

## Supplementary Information

### Copper-Catalyzed Deaminative Alkynylation of Secondary Amines with Alkynes: Selectivity Switch in the Synthesis of Diversified Propargylamines

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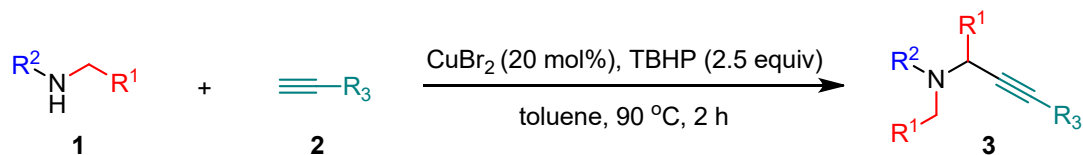
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## 1. General Information

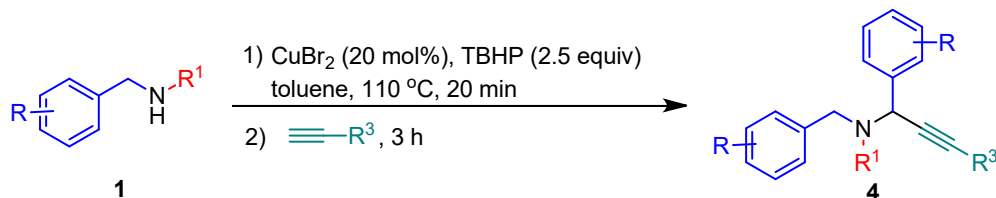
All commercially available reagents were used without purification unless otherwise noted. Visualization of the compounds was accomplished with UV light (254 nm) or iodine. HPLC analysis was performed on an Agilent 1260 infinity II chromatograph with an Eclipse plus C18 column (4.6 mm × 150 mm, 3.5 μm, P/N 959963-902). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> operating at 400 MHz and 600 MHz. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent CDCl<sub>3</sub> (7.26 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl<sub>3</sub> (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 Q-Exacte Spectrometer (Thermo, USA).

## 2. General Procedure for the Synthesis of Propargylamines 3



Amines **1** (2.0 mmol), CuBr<sub>2</sub> (22.33 mg 20 mol %), 70% TBHP (160 mg, 1.25 mmol), alkynes **2** (0.5 mmol), and toluene (3 mL) were charged into a 25 mL tube along with a magnetic stir bar. The mixture was stirred in an oil bath at 90 °C for 2 hours until alkynes **2** were completely consumed, monitoring with TLC. Subsequently, the mixture was cooled to room temperature and purified by running column chromatography on silica gel using petroleum ether/ethyl acetate. Flash column chromatography was performed on silica gel (100–200 mesh).

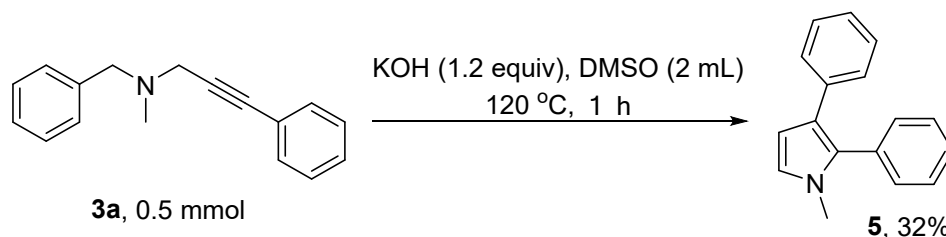
## 3. General Procedure for the Synthesis of Propargylamines 4



Amines **1** (2.0 mmol), CuBr<sub>2</sub> (22.33 mg 20 mol %), 70% TBHP (160 mg, 1.25 mmol), and toluene (1 mL) were charged into a 25 mL tube along with a magnetic stir bar. The mixture was stirred in an oil bath at 110 °C for 20 min; then, alkynes **2** (0.5 mmol) were added into the reaction system,

and the resulting mixture was stirred at 110 °C for another 3 hours. Subsequently, the mixture was cooled to room temperature and purified by running column chromatography on silica gel using petroleum ether/ethyl acetate. Flash column chromatography was performed on silica gel (200–300 mesh).

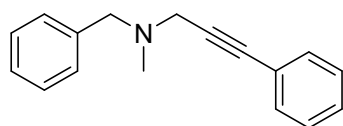
#### 4. Procedure for the Synthesis of 1-Methyl-2,3-diphenyl-1H-pyrrole 5



Amines **3a** (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<sub>4</sub>. After that, the mixture was purified by running column chromatography on silica gel using petroleum ether/ethyl acetate =40:1. Flash column chromatography was performed on silica gel (100–200 mesh). The product **5a** was obtained (37.3 mg, 32%) as colorless oil.

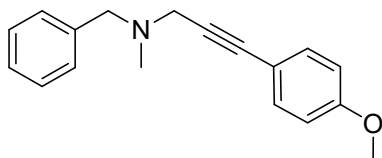
#### 5. <sup>1</sup>H NMR and <sup>13</sup>C NMR Data of Products 3–5

##### *N*-benzyl-*N*-methyl-3-phenylprop-2-yn-1-amine (**3a**)



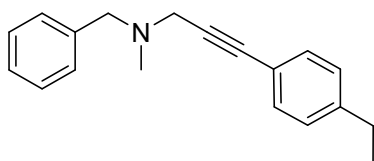
(98.7 mg, 84%) as light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47-7.26 (m, 9H), 3.64 (s, 2H), 3.51 (s, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 137.9, 131.3, 132.7, 128.8, 127.9, 127.8, 127.6, 126.8, 122.8, 85.3, 83.9, 59.8, 45.3, 41.5. LC-MS m/z (ESI<sup>+</sup>): Calculated for C<sub>17</sub>H<sub>17</sub>N ([M+H]<sup>+</sup>): 236.1, found: 236.1. Known compound<sup>[1]</sup>.

##### *N*-benzyl-3-(4-methoxyphenyl)-*N*-methylprop-2-yn-1-amine (**3b**)



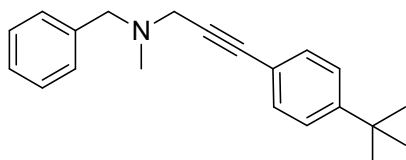
(103.3 mg, 78%) as light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.26 (m, 7H), 6.85-6.83 (m, 2H), 3.80 (s, 3H), 3.63 (s, 2H), 3.49 (s, 2H), 2.39 (s, 3H).  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 138.0, 132.7, 128.8, 127.8, 126.8, 115.0, 113.4, 85.0, 82.4, 59.8, 54.8, 45.4, 41.5. LC-MS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{18}\text{H}_{19}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ): 266.2, found: 266.2. Known compound [2].

***N*-benzyl-3-(4-ethylphenyl)-*N*-methylprop-2-yn-1-amine (3c)**



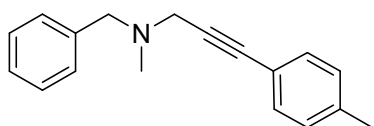
(107.8 mg, 82%) as light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.13 (m, 9H), 3.63 (s, 3H), 3.50 (s, 2H), 2.66 (q,  $J = 22.8$  Hz, 2H), 2.39 (s, 3H), 1.24 (t,  $J = 15.2$  Hz 3H).  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 138.0, 131.3, 128.8, 127.9, 127.4, 126.8, 120.0, 85.4, 83.1, 59.8, 45.3, 41.5, 28.3, 15.0. HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{19}\text{H}_{21}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 264.1747, found: 264.1746.

***N*-benzyl-3-(4-(tert-butyl)phenyl)-*N*-methylprop-2-yn-1-amine (3d)**



(122.3 mg, 84%) as light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.36 (m, 9H), 3.64 (s, 2H), 3.51 (s, 2H), 2.40 (s, 3H), 1.32 (s, 9H).  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 138.0, 131.0, 128.8, 127.9, 126.8, 124.8, 119.8, 85.4, 83.1, 59.8, 45.3, 41.5, 34.3, 30.7. LC-MS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{21}\text{H}_{25}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 292.2, found: 292.2. Known compound [3].

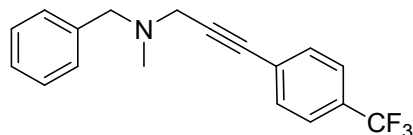
***N*-benzyl-*N*-methyl-3-(*p*-tolyl)prop-2-yn-1-amine (3e)**



(100.8 mg, 81%) as light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.10 (m, 9H), 3.63 (s, 2H), 3.50 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  138.0, 137.6, 131.2, 128.8,

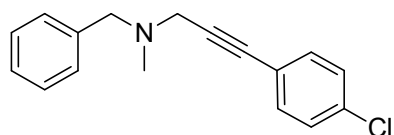
128.6, 127.9, 126.7, 119.8, 85.3, 83.2, 59.8, 45.3, 41.5, 21.0. LC-MS m/z (ESI<sup>+</sup>): Calculated for C<sub>18</sub>H<sub>19</sub>N ([M+H]<sup>+</sup>): 250.2, found: 250.1. Known compound<sup>[4]</sup>

***N*-benzyl-*N*-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (3f)**



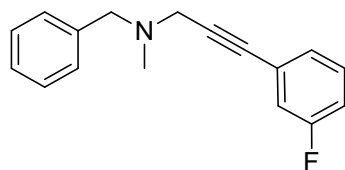
(106.1 mg, 70%) as light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58-7.27 (m, 9H), 3.64 (s, 2H), 3.53 (s, 2H), 2.41 (s, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 137.8, 131.5, 128.7, 127.9, 126.9, 124.8, 124.7, 86.8, 84.0, 59.9, 45.2, 41.6. <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) δ -62.8 (s). LC-MS m/z (ESI<sup>+</sup>): Calculated for C<sub>18</sub>H<sub>16</sub>F<sub>3</sub>N ([M+H]<sup>+</sup>): 304.1, found: 304.1. Known compound<sup>[2]</sup>

***N*-benzyl-3-(4-chlorophenyl)-*N*-methylprop-2-yn-1-amine (3g)**



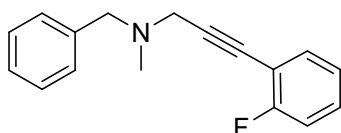
(100.8 mg, 75%) as light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43-7.31 (m, 9H), 3.67 (s, 2H), 3.54 (s, 2H), 2.44 (s, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 137.9, 133.6, 132.5, 128.7, 128.1, 127.9, 126.8, 85.1, 84.1, 59.9, 45.3, 41.6. LC-MS m/z (ESI<sup>+</sup>): Calculated for C<sub>17</sub>H<sub>16</sub>ClN ([M+H]<sup>+</sup>): 270.1, found: 270.1. Known compound<sup>[5]</sup>

***N*-benzyl-3-(3-fluorophenyl)-*N*-methylprop-2-yn-1-amine (3h)**



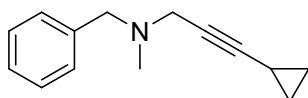
(89.8 mg, 71%) as light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38-6.99 (m, 9H), 3.63 (s, 2H), 3.51 (s, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 163.1, 160.7, 137.9, 128.7, 127.9, 127.2, 127.1, 126.8, 118.2, 118.0, 115.0, 114.8, 85.1, 84.1, 59.8, 45.2, 41.5. <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) δ -113.0 (s). HRMS m/z (ESI<sup>+</sup>): Calculated for C<sub>17</sub>H<sub>16</sub>FN ([M+H]<sup>+</sup>): 254.1340, found: 254.1340.

***N*-benzyl-3-(2-fluorophenyl)-*N*-methylprop-2-yn-1-amine (3i)**



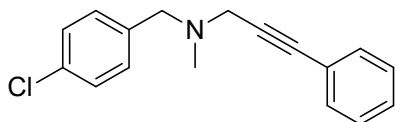
(83.5 mg, 66%) as light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.05 (m, 9H), 3.65 (s, 2H), 3.55 (s, 2H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 138.0, 132.7, 128.8, 126.8, 115.0, 113.4, 85.0, 82.4, 59.8, 54.8, 45.4, 41.5.  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.1 (s). HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{17}\text{H}_{16}\text{FN}$  ( $[\text{M}+\text{H}]^+$ ): 254.1340, found: 254.1334.

***N*-benzyl-3-cyclopropyl-*N*-methylprop-2-yn-1-amine(3j)**



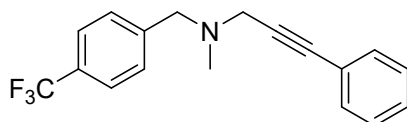
(31.8 mg, 32%) as light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.56 (m, 5H), 3.57 (s, 2H), 3.27 (d,  $J = 2.0$  Hz 2H), 2.32 (s, 3H), 1.33-1.28 (m, 1H), 0.82-0.69 (m, 4H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 129.2, 128.2, 127.1, 88.8, 70.0, 60.2, 45.5, 41.8, 8.31, -0.44. LC-MS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{14}\text{H}_{17}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 200.1, found: 200.1. Known compound<sup>[5]</sup>

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



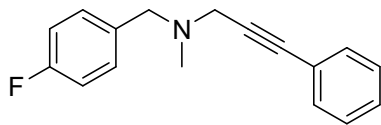
(98.2 mg, 73%) as light yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.49 (m, 2H), 7.35-7.34 (m, 7H), 3.64 (s, 2H), 3.54 (s, 2H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0, 131.7, 130.5, 128.5, 128.3, 128.1, 123.2, 85.8, 84.1, 59.4, 45.7, 41.9. LC-MS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{17}\text{H}_{16}\text{ClN}$  ( $[\text{M}+\text{H}]^+$ ): 270.1, found: 270.1. Known compound<sup>[6]</sup>

***N*-methyl-3-phenyl-*N*-(4-(trifluoromethyl)benzyl)prop-2-yn-1-amine(3l)**



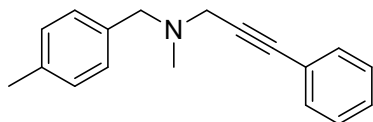
(113.6 mg, 75%) as light yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.62 (m, 2H), 7.54-7.50 (m, 4H), 7.37-7.35 (m, 3H), 3.74 (s, 2H), 3.57 (s, 2H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 131.7, 129.3, 128.3, 128.1, 125.3, 125.2, 123.1, 85.9, 84.0, 59.7, 45.9, 42.0. HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{17}\text{H}_{16}\text{F}_3\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 304.1308, found: 304.1304.

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



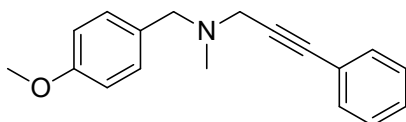
(88.6 mg, 70%) as light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.49 (m, 2H), 7.39-7.34 (m, 5H), 7.07-7.03 (m, 2H), 3.64 (s, 2H), 3.54 (s, 2H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 161.3, 134.2, 131.7, 130.7, 128.3, 128.1, 123.2, 115.2, 115.0, 85.8, 84.2, 59.4, 45.6, 41.9. HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{17}\text{H}_{16}\text{FN}$  ( $[\text{M}+\text{H}]^+$ ): 254.1340, found: 254.1340.

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



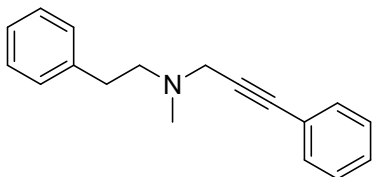
(98.3 mg, 70%) as light yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.51 (m, 2H), 7.37-7.18 (m, 7H), 3.66 (s, 2H), 3.55 (s, 2H), 2.45 (s, 3H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 135.3, 131.7, 129.2, 129.0, 128.3, 128.0, 123.3, 85.7, 84.5, 60.0, 45.6, 42.0, 21.1. HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{18}\text{H}_{19}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 250.1590, found: 250.1593.

***N*-(4-methoxybenzyl)-*N*-methyl-3-phenylprop-2-yn-1-amine(3o)**



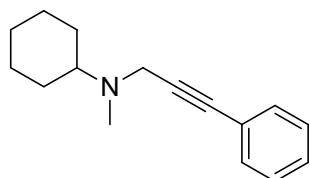
(107.3 mg, 81%) as light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.31 (m, 7H), 6.92-6.89 (m, 2H), 3.83 (s, 3H), 3.62 (s, 2H), 3.53 (s, 2H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 131.3, 130.0, 129.9, 127.8, 127.5, 122.9, 113.2, 85.2, 84.0, 59.1, 54.8, 45.0, 41.4. LC-MS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{18}\text{H}_{19}\text{ON}$  ( $[\text{M}+\text{H}]^+$ ): 266.2, found: 266.1. Known compound <sup>[6]</sup>

***N*-methyl-*N*-phenethyl-3-phenylprop-2-yn-1-amine(3p)**



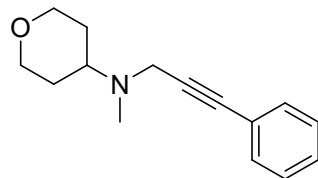
(94.7 mg, 76%) as yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.47 (m, 2H), 7.35-7.24 (m, 7H), 3.67 (s, 2H), 2.89-2.86 (m, 2H), 2.82-2.80 (m, 2H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 131.7, 128.7, 128.4, 128.3, 128.0, 126.1, 123.2, 85.5, 84.3, 57.7, 46.5, 42.1, 34.4. HRMS  $m/z$  ( $\text{ESI}^+$ ): Calculated for  $\text{C}_{18}\text{H}_{19}\text{ON}$  ( $[\text{M}+\text{H}]^+$ ): 250.1590, found: 250.1594.

***N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)cyclohexanamine (3q)**



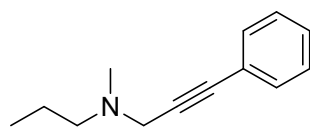
(65.8 mg, 58%) as light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.42 (m, 2H), 7.32-7.29 (m, 3H), 3.66 (s, 2H), 2.48-2.45 (m, 4H), 2.00-1.97 (m, 2H), 1.83-1.80 (m, 2H), 1.66-1.62 (m, 1H), 1.32-1.17 (m, 5H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  131.2, 127.7, 127.4, 122.9, 85.0, 84.4, 60.6, 43.2, 29.3, 25.6, 25.1. LC-MS  $m/z$  ( $\text{ESI}^+$ ): Calculated for  $\text{C}_{16}\text{H}_{21}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 228.2, found: 288.2. Known compound [1]

***N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)tetrahydro-2*H*-pyran-4-amine (3r)**



(61.8 mg, 54%) as light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45-7.43 (m, 2H), 7.32-7.30 (m, 3H), 4.05-4.01 (m, 4H), 3.67 (s, 2H), 3.45-3.38 (m, 2H), 2.63-2.60 (m, 1H), 2.44 (s, 3H), 1.90-1.86 (m, 2H), 1.59-1.55 (m, 2H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  131.2, 127.8, 127.6, 122.7, 84.9, 84.1, 66.6, 57.7, 42.9, 38.0, 30.1. HRMS  $m/z$  ( $\text{ESI}^+$ ): Calculated for  $\text{C}_{16}\text{H}_{21}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 230.1539, found: 230.1535.

***N*-methyl-3-phenyl-*N*-propylprop-2-yn-1-amine (3s')**



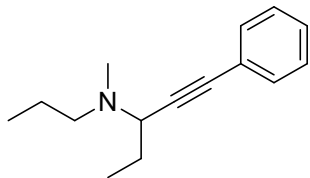
(32.7 mg, 35%) as light yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.45 (m, 2H), 7.31-7.30 (m, 3H), 3.56 (s, 2H), 2.47-2.45 (m, 2H), 2.39 (s, 3H), 1.56-1.53 (m, 2H), 0.97 (t,  $J = 15.0$  Hz 3H).  $^{13}\text{C}$



NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  131.7, 128.2, 127.9, 123.3, 85.2, 84.6, 58.0, 46.4, 41.9, 20.8, 11.9.

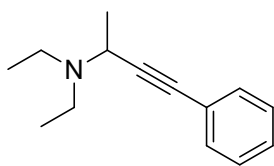
HRMS m/z (ESI<sup>+</sup>): Calculated for C<sub>13</sub>H<sub>17</sub>N ([M+H]<sup>+</sup>): 188.1434, found: 188.1434.

***N*-methyl-1-phenyl-*N*-propylpent-1-yn-3-amine(3s)**



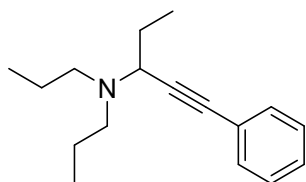
(54.9 mg, 51%) as light yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.47-7.45 (m, 2H), .7.32-7.31 (m, 3H), 3.54-3.51 (m, 1H), 2.52-2.42 (m, 2H), 2.32 (s, 3H), 1.77-1.73 (m, 2H), 1.56-1.53 (m, 2H), 1.10(t, *J* = 14.4 Hz 3H), 0.96 (t, *J* = 15.0 Hz 3H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  131.7, 128.2, 127.7, 123.6, 87.7, 85.5, 58.6, 56.7, 38.0, 27.1, 21.1, 11.9, 11.4. HRMS m/z (ESI<sup>+</sup>): Calculated for C<sub>15</sub>H<sub>21</sub>N ([M+H]<sup>+</sup>): 216.1747, found: 216.1736.

***N,N*-diethyl-4-phenylbut-3-yn-2-amine (3t)**



(62.3 mg, 62%) as light yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.44-7.43 (m, 2H), .7.31-7.30 (m, 3H), 3.95-3.93 (m, 1H), 2.80-2.74 (m, 2H), 2.56-2.53 (m, 2H), 1.45 (d, *J* = 6.6 Hz 3H), 1.15 (d, *J* = 14.4 Hz 6H), 1.90-1.86 (m, 2H) 1.59-1.55 (m, 2H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  131.6, 128.2, 127.7, 123.5, 89.5, 84.0, 48.3, 44.6, 20.1, 13.6. LC-MS m/z (ESI<sup>+</sup>): Calculated for C<sub>14</sub>H<sub>19</sub>N ([M+H]<sup>+</sup>): 202.2, found: 202.1. Known compound<sup>[7]</sup>

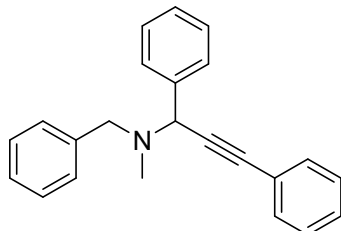
**1-phenyl-*N,N*-dipropylpent-1-yn-3-amine(3u)**



(85.1 mg, 70%) as light yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.46-7.45 (m, 2H), .7.32-7.31 (m, 3H), 3.57 (t, *J* = 15.6 Hz 1H), 2.57-2.52 (m, 2H), 2.47-2.43 (m, 2H), 1.74-1.71 (m, 2H), 1.55-1.47 (m, 4H), 1.08(t, *J* = 15.0 Hz 3H), 0.95 (t, *J* = 15.0 Hz 6H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  131.7,

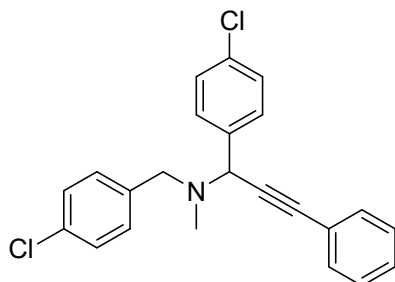
128.2, 127.6, 123.7, 89.2, 84.4, 56.0, 53.6, 27.4, 21.7, 12.0, 11.4. LC-MS m/z (ESI<sup>+</sup>): Calculated for C<sub>17</sub>H<sub>25</sub>N ([M+H]<sup>+</sup>): 244.2, found: 244.2. Known compound [7]

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



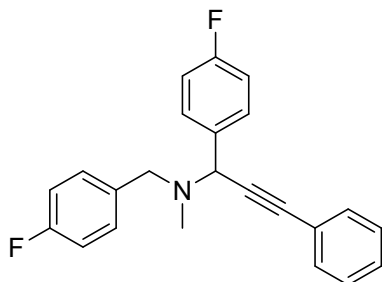
(124.4 mg, 80%) as yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.68-7.67 (d, *J* = 7.8 Hz 2H), .7.57-7.56 (m, 2H), 7.42-7.40 (d, *J* = 7.8 Hz 2H), 7.36-7.22 (m, 9H), 4.91 (s, 1H), 3.73-3.62 (m, 2H), 2.24 (s, 3H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) δ 139.3, 139.1, 131.9, 129.1, 128.4, 128.2, 127.6, 127.1, 123.3, 88.7, 84.8 59.6, 59.0, 38.1. LC-MS m/z (ESI<sup>+</sup>): Calculated for C<sub>23</sub>H<sub>21</sub>N ([M+H]<sup>+</sup>): 312.2, found: 312.2. Known compound [5]

***N*-(4-chlorobenzyl)-1-(4-chlorophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine(4b)**



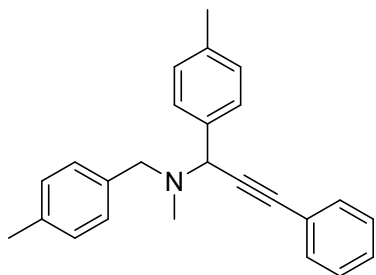
(142.1 mg, 75%) as yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64-7.58 (m, 4H), .7.41-7.34 (m, 9H), 4.48 (s, 1H), 3.70-3.60 (m, 2H), 2.24 (s, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 137.1, 137.0, 132.9, 132.4, 131.4, 129.8, 129.2, 128.0, 127.9, 127.8, 122.4, 88.6, 83.3, 58.6, 57.6, 37.5. HRMS m/z (ESI<sup>+</sup>): Calculated for C<sub>23</sub>H<sub>19</sub>Cl<sub>2</sub>N ([M+H]<sup>+</sup>): 380.0967, found: 380.0949.

***N*-(4-fluorobenzyl)-1-(4-fluorophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine(4c)**



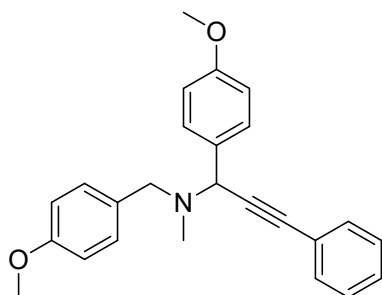
(119.7 mg, 75%) as yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69-7.61 (m, 4H), 7.42-7.40 (m, 5H), 7.12-7.06 (m, 4H), 4.91 (s, 1H), 3.73-3.63 (m, 2H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  163.0, 162.8, 160.6, 160.4, 134.4, 134.3, 134.2, 131.4, 130.0, 129.9, 129.5, 129.4, 127.9, 122.5, 114.8, 114.6, 114.4, 88.5, 83.7, 58.4, 57.6, 37.4. HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{23}\text{H}_{19}\text{F}_2\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 348.1558, found: 348.1547.

***N*-methyl-*N*-(4-methylbenzyl)-3-phenyl-1-(*p*-tolyl)prop-2-yn-1-amine(4d)**



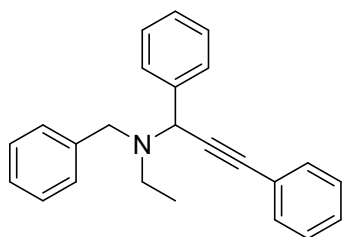
(130.6 mg, 77%) as yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.38 (m, 9H), 7.25-7.21 (m, 4H), 4.96 (s, 1H), 3.79-3.66 (m, 2H), 2.43 (d,  $J = 4.4$  Hz 6H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  136.6, 136.1, 135.8, 135.7, 131.4, 128.5, 128.4, 127.9, 127.8, 127.7, 123.0, 84.9, 84.7, 58.8, 58.2, 37.5, 20.7. HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{25}\text{H}_{25}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 340.2060, found: 340.2044.

***N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine(4e)**



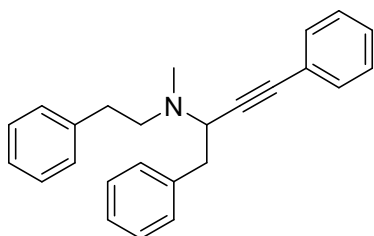
(146.5 mg, 79%) as yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.39 (m, 9H), 6.98-6.94 (m, 4H), 4.94 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.75-3.62 (m, 2H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 158.3, 131.4, 130.9, 130.8, 129.7, 129.0, 127.9, 127.7, 122.9, 113.3, 113.0, 88.0, 84.7, 58.3, 57.7, 37.3. HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{25}\text{H}_{25}\text{NO}_2$  ( $[\text{M}+\text{H}]^+$ ): 372.1958, found: 372.1937.

***N*-benzyl-*N*-ethyl-1,3-diphenylprop-2-yn-1-amine(4f)**



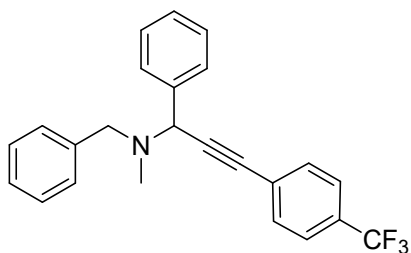
(105.6 mg, 65%) as yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81-7.79 (d,  $J = 8.0$  Hz 2H), .7.66-7.64 (m, 2H), 7.50-7.28 (m, 11H), 5.08 (s, 1H), 3.95-3.60 (m, 2H), 2.70 (q,  $J = 21.6$  Hz 2H), 1.21 (t,  $J = 14.4$  Hz 3H).  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 139.2, 131.5, 128.4, 127.9, 127.8, 127.7, 127.6, 126.9, 126.4, 123.0, 87.6, 85.0, 54.5, 44.0, 13.2. LC-MS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{24}\text{H}_{23}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 326.2, found: 326.2. Known compound<sup>[8]</sup>

***N*-methyl-*N*-phenethyl-1,4-diphenylbut-3-yn-2-amine (4g)**



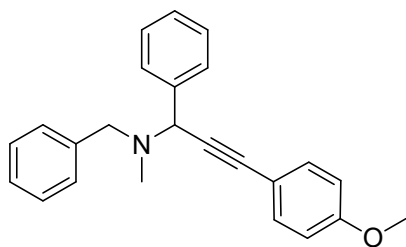
(110.2 mg, 65%) as light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44-7.26 (m, 15H), 3.97 (t,  $J = 14.8$  Hz 1H), 3.08-3.05 (m, 2H), 2.92-2.83 (m, 4H), 2.52 (s, 3H).  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 138.4, 131.2, 129.0, 128.4, 127.9, 127.8, 127.5, 126.0, 125.6, 123.0, 86.4, 84.3, 58.7, 56.4, 40.0, 37.8, 34.3. HRMS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{25}\text{H}_{25}\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 340.2060, found: 340.2061.

***N*-benzyl-*N*-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (4h)**



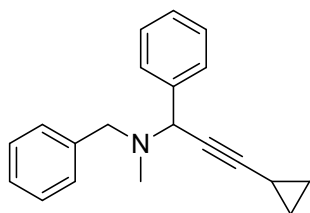
(130.8 mg, 69%) as light yellow oil.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.67 (m, 6H), 7.49-7.33 (m, 8H) 5.01 (s, 1H) 3.82-3.69 (m, 2H) 2.32 (s, 3H).  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 138.6, 132.2, 130.1, 129.9, 129.0, 128.4, 128.3, 127.7, 127.2, 127.0, 125.3, 124.9, 123.1, 87.7, 87.4, 59.6, 59.0, 38.1. LC-MS  $m/z$  (ESI $^+$ ): Calculated for  $\text{C}_{24}\text{H}_{20}\text{F}_3\text{N}$  ( $[\text{M}+\text{H}]^+$ ): 380.2, found: 380.2. Known compound<sup>[8]</sup>

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



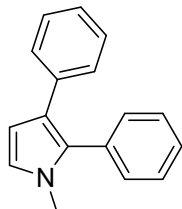
(138.2 mg, 81%) as colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.58-7.56 (m, 2H), 7.49-7.28 (m, 8H), 6.95-6.94 (m, 2H) 4.97 (s, 1H), 3.88 (s, 3H), 3.79-3.69 (m, 2H), 2.30 (s, 3H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) δ 159.6, 139.4, 139.3, 133.3, 129.1, 128.4, 128.3, 128.2, 127.5, 127.1, 88.5, 83.2, 59.7, 59.0, 55.4, 38.1. LC-MS *m/z* (ESI<sup>+</sup>): Calculated for C<sub>24</sub>H<sub>23</sub>NO ([M+H]<sup>+</sup>): 342.2, found: 342.2. Known compound<sup>[8]</sup>

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



(20.6 mg, 15%) as light yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.66-7.65 (m, 2H), 7.45-7.30 (m, 8H), 7.49-7.28 (m, 8H), 4.71 (s, 1H) 3.69-3.57 (m, 2H), 2.20 (s, 3H), 1.49-1.46 (m, 1H), 0.93-0.84 (m, 4H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) δ 139.7, 139.6, 129.0, 128.4, 128.3, 128.0, 127.3, 127.0, 92.1, 70.1, 59.2, 58.8, 37.9, 8.7, -0.3. LC-MS *m/z* (ESI<sup>+</sup>): Calculated for C<sub>20</sub>H<sub>21</sub>N ([M+H]<sup>+</sup>): 276.2, found:276.2. Known compound<sup>[8]</sup>

**1-Methyl-2,3-diphenyl-1*H*-pyrrole (5)**



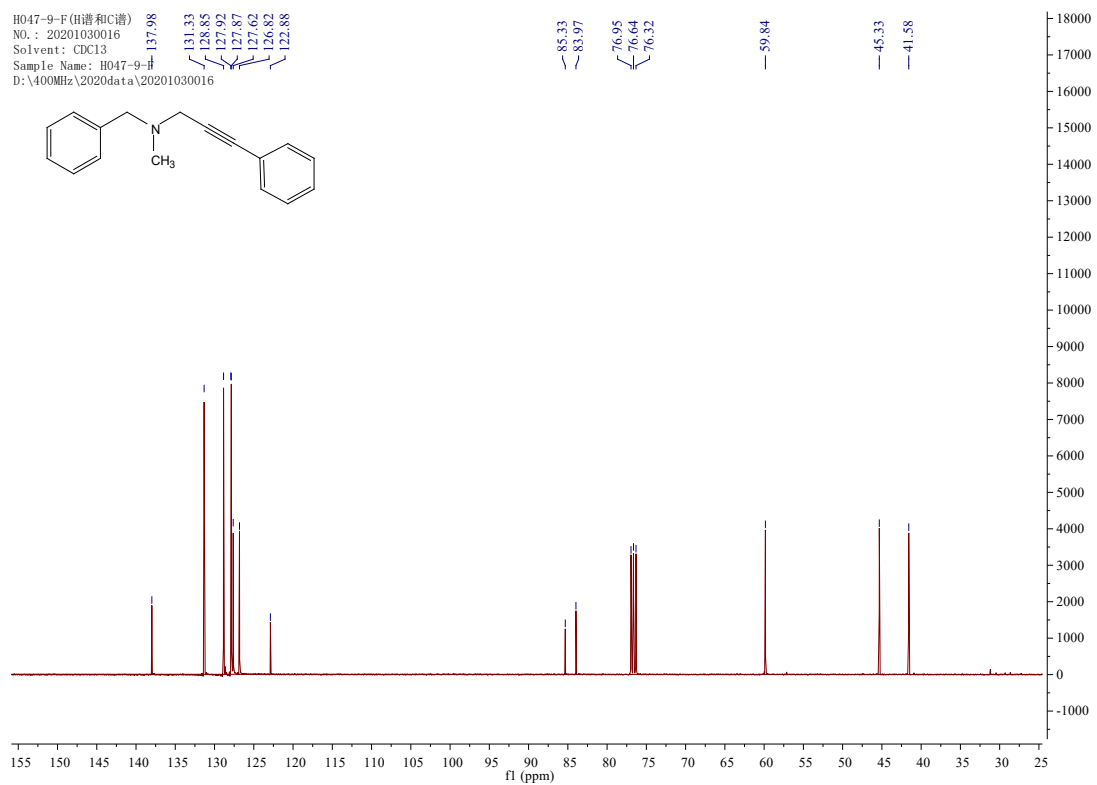
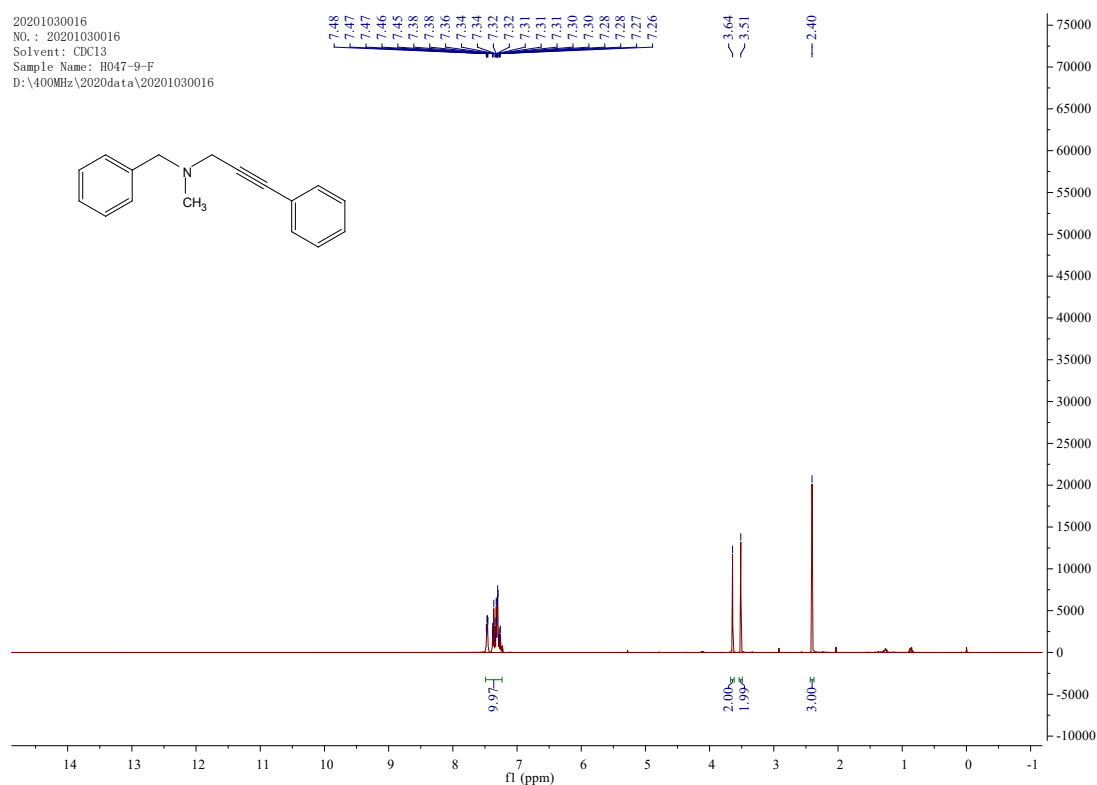
(37.3 mg, 32%) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.31 (m, 5H), 7.24-7.19 (m, 4H), 7.13-7.10 (m, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 6.45 (d, *J* = 3.0 Hz, 1H), 3.55 (s, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 136.2, 132.4, 130.6, 130.2, 128.0, 127.6, 127.3, 127.1, 124.6, 122.4, 121.8,

107.4, 34.3. LC-MS m/z (ESI<sup>+</sup>): Calculated for C<sub>20</sub>H<sub>21</sub>N ([M+H]<sup>+</sup>): 234.1, found:234.1. Known compound<sup>[9]</sup>

## 6. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

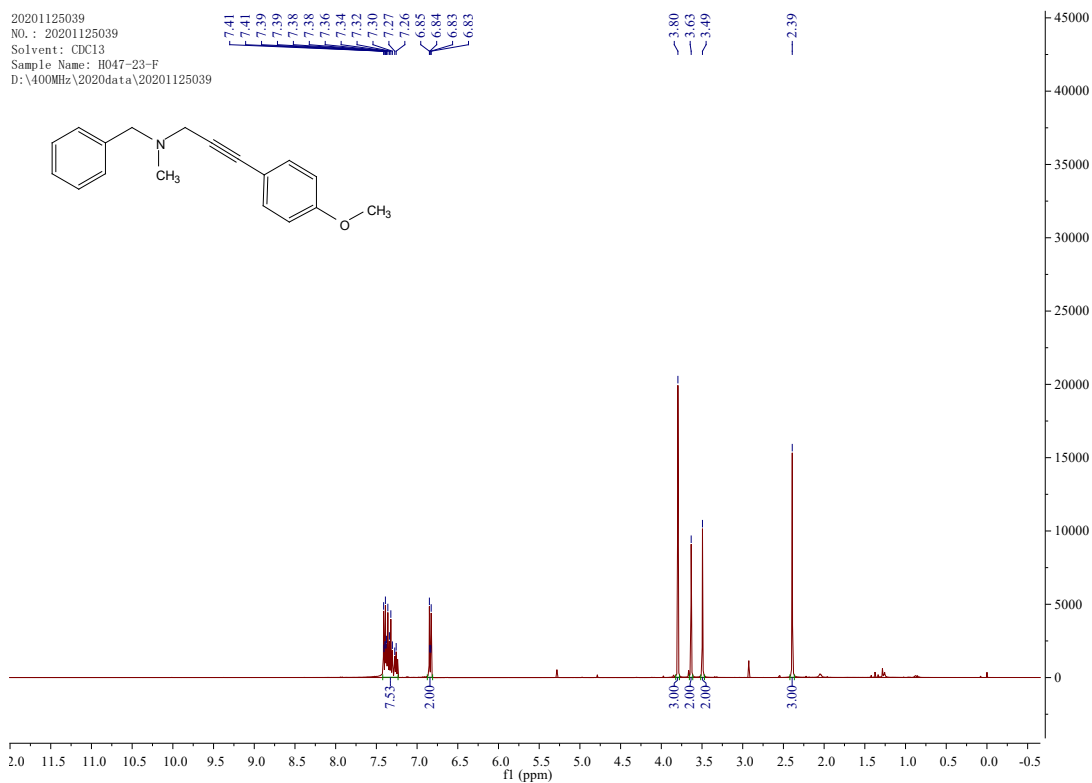
(3a)

20201030016  
 NO.: 20201030016  
 Solvent:  $\text{CDCl}_3$   
 Sample Name: H047-9-F  
 D:\400MHz\2020data\20201030016

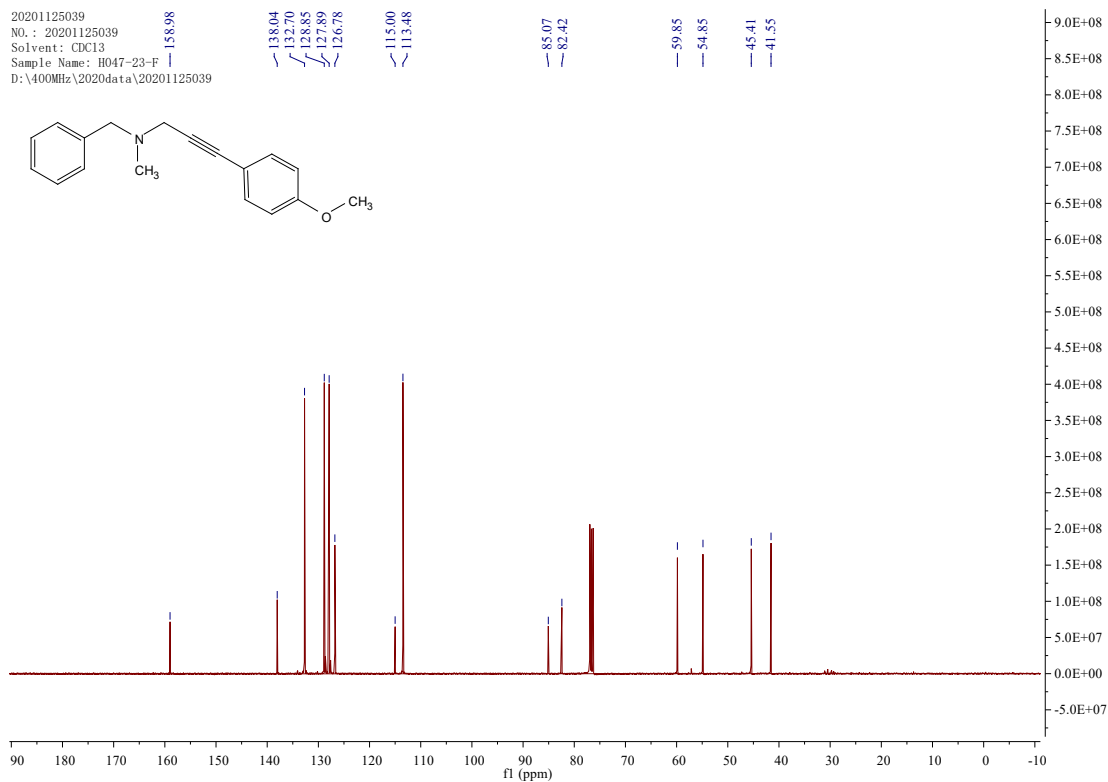


**(3b)**

20201125039  
NO.: 20201125039  
Solvent: CDC13  
Sample Name: H047-23-F  
D:\400MHz\2020data\20201125039



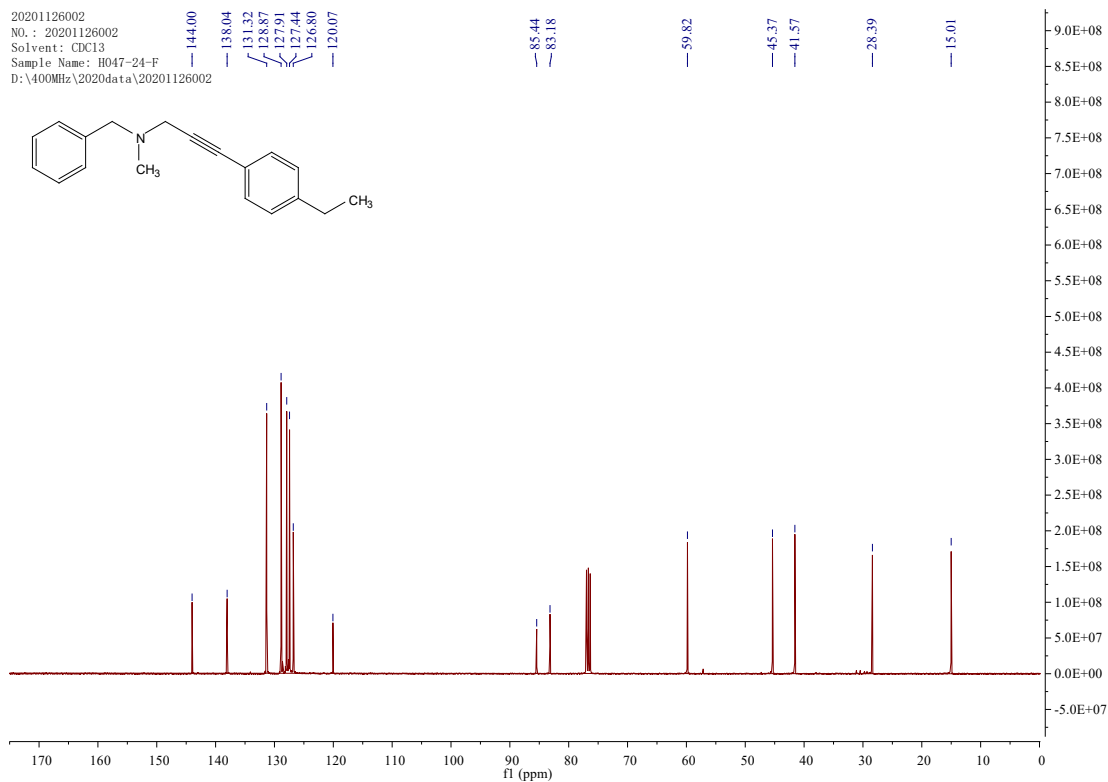
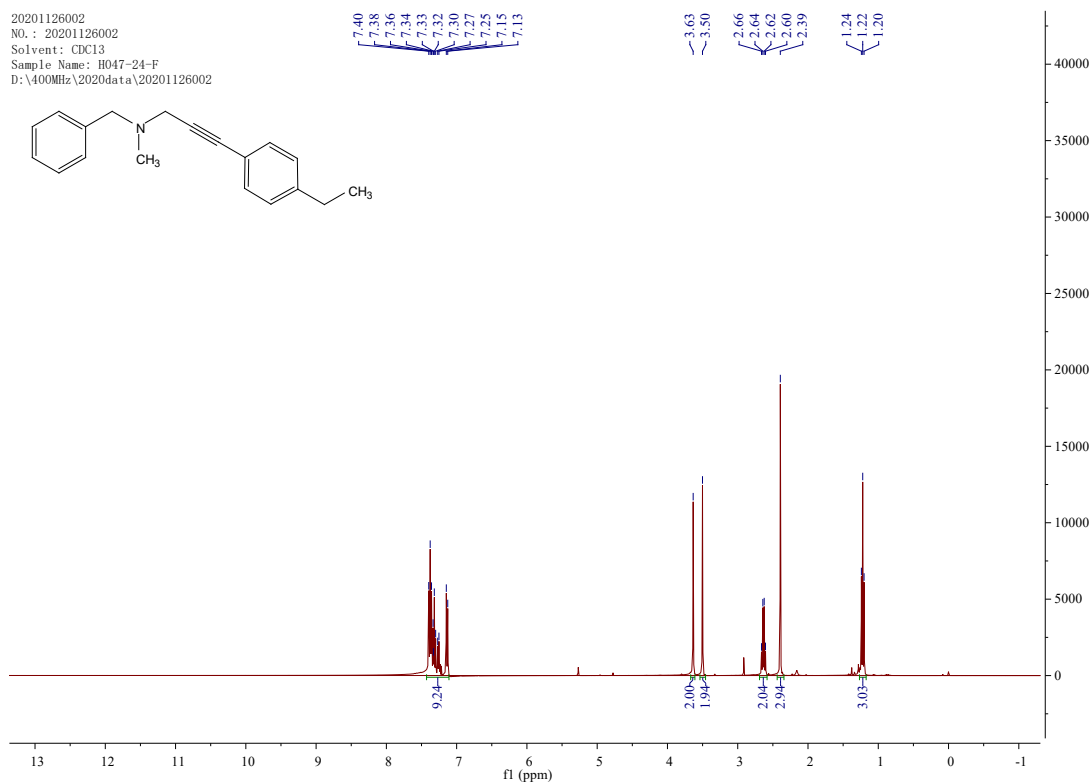
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NO.: 20201125039  
Solvent: CDC13  
Sample Name: H047-23-F  
D:\400MHz\2020data\20201125039





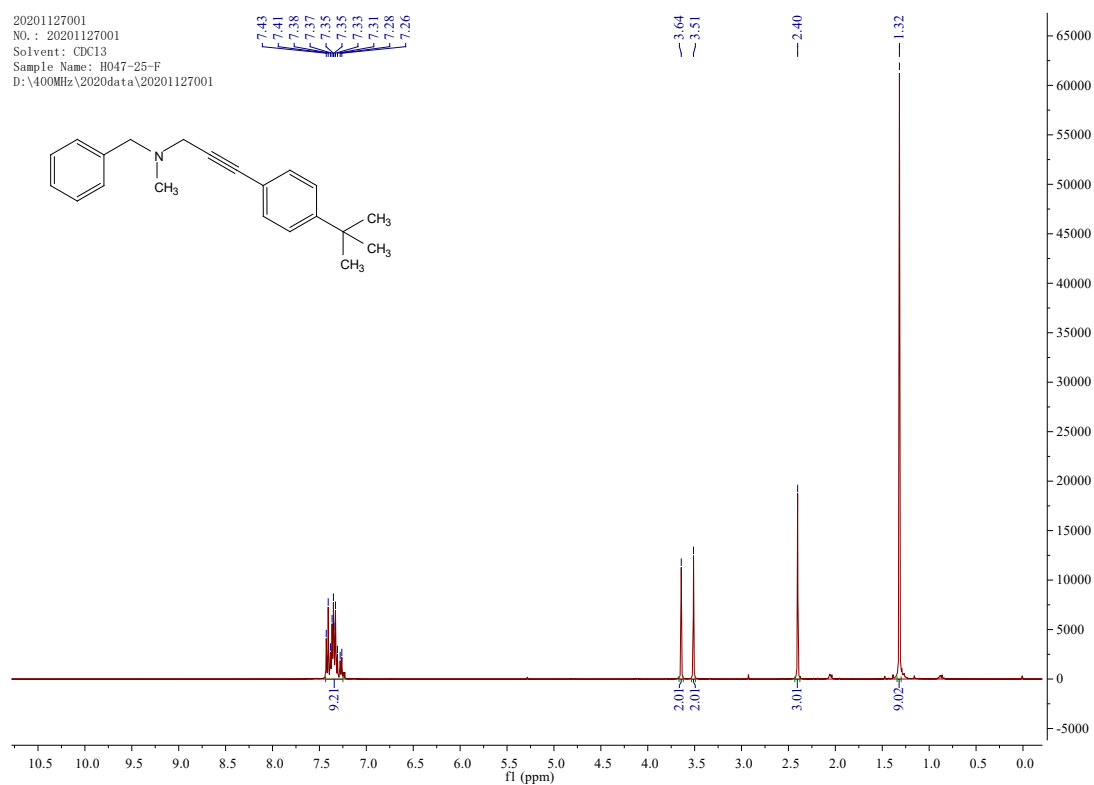
**(3c)**

20201126002  
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Sample Name: H047-24-F  
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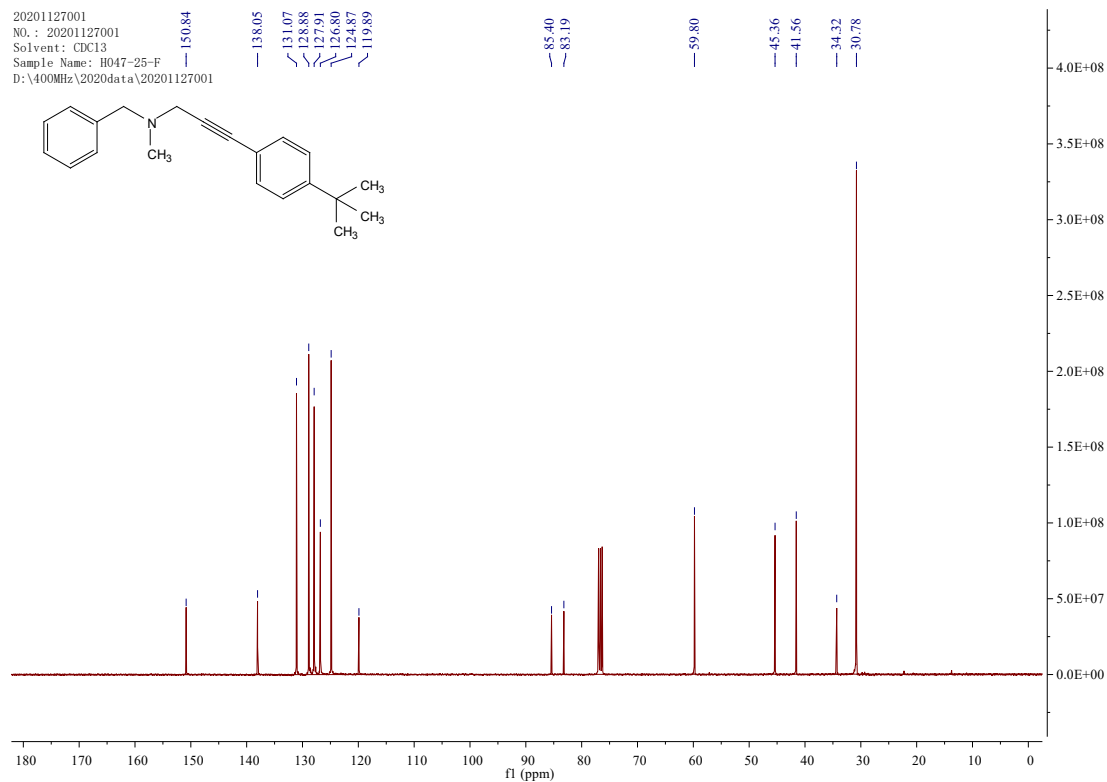


**(3d)**

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Solvent: CDC13  
Sample Name: H047-25-F  
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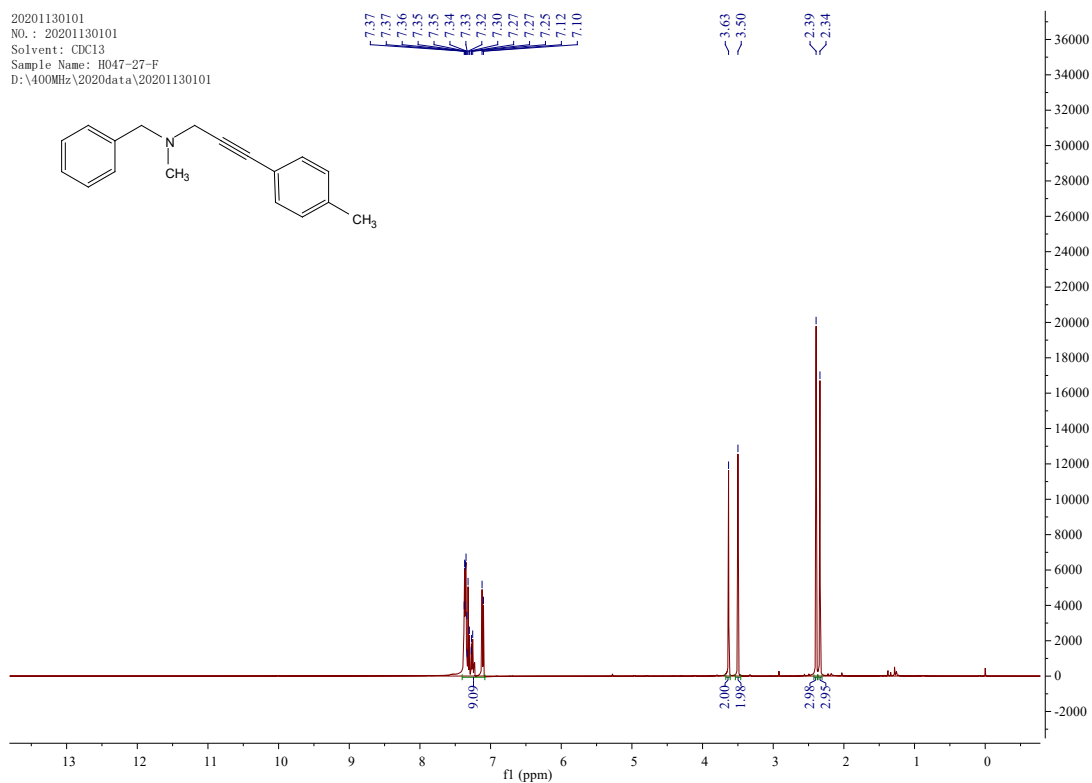


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Solvent: CDC13  
Sample Name: H047-25-F  
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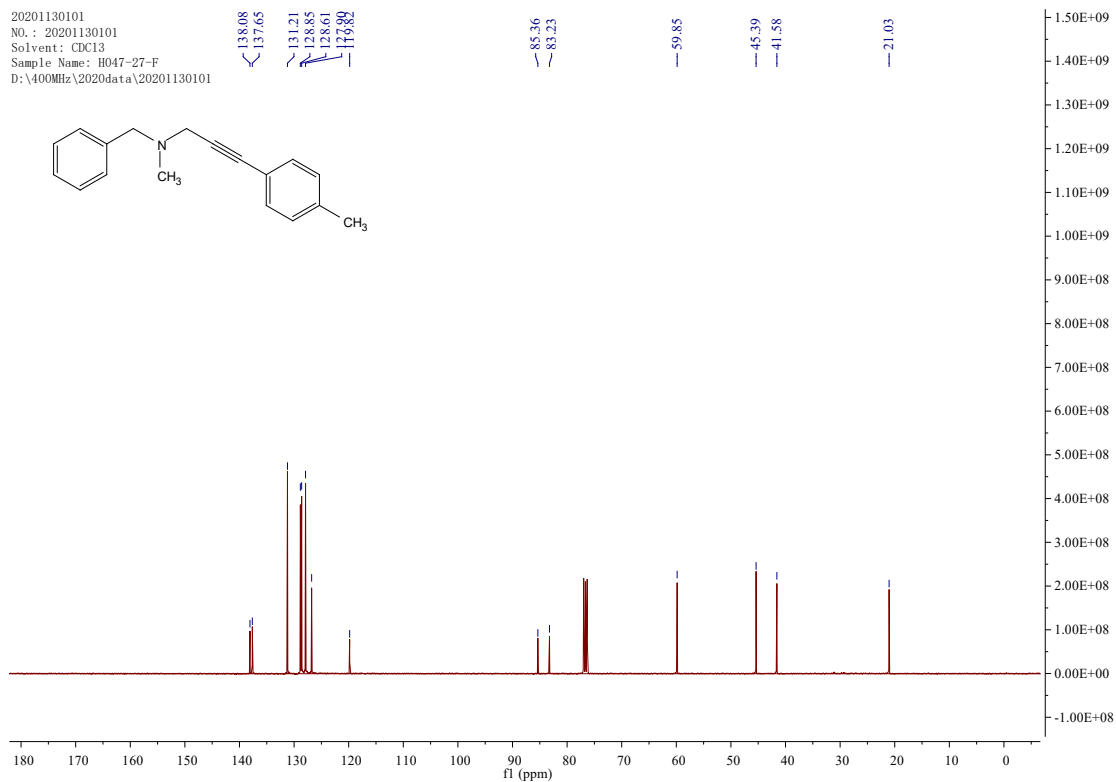


**(3e)**

20201130101  
NO.: 20201130101  
Solvent: CDC13  
Sample Name: H047-27-F  
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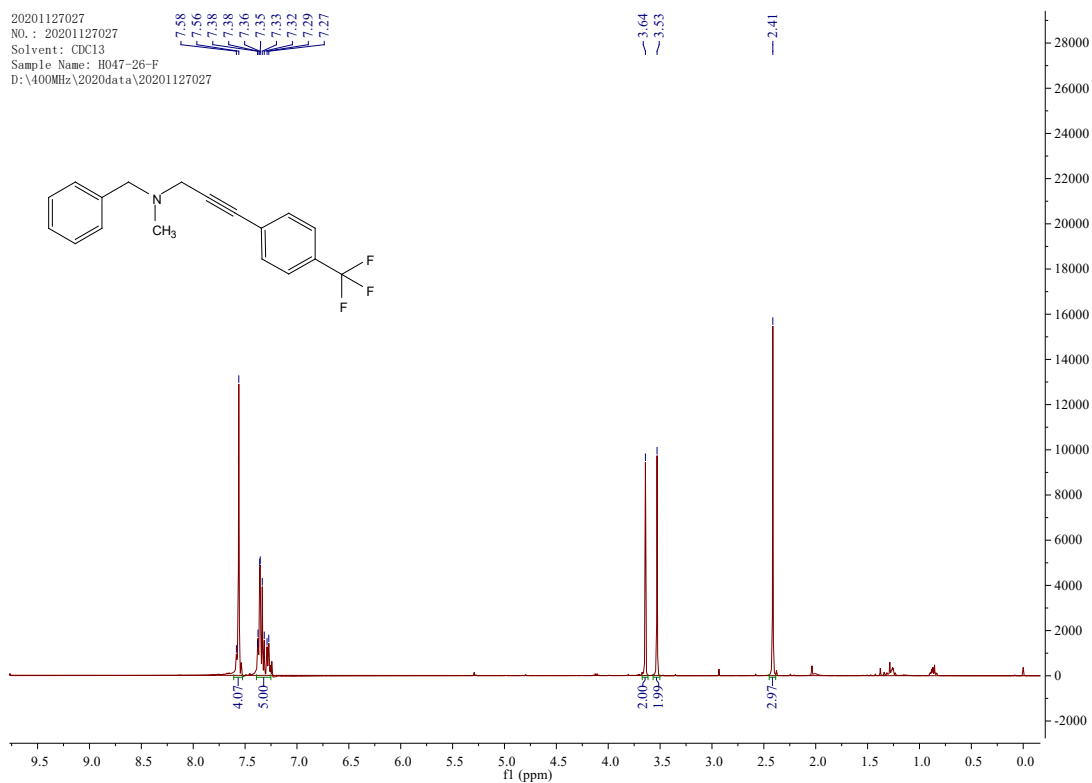


20201130101  
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Solvent: CDC13  
Sample Name: H047-27-F  
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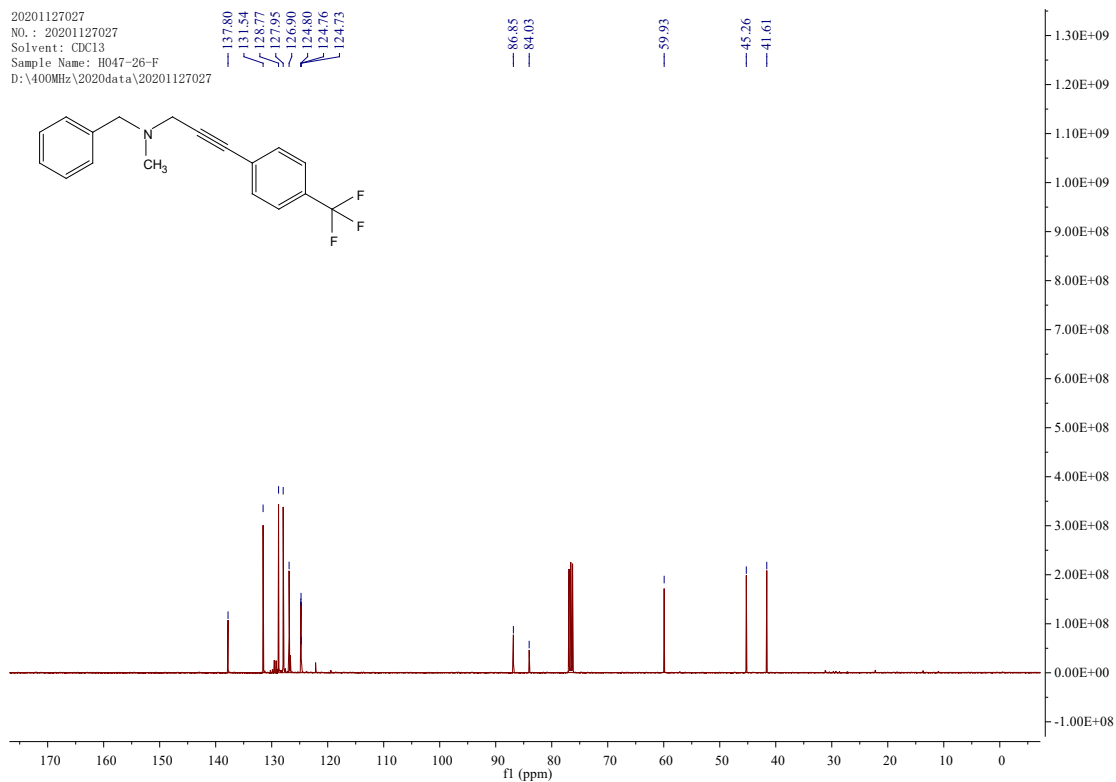


(3f)

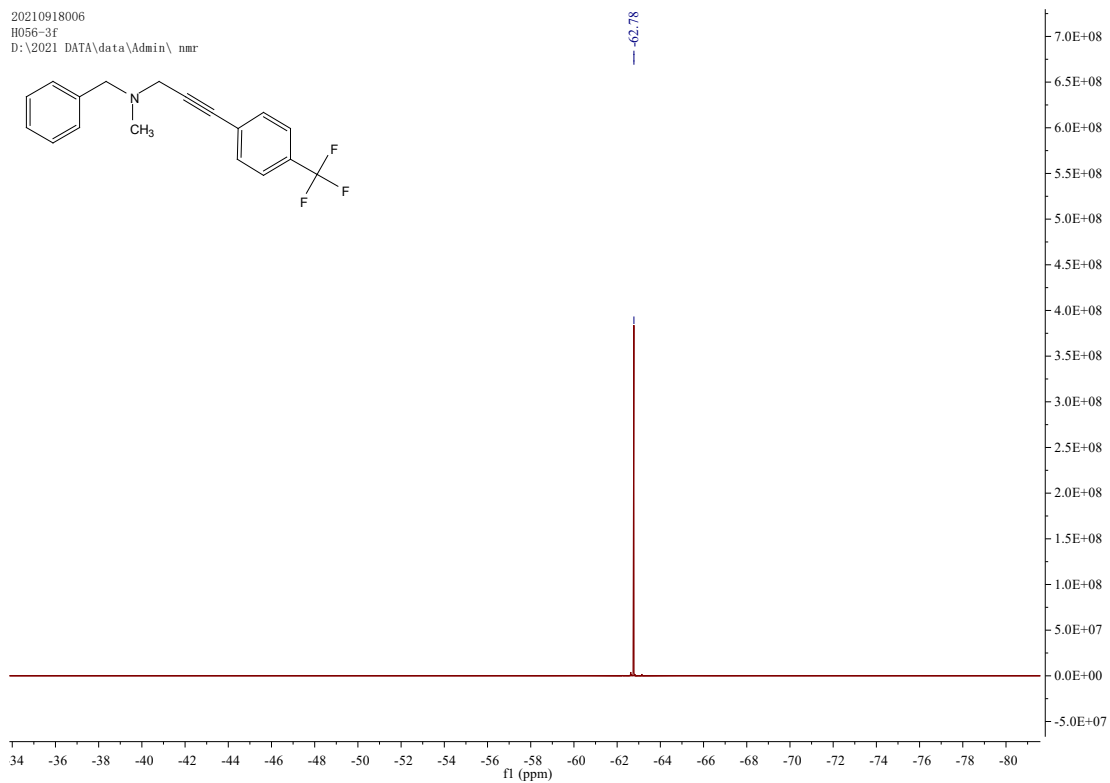
20201127027  
NO.: 20201127027  
Solvent: CDCl3  
Sample Name: H047-26-F  
D:\400MHz\2020data\20201127027



20201127027  
NO.: 20201127027  
Solvent: CDCl3  
Sample Name: H047-26-F  
D:\400MHz\2020data\20201127027

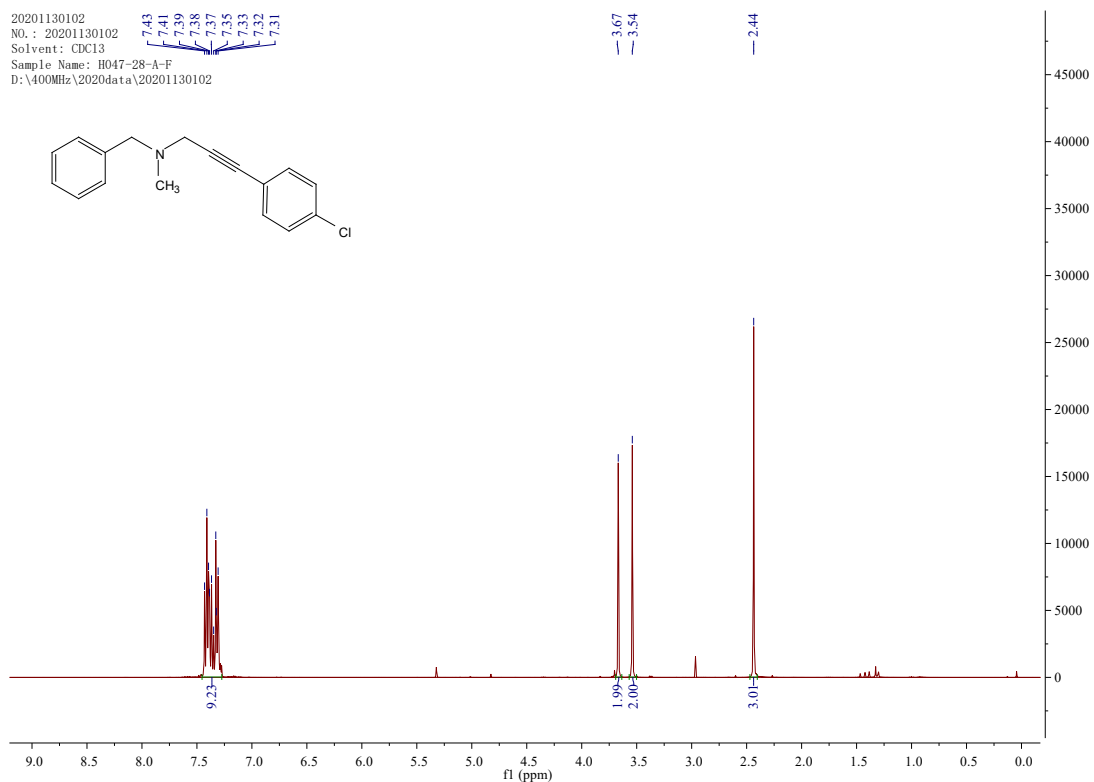


20210918006  
H056-3f  
D:\2021 DATA\data\Admin\ nmr

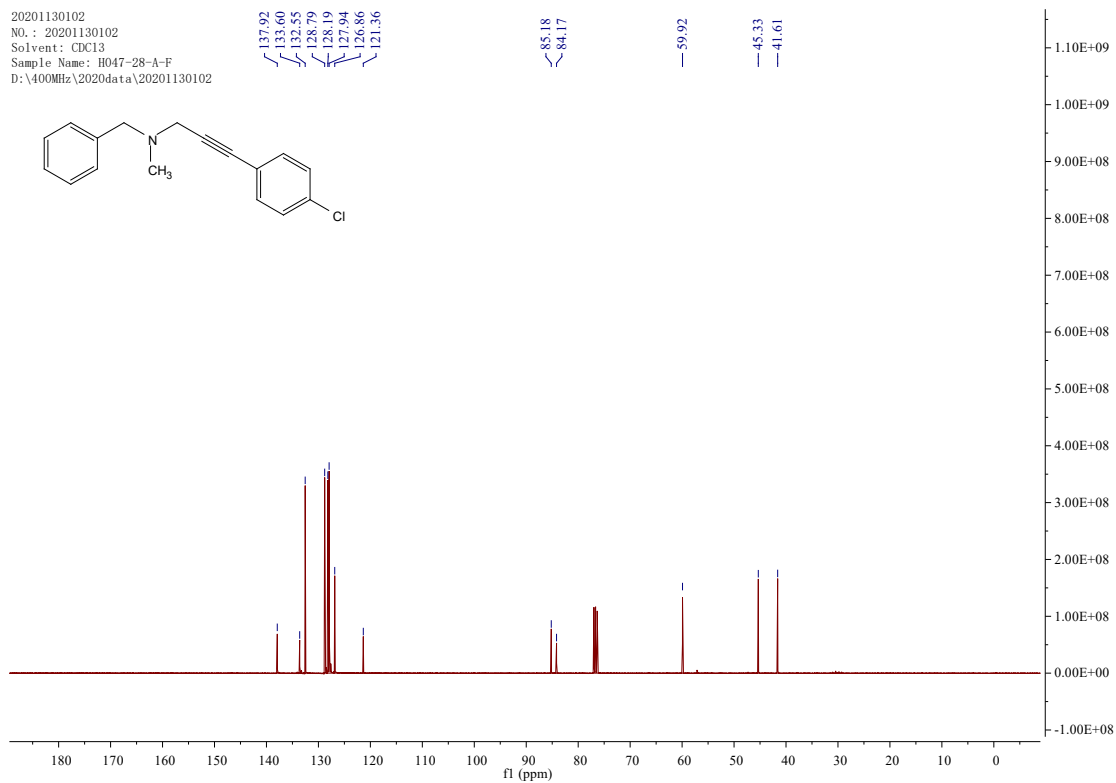


(3g)

20201130102  
NO.: 20201130102  
Solvent: CDCl3  
Sample Name: H047-28-A-F  
D:\400MHz\2020data\20201130102

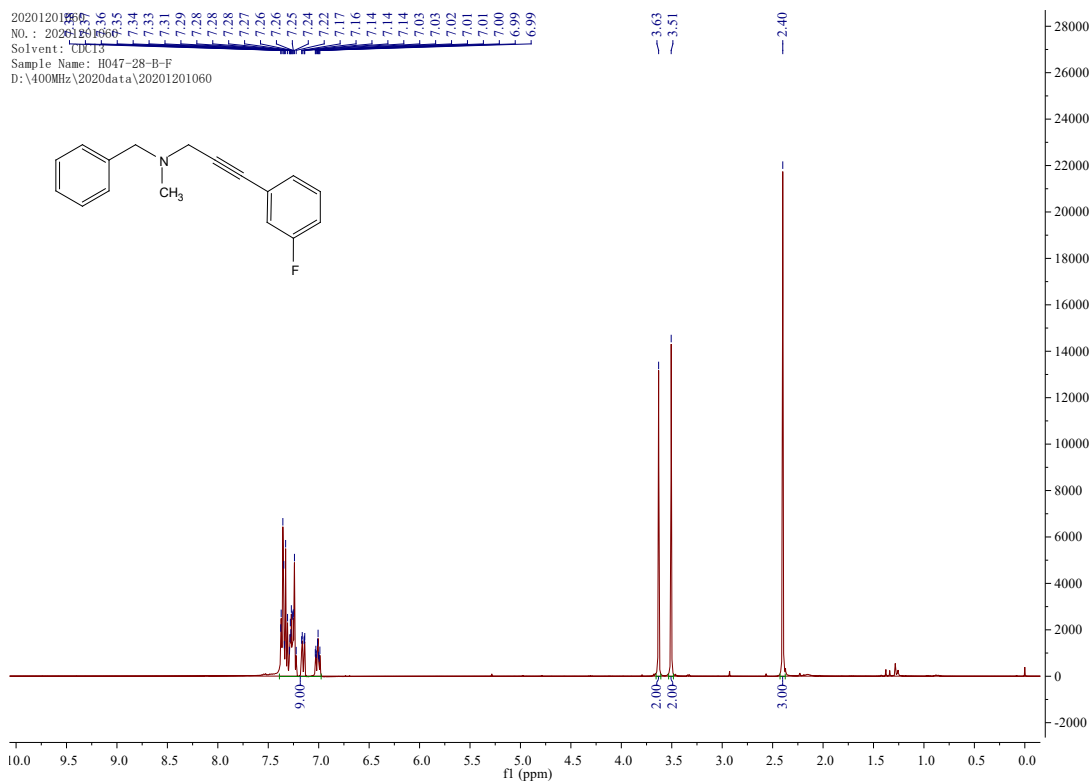


20201130102  
 NO.: 20201130102  
 Solvent: CDCl3  
 Sample Name: H047-28-A-F  
 D:\400MHz\2020data\20201130102

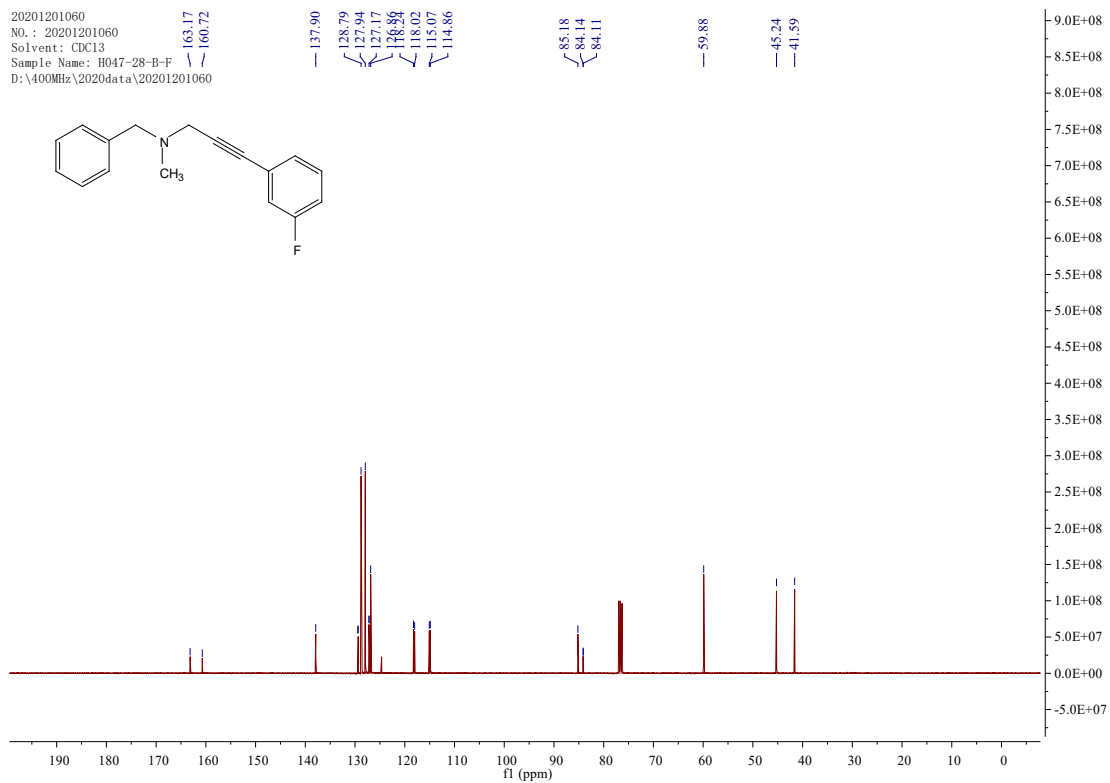


**(3h)**

20201201060  
 NO.: 20201201060  
 Solvent: CDCl3  
 Sample Name: H047-28-B-F  
 D:\400MHz\2020data\20201201060



20201201060  
NO.: 20201201060  
Solvent: CDCl3  
Sample Name: H047-28-B-F  
D:\400MHz\2020data\20201201060

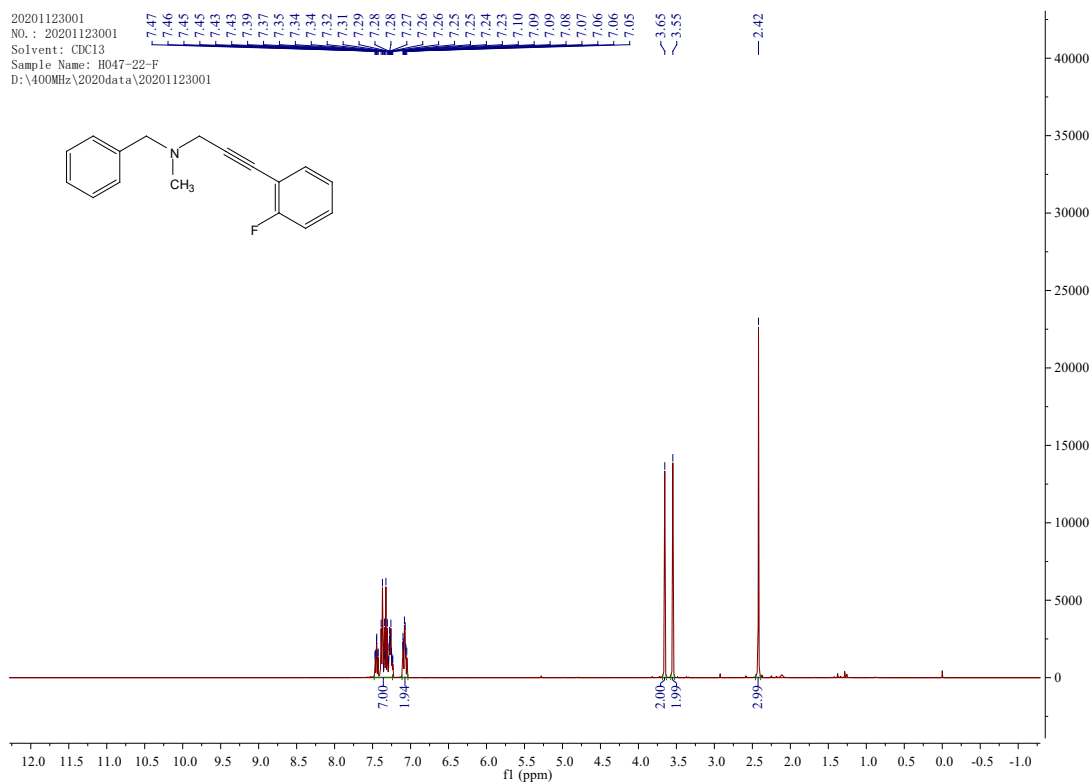


20210918007  
H056-3h  
D:\2021 DATA\data\Admin\ nmr

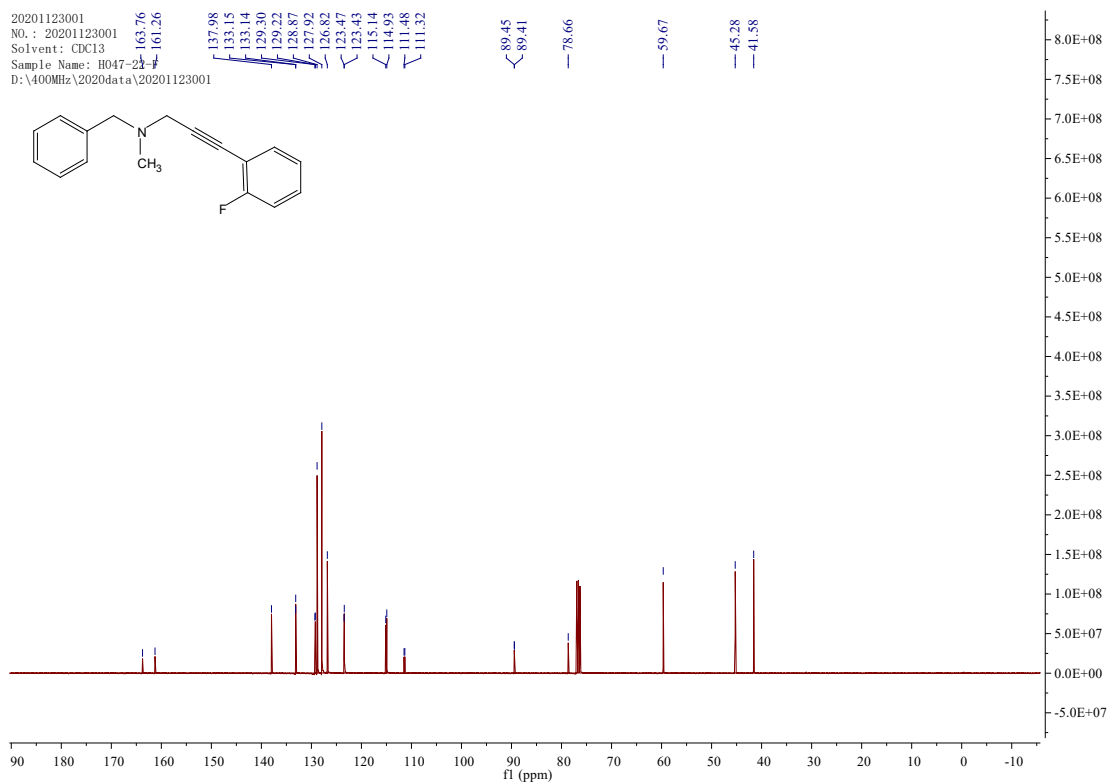


(3i)

20201123001  
NO.: 20201123001  
Solvent: CDC13  
Sample Name: H047-22-F  
D:\400MHz\2020data\20201123001

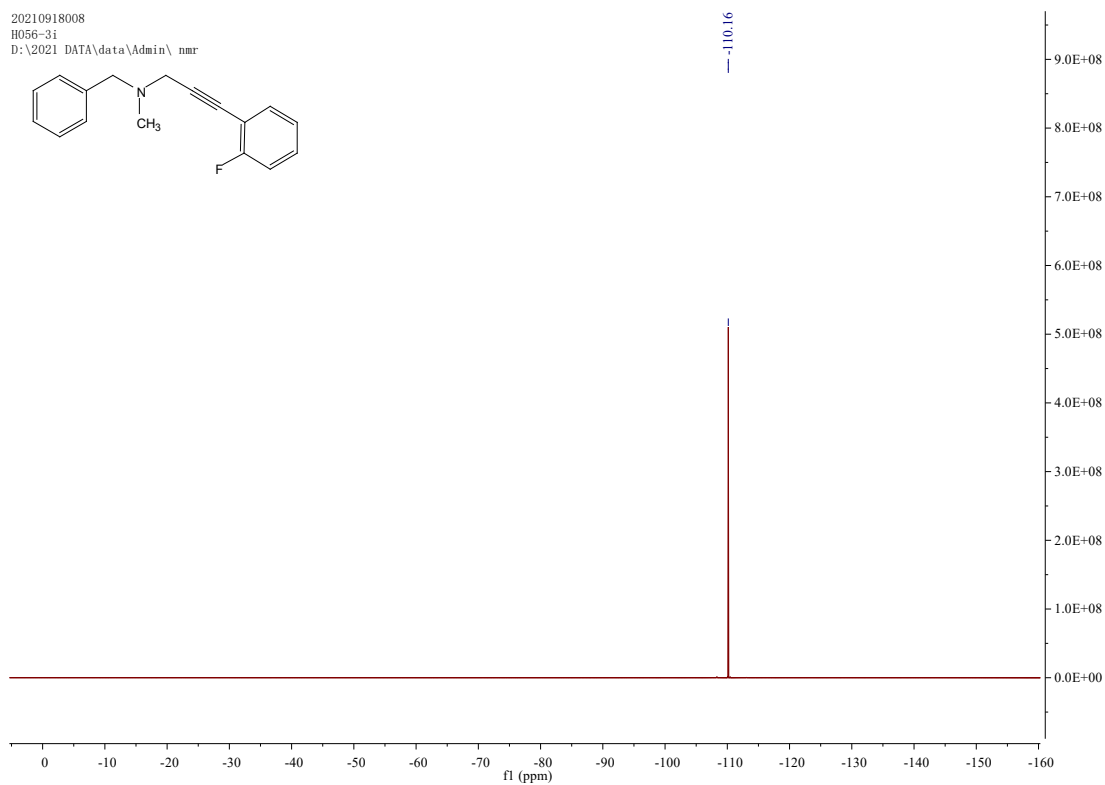
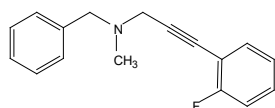


20201123001  
NO.: 20201123001  
Solvent: CDC13  
Sample Name: H047-22-F  
D:\400MHz\2020data\20201123001



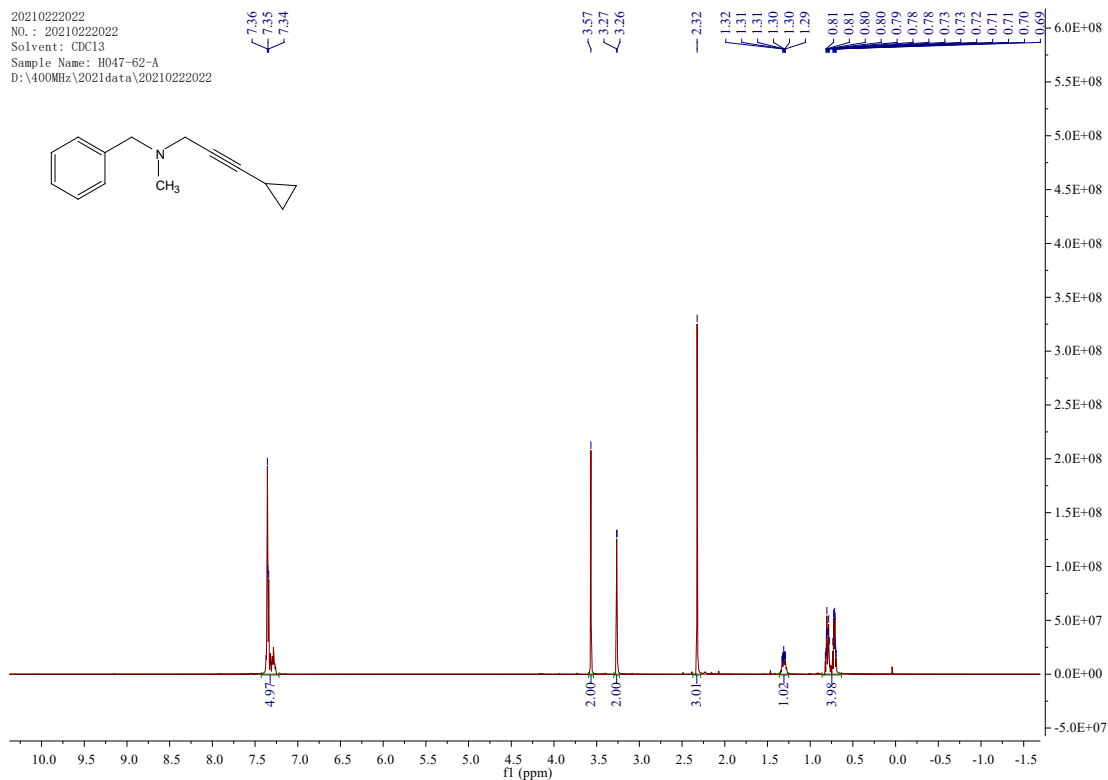
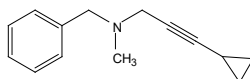


20210918008  
 H056-3i  
 D:\2021 DATA\data\Admin\ nmr

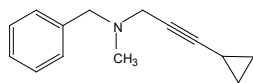
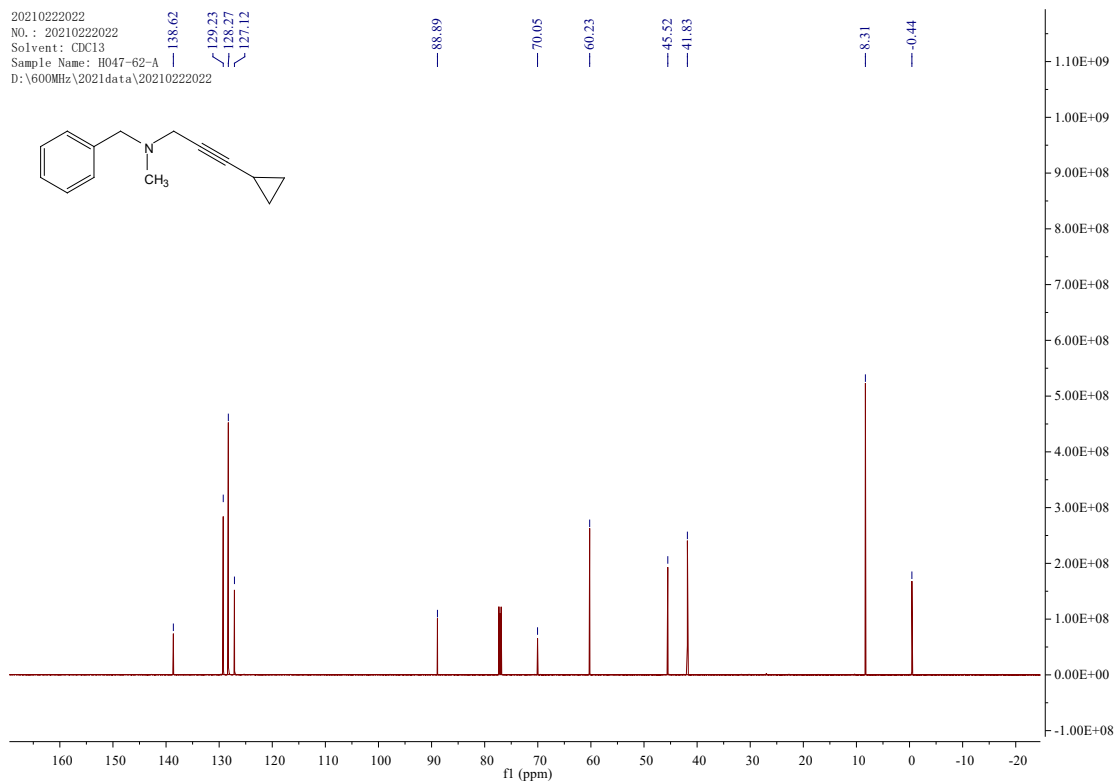


(3j)

20210222022  
 NO : 20210222022  
 Solvent: CDCl3  
 Sample Name: H047-62-A  
 D:\400MHz\2021data\20210222022

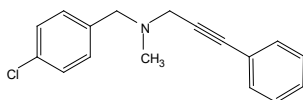
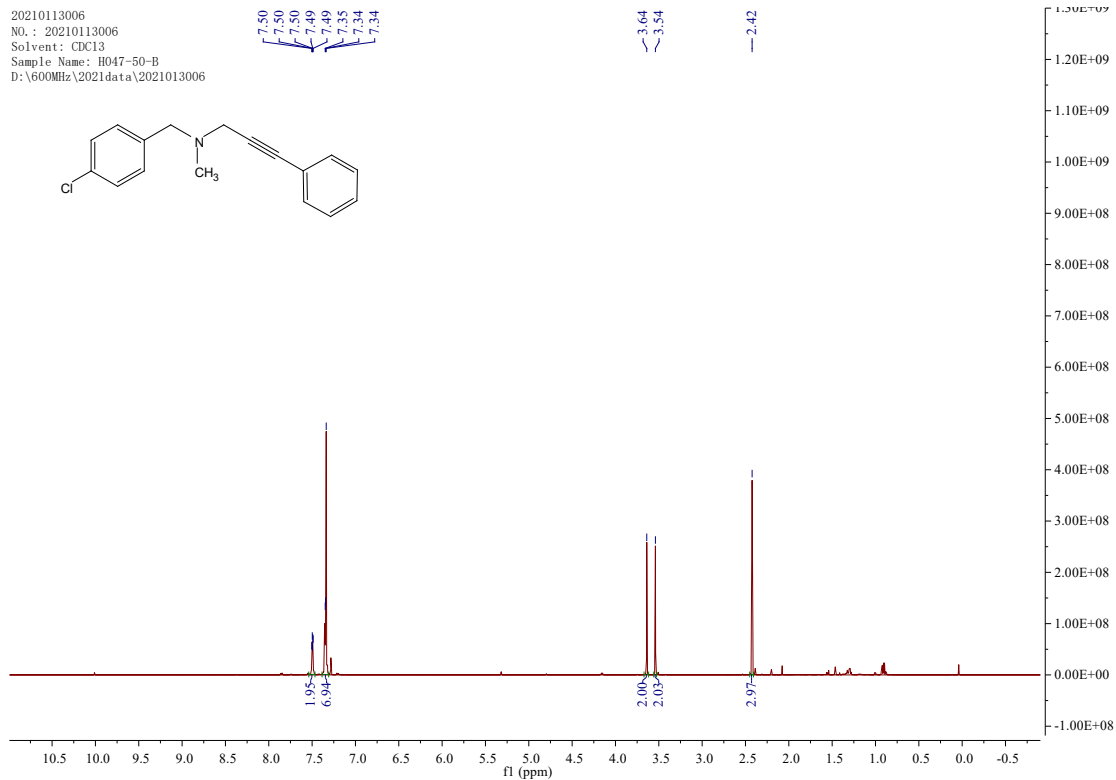


20210222022  
 NO.: 20210222022  
 Solvent: CDCl3  
 Sample Name: H047-62-A  
 D:\600MHz\2021data\20210222022

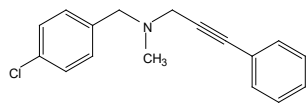
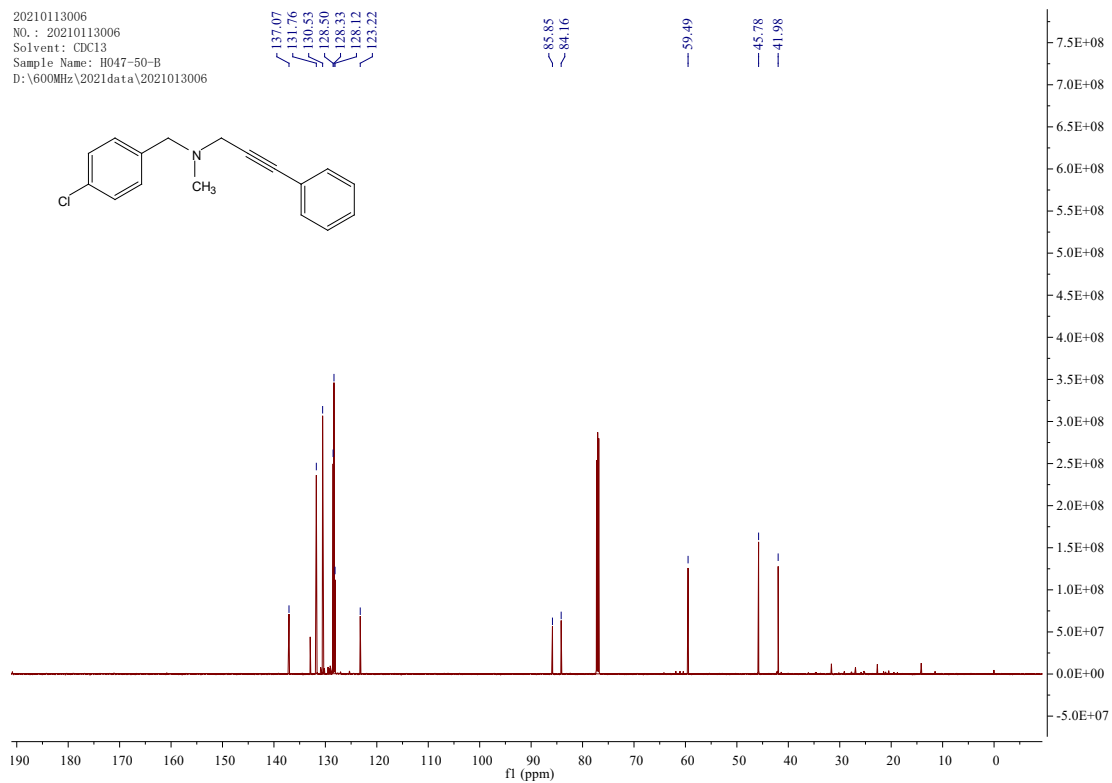


**(3k)**

20210113006  
 NO.: 20210113006  
 Solvent: CDCl3  
 Sample Name: H047-50-B  
 D:\600MHz\2021data\20210113006

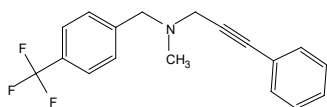
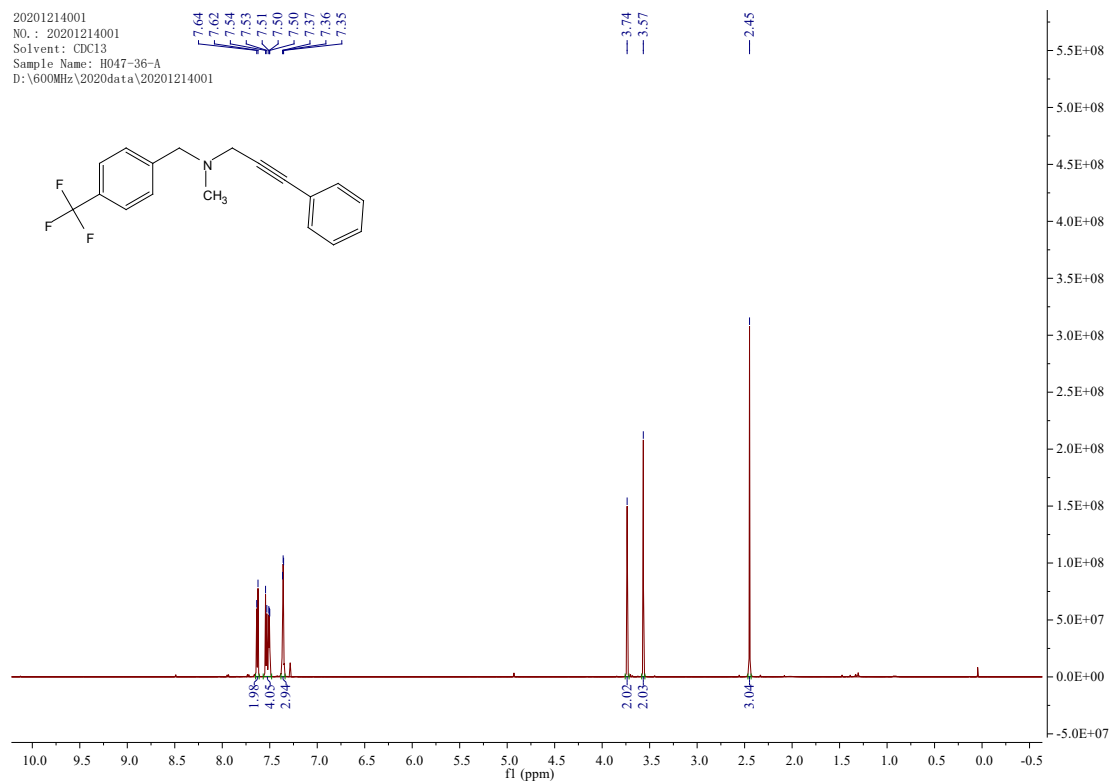


20210113006  
 NO.: 20210113006  
 Solvent: CDCl3  
 Sample Name: H047-50-B  
 D:\600MHz\2021data\2021013006

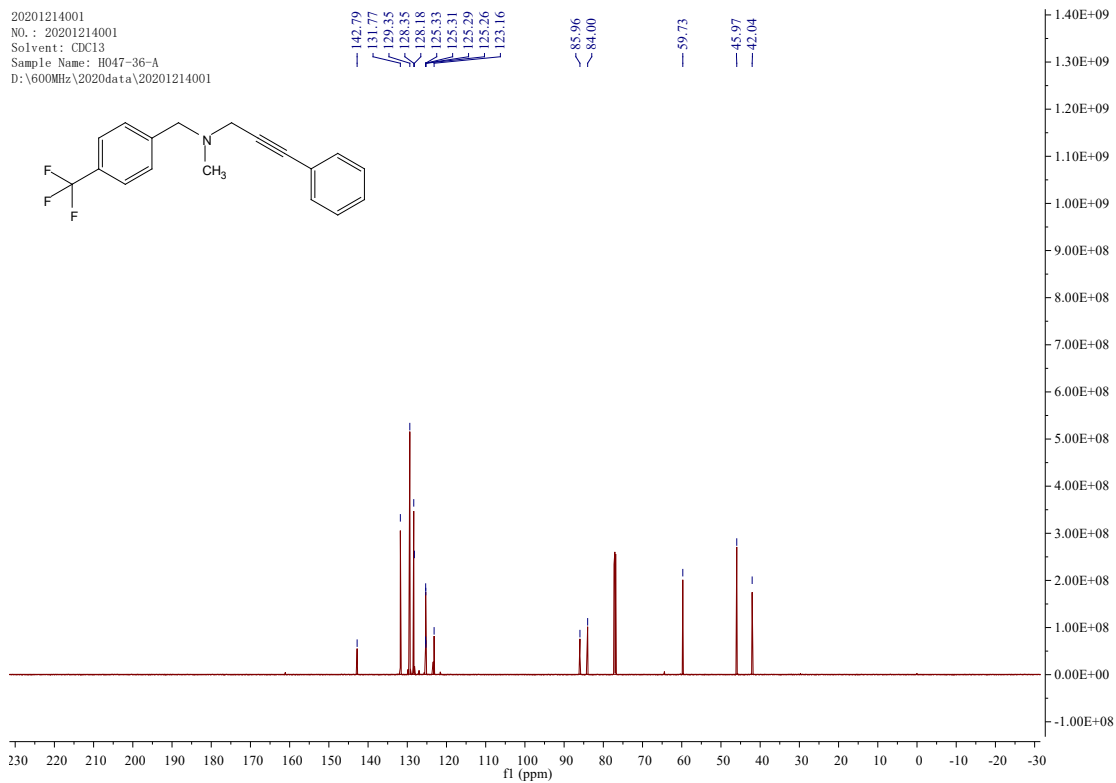


**(31)**

20201214001  
 NO.: 20201214001  
 Solvent: CDCl3  
 Sample Name: H047-36-A  
 D:\600MHz\2020data\20201214001

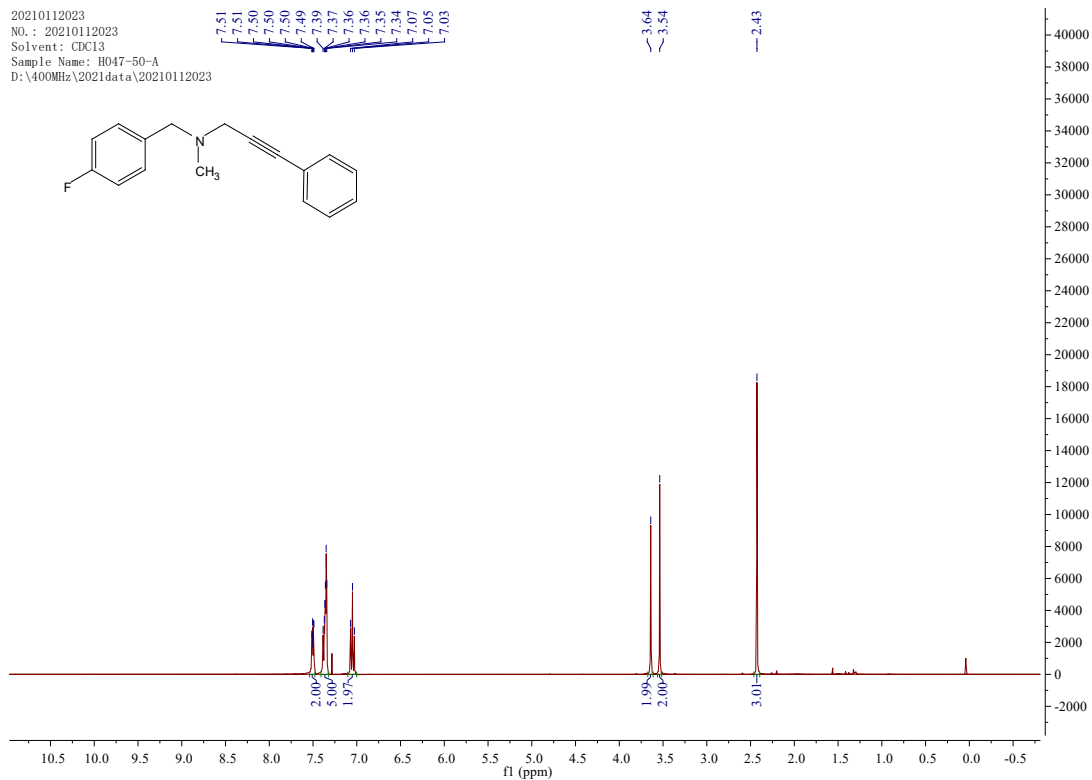


20201214001  
 NO.: 20201214001  
 Solvent: CDCl3  
 Sample Name: H047-36-A  
 D:\600MHz\2020data\20201214001

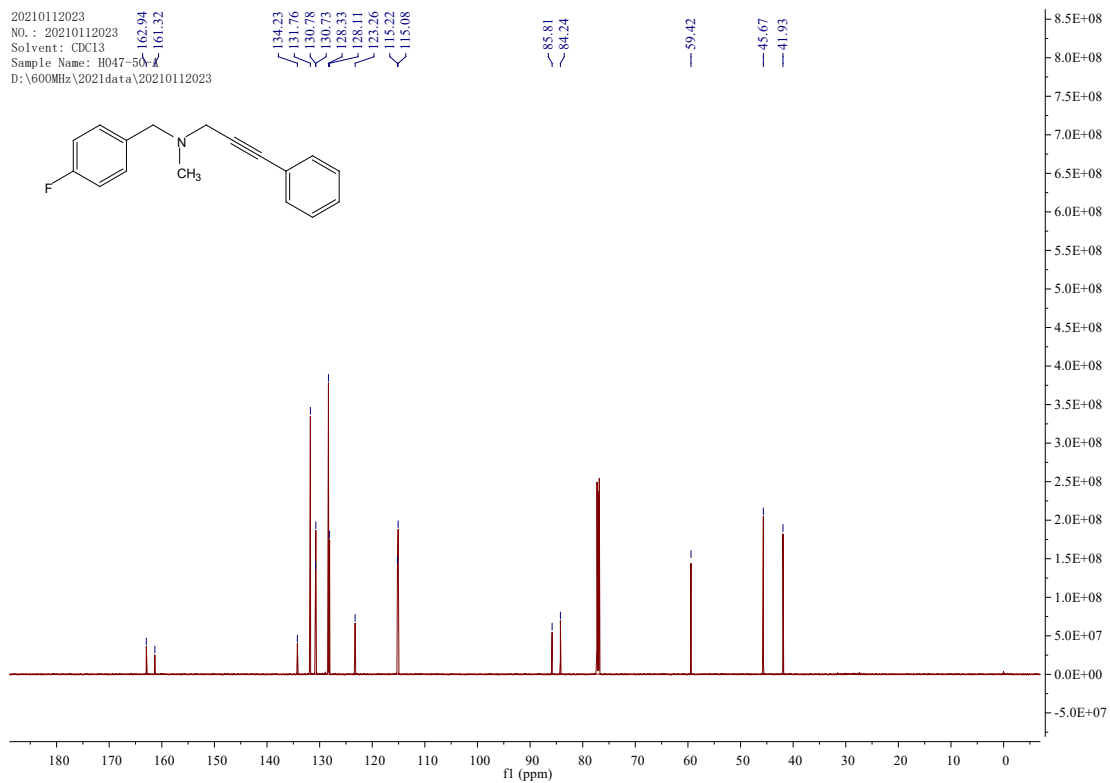


**(3m)**

20210112023  
 NO.: 20210112023  
 Solvent: CDCl3  
 Sample Name: H047-50-A  
 D:\400MHz\2021data\20210112023

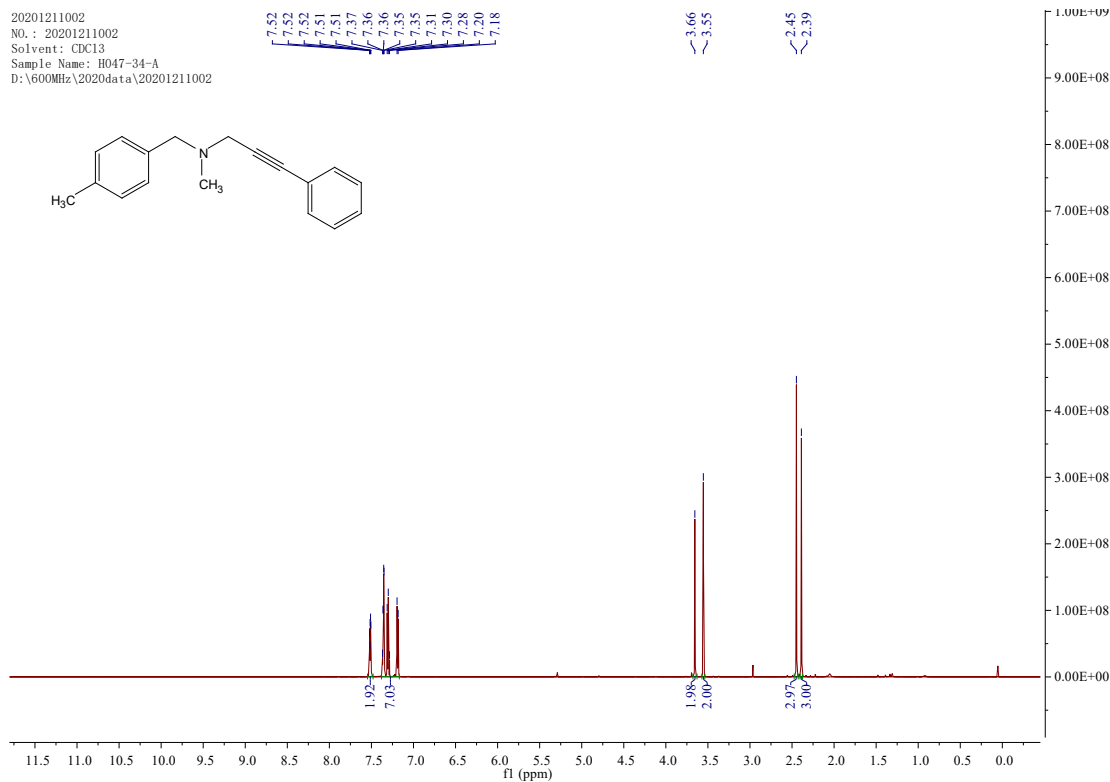


20210112023  
 NO.: 20210112023  
 Solvent: CDCl3  
 Sample Name: H047-50-A  
 D:\600MHz\2021data\20210112023

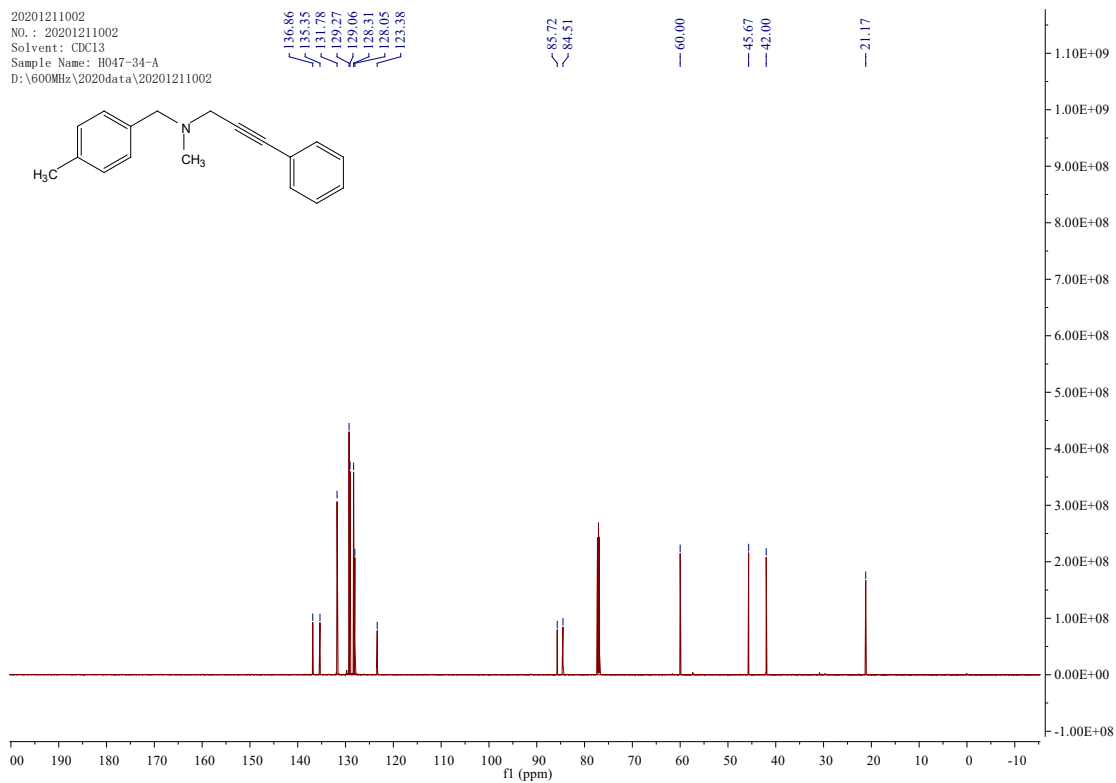


**(3n)**

20201211002  
 NO.: 20201211002  
 Solvent: CDCl3  
 Sample Name: H047-34-A  
 D:\600MHz\2020data\20201211002

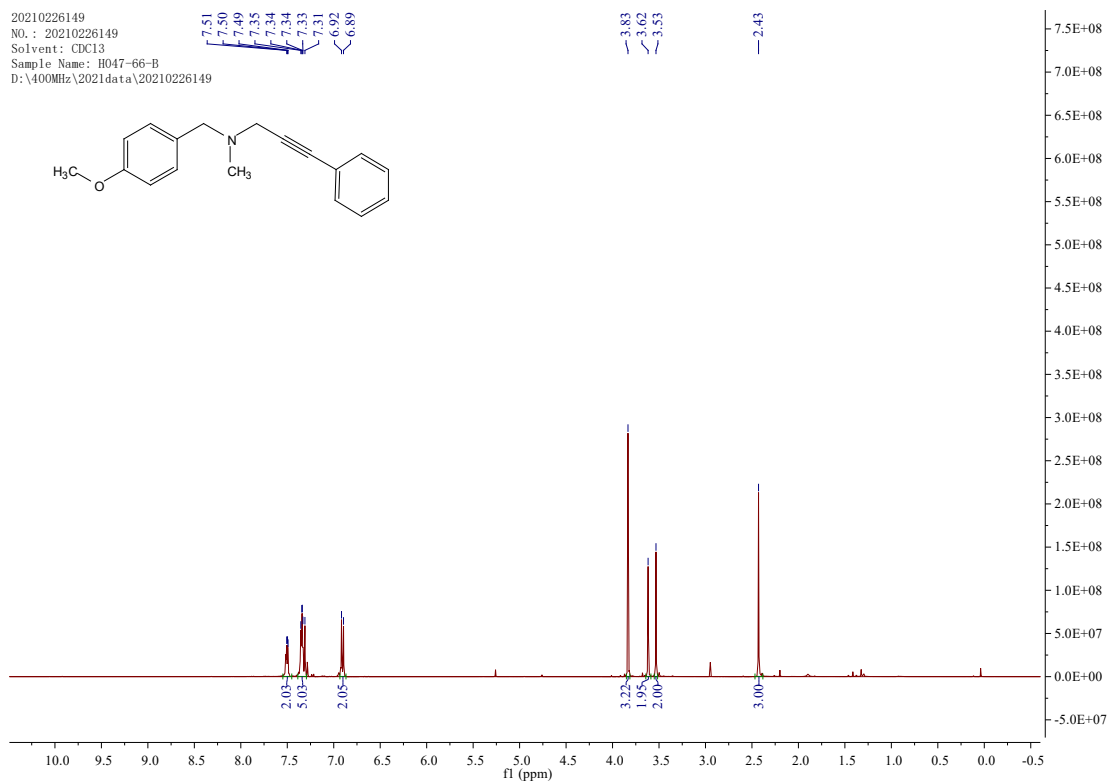


20201211002  
 NO.: 20201211002  
 Solvent: CDCl3  
 Sample Name: H047-34-A  
 D:\600MHz\2020data\20201211002

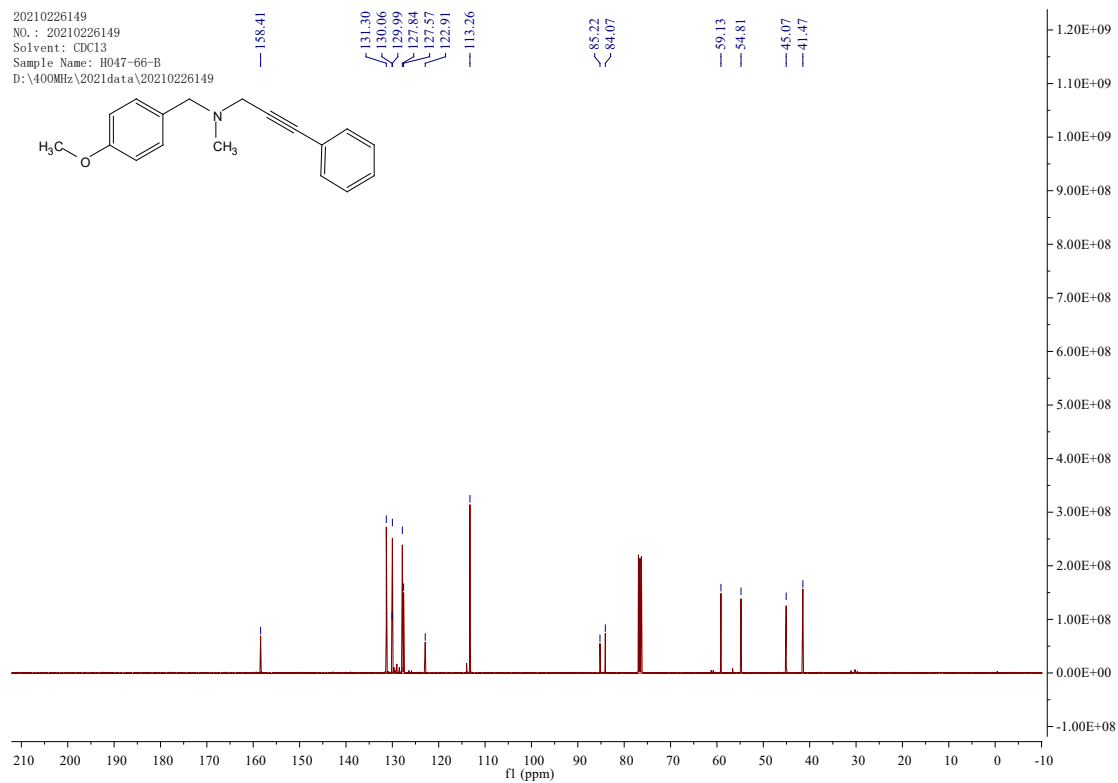


**(30)**

20210226149  
 NO.: 20210226149  
 Solvent: CDCl3  
 Sample Name: H047-66-B  
 D:\400MHz\2021data\20210226149

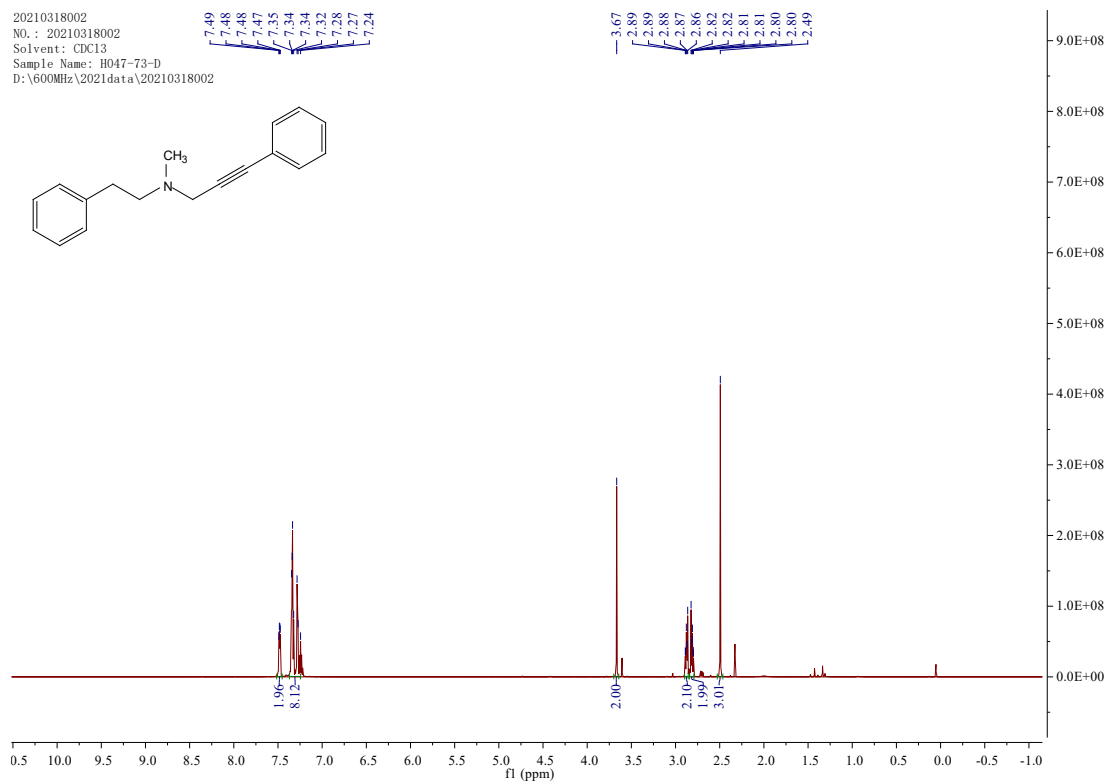


20210226149  
 NO.: 20210226149  
 Solvent: CDCl3  
 Sample Name: H047-66-B  
 D:\400MHz\2021data\20210226149

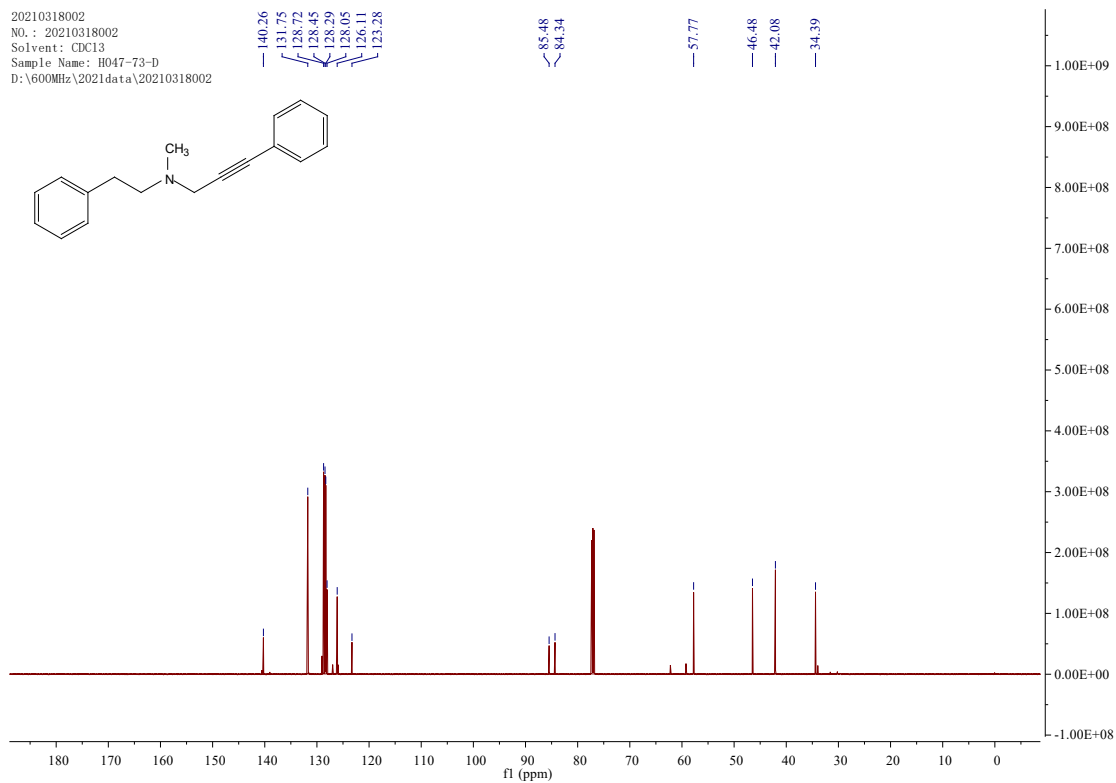


**(3p)**

20210318002  
 NO.: 20210318002  
 Solvent: CDCl3  
 Sample Name: H047-73-D  
 D:\600MHz\2021data\20210318002

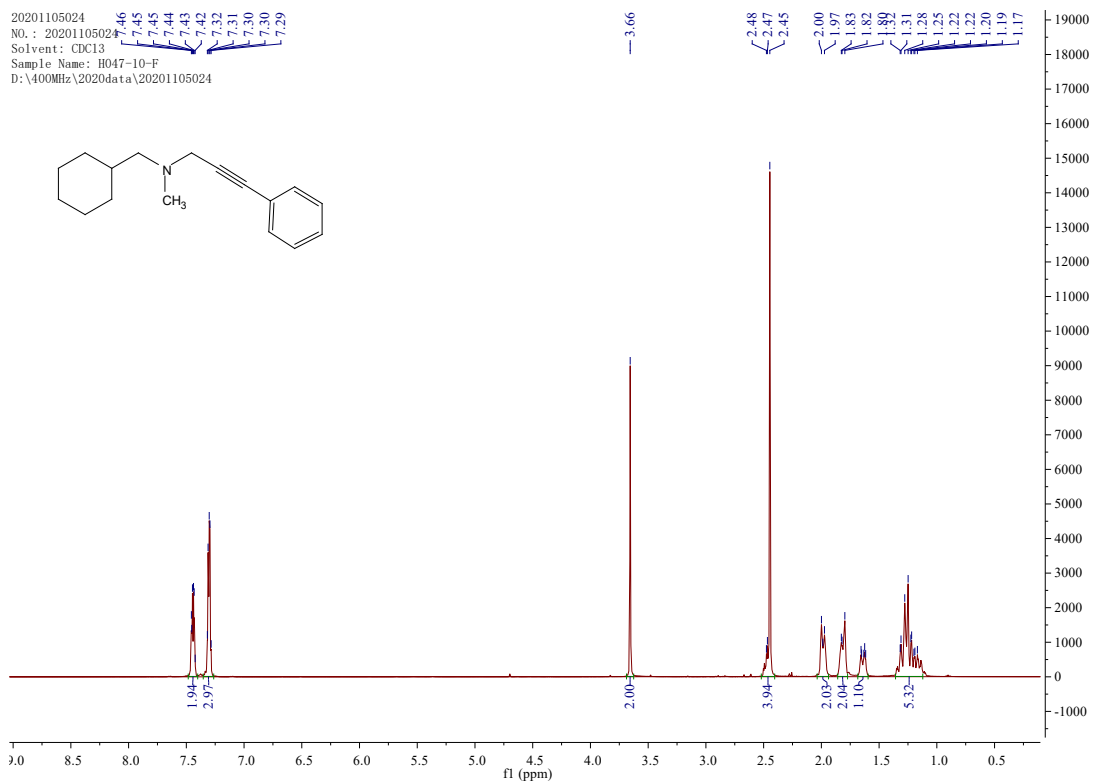


20210318002  
 NO.: 20210318002  
 Solvent: CDCl3  
 Sample Name: H047-73-D  
 D:\600MHz\2021data\20210318002



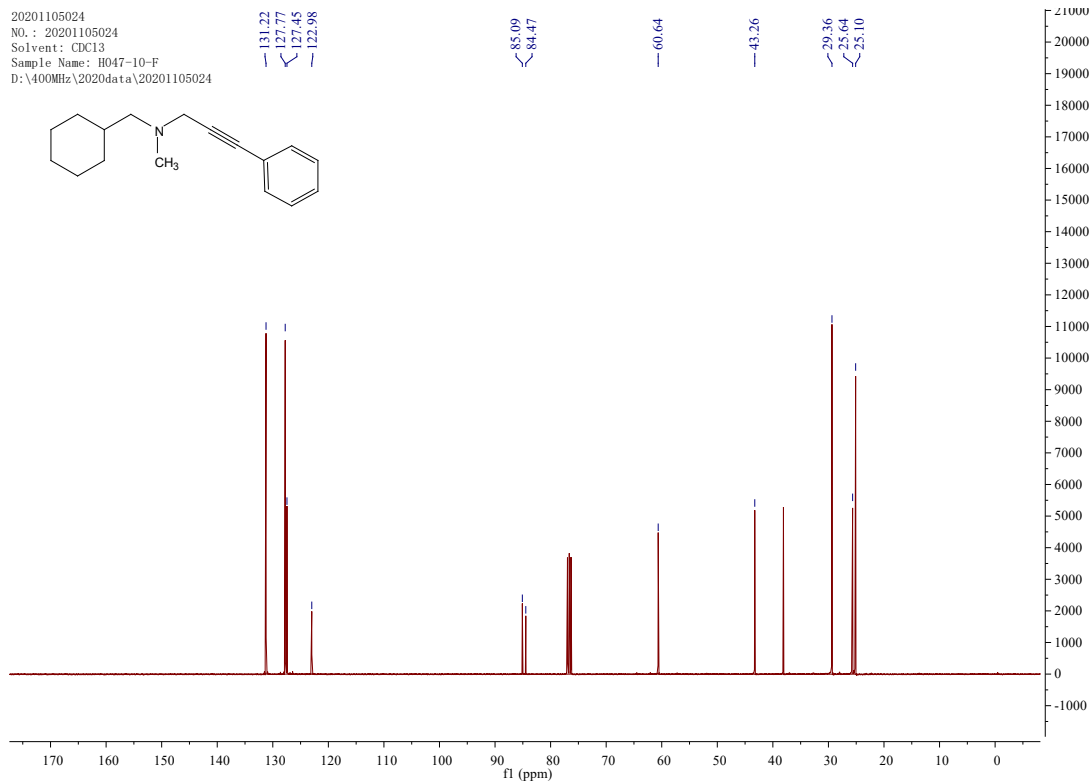
**(3q)**

20201105024  
 NO.: 20201105024  
 Solvent: CDCl3  
 Sample Name: H047-10-F  
 D:\400MHz\2020data\20201105024



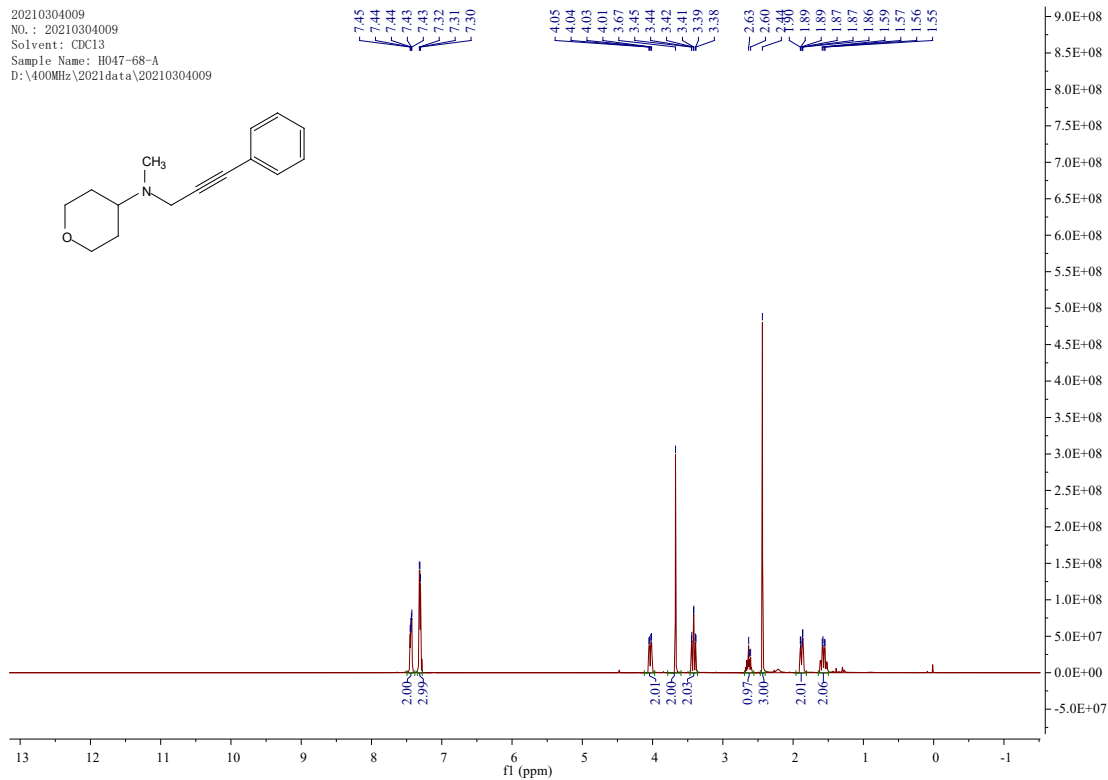


20201105024  
 NO.: 20201105024  
 Solvent: CDCl3  
 Sample Name: H047-10-F  
 D:\400MHz\2020data\20201105024

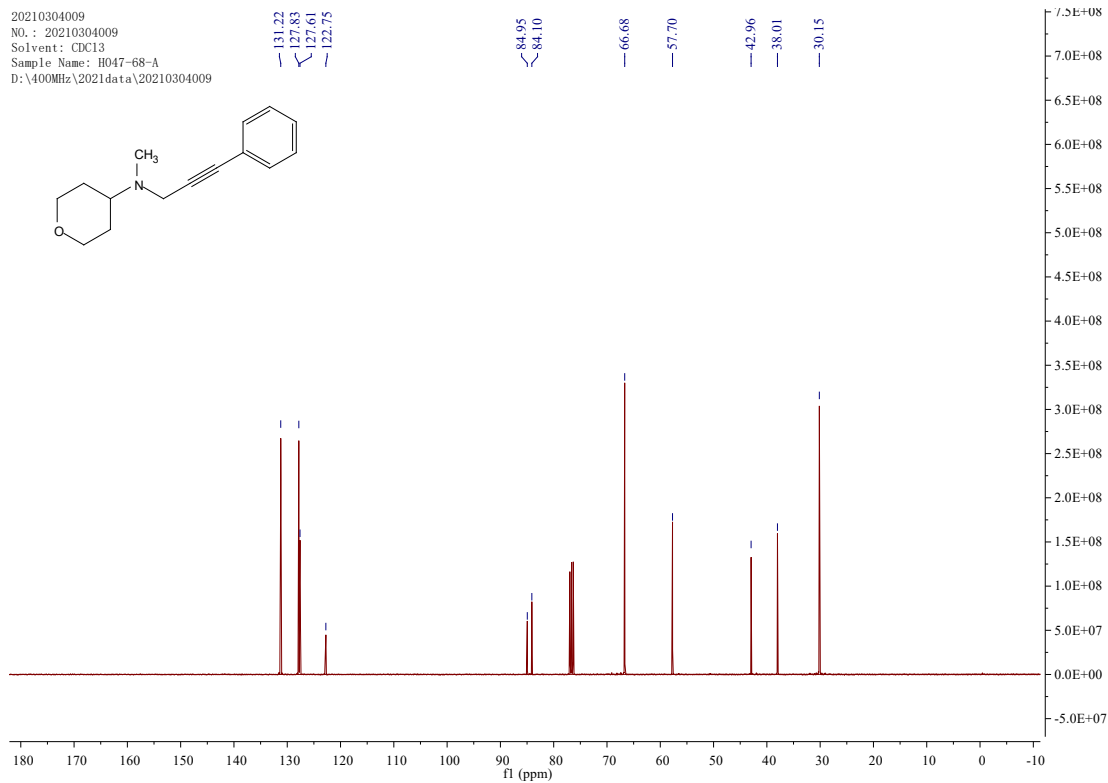


**(3r)**

20210304009  
 NO.: 20210304009  
 Solvent: CDCl3  
 Sample Name: H047-68-A  
 D:\400MHz\2021data\20210304009

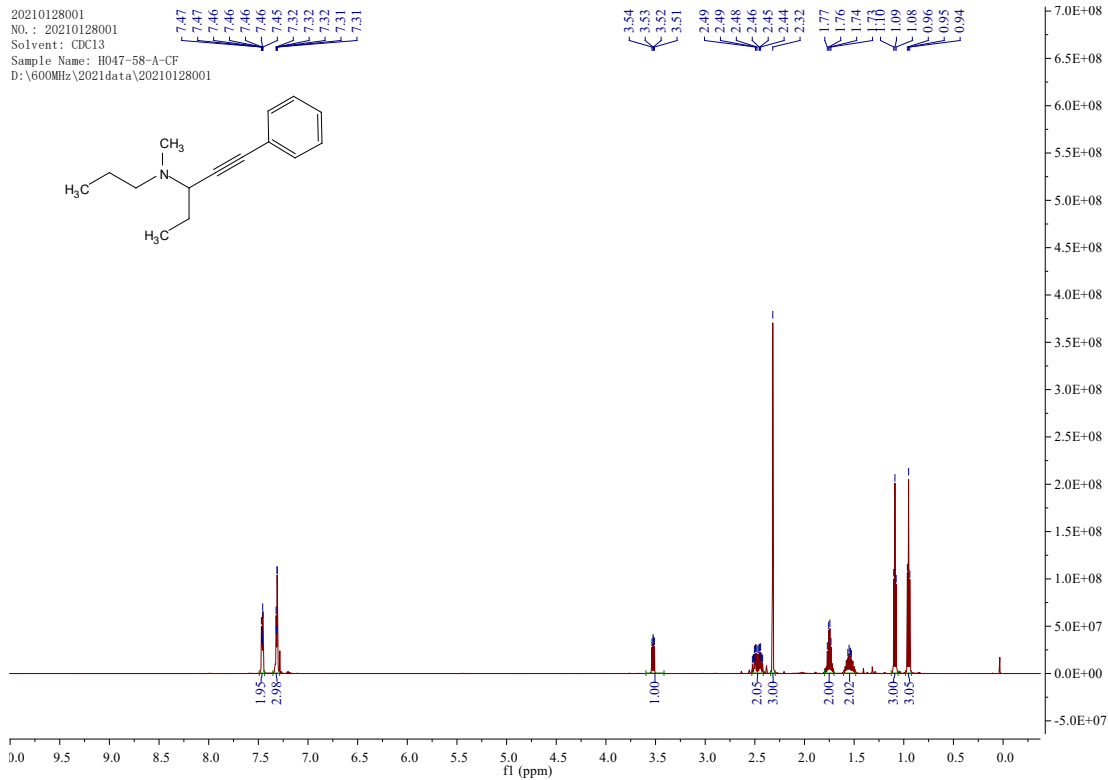


20210304009  
 NO.: 20210304009  
 Solvent: CDC13  
 Sample Name: H047-68-A  
 D:\400MHz\2021data\20210304009

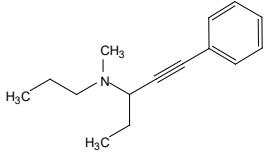
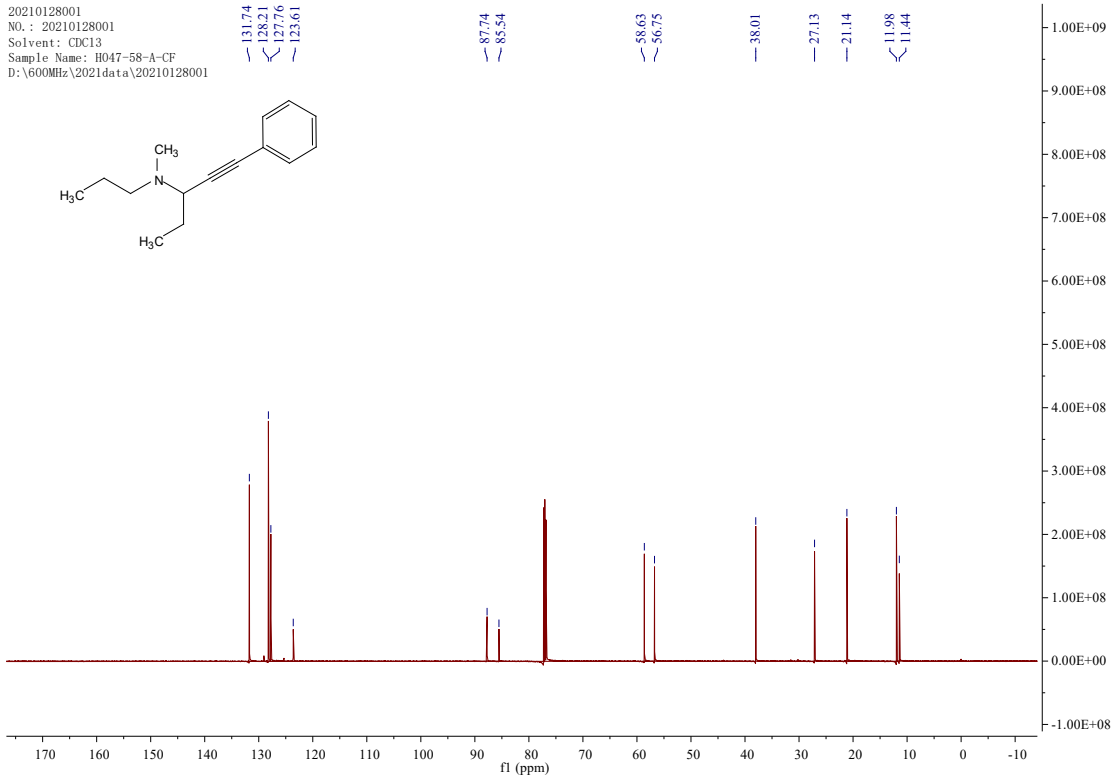


**(3s)**

20210128001  
 NO.: 20210128001  
 Solvent: CDC13  
 Sample Name: H047-58-A-CF  
 D:\600MHz\2021data\20210128001

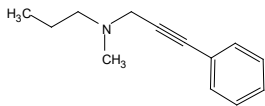
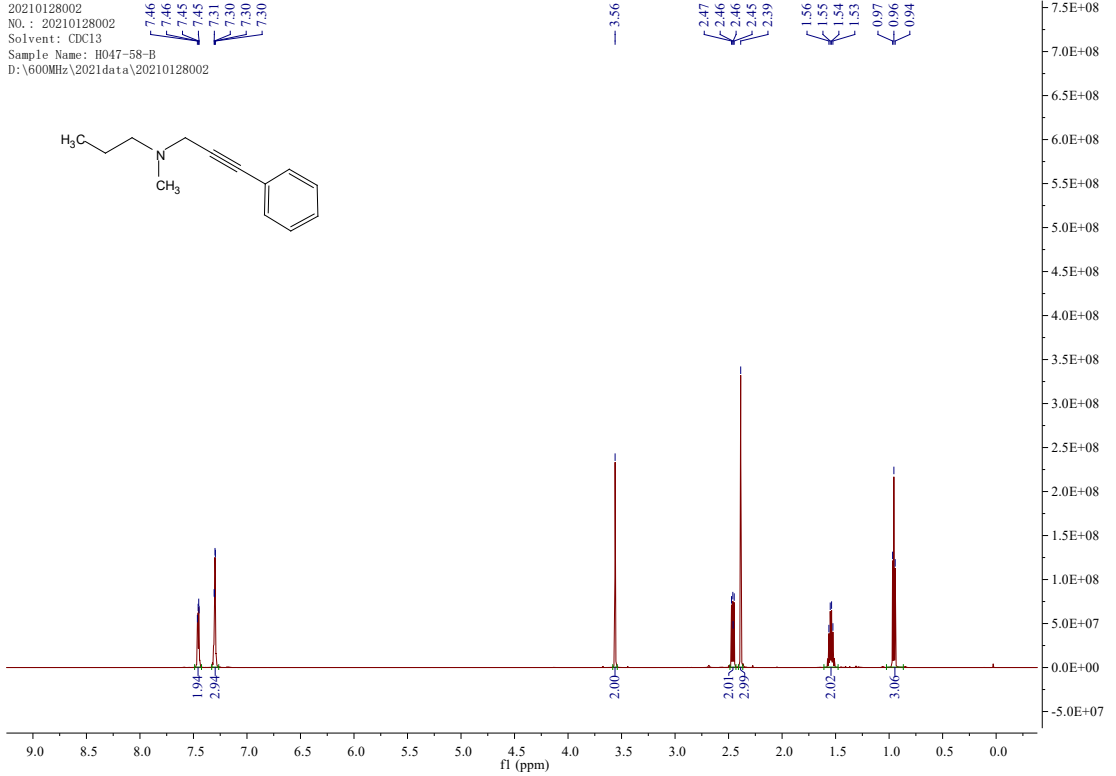


20210128001  
 NO.: 20210128001  
 Solvent: CDC13  
 Sample Name: H047-58-A-CF  
 D:\600MHz\2021data\20210128001

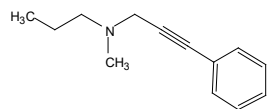
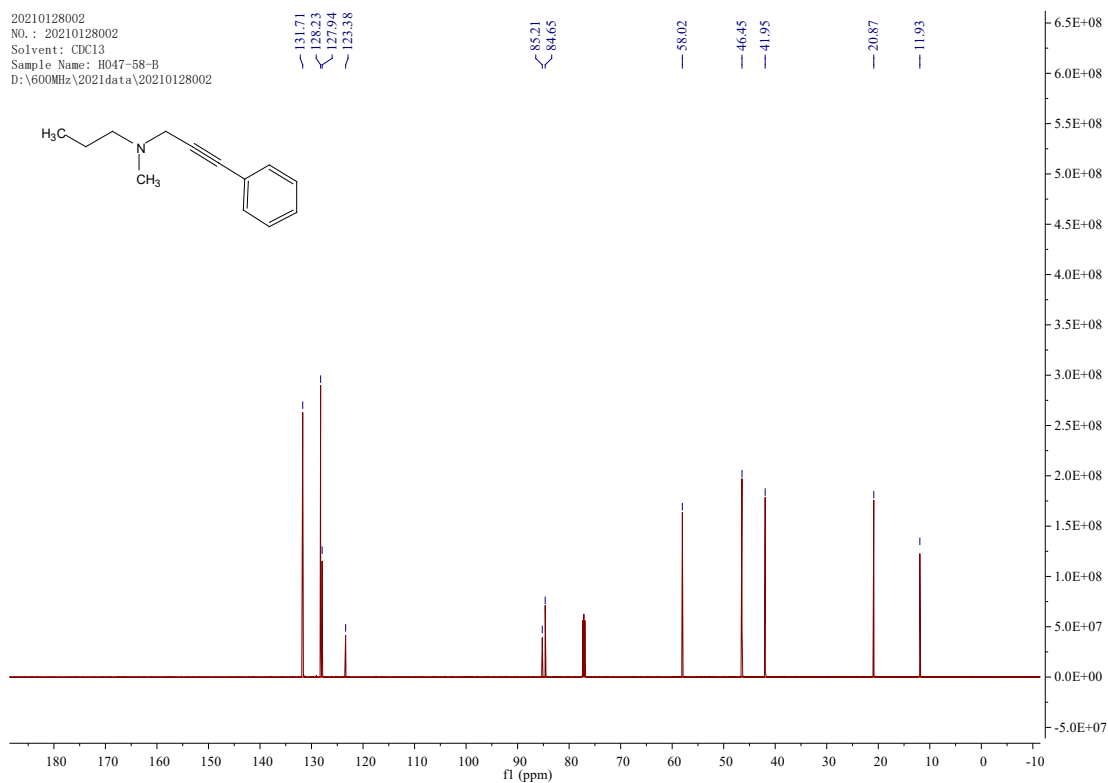


**(3s')**

20210128002  
 NO.: 20210128002  
 Solvent: CDC13  
 Sample Name: H047-58-B  
 D:\600MHz\2021data\20210128002

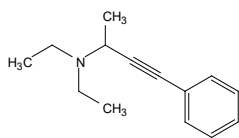
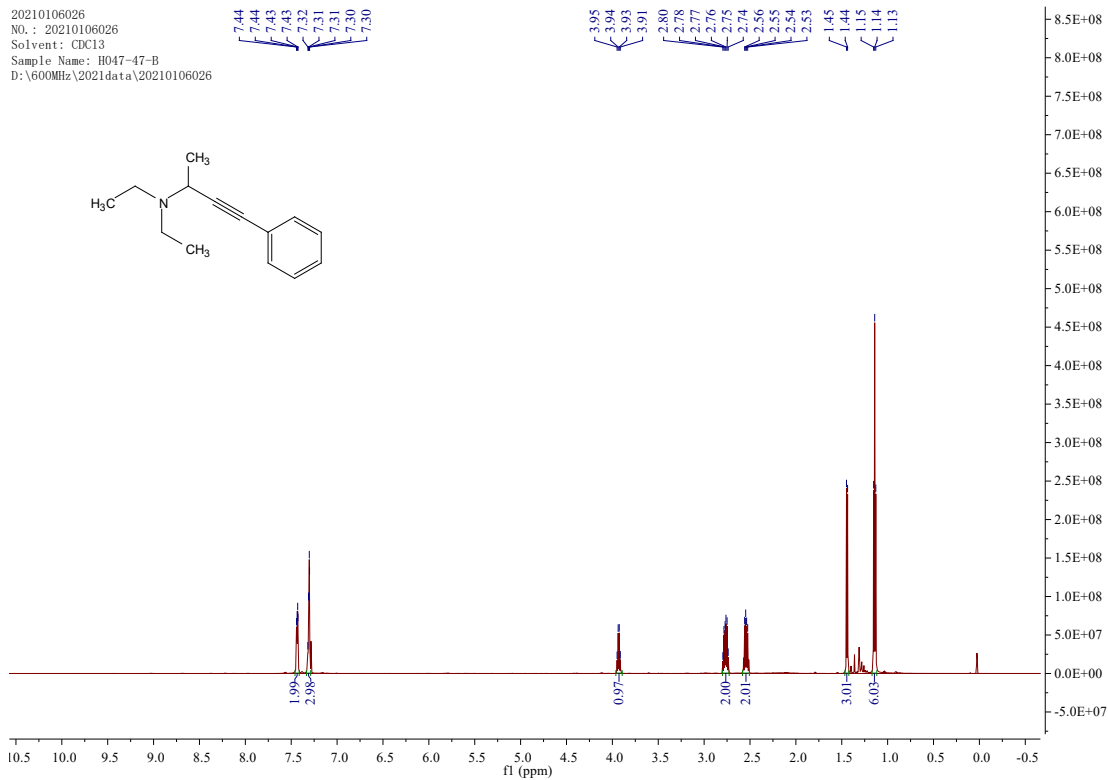


20210128002  
 NO.: 20210128002  
 Solvent: CDC13  
 Sample Name: H047-58-B  
 D:\600MHz\2021data\20210128002

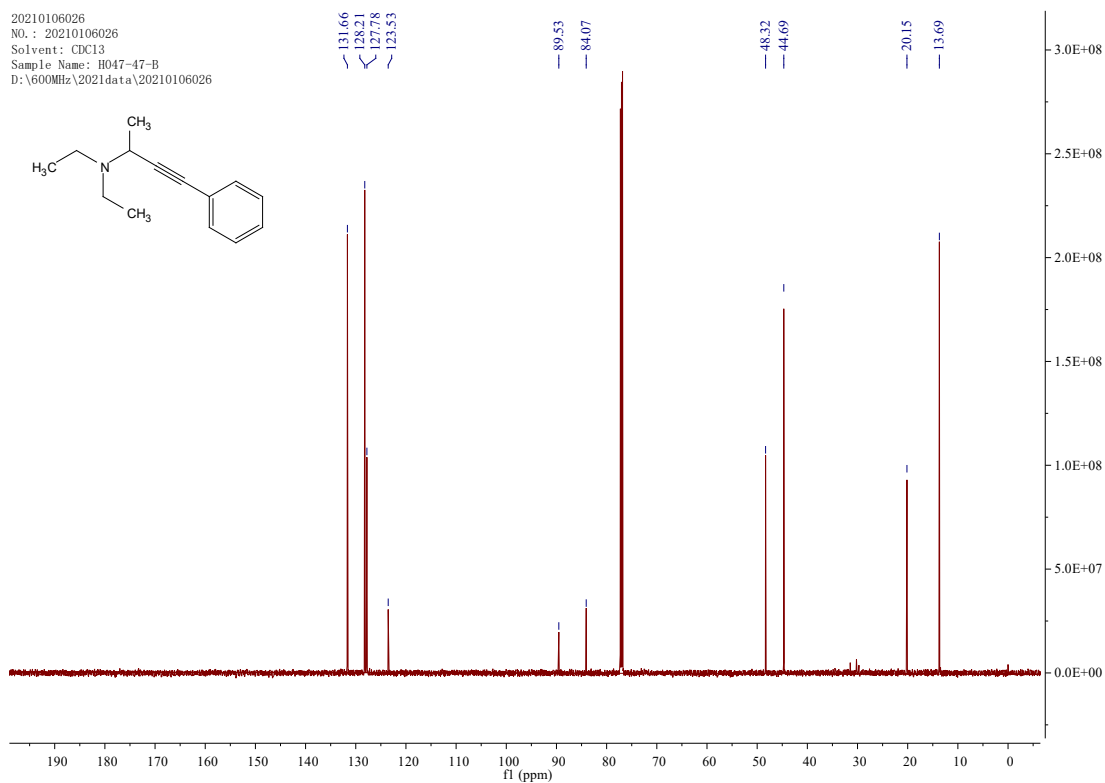


**(3t)**

20210106026  
 NO.: 20210106026  
 Solvent: CDC13  
 Sample Name: H047-47-B  
 D:\600MHz\2021data\20210106026

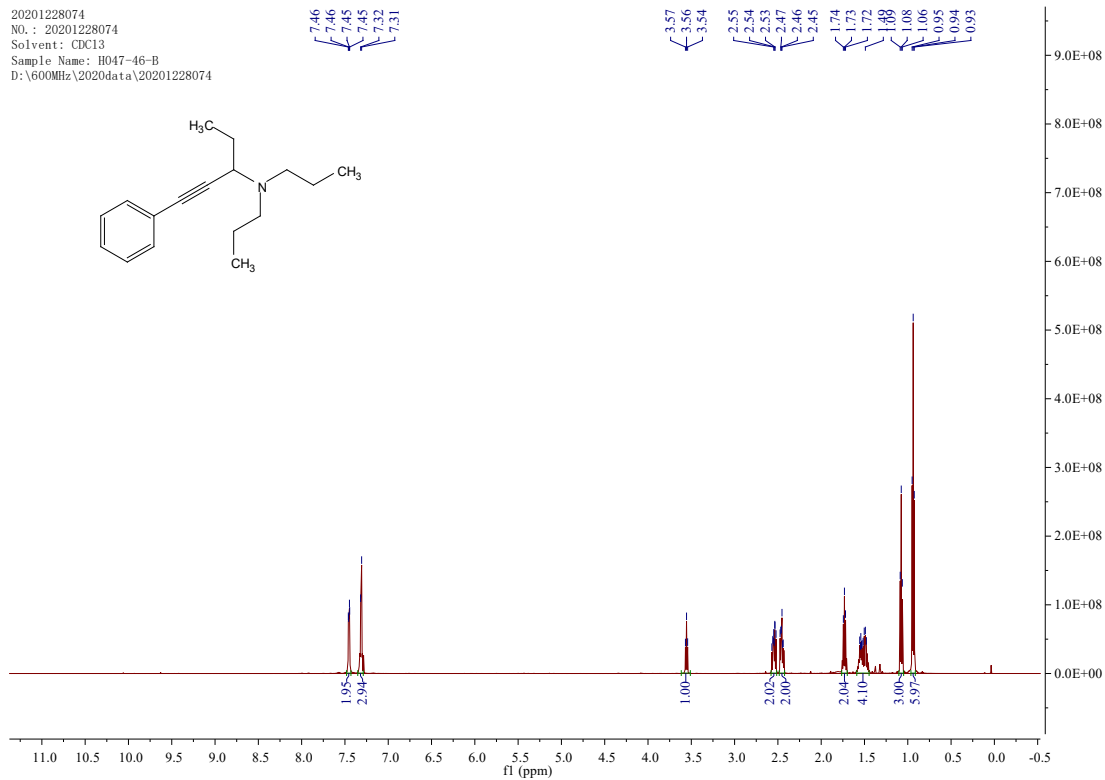


20210106026  
 NO.: 20210106026  
 Solvent: CDC13  
 Sample Name: H047-47-B  
 D:\600MHz\2021data\20210106026

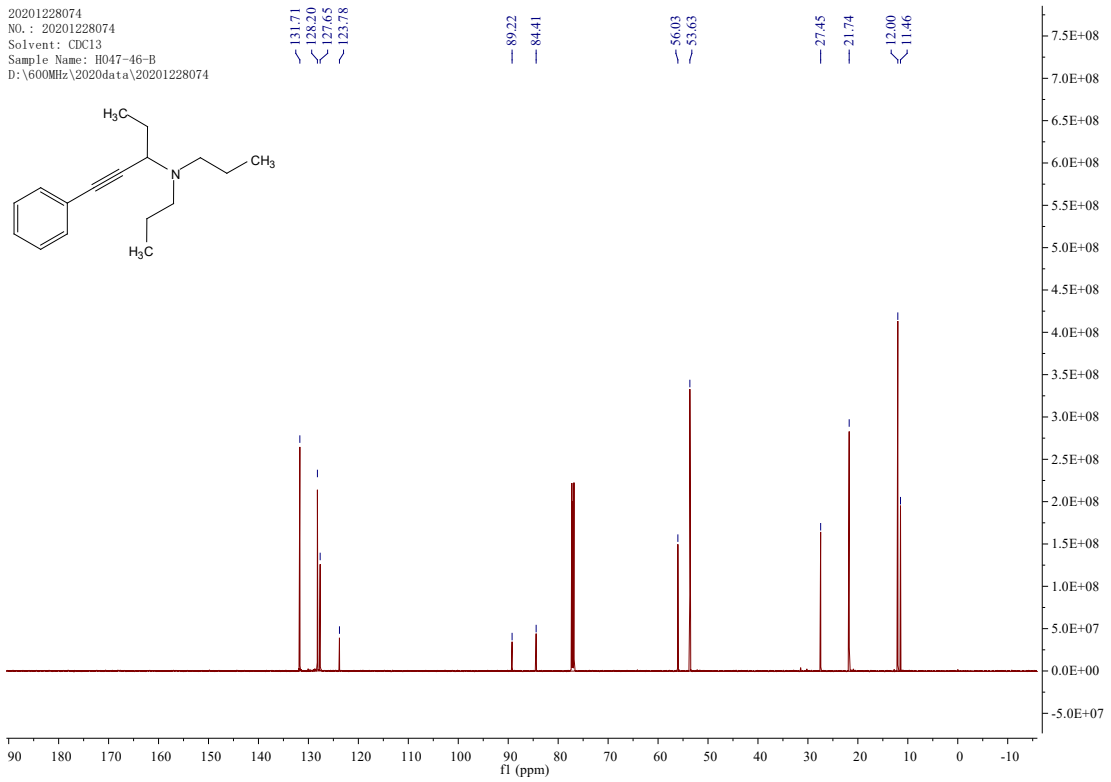


**(3u)**

20201228074  
 NO.: 20201228074  
 Solvent: CDC13  
 Sample Name: H047-46-B  
 D:\600MHz\2020data\20201228074

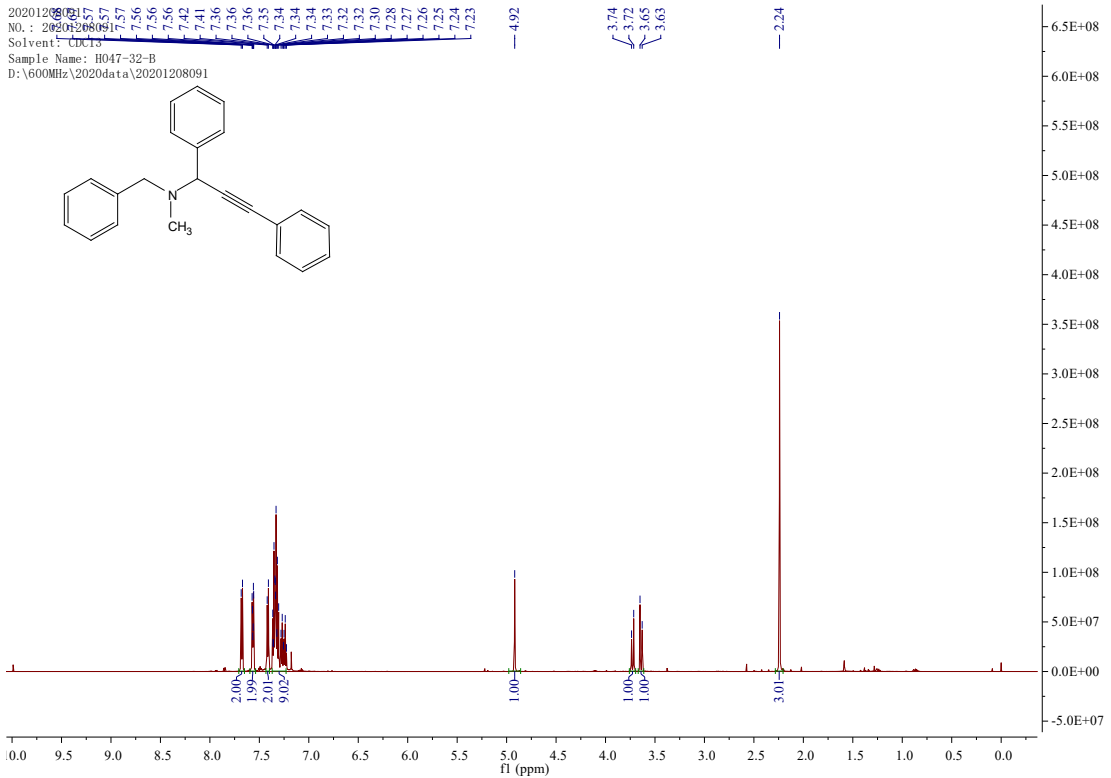


20201228074  
 NO.: 20201228074  
 Solvent: CDC13  
 Sample Name: H047-46-B  
 D:\600MHz\2020data\20201228074

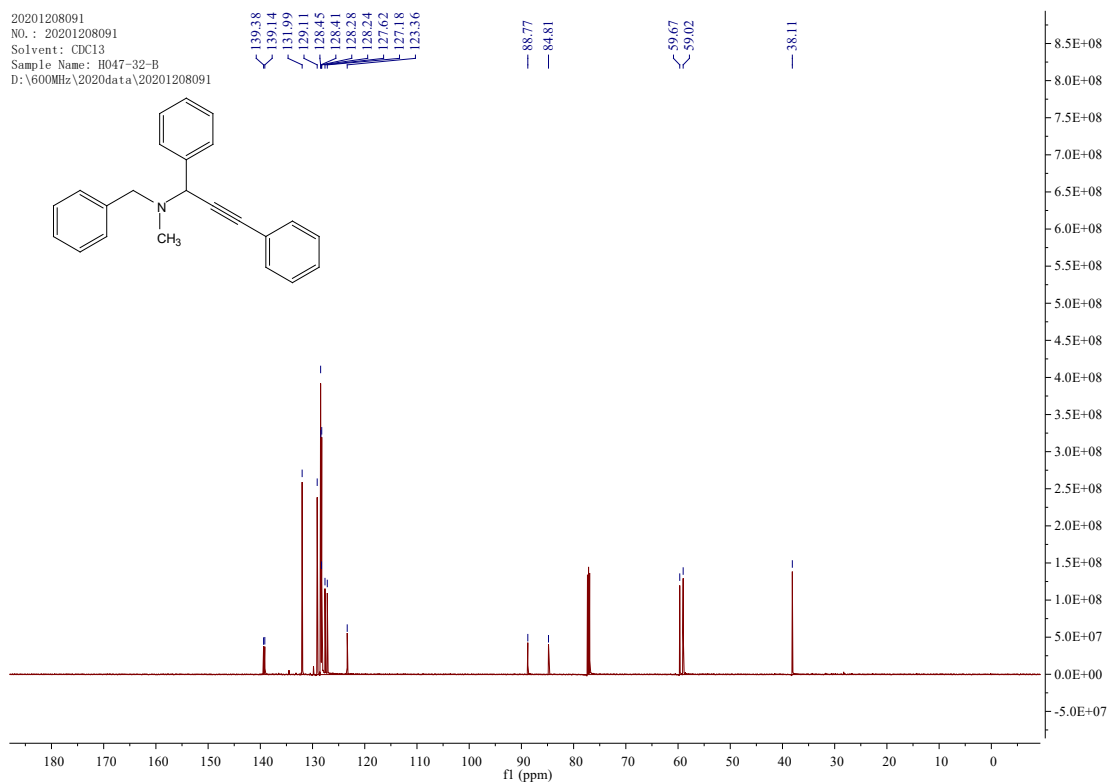


**(4a)**

20201208091  
 NO.: 20201208091  
 Solvent: CDC13  
 Sample Name: H047-32-B  
 D:\600MHz\2020data\20201208091

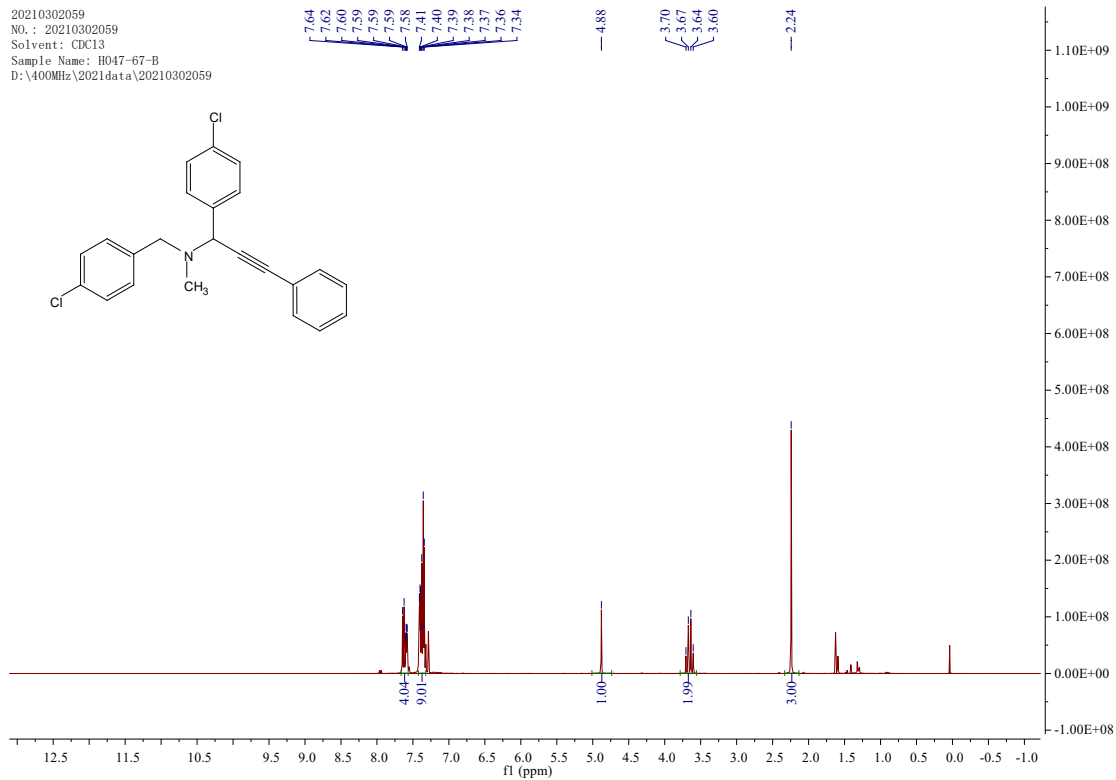


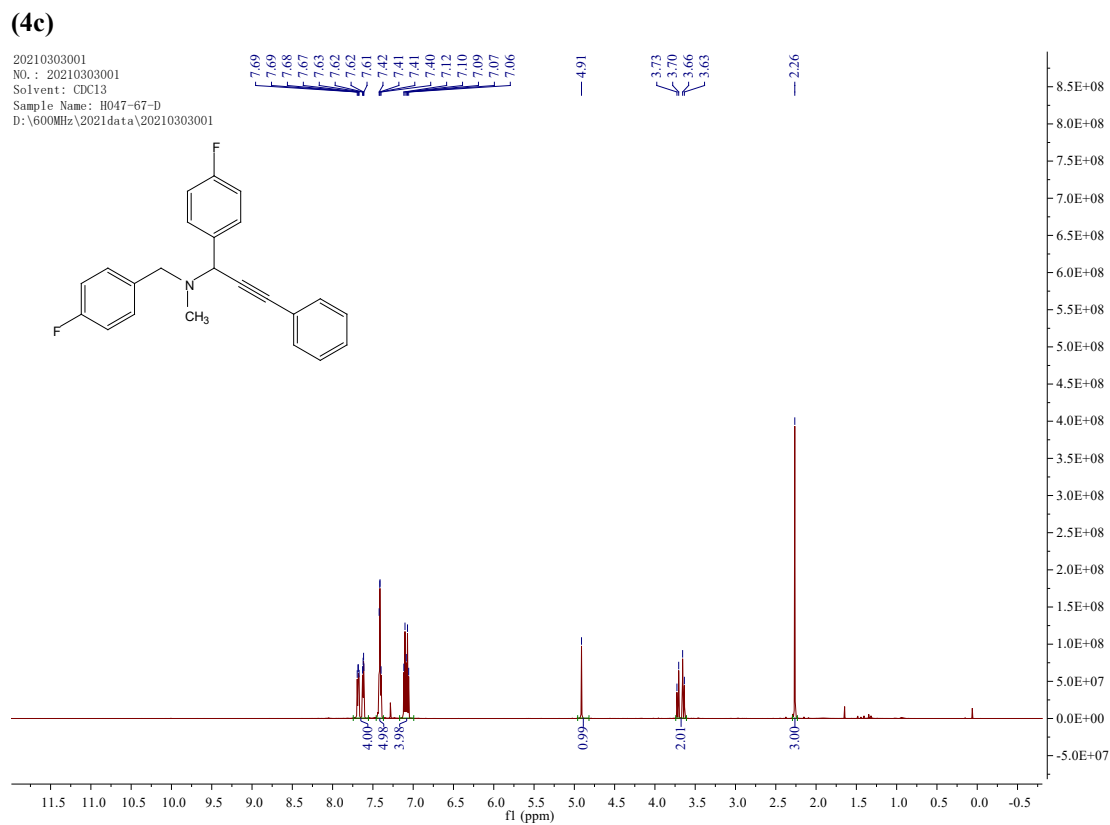
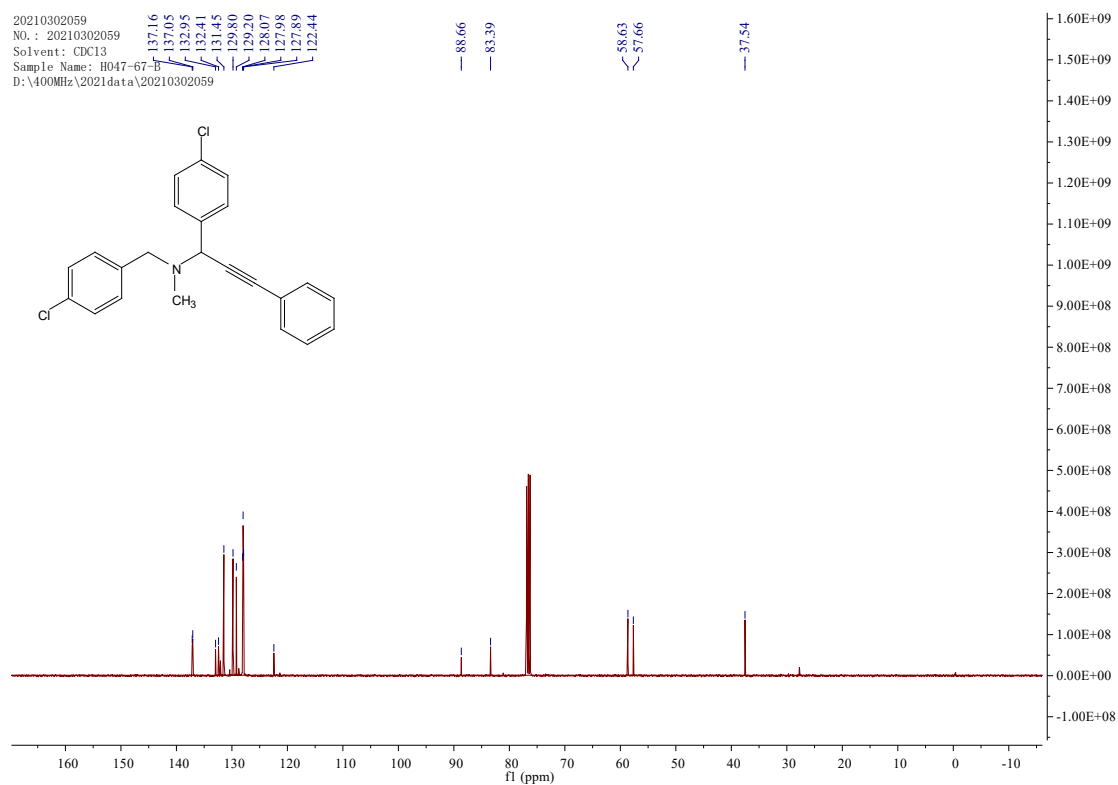
20201208091  
 NO.: 20201208091  
 Solvent: CDC13  
 Sample Name: H047-32-B  
 D:\600MHz\2020data\20201208091



**(4b)**

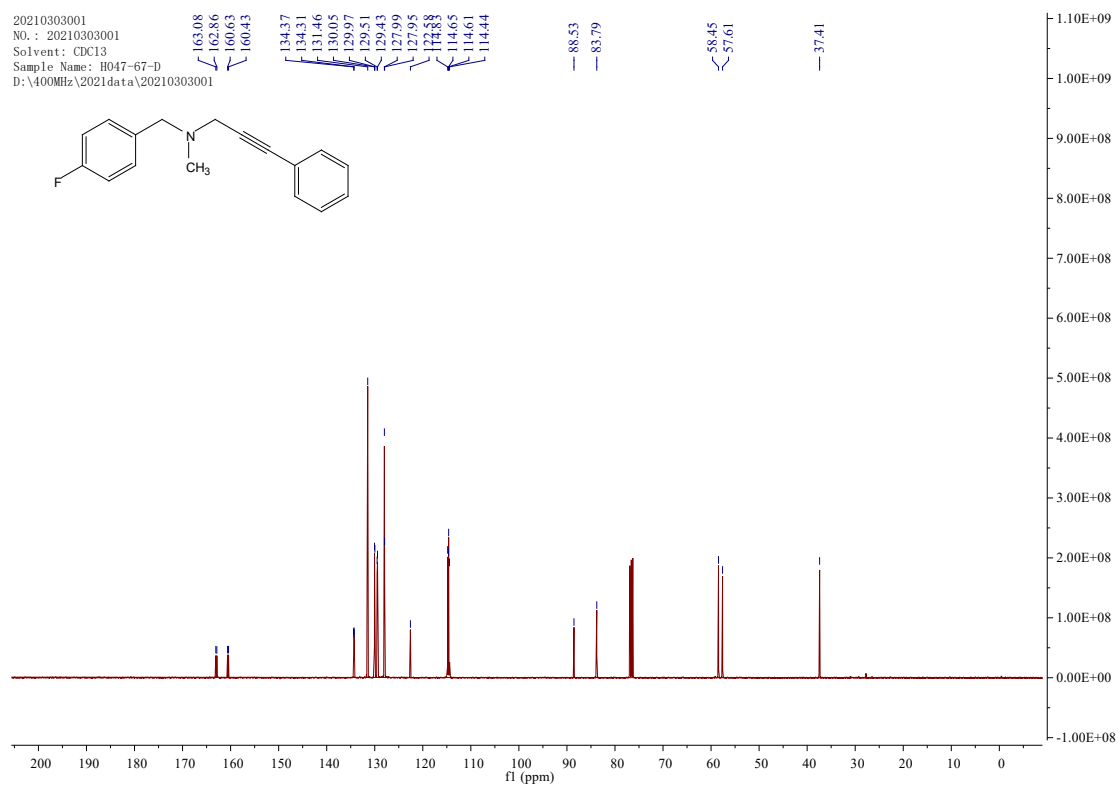
20210302059  
 NO.: 20210302059  
 Solvent: CDC13  
 Sample Name: H047-67-B  
 D:\400MHz\2021data\20210302059





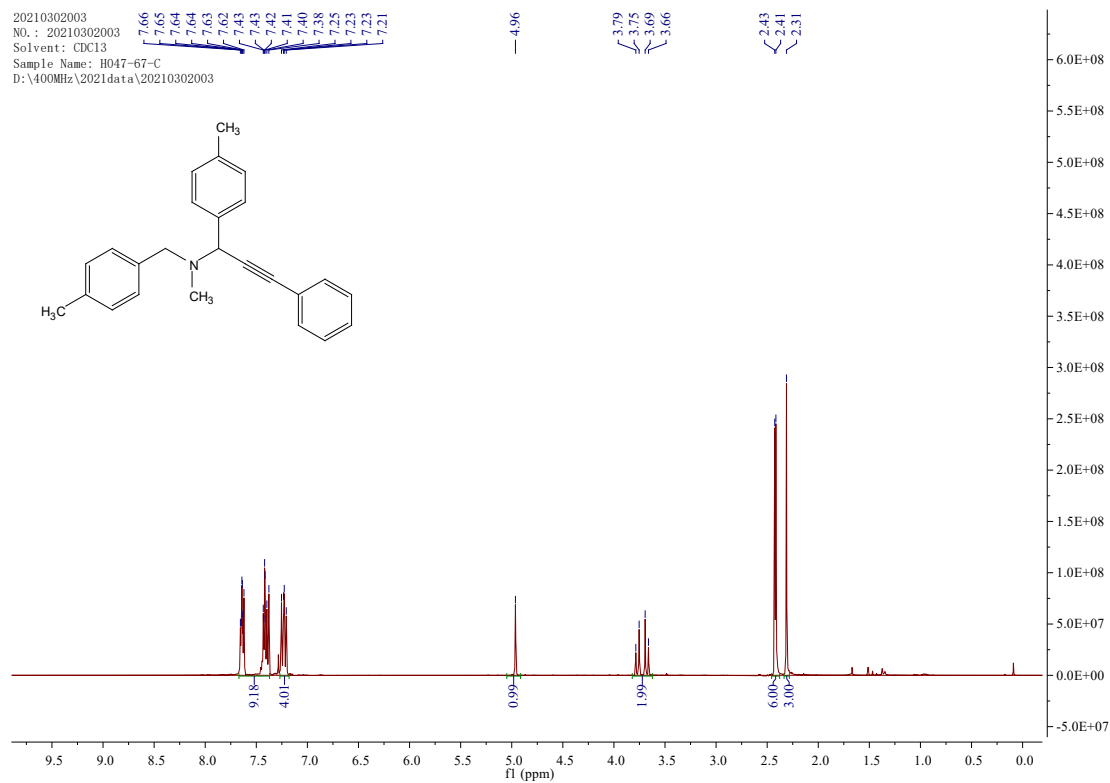


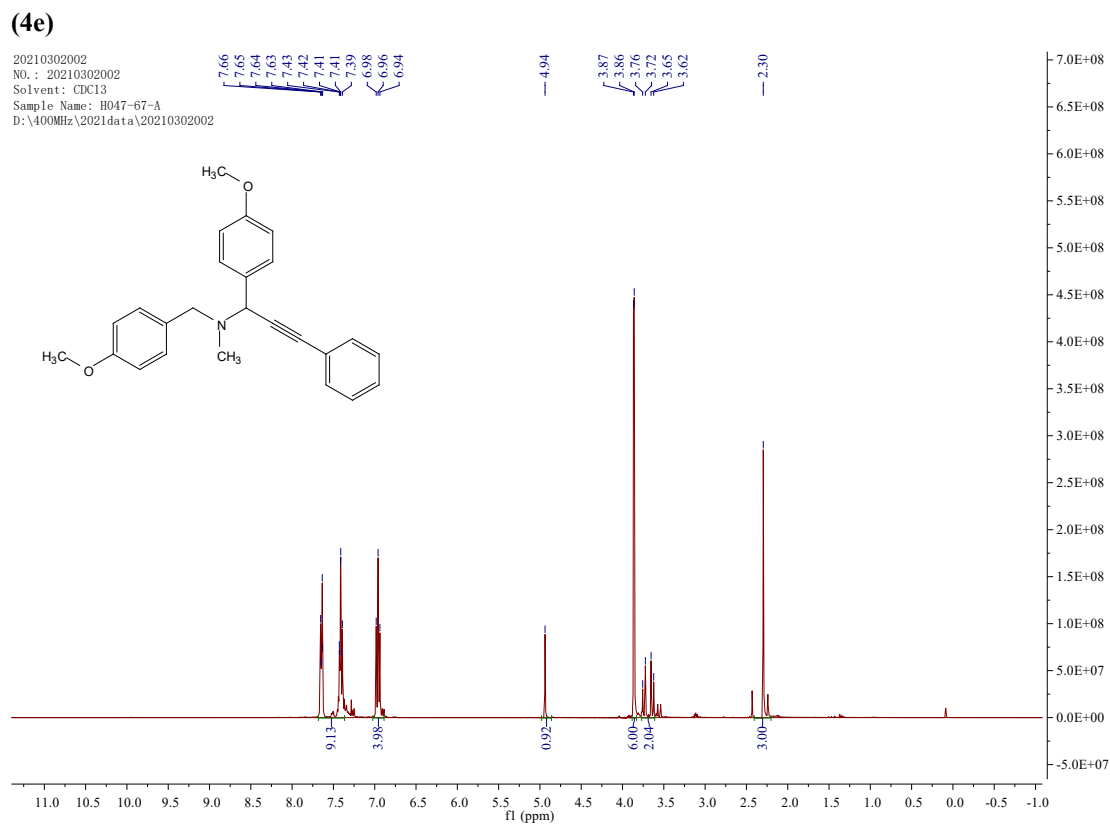
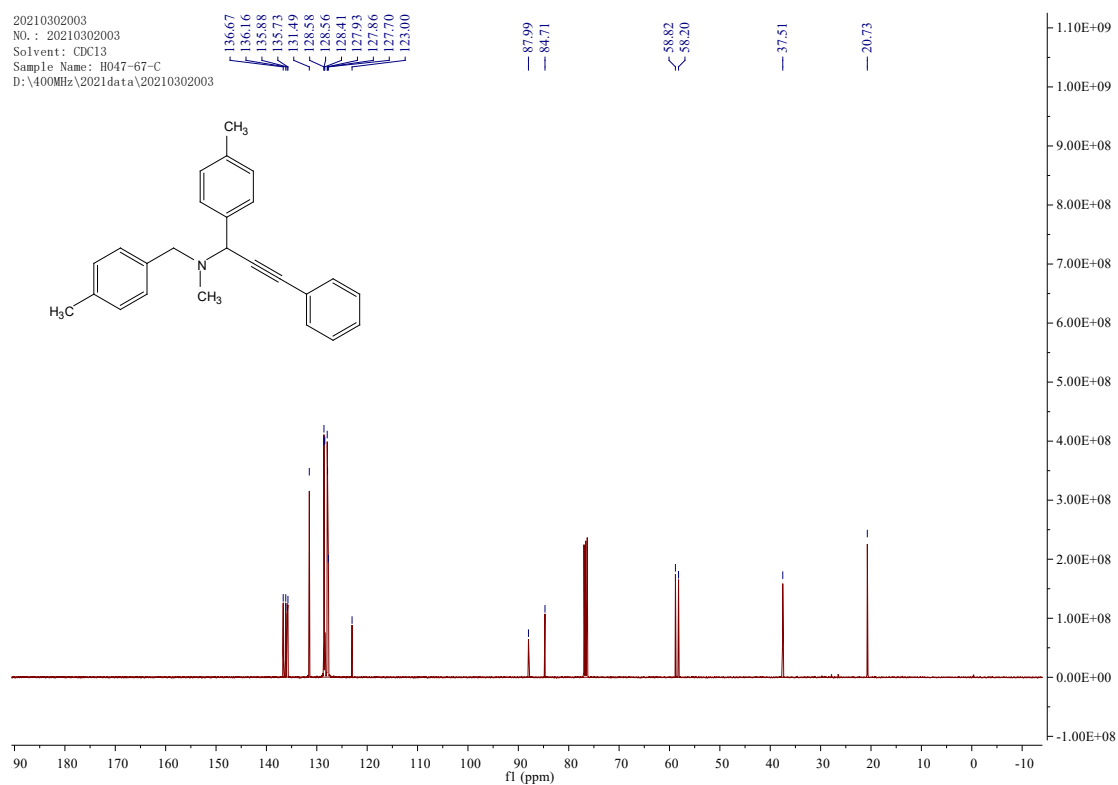
20210303001  
 NO.: 20210303001  
 Solvent: CDC13  
 Sample Name: H047-67-D  
 D:\400MHz\2021data\20210303001



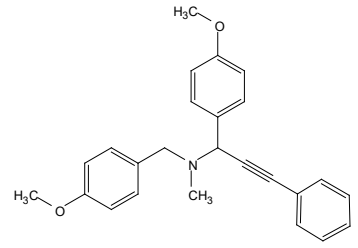
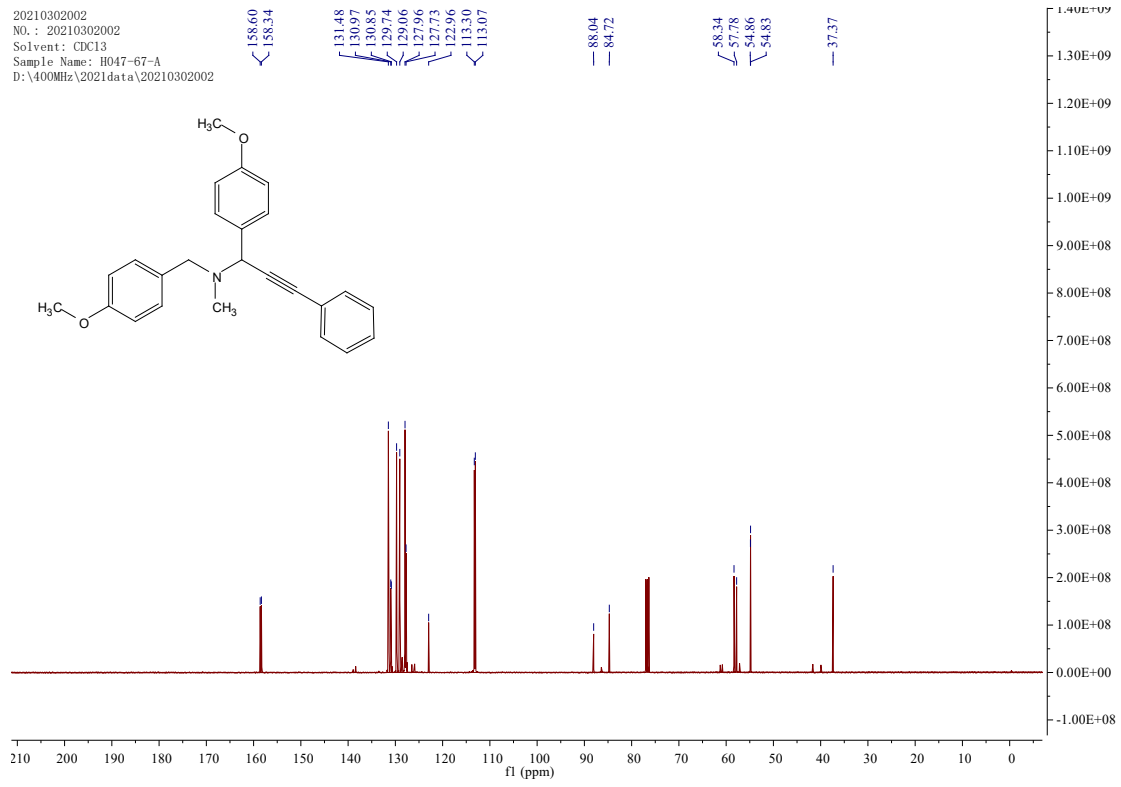
**(4d)**

20210302003  
 NO.: 20210302003  
 Solvent: CDC13  
 Sample Name: H047-67-C  
 D:\400MHz\2021data\20210302003



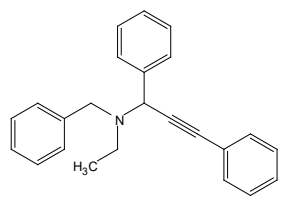
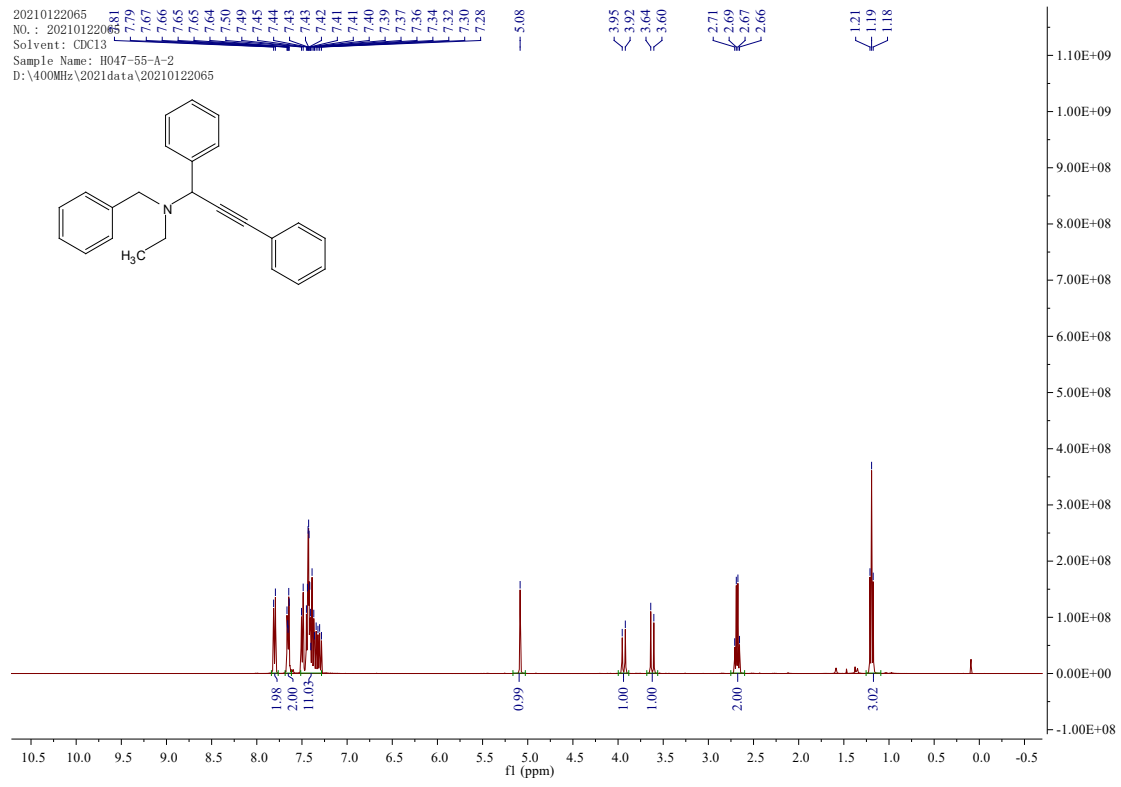


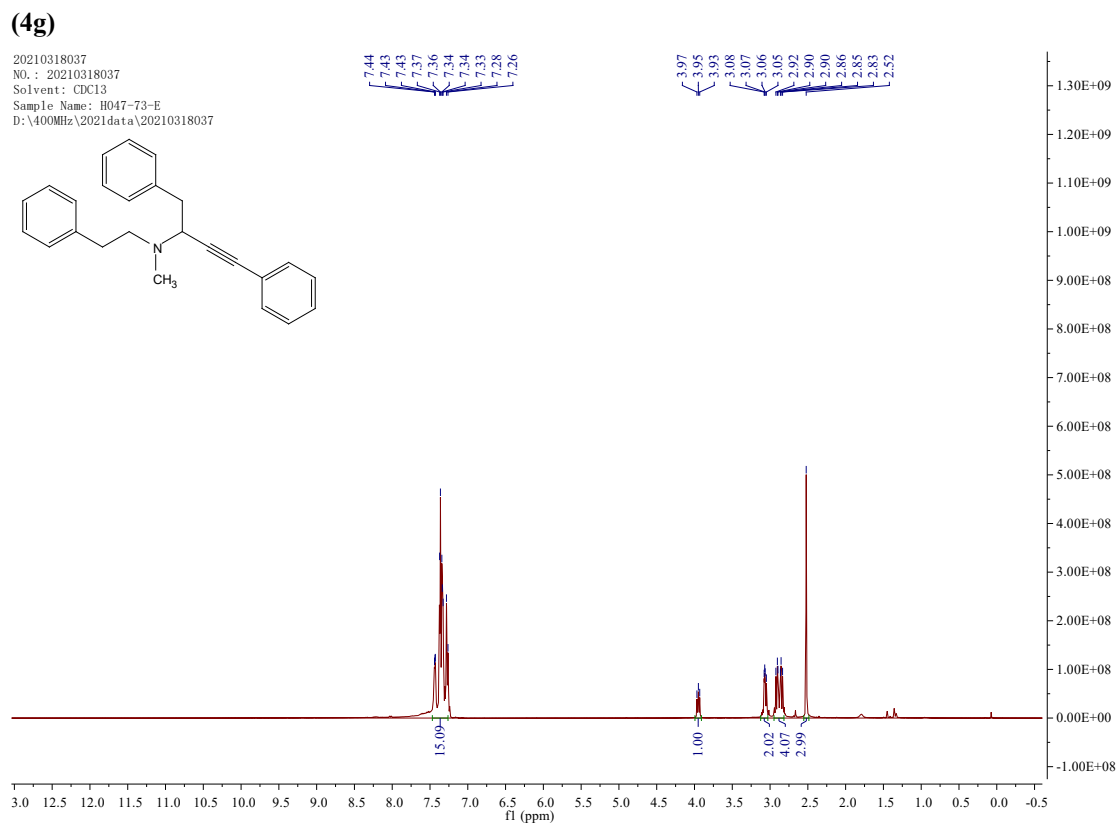
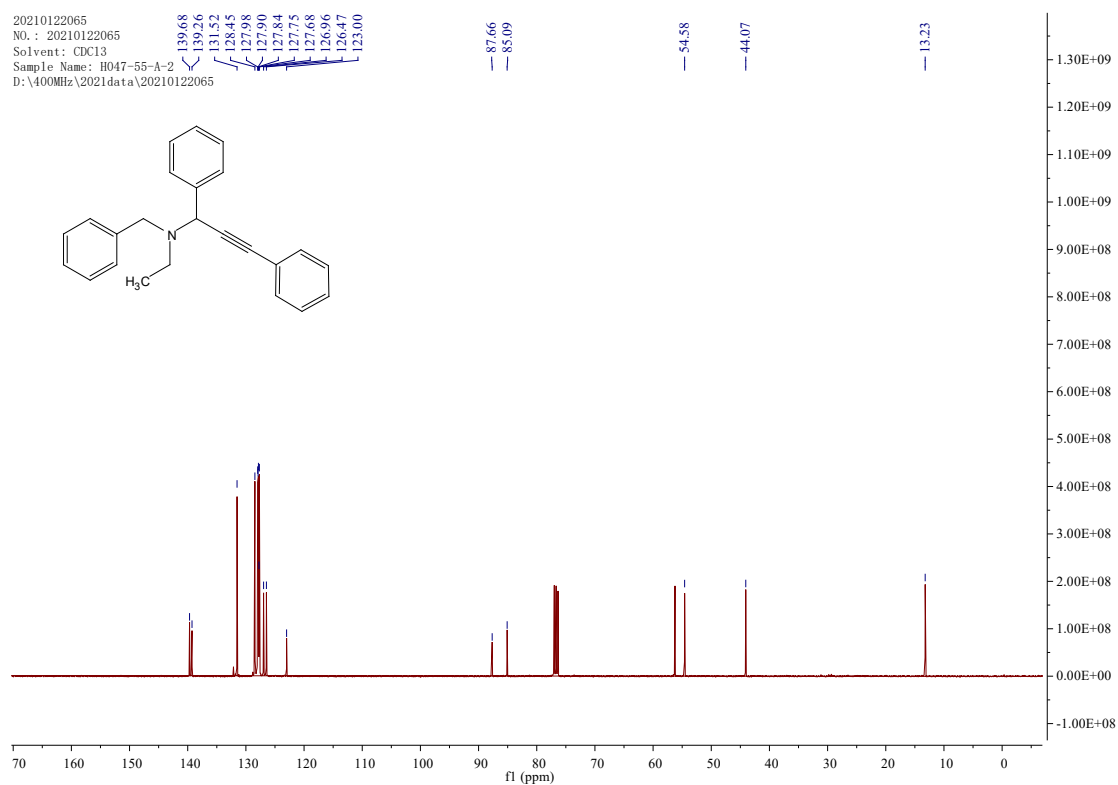
20210302002  
 NO.: 20210302002  
 Solvent: CDC13  
 Sample Name: H047-67-A  
 D:\400MHz\2021data\20210302002

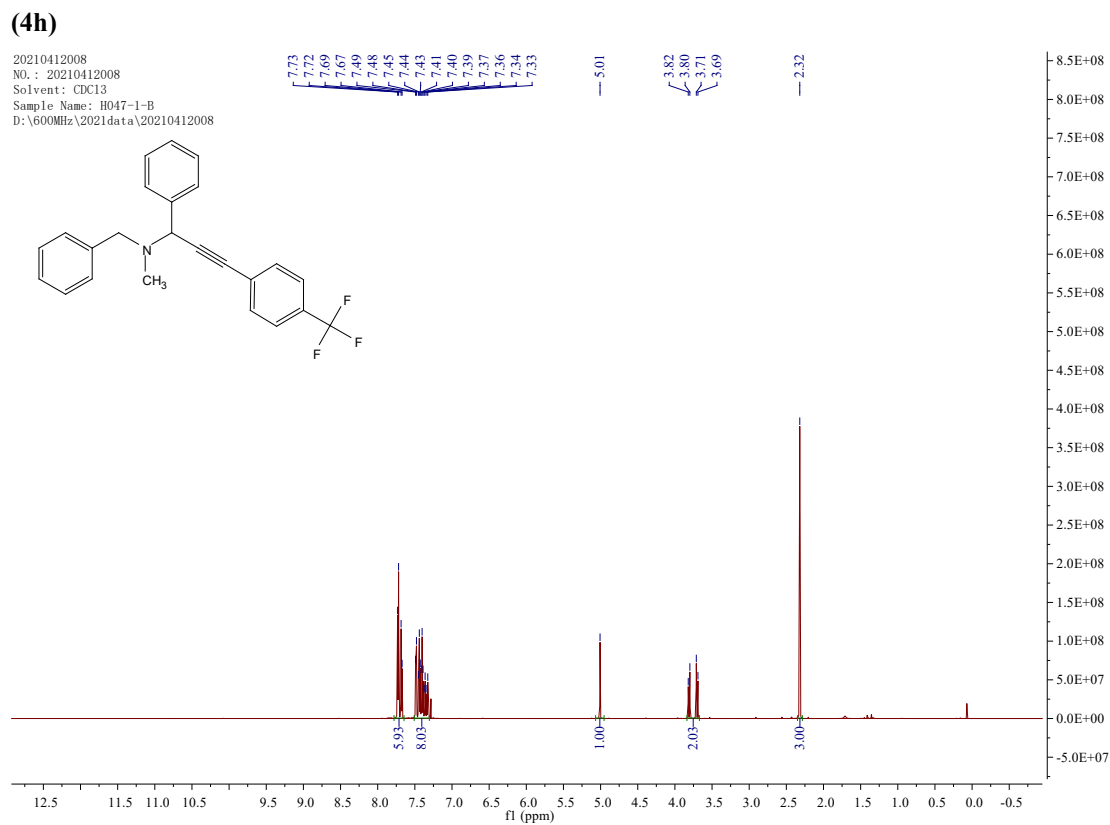
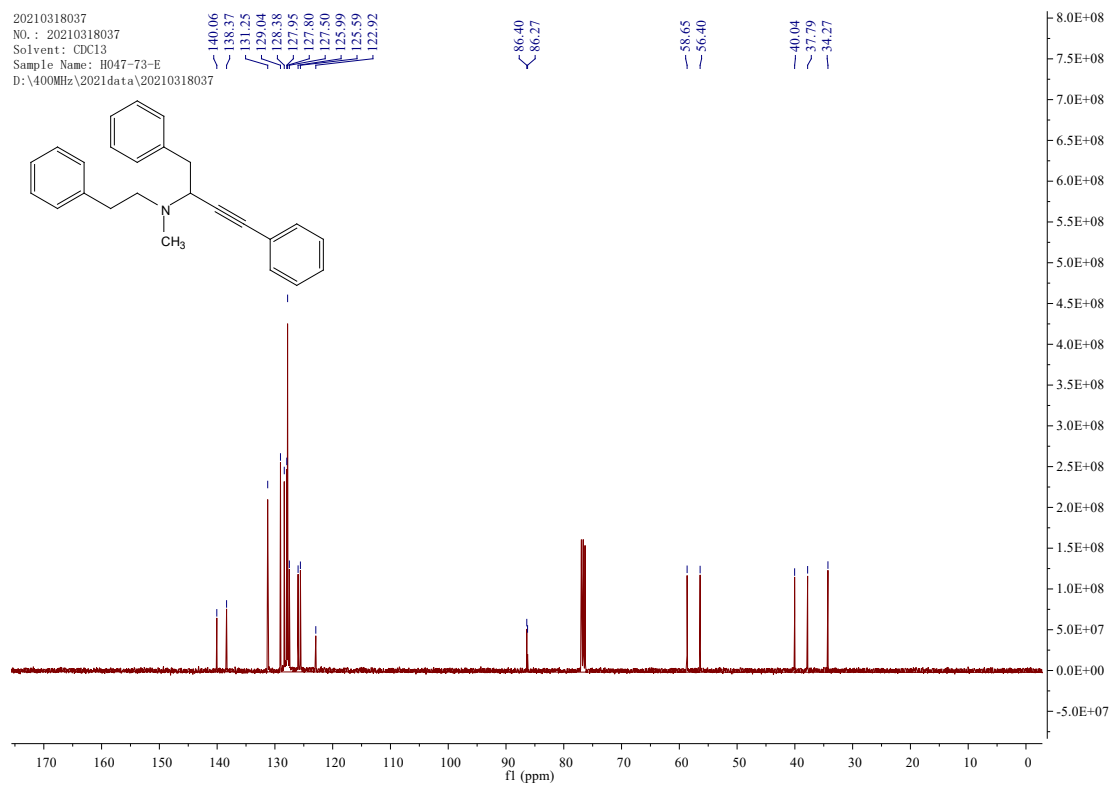


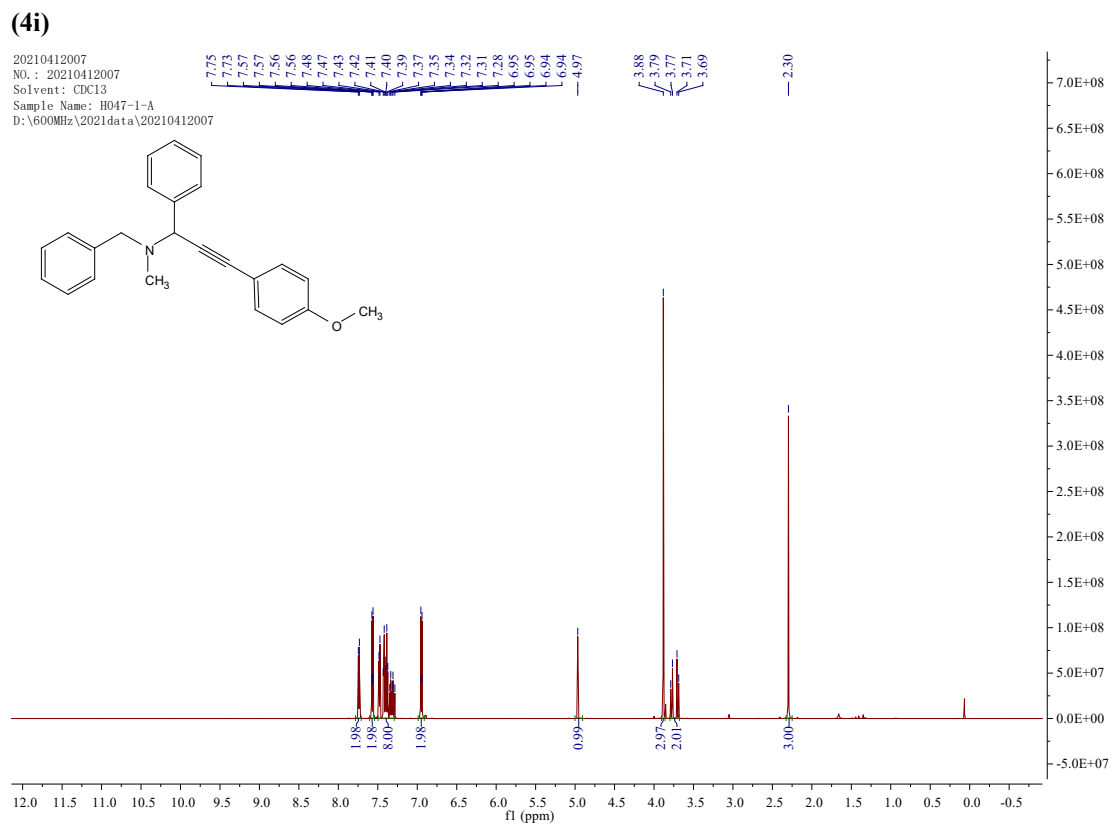
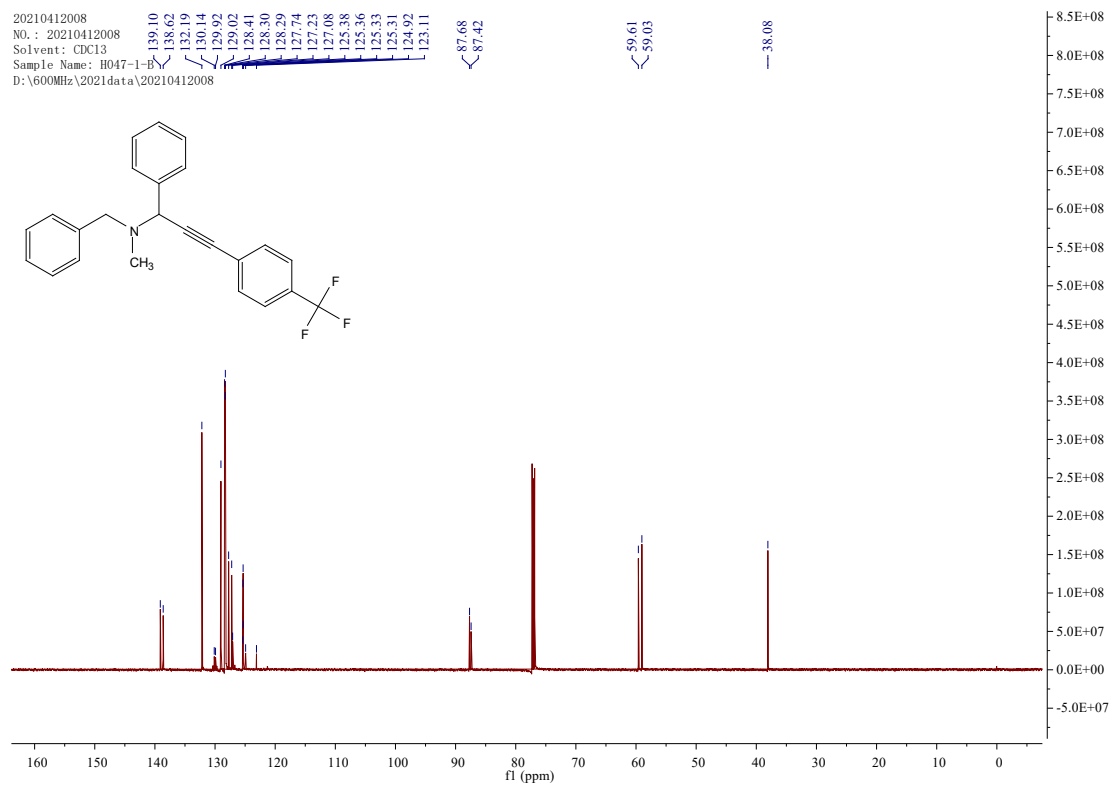
**(4f)**

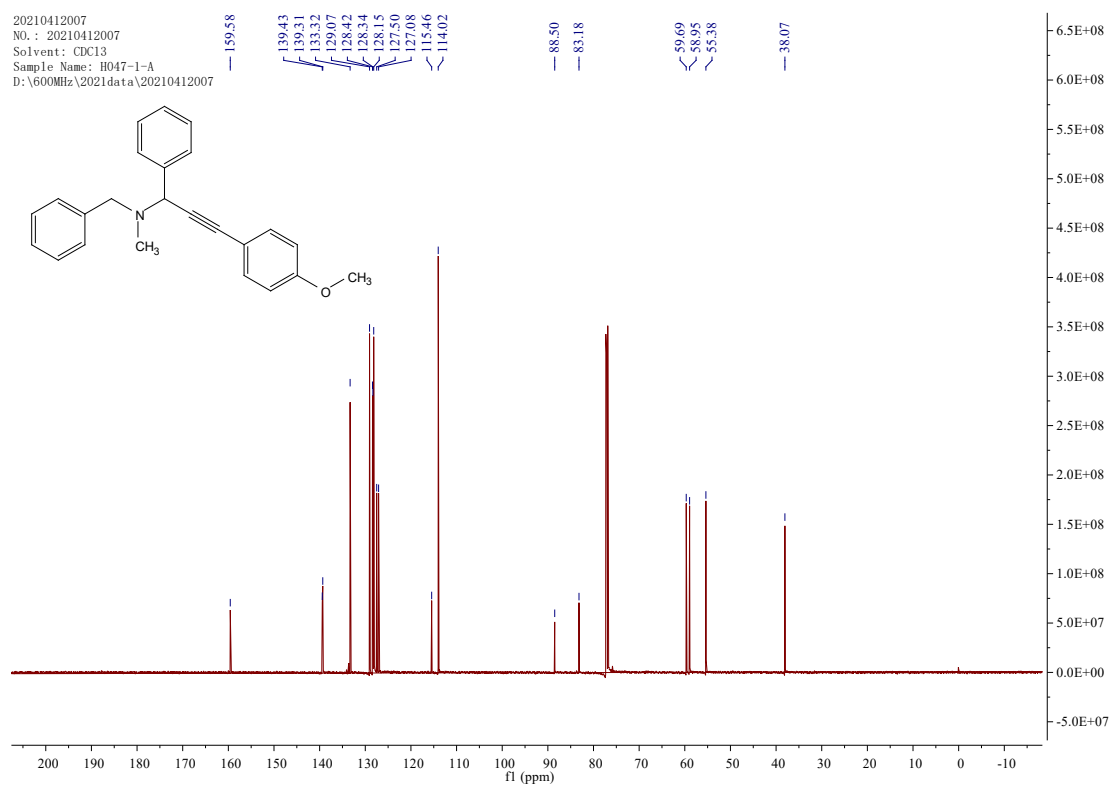
20210122065  
 NO.: 20210122065  
 Solvent: CDC13  
 Sample Name: H047-55-A-2  
 D:\400MHz\2021data\20210122065



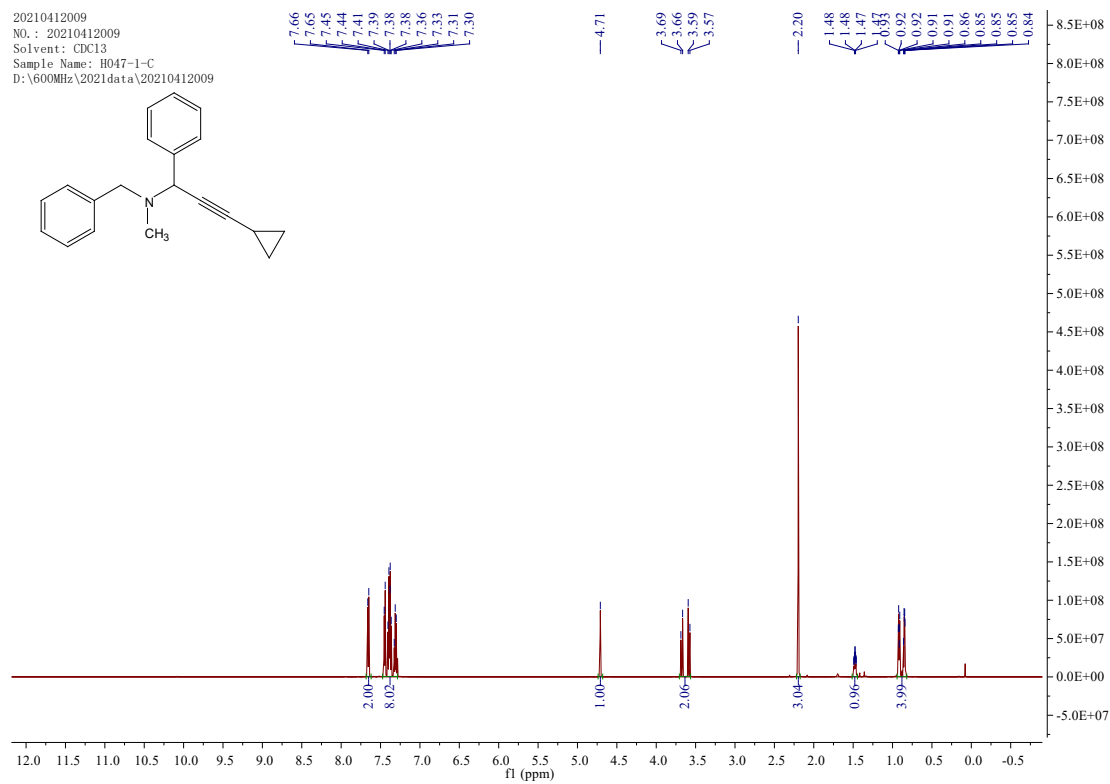




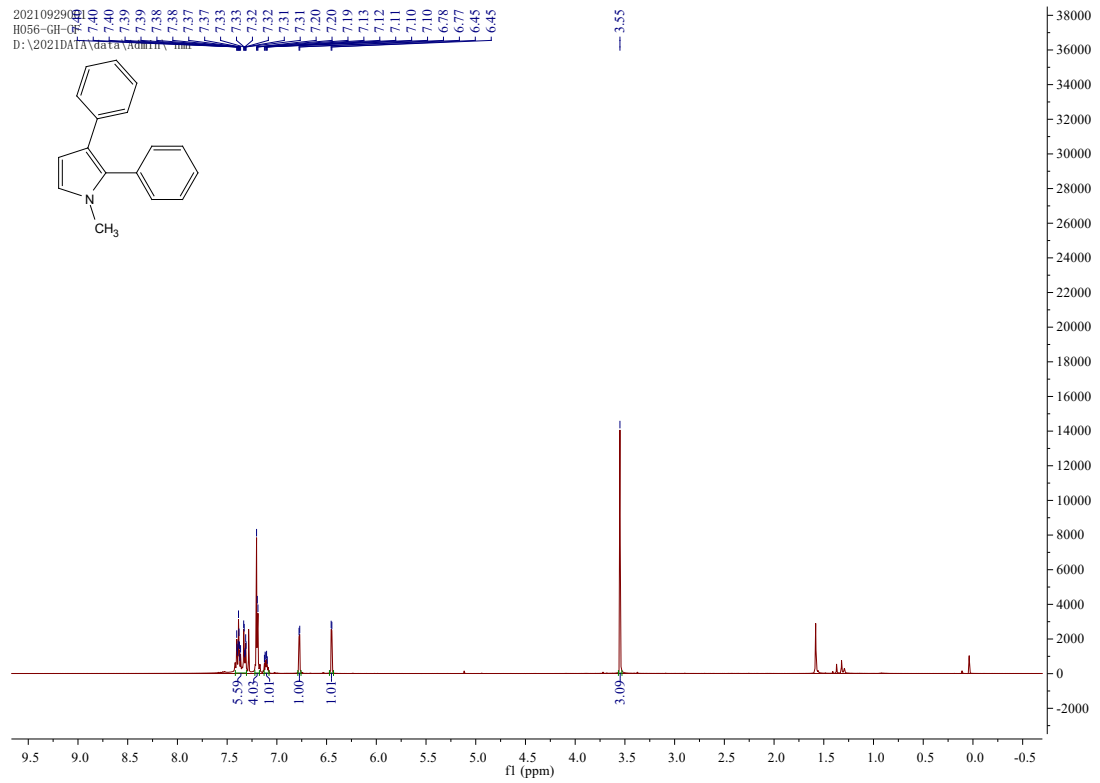
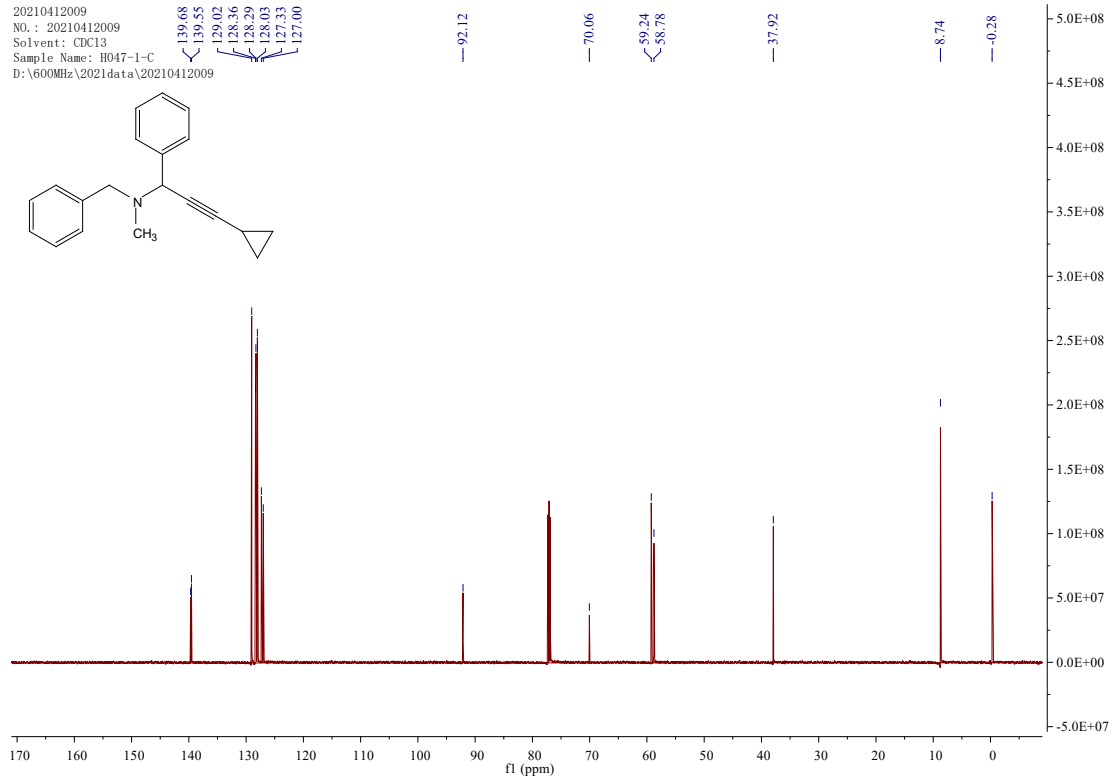




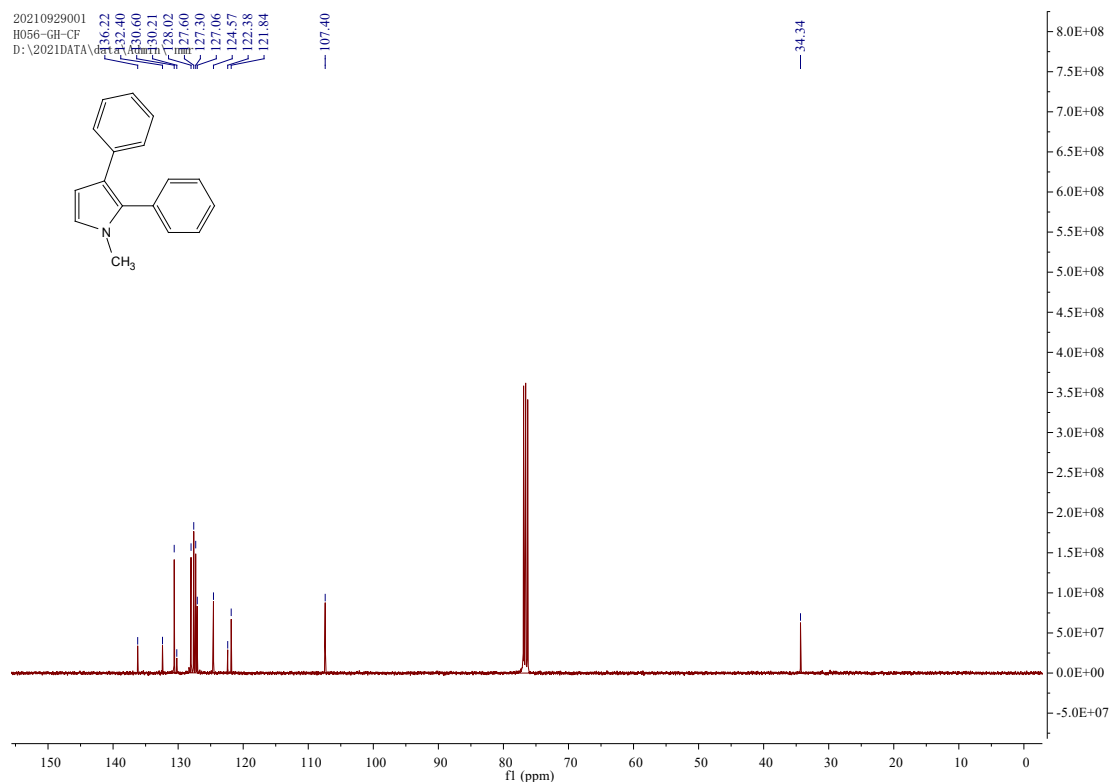
**(4j)**



20210412009  
 NO.: 20210412009  
 Solvent: CDCl3  
 Sample Name: H047-1-C  
 D:\600MHz\2021data\20210412009







## References

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