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*Electronic Supplementary Information (ESI) for*

# Aerobic cross-dehydrogenative coupling of terminal alkynes and tertiary amines by a combined catalyst of $Zn^{2+}$ and OMS-2

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## Full experimental details

**Instruments and reagents:** GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a Rxi-5 Sil capillary column. GC-MS spectra were recorded on Shimadzu GCMS-QP2010 equipped with a InertCap 5 capillary column at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded on JEOL JNM-ECA-500. $^1H$ and $^{13}C$ NMR spectra were measured at 500.2 and 125.8 MHz, respectively, using tetramethylsilane (TMS) as an internal reference ($\delta = 0$ ppm). OMS-2 (BET surface area: 90 $m^2\,g^{-1}$)[S1] was prepared according to the literature procedures. Activated $MnO_2$ (Cat. No. 217646-5G, for organic oxidations, Aldrich), β-$MnO_2$ (BET surface area: 36 $m^2g^{-1}$, Cat. No. 133-09681, Wako) were commercially available. Solvents and substrates were obtained from Kanto Chemical, TCI, Wako, or Aldrich (reagent grade), and purified prior to the use (if required).[S2]

**A typical procedure for CDC of terminal alkynes and tertiary amines:** Into a Pyrex glass reactor (volume: ca. 20 mL) were successively placed $ZnBr_2$ (11.3 mg, 0.05 mmol), OMS-2 (100 mg), **1** (1 mmol), **2** (2 mmol), CPME (2 mL), and a Teflon-coated magnetic stir bar, and the reaction mixture was purged with oxygen gas, and then vigorously stirred at 100 °C. After the reaction was completed, an internal standard (diphenyl) was added to the reaction mixture, and the conversions of **1** and **2** and the product yield were determined by GC analysis. As for isolation of propargylamine products, an internal standard was not added. After the reaction, OMS-2 was filtered off (>97 % recovery), and then the filtrate was concentrated by evaporation of CPME. The crude product was subjected to column chromatography on silica gel (typically using *n*-hexane/diethylether as the eluent), giving the pure propargylamines. The products were identified by GC-MS and NMR ($^1$H and $^{13}$C) analyses.

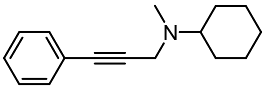
**Reuse of OMS-2:** The CDC of **1a** and **2a** was carried out with fresh OMS-2 as above-described experimental procedure. After the reaction, OMS was retrieved by filtration, washed with acetone and water, and then calcined at 300 °C for 2 h. Into a Pyrex glass reactor (volume: ca. 20 mL) were successively placed $ZnBr_2$ (11.3 mg, 0.05 mmol), the retrieved OMS-2 (100 mg), **1a** (1 mmol), **2a** (2 mmol), CPME (2 mL), and a Teflon-coated magnetic stir bar, and the reaction mixture was purged with oxygen gas, and then vigorously stirred at 100 °C for 8 h. After the reaction was completed, an internal standard (diphenyl) was added to the reaction mixture, and the conversions of **1a** and **2a** and the yield of **3aa** were determined by GC analysis. The reuse experiments were repeated 3 times.

## Additional references

S1 R. N. DeGuzman, Y.-F. Shen, E. J. Neth, S. L. Suib, C.-L. O'Young, S. Levine and J. M. Newsam, *Chem. Mater.*, 1994, **6**, 815.

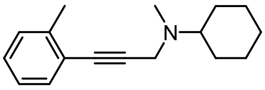
S2 *Purification of Laboratory Chemicals*, 3rd ed. (Eds.: D. D. Perrin and W. L. F. Armarego), Pergamon Press, Oxford, 1988.

## Spectral data of propargylamines



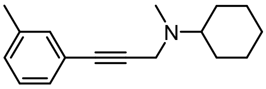
**3aa**

***N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)cyclohexanamine (3aa):** $^1$H NMR (500.2 MHz, CDCl$_3$, TMS): $\delta$ 1.09−1.32 (m, 5H), 1.60−1.64 (m, 1H), 1.78−1.81 (m, 2H), 1.95−1.98 (m, 2H), 2.41−2.46 (m, 4H), 3.63 (s, 2H), 7.27−7.31 (m, 3H), 7.41−7.44 (m, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, CDCl$_3$, TMS): $\delta$ 25.67, 26.23, 29.96, 38.68, 43.82, 61.16, 84.92, 85.80, 123.58, 127.98, 128.32, 131.78. MS (EI): *m*/*z* (%) : 227 (11) [$M^+$], 184 (19), 171 (29), 170 (35), 116 (33), 115 (100), 94 (43), 89 (11), 82 (10), 70 (21), 68 (27), 55 (18).



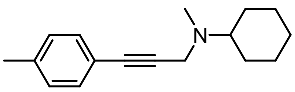
**3ba**

***N*-methyl-*N*-(3-(*o*-tolyl)prop-2-yn-1-yl)cyclohexanamine (3ba):** $^1$H NMR (500.2 MHz, CDCl$_3$, TMS): $\delta$ 1.10−1.31 (m, 5H), 1.60−1.63 (m, 1H), 1.78−1.80 (m, 2H), 1.98−2.00 (m, 2H), 2.43−2.48 (m, 7H), 3.70 (s, 2H), 7.10−7.14 (m, 1H), 7.17−7.21 (m, 2H), 7.39 (t, $J$ = 7.5 Hz, 1H). $^{13}$C{$^1$H} NMR (125.8 MHz, CDCl$_3$, TMS): $\delta$ 21.02, 25.63, 26.22, 30.16, 38.90, 44.00, 60.92, 83.91, 89.48, 123.42, 125.58, 127.99, 129.46, 132.12, 140.10. MS (EI): *m*/*z* (%) : 241 (29) [$M^+$], 240 (12), 199 (11), 198 (42), 185 (63), 184 (64), 170 (16), 158 (11), 150 (15), 130 (18), 129 (100), 128 (95), 127 (38), 115 (19), 104 (25), 94 (68), 77 (11), 68 (15), 55 (17).



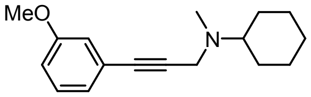
**3ca**

***N*-methyl-*N*-(3-(*m*-tolyl)prop-2-yn-1-yl)cyclohexanamine (3ca):** $^1$H NMR (500.2 MHz, CDCl$_3$, TMS): $\delta$ 1.09−1.32 (m, 5H), 1.60−1.64 (m, 1H), 1.77−1.81 (m, 2H), 1.95−1.97 (m, 2H), 2.32 (s, 3H), 2.40−2.46 (m, 4H), 3.63 (s, 2H), 7.09 (d, $J$ = 7.5 Hz, 1H), 7.18 (t, $J$ = 7.5 Hz, 1H), 7.22−7.26 (m, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, CDCl$_3$, TMS): $\delta$ 21.30, 25.65, 26.23, 29.98, 38.68, 43.81, 61.10, 85.08, 85.34, 123.37, 128.22, 128.84, 128.86, 132.35, 137.96. MS (EI): *m*/*z* (%) : 241 (24) [$M^+$], 198 (31), 185 (52), 184 (61), 158 (11), 150 (12), 130 (22), 129 (100), 128 (35), 127 (16), 115 (18), 94 (76), 68 (14), 55 (13).



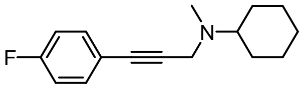
**3da**

**$N$-methyl-$N$-(3-($p$-tolyl)prop-2-yn-1-yl)cyclohexanamine (3da):** $^1$H NMR (500.2 MHz, CDCl$_3$, TMS): $\delta$ 1.09−1.31 (m, 5H), 1.60−1.63 (m, 1H), 1.77−1.80 (m, 2H), 1.95−1.97 (m, 2H), 2.33 (s, 3H), 2.40−2.46 (m, 4H), 3.61 (s, 2H), 7.09 (d, $J$ = 8.0 Hz, 2H), 7.31 (d, $J$ = 8.0 Hz, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, CDCl$_3$, TMS): $\delta$ 21.50, 25.66, 26.22, 29.93, 38.64, 43.82, 61.13, 84.95, 84.98, 120.49, 129.05, 131.63, 137.98. MS (EI): $m/z$ (%) : 241 (23) [$M^+$], 198 (26), 185 (46), 184 (56), 170 (10), 158 (11), 150 (10), 130 (19), 129 (100), 128 (36), 127 (16), 115 (14), 94 (70), 68 (11), 55 (12).



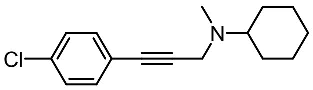
**3ea**

**$N$-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-$N$-methylcyclohexanamine (3ea):** $^1$H NMR (500.2 MHz, CDCl$_3$, TMS): $\delta$ 1.09−1.32 (m, 5H), 1.60−1.64 (m, 1H), 1.78−1.81 (m, 2H), 1.95−1.97 (m, 2H), 2.40−2.46 (m, 4H), 3.62 (s, 2H), 3.79 (s, 3H), 6.85 (ddd, $J$ = 8.5, 2.5 and 1.0 Hz, 1H), 6.96 (dd, $J$ = 2.5 and 1.5 Hz, 1H), 7.02 (dt, $J$ = 7.5 and 1.0 Hz, 1H), 7.20 (t, $J$ = 8.0 Hz, 1H). $^{13}$C{$^1$H} NMR (125.8 MHz, CDCl$_3$, TMS): $\delta$ 25.66, 26.22, 29.94, 38.68, 43.80, 55.34, 61.18, 84.81, 85.72, 114.47, 116.74, 124.32, 124.57, 129.37, 159.37. MS (EI): $m/z$ (%) : 257 (37) [$M^+$], 256 (12), 215 (10), 214 (34), 201 (66), 200 (68), 174 (12), 150 (16), 146 (27), 145 (98), 115 (24), 107 (10), 103 (15), 102 (25), 95 (10), 94 (100), 77 (10), 68 (18), 55 (17).



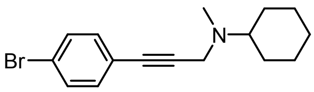
**3fa**

**$N$-(3-(4-fluorophenyl)prop-2-yn-1-yl)-$N$-methylcyclohexanamine (3fa):** $^1$H NMR (500.2 MHz, CDCl$_3$, TMS): $\delta$ 1.09−1.32 (m, 5H), 1.59−1.64 (m, 1H), 1.78−1.81 (m, 2H), 1.94−1.96 (m, 2H), 2.39−2.45 (m, 4H), 3.61 (s, 2H), 6.98 (tt, $J$ = 8.5 and 2.0 Hz, 2H), 7.37−7.41 (m, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, CDCl$_3$, TMS): $\delta$ 25.65, 26.22, 29.91, 38.63, 43.76, 61.23, 83.79, 85.54, 115.53 (d, $J$ = 21.6 Hz), 119.64 (d, $J$ = 3.5 Hz), 133.58 (d, $J$ = 8.3 Hz), 162.37 (d, $J$ = 249.6 Hz). MS (EI): $m/z$ (%) : 245 (16) [$M^+$], 202 (22), 189 (37), 188 (46), 134 (20), 133 (100), 94 (51), 68 (12), 55 (11).



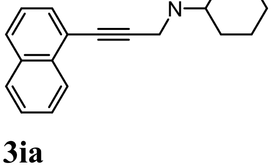
**3ga**

***N*-(3-(4-chlorophenyl)prop-2-yn-1-yl)-*N*-methylcyclohexanamine (3ga):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 1.09−1.31 (m, 5H), 1.60−1.63 (m, 1H), 1.78−1.81 (m, 2H), 1.93−1.95 (m, 2H), 2.39−2.44 (m, 4H), 3.61 (s, 2H), 7.26 (dt, $J$ = 8.5 and 2.0 Hz, 2H), 7.34 (dt, $J$ = 9.0 and 2.0 Hz, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 25.63, 26.20, 29.89, 38.64, 43.78, 61.24, 83.77, 86.98, 122.04, 128.62, 132.97, 133.95. MS (EI): *m*/*z* (%) : 261 (21) [$M^+$], 220 (11), 218 (32), 207 (18), 206 (26), 205 (52), 204 (62), 178 (10), 170 (14), 152 (10), 151 (35), 150 (33), 149 (100), 115 (27), 114 (27), 113 (13), 94 (100), 68 (17), 55 (20),



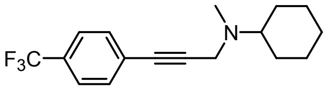
**3ha**

***N*-(3-(4-bromophenyl)prop-2-yn-1-yl)-*N*-methylcyclohexanamine (3ha):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 1.09−1.31 (m, 5H), 1.60−1.64 (m, 1H), 1.78−1.81 (m, 2H), 1.93−1.95 (m, 2H), 2.38−2.44 (m, 4H), 3.60 (s, 2H), 7.27 (dt, $J$ = 8.5 and 2.0 Hz, 2H), 7.42 (dt, $J$ = 9.0 and 2.0 Hz, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 25.64, 26.21, 29.90, 38.65, 43.80, 61.26, 83.85, 87.22, 122.14, 122.52, 131.56, 133.23. MS (EI): *m*/*z* (%) : 307 (19), 306 (9) [$M^+$], 305 (20), 264 (23), 262 (23), 251 (45), 250 (52), 249 (47), 248 (48), 196 (16), 195 (53), 194 (15), 193 (53), 183 (10), 182 (12), 170 (17), 169 (12), 150 (18), 115 (36), 114 (42), 113 (16), 94 (100), 88 (12), 70 (10), 68 (22), 55 (20).



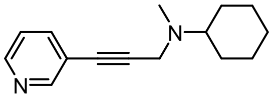
**3ia**

***N*-methyl-*N*-(3-(naphthalen-1-yl)prop-2-yn-1-yl)cyclohexanamine (3ia):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 1.11−1.34 (m, 5H), 1.61−1.64 (m, 1H), 1.79−1.82 (m, 2H), 2.02−2.04 (m, 2H), 2.50−2.56 (m, 4H), 3.80 (s, 2H), 7.38−7.41 (m, 1H), 7.47−7.51 (m, 1H), 7.53−7.57 (m, 1H), 7.65 (dd, $J$ = 7.0 and 1.0 Hz, 1H), 7.78 (d, $J$ = 8.5 Hz, 1H), 7.82 (d, $J$ = 8.0 Hz, 1H), 8.35 (d, $J$ = 8.5 Hz, 1H). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 25.63, 26.22, 30.16, 39.00, 44.14, 61.08, 83.06, 90.65, 121.28, 125.30, 126.35, 126.38, 126.69, 128.33, 128.42, 130.48, 133.28, 133.53. MS (EI): *m*/*z* (%) : 277 (20) [$M^+$], 234 (18), 221 (31), 220 (38), 166 (19), 165 (100), 164 (20), 163 (14), 94 (41), 68 (11).



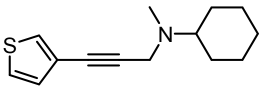
**3ja**

***N*-methyl-*N*-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)cyclohexanamine (3ja):** $^{1}$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 1.10−1.32 (m, 5H), 1.61−1.64 (m, 1H), 1.79−1.82 (m, 2H), 1.94−1.97 (m, 2H), 2.40−2.46 (m, 4H), 3.64 (s, 2H), 7.51−7.56 (m, 4H). $^{13}$C{$^{1}$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 25.65, 26.20, 29.92, 38.68, 43.79, 61.35, 83.69, 88.77, 124.07 (q, *J* = 272.0 Hz), 125.26 (q, *J* = 4.8 Hz), 127.41, 129.79 (q, *J* = 98.5 Hz), 132.01. MS (EI): *m*/*z* (%) : 295 (26) [$M^+$], 253 (13), 252 (52), 240 (11), 239 (83), 238 (90), 212 (12), 184 (16), 183 (97), 182 (13), 150 (15), 133 (19), 115 (12), 94 (100), 68 (12), 55 (17).



**3ka**

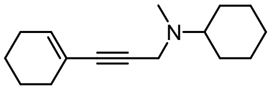
***N*-methyl-*N*-(3-(pyridin-3-yl)prop-2-yn-1-yl)cyclohexanamine (3ka):** $^{1}$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 1.10−1.32 (m, 5H), 1.61−1.64 (m, 1H), 1.79−1.82 (m, 2H), 1.94−1.96 (m, 2H), 2.40−2.46 (m, 4H), 3.64 (s, 2H), 7.21−7.24 (m, 1H), 7.70 (dt, *J* = 8.0 and 2.0 Hz, 1H), 8.50 (dd, *J* = 5.0 and 2.0 Hz, 1H), 8.66 (d, *J* = 1.5 Hz, 1H). $^{13}$C{$^{1}$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 25.58, 26.14, 29.85, 38.62, 43.75, 61.26, 81.56, 89.55, 120.62, 122.95, 138.57, 148.35, 152.48. MS (EI): *m*/*z* (%) : 228 (25) [$M^+$], 186 (12), 185 (53), 173 (11), 172 (82), 171 (89), 150 (17), 145 (14), 144 (10), 130 (12), 119 (10), 117 (35), 116 (100), 94 (100), 90 (13), 89 (46), 82 (11), 70 (15), 68 (31), 63 (28), 55 (28).



**3la**

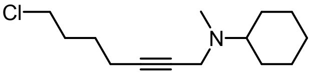
***N*-methyl-*N*-(3-(thiophen-3-yl)prop-2-yn-1-yl)cyclohexanamine (3la):** $^{1}$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 1.09−1.31 (m, 5H), 1.60−1.63 (m, 1H), 1.77−1.81 (m, 2H), 1.93−1.96 (m, 2H), 2.39−2.45 (m, 4H), 3.60 (s, 2H), 7.09 (dd, *J* = 5.0 and 1.0 Hz, 1H), 7.23 (dd, *J* = 5.0 and 2.8 Hz, 1H), 7.39 (d, *J* = 3.0 Hz, 1H). $^{13}$C{$^{1}$H} NMR (125.8

MHz, $CDCl_3$, TMS): *δ* 25.65, 26.23, 29.90, 38.63, 43.81, 61.16, 79.87, 85.42, 122.55, 125.16, 128.28, 130.13. MS (EI): *m*/*z* (%) : 233 (20) [*M*$^+$], 190 (25), 177 (45), 176 (60), 150 (17), 122 (29), 121 (100), 94 (45), 82 (10), 77 (19), 70 (12), 68 (25), 55 (20).



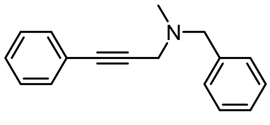
**3ma**

***N*-(3-(cyclohex-1-en-1-yl)prop-2-yn-1-yl)-*N*-methylcyclohexanamine (3ma):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): *δ* 1.08−1.30 (m, 5H), 1.55−1.65 (m, 5H), 1.75−1.79 (m, 2H), 1.90−1.93 (m, 2H), 2.06−2.13 (m, 4H), 2.33−2.39 (m, 4H), 3.51 (s, 2H), 6.04−6.06 (m, 1H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, TMS): *δ* 21.62, 22.41, 25.60, 26.18, 29.53, 29.89, 38.49, 43.68, 60.93, 82.62, 86.70, 120.77, 133.90. MS (EI): *m*/*z* (%) : 232 (10), 231 (61) [*M*$^+$], 230 (16), 202 (10), 189 (20), 188 (69), 176 (14), 175 (97), 174 (72), 160 (34), 150 (18), 148 (22), 147 (22), 146 (37), 134 (12), 133 (12), 132 (29), 120 (30), 119 (35), 118 (12), 117 (22), 115 (15), 112 (10), 108 (16), 107 (11), 105 (15), 104 (10), 103 (12), 95 (15), 94 (79), 93 (13), 92 (22), 91 (100), 87 (10), 82 (19), 81 (48), 79 (33), 78 (15), 77 (31), 70 (36), 68 (33), 67 (12), 65 (24), 57 (10), 55 (35), 53 (12), 51 (11).



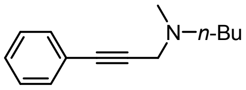
**3na**

***N*-(7-chlorohept-2-yn-1-yl)-*N*-methylcyclohexanamine (3na):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): *δ* 1.07−1.29 (m, 5H), 1.59−1.69 (m, 3H), 1.76−1.79 (m, 2H), 1.88−1.93 (m, 4H), 2.25 (tt, *J* = 7.0 and 2.0 Hz, 2H), 2.31−2.37 (m, 4H), 3.36 (t, *J* = 2.0 Hz, 2H), 3.56 (t, *J* = 7.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, TMS): *δ* 18.16, 25.67, 26.13, 26.22, 29.79, 31.69, 38.45, 43.33, 44.63, 60.97, 76.65, 83.88. MS (EI): *m*/*z* (%) : 241 (15) [*M*$^+$], 206 (14), 200 (14), 198 (42), 185 (11), 184 (23), 164 (40), 150 (45), 148 (20), 122 (10), 120 (11), 109 (12), 108 (100), 107 (15), 95 (22), 94 (35), 91 (12), 82 (26), 81 (13), 79 (12), 77 (14), 70 (17), 68 (25), 67 (17), 65 (11), 55 (29), 54 (14), 53 (15).



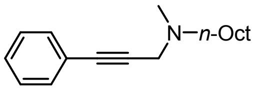
**3ab**

***N*-benzyl-*N*-methyl-3-phenylprop-2-yn-1-amine (3ab):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 2.40 (s, 3H), 3.51 (s, 2H), 3.64 (s, 2H), 7.26 (tt, $J$ = 7.0 and 2.0 Hz, 1H), 7.28−7.33 (m, 5H), 7.36−7.38 (m, 2H), 7.45−7.48 (m, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 42.12, 45.89, 60.40, 84.60, 85.81, 123.46, 127.32, 128.12, 128.39, 128.44, 129.35, 131.85, 138.62. MS (EI): $m/z$ (%) : 235 (25) [$M^+$], 234 (31), 158 (43), 144 (26), 118 (10), 116 (15), 115 (100), 92 (10), 91 (60), 89 (12), 65 (16).



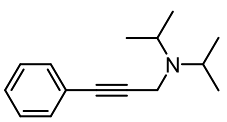
**3ac**

***N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)butan-1-amine (3ac):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 0.93 (t, $J$ = 7.3 Hz, 3H), 1.36 (sext, $J$ = 7.4 Hz, 2H), 1.45−1.51 (m, 2H), 2.36 (s, 3H), 2.45−2.49 (m, 2H), 3.54 (s, 2H), 7.26−7.31 (m, 3H), 7.41−7.45 (m, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 14.11, 20.70, 29.91, 42.08, 46.52, 55.83, 84.74, 85.27, 123.45, 127.98, 128.29, 131.76. MS (EI): $m/z$ (%) : 201 (3) [$M^+$], 158 (54), 116 (11), 115 (100).



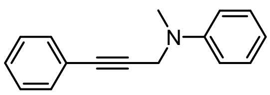
**3ad**

***N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)octan-1-amine (3ad):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 0.88 (t, $J$ = 7.0 Hz, 3H), 1.27−1.31 (m, 10H), 1.49 (quin, $J$ = 7.3 Hz, 2H), 2.36 (s, 3H), 2.45−2.48 (m, 2H), 3.54 (s, 2H), 7.27−7.30 (m, 3H), 7.41−7.45 (m, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 14.21, 22.77, 27.62, 27.80, 29.39, 29.67, 31.97, 42.13, 46.54, 56.21, 84.77, 85.31, 123.49, 128.02, 128.31, 131.81. MS (EI): $m/z$ (%) : 257 (3) [$M^+$], 159 (11), 158 (86), 116 (11), 115 (100).



**3ae**

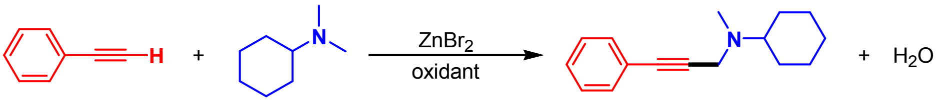
***N*,*N*-diisopropyl-3-phenylprop-2-yn-1-amine (3ae):** $^1$H NMR (500.2 MHz, $CDCl_3$, TMS): $\delta$ 1.15 (d, $J$ = 6.5 Hz, 12H), 3.25 (sep, $J$ = 6.5 Hz, 2H), 3.65 (s, 2H), 7.24−7.29 (m, 3H), 7.37−7.42 (m, 2H). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$, TMS): $\delta$ 20.79, 34.91, 48.62, 83.57, 89.20, 123.95, 127.78, 128.28, 131.53. MS (EI): $m/z$ (%) : 215 (5) [$M^+$], 200 (50), 116 (16), 115 (100).



**3af**

***N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)aniline (3af):** MS (EI): *m*/*z* (%) : 222 (14), 221 (81) [$M^+$], 220 (69), 144 (22), 116 (12), 115 (100), 106 (11), 104 (18), 89 (15), 77 (32), 63 (10), 51 (12).

**Table S1** Effect of oxidants on the CDC of phenylacetylene (**1a**) and *N,N*-dimethylcyclohexylamine (**2a**)[a]

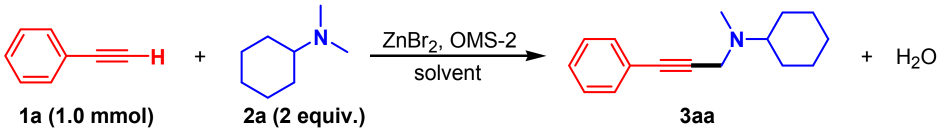


**1a (1.0 mmol)** **2a (2 equiv.)** **3aa**

| Entry | Oxidant | Conv. (%) | | Yield of **3aa** (%) |
|---|---|---|---|---|
| | | **1a** | **2a** | |
| 1 | OMS-2/$O_2$ | 95 | 56 | 85 |
| 2 | Activated $MnO_2$[b]/$O_2$ | 6 | <1 | 1 |
| 3 | β-$MnO_2$/$O_2$ | 48 | 26 | 38 |
| 4 | TBHP[c]/$O_2$ | 6 | 15 | 1 |

[a] Reaction conditions: $ZnBr_2$ (5 mol%), oxidant (100 mg), **1a** (1.0 mmol), **2a** (2.0 mmol), CPME (2 mL), 100 °C, $O_2$ (1 atm), 8 h. Conversion and yield were determined by GC analysis. [b] Commercially available. [c] 1.0 mmol of 70 % TBHP in water was utilized.

**Table S2** Effect of solvents on the CDC of phenylacetylene (**1a**) and *N,N*-dimethylcyclohexylamine (**2a**)[a]



| Entry | Solvent | Conv. (%) | | Yield of **3aa** (%) |
|---|---|---|---|---|
| | | **1a** | **2a** | |
| 1 | Toluene | 87 | 54 | 68 |
| 2 | $PhCF_3$ | 93 | 55 | 76 |
| 3 | *N*-Methylpyrrolidone | 71 | 74 | 44 |
| 4 | *N,N*-Dimethylformamide | 77 | 75 | 49 |
| 5 | *N,N*-Dimethylacetamide | 79 | 63 | 58 |
| 6 | 1,4-Dioxane | 54 | 37 | 39 |
| 7 | Dimethylsulfoxide | 81 | 77 | 48 |
| **8** | **Cyclopentylmethylether** | **95** | **56** | **85** |
| 9 | Diethylcarbonate | 92 | 67 | 73 |

[a] Reaction conditions: $ZnBr_2$ (5 mol%), OMS-2 (100 mg), **1a** (1.0 mmol), **2a** (2.0 mmol), solvent (2 mL), 100 °C, $O_2$ (1 atm), 8 h. Conversion and yield were determined by GC analysis.

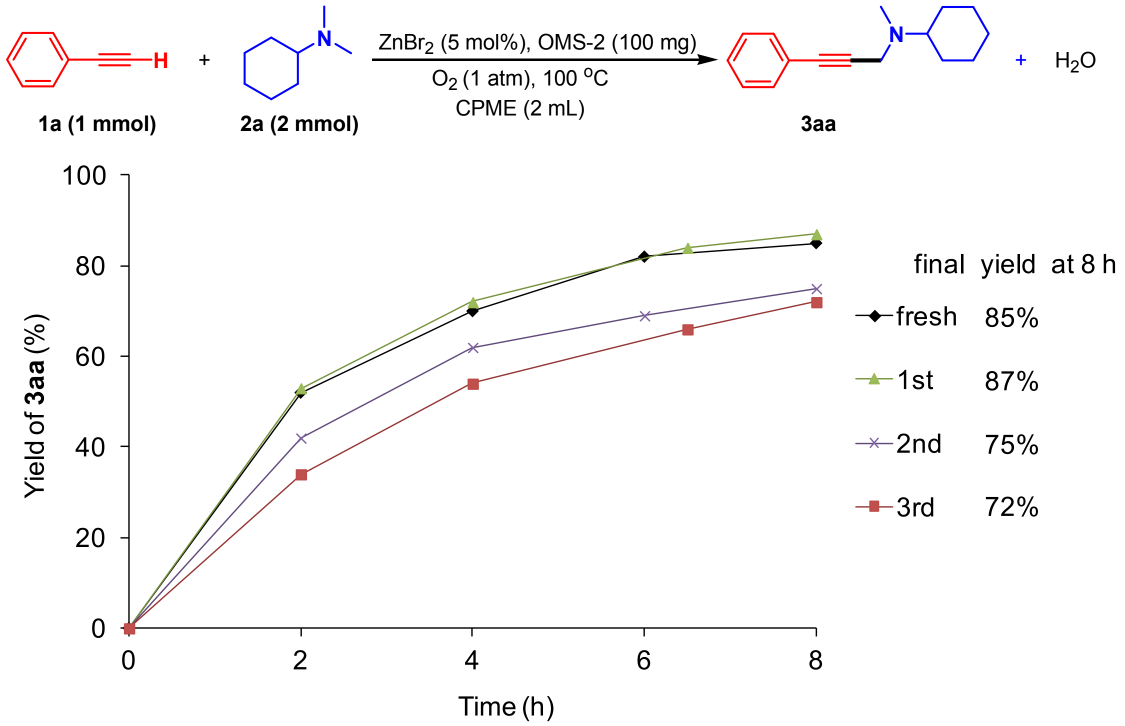


**Fig. S1** The reaction profiles for the reuse experiments. The reaction conditions were the same as those described in Table 1.

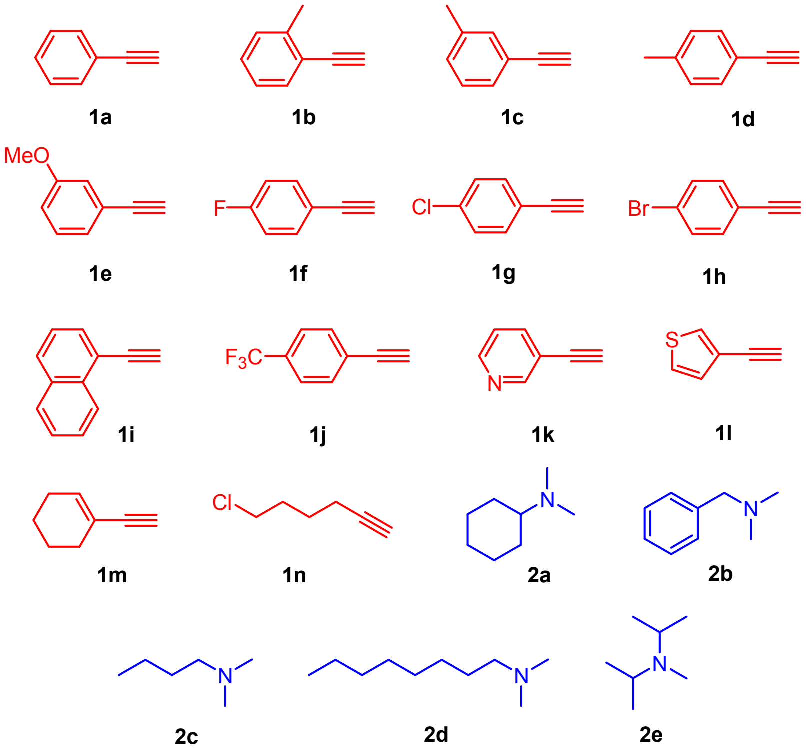
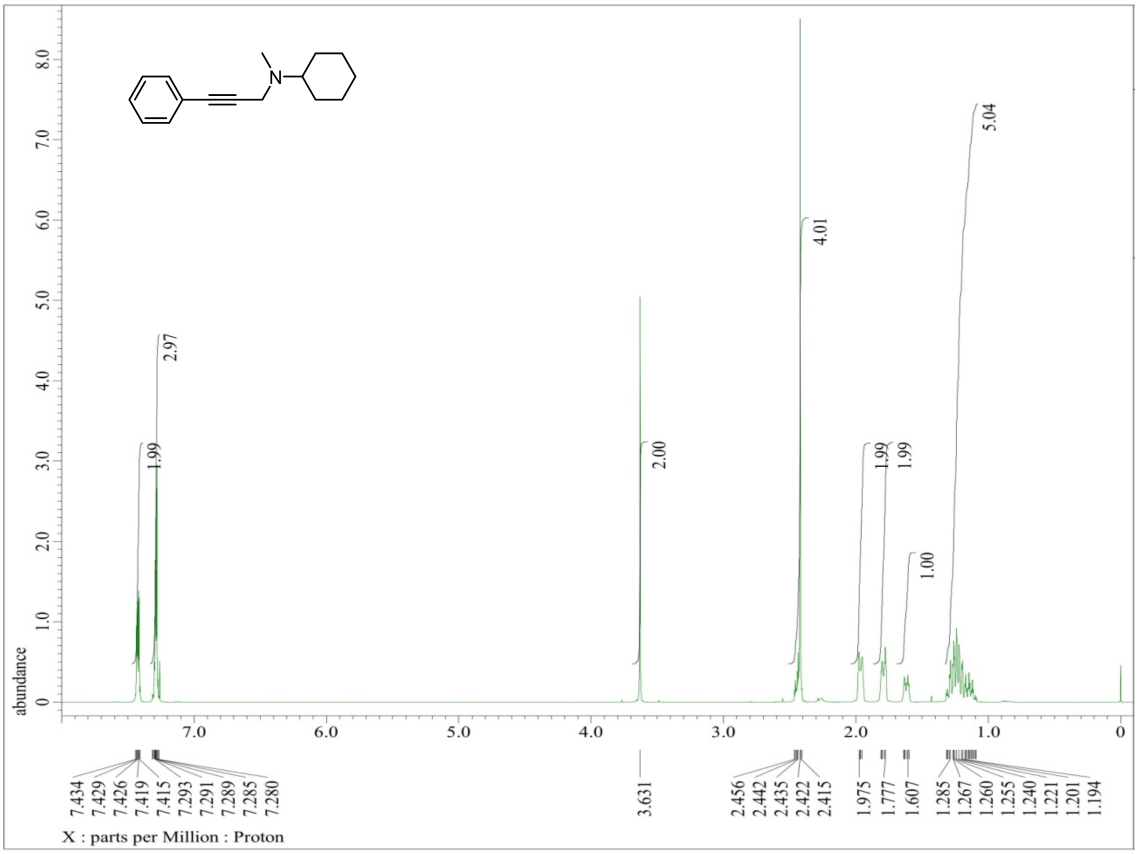


**Fig. S2** Terminal alkynes and tertiary amines used in this study.

## **NMR Spectra**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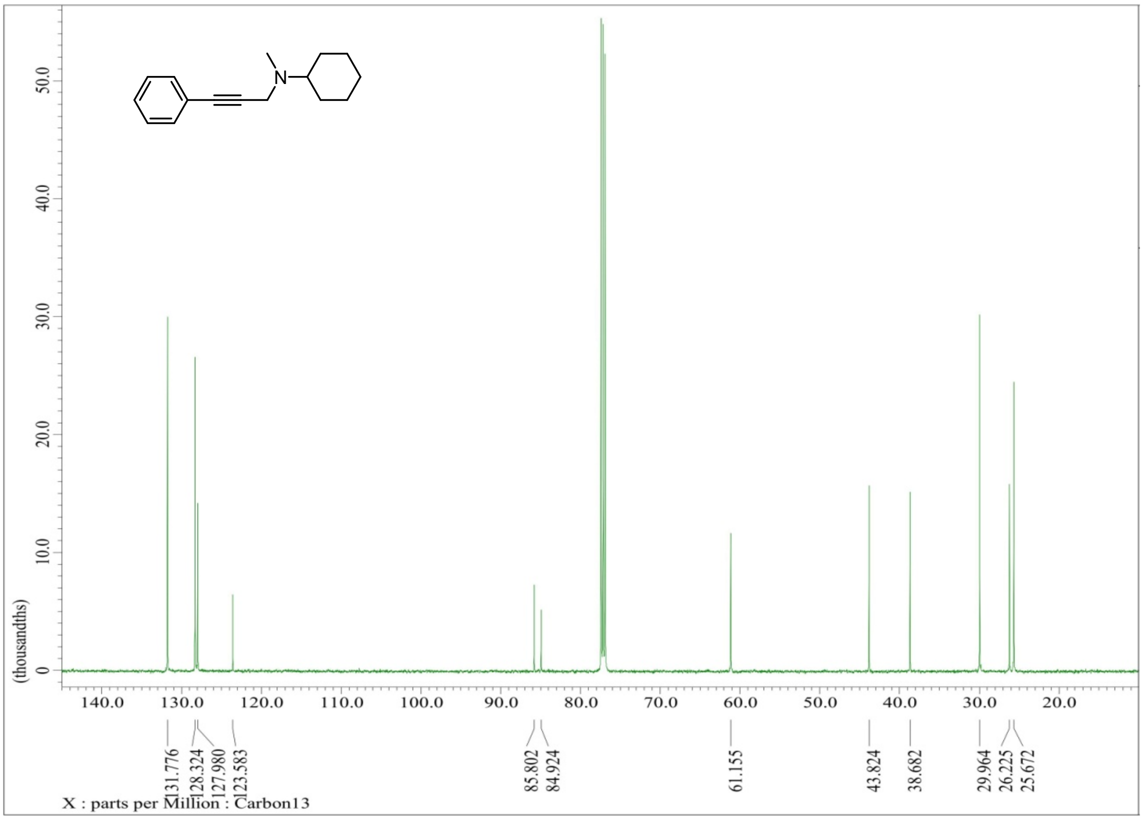
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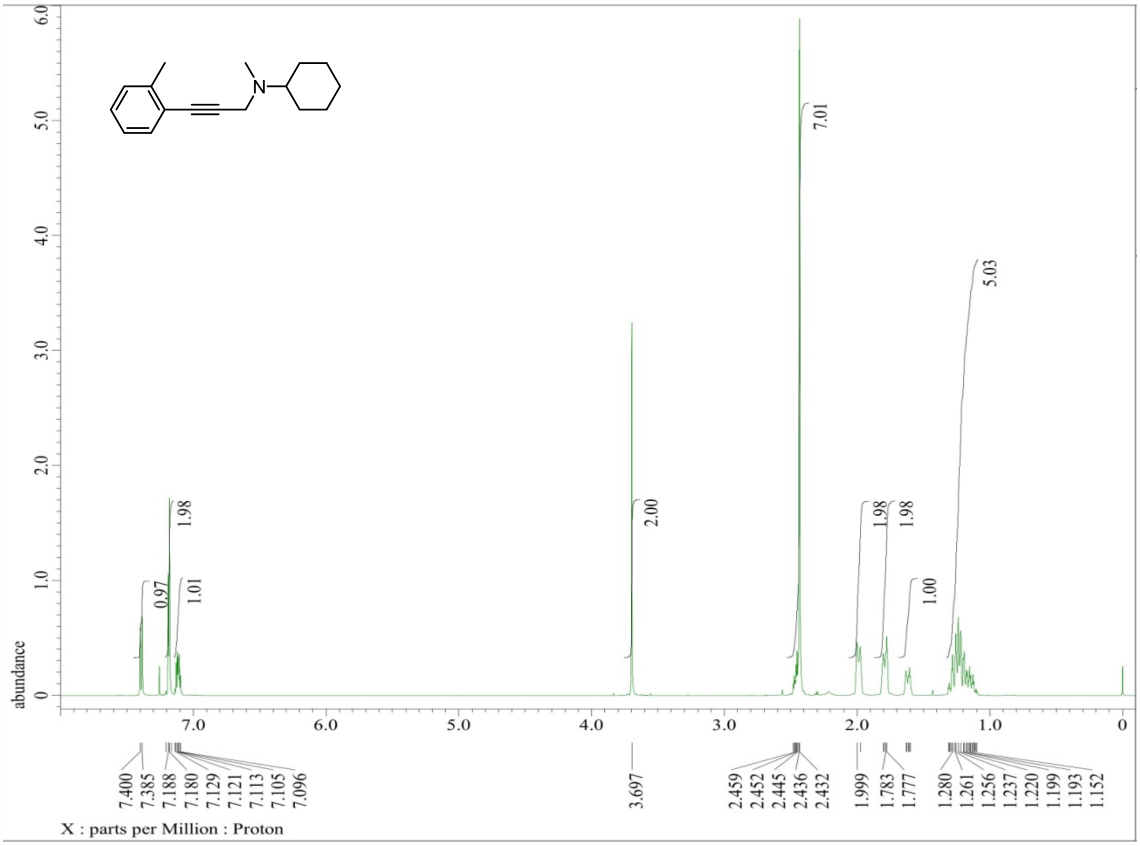
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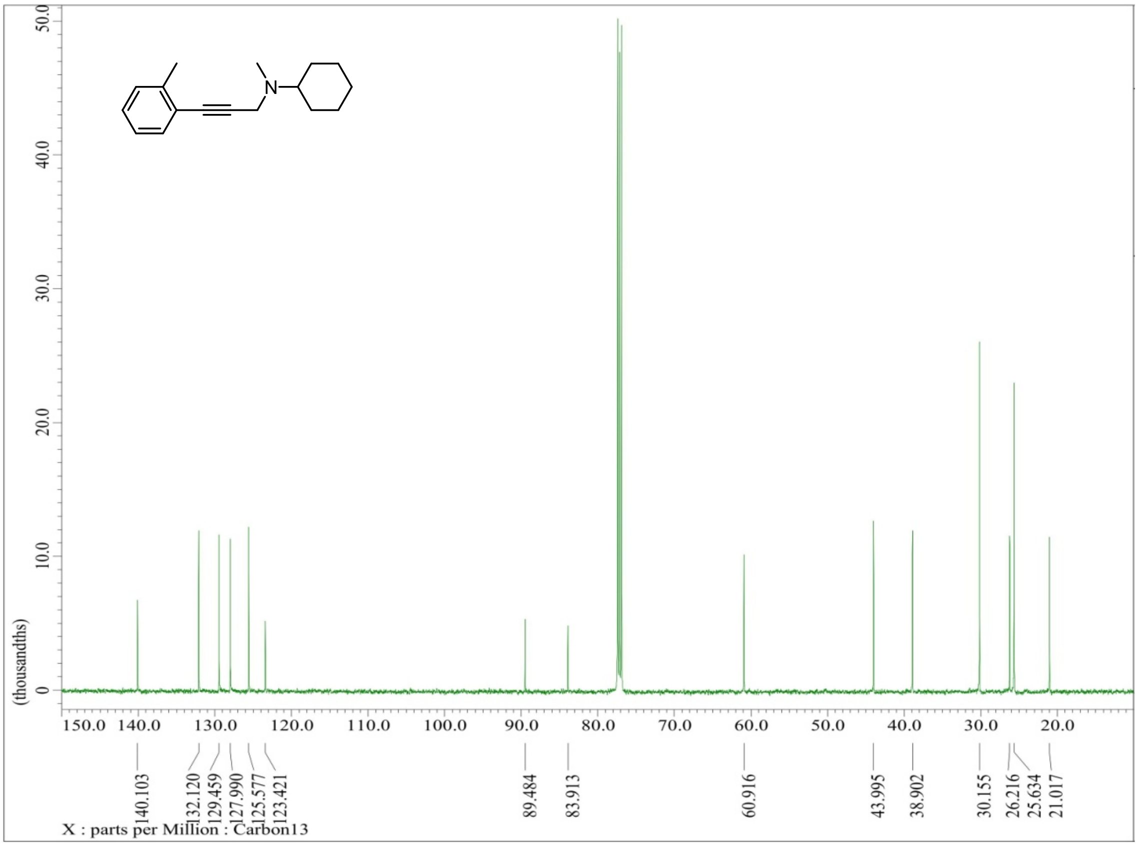
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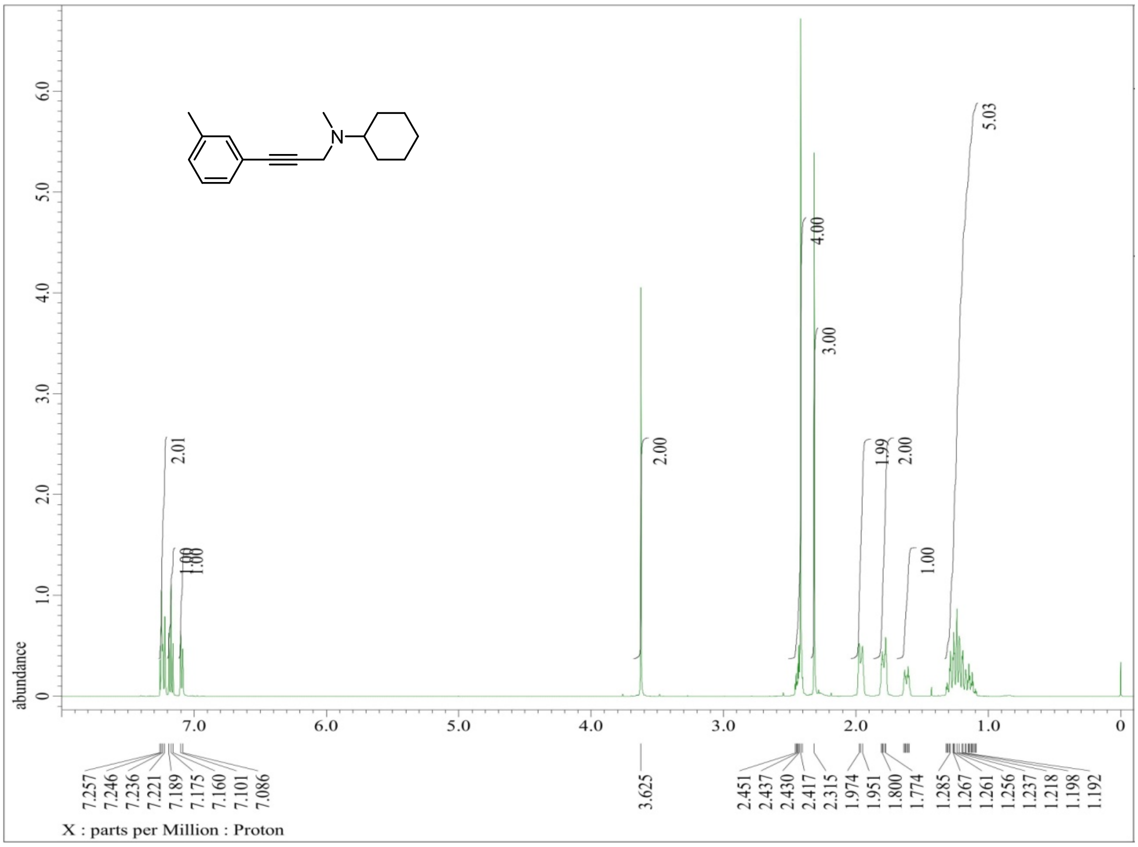
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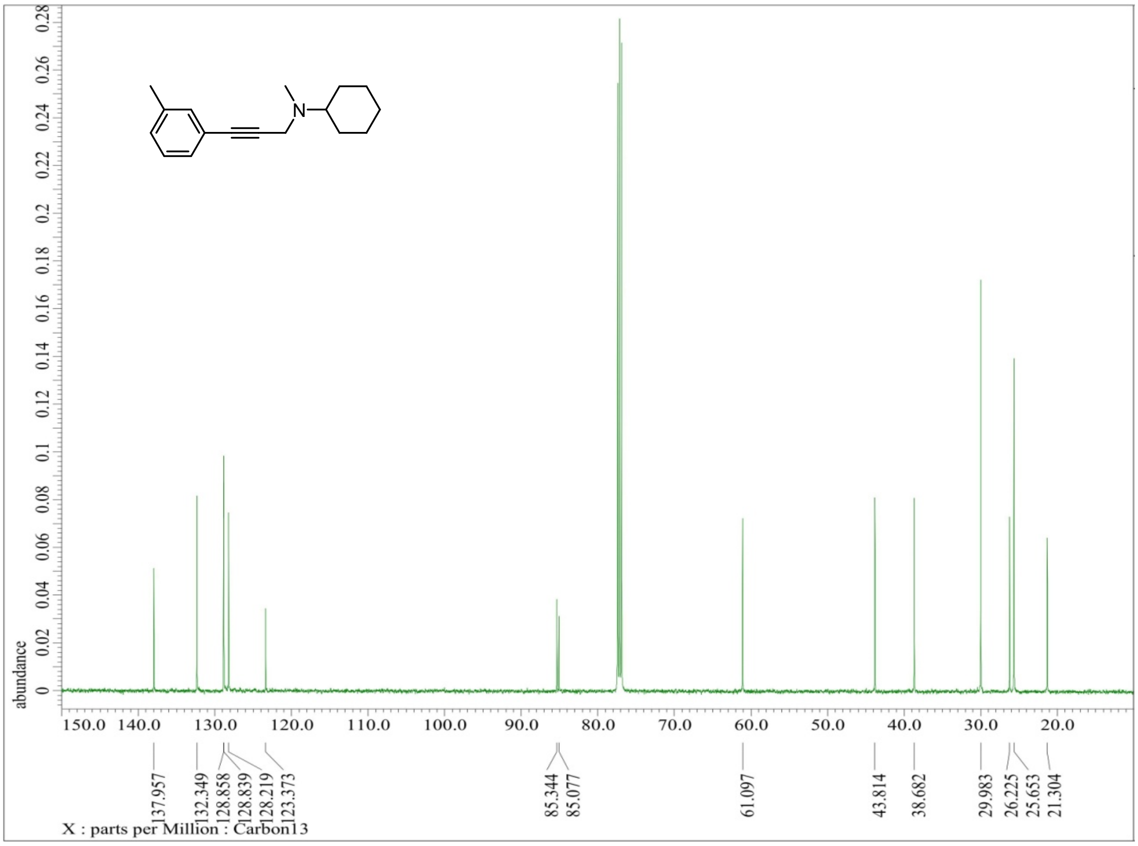
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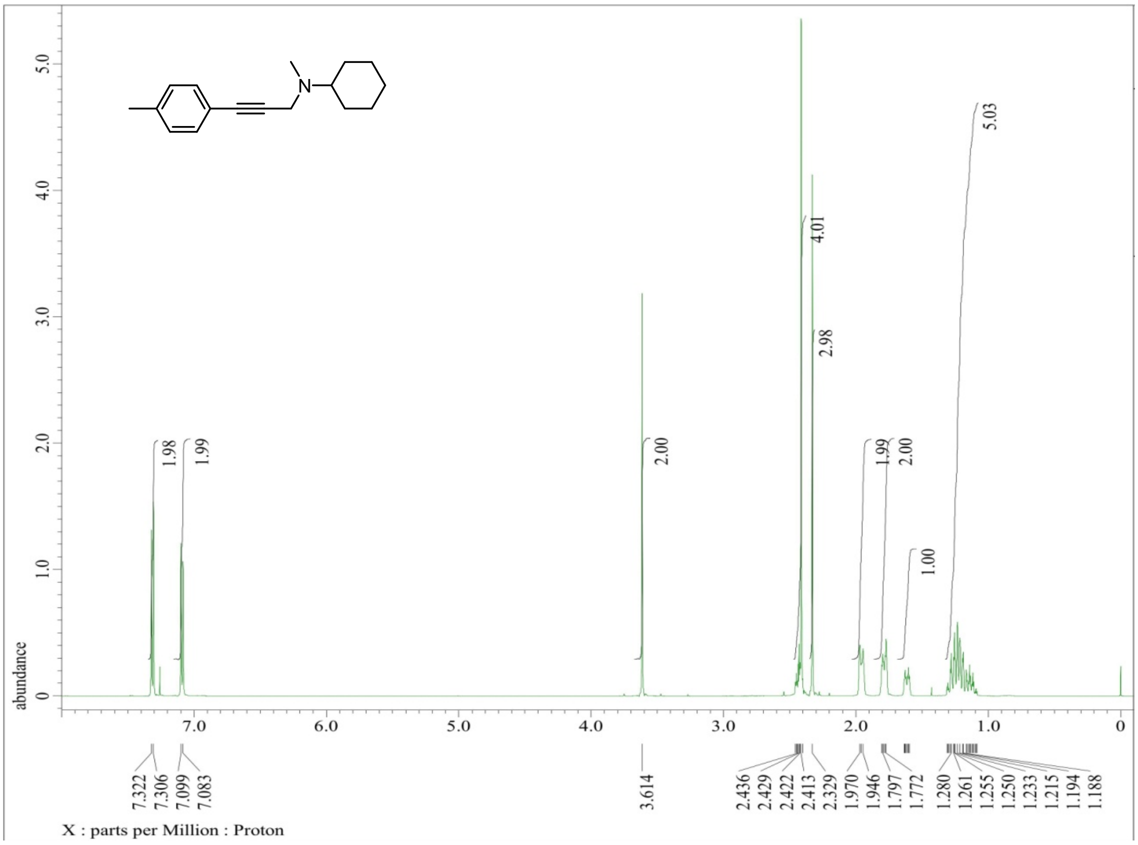
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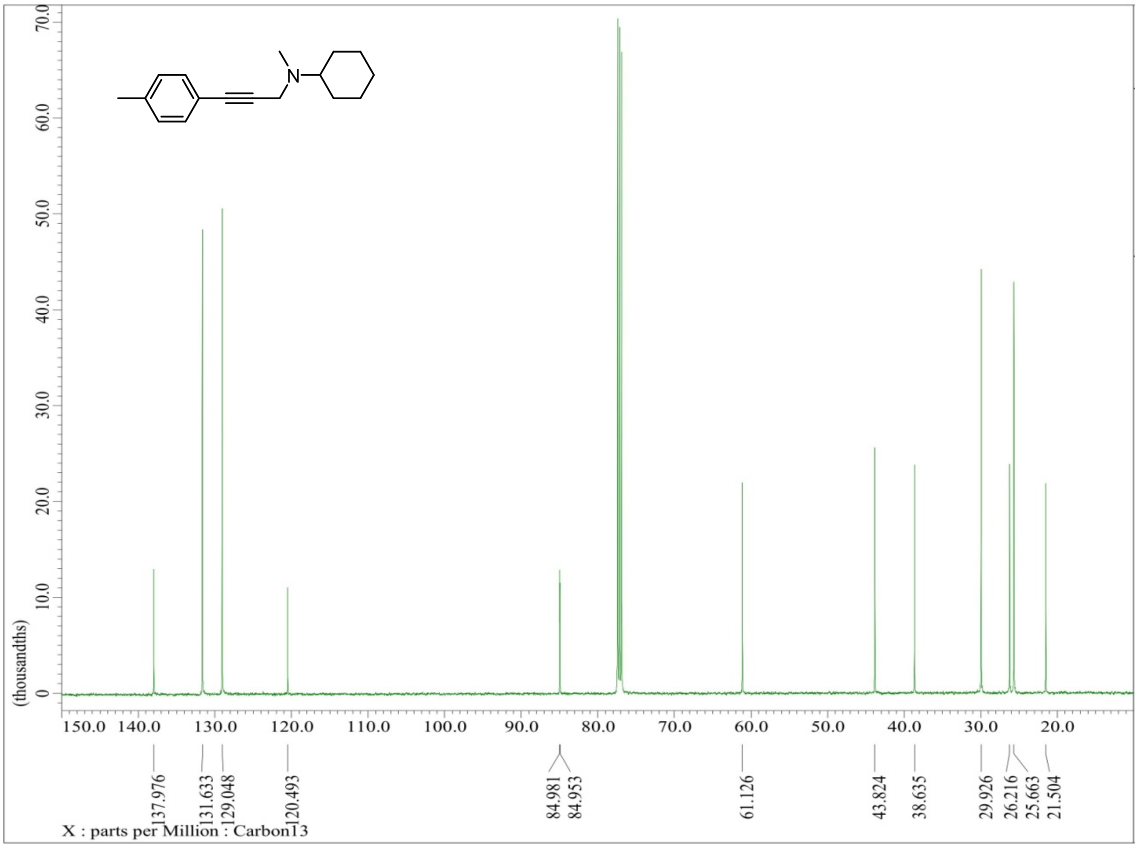
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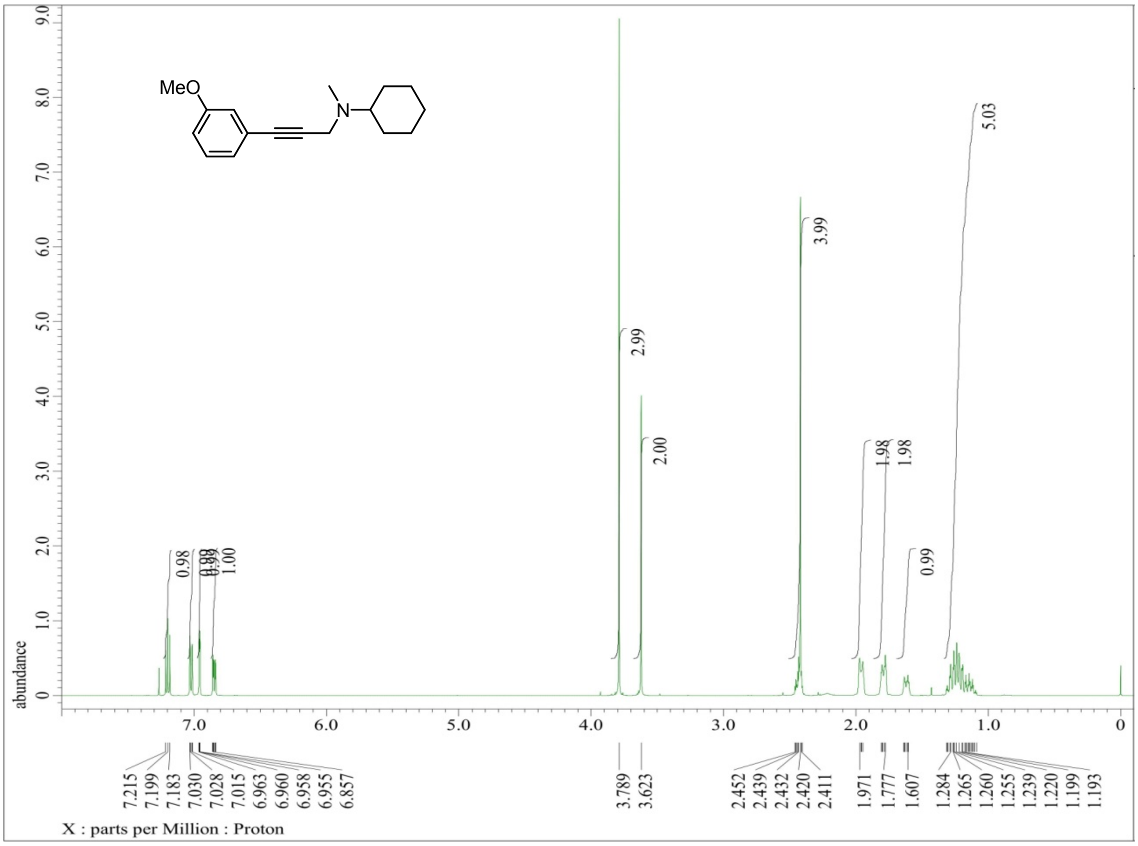
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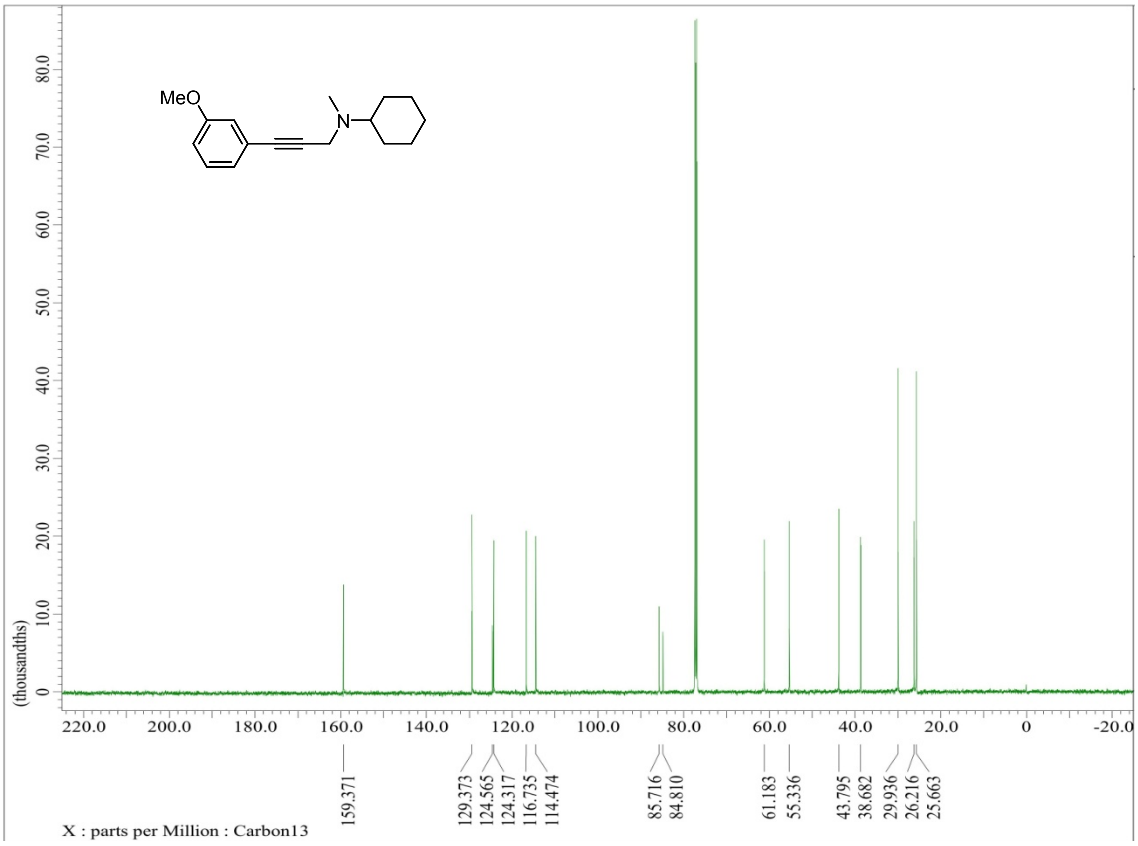
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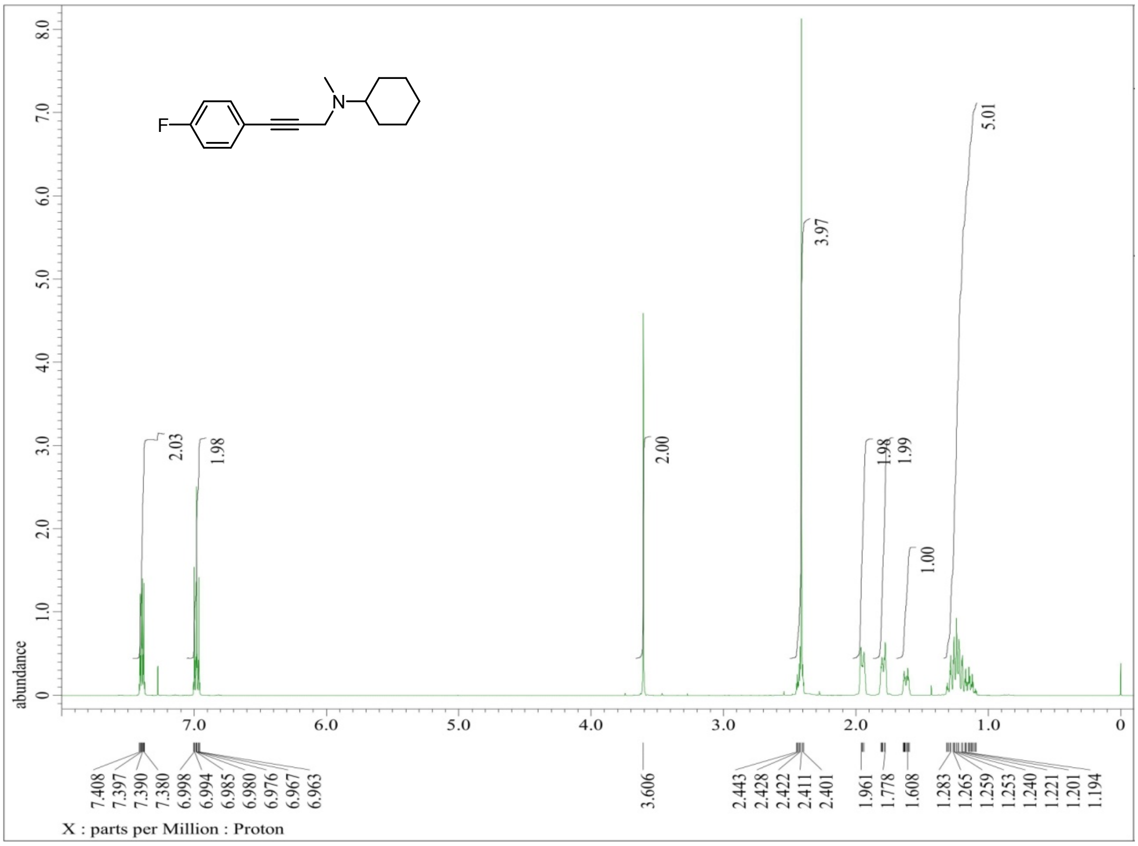
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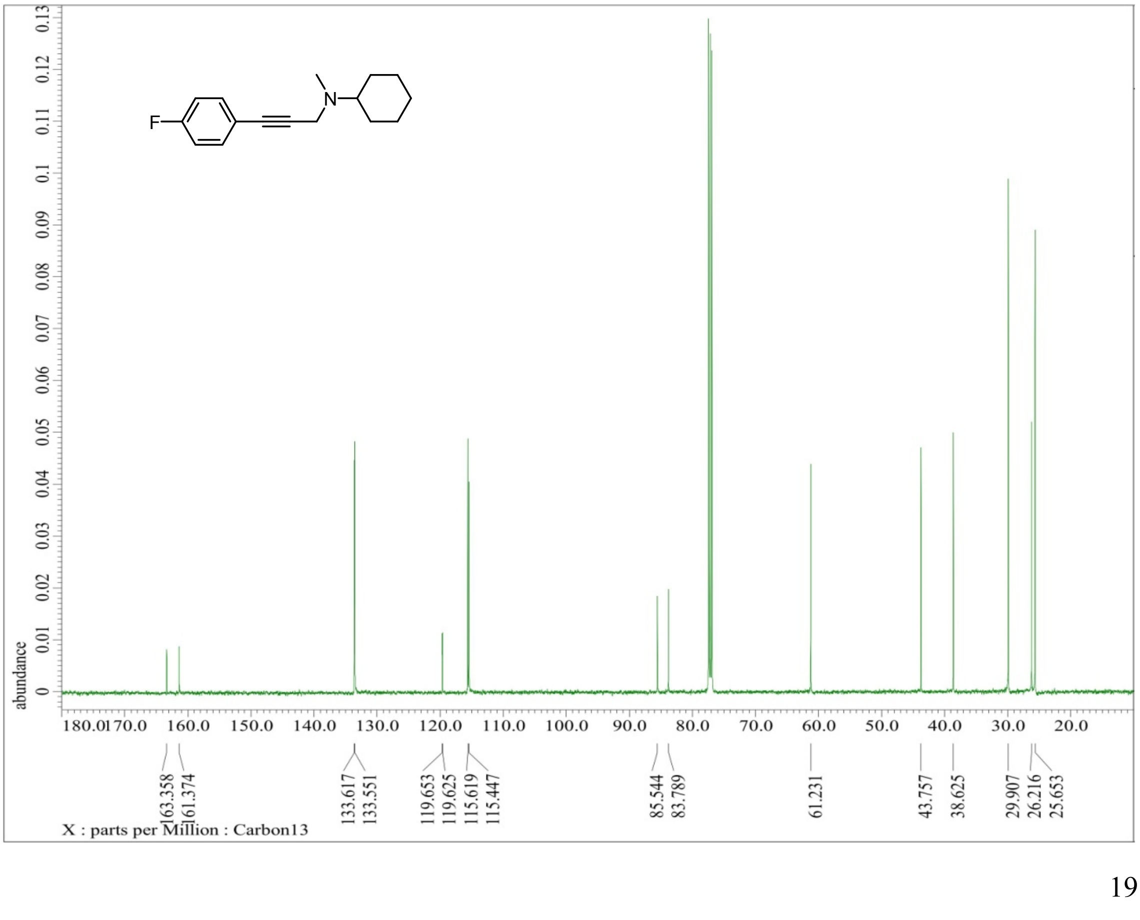
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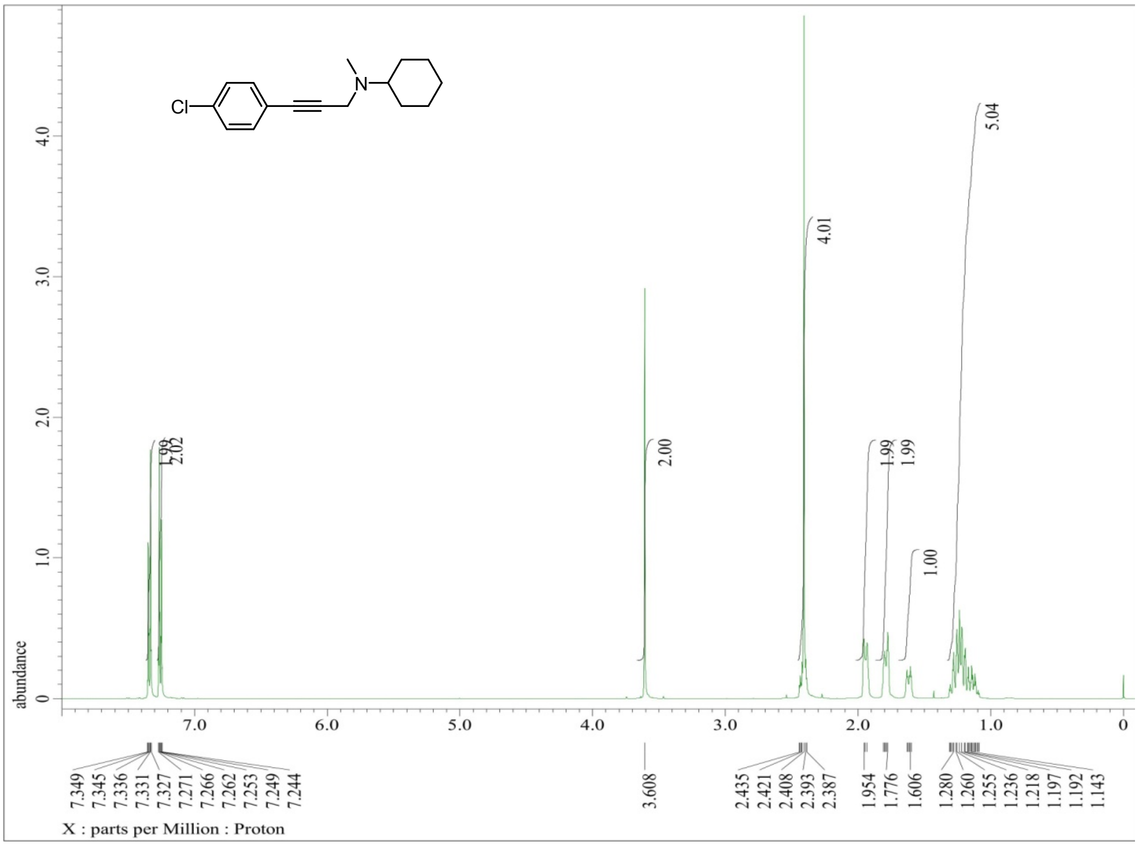
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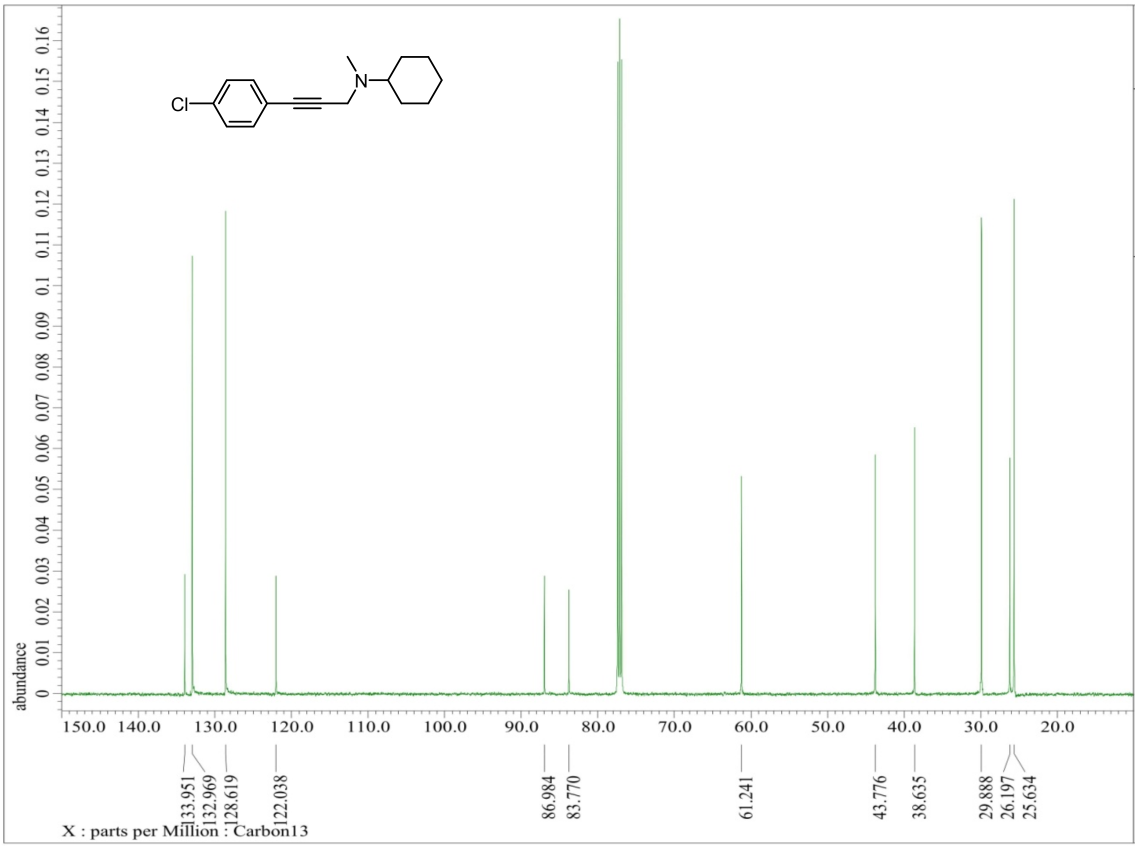
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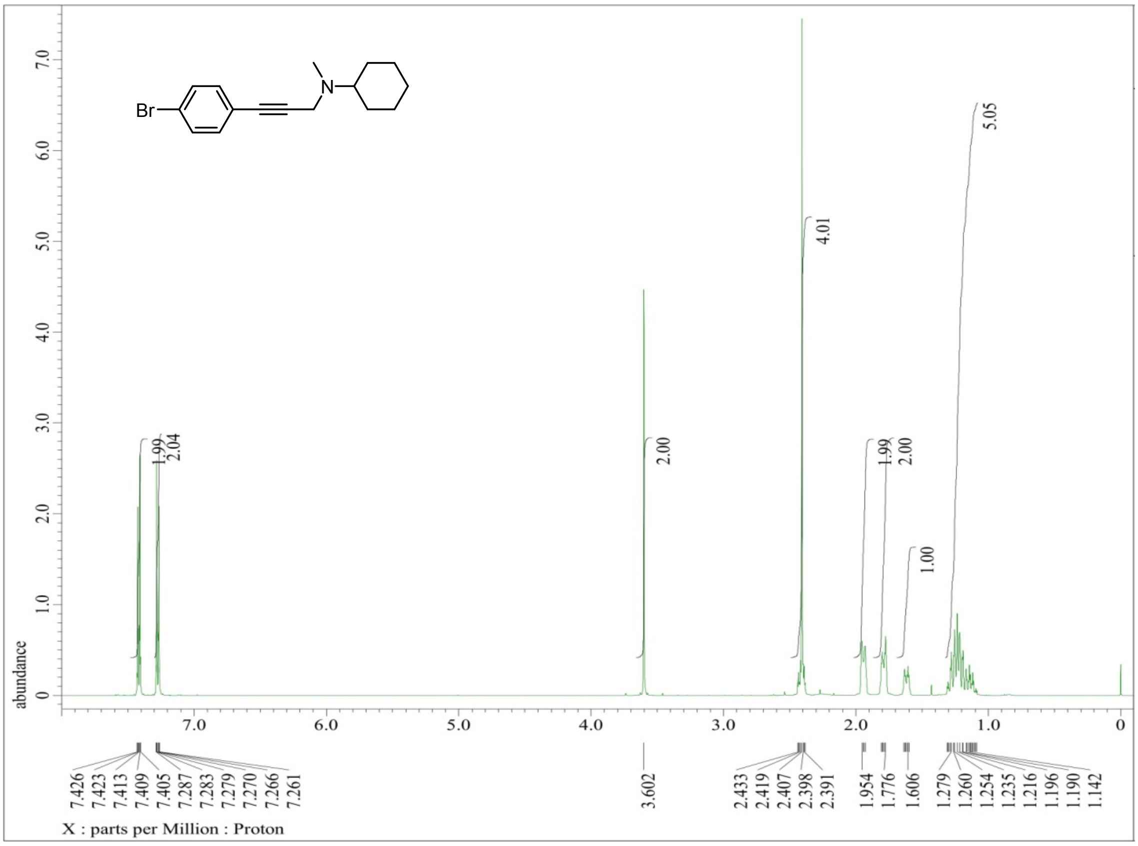
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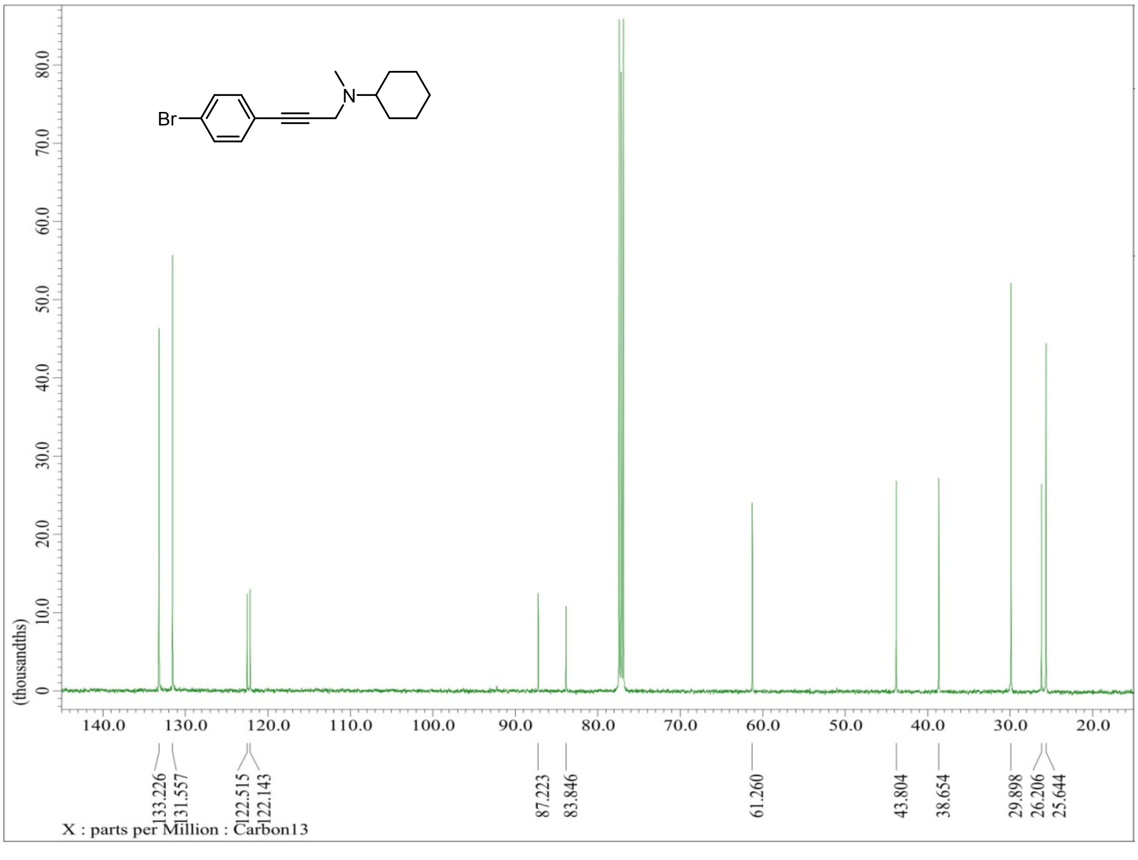
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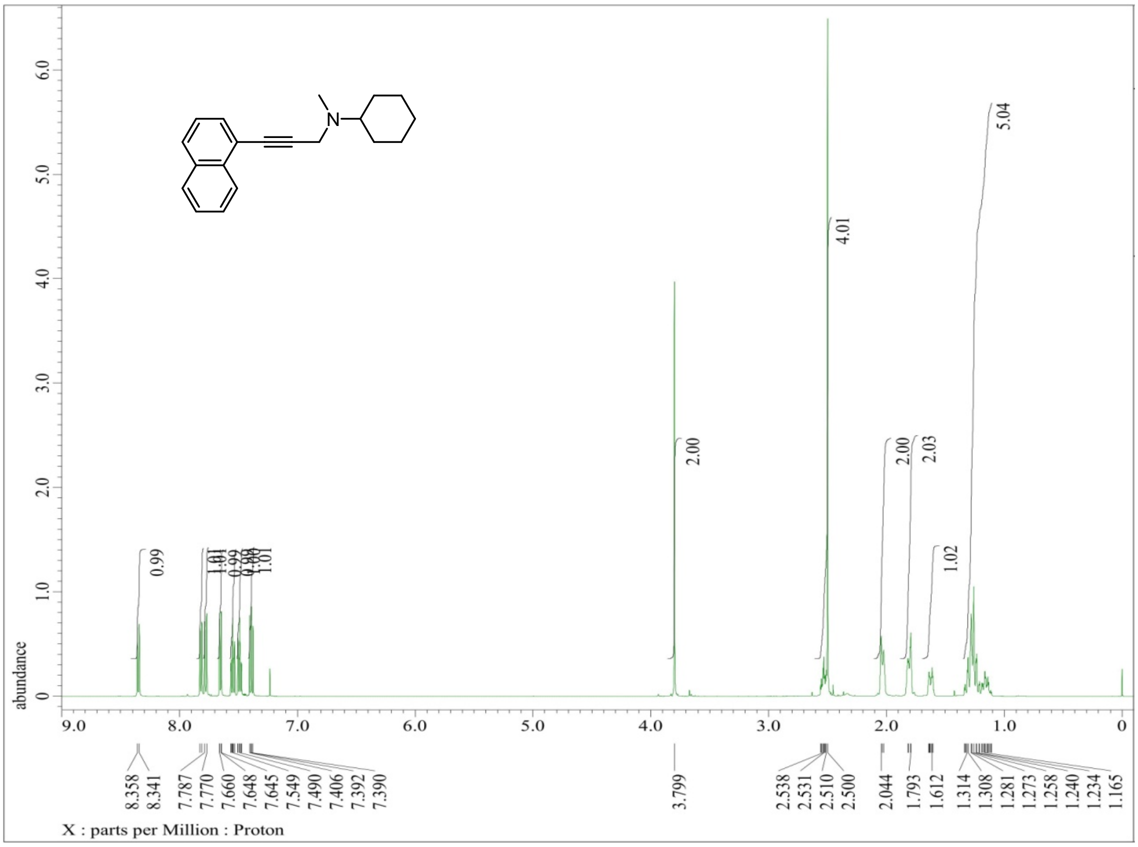
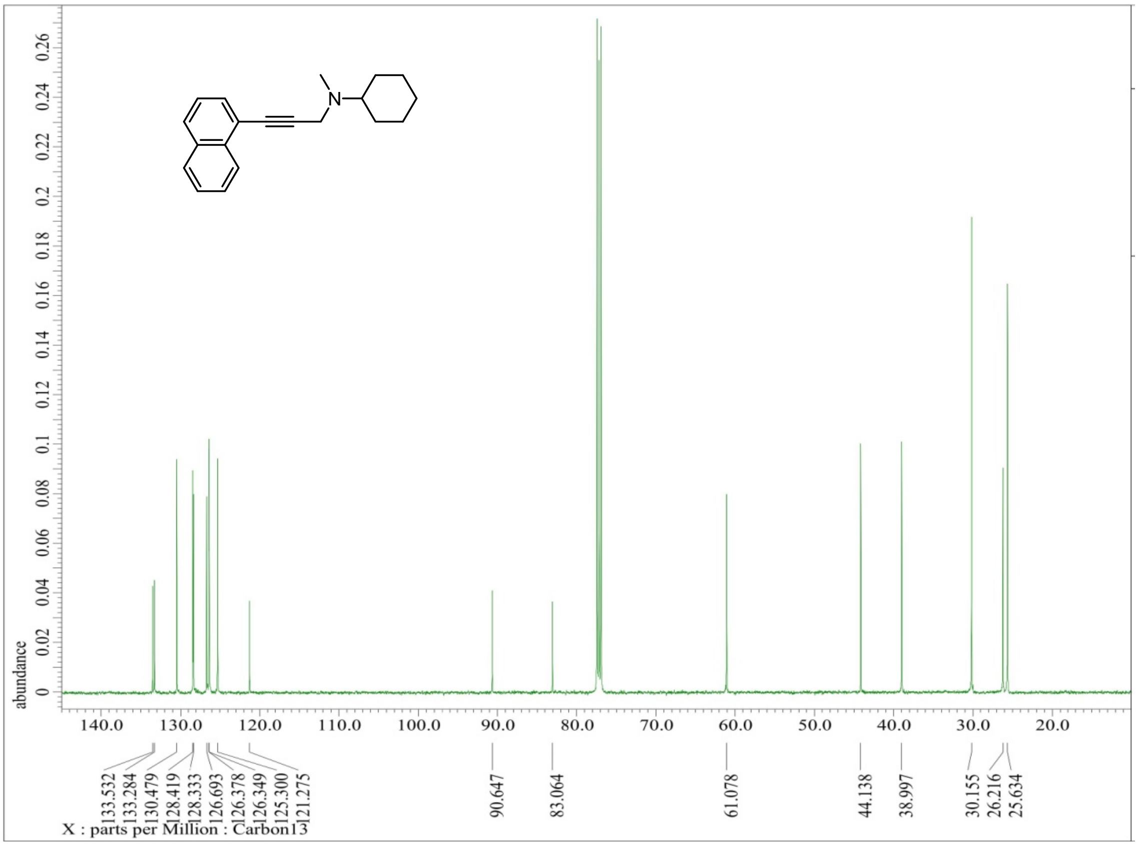
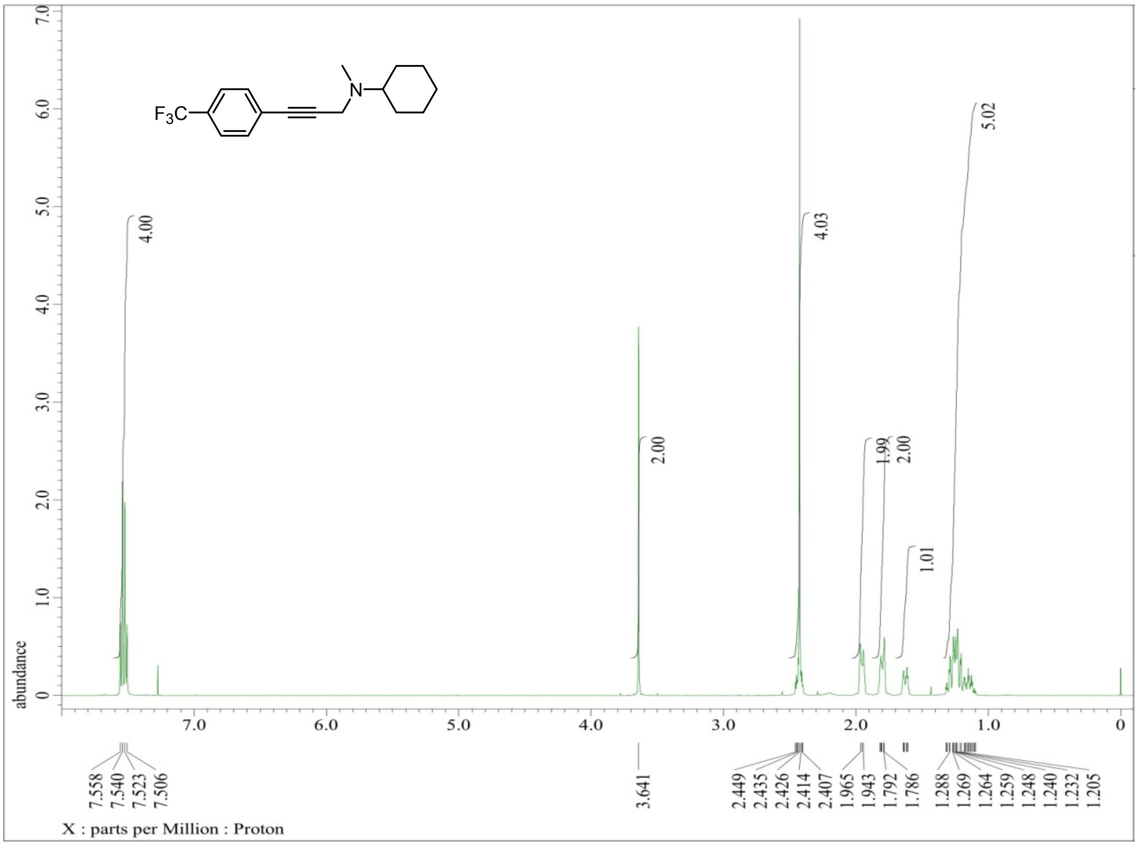
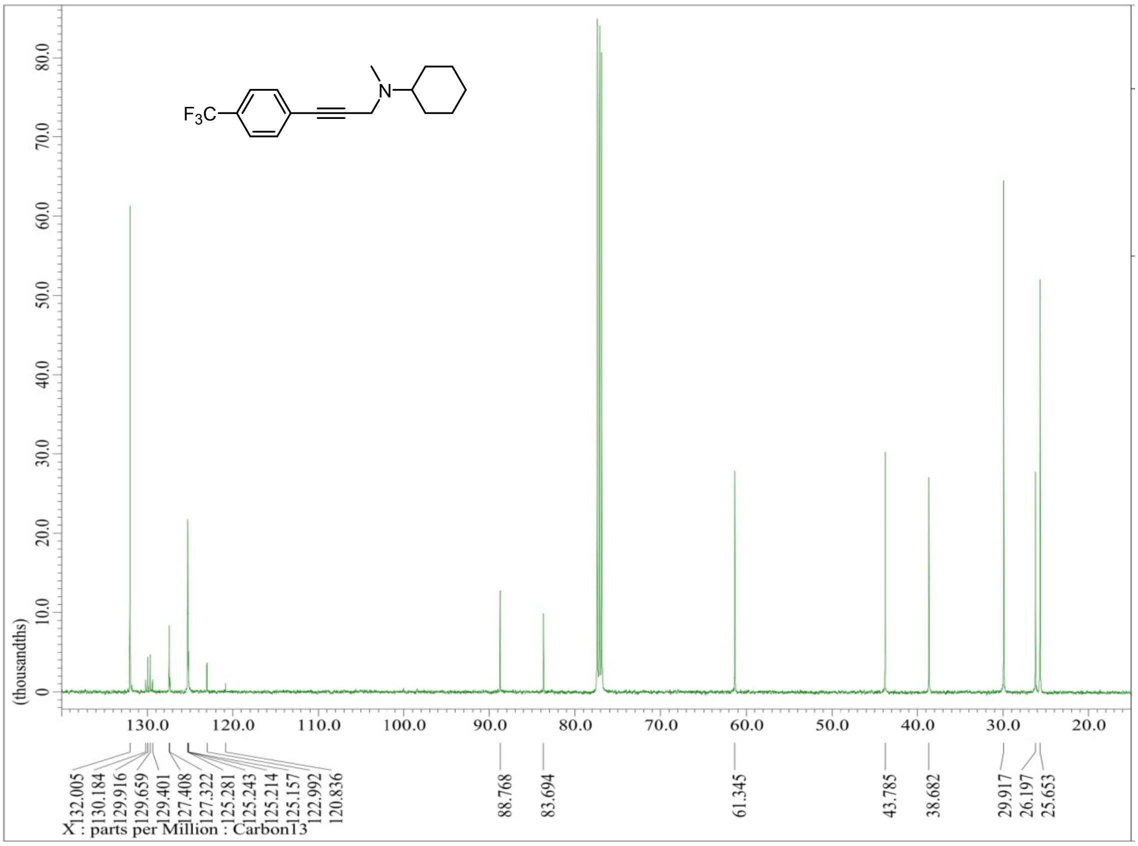
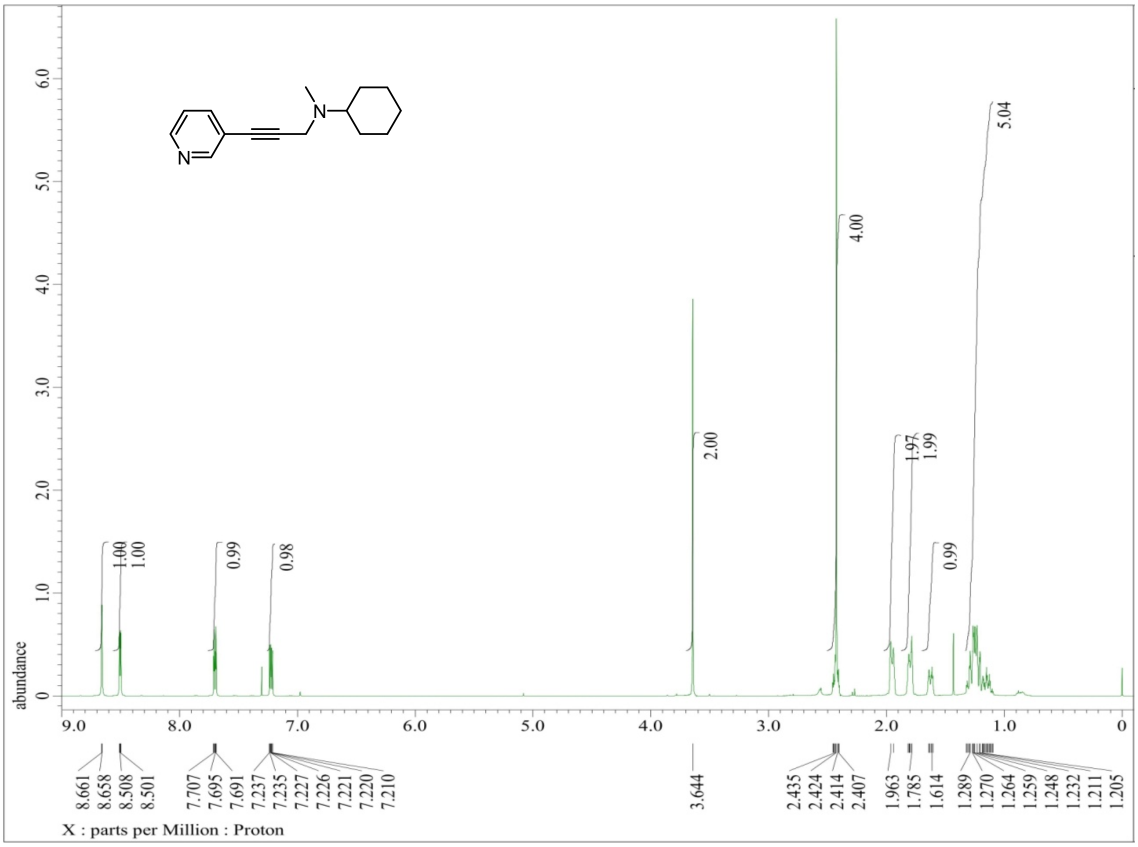
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
133.226
131.557
122.515
122.143
87.223
83.846
61.260
43.804
38.654
29.898
26.206
25.644
X : parts per Million : Carbon13

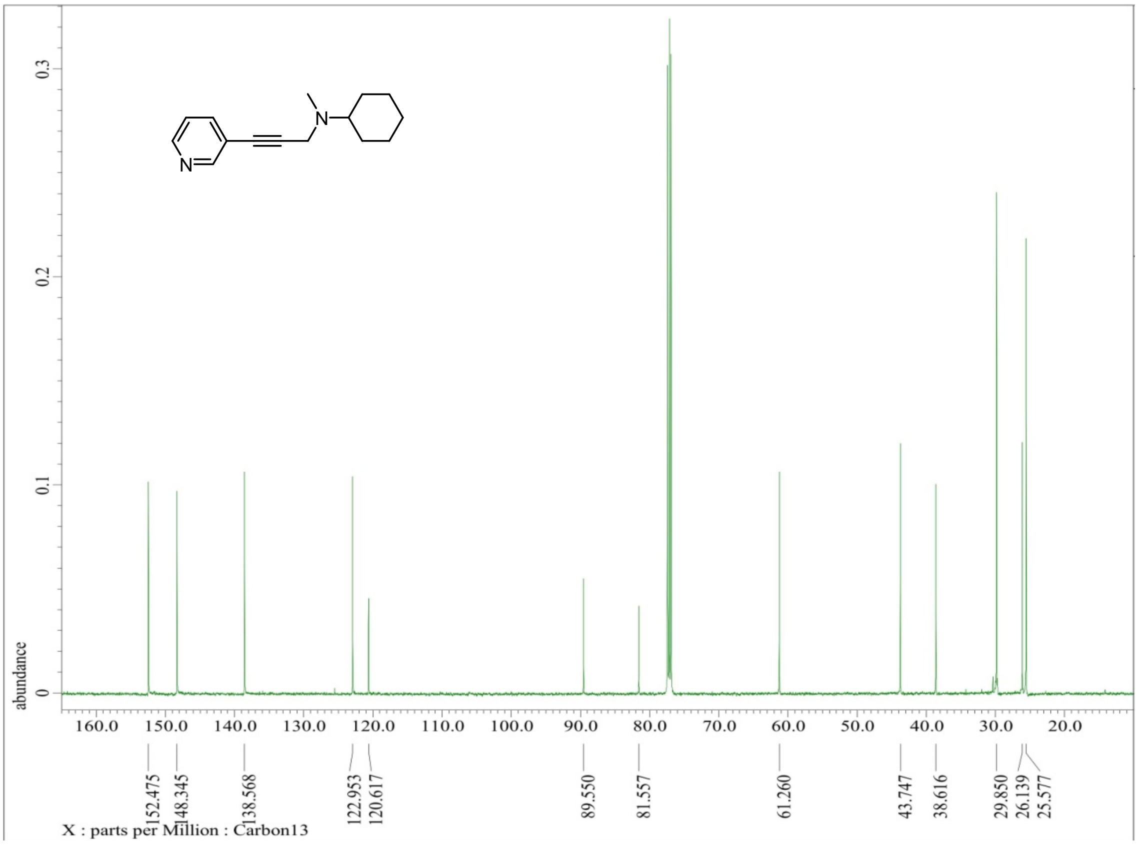

N
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
0.99
1.01
0.99
1.00
1.01
2.00
4.01
2.00
2.03
1.02
5.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.358
8.341
7.787
7.770
7.660
7.648
7.645
7.549
7.490
7.406
7.392
7.390
3.799
2.538
2.531
2.510
2.500
2.044
1.793
1.612
1.314
1.308
1.281
1.273
1.258
1.240
1.234
1.165
X : parts per Million : Proton

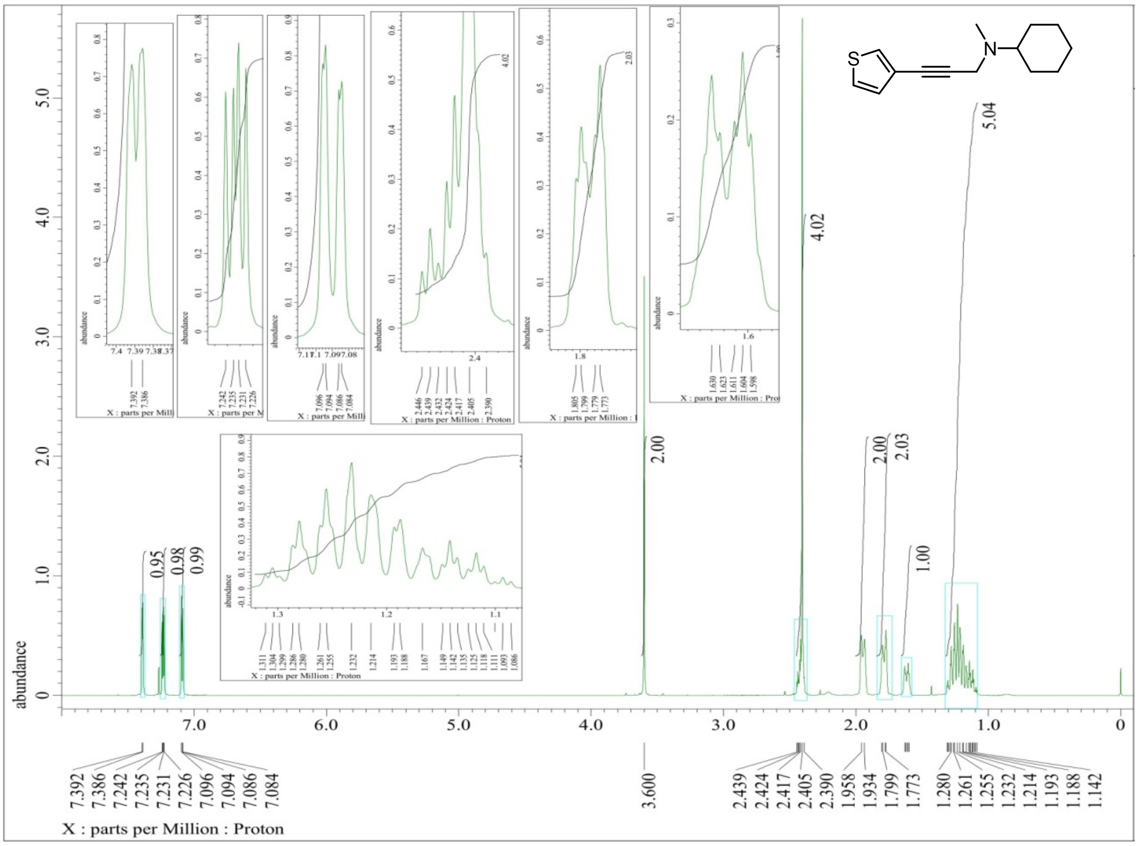

N
abundance
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
133.532
133.284
130.479
128.419
128.333
126.693
126.378
126.349
125.300
121.275
90.647
83.064
61.078
44.138
38.997
30.155
26.216
25.634
X : parts per Million : Carbon13

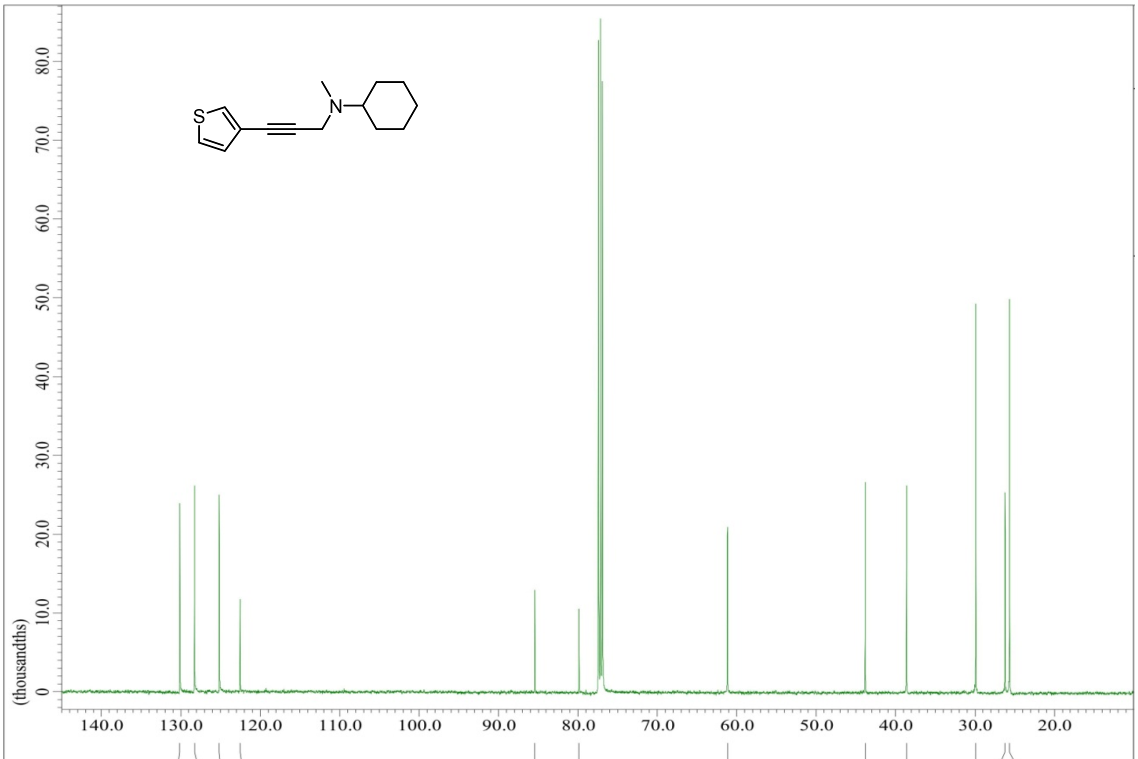

F3C
N
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
4.00
2.00
4.03
1.99
2.00
1.01
5.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.558
7.540
7.523
7.506
3.641
2.449
2.435
2.426
2.414
2.407
1.965
1.943
1.792
1.786
1.288
1.269
1.264
1.259
1.248
1.240
1.232
1.205
X : parts per Million : Proton

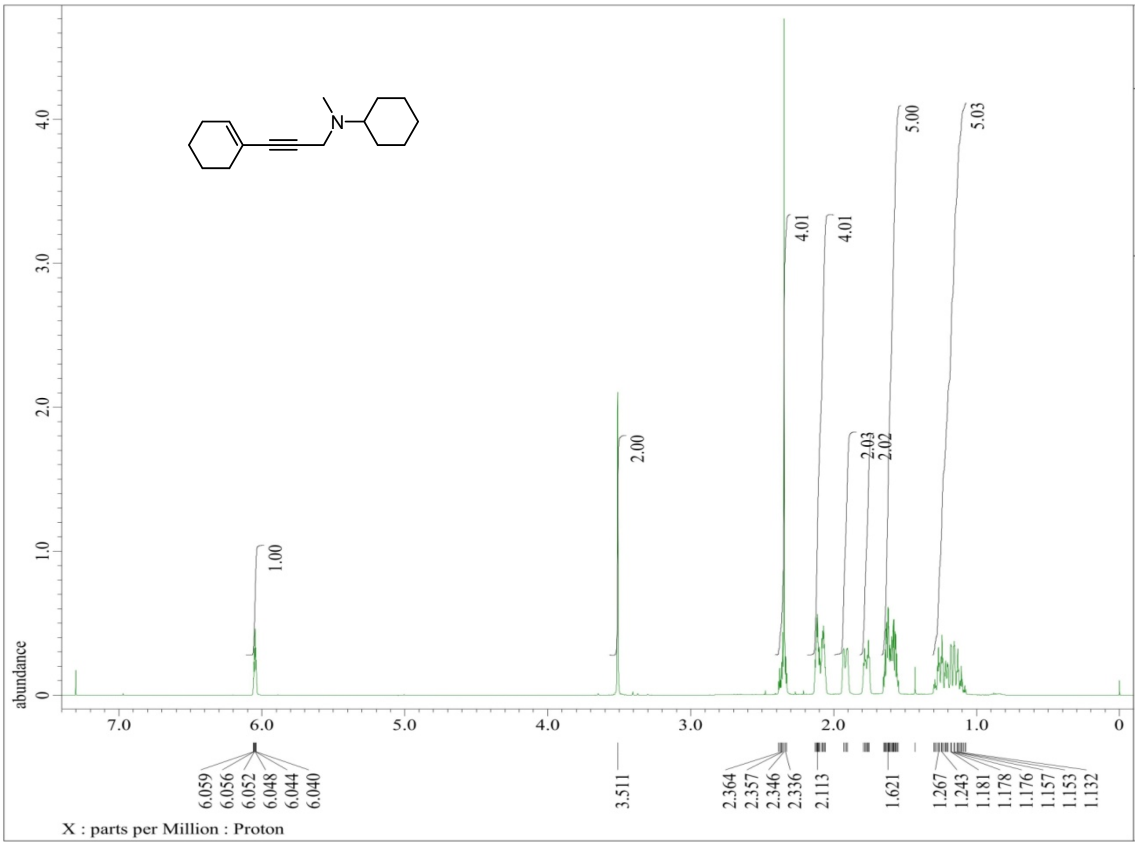

F3C
N
(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
132.005
130.184
129.916
129.659
129.401
127.408
127.322
125.281
125.243
125.214
125.157
122.992
120.836
88.768
83.694
61.345
43.785
38.682
29.917
26.197
25.653
X : parts per Million : Carbon13

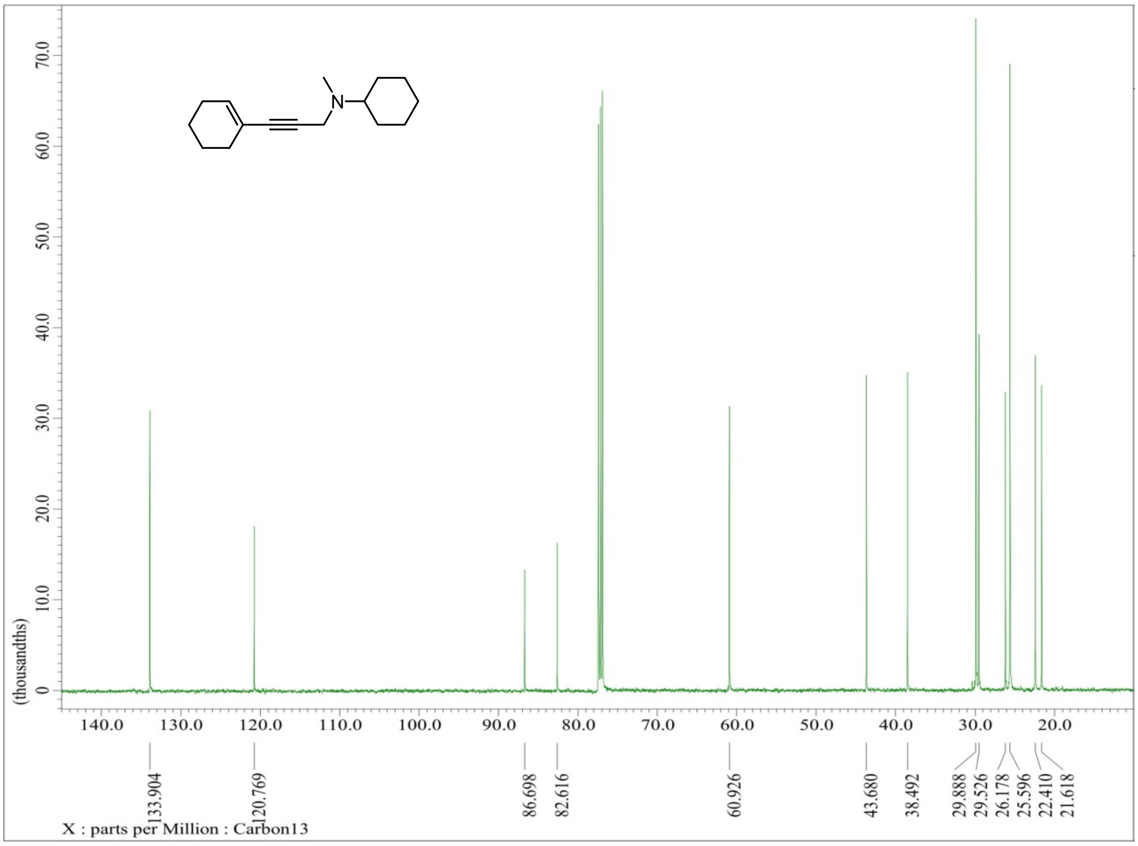

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.00
1.00
0.99
0.98
2.00
4.00
1.97
1.99
0.99
5.04
8.661
8.658
8.508
8.501
7.707
7.695
7.691
7.237
7.235
7.227
7.226
7.221
7.220
7.210
3.644
2.435
2.424
2.414
2.407
1.963
1.785
1.614
1.289
1.270
1.264
1.259
1.248
1.232
1.211
1.205
N
N
X : parts per Million : Proton

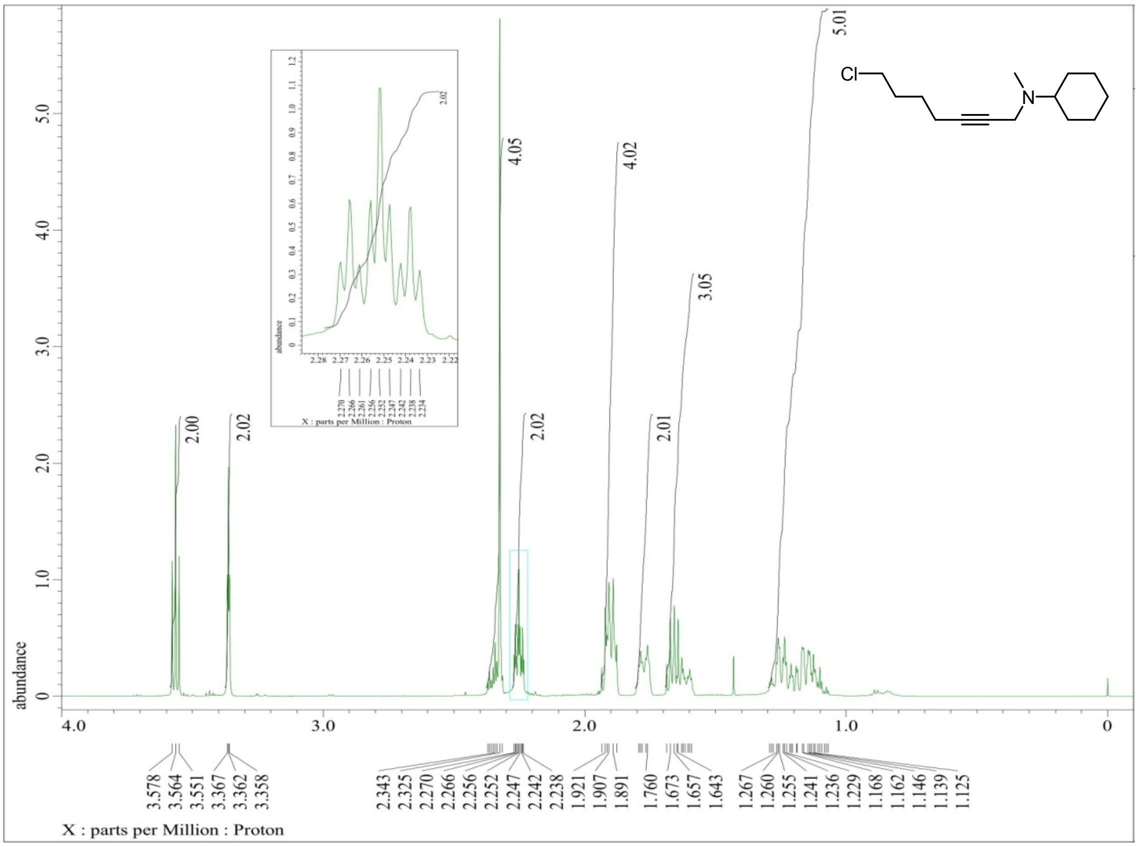

abundance
0
0.1
0.2
0.3
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
152.475
148.345
138.568
122.953
120.617
89.550
81.557
61.260
43.747
38.616
29.850
26.139
25.577
N
N
X : parts per Million : Carbon13


S
N
abundance
0
1.0
2.0
3.0
4.0
5.0
0.95
0.98
0.99
2.00
4.02
2.00
2.03
1.00
5.04
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.392
7.386
7.242
7.235
7.231
7.226
7.096
7.094
7.086
7.084
3.600
2.439
2.424
2.417
2.405
2.390
1.958
1.934
1.799
1.773
1.280
1.261
1.255
1.232
1.214
1.193
1.188
1.142
X : parts per Million : Proton

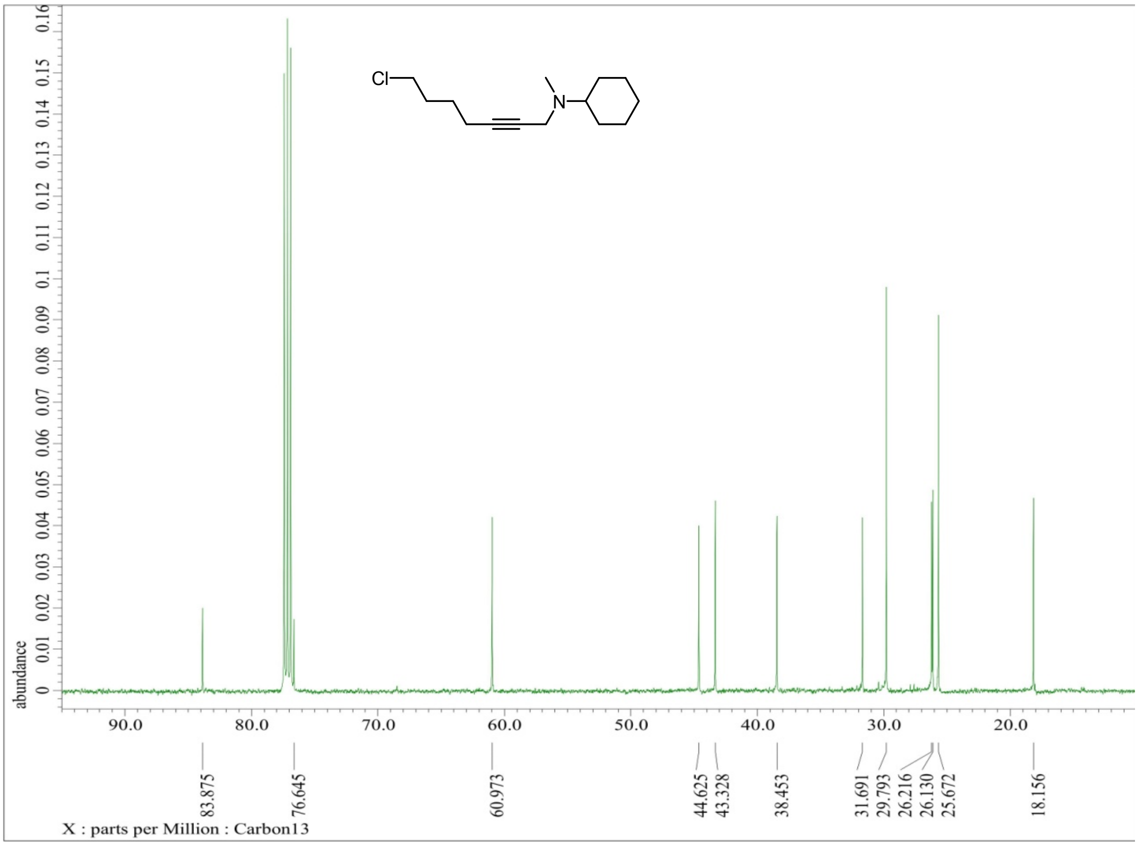

S
N
(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
130.126
128.276
125.157
122.553
85.420
79.869
61.164
43.814
38.625
29.898
26.225
25.653
X : parts per Million : Carbon13


abundance
0
1.0
2.0
3.0
4.0
1.00
2.00
4.01
4.01
2.03
2.02
5.00
5.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
6.059
6.056
6.052
6.048
6.044
6.040
3.511
2.364
2.357
2.346
2.336
2.113
1.621
1.267
1.243
1.181
1.178
1.176
1.157
1.153
1.132
N
X : parts per Million : Proton

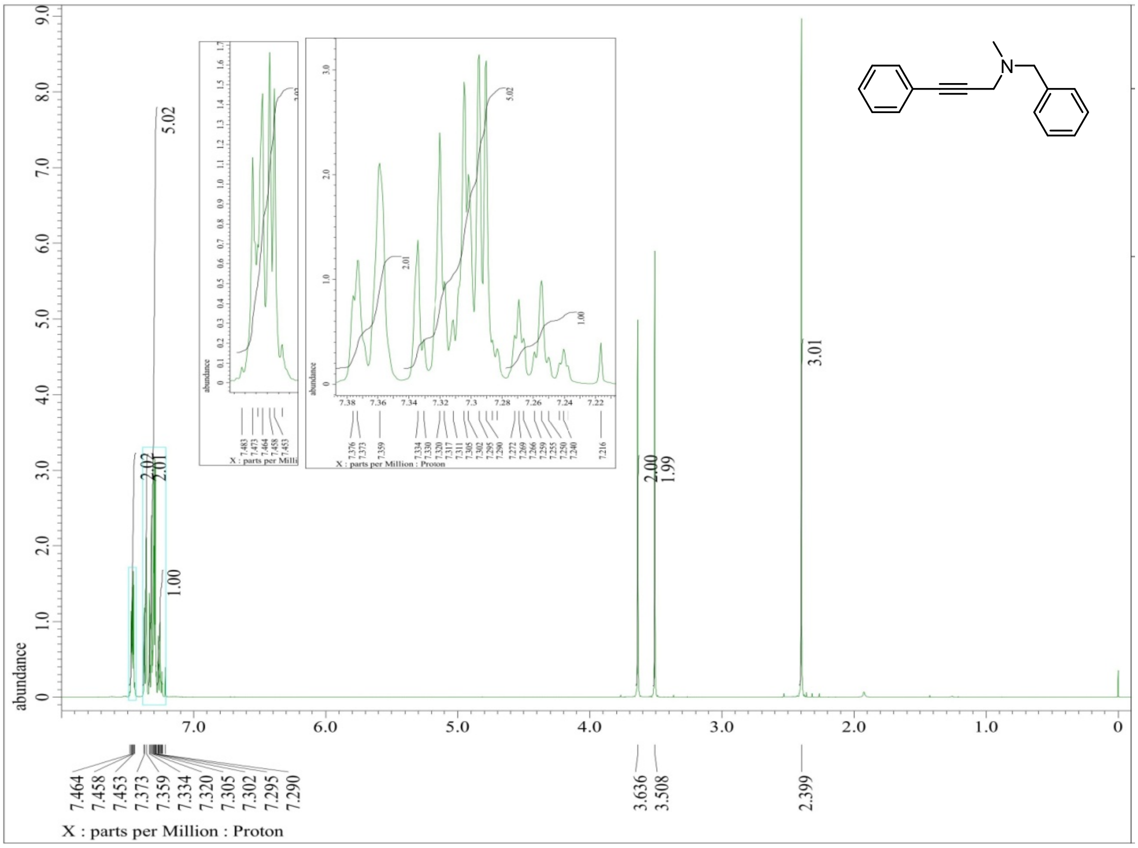

(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
133.904
120.769
86.698
82.616
60.926
43.680
38.492
29.888
29.526
26.178
25.596
22.410
21.618
N
X : parts per Million : Carbon13

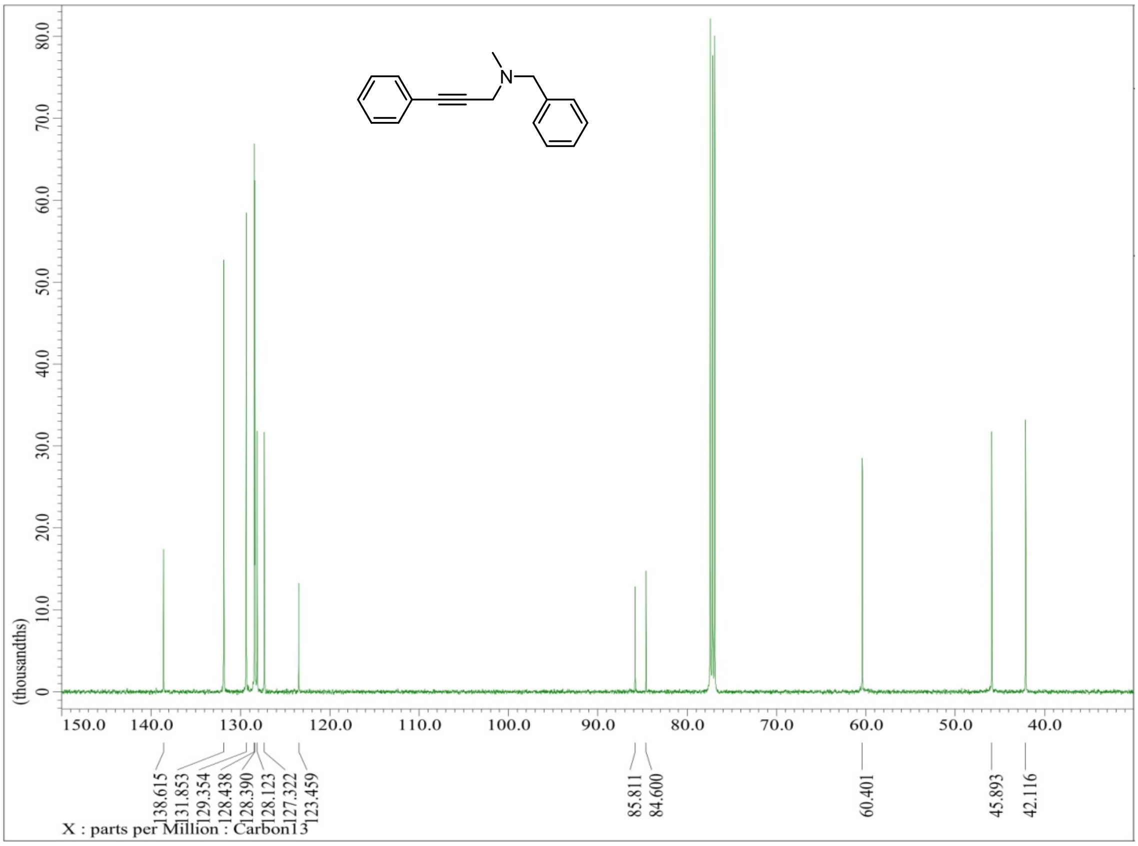


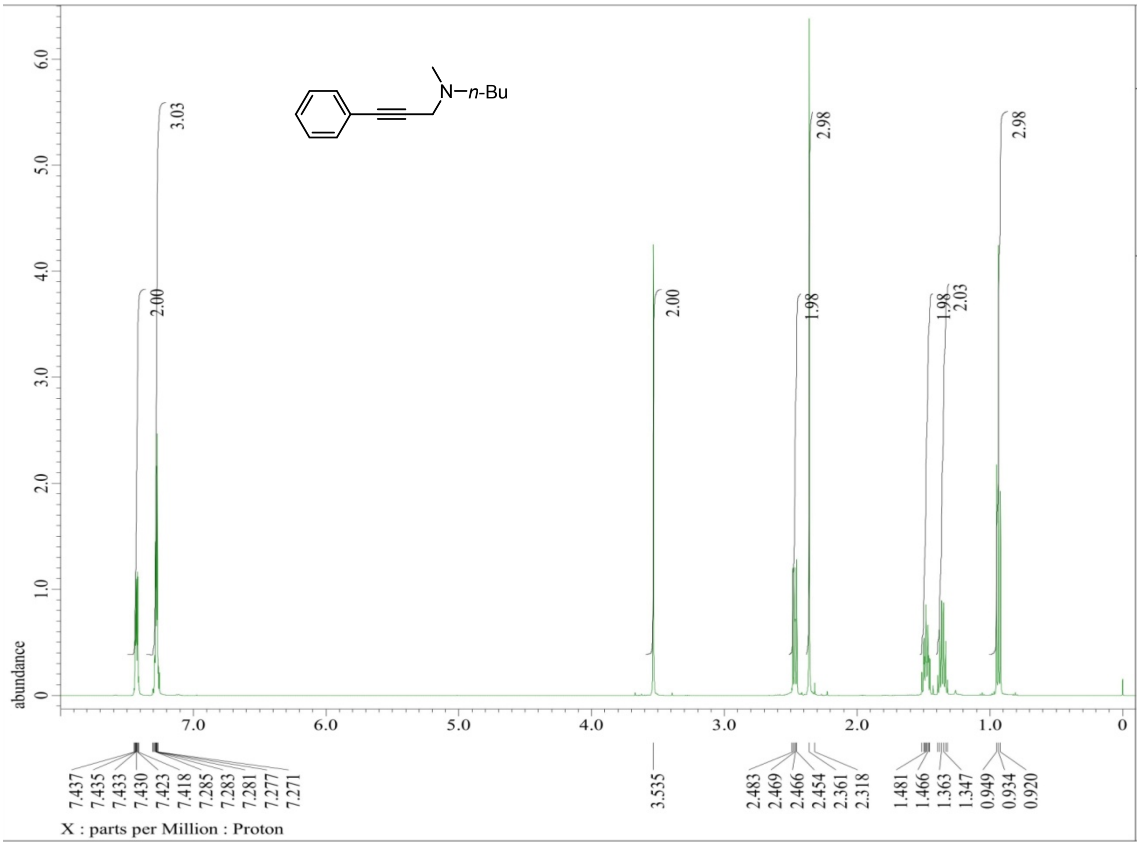
Cl
N
abundance
5.0
4.0
3.0
2.0
1.0
0
4.0
3.0
2.0
1.0
0
2.00
2.02
4.05
2.02
4.02
2.01
3.05
5.01
3.578
3.564
3.551
3.367
3.362
3.358
2.343
2.325
2.270
2.266
2.256
2.252
2.247
2.242
2.238
1.921
1.907
1.891
1.760
1.673
1.657
1.643
1.267
1.260
1.255
1.241
1.236
1.229
1.168
1.162
1.146
1.139
1.125
X : parts per Million : Proton

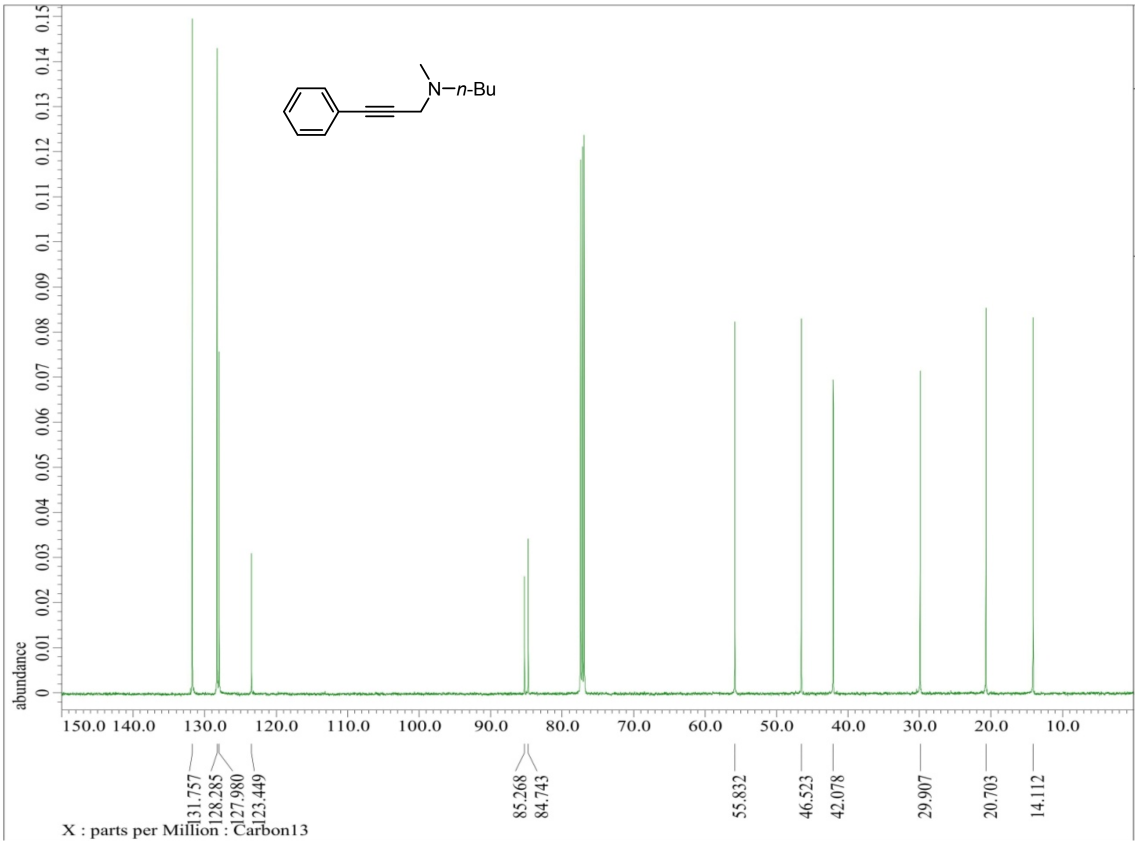


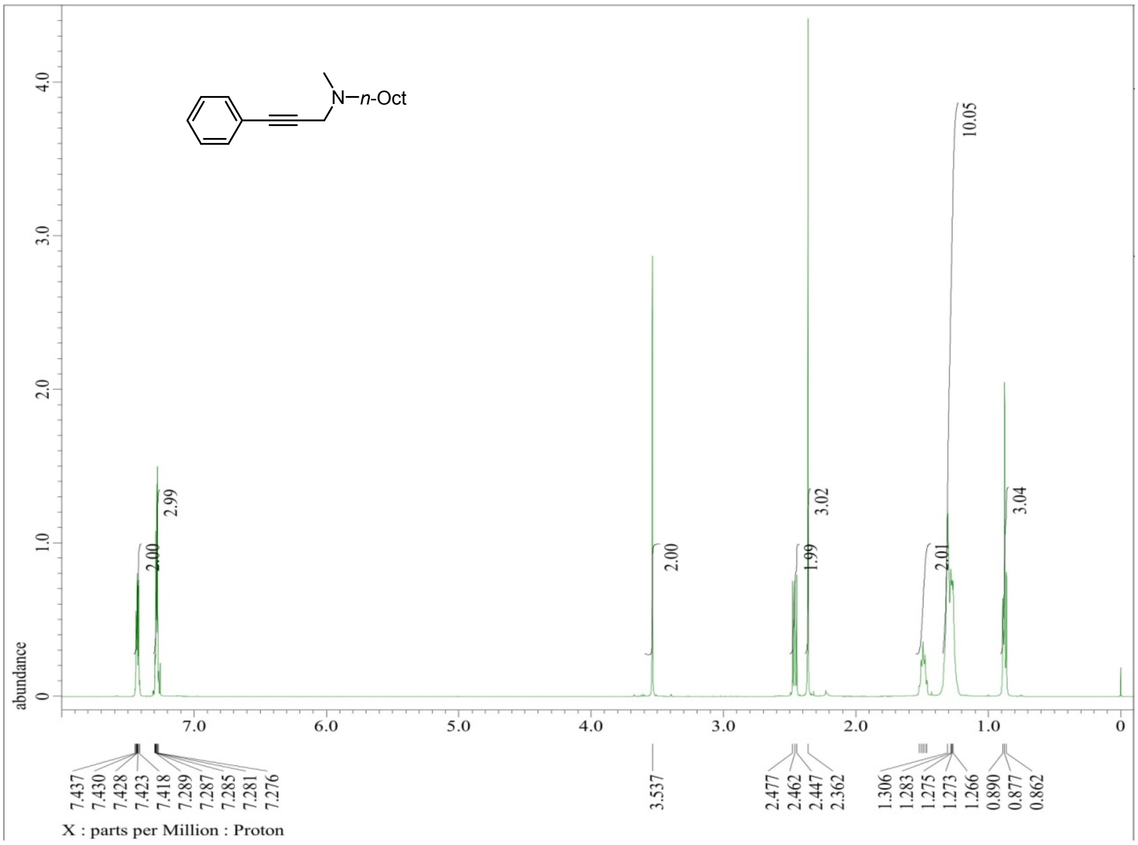
Cl
N
abundance
0.16
0.15
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
83.875
76.645
60.973
44.625
43.328
38.453
31.691
29.793
26.216
26.130
25.672
18.156
X : parts per Million : Carbon13

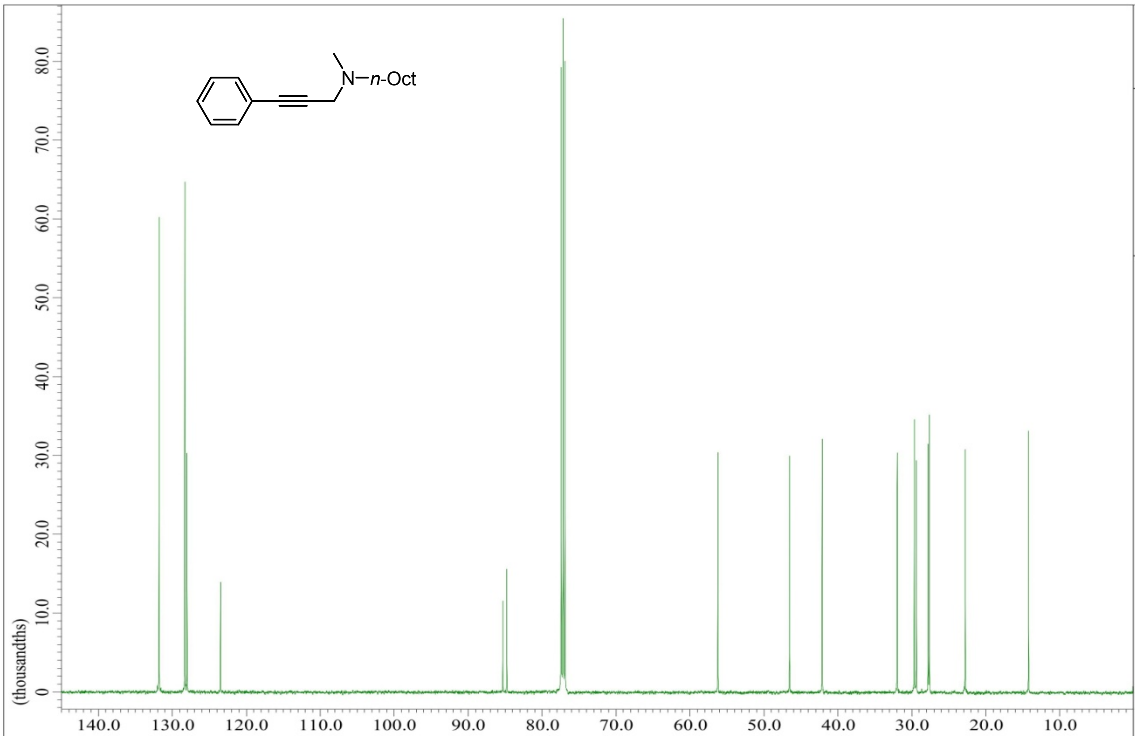

abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.02
2.02
2.01
1.00
2.00
1.99
3.01
N
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.464
7.458
7.453
7.373
7.359
7.334
7.320
7.305
7.302
7.295
7.290
3.636
3.508
2.399
X : parts per Million : Proton
7.483
7.473
7.464
7.458
7.453
X : parts per Million
7.376
7.373
7.359
7.334
7.330
7.320
7.317
7.311
7.305
7.302
7.295
7.290
7.272
7.269
7.266
7.259
7.255
7.250
7.240
7.216
X : parts per Million : Proton
2.01
5.02
1.00

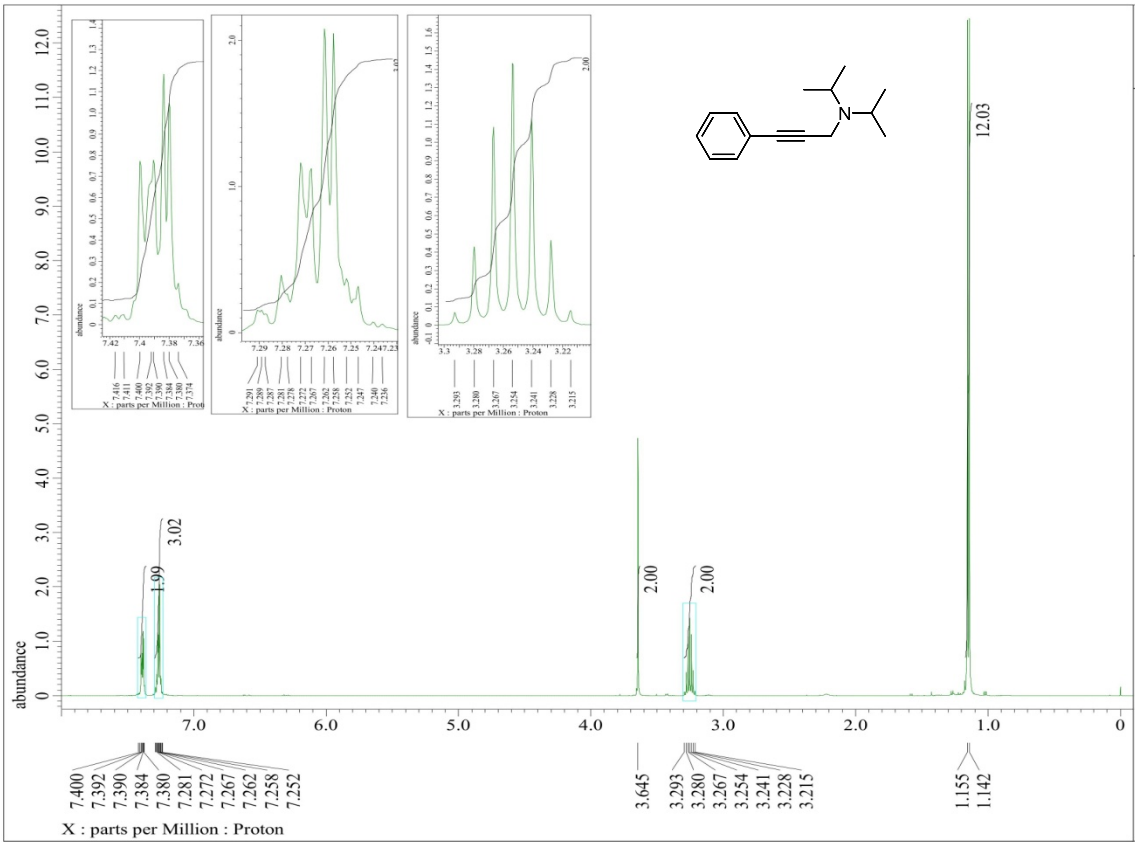

(thousandths)
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
N
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
138.615
131.853
129.354
128.438
128.390
128.123
127.322
123.459
85.811
84.600
60.401
45.893
42.116
X : parts per Million : Carbon13

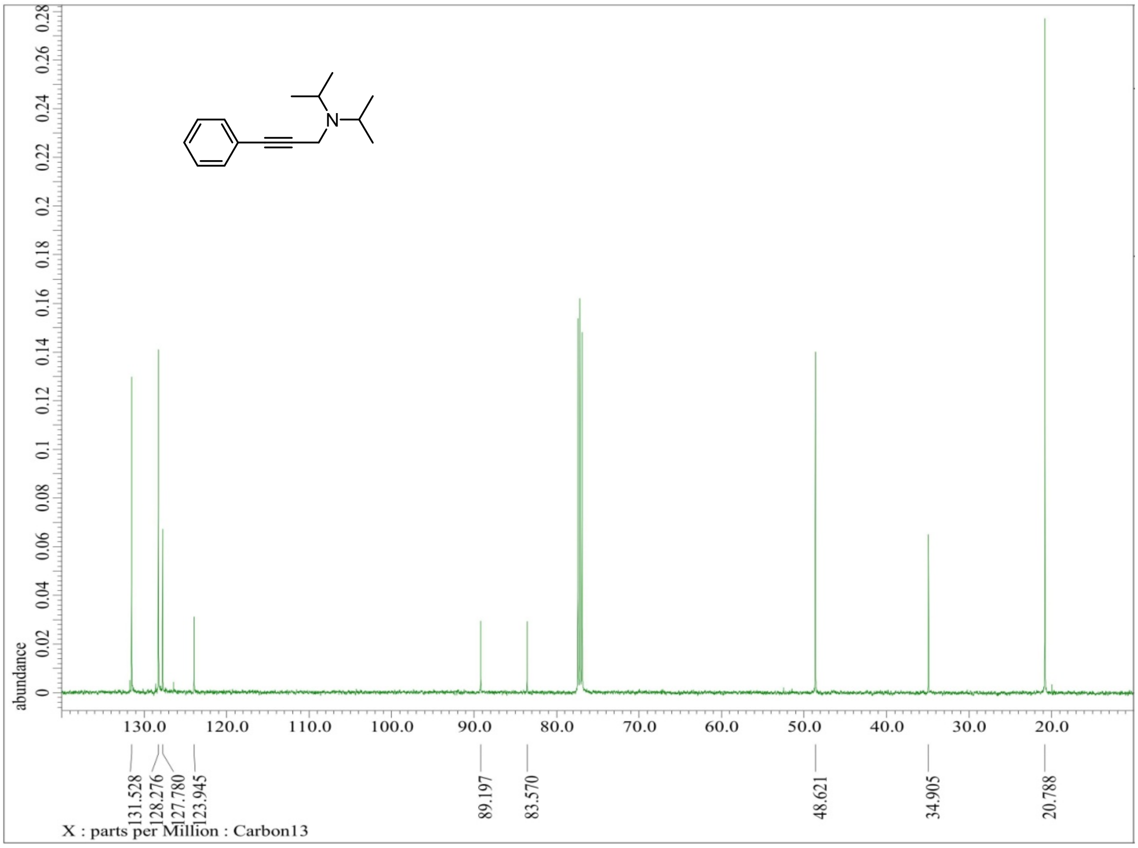

N−n-Bu
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
2.00
3.03
2.00
1.98
2.98
1.98
2.03
2.98
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.437
7.435
7.433
7.430
7.423
7.418
7.285
7.283
7.281
7.277
7.271
3.535
2.483
2.469
2.466
2.454
2.361
2.318
1.481
1.466
1.363
1.347
0.949
0.934
0.920
X : parts per Million : Proton


N−n-Bu
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
131.757
128.285
127.980
123.449
85.268
84.743
55.832
46.523
42.078
29.907
20.703
14.112
X : parts per Million : Carbon13


N−n-Oct
4.0
3.0
2.0
1.0
0
abundance
2.00
2.99
2.00
1.99
3.02
2.01
10.05
3.04
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.437
7.430
7.428
7.423
7.418
7.289
7.287
7.285
7.281
7.276
3.537
2.477
2.462
2.447
2.362
1.306
1.283
1.275
1.273
1.266
0.890
0.877
0.862
X : parts per Million : Proton


N−n-Oct
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
(thousandths)
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
131.805
128.314
128.018
123.488
85.306
84.772
56.214
46.542
42.126
31.967
29.669
29.392
27.799
27.618
22.772
14.207
X : parts per Million : Carbon13


N
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.99
3.02
2.00
2.00
12.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.400
7.392
7.390
7.384
7.380
7.281
7.272
7.267
7.262
7.258
7.252
3.645
3.293
3.280
3.267
3.254
3.241
3.228
3.215
1.155
1.142
X : parts per Million : Proton
7.416
7.411
7.400
7.392
7.390
7.384
7.380
7.374
7.291
7.289
7.287
7.281
7.278
7.272
7.267
7.262
7.258
7.252
7.247
7.240
7.236
3.293
3.280
3.267
3.254
3.241
3.228
3.215


N
abundance
0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
131.528
128.276
127.780
123.945
89.197
83.570
48.621
34.905
20.788
X : parts per Million : Carbon13