# Supporting Information

## Recyclable $Cu/C_3N_4$ Composite Catalyzed AHA/$A^3$ Coupling Reactions for the Synthesis of Propargylamines

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## Preparation and characterization of catalyst

The $Cu/C_3N_4$ catalyst was synthesized following the reported method.[1] Typically, melamide (2 g) was uniformly mixed with copper(II) acetate (625 mg). The resulting mixture was then heated to 550 °C with 2°C/min in a tube furnace under $N_2$ atmosphere and kept for 2 h. After cooling to room temperature, the final solid product (Cu-doped $C_3N_4$) was collected without further purification.

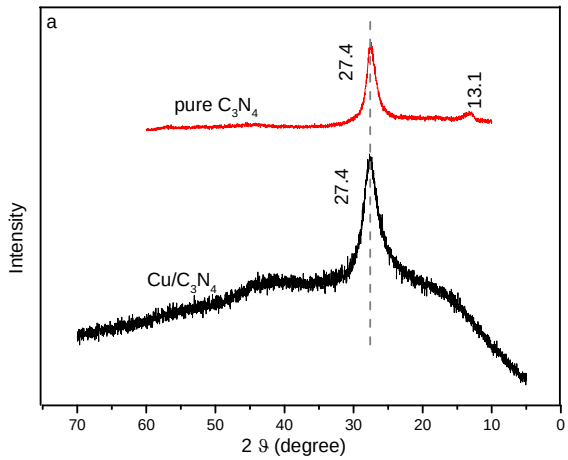



**Figure S1.** XRD patterns of pure $C_3N_4$ and $Cu/C_3N_4$

Figure S1 shows the XRD patterns of pure $C_3N_4$ and 20% $Cu/C_3N_4$. It was found that the XRD pattern of 20% $Cu/C_3N_4$ was similar to pure $C_3N_4$. This result indicates that the structure of $C_3N_4$ remains unchanged when copper ions were host by coordination with the N atom.

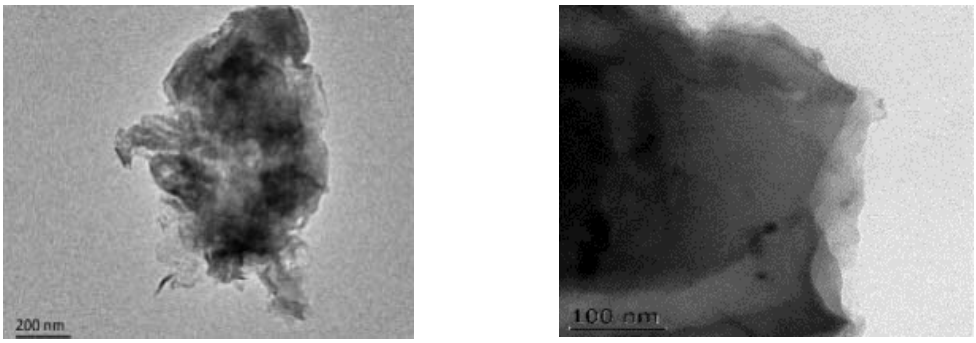



**Figure S2.** TEM images of $Cu/C_3N_4$

Figure S2 shows the TEM pattern of 20% Cu/$C_3N_4$. From the images, Cu/$C_3N_4$ maintains the flexible sheet-like morphology of $C_3N_4$ with no nanoparticles, possibly from Cu species, being observed on it.

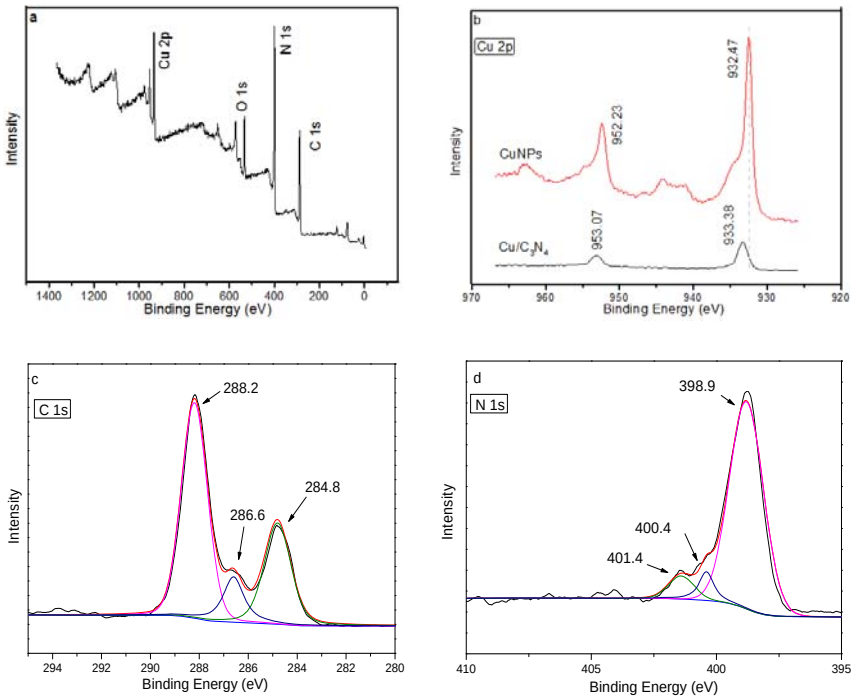
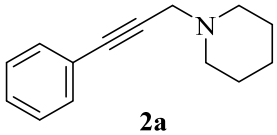



**Figure S3.** The XPS spectrum of 20% Cu/$C_3N_4$: (a) survey, (b) Cu 2p, (c) C 1s, (d) N 1s.

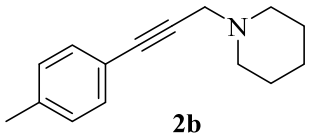
The X-ray photoelectron spectroscopy (XPS) patterns of Cu/$C_3N_4$ were shown in Figure S3. The binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ shift to 933.38 and 953.07 eV, respectively, indicating Cu (0) makes up a majority of the Cu present. Moreover, Cu NPs were also synthesized and tested as contrast, and it can be seen from Figure S3 (b) that the binding energy values of Cu 2p in Cu/$C_3N_4$ is slightly higher than these of Cu NPs. The shift might result from the strong interaction between Cu NPs and $C_3N_4$.[2] The C 1s at 288.24 eV and N 1s at 398.78 eV are assigned to the $sp^2$ C=N bond in the striazine ring. The peaks at 288.24 eV and 284.83 eV in the C 1s zone are attributed to electrons originating from a $sp^2$ C atom attached to an $NH_2$ group and to an aromatic carbon atom.[3]

## Characterization for compounds 2 & 4



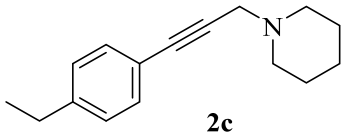
**2a**

**1-(3-phenylprop-2-yn-1-yl)piperidine (2a, 94%)** [4]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.37-7.36 (m, 2H), 7.22-7.20 (m, 3H), 3.43 (s, 2H), 2.52 (br, 4H), 1.60-1.57 (m, 2H), 1.38 (br, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 131.7, 128.2, 128.0, 123.3, 85.0, 53.5, 48.5, 25.9, 24.0.



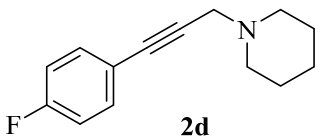
**2b**

**1-(3-(p-tolyl)prop-2-yn-1-yl)piperidine (2b, 91%)** [4]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.33 (d, $J$ = 7.6 Hz, 2H), 7.09 (d, $J$ = 7.6 Hz, 2H), 3.46 (s, 2H), 2.57 (br, 4H), 2.33 (s, 3H), 1.67-1.61 (m, 4H); 1.44 (br, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 138.0, 131.6, 129.0, 120.3, 85.1, 84.3, 53.5, 48.5, 26.0, 24.0, 21.4.



**2c**

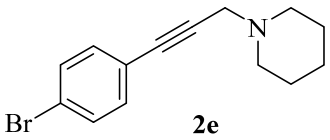
**1-(3-(4-ethylphenyl)prop-2-yn-1-yl)piperidine (2c, 88%)** [4]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.28 (d, $J$ = 8.0 Hz, 2H), 7.05 (d, $J$ = 8.0 Hz, 2H), 3.40 (s, 2H), 2.58-2.50 (m, 6H), 1.58-1.55 (m, 4H), 1.37 (br, 2H), 1.14 (t, $J$ = 7.6 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$:143.3, 130.7, 126.8, 119.4, 84.2, 83.1, 52.4, 47.4, 27.8, 24.9, 22.9, 14.4.



**2d**

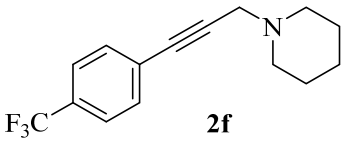
**1-(3-(4-fluorophenyl)prop-2-yn-1-yl)piperidine (2d, 85%)** [4]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.40 (dd, $J_1$ = 5.6 Hz, $J_2$ = 8.0 Hz, 2H), 7.01-6.96 (m, 2H), 3.45 (s, 2H), 2.56 (br, 4H), 1.67-1.62 (m, 4H), 1.45 (br, 2H); **$^{13}$C NMR** (101 MHz,

$CDCl_3$) $\delta$: 162.3 (d, $J$ = 250.5 Hz), 133.5 (d, $J$ = 8.1 Hz), 119.4 (d, $J$ = 3.0 Hz), 115.5 (d, $J$ = 11.11 Hz), 84.8, 83.9, 53.5, 48.5, 26.0, 24.0.



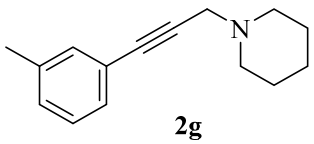

**2e**

**1-(3-(4-bromophenyl)prop-2-yn-1-yl)piperidine (2e, 92%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.42 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 3.45 (s, 2H), 2.56 (br, 4H), 1.67-1.62 (m, 4H), 1.46-1.45 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$: 159.4, 133.1, 115.5, 113.9, 84.8, 83.5, 55.3, 53.5, 48.5, 26.0, 24.0.



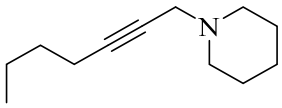

**2f**

**1-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)piperidine (2f, 90%)**: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.57-7.52 (m, 4H), 3.49 (s, 2H), 2.57 (br, 4H), 1.68-1.63 (m, 4H), 1.46 (br, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 132.0, 129.8 (q, $J$ = 32.8 Hz), 127.2 (d, $J$ = 1.0 Hz), 125.2 (dd, $J_1$ = 3.7 Hz, $J_2$ = 7.6 Hz), 124.0 (q, $J$ = 273.2 Hz), 87.9, 83.8, 53.6, 48.5, 26.0, 23.9; MS (EI) m/z (%): 267 ($M^+$), 238, 225, 211, 183 (100), 164, 143, 133, 115, 84, 42; HRMS calcd for $C_{15}H_{16}NF_3$: 267.1235; found 267.1241.



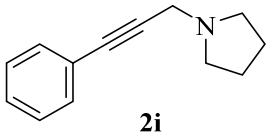

**2g**

**1-(3-(m-tolyl)prop-2-yn-1-yl)piperidine (2g, 95%)** [4]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.26-7.23 (m, 2H), 7.20-7.16 (m, 1H), 7.11-7.10 (m, 1H), 3.48 (s, 2H), 2.57 (br, 4H), 2.32 (s, 3H), 1.67-1.62 (m, 4H), 1.45 (br, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$ $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$: 137.9, 132.3, 128.9, 128.8, 128.1, 123.1, 85.2, 84.6, 53.4, 48.5, 26.0, 23.9, 21.2.



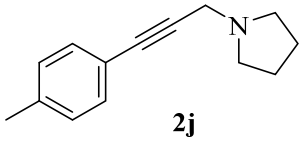

**2h**

**1-(hept-2-yn-1-yl)piperidine (2h, 45%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 3.14 (s, 2H), 2.41 (br, 4H), 2.14-2.11 (m, 2H), 1.56-1.53 (m, 4H), 1.46-1.31 (m, 6H), 0.84 (t, $J$ = 6.8 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 84.1, 74.2, 52.4, 47.1, 30.0, 24.9, 23.0, 21.0, 17.4, 12.6.



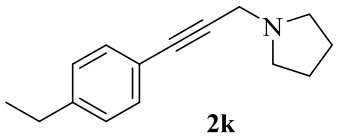
**2i**

**1-(3-phenylprop-2-yn-1-yl)pyrrolidine (2i, 85%)** [4]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.44-7.42 (m, 2H), 7.30-7.28 (m, 3H), 3.63 (s, 2H), 2.70-2.69 (m, 4H), 1.86-1.83 (m, 4H), 1.74 (br, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 131.7, 128.2, 128.0, 123.3, 85.4, 84.4, 52.7, 43.9, 23.8.



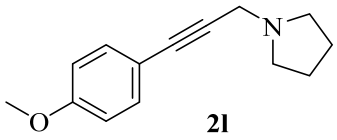
**2j**

**1-(3-(p-tolyl)prop-2-yn-1-yl)pyrrolidine (2j, 81%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.32 (d, $J$ = 8.0 Hz, 2H), 7.10 (d, $J$ = 7.6 Hz, 2H), 3.62 (s, 2H), 2.69 (br, 4H), 2.33 (s, 3H), 1.87-1.80 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 137.0, 130.6, 128.0, 119.2, 83.6, 83.4, 51.7, 42.9, 22.8, 20.4.



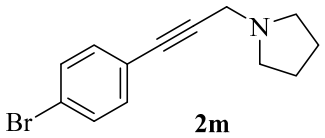
**2k**

**1-(3-(4-ethylphenyl)prop-2-yn-1-yl)pyrrolidine (2k, 78%)**: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.28 (d, $J$ = 8.0 Hz, 2H), 7.05 (d, $J$ = 8.0 Hz, 2H), 3.55 (s, 2H), 2.62-2.61 (m, 4H), 2.56 (q, $J$ = 7.6 Hz, 2H), 1.77-1.75 (m, 4H), 1.15 (t, $J$ = 7.6 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 143.3, 130.7, 126.8, 119.4, 83.6, 83.5, 51.6, 42.8, 27.8, 22.8, 14.3; MS (EI) m/z (%): 213 ($M^+$), 198, 184 (100), 170, 143, 128, 115, 99, 83, 70, 42; HRMS calcd for $C_{15}H_{19}N$: 213.1517; found 213.1514.



**2l**

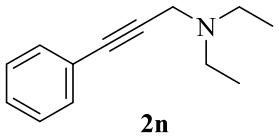
**1-(3-(4-methoxyphenyl)prop-2-yn-1-yl)pyrrolidine (2l, 84%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.36 (d, $J$ = 8.8 Hz, 2H), 6.82 (d, $J$ = 8.8 Hz, 2H), 3.80 (s, 3H), 3.61 (s, 2H), 2.69 (br, 4H), 1.83-1.82 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): $\delta$: 158.4, 132.1, 114.4, 112.8, 83.1, 82.8, 54.3, 51.7, 42.9, 22.8.



**2m**

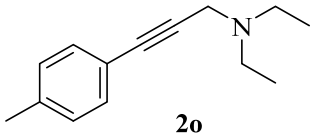
**1-(3-(4-bromophenyl)prop-2-yn-1-yl)pyrrolidine (2m, 81%)** [5]: Yellow liquid. **$^1$H**

**NMR** (400 MHz, $CDCl_3$) $\delta$: 7.42 (d, $J$ = 8.4 Hz, 2H), 7.28 (d, $J$ = 8.4 Hz, 2H), 3.60 (s, 2H), 2.68 (br, 4H), 1.84-1.83 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 133.2, 131.5, 122.3, 122.2, 86.8, 83.3, 52.8, 43.9, 23.8.



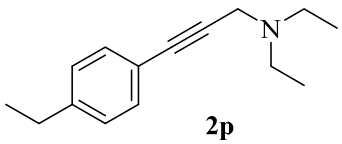
**2n**

**N,N-diethyl-3-phenylprop-2-yn-1-amine (2n 90%)** [4]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.36-7.34 (m, 2H), 7.23-7.19 (m, 3H), 3.58 (s, 2H), 2.57 (q, $J$ = 7.2 Hz, 4H), 1.05 (t, $J$ = 7.2 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 131.7, 128.3, 128.0, 123.4, 85.1, 84.3, 47.3, 41.5, 12.6.



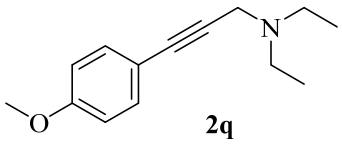
**2o**

**N,N-diethyl-3-(p-tolyl)prop-2-yn-1-amine (2o, 90%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.24 (d, $J$ = 7.6 Hz, 2H), 7.02 (d, $J$ = 7.6 Hz, 2H), 3.56 (s, 2H), 2.55 (q, $J$ = 7.2 Hz, 4H), 2.26 (s, 3H), 1.04 (t, $J$ = 7.2 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 136.9, 130.6, 128.0, 119.3, 84.0, 82.5, 46.3, 40.4, 20.4, 11.6.



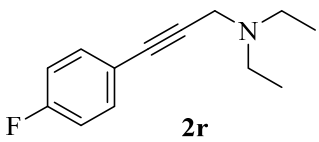
**2p**

**N,N-diethyl-3-(4-ethylphenyl)prop-2-yn-1-amine (2p, 82%)**: Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.27 (d, $J$ = 8.0 Hz, 2H), 7.05 (d, $J$ = 8.0 Hz, 2H), 3.56 (s, 2H), 2.55 (q, $J$ = 7.2 Hz, 6H), 1.14 (t, $J$ = 7.6 Hz, 3H), 1.04 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$: 144.3, 131.7, 127.8, 120.6, 85.1, 83.6, 47.3, 41.5, 28.8, 15.4, 12.6; MS (EI) m/z (%): 215 ($M^+$), 200, 143 (100), 128, 115, 102, 93, 56, 42; HRMS calcd for $C_{15}H_{21}N$: 215.1674; found 215.1678.



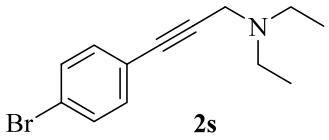
**2q**

**N,N-diethyl-3-(4-methoxyphenyl)prop-2-yn-1-amine (2q, 85%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.36 (d, $J$ = 8.4 Hz, 2H), 6.82 (d, $J$ = 8.4 Hz, 2H), 3.80 (s, 3H), 3.63 (s, 2H), 2.63 (q, $J$ = 7.2 Hz, 4H), 1.12 (t, $J$ = 6.8 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 159.3, 133.1, 115.5, 113.9, 84.8, 82.7, 55.3, 47.3, 41.5, 12.6.



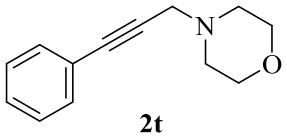

**2r**

**N,N-diethyl-3-(4-fluorophenyl)prop-2-yn-1-amine (2r, 86%)** [6]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.39 (dd, $J_1$ = 5.6 Hz, $J_2$ = 8.0 Hz, 2H), 7.01-6.96 (m, 2H), 3.62 (s, 2H), 2.62 (q, $J$ = 7.2 Hz, 4H), 1.12 (t, $J$ =7.2 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 162.3 (d, $J$ = 250.5 Hz), 133.6, 119.4, 115.5 (d, $J$ = 22.2 Hz), 84.2, 83.9, 47.3, 41.5, 12.6.



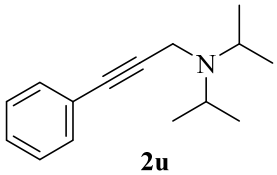

**2s**

**3-(4-bromophenyl)-N,N-diethylprop-2-yn-1-amine (2s, 88%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.35 (d, $J$ = 8.4 Hz, 2H), 7.20 (d, $J$ = 8.0 Hz, 2H), 3.55 (s, 2H), 2.55 (q, $J$ = 7.2 Hz, 4H), 1.04 (t, $J$ = 7.2 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 133.2, 131.5, 122.3, 122.1, 85.8, 84.0, 47.4, 41.5, 12.6.



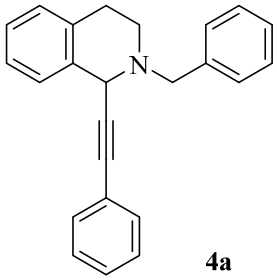

**2t**

**4-(3-phenylprop-2-yn-1-yl)morpholine (2t, 46%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.45-7.43 (m, 2H), 7.31-7.30 (m, 3H), 3.79-3.77 (m, 4H), 3.51 (s, 2H), 2.65 (t, $J$ = 4.4 Hz, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 131.7, 128.2, 123.0, 85.6, 84.0, 66.9, 52.5, 48.1.



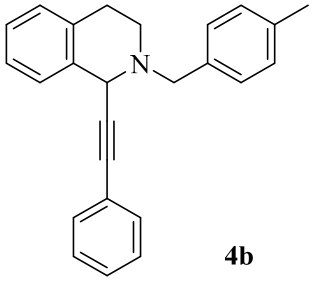

**2u**

**N,N-diisopropyl-3-phenylprop-2-yn-1-amine (2u, 20%)** [5]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.41-7.38 (m, 2H), 7.30-7.27 (m, 3H), 3.67 (s, 2H), 3.21-3.24 (m, 2H), 1.16 (d, $J$ = 6.8 Hz, 12H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 131.5, 128.2, 127.8, 123.8, 88.9, 83.6, 48.6, 34.8, 20.6.



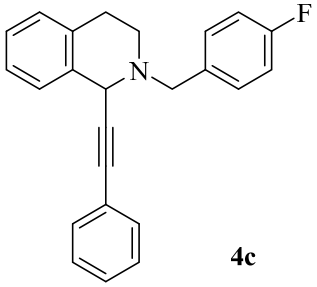
**4a**

**2-benzyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4a, 96%)** [7]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.51-7.45 (m, 4H), 7.37-7.34 (m, 2H), 7.30-7.25 (m, 7H), 7.19-7.13 (m, 3H), 4.84 (s, 1H), 4.02 (d, $J$ = 13.6 Hz, 1H), 3.97 (d, $J$ = 13.6 Hz, 1H), 3.14-3.09 (m, 2H), 2.91-2.82 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 137.3, 134.4, 133.0, 130.8, 128.3, 128.0, 127.3, 127.2, 127.0, 126.8, 126.2, 125.9, 124.8, 122.2, 86.5, 85.8, 58.5, 53.3, 44.7, 28.0.



**4b**

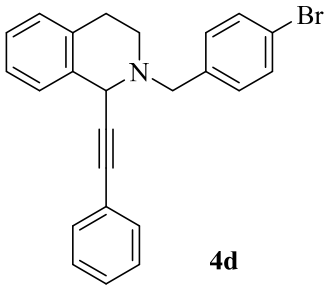
**2-(4-methylbenzyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4b, 92%)** [7]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.44-7.43 (m, 2H), 7.36-7.34 (m, 2H), 7.28-7.24 (m, 4H), 7.16-7.11 (m, 5H), 4.78 (s, 1H), 3.91 (d, $J$ = 12.0 Hz, 1H), 3.87 (d, $J$ = 12.0 Hz, 1H), 3.09-2.98 (m, 2H), 2.84-2.78 (m, 2H), 2.35 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 136.8, 135.5, 135.1, 134.1, 131.8, 129.3, 129.0, 128.2, 128.0, 127.8, 126.9, 125.8, 123.3, 87.5, 86.9, 59.4, 54.3, 45.7, 29.0, 21.2.



**4c**

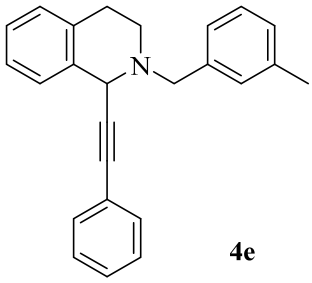
**2-(4-fluorobenzyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4c, 94%)** [7]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.35-7.32 (m, 4H), 7.20-7.16 (m, 4H), 7.08-7.03 (m, 3H), 6.96-6.92 (m, 2H), 4.67 (s, 1H), 3.82 (d, $J$ = 16.0 Hz, 1H), 3.78 (d, $J$ = 16.0 Hz, 1H), 3.01-2.92 (m, 2H), 2.73-2.70 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$):

$\delta$: 161.1 (d, $J$ = 246.4 Hz), 134.3, 133.0, 130.7, 129.7 (d, $J$ = 8.0 Hz), 128.0, 127.2, 127.1, 126.8, 126.0, 124.8, 122.1, 114.1 (d, $J$ = 22.2 Hz), 86.3, 85.9, 57.8, 53.2, 44.7, 28.0.



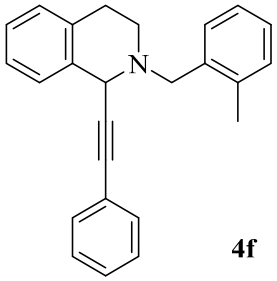

**4d**

**2-(4-bromobenzyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4d, 96%)** [7]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.62-7.60 (m, 2H), 7.51-7.49 (m, 4H), 7.33 (br, 3H), 7.11-7.10 (m, 3H), 7.01-7.00 (m, 1H), 5.01 (s, 1H), 3.85 (d, $J$ = 14.8 Hz, 1H), 3.80 (d, $J$ = 14.8 Hz, 1H), 2.94-2.87 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 137.4, 135.0, 134.2, 131.8, 131.4, 130.2, 128.7, 128.4, 128.3, 126.7, 126.1, 125.6, 122.7, 121.7, 89.0, 84.2, 61.0, 52.2, 47.2, 29.6.



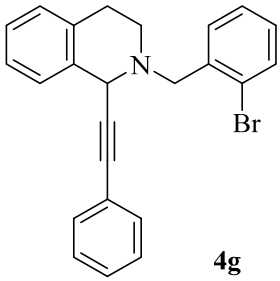

**4e**

**2-(3-methylbenzyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4e, 95%)** [7]: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.45-7.44 (m, 2H), 7.29-7.23 (m, 7H), 7.16-7.08 (m, 4H), 4.80 (s, 1H), 3.92 (d, $J$ = 12.0 Hz, 1H), 3.86 (d, $J$ = 12.0 Hz, 1H), 3.07-2.99 (m, 2H), 2.84-2.79 (m, 2H), 2.35 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 138.3, 138.0, 135.6, 134.2, 131.9, 130.1, 129.1, 128.3, 128.2, 128.1, 128.0, 127.9, 127.0, 126.4, 125.9, 123.4, 87.7, 86.9, 59.7, 54.5, 45.8, 29.1, 21.5.



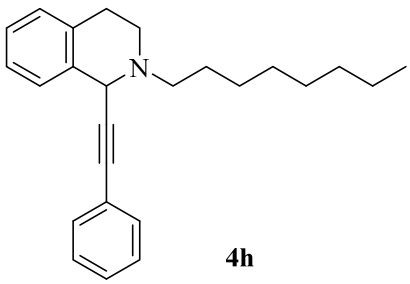
**4f**

**2-(2-methylbenzyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4f, 95%)** [7]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.44-7.43 (m, 3H), 7.28-7.23 (m, 4H), 7.17-7.11 (m, 6H), 4.77 (s, 1H), 3.93 (d, $J$ = 13.2 Hz, 1H), 3.87 (d, $J$ = 13.2 Hz, 1H), 3.11-2.97 (m, 2H), 2.82-2.75 (m, 2H), 2.42 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 137.9, 136.3, 135.7, 134.2, 131.7, 130.3, 130.0, 129.0, 128.2, 128.0, 127.8, 127.2, 126.8, 125.8, 125.6, 123.3, 87.8, 86.8, 57.5, 54.4, 45.7, 29.0, 19.3.



**4g**

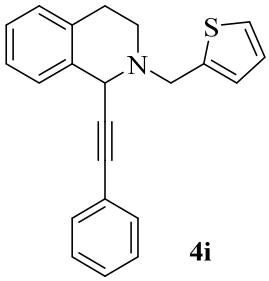
**2-(2-bromobenzyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4g, 91%)** [7]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.51-7.49 (m, 2H), 7.47-7.45 (m, 2H), 7.20-7.18 (m, 5H), 7.07-6.99 (m, 4H), 4.78 (s, 1H), 3.97 (d, $J$ = 14.4 Hz, 1H), 3.92 (d, $J$ = 14.4 Hz, 1H), 3.08-2.90 (m, 2H), 2.75-2.67 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 136.8, 134.4, 133.0, 131.8, 130.8, 129.6, 128.0, 127.5, 127.1, 127.0, 126.7, 126.2, 125.9, 124.8, 123.8, 122.2, 86.6, 85.7, 57.8, 53.7, 44.7, 28.1.



**4h**

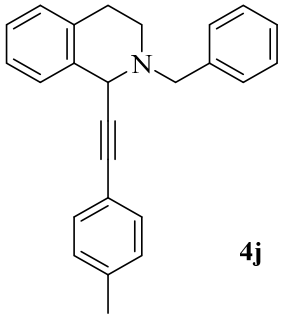
**2-octyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (4h, 72%)**: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.41-7.40 (m, 2H), 7.27-7.25 (m, 3H), 7.11-7.07 (m, 4H), 3.94 (d, $J$ = 14.8 Hz, 1H), 3.79 (d, $J$ = 14.8 Hz, 1H), 3.81 (s, 1H), 3.05-2.92 (m,

3H), 2.82-2.78 (m, 1H), 1.84-1.81 (m, 2H), 1.62-1.47 (m, 2H), 1.35-1.26 (m, 9H), 0.88-0.87 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 135.1, 134.4, 131.7, 128.7, 128.2, 127.9, 126.8, 126.0, 125.6, 123.3, 87.3, 86.1, 57.9, 51.9, 47.4, 31.9, 29.5, 29.4, 29.2, 26.8, 22.7, 14.0; MS (EI) m/z (%): 345 ($M^+$, 100), 297, 296, 258, 242, 227, 194, 160. HRMS calcd for $C_{25}H_{31}N$: 345.2457; found 345.2446.



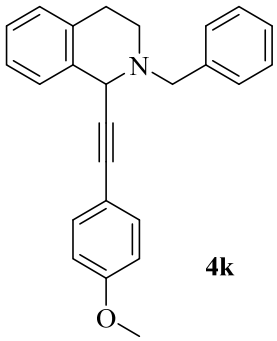

**4i**

**1-(phenylethynyl)-2-(thiophen-2-ylmethyl)-1,2,3,4-tetrahydroisoquinoline (4i, 95%)**: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.45 (br, 2H), 7.31-7.28 (m, 5H), 7.19-7.13 (m, 4H), 7.00 (br, 1H), 4.95 (s, 1H), 4.26-4.18 (m, 2H), 3.16-3.14 (m, 2H), 2.99-2.86 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 140.9, 134.2, 133.0, 130.8, 128.0, 127.2, 127.1, 126.8, 125.9, 125.5, 125.3, 124.8, 124.2, 122.1, 86.2, 85.9, 53.2, 53.0, 44.6, 28.0; MS (EI) m/z (%): 329 ($M^+$), 296, 252, 202, 145 (100), 132, 105, 97; HRMS calcd for $C_{22}H_{19}NS$: 329.1238; found 329.1226.



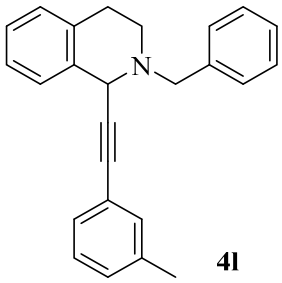

**4j**

**2-benzyl-1-(2-(4-methphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (4j, 99%)**: Yellow liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.39 (d, $J$ = 7.2 Hz, 2H), 7.27-7.24 (m, 4H), 7.21-7.17 (m, 3H), 7.08-7.01 (m, 5H), 4.70 (s, 1H), 3.87 (d, $J$ = 12.0 Hz, 1H), 3.82 (d, $J$ = 12.0 Hz, 1H), 3.04-2.91 (m, 2H), 2.76-2.70 (m, 2H), 2.26 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 137.3, 137.1, 134.6, 133.0, 130.6, 128.3, 127.9, 127.3, 126.8, 126.1, 125.9, 124.8, 119.1, 85.9, 85.7, 58.5, 53.4, 44.7, 28.0, 20.4; MS (EI) m/z (%): 337 ($M^+$), 336, 335 (100), 334, 333, 318, 304, 291, 241, 215, 201, 152; HRMS calcd for $C_{25}H_{23}N$: 337.1830; found 337.1822.



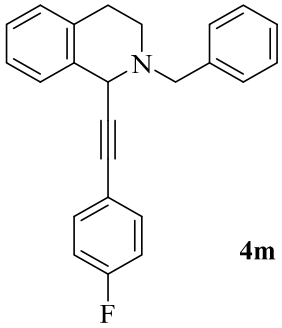
**4k**

**2-benzyl-1-(2-(4-methoxyphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (4k, 93%)** [7]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.46 (d, $J$ = 7.6 Hz, 2H), 7.39-7.31 (m, 4H), 7.29-7.22 (m, 2H), 7.15-7.10 (m, 3H), 6.82-6.80 (m, 2H), 4.77 (s, 1H), 3.94 (d, $J$ = 13.2 Hz, 1H), 3.89 (d, $J$ = 13.2 Hz, 1H), 3.78 (s, 3H), 3.11-2.99 (m, 2H), 2.81-2.78 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 159.4, 138.4, 135.7, 134.0, 133.2, 129.3, 129.0, 128.3, 127.8, 127.1, 126.8, 125.8, 115.4, 113.8, 86.6, 86.0, 59.6, 55.3, 54.4, 45.7, 29.0.



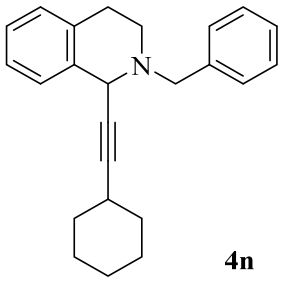
**4l**

**2-Benzyl-1-(2-(3-methphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline (4l, 99%)**: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.46 (d, $J$ = 7.6 Hz, 2H), 7.35-7.31 (m, 2H), 7.29-7.24 (m, 4H), 7.19-7.08 (m, 5H), 4.78 (s, 1H), 3.95 (d, $J$ = 13.2 Hz, 1H), 3.91(d, $J$ = 13.2 Hz, 1H), 3.11-2.98 (m, 2H), 2.84-2.77 (m, 2H), 2.30 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 138.3, 137.9, 135.6, 134.1, 132.4, 129.4, 129.1, 129.0, 128.9, 128.4, 128.2, 127.9, 127.2, 127.0, 125.9, 123.1, 87.1, 59.6, 54.4, 45.8, 29.1, 21.2; MS (EI) m/z (%): 337 ($M^+$) 336 (100), 310, 260, 246, 222, 218, 202, 116, 91. HRMS calcd for $C_{25}H_{23}N$: 337.1830; found 337.1825.



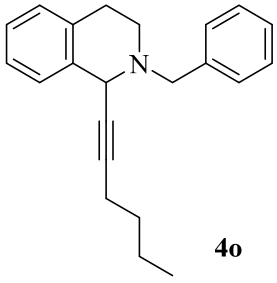
**4m**

**2-benzyl-1-((4-fluorophenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline** (**4m, 90%**) [8]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.47-7.40 (m, 4H), 7.34 (t, $J$ = 6.8 Hz, 2H), 7.30-7.25 (m, 2H), 7.17-7.12 (m, 3H), 6.99 (t, $J$ = 8.4 Hz, 2H), 4.78 (s, 1H), 3.94 (d, $J$ = 13.2 Hz, 1H), 3.89 (d, $J$ = 13.2 Hz, 1H), 3.10-3.00 (m, 2H), 2.82-2.79 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 162.4 (d, $J$ = 249.5 Hz), 138.2, 135.3, 134.0, 133.6 (d, $J$ = 9.1 Hz), 129.3, 129.0, 128.4, 127.8, 127.2, 127.0, 125.9, 119.3 (d, $J$ = 3.0 Hz), 115.4 (d, $J$ = 33.3 Hz), 87.2, 85.8, 59.6, 54.3, 45.6, 29.0.



**4n**

**2-benzyl-1-(2-cyclohexylethynyl)-1,2,3,4-tetrahydroisoquinoline (4n, 99%)** [9]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.45-7.43 (m, 2H), 7.34-7.33 (m, 2H), 7.28-7.24 (m, 1H), 7.20-7.19 (m, 1H), 7.12-7.07 (m, 3H), 4.54 (s, 1H), 3.90 (d, $J$ = 13.2 Hz, 1H), 3.80 (d, $J$ = 13.2 Hz, 1H), 3.02-2.92 (m, 2H), 2.80-2.70 (m, 2H), 2.44 (s, 1H), 1.80-1.71 (m, 5H), 1.49-1.44 (m, 3H), 1.36-1.31 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 138.6, 136.4, 133.9, 129.4, 128.9, 128.3, 127.8, 127.1, 126.7, 125.7, 91.4, 77.8, 59.5, 54.1, 45.7, 33.1, 33.0, 29.2, 29.1, 26.0, 24.9.



**4o**

**2-benzyl-1-(hex-1-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline (4o, 92%)** [9]: Yellow liquid. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$: 7.43 (d, $J$ = 7.2 Hz, 2H), 7.34-7.31 (m, 2H), 7.28-7.23 (m, 1H), 7.20-7.18 (m, 1H), 7.13-7.09 (m, 3H), 4.54 (s, 1H), 3.88 (d, $J$ = 13.2 Hz, 1H), 3.79 (d, $J$ = 13.2 Hz, 1H), 3.01-2.91 (m, 2H), 2.77-2.72 (m, 2H), 2.24 (t, $J$ = 7.2 Hz, 2H), 1.54-1.41 (m, 4H), 0.92 (t, $J$ = 7.2 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$: 138.6, 136.4, 133.9, 129.3, 128.9, 128.3, 127.8, 127.1, 126.7, 125.7, 87.2, 77.9, 59.5, 54.2, 45.6, 31.2, 29.1, 22.1, 18.6, 13.7.

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[8] W. Lin, T. Cao, W. Fan, Y. Han, J. Kuang, H. Luo, B. Miao, X. Tang, Q. Yu, W. Yuan, J. Zhang, C. Zhu and S. Ma, *Angew. Chem., Int. Ed.,* 2014, **53**, 277.

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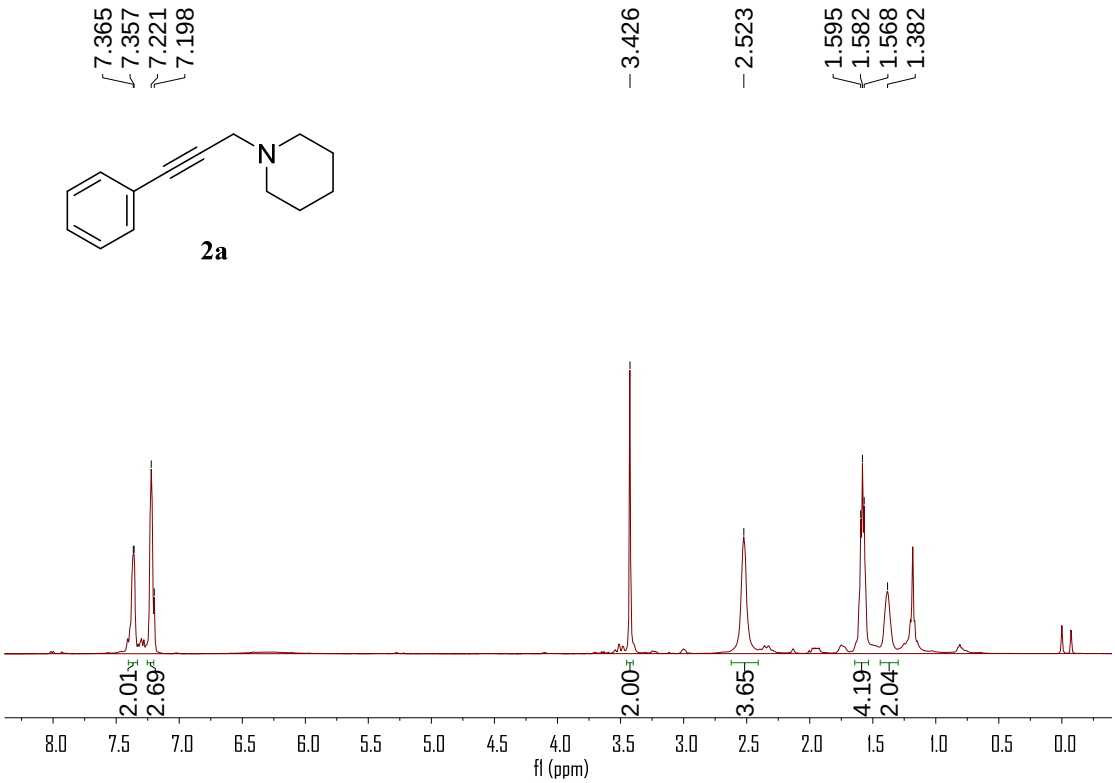
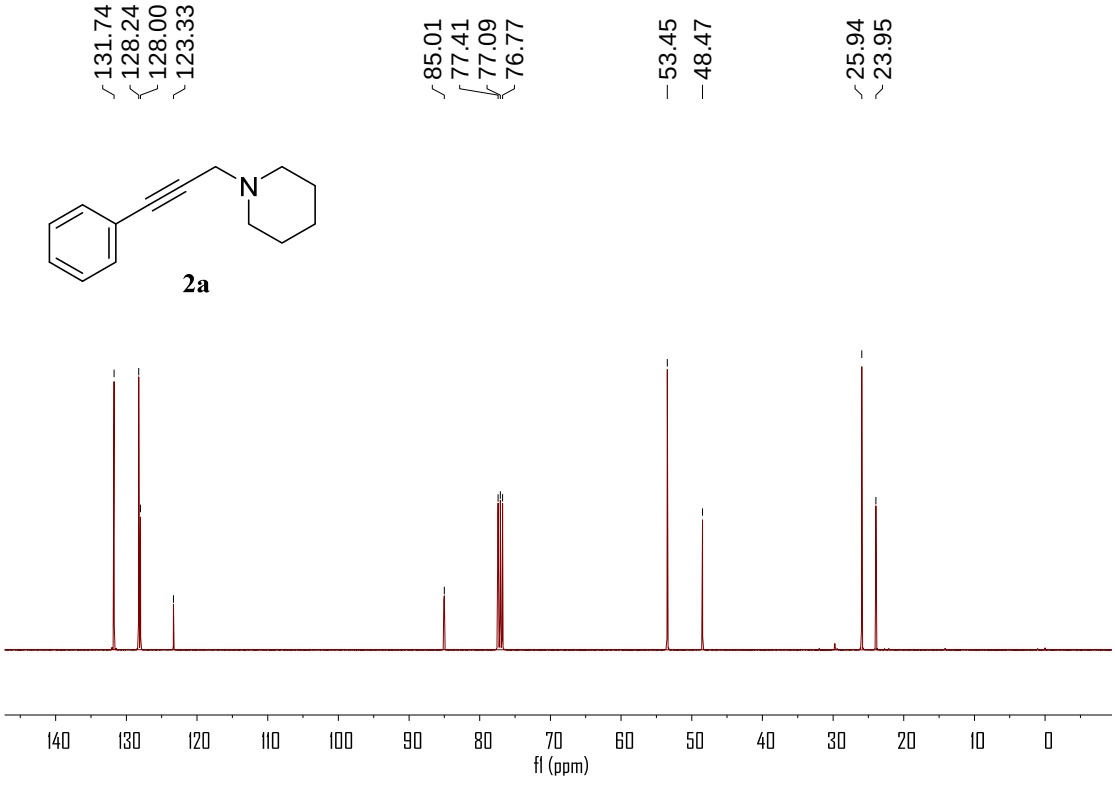
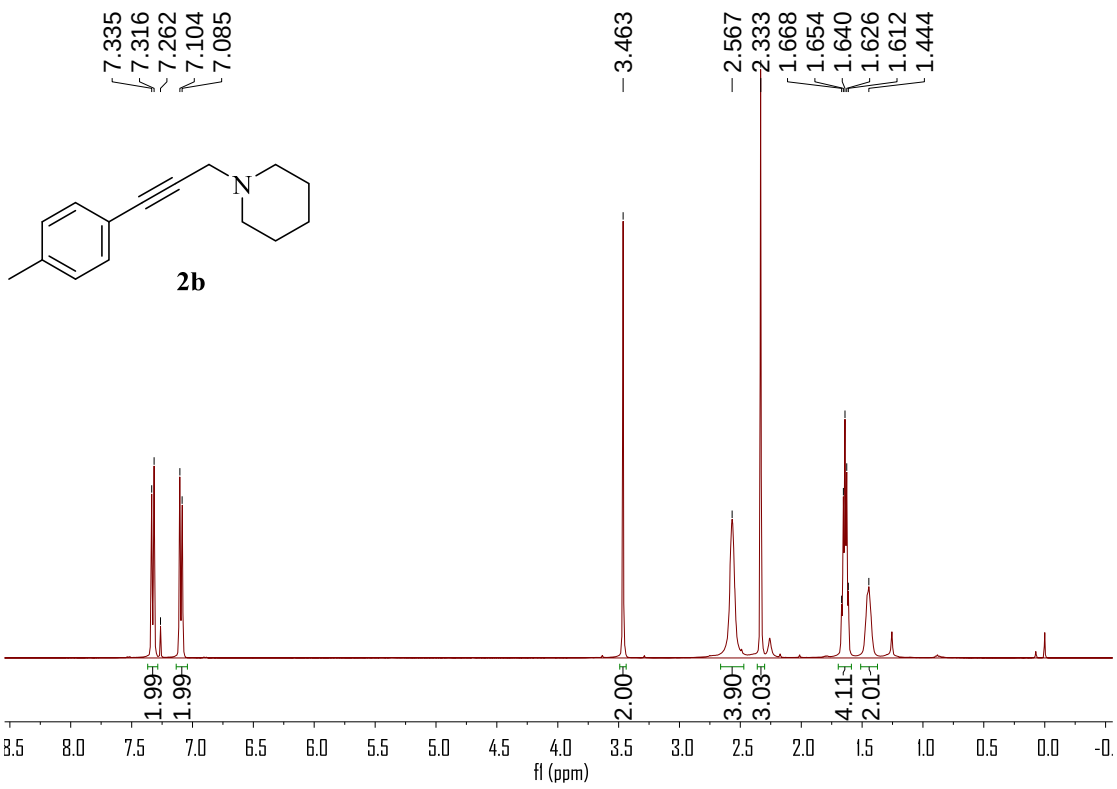



**2a** $^{1}$H NMR

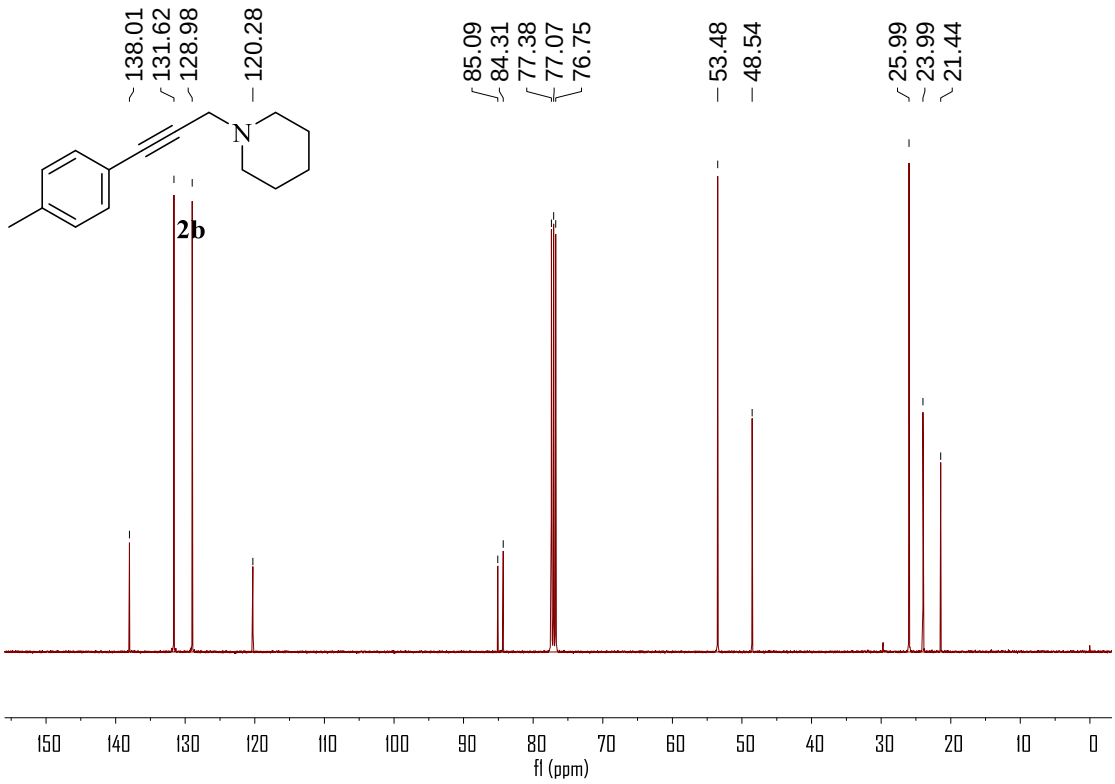



**2a** $^{13}$C NMR

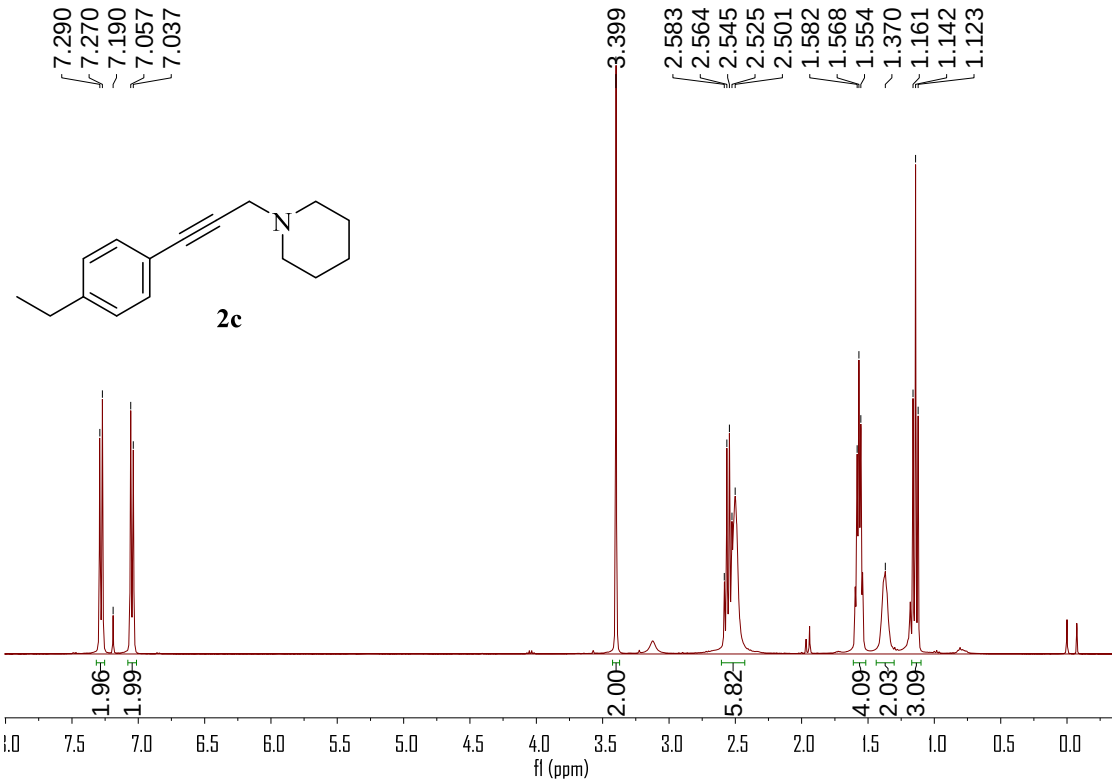

7.335
7.316
7.262
7.104
7.085
3.463
2.567
2.333
1.668
1.654
1.640
1.626
1.612
1.444
N
1.99
1.99
2.00
3.90
3.03
4.11
2.01
f1 (ppm)

**2b**

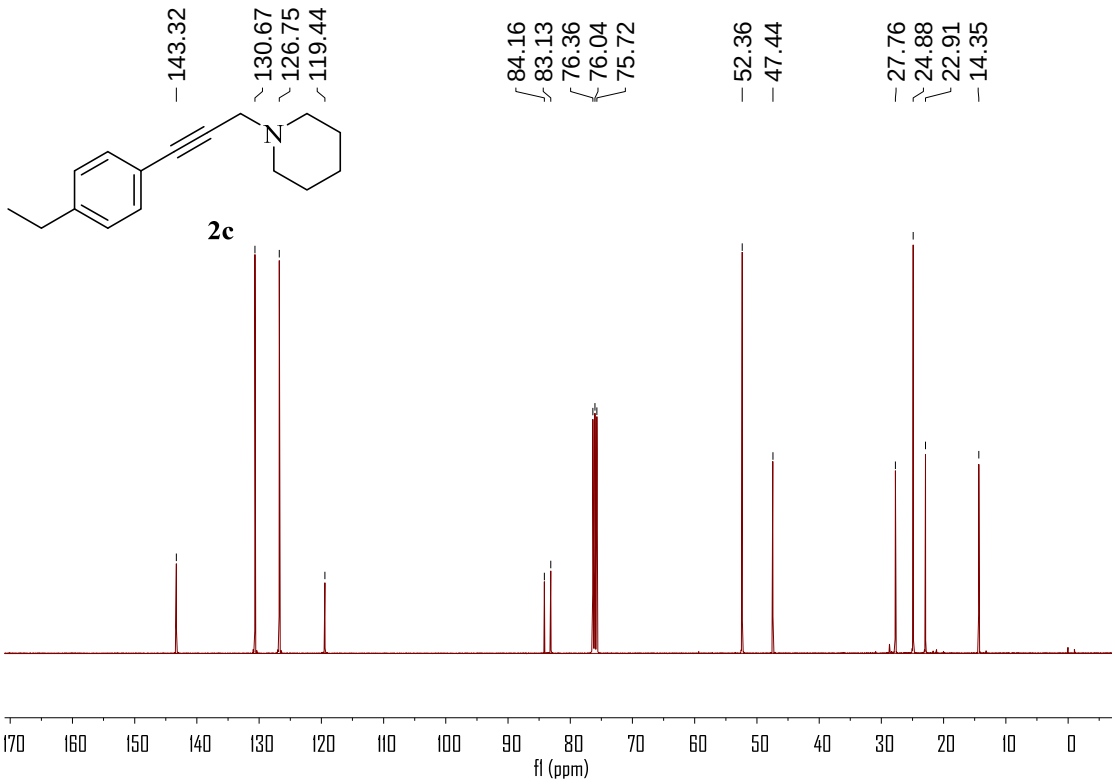
**2b** $^{1}$H NMR



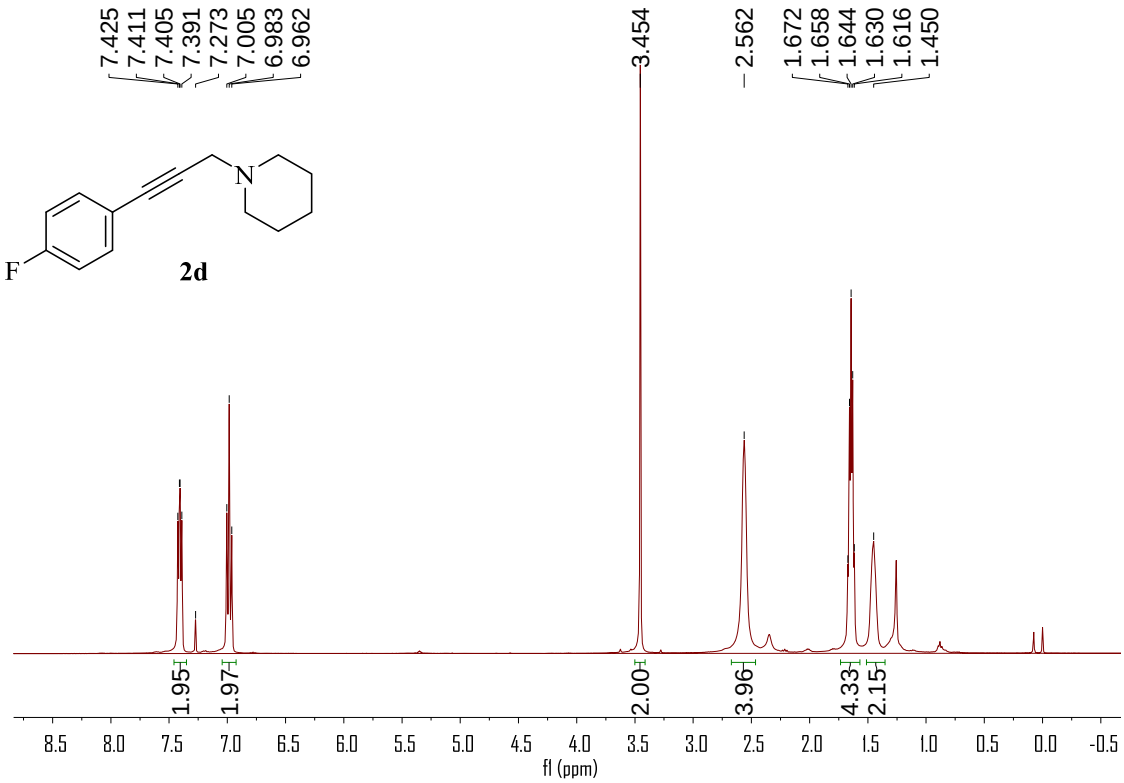

**2b** $^{13}$C NMR



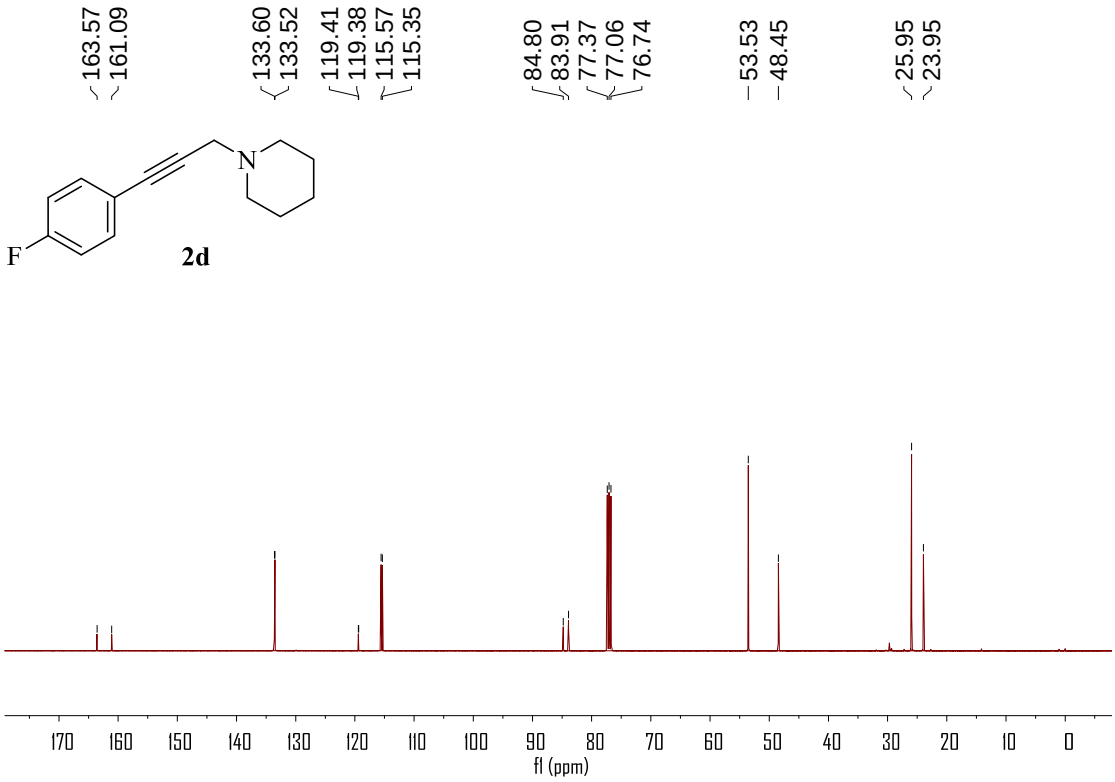

**2c** $^{1}$H NMR



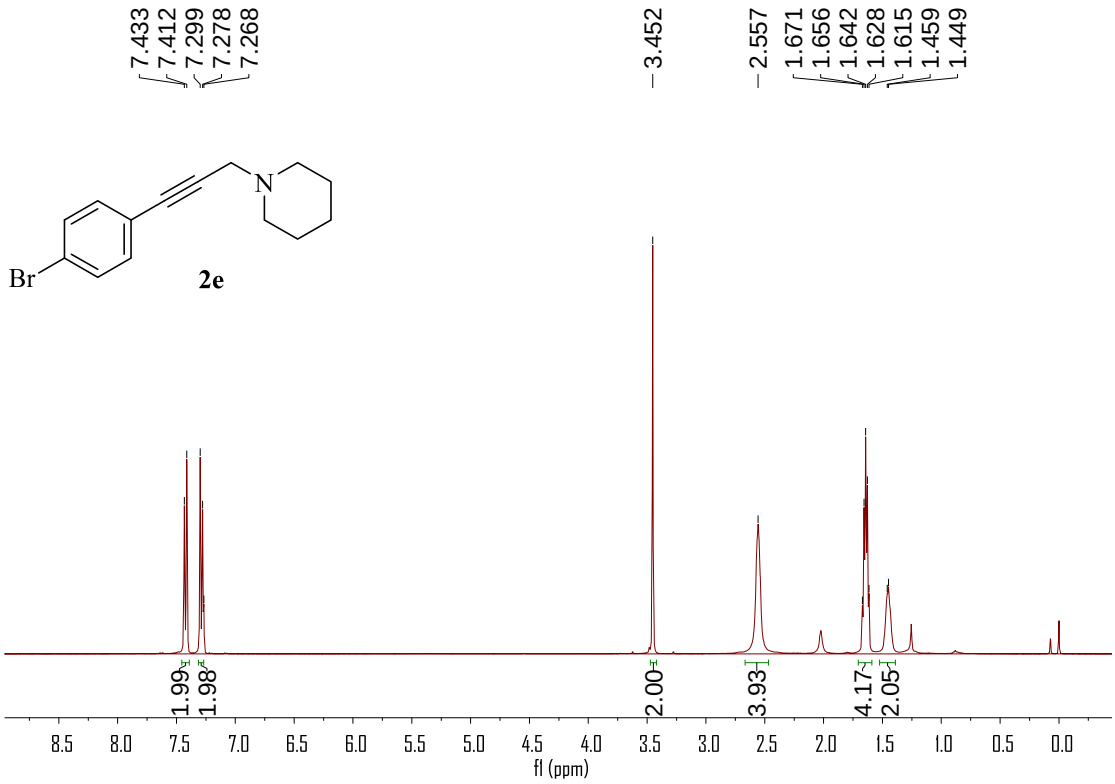

**2c** $^{13}$C NMR



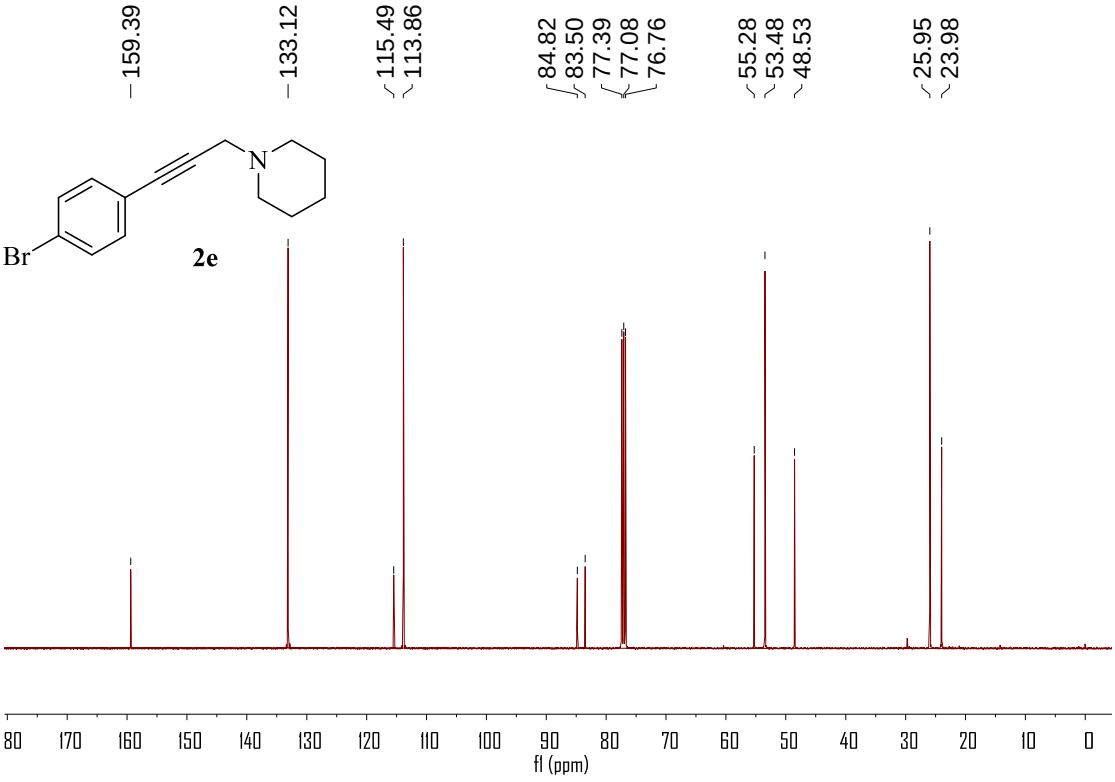

**2d** $^{1}$H NMR


163.57
161.09
133.60
133.52
119.41
119.38
115.57
115.35
84.80
83.91
77.37
77.06
76.74
53.53
48.45
25.95
23.95
N
F
2d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

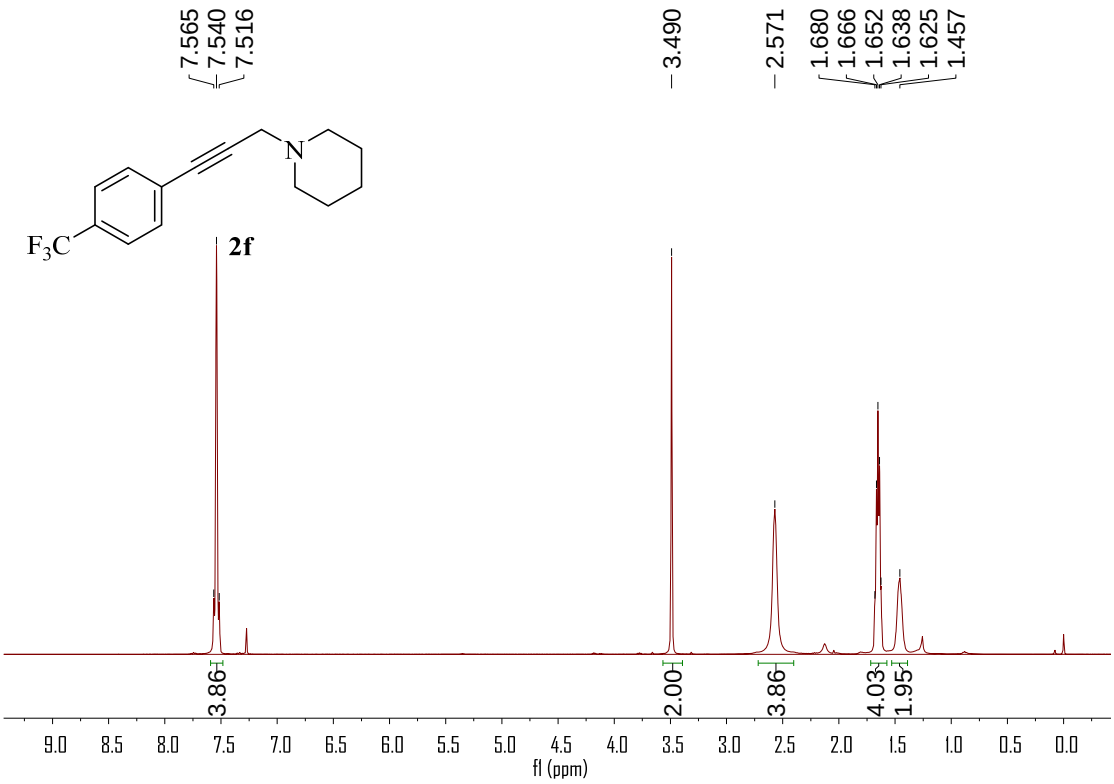
**2d** $^{13}$C NMR



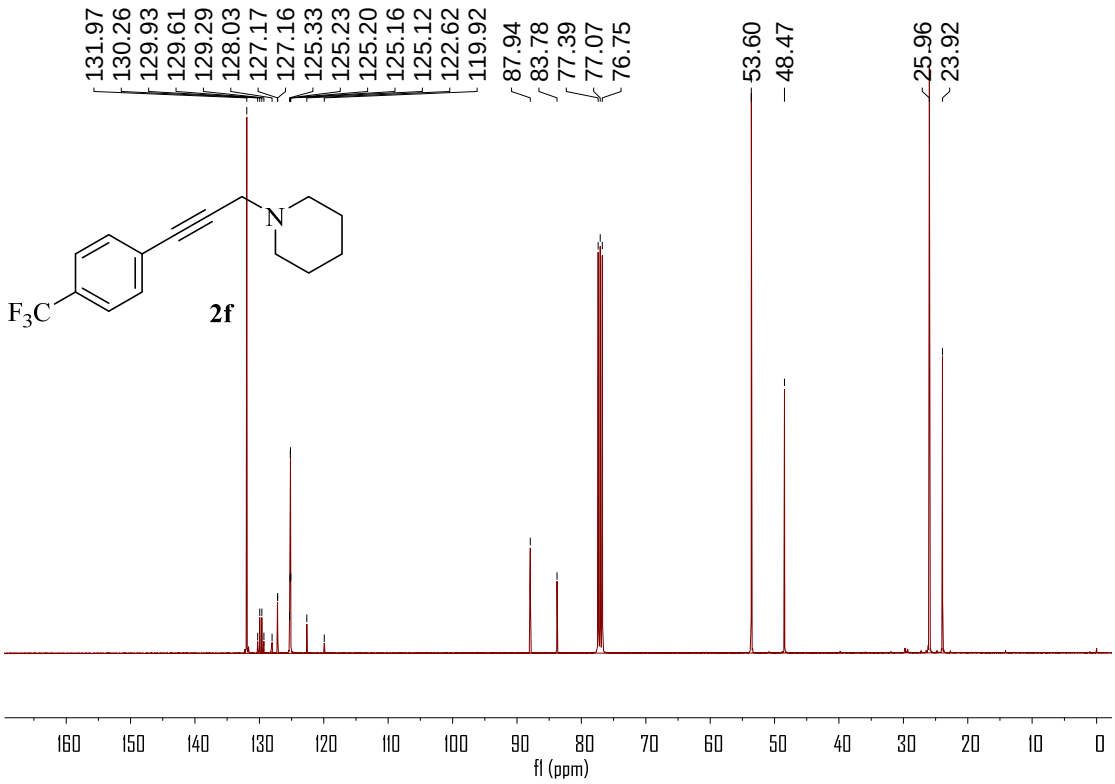

**2e** $^{1}$H NMR



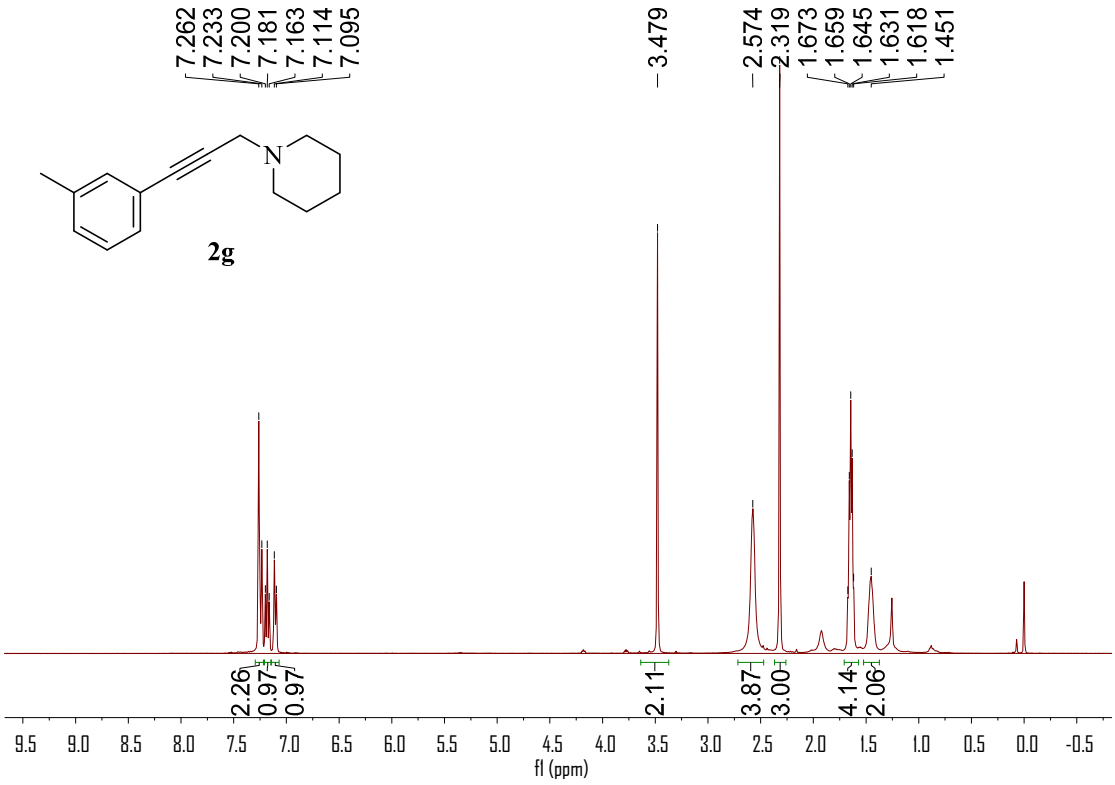

**2e** $^{13}$C NMR


7.565
7.540
7.516
3.490
2.571
1.680
1.666
1.652
1.638
1.625
1.457
N
F3C
2f
3.86
2.00
3.86
4.03
1.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

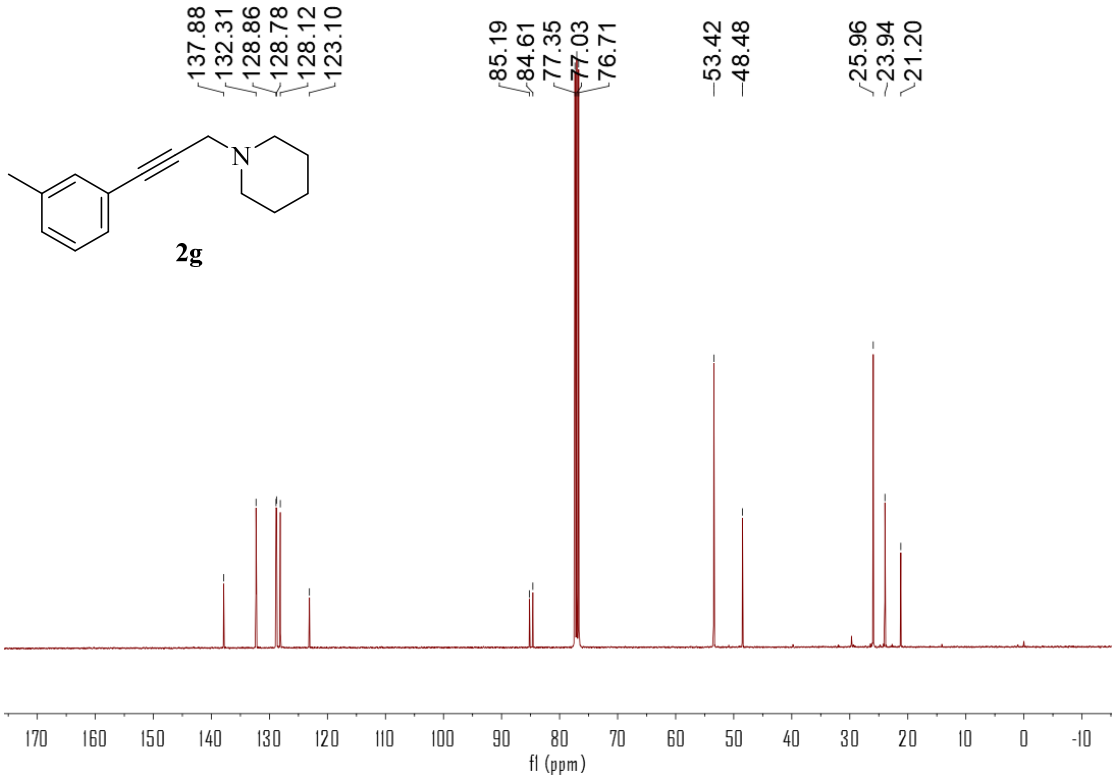
**2f** $^{1}$H NMR



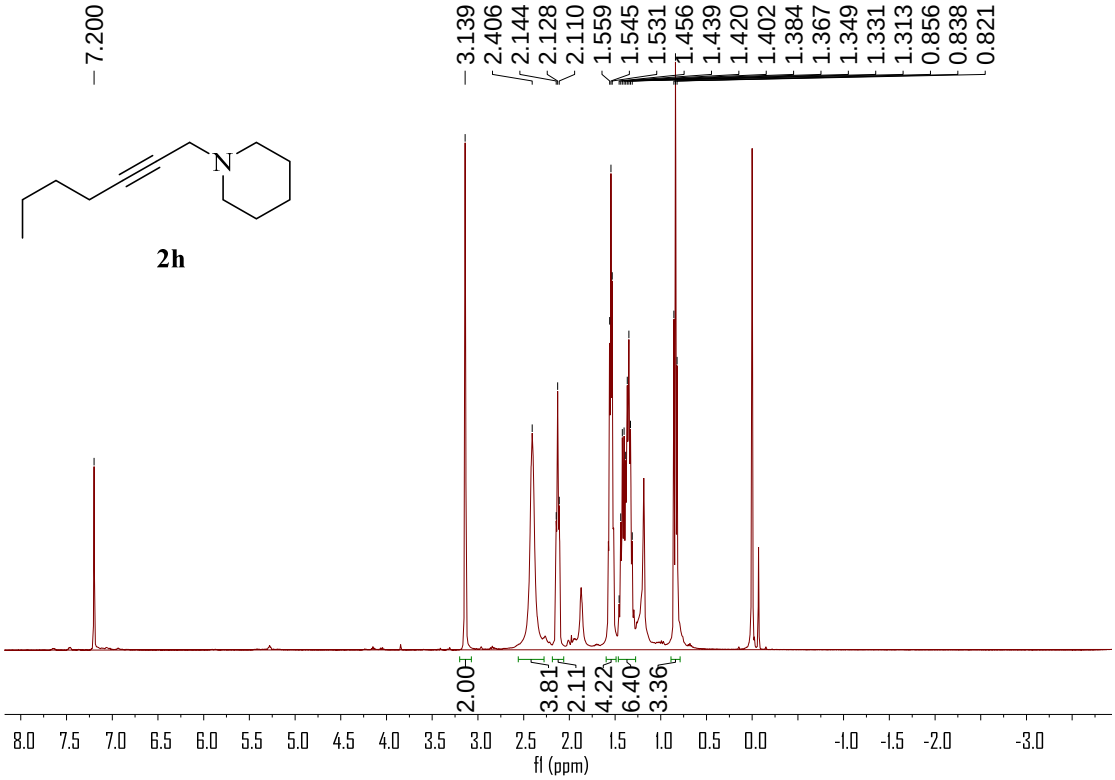

**2f** $^{13}$C NMR



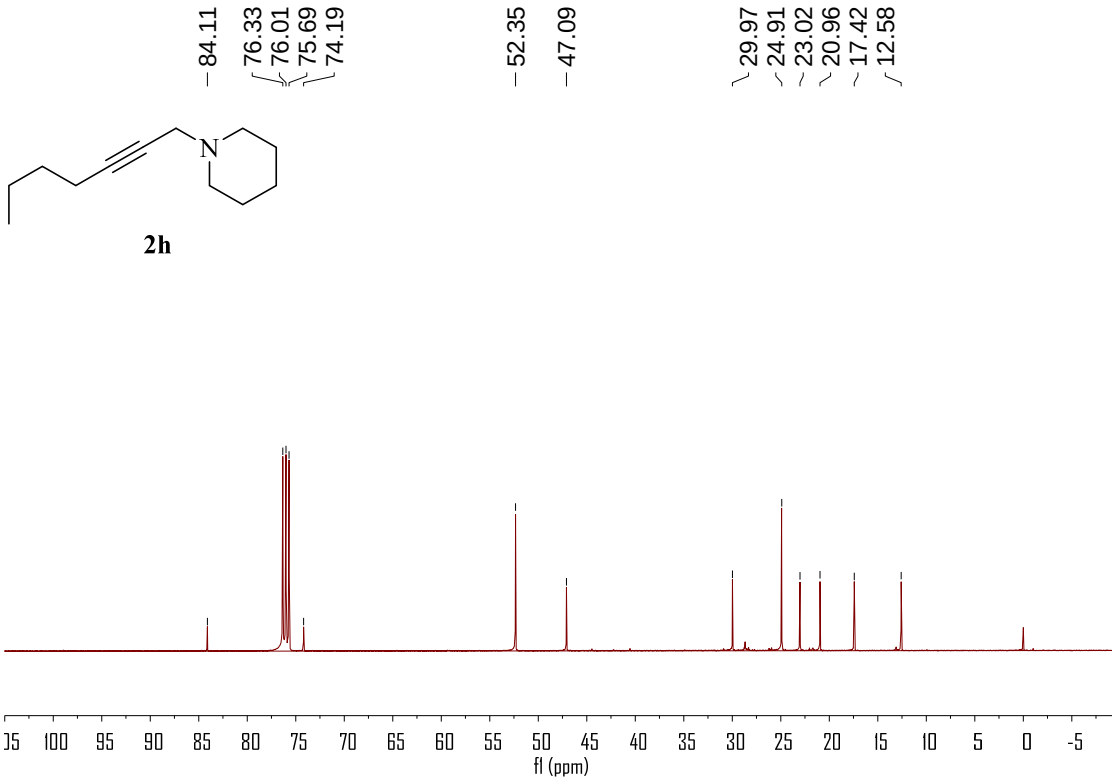

**2g** $^{1}$H NMR



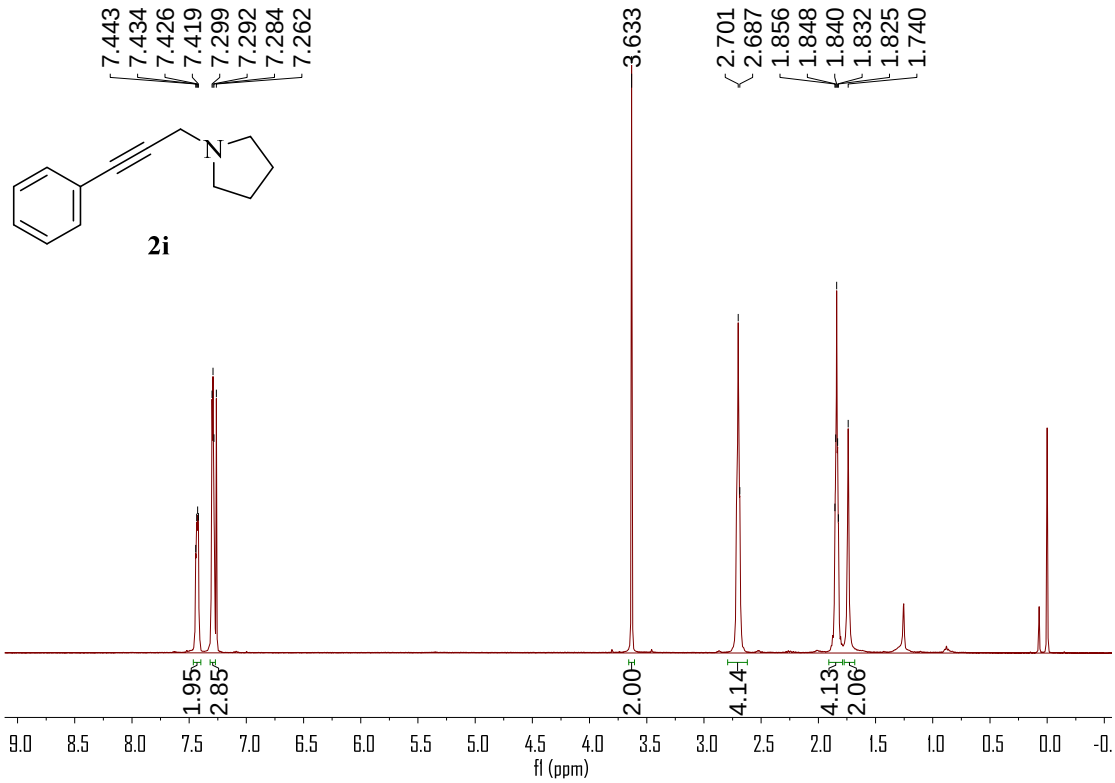

**2g** $^{13}$C NMR



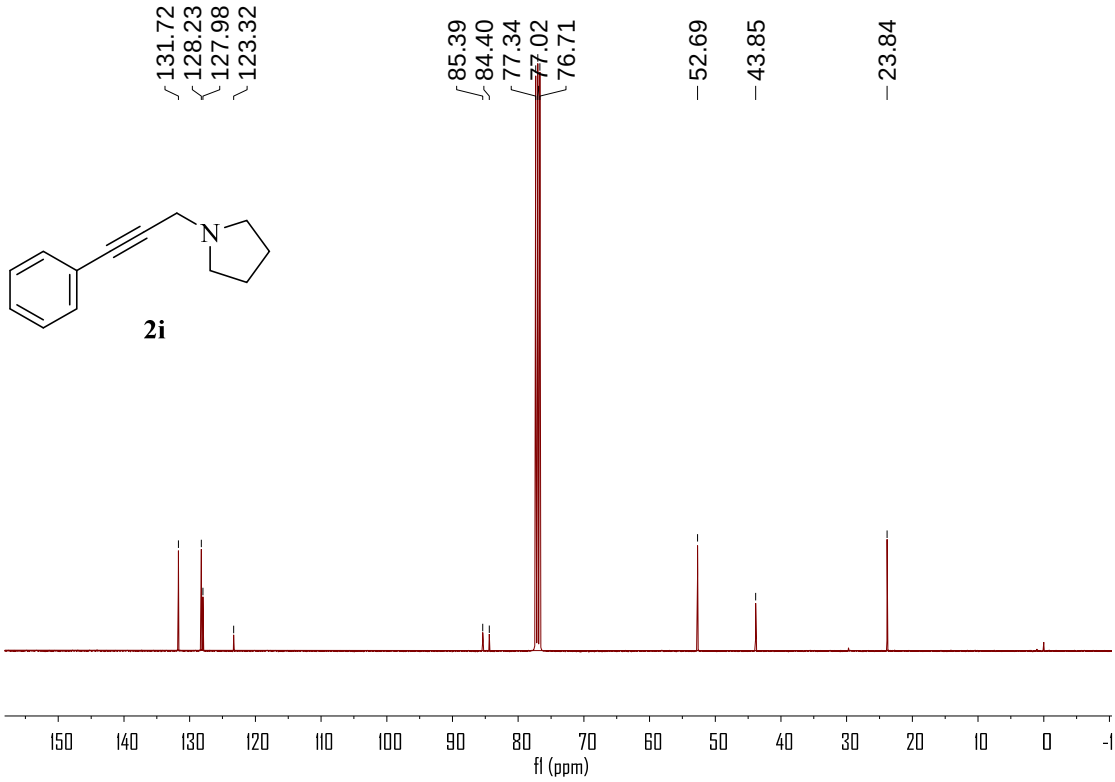

**2h** $^{1}$H NMR



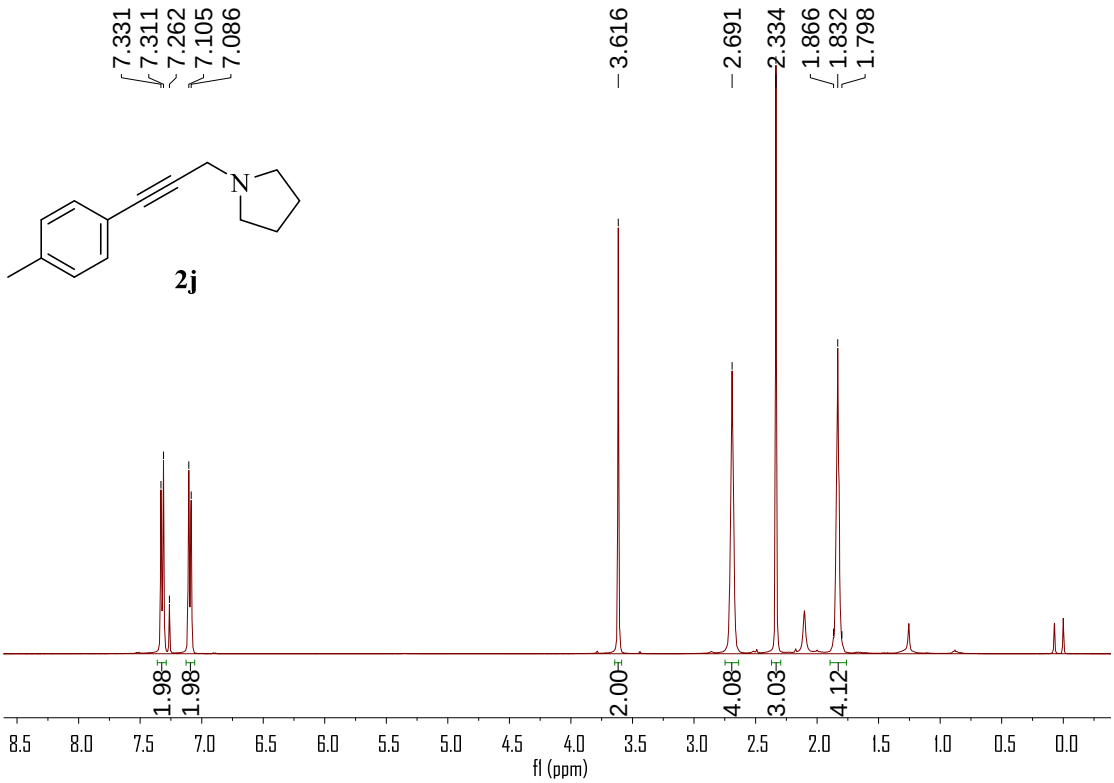

**2h** $^{13}$C NMR



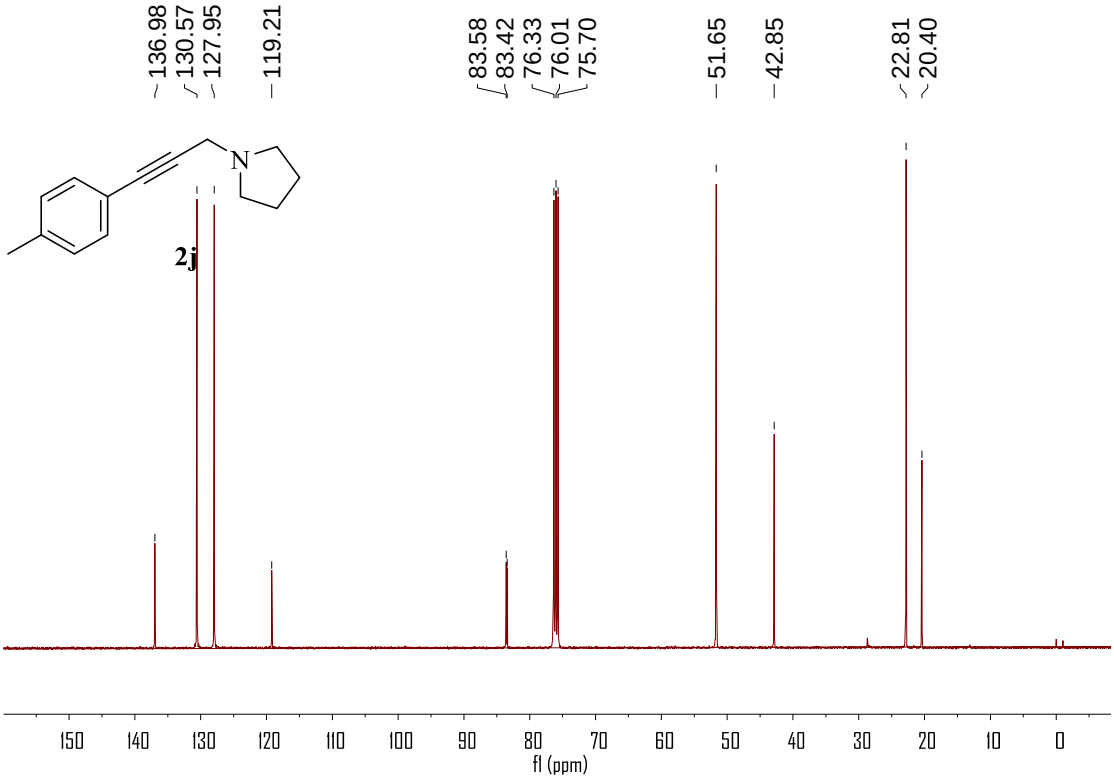

**2i** $^{1}$H NMR


131.72
128.23
127.98
123.32
85.39
84.40
77.34
77.02
76.71
52.69
43.85
23.84
N
2i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

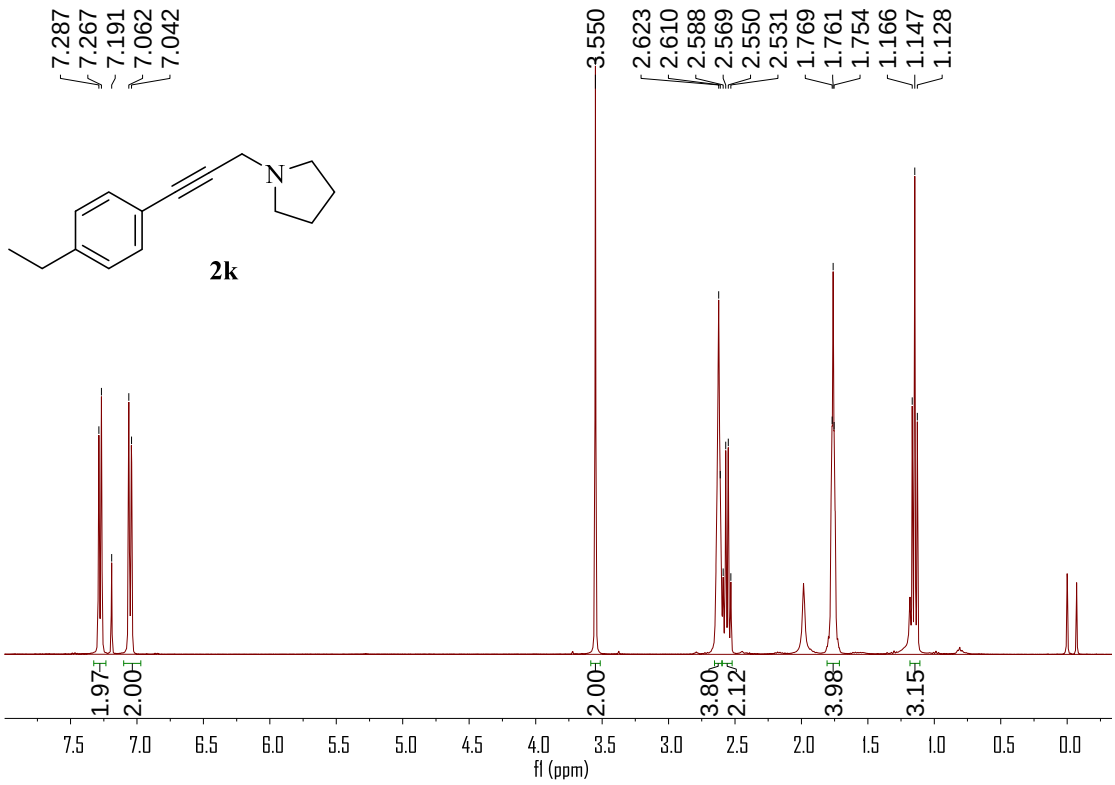
**2i** $^{13}$C NMR



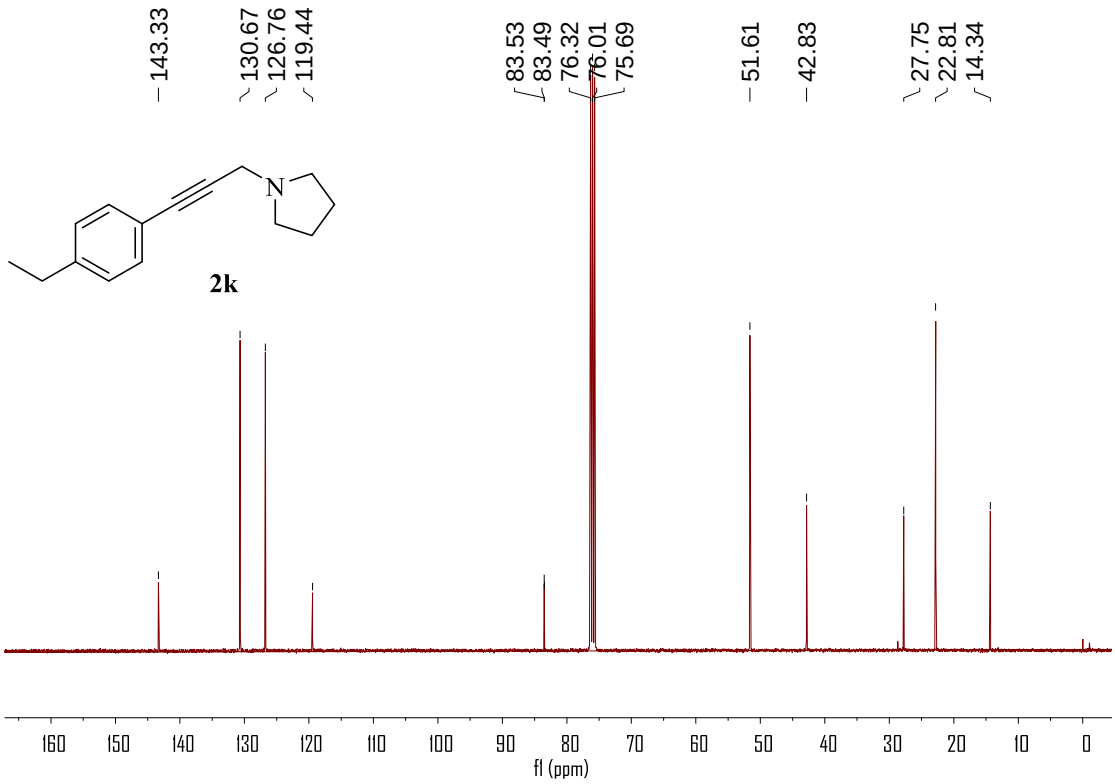

**2j** $^{1}$H NMR



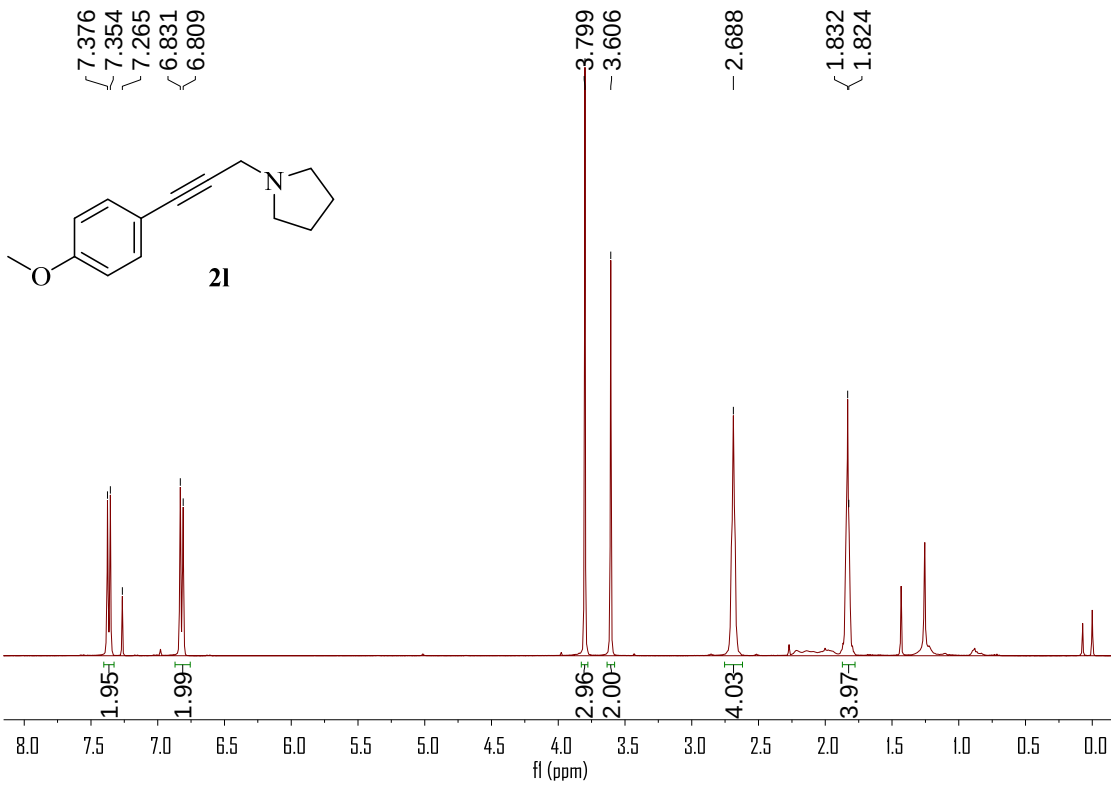

**2j** $^{13}$C NMR


7.287
7.267
7.191
7.062
7.042
3.550
2.623
2.610
2.588
2.569
2.550
2.531
1.769
1.761
1.754
1.166
1.147
1.128
N
2k
1.97
2.00
2.00
3.80
2.12
3.98
3.15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

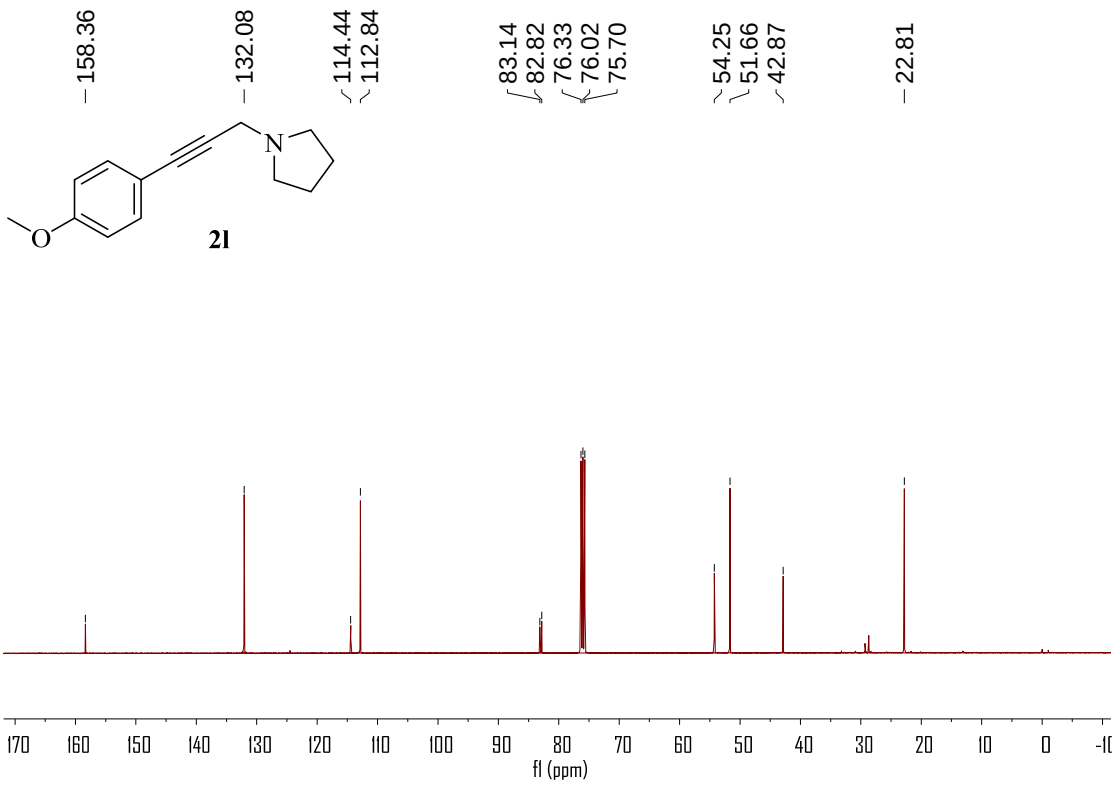
**2k** $^{1}$H NMR


143.33
130.67
126.76
119.44
83.53
83.49
76.32
76.01
75.69
51.61
42.83
27.75
22.81
14.34
N
2k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

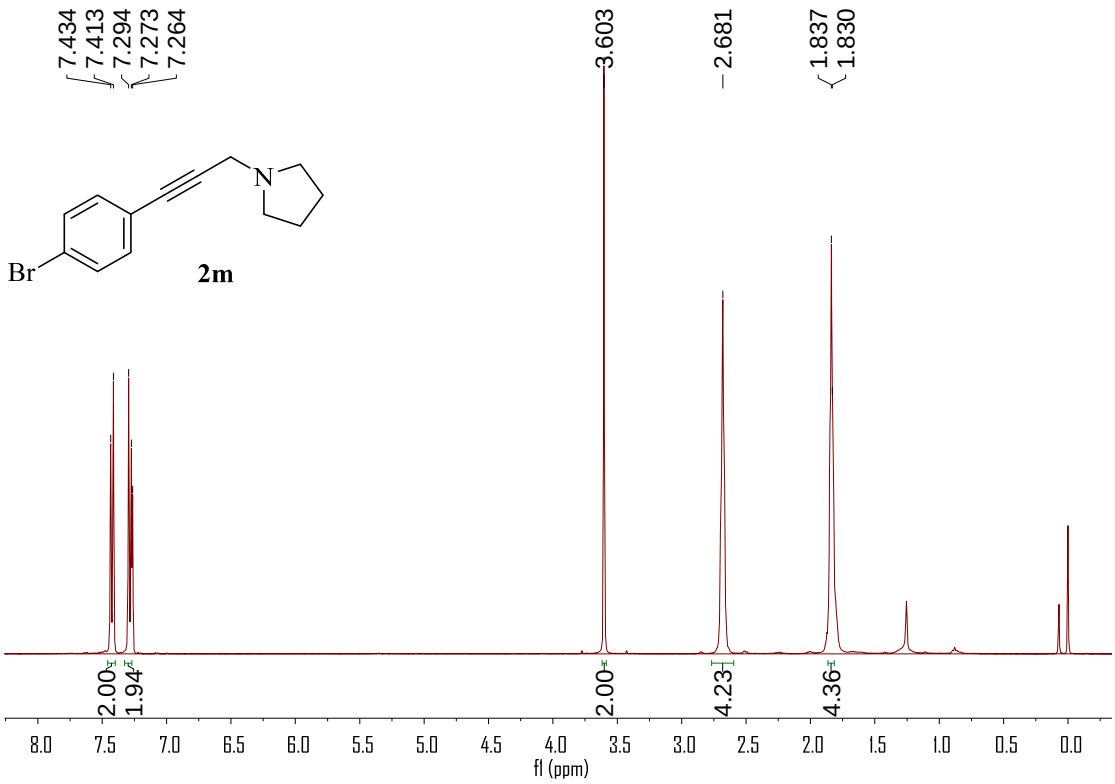
**2k** $^{13}$C NMR



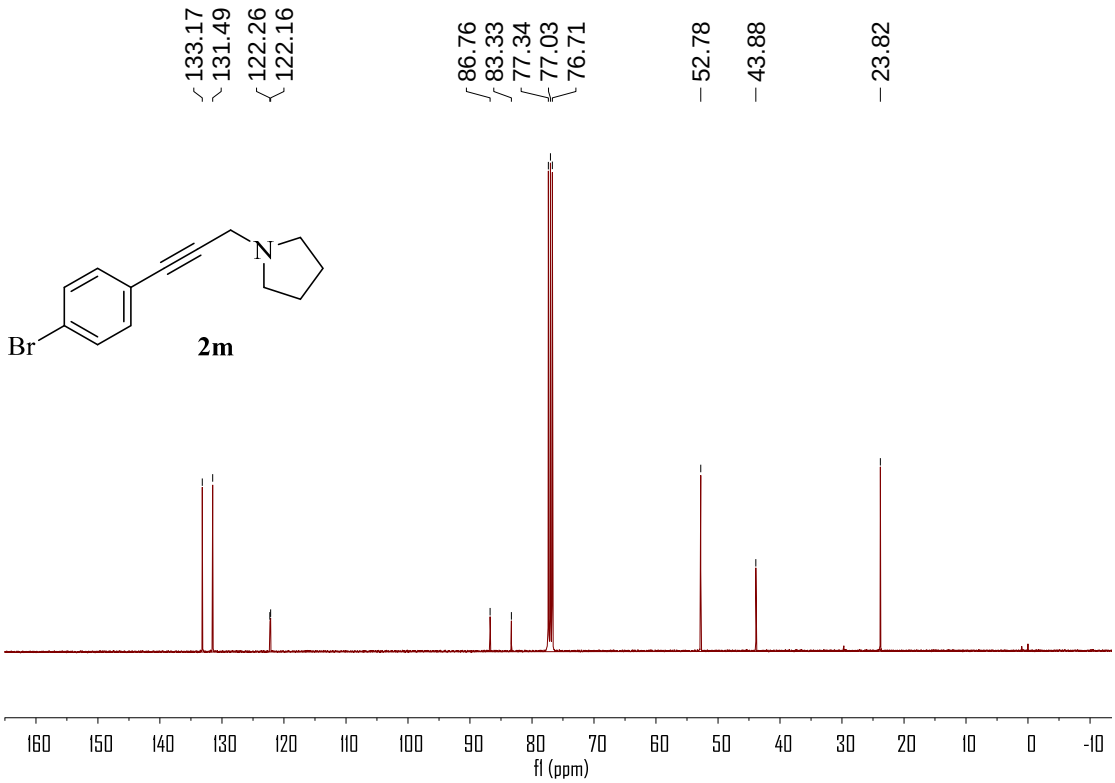

**2l** $^{1}$H NMR



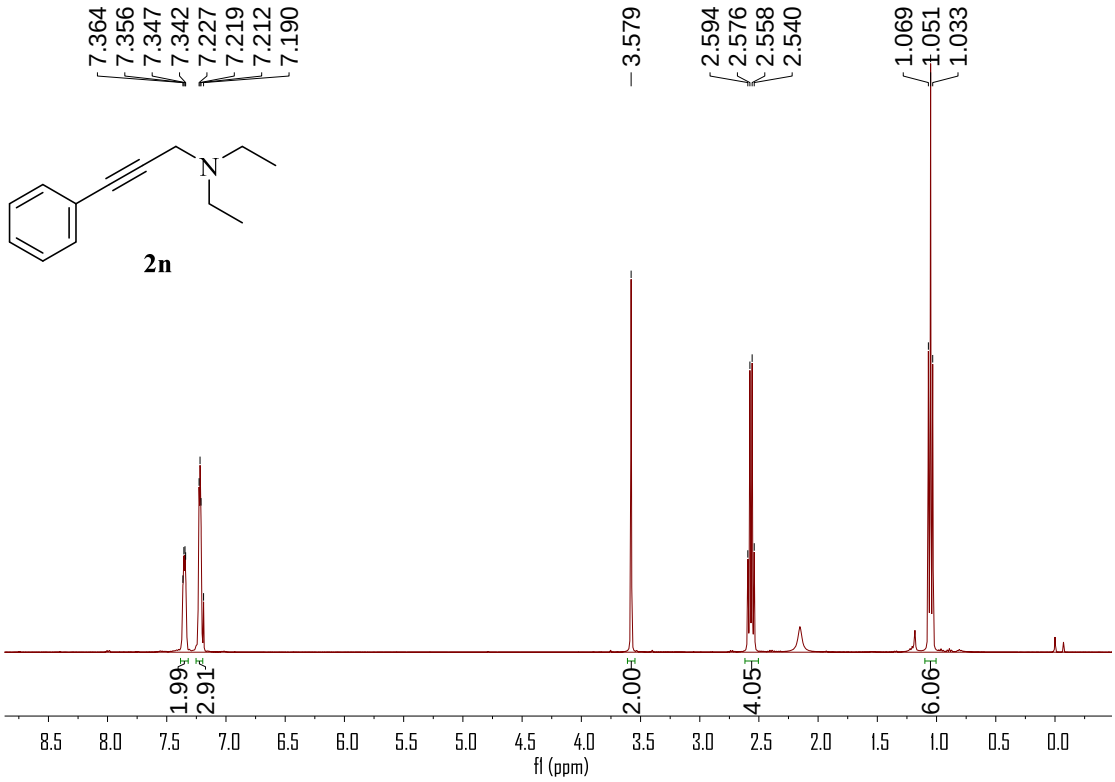

**2l** $^{13}$C NMR


7.434
7.413
7.294
7.273
7.264
3.603
2.681
1.837
1.830
N
Br
2m
2.00
1.94
2.00
4.23
4.36
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

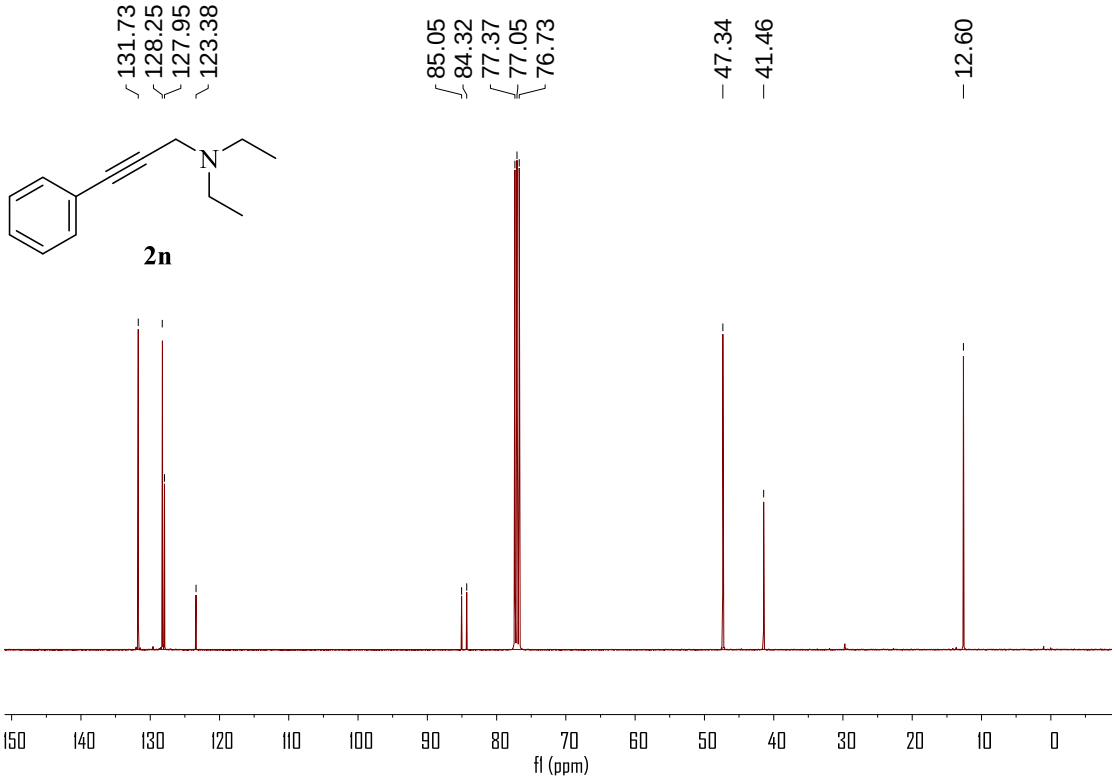
**2m** $^{1}$H NMR


133.17
131.49
122.26
122.16
86.76
83.33
77.34
77.03
76.71
52.78
43.88
23.82
Br
N
2m
f1 (ppm)

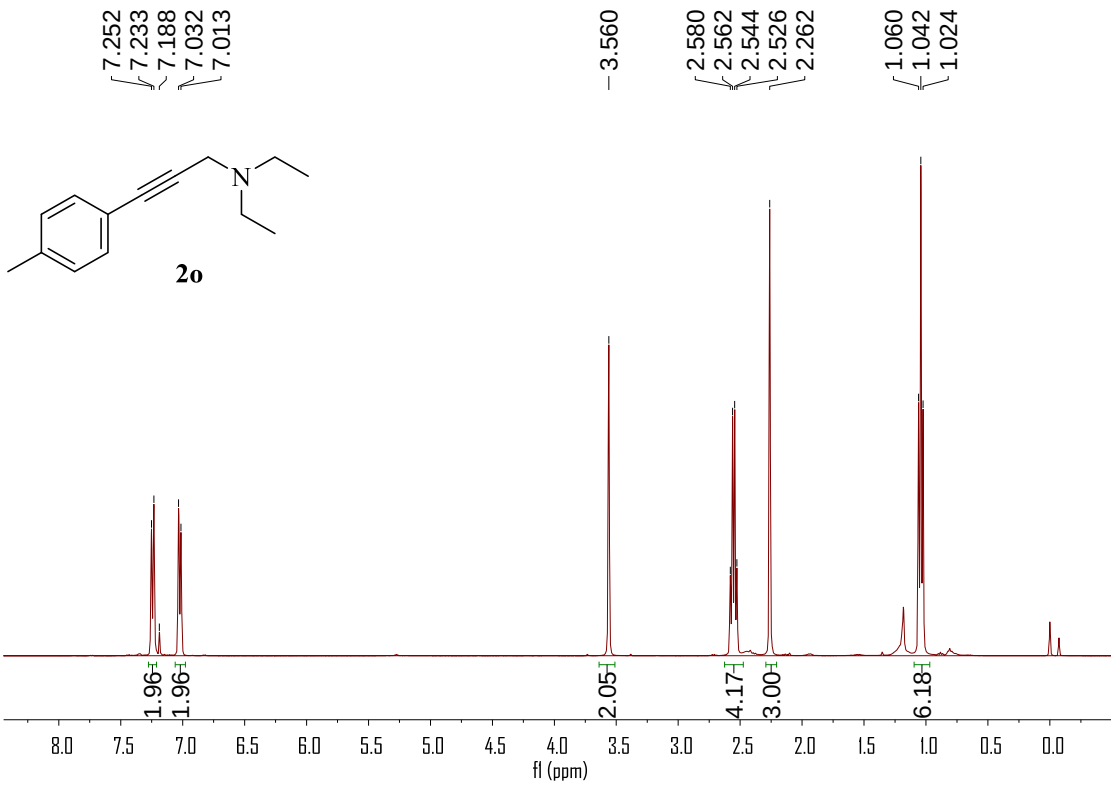
**2m** $^{13}$C NMR


7.364
7.356
7.347
7.342
7.227
7.219
7.212
7.190
3.579
2.594
2.576
2.558
2.540
1.069
1.051
1.033
N
2n
1.99
2.91
2.00
4.05
6.06
f1 (ppm)

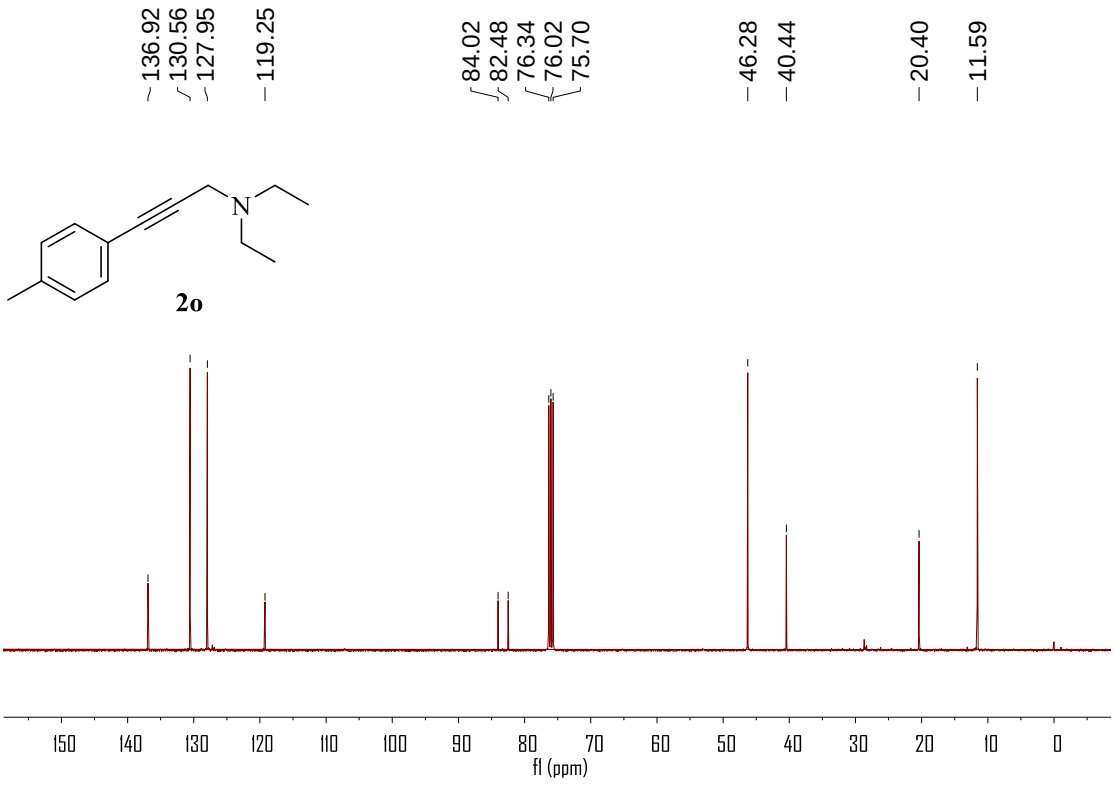
**2n** $^{1}$H NMR



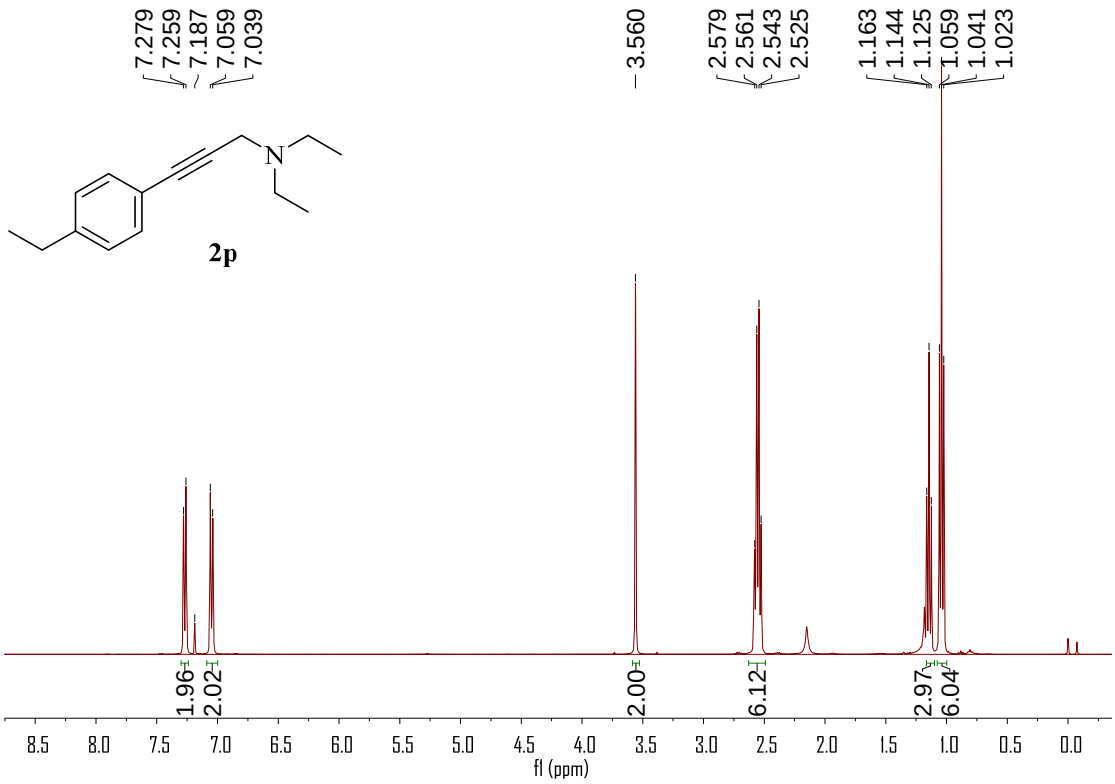

**2n** $^{13}$C NMR



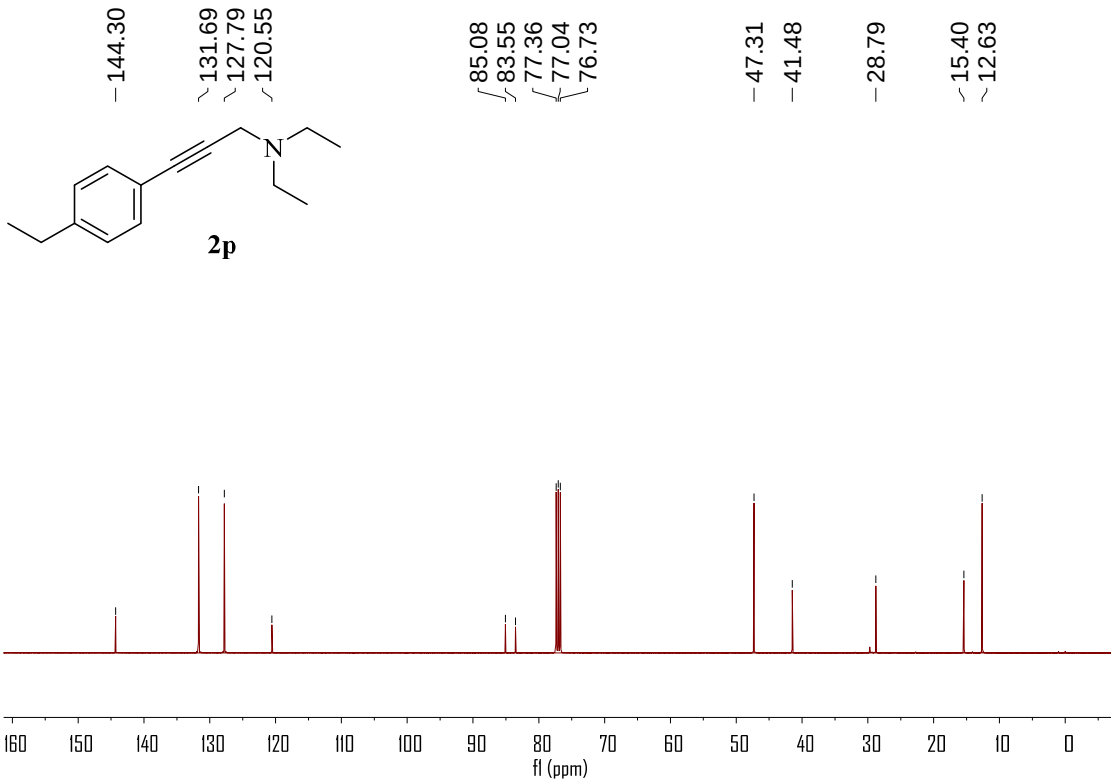

**2o** $^{1}$H NMR



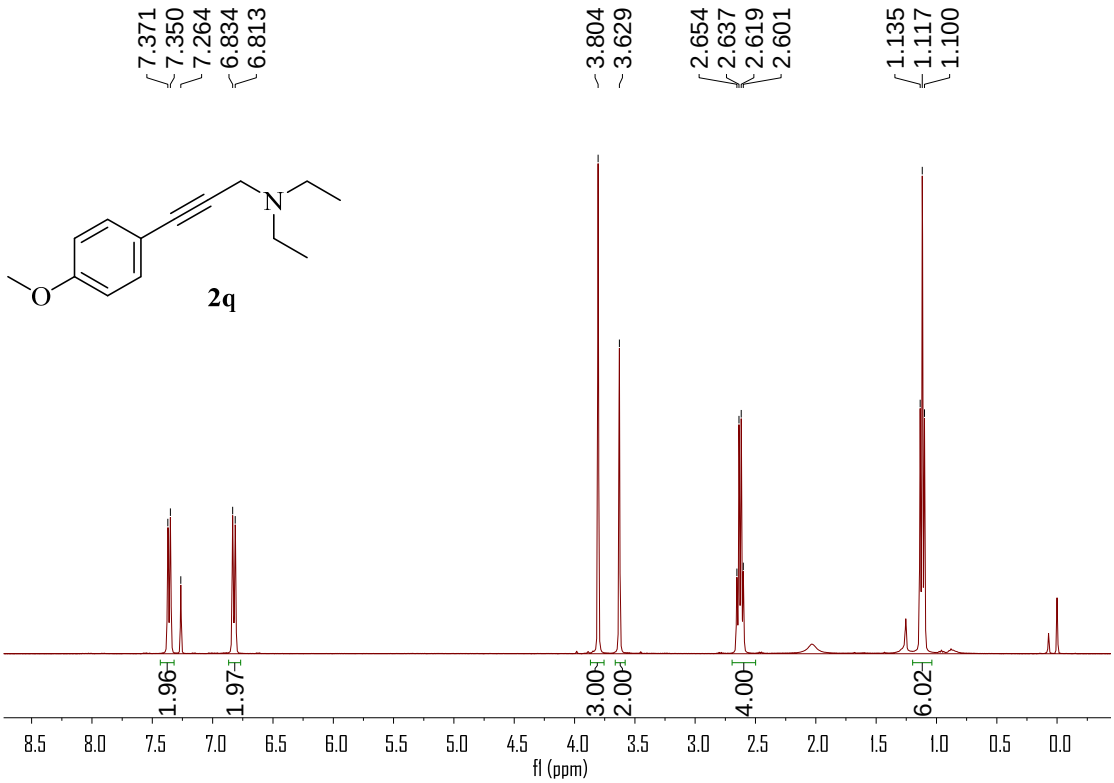

**2o** $^{13}$C NMR


7.279
7.259
7.187
7.059
7.039
3.560
2.579
2.561
2.543
2.525
1.163
1.144
1.125
1.059
1.041
1.023
N
2p
1.96
2.02
2.00
6.12
2.97
6.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

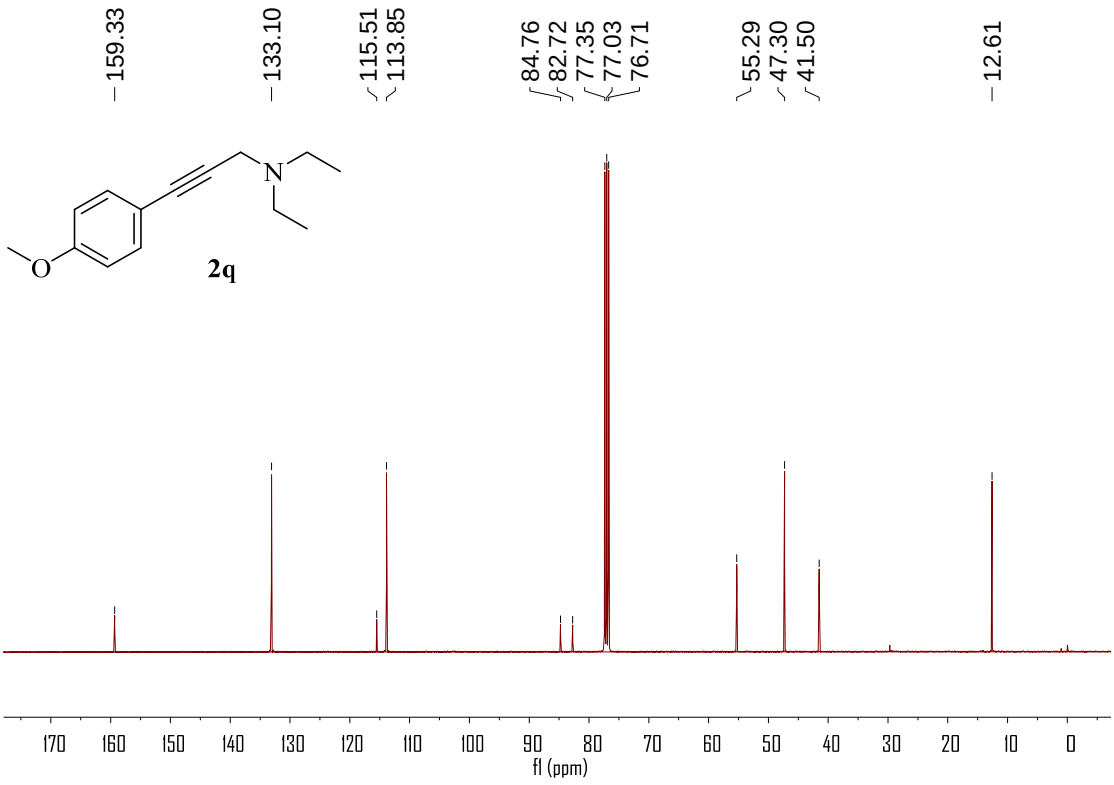
**2p** $^{1}$H NMR


144.30
131.69
127.79
120.55
85.08
83.55
77.36
77.04
76.73
47.31
41.48
28.79
15.40
12.63
N
2p
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

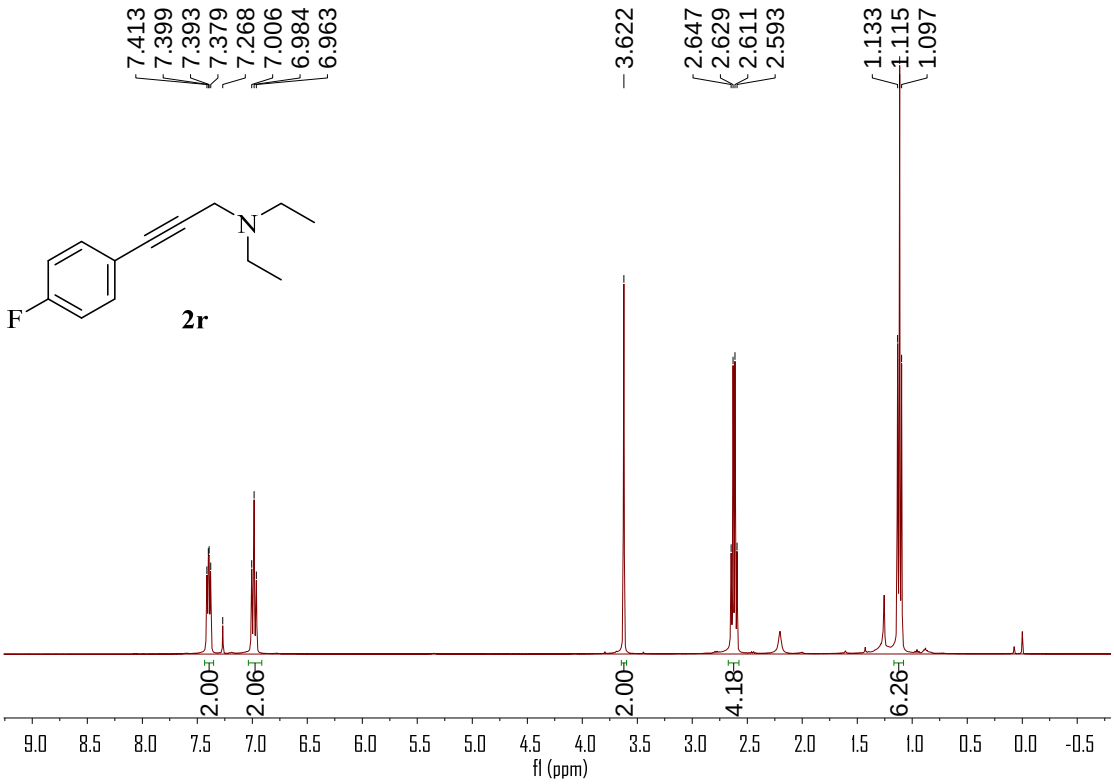
**2p** $^{13}$C NMR



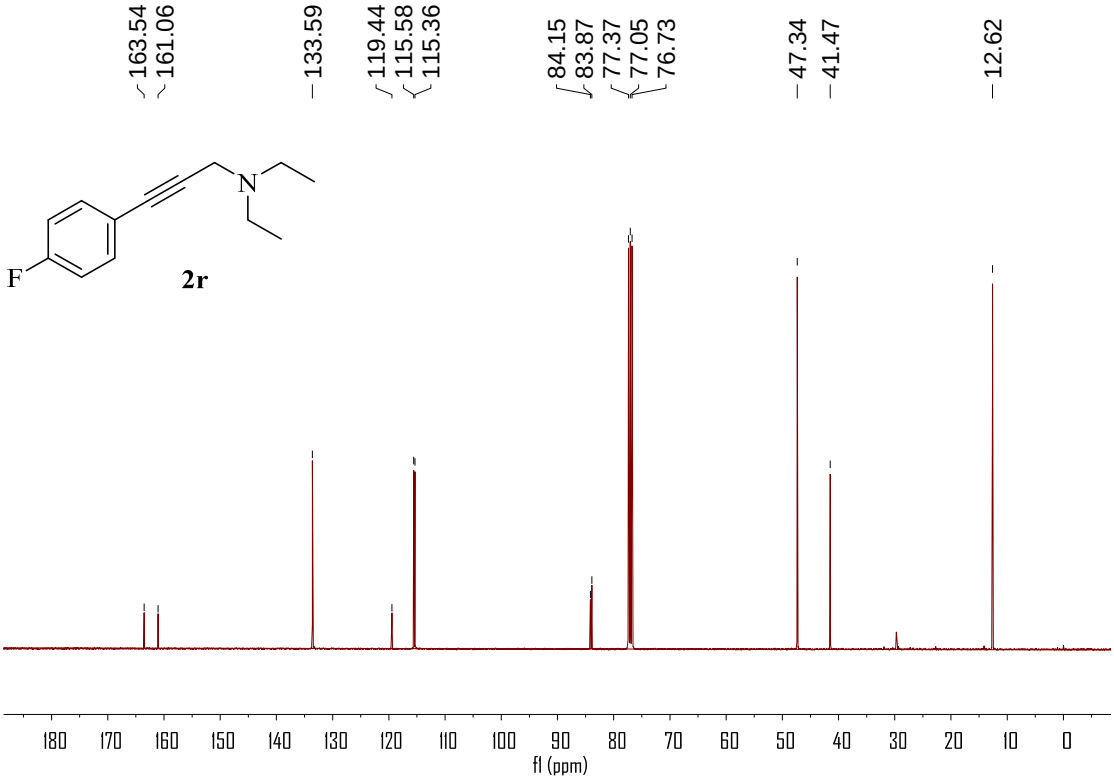

**2q** $^{1}$H NMR



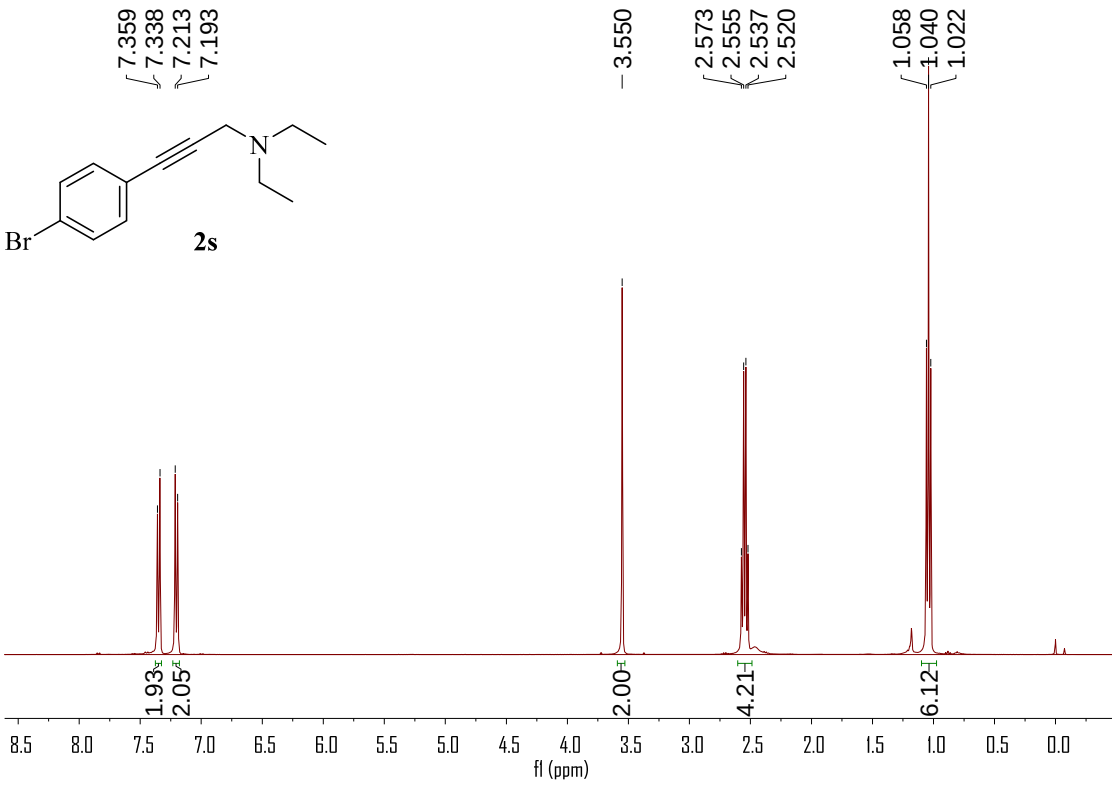

**2q** $^{13}$C NMR



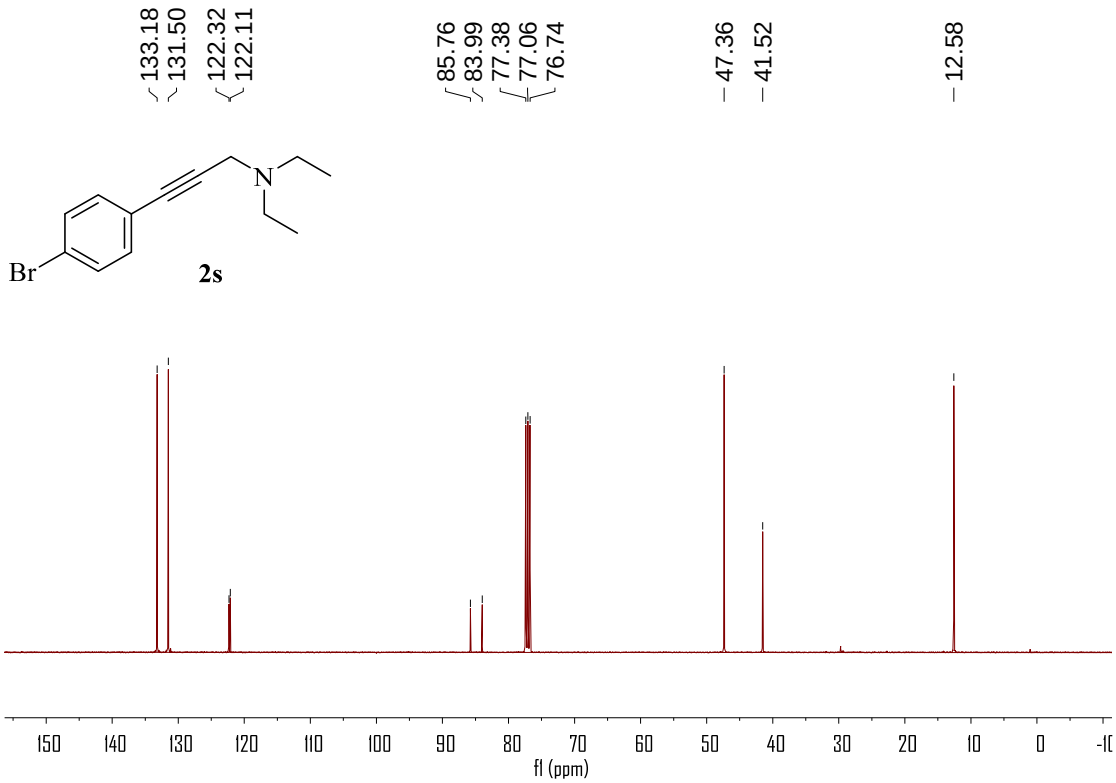

**2r** $^{1}$H NMR



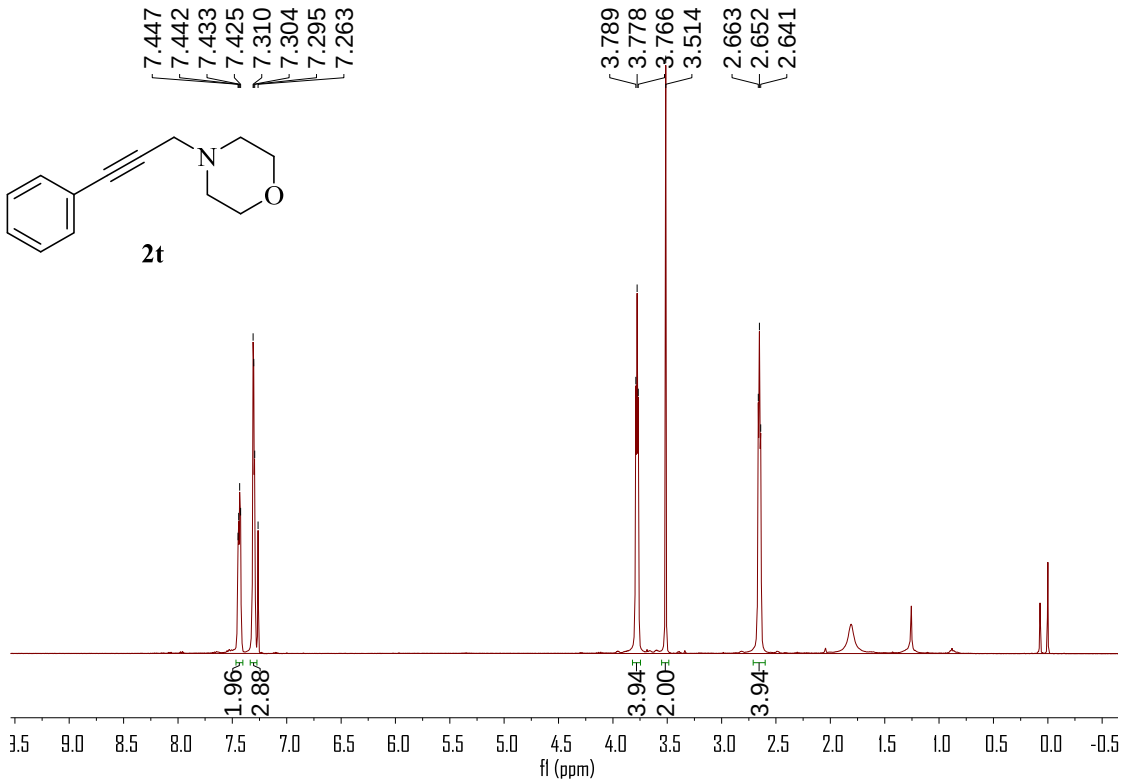

**2r** $^{13}$C NMR


7.359
7.338
7.213
7.193
3.550
2.573
2.555
2.537
2.520
1.058
1.040
1.022
N
Br
2s
1.93
2.05
2.00
4.21
6.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

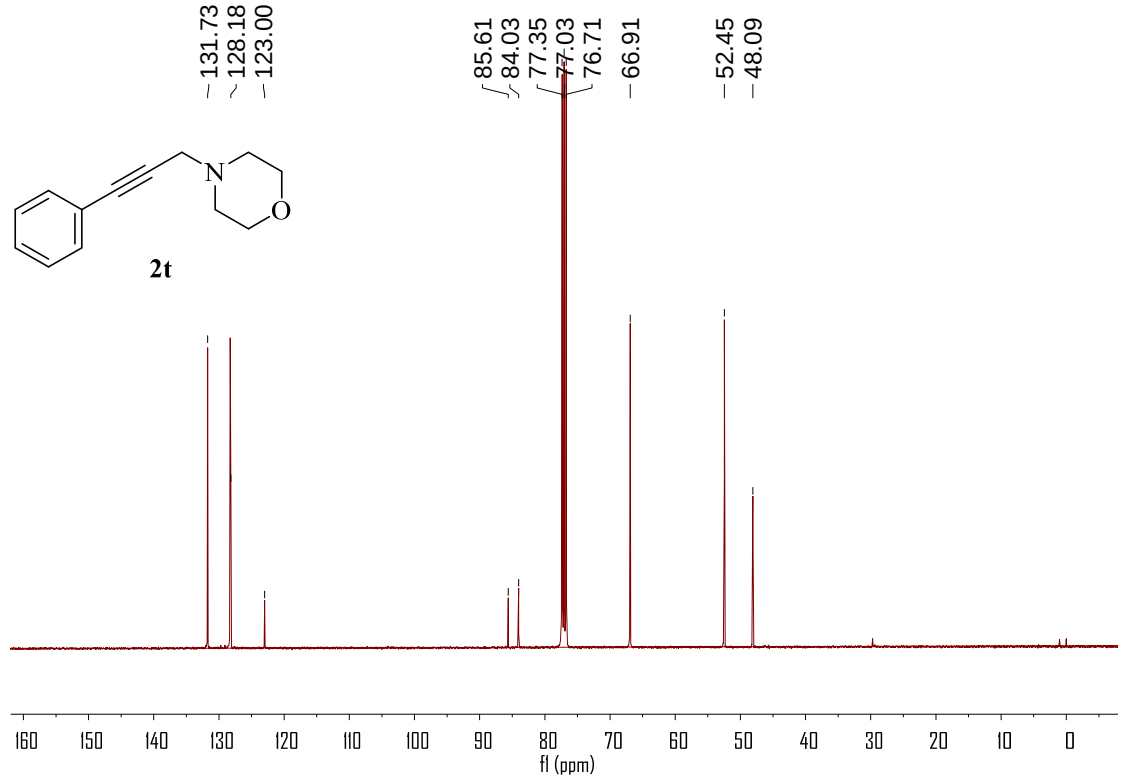
**2s** $^{1}$H NMR


133.18
131.50
122.32
122.11
85.76
83.99
77.38
77.06
76.74
47.36
41.52
12.58
N
Br
2s
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

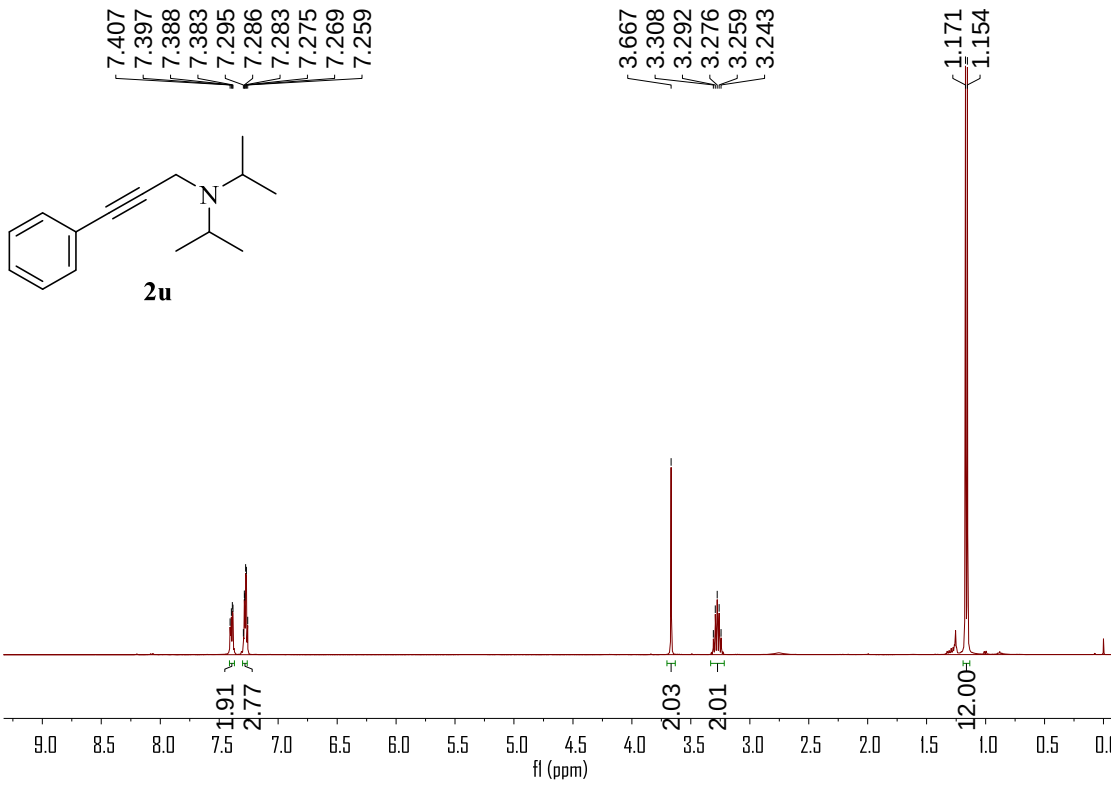
**2s** $^{13}$C NMR




**2t** $^{1}$H NMR

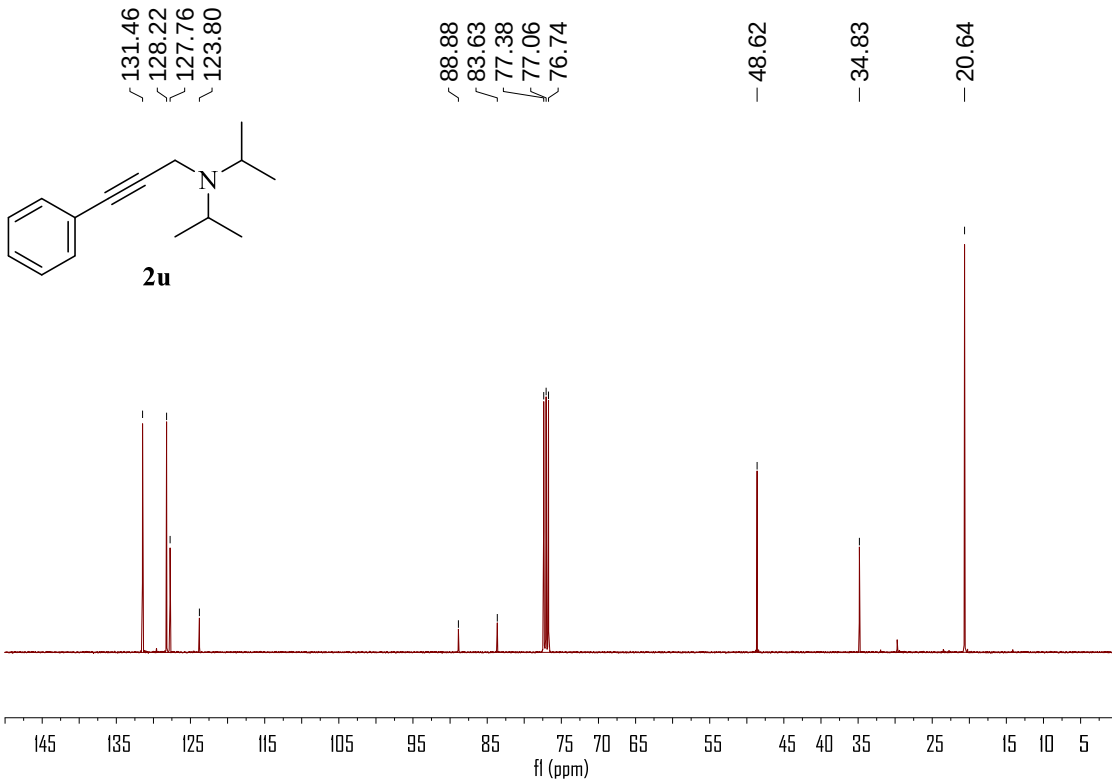



**2t** $^{13}$C NMR

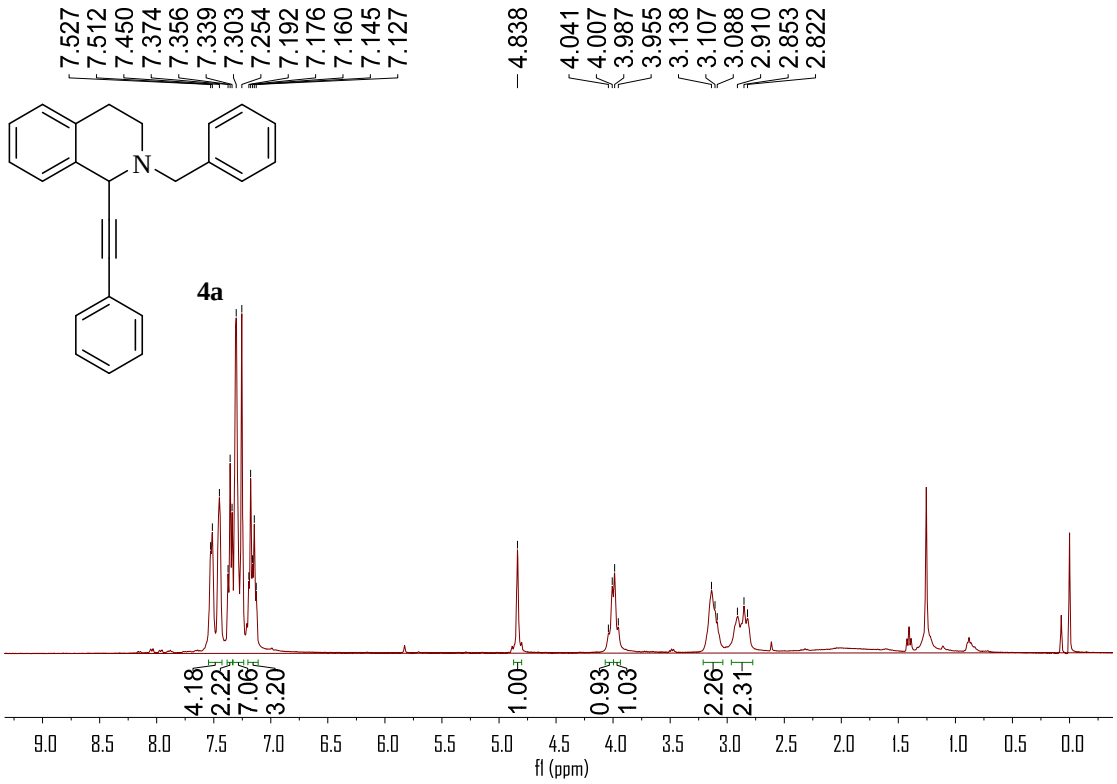

7.407
7.397
7.388
7.383
7.295
7.286
7.283
7.275
7.269
7.259
3.667
3.308
3.292
3.276
3.259
3.243
1.171
1.154
N
1.91
2.77
2.03
2.01
12.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

**2u**

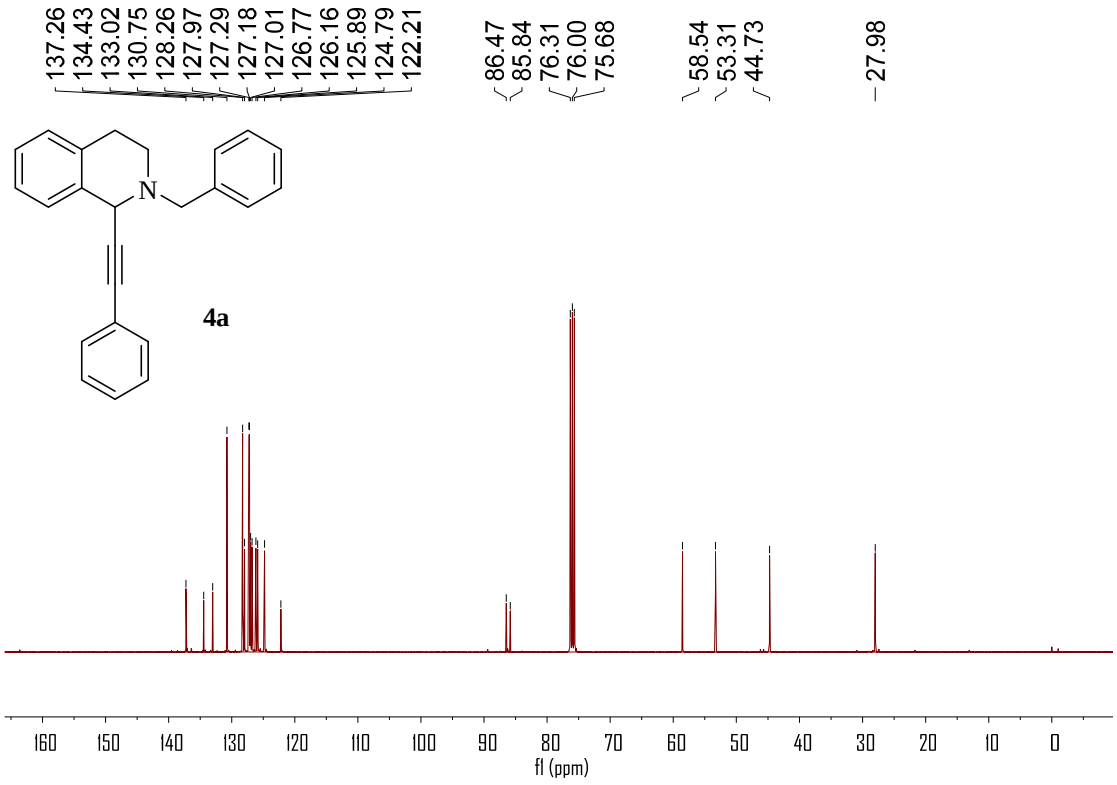
**2u** $^{1}$H NMR


131.46
128.22
127.76
123.80
88.88
83.63
77.38
77.06
76.74
48.62
34.83
20.64
N
2u
145
135
125
115
105
95
85
75
70
65
55
45
40
35
25
15
10
5
f1 (ppm)

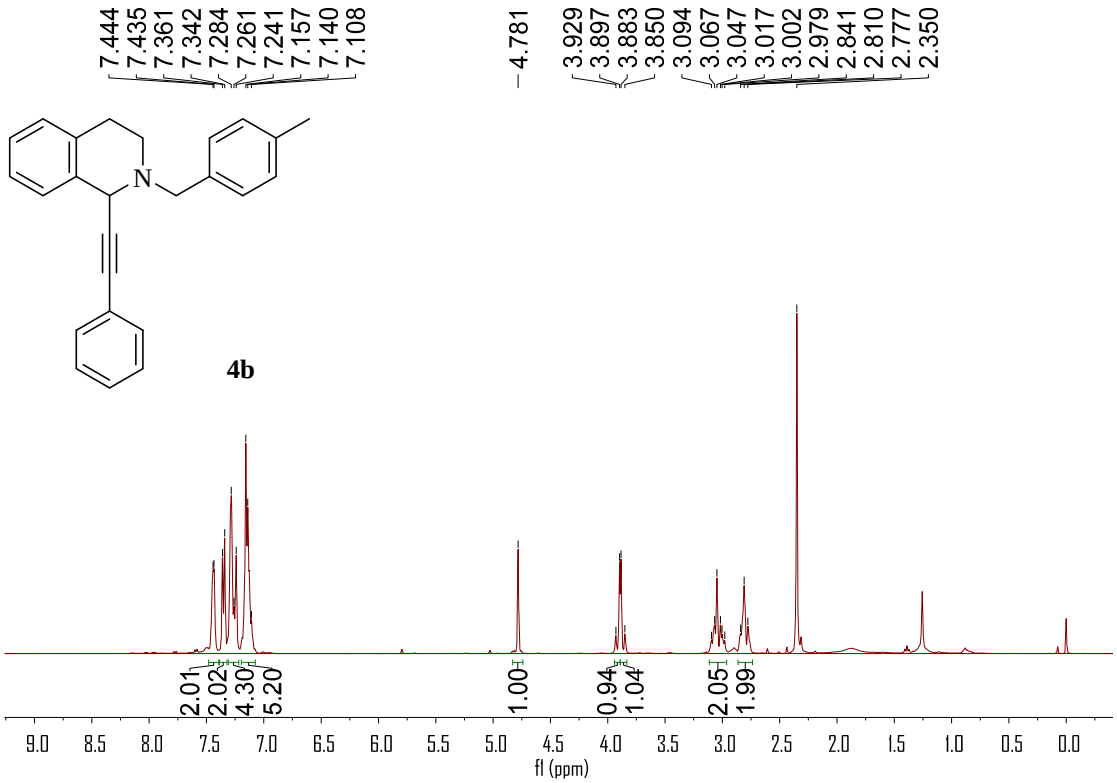
**2u** $^{13}$C NMR



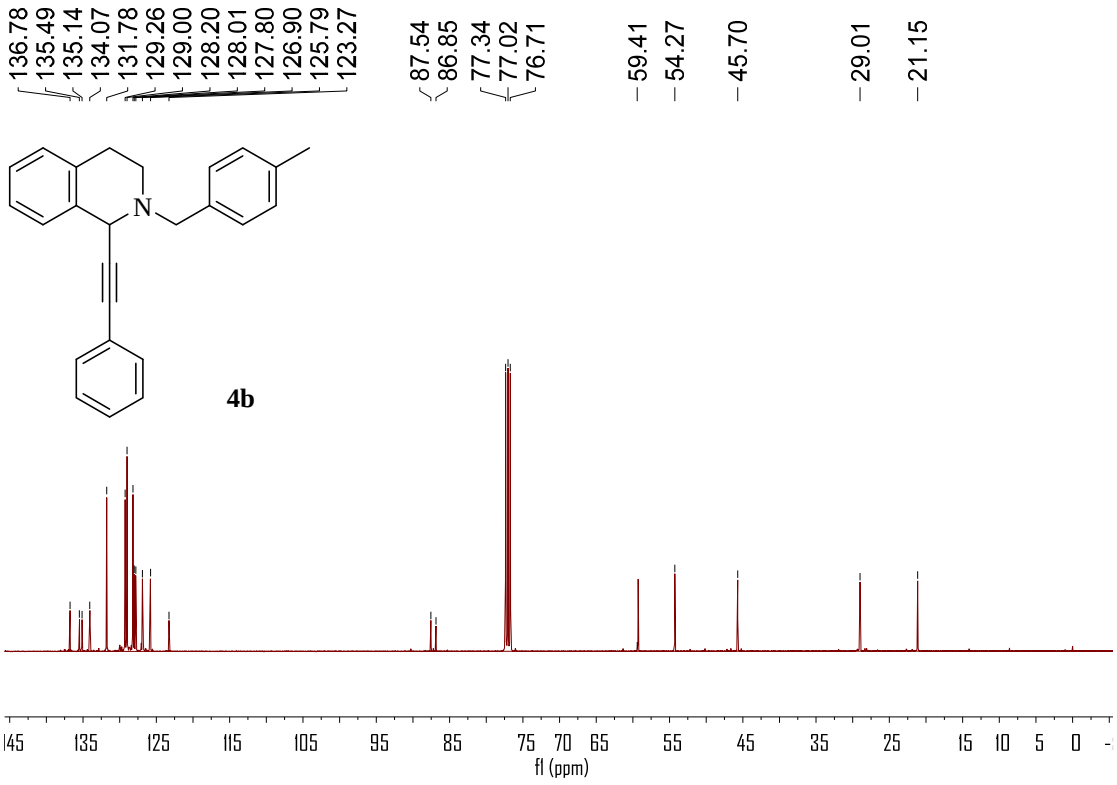

**4a** $^{1}$H NMR



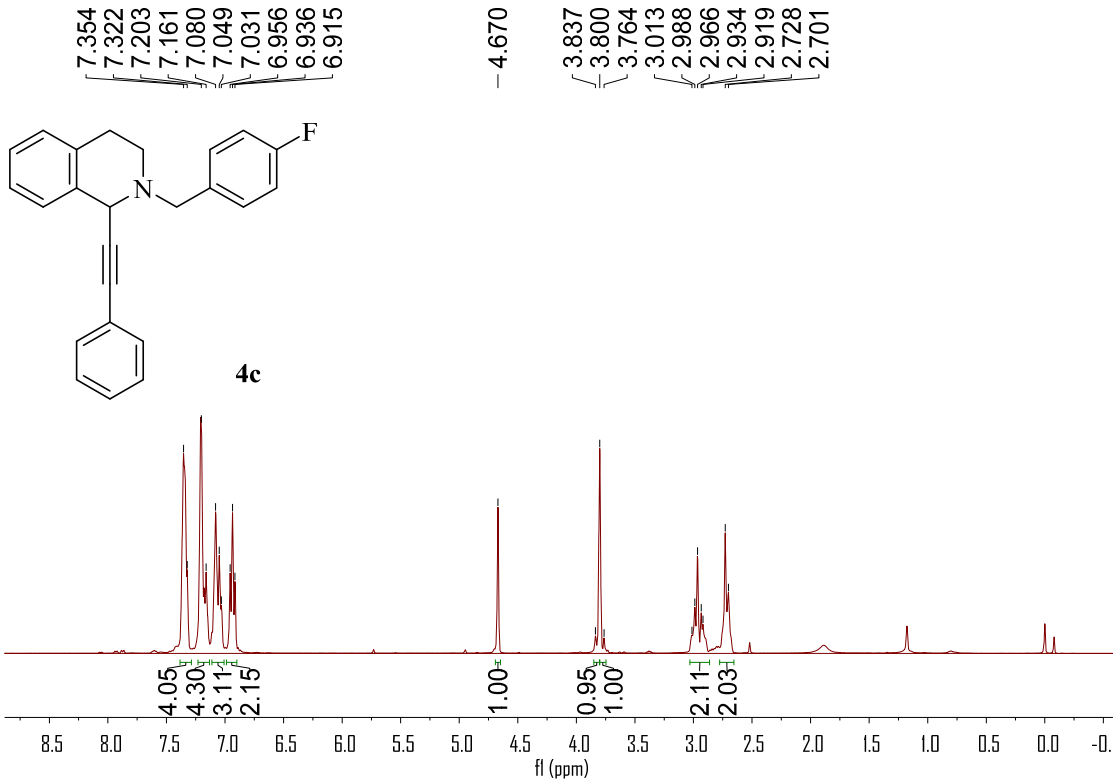

**4a** $^{13}$C NMR



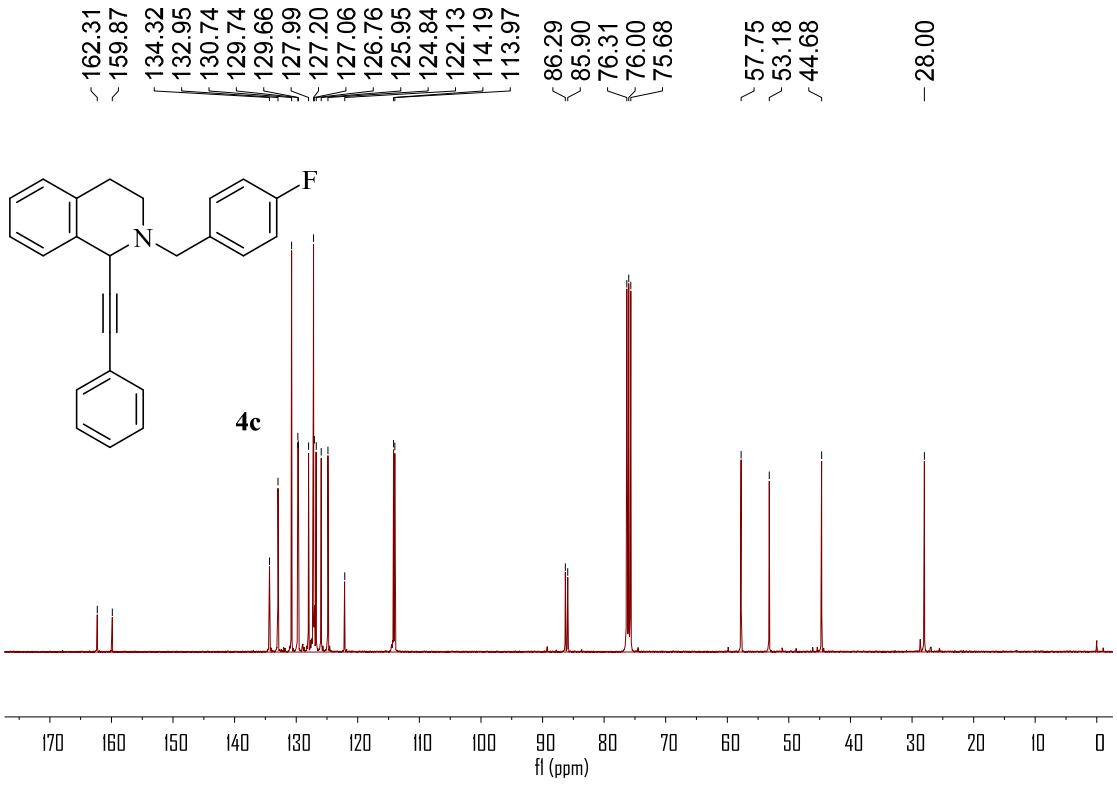

**4b** $^{1}$H NMR



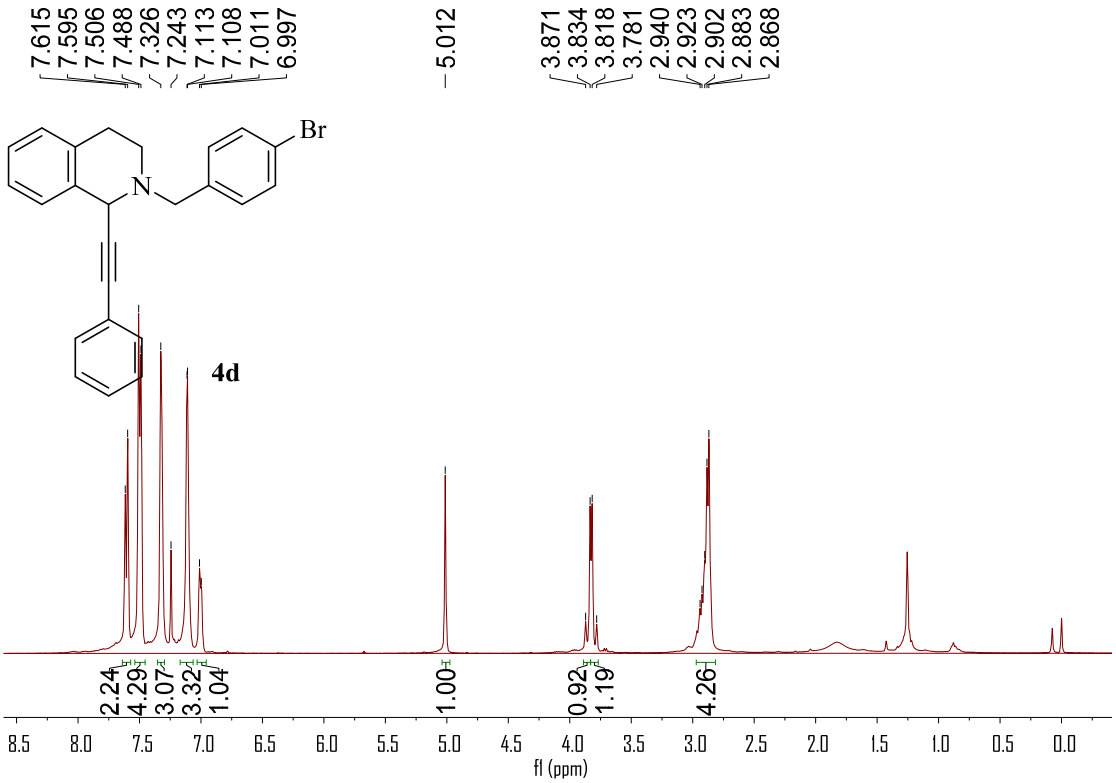

**4b** $^{13}$C NMR



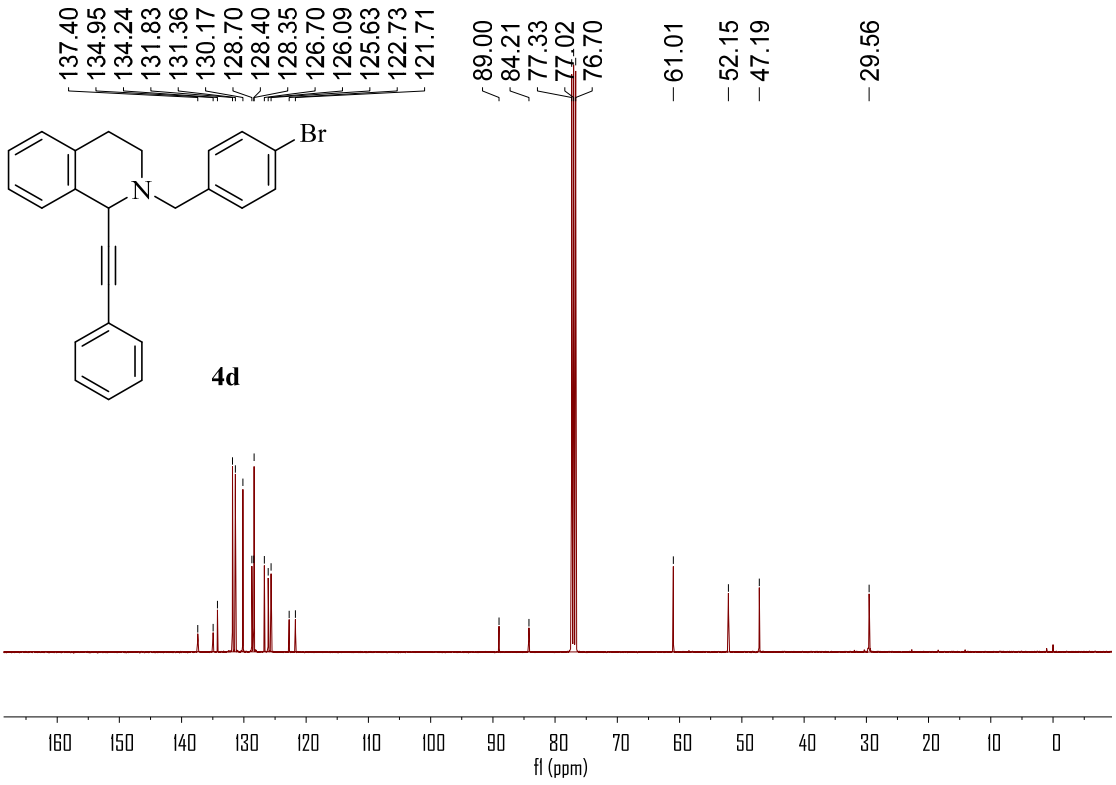

**4c** $^{1}$H NMR



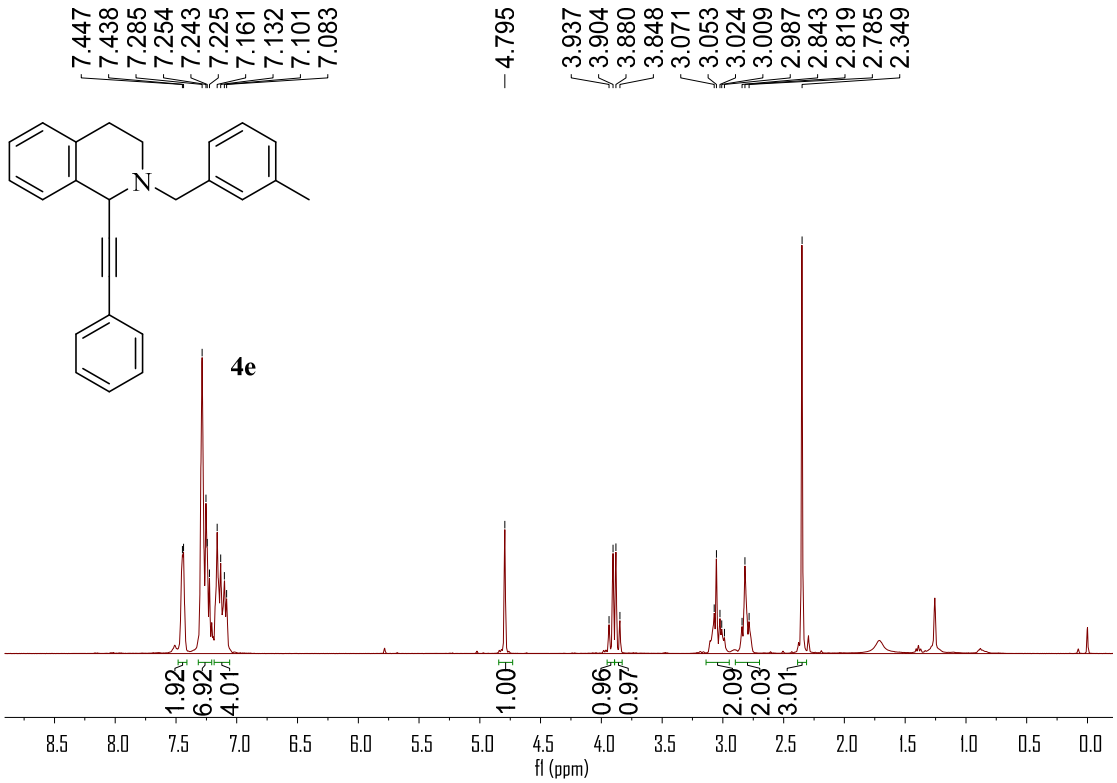

**4c** $^{13}$C NMR



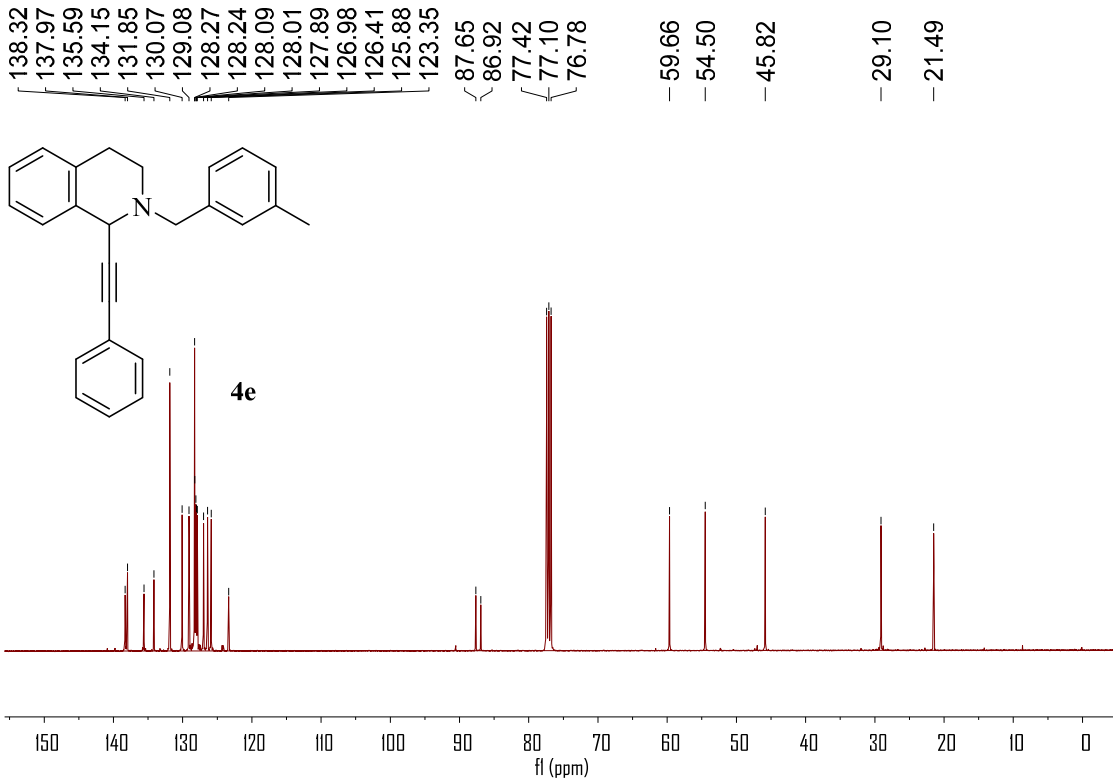

**4d** $^{1}$H NMR



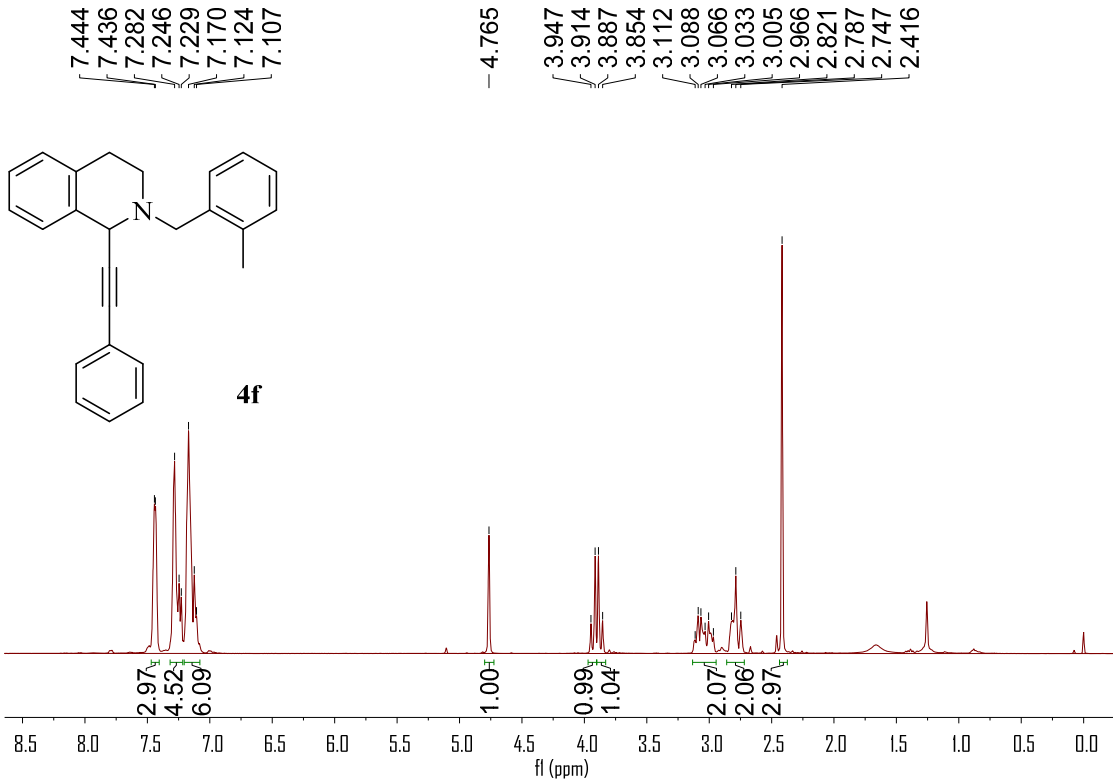

**4d** $^{13}$C NMR



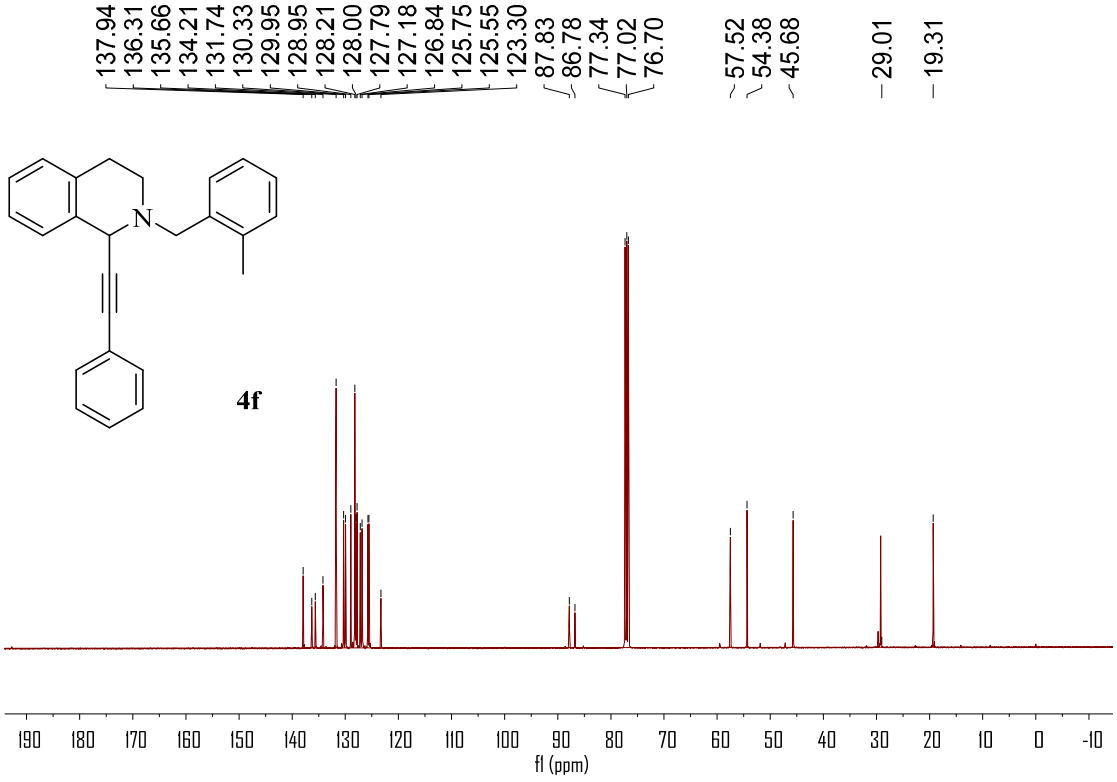

**4e** $^{1}$H NMR



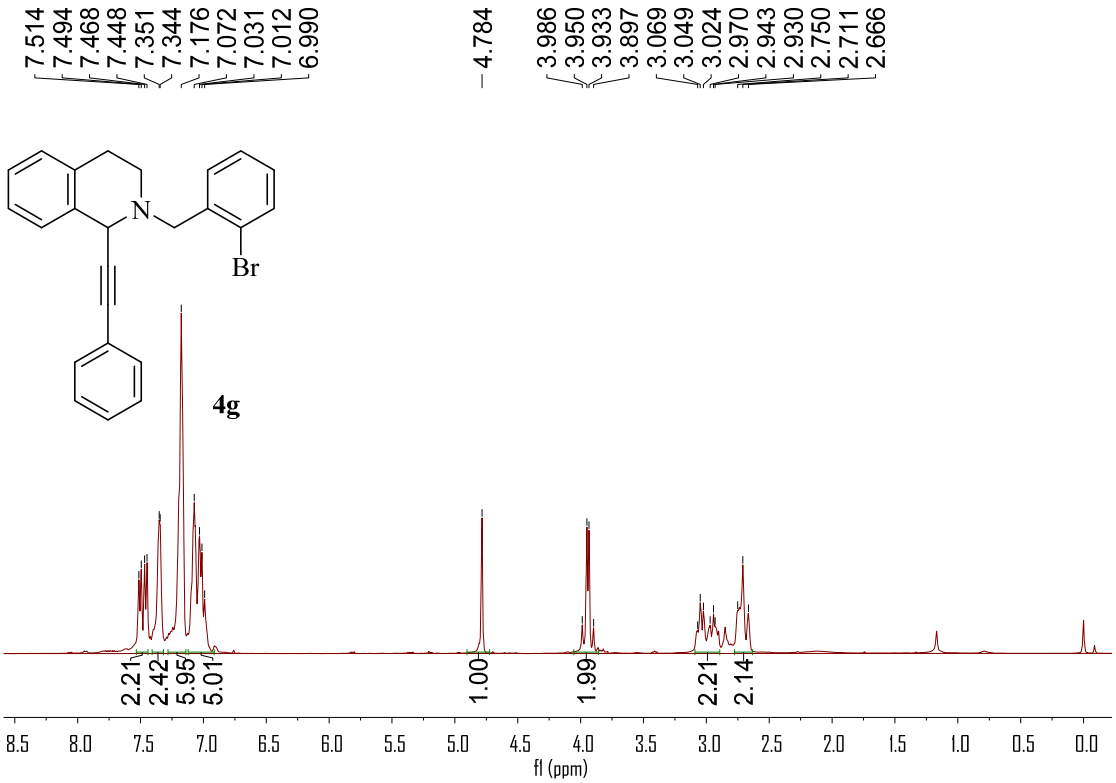

**4e** $^{13}$C NMR



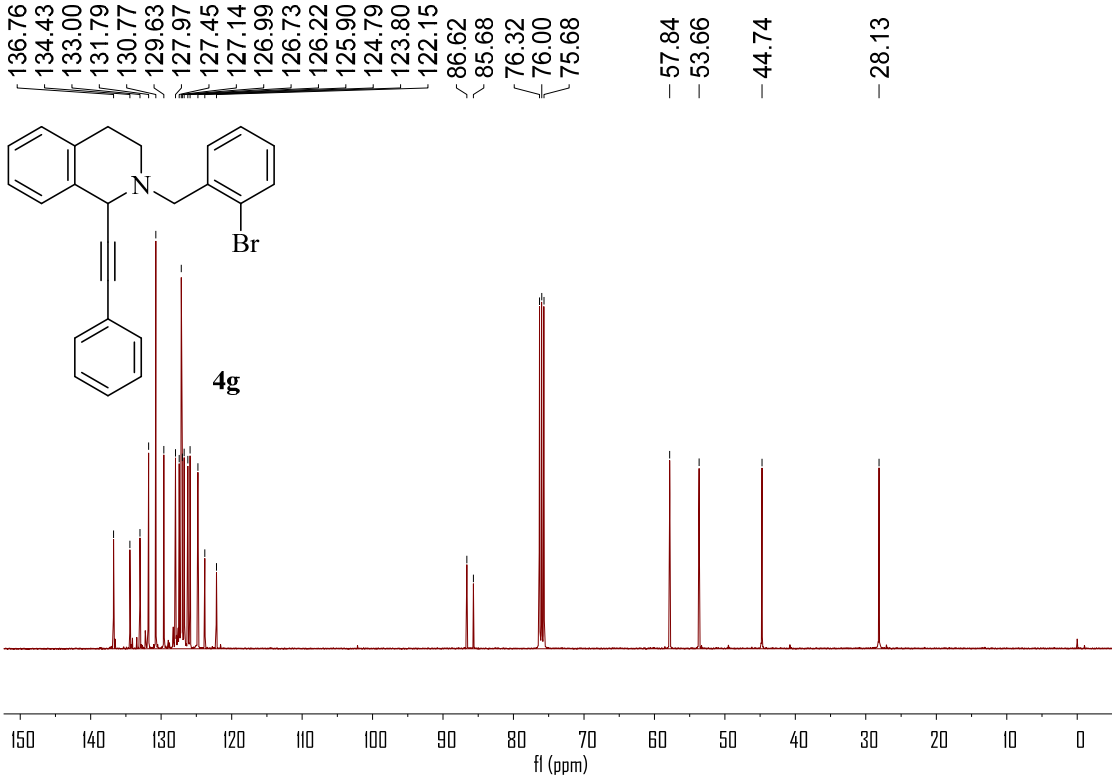

**4f** $^{1}$H NMR



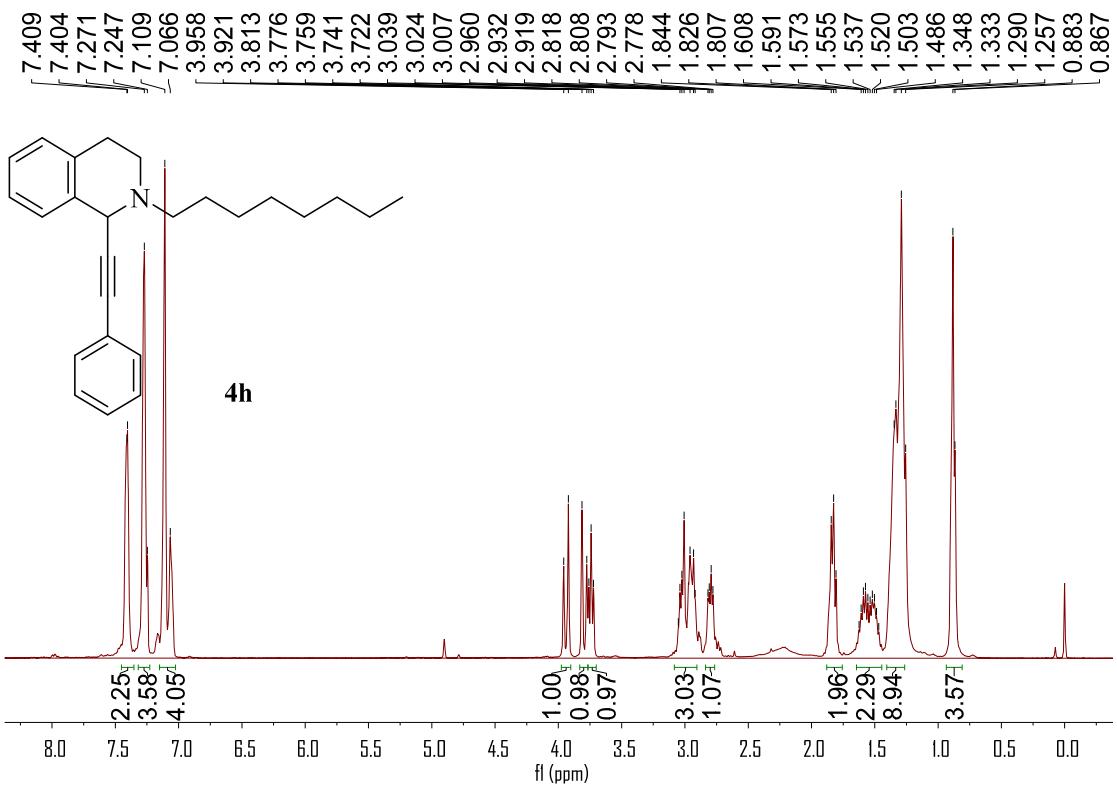

**4f** $^{13}$C NMR



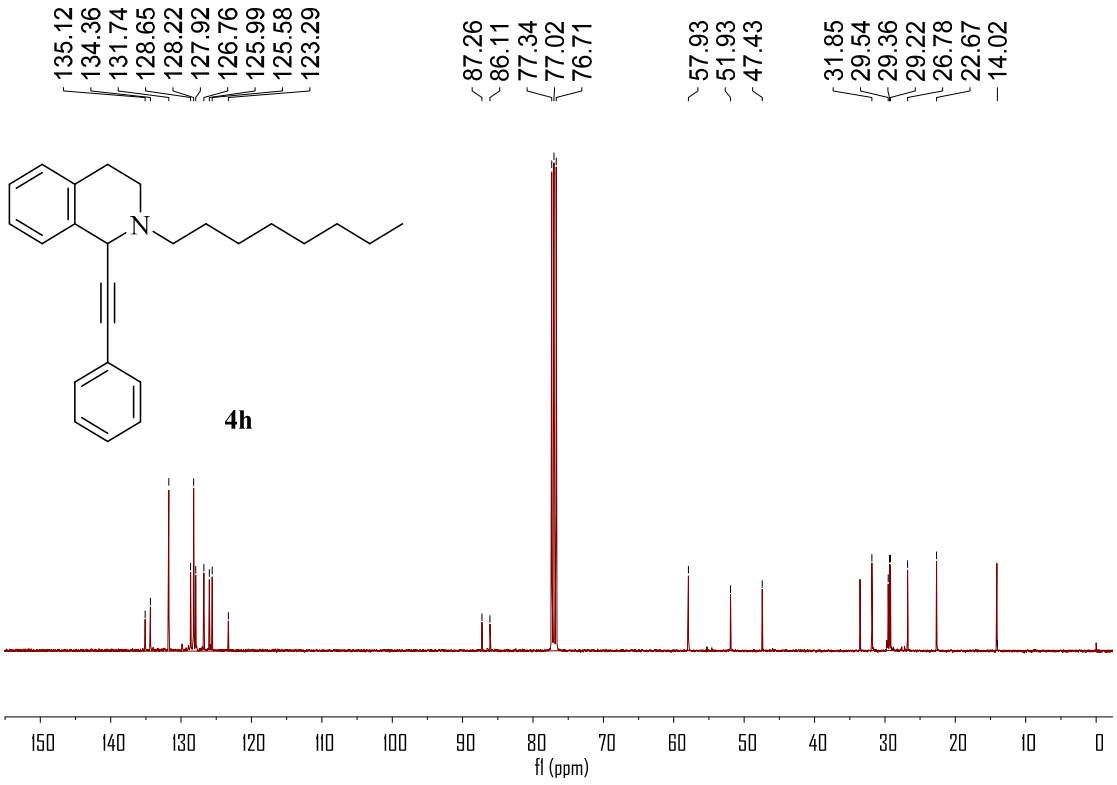

**4g** $^{1}$H NMR



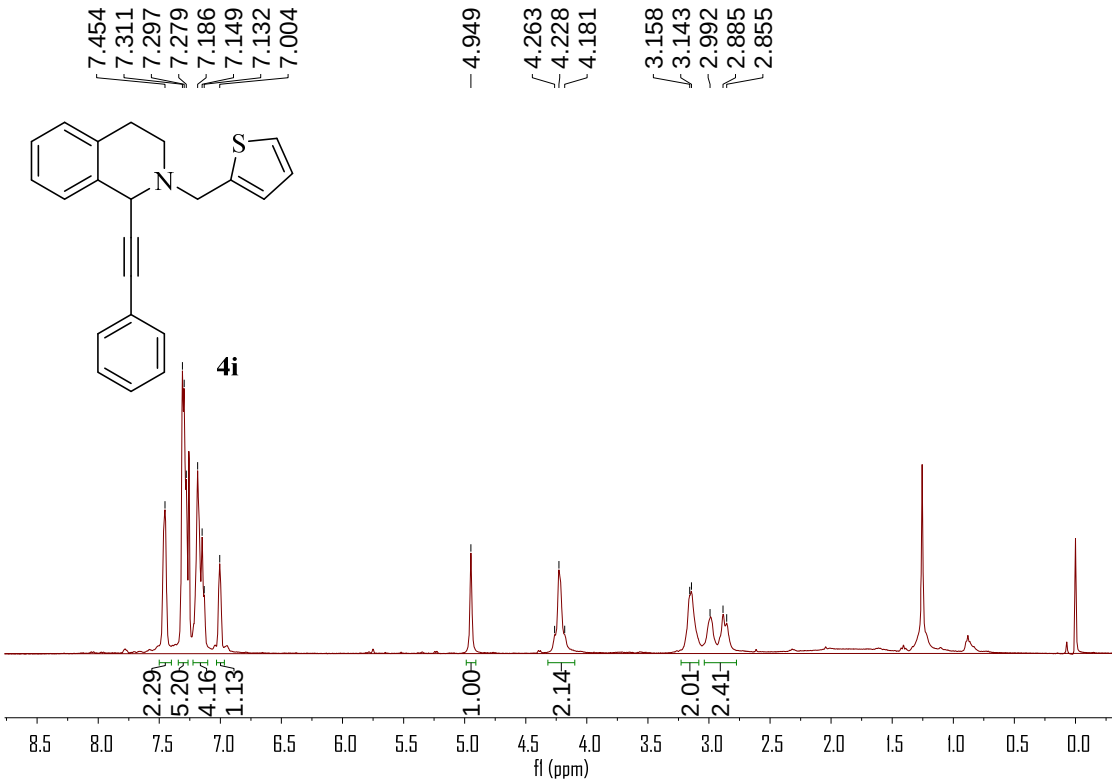

**4g** $^{13}$C NMR



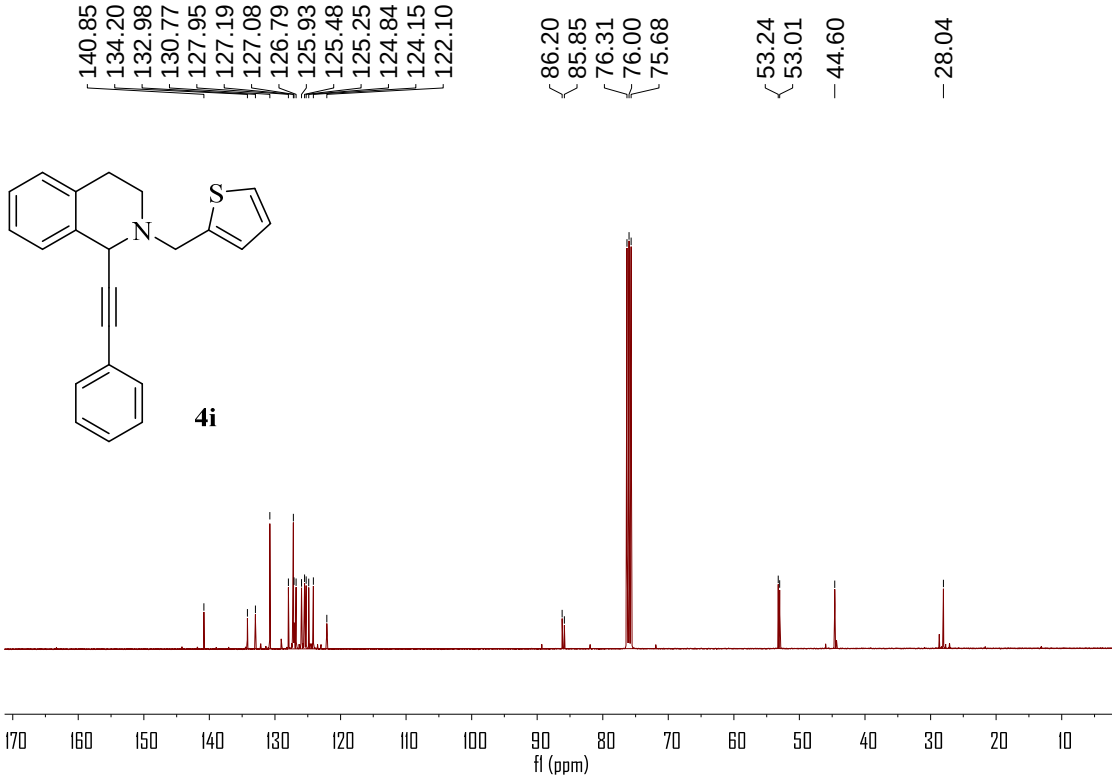

**4h** $^{1}$H NMR



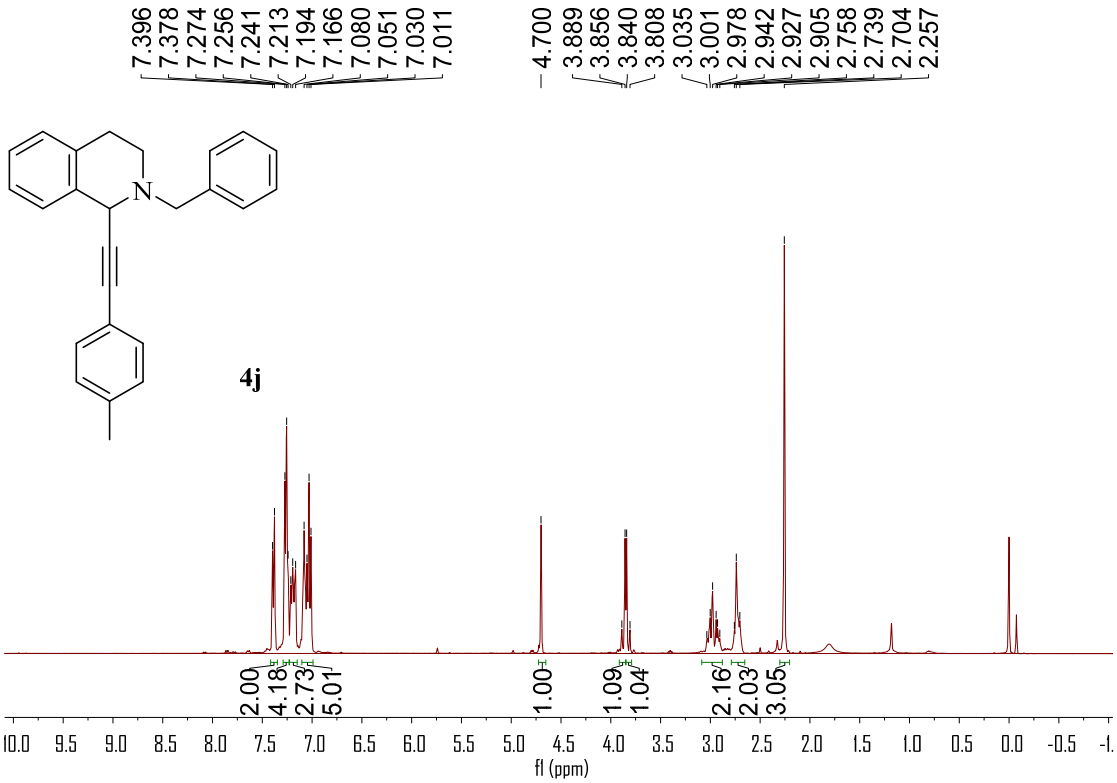

**4h** $^{13}$C NMR



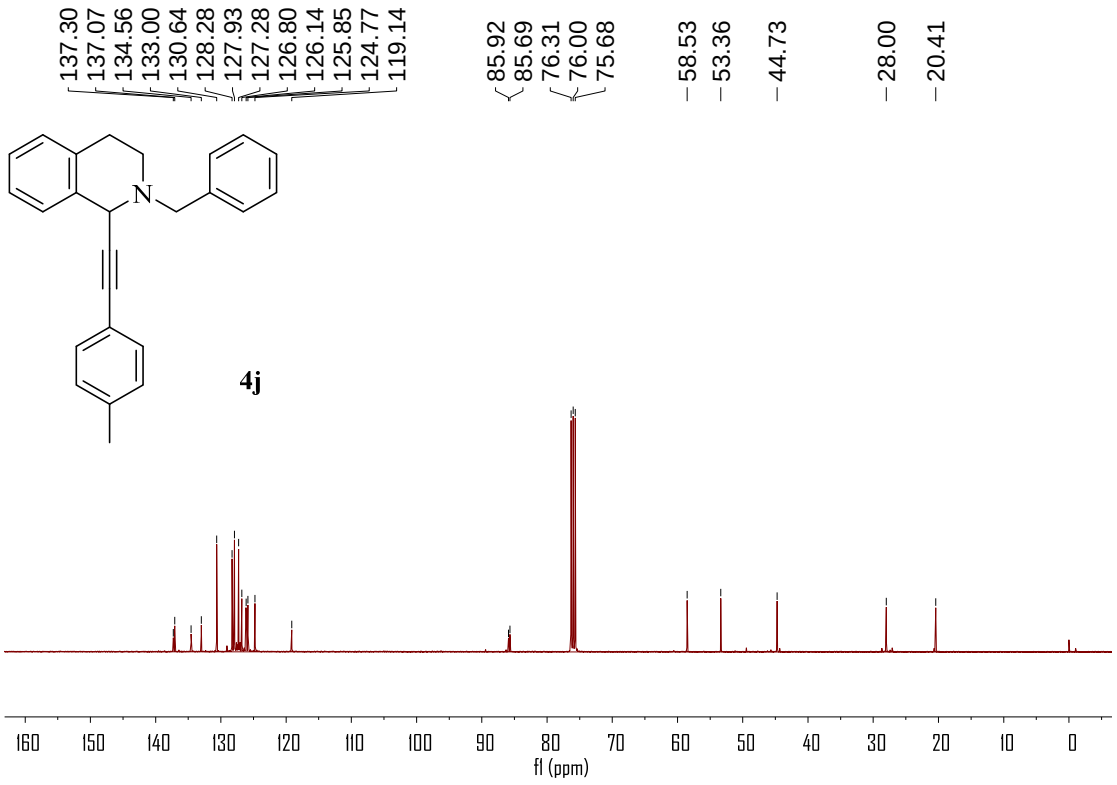

**4i** $^{1}$H NMR



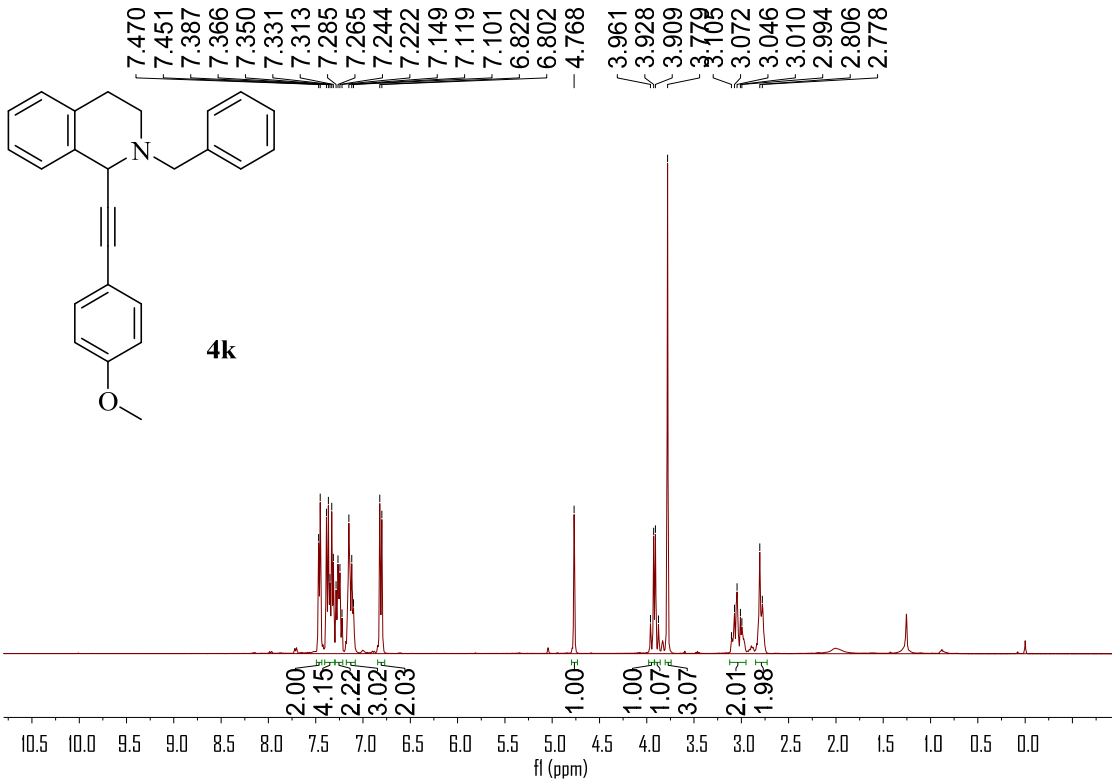

**4i** $^{13}$C NMR



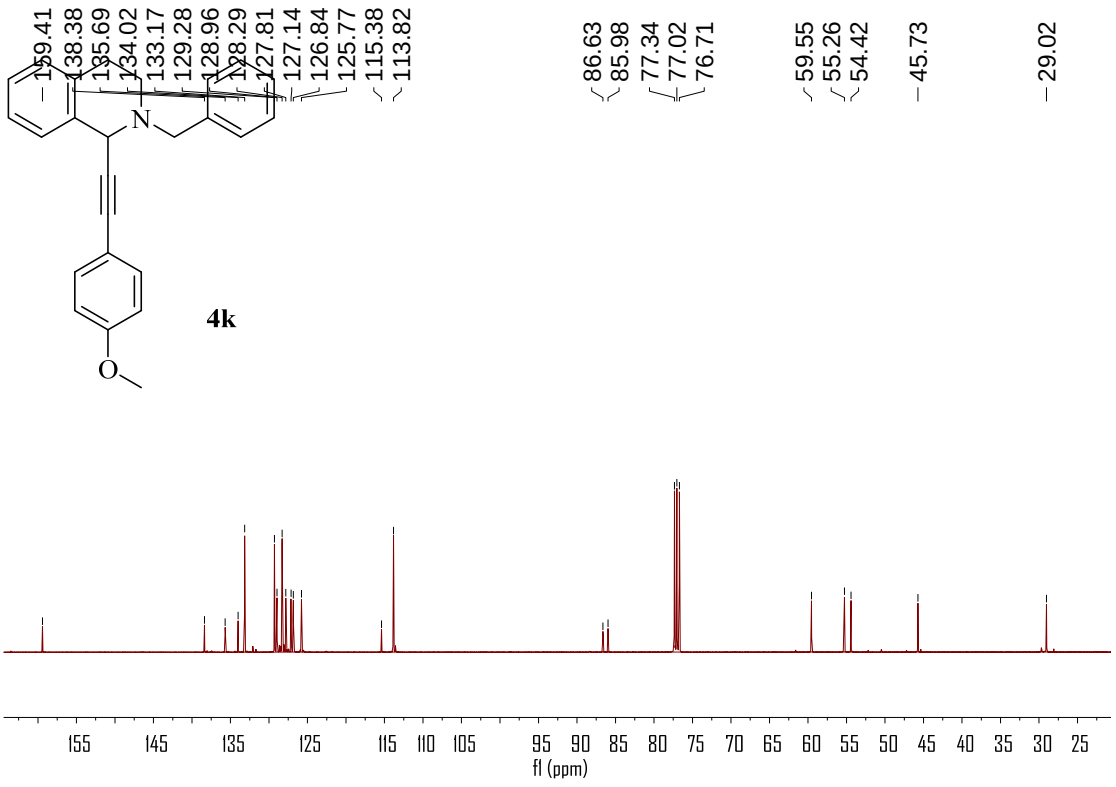

**4j** $^{1}$H NMR



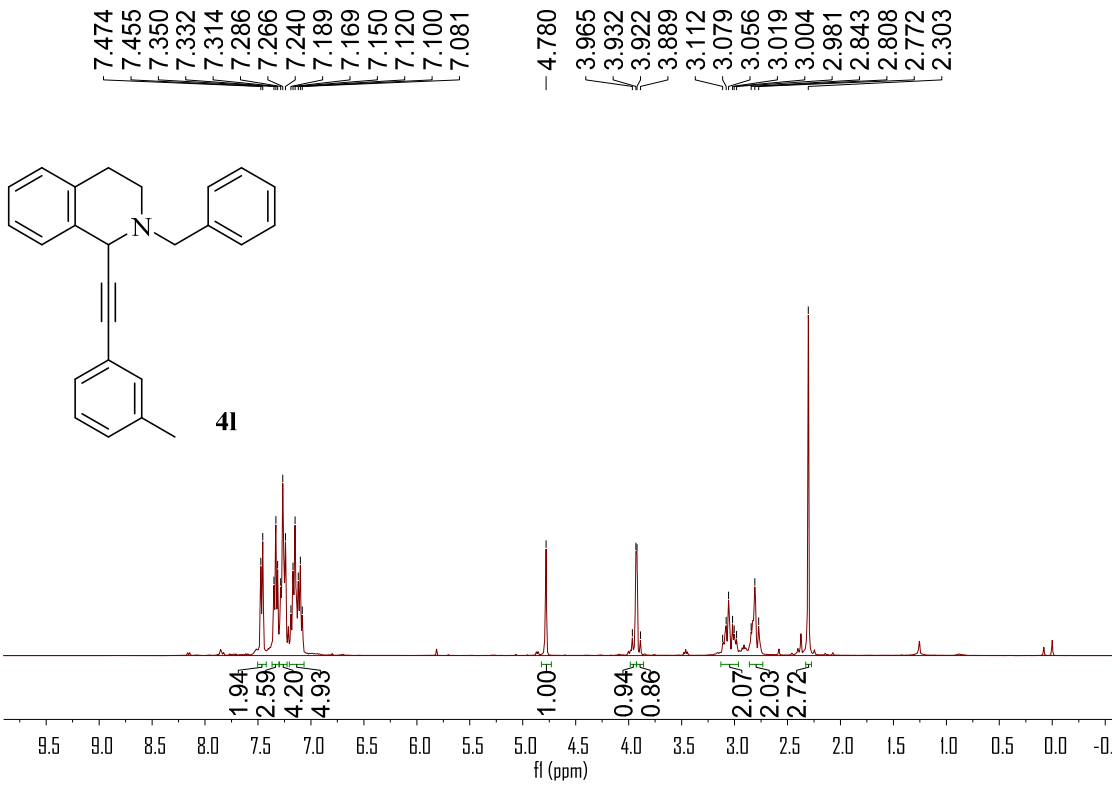

**4j** $^{13}$C NMR



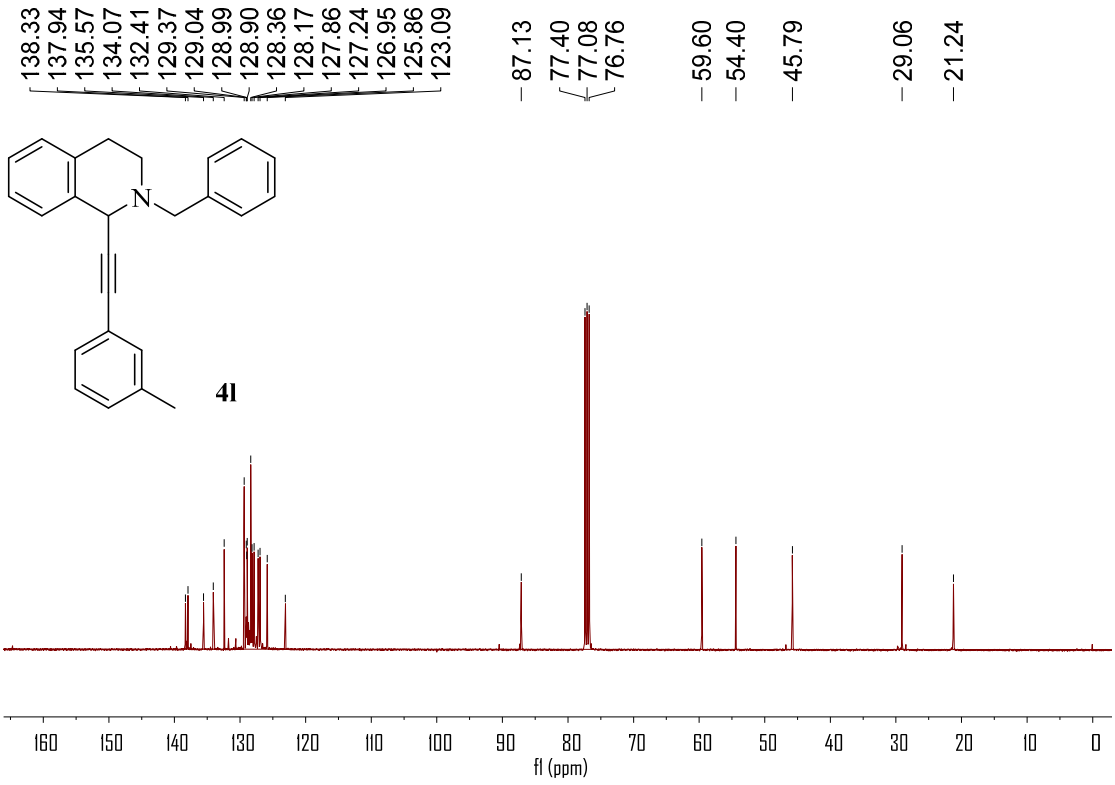

**4k** $^{1}$H NMR



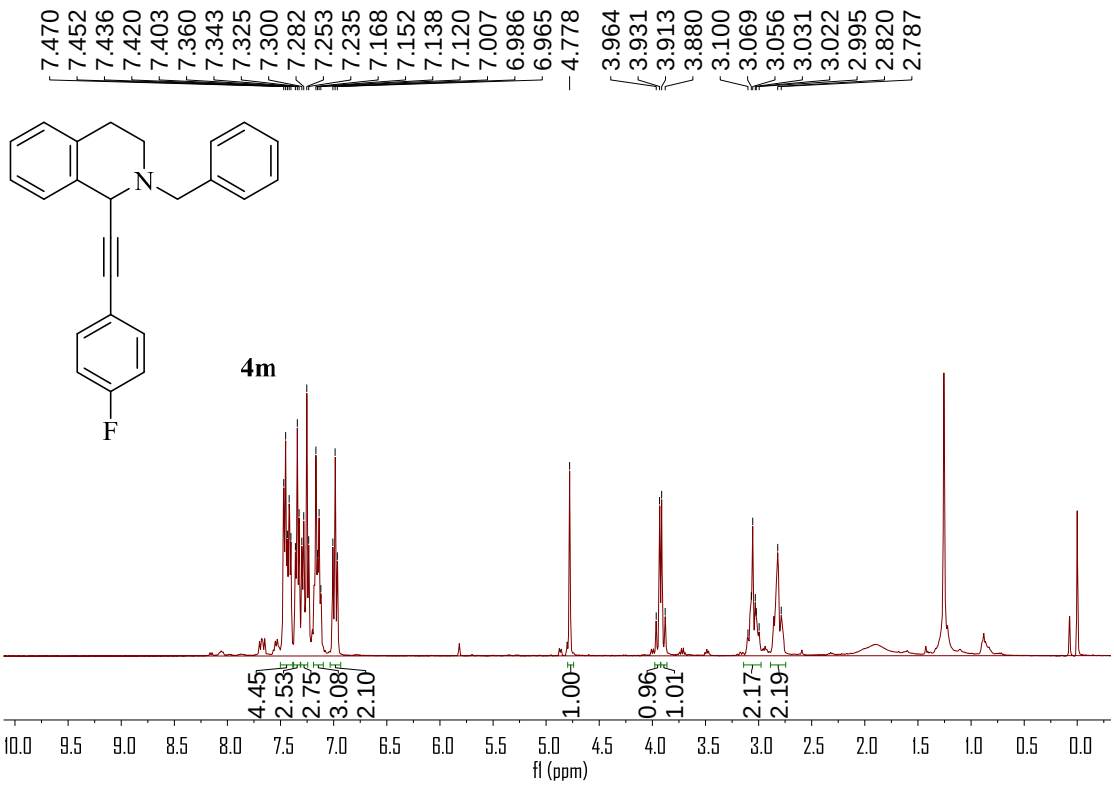

**4k** $^{13}$C NMR



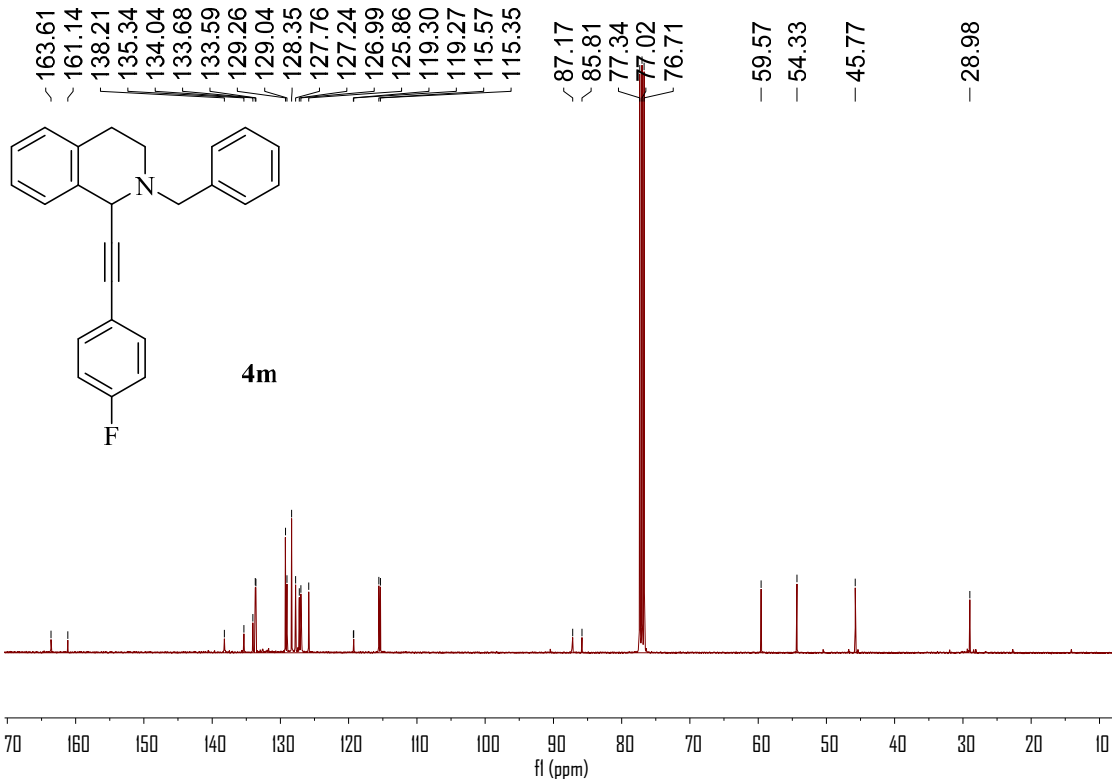

**4l** $^{1}$H NMR



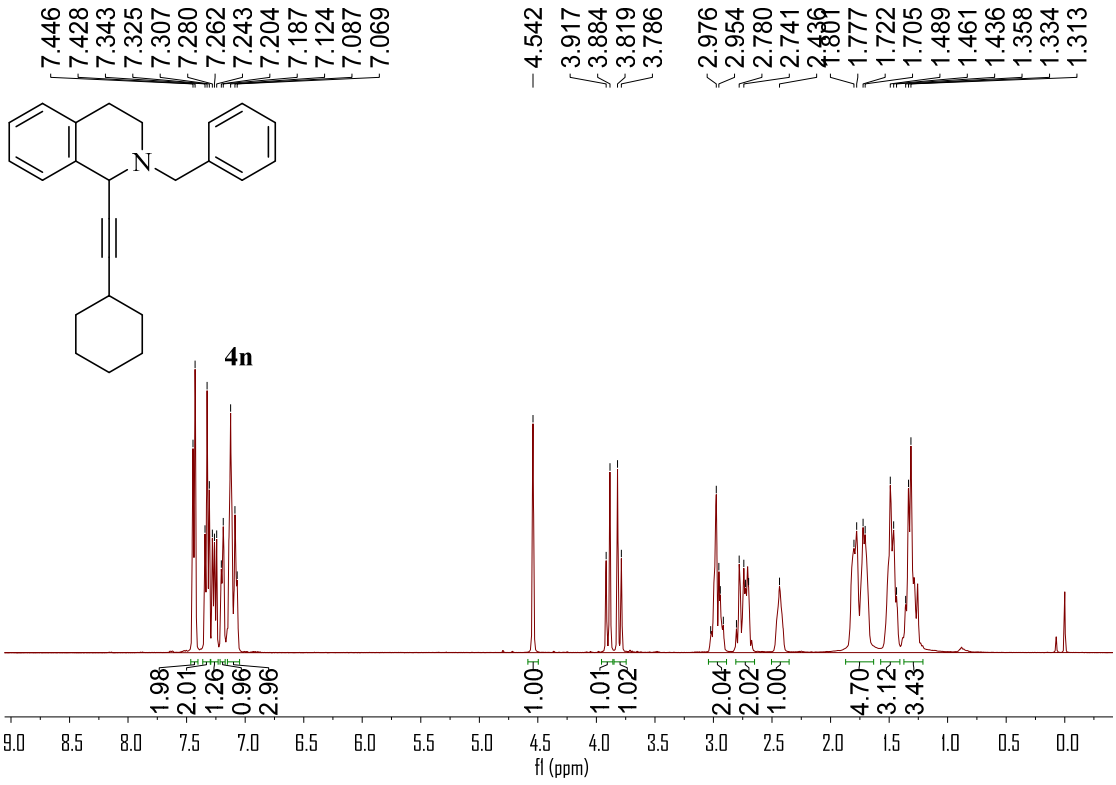

**4l** $^{13}$C NMR


7.470
7.452
7.436
7.420
7.403
7.360
7.343
7.325
7.300
7.282
7.253
7.235
7.168
7.152
7.138
7.120
7.007
6.986
6.965
4.778
3.964
3.931
3.913
3.880
3.100
3.069
3.056
3.031
3.022
2.995
2.820
2.787
N
F
4m
4.45
2.53
2.75
3.08
2.10
1.00
0.96
1.01
2.17
2.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

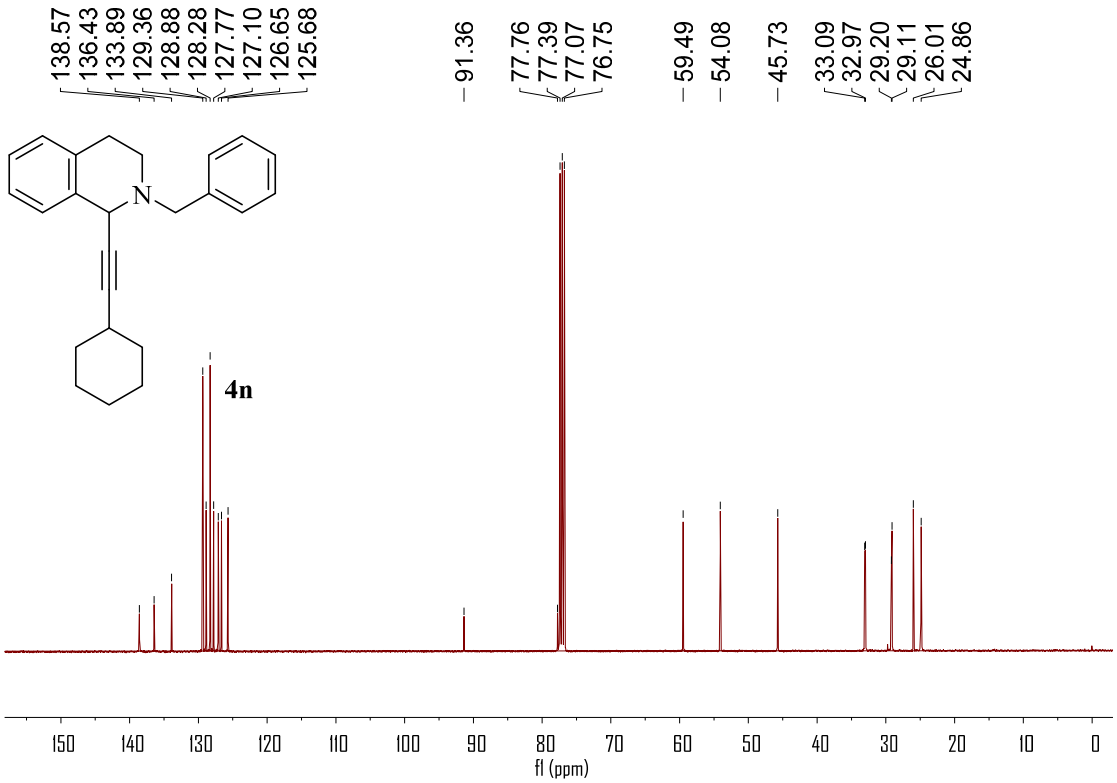
**4m** $^{1}$H NMR



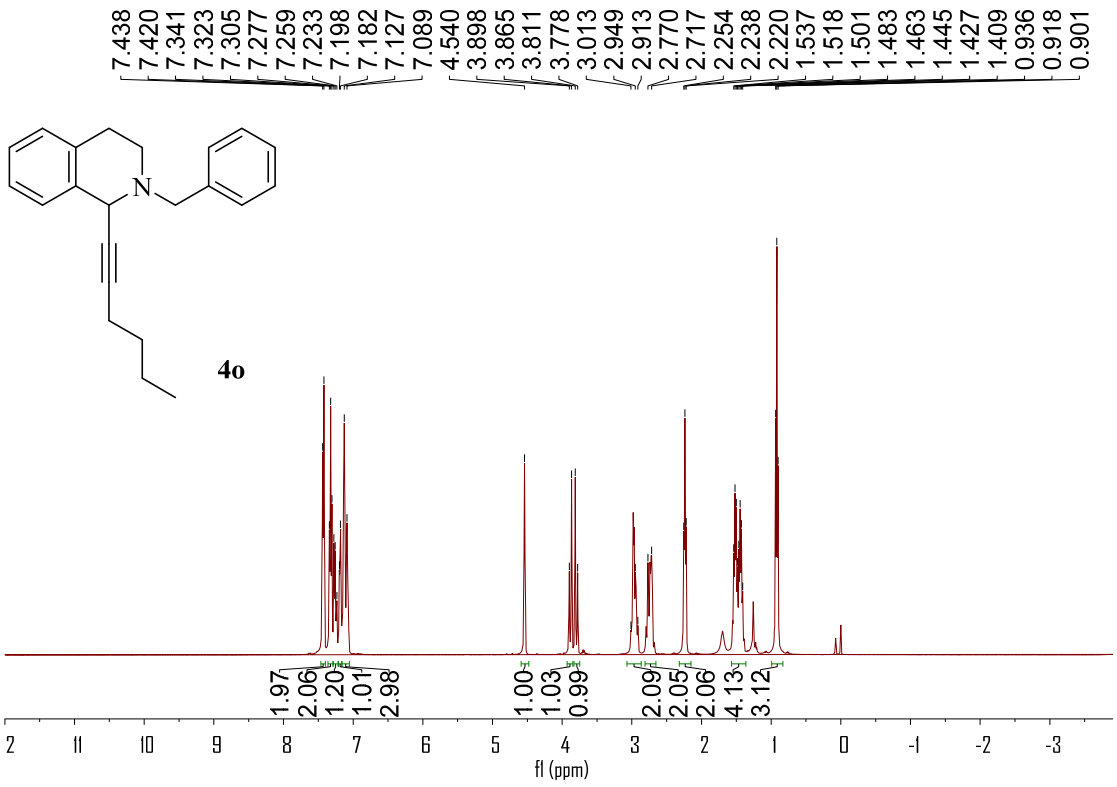

**4m** $^{13}$C NMR



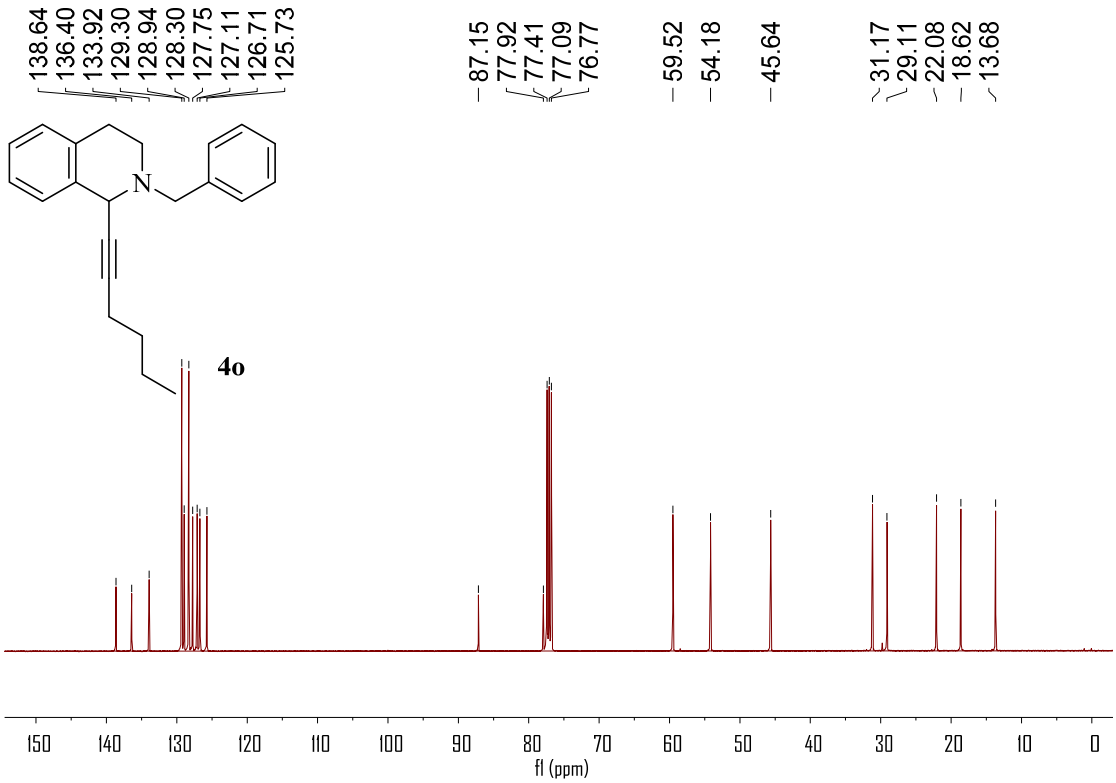

**4n** $^{1}$H NMR




**4n** $^{13}$C NMR




**4o** $^{1}$H NMR


138.64
136.40
133.92
129.30
128.94
128.30
127.75
127.11
126.71
125.73
87.15
77.92
77.41
77.09
76.77
59.52
54.18
45.64
31.17
29.11
22.08
18.62
13.68
N
4o
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**4o** $^{13}$C NMR