

# Supporting Information

for

## **Highly Efficient Synthesis of Tri- and Tetrasubstituted Conjugated Enynes from Brønsted Acid-Catalyzed Alkoxylation of 1-Cyclopropylprop-2-yn-1-ols with Alcohols**

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**General remarks:** All reactions were performed under an argon atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. TfOH was used as stock solutions in the alcohol nucleophile **2** (e.g. for 0.01 mol% of TfOH, a stock solution containing 0.88  $\mu\text{L}$  of TfOH in 1 L of **2** was prepared). Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (EtOAc: *n*-hexane as eluant).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on 300, 400 and 500 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. Infrared spectra were recorded on a FTIR spectrometer. Solid samples were examined as a thin film between NaCl salt plates. Low resolution mass spectra were determined on a mass spectrometer and reported in units of mass to charge (*m/z*). High resolution mass spectra (HRMS) were obtained on a LC/HRMS mass spectrometer.

## Experimental Procedure for Preparation of Substituted

**1-Cyclopropyl-2-propyn-1-ols (1a)-(1p) and (1w) & (1y)-(1δ):** To a solution of the alkyne (3.3 mmol) in THF (15 mL) was added LDA (2.0 M in THF, 1.8 mL) at  $-78^{\circ}\text{C}$ . The resulting solution was stirred for 1 h at prior to slow addition of cyclopropyl ketone (3 mmol) in THF (2 mL) at  $-78^{\circ}\text{C}$ . The reaction mixture was slowly warmed up to room temperature and stirred for a further 10 h. On completion, the reaction mixture was quenched by adding saturated  $\text{NH}_4\text{Cl}$  (10 mL) and extracted with  $\text{Et}_2\text{O}$  (2 x 25 mL). The combined organic layers were washed with brine, dried over  $\text{Mg}_2\text{SO}_4$ , and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane: EtOAc = 9: 1) gave the title compound.

**Experimental Procedure for the Preparation of 1-Cyclopropyl-2-propyn-1-ols (1q)-(1v) and (1x):**<sup>S1</sup> For **(1q)-(1t)**: To a solution of cyclopropylmagnesium bromide (0.5 M THF solution; 3.3 mL, 1.6 mmol) in THF (5 mL) at  $0^{\circ}\text{C}$  was added dropwise a solution of ketone (1.3 mmol) in THF (3 mL). For **(1u)-(1v)**: To a solution of ethynylmagnesium bromide (0.5 M THF solution; 12.4 mL, 6.2 mmol) in THF (5 mL) at  $0^{\circ}\text{C}$  was added dropwise a solution of cyclopropyl ketone (3 mmol) in diethyl ether (10 mL). For **(1x)**: To a solution of vinylmagnesium bromide (1.0 M THF solution; 0.6 mL, 0.54 mmol) in THF (3 mL) at  $0^{\circ}\text{C}$  was added dropwise a solution of cyclopropyl ketone (0.36 mmol) in THF (2 mL). The resulting mixture was stirred at room temperature for 15 h. The mixture was treated with saturated  $\text{NH}_4\text{Cl}$  aq. (10 mL). The organic layer was extracted with diethyl ether (10 mL x 3). The combined organic layers were dried over anhydrous  $\text{MgSO}_4$ , and concentrated under reduced pressure.

Purification by flash column chromatography on silica gel (eluent: *n*-hexane: EtOAc =

9: 1) gave the title compound.

**Cyclopropyl-1,3-diphenylprop-2-yn-1-ol (1a):**<sup>S2</sup> Yield 65%; white solid; m.p. 69-71 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.76-7.74 (m, 2H), 7.46-7.25 (m, 8H), 2.54 (s, 1H), 1.49-1.44 (m, 1H), 0.90-0.85 (m, 1H), 0.75-0.60 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  144.9, 131.9, 128.6, 128.4, 128.3, 127.8, 125.59, 122.5, 89.1, 86.1, 75.0, 23.9, 3.4, 2.6.

**1-Cyclopropyl-1-(4-fluorophenyl)-3-phenylprop-2-yn-1-ol (1b):**<sup>S2</sup> Yield 80%; pale yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.72-7.68 (m, 2H), 7.44-7.25 (m, 5H), 7.07-7.03 (m, 2H), 1.61-1.39 (m, 1H), 0.87-0.56 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  163.3, 161.3, 140.6, 131.8, 128.7, 128.3, 127.2, 122.1, 115.0 (d, 1C,  $J_{C-F}$  = 83.2 Hz), 88.6, 86.2, 74.5, 23.9, 3.3, 2.4.

**1-(4-Chlorophenyl)-1-cyclopropyl-3-phenylprop-2-yn-1-ol (1c):**<sup>S2</sup> Yield 78%; pale yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.70-7.28 (m, 9H), 2.5 (s, 1H), 1.45-1.43 (m, 1H), 0.89-0.63 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  143.3, 133.5, 131.8, 128.7, 128.37, 128.34, 126.9, 122.1, 88.3, 86.3, 74.5, 23.9, 3.4, 2.4.

**1-Cyclopropyl-3-(4-methoxy-2-methylphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (1d):** Yield: 68%; pale yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.67 (d, 2H,  $J$  = 8.7 Hz), 7.33 (d, 1H,  $J$  = 8.4 Hz), 6.91 (d, 2H,  $J$  = 8.7 Hz), 6.73 (d, 1H,  $J$  = 1.9 Hz), 6.66 (dd, 1H,  $J$  = 8.4, 2.3 Hz), 3.82 (s, 3H), 3.79 (s, 3H), 2.46 (d, 1H,  $J$  = 3.5 Hz), 1.42-1.48 (m, 1H), 0.84-0.88 (m, 1H), 0.65-0.68 (m, 1H), 0.57-0.62 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  159.6, 159.0, 142.0, 137.5, 133.5, 126.8, 115.1, 114.6, 113.4, 111.2, 91.7, 84.8, 77.4, 77.1, 76.9, 74.9, 55.3, 55.2, 23.8, 21.1, 2.6, 2.2; IR (neat, cm<sup>-1</sup>): 3419, 3018, 2399, 1635, 1508, 1419, 1215, 1037, 927, 756, 669; HRMS

(ESI): calcd for  $C_{21}H_{22}O_3Na$  345.1467, found 345.1469.

**1-Cyclopropyl-1-(4-methoxyphenyl)-3-(2,4,5-trimethylphenyl)prop-2-yn-1-ol (1e):**

Yield 70%; pale yellow oil;  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  7.68 (d, 2H,  $J$  = 8.6 Hz), 7.18 (s, 1H), 6.97 (s, 1H), 6.91 (d, 2H,  $J$  = 8.7 Hz), 3.82 (s, 3H), 2.5 (s, 1H), 2.36 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H), 1.48-1.43 (m, 1H), 0.90-0.86 (m, 1H), 0.70-0.66 (m, 1H), 0.61-0.54 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz):  $\delta$  159.0, 137.4, 137.3, 133.7, 133.1, 130.8, 126.7, 119.3, 113.4, 91.8, 85.2, 75.0, 55.3, 23.7, 20.2, 19.6, 19.0, 3.2, 2.5; IR (neat,  $cm^{-1}$ ): 3419, 3018, 2399, 1635, 1508, 1215, 927, 756, 669; HRMS (ESI): calcd for  $C_{22}H_{25}O_2$  321.1855, found 321.1859.

**1-Cyclopropyl-3-(4-(trifluoromethyl)phenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (1f):**

Yield 72%; pale yellow oil;  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  7.65 (d, 2H,  $J$  = 8.6 Hz), 7.55 (q, 4H,  $J$  = 8.2 Hz), 6.92 (d, 2H,  $J$  = 8.6 Hz), 3.82 (s, 3H), 2.5 (s, 1H), 1.50-1.45 (m, 1H), 0.82-0.81 (m, 1H), 0.68-0.61 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz):  $\delta$  159.2, 136.5, 132.0, 130.1, 126.7, 126.2, 125.27, 125.24, 113.6, 91.8, 84.4, 74.4, 55.3, 23.5, 3.1, 2.4; IR (neat,  $cm^{-1}$ ): 3421, 3018, 2399, 1635, 1323, 1215, 756, 669; HRMS (ESI): calcd for  $C_{20}H_{18}F_3O_2$  347.1259, found 347.1258.

**1-Cyclopropyl-1-(4-fluorophenyl)-3-(4-methoxy-2-methylphenyl)prop-2-yn-1-ol (1g):**

Yield 75%; pale yellow oil;  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  7.73-7.70 (m, 2H), 7.33 (d, 1H,  $J$  = 8.5 Hz), 7.07-7.04 (m, 2H), 6.74-6.66 (m, 2H), 3.79 (s, 3H), 2.50 (s, 1H), 2.40 (s, 3H), 1.45-1.40 (m, 1H), 0.90-0.84 (m, 1H), 0.73-0.68 (m, 1H), 0.64-0.56 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz):  $\delta$  163.2, 161.3, 159.8, 142.0, 141.0, 133.5, 127.3 (d, 1C,  $J_{C-F}$  = 32.3 Hz), 114.9 (t, 1C,  $J_{C-F}$  = 81.1 Hz), 114.2, 111.2, 91.0, 85.2,

74.8, 55.2, 23.9, 21.0, 3.4, 2.5; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1604, 1421, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{19}\text{FO}_2\text{Na}$  333.1267, found 333.1257.

**1-Cyclopropyl-1-(4-fluorophenyl)-3-(pyridin-2-yl)prop-2-yn-1-ol (1h):** Yield 72%; white solid; m.p. 132-234 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.56 (d, 1H,  $J = 4.2$  Hz), 7.75 (q, 2H,  $J = 5.5$  Hz), 7.66 (t, 1H,  $J = 7.1$  Hz), 7.43 (d, 1H,  $J = 7.7$  Hz), 7.25 (t, 1H,  $J = 6.1$  Hz), 7.06 (t, 2H,  $J = 8.6$  Hz), 3.41 (s, 1H), 1.45-1.50 (m, 1H), 0.87-0.90 (m, 1H), 0.76-0.79 (m, 1H), 0.59-0.66 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  163.2, 161.2, 149.7, 142.4, 140.5, 136.3, 127.4 (t, 1C,  $J_{\text{C-F}} = 41.6$  Hz), 123.1, 114.8 (d, 1C,  $J_{\text{C-F}} = 85$  Hz), 90.08, 84.7, 73.6, 23.8, 3.1, 2.5; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1651, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{17}\text{H}_{15}\text{FNO}$  268.1138, found 267.1136.

**1-Cyclopropyl-1-(4-methoxyphenyl)-3-(pyridin-2-yl)prop-2-yn-1-ol (1i):** Yield 69%; light brown solid; m.p. 84-86 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.53-8.52 (m, 1H), 7.68-7.66 (m, 2H), 7.63-7.59 (m, 1H), 7.39 (d, 1H,  $J = 7.8$  Hz), 7.25-7.19 (m, 1H), 6.90-6.87 (m, 2H), 6.90-6.87 (m, 2H), 3.79 (s, 3H), 3.41 (s, 1H), 1.50-1.44 (m, 1H), 0.86-0.82 (m, 1H), 0.74-0.71 (m, 1H), 0.61-0.55 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.0, 149.8, 142.7, 136.8, 136.2, 127.2, 126.9, 123.0, 113.4, 90.4, 84.6, 73.7, 55.2, 23.6, 3.0, 2.4; IR (neat,  $\text{cm}^{-1}$ ): 3421, 3018, 2399, 1635, 1419, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}_2$  280.1338, found 280.1340.

**4-(3-Cyclopropyl-3-(4-fluorophenyl)-3-hydroxyprop-1-ynyl)benzonitrile (1j):** Yield 70%; white solid; m.p. 78-80 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.67 (q, 2H,  $J = 5.3$  Hz), 7.6-7.5 (m, 4H), 7.06 (t, 1H,  $J = 8.6$  Hz), 2.56 (s, 1H), 1.47-1.42 (m, 1H),



0.82-0.78 (m, 1H), 0.71-0.60 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  163.3, 161.4, 139.9, 132.3, 132.0, 127.20 (t, 1C,  $J_{\text{C-F}} = 31.5$  Hz), 118.3, 115.1 (d, 1C,  $J_{\text{C-F}} = 84.9$  Hz), 112.0, 93.4, 84.3, 74.2, 23.7, 3.3, 2.4; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1506, 1423, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{19}\text{H}_{15}\text{FNO}$  292.1138, found 292.1142.

**4-(3-Hydroxy-3-phenyl-3-(2-phenylcyclopropyl)prop-1-ynyl)benzonitrile (1k):**

Yield 68%; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.78 (d, 2H,  $J = 7.4$ ), 7.65-7.58 (m, 4H), 7.47-7.14 (m, 8H), 2.93 (s, 1H), 2.48-2.44 (m, 1H), 1.85-1.81 (m, 1H), 1.45-1.41 (m, 1H), 1.14-1.11 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  143.9, 141.7, 132.4, 132.1, 128.5, 128.4, 128.1, 127.2, 126.2, 125.9, 125.4, 118.3, 112.0, 94.1, 84.5, 74.1, 34.5, 20.7, 13.4; IR (neat,  $\text{cm}^{-1}$ ): 3427, 3018, 2399, 1643, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{25}\text{H}_{19}\text{NONa}$  372.1364, found 372.1350.

**1-Cyclopropyl-3-(2-methoxynaphthalen-6-yl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (1l):**

**1 (1l):** Yield 67%; white solid; m.p. 95-97 °C:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.88 (s, 1H), 7.71-7.65 (m, 4H), 7.44 (dd, 1H,  $J = 8.4, 1.4$  Hz), 7.16-7.09 (m, 2H), 6.93 (d, 2H,  $J = 8.8$  Hz), 3.92 (s, 3H), 3.83 (s, 3H), 2.56 (s, 1H), 1.51-1.46 (m, 1H), 0.92-0.86 (m, 1H), 0.75-0.71 (m, 1H), 0.66-0.58 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.1, 158.3, 137.2, 134.2, 131.5, 129.3, 129.0, 128.3, 126.8, 119.5, 117.3, 113.5, 105.8, 88.8, 86.4, 74.6, 55.36, 55.33, 23.8, 3.2, 2.5; IR (neat,  $\text{cm}^{-1}$ ): 3427, 3304, 3018, 2358, 1645, 1489, 1215, 1093, 756, 669; HRMS (ESI): calcd for  $\text{C}_{24}\text{H}_{22}\text{O}_3\text{Na}$  381.1467, found 381.1451.

**3-(2-Methoxynaphthalen-6-yl)-1-phenyl-1-(2-phenylcyclopropyl)prop-2-yn-1-ol**

**(1m):** Yield: 66%; pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.97 (s, 1H), 7.86 (d, 2H,  $J = 7.4$  Hz), 7.74-7.71 (m, 2H), 7.54-7.44 (m, 4H), 7.39-7.12 (m, 7H), 3.96 (s, 3H), 2.45-2.42 (m, 1H), 1.88-1.83 (m, 1H), 1.66-1.62 (m, 1H), 1.17-1.12 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  158.4, 144.7, 141.8, 134.3, 131.7, 129.3, 129.0, 128.5, 128.4, 128.3, 127.9, 126.9, 126.5, 125.8, 125.5, 119.5, 117.1, 105.8, 89.0, 87.0, 74.2, 55.3, 34.3, 21.5, 12.2; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1635, 1215, 756, 669; HRMS (ESI): calcd for  $\text{C}_{29}\text{H}_{25}\text{O}_2$  405.1855, found 405.1864.

**1-Cyclopropyl-3-(naphthalen-1-yl)-1-phenylprop-2-yn-1-ol (1n):** Yield 85%; light brown oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.28 (d, 1H,  $J = 8.1$  Hz), 7.86-7.33 (m, 11H), 2.66 (s, 1H), 1.58-1.53 (m, 1H), 1.02-0.82 (m, 2H), 0.72-0.67 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  144.8, 133.3, 133.1, 130.9, 129.0, 128.35, 128.32, 127.8, 126.9, 126.4, 125.9, 125.5, 125.1, 120.0, 93.9, 84.2, 75.3, 23.9, 3.4, 2.6; IR (neat,  $\text{cm}^{-1}$ ): 3415, 3018, 1215, 756, 699, 667; HRMS (ESI): calcd for  $\text{C}_{22}\text{H}_{19}\text{O}$  299.1436, found 299.1422.

**1-(4-Chlorophenyl)-1-cyclopropylnon-2-yn-1-ol (1o):** Yield 65%; pale yellow oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.59 (d, 2H,  $J = 8.5$  Hz), 7.31 (d, 2H,  $J = 8.5$  Hz), 2.34 (s, 1H), 2.23 (t, 2H,  $J = 7.05$  Hz), 1.48-1.56 (m, 2H), 1.26-1.41 (m, 7H), 0.89 (t, 3H,  $J = 6.9$  Hz), 0.74-0.77 (m, 1H), 0.50-0.60 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  128.2, 126.9, 87.4, 79.4, 74.29, 31.27, 28.58, 28.53, 23.8, 22.6, 18.6, 14.0, 3.3, 2.3; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2931, 2399, 1645, 1215, 756, 669; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{24}\text{ClO}$  291.1516, found 291.1527.

**1-cyclopropyl-1-phenylhept-2-yn-1-ol (1p):** Yield 60%; colorless oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.66 (d, 2H,  $J = 7.8$  Hz), 7.35-7.22 (m, 3H), 2.25 (s, 1H), 2.23 (t, 2H,  $J = 7.0$  Hz), 1.53-1.47 (m, 2H), 1.44-1.37 (m, 2H), 1.34-1.29 (m, 1H), 0.91 (t, 3H,  $J = 7.2$  Hz), 0.78-0.74 (m, 1H), 0.60-0.46 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  145.5, 128.0, 127.4, 125.4, 86.8, 79.9, 74.7, 30.8, 23.7, 22.0, 18.3, 13.6, 3.2, 2.3; IR (neat,  $\text{cm}^{-1}$ ): 3410, 3019, 1215, 1030, 758, 699, 669; HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{20}\text{ONa}$  251.1412, found 251.1408.

**1-Cyclopropyl-1-(1-methylcyclohexyl)-3-phenylprop-2-yn-1-ol (1q):** Yield 78%; pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.40-7.25 (m, 5H), 1.91 (s, 1H), 1.77-1.60 (m, 7H), 1.58-1.39 (m, 2H), 1.33-1.25 (m, 1H), 1.16 (s, 3H), 1.14-1.09 (m, 1H), 0.68-0.56 (m, 3H), 0.47-0.41 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  131.6, 128.2, 128.1, 122.9, 88.8, 85.8, 80.3, 42.4, 32.4, 31.5, 26.3, 22.1, 22.0, 17.9, 15.7, 4.6, 0.5; IR (neat,  $\text{cm}^{-1}$ ): 3415, 3018, 1215, 759, 699, 667; HRMS (ESI): calcd for  $\text{C}_{19}\text{H}_{25}\text{O}$  269.1905, found 269.1918.

**3-Cyclopropyl-4,4-dimethyl-1-phenylpent-1-yn-3-ol (1r):** Yield 82%; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.41-7.28 (m, 5H), 1.93 (s, 1H), 1.32-1.26 (m, 1H), 1.16 (s, 9H), 0.68-0.58 (m, 3H), 0.49-0.41 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  131.6, 128.26, 128.21, 122.8, 88.7, 85.4, 79.3, 39.7, 25.7, 16.3, 4.6, 0.7; IR (neat,  $\text{cm}^{-1}$ ): 3425, 3018, 1215, 757, 699, 667; HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{20}\text{ONa}$  251.1412, found 251.1421.

**3-Cyclopropyl-2,2-dimethylundec-4-yn-3-ol (1s):** Yield 80%; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  2.17 (t, 2H,  $J = 6.9$  Hz), 1.75 (s, 1H), 1.50-1.44 (m, 2H),

1.40-1.15 (m, 7H), 1.08 (s, 9H), 0.89 (t, 3H,  $J = 6.9$  Hz), 0.55-0.52 (m, 3H), 0.39-0.34 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  85.8, 79.08, 79.00, 39.4, 31.2, 28.7, 28.5, 25.6, 22.5, 18.5, 16.1, 14.0, 4.6, 0.5; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2921, 2299, 1645, 1215, 756, 667; HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{29}\text{O}$  237.2218, found 237.2217.

**7-Cyclopropylpentadec-8-yn-7-ol (1t):** Yield 75%; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  2.08 (t, 2H,  $J = 6.9$  Hz), 2.04 (s, 1H), 1.66-1.60 (m, 2H), 1.48-1.17 (m, 16H), 1.00-0.94 (m, 1H), 0.83-0.80 (m, 6H), 0.50-0.28 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  85.2, 79.8, 73.3, 67.8, 43.2, 31.8, 31.2, 29.5, 28.7, 28.4, 25.5, 24.5, 22.6, 22.5, 20.8, 18.4, 14.0, 13.9, 2.8, 0.6; IR (neat,  $\text{cm}^{-1}$ ): 3421, 3018, 2928, 2358, 1634, 1215, 1109, 757, 669; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{33}\text{O}$  265.2531, found 265.2536.

**1-(4-Chlorophenyl)-1-cyclopropylprop-2-yn-1-ol (1u):**<sup>S1</sup> Yield 70%; brown oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.62-7.60 (m, 2H), 7.36-7.33 (m, 2H), 2.87 (s, 1H), 2.61 (s, 1H), 1.37-1.31 (m, 1H), 0.83-0.75 (m, 1H), 0.68-0.54 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  142.8, 133.5, 128.3, 126.9, 83.3, 74.4, 73.8, 23.4, 3.2, 2.3.

**1-Cyclopropyl-1-phenylprop-2-yn-1-ol (1v):** Yield 87%; brown color oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.68 (d, 2H,  $J = 8.0$  Hz), 7.38-7.29 (m, 3H), 2.58 (s, 1H), 2.45 (s, 1H), 1.41-1.36 (m, 1H), 0.80-0.78 (m, 1H), 0.68-0.56 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  144.2, 128.2, 127.8, 125.3, 83.8, 74.2, 74.1, 23.4, 3.2, 2.2; IR (neat,  $\text{cm}^{-1}$ ): 3435, 3018, 1643, 1215, 756, 460; HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{13}\text{O}$  173.0966, found 173.0960.

**3-Cyclopropyl-1,5-diphenylpenta-1,4-diyn-3-ol (1w):** Yield 86%; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.49-7.25 (m, 10H), 2.71 (s, 1H), 1.71-1.62 (m, 1H),

0.85-0.82 (m, 2H), 0.70-0.66 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  131.9, 128.7, 128.2, 122.0, 87.6, 83.6, 66.4, 22.5, 2.7; IR (neat,  $\text{cm}^{-1}$ ): 3421, 3018, 2399, 1635, 1323; 1215, 756, 669; HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{16}\text{ONa}$  295.1099, found 295.1085.

**5-Phenyl-3-(2-phenylcyclopropyl)pent-1-en-4-yn-3-ol (1x):** Yield 74%; pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.46-7.12 (m, 10H), 6.13-6.07 (m, 1H), 5.64 (d, 1H,  $J = 17.0$  Hz), 5.24 (d, 1H,  $J = 10.2$  Hz), 2.33-2.29 (m, 1H), 2.24 (s, 1H), 1.61-1.56 (m, 1H), 1.28-1.25 (m, 1H), 1.03-0.87 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  142.0, 140.2, 131.8, 129.9, 128.6, 128.3, 126.2, 125.7, 122.2, 114.5, 87.7, 86.4, 72.8, 32.0, 20.0, 12.7; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2398, 1645, 1215, 757, 665; HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{19}\text{O}$  275.1436, found 275.1425.

**1-(1-Methyl-2-phenylcyclopropyl)-1,3-diphenylprop-2-yn-1-ol (1y):** Yield 85%; pale yellow oil; mixture of diastereomers A: B = 3: 2;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.83-7.20 (m, 26H), 2.93-2.86 (m, 1H), 2.57 (s, 1H, diastereomer A), 2.56 (s, 1H, diastereomer B), 1.77-1.73 (m, 1H, diastereomer B), 1.65-1.61 (m, 1H, diastereomer A), 0.99-0.94 (m, 1H), 0.79 (s, 3H, diastereomer A), 0.73 (s, 3H, diastereomer B);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  143.49, 143.47, 139.2, 139.1, 129.3, 129.2, 128.6, 128.45, 128.41, 128.07, 128.04, 127.84, 127.80, 126.4, 125.9, 122.58, 122.56, 91.0, 90.9, 85.9, 85.8, 77.3, 76.33, 76.31, 31.7, 31.6, 26.0, 25.3, 15.7, 15.6, 15.5, 14.5; IR (neat,  $\text{cm}^{-1}$ ): 3415, 3019, 1215, 757, 668; HRMS (ESI): calcd for  $\text{C}_{25}\text{H}_{23}\text{O}$  339.1749, found 339.1744.

**3-(6-Methoxynaphthalen-2-yl)-1-(1-methyl-2-phenylcyclopropyl)-1-phenylprop-2-yn-1-ol (1z):** Yield 82%; pale yellow oil; mixture of diastereomers A: B = 3: 2;  $^1\text{H}$

NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.91-7.07 (m, 32H), 3.879 (s, 3H, diastereomer B), 3.875 (s, 3H, diastereomer A), 2.91-2.84 (m, 1H), 2.61 (s, 2H), 1.74-1.70 (m, 1H, diastereomer B), 1.63-1.59 (m, 1H, diastereomer A), 0.95-0.90 (m, 1H), 0.75 (s, 3H, diastereomer A), 0.69 (s, 3H, diastereomer B); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  158.43, 158.42, 143.65, 143.60, 139.27, 139.21, 134.3, 131.6, 129.3, 129.2, 129.1, 129.0, 128.46, 128.44, 128.3, 128.1, 128.0, 127.8, 127.7, 126.9, 126.8, 126.6, 126.4, 126.3, 125.9, 119.58, 119.55, 117.3, 105.8, 90.6, 90.5, 86.4, 86.3, 77.3, 76.4, 76.3, 55.3, 31.8, 31.7, 26.1, 25.3, 15.7, 15.6, 15.5, 14.6, 14.2; IR (neat, cm<sup>-1</sup>): 3417, 3019, 1215, 756, 668; HRMS (ESI): calcd for C<sub>30</sub>H<sub>27</sub>O<sub>2</sub> 419.2011, found 419.2020.

**1-(4-Chlorophenyl)-1-cyclopropyl-3-(thiophen-2-yl)prop-2-yn-1-ol (1 $\alpha$ ):** Yield 65%; pale yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.66-7.63 (m, 2H), 7.459-7.451 (m, 1H), 7.35-7.26 (m, 3H), 7.10-7.09 (m, 1H), 2.49 (s, 1H), 1.43-1.37 (m, 1H), 0.85-0.81 (m, 1H), 0.71-0.67 (m, 1H), 0.63-0.57 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  143.4, 133.5, 129.9, 129.3, 128.3, 127.0, 125.5, 121.1, 88.2, 81.4, 74.4, 23.8, 3.3, 2.5; IR (neat, cm<sup>-1</sup>): 3585, 3419, 3018, 2399, 1489, 1215, 1091, 1033, 927, 756, 669; HRMS (ESI): calcd for C<sub>16</sub>H<sub>14</sub>ClOS 289.0454, found 289.0455.

**1-(2-(Furan-2-yl)cyclopropyl)-1,3-diphenylprop-2-yn-1-ol (1 $\beta$ ):** Yield 60%; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.78-7.77 (m, 2H), 7.51-7.25 (m, 9H), 6.28 (q, 1H, *J* = 1.8Hz), 6.02 (d, 1H, *J* = 3.1Hz), 2.72 (s, 1H), 2.53-2.49 (m, 1H), 1.92-1.88 (m, 1H), 1.36-1.32 (m, 1H), 1.14-1.10 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  155.5, 144.2, 140.7, 131.8, 128.7, 128.4, 127.9, 125.4, 122.1, 110.3, 104.1, 88.6, 86.7, 74.2, 32.4, 14.2, 11.59; IR (neat, cm<sup>-1</sup>): 3419, 3018, 2092, 1639, 1521,

1423, 1215, 927, 765, 669; HRMS (ESI): calcd for C<sub>22</sub>H<sub>19</sub>O<sub>2</sub> 315.1385, found 315.1397.

**1,3-Diphenyl-1-(2-(thiophen-2-yl)cyclopropyl)prop-2-yn-1-ol (1 $\chi$ ):** Yield 83%; light brown oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.80-7.78 (m, 2H), 7.51-7.33 (m, 8H), 7.05-6.71 (m, 3H), 2.66 (s, 1H), 2.52-2.48 (m, 1H), 1.83-1.78 (m, 1H), 1.62-1.57 (m, 1H), 1.16-1.09 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  146.1, 144.3, 131.9, 128.8, 128.46, 128.43, 128.0, 126.8, 125.4, 123.3, 122.7, 122.2, 89.1, 86.6, 73.7, 35.0, 16.6, 13.2; IR (neat, cm<sup>-1</sup>): 3415, 3018, 1489, 1446, 1215, 1029, 756, 669, 449; HRMS (ESI): calcd for C<sub>22</sub>H<sub>19</sub>OS 331.1157, found 331.1168.

**1-Cyclopropyl-3-phenylprop-2-yn-1-ol (1 $\delta$ ):** Yield 80%; light yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.39-7.37 (m, 2H), 7.27-7.25 (m, 3H), 4.40 (t, 1H, *J* = 5.5 Hz), 2.07 (d, 1H, *J* = 5.2 Hz), 1.35-1.27 (m, 1H), 0.60-0.45 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  131.7, 128.4, 128.2, 122.5, 87.8, 85.0, 66.2, 17.2 3.3, 1.6; IR (neat, cm<sup>-1</sup>): 3415, 3018, 1215, 1027, 756, 667; HRMS (ESI): calcd for C<sub>12</sub>H<sub>13</sub>O 173.0966, found 173.0974.

**(Z)-1-(6-Ethoxy-1-phenylhex-3-en-1-yn-3-yl)-4-fluorobenzene (3b):** Colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.66-7.63 (m, 2H), 7.54-7.53 (m, 2H), 7.37-7.35 (m, 3H), 7.05 (t, 2H, *J* = 8.6 Hz), 6.47 (t, 1H, *J* = 7.3 Hz) 3.63 (t, 2H, *J* = 6.7 Hz), 3.56 (q, 2H, *J* = 7.0 Hz), 2.88 (q, 2H, *J* = 6.9 Hz), 1.25 (t, 3H, *J* = 7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  163.4, 161.4, 134.4, 134.2, 134.1, 131.5, 128.4, 127.7 (d, 1C, *J*<sub>C-F</sub> = 32.2 Hz), 123.8, 123.2, 115.3 (d, 1C, *J*<sub>C-F</sub> = 85.5 Hz), 95.7, 86.3, 69.4, 66.2, 32.0, 15.2; IR (neat, cm<sup>-1</sup>): 3437, 2866, 1602, 1506, 1232, 1109, 833, 754, 460; HRMS (ESI): calcd

for C<sub>20</sub>H<sub>20</sub>O 295.1498, found 295.1493.

**(Z)-1-Chloro-4-(6-ethoxy-1-phenylhex-3-en-1-yn-3-yl)benzene (3c):** Colorless oil;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.61-7.52 (m, 4H), 7.37-7.32 (m, 5H), 6.52 (t, 1H,  $J$  = 7.3 Hz) 3.63 (t, 2H,  $J$  = 6.7 Hz), 3.56 (q, 2H,  $J$  = 7.0 Hz), 2.88 (q, 2H,  $J$  = 6.8 Hz), 1.24 (t, 3H,  $J$  = 7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  136.5, 135.1, 133.4, 131.5, 128.5, 128.49, 128.43, 127.3, 123.8, 123.1, 95.9, 86.1, 69.3, 66.2, 32.0, 15.2; IR (neat, cm<sup>-1</sup>): 3439, 3018, 1643, 1489, 1215, 1095, 756, 464; HRMS (ESI): calcd for C<sub>20</sub>H<sub>20</sub>OCl 311.1203, found 311.1208.

**1-((Z)-6-Ethoxy-1-(4-methoxy-2-methylphenyl)hex-3-en-1-yn-3-yl)-4-methoxybenzene (3d):** Yellow oil;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.61 (d, 2H,  $J$  = 8.5 Hz), 7.42 (d, 1H,  $J$  = 8.4 Hz), 6.9 (d, 2H,  $J$  = 2.7 Hz), 6.78-6.70 (m, 2H), 6.37 (t, 1H,  $J$  = 7.3 Hz), 3.82 (s, 3H), 3.81 (s, 3H), 3.61 (t, 3H,  $J$  = 6.8 Hz), 3.53 (q, 2H,  $J$  = 7.0 Hz), 2.84 (q, 2H,  $J$  = 7.0 Hz), 2.49 (s, 3H), 1.23 (t, 3H,  $J$  = 7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  159.6, 159.2, 141.7, 133.3, 131.5, 131.0, 127.2, 124.7, 115.6, 115.1, 113.7, 113.3, 94.5, 89.3, 69.6, 66.1, 55.3, 55.2, 32.0, 21.3, 15.2; IR (neat, cm<sup>-1</sup>): 3419, 3018, 2399, 1602, 1508, 1215, 116, 1035, 929, 756, 669; HRMS (ESI): calcd for C<sub>23</sub>H<sub>27</sub>O<sub>3</sub> 351.1960, found 351.1961.

**1-((Z)-6-Ethoxy-3-(4-methoxyphenyl)hex-3-en-1-ynyl)-2,4,5-trimethylbenzene (3e):** Pale yellow oil;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.63-7.60 (m, 2H), 7.27 (s, 1H), 7.00 (s, 1H), 6.90-6.87 (m, 2H), 6.38 (t, 1H,  $J$  = 7.3 Hz), 3.82 (s, 3H), 3.61 (t, 2H,  $J$  = 6.8 Hz), 3.54 (q, 2H,  $J$  = 7.2 Hz), 2.85 (q, 2H,  $J$  = 6.9 Hz), 2.43 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H), 1.22 (t, 3H,  $J$  = 7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  159.2, 137.2,



137.1, 133.7, 132.9, 131.8, 131.0, 130.9, 127.2, 124.7, 120.4, 113.71, 94.8, 89.6, 69.6, 66.1, 55.3, 32.0, 20.4, 19.7, 19.0, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2358, 1600, 1215, 1109, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{24}\text{H}_{29}\text{O}_2$  349.2168, found 349.2169.

**1-((Z)-6-Ethoxy-3-(4-methoxyphenyl)hex-3-en-1-ynyl)-4-(trifluoromethyl)benzene (3f):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.62-7.56 (m, 6H), 6.90-6.88 (m, 2H), 6.45 (t, 1H,  $J = 7.3$  Hz), 3.82 (s, 3H), 3.61 (t, 2H,  $J = 6.7$  Hz), 3.54 (q, 2H,  $J = 7.0$  Hz), 2.84 (q, 2H,  $J = 6.9$  Hz), 1.22 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.4, 134.0, 131.7, 130.3, 127.2, 127.1, 125.3, 125.28, 125.25, 123.8, 113.8, 93.8, 89.2, 69.4, 66.2, 55.3, 32.0, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1600, 1519, 1323, 1215, 1132, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{22}\text{H}_{22}\text{F}_3\text{O}_2$  375.1572, found 375.1559.

**1-((Z)-6-Ethoxy-1-(4-methoxy-2-methylphenyl)hex-3-en-1-yn-3-yl)-4-fluorobenzene (3g):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.66-7.62 (m, 2H), 7.42 (d, 1H,  $J = 8.5$  Hz), 7.06-7.02 (m, 2H), 6.78-6.71 (m, 2H), 6.40 (t, 1H,  $J = 7.3$  Hz), 3.81 (s, 3H), 3.61 (t, 2H,  $J = 6.7$  Hz), 3.54 (q, 2H,  $J = 7.0$  Hz), 2.85 (q, 2H,  $J = 6.9$  Hz), 2.48 (s, 3H), 1.22 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  163.3, 161.4, 159.7, 141.7, 134.5 (d, 1C,  $J_{\text{C-F}} = 12.2$  Hz), 133.3 (d, 1C,  $J_{\text{C-F}} = 30.1$ ), 127.70 (d, 1C,  $J_{\text{C-F}} = 31.9$  Hz), 124.3, 115.4, 115.2 (d, 1C,  $J_{\text{C-F}} = 30.9$  Hz), 115.0, 111.3, 94.8, 88.9, 69.4, 66.2, 55.2, 32.0, 21.3, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3421, 3018, 2399, 1602, 1508, 1423, 1215, 927, 769, 756, 669; HRMS (ESI): calcd for  $\text{C}_{22}\text{H}_{23}\text{FO}_2\text{Na}$  361.1580, found 361.1584.

**2-((Z)-6-Ethoxy-3-(4-fluorophenyl)hex-3-en-1-ynyl)pyridine (3h):** Pale yellow oil;

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.60 (dq, 1H,  $J = 4.9, 0.85$  Hz), 7.67-7.62 (m, 3H), 7.50 (dt, 1H,  $J = 7.8, 0.9$  Hz), 7.25-7.23 (m, 1H), 7.05-7.01 (m, 2H), 6.55 (t, 1H,  $J = 7.3$  Hz), 3.61 (t, 2H,  $J = 6.4$  Hz), 3.53 (q, 2H,  $J = 7.0$  Hz), 2.88 (q, 2H,  $J = 6.7$  Hz), 1.21 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  163.4, 161.4, 150.1, 143.3, 136.5, 136.1, 133.6 (d, 1C,  $J_{\text{C-F}} = 12.1$  Hz), 127.70 (d, 1C,  $J_{\text{C-F}} = 32.1$  Hz), 127.2, 123.1, 123.8, 115.2 (d, 1C,  $J_{\text{C-F}} = 86.0$  Hz), 94.8, 86.1, 69.3, 66.2, 32.1, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1647, 1429, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{19}\text{H}_{19}\text{FNO}$  296.1451, found 295.1449.

**2-((Z)-6-Ethoxy-3-(4-methoxyphenyl)hex-3-en-1-ynyl)pyridine (3i):** Light brown oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.61 (d, 1H,  $J = 4.3$  Hz), 7.67-7.59 (m, 3H), 7.49 (d, 1H,  $J = 7.8$  Hz), 7.23-7.21 (m, 1H), 6.87 (d, 2H,  $J = 8.7$  Hz), 6.50 (t, 1H,  $J = 7.3$  Hz), 3.8 (s, 3H), 3.60 (t, 2H,  $J = 6.6$  Hz), 3.52 (q, 2H,  $J = 7.0$  Hz), 2.87 (q, 2H,  $J = 6.8$  Hz), 1.21 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.3, 150.1, 143.6, 136.1, 134.8, 130.2, 127.29, 127.24, 123.5, 122.7, 113.7, 94.4, 86.6, 69.5, 66.2, 55.3, 32.0, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3417, 3018, 2399, 1635, 1510, 1429, 1215, 927, 756, 669, 445; HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{22}\text{NO}_2$  308.1651, found 308.1650.

**4-((Z)-6-Ethoxy-3-(4-fluorophenyl)hex-3-en-1-ynyl)benzonitrile (3j):** White solid; m.p. 47-49  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.64-7.57 (m, 6H), 7.04 (t, 2H,  $J = 8.5$  Hz), 6.52 (t, 1H,  $J = 7.3$  Hz), 3.61 (t, 3H,  $J = 6.6$  Hz), 3.54 (q, 2H,  $J = 6.9$  Hz), 2.83 (q, 2H,  $J = 6.8$  Hz), 1.22 (t, 3H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  163.5, 161.5, 136.5, 133.6, 132.1 (d, 1C,  $J_{\text{C-F}} = 38.3$  Hz), 128.0, 127.6 (d, 1C,  $J_{\text{C-F}} = 32.2$  Hz), 123.3, 118.4, 115.3 (d, 1C,  $J_{\text{C-F}} = 86.2$  Hz), 111.6, 93.8, 90.7, 69.2, 66.3, 32.1, 15.2;

IR (neat,  $\text{cm}^{-1}$ ): 3421, 3018, 2399, 1635, 1215, 927, 756, 669, 505; HRMS (ESI): calcd for  $\text{C}_{21}\text{H}_{19}\text{FNO}$  320.1451, found 320.1456.

**4-((Z)-6-Ethoxy-3,6-diphenylhex-3-en-1-ynyl)benzonitrile (3k):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.79-7.42 (m, 6H), 7.39-7.29 (m, 8H), 6.57 (t, 1H,  $J = 7.3$  Hz), 4.48-4.45 (m, 1H), 3.48-3.37 (m, 2H), 3.07-2.94 (m, 2H), 1.22 (t, 3H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  142.2, 137.6, 136.3, 132.07, 132.04, 128.53, 128.50, 128.2, 127.9, 127.7, 126.5, 126.0, 124.5, 118.5, 111.5, 93.6, 91.2, 81.3, 64.3, 40.2, 15.4; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1635, 1215, 756, 669; HRMS (ESI): calcd for  $\text{C}_{27}\text{H}_{24}\text{NO}$  378.1858, found 378.1849.

**2-((Z)-6-Ethoxy-3-(4-methoxyphenyl)hex-3-en-1-ynyl)-6-methoxynaphthalene (3l):** Yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.96 (s, 1H), 7.70 (t, 2H,  $J = 8.4$  Hz), 7.64 (d, 2H,  $J = 8.7$  Hz), 7.17-7.11 (m, 2H), 6.91 (d, 2H,  $J = 8.7$  Hz), 6.42 (t, 1H,  $J = 7.3$  Hz), 3.93 (s, 3H), 3.83 (s, 3H), 3.64 (t, 2H,  $J = 6.8$  Hz), 3.56 (q, 2H,  $J = 6.9$  Hz), 2.90 (q, 2H,  $J = 6.9$  Hz), 1.24 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.2, 158.3, 134.1, 132.4, 131.1, 130.8, 129.3, 129.0, 128.5, 127.2, 126.8, 124.3, 119.4, 118.3, 105.8, 96.0, 86.4, 69.6, 66.2, 55.3, 32.0, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1635, 1419, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{26}\text{H}_{26}\text{O}_3\text{Na}$  409.1780, found 409.1772.

**2-((Z)-6-Ethoxy-3,6-diphenylhex-3-en-1-ynyl)-6-methoxynaphthalene (3m):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.96 (s, 1H), 7.73-7.68 (m, 4H), 7.54-7.52 (m, 1H), 7.44-7.37 (m, 6H), 7.33-7.30 (m, 2H), 7.19 (dd, 1H,  $J = 8.9, 2.5$  Hz), 7.13 (d, 1H,  $J = 2.3$  Hz), 6.52 (t, 1H,  $J = 7.3$  Hz), 4.51 (t, 1H,  $J = 6.7$  Hz), 3.94 (s, 3H),

3.51-3.40 (m, 2H), 3.14-3.02 (m, 2H), 1.25 (t, 3H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  158.3, 142.5, 138.3, 134.2, 134.1, 131.2, 129.3, 129.0, 128.5, 128.47, 128.4, 127.7, 127.6, 126.8, 126.6, 126.1, 125.1, 119.4, 118.3, 105.8, 96.2, 86.4, 81.6, 64.3, 55.3, 40.1, 15.4; IR (neat,  $\text{cm}^{-1}$ ): 3421, 3018, 2399, 1647, 1215, 756, 669; HRMS (ESI): calcd for  $\text{C}_{31}\text{H}_{29}\text{O}_2$  433.2168, found 433.2177.

**(Z)-1-(6-Ethoxy-3-phenylhex-3-en-1-ynyl)naphthalene (3n):** Colorless oil; Yield 97 %;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.41 (d, 1H,  $J = 8.3$  Hz) 7.85-7.28 (m, 11H), 6.58 (t, 1H,  $J = 7.3$  Hz) 3.66 (t, 2H,  $J = 6.7$  Hz), 3.55 (q, 2H,  $J = 7.0$  Hz), 2.98 (q, 2H,  $J = 6.9$  Hz), 1.23 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  138.2, 134.9, 133.29, 133.25, 130.6, 128.8, 128.5, 128.3, 127.7, 126.9, 126.4, 126.3, 126.2, 125.3, 125.2, 121.1, 93.7, 91.5, 69.5, 66.3, 32.2, 15.3; IR (neat,  $\text{cm}^{-1}$ ): 3439, 3019, 1215, 756, 669; HRMS (ESI): calcd for  $\text{C}_{24}\text{H}_{23}\text{O}$  327.1749, found 327.1743.

**1-Chloro-4-((Z)-1-ethoxydodec-3-en-5-yn-4-yl)benzene (3o):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.56-7.55 (m, 2H,  $J = 8.5$  Hz), 7.30 (d, 2H,  $J = 8.6$  Hz), 6.38 (t, 1H,  $J = 7.2$  Hz), 3.60-3.50 (m, 4H), 2.77 (q, 2H,  $J = 6.9$  Hz), 2.4 (t, 2H,  $J = 7.0$  Hz), 1.68-1.58 (m, 2H), 1.53-1.45 (m, 2H), 1.43-1.31 (m, 4H), 1.24 (t, 3H,  $J = 7.0$  Hz), 0.93 (t, 3H,  $J = 6.7$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  137.1, 133.3, 133.0, 128.2, 127.2, 124.2, 97.2, 69.4, 66.1, 31.8, 31.3, 28.8, 28.6, 22.5, 19.5, 15.2, 14.0; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2929, 2358, 1645, 1215, 1109, 756, 669; HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{28}\text{ClO}$  319.1829, found 319.1843.

**(Z)-(1-Ethoxydec-3-en-5-yn-4-yl)benzene (3p):** Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.59-7.21 (m, 5H), 6.37 (t, 1H,  $J = 7.2$  Hz) 3.55 (t, 2H,  $J = 6.8$  Hz), 3.52 (q,

2H,  $J = 7.0$  Hz), 2.76 (q, 2H,  $J = 7.0$  Hz), 2.45 (t, 2H  $J = 7.0$  Hz), 1.62-1.57 (m, 2H), 1.52-1.45 (m, 2H), 1.22 (t, 3H,  $J = 7.0$  Hz), 0.94 (t, 3H,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  138.6, 132.8, 128.2, 128.0, 127.7, 127.3, 126.1, 126.0, 125.3, 96.7, 77.6, 69.5, 66.1, 31.8, 31.0, 22.0, 19.3, 15.2, 13.6; IR (neat,  $\text{cm}^{-1}$ ): 3435, 2960, 1493, 1216, 1105, 756, 694, 667; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{25}\text{O}$  257.1905, found 257.1904.

**(Z)-(6-Ethoxy-3-(1-methylcyclohexyl)hex-3-en-1-ynyl)benzene (3q):** Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.44-7.24 (m, 5H), 5.82 (t, 1H,  $J = 7.1$  Hz) 3.52-3.48 (m, 4H), 2.71 (q, 2H,  $J = 7.0$  Hz), 1.83-1.39 (m, 10H), 1.20 (t, 3H,  $J = 6.9$  Hz), 1.11 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  133.7, 131.3, 131.0, 128.2, 127.7, 124.0, 94.7, 87.5, 69.8, 66.0, 38.6, 36.8, 31.5, 26.3, 22.4, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3429, 3018, 1656, 1489, 1215, 1095, 757, 464; HRMS (ESI): calcd for  $\text{C}_{21}\text{H}_{29}\text{O}$  297.2218, found 297.2226.

**(Z)-(3-Tert-butyl-6-ethoxyhex-3-en-1-ynyl)benzene (3r):** Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.43-7.26 (m, 5H), 5.78 (t, 1H,  $J = 7.1$  Hz) 3.51-3.46 (m, 4H), 2.64 (q, 2H,  $J = 7.0$  Hz), 1.19 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  134.7, 131.3, 129.4, 128.2, 127.8, 123.9, 95.2, 87.3, 69.8, 66.0, 35.7, 31.4, 29.4, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 1643, 1490, 1215, 1095, 756; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{25}\text{O}$  257.1905, found 257.1906.

**(Z)-4-Tert-Butyl-1-ethoxydodec-3-en-5-yne (3s):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  5.57 (t, 1H,  $J = 7.0$  Hz), 3.44-3.35 (m, 4H), 2.50 (q, 2H,  $J = 7.0$  Hz), 2.29 (t, 2H,  $J = 6.9$  Hz), 1.55-1.18 (m, 8H), 1.13 (t, 3H,  $J = 7.0$  Hz), 1.02 (s, 9H), 0.82 (t, 3H,  $J = 6.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  135.2, 127.2, 96.0, 77.9, 69.9,

65.9, 35.6, 31.3, 31.1, 29.2, 28.9, 28.5, 22.5, 19.5, 15.2, 14.0; IR (neat,  $\text{cm}^{-1}$ ): 3422, 3018, 2925, 2358, 1645, 1215, 1109, 756, 667; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{33}\text{O}$  265.2531, found 265.2541.

**(Z)-9-(3-Ethoxypropylidene)pentadec-7-yne (3t):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.55 (t, 1H,  $J = 7.1$  Hz), 3.46 (q, 2H,  $J = 7.0$  Hz), 3.39 (t, 2H,  $J = 7.0$  Hz), 2.49 (q, 2H,  $J = 7.0$  Hz), 2.29 (t, 2H,  $J = 7.0$  Hz), 2.02 (t, 2H,  $J = 7.4$  Hz), 1.51-1.22 (m, 16H), 1.15 (t, 3H,  $J = 7.0$  Hz), 0.86-0.81 (m, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  131.3, 125.4, 94.7, 78.9, 69.8, 65.9, 37.5, 31.7, 31.3, 30.9, 28.9, 28.6, 28.5, 28.4, 22.6, 22.5, 19.5, 15.2, 14.09, 14.04; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2928, 2358, 1645, 1215, 1109, 756, 667; HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{37}\text{O}$  293.2844, found 293.2846.

**1-Chloro-4-((E)-6-ethoxyhex-3-en-1-yn-3-yl)benzene (3u):** Yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.57-7.52 (m, 2H), 7.33-7.28 (m, 2H), 6.56 (t, 1H,  $J = 7.3$  Hz), 3.6-3.5 (m, 4H), 3.3 (s, 1H), 2.80 (q, 2H,  $J = 6.7$  Hz), 1.24 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  136.8, 135.9, 133.4, 128.4, 127.2, 122.9, 83.7, 80.2, 69.1, 66.2, 31.9, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1645, 1419, 1215, 1111, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{16}\text{ClO}$  235.0890, found 235.0894.

**(E)-(6-Ethoxyhex-3-en-1-yn-3-yl)benzene (3v):** Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.82 (d, 2H,  $J = 7.8$  Hz), 7.62-7.26 (m, 3H), 6.56 (t, 1H,  $J = 7.3$  Hz), 3.60-3.50 (m, 4H), 3.35 (s, 1H), 2.81 (q, 2H,  $J = 6.8$  Hz), 1.23 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  137.5, 136.4, 128.3, 127.7, 125.9, 124.0, 83.4, 80.7, 69.3, 66.2, 31.9, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3435, 2870, 1643, 1215, 1109, 756; HRMS (ESI):

calcd for C<sub>14</sub>H<sub>17</sub>O 201.1279, found 201.1278.

**(3-(3-Ethoxypropylidene)penta-1,4-diyne-1,5-diyl)dibenzene (3w):** Colorless oil;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.63-7.39 (m, 10H), 6.60 (t, 1H,  $J$  = 7.4 Hz) 3.65 (t, 2H,  $J$  = 6.6 Hz), 3.63 (q, 2H,  $J$  = 6.9 Hz), 2.88 (q, 2H,  $J$  = 6.9 Hz), 1.30 (t, 3H,  $J$  = 6.9 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  145.5, 131.6, 128.5, 128.3, 128.2, 122.9, 122.8, 107.0, 93.2, 87.2, 86.9, 84.6, 68.9, 66.2, 31.6, 15.2; IR (neat, cm<sup>-1</sup>): 3421, 3018, 2399, 1647, 1215, 756, 669; HRMS (ESI): calcd for C<sub>22</sub>H<sub>20</sub>ONa 323.1412, found 323.1414.

**(Z)-(6-Ethoxy-3-vinylhex-3-en-1-yne-1,6-diyl)dibenzene (3x):** Pale yellow oil;

mixture of *E/Z* isomers = 5: 1; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.40-7.18 (m, 13H), 6.55-6.50 (m, 1H, *E* or *Z* regioisomer), 6.30-6.24 (m, 1H, *E* or *Z* regioisomer), 6.03 (t, 1H,  $J$  = 7.4 Hz, *E* or *Z* regioisomer), 5.93 (t, 1H,  $J$  = 7.3 Hz, *E* or *Z* regioisomer), 5.71 (d, 1H,  $J$  = 16.7 Hz, *E* or *Z* regioisomer), 5.58 (d, 1H,  $J$  = 16.9 Hz, *E* or *Z* regioisomer), 5.22 (d, 1H,  $J$  = 9.9 Hz, *E* or *Z* regioisomer), 5.10 (d, 1H,  $J$  = 10.2 Hz, *E* or *Z* regioisomer), 4.30 (t, 1H,  $J$  = 6.8 Hz, *E* or *Z* regioisomer), 4.23 (t, 1H,  $J$  = 6.7 Hz, *E* or *Z* regioisomer), 3.36-3.26 (m, 2H), 2.87-2.69 (m, 2H, *E* or *Z* regioisomer), 2.61-2.55 (m, 2H, *E* or *Z* regioisomer), 1.11 (t, 3H,  $J$  = 7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  142.3, 137.6, 136.5, 135.8, 131.5, 130.4, 128.49, 128.40, 128.3, 128.2, 128.0, 127.5, 126.5, 124.8, 123.3, 115.3, 96.2, 84.0, 81.3, 81.2, 64.2, 39.4, 15.3, 1.0; IR (neat, cm<sup>-1</sup>): 3419, 3018, 2375, 1636, 1215, 756, 669; HRMS (ESI): calcd for C<sub>22</sub>H<sub>23</sub>O 303.1749, found 303.1737.

**2-(6-Ethoxy-4-methyl-3,6-diphenylhex-3-en-1-ynyl)-6-methoxynaphthalene (3z):**

Colorless oil; mixture of *E/Z* isomers = 3: 1; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.74-6.97

(m, 23H), 4.64 (t, 1H,  $J = 6.9$  Hz, *E* or *Z* regioisomer), 4.30 (q, 1H,  $J = 5.9$  Hz, *E* or *Z* regioisomer), 3.81 (s, 3H, *E* or *Z* regioisomer), 3.80 (s, 3H, *E* or *Z* regioisomer), 3.42-3.16 (m, 3H), 2.98-2.90 (m, 2H, *E* or *Z* regioisomer), 2.63-2.36 (m, 2H, *E* or *Z* regioisomer), 2.20 (s, 3H, *E* or *Z* regioisomer), 1.68 (s, 3H, *E* or *Z* regioisomer), 1.11 (t, 3H,  $J = 7.0$  Hz, *E* or *Z* regioisomer), 1.06 (t, 3H,  $J = 6.9$  Hz, *E* or *Z* regioisomer);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.17, 158.13, 144.5, 143.4, 142.7, 142.4, 139.4, 139.3, 133.8, 130.76, 130.70, 129.3, 129.2, 129.1, 129.05, 129.02, 128.5, 128.3, 128.2, 128.14, 128.111, 127.5, 127.4, 126.9, 126.8, 126.7, 126.69, 126.66, 126.4, 121.6, 121.1, 119.3, 119.2, 118.9, 105.86, 105.83, 93.9 (*E* or *Z* regioisomer), 93.6 (*E* or *Z* regioisomer), 90.2 (*E* or *Z* regioisomer), 89.9 (*E* or *Z* regioisomer), 81.8, 80.7, 77.2, 64.3, 64.2, 55.3, 46.3, 43.3, 22.1, 21.5, 15.4, 15.3; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3019, 1601, 1215, 748, 701, 668; HRMS (ESI): calcd for  $\text{C}_{32}\text{H}_{31}\text{O}_2$  447.2324, found 447.2328.

**2-((*Z*)-3-(4-Chlorophenyl)-6-ethoxyhex-3-en-1-ynyl)thiophene (3 $\alpha$ ):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.58-7.56 (m, 2H), 7.51-7.50 (m, 1H), 7.32-7.30 (m, 3H), 7.18-7.17 (m, 1H), 6.48 (t, 1H,  $J = 7.3$  Hz), 3.60 (t, 2H,  $J = 6.6$  Hz), 3.54 (q, 2H,  $J = 7.0$  Hz), 2.83 (q, 2H,  $J = 6.8$  Hz), 1.22 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  136.5, 135.0, 133.4, 129.8, 128.6, 128.4, 127.3, 125.5, 123.8, 122.1, 90.9, 85.6, 69.3, 66.2, 32.0, 15.2; IR (neat,  $\text{cm}^{-1}$ ): 3684, 3018, 2399, 1521, 1421, 1215, 756, 669; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{17}\text{ClOSNa}$  339.0586, found 339.0576.

**(*Z*)-2-(1-Ethoxy-4,6-diphenylhex-3-en-5-ynyl)furan (3 $\beta$ ):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.66-7.55 (m, 4H), 7.44-7.28 (m, 7H), 6.47 (t, 1H,  $J = 7.3$  Hz), 6.37-6.35 (m, 2H), 4.55 (t, 1H,  $J = 6.9$  Hz), 3.60-3.48 (m, 2H), 3.19-3.16 (m, 2H),



1.24 (t, 3H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  154.4, 142.3, 138.0, 133.4, 131.5, 128.38, 128.36, 128.3, 127.6, 126.1, 125.2, 123.3, 110.0, 107.7, 95.7, 86.5, 74.1, 64.3, 36.1, 15.3; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 2092, 1639, 1423, 1215, 927, 777, 744, 669; HRMS (ESI): calcd for  $\text{C}_{24}\text{H}_{23}\text{O}_2$  343.1698, found 343.1711.

**(Z)-2-(1-Ethoxy-4,6-diphenylhex-3-en-5-ynyl)thiophene (3 $\chi$ ):** Light brown oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.64 (d, 2H,  $J = 7.3$  Hz), 7.53-7.26 (m, 9H), 7.01-6.96 (m, 2H), 6.48 (t, 1H,  $J = 7.3$  Hz), 4.74 (t, 1H,  $J = 6.7$  Hz), 3.59-3.42 (m, 2H), 3.19-3.04 (m, 2H), 1.22 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  146.4, 138.1, 133.6, 131.6, 128.4, 128.38, 128.34, 127.7, 126.4, 126.1, 125.3, 124.9, 123.3, 95.7, 86.6, 76.9, 64.3, 40.1, 15.3; IR (neat,  $\text{cm}^{-1}$ ): 3417, 3018, 1643, 1215, 756, 453; HRMS (ESI): calcd for  $\text{C}_{24}\text{H}_{23}\text{OS}$  359.1470, found 359.1472.

**(Z)-6-(2-(Allyloxy)ethoxy)-1,3-diphenylhex-3-en-1-yne (3 $\epsilon$ ):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.72 (d, 2H,  $J = 7.2$  Hz), 7.59-7.56 (m, 2H), 7.42-7.32 (m, 6H), 6.57 (t, 1H,  $J = 7.3$  Hz), 6.03-5.90 (m, 1H), 5.35-5.20 (m, 2H), 4.08 (d, 2H,  $J = 5.6$  Hz), 3.75-3.64 (m, 6H), 2.94 (q, 2H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  138.0, 134.8, 134.5, 131.5, 128.4, 128.3, 127.6, 126.0, 124.9, 123.4, 117.1, 95.6, 86.6, 72.3, 70.2, 69.4, 31.9; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1647, 1215, 1122, 929, 756, 669; HRMS (ESI): calcd for  $\text{C}_{23}\text{H}_{25}\text{O}_2$  333.1855, found 333.1853.

**(Z)-6-(Allyloxy)-1,3-diphenylhex-3-en-1-yne (3 $\phi$ ):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.72-7.69 (m, 2H), 7.59-7.53 (m, 2H), 7.41-7.30 (m, 6H), 6.56 (t, 1H,  $J = 7.3$  Hz), 5.98-5.91 (m, 1H), 5.37-5.20 (m, 2H), 4.06 (dt, 2H,  $J = 9.3, 1.3$  Hz), 3.67 (t, 2H,  $J = 6.7$  Hz), 2.92 (q, 2H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  138.0, 134.8,

134.5, 131.5, 128.41, 128.40, 128.3, 127.6, 126.0, 125.0, 123.4, 117.0, 95.6, 86.6, 71.9, 69.2, 32.0; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1647, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{21}\text{H}_{21}\text{O}$  289.1592, found 289.1595.

**(Z)-6-(Pentan-3-yloxy)-1,3-diphenylhex-3-en-1-yne (3 $\gamma$ ):** Pale yellow oil; Yield 86 %:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.68 (d, 2H,  $J = 7.2$  Hz), 7.54 (m, 2H), 7.40-7.29 (m, 6H), 6.58 (t, 1H,  $J = 7.3$  Hz), 3.65 (t, 2H,  $J = 6.7$  Hz), 3.23-3.16 (m, 1H), 2.87 (q, 2H,  $J = 6.8$  Hz), 1.63-1.50 (m, 4H), 0.94 (t, 6H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  138.1, 135.1, 131.5, 128.4, 128.3, 128.2, 127.6, 126.0, 124.7, 123.4, 95.5, 86.7, 82.0, 67.8, 32.5, 26.1, 9.7; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1647, 1419, 1215, 927, 756, 669; HRMS (ESI): calcd for  $\text{C}_{23}\text{H}_{27}\text{O}$  319.2062, found 319.2056.

**(Z)-6-tert-Butoxy-1,3-diphenylhex-3-en-1-yne (3 $\eta$ ):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.72-7.69 (m, 2H), 7.58-7.55 (m, 2H), 7.42-7.30 (m, 6H), 6.57 (t, 1H,  $J = 7.3$  Hz), 3.58 (t, 2H,  $J = 6.8$  Hz), 2.85 (q, 2H,  $J = 7.0$  Hz), 1.26 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  138.2, 135.2, 131.5, 128.4, 128.3, 128.2, 127.6, 126.0, 124.6, 123.5, 95.4, 86.7, 72.9, 60.8, 32.9, 27.6; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1635, 1215, 756, 669; HRMS (ESI): calcd for  $\text{C}_{22}\text{H}_{25}\text{O}$  305.1905, found 305.1896.

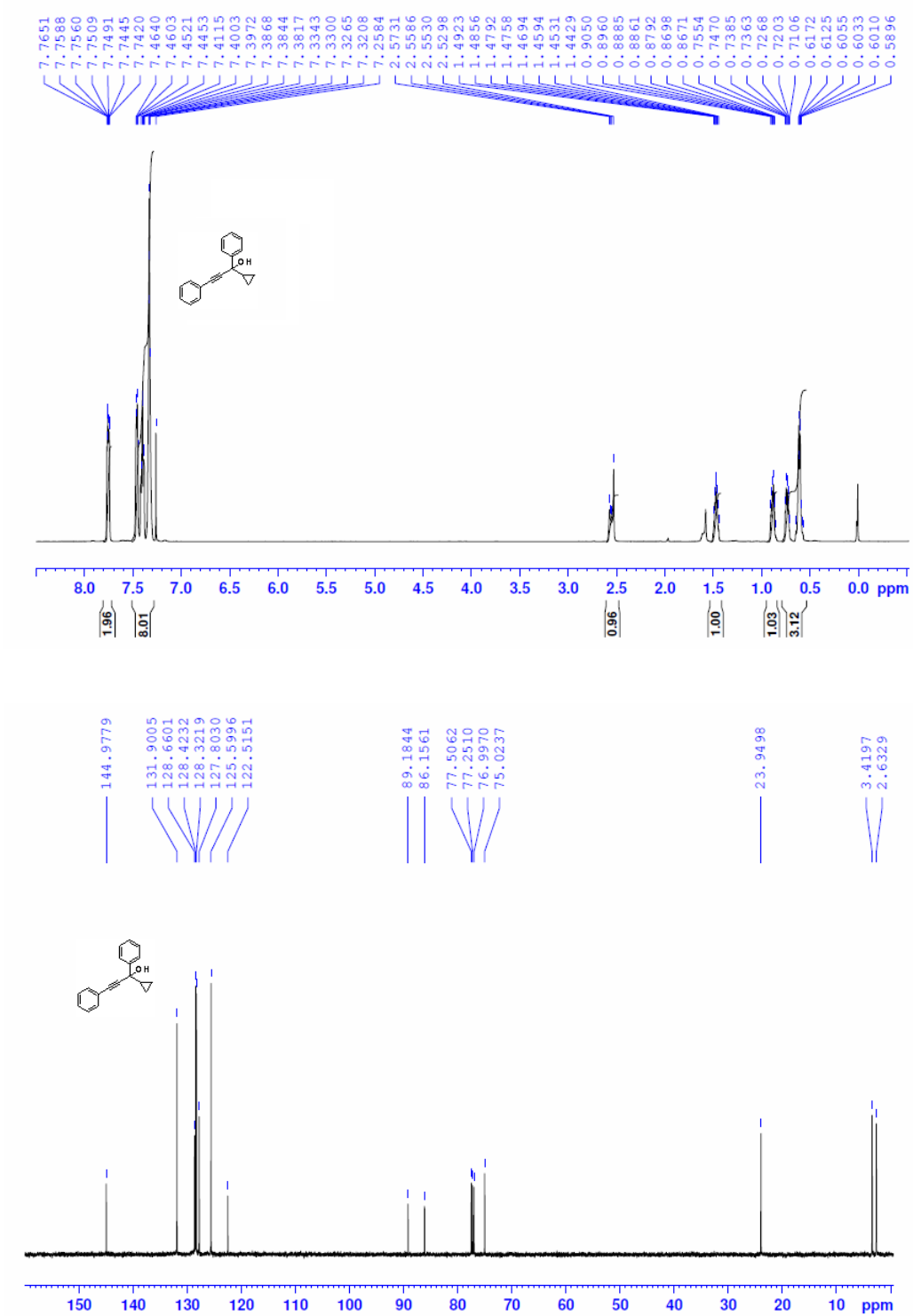
**(Z)-6-(Cyclohexyloxy)-1,3-diphenylhex-3-en-1-yne (3 $\iota$ ):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.73-7.70 (m, 2H), 7.59-7.54 (m, 2H), 7.42-7.31 (m, 6H), 6.58 (t, 1H,  $J = 7.3$  Hz), 3.69 (t, 2H,  $J = 6.7$  Hz), 3.36-3.29 (m, 1H), 2.90 (q, 2H,  $J = 6.9$  Hz), 2.00-1.97 (m, 2H), 1.79-1.78 (m, 2H), 1.58-1.55 (m, 1H), 1.41-1.24 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  138.1, 135.0, 131.5, 128.4, 128.3, 128.2, 127.6, 126.0,

124.7, 123.4, 95.5, 86.7, 76.6, 66.7, 32.5, 32.3, 25.8, 24.2; IR (neat,  $\text{cm}^{-1}$ ): 3419, 3018, 2399, 1647, 1419, 1215, 927 756, 669; HRMS (ESI): calcd for  $\text{C}_{24}\text{H}_{27}\text{O}$  331.2062, found 331.2072.

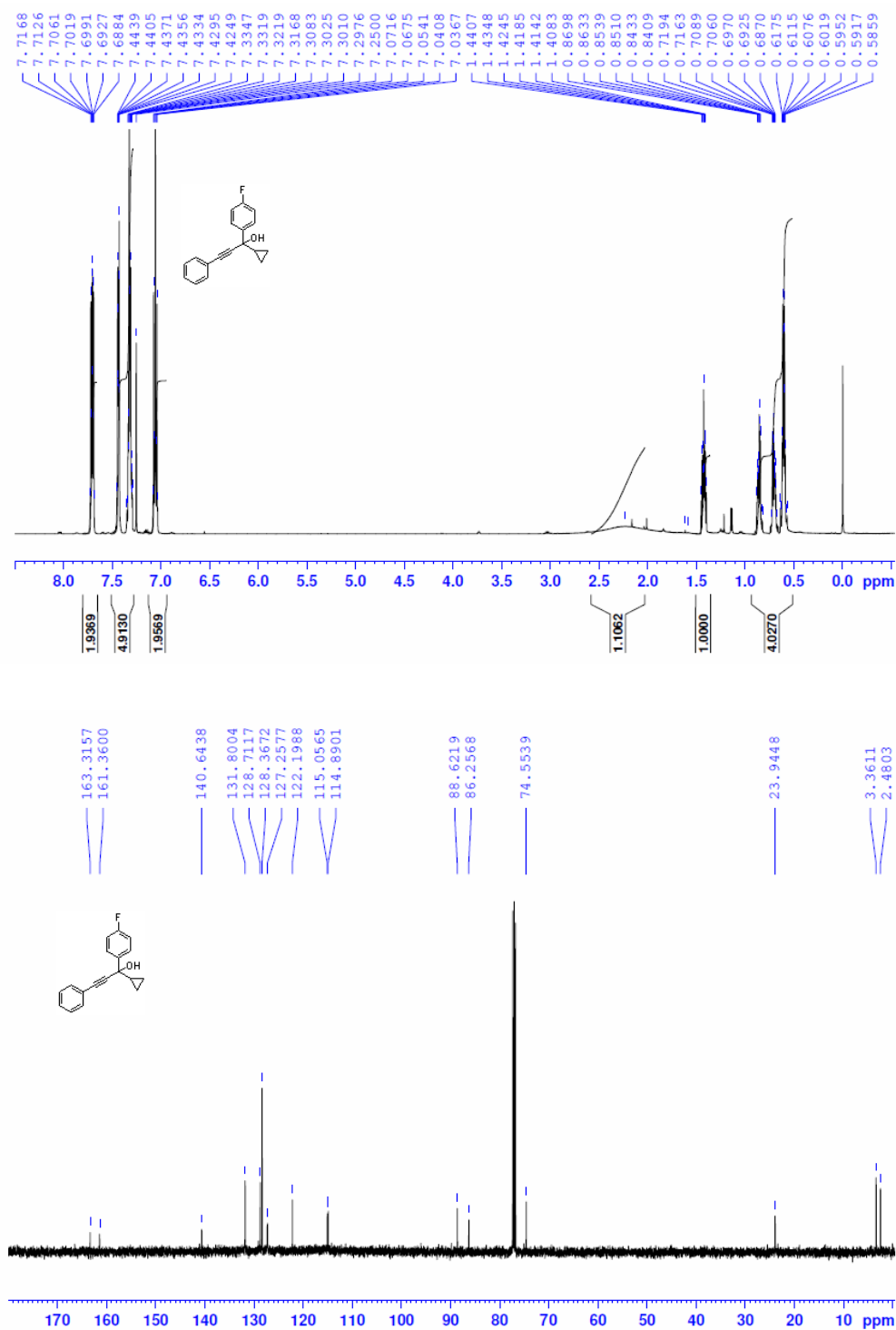
**(Z)-Pentadec-6-en-8-yn-7-ylcyclopropane (4):** Pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.71 (t, 1H,  $J = 7.3$  Hz), 2.32-2.18 (m, 4H), 1.54-1.24 (m, 15H), 0.90-0.86 (m, 6H), 0.65-0.53 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  134.4, 125.2, 94.5, 75.7, 31.5, 31.3, 30.4, 29.0, 28.9, 28.4, 22.59, 22.56, 19.3, 16.2, 14.0, 5.3, 4.9; IR (neat,  $\text{cm}^{-1}$ ): 3421, 3018, 2928, 2358, 1634, 1215, 1109, 757, 669; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{31}$  247.2426, found 247.2437.

**(3-Cyclopropyl-3-ethoxyprop-1-ynyl)benzene (5):** Light yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.43-7.24 (m, 5H), 4.12 (d, 1H,  $J = 8.4$  Hz), 3.90-3.80 (m, 1H), 3.59-3.47 (m, 1H), 1.29-1.18 (m, 4H), 0.59-0.45 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  131.7, 131.4, 128.29, 128.24, 122.7, 86.5, 85.5, 73.2, 64.1, 15.2, 15.1, 3.1, 1.9; IR (neat,  $\text{cm}^{-1}$ ): 3439, 3019, 1490, 1215, 1077, 753, 691, 667; HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{17}\text{O}$  201.1279, found 201.1273.

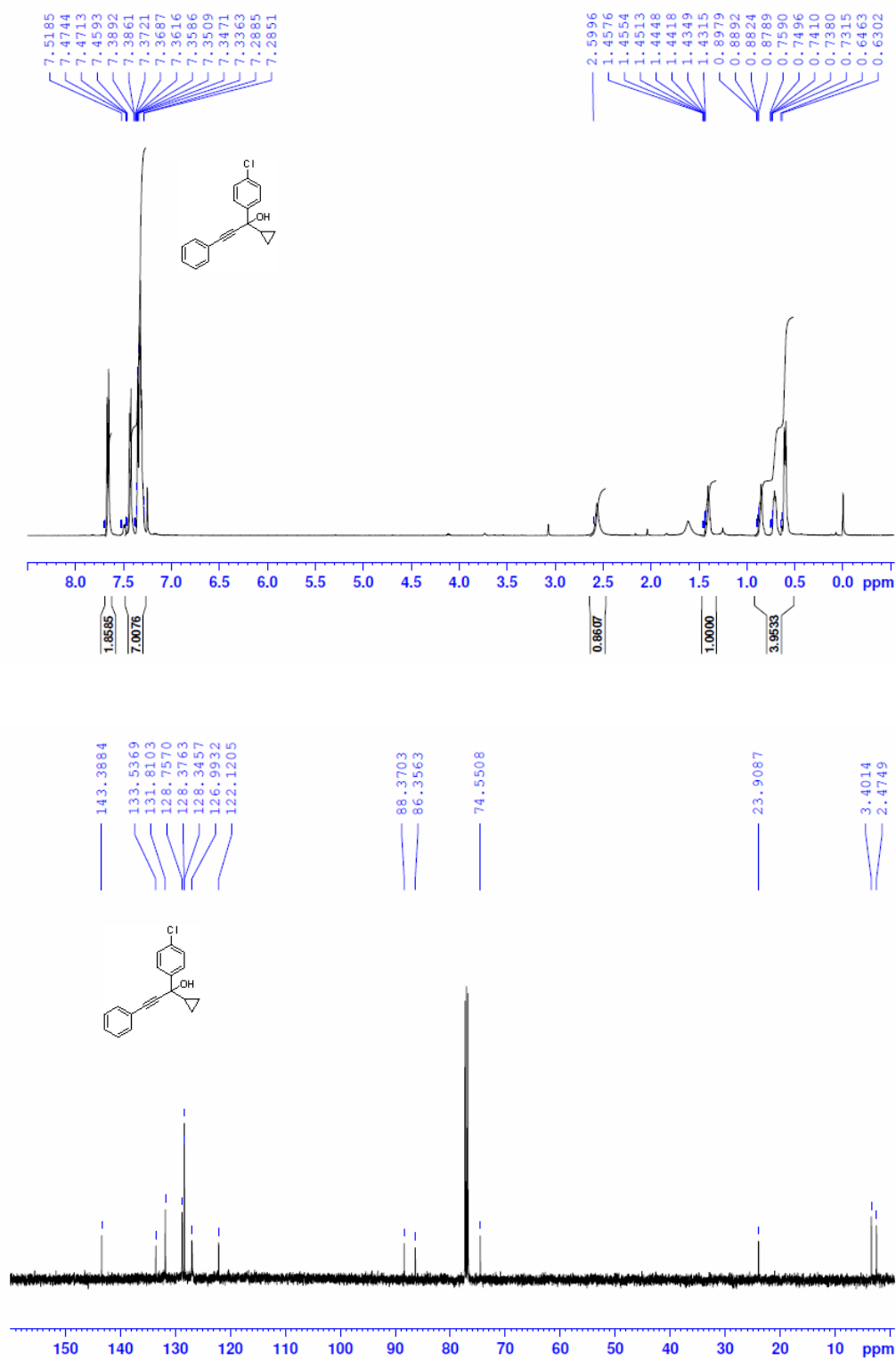
**Figure S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Cyclopropyl-1,3-diphenylprop-2-yn-1-ol (**1a**)<sup>S2</sup>



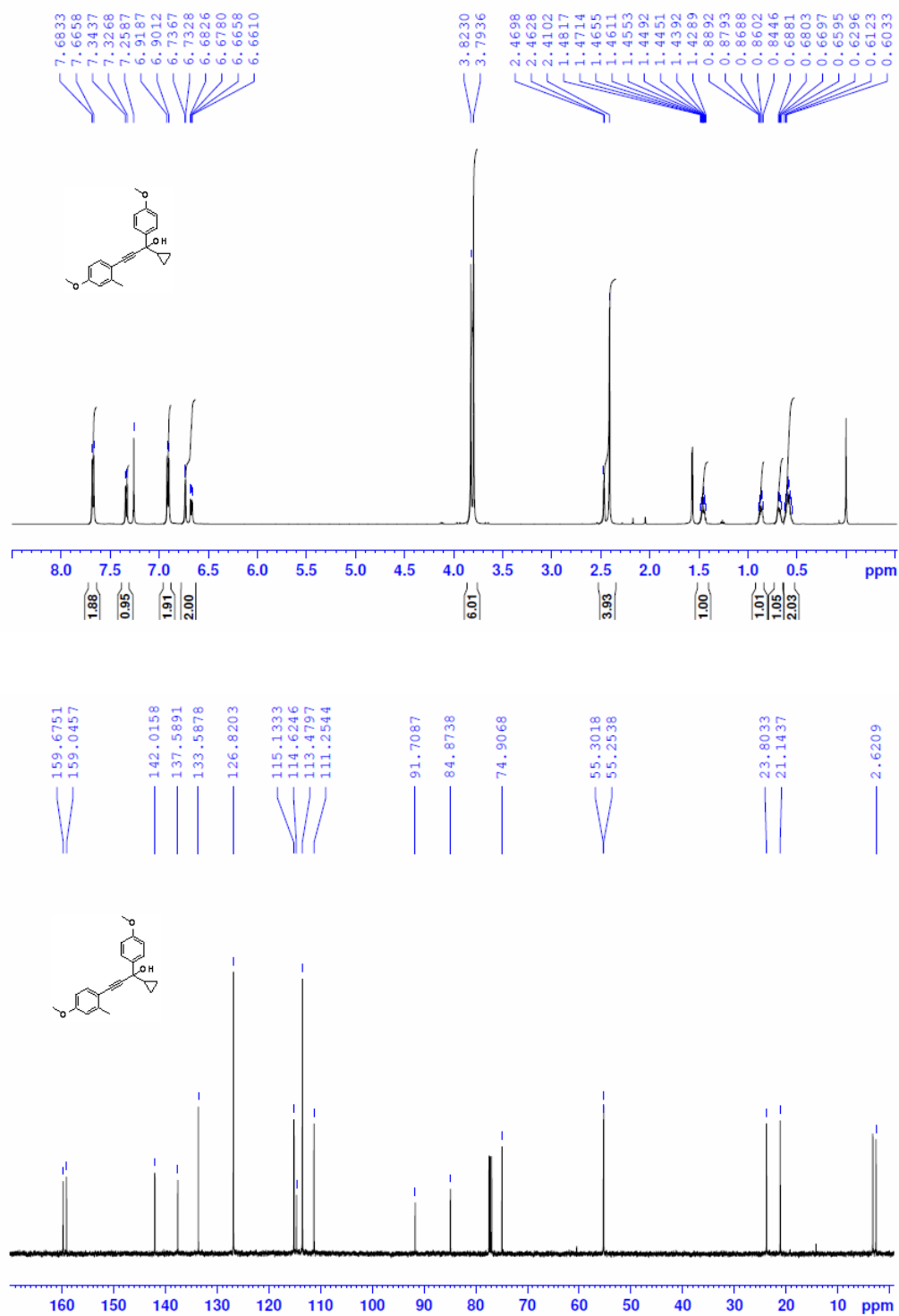
**Figure S2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-1-(4-fluorophenyl)-3-phenyl prop-2-yn-1-ol (**1b**)<sup>S2</sup>



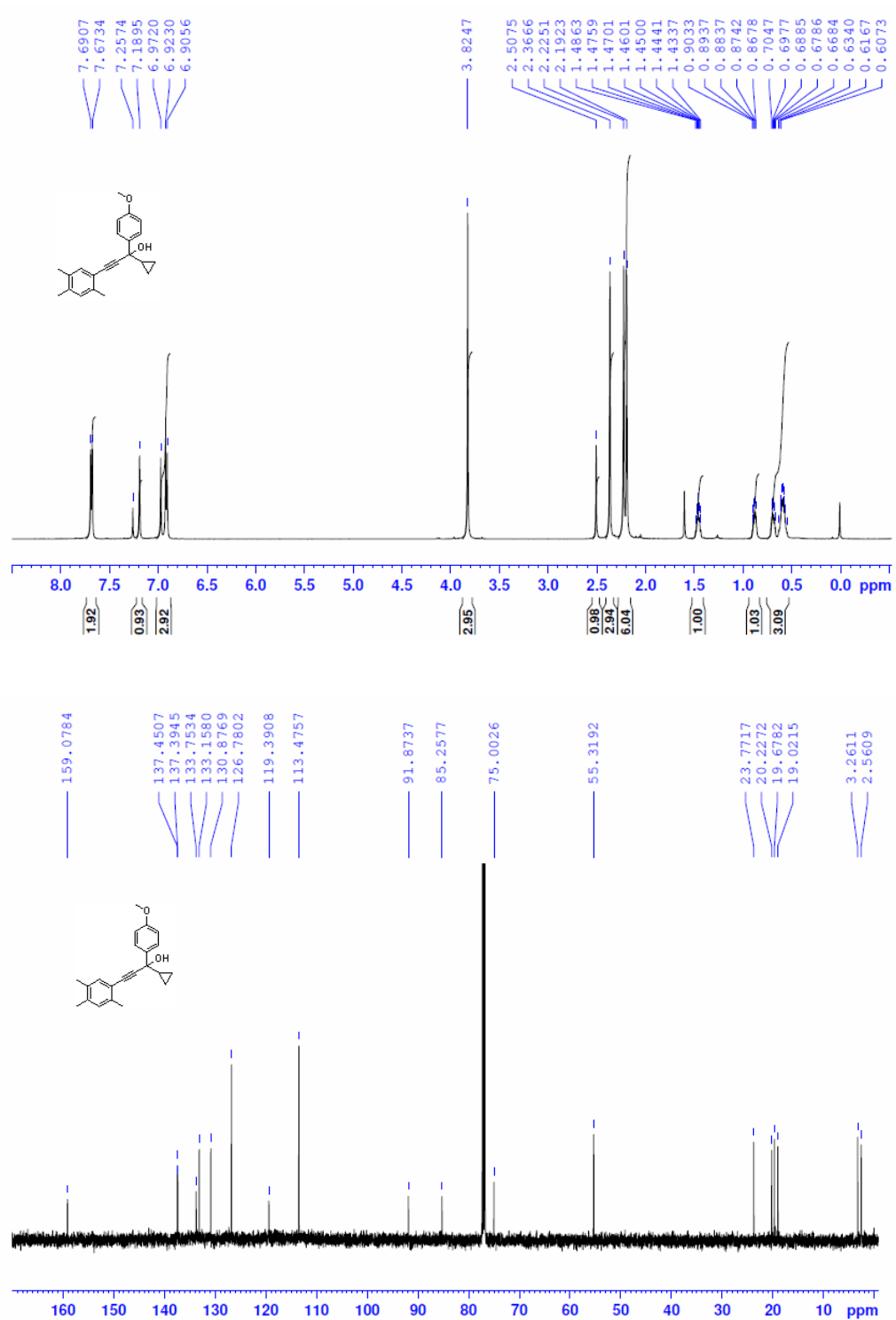
**Figure S3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-(4-Chlorophenyl)-1-cyclopropyl-3-phenylprop-2-yn-1-ol (**1c**)<sup>S2</sup>



**Figure S4.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-3-(4-methoxy-2-methylphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (**1d**)

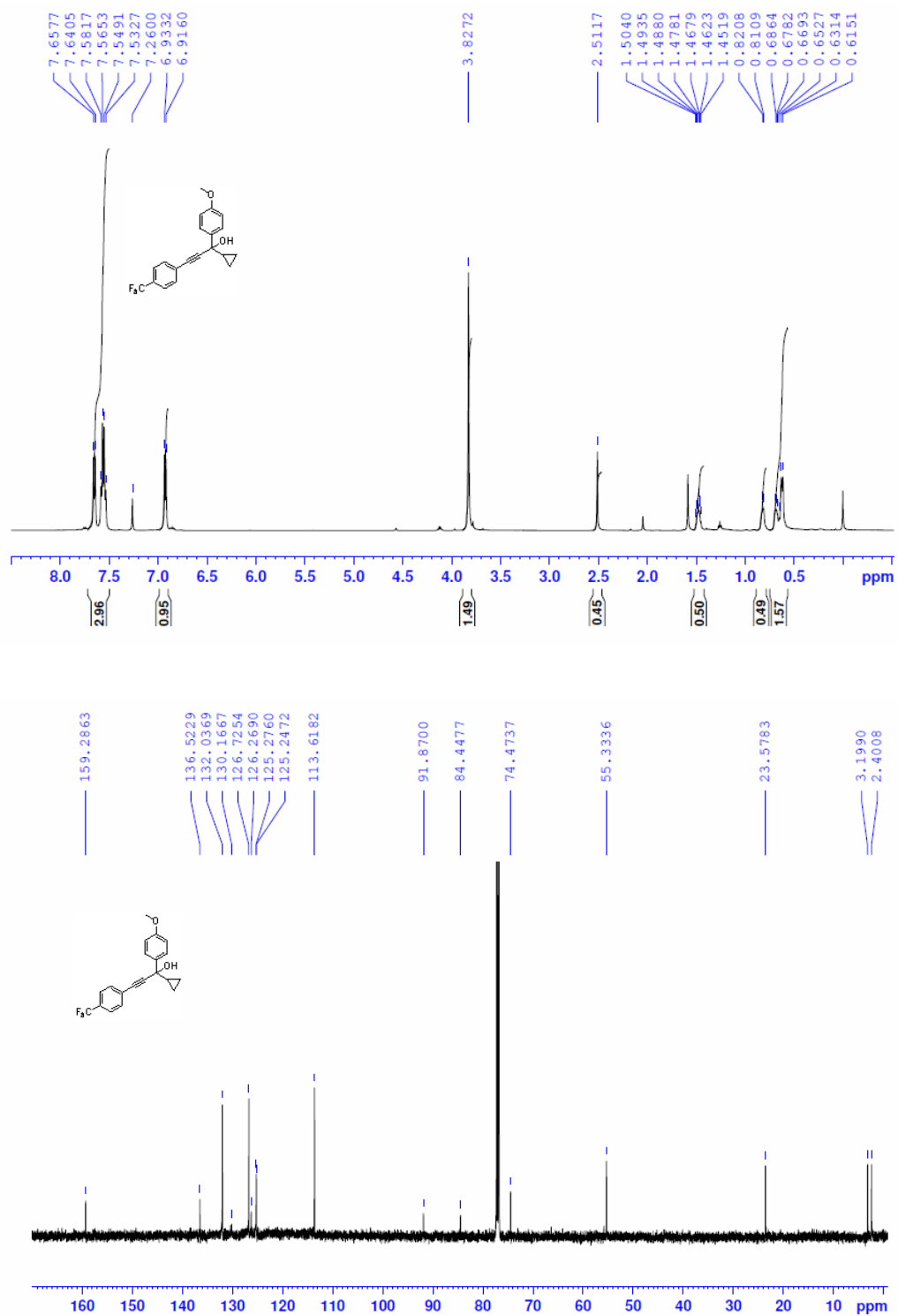


**Figure S5.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-1-(4-methoxyphenyl)-3-(2,4,5-trimethylphenyl)prop-2-yn-1-ol (**1e**)

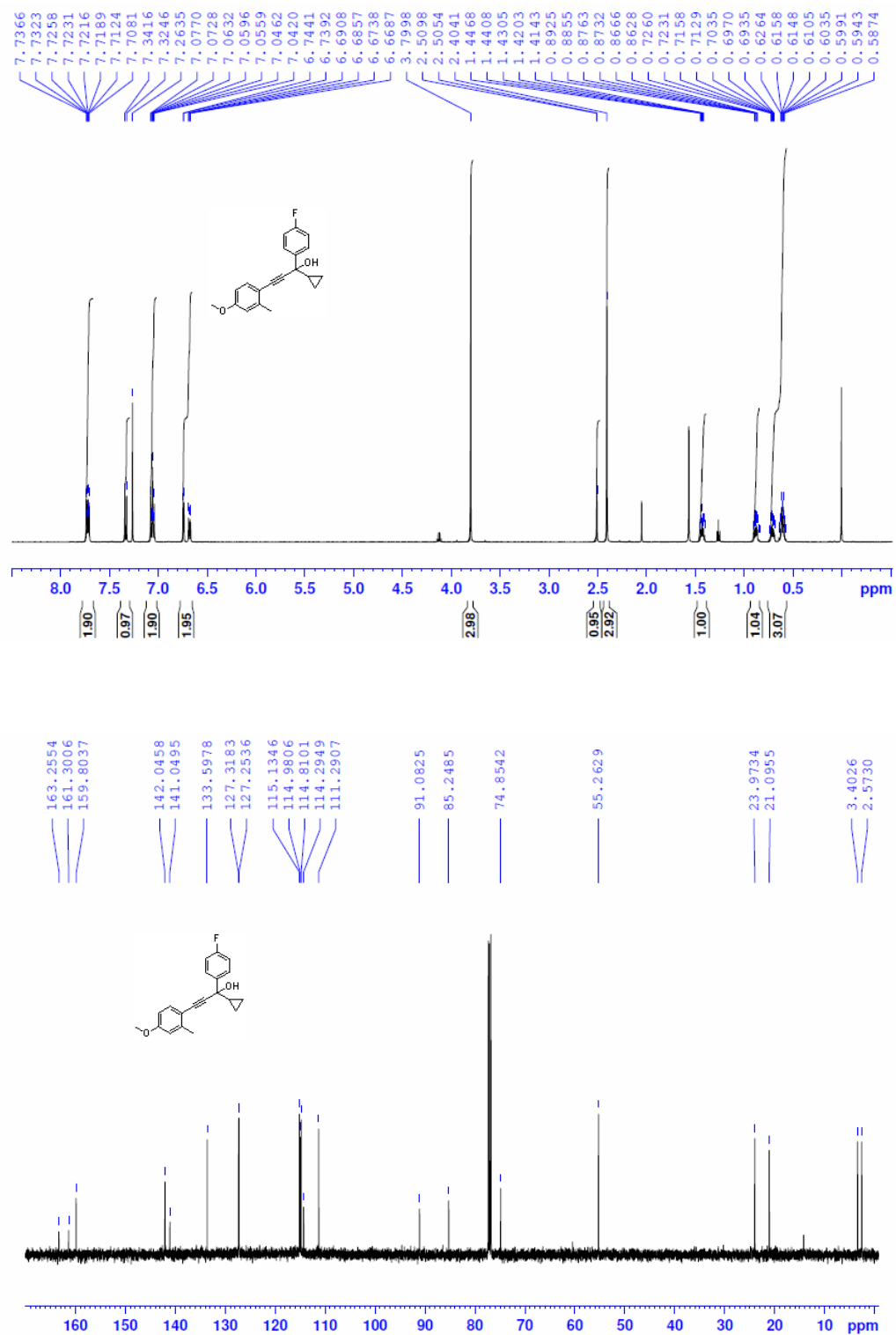




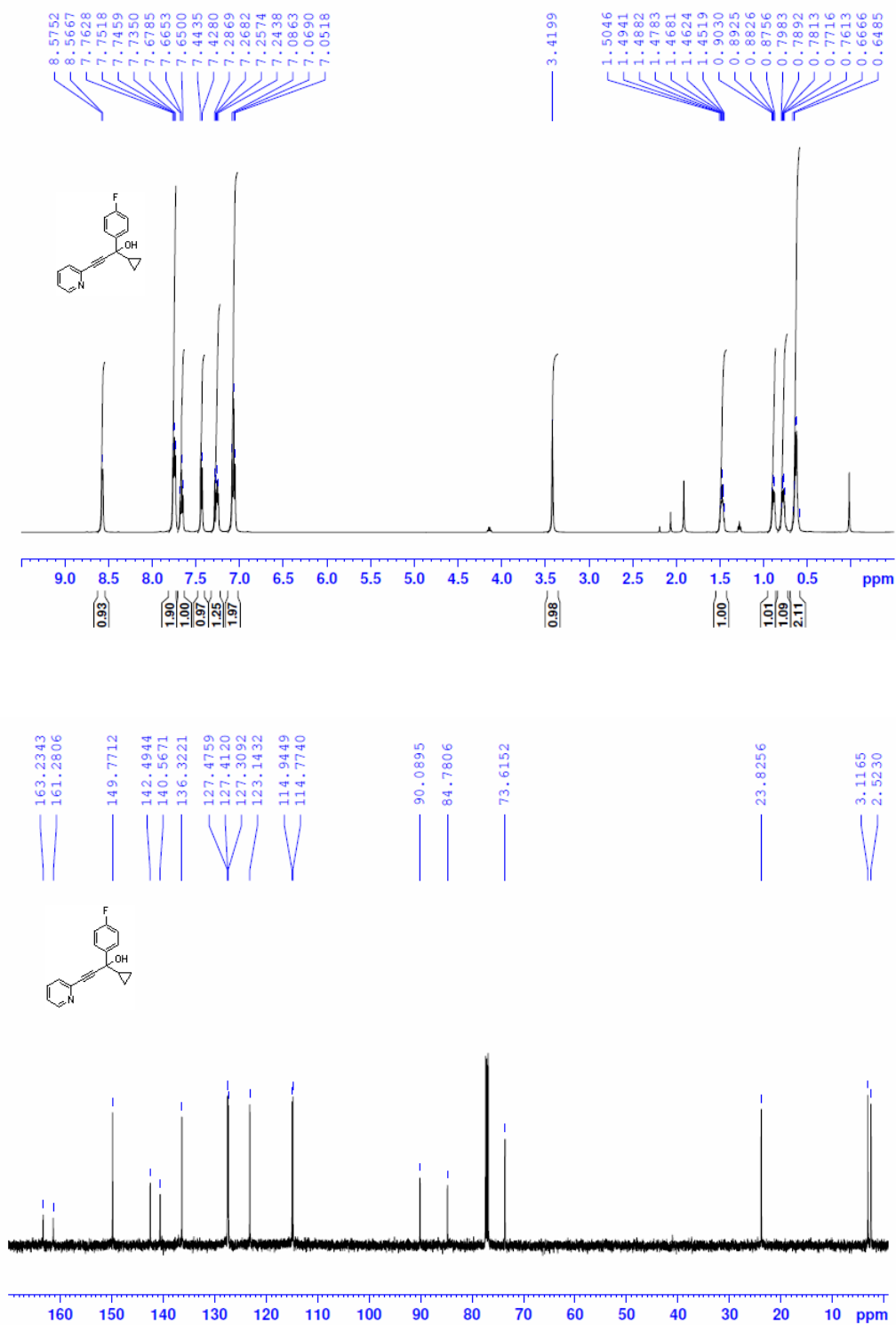
**Figure S6.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-3-(4-(trifluoromethyl)phenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (**1f**)



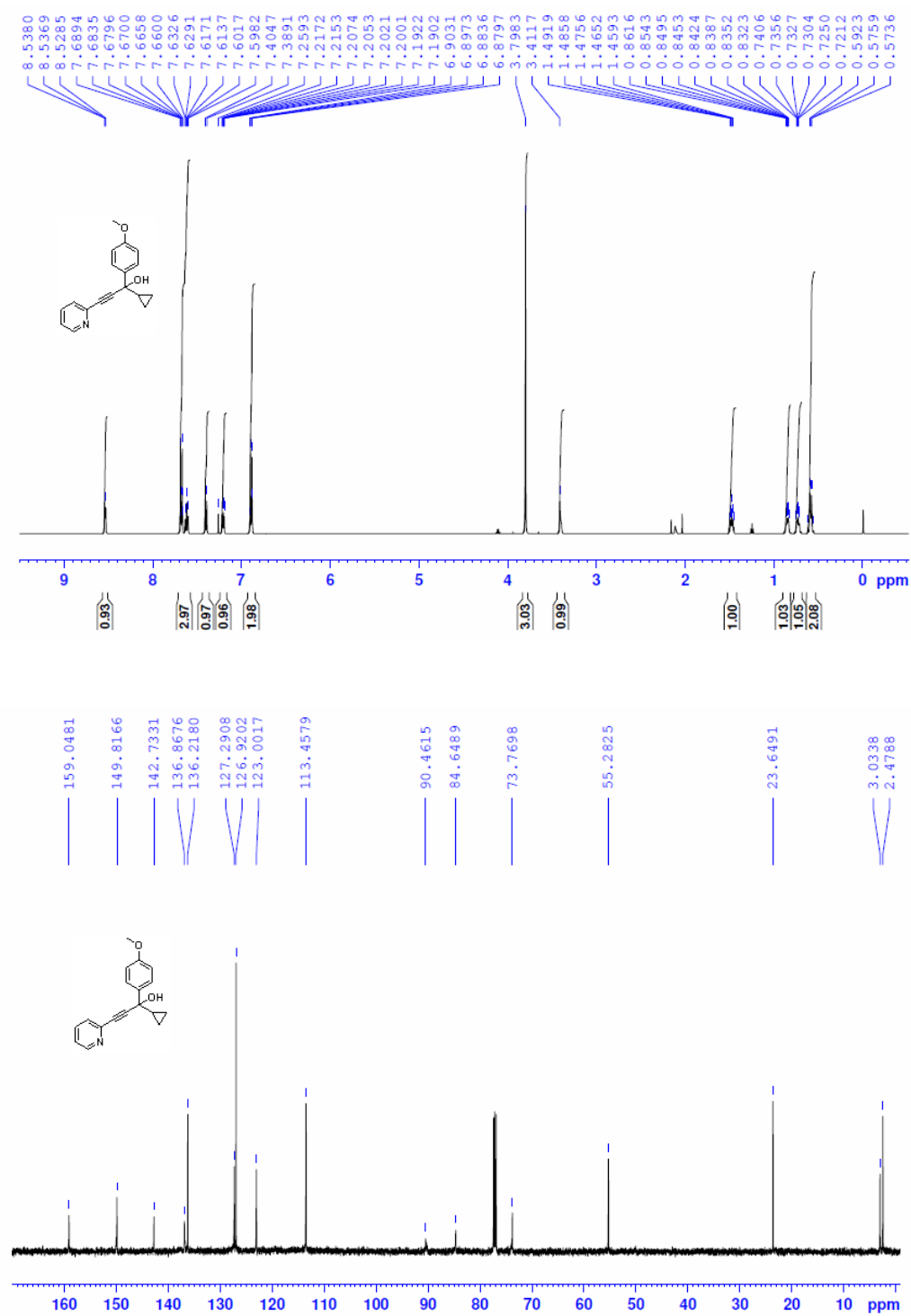
**Figure S7.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-1-(4-fluorophenyl)-3-(4-methoxy-2-methylphenyl)prop-2-yn-1-ol (**1g**)



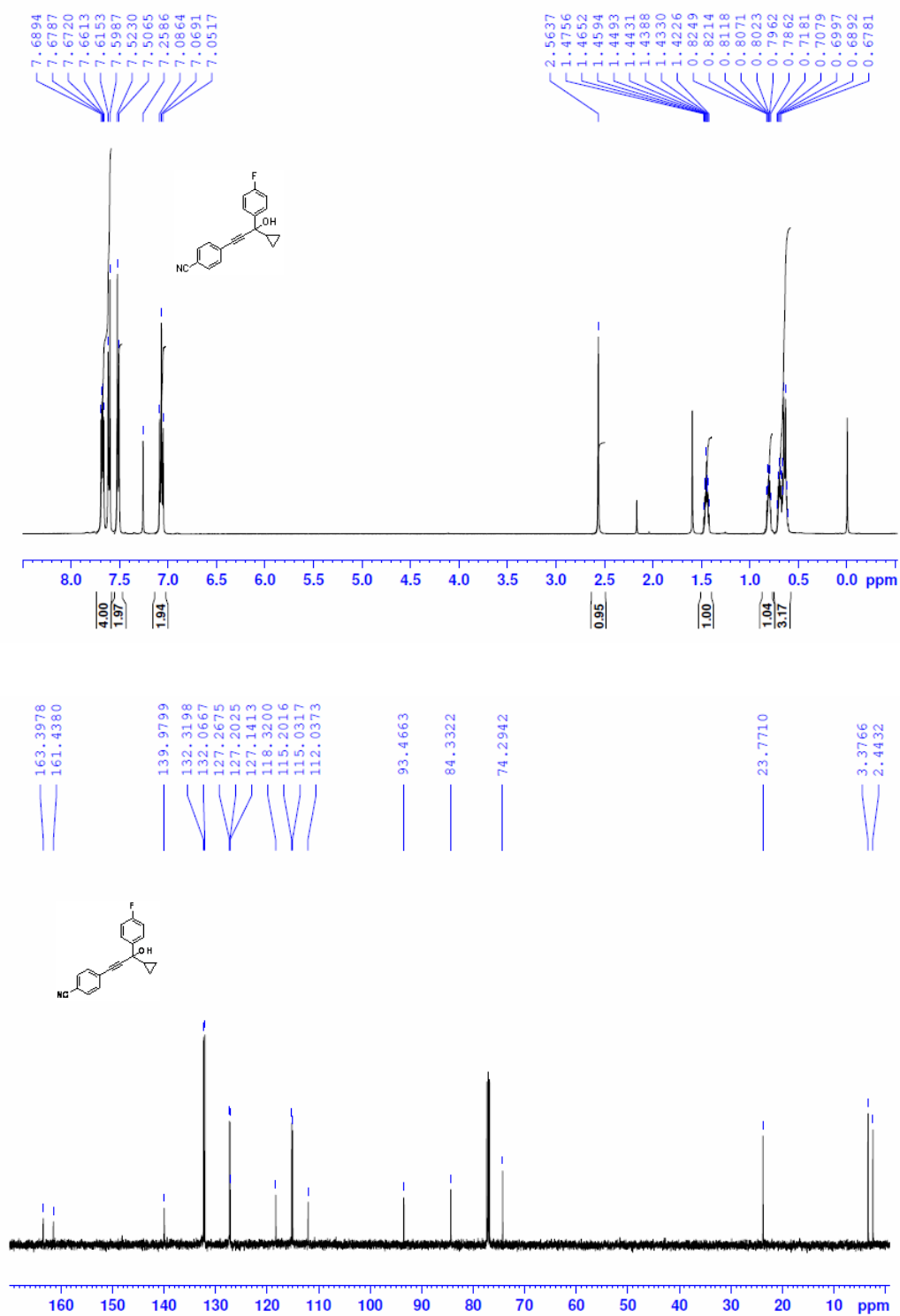
**Figure S8.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-1-(4-fluorophenyl)-3-(pyridin-2-yl)prop-2-yn-1-ol (**1h**)



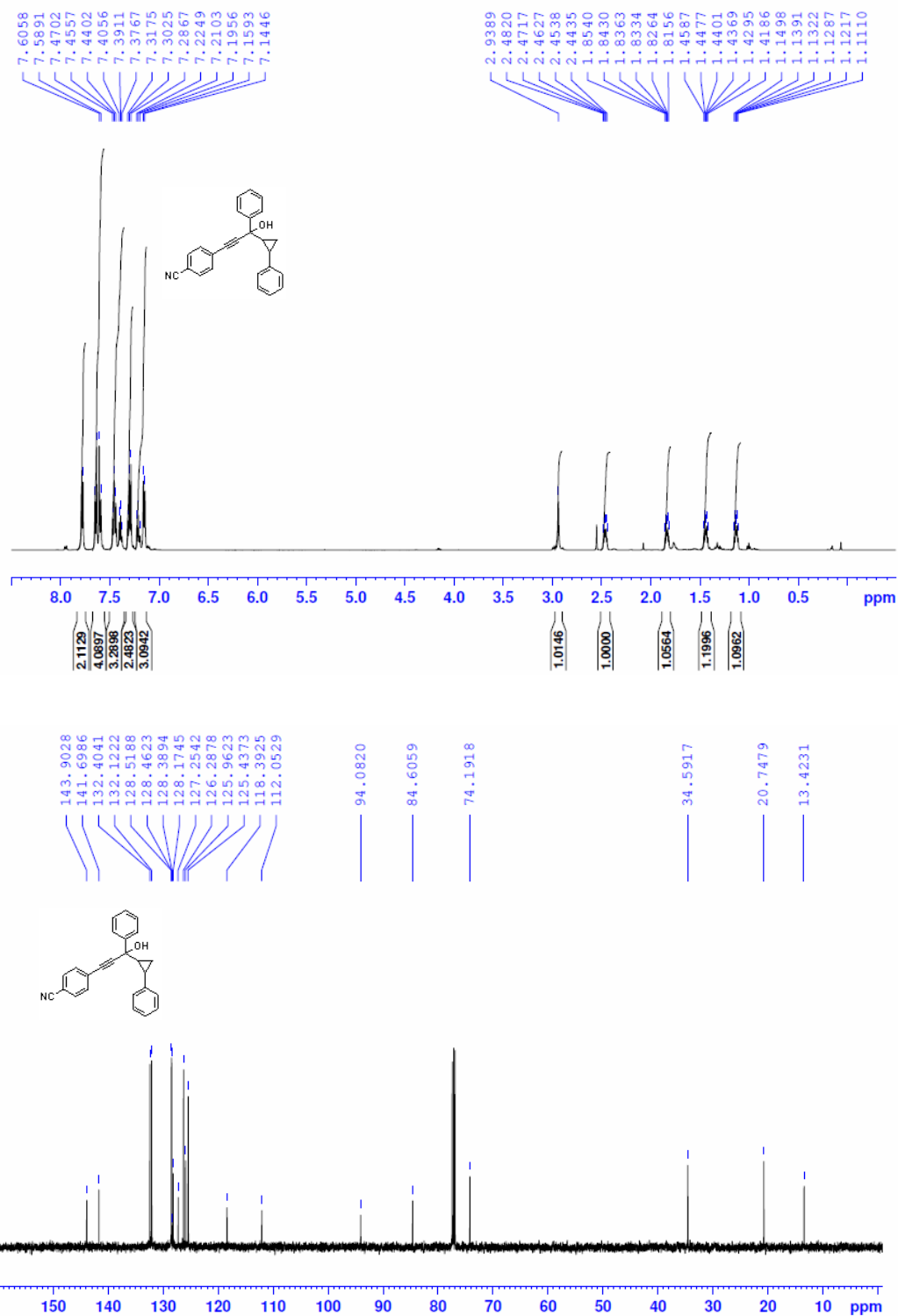
**Figure S9.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-1-(4-methoxyphenyl)-3-(pyridin-2-yl)prop-2-yn-1-ol (**1i**)



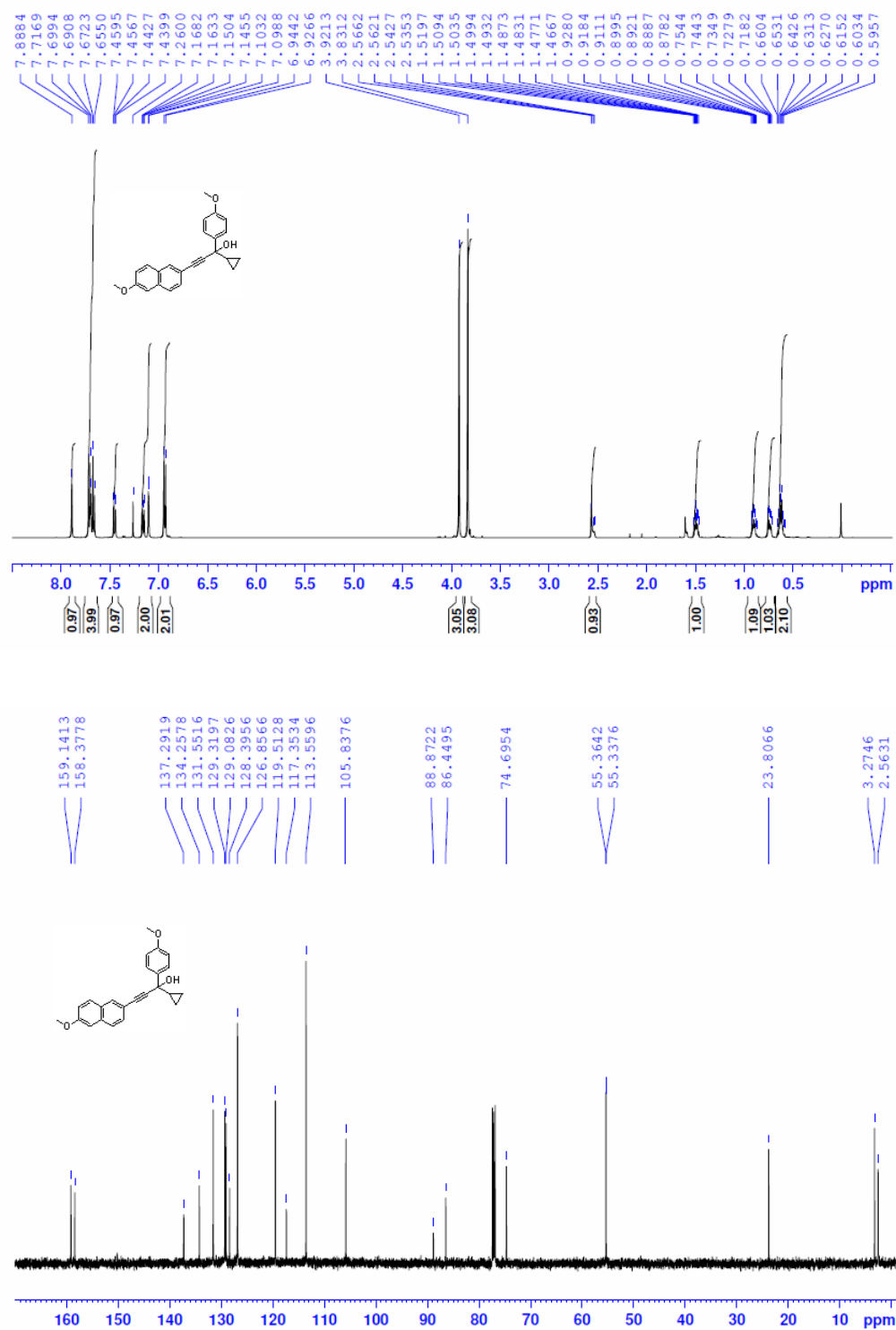
**Figure S10.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 4-(3-Cyclopropyl-3-(4-fluorophenyl)-3-hydroxyprop-1-ynyl)benzonitrile (**1j**)



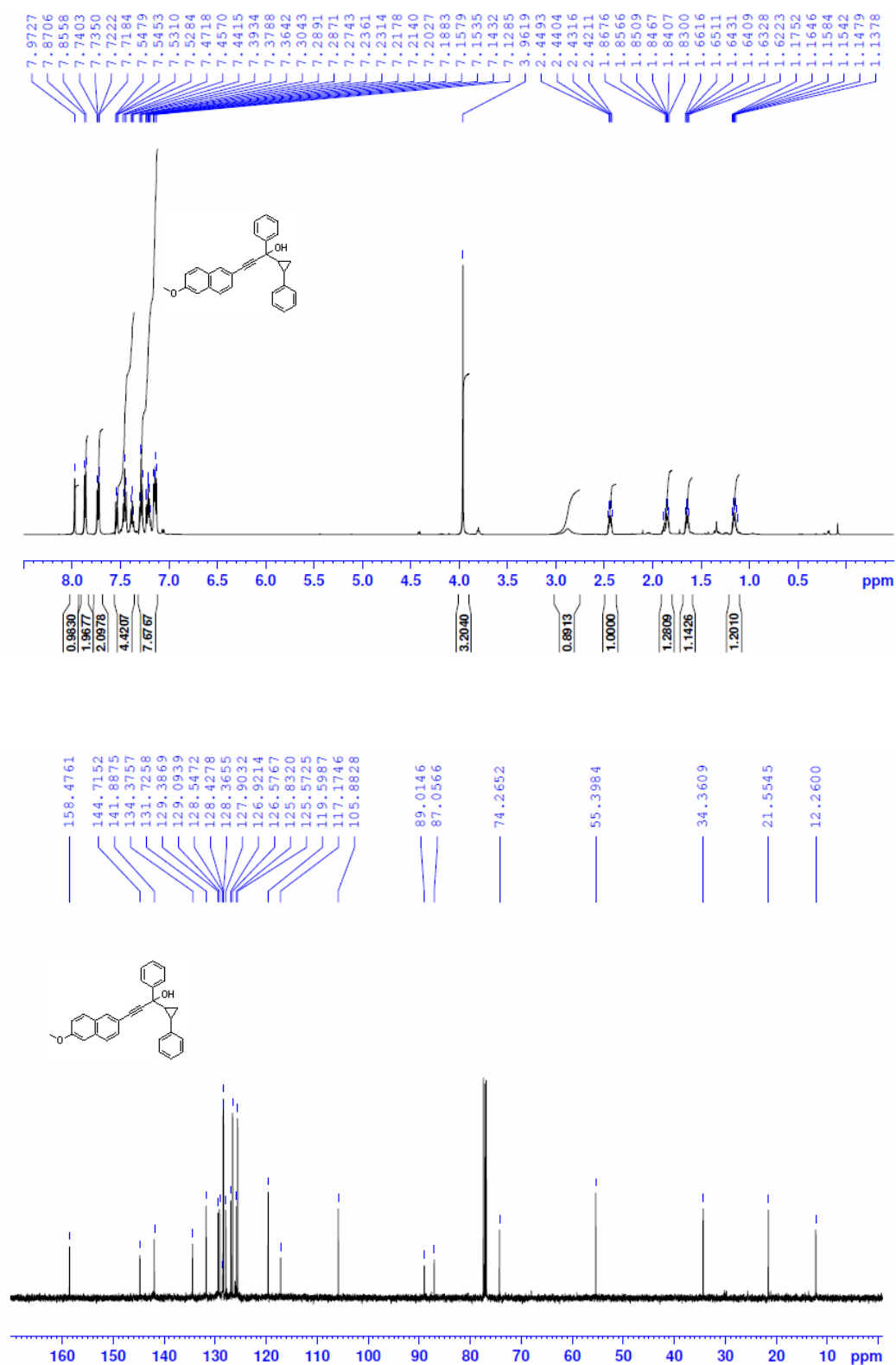
**Figure S11.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 4-(3-Hydroxy-3-phenyl-3-(2-phenylcyclopropyl)prop-1-ynyl)benzonitrile (**1k**)



**Figure S12.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-3-(2-methoxynaphthalen-6-yl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (**II**)

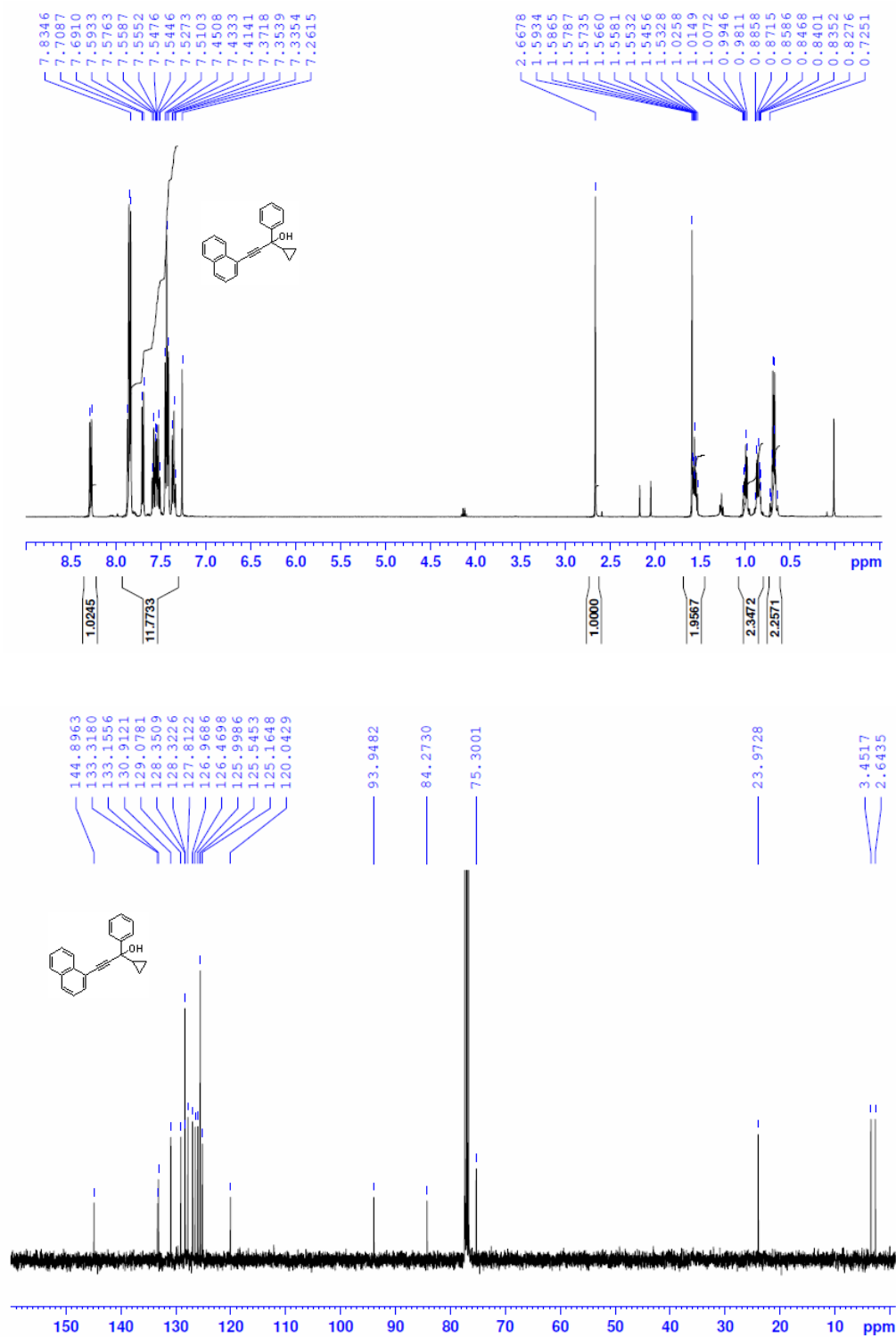


**Figure S13.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 3-(2-Methoxynaphthalen-6-yl)-1-phenyl-1-(2-phenylcyclopropyl)prop-2-yn-1-ol (**1m**)

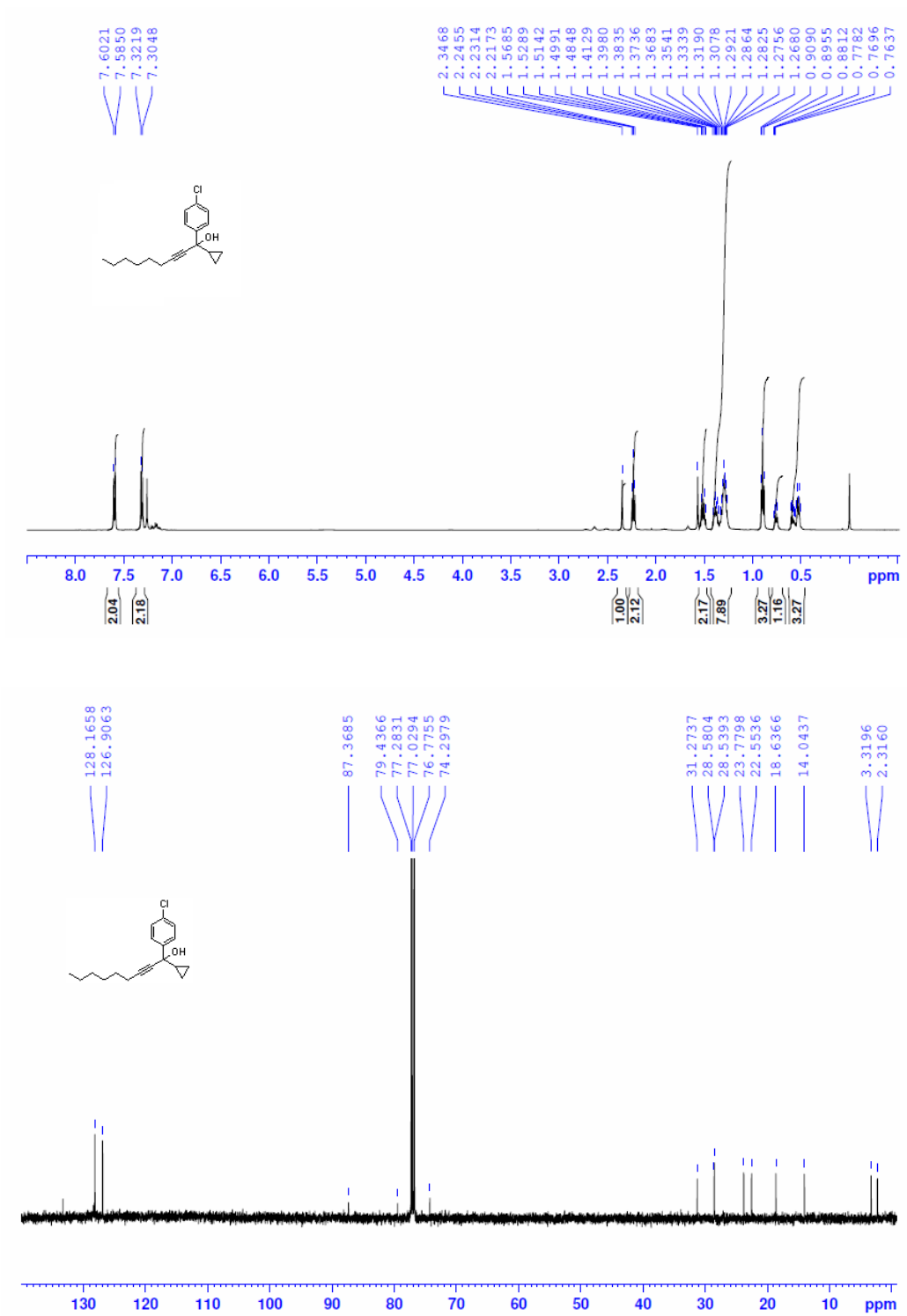




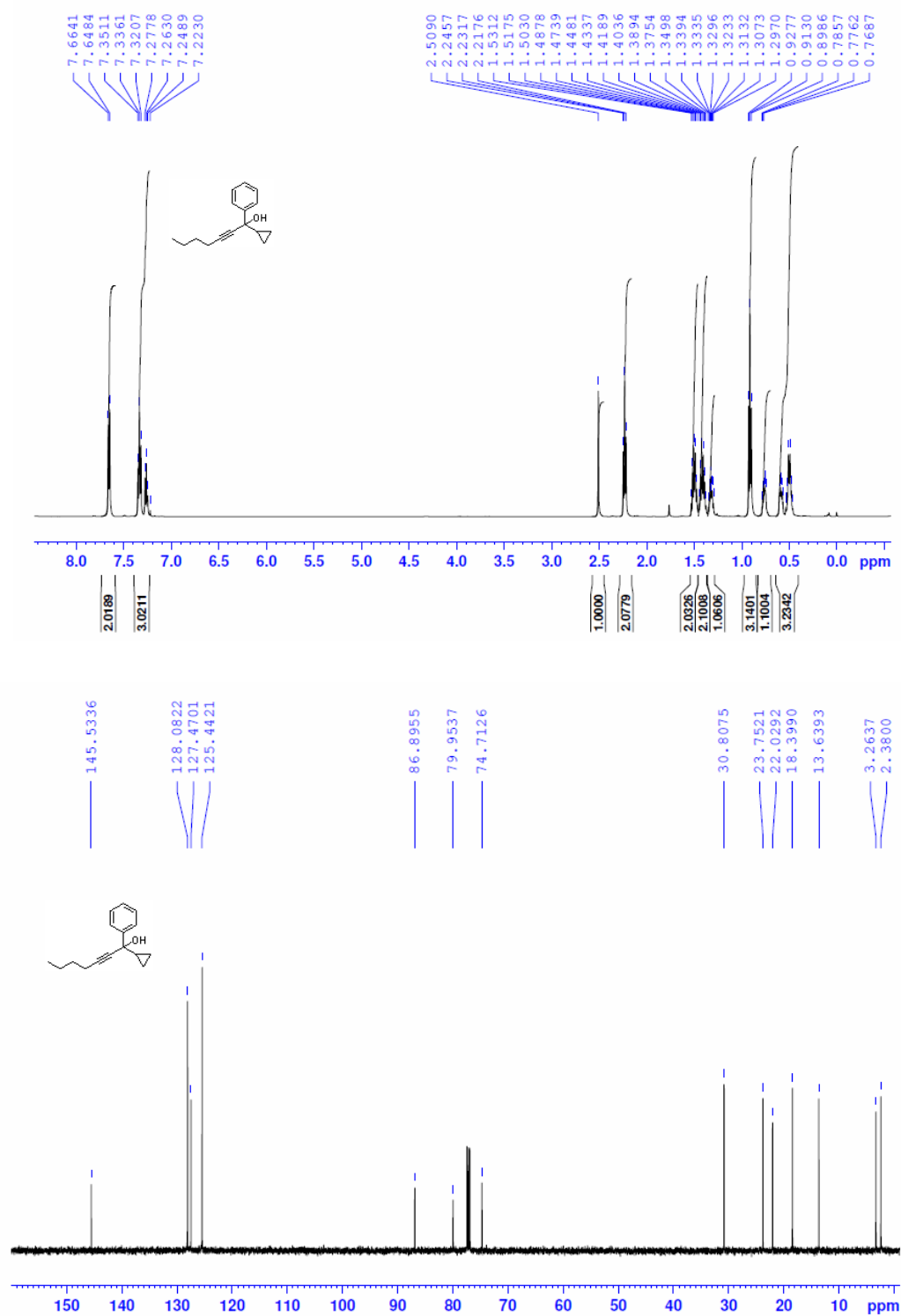
**Figure S14.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-3-(naphthalen-1-yl)-1-phenylprop-2-yn-1-ol (**1n**)



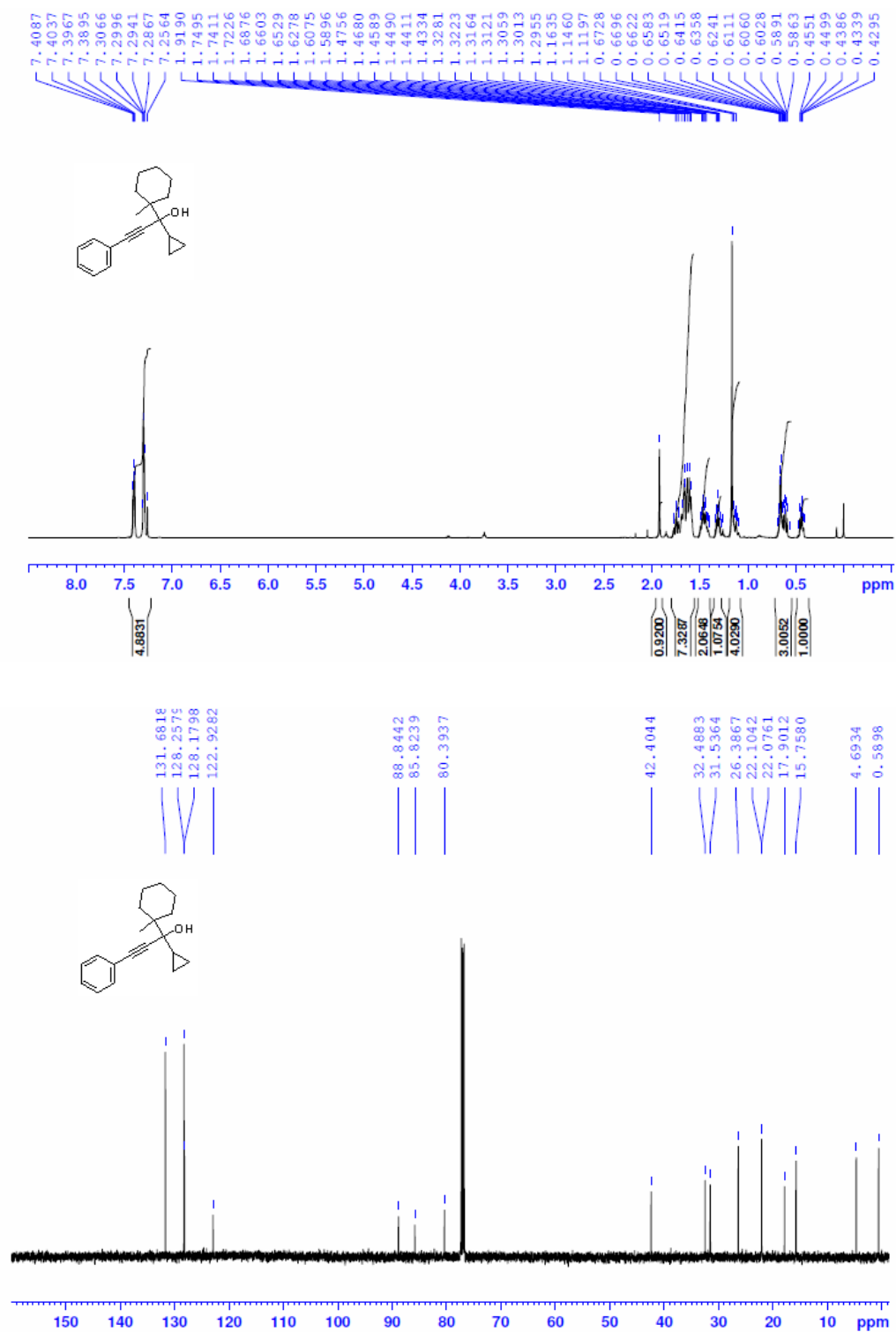
**Figure S15.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-(4-Chlorophenyl)-1-cyclopropylnon-2-yn-1-ol (**1o**)



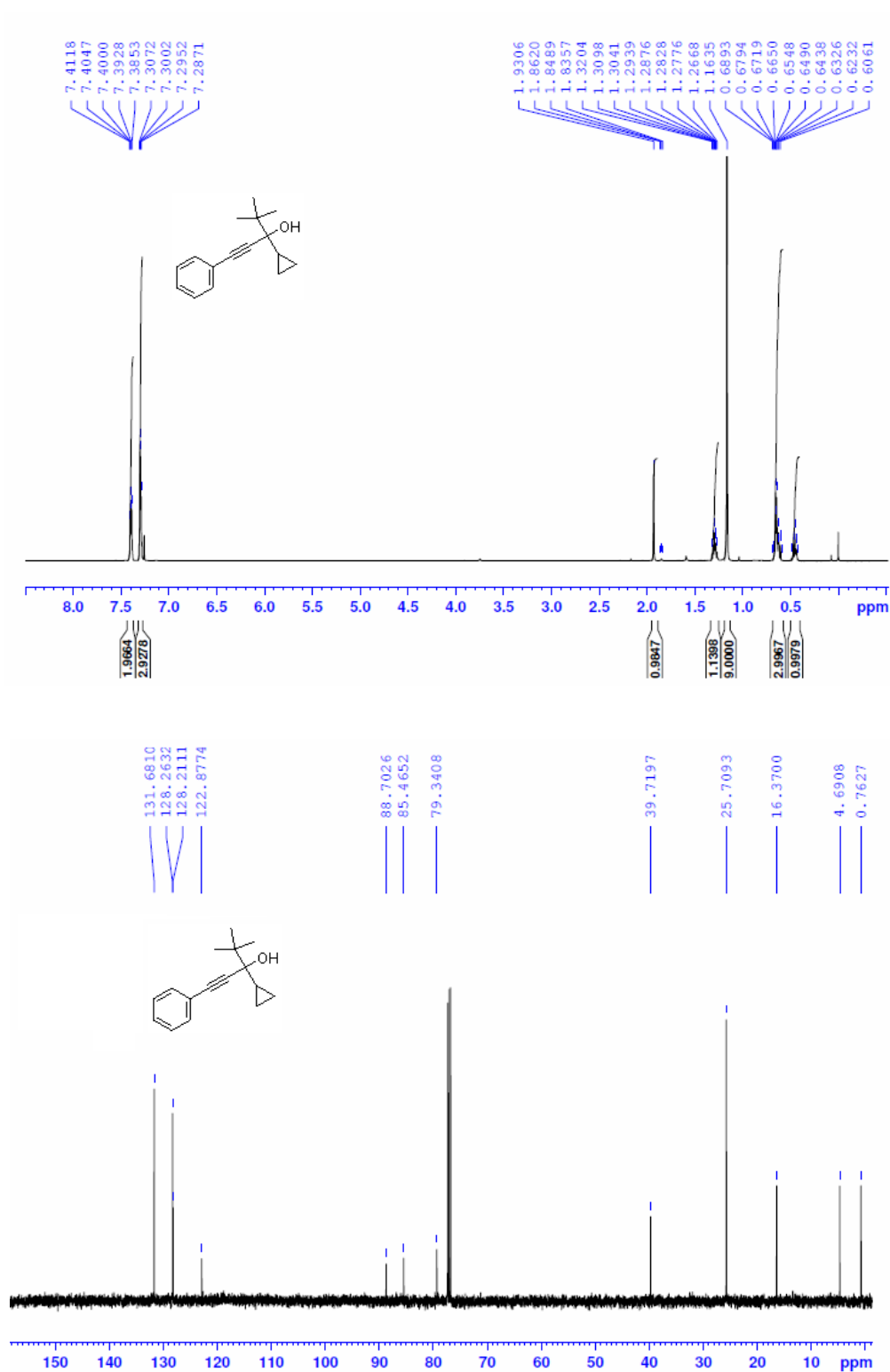
**Figure S16.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-1-phenylhept-2-yn-1-ol (**1p**)



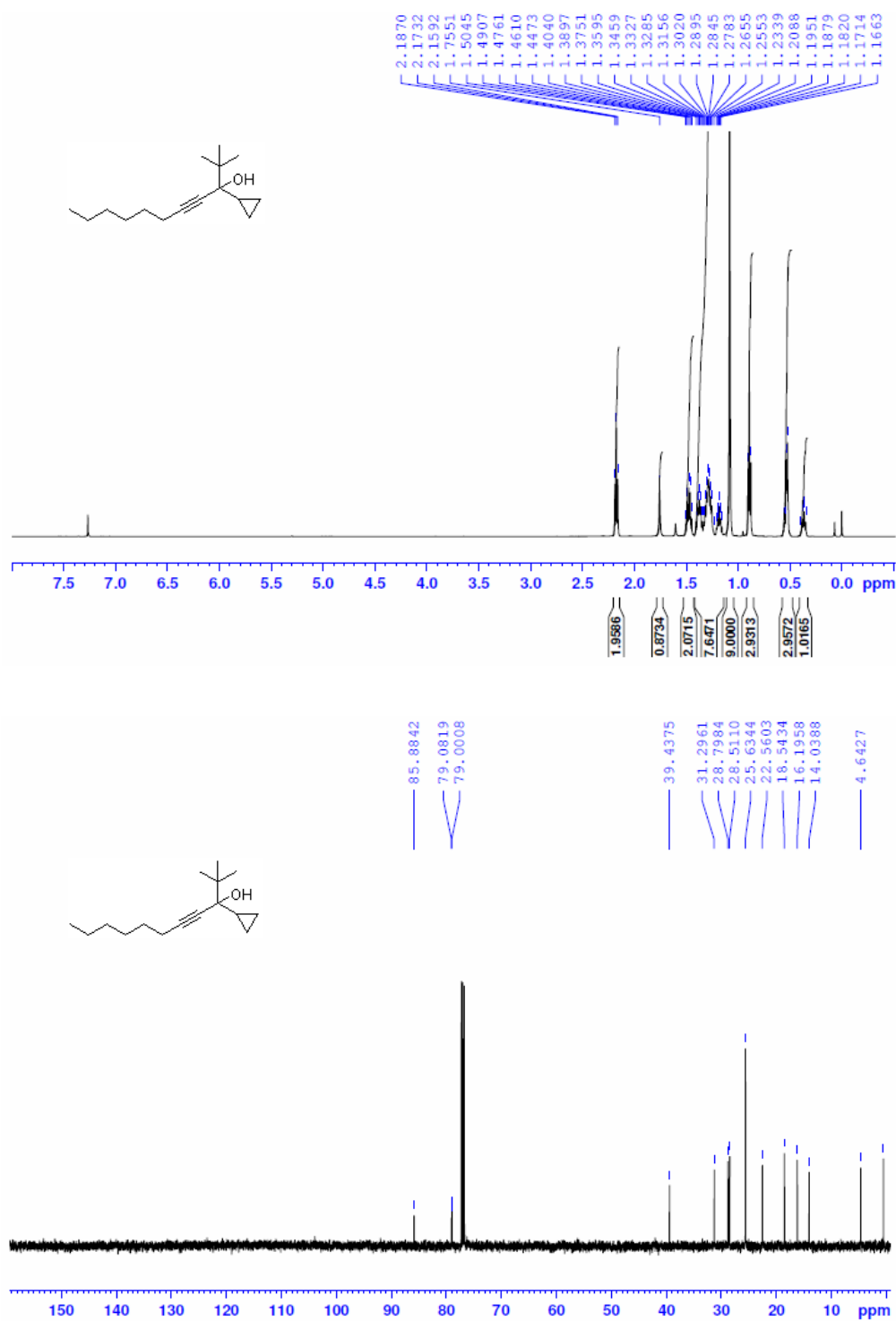
**Figure S17.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1-Cyclopropyl-1-(1-methylcyclohexyl)-3-phenylprop-2-yn-1-ol (**1q**)



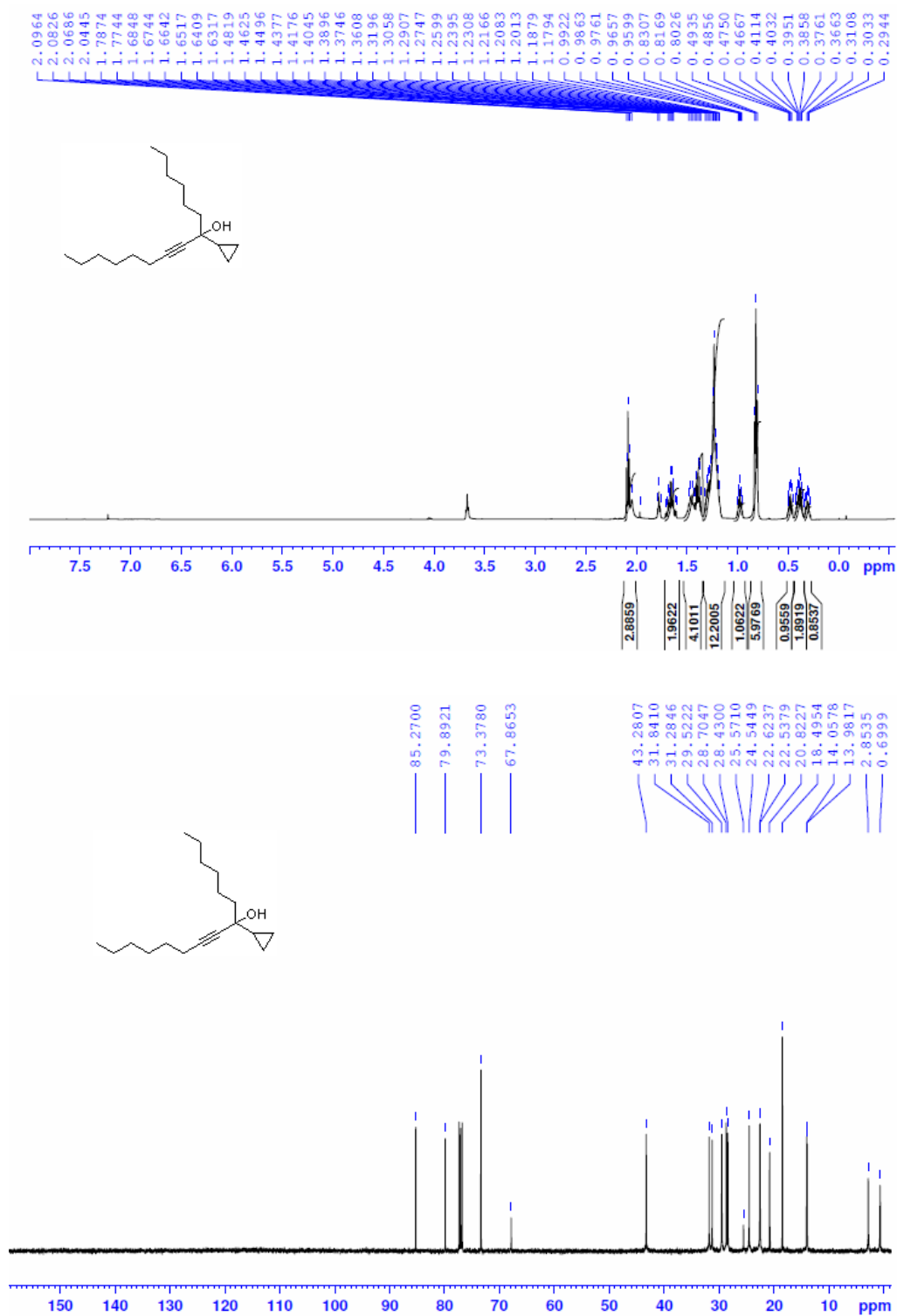
**Figure S18.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3-Cyclopropyl-4,4-dimethyl-1-phenylpent-1-yn-3-ol (**1r**)



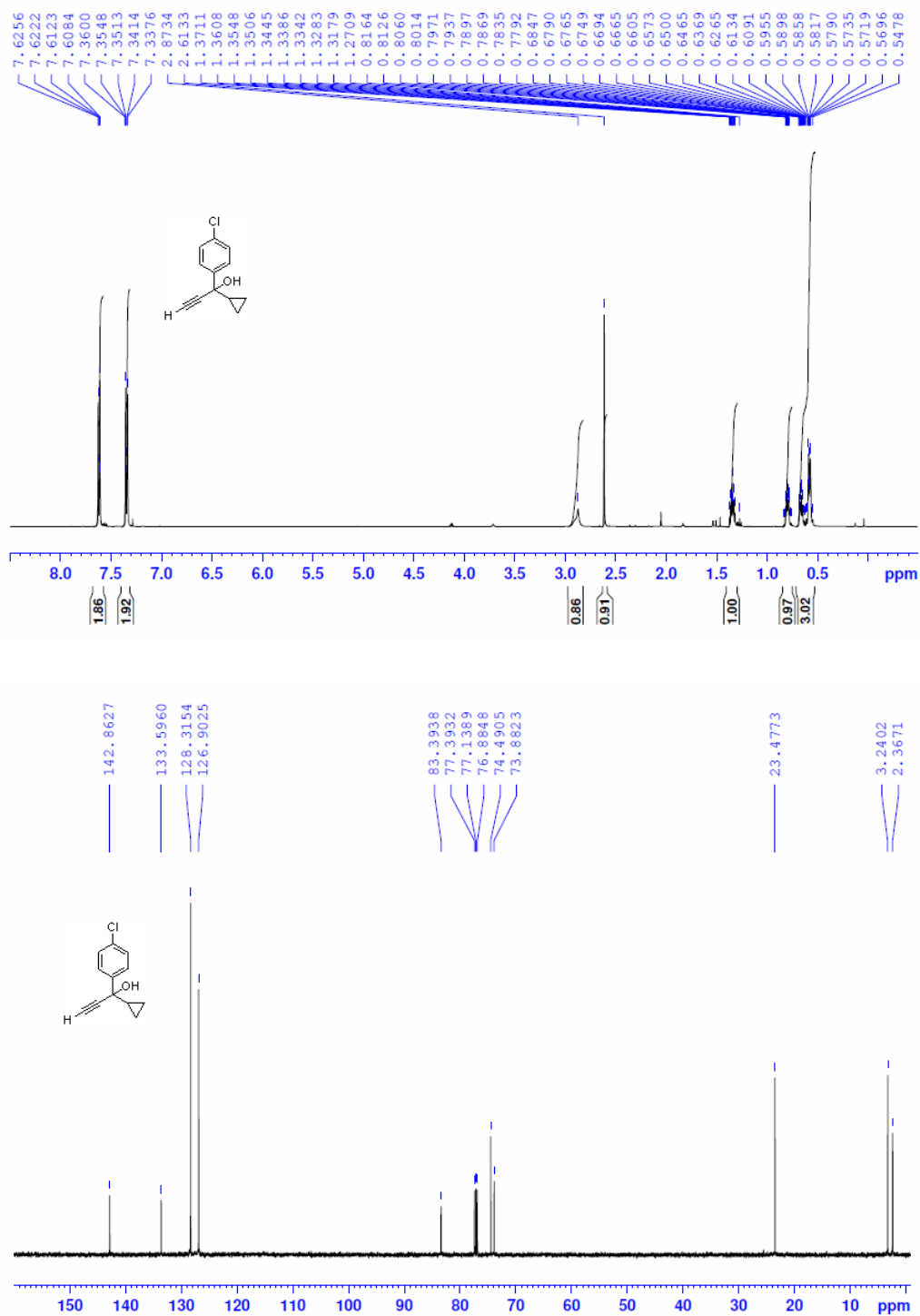
**Figure S19.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3-Cyclopropyl-2,2-dimethylundec-4-yn-3-ol (**1s**)



**Figure S20.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 7-Cyclopropylpentadec-8-yn-7-ol (**1t**)

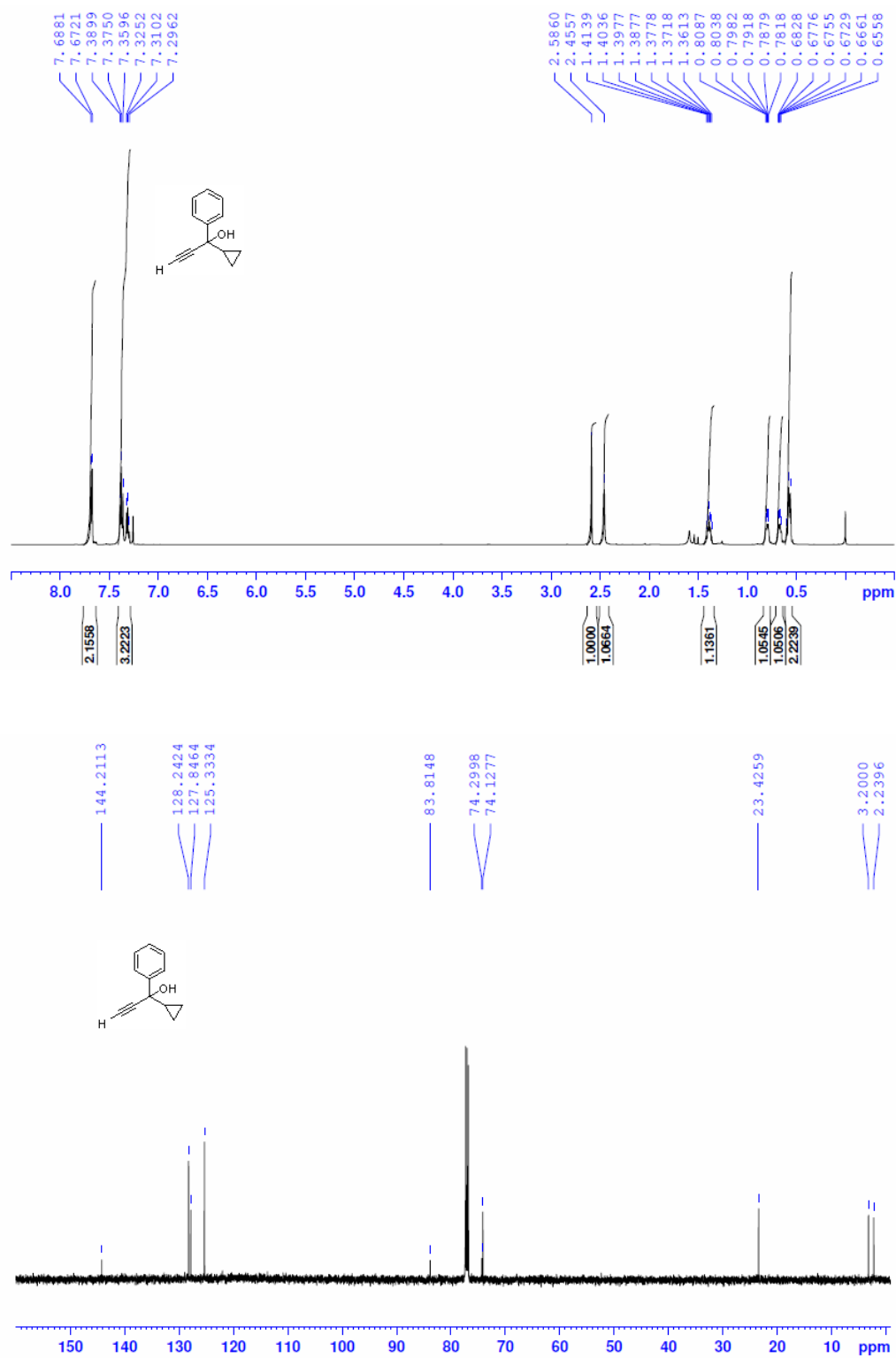


**Figure S21.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-(4-Chlorophenyl)-1-cyclopropylprop-2-yn-1-ol (**1u**)<sup>S1</sup>

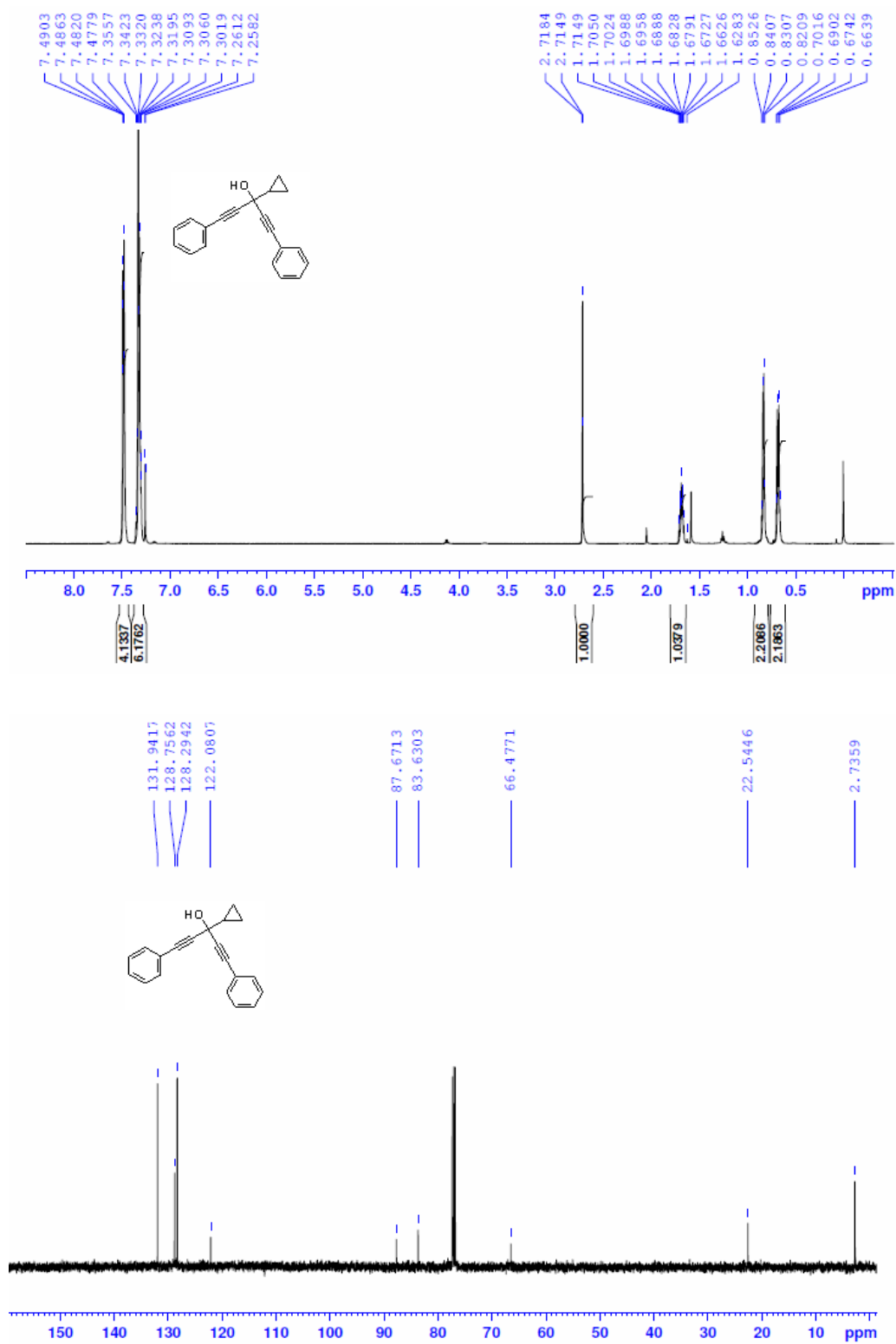




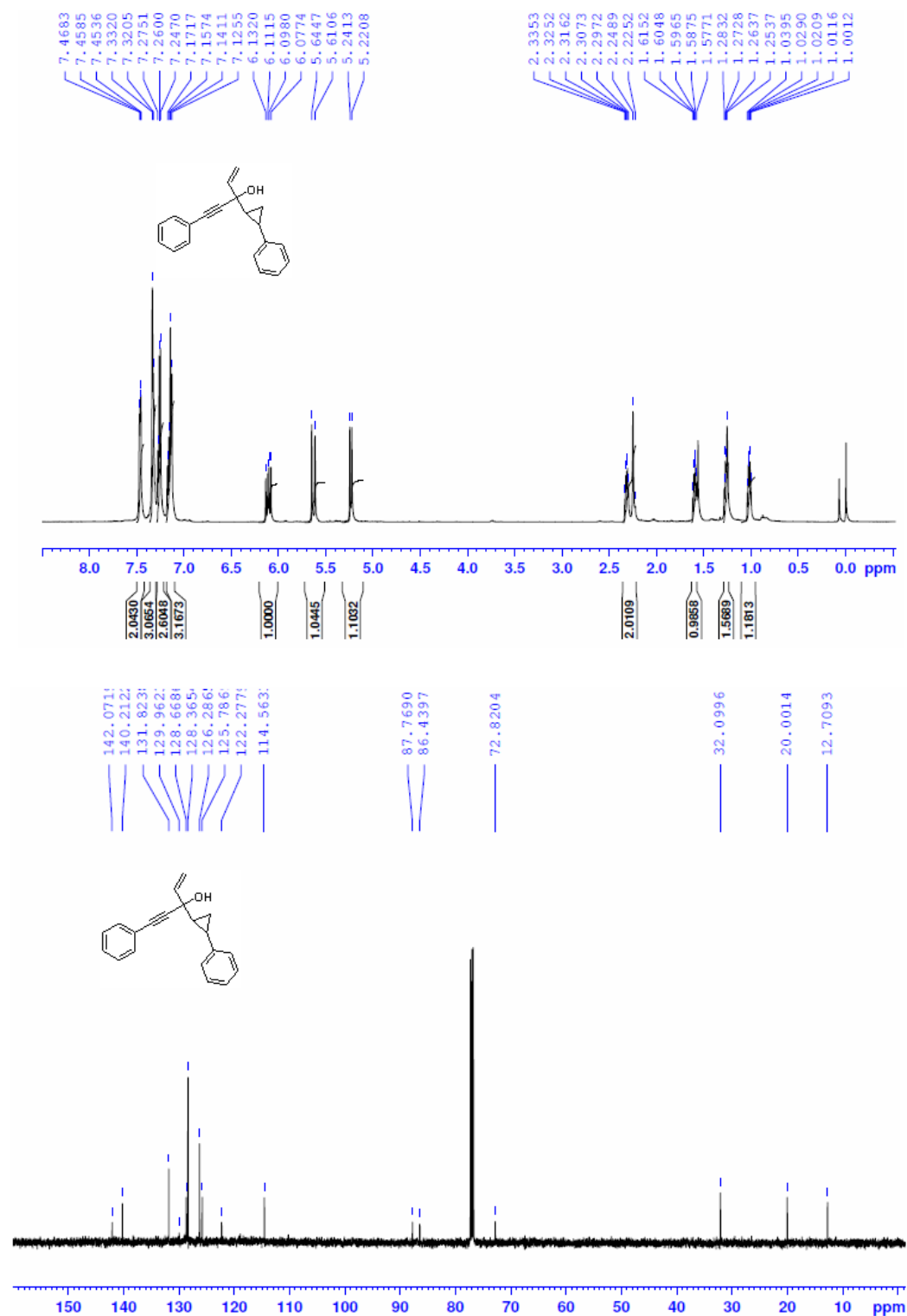
**Figure S22.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-1-phenylprop-2-yn-1-ol (**1v**)



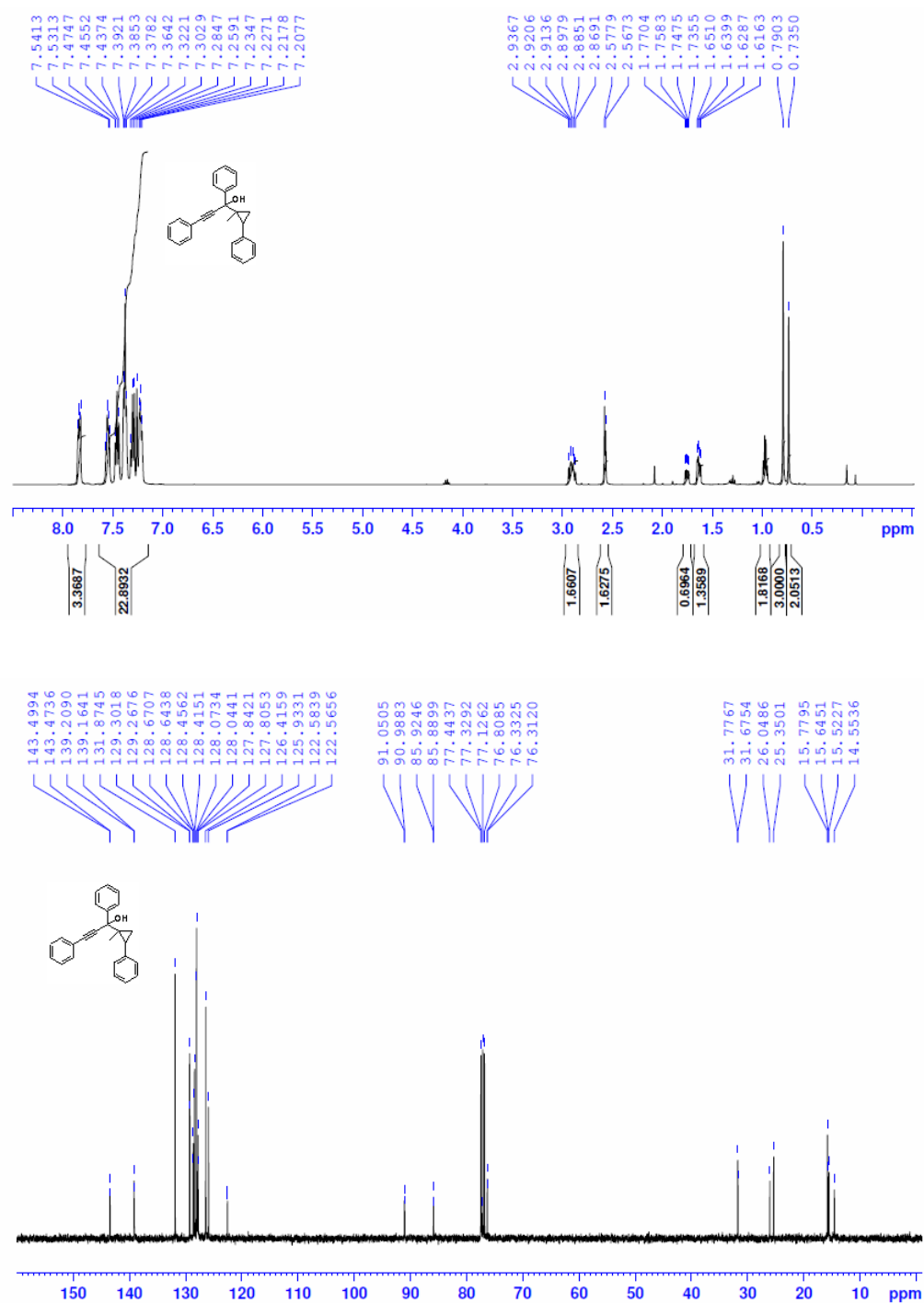
**Figure S23.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3-Cyclopropyl-1,5-diphenylpenta-1,4-diy-3-ol (**1w**)



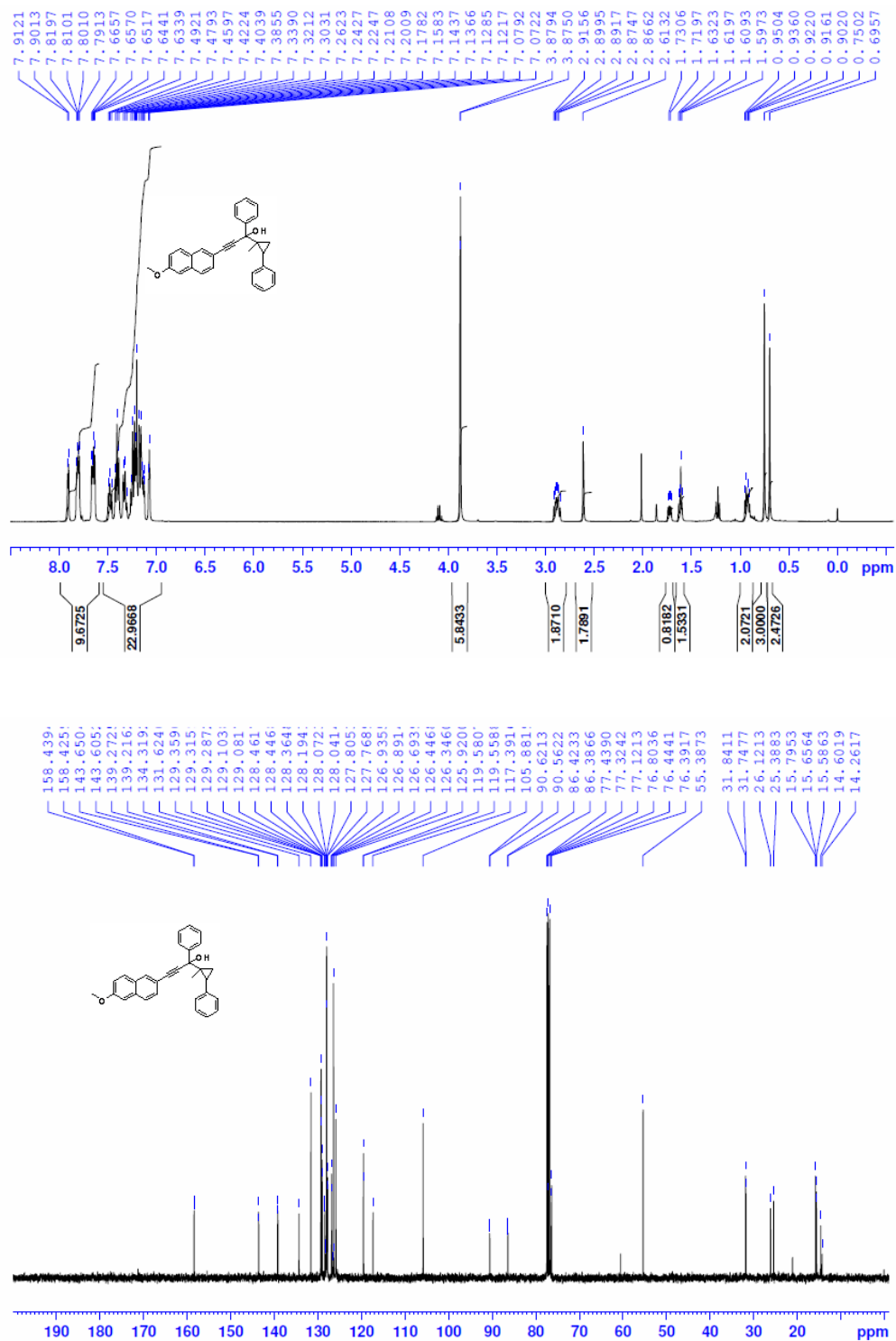
**Figure S24.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5-Phenyl-3-(2-phenylcyclopropyl)pent-1-en-4-yn-3-ol (**1x**)



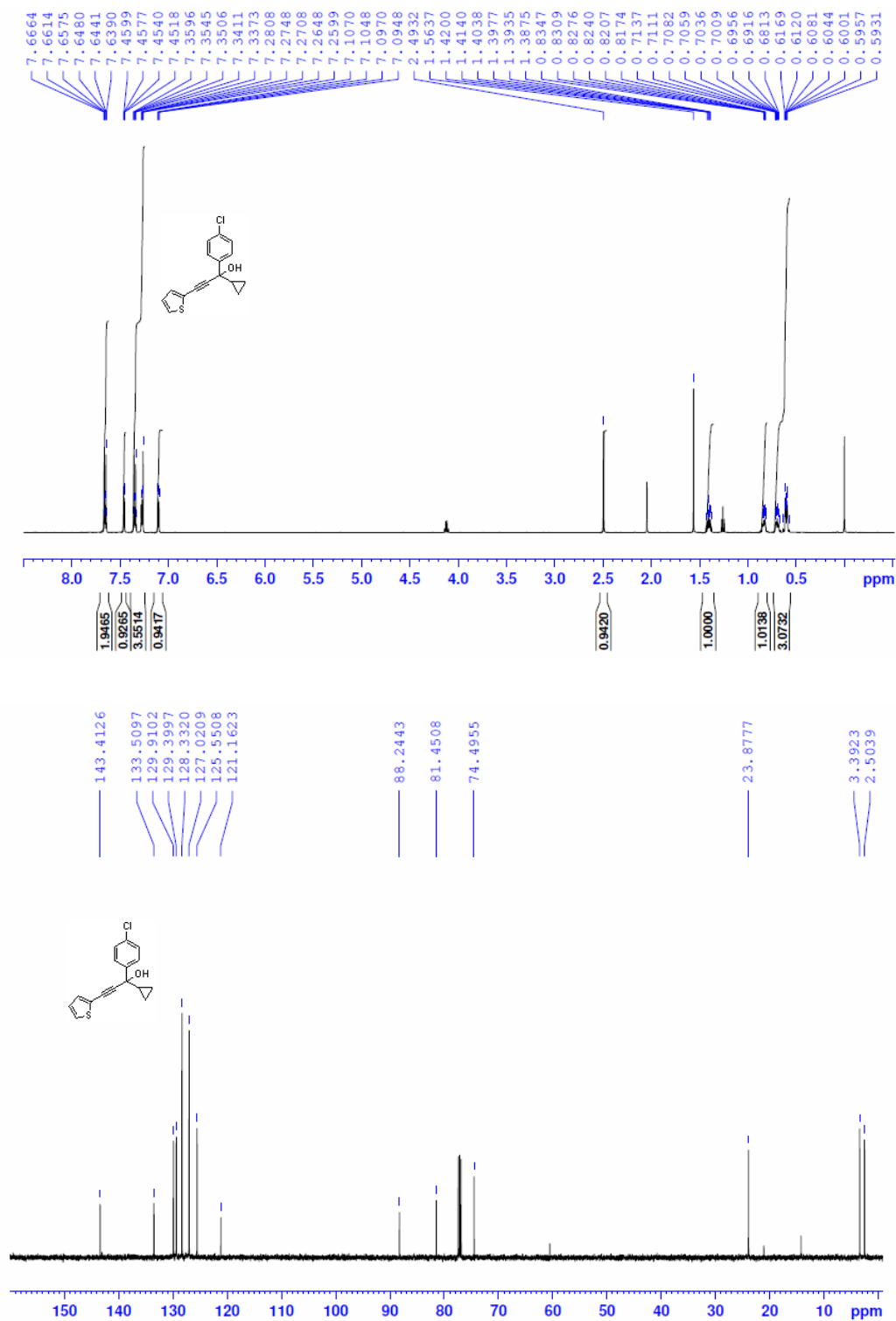
**Figure S25.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-(1-Methyl-2-phenylcyclopropyl)-1,3-diphenylprop-2-yn-1-ol (**1y**)



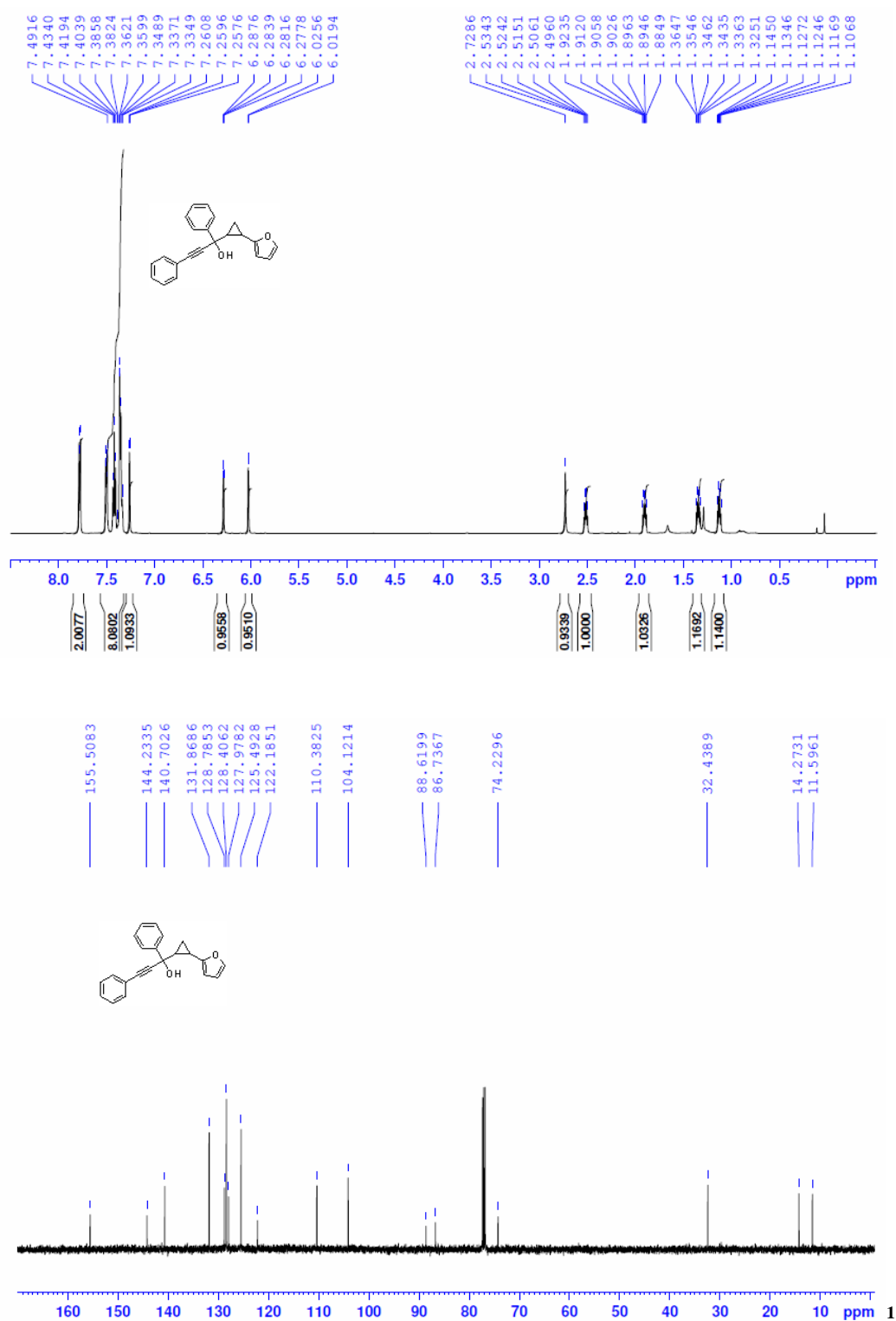
**Figure S26.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 3-(6-Methoxynaphthalen-2-yl)-1-(1-methyl-2-phenylcyclopropyl)-1-phenylprop-2-yn-1-ol (**1z**)



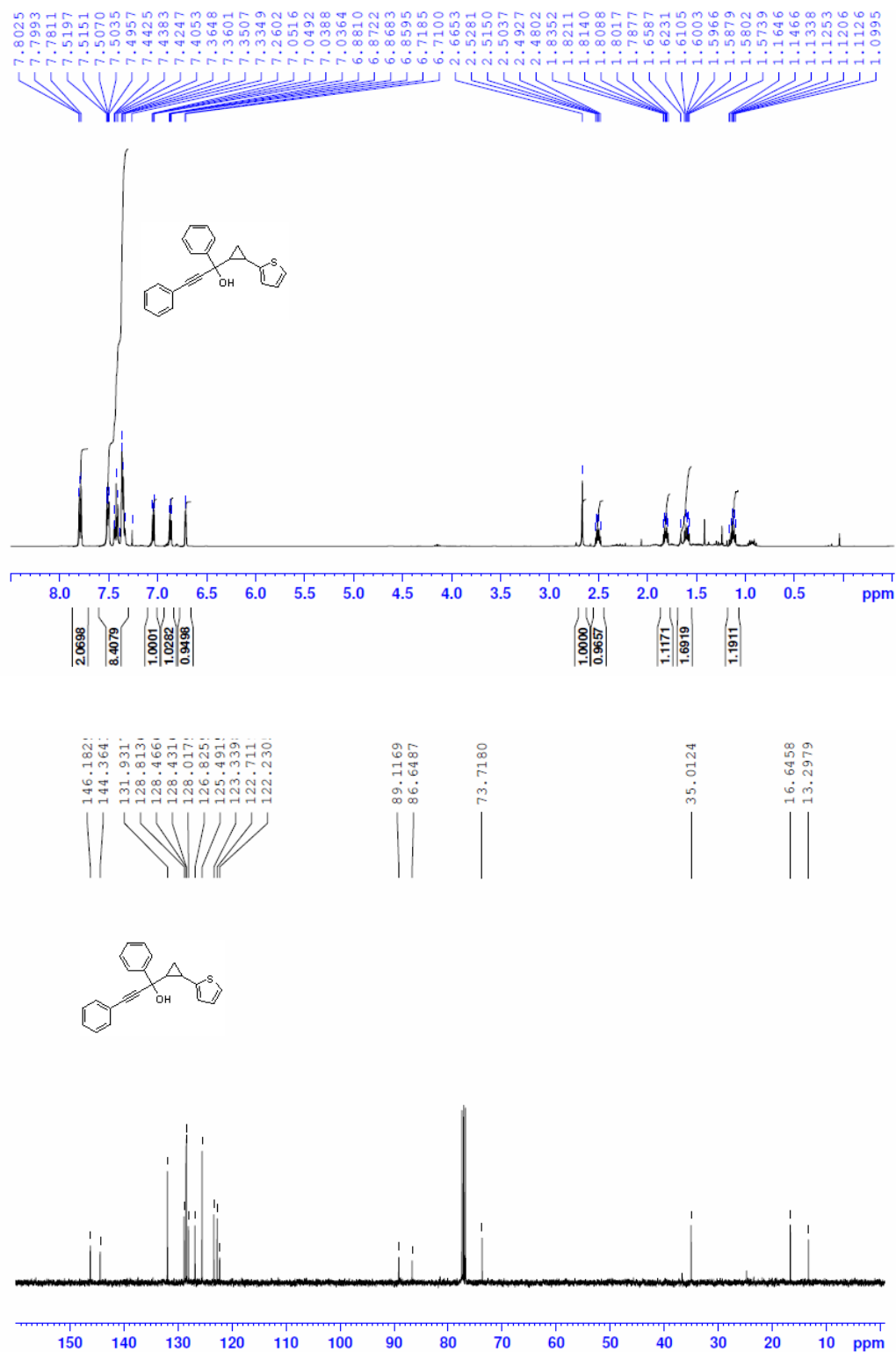
**Figure S27.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-(4-Chlorophenyl)-1-cyclopropyl-3-(thiophen-2-yl)prop-2-yn-1-ol (**1a**)



**Figure S28.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-(2-(Furan-2-yl)cyclopropyl)-1,3-diphenyl prop-2-yn-1-ol (**1 $\beta$** )

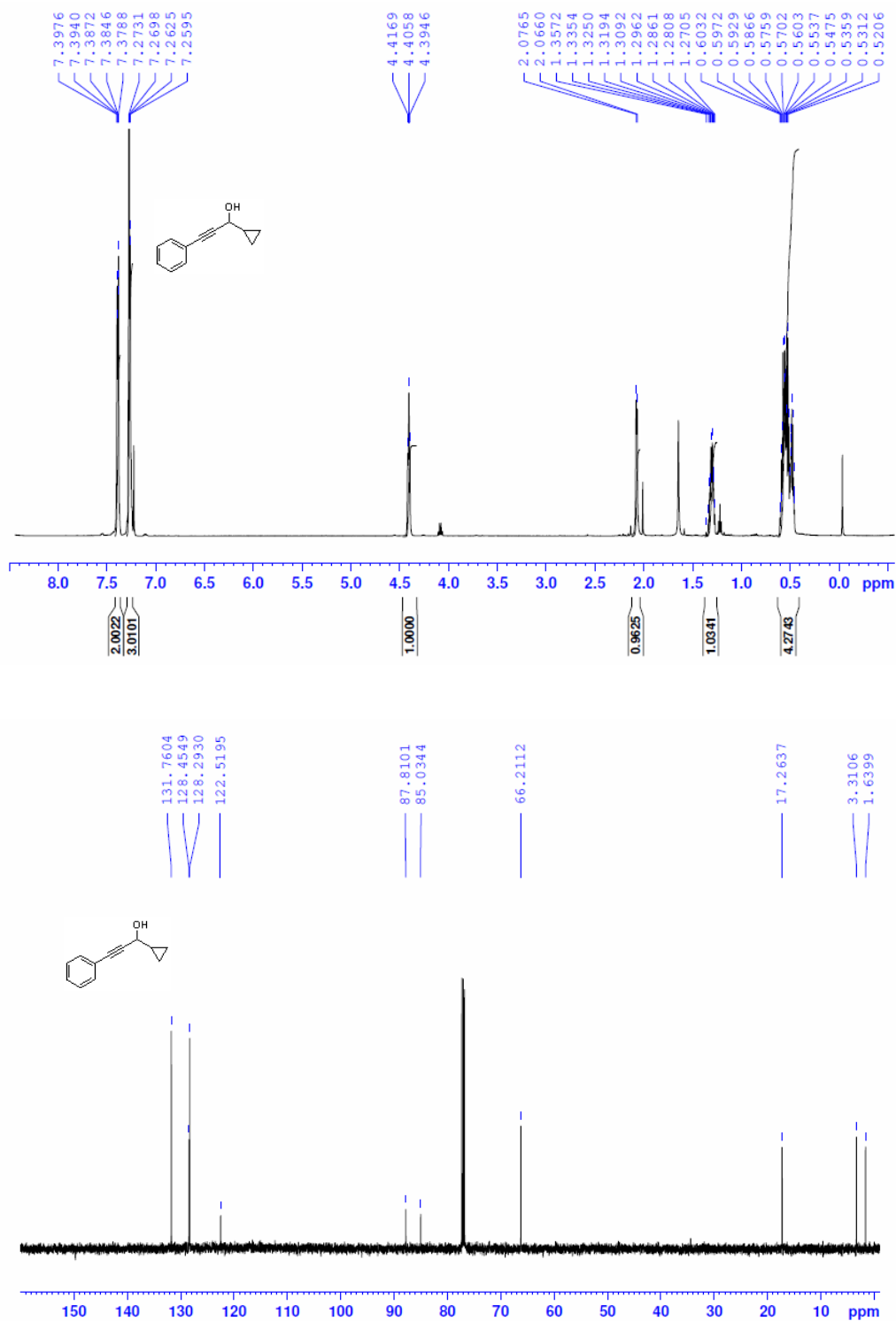


**Figure S29.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1,3-Diphenyl-1-(2-(thiophen-2-yl)cyclopropyl)prop-2-yn-1-ol (**1x**)



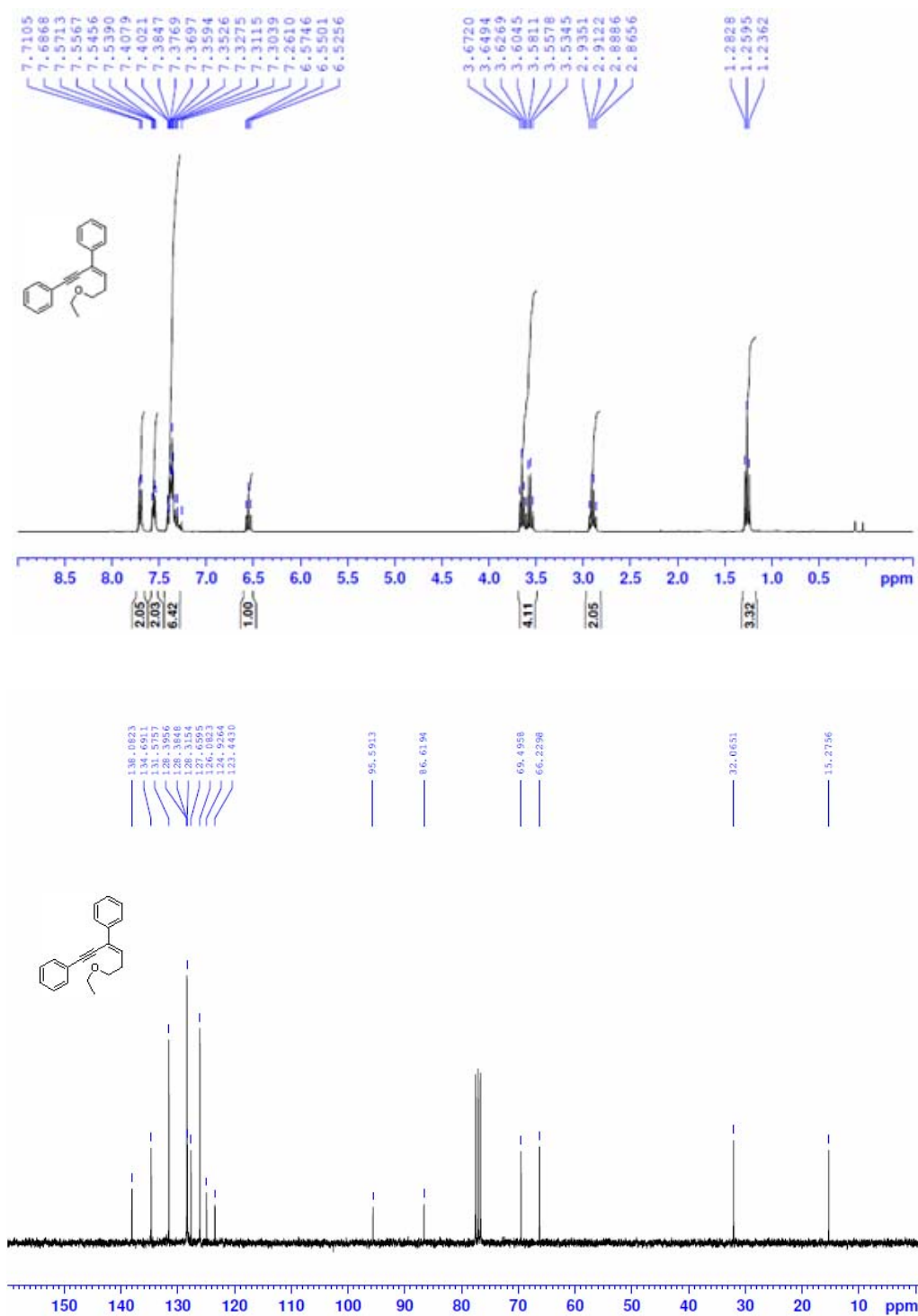


**Figure S30.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Cyclopropyl-3-phenylprop-2-yn-1-ol (**18**)

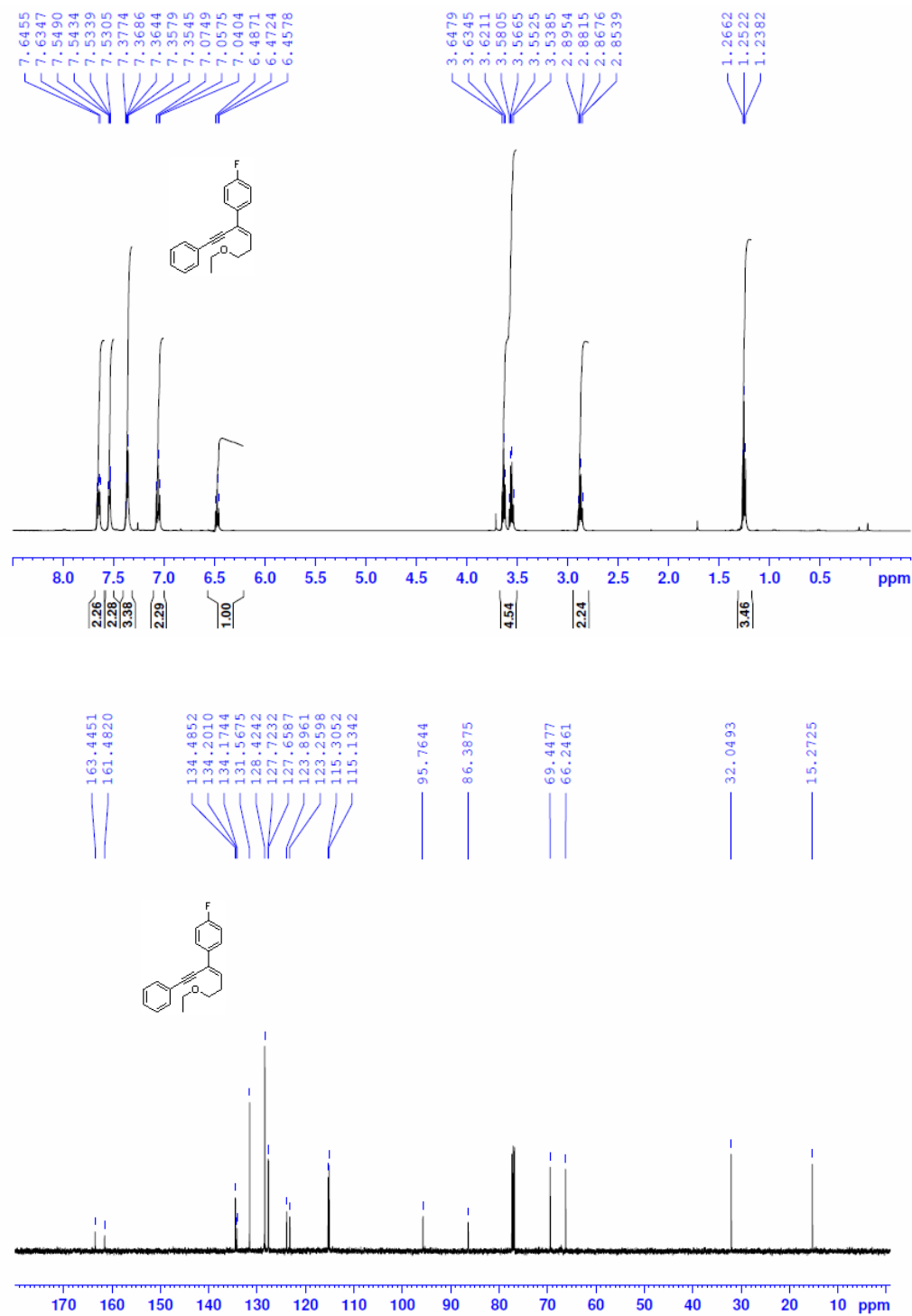


**Figure S31.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-6-Ethoxy-1,3-diphenylhex-3-en-1-yne

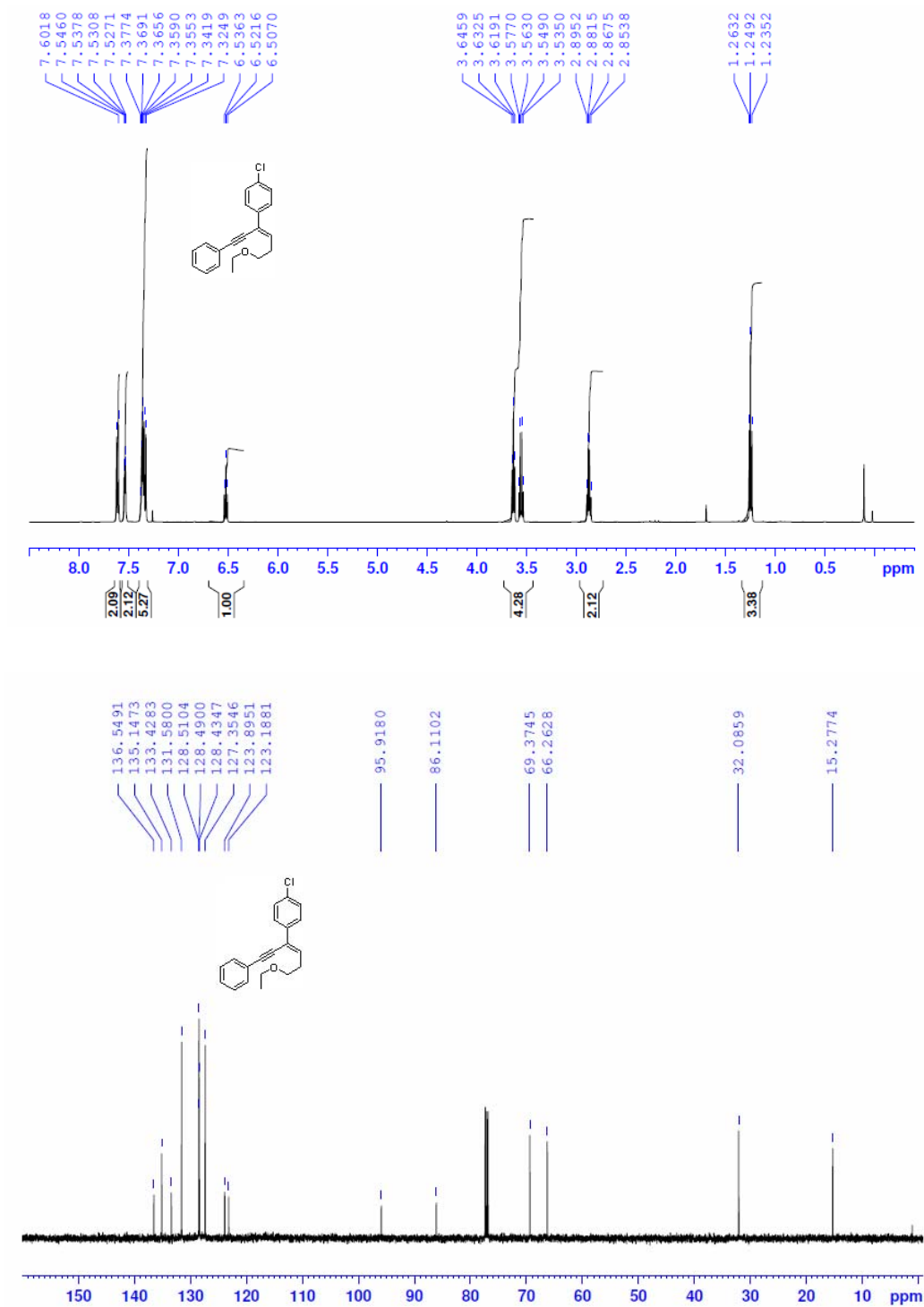
(3a)



**Figure S32.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-1-(6-Ethoxy-1-phenylhex-3-en-1-yn-3-yl)-4-fluorobenzene (**3b**)



**Figure S33.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-1-Chloro-4-(6-ethoxy-1-phenylhex-3-en-1-yn-3-yl)benzene (**3c**)



The figure displays the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 10, which is 1-(4-methoxyphenyl)-2-(4-methoxyphenyl)ethynyl-1H-imidazole. The chemical structure is shown above the spectra.

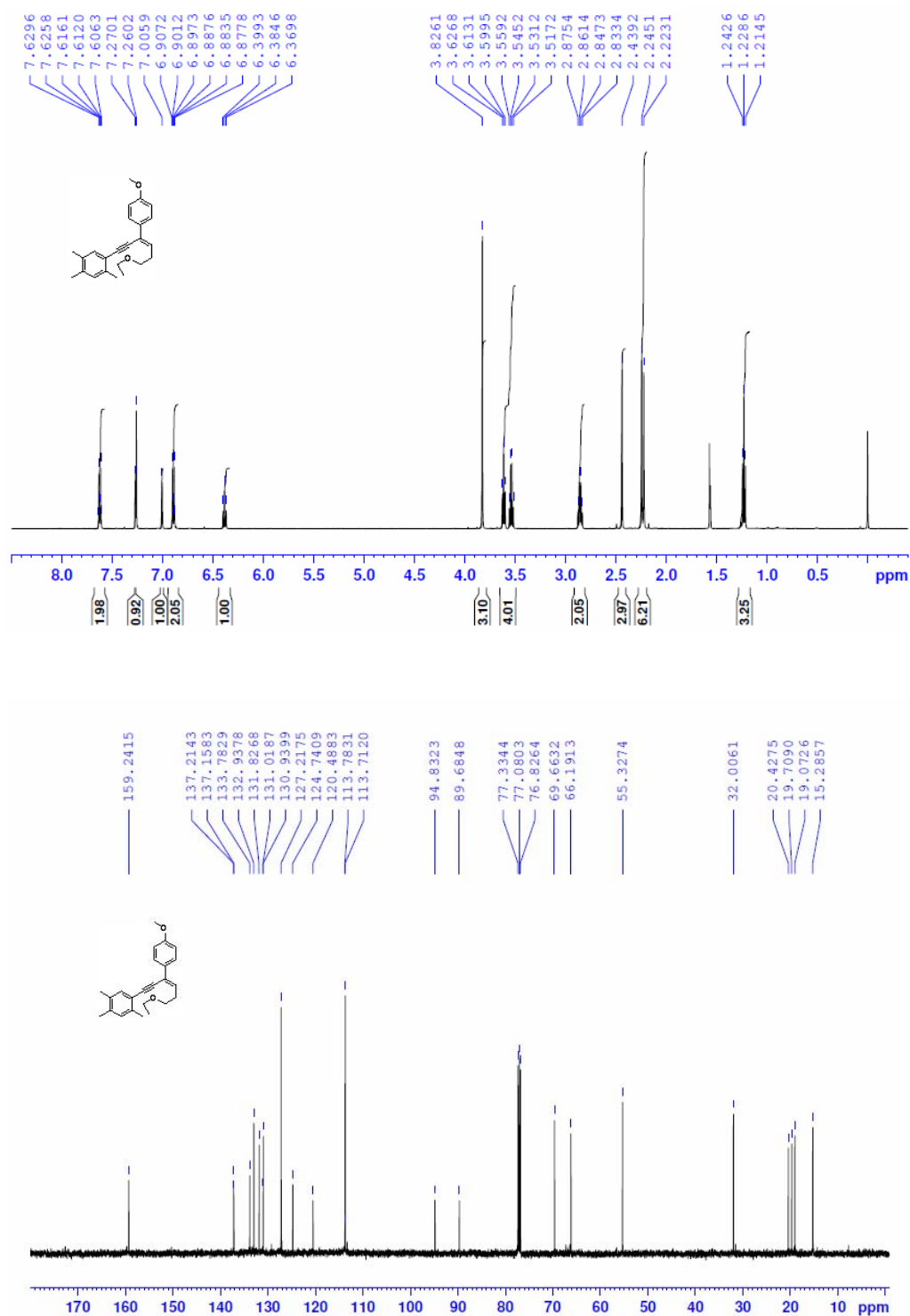
**$^1\text{H}$  NMR Spectrum (Top):** The spectrum is recorded in  $\text{CDCl}_3$  and shows peaks in the aromatic region (6.3–7.7 ppm) and aliphatic region (2.4–3.9 ppm). Integration values are provided below the baseline.

Chemical Shift (ppm)	Integration
7.6264, 7.6093, 7.4354, 7.4185	2.09
6.9062, 6.9007, 6.8835, 6.7826, 6.7778	0.96
6.7624, 6.7576, 6.7403, 6.7303, 6.7250, 6.7133, 6.7082, 6.3859, 6.3713, 6.3566	2.20, 2.19, 1.00
3.8380, 3.8271, 3.8166, 3.6260, 3.6123, 3.5986, 3.5601, 3.5461, 3.5321, 3.5181	6.66, 4.03
2.8710, 2.8570, 2.8430, 2.8291, 2.4936	2.04, 2.98
1.2441, 1.2301, 1.2161	3.00

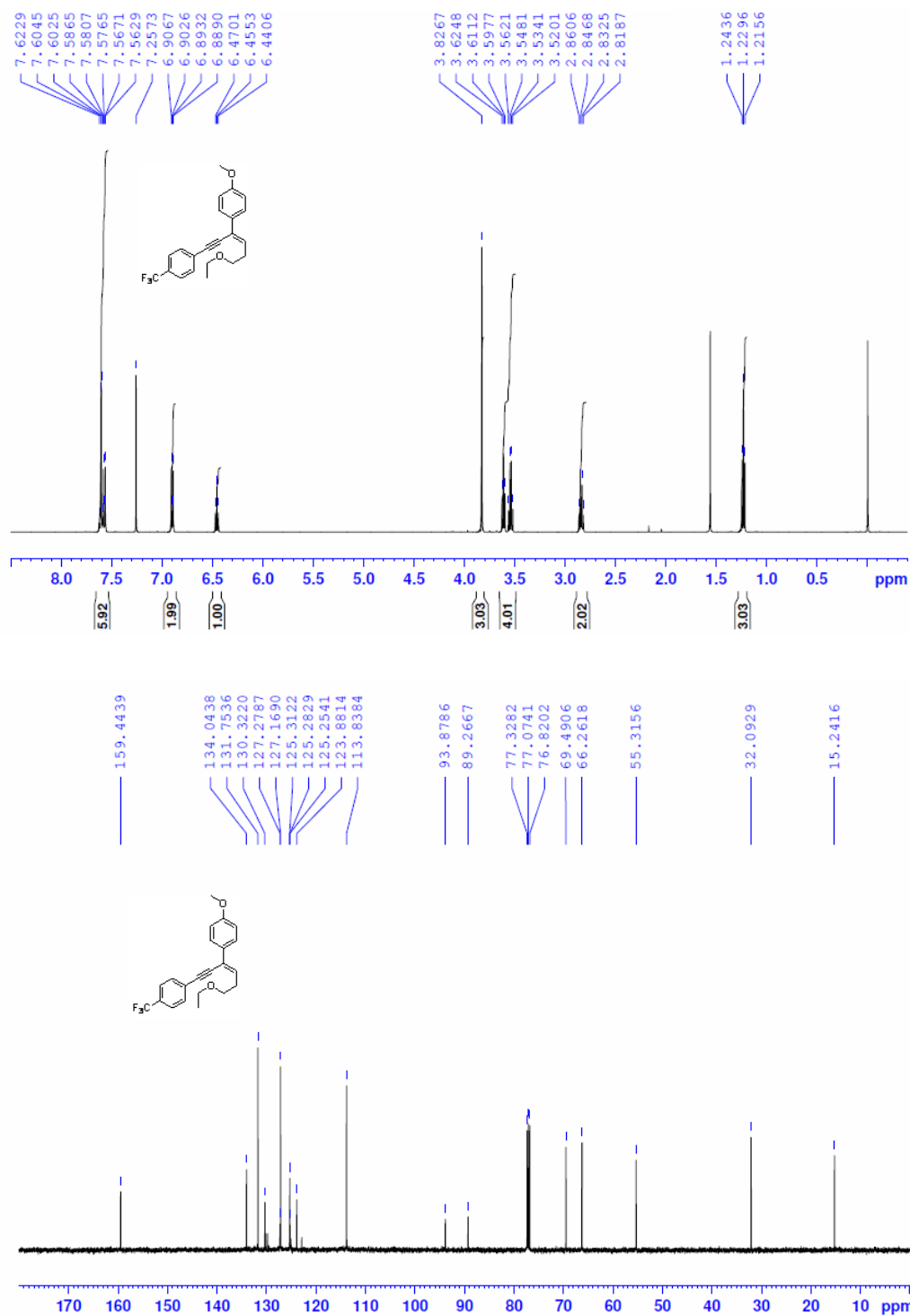
**$^{13}\text{C}$  NMR Spectrum (Bottom):** The spectrum is recorded in  $\text{CDCl}_3$  and shows peaks in the aromatic region (111–159 ppm), solvent region (77 ppm), and aliphatic region (15–32 ppm).

Chemical Shift (ppm)
159.6022, 159.2398
141.7350
133.3432, 131.5820, 131.0410, 127.2109, 124.7476
115.6563, 115.1498, 113.7109, 111.3361
94.5279, 89.3237
69.6563, 66.1930
55.3221, 55.2620
32.0118, 21.3397, 15.2906

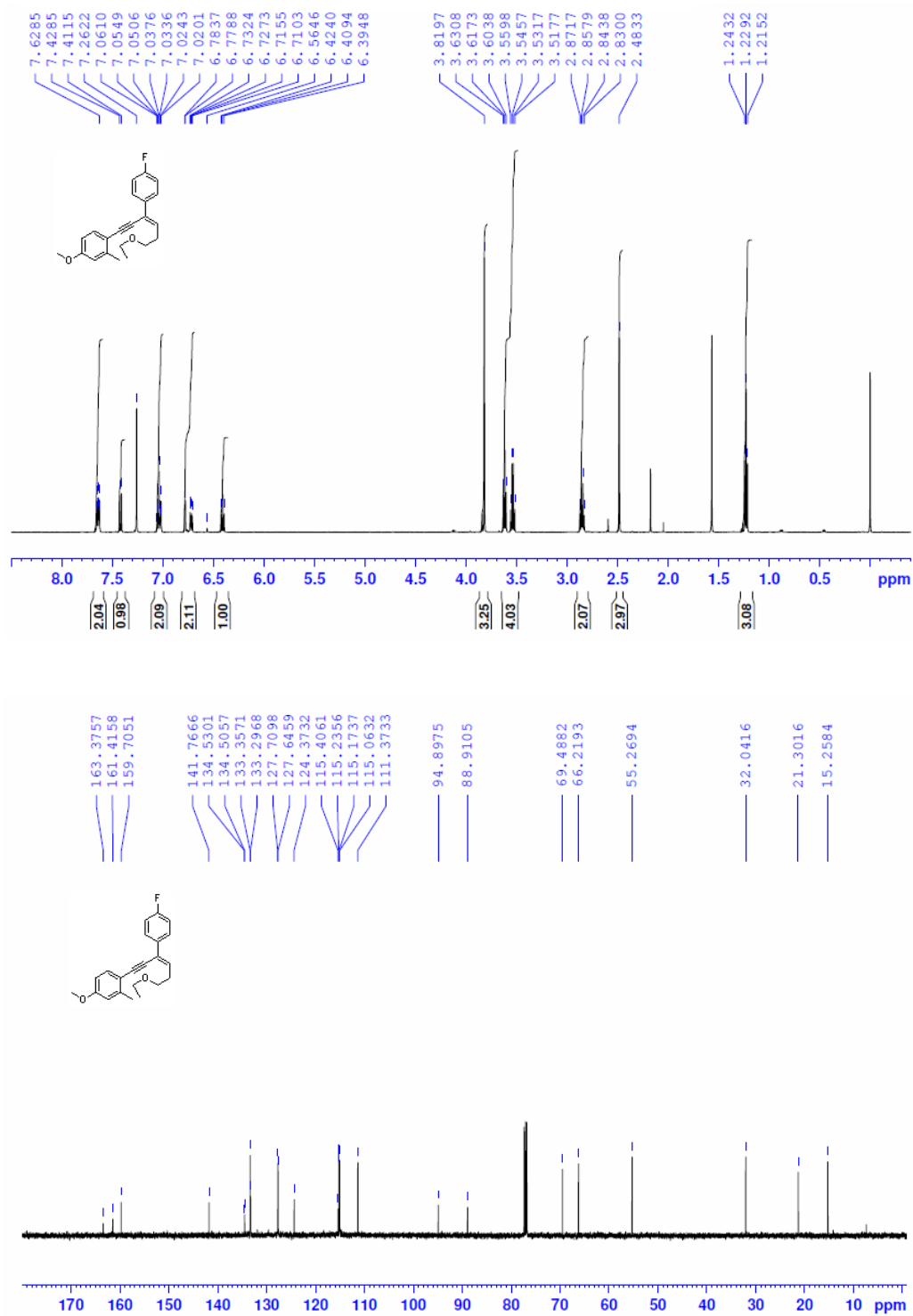
**Figure S35.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-((Z)-6-Ethoxy-3-(4-methoxyphenyl)hex-3-en-1-ynyl)-2,4,5-trimethylbenzene (**3e**)



**Figure S36.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-((Z)-6-Ethoxy-3-(4-methoxyphenyl)hex-3-en-1-ynyl)-4-(trifluoromethyl)benzene (**3f**)

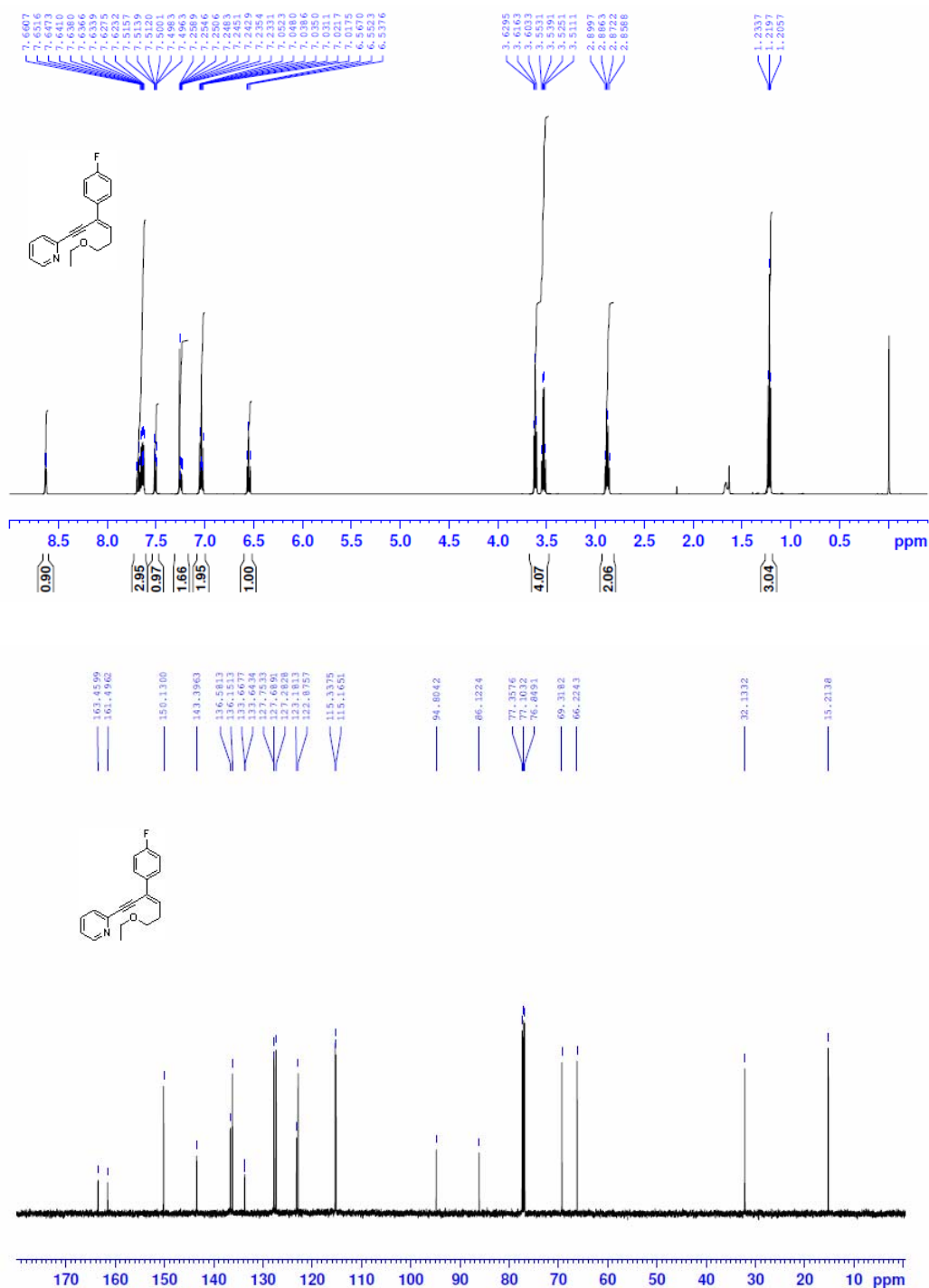


**Figure S37.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-((*Z*)-6-Ethoxy-1-(4-methoxy-2-methylphenyl)hex-3-en-1-yn-3-yl)-4-fluorobenzene (**3g**)

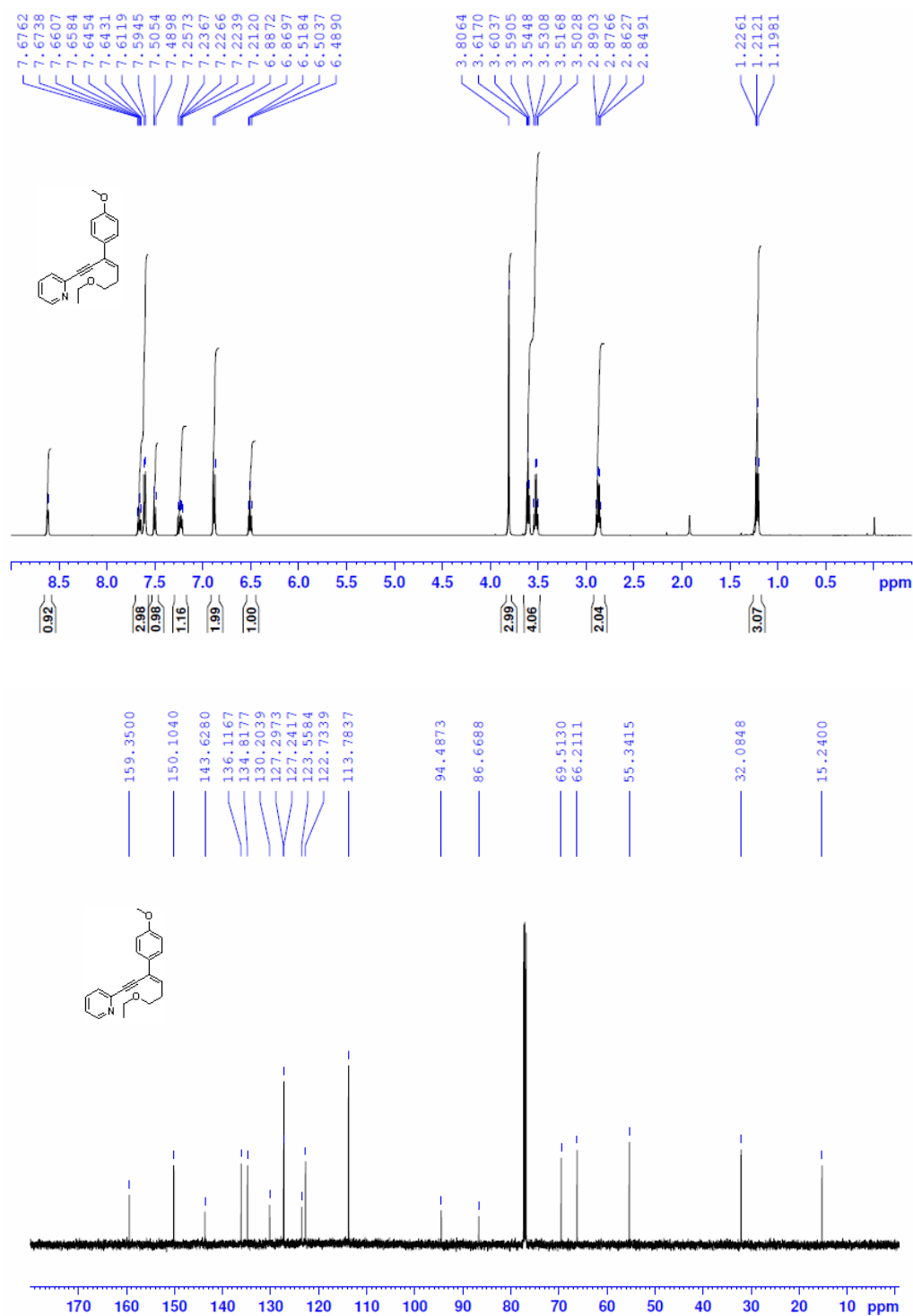




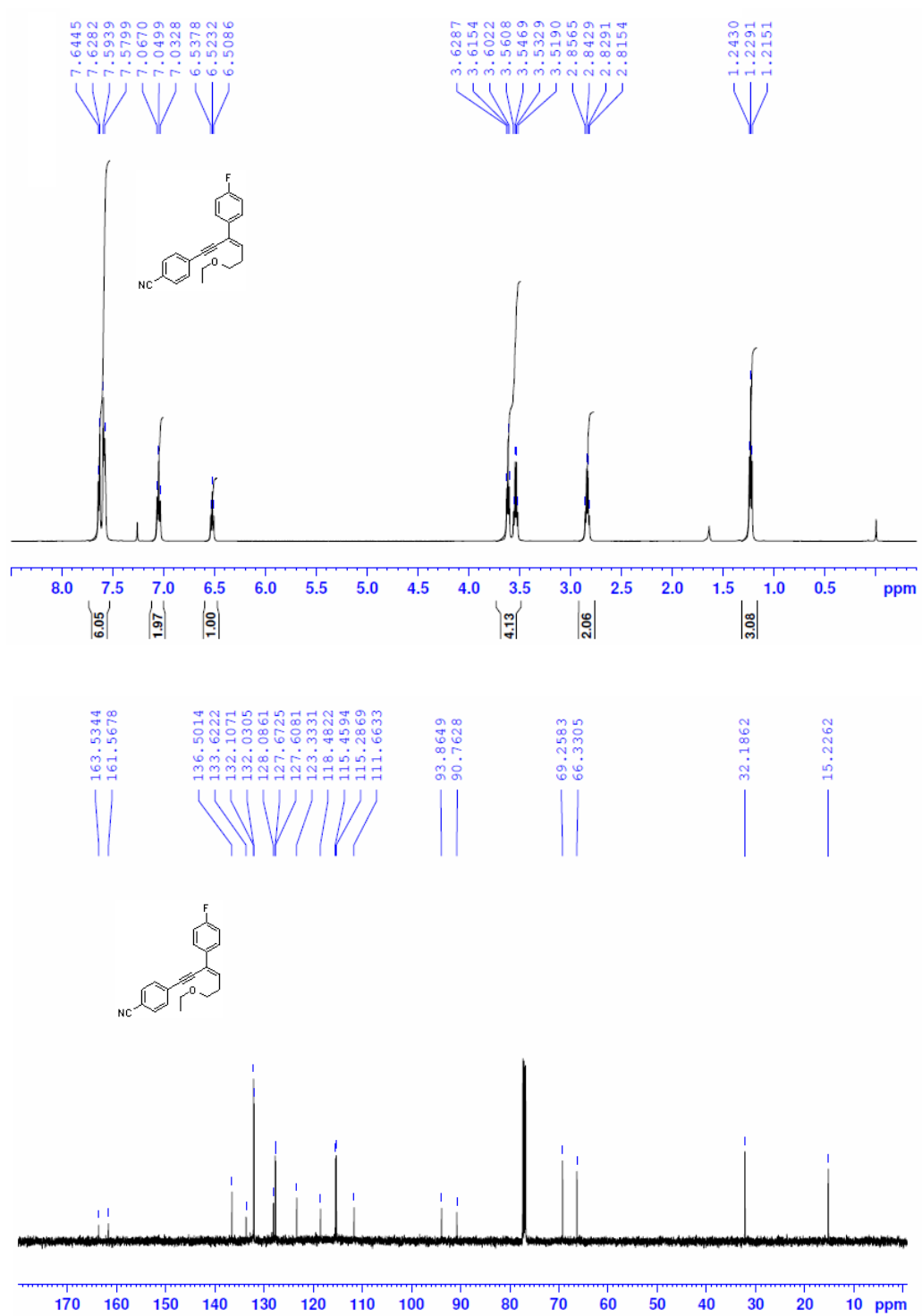
**Figure S38.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 2-((Z)-6-Ethoxy-3-(4-fluorophenyl)hex-3-en-1-ynyl)pyridine (**3h**)



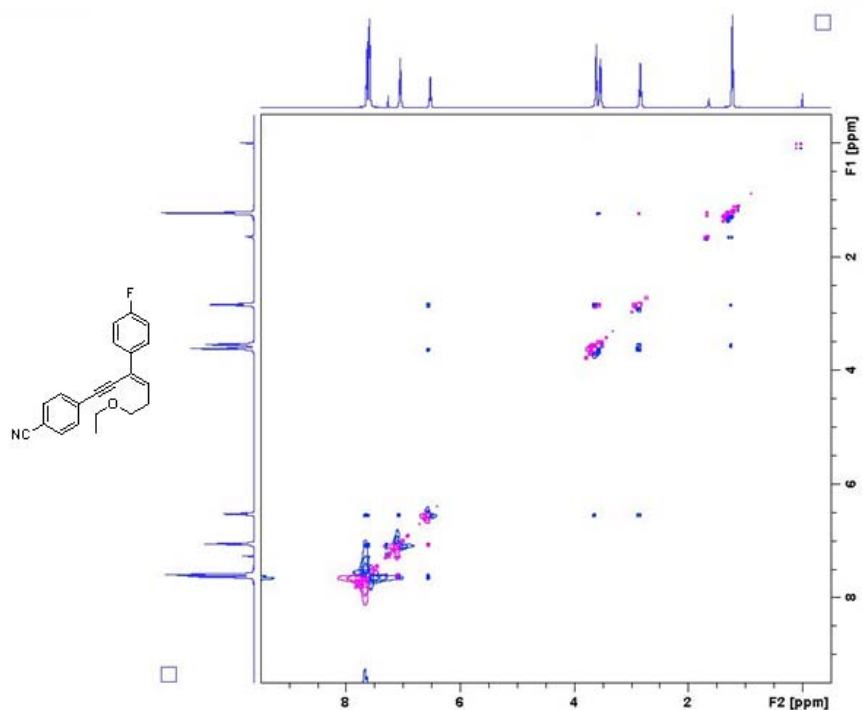
**Figure S39.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 2-((Z)-6-Ethoxy-3-(4-methoxyphenyl)hex-3-en-1-ynyl)pyridine (**3i**)



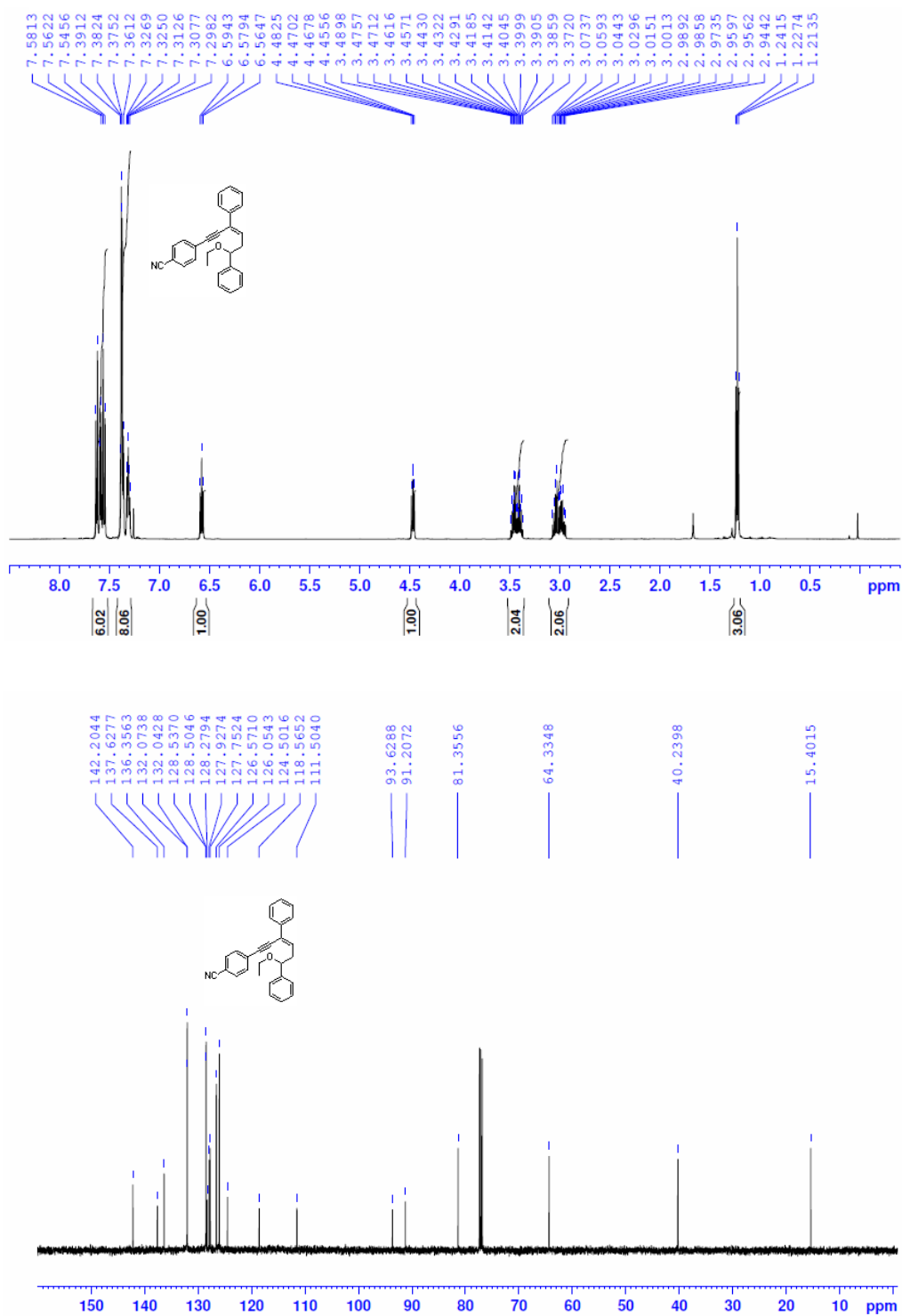
**Figure S40.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 4-((Z)-6-Ethoxy-3-(4-fluorophenyl)hex-3-en-1-ynyl)benzonitrile (**3j**)



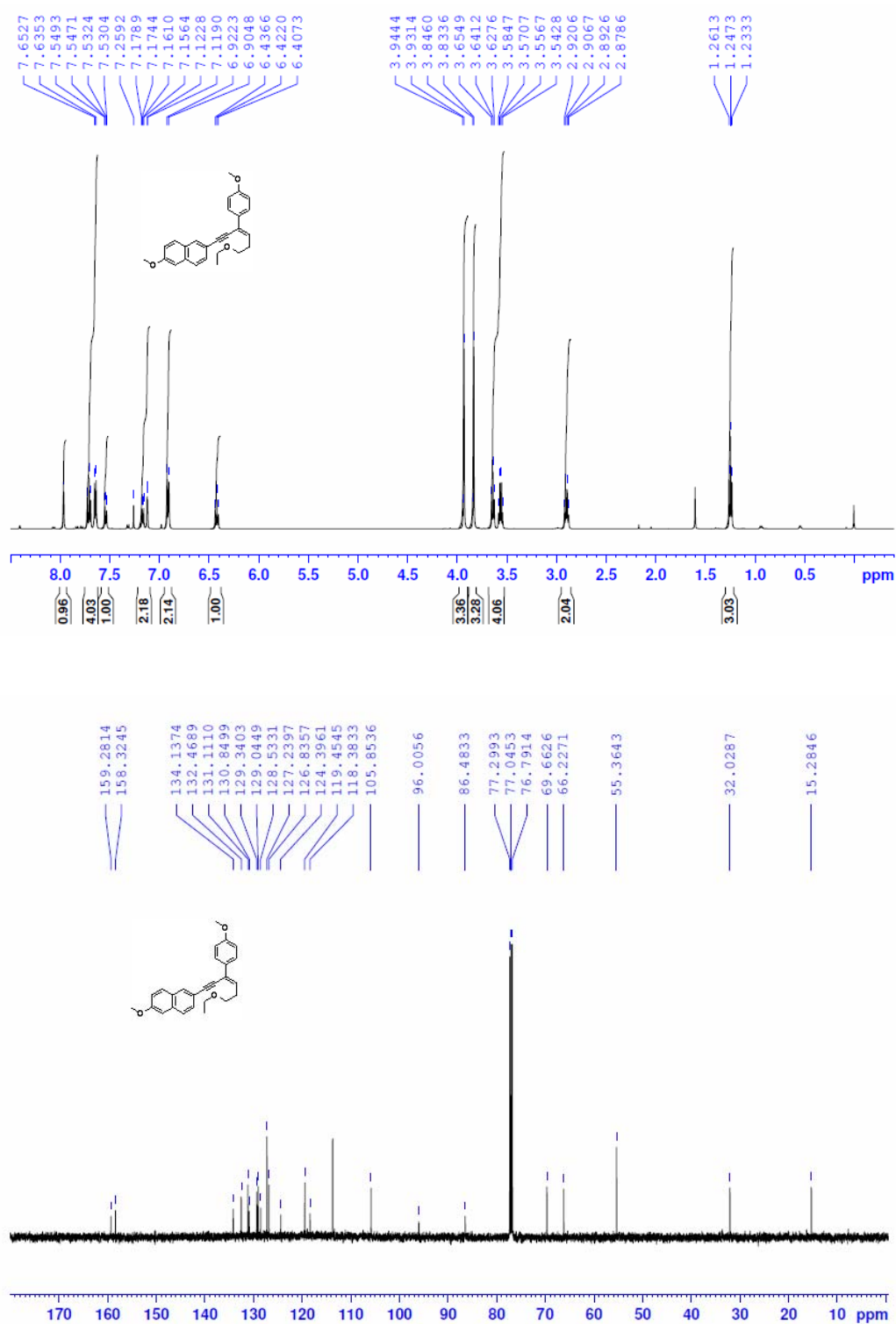
**Figure S41.** NOESY Spectrum of 4-((*Z*)-6-Ethoxy-3-(4-fluorophenyl)hex-3-en-1-ynyl)benzonitrile (**3j**)



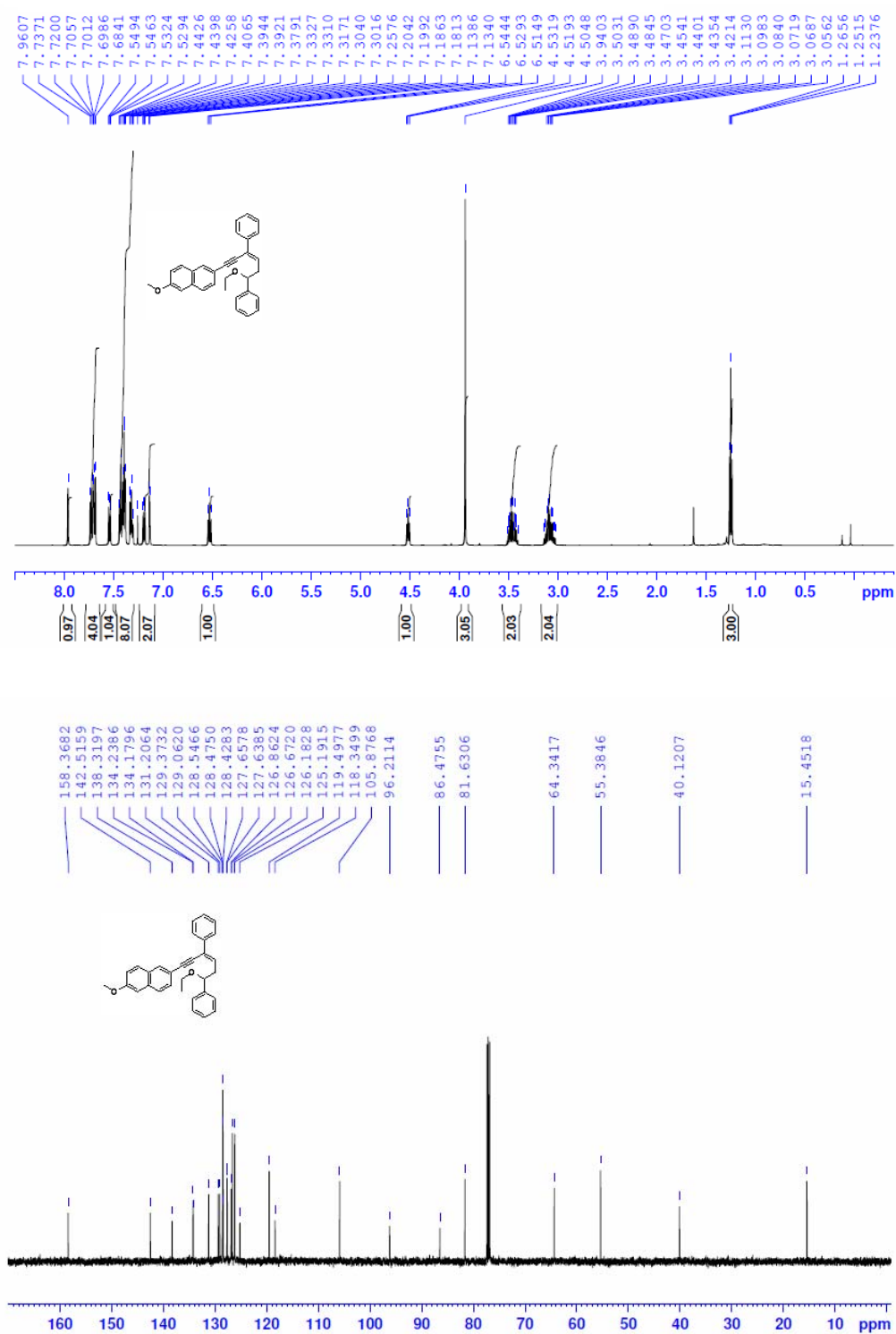
**Figure S42.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 4-((Z)-6-Ethoxy-3,6-diphenylhex-3-en-1-ynyl)benzonitrile (**3k**)



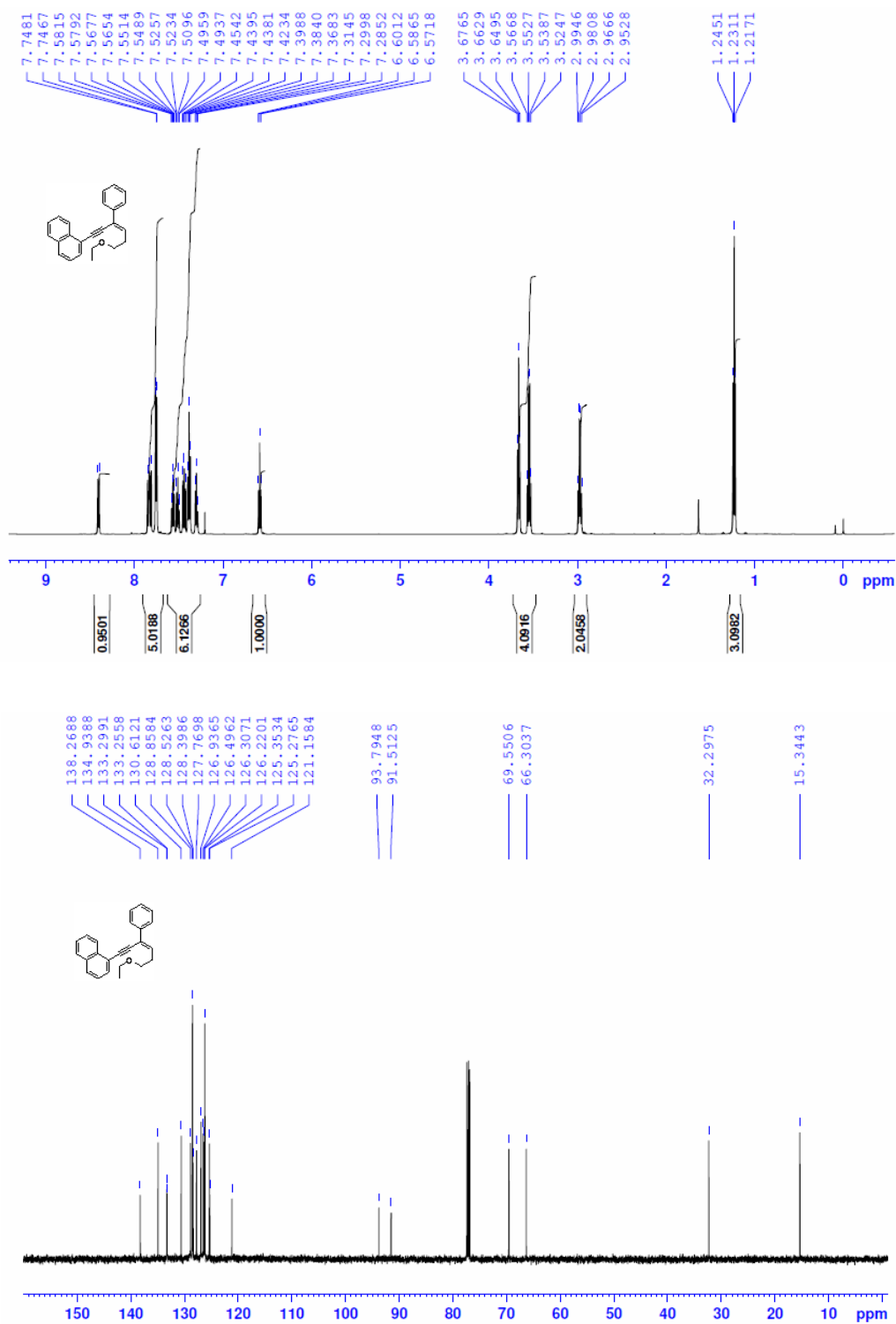
**Figure S43.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 2-((Z)-6-Ethoxy-3-(4-methoxyphenyl)hex-3-en-1-ynyl)-6-methoxynaphthalene (**3I**)



**Figure S44.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 2-((Z)-6-Ethoxy-3,6-diphenylhex-3-en-1-ynyl)-6-methoxynaphthalene (**3m**)

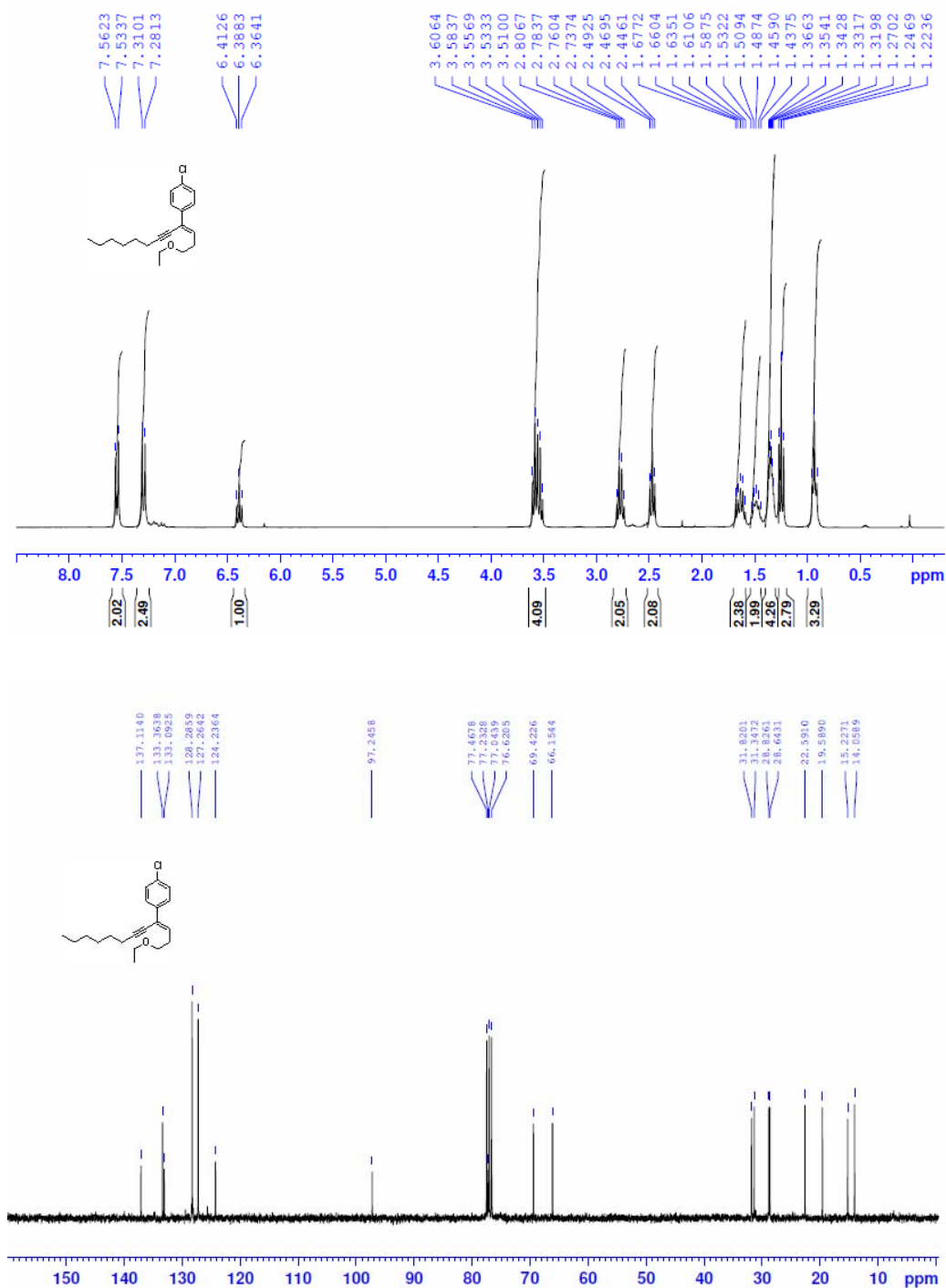


**Figure S45.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-1-(6-ethoxy-3-phenylhex-3-en-1-ynyl)naphthalene (**3n**)

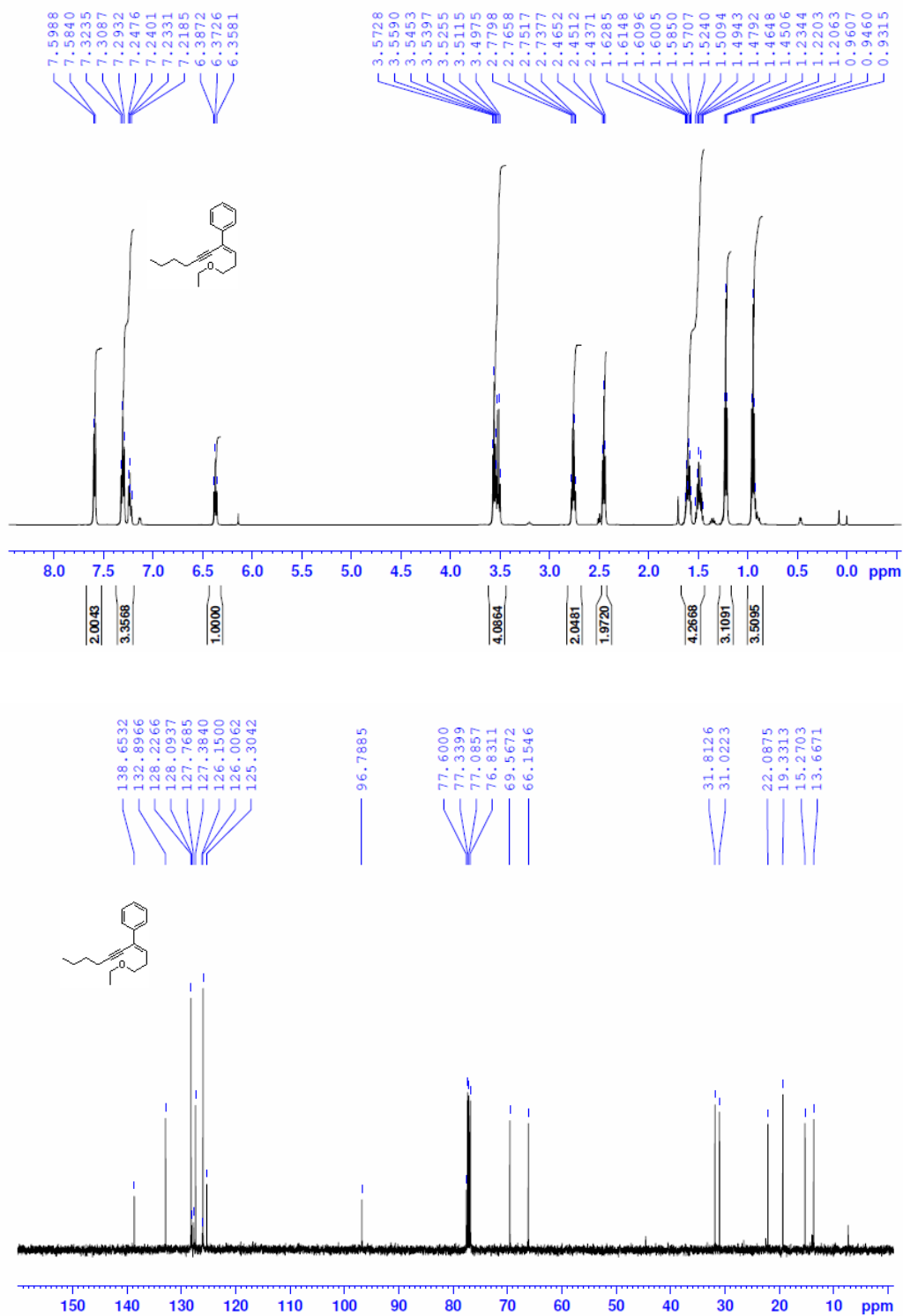




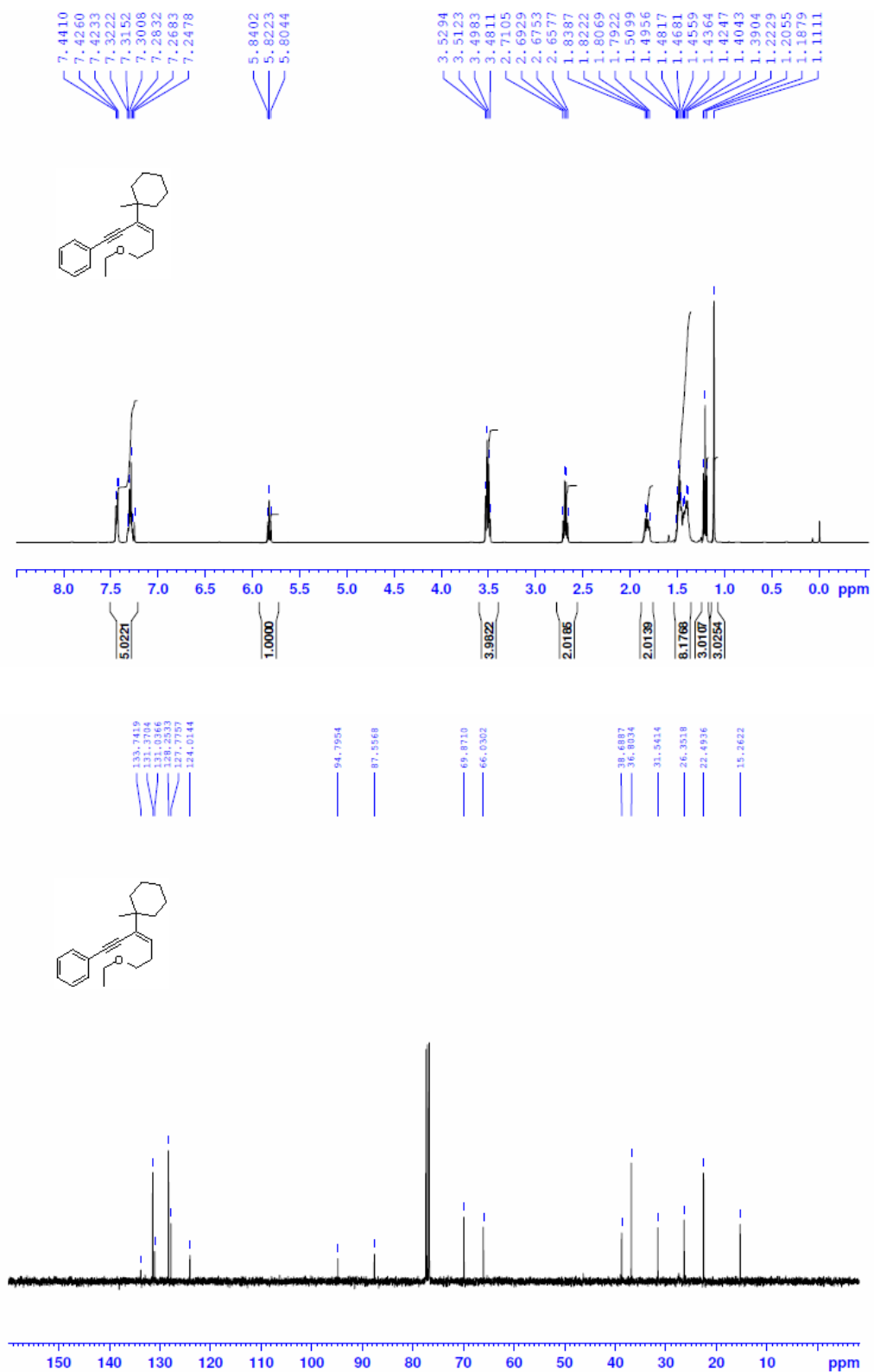
**Figure S46.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Chloro-4-((*Z*)-1-ethoxydodec-3-en-5-yn-4-yl)benzene (**30**)



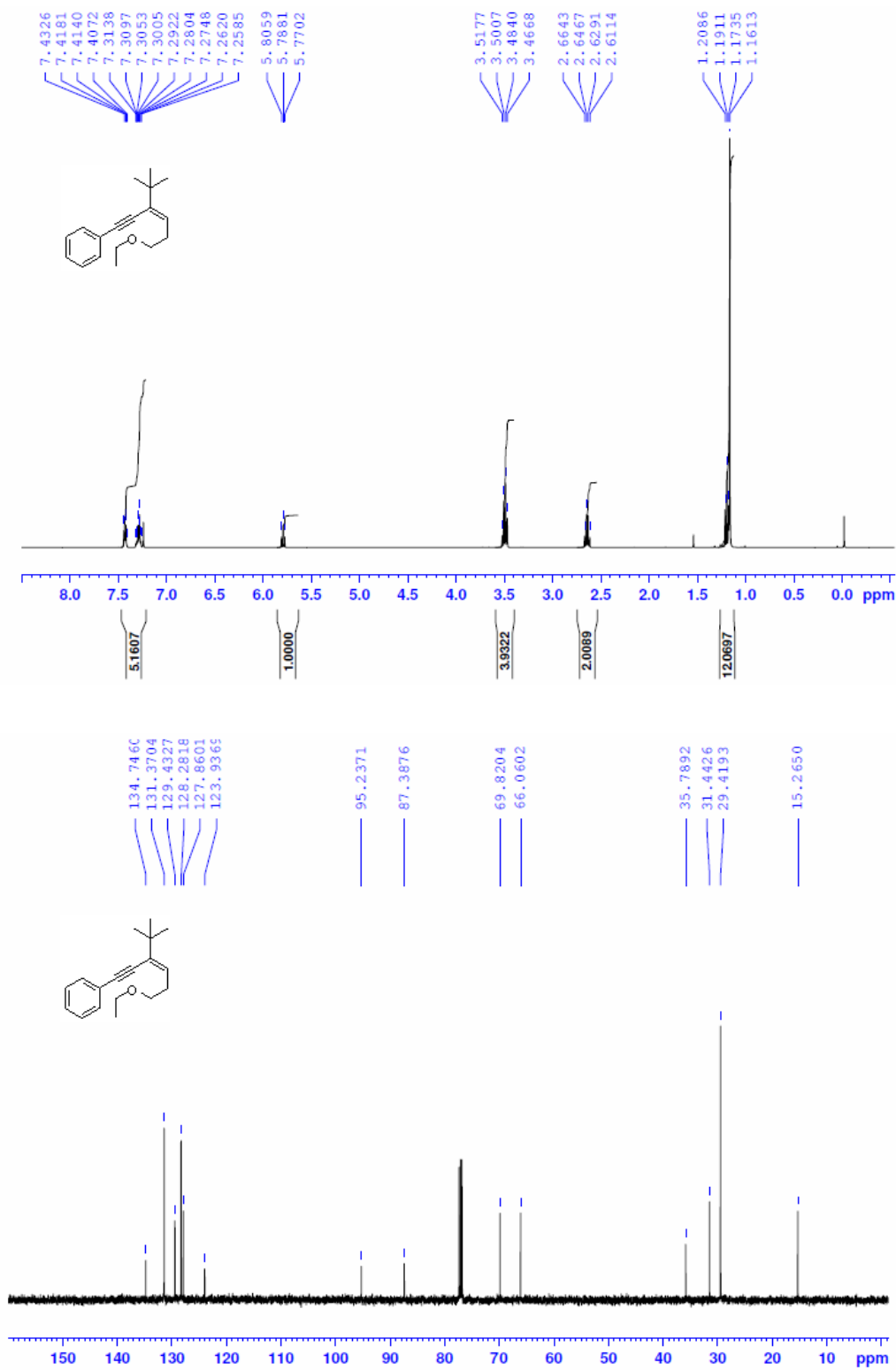
**Figure S47.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-(1-Ethoxydec-3-en-5-yn-4-yl)benzene (**3p**)



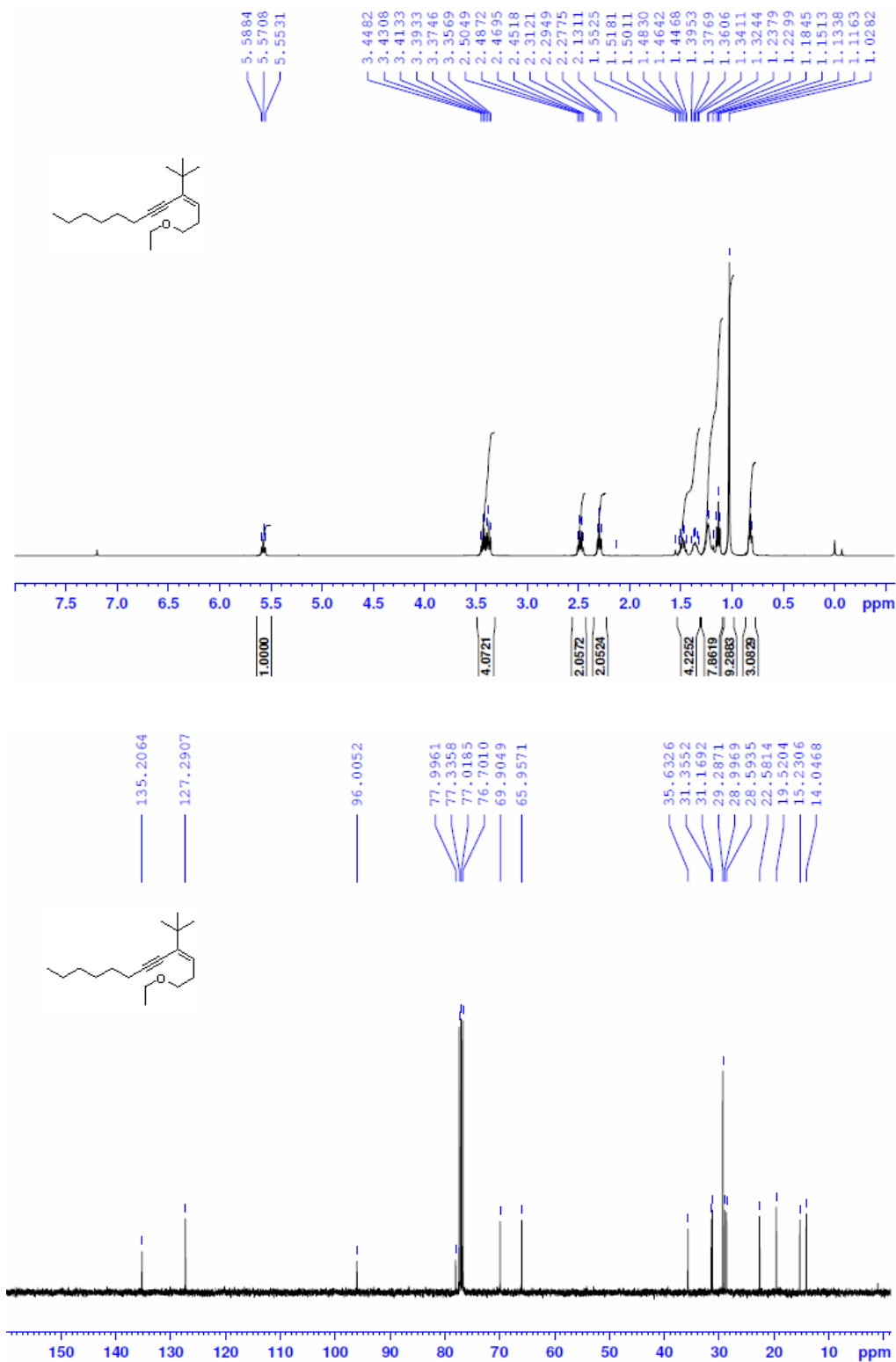
**Figure S48.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (Z)-(6-Ethoxy-3-(1-methylcyclohexyl)hex-3-en-1-ynyl)benzene (**3q**)



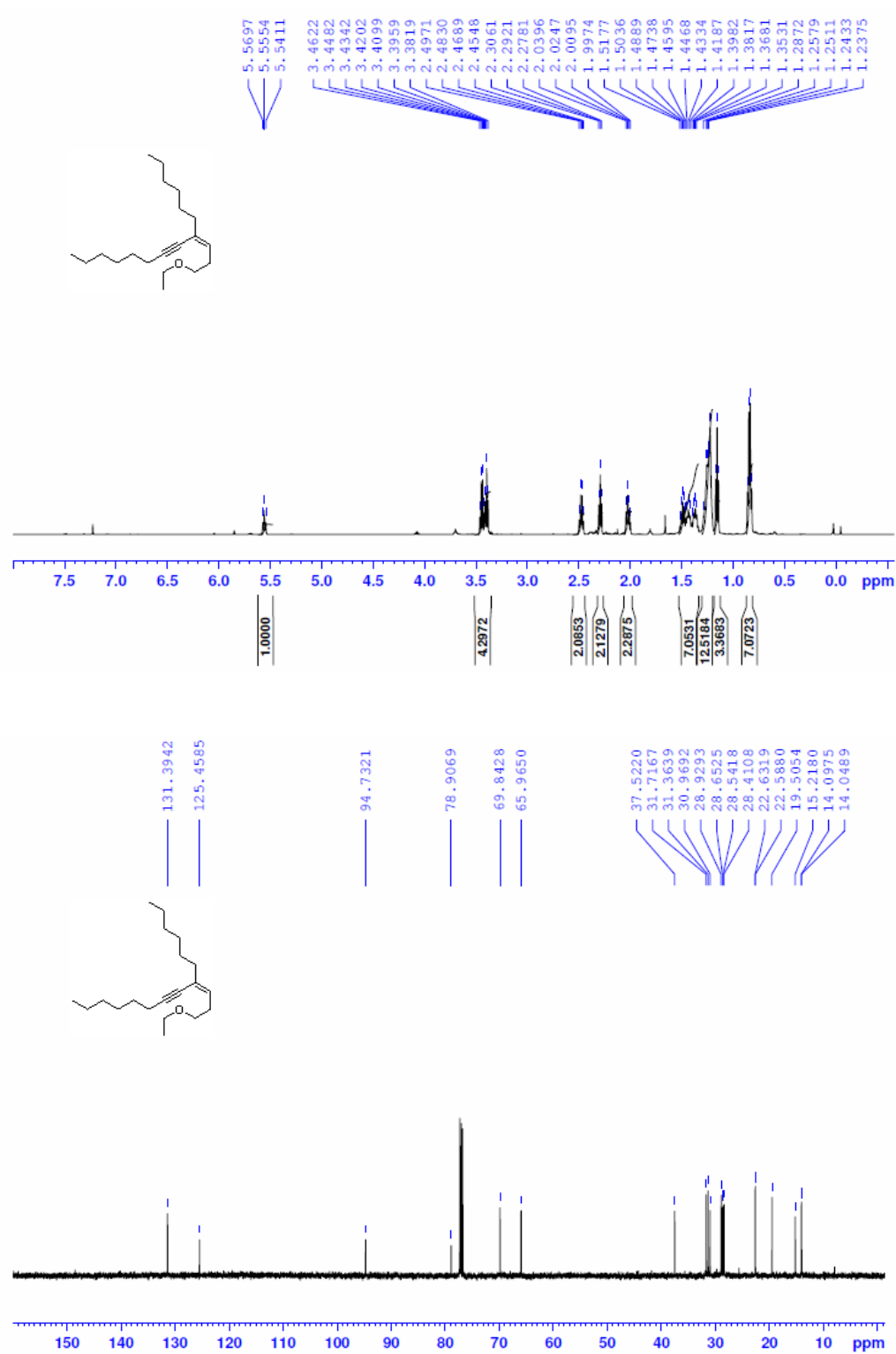
**Figure S49.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (Z)-(3-tert-butyl-6-ethoxyhex-3-en-1-ynyl) benzene (**3r**)



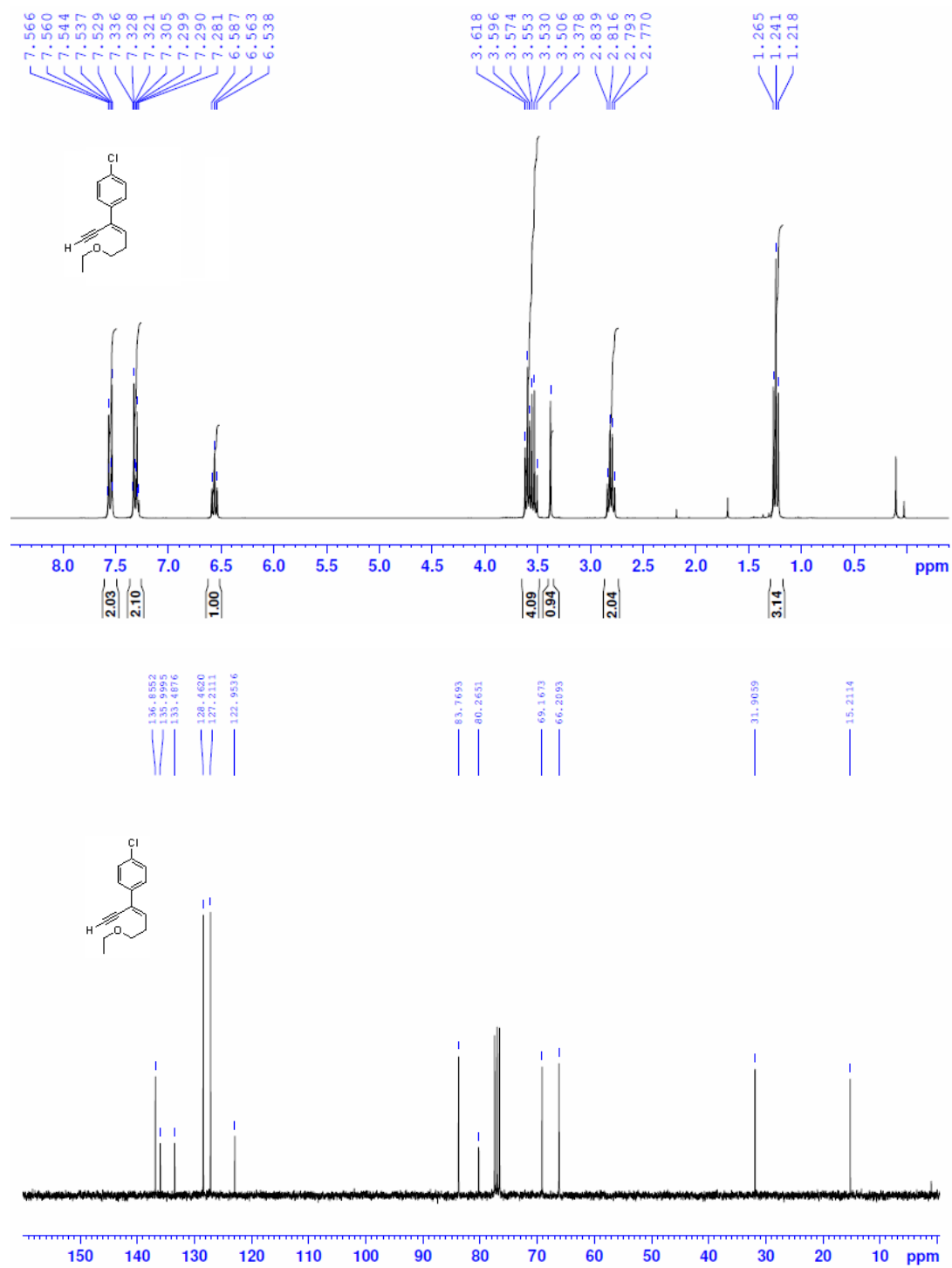
**Figure S50.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (Z)-4-Tert-butyl-1-ethoxydodec-3-en-5-yne (**3s**)



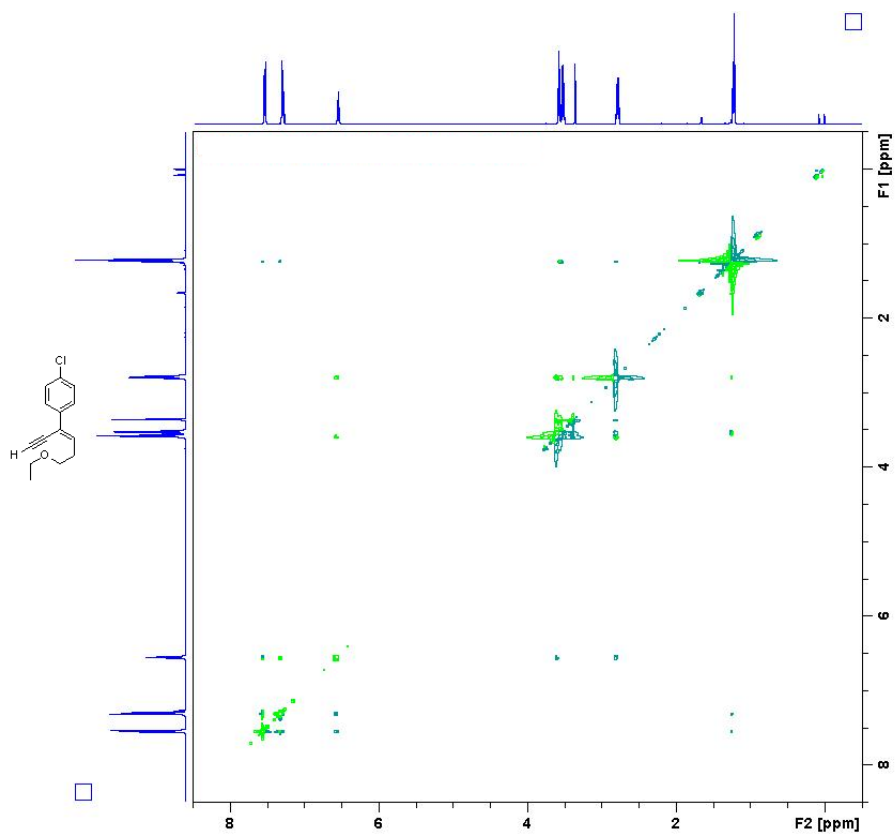
**Figure S51.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (Z)-9-(3-Ethoxypropylidene)pentadec-7-yne (**3t**)



**Figure S52.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 1-Chloro-4-((*E*)-6-ethoxyhex-3-en-1-yn-3-yl) benzene (**3u**)

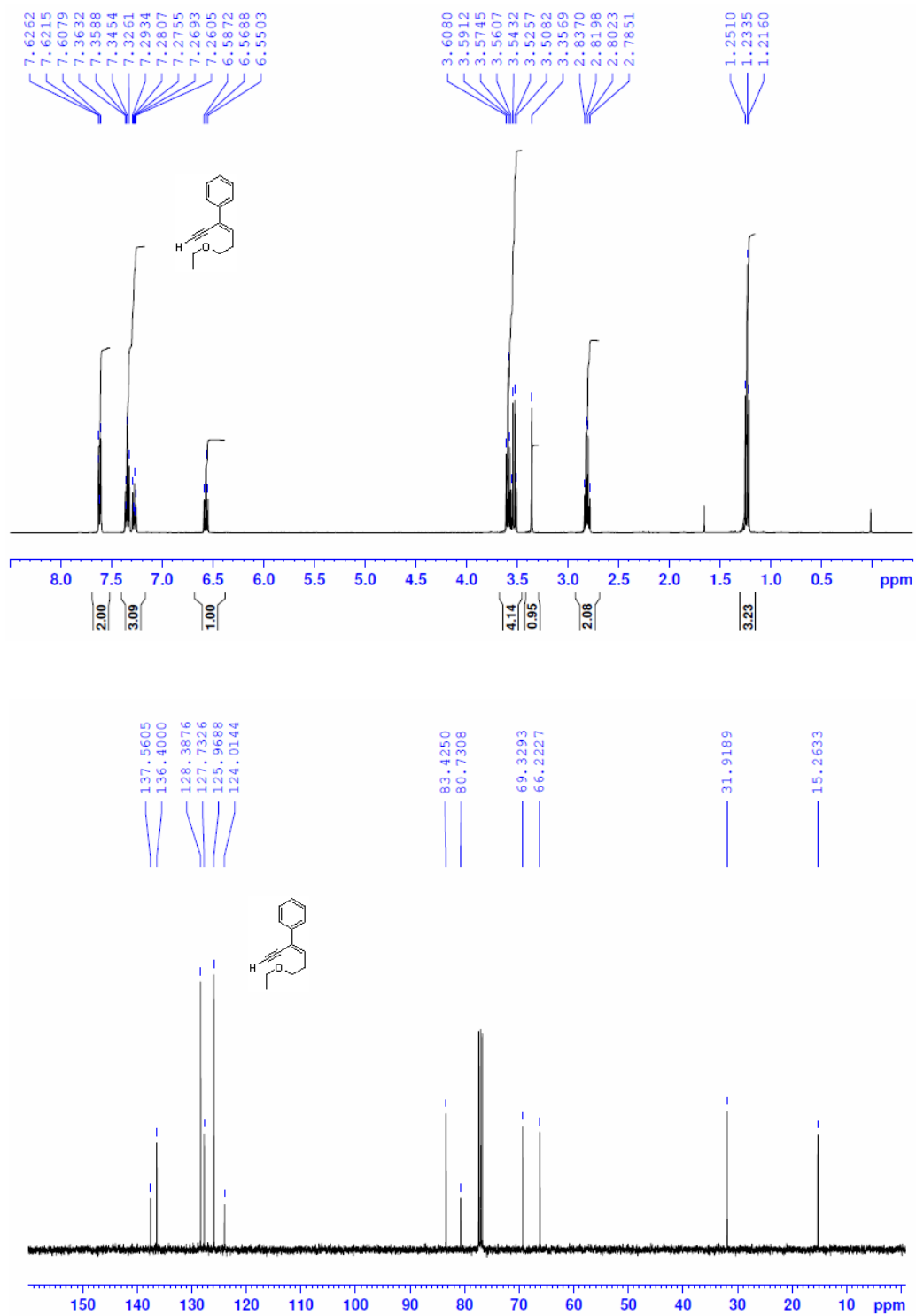


**Figure S53.** NOESY Spectrum of 1-Chloro-4-((*E*)-6-ethoxyhex-3-en-1-yn-3-yl)benzene (**3u**)

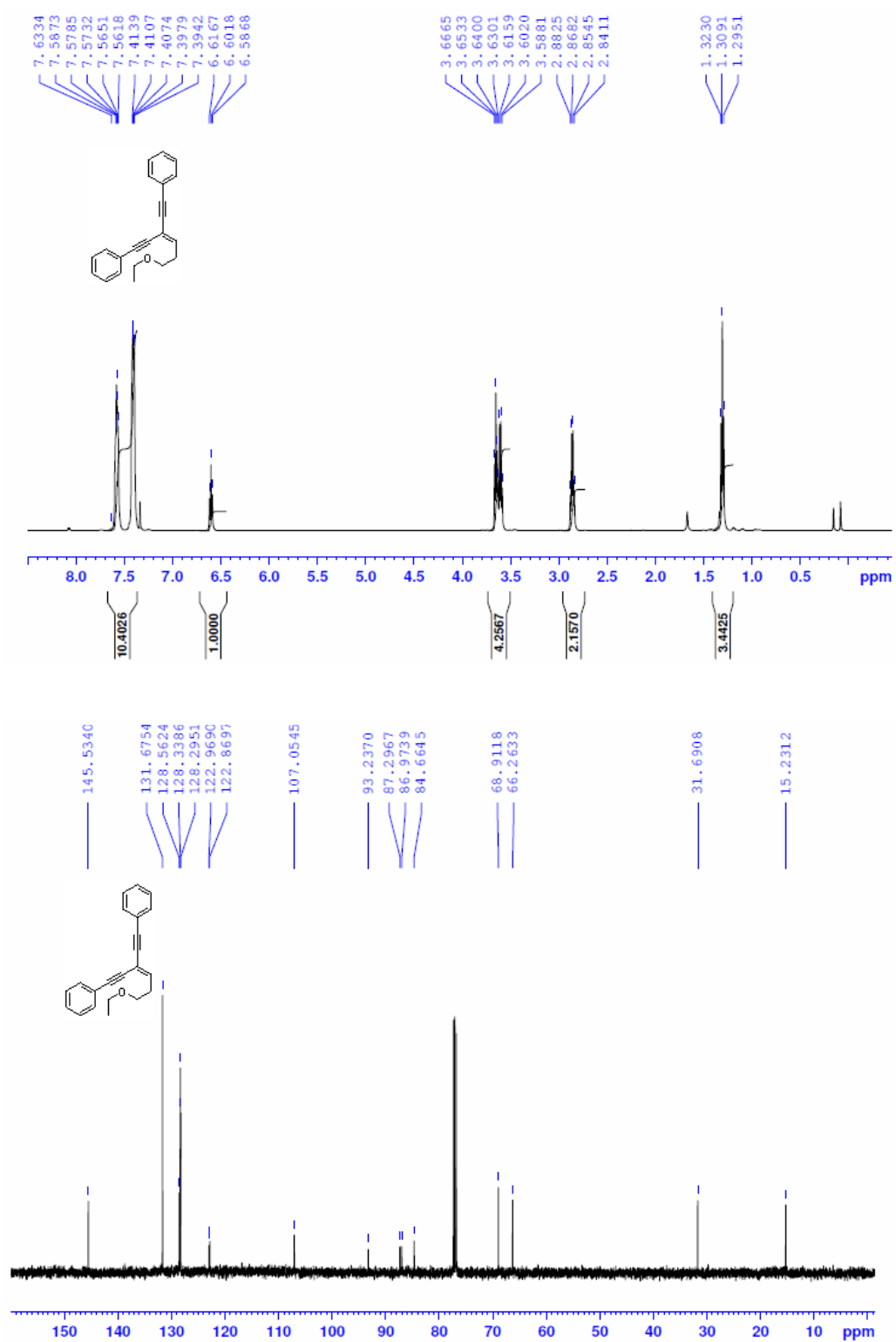




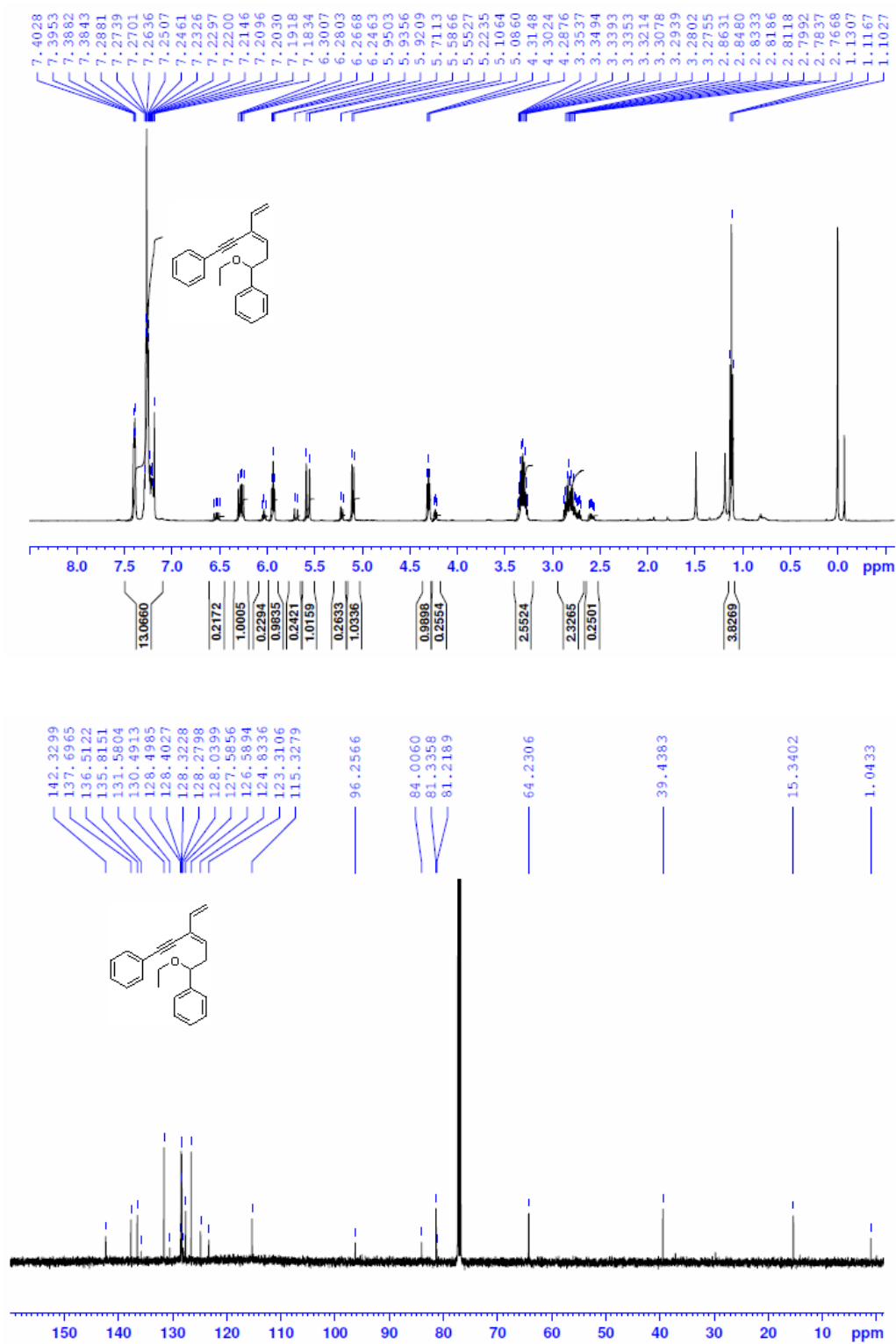
**Figure S54.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (*E*)-(6-Ethoxyhex-3-en-1-yn-3-yl)benzene (**3v**)



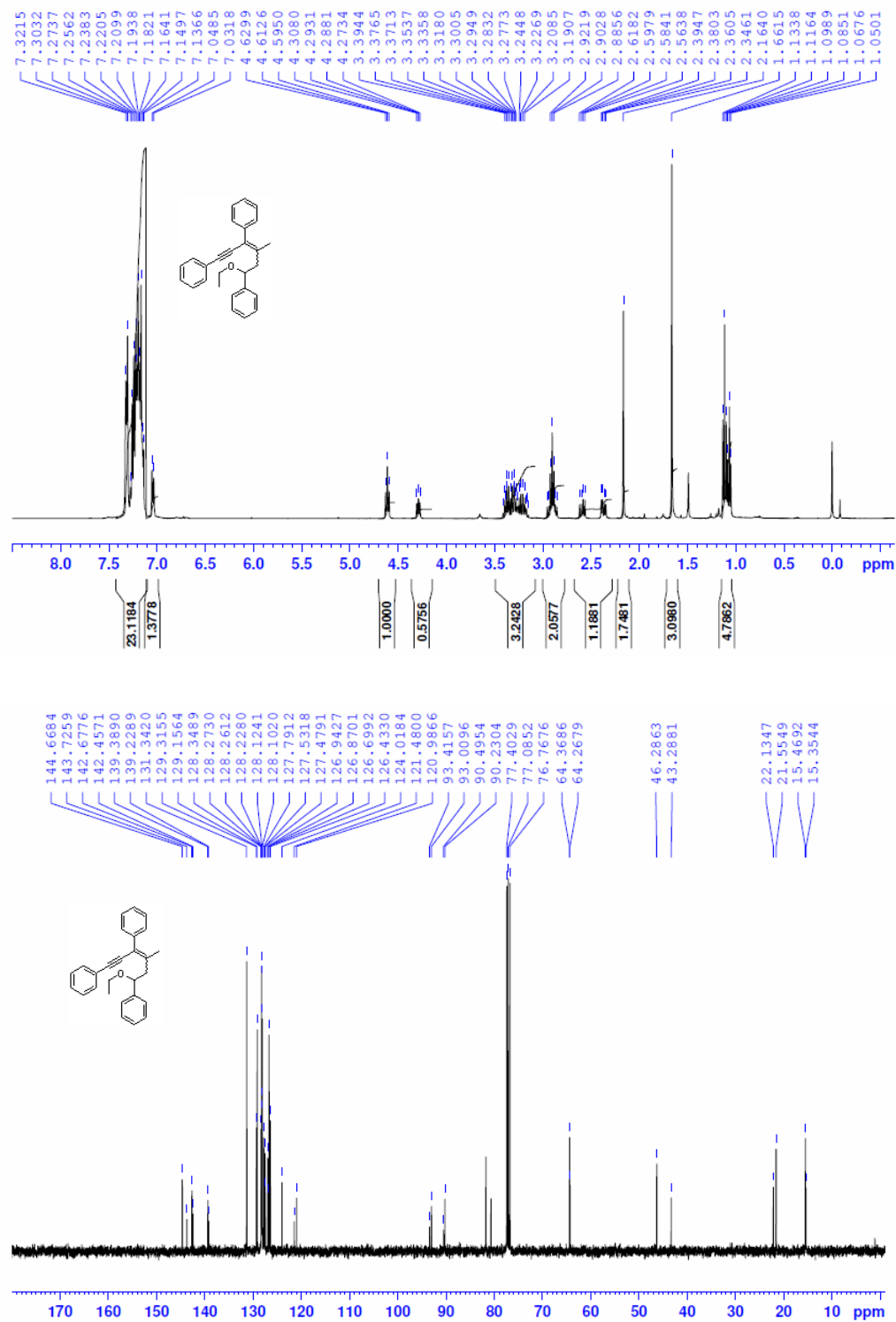
**Figure S55.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (3-(3-Ethoxypropylidene)penta-1,4-diyne-1,5-diyl)dibenzene (**3w**)



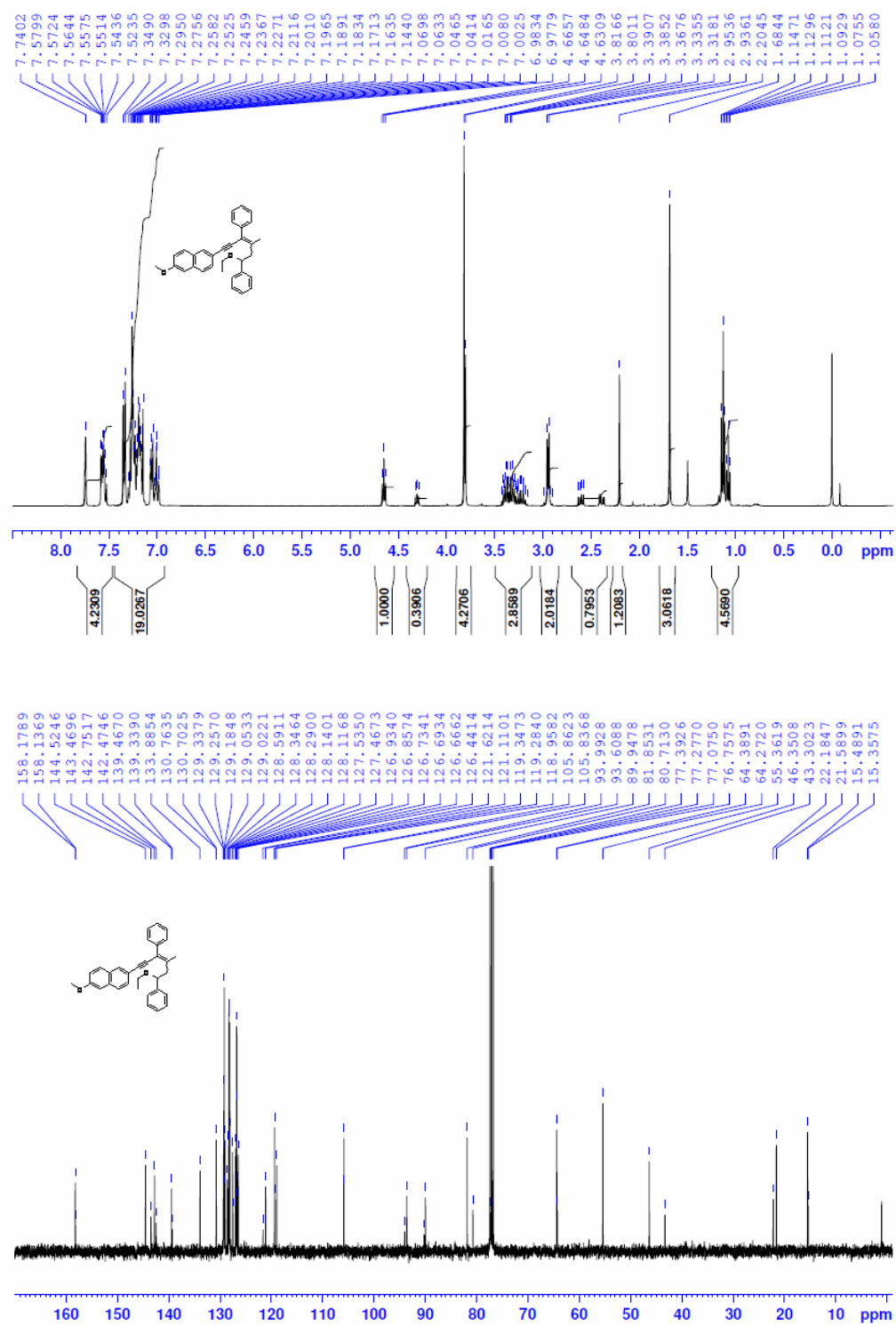
**Figure S56.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (Z)-(6-Ethoxy-3-vinylhex-3-en-1-yne-1,6-diyl) dibenzene (**3x**)



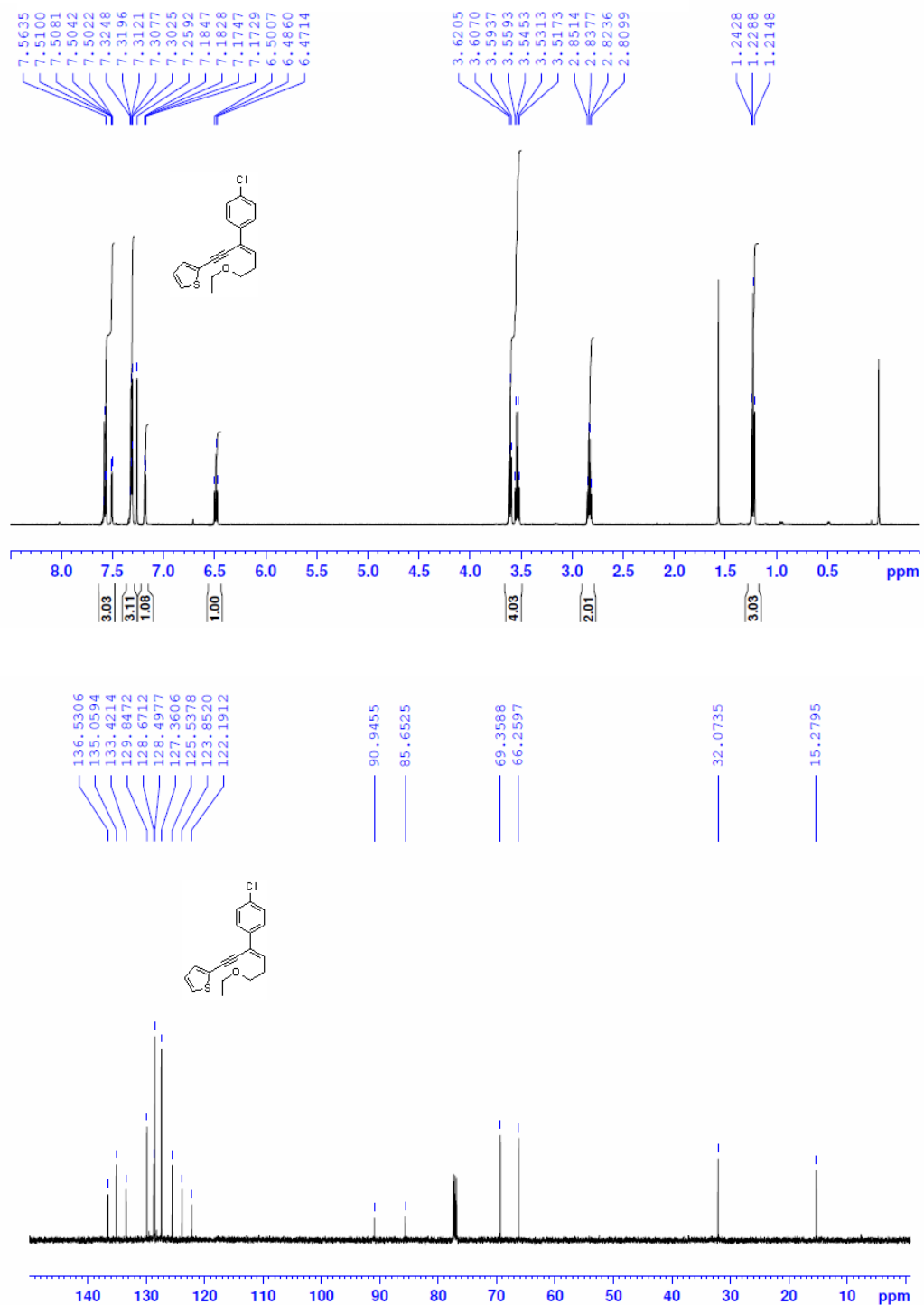
**Figure S57.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (6-Ethoxy-4-methyl-6-phenylhex-3-en-1-yn-1,3-diyl)dibenzene (**3y**)



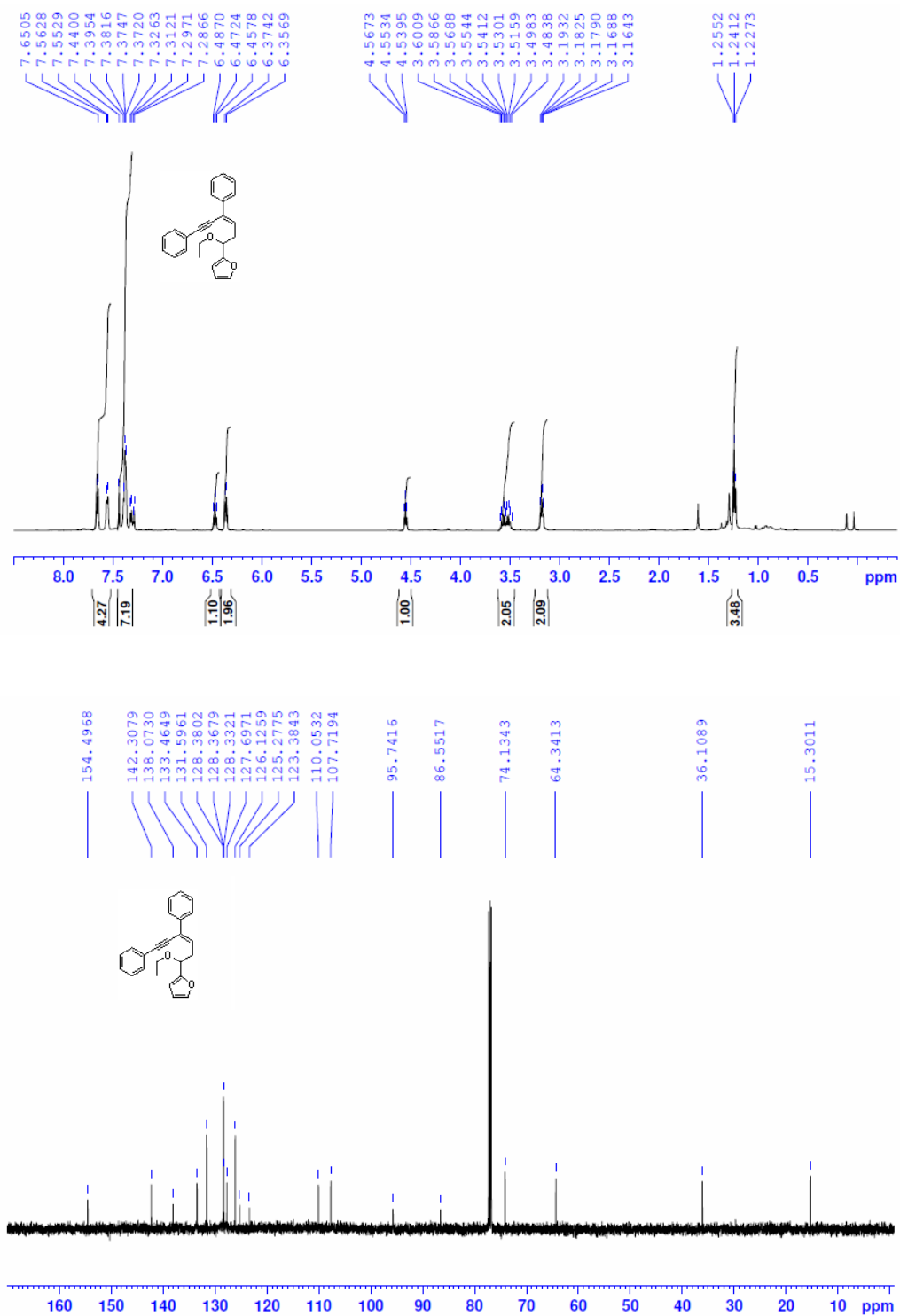
**Figure S58.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 2-(6-Ethoxy-4-methyl-3,6-diphenylhex-3-en-1-ynyl)-6-methoxynaphthalene (**3z**)



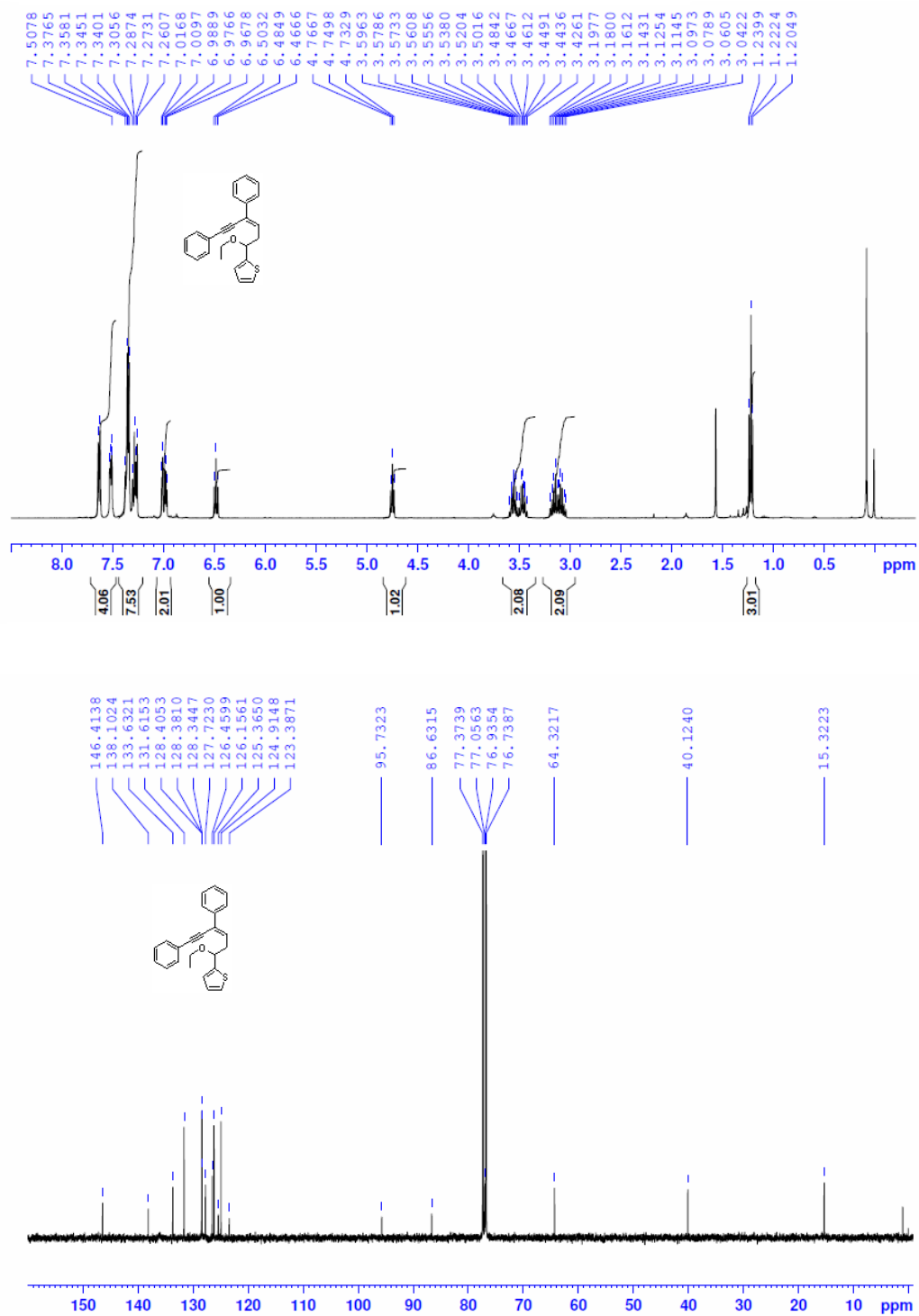
**Figure S59.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 2-((Z)-3-(4-Chlorophenyl)-6-ethoxyhex-3-en-1-ynyl)thiophene (**3a**)



**Figure S60.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-2-(1-Ethoxy-4,6-diphenylhex-3-en-5-ynyl)furan (**3 $\beta$** )

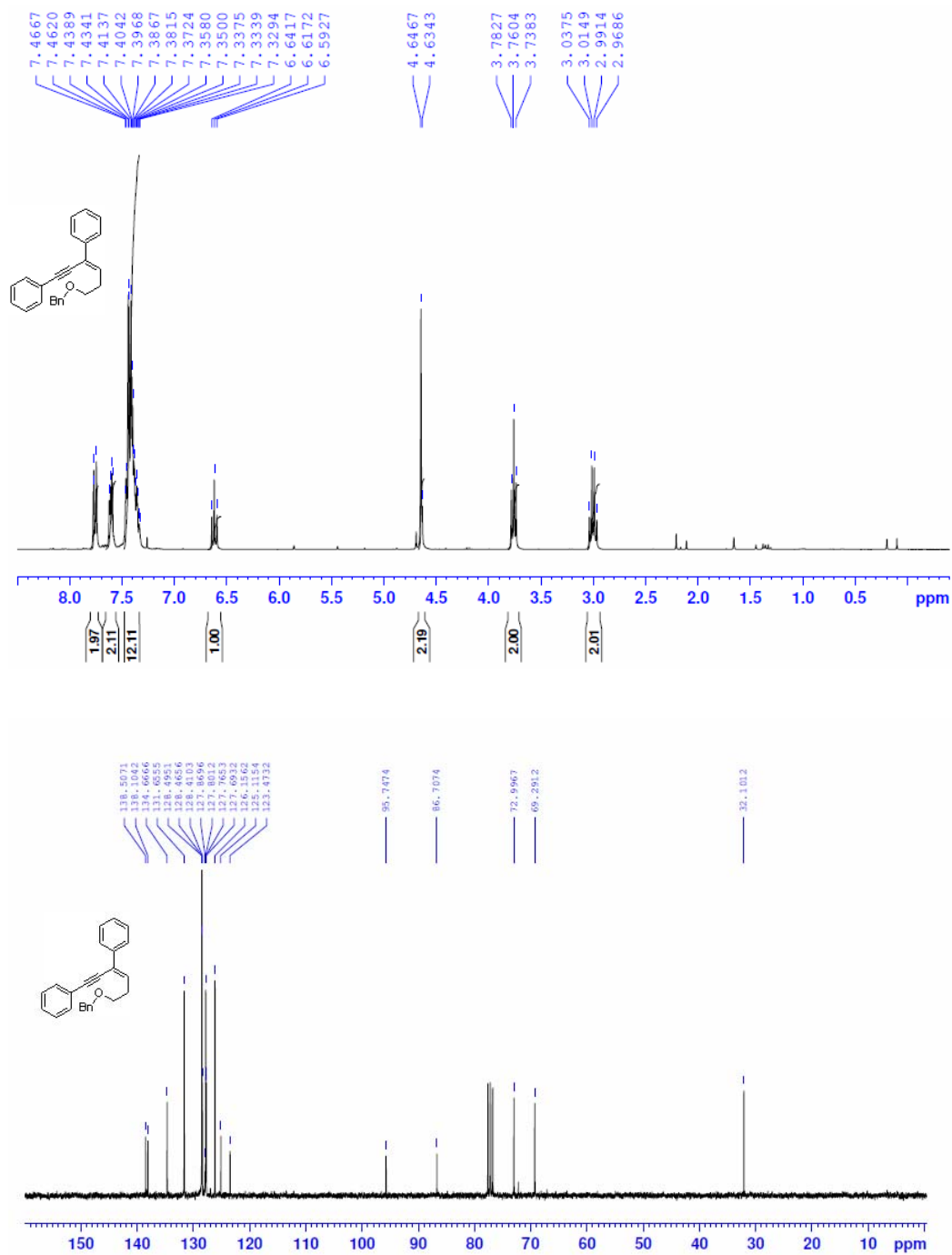


**Figure S61.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-2-(1-Ethoxy-4,6-diphenylhex-3-en-5-ynyl)thiophene (**3 $\chi$** )

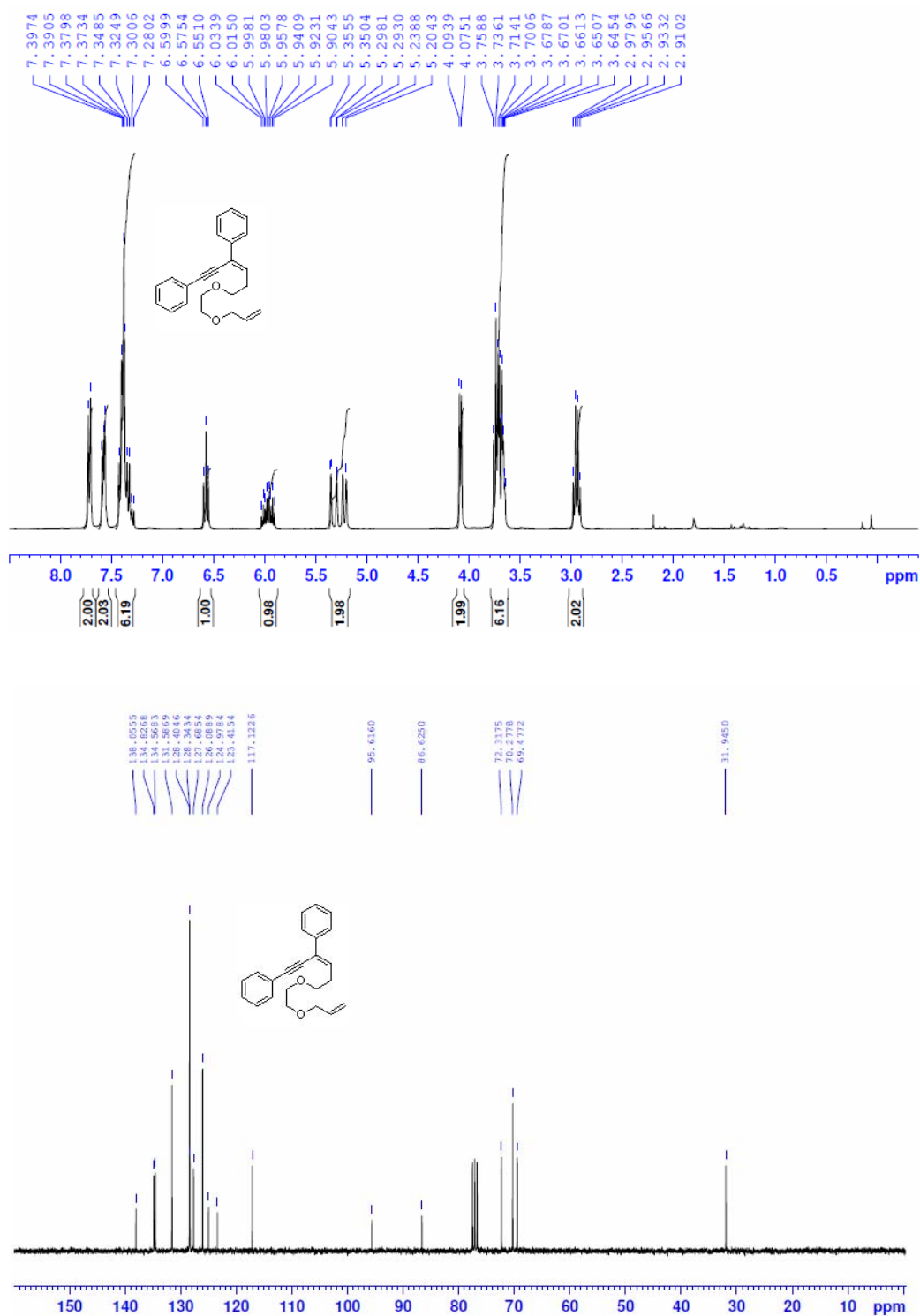




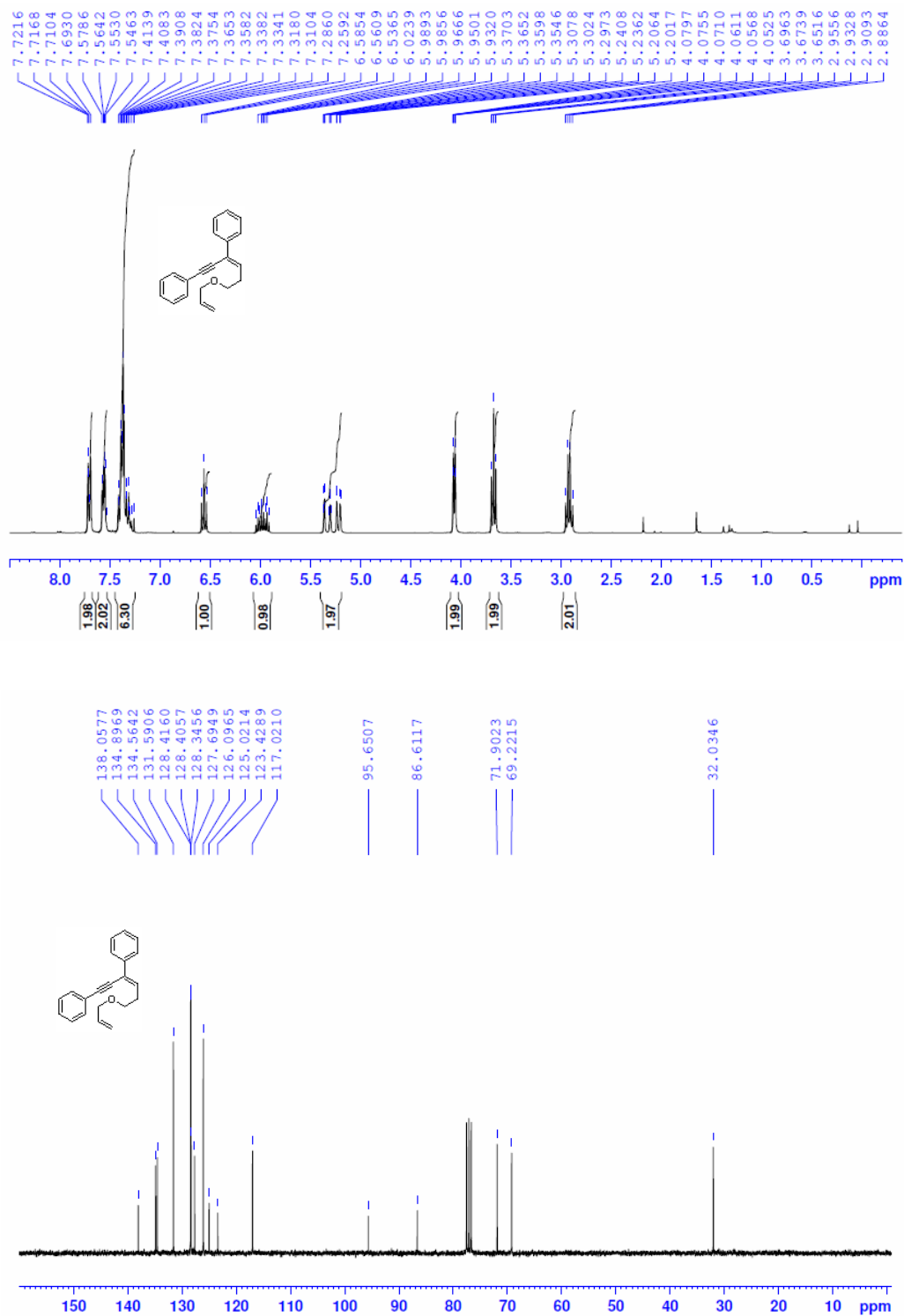
**Figure S62.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-6-(Benzyloxy)-1,3-diphenylhex-3-en-1-yne (**3d**)



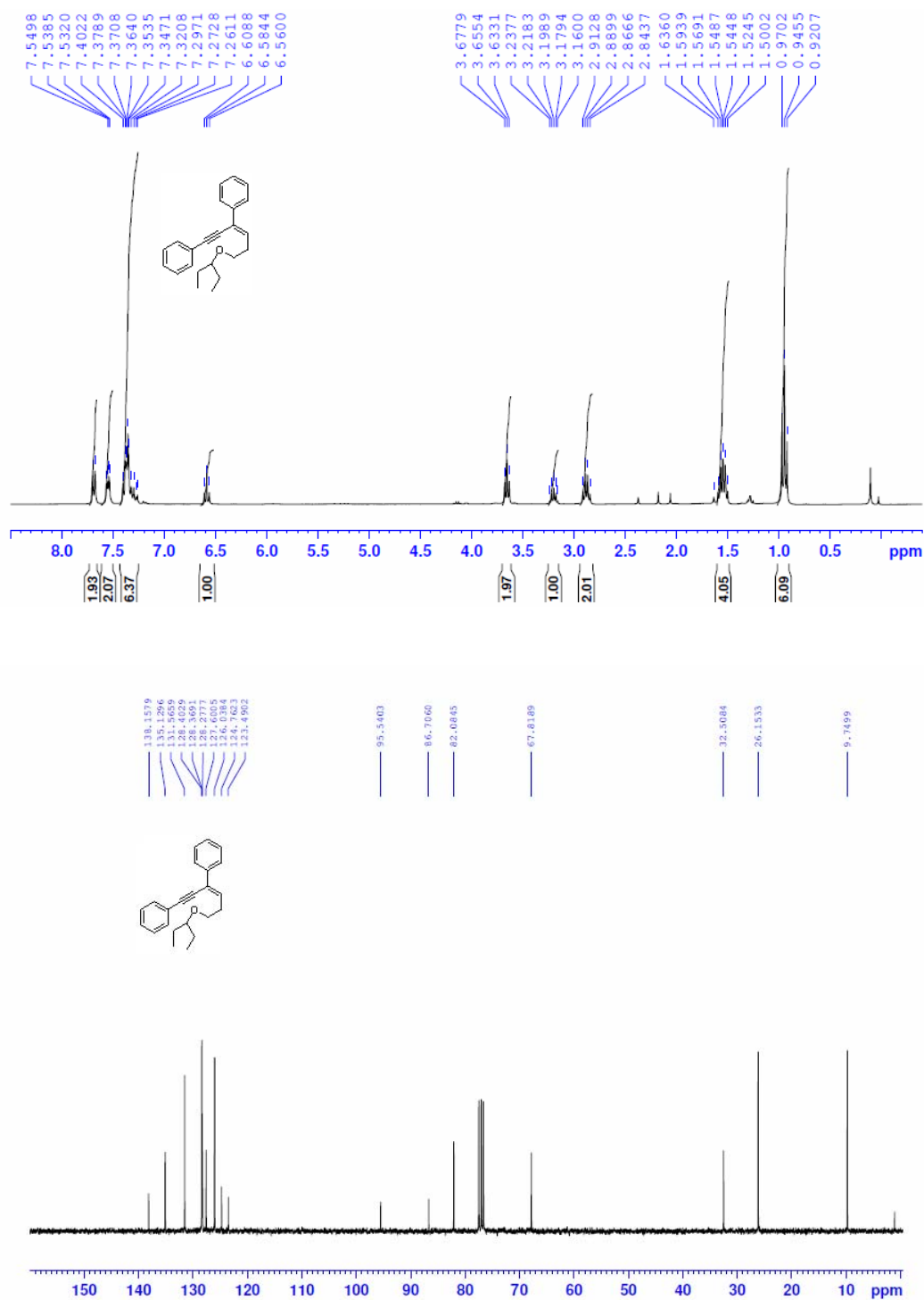
**Figure S63.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-6-(2-(Allyloxy)ethoxy)-1,3-diphenylhex-3-en-1-yne (**3e**)



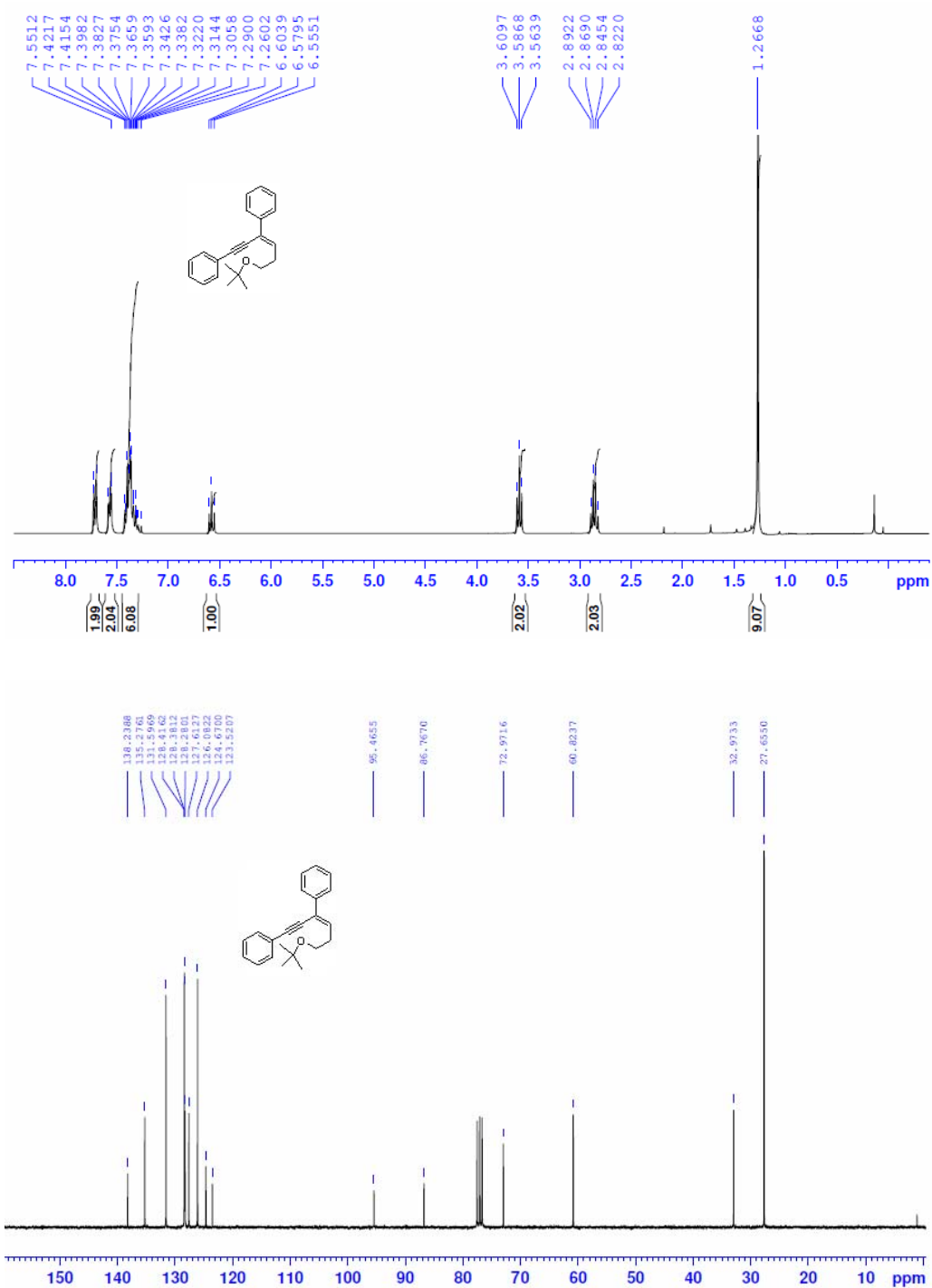
**Figure S64.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-6-(Allyloxy)-1,3-diphenylhex-3-en-1-yne (**3 $\phi$** )



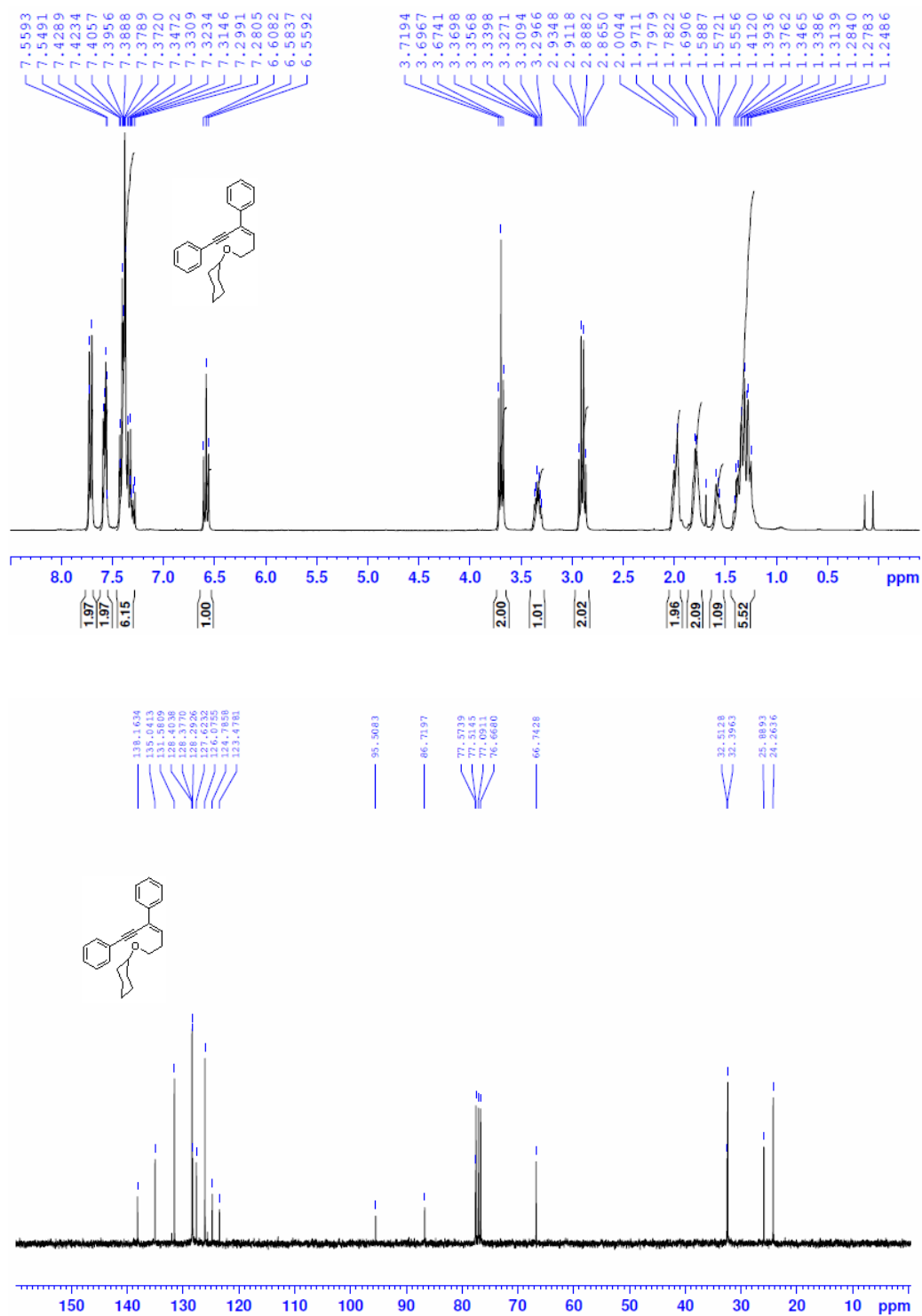
**Figure S65.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-6-(Pentan-3-yloxy)-1,3-diphenylhex-3-en-1-yne (**3y**)



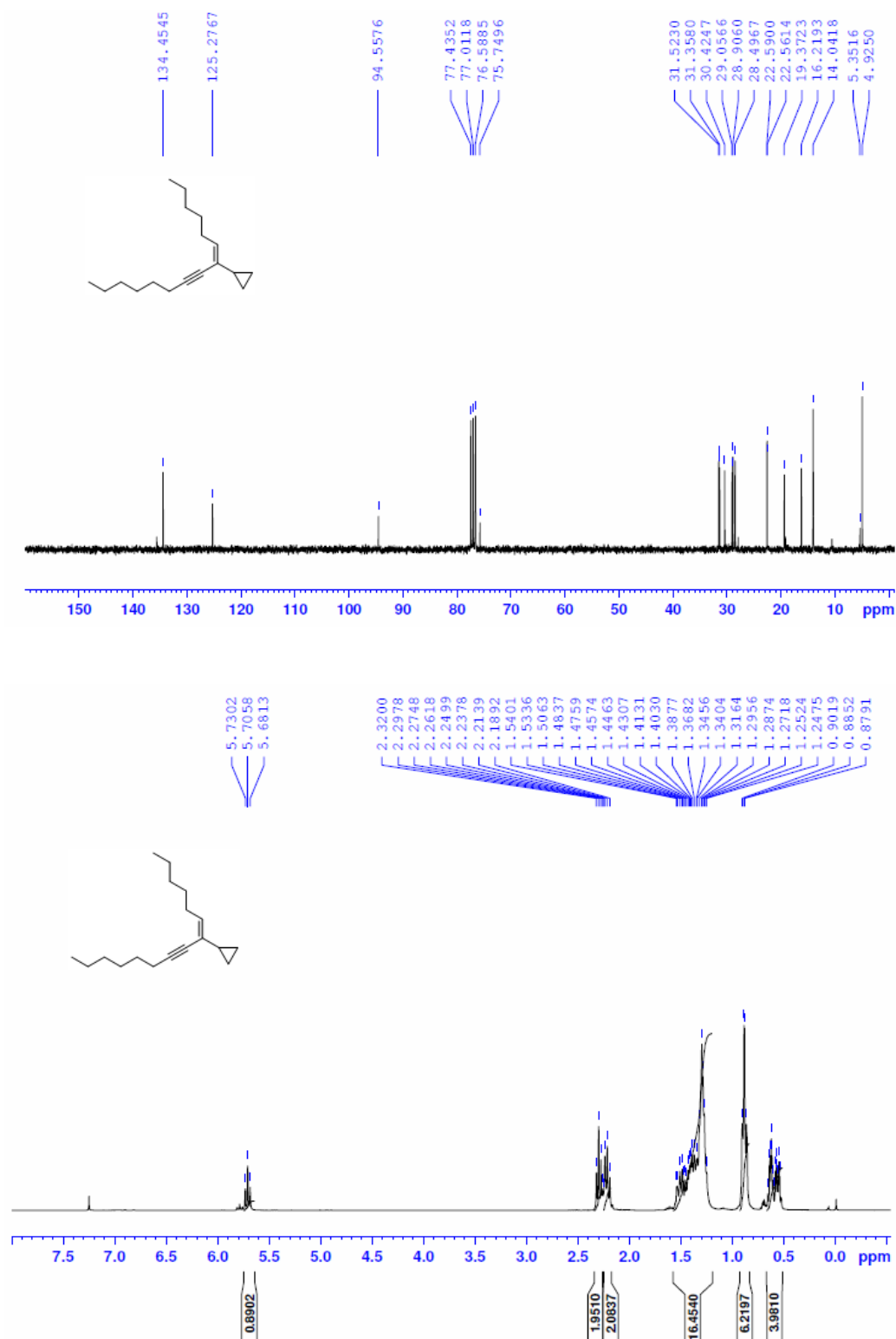
**Figure S66.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-6-tert-Butoxy-1,3-diphenylhex-3-en-1-yne (**3 $\eta$** )



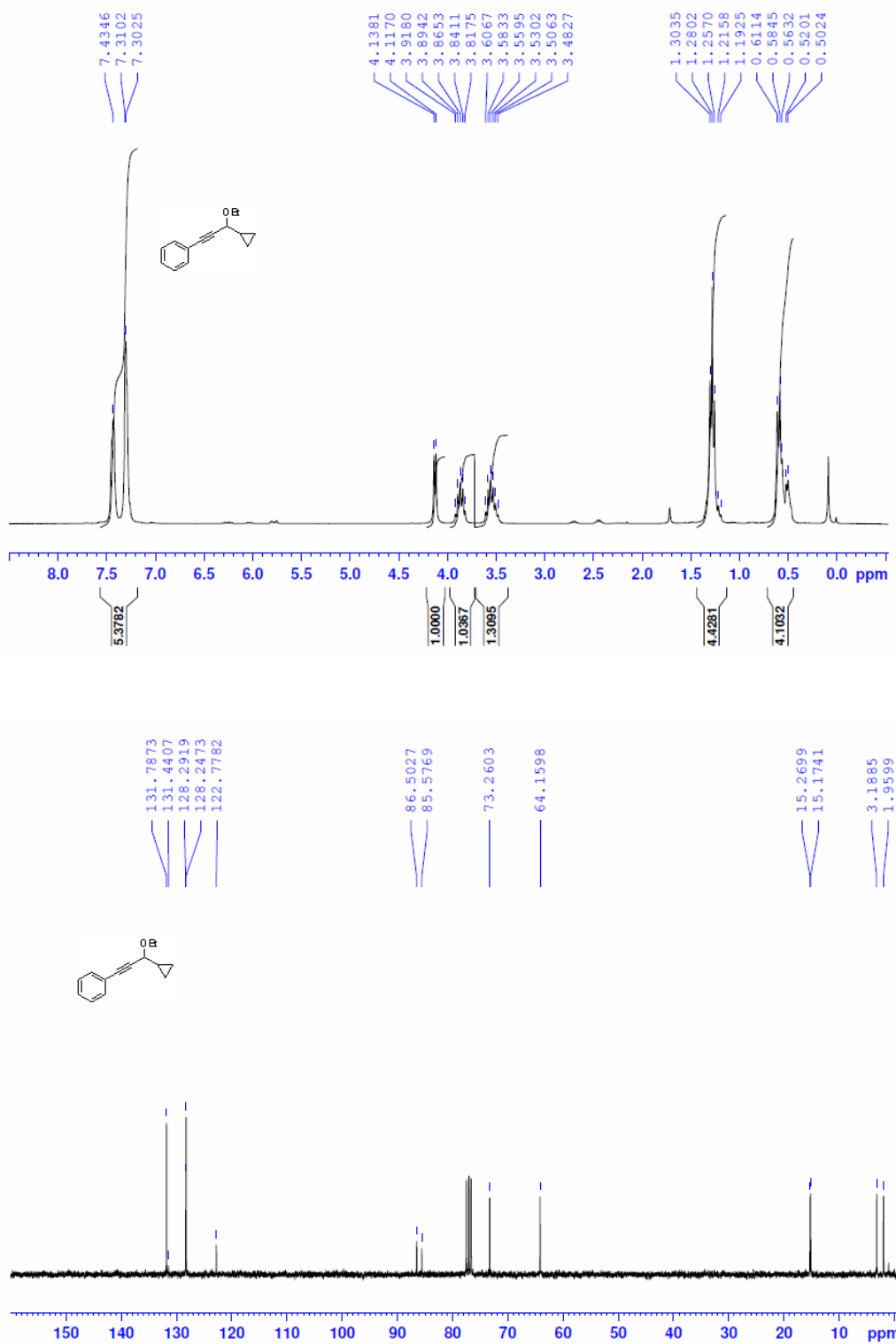
**Figure S67.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (Z)-6-(Cyclohexyloxy)-1,3-diphenylhex-3-en-1-yne (**3t**)



**Figure S68.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (Z)-Pentadec-6-en-8-yn-7-ylcyclopropane (**4**)



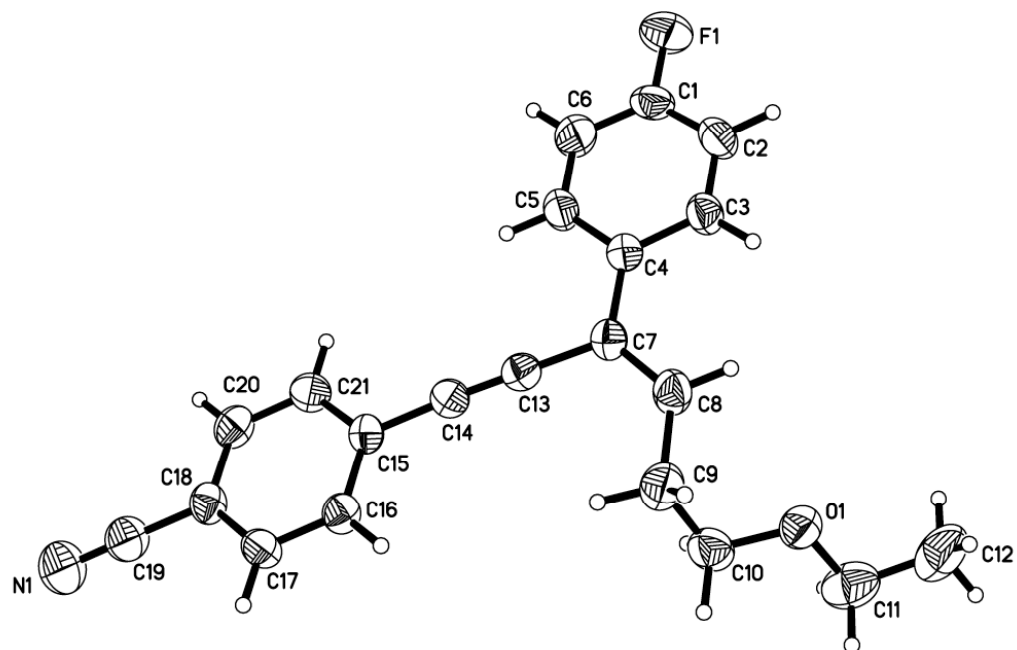
**Figure S69.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of (3-Cyclopropyl-3-ethoxyprop-1-ynyl) benzene (**5**)





**Figure S70.** ORTEP Drawing of 4-((Z)-6-Ethoxy-3-(4-fluorophenyl)hex-3-en-1-ynyl)

benzonitrile (**3j**) with Thermal Ellipsoids at 50% Probability levels<sup>S3</sup>



## References

- S1. Yamauchi, Y.; Onodera, G.; Sakata, K.; Yuki, M.; Miyake, Y.; Uemura, S.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 5175.
- S2. Rao, W.; Zhang, X.; Sze, E. M. L.; Chan, P. W. H. *J. Org. Chem.* **2009**, *74*, 1740.  
(b) Rao, W.; Chan, P. W. H. *Chem. Eur. J.* **2008**, *14*, 10486.
- S3. CCDC 720922 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).