Supplementary Information for

Double addition of organoaluminum reagents onto nitriles to access diethynyl carbinamines

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I. General information

All reactions were performed under Argon atmosphere and the glassware was dried in the oven at 100 °C. Toluene, THF, Et_2O and DCM were purified by passing through neutral alumina column under argon (Glass Technology GT S100 device). 1,2-Dichloroethane was distilled from CaH_2 before use. Trimethylsilylacetylene was purchased from TCI. Hex-1-yne, phenylacetylene, Me_2AlCl solution (0.9 M in *n*-heptane) and Me_3Al (2 M in toluene) were purchased from Sigma-Aldrich. *n*-BuLi solution (2.5 M in *n*-hexane) were purchased from Sigma-Aldrich and titrated before use.[1] Acyl cyanohydrins **4a-o** and **4r-t**,[2] cyanoester **4p**,[2a] cyanoester **4q**,[3] and cyanocarbamate **4u**[2a] were prepared by following reported procedure. The microwave reactions were performed using the CEM Discover SP® device. Thin layer chromatographies (TLC) were performed with Merck Silica 60 F254 plates. $KMnO_4$ solution was used for the revelation. Column chromatographies were carried out using silica gel 60 (40 - 63 µm) from Merck or the automatic chromatography device Reveleris X2. The spectroscopy ^{1}H-NMR (400 MHz or 500 MHz) and ^{13}C-NMR (100.6 MHz or 126 MHz) were recorded on Brucker AVANCE 400 and AVANCE NEO 500Hz spectrometer. Me_4Si was used as an intern reference in $CDCl_3$ NMR solvent. Chemical shifts (δ) are expressed in parts per million (ppm) units, relative to the residual solvent peak. Coupling constants (J) are expressed in Hertz (Hz). The multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quadruplet (q), multiplet (m) and broad signal (bs). IR spectra were obtained on a Perkin Elmer Spectrum One spectrometer on a single reflection diamond ATR unit. High resolution mass spectra (HRMS) were recorded on a the MicroTOF Bruker or AccuTOF device. Melting points were measured on Buchi melting point B-540 apparatus.

[1] Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

[2] (a) Setzer, P.; Forcher, G.; Boeda, F.; Pearson-Long, M. S. M.; Bertus, P. *Eur. J. Org. Chem.* **2014**, 171. (b) F. Boukattaya, F.; Caillé, J.; Ammar, H.; Rouzier, F.; Boeda, F.; Pearson-Long, M. S. M.; Bertus, P. *Synthesis*, **2016**, *48*, 906.

[3] Caillé, J.; Pantin, M.; Boeda, F.; Pearson-Long, M. S. M.; Bertus, P. *Synthesis* **2019**, *51*, 1329.

II. General procedures for organoalanes preparation

General procedure for the preparation of dimethylhexynylaluminum and dimethylphenylethynylaluminum solutions by alumination catalyzed by Et_3N (Method A)

A dry and argon-flushed flask equipped with a condenser was charged with a commercial trimethylaluminum solution (10 mL, 2 M in heptane, 20 mmol, ***CAUTION: trimethylaluminum is flammable***). Distilled triethylamine (0.28 mL, 2 mmol) was then added dropwise by a syringe and the solution was stirred for 5 min. The freshly distilled appropriate alkyne (22 mmol) was added dropwise. The mixture was stirred at 60 ^oC for 6 h, until the gas evolution ceased. The organoaluminum solution can be stored under argon in the dark for several days. [4] In general, the concentration of the solution was 1.6 M.

The organoaluminum solution can also be prepared using microwave activation: A dry and argon-flushed microwave-tube was successively charged with a commercial trimethylaluminum solution (10 mL, 2 M in heptane, 20 mmol, ***CAUTION: trimethylaluminum is flammable***), freshly distilled triethylamine (0.28 mL, 2 mmol) and the appropriate alkyne (22 mmol). The reaction was heated at 70 ^oC by using a microwave (150 W) for a period of 1 h. The organoaluminum solution can be stored under argon in the dark for several days. In general, the concentration of the solution was 1.6 M.

General procedure for the preparation of dimethylhexynylaluminum, dimethylphenylethynylaluminum and dimethyltrimethylsilylethynylaluminum solutions by transmetalation (Method B)

A Schlenk flask, dried and flushed with argon, was charged with the appropriate alkyne (10 mmol) and toluene (20 mL). A solution of *n*-BuLi (V = 5.6 mL, 10 mmol, 1.78 M in *n*-hexane) titrated using diphenyl acetic acid,[5] was added dropwise at -35 °C. A solution of Me_2AlCl (11 mL, 10 mmol, 0.9 M in *n*-heptane) was then added dropwise at the same temperature. The resulting mixture was stirred at 10 °C for 5 h to complete the conversion. The organoaluminum solution can be stored under argon in the dark for 5 days. In general, the concentration of the solution was 0.2 M.

[4] Feuvrie, C.; Blanchet, J.; Bonin, M.; Micouin, L. *Org. Lett.*, **2004**, *6*, 2333.
[5] Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

General procedure for titration of organoalanes solutions:[2b]

To a solution of *p*-chlorobenzaldehyde (281 mg, 2 mmol) in toluene or CH_2Cl_2 (2 mL) under argon at room temperature was added dropwise the freshly prepared organoaluminum solution (1 mmol). The solution was stirred at room temperature for 30 min, then cooled down to 0 °C. A saturated Rochelle's salt solution was added (5 mL) and the resulting mixture was stirred for 20 min. The two phases were separated and the organic phase was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was analyzed by ^{1}H-NMR ($CDCl_3$) and the concentration was determined by the integration of the -CHOH signal of the alcohol and the CHO signal of the residual starting aldehyde.

III. Synthesis and analytical data of compounds 5a-w

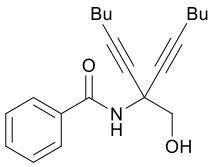
Conditions A - General procedure:

A dry and argon-flushed flask was charged with the appropriate acyl cyanohydrin **4** (1 mmol) and anhydrous DCM (4 mL) and the solution was warmed up to 40 °C. The appropriate organoalane solution prepared by method **A** (2.1 equiv) was added dropwise over 1 min and the resulting mixture was stirred at 40 °C for 1 h. The solution was cooled down to room temperature, then quenched by pouring the reaction mixture into a slurry of Merck silica gel 60 (5 g, 230– 400 mesh) in $CHCl_3$ (20 mL). The suspension was stirred for 1 h at room temperature and then filtered. The silica residue was washed with EtOAc and the filtrate was concentrated under reduced pressure to provide the crude di-addition product **5**, which was purified by column chromatography on silica gel when required.

Conditions B - General procedure:

The appropriate organoalane solution prepared using method **B** (2.5 equiv) was added dropwise to a solution of the appropriate acyl cyanohydrin **4** (1.0 mmol) in toluene (4 mL) at room temperature and the solution was stirred at 60 °C for 1 h. The progress of the reaction was monitored by TLC. The reaction was quenched by pouring the reaction mixture into a slurry of Merck silica gel 60 (5 g, 230–400 mesh) in $CHCl_3$ (20 mL). The suspension was stirred for 1 h at room temperature and then filtered. The silica residue was washed with EtOAc and the filtrate was concentrated under reduced pressure to provide the crude di-addition product **5**, which was purified by column chromatography on silica gel when required.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)benzamide (5a)**



The hydroxyamide **5a** was prepared using conditions **A**, and was isolated pure (315 mg, 97% yield) as white crystals without any further purification. The reaction was also performed on 5 mmol of **5a** to provide **5a** in 97% yield (1.58 g).

Rf ~0.30 (cyclohexane/EtOAc 8:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.77 (m, 2H, H_{Ar}), 7.51 (m, 1H, H_{Ar}), 7.47–7.41 (m, 2H, H_{Ar}), 6.65 (bs, 1H, NH), 4.00 (d, *J* = 6.5 Hz, 2H, CH_2OH), 3.69 (t, *J* = 6.5 Hz, 1H, OH), 2.25 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.58–1.47 (m, 4H, 2 *CH_2*CH_2CH_3), 1.47 – 1.34 (m, 4H, 2 CH_2*CH_2*CH_3), 0.90 (t, *J* = 7.2 Hz, 6H, 2 CH_3).

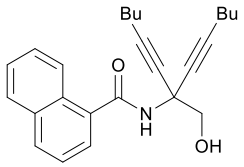
^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.1 (C=O), 134.5 (C_{Ar}), 132.2 (CH_{Ar}), 128.9 (2 CH_{Ar}), 127.5 (2 CH_{Ar}), 85.2 (2 *C*≡C), 77.0 (2 C≡*C*), 70.6 (CH_2OH), 51.4 (C-NH), 30.8 (2 *CH_2*CH_2CH_3), 22.3 (2 CH_2*CH_2*CH_3), 18.8 (2 C≡C-*CH_2*), 13.9 (2 CH_3).

IR (neat): ν = 3469, 3387, 2933, 2240, 1640, 1529, 1491, 1294, 1197, 1082, 933 cm^{-1}.

HRMS (ESI+): *m/z* ($M+Na^+$) calcd for $C_{21}H_{27}NNaO_2$: 348.1934, found: 348.1945.

Mp = 103 °C.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-1-naphthamide (5b)**



The hydroxyamide **5b** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 7:3) as eluent provided **5b** (327 mg, 87% yield) as white crystals.

Rf ~ 0.35 (cyclohexane/EtOAc 8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (m, 1H, H_{Ar}), 7.93 (m, 1H, H_{Ar}), 7.87 (m, 1H, H_{Ar}), 7.65 (dd, *J* = 7.0, 1.3 Hz, 1H, H_{Ar}), 7.59 – 7.51 (m, 2H, H_{Ar}), 7.47 (dd, *J* = 8.3, 7.0 Hz, 1H, H_{Ar}), 6.55 (bs, 1 H, NH), 4.06 (d, *J* =

7.1 Hz, 2H, CH_2OH), 3.75 (t, *J* = 7.1 Hz, 1 H, OH), 2.28 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.61–1.48 (m, 4H, 2 $CH_2CH_2CH_3$), 1.50 – 1.37 (m, 4H, 2 $CH_2CH_2CH_3$), 0.92 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

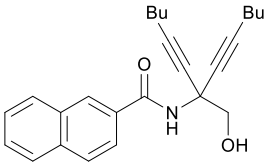
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3 (C=O), 134.1 (C_{Ar}), 134.0 (C_{Ar}), 131.2 (CH_{Ar}), 130.5 (C_{Ar}), 128.6 (CH_{Ar}), 127.5 (CH_{Ar}), 126.8 (CH_{Ar}), 125.6 (CH_{Ar}), 125.4 (CH_{Ar}), 125.0 (CH_{Ar}), 85.3 (2 *C*≡C), 76.9 (2 C≡*C*), 70.4 (CH_2OH), 51.6 (C-NH), 30.8 (2 $CH_2CH_2CH_3$), 22.3 (2 $CH_2CH_2CH_3$), 18.8 (2 C≡C-CH_2), 13.9 (2 CH_3).

IR (neat): ν = 3428, 3353, 2929, 2873, 1659, 1488, 1261, 1097, 780 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{25}H_{30}NO_2$: 376.2258, found: 376.2264.

Mp = 77 °C.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-2-naphthamide (5c)**



The hydroxyamide **5c** was prepared using conditions **B**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 7:3) as eluent provided **5c** (375 mg, quantitative yield) as white crystals.

Rf ~ 0.35 (Cyclohexane/EtOAc 8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.8 Hz, 1H, H_{Ar}), 8.09 – 7.78 (m, 4H, H_{Ar}), 7.59 – 7.53 (m, 2H, H_{Ar}), 6.80 (bs, 1H, NH), 4.04 (d, *J* = 7.1 Hz, 2H, CH_2OH), 3.69 (t, *J* = 7.1 Hz, 1H, OH), 2.27 (t, *J* = 7.2 Hz, 4H, 2 C≡C-CH_2), 1.58 – 1.50 (m, 4H, 2 $CH_2CH_2CH_3$), 1.46 – 1.38 (m, 4H, 2 $CH_2CH_2CH_3$), 0.91 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

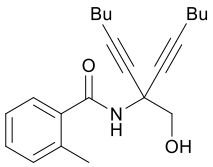
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2 (C=O), 135.2 (C_{Ar}), 132.9 (C_{Ar}), 131.6 (C_{Ar}), 129.3 (CH_{Ar}), 128.8 (CH_{Ar}), 128.2 (CH_{Ar}), 128.1 (CH_{Ar}), 128.1 (CH_{Ar}), 127.1 (CH_{Ar}), 124.0 (CH_{Ar}), 85.2 (2 *C*≡C), 77.0 (2 C≡*C*), 70.6 (CH_2OH), 51.4 (C-NH), 30.8 (2 $CH_2CH_2CH_3$), 22.3 (2 $CH_2CH_2CH_3$), 18.8 *(2* C≡C-CH_2), 13.9 (2 CH_3).

IR (neat): ν = 3450, 3316, 2933, 2244, 1622, 1536, 1309, 1082, 784 cm^{-1}.

HRMS (ESI+): *m/z* ($M+Na^+$) calcd for $C_{25}H_{29}NNaO_2$: 398.2090, found: 398.2090.

Mp = 106 °C.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-2-methylbenzamide (5d)**



The hydroxyamide **5d** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5) as eluent provided **5d** (291 mg, 86% yield) as a yellow oil.

Rf ~ 0.30 (Cyclohexane/EtOAc 8:2).

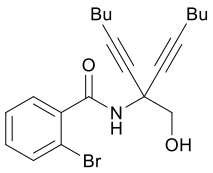
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.6, 1.5 Hz, 1H, H_{Ar}), 7.35 – 7.29 (m, 1H, H_{Ar}), 7.24 – 7.17 (m, 2H, H_{Ar}), 6.31 (bs, 1H, NH), 3.98 (d, *J* = 7.0 Hz, 2H, CH_2OH), 3.75 (t, *J* = 7.0 Hz, 1H, OH), 2.46 (s, 3H, $C_6H_4\mathit{CH_3}$), 2.25 (t, *J* = 7.1 Hz, 4H, 2 C≡C-$\mathit{CH_2}$), 1.57 – 1.47 (m, 4H, 2 $\mathit{CH_2}CH_2CH_3$), 1.46 – 1.36 (m, 4H, 2 $CH_2\mathit{CH_2}CH_3$), 0.91 (t, *J* = 7.2 Hz, 6H, 2 CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ 169.8 (C=O), 136.7 (CH_{Ar}), 136.1 (C_{Ar}), 131.4 (CH_{Ar}), 130.5 (CH_{Ar}), 127.1 (CH_{Ar}), 126.1 (*C*-CH_3), 85.2 (2 C≡C), 76.9 (2 C≡C), 70.5 (CH_2OH), 51.5 (C-NH), 30.8 (2 $\mathit{CH_2}CH_2CH_3$), 22.3 (2 $CH_2\mathit{CH_2}CH_3$), 19.9 ($C_6H_4\mathit{C}H_3$), 18.8 (2 C≡C-$\mathit{CH_2}$), 13.9 (2 CH_3).

IR (neat): ν = 3491, 3294, 2933, 2244, 1640, 1532, 1313, 1082, 754 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{22}H_{30}NO_2$: 340.2271, found: 340.2273.

2-Bromo-*N*-(7-(hydroxymethyl)trideca-5,8-diyn-7-yl)benzamide (5e)



The hydroxyamide **5e** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 7:3) as eluent provided **5e** (322 mg, 80% yield) as yellow crystals.

Rf ~ 0.30 (Cyclohexane/EtOAc 8:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H, H_{Ar}), 7.36 (td, *J* = 7.7, 1.3 Hz, 1 H, H_{Ar}), 7.28 (td, *J* = 7.7, 1.8 Hz, 1H, H_{Ar}), 6.56 (bs, 1H, NH), 4.00 (d, *J* = 5.9 Hz, 2H, CH_2OH), 3.48 (t, *J* = 5.9 Hz, 1H, OH), 2.26 (t, *J*

= 7.1 Hz, 4H, 2 C≡C-CH_2), 1.58 – 1.47 (m, 4H, 2 *CH_2*CH_2CH_3), 1.47 – 1.36 (m, 4H, 2 CH_2*CH_2*CH_3), 0.91 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

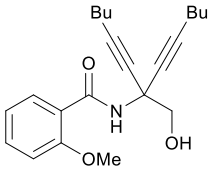
^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.0 (C=O), 137.6 (C_{Ar}), 133.7 (CH_{Ar}), 131.8 (CH_{Ar}), 130.0 (CH_{Ar}), 127.9 (CH_{Ar}), 119.7 (C-Br), 85.4 (2 *C*≡C), 76.6 (2 C≡*C*), 70.2 (CH_2OH), 51.6 (C-NH), 30.8 (2 *C*$H_2CH_2CH_3$), 22.3 (2 CH_2*C*H_2CH_3), 18.8 (2 C≡C-*C*H_2), 13.9 (2 CH_3).

IR (neat): ν = 3491, 3294, 2933, 2244, 1640, 1532, 1313, 1201, 1082, 754 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{21}H_{27}BrNO_2$: 404.1220, found: 404.1220.

Mp = 110 °C.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-2-methoxybenzamide (5f)**



The hydroxyamide **5f** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 7:3) as eluent provided **5f** (276 mg, 78% yield) as yellow crystals.

Rf ~ 0.40 (cyclohexane/EtOAc 8:2)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.65 (bs, 1H, H_{Ar}), 8.22 (dd, J = 7.5, 1.9 Hz, 1H, H_{Ar}), 7.46 (ddd, J = 8.3, 7.5, 1.9 Hz, 1H, H_{Ar}), 7.08 (ddd, J = 8.3, 7.5, 1.0 Hz, 1H, H_{Ar}), 6.97 (bs, 1H, NH), 4.09 (m, 1H, OH), 3.98 (d, J = 7.0 Hz, 2H, CH_2OH), 3.97 (s, 3H, OCH_3), 2.25 (t, J = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.55 – 1.46 (m, 4H, *CH_2CH_2*CH_3), 1.45 – 1.38 (m, 4H, *CH_2CH_2*CH_3), 0.9 (t, J = 7.3 Hz, 6H, 2 CH_3).

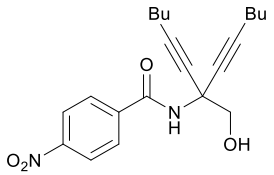
^{13}C-NMR (126 MHz, $CDCl_3$) δ 157.9 (C=O), 133.6 (C_{Ar}), 132.8 (2 CH_{Ar}), 121.7 (2 CH_{Ar}), 121.4 (C_{Ar}), 111.7 (2 *C*≡C), 84.7 (2 C≡*C*), 71.1 (CH_2OH), 56.4 (OCH_3), 51.2 (C-NH), 30.9 (2 *C*$H_2CH_2CH_3$), 22.3 (2 CH_2*C*H_2CH_3), 18.8 (2 C≡C-*C*H_2), 13.9 (2 CH_3).

IR (neat): ν = 3353, 2933, 2873, 1655, 1521, 1484, 1242, 1019, 762 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{22}H_{30}NO_3$: 356.2220, found: 356.2223.

Mp = 64 °C.

***N*-(7-(hydroxymethyl)trideca-5,8-diyn-7-yl)-4-nitrobenzamide (5g)**



The hydroxyamide **5g** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 7:3) as eluent provided **5g** (326 mg, 88% yield) as yellow crystals.

Rf ~ 0.28 (Cyclohexane/EtOAc 8:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.25 (m, 2H, H_{Ar}), 7.99 – 7.93 (m, 2H, H_{Ar}), 6.75 (bs, 1H, NH), 3.99 (s, 2H, CH_2OH), 3.08 (br, 1H, OH), 2.25 (t, *J* = 7.2 Hz, 4H, 2 C≡C-CH_2), 1.56-1.46 (m, 4H, 2 *CH_2*CH_2CH_3), 1.45 – 1.34 (m, 4H, 2 CH_2*CH_2*CH_3), 0.90 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

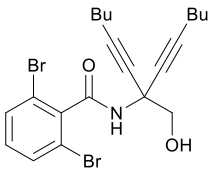
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8 (C=O), 150.1 (C_{Ar}), 140.1 (C-NO_2), 128.7 (2 CH_{Ar}), 124.1 (2 CH_{Ar}), 85.5 (2 *C*≡C), 76.4 (2 C≡*C*), 70.1 (CH_2OH), 51.0 (C-NH), 30.8 (2 *CH_2*CH_2CH_3), 22.3 (2 CH_2*CH_2*CH_3), 18.8 (2 C≡C-CH_2), 13.9 (2 CH_3).

IR (neat): ν = 3394, 2959, 2933, 2244, 1644, 1529, 1350, 1078, 851 cm^{-1}.

HRMS (ESI+): *m/z* (M+Na^+) calcd for $C_{21}H_{26}N_2NaO_4$: 393.1785, found: 393.1788.

Mp = 112 °C.

2,6-Dibromo-*N*-(7-(hydroxymethyl)trideca-5,8-diyn-7-yl)benzamide (5h)



The hydroxyamide **5h** was prepared using conditions **B**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (9:1 to 7:3) as eluent provided **5g** (390 mg, 81% yield) as a yellow oil.

Rf ~ 0.30 (Toluene/EtOAc 9:1)

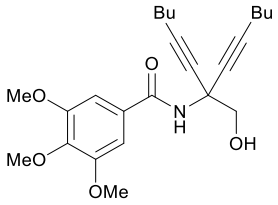
4.04 (d, *J* = 2.2 Hz, 2H, CH_2OH), 3.28 (bs, 1H, OH), 2.26 (t, *J* = 7.1Hz, 4H, 2 C≡C-CH_2), 1.58 – 1.46 (m, 4H, 2 *CH_2*CH_2CH_3), 1.45 – 1.37 (m, 4H, 2 *CH_2*CH_2CH_3), 0.91 (t, 7,1 Hz, 6H, 2 CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4 (*C*=O), 139.3 (C_{Ar}), 132.1 (2 CH_{Ar}), 131.8 (CH_{Ar}), 120.9 (2 C_{Ar}-Br), 85.7 (2 *C*≡C), 76.2 (2 C≡*C*$_9$), 69.9 (CH_2OH), 51.8 (C-NH), 30.8 (2 *CH_2*CH_2CH_3), 22.3 (2 CH_2*CH_2*CH_3), 18.8 (2 C≡C-CH_2), 14.0 (2 CH_3).

IR (neat): ν = 3490, 3294, 2930, 2249, 1640, 1532, 1327, 1201, 1082, 733 cm^{-1}.

HRMS (ESI+): *m/z* (M+Na^+) calcd for $C_{21}H_{25}Br_2NNaO_2$: 504.0140, found: 504.0144.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-3,4,5-trimethoxybenzamide (5i)**



The hydroxyamide **5i** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 7:3) as eluent provided **5i** (306 mg, 74% yield) as a yellow solid.

Rf ~ 0.15 (Cyclohexane/EtOAc 8:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 2H, H_{Ar}), 6.56 (bs, 1H, NH), 3.99 (d, *J* = 7.1 Hz, 2H, *CH_2*OH), 3.90 (s, 6H, 2 OCH_3), 3.87 (s, 3H, OCH_3), 3.58 (t, *J* = 7.1 Hz, 1H, OH), 2.25 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.57 – 1.47 (m, 4H, 2 *CH_2*CH_2CH_3), 1.46 – 1.35 (m, 4H, 2 CH_2*CH_2*CH_3) 0.90 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

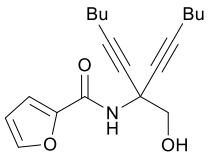
^{13}C NMR (100.6 MHz, $CDCl_3$) δ 166.8 (C=O), 153.5 (2 CH_3O*C_{Ar}*), 141.6 (CH_3O*C_{Ar}*), 129.8 (C_{Ar}), 105.0 (2 CH_{Ar}), 85.1 (2 *C*≡C), 76.9 (2 C≡*C*), 70.5 (CH_2OH), 61.2 (OCH_3), 56.7 (2 OCH_3), 51.3 (C-NH), 30.8 (2 *C*$H_2CH_2CH_3$), 22.3 (2 CH_2*C*H_2CH_3), 18.8 (2 C≡C-*C*H_2), 13.9 (2 CH_3).

IR (neat): ν = 3491, 2959, 2933, 2259, 1499, 1335, 1130, 1078 cm^{-1}.

HRMS (ESI+): *m/z* (M+H^+) calcd for $C_{24}H_{34}NO_5$: 416.2431, found: 416.2433.

Mp = 68°C.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)furan-2-carboxamide (5j)**



The hydroxyamide **5j** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 7:3) as eluent provided **5j** (281 mg, 89% yield) as yellow crystals.

Rf ~ 0.20 (cyclohexane/EtOAc 8:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 1.8, 0.8 Hz, 1H, O-CH_{Ar}), 7.15 (dd, *J* = 3.5, 0.8 Hz, 1H, OCH=CH-*CH_{Ar}*), 6.85 (bs, 1H, NH), 6.50 (dd, *J* = 3.5, 1.8 Hz, 1H, OCH=*CH_{Ar}*), 3.98 (d, *J* = 7.0 Hz, 2H, CH_2OH), 3.62 (t, *J* = 7.1 Hz, 1H, OH), 2.24 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.56 – 1.47 (m, 4H, 2 *CH_2*CH_2CH_3), 1.45 – 1.35 (m, 4H, 2 CH_2*CH_2*CH_3) , 0.90 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

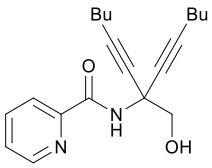
^{13}C NMR (100.6 MHz, $CDCl_3$) δ 157.8 (C=O), 147.8 (OC_{Ar}), 144.5 (OCH_{Ar}), 115.5 (OCH=CH-*CH_{Ar}*), 112.6 (OCH=*CH_{Ar}*), 85.3 (2 *C*≡C), 76.7 (2 C≡*C*), 70.4 (CH_2OH), 51.1 (C-NH), 30.8 (2 *CH_2*CH_2CH_3), 22.3 (2 CH_2*CH_2*CH_3), 18.8 (2 C≡C-*CH_2*), 13.9 (2 CH_3).

IR (neat): ν = 3394, 2959, 2933, 2240, 1640, 1309, 1194, 1082 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{19}H_{26}NO_3$: 316.1907, found: 316.1905.

Mp = 55 °C.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)picolinamide (5k)**



The hydroxyamide **5k** was prepared using conditions **B** with 4 equivalents of dimethylhexynylaluminum reagent (4 mmol). After reaction at 60 °C for 1 h, the reaction solution was cooled down to room temperature and poured into 4:1 THF/H_2O mixture (5 mL). The resulting mixture was stirred for 20 min at room temperature, then filtered on celite. The filtrate was concentrated under reduced pressure and purification by column chromatography on silica gel using

cyclohexane/EtOAc (6:4) containing Et_3N (3 vol%) as eluent provided **5k** (247 mg, 76% yield) as a brown oil.

Rf ~ 0.29 (Cyclohexane/ EtOAc 6:4).

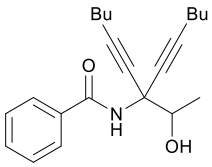
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 2.0 Hz, 1H, CH_{Ar}), 8.68 (dd, *J* = 5.0, 1.6 Hz, 1H, CH_{Ar}), 8.11 (dd, *J* = 8.0, 2.0 Hz, 1 H, CH_{Ar}), 7.35 (dd, *J* = 8.0, 5.0 Hz, 1H, CH_{Ar}), 6.90 (bs, 1H, NH), 3.99 (s, 2H, C*H*$_2$OH), 2.22 (t, *J* = 7.2 Hz, 4H, 2 C≡C-CH_2), 1.54 – 1.44 (m, 2H, 2 *CH*$_2$$CH_2CH_3$), 1.43 – 1.32 (m, 2H, 2 CH_2*CH*$_2$$CH_3$), 0.88 (t, *J* = 7.2 Hz, 6H, 2 CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0 (C=O), 152.6 (CH_{Ar}), 148.4 (CH_{Ar}), 135.7 (CH_{Ar}), 130.4 (C_{Ar}), 123.8 (CH_{Ar}), 85.2 (2 *C*≡C), 76.8 (2 C≡*C*), 70.0 (CH_2OH), 51.0 (C-NH), 30.8 (2 *C*$H_2CH_2CH_3$), 22.3 (2 CH_2*C*H_2CH_3), 18.8 (2 C≡C-*C*H_2), 13.9 (2 CH_3).

IR (neat): ν = 3335, 2959, 2933, 2244, 1659, 1525, 1305, 1201, 1078, 707 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{20}H_{27}N_2O_2$: 327.2067, found: 327.2066.

***N*-(7-(1-Hydroxyethyl)trideca-5,8-diyn-7-yl)benzamide (5l)**



The hydroxyamide **5l** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5l** (279 mg, 82% yield) as a white solid.

Rf ~ 0.32 (cyclohexane/EtOAc 8:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H, CH_{Ar}), 7.55 – 7.47 (m, 1H, H_{Ar}), 7.47 – 7.38 (m, 2H, H_{Ar}), 6.70 (bs, 1H, NH), 4.23 (m, 1H, CHOH), 3.41 (m, 1H, OH), 2.31 – 2.19 (m, 4H, 2 C≡C-CH_2), 1.58 – 1.49 (m, 4H, 2 *CH*$_2$$CH_2CH_3$), 1.44 (d, *J* = 2.9 Hz, 3H, *CH*$_3$-CHOH) 1.46 – 1.38 (m, 4H, 2 CH_2*CH*$_2$$CH_3$), 0.97 – 0.84 (m, 6H, 2 CH_3).

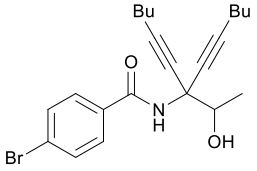
^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.0 (C=O), 134.7 (C_{Ar}), 132.1 (CH_{Ar}), 128.9 (2 CH_{Ar}), 127.5 (2 CH_{Ar}), 85.5 (*C*≡C), 85.1 (C≡*C*), 77.6 (*C*≡C), 76.5 (C≡*C*), 73.9 (CHOH), 54.8 (C-NH), 30.9 (*C*$H_2CH_2CH_3$), 30.8 (*C*$H_2CH_2CH_3$), 22.3 (CH_2*C*H_2CH_3), 22.3 (CH_2*C*H_2CH_3), 18.8 (2 C≡C-*C*H_2), 18.8 (*CH*$_3$CHOH), 13.9 (2 CH_3).

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{22}H_{30}NO_2$: 340.2271, found: 340.2267.

IR (neat): ν = 3417, 3383 2959, 2933, 2873, 2244, 1663, 1477, 1287, 1145 cm^{-1}.

Mp = 105 °C.

4-Bromo-*N*-(7-(1-hydroxyethyl)trideca-5,8-diyn-7-yl)benzamide (5m)



The hydroxyamide **5m** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5m** (350 mg, 84% yield) as yellow crystals.

Rf ~ 0.25 (cyclohexane/EtOAc 8:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H, 2 *o*-CH_{Ar}), 7.60 – 7.53 (m, 2H, 2 *m*-CH_{Ar}), 6.67 (bs, 1H, NH), 4.19 (dq, *J* = 7.6, 6.2 Hz, 1H, *CH*-OH), 3.07 (d, *J* = 7.6 Hz, 1H, OH), 2.25 (t, *J* = 7.0 Hz, 4H, 2 C≡C-CH_2), 1.57 – 1.46 (m, 4H, 2 $CH_2CH_2CH_3$), 1.44 (d, J = 6.2 Hz, 3H, CH_3-CHOH), 1.45 – 1.34 (m, 4H, 2 $CH_2CH_2CH_3$) 0.90 (t, *J* = 7.3 Hz, 3H, CH_3), 0.89 (t, *J* = 7.3 Hz, 3H, CH_3).

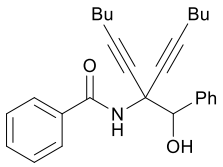
^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.9 (C=O), 133.5 (CBr), 132.0 (2 *m*-CH_{Ar}), 129.1 (2 *o*-CH_{Ar}), 126.7 (C_{Ar}), 85.5 (*C*≡C), 85.0 (*C*≡C), 76.2 (2 C≡*C*), 73.8 (CHOH), 54.5 (C-NH), 30.8 (2 $CH_2CH_2CH_3$), 22.3 (2 $CH_2CH_2CH_3$), 18.8 (2 C≡C-CH_2), 18.7 (CH_3CHOH), 13.9 (2 CH_3).

IR (neat): ν = 3506, 3327, 2955, 2929, 1629, 1540, 1320, 1015, 851, 762 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{22}H_{29}BrNO_2$: 418.1376, found: 418.1379.

Mp = 107 °C.

***N*-(7-(Hydroxy(phenyl)methyl)trideca-5,8-diyn-7-yl)benzamide (5n)**



The hydroxyamide **5n** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5n** (306 mg, 76% yield) as yellow crystals.

Rf ~ 0.40 (cyclohexane/EtOAc 8:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H, H_{Ar}), 7.56 – 7.51 (m, 2H, H_{Ar}), 7.51 – 7.46 (m, 1H, H_{Ar}), 7.43 – 7.36 (m, 2H, H_{Ar}), 7.32 – 7.24 (m, 3H, H_{Ar}), 6.49 (bs, 1H, NH), 5.25 (s, 1H, *CH*OH), 5.07 (bs, 1H, OH), 2.29 – 2.23 (m, 2H, C≡C-CH_2), 2.23 – 2.18 (m, 2H, C≡C-CH_2), 1.57 – 1.43 (m, 4H, 2 *CH_2*CH_2CH_3), 1.44 – 1.30 (m, 4H, 2 CH_2*CH_2*CH_3), 0.91 (t, *J* = 7.3 Hz, 3H, CH_3), 0.88 (t, *J* = 7.3 Hz, 3H, CH_3).

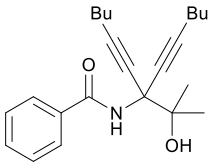
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7 (C=O), 139.2 (C_{Ar}), 134.3 (C_{Ar}), 132.2 (CH_{Ar}), 128.9 (2 CH_{Ar}), 128.4 (2 CH_{Ar}), 128.3 (CH_{Ar}), 127.7 (2 CH_{Ar}), 127.4 (2 CH_{Ar}), 86.7 (*C*≡C), 86.7 (*C*≡C), 79.6 (CH-OH), 76.9 (C≡*C*), 76.8 (C≡*C*), 55.7 (C-NH), 30.6 (2 *C*$H_2CH_2CH_3$), 22.3 (2 CH_2*CH_2*CH_3), 18.8 (2 C≡C-*CH_2*), 13.9 (2 CH_3).

IR (neat): ν = 3383 2959, 2933, 2244, 1640, 1525, 1290, 1186, 1033 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{27}H_{32}NO_2$: 402.2428, found: 402.2431.

Mp = 101 °C.

***N*-(7-(2-Hydroxypropan-2-yl)trideca-5,8-diyn-7-yl)benzamide (5o)**



The hydroxyamide **5o** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5o** (280 mg, 79% yield) as yellow crystals.

Rf ~ 0.40 (cyclohexane/EtOAc 8:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H, H_{Ar}), 7.51 – 7.46 (m, 1H, H_{Ar}), 7.45 – 7.39 (m, 2H, H_{Ar}), 6.78 (bs, 1H, NH), 3.95 (bs, 1H, OH), 2.29 – 2.20 (m, 4H, 2 C≡C-CH_2), 1.55 – 1.45 (m, 4H, 2 $CH_2CH_2CH_3$), 1.49 (s, 6H, 2 CH_3-C-OH), 1.41 – 1.35 (m, 4H, 2 $CH_2CH_2CH_3$), 0.88 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

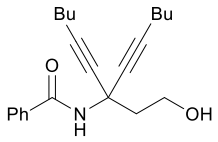
^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.2 (C=O), 134.8 (C_{Ar}), 132.0 (CH_{Ar}), 128.8 (2 CH_{Ar}), 127.5 (2 CH_{Ar}), 84.7 (2 C≡C), 77.6 (2 C≡C), 77.1 (C-OH), 57.8 (C-NH), 30.8 (2 $CH_2CH_2CH_3$), 25.6 (2 CH_3-CH-OH), 22.3 (2 $CH_2CH_2CH_3$), 18.8 (2 C≡C-CH_2), 13.8 (2 CH_3).

IR (neat): ν = 3357, 2959, 2933, 2244, 1666, 1477, 1164, 709 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{23}H_{32}NO_2$: 354.2428, found: 354.2420.

Mp = 60 °C.

***N*-(7-(2-Hydroxyethyl)trideca-5,8-diyn-7-yl)benzamide (5p)**



The hydroxyamide **5p** was prepared using conditions **B** with 4 equivalents of dimethylhexynylaluminum reagent (4 mmol). Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5p** (153 mg, 45% yield) as a yellow oil.

Rf ~ 0.14 (cyclohexane/EtOAc 8:2)

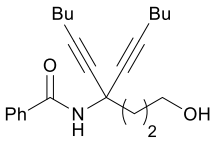
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H, 2 CH_{Ar}), 7.53 – 7.46 (m, 1H, CH_{Ar}), 7.44 – 7.35 (m, 2H, 2 CH_{Ar}), 4.07 (t, *J* = 5.3 Hz, 2H, CH_2OH), 2.44 (m, 2H, CH_2 CH_2OH), 2.23 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.54 – 1.47 (m, 4H, 2 $CH_2CH_2CH_3$), 1.43 – 1.36 (m, 4H, 2 $CH_2CH_2CH_3$), 0.89 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0 (C=O), 135.0 (C_{Ar}), 131.8 (CH_{Ar}), 128.8 (2 CH_{Ar}), 127.4 (2 CH_{Ar}), 83.5 (2 C≡C), 79.5 (2 C≡C), 60.4 (CH_2OH), 47.4 (C-NH), 44.8 (CH_2CH_2OH), 30.9 (2 $CH_2CH_2CH_3$), 22.3 (2 $CH_2CH_2CH_3$), 18.8 (2 C≡C-CH_2), 14.0 (2 CH_3).

IR (neat): ν = 3209, 2934, 1659, 1451, 1171, 1048, 1013, 890 cm^{-1}.

HRMS (ESI+): *m/z* ($M+Na^+$) calcd for $C_{22}H_{29}NaNO_2$: 362.2099, found: 362.2090.

***N*-(7-(2-Hydroxyethyl)trideca-5,8-diyn-7-yl)benzamide (5q)**



The hydroxyamide **5q** was prepared using conditions **B** with 4 equivalents of dimethylhexynylaluminum reagent (4 mmol). Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5q** (95 mg, 27% yield) as a yellow oil.

Rf ~ 0.14 (cyclohexane/EtOAc 8:2)

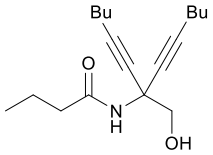
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H, H_{Ar}), 7.53 – 7.44 (m, 1H, H_{Ar}), 7.45 – 7.33 (m, 2H, H_{Ar}), 6.68 (bs, 1H, NH), 3.73 (t, *J* = 6.4 Hz, 2H, CH_2OH), 2.40 – 2.31 (m, 2H, $CH_2CH_2CH_2OH$), 2.23 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.94 – 1.82 (m, 2H, $CH_2CH_2CH_2OH$), 1.56 – 1.46 (m, 4H, 2 $CH_2CH_2CH_3$), 1.46 – 1.35 (m, 4H, 2 $CH_2CH_2CH_3$), 0.90 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (C=O), 135.1 (C_{Ar}), 131.8 (CH_{Ar}), 128.8 (2 CH_{Ar}), 127.3 (2 CH_{Ar}), 83.4 (2 *C*≡C), 79.6 (2 C≡*C*), 62.7 (CH_2OH), 48.8 (C-NH), 38.1 ($CH_2CH_2CH_2OH$), 30.9 (2 $CH_2CH_2CH_3$), 28.5 ($CH_2CH_2CH_2OH$), 22.3 (2 $CH_2CH_2CH_3$), 18.8 (2 C≡C-CH_2), 13.9 (2 CH_3).

IR (neat): ν = 3204, 2933, 1659, 1451, 1171, 1048, 1019, 888 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{23}H_{32}NO_2$: 354.2428, found: 354.2422.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)butyramide (5r)**



The hydroxyamide **5r** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5r** (251 mg, 86% yield) as a yellow oil.

Rf ~ 0.40 (Cyclohexane/EtOAc 8:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.10 (bs, 1H, NH), 4.14 – 4.05 (bs, 1H, OH), 3.85 (s, 2H, CH_2OH), 2.20 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 2.15 (t, *J* = 7.1 Hz, 2H, $CH_2C=O$), 1.65 (m, 2H, $CH_3CH_2CH_2C=O$), 1.51 – 1.42 (m,

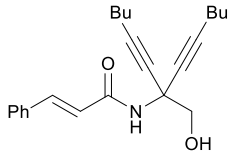
4H, 2 $CH_2CH_2CH_3$), 1.42 – 1.31 (m, 4H, 2 $CH_2CH_2CH_3$), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3), 0.88 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0 (C=O), 84.8 (2 *C*≡C), 77.0 (2 C≡*C*), 70.5 (CH_2OH), 51.1 (C-NH), 39.0 (CH_2C=O), 30.7 (2 $CH_2CH_2CH_3$), 22.2 (2 $CH_2CH_2CH_3$), 19.3 ($CH_3CH_2CH_2C$=O), 18.7 (2 C≡C-CH_2), 13.9 (2 CH_3), 13.8 ($CH_3CH_2CH_2C$=O).

IR (neat): ν = 34987, 3378, 2959, 2933, 2244, 1495, 1335, 1130, 1082 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{18}H_{30}NO_2$: 292.2271, found: 292.2264.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)cinnamamide (5s)**



The hydroxyamide **5s** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5s** (308 mg, 88% yield) as a white solid.

Rf ~ 0.20 (cyclohexane/EtOAc 8:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 15.6 Hz, 1H, CH=*CH*-CO), 7.54 – 7.46 (m, 2H, H_{Ar}), 7.40 – 7.32 (m, 3H, H_{Ar}), 6.41 (d, *J* = 15.6 Hz, 1H, *CH*=CH-CO), 6.30 (bs, 1H, NH), 4.01 (bs, 1H, OH), 3.96 (d, *J* = 5.8 Hz, 2H, CH_2OH), 2.24 (t, *J* = 7.2 Hz, 4H, 2 C≡C-CH_2), 1.56 – 1.46 (m, 4H, 2 $CH_2CH_2CH_3$), 1.45 – 1.34 (m, 4H, 2 $CH_2CH_2CH_3$), 0.90 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

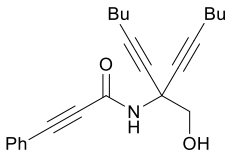
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6 (C=O), 142.6 (CH=*C*H-CO), 134.9 (C_{Ar}), 130.2 (CH_{Ar}), 129.2 (2 CH_{Ar}), 128.3 (2 CH_{Ar}), 120.4 (*C*H=CH-CO), 85.2 (2 *C*≡C), 77.0 (2 C≡*C*), 70.7 (CH_2OH), 51.4 (C-NH), 30.8 (2 $CH_2CH_2CH_3$), 22.3 (2 $CH_2CH_2CH_3$), 18.8 (2 C≡C-CH_2), 13.9 (2 CH_3).

IR (neat): ν = 3339, 2959, 2929, 2244, 1659, 1614, 1521, 1220, 1093, 1078, 981, 776 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{23}H_{30}NO_2$: 352.2271, found: 352.2262.

Mp = 69°C.

***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-3-phenylpropiolamide (5t)**



The hydroxyamide **5t** was prepared using conditions **B**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (8:2) as eluent provided **5t** (287 mg, 82% yield) as a yellow oil.

Rf ~ 0.35 (Cyclohexane/EtOAc 7:3)

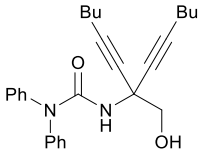
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H, H_{Ar}), 7.46 – 7.39 (m, 1H, H_{Ar}), 7.39 – 7.31 (m, 2H, H_{Ar}) 6.46 (bs, 1H, NH), 3.92 (d, *J* = 7.2 Hz, 2H, CH_2OH), 3.05 (t, *J* = 7.2 Hz, 1H, OH), 2.24 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.56 – 1.47 (m, 4H, 2 $CH_2CH_2CH_3$), 1.47 – 1.35 (m, 4H, 2 $CH_2CH_2CH_3$), 0.91 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.9 (2 CH_{Ar}), 130.6 (CH_{Ar}), 128.9 (2 CH_{Ar}), 120.4 (C_{Ar}), 85.6 (2 C≡C-C_4H_9), 85.4 (C≡C-Ph), 83.2 (2 C≡C-C_4H_9), 76.2 (C≡C-Ph), 70.0 (CH_2OH), 51.2 (C-NH), 30.8 (2 $CH_2CH_2CH_3$), 22.3 (2 $CH_2CH_2CH_3$), 18.8 (2 C≡C-CH_2), 13.9 (2 CH_3).

IR (neat): ν = 3335, 2933, 2218, 1640, 1491, 1156, 1089, 736 cm^{-1}.

HRMS (ESI+): *m/z* ($M+Na^+$) calcd for $C_{23}H_{27}NNaO_2$: 372.1925, found: 372.1934.

3-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-1,1-diphenylurea (5u)



The hydroxyurea **5u** was prepared using conditions **B**, and was isolated pure in a 98% yield (407 mg, 98%) as a yellow oil without any further purification.

Rf ~ 0.30 (Cyclohexane/EtOAc 7:3).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 4H, H_{Ar}), 7.29 – 7.26 (m, 4H, H_{Ar}), 7.25 – 7.20 (m, 2H, H_{Ar}), 5.21 (bs, 1H, NH), 4.17 (t, *J* = 6.7 Hz, 1H, OH), 3.89 (d, *J* = 6.7 Hz, 2H, CH_2OH), 2.20 (t, *J* = 7.1 Hz, 4H, 2 C≡C-CH_2), 1.55 – 1.42 (m, 4H, 2 $CH_2CH_2CH_3$), 1.41 – 1.29 (m, 4H, 2 $CH_2CH_2CH_3$), 0.89 (t, *J* = 7.3 Hz, 6H, 2 CH_3).

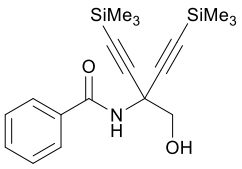
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1 (C=O), 143.2 (2 C_{Ar}), 130.2 (4 CH_{Ar}), 128.1 (4 CH_{Ar}), 127.2 (2 CH_{Ar}), 85.2 (2 *C*≡C), 77.9 (2 C≡*C*), 71.5 (CH_2OH), 52.1 (C-NH), 31.2 (2 *C*$H_2CH_2CH_3$), 22.6 (2 CH_2*C*H_2CH_3), 19.1 (2 C≡C-*C*H_2), 14.5 (2 CH_3).

IR (neat): ν = 3339, 2959, 2929, 2244, 1659, 1614, 1491, 1220, 1093, 1078, 981, 776 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{27}H_{33}N_2O_2$: 417.2537, found: 417.2534.

Mp = 68°C.

***N*-(3-(Hydroxymethyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-yl)benzamide (5v)[6]**



The hydroxyamide **5v** was prepared using conditions **B**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (8:2) as eluent provided **5v** (243 mg, 68% yield) as white crystals.

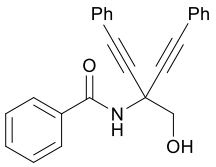
Rf ~ 0.20 (cyclohexane/EtOAc 8:2).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H, H_{Ar}), 7.58 – 7.49 (m, 1 H, H_{Ar}), 7.45 (m, 2H, H_{Ar}), 6.61 (bs, 1 h, NH), 4.05 (d, J = 7.1 Hz, 2H, CH_2OH), 3.61 (t, J = 7.1 Hz, 1 H, OH), 0.20 (s, 18H, CH_3).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.8 (C=O), 134.3 (C_{Ar}), 132.2 (CH_{Ar}), 128.9 (2 CH_{Ar}), 127.4 (2 CH_{Ar}), 100.6 (2 *C*≡C), 89.7 (2 C≡*C*), 70.0 (CH_2OH), 52.0 (C-NH), 0.0 (2 *C*H_3).

[6]Boukattaya, F.; Stanovych, A.; Setzer, P.; Abid, S.; Ammar,H.; Pearson-Long, M. S. M.; Bertus, P. *Chem. Commun.* **2012**, *48*, 8655.

***N*-(3-(Hydroxymethyl)-1,5-diphenylpenta-1,4-diyn-3-yl)benzamide (5w)**[6]



The hydroxyamide **5w** was prepared using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (95:5 to 8:2) as eluent provided **5w** (322 mg, 88% yield) as white crystals.

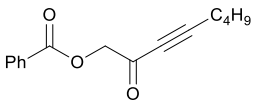
Rf ~ 0.15 (cyclohexane/EtOAc 8:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H, H_{Ar}), 7.57 – 7.50 (m, 5H, H_{Ar}), 7.49 – 7.44 (m, 2H, H_{Ar}), 7.35 – 7.29 (m, 6H, H_{Ar}), 6.90 (s, 1H, NH), 4.27 (d, *J* = 6.9 Hz, 2H, *CH*$_2$OH), 3.74 (t, *J* = 6.9 Hz, 1H, OH).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (C=O), 133.5 (C_{Ar}), 131.7 (4 CH_{Ar}), 131.6 (CH_{Ar}), 128.5 (2 CH_{Ar}), 128.3 (2 CH_{Ar}), 127.8 (2 CH_{Ar}), 126.9 (4 CH_{Ar}), 121.4 (2 C_{Ar}), 84.5 (2 *C*≡C), 83.9 (2 C≡*C*), 69.6 (CH_2OH), 51.2 (C-NH).

IV. Analytical data of byproducts 7a, 8a, 7h, 6k, 8u

2-Oxooct-3-yn-1-yl benzoate (7a)



Colorless oil.

Rf ~ 0.75 (cyclohexane/EtOAc 8:2)

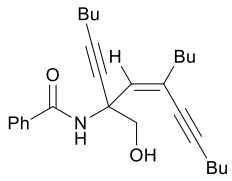
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34–8.09 (m, 2H, H_{Ar}), 7.59 (m, 1H, H_{Ar}), 7.50–7.43 (m, 2H, H_{Ar}), 4.94 (s, 2H, OCH_2), 2.36 (t, J = 7.0 Hz, 2H, C≡C-CH_2), 1.55–1.45 (m, 2H, CH_2), 1.55–1.45 (m, 2H, CH_2), 0.87 (t, J = 7.3 Hz, 3H, CH_3).

^{13}C-NMR (100.6 MHz, $CDCl_3$) δ 181.4 (C=O), 166.0 (C=O), 133.8 (CH_{Ar}), 130.3 (2 CH_{Ar}), 129.6 (C_{Ar}), 128.8 (2 CH_{Ar}), 99.2 (*C*≡C), 78.4 (C≡*C*), 69.4 (OCH_2), 29.8 (*CH_2*CH_2CH_3), 22.2 (CH_2*CH_2*CH_3), 19.1 (C≡C-*CH_2*), 13.7 (CH_3).

IR (neat): ν = 2962, 2933, 2873, 2214, 1730, 1700, 1454, 1417, 1373, 1275, 1179, 1115, 1022 cm^{-1}.

HRMS (ESI+): *m/z* ($M+Na^+$) calcd for $C_{15}H_{16}NaO_3$: 267.0992, found: 267.0999.

***N*-(9-Butyl-7-(hydroxymethyl)pentadeca-8-en-5,10-diyn-7-yl)benzamide (8a)**



Yellow oil.

Rf ~ 0.40 (cyclohexane/EtOAc 8:2)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H, H_{Ar}), 7.54 – 7.46 (m, 1 H, H_{Ar}), 7.43 (dd, *J* = 8.3, 6.9 Hz, 2H, H_{Ar}), 7.31 (bs, 1H, NH), 5.96 (t, *J* = 1.3 Hz, 1H, CH=C), 4.43 (bs, 1H, OH), 4.03 (d, *J* = 11.4 Hz, 1H, C*H_2*OH), 3.96 (d, *J* = 11.4 Hz, 1H, C*H_2*OH), 2.24 (m, 2H, C≡C-CH_2), 2.18 – 2.14 (m, 4H, C=C-CH_2, C=C-C≡C-CH_2), 1.54 – 1.28 (m, 12H, 3 C*H_2*C*H_2*CH_3), 0.90 (t, *J* = 7.5 Hz, 3H, CH_3), 0.90 (t, *J* = 7.5 Hz, 3H, CH_3), 0.83 (t, *J* = 7.0 Hz, 3H, CH_3).

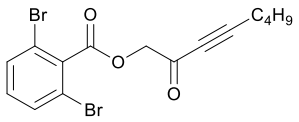
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3 (C=O), 134.9 (C_{Ar}), 133.6 (C=*C*H), 131.9 (CH_{Ar}), 128.8 (2 CH_{Ar}), 127.5 (2 CH_{Ar}), 126.3 (*C*=CH), 100.0 (*C*≡C), 85.3 (C≡*C*), 78.9 (C≡C), 78.8 (C≡C), 69.6 (CH_2-OH), 57.6 (C-NH), 38.8 (C=C-*CH_2*), 31.1 (CH_2), 30.9 (CH_2), 30.7 (CH_2), 22.3 (CH_2), 22.3 (CH_2), 22.2 (CH_2), 19.7 (C≡C-*CH_2*), 18.8 (C=C-C≡C-*CH_2*), 14.2 (CH_3), 13.9 (CH_3), 13.9 (CH_3).

IR (neat): ν =3391, 2933, 2862, 1655, 1484, 1465, 1294, 1074, 713 cm^{-1}.

HRMS (ESI+): *m/z* ($M+Na^+$) calcd for $C_{27}H_{37}NNaO_2$: 430.2717, found: 430.2728.

The alkene *Z* configuration was determined thanks to 1D (^{1}H, ^{13}C) and 2D (COSY, HMBC) NMR analyses, and NOESY experiments (see section V to see spectra and comments).

2-Oxooct-3-yn-1-yl 2,6-dibromobenzoate (7h)



The ketone **7h** was obtained as the main product from acyl cyanohydrin **4h** using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (9:1 to 7:3) as eluent provided **7h** (299 mg, 75% yield) as a yellow oil.

Rf ~ 0.70 (Toluene/EtOAc 9:1)

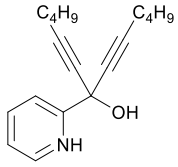
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H, H_{Ar}), 7.15 (t, *J* = 8.0 Hz, 1H, H_{Ar}), 4.98 (s, 2H, CH_2CO), 2.41 (t, *J* = 7.1 Hz, 2H, C≡C-CH_2), 1.57 (m, 2H, $CH_2CH_2CH_3$), 1.43 (m, 2H, $CH_2CH_2CH_3$), 0.91 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7 ($CH_2C{=}O$), 164.7 (*C*=O), 136.1 (C_{Ar}), 131.4 (CH_{Ar}), 131.2 (2 CH_{Ar}), 119.7 (2 C_{Ar}-Br), 98.7 (*C*≡C), 77.7 (C≡*C*), 69.3 (CH_2CO), 29.1 ($CH_2CH_2CH_3$), 21.5 ($CH_2CH_2CH_3$), 18.5 (C≡C-CH_2), 13.0 (CH_3).

IR (neat)**:** ν =2959, 2933, 2862, 2214, 1741, 1693, 1249, 1112, 1033, 747 cm^{-1}.

HRMS (ESI+): *m/z* (M+Na^+) calcd for $C_{15}H_{14}Br_2NaO_3$: 422.9201, found: 422.9202.

7-(Pyridin-2-yl)trideca-5,8-diyn-7-ol (6k)



The tertiary alcohol **6k** was obtained as by-product from acyl cyanohydrin **4k** using conditions **A** with 4 equivalents of dimethylhexynylaluminum reagent (4 mmol). Purification by column chromatography on silica gel using petroleum ether/EtOAc (95:5 to 0/100) with Et_3N (3 vol.%) as eluent provided **6k** (29 mg, 11% yield) as a yellow oil.

Rf ~ 0.75 (PE/EtOAc 6:4)

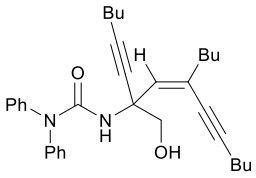
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (dd, *J* = 2.4, 0.8 Hz, 1H, N=CH_{Ar}), 8.53 (dd, *J* = 4.8, 1.7 Hz, 1H, H_{Ar}), 8.07 (ddd, *J* = 8.0, 2.4, 1.7 Hz, 1H, H_{Ar}), 7.28 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1H, H_{Ar}), 2.27 (t, *J* = 7.0 Hz, 4H, 2 C≡C-CH_2), 1.72 – 1.45 (m, 4H, 2 $CH_2CH_2CH_3$), 1.45 – 1.32 (m, 4H, 2 $CH_2CH_2CH_3$), 0.89 (t, *J* = 7.5 Hz, 6H, 2 CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4 (CH_{Ar}), 148.0 (CH_{Ar}=N), 139.4 (C_{Ar}), 134.0 (CH_{Ar}), 123.3 (CH_{Ar}), 86.7 (2 *C*≡C-CH_2), 80.9 (2 C≡*C*-CH_2), 63.8 (C-OH), 30.7 (2 *CH_2*CH_2CH_3), 22.3 (2 CH_2*CH_2*CH_3), 18.8 (2 C≡C-*CH_2*), 13.9 (2 CH_3).

IR (Neat): ν = 2933, 2240, 1778, 1169, 1249, 1097, 929, 762 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{18}H_{24}NO_3$: 270.1852, found: 270.1860.

3-(9-Butyl-7-(hydroxymethyl)pentadeca-8-en-5,10-diyn-7-yl)-1,1-diphenylurea (8u)



This triple addition product **8u** was obtained as by-product from cyanocarbamate **4u** using conditions **A**. Purification by column chromatography on silica gel using cyclohexane/EtOAc (7:3 to 0:100) as eluent provided **8u** (121 mg, 24% yield) as a yellow oil.

Rf ~ 0.35 (Cyclohexane/EtOAc 7:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H, H_{Ar}), 7.29 – 7.24 (m, 4H, H_{Ar}), 7.23 – 7.18 (m, 2H, H_{Ar}) 5.98 (s, 1H, C=CH), 5.66 (bs, 1H, NH), 4.36 (dd, *J* = 8.0, 5.2 Hz, 1H, OH), 3.96 (dd, *J* = 11.2, 8.0 Hz, 1H, C*H*OH), 3.90 (dd, *J* = 11.2, 5.2 Hz, 1H, C*H*OH), 2.22 – 2.14 (m, 4H, 2 *CH_2*$CH_2CH_2CH_3$), 2.14 – 2.08 (m, 2H, *CH_2*$CH_2CH_2CH_3$), 1.57 – 1.20 (m, 12H, 3 CH_2*CH_2*CH_2*CH_3), 0.93 – 0.85 (m, 9H, 3 CH_3).

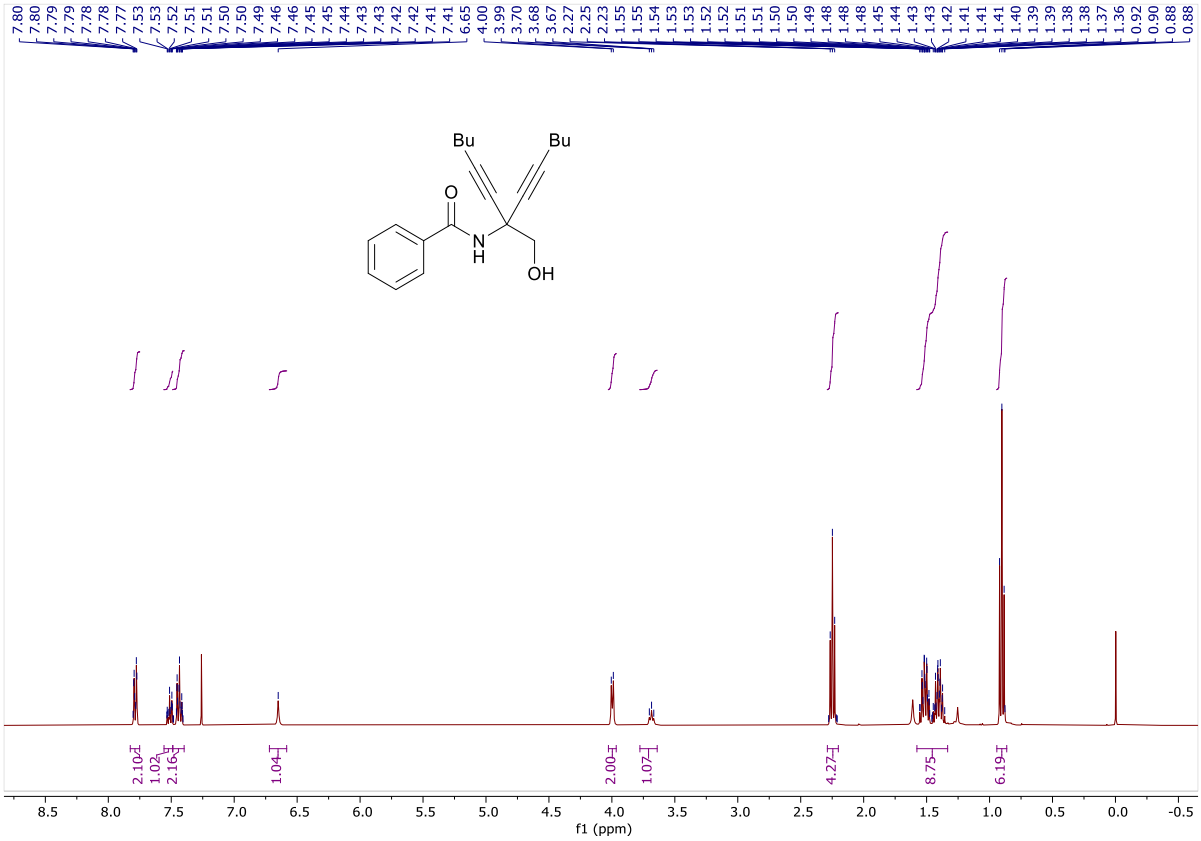
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1 (C=O), 143.1 (2 C_{Ar}) , 134.1 (*C*H=C), 129.6 (2 CH_{Ar}), 127.7 (4 CH_{Ar}), 126.5 (4 CH_{Ar}), 126.4 (CH=*C*), 99.5 (C≡C), 84.7 (C≡C), 79.4 (C≡C), 78.7 (C≡C), 69.8 (CH_2OH), 57.2 (C-NH), 38.7 (CH=C-*CH_2*), 31.2 (*$CH_2CH_2CH_3$*), 31.0 (*$CH_2CH_2CH_3$*), 30.7 (*$CH_2CH_2CH_3$*), 22.4 (CH_2*CH_2CH_3*), 22.2 (CH_2*CH_2CH_3*), 22.2 (CH_2*CH_2CH_3*), 19.8 (C≡C-*CH_2*), 18.8 (C≡C-*CH_2*), 14.3 (CH_3), 14.0 (2 CH_3).

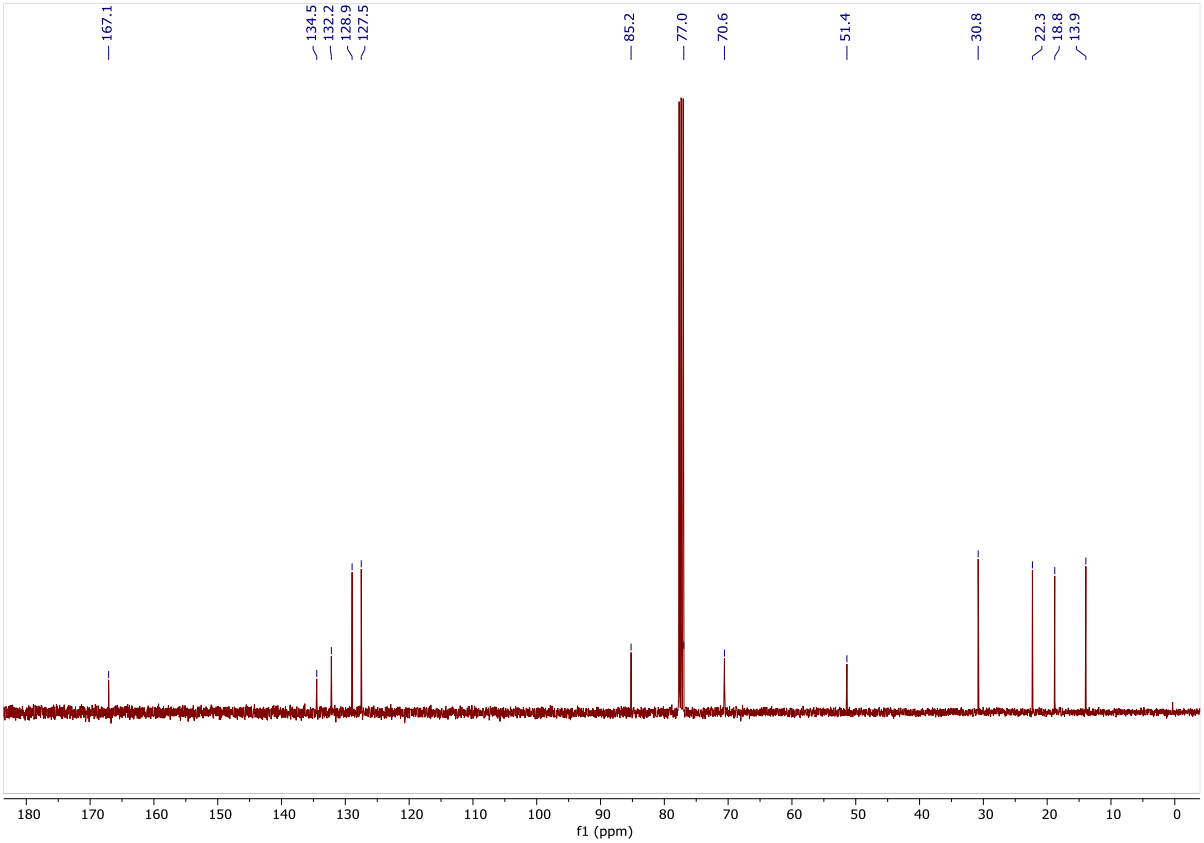
IR (neat): ν = 3335, 2959, 2929, 2244, 1659, 1491, 1201, 1093, 1078, 762 cm^{-1}.

HRMS (ESI+): *m/z* ($M+H^+$) calcd for $C_{33}H_{43}N_2O_2$: 499.3319, found: 499.3314.

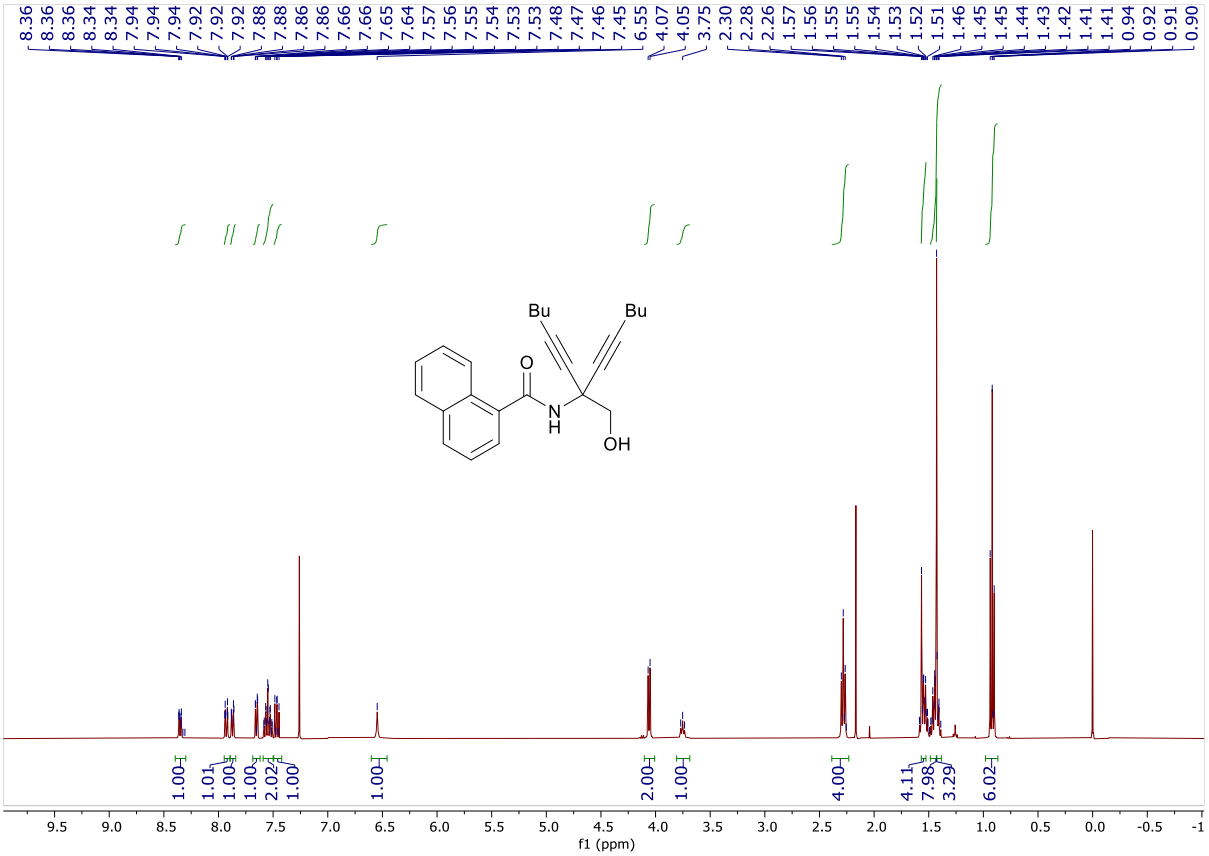
V. Copies of ^{1}H and ^{13}C NMR spectra of new compounds

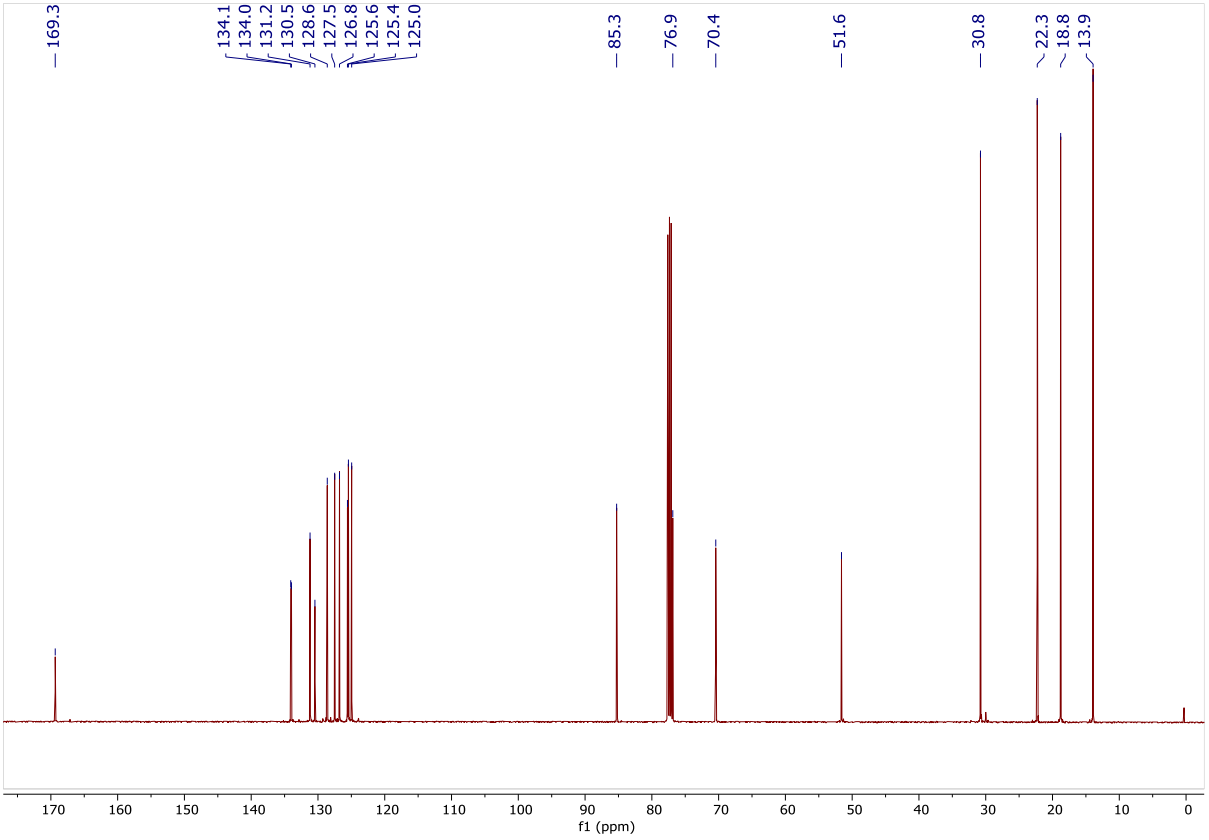
N-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)benzamide (5a)



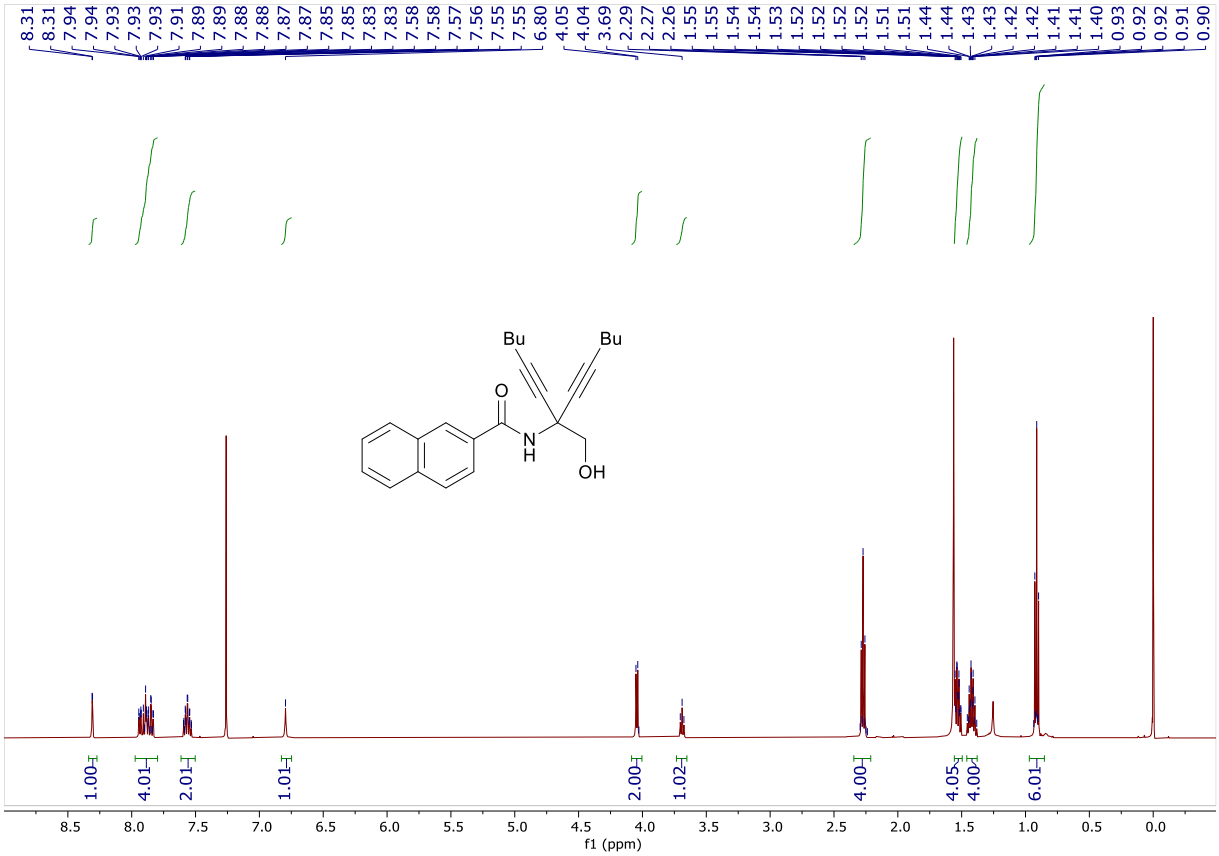


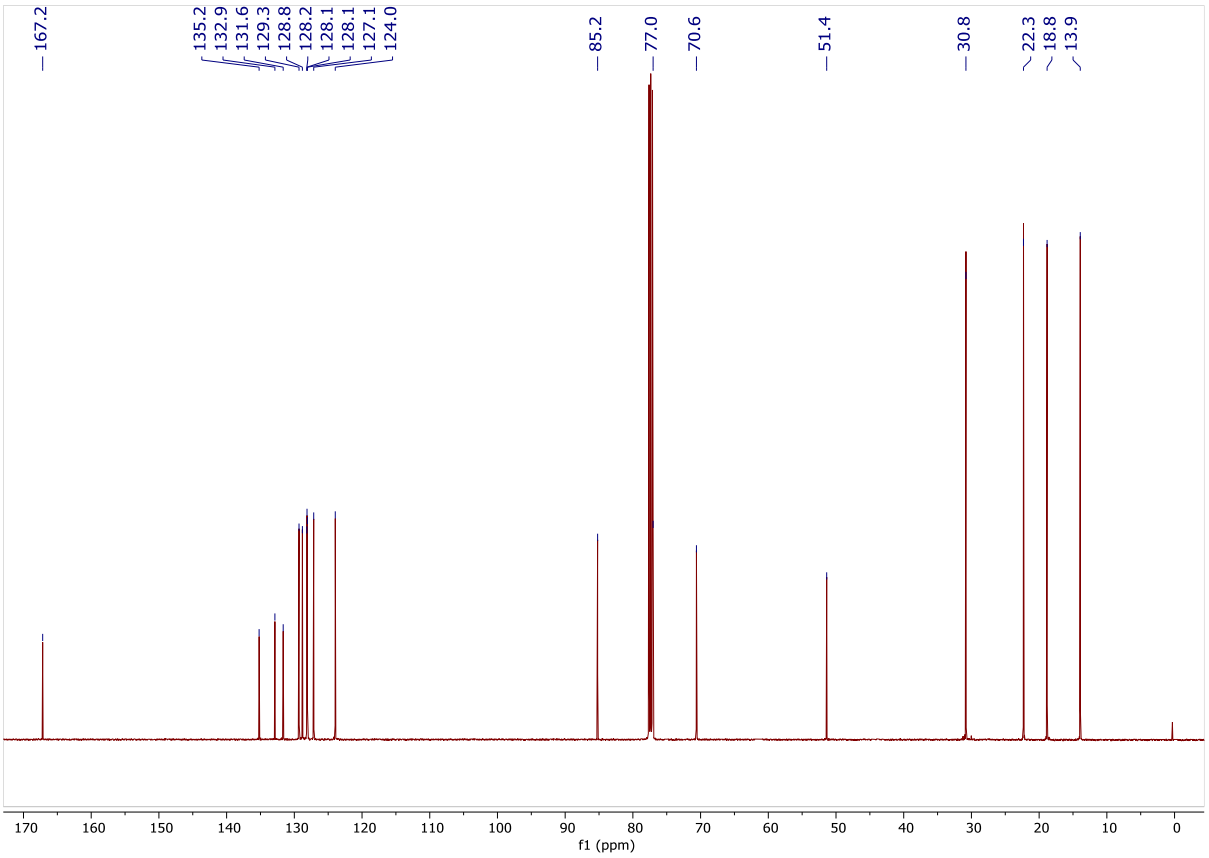
***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-1-naphthamide (5b)**



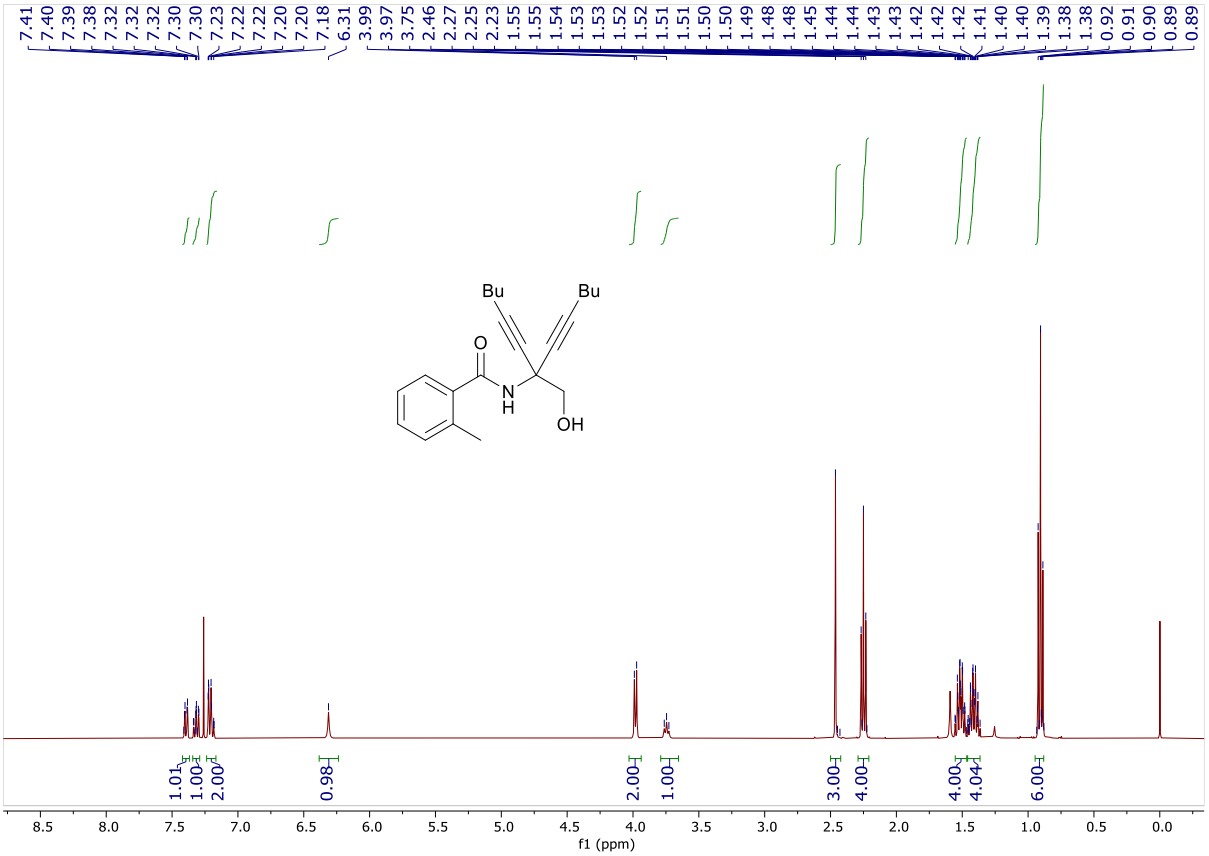


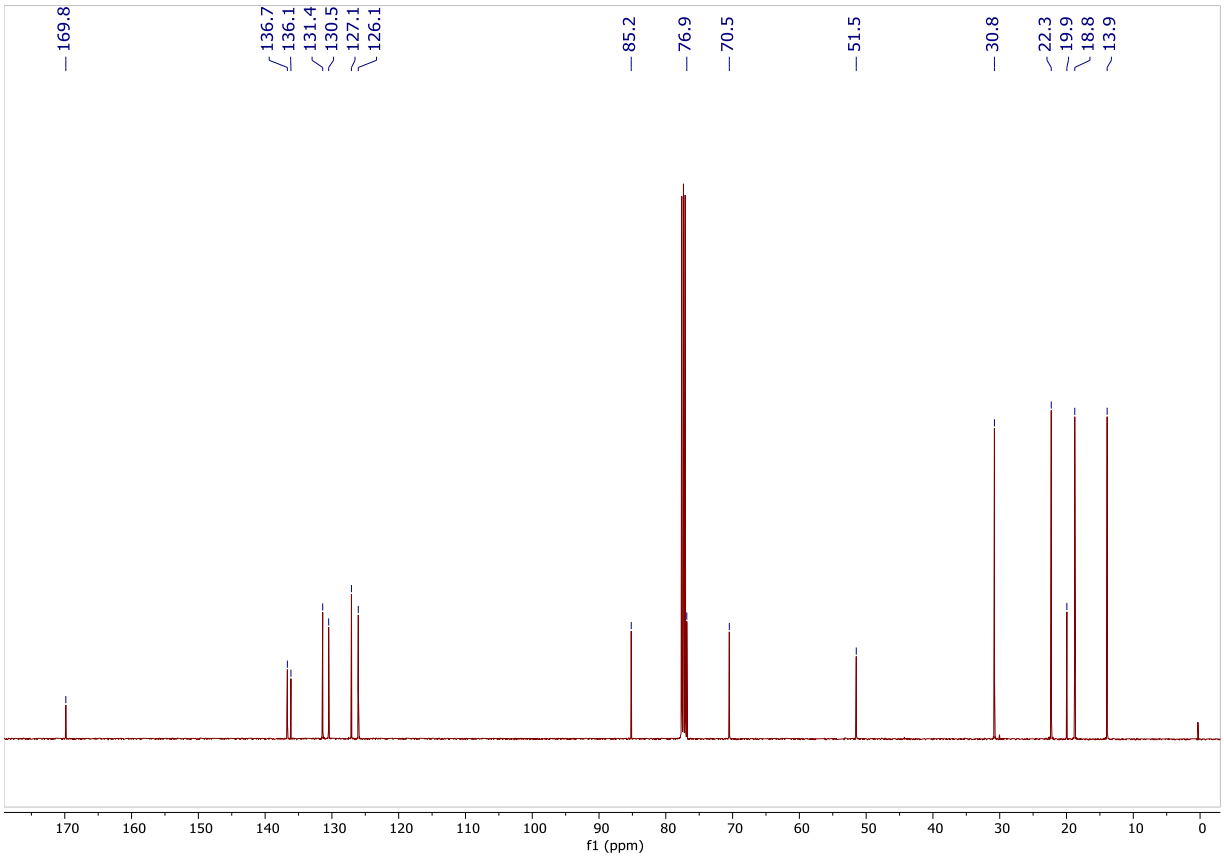
_N_-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-2-naphthamide (5c)



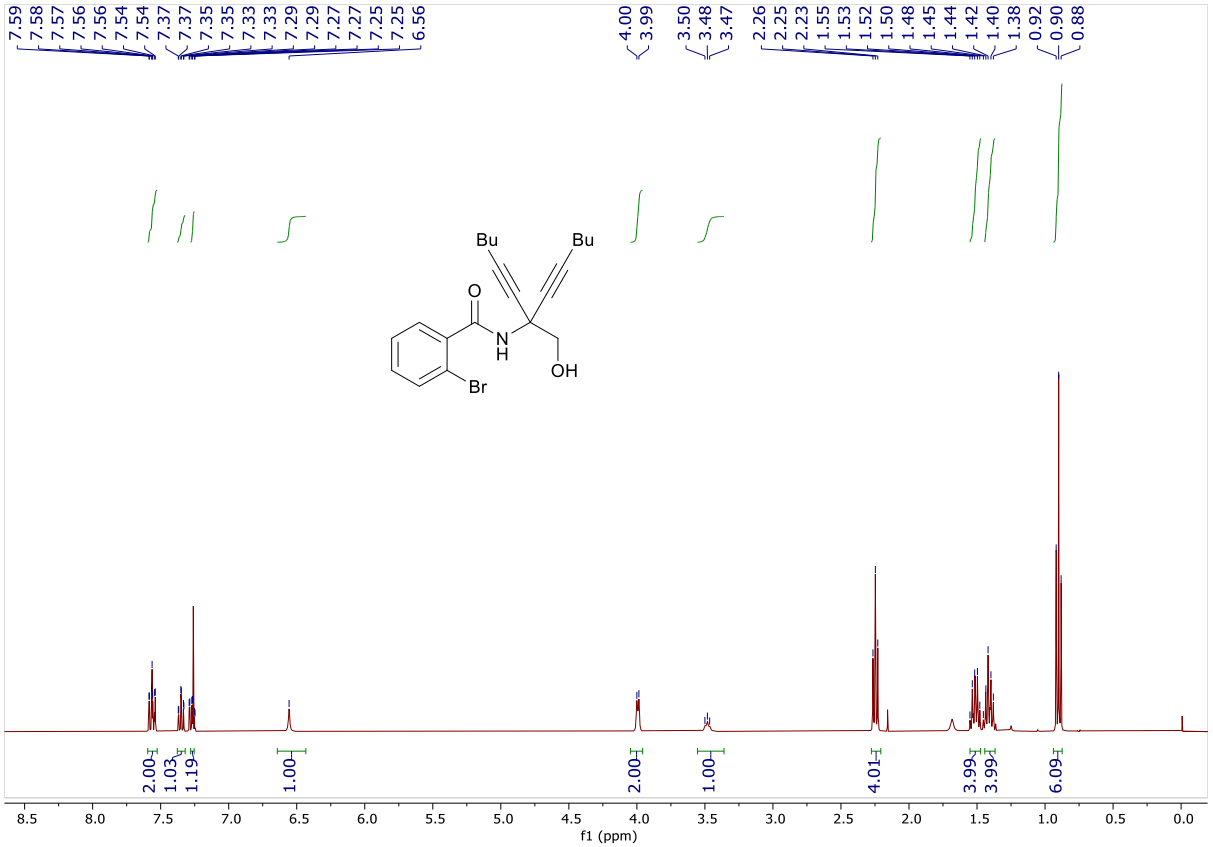


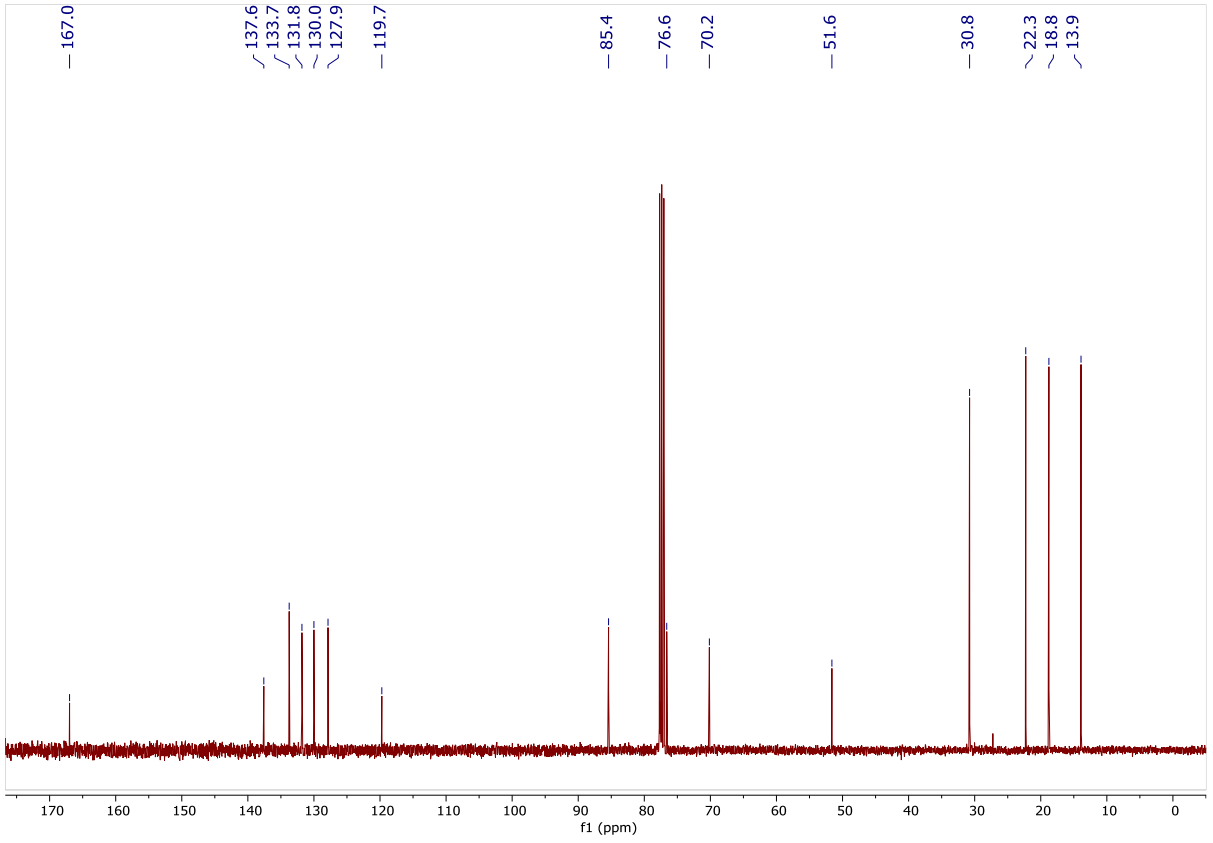
***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-2-methylbenzamide (5d)**



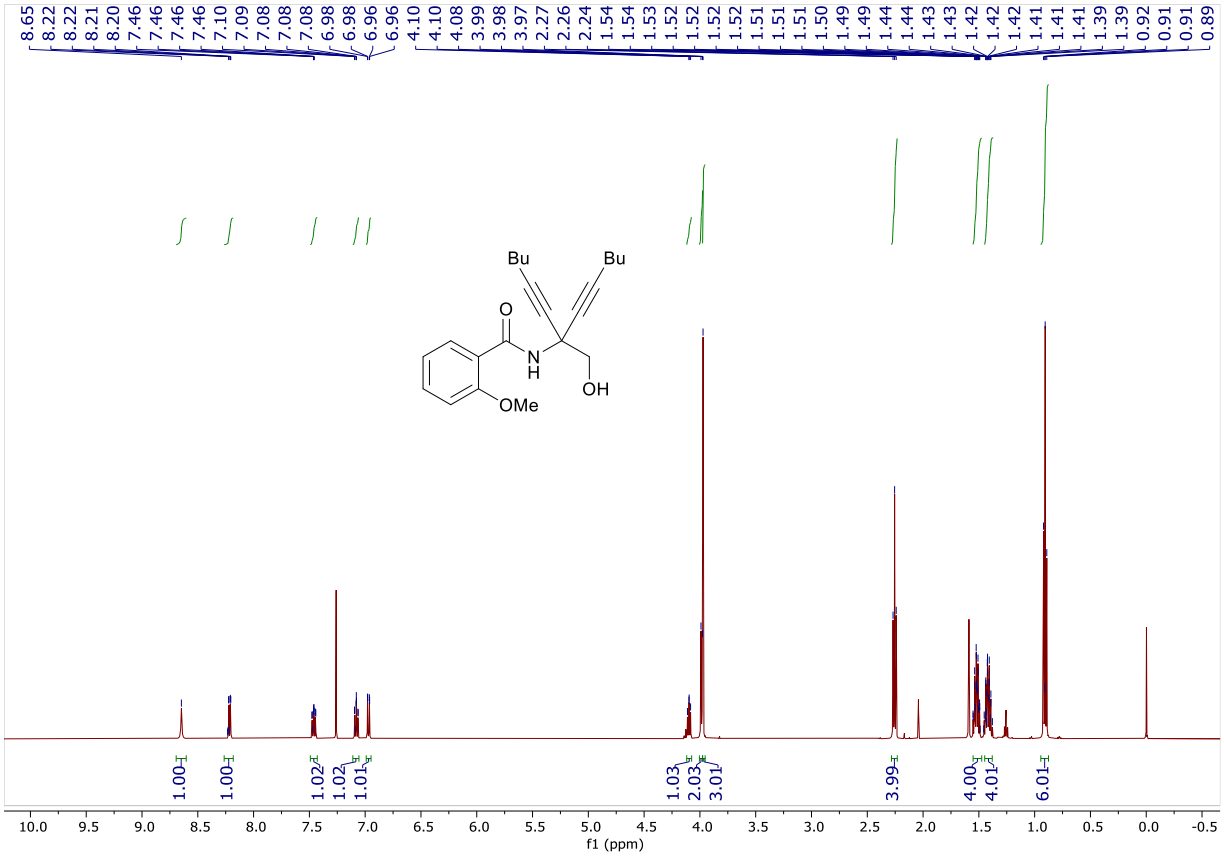


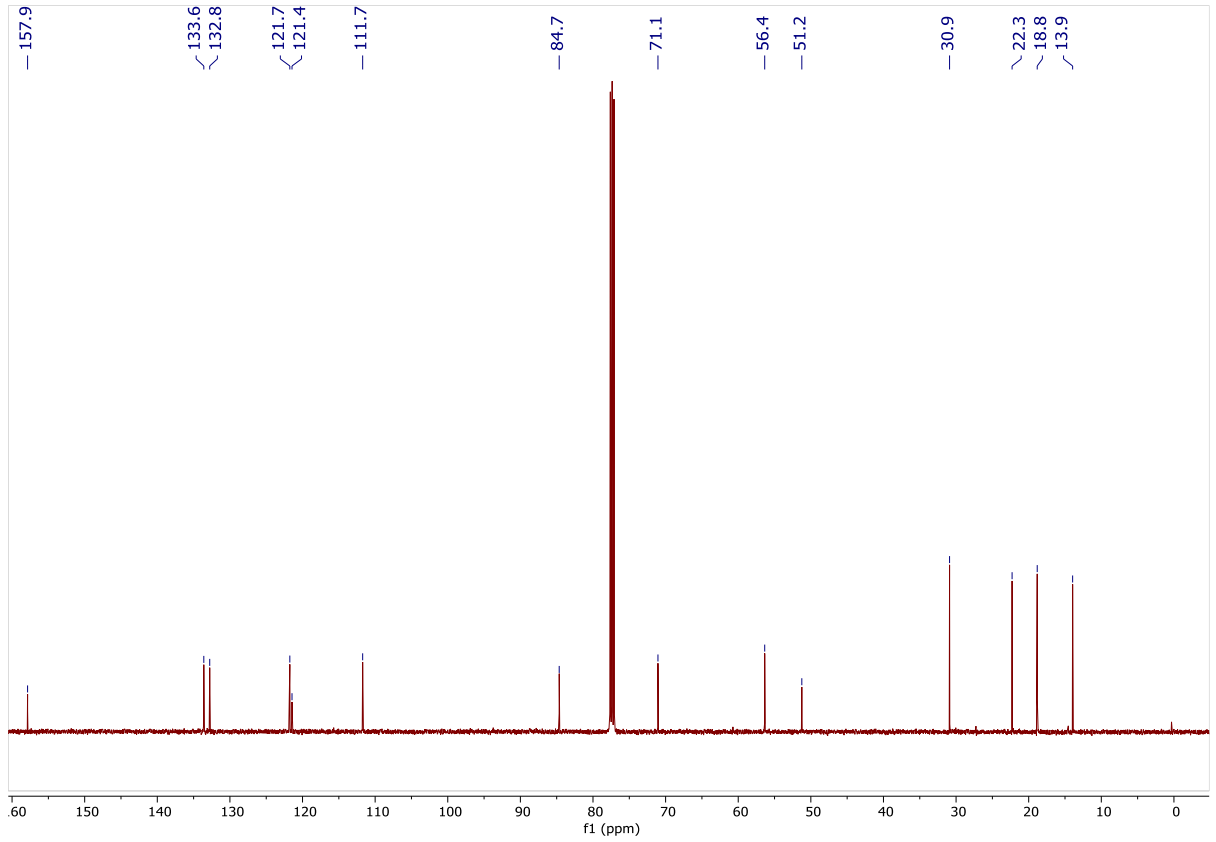
2-Bromo-*N*-(7-(hydroxymethyl)trideca-5,8-diyn-7-yl)benzamide (5e)



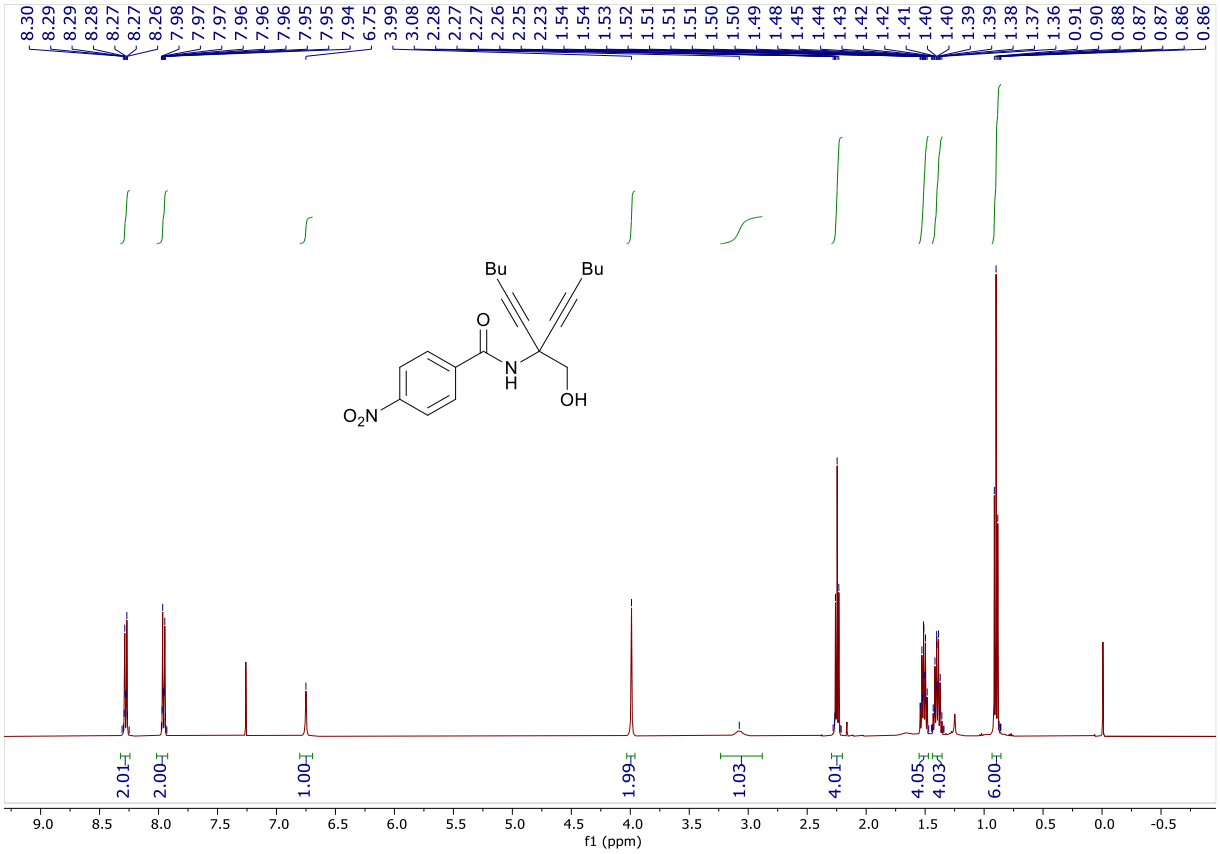


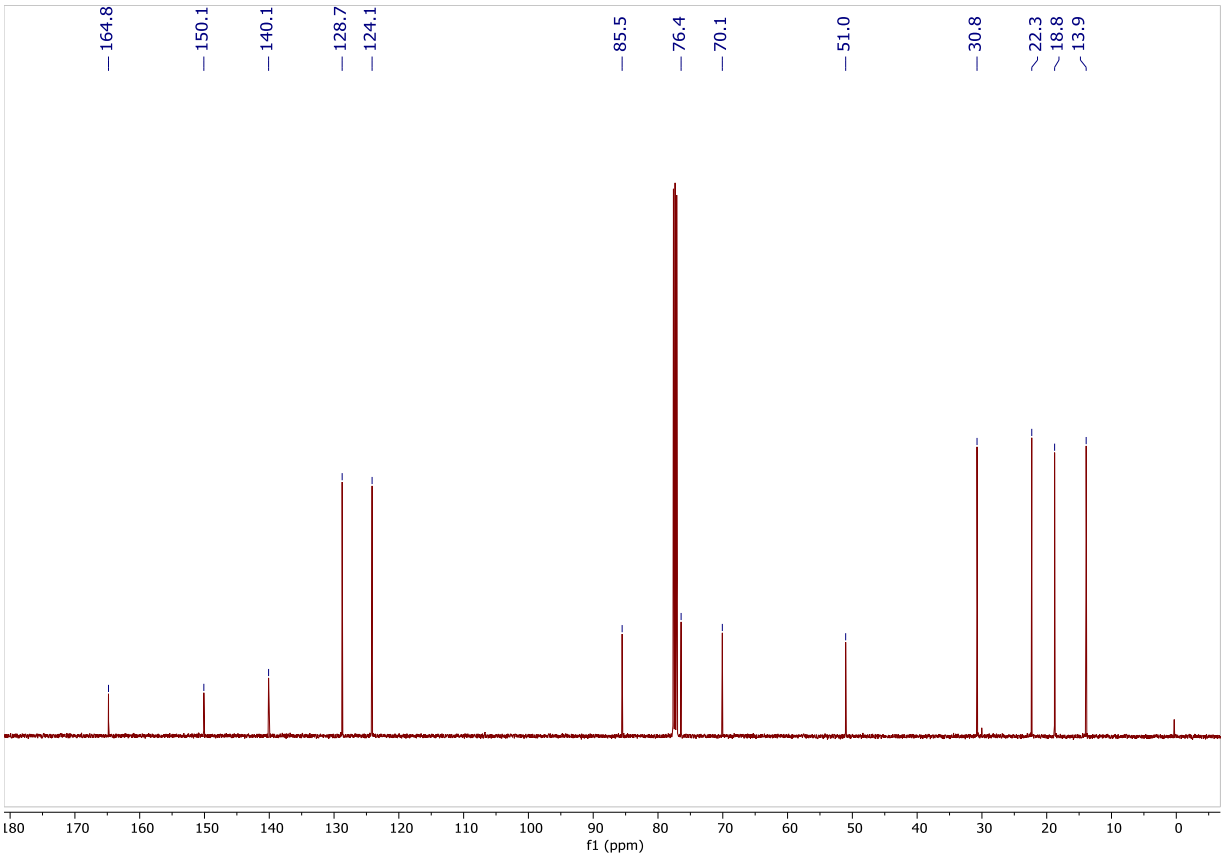
***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-2-methoxybenzamide (5f)**



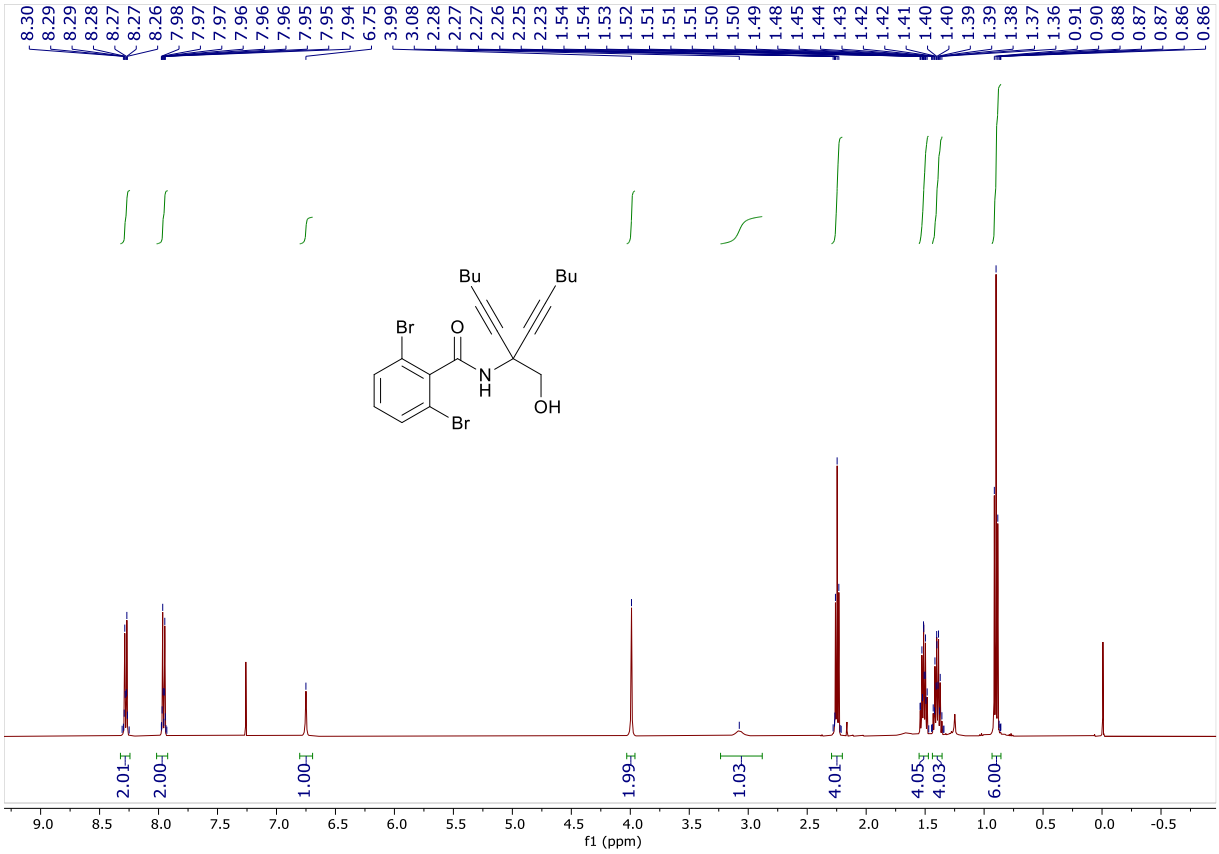


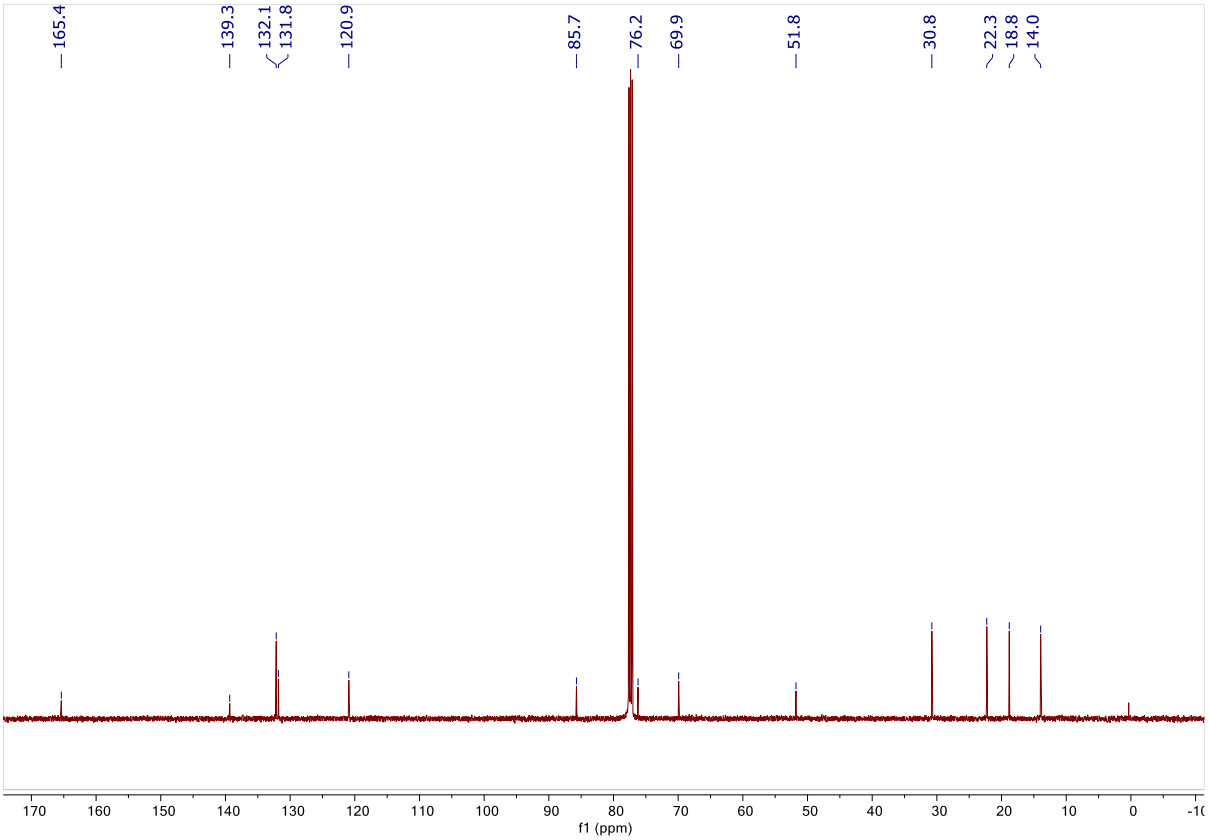
***N*-(7-(hydroxymethyl)trideca-5,8-diyn-7-yl)-4-nitrobenzamide (5g)**



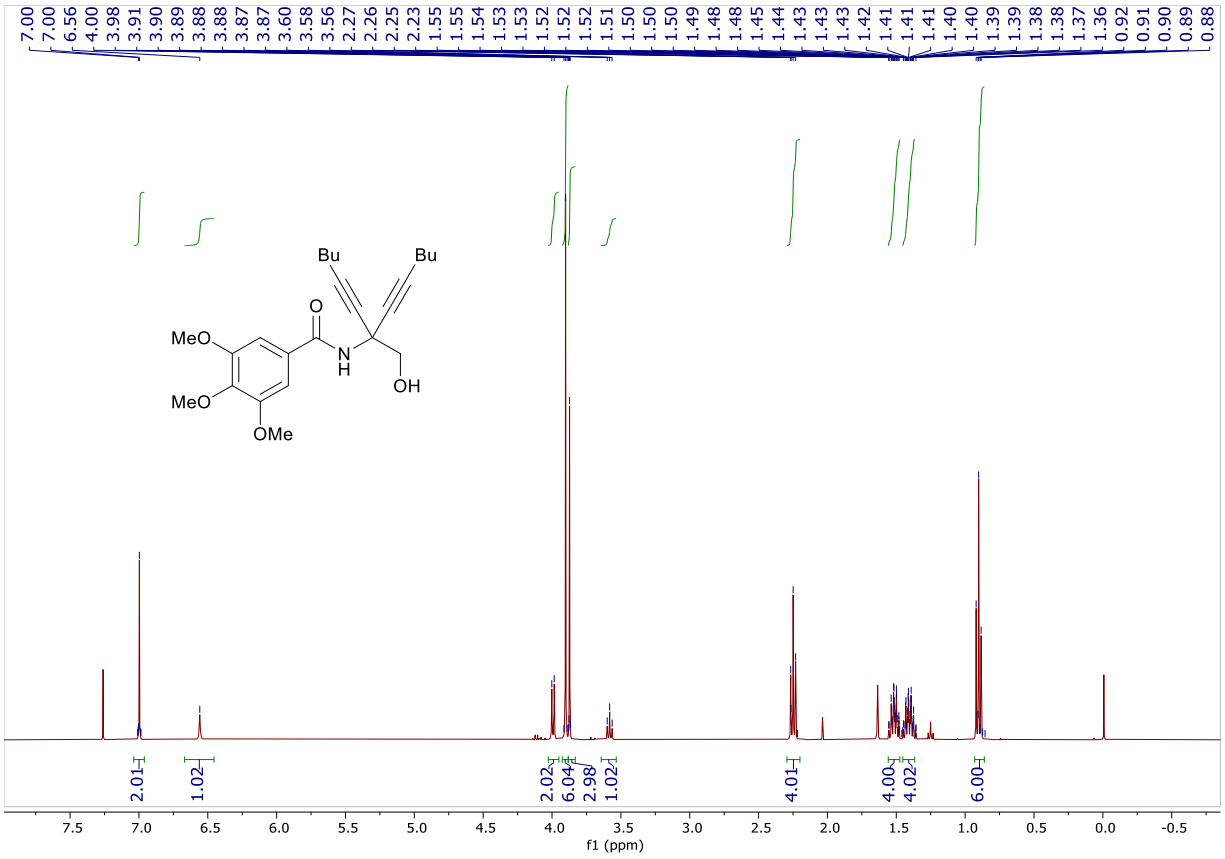


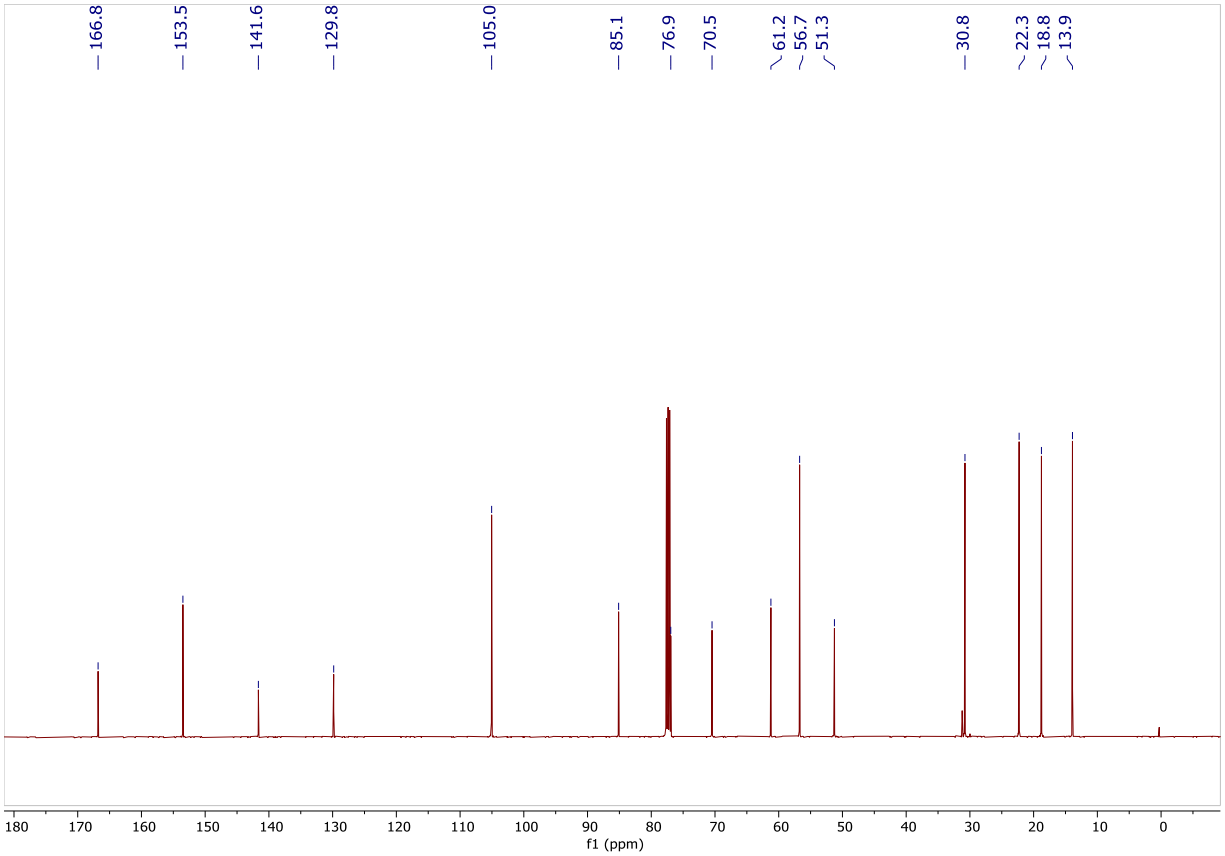
2,6-Dibromo-*N*-(7-(hydroxymethyl)trideca-5,8-diyn-7-yl)benzamide (5h)



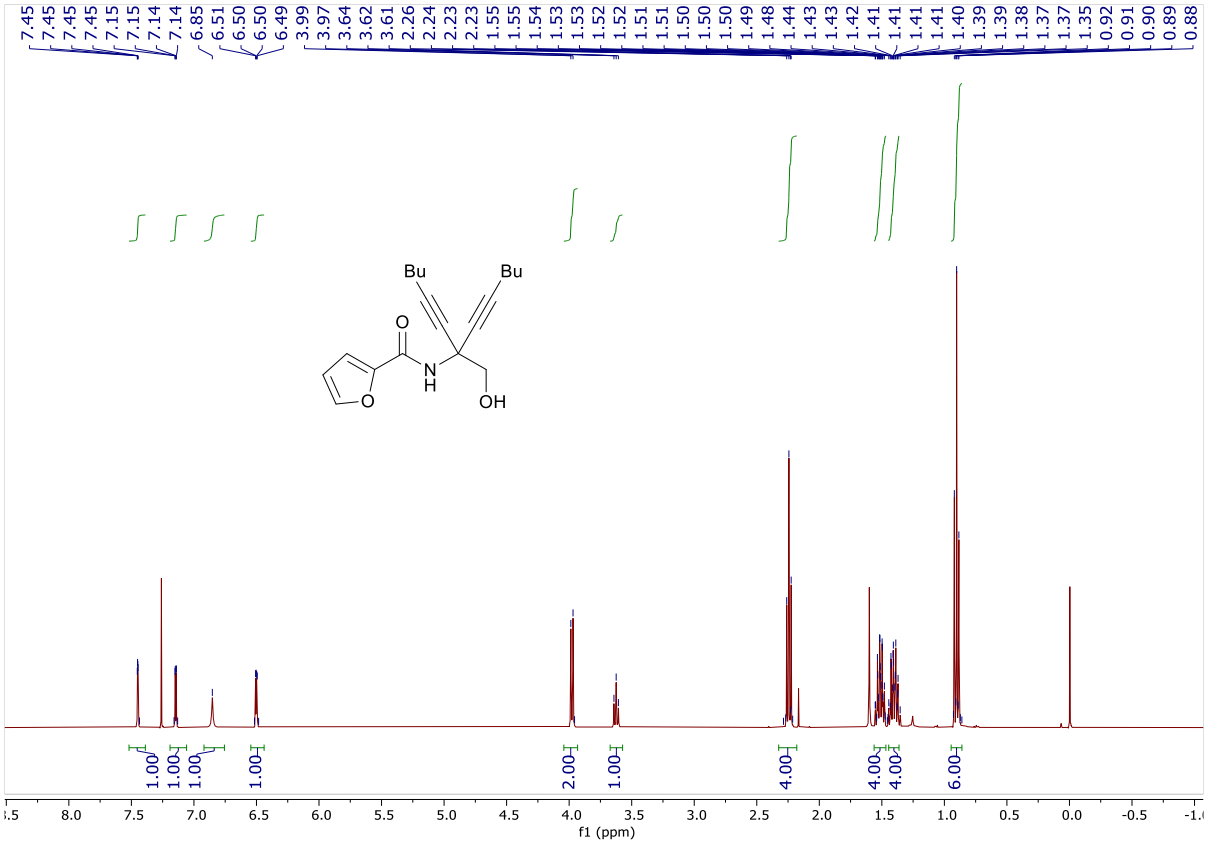


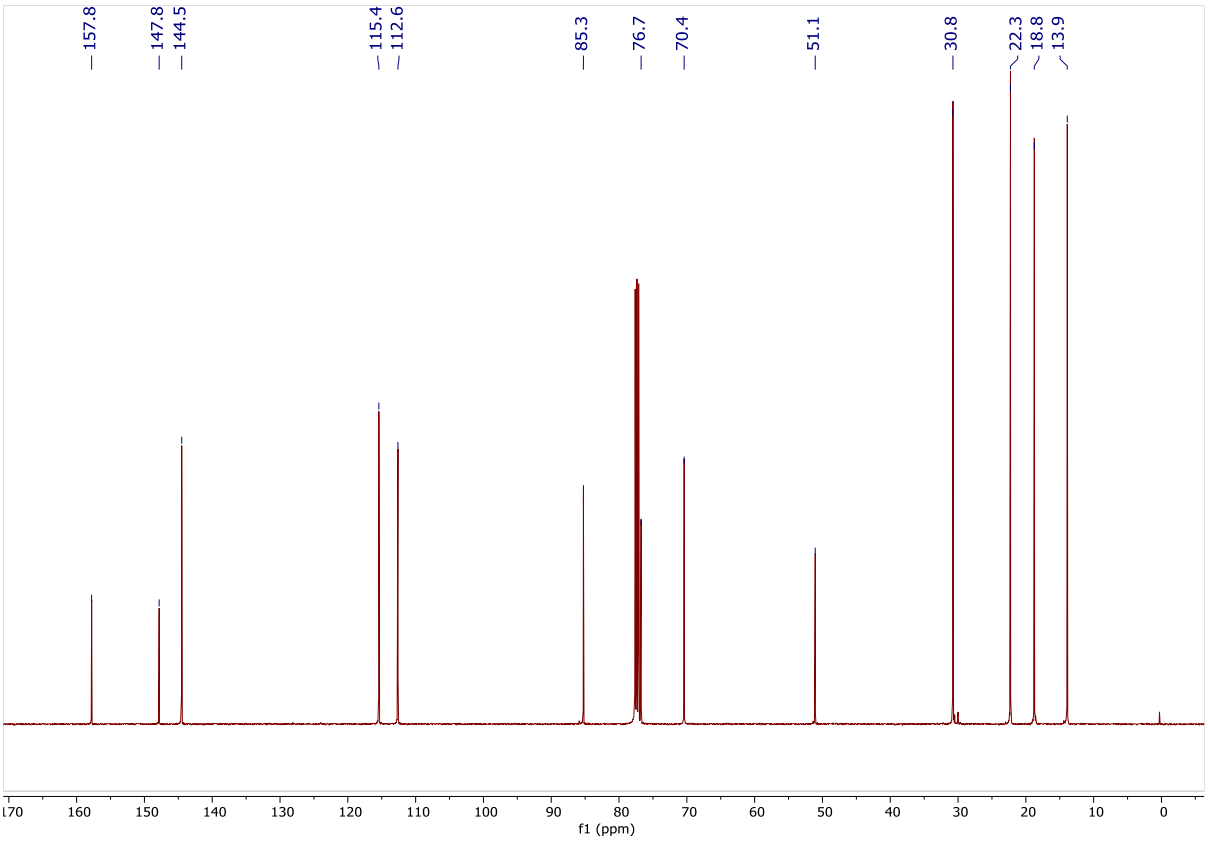
***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-3,4,5-trimethoxybenzamide (5i)**



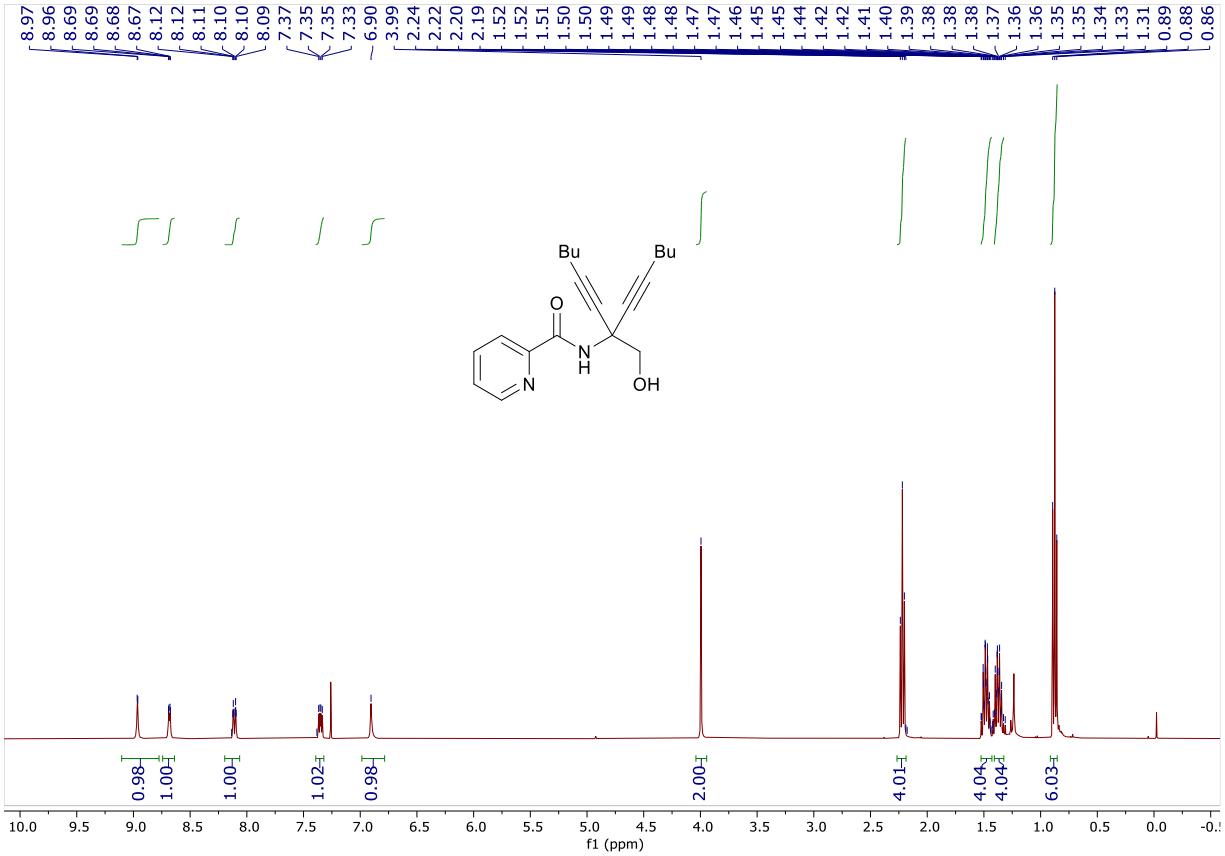


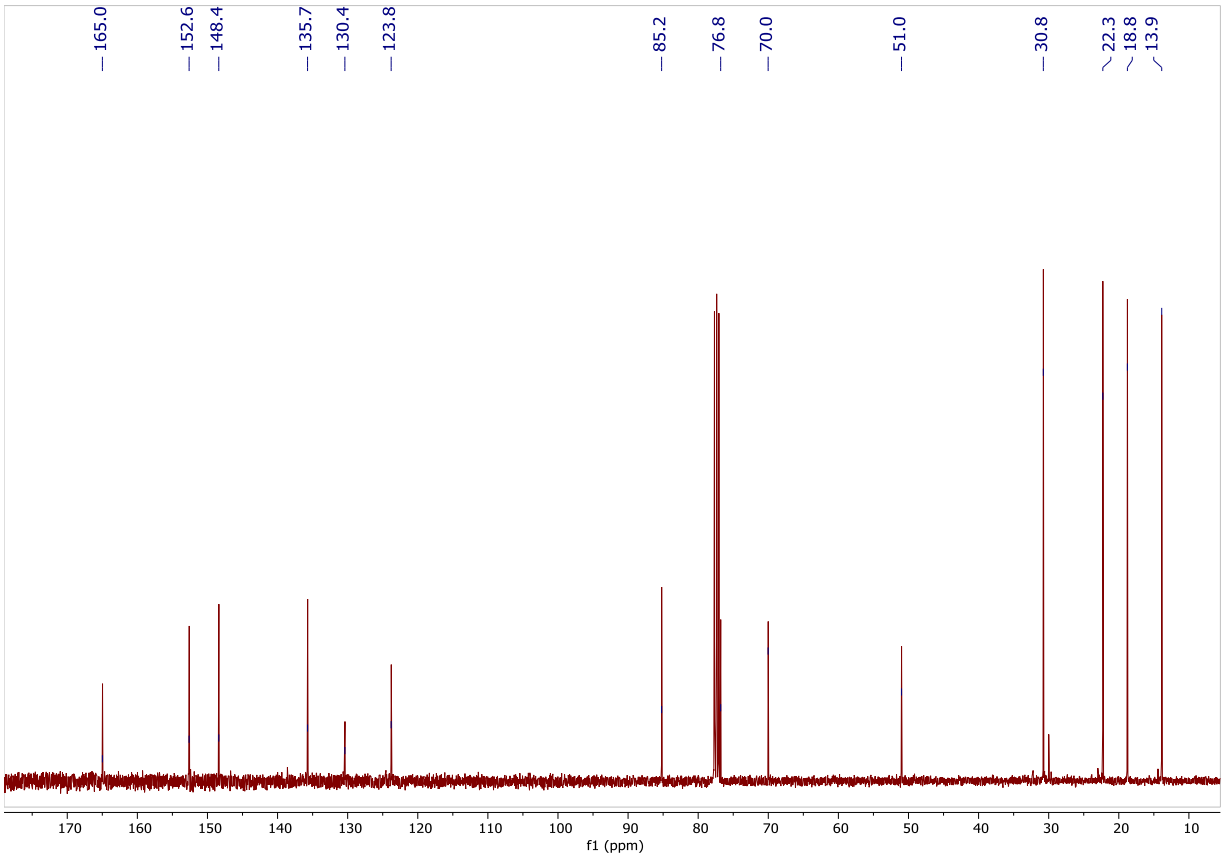
***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)furan-2-carboxamide (5j)**



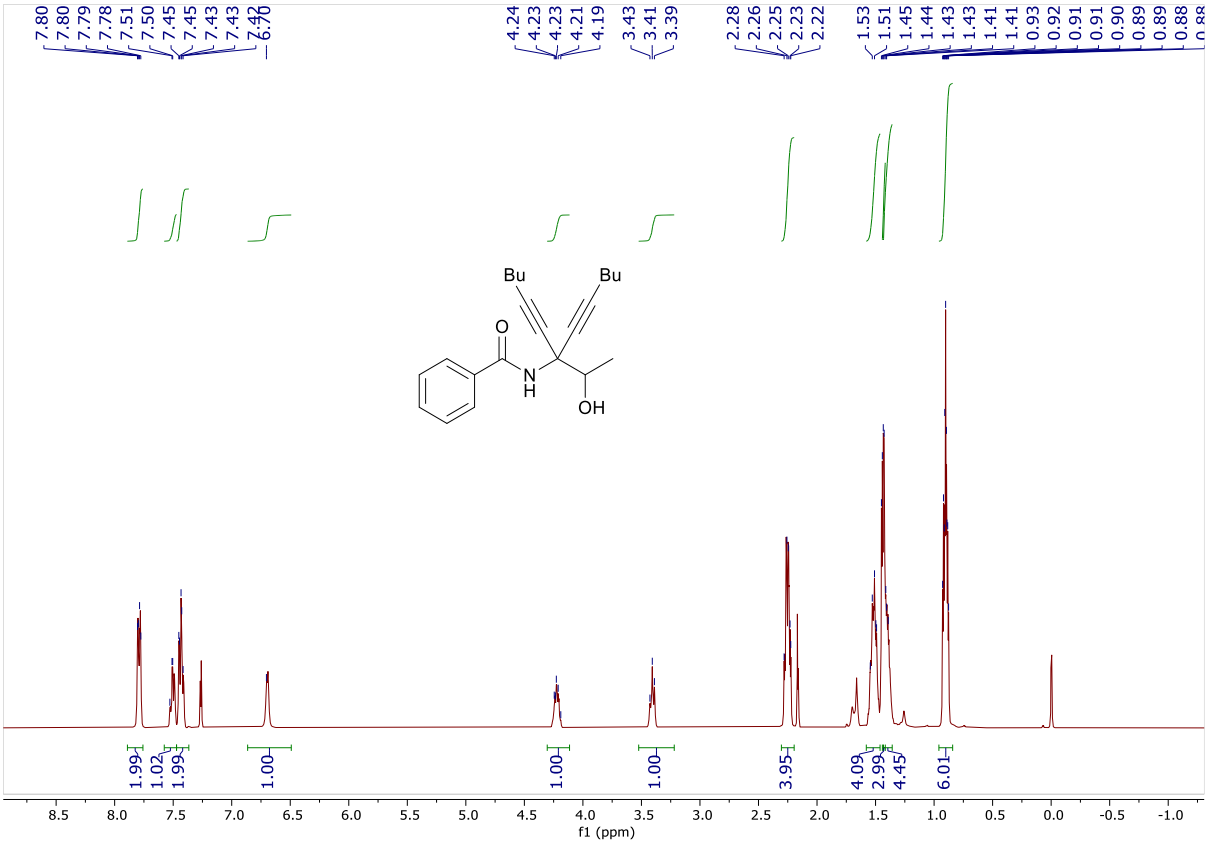


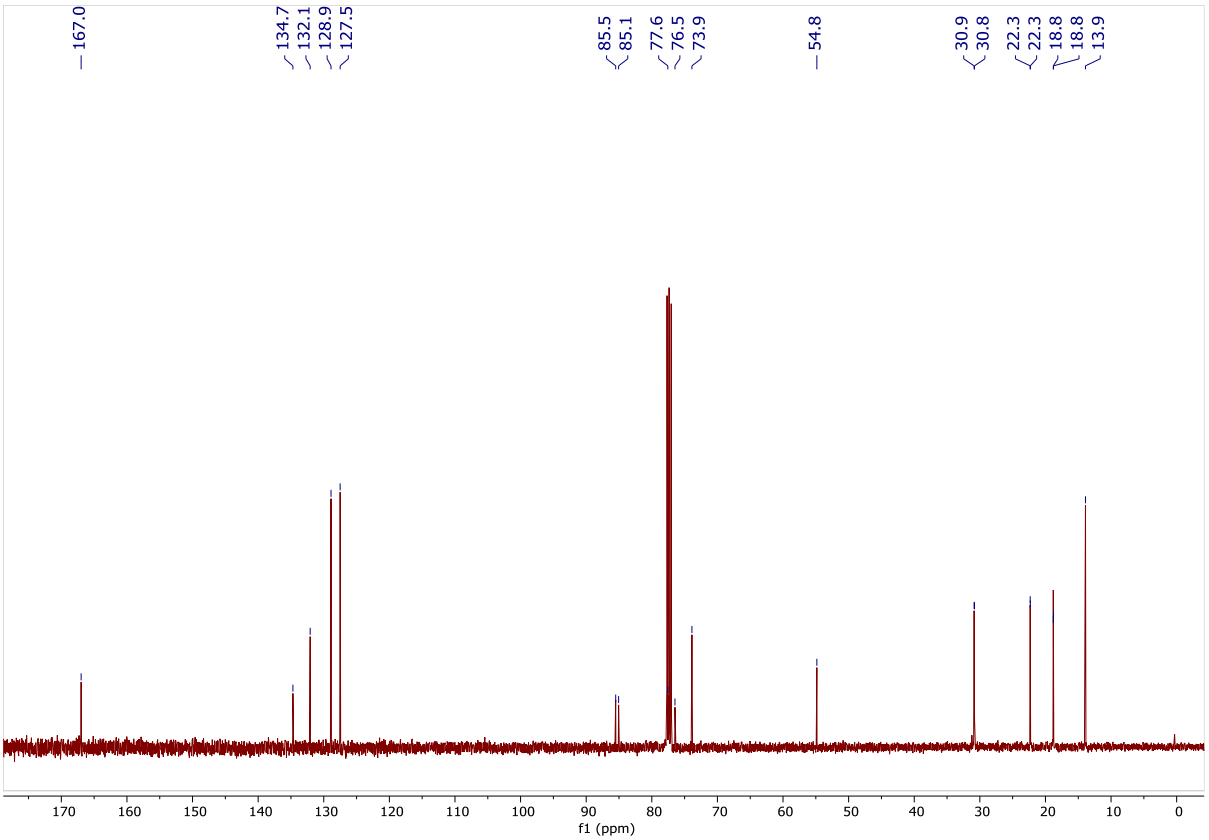
***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)picolinamide (5k)**



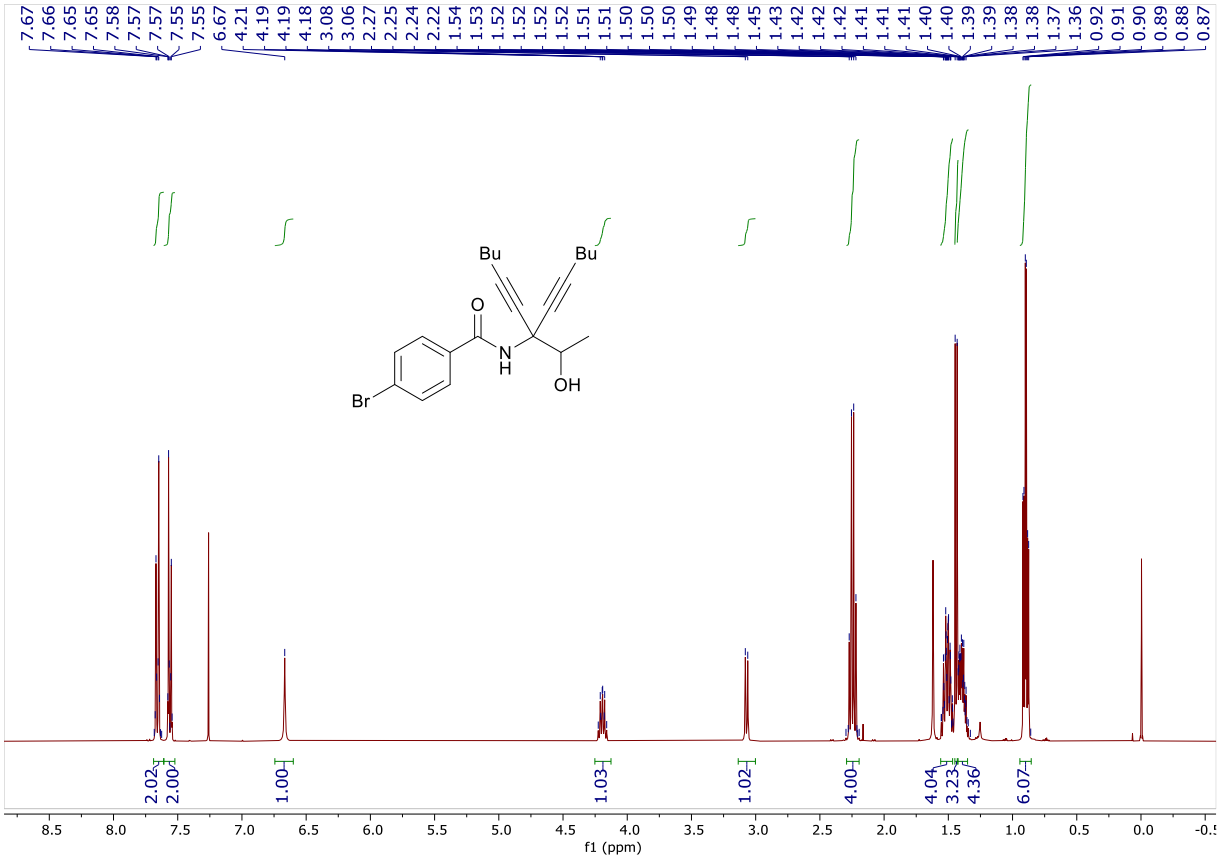


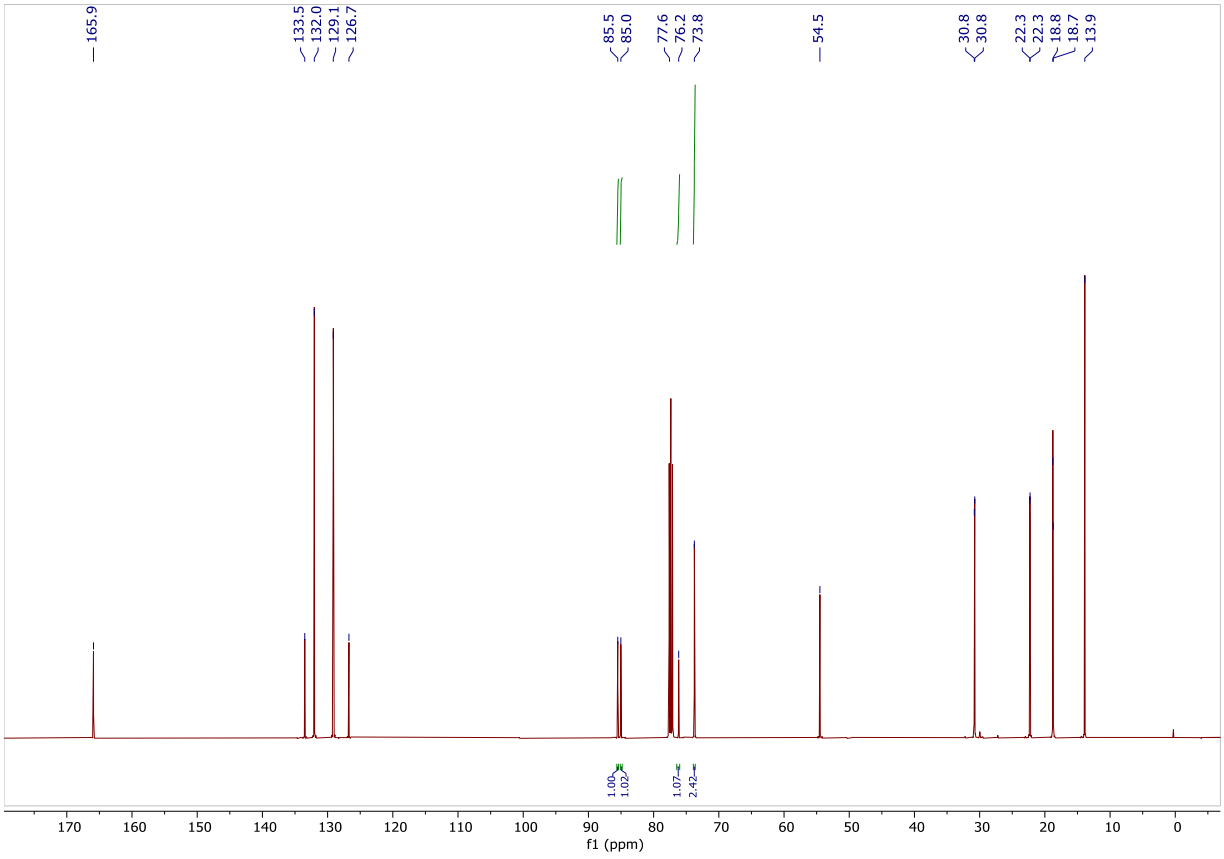
***N*-(7-(1-Hydroxyethyl)trideca-5,8-diyn-7-yl)benzamide (5l)**



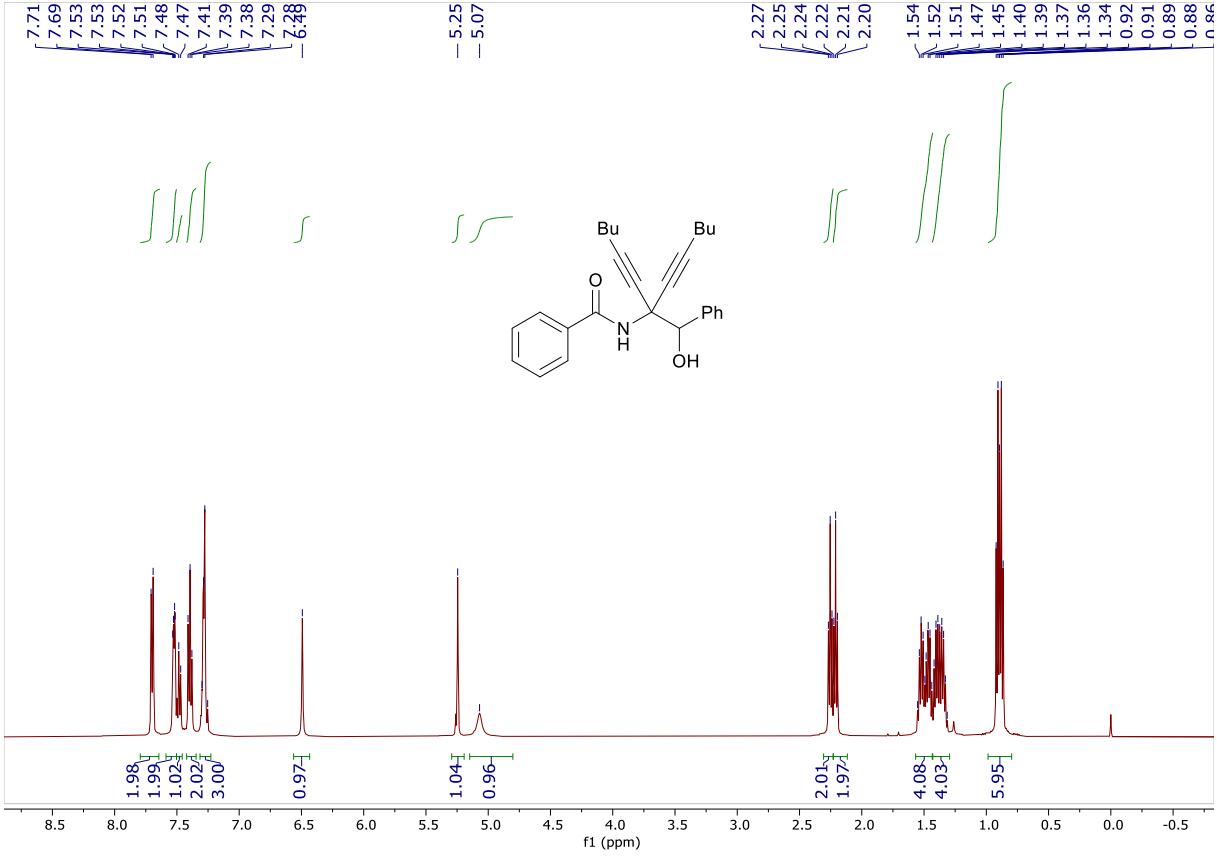


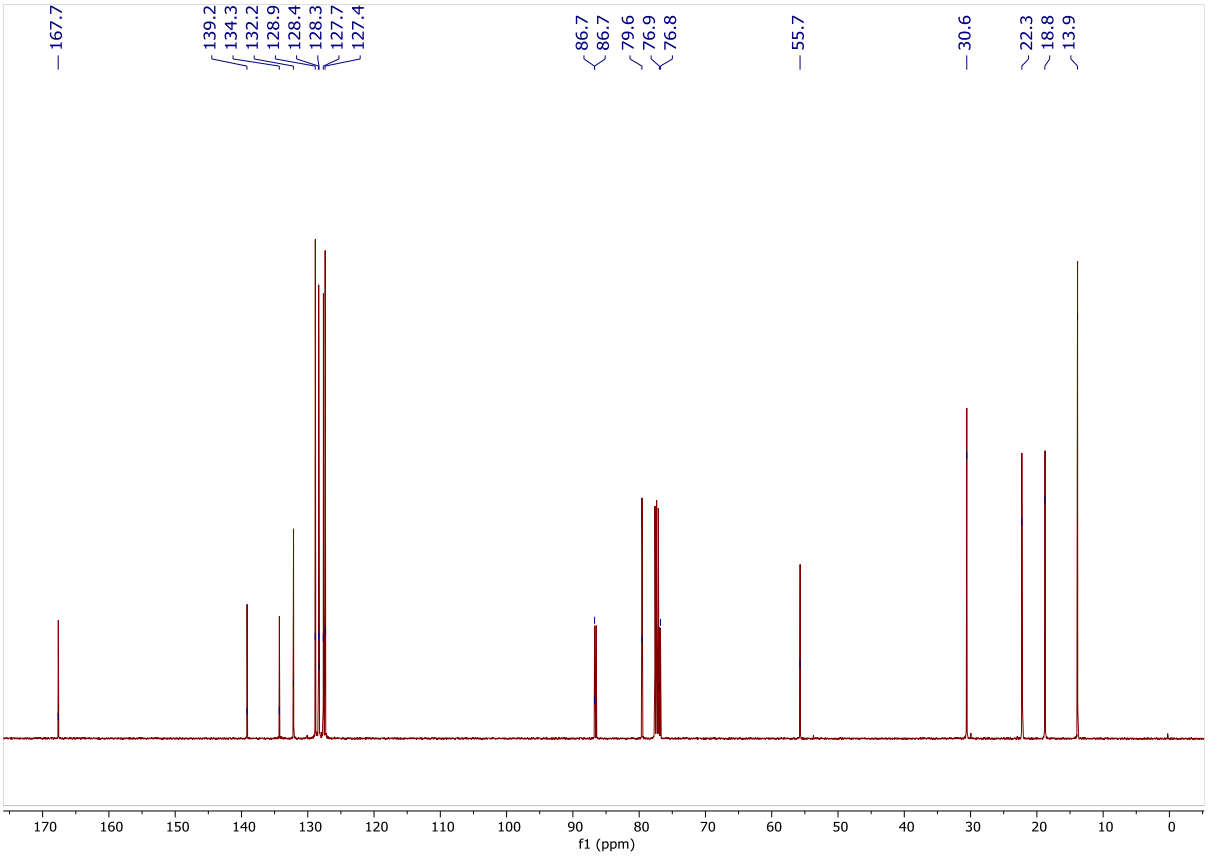
4-Bromo-*N*-(7-(1-hydroxyethyl)trideca-5,8-diyn-7-yl)benzamide (5m)



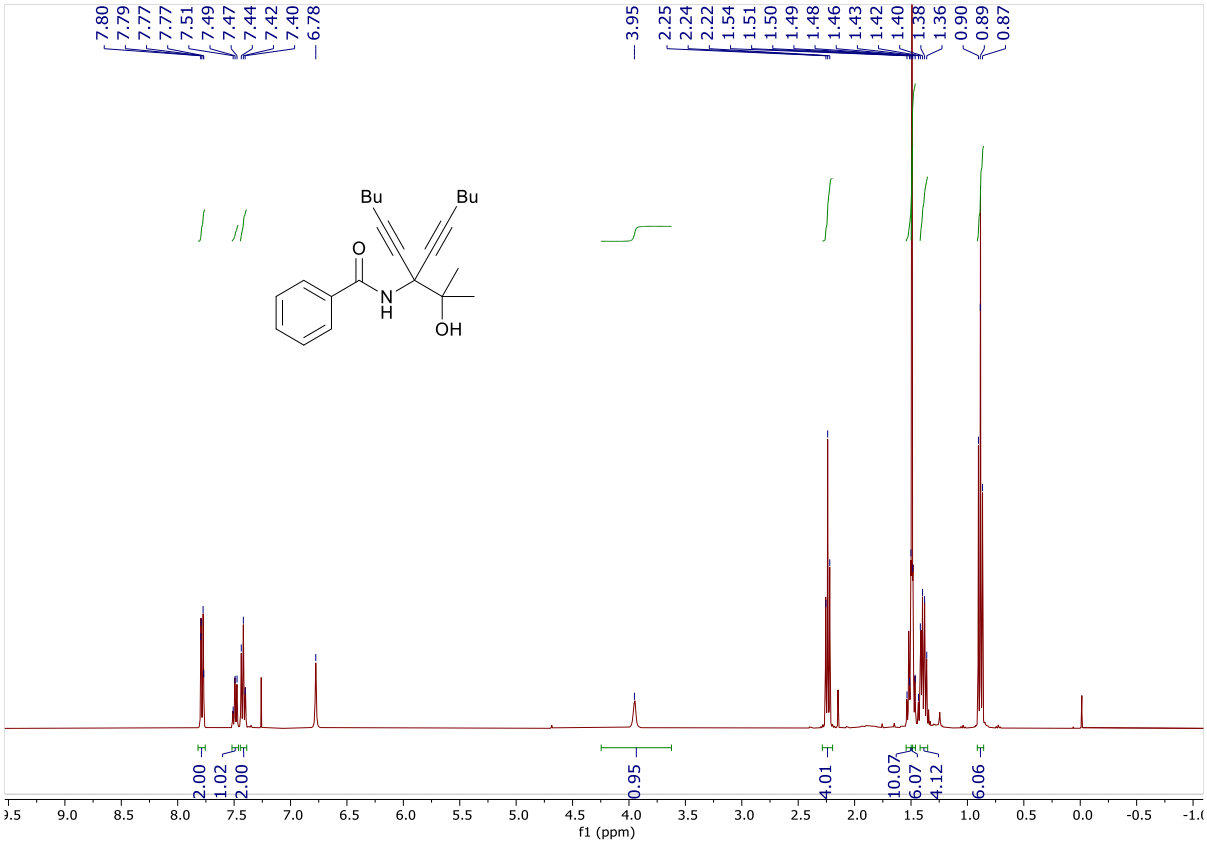


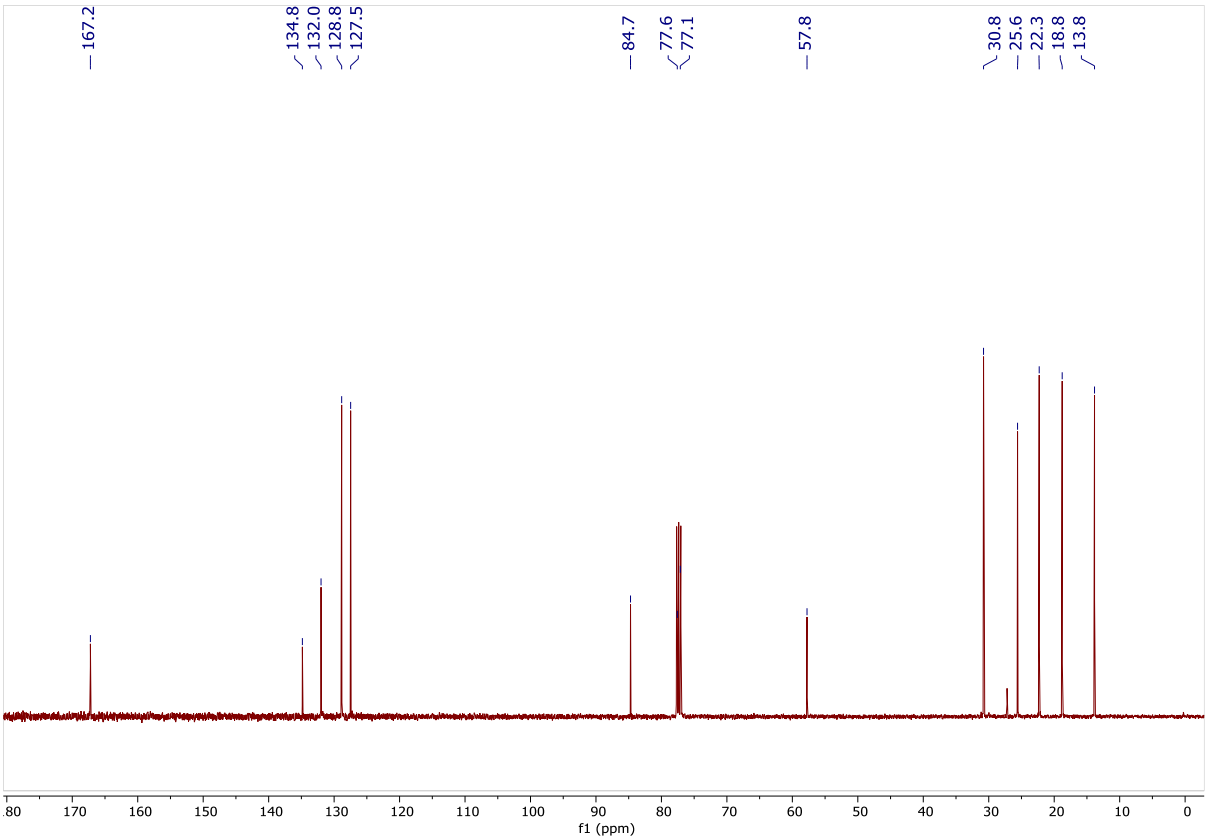
***N*-(7-(Hydroxy(phenyl)methyl)trideca-5,8-diyn-7-yl)benzamide (5n)**



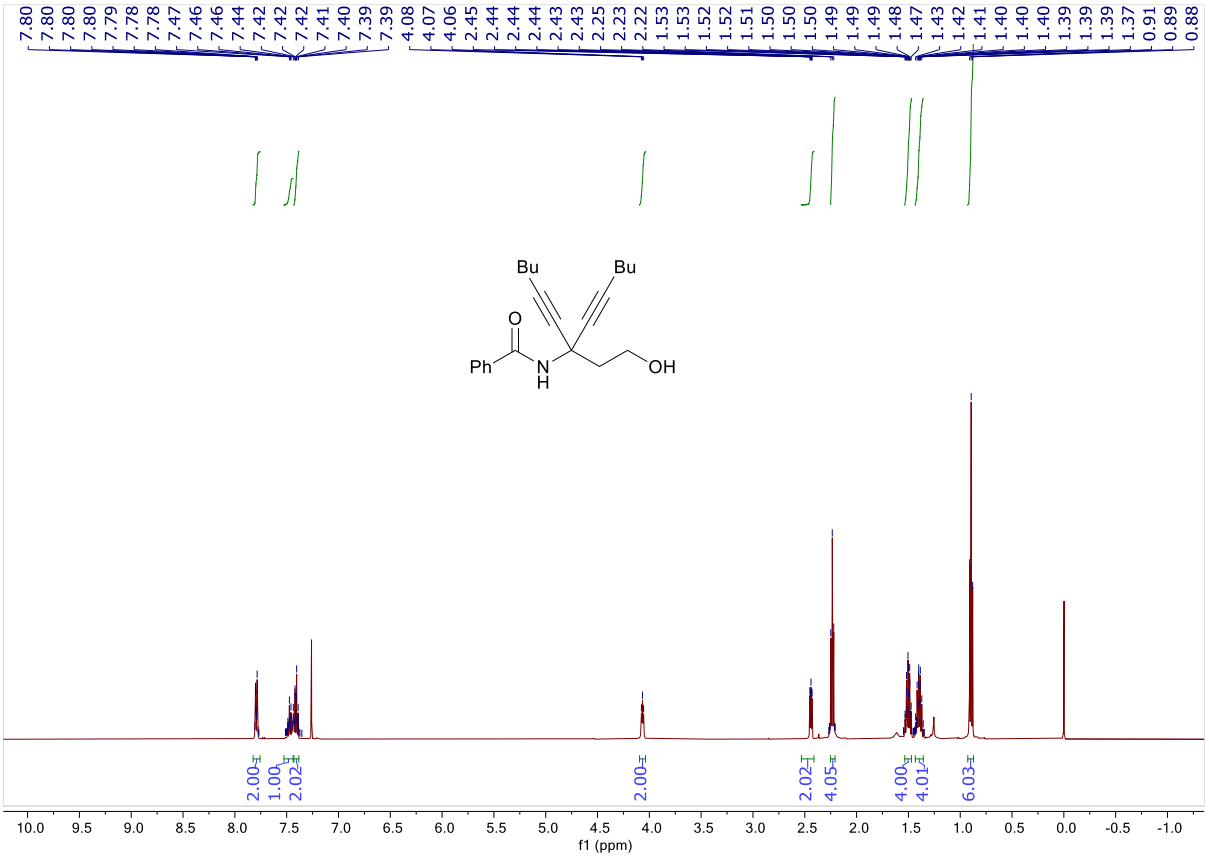


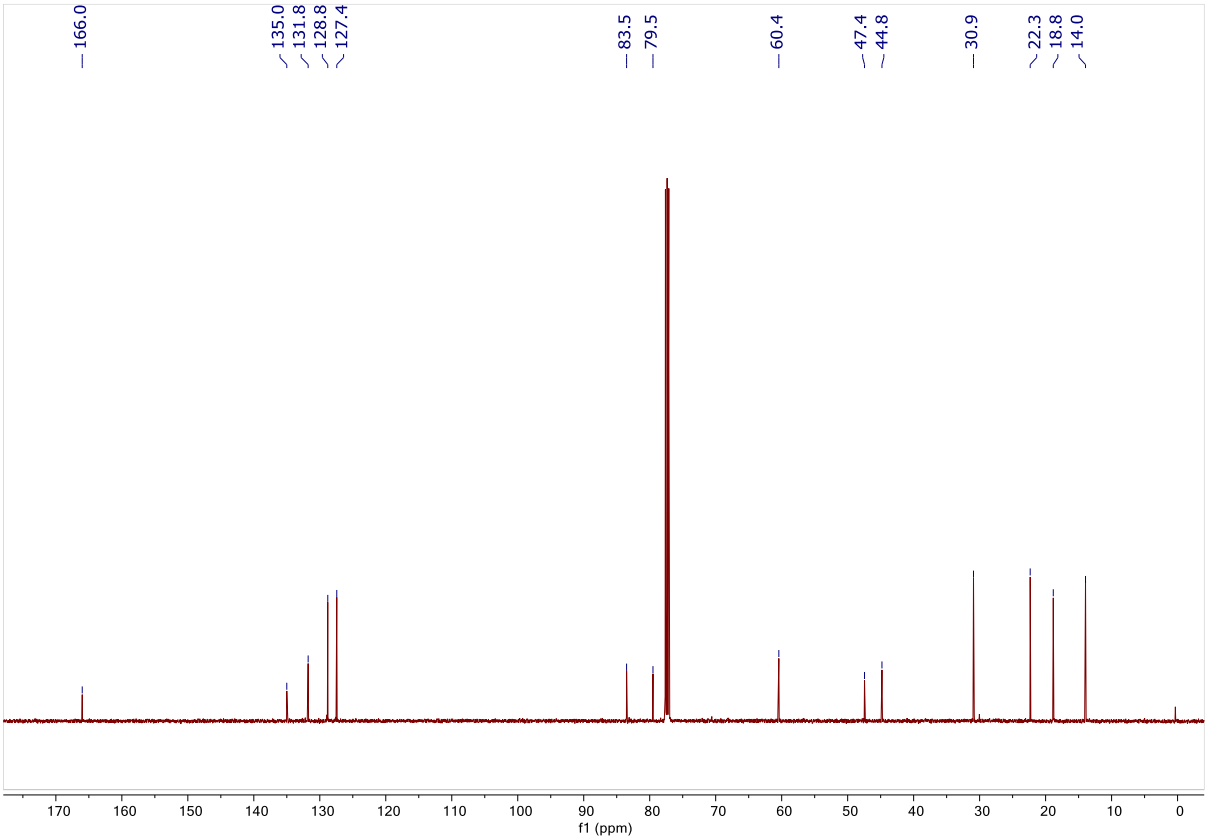
***N*-(7-(2-Hydroxypropan-2-yl)trideca-5,8-diyn-7-yl)benzamide(5o)**



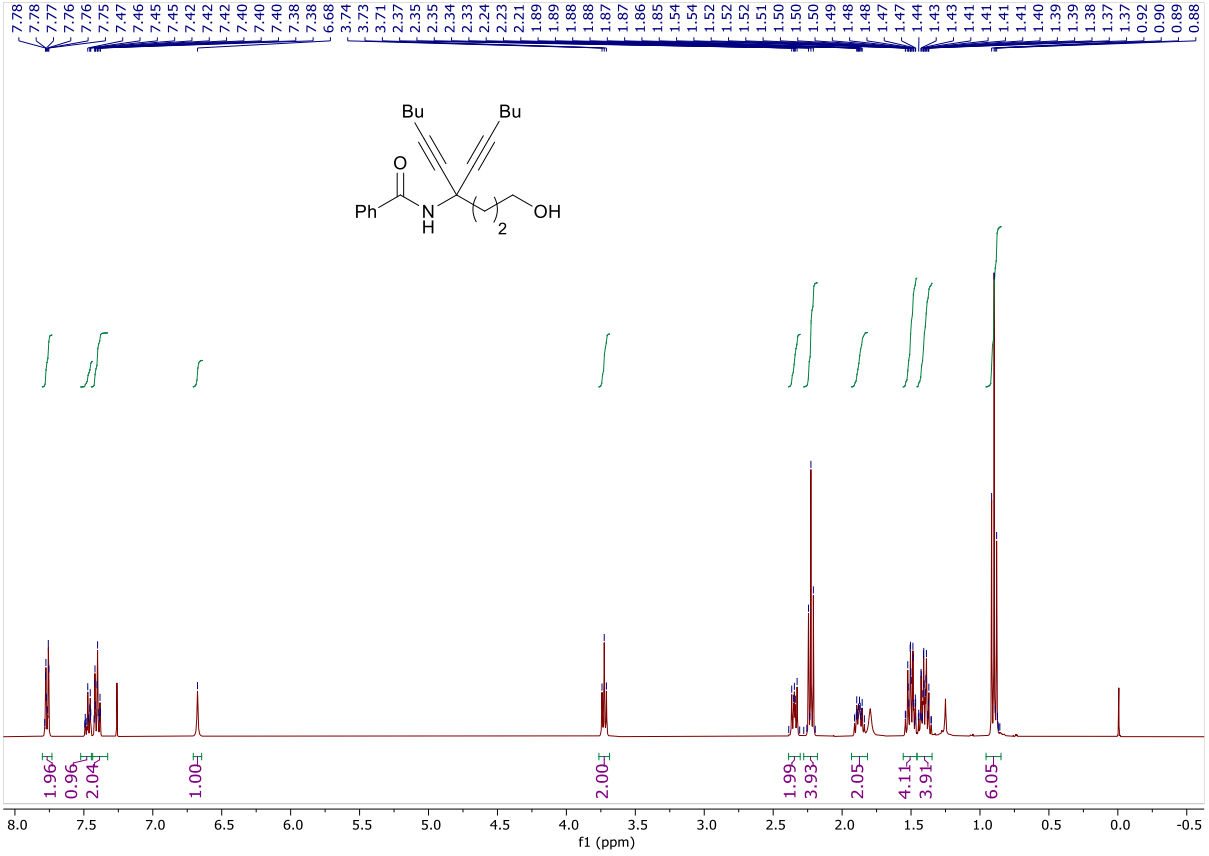


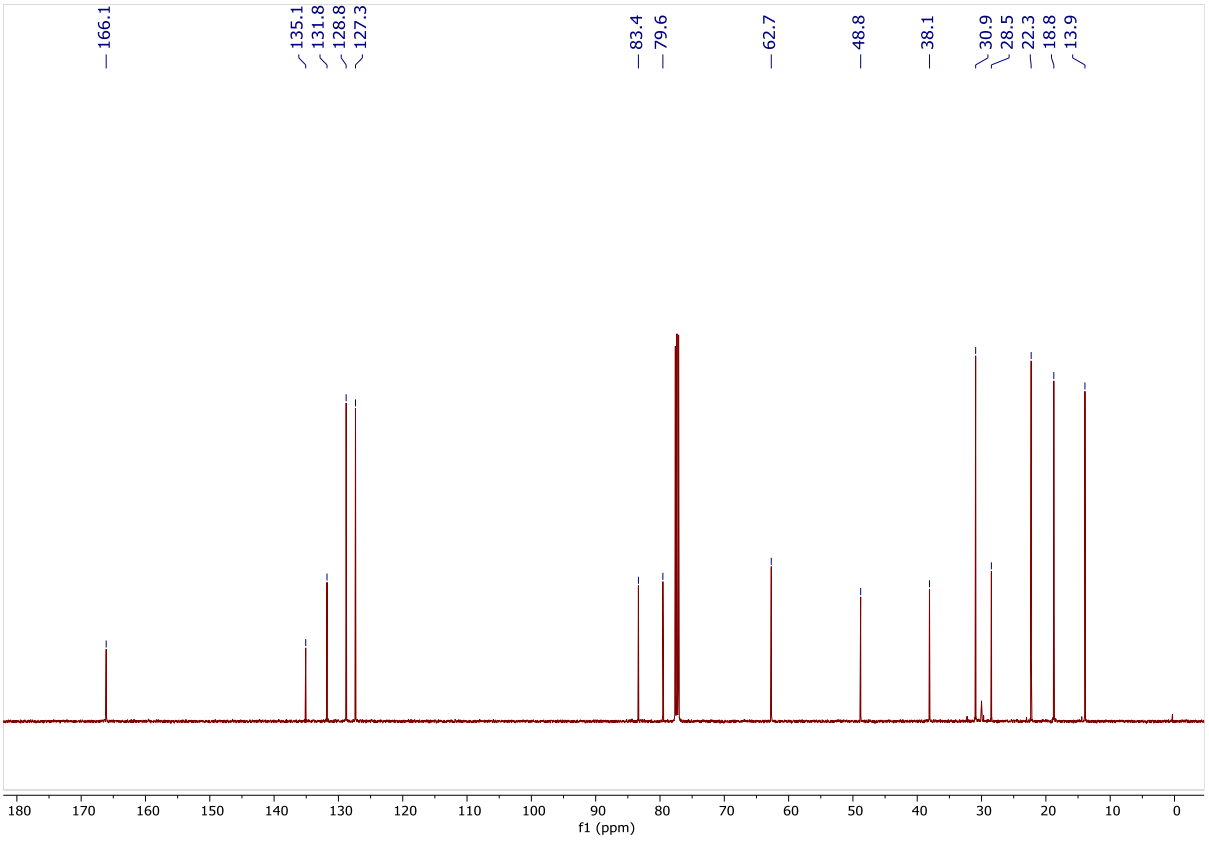
***N*-(7-(2-Hydroxyethyl)trideca-5,8-diyn-7-yl)benzamide (5p)**



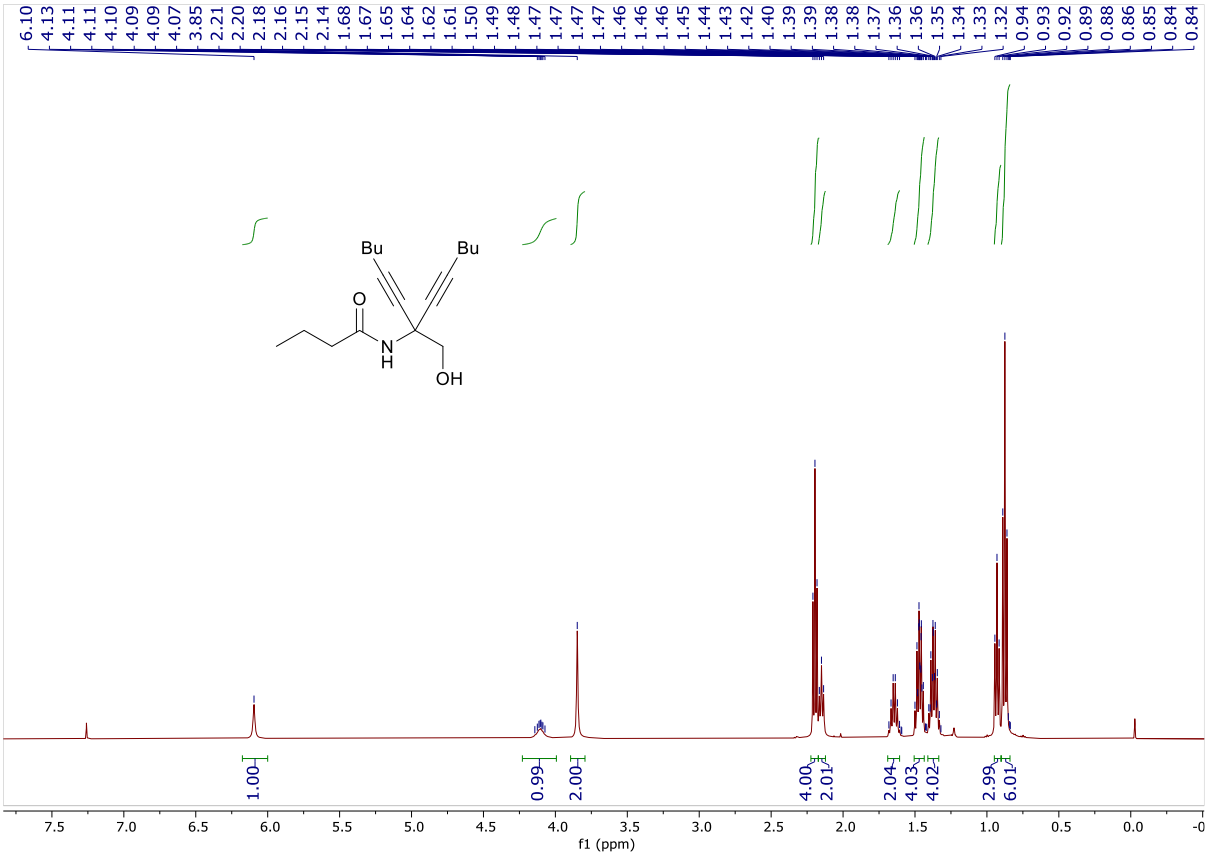


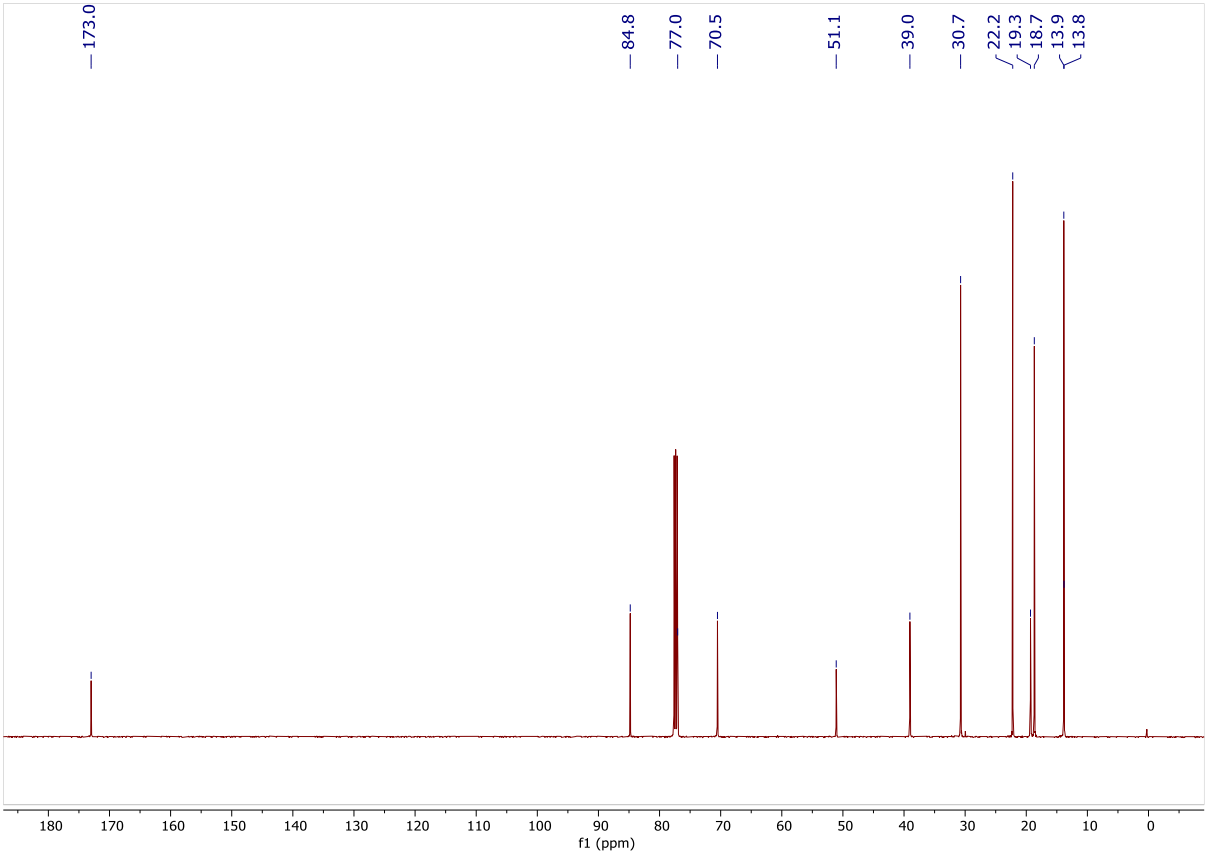
N-(7-(2-Hydroxyethyl)trideca-5,8-diyn-7-yl)benzamide (5q)



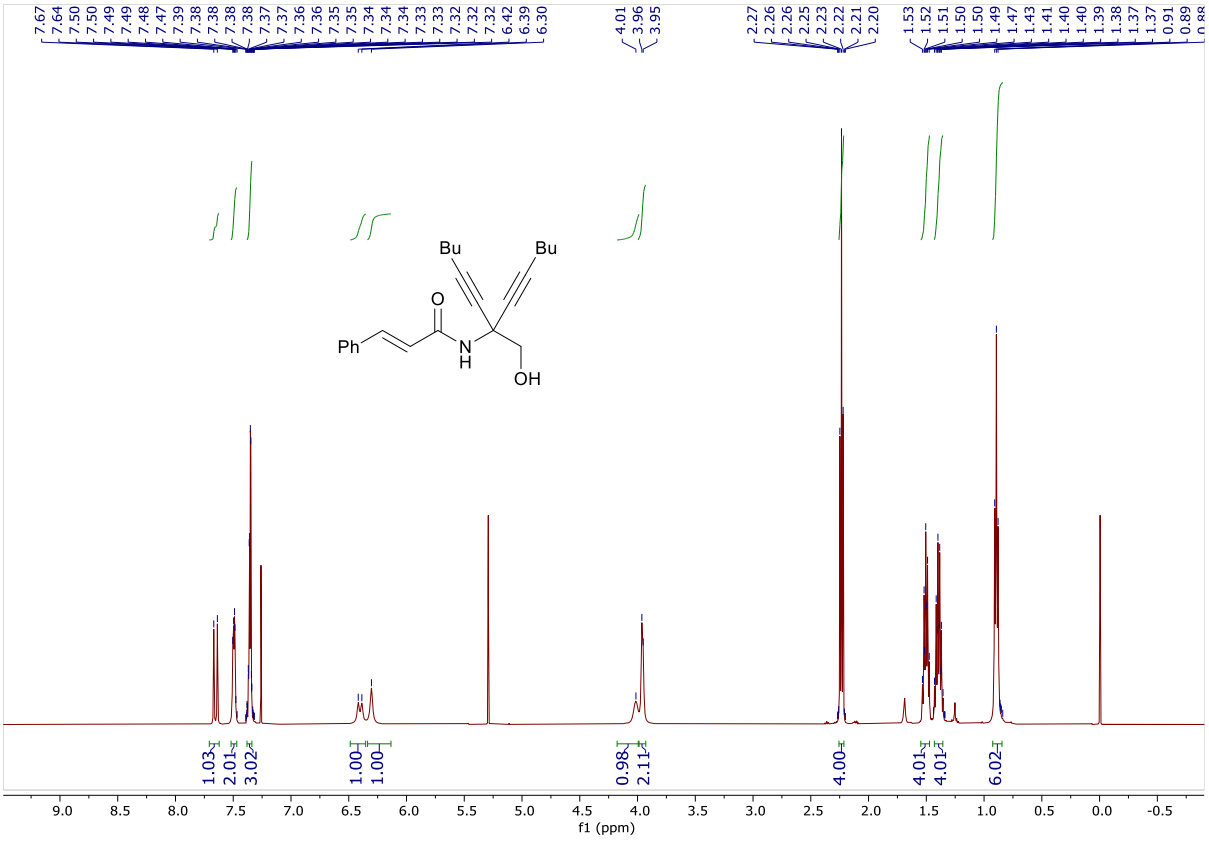


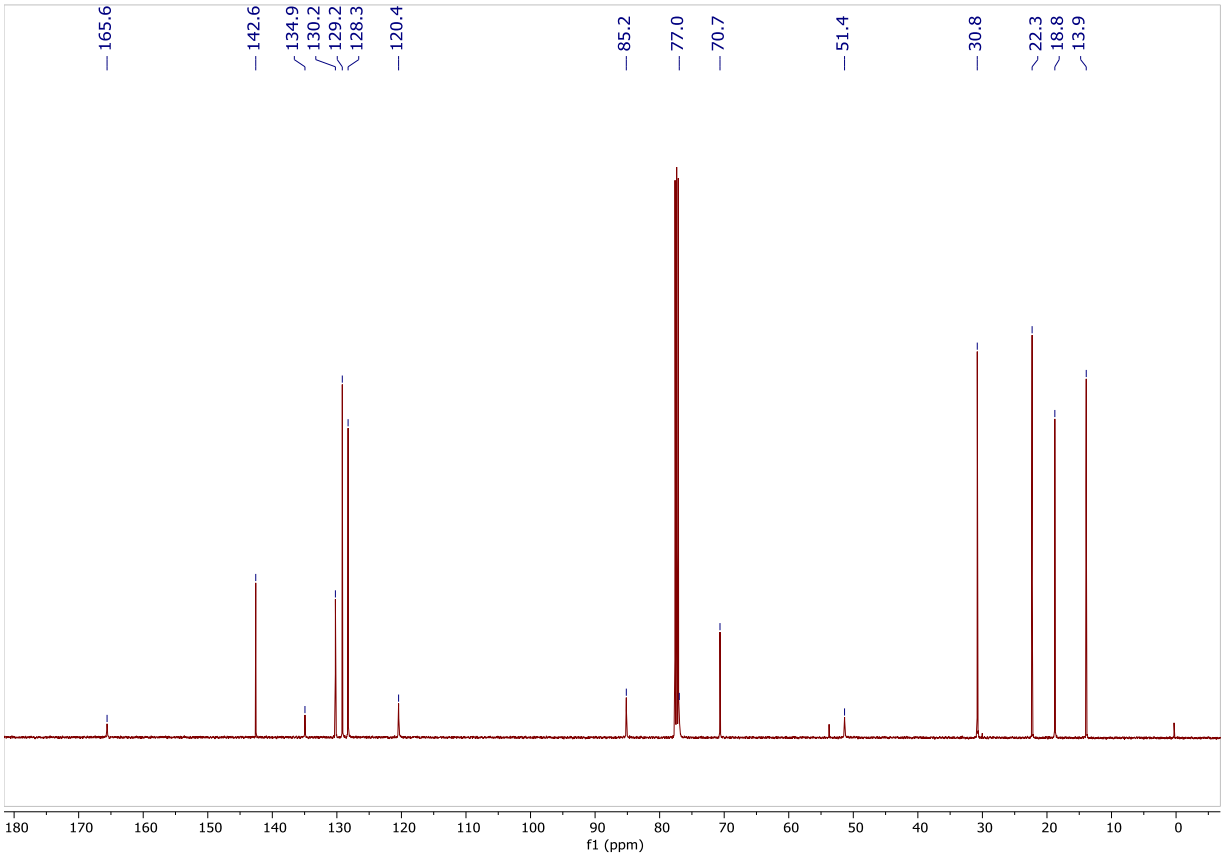
***N*-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)butyramide (5r)**



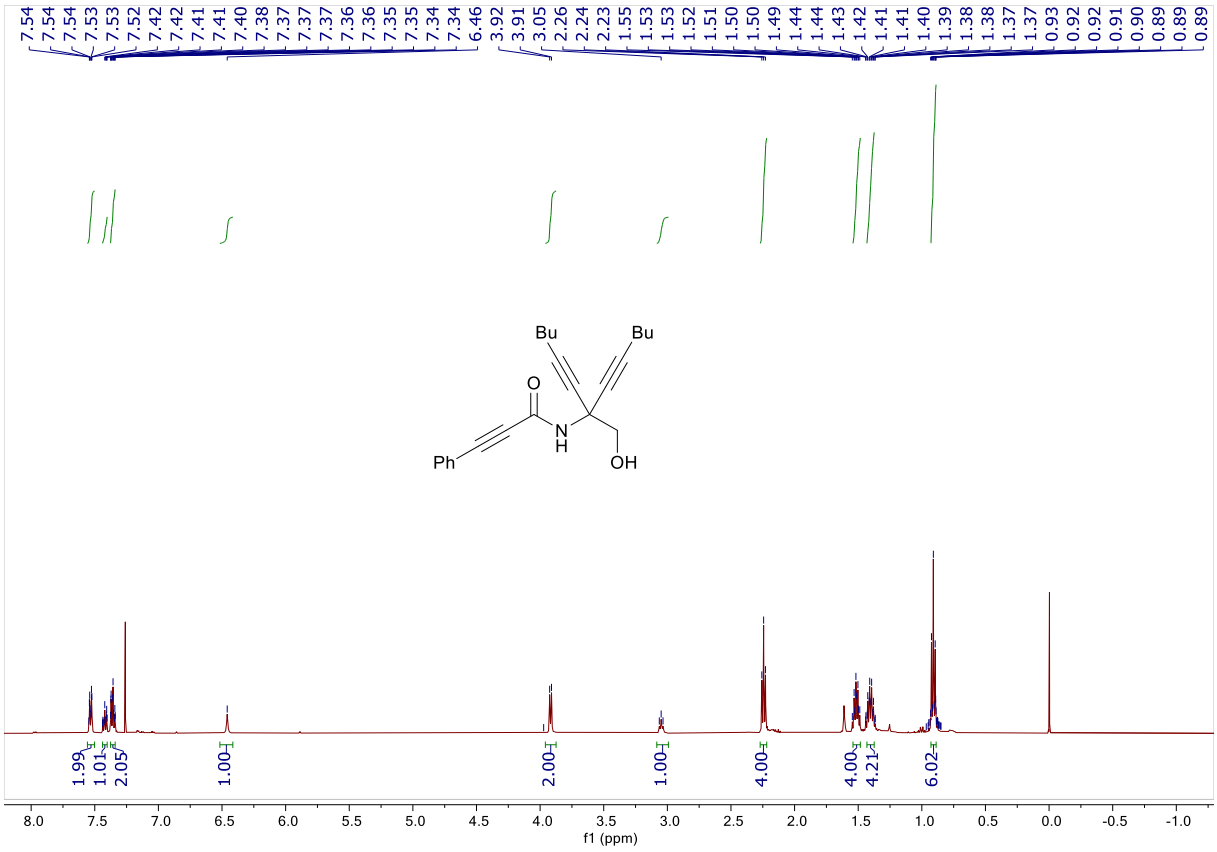


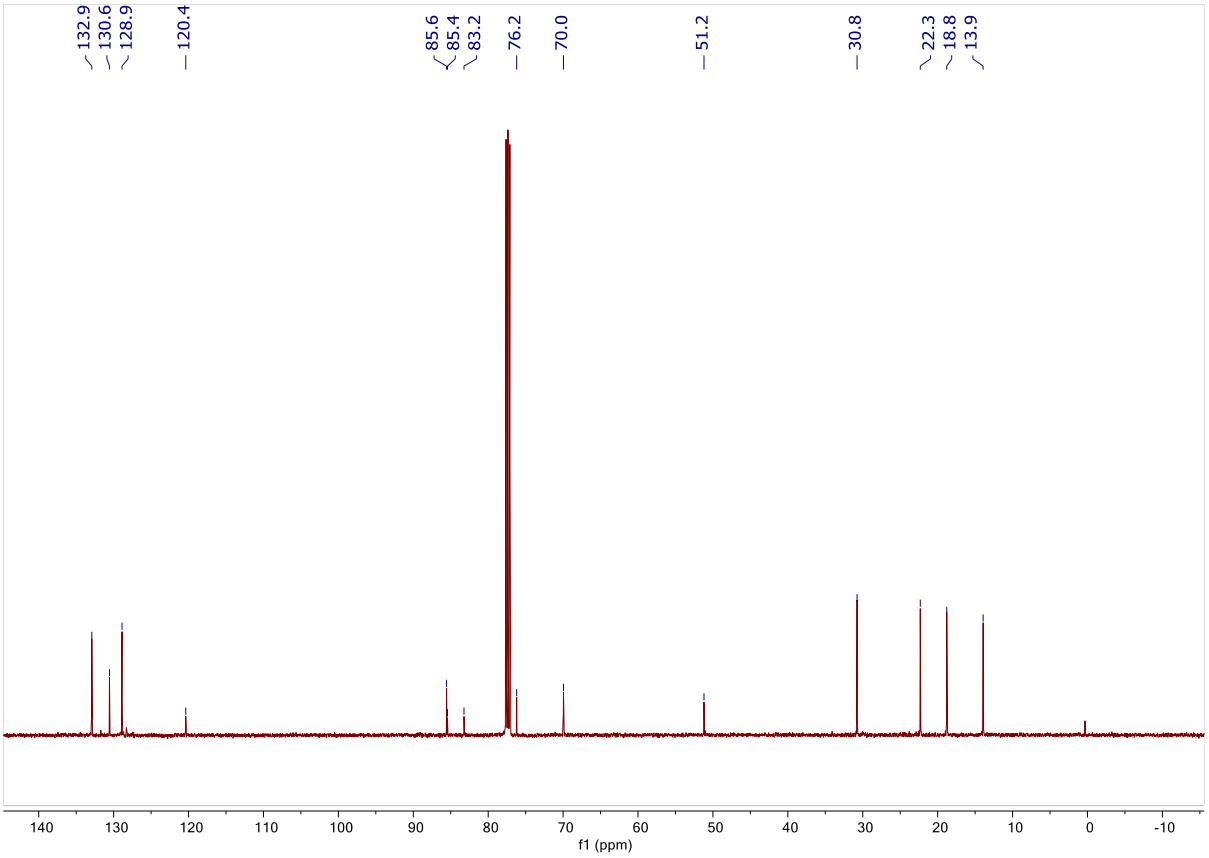
N-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)cinnamamide (5s)



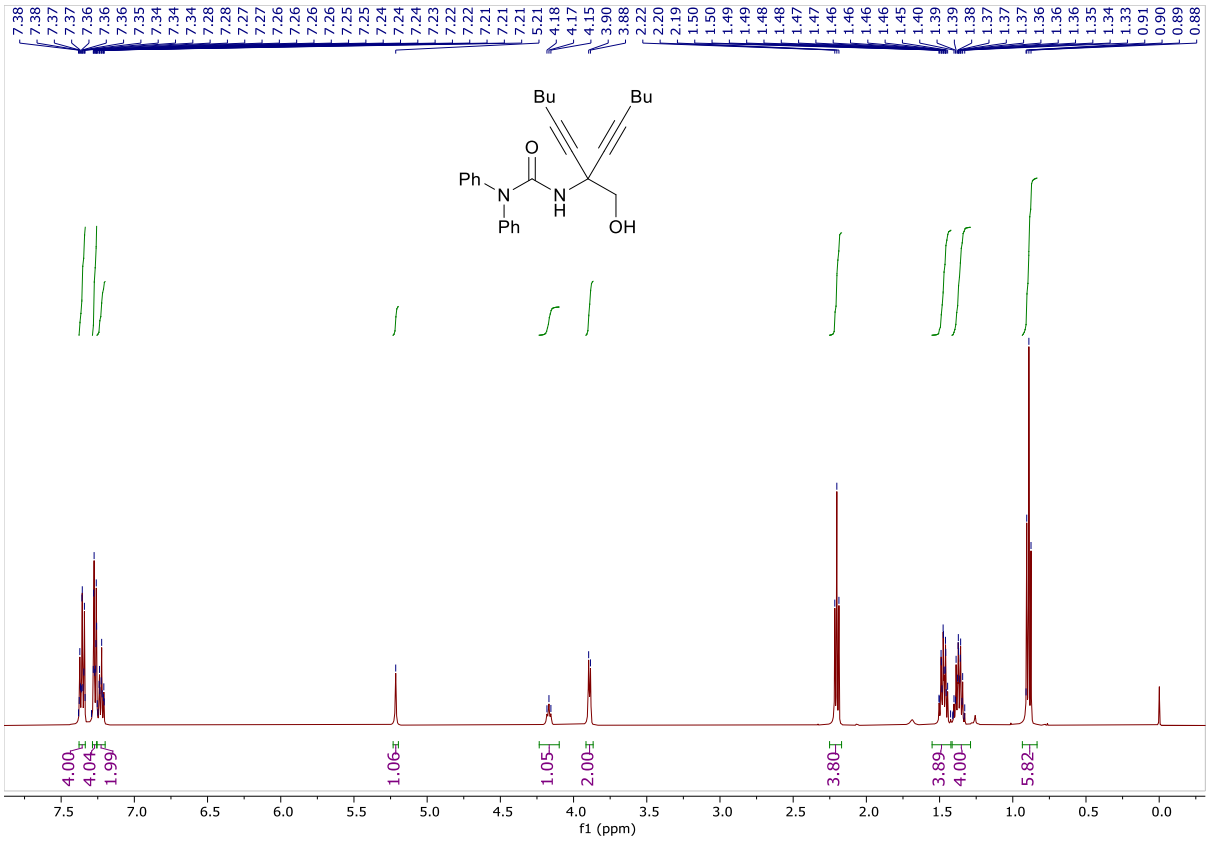


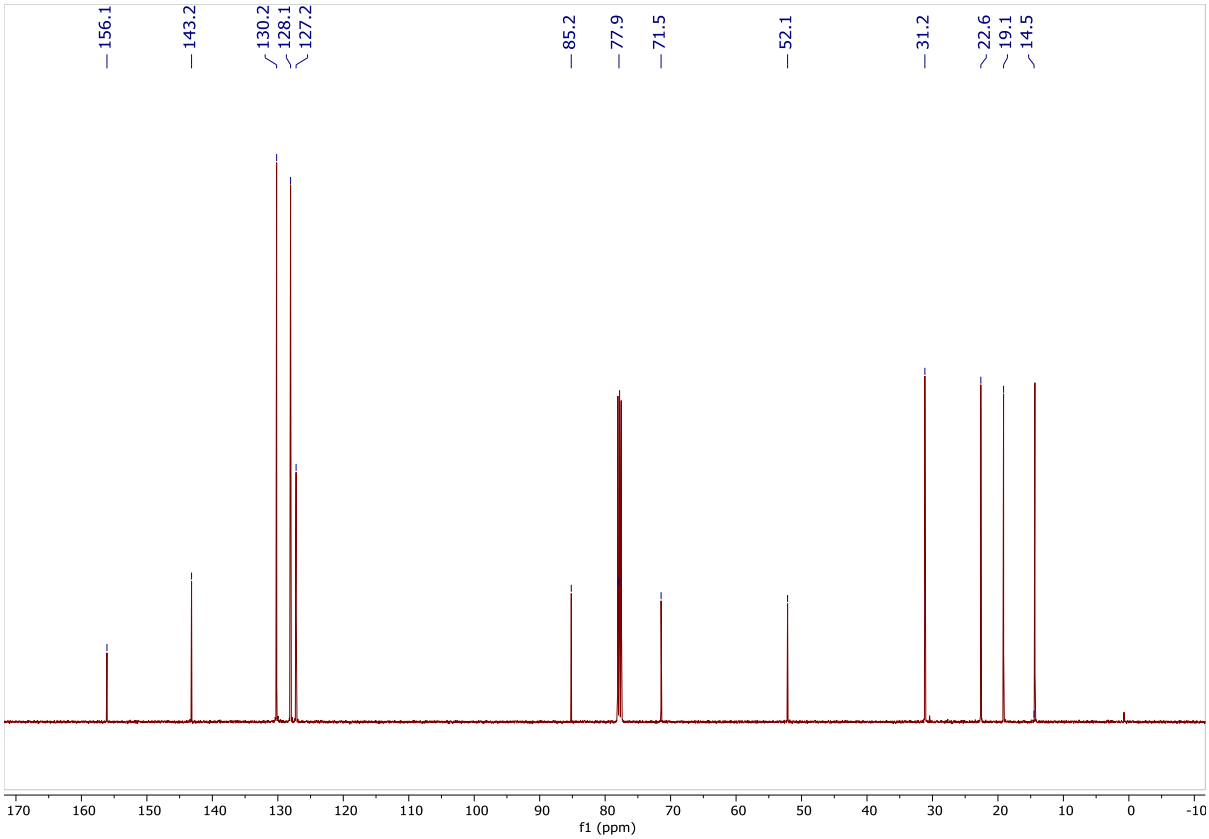
N-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-3-phenylpropiolamide (5t)



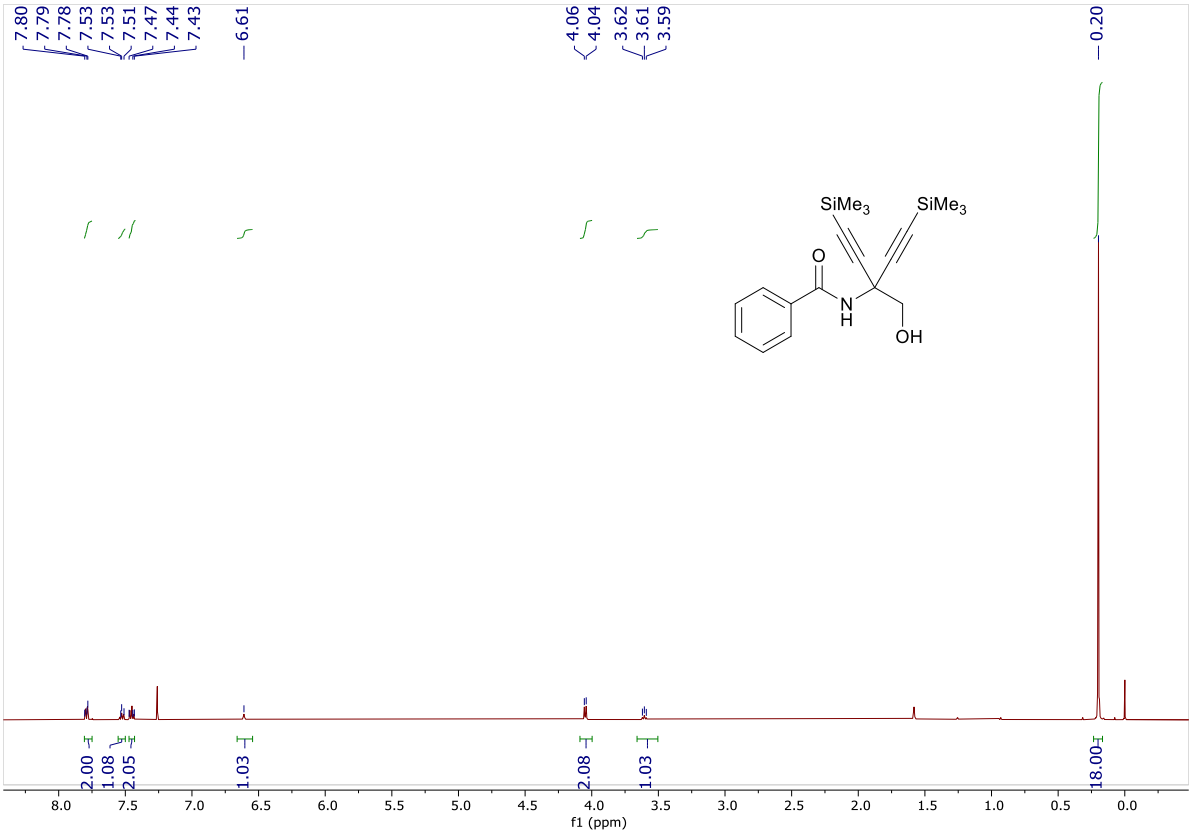


3-(7-(Hydroxymethyl)trideca-5,8-diyn-7-yl)-1,1-diphenylurea (5u)

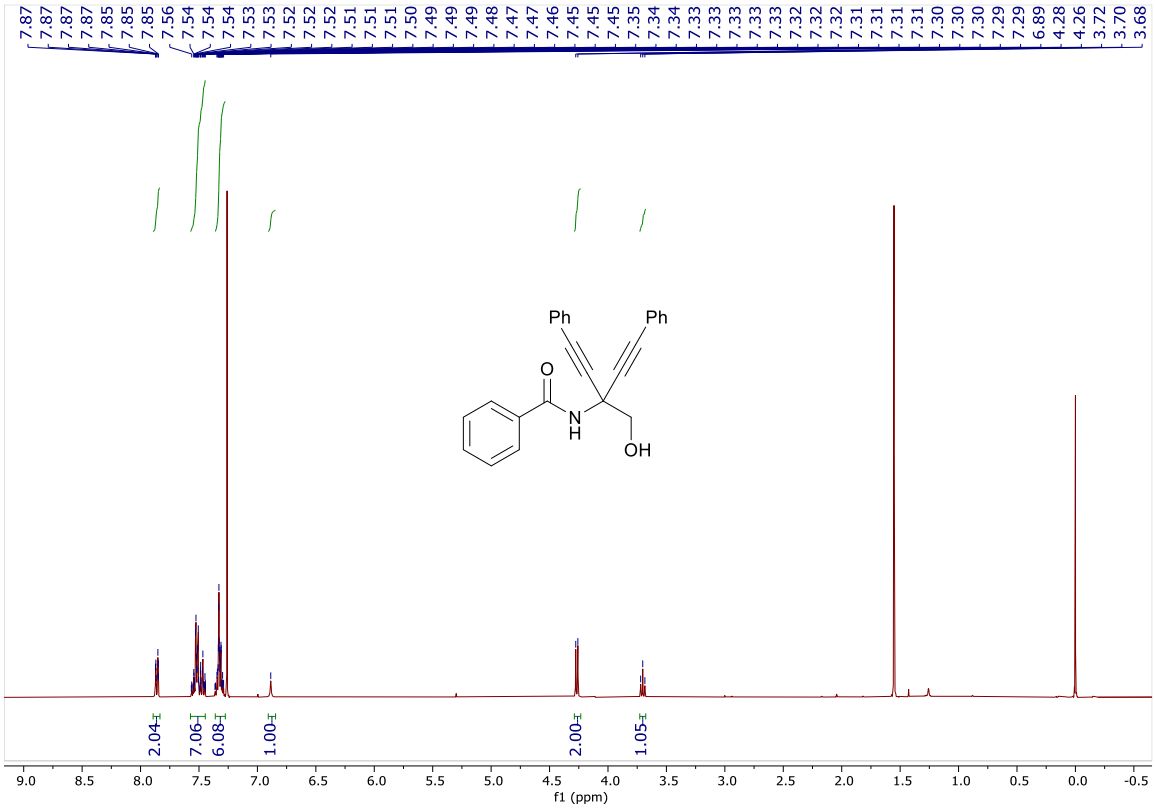




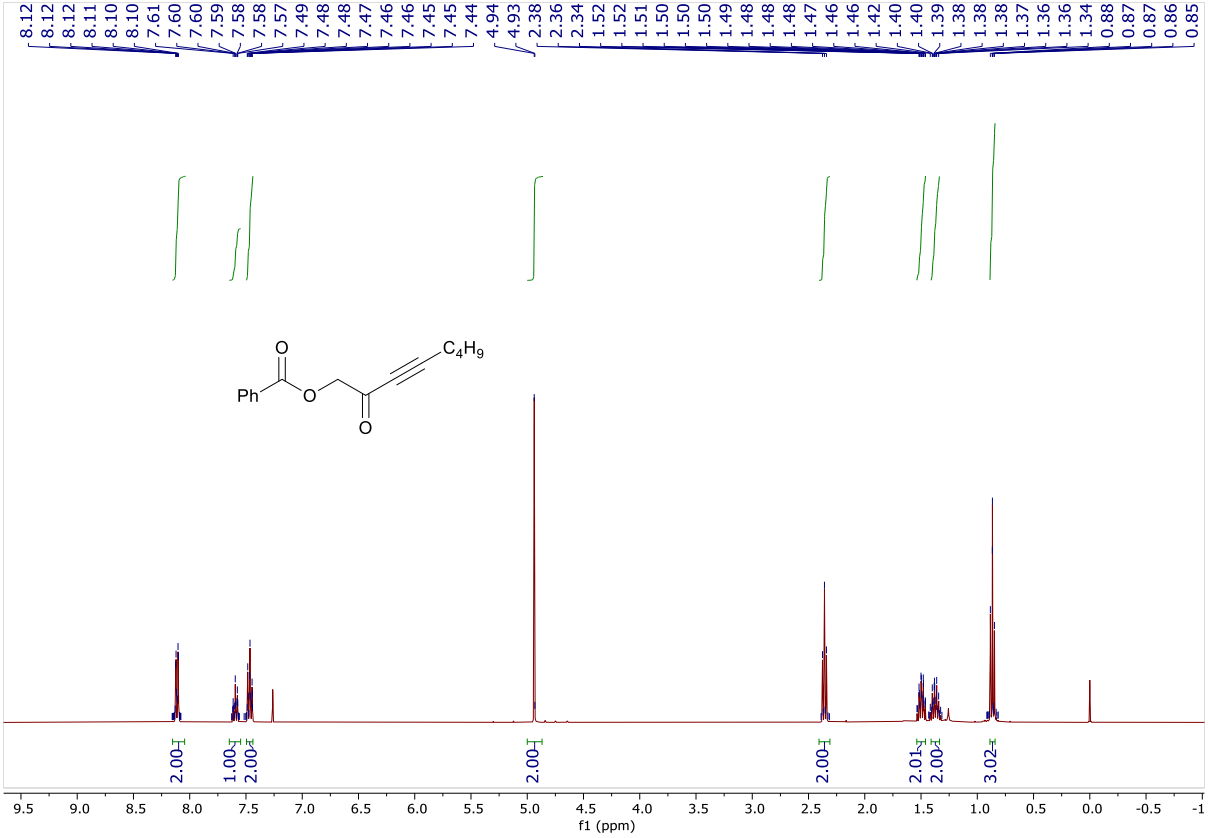
***N*-(3-(Hydroxymethyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-yl)benzamide (5v)**

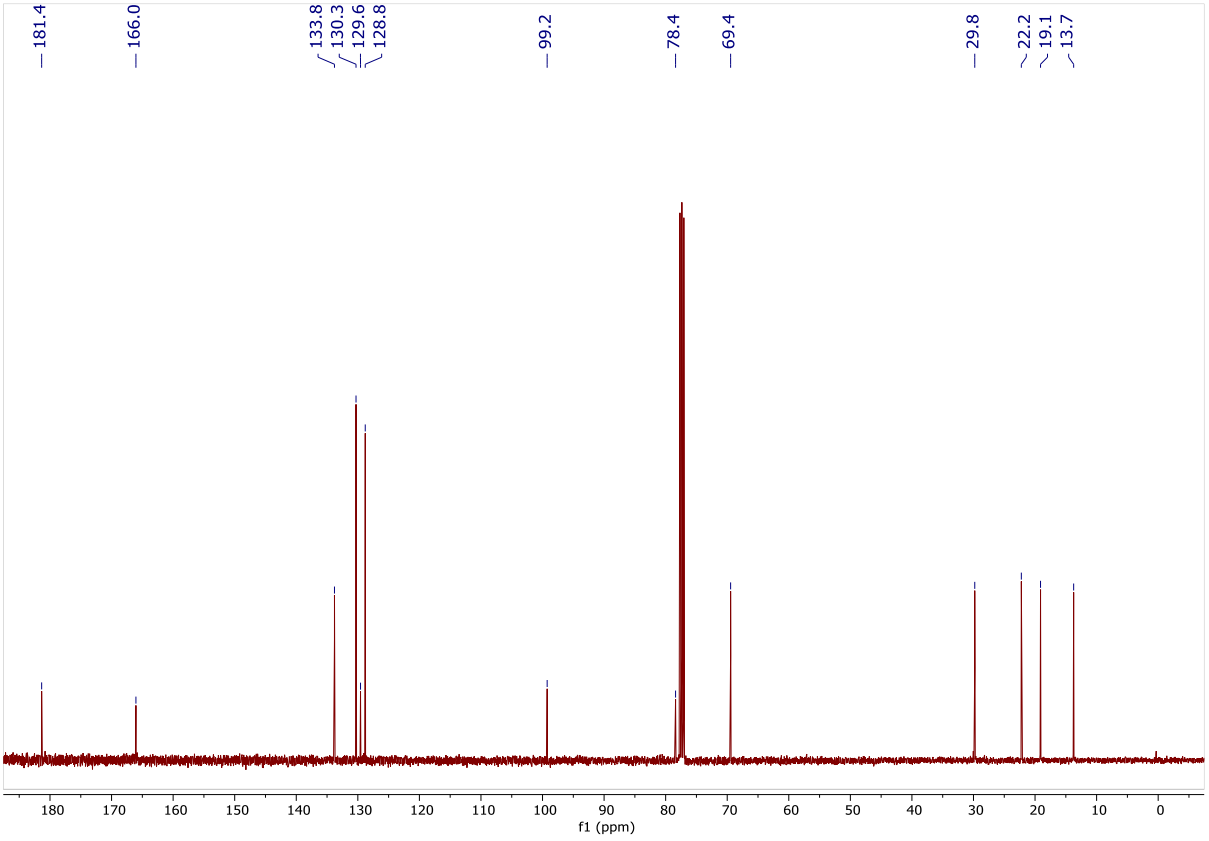


***N*-(3-(Hydroxymethyl)-1,5-diphenylpenta-1,4-diyn-3-yl)benzamide (5w)**

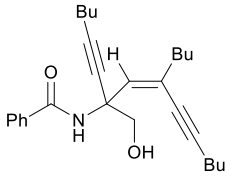


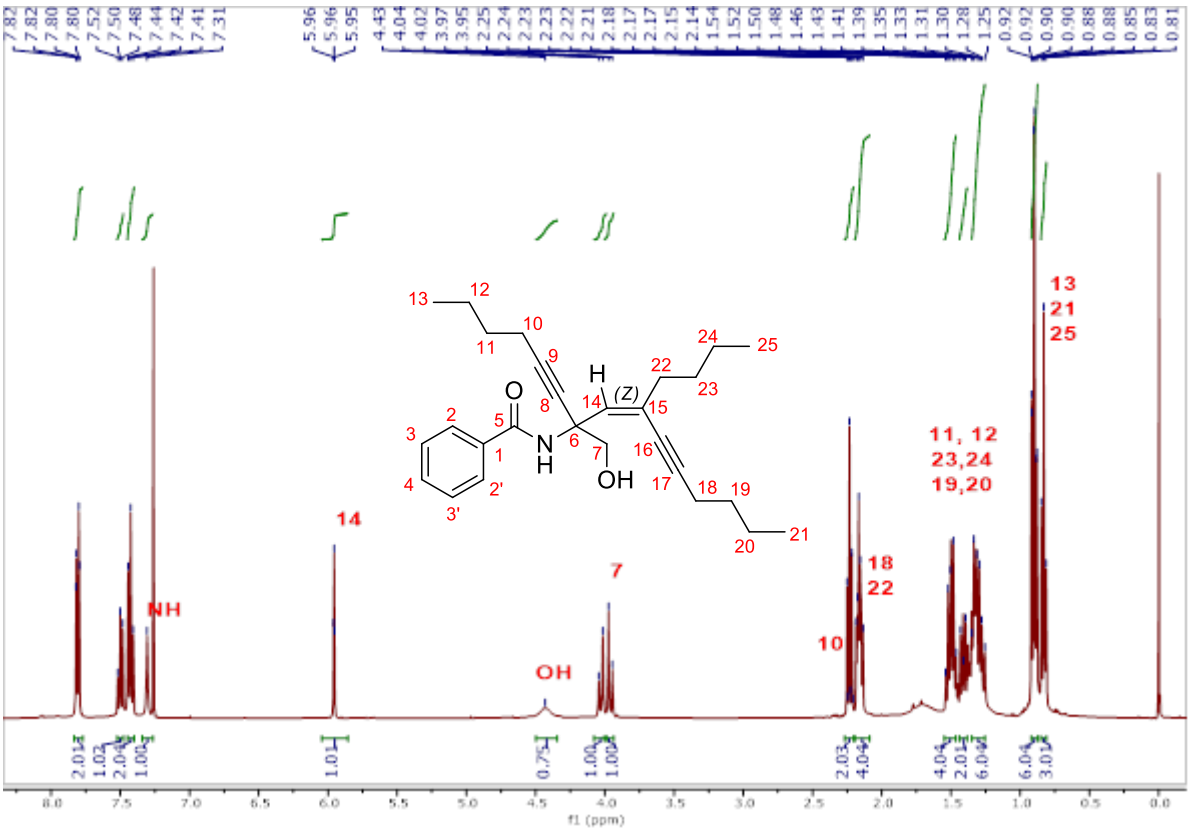
2-Oxooct-3-yn-1-yl benzoate (7a)

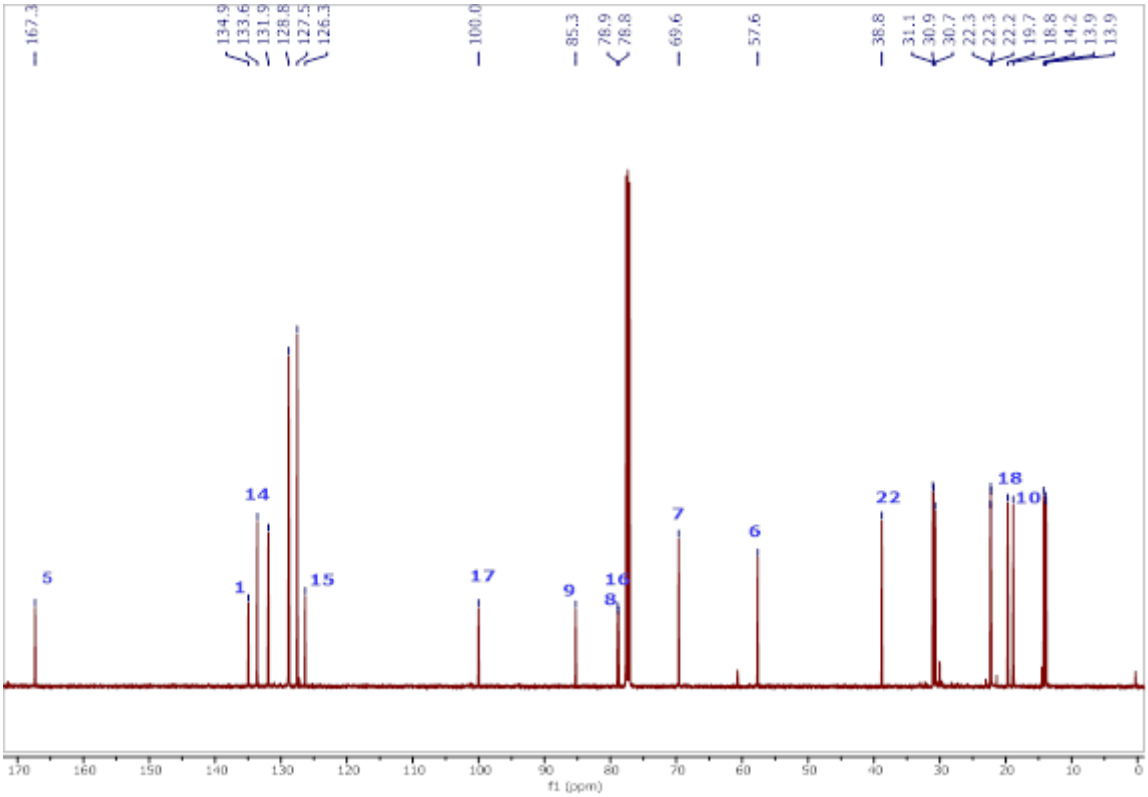




***N*-(9-Butyl-7-(hydroxymethyl)pentadeca-8-en-5,10-diyn-7-yl)benzamide (8a)**

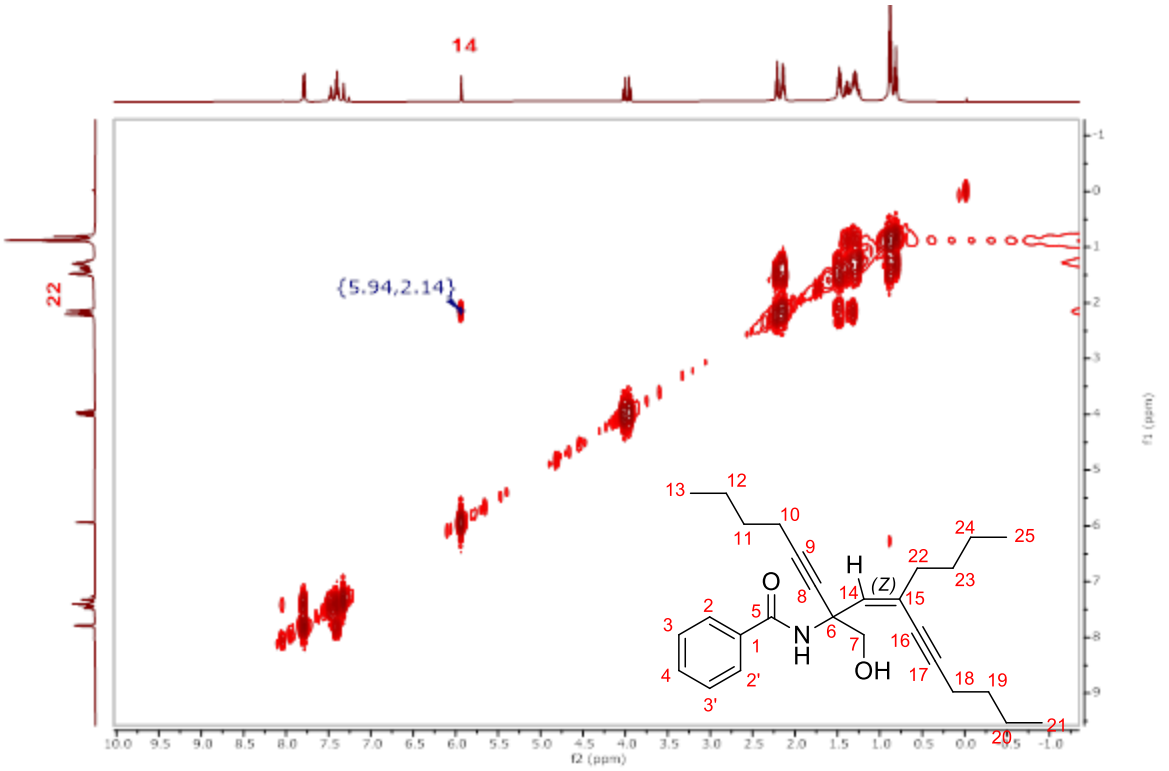


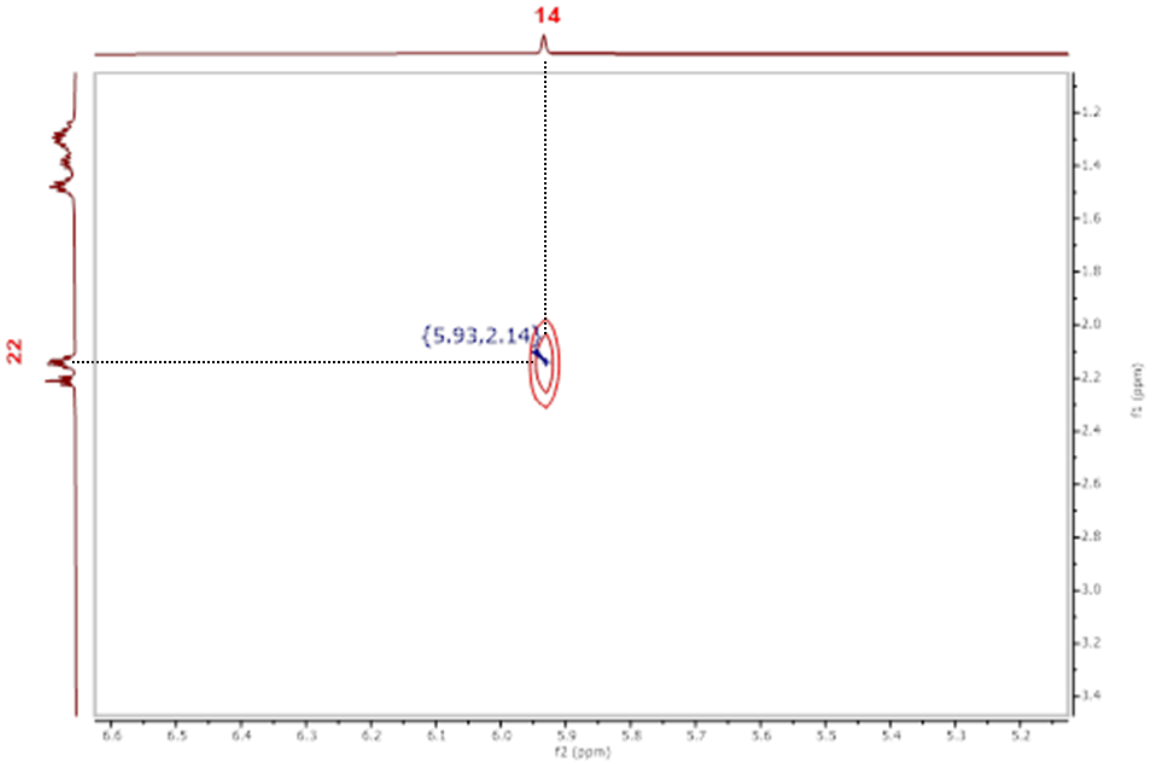




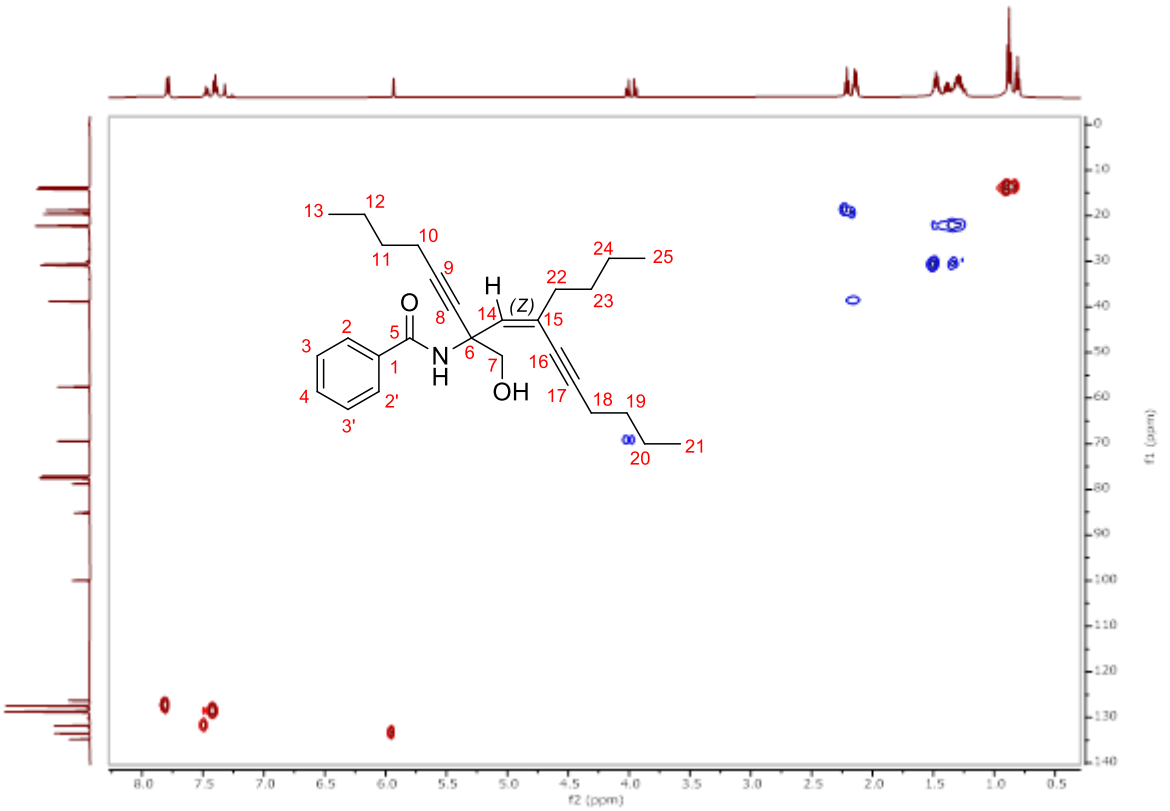
COSY experiment

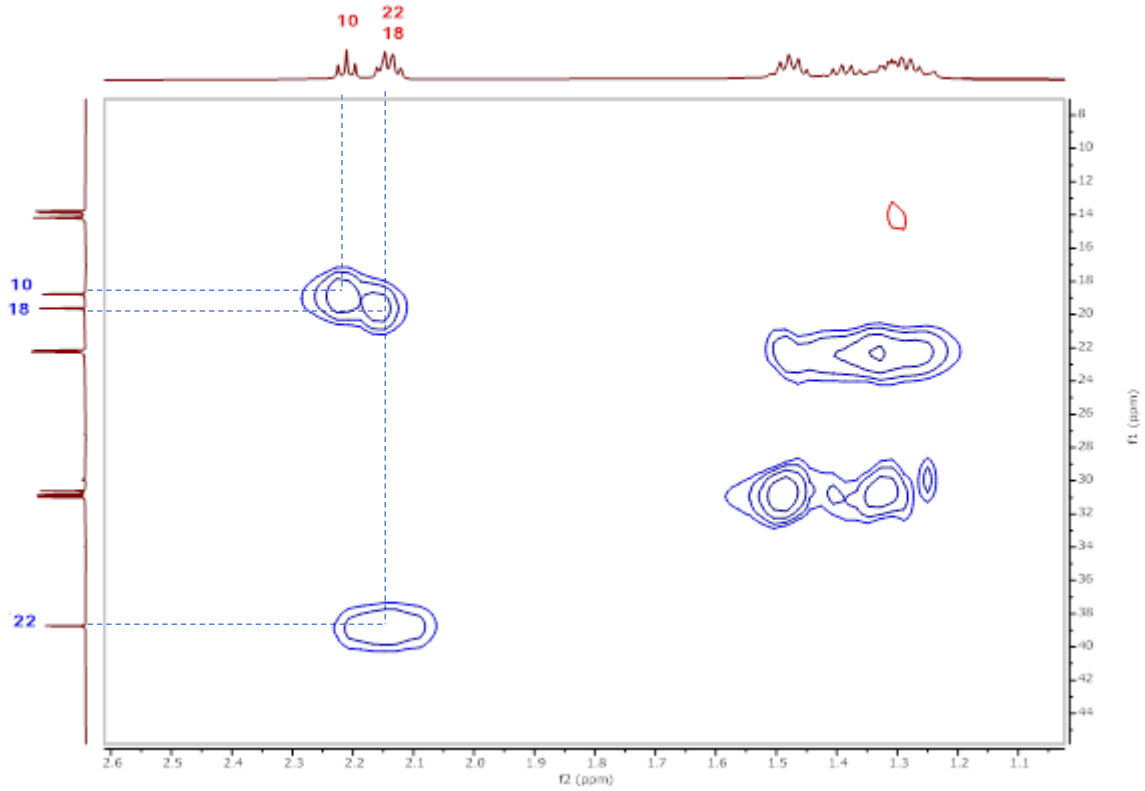
^{1}H NMR allows to assign aromatic, alkyl hydrogen, CH_2OH signals and H14 signal is a triplet at 5.96 ppm (weak coupling constant of 1.3 Hz meaning a $^{4}J_{H,H}$ coupling constant). COSY experiment shows a correlation between H14 and one of the two CH_2 signals in the multiplet at 2.14 – 2.18 ppm. H14 can only couple with H22 in its close neighbourhood through a $^{4}J_{H,H}$ spin-spin correlation. H22 and C22 are thus identified (see HSQC experiment).





HSQC experiment

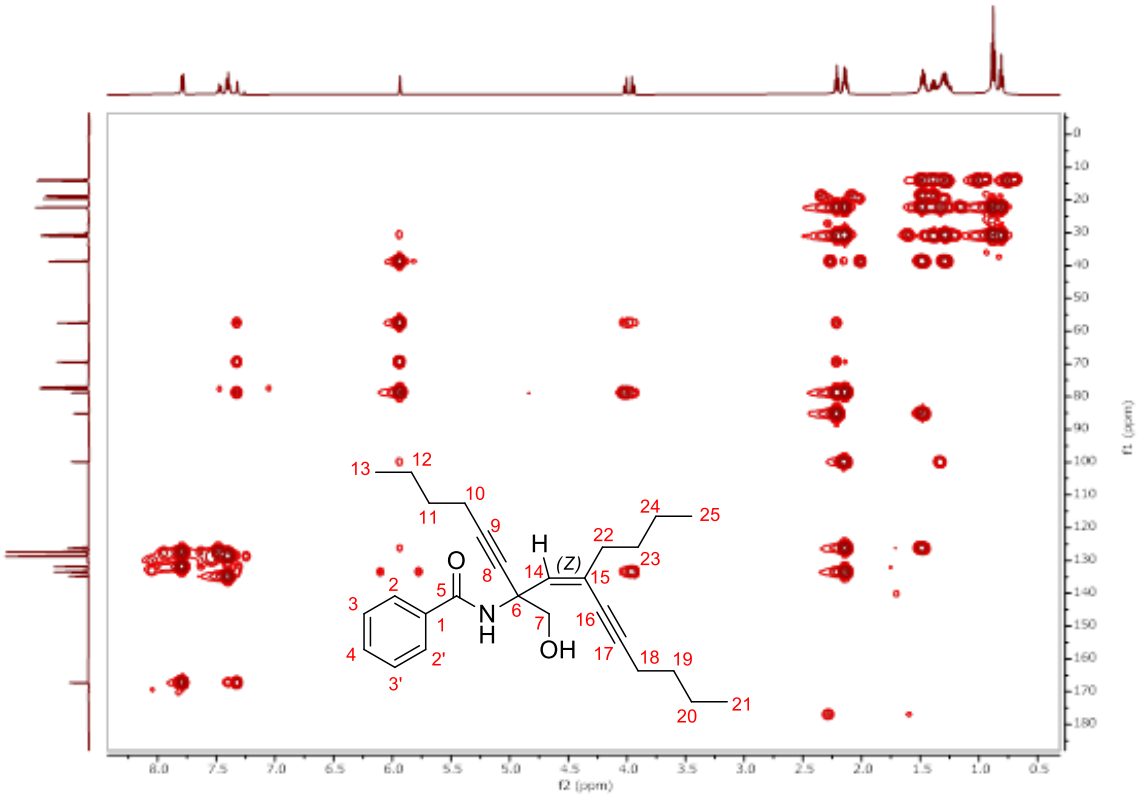


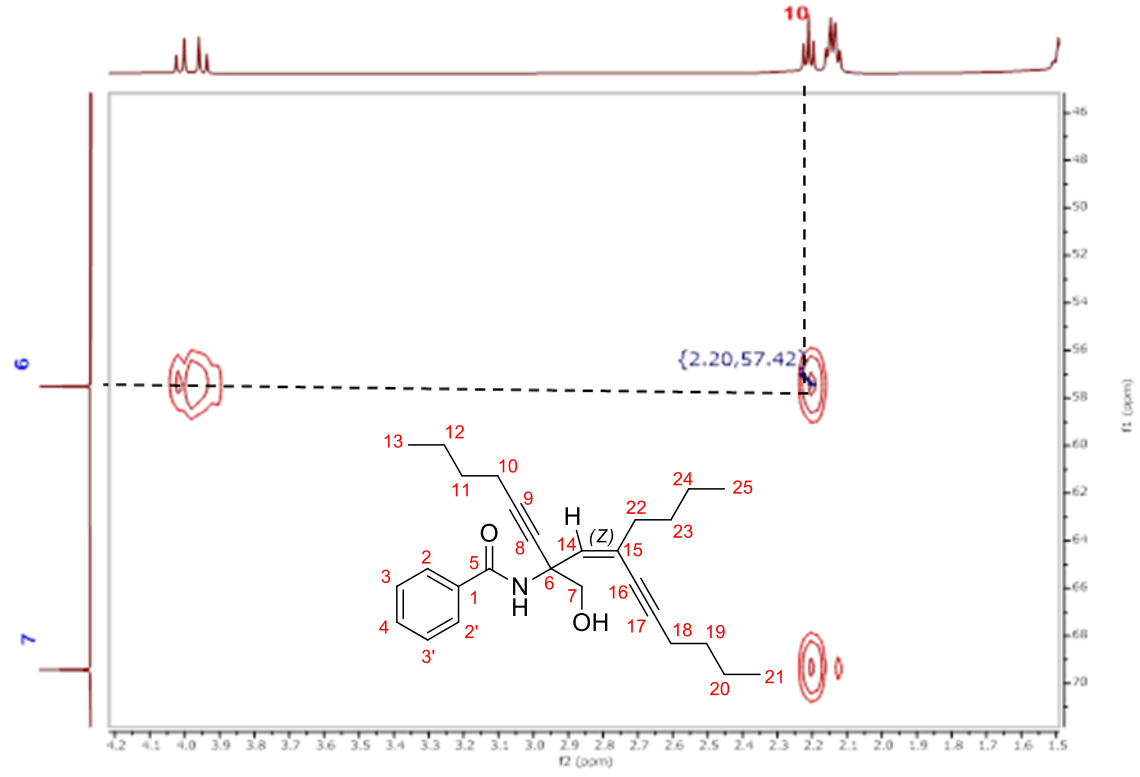


HMBC experiment

HMBC experiment shows a correlation between the quaternary carbon C6 and the multiplet at 2.24 ppm which corresponds to only one CH2 signal. C6 can only couple with H22 and H10 through a $^{4}J_{H,C}$ spin-spin correlation. Since H22 has already been assigned, the signal at 2.24 ppm is assigned to H10.

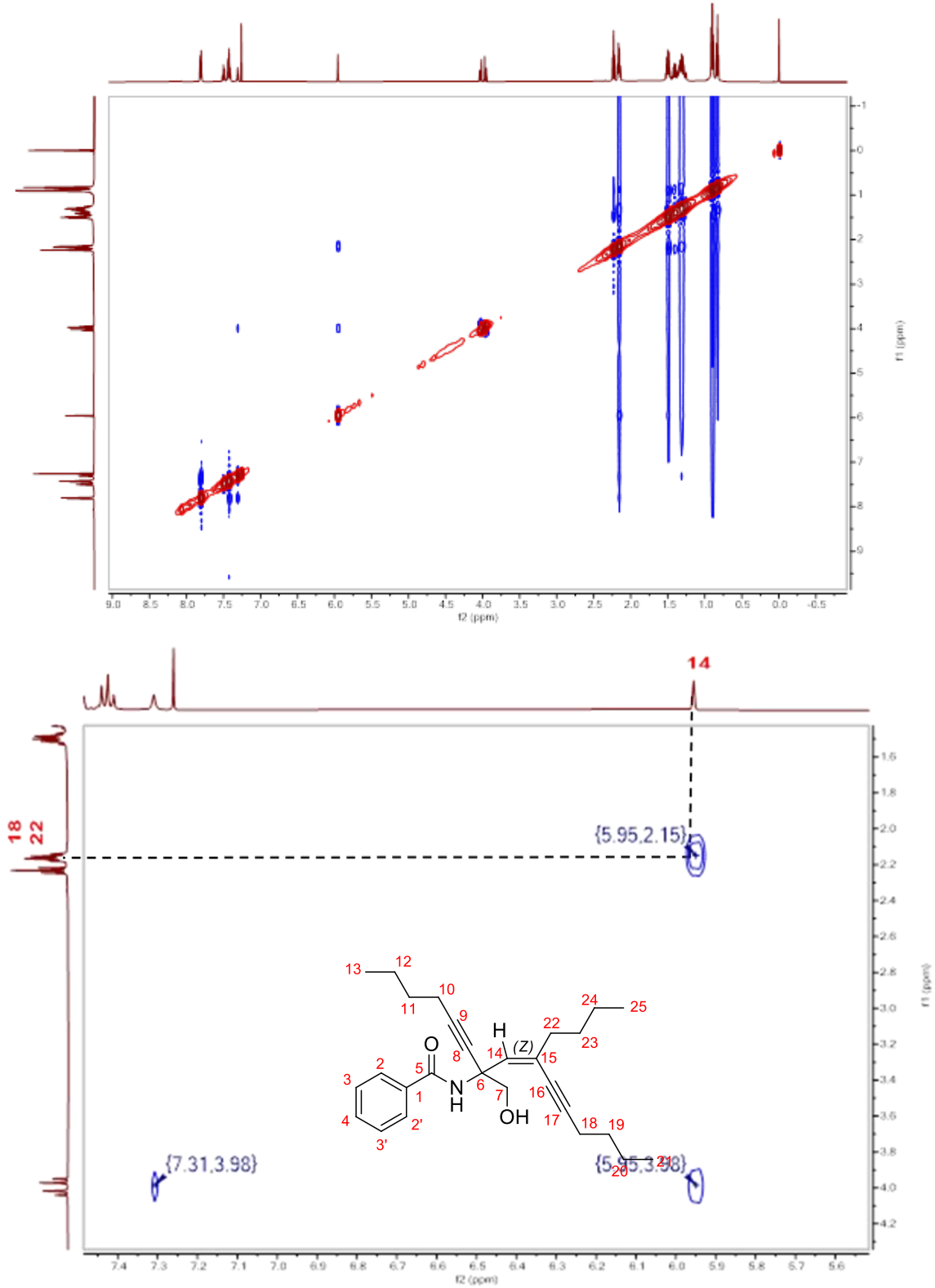
As a result, the other CH_2 signal present in the multiplet at 2.14 – 2.18 ppm is assigned to H18.



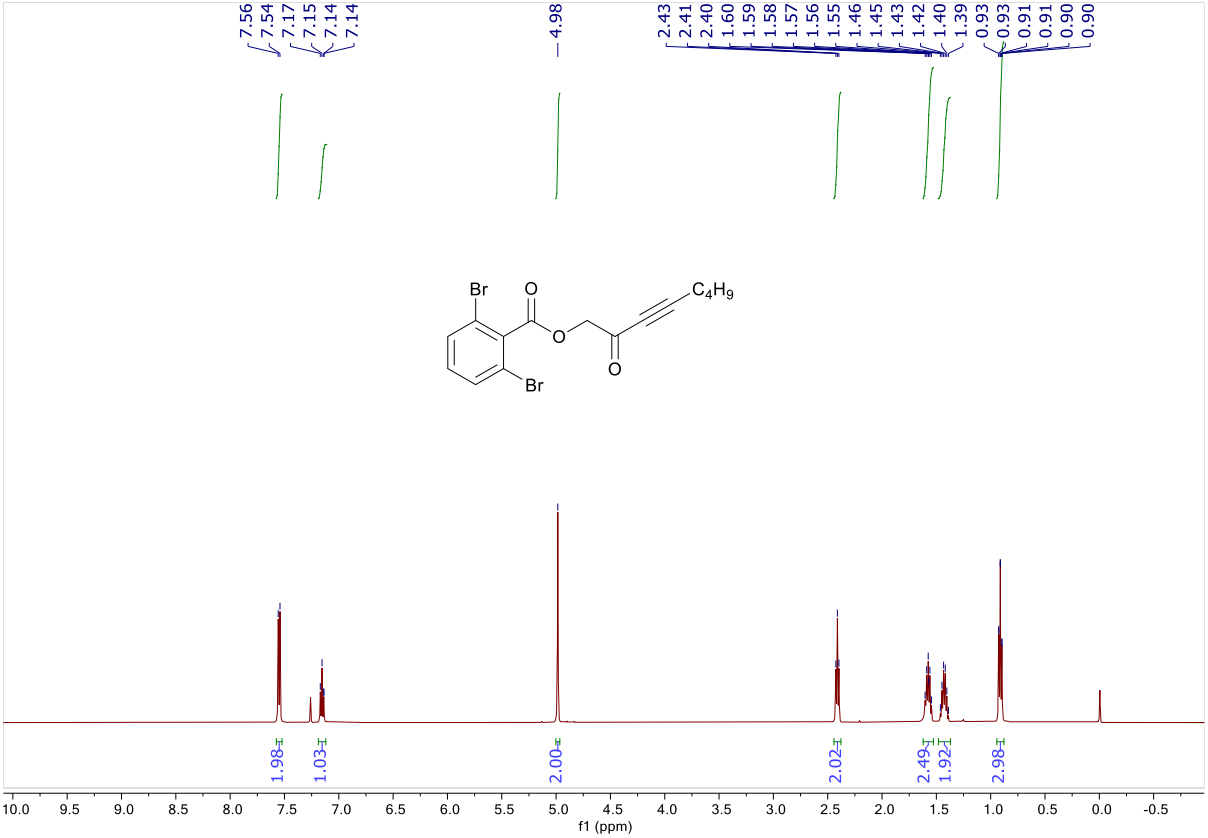


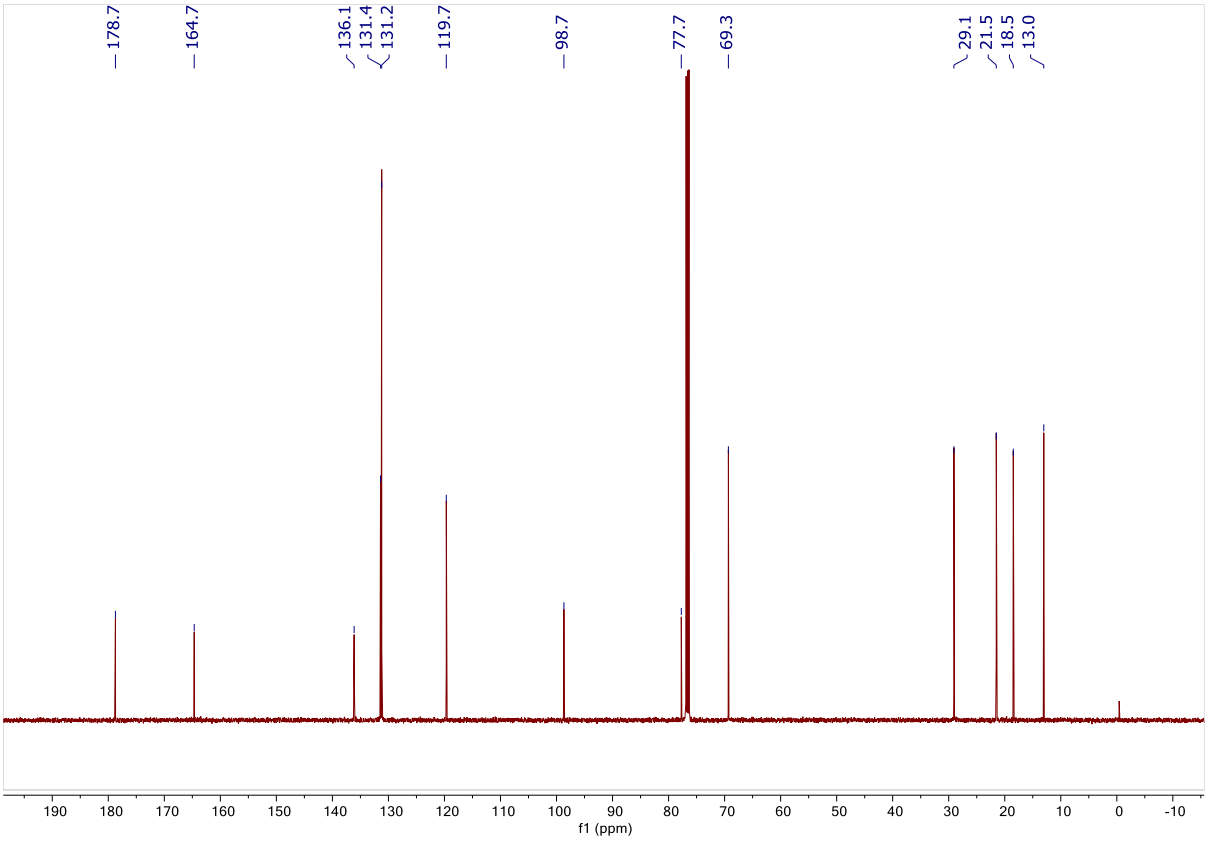
NOESY experiment

NOESY experiment shows through-*space* interaction between H14 and the multiplet at 2.18 – 2.14 which corresponds to H22 and H18. Due to the planar structure of the alkene moiety, H14 can only interact with H22 (H18 being too far). As a result, the configuration of the alkene function is assigned to *Z*.

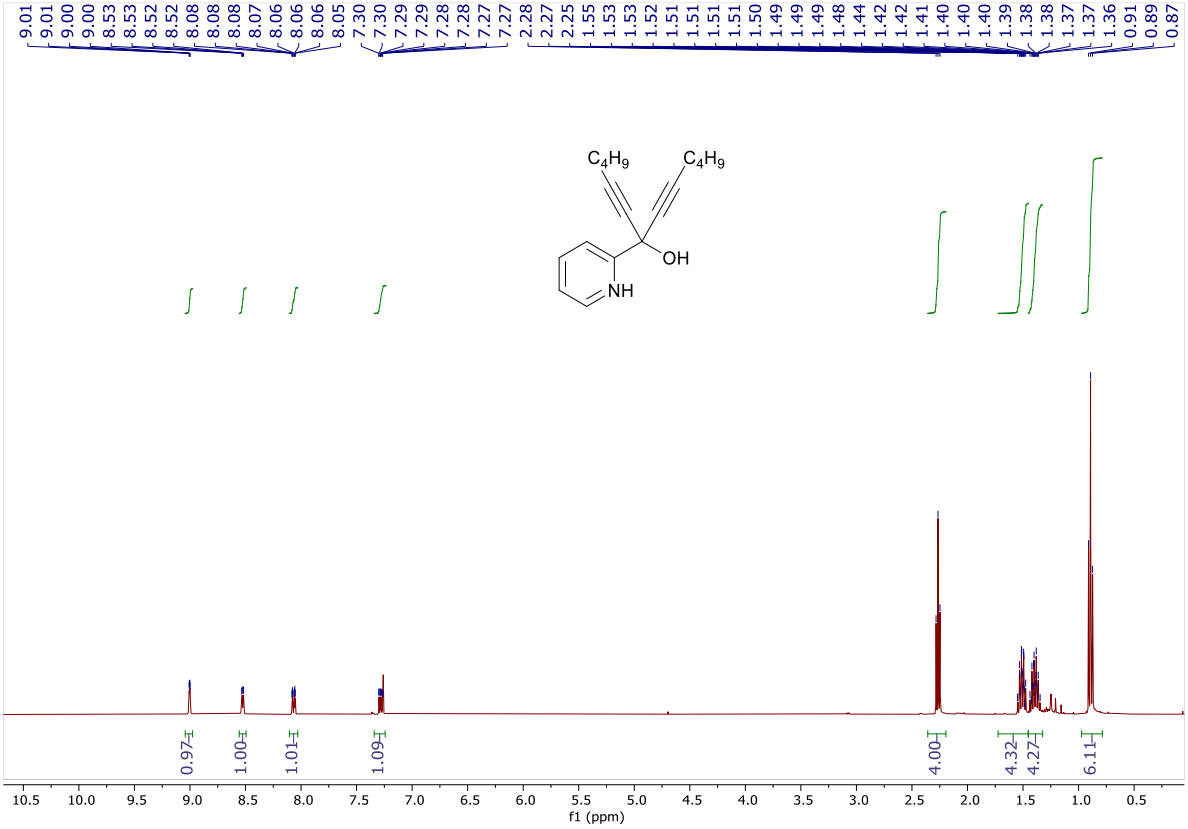


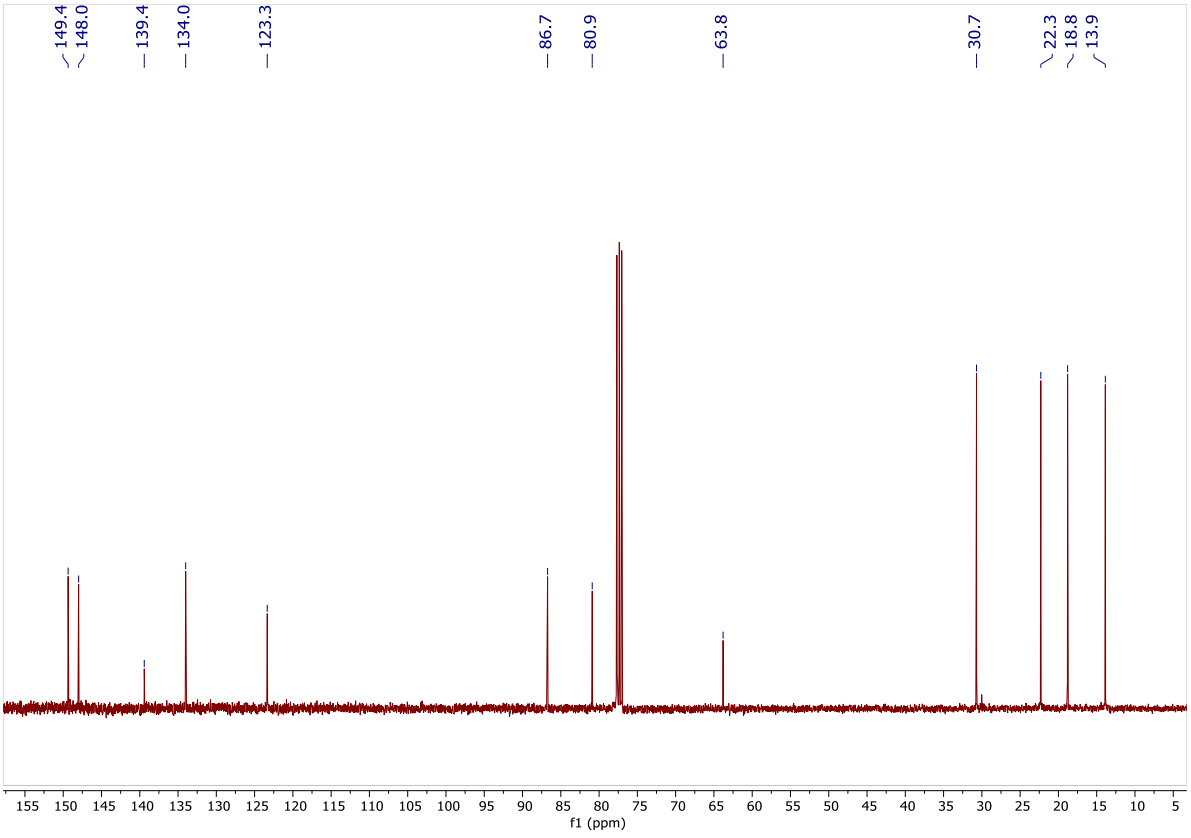
2-Oxooct-3-yn-1-yl 2,6-dibromobenzoate (7h)





7-(Pyridin-2-yl)trideca-5,8-diyn-7-ol (6k)





3-(9-Butyl-7-(hydroxymethyl)pentadeca-8-en-5,10-diyn-7-yl)-1,1-diphenylurea (8u)