Supporting Online Information.

Preparation of Conjugated 1,3-Eneynes using Rh(III) Catalysed Alkynylation of Alkenes via C-H activation

*Karl D. Collins, Fabian Lied, Frank Glorius**

Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut
Corrensstraße 40, 48149 Münster, Germany

1. General Experimental Details

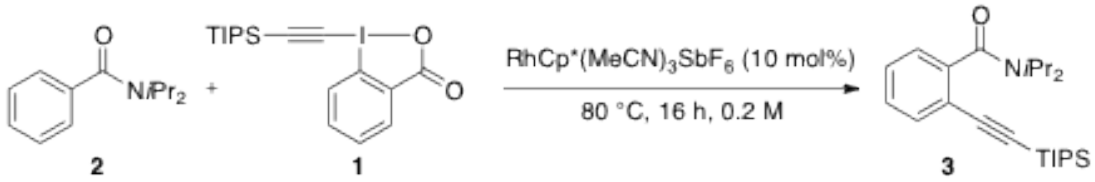
All rhodium (III) catalysed reactions were undertaken in oven dried (~80 °C) reaction vessels with Teflon screw caps under an atmosphere of air, using anhydrous solvents. The reaction is insensitive to atmospheric moisture, and oven drying was primarily for convenience. All commercial reagents were used as supplied.

Reaction solvents were dried using distillation over an appropriate drying agent or stored over molecular sieves from purchase: THF (Sodium), CH_2Cl_2 (CaH_2), DCE (molecular sieves). All solvents used for purification were distilled. Column chromatography was carried out using 40-63 mesh silica gel. Routine TLC analysis was carried out on aluminum sheets coated with silica gel 60 F254, 0.2 mm thickness. Plates were viewed using a 254 nm ultraviolet lamp or developed using $KMnO_4$.

NMR-spectra were recorded on a 300 or 400 MHz spectrometers with chemical shifts (δ) being reported in ppm relative to residual chloroform (^1H = 7.26 or ^{13}C = 77.2), Coupling constants (*J*) are quoted in Hertz (Hz). High-resolution mass spectra were obtained using ESI unless otherwise noted. Infra-red spectra were recorded neat using FT/IR spectrometers. GCMS retention times are quoted in minutes for the method "(50_40)": injection temperature 50°C, hold *T* for 3 min, ramp 40°C/min, final temperature 280 °C, hold *T* for 3 minutes.

2. Reaction optimization

2.1 Initial Screen



Tables show deviation from optimal reaction conditions: **2** (0.200 mmol), **1** (2.0 eq), $RhCp^*(MeCN)_3(SbF_6)_2$ (10 mol%), CH_2Cl_2 (1.5 mL), 80 °C, 16 h.

Solvent	GC yield %	Concentration	GC yield %	Eq **1**	GC yield %
DCE	42	0.2 M	49	2	57
MeOH	8	0.133 M	57	1.5	51
EtOH	2	0.4 M	20	1	36
DMF	5	Temperature	GC yield %		
Dioxane	20	80 °C (DCE)	42		
THF	13	60 °C (DCE)	5		
MeCN	11	Catalyst	GC yield %		
DCM	49	10 mol% (0.2 M)	51		
PhCl	28	5 mol% (0.2 M)	38		

2.2 Additive Screen

Whilst investigating the alkynylation of arene **2** we undertook an extensive screen of additives. All reactions were performed **under an atmosphere of air** using the reported conditions on a 0.03 mmol scale in a multiwall plate. Unfortunately all experiments were unsuccessful with regard to increasing the yield of alkynylated compound **3**. A list of additives screened is given below:

PIDA (0.5 eq)
TsOH (0.5 eq)
PIDA and TsOH (0.5 eq each)
AcOH (0.5 eq)
AuCl (0.1 eq)
TFA (1.2 eq)
AuCl (0.1 eq) and TFA (1.2 eq)
TIPSCl (1 eq)
LiCl (1 eq)
LiCl (2 eq)
Et_3N (1 eq)
DIPEA (1 eq)

DBU (1 eq)
2,5-*t*butylpyridine (1 eq)
LiCl (2 eq) and Et_3N (1 eq)
Ag_2O (1 eq)
Ag_2CO_3 (1 eq)
CuCl (1 eq)
AuCl (1 eq)
CuI (1 eq)
$CuCl_2$ (1 eq)
Li_2CO_3 (1 eq)
Na_2CO_3 (1 eq)
K_2CO_3 (1 eq)
NaOAc (1 eq)
KOAc (1 eq)
NaOH (1 eq)
NaOtBu (1 eq)
Tetramethylguanadine (1 eq)
Bu_4NOH (1 eq)
Bu_4POH (1 eq)
$ClCH_2COOH$ (1 eq)
Cl_3CCOOH (1 eq)
MsOH (1 eq)
TfOH (1 eq)
3,3-Dimethylbutanoic acid (1 eq)
$TiCl_4$ (1 eq)
$SnCl_2$ (1 eq)
$Zn(OAc)_2•2H_2O$ (1 eq)
Ni(OAc) $_2$•4H2O (1 eq)
$MgCl_2$ (1 eq)
$Cu(OH)_2$ (1 eq)
CsOAc (1 eq)
$Al(OTf)_3$ (1 eq)
$Zn(OTf)_2$ (1 eq)
$ZnCl_2$ (1 eq)
$Yb(OAc)_3•4H_2O$ (1 eq)
$Yb(OTf)_3$ (1 eq)
Cu(OAc) (1 eq)
$AgPF_6$ (1 eq)
$AgSbF_6$ (1 eq)
AgOAc (1 eq)
$Cu(OAc)_2$ (1 eq)

The following additives were screened on a 0.2 mmol scale:

PivOH (0.5 eq) and CsOPiv (0.2 eq)
PivOH (0.2 eq) and CsOPiv (0.5 eq)
PivOH (0.5 eq) and CsOPiv (0.5 eq)
PivOH (0.5 eq)
PivOH (1.0 eq)
CsOPiv (0.5 eq)

CsOPiv (1.0 eq)
TMSOTf (1 eq)
H_2O (10% v/v)

2.3 Re-optimization for substrate 4a

For substrate **4a** we were able to show that reaction proceeds equally well in DCE or DCM at 60 °C with 5 mol% catalyst loading. Unfortunately when these conditions were applied in the preparation of **5g** and **5i** the yields were 13% and 20% respectively (compared to 45% and 84% for the reported conditions), and hence these conditions were not explored any further. We also demonstrated that using 1.5 equivalents of **1** (81% yield) and a single equivalent (57% yield) was detrimental to the reaction.

3. Synthesis and Characterization Data

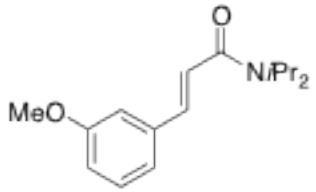
3.1 Substrate Preparation

Substrates previously reported by the Glorius group were prepared using the established procedures.[1,2]

General procedure for synthesis of cinnamic amide substrates

All reactions were carried out in oven-dried glassware, under an atmosphere of argon and using dried solvents.

To a solution of cinnamic acid (3.00 mmol, 1.00 eq) and *N,N*-dimethylformamide (346 μL, 4.50 mmol, 1.5 eq) in CH_2Cl_2 (6.0 mL) at 0 °C was added drop wise oxalylchloride (256 μL, 2.94 mmol, 0.98 eq). The solution was stirred at room temperature for 4 h prior to the addition of diisopropylamine (953 μL, 6.75 mmol, 2.25 eq) as a solution in CH_2Cl_2 (13.5 mL) in one portion. The resulting mixture was stirred for at least 2 h (monitor by TLC) at room temperature and then filtered through a short plug of silica. The organic phase was washed with aqueous NaOH (2N, 20 mL), aqueous HCl (1N, 20 mL) and saturated aqueous NaCl (20 mL), dried ($MgSO_4$), concentrated *in vacuo* then and purified.

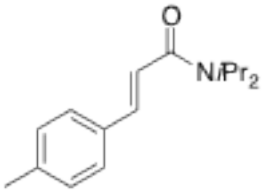


(*E*)-*N*,*N*-Diisopropyl-3-(3-methoxyphenyl)acrylamide I

Reaction of (*E*)-3-(3-methoxyphenyl)acrylic acid (535 mg, 3.00 mmol, 1.0 eq) following purification on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **I** (115 mg, 0.440 mmol, 15%) as a white solid. Note: Actual yield is much higher; material was lost due to experimental error.

[1] N. Kuhl, N. Schröder and F. Glorius, *Org. Lett.* 2013, **15**, 3860.
[2] N. Schröder, J. Wencel-Delord and F. Glorius, *J. Am. Chem. Soc.* 2012, **134**, 8298.

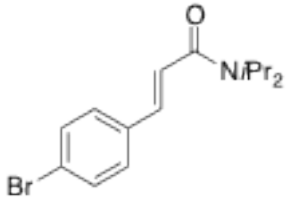
R_f (20% EtOAc in pentane) = 0.22; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (br.s, 12H, 4 × CHCH_3), 3.79 (s, 3H, CH_3), 3.81 (br.s, 1H, NCH), 4.08 (br.s, 1H, NCH), 6.79 (d, *J* = 15.5 Hz, 1H, CH), 6.82-6.87 (m, 1H, ArH), 6.97-7.01 (m, 1H, ArH), 7.07 (d, *J* = 7.7 Hz, 1H, ArH), 7.25 (t, *J* = 7.9 Hz, 1H, ArH), 7.52 (d, *J* = 15.5 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 21.6, 45.9, 48.0, 55.3, 113.1, 114.5, 120.1, 121.0, 129.7, 137.1, 140.7, 159.8, 166.1; υ_{max} (neat)/ cm^{-1}: 2967, 2942, 2864, 1645, 1595, 1443, 1393, 1369, 1339, 1269, 1211, 1153, 1132, 1121, 1045, 978, 882, 853, 770, 702, 681; GC-MS (EI): t_R (50_40): 9.6 min; *m/z* (%): 161 (100); *m/z* (ESI): Found (M + H), 262.1802. $C_{16}H_{23}NO_2H$ requires *M*, 262.1807.



(*E*)-*N,N*-Diisopropyl-3-(*p*-tolyl)acrylamide II

Reaction of (*E*)-3-(*p*-tolyl)acrylic acid (489 mg, 3.00 mmol, 1.0 eq) following purification on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **II** (495 mg, 2.02 mmol, 67%) as a white solid.

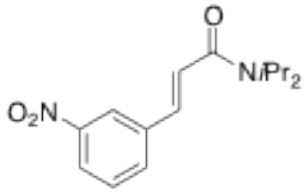
R_f (20% EtOAc in pentane) = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (br.s, 12H, 4 × CHCH_3), 2.35 (s, 3H, CH_3), 3.85 (br.s, 1H, NCH), 4.10 (br.s, 1H, NCH), 6.78 (d, *J* = 15.4 Hz, 1H, CH), 7.15 (d, *J* = 8.1 Hz, 2H, 2 × ArH), 7.39 (d, *J* = 8.1 Hz, 2H, 2 × ArH), 7.56 (d, *J* = 15.4 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 21.4, 21.7, 45.9, 47.9, 119.5, 127.5, 129.4, 132.9, 139.4, 140.9, 166.3; υ_{max} (neat)/ cm^{-1}: 2967, 1645, 1601, 1514, 1437, 1370, 1333, 1260, 1209, 1150, 1130, 1044, 11360, 808, 729, 611; GC-MS (EI): t_R (50_40): 9.2 min; *m/z* (%): 145 (100); *m/z* (ESI): Found (M + H), 246.1852. $C_{16}H_{23}NOH$ requires *M*, 246.1858.



(*E*)-3-(4-Bromophenyl)-*N,N*-diisopropylacrylamide III

Reaction of (*E*)-3-(4-bromophenyl)acrylic acid (681 mg, 3.00 mmol, 1.00 eq) following purification on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **III** (592 mg, 1.91 mmol, 64%) as a white solid.

R_f (20% EtOAc in pentane) = 0.31; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (br.s, 6H, 2 × CHCH_3), 1.38 (br.s, 6H, 2 × CHCH_3), 3.83 (br.s, 1H, NCH), 4.08 (br.s, 1H, NCH), 6.81 (d, *J* = 15.5 Hz, 1H, CH), 7.35 (d, *J* = 8.5 Hz, 2H, 2 × ArH), 7.43-7.56 (m, 3H, 2 × ArH, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 21.7, 45.9, 48.1, 121.3, 123.2, 129.0, 131.9, 134.6, 139.6, 165.8; υ_{max} (neat)/ cm^{-1}: 2969, 2930, 1643, 1601, 1474, 1456, 1437, 1397, 1370, 1333, 1254, 1206, 1152, 1132, 1071, 1044, 814, 768, 723, 606; GC-MS (EI): t_R (50_40): 9.7 min; *m/z* (%): 211 (99), 209 (100), 102 (57), 86 (27); *m/z* (ESI): Found (M + Na), 332.0620. $C_{15}H_{20}BrNONa$ requires *M*, 332.0626.

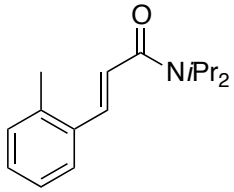


(*E*)-*N,N*-Diisopropyl-3-(3-nitrophenyl)acrylamide IV

Reaction of (*E*)-3-(3-nitrophenyl)acrylic acid (579 mg, 3.00 mmol, 1.00 eq) following purification on silica gel using automated MPLC and eluting with a gradient of 7-60% EtOAc in pentane gave **IV** (493 mg, 1.78 mmol, 59%) as a white solid.

R_f (20% EtOAc in pentane) = 0.14; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (br.s, 6H, 2 × CHCH_3), 1.40 (br.s, 6H, 2 × CHCH_3), 3.78 (br.s, 1H, NCH), 4.13 (br.s, 1H, NCH), 6.95 (d, *J* = 15.5 Hz, 1H, CH), 7.49-7.63 (m, 2H, ArH, CH), 7.75 (d, *J* = 7.8 Hz, 1H, ArH), 8.15 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H, ArH), 8.34 (t, *J* = 2.0 Hz, 1H, ArH); ^{13}C

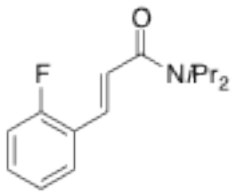
NMR (75 MHz, $CDCl_3$) δ 20.6, 21.6, 46.1, 48.5, 121.4, 123.6, 123.7, 129.8, 133.8, 137.4, 138.2, 148.6, 165.1; υ_{max} (neat)/ cm^{-1}: 2967, 1645, 1607, 1526, 1474, 1447, 1437, 1370, 1339, 1258, 1213, 1155, 1136, 1096, 1045, 990, 922, 907, 835, 808, 737, 702, 675, 667, 617; GC-MS (EI): t_R (50_40): 10.1 min; *m/z* (%): 176 (100), 102 (46), 86 (58); *m/z* (ESI): Found (M + H), 277.1547. $C_{15}H_{20}N_2O_3H$ requires *M*, 277.1552.



(*E*)-*N,N*-Diisopropyl-3-(*o*-tolyl)acrylamide V

Reaction of (*E*)-3-(*o*-tolyl)acrylic acid (487 mg, 3.00 mmol, 1.00 eq) following purification on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **V** (439 mg, 1.79 mmol, 60%) as a white solid.

R_f (20% EtOAc in pentane) = 0.37; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (br.s, 6H, 2 × CHC*H*$_3$), 1.39 (br.s, 6H, 2 × CHC*H*$_3$), 2.42 (s, 3H, CH_3), 3.86 (br.s, 1H, NCH), 4.11 (br.s, 1H, NCH), 6.74 (d, *J* = 15.3 Hz, 1H, CH), 7.14-7.27 (m, 3H, 3 × ArH), 7.51 (d, *J* = 7.4 Hz, 1H, ArH), 7.85 (d, *J* = 15.3 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 20.7, 21.6, 45.9, 48.0, 121.9, 125.9, 126.1, 129.0, 130.6, 134.8, 137.3, 138.6, 166.2; υ_{max} (neat)/ cm^{-1}: 2969, 1643, 1605, 1437, 1370, 1333, 1292, 1252, 1207, 1152, 1126, 1044, 974, 903, 851, 762, 731, 615; GC-MS (EI): t_R (50_40): 9.8 min; *m/z* (%): 230 (33), 145 (100), 115 (37); *m/z* (ESI): Found (M + H), 246.1852. $C_{16}H_{23}NOH$ requires *M*, 246.1858.

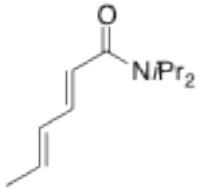


(*E*)-3-(2-Fluorophenyl)-*N,N*-diisopropylacrylamide VI

Reaction of (*E*)-3-(2-fluorophenyl)acrylic acid (498 mg, 3.00 mmol, 1.00 eq following purification on silica gel using automated MPLC and eluting with a

gradient of 5-20% EtOAc in pentane gave **VI** (331 mg, 1.33 mmol, 44%) as a colorless oil.

R_f (20% EtOAc in pentane) = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (br.s, 6H, 2 × CHC*H*$_3$), 1.36 (br.s, 6H, 2 × CHC*H*$_3$), 3.88 (br.s, 1H, NCH), 4.07 (br.s, 1H, NCH), 6.97 (d, *J* = 15.7 Hz, 1H, CH), 7.01-7.16 (m, 2H, 2 × ArH), 7.27 (tdd, *J* = 7.5, 5.2, 1.8 Hz, 1H, ArH), 7.47 (td, *J* = 7.6, 1.8 Hz, 1H, ArH), 7.62 (d, *J* = 15.7 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 21.7, 45.9, 48.0, 116.0 (d, *J* = 22 Hz), 123.8 (d, *J* = 8 Hz), 124.3 (d, *J* = 4 Hz), 129.6 (d, *J* = 4 Hz), 130.4 (d, *J* = 9 Hz), 133.8 (d, *J* = 1 Hz), 159.5, 162.8, 166.1; υ_{max} (neat)/ cm^{-1}: 2969, 1645, 1601, 1489, 1456, 1437, 1371, 1333, 1287, 1211, 1152, 1132, 1045, 976, 818, 758, 615; GC-MS (EI): t_R (50_40): 8.9 min; *m/z* (%): 249 (25), 149 (100), 101 (26); *m/z* (ESI): Found (M + H), 250.1602. $C_{15}H_{20}FNOH$ requires *M*, 250.1607.

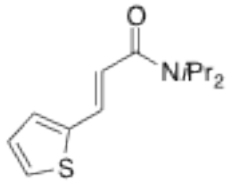


(2*E*,4*E*)-*N*,*N*-Diisopropylhexa-2,4-dienamide VII

Reaction of (2*E*,4*E*)-hexa-2,4-dienoic acid following purification on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **VII** (314 mg, 1.61 mmol, 54%) as a yellow oil.

R_f (20% EtOAc in pentane) = 0.31; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (br.s, 12H, 4 × CHC*H*$_3$), 1.76 (d, *J* = 6.73 Hz, 3H, CH_3), 3.74 (br.s, 1H, NCH), 3.95 (br.s, 1H, NCH), 5.88-6.06 (m, 1H, CH), 6.07-6.23 (m, 2H, 2 × CH), 7.12 (dd, *J* = 14.7, 10.8 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 20.6, 21.3, 45.5, 47.7, 121.1, 130.25, 136.2, 141.3, 166.3. Data is consistent with the literature.[3]

[3] L. Ferrie and J. Cossy, J. *Organomet. Chem.* 2006, **691**, 5456.



(*E*)-*N,N*-Diisopropyl-3-(thiophen-2-yl)acrylamide VIII

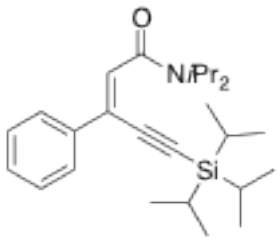
Reaction of (*E*)-3-(thiophen-2-yl)acrylic acid (463 mg, 3.00 mmol, 1.00 eq) following purification on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **VIII** (340 mg, 1.43 mmol, 48%) as a pale yellow solid.

R_f (20% EtOAc in pentane) = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (br.s, 12H, 4 × CHCH_3), 3.85 (br.s, 1H, NCH), 4.02 (br.s, 1H, NCH), 6.51 (d, *J* = 15.1 Hz, 1H, CH), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H, ArH), 7.13 (d, *J* = 3.6 Hz, 1H, ArH), 7.24 (d, *J* = 5.1 Hz, 1H, ArH), 7.69 (d, *J* = 15.1 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 21.6, 45.8, 47.7, 119.3, 126.6, 127.8, 129.5, 133.7, 140.7, 165.5. Data is consistent with the literature.[2]

3.2 Catalysis Reactions

General procedure for the alkynylation of alkenes and arenes

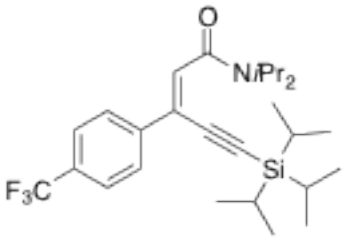
To a solution of cinnamic amide or benzamide (0.200 mmol, 1.0 eq) and RhCp*$(MeCN)_3(SbF_6)_2$ (17 mg, 10 mol%) in DCM (1.5 mL) was added TIPS-EBX **1** (171 mg, 0.400 mmol, 2.0 eq) and the reaction stirred for 16 h at 80 °C. After cooling, the reaction was filtered through a short plug of silica and then purified. **Note:** Reactions should be heated directly after the addition of **1** or a decrease in yield is observed.



(*Z*)-*N*,*N*-Diisopropyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 5a

The reaction of *N*,*N*-diisopropylcinnamamide (0.200 mmol, 46 mg, 1.0 eq) following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **5a** (77 mg, 0.188 mmol, 94 %) as a white solid.

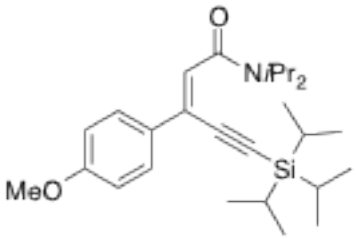
R_f (10% EtOAc in pentane) = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 21H, TIPS), 1.21 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.47 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 3.56 (dt, *J* = 13.2, 7.0 Hz, 1H, NCH), 4.10 (dt, *J* = 13.6, 7.0 Hz, 1H, NCH), 6.62 (s, 1H, CH), 7.28-7.42 (m, 3H, 3 × ArH), 7.65-7.73 (m, 2H, 2 × ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4, 18.7, 20.6, 21.2, 45.6, 50.3, 99.0, 102.6, 126.1, 126.3, 128.4, 128.5, 130.2, 137.0, 166.5; υ_{max} (neat)/ cm^{-1}: 2942, 2864, 1630, 1495, 1449, 1435, 1370, 1341, 1316, 1213, 1155, 1136, 1049, 1038, 1024, 997, 882, 762, 750, 692, 677, 631; GC-MS (EI): t_R (50_40): 11.5 min; *m/z* (%): 369 (54), 368 (100), 327 (30), 326 (95), 284 (30); *m/z* (ESI): Found (M + H), 412.3030. $C_{26}H_{41}NOSiH$ requires *M*, 412.3036.



(*Z*)-*N*,*N*-Diisopropyl-3-(4-(trifluoromethyl)phenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5b

The reaction of (*E*)-*N*,*N*-diisopropyl-3-(4-(trifluoromethyl)phenyl)acrylamide (0.200 mmol, 46 mg, 1.0 eq) following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **5b** (85 mg, 0.178 mmol, 89%) as a white solid.

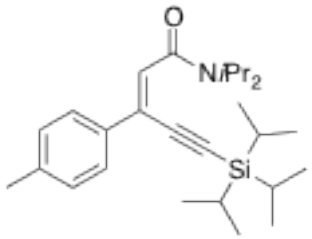
R_f (10% EtOAc in pentane) = 0.21; 1H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 21H, TIPS), 1.22 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.48 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 3.57 (p, *J* = 6.9 Hz, 1H, NCH), 4.05 (p, *J* = 6.6 Hz, 1H, NCH), 6.78 (s, 1H, C=CH), 7.62 (d, *J* = 8.3 Hz, 2H, 2 × ArH), 7.79 (d, *J* = 8.2 Hz, 2H, 2 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.5, 18.8, 20.7, 21.4, 45.9, 50.5, 100.2, 102.0, 124.6 (q, *J* = 272 Hz) 125.0, 125.4 (q, *J* = 3.8 Hz), 126.7, 130.4 (q, *J* = 33 Hz), 131.9, 140.5 (d, *J* = 2 Hz), 166.0; υ_{max} (neat)/ cm^{-1}: 2943, 2866, 1620, 1442, 1319, 1115, 1070; GC-MS (EI): t_R (50_40): 6.2 min; *m/z* (%): 436 (100), 394 (95), 352 (56) 303 (63); *m/z* (ESI): Found (M + H), 480.2904. $C_{27}H_{41}F_3NOSi$ requires *M*, 480.2910.



(*Z*)-*N*,*N*-Diisopropyl-3-(4-methoxyphenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5c

The reaction of (*E*)-*N*,*N*-diisopropyl-3-(4-methoxyphenyl)acrylamide (0.200 mmol, 52 mg, 1.0 eq) following column chromatography on silica gel, eluting with 15% EtOAc in pentane gave **5c** (79 mg, 0.180 mmol, 90 %) as a white solid.

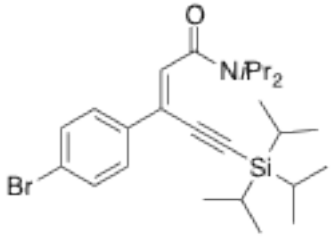
R_f (25% EtOAc in pentane) = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 21H, TIPS), 1.21 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.47 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 3.56 (p, *J* = 6.9 Hz, 1H, NCH), 3.83 (s, 3H, OMe), 4.01 – 4.23 (m, 1H, NCH), 6.61 (s, 1H, C=CH), 6.89 (d, *J* = 8.9 Hz, 2H, 2 × ArH), 7.62 (d, *J* = 8.9 Hz, 2H, 2 × ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.5, 18.9, 20.7, 21.4, 45.7, 50.3, 55.5, 98.8, 103.0, 113.9, 125.7, 127.7, 128.6, 129.7, 160.1, 166.9; υ_{max} (neat)/ cm^{-1}: 2941, 2864, 1622, 1508, 1437, 1246, 1182, 1024, 883; GC-MS was uninformative; *m/z* (ESI): Found (M + H), 442.3136. $C_{27}H_{44}NO_2Si$ requires *M*, 442.3141.



(*Z*)-*N*,*N*-Diisopropyl-3-(*p*-tolyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5d

The reaction of (*E*)-*N*,*N*-diisopropyl-3-(*p*-tolyl)acrylamide (0.200 mmol, 49 mg, 1.0 eq) following column chromatography on silica gel, eluting with 7.5% EtOAc in pentane gave **5d** (69 mg, 0.162 mmol, 81 %) as a brown oil.

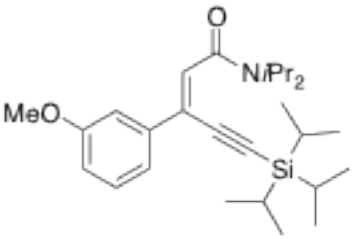
R_f (10% EtOAc in pentane) = 0.52; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 – 1.17 (m, 21H, TIPS), 1.21 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.47 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 2.36 (s, 3H, CH_3), 3.56 (p, *J* = 6.7 Hz, 1H, NCH), 4.02 – 4.21 (m, 1H, NCH), 6.68 (s, 1H, C=CH), 7.17 (d, *J* = 8.0 Hz, 2H, 2 × ArH), 7.58 (d, *J* = 8.1 Hz, 2H, 2 × ArH). ^{13}C NMR (101 MHz, CDCl3) δ 11.4, 18.7, 20.6, 21.2, 45.6, 50.2, 98.7, 102.8, 125.9, 126.2, 129.1, 129.4, 134.1, 138.5, 166.7; υ_{max} (neat)/ cm^{-1}: 2941, 2864, 1627, 1437, 1339, 882, 814; GC-MS (EI): t_R (50_40): 12.1 min; *m/z* (%): 383 (50), 382 (100), 368 (57), 340 (79), 207 (66); *m/z* (ESI): Found (M + H), 426.3187. $C_{27}H_{44}NOSi$ requires *M*, 426.3192.



(*Z*)-3-(4-Bromophenyl)-*N*,*N*-diisopropyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 5e

The reaction of (*E*)-3-(4-bromophenyl)-*N*,*N*-diisopropylacrylamide (0.200 mmol, 62 mg, 1.0 eq) following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **5e** (64 mg, 0.130 mmol, 65 %) as a white solid.

R_f (10% EtOAc in pentane) = 0.18; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 21H, TIPS), 1.21 (d, *J* = 6.7 Hz, 6H, 2 × CHCH_3), 1.46 (d, *J* = 6.8 Hz, 6H, 2 × CHCH_3), 3.55 (p, *J* = 6.8 Hz, 1H, NCH), 3.91 – 4.25 (m, 1H, NCH), 6.69 (s, 1H, C=CH), 7.39 – 7.68 (m, 4H, 4 × ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.5, 18.8, 20.7, 21.4, 45.8, 50.4, 99.7, 102.2, 122.8, 125.2, 128.0, 130.7, 131.7, 136.2, 166.3; υ_{max} (neat)/ cm^{-1}: 2943, 2864, 1624, 1339, 1007, 839; GC-MS was uninformative; *m/z* (ESI): Found (M + H), 490.2116. $C_{26}H_{41}BrNOSi$ requires *M*, 490.2141.

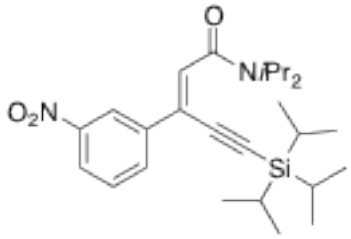


(*Z*)-*N*,*N*-Diisopropyl-3-(3-methoxyphenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5f

The reaction of (*E*)-3-(4-bromophenyl)-*N*,*N*-diisopropylacrylamide (0.200 mmol, 52 mg, 1.0 eq) following column chromatography on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **5f** (81 mg, 0.184 mmol, 92%) as a white solid.

R_f (10% EtOAc in pentane) = 0.13; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 21H, TIPS), 1.22 (d, *J* = 6.7 Hz, 6H, 2 × CHCH_3), 1.48 (d, *J* = 6.8 Hz, 6H, 2 × CHCH_3),

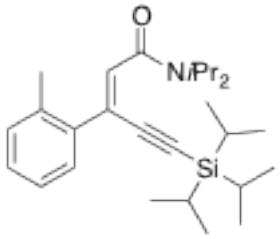
3.56 (p, J = 6.8 Hz, 1H, NCH), 3.82 (s, 3H, CH_3), 4.10 (p, J = 6.7 Hz, 1H, NCH), 6.72 (s, 1H, CH), 6.83-6.93 (m, 1H, ArH), 7.24-7.29 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4, 18.7, 20.6, 21.2, 45.6, 50.2, 55.3, 98.9, 102.6, 111.8, 114.6, 118.5, 125.9, 129.3, 130.6, 138.6, 159.6, 166.4; υ_{max} (neat)/ cm^{-1}: 2965, 2942, 1864, 1628, 1597, 1578, 1489, 1437, 1370, 1339, 1287, 1261, 1204, 1136, 1047, 1034, 995, 883, 783, 723, 677, 660, 633; GC-MS (EI): t_R (50_40): 12.9 min; *m/z* (%): 399 (54), 398 (100), 356 (45); *m/z* (ESI): Found (M + H), 442.3136. $C_{27}H_{43}NO_2SiH$ requires M, 442.3141.



(*Z*)-*N*,*N*-Diisopropyl-3-(3-nitrophenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5g

The reaction of (*E*)-*N*,*N*-diisopropyl-3-(3-nitrophenyl)acrylamide (0.200 mmol, 46 mg, 1.0 eq) following column chromatography on silica gel, eluting with 20% EtOAc in pentane gave **5g** (41 mg, 0.09 mmol, 45 %) as an orange solid.

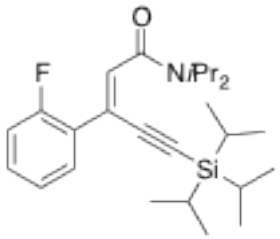
R_f (pentane) = 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 21H, TIPS), 1.24 (d, J = 6.7 Hz, 6H, 2 × CHCH_3), 1.49 (d, J = 6.8 Hz, 6H, 2 × CHCH_3), 3.56 (p, J = 6.8 Hz, 1H, NCH), 4.06 (p, J = 6.8 Hz, 1H, NCH), 6.84 (s, 1H, C=CH), 7.55 (t, J = 8.0 Hz, 1H, ArH), 7.99 (ddd, J = 7.9, 1.9, 1.0 Hz, 1H, ArH), 8.18 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H, ArH), 8.59 (t, J = 2.0 Hz, 1H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.5, 18.8, 20.6, 21.4, 45.9, 50.6, 101.0, 101.6, 121.7, 123.3, 124.1, 129.5, 139.0, 148.6, 165.7; υ_{max} (neat)/ cm^{-1}: 2943, 2866, 1620, 1531, 1342, 883; GC-MS was uninformative; *m/z* (ESI): Found (M + Na), 457.2878. $C_{26}H_{41}N_2O_3Si$ requires M, 457.2886.



(*Z*)-*N*,*N*-Diisopropyl-3-(*o*-tolyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5h

The reaction of (*E*)-*N*,*N*-diisopropyl-3-(*o*-tolyl)acrylamide (0.200 mmol, 50 mg, 1.0 eq) following column chromatography on silica gel, eluting with 5% EtOAc in pentane gave **5h** (32 mg, 0.076 mmol, 38 %) as an orange oil white solid.

R_f (10% EtOAc in pentane) = 0.32; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (s, 21H, TIPS), 1.24 (d, *J* = 6.8 Hz, 6H, 2 × CHCH_3), 1.48 (d, *J* = 6.8 Hz, 6H, 2 × CHCH_3), 2.47 (s, 3H, CH_3), 3.41 – 3.65 (m, 1H, NCH), 4.19 (p, *J* = 6.8 Hz, 1H, NCH), 6.29 (s, 1H, C=CH), 7.10 – 7.24 (m, 3H, 3 × ArH), 7.27 – 7.33 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.3, 18.6, 20.3, 20.6, 21.2, 45.6, 50.3, 99.1, 103.1, 125.9, 126.8, 127.9, 128.7, 130.4, 134.9, 135.7, 138.8, 166.1; υ_{max} (neat)/ cm^{-1}: 2924, 2864, 1805, 1699, 1205, 976; GC-MS (EI): t_R (50_40): 11.2 min; *m/z* (%): 268 (100); *m/z* (ESI): Found (M + H), 426.3187. $C_{27}H_{44}NOSi$ requires *M*, 426.3192.

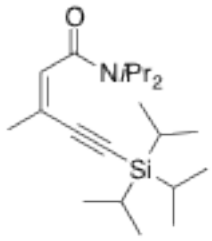


(*Z*)-3-(2-Fluorophenyl)-*N*,*N*-diisopropyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 5i

The reaction of (*E*)-3-(2-fluorophenyl)-*N*,*N*-diisopropylacrylamide (0.200 mmol, 46 mg, 1.0 eq) following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **5i** (77 mg, 0.188 mmol, 94 %) as an orange oil.

R_f (5% EtOAc in pentane) = 0.16; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 21H, TIPS), 1.23 (d, *J* = 6.7 Hz, 6H, 2 × CH_2CH_3), 1.47 (d, *J* = 6.8 Hz, 6H, 2 × CH_2CH_3), 3.57 (p, *J* = 6.8 Hz, 1H, NCH), 4.16 (p, *J* = 6.7 Hz, 1H, NCH), 6.84 (s, 1H, C=CH), 7.07 (ddd,

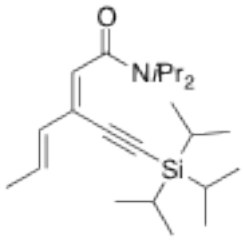
J = 11.7, 8.2, 1.3 Hz, 1H, ArH), 7.15 (td, *J* = 7.6, 1.3 Hz, 1H, ArH), 7.23 – 7.31 (m, 1H, ArH), 7.73 (td, *J* = 7.9, 1.8 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.4, 18.7, 20.6, 21.2, 45.5, 50.1, 97.9, 102.7, 116.1 (d, *J* = 23.1 Hz), 120.5, 124.0 (d, *J* = 3.6 Hz), 129.6 (d, *J* = 8.8 Hz), 130.8, 135.5 (d, *J* = 10.2 Hz), 166.3; υ_{max} (neat)/ cm^{-1}: 2943, 2864, 1634, 1437, 1340, 1213, 881, 758; GC-MS (EI): t_R (50_40): 11.2 min; *m/z* (%): 386 (69), 344 (48), 302 (79), 297 (100); *m/z* (ESI): Found (M + H), 430.2936. $C_{26}H_{41}FNOSi$ requires *M*, 430.2941.



(*Z*)-*N*,*N*-Diisopropyl-3-methyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 6

The reaction of (*E*)-*N*,*N*-diisopropylbut-2-enamide (0.200 mmol, 34 mg, 1.0 eq) following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **5i** (18 mg, 0.052 mmol, 26 %) yellow oil

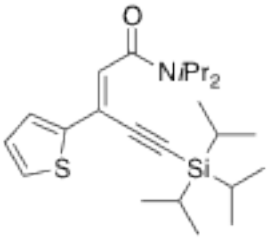
R_f (5% EtOAc in pentane) = 0.19; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (s, 21H, TIPS), 1.18 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.41 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 1.95 (d, *J* = 1.5 Hz, 3H, CH_3), 3.48 (p, *J* = 6.7 Hz, 1H, NCH), 4.07 (p, *J* = 6.8 Hz, 1H, NCH), 6.06 (q, *J* = 1.5 Hz, 1H, C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4, 18.8, 20.7, 21.3, 24.3, 45.6, 50.2, 96.5, 105.2, 122.5, 131.4, 166.8; υ_{max} (neat)/ cm^{-1}: 1712, 1622, 1608, 1510, 1441, 1339, 1219, 1033, 829; GC-MS (EI): t_R (50_40): 9.5 min; *m/z* (%): 306 (39), 264 (100), 222 (51), 207 (55); *m/z* (ESI): Found (M + H), 350.2874. $C_{21}H_{40}NOSi$ requires *M*, 350.2879.



(2*Z*,4*E*)-*N*,*N*-Diisopropyl-3-((triisopropylsilyl)ethynyl)hexa-2,4-dienamide 7

The reaction of (2*E*,4*E*)-*N*,*N*-diisopropylhexa-2,4-dienamide (0.200 mmol, 39 mg, 1.0 eq) following column chromatography on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **7** (45 mg, 0.119 mmol, 60%) as a white solid.

R_f (10% EtOAc in pentane) = 0.22; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 21H, TIPS), 1.17 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.42 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 1.82 (dd, *J* = 6.9, 1.1 Hz, 3H, CH_3), 3.49 (p, *J* = 6.8 Hz, 1H, NCH), 4.03 (p, *J* = 6.6 Hz, 1H, NCH), 6.00 (dd, *J* = 15.0, 1.8 Hz, 1H, CH), 6.09 (s, 1H, CH), 6.27 (dq, *J* = 15.0, 6.9 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.3, 18.0, 18.7, 20.5, 21.1, 45.4, 50.1, 98.3, 100.9, 125.2, 130.4, 130.6, 131.2, 166.4; υ_{max} (neat)/ cm^{-1}: 2942, 2864, 2145, 1618, 1437, 1370, 1356, 1317, 1211, 1152, 1136, 1047, 997, 961, 883, 806, 698, 675, 656, 623, 610; GC-MS (EI): t_R (50_40) 10.1 min; *m/z* (%): 375 (93), 332 (51), 318 (31), 291 (90), 290 (91), 276 (39), 248 (50), 246 (100), 43 (33); *m/z* (ESI): Found (M + H), 376.3030. $C_{23}H_{41}NOSiH$ requires *M*, 376.3036.

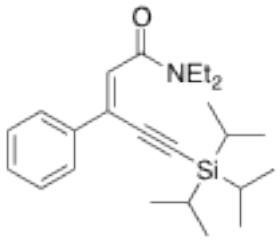


(*E*)-*N*,*N*-Diisopropyl-3-(thiophen-2-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 10

The reaction of (*E*)-*N*,*N*-diisopropyl-3-(thiophen-2-yl)acrylamide (0.200 mmol, 47 mg, 1.0 eq) following column chromatography on silica gel using automated MPLC and eluting with a gradient of 5-20% EtOAc in pentane gave **10** (69 mg, 0.164 mmol, 82%) as a yellow solid.

R_f (10% EtOAc in pentane) = 0.24; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 21H, TIPS), 1.21 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.45 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 3.55 (p, *J* = 6.7 Hz, 1H, NCH), 4.09 (p, *J* = 6.7 Hz, 1H, NCH), 6.62 (s, 1H, CH), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H, ArH), 7.23 (dd, *J* = 5.1, 1.2 Hz, 1H, ArH), 7.33 (dd, *J* = 3.6, 1.2 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.3, 18.7, 20.5, 21.2, 45.6, 50.2, 98.2, 101.6, 120.4, 125.7, 126.2, 127.6, 127.8, 142.3, 165.7; υ_{max} (neat)/ cm^{-1}: 2940,

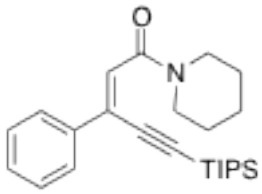
2864, 1620, 1586, 1439, 1366, 1335, 1248, 1215, 1157, 1134, 1049, 999, 883, 856, 826, 696, 677, 627; GC-MS (EI): t_R (50_40): 11.7 min; *m/z* (%): 375 (77), 374 (60), 333 (40), 332 (100), 318 (26), 290 (25); *m/z* (ESI): Found (M + H), 418.2594. $C_{24}H_{39}NOSSiH$ requires *M*, 418.2600.



(*Z*)-*N*,*N*-Diethyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 11

The reaction of *N*,*N*-diethylcinnamamide (0.200 mmol, 40 mg, 1.0 eq) following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **11** (58 mg, 0.152 mmol, 76 %) as yellow oil.

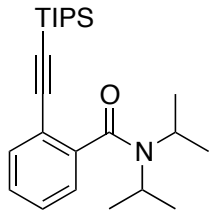
R_f (10% EtOAc in pentane) = 0.21; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 21H, TIPS), 1.19 (q, *J* = 7.2 Hz, 6H, 2 × CH_2CH_3), 3.42 (q, *J* = 7.2 Hz, 4H, CH_2CH_3), 3.48 (q, *J* = 7.2 Hz, 4H, CH_2CH_3), 6.74 (s, 1H, C=CH), 7.29 – 7.42 (m, 3H, 3 × ArH), 7.63 – 7.72 (m, 2H, 2 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.4, 13.3, 14.8, 18.8, 39.6, 43.1, 99.8, 102.6, 126.5, 127.4, 128.6, 128.8, 128.8, 136.8, 167.1; υ_{max} (neat)/ cm^{-1}: 2934, 2862, 1629, 1464, 1435, 1265, 1234, 1013, 882; GC-MS (EI): t_R (50_40): 11.2 min; *m/z* (%): 341 (35), 340 (100); *m/z* (ESI): Found (M + H), 384.2717. $C_{24}H_{37}NOSi$ requires *M*, 384.2723.



(*Z*)-3-Phenyl-1-(piperidin-1-yl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one 12

The reaction of (*E*)-3-phenyl-1-(piperidin-1-yl)prop-2-en-1-one (0.200 mmol, 42 mg, 1.0 eq) following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **5i** (49 mg, 0.124 mmol, 62 %) as a yellow oil.

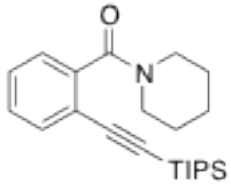
R_f (10% EtOAc in pentane) = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (s, 21H, TIPS), 1.41 – 1.74 (m, 6H, 3 × CH_2), 3.54 (t, *J* = 5.5 Hz, 2H, NCH_2), 3.64 (t, *J* = 5.4 Hz, 2H, NCH_2), 6.71 (s, 1H, C=CH), 7.30 – 7.45 (m, 3H, 3 × ArH), 7.61 – 7.72 (m, 2H, 2 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.5, 18.8, 24.8, 25.5, 26.9, 42.5, 47.8, 99.7, 102.5, 126.4, 127.2, 128.4, 128.6, 128.9, 136.5, 166.2; υ_{max} (neat)/ cm^{-1}: 2941, 2864, 1631, 1460, 1427, 1273, 1012; GC-MS (EI): t_R (50_40): 12.9 min; *m/z* (%): 353 (34), 352 (100); *m/z* (ESI): Found (M + H), 396.2717. $C_{25}H_{38}NOSi$ requires *M*, 396.2723.



***N*,*N*-Diisopropyl-2-((triisopropylsilyl)ethynyl)benzamide 3**

The reaction of *N*,*N*-diisopropylbenzamide (0.200 mmol, 41 mg, 1.0 eq) following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **3** (42 mg, 0.108 mmol, 54 %) as a yellow oil.

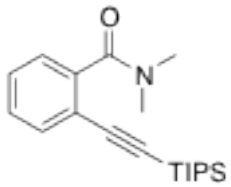
R_f (20% EtOAc in pentane) = 0.21; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.11 (s, 21H, TIPS), 1.21 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.54 (d, *J* = 6.8 Hz, 3H, CHCH_3), 1.57 (d, *J* = 6.8 Hz, 3H, CHCH_3), 3.50 (p, *J* = 6.8 Hz, 1H, NCH), 3.63 (p, *J* = 6.6 Hz, 1H, CHCH_3), 7.14 (dd, *J* = 7.6, 1.4 Hz, 1H, ArH), 7.23 – 7.33 (m, 2H, 2 × ArH), 7.51 (dd, *J* = 7.2, 1.8 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.5, 18.8, 18.8, 20.7, 20.8, 21.1, 45.9, 51.2, 94.5, 104.7, 120.0, 125.2, 127.8, 128.6, 134.1, 141.2, 169.2; υ_{max} (neat)/ cm^{-1}:2943, 2864, 1635, 1339, 1209, 983; GC-MS (EI): t_R (50_40): 10.7 min; *m/z* (%): 343 (41), 342 (100), 300 (54); *m/z* (ESI): Found (M + H), 386.2874. $C_{24}H_{40}NOSi$ requires *M*, 386.2879.



Piperidin-1-yl(2-((triisopropylsilyl)ethynyl)phenyl)methanone 13

The reaction of phenyl(piperidin-1-yl)methanone (0.200 mmol, 38 mg, 1.0 eq) following column chromatography on silica gel, using automated MPLC and eluting with a gradient of 7-50% EtOAc in pentane gave **13** (54 mg, 0.146 mmol, 73%) as a red oil.

R_f (20% EtOAc in pentane) = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (s, 21H, TIPS), 1.25-1.67 (m, 6H, 2 × CH_2), 3.01-3.37 (m, 3H from 2 × CH_2), 4.03 (d, J = 12.9 Hz, 1H from CH_2), 7.17-7.32 (m, 3H, 3 × ArH), 7.38-7.46 (m, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.3, 18.7, 24.6, 25.5, 26.4, 42.6, 47.9, 94.4, 104.1, 120.2, 126.1, 128.3, 128.6, 133.0, 139.8, 168.4; υ_{max} (neat)/ cm^{-1}: 2940, 2864, 1717, 1638, 1447, 1429, 1287, 1256, 1240, 1090, 997, 882, 839, 822, 756, 700, 677, 662; GC-MS (EI): t_R (50_40): 11.4 min; *m/z* (%): 327 (36), 326 (100); *m/z* (ESI): Found (M + H), 370.2561. $C_{23}H_{35}NOSiH$ requires *M*, 370.2566.

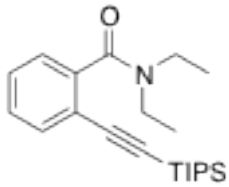


***N*,*N*-Dimethyl-2-((triisopropylsilyl)ethynyl)benzamide 14**

The reaction of *N*,*N*-dimethylbenzamide (0.200 mmol, 30 mg, 1.0 eq) following column chromatography on silica gel, using automated MPLC and eluting with a gradient of 7-50% EtOAc in pentane gave **14** (41 mg, 0.124 mmol, 62%) as a red oil.

R_f (20% EtOAc in pentane) = 0.11; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (s, 21H, TIPS) 2.83 (s, 3H, CH_3) 3.03 (s, 3H, CH_3) 7.18-7.46 (m, 4H, 4 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 10.2, 17.6, 33.8, 37.3, 93.2, 102.9, 119.2, 125.4, 127.5, 127.8, 131.7, 138.8, 169.1; υ_{max} (neat)/ cm^{-1}: 2942, 2864, 1636, 1506, 1437, 1395, 1339, 1260, 1206, 1072, 995, 882, 837, 756, 710, 677, 664, 644; GC-MS (EI): t_R (50_40):

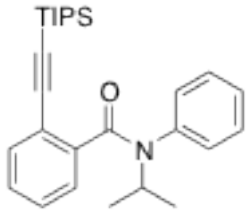
10.0 min; *m/z* (%): 287 (32), 286 (100); *m/z* (ESI): Found (M + H), 330.2248. $C_{20}H_{31}NOSiH$ requires *M*, 330.2253.



***N*,*N*-Diethyl-2-((triisopropylsilyl)ethynyl)benzamide 15**

The reaction of *N*,*N*-diethylbenzamide (0.200 mmol, 36 mg, 1.0 eq) following column chromatography on silica gel, eluting with 15% EtOAc in pentane gave **15** (16 mg, 0.046 mmol, 23 %) as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62 – 1.12 (m, 25H, TIPS, CH_2CH_3), 1.20 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 3.12 (br. s, 2H, NCH_2), 3.49 (br. d, *J* = 28.4 Hz, 2H NCH_2), 6.90 – 7.36 (m, 3H, 3 × ArH), 7.37 – 7.56 (m, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.3, 13.1, 14.2, 18.7, 39.4, 43.2, 94.5, 104.1, 120.2, 126.1, 128.2, 128.5, 133.3, 140.1, 169.4; υ_{max} (neat)/ cm^{-1}: 2943, 2866, 1734, 1635, 1290, 1084, 883; *m/z* (ESI): Found (M + Na), 380.2388. $C_{22}H_{35}NNaOSi$ requires *M*, 380.2386.

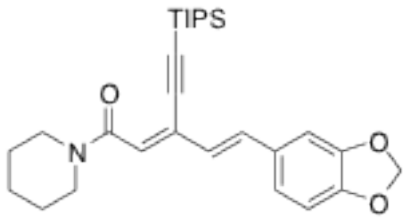


***N*-Isopropyl-*N*-phenyl-2-((triisopropylsilyl)ethynyl)benzamide 16**

The reaction of *N*-isopropyl-*N*-phenylacetamide (0.200 mmol, 48 mg, 1.0 eq) following column chromatography on silica gel eluting with 10% EtOAc in pentane gave **17** (61 mg, 0.146 mmol, 73%) as a white solid.

R_f (20% EtOAc in pentane) = 0,48; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13-1.27 (m, 27H, TIPS, 2 × $CHCH_3$), 5.15 (p, *J* = 6.8 Hz, 1H, NCH), 6.92-7.33 (m, 9H, 9 × ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 11.4, 18.7, 21.0, 46.5, 94.6, 105.1, 120.7, 126.7, 127.5, 127.5, 128.3, 128.6, 128.9, 130.4, 130.6, 133.0, 138.4, 140.7, 169.2; υ_{max} (neat)/ cm^{-1}: 2942, 2864, 2155, 1643, 1593, 1497, 1462, 1393, 1348, 1256, 1121, 1096, 1076, 1018, 993, 882, 853, 816, 768, 702, 667, 625; GC-MS (EI): t_R (50_40): 12.0 min; *m/z*

(%): 377 (49), 376 (100), 334 (59); *m/z* (ESI): Found (M + H), 420.2717. $C_{27}H_{37}NOSiH$ requires *M*, 420.2723.

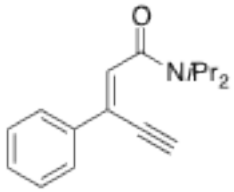


(2*Z*,4*E*)-5-(Benzo[*d*][1,3]dioxol-5-yl)-1-(piperidin-1-yl)-3-((triisopropylsilyl)ethynyl)penta-2,4-dien-1-one 22

The reaction of piperine (0.200 mmol, 57 mg, 1.0 eq) following column chromatography on silica gel, eluting with 25% EtOAc in pentane gave **22** (16 mg, 0.036 mmol, 30 %) as a colourless oil.

R_f (20% EtOAc in pentane) = 0.12; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 21H, TIPS), 1.51 – 1.70 (m, 6H, 3 × CH_2), 3.51 (t, *J* = 5.5 Hz, 2H, NCH_2), 3.61 (t, *J* = 5.4 Hz, 2H, NCH_2), 5.97 (s, 2H, OCH_2O), 6.26 (s, 1H, CH=C), 6.56 (d, *J* = 15.6 Hz, 1H, 1H from CH=CH), 6.77 (d, *J* = 8.3 Hz, 1H, ArH), 6.85 (dd, *J* = 8.3, 1.8 Hz, 1H, ArH), 6.94 (d, *J* = 1.7 Hz, 1H, ArH), 7.08 (d, *J* = 15.6 Hz, 1H, 1H from CH=CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.3, 18.7, 24.6, 25.4, 26.8, 42.4, 47.8, 99.8, 100.5, 101.2, 105.8, 108.5, 122.2, 125.8, 126.6, 129.5, 130.9, 134.3, 147.9, 148.1, 165.8; υ_{max} (neat)/ cm^{-1}: 2939; 2891; 2862; 1624, 1440, 1250, 1229, 1038, 881; GC-MS was uninformative; *m/z* (ESI): Found (M + H), 466.2778. $C_{28}H_{40}NO_3Si$ requires *M*, 466.2777.

Derivatisation of products

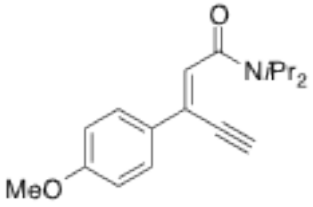


(*E*)-*N*,*N*-Diisopropyl-3-phenylpent-2-en-4-ynamide 18

Reaction was undertaken in an oven dried (80 °C) flask under an atmosphere of argon. To a solution of **5a** (0.200 mmol, 82 mg, 1.0 eq) in THF (7.2 mL) was added

drop wise at 0°C TBAF (1M in THF, 220 μL, 0.220 mmol, 1.1 eq) and the reaction stirred for 3 h. The solvent was removed *in vacuo*, the residue dissolved in Et_2O (15 mL) and the organic phase washed with saturated sodium hydrogen carbonate (15 mL). The aqueous phase was separated, washed with Et_2O (2 × 15 mL), and the combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography on silica gel, eluting with 15% EtOAc in pentane gave **18** (51 mg, 0.200 mmol, >95%) as a colourless oil.

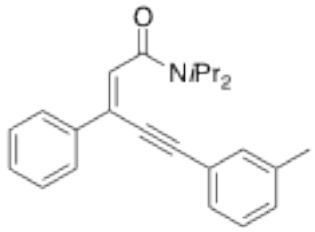
R_f (20% EtOAc in pentane) = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.49 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 3.37 (s, 1H, C≡CH), 3.58 (p, *J* = 6.8 Hz, 1H, NCH), 4.10 (p, *J* = 6.7 Hz, 1H, NCH), 6.81 (s, 1H, C=CH), 7.31 – 7.46 (m, 3H, 3 × ArH), 7.58 – 7.75 (m, 2H, 2 × ArH); υ_{max} (neat)/ cm^{-1}: 3207; 1620; 1440, 1350, 1221 761; ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 23.2, 47.7, 52.3, 81.8, 86.7, 127.4, 128.2, 130.5, 130.8, 133.1, 138.2, 168.3; *m/z* (ESI): Found (M + H), 256.1696. $C_{17}H_{22}NO$ requires *M*, 256.1701.



(*E*)-*N*,*N*-Diisopropyl-3-(4-methoxyphenyl)pent-2-en-4-ynamide 19

Reaction was undertaken in an oven dried (80 °C) flask under an atmosphere of argon. To a solution of **5c** (0.143 mmol, 41 mg, 1.0 eq) in THF (9.0 mL) was added drop wise at 0°C TBAF (1M in THF, 265 μL, 0.265 mmol, 1.9 eq) and the reaction stirred for 3 h. The solvent was removed *in vacuo*, the residue dissolved in Et_2O (15 mL) and the organic phase washed with saturated sodium hydrogen carbonate (15 mL). The aqueous phase was separated, washed with Et_2O (2 × 15 mL), and the combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography on silica gel, eluting with 25% EtOAc in pentane gave **19** (51 mg, 0.129 mmol, 90%) as a colourless oil.

R_f (20% EtOAc in pentane) = 0.13; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.48 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 3.35 (d, *J* = 0.4 Hz, 1H, C≡CH), 3.57 (p, *J* = 6.6 Hz, 1H, CHN), 3.82 (s, 3H, OMe), 4.10 (p, *J* = 6.3 Hz, 1H, CHN), 6.70 (d, *J* = 0.4 Hz, 1H, C=CH), 6.89 (d, *J* = 8.8 Hz, 2H, 2 × ArH), 7.60 (d, *J* = 8.9 Hz, 2H, 2 × ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 21.4, 45.8, 50.4, 55.5, 80.2, 84.7, 114.0, 125.2, 127.7, 129.0, 129.3, 160.3, 166.7; GC-MS (EI): t_R (50_40): 9.9 min; υ_{max} (neat)/ cm^{-1}: 2942, 2924, 2864, 1616, 1456, 1437, 1307, 1136, 885, 785; *m/z* (%): 281 (33), 207 (63), 185 (100); *m/z* (ESI): Found (2M + Na), 593.3350. $C_{36}H_{46}N_2NaO_4$ requires *M*, 593.3355.



(*Z*)-*N*,*N*-Diisopropyl-3-phenyl-5-(*m*-tolyl)pent-2-en-4-ynamide 20

Reaction was undertaken in a flame dried reaction vessel (hot air gun, 600 °C, 1 min) with a Teflon screw caps under an atmosphere of argon. To a solution of **5a** (0.200 mmol, 82 mg, 1.0 eq) in THF (1.0 mL) was added drop wise at 0°C TBAF (1M in THF, 265 μL, 0.265 mmol, 1.9 eq) and the reaction stirred for 3 h. To the reaction was then added consecutively 3-iodotoluene (0.240 mmol, 31 μL, 1.2 eq), $PdCl_2(PPh_3)_2$ (11mg, 0.016 mmol, 8 mol%), CuI (0.22 eq, 42 mg, 1.2 eq) and the reaction stirred at room temperature overnight. The reaction was concentrated *in vacuo* directly onto silica and following column chromatography on silica gel, eluting with 10% EtOAc in pentane gave **20** (35 mg, 0.100 mmol, 50%) as a brown oil.

R_f (20% EtOAc in pentane) = 0.13; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, *J* = 6.7 Hz, 6H, 2 × CHC*H*$_3$), 1.46 (d, *J* = 6.8 Hz, 6H, 2 × CHC*H*$_3$), 2.26 (s, 3H, CH_3), 3.50 (p, *J* = 6.8 Hz, 1H, NCH), 4.14 (p, *J* = 6.7 Hz, 1H, NCH), 6.69 (s, 1H, C=CH), 6.88 – 7.44 (m, 7H, 7 × ArH), 7.53 – 7.79 (m, 2H, 2 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.7, 21.4, 21.4, 45.9, 50.6, 85.7, 96.7, 122.8, 126.0, 126.4, 128.4, 128.7, 128.8, 128.9, 129.4, 129.7, 132.4, 136.9, 138.1, 167.1; υ_{max} (neat)/ cm^{-1}: 2950, 1624, 1437,

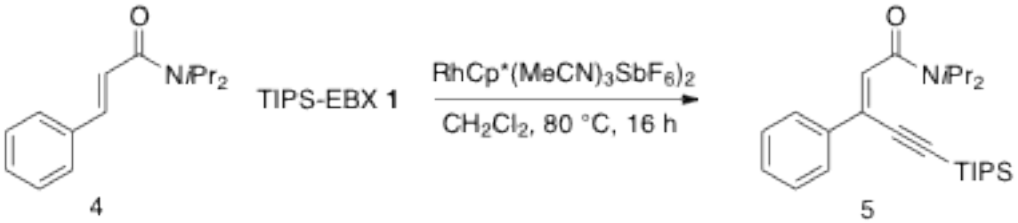
1354, 1325, 1136, 785, 761; *m/z* (ESI): Found (M + H), 346.2171. $C_{24}H_{28}NO$ requires *M*, 346.2171.

4. Robustness Screen results

A simplified robustness screen as recently reported[4] has been undertaken to evaluate the tolerance of this reaction to the given functionalities and chemical motifs, as well as the stability of these 'additives' to the reaction conditions. This procedure requires the undertaking of a standard reaction in the presence of one molar equivalent of a given additive (functional group or heterocycle). After the pre-determined reaction time, the yield of the product, the starting material remaining, and the additive remaining is determined by GC analysis.

The calibration of the additives, starting materials and the product of the reaction was undertaken using the single point calibration technique for gas chromatography (GC) analysis as previously described. Evaluation of two groups of additives, 'functional groups' (Group A) and 'heterocycles' (Group B) as previously reported was undertaken.

Excluding reaction time and GC running time, the whole screen was undertaken in approximately 8 h including control experiments and analysis.



The standard reaction evaluated.

Sample procedure:

1) To 11 oven-dried Schlenk flasks under air was added RhCp*$(MeCN)_3(SbF_6)$ (0.01 mmol, 8 mg, 10 mol%).

[4] (a) K. D. Collins and F. Glorius, *Nature Chem.,* 2013, **5**, 597; (b) K. D. Collins and F. Glorius, *Tetrahedron*., 2013, **69**, 7817; (c) K. D. Collins, A. Rühling, and F. Glorius, *Nat. Protoc.,* 2014, accepted.

2) A stock solution of *N*,*N*-diisopropylcinnamamide **4** (1.20 mmol, 276 mg, 1 eq.), (12 × 0.100 mmol = 1.20 mmol scale) in CH_2Cl_2 (9.0 mL) was prepared, and the mixture stirred until complete dissolution of the reagent had occurred.
3) A portion of the stock reaction mixture (0.75 mL, ~0.100 mmol) was then added *via* syringe (1 mL) to each Schlenk flask containing the catalyst. The corresponding additive (0.100 mmol) followed immediately by TIPS-EBX **4** (86 mg, 0.200mmol, 2 eq) was added to each reaction vessel, the vessel sealed and then the heated directly for 16 h at 80 °C in an oil bath.
4) Once cooled, mesitylene (28 μL, 0.200 mmol, 1 eq) was added to each reaction, and analysis by GC was undertaken.

Note:

- Change in volume of stock solution due to addition of starting materials was not accounted for, hence a control reaction (no additive) is undertaken to determine the maximum yield of reaction in the screen.
- ***N*-methylimidazole** and **dodecylamine** should be filtered through Celite and not silica when preparing samples for GC analysis.
- Following the original screen 5 reactions were repeated to ensure consistency and reproducibility of the data.

Group A - Functional Groups

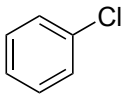
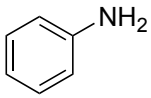
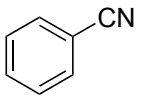
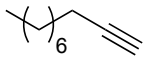
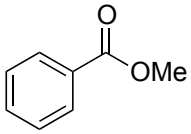
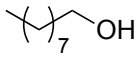
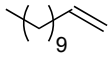
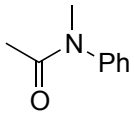
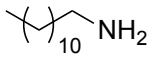
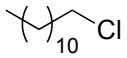
Entry		Amount (0.100 mmol)	Yield of **5a** %	Additive remaining %[a]	SM remaining % **4a**
A1		10.5 μL	✓ 87	✓ >95	0
A2		9.5 μL	X 0	X 29	63
A3		10.5 μL	✓ 79	✓ >95	<5
A4		18.5 μL	X 0 (0)	- 38 (41)	91 (92)
A5		14 μL	✓ 83 (89)	✓ >95 (>95)	0 (0)
A6		16 μL	X 22	X 0	66
A7		22.5 μL	✓ 82	✓ 78	0
A8		15 mg	✓ 87	✓ >95	0
A9		18.5 mg	X 18	X 0	66
A10		24 μL	✓ 76 (80)	✓ >95 (>95)	0 (0)
A11	none	-	✓ 84	-	0

Table 1. Table shows the affect of a given additive on the standard reaction. The yield of **5a**, and the additive and starting material **4a** remaining after reaction are given. Color-coding should help the ready assessment of the data: green (above 66%), yellow (34-66%), red (below 34%). All yields are GC yields. SM is starting material. Yields in parenthesis are of the control group: selected experiments were repeated to ensure consistency and reproducibility of the data.

Group B - Heterocycles

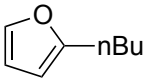
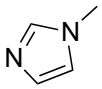
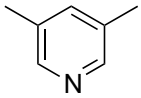
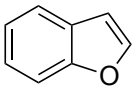
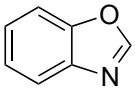
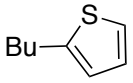
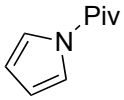
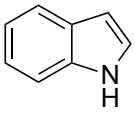
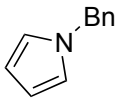
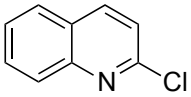
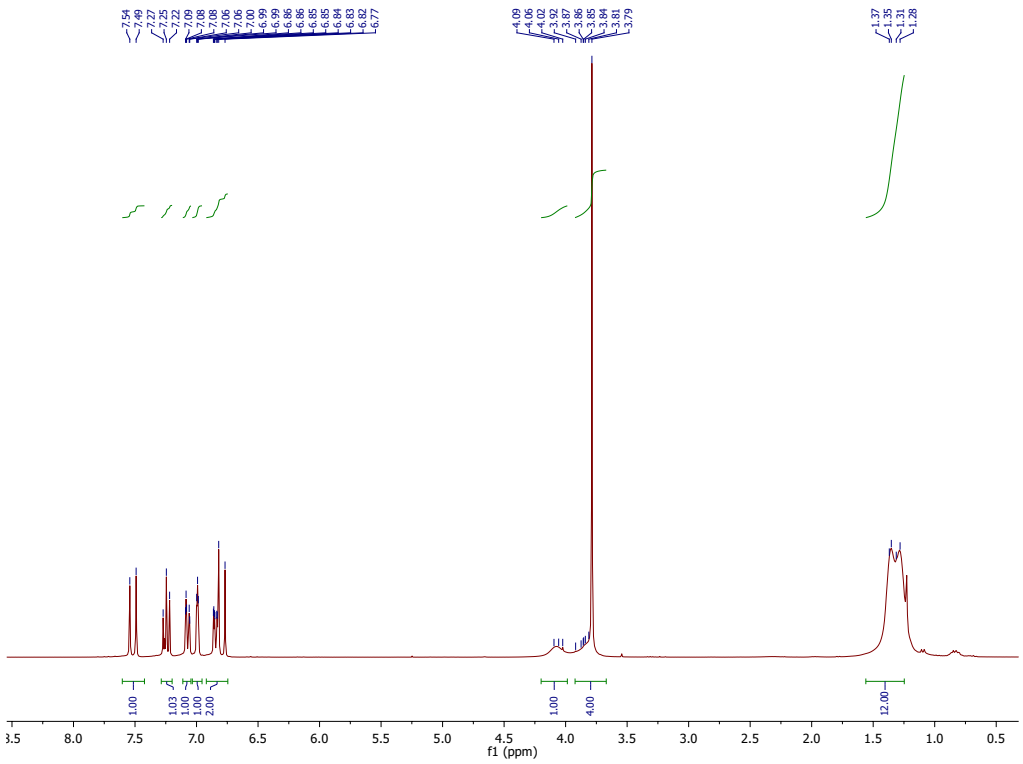
Entry		Amount (0.100 mmol)	Yield of **5a** %		Additive remaining %[a]		SM remaining % **4a**
B1		15 μL	-	52	X	8	16
B2		8 μL	X	0	✓	88	90
B3		11 μL	X	0	-	62	90
B4		11 μL	✓	80 (82)	✓	94 (88)	11 (0)
B5		12 mg	-	52	-	62	40
B6		14.5 μL	✓	82	✓	84	10
B7		15 mg	-	39	X	0	53
B8		12 mg	X	26	X	0	29
B9		15 μL	-	60	X	0	36
B10		17 mg	✓	85 (82)	✓	84 (95)	7 (0)
B11	none	-	✓	86	-		0

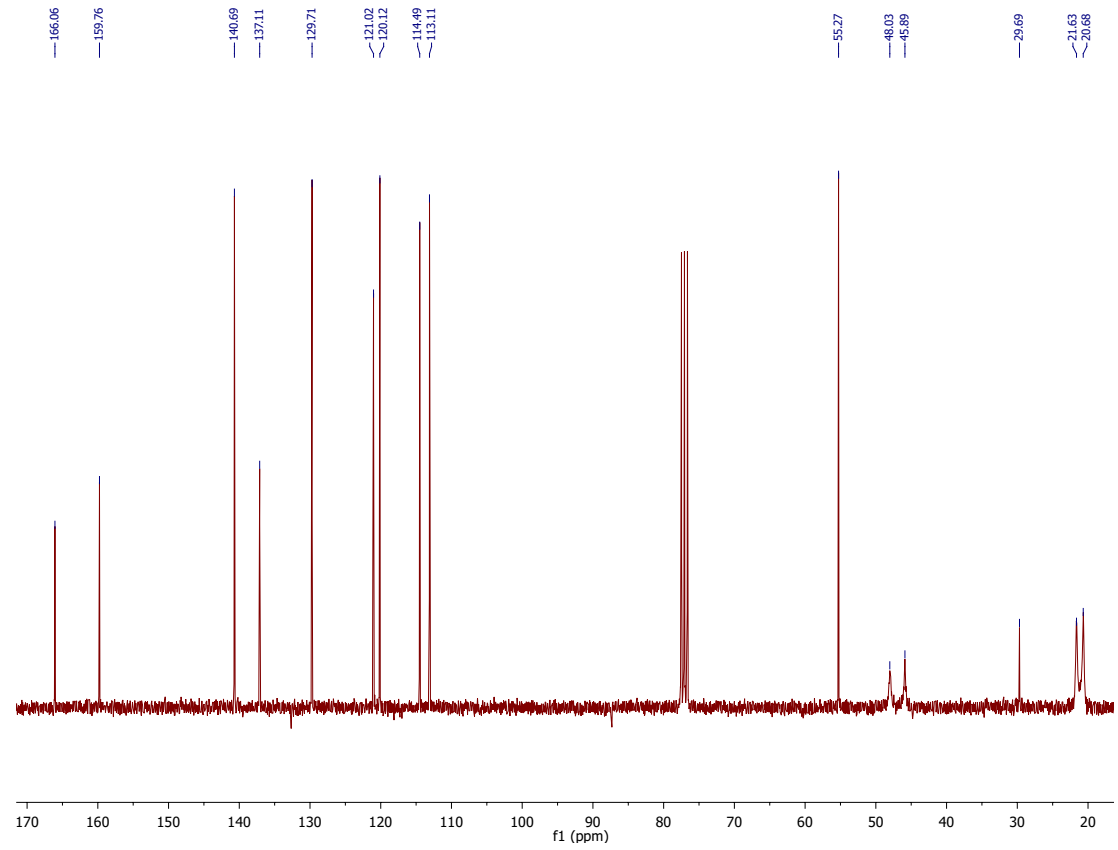
Table 2. Table shows the affect of a given additive on the standard reaction. The yield of **5a**, and the additive and starting material **1a** remaining after reaction are given. Color-coding should help the ready assessment of the data: green (above 66%), yellow (34-66%), red (below 34%). All yields are GC yields. SM is starting material. Yields in parenthesis are of the control group; selected experiments were repeated to ensure consistency and reproducibility of the data.

The screen demonstrated that the reaction was tolerant of an aromatic chloride, nitrile, ester and tertiary amide, with these functionalities showing high stability under reaction conditions. Alkyl chlorides and a terminal olefin were also stable under the reaction conditions and did not inhibit reaction. Aliphatic and aromatic amines, a primary alcohol and a terminal alkyne were all shown to inhibit the reaction. Of the heterocycles screened, azacycles were typically detrimental to the reaction or unstable to the reaction conditions with the exception of 2-chloroquinoline. Furan inhibited the reaction, though benzofuran and thiophene did not, and were stable to the reaction conditions.

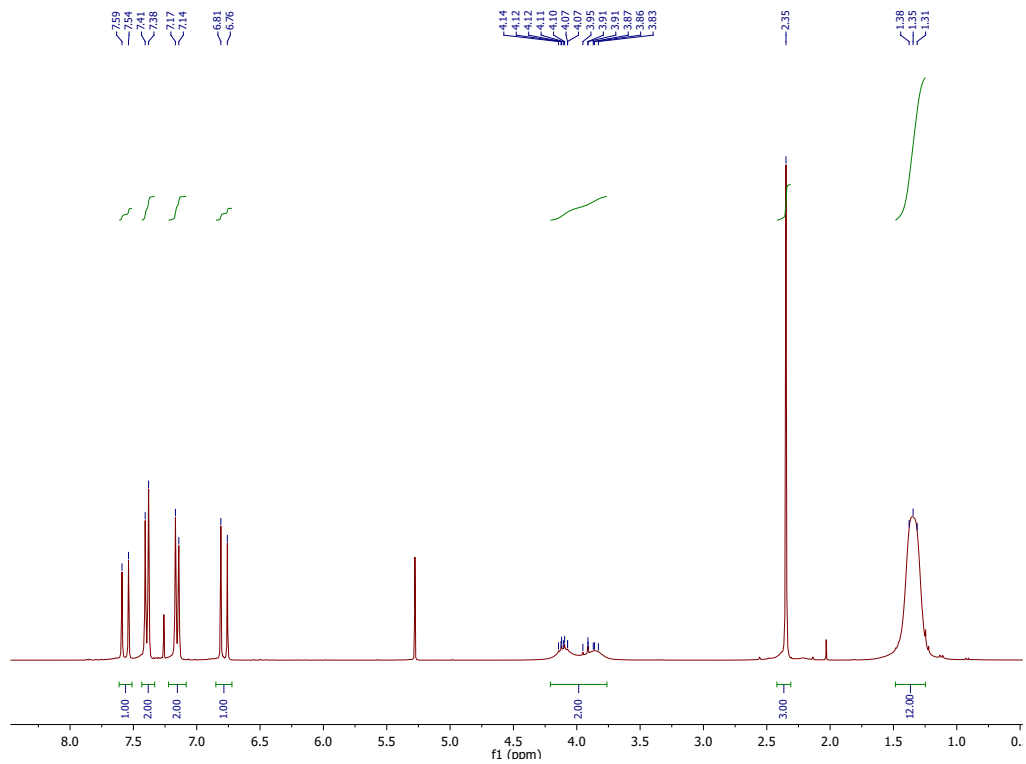
5. NMR Spectra

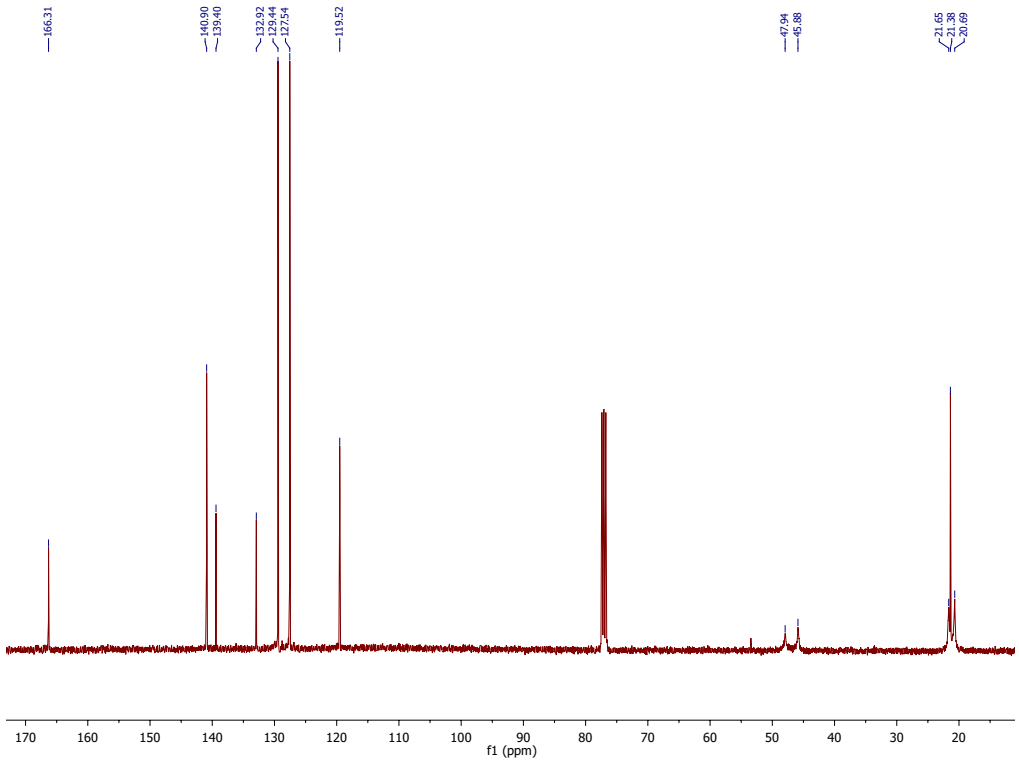
(*E*)-*N*,*N*-Diisopropyl-3-(3-methoxyphenyl)acrylamide I



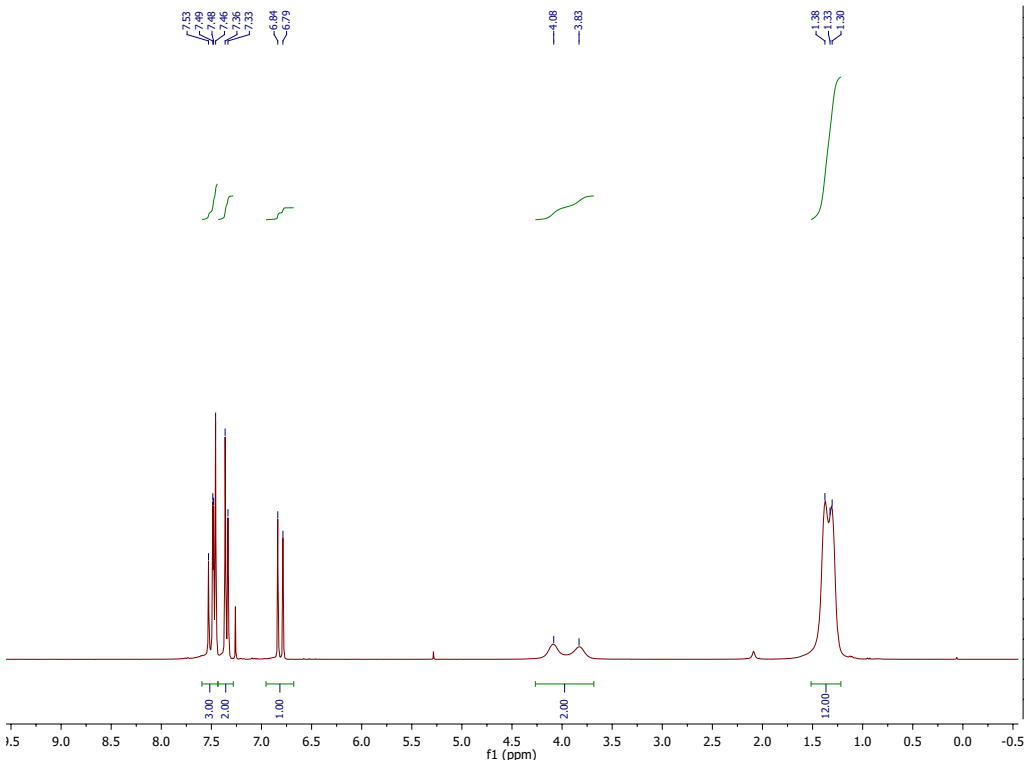


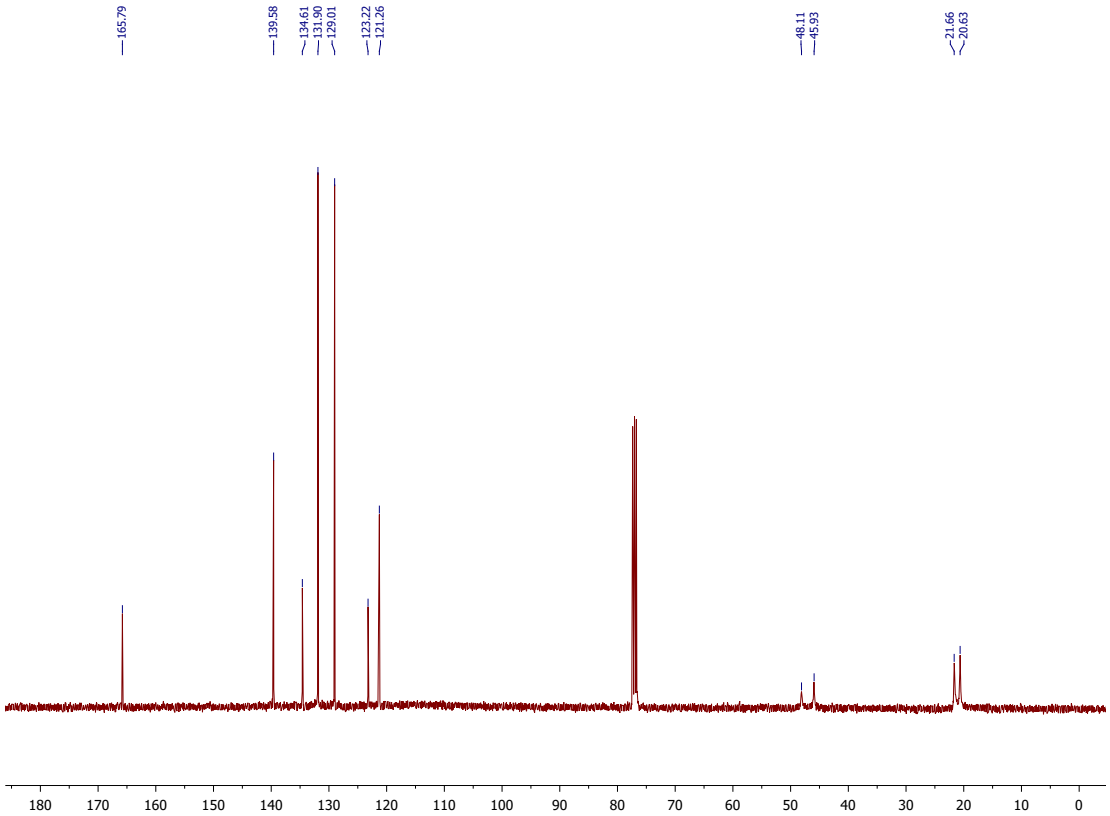
(*E*)-*N*,*N*-Diisopropyl-3-(*p*-tolyl)acrylamide II



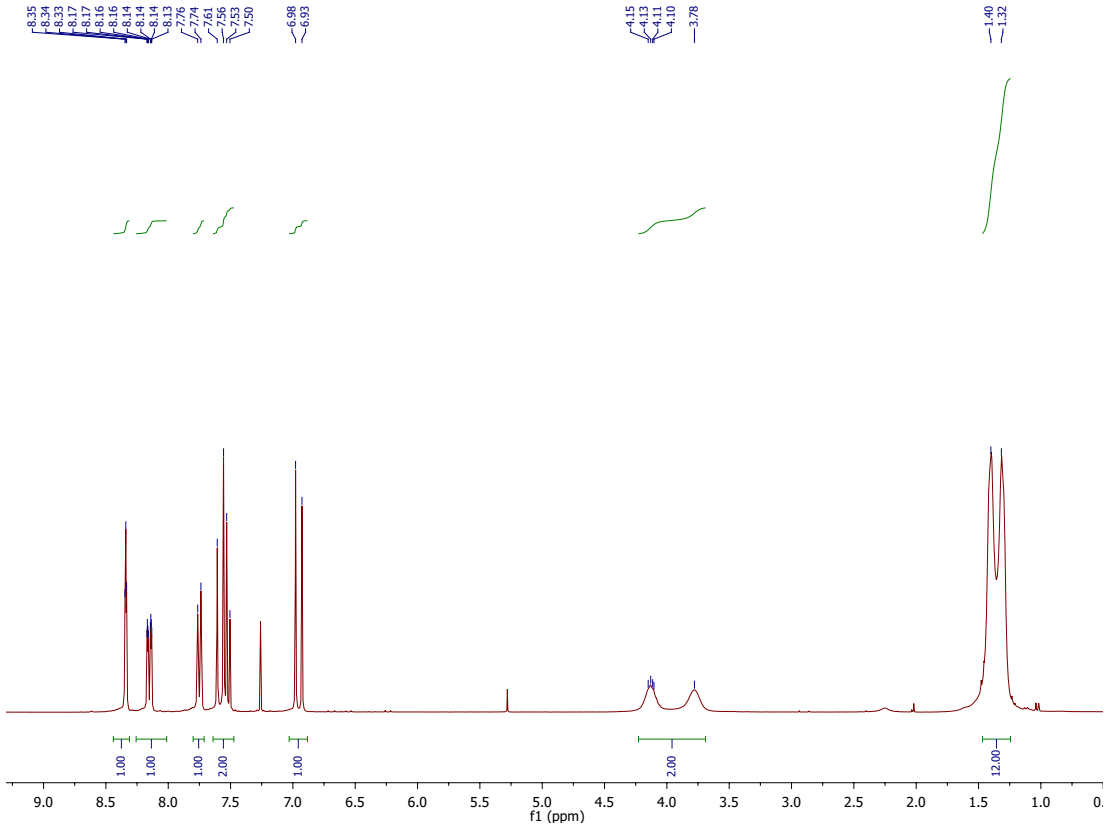


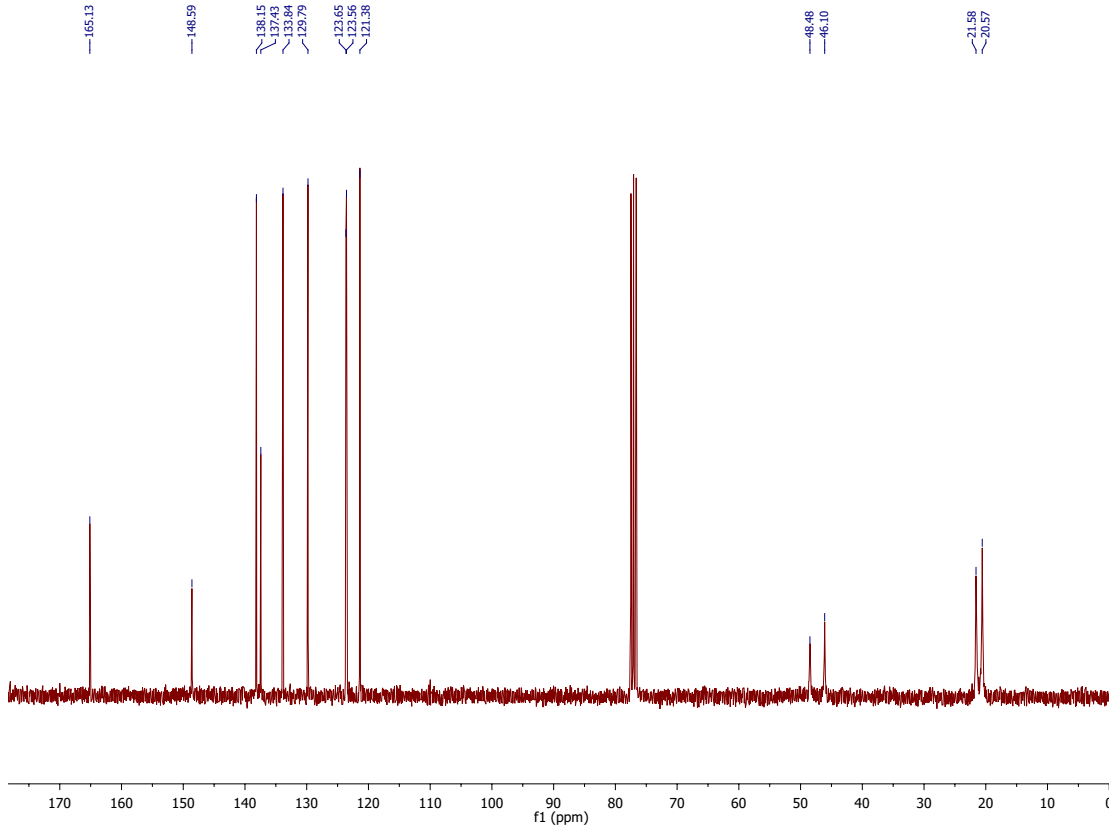
(*E*)-3-(4-Bromophenyl)-*N*,*N*-diisopropylacrylamide III



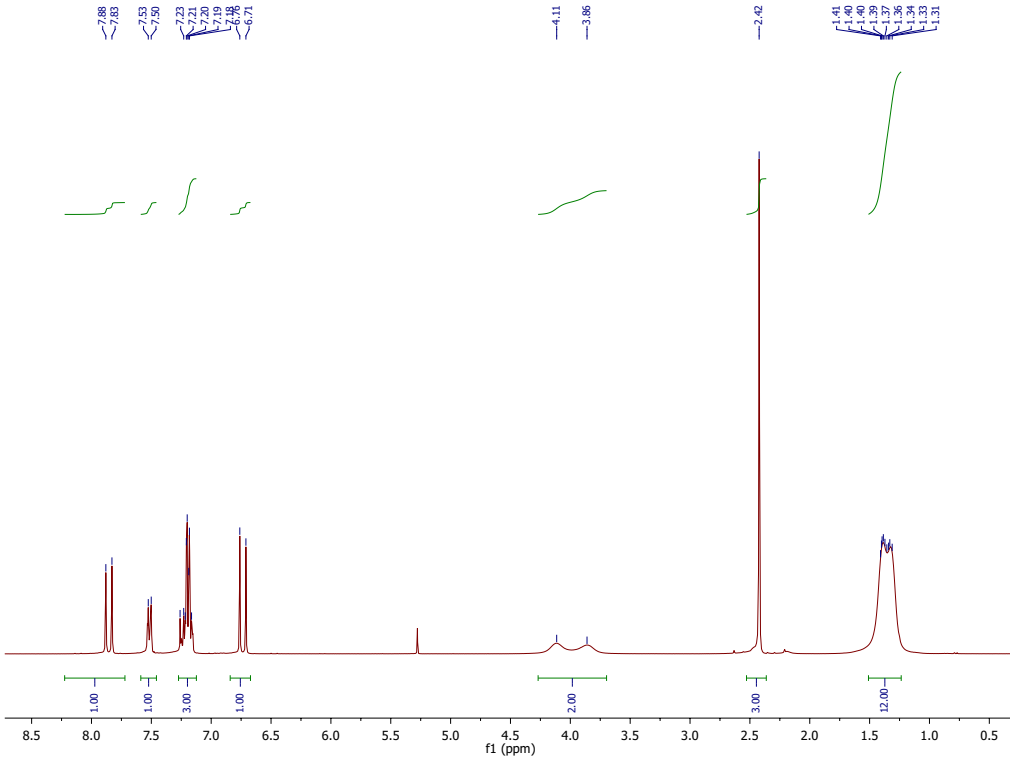


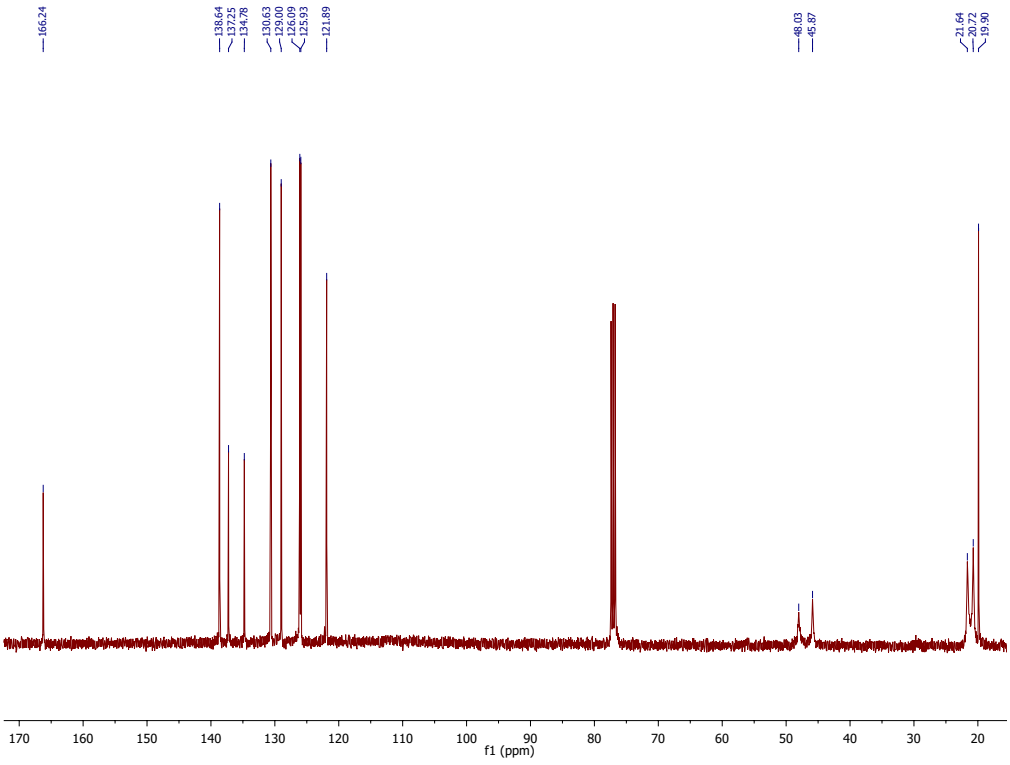
(*E*)-*N*,*N*-Diisopropyl-3-(3-nitrophenyl)acrylamide IV



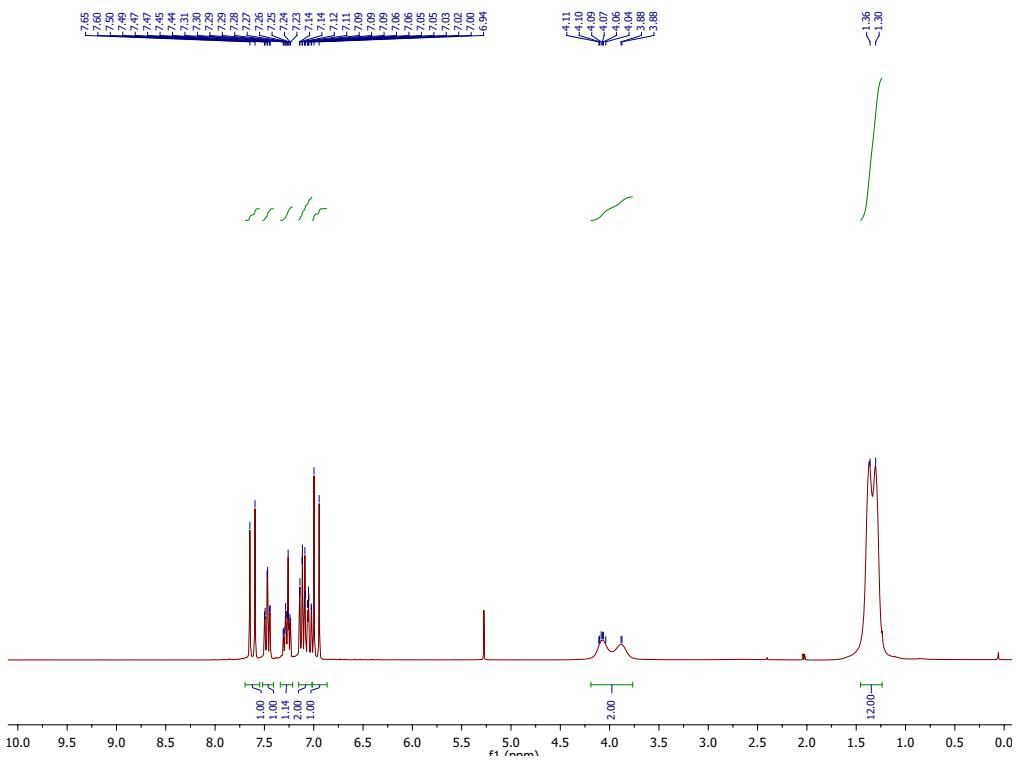


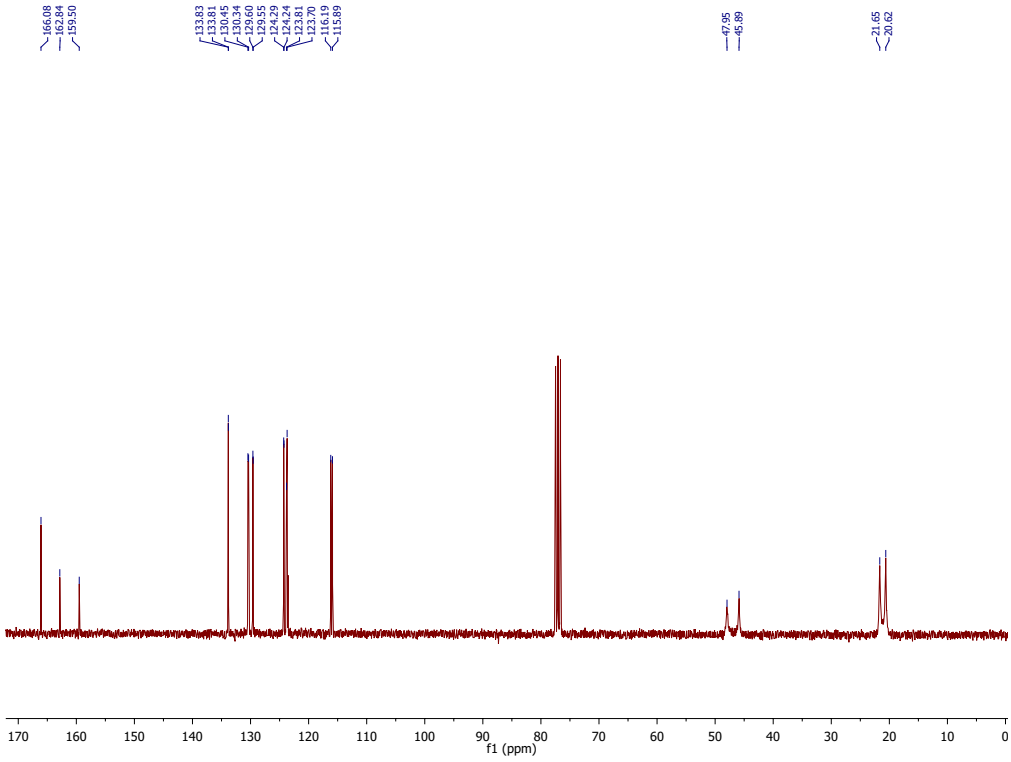
(*E*)-*N*,*N*-Diisopropyl-3-(*o*-tolyl)acrylamide V



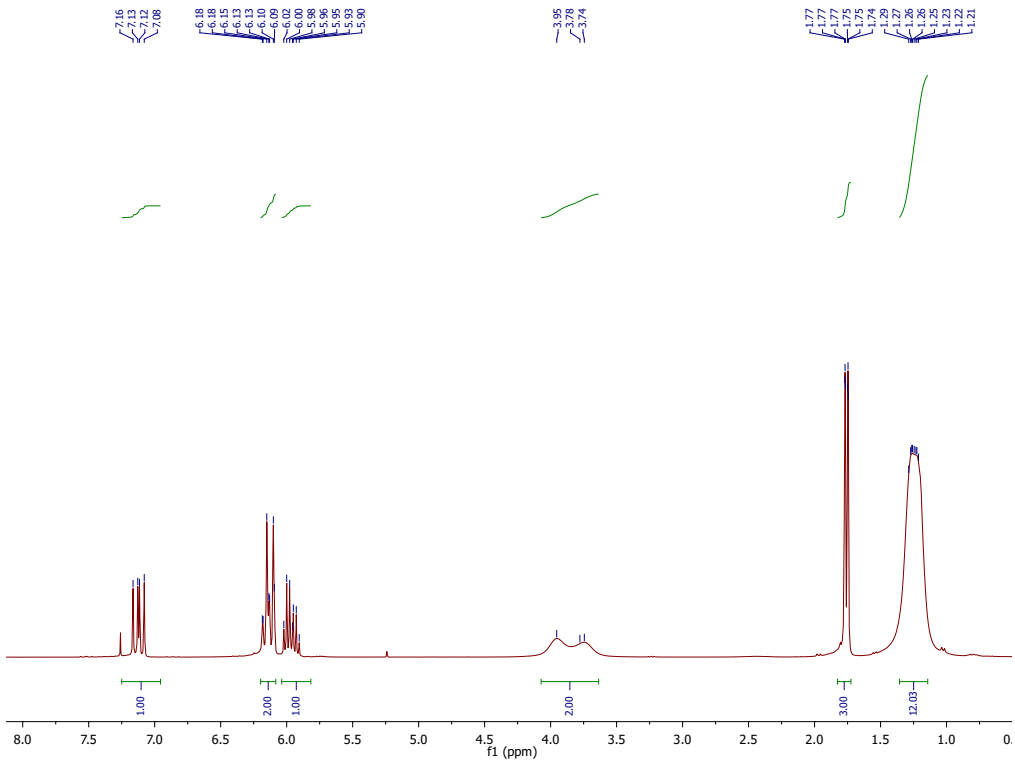


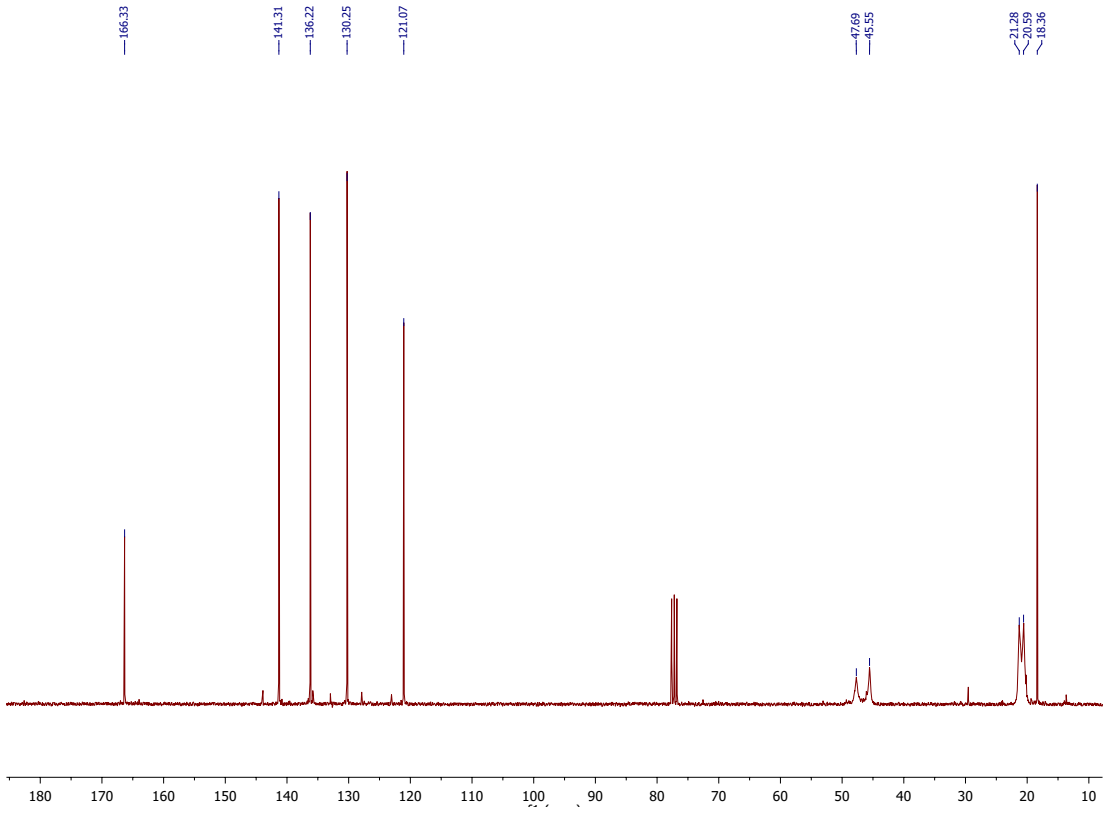
(*E*)-3-(2-Fluorophenyl)-*N*,*N*-diisopropylacrylamide VI



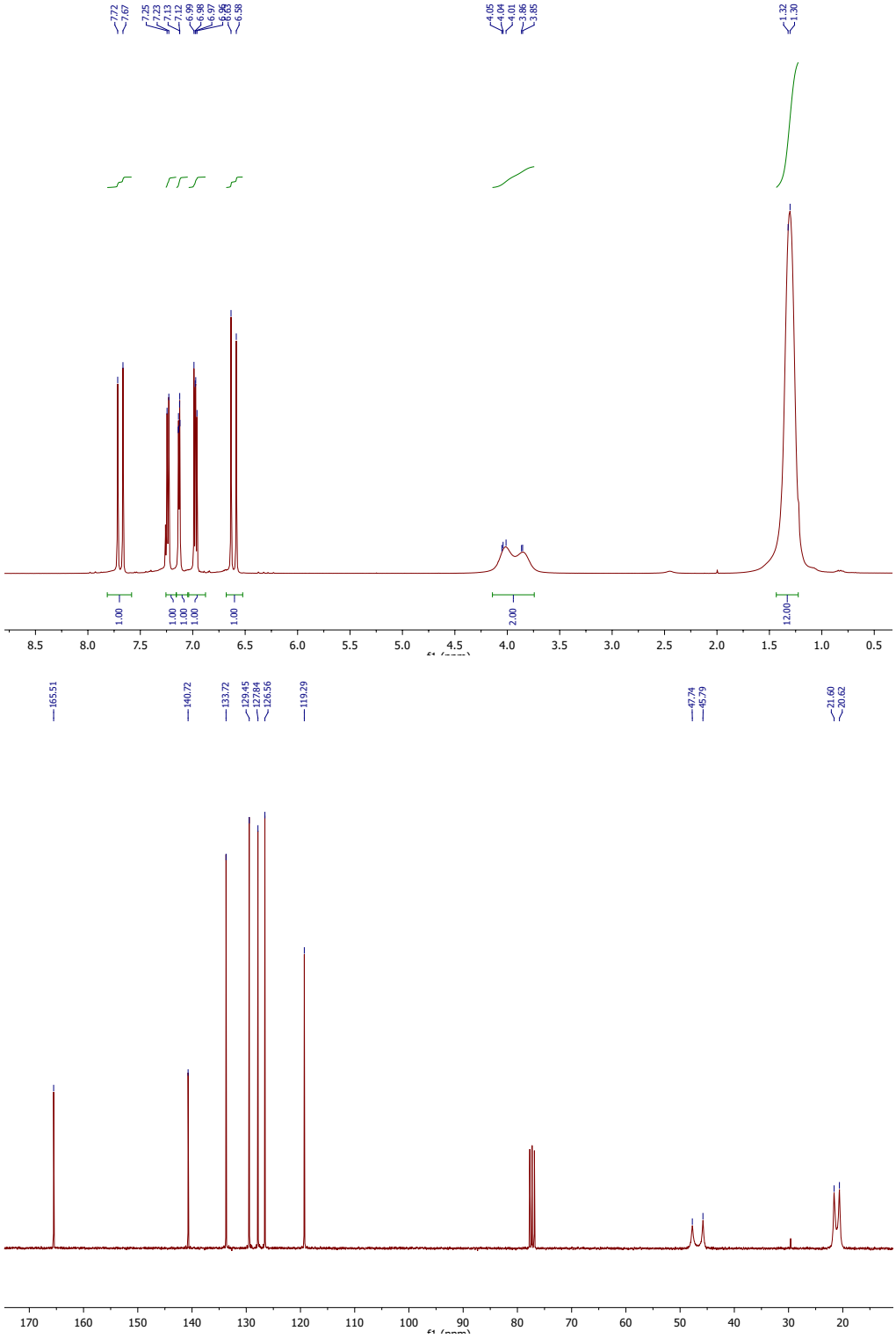


(2*E*,4*E*)-*N*,*N*-Diisopropylhexa-2,4-dienamide VII

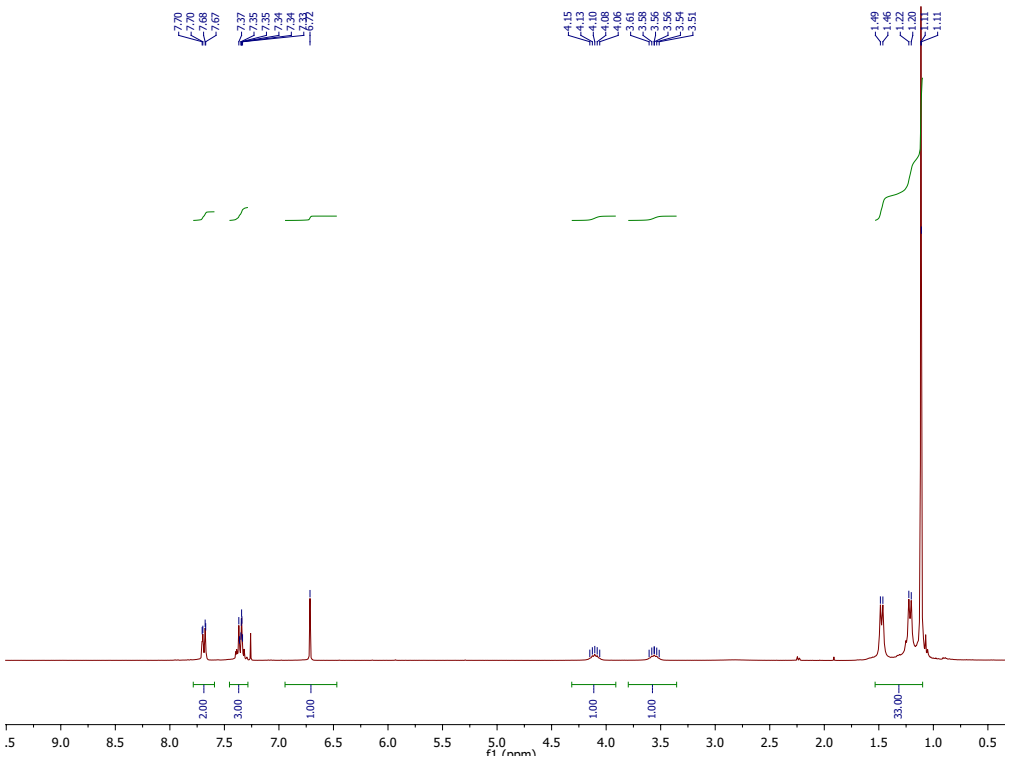


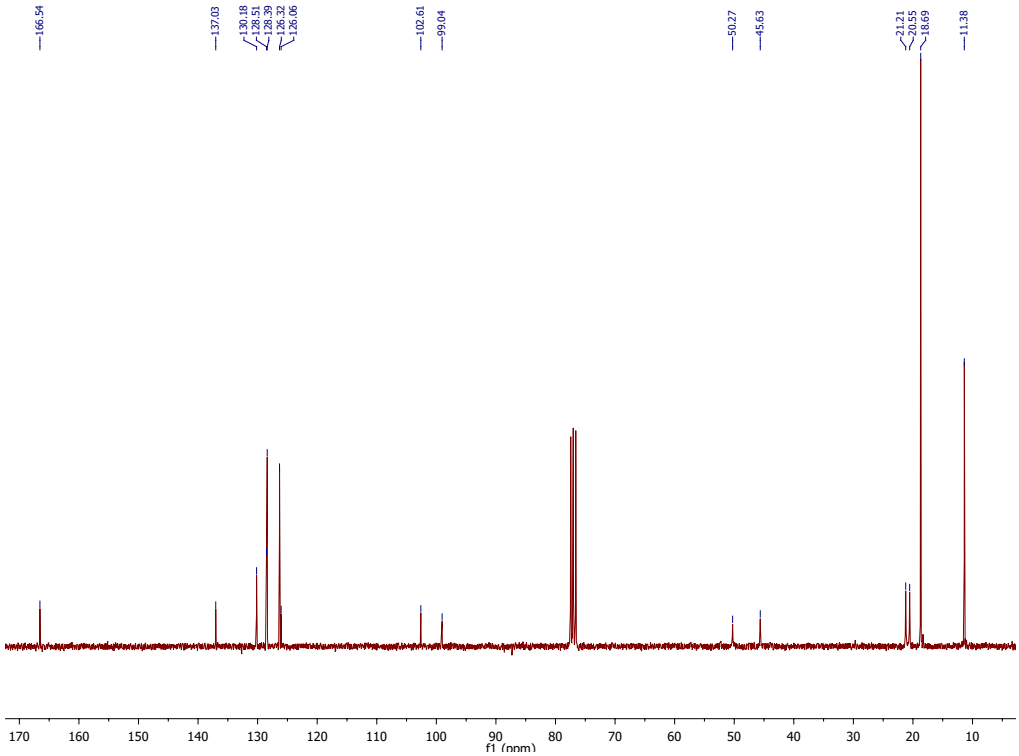


(*E*)-*N*,*N*-Diisopropyl-3-(thiophen-2-yl)acrylamide VIII

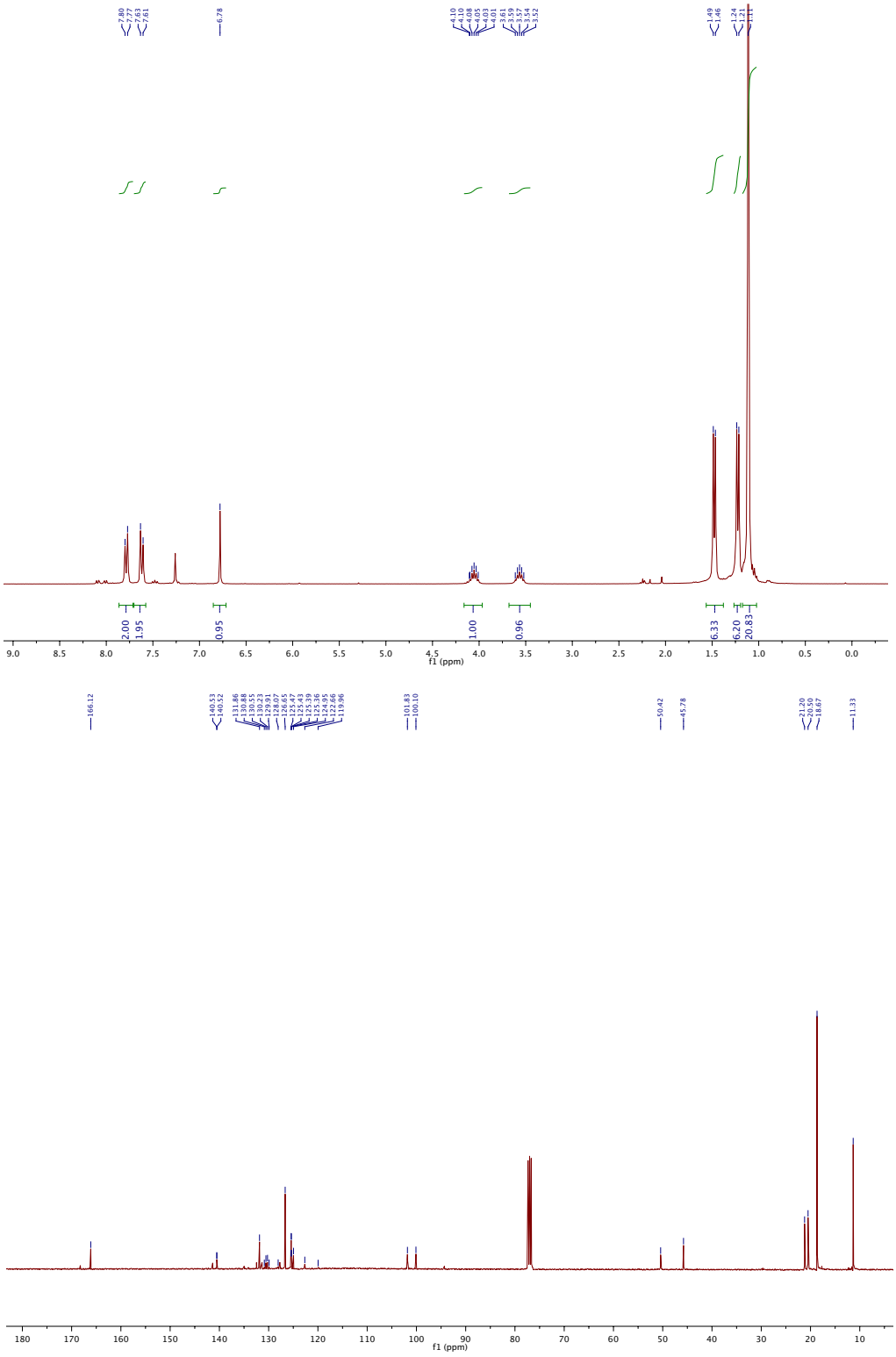


(*Z*)-*N*,*N*-Diisopropyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 5a

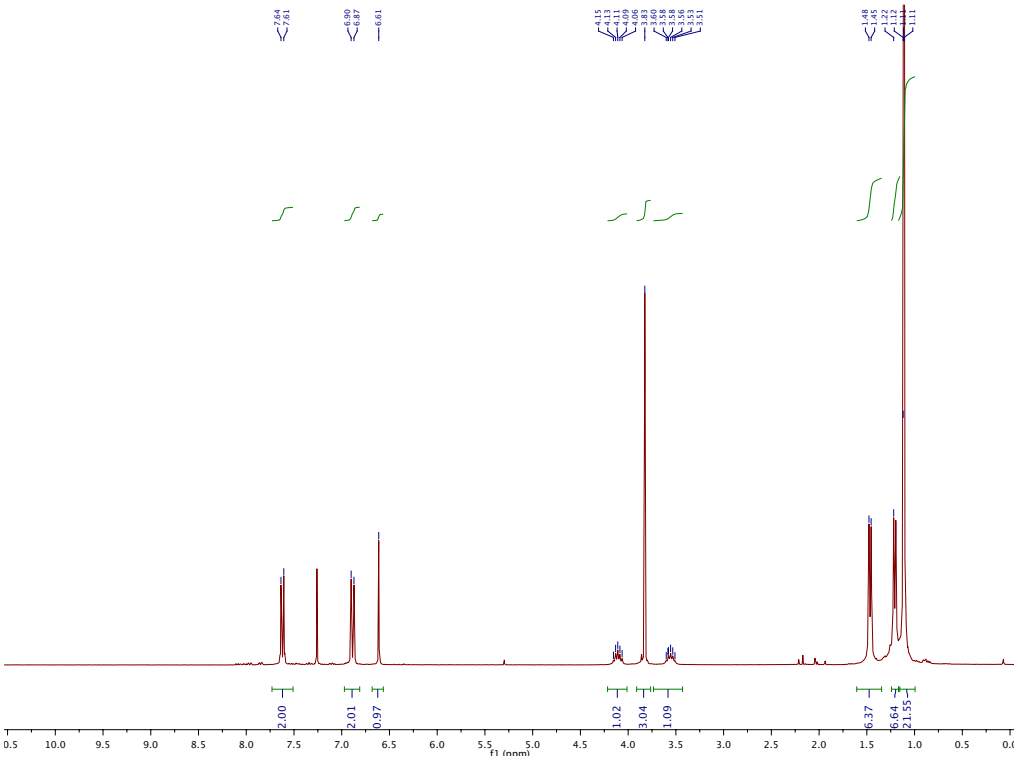


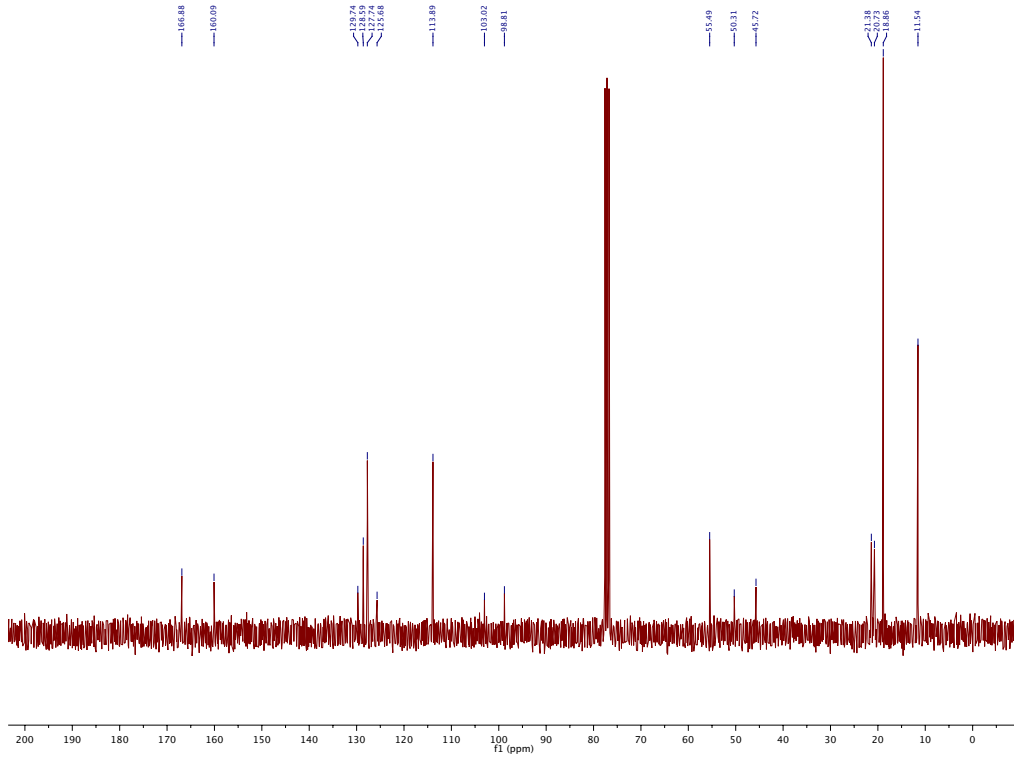


(*Z*)-*N*,*N*-Diisopropyl-3-(4-(trifluoromethyl)phenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5b

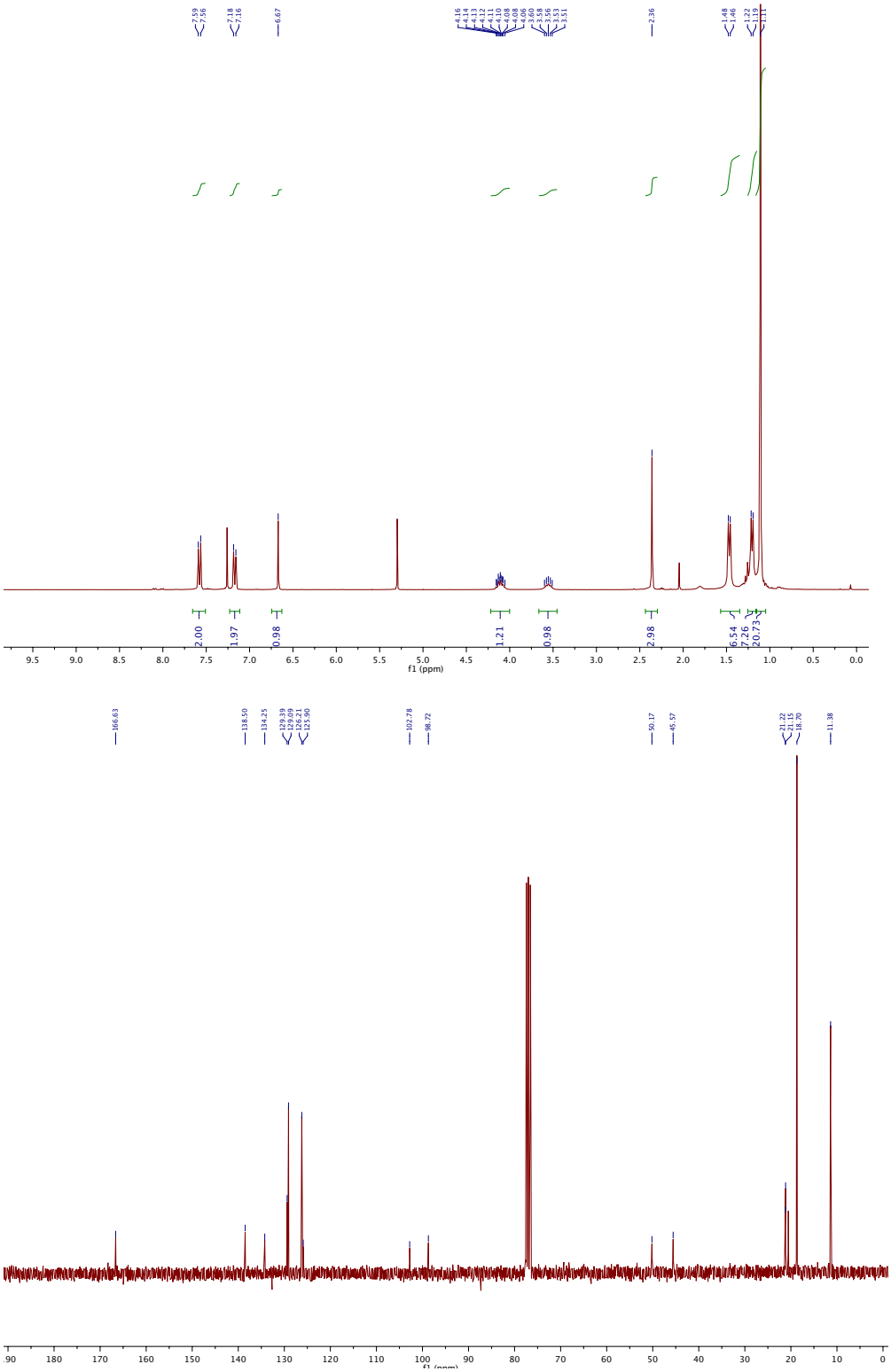


(*Z*)-*N*,*N*-Diisopropyl-3-(4-methoxyphenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5c

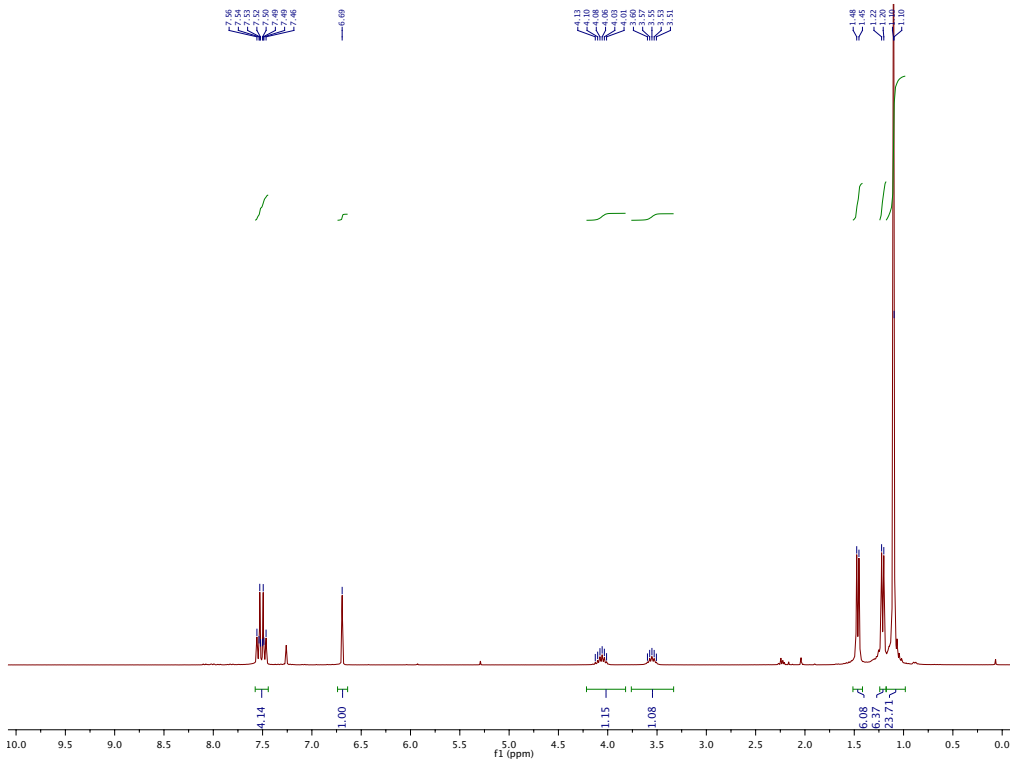


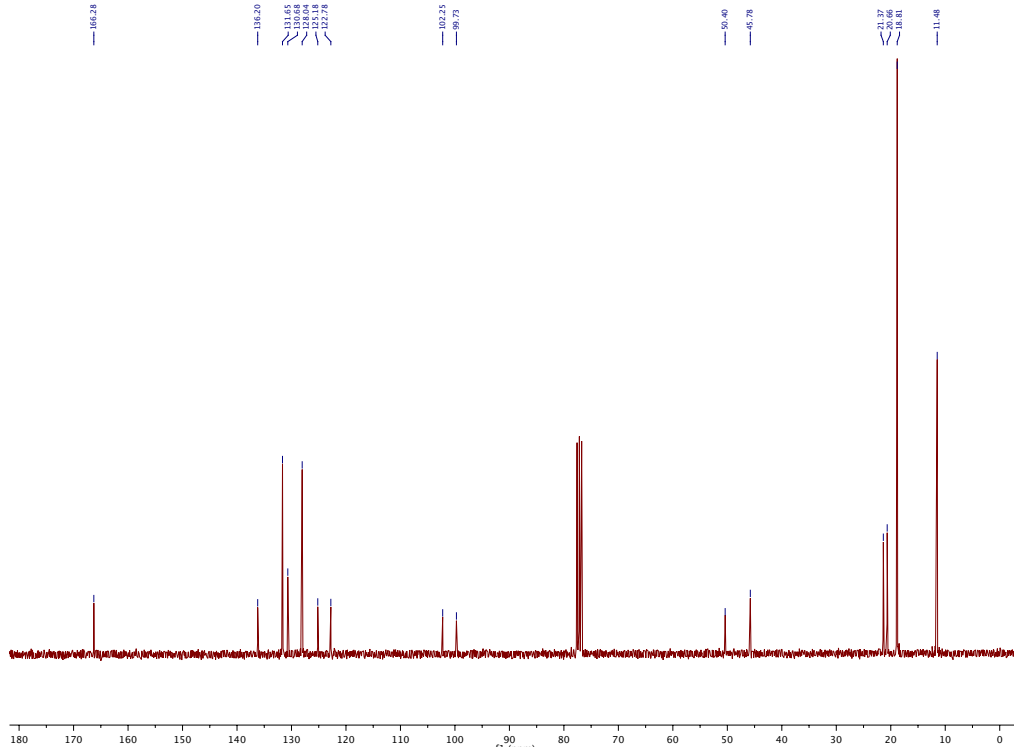


(*Z*)-*N*,*N*-Diisopropyl-3-(*p*-tolyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5d

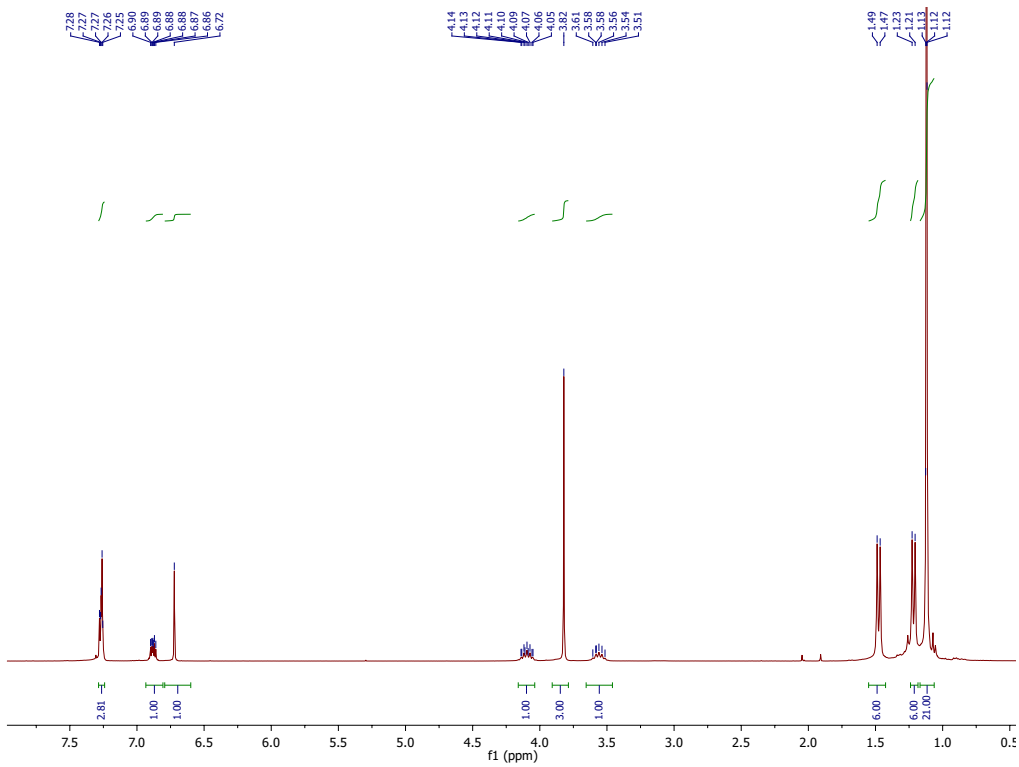


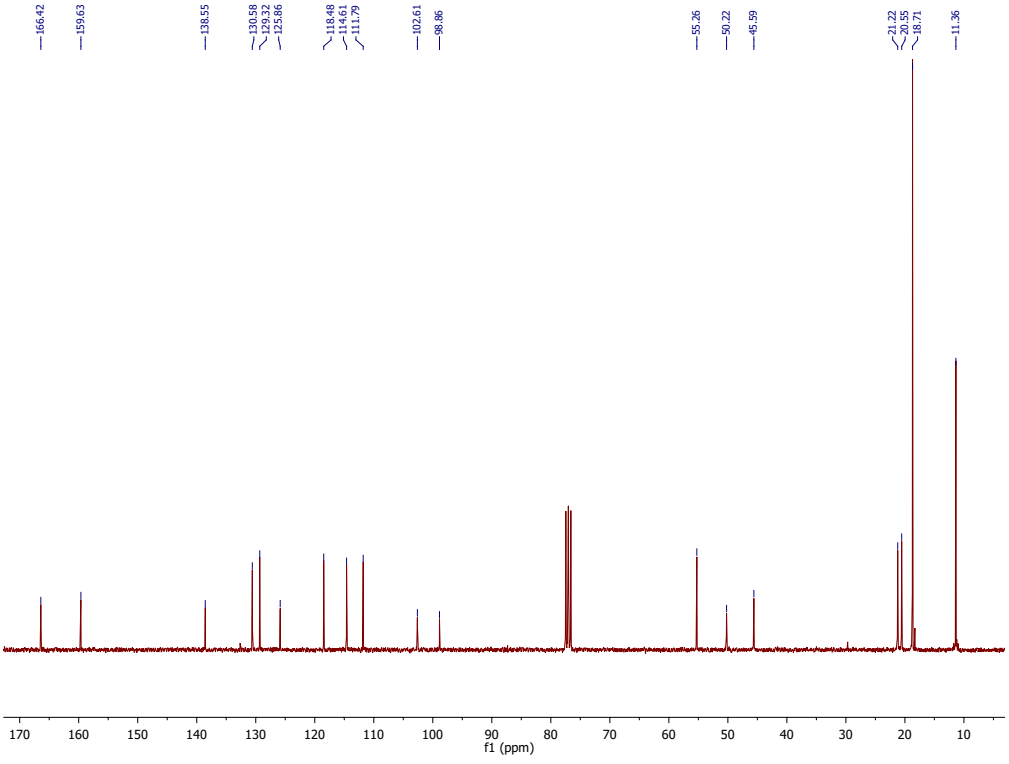
(*Z*)-3-(4-Bromophenyl)-*N*,*N*-diisopropyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 5e





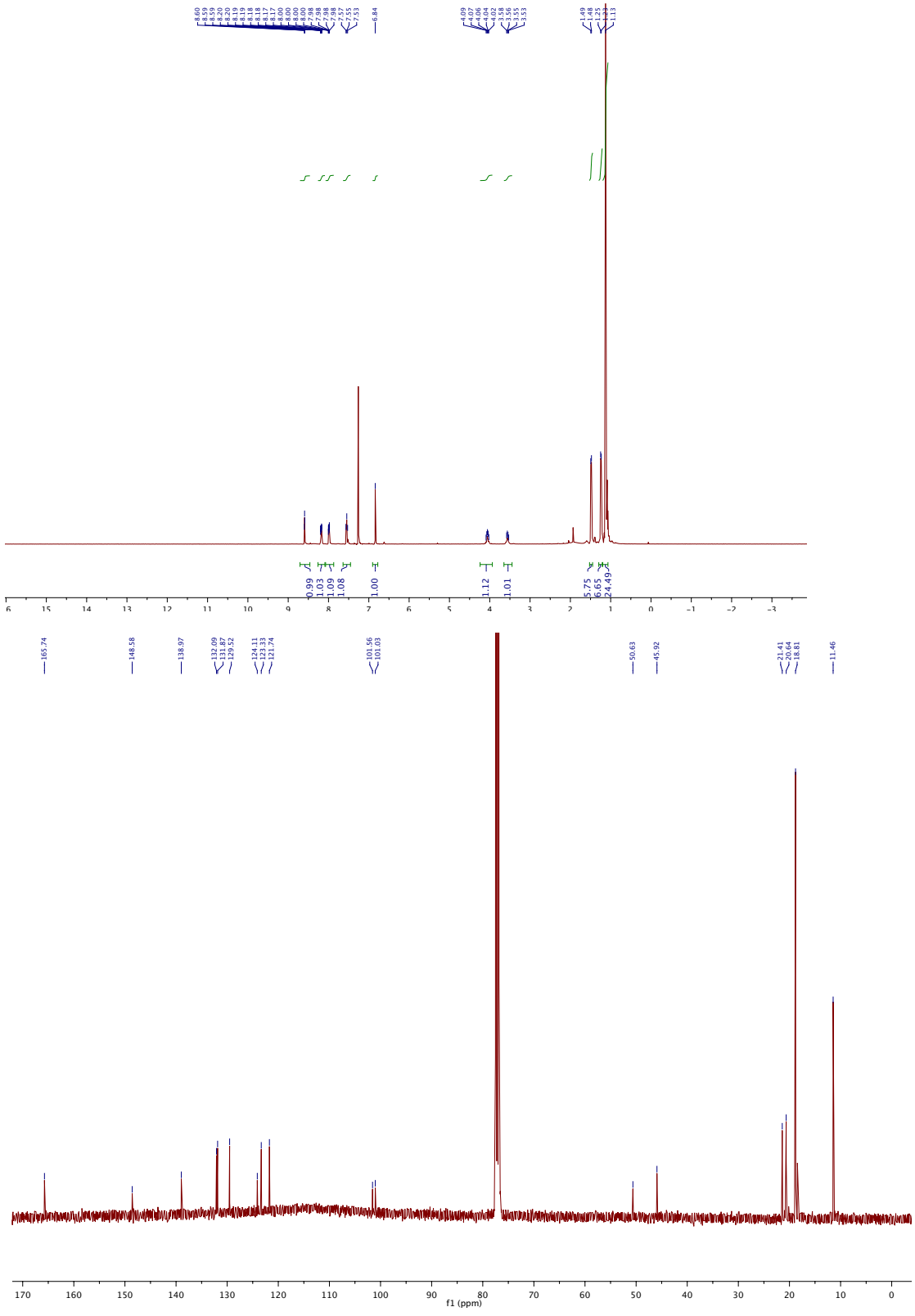
(*Z*)-*N*,*N*-Diisopropyl-3-(3-methoxyphenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5f



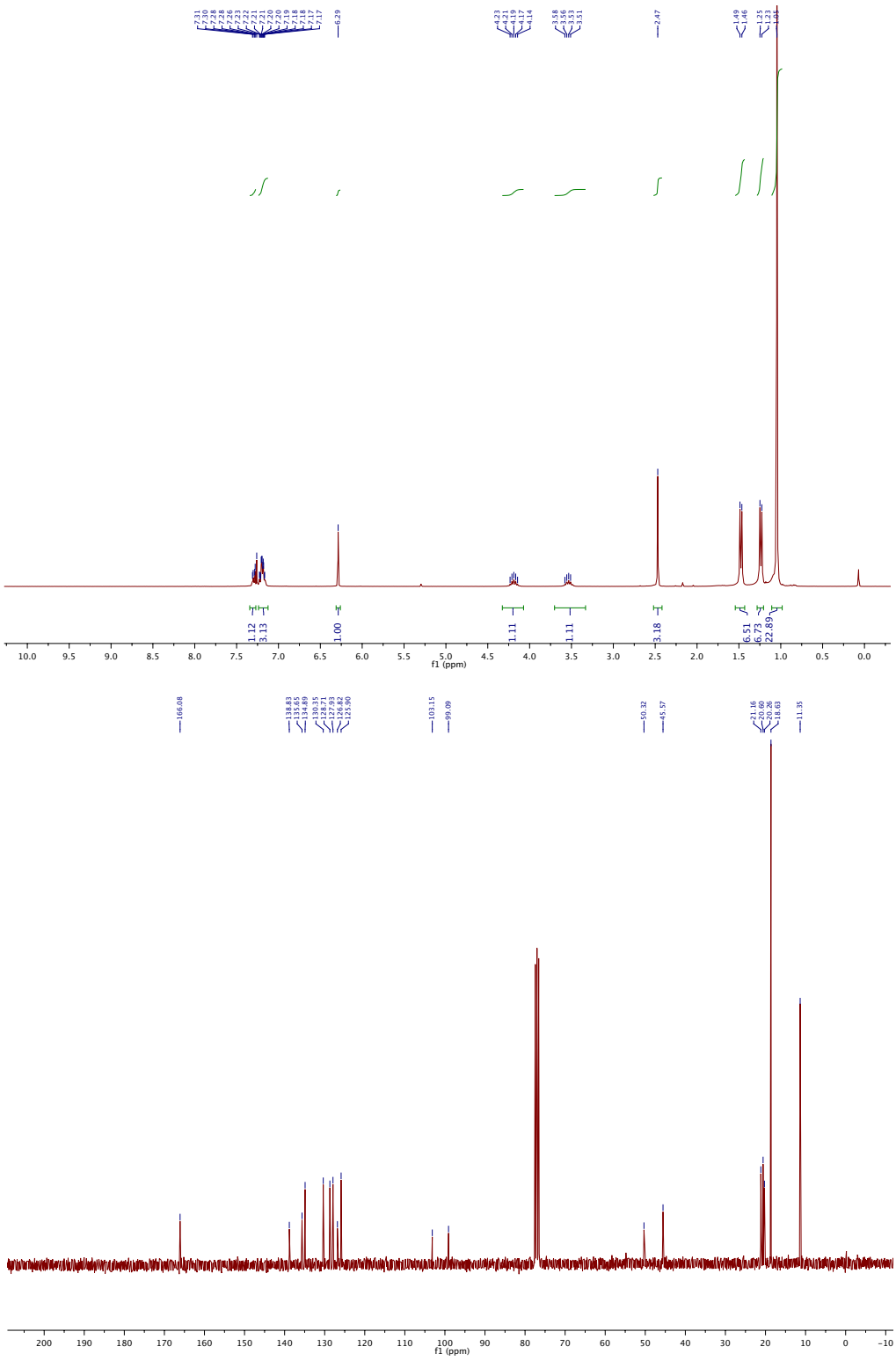


(*Z*)-*N*,*N*-Diisopropyl-3-(3-nitrophenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

5g

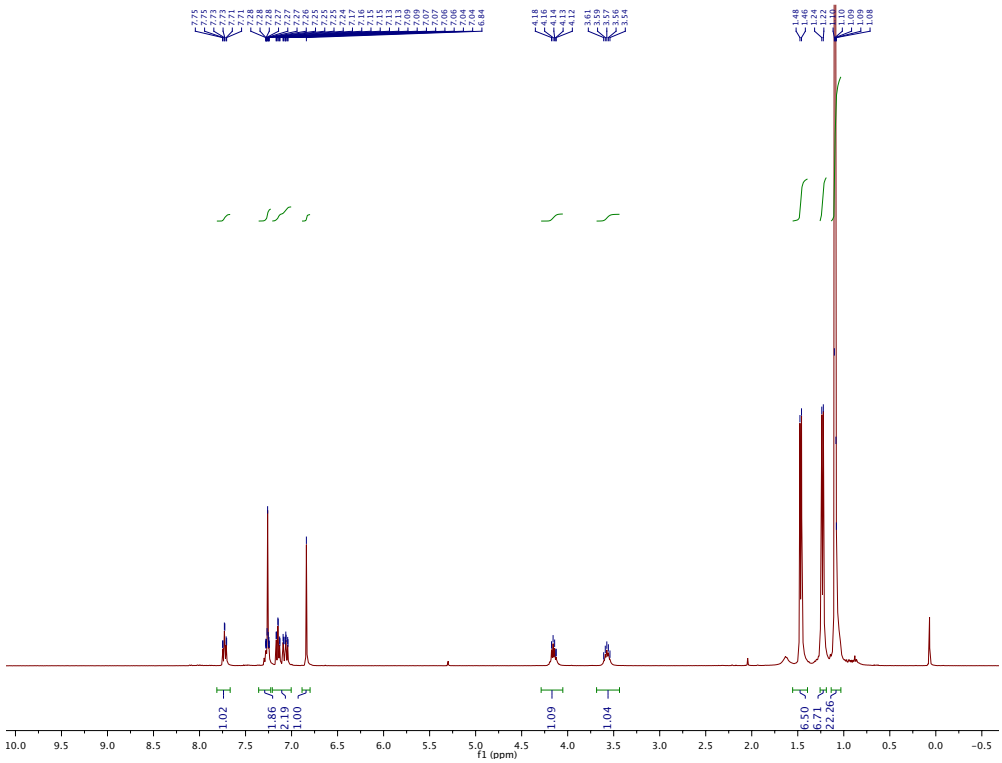


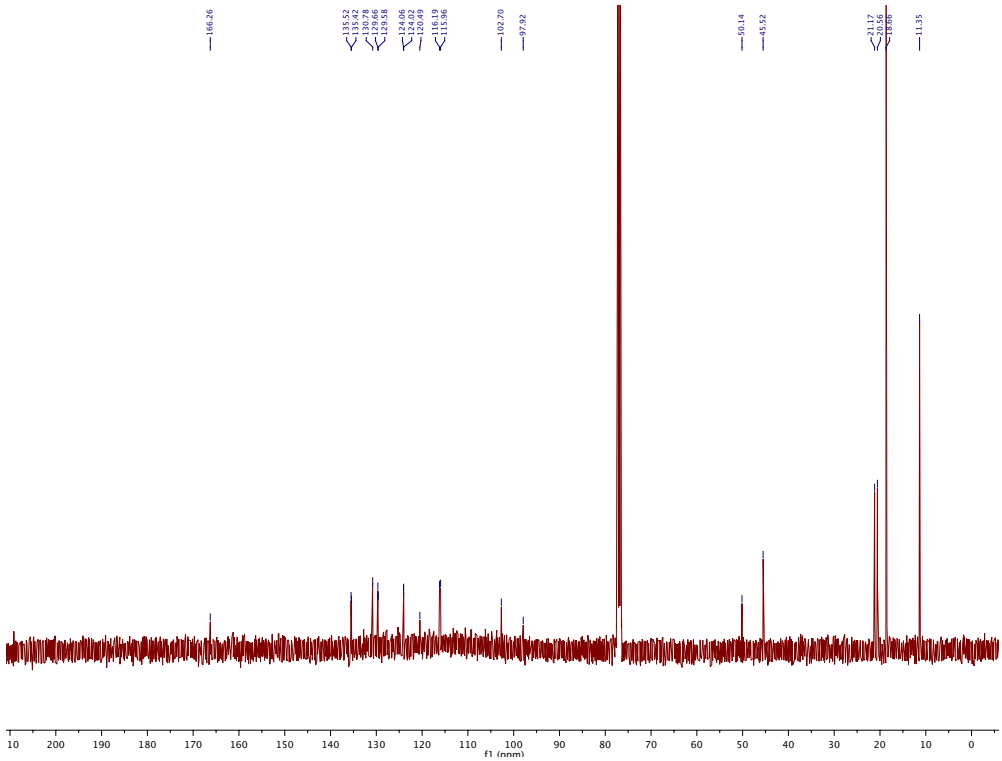
(*Z*)-*N*,*N*-Diisopropyl-3-(*o*-tolyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 5h



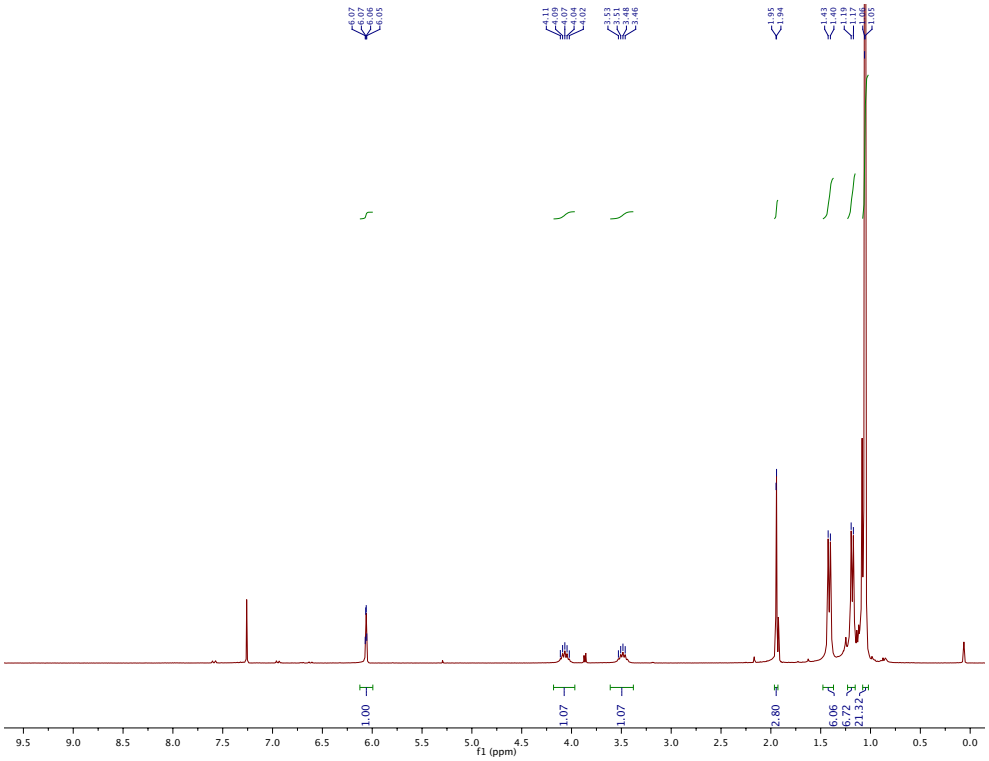
(*Z*)-3-(2-Fluorophenyl)-*N*,*N*-diisopropyl-5-(triisopropylsilyl)pent-2-en-4-ynamide

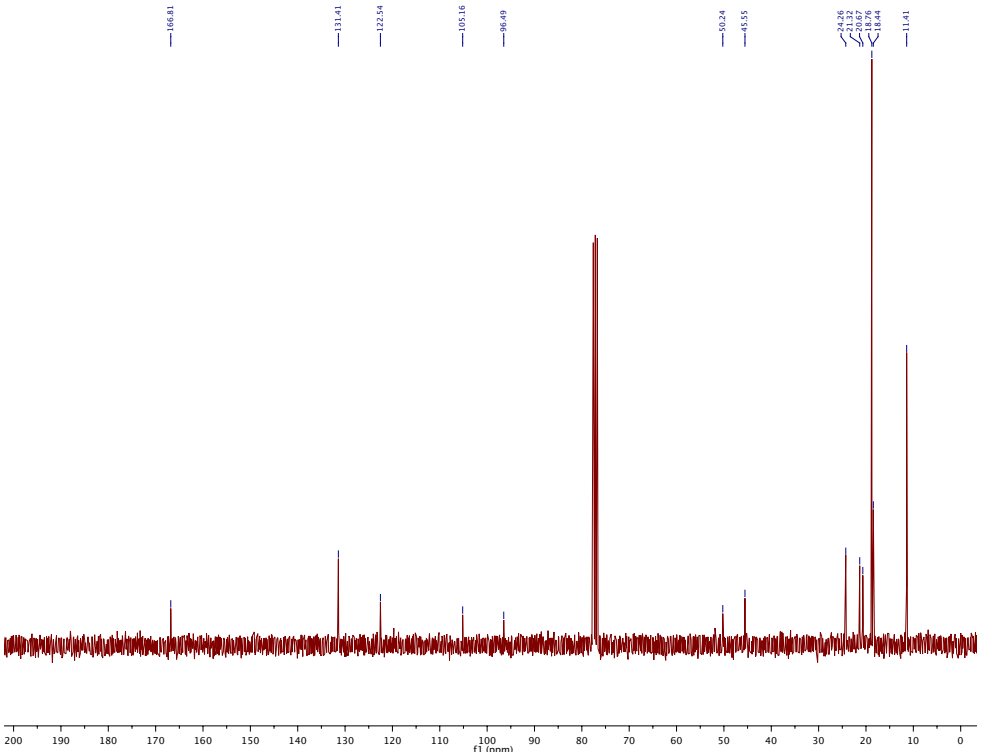
5i



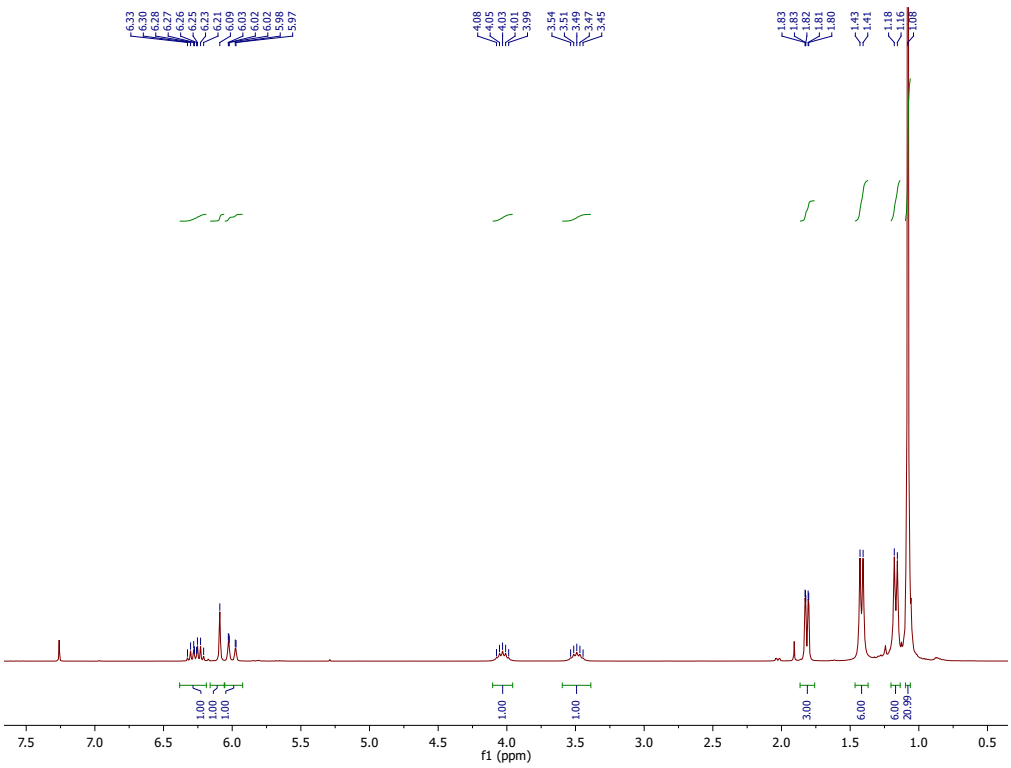


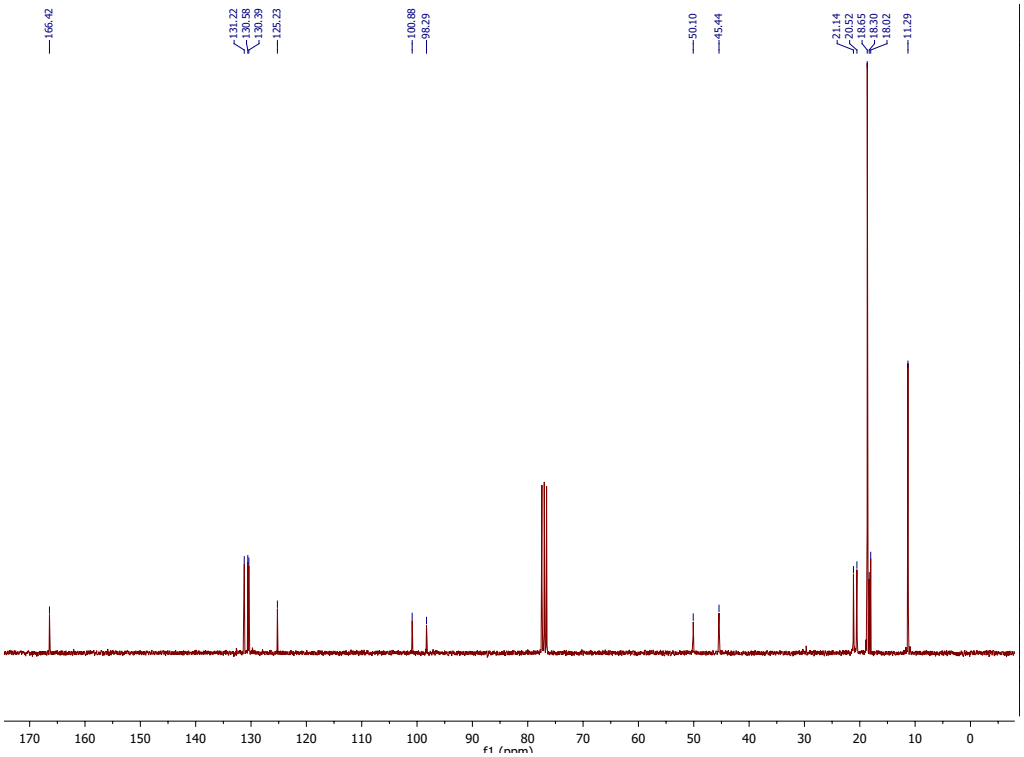
(*Z*)-*N*,*N*-Diisopropyl-3-methyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 6



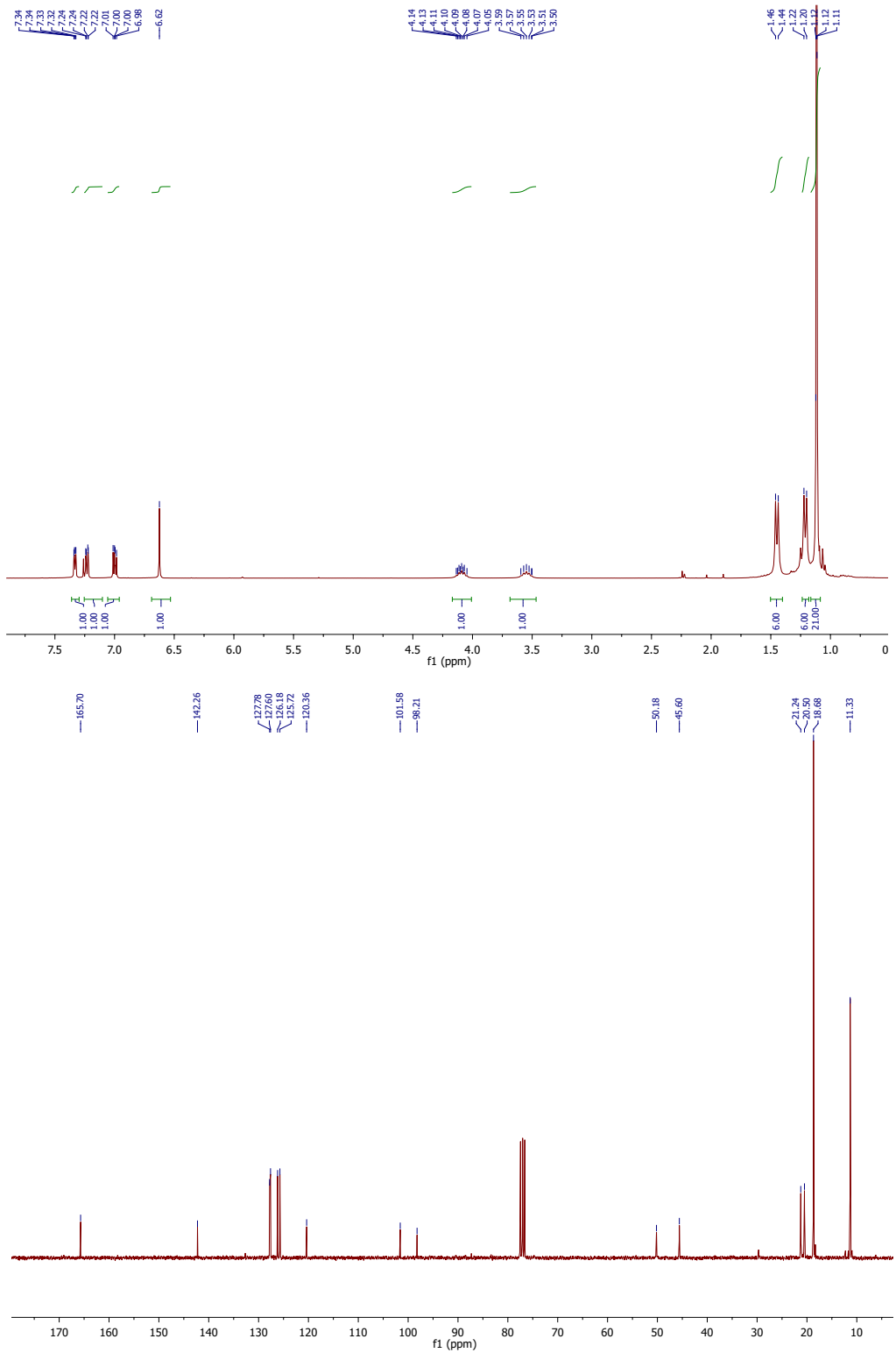


(2*Z*,4*E*)-*N*,*N*-Diisopropyl-3-((triisopropylsilyl)ethynyl)hexa-2,4-dienamide 7

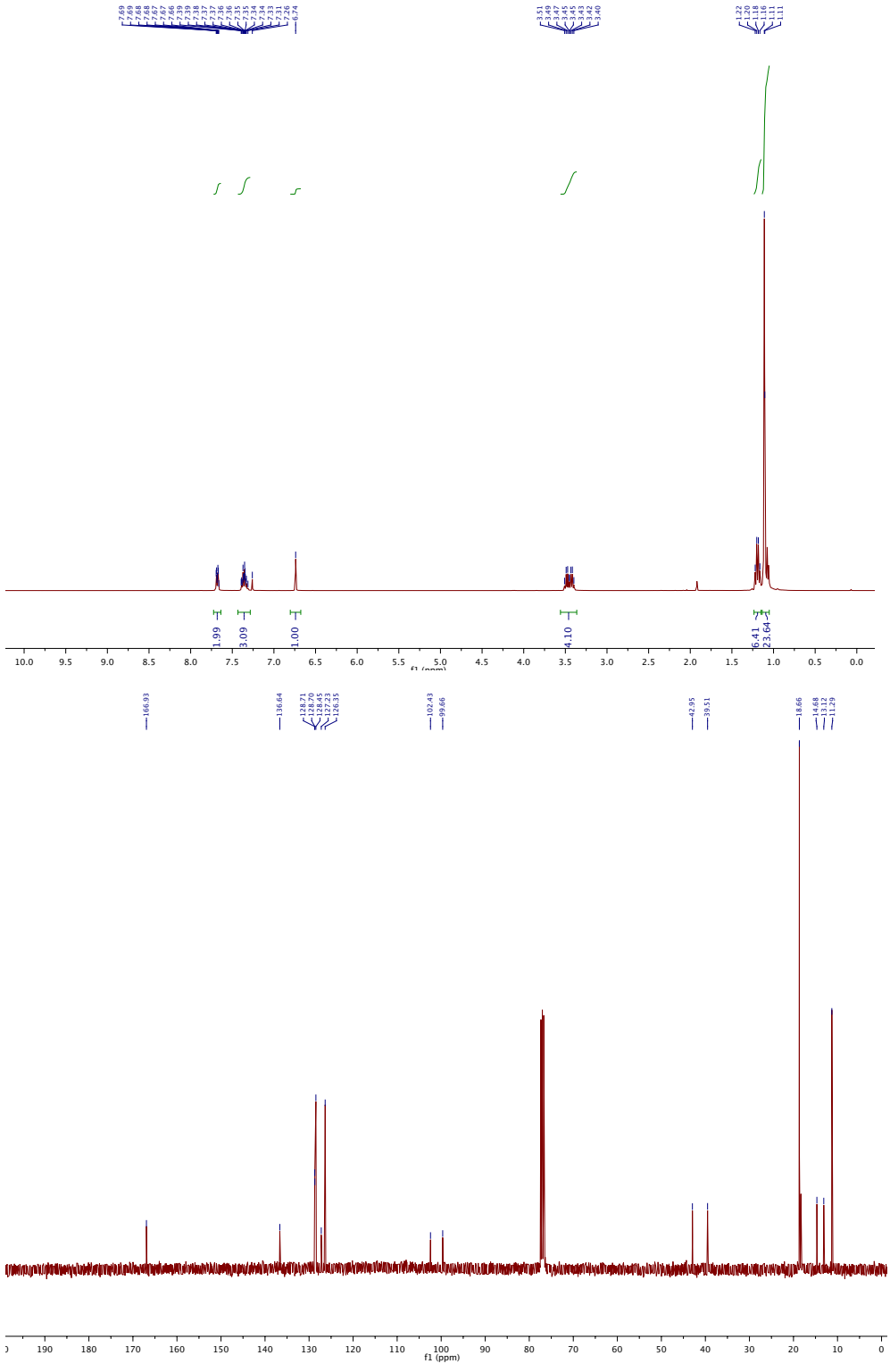




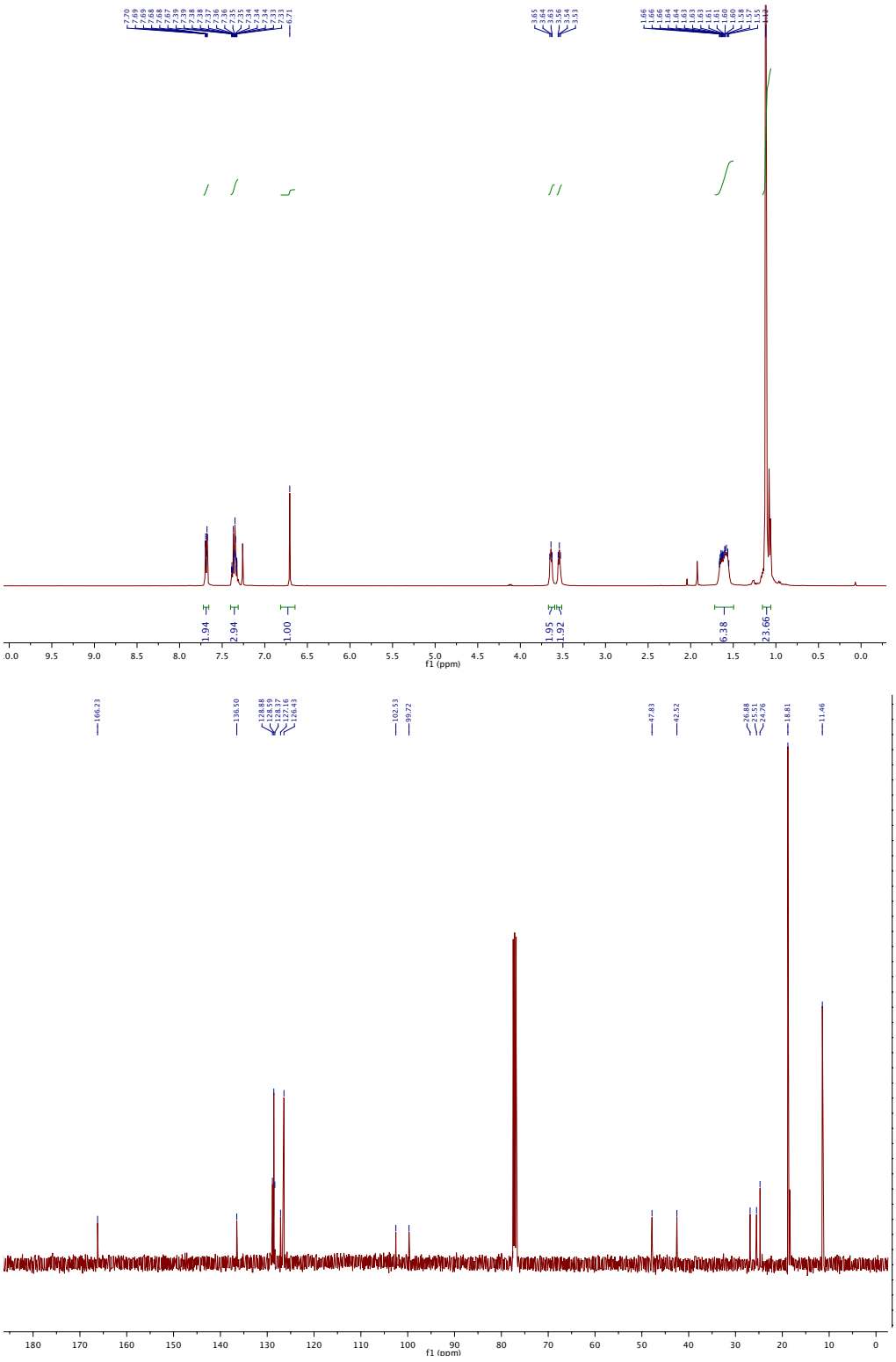
(*E*)-*N*,*N*-Diisopropyl-3-(thiophen-2-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide 10



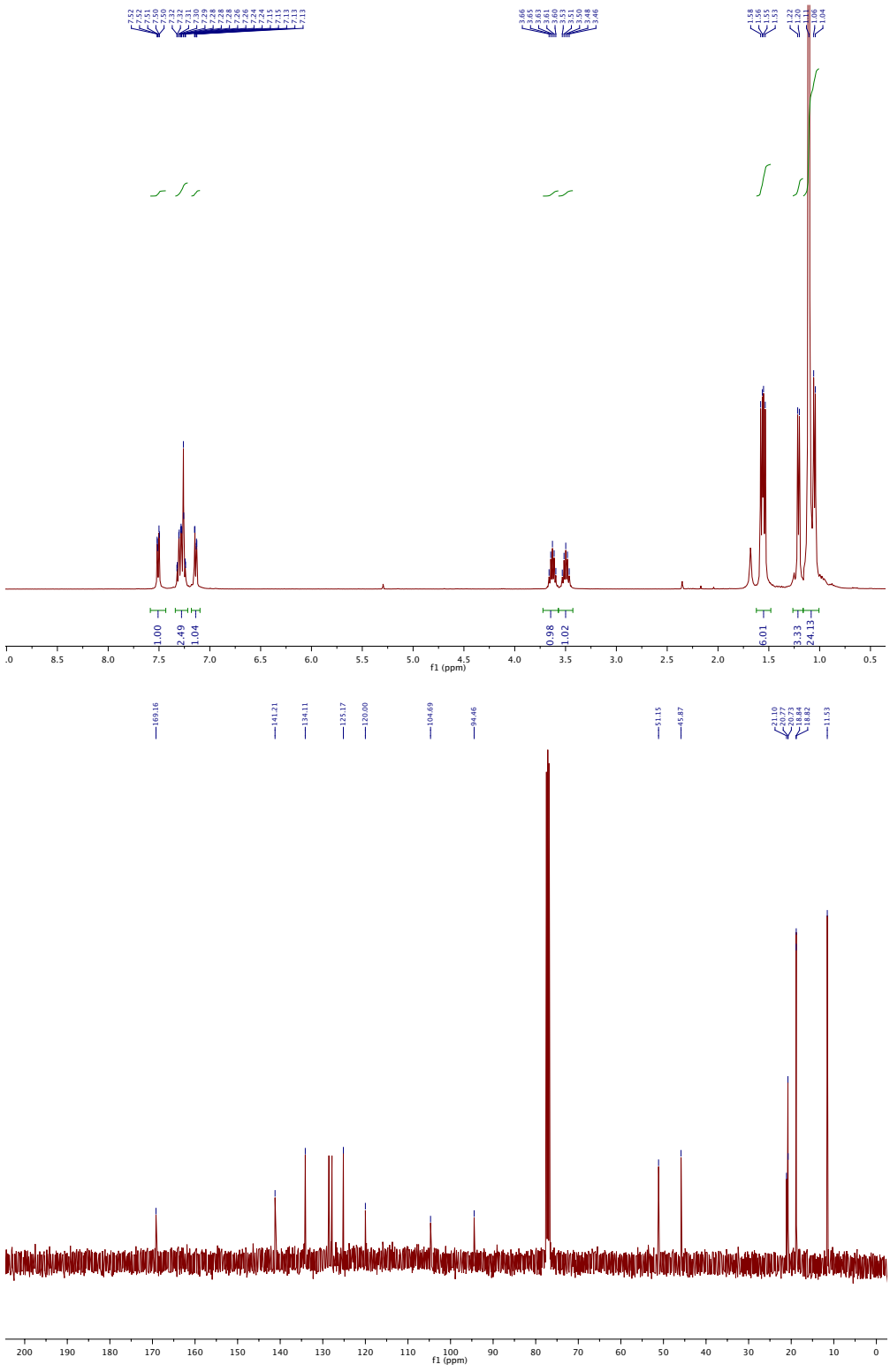
(*Z*)-*N*,*N*-Diethyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide 11



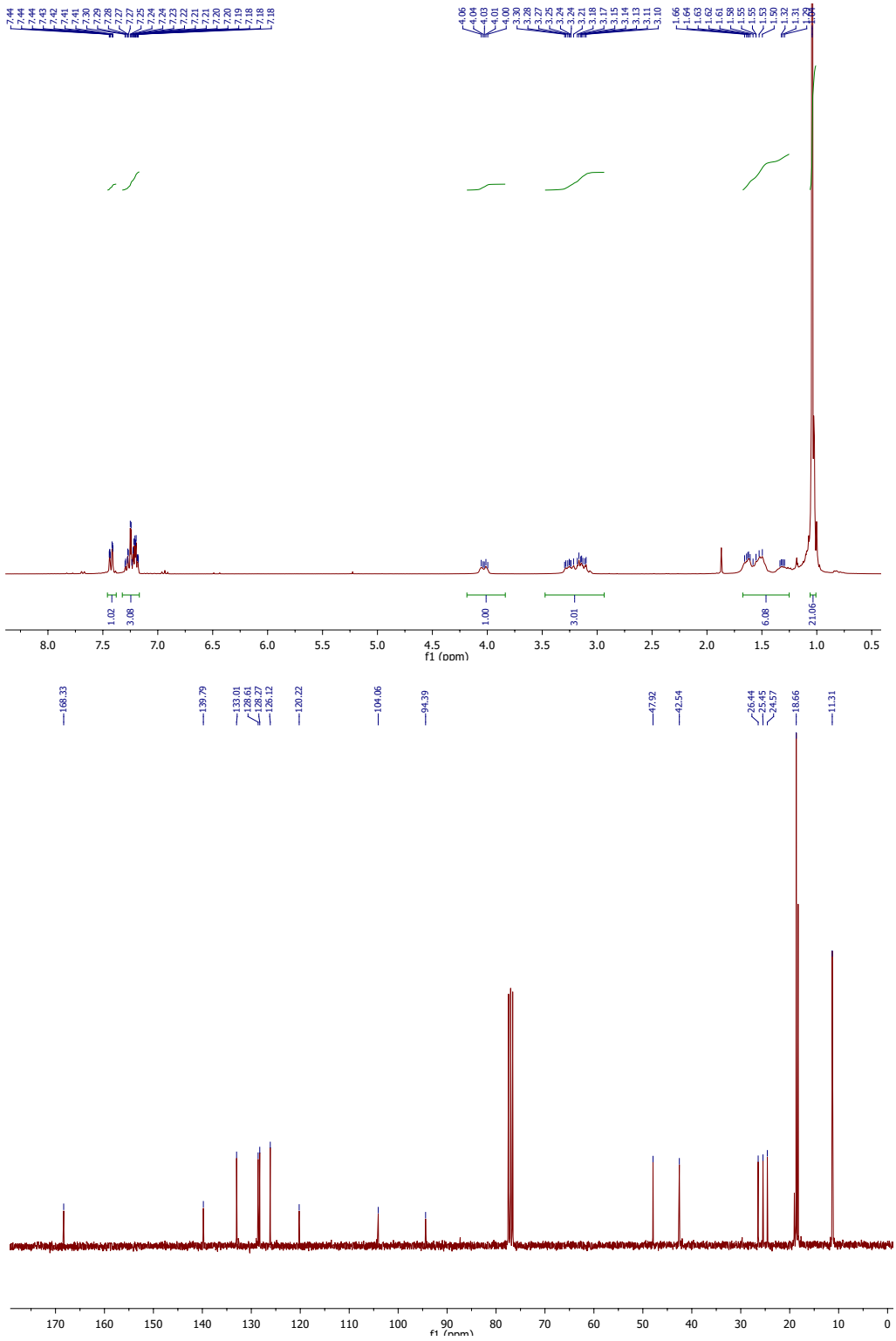
(*Z*)-3-Phenyl-1-(piperidin-1-yl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one 12



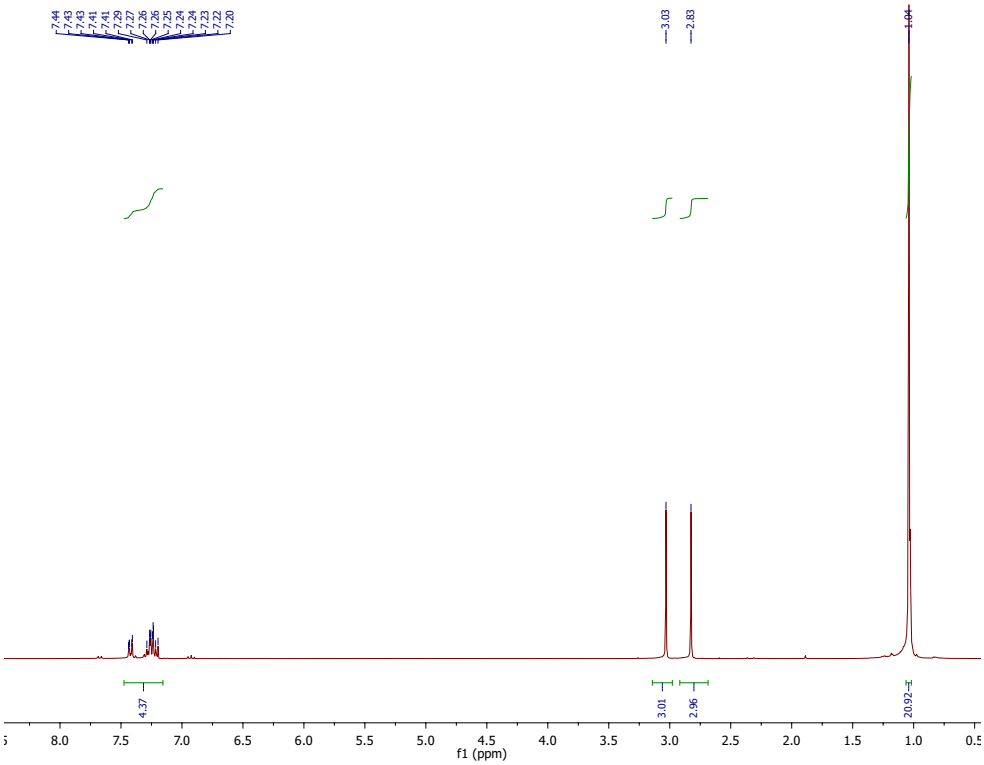
N,*N*-diisopropyl-2-((triisopropylsilyl)ethynyl)benzamide 3

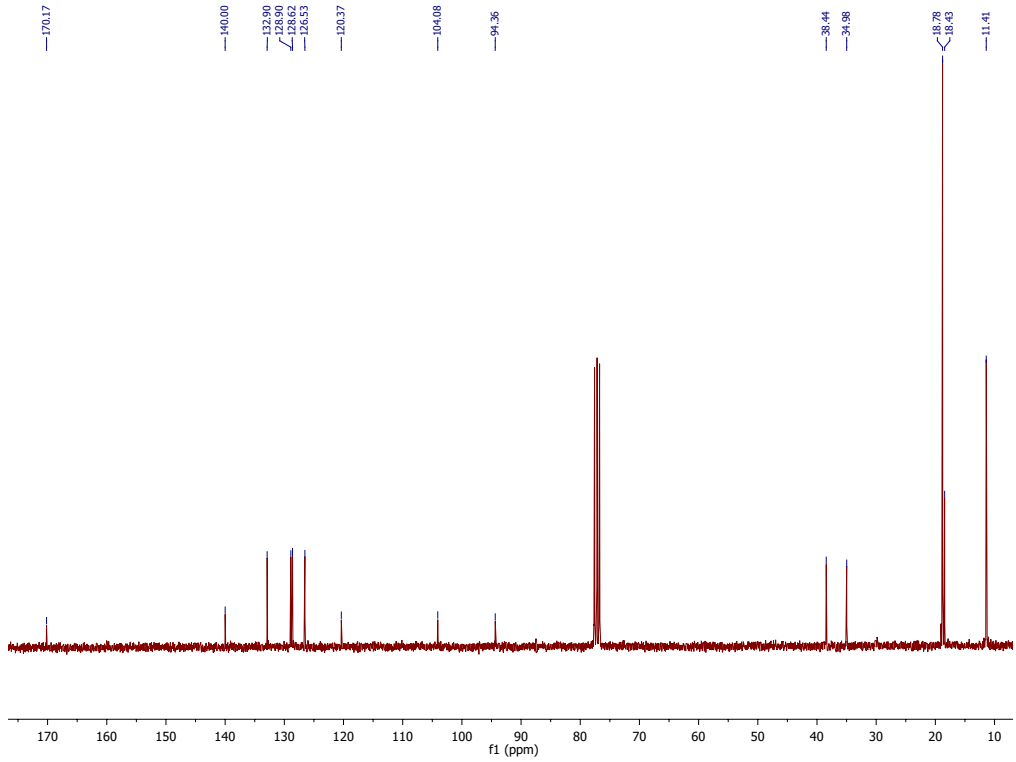


Piperidin-1-yl(2-((triisopropylsilyl)ethynyl)phenyl)methanone 13

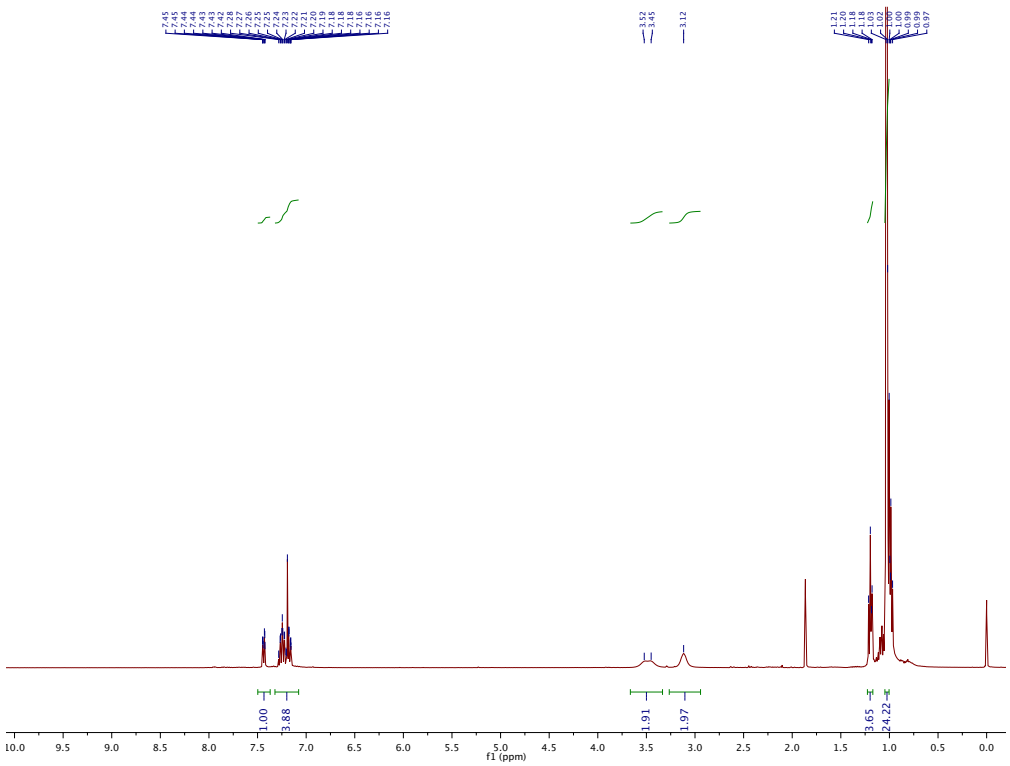


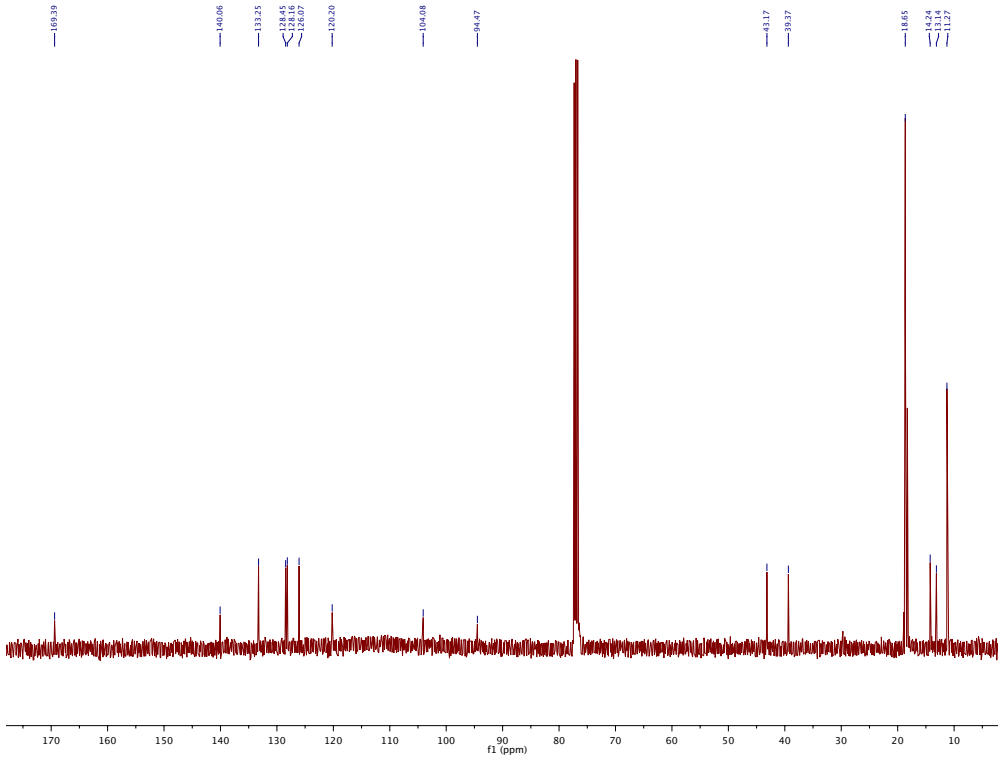
N,*N*-Dimethyl-2-((triisopropylsilyl)ethynyl)benzamide 14



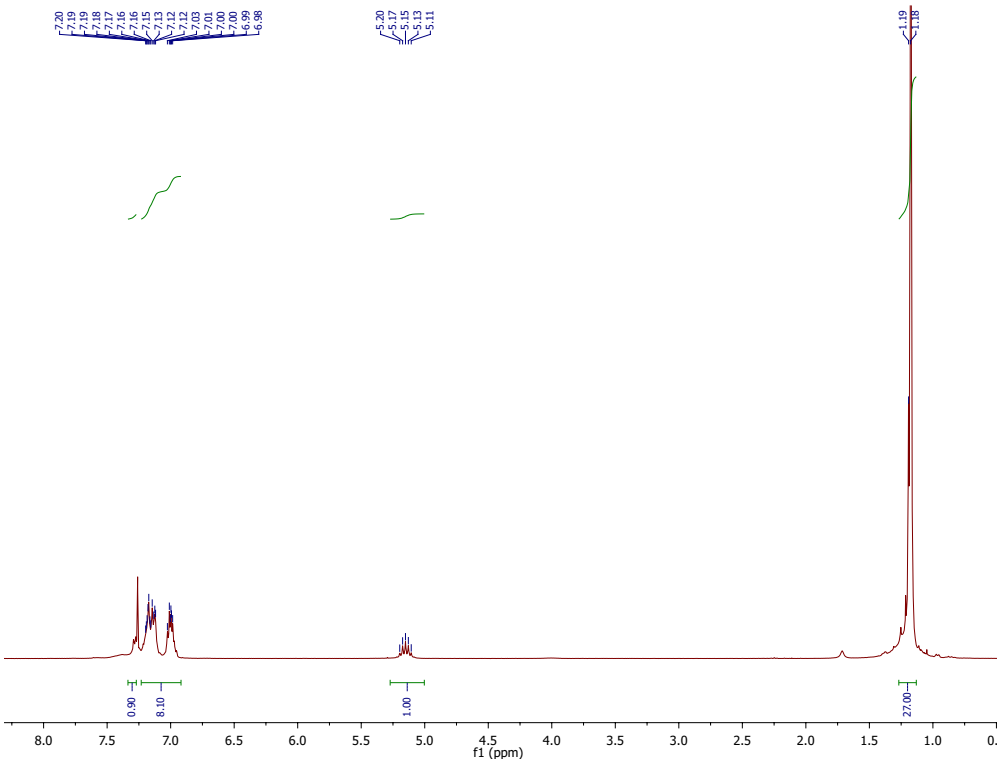


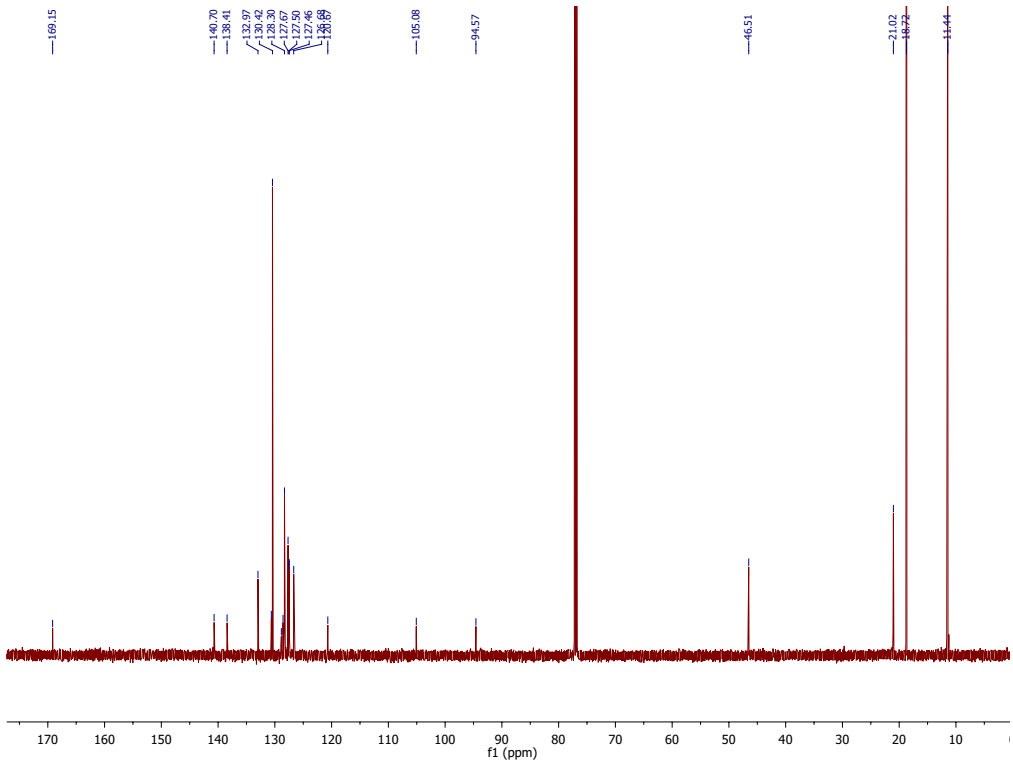
N,*N*-Diethyl-2-((triisopropylsilyl)ethynyl)benzamide 15



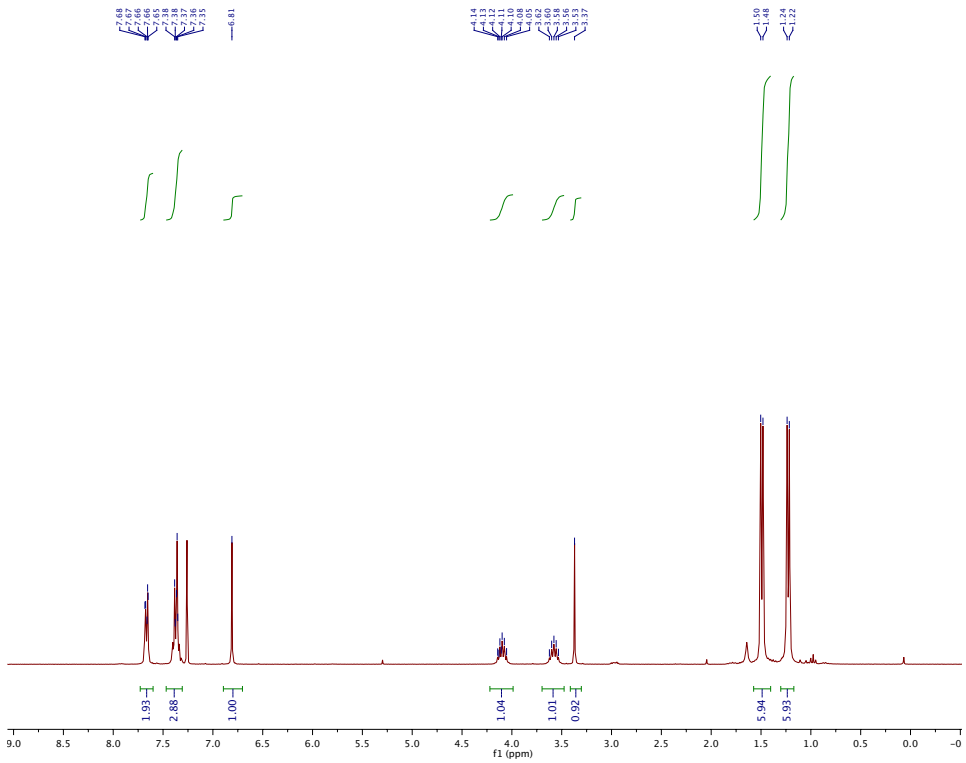


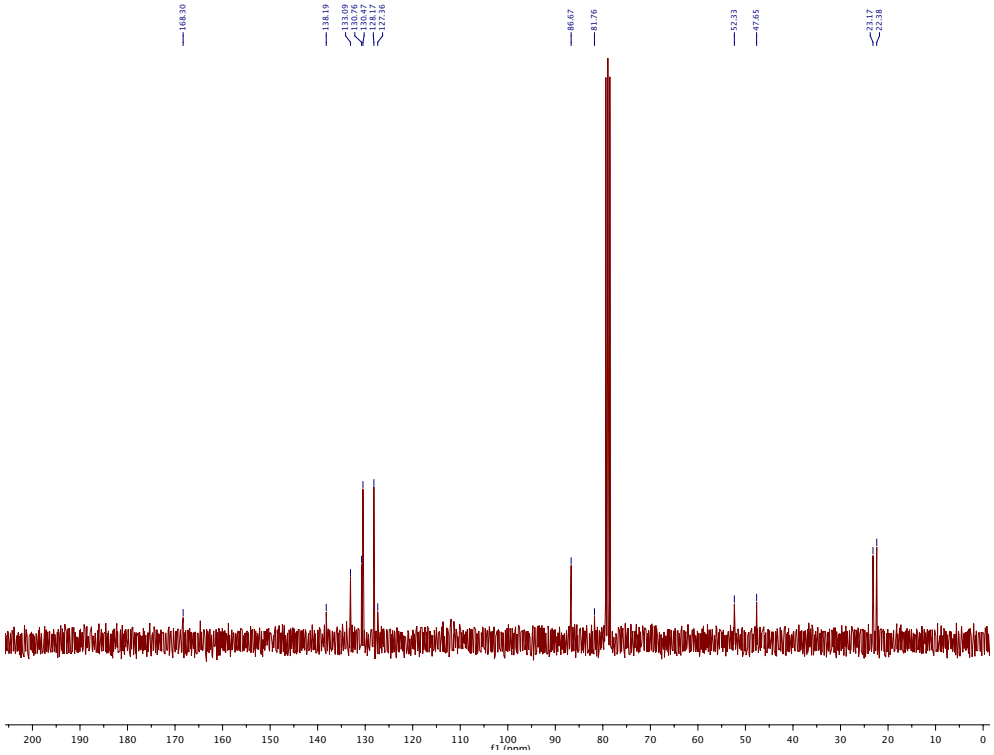
N-Isopropyl-*N*-phenyl-2-((triisopropylsilyl)ethynyl)benzamide 16



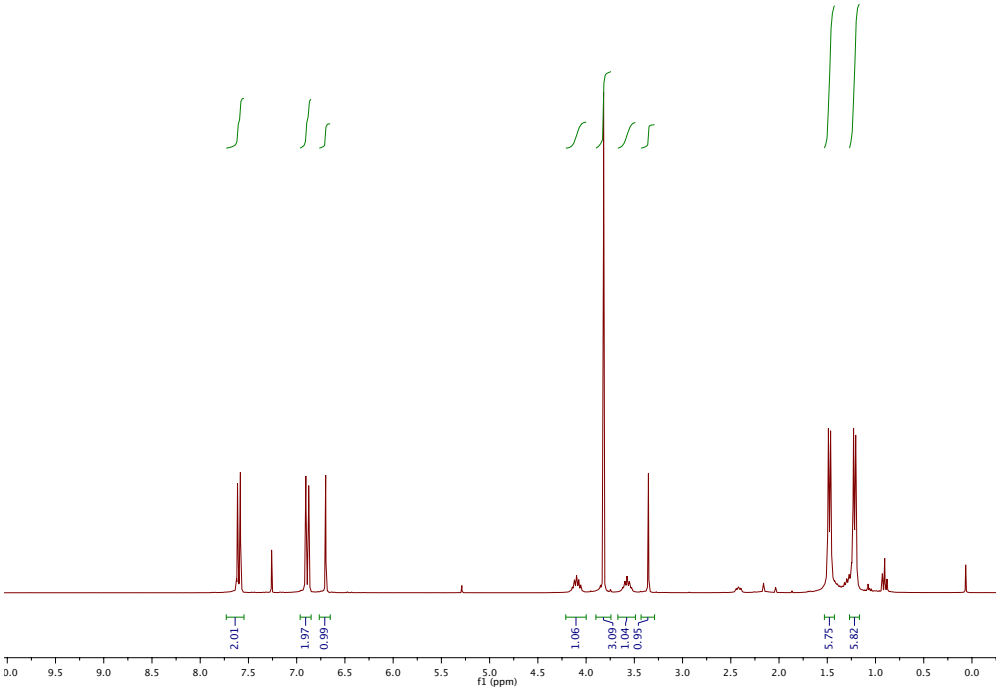


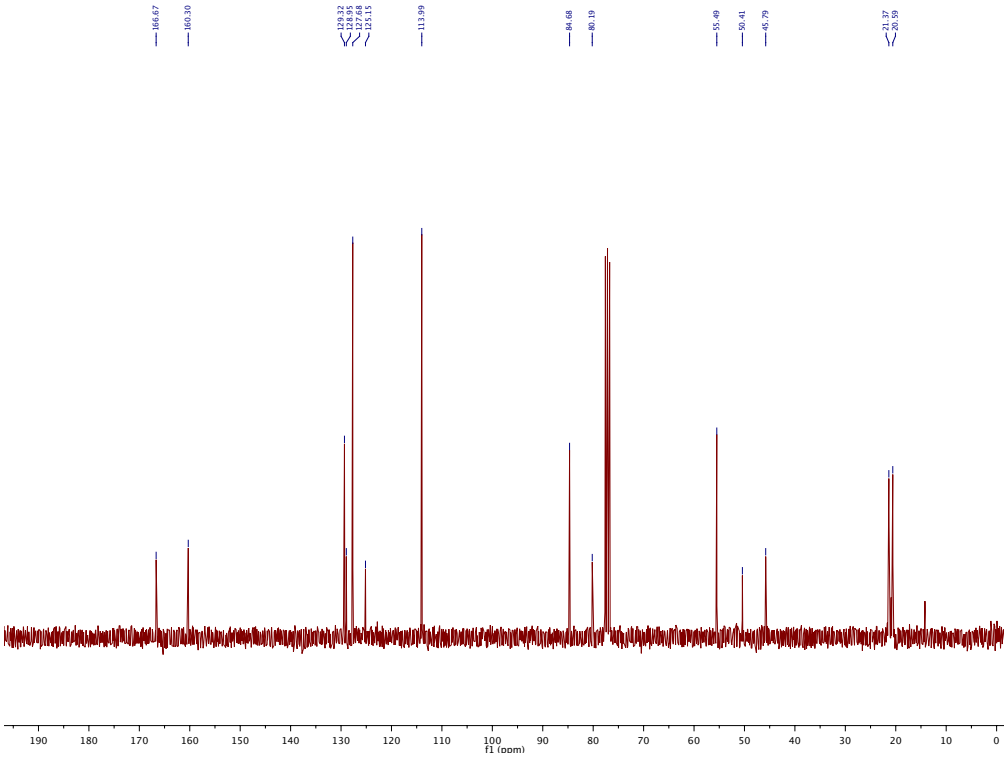
(*E*)-*N*,*N*-Diisopropyl-3-phenylpent-2-en-4-ynamide 18



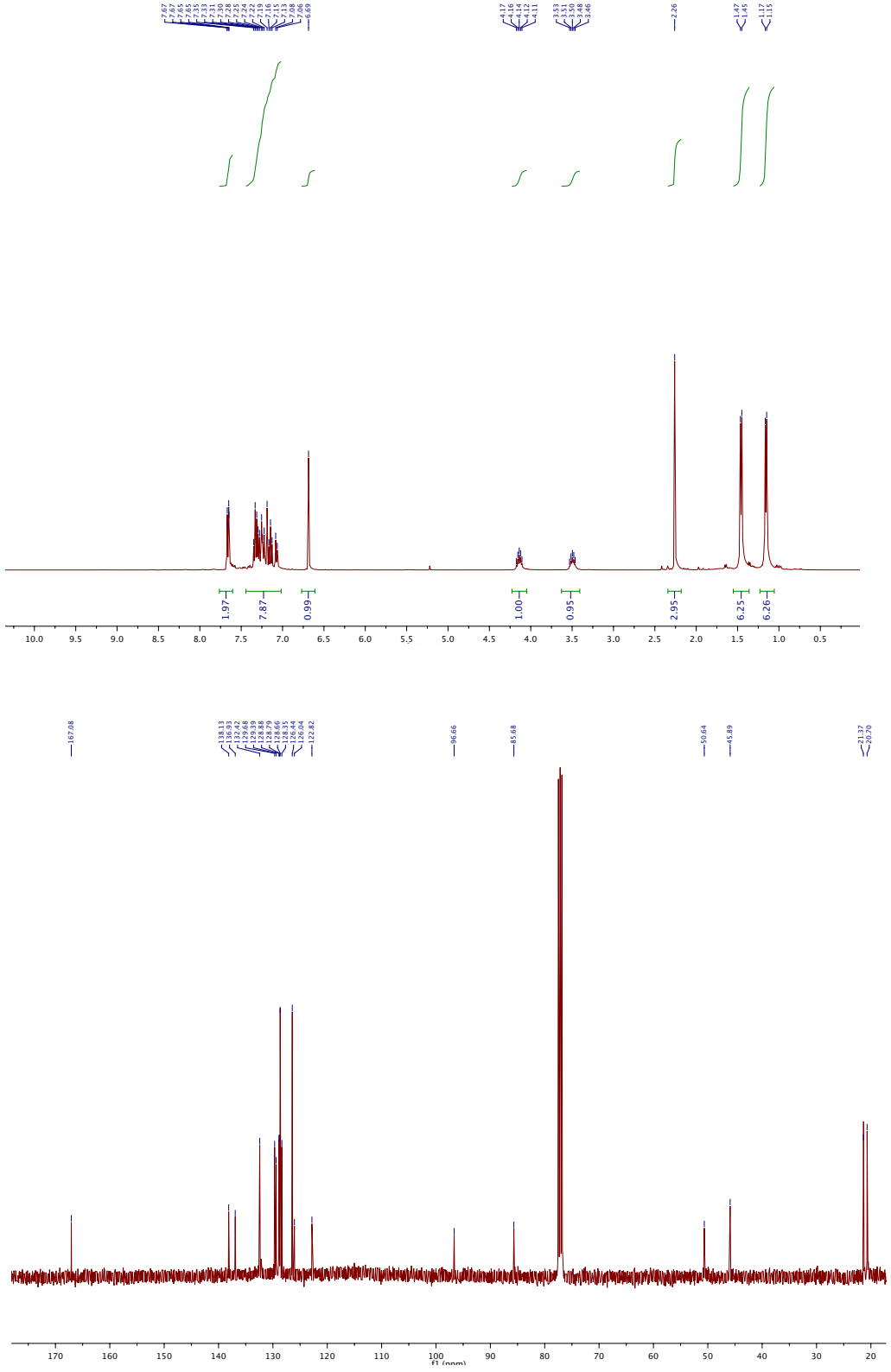


(*E*)-*N*,*N*-Diisopropyl-3-(4-methoxyphenyl)pent-2-en-4-ynamide 19





(*Z*)-*N*,*N*-Diisopropyl-3-phenyl-5-(*o*-tolyl)pent-2-en-4-ynamide 20



(2*Z*,4*E*)-5-(Benzo[*d*][1,3]dioxol-5-yl)-1-(piperidin-1-yl)-3-((triisopropylsilyl)ethynyl)penta-2,4-dien-1-one 22