Zn(II) Chloride-Catalyzed Direct Coupling of Various Alkynes with Acetals: Facile and Inexpensive Access to Funcionalized Propargyl Ethers

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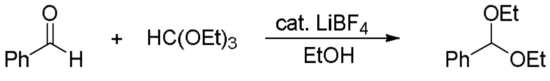
Supporting Information

General. New compounds were characterized by ^{1}H, ^{13}C, DEPT, COSY, HMQC, HMBC, IR, MS, HRMS, and elemental analysis. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were obtained with TMS as an internal standard. IR spectra were recorded as thin films. All reactions were carried out under nitrogen. GLC analyses were performed with FID using a capillary column (Rxi-5SiI MS; 30 m × 0.25 mm) and hexadecane as an internal standard. Column chromatography was performed on silica gel (MERK C60 or Fuji Silysia FL100DX). Bulb-to-Bulb distillation (Kugelrohr) was accomplished at the oven temperature and pressure indicated. Recycle GPC was performed with $CHCl_3$ as the eluent. Yields were determined by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard.

Materials. Dehydrated toluene and tetrahydrofuran were purchased and used as obtained. Catalysts examined in Table 1 were also purchased from commercial sources. Benzaldehyde dimethyl acetal (**1a**), *p*-anisaldehyde dimethyl acetal (**1e**), and 1,1-dimethoxy hexane (**1i**) were purchased from commercial sources. Benzaldehyde diethyl acetal (**1b**) was prepared by known method.[1] Other acetals such as **1c**, **1d**[1], **1f**[1], **1g**[2], and **1h**[3] were synthesized by known methods. Alkynes **2a-2k** and other reagents were also purchased from commercial sources.

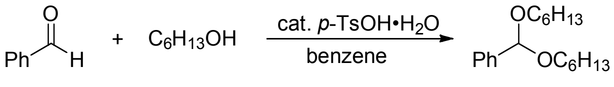
Preparation of benzaldehyde diethyl acetal (1b)[1]



1b

To a solution of benzaldehyde (3.25 g, 30.6 mmol) and $LiBF_4$ (0.0900 g, 0.961 mmol) in EtOH (15 mL) was added triethyl orthoformate (5.17 g, 34.9 mmol). The mixture was stirred at 50 °C overnight and quenched by saturated $NaHCO_3$ aq (30 mL) followed by extraction with ethyl acetate (3 x 50 mL). The collected organic layer was washed with brine (2 x 30 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product **1c** (4.39g, 80%) whose analytical data agreed with previous report.[4] ^1H and ^{13}C NMR charts are listed in Product Data.

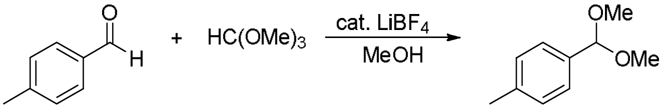
Preparation of benzaldehyde dihexyl acetal (1c)



1c

To a solution of 1-hexanol (65.3 mmol, 6.67 g) and benzaldehyde (30.1 mmol, 3.19 g) in benzene (25 mL) was added *p*-TsOH (0.294 mmol, 0.0560 g). The mixture was heated at 90 °C for 27 h removing H_2O with Dean-Stark apparatus. The reaction mixture was quenched with saturated $NaHCO_3$ aq (50 mL) and extracted with ethyl acetate (3 x 50 mL). The collected organic layer was dried (MgSO4) and concentrated to give a crude product. The product was purified by distillation under reduced pressure to afford the product **1c** as a colorless oil (6.45 g, 73%). bp: 113 °C/0.093 torr IR (neat): 2931, 1103 (C-O-C) cm^{-1} ^1H NMR: (400 MHz, $CDCl_3$) 7.47 (d, $J = 7.2$ Hz, 2H, *o*), 7.38-7.26 (m, 3H, Ar), 5.51 (s, 1H, PhCH), 3.56-3.24 (m, 4H, OCH_2 x 2), 1.60 (quint, $J = 7.0$ Hz, 4H, OCH_2CH_2 x 2), 1.40-1.26 (m, 12H, $OCH_2CH_2(CH_2)_3$ x 2), 0.88 (t, $J = 6.8$ Hz, 6H, CH_3 x 2) ^{13}C NMR: (100 MHz, $CDCl_3$) 139.15 (-, *i*), 128.16 (+), 128.09 (+), 126.68 (+, *o*), 101.52 (+, PhCH), 65.45 (-, OCH_2), 31.67 (-, $CH_3CH_2CH_2$), 29.72 (-, OCH_2CH_2), 25.95 (-, $OCH_2CH_2CH_2$), 22.62 (-, CH_3CH_2), 14.04 (+, CH_3) MS: (EI, 70 eV) *m/z* 292 (M^+, 0.23), 191 (M^+ - OC_6H_{13}, 100), 107 (76) HRMS: (EI, 70 eV) Calculated ($C_{19}H_{32}O$) 292.2402 (M^+) Found: 292.2405 Analysis: $C_{19}H_{32}O_2$ (292.46) Calcd: C, 78.03; H, 11.03 Found: C, 78.03; H, 10.85

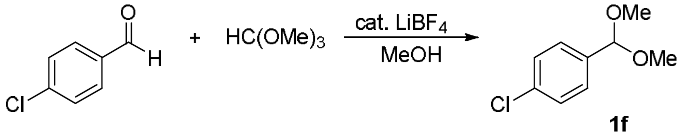
Preparation of *p*-tolualdehyde dimethyl acetal (1d)[1]



1d

To a solution of 4-methylbenzaldehyde (3.81 g, 31.7 mmol) and $LiBF_4$ (0.0914 g, 0.974 mmol) in MeOH (15 mL) was added trimethyl orthoformate (4.25 g, 40.0 mmol). The mixture was refluxed overnight and quenched by saturated $NaHCO_3$ aq (30 mL) followed by extraction with ethyl acetate (3 x 50 mL). The collected organic layer was washed with brine (2 x 30 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product **1d** (4.32 g, 82%) whose analytical data agreed with previous report.[5] ^{1}H and ^{13}C NMR charts are listed in Product Data.

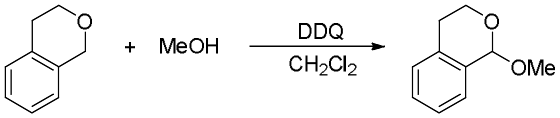
Preparation of *p*-chloroaldehyde dimethyl acetal (1f)[1]



1f

To a solution of 4-chlorobenzaldehyde (4.20 g, 29.9 mmol) and $LiBF_4$ (0.280 g, 2.99 mmol) in MeOH (15 mL) was added trimethyl orthoformate (4.44 g, 41.8 mmol). The mixture was refluxed overnight and quenched by saturated $NaHCO_3$ aq (30 mL) followed by extraction with ethyl acetate (3 x 50 mL). The collected organic layer was washed with brine (2 x 30 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product **1d** (4.60 g, 82%) whose analytical data agreed with previous report.[6] ^{1}H and ^{13}C NMR charts are listed in Product Data.

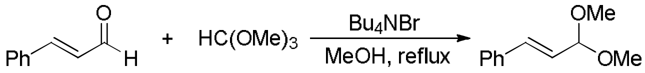
Preparation of 1-methoxyisochroman (1g)[2]



1g

To a solution of DDQ (5.57 g, 24.5 mmol) in CH_2Cl_2 (100 mL) was added MeOH (0.847 g, 26.4 mmol) and isochroman (2.66 g, 19.8 mmol). The mixture was stirred at ambient temperature for 27 h and quenched by saturated $NaHCO_3$ aq (30 mL). The resulting solid was filtered through celite and the aqueous layer was separated. The organic layer was washed with saturated $NaHCO_3$ aq (3 x 50 mL) and brine (2 x 50 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product **1g** (1.65 g, 51%) whose analytical data agreed with previous report.[2] ^{1}H and ^{13}C NMR charts are listed in Product Data.

Preparation of 1-methoxyisochroman (1h)[3]



1h

To a solution of cinnamaldehyde (2.66 g, 20.1 mmol) and trimethyl orthoformate (2.39 g, 22.5 mmol) in MeOH (20 mL) was added tetrabutylammmonium bromide (0.0966 g, 0.200 mmol). The mixture was reluxed overnight and quenched by saturated $NaHCO_3$ aq (30 mL) followed by extraction with ethyl acetate (3 x 50 mL). The collected organic layer was washed with brine (2 x 30 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product **1g** (3.19 g, 89%) whose analytical data agreed with previous report.[7] ^1H and ^{13}C NMR charts are listed in Product Data.

Experimental Procedure for Scheme 1: To a solution of benzaldehyde dimethyl acetal (**1a**) (2.0 mmol) and 1-decyne (**2a**) (1.0 mmol) in toluene (1 mL) was added catalyst (0.01 mmol) and stirred at 130 °C for 24 h. H_2O (10 mL) was then added to the reaction mixture, which was extracted with diethyl ether (3 x 10 mL). The collected organic layers were dried ($MgSO_4$) and evaporated to give the crude product, which was analyzed by ^1H NMR.

Experimental Procedure for Table 2: To a solution of benzaldehyde dimethyl acetal (**1a**) (2.0 mmol) and alkyne **2** (1.0 mmol) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (10 μL, 0.010 mmol) and heated at 130 °C for 12 h. The mixture was then evaporated to give the crude product, which was analyzed by ^1H NMR. The detail of further purification was described in Product Data.

Experimental Procedure for Table 3: To a solution acetal **1** (2.0 mmol) and 1-decyne (**2a**) (1.0 mmol) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (10 μL, 0.010 mmol) and heated at 130 °C for 12 h. The mixture was then evaporated to give the crude product, which was analyzed by ^1H NMR. The detail of further purification was described in Product Data.

Experimental Procedure for Scheme 2 (in a sealed vessel): To a solution benzaldehyde dimethyl acetal (**1a**) (0.317 g, 2.08 mmol) and 1-decyne (**2a**) (0.144 g, 1.04 mmol) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (10 μL, 0.010 mmol). The reaction vessel was sealed and heated at 130 °C for 12 h. The mixture was then evaporated to give the crude product, which was analyzed by ^1H NMR.

Experimental Procedure for Scheme 2 (with MeOH): To a solution benzaldehyde dimethyl acetal (**1a**) (0.317 g, 2.08 mmol) and 1-decyne (**2a**) (0.144 g, 1.04 mmol) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (10 μL, 0.010 mmol) and MeOH (0.2

mL). The reaction vessel was sealed and heated at 130 °C for 12 h. The mixture was then evaporated to give the crude product, which was analyzed by ^{1}H NMR.

Experimental Procedure for Scheme 3: To a solution (bromoethynyl)benzene **4** (0.188 g, 1.04 mmol) and zinc dust (0.0667 g, 1.02 mmol) in THF (1 mL) was added I_2 (0.0156 g, 0.0615 mmol). The mixture was stirred at room temperature for 1 h and evaporated. The residue was dissolved in toluene (1 mL) and benzaldehyde dimethyl acetal (**1a**) (0.304 g, 1.99 mmol) was added. The mixture was heated at 130 °C for 12 h. H_2O (10 mL) was added to the reaction mixture, which was extracted with diethyl ether (3 x 10 mL). The collected organic layer was dried ($MgSO_4$) and evaporated to give the crude product, which was analyzed by ^{1}H NMR.

Experimental Procedure for Scheme 4: To a solution of benzaldehyde (**6**) (0.218 g, 2.06 mmol) and phenylacetylene (**2c**) (0.105 g, 1.03 mmol) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (10 μL, 0.010 mmol). The mixture was heated at 130 °C for 12 h. The mixture was evaporated to give the crude product, which was analyzed by ^{1}H NMR.

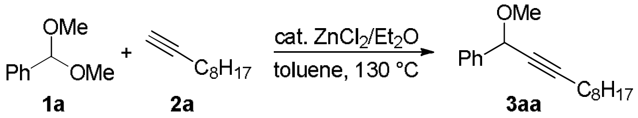
Experimental Procedure for Scheme 5: To a solution of benzaldehyde dimethyl acetal (**1a**) (0.309 g, 2.03 mmol) and 1-decyne (**2a**) (0.137 g, 0.0993 mmol) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (10 μL, 0.010 mmol) and stirred at 130 °C for 12 h. The mixture was then allowed to cool to room temperature and allyl(chloro)dimethylsilane (0.409 g, 3.04 mmol) was added. The mixture was stirred at room temperature for 30 min and evaporated to give the crude product, which was analyzed by ^{1}H NMR. The detail of further purification was described in Product Data.

Experimental Procedure for the Reaction of isolated 3aa with allyl(chloro)dimethylsilane (10) in the absence of $ZnCl_2/Et_2O$: A solution of **3aa** (0.125 g, 0.0484 mmol) and 1-decyne (**2a**) (0.106 g, 0.0787 mmol) in toluene was stirred in a N_2 filled glove box at room temperature for 30 min. The mixture was then evaporated. The residue was analyzed by ^{1}H NMR. No product was given.

Experimental Procedure for the Reaction of isolated 3aa with allyl(chloro)dimethylsilane (10) along with $ZnCl_2/Et_2O$ catalyst: To a solution of **3aa** (0.127 g, 0.0491 mmol) and 1-decyne (**2a**) (0.108 g, 0.0802 mmol) in toluene was added 1.0 M $ZnCl_2/Et_2O$ (5 μL, 0.005 mmol) and the mixture was stirred in a N_2 filled glove box at room temperature for 30 min. The mixture was then evaporated to give the crude.

The residue was analyzed by ^{1}H NMR. The product **11** was given in 73% yield.

Experimental Procedure for Kinetic Study for the Reaction of 1a with 2a



(S-1)

The rate equation for eq S-1 can be described as
$v = k[\mathbf{1a}]^a[\mathbf{2a}]^b[\mathrm{ZnCl_2}]^c$.

(Order with respect to concentration in 1a); A solution of 1-decyne (**2a**) (10 mmol) and hexadecane (3 mmol) in toluene (50 mL) was prepared and divided into four reaction tubes by 5 mL. To each tube was added benzaldehyde dimethyl acetal (**1a**) (0.2, 0.3, 0.5, 0.75 mmol) and 1.0 M $ZnCl_2/Et_2O$ (10 μL, 0.01 mmol). The reaction mixtures were heated at 130 °C. The yields of **3aa** in every 10 min were determined by GC analysis and the results were shown in Figure S-1. The reaction order a was found to be 1 by plotting equation $\ln(v) = \ln(k) + a\ln[\mathbf{1a}] + b\ln[\mathbf{2a}] + c\ln[\mathrm{ZnCl_2}]$ as shown in Figure S-2.

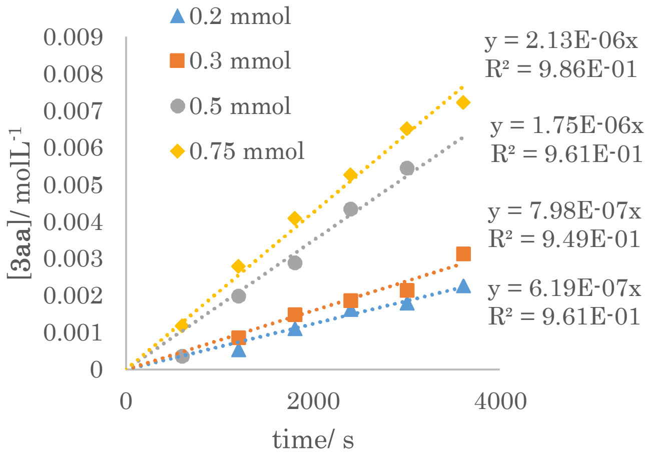


Figure S-1. Plotts of [**3aa**] vs. time at different [**1a**] concentrations.

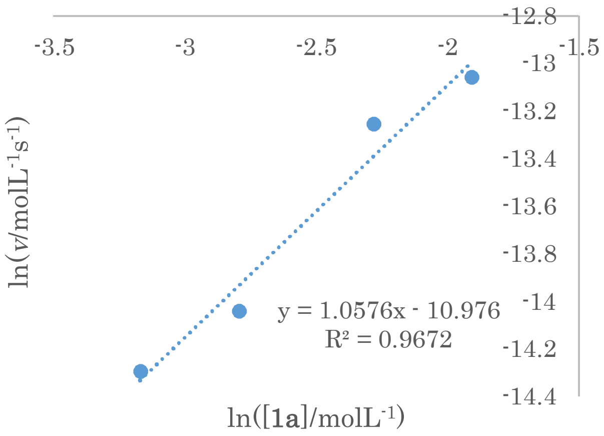


Figure S-2. Determination of order a by plotting equation ln(v) = ln(k) + $a$ln[**1a**] + $b$ln[**2a**] + $c$ln[$ZnCl_2$].

(Order with respect to concentration in 2a); A solution of benzaldehyde dimethyl acetal (**1a**) (10 mmol), 1.0 M $ZnCl_2/Et_2O$ (0.1 mmol), and hexadecane (3 mmol) in toluene (50 mL) was prepared and divided into four reaction tubes by 5 mL. To each tube was added 1-decyne (**2a**) (0.2, 0.3, 0.4, 0.5 mmol). The reaction mixtures were heated at 130 °C. The yields of **3aa** in every 10 min were determined by GC analysis and the results were shown in Figure S-3. The reaction order b was found to be 1 by plotting equation ln(v) = ln(k) + $a$ln[**1a**] + $b$ln[**2a**] + $c$ln[$ZnCl_2$] as shown in Figure S-4.

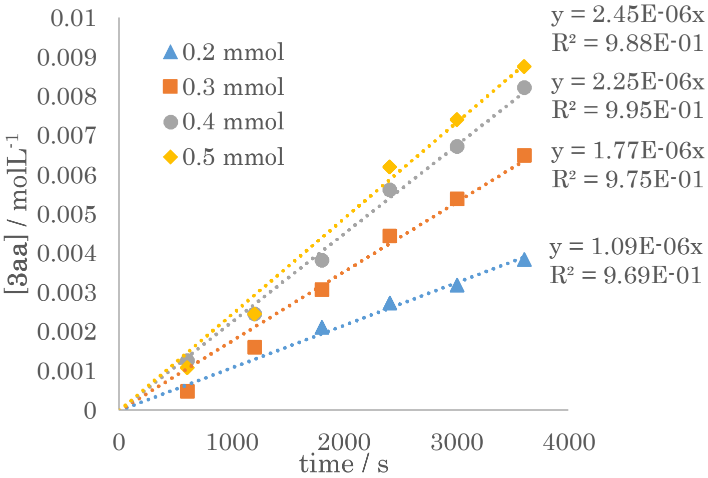


Figure S-3. Plotts of [**3aa**] vs. time at different [**2a**] concentrations.

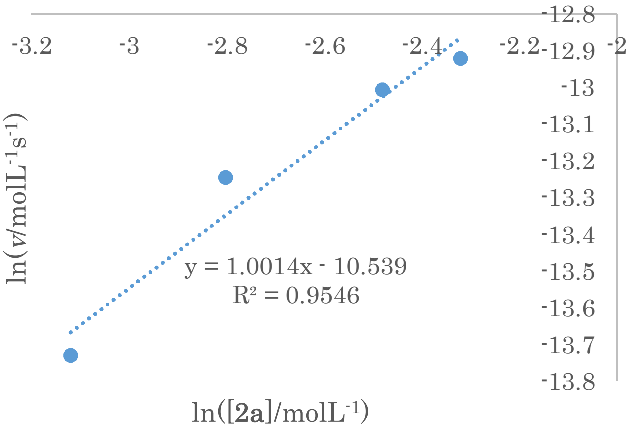


Figure S-4. Determination of order *b* by plotting equation ln(v) = ln(k) + $a$ln[**1a**] + $b$ln[**2a**] + $c$ln[$ZnCl_2$].

(Order with respect to concentration in $ZnCl_2$); A solution of benzaldehyde dimethyl acetal (**1a**) (10 mmol), 1-decyne (**2a**) (10 mmol), and hexadecane (3 mmol) in toluene (50 mL) was prepared and divided into four reaction tubes by 5 mL. To each tube was added 1.0 M $ZnCl_2$/Et_2O (0.005, 0.01, 0.02, 0.03 mmol). The reaction mixtures were heated at 130 °C. The yields of **3aa** in every 10 min were determined by GC analysis and the results were shown in Figure S-5. The reaction order *c* was found to be 1 by plotting equation ln(v) = ln(k) + $a$ln[**1a**] + $b$ln[**2a**] + $c$ln[$ZnCl_2$] as shown in Figure S-6.

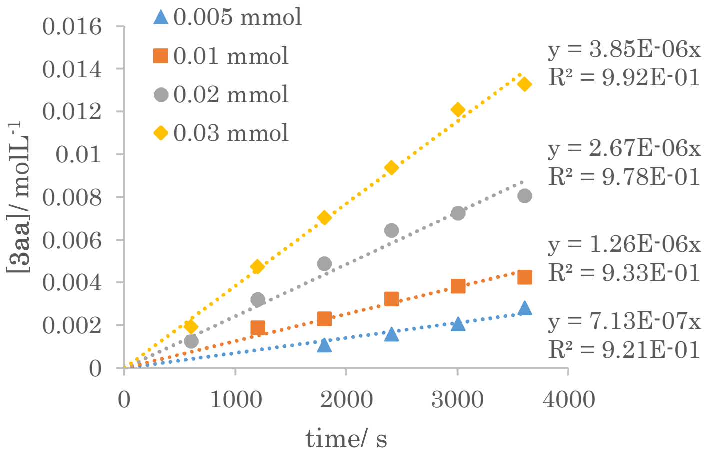


Figure S-5. Plotts of [**3aa**] vs. time at different [$ZnCl_2$] concentrations.

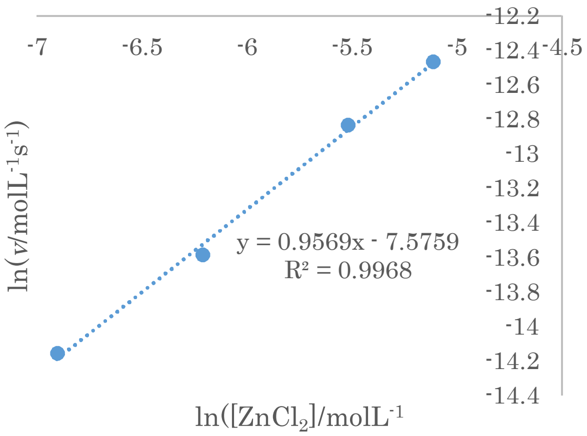


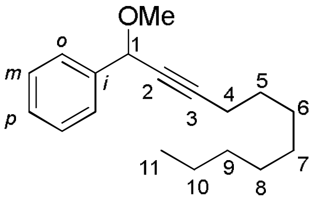
Figure S-6. Determination of order *c* by plotting equation ln(*v*) = ln(*k*) + *a*ln[**1a**] + *b*ln[**2a**] + *c*ln[$ZnCl_2$].

The value of *k* is determined by the average of rate constants given from Figure S-2, S-4, and S-6;
k = 4.06 x 10^{-2} $mol^{-2}L^{2}s^{-1}$. *T* = 130 °C

Product Data. Spectral data for the products are shown below.

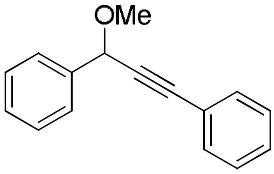
Almost all the products **3** were getting decomposed rapidly under air or gradually under N_2. NMR spectra were measured using a sealed NMR tube prepared in a N_2 filled glove box soon after purification. Although elementary analysis of the products **3** was difficult, HRMS was used as an alternative for identification of the products.

1-Methoxy-1-phenyl-2-undecyne (3aa)



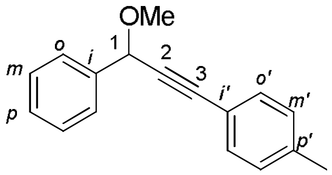
To a solution of 1-decyne (0.0982 mmol, 0.136 g) and benzaldehyde dimethyl acetal (1.99 mmol, 0.304 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.01 mmol, 10 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.218 g, 86%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 160 °C /0.42 torr ^{1}H NMR:(400 MHz, $CDCl_3$)7.50 (d, *J* = 6.8 Hz, 2H, *o*), 7.39-7.24 (m, 3H, *m* and *p*), 5.07 (t, *J* = 1.8 Hz, 1H, 1-H), 3.40 (s, 3H, OMe), 2.28 (td, *J* = 7.1, 1.9 Hz, 2H, 4-H_2), 1.55 (quint, *J* = 7.1 Hz, 2H, 5-H_2), 1.47-1.16 (m, 10H, 6-H_2, 7-H_2, 8-H_2, 9-H_2, and 10-H_2), 0.88 (t, *J* = 6.9 Hz, 11-H_3) ^{13}C NMR: (100 MHz, $CDCl_3$) 139.10 (*i*), 128.36 (+, *m*), 128.19 (+, *p*), 127.40 (+, *o*), 88.72 (C-3), 77.55 (C-2), 73.22 (+, C-1), 55.58 (+, OCH_3), 31.8 (-, C-9), 29.18 (-), 29.04 (-), 28.87 (-), 28.62 (-), 22.64 (-, C-10), 18.81 (-, C-4), 14.09 (+, C-11) MS: (EI, 70 eV) *m*/*z* 258 (M^+, 100), 257 (36), 159 (M^+ - C_7H_{15}, 44), 145 (M^+ - C_8H_{17}, 24), 129 (34), 128 ($C_6H_5CH_2C{\equiv}CCH$, 31), 121 (C_6H_5CHOMe, 9), 117 (23), 115 (22), 91 (31) HRMS: (EI, 70 eV) Calculated ($C_{18}H_{26}O$) 258.1984 (M^+) Found: 258.1985

1-Methoxy-1,3-diphenyl-2-propyne (3ab)



To a solution of 1-decyne (0.104 mmol, 0.107 g) and benzaldehyde dimethyl acetal (1.97 mmol, 0.300 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.03 mmol, 30 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.199 g, 86%). The analytical data agreed with previous report.[5]

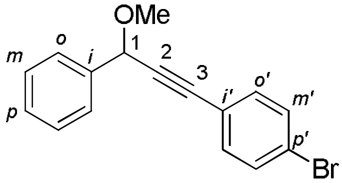
1-Methoxy-1-phenyl-3-(4-methylphenyl)-2-propyne (3ac)



To a solution of *p*-ethynyltoluene (0.0997 mmol, 0.116 g) and benzaldehyde dimethyl acetal (2.03 mmol, 0.309 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.05 mmol, 50 μL). The mixture was heated for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.101 g, 43%). ^{1}H NMR: (400 MHz, $CDCl_3$) 7.57 (d, *J* = 7.7 Hz, 2H, *o*), 7.36-7.29 (m, 5H, *m*, *p*, and *o*'), 7.09 (d, *J* = 7.7 Hz, 2H, *m*'), 5.29 (s, 1H, 1-H), 3.47 (s, 3H, OMe), 2.31 (s, 3H, Ar-Me) ^{13}C NMR: (100 MHz, $CDCl_3$) 138.59, 138.56, 131.62 (+), 128.97 (+), 128.41 (+), 128.32 (+), 127.43 (+), 119.42 (*i*'), 87.84, 85.91, 73.46 (+, C-1), 55.78 (+, OMe), 21.38

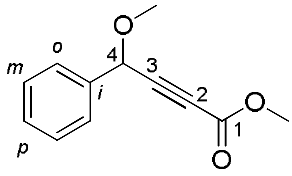
(+, Ar-Me) MS: (EI, 70 eV) *m*/*z* 236 (M^+, 34), 221 (M^+ - CH_3, 64), 206 (23), 205 (M^+ - OMe, 100), 178 (23) HRMS: (EI, 70 eV) Calculated ($C_{17}H_{16}O$) 236.1201 (M^+) Found: 236.1200

1-Methoxy-1-phenyl-3-(4-bromophenyl)-2-propyne (3ad)



To a solution of 1-bromo-4-ethynylbenzene (0.102 mmol, 0.184 g) and benzaldehyde dimethyl acetal (2.01 mmol, 0.306 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.01 mmol, 10 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.301 g, 98%). ^{1}H NMR: (400 MHz, $CDCl_3$) 7.57-7.54 (m, 2H, *o*), 7.47-7.32 (m, 7H, *m*, *p*, *o*', and *p*'), 5.28 (s, 1H, 1-H), 3.48 (s, 3H, OMe) ^{13}C NMR: (100 MHz, $CDCl_3$) 138.27 (*i*), 133.21 (+), 131.56 (+), 128.56 (+), 128.54 (+), 127.43 (+, *o*), 122.81 (*p*'), 121.47 (*i*'), 87.92, 86.57, 73.49 (+, C-1), 56.02 (+, OMe) MS: (EI, 70 eV) *m*/*z* 302 (M^+ + 2, 31), 301 (27), 300 (M^+, 31), 287 (M^+ + 2 - CH_3, 42), 285 (M^+ - CH_3, 45), 272 (22), 271 (M^+ + 2 - OMe, 100), 270 (23), 269 (M^+ - OMe, 92), 221 (M^+ - Br, 29), 206 (M^+ - OMe - Br, 27), 192 (31), 191 (33), 190 (25), 189 (79), 178 (M^+ - PhCHOMe, 61), 105 (21), 95 (42), 77 (Ph, 21) HRMS: (EI, 70 eV) Calculated ($C_{16}H_{13}BrO$) 300.0150 (M^+) Found: 300.0147

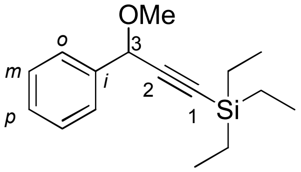
Methyl 4-methoxy-4-phenylbut-2-ynoate (3ae)



To a solution of methyl propiolate (0.105 mmol, 0.0883 g) and benzaldehyde dimethyl acetal (2.02 mmol, 0.308 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.03 mmol, 30 μL). The mixture was heated for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.172 g, 80%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 150 °C /0.23 torr IR: (neat) 2237 (C≡C), 1720 (C=O) cm^{-1} ^{1}H

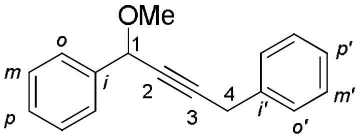
NMR: (400 MHz, $CDCl_3$) 7.49-7.46 (m, 2H, *o*), 7.41-7.33 (m, 3H, *m* and *p*), 5.18 (s, 1H, 4-H), 3.79 (s, 3H, 1-OMe), 3.46 (s, 3H, 4-OMe) ^{13}C NMR: (100 MHz, $CDCl_3$) 153.56 (C-1), 136.45 (*i*), 128.92 (+, *p*) 128.67 (+, *m*), 127.29 (+, *o*), 84.62 (C-3), 78.73 (C-2), 72.66 (+, C-4), 56.42 (+, 4-OMe), 52.79 (+, 1-OMe) MS: (EI, 70 eV) *m*/*z* 204 (M^+, 73), 189 (M^+ - CH_3, 100), 173 (M^+ - OMe, 58), 145 (M^+ - COOMe, 80), 121 (C_6H_5CHOMe, 42), 115 (51), 114 (22) HRMS: (EI, 70 eV) Calculated ($C_{12}H_{12}O_3$) 204.0786 (M^+) Found: 204.0785

1-Triethylsilyl-3-methoxy-3-phenylpropyne (3af)



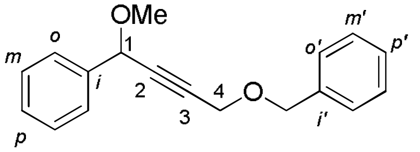
To a solution of triethyl ethynylsilane (1.01 mmol, 0.142 g) and benzaldehyde dimethyl acetal (2.03 mmol, 0.309 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.01 mmol, 10 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.228 g, 86%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 140 °C /0.34 torr. IR: (neat) 2168 (C≡C) cm^{-1} ^1H NMR: (400 MHz, $CDCl_3$) 7.53 (d, *J* = 7.2 Hz, 2H, *o*), 7.39-7.30 (m, 3H, *m* and *p*), 5.13 (s, 1H, 3-H), 3.43 (s, 3H, OCH_3), 1.02 (t, *J* = 8.0 Hz, 9H, $Si(CH_2CH_3)_3$), 0.64 (q, *J* = 8.0 Hz, 6H, $Si(CH_2CH_3)_3$) ^{13}C NMR: (100 MHz, $CDCl_3$)139.27 (*i*), 128.37 (+, *m*), 128.34 (+, *p*), 127.56 (+, *o*), 103.73 (C-2), 90.35 (C-1), 73.35 (+, C-3), 55.54 (+, OCH_3), 7.46 (+, $SiCH_2CH_3$), 4.31 (-, $SiCH_2$) ^{29}Si NMR: (78.5 MHz, $CDCl_3$ external standard = $SiMe_4$ in $CDCl_3$) -6.90 MS: (EI, 70 eV) *m*/*z* 260 (M^+, 49), 245 (M^+ - CH_3, 22), 189 (100), 113 (22) HRMS: (EI, 70 eV) Calculated ($C_{16}H_{24}OSi$) 260.1596 (M^+) Found: 260.1595

1-Methoxy-1,4-diphenyl-2-butyne (3ag)



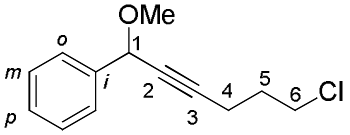
To a solution of 3-phenyl-1-propyne (0.0987 mmol, 0.115 g) and benzaldehyde dimethyl acetal (2.03 mmol, 0.308 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.01 mmol, 10 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.220 g, 94%). Further purification was performed by distillation under reduced pressure to afford the product (0.201 g, 85%). bp: 125 °C /0.21 torr ^{1}H NMR: (400 MHz, $CDCl_3$) 7.56 (d, J = 7.2 Hz, 2H, *o*), 7.42-7.24 (m, 8H, Ar), 5.14 (s, 1H, 1-H), 3.71 (s, 2H, 4-H_2), 3.43 (s, 3H, OMe) ^{13}C NMR: (100 MHz, $CDCl_3$) 138.85 (*i*), 136.43 (*i*'), 128.49 (+), 128.41 (+), 128.28 (+), 127.84 (+), 127.39 (+), 126.60 (+, *o*), 85.83 (C-3), 79.91 (C-2), 73.23 (+, C-1), 55.77 (+, OMe), 25.18 (-, C-2) MS: (EI, 70 eV) *m*/*z* 236 (M^+, 100), 235 (29), 205 (M^+ - OMe, 48), 204 (32), 203 (31), 202 (28), 145 (M^+ - $C_6H_5CH_2$, 37), 115 ($C{\equiv}CCH_2C_6H_5$, 20) HRMS: (EI, 70 eV) Calculated ($C_{17}H_{16}O$) 236.1201 (M^+) Found: 236.1195

4-Benzyloxy-1-methoxy-1-phenyl-2-butyne (3ah)



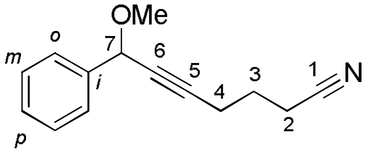
To a solution of benzyl propargyl ether (0.0988 mmol, 0.145 g) and benzaldehyde dimethyl acetal (2.03 mmol, 0.308 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.03 mmol, 30 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.203 g, 77%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 140 °C /0.19 torr ^{1}H NMR: (400 MHz, $CDCl_3$) 7.51 (d, J = 7.2 Hz, 2H, *o*), 7.39-7.23 (m, 8H, Ar), 5.14 (t, J = 1.7 Hz, 1H, 1-H), 4.61 (s, 2H, $CH_2C_6H_5$), 4.28 (d, J = 1.7 Hz, 1H, 4-H), 3.44 (s, 3H, OMe) ^{13}C NMR: (100 MHz, $CDCl_3$) 138.26 (*i*), 137.28 (*i'*), 128.47 (+), 128.41 (+), 128.08 (+), 127.86 (+), 127.32 (+, *o*), 84.13, 83.68, 73.03 (+, C-1), 71.56 (-, CH_2Ph), 57.38 (-, C-4), 55.94 (+, OMe) MS: (EI, 70 eV) *m*/*z* 205 (45), 204 (26), 159 (M^+ - OCH_2Ph, 21), 145 (M^+ - CH_2OCH_2Ph, 36), 128 ($PhCHCC{\equiv}CH_2$, 57) 121 (CH_2OCH_2Ph, 26), 115 (31), 91 (CH_2Ph, 100) HRMS: (EI, 70 eV) Calculated ($C_{18}H_{18}O_2$) 266.1307 (M^+) Found: 266.1305

6-Chloro-1-methoxy-1-phenyl-2-hexyne (3ai)



To a solution of 5-chloro-1-pentyne (1.01 mmol, 0.103 g) and benzaldehyde dimethyl acetal (2.03 mmol, 0.308 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.01 mmol, 10 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.174 g, 78%). Further purification was performed by distillation under reduced pressure to afford the product (0.126, 57%).bp: 140 °C /0.33 torr ^{1}H NMR: (400 MHz, $CDCl_3$) 7.48 (d, J = 7.2 Hz, *o*), 7.39-7.25 (m, 3H, *m* and *p*), 5.06 (s, 1H, 1-H), 3.65 (t, J = 6.3 Hz, 2H, 6-H_2), 3.40 (s, 3H, OCH_3), 2.49 (td, J = 6.8, 1.9 Hz, 2H, 4-H_2), 2.00 (tt, J = 6.8, 6.3 Hz, 2H, 5-H_2) ^{13}C NMR: (100 MHz, $CDCl_3$) 139.12 (*i*), 128.74 (+, *m*), 128.63 (+, *p*), 127.62 (+, *o*), 86.69 (C-3), 79.10 (C-2), 73.45 (+, C-1), 56.02 (+, OCH_3), 43.92 (-, C-6), 31.56 (-, C-5), 16.58 (-, C-4) MS: (EI, 70 eV) *m*/*z* 224 (32), 223 (26), 222 (M^+, 100), 191 (M^+ - CH_3, 47), 159 (M^+ - CH_2CH_2Cl, 37), 155 (24), 145 (M^+ - $CH_2CH_2CH_2Cl$, 31)、129 (29), 128 (34), 127 (15) HRMS: (EI, 70 eV) Calculated ($C_{13}H_{15}ClO$) 222.0811 (M^+) Found: 222.0808

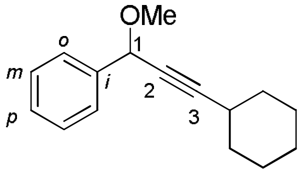
7-Methoxy-7-phenyl-5-heptynenitrile (3aj)



To a solution of 5-hexynenitrile (0.103 mmol, 0.0959 g) and benzaldehyde dimethyl acetal (2.04 mmol, 0.311 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.03 mmol, 30 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to eliminate toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.180 g, 82%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 145 °C /0.12 torr IR: (neat) 2249 (C≡N) cm^{-1} ^{1}H NMR: (400 MHz, $CDCl_3$) 7.48-7.45 (m, 2H, *o*), 7.39-7.30 (m, 3H, *m* and *p*), 5.05 (t, J = 1.9 Hz, 1H, 7-H), 3.40 (s, 3H, OMe), 2.53-2.46 (m, 4H, 2-H_2 and 4-H_2), 1.92 (quint, J = 7.0 Hz, 2H, 3-H_2) ^{13}C NMR: (100 MHz, $CDCl_3$) 138.64 (*i*), 128.45 (+, *o*) 128.36 (+, *p*), 127.18 (+, *m*), 118.97 (C-1), 85.22 (C-5), 79.86 (C-6), 73.06 (+, C-7), 55.78 (+, OMe), 24.44 (-, C-3), 17.91 (-, C-2), 16.11 (-, C-4) MS: (EI, 70 eV) *m*/*z* 213 (M^+, 4), 198 (M^+ - CH_3, 41), 182 (M^+ - OMe, 98), 181 (51), 180 (19), 159 (M^+ - CH_2CH_2CN, 17), 153 (29), 145 (M^+ - $CH_2CH_2CH_2CN$, 18), 142 ($C_6H_5CC{\equiv}CCH_2CH_2$, 26), 141 (100), 129 (21), 128 ($PhCC{\equiv}CCH_2$, 31), 115 (33) HRMS: (EI, 70 eV) Calculated ($C_{14}H_{15}NO$) 213.1154 (M^+)

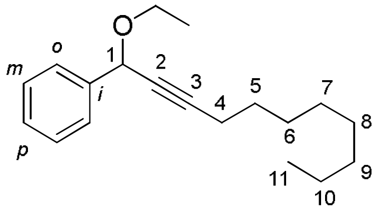
Found: 213.1147

3-Cyclohexyl-1-methoxy-1-phenyl-2-propyne (3ak)



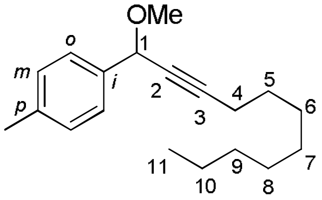
To a solution of cyclohexylacetylene (1.02 mmol, 0.110 g) and benzaldehyde dimethyl acetal (1.98 mmol, 0.302 g) in toluene (1 mL) was added 1.0 M $\mathrm{ZnCl_2}$ in $\mathrm{Et_2O}$ (0.01 mmol 10 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (70 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.189 g, 81%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 120 °C /0.11 torr IR: (neat) 2229 (C≡C) $\mathrm{cm^{-1}}$ ^{1}H NMR: (400 MHz, $\mathrm{CDCl_3}$) 7.51 (d, *J* = 7.2 Hz, 2H, *o*), 7.38-7.25 (m, 3H, *m* and *p*), 5.10 (t, *J* = 1.9 Hz, 1H, 1-H), 3.40 (s, 3H, $\mathrm{OCH_3}$), 2.55-2.38 (m, 1H, C≡CCH), 1.89-1.77 (m, 2H, $\mathrm{CHCH}H$ x 2), 1.77-1.60 (m, 3H, $\mathrm{CHC}H\mathrm{H}$ x 2 and $\mathrm{CHCH_2CH_2CH}H$), 1.59-1.40 (m, 2H, $\mathrm{CHCH_2CH}H$ x 2), 1.40-1.11 (m, 3H, $\mathrm{CHCH_2C}H\mathrm{H}$ x 2 and $\mathrm{CHCH_2CH_2C}H\mathrm{H}$) ^{13}C NMR: (100 MHz, $\mathrm{CDCl_3}$) 139.12 (*i*), 128.32 (+, *m*), 128.16 (+, *p*), 127.48 (+, *o*), 92.80 (C-2), 73.16 (+, C-1), 55.43 (+, $\mathrm{OCH_3}$), 32.60 (-, $\mathrm{CH}C\mathrm{H_2}$), 29.11 (-, C≡C*C*H), 25.86 (-, $\mathrm{CHCH_2}C\mathrm{H_2}$), 24.80 (-, $\mathrm{CHCH_2CH_2}C\mathrm{H_2}$) MS: (EI, 70 eV) *m*/*z* 228 ($\mathrm{M^+}$, 100), 227 (28), 197 ($\mathrm{M^+}$ - OMe, 20), 145 ($\mathrm{M^+}$ - $\mathrm{C_6H_{11}}$, 48), 141 (23), 115 (31), 91 (33) HRMS: (EI, 70 eV) Calculated ($\mathrm{C_{16}H_{20}O}$) 228.1514 ($\mathrm{M^+}$) Found: 228.1512

1-Ethoxy-1-phenyl-2-undecyne (3ba)



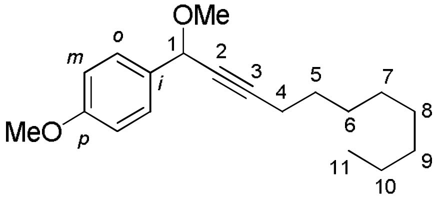
To a solution of 1-decyne (0.103 mmol, 0.142 g) and benzaldehyde diethyl acetal (2.05 mmol, 0.371 g) in toluene (1 mL) was added 1.0 M $\mathrm{ZnCl_2}$ in $\mathrm{Et_2O}$ (0.05 mmol, 50 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (80 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.160 g, 77%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 170 °C /0.73 torr IR: (neat) 2345 (C≡C) cm^{-1} ^{1}H NMR: (400 MHz, CDCl$_3$) 7.51 (d, *J* = 7.2 Hz, 2H, *o*), 7.38-7.26 (m, 3H, *m* and *p*), 5.15 (s, 1H, 1-H), 3.73-3.66 (m, 1H, OC*H*HCH$_3$), 3.56-3.49 (m, 1H, OCH*H*CH$_3$), 2.27 (td, *J* = 7.1, 2.1 Hz, 2H, 4-H$_2$), 1.54 (quint, *J* = 7.0 Hz, 2H, 5-H$_2$), 1.42-1.19 (m, 13H, 10H, 6H$_2$, 7H$_2$, 8H$_2$, 9H$_2$, 10H$_2$, and OCH$_2$C*H*$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, 11-H$_3$) ^{13}C NMR: (100 MHz, CDCl$_3$) 139.62 (*i*), 128.34 (+, *m*) 128.04 (+, *p*), 127.38 (+, *o*), 88.21 (C-3), 78.19 (C-2), 71.63 (+, C-1), 63.52 (-, O*C*H$_2$CH$_3$), 31.81 (-, C-9), 29.18 (-), 29.06 (-), 28.88 (-), 28.63 (-), 22.66 (-, C-10), 18.86 (-, C-4), 15.18 (+, OCH$_2$*C*H$_3$), 14.09 (+, C-11) MS: (EI, 70 eV) *m*/*z* 273 (23), 272 (M$^+$, 100), 271 (28), 173 (M$^+$ - (CH$_2$)$_6$CH$_3$, 15), 159 (M$^+$ - (CH$_2$)$_7$CH$_3$, 7), 145 (23), 131 (20), 129 (35), 128 (29), 117 (34), 115 (22), 91 (44) HRMS: (EI, 70 eV) Calculated (C$_{19}$H$_{28}$O) 272.2140 (M$^+$) Found: 272.2139

1-Methoxy-1-(4-methylphenyl)-2-undecyne (3da)



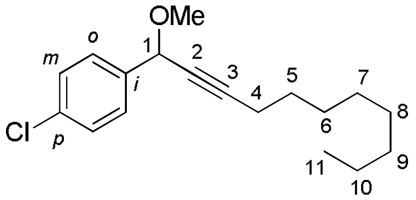
To a solution of 1-decyne (0.103 mmol, 0.142 g) and *p*-tolualdehyde dimethyl acetal (1.99 mmol, 0.330 g) in toluene (1 mL) was added 1.0 M ZnCl$_2$ in Et$_2$O (0.01 mmol, 10 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (80 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.222 g, 89%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 160 °C /0.42 torr ^{1}H NMR: (400 MHz, CDCl$_3$) 7.38 (d, *J* = 8.2 Hz, 2H, *o*), 7.16 (d, *J* = 7.7 Hz, 2H, *m*), 5.03 (s, 1H, 1-H), 3.38 (s, 3H, OMe), 2.34 (s, 3H, *p*-Me), 2.27 (td, *J* = 7.0, 1.8 Hz, 2H, 4-H$_2$), 1.54 (quit, *J* = 7.0 Hz, 2H, 5-H$_2$), 1.43-1.20 (m, 10H, 6-H$_2$, 7-H$_2$, 8-H$_2$, 9-H$_2$, and 10-H$_2$), 0.88 (t, *J* = 6.8 Hz, 11-H$_3$) ^{13}C NMR: (100 MHz, CDCl$_3$) 137.94 (*p*), 136.18 (*i*), 129.02 (+, *m*), 127.36 (+, *o*), 88.44 (C-3), 77.74 (C-2), 73.03 (+, C-1), 55.44 (+, OCH$_3$), 31.8 (-, C-9), 29.18 (-), 29.05 (-), 28.86 (-), 28.63 (-), 22.64 (-, C-10), 21.15 (+, *p*-Me), 18.82 (-, C-4), 14.08 (+, C-11) MS: (EI, 70 eV) *m*/*z* 272 (M$^+$, 75), 257 (M$^+$ - Me, 100), 173 (M$^+$ - (CH$_2$)$_6$CH$_3$, 20), 159 (M$^+$ - (CH$_2$)$_6$CH$_3$, 22), 105 (27) HRMS: (EI, 70 eV) Calculated (C$_{19}$H$_{28}$O) 272.2140 (M $^+$) Found: 272.2140

1-Methoxy-1-(4-methoxyphenyl)-2-undecyne (3ea)



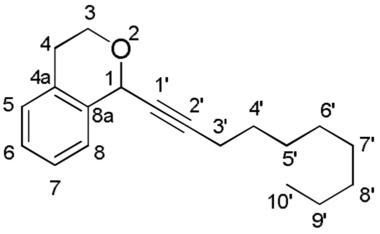
To a solution of 1-decyne (0.101 mmol, 0.140 g) and *p*-anisaldehyde dimethyl acetal (2.01 mmol, 0.366 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.03 mmol, 30 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (90 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.250 g, 85%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 135 °C /0.27 torr ^{1}H NMR: (400 MHz, $CDCl_3$) 7.42 (d, *J* = 8.7 Hz, 2H, *o*), 6.88 (d, *J* = 8.7 Hz, 2H, *m*), 5.02 (t, *J* = 1.9 Hz, 1H, 1-H), 3.80 (s, 3H, *p*-OMe), 3.37 (s, 3H, 1-OMe), 2.27 (td, *J* = 7.0, 1.9 Hz, 2H, 4-H_2), 1.59-1.51 (quint, *J* = 7.0 Hz, 2H, 5-H_2), 1.48-1.17 (m, 10H, 6-H_2, 7-H_2, 8-H_2, 9-H_2, and 10-H_2), 0.88 (t, *J* = 6.8 Hz, 3H, 11-H_3) ^{13}C NMR: (100 MHz, $CDCl_3$) 159.56 (*p*), 131.39 (*i*), 128.78 (+, *o*), 113.70 (+, *m*), 88.47 (C-3), 77.77 (C-2), 72.77 (+, C-1), 55.34 (+), 55.26 (+), 31.80 (-, C-9), 29.18 (-), 29.05 (-), 28.88 (-), 28.65 (-), 22.64 (-, C-10), 18.82 (-, C-4), 14.07 (+, C-11) MS: (EI, 70 eV) *m*/*z* 288 (M^+, 74), 258 (20), 257 (M^+ - OMe, 100), 189 (M^+ - $(CH_2)_6CH_3$, 14), 175 (M^+ - $(CH_2)_7CH_3$, 12), 159 (23), 121 (42) HRMS: (EI, 70 eV) Calculated ($C_{19}H_{28}O_2$) 288.2089 (M^+) Found: 288.2090

1-Methoxy-1-(4-chlorophenyl)-2-undecyne (3fa)



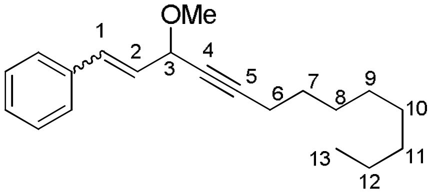
To a solution of 1-decyne (0.102 mmol, 0.142 g) and *p*-chlorobenzaldehyde dimethyl acetal (2.01 mmol, 0.375 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.05 mmol, 50 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was evaporated to remove toluene and acetal (90 °C, 0.083 torr). The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a colorless oil (0.271 g, 90%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 170 °C /0.68 torr ^{1}H NMR: (400 MHz, $CDCl_3$) 7.44 (d, *J* = 8.7 Hz, 2H, *m*), 7.32 (d, *J* = 8.2 Hz, 2H, *o*), 5.04 (s, 1H, 1-H), 3.39 (s, 3H, OMe), 2.28 (td, *J* = 7.0, 1.9 Hz, 2H, 4-H_2), 1.54 (quint, *J* = 7.0 Hz, 2H, 5-H_2), 1.44-1.15 (m, 10H, 6H_2, 7H_2, 8H_2, 9H_2, and 10H_2), 0.88 (t, *J* = 6.8 Hz, 3H, 11-H_3) ^{13}C NMR: (100 MHz, $CDCl_3$) 137.72 (*p*), 133.96 (*i*), 128.73 (+, *m*), 128.48 (+, *o*), 89.09 (C-3), 77.15 (C-2), 72.45 (+, C-1), 55.58 (+, OMe), 31.79 (-, C-9), 29.16 (-), 29.03 (-), 28.85 (-), 28.57 (-), 22.63 (-, C-10), 18.77 (-, C-4), 14.06 (+, C-11) MS: (EI, 70 eV) *m*/*z* 294 (26), 293 (20), 292 (M^+, 78), 257 (M^+ - Cl, 100), 193 (M^+ - $(CH_2)_6CH_3$, 23), 179 (M^+ - $(CH_2)_7CH_3$, 19), 165 (28), 159 (24), 127 (24), 125 ($C(CH_2)_7CH_3$, 42), 55 (20) HRMS: (EI, 70 eV) Calculated ($C_{18}H_{25}ClO$) 292.1594 (M^+) Found: 292.1593

1-(Dec-1-ynyl)isochroman (3ga)



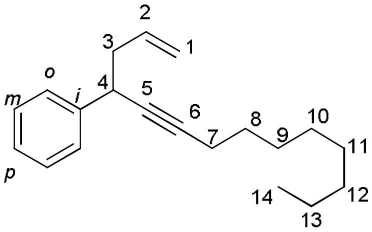
To a solution of 1-decyne (0.101 mmol, 0.140 g) and isochroman (1.98 mmol, 0.326 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.01 mmol, 10 µL). The mixture was heated at 130 °C for 12 h. The reaction mixture was purified by silica column gel chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.233 g, 85%). Further purification was performed by distillation under reduced pressure to afford the product. bp: 150 °C /0.23 torr ^{1}H NMR: (400 MHz, $CDCl_3$) 7.30-7.24 (m, 1H, Ar), 7,21-7.17 (m, 2H, Ar), 7.11-7.06 (m, 1H, 5-H), 5.52 (s, 1H, 1-H), 4.23 (dt, *J* = 12.4, 6.1 Hz, 1H, 3-*H*H), 3.93 (dt, *J* = 12.4, 6.1 Hz, 1H, 3-H*H*), 2.86 (t, *J* = 6.1 Hz, 2H, 4-H_2), 2.23 (td, *J* = 7.1, 2.3 Hz, 2H, $C{\equiv}CCH_2$), 1.52 (quint, *J* = 6.8 Hz, 2H, $C{\equiv}CCH_2C\mathit{H}_2$), 1.44-1.16 (m, 10H, $C{\equiv}CCH_2CH_2(C\mathit{H}_2)_5$), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3) ^{13}C NMR: (100 MHz, $CDCl_3$) 135.66 (8*a*), 132.64 (4*a*), 128.80(+), 126.98 (+), 126.18 (+), 125.93 (+), 86.66 ($C{\equiv}\mathit{C}CH_2$), 79.03 ($CH\mathit{C}{\equiv}C$), 67.20 (+, C-1), 62.60 (-, C-3), 31.79 (-, $CH_3CH_2\mathit{C}H_2$), 29.16 (-), 29.04 (-), 28.86 (-), 28.533 (-), 28.06 (-), 22.64 (-, $CH_3\mathit{C}H_2$), 18.81 (-, $C{\equiv}C\mathit{C}H_2$), 14.08 (+, CH_3) MS: (EI, 70 eV) *m*/*z* 270 (M^+, 72), 269 (43), 185 (M^+ - $(CH_2)_5CH_3$, 19), 172, (26), 171 (M^+ - $(CH_2)_6CH_3$, 100), 158 (43), 157 (M^+ - $(CH_2)_7CH_3$, 23), 128 (20) HRMS: (EI, 70 eV) Calculated ($C_{19}H_{26}O$) 270.1984 (M^+) Found: 270.1979

1-Phenyl-3-methoxytridec-1-en-4-yne (3ha)



To a solution of 1-decyne (0.0972 mmol, 0.134 g) and (*E*)-cinnamaldehyde dimethyl acetal (2.00 mmol, 0.356 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.05 mmol, 50 μL). The mixture was heated at 130 °C for 12 h. The reaction mixture was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20), giving the product as a yellow oil (0.216 g, 78%, *E*/*Z* = 66/34). Further purification was performed under reduced pressure to afford the product. The isomers were separated by GPC. bp: 160 °C /0.13 torr IR: (neat) 2213 (C≡C) cm^{-1} ^1H NMR: (400 MHz, $CDCl_3$) (*E*-isomer) 7.36-7.25 (m, 5H, Ar), 6.08 (dd, *J* = 15.9, 6.8 Hz, 1H, 2-H), 5.71 (d, *J* = 15.9 Hz, 1H, 1-H), 4.63 (d, *J* = 6.8 Hz, 1H, 3-H), 3.32 (s, OMe), 2.27 (td, *J* = 7.0, 1.9 Hz, 2H, 6-H_2), 1.52-1.35 (m, 2H, 7-H_2), 1.42-1.03 (m, 10H, 8H_2, 9H_2, 10H_2, 11H_2, and 12H_2), 0.87 (t, *J* = 6.6 Hz, 3H, 13-H_3) (*Z*-isomer) 7.40-7.25 (m, 5H, Ar), 5.89 (dd, *J* = 10.6, 8.9 Hz, 1H, 2-H), 5.68-5.63 (m, 1H, 1-H), 5.27 (d, *J* = 8.9 Hz, 1H, 3-H), 3.38 (s, OMe), 2.39 (td, *J* = 6.9, 2.1 Hz, 2H, 6-H_2), 1.62-1.46 (m, 2H, 7-H_2), 1.37-1.12 (m, 10H, 8H_2, 9H_2, 10H_2, 11H_2, and 12H_2), 0.92-0.86 (m, 3H, 13-H_3) ^{13}C NMR: (100 MHz, $CDCl_3$) (*E*-isomer) 141.55 (+, C-2), 140.29 (*i*), 128.50 , 127.80 , 126.84 , 111.89 (+, C-1), 91.76 (C-5), 83.70 (+, C-3), 78.28 (C-4), 56.48 (+, OMe), 31.82 (-, C-7), 29.16 (-), 29.08 (-), 28.88 (-), 28.67 (-), 22.64 (-, C-12), 19.38 (-, C-6), 14.08 (+, C-13) (*Z*-isomer) 141.29 (+, C-2), 128.44 (+), 127.57 (+), 126.26 (+), 111.87 (+, C-1), 96.33 (C-5), 80.59 (+, C-3), 56.40 (+, OMe), 31.84 (-, C-7), 29.24 (-), 29.13 (-), 28.96 (-), 28.74 (-), 22.65 (-, C-12), 19.56 (-, C-6), 14.08 (+, C-13) MS: (EI, 70 eV) *m*/*z* 285 (20), 284 (M^+, 98), 283 (33), 199 (43), 186 (100), 185 (M^+ - $(CH_2)_6CH_3$, 56), 171 (M^+ - $(CH_2)_7CH_3$, 63), 167 (21), 155 (40), 154 (20), 153 (33), 152 (24), 129 (20), 128 (22), 121 (23), 115 (24), 105 (46), 91 (55), 77 (C_6H_5, 29) HRMS: (EI, 70 eV) Calculated ($C_{20}H_{28}O$) 284.2140 (M^+) Found: 284.2138

4-Phenyltetradec-1-en-5-yne (11)



To a solution of 1-decyne (0.0993 mmol, 0.137 g) and benzaldehyde dimethyl acetal (2.00 mmol, 0.309 g) in toluene (1 mL) was added 1.0 M $ZnCl_2$ in Et_2O (0.03 mmol, 30 μL). The mixture was heated at 130 °C for 12 h The reaction mixture was cooled to room temperature. Allylchlorodimethylsilane (0.304 mmol, 0.409 g) was added to the mixture, which was stirred at room temperature for 30 min. The mixture was purified by silica gel column chromatography (hexane 300 mL), giving the product as a yellow oil (0.165 g, 62%). Further purification was performed under reduced pressure to afford the product. bp: 130 °C /0.18 torr IR: (neat) 2206 (C≡C) cm^{-1} ^1H NMR: (400 MHz, $CDCl_3$) 7.41-7.11 (m, 5H, Ar), 5.85 (dddd, J = 15.6, 10.0, 7.6, 7.2 Hz, 1H, 2-H), 5.07-5.01 (m, 2H, 1-H_2), 3.66 (ddt, J = 7.6, 7.2, 2.0 Hz, 1H, 4-H), 2.48-2.44 (m, 2H, 3-H_2), 2.22 (td, J = 6.8, 2.4 Hz, 2H, 7-H_2), 1.54-1.28 (m, 12H, 8H_2, 9H_2, 10H_2, 11H_2, 12H_2 and 13H_2), 0.88 (t, J = 6.8 Hz, 3H, 14-H_3) ^{13}C NMR: (100 MHz, $CDCl_3$) 142.17 (*i*), 135.83 (+, C-2), 128.29, 127.47, 126.54, 116.60 (-, C-1), 83.82 (C-6), 81.09 (C-5), 43.07 (-, C-3), 38.04 (+, C-4), 31.83 (-, C-8), 29.22 (-), 29.10 (-), 29.05 (-), 28.85 (-), 22.67 (-, C-13), 18.81 (-, C-7), 14.10 (+, C-14) MS: (CI, 200 eV) *m*/*z* 269 (M^++1, 100), 267 (22), 227 (M^++1 - $CH_2CH{=}CH_2$, 72), 171 (38), 131 ($PhCHCH_2CH{=}CH_2$, 21) HRMS: (CI, 200 eV) Calculated ($C_{20}H_{29}$) 269.2269 (M^++1) Found: 269.2271

References

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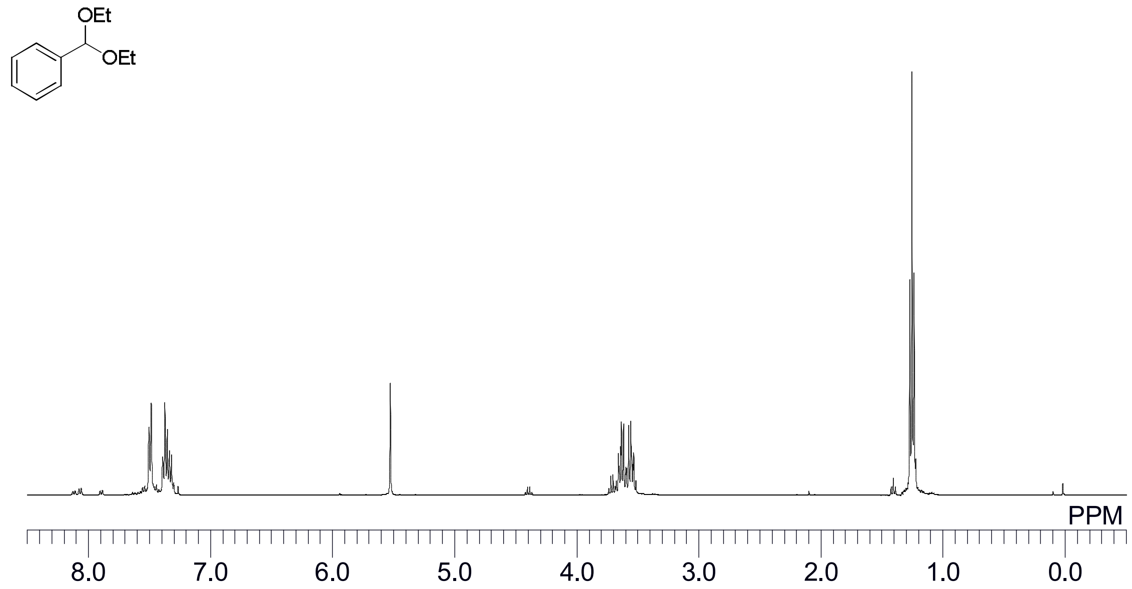
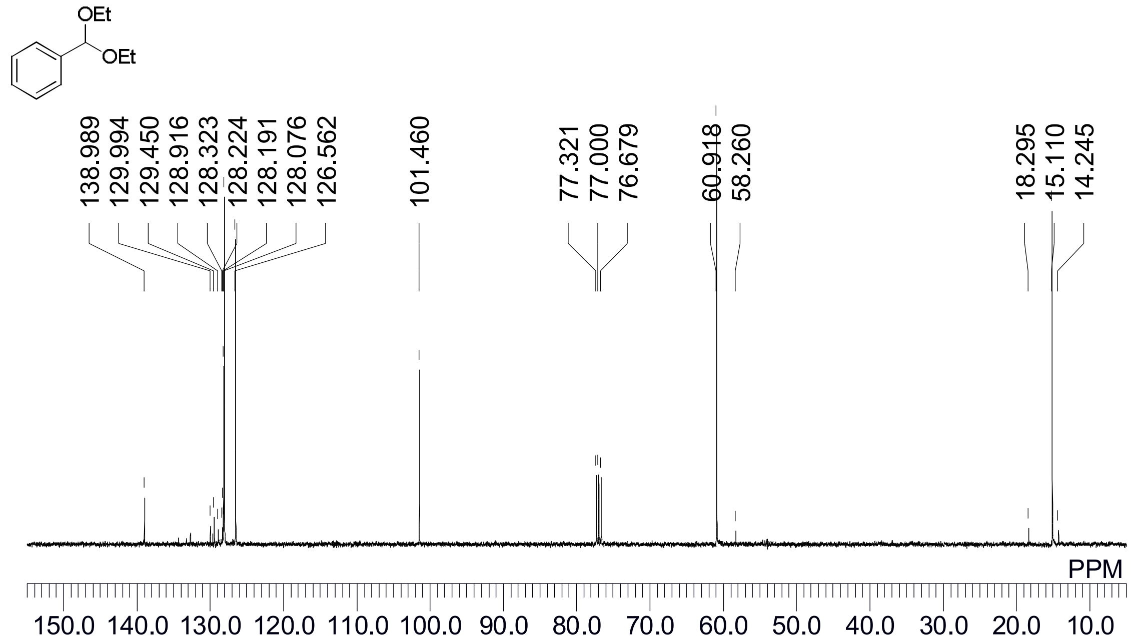
Benzaldehyde diethyl acetal (1b)

^{1}H NMR (400 MHz, in CDCl$_3$)

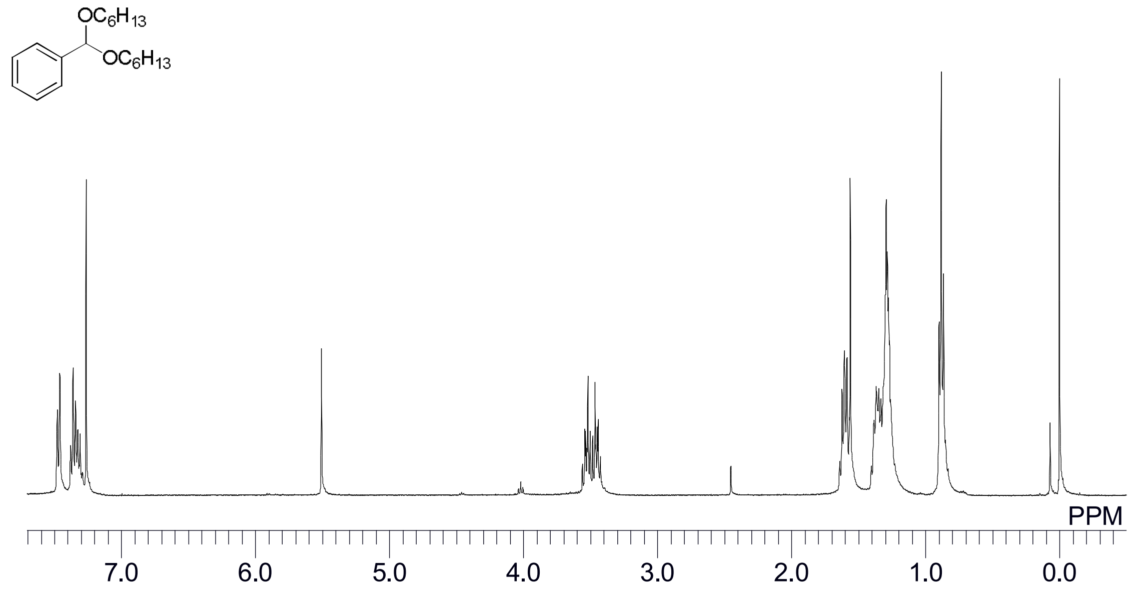


^{13}C NMR (100 MHz, in CDCl$_3$)

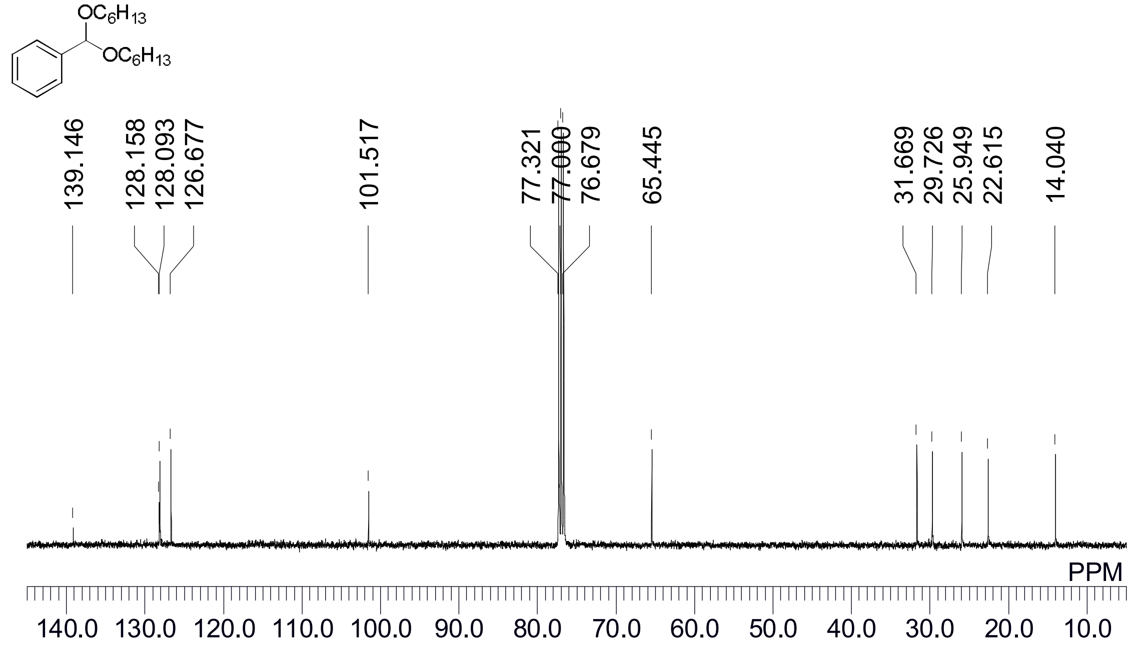


Benzaldehyde dihexyl acetal (1c)

^{1}H NMR (400 MHz, in CDCl$_3$)

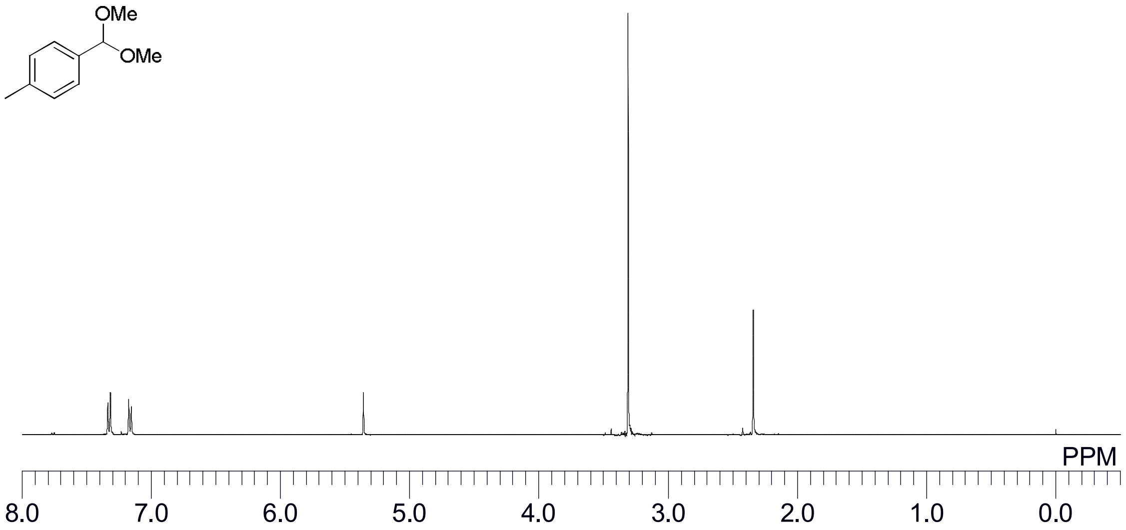


^{13}C NMR (100 MHz, in CDCl$_3$)

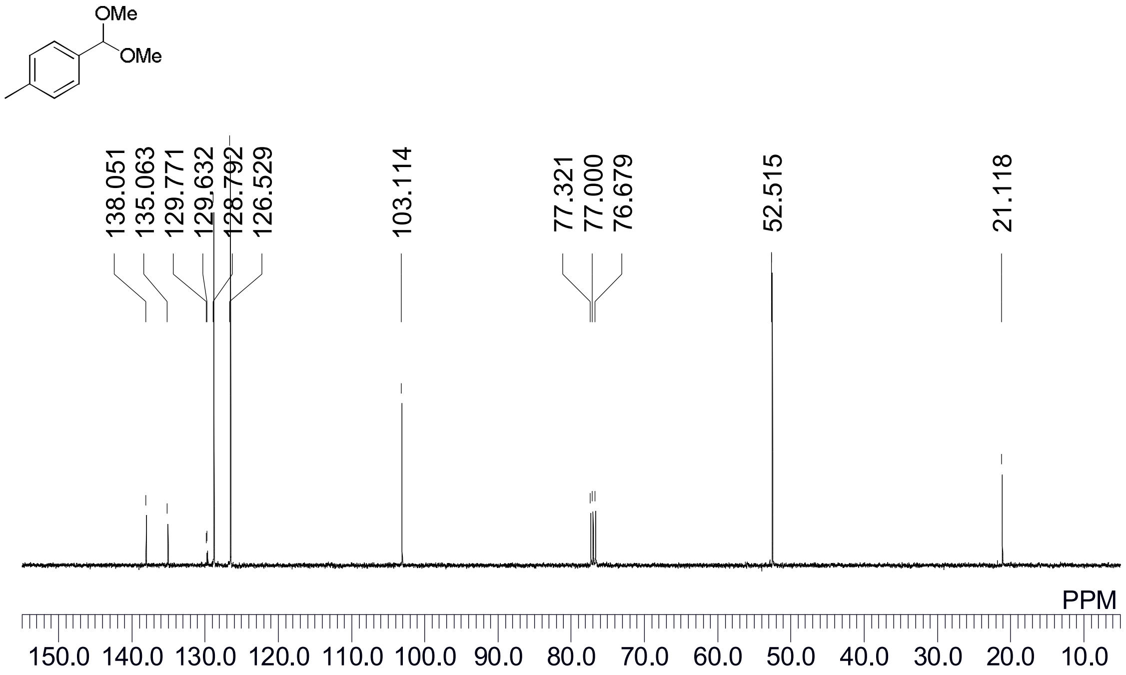


p-Tolualdehyde dimethyl acetal (1d)

^{1}H NMR (400 MHz, in CDCl$_3$)

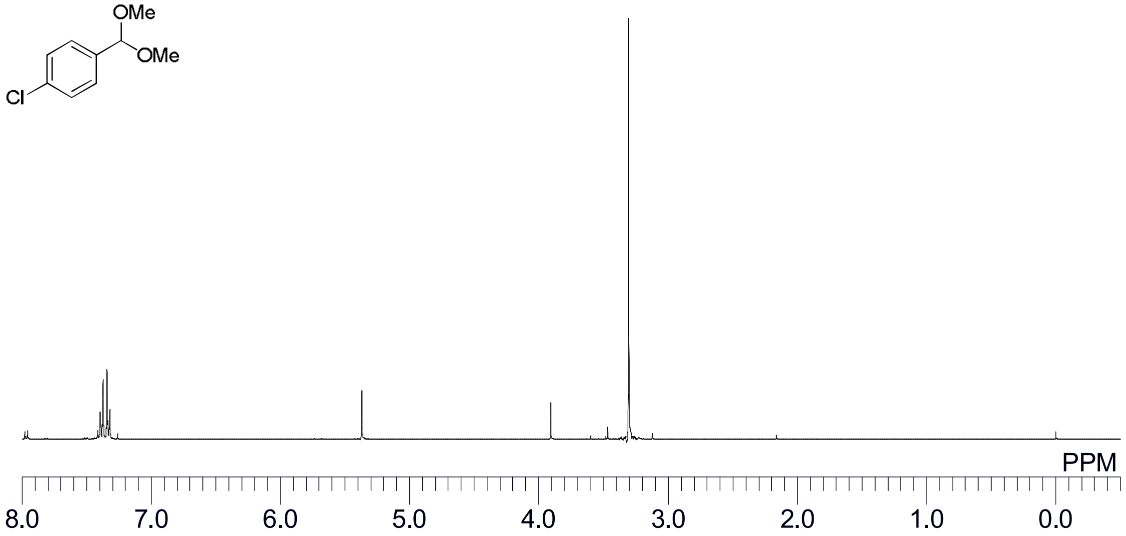


^{13}C NMR (100 MHz, in CDCl$_3$)

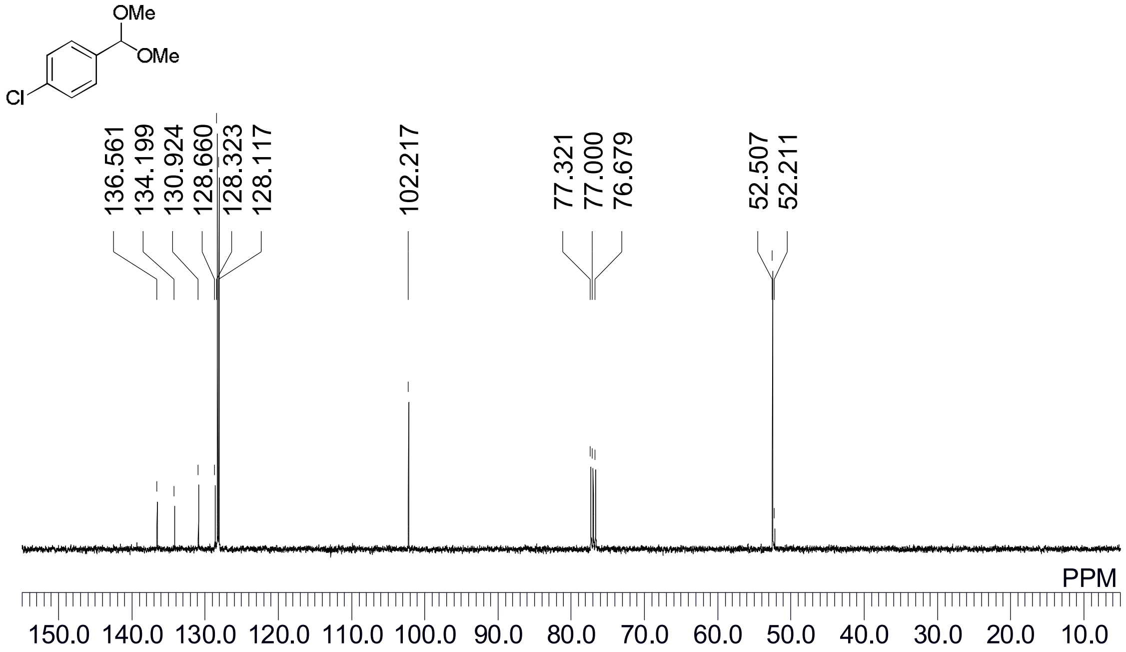


p-Chloroaldehyde dimethyl acetal (1c)

^{1}H NMR (400 MHz, in $CDCl_3$)

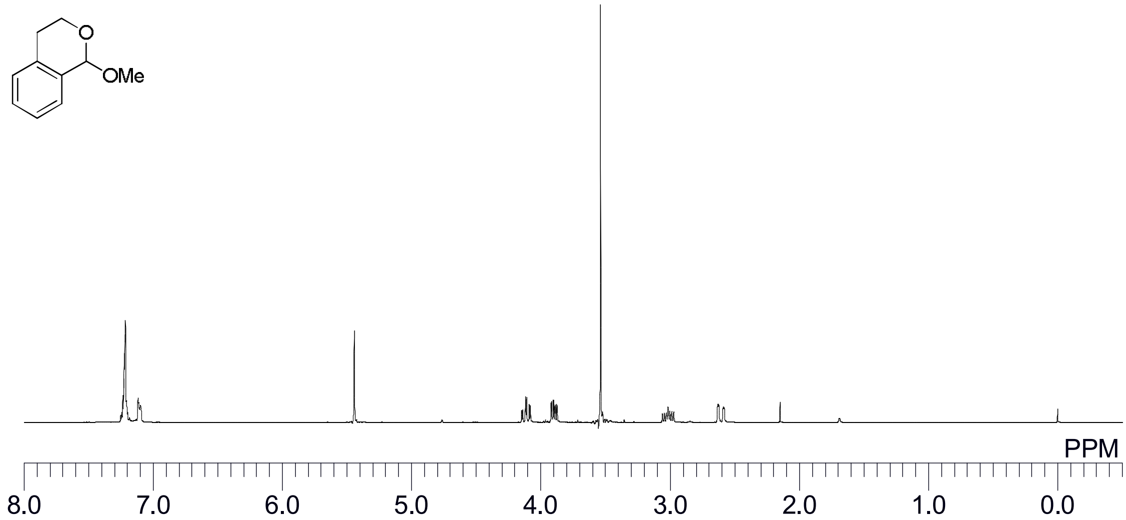


^{13}C NMR (100 MHz, in $CDCl_3$)

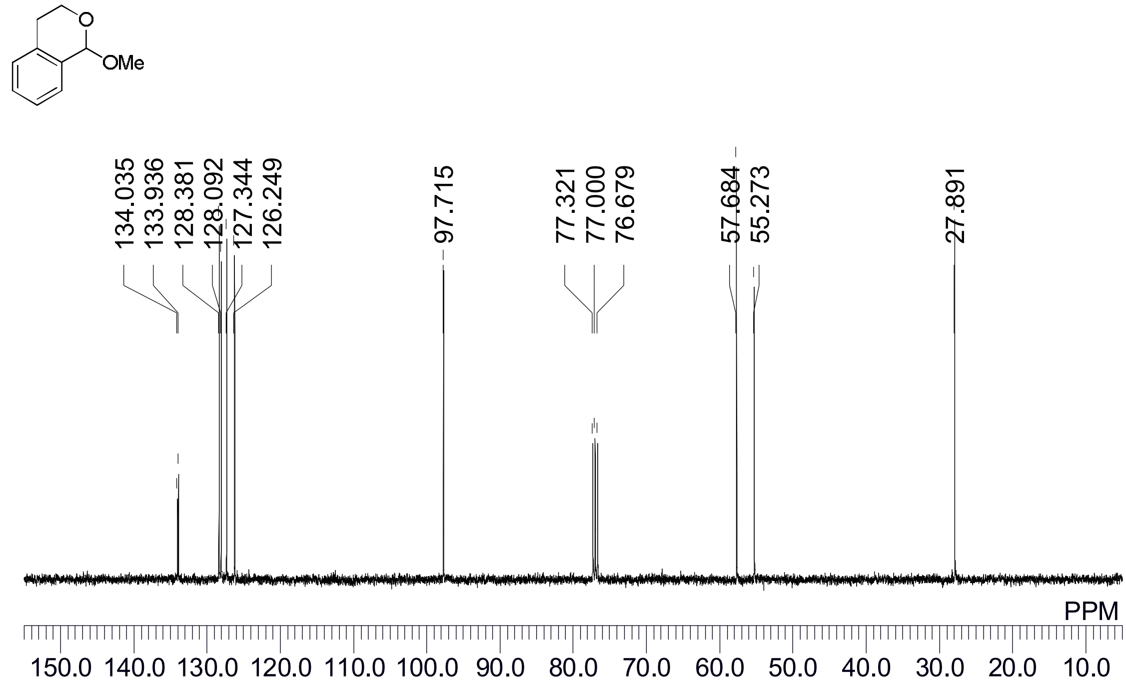


1-Methoxyisochroman (1g)

^{1}H NMR (400 MHz, in $CDCl_3$)

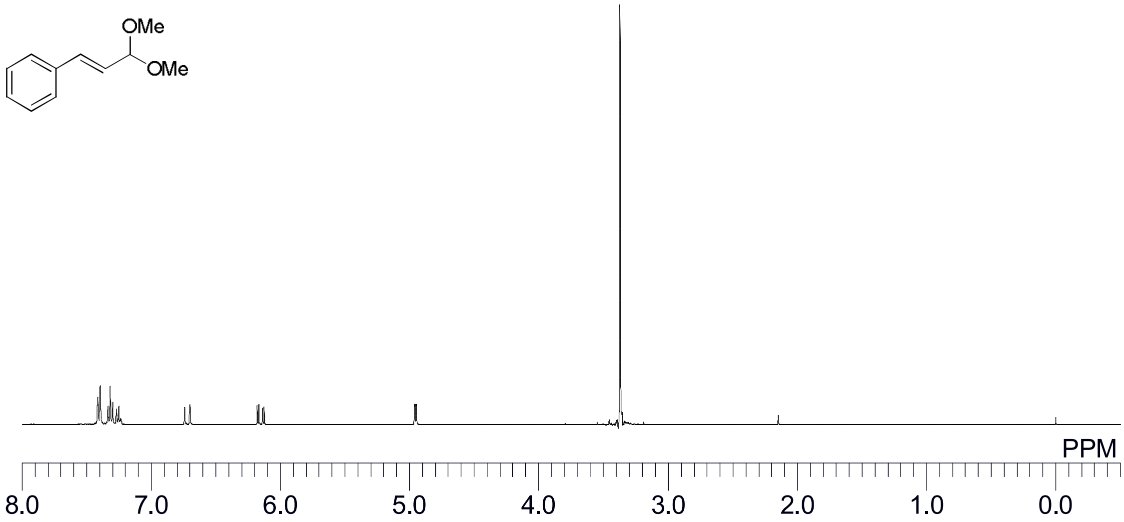


^{13}C NMR (100 MHz, in $CDCl_3$)

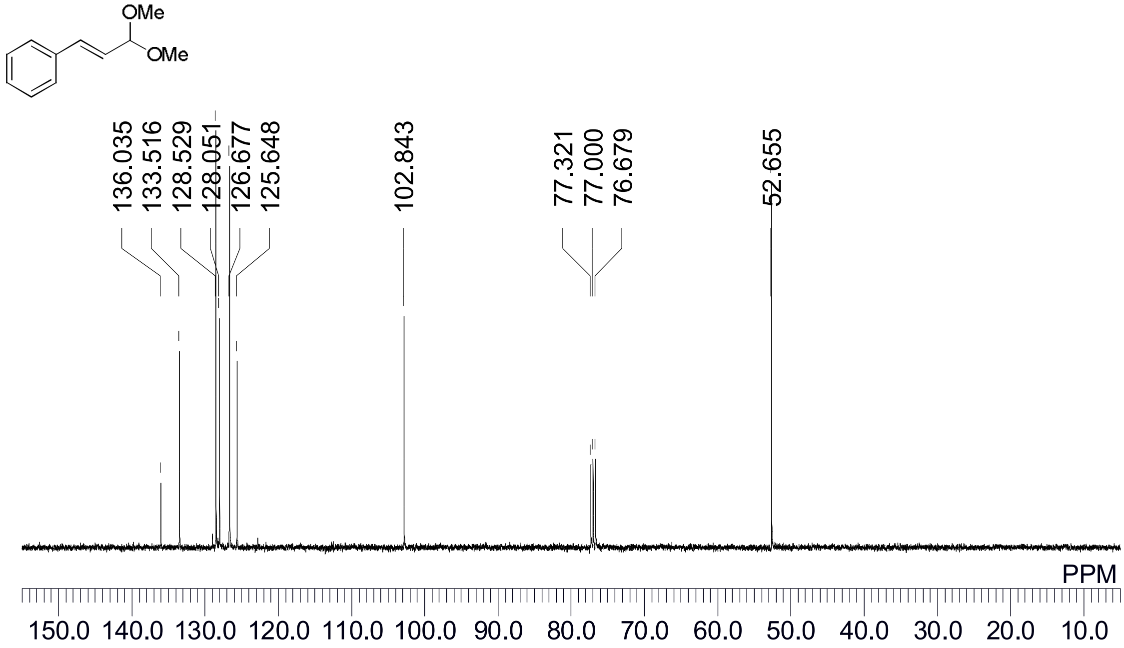


(*E*)-Cinnamaldehyde dimethyl acetal (1h)

^{1}H NMR (400 MHz, in CDCl$_3$)

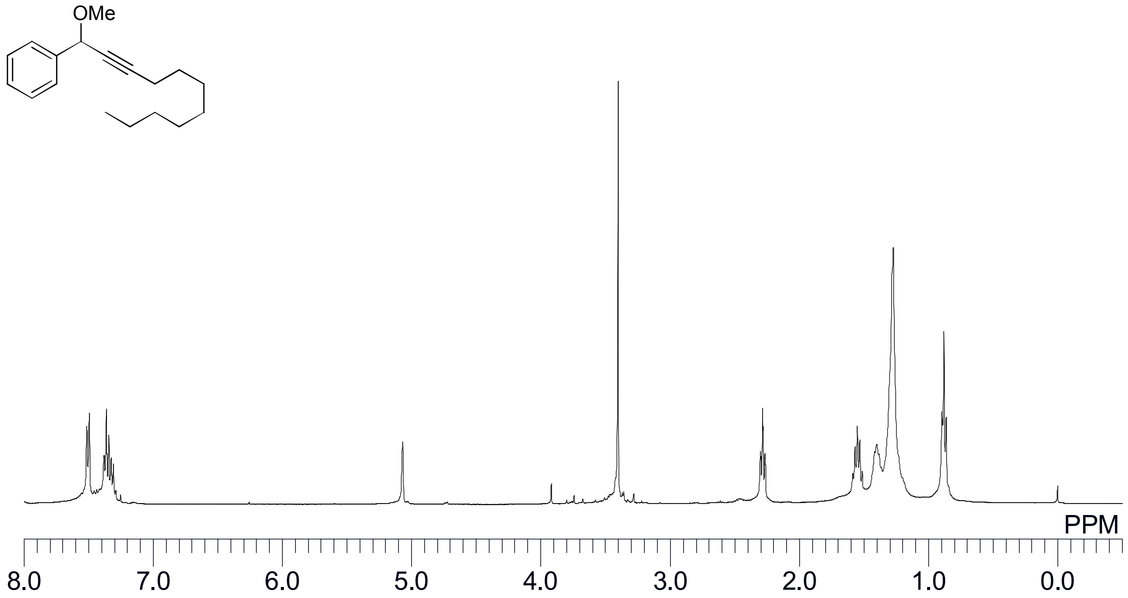


^{13}C NMR (100 MHz, in CDCl$_3$)

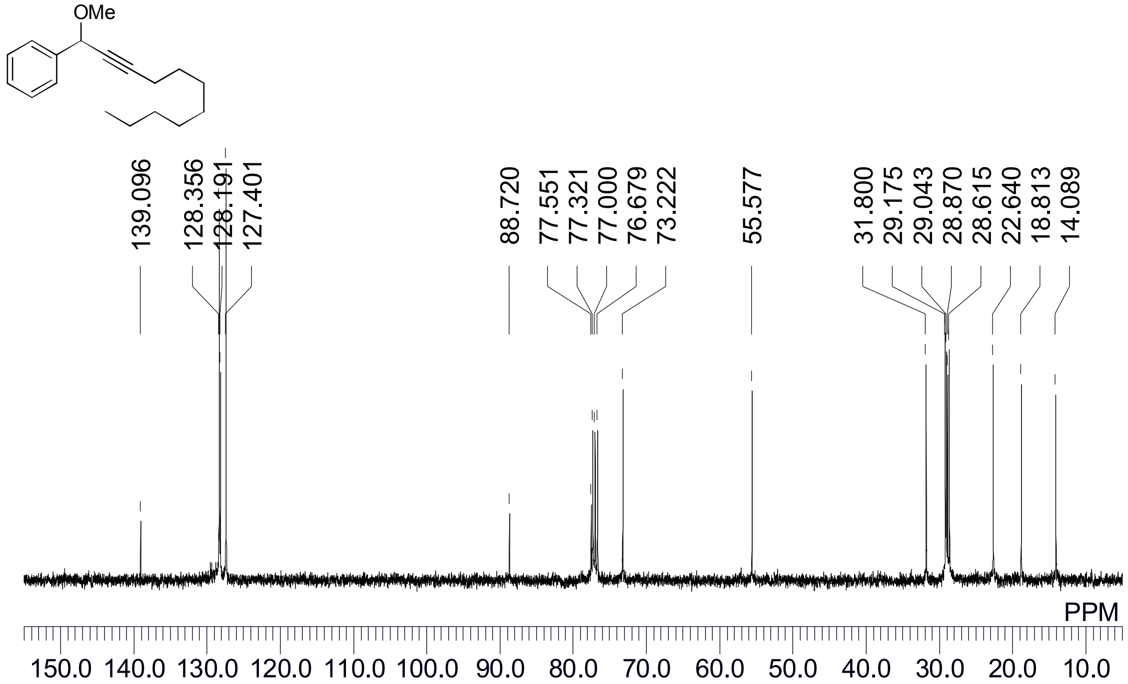


1-Methoxy-1-phenyl-2-undecyne (3aa)

^{1}H NMR (400 MHz, in CDCl$_3$)

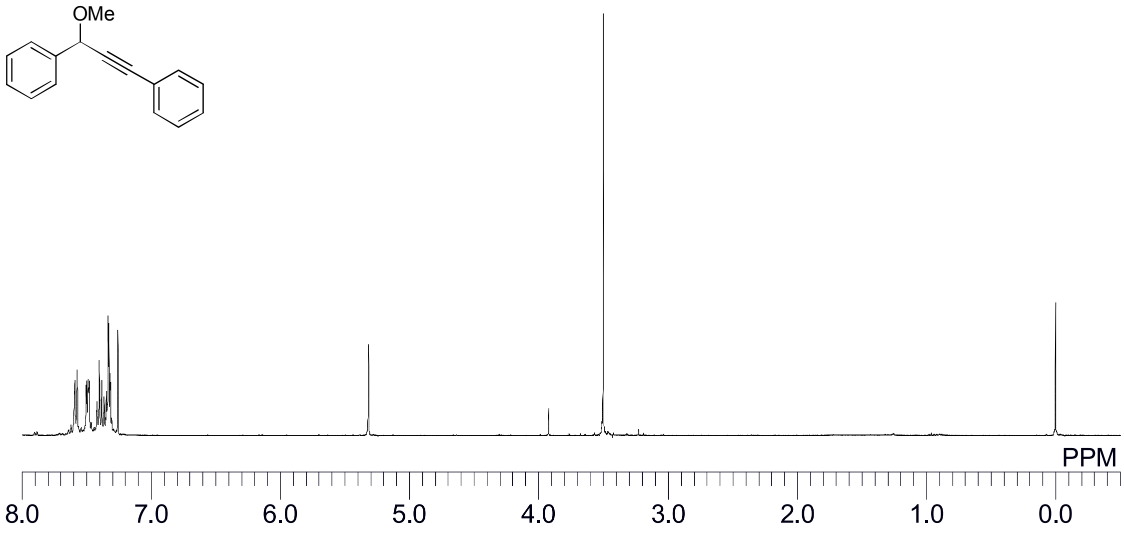


^{13}C NMR (100 MHz, in CDCl$_3$)

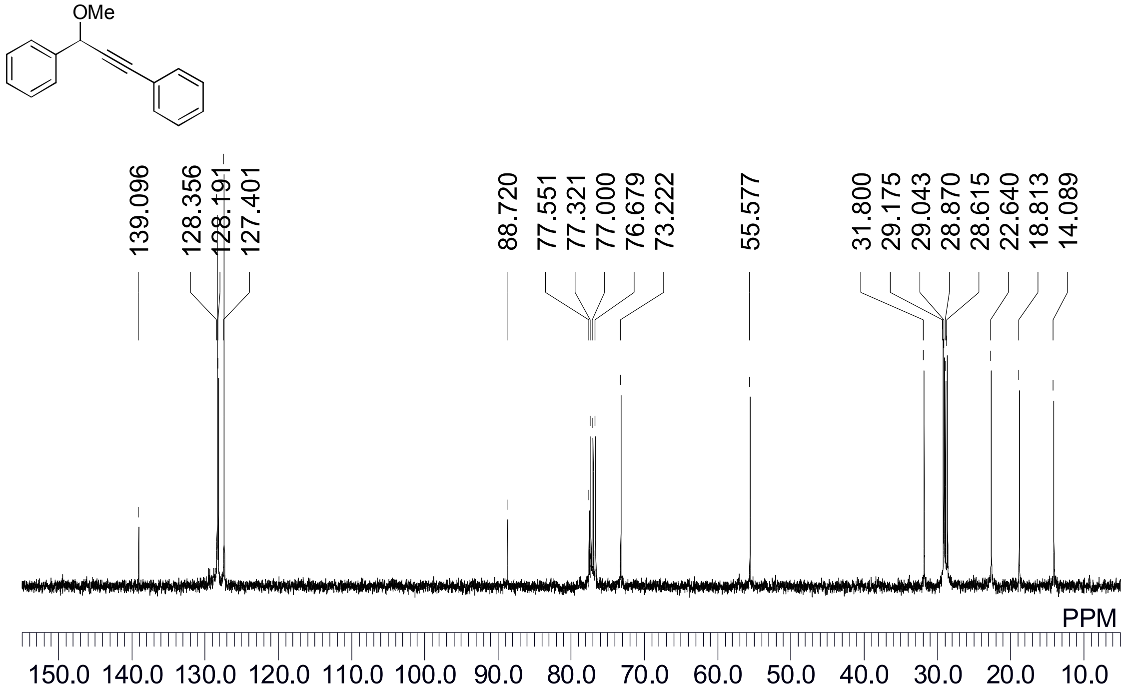


1-Methoxy-1,3-diphenyl-2-propyne (3ab)

^{1}H NMR (400 MHz, in $CDCl_3$

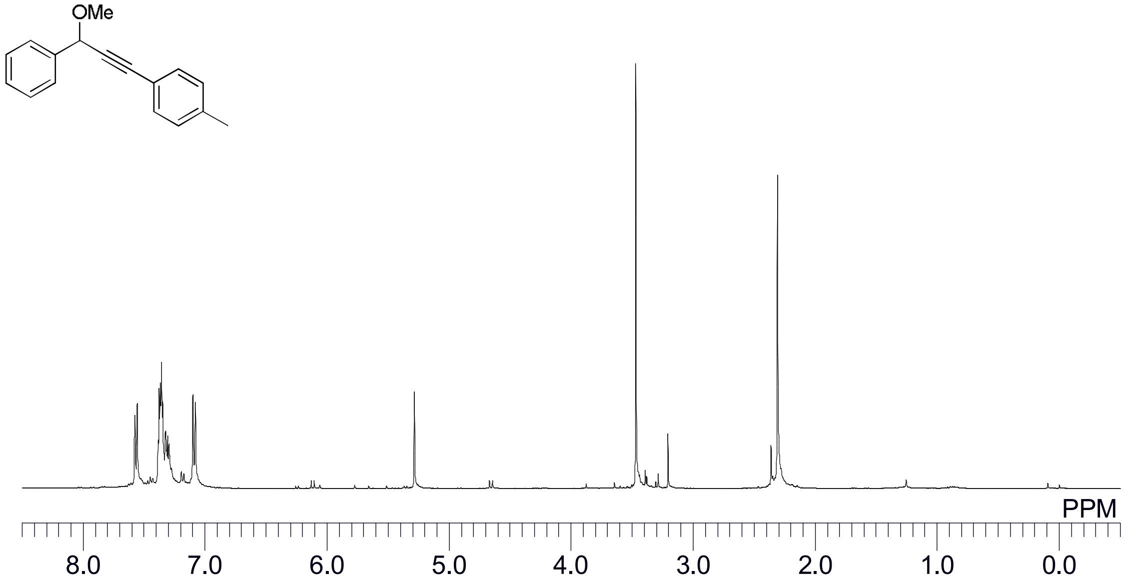


^{13}C NMR (100 MHz, in $CDCl_3$)

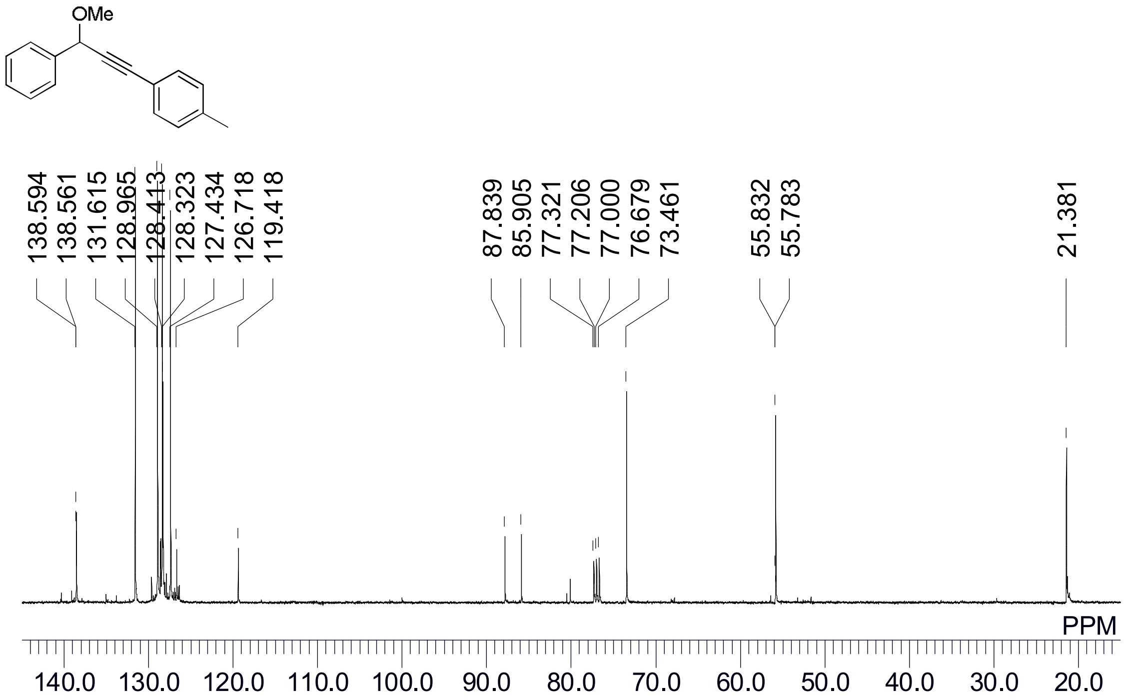


1-Methoxy-1-phenyl-3-(4-methylphenyl)-2-propyne (3ac)

^{1}H NMR (400 MHz, in CDCl$_3$)

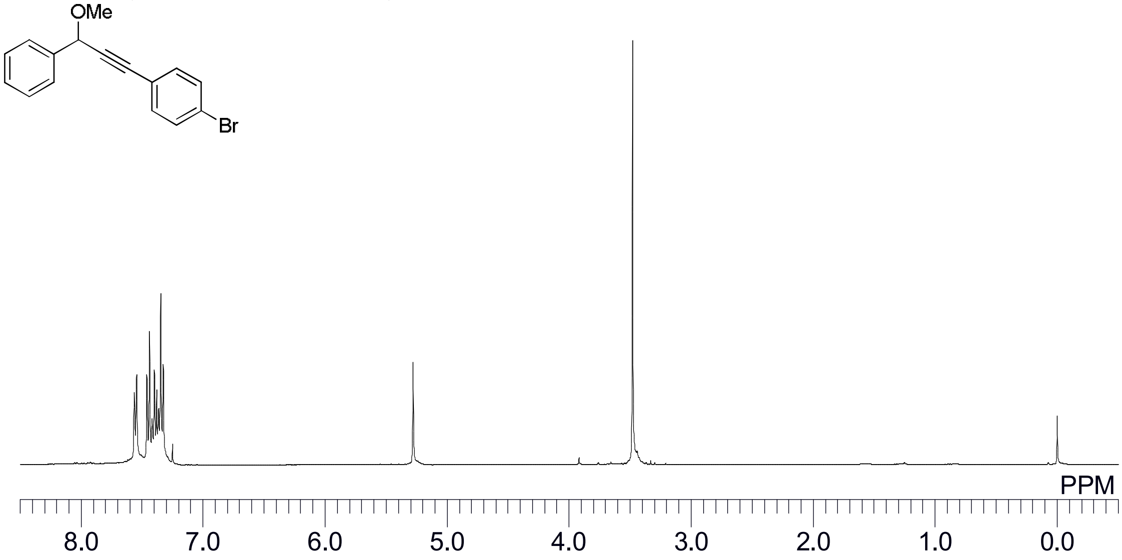


^{13}C NMR (100 MHz, in CDCl$_3$)

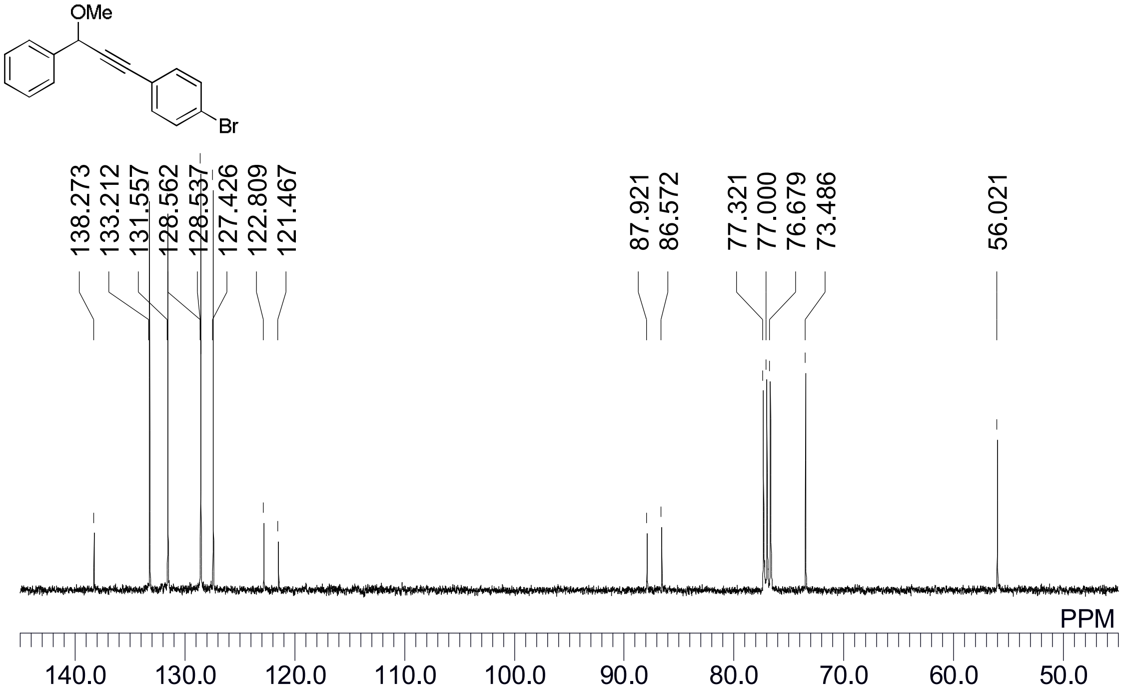


1-Methoxy-1-phenyl-3-(4-bromophenyl)-2-propyne (3ad)

^{1}H NMR (400 MHz, in CDCl$_3$)

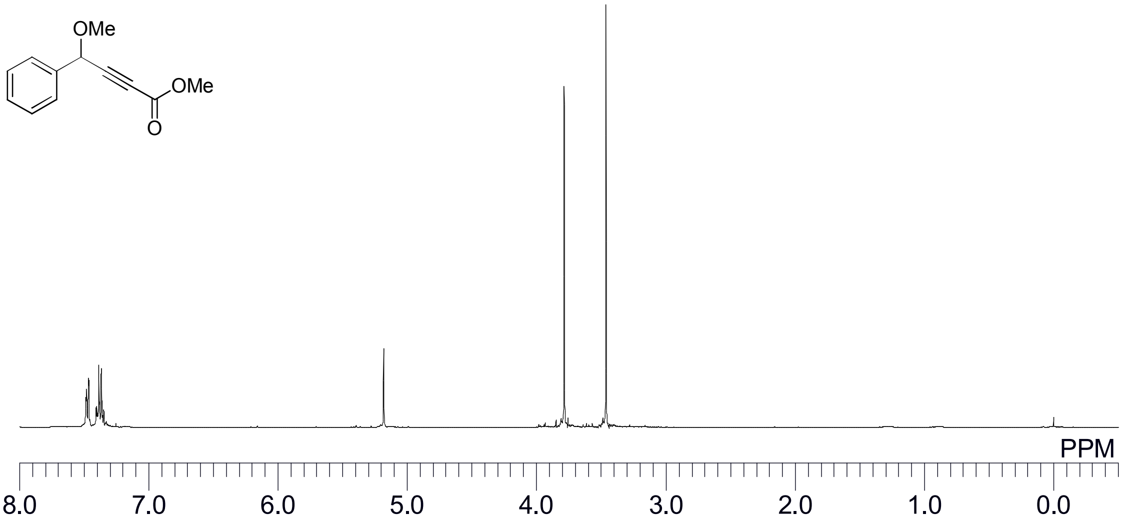


^{13}C NMR (100 MHz, in CDCl$_3$)

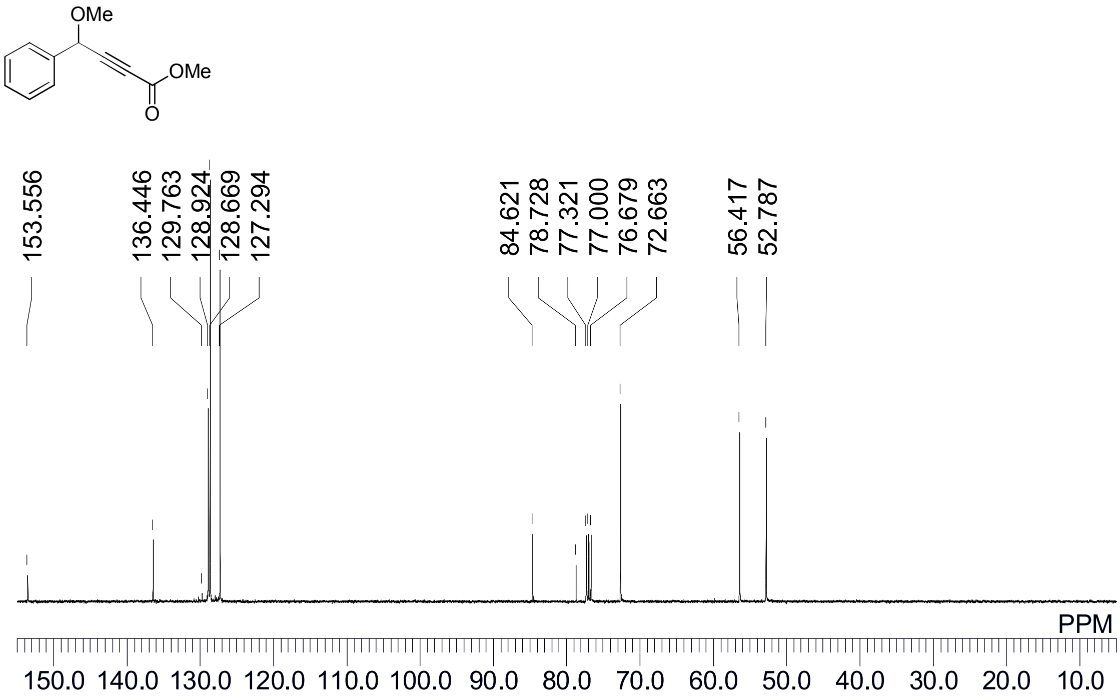


Methyl 4-methoxy-4-phenylbut-2-ynoate (3ae)

^{1}H NMR (400 MHz, in $CDCl_3$)

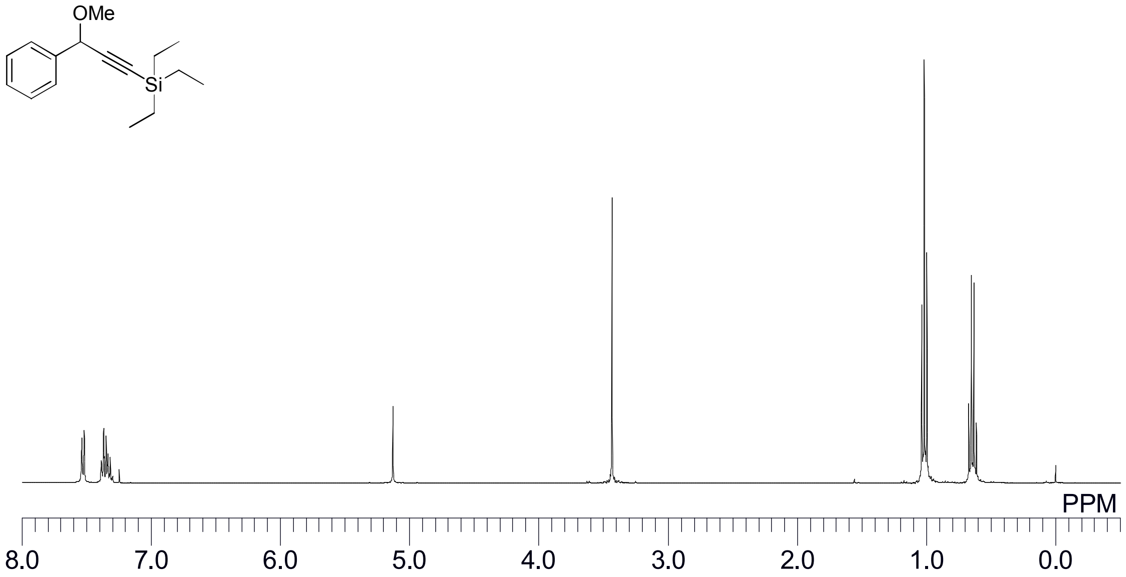


^{13}C NMR (100 MHz, in $CDCl_3$)

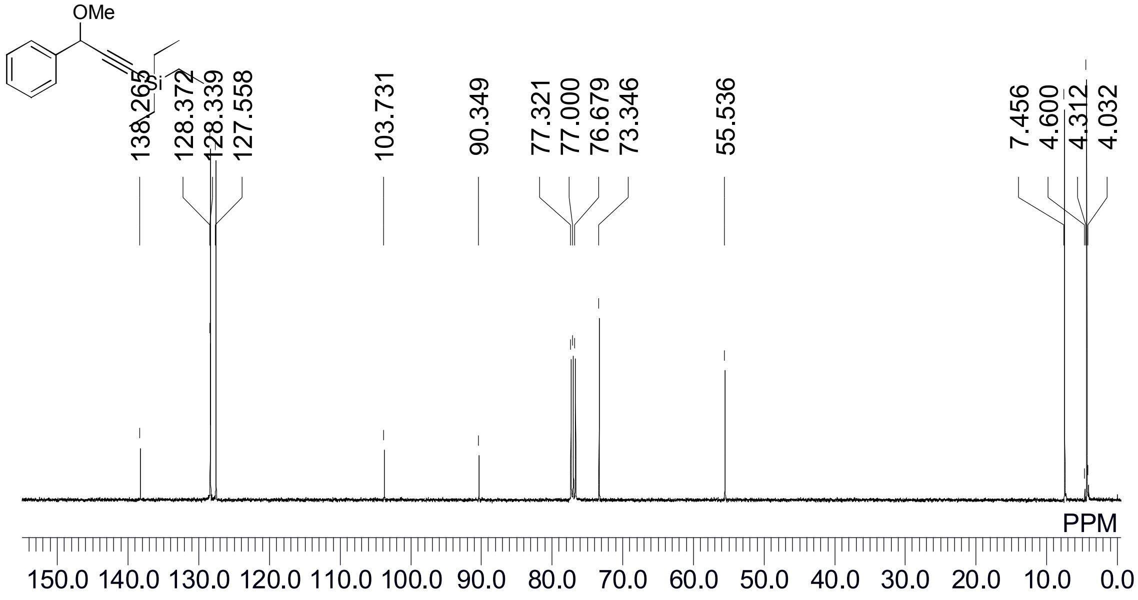


Triethyl(3-methoxy-3-phenylprop-1-ynyl)silane (3af)

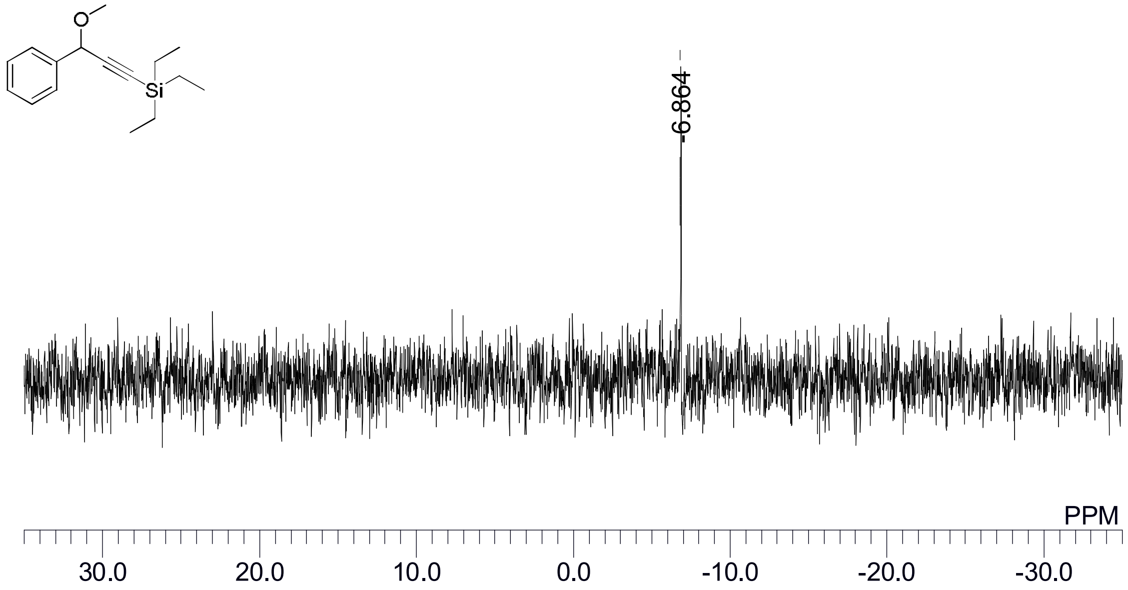
^{1}H NMR (400 MHz, in CDCl$_3$)



^{13}C NMR (100 MHz, in CDCl$_3$)

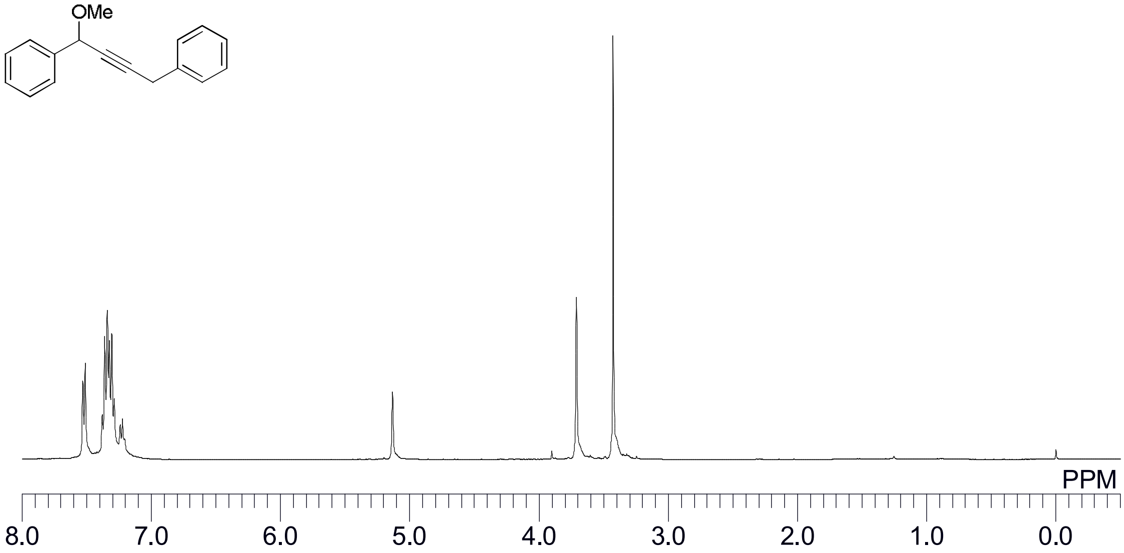


^{29}Si NMR (78.5 MHz, in $CDCl_3$ external standard = $SiMe_4$ in $CDCl_3$)

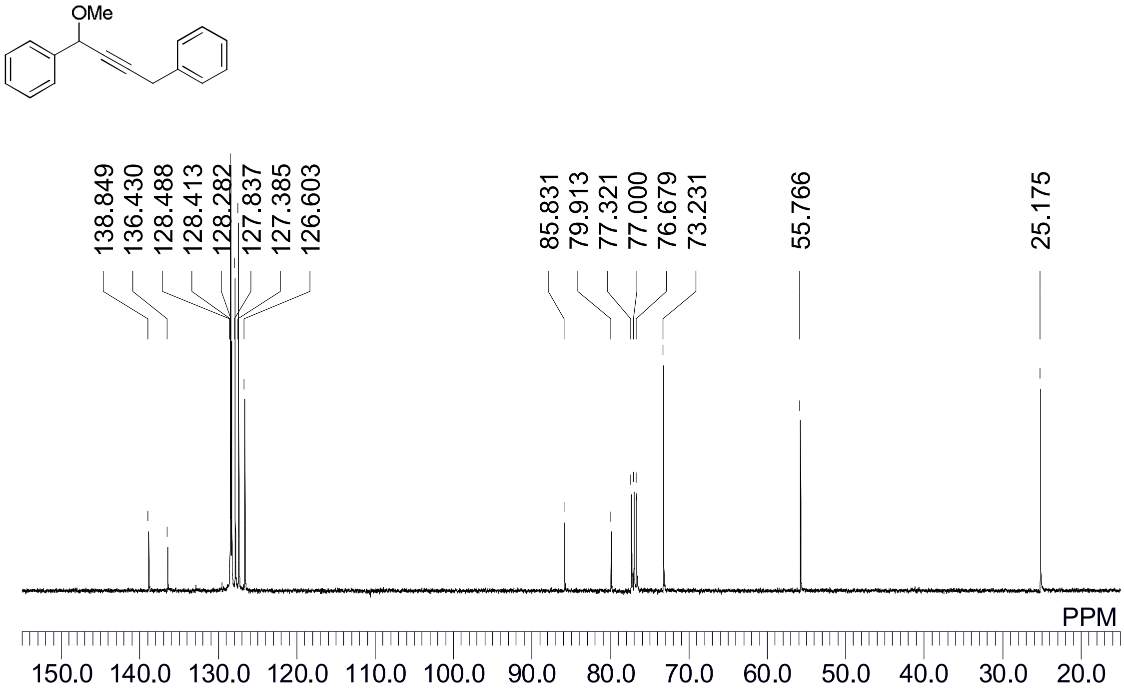


1-Methoxy-1,4-diphenyl-2-butyne (3ag)

^{1}H NMR (400 MHz, in CDCl$_3$)

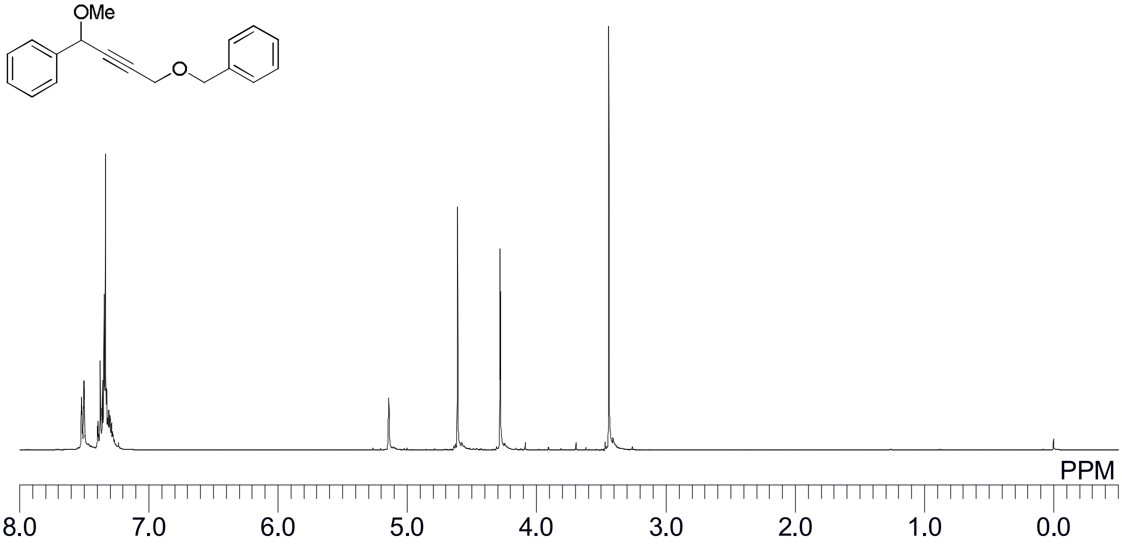


^{13}C NMR (100 MHz, in CDCl$_3$)

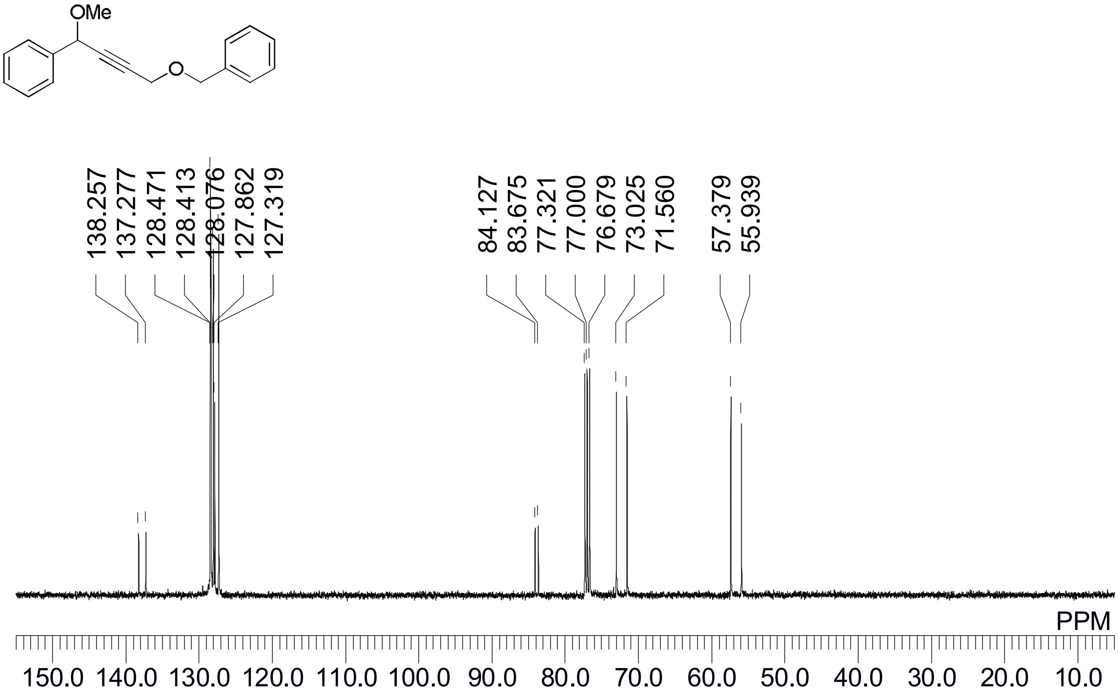


4-Benzyloxy-1-methoxy-1-phenyl-2-butyne (3ah)

^{1}H NMR (400 MHz, in CDCl$_3$)

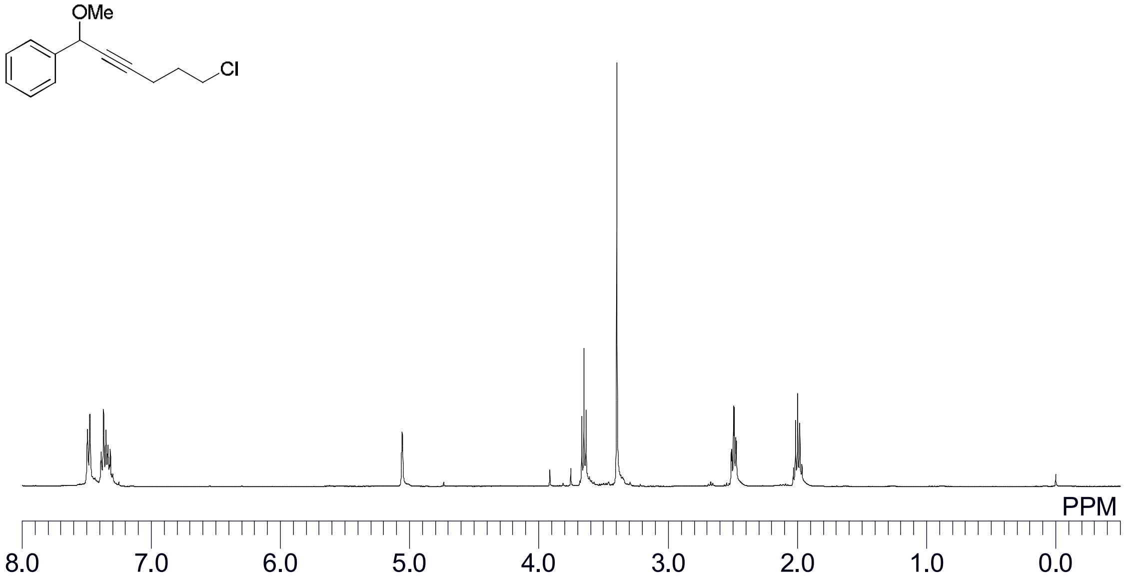


^{13}C NMR (100 MHz, in CDCl$_3$)

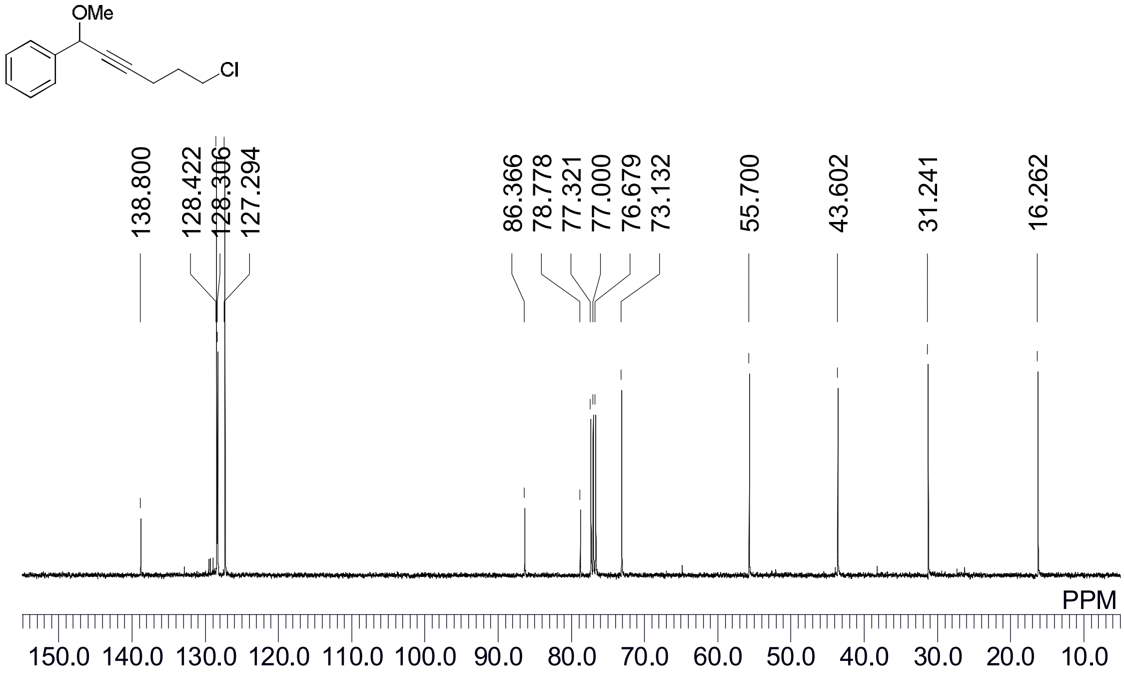


6-Chloro-1-methoxy-1-phenyl-2-hexyne (3ai)

^{1}H NMR (400 MHz, in CDCl$_3$)

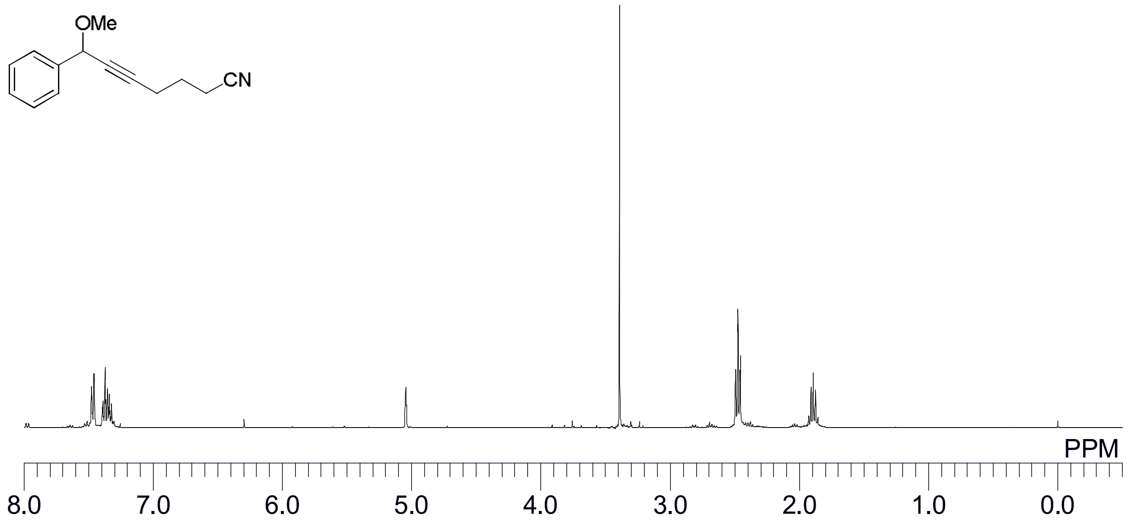


^{13}C NMR (100 MHz, in CDCl$_3$)

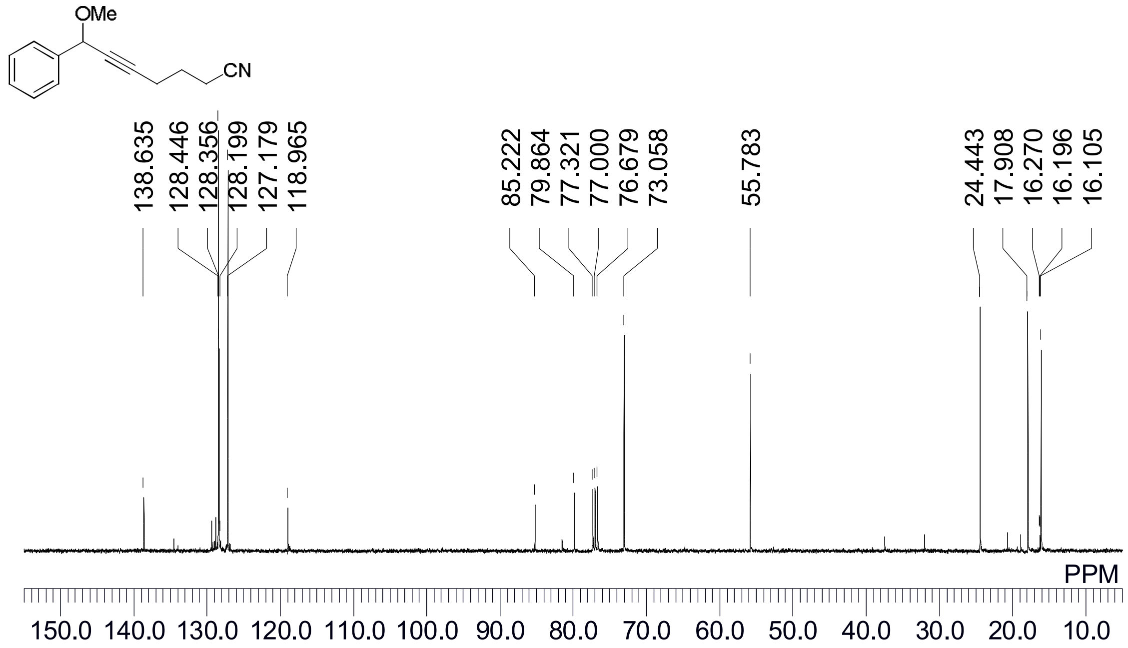


7-Methoxy-7-phenyl-5-heptynenitrile (3aj)

^{1}H NMR (400 MHz, in $CDCl_3$)

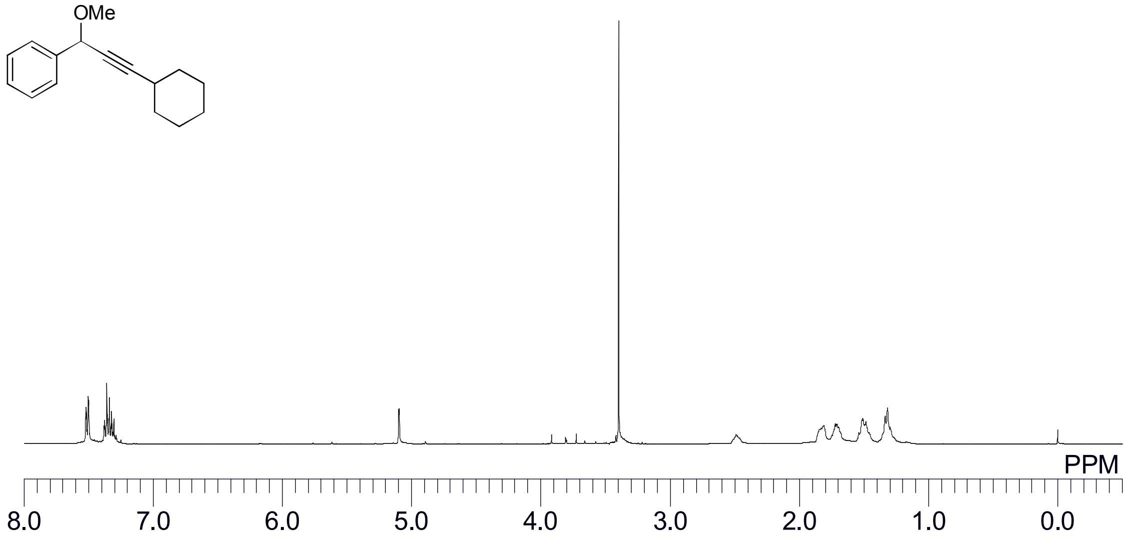


^{13}C NMR (100 MHz, in $CDCl_3$)

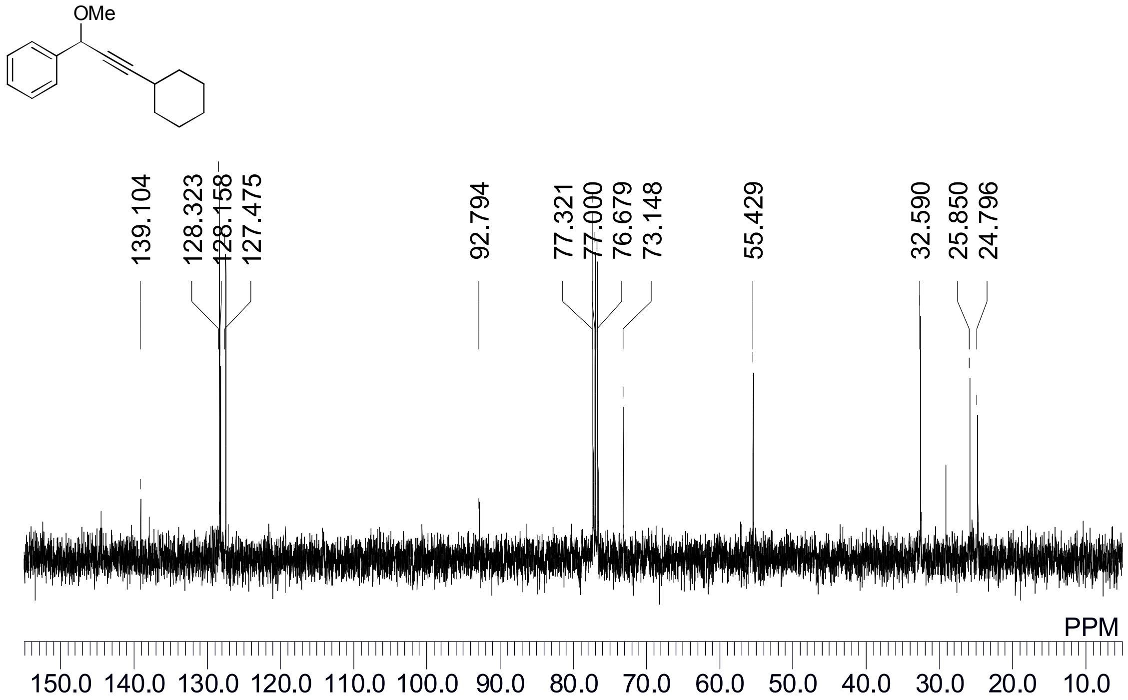


3-Cyclohexyl-1-methoxy-1-phenyl-2-propyne (3ak)

^{1}H NMR (400 MHz, in $CDCl_3$)

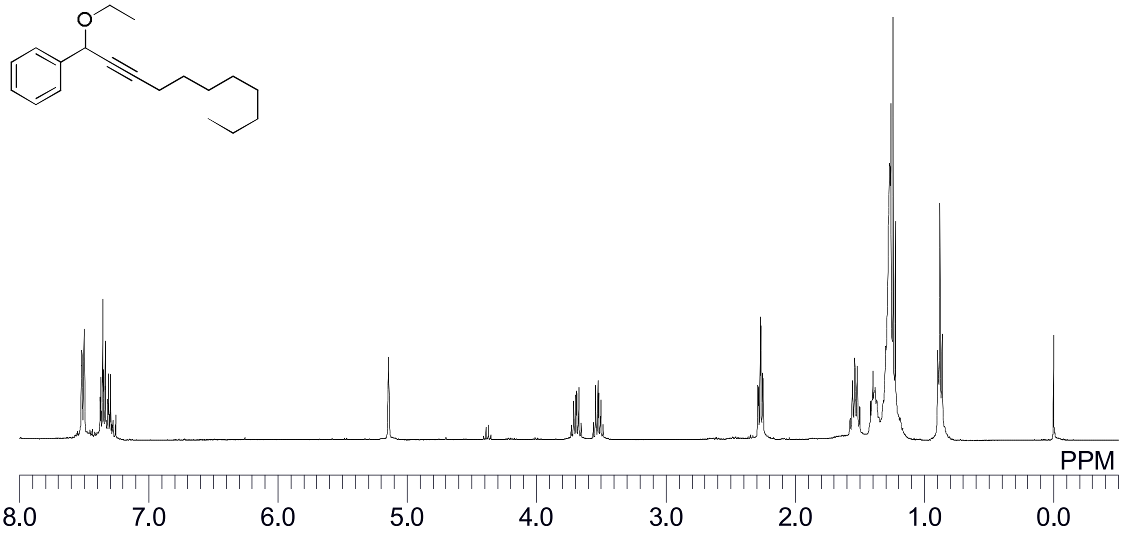


^{13}C NMR (100 MHz, in $CDCl_3$)

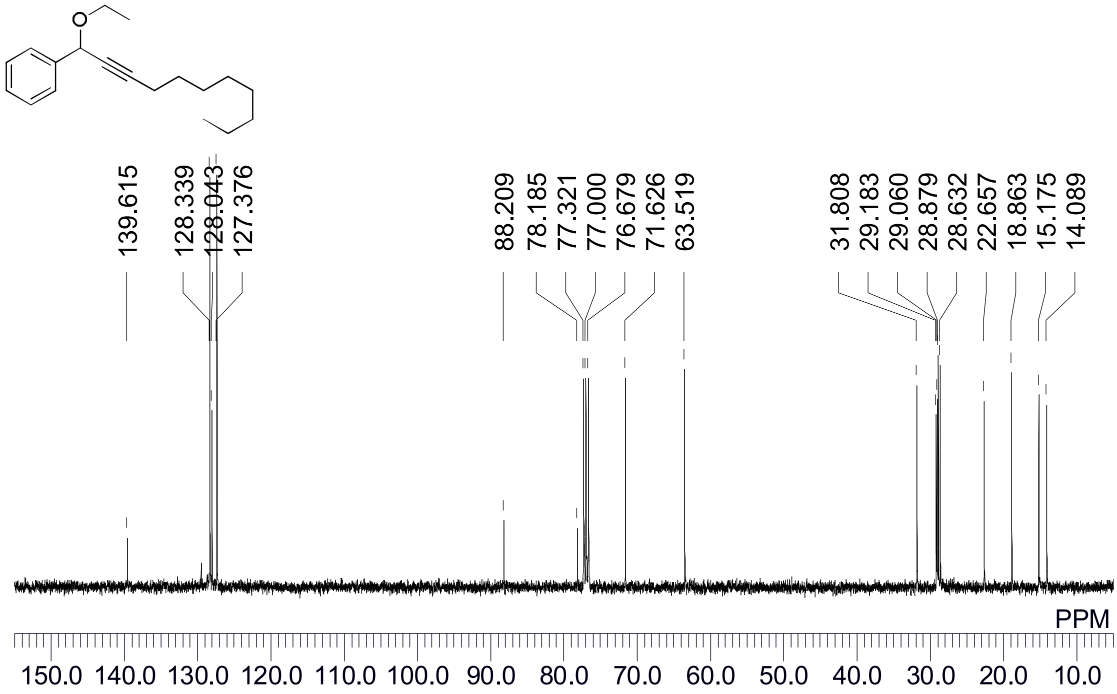


1-Ethoxy-1-phenyl-2-undecyne (3ba)

^{1}H NMR (400 MHz, in CDCl$_3$)

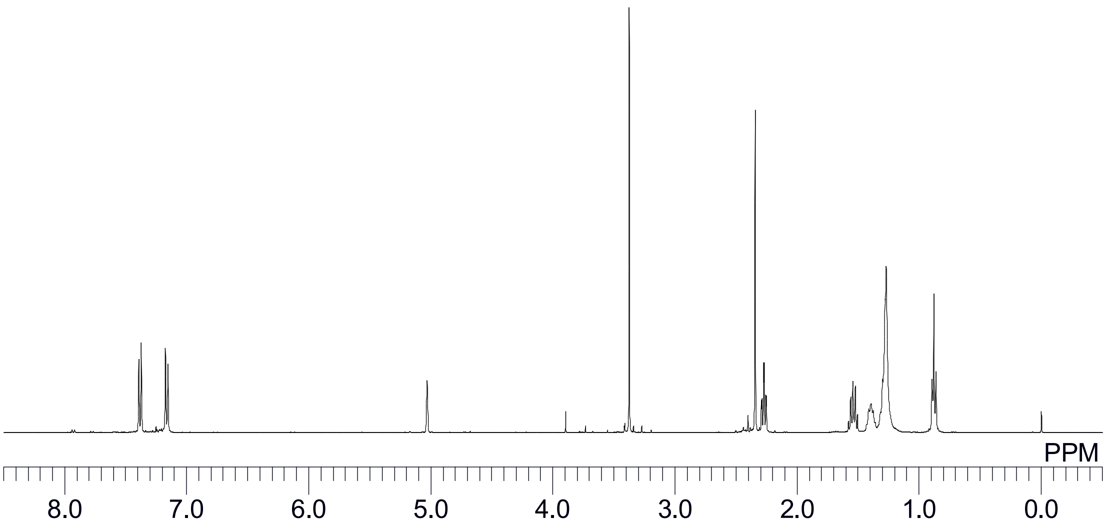


^{13}C NMR (100 MHz, in CDCl$_3$)

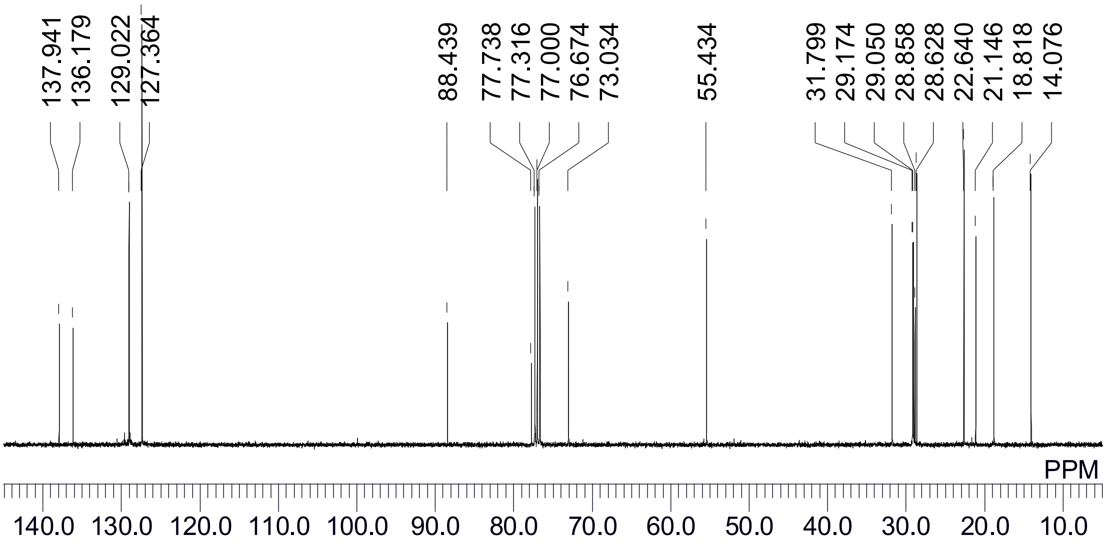


1-Methoxy-1-(4-methyl)phenyl-2-undecyne (3da)

^{1}H NMR (400 MHz, in CDCl$_3$)

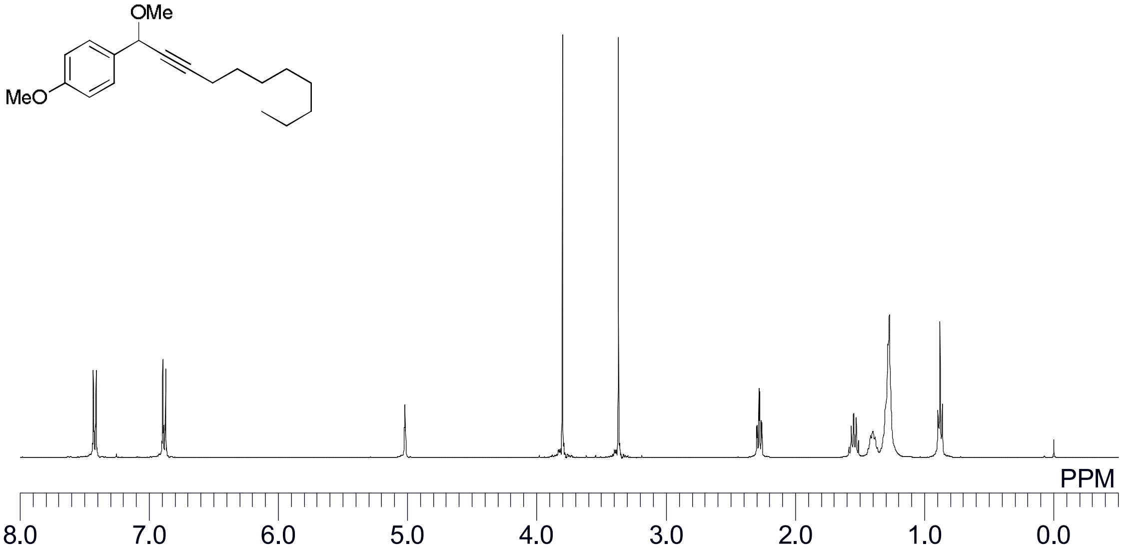


^{13}C NMR (100 MHz, in CDCl$_3$)

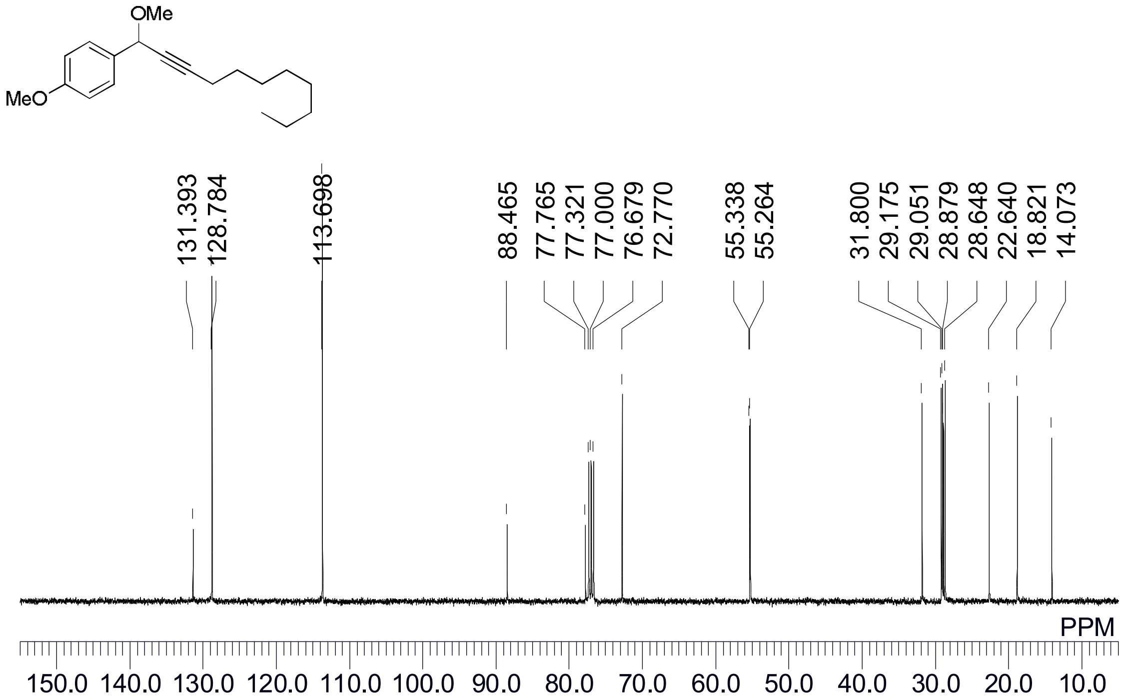


1-Methoxy-1-(4-methoxyphenyl)-2-undecyne (3ea)

^{1}H NMR (400 MHz, in CDCl$_3$)

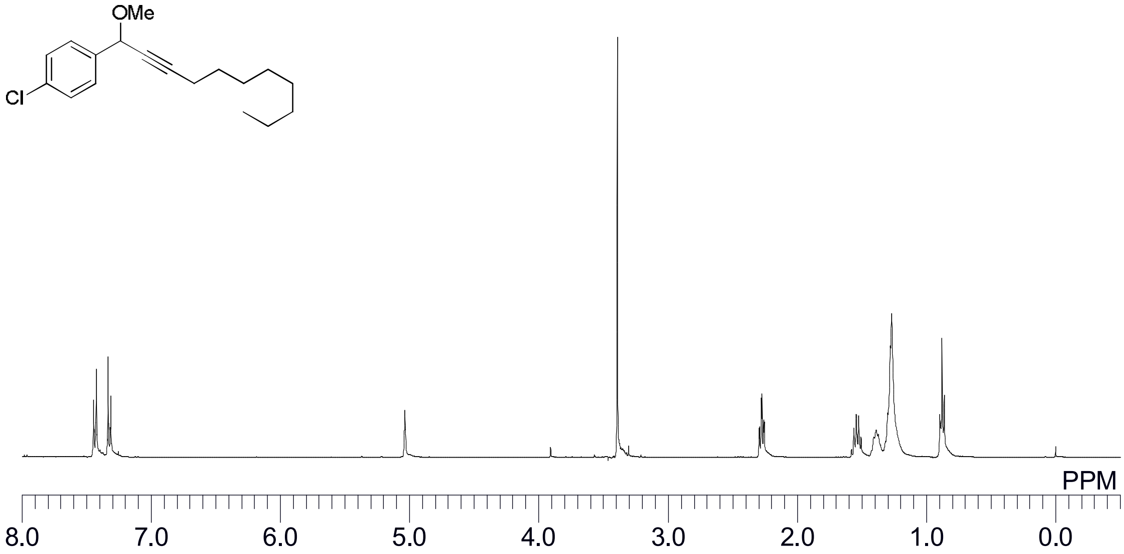


^{13}C NMR (100 MHz, in CDCl$_3$)

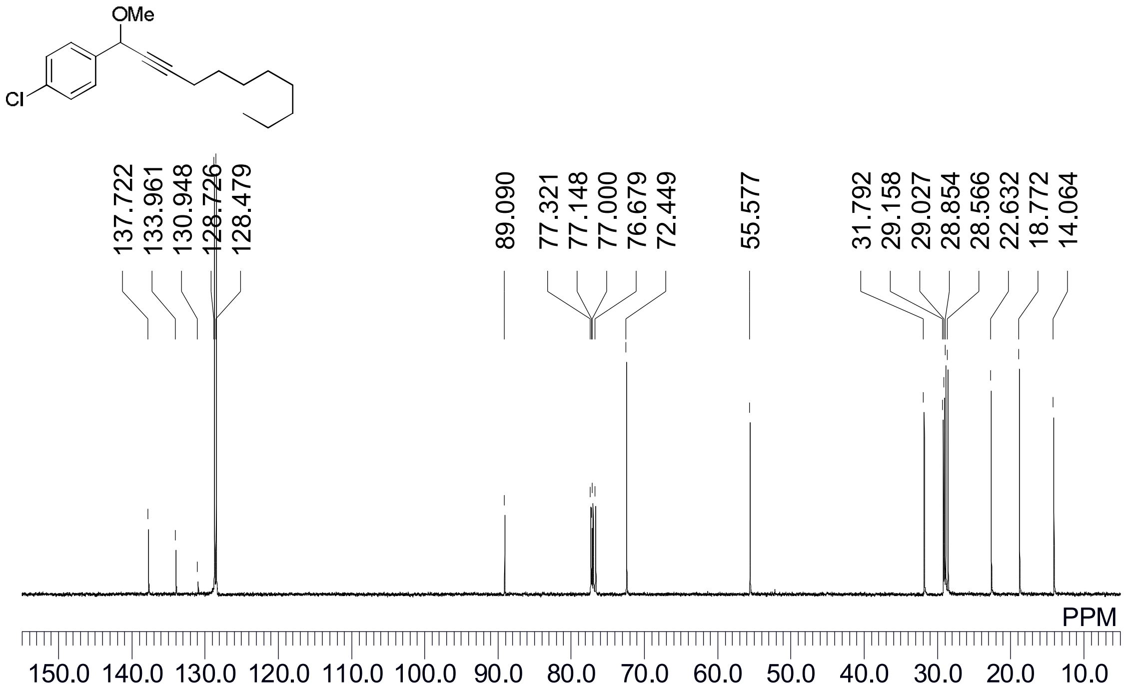


1-Methoxy-1-(4-chlorophenyl)-2-undecyne (3fa)

^{1}H NMR (400 MHz, in CDCl$_3$)

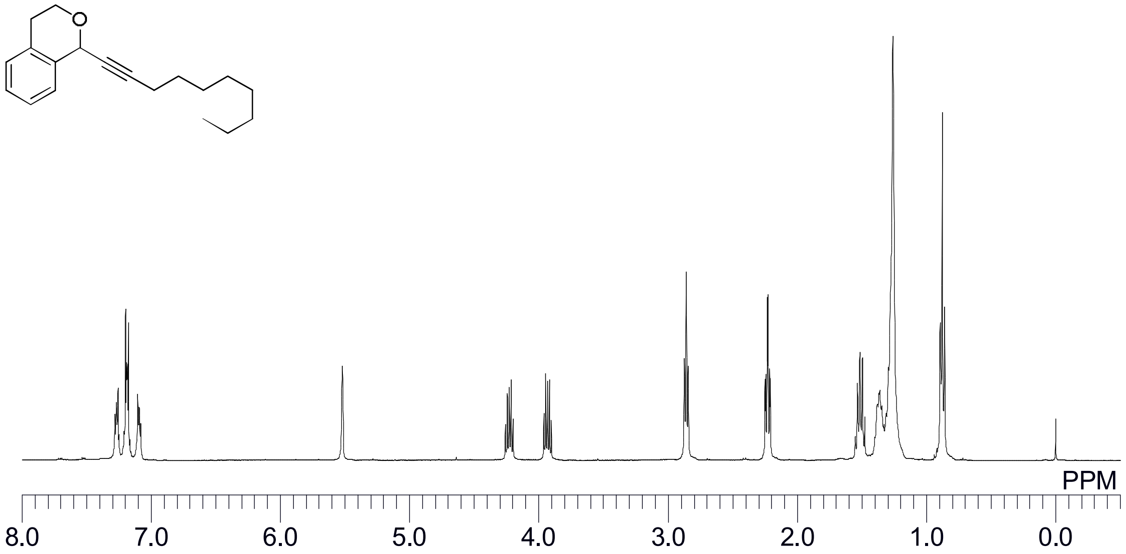


^{13}C NMR (100 MHz, in CDCl$_3$)

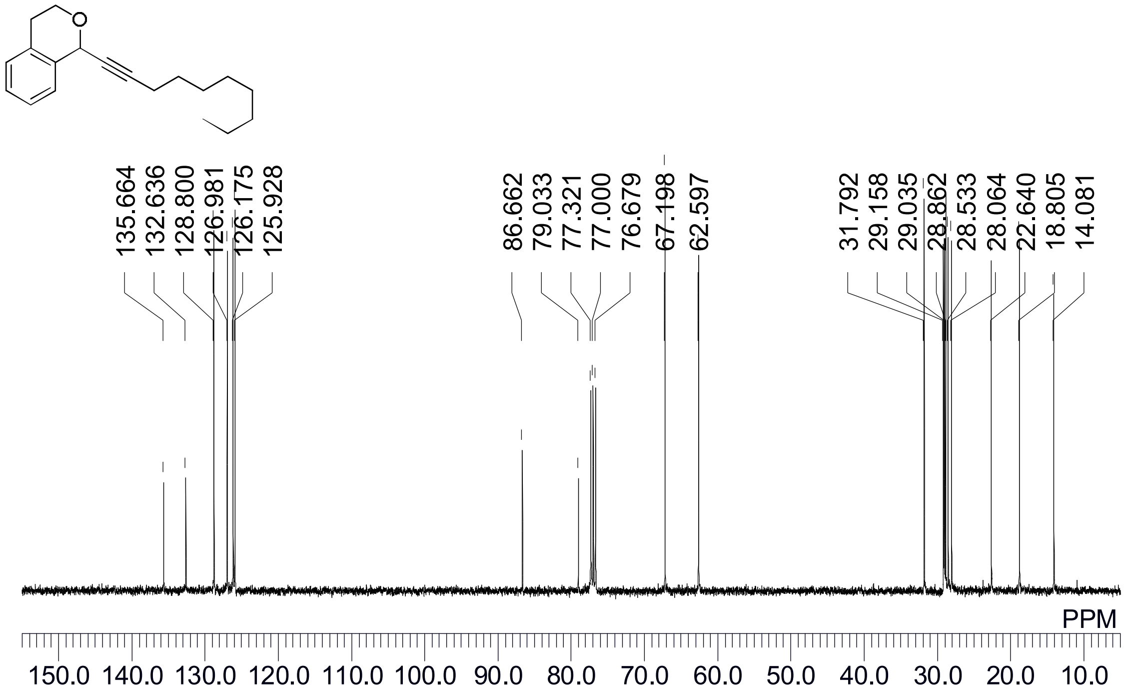


1-(Dec-1-ynyl)isochroman (3ga)

^{1}H NMR (400 MHz, in $CDCl_3$)



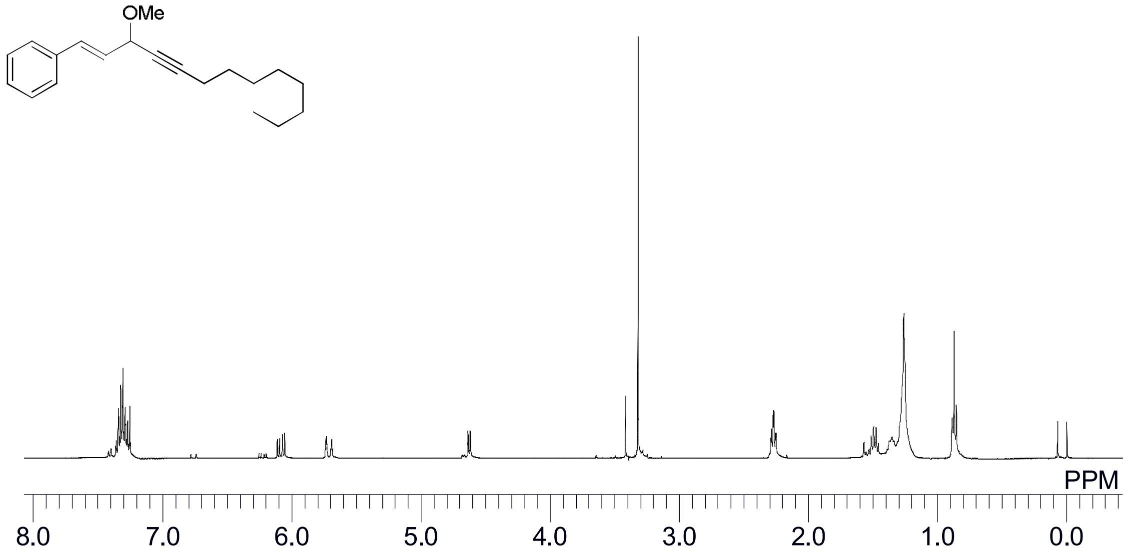
^{13}C NMR (100 MHz, in $CDCl_3$)



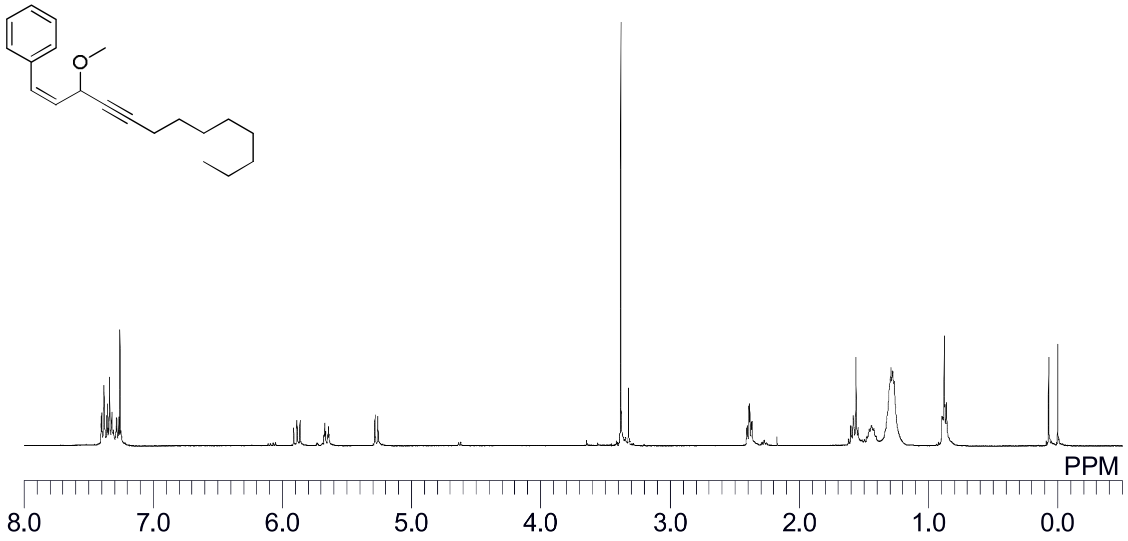
1-Phenyl-3-methoxytridec-1-en-4-yne (3ha)

^1H NMR (400 MHz, in $CDCl_3$)

(*E*-isomer)

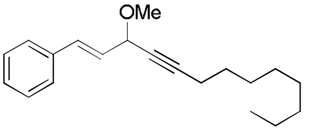


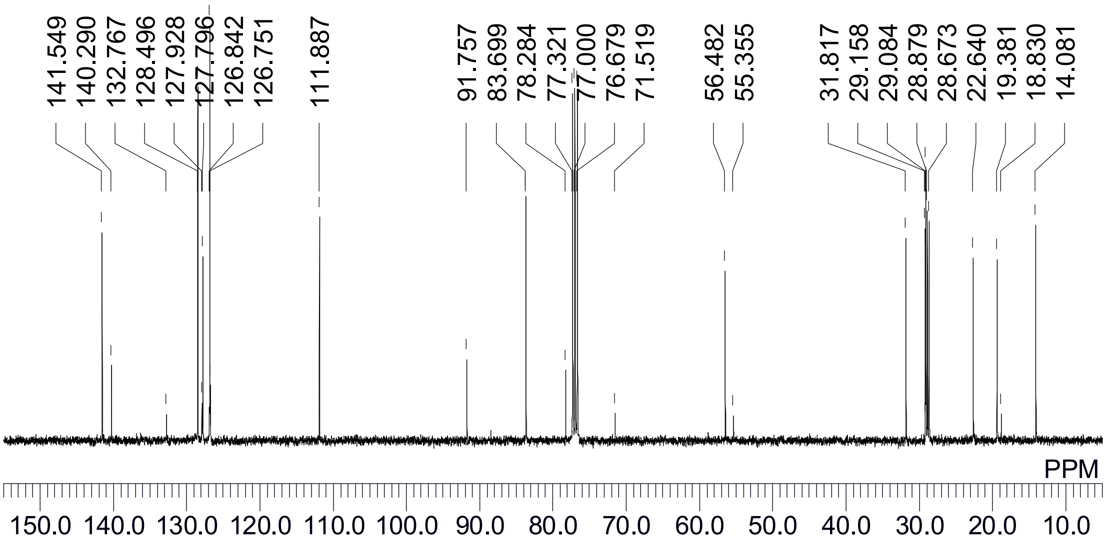
(*Z*-isomer)



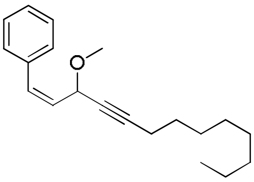
^{13}C NMR (100 MHz, in $CDCl_3$)

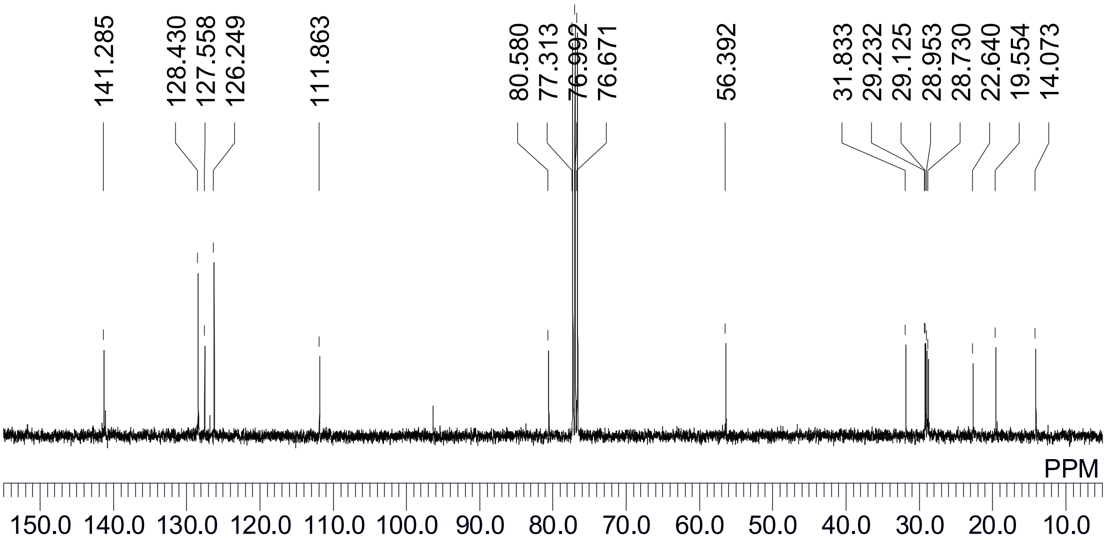
(*E*-isomer)





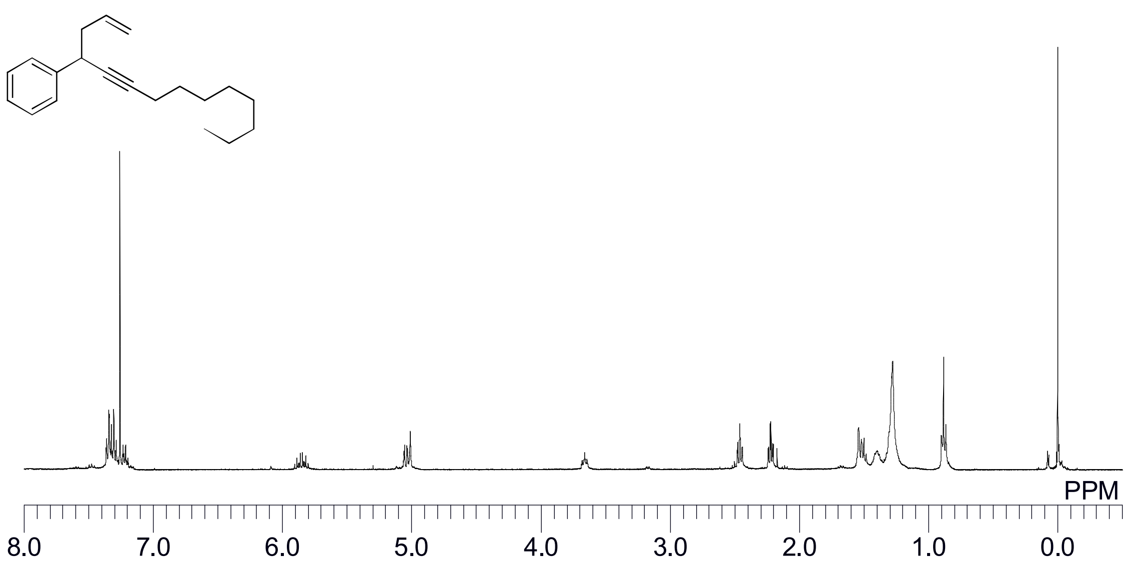
(*Z*-isomer)





4-Phenyltetradec-1-en-5-yne (11)

^{1}H NMR (400 MHz, in CDCl$_3$)



^{13}C NMR (100 MHz, in CDCl$_3$)