Light Mediated Preparation of Palladium Nanoparticles as Catalysts for Alkyne *cis*-Semihydrogenation

Florian Mäsing,[+] Harald Nüsse,[#] Jürgen Klingauf,[#] and Armido Studer[+]*

[+] Institute of Organic Chemistry, University of Münster, Corrensstrasse 40, 48149 Münster, Germany

[#] Institute of Medical Physics and Biophysics, University of Münster, Robert-Koch-Strasse 31, 48149 Münster, Germany

Supporting Information

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Abbreviations

atm	standard atmosphere
d	diameter
DCM	dichloromethane
DMF	dimethylformamide
equiv.	equivalents
EtOAc	ethyl acetate
g	grams
h	hours
λ	wavelength
L	litres
m	milli
M	molar
min	minutes
mol	moles
nm	nanometers
MTBE	methyl *tert*-butyl ether
UV	ultraviolet
°C	degree Celsius

General Information

Commercially available chemicals were purchased from *Sigma-Aldrich*, *Fisher Scientific*, *Fluka*, *Acros Organics*, *Alfa Aesar* or *TCI Germany*. Dimethylformamide (extra pure) was purchased for *Acros Organics* and $Pd(OAc)_2$ ≥99.9% from *Sigma Aldrich*. Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide was purchased from *Sigma Aldrich*, whereas diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide was purchased from *TCI*.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on an *Agilent DD2 600* (600 MHz), *Bruker AV 400 (400 MHz), Bruker AV 300* (300 MHz) or *Bruker dpx 300* (300 MHz) spectrometer. Chemical shifts δ in ppm are referenced to the solvent residual peak as an internal standard. Multiplicities of signals were abbreviated with *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), quin (quintet), sext (sextet), *m* (multiplet) and *br* (broad signal). Coupling constants *J* were reported in Hz.

TEM-images were recorded on a *Philips CM10 TEM* (100 kV) at the *University of Münster*. TEM was combined with a *CMOS UI-1480-M-G* camera from *IDS Imaging Development Systems GmbH*. Analysis of TEM-images was performed using *Gatan Microscopy Suite, DigitalMicrograph V. 2.30* software.

High resolution electrospray ionisation mass spectra HRMS (ESI) were recorded on a *Bruker Daltonics MicroTof* mass spectrometer.

High resolution atmospheric pressure chemical ionization mass spectra HRMS (APCI) were recorded on a *Thermo Scientific Orbitrap LTQ XL* mass spectrometer.

GC-MS chromatograms were recorded on an *Agilent Technologies 7890A* GC-system equipped with an *Agilent 5975C VL MSD* (EI) detector and a HP-5MS column with helium as carrier gas; the major signals are quoted as ratio of m/z in Daltons; the method used starts with the injection temperature T0, after holding this temperature for 3 min, the column is heated to temperature T1 (ramp) and this temperature is held for an additional time t (method 50_40: T0 = 50 °C, T1 = 290 °C, ramp = 40 °C/min, t = 10 min).

GC-FID was conducted on an *Agilent GC 6890* equipped with a Flame Ionization Detection (FID) and a *Agilent HP-1*, *Methyl Siloxan*, *Model No: 19091Z-413* column using H_2 as carrier gas with a flow rate of 1.5 mL/min. The method used starts with the injection temperature T0, the column is heated to temperature T1 (ramp) and this temperature is held for an additional time t (T0 = 50 °C, T1 = 300 °C, ramp = 10 °C/min, t = 15 min).

Chiral GC-FID was conducted on a Agilent GC 6890 equipped with a Flame Ionization Detection (FID) and a *Supelco 24304 Beta Dex 120* column using H_2 as carrier gas with a flow rate of 1.5 mL/min. The method used starts with the injection temperature T0, the column is heated to temperature T1 (ramp) and T2 (ramp) and this temperature is held for an additional time t (T0 = 50 °C, T1 = 110 °C, ramp = 0.5 °C/min, T2 = 200, ramp = 6 °C/min, t = 15 min).

IR spectra were recorded on a *Digilab FTS 3100* spectrometer combined with a *Specac MKII Golden Gate Single Reflection ATR System*. Signals were given in wavenumbers $\tilde{\nu}\,(\mathrm{cm}^{-1})$. Intensities were abbreviated with (*vs*) very strong, (*s*) strong, (*m*) medium, (*w*) weak, (*vw*) very weak and (*br*) broad.

Photoreactions were carried out in quartz tubes. Irradiation was performed in a photo reactor *Photoreaktor 400m Blende* (Hg light-source; λ = 254 nm, max. 40 W light intensity) from *Gräntzel Karlsruhe*.

Photochemical Preparation of Pd Nanoparticles

Pd@1*

Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (16.7 mg, 40.0 µmol, 20 equiv.) and DMF (9.6 mL) were added to an argon purged quartz tube. $Pd(OAc)_2$ (5.00 mM in DMF, 400 µL, 2.00 µmol, 1.0 equiv.) was added and the resulting mixture was irradiated in a photoreactor for 10 min with UV-light (λ= 254 nm) at room temperature to obtain a brown solution. The irradiated solution was directly used for TEM-analysis (2.8±1.0 nm). Mean diameter d and standard deviation σ were determined considering 250 particles.

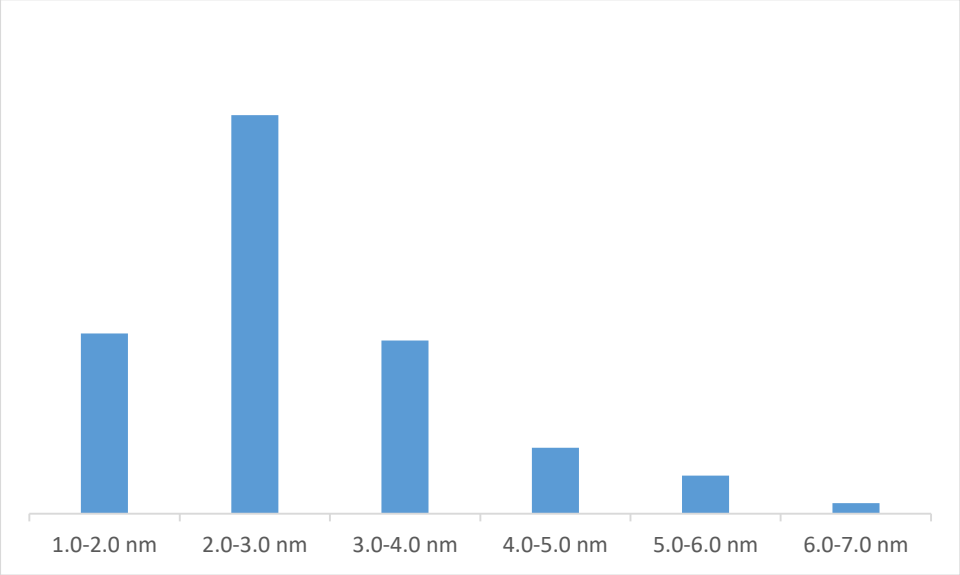


Figure S1: Size distribution of Pd@**1***.

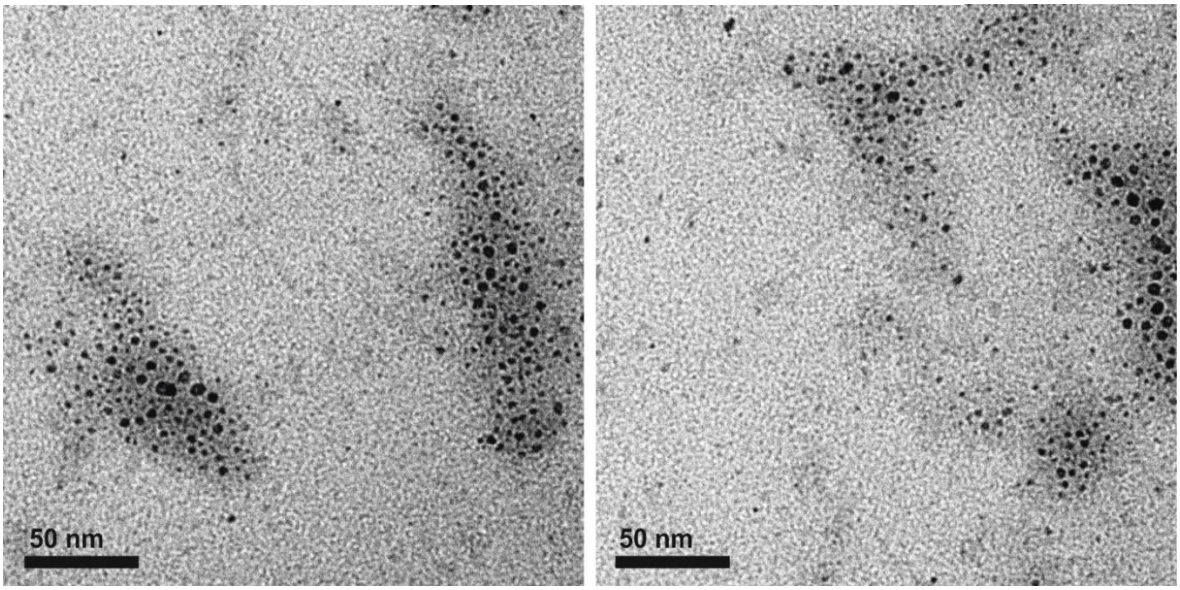


Figure S2: TEM-images of Pd@**1***.

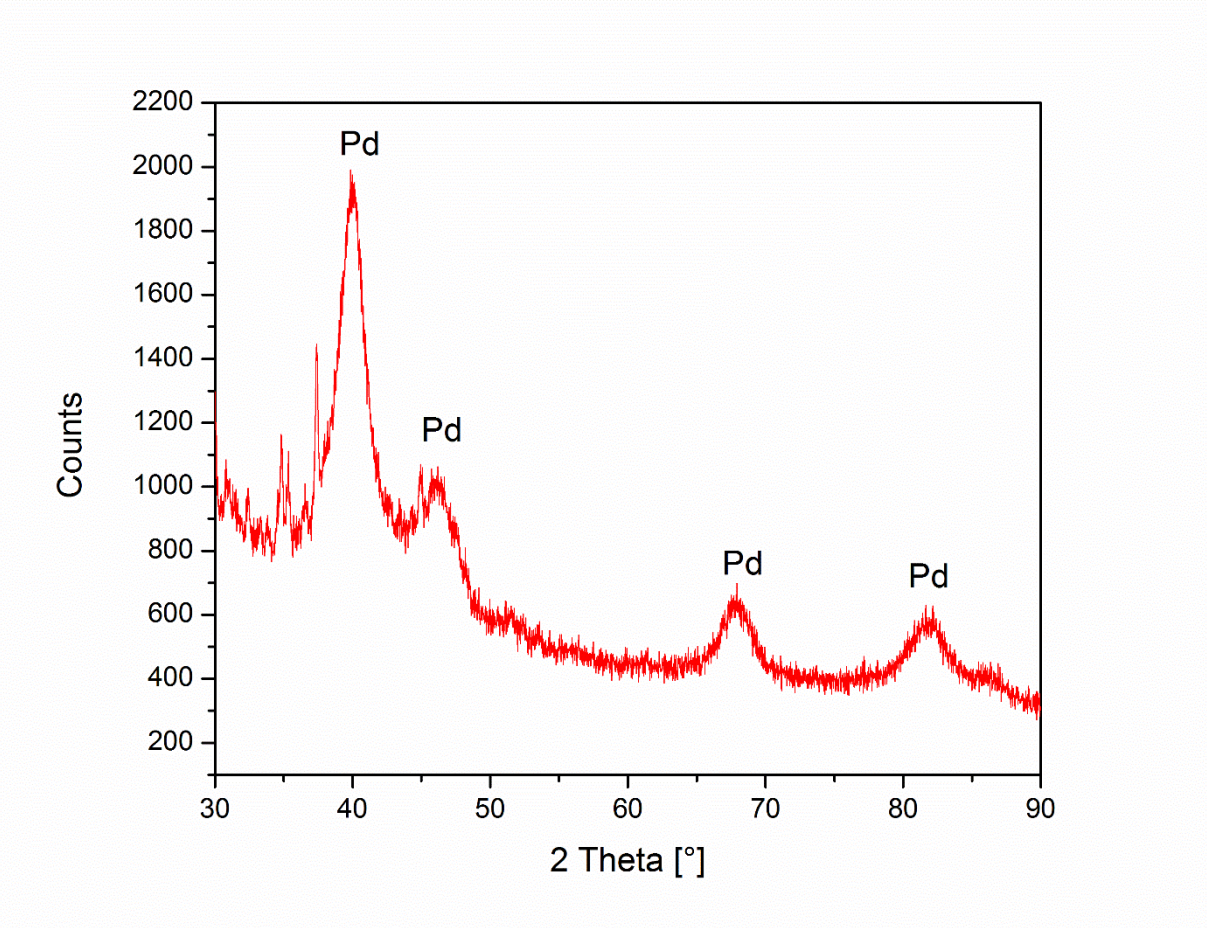


Figure S3: XRD pattern of Pd@**1***.

Pd@2*

Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (13.9 mg, 40.0 µmol, 20 equiv.) and DMF (9.6 mL) were added to an argon purged quartz tube. $Pd(OAc)_2$ (5.00 mM in DMF, 400 µL, 2.00 µmol, 1.0 equiv.) was added and the resulting mixture was irradiated in a photoreactor for 10 min with UV-light (λ= 254 nm) at room temperature to obtain a yellow solution. The irradiated solution was directly used for TEM-analysis (177±126 nm). Mean diameter d and standard deviation σ were determined considering 250 particles.

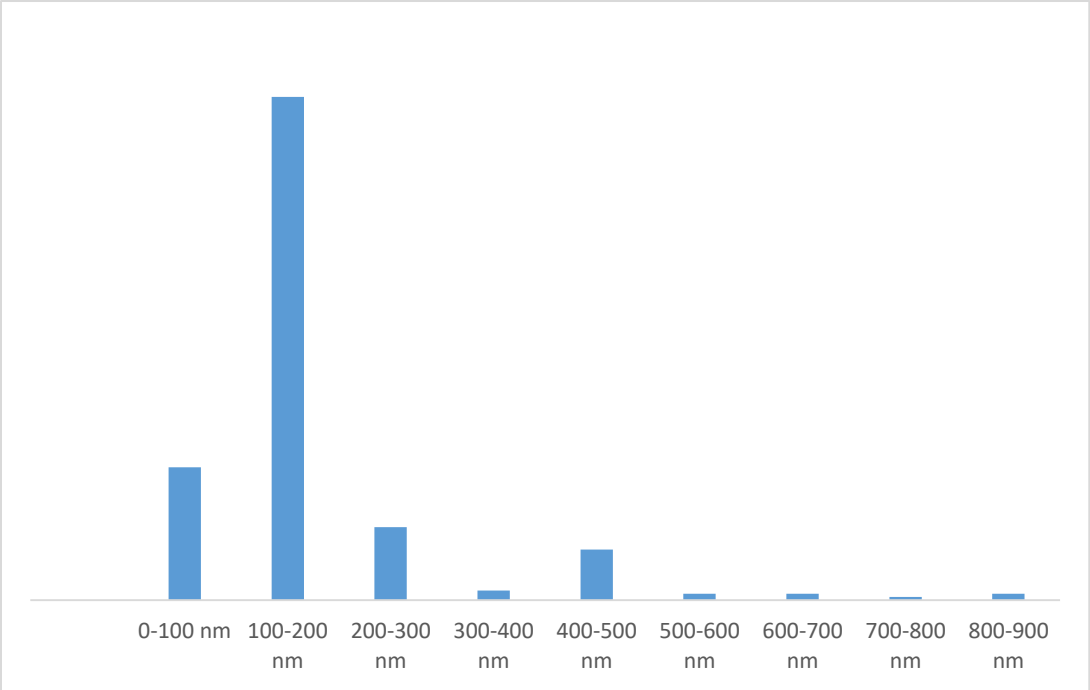


Figure S4: Size distribution of Pd@**2***.

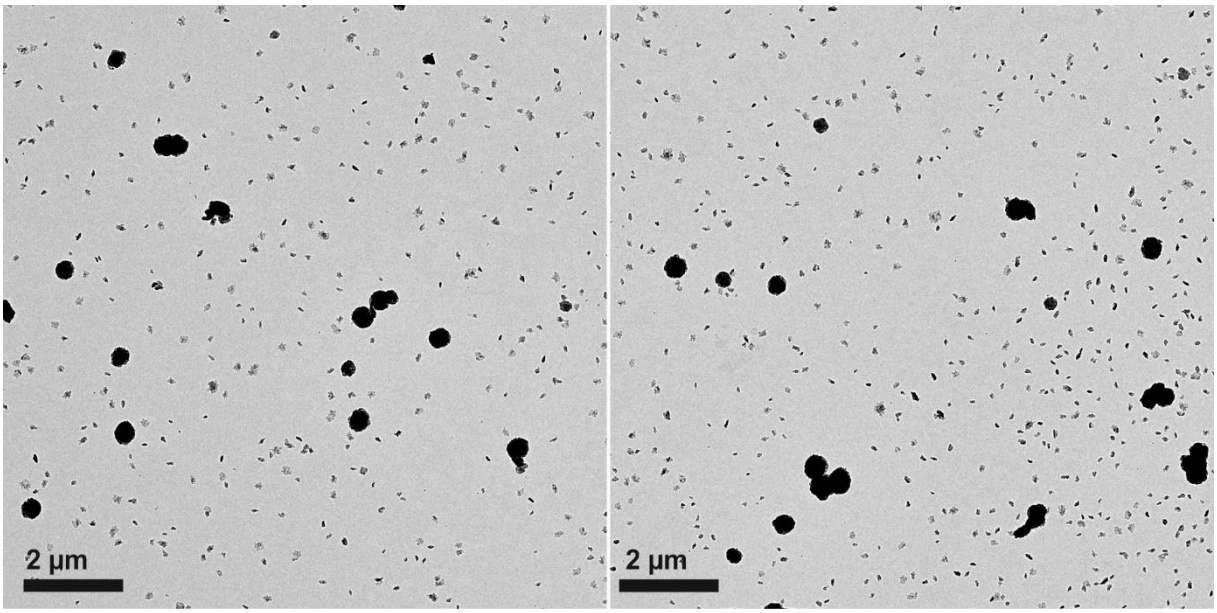
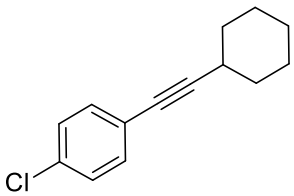


Figure S5: TEM-images of Pd@**2***.

Synthesis of Alkynes

Most alkynes were prepared according to a method previously published from our group.[1] The preparation of other alkynes is described below.

1-Chloro-4-(cyclohexylethynyl)benzene (9l)



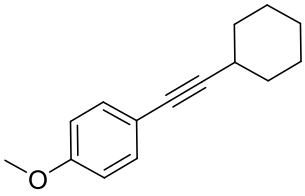
According to a modified procedure of *Studer et al.*[1] 1-chloro-4-iodobenzene (1.00 g, 4.19 mmol, 1.0 equiv.), ethynylcyclohexane (0.544 g, 5.03 mmol, 1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (29.4 mg, 41.9 µmol, 1 mol %) and CuI (16.0 mg, 84.0 µmol, 2 mol %) were added to NEt_3 (5 mL) and the mixture was stirred overnight at room temperature. The reaction mixture was poured on water and the organic components were extracted with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The title compound was isolated after purification by column chromatography (SiO_2, pentane) as colourless oil (871 mg, 3.98 mmol, 95 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.32 (*d*, *J*= 8.6 Hz, 2H, CH_{Aryl}), 7.24 (*d*, *J*= 8.6 Hz, 2H, CH_{Aryl}), 2.63-2.52 (*m*, 1H, C*H*), 1.93-1.82 (*m*, 2H, CH_2), 1.82-1.67 (*m*, 2H, CH_2), 1.62-1.45 (*m*, 3H, 1.5 x CH_2), 1.43-1.26 (*m*, 3H, 1.5 x CH_2).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 133.5 (C_q), 132.9 (CH_{Aryl}), 128.6 (CH_{Aryl}), 122.8 (C_q), 95.7 (C_q), 79.7 (C_q), 32.8 (CH_2), 29.8 (*C*H), 26.1 (CH_2), 25.1 (CH_2).

The recorded spectroscopic data correlate with those reported in literature.[2]

1-(Cyclohexylethynyl)-4-methoxybenzene (9m)



According to a modified procedure of *Studer et al.*[1] 1-iodo-4-methoxybenzene (500 mg, 2.14 mmol, 1.0 equiv.), ethynylcyclohexane (277 mg, 2.56 mmol, 1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (15.0 mg, 21.4 µmol, 1 mol %) and CuI (8.20 mg, 43.1 µmol, 2 mol %) were added to NEt_3 (5 mL) and the mixture was stirred overnight at room temperature. The reaction mixture was poured on water and the organic components were extracted with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The title compound was isolated after purification by column chromatography (SiO_2, pentane/MTBE 20 : 1) as colourless oil (434 mg, 2.03 mmol, 95 %).

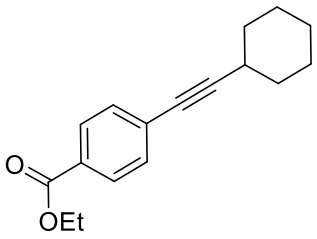
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33 (*d*, *J*= 8.9 Hz, 2H, CH_{Aryl}), 6.81 (*d*, *J*= 8.9 Hz, 2H, CH_{Aryl}), 3.79 (*s*, 3H, CH_3), 2.62-2.51 (*m*, 1H, C*H*), 1.94-1.83 (*m*, 2H, CH_2), 1.83-1.69 (*m*, 2H, CH_2), 1.60-1.45 (*m*, 3H, 1.5 x CH_2), 1.42-1.25 (*m*, 3H, 1.5 x CH_2).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 159.1 (C_q), 133.0 (CH_{Aryl}), 116.5 (C_q), 113.9 (CH_{Aryl}), 93.0 (C_q), 80.3 (C_q), 55.4 (CH_3), 33.0 (CH_2), 29.9 (CH), 26.1 (CH_2), 25.1 (CH_2).

HRMS (ESI): m/z calculated for $[C_{15}H_{18}ONa]^+$ 237.1250; found 237.1251.

The recorded spectroscopic data correlate with those reported in literature.[3]

Ethyl 4-(cyclohexylethynyl)benzoate (9n)



According to a modified procedure of *Studer et al.*[1] ethyl 4-iodobenzoate (1.66 g, 6.01 mmol, 1.0 equiv.), ethynylcyclohexane (779 mg, 7.20 mmol, 1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (42.0 mg, 59.8 µmol, 1 mol %) and CuI (14.0 mg, 73.5 µmol, 1.2 mol %) were added to NEt_3 (15 mL) and the mixture was stirred overnight at room temperature. The reaction mixture was poured on water and the organic components were extracted with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The title compound was isolated after purification by column chromatography (SiO_2, pentane/EtOAc 200 : 1) as colourless oil (1.29 g, 5.03 mmol, 84 %).

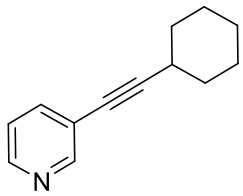
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.95 (*d*, *J*= 8.5 Hz, 2H, C*H*$_{Aryl}$), 7.44 (*d*, *J*= 8.5 Hz, 2H, C*H*$_{Aryl}$), 4.36 (*q*, *J*= 7.1 Hz, 2H, OC*H*$_2$), 2.66-2.55 (*m*, 1H, C*H*), 1.94-1.83 (*m*, 2H, C*H*$_2$), 1.82-1.70 (*m*, 2H, C*H*$_2$), 1.62-1.46 (*m*, 3H, 1.5 x C*H*$_2$), 1.44-1.30 (*m*, 6H, 1.5 x C*H*2, C*H*3).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 166.3 (*C*OO), 131.6 (CH_{Aryl}), 129.4 (CH_{Aryl}), 129.3 (C_q), 129.0 (C_q), 98.0 (C_q), 80.3 (C_q), 61.1 (OCH_2), 32.7 (CH_2), 29.9 (CH), 26.0 (CH_2), 25.0 (CH_2), 14.5 (CH_3).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2931 (*m*), 2854 (*w*), 1717 (*s*), 1606 (m), 1449 (*w*), 1405 (*w*), 1367 (*w*), 1270 (*vs*), 1174 (*m*), 1105 (*s*), 1019 (*w*), 857 (*w*), 769 (*m*), 697 (*w*).

HRMS (ESI): m/z calculated for $[C_{17}H_{20}O_2Na]^+$ 279.1356; found 279.1362.

3-(Cyclohexylethynyl)pyridine (9o)



According to a modified procedure of *Studer et al.*[1] 3-iodopyridine (250 mg, 1.22 mmol, 1.0 equiv.), ethynylcyclohexane (158 mg, 1.46 mmol, 1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (8.80 mg, 12.5 µmol, 1 mol %) and CuI (4.60 mg, 24.2 µmol, 2 mol %) were added to NEt_3 (3 mL) and the mixture was stirred overnight at room temperature. The reaction mixture was poured on water and the organic components were extracted with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The title compound was isolated after purification by column chromatography (SiO_2, pentane/MTBE 1 : 1) as slightly yellow oil (202 mg, 1.09 mmol, 89 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.62 (*s*, 1H, CH_{Aryl}), 8.47 (*d*, *J*= 4.8 Hz, 1H, CH_{Aryl}), 7.66 (*dt*, *J*= 7.9 Hz, *J*= 1.9 Hz, 1H, CH_{Aryl}), 7.19 (*dd*, *J*= 7.9 Hz, *J*= 4.8 Hz. 1H, CH_{Aryl}), 2.65-2.54 (*m*, 1H, C*H*), 1.94-1.82 (*m*, 2H, CH_2), 1.82-1.69 (*m*, 2H, CH_2), 1.61-1.46 (*m*, 3H, 1.5 x CH_2), 1.43-1.30 (*m*, 3H, 1.5 x CH_2).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 152.5 (*C*H_{Aryl}), 148.0 (*C*H_{Aryl}), 138.5 (*C*H_{Aryl}), 123.0 (*C*H_{Aryl}), 121.4 (C_q), 98.2 (C_q), 77.5 (C_q), 32.7 (*C*H_2), 29.9 (*C*H), 26.0 (*C*H_2), 25.0 (*C*H_2).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2927 (*vs*), 2854 (*s*), 1559 (*w*), 1476 (*m*), 1449 (*m*), 1406 (*s*), 1185 (*w*), 1022 (*m*), 952 (*w*), 889 (*w*), 803 (*s*), 705 (*s*).

HRMS (ESI): m/z calculated for $[C_{13}H_{15}NH]^+$ 186.1277, found 186.1282.

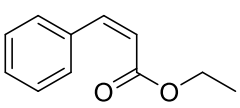
Catalysis

General Procedure 1: Pd@1* catalyzed semihydrogenation of internal alkynes

The irradiated Pd@**1*** stock-solution (5.00 mL, 1.00 µmol of Pd@**1***-catalyst, 1 mol %) was carefully evaporated to dryness and diluted in DMF to a volume of 1 mL. To the catalyst solution the alkynes **9a-s** (0.100 mmol, 1.0 equiv.) and the internal standard mesitylene (14 µL, 0.100 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at room temperature or 40 °C under H_2-atmosphere (balloon, 1 atm) for 2.5-24 h. Conversion of alkynes, yields and Z/E-ratio of alkenes were determined by GC-analysis by using the internal standard technique. In addition, isolated yields of the

desired Z-alkenes were determined after purification by column chromatography. Remaining Pd-content in the product *Z*-alkenes after column chromatography was not quantified since we do not have access to ICP.

Ethyl (*Z*)-3-phenylacrylate (10a)



The title compound was prepared according to the general procedure 1 with ethyl 3-phenylpropiolate (17.4 mg) for 3 h at 40 °C. The reaction outcome was analyzed by GC: conv. of ethyl 3-phenylpropiolate >99 %, yield of ethyl 3-phenylacrylate 99 %, ratio of stereoisomers Z/E 99:1, ethyl 3-phenylpropanoate <1 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 10:1) as colourless oil (16.1 mg, 0.0914 mmol, 91 %).

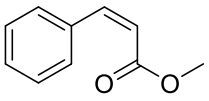
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.61-7.54 (*m*, 2H, C*H*$_{Aryl}$), 7.39-7.30 (*m*, 3H, C*H*$_{Aryl}$), 6.95 (*d*, *J*= 12.7 Hz, 1H, -C*H*=), 5.95 (*d*, *J*= 12.7 Hz, 1H, -C*H*=), 4.18 (*q*; *J*= 7.1 Hz, 2H, C*H*$_2$), 1.24 (*t*, *J*= 7.1Hz, 3H, C*H*$_3$).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 166.3 (C_q), 143.0 (*C*H), 135.1 (C_q), 129.8 (*C*H), 129.1 (*C*H), 128.1 (*C*H), 120.1 (*C*H), 60.4 (*C*H$_2$), 14.2 (*C*H$_3$).

HRMS (ESI): m/z calculated for $[C_{11}H_{12}O_2Na]^+$ 199.0730; found 199.0738.

The recorded spectroscopic data correlate with those reported in literature.[4]

Methyl (*Z*)-3-phenylacrylate (10b)



The title compound was prepared according to the general procedure 1 with methyl 3-phenylpropiolate (16.0 mg) for 4.5 h at room temperature. The reaction outcome was analyzed by GC: conv. of methyl 3-phenylpropiolate >99 %, yield of methyl 3-phenylacrylate 99 %, ratio of stereoisomers Z/E 99:1, methyl 3-phenylpropanoate <1 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 10:1) as colourless oil (15.0 mg, 0.0925 mmol, 93 %).

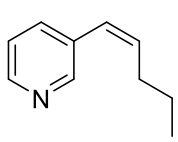
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.62-7.56 (*m*, 2H, C*H*$_{Aryl}$), 7.40-7.32 (*m*, 3H, C*H*$_{Aryl}$); 6.96 (*d*; *J*= 12.7 Hz, 1H, C*H*=), 5.96 (*d*, *J*= 12.7 Hz, 1H, C*H*=), 3.72 (*s*, 3H, C*H*$_3$).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 166.7 (C_q), 143.6 (*C*H), 134.9 (C_q), 129.8 (*C*H), 129.2 (*C*H), 128.2 (*C*H), 119.4 (*C*H); 51.5 (CH_3).

HRMS (ESI): m/z calculated for $[C_{10}H_{10}O_2Na]^+$ 185.0573; found 185.0589.

The recorded spectroscopic data correlate with those reported in literature.[5]

(*Z*)-3-(Pent-1-en-1-yl)pyridine (10c)



The title compound was prepared according to the general procedure 1 with 3-(pent-1-yn-1-yl)pyridine (14.5 mg) for 3.5 h at 40 °C. The reaction outcome was analyzed by GC: conv. of 3-(pent-1-yn-1-yl)pyridine 99 %, yield of 3-(pent-1-en-1-yl)pyridine 99 %, ratio of stereoisomers Z/E 99:1. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 10:1) as colourless oil (13.7 mg, 0.0931 mmol, 93 %).

^{1}H-NMR (600 MHz, CD_2Cl_2): δ (ppm) 8.51 (*d*, *J*=2.2 Hz, 1H, C*H*$_{Aryl}$), 8.41 (*dd*, *J*= 4.8 Hz, *J*= 1.6 Hz, 1H, C*H*$_{Aryl}$), 7.59 (*dt*, *J*= 7.9 Hz, 2.0 Hz, 1H, C*H*$_{Aryl}$), 7.25 (*ddd*, *J*= 7.9 Hz, *J*= 4.8 Hz, *J*= 0.9Hz, 1H, C*H*$_{Aryl}$), 6.38 (*dt*, *J*= 11.8 Hz, *J*= 2.0 Hz, 1H, -C*H*=), 5.82 (*dt*, *J*= 11.8 Hz, *J*= 7.3 Hz, 1H, =C*H*-), 2.29 (*qd*, *J*= 7.4 Hz, J= 1.8 Hz, 2H, C*H*$_2$), 1.49 (*sext*, *J*= 7.4 Hz, 2H, C*H*$_2$), 0.94 (*t*, *J*= 7.4 Hz, 3H, C*H*$_3$).

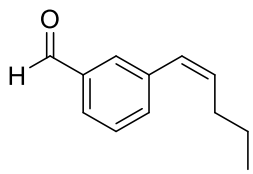
^{13}C-NMR (151 MHz, CD_2Cl_2): δ (ppm) 150.5 (*C*H$_{Aryl}$), 148.1 (*C*H$_{Aryl}$), 136.1 (*C*H$_{Aryl}$), 135.9 (=*C*H-CH$_2$), 133.9 (C_q), 125.8 (-*C*H=), 123.5 (*C*H$_{Aryl}$), 31.2 (*C*H$_2$), 23.6 (*C*H$_2$), 14.1 (*C*H$_3$).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 3012 (*w*), 2959 (*m*), 2871 (*w*), 1565 (*w*), 1462 (*w*), 1420 (*w*), 1024 (*w*), 823 (*m*), 711 (*s*).

HRMS (ESI): m/z calculated for $[C_{10}H_{13}NH]^+$ 148.1121; found 148.1118.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-3-(Pent-1-en-1-yl)benzaldehyde (10d)



The title compound was prepared according to the general procedure 1 with 3-(pent-1-yn-1-yl)benzaldehyde (17.2 mg) for 3 h at 40 °C. The reaction outcome was analyzed by GC: conv. of 3-(pent-1-yn-1-yl)benzaldehyde 98 %, yield of 3-(pent-1-en-1-yl)benzaldehyde 95 %, ratio of stereoisomers Z/E 99:1, 3-pentylbenzaldehyde 3 %.

Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 20:1) as colourless oil (15.5 mg, 0.0889 mmol, 89 %).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 10.02 (*s*, 1H, C*H*O) 7.77 (*t*, *J*= 1.7Hz, 1H, CH_{Aryl}), 7.74 (*dt*, *J*= 7.4, *J*= 1.6 Hz, 1H, CH_{Aryl}), 7.54-7.48 (*m*, 2H, CH_{Aryl}), 6.46 (*dt*, *J*= 11.7 Hz, *J*= 2.0 Hz, 1H, -C*H*=), 5.78 (*dt*, J= 11.7 Hz, 7.3 Hz, 1H, CH_2-C*H*=), 2.31 (*qd*, *J*= 7.4 Hz, *J*= 1.9 Hz, 2H, CH_2), 1.50 (*sext*, *J*= 7.4 Hz, 2H, CH_2), 0.94 (*t*, *J*= 7.4Hz, 3H, CH_3).

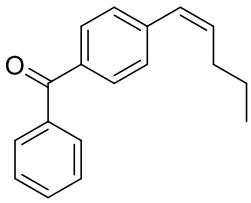
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 192.6 (*C*HO), 138.9 (C_q), 136.5 (C_q), 134.9 (2 x C; *C*H_{Aryl}, =*C*-CH_2), 130.0 (*C*H_{Aryl}), 129.0 (*C*H_{Aryl}), 127.9 (*C*H_{Aryl}), 127.7 (-*C*H=), 30.8 (*C*H_2), 23.2 (*C*H_2), 14.0 (*C*H_3).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2959 (*w*), 2871 (*w*), 2724 (*vw*), 1701 (*vs*), 1599 (*w*), 1460 (*w*), 1379 (*w*), 1224 (*w*), 1141 (*w*), 806 (*m*), 684 (*w*).

HRMS (ESI): m/z calculated for $[C_{12}H_{14}ONa]^+$ 197.0937; found 197.0944.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-(4-(Pent-1-en-1-yl)phenyl)(phenyl)methanone (10e)



The title compound was prepared according to the general procedure 1 with (4-(pent-1-yn-1-yl)phenyl)(phenyl)methanone (24.8 mg) for 3.5 h at room temperature. The reaction outcome was analyzed by GC: conv. of (4-(pent-1-yn-1-yl)phenyl)(phenyl) methanone >99 %, yield of (4-(pent-1-en-1-yl)phenyl)(phenyl)methanone 97 %, ratio of stereoisomers Z/E 97:3, (4-pentylphenyl)(phenyl)methanone 2 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 20:1) as colourless oil (22.5 mg, 0.0899 mmol, 90 %).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 7.82-7.78 (*m*, 4H, CH_{Aryl}), 7.58 (*t*, *J*= 7.4 Hz, 1H, CH_{Aryl}), 7.48 (*t*, *J*= 7.4 Hz, 2H, CH_{Aryl}), 7.38 (*d*, *J*= 8.2 Hz, 2H, CH_{Aryl}), 6.47 (*dt*, *J*= 11.7 Hz, *J*= 2.0 Hz, 1H, -C*H*=), 5.81 (*dt*, *J*= 11.7 Hz, *J*= 7.3 Hz, 1H, =C*H*-CH_2), 2.35 (*qd*, *J*= 7.3 Hz, *J*= 1.9 Hz, 2H, CH_2), 1.51 (*sext*, *J*= 7.4 Hz, 2H, CH_2), 0.96 (*t*, *J*= 7.4 Hz, 3H, CH_3).

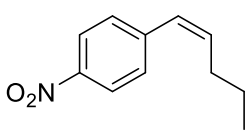
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 196.4 (*C*O), 142.3 (C_q), 138.0 (C_q), 135.5 (2 x C, =*C*H-CH_2 overlapping with C_q), 132.4 (*C*H_{Aryl}), 130.3 (*C*H_{Aryl}), 130.1 (*C*H_{Aryl}), 128.7 (*C*H_{Aryl}), 128.4 (*C*H_{Aryl}), 128.2 (-*C*H=), 31.0 (*C*H_2), 23.2 (*C*H_2), 14.0 (*C*H_3).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2958 (w), 2932 (w), 2870 (w), 1656 (s), 1603 (m), 1447 (w), 1309 (m), 1278 (s), 1177 (w), 938 (w), 924 (w), 859 (w), 701 (m).

HRMS (ESI): m/z calculated for $[C_{18}H_{18}ONa]^+$ 273.1250; found 273.1266.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-1-Nitro-4-(pent-1-en-1-yl)benzene (10f)



The title compound was prepared according to the general procedure 1 with 1-nitro-4-(pent-1-yn-1-yl)benzene (18.9 mg) for 3.5 h at room temperature. The reaction outcome was analyzed by GC: conv. of 1-nitro-4-(pent-1-yn-1-yl)benzene 93 %, yield of 1-nitro-4-(pent-1-en-1-yl)benzene 92 %, ratio of stereoisomers Z/E 98:2, 1-nitro-4-pentylbenzene 1 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 100:1) as slightly yellow oil (15.8 mg, 0.0826 mmol, 83 %).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 8.19 (*d*, *J*= 8.8 Hz, 2H, CH_{Aryl}), 7.41 (*d*, *J*= 8.8 Hz, 2H, CH_{Aryl}), 6.46 (*dt*, *J*= 11.8 Hz, *J*= 1.9 Hz, 1H, -C*H*=), 5.87 (*dt*, *J*= 11.8, *J*= 7.4 Hz, 1H, =C*H*-CH_2), 2.31 (*qd*, *J*= 7.4 Hz, *J*= 1.9 Hz, 2H, CH_2), 1.50 (*sext*, *J*= 7.4 Hz, 2H, CH_2), 0.95 (*t*, *J*= 7.4 Hz, 3H, CH_3).

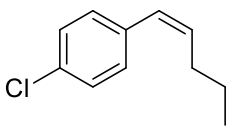
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 146.3 (C_q, weak signal), 144.7 (C_q), 137.1 (=*C*H-CH_2), 129.5 (CH_{Aryl}), 127.3 (-*C*H=), 123.6 (CH_{Aryl}), 31.0 (CH_2), 23.1 (CH_2), 14.0 (CH_3).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2961 (*w*), 2930 (*vw*), 2872 (*vw*), 1596 (*m*), 1515 (*s*), 1341 (*vs*), 1109 (*w*), 856 (*m*).

HRMS (APCI) m/z calculated for $[C_{11}H_{13}NO_2H]^+$ 192.1019; found 192.1016.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-1-Chloro-4-(pent-1-en-1-yl)benzene (10g)



The title compound was prepared according to the general procedure 1 with 1-chloro-4-(pent-1-yn-1-yl)benzene (17.9 mg) for 3 h at room temperature. The reaction outcome was analyzed by GC: conv. of 1-chloro-4-(pent-1-yn-1-yl)benzene 99 %, yield of 1-chloro-4-(pent-1-en-1-yl)benzene 97 %, ratio of stereoisomers Z/E 98:2, 1-chloro-4-pentylbenzene 2 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane) as colourless oil (15.4 mg, 0.0852 mmol, 85 %).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 7.29 (*d*, *J*= 8.5 Hz, 2H, CH_{Aryl}), 7.20 (*d*, *J*= 8.5 Hz, 2H, CH_{Aryl}), 6.36 (*dt*, *J*= 11.7 Hz, *J*= 1.9 Hz, 1H, -C*H*=), 5.69 (*dt*, *J*= 11.7 Hz, *J*= 7.3 Hz, 1H, =C*H*-CH_2), 2.27 (*qd*, *J*= 7.3 Hz, *J*= 1.9 Hz, 2H, CH_2), 1.48 (*sext*, *J*= 7.4 Hz, 2H, CH_2), 0.94 (*t*, *J*= 7.4 Hz, 3H, CH_3).

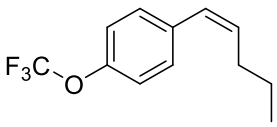
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 136.4 (C_q), 133.9 (=*C*H-CH_2), 132.3 (C_q), 130.2 (*C*H_{Aryl}), 128.4 (*C*H_{Aryl}), 127.8 (-*C*H=), 30.8 (*C*H_2), 23.2 (*C*H_2), 14.0 (*C*H_3).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 3012 (*w*), 2960 (*m*), 2871 (*w*), 1491 (*s*), 1092 (*s*), 1014 (*m*), 839 (*s*), 797 (*w*).

GC/MS (EI): m/z (%) 180.1 (37) $[C_{11}H_{13}Cl]^+$, 151.0 (94), 138.0 (37), 127.0 (15), 115.1 (100), 103.0 (12), 89.1 (14), 75.0 (12), 63.0 (12), 51.0 (8), 39.1 (10).

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-1-(Pent-1-en-1-yl)-4-(trifluoromethoxy)benzene (10h)



The title compound was prepared according to the general procedure 1 with 1-(pent-1-yn-1-yl)-4-(trifluoromethoxy)benzene (22.8 mg) for 8 h at room temperature. The reaction outcome was analyzed by GC: conv. of 1-(pent-1-yn-1-yl)-4-(trifluoromethoxy)benzene 97 %, yield of 1-(pent-1-en-1-yl)-4-(trifluoromethoxy)benzene 96 %, ratio of stereoisomers *Z*/E 99:1, 1-pentyl-4-(trifluoromethoxy)benzene <1 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 100:1) as colourless oil (19.4 mg, 0.0843 mmol, 84 %).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 7.28 (*d*, *J*= 8.7 Hz, 2H, CH_{Aryl}), 7.17 (*d*, *J*= 8.7 Hz, 2H, CH_{Aryl}), 6.39 (*dt*, *J*= 11.7 Hz, *J*= 2.0 Hz, 1H, -C*H*=), 5.71 (*dt*, *J*= 11.7 Hz, *J*= 7.3 Hz, 1H, =C*H*-CH_2), 2.28 (*qd*, *J*= 7.3 Hz, *J*= 1.9 Hz, 2H, CH_2), 1.48 (*sext*, *J*= 7.4 Hz, 2H, CH_2), 0.94 (*t*, *J*= 7.4 Hz, 3H. CH_3).

^{19}F-NMR (564 MHz, $CDCl_3$): δ (ppm) -57.9 (*s*, 3F, C*F*3).

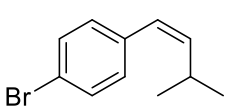
^{13}C-NMR {^{19}F} (151 MHz, $CDCl_3$): δ (ppm) 147.7 (C_q), 136.7 (C_q), 134.1 (=*C*H-CH_2), 130.2 (*C*H_{Aryl}), 127.6 (-*C*H=), 120.8 (*C*H_{Aryl}), 120.7 (O*C*F_3), 30.7 (*C*H_2), 23.2 (*C*H_2), 14.0 (*C*H_3).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2963 (*w*), 2934 (*vw*), 2875 (*vw*), 1508 (*m*), 1257 (*vs*), 1208 (*vs*), 1162 (*vs*), 854 (*w*).

HRMS (APCI) m/z calculated for $[C_{12}H_{13}F_3O]^+$ 230.0913; found 230.0909.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-1-Bromo-4-(3-methylbut-1-en-1-yl)benzene (10i)



The title compound was prepared according to the general procedure 1 with 1-bromo-4-(3-methylbut-1-yn-1-yl)benzene (22.3 mg) for 3.5 h at 40 °C with 2 mol % catalyst. The reaction outcome was analyzed by GC: conv. of 1-bromo-4-(3-methylbut-1-yn-1-yl)benzene 99%, yield of 1-bromo-4-(3-methylbut-1-en-1-yl)benzene 97 %, ratio of stereoisomers Z/E 98:2, 1-bromo-4-isopentylbenzene 2 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane) as colourless oil (20.3 mg, 0.0902 mmol, 90 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (*d*, *J*= 8.5 Hz, 2H, C*H*$_{Aryl}$), 7.12 (*d*, *J*= 8.5 Hz, 2H, C*H*$_{Aryl}$), 6.22 (*d*, *J*= 11.6 Hz, 1H, -C*H*=), 5.50 (*dd*, *J*= 11.6 Hz, J= 10.3 Hz, 1H, =C*H*-CH), 2.89-2.76 (*m*, 1H, C*H*), 1.03 (*d*, *J*= 6.6 Hz, 6H, 2 x C*H*$_3$).

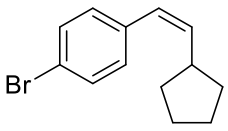
^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 141.3 (=*C*H-CH), 136.9 (*C*$_q$), 131.4 (*C*H$_{Aryl}$), 130.4 (*C*H$_{Aryl}$), 125.4 (-*C*H=), 120.4 (*C*$_q$), 27.3 (*C*H), 23.2 (2 x *C*H$_3$).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 3005 (*w*), 2961 (*m*), 2866 (*w*), 1486 (*s*), 1457 (*w*), 1072 (*m*), 1010 (*m*), 928 (*w*), 864 (*w*), 828 (*m*), 775 (*m*).

HRMS (APCI) m/z calculated for $[C_{11}H_{13}Br]^+$ 224.0195; found 224.0192.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-1-Bromo-4-(2-cyclopentylvinyl)benzene (10j)



The title compound was prepared according to the general procedure 1 with 1-bromo-4-(cyclopentylethynyl)benzene (24.9 mg) for 4 h at 40 °C. The reaction outcome was analyzed by GC: conv. of 1-bromo-4-(cyclopentylethynyl)benzene 98 %, yield of 1-bromo-4-(2-cyclopentylvinyl)benzene 97 %, ratio of stereoisomers Z/E 99:1, 1-bromo-4-(2-cyclopentylethyl)benzene 1 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane) as colourless oil (22.6 mg, 0.0900 mmol, 90 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (*d*, *J*= 8.5 Hz, 2H, CH_{Aryl}), 7.14 (*d*, *J*= 8.5 Hz, 2H, CH_{Aryl}), 6.28 (*d*, *J*= 11.5 Hz, 1H, -C*H*=), 5.61 (*dd*, *J*= 11.5 Hz, *J*= 10.1 Hz, 1H, =C*H*-CH), 2.94-2.82 (*m*, 1H, C*H*), 1.90-1.80 (*m*, 2H, CH_2), 1.77-1.66 (*m*, 2H, CH_2), 1.64-1.56 (*m*, 2H, CH_2), 1.40-1.29 (*m*, 2H, CH_2).

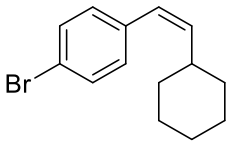
^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 139.3 (=*C*H-CH), 136.9 (C_q), 131.3 (*C*H_{Aryl}), 130.4 (*C*H_{Aryl}), 126.3 (-*C*H=), 120.4 (C_q), 38.9 (*C*H), 34.3 (2 x *C*H_2), 25.7 (2 x *C*H_2).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 3005 (*w*), 2954 (*vs*), 2867 (*m*), 1485 (*s*), 1450 (*w*), 1072 (*m*), 1010 (*s*), 836 (*m*).

HRMS (APCI) m/z calculated for $[C_{13}H_{15}Br]^+$ 250.0352; found 250.0347.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-1-Bromo-4-(2-cyclohexylvinyl)benzene (10k)



The title compound was prepared according to the general procedure 1 with 1-bromo-4-(cyclohexylethynyl)benzene (26.3 mg) for 4.5 h at 40 °C. The reaction outcome was analyzed by GC: conv. of 1-bromo-4-(cyclohexylethynyl)benzene 96 %, yield of 1-bromo-4-(2-cyclohexylvinyl)benzene 93 %, ratio of stereoisomers Z/E 98:2, 1-bromo-4-(2-cyclohexylethyl)benzene 3 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane) as colourless oil (23.5 mg, 0.0886 mmol, 89 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45 (*d*, *J*= 8.5 Hz, 2H, CH_{Aryl}), 7.12 (*d*, *J*= 8.5 Hz, 2H, CH_{Aryl}), 6.23 (*d*, *J*= 11.7 Hz, 1H, -C*H*=), 5.52 (*dd*, *J*= 11.7 Hz, *J*= 10.2 Hz, 1H, =C*H*-CH), 2.59-2.44 (*m*, 1H, C*H*), 1.77-1.61 (*m*, 5H, 2.5 x CH_2), 1.34-1.10 (*m*, 5H, 2.5 x CH_2).

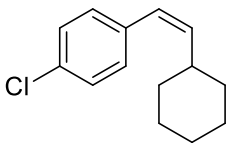
^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 139.9 (=*C*H-CH), 137.0 (C_q), 131.4 (*C*H_{Aryl}), 130.3 (*C*H_{Aryl}), 125.9 (-*C*H=), 120.4 (C_q), 37.1 (*C*H), 33.3 (2 x *C*H_2), 26.1 (*C*H_2), 25.8 (2 x *C*H_2).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 3005 (*w*), 2922 (*vs*), 2849 (*m*), 1485 (*s*), 1448 (*m*), 1392 (*w*), 1071 (*m*), 1010 (*m*), 956 (*m*), 890 (*m*), 838 (*s*), 806 (*m*), 780 (*w*), 746 (*w*), 714 (*w*).

HRMS (APCI) m/z calculated for $[C_{14}H_{17}Br]^+$ 264.0508; found 264.0504.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-1-Chloro-4-(2-cyclohexylvinyl)benzene (10l)



The title compound was prepared according to the general procedure 1 with 1-chloro-4-(cyclohexylethynyl)benzene (21.9 mg) for 2.5 h at 40 °C. The reaction outcome was analyzed by GC: conv. of 1-chloro-4-(cyclohexylethynyl)benzene >99 %, yield of 1-chloro-4-(2-cyclohexylvinyl)benzene 93 %, ratio of stereoisomers Z/E 98:2, 1-chloro-4-(2-cyclohexylethyl)benzene 6 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane) as colourless oil (18.2 mg, 0.0824 mmol, 82 %).

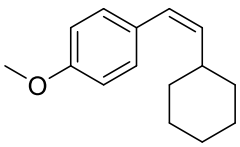
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.29 (*d*, *J*= 8.5 Hz, 2H, CH_{Aryl}), 7.18 (*d*, *J*= 8.5 Hz, 2H, CH_{Aryl}), 6.25 (*d*, *J*= 11.6 Hz, 1H, C*H*=), 5.51 (*dd*, *J*= 11.6 Hz, *J*= 10.1 Hz, 1H, C*H*=), 2.61-2.47 (*m*, 1H, C*H*), 1.80-1.60 (*m*, 5H, 2.5 x CH_2), 1.36-1.09 (*m*, 5H, 2.5 x CH_2).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 139.8 (*C*H=), 136.6 (C_q), 132.3 (C_q), 130.0 (*C*H_{Aryl}), 128.5 (*C*H_{Aryl}), 125.9 (*C*H=); 37.1 (*C*H); 33.3 (*C*H_2); 26.2 (*C*H_2), 25.8 (*C*H_2).

GC/MS (EI): m/z (%) 220.1 (22) $[C_{14}H_{17}Cl]^+$, 177.1 (6), 163.0 (6), 151.0 (6), 138.0 (100), 129.1 (28), 115.1 (19), 95.1 (13), 77.1 (6), 67.1 (6).

The recorded spectroscopic data correlate with those reported in literature.[6]

(*Z*)-1-(2-Cyclohexylvinyl)-4-methoxybenzene (10m)



The title compound was prepared according to the general procedure 1 with 1-(cyclohexylethynyl)-4-methoxybenzene (21.4 mg) for 9 h at 40 °C. The reaction outcome was analyzed by GC: conv. of 1-(cyclohexylethynyl)-4-methoxybenzene 94 %, yield of 1-(2-cyclohexylvinyl)-4-methoxybenzene 90 %, ratio of stereoisomers Z/E 99:1, 1-(2-cyclohexylethyl)-4-methoxybenzene 4 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 20 : 1) as colourless oil (18.3 mg, 0.0846 mmol, 85 %).

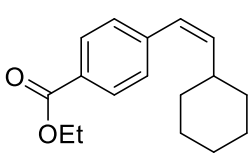
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.21 (*d*, *J*= 8.7 Hz, 2H, CH_{Aryl}), 6.88 (*d*, *J*= 8.7 Hz, 2H, CH_{Aryl}), 6.25 (*d*, *J*= 11.7 Hz, 1H, C*H*=), 5.40 (*dd*, *J*= 11.7 Hz, *J*= 10.0 Hz, 1H, C*H*=); 3.82 (*s*, 3H, CH_3); 2.65-2.48 (*m*, 1H, C*H*), 1.81-1.60 (*m*, 5H, 2.5 x CH_2), 1.38-1.08 (*m*, 5H, 2.5 x CH_2).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 158.4 (C_q), 137.7 (CH=), 130.8 (C_q), 129.9 (CH_{Aryl}), 126.4 (CH=), 113.8 (CH_{Aryl}), 55.4 (CH_3), 37.1 (CH), 33.5 (CH_2), 26.2 (CH_2), 25.9 (CH_2).

HRMS (ESI): m/z calculated for $[C_{15}H_{20}ONa]^+$ 239.1406; found 239.1481.

The recorded spectroscopic data correlate with those reported in literature.[6]

Ethyl (*Z*)-4-(2-cyclohexylvinyl)benzoate (10n)



The title compound was prepared according to the general procedure 1 with ethyl 4-(cyclohexylethynyl)benzoate (25.6 mg) for 4 h at 40 °C. The reaction outcome was analyzed by GC: Conv. of ethyl 4-(cyclohexylethynyl)benzoate 98 %, yield of ethyl 4-(2-cyclohexylvinyl)benzoate 96 %, ratio of stereoisomers Z/E 99:1, ethyl 4-(2-cyclohexylethyl)benzoate 2 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 20 : 1) as colourless oil (23.5 mmol, 0.0909 mmol, 91 %).

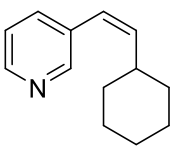
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00 (*d*, *J*= 8.4 Hz, 2H, C*H*$_{Aryl}$), 7.31 (*d, J*= 8.4 Hz, 2H, C*H*$_{Aryl}$), 6.33 (*d*, *J*= 11.7 Hz, 1H, C*H*=), 5.58 (*dd*, *J*= 11.7 Hz, *J*= 10.2 Hz, 1H, C*H*=), 4.37 (*q*, *J*= 7.1 Hz, 2H, OC*H*$_2$), 2.60-2.48 (*m*, 1H, C*H*), 1.76-1.62 (*m*, 5H, 2.5 x C*H*$_2$), 1.39 (*t*, *J*= 7.1 Hz, 3H, C*H*$_3$), 1.33-1.11 (*m*, 5H, 2.5 x C*H*$_2$).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 166.7 (*C*OO), 142.7 (*C*$_q$), 141.1 (*C*H=), 129.6 (*C*H$_{Aryl}$), 128.6 (*C*H$_{Aryl}$), 128.5 (*C*$_q$), 126.3 (*C*H=), 61.0 (O*C*H$_2$), 37.3 (*C*H), 33.2 (*C*H$_2$), 26.1 (*C*H$_2$), 25.8 (*C*H$_2$), 14.5 (*C*H$_3$).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2923 (*m*), 2851 (*w*), 1717 (*vs*), 1609 (*w*), 1448 (*w*), 1367 (*w*), 1274 (*vs*), 1177 (*m*), 1102 (*s*), 1020 (*w*), 866 (*w*), 788 (*w*), 708 (*w*).

HRMS (ESI): m/z calculated for $[C_{17}H_{22}O_2Na]^+$ 281.1512; found 281.1512.

(Z)-3-(2-Cyclohexylvinyl)pyridine (10o)



The title compound was prepared according to the general procedure 1 with 3-(cyclohexylethynyl)pyridine (18.5 mg) for 24 h at 40 °C with 2 mol % catalyst. The reaction outcome was analyzed by GC: conv. of 3-(cyclohexylethynyl)pyridine 85 %, yield of 3-(2-cyclohexylvinyl)pyridine 84 %, ratio of stereoisomers Z/E 98:2, 3-(2-cyclohexylethyl)pyridine 1 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE, first 10 : 1, then 1 : 1) as slightly yellow oil (13.9 mg, 0.0742 mmol, 74 %).

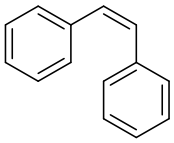
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 8.52 (*d*, *J*= 2.2 Hz, 1H, CH_{Aryl}), 8.45 (*dd*, *J*= 4.8 Hz, *J*= 1.7 Hz, 1H, CH_{Aryl}), 7.54 (*dt*, *J*= 7.9 Hz, *J*= 1.9 Hz, 1H, CH_{Aryl}), 7.26-7.24 (*m*, 1H, CH_{Aryl}), 6.25 (*d*, *J*= 11.7 Hz, 1H, C*H*=), 5.62 (*dd*, *J*= 11.7 Hz, *J*= 10.2 Hz, 1H, C*H*=), 2.52-2.44 (*m*, 1H, C*H*), 1.75-1.69 (*m*, 4H, 2 x CH_2), 1.69-1.63 (*m*, 1H, 0.5 x CH_2), 1.31-1.14 (*m*, 5H, 2.5 x CH_2).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 149.9 (*C*H), 147.6 (*C*H), 141.4 (*C*H), 135.7 (*C*H), 133.7 (C_q), 123.4 (*C*H), 123.3 (*C*H), 37.2 (*C*H), 33.3 (CH_2), 26.1 (CH_2), 25.7 (CH_2).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2923 (*vs*), 2850 (*m*), 1565 (*w*), 1475 (*vw*), 1449 (*w*), 1420 (*vw*), 1398 (*vw*), 1024 (*w*), 958 (*w*), 890 (*w*), 829 (*w*), 804 (*w*), 712 (*m*).

HRMS (ESI): m/z calculated for $[C_{13}H_{17}NH]^+$ 188.1434; found 188.1433.

(*Z*)-1,2-Diphenylethene (10p)



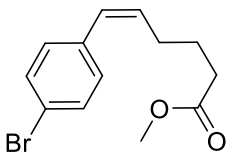
The title compound was prepared according to the general procedure 1 with 1,2-diphenylethyne (17.8 mg) at 40 °C for 3 h with 2 mol % catalyst. The reaction outcome was analyzed by GC: conv. of 1,2-diphenylethyne >99 %, yield of 1,2-diphenylethene 99 %, ratio of stereoisomers Z/E 97:3, 1,2-diphenylethane <1 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane) as colourless oil (13.1 mg, 0.0727 mmol, 73 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 6.60 (*s*, 2H, 2 x =C*H*-), 7.29-7.15 (*m*, 10H, CH_{Aryl}).

GC/MS (EI): m/z (%) 180.1 (100) $[C_{14}H_{12}]^+$, 165.1 (50), 152.1 (15), 139.1 (4), 115.1 (4), 102.1 (8), 89.1 (19), 76.1 (12).

The recorded spectroscopic data correlate with those reported in literature.[1b]

Methyl (*Z*)-6-(4-bromophenyl)hex-5-enoate (10q)



The title compound was prepared according to the general procedure 1 with methyl 6-(4-bromophenyl)hex-5-ynoate (28.1 mg) at room temperature for 6 h. The reaction outcome was analyzed by GC: conv. of methyl 6-(4-bromophenyl)hex-5-ynoate 97 %, yield of methyl 6-(4-bromophenyl)hex-5-enoate 96 %, ratio of stereoisomers Z/E 99:1, methyl 6-(4-bromophenyl)hexanoate <1 %. Furthermore, the product was isolated after purification

by column chromatography (SiO_2, pentane : MTBE 10 : 1) as colourless oil (26.5 mg, 0.0936 mmol, 94 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (*d*, *J*= 8.4 Hz, 2H, CH_{Aryl}), 7.12 (*d*, *J*= 8.4 Hz, 2H, CH_{Aryl}), 6.38 (*dt*, *J*= 11.7 Hz, *J*= 1.9 Hz, 1H, -C*H*=), 5.65 (*dt*, *J*= 11.7 Hz, *J*= 7.4 Hz, 1H, =C*H*-CH_2), 3.64 (*s*, 3H, OCH_3), 2.35-2.28 (*m*, 4H, 2 x CH_2), 1.77 (*quin*, *J*= 7.6 Hz, 2H, CH_2).

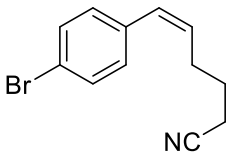
^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 173.9 (*C*OO), 136.4 (C_q), 132.5 (=*C*H-CH_2), 131.4 (*C*H_{Aryl}), 130.5 (*C*H_{Aryl}), 128.8 (-*C*H=), 120.6 (C_q), 51.7 (O*C*H_3), 33.6 (*C*H_2), 28.0 (*C*H_2), 25.1 (*C*H_2).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 2949 (*w*), 1734 (*vs*), 1487 (*m*), 1436 (*w*), 1173 (*m*), 1152 (*m*), 1072 (*m*), 1009 (*m*), 838 (*m*).

HRMS (ESI): m/z calculated for $[C_{13}H_{15}BrO_2Na]^+$ 305.0148; found 305.0152.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-6-(4-Bromophenyl)hex-5-enenitrile (10r)



The title compound was prepared according to the general procedure 1 with 6-(4-bromophenyl)hex-5-ynenitrile (24.8 mg) for 6.5 h at 40 °C. The reaction outcome was analyzed by GC: conv. of 6-(4-bromophenyl)hex-5-ynenitrile 98 %, yield of 6-(4-bromophenyl)hex-5-enenitrile 97 %, ratio of stereoisomers Z/E 99:1, 6-(4-bromophenyl)hexanenitrile 1 %. Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane : MTBE 1 : 1) as colourless oil (22.3 mg, 0.0892 mmol, 89 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (*d*, *J*= 8.4 Hz, 2H, CH_{Aryl}), 7.11 (*d*, *J*= 8.4 Hz, 2H, CH_{Aryl}), 6.45 (*dt*, *J*= 11.6 Hz, *J*= 1.9 Hz, 1H, -C*H*=), 5.62 (*dt*, *J*= 11.6 Hz, *J*= 7.2 Hz, 1H, =C*H*-CH_2), 2.44 (*qd*, *J*= 7.4 Hz, *J*= 1.8 Hz, 2H, CH_2), 2.34 (*t*, *J*= 7.2 Hz, 2H, CH_2), 1.80 (*quin*, *J*= 7.3 Hz, 2H, CH_2).

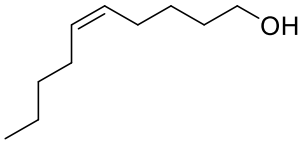
^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 136.0 (C_q), 131.6 (*C*H_{Aryl}), 130.6 (=*C*H-CH_2), 130.4 (*C*H_{Aryl}), 130.0 (-*C*H=), 121.0 (C_q), 119.5 (C_q), 27.5 (*C*H_2), 25.7 (*C*H_2), 16.8 (*C*H_2).

IR (ATR, neat): $\tilde{\nu}$ (cm^{-1}) 3013 (*w*), 2934 (*w*), 1487 (*s*), 1457 (*w*), 1424 (*w*), 1392 (*w*), 1072 (*m*), 1009 (*m*), 837 (*m*).

HRMS (ESI): m/z calculated for $[C_{12}H_{12}BrNNa]^+$ 272.0045; found 272.0051.

The recorded spectroscopic data correlate with those reported in literature.[1b]

(*Z*)-Dec-5-en-1-ol (10s)



The title compound was prepared according to the general procedure 1 with dec-5-yn-1-ol (15.4 mg) for 2.5 h at 40 °C. The reaction outcome was analyzed by GC: conv. of dec-5-yn-1-ol >99 %, yield of dec-5-en-1-ol 99 %, ratio of stereoisomers Z/E 96:4 (determined by chiral GC). Furthermore, the product was isolated after purification by column chromatography (SiO_2, pentane/MTBE 1:1) as colourless oil (14.0 mg, 0.0896 mmol, 90 %).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 5.40-5.31 (*m*, 2H, 2 x =C*H*), 3.65 (*t*, *J*= 6.7 Hz, 2H, CH_2), 2.06 (*q*, *J*= 6.9 Hz, 2H, CH_2), 2.04-1.99 (*m*, 2H, CH_2), 1.60-1.55 (*m*, 2H, CH_2), 1.45-1.38 (*m*, 3H, CH_2, O*H*), 1.34-1.28 (*m*, 4H, 2 x CH_2), 0.89 (*t*, *J*= 7.0 Hz, 3H, CH_3).

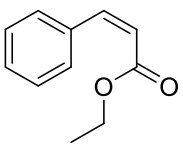
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 130.5 (=*C*H), 129.4 (=*C*H), 63.0 (*C*H_2OH), 32.5 (*C*H_2), 32.1 (*C*H_2), 27.1 (*C*H_2), 27.0 (*C*H_2), 26.0 (*C*H_2), 22.5 (*C*H_2), 14.1 (*C*H_3).

HRMS (ESI): m/z calculated for $[C_{10}H_{20}ONa]^+$ 179.1406; found 179.1409.

The recorded spectroscopic data correlate with those reported in literature.[1b]

Reaction in 1 mmol scale

Ethyl (*Z*)-3-phenylacrylate (10a)



The irradiated Pd@**1*** stock-solution (50.0 mL, 10.0 µmol of Pd@**1***-catalyst, 1 mol %) was carefully evaporated to dryness and diluted in DMF to a volume of 10 mL. To the catalyst solution ethyl 3-phenylpropiolate (174 mg, 1.00 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at 40 °C under H_2-atmosphere (balloon, 1 atm) for 1 h. The solvent was removed *in vacuo* and the title compound was isolated after purification by column chromatography (SiO_2, pentane/MTBE 10:1) as yellow oil (158 mg, 0.897 mmol, 90 %, Z/E-ratio 99/1).

NMR Spectra of New Compounds and Z-Alkenes

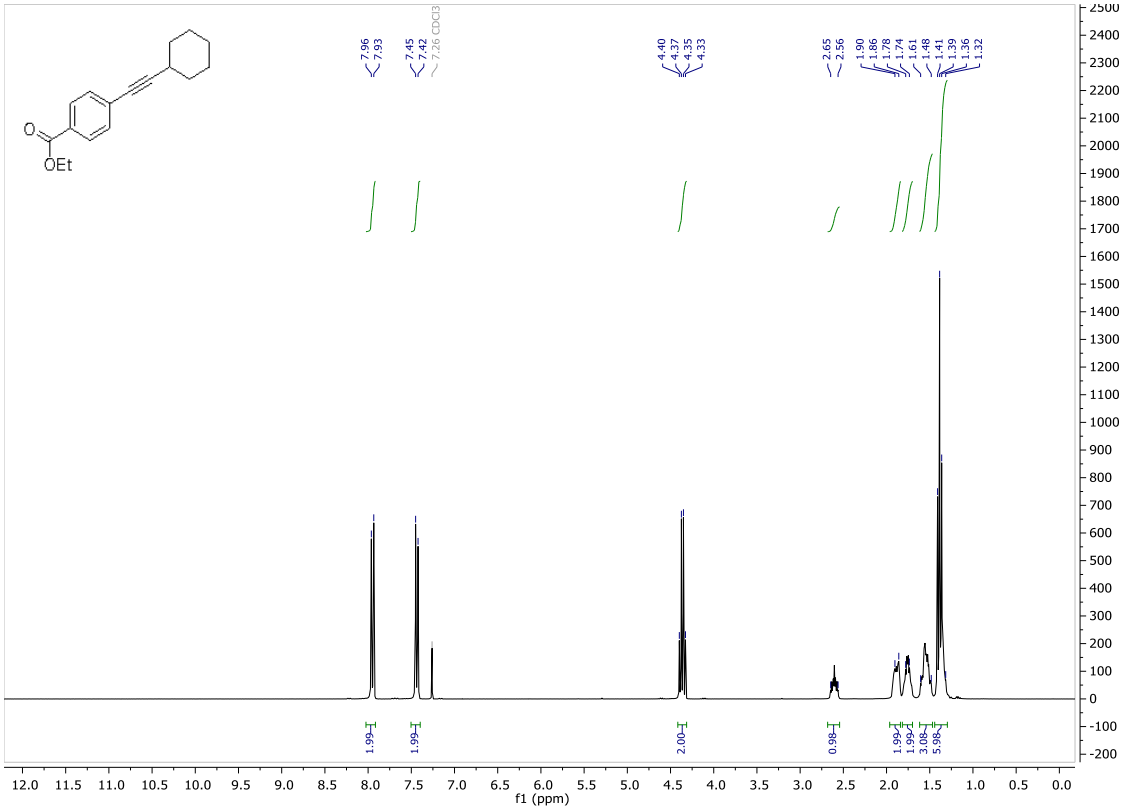


Figure S6: ^{1}H-NMR spectrum of ethyl 4-(cyclohexylethynyl)benzoate (**9n**).

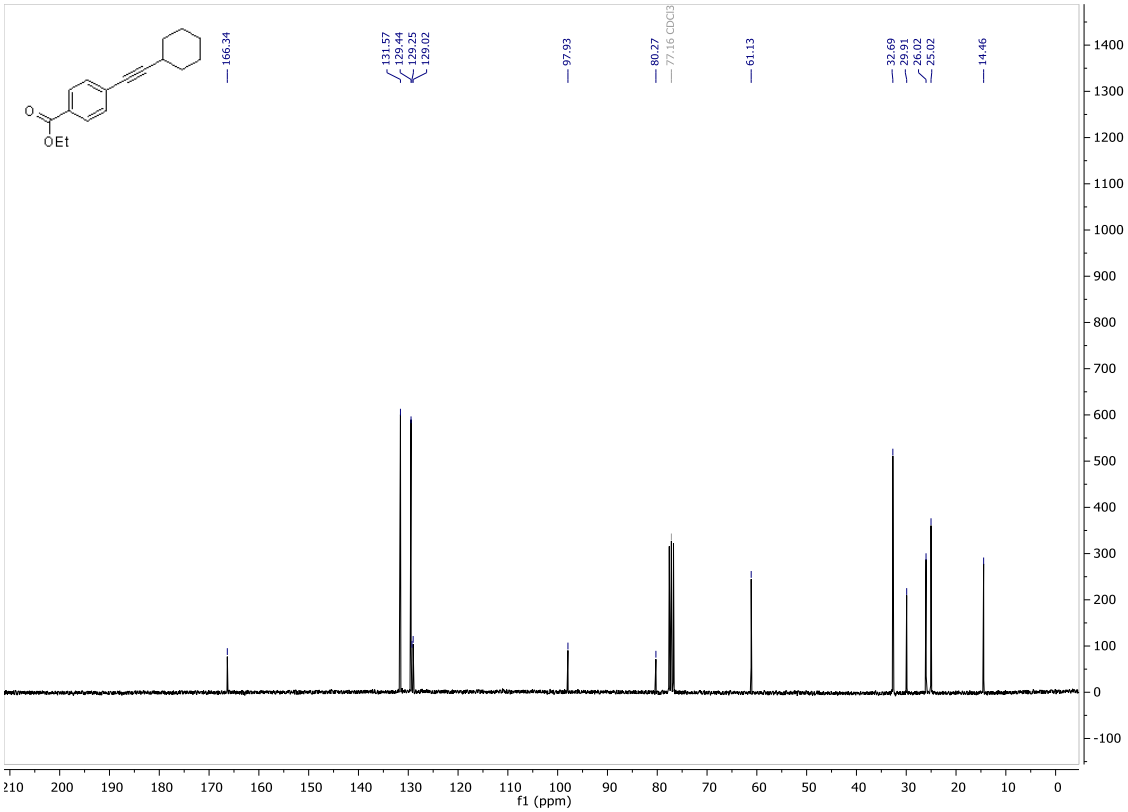


Figure S7: ^{13}C-NMR spectrum of ethyl 4-(cyclohexylethynyl)benzoate (**9n**).

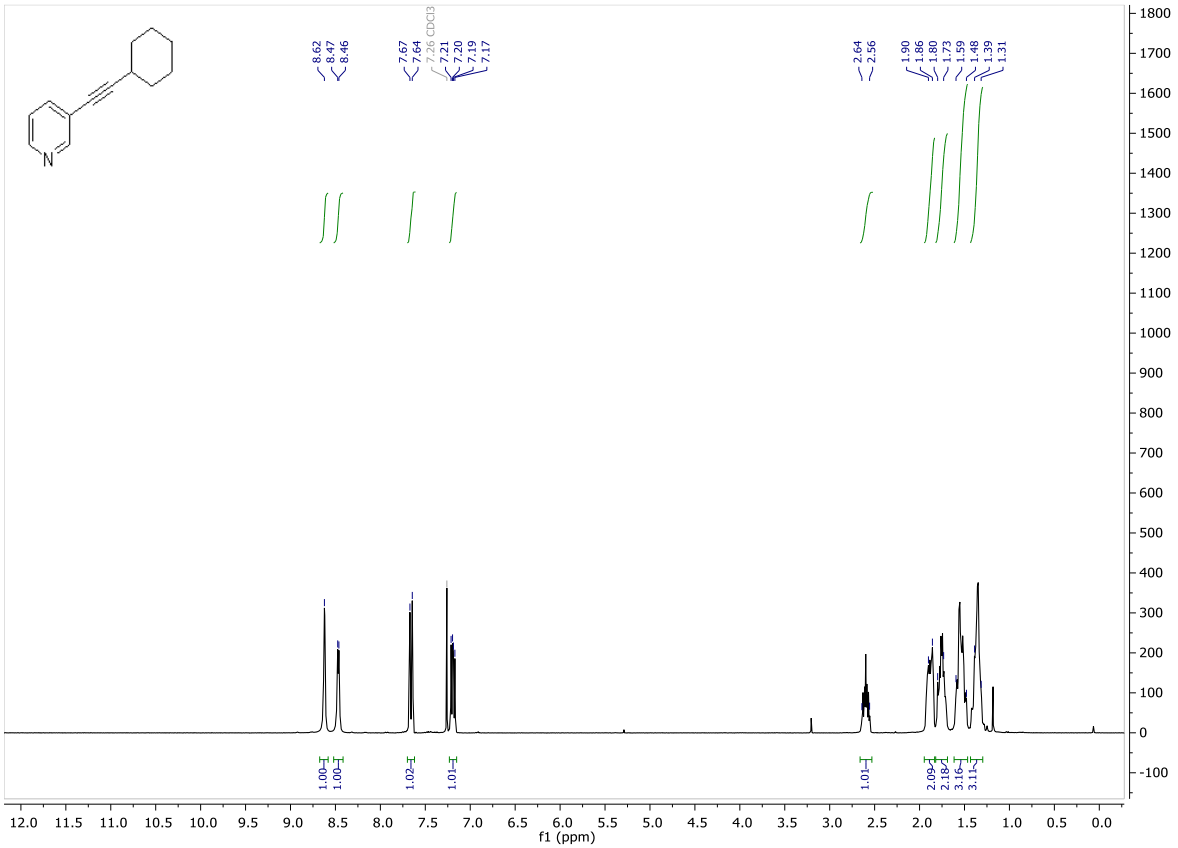


Figure S8: ^{1}H-NMR spectrum of 3-(cyclohexylethynyl)pyridine (**9o**).

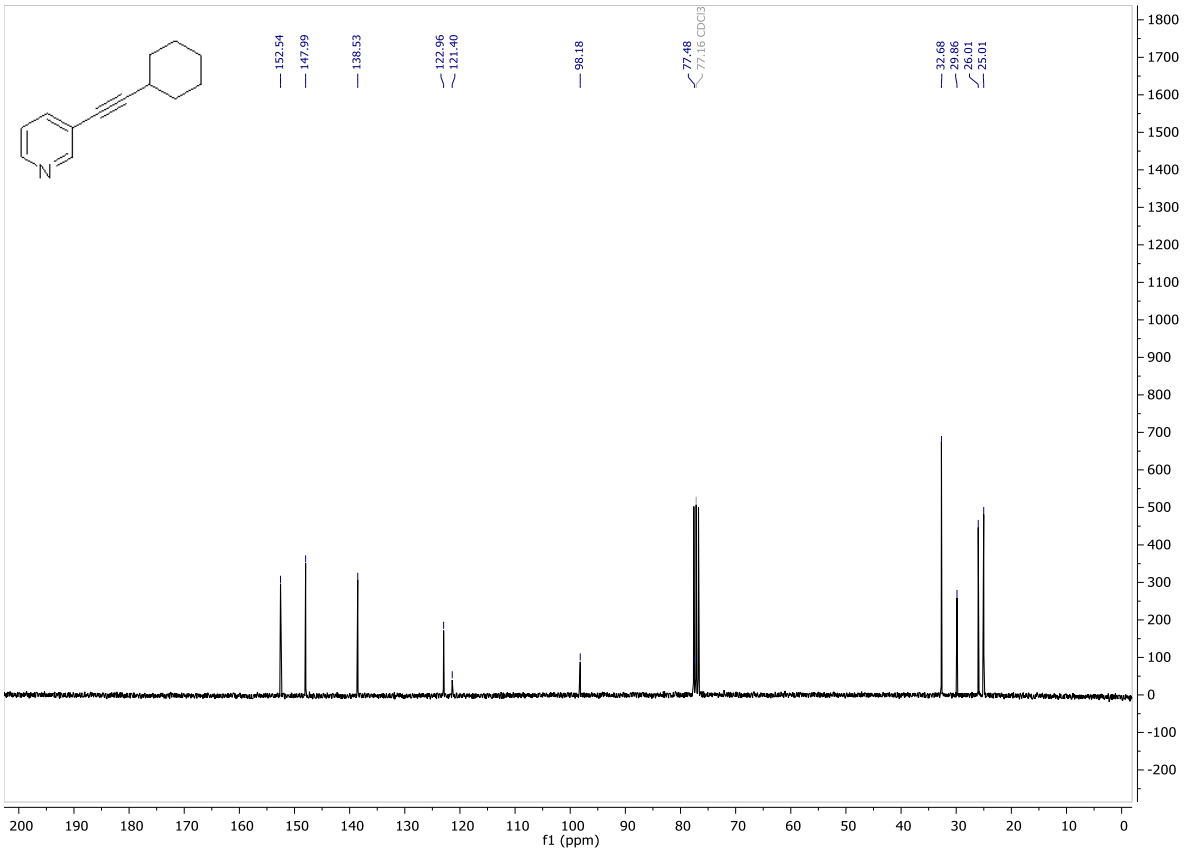


Figure S9: ^{13}C-NMR spectrum of 3-(cyclohexylethynyl)pyridine (**9o**).

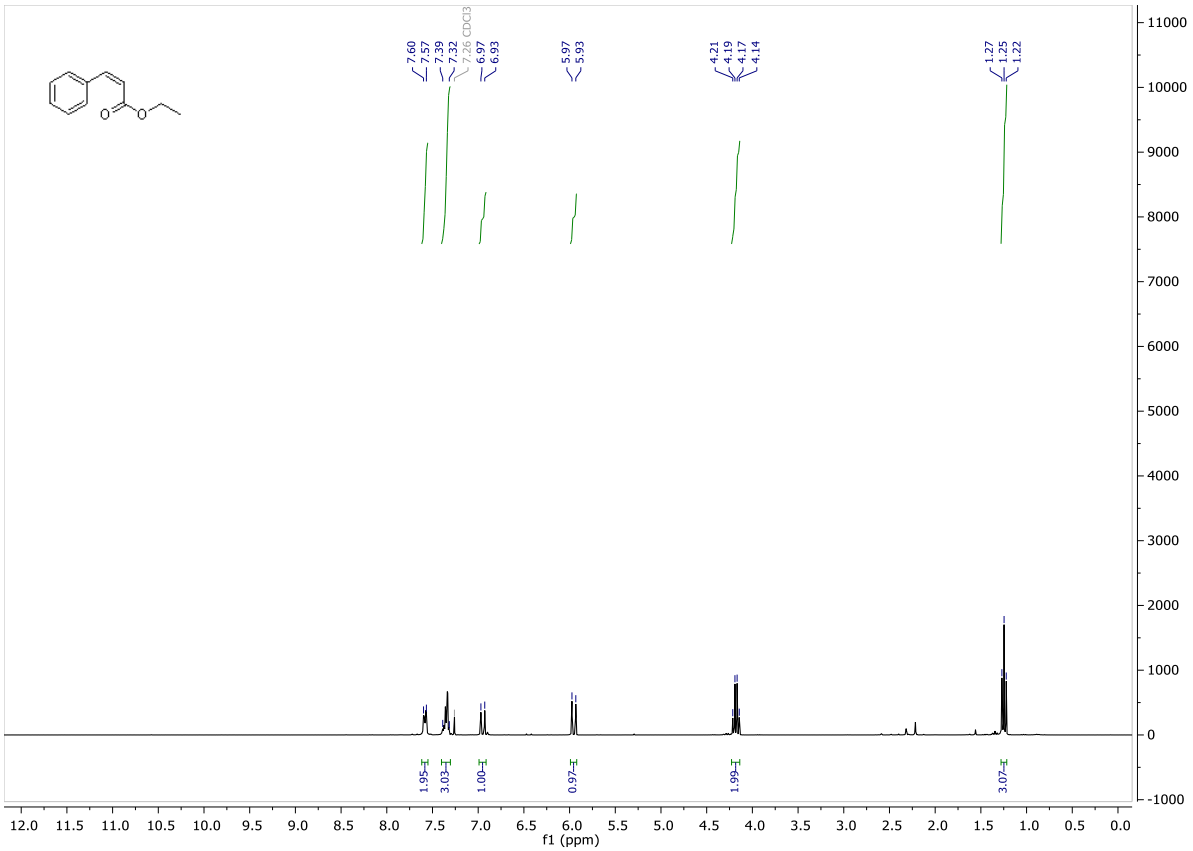


Figure S10: ^{1}H-NMR spectrum of ethyl (*Z*)-3-phenylacrylate (**10a**).

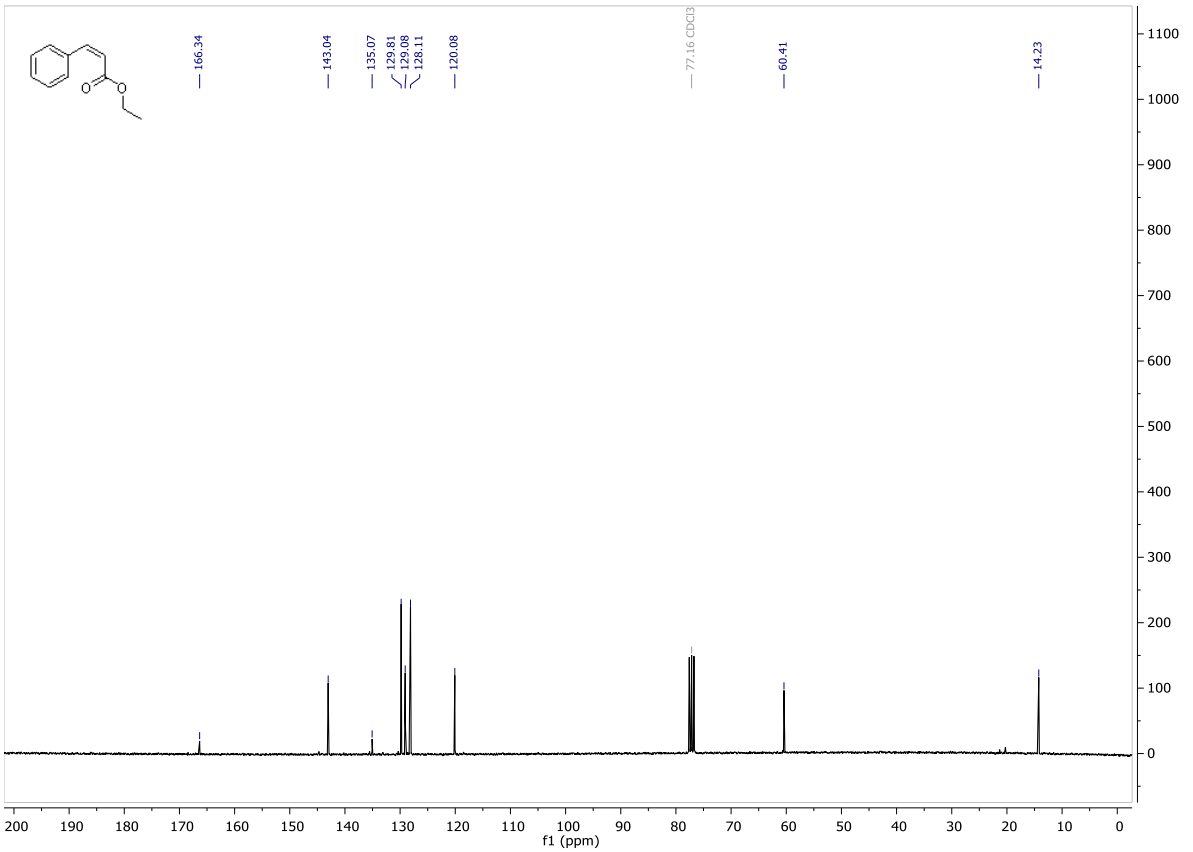


Figure S11: ^{13}C-NMR spectrum of ethyl (*Z*)-3-phenylacrylate (**10a**).

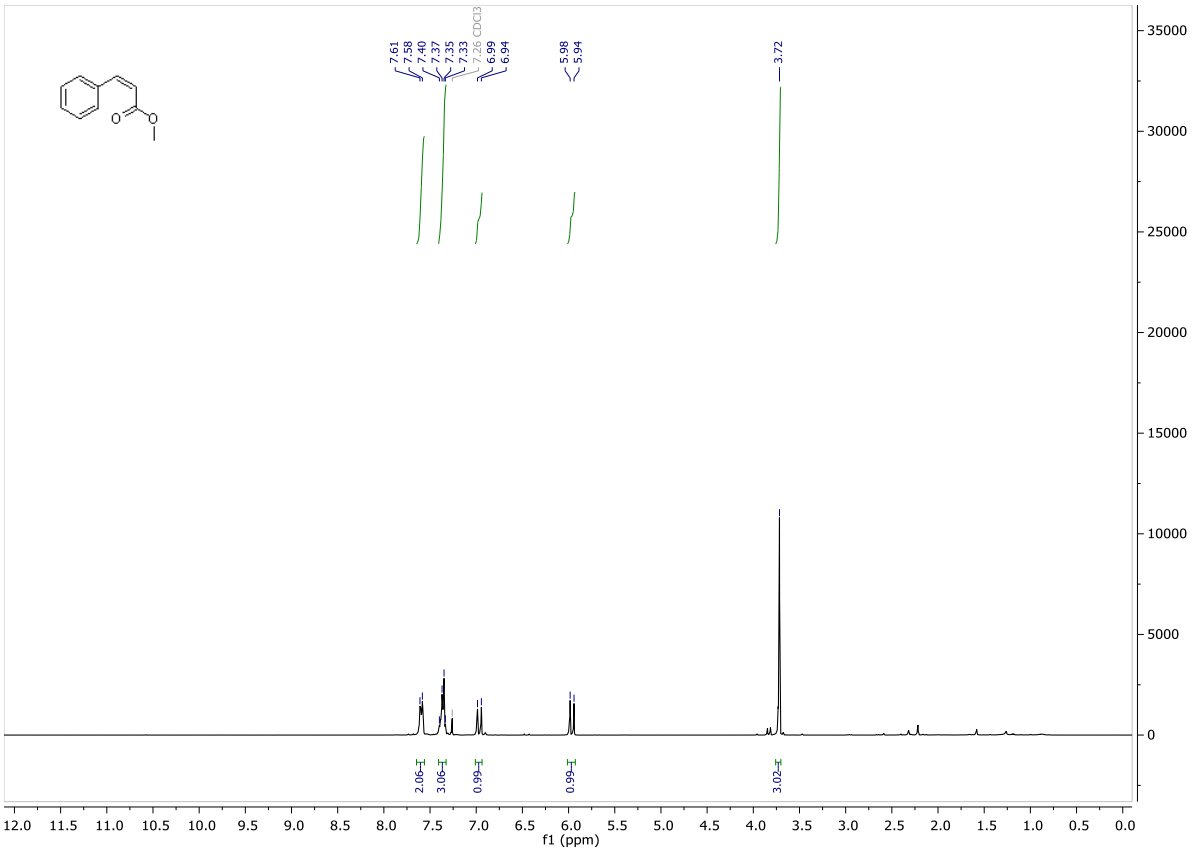


Figure S12: ^{1}H-NMR spectrum of methyl (Z)-3-phenylacrylate (**10b**).

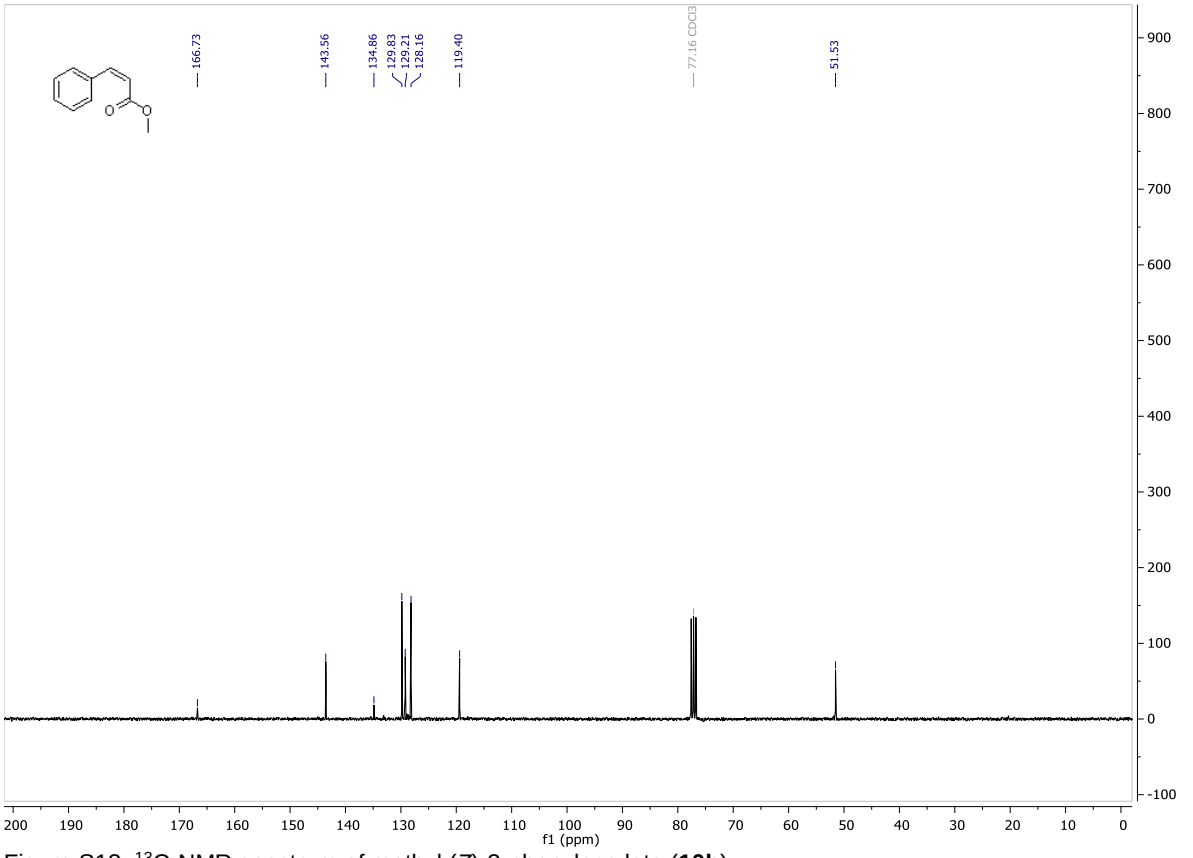


Figure S13: ^{13}C-NMR spectrum of methyl (*Z*)-3-phenylacrylate (**10b**).

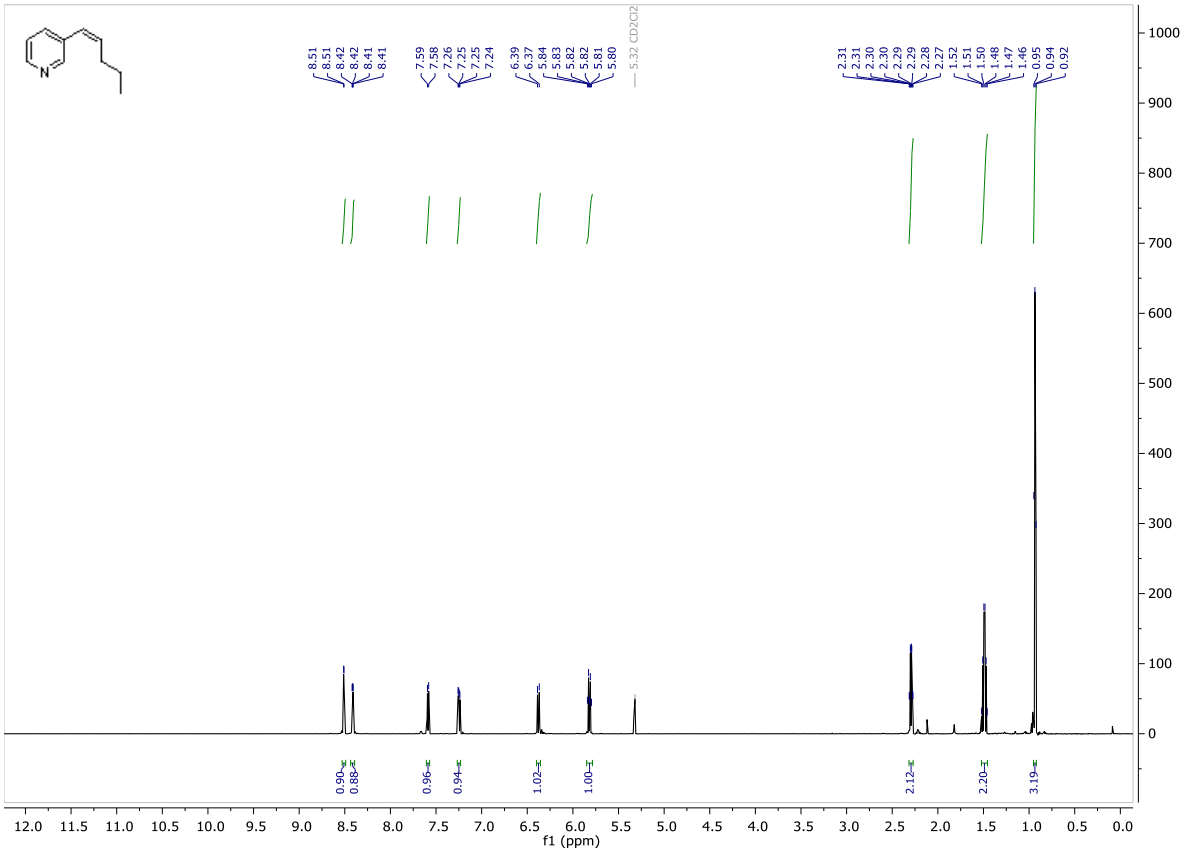


Figure S14: ^{1}H-NMR spectrum of (*Z*)-3-(pent-1-en-1-yl)pyridine (**10c**).

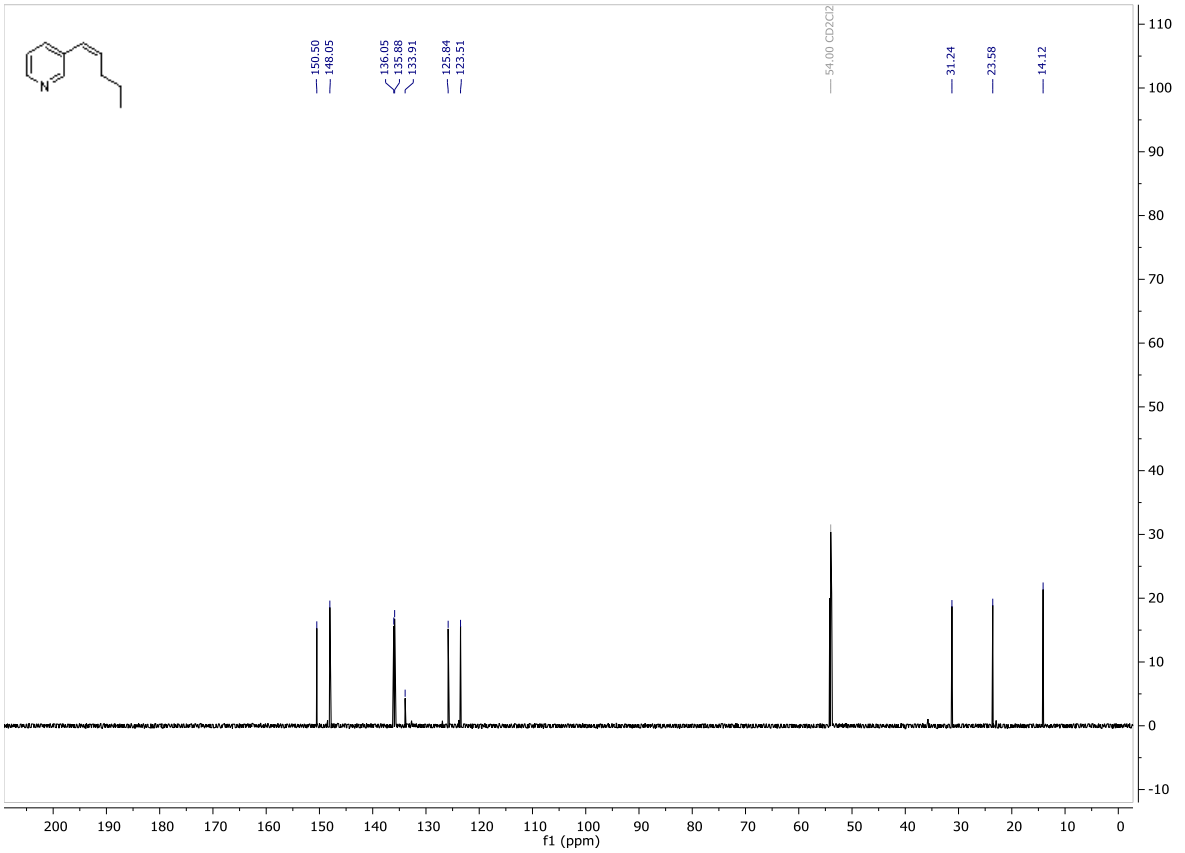


Figure S15: ^{13}C-NMR spectrum of (*Z*)-3-(pent-1-en-1-yl)pyridine (**10c**).

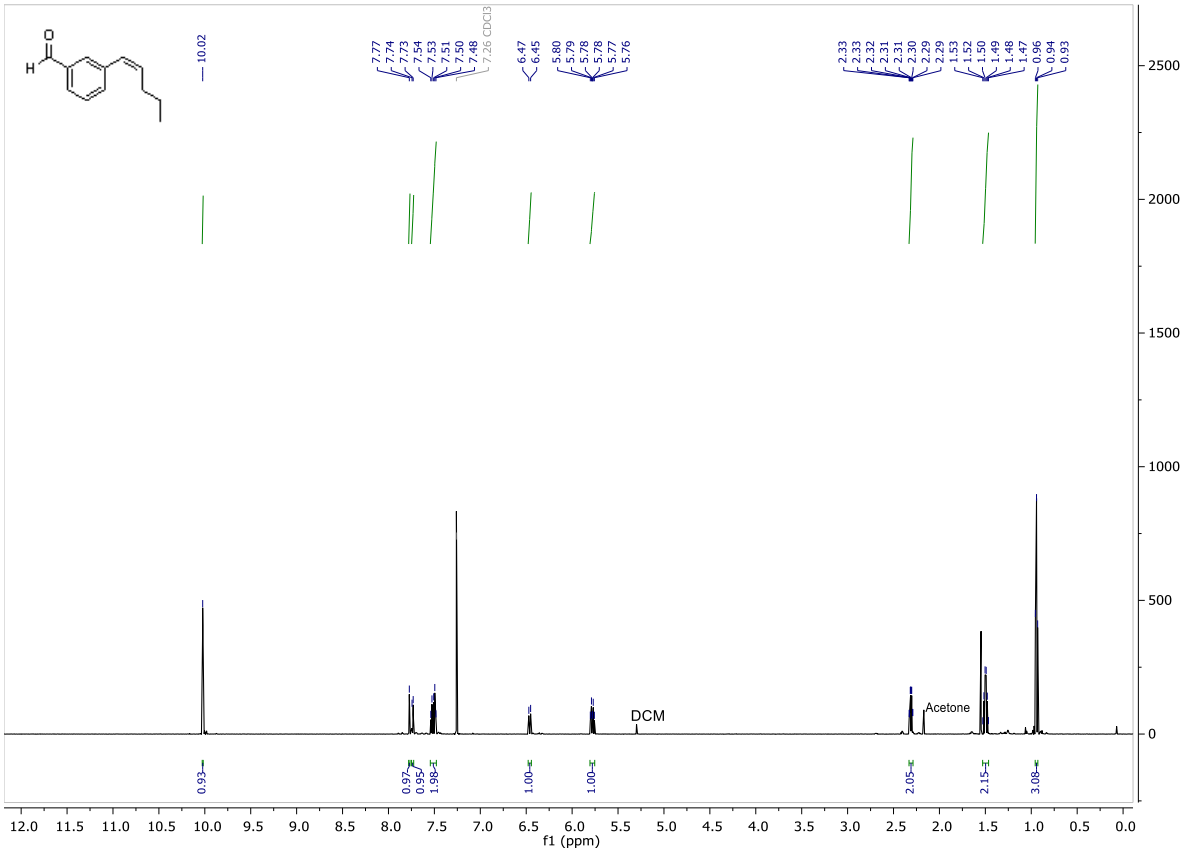


Figure S16: ^{1}H-NMR spectrum of (*Z*)-3-(pent-1-en-1-yl)benzaldehyde (**10d**).

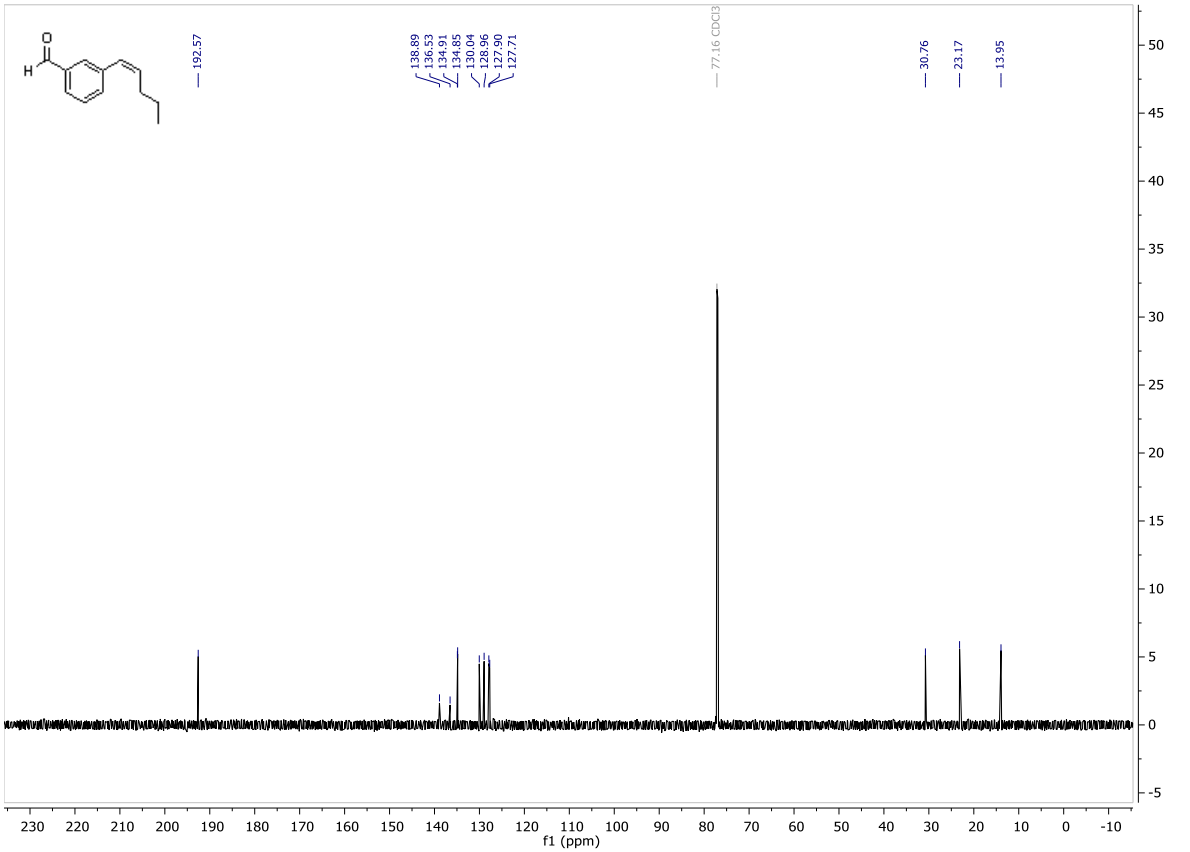


Figure S17: ^{13}C-NMR spectrum of (*Z*)-3-(pent-1-en-1-yl)benzaldehyde (**10d**).

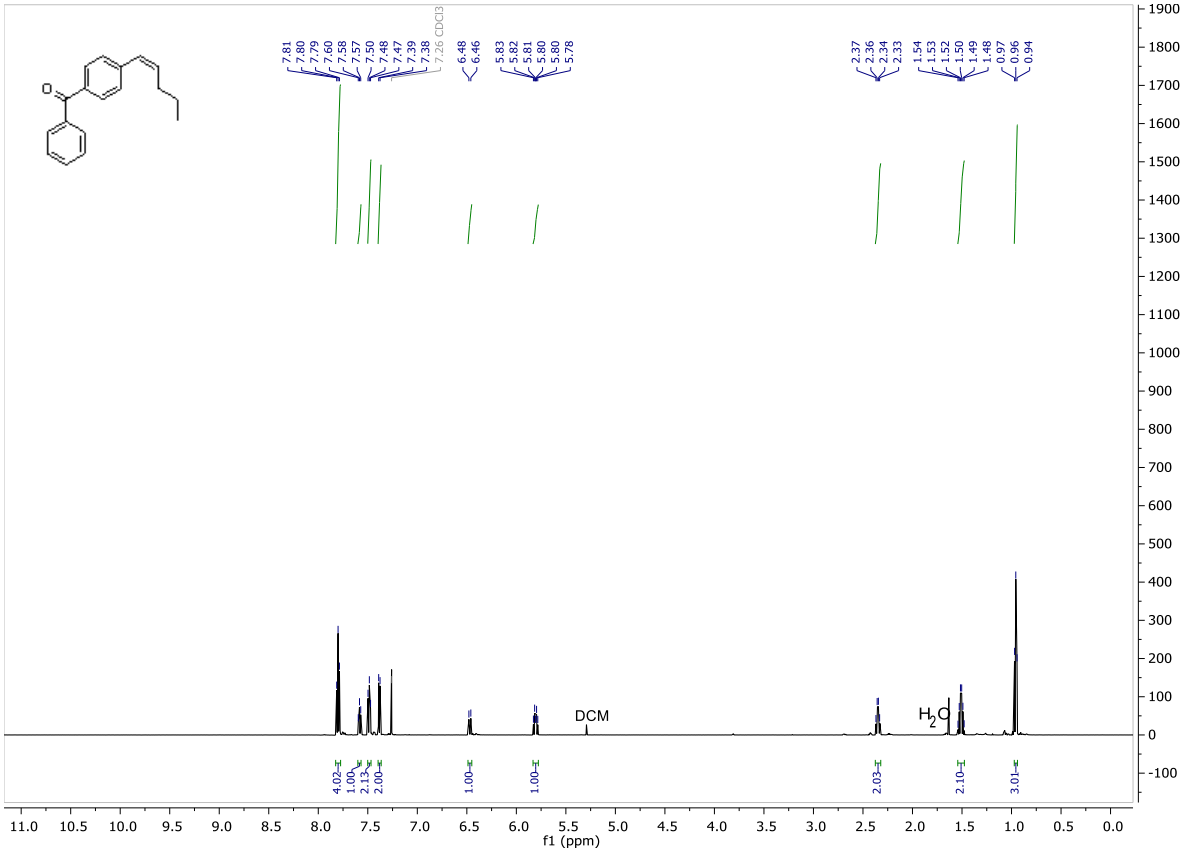


Figure S18: ^{1}H-NMR spectrum of (*Z*)-(4-(pent-1-en-1-yl)phenyl)(phenyl)methanone (**10e**).

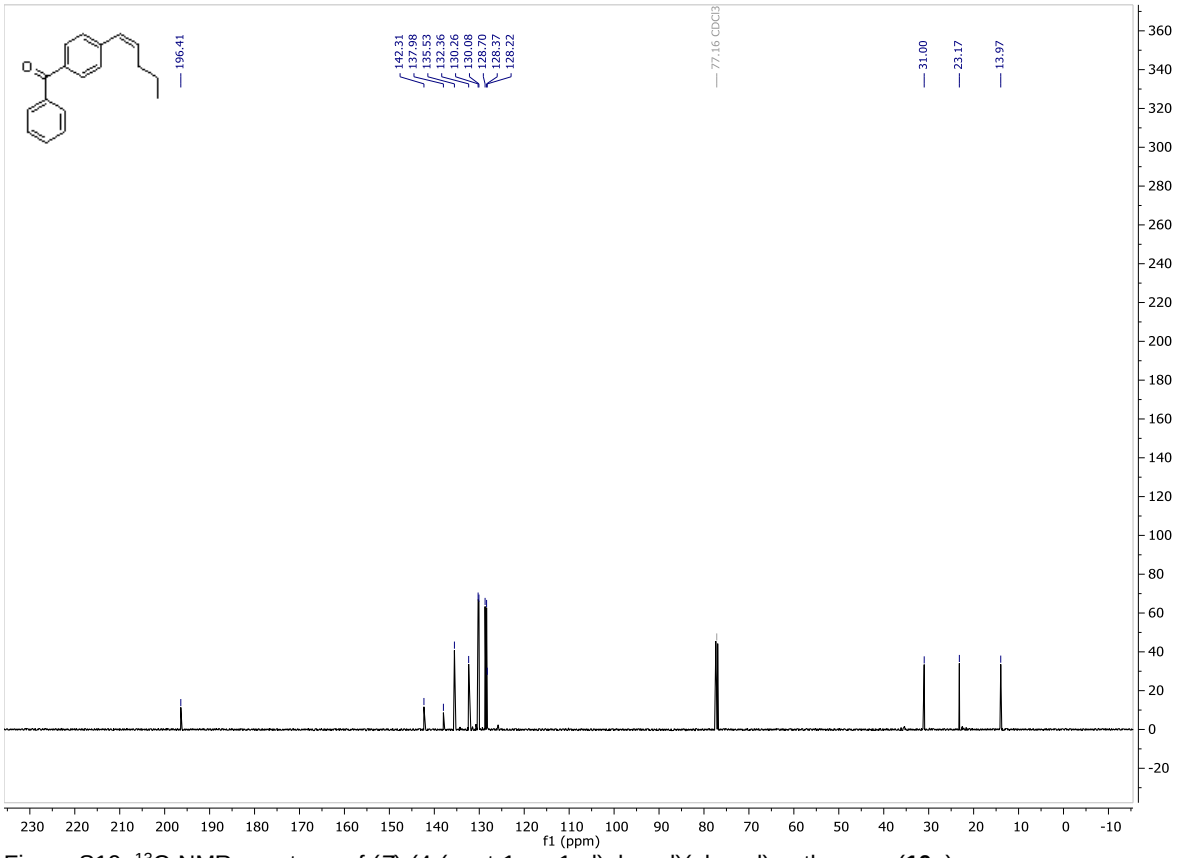


Figure S19: ^{13}C-NMR spectrum of (*Z*)-(4-(pent-1-en-1-yl)phenyl)(phenyl)methanone (**10e**).

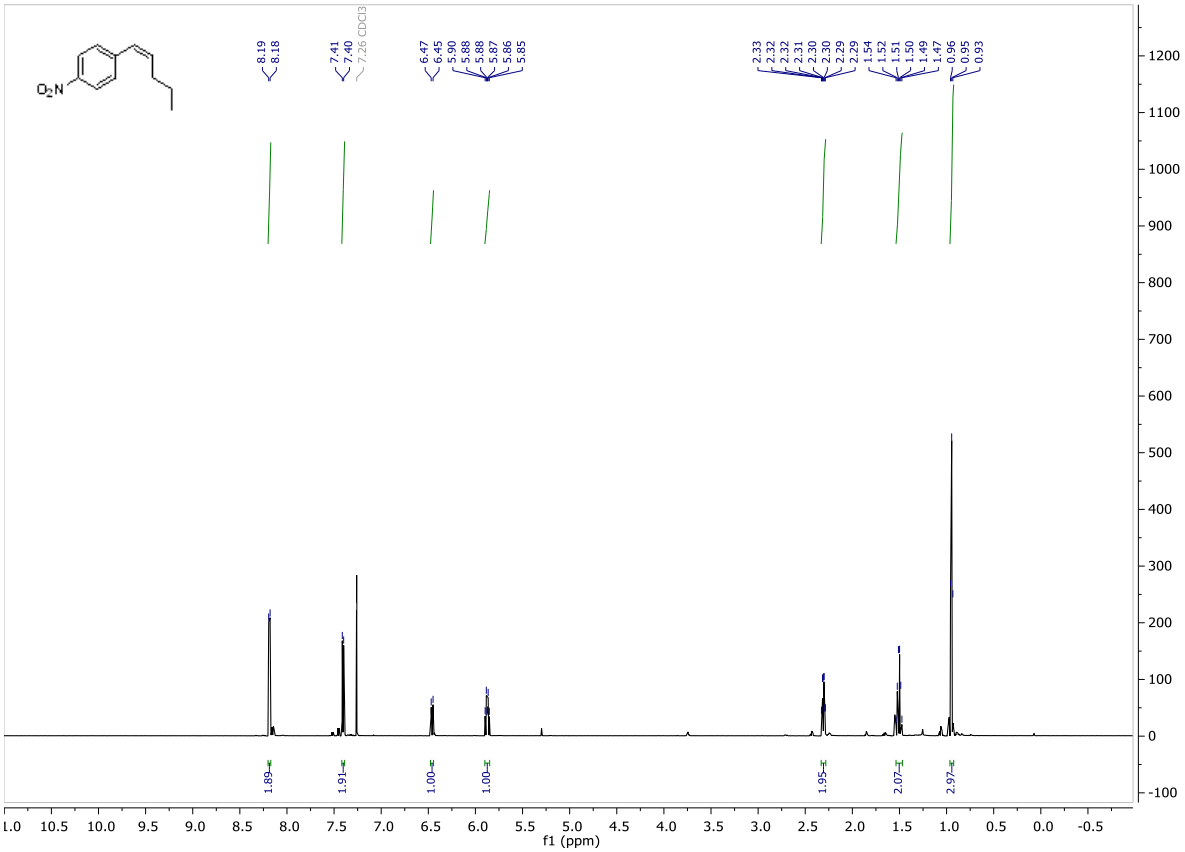


Figure S20: ^{1}H-NMR spectrum of (*Z*)-1-nitro-4-(pent-1-en-1-yl)benzene (**10f**).

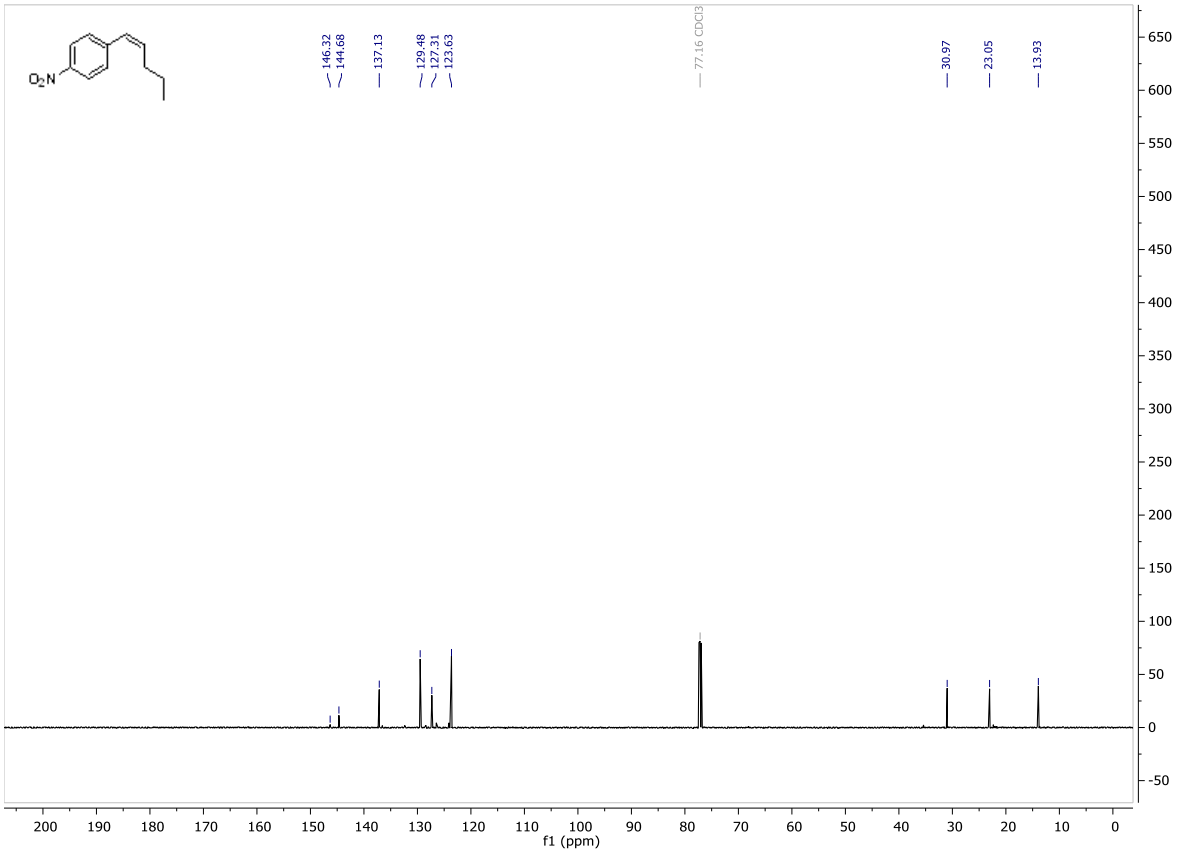


Figure S21: ^{13}C-NMR spectrum of (*Z*)-1-nitro-4-(pent-1-en-1-yl)benzene (**10f**).

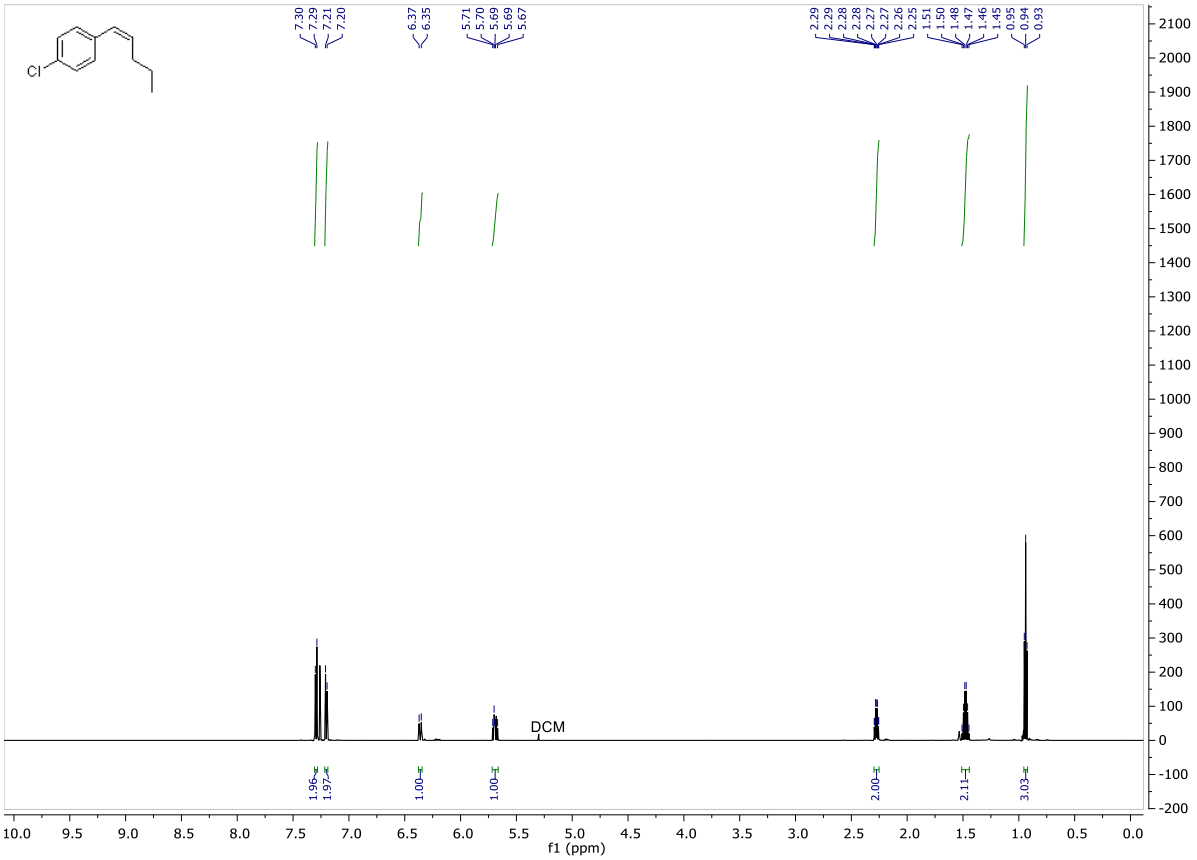


Figure S22: ^{1}H-NMR spectrum of (*Z*)-1-Chloro-4-(pent-1-en-1-yl)benzene (**10g**).

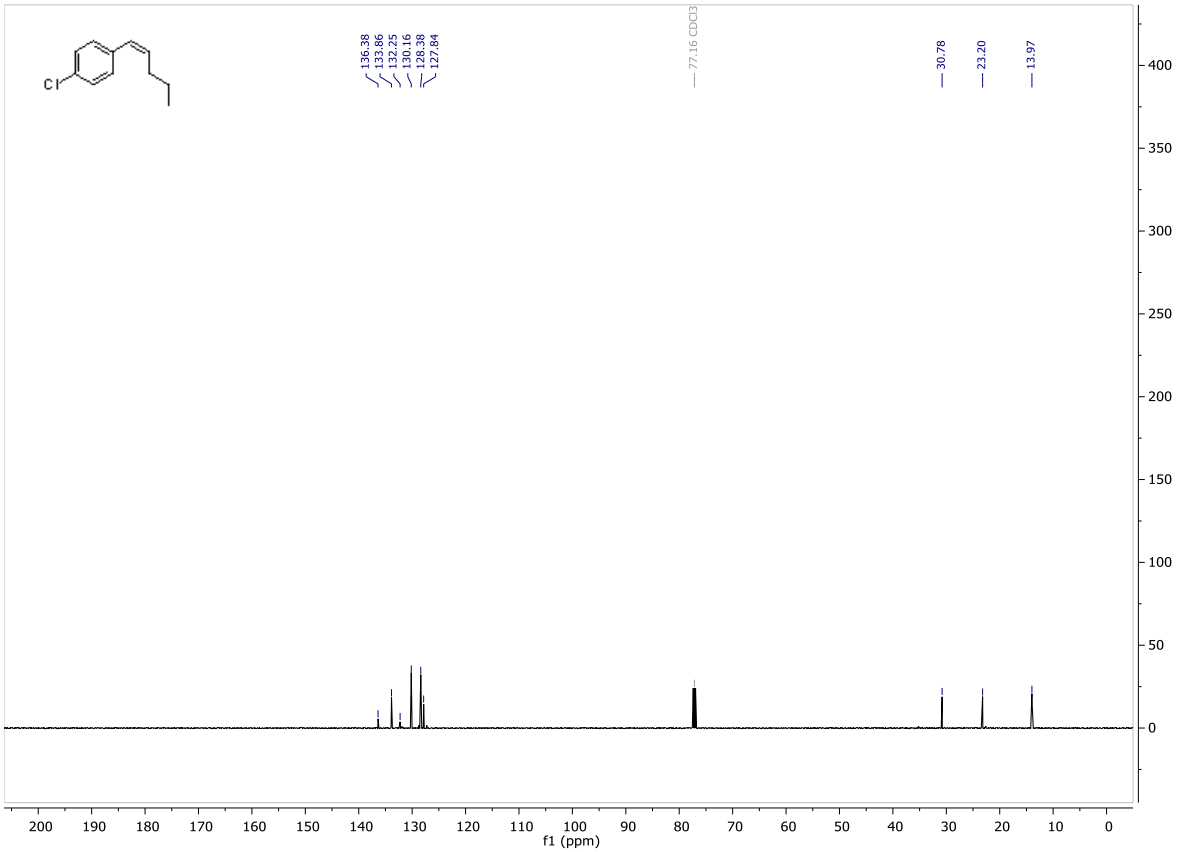


Figure S23: ^{13}C-NMR spectrum of (*Z*)-1-Chloro-4-(pent-1-en-1-yl)benzene (**10g**).

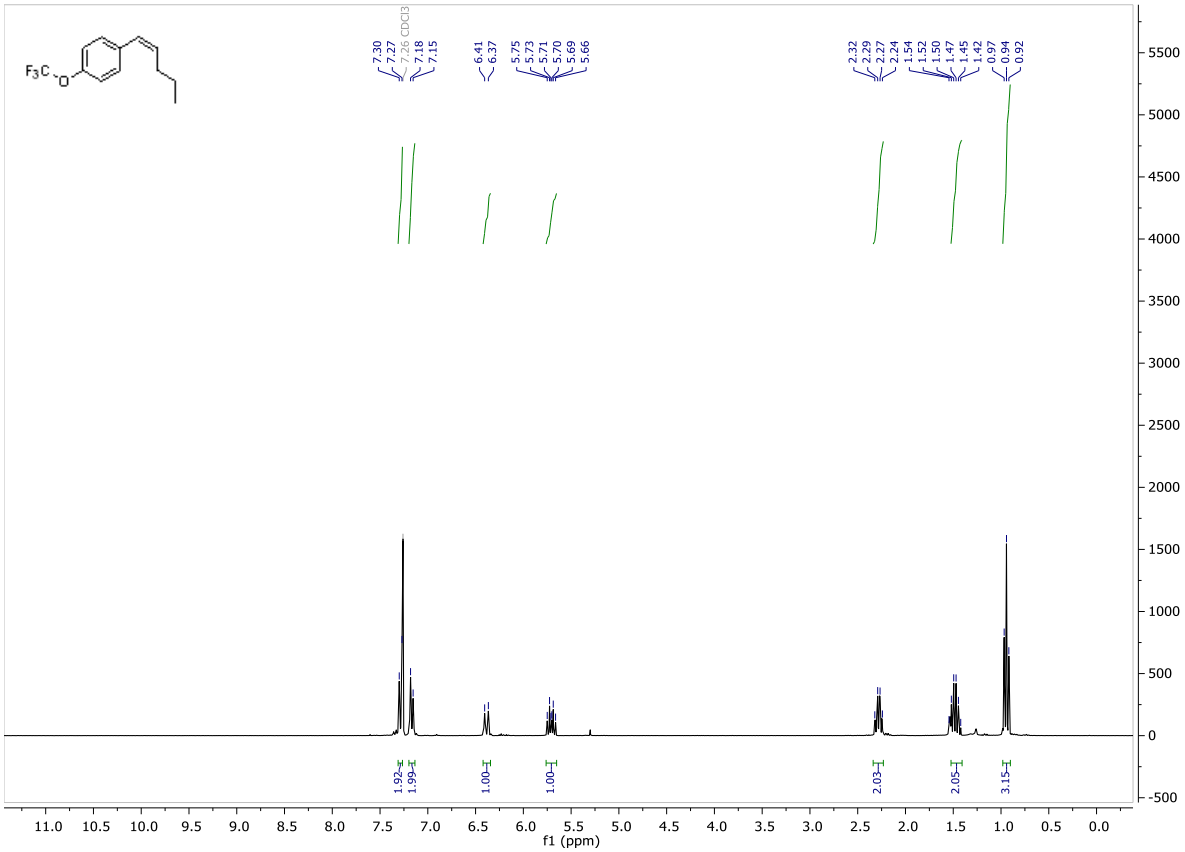


Figure S24: ^{1}H-NMR spectrum of (Z)-1-(Pent-1-en-1-yl)-4-(trifluoromethoxy)benzene (**10h**).

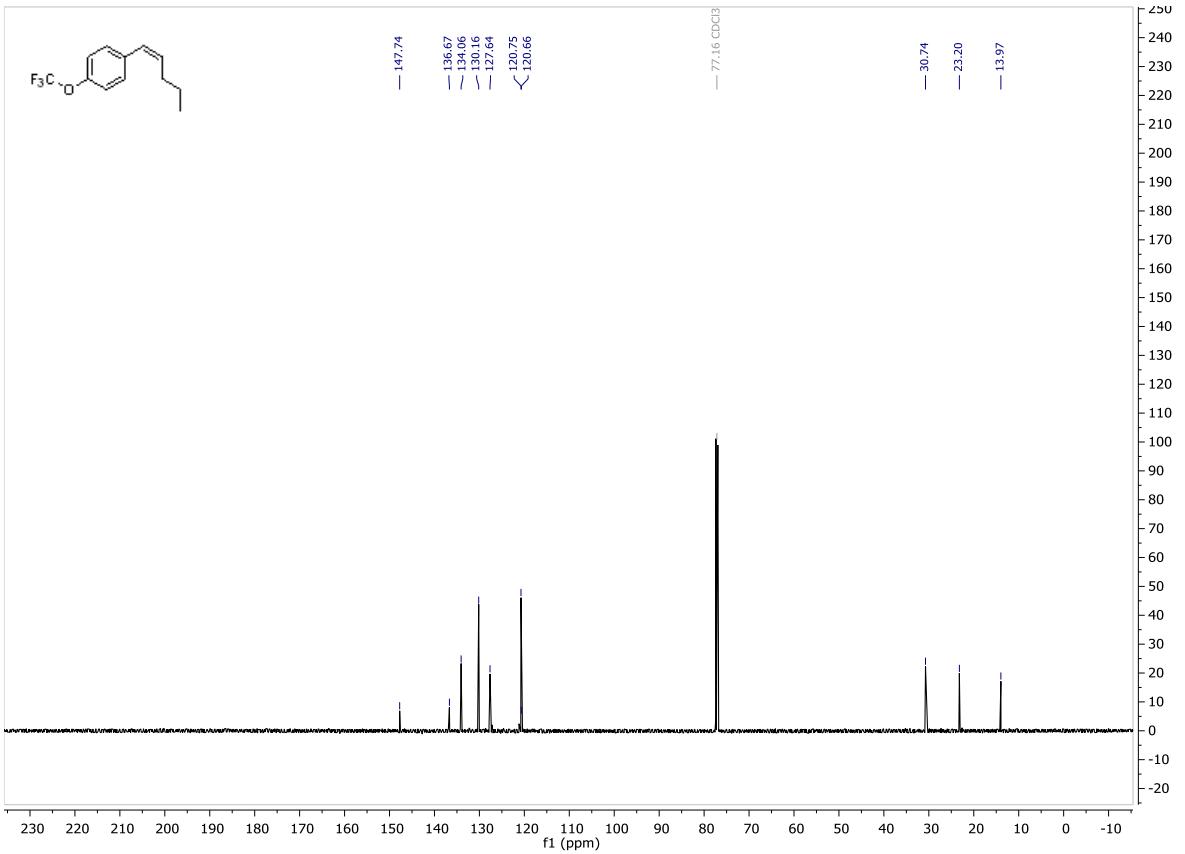


Figure S25: ^{13}C {^{19}F}-NMR spectrum of (Z)-1-(Pent-1-en-1-yl)-4-(trifluoromethoxy)benzene (**10h**).

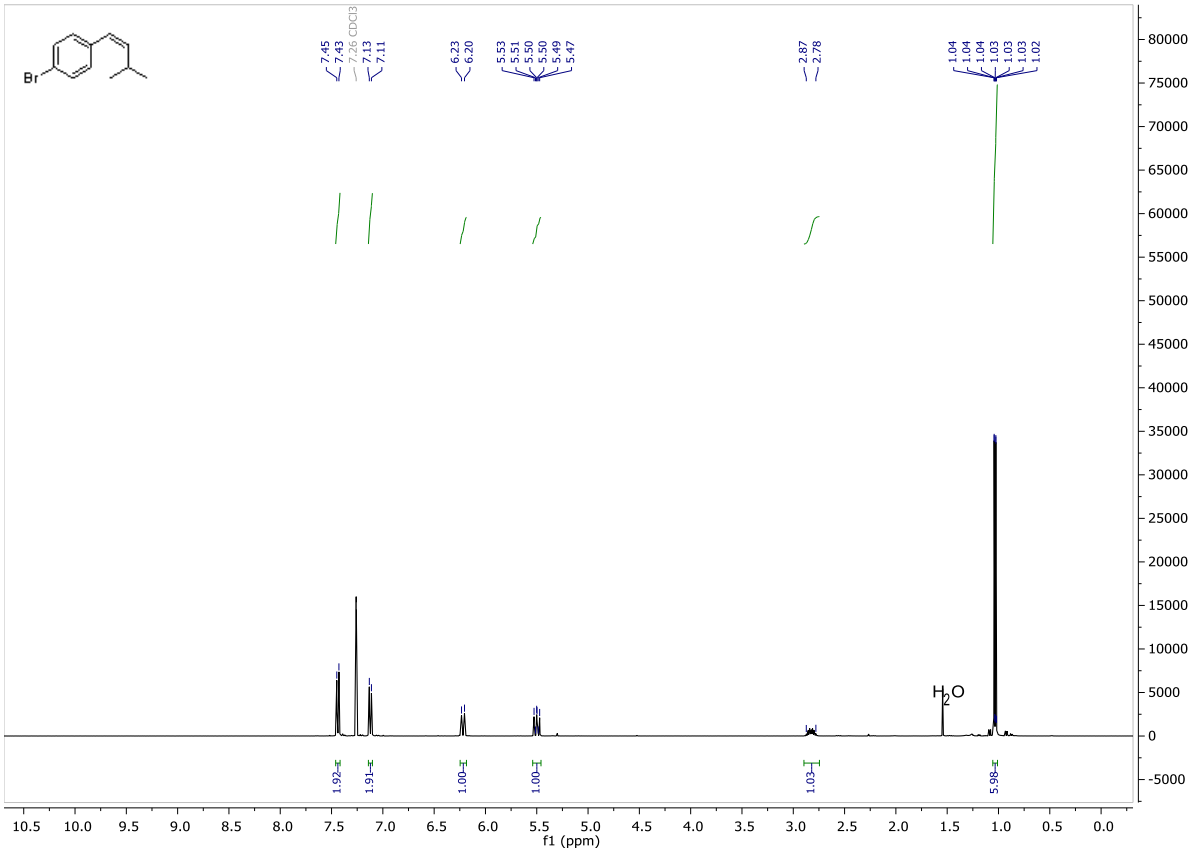


Figure S26: ^{1}H-NMR spectrum of (*Z*)-1-bromo-4-(3-methylbut-1-en-1-yl)benzene (**10i**).

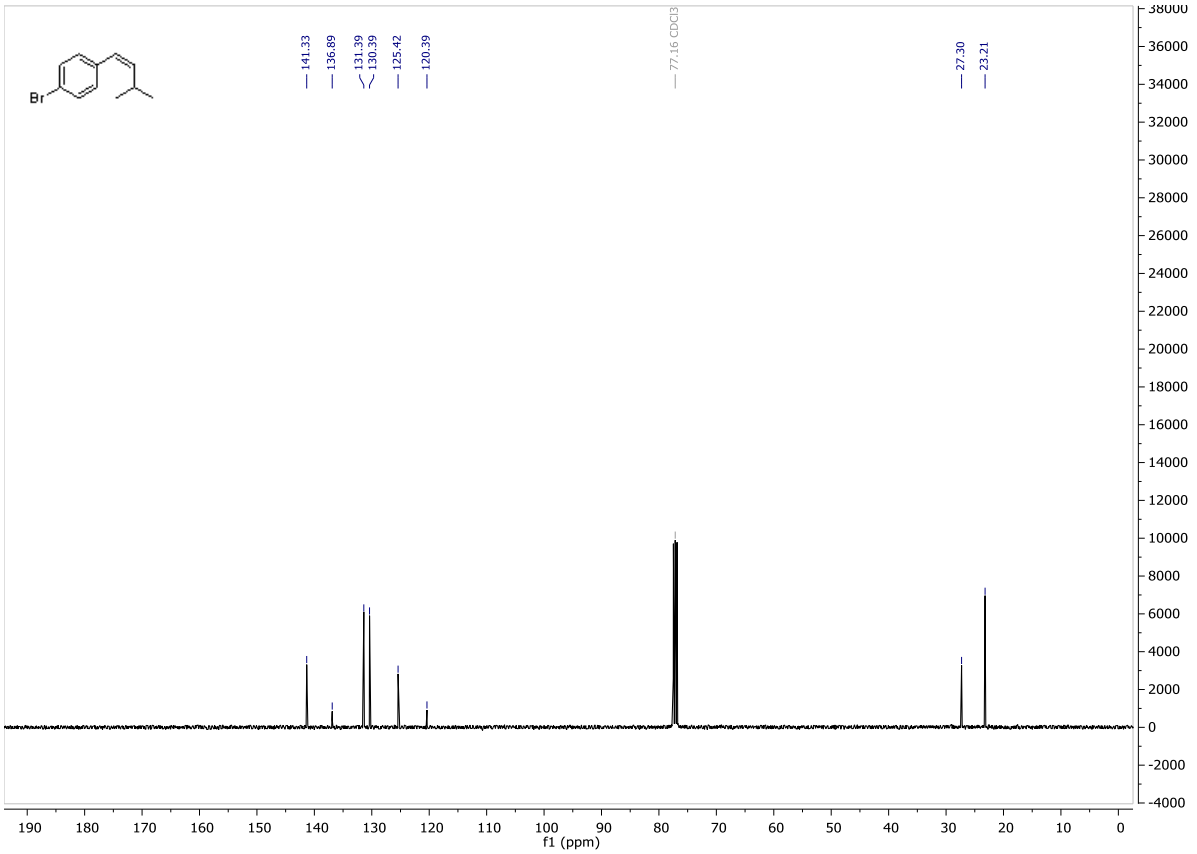


Figure S27: ^{13}C-NMR spectrum of (*Z*)-1-bromo-4-(3-methylbut-1-en-1-yl)benzene (**10i**).

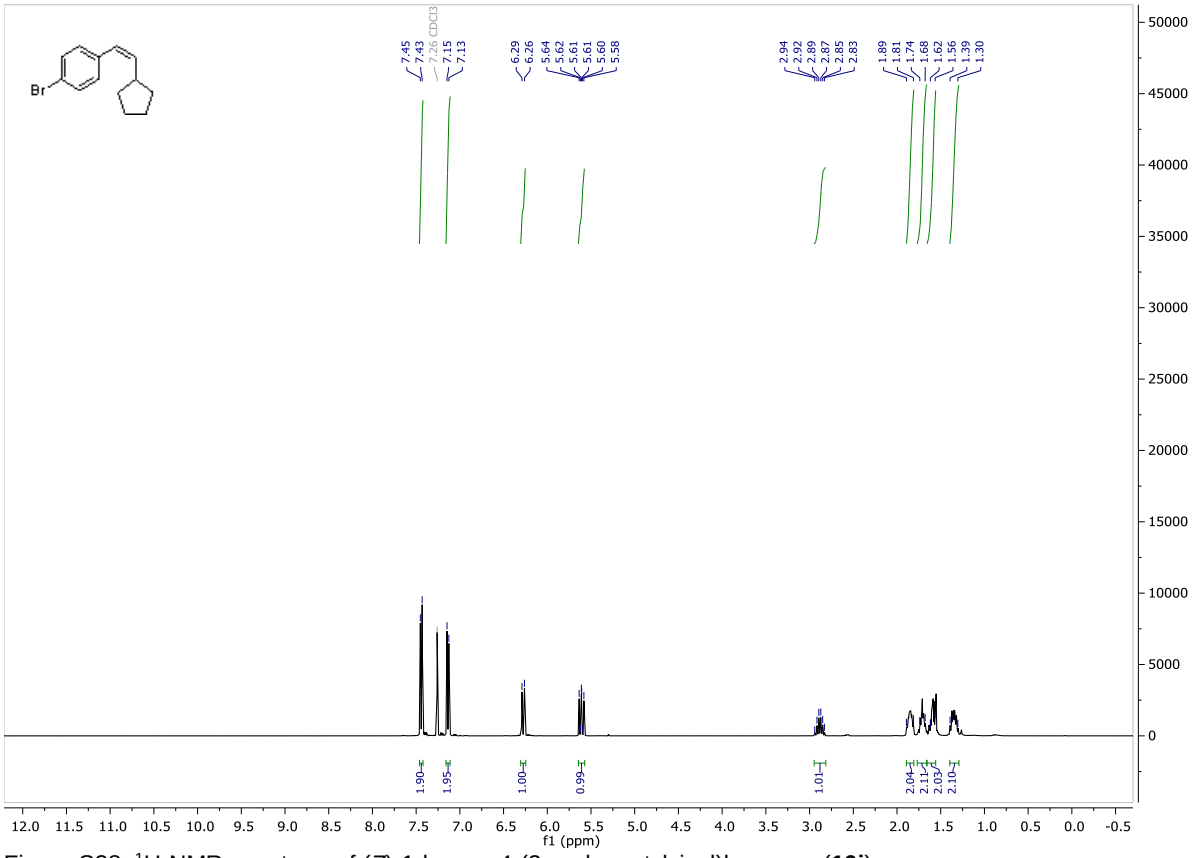


Figure S28: ^{1}H-NMR spectrum of (*Z*)-1-bromo-4-(2-cyclopentylvinyl)benzene (**10j**).

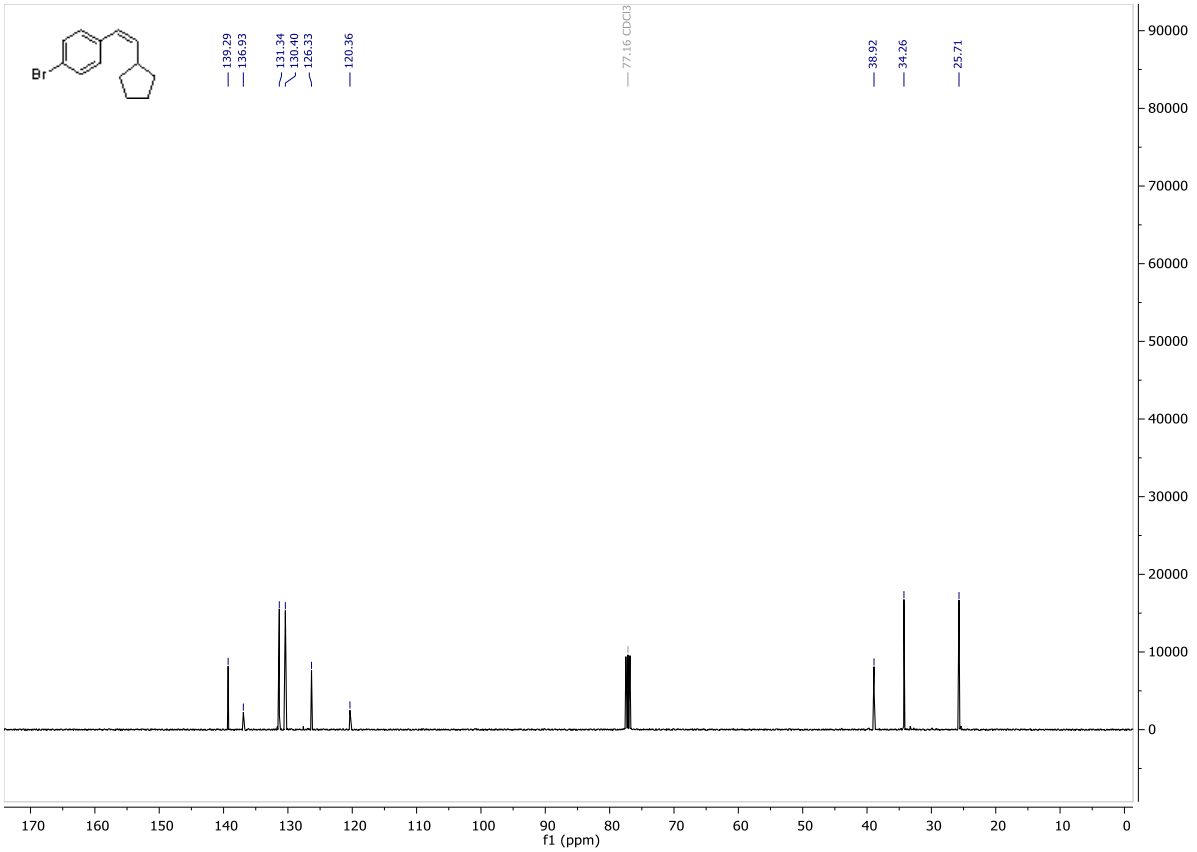


Figure S29: ^{13}C-NMR spectrum of (*Z*)-1-bromo-4-(2-cyclopentylvinyl)benzene (**10j**).

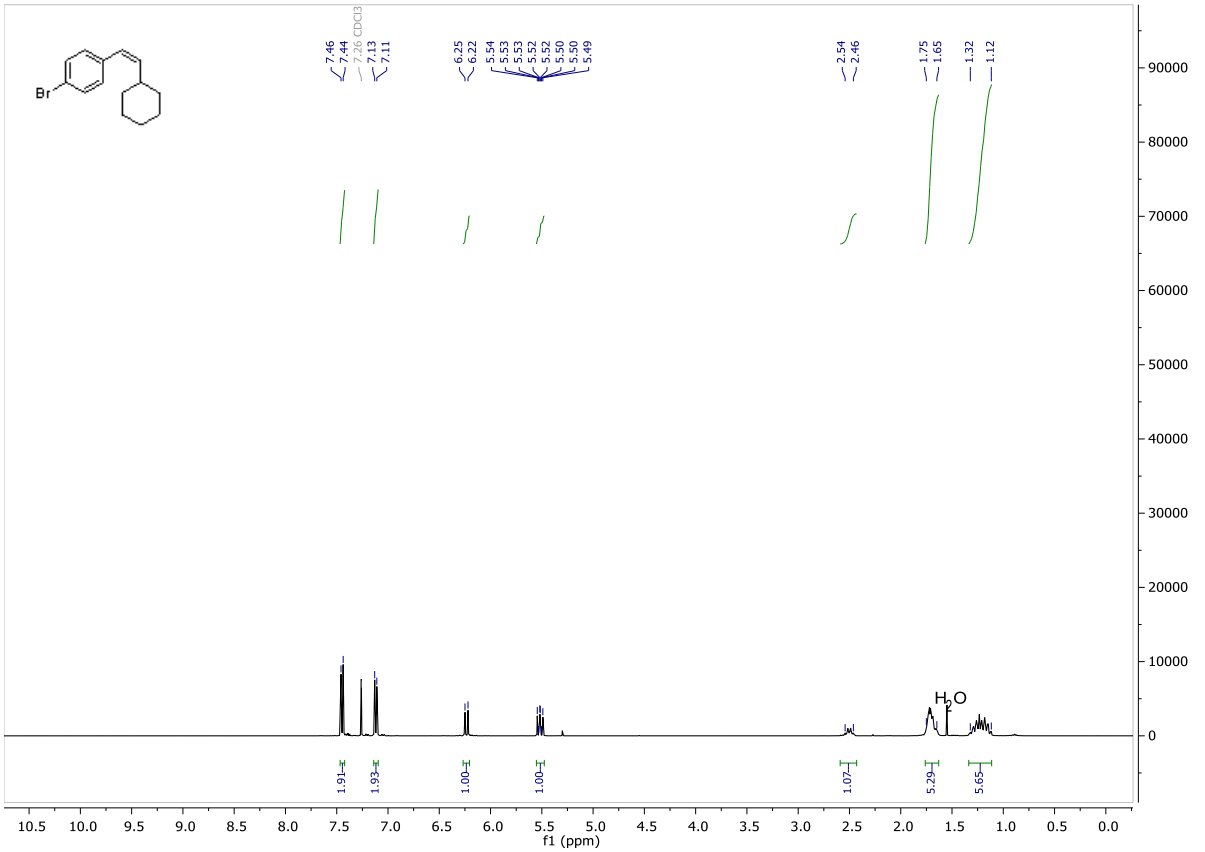


Figure S30: ^{1}H-NMR spectrum of (*Z*)-1-bromo-4-(2-cyclohexylvinyl)benzene (**10k**).

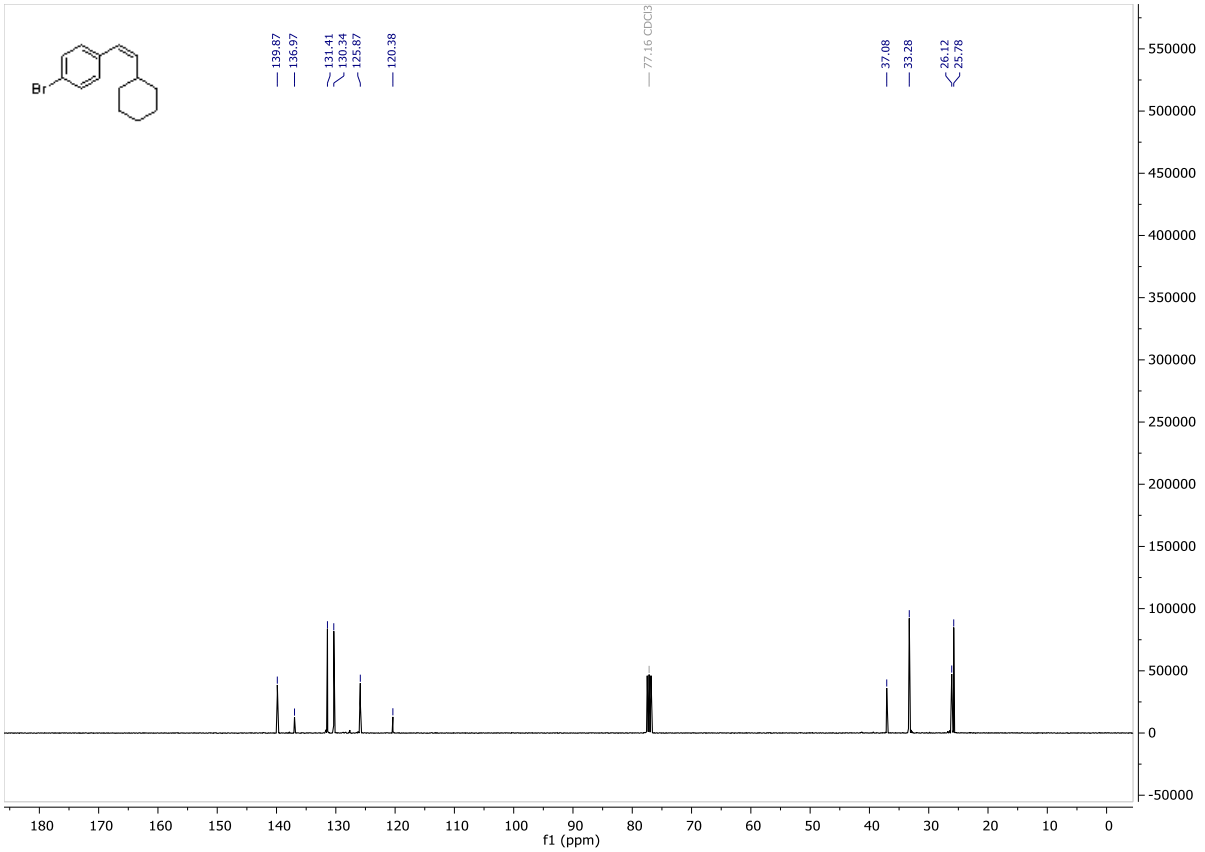


Figure S31: ^{13}C-NMR spectrum of (*Z*)-1-bromo-4-(2-cyclohexylvinyl)benzene (**10k**).

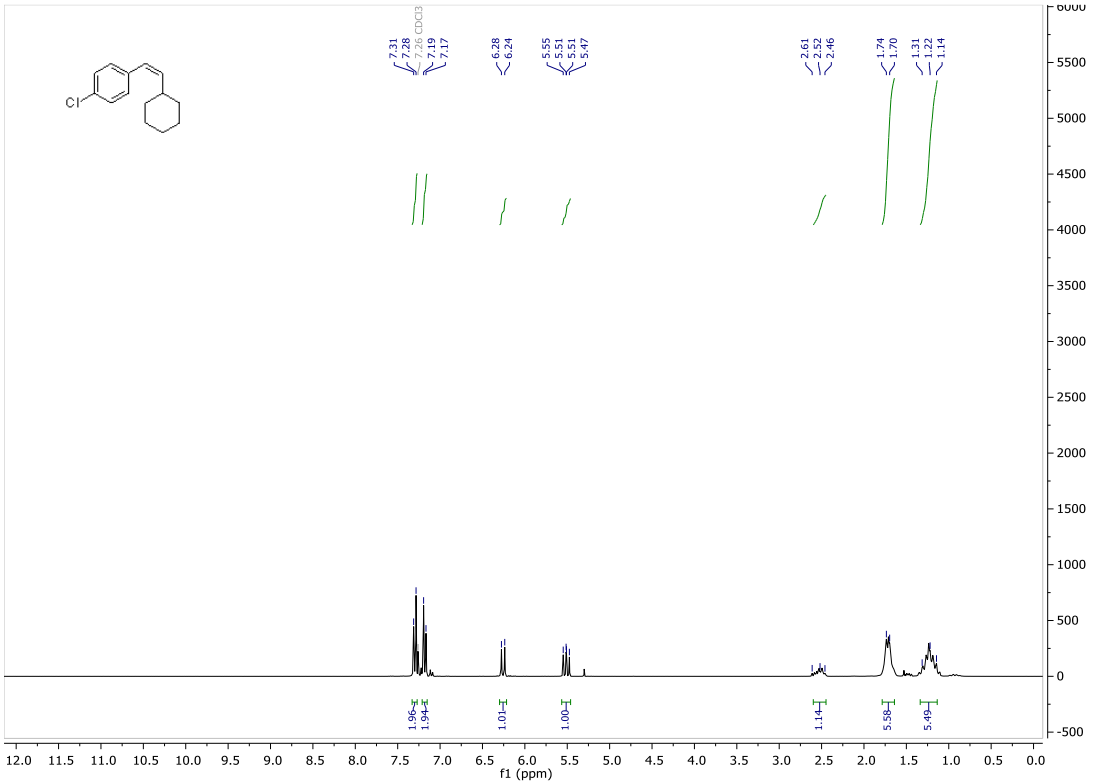


Figure S32: ^{1}H-NMR spectrum of (*Z*)-1-chloro-4-(2-cyclohexylvinyl)benzene (**10l**).

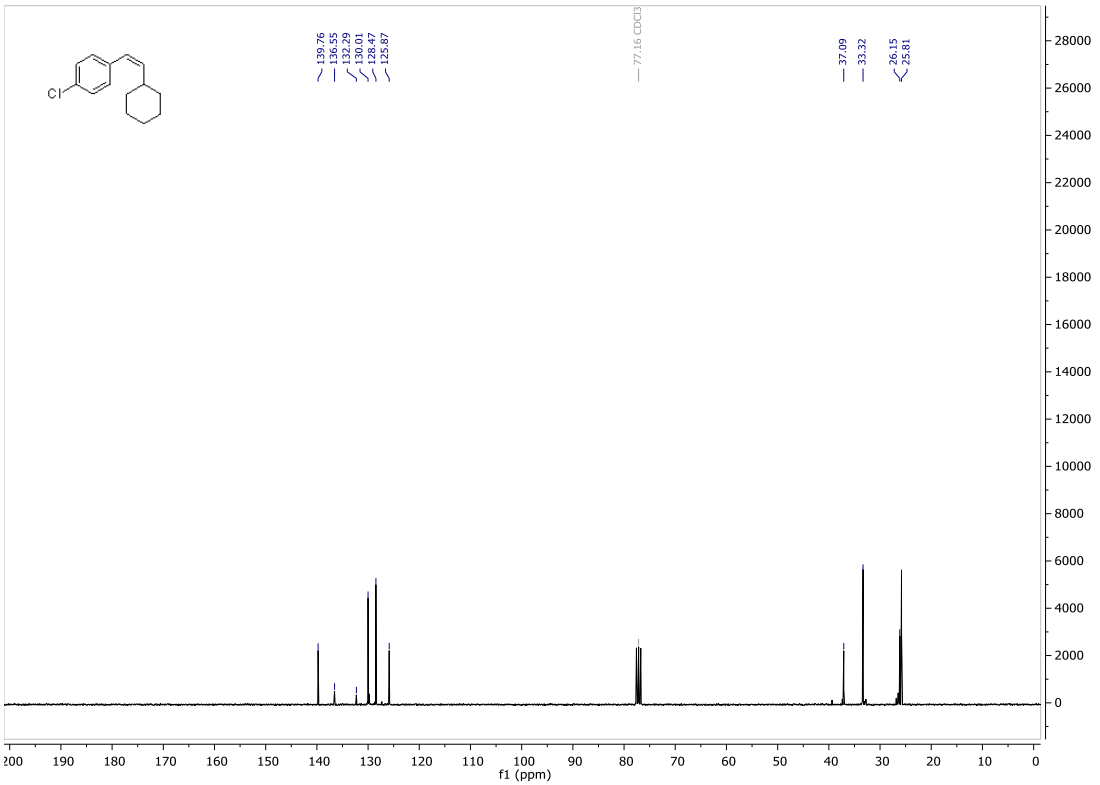


Figure S33: ^{13}C-NMR spectrum of (*Z*)-1-chloro-4-(2-cyclohexylvinyl)benzene (**10l**).

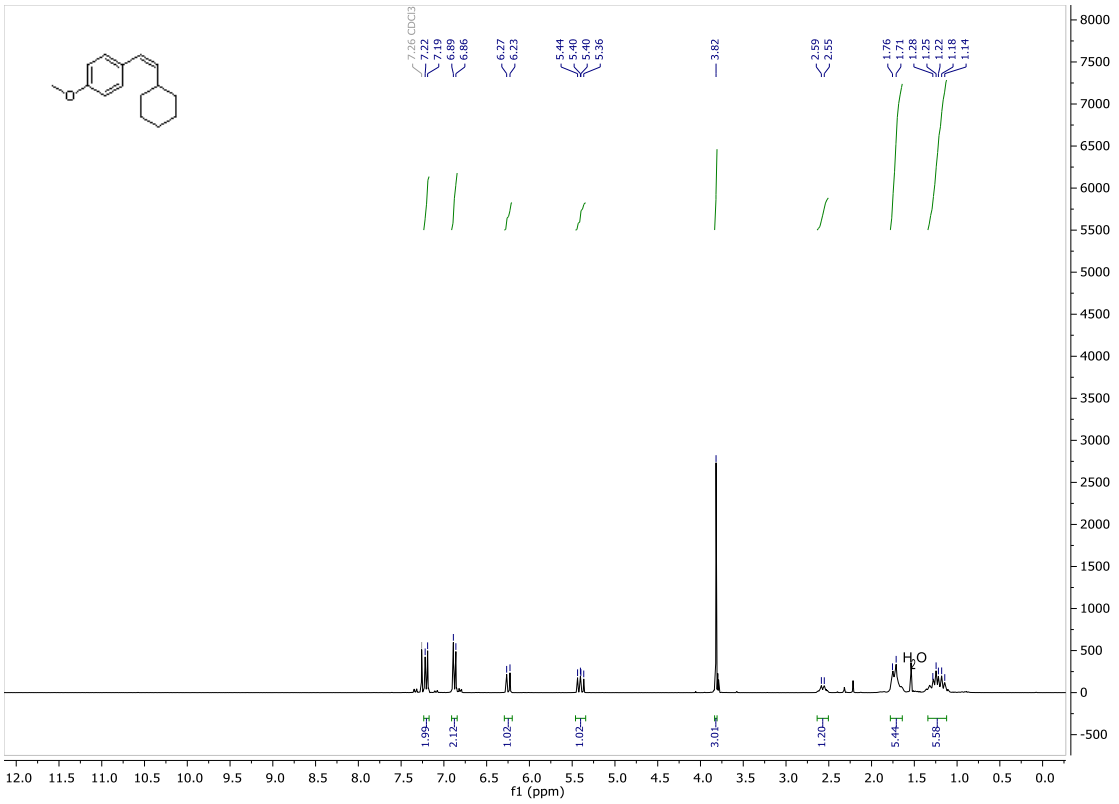


Figure S34: ^{1}H-NMR spectrum of (*Z*)-1-(2-cyclohexylvinyl)-4-methoxybenzene (**10m**).

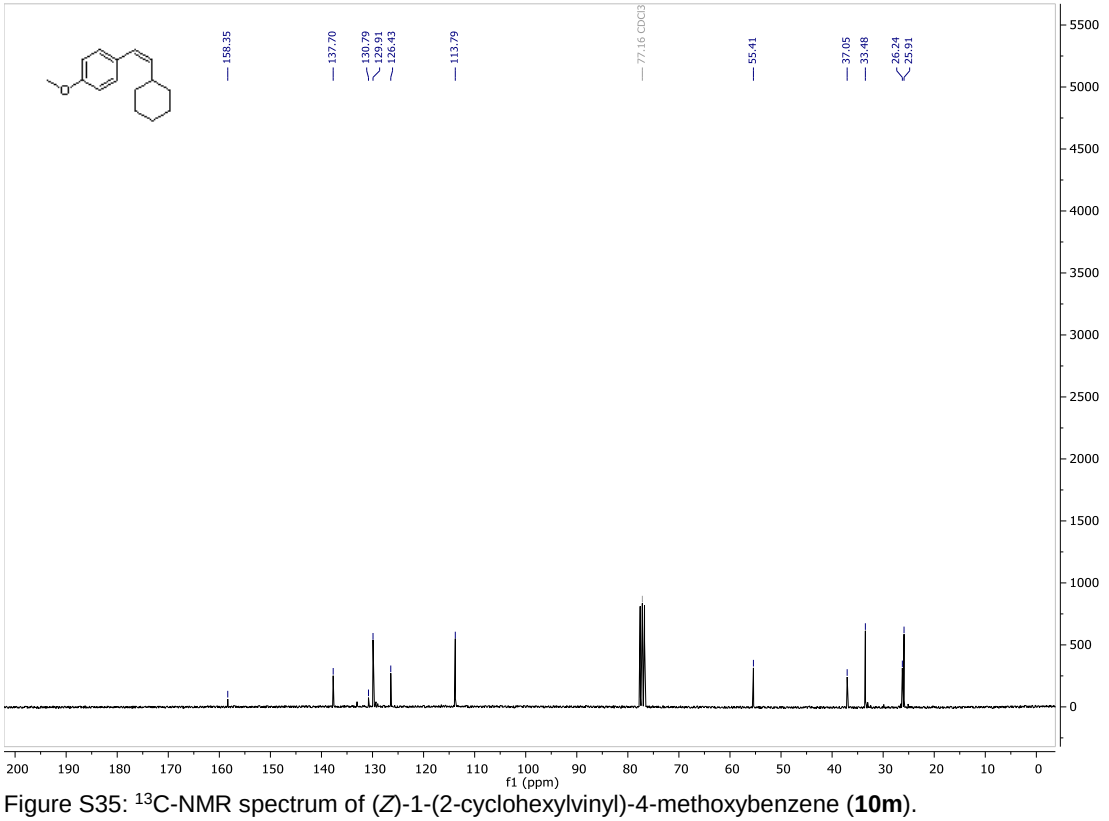


Figure S35: ^{13}C-NMR spectrum of (*Z*)-1-(2-cyclohexylvinyl)-4-methoxybenzene (**10m**).

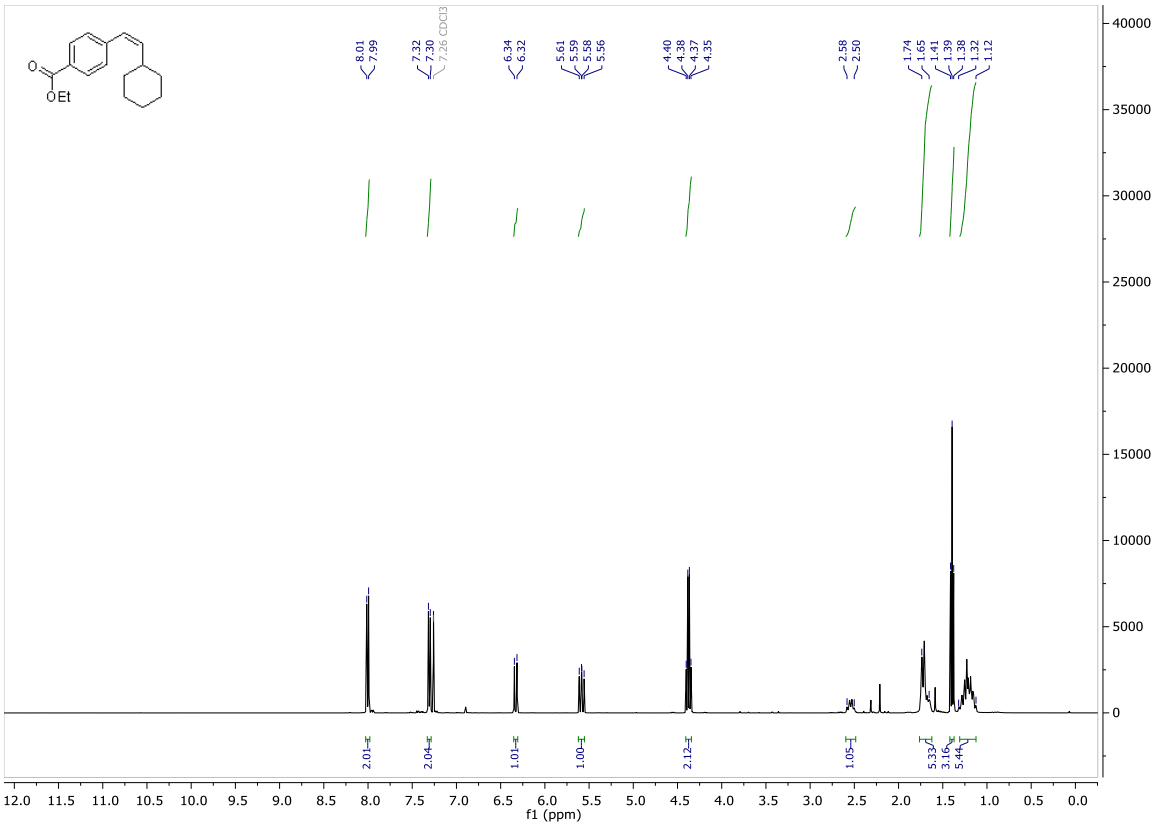


Figure S36: ^{1}H-NMR spectrum of ethyl (*Z*)-4-(2-cyclohexylvinyl)benzoate (**10n**).

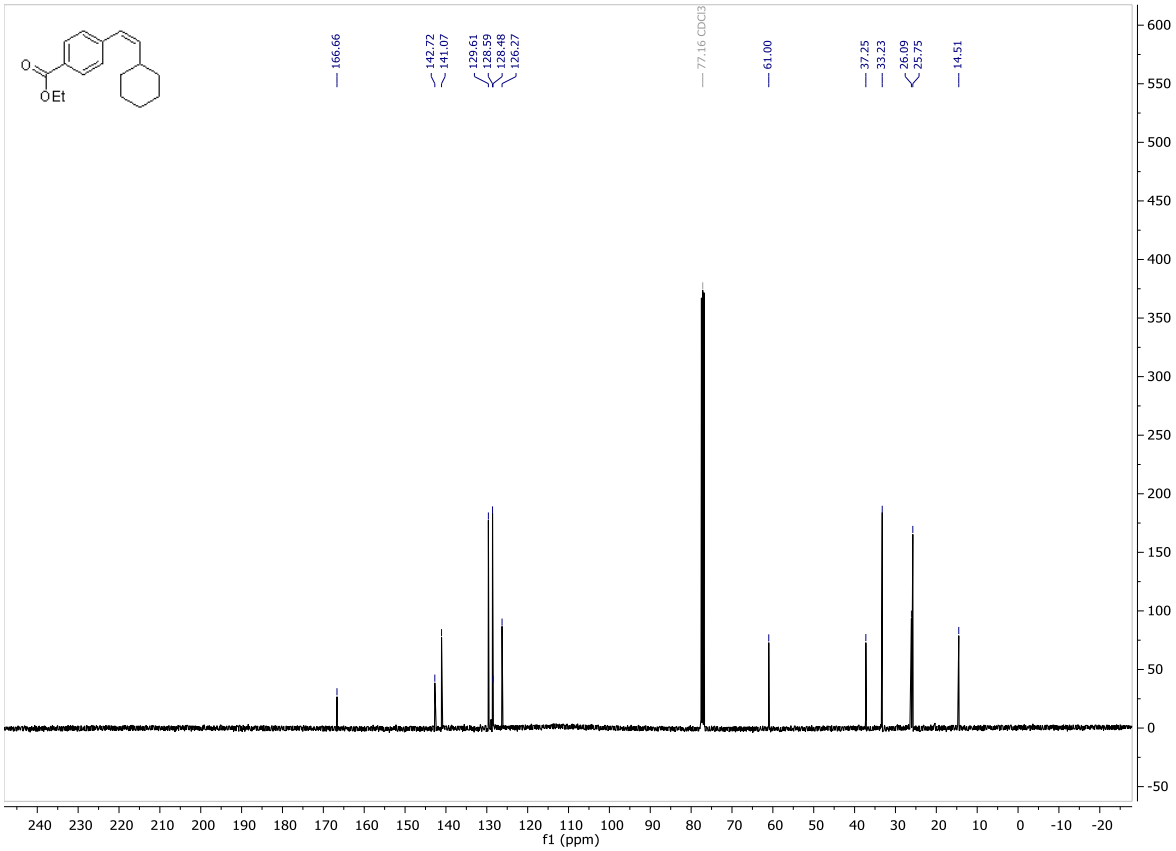


Figure S37: ^{13}C-NMR spectrum of ethyl (*Z*)-4-(2-cyclohexylvinyl)benzoate (**10n**).

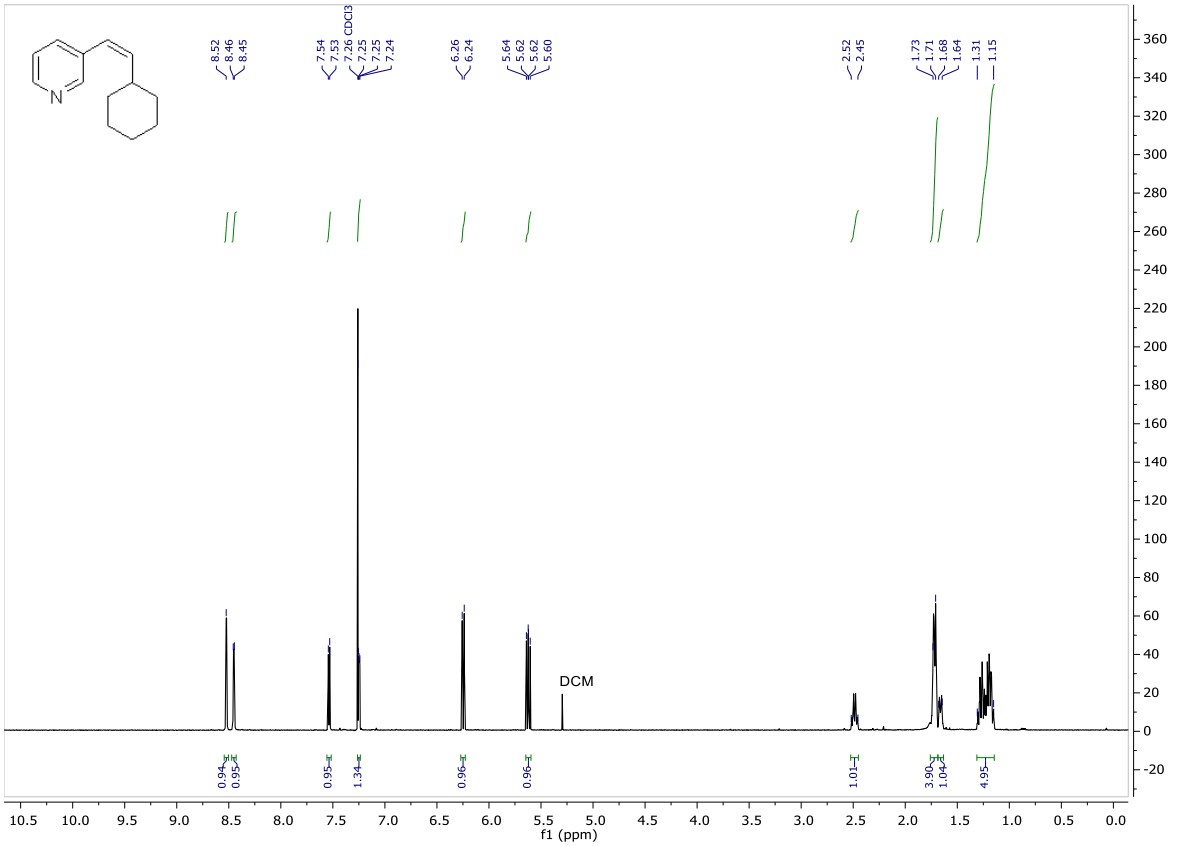


Figure S38: ^{1}H-NMR spectrum of (*Z*)-3-(2-cyclohexylvinyl)pyridine (**10o**).

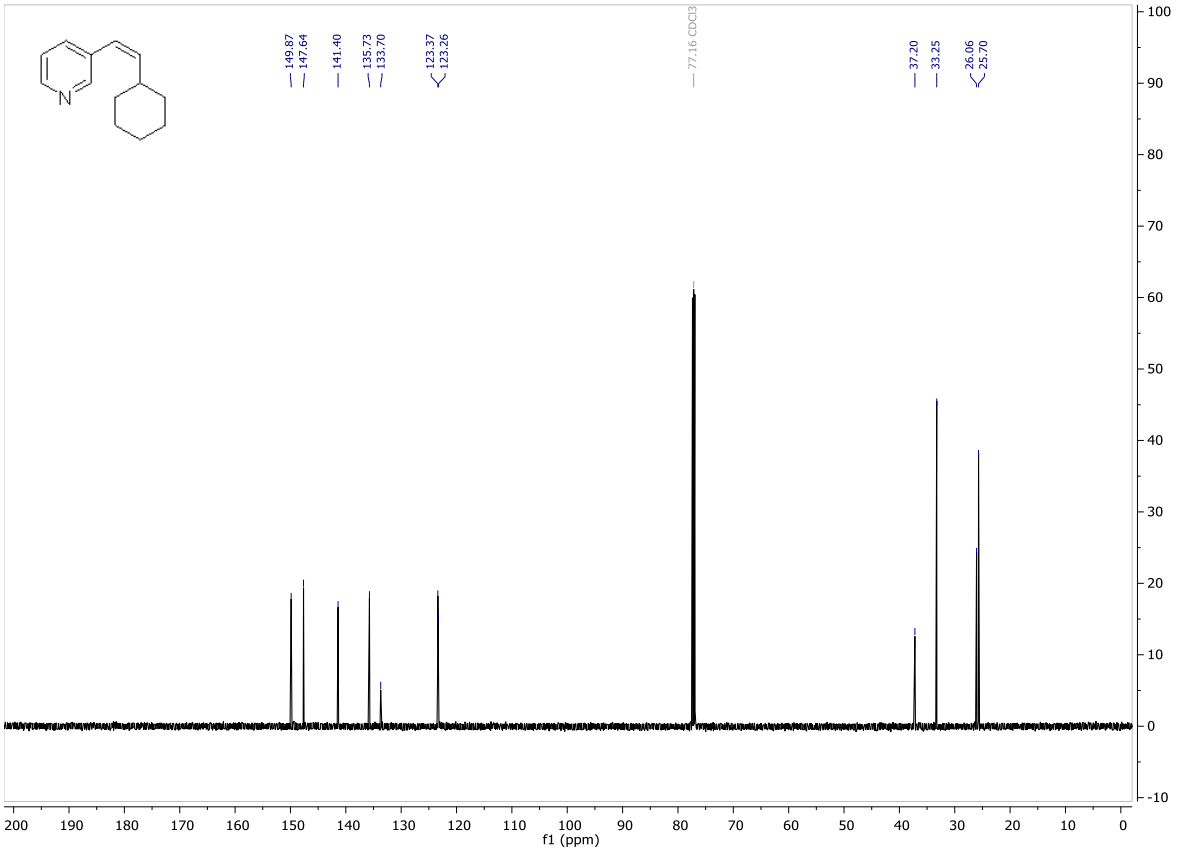


Figure S39: ^{13}C-NMR spectrum of (*Z*)-3-(2-cyclohexylvinyl)pyridine (**10o**).

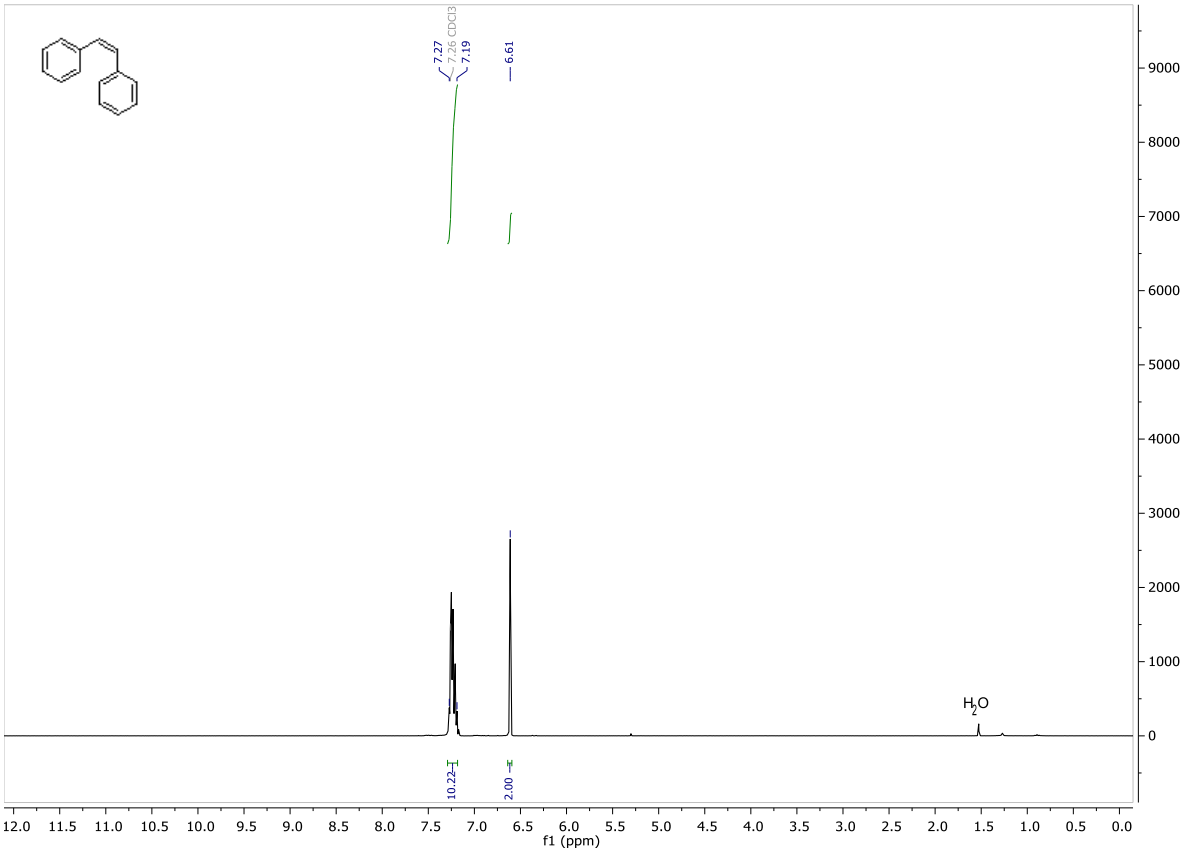


Figure S40: ^{1}H-NMR spectrum of (*Z*)-1,2-diphenylethene (**10p**).

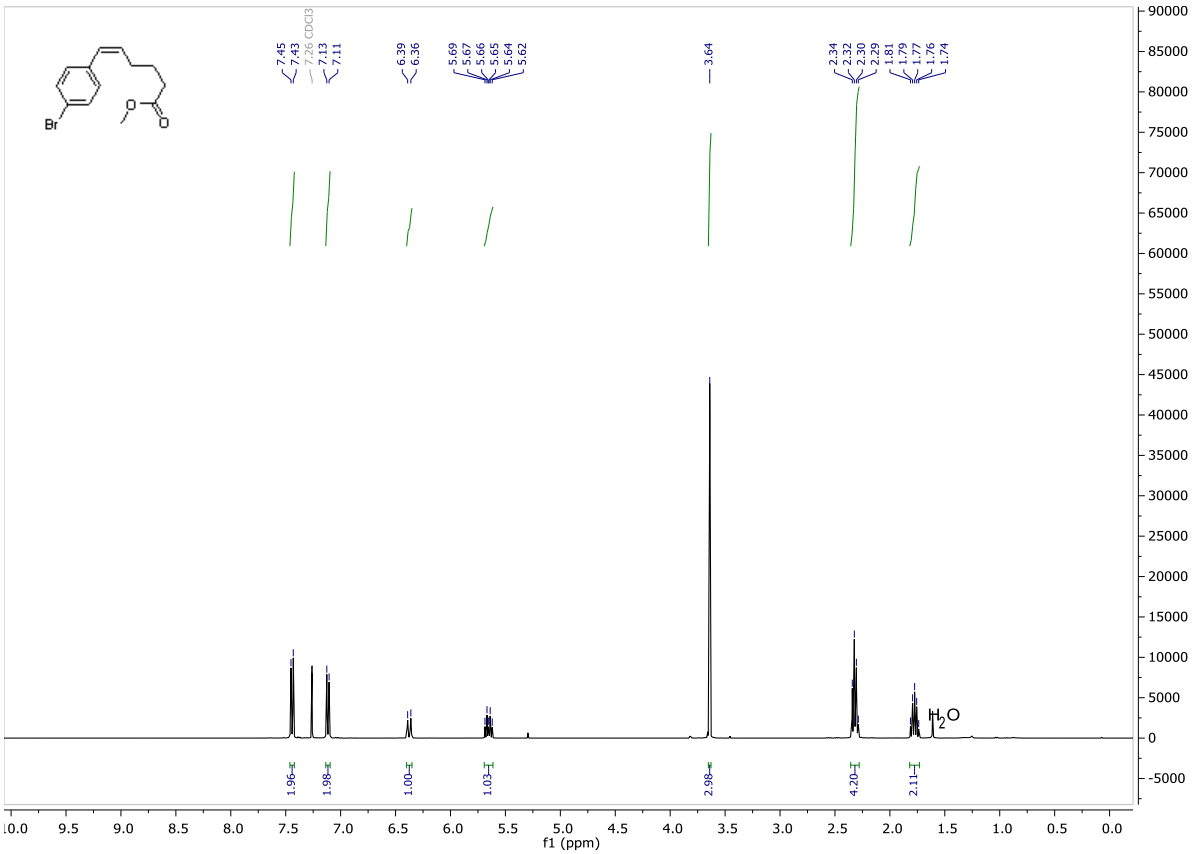


Figure S41: ^{1}H-NMR spectrum of methyl (*Z*)-6-(4-bromophenyl)hex-5-enoate (**10q**).

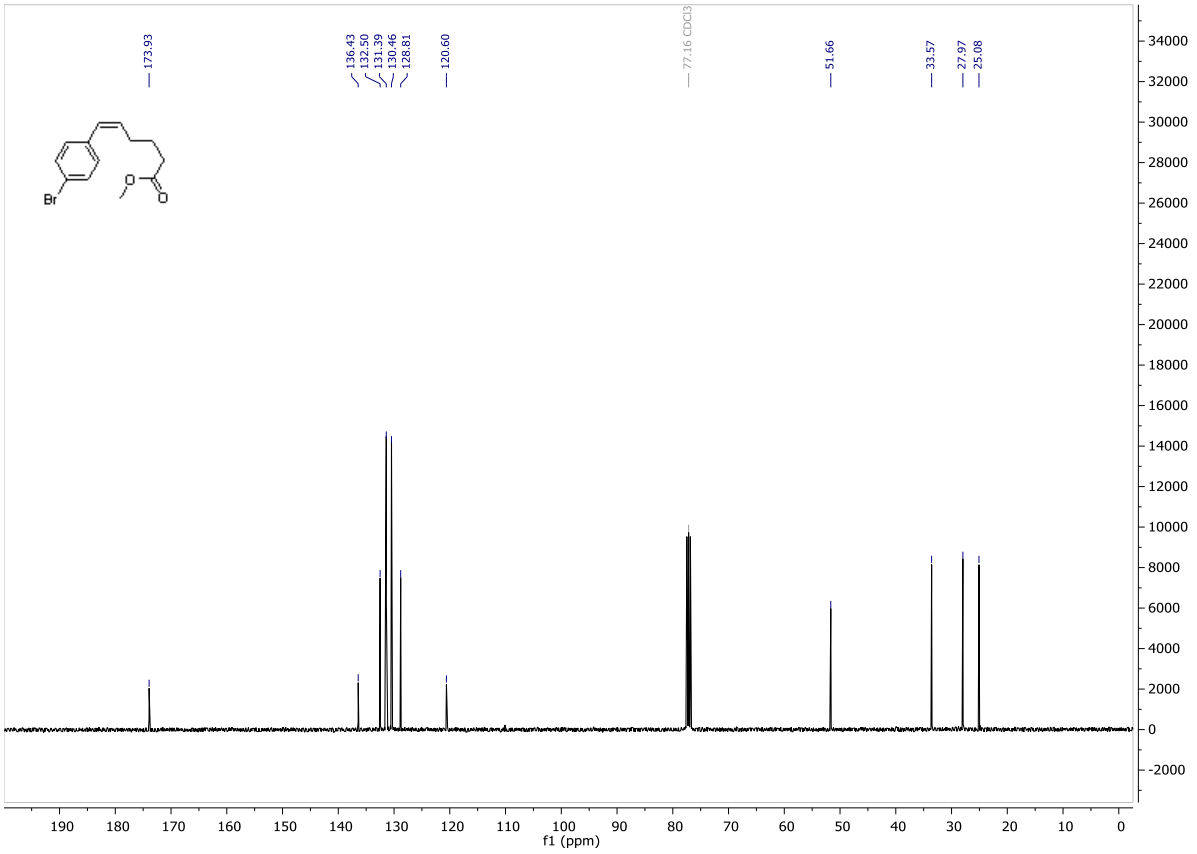


Figure S42: ^{13}C-NMR spectrum of methyl (*Z*)-6-(4-bromophenyl)hex-5-enoate (**10q**).

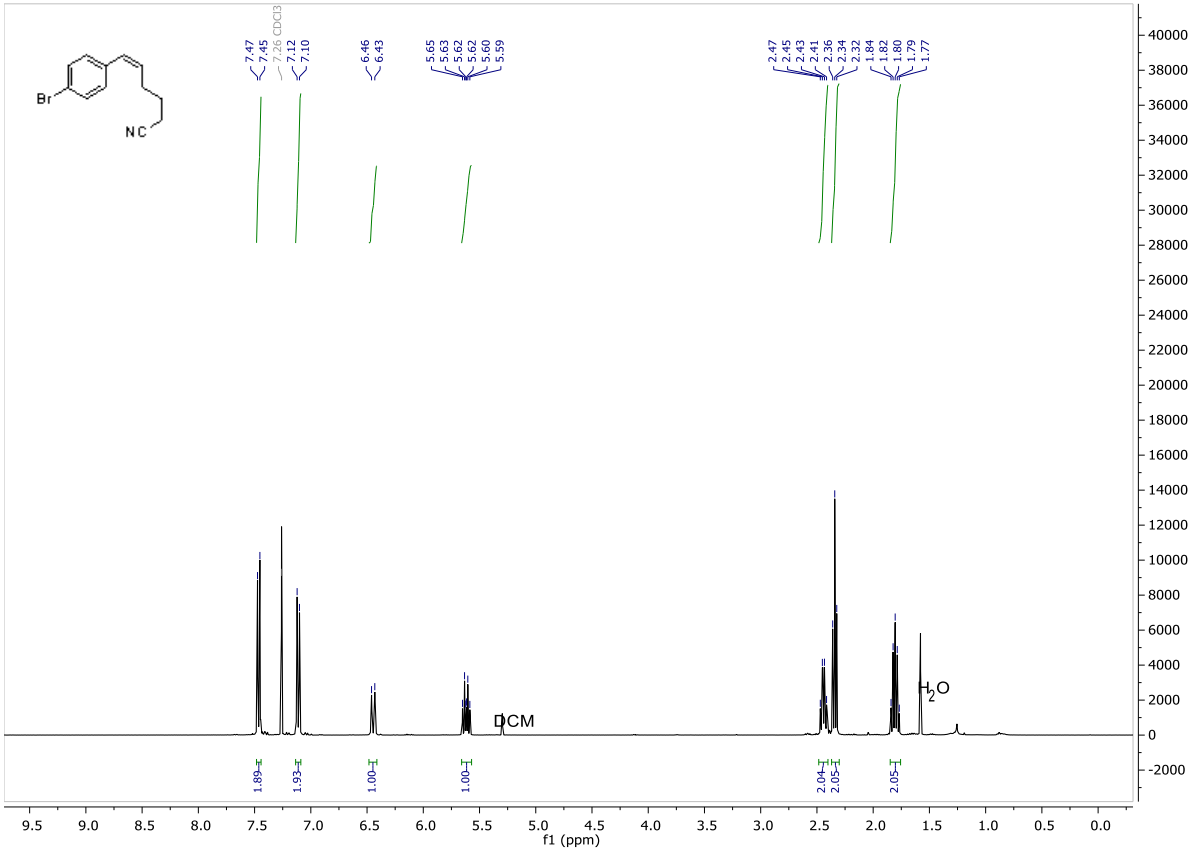


Figure S43: ^{1}H-NMR spectrum of (*Z*)-6-(4-bromophenyl)hex-5-enenitrile (**10r**).

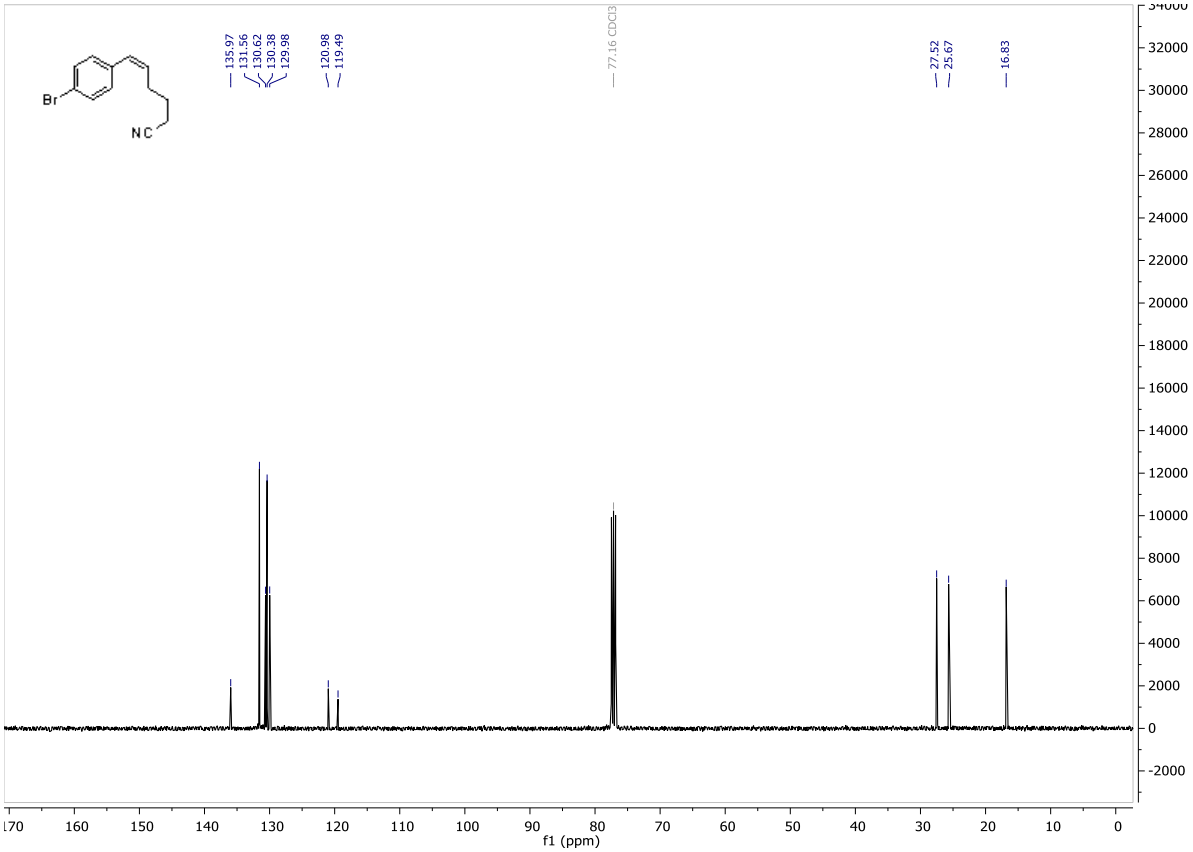


Figure S44: ^{13}C-NMR spectrum of (*Z*)-6-(4-bromophenyl)hex-5-enenitrile (**10r**).

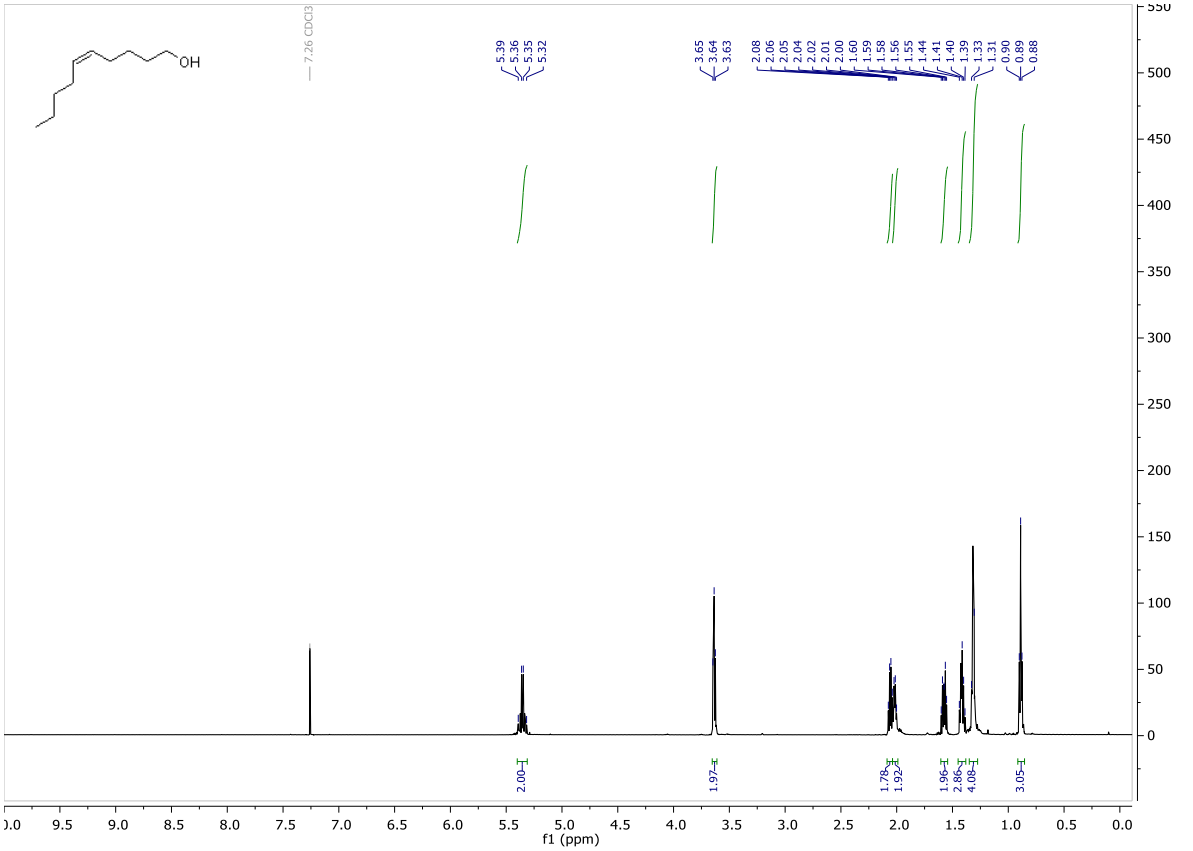


Figure S45: ^{1}H-NMR spectrum of (*Z*)-dec-5-en-1-ol (**10s**).

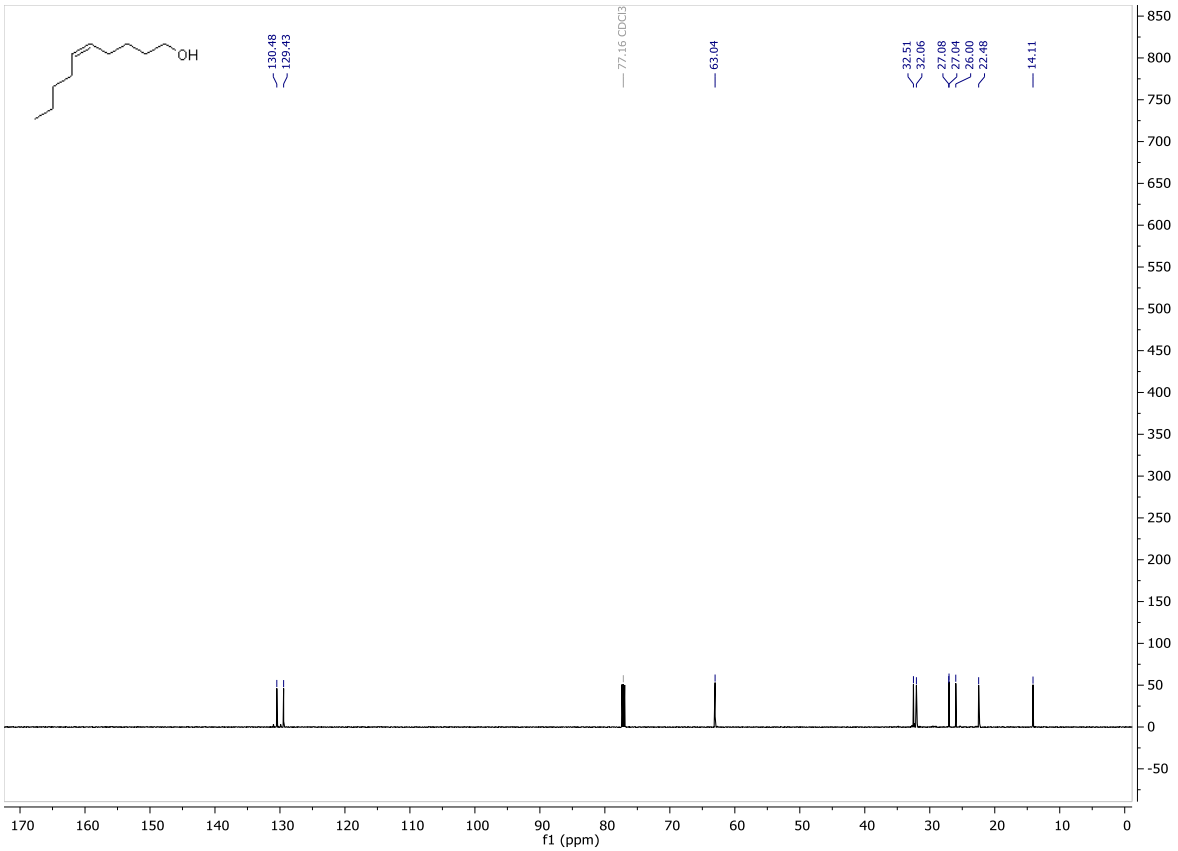


Figure S46: ^{13}C-NMR spectrum of (*Z*)-dec-5-en-1-ol (**10s**).

GC Traces

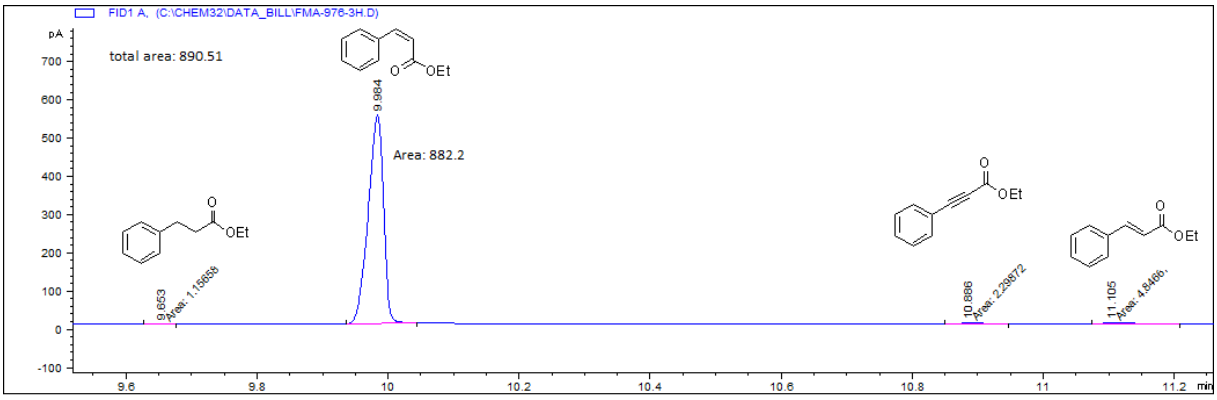


Figure S47: GC-FID trace with the hydrogenation products derived from alkyne **9a**.

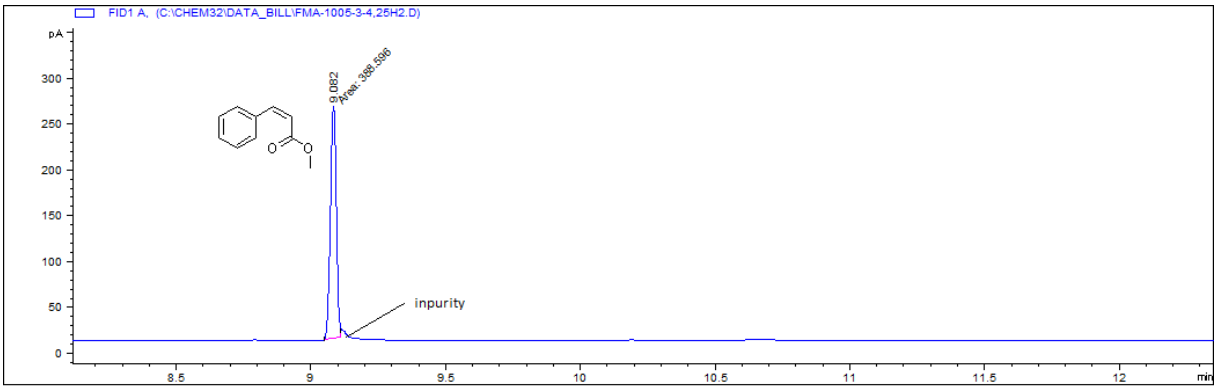


Figure S48: GC-FID trace with the hydrogenation products derived from alkyne **9b**.

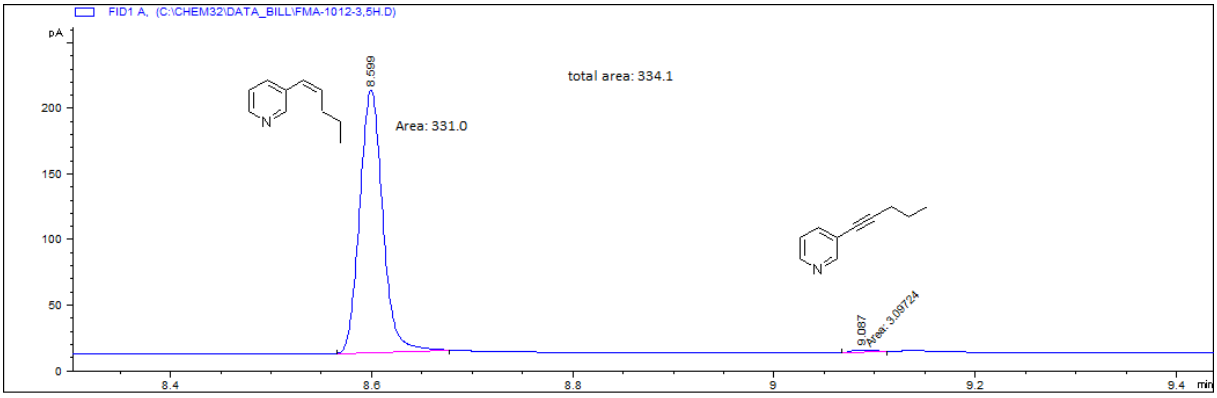


Figure S49: GC-FID trace with the hydrogenation products derived from alkyne **9c**.

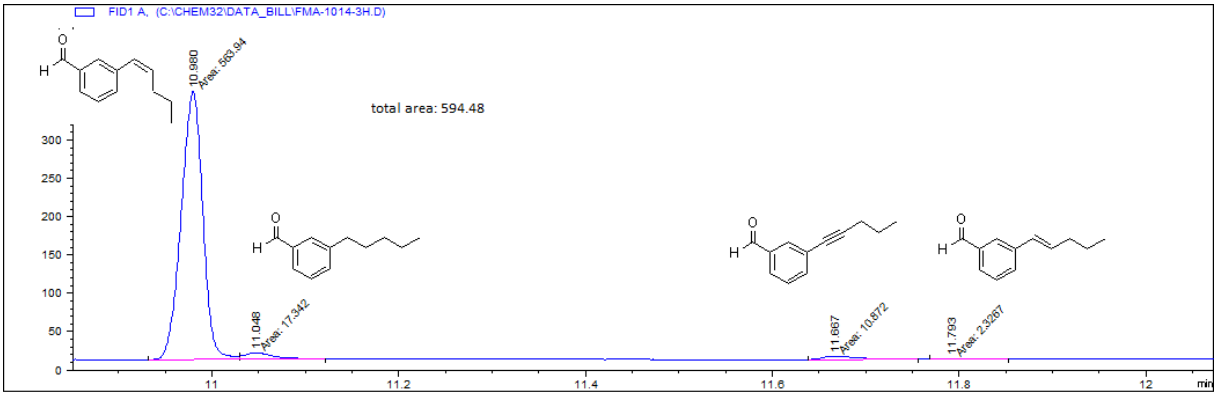


Figure S50: GC-FID trace with the hydrogenation products derived from alkyne **9d**.

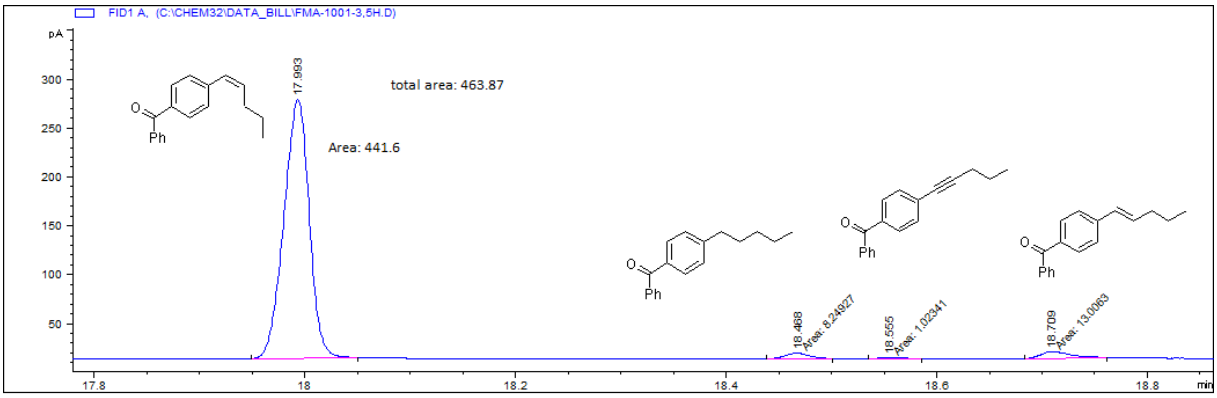


Figure S51: GC-FID trace with the hydrogenation products derived from alkyne **9e**.

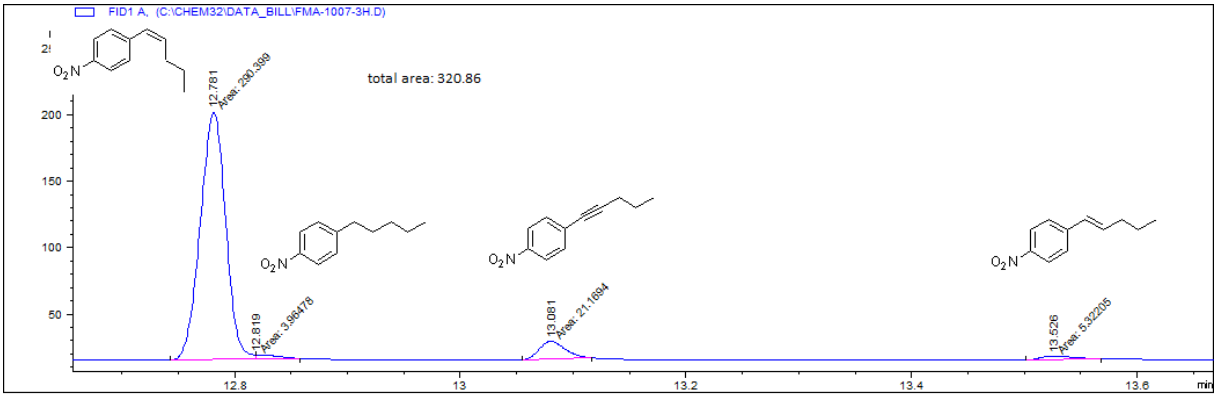


Figure S52: GC-FID trace with the hydrogenation products derived from alkyne **9f**.

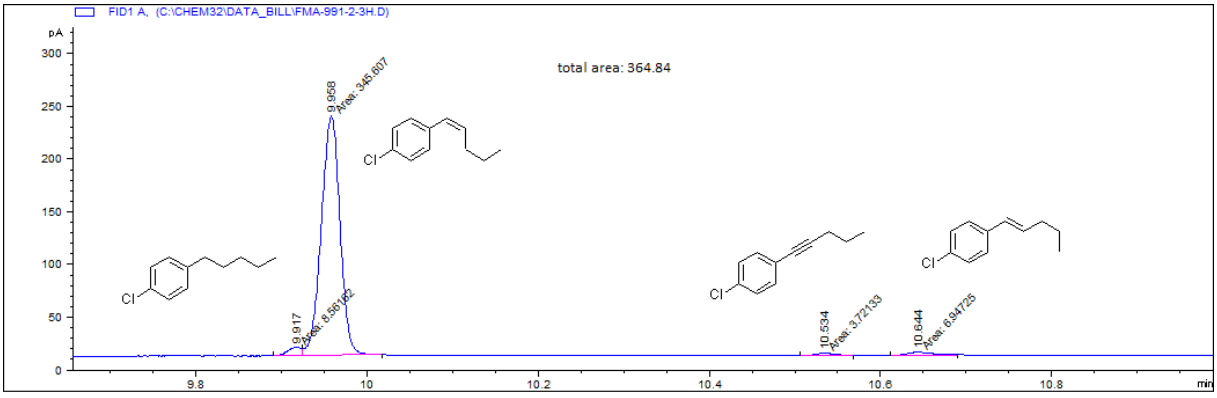


Figure S53: GC-FID trace with the hydrogenation products derived from alkyne **9g**.

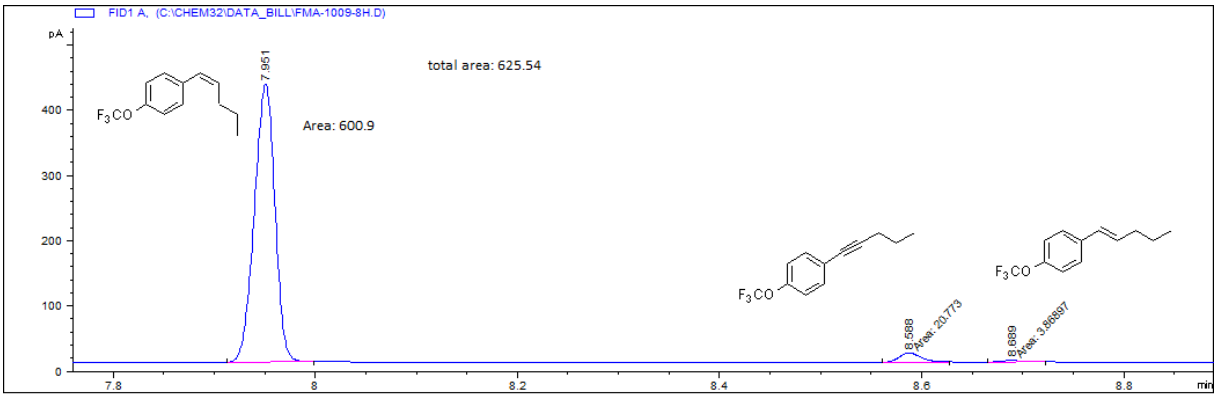


Figure S54: GC-FID trace with the hydrogenation products derived from alkyne **9h**.

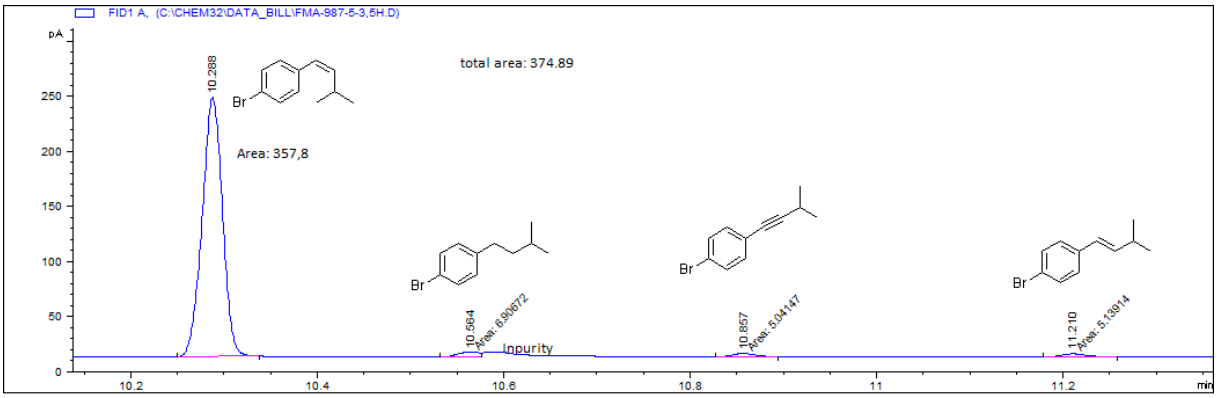


Figure S55: GC-FID trace with the hydrogenation products derived from alkyne **9i**.

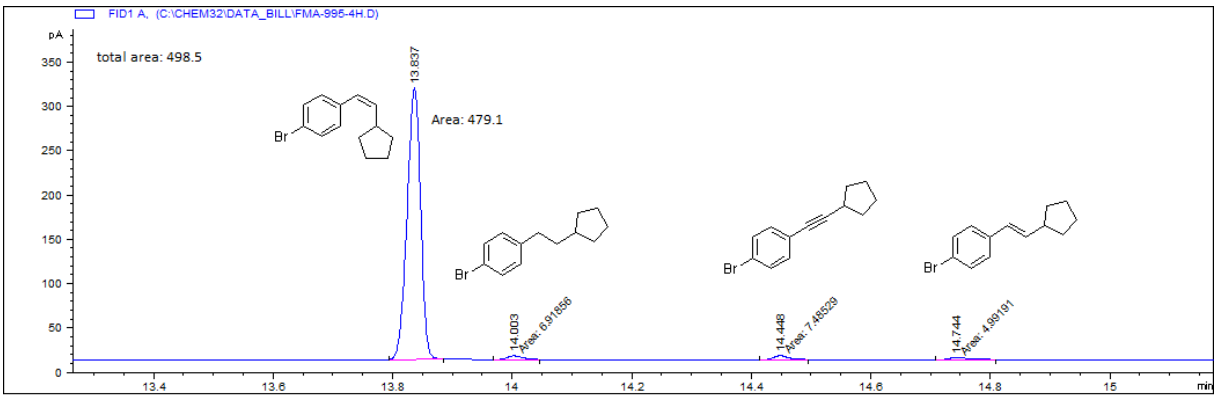


Figure S56: GC-FID trace with the hydrogenation products derived from alkyne **9j**.

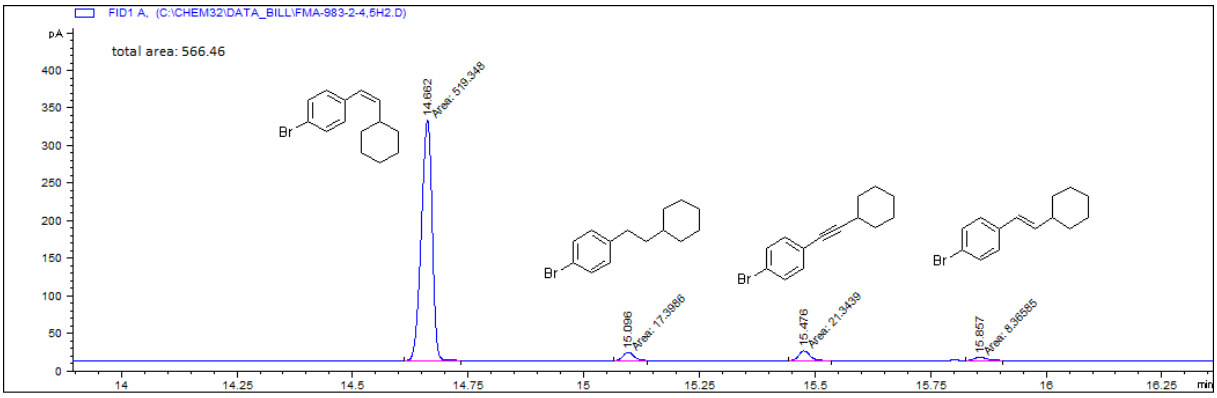


Figure S57: GC-FID trace with the hydrogenation products derived from alkyne **9k**.

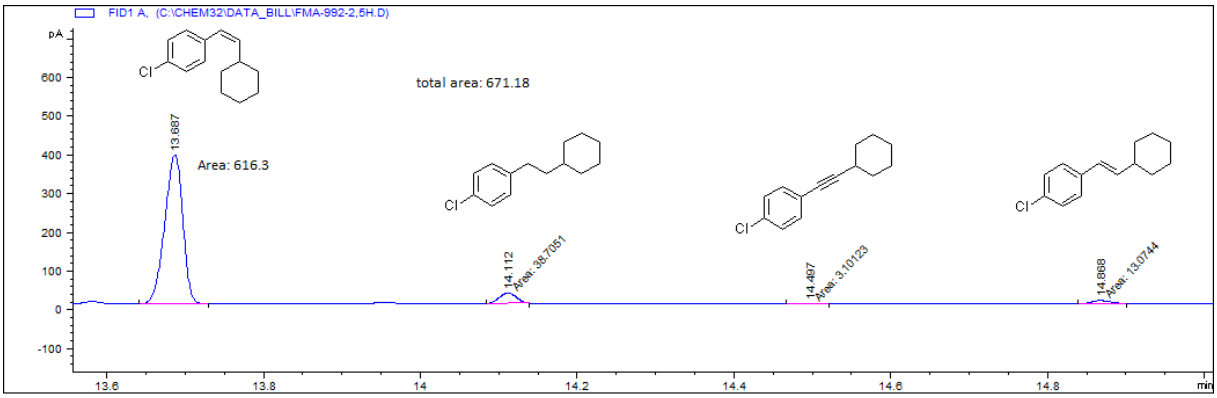


Figure S58: GC-FID trace with the hydrogenation products derived from alkyne **9l**.

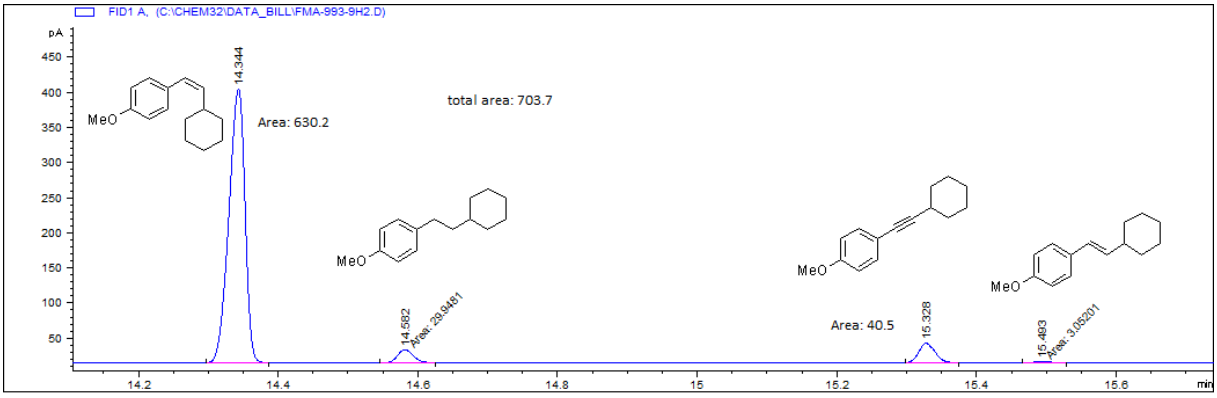


Figure S59: GC-FID trace with the hydrogenation products derived from alkyne **9m**.

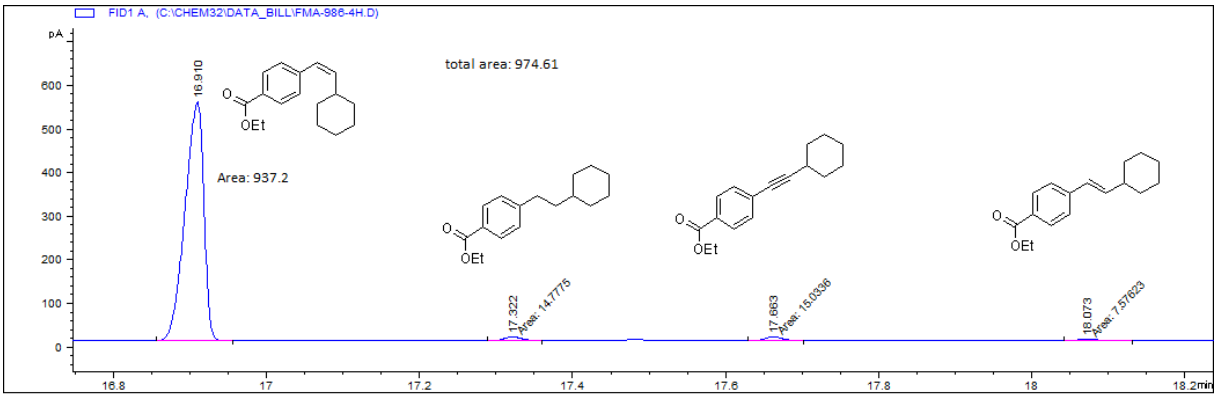


Figure S60: GC-FID trace with the hydrogenation products derived from alkyne **9n**.

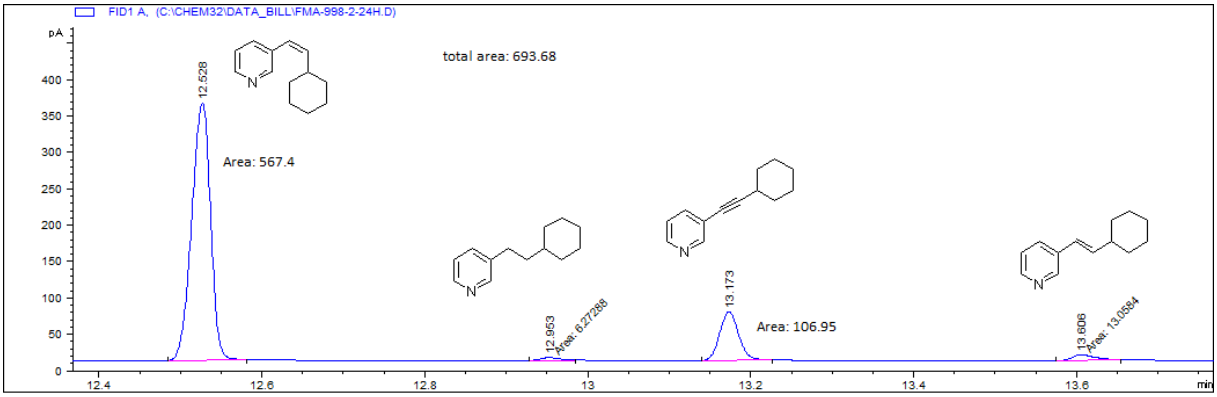


Figure S61: GC-FID trace with the hydrogenation products derived from alkyne **9o**.

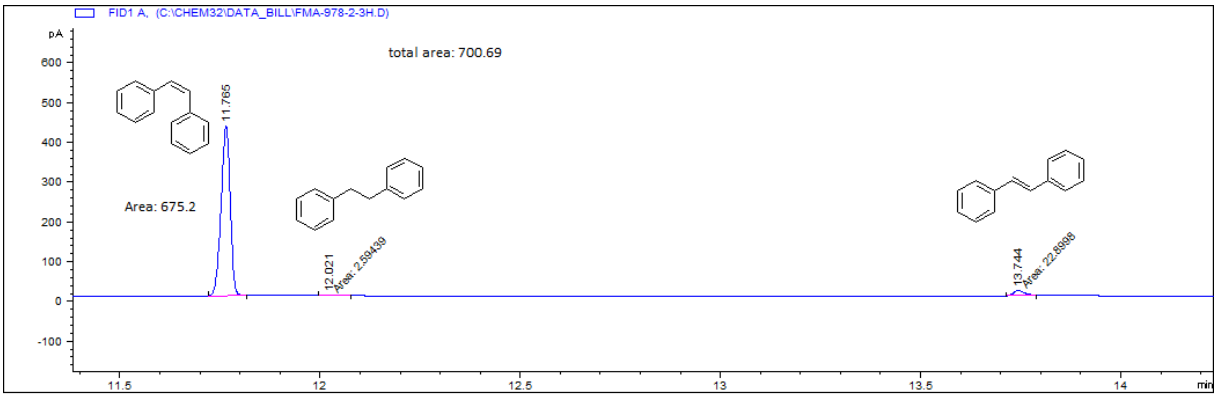


Figure S62: GC-FID trace with the hydrogenation products derived from alkyne **9p**.

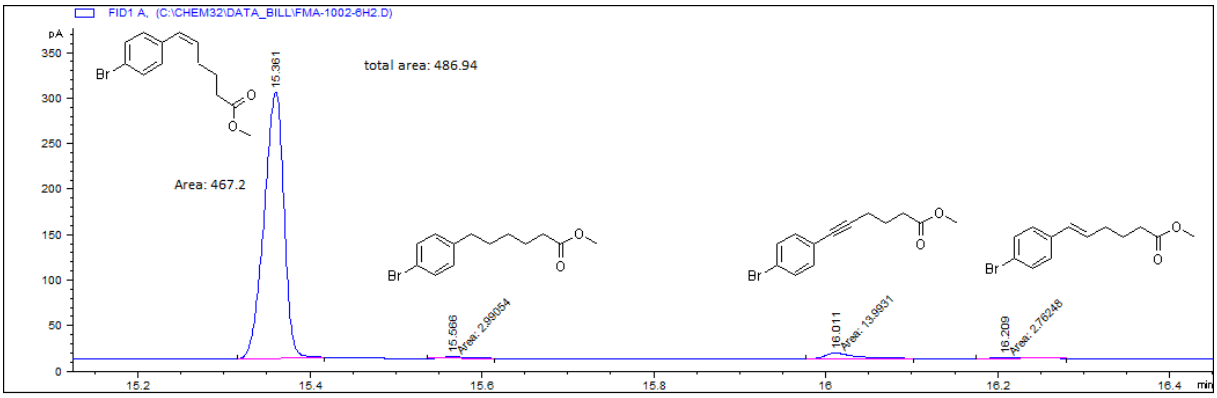


Figure S63: GC-FID trace with the hydrogenation products derived from alkyne **9q**.

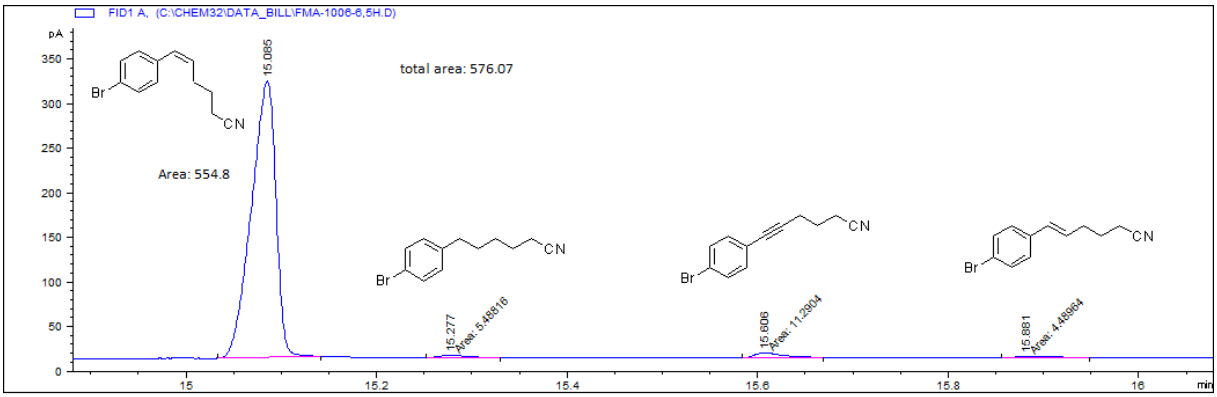


Figure S64: GC-FID trace with the hydrogenation products derived from alkyne **9r**.

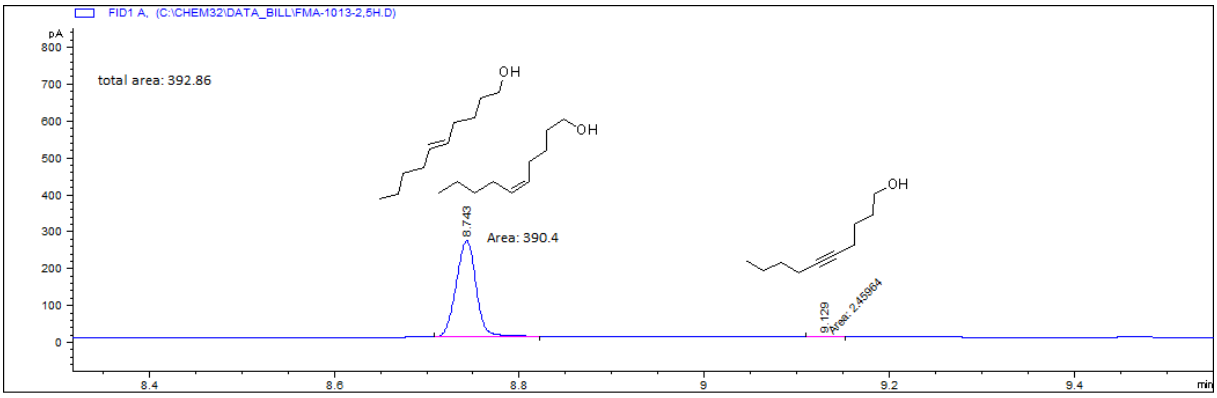


Figure S65: GC-FID trace with the hydrogenation products derived from alkyne **9s**.

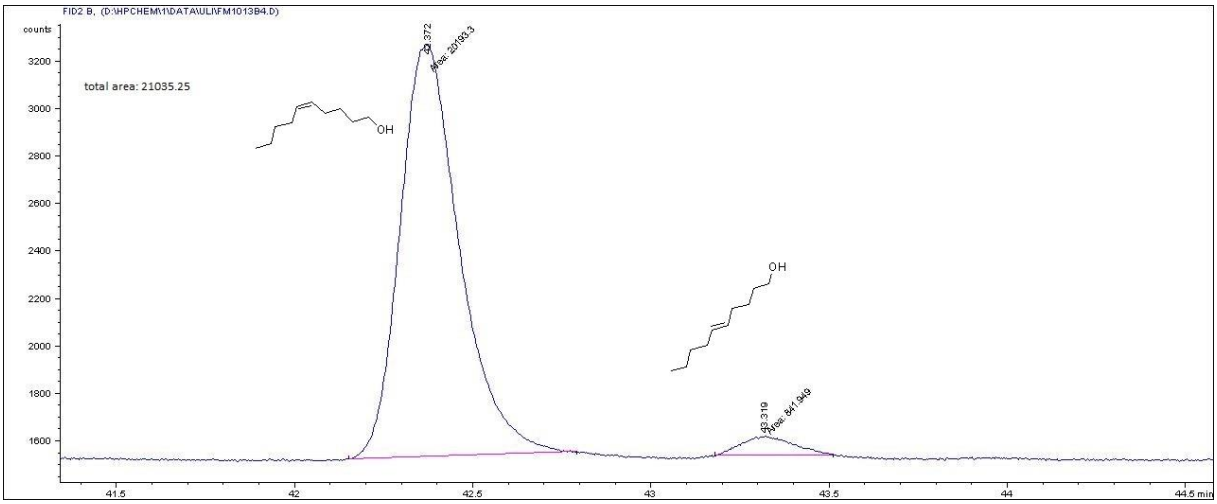


Figure S66: Chiral GC-FID trace with Z/E isomers of **10s**.

References

(1) (a) Wang, X.; Studer, A. *J. Am. Chem. Soc*. **2016**, *138*, 2977-2980; (b) Mäsing, F.; Wang, X.; Nüsse, H.; Klingauf, J.; Studer, A. *Chem. Eur. J*. **2017**, *23*, 6014-6018.

(2) Gil-Moltó, J.; Nájera, C. *Eur. J. Org. Chem*. **2005**, 4073-4081.

(3) Yang, J.; Zhang, J.; Qi, L.; Hu, C.; Chen, Y. *Chem. Commun*. **2015**, *51*, 5275-5278.

(4) Walter, C.; Oestreich, M. *Angew. Chem. Int. Ed*. **2008**, *47*, 3818-3820.

(5) Belger, C.; Neisius, N. M.; Plietker, B. *Chem. Eur. J*. **2010**, *16*, 12214-12220.

(6) Cheung, C. W.; Zhurkin, F. E.; Hu, X. *J. Am. Chem. Soc*. **2015**, *137*, 4932-4935.