Experimental Section

General Information. Tetrahydrofuran was purified according to the method of Grubbs.[1] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on Geduran Silica Gel 60 40-63 mesh according to the method of Still.[2] Thin-layer chromatography (TLC) was performed on Merck 0.20 mm silica gel 60-F_{254} plates. Visualisation of the developed chromatogram was performed by UV (254 nm) and fluorescence quenching using potassium permanganate or phosphomolybdic acid. Gas Liquid Chromatography (GLC) assays to optimize the reaction were developed using standard samples. ^{1}H, and ^{13}C NMR spectra were recorded on Brücker AC-300 (300 MHz and 75 MHz respectively) as noted, and are internally referenced to residual solvent signals ($CDCl_3$ or CD_2Cl_2). Data for ^{1}H and ^{13}C NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, hept = heptuplet, m = multiplet), coupling constant, integration and assignment. IR spectra were recorded on a Brucker Tensor (Attenuated Total Reflection) spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the Ecole Polytechnique Mass Spectral facility. Gas Liquid Chromatography (GLC) was performed on a Perichrom PR 2100 2317 Series gas chromatograph equipped with a split-mode, capillary injection system and flame ionisation detectors using a SGE apolar ID-BP1 (25 m x 0.32 mm) column.
Filtration of arylzinc containing solutions was carried on using Whatman PTFE syringe filter ReZist-30 0.45 µm.
$CoBr_2$(bipy) was prepared according to Labbé and Buriez.[3]
Anhydrous $CoBr_2$ was purchased from Alfa Aesar; Zinc dust was purchased from Sigma-Aldrich. Acetonitrile was purchased from Sigma-Aldrich and used without further purification. Allyl chloride, trifluoroacetic acid, 2,2'-bipyridyl, all aryl halides, and alkynes **2a**, **2b**, **2c**, **2g** and **2k** were purchased from the usual suppliers (Sigma-Aldrich, Alfa Aesar and Acros Organics) and used as received. Alkyne **2d** was synthesised as reported in the litterature[4].

Synthesis of starting materials:

General Procedure 1, Sonogashira coupling:

To a solution of $PdCl_2(PPh_3)_2$ (351 mg, 0.5 mmol, 5 mol%), CuI (190 mg, 0.1 mmol, 10 mol%) in NEt_3 (20 mL), were added ArBr (for **2h**, **2i** and **2j**) or ArI (for **2e** and **2f**) (10 mmol, 1 equiv), and the terminal alkyne (12 mmol, 1.2 equiv). The medium was stirred at 40 °C until total consumption of the starting aryl halide (GC on hydrolysed aliquots). The reaction mixture was cooled to rt, and saturated aqueous NH_4Cl (40 mL) was added. The mixture was extracted 3 times with Et_2O (40 mL). The combined organic phases were washed with H_2O (40 mL) and Brine (40 mL), dried over $MgSO_4$, and the solvents were evaporated to afford the crude material, which was purified by column chromatography (SiO_2, Petroleum Ether/ Ethyl Acetate).

Synthesis of Arylzinc, and carbozincation, general procedure:

General Procedure 2: arylzinc preparation and carbometallation:

Preparation of the arylzinc:

To a solution of $CoBr_2$(bipy) (1 mmol, 375 mg, 10 mol%) and Zn dust (20 mmol, 1.3 g, 2 equiv) in MeCN (8 mL) were added AllylCl (0.25 mL, 3mmol, 30 mol%) and TFA (0.1 mL), under vigorous stirring. This caused a rise in temperature and a change of the color of the mixture from blue to orange to dark grey. Once the orange tinge of the mixture had disappeared, ArBr (10 mmol, 1 equiv) was added. The reaction was followed by GC on iodolysed aliquots. Once all the starting bromide was consumed, stirring was interrupted; the reaction medium was taken in a 10 mL syringe, and filtered through a syringe filter. The starting flask was rinsed with MeCN (7 mL), which was filtered in the same manner, providing 15mL of a cobalt-containing arylzinc bromide solution. An internal standard was added (decane or dodecane), and the solution was titrated by GC on an iodolysed aliquot.

Carbozincation:

The solution of arylzinc bromide was cooled to 0°C, and the alkyne (0.33 equiv vs ArZnBr) was added. The reaction was then stirred at room temperature, and followed by GC on hydrolysed aliquots, until all of the alkyne was consumed. Aqueous hydrochloric acid (ca 2M, 20 mL) and Et_2O (20 mL) were then added to the reaction mixture and stirred for 5 min. The phases were separated, and the aqueous phase was extracted 3 times with Et_2O (20 mL). The combined organic phases were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, and the solvents were evaporated to afford the crude material, which was purified by column chromatography (SiO_2, Petroleum Ether/ Ethyl Acetate).

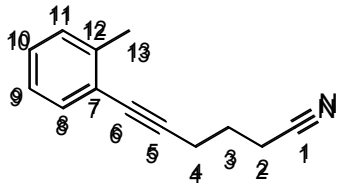
Post functionnalisation:

With I_2: Instead of quenching with HCl, I_2 (2.54 g, 10 mmol) was added to the medium, which was stirred for 15 min. Saturated aqueous $Na_2S_2O_3$ was added (30mL), and the mixture was extracted 4 times with Et_2O (20 mL). The combined organic phases were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, and the solvents were evaporated to afford the crude material, which was purified by column chromatography (SiO_2, Pentane).

Negishi cross-coupling: Instead of quenching with HCl, the reaction mixture was cooled to 0°C, and $Pd(dba)_2$ (71.9 mg, 0.125 mmol, 5 mol%), PPh_3 (75.6 mg, 0.25 mmol, 10 mol%), and PhI (1,1 mL, 10 mmol, 5 equiv) in THF (10mL) were added. The medium was stirred overnight, quenched with saturated aqueous NH_4Cl (20 mL), and extracted 3 times with Et_2O (20 mL). The combined organic phases were washed with H_2O (20 mL) and brine (20 mL), dried over $MgSO_4$, and the solvents were evaporated to afford the crude material, which was purified by column chromatography (SiO_2, Petroleum Ether/ Ethyl Acetate: 75/25 then 7/3).

Characterisation data

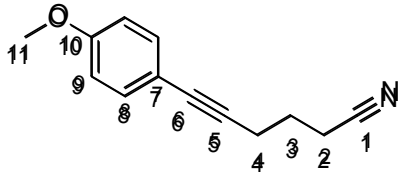
6-o-Tolyl-hex-5-ynenitrile (**2e**) (CAS: 1352643-10-7)



Pale yellow oil
Chemical Formula: $C_{13}H_{13}N$
Exact Mass: 183.1048
Molecular Weight: 183.2490

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.36 (d, *J*=7.4Hz, 1H, H_8), 7.2 (m, 2H, H_9&H_{10}), 7.12 (m, 1H, H_{11}), 2.64 (t, *J*=6.8Hz, 2H, H_2), 2.57 (t, *J*=7.2Hz, 2H, H_4), 2.41 (s, 3H, H_{13}), 2.64 (qt, *J*=7Hz, 2H, H_3)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 140.6 (C_q, C_{12}), 132.4 (CH, C_8), 129.9 (CH, C_{11}), 128.5 (CH, C_{10}), 126.1 (CH, C_9), 123.7 (C_q, C_7), 119.8 (C_q, C_1), 91.8 (C_q, C_5), 81.47 (C_q, C_6), 25.5 (CH_2, C_3), 21.0 (CH_3, C_{13}), 19.2 (CH_2, C_2), 16.8 (CH_2, C_4)
IR (neat, cm^{-1}): 3052, 2946, 2831, 2249, 2194, 1486, 1455
HRMS ($C_{13}H_{13}N$): calc: 183.1048, found 183.1048

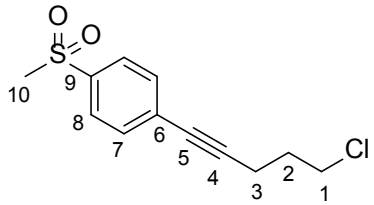
6-(4-Methoxy-phenyl)-hex-5-ynenitrile (**2f**) (CAS: 748770-70-9)



Yellow oil
Chemical Formula: $C_{13}H_{13}NO$
Exact Mass: 199.0997
Molecular Weight: 199.2484

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.33 (d, *J*=8.9Hz, 2H, H_9), 6.83 (d, *J*=8.9Hz, 2H, H_8), 3.30 (s, 3H, H_{11}), 2.56 (m, 4H, H_2 & H_4), 1.95 (qt, *J*=7Hz, 2H, H_3)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 159.6 (C_q, C_{10}), 133.1 (CH, C_8), 119.4 (C_q, C_1), 115.5 (C_q, C_7), 114.1 (CH, C_9), 85.5 (C_q, C_5), 82.4 (C_q, C_6), 55.4 (CH_3, C_{11}), 24.9 (CH_3, C_3), 18.7 (CH_2, C_2), 16.4 (CH_2, C_4)
IR (neat, cm^{-1}): 3056, 2940, 2838, 2248, 2245, 1607, 1509, 1289, 1245
HRMS ($C_{13}H_{13}NO$): calc: 199.0997, found 199.1003

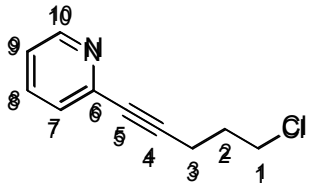
1-(5-Chloro-pent-1-ynyl)-4-methanesulfonyl-benzene (**2h**)



Yellow cristals, mp: 47-49°
Chemical Formula: $C_{12}H_{13}ClO_2S$
Exact Mass: 256.0325
Molecular Weight: 256.7484

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.84 (d, *J*= 8.5 Hz, 2H, H_8), 7.58 (d, *J*= 8.5 Hz, 2H, H_7), 3.72 (t, *J*= 6.4 Hz, 2H, H_1), 3.02 (s, 3H, H_{10}), 2.65 (t, *J*= 6.8 Hz, 2H, H_3), 2.08 (t, *J*= 6.6 Hz, 2H, H_2)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 140.1 (C_q, C_9), 132.9 (CH, C_7), 130.0 (C_q, C_6), 127.9 (CH, C_6), 93.4 (C_q, C_4), 80.5 (C_q, C_5), 44.9 (CH_3, C_{10}), 44.3 (CH_2, C_1), 31.8 (CH_2, C_2), 17.5 (CH_2, C_3)
IR (neat, cm^{-1}): 3018, 2926, 2854, 2232, 1593, 1576, 1307, 1160, 840
HRMS ($C_{12}H_{13}ClO_2S$): calc: 256.0325, found 256.0325

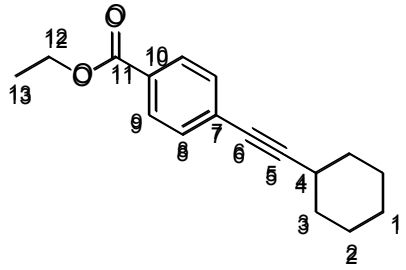
2-(5-Chloro-pent-1-ynyl)-pyridine (**2i**) (CAS: 872368-11-1)



Yellow oil
Chemical Formula: $C_{10}H_{10}ClN$
Exact Mass: 179.0502
Molecular Weight: 179.6461

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 8.53 (d, *J*=4.2Hz, 1H, H_{10}), 7.61 (td, *J*=7.7Hz, *J*=1.8Hz 1H, H_7), 7.36 (m, 1H, H_8), 7.19 (m, 1H, H_9), 3.7 (t, *J*=6.3Hz, 2H, H_1), 2.63 (t, *J*=6.9Hz, 2H, H_3), 2.08 (qt, *J*=6.6Hz, 2H, H_3)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 150.0 (CH, C_{10}), 143.7 (C_q, C_6), 136.2 (CH, C_8), 127.0 (CH, C_7), 122.6 (CH, C_9), 88.8 (C_q, C_5), 81.4 (C_q, C_4), 43.8 (CH_2, C_1), 31.3 (CH_2, C_2), 16.9 (CH_2, C_3)
IR (neat, cm^{-1}): 3051, 2960, 2230, 1582, 1561, 1464, 1427, 854
HRMS ($C_{10}H_{10}ClN$): calc: 179.0502, found 179.0502

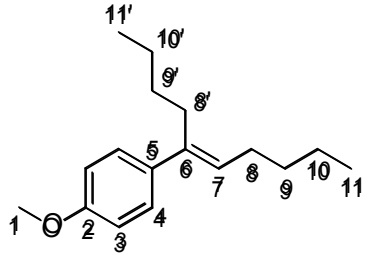
4-Cyclohexylethynyl-benzoic acid ethyl ester (**2j**)



Orange oil
Chemical Formula: $C_{17}H_{20}O_2$
Exact Mass: 256.1463
Molecular Weight: 256.3395

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.95 (d, *J*=8.6Hz, 2H, H_{10}), 7.44 (td, *J*=8.5Hz, 2H, H_7), 4.37 (q, *J*=7.1Hz, 2H, H_{12}), 2.60 (m, 1H, H_4), 1.89 (m, 2H, H_3), 1.76 (m, 2H, $H_{3'}$), 1.65-1.5 (m, 4H, H_2), 1.45-1.3 (2 signals coalesce, 5H, H_1 & H_{13})
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 166.4 (C_q, C_{11}), 131.6 (CH, C_8), 129.5 (CH, C_9), 129.3 (C_q, C_{10}), 129.1 (C_q, C_7), 98.0 (C_q, C_6), 80.3 (C_q, C_5), 61.2 (CH_2, C_{12}), 32.7 (CH_2, C_3), 29.9 (CH, C_4), 26.1 (CH_2, C_2), 25.0 (CH_2, C_1), 14.5 (CH_3, C_{13})
IR (neat, cm^{-1}): 2982, 2932, 2855, 2229, 1716, 1606, 1270
HRMS ($C_{17}H_{20}O_2$): calc: 256.1463, found 256.1470

(*E*)-1-(1-Butyl-hex-1-enyl)-4-methoxy-benzene (**3aa**)

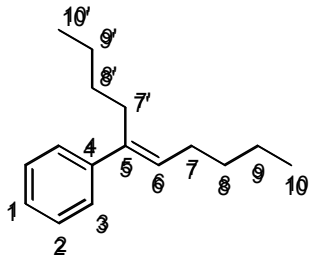


Pale yellow oil
Chemical Formula: $C_{17}H_{26}O$
Exact Mass: 246.1984
Molecular Weight: 246.3877

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.32 (d, *J*=8.6 Hz, 2H, H_4), 6.88 (d, *J*=8.7Hz, 2H, H_3), 5.62 (t, *J*=7.2Hz, 1H, H_7), 3.25 (s, 3H, H_1), 2.50 (t, *J*=7.1Hz, 2H, $H_{8'}$), 2.22 (m, 2H, H_8), 1.50-1.25 (m, 8H, H_9 & $H_{9'}$& H_{10}& $H_{10'}$), 0.98-0.82 (m, 6H, H_{11} & $H_{11'}$)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 159.0 (C_q, C_2), 140.0 (C_q, C_6), 136.6 (C_q, C_5), 128.2 (CH, C_7), 127.8 (CH, C_4), 114.0 (CH, C_3), 55.8 (CH_3, C_1), 32.9 (CH_2, C_9), 31.6 (CH_2, $C_{9'}$), 30.0 (CH_2, $C_{8'}$), 28.8 (CH_2, C_8), 23.3 (CH_2, $C_{10or10'}$), 23.1 (CH_2, $C_{10or10'}$), 14.4 (CH_3, $C_{11or11'}$), 14.3 (CH_3, $C_{11or11'}$)

IR (neat, cm^{-1}): 2959, 2930, 2860, 1607, 1510, 1465, 1244, 953
HRMS ($C_{17}H_{26}O$): calc: 246.1984, found 246.1980

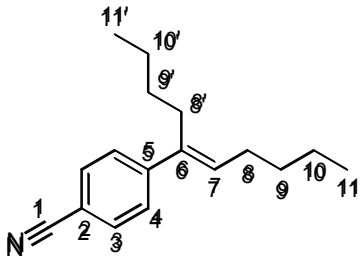
(*E*)-(1-Butyl-hex-1-enyl)-benzene (**3ba**) (CAS: 6619-22-5)



Colorless oil
Chemical Formula: $C_{16}H_{24}$
Exact Mass: 216.1878
Molecular Weight: 216.3618

^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.42-7.30 (m, 4H, H_2 & H_3), 7.30-7.22 (m, 1H, H_1), 5.69 (t, *J*=7.3Hz, 1H, H_6), 2.54 (m, 2H, H_7), 2.25 (q, 2H, $H_{7'}$), 1.53-1.33 (m, 8H, H_8 & $H_{8'}$& H_9& $H_{9'}$), 1.02-0.88 (m, 6H, H_{10} & $H_{10'}$)
^{13}C NMR (δ, $CDCl_3$, 75 MHz): 143.7 (C_q, C_5), 140.2 (C_q, C_4), 129.3 (CH, C_1), 128.2 (CH, C_3), 126.5 (CH, C_2 & C_5), 32.3 (CH_2, $C_{7'}$), 31.1 (CH_2, C_8), 29.6 (CH_2, $C_{8'}$), 28.4 (CH_2, C_7), 22.9 (CH_2, $C_{9or9'}$), 22.6 (CH_2, $C_{9or9'}$), 14.2 (CH_3, $C_{10or10'}$), 14.1 (CH_3, $C_{10or10'}$)
IR (neat, cm^{-1}): 3068, 2969, 2878, 1687, 1596, 1448
HRMS ($C_{16}H_{24}$): calc: 216.1878, found 216.1877

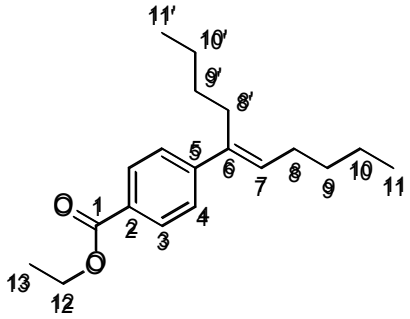
(*E*)-4-(1-Butyl-hex-1-enyl)-benzonitrile (**3ca**)



Orange oil
Chemical Formula: $C_{17}H_{26}N$
Exact Mass: 241.1830
Molecular Weight: 241.3712

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.58 (d, *J*=8.6 Hz, 2H, H_4), 7.44 (d, *J*=8.6Hz, 2H, H_3), 5.78 (t, *J*=7.3Hz, 1H, H_7), 2.50 (t, *J*=7.3Hz, 2H, $H_{8'}$), 2.22 (q, *J*=7.3Hz, 2H, H_8), 1.50-1.25 (m, 8H, H_9 & $H_{9'}$& H_{10}& $H_{10'}$), 0.98-0.82 (m, 6H, H_{11} & $H_{11'}$)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 148.7 (C_q, C_6), 139.5 (C_q, C_5), 132.9 (CH, C_7), 132.6 (CH, C_4), 127.4 (CH, C_3), 119.7 (C_q, C_1), 110.4 (C_q, C_2), 32.4 (CH_2, $C_{8'}$), 31.4 (CH_2, C_9), 29.5 (CH_2, $C_{9'}$), 29.0 (CH_2, C_8), 23.2 (CH_2, $C_{10'or10}$), 23.1 (CH_2, $C_{10'or10}$), 14.3 (CH_3, $C_{11'or11}$), 14.2 (CH_3, $C_{11'or11}$)
IR (neat, cm^{-1}): 2956, 2872, 2226, 1604, 1503, 1466, 832
HRMS ($C_{17}H_{26}N$): calc: : 241.1830, found 241.1837

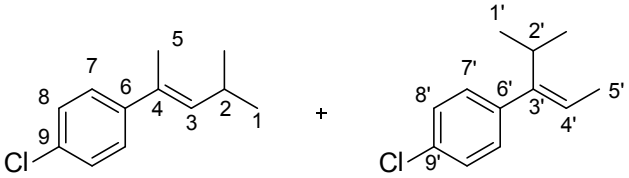
(*E*)-4-(1-Butyl-hex-1-enyl)-benzoic acid ethyl ester (**3da**)



Yellow oil
Chemical Formula: $C_{19}H_{28}O_2$
Exact Mass: 288.2089
Molecular Weight: 288.4244

^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.97 (d, *J*=8.5 Hz, 2H, H_3), 7.39 (d, *J*=8.5 Hz, 2H, H_4), 5.74 (t, *J*=7.3Hz, 1H, H_7), 4.37 (t, *J*=7.1Hz, 2H, H_{12}), 2.50 (t, *J*=7.2Hz, 2H, $H_{8'}$), 2.21 (q, *J*=7.2Hz, 2H, H_8), 1.50-1.25 (m, 11H, H_9 & $H_{9'}$& H_{10}& $H_{10'}$ & H_{13}), 0.98-0.82 (m, 6H, H_{11} & $H_{11'}$)
^{13}C NMR (δ, $CDCl_3$, 75 MHz): 166.6 (C_q, C_1), 148.1 (C_q, C_6), 139.5 (C_q, C_5), 131.0 (CH, C_7), 129.5 (CH, C_3), 128.4 (C_q, C_2), 126.1 (CH, C_4), 60.7 (CH_2, C_{12}), 31.9 (CH_2, $C_{9or9'}$), 30.9 (CH_2, $C_{9or9'}$), 29.2 (CH_2, $C_{8'}$), 28.4 (CH_2, C_8), 22.6 (CH_2, $C_{10'or10}$), 22.5 (CH_2, $C_{10'or10}$), 14.4 (CH_3, C_{13}), 14.0 (CH_3, $C_{11'or11}$), 13.9 (CH_3, $C_{11'or11}$)
IR (neat, cm^{-1}): 3055, 2988, 1710, 1606, 1422, 1264, 1111, 896
HRMS ($C_{19}H_{28}O_2$): calc: : 288.2089, found 288.2088

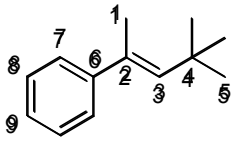
(*E*)1-Chloro-4-(1,3-dimethyl-but-1-enyl)-benzene / 1-Chloro-4-(1-isopropyl-propenyl)-benzene (**3fb + 3fb'**)



Colorless oil
Chemical Formula: $C_{12}H_{15}Cl$
Exact Mass: 194.0862
Molecular Weight: 194.7005

^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.32-7.21 (m, 8H, H_{Ar}), 7.10-7.06 (m, 2H, H_{Ar}), 5.59 (dq, *J*=9.1Hz, *J*=1.3Hz, 1.5H, H_3), 5.33 (q, *J*=6.8Hz, 1H, $H_{4'}$), 3.05 (hept, *J*=6.7Hz, 1H, $H_{2'}$), 2.68 (dhept, *J*=9.2Hz, *J*=6.8Hz, 1H, H_3), 2.01 (d, *J*=1.3Hz, 4.5H, H_5), 1.76 (d, *J*=6.9Hz, 3H, $H_{5'}$), 1.04 (d, *J*=6.9Hz, 9H, H_1), 1.02 (d, *J*=6.6Hz, 6H, $H_{1'}$)
^{13}C NMR (δ, $CDCl_3$, 75 MHz): 146.6 (C_q, C_{Ar}), 142.6 (C_q, C_{Ar}), 142.1 (C_q, C_{Ar}), 136.8 (CH, C_3), 132.2 (C_q, C_{Ar}), 132.1 (C_q, C_{Ar}), 131.5 (C_q, C_{Ar}), 130.1 (CH, C_{Ar}), 128.3 (CH, C_{Ar}), 127.8 (CH, C_{Ar}), 127.1 (CH, C_{Ar}), 123.4 (CH, $C_{4'}$), 28.9 (CH, $C_{2'}$), 28.1 (CH, C_2), 23.0 (CH_3, C_1), 21.7 (CH_3, $C_{1'}$), 15.8 (CH_3, C_5), 13.4 (CH_3, $C_{5'}$)
IR (neat, cm^{-1}): 2959, 2868, 1690, 1644, 1592, 1492, 1402, 1381, 1361, 1094, 1012, 819
HRMS ($C_{12}H_{15}Cl$): calc: 194.0862, found 194.0852

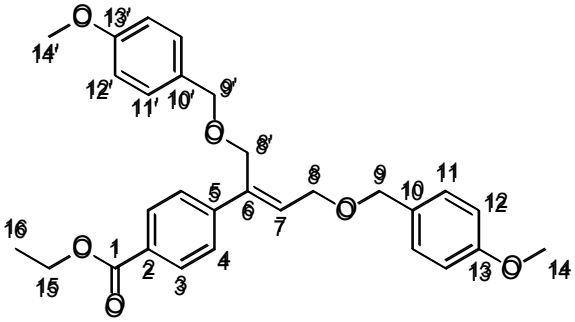
(*E*)-(1,3,3-Trimethyl-but-1-enyl)-benzene (**3bc**) (CAS: 32347-01-6)



Colorless oil
Chemical Formula: $C_{13}H_{18}$
Exact Mass: 174.1409
Molecular Weight: 174.2820

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.38-7.27 (m, 4H, H_7 & H_8), 7.24-7.17 (m, 1H, H_9), 5.75 (q, *J*=1.2Hz, 1H, H_3), 2.16 (d, *J*=1.3Hz, 3H, H_1), 1.24 (s, 9H, H_5)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 146.8 (C_q, C_2), 139.8 (CH, C_3), 135.0 (C_q, C_6), 128.6 (CH, C_8), 126.9 (CH, C_9), 126.5 (CH, C_7), 33.2 (C_q, C_4), 31.3 (CH_3, C_5), 17.6 (CH_3, C_1)
IR (neat, cm^{-1}): 3056, 2959, 2868, 1647, 1598, 1492, 1443, 896
HRMS ($C_{13}H_{18}$): calc: 174.1409, found 174.1404

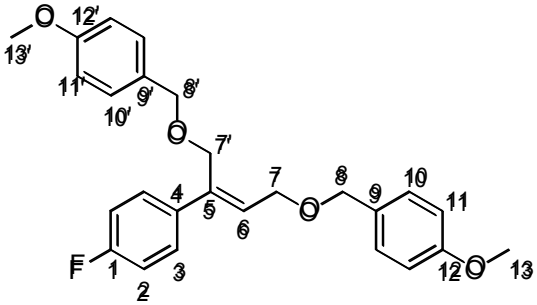
(*Z*)-1,4-Bis[(4-methoxyphenyl)methoxy]-2-(4-ethoxycarbonylphenyl)-but-2-ene (**3dd**)



Colorless oil
Chemical Formula: $C_{29}H_{32}O_6$
Exact Mass: 476.2199
Molecular Weight: 476.5608

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 8.01 (d, *J*=8.3Hz, 2H, H_3), 7.54 (d, *J*=8.3Hz, 2H, H_4), 7.30 (d, *J*=8.5Hz, 2H, $H_{11or11'}$), 7.21 (t, *J*=8.5Hz, 2H, $H_{11or11'}$), 6.89 (m, 4H, H_{12} & $H_{12'}$), 6.25 (t, *J*=6.3Hz, 1H, H_7), 4.49 (s, 2H, $H_{9'}$), 4.43-4.33 (m, 6H, H_{15} & H_9 &$H_{8'}$), 4.25 (d, *J*=6.3Hz, 2H, H_8), 3.80 (2 signals coalesce, 6H, $H_{14'}$ & H_{14}), 1.40 (t, *J*=7.12Hz, 3H, H_{16})
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 166.8 (C_q, C_1), 160.8 (2 signals coalesce, C_q, C_{13} & $C_{13'}$), 145.8 (C_q, C_5), 138.8 (C_q, C_6), 132.0 (CH, C_7), 131.0 (C_q, $C_{10or10'}$), 130.8 (C_q, $C_{10or10'}$), 130.0 (3 signals coalesce CH, C_3 & C_{11} & $C_{11'}$), 126.9 (CH, C_4) , 114.3 (2 signals coalesce, CH, C_{12} & $C_{12'}$), 72.8 (CH_2, $C_{9'}$), 72.4 (CH_2, C_9), 66.8 (2 signals coalesce CH_2, C_8 & $C_{8'}$), 61.44 (CH_2, C_{15}), 55.8 (CH_3, C_{14} & $C_{14'}$), 14.7 (CH_3, C_{16}). C_2 disappears under the signal around 130.0 ppm
IR (neat, cm^{-1}): 3055, 2926, 2854, 1713, 1610, 1513, 1464, 1274, 1247, 1103, 819
HRMS ($C_{29}H_{32}O_6$): calc: 476.2199, found 476.2195

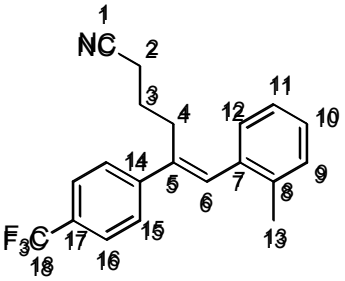
(*Z*)-1,4-Bis[(4-methoxyphenyl)methoxy]-2-(4-fluorophenyl)-but-2-ene (**3gd**)



Colorless oil
Chemical Formula: $C_{26}H_{27}FO_4$
Exact Mass: 422.1893
Molecular Weight: 422.4886

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.42 (m, 2H, H_3), 7.27 (d, *J*=8.4Hz, 2H, $H_{10or10'}$), 7.17 (d, *J*=8.4Hz, 2H, $H_{10or10'}$), 7.02 (t, *J*=8.8Hz, 2H, H_2), 6.86 (t, *J*=8.9Hz, 4H, H_{11} & $H_{11'}$), 6.06 (t, *J*=6.4Hz, 1H, H_6), 4.44 (s, 2H, $H_{8'}$), 4.38 (s, 2H, H_8), 4.32 (s, 2H, $H_{7'}$), 4.18 (d, *J*=6.4Hz, 2H, H_7), 3.79 (2 signals coalesce, 6H, $H_{13'}$ & H_{13})
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 162.8 (d, $J^1_{C\text{-}F}$= 245 Hz, C_q, C_1), 159.9 (C_q, $C_{12\ \&12'}$), 138.6 (C_q, C_5), 137.5 (d, $J^4_{C\text{-}F}$= 3.27 Hz, C_q, C_4), 131.1 (C_q, $C_{9or\ 9'}$), 130.9 (C_q, $C_{9or\ 9'}$), 130.0 (CH, $C_{10\ \&\ 10'}$), 129.9 (CH, C_6), 128.7 (d, $J^3_{C\text{-}F}$= 8 Hz, CH, C_3), 115.5 (d, $J^2_{C\text{-}F}$= 21.4 Hz, CH, C_2), 114.3 (CH, $C_{11or\ 11'}$), 114.2 (CH, $C_{11or\ 11'}$), 72.7 (CH_2, $C_{8\ or\ 8'}$), 72.3 (CH_2, $C_{8\ or\ 8'}$), 67.1 (CH_2, $C_{7\ or\ 7'}$), 66.8 (CH_2, $C_{7\ or\ 7'}$), 55.8 (CH_3, $C_{13\ \&\ 13'}$)
IR (neat, cm^{-1}): 3055, 2926, 2837, 1601, 1509, 1464, 1244, 1030, 816
HRMS ($C_{26}H_{27}FO_4$): calc: 422.1893, found 422.1876

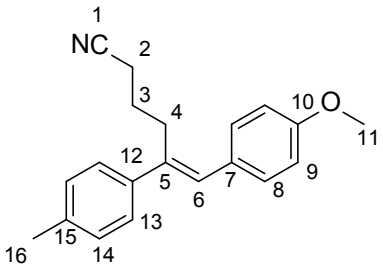
(*E*)-6-o-Tolyl-5-(4-trifluoromethyl-phenyl)-hex-5-enenitrile (**3he**)



Colorless oil
Chemical Formula: $C_{20}H_{18}F_3N$
Exact Mass: 329.1391
Molecular Weight: 329.3588

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.65 (m, 4H, H_{15} & H_{16}), 7.23 (m, 4H, H_9& H_{10} & H_{11} &H_{12}), 6.86 (s, 1H, H_6), 2.72 (m, 2H, H_4), 2.29 (s, 3H, H_{13}), 2.2 (t, *J*=7.2Hz, 2H, H_2), 1.65 (qt, *J*=7.3Hz, 2H, H_3)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 146.1 (C_q, C_{12}), 140.6 (C_q, C_{12}), 137.3 (C_q, C_8), 137.0 (C_q, C_{11}), 131.6 (CH, C_{10}), 130.6 (CH, C_9), 129.9 (q, $J^2_{C\text{-}F}$=32.3 Hz, C_q, C_{17}), 129.1 (CH, C_7), 128.1 (CH, C_{12}), 127.6 (CH, C_{12}), 126.3 (CH, C_{12}), 126.1 (q, $J^3_{C\text{-}F}$=3.8 Hz, CH, C_{16}), 125.0 (q, $J^1_{C\text{-}F}$=272 Hz, C_q, C_{18}) 119.8 (C_q, C_1), 29.5 (CH_2, C_3), 24.9 (CH_3, C_{13}), 20.3 (CH_3, C_2), 17.3 (CH_2, C_4)
IR (neat, cm^{-1}): 2945, 2881, 2248, 1616, 1524, 1482, 1409, 1114
HRMS ($C_{20}H_{18}F_3N$): calc: 329.1391, found 329.1376

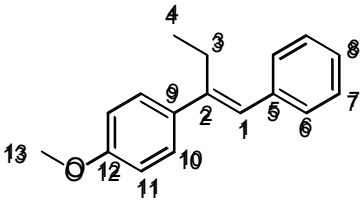
(*E*)-6-(4-Methoxy-phenyl)-5-p-tolyl-hex-5-enenitrile (**3if**)



Yellow oil
Chemical Formula: $C_{20}H_{21}NO$
Exact Mass: 291.1623
Molecular Weight: 291.3868

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.34 (d, *J*=8.1Hz, 2H, H_{13}), 7.25 (d, *J*=8.4Hz, 2H, H_8) , 7.19 (d, *J*=7.9 Hz, 2H, H_{14}) , 6.92 (d, *J*=8.8Hz, 2H, H_9), 6.71 (s, 1H, H_6), 3.82 (s, 3H, H_{11}), 2.86-2.80 (m, 2H, H_4), 2.36 (s, 3H, H_{16}), 2.27 (t, *J*=7.2Hz, 2H, H_2), 1.79-1.68 (m, 2H, H_3)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 159.1 (C_q, C_{10}), 139.9 (C_q, C_5), 137.8 (C_q, C_{15}), 130.9 (2 signals overlap, C_q, C_7 & C_{12}), 130.4 (CH, C_8), 129.8 (CH, C_{14}), 129.1 (CH, C_6), 126.9 (CH, C_{13}), 120.1 (C_q, C_1), 114.3 (CH, C_9), 55.8 (CH_3, C_{11}), 29.5 (CH_2, C_4), 25.1 (CH_2, C_3), 21.4 (CH_3, C_{16}), 17.4 (CH_2, C_2)
IR (neat, cm^{-1}): 3026, 2958, 2836, 2246,1606, 1510; 1463, 1247,1176, 813
HRMS ($C_{20}H_{21}NO$): calc: 291.1623, found 291.1622

(*E*)-2-(4-methoxy-phenyl)-1-phenyl-but-1-ene (**3ag**) (CAS: 101594-21-2)

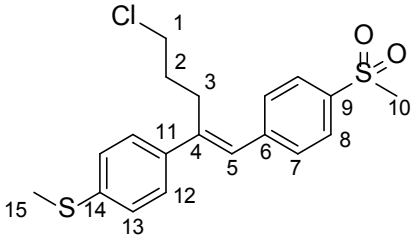


White solid, mp: 56-58°
Chemical Formula: $C_{17}H_{18}O$
Exact Mass: 238.1358
Molecular Weight: 238.3242

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.42 (d, *J*=8.7Hz, 2H, H_{11}), 7.31 (m, 5H, H_6& H_7 & H_8), 6.91 (d, *J*=8.7Hz, 2H, H_{10}), 6.65 (s, 1H, H_1), 3.82 (s, 3H, H_{13}), 2.72 (q, *J*=7.5Hz, 2H, H_3), 1.05 (t, *J*=7.5Hz, 3H, H_4)

^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 159.7 (C_q, C_{12}), 144.5 (C_q, C_2), 139.2 (C_q, C_5), 135.5 (C_q, C_9), 129.3 (CH, C_7), 128.8 (CH, C_6), 128.2 (CH, C_{11}), 126.9 (CH, C_8), 126.7 (CH, C_1), 114.3 (CH, C_{10}), 55.9 (CH_3, C_{13}), 23.7 (CH_2, C_3), 13.9 (CH_3, C_4)
IR (neat, cm^{-1}): 3054, 2983, 1606, 1511, 1265, 896
HRMS ($C_{17}H_{18}O$): calc: 238.1358, found 238.1357

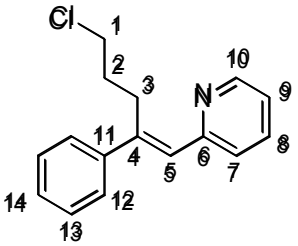
(*E*)-1-[5-Chloro-2-(4-Methylsulfanyl-phenyl)-pent-1-enyl]-4-methanesulfonyl-benzene (**3jh**)



White amorphous solid, mp: 101-103°
Chemical Formula: $C_{19}H_{21}ClO_2S_2$
Exact Mass: 380.0671
Molecular Weight: 380.9518

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.92 (d, *J*=8.4Hz, 2H, H_8), 7.53 (d, *J*=8.2Hz, *2*H, H_7), 7.43 (d, *J*=8.5Hz, 2H, H_{12}), 7.27 (d, *J*=8.5Hz, 2H, H_{13}), 6.80 (s, 1H, H_5), 3.51 (t, *J*=6.4Hz , 2H, H_1), 3.06 (s, 3H, H_{10}), 2.89-2.83 (m, 2H, H_3), 2.51 (s, 3H, H_{15}), 1.93-1.82 (m, 2H, H_1).
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 144.3 (C_q, C_4), 144.1 (C_q, C_9), 139.2 (C_q, $C_{14\,\&\,11}$, 2 signals overlap), 138.7 (C_q, C_6), 130.1 (CH, C_7), 127.9 (CH, C_8), 127.5 (CH, C_{12}), 127.4 (CH, C_5), 126.8 (CH, C_{13}), 45.4 (CH_2, C_1), 45.0 (CH_3, C_{10}), 32.0 (CH_2, C_2), 27.9 (CH_2, C_3), 15.9 (CH_3, C_{15}).
IR (neat, cm^{-1}): 3012, 2923, 2861, 1641, 1588, 1548, 1301, 1146, 965, 768
HRMS ($C_{19}H_{21}ClO_2S_2$): calc: 380.0671, found 380.0710

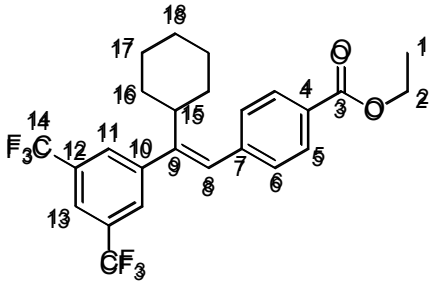
(*E*)-2-(5-Chloro-2-phenyl-pent-1-enyl)-pyridine (**3bi**)



Colorless oil
Chemical Formula: $C_{16}H_{16}ClN$
Exact Mass: 257.10
Molecular Weight: 257,76

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 8.64-8.61 (m, 1H, H_{10}), 7.67 (td, *J*=7.7Hz, *J*=1.9Hz, 1H, H_8), 7.56-7.50 (m, 2H, H_7& H_9), 7.43-7.26 (m, 4H, H_{12}& H_{13}), 7.13 (ddd, *J*=7.5 Hz, *J*=4.8 Hz, *J*=1.0Hz , 1H, H_{14}), 6.74 (s, 1H, H_5), 3.60 (t, *J*=6.9Hz , 2H, H_1), 3.34-3.25 (m, 2H, H_3), 1.97 (p, *J*=6.9Hz, 2H, H_1), 1.65 (qt, *J*=7.3Hz, 2H, H_3).
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 157.3 (C_q, C_6), 149.7 (CH, C_{10}), 146.4 (C_q, C_4), 143.5 (C_q, C_{11}), 136.6 (CH, C_8), 129.0 (CH, C_{13}), 128.3 (CH, C_{14}), 128.2 (CH, C_7), 127.2 (CH, C_{12}), 125.4 (CH, C_9), 121.7 (CH, C_5), 45.9 (CH_2, C_1), 32.5 (CH_2, C_3), 28.6 (CH_2, C_2).
Due to the instability of this product, no other analysis could be performed.

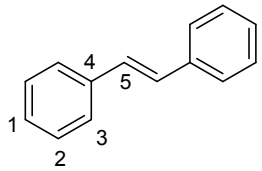
(*E*)-4-[2-(3,5-Bis-trifluoromethyl-phenyl)-2-cyclohexyl-vinyl]-benzoic acid ethyl ester (**3kj**)



Colorless oil
Chemical Formula: $C_{25}H_{24}F_6O_2$
Exact Mass: 470.1680
Molecular Weight: 470.4473

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 8.05 (d, *J*=8.3Hz, 2H, H_5), 7.87 (s, 1H, H_{13}), 7.74 (s, 2H, H_{11}), 7.40 (d, *J*=8.3Hz, 2H, H_6), 6.39 (s, 1H, H_8), 4.37 (q, *J*=7.1Hz, 2H, H_2), 2.93 (m, 1H, H_{15}), 1.81-1.58 (m, 5H), 1.40 (t, *J*=7.1Hz, 2H, H_1), 1.30-1.15 (m, 5H)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 166.7 (C_q, C_3), 149.0 (C_q, C_{10}), 145.3 (C_q, C_9), 142.0 (C_q, C_4), 131.4 (q, $J^2_{C\text{-}F}$= 33.1 Hz, C_q, C_{12}), 130.3 (CH, C_8), 130.1 (CH, C_5), 129.8 (C_q, C_7), 129.5 (br, CH, C_{11}), 129.3 (CH, C_6), 124.1 (q, $J^1_{C\text{-}F}$= 272.6 Hz, C_q, C_{14}), 121.4 (hept, $J^3_{C\text{-}F}$= 4.4 Hz, CH, C_{13}), 61.6 (CH_2, C_2), 41.0 (CH, C_{15}), 32.5 (CH_2, C_{16}), 26.7 (CH_2, C_{18}), 26.3 (CH_2, C_{17}), 14.7 (CH_3, C_1)
IR (neat, cm^{-1}): 2932, 2856, 1716, 1607, 1381, 1265, 1133, 1104, 900
HRMS ($C_{25}H_{24}F_6O_2$): calc: 470.1680, found 470.1683

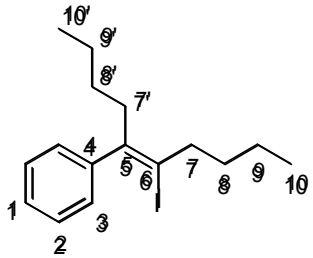
(*E*)-1,2-diphenylethene (**3bk**) (CAS: 103-30-0)



white solid, mp: 121-123°C
Chemical Formula: $C_{14}H_{12}$
Exact Mass: (Calc) 180.0939
Molecular Weight: 180.2451

^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.57-7.52 (m, 4H, H_1 & H_3), 7.42-7.33 (m, 4H, H_2), 7.28 (tt, *J*= 7.0 Hz, *J*= 1.3 Hz, 2H, H_1), 7.14 (s, 2H, H_5)
^{13}C NMR (δ, $CDCl_3$, 75 MHz): 137.5 (C_q, C_4), 128.9 (CH, C_5), 128.8 (CH, C_2), 127.8 (C_q, C_1), 126.7 (CH, C_3)
IR (neat, cm^{-1}): 3031, 2957, 1598, 1492, 1444, 857

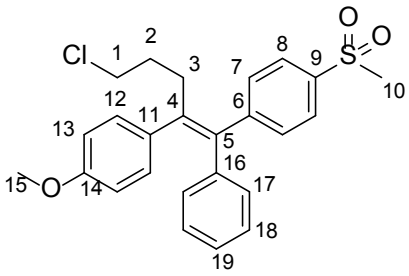
(*Z*)-(1-Butyl-2-iodo-hex-1-enyl)-benzene (**4**)



Colorless oil
Chemical Formula: $C_{16}H_{23}I$
Exact Mass: 342.0844
Molecular Weight: 342.2583

^{1}H NMR (δ, CD_2Cl_2, 300 MHz): 7.37-7.22 (m, 3H, H_1 & H_3), 7.09-7.03 (m, 2H, H_2), 2.68 (m, 2H, $H_{7or7'}$), 2.47 (m, 2H, $H_{7or7'}$), 1.65-1.55 (m, 2H, $H_{8or8'}$), 1.48-1.34 (m, 2H, $H_{8or8'}$), 1.30-1.23 (m, 4H, H_9 & $H_{9'}$), 0.98 (t, *J*= 7.3 Hz, 3H, $H_{10or10'}$), 0.88-0.81 (m, 3H, $H_{10or10'}$)
^{13}C NMR (δ, CD_2Cl_2, 75 MHz): 148.3 (C_q,C_5), 147.9 (C_q,C_4), 128.9 (CH,C_{2or3}), 128.6 (CH,C_{2or3}), 127.4 (CH,C_1), 106.8 (C_q,C_6), 41.6 (CH_2,$C_{7or7'}$), 35.0 (CH_2,$C_{7or7'}$), 32.6 (CH_2,$C_{8or8'}$), 30.1 (CH_2,$C_{8or8'}$), 23.0 (CH_2,$C_{9or9'}$), 22.4 (CH_2,$C_{9or9'}$), 14.4 (CH_3,$C_{10or10'}$), 14.2 (CH_3,$C_{10or10'}$)
HRMS ($C_{16}H_{23}I$): calc: 342.0844, found 342.0828

(*E*)-1-[5-Chloro-2-(4-Methoxy-phenyl)-1-Phenyl-pent-1-enyl]-4-methanesulfonyl-benzene (**5**):



White solid, mp: 148-150°
Chemical Formula: $C_{25}H_{25}ClO_3S$
Exact Mass: 440.1213
Molecular Weight: 440.9822

^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.92 (d, *J*= 8.4 Hz, 2H, H_8), 7.46 (d, *J*= 8.4 Hz, 2H, H_7), 7.09-7.04 (m, 5H, H_{12}, H_{17} & H_{19}), 6.92 (dd, *J*= 7.5 Hz, *J*= 2.6 Hz, 2H, H_{18}), 6.74 (d, *J*= 8.8 Hz, 2H, H_{13}), 3.74 (s, 3H, H_{15}), 3.43 (t, *J*= 6.6 Hz, 2H, H_1), 3.07 (s, 3H, H_{10}), 2.58-2.52 (m, 2H, H_3), 1.86-1.75 (m, 2H, H_2)
^{13}C NMR (δ, $CDCl_3$, 75 MHz): 159.1 (C_q, C_{14}), 149.6 (C_q, C_9), 142.7 (C_q, C_{16}), 141.1 (C_q, C_4), 139.5 (C_q, C_6), 138.7 (C_q, C_{11}), 133.6 (C_q, C_5), 131.2 (CH, C_{18}), 131.1 (CH, C_{17}), 130.9 (CH, C_7), 128.3 (CH, C_{12}), 128.0 (CH, C_8), 126.8 (CH, C_{19}), 114.0 (CH, C_{13}), 55.6 (CH_3, C_{15}), 45.5 (CH_2, C_1), 45.0 (CH_3, C_{10}), 33.7 (CH_2, C_3), 32.4 (CH_2, C_2)
IR (neat, cm^{-1}): 3018, 2926, 2854, 1508, 1313, 1244, 1147, 953, 840
HRMS ($C_{25}H_{25}ClO_3S$): calc: 440.1213, found 440.1229

[1] A.B. Pangborn; M.A. Giardello; R.H. Grubbs; R.K. Tosen; F.J. Timmers *Organometallics, 1996*, **15**, 1518.
[2] W.C. Still; M. Kahn; A. Mitra J. *J. Org. Chem. 1978*, **43**, 2923.
[3] L. Polleux; E. Labbé; O. Buriez; J. Périchon *Chem. Eur. J., 2005*, **11**, 4678.
[4] K.C. Nicolaou; E.W. Yue; S. la Greca; J.E. Leresche; T. Tsuri; Y. Naniwa; F. de Riccardis *Chem. Eur. J. , 1995*, **1**, 467-494.