Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

From 1,2-difunctionalisation to cyanide-transfer cascades – Pd-catalysed cyanosulfenylation of internal (oligo)alkynes

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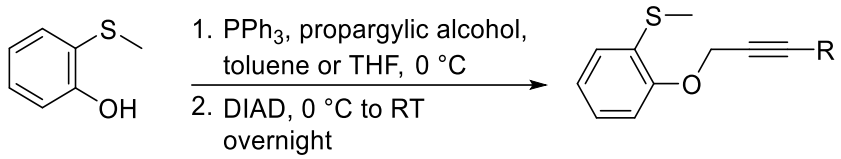
1) General Experimental

All solvents were dried and stored over molecular sieves under argon atmosphere unless otherwise stated. Air- and moisture-sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated.

Proton (^{1}H), carbon (^{13}C) and fluorine (^{19}F) NMR spectra were recorded on a Bruker AV300, Bruker AVIII400, Bruker AVIIIHD500 or Bruker AVII600 instrument using the residual signals from $CHCl_3$, δ = 7.26 ppm and δ = 77.16 ppm, as internal reference for ^{1}H and ^{13}C chemical shifts, respectively. Additionally, tetramethylsilane (TMS; δ = 0.00 ppm; 0.03%) was added to NMR samples. The following abbreviations were used for ^{1}H and ^{13}C NMR chemical shifts: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet/quintet, m = multiplet and combinations therof. GC-HRMS mass spectrometry was carried out on an Agilent 6890 gas chromatograph coupled to a JMS-T100GC (GCAccuTOF, JEOL, Japan) time of flight mass spectrometer in electron ionization (EI) mode. ESI-HRMS mass spectrometry was carried out on an FTICR instrument. EI-HRSM mass spectrometry was carried out on JOEL AccuTOF GC JMS-T100GC instrument. IR spectra were recorded on an ATR spectrometer Tensor 27 from Bruker. Melting Points were recorded with a Büchi SMP-20 and Büchi M-560 melting point meter and are uncorrected. Semi-preparative HPLC were conducted using an Agilent 1260 Infinity system with an Agilent Pursuit XRs 5 C18 column (250 x 10 mm) or an Agilent Polaris 5 C8-A column (250 x 10 mm) with CH_3CN/H_2O (isocratic or gradient) as eluent mixture.

2) General Procedures

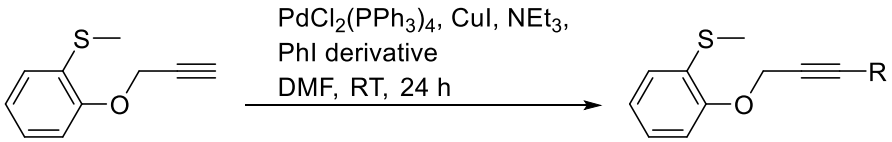
General Procedure (GP 1) for the preparation of propargylic ethers 11



A solution of **SM1** (1.00 equiv., 0.14 - 0.36 M), PPh_3 (1.10 - 1.50 equiv.) and the corresponding propargylic alcohol (1.00 - 1.50 equiv.) in dry toluene or THF was cooled to 0 °C. DIAD (1.10 – 1.50 equiv., 0.27 - 0.59 M) in dry toluene or THF was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography gave the desired products.

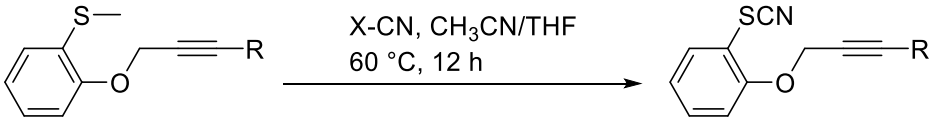
Carried out in accordance to a reported procedure.[1]

General Procedure (GP 2) for the preparation of propargylic ethers 11[2]



To a mixture of **SM2**, $PdCl_2(PPh_3)_2$ (0.03 equiv.), CuI (0.06 equiv.) in triethylamine (and DMF) was added the corresponding iodobenzene derivative. After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether, washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography.

General Procedure (GP 3) for the preparation of thiocyanatobenzenes 1

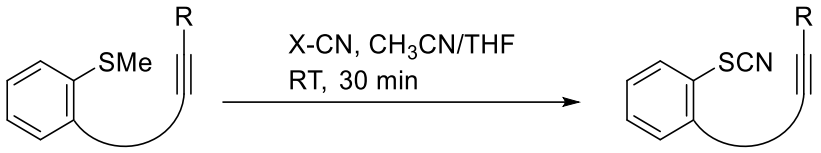


[1] H. Murase, K. Senda, M. Senoo, T. Hata and H. Urabe, *Chem. Eur. J.*, 2014, **20**, 317.

[2] a) M. Ahmad, A.-C. Gaumont, M. Durandetti and J. Maddaluno, *Angew. Chem. Int. Ed.*, 2017, **56**, 2464,S. A. Worlikar, T. Kesharwani, T. Yao and R. C. Larock, *J. Org. Chem.*, 2007, **72**, 1347.

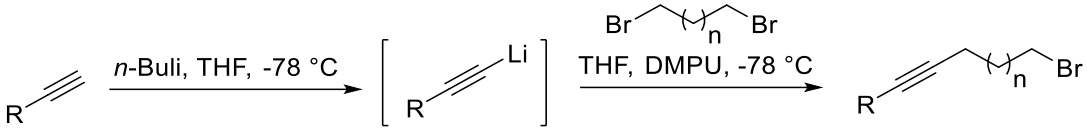
Following a modified reported procedure[3] 3,5-bis(trifluoromethyl)phenyl(cyano)iodoniumtriflate[4] (X-CN, 2.00 equiv.) was weighed into a sealable tube and a solution of the thioether (1.00 equiv.) in a mixture of CH_3CN/THF (1:1) was added and the tube was capped. The (often) resulting brown solution was heated to 60 °C and stirred for 12 h. After cooling, the solvent was removed and the product was obtained after silica gel column chromatography.

General Procedure (GP 3, alternative B) for the preparation of aromatic thiocyanates



To a stirred solution of the thioether (1.00 equiv.) in a mixture of CH_3CN/THF (1:1, 0.35 mM) was smoothly added 3,5-bis(trifluoromethyl)phenyl(cyano)iodoniumtriflate (X-CN, 1.00 equiv.). After 10 min the reaction progress was controlled by TLC and the reaction was stopped after 30 min. The solvent was removed and the product was obtained after silica gel column chromatography.

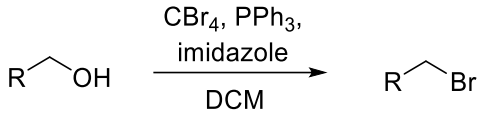
General Procedure (GP 4) for the preparation of alkyne substituted alkyl bromides 13.1 from alkyl dibromides[5]



To a stirred solution of the alkyne (1.0 equiv.) in THF (0.2 M) was added *n*-butyllithium (2.5 M solution in THF, 1.1 equiv) slowly at −78 °C. The clear solution was allowed to warm to ambient temperature over 0.5 hours. First DMPU (1.2 equiv.) and then the alkyl dibromide were added at −78 °C. The reaction mixture was again allowed to warm to ambient temperature over 2 h. Remaining organolithium compounds were quenched by the addition of water. The resulting mixture was extracted with diethyl ether. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography.

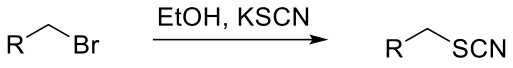
[3] D. Zhu, D. Chang and L. Shi, *Chem. Commun.*, 2015, **51**, 7180.
[4] R. Frei, T. Courant, M. D. Wodrich and J. Waser, *Chem. Eur. J.*, 2015, **21**, 2662.
[5] Y. Wang, C. Chen, S. Zhang, Z. Lou, X. Su, L. Wen and M. Li, *Org. Lett.*, 2013, **15**, 4794.

General Procedure (GP 5) for the preparation of alkyne substituted alkyl bromides 13.1 from alkyl alcohols



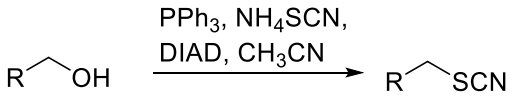
The alcohol (1.0 equiv.), imidazole (2.0 equiv.) and PPh_3 (2.0 equiv.) were dissolved in Et_2O/CH_3CN (4:1, 0.8 M). CBr_4 (1.9 equiv.) was slowly added to the stirred solution at ambient temperature. After a few seconds a colorless precipitate was formed. The mixture was stirred for 1 h, diluted with an excess of pentane and filtrated. The filter cake was washed with additional pentane. The filtrate was concentrated in vacuo and the crude product was purified by flash column chromatography (pentane).

General Procedure (GP 6) for the preparation of aliphatic thiocyanates 3 (via S_N)[5]



A solution of the bromide (1.0 equiv.) and KSCN (1.5 equiv.) in EtOH (1 M) in a capped tube as stirred for 12 h at 85 °C. The reaction mixture was cooled to ambient temperature, diluted with water and extracted with DCM. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvents in vacuo the crude product was purified by flash column chromatography (pentane/ EtOAc = 10:1).

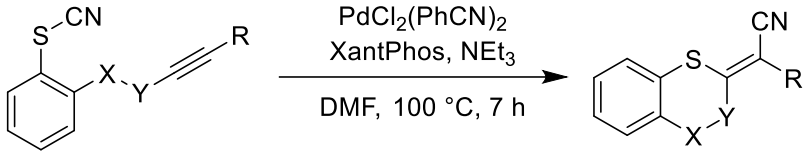
General Procedure (GP 7) for the preparation of aliphatic thiocyanates 3 (via MITSUNOBU)[6]



The alcohol (1.0 equiv.), PPh_3 (2.0 equiv.) and NH_4SCN (2.0 equiv.) were dissolved in CH_3CN (6 mL). DIAD (2.0 equiv.) was added slowly to the solution and the reaction mixture was stirred overnight at RT. After the solvent was evaporated *in vacuo*, the crude product was purified by flash column chromatography to afford the pure title product.

[6] N. Iranpoor, H. Firouzabadi, B. Akhlaghinia and R. Azadi, *Synthesis*, 2003, **2004**, 92.

General Procedure (GP CAT1) for the transformation of thiocyanates

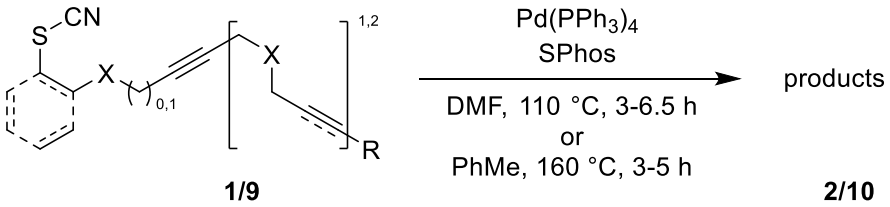


1 **2**

A solution of the substrate in DMF (5 ml per 100 µmol) was degassed with argon for 20 min. Afterwards, triethylamine (5.0 equiv.), bis(benzonitrile)palladium dichloride (10 mol%) and XantPhos (20 mol%) were added and the reaction mixture was degassed for another 10 min while pre-stirring for 30 min at RT in a sealable flask. Subsequently, the reaction was heated for at least 7 h (or until full consumption of starting material; control by TLC) at 100 °C.

DMF was co-evaporated (4-5 times) with toluene until dryness. The residue was then purified by flash column chromatography.

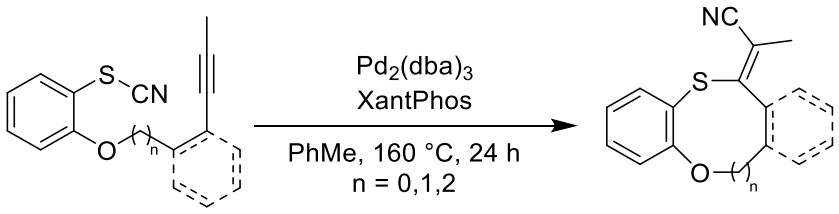
General Procedure (GP CAT2) for the transformation of thiocyanates



1/9 **2/10**

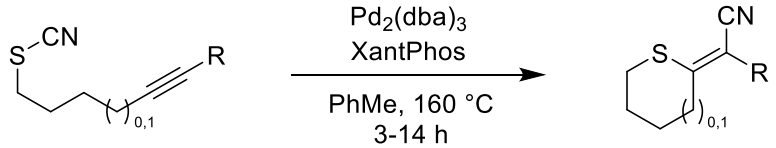
In a flask or tube three fifth of the solvent needed for the catalysis (5 ml for 100 µmol of substrate) were added to $Pd(PPh_3)_4$ (5 mol%) and SPhos (20 mol%). This mixture was prestirred for 30-45 min and then transferred to a tube with stirring bar containing the substrate in the remaining two fifth of solvent. The tube was sealed and the reaction mixture was stirred at 110 °C for the respective time. After cooling, the solvent was removed under reduced pressure (co-evaporation in with PhMe in case of DMF). The residue was then purified by flash column chromatography.

General Procedure (GP CAT2, alternative B) for the transformation of thiocyanates



In a flask or tube three fifth of the solvent needed for the catalysis (5 ml for 100 µmol of substrate) were added to $Pd_2(dba)_3$ (10 mol%) and XantPhos (20 mol%). This mixture was prestirred for 30-45 min and then transferred to a tube with stirring bar containing the substrate in the remaining two fifth of solvent. The tube was sealed and the reaction mixture was stirred at 160 °C for the respective time. After cooling, the solvent was removed under reduced pressure. The residue was then purified by flash column chromatography.

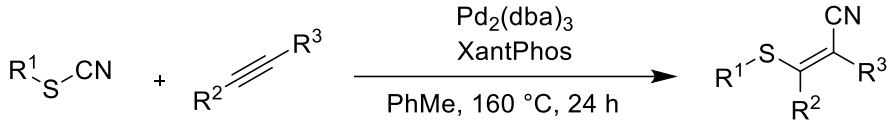
General Procedure (GP CAT3) for the transformation of thiocyanates



3 **4**

The substrate (1.0 equiv.) was weighed in a microwave vial and dissolved in thoroughly degassed toluene (5 mL) Then, $Pd_2(dba)_3$ (10 mol%) and XantPhos (20 mol%). were added. The microwave vial was capped and the solution was stirred at 160 °C for 3-14 hours. The solvent was evaporated in vacuo and the product was purified by flash column chromatography.

General Procedure (GP CAT4) for the intermolecular cyanosulfenylation

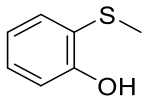


7a **7b** **8**

$Pd_2(dba)_3$ (10 mol%) and XantPhos (20 mol%). were added to a sealable flask and dissolved in thoroughly degassed PhMe. After 30 min of pre-stirring at RT the substrates **7a** (1.0 equiv.) and **7b** (2.0 equiv.) were added successively. The microwave vial was capped and the solution was stirred at 160 °C for 24 hours. The solvent was evaporated *in vacuo* and the product was purified by flash column chromatography.

3) Preparation of Starting Materials

2-(Methylthio)phenol (SM1)

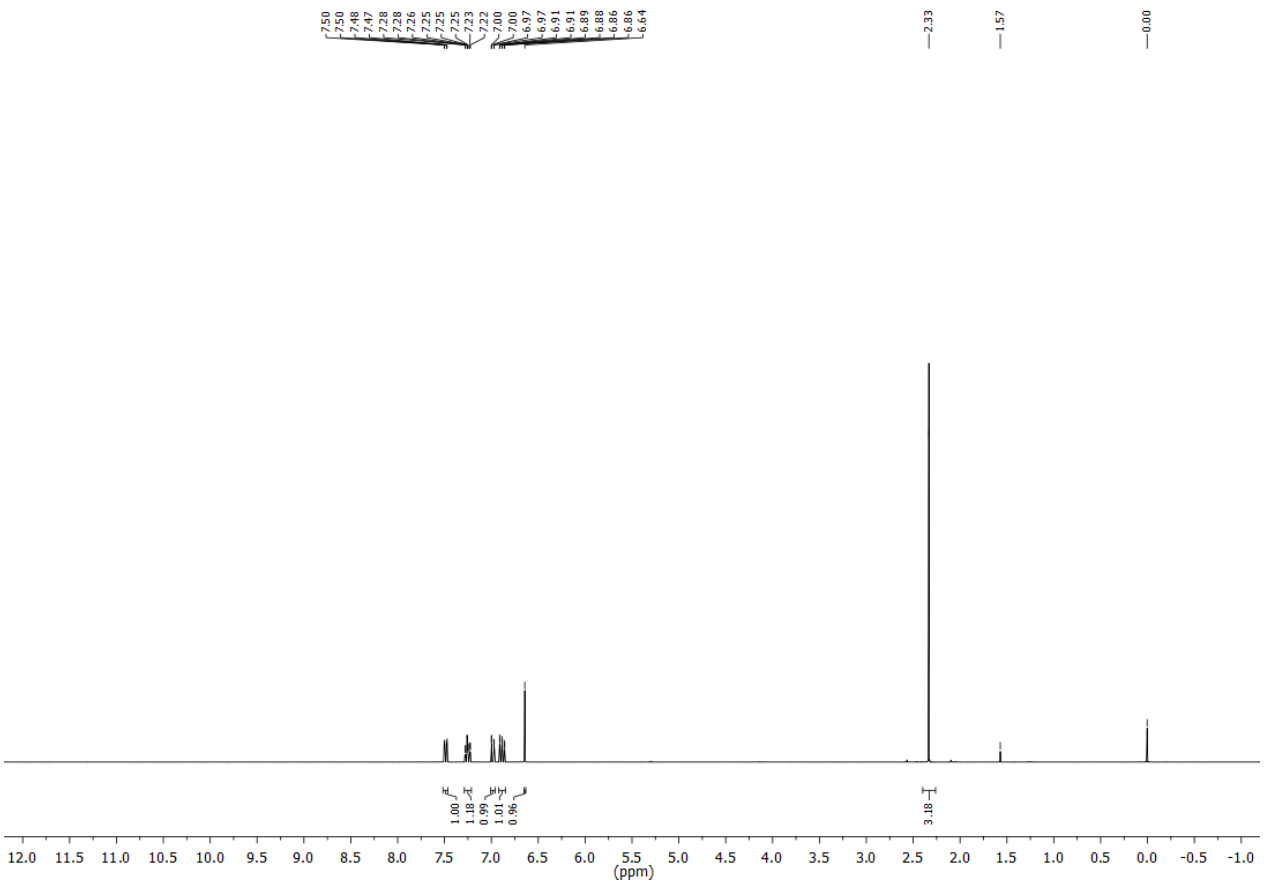


Following a reported procedure[7] phenol (9.40 g, 100.00 mmol, 1.00 equiv.) was dissolved in dry toluene (150 mL). To the stirred solution $AlCl_3$ (16.00 g, 120.00 mmol, 1.20 equiv.) and dimethyl disulfide (28.30 g, 27.1 ml, 300.00 mmol, 3.00 equiv.) were added. The solution was then heated to 105 °C for 12 h. Afterwards, it was cooled to 40 °C and hydrolyzed with hydrochloric acid (10%, 100 ml). The mixture was extracted with DCM (5 x 160 ml) and the combined organic layers were washed with water, brine, dried over Na_2SO_4 and concentrated under reduced pressure. Silica gel column chromatography (*n*-pentane:EtOAc = 20:1) gave the desired product **SM1** (10.9 g, 77.7 mmol, 77%) as pale yellow oil.

R_f = 0.61 (*n*-pentane:EtOAc = 20:1).

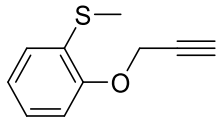
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.33 (s, 3H), 6.64 (s, 1H), 6.88 (td, *J* = 7.5, 1.4 Hz, 1H), 6.99 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.25 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H).

[7] EP 0318394 A2, 1989.



^{1}H-NMR (300 MHz, $CDCl_3$).

1-(Methylthio)-2-(2-propyn-1-yloxy)benzene (SM2)



To a solution of **SM1** (750.0 mg, 5.35 mmol, 1.00 equiv.) in acetone (5 ml) was added K_2CO_3 (2.22 g, 16.06 mmol, 3.00 equiv.) followed by dropwise addition of propargyl bromide (760.0 mg, 0.49 ml, 6.38 mmol, 1.20 equiv.). The mixture was stirred overnight, filtered and the solvent was removed under reduced pressure. Silica gel column chromatography (*n*-pentane:EtOAc = 100:1 → 60:1) gave the desired product **SM2** (336 mg, 1.15 mmol, 60%) as a colorless oil which crystallized slowly to a colorless solid. Carried out in accordance to a reported procedure.[8]

m.p.: 36 °C.

R_f = 0.17 (*n*-pentane:EtOAc = 50:1).

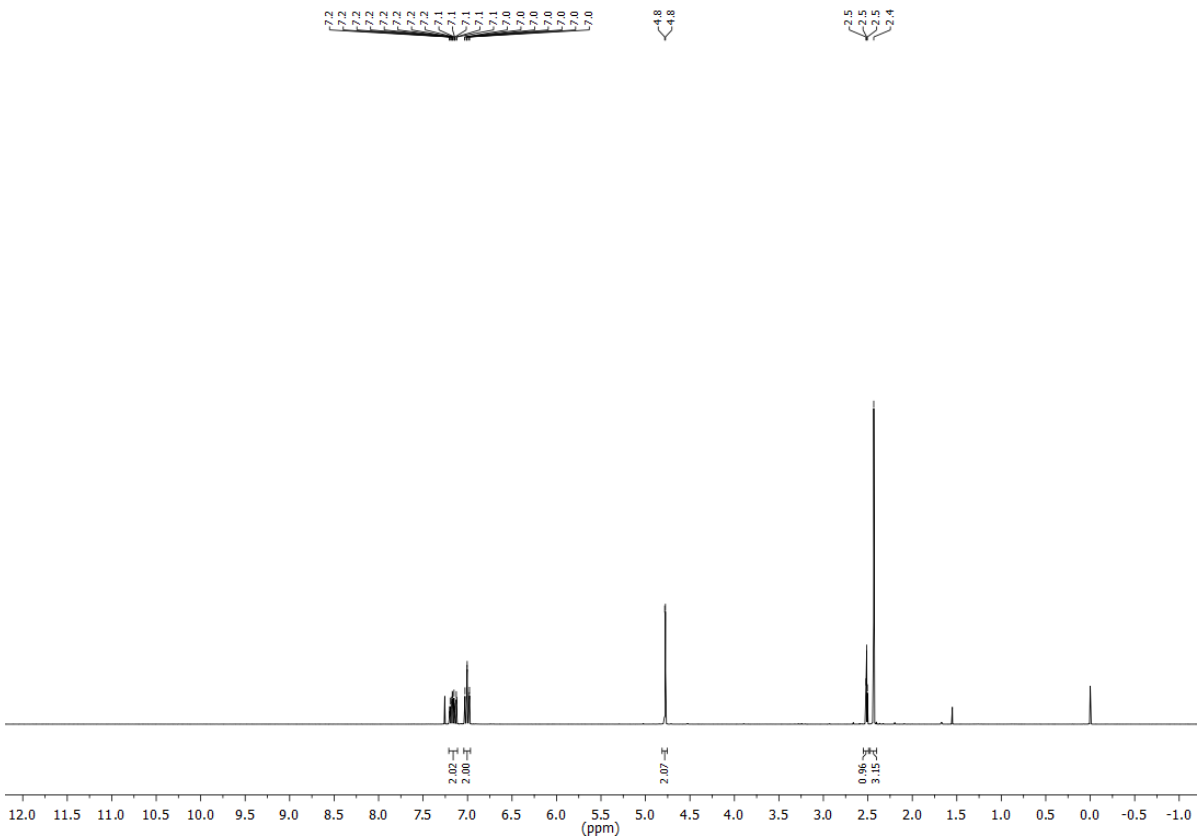
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.21 – 7.12 (m, 2H), 7.04 – 6.97 (m, 2H), 4.78 (d, *J* = 2.3 Hz, 2H), 2.51 (t, *J* = 2.4 Hz, 1H), 2.43 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.8, 56.4, 75.7, 78.4, 112.3, 122.2, 125.7, 126.5, 127.8, 154.3.

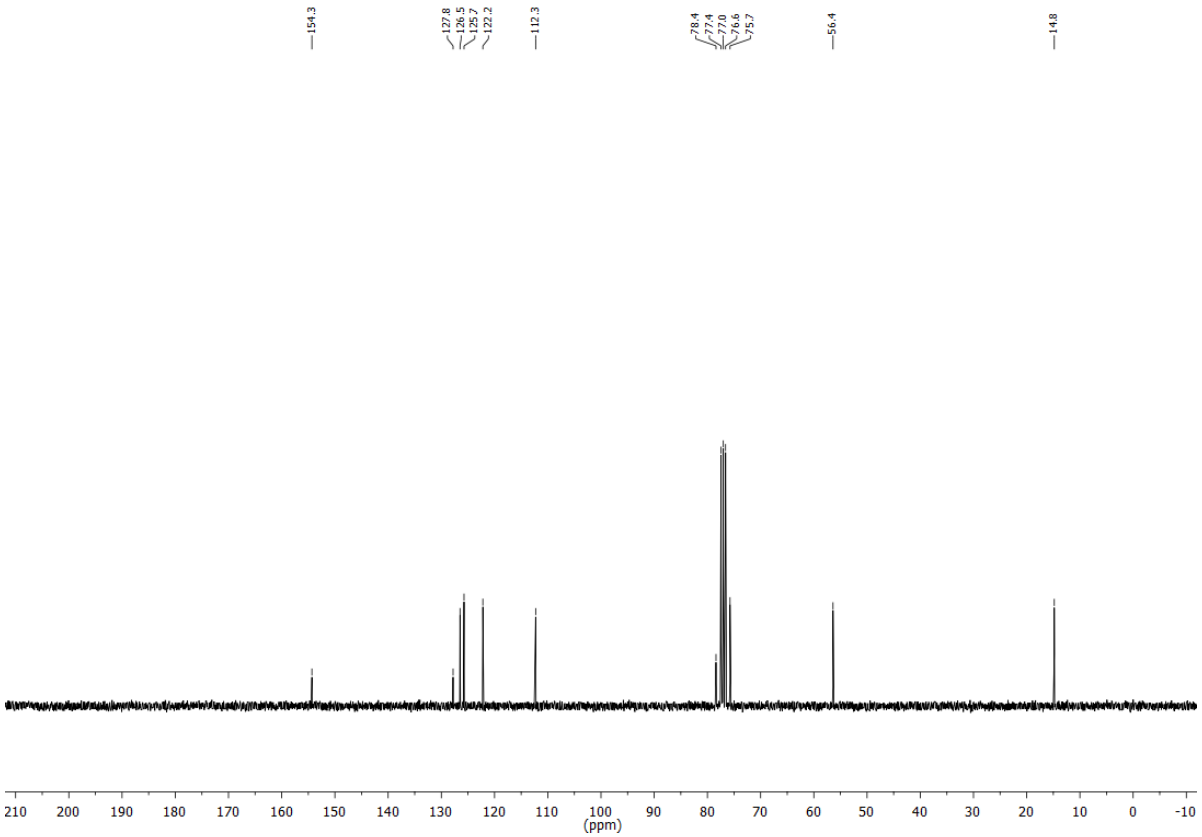
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3284, 2920, 2121, 1576, 1472, 1441, 1214, 1137, 1071.

$C_{10}H_{10}OS$ calcd. for $[M+H]^+$.: 179.0525, found: 179.0526 (ESI-HRMS).

[8] M. van Scherpenzeel, E. E. Moret, L. Ballell, R. M. J. Liskamp, U. J. Nilsson, H. Leffler and R. J. Pieters, *ChemBioChem*, 2009, **10**, 1724.

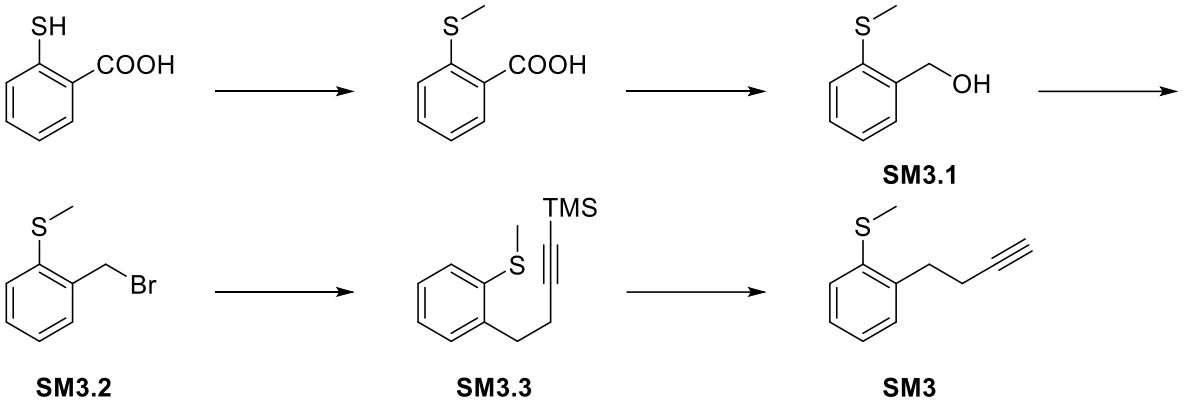


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(but-3-yn-1-yl)benzene (SM3)



2-(Methylthio)benzyl bromide was synthesized according literature-known procedures starting from thiosalicylic acid.[9,10]

Subsequently, compound **SM3.3** was prepared from bromide **SM3.2** (2.17 g, 10.00 mmol, 1.00 equiv.) and 1-(trimethylsilyl)propyne (1.34 g, 1.78 ml, 12.00 mmol, 1.20 equiv.) in accordance to a reported procedure.[11] The crude product **SM3.1** was then directly subjected to a described desilylation protocol[11] to obtain **SM3** (1.28 g, 7.28 mmol, 73% over two steps) as colorless oil.

R_f = 0.59 (*n*-pentane:EtOAc = 50:1).

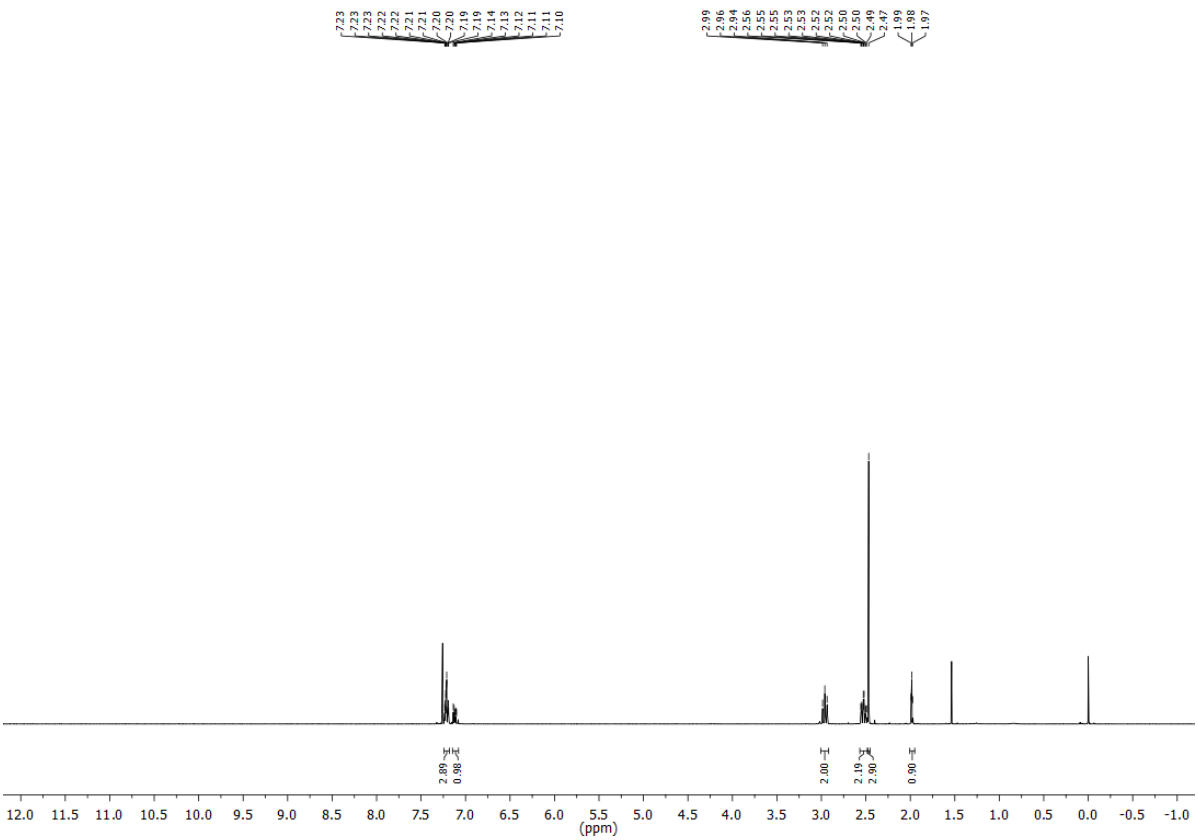
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.98 (t, *J* = 2.6 Hz, 1H), 2.47 (s, 3H), 2.48 – 2.56 (m, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 7.10 – 7.14 (m, 1H), 7.18 – 7.24 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 15.9, 18.8, 32.8, 68.9, 83.8, 125.0, 125.8, 127.3, 129.4, 137.2, 138.2.

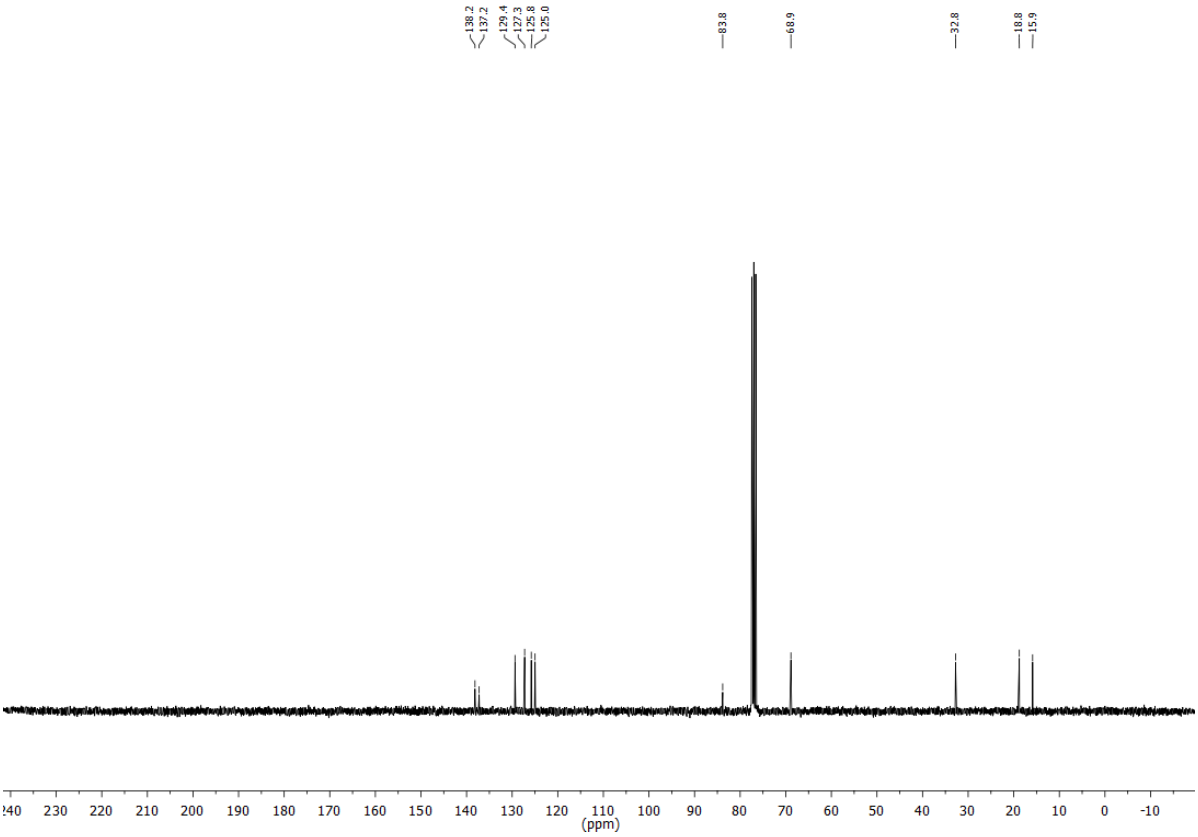
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2920, 2863, 2116, 1588, 1467, 1435, 1067, 1043.

$C_{11}H_{12}S$ calcd.: 176.0660, found: 176.0664 (GC-HRMS).

[9] H. V. Huynh, C. H. Yeo and Y. X. Chew, *Organometallics*, 2010, **29**, 1479.
[10] D. J. Smith, G. P. A. Yap, J. A. Kelley and J. P. Schneider, *J. Org. Chem.*, 2011, **76**, 1513.
[11] D.-Q. Chen, C.-H. Guo, H.-R. Zhang, D.-P. Jin, X.-S. Li, P. Gao, X.-X. Wu, X.-Y. Liu and Y.-M. Liang, *Green Chem.*, 2016, **18**, 4176.



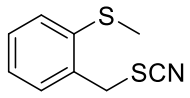
^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

Further Starting Materials

1-(Methylthio)-2-(thiocyanatomethyl)benzene (5.1b)



Procedure similar to GP7.

The alcohol **SM3.1** (926 mg, 6.0 mmol, 1.0 equiv., in 2 ml of CH_3CN for transfer), PPh_3 (3.15 g, 12.0 mmol, 2.0 equiv.) and NH_4SCN (914 mg, 12.0 mmol, 2.0 equiv.) were dissolved in CH_3CN (12 mL). DEAD (2.09 g, 1.88 ml, 12.0 mmol, 2.0 equiv.) was added slowly to the solution and the reaction mixture was stirred for 9 h. After the solvent was evaporated *in vacuo*, the crude product was purified by flash column chromatography (*n*-pentane:EtOAc = 50:1→20:1) to afford the pure title product as a colorless oil (537 mg, 2.75 mmol, 46%).

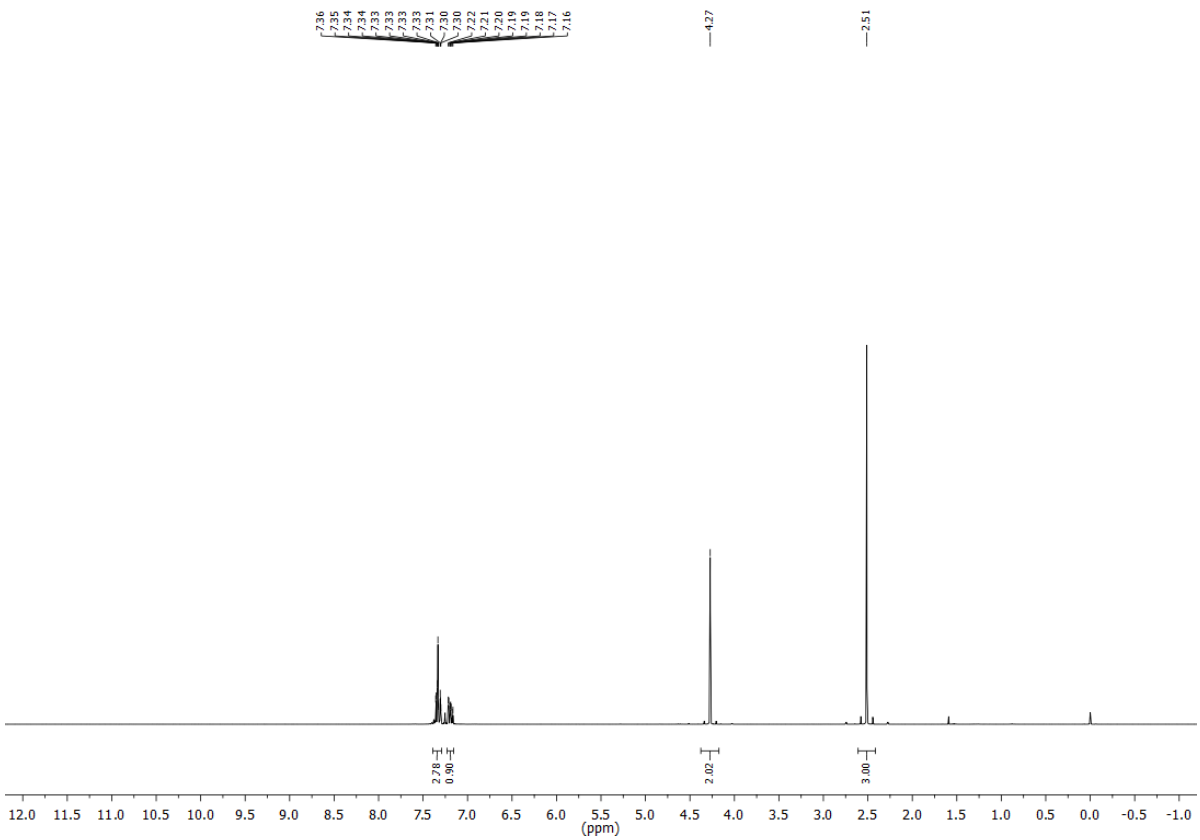
R_f = 0.31 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.51 (s, 3H), 4.27 (s, 2H), 7.19 (ddd, *J* = 7.8, 6.1, 2.5 Hz, 1H), 7.29 – 7.39 (m, 3H).

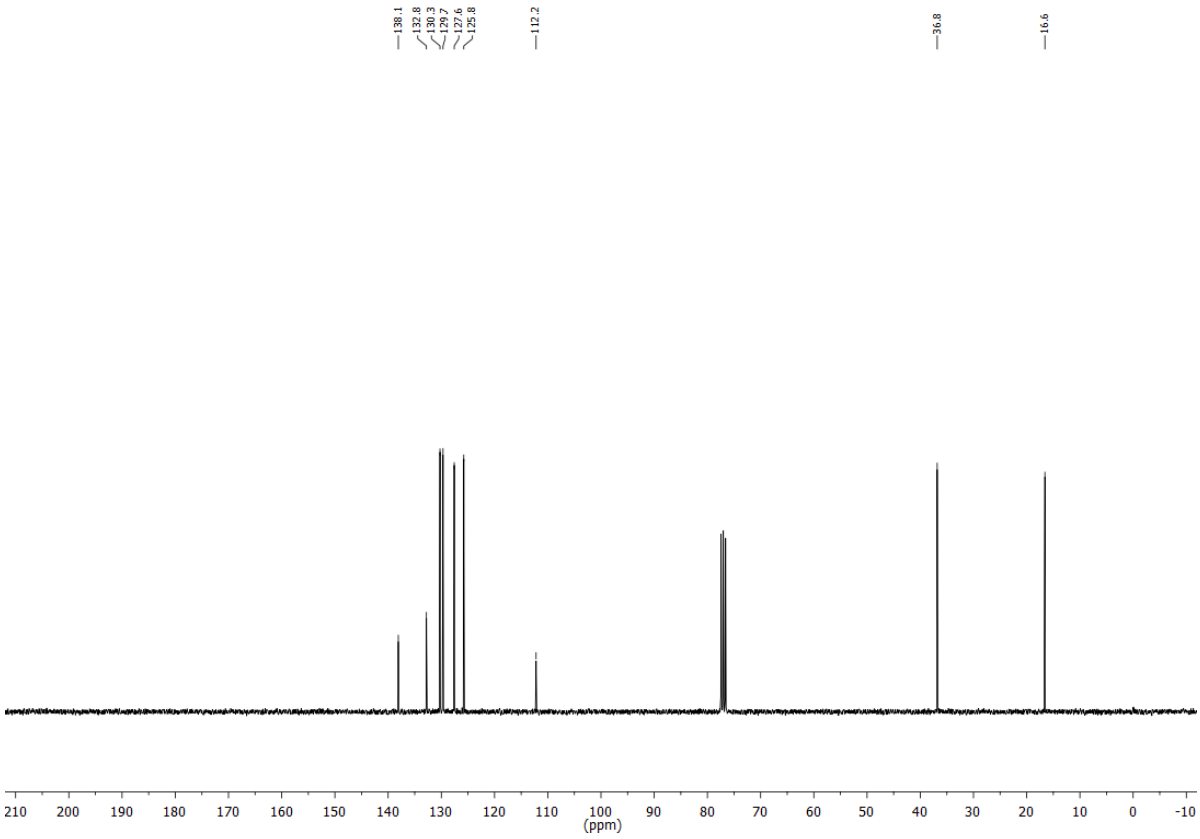
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.6, 36.8, 112.2, 125.8, 127.6, 129.7, 130.3, 132.8, 138.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3059, 2990, 2921, 2834, 2149, 1584, 1467, 1432, 1239, 1055, 1041, 963.

$C_9H_9NS_2$ calcd.: 195.0176, found: 195.0180 (GC-HRMS).

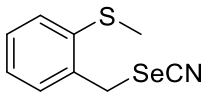


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(selenocyanatomethyl)benzene (5.1d)



According to a reported procedure[12], the bromide **SM3.2** (2.17 g, 10.0 mmol, 1.0 equiv.) was dissolved in DMF (80 mL). KSeCN (1.44 g, 10.0 mmol, 1.0 equiv.) was added to the solution and the reaction mixture was stirred for 2 h. Then, Et_2O (20 ml) and water (20 ml) were added and the mixture was stirred for a short time. After transfer to a separation funnel, the organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 50 ml). The combined organic phases were washed with water and brine and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (*n*-pentane:EtOAc = 50:1→10:1) to afford the pure title product as a colorless solid (2,01 g, 8.30 mmol, 83%).

m.p.: 85 °C.

R_f = 0.28 (*n*-pentane:EtOAc = 20:1).

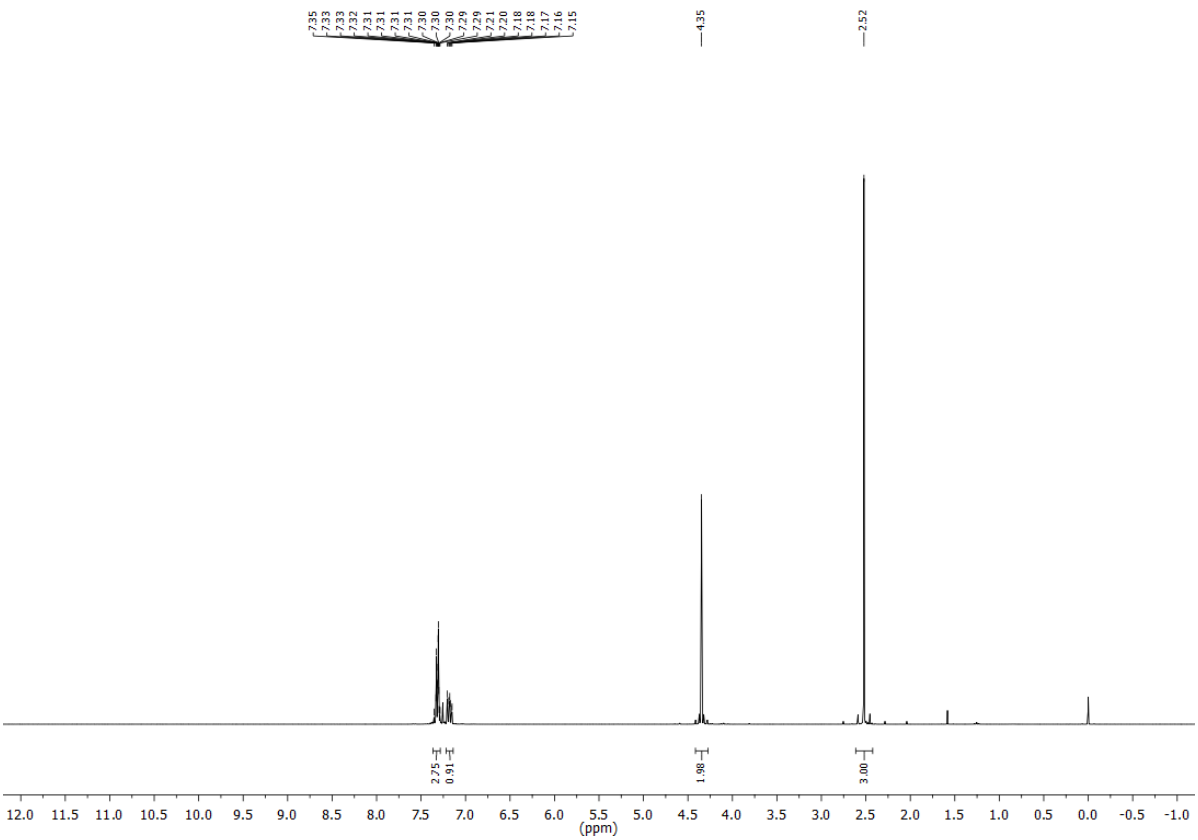
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.52 (s, 3H), 4.35 (s, 2H), 7.12 – 7.22 (m, 1H), 7.28 – 7.37 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.5, 31.7, 102.6, 125.8, 127.4, 129.4, 129.8, 134.4, 137.7.

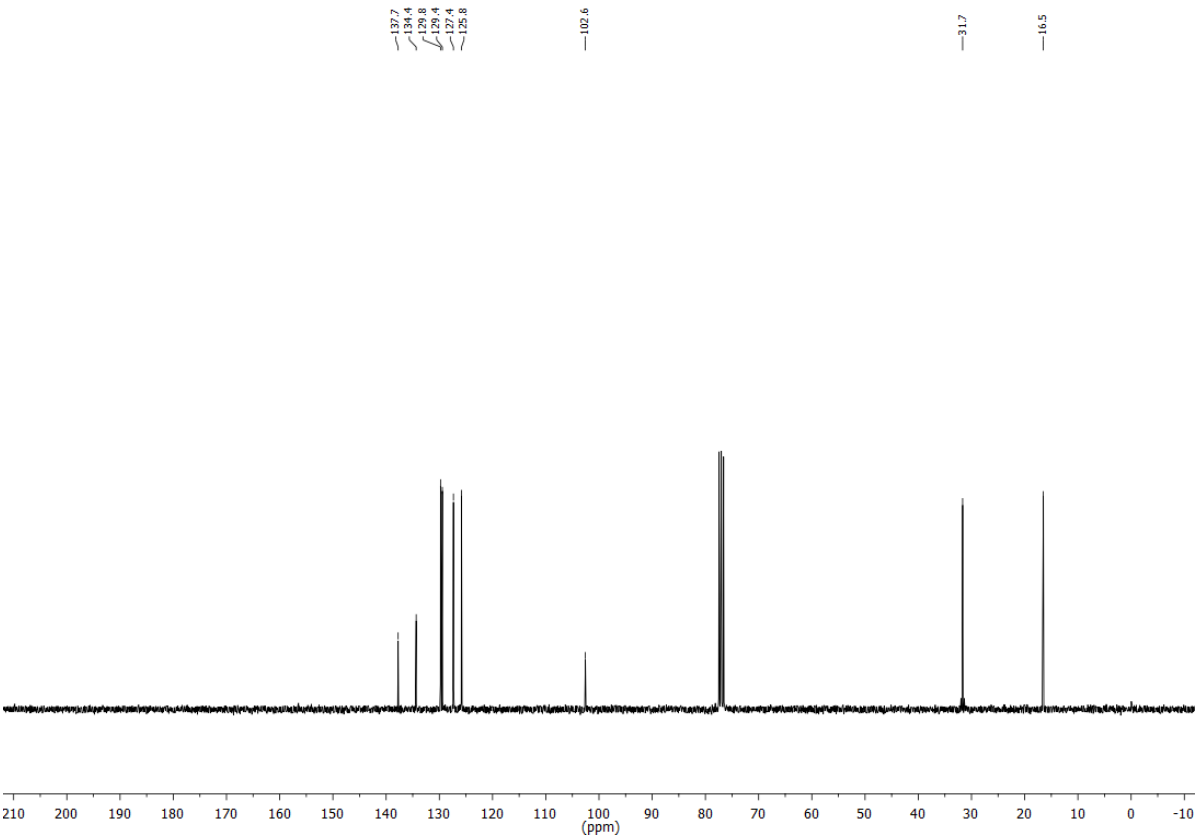
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3057, 2967, 2916, 2852, 2150, 1577, 1466, 1426, 1201, 1036.

C_9H_9NSSe calcd.: 242.9621, found: 242.9626 (GC-HRMS).

[12] A. A. Heredia and A. B. Peñéñory, *RSC Adv.*, 2015, **5**, 105699.

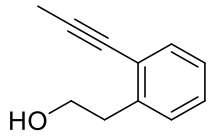


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

2-(2-(Prop-1-yn-1-yl)phenyl)ethan-1-ol (5.1e)



Similar to the synthesis of **11s**, 2-(2-iodophenyl)ethan-1-ol (5.20 g, 21.0 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (295 mg, 2 mol%) and CuI (160 mg, 4 mol%) were dissolved in triethylamine (60 ml). Afterwards, propyne (22.0 ml, 22.0 mmol, 1.0 M in THF, 1.05 equiv.) was added via syringe. After stirring overnight, saturated NH_4Cl solution was added and the mixture was extracted with Et_2O (3 x 100 ml). The combined organic phases were washed with brine, dried over Na_2SO_4, filtrated and evaporated. Silica gel column chromatography (*n*-pentane:EtOAc = 10:1 → 4:1) gave the desired product **5.1e** (3.28 g, 20.5 mmol, 98%) as a brown oil.

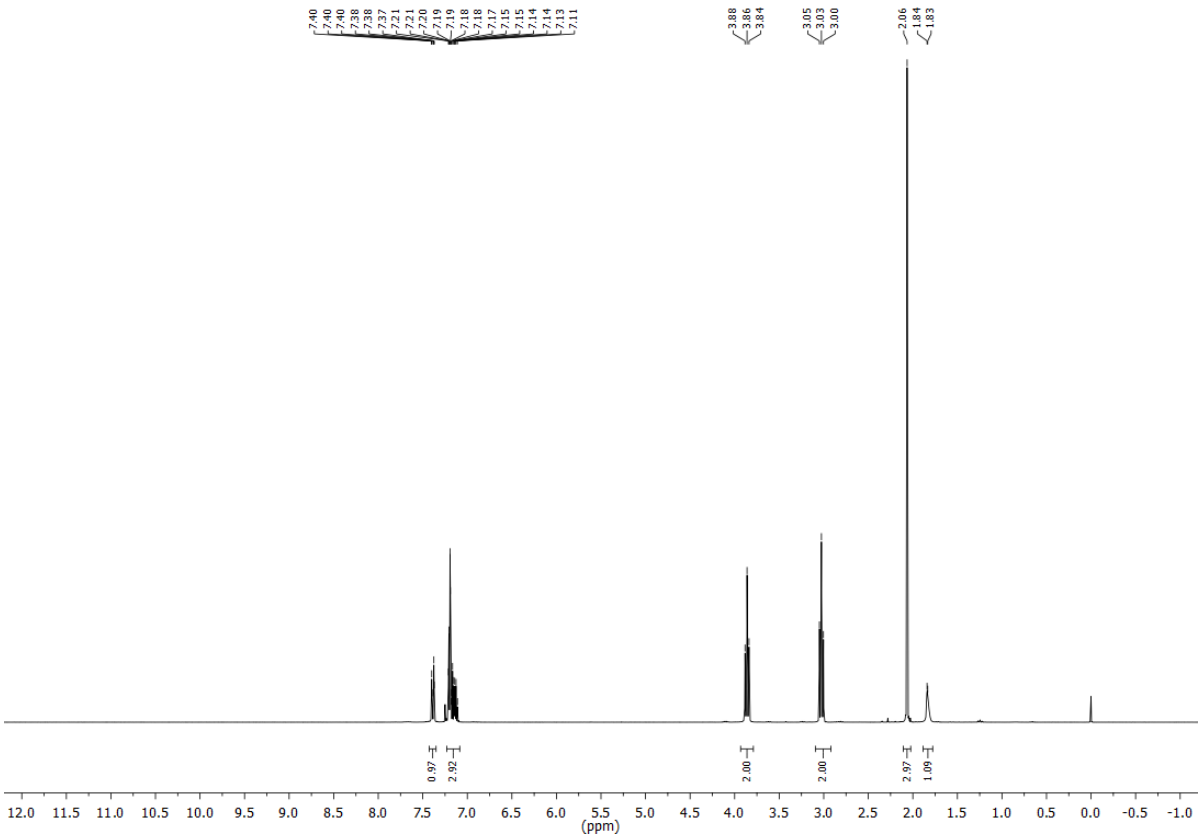
R_f = 0.31 (*n*-pentane:EtOAc = 4:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.84 (s, 1H), 2.06 (s, 3H), 3.03 (t, *J*=6.8, 2H), 3.86 (t, *J*=6.7, 2H), 7.10 – 7.23 (m, 3H), 7.39 (dt, *J*=7.2, 1.2, 1H).

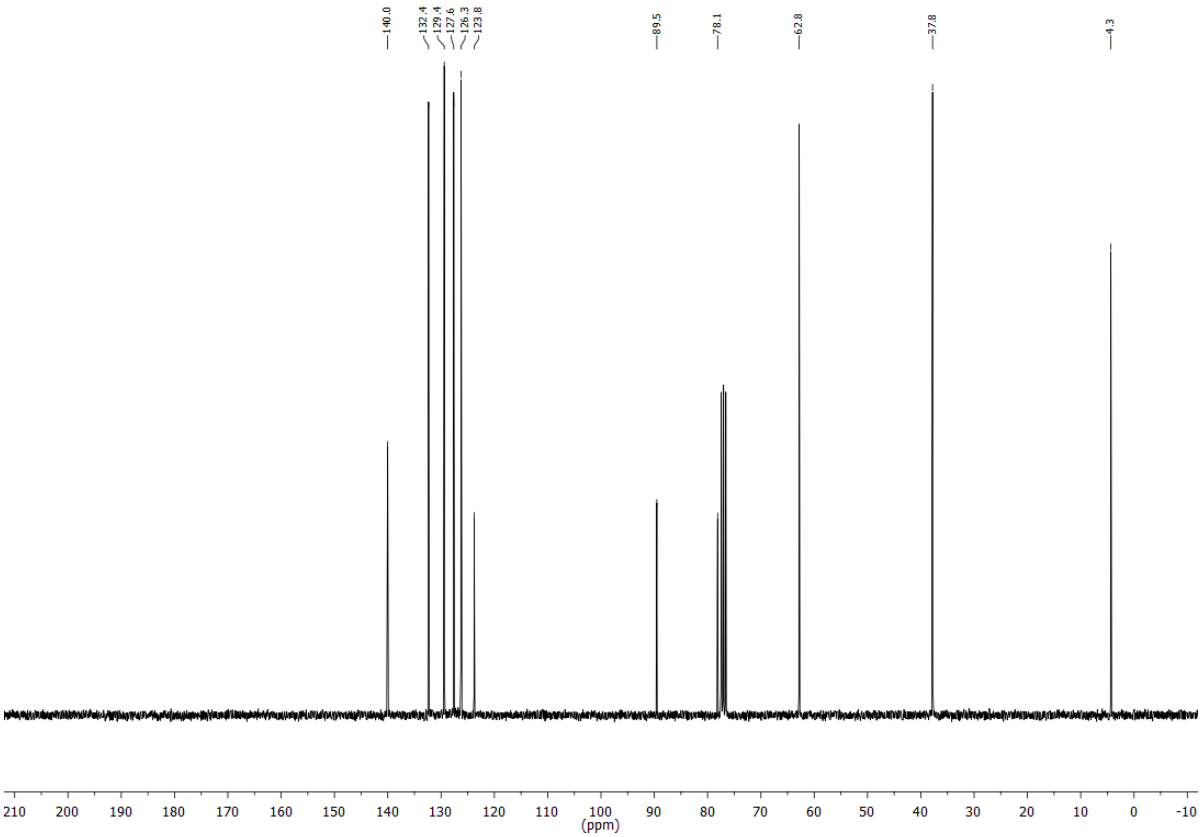
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.3, 37.8, 62.8, 78.1, 89.5, 123.8, 126.3, 127.6, 129.4, 132.4, 140.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3328, 3063, 3023, 2949, 2921, 2876, 1482, 1441, 1040.

$C_{11}H_{12}O$ calcd.: 160.0888, found: 160.0880 (GC-HRMS).

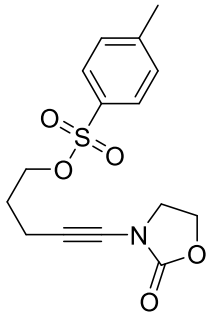


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

5-(2-Oxooxazolidin-3-yl)pent-4-yn-1-yl 4-methylbenzenesulfonate (15g)



Following a reported procedure[13] $CuCl_2$ (135 mg, 1.00 mmol, 0.2 equiv.), 2-oxazolidinone (2.18 g, 25.00 mmol, 5.0 equiv.) and Na_2CO_3 (1.06 g, 10.00 mmol, 2.0 equiv.) were weighed in a three-necked round bottom flask. The reaction vessel was purged with oxygen gas (balloon) for 15 min. Afterwards, a solution of pyridine (0.81 ml, 10.00 mmol, 2.0 equiv.) in dry toluene (25 ml) was added via a syringe. The oxidative atmosphere was maintained by connection of a balloon filled with oxygen gas via syringe with needle. The mixture was heated to 70 °C, followed by the dropwise addition (over 4 h) of pent-4-yn-1-yl 4-methylbenzenesulfonate[14] (1.19 g, 5.00 mmol, 1.0 equiv.) in dry toluene (25 ml). Upon completion, the reaction mixture was allowed to stir for another 4 h at 70 °C. The mixture was cooled to RT, filtrated (flask rinsed with toluene) and the filtrate evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 4:1→2:1→1:2) to obtain the product (467 mg, 1.44 mmol, 29%) as colorless oil.

R_f = 0.09 (*n*-pentane:EtOAc = 2:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.81 – 1.92 (m, 2H), 2.39 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 3.80 – 3.88 (m, 2H), 4.14 (t, *J* = 6.1 Hz, 2H), 4.37 – 4.46 (m, 2H), 7.33 – 7.42 (m, 2H), 7.76 – 7.82 (m, 2H).

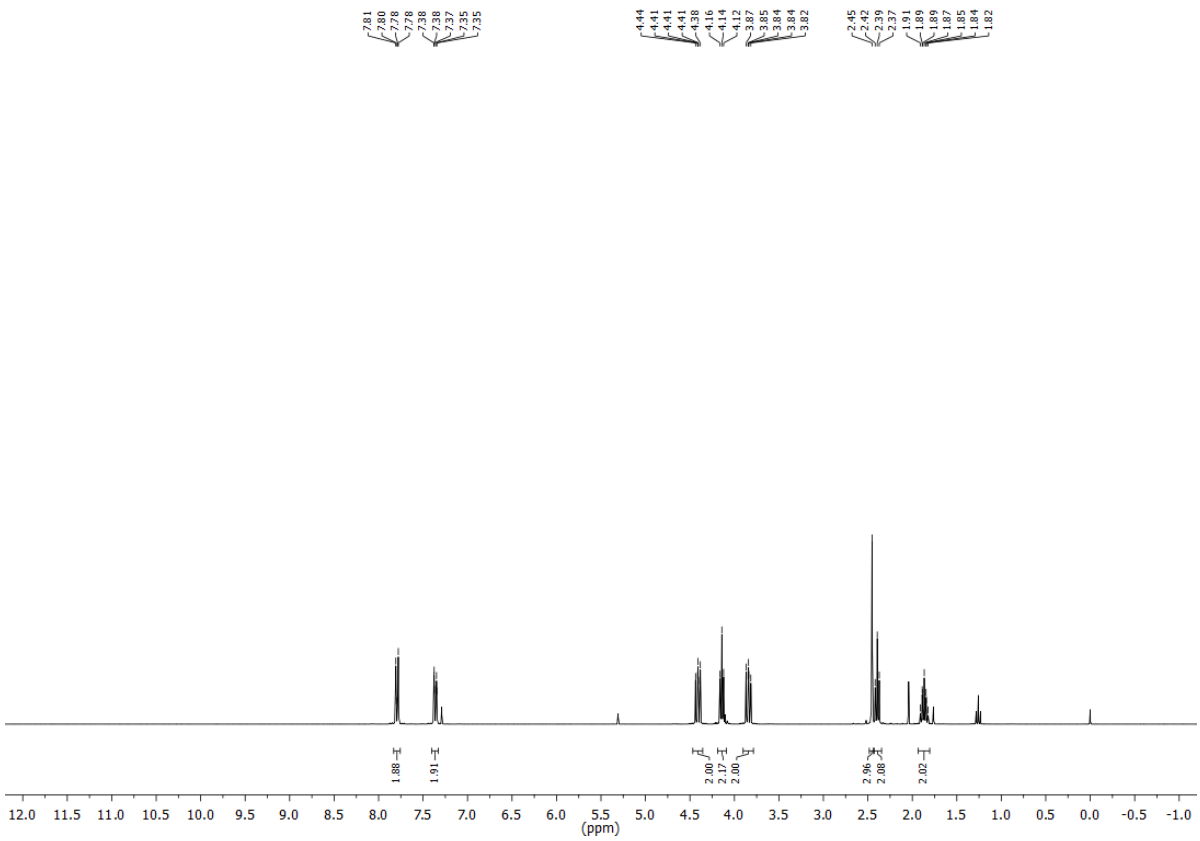
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.7, 21.5, 27.9, 46.8, 62.9, 68.8, 68.9, 71.1, 127.8, 129.8, 132.8, 144.8, 156.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2964, 2922, 2270, 1763, 1416, 1353, 1172, 1114, 921.

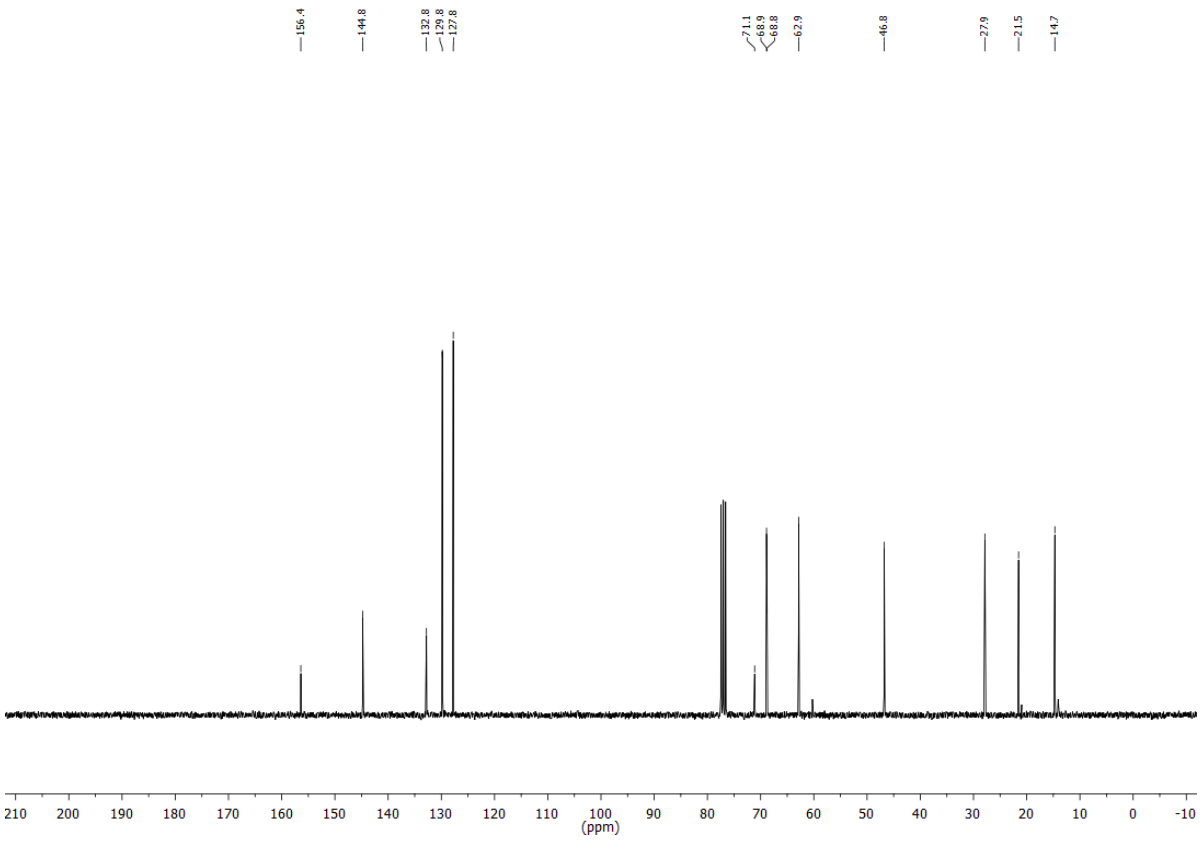
$C_{15}H_{17}NO_5S$ calcd.: 346.0720, found: 346.0722 $[M+Na]^+$ (ESI-HRMS).

[13] T. Hamada, X. Ye and S. S. Stahl, *J. Am. Chem. Soc.*, 2008, **130**, 833.

[14] A. Hoshi, T. Sakamoto, J. Takayama, M. Xuan, M. Okazaki, T. L. Hartman, R. W. Buckheit, C. Pannecouque and M. Cushman, *Bioorg. Med. Chem.*, 2016, **24**, 3006.

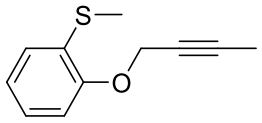


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(but-2-yn-1-yloxy)benzene (11a)



Compound **11a** was synthesized according GP1.

A solution of **SM1** (1.50 g, 10.71 mmol, 1.00 equiv.), PPh_3 (3.10 g, 11.78 mmol, 1.10 equiv.) and 2-butyn-1-ol (830.0 mg, 11.78 mmol, 1.10 equiv.) in dry toluene (30 ml) was cooled to 0 °C. DIAD (2.40 g, 2.33 ml, 11.78 mmol, 1.10 equiv.) in dry toluene (20 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 50:1) gave the desired product (1.7 g, 9.00 mmol, 84%) as colorless oil.

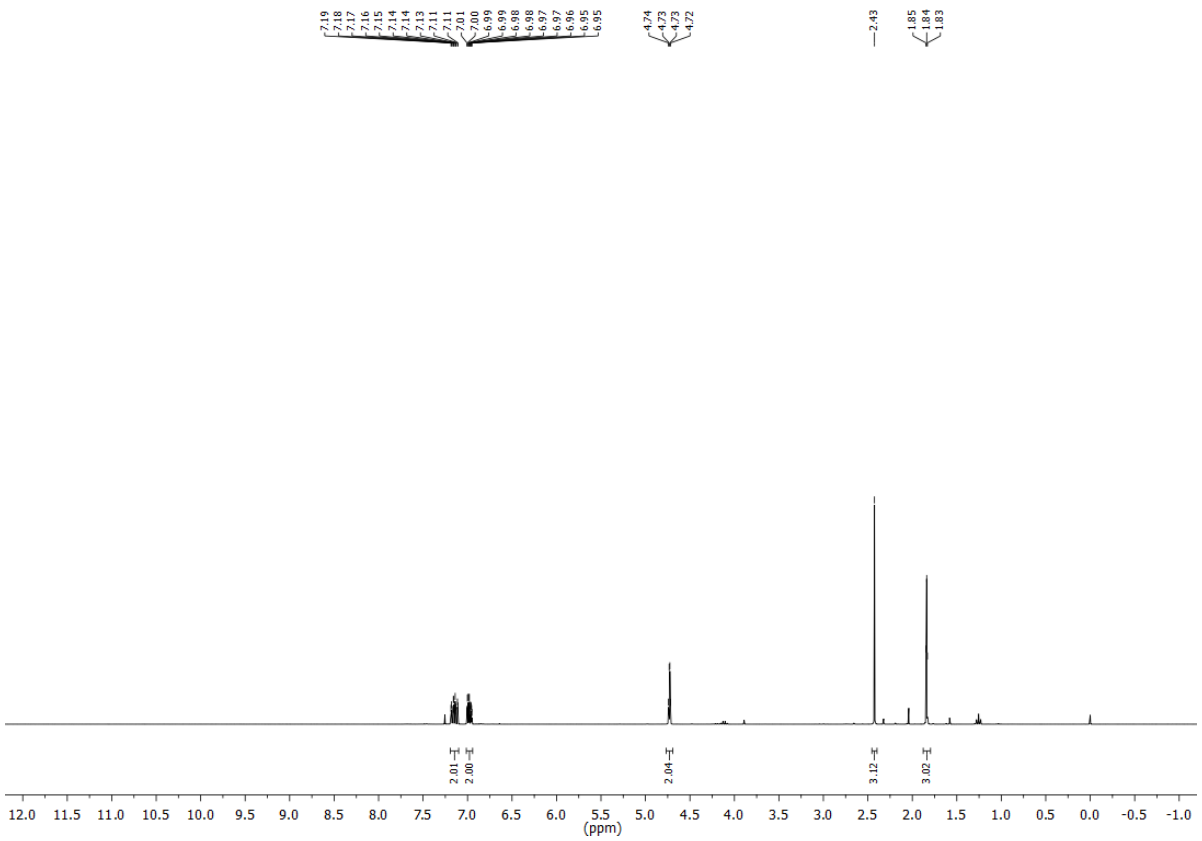
R_f = 0.33 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.84 (t, *J* = 2.3 Hz, 3H), 2.43 (s, 3H), 4.73 (q, *J* = 2.3 Hz, 2H), 6.94 – 7.01 (m, 2H), 7.10 – 7.19 (m, 2H).

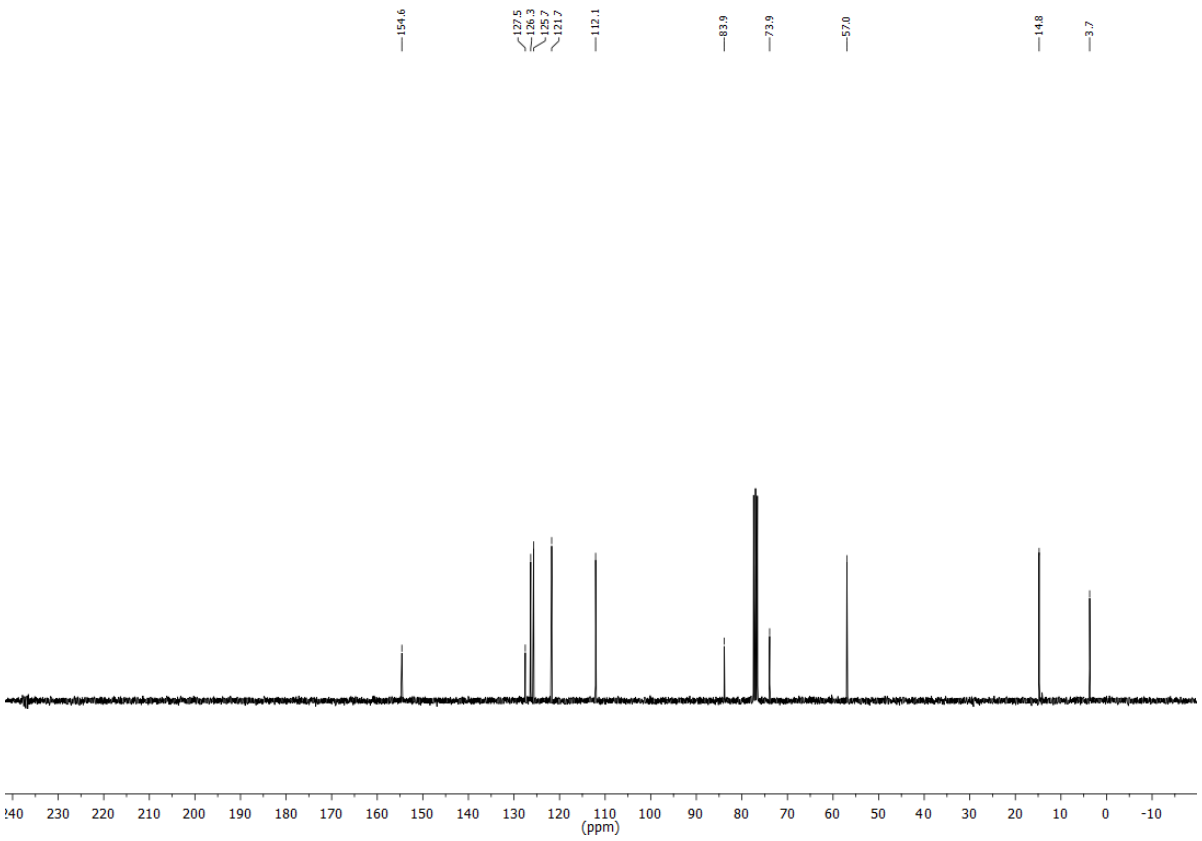
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.7, 14.8, 57.0, 73.9, 83.9, 112.1, 121.7, 125.7, 126.3, 127.5, 154.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2957, 2229, 1576, 1472, 1441, 1216, 999.

$C_{11}H_{12}OS$ calcd.: 192.0609, found: 192.0626 (GC-HRMS).

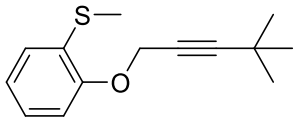


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(but-2-yn-1-yloxy)benzene (11b)



Compound **11b** was synthesized according GP1.

A solution of **SM1** (200.0 mg, 1.44 mmol, 1.00 equiv.), PPh_3 (568.0 mg, 2.16 mmol, 1.50 equiv.) and 4,4-dimethyl-2-pentyn-1-ol[15] (162.0 mg, 1.44 mmol, 1.00 equiv.) in dry toluene (10 ml) was cooled to 0 °C. DIAD (438.0 mg, 0.44 ml, 11.78 mmol, 1.10 equiv.) in dry toluene (8 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 150:1) gave the desired product (98 mg, 0.42 mmol, 29%) as colorless oil.

As 4,4-dimethyl-2-pentyn-1-ol was used without further purification after synthesis, the by-product **11b*** was also formed and isolated in 14% yield (see next page).

R_f = 0.21 (*n*-pentane:EtOAc = 50:1).

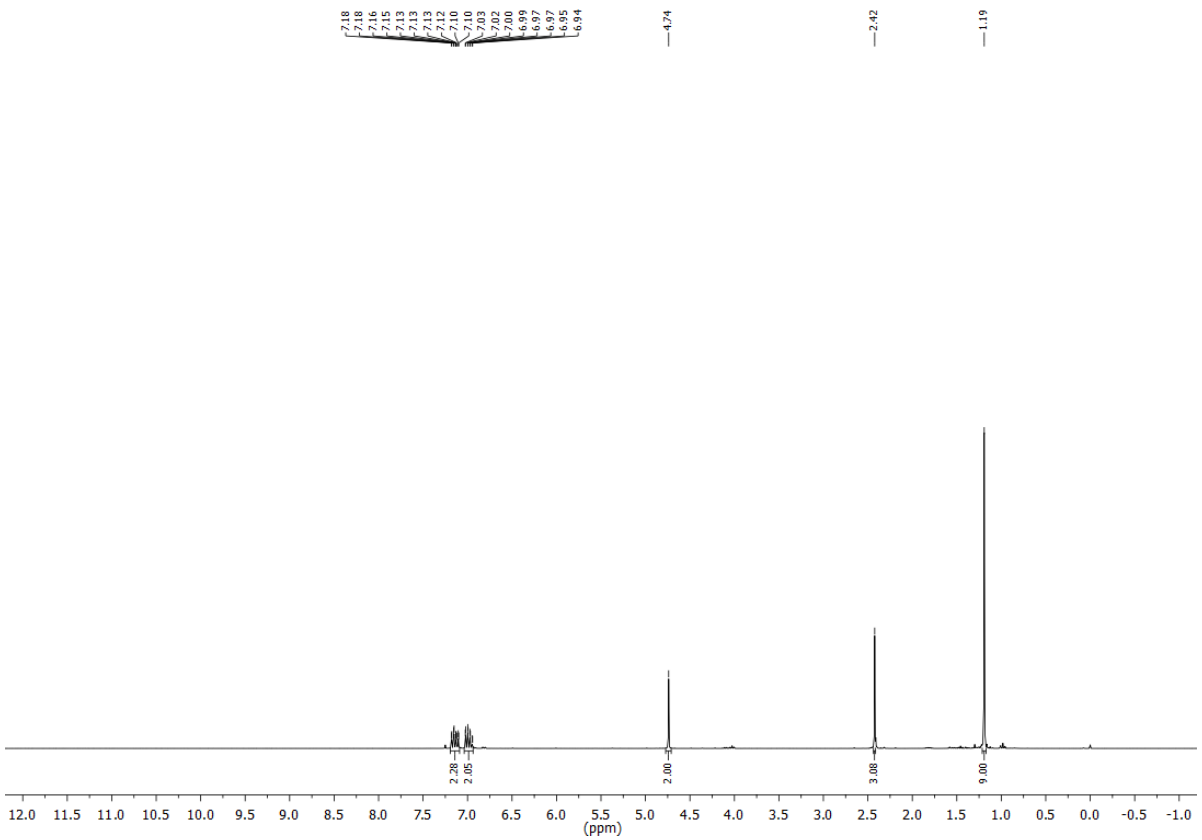
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.19 (s, 9H), 2.42 (s, 3H), 4.74 (s, 2H), 6.93 – 7.03 (m, 2H), 7.09 – 7.20 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.8, 27.4, 30.7, 57.3, 73.4, 96.6, 112.7, 121.7, 125.6, 126.3, 127.6, 154.8.

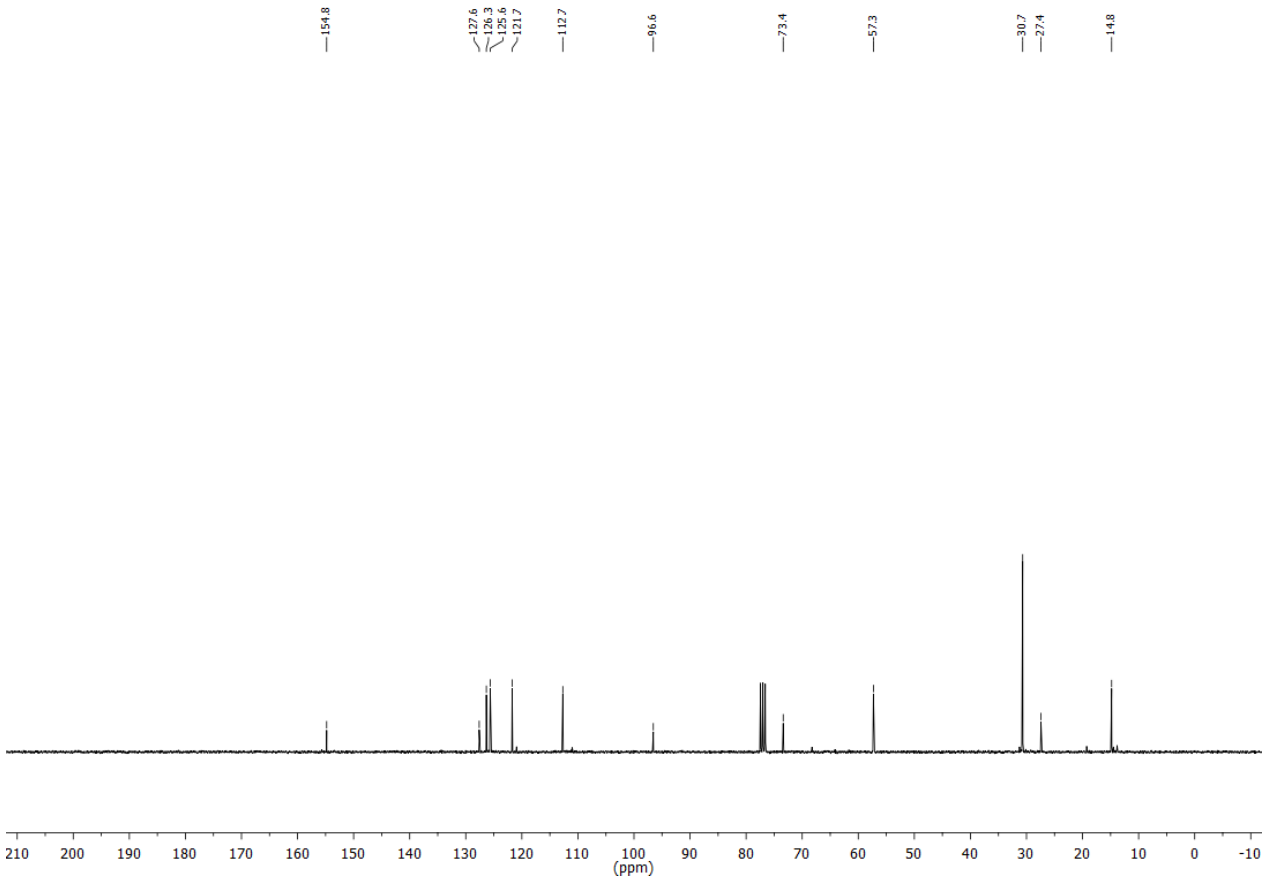
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2968, 2923, 2866, 2238, 1578, 1473, 1444, 1263, 1216.

$C_{14}H_{18}OS$ calcd.: 234.1078, found: 234.1091 (GC-HRMS).

[15] I. Chatterjee, R. Fröhlich and A. Studer, *Angew. Chem. Int. Ed.*, 2011, **50**, 11257.

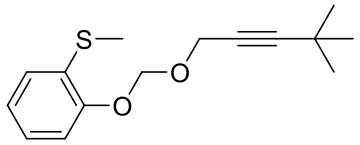


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(((4,4-dimethylpent-2-yn-1-yl)oxy)methoxy)benzene (11b*)



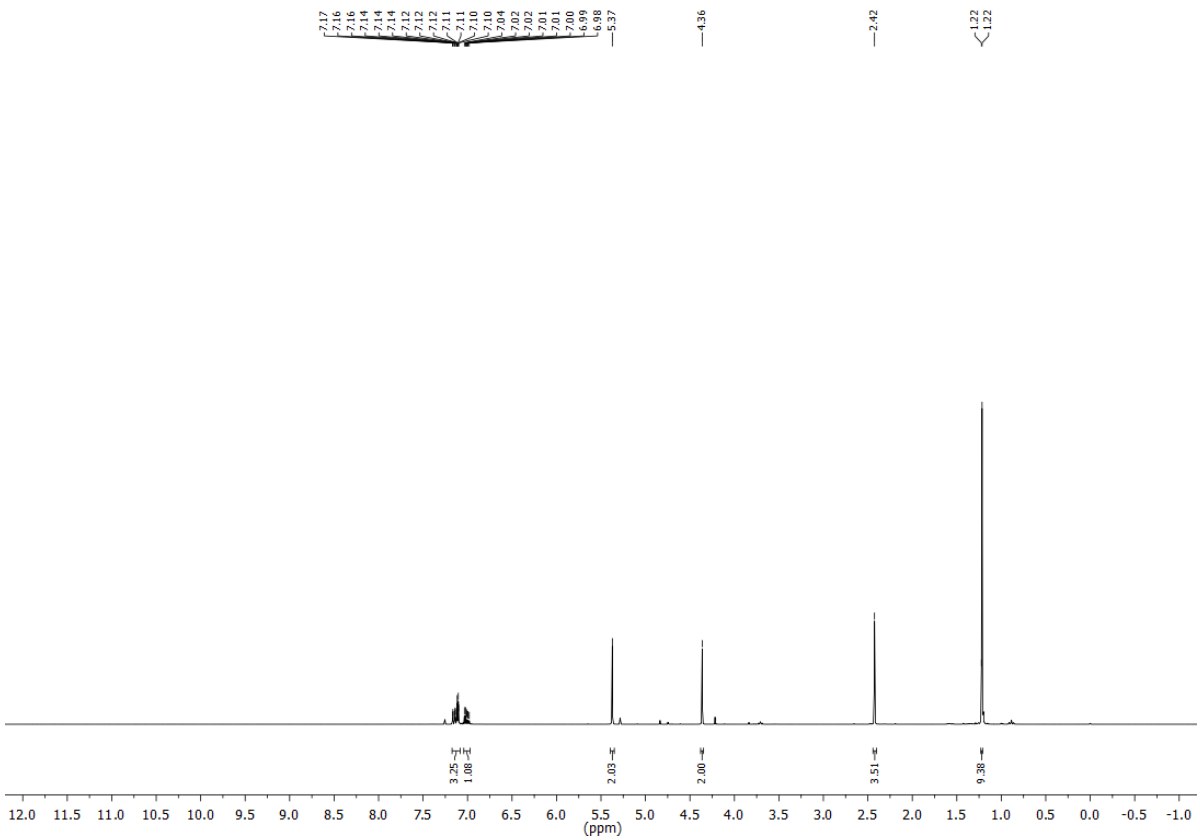
R_f = 0.37 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 6H), 1.22 (s, 3H), 2.42 (s, 3H), 4.36 (s, 2H), 5.37 (s, 2H), 6.95 – 7.07 (m, 1H), 7.07 – 7.20 (m, 3H).

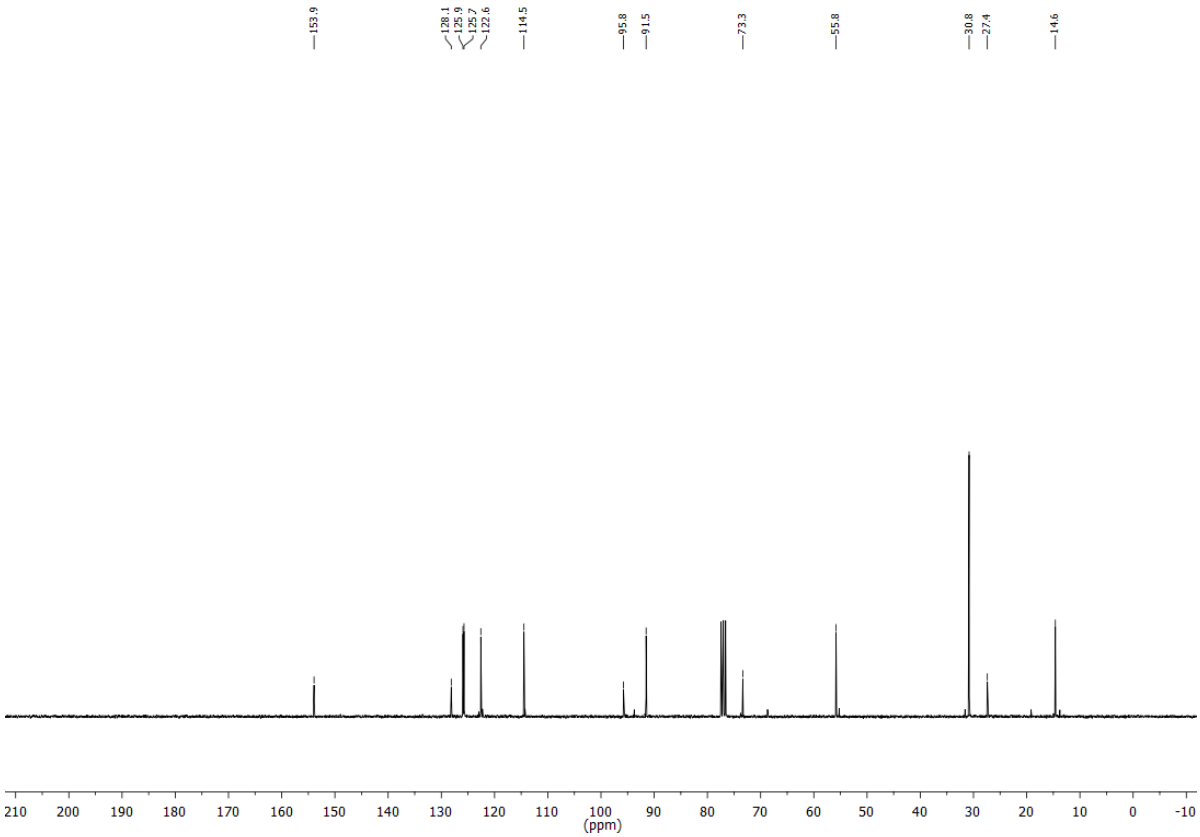
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.6, 27.4, 30.8, 55.8, 73.3, 91.5, 95.8, 114.5, 122.6, 125.7, 125.9, 128.1, 153.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 2968, 2867, 2238, 1578, 1474, 1443, 1218, 1064.

$C_{15}H_{20}O_2S$ calcd.: 264.1184, found: 264.1199 (GC-HRMS).

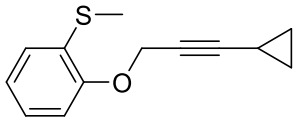


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-cyclopropylprop-2-yn-1-yl)oxy)benzene (11c)



Compound **11c** was synthesized according GP1.

A solution of **SM1** (810.0 mg, 5.77 mmol, 1.00 equiv.), PPh_3 (2.30 g, 8.66 mmol, 1.50 equiv.) and 3-cyclopropyl-2-propyn-1-ol[16] (555.0 mg, 5.77 mmol, 1.00 equiv.) in dry THF (40 ml) was cooled to 0 °C. DIAD (1.80 g, 1.70 ml, 8.66 mmol, 1.50 equiv.) in dry THF (32 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 50:1) gave the desired product (541 mg, 2.48 mmol, 43%) as a colorless oil.

R_f = 0.39 (*n*-pentane:EtOAc = 50:1).

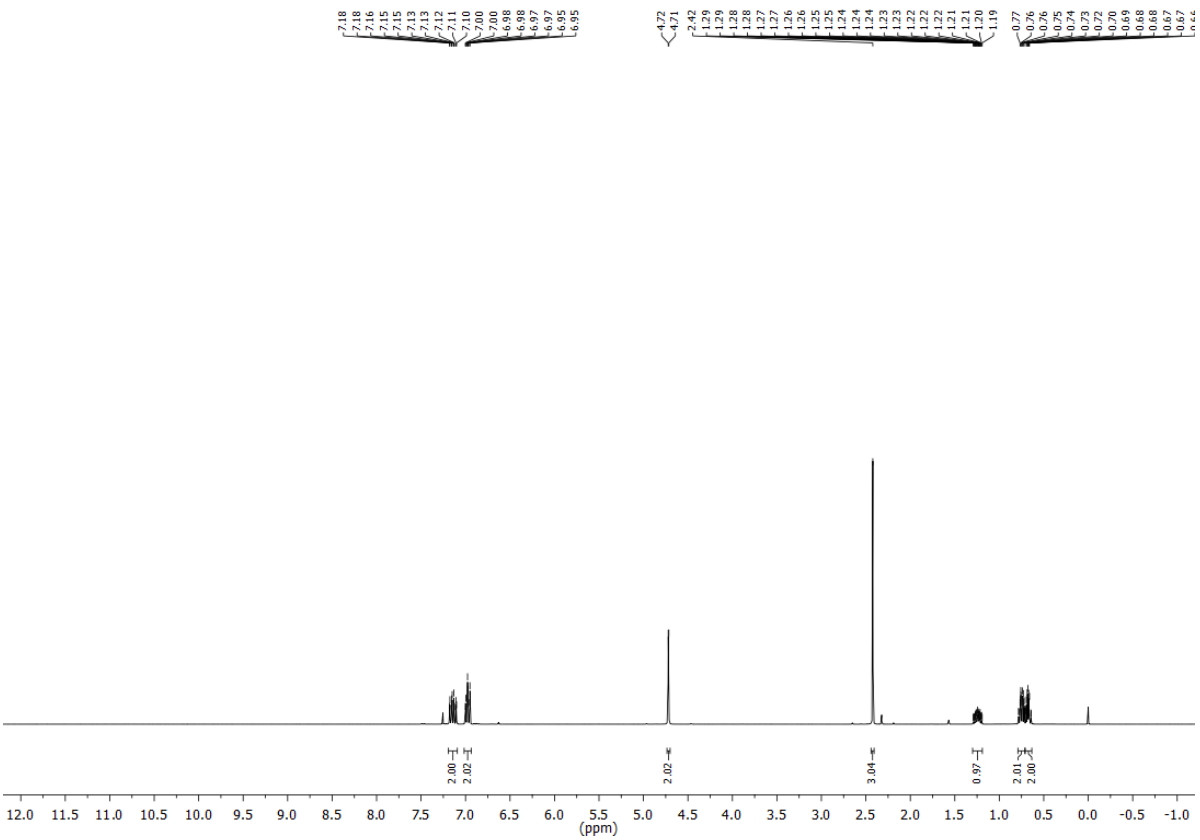
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.64 – 0.71 (m, 2H), 0.71 – 0.79 (m, 2H), 1.19 – 1.30 (m, 1H), 2.42 (s, 3H), 4.72 (d, *J* = 2.0 Hz, 2H), 6.98 (ddd, *J* = 8.0, 6.6, 1.3 Hz, 2H), 7.10 – 7.19 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = -0.6, 8.1, 14.7, 57.0, 70.0, 91.4, 112.2, 121.7, 125.6, 126.2, 127.5, 154.6.

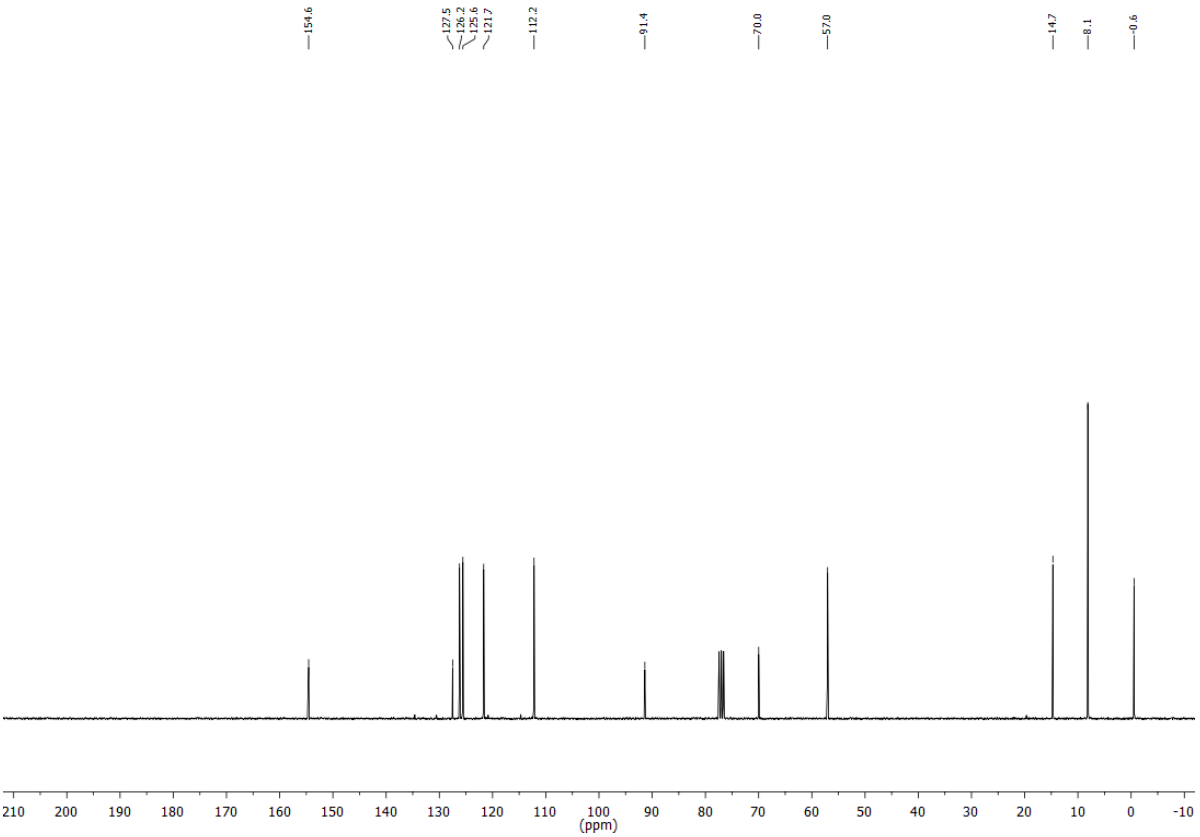
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3012, 2925, 2864, 2236, 2157, 1581, 1474, 1226, 1059.

$C_{13}H_{14}OS$ calcd.: 218.0765, found: 218.0755 (GC-HRMS).

[16] E. Matoušová, R. Gyepes, I. Císařová and M. Kotora, *Adv. Synth. Catal.*, 2016, **358**, 254.

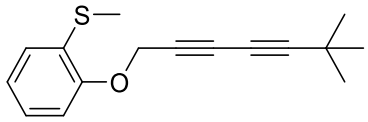


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((6,6-dimethylhepta-2,4-diyn-1-yl)oxy)benzene (11d)



Compound **11d** was synthesized according GP1.

A solution of **SM1** (300.0 mg, 2.16 mmol, 1.00 equiv.), PPh_3 (852 mg, 3.24 mmol, 1.50 equiv.) and 6,6-dimethyl-2,4-heptadiyn-1-ol[17] (442 mg, 3.24 mmol, 1.50 equiv.) in dry toluene (15 ml) was cooled to 0 °C. DIAD (657 mg, 0.66 ml, 3.24 mmol, 1.50 equiv.) in dry toluene (12 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 50:1) gave the desired product (457 mg, 1.77 mmol, 82%) as a colorless oil.

R_f = 0.29 (*n*-pentane:EtOAc = 50:1).

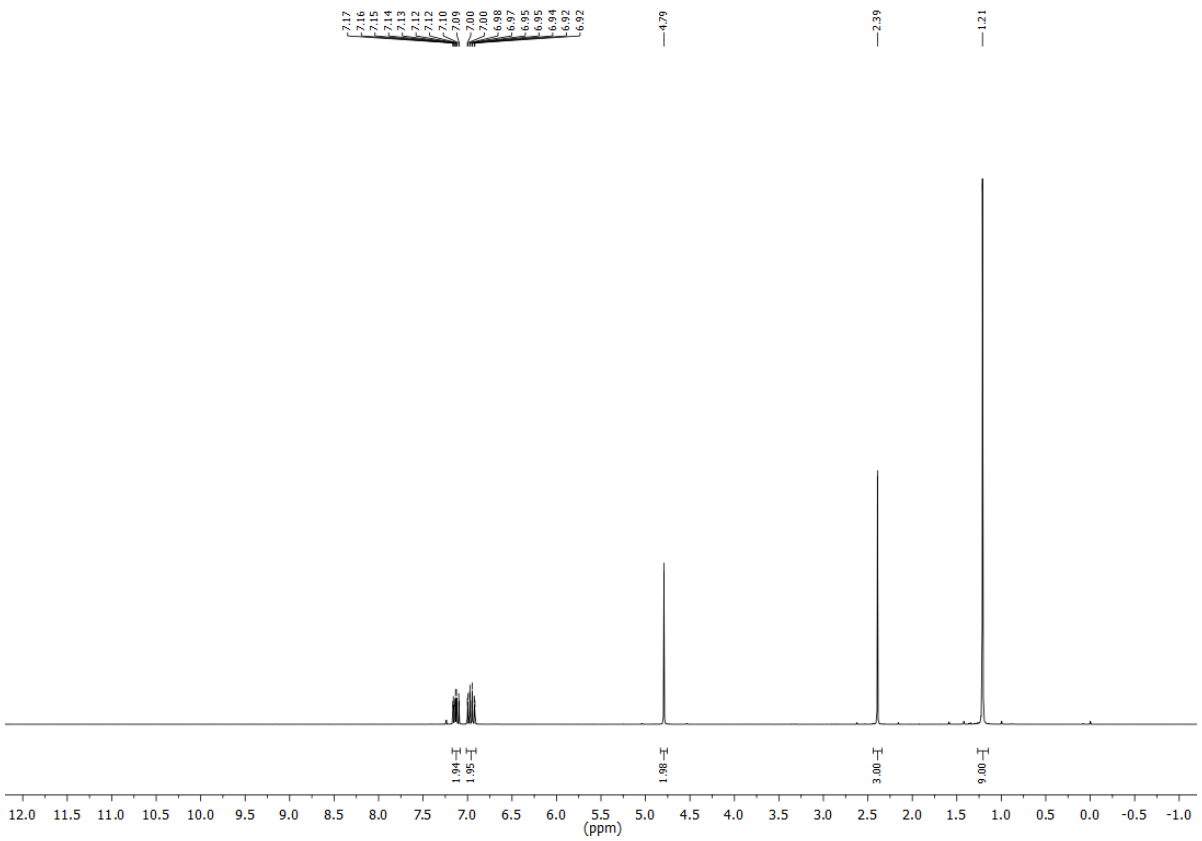
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 9H), 2.39 (s, 3H), 4.79 (s, 2H), 6.91 – 7.01 (m, 2H), 7.09 – 7.17 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.6, 27.8, 30.2, 56.7, 63.1, 71.2, 72.1, 89.3, 112.0, 122.0, 125.7, 126.3, 127.6, 154.2.

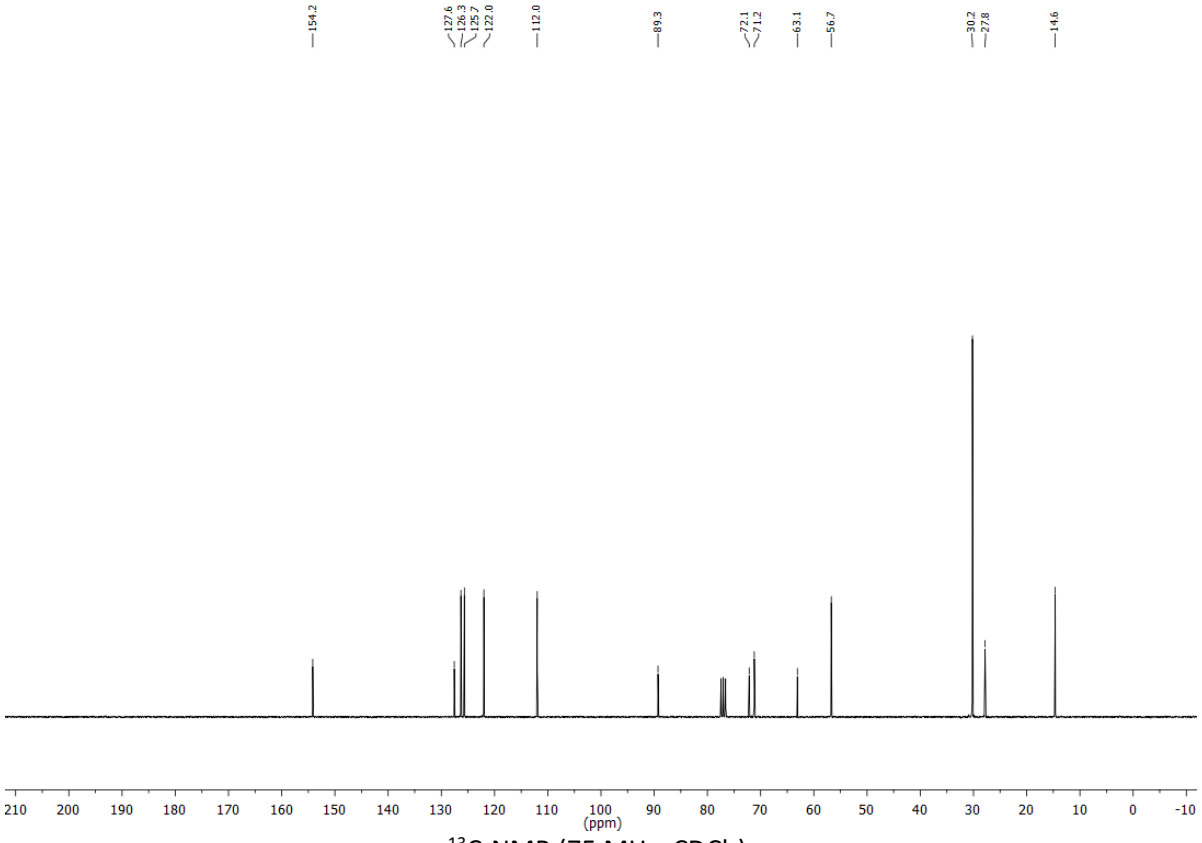
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2970, 2921, 2865, 2251, 1774, 1577, 1472, 1444, 1213, 1008.

$C_{16}H_{18}OS$ calcd.: 258.1078, found: 258.1091 (GC-HRMS).

[17] N. P. Bowling, N. J. Burrmann, R. J. Halter, J. A. Hodges and R. J. McMahon, *J. Org. Chem.*, 2010, **75**, 6382.

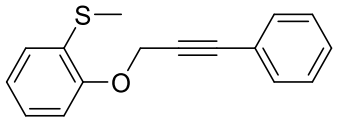


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (11e)



Compound **11e** was synthesized according GP1.

A solution of **SM1** (100.0 mg, 0.72 mmol, 1.00 equiv.), PPh_3 (284.0 mg, 1.08 mmol, 1.50 equiv.) and 3-phenyl-2-propyn-1-ol (96.0 mg, 0.72 mmol, 1.00 equiv.) in dry toluene (5 ml) was cooled to 0 °C. DIAD (219 mg, 0.22 ml, 1.08 mmol, 1.50 equiv.) in dry toluene (4 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 50:1) gave the desired product (73 mg, 0.29 mmol, 40%) as colorless oil which crystallized slowly to a colorless solid.

m.p.: 43 °C.

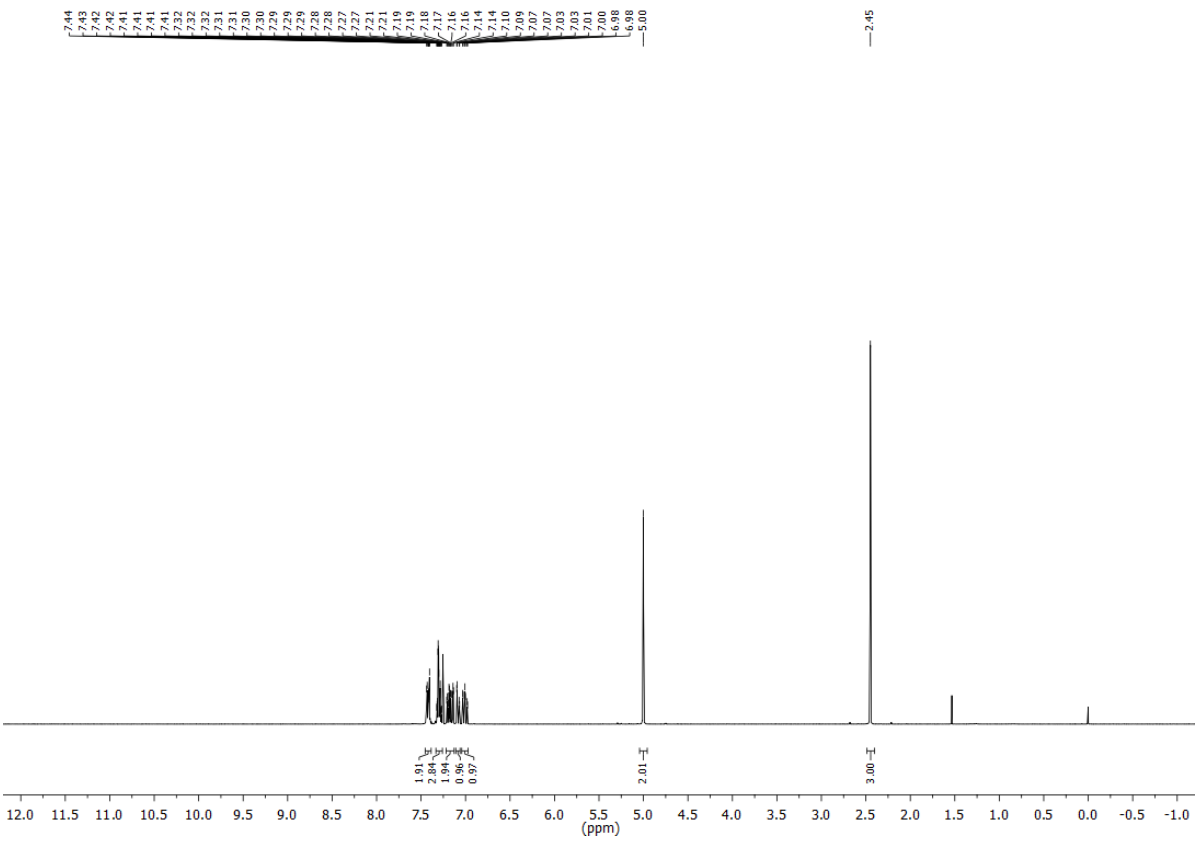
$\mathbf{R_f}$ = 0.19 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 5.00 (s, 2H), 7.00 (td, *J* = 7.4, 1.4 Hz, 1H), 7.08 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.13 – 7.22 (m, 2H), 7.26 – 7.34 (m, 3H), 7.39 – 7.46 (m, 2H).

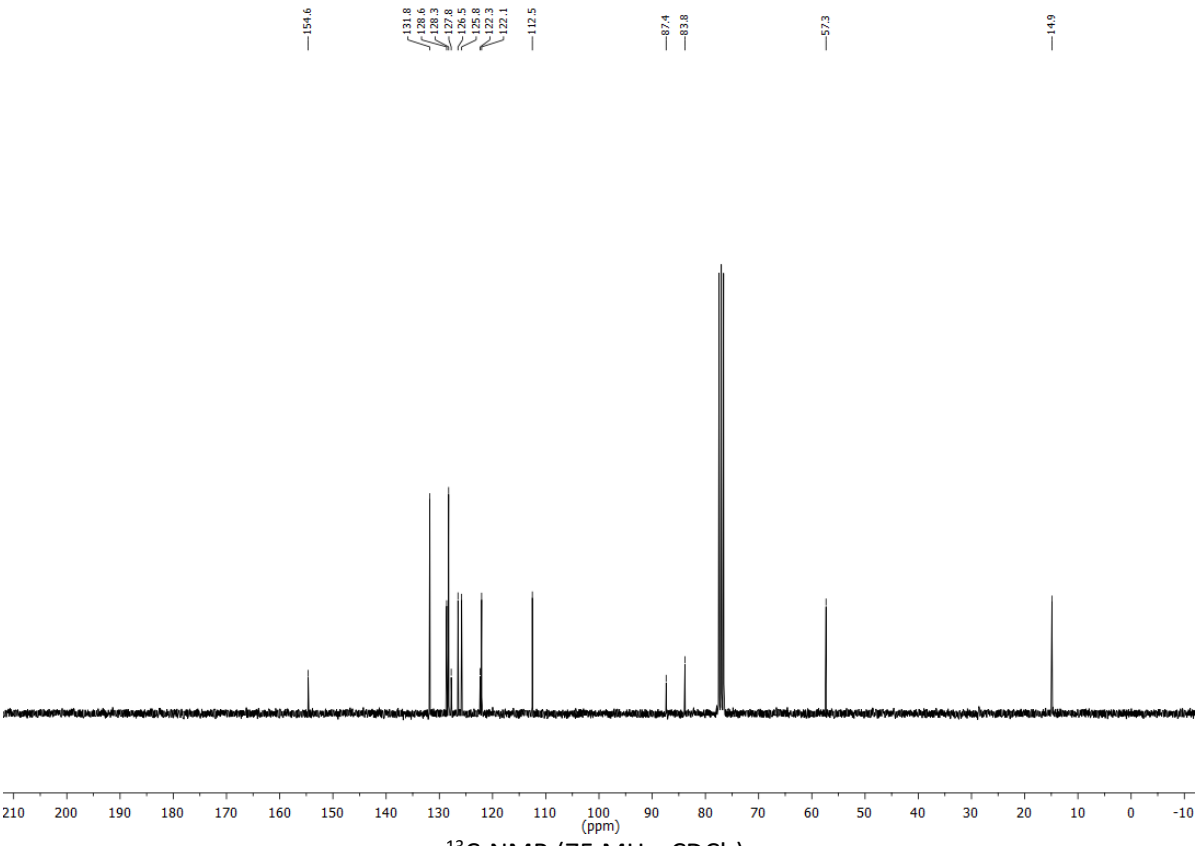
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.9, 57.3, 83.8, 87.4, 112.5, 122.1, 122.3, 125.8, 126.5, 127.8, 128.3, 128.6, 131.8, 154.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3059, 2918, 2237, 1575, 1472, 1441, 1214, 1014.

$C_{16}H_{14}OS$ calcd.: 254.0765, found: 254.0775 (GC-HRMS).

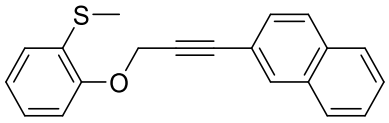


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(2-naphthyl)prop-2-yn-1-yl)oxy)benzene (11f)



Compound **11f** was synthesized according GP2.

To a mixture of **SM2** (200.0 mg, 1.12 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and CuI (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 2-iodonaphthalene (343.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with sat. NH_4Cl-solution, diluted with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) which afforded an off-colorless solid (149 mg, 0.49 mmol, 44%).

m.p.: 84 °C.

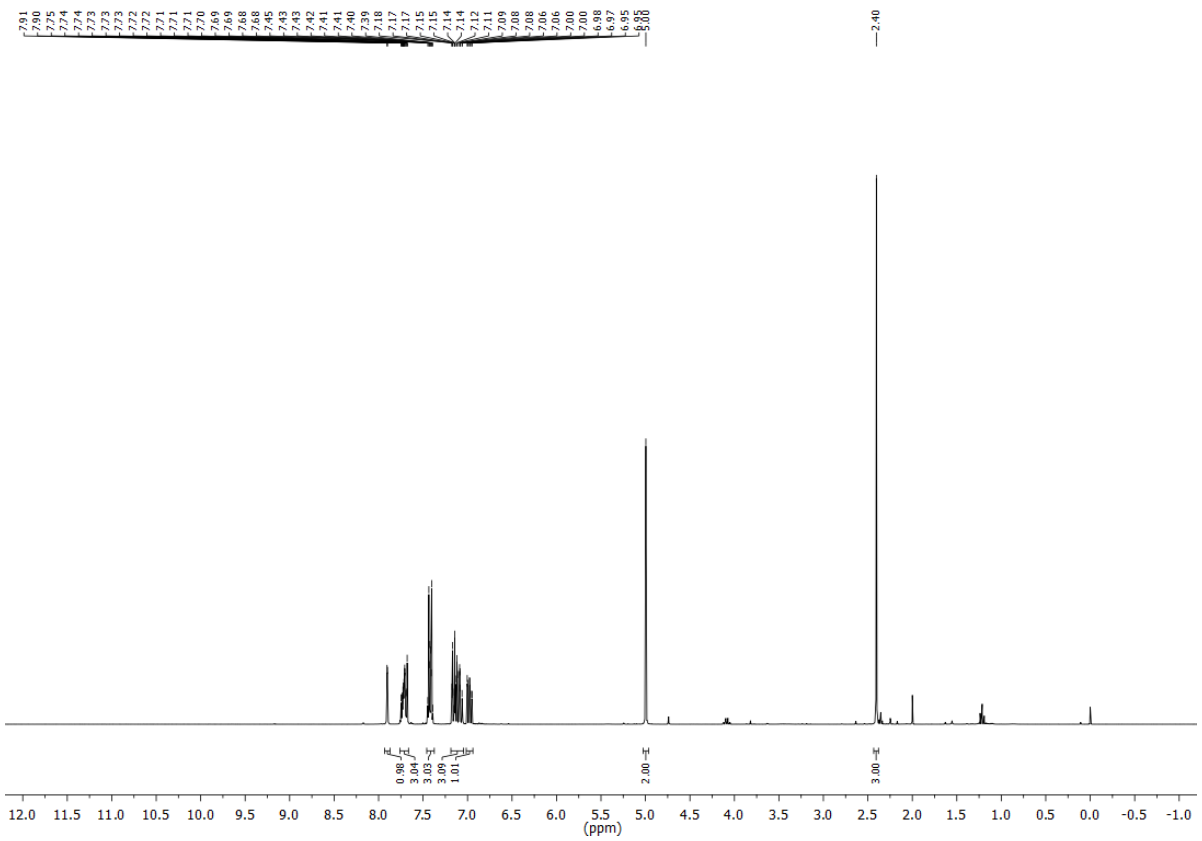
R_f = 0.25 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 5.00 (s, 2H), 6.95 – 7.01 (m, 1H), 7.04 – 7.20 (m, 3H), 7.38 – 7.46 (m, 3H), 7.66 – 7.77 (m, 3H), 7.90 (d, *J* = 1.6 Hz, 1H).

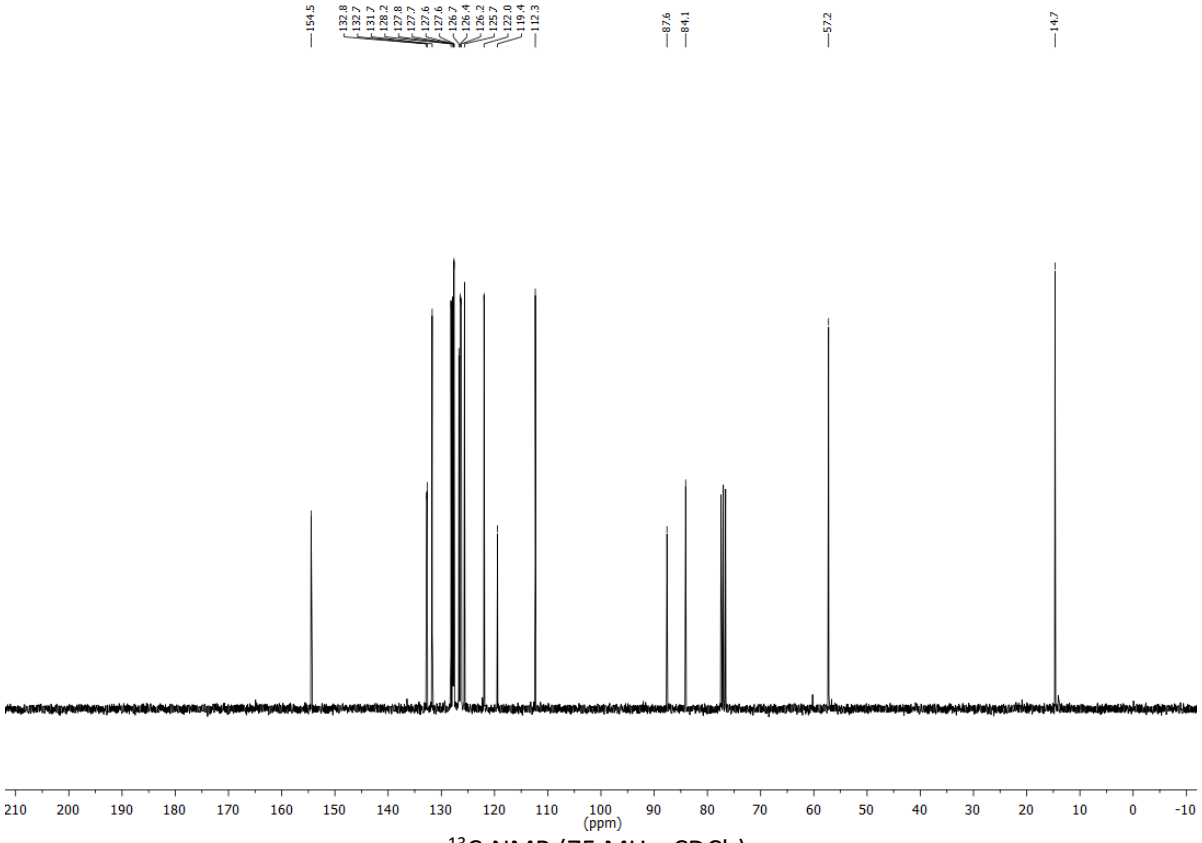
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.7, 57.2, 84.1, 87.6, 112.3, 119.4, 122.0, 125.7, 126.2, 126.4, 126.7, 127.6, 127.6, 127.7, 127.8, 128.2, 131.7, 132.7, 132.8, 154.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3052, 2992, 2920, 2856, 2235, 1593, 1499, 1475, 1379, 1227, 1071, 1016.

$C_{20}H_{16}OS$ calcd.: 304.0922, found: 304.0900 (GC-HRMS).

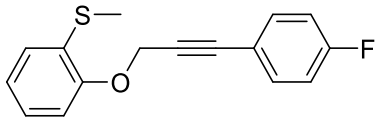


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)benzene (11g)



Compound **11g** was synthesized according GP2.

To a mixture of **SM2** (100.0 mg, 0.56 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (12.0 mg, 17.1 µmol, 0.03 equiv.) and CuI (7.0 mg, 36.8 µmol, 0.06 equiv.) in dry triethylamine (4 ml) was added 4-fluoroiodobenzene (149.0 mg, 0.67 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) which afforded an off-colorless solid (93 mg, 0.34 mmol, 61%).

m.p.: 67 °C.

$\mathbf{R_f}$ = 0.19 (*n*-pentane:EtOAc = 50:1).

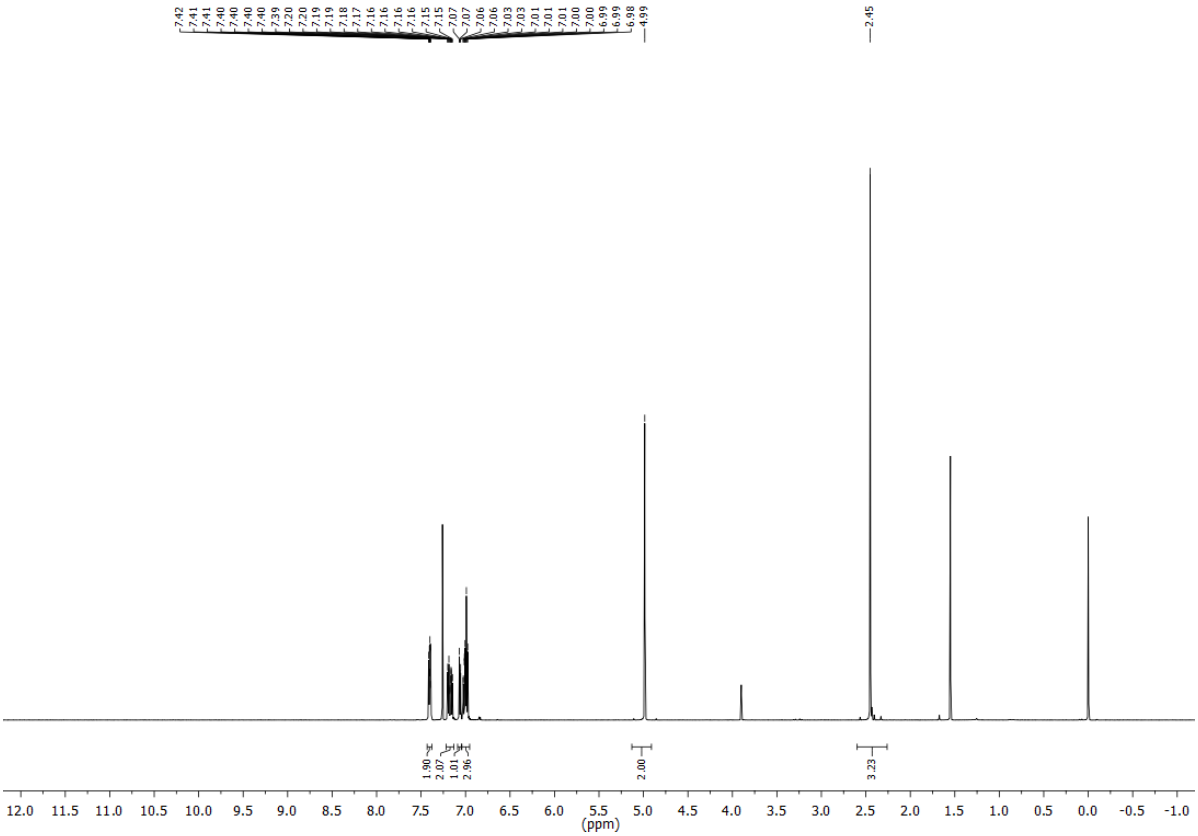
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 4.98 (s, 2H), 6.92 – 7.09 (m, 4H), 7.12 – 7.22 (m, 2H), 7.36 – 7.44 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.8, 57.2 , 83.6 (d, *J* = 1.5 Hz), 86.3 , 112.4 , 115.6 (d, *J* = 22.1 Hz), 118.4 (d, *J* = 3.6 Hz), 122.1 , 125.8 , 126.40 , 127.8 , 133.8 (d, *J* = 8.5 Hz), 154.5 , 162.7 (d, *J* = 250.0 Hz).

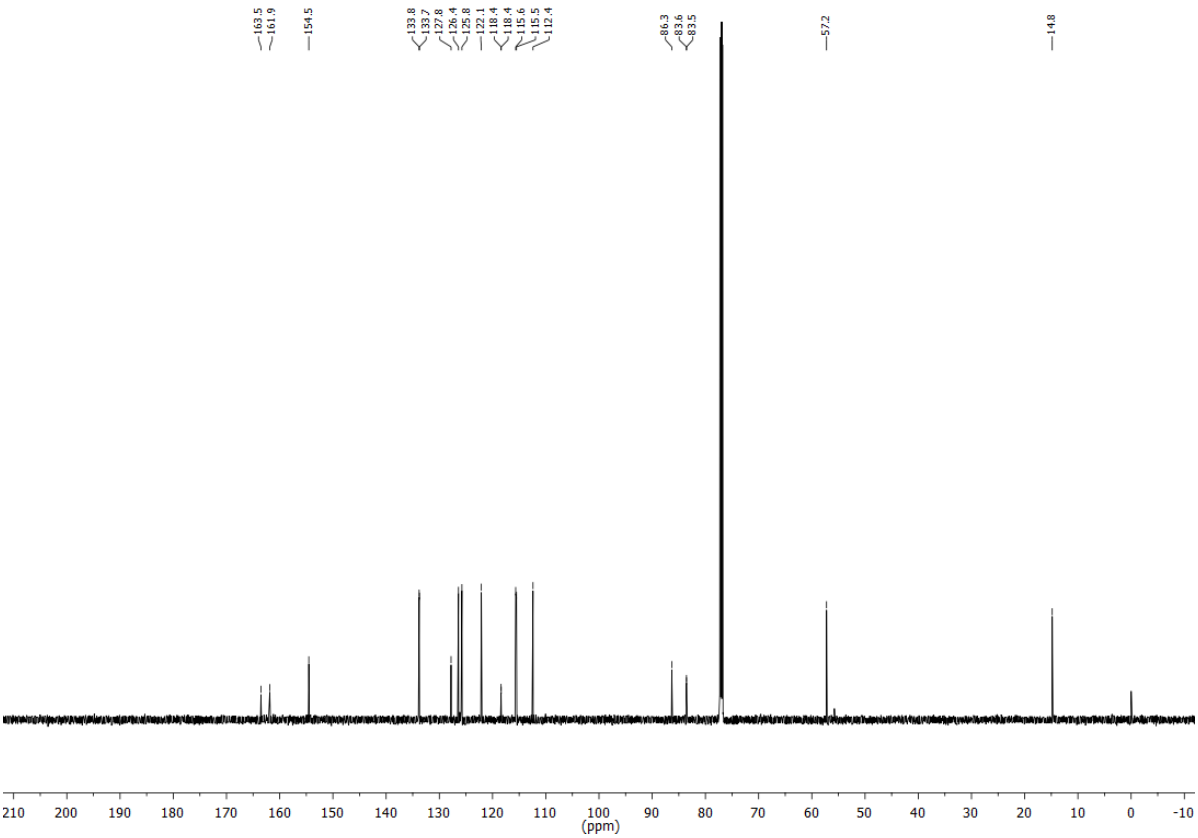
^{19}F-NMR (283 MHz, $CDCl_3$): δ = -110.73

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2853, 2231, 1503, 1476, 1226, 1018.

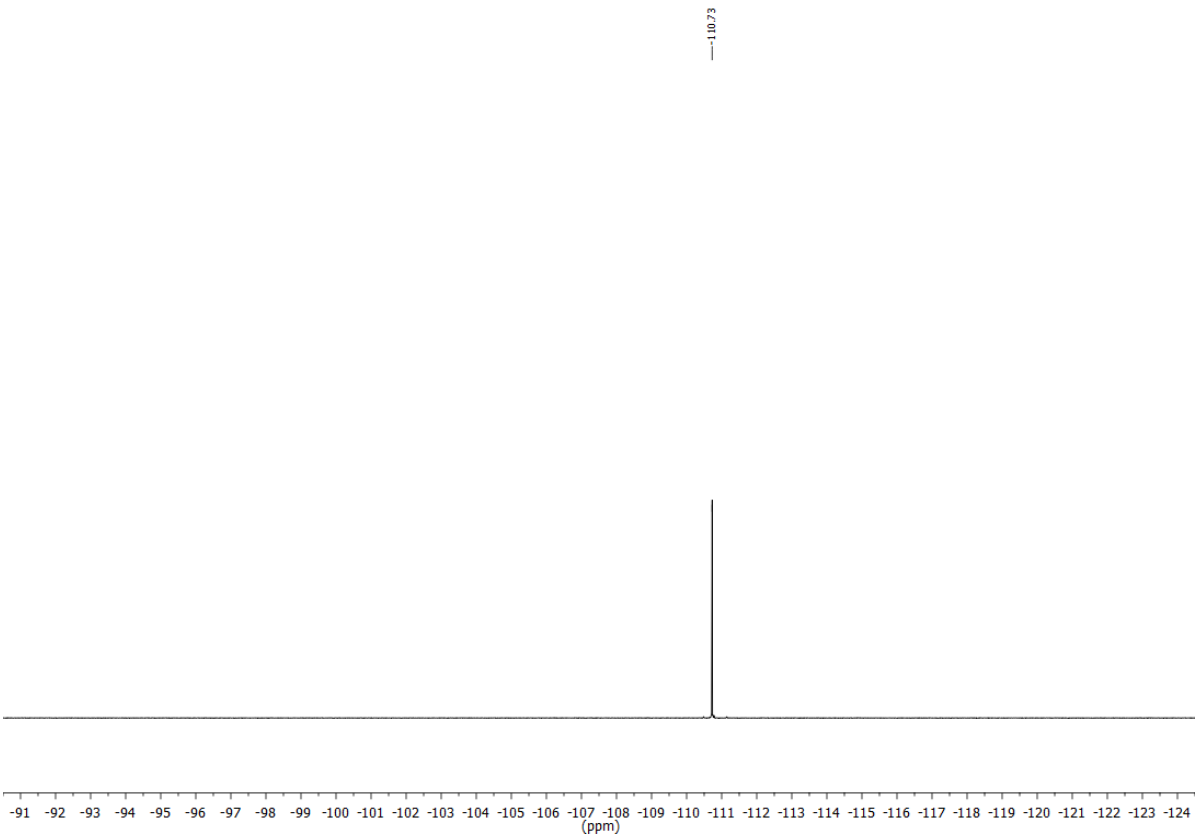
$C_{16}H_{13}FOS$ calcd.: 272.0671, found: 272.0671 (GC-HRMS).



^{1}H-NMR (300 MHz, $CDCl_3$).

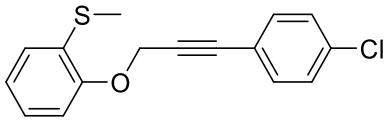


^{13}C-NMR (75 MHz, $CDCl_3$).



^{19}F-NMR (283 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)benzene (11h)



Compound **11h** was synthesized according GP2.

To a mixture of **SM2** (200.0 mg, 1.12 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and CuI (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 1-chloro-4-iodobenzene (322.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with sat. NH_4Cl-solution, diluted with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) which afforded a colorless solid (215 mg, 0.74 mmol, 67%).

m.p.: 72 °C.

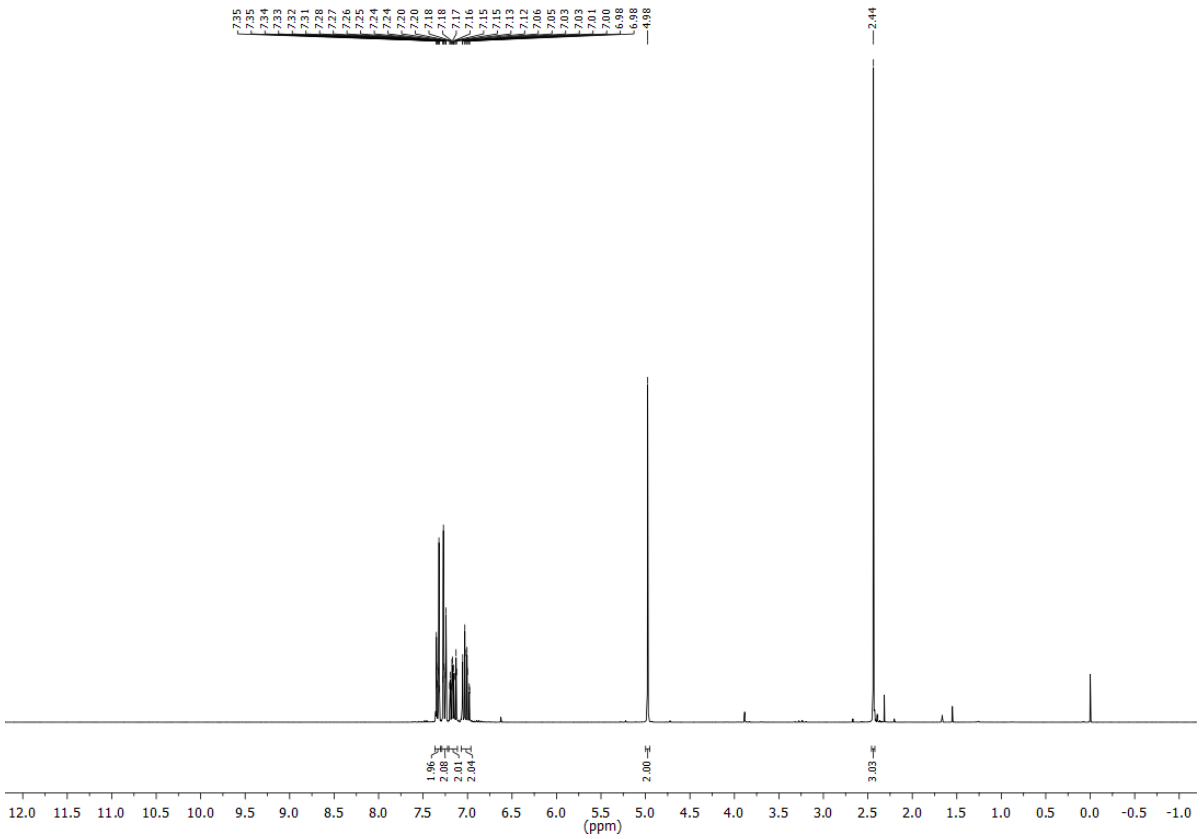
R_f = 0.16 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 4.98 (s, 2H), 6.96 – 7.07 (m, 2H), 7.11 – 7.21 (m, 2H), 7.23 – 7.29 (m, 2H), 7.30 – 7.37 (m, 2H).

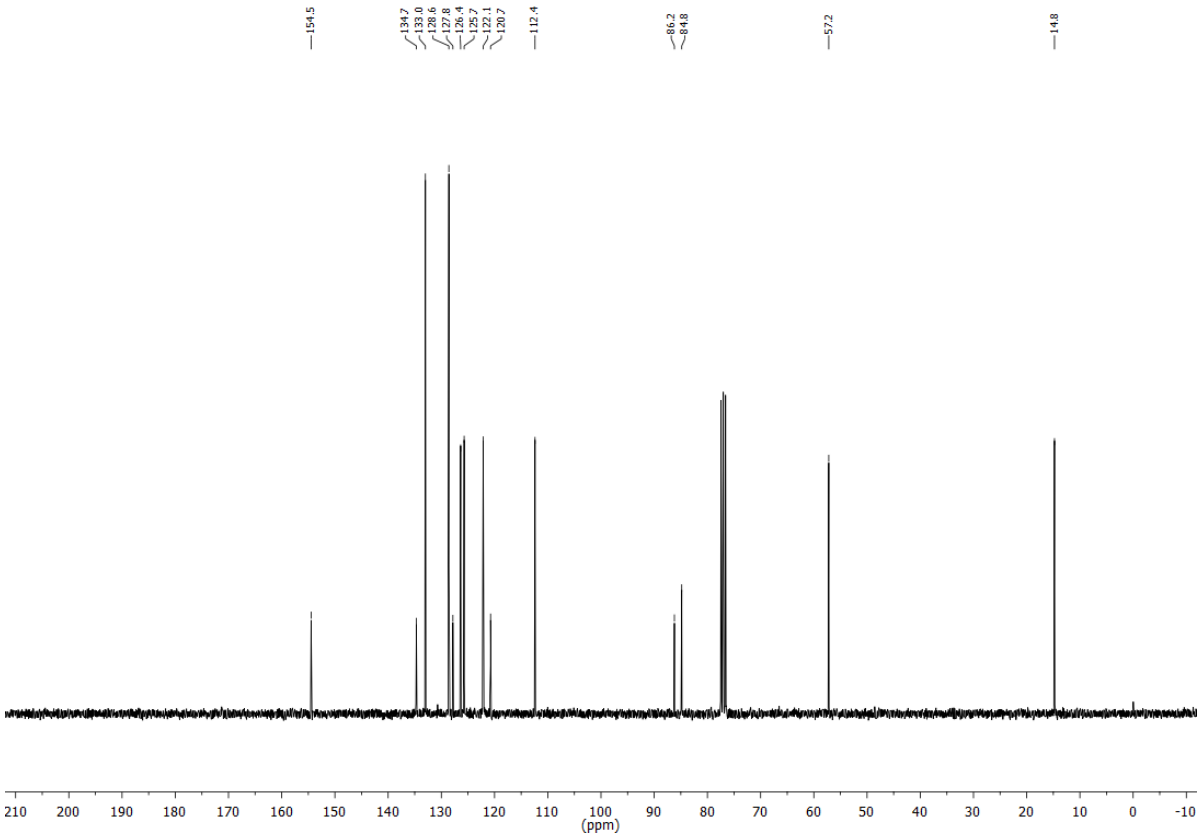
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.8, 57.2, 84.8, 86.2, 112.4, 120.7, 122.1, 125.7, 126.4, 127.8, 128.6, 133.0, 134.7, 154.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2918, 2860, 2238, 1575, 1471, 1441, 1214, 1013.

$C_{16}H_{13}ClOS$ calcd.: 288.0376, found: 288.0399 (GC-HRMS).

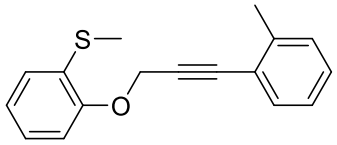


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(*o*-tolyl)prop-2-yn-1-yl)oxy)benzene (11i)



Compound **11i** was synthesized according GP2.

To a mixture of **SM2** (200.0 mg, 1.12 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and CuI (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 2-iodotoluene (295.0 mg, 0.17 ml, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) which afforded a colorless solid (151 mg, 0.56 mmol, 50%).

m.p.: 58 °C.

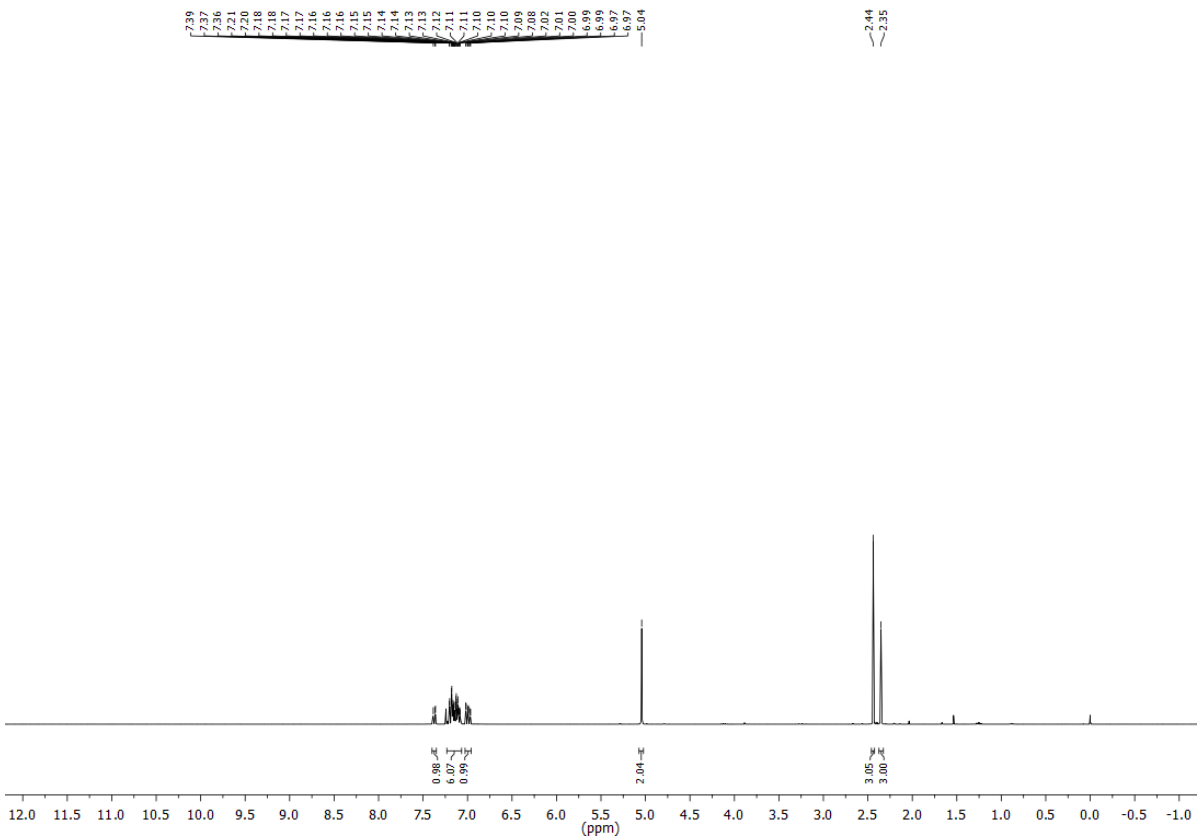
R_f = 0.19 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3H), 2.44 (s, 3H), 5.04 (s, 2H), 6.96 – 7.03 (m, 1H), 7.06 – 7.23 (m, 6H), 7.35 – 7.40 (m, 1H).

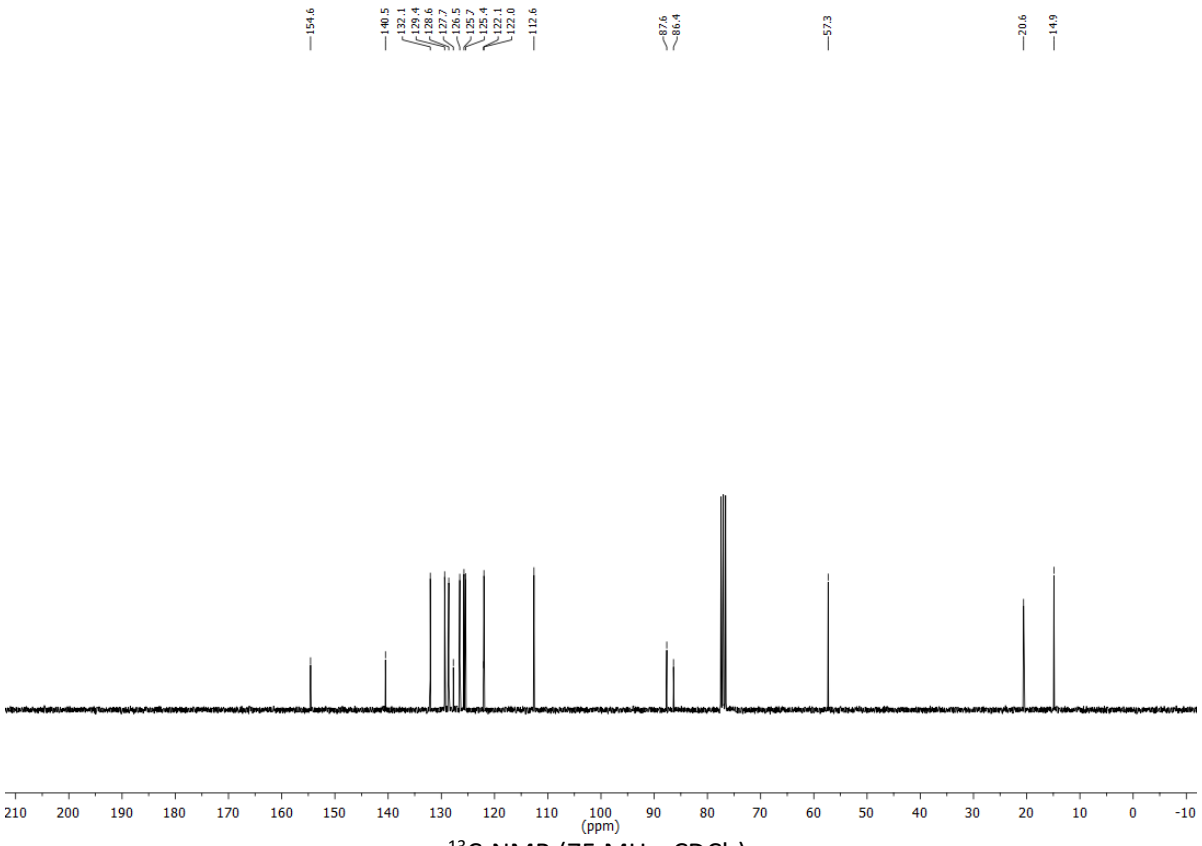
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.9, 20.6, 57.3, 86.4, 87.6, 112.6, 122.0, 122.1, 125.4, 125.7, 126.5, 127.7, 128.6, 129.4, 132.1, 140.5, 154.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2976, 2919, 2236, 1573, 1471, 1441, 1214, 1011.

$C_{17}H_{16}OS$ calcd.: 268.0922, found: 268.0937 (GC-HRMS).

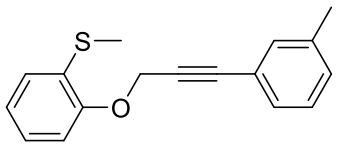


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(*m*-tolyl)prop-2-yn-1-yl)oxy)benzene (11j)



Compound **11j** was synthesized according GP2.

To a mixture of **SM2** (200.0 mg, 1.12 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and CuI (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 3-iodotoluene (295.0 mg, 0.17 ml, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) which afforded an orange oil (199 mg, 0.74 mmol, 66%).

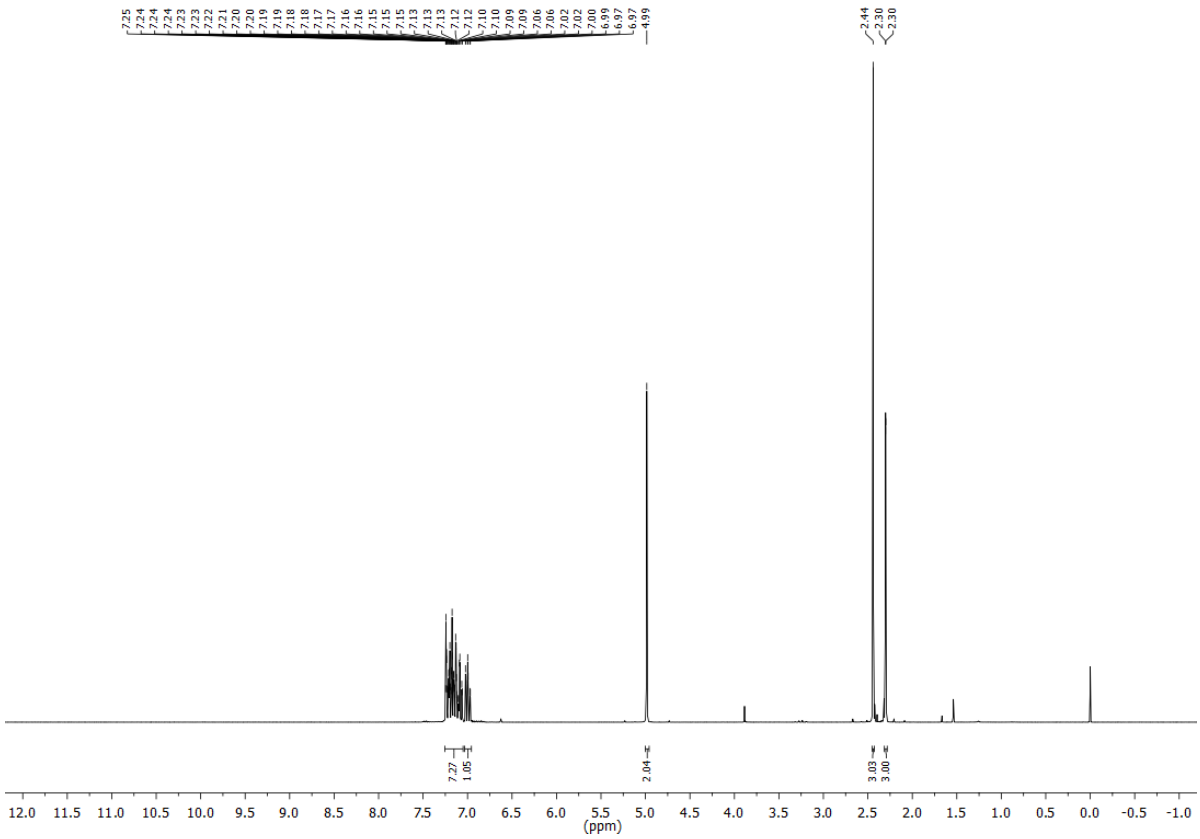
R_f = 0.16 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.30 (d, *J* = 0.7 Hz, 3H), 2.44 (s, 3H), 4.99 (s, 2H), 7.00 (td, *J* = 7.4, 1.5 Hz, 1H), 7.05 – 7.25 (m, 7H).

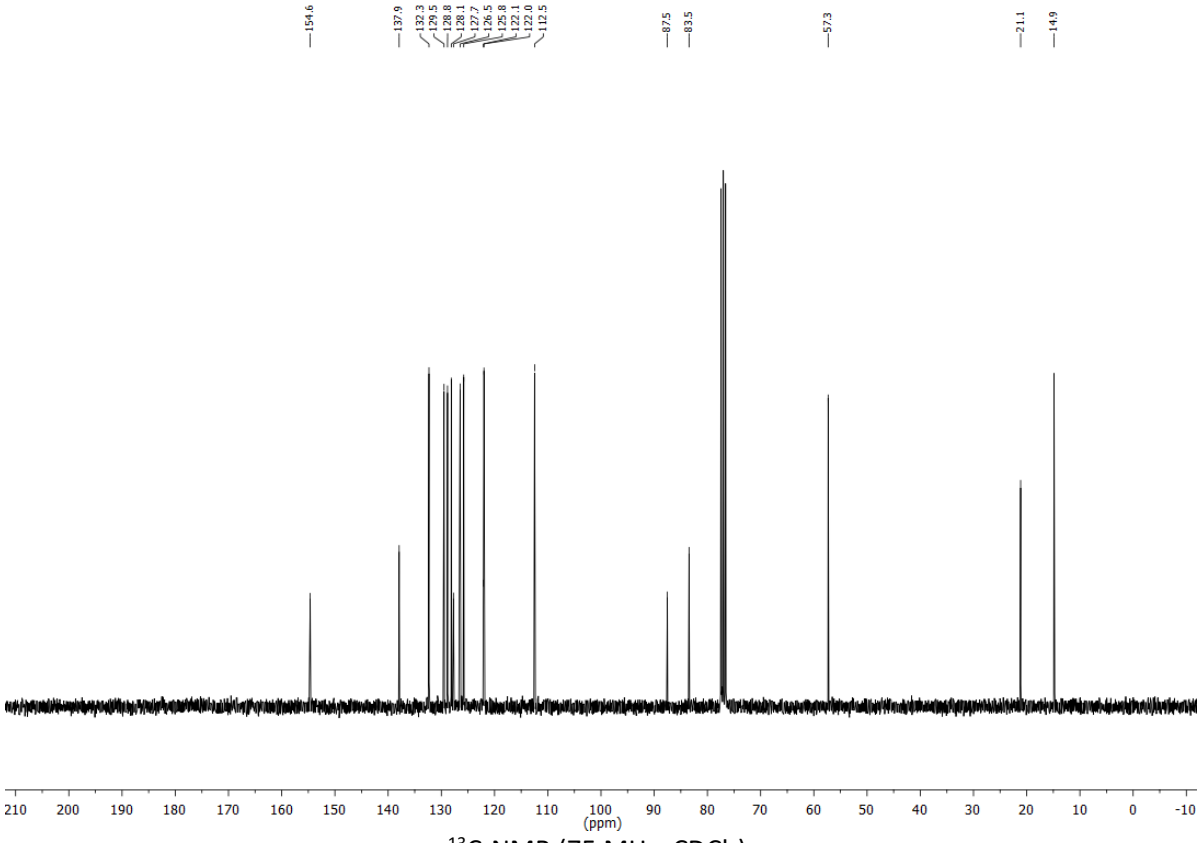
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.9, 21.1, 57.3, 83.5, 87.5, 112.5, 122.0, 122.1, 125.8, 126.5, 127.7, 128.1, 128.8, 129.5, 132.3, 137.9, 154.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3059, 2918, 2860, 2229, 1576, 1472, 1441, 1214, 999.

$C_{17}H_{16}OS$ calcd.: 268.0922, found: 268.0942 (GC-HRMS).

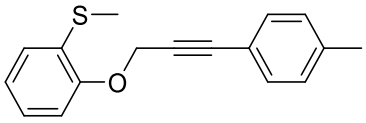


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(*p*-tolyl)prop-2-yn-1-yl)oxy)benzene (11k)



Compound **11h** was synthesized according GP2.

To a mixture of **SM2** (200.0 mg, 1.12 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and CuI (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 4-iodotoluene (295.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) which afforded a colorless solid (130 mg, 0.48 mmol, 43%).

m.p.: 52 °C.

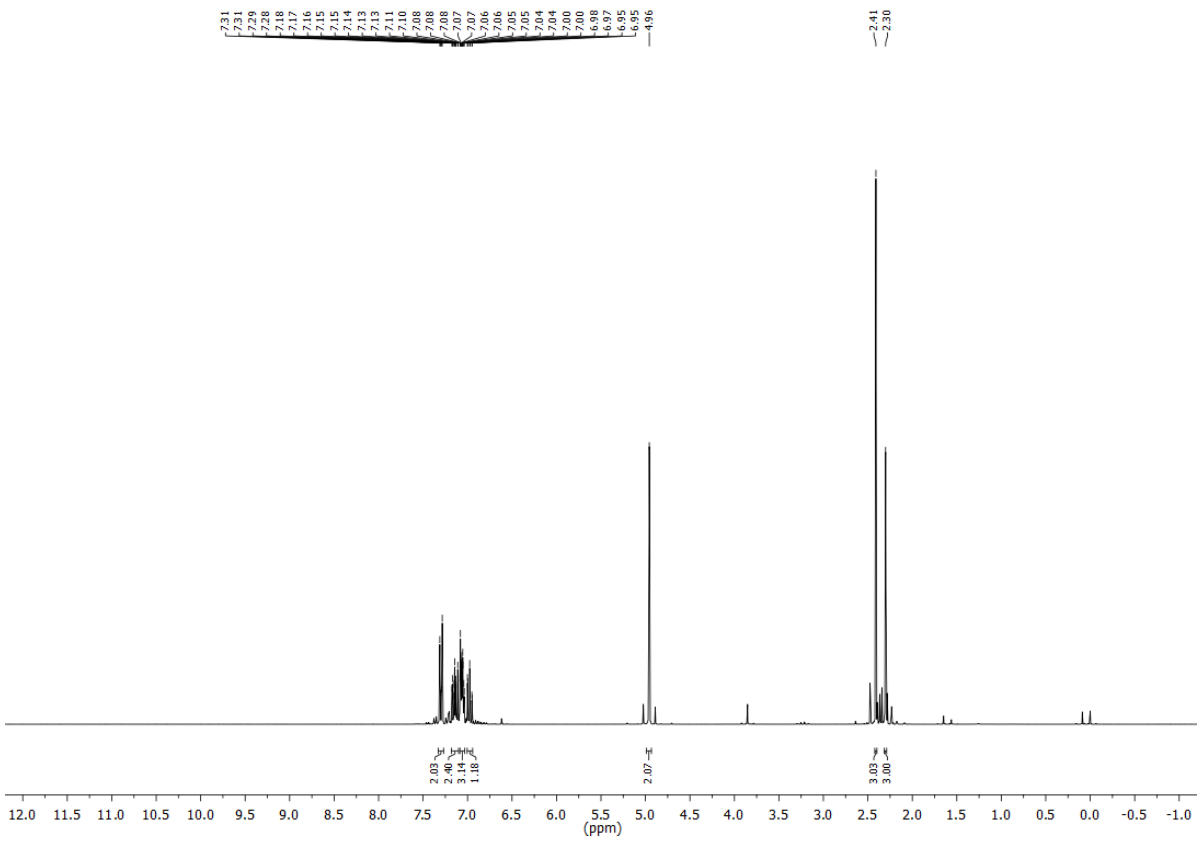
R_f = 0.19 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 2.41 (s, 3H), 4.96 (s, 2H), 6.97 (td, *J* = 7.5, 1.5 Hz, 1H), 7.03 – 7.09 (m, 3H), 7.10 – 7.18 (m, 2H), 7.27 – 7.33 (m, 2H).

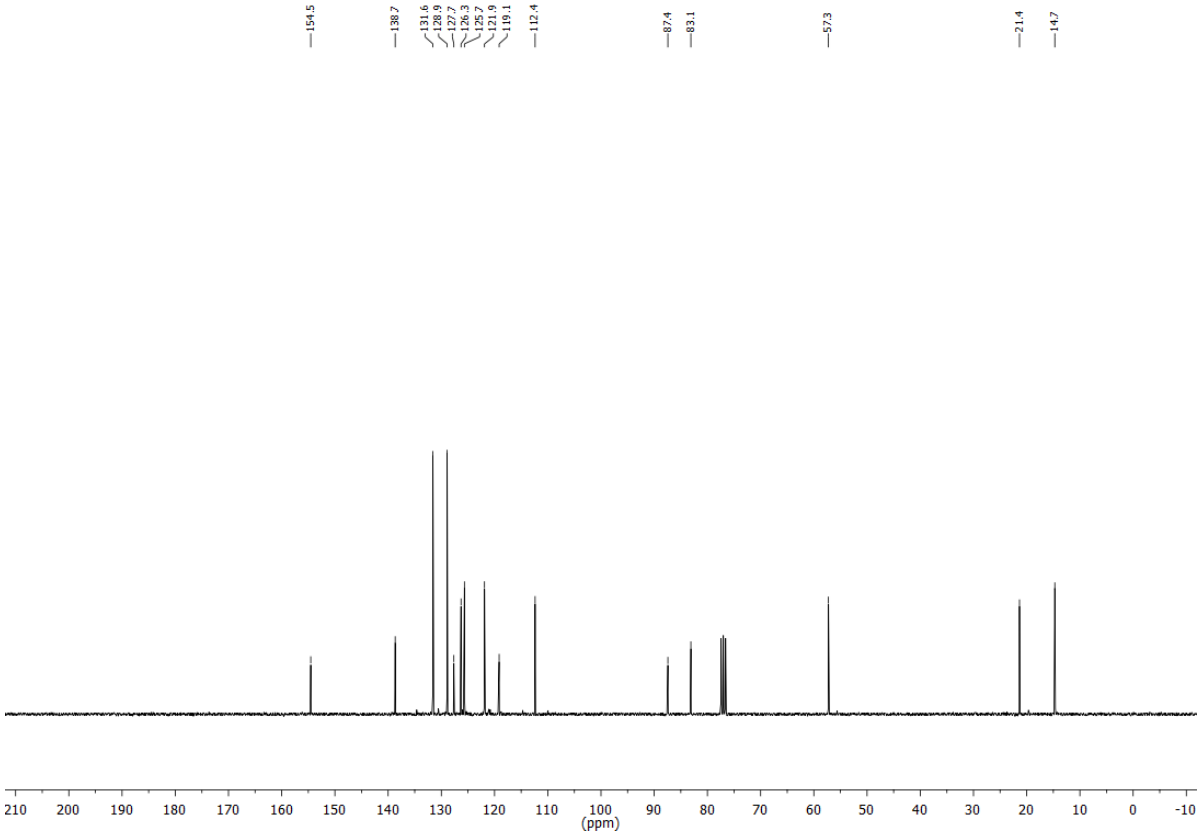
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.7, 21.4, 57.3, 83.1, 87.4, 112.4, 119.1, 121.9, 125.7, 126.3, 127.7, 128.9, 131.6, 138.7, 154.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2920, 2865, 2225, 1603, 1509, 1377, 1220, 1023.

$C_{17}H_{16}OS$ calcd.: 268.0922, found: 268.0947 (GC-HRMS).

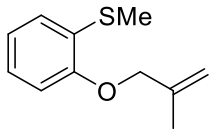


^{1}H-NMR (300 MHz, $CDCl_3$).



^{1}H-NMR (300 MHz, $CDCl_3$).

1-(Methylthio)- 2-((2-methylallyl)oxy)benzene (11l)



According to a reported procedure[18], a suspension of **SM1** (562.0 mg, 4.0 mmol, 1.0 equiv.) and K_2CO_3 (1.11 g, 8.0 mmol, 2.0 equiv.) in DMF (20 ml) was treated with 3-bromo-2-methyl-1-propene (648.0 mg, 0.49 ml, 4.8 mmol, 1.2 equiv.). The mixture was stirred at RT for 18 h. It was then quenched with H_2O, extracted with Et_2O (3 x 50 ml), washed with brine and dried over Na_2SO_4. The solvent was evaporated *in vacuo* to obtain the product as a pale yellow oil (777 mg, 4.33 mmol, quant.) which was used without further purification.

R_f = 0.61 (*n*-pentane:EtOAc = 20:1).

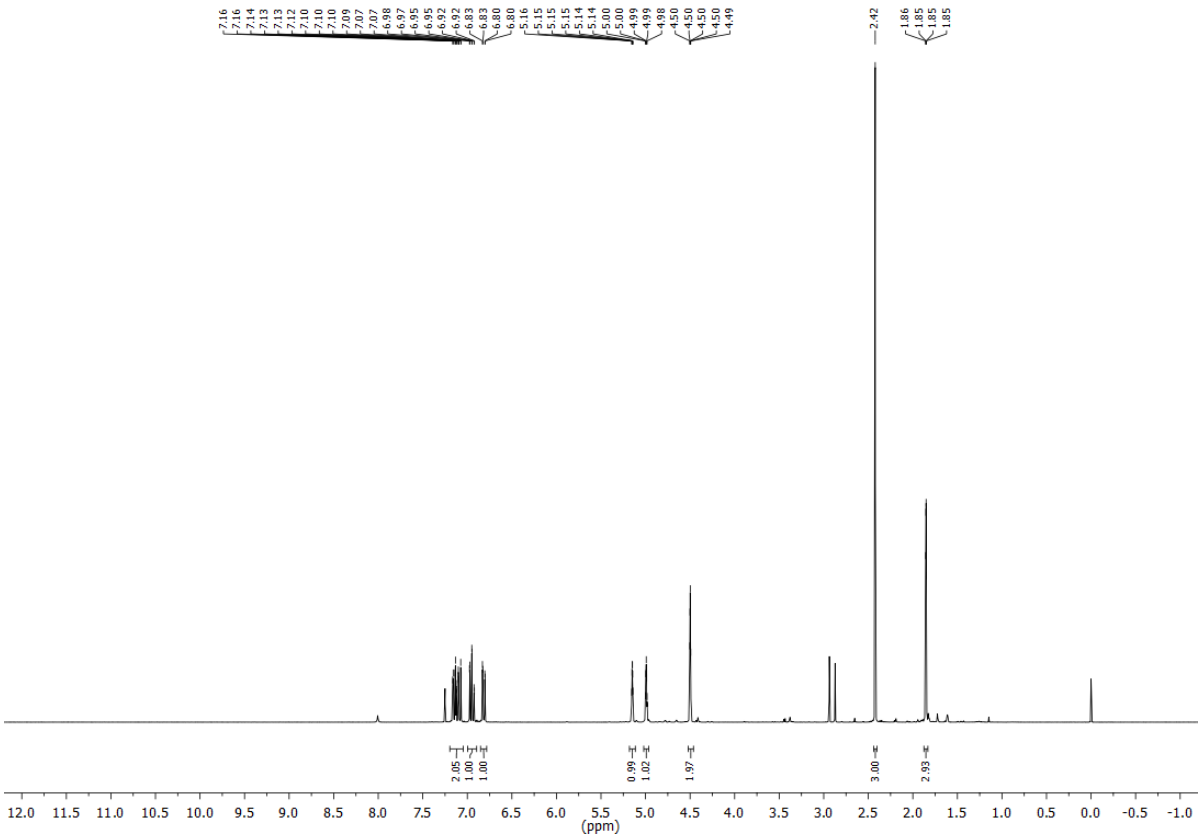
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.85 (dd, *J*=1.6, 0.8, 3H), 2.42 (s, 3H), 4.50 (q, *J*=1.1, 0.6, 2H), 4.99 (p, *J*=1.3, 1H), 5.15 (dq, *J*=1.6, 0.8, 1H), 6.81 (dd, *J*=8.0, 1.3, 1H), 6.95 (td, *J*=7.6, 1.3, 1H), 7.06 – 7.19 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.5, 19.4, 72.0, 111.4, 112.5, 121.3, 125.6, 125.8, 127.5, 140.6, 155.2.

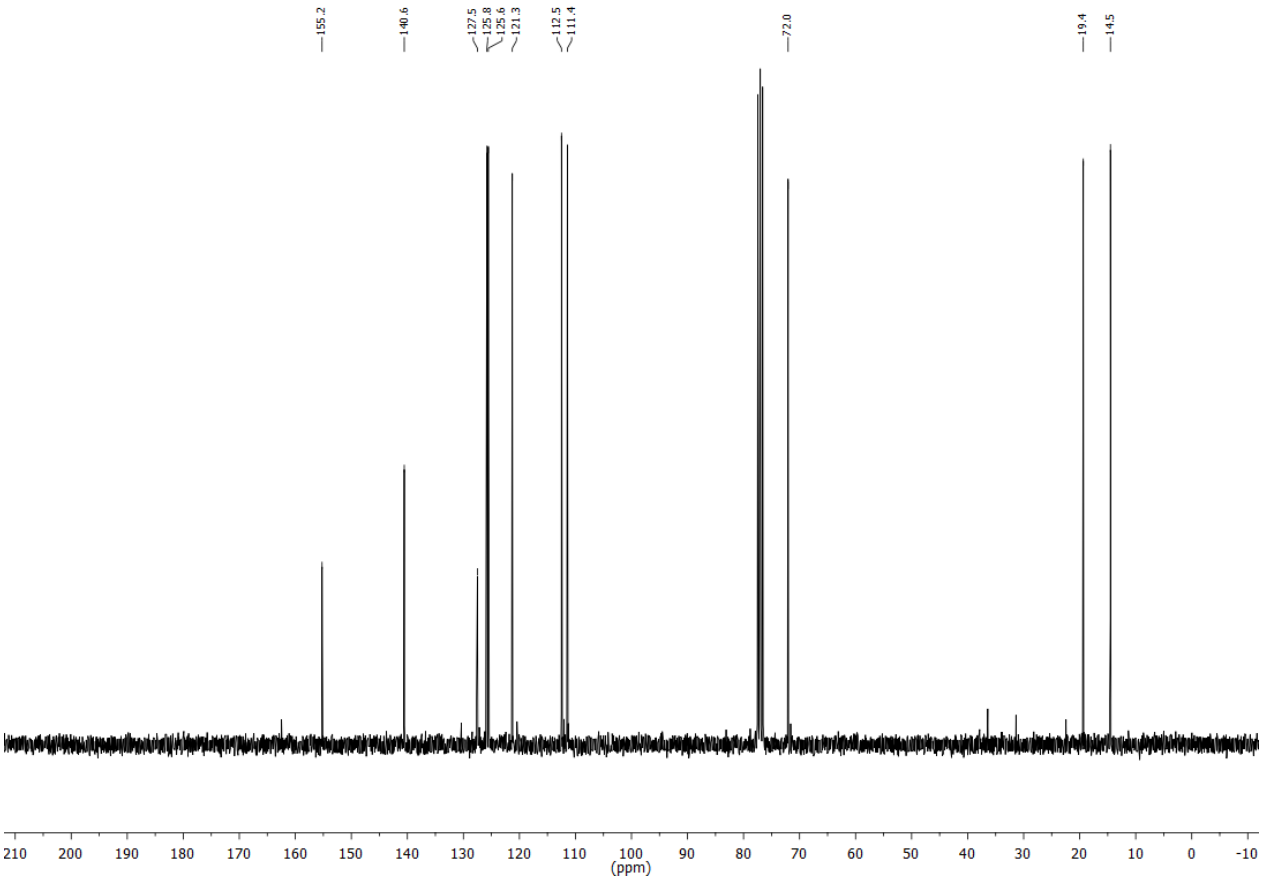
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3068, 2979, 2919, 2860, 1674, 1577, 1471, 1441, 1075, 1008.

$C_{11}H_{14}OS$ calcd.: 194.0765, found: 194.0773 (GC-HRMS).

[18] J. F. M. Hewitt, L. Williams, P. Aggarwal, C. D. Smith and D. J. France, *Chem. Sci.*, 2013, **4**, 3538.

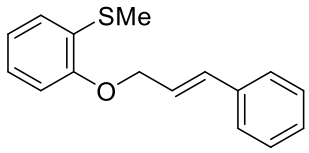


^{1}H-NMR (300 MHz, $CDCl_3$).



^{1}H-NMR (300 MHz, $CDCl_3$).

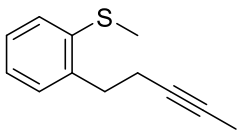
1-(Methylthio)- 2-(cinnamyloxy)benzene (11m)



Following a reported procedure[19], a solution of **SM1** (701 mg, 5.0 mmol, 1.0 equiv.) in THF (50 ml) was cooled to 0 °C and treated with NaH (400 mg of 60% dispersion, 10.0 mmol, 2.0 equiv.). After 30 min of stirring, cinnamyl bromide (1.97 g, 10.0 mmol, 2.0 equiv.) in THF (20 ml) followed by TBAI (277.0 mg, 0.75 mmol, 0.15 equiv.) were added, the reaction was warmed to RT and stirred overnight. It was then quenched with sat. NH_4Cl solution at 0 °C, diluted with H_2O, extracted with Et_2O (3 x 50 ml), washed with brine and dried over Na_2SO_4. The solvent was evaporated *in vacuo* to obtain an isomeric mixture after flash column chromatography (*n*-pentane:EtOAc = 50:1) as a colorless oil (1.04 g). This was used without further purification.

[19] T. Schitter, P. G. Jones and D. B. Werz, *Chem. Eur. J.*, 2018, **24**, 13446.

1-(Methylthio)-2-(pent-3-yn-1-yl)benzene (11n)



A solution of **SM3** (530.0 mg, 3.00 mmol, 1.00 equiv.) in dry THF (6 ml) was cooled to -78 °C. Then, *n*-butyllithium was added dropwise over 30 min to the stirred solution. After completion, the reaction mixture was stirred for 1 h at -78 °C. Afterwards, methyl iodide (426.0 mg, 3.00 mmol, 190.0 µl, 1.00 equiv.) was added, the mixture warmed to RT and stirred overnight. It was then quenched with sat. NH_4Cl solution, extracted with Et_2O (3 x 40 ml), washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 80:1) gave the desired product (505 mg, 2.65 mmol, 88%) as colorless oil.

Carried out in accordance to a reported procedure.[20]

R_f = 0.67 (*n*-pentane:EtOAc = 20:1).

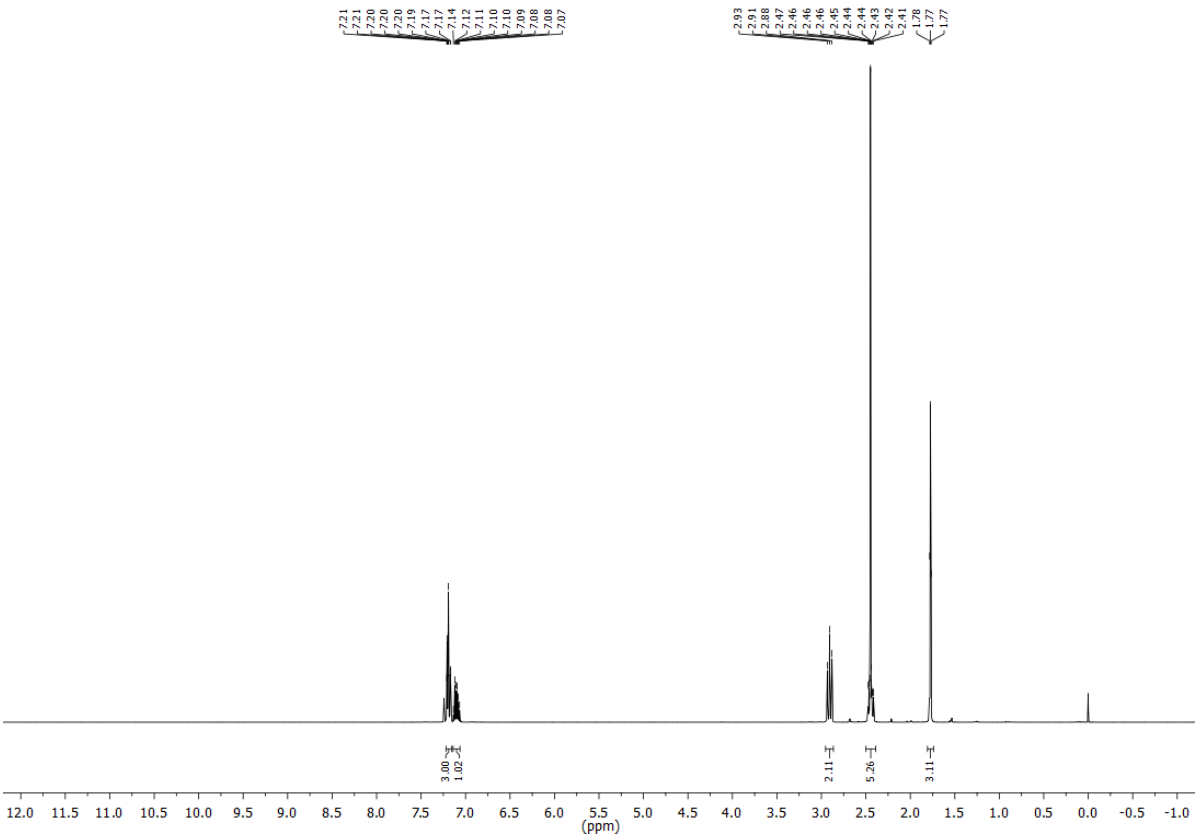
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.77 (t, *J* = 2.5 Hz, 3H), 2.39 – 2.51 (m, 5H), 2.87 – 2.94 (m, 2H), 7.06 – 7.14 (m, 1H), 7.15 – 7.22 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.5, 15.8, 19.2, 33.4, 76.2, 78.5, 124.9, 125.7, 127.0, 129.2, 137.2, 138.7.

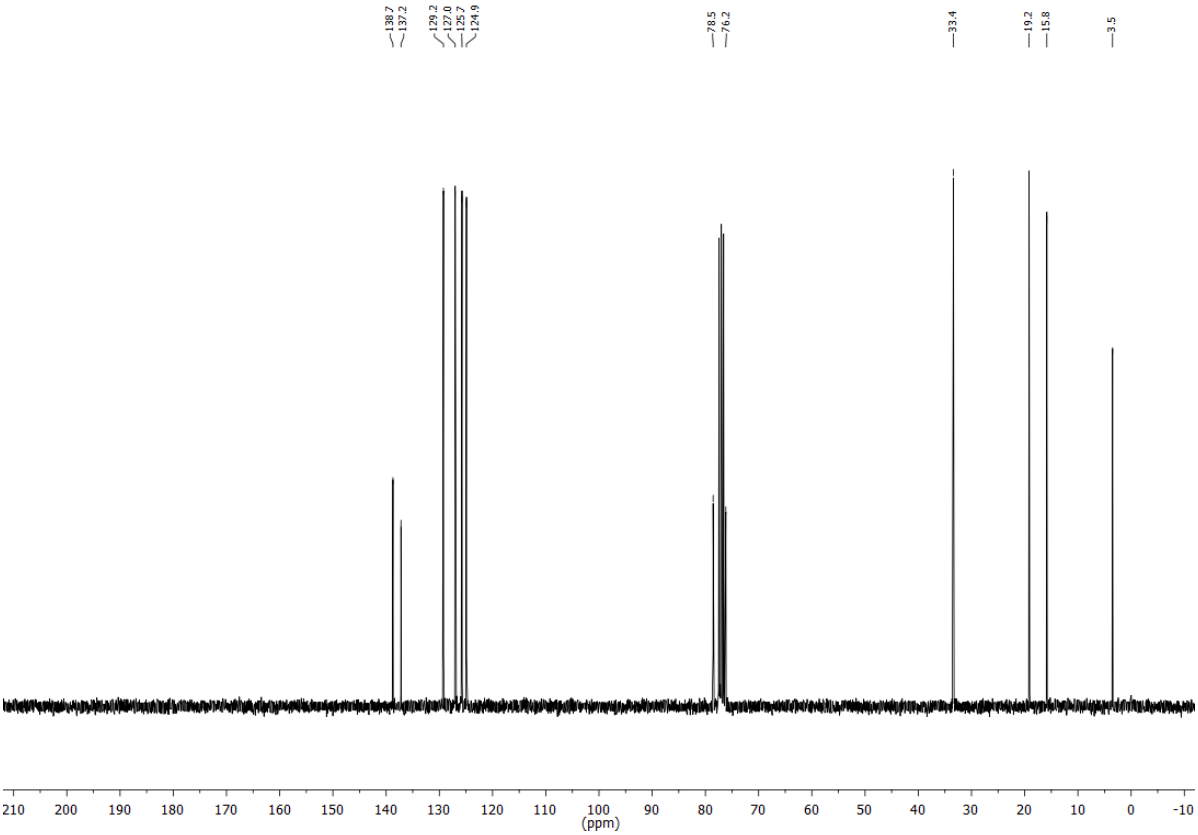
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2917, 2856, 1588, 1467, 1436, 1042.

$C_{12}H_{14}S$ calcd.: 190.0816, found: 190.0819 (GC-HRMS).

[20] E. H. P. Tan, G. C. Lloyd-Jones, J. N. Harvey, A. J. J. Lennox and B. M. Mills, *Angew. Chem.*, 2011, **123**, 9776.

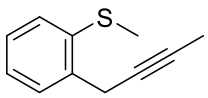


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(but-2-yn-1-yl)benzene (11o)



Propyne (5.52 mmol, 1 M in THF, 1.20 equiv.) in additional dry THF (40 ml) was treated with *n*-butyllithium at -78 °C. The reaction was kept at this temperature and stirred for further 2 h. A solution of 2-methylthio benzylbromide **SM3.2** (4.60 mmol, 1.00 g, 1.00 equiv.) in dry THF (10 ml) was added and the reaction mixture warmed to RT and quenched after 24 h with brine, diluted with water, extracted with Et_2O (3 x 50 ml) and dried over Na_2SO_4. After evaporation, the residue was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product as colorless oil (490 mg, 2.78 mmol, 60%).

Carried out in accordance to a reported procedure.[11]

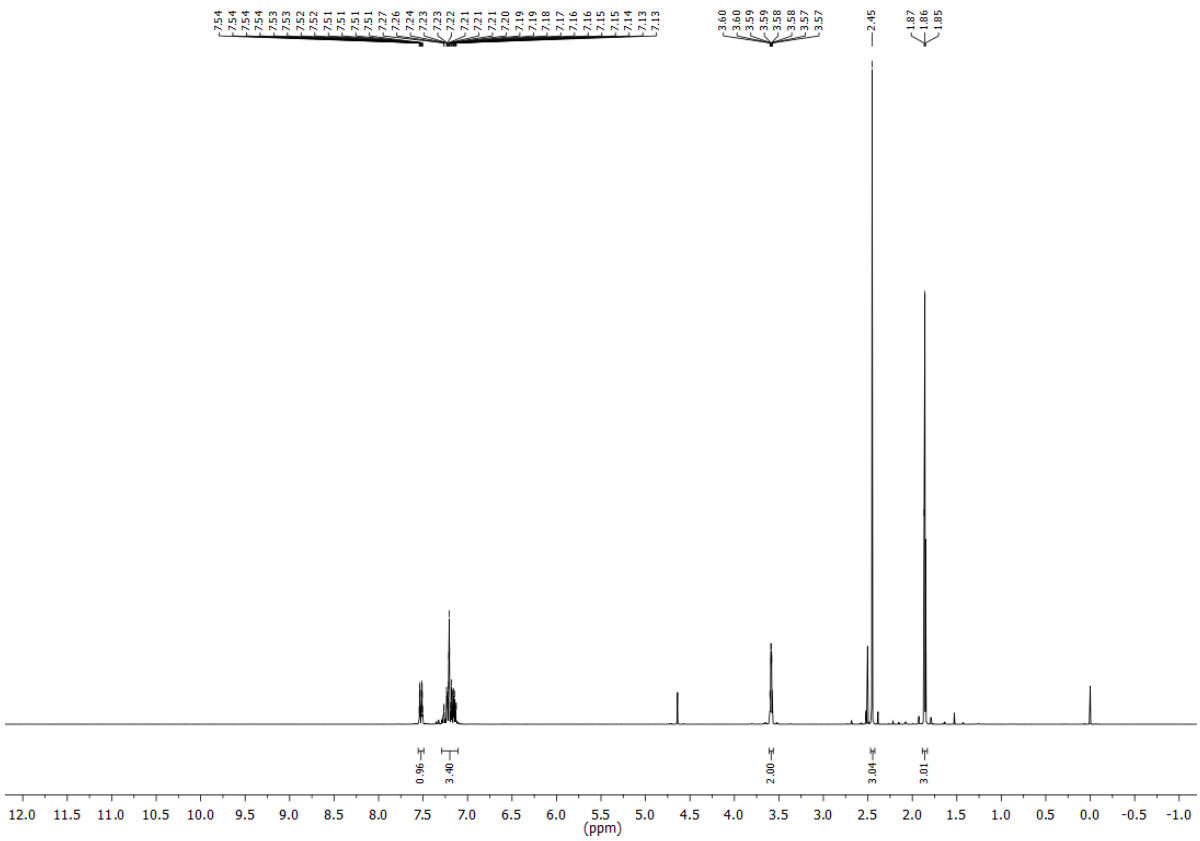
R_f = 0.52 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.86 (t, *J* = 2.6 Hz, 3H), 2.45 (s, 3H), 3.59 (q, *J* = 2.6, 2H), 7.11 – 7.29 (m, 3H), 7.52 (m, 1H).

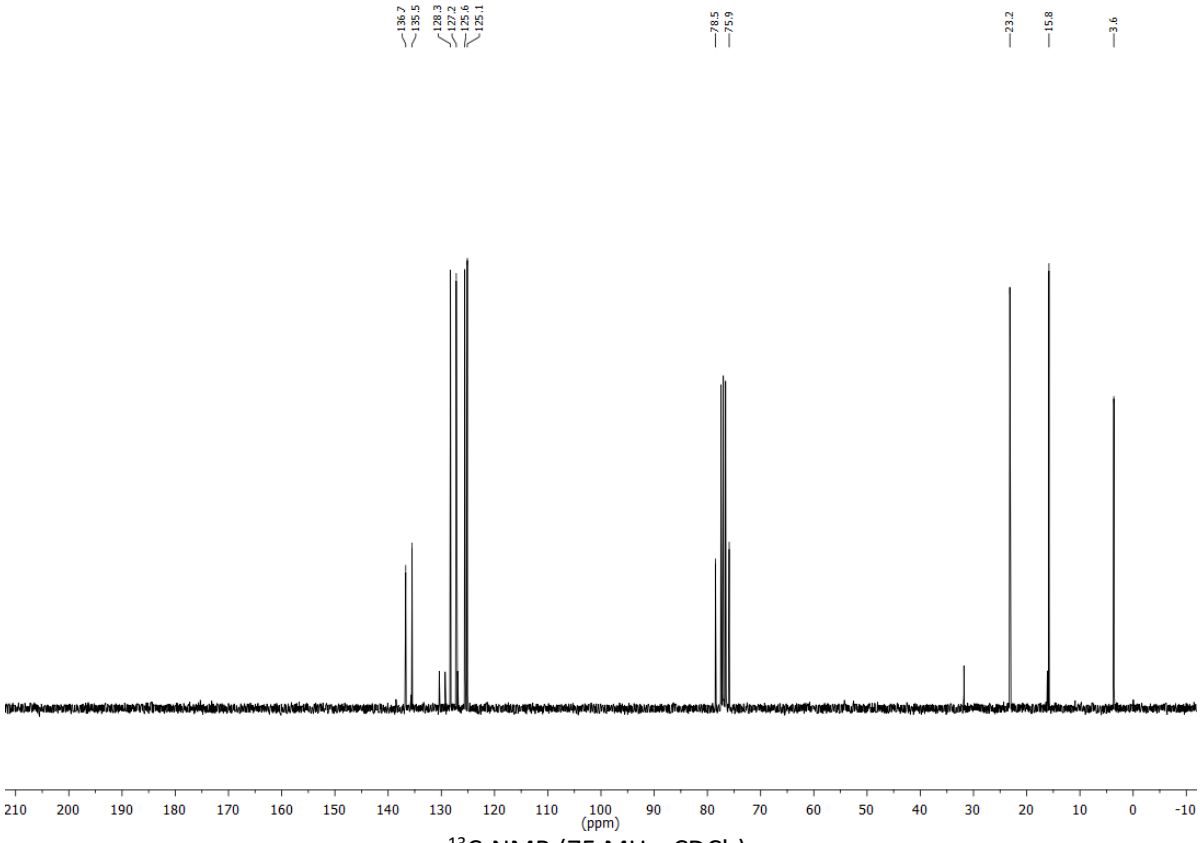
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.6, 15.8, 23.2, 75.9, 78.5, 125.1, 125.6, 127.2, 128.3, 135.5, 136.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2913, 2865, 1581, 1436, 1419, 1269, 1038, 963.

$C_{11}H_{12}S$ calcd.: 176.0660, found: 176.0657 (GC-HRMS).

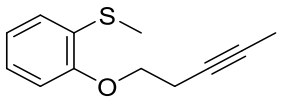


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((pent-3-yn-1-yl)oxy)benzene (11p)



Compound **11p** was synthesized according GP1.

A solution of **SM1** (350.0 mg, 2.50 mmol, 1.00 equiv.), PPh_3 (980.0 mg, 3.75 mmol, 1.50 equiv.) and 3-pentyn-1-ol (315.0 mg, 0.35 ml, 3.75 mmol, 1.50 equiv.) in dry toluene (15 ml) was cooled to 0 °C. DIAD (760 mg, 0.74 ml, 3.75 mmol, 1.50 equiv.) in dry toluene (12 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 50:1) gave the desired product (490 mg, 2.40 mmol, 96%) as a colorless solid.

m.p.: 69 °C.

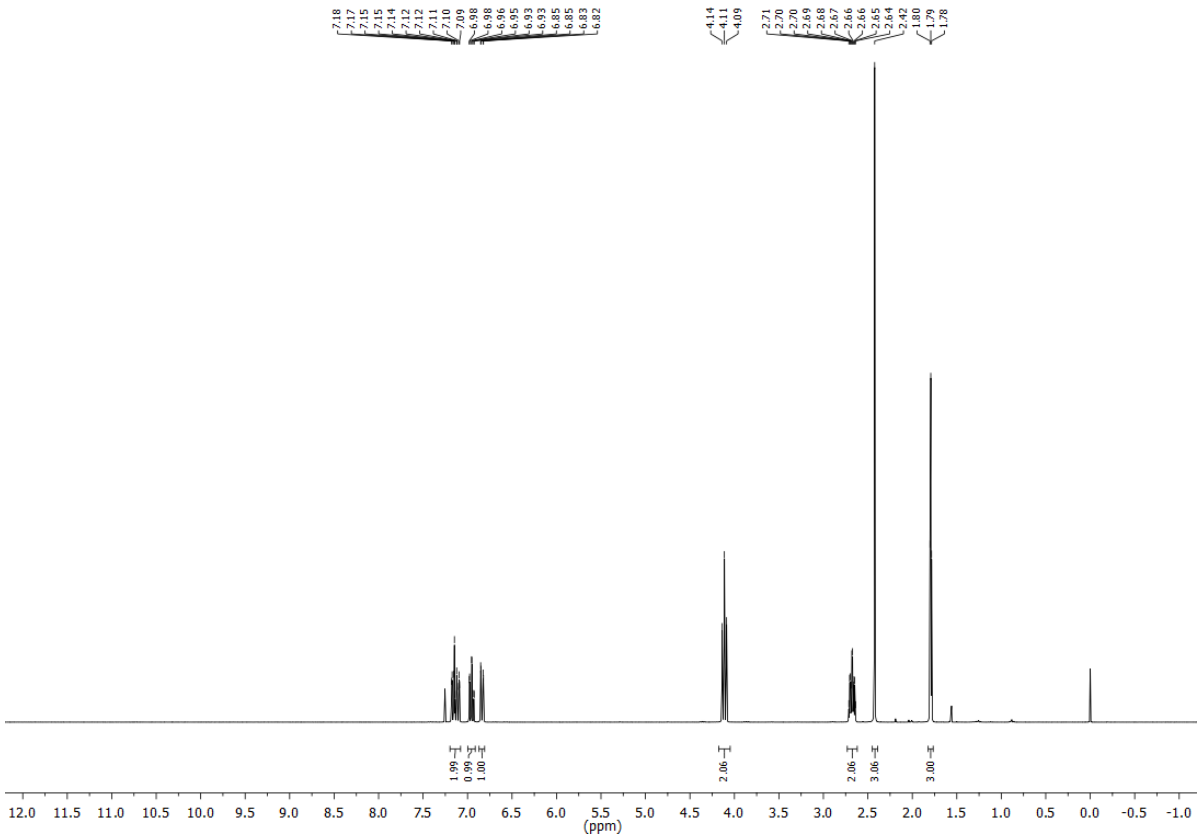
R_f = 0.70 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.79 (t, *J* = 2.6 Hz, 3H), 2.42 (s, 3H), 2.68 (tq, *J* = 7.5, 2.6 Hz, 2H), 4.11 (t, *J* = 7.4 Hz, 2H), 6.84 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.95 (td, *J* = 7.6, 1.3 Hz, 1H), 7.08 – 7.19 (m, 2H).

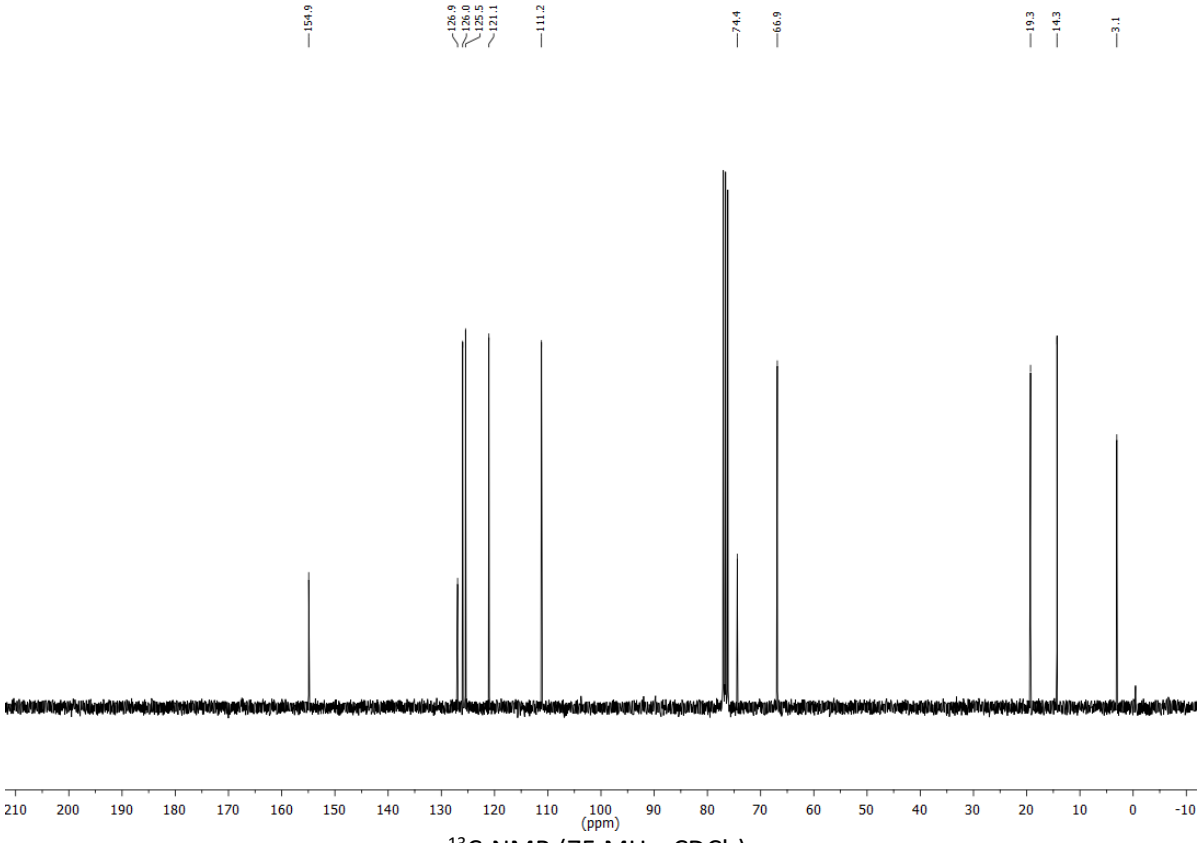
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.1, 14.3, 19.3, 66.9, 74.4, 111.2, 121.1, 125.5, 126.0, 126.9, 154.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3064, 2916, 2878, 2848, 1575, 1440, 1235, 1073, 1023.

$C_{12}H_{14}OS$ calcd.: 206.0765, found: 206.0781 (GC-HRMS).

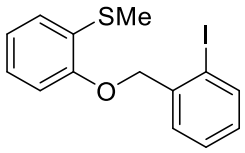


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((2-iodobenzyl)oxy)benzene (11.1q)



According to a reported procedure[21], a solution of **SM1** (1.68 g, 12.0 mmol, 1.2 equiv.) in DMF (20 ml) was treated with K_2CO_3 (4.15 g, 30.0 mmol, 3.0 equiv.). After 10 min of stirring, 1-(bromomethyl)-2-iodobenzene (2.97 g, 10.0 mmol, 1.0 equiv.) was added and the reaction was stirred overnight. It was then quenched with H_2O, extracted with Et_2O (3 x 100 ml), washed with brine and dried over Na_2SO_4. The solvent was evaporated *in vacuo* to obtain the product as a colorless solid (3.55 g, 9.96 mmol, quant.) which was used without further purification.

m.p.: 73 °C.

R_f = 0.53 (*n*-pentane:EtOAc = 20:1).

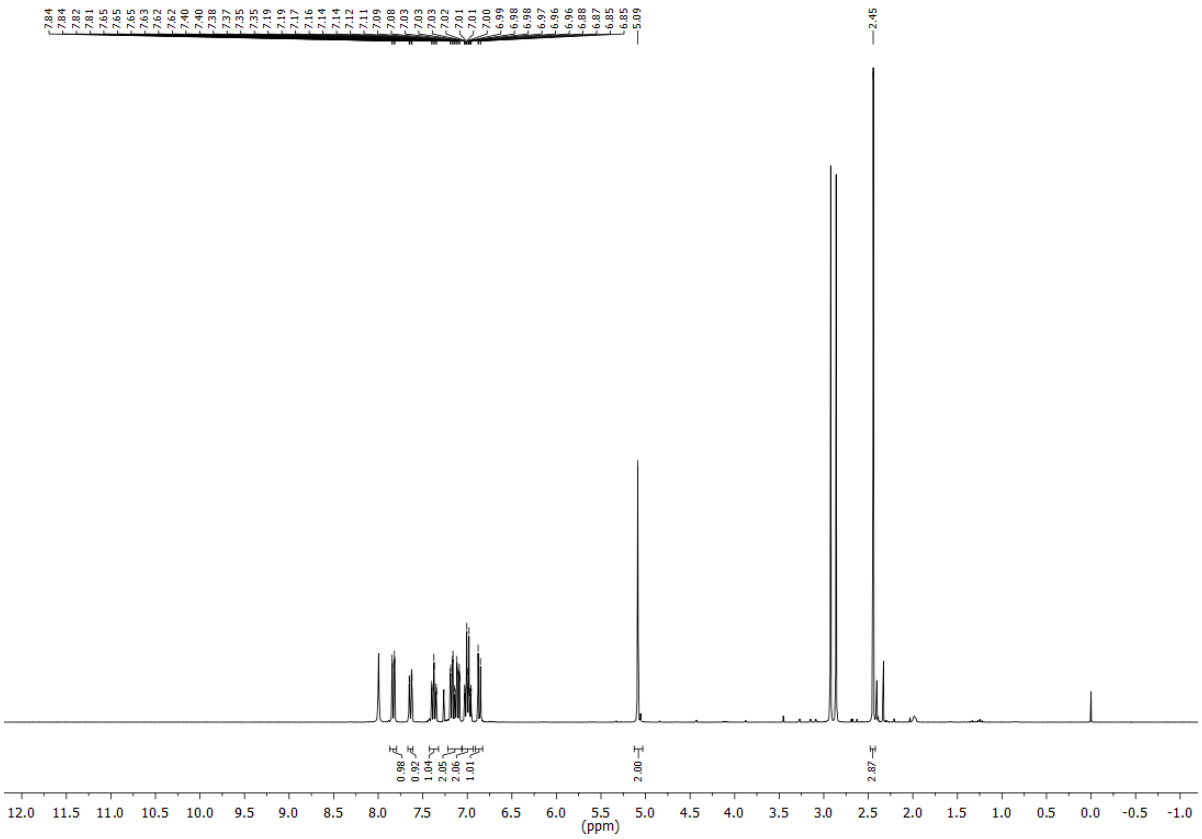
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 5.09 (s, 2H), 6.86 (dd, *J*=8.1, 1.3, 1H), 6.99 (tdd, *J*=7.6, 5.7, 1.5, 2H), 7.06 – 7.20 (m, 2H), 7.37 (td, *J*=7.6, 1.3, 1H), 7.61 – 7.67 (m, 1H), 7.83 (dd, *J*=7.9, 1.2, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.5, 74.1, 96.2, 111.7, 121.7, 125.6, 125.8, 127.6, 128.1, 128.4, 129.2, 138.9, 154.7, 162.4.

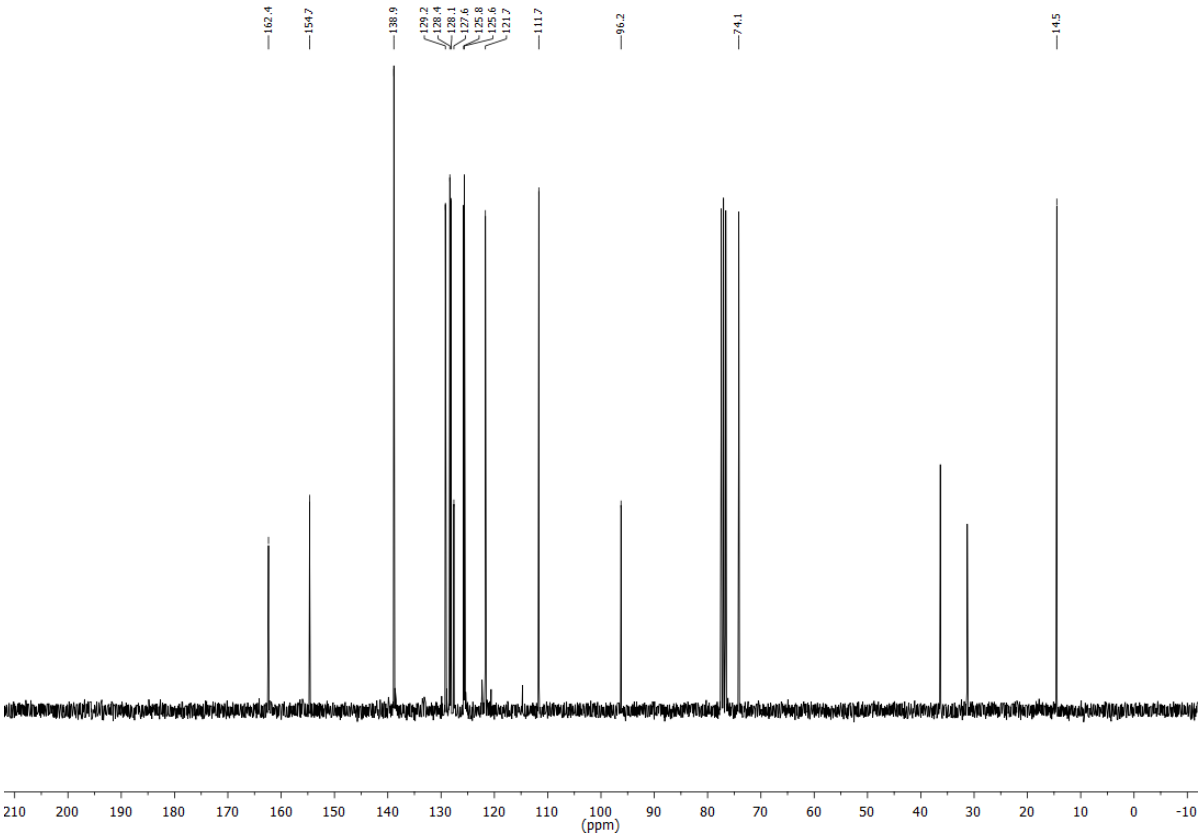
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2911, 2849, 1669, 1570, 1473, 1434, 1237, 1038, 1002.

$C_{14}H_{13}IOS$ calcd.: 355.9732, found: 355.9754 (GC-HRMS).

[21] H.-X. Zheng, X.-H. Shan, J.-P. Qu and Y.-B. Kang, *Org. Lett.*, 2018, **20**, 3310.

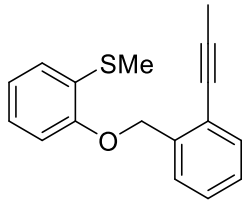


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)- 2-((2-(prop-1-yn-1-yl)benzyl)oxy)benzene (11.2q)



Similar to the synthesis of **11s**, compound **11.1q** (1.78 g, 5.0 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (71 mg, 2 mol%) and CuI (39 mg, 4 mol%) were dissolved in triethylamine (15 ml). Afterwards, propyne (5.0 ml, 5.0 mmol, 1.0 M in THF) was added via syringe. After stirring overnight, saturated NH_4Cl solution was added and the mixture was extracted with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtrated and evaporated. Silica gel column chromatography (*n*-pentane:EtOAc = 50:1 → 20:1) gave the desired product **11.2q** (990 mg, 3.69 mmol, 74%) as off-colorless oil.

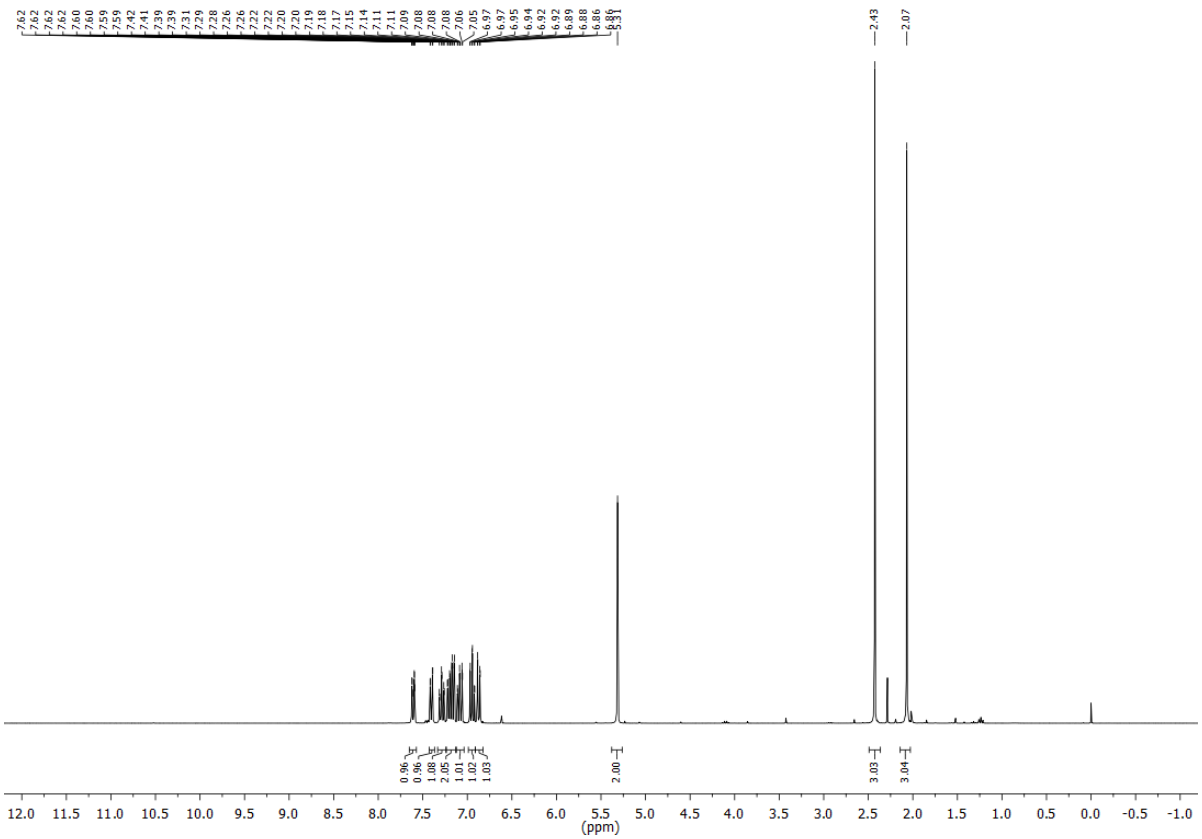
R_f = 0.47 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3H), 2.43 (s, 3H), 5.31 (s, 2H), 6.87 (dd, *J*=8.1, 1.3, 1H), 6.94 (td, *J*=7.6, 1.3, 1H), 7.08 (ddd, *J*=8.0, 7.4, 1.7, 1H), 7.18 (ddd, *J*=14.6, 7.5, 1.6, 2H), 7.29 (td, *J*=7.6, 1.5, 1H), 7.40 (dd, *J*=7.5, 1.5, 1H), 7.61 (dq, *J*=7.7, 0.8, 1H).

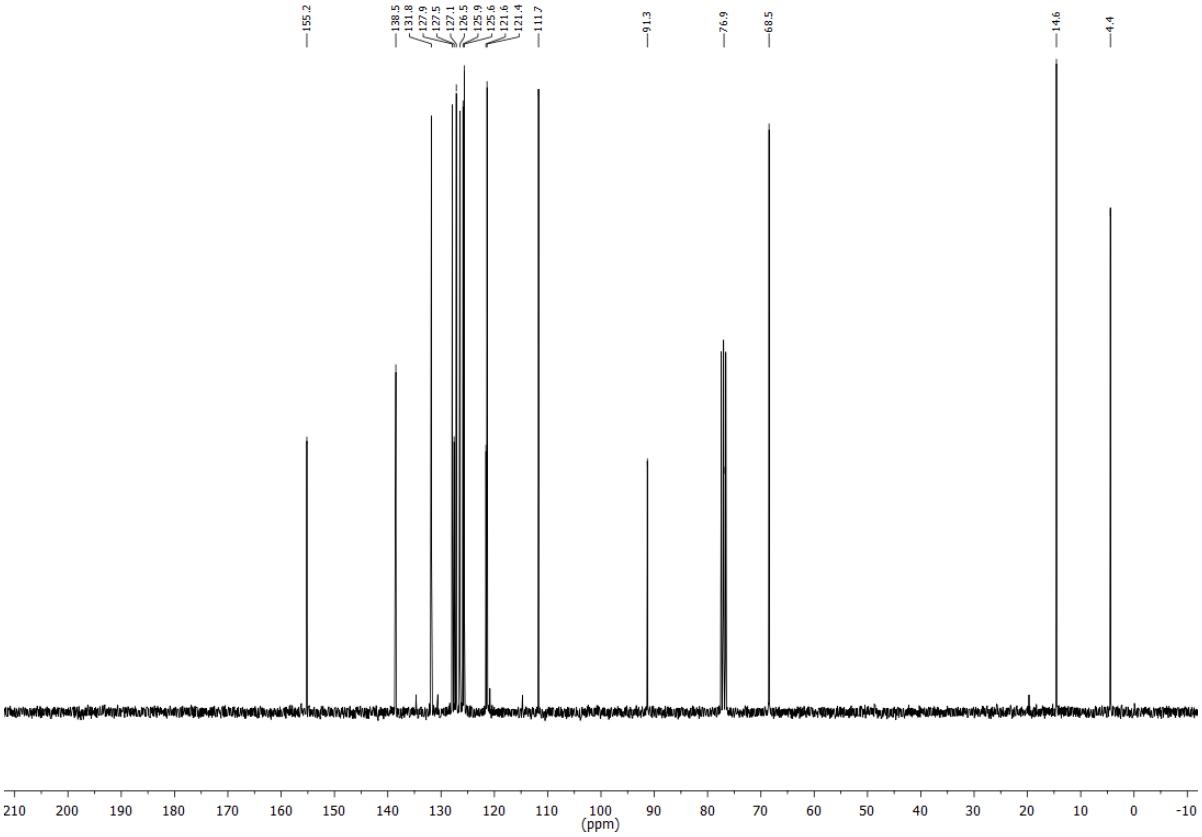
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.4, 14.6, 68.5, 76.9, 91.3, 111.7, 121.4, 121.6, 125.6, 125.9, 126.5, 127.1, 127.5, 127.9, 131.8, 138.5, 155.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3062, 2917, 2851, 1576, 1473, 1440, 1229, 1073, 1032.

$C_{17}H_{16}OS$ calcd.: 268.0922, found: 268.0903 (GC-HRMS).

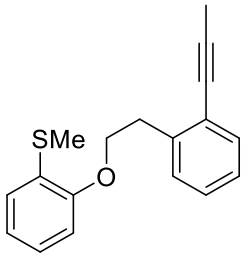


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)- 2-(2-(prop-1-yn-1-yl)phenethoxy)benzene (11r)



Compound **11r** was synthesized according GP1.

A solution of **SM1** (701.0 mg, 5.00 mmol, 1.00 equiv.), PPh_3 (1.97 g, 7.50 mmol, 1.50 equiv.) and alcohol **5.1e** (962.0 mg, 6.00 mmol, 1.20 equiv.) in dry toluene (30 ml) was cooled to 0 °C. DIAD (1.52 g, 1.50 ml, 7.50 mmol, 1.50 equiv.) in dry toluene (24 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 50:1) gave the desired product (714 mg, 2.53 mmol, 51%) as a pale yellow oil.

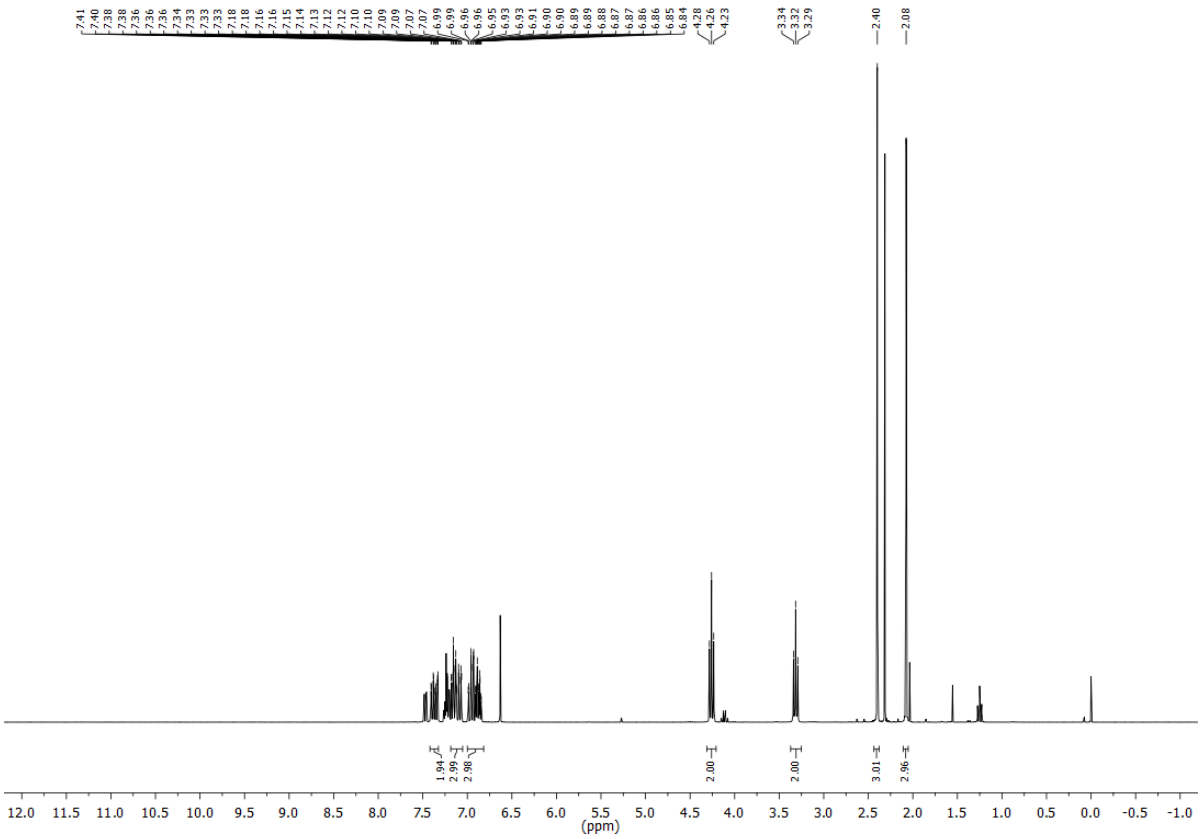
R_f = 0.47 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.08 (s, 3H), 2.40 (s, 3H), 3.32 (t, *J*=7.3, 2H), 4.26 (t, *J*=7.3, 2H), 6.82 – 7.02 (m, 3H), 7.05 – 7.19 (m, 3H), 7.31 – 7.42 (m, 2H).

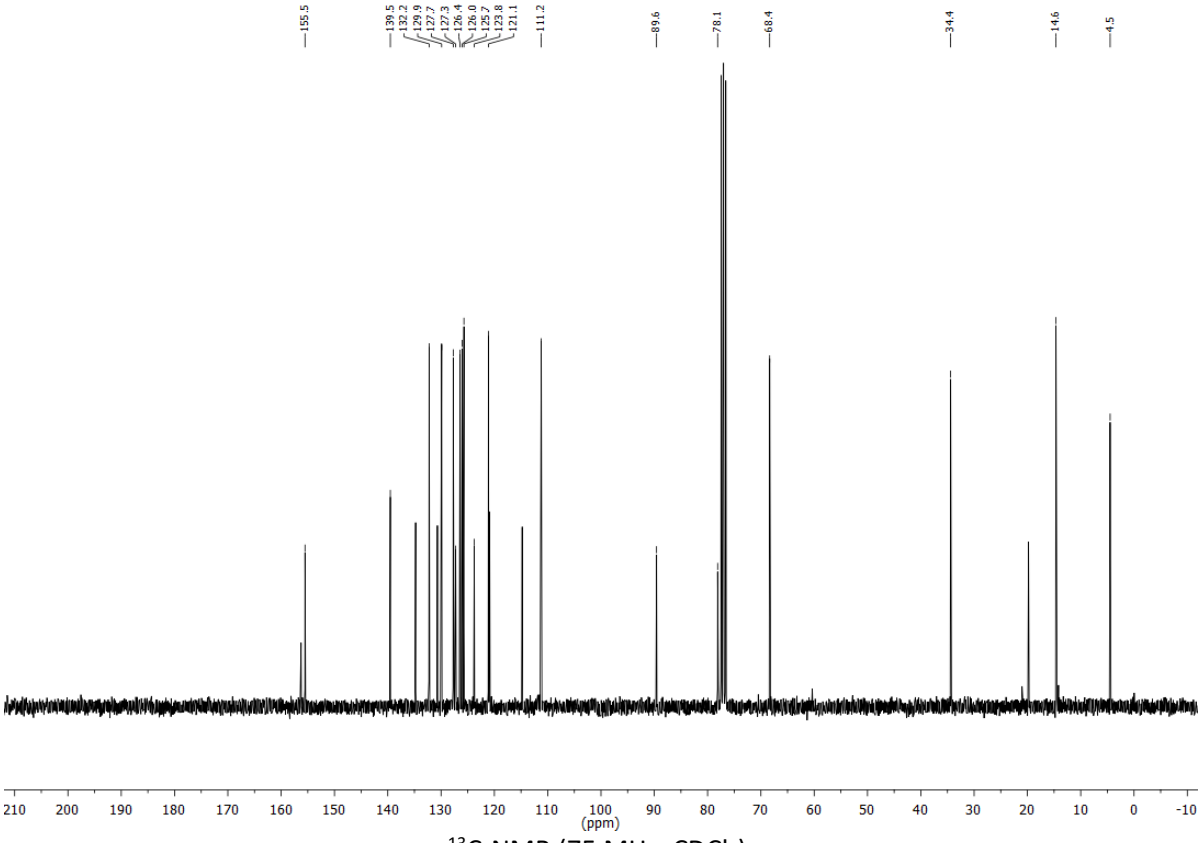
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.5, 14.6, 34.4, 68.4, 78.1, 89.6, 111.2, 121.1, 123.8, 125.7, 126.0, 126.4, 127.3, 127.7, 129.9, 132.2, 139.5, 155.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3062, 3022, 2920, 2861, 1575, 1470, 1436, 1235, 1071, 1015.

$C_{18}H_{18}OS$ calcd.: 282.1078, found: 282.1053 (GC-HRMS).

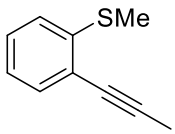


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(prop-1-yn-1-yl)benzene (11s)



According to a reported procedure[22] 2-iodothioanisole (1.25 g, 5.0 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (71 mg, 2 mol%) and CuI (39 mg, 4 mol%) were dissolved in triethylamine (15 ml). The reaction was stirred at RT and propyne (5.0 ml, 5.0 mmol, 1.0 M in THF) was added via syringe. After 5.5 h, saturated NH_4Cl solution was added and the mixture was extracted with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtrated and evaporated. Silica gel column chromatography (*n*-pentane:EtOAc = 80:1) gave the desired product **11s** (723 mg, 4.46 mmol, 89%) as pale orange solid.

m.p.: 30 °C.

$\mathbf{R_f}$ = 0.51 (*n*-pentane:EtOAc = 50:1).

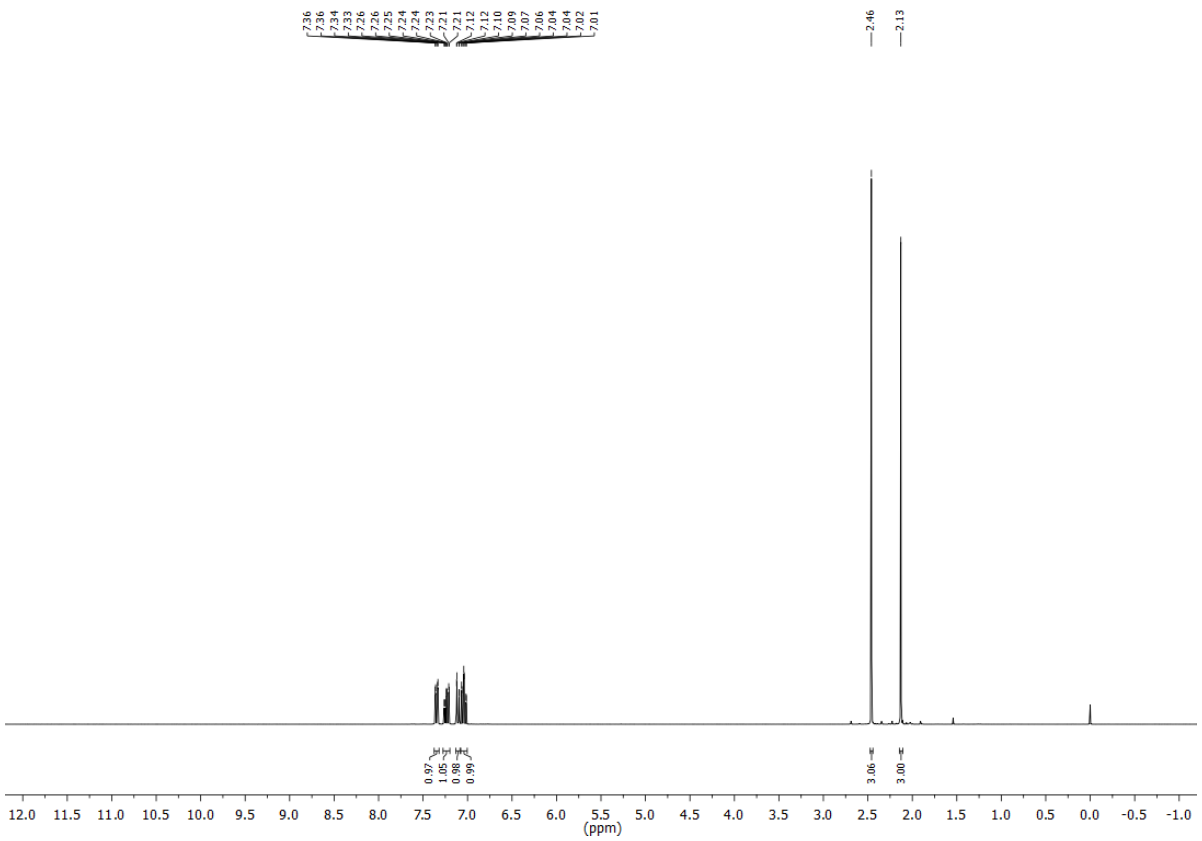
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3H), 2.46 (s, 3H), 7.04 (td, *J* = 7.5, 1.3 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.20 – 7.27 (m, 1H), 7.35 (dd, *J* = 7.6, 1.5 Hz, 1H).

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3055, 2982, 2915, 2846, 2230, 1580, 1462, 1431, 1275, 1073, 1035.

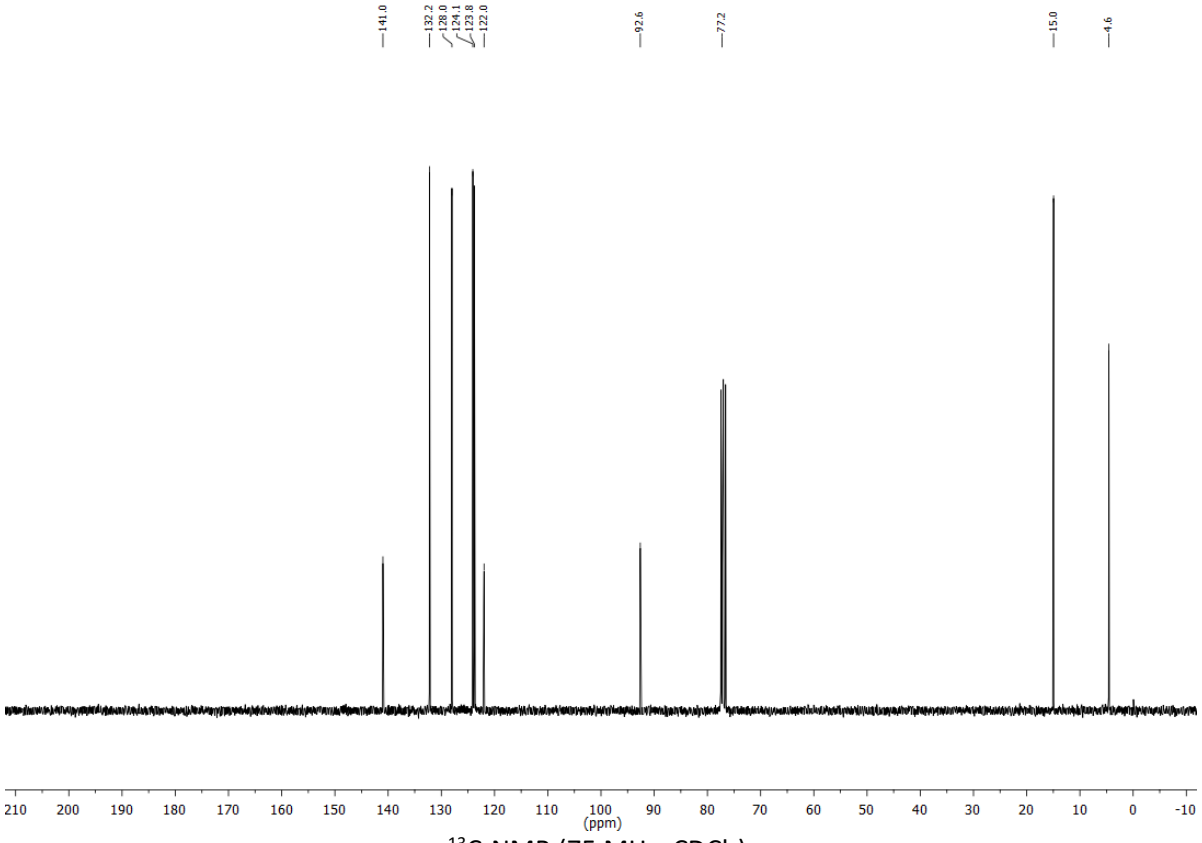
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.6, 15.0, 77.2, 92.6, 122.0, 123.8, 124.1, 128.0, 132.2, 141.0.

$C_{10}H_{10}S$ calcd.: 162.0503, found: 162.0509 (GC-HRMS).

[22] S. Gao, Z. Wu, X. Fang, A. Lin and H. Yao, *Org. Lett.*, 2016, **18**, 3906.

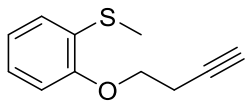


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((but-3-yn-1-yl)oxy)benzene (11t)



A solution of **SM1** (500.0 mg, 3.57 mmol, 1.00 equiv.), PPh_3 (940.0 mg, 3.57 mmol, 1.00 equiv.) and 3-butyn-1-ol (250.0 mg, 0.27 ml, 3.57 mmol, 1.00 equiv.) in dry toluene (10 ml) was cooled to 0 °C. DEAD (630 mg, 0.57 ml, 3.57 mmol, 1.00 equiv.) in dry toluene (2 ml) was added to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred for 17 h. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 40:1) gave the desired product (200 mg, 1.04 mmol, 29%) as colorless solid.

Carried out in accordance to a reported procedure.[1]

m.p.: 71 °C.

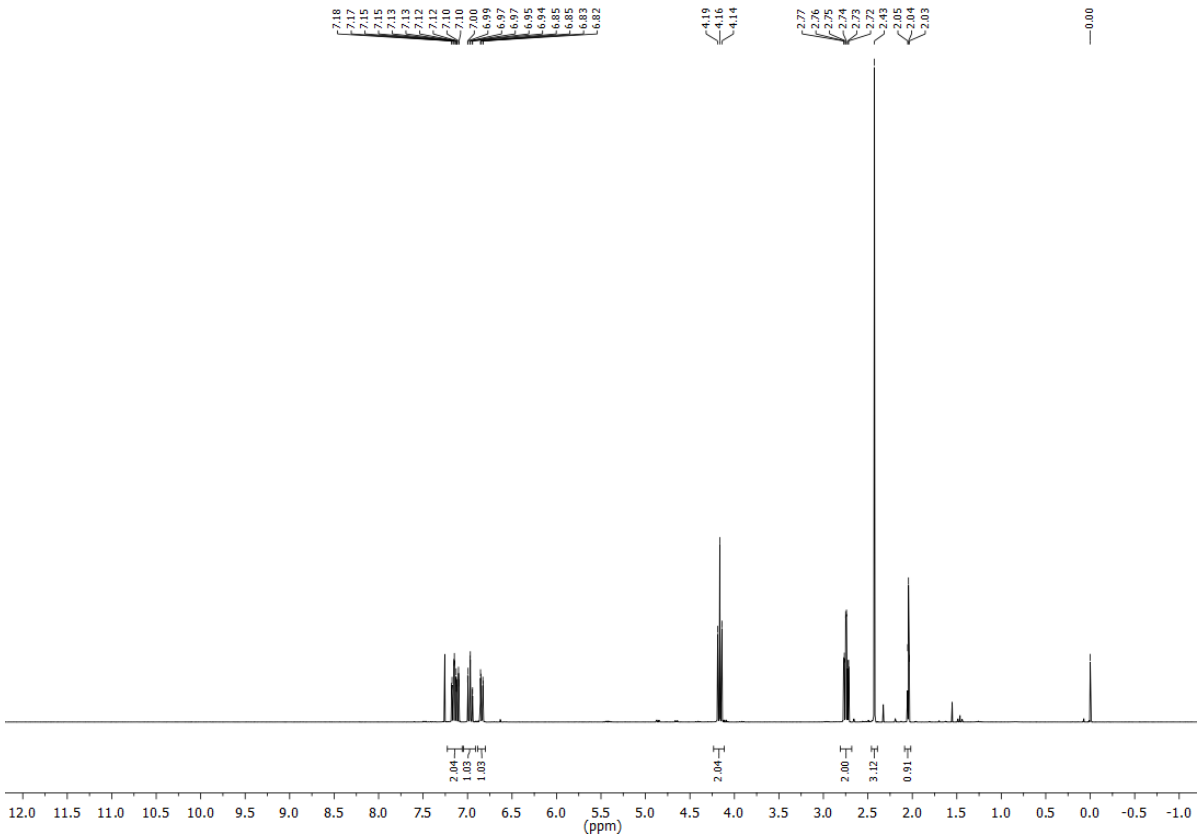
R_f = 0.35 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.04 (t, *J* = 2.7 Hz, 1H), 2.43 (s, 3H), 2.74 (td, *J* = 7.2, 2.7 Hz, 2H), 4.16 (t, *J* = 7.2 Hz, 2H), 6.84 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.97 (td, *J* = 7.6, 1.3 Hz, 1H), 7.09 – 7.19 (m, 2H).

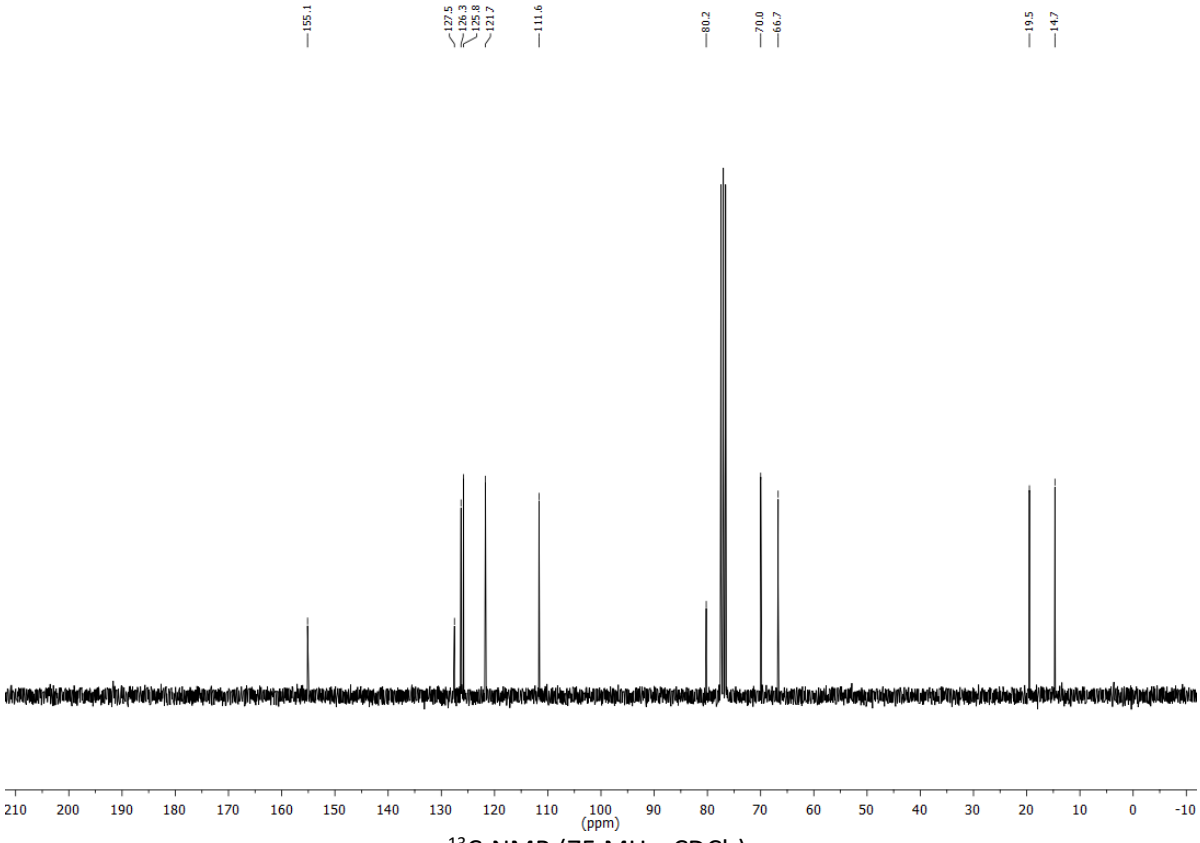
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.7, 19.5, 66.7, 70.0, 80.2, 111.6, 121.7, 125.8, 126.3, 127.5, 155.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3275, 3062, 2955, 1577, 1439, 1237, 1023.

$C_{11}H_{12}OS$ calcd.: 192.0609, found: 192.0624 (GC-HRMS).

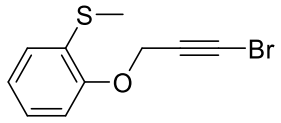


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-bromoprop-2-yn-1-yl)oxy)benzene (11u)



A solution of **SM1** (457.0 mg, 3.26 mmol, 1.00 equiv.) and 3-bromoprop-2-yn-1-yl 4-methylbenzenesulfonate[23] (1.13 g, 3.91 mmol, 1.20 equiv.) in dry DMF (35 ml) was treated with potassium carbonate (8.15 mmol, 1.13 g, 2.5 equiv.). After stirring overnight, the solvent was removed under reduced pressure via co-evaporation with toluene. The crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 80:1) to afford the title compound (596 mg, 2.32 mmol, 71%) as off-white solid.

Carried out in accordance to a reported procedure.[24]

m.p.: 64 °C.

R_f = 0.33 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 4.79 (s, 2H), 6.93 – 7.04 (m, 2H), 7.12 – 7.20 (m, 2H).

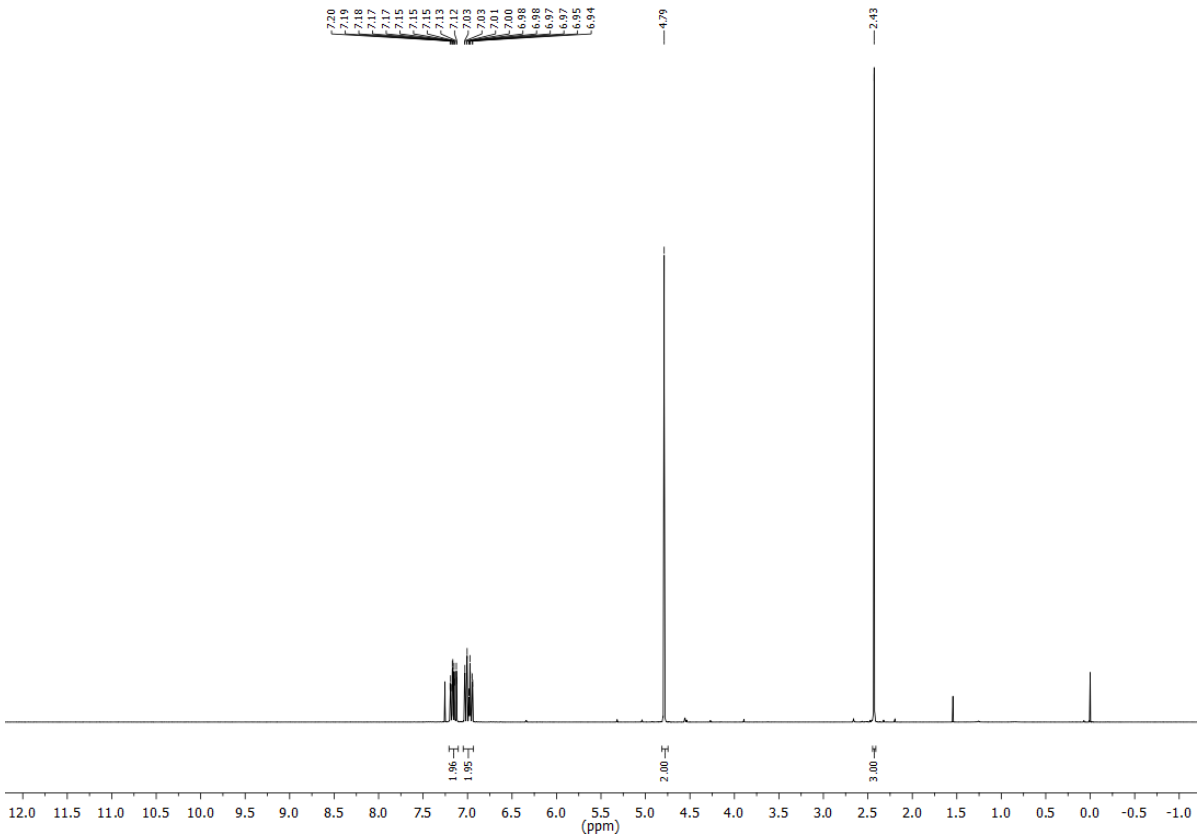
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.8, 47.9, 57.3, 74.9, 112.2, 122.2, 125.8, 126.5, 127.8, 154.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3062, 2988, 2921, 2211, 1575, 1473, 1438, 1215, 1073, 1035.

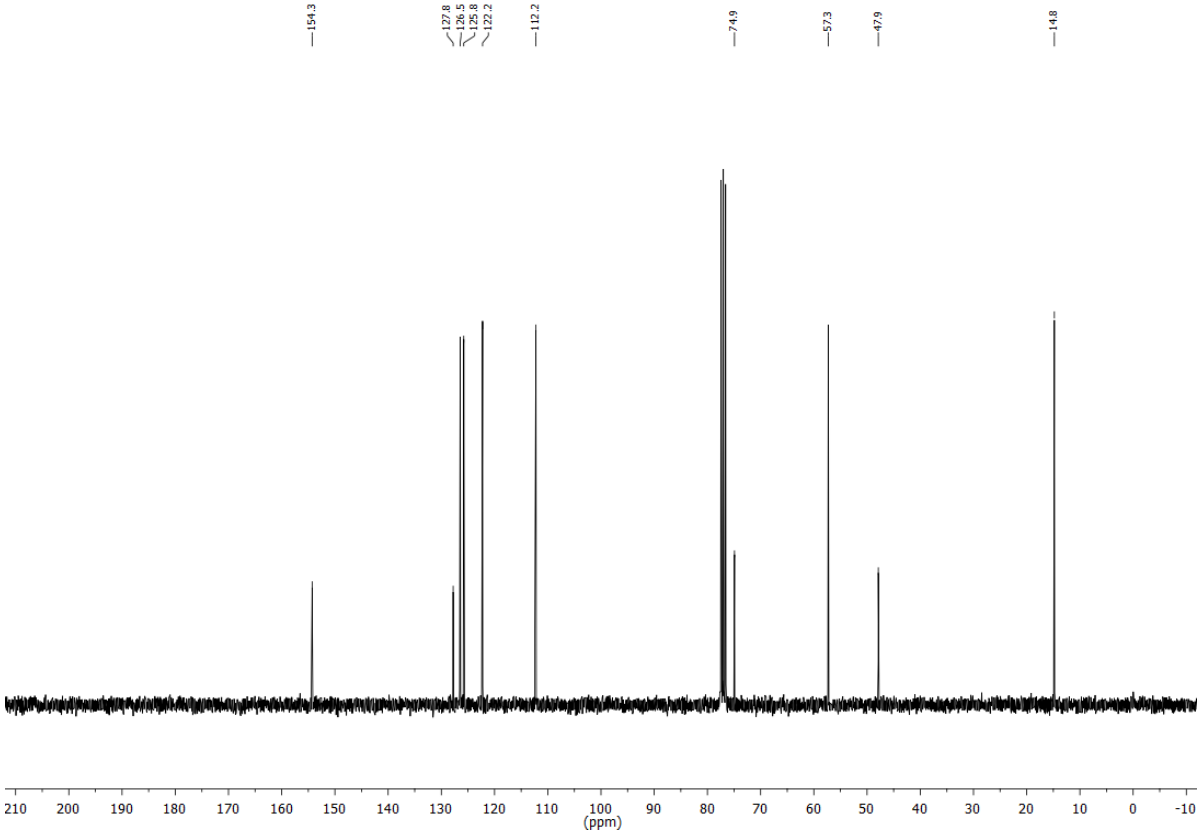
$C_{10}H_9BrOS$ calcd.: 257.9537, found: 257.9558 (GC-HRMS).

[23] CA2141376 A1.

[24] B. Findlay, G. G. Zhanel and F. Schweizer, *Bioorg. Med. Chem. Lett.*, 2012, **22**, 1499.

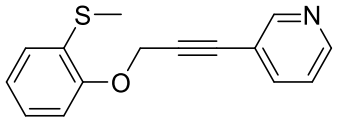


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(3-pyridyl)prop-2-yn-1-yl)oxy)benzene (11v)



Compound **11r** was synthesized according GP2.

To a mixture of **SM2** (100.0 mg, 0.56 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (12.0 mg, 17.1 µmol, 0.03 equiv.) and CuI (7.0 mg, 36.8 µmol, 0.06 equiv.) in dry triethylamine (4 ml) was added 3-iodopyridine (138.0 mg, 0.67 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 20:1) which afforded a pale yellow solid (104 mg, 0.41 mmol, 73%).

m.p.: 49 °C.

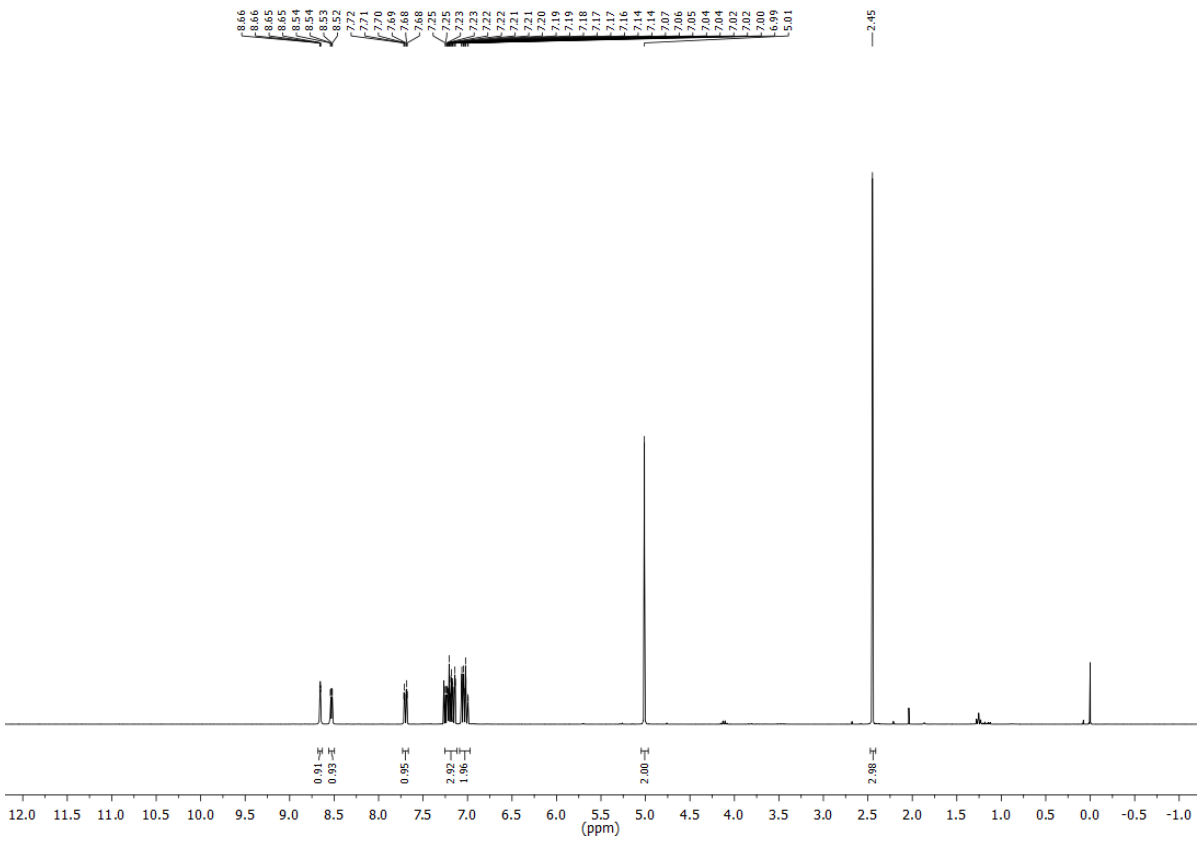
$\mathbf{R_f}$ = 0.06 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 2H), 5.01 (s, 2H), 6.99 – 7.08 (m, 2H), 7.13 – 7.25 (m, 3H), 7.70 (dt, *J* = 7.9, 1.9 Hz, 1H), 8.53 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.66 (dd, *J* = 2.2, 0.9 Hz, 1H).

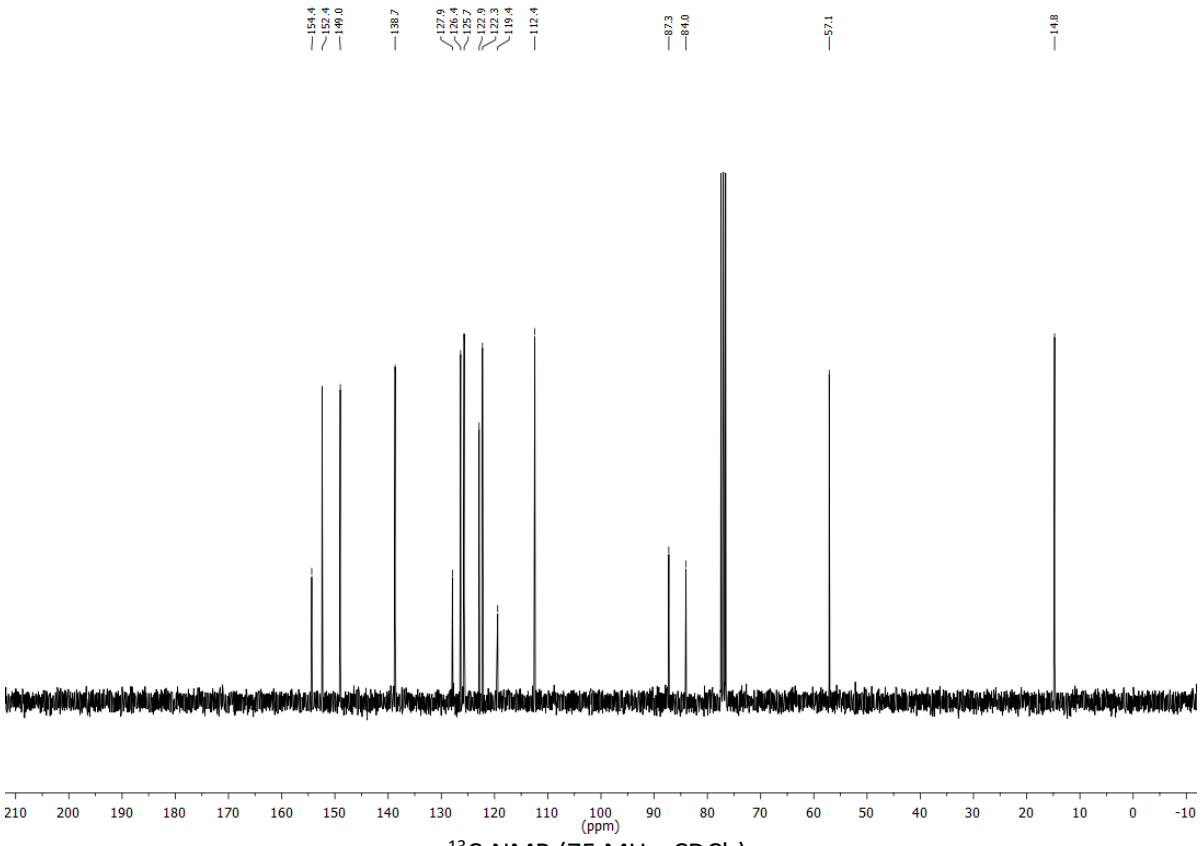
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.8, 57.1, 84.0, 87.3, 112.4, 119.4, 122.3, 122.9, 125.7, 126.4, 127.9, 138.7, 149.0, 152.4, 154.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3060, 2919, 2861, 2241, 1576, 1472, 1441, 1214, 1012.

$C_{15}H_{13}NOS$ calcd.: 255.0718, found: 255.0717 (GC-HRMS).

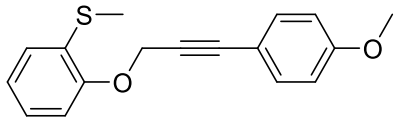


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzene (11w)



Compound **11w** was synthesized according GP2.

To a mixture of **SM2** (200.0 mg, 1.12 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and CuI (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) was added 4-iodoanisole (316.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) which afforded an off-white solid (181 mg, 0.64 mmol, 57%).

m.p.: 73 °C.

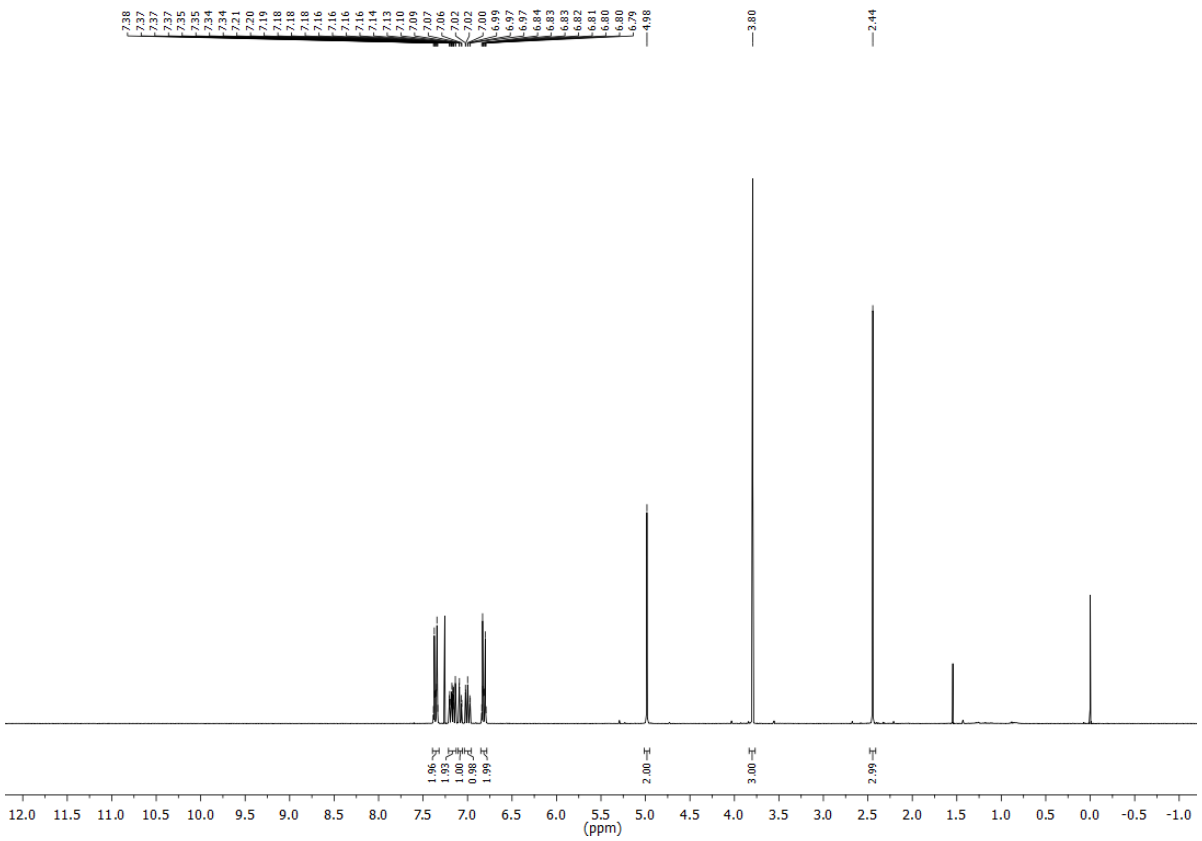
$\mathbf{R_f}$ = 0.40 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 3.80 (s, 3H), 4.98 (s, 2H), 6.79 – 6.84 (m, 2H), 7.00 (td, *J* = 7.4, 1.4 Hz, 1H), 7.08 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.13 – 7.21 (m, 2H), 7.33 – 7.39 (m, 2H).

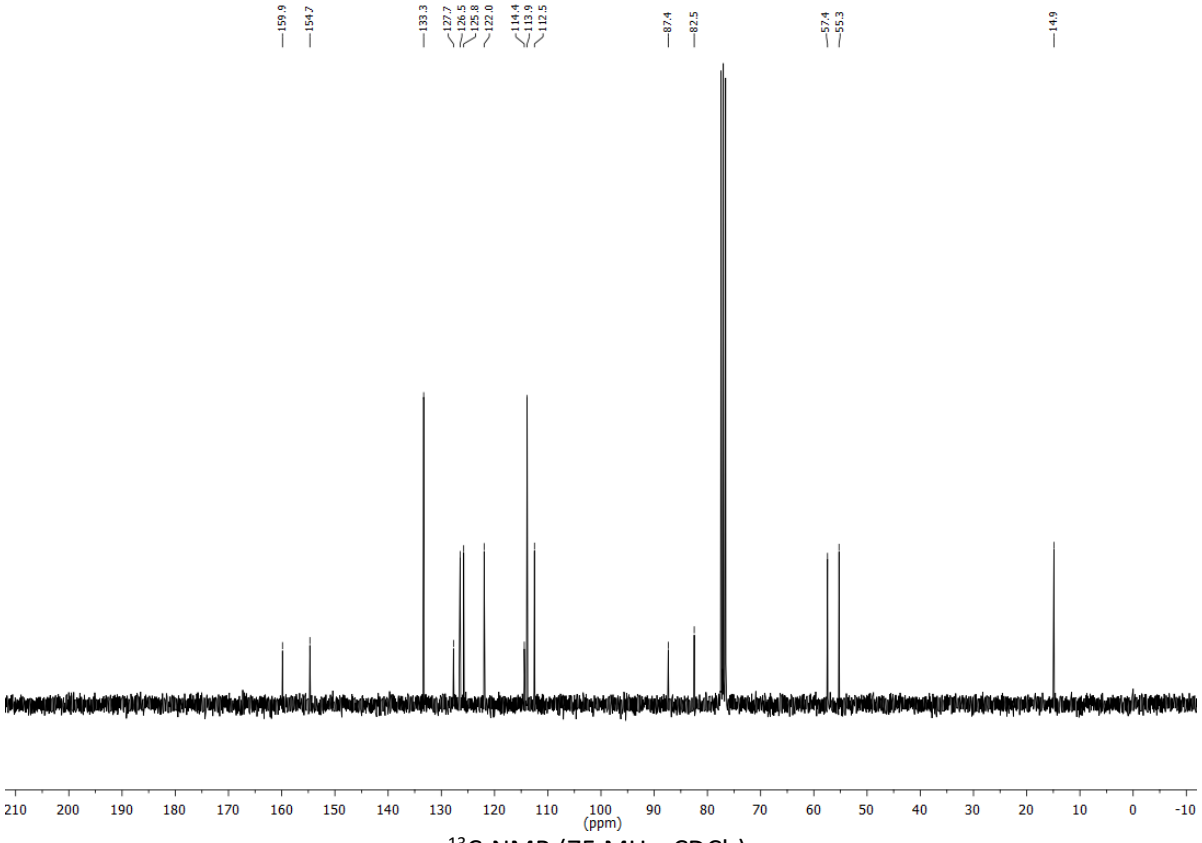
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.9, 55.3, 57.4, 82.5, 87.4, 112.5, 113.9, 114.4, 122.0, 125.8, 126.5, 127.7, 133.3, 154.7, 159.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3003, 2927, 2910, 2840, 2226, 1601, 1507, 1437, 1224, 1073, 1025.

$C_{17}H_{16}O_2S$ calcd.: 284.0871, found: 284.0882 (GC-HRMS).

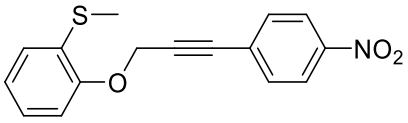


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((3-(4-nitrophenylp)rop-2-yn-1-yl)oxy)benzene (11x)



Compound **11x** was synthesized according GP2.

To a mixture of **SM2** (200.0 mg, 1.12 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and CuI (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) was added 1-iodo-4-nitrobenzene (337.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) which afforded a yellow oil (309 mg, 1.03 mmol, 92%).

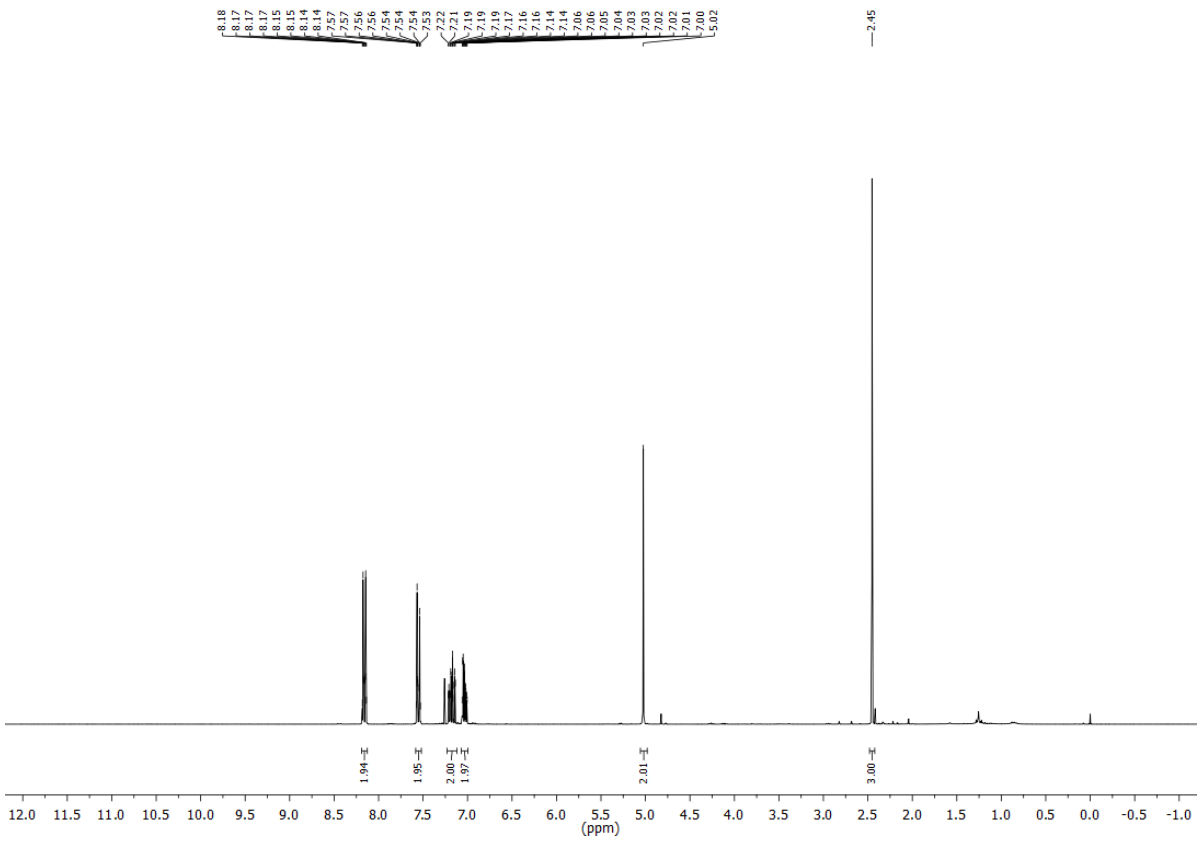
R_f = 0.34 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 5.02 (s, 2H), 7.00 – 7.07 (m, 2H), 7.13 – 7.23 (m, 2H), 7.52 – 7.59 (m, 2H), 8.13 – 8.19 (m, 2H).

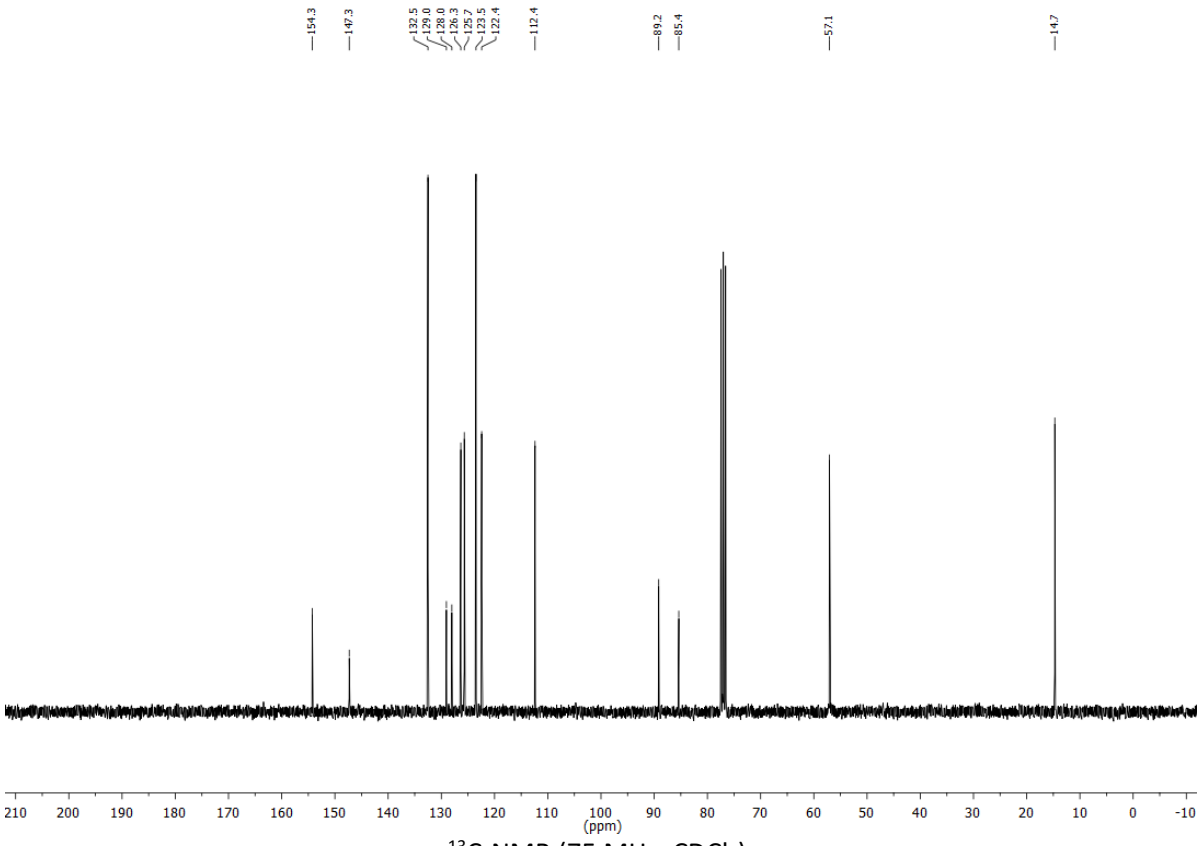
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.7, 57.1, 85.4, 89.2, 112.4, 122.4, 123.5, 125.7, 126.3, 128.0, 129.0, 132.5, 147.3, 154.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3066, 2921, 2853, 2246, 1592, 1516, 1340, 1214, 1016.

$C_{16}H_{13}NO_3S$ calcd.: 322.0508, found: 322.0511 $[M+Na]^+$ (ESI-HRMS).

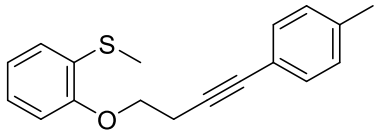


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((4-(*p*-tolyl)but-3-yn-1-yl)oxy)benzene (11y)



A mixture of 4-iodotoluene (377.0 mg, 1.73 mmol, 1.00 equiv.)., $PdCl_2(PPh_3)_2$ (24.3 mg, 34.6 µmol, 0.02 equiv.) and CuI (5.0 mg, 26.0 µmol, 0.015 equiv.) in dry triethylamine (8 ml) was stirred for 30 min. Then, **11t** (220.0 mg, 1.15 mmol, 0.66 equiv.) in dry triethylamine/DMF (1:1, 4 ml) was added dropwise. After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether, washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography (*n*-pentane:EtOAc = 70:1→50:1) which afforded a white solid (205 mg, 0.73 mmol, 63%).

Carried out in accordance to a reported procedure.[2]

m.p.: 82 °C.

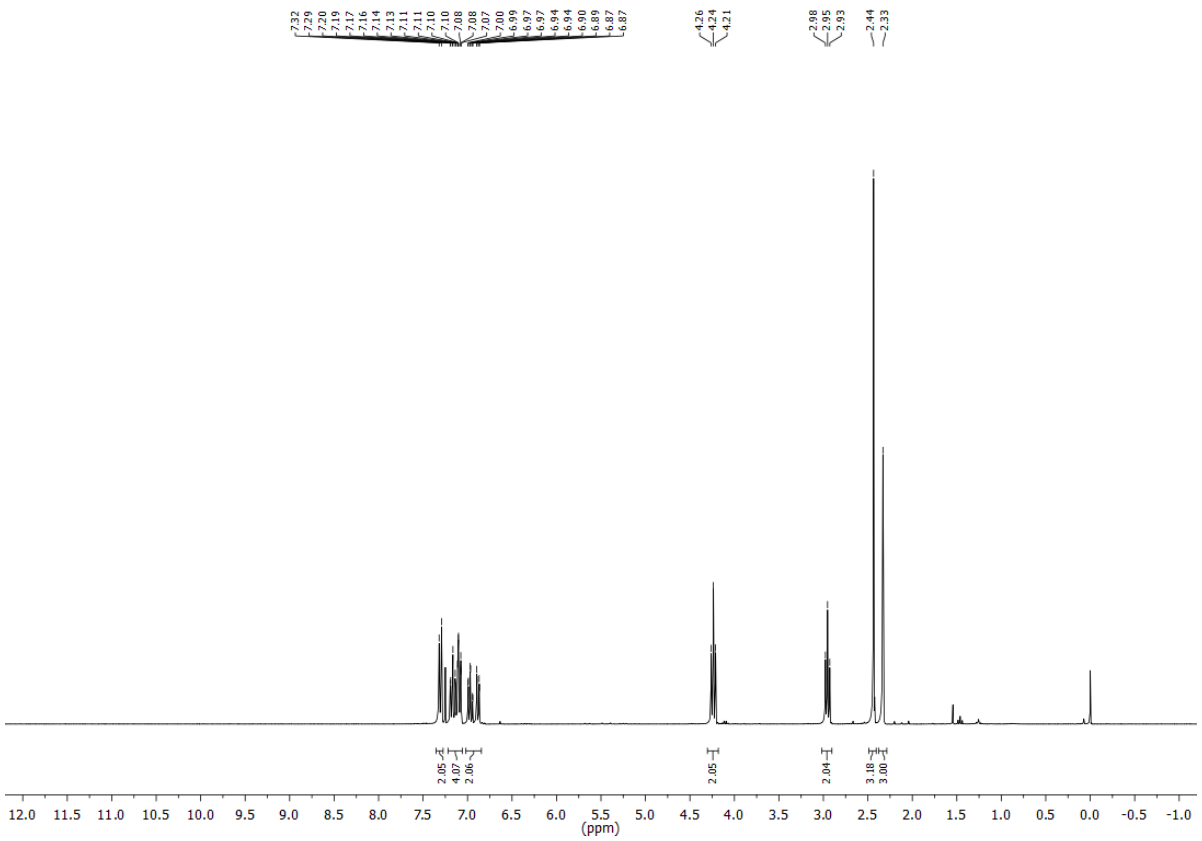
R_f = 0.38 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.44 (s, 3H), 2.95 (t, *J* = 7.3 Hz, 2H), 4.24 (t, *J* = 7.3 Hz, 2H), 6.86 – 7.00 (m, 2H), 7.06 – 7.20 (m, 4H), 7.31 (d, *J* = 8.1 Hz, 2H).

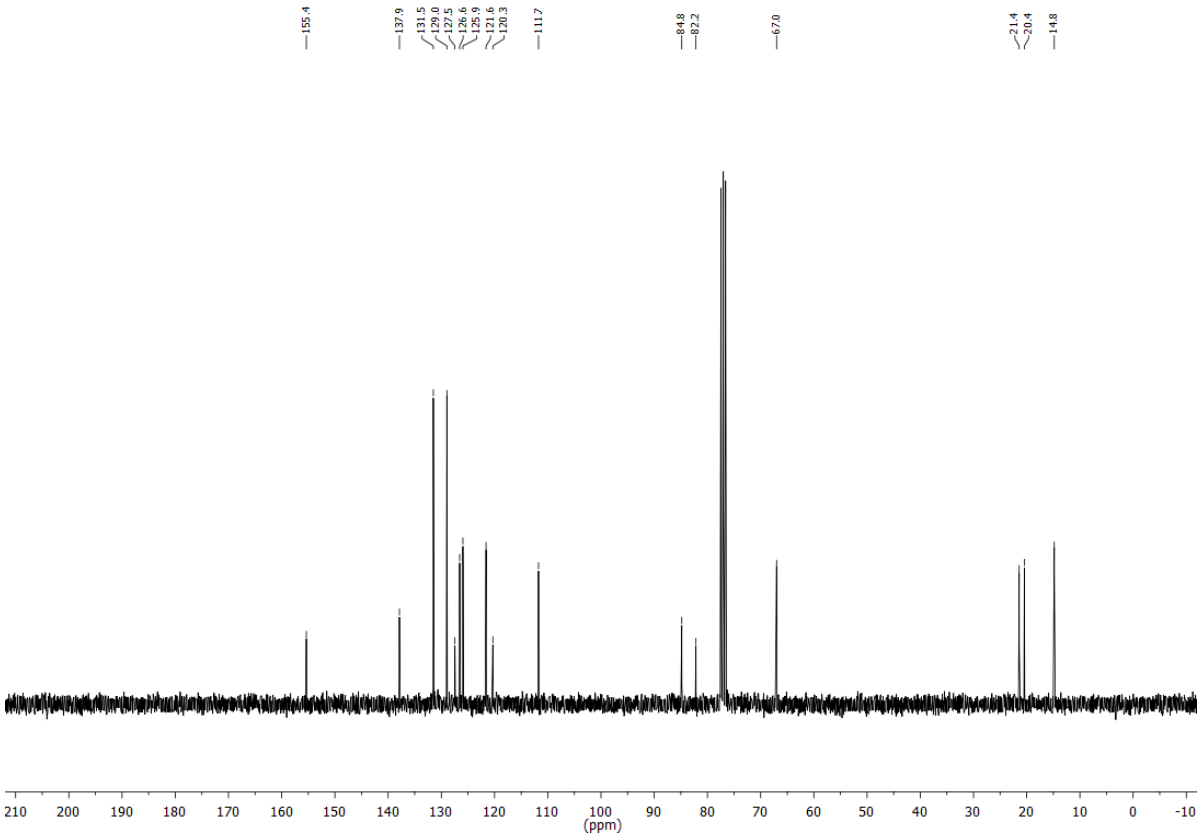
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.8, 20.4, 21.4, 67.0, 82.2, 84.8, 111.7, 120.3, 121.6, 125.9, 126.6, 127.5, 129.0, 131.5, 137.9, 155.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3019, 2918, 2887, 2224, 1576, 1463, 1236, 1021.

$C_{18}H_{18}OS$ calcd.: 282.1078, found: 282.1080 (GC-HRMS).

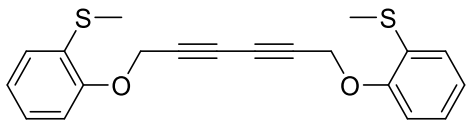


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1,6-Bis(2-(methylthio)phenoxy)hexa-2,4-diyne (11z)



To a mixture of **SM2** (430.0 mg, 2.42 mmol, 1.00 equiv.)., $PdCl_2(PPh_3)_2$ (34.0 mg, 48.4 µmol, 0.04 equiv.) and CuI (23.0 mg, 0.12 mmol, 0.10 equiv.) in dry triethylamine (5 ml) and dry DMF (4 ml) was added iodine (610 mg, 2.44 mmol, 1.01 equiv.) at RT. After stirring for 2.5 h the reaction was quenched with NH_4Cl-solution, extracted with diethyl ether (3 x 50 ml), washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column (*n*-pentane:EtOAc = 60:1→10:1) which afforded a colorless solid (261 mg, 0.74 mmol, 61%).

Carried out in accordance to a reported procedure.[2a]

m.p.: 106 °C.

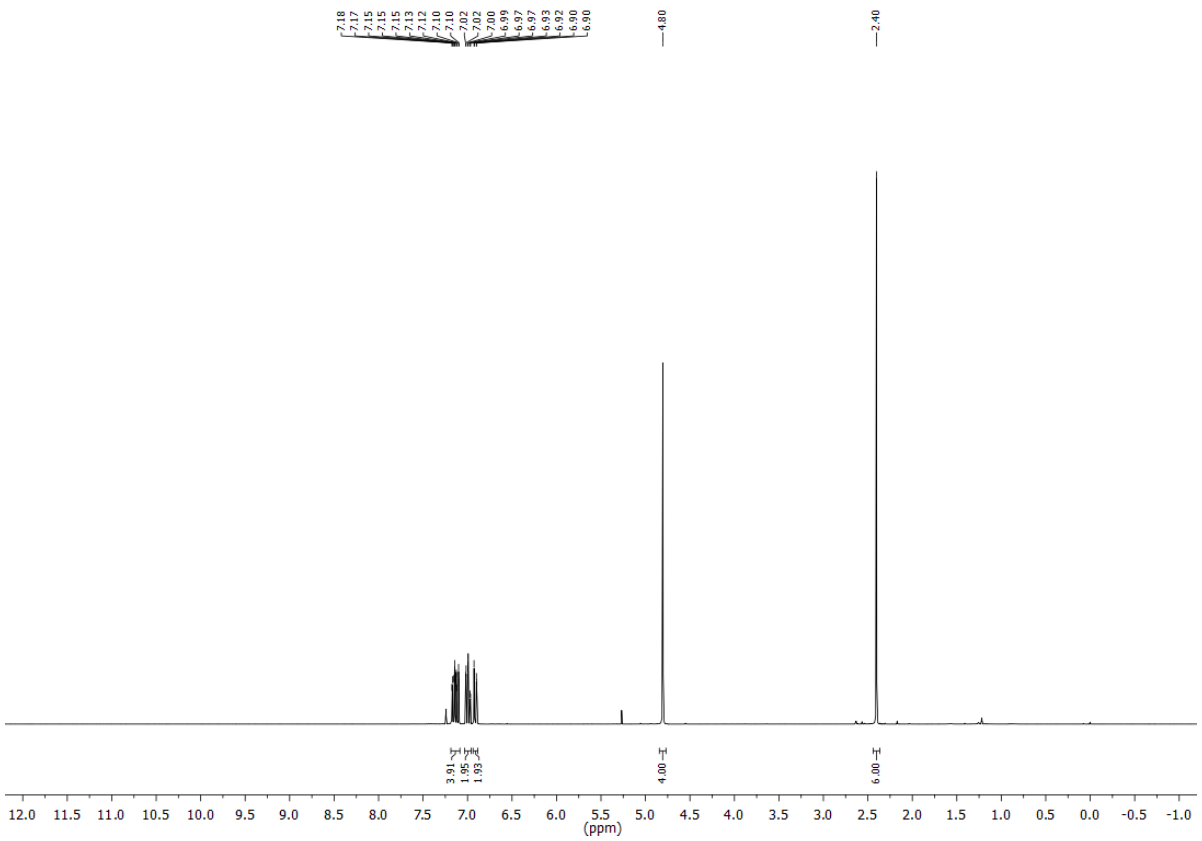
R_f = 0.19 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 6H), 4.80 (s, 4H), 6.91 (dd, *J* = 8.0, 1.3 Hz, 2H), 6.99 (td, *J* = 7.6, 1.3 Hz, 2H), 7.08 – 7.19 (m, 4H).

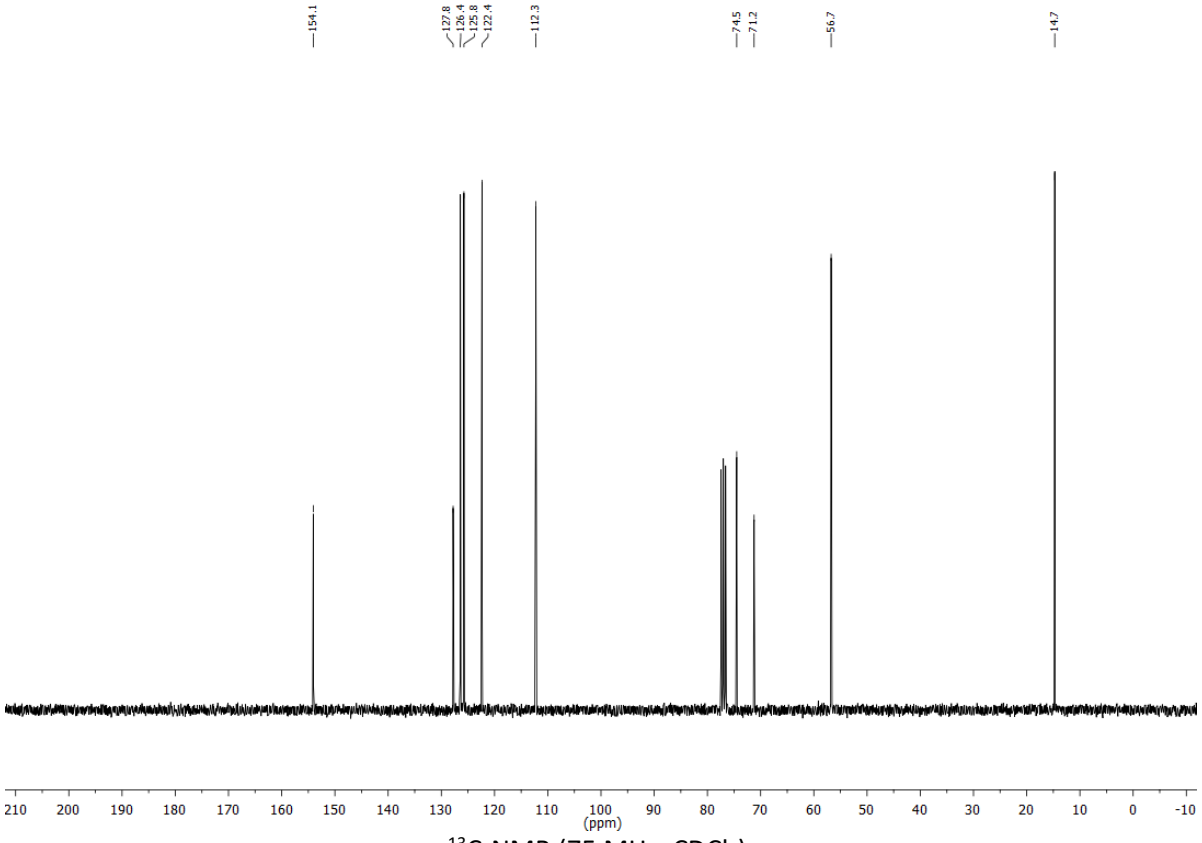
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.7, 56.7, 71.2, 74.5, 112.3, 122.4, 125.8, 126.4, 127.8, 154.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3106, 2920, 2855, 2165, 1573, 1474, 1438, 1366, 1221, 1012.

$C_{20}H_{18}O_2S_2$ calcd.: 377.0640, found: 377.0641 $[M+Na]^+$ (ESI-HRMS).

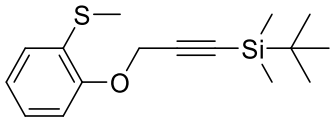


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-[[3-[(1,1-dimethylethyl)dimethylsilyl]-2-propyn-1-yl]oxy]benzene (15a)



Compound **15a** was synthesized according GP1.

A solution of **SM1** (300.0 mg, 2.16 mmol, 1.00 equiv.), PPh_3 (852 mg, 3.24 mmol, 1.50 equiv.) and 3-[(1,1-Dimethylethyl)dimethylsilyl]-2-propyn-1-ol[25] (552 mg, 3.24 mmol, 1.50 equiv.) in dry toluene (15 ml) was cooled to 0 °C. DIAD (657 mg, 0.66 ml, 3.24 mmol, 1.50 equiv.) in dry toluene (12 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 50:1) gave the desired product (524 mg, 1.79 mmol, 83%) as colorless oil.

R_f = 0.33 (*n*-pentane:EtOAc = 50:1).

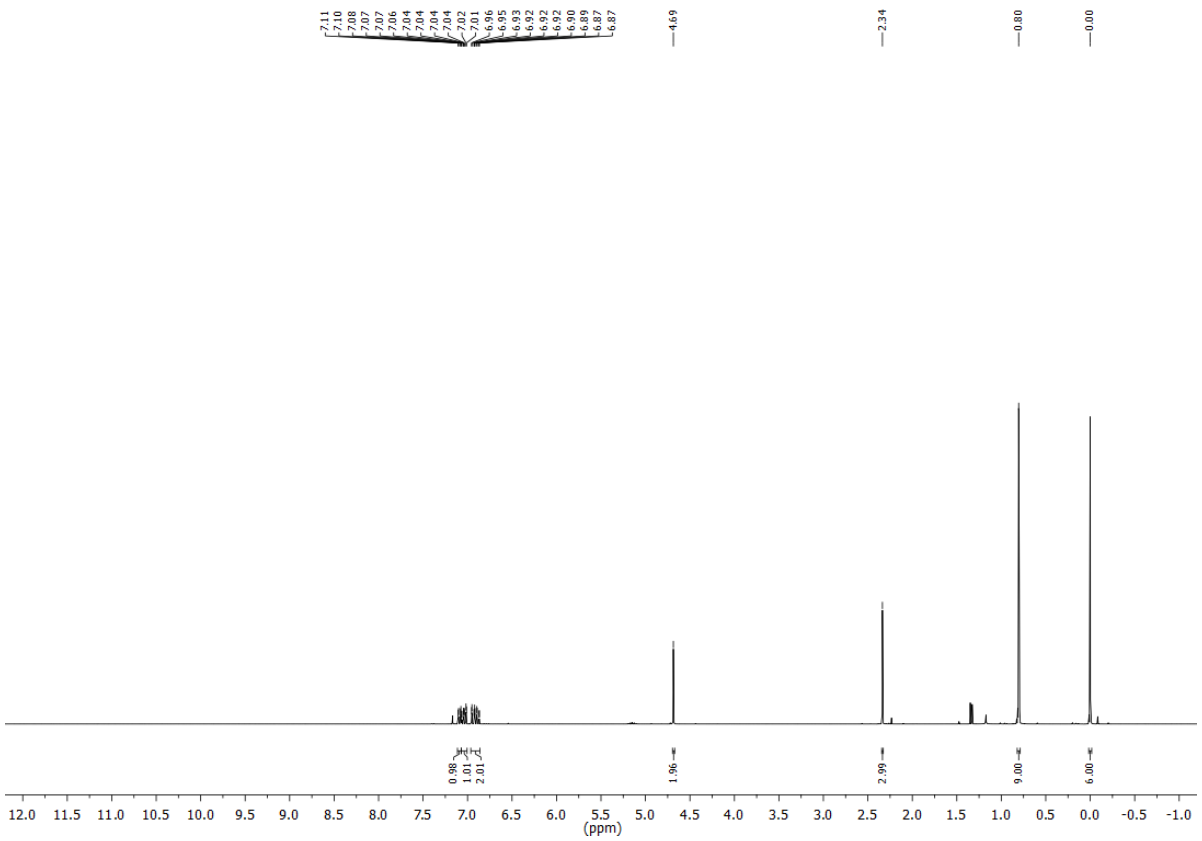
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 6H), 0.80 (s, 9H), 2.34 (s, 3H), 4.69 (s, 2H), 6.86 – 6.96 (m, 2H), 7.04 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.7 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = -4.9, 14.8, 16.4, 25.9, 57.3, 91.2, 100.6, 112.8, 121.9, 125.6, 126.4, 127.7, 154.5.

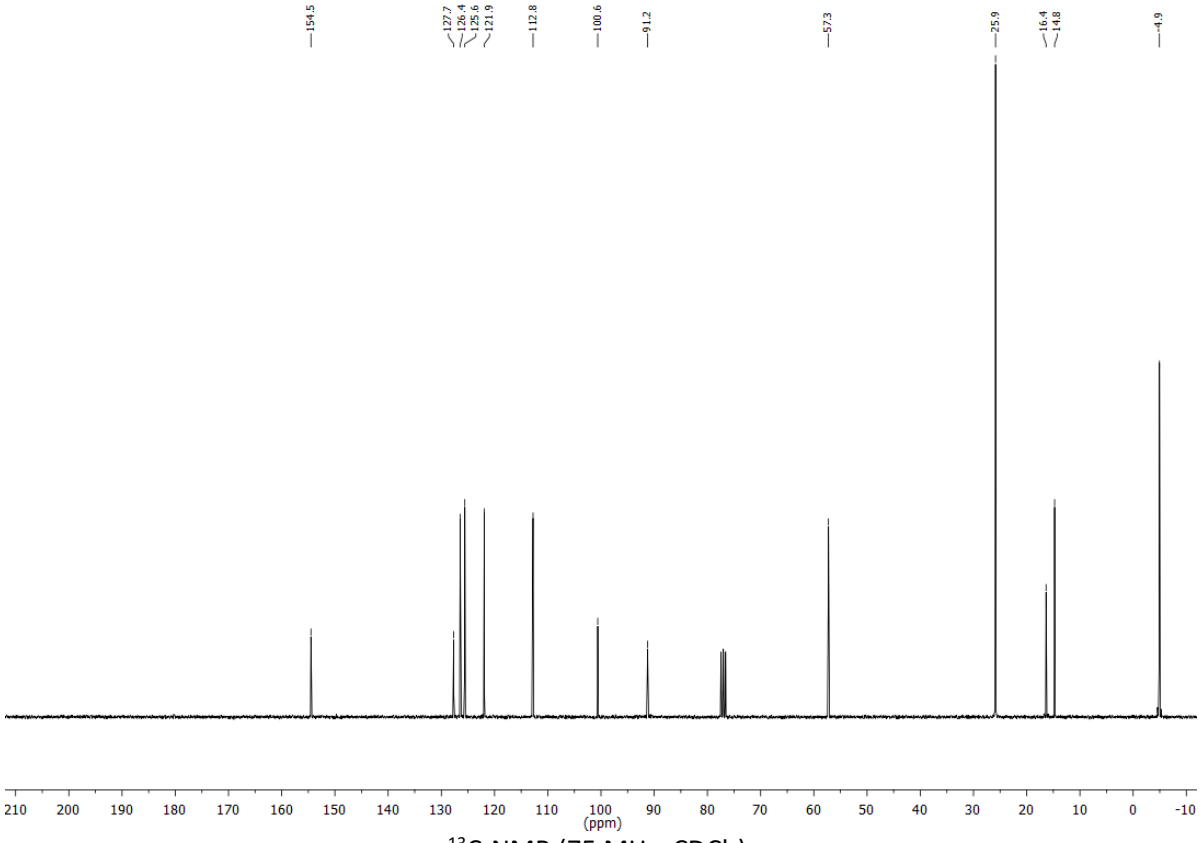
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 2928, 2856, 2178, 1775, 1578, 1471, 1443, 1250, 1216, 1029.

$C_{16}H_{24}OSSi$ calcd.: 292.1317, found: 292.1327 (GC-HRMS).

[25] C. D. McCune, M. L. Beio, J. A. Friest, S. Ginotra and D. B. Berkowitz, *Tetrahedron Lett.*, 2015, **56**, 3575.

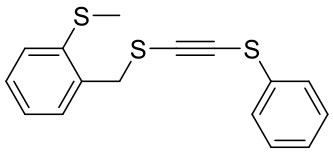


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-((((phenylthio)ethynyl)thio)methyl)benzene (15b)



According to a reported procedure[26] *n*-butyllithium (1.65 ml, 2.64 mmol, 1.05 equiv., 1.6 M in hexane) was added dropwise over a period of 10 min to a solution of ethynyl(phenyl)sulfane[27] (355 mg, 2.64 mmol, 1.05 equiv.) in dry THF (62 ml) at -25 °C. The solution was stirred for 2 h at -40 °C. Afterwards, compound **5.1b** (491 mg, 2.51 mmol, 1.00 equiv.) was dissolved in dry THF (31 ml) and was added dropwise within a period of 1.5 h. The mixture was then stirred for 1 h. After warming to RT, the reaction was quenched with sat. NH_4Cl solution and diluted with water. The mixture was extracted with Et_2O (3 x 50 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (*n*-pentane:EtOAc = 100:1) to afford a yellow oil (243 mg, 0.82 mmol, 33%)

R_f = 0.57 (*n*-pentane:EtOAc = 20:1).

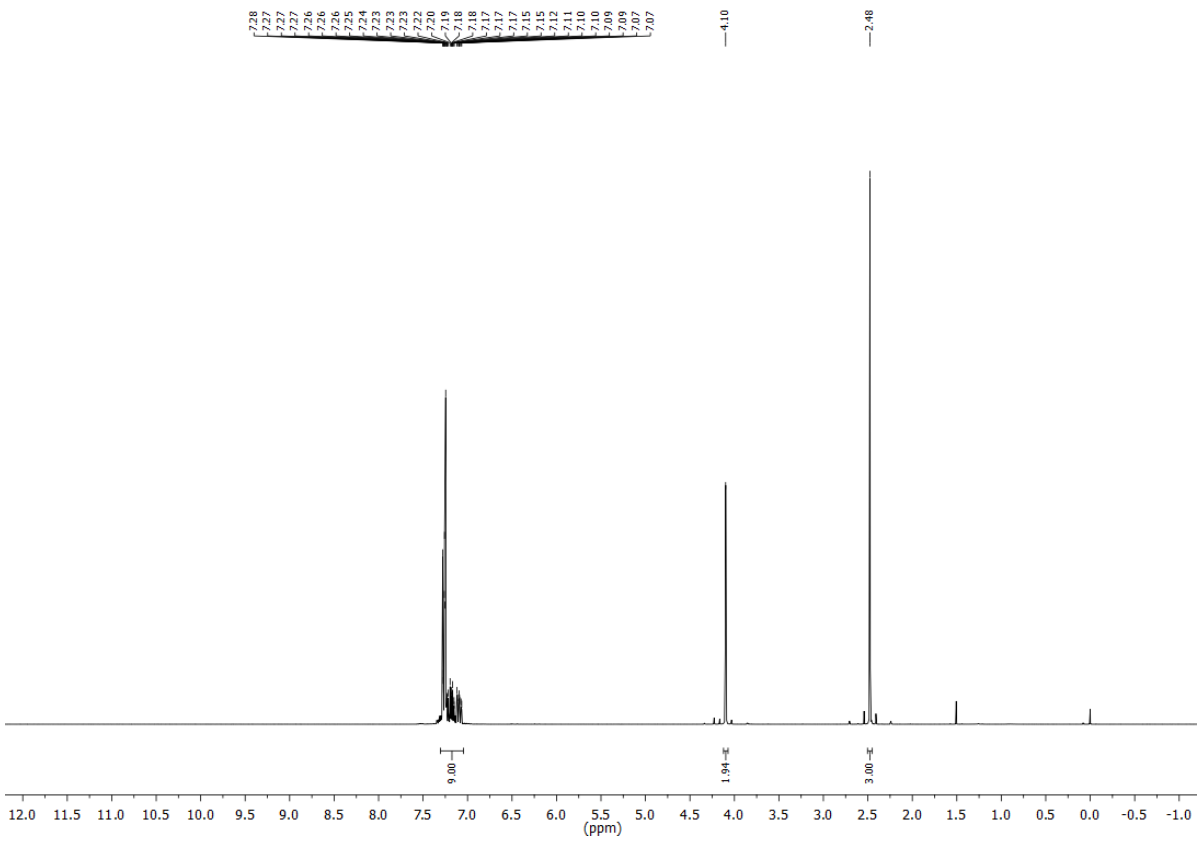
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 4.10 (s, 2H), 7.05 – 7.31 (m, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.5, 39.7, 83.8, 92.2, 125.2, 125.7, 126.4, 127.0, 128.6, 129.0, 130.4, 133.7, 134.6, 137.8.

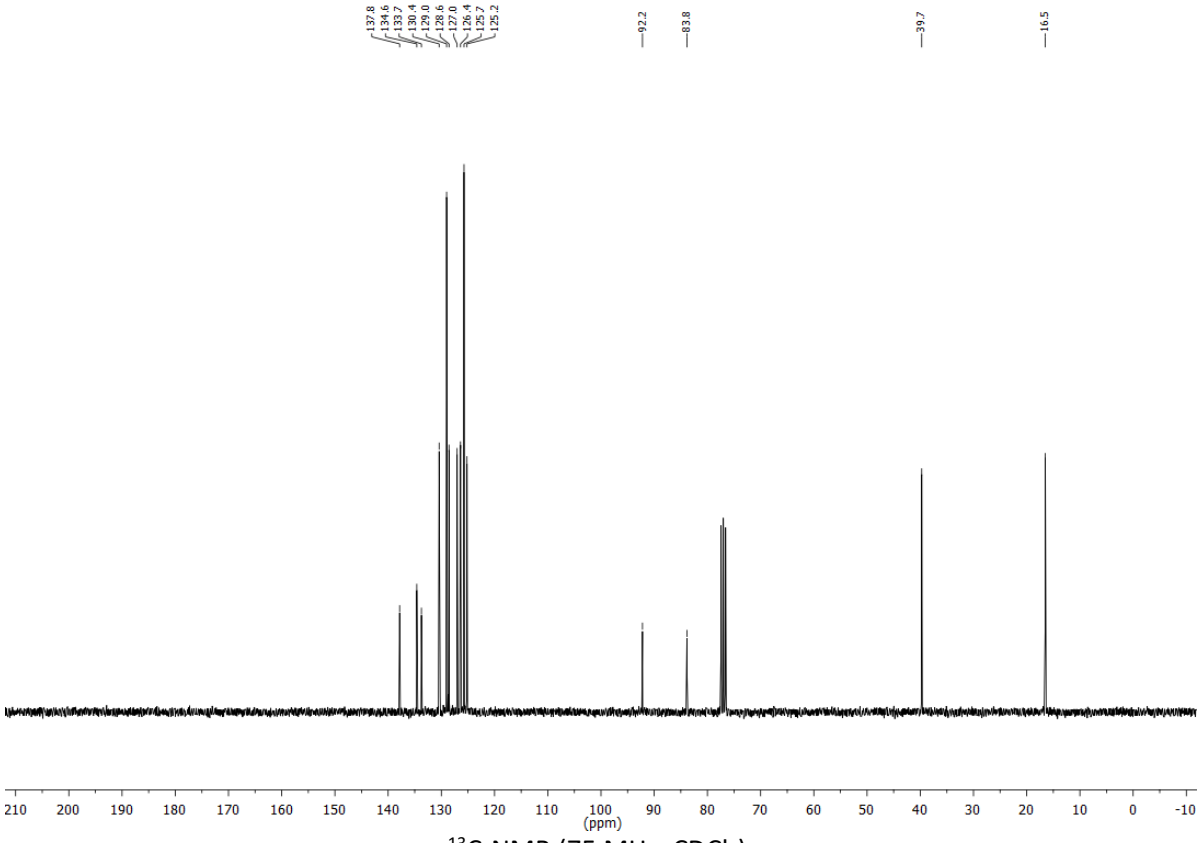
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3055, 2984, 2917, 1579, 1470, 1433, 1228, 1068, 960.

$C_{16}H_{14}S_3$ calcd.: 302.0258, found: 302.0238 (GC-HRMS).

[26] A. Lari, C. Bleiholder, F. Rominger and R. Gleiter, *Eur. J. Org. Chem.*, 2009, **2009**, 2765.
[27] D. Nitsch, S. M. Huber, A. Pöthig, A. Narayanan, G. A. Olah, G. K. S. Prakash and T. Bach, *J. Am. Chem. Soc.*, 2014, **136**, 2851.

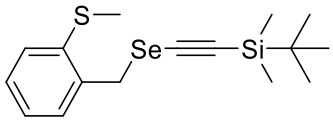


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(3-((1,1-dimethylethyl)dimethylsilyl)-2-((ethynylselanyl)methyl))benzene (15d)



According to a reported procedure[26] *n*-butyllithium (2.63 ml, 4.20 mmol, 1.05 equiv., 1.6 M in hexane) was added dropwise over a period of 10 min to a solution of (*tert*-butyldimethylsilyl)acetylene (562 mg, 0.75 ml, 4.20 mmol, 1.05 equiv.) in dry THF (100 ml) at -25 °C. The solution was stirred for 2 h at -40 °C. Afterwards, compound 5.1d (969 mg, 4.00 mmol, 1.00 equiv.) was dissolved in dry THF (50 ml) and was added dropwise within a period of 1.5 h. The mixture was then stirred for 1 h. After warming to RT, the reaction was quenched with sat. NH_4Cl solution and diluted with water. The mixture was extracted with Et_2O (1 x 50 ml, 2 x 100 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (*n*-pentane:EtOAc = 100:1) to afford a yellow oil (1.19 g, 3.35 mmol, 84%)

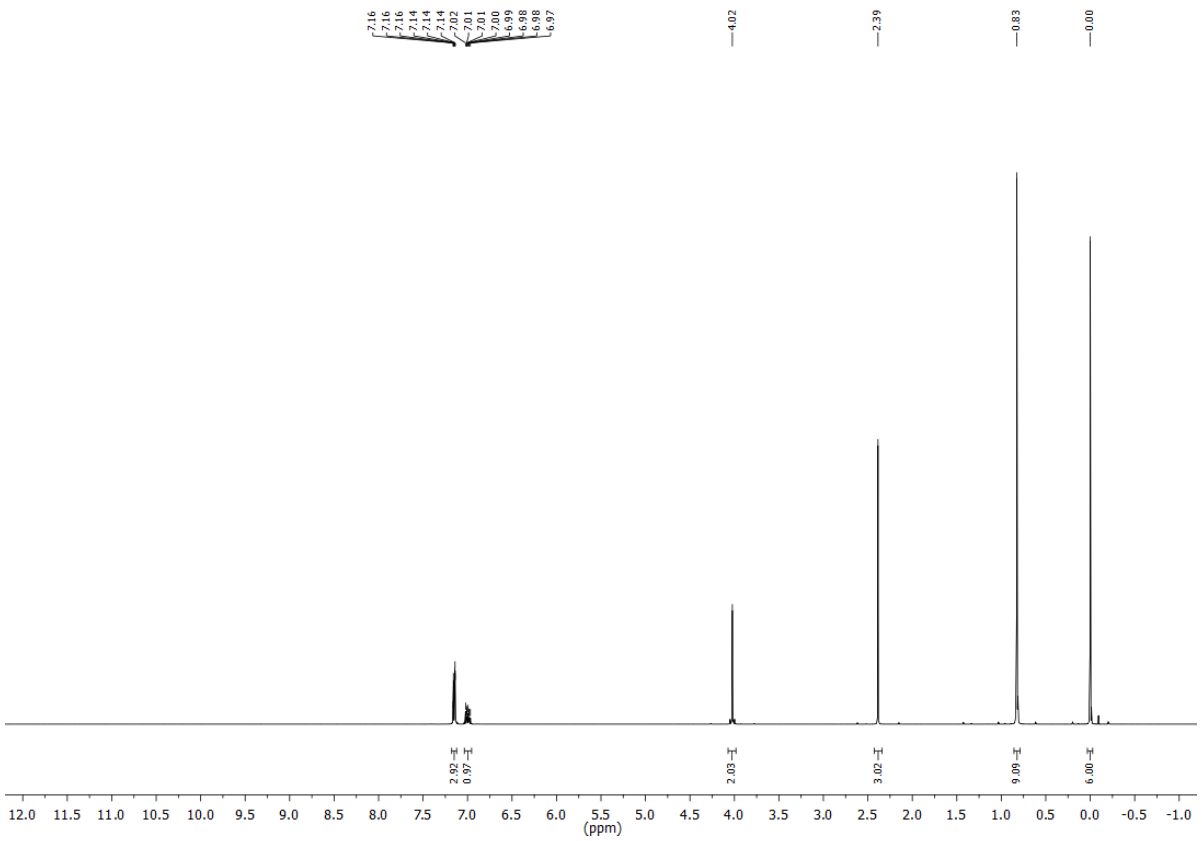
R_f = 0.74 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 6H), 0.83 (s, 9H), 2.39 (s, 3H), 4.02 (s, 2H), 6.96 – 7.04 (m, 1H), 7.12 – 7.18 (m, 3H).

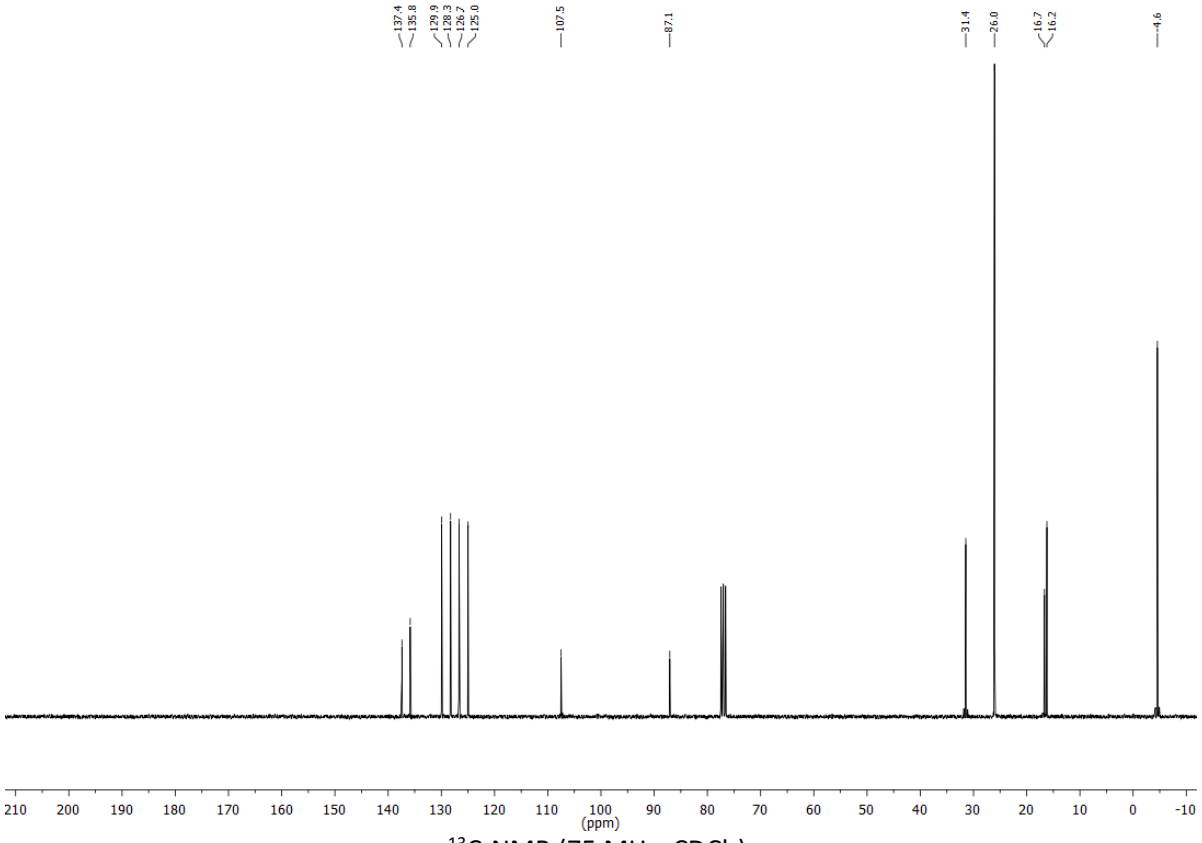
^{13}C-NMR (75 MHz, $CDCl_3$): δ = -4.6, 16.2, 16.7, 26.0, 31.4, 87.1, 107.5, 125.0, 126.7, 128.3, 129.9, 135.8, 137.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2926, 2886, 2852, 2078, 1584, 1464, 1433, 1251, 1187.

$C_{16}H_{24}SSeSi$ calcd.: 356.0533, found: 356.0543 (GC-HRMS).

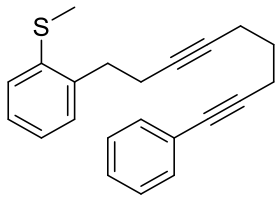


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(9-phenylnona-3,8-diyn-1-yl)benzene (19a)



Following a reported procedure[28], *n*-butyllithium (1.50 ml, 3.75 mmol, 1.10 equiv., 2.5 M in hexane) was added dropwise over a period of 30 min to a solution of **SM3** (600 mg, 3.40 mmol, 1.00 equiv.) in THF (6 ml) and DMPU (0.75 ml) at -78 °C. The mixture was then allowed to stir 1h at ambient temperature. After this time, it was recooled to -78 °C and (5-iodopent-1-yn-1-yl)benzene[31] (1.02 g, 3.75 mmol, 1.10 equiv.) was added via syringe. The temperature was kept at -78 °C for one further hour. The mixture was then warmed to RT and stirred overnight. After quenching with sat. NH_4Cl solution, the mixture was extracted with Et_2O (3 x 50 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (*n*-pentane:EtOAc = 100:1) to afford a colorless oil (862 mg, 2.71 mmol, 80%).

R_f = 0.60 (*n*-pentane:EtOAc = 20:1).

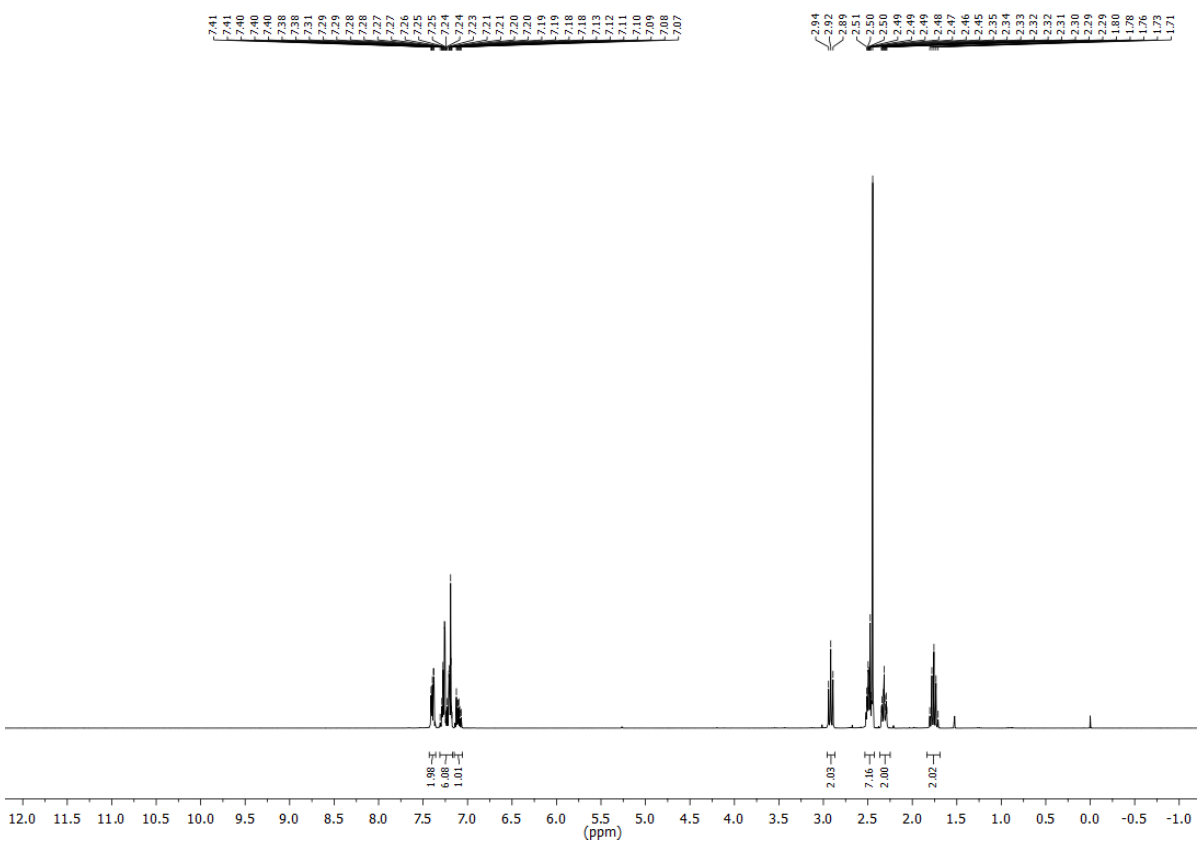
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.76 (p, *J* = 7.0 Hz, 2H), 2.32 (tt, *J* = 6.9, 2.4 Hz, 2H), 2.45 (s, 3H), 2.46 – 2.53 (m, 4H), 2.92 (t, *J* = 7.5 Hz, 2H), 7.07 – 7.15 (m, 1H), 7.17 – 7.31 (m, 6H), 7.37 – 7.43 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 15.8, 18.0, 18.5, 19.2, 28.2, 33.3, 79.9, 80.1, 81.0, 89.5, 123.9, 124.8, 125.6, 127.0, 127.5, 128.1, 129.4, 131.5, 137.2, 138.6.

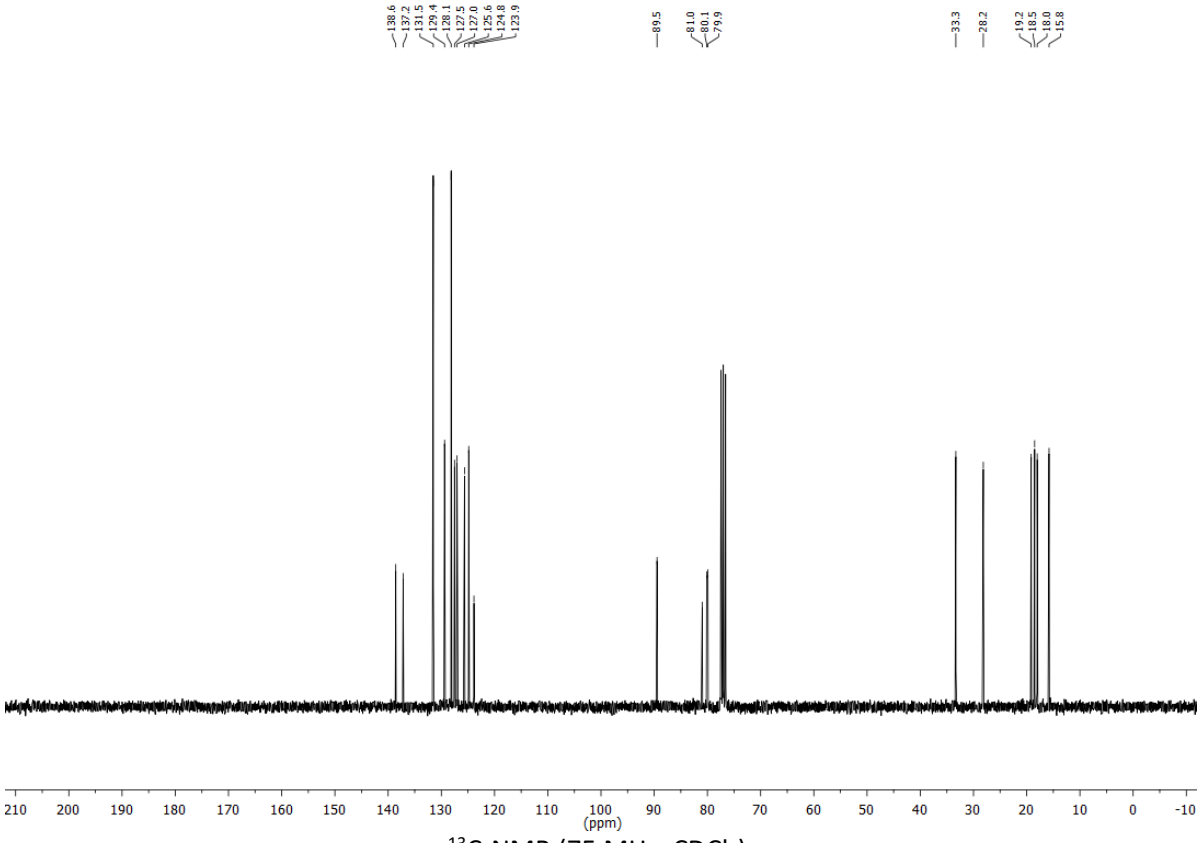
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2924, 2862, 2838, 1593, 1434, 1335, 1066, 1042.

$C_{22}H_{22}S$ calcd.: 318.1442, found: 318.1473 (GC-HRMS).

[28] M. Puigmartí, M. Bosch and A. Guerrero, *Synthesis*, 2015, **47**, 961.

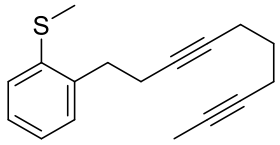


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(deca-3,8-diyn-1-yl)benzene (19b)



Following a reported procedure,[25] *n*-butyllithium (0.66 ml, 1.65 mmol, 1.10 equiv., 2.5 M in hexane) was added dropwise over a period of 30 min to a solution of **SM3** (265 mg, 1.50 mmol, 1.00 equiv.) in THF (3.3 ml) and DMPU (0.33 ml) at -78 °C. The mixture was then allowed to stir 1h at ambient temperature. After this time, it was recooled to -78 °C and 6-iodohex-2-yne[31] (344 mg, 1.65 mmol, 1.10 equiv.) was added via syringe. The temperature was kept at -78 °C for one further hour. The mixture was then warmed to RT and stirred for 6 h. After quenching with sat. NH_4Cl solution, the mixture was extracted with Et_2O (3 x 50 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (*n*-pentane:EtOAc = 100:1) to afford a colorless oil (300 mg, 1.17 mmol, 78%).

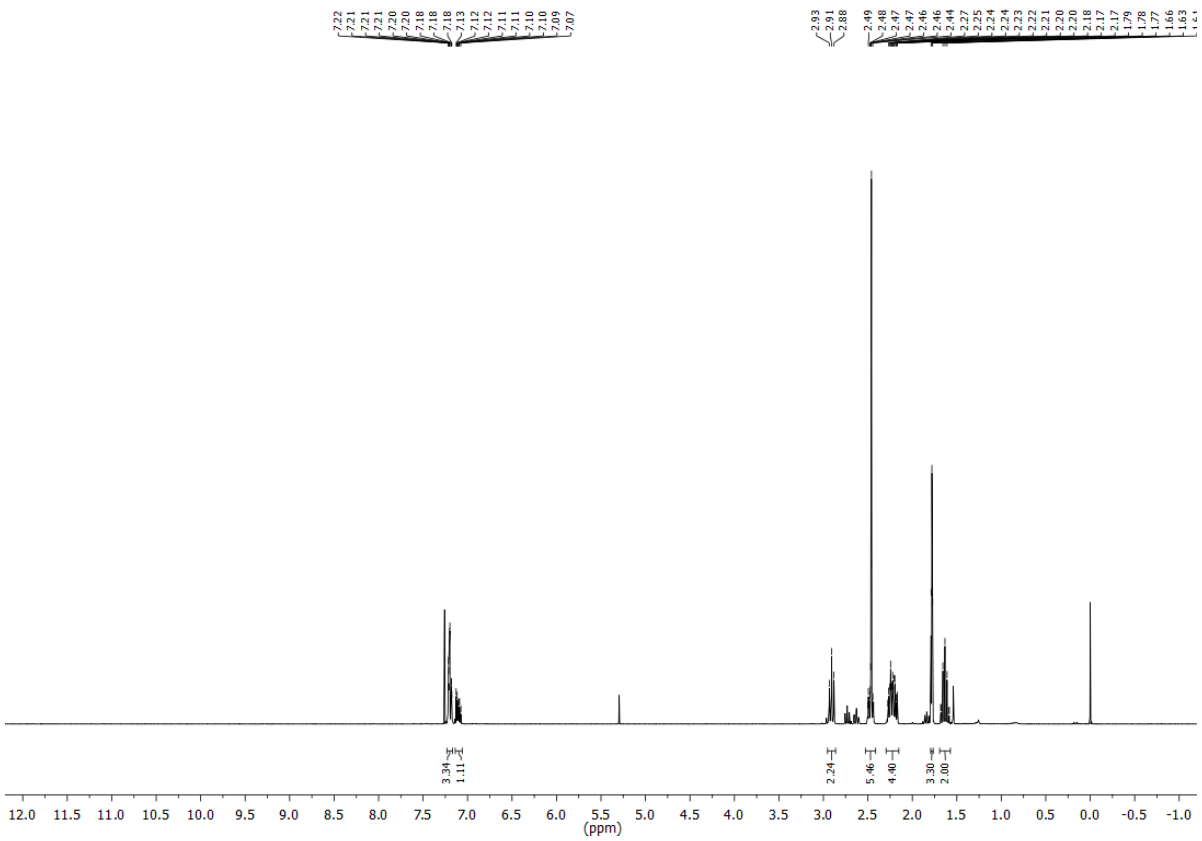
R_f = 0.36 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.58 – 1.69 (m, 2H), 1.78 (t, *J* = 2.6 Hz, 3H), 2.14 – 2.30 (m, 4H), 2.46 (s, 3H), 2.43 – 2.51 (m, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 7.07 – 7.13 (m, 1H), 7.17 – 7.22 (m, 3H).

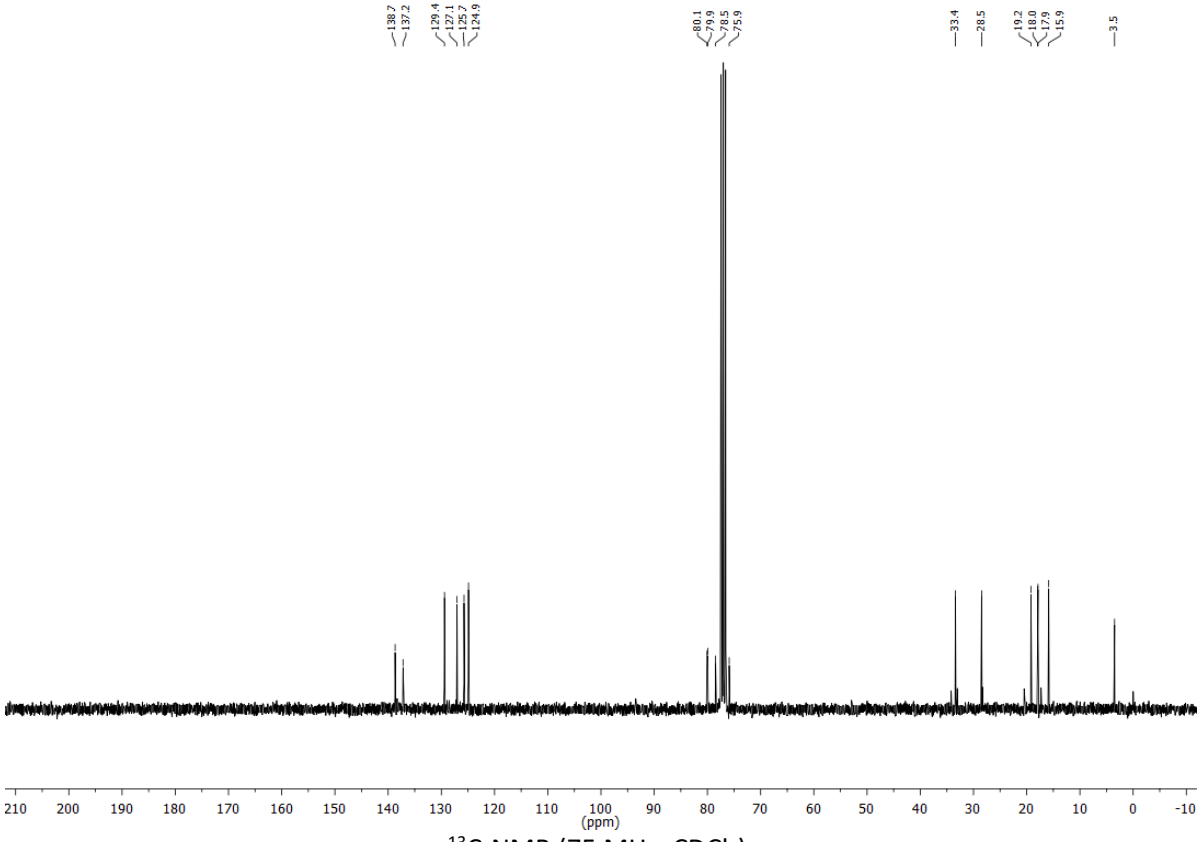
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.5, 15.9, 17.9, 18.0, 19.2, 28.5, 33.4, 75.9, 78.5, 79.9, 80.1, 124.9, 125.7, 127.1, 129.4, 137.2, 138.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2916, 2859, 1588, 1435, 1336, 1043, 863.

$C_{17}H_{20}S$ calcd.: 256.1286, found: 256.1274 (GC-HRMS).

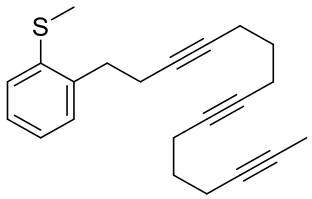


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(pentadeca-3,8,13-triyn-1-yl)benzene (19d)



Following a reported procedure,[25] *n*-butyllithium (0.66 ml, 1.65 mmol, 1.10 equiv., 2.5 M in hexane) was added dropwise over a period of 30 min to a solution of **SM3** (265 mg, 1.50 mmol, 1.00 equiv.) in THF (3.3 ml) and DMPU (0.33 ml) at -78 °C. The mixture was then allowed to stir 1h at ambient temperature. After this time, it was recooled to -78 °C and 11-iodoundeca-2,7-diyne (344 mg, 1.65 mmol, 1.10 equiv., from 6-iodohex-2-yne and *tert*-butyldimethyl(pent-4-yn-1-yloxy)silane, according the literature[25,29,31]) was added via syringe. The temperature was kept at -78 °C for one further hour. The mixture was then warmed to RT and stirred for 6 h. After quenching with sat. NH_4Cl solution, the mixture was extracted with Et_2O (3 x 50 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (*n*-pentane:EtOAc = 100:1) to afford a colorless oil (300 mg, 1.17 mmol, 78%).

R_f = 0.34 (*n*-pentane:EtOAc = 50:1).

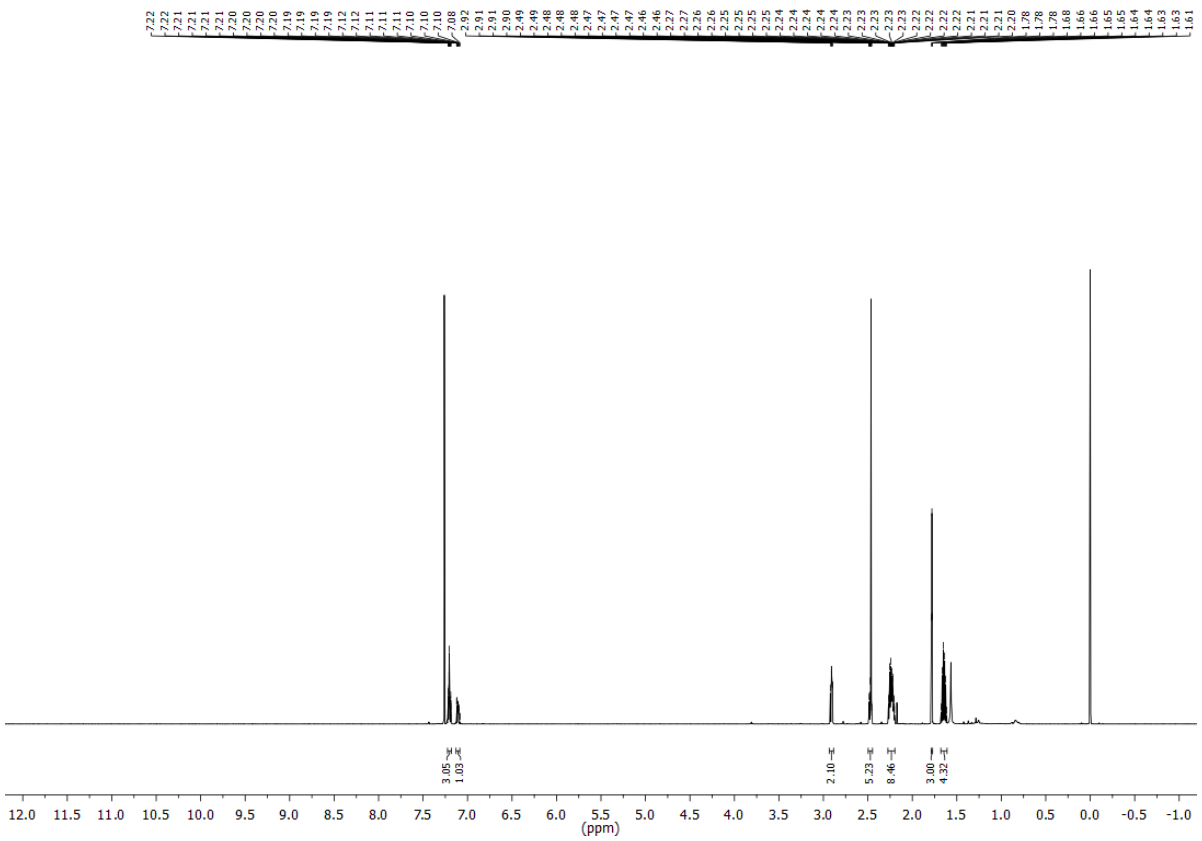
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.64 (dp, *J* = 9.0, 7.0 Hz, 4H), 1.78 (t, *J* = 2.5 Hz, 3H), 2.20 – 2.28 (m, 8H), 2.46 (s, 3H), 2.44 – 2.51 (m, 2H), 2.91 (dd, *J* = 7.9, 7.3 Hz, 2H), 7.11 (ddd, *J* = 7.6, 5.8, 2.7 Hz, 1H), 7.18 – 7.22 (m, 3H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ = 3.5, 15.9, 17.9, 17.9, 17.9, 18.0, 19.2, 28.5, 28.5, 33.4, 76.0, 78.4, 79.8, 79.9, 80.0, 80.1, 124.9, 125.7, 127.1, 129.4, 137.2, 138.7.

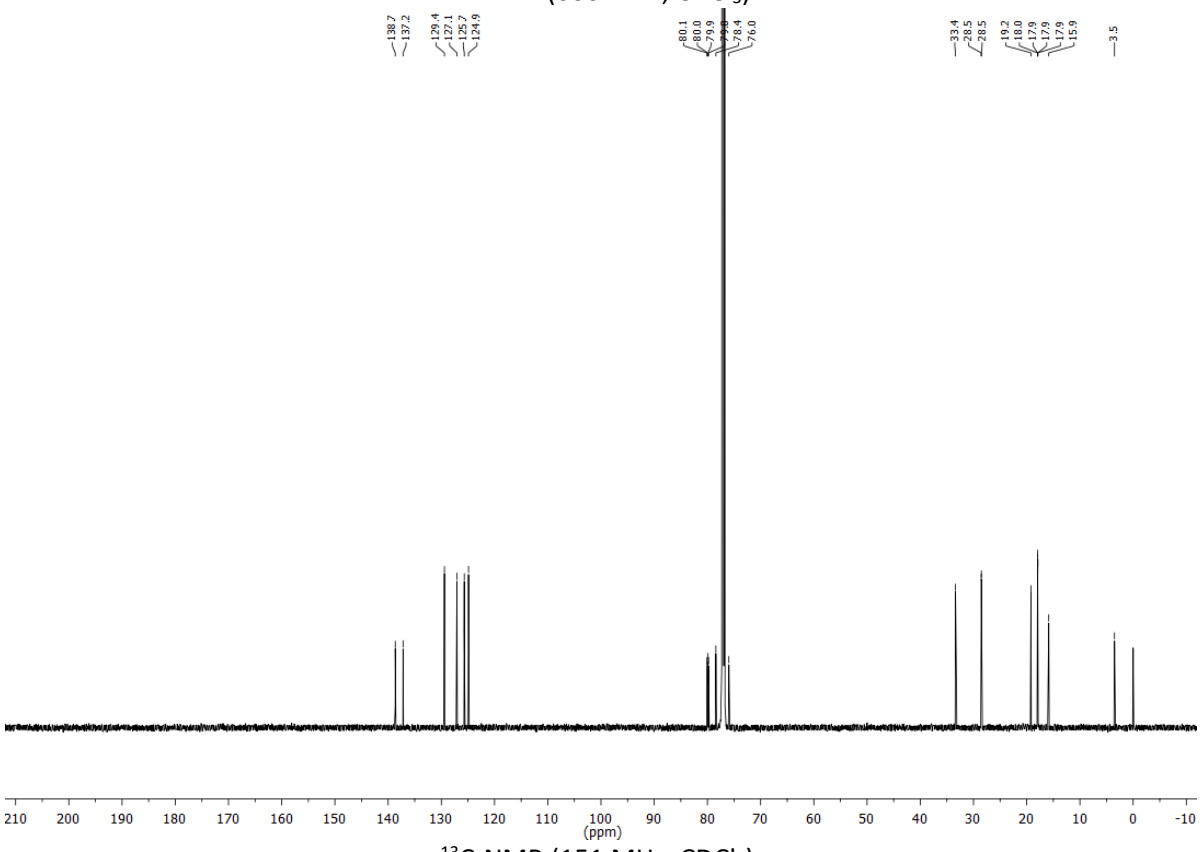
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2920, 2850, 1587, 1436, 1335, 1043, 963.

$C_{22}H_{26}S$ calcd.: 322.17497, found: 322.17499 (GC-HRMS).

[29] S. Hötling, B. Haberlag, M. Tamm, J. Collatz, P. Mack, J. L. M. Steidle, M. Vences and S. Schulz, *Chem. Eur. J.*, 2014, **20**, 3183.

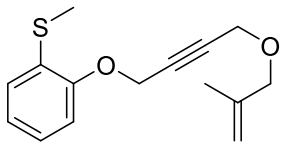


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

1-(Methylthio)-2-((4-((2-methylallyl)oxy)but-2-yn-1-yl)oxy)benzene (19e)



SM1 (350 mg, 2.50 mmol, 1.0 equiv.), PPh_3 (980 mg, 3.75 mmol, 1.5 equiv.) and 4-(2-methylallyloxy)-2-butyne-1-ol[30] (530 mg, 3.75 mmol, 1.5 equiv.) were dissolved in toluene (17 ml) and cooled to 0 °C. To this solution DIAD (0.74 ml, 760 mg, 3.75 mmol, 1.5 equiv.) in toluene (15 ml) was added dropwise. Afterwards, the mixture was warmed to RT and stirred overnight. The solvent was evaporated and the crude product purified by flash column chromatography (*n*-pentane:EtOAc = 50:1) to afford a colorless oil (520 mg, 1.98 mmol, 80%).

R_f = 0.27 (*n*-pentane:EtOAc = 50:1).

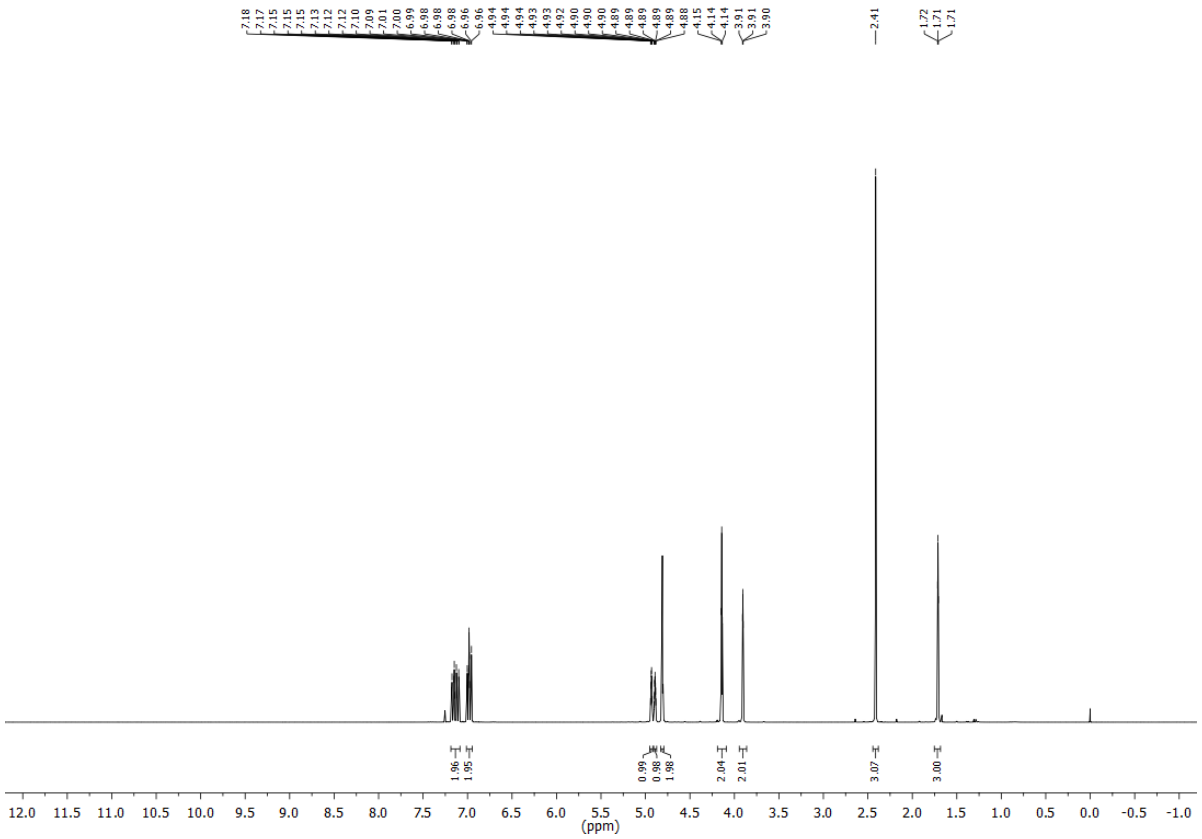
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.71 (t, *J* = 1.3 Hz, 3H), 2.41 (s, 3H), 3.90 – 3.91 (m, 2H), 4.14 (t, *J* = 1.8 Hz, 2H), 4.89 (ddq, *J* = 2.1, 1.5, 0.8 Hz, 1H), 4.93 (dq, *J* = 2.2, 1.1 Hz, 1H), 6.98 (ddd, *J* = 8.1, 6.3, 1.3 Hz, 2H), 7.09 – 7.19 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.7, 19.4, 56.5, 57.0, 73.4, 80.9, 83.6, 112.2, 112.9, 121.9, 125.6, 126.3, 127.6, 141.2, 154.3.

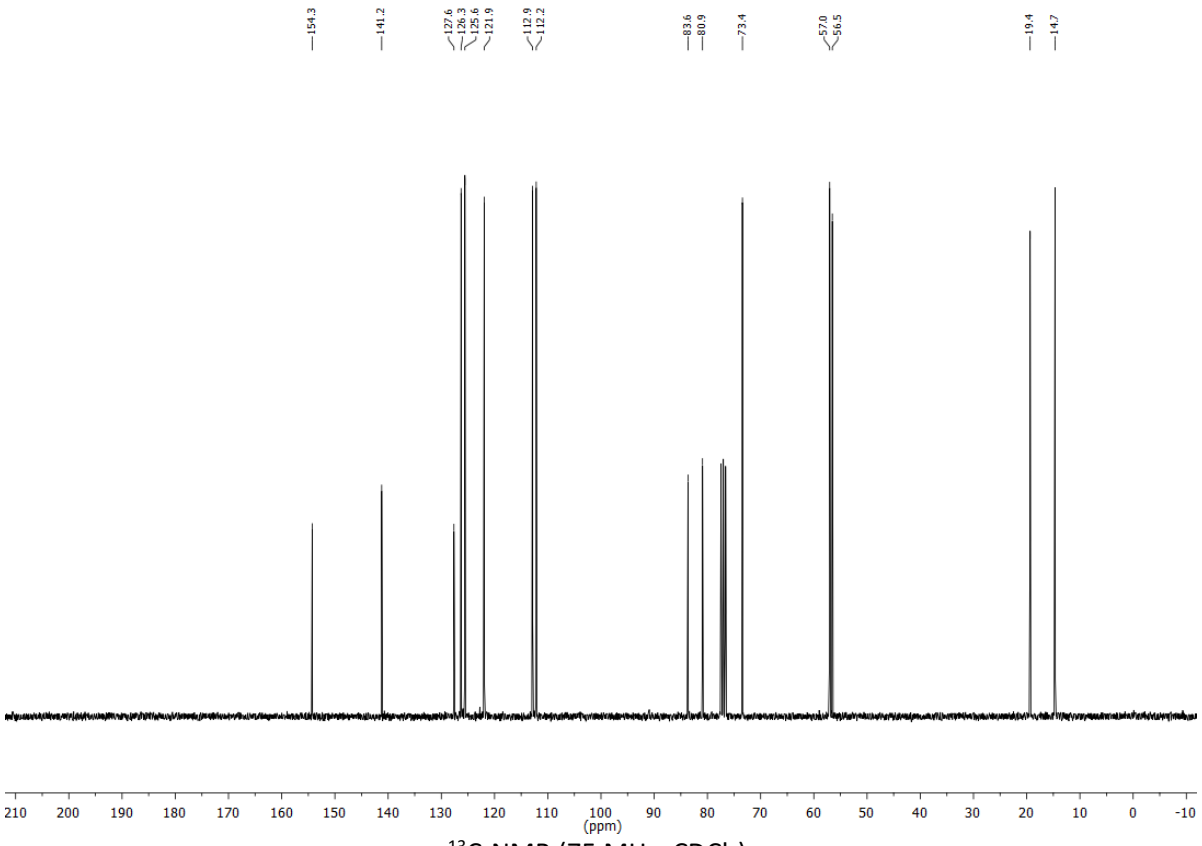
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3068, 2977, 2918, 2852, 1577, 1471, 1443, 1356, 1217, 1129, 1073, 1004.

$C_{15}H_{18}O_2S$ calcd.: 262.1028, found: 262.10465 (GC-HRMS).

[30] B. M. Trost and A. W. Franz, *J. Am. Chem. Soc.*, 2010, **132**, 18429.

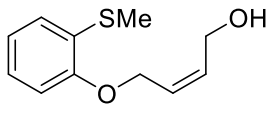


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(*Z*)-4-(2-(Methylthio)phenoxy)but-2-en-1-ol (19.1f)



Compound **19.1f** was synthesized according GP1.

A solution of **SM1** (1.40 g, 10.00 mmol, 1.00 equiv.), PPh_3 (2.62 g, 10.00 mmol, 1.00 equiv.) and (*Z*)-but-2-ene-1,4-diol (882.0 mg, 10.00 mmol, 1.00 equiv.) in dry toluene (60 ml) was cooled to 0 °C. DIAD (2.02 g, 1.96 ml, 10.00 mmol, 1.00 equiv.) in dry toluene (48 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred for 48 h. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 4:1→2:1) gave the desired product (827 mg, 3.93 mmol, 39%) as a colorless oil.

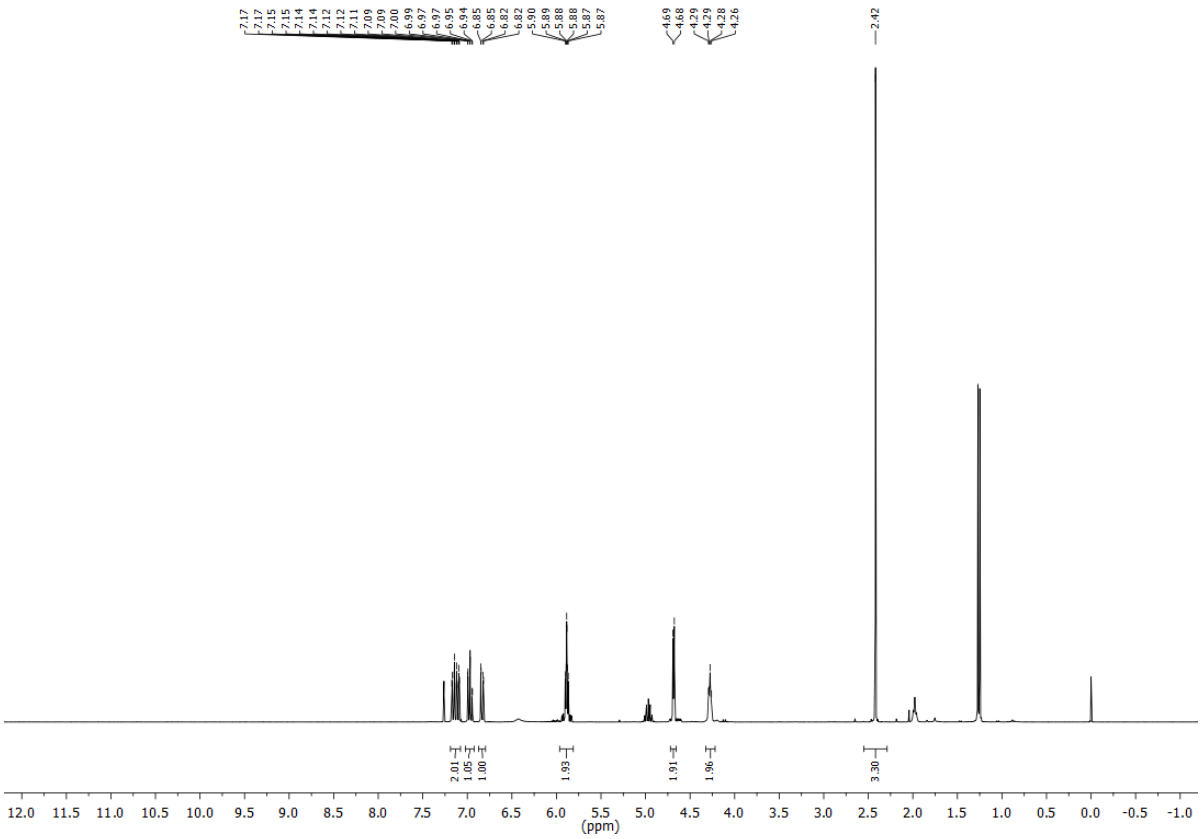
R_f = 0.17 (*n*-pentane:EtOAc = 4:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 4.22 – 4.33 (m, 2H), 4.68 (d, *J*=4.5, 2H), 5.84 – 5.92 (m, 2H), 6.83 (dd, *J*=8.1, 1.3, 1H), 6.97 (td, *J*=7.6, 1.3, 1H), 7.08 – 7.20 (m, 2H).

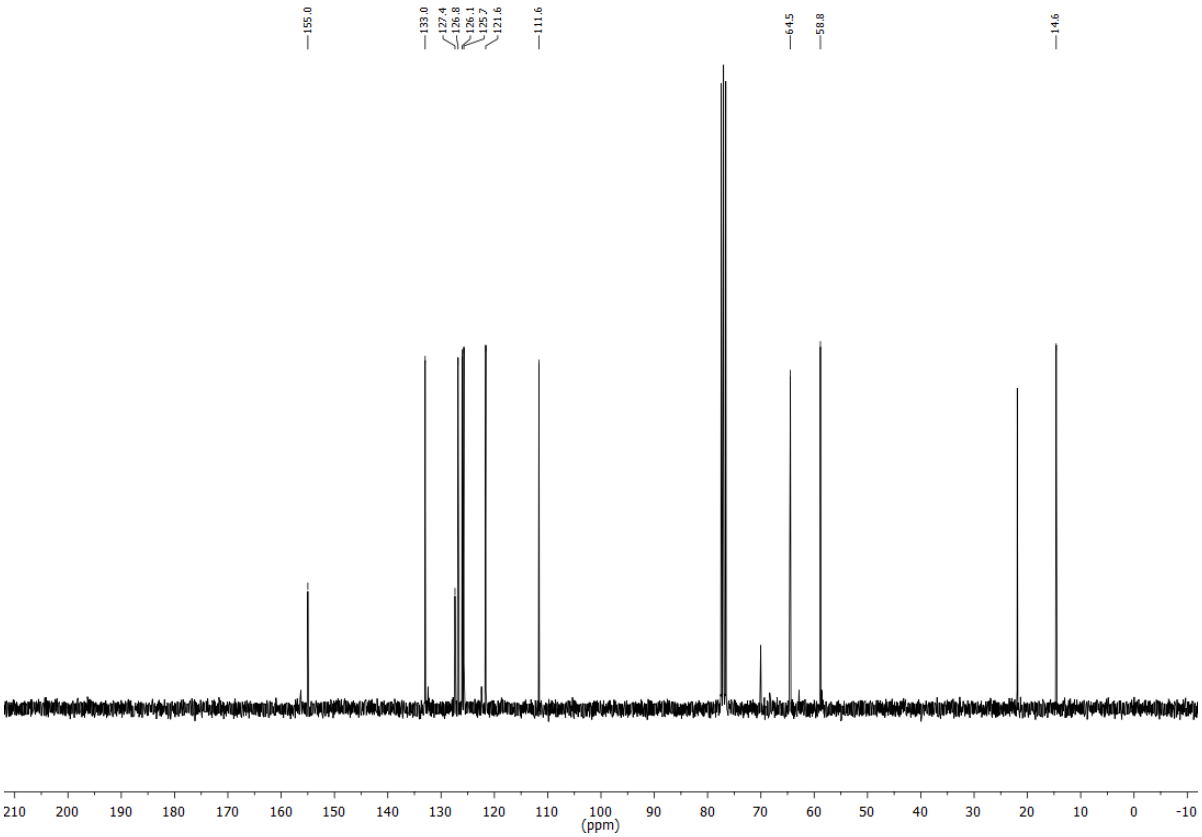
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.6, 58.8, 64.5, 111.6, 121.6, 125.7, 126.1, 126.8, 127.4, 133.0, 155.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3314, 3061, 3024, 2980, 2923, 2870, 1713, 1576, 1470, 1440, 1226, 1011.

$C_{11}H_{14}O_2S$ calcd.: 210.0715, found: 210.0731 (GC-HRMS).

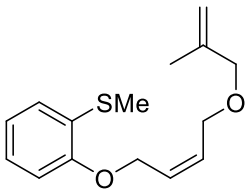


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(*Z*)-Methyl(2-((4-((2-methylallyl)oxy)but-2-en-1-yl)oxy)phenyl)sulfane (19.2f)



Following a reported procedure[31], a solution of **19.1f** (483 mg, 2.3 mmol, 1.0 equiv.) in DMF (12 ml) was cooled to 0 °C and treated with NaH (148 mg of 60% dispersion, 3.7 mmol, 1.61 equiv.). After 30 min of stirring, 3-bromo-2-methyl-1-propene (378.0 mg, 0.29 ml, 2.8 mmol, 1.22 equiv.) in DMF (14 ml) followed by TBAI (130.0 mg, 0.35 mmol, 0.15 equiv.) were added, the reaction was warmed to RT and stirred overnight. It was then quenched with H_2O at 0 °C, extracted with Et_2O (3 x 50 ml), washed with brine and dried over Na_2SO_4. The solvent was evaporated *in vacuo* to obtain the product after flash column chromatography (*n*-pentane:EtOAc = 40:1→20:1) as a colorless oil (1.42 mmol, 375 mg, 62%).

R_f = 0.35 (*n*-pentane:EtOAc = 20:1).

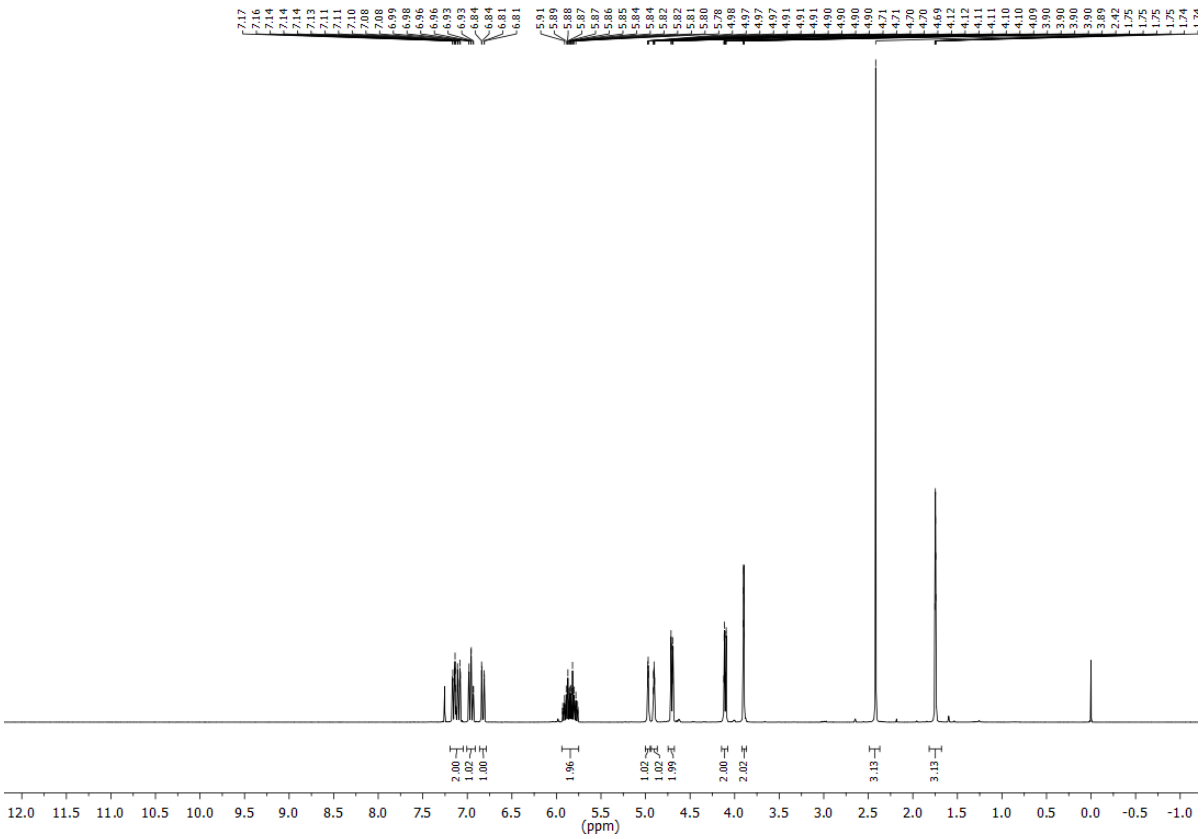
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.68 – 1.79 (m, 3H), 2.42 (s, 3H), 3.84 – 3.96 (m, 2H), 4.11 (dt, *J*=5.6, 1.1, 2H), 4.70 (dd, *J*=5.6, 1.2, 2H), 4.90 (ddd, *J*=2.1, 1.5, 0.7, 1H), 4.97 (dd, *J*=2.2, 1.1, 1H), 5.69 – 5.97 (m, 2H), 6.82 (dd, *J*=8.1, 1.3, 1H), 6.96 (td, *J*=7.6, 1.3, 1H), 7.07 – 7.19 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.6, 19.5, 64.9, 65.8, 74.3, 111.6, 112.3, 121.5, 125.7, 126.0, 127.5, 127.8, 129.9, 142.0, 155.1.

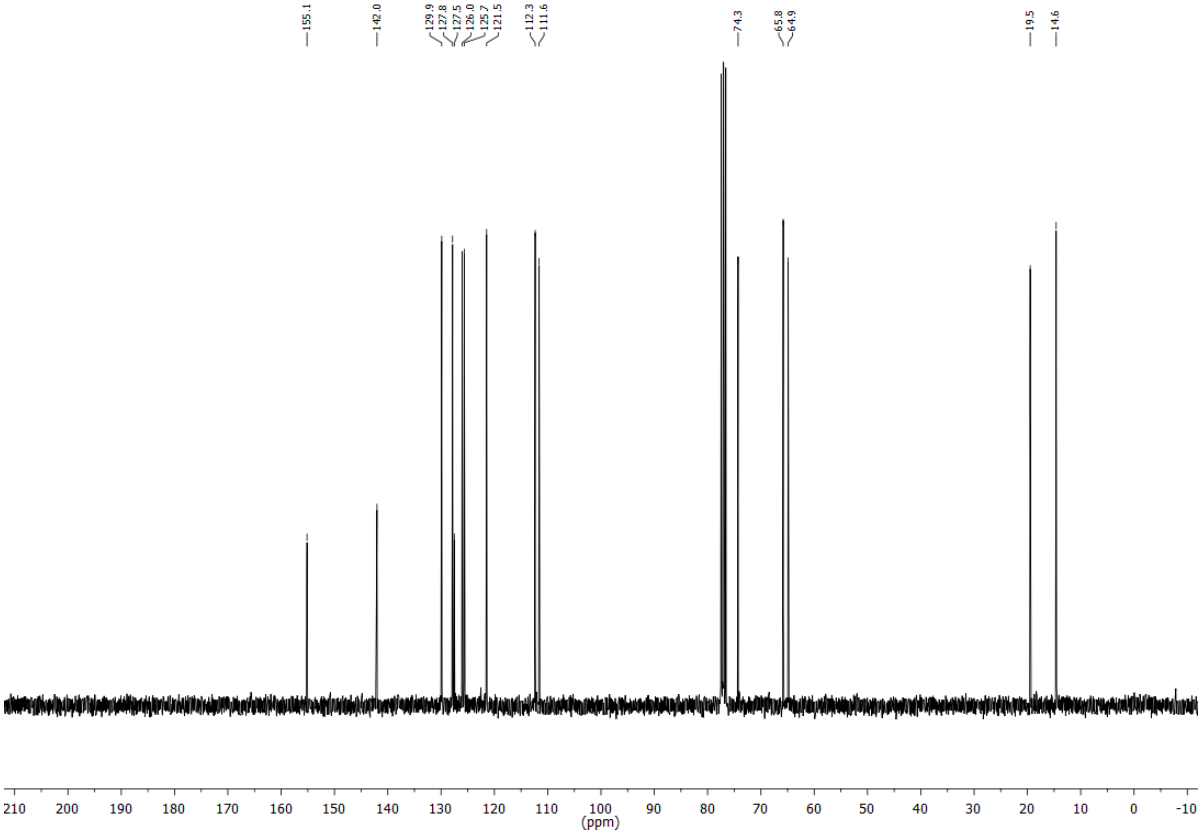
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3067, 3025, 2976, 2918, 2854, 1577, 1470, 1442, 1228, 1075, 1009.

$C_{15}H_{20}O_2S$ calcd.: 264.1184, found: 264.1207 (GC-HRMS).

[31] T. Schitter, P. G. Jones and D. B. Werz, *Chem. Eur. J.*, 2018, **24**, 13446.



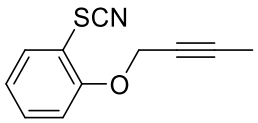
^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

Synthesis of Thiocyanates 4

1-(But-2-yn-1-yloxy)-2-thiocyanatobenzene (1a)



Thiocyanate **1a** was synthesized from compound **11a** (1.6 g, 8.32 mmol) according GP 3. A mixture of CH_3CN/THF (1:1, 32 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) to obtain the product (887 mg, 4.32 mmol, 52%) as colorless solid.

m.p.: 43 °C.

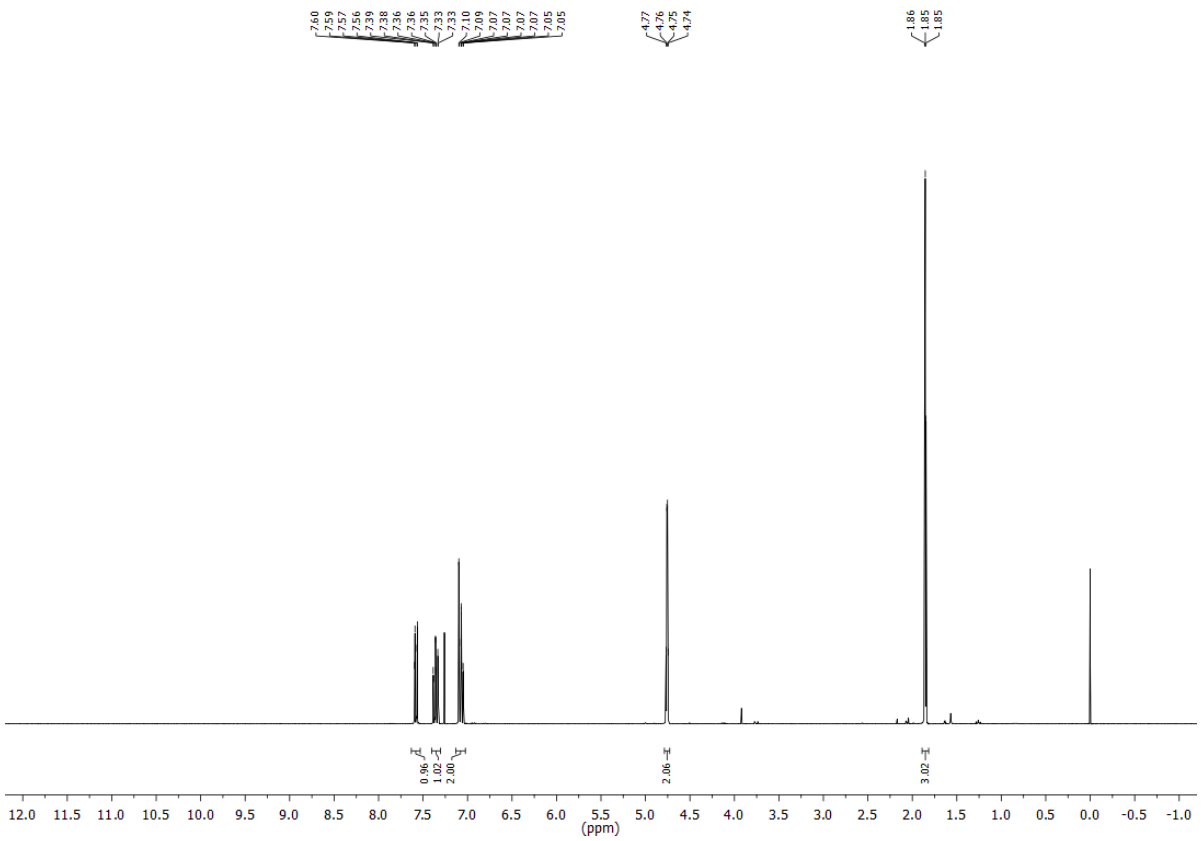
R_f = 0.67 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.85 (t, *J* = 2.4 Hz, 3H), 4.76 (q, *J* = 2.4 Hz, 2H), 7.04 – 7.10 (m, 2H), 7.32 – 7.39 (m, 1H), 7.58 (dd, *J* = 8.2, 1.6 Hz, 1H).

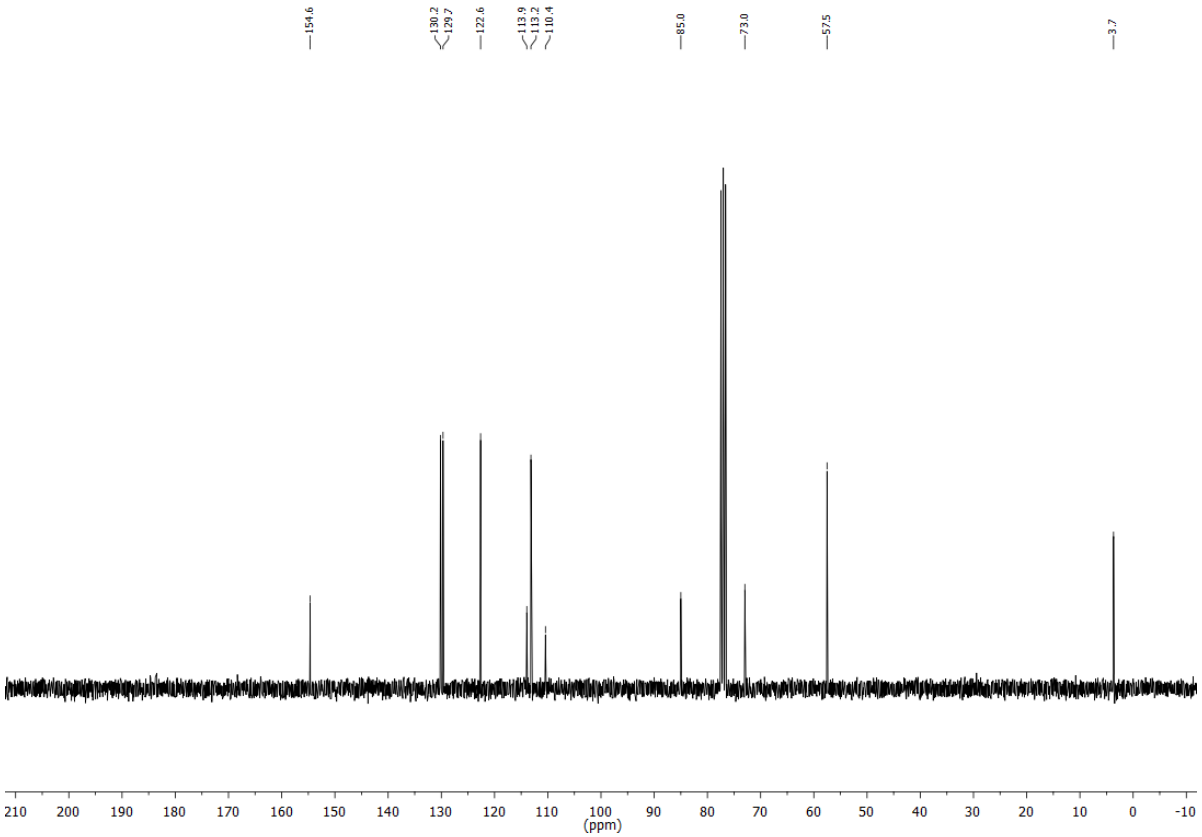
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.7, 57.5, 73.0, 85.0, 110.4, 113.2, 113.9, 122.6, 129.7, 130.2, 154.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3066, 2967, 2159, 1579, 1473, 1447, 1224, 1143, 1060.

$C_{11}H_9NOS$ calcd.: 202.0332 [M-H], found: 202.0346 (GC-HRMS).

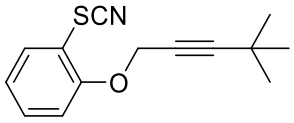


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((4,4-Dimethylpent-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1b)



Thiocyanate **1b** was synthesized from compound **11b** (105 mg, 448 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 2.0 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (52 mg, 212 µmol, 47%) as colorless oil.

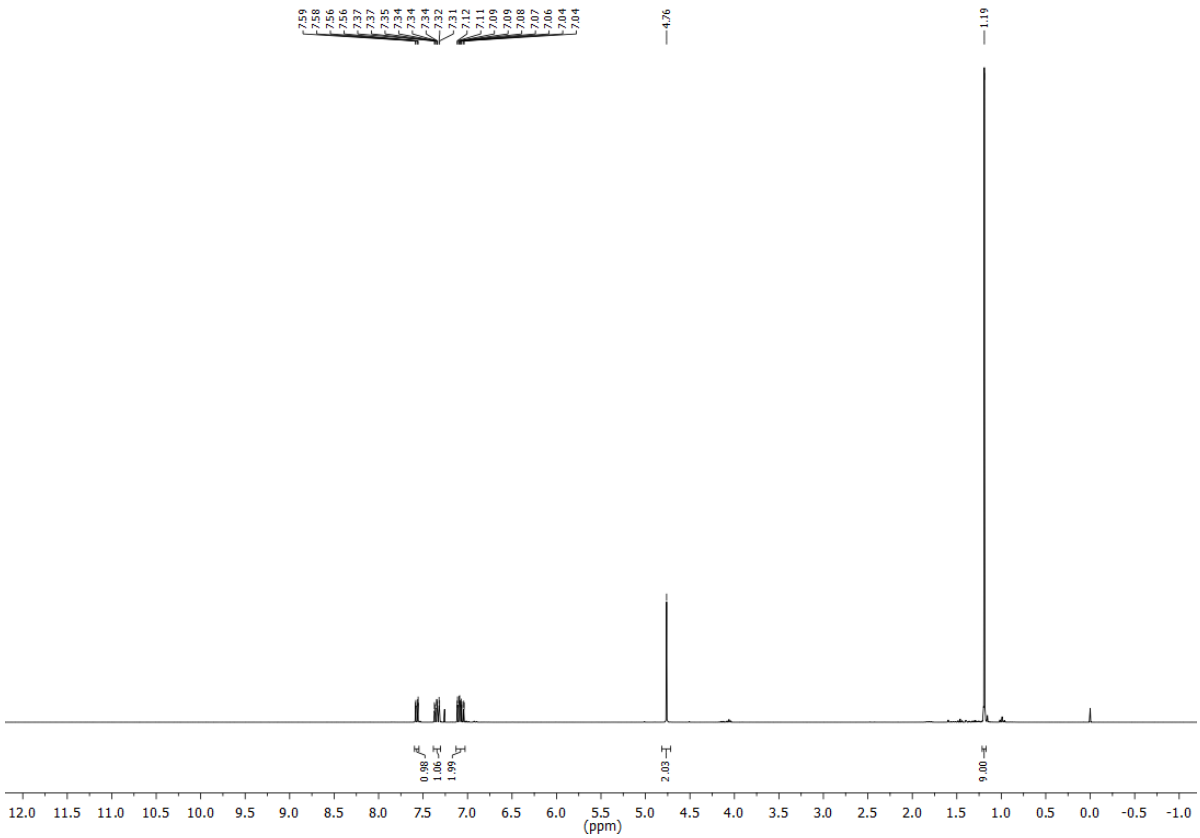
R_f = 0.34 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.19 (s, 9H), 4.76 (s, 2H), 7.03 – 7.12 (m, 2H), 7.34 (ddd, *J* = 8.4, 7.5, 1.6 Hz, 1H), 7.55 – 7.59 (m, 1H).

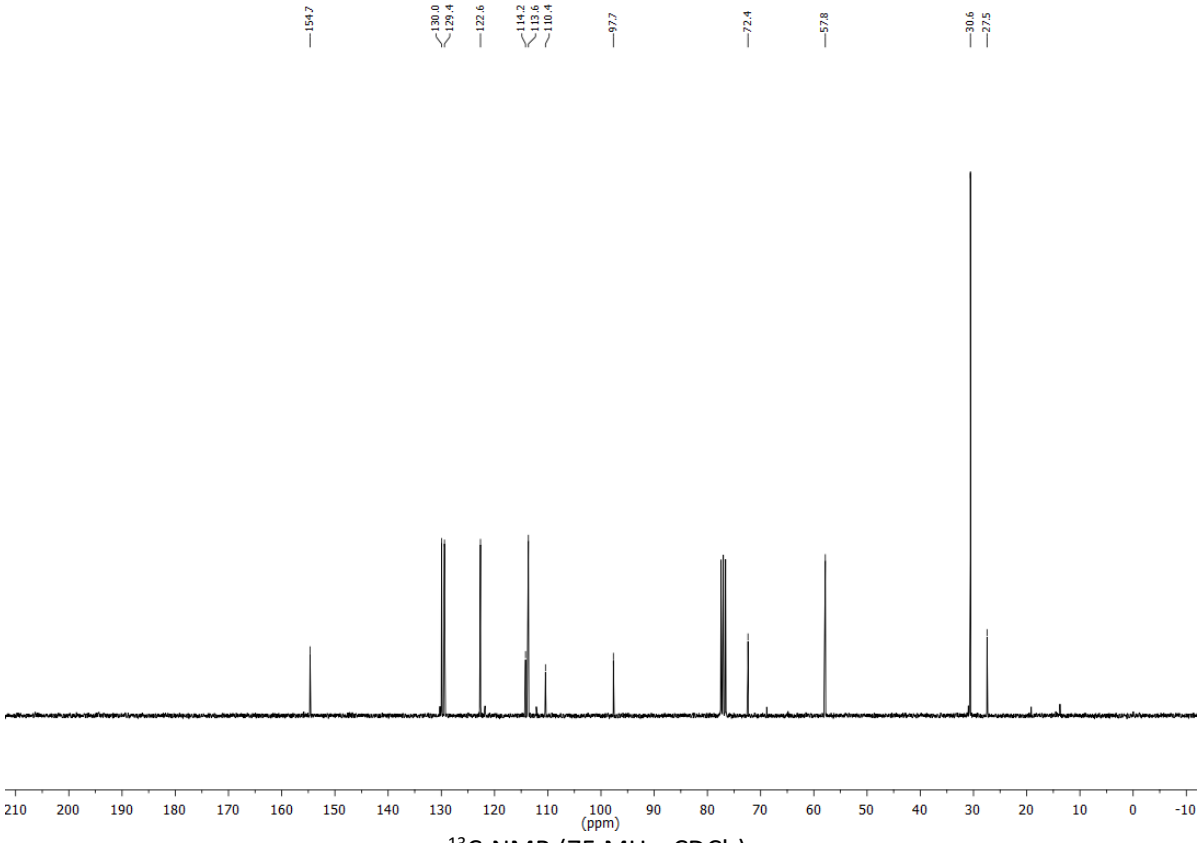
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 27.5, 30.6, 57.8, 72.4, 97.7, 110.4, 113.6, 114.2, 122.6, 129.4, 130.0, 154.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2969, 2929, 2869, 2239, 2158, 1582, 1475, 1227, 1066.

$C_{14}H_{15}NOS$ calcd.: 268.0767, found: 268.0769 $[M+Na]^+$ (ESI-HRMS).

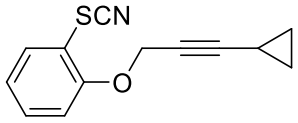


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-Cyclopropyl-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1c)



Thiocyanate **1c** was synthesized from compound **11c** (211 mg, 0.97 mmol) according GP 3. A mixture of CH_3CN/THF (1:1, 5.6 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) to obtain the product (24 mg, 104 µmol, 11%) as colorless oil.

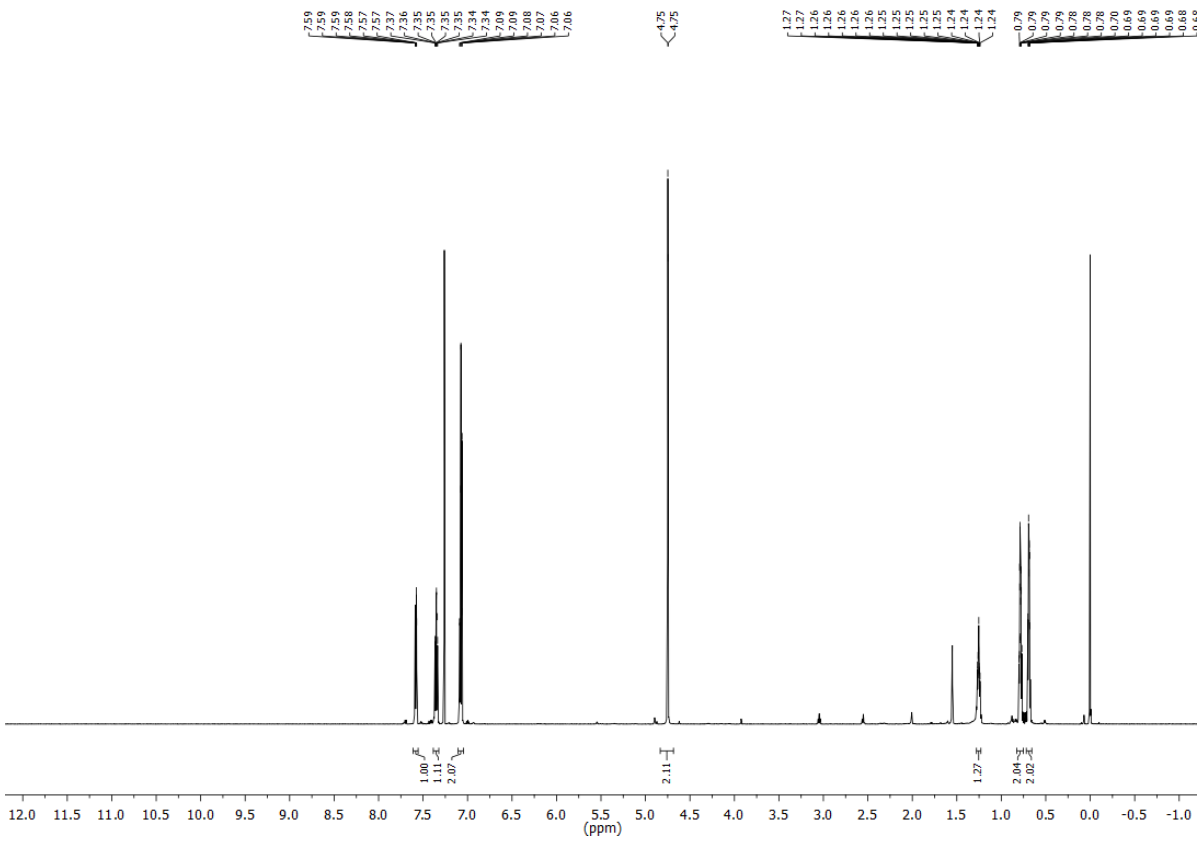
R_f = 0.48 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.66 – 0.71 (m, 2H), 0.75 – 0.82 (m, 2H), 1.22 – 1.29 (m, 1H), 4.75 (d, *J* = 1.9 Hz, 2H), 7.08 (td, *J* = 7.6, 1.2 Hz, 2H), 7.34 – 7.37 (m, 1H), 7.57 – 7.59 (m, 1H).

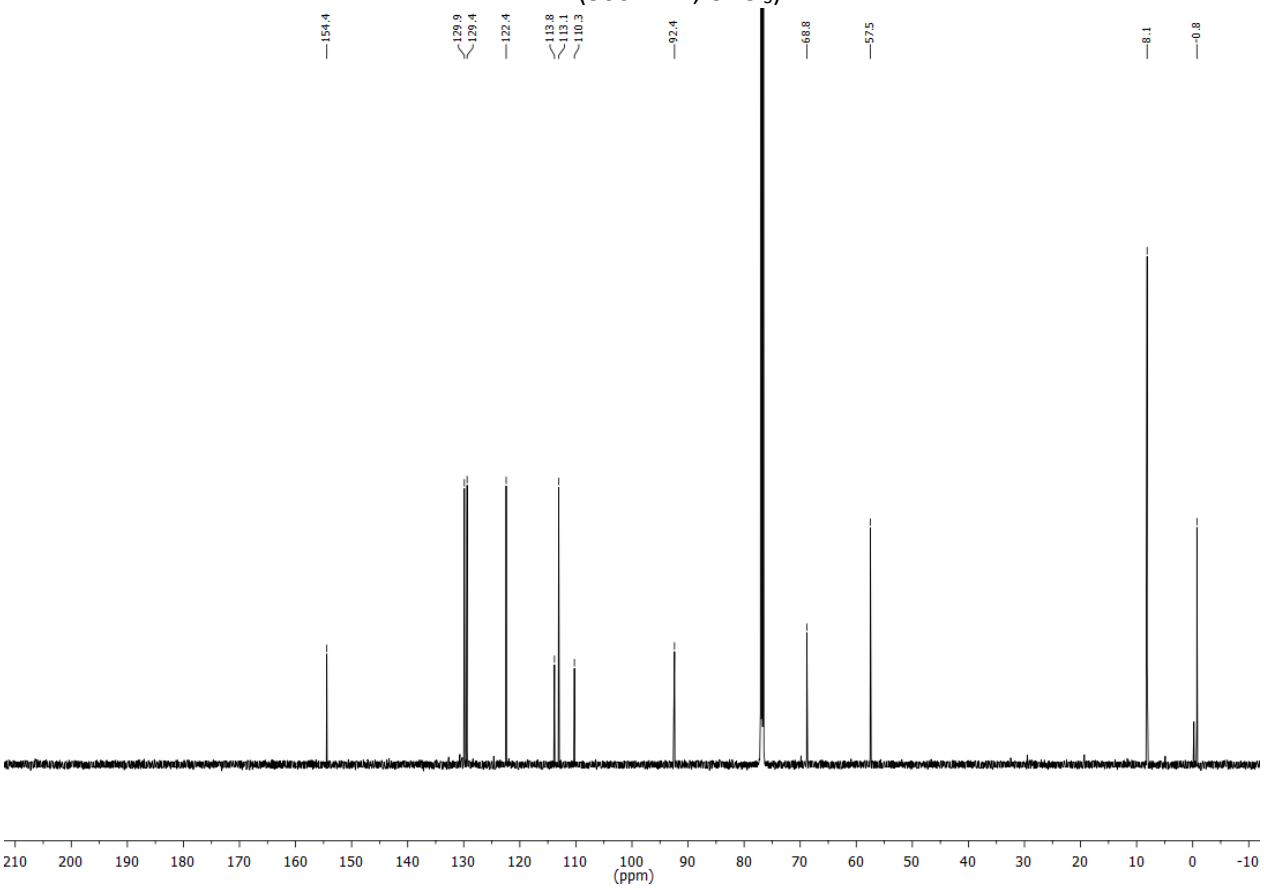
^{13}C-NMR (75 MHz, $CDCl_3$): δ = -0.8, 8.1, 57.5, 68.8, 92.4, 110.3, 113.1, 113.8, 122.4, 129.4, 129.9, 154.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3012, 2925, 2864, 2236, 2157, 1581, 1474, 1226, 1059.

$C_{13}H_{11}NOS$ calcd.: 229.0561, found: 229.0563 (GC-HRMS).

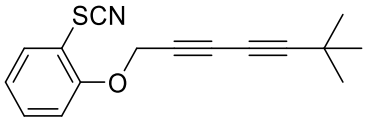


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((6,6-Dimethylhepta-2,4-diyn-1-yl)oxy)-2-thiocyanatobenzene (1d)



Thiocyanate **1d** was synthesized from compound **11d** (200 mg, 774 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 4.4 ml) was used as solvent. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (*n*-pentane:EtOAc = 60:1) the product was obtained as a colorless solid (116 mg, 431 µmol, 56%).

m.p.: 49 °C

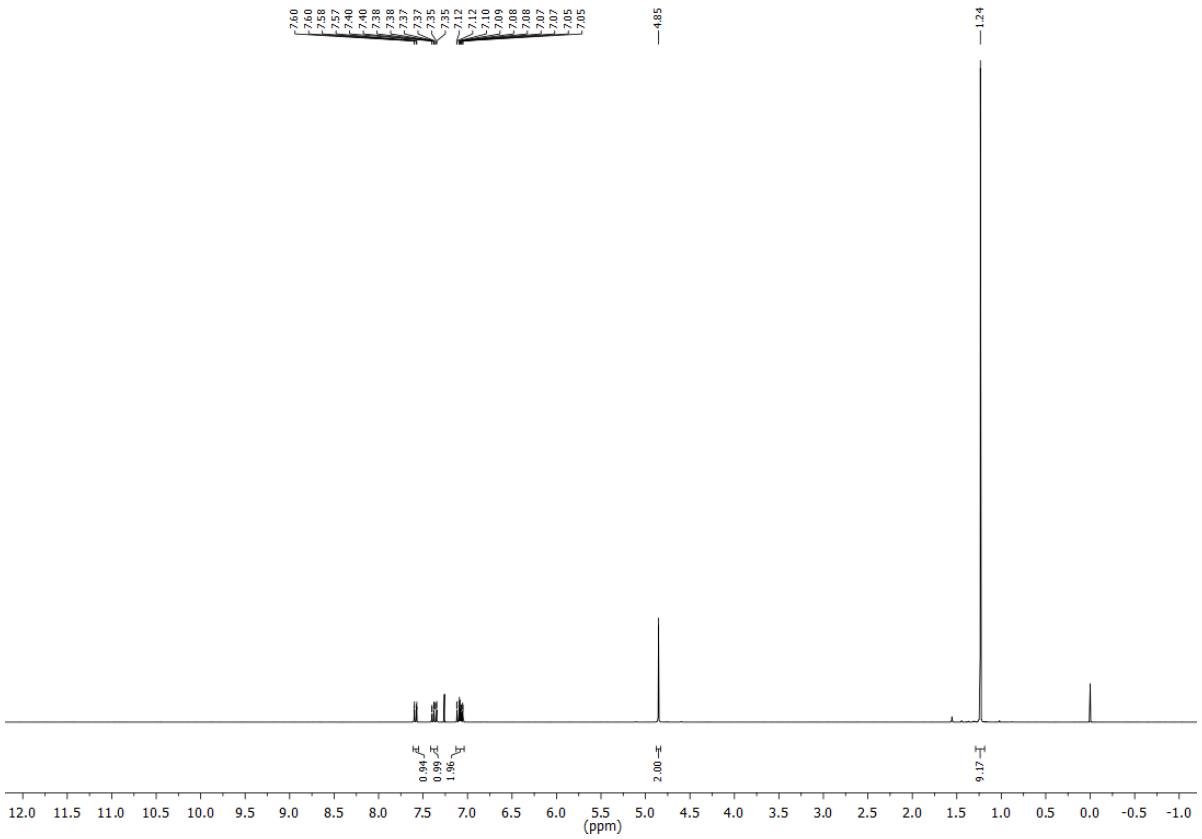
R_f = 0.18 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 9H), 4.85 (s, 2H), 7.05 – 7.13 (m, 2H), 7.37 (ddd, *J* = 8.1, 7.6, 1.6 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.6 Hz, 1H).

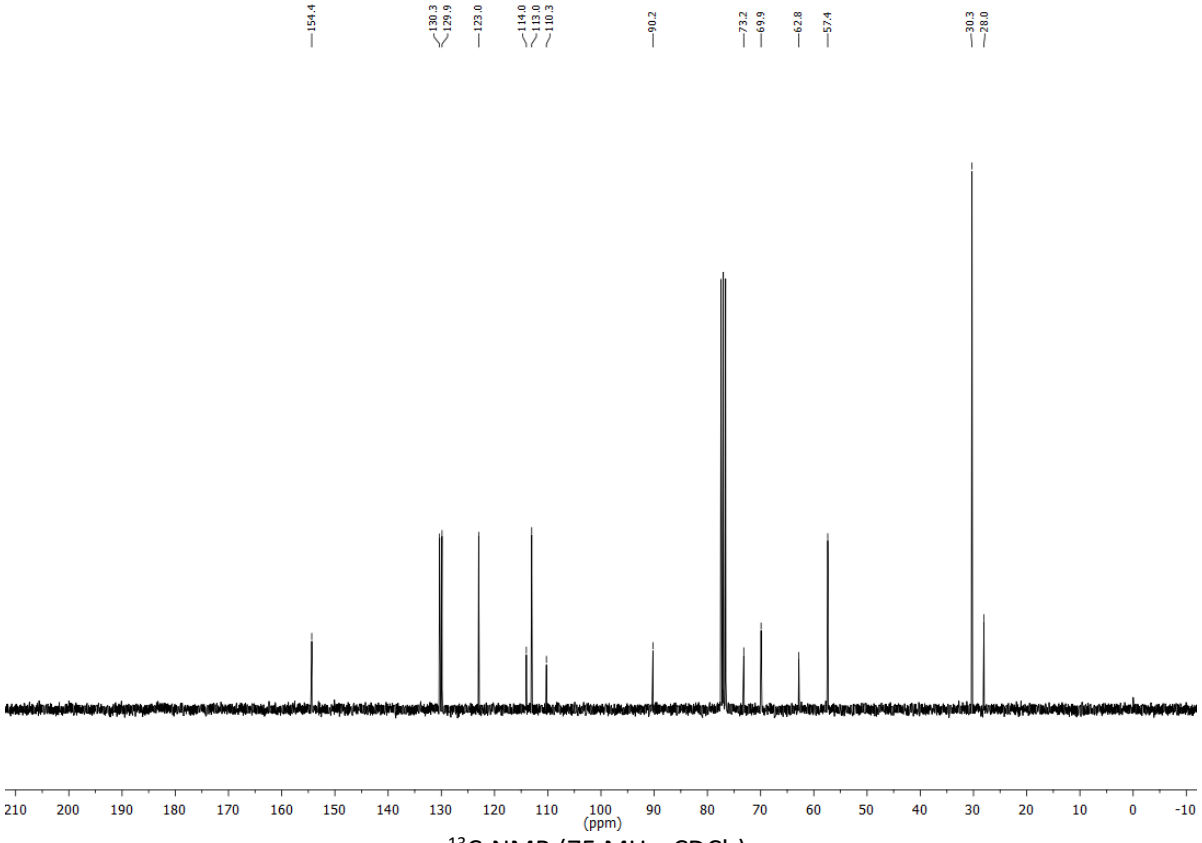
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 28.0, 30.3, 57.4, 62.8, 69.9, 73.2, 90.2, 110.3, 113.0, 114.0, 123.0, 129.9, 130.3, 154.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2972, 2931, 2868, 2246, 2158, 1580, 1474, 1449, 1284, 1222, 1165.

$C_{16}H_{15}NOS$ calcd.: 269.0874, found: 269.0895 (GC-HRMS).

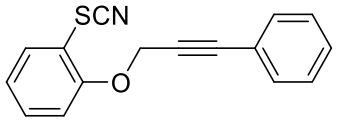


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-Phenylprop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1e)



Thiocyanate **1e** was synthesized from compound **11e** (201 mg, 790 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 4.6 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (107 mg, 403 µmol, 51%) as pale yellow solid.

m.p.: 39 °C.

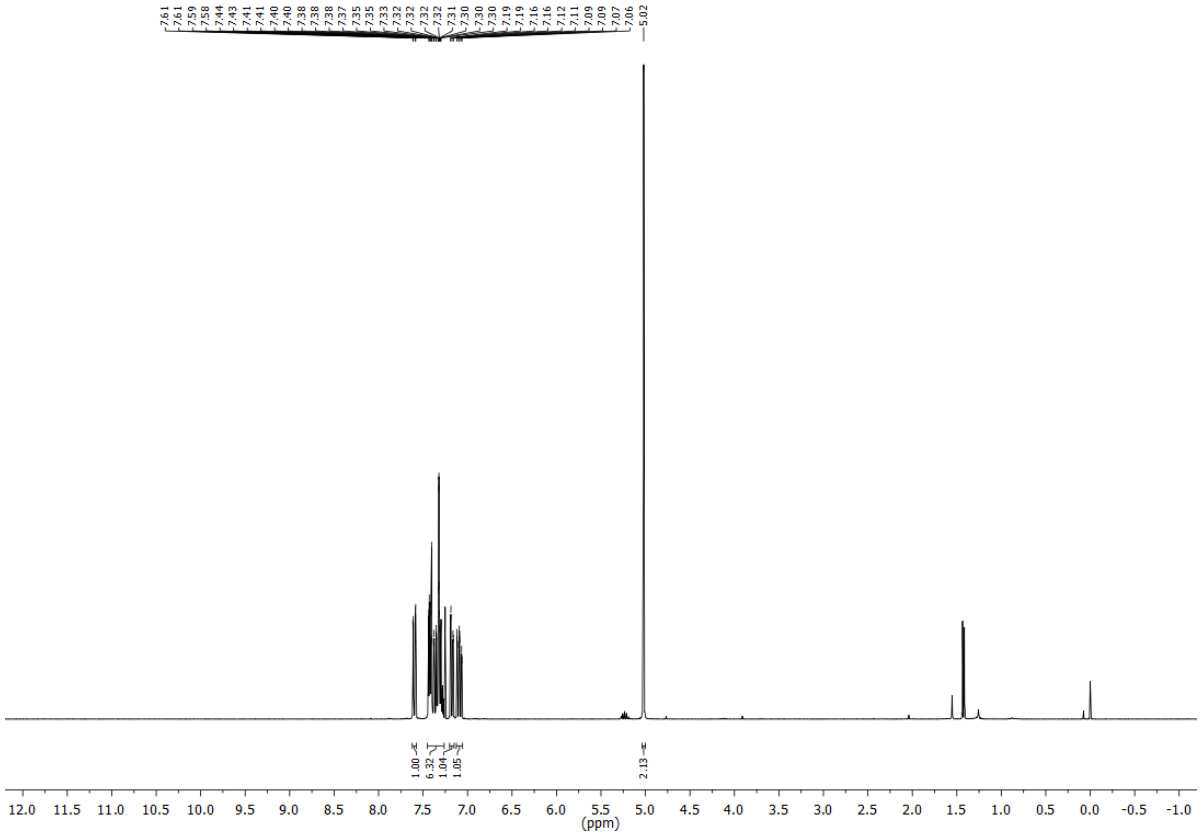
$\mathbf{R_f}$ = 0.13 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.02 (s, 2H), 7.06 – 7.12 (m, 1H), 7.18 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.26 – 7.45 (m, 6H), 7.60 (dd, *J* = 7.9, 1.6 Hz, 1H).

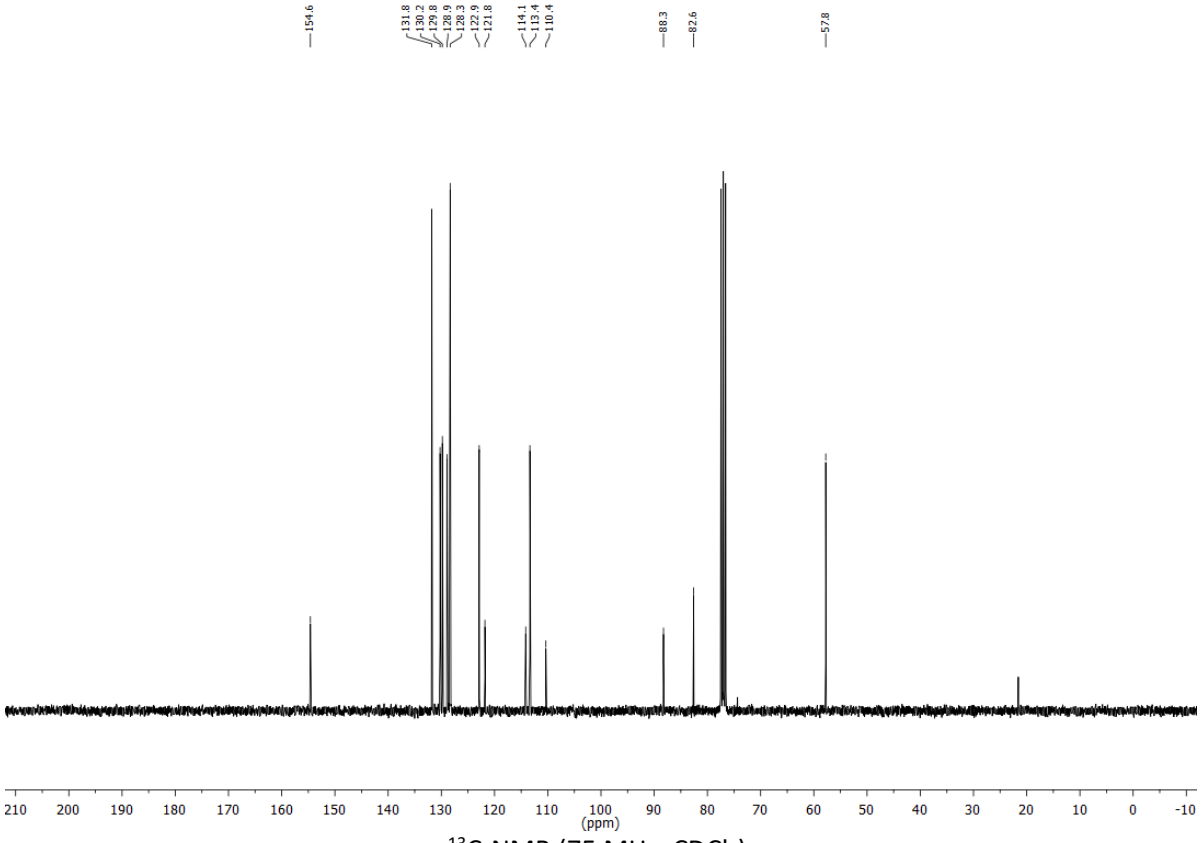
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 57.8, 82.6, 88.3, 110.4, 113.4, 114.1, 121.8, 122.9, 128.3, 128.9, 129.8, 130.2, 131.8, 154.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 2921, 2866, 2238, 2157, 1580, 1474, 1446, 1223, 1062.

$C_{16}H_{11}NOS$ calcd.: 288.0454, found: 288.0455 $[M+Na]^+$ (ESI-HRMS).

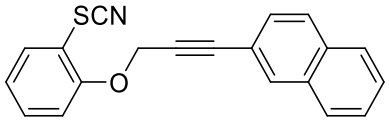


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-(2-Naphthyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1f)



Thiocyanate **1f** was synthesized from compound **11f** (143 mg, 469 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 2.8 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (62 mg, 196 µmol, 42%) as colorless solid.

m.p.: 55 °C.

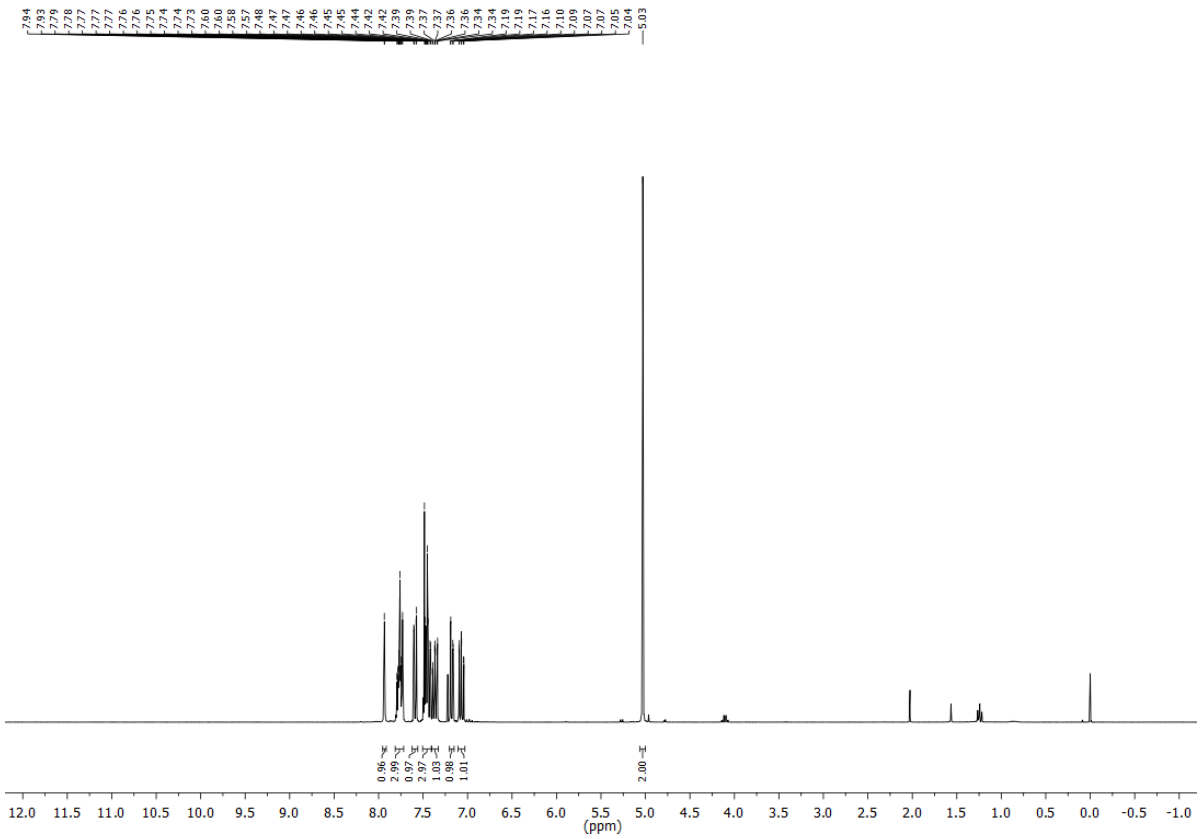
R_f = 0.12 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.03 (s, 2H), 7.07 (td, *J* = 7.7, 1.3 Hz, 1H), 7.18 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.37 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1H), 7.41 – 7.50 (m, 3H), 7.59 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.71 – 7.81 (m, 3H), 7.93 (d, *J* = 1.4 Hz, 1H).

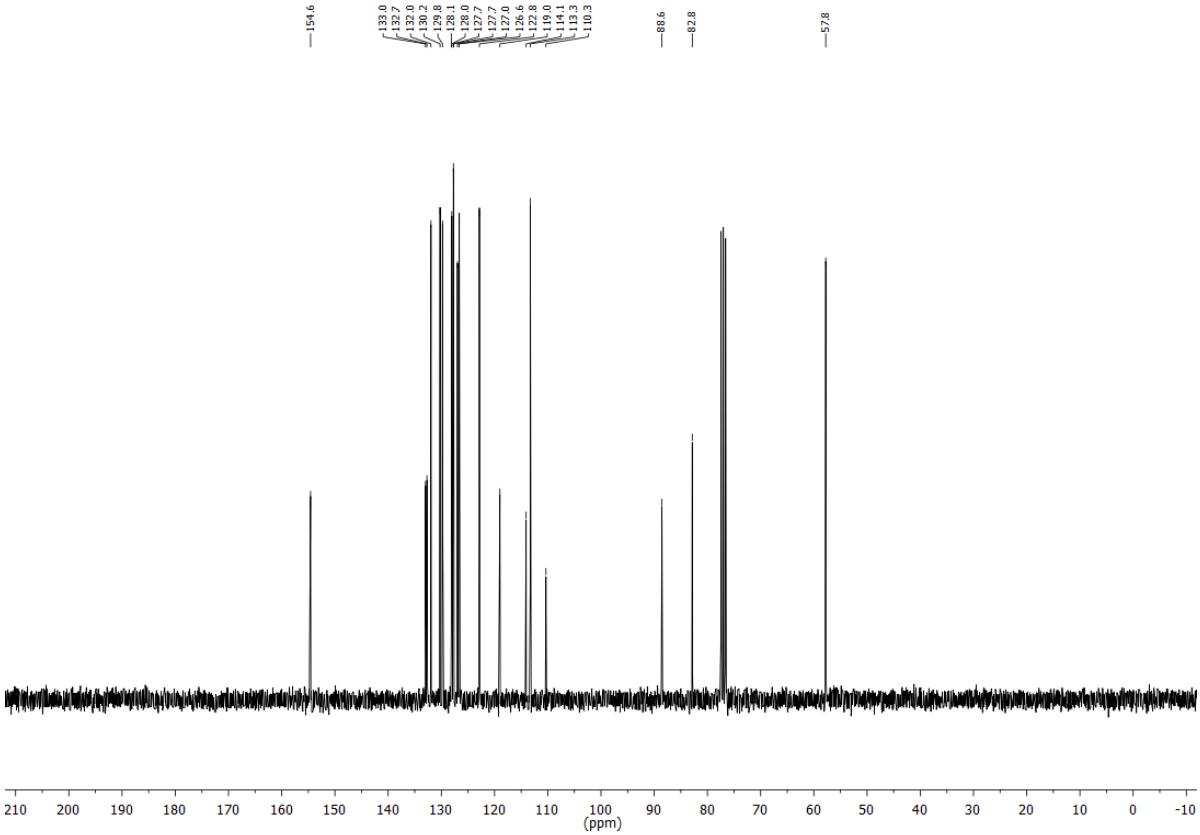
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 57.8, 82.8, 88.6, 110.3, 113.3, 114.1, 119.0, 122.8, 126.6, 127.0, 127.7, 127.7, 128.0, 128.1, 129.8, 130.2, 132.0, 132.7, 133.0, 154.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3062, 2963, 2925, 2226, 2148, 1580, 1499, 1474, 1295, 1223, 1014.

$C_{20}H_{13}NOS$ calcd.: 315.0718, found: 315.0722 (GC-HRMS).

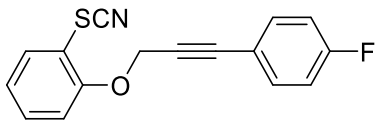


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-(4-Fluorophenyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1g)



Thiocyanate **1g** was synthesized from compound **11g** (85 mg, 312 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 1.6 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (43 mg, 152 µmol, 49%) as colorless solid.

m.p.: 92 °C.

R_f = 0.08 (*n*-pentane:EtOAc = 50:1).

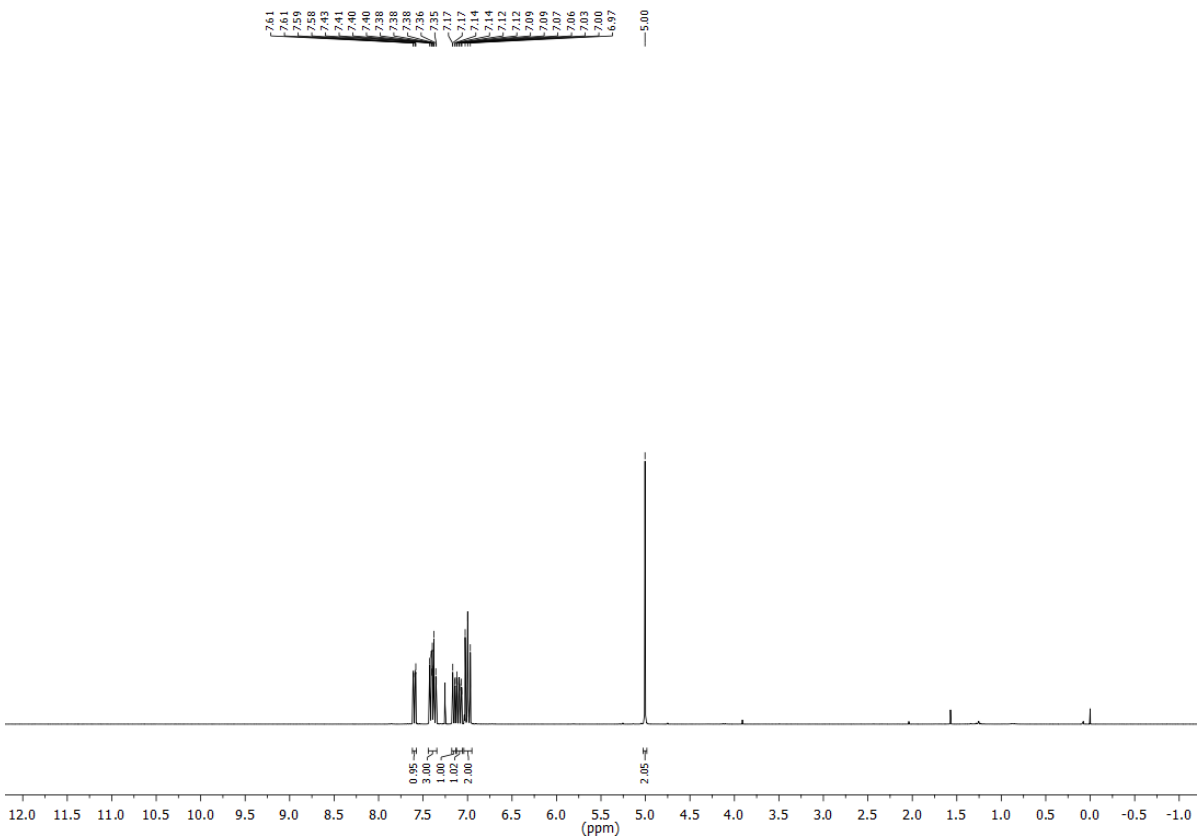
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.00 (s, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 7.06 – 7.12 (m, 1H), 7.15 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.35 – 7.44 (m, 3H), 7.60 (dd, *J* = 7.9, 1.6 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 57.7, 82.3, 82.4, 87.2, 110.3, 113.3, 114.1, 115.5, 115.8, 117.9, 117.9, 122.9, 129.9, 130.3, 133.7, 133.9, 154.6, 161.2, 164.5.

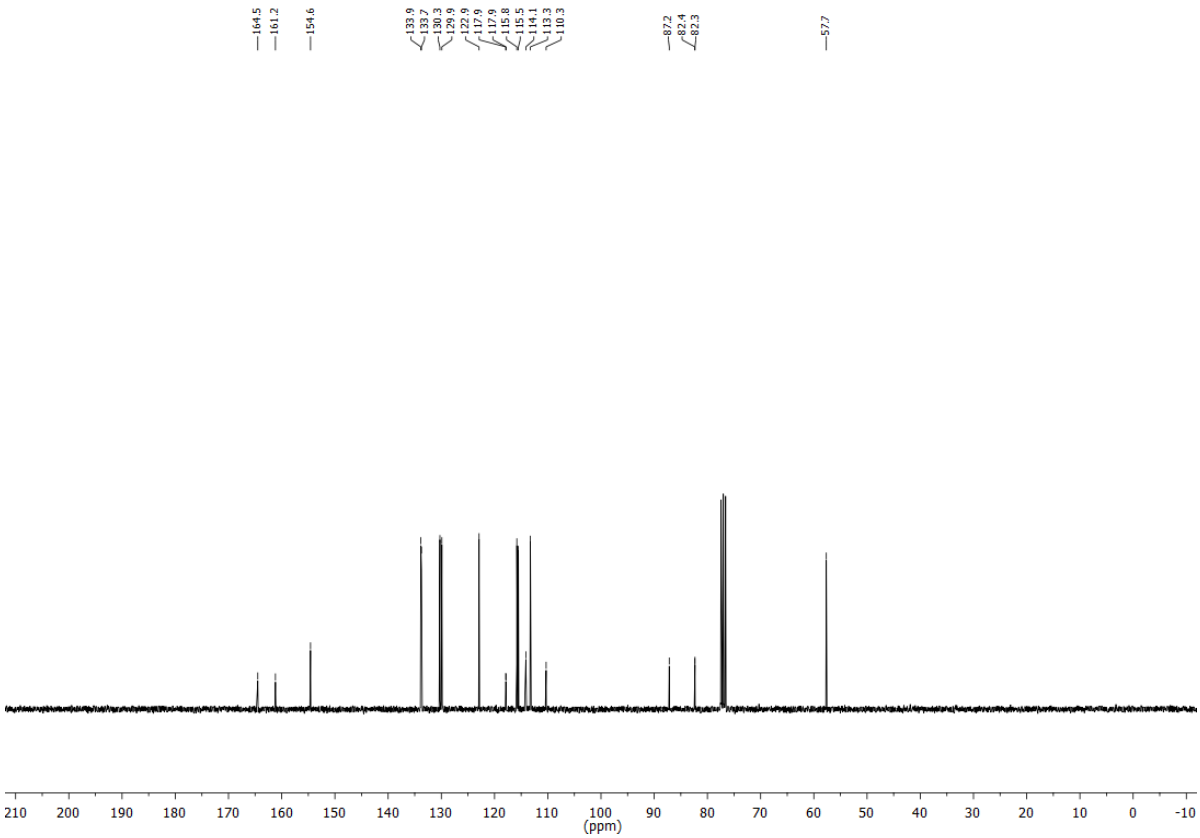
^{19}F-NMR (283 MHz, $CDCl_3$): δ = -110.07

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3101, 3068, 2932, 2242, 2150, 1580, 1502, 1472, 1449, 1278, 1212, 1009.

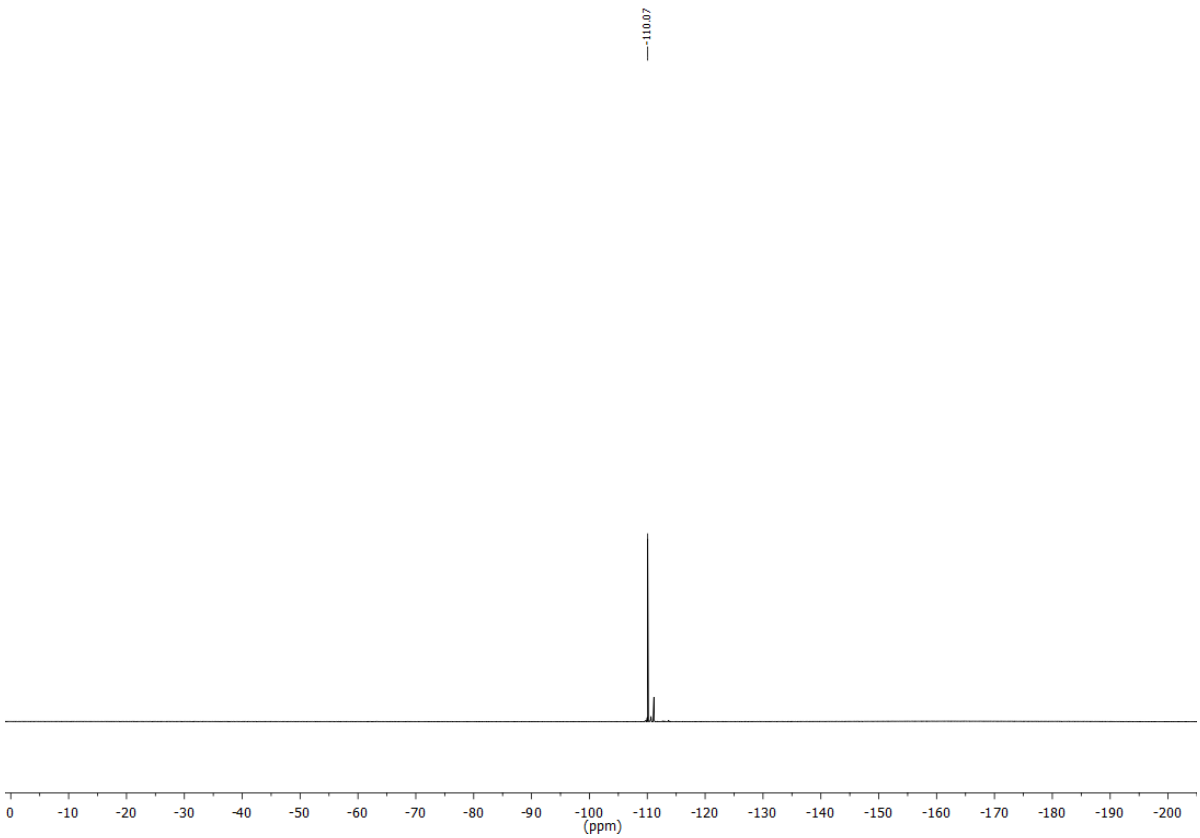
$C_{16}H_{10}FNOS$ calcd.: 306.0359, found: 306.0361 $[M+Na]^+$ (ESI-HRMS).



^{1}H-NMR (300 MHz, $CDCl_3$).

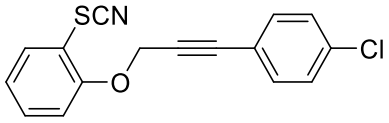


^{13}C-NMR (75 MHz, $CDCl_3$).



^{19}F-NMR (283 MHz, $CDCl_3$).

1-((3-(4-Chlorophenyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1h)



Thiocyanate **1h** was synthesized from compound **11h** (165 mg, 571 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 3.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (87 mg, 290 µmol, 51%) as yellow solid.

m.p.: 53 °C.

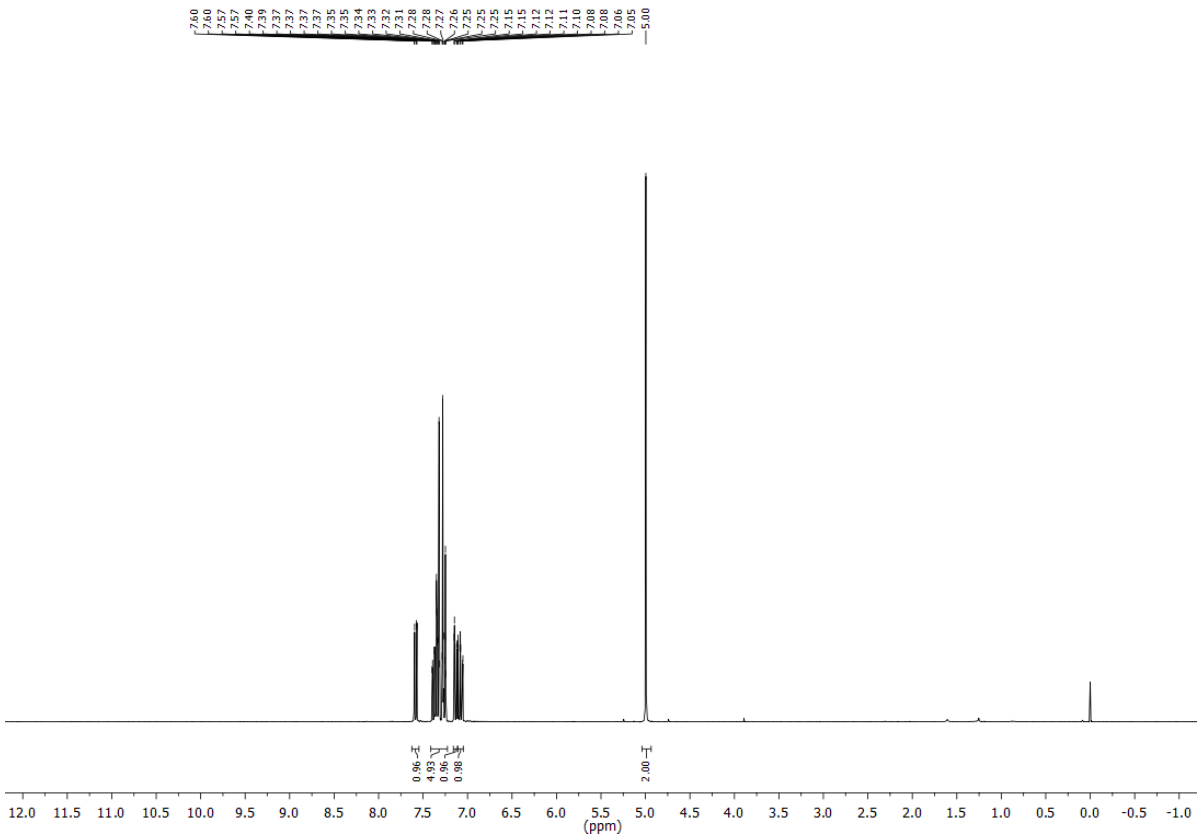
$\mathbf{R_f}$ = 0.17 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.00 (s, 2H), 7.05 – 7.11 (m, 1H), 7.14 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.23 – 7.41 (m, 5H), 7.58 (dd, *J* = 7.9, 1.6 Hz, 1H).

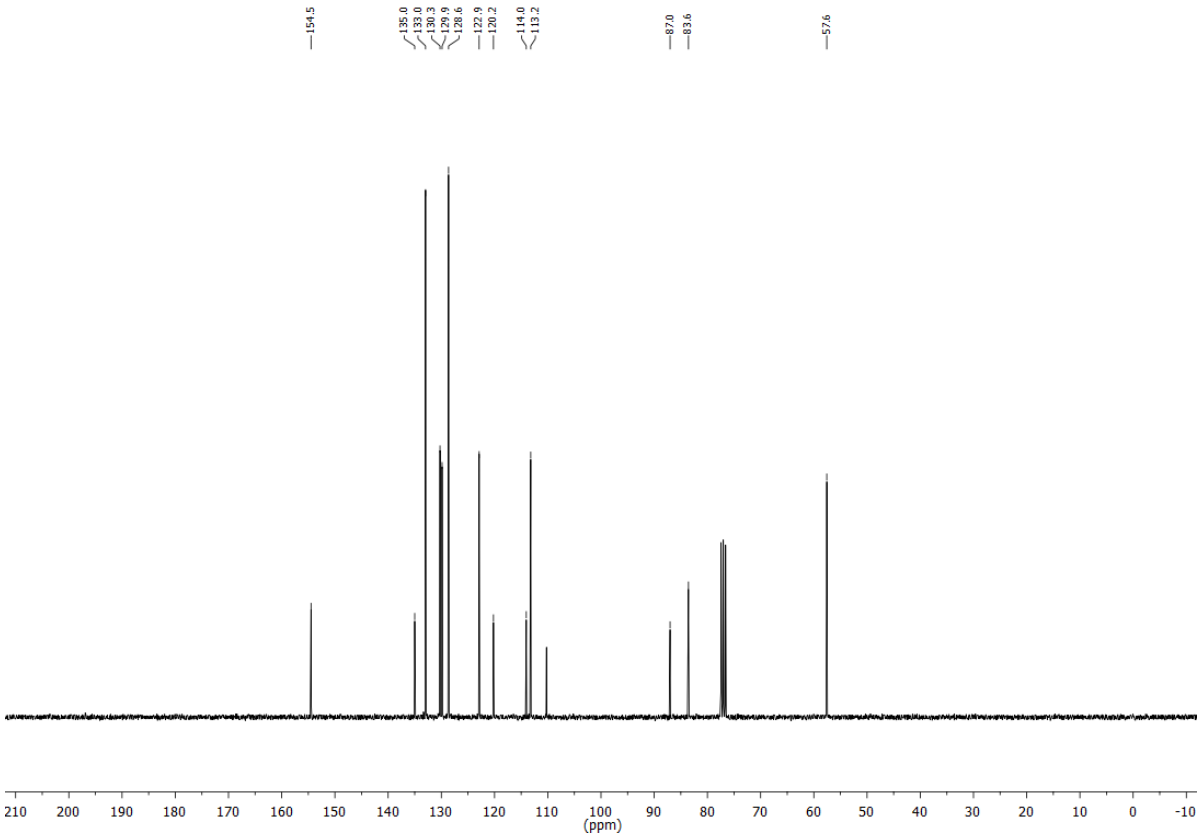
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 57.6, 83.6, 87.0, 113.2, 114.0, 120.2, 122.9, 128.6, 129.9, 130.3, 133.0, 135.0, 154.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3083, 3057, 2923, 2856, 2254, 2154, 1578, 1476, 1443, 1382, 1290, 1240, 1012.

$C_{16}H_{10}ClNOS$ calcd.: 322.0064, found: 322.0065 $[M+Na]^+$ (ESI-HRMS).

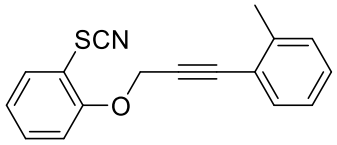


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-(*o*-Tolyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1i)



Thiocyanate **1i** was synthesized from compound **11i** (119 mg, 444 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 2.4 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (54 mg, 193 µmol, 43%) as pale yellow oil.

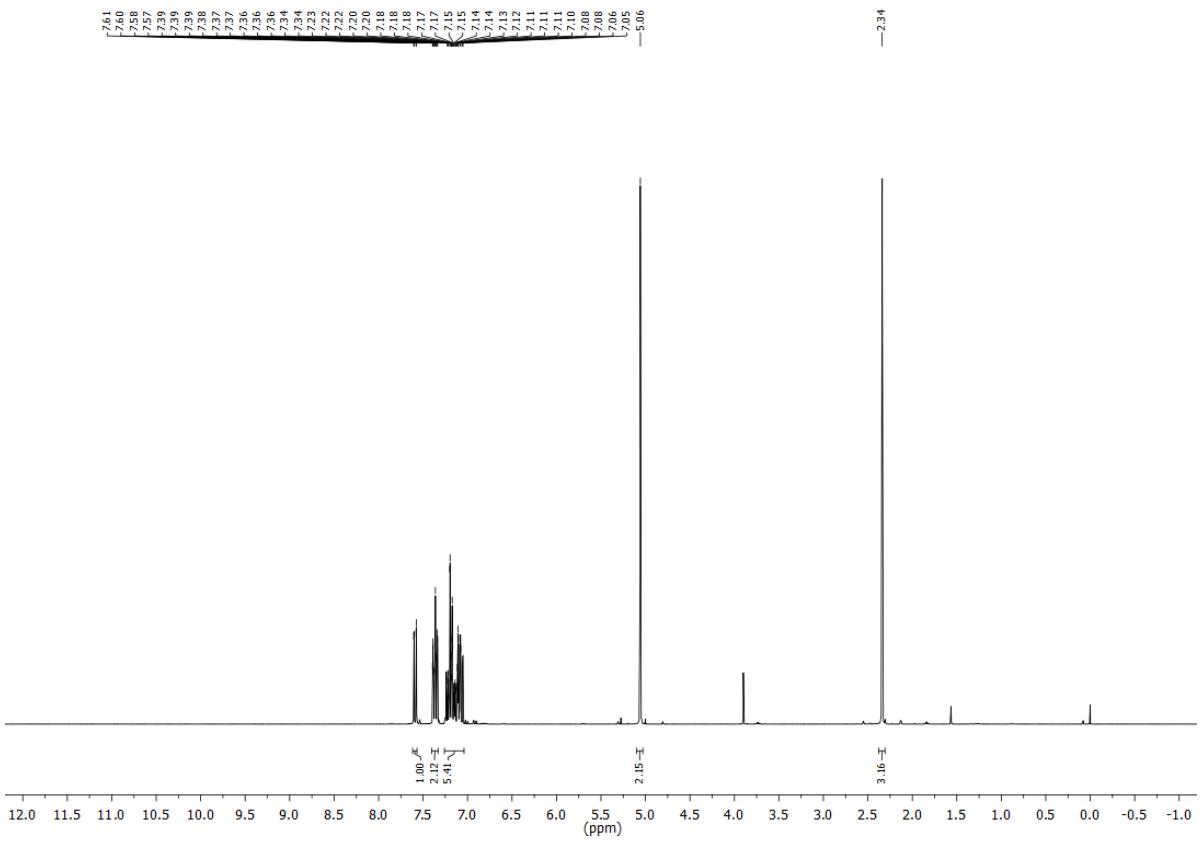
R_f = 0.13 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 5.06 (s, 2H), 7.04 – 7.26 (m, 5H), 7.33 – 7.41 (m, 2H), 7.59 (dd, *J* = 7.9, 1.6 Hz, 1H).

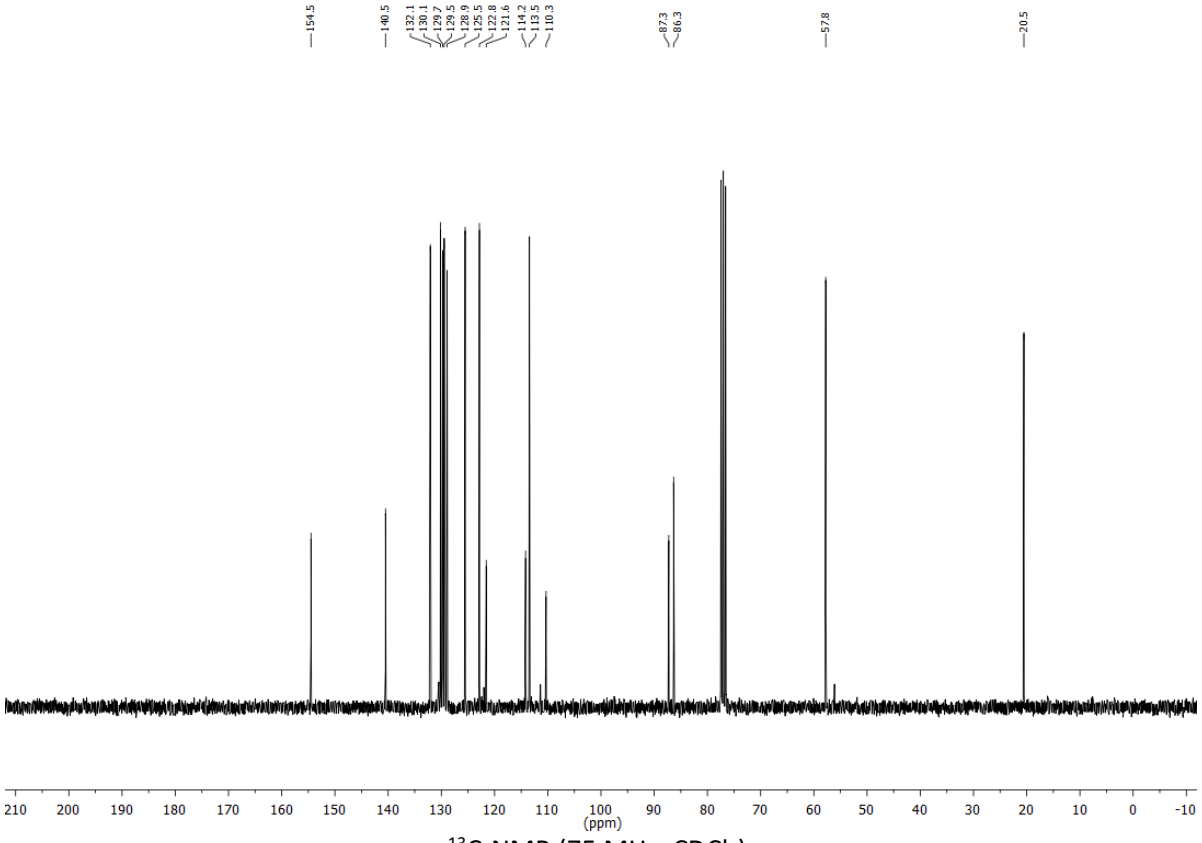
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 20.5, 57.8, 86.3, 87.3, 110.3, 113.5, 114.2, 121.6, 122.8, 125.5, 128.9, 129.5, 129.7, 130.1, 132.1, 140.5, 154.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 2917, 2869, 2232, 2157, 1580, 1475, 1449, 1222, 1007.

$C_{17}H_{13}NOS$ calcd.: 302.0610, found: 302.0612 $[M+Na]^+$ (ESI-HRMS).

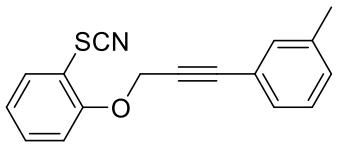


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-(*m*-Tolyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1j)



Thiocyanate **1j** was synthesized from compound **11j** (164 mg, 611 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 3.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (74 mg, 265 µmol, 43%) as pale yellow oil.

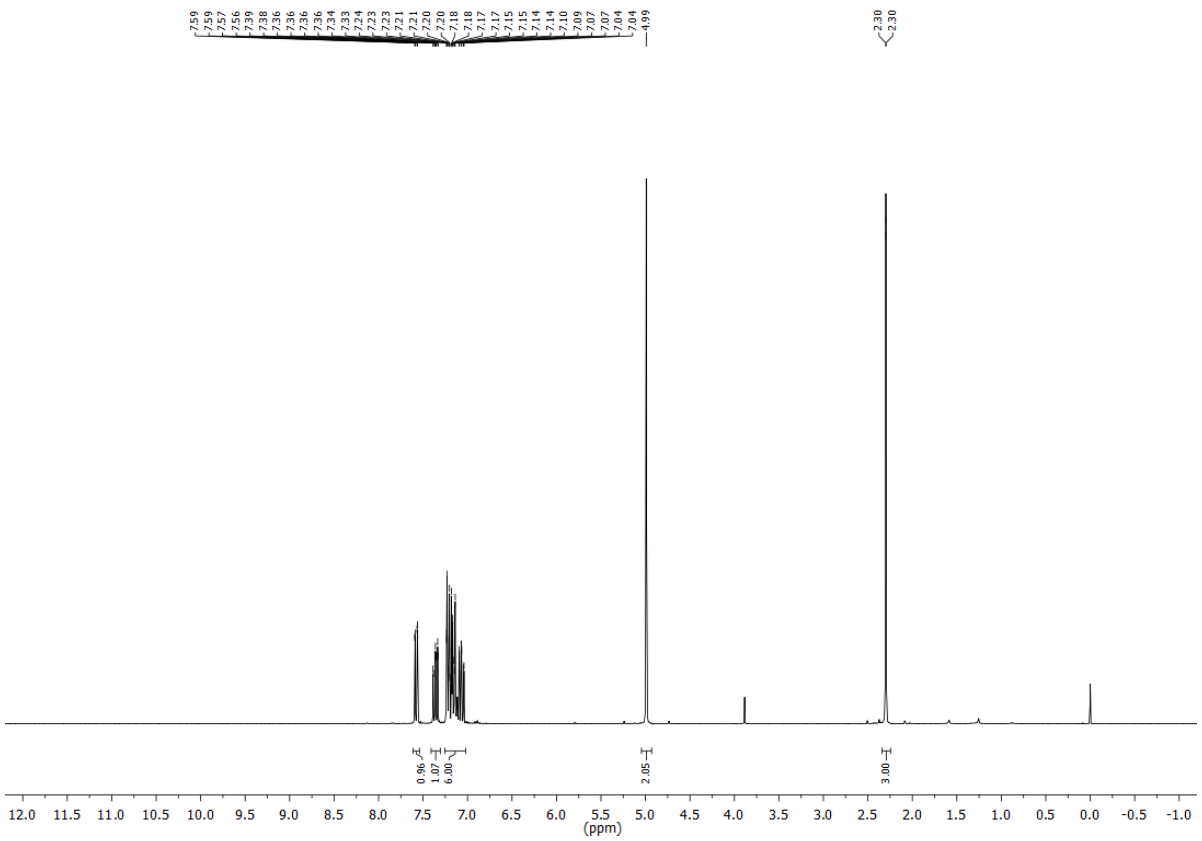
R_f = 0.21 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.30 (d, *J* = 0.7 Hz, 3H), 4.99 (s, 2H), 7.03 – 7.26 (m, 6H), 7.36 (ddd, *J* = 8.2, 7.4, 1.5 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.6 Hz, 1H).

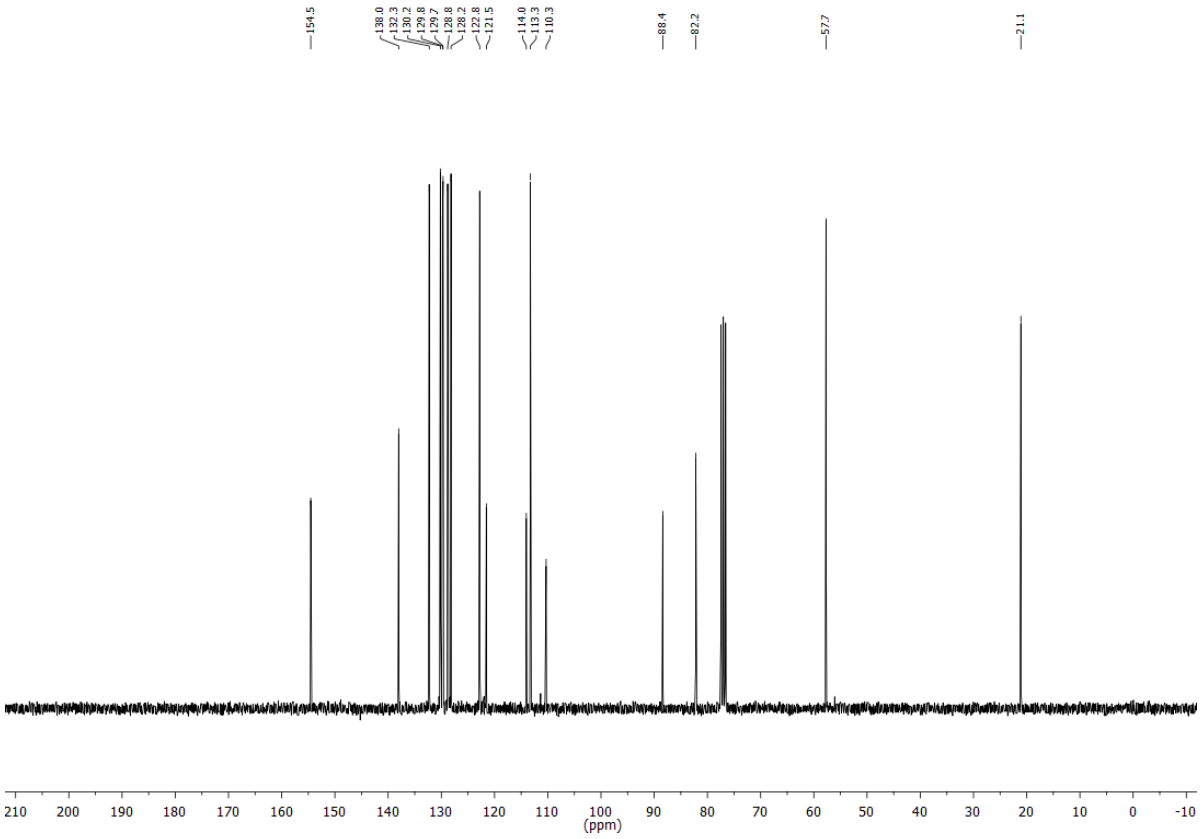
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 21.1, 57.7, 82.2, 88.4, 110.3, 113.3, 114.0, 121.5, 122.8, 128.2, 128.8, 129.7, 129.8, 130.2, 132.3, 138.0, 154.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 2920, 2863, 2230, 2157, 1580, 1475, 1447, 1281, 1223, 1061.

$C_{17}H_{13}NOS$ calcd.: 302.0610, found: 302.0612 $[M+Na]^+$ (ESI-HRMS).

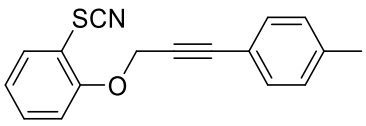


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-(*p*-Tolyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1k)



Thiocyanate **1k** was synthesized from compound **11k** (118 mg, 440 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 2.4 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (30 mg, 107 µmol, 24%) as off-white solid.

m.p.: 74 °C.

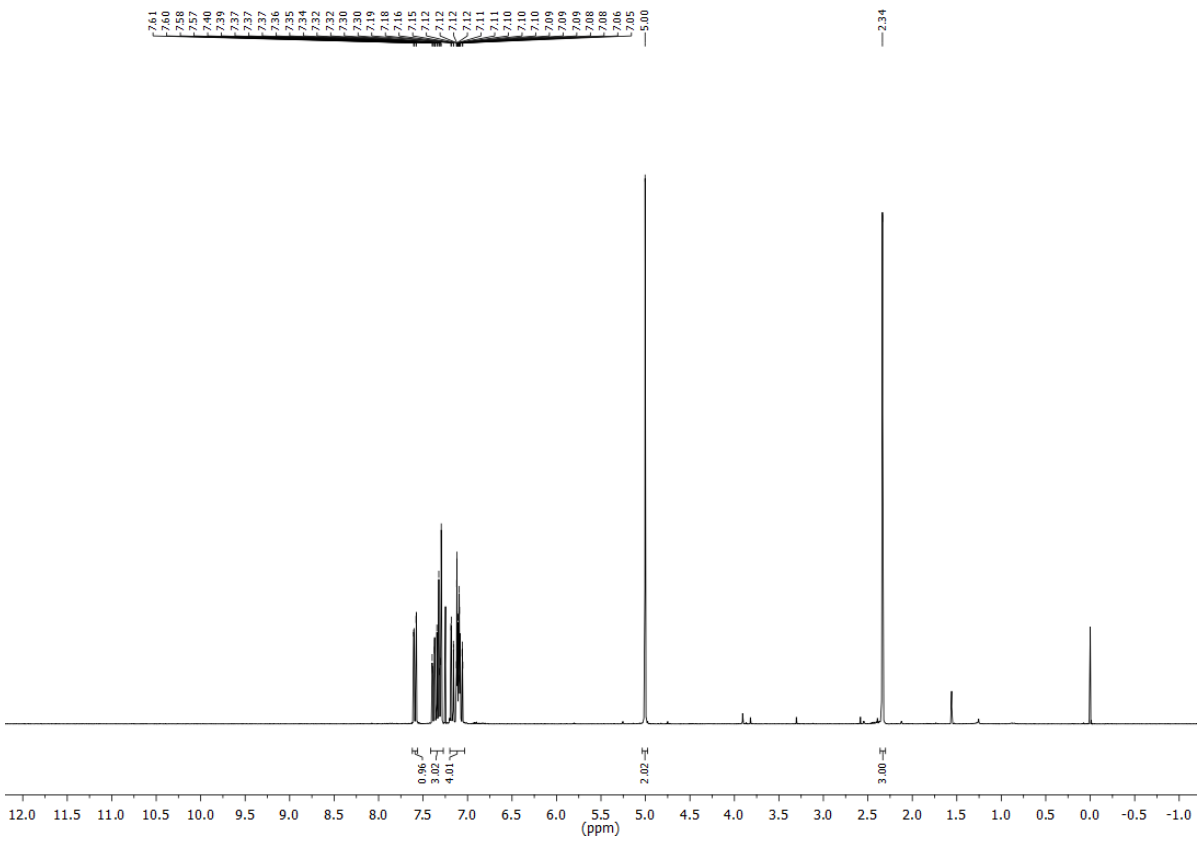
R_f = 0.21 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 5.00 (s, 2H), 7.05 – 7.20 (m, 4H), 7.28 – 7.42 (m, 3H), 7.59 (dd, *J* = 7.9, 1.6 Hz, 1H).

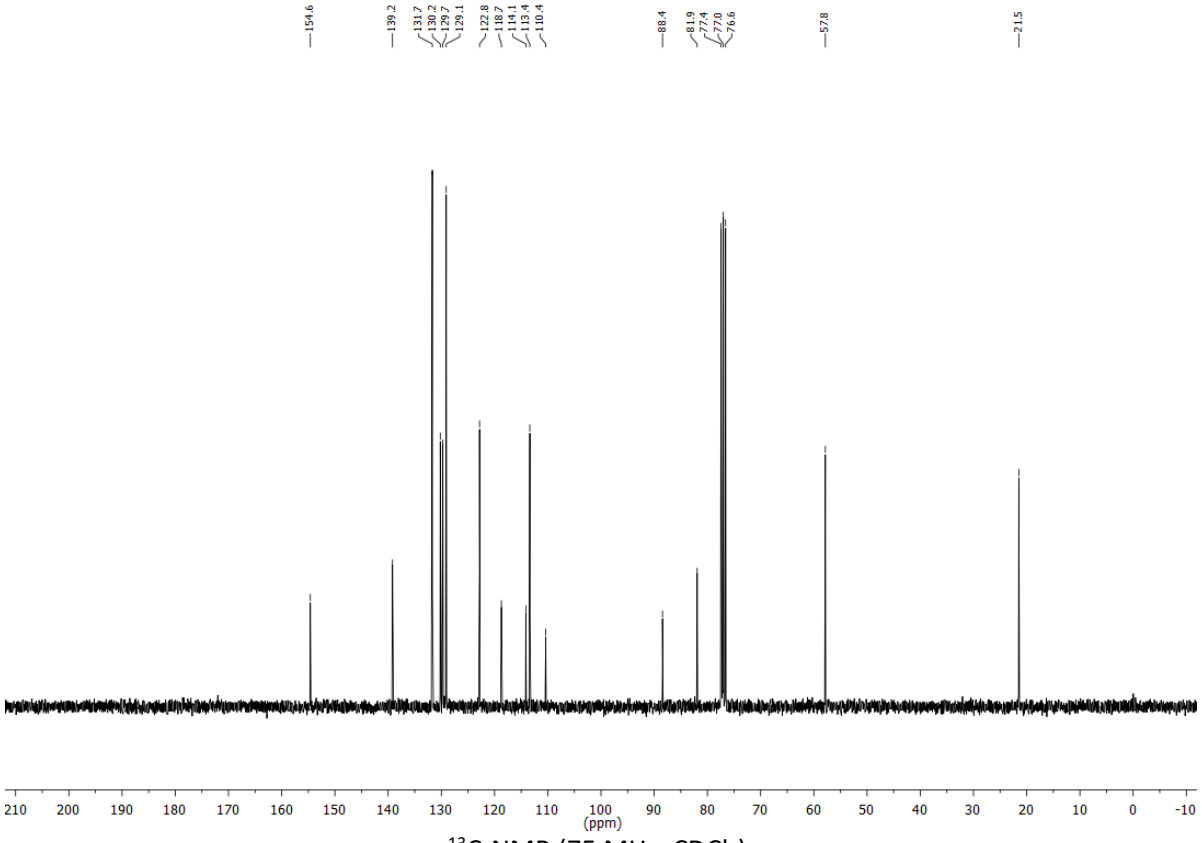
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 21.5, 57.8, 76.6, 77.0, 77.4, 81.9, 88.4, 110.4, 113.4, 114.1, 118.7, 122.8, 129.1, 129.7, 130.2, 131.7, 139.2, 154.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3032, 2919, 2856, 2224, 2158, 1577, 1475, 1443, 1374, 1230, 1008.

$C_{17}H_{13}NOS$ calcd.: 302.0610, found: 302.0611 $[M+Na]^+$ (ESI-HRMS).

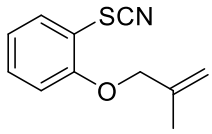


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((2-Methylallyl)oxy)-2-thiocyanatobenzene (1l)



Compound **1l** was synthesized according GP3 (alternative B) from substrate **11l** (2.0 mmol, 389.0 mg). The desired product was obtained after flash column chromatography (*n*-pentane:EtOAc = 50:1) as a colorless oil (0.68 mmol, 140.0 mg, 34%).

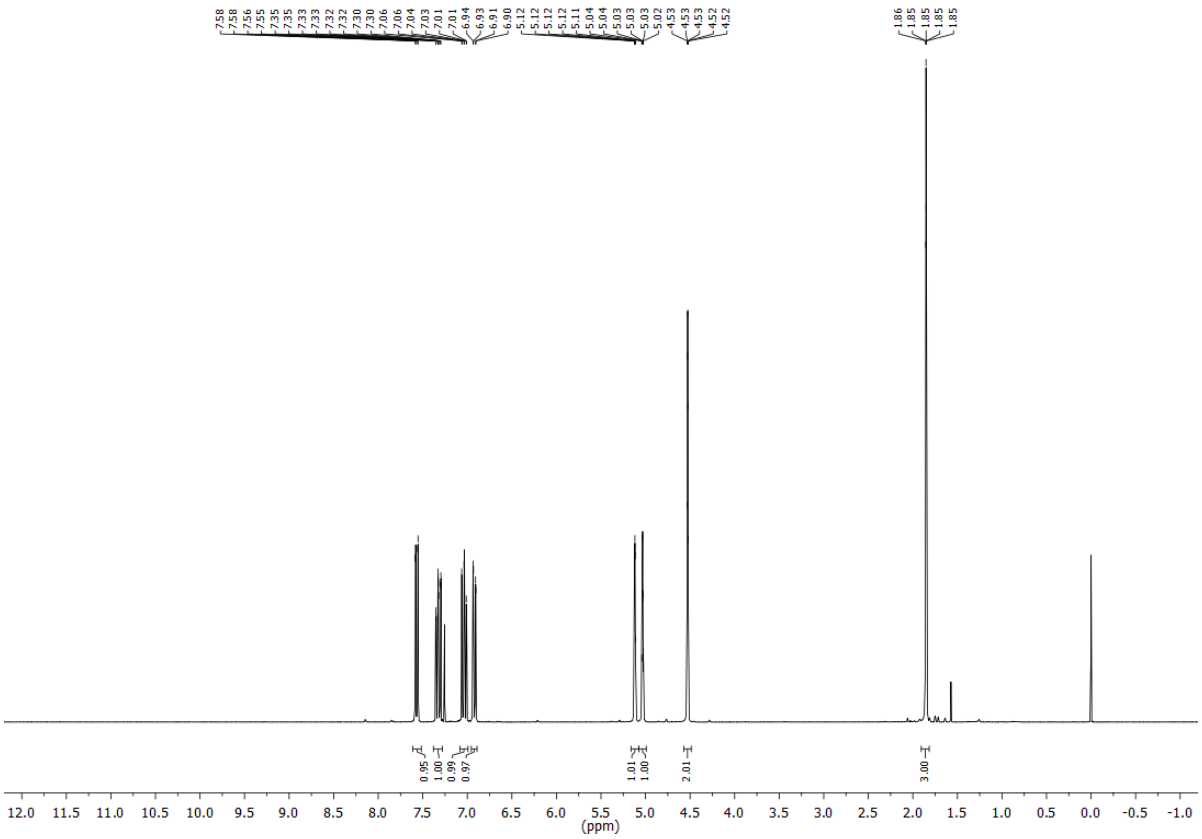
R_f = 0.40 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.80 – 1.91 (m, 3H), 4.53 (p, *J*=0.8, 2H), 4.99 – 5.06 (m, 1H), 5.12 (dd, *J*=1.5, 0.9, 1H), 6.92 (dd, *J*=8.2, 1.2, 1H), 7.04 (td, *J*=7.6, 1.1, 1H), 7.33 (ddd, *J*=8.3, 7.6, 1.7, 1H), 7.57 (dd, *J*=7.8, 1.6, 1H).

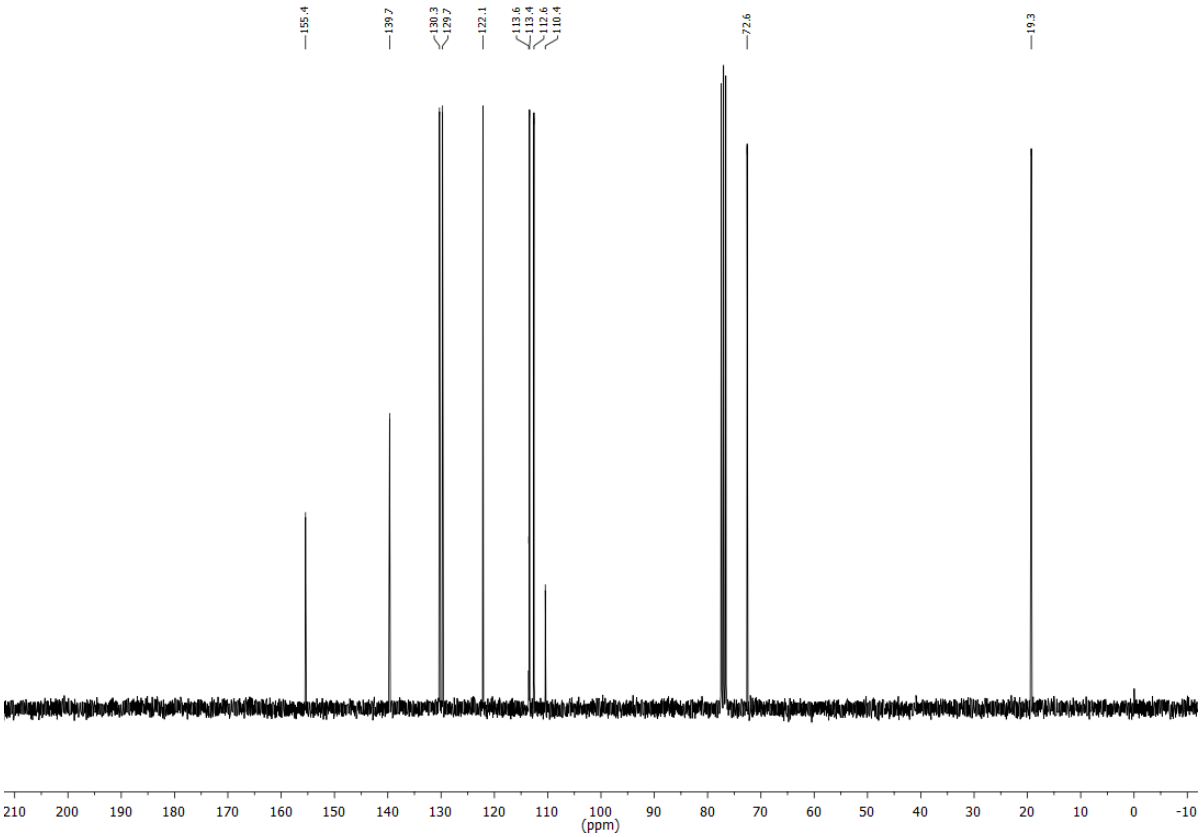
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 19.3, 72.6, 110.4, 112.6, 113.4, 113.6, 122.1, 129.7, 130.3, 139.7, 155.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3075, 2977, 2940, 2864, 2158, 1740, 1582, 1476, 1446, 1235, 1062, 1002.

$C_{11}H_{11}NOS$ calcd.: 205.0561, found: 205.0582 (GC-HRMS).

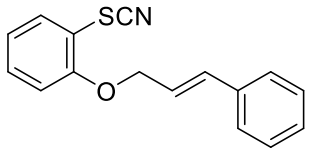


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Cinnamyloxy)-2-thiocyanatobenzene (1m)



Compound **1m** was synthesized according GP3 (alternative B) from substrate **11m** (3.86 mmol, 990.0 mg, isomeric mixture). The desired product was obtained after flash column chromatography (*n*-pentane:EtOAc = 30:1) as a yellow oil (1.26 mmol, 338.0 mg, 33%).

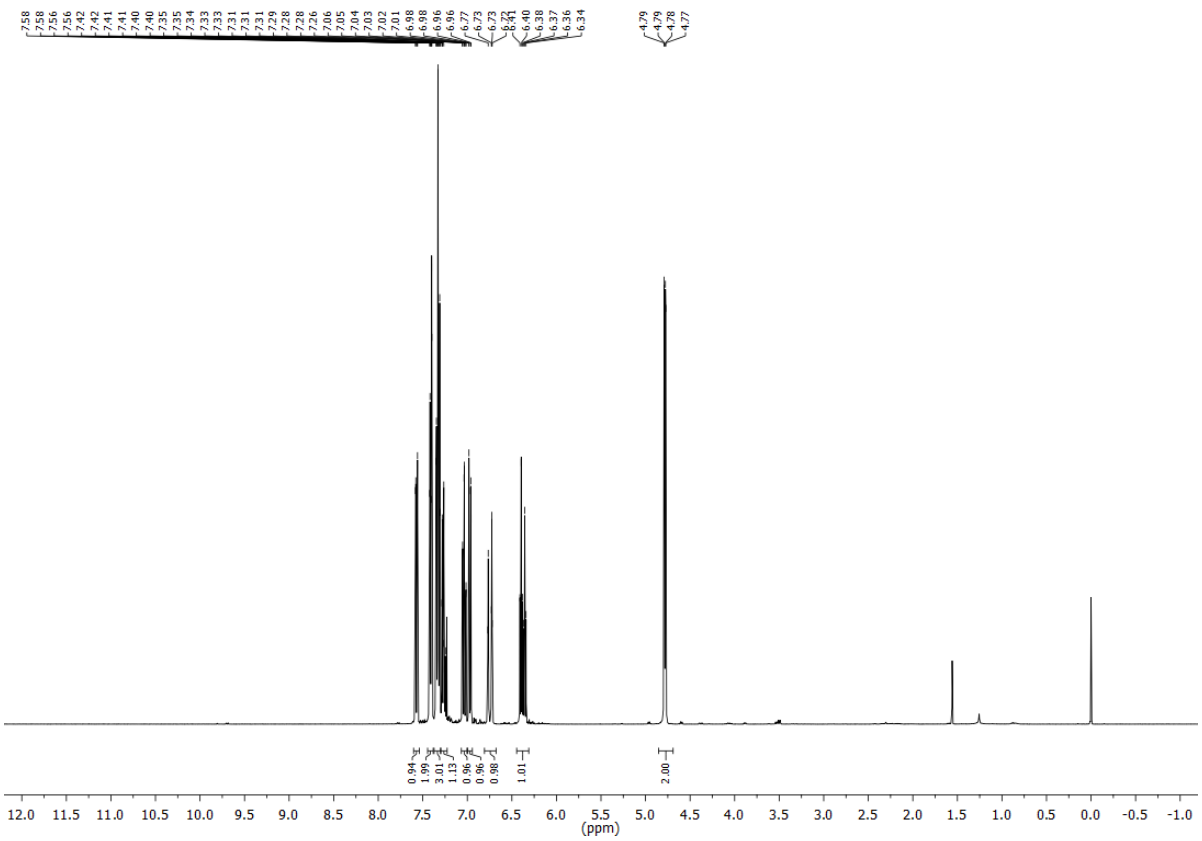
R_f = 0.43 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.78 (dd, *J*=5.7, 1.5, 2H), 6.38 (dt, *J*=16.1, 5.8, 1H), 6.75 (dt, *J*=16.1, 1.7, 1H), 6.97 (dd, *J*=8.3, 1.2, 1H), 7.03 (td, *J*=7.7, 1.2, 1H), 7.22 – 7.29 (m, 1H), 7.33 (m, 3H), 7.39 – 7.44 (m, 2H), 7.57 (dd, *J*=7.9, 1.6, 1H).

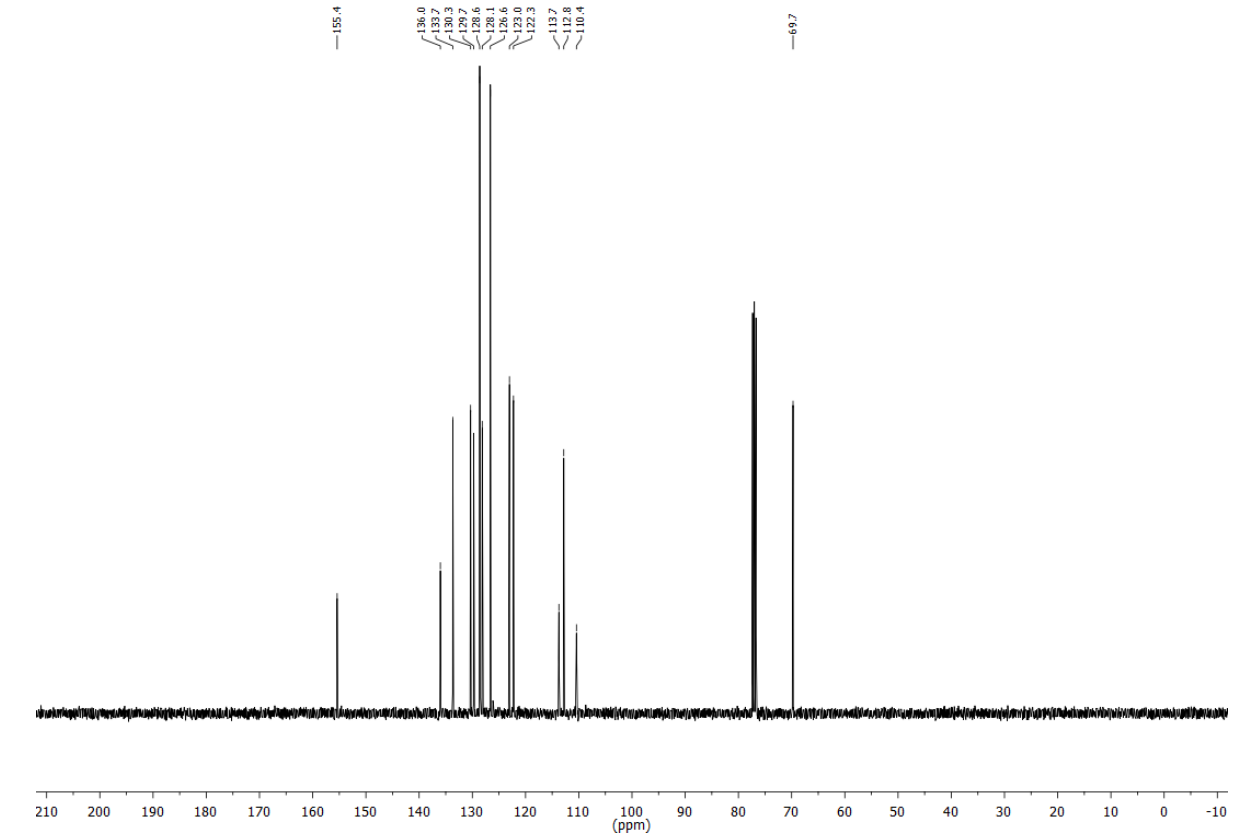
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 69.7, 110.4, 112.8, 113.7, 122.3, 123.0, 126.6 (2 C), 128.1, 128.6 (2 C), 129.7, 130.3, 133.7, 136.0, 155.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3059, 3027, 2926, 2866, 2156, 1580, 1475, 1447, 1240, 964.

$C_{16}H_{13}NOS$ calcd.: 290.0610 [M+Na^+], found: 290.0613 [M+Na^+] (ESI-HRMS).

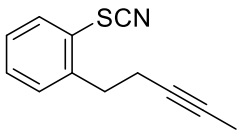


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Pent-3-yn-1-yl)-2-thiocyanatobenzene (1n)



Thiocyanate **1n** was synthesized from compound **11n** (94 mg, 367 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 2.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) to obtain the product (36 mg, 134 µmol, 37%) as colorless oil.

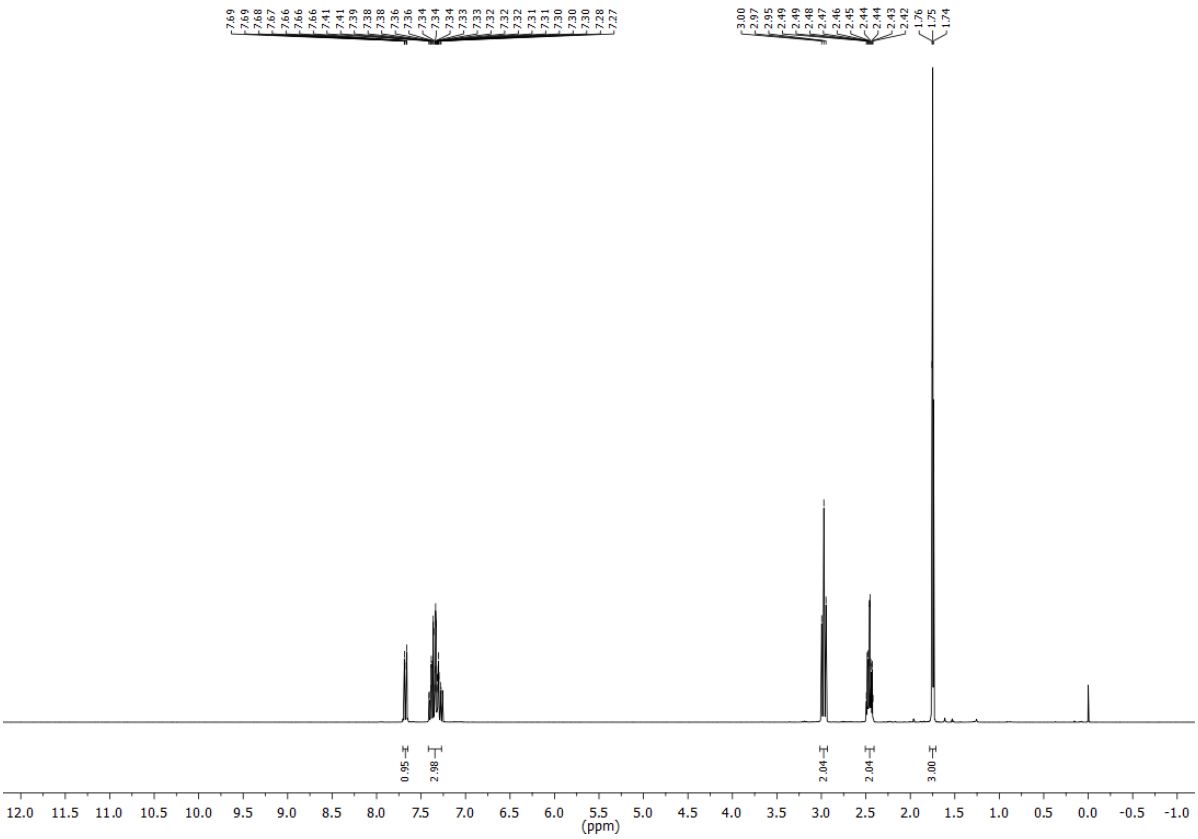
R_f = 0.43 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.75 (t, *J* = 2.5 Hz, 3H), 2.46 (tq, *J* = 7.4, 2.5 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.42 (m, 3H), 7.65 – 7.70 (m, 1H).

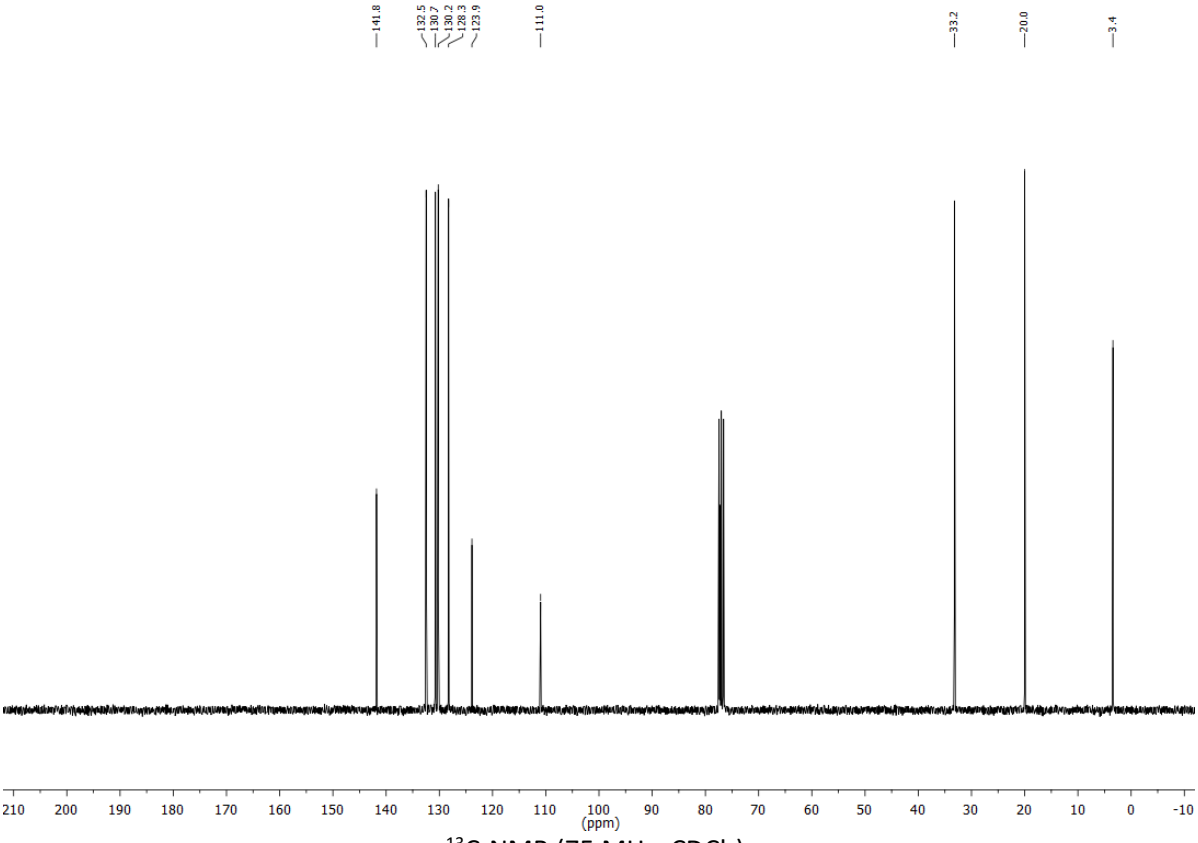
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.4, 20.0, 33.2, 111.0, 123.9, 128.3, 130.2, 130.7, 132.5, 141.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3062, 2917, 2853, 2155, 1469, 1440, 1039.

$C_{12}H_{11}NS$ calcd.: 200.0539, found: 200.0549 $[M-H]^-$ (GC-HRMS).

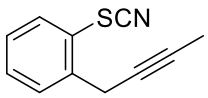


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(But-2-yn-1-yl)-2-thiocyanatobenzene (1o)



Thiocyanate **1o** was synthesized from compound **11o** (177 mg, 1.0 mmol) according GP 3. A mixture of CH_3CN/THF (1:1, 5.8 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 100:1) to obtain the product (13 mg, 69 µmol, 7%) as colorless oil.

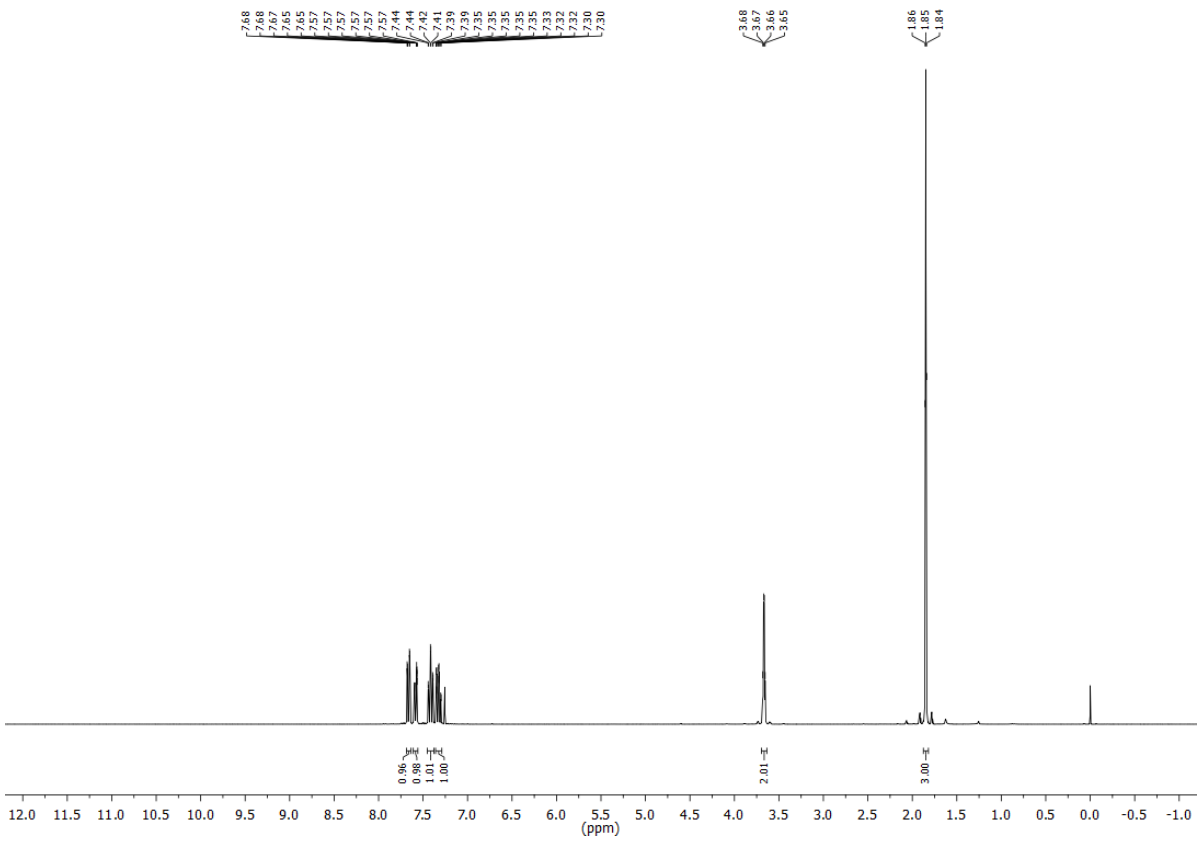
R_f = 0.36 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.85 (t, *J* = 2.6 Hz, 3H), 3.67 (q, *J* = 2.6 Hz, 2H), 7.29 – 7.36 (m, 1H), 7.42 (td, *J* = 7.5, 1.4 Hz, 1H), 7.56 – 7.60 (m, 1H), 7.64 – 7.69 (m, 1H).

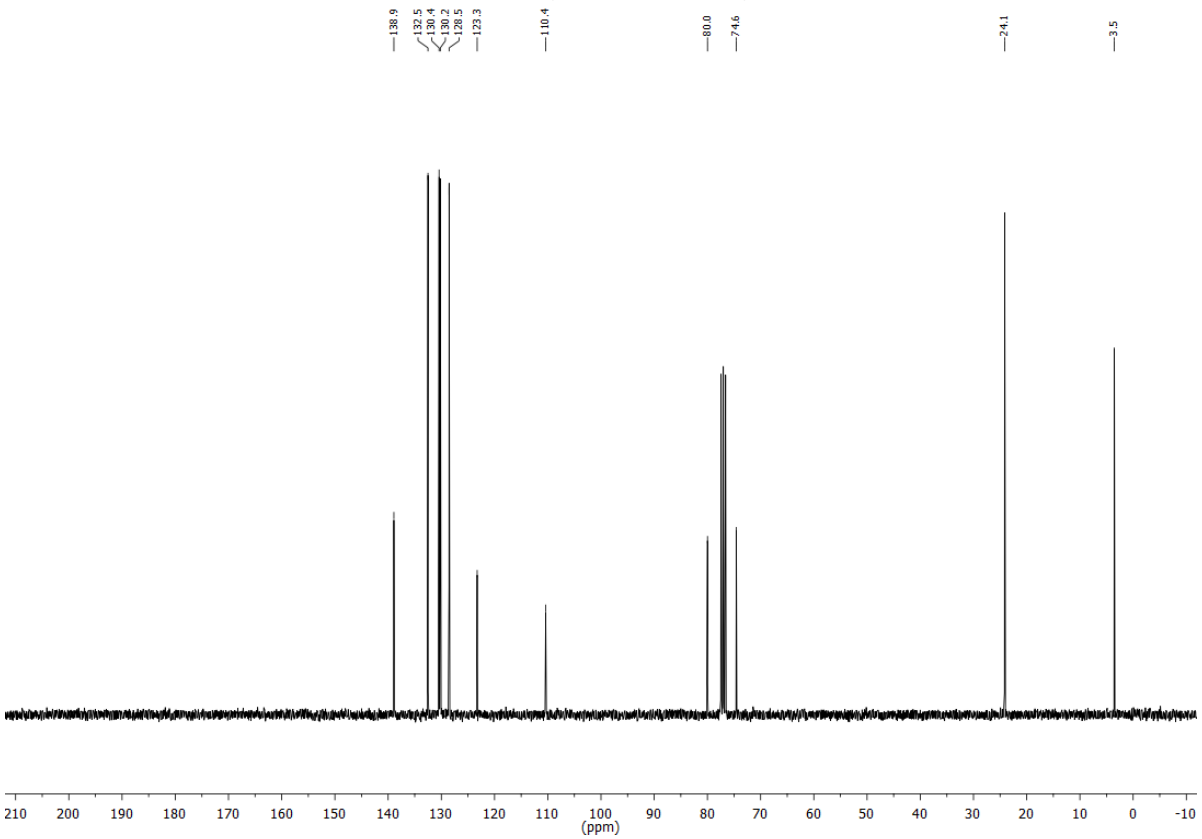
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.5, 24.1, 74.6, 80.0, 110.4, 123.3, 128.5, 130.2, 130.4, 132.5, 138.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 2917, 2878, 2853, 2812, 2152, 1579, 1467, 1416, 1322, 1029.

$C_{11}H_9NS$ calcd.: 187.0456, found: 187.0445 (GC-HRMS).

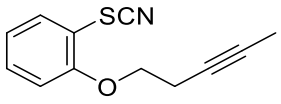


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((Pent-3-yn-1-yl)oxy)-2-thiocyanatobenzene (1p)



Thiocyanate **1p** was synthesized from compound **11p** (260 mg, 1.26 mmol) according GP 3. A mixture of CH_3CN/THF (1:1, 7.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) to obtain the product (157 mg, 720 µmol, 57%) as colorless solid.

m.p.: 59 °C.

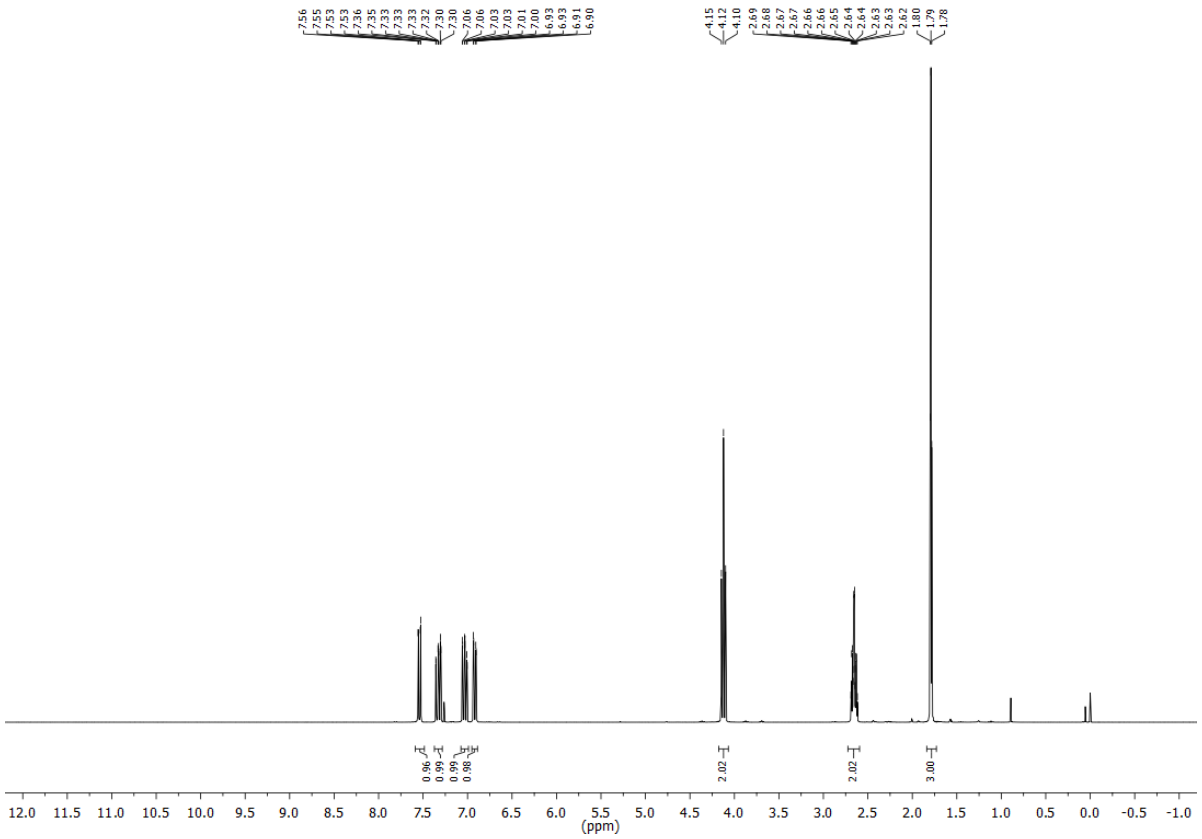
$\mathbf{R_f}$ = 0.46 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.79 (t, *J* = 2.6 Hz, 3H), 2.65 (tq, *J* = 7.1, 2.5 Hz, 2H), 4.12 (t, *J* = 7.1 Hz, 2H), 6.92 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.99 – 7.07 (m, 1H), 7.33 (ddd, *J* = 8.2, 7.4, 1.5 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.6 Hz, 1H).

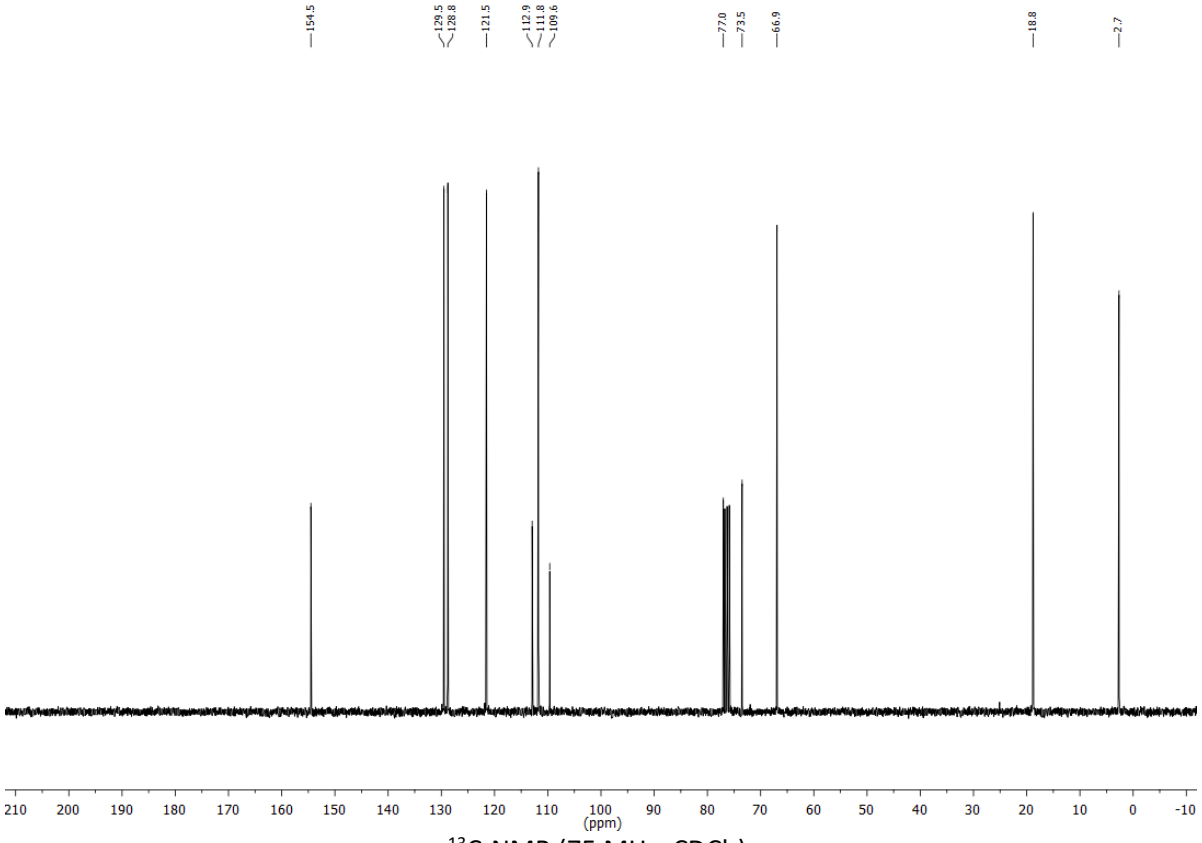
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 2.7, 18.8, 66.9, 73.5, 77.0, 109.6, 111.8, 112.9, 121.5, 128.8, 129.5, 154.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3084, 2948, 2922, 2881, 2159, 1581, 1481, 1447, 1244, 1062, 1026.

$C_{12}H_{11}NOS$ calcd.: 217.0561, found: 217.0572 (GC-HRMS).

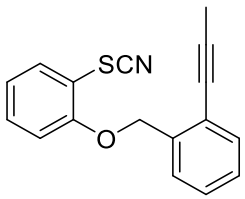


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((2-(Prop-1-yn-1-yl)benzyl)oxy)-2-thiocyanatobenzene (1q)



Compound **1q** was synthesized according GP3 (alternative B) from substrate **11q** (2.1 mmol, 564.0 mg). The desired product was obtained after flash column chromatography (*n*-pentane:EtOAc = 20:1) as a colorless solid (1.29 mmol, 359.0 mg, 61%).

m.p.: 80 °C.

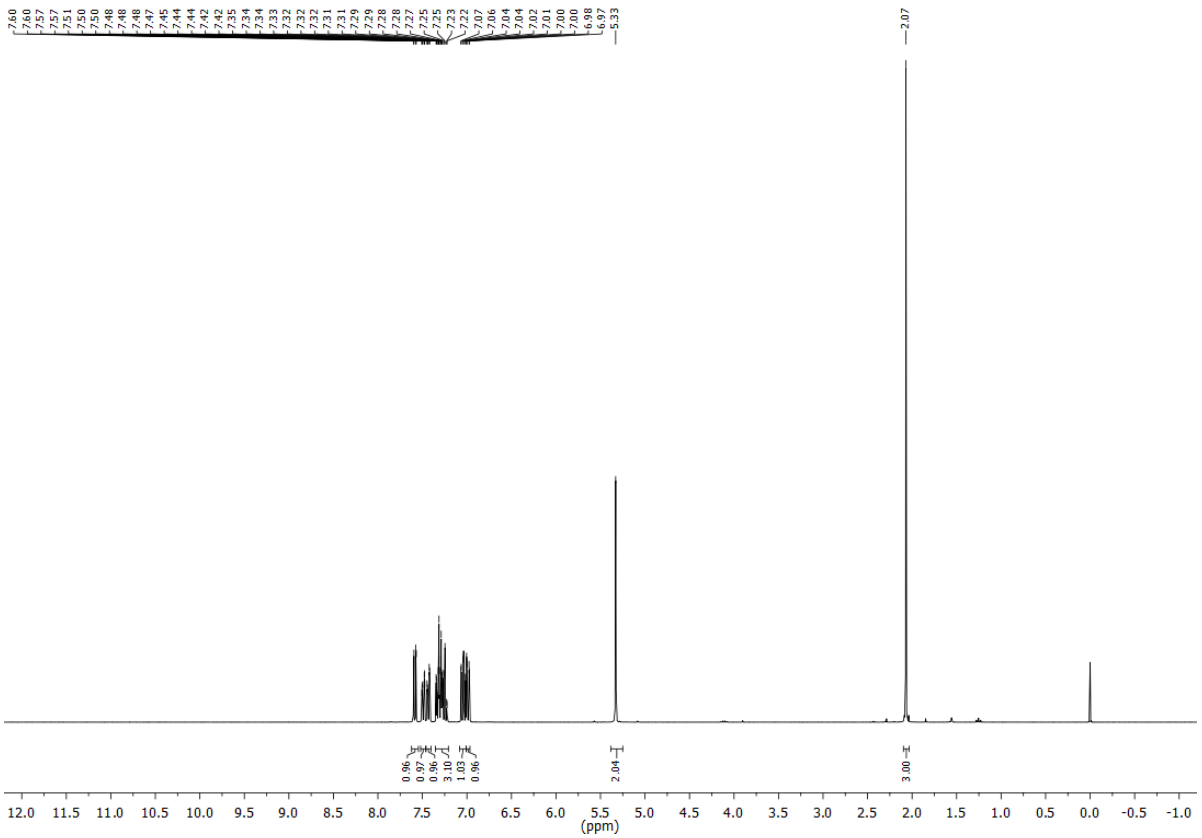
R_f = 0.28 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3H), 5.33 (s, 2H), 6.99 (dd, *J*=8.3, 1.2, 1H), 7.01 – 7.08 (m, 1H), 7.21 – 7.36 (m, 3H), 7.43 (dd, *J*=7.5, 1.6, 1H), 7.47 – 7.51 (m, 1H), 7.58 (dd, *J*=7.9, 1.6, 1H).

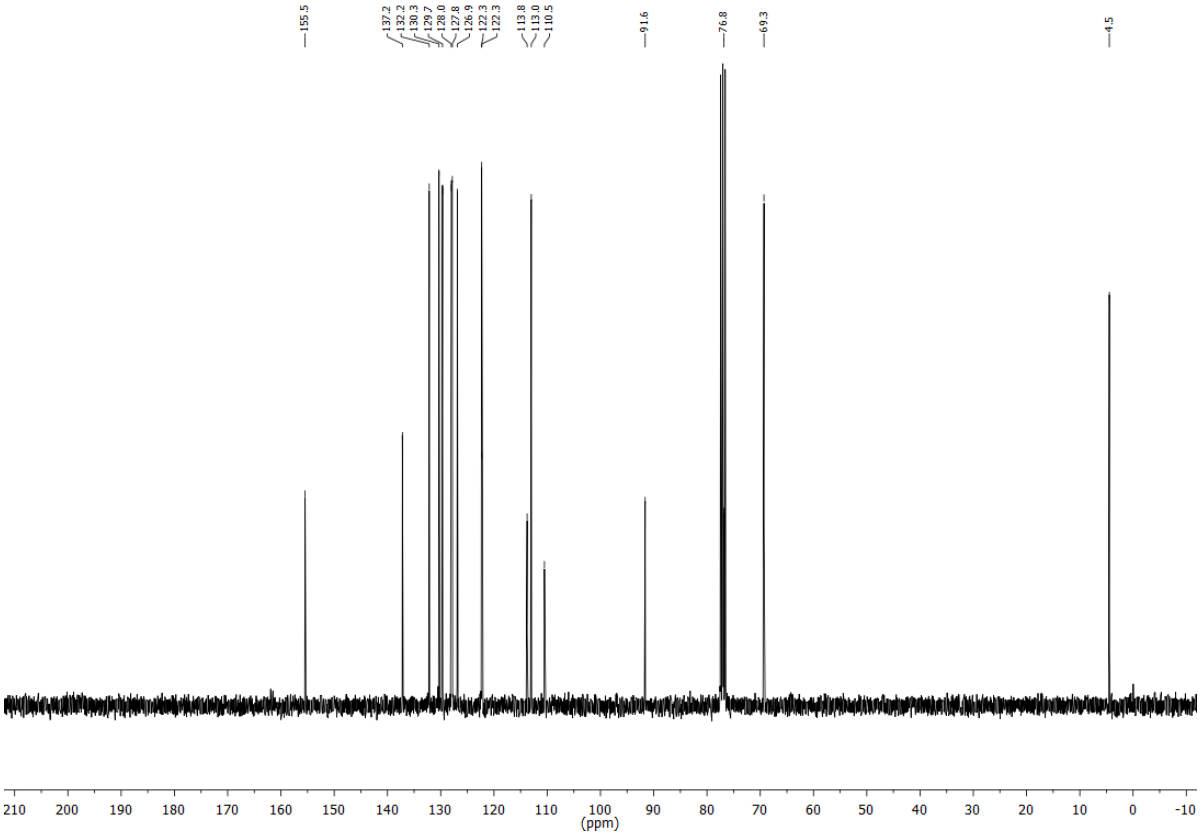
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.5, 69.3, 76.8, 91.6, 110.5, 113.0, 113.8, 122.3, 122.3, 126.9, 127.8, 128.0, 129.7, 130.3, 132.2, 137.2, 155.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3097, 3063, 2911, 2850, 2155, 1850, 1480, 1441, 1245, 1022.

$C_{17}H_{13}NOS$ calcd.: 279.0718, found: 279.0729 (GC-HRMS).

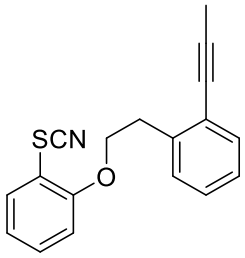


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(2-(Prop-1-yn-1-yl)phenethoxy)-2-thiocyanatobenzene (1r)



Compound **1r** was synthesized according GP3 (alternative B, 1.1 equiv. of X-CN) from substrate **11r** (2.5 mmol, 711.0 mg). The desired product was obtained after flash column chromatography (*n*-pentane:EtOAc = 20:1) as a colorless oil (0.84 mmol, 247.0 mg, 34%).

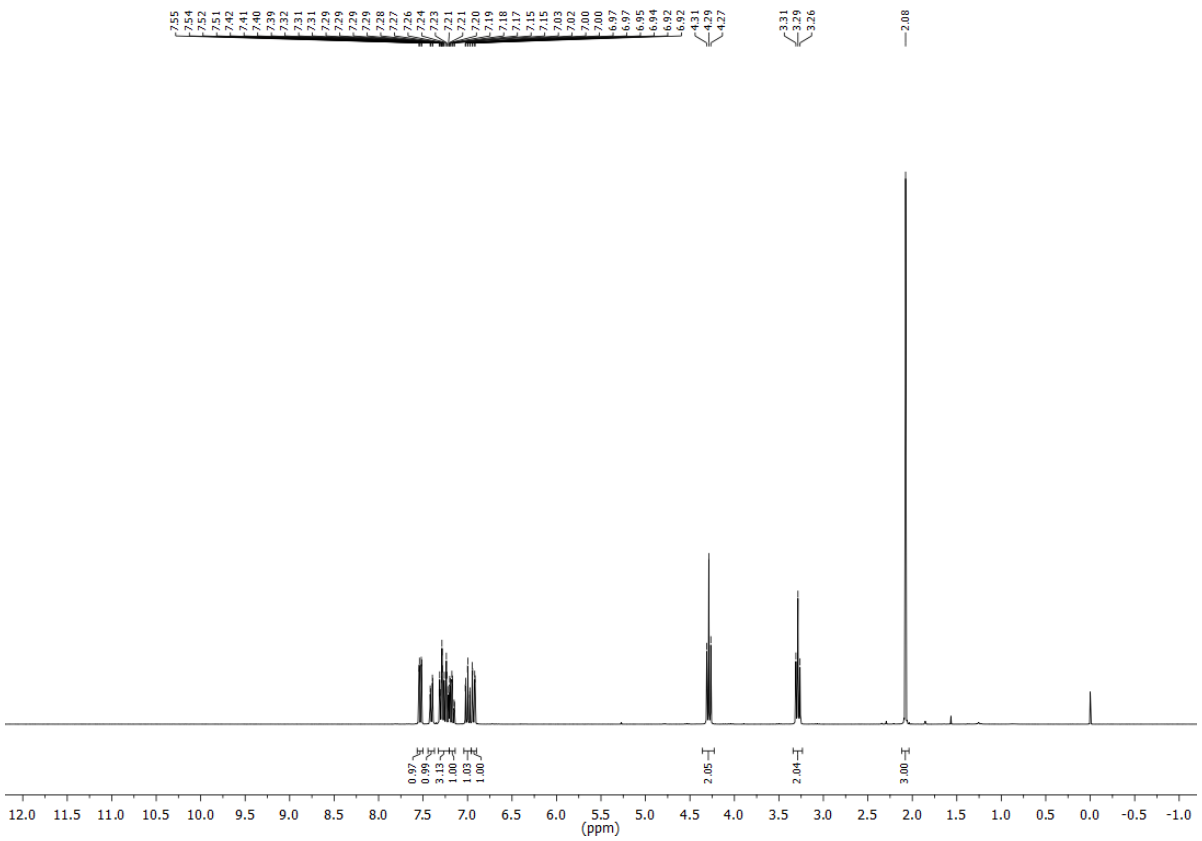
R_f = 0.26 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.08 (s, 3H), 3.29 (t, *J*=6.9, 2H), 4.29 (t, *J*=6.9, 2H), 6.93 (dd, *J*=8.2, 1.2, 1H), 7.00 (td, *J*=7.7, 1.3, 1H), 7.17 (td, *J*=7.4, 1.8, 1H), 7.21 – 7.32 (m, 3H), 7.40 (dd, *J*=7.4, 1.7, 1H), 7.53 (dd, *J*=7.9, 1.6, 1H).

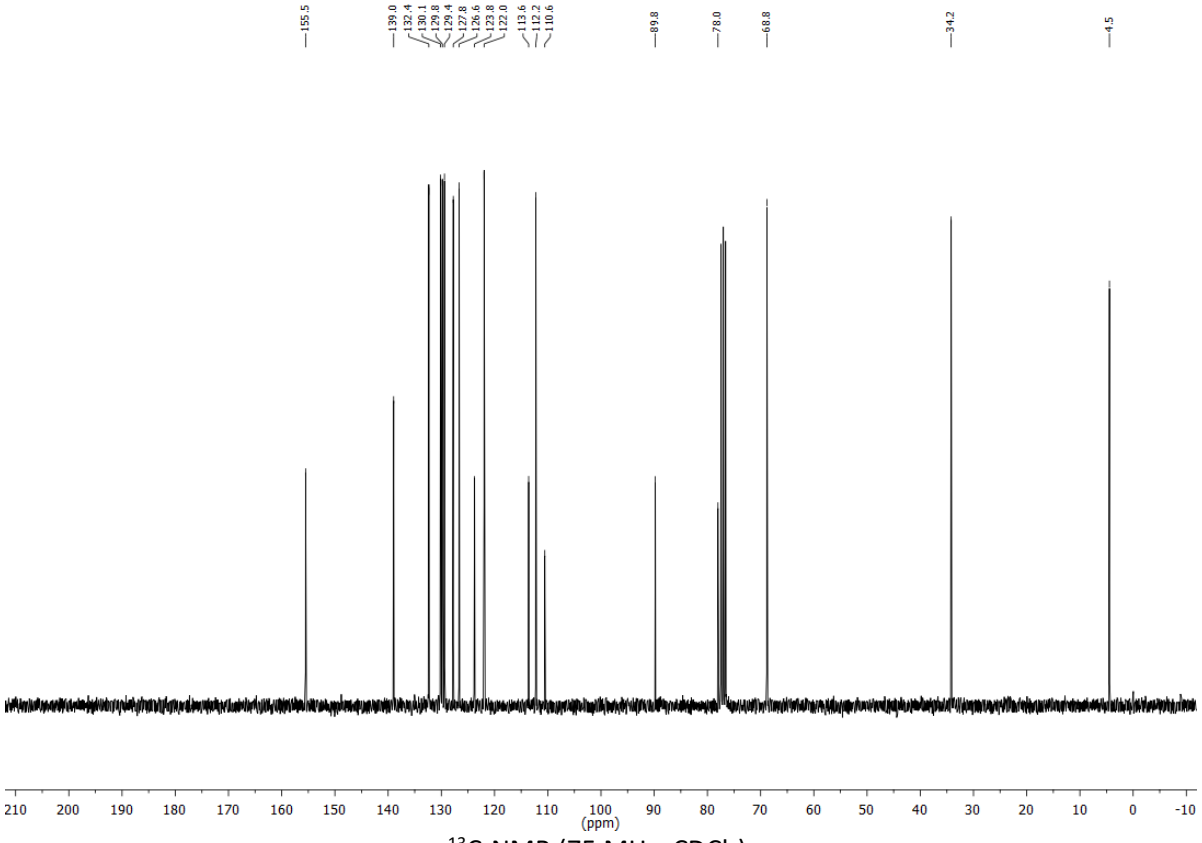
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.5, 34.2, 68.8, 78.0, 89.8, 110.6, 112.2, 113.6, 122.0, 123.8, 126.6, 127.8, 129.4, 129.8, 130.1, 132.4, 139.0, 155.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3065, 3024, 3923, 2882, 2853, 2157, 1582, 1474, 1284, 1244, 1060, 1012.

$C_{18}H_{15}NOS$ calcd.: 293.0874, found: 293.0849 (GC-HRMS).

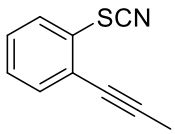


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(prop-1-yn-1-yl)benzene (1s)



Thiocyanate **1s** was synthesized from compound **11s** (170 mg, 1.05 mmol) according GP 3. A mixture of CH_3CN/THF (1:1, 6.0 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 60:1) to obtain the product (71 mg, 410 µmol, 39%) as yellow oil.

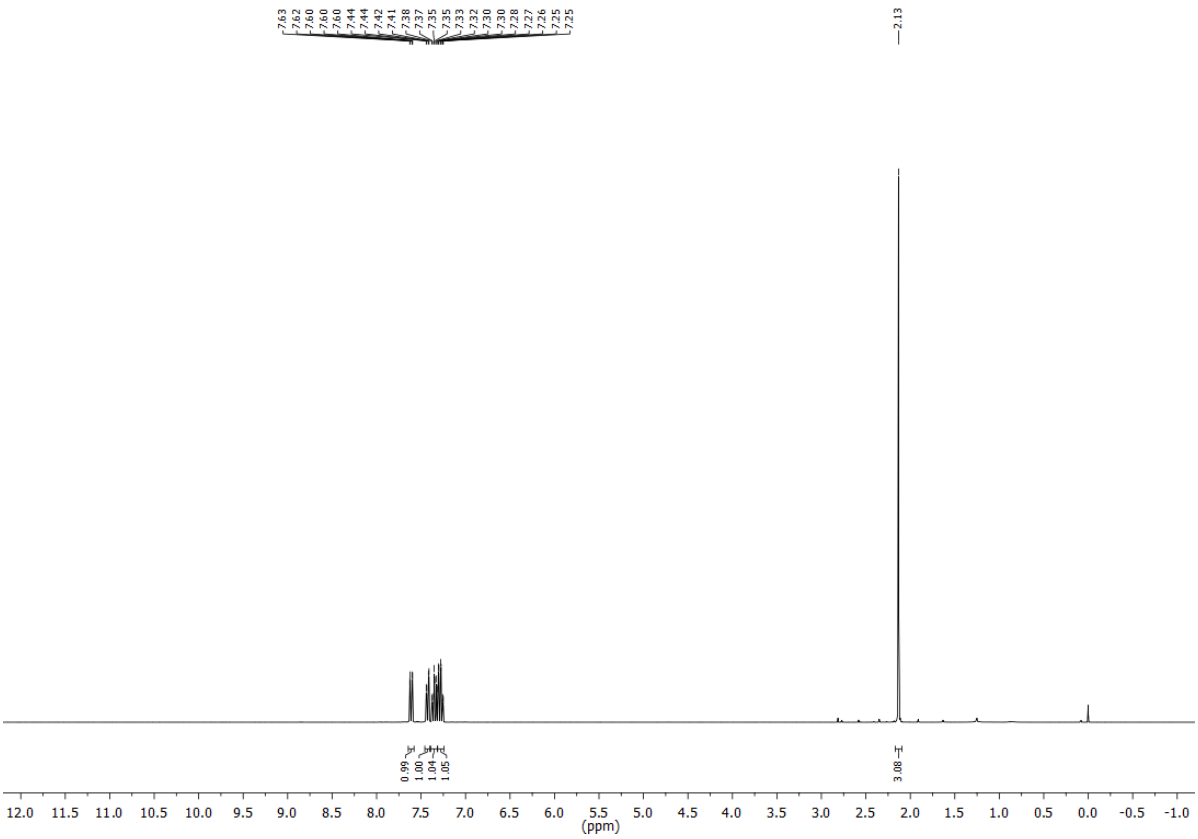
R_f = 0.65 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3H), 7.25 – 7.31 (m, 1H), 7.35 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.59 – 7.64 (m, 1H).

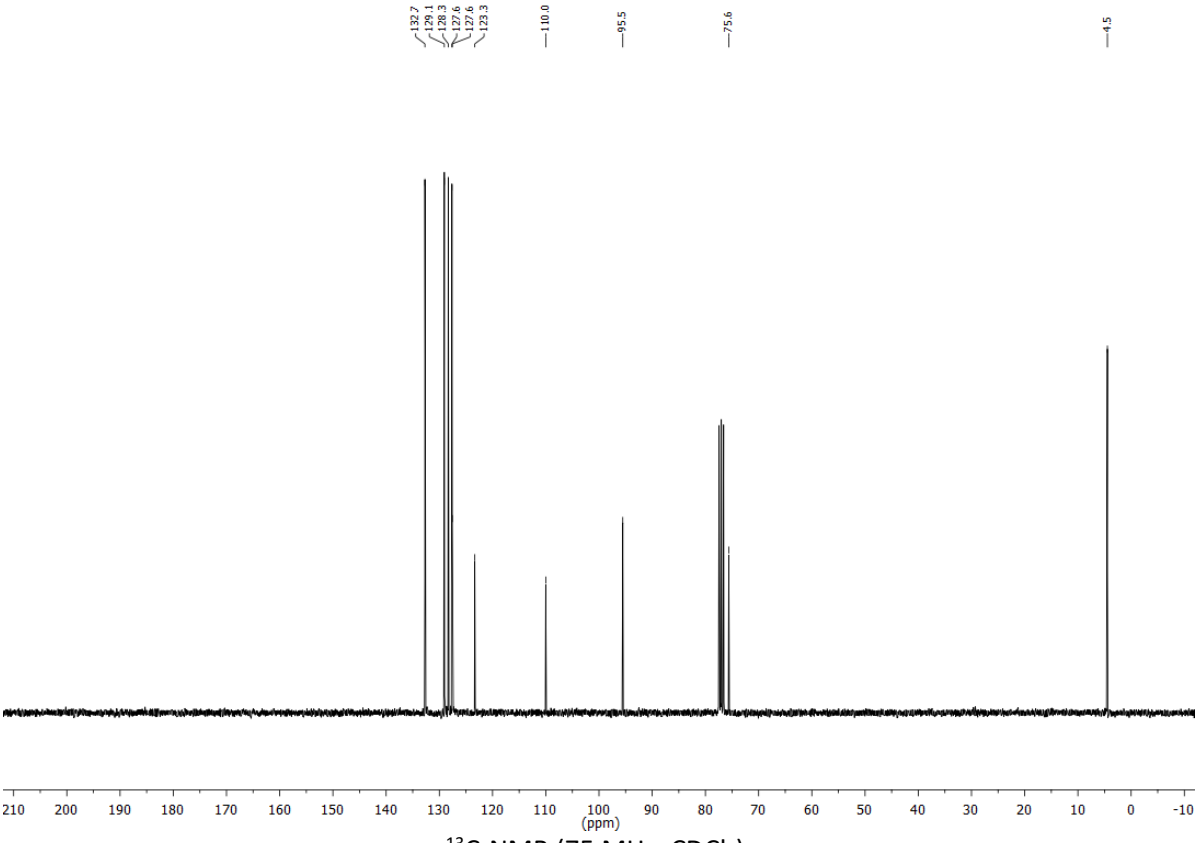
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.5, 75.6, 95.5, 110.0, 123.3, 127.6, 127.6, 128.3, 129.1, 132.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 2917, 2848, 2157, 1466, 1434, 1062, 1029.

$C_{10}H_7NS$ calcd.: 173.0299, found: 173.0305 (GC-HRMS).

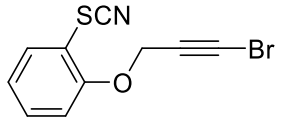


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-Bromoprop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1u)



Thiocyanate **1u** was synthesized from compound **11u** (155 mg, 0.60 mmol) according GP 3. A mixture of CH_3CN/THF (1:1, 3.4 ml) was used as solvent. The reaction mixture was directly added to a silica gel column. After elution (*n*-pentane:EtOAc = 20:1), the product was obtained as colorless solid (86 mg, 0.32 mmol, 53%).

m.p.: 50 °C.

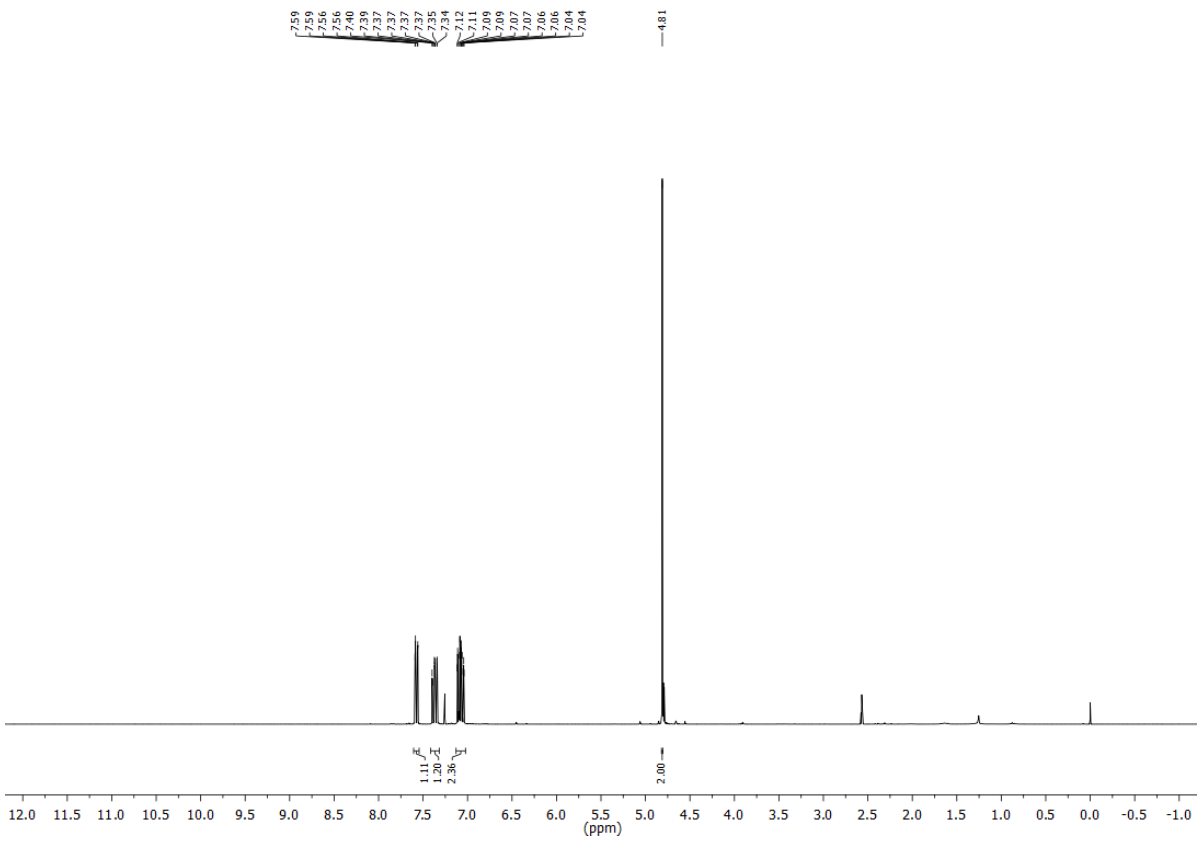
R_f = 0.16 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.81 (s, 2H), 7.03 – 7.13 (m, 2H), 7.37 (ddd, *J* = 8.3, 7.6, 1.6 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.5 Hz, 1H).

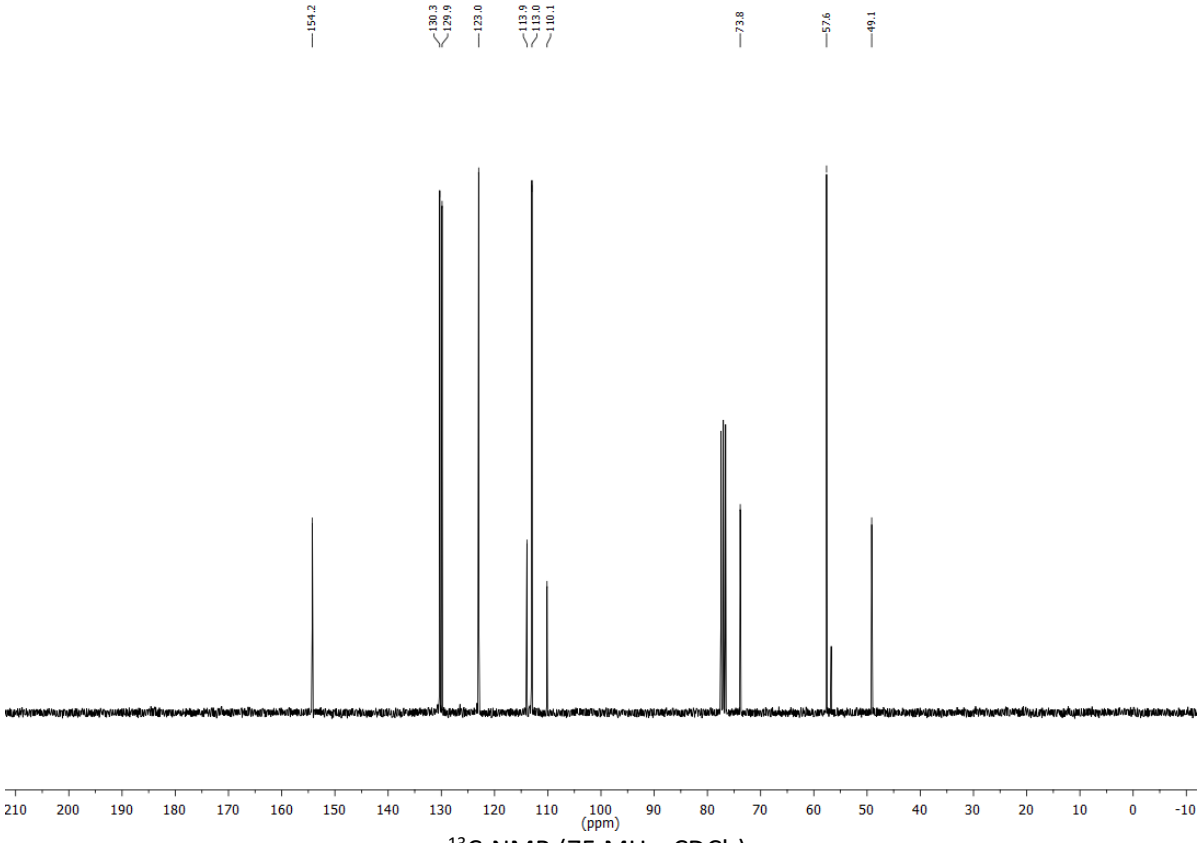
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 49.1, 57.6, 73.8, 110.1, 113.0, 113.9, 123.0, 129.9, 130.3, 154.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3283, 3096, 3067, 2928, 2231, 2155, 1580, 1501, 1475, 1365, 1289, 1241, 1064, 996.

$C_{10}H_6BrNOS$ calcd.: 268.9333, found: 268.9347 (GC-HRMS).

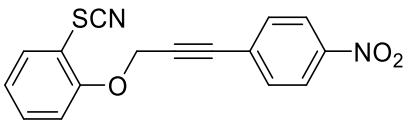


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((3-(4-Nitrophenylp)rop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1x)



Thiocyanate **1x** was synthesized from compound **11x** (264 mg, 882 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 5.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 20:1) to obtain the product (156 mg, 502 µmol, 57%) as off-white/beige solid.

m.p.: 97 °C.

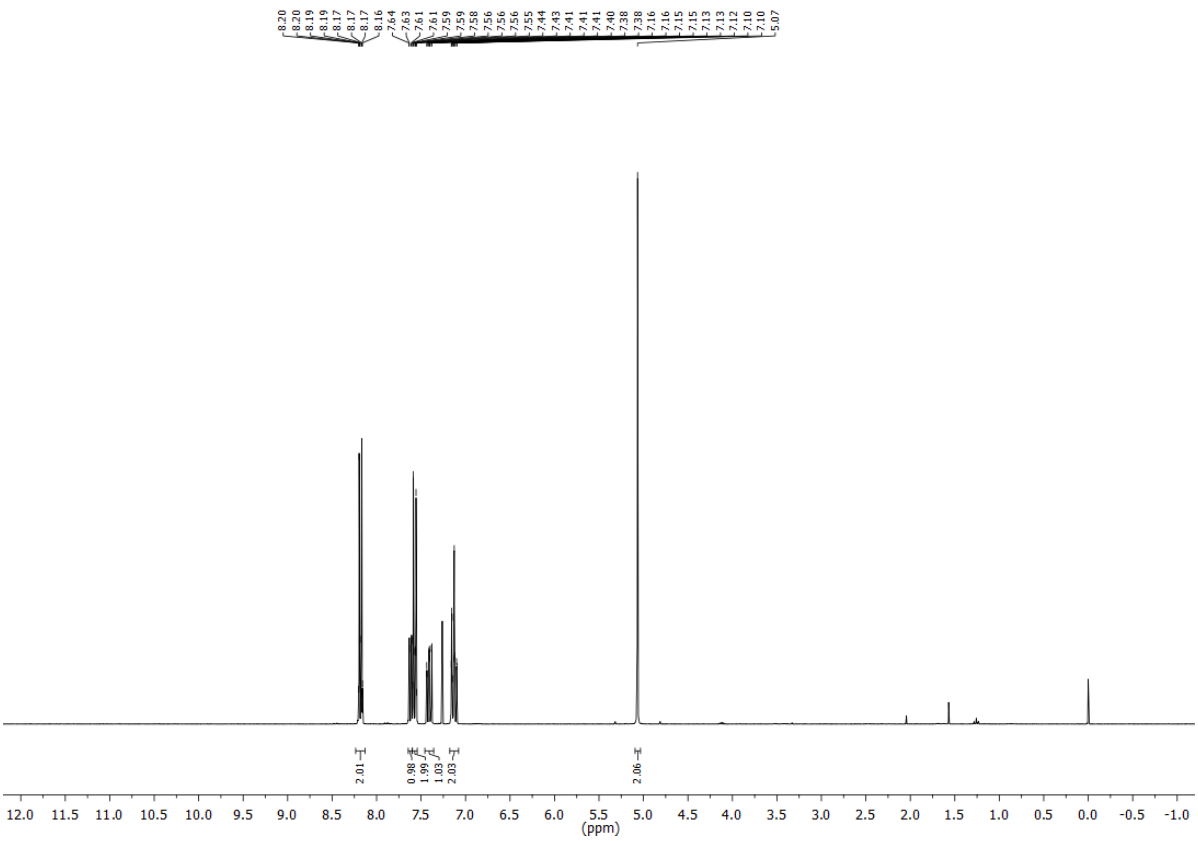
R_f = 0.46 (*n*-pentane:EtOAc = 4:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.07 (s, 2H), 7.09 – 7.18 (m, 2H), 7.41 (ddd, *J* = 8.3, 7.4, 1.6 Hz, 1H), 7.55 – 7.60 (m, 2H), 7.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.15 – 8.21 (m, 2H).

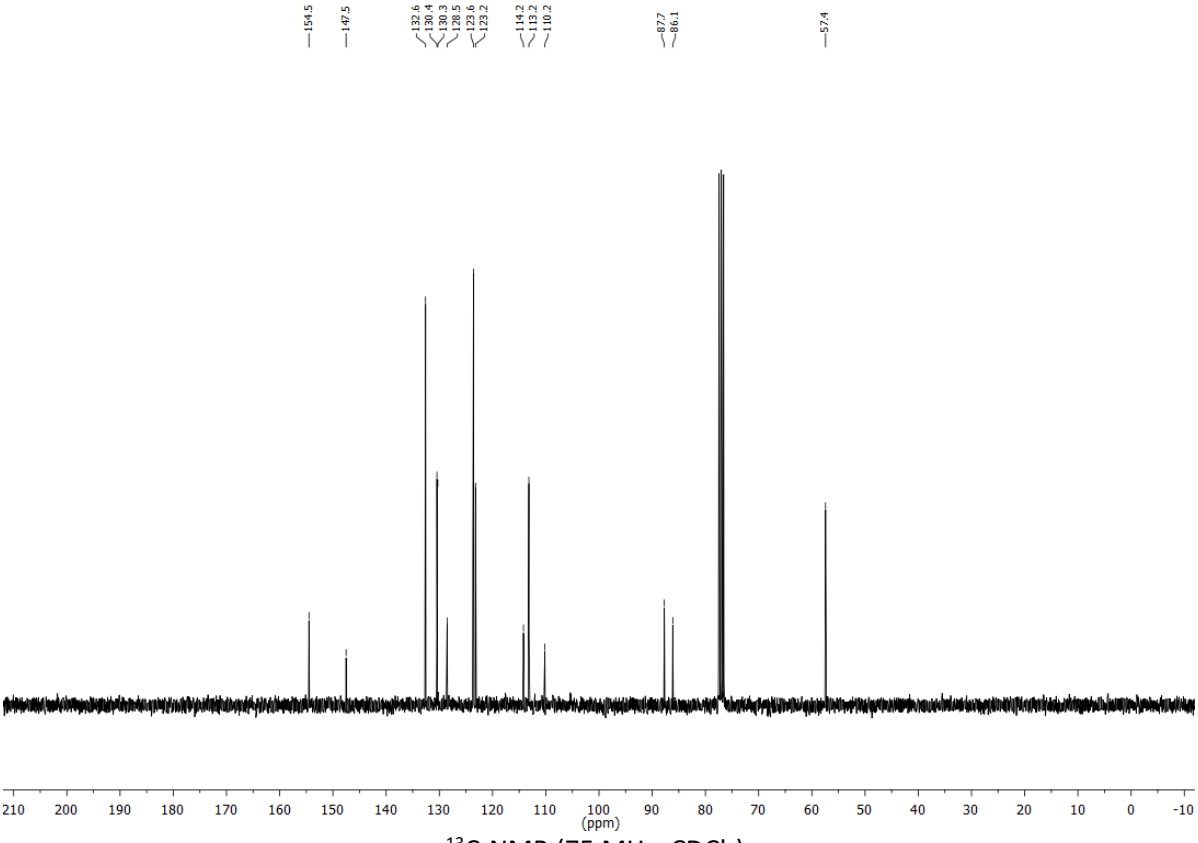
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 57.4, 86.1, 87.7, 110.2, 113.2, 114.2, 123.2, 123.6, 128.5, 130.3, 130.4, 132.6, 147.5, 154.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3106, 3070, 2934, 2839, 2156, 1585, 1515, 1472, 1446, 1337, 1063, 1011.

$C_{16}H_{10}N_2O_3S$ calcd.: 333.0304, found: 333.0306 $[M+Na]^+$ (ESI-HRMS).

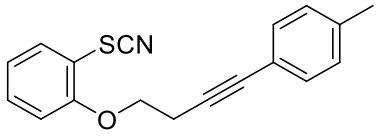


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((4-(*p*-Tolyl)but-3-yn-1-yl)oxy)-2-thiocyanatobenzene (1y)



Thiocyanate **1y** was synthesized from compound **11y** (186 mg, 0.66 mmol) according GP 3. A mixture of CH_3CN/THF (1:2, 6.0 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 50:1) to obtain the product (44 mg, 150 µmol, 23%) as colorless solid.

m.p.: 63 °C.

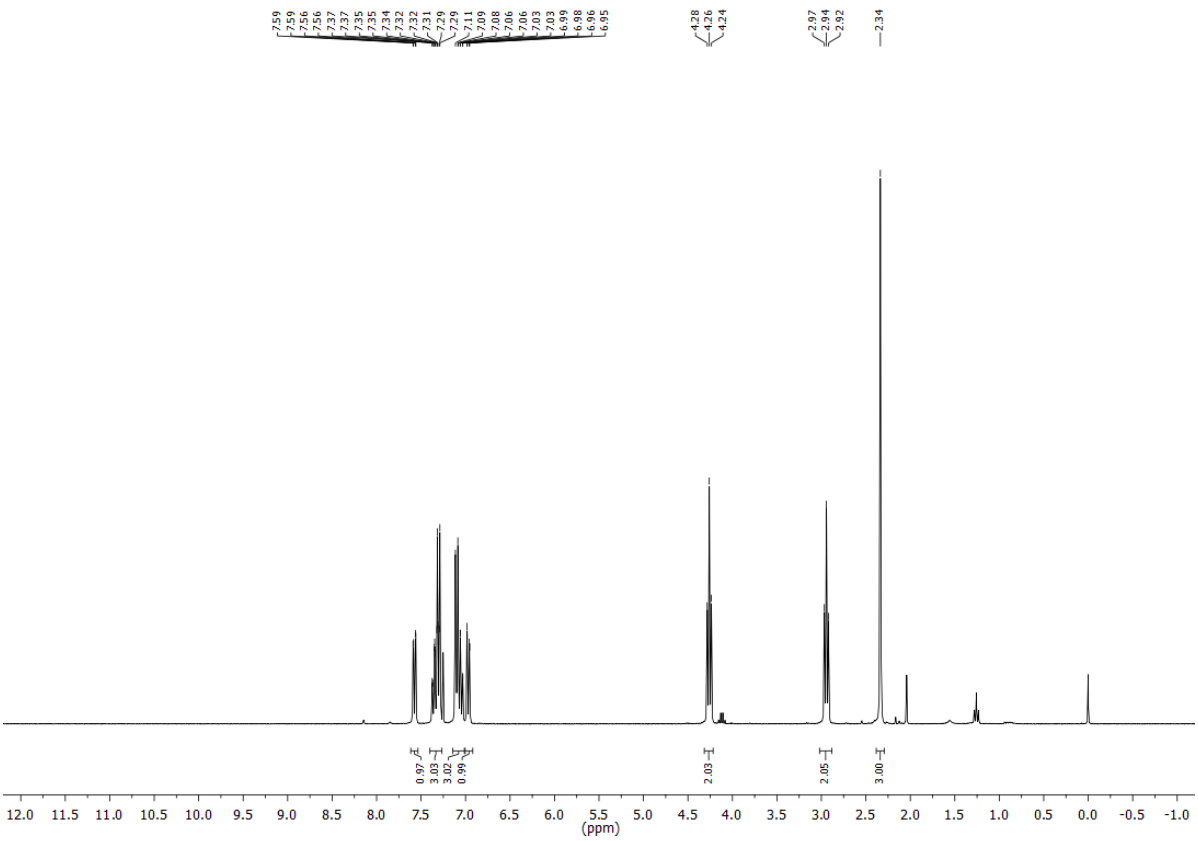
R_f = 0.16 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 2.94 (t, *J* = 7.0 Hz, 2H), 4.26 (t, *J* = 7.0 Hz, 2H), 6.97 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.02 – 7.14 (m, 3H), 7.27 – 7.40 (m, 3H), 7.57 (dd, *J* = 7.9, 1.6 Hz, 1H).

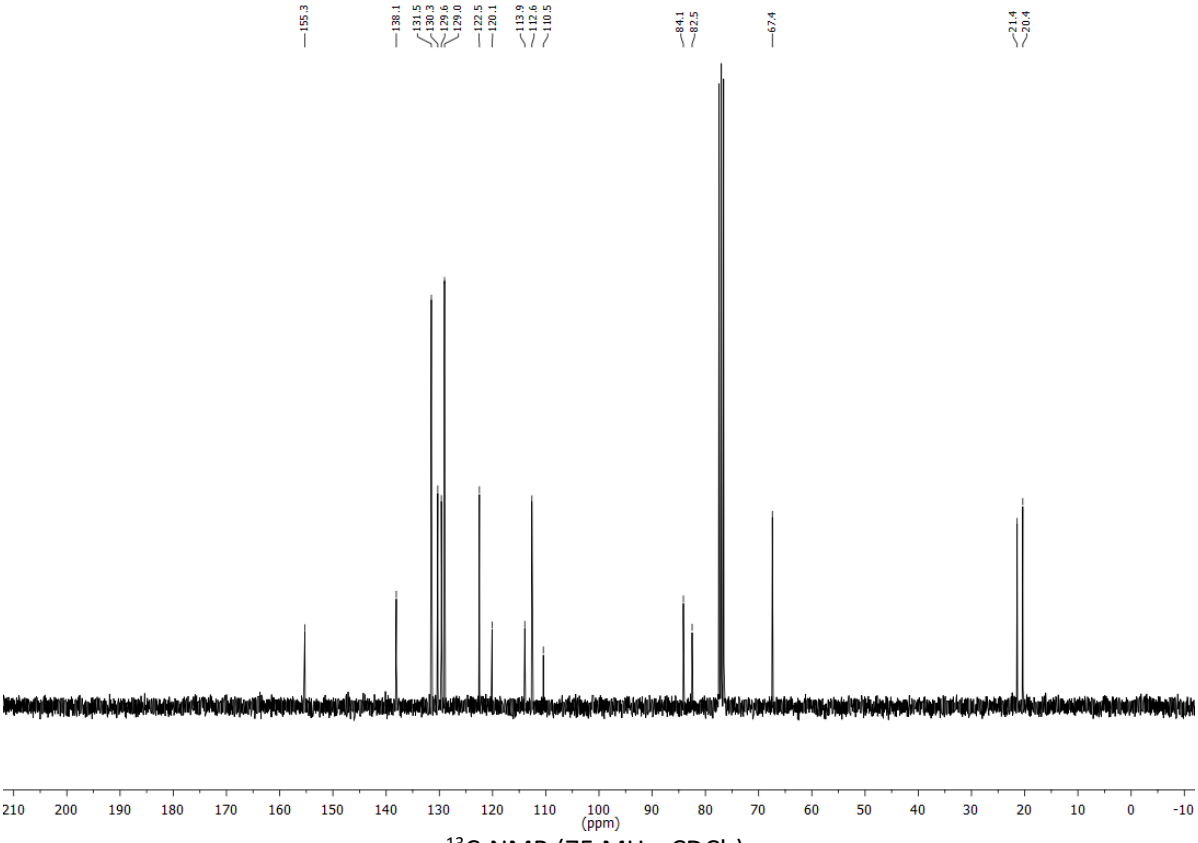
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 20.4, 21.4, 67.4, 82.5, 84.1, 110.5, 112.6, 113.9, 120.1, 122.5, 129.0, 129.6, 130.3, 131.5, 138.1, 155.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3097, 3067, 2953, 2921, 2162, 1583, 1482, 1385, 1288, 1251, 1062, 1038, 1019.

$C_{18}H_{15}NOS$ calcd.: 293.0874, found: 293.0903 (GC-HRMS).

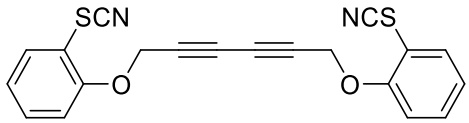


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1,6-Bis(2-thiocyanatophenoxy)hexa-2,4-diyne (1z)



Thiocyanate **1v** was synthesized from compound **11z** (261 mg, 736 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 4.2 ml) as solvent and 3.0 equiv. of X-CN were used for the reaction. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (*n*-pentane:EtOAc = 100:1) the product (122 mg, 324 µmol, 44%) was obtained as colorless solid.

m.p.: 128 °C.

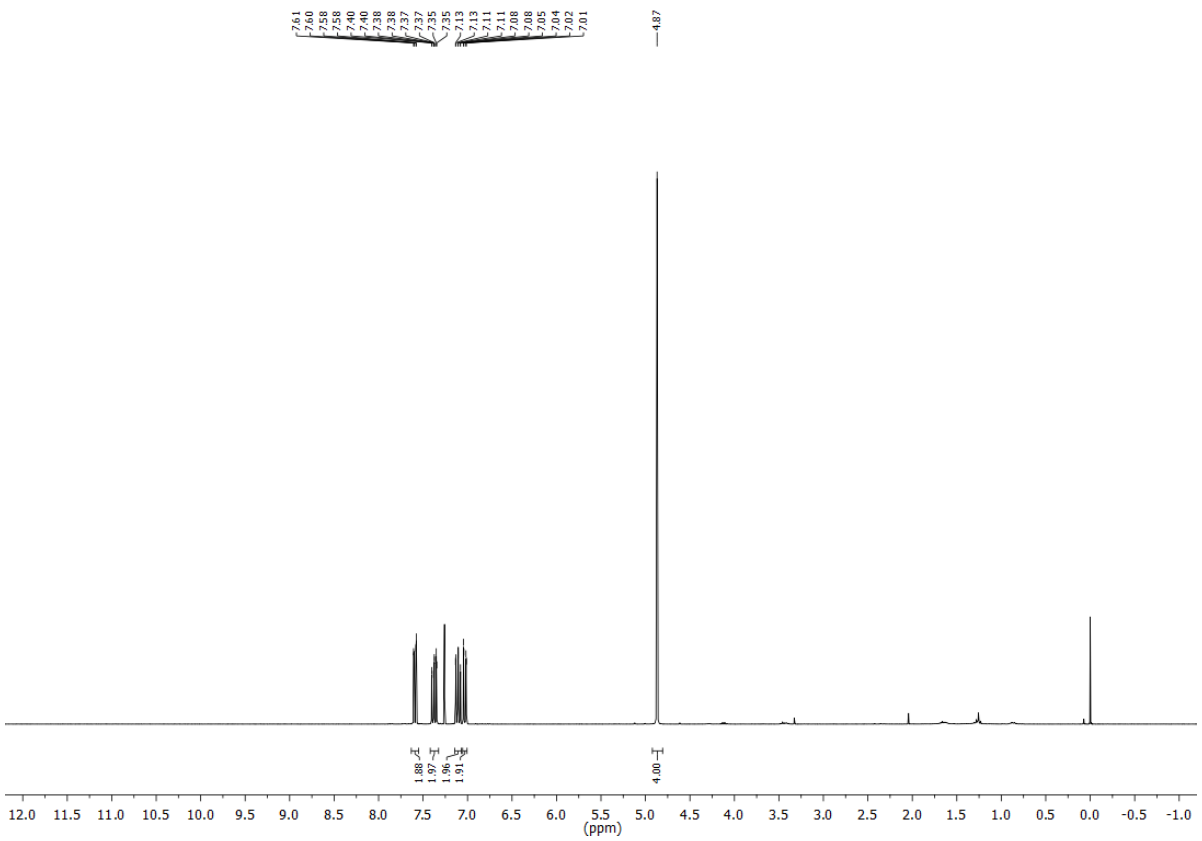
R_f = 0.29 (*n*-pentane:EtOAc = 4:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.87 (s, 4H), 7.03 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.07 – 7.14 (m, 2H), 7.38 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 2H), 7.59 (dd, *J* = 7.8, 1.6 Hz, 2H).

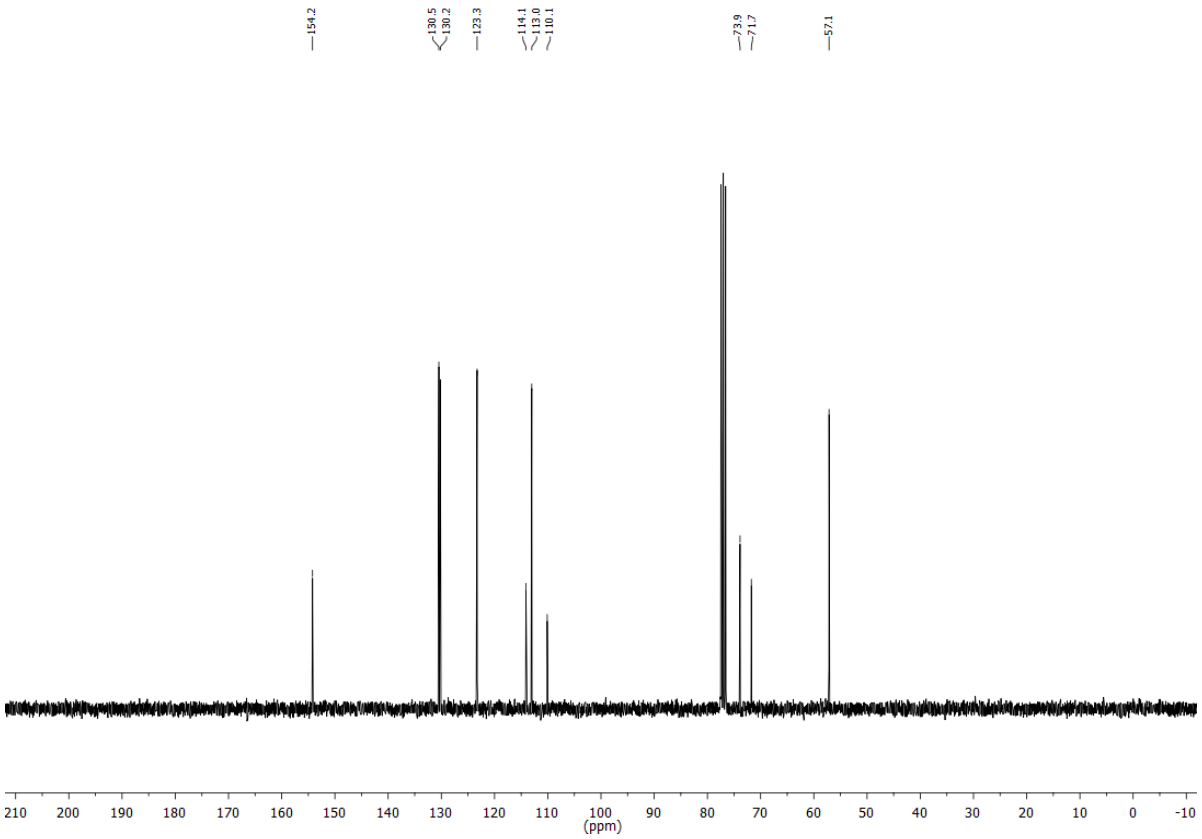
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 57.1, 71.7, 73.9, 110.1, 113.0, 114.1, 123.3, 130.2, 130.5, 154.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2926, 2854, 2155, 1577, 1471, 1447, 1284, 1215, 1061, 1011.

$C_{20}H_{12}N_2O_2S_2$ calcd.: 399.0232, found: 399.0233 $[M+Na]^+$ (ESI-HRMS).

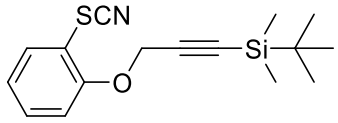


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-[[3-[(1,1-Dimethylethyl)dimethylsilyl]-2-propyn-1-yl]oxy]-2-thiocyanatobenzene (5a)



Thiocyanate **5a** was synthesized from compound **15a** (200 mg, 684 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 4.0 ml) was used as solvent. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (*n*-pentane:EtOAc = 60:1) the product was obtained as a pale yellow oil (122 mg, 402 µmol, 59%).

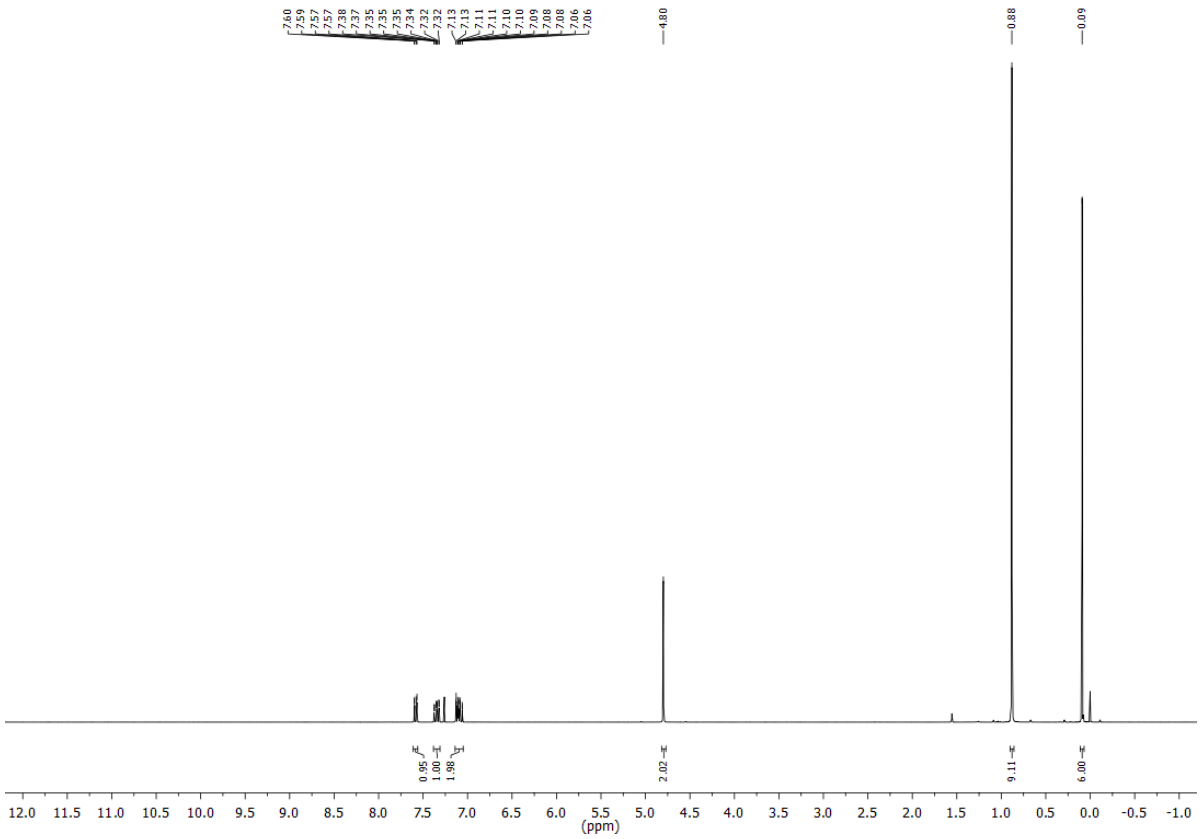
R_f = 0.27 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.09 (s, 6H), 0.88 (s, 9H), 4.80 (s, 2H), 7.05 – 7.13 (m, 2H), 7.35 (ddd, *J* = 8.3, 7.4, 1.6 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.6 Hz, 1H).

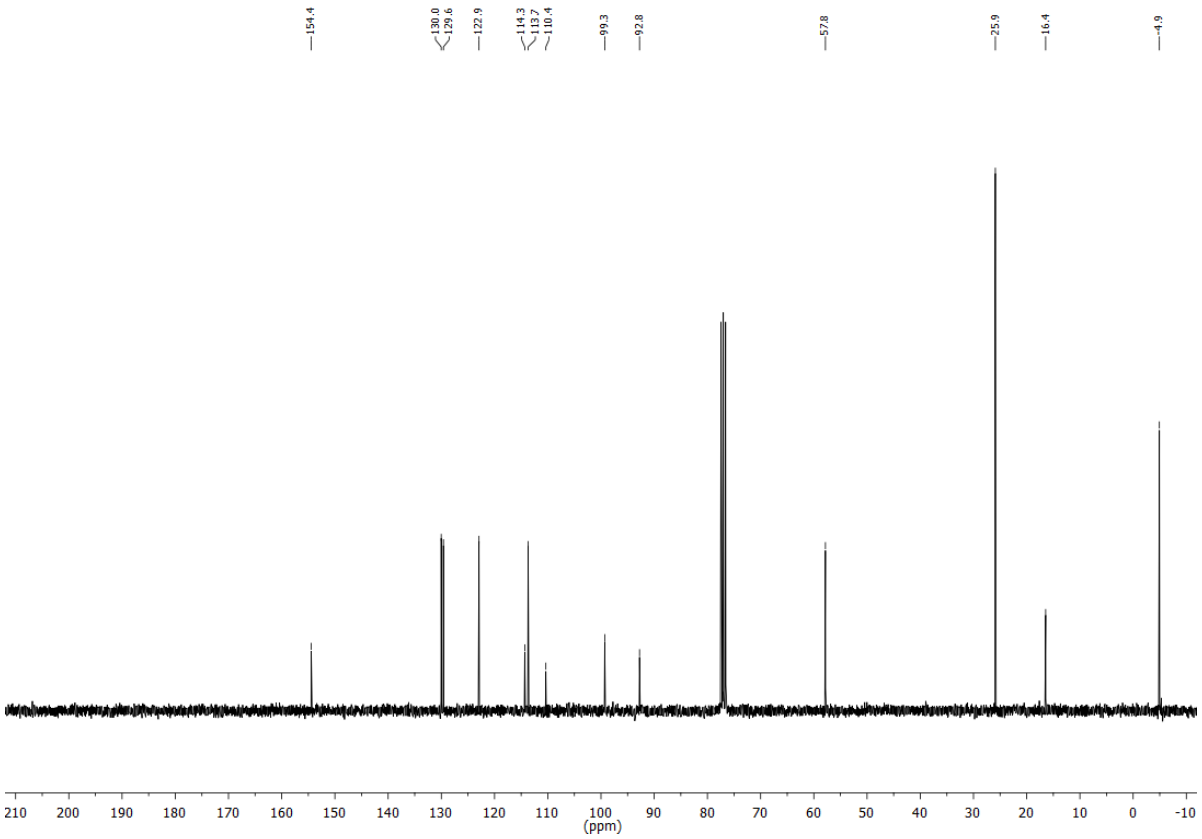
^{13}C-NMR (75 MHz, $CDCl_3$): δ = -4.9, 16.4, 25.9, 57.8, 92.8, 99.3, 110.4, 113.7, 114.3, 122.9, 129.6, 130.0, 154.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3069, 2953, 2930, 2857, 2159, 1582, 1475, 1282, 1250, 1225, 1028.

$C_{16}H_{21}NOSSi$ calcd.: 288.0878, found: 288.0886 [M-CH_3] (GC-HRMS).

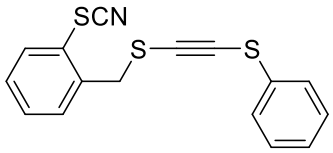


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((((Phenylthio)ethynyl)thio)methyl)-2-thiocyanatobenzene (5b)



3,5-Bis(trifluoromethyl)phenyl(cyano)iodoniumtriflate (X-CN, 340 mg, 0.66 mmol, 1.00 equiv.) was weighed into a sealable tube and a solution of the compound **15b** (201 mg, 0.66 mmol, 1.00 equiv.) in a mixture of CH_3CN/THF (1.9 ml/1.9 ml) was added and the tube capped. The solution was stirred for 20 min at RT. The solvent was removed and the crude mixture redissolved in DCM for adsorption on silica gel. The product was purified via flash column chromatography (*n*-pentane:EtOAc = 60:1) to afford a yellow oil (41 mg, 0.13 mmol, 20%).

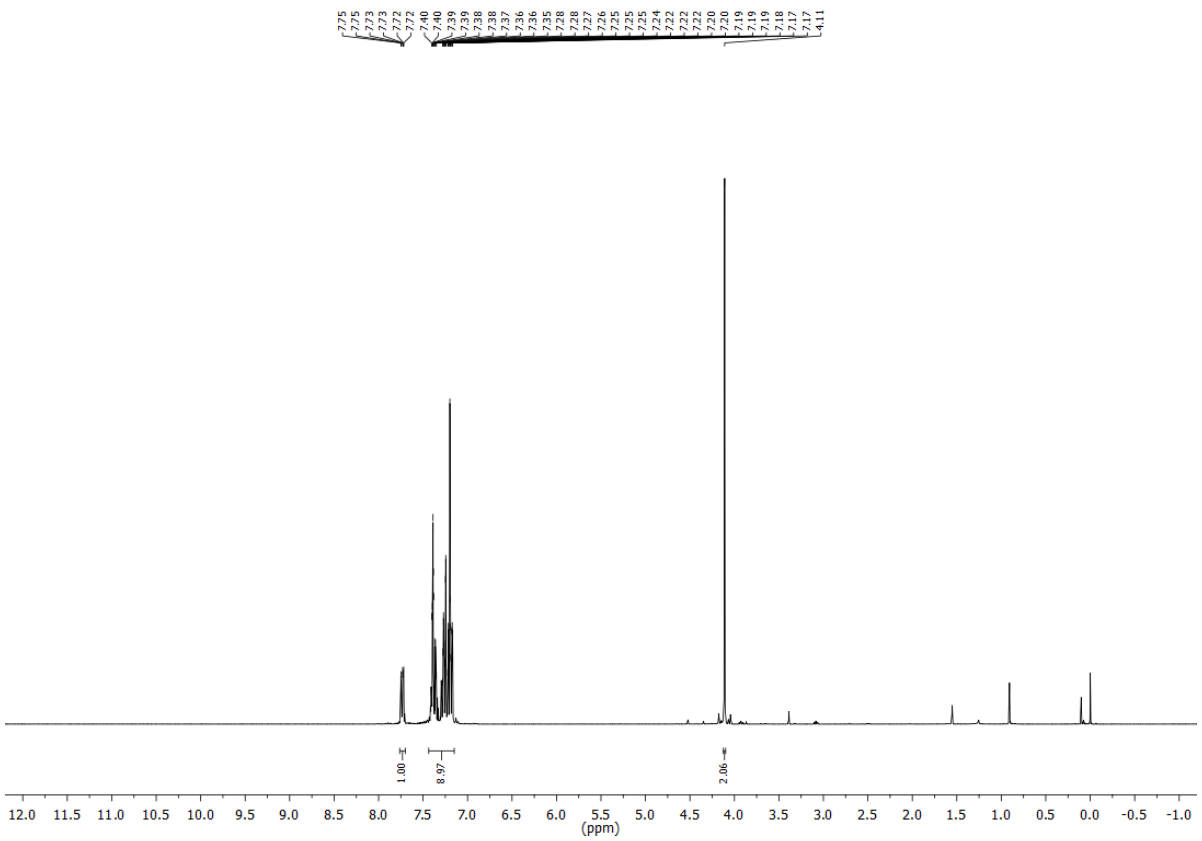
R_f = 0.31 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 4.10 (s, 2H), 7.05 – 7.31 (m, 9H).

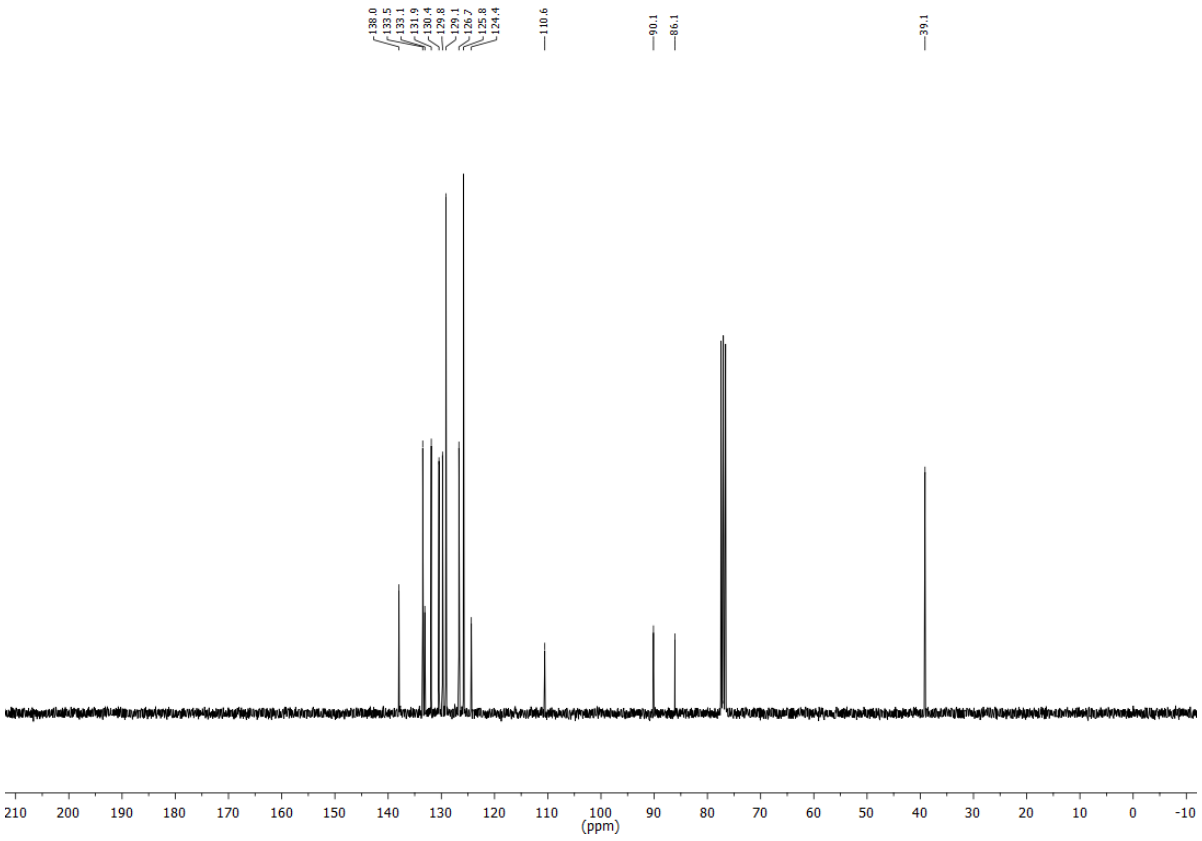
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.5, 39.7, 83.8, 92.2, 125.2, 125.7, 126.4, 127.0, 128.6, 129.0, 130.4, 133.7, 134.6, 137.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2929, 2848, 2153, 1578, 1472, 1435, 1198, 1025.

$C_{16}H_{11}NS_3$ calcd.: 335.9946, found: 335.9949 $[M+Na]^+$ (ESI-HRMS).

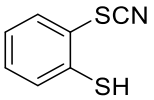


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

2-Thiocyanatobenzenethiol (15.1c)



Following a reported procedure[4] 1,2-benzenedithiol (142 mg, 1.00 mmol, 1.00 equiv.) was dissolved in THF (10 ml). To this solution DBU (160 mg, 157 µl, 1.05 mmol, 1.05 equiv.) and then CDBX[4] (287 mg, 1.00 mmol, 1.00 equiv.) were added to the open flask. The mixture was stirred for 5 min at RT, quenched with aq. citric acid (5%, 20 ml) and extracted with EtOAc (3 x 20 ml). The combined organic layers were dried over Na_2SO_4, filtrated and the solvent was removed *in vacuo*. The product was purified via flash column chromatography (DCM) to afford a light pink solid (113 mg, 0.68 mmol, 68%).

m.p.: 126 °C.

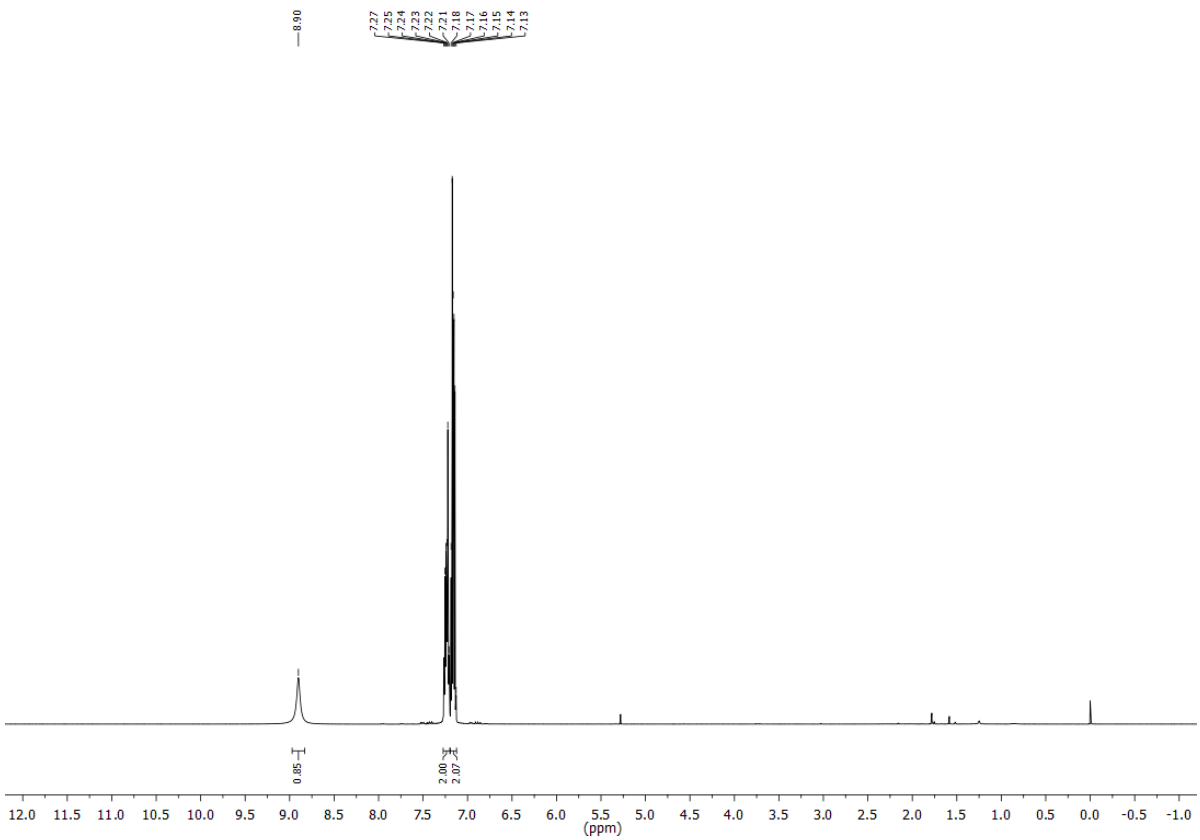
R_f = 0.10 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.13 – 7.19 (m, 2H), 7.20 – 7.28 (m, 2H), 8.90 (s, 1H).

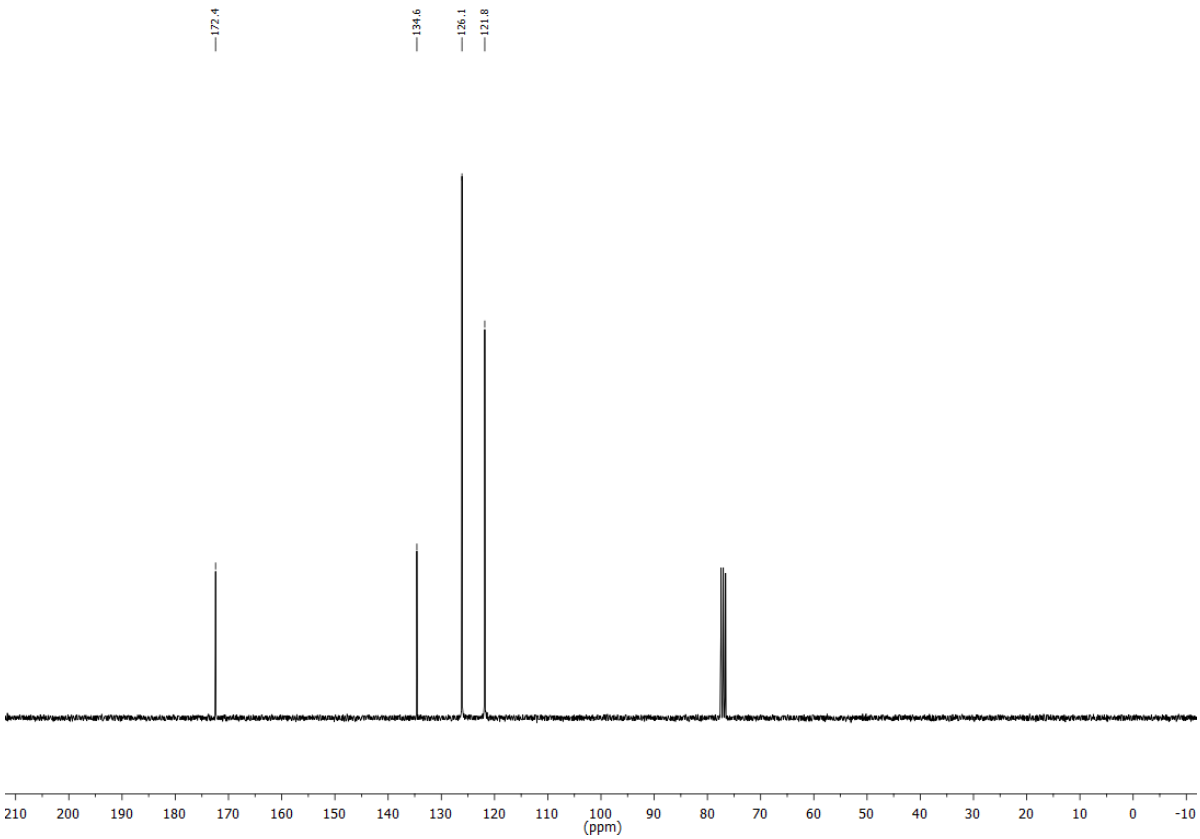
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 121.8 (2C), 126.1 (3C), 134.6, 172.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3174, 3049, 1697, 1547, 1430, 1231.

$C_7H_5NS_2$ calcd.: 166.9863, found: 166.9890 (GC-HRMS).

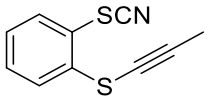


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Prop-1-yn-1-ylthio)-2-thiocyanatobenzene (5c)



According a reported procedure[32] compound **15.1c** (50 mg, 0.30 mmol, 1.00 equiv.) was dissolved in dry THF (4 ml) and TMG (38 mg, 42 µl, 0.33 mmol, 1.10 equiv.) was added. The Me-EBX reagent[28] (95 mg, 0.33 mmol, 1.10 equiv.) was added after 5 min of stirring and 15 min later, the mixture was quenched with water and showed then a blue color. The mixture was extracted with Et_2O, dried over Na_2SO_4 and evaporated under reduced pressure. Flash column chromatography (*n*-pentane/1% NEt_3) furnished the desired product as a pale yellow oil (21 mg, 0.10 mmol, 34%).

R_f = 0.23 (*n*-pentane:EtOAc = 50:1).

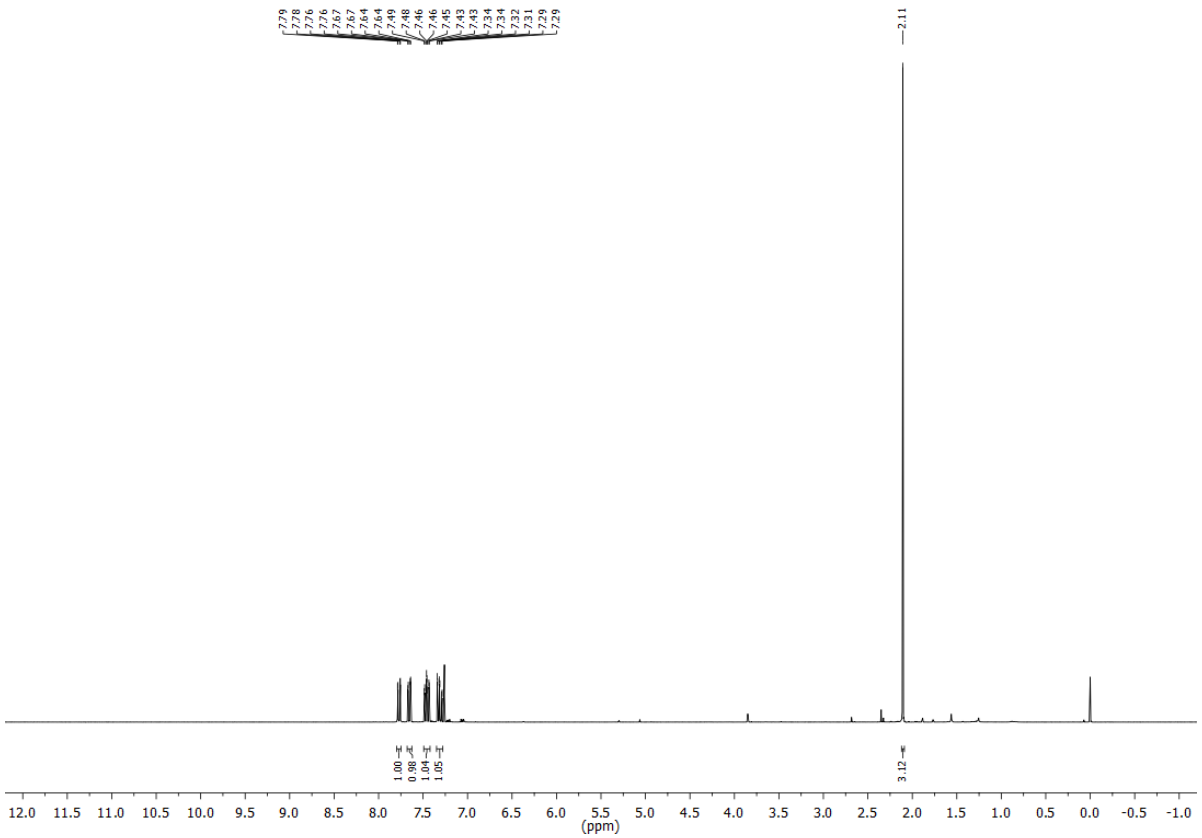
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.11 (s, 3H), 7.28 – 7.35 (m, 1H), 7.43 – 7.49 (m, 1H), 7.66 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.77 (dd, *J* = 7.9, 1.4 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 5.3, 62.5, 96.8, 109.5, 122.1, 128.3, 129.2, 131.1, 133.1, 137.2.

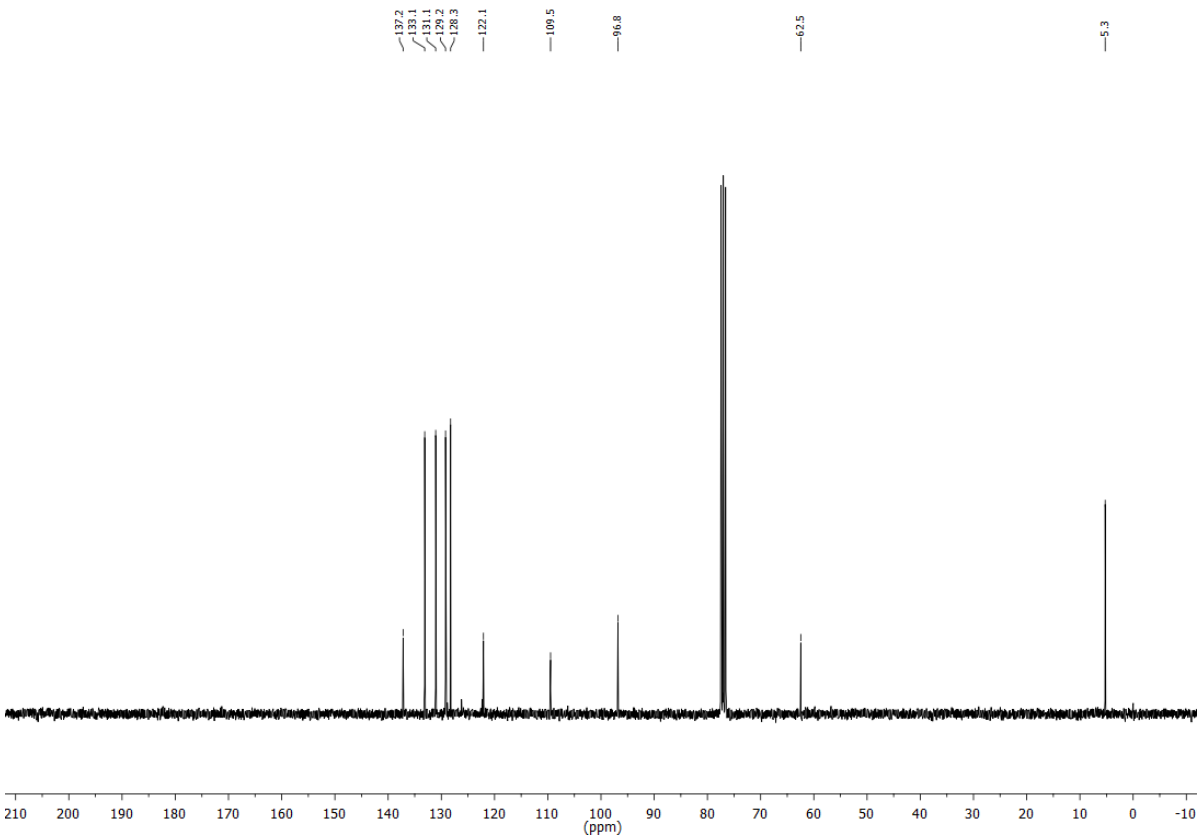
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3059, 2955, 2915, 2844, 2201, 2156, 1727, 1568, 1438, 1263, 1028.

$C_{10}H_7NS_2$ calcd.: 205.0020, found: 204.9995 (GC-HRMS).

[32] S. Racine, B. Hegedüs, R. Scopelliti and J. Waser, *Chem. Eur. J.*, 2016, **22**, 11997..

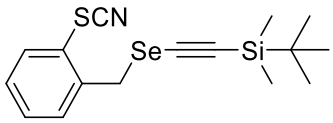


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Methylthio)-2-(3-((1,1-dimethylethyl)dimethylsilyl)-2-((ethynylselanyl)methyl))benzene (5d)



3,5-Bis(trifluoromethyl)phenyl(cyano)iodoniumtriflate (X-CN, 541 mg, 1.05 mmol, 1.00 equiv.) was weighed into a sealable tube and a solution of the compound **15d** (375 mg, 1.05 mmol, 1.00 equiv.) in a mixture of CH_3CN/THF (3.0 ml/3.0 ml) was added and the tube capped. The solution was stirred for 30 min at RT and then filtered through a short plug of silica. The reaction flask was rinsed with DCM and the plug was washed 4 times with the later eluent. The crude mixture was adsorbed on silica gel. The product was purified via flash column chromatography (*n*-pentane:EtOAc = 60:1) to afford an orange oil (122 mg, 0.33 mmol, 31%).

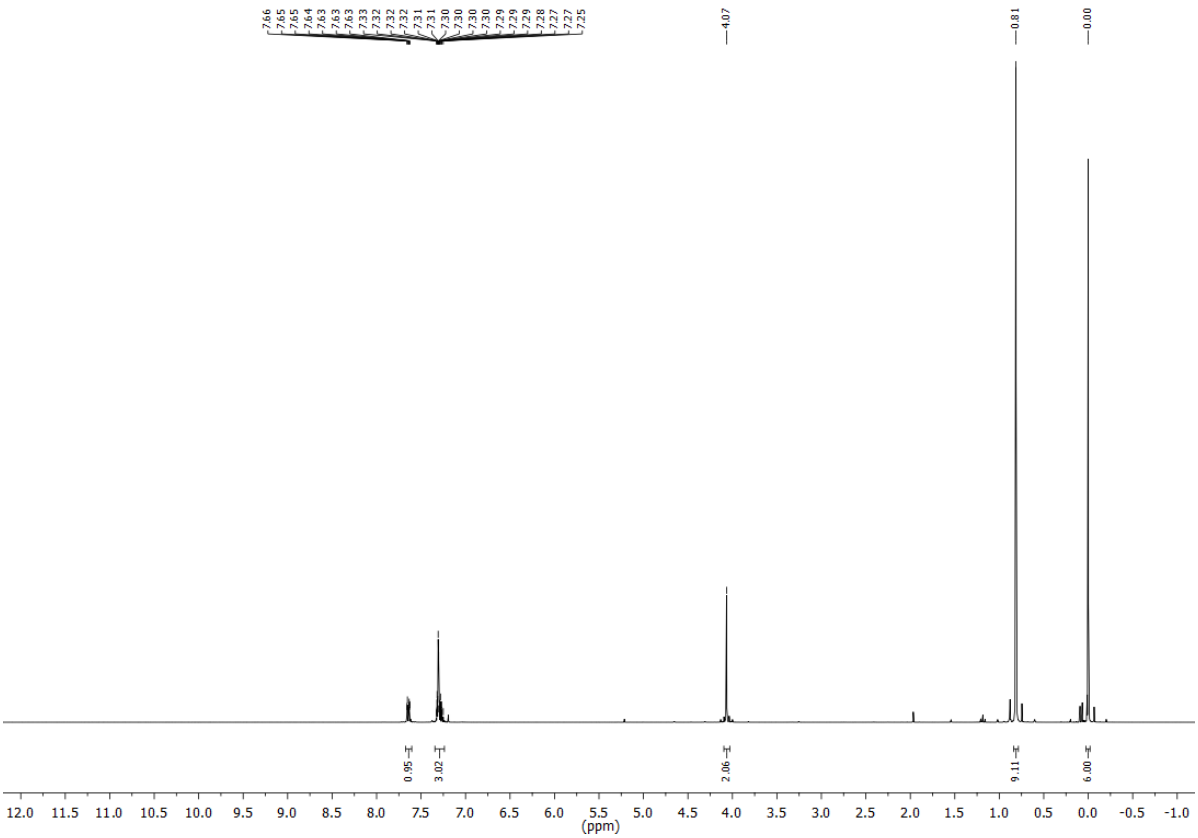
R_f = 0.50 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 6H), 0.81 (s, 9H), 4.07 (s, 2H), 7.24 – 7.34 (m, 3H), 7.60 – 7.68 (m, 1H).

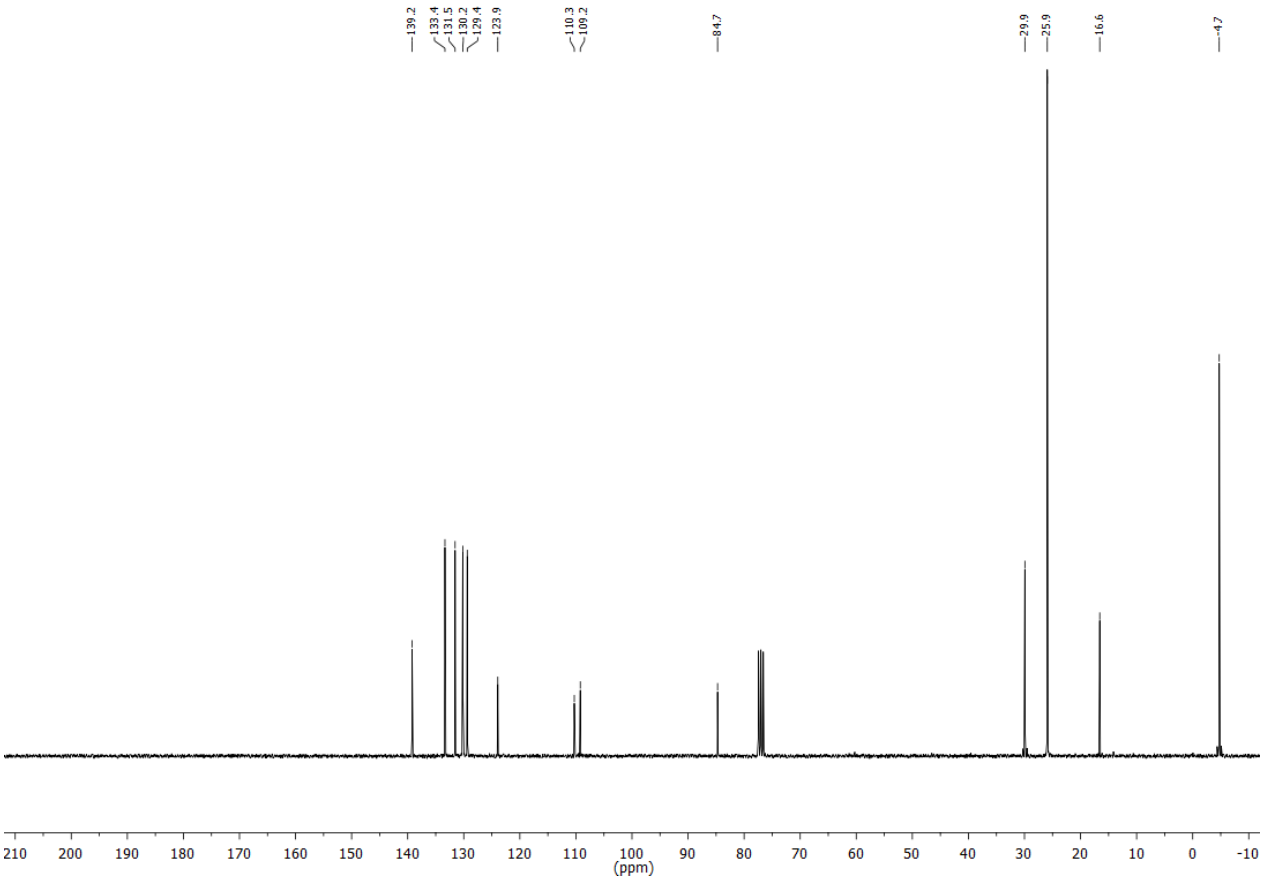
^{13}C-NMR (75 MHz, $CDCl_3$): δ = -4.7, 16.6, 25.9, 29.9, 84.7, 109.2, 110.3, 123.9, 129.4, 130.2, 131.5, 133.4, 139.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2951, 2928, 2890, 2855, 2155, 2078, 1466, 1361, 1253, 1182.

$C_{16}H_{21}NSSeSi$ calcd.: 309.9625, found: 309.9649 [M-TBS] (GC-HRMS).

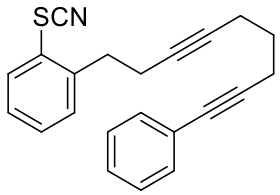


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(9-Phenylnona-3,8-diyn-1-yl)-2-thiocyanatobenzene (9a)



Thiocyanate **9a** was synthesized from compound **19a** (105 mg, 330 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 2.0 ml) was used as solvent. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (*n*-pentane:EtOAc = 50:1) the product was obtained as a colorless oil (44 mg, 133 µmol, 40%).

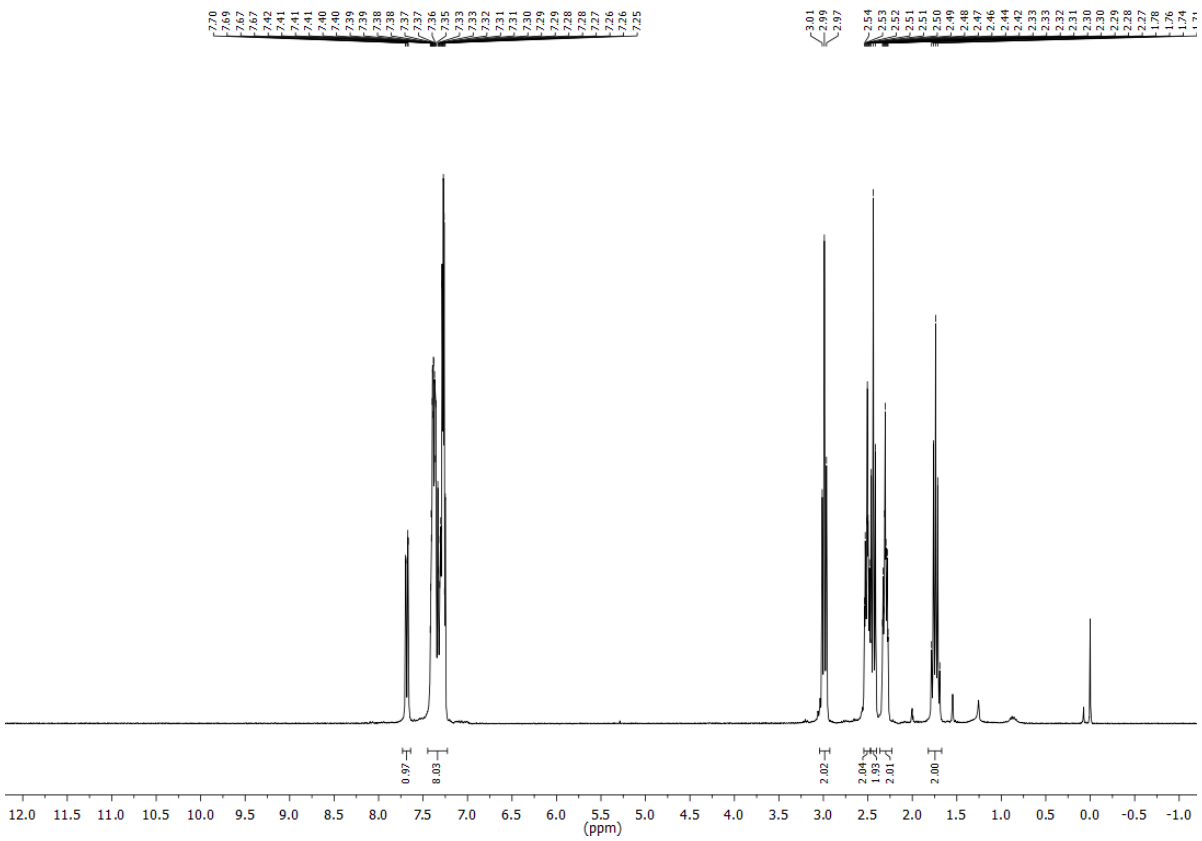
R_f = 0.36 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.74 (p, *J* = 7.0 Hz, 2H), 2.30 (tt, *J* = 7.0, 2.3 Hz, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.50 (tt, *J* = 7.3, 2.4 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 7.24 – 7.43 (m, 8H), 7.68 (dd, *J* = 7.8, 1.4 Hz, 1H).

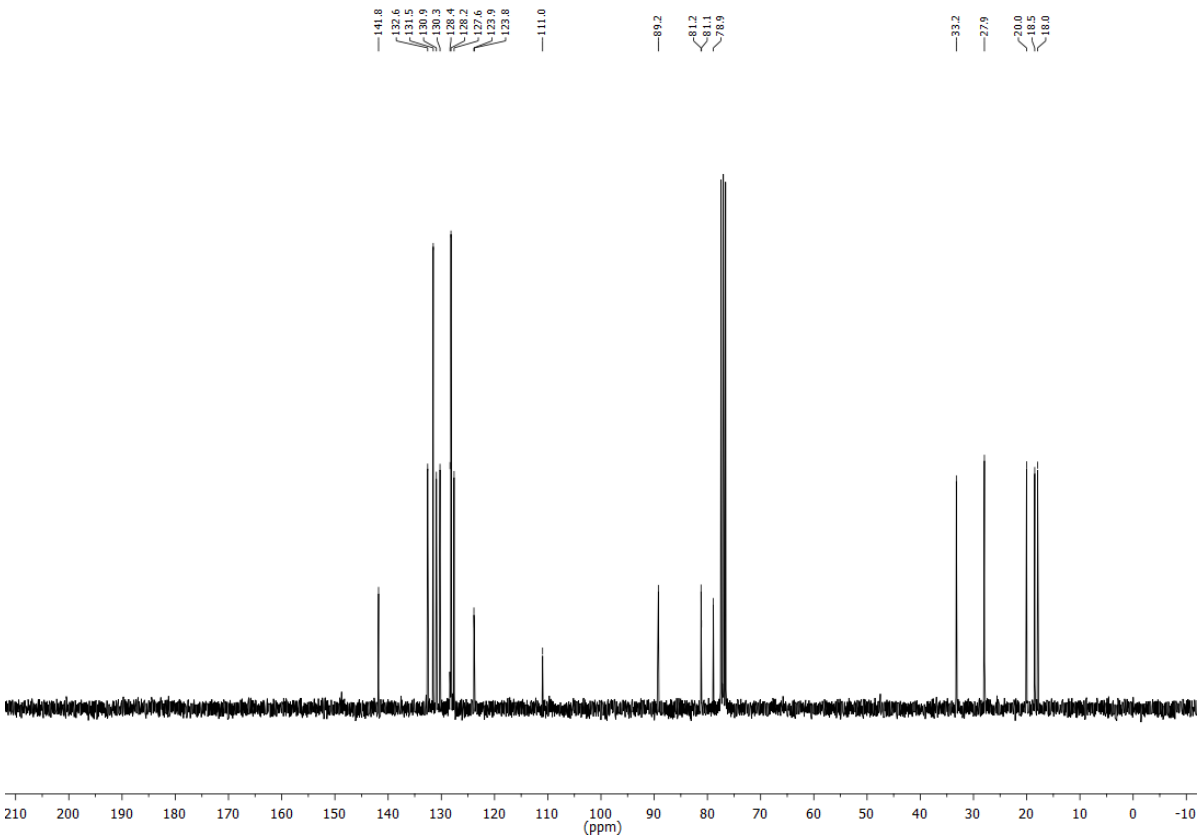
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 18.0, 18.5, 20.0, 27.9, 33.2, 78.9, 81.1, 81.2, 89.2, 111.0, 123.8, 123.9, 127.6, 128.2, 128.4, 130.3, 130.9, 131.5, 132.6, 141.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2937, 2866, 2838, 2155, 1596, 1482, 1436, 1337, 1033.

$C_{22}H_{19}NS$ calcd.: 329.1238, found: 329.1233 (GC-HRMS).

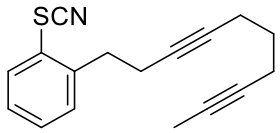


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Deca-3,8-diyn-1-yl)-2-thiocyanatobenzene (9b)



Thiocyanate **9b** was synthesized from compound **19b** (94 mg, 367 µmol) according GP 3. A mixture of CH_3CN/THF (1:1, 2.2 ml) was used as solvent. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (*n*-pentane:EtOAc = 60:1) the product was obtained as a colorless oil (36 mg, 134 µmol, 37%).

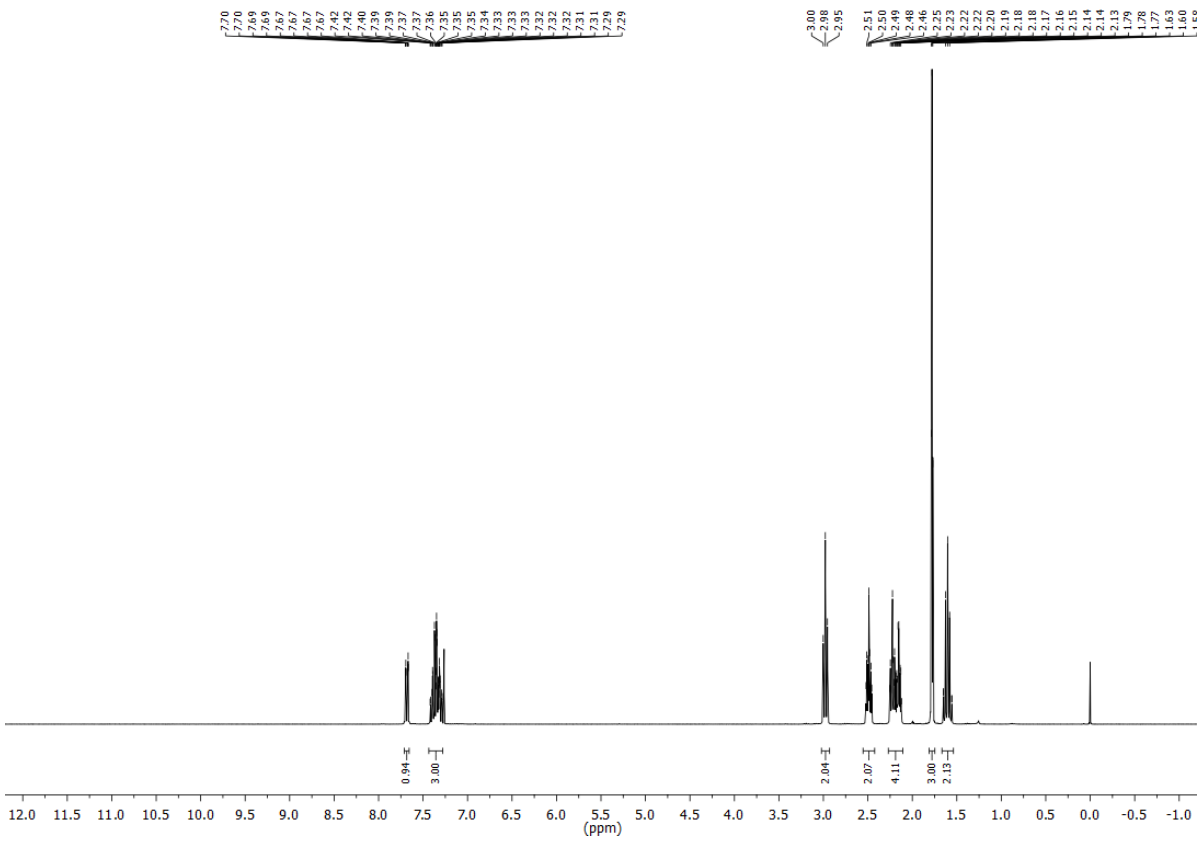
R_f = 0.34 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.55 – 1.66 (m, 2H), 1.78 (t, *J* = 2.5 Hz, 3H), 2.15 (tt, *J* = 7.0, 2.6 Hz, 2H), 2.22 (tt, *J* = 6.9, 2.3 Hz, 2H), 2.49 (tt, *J* = 7.2, 2.3 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.43 (m, 3H), 7.68 (ddd, *J* = 7.7, 1.5, 0.7 Hz, 1H).

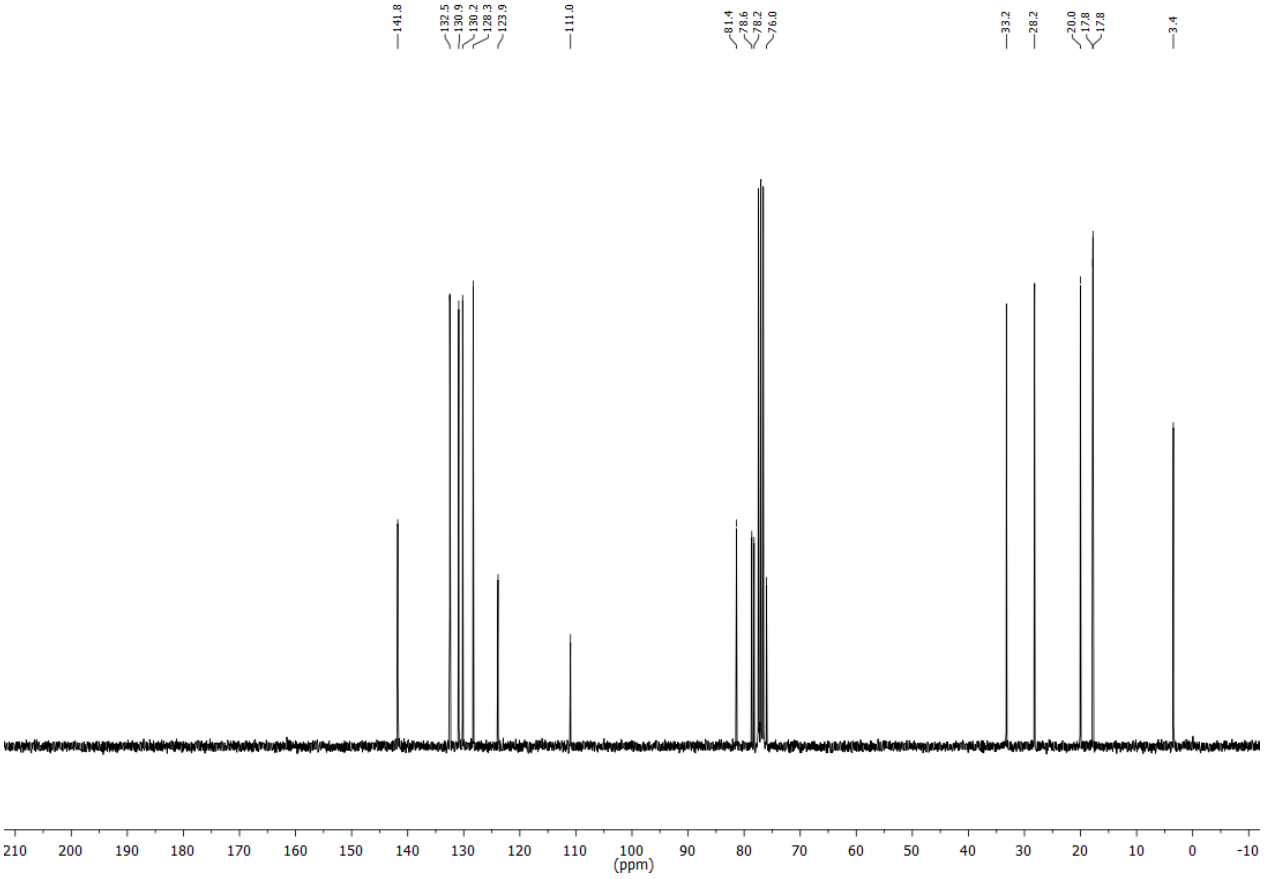
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.4, 17.8, 17.8, 20.0, 28.2, 33.2, 76.0, 78.2, 78.6, 81.4, 111.0, 123.9, 128.3, 130.2, 130.9, 132.5, 141.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2939, 2913, 2862, 2844, 2156, 1472, 1437, 1338, 1035.

$C_{17}H_{17}NS$ calcd.: 266.1003, found: 266.1012 (GC-HRMS).

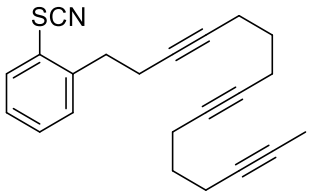


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Pentadeca-3,8,13-triyn-1-yl)-2-thiocyanatobenzene (9d)



Thiocyanate **9d** was synthesized from compound **19d** (258 mg, 0.80 mmol) according GP 3. A mixture of CH_3CN/THF (1:2, 4.6 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 50:1) to obtain the product (37 mg, 135 µmol, 8%) as colorless oil.

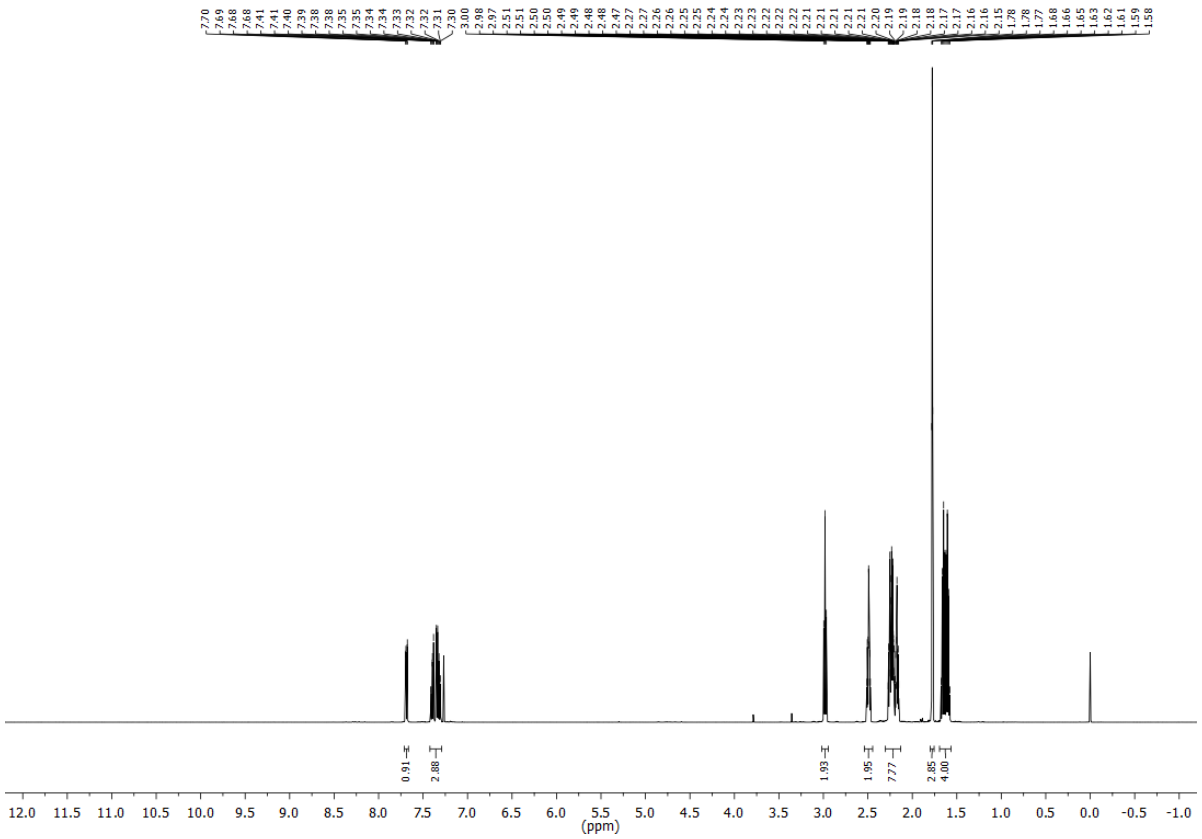
R_f = 0.21 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.63 (dp, *J* = 21.1, 7.0 Hz, 4H), 1.78 (t, *J* = 2.6 Hz, 3H), 2.14 – 2.29 (m, 8H), 2.49 (tt, *J* = 7.1, 2.4 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 7.30 – 7.42 (m, 3H), 7.69 (dd, *J* = 7.8, 1.3 Hz, 1H).

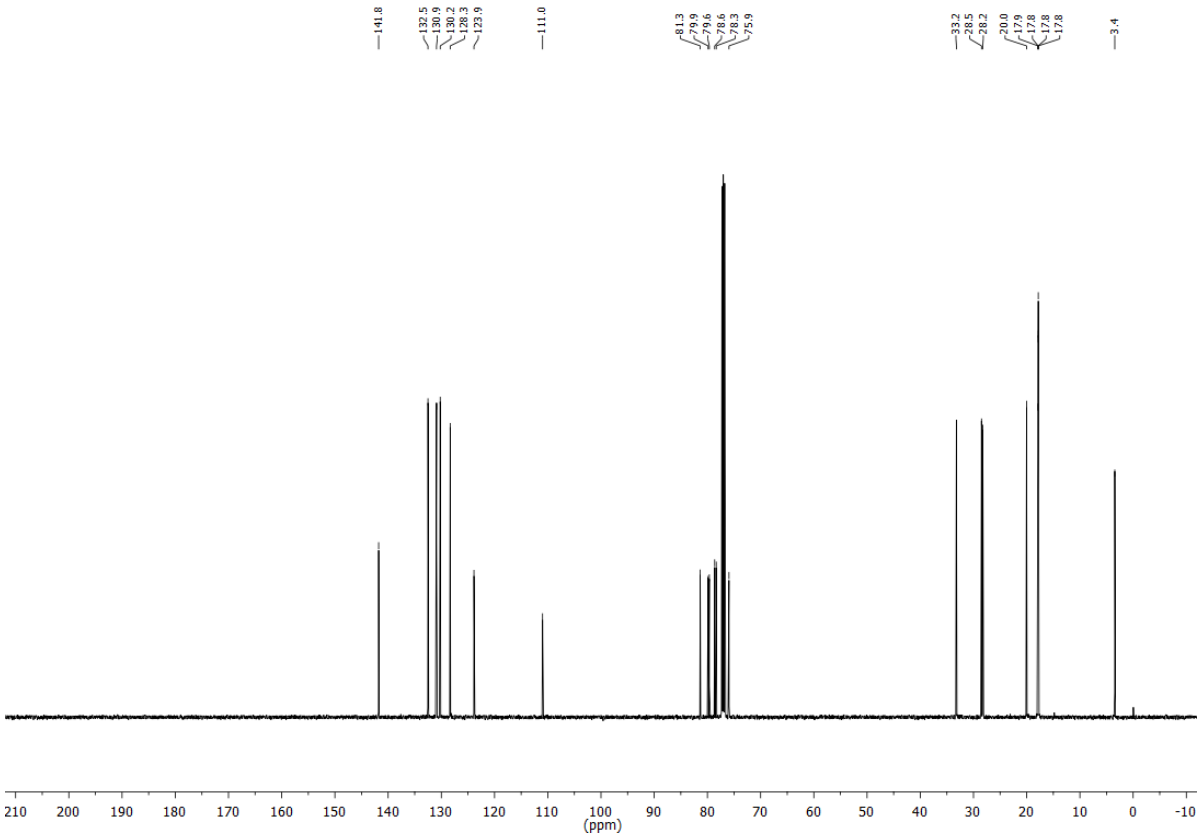
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 3.4, 17.8, 17.8, 17.8, 17.9, 20.0, 28.2, 28.5, 33.2, 75.9, 78.3, 78.6, 79.6, 79.9, 81.3, 111.0, 123.9, 128.3, 130.2, 130.9, 132.5, 141.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2937, 2862, 2841, 2156, 1472, 1435, 1337, 1036.

$C_{22}H_{23}NS$ calcd.: 333.1546, found: 333.1529 (EI-HRMS).

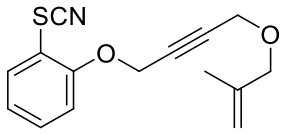


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

1-((4-((2-Methylallyl)oxy)but-2-yn-1-yl)oxy)-2-thiocyanatobenzene (9e)



Thiocyanate **9e** was synthesized from compound **19e** (424 mg, 1.62 mmol) according GP 3. A mixture of CH_3CN/THF (1:2, 9.0 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (*n*-pentane:EtOAc = 40:1→20:1) to obtain the product (37 mg, 135 µmol, 8%) as colorless oil.

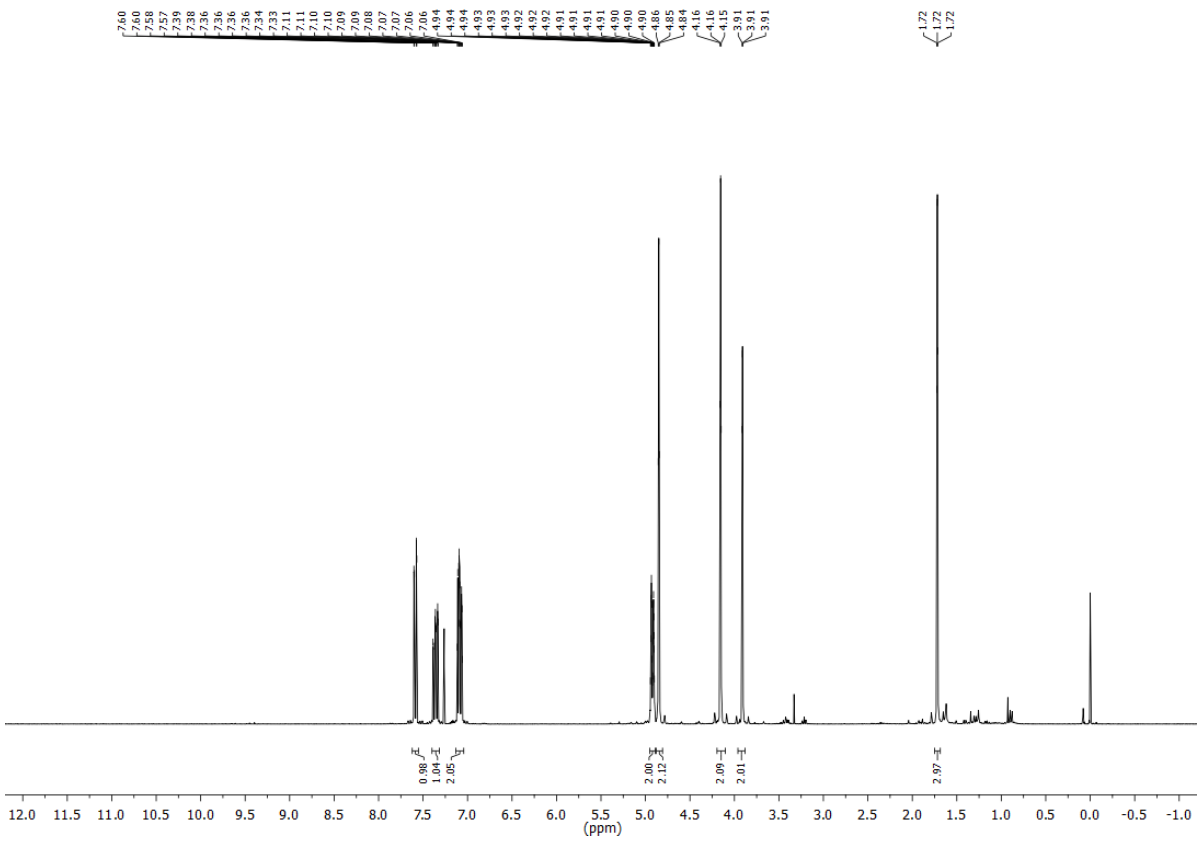
R_f = 0.23 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.72 (t, *J* = 1.3 Hz, 3H), 3.88 – 3.92 (m, 2H), 4.15 (t, *J* = 1.8 Hz, 2H), 4.85 (t, *J* = 1.8 Hz, 2H), 4.88 – 4.96 (m, 2H), 7.05 – 7.13 (m, 2H), 7.36 (ddd, *J* = 8.4, 7.4, 1.6 Hz, 1H), 7.59 (dd, *J* = 8.1, 1.5 Hz, 1H).

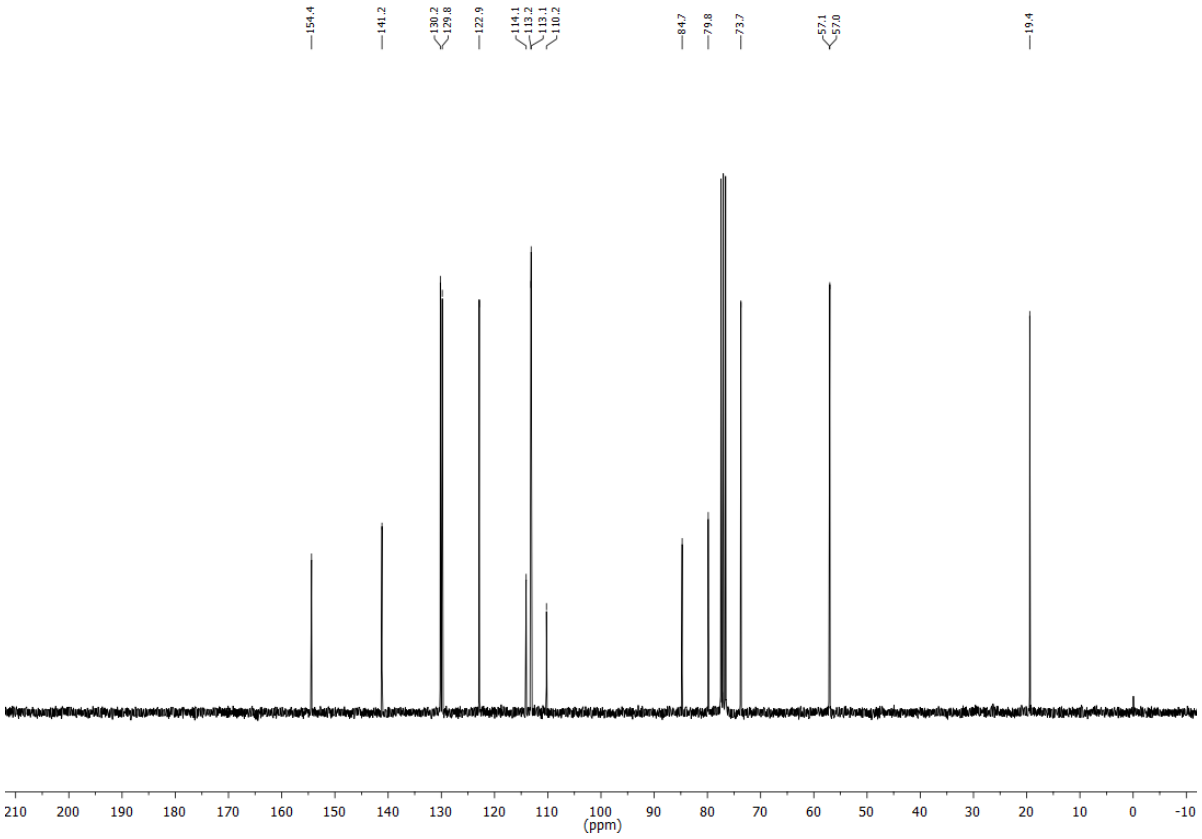
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 19.4, 57.0, 57.1, 73.7, 79.8, 84.7, 110.2, 113.1, 113.2, 114.1, 122.9, 129.8, 130.2, 141.2, 154.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3072, 2923, 2855, 2158, 1582, 1474, 1448, 1360, 1287, 1228, 1130, 1068, 998.

$C_{15}H_{15}NO_2S$ calcd.: 273.0818, found: 273.0820 (EI-HRMS).

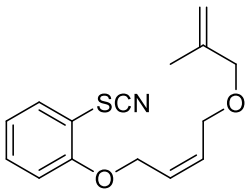


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(*Z*)-1-((4-((2-Methylallyl)oxy)but-2-en-1-yl)oxy)-2-thiocyanatobenzene (9f)



Compound **9f** was synthesized according GP3 (alternative B) from substrate **19.2f** (1.3 mmol, 341.0 mg). The desired product was obtained after flash column chromatography (*n*-pentane:EtOAc = 20:1) as a colorless oil (0.10 mmol, 27.6 mg, 8%).

R_f = 0.45 (*n*-pentane:EtOAc = 10:1).

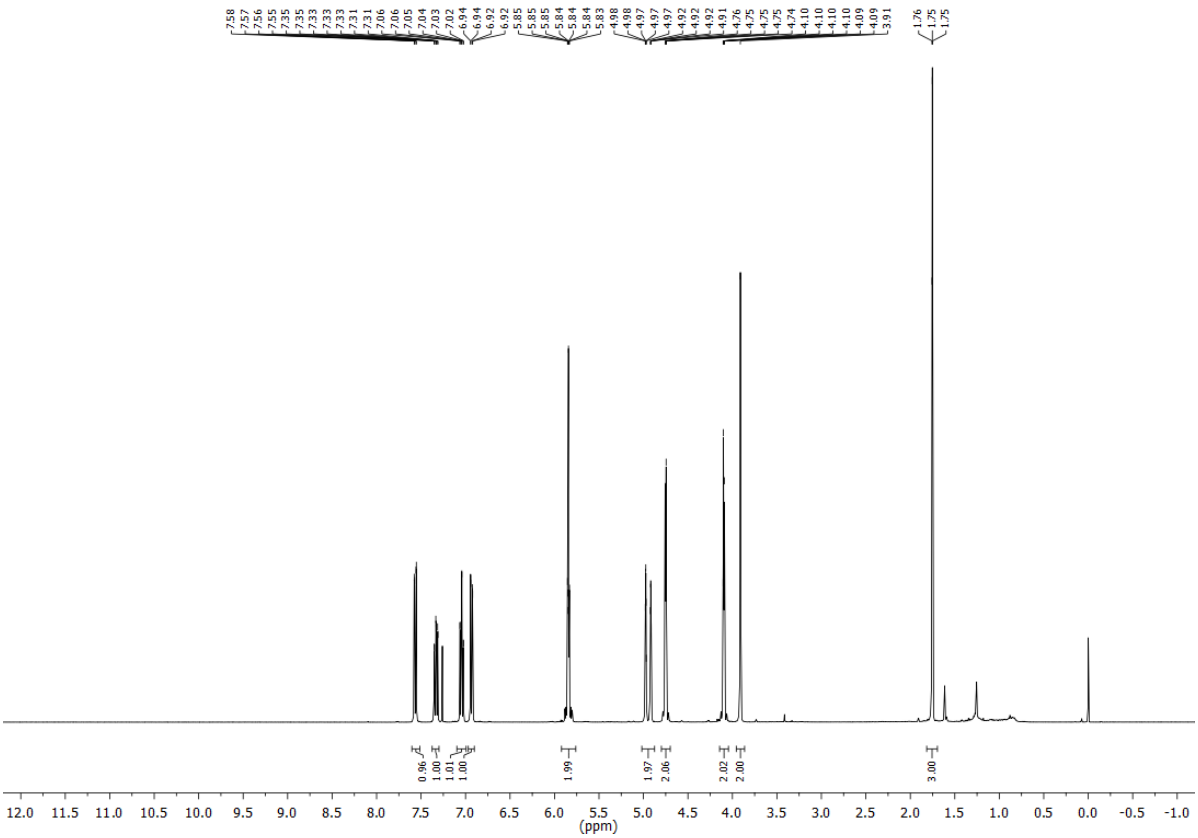
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.75 (s, 4H), 3.91 (s, 2H), 4.06 – 4.15 (m, 2H), 4.69 – 4.84 (m, 2H), 4.95 (ddd, *J*=23.1, 2.2, 1.3, 2H), 5.79 – 5.92 (m, 2H), 6.93 (dd, *J*=8.3, 1.1, 1H), 7.04 (td, *J*=7.6, 1.2, 1H), 7.30 – 7.37 (m, 1H), 7.57 (dd, *J*=7.9, 1.6, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 19.5, 65.4, 65.8, 74.4, 110.4, 112.5, 112.6, 113.7, 122.3, 126.7, 129.8, 130.3, 130.6, 141.9, 155.3.

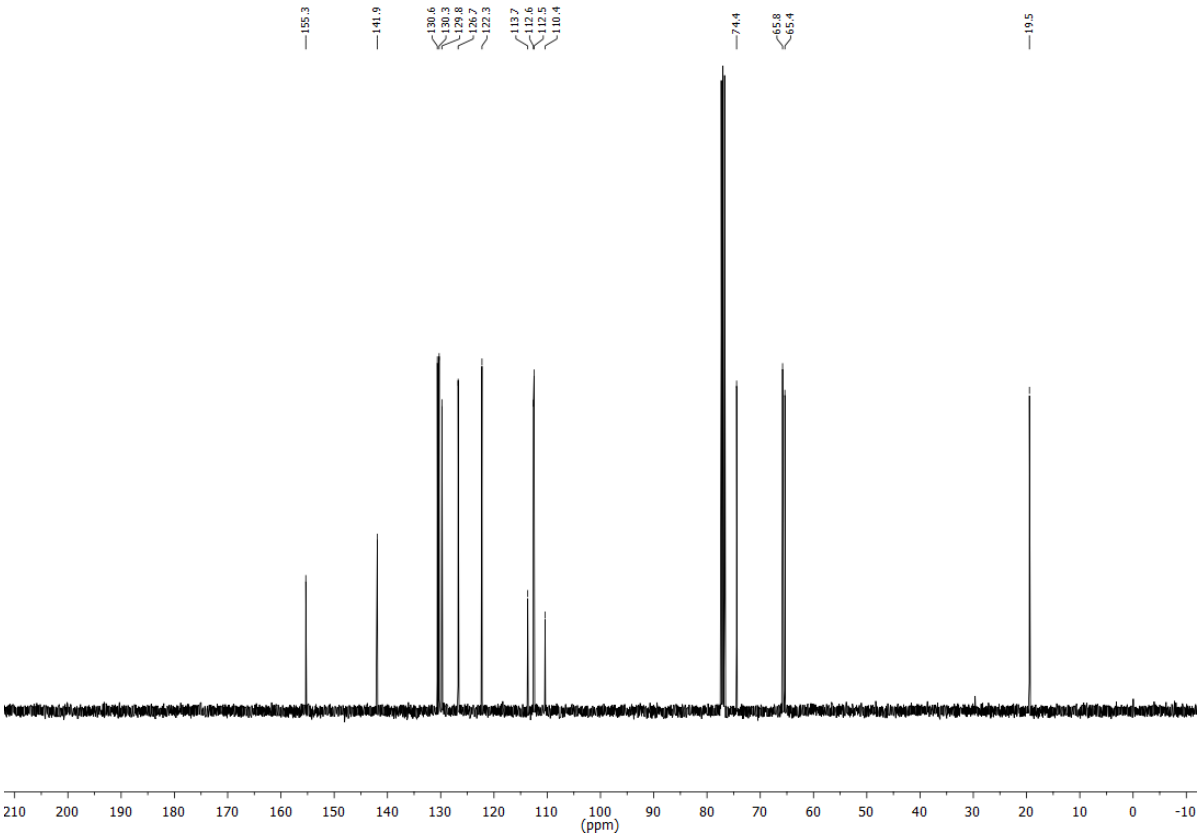
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3074, 3030, 2972, 2918, 2853, 2158, 1582, 1476, 1446, 1297, 1281, 1060, 997.

$C_{15}H_{17}NO_2S$ calcd.: 275.0980, found: 275.0985 (GC-HRMS).

Compound **9f** was synthesized to do a cascade reaction with an alkene-alkene system. Unfortunately, the isolation of the desired product was not possible. The GC-MS showed only traces of a new peak with the right mass.

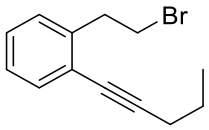


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

1-(2-Bromoethyl)-2-(pent-1-yn-1-yl)benzene (13.1e)



2-(2-(Pent-1-yn-1-yl)phenyl)ethan-1-ol[33] (339 mg, 1.80 mmol) was converted via the aforementioned general procedure (GP 5) to afford the title compound **13.1d** as a slightly yellow oil (382 mg, 1.52 mmol, 85 %).

R_f = 0.61 (*n*-pentane).

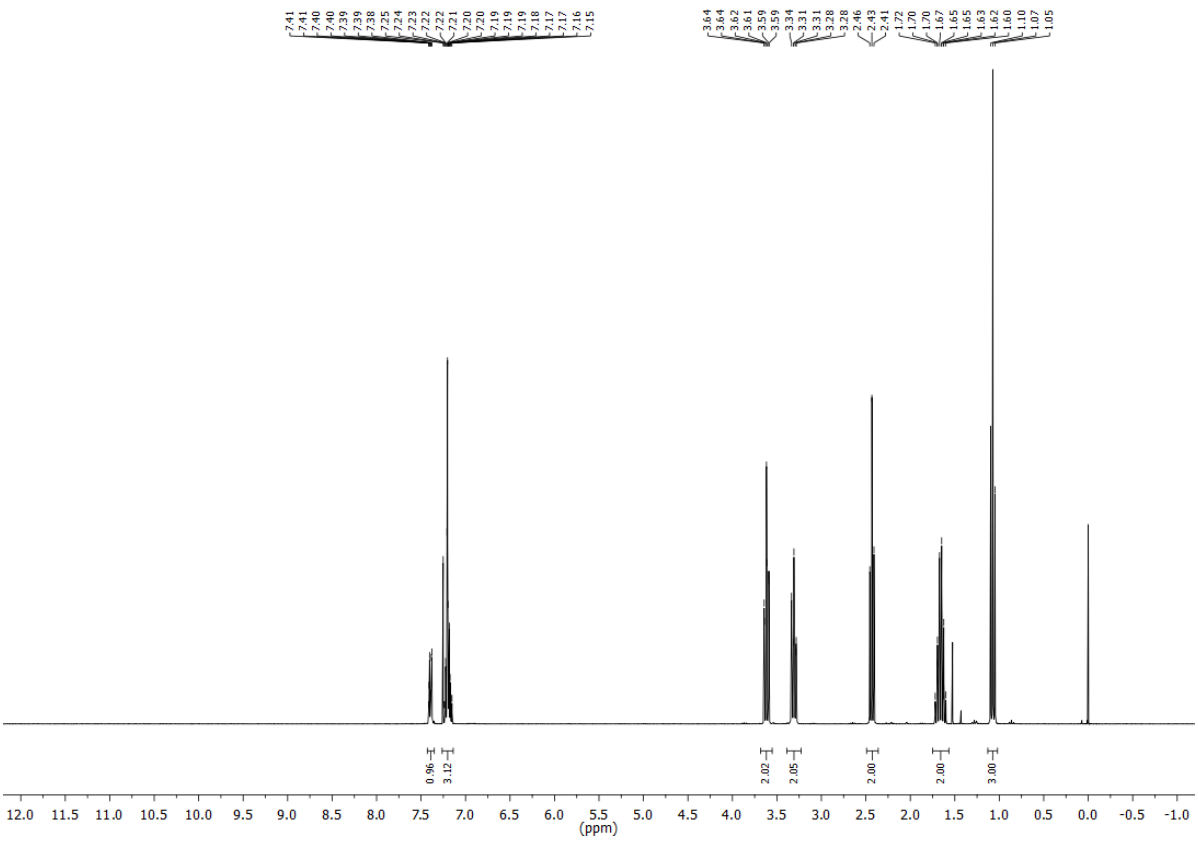
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.42-7.37 (m, 1H), 7.24-7.15 (m, 3H), 3.65-3.58 (m, 2H), 3.31 (t, *J* = 7.9 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.66 (s, *J* = 7.3 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 140.5, 132.4, 129.3, 127.7, 126.9, 123.7, 94.7, 78.6, 38.5, 31.9, 22.3, 21.5, 13.6.

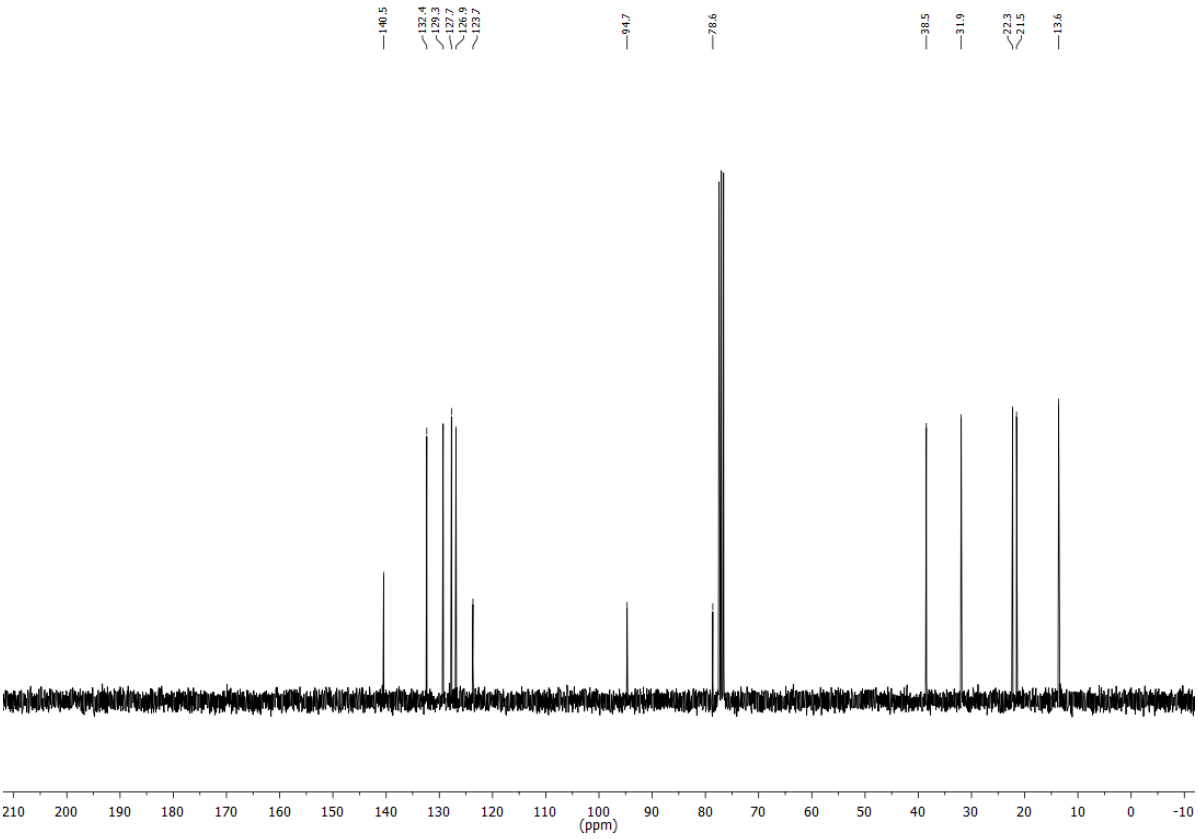
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3065, 3022, 2963, 2932, 2870, 2232, 1484, 1448, 1214, 1040.

$C_{13}H_{15}Br$ calcd.: 250.0357, found: 250.0364 (GC-HRMS).

[33] C. Wang, D. Abegg, D. G. Hoch and A. Adibekian, *Angew. Chem. Int. Ed.*, 2016, **55**, 2911.

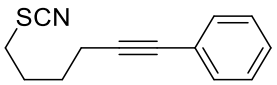


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(6-Thiocyanatohex-1-yn-1-yl)benzene (3a)



(6-Bromohex-1-yn-1-yl)benzene (550 mg, 2.32 mmol, prepared via GP 5) was converted via the aforementioned general procedure (GP 6) to afford the title compound **3a** as a colorless oil (437 mg, 2.03 mmol, 87%).

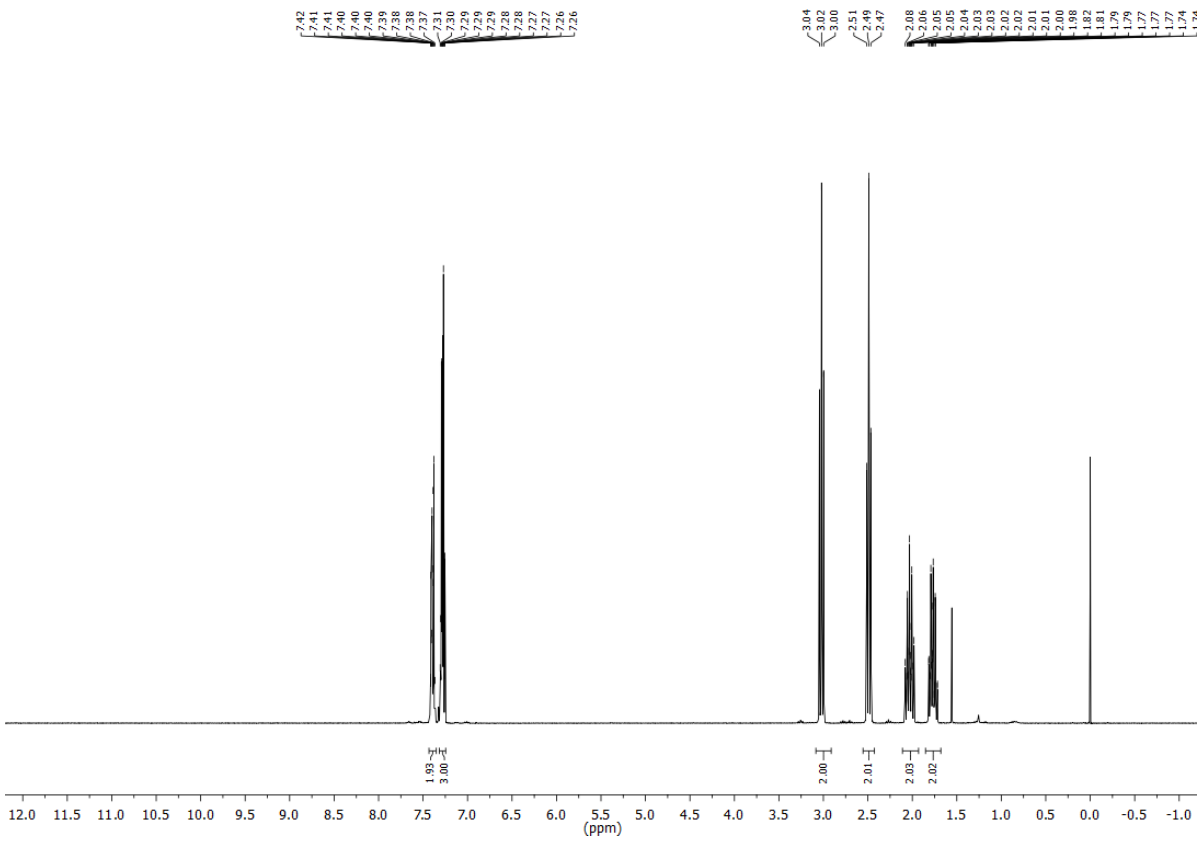
R_f = 0.50 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.43-7.36 (m, 2H), 7.33-7.24 (m, 3H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 6.9 Hz, 2H), 2.09-1.97 (m, 2H), 1.83-1.70 (m, 2H).

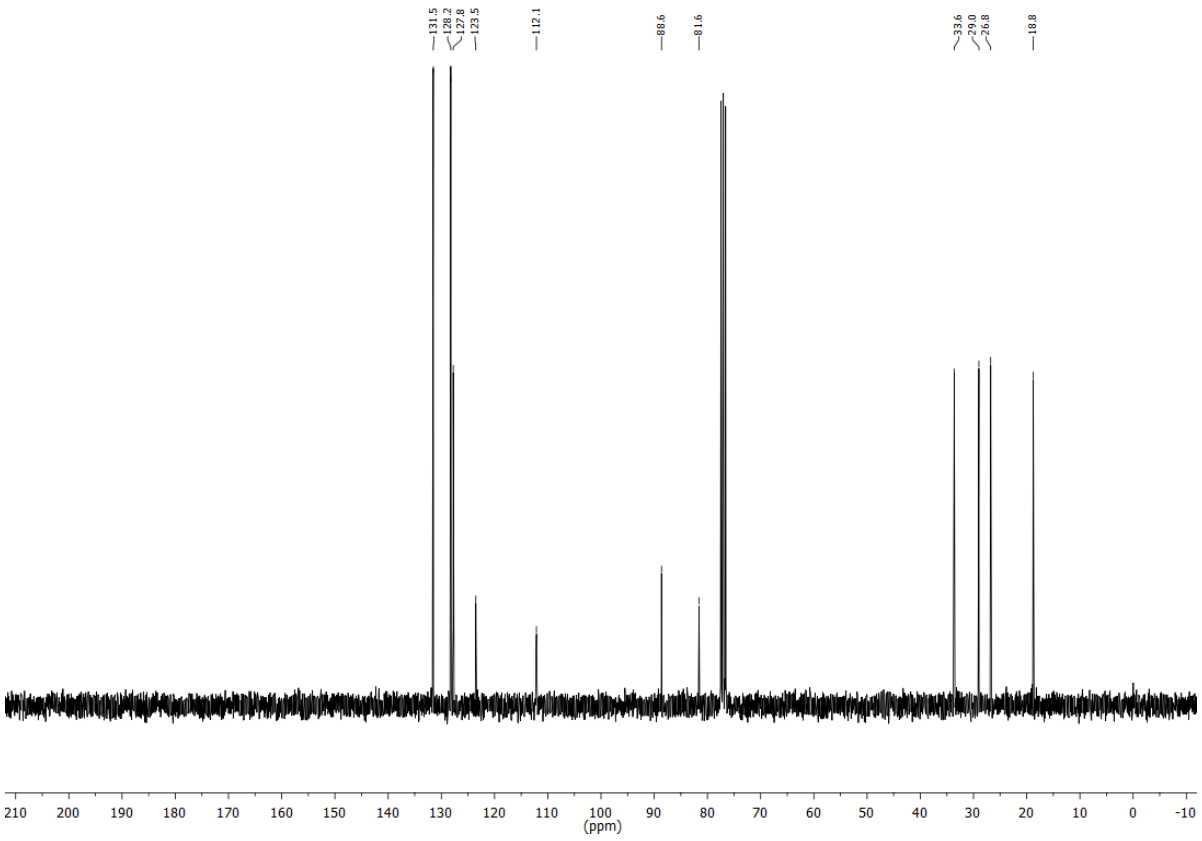
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 131.5, 128.2, 127.8, 123.5, 112.1, 88.6, 81.6, 33.6, 29.0, 26.8, 18.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3078, 3056, 2941, 2863, 2230, 2153, 1598, 1489, 1439.

$C_{13}H_{13}NS$ calcd.: 215.0769, found: 215.0771 (GC-HRMS).

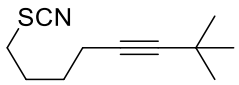


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

2,2-Dimethyl-8-thiocyanatooct-3-yne (3b)



8-Bromo-2,2-dimethyloct-3-yne (prepared via GP 4, used crude) was converted via the aforementioned general procedure (GP 6) to afford the title compound **3b** as a colorless oil (19 mg, 0.10 mmol, 10% over two steps).

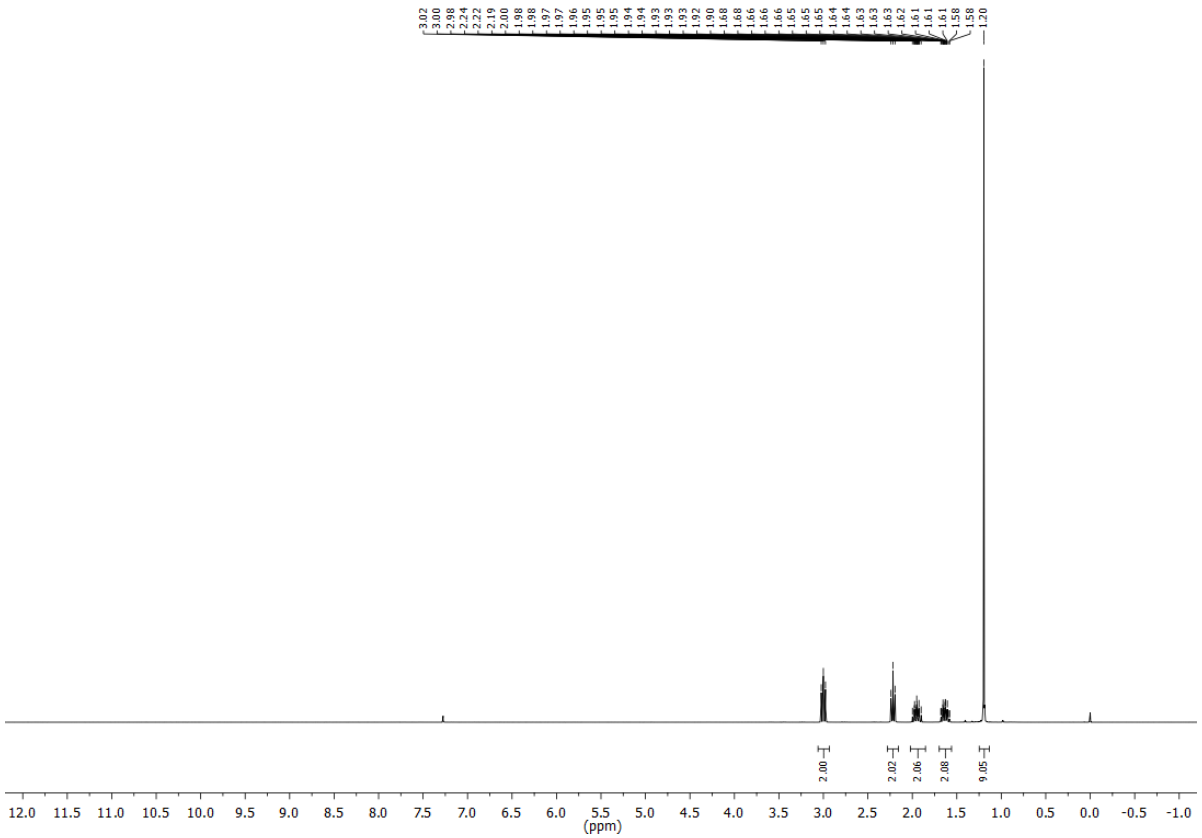
R_f = 0.31 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 9H), 1.57 – 1.69 (m, 2H), 1.89 – 2.01 (m, 2H), 2.22 (t, *J* = 6.8 Hz, 2H), 2.97 – 3.03 (m, 2H).

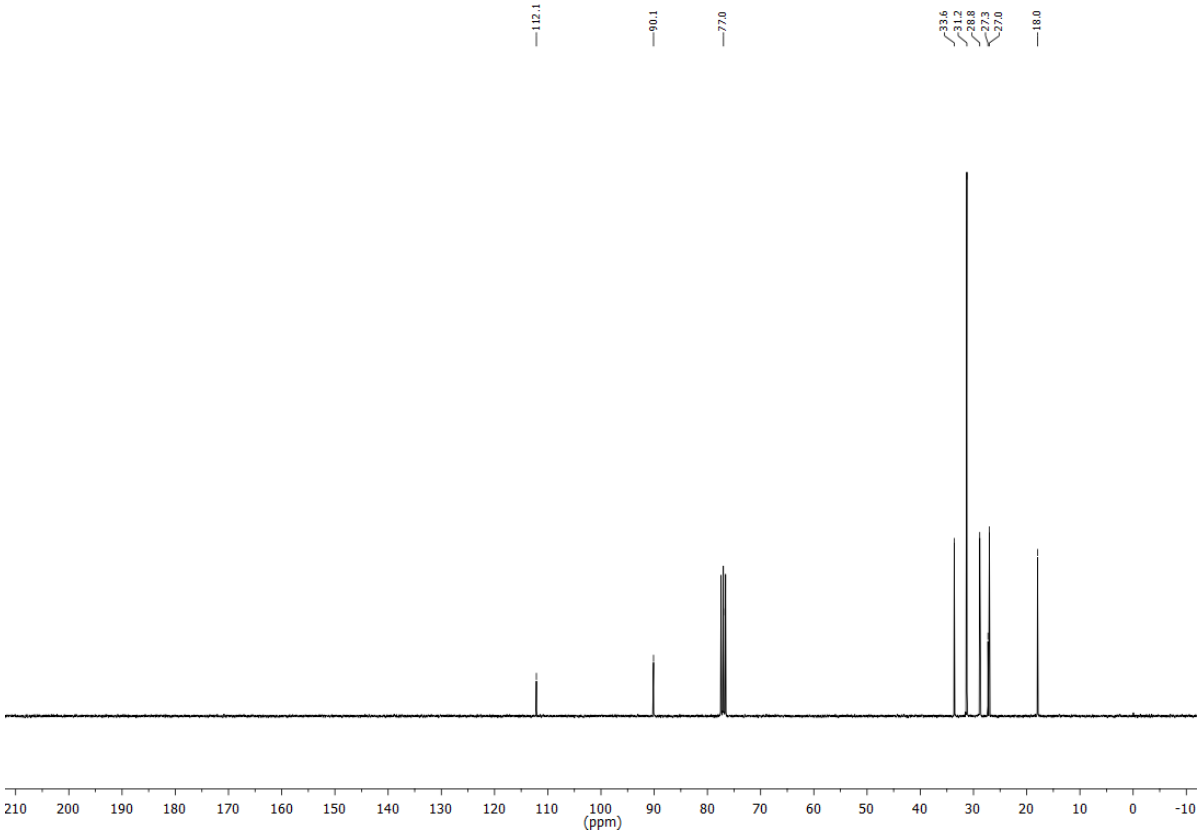
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 18.0, 27.0, 27.3, 28.8, 31.2, 33.6, 77.0, 90.1, 112.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2967, 2866, 2154, 1454, 1362, 1265, 1205, 1064.

$C_{11}H_{17}NS$ calcd.: 195.1082, found: 195.1062 (GC-HRMS).

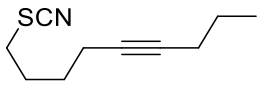


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

9-Thiocyanatonon-4-yne (3c)



9-Bromonon-4-yne (450 mg, 2.22 mmol, prepared via GP 4) was converted via the aforementioned general procedure (GP 6) to afford the title compound **3c** as a colorless oil (301 mg, 1.66 mmol, 75%).

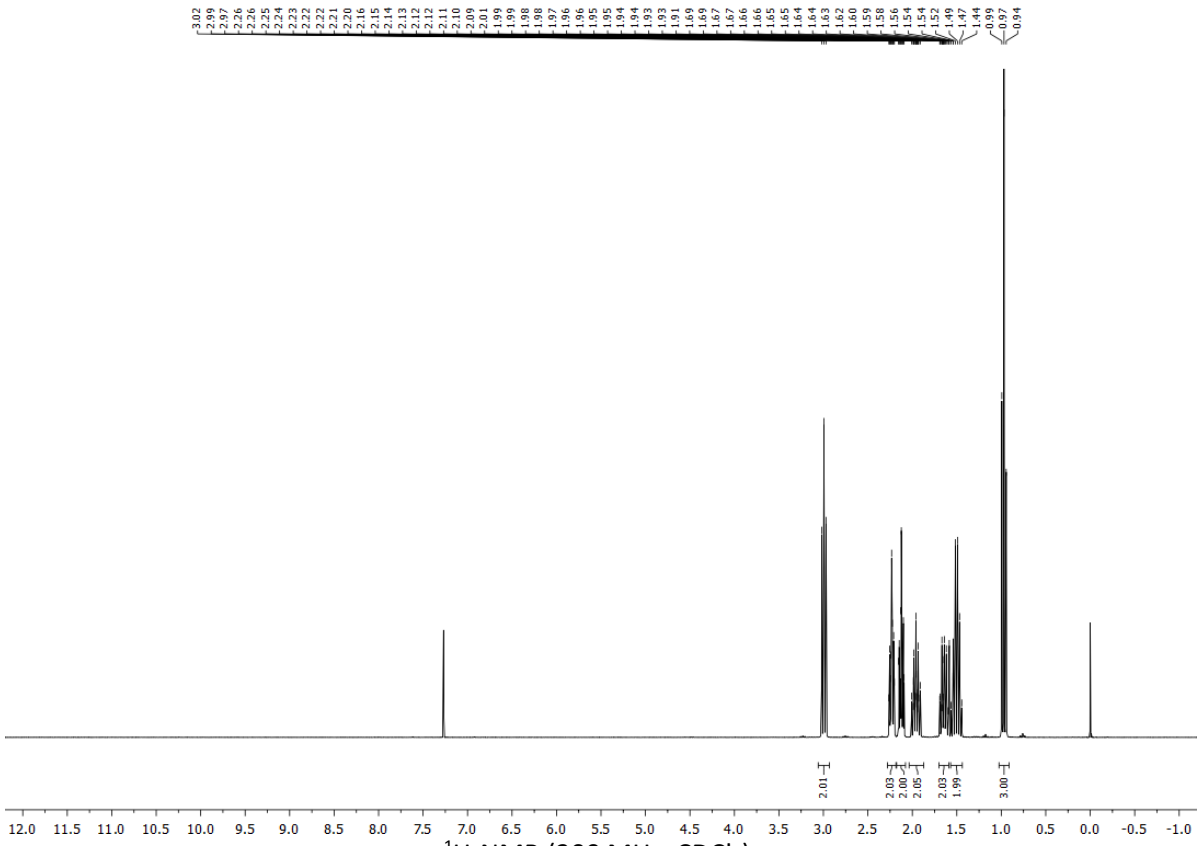
R_f = 0.62 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.99 (t, J = 7.3 Hz, 1H), 2.23 (tt, J = 6.8, 2.4 Hz, 1H), 2.12 (tt, J = 7.0, 2.3 Hz, 1H), 2.03-1.89 (m, 1H), 1.70-1.59 (m, 1H), 1.51 (s, J = 7.0 Hz, 1H), 0.97 (t, J = 7.4 Hz, 2H).

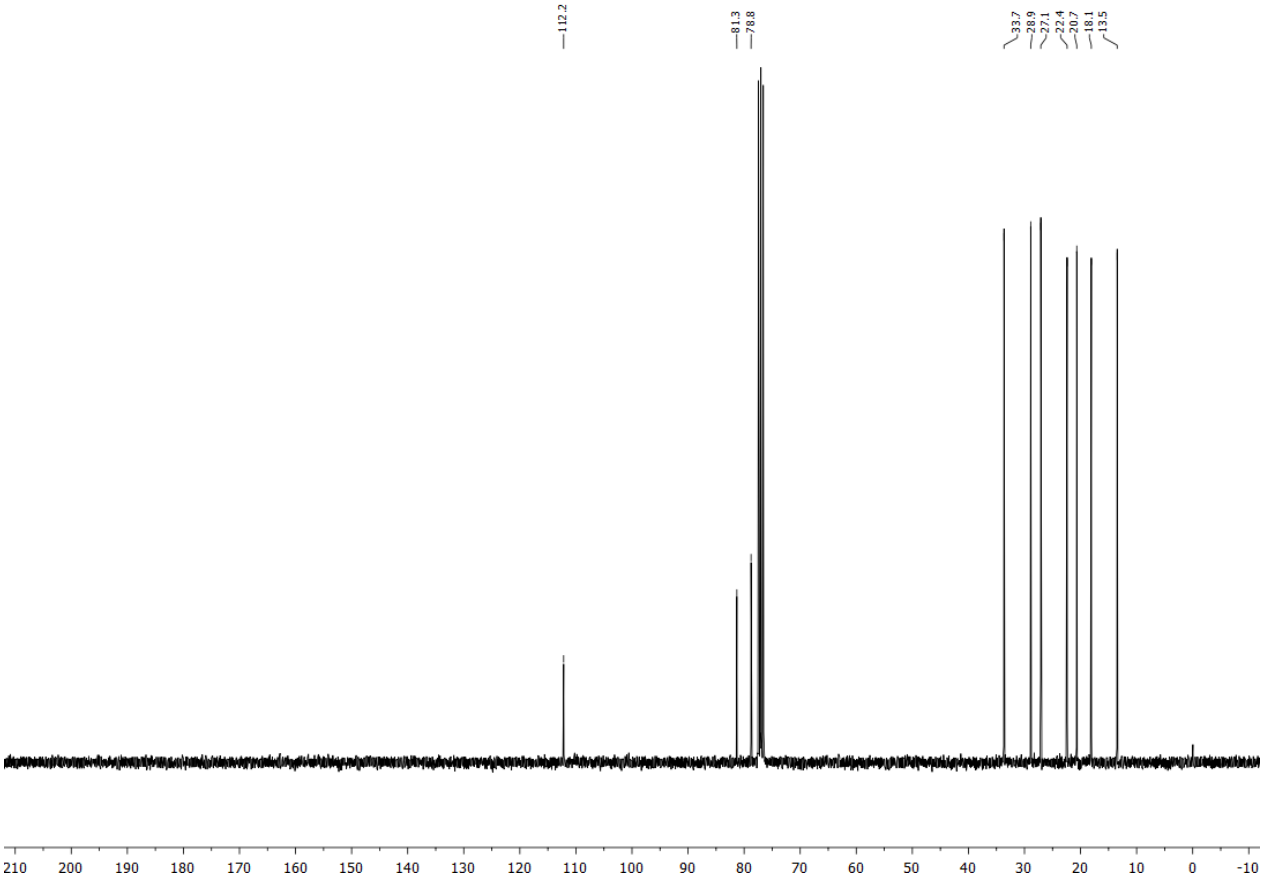
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 112.2, 81.3, 78.8, 33.7, 28.9, 27.1, 22.4, 20.7, 18.1, 13.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2960, 2934, 2869, 2154, 1455, 1435, 1335.

$C_{10}H_{15}NS$ calcd.: 181.0925, found: 181.0918 (GC-HRMS).

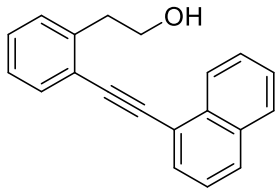


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

2-(2-(Naphthalen-1-ylethynyl)phenyl)ethan-1-ol (13d)



According to a reported procedure[34], to a solution of 2-(2-iodophenyl)ethan-1-ol (993 mg, 4.0 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (85 mg, 3 mol%) and CuI (38 mg, 5 mol%) in degassed triethylamine (20 ml) and degassed THF (30 mol) was added a solution of 1-ethynylnaphthalene (7321 mg, 4.8 mmol, 1.2 equiv.) in degassed THF (10 ml). Afterwards, propyne (10.0 ml, 10.0 mmol, 1.0 M in THF, 1.00 equiv.) was added via syringe. After stirring overnight, the reaction mixture was diluted with EtOAc (60 ml) and washed with brine (3 x 60 ml). The organic phase was washed with brine, dried over Na_2SO_4, filtrated and evaporated. Silica gel column chromatography (*n*-pentane:EtOAc = 10:1→4:1) gave the desired product **13d** (1.08 g, 3.97 mmol, quant.) as brownish solid.

m.p.: 68 °C.

R_f = 0.27 (*n*-pentane:EtOAc = 4:1).

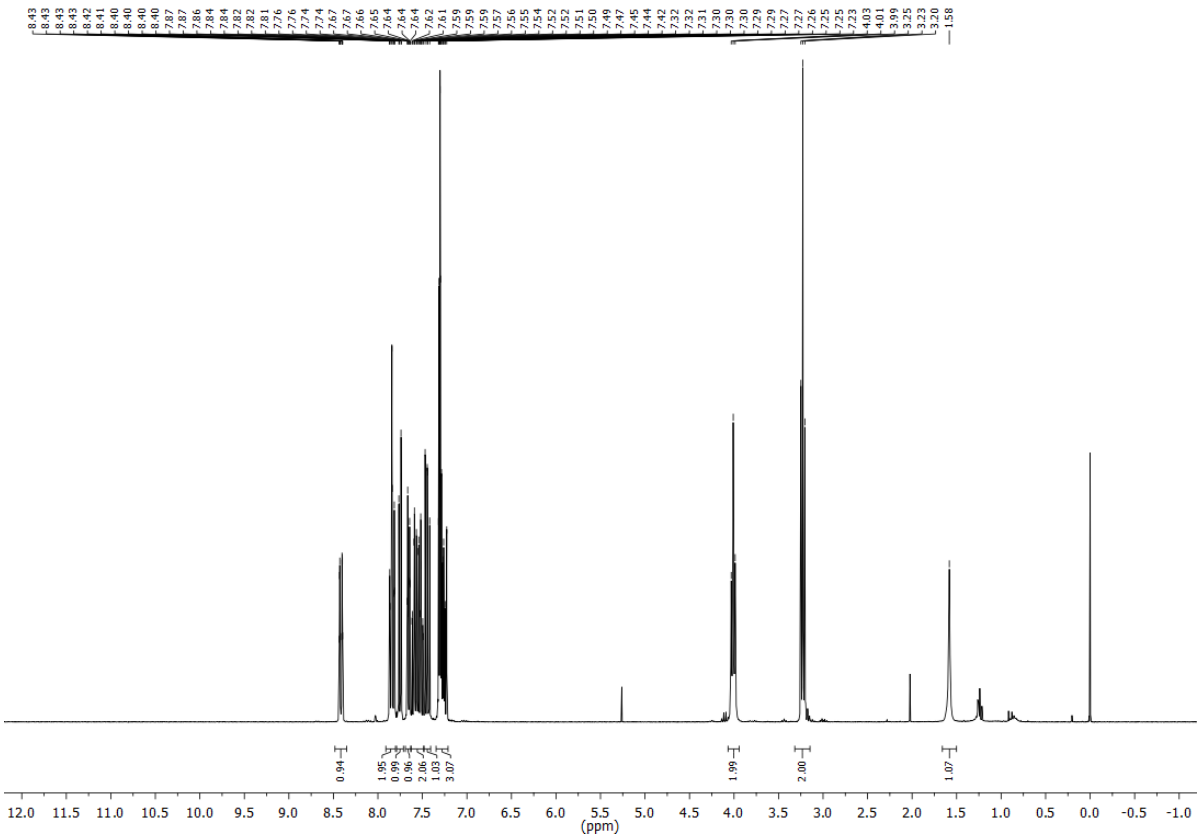
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.58 (s, 1H), 3.23 (t, *J*=6.7, 2H), 4.01 (t, *J*=6.7, 2H), 7.22 – 7.34 (m, 3H), 7.44 (dd, *J*=8.3, 7.1, 1H), 7.49 – 7.62 (m, 2H), 7.63 – 7.68 (m, 1H), 7.75 (dd, *J*=7.1, 1.2, 1H), 7.80 – 7.89 (m, 2H), 8.41 (ddt, *J*=8.3, 1.4, 0.8, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 38.2, 62.9, 91.4, 92.7, 120.9, 123.2, 125.3, 126.1, 126.4, 126.6, 126.9, 128.3, 128.6, 128.8, 129.8, 130.5, 132.6, 133.1, 133.2, 140.3.

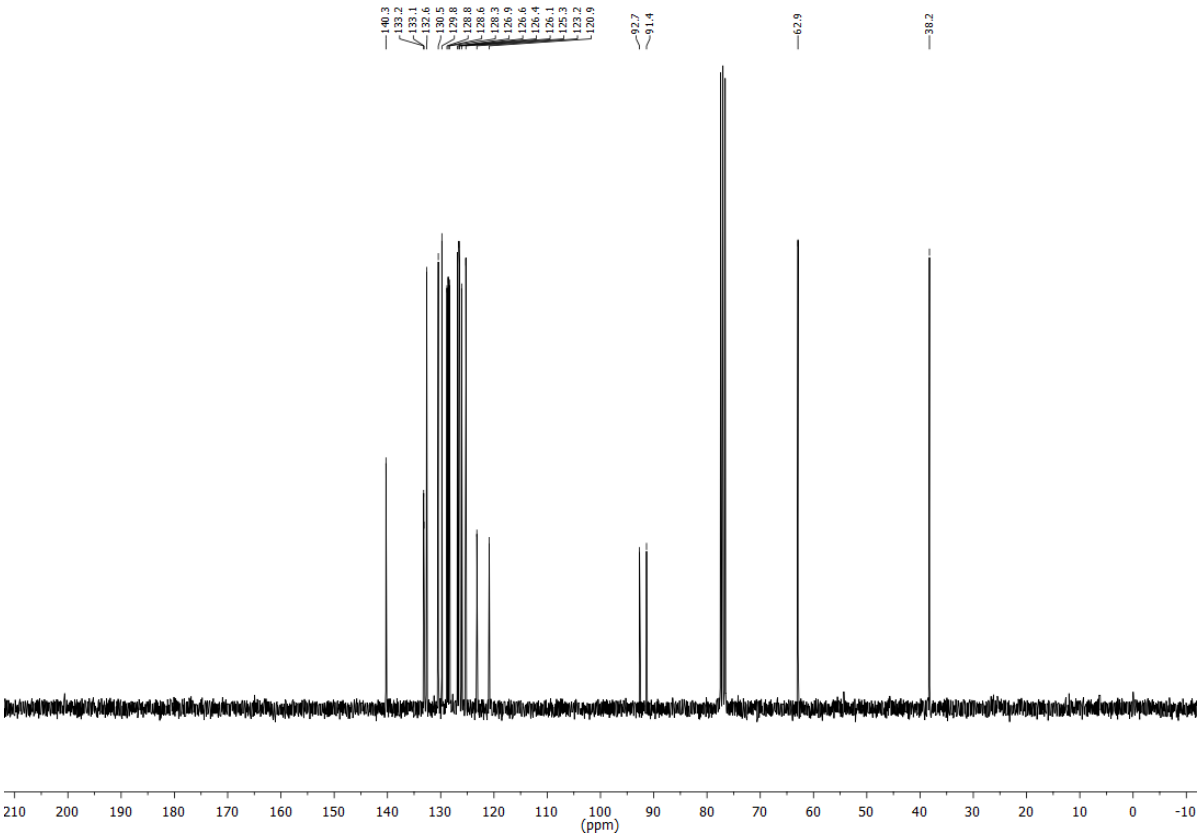
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3216, 3052, 2941, 2861, 1578, 1445, 1385, 1031.

$C_{20}H_{16}O$ calcd.: 272.1201, found: 272.1224 (GC-HRMS).

[34] X. He, Y. Li, M. Wang, H.-X. Chen, B. Chen, H. Liang, Y. Zhang, J. Pang and L. Qiu, *Org. Biomol. Chem.*, 2018, **16**, 5533.

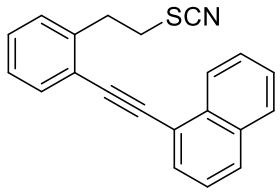


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-((2-(2-Thiocyanatoethyl)phenyl)ethynyl)naphthalene (3d)



Alcohol **13d** (415 mg, 1.52 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **3d** as a colorless oil (391.0 mg, 1.25 mmol, 82%).

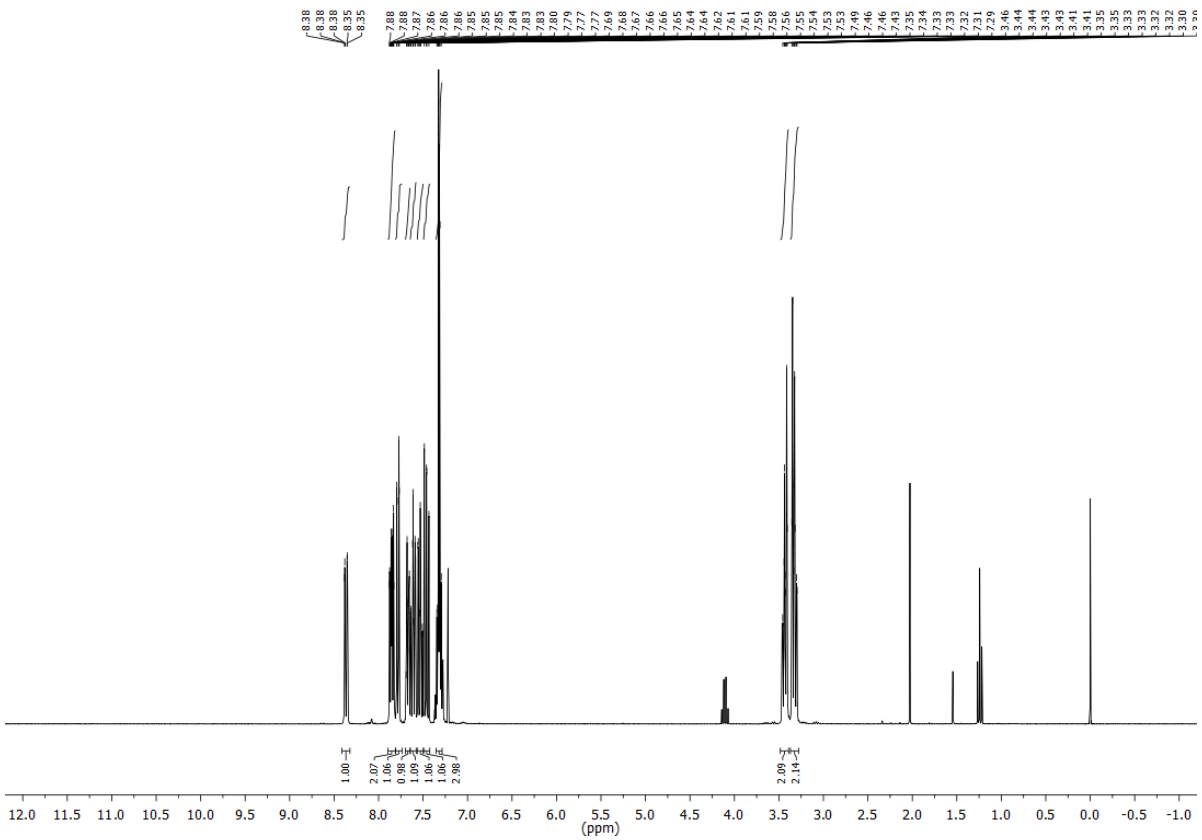
$\mathbf{R_f}$ = 0.19 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.28 – 3.37 (m, 2H), 3.39 – 3.50 (m, 2H), 7.29 – 7.35 (m, 3H), 7.46 (dd, *J*=8.3, 7.2, 1H), 7.53 (ddd, *J*=8.2, 6.8, 1.3, 1H), 7.61 (ddd, *J*=8.3, 6.8, 1.4, 1H), 7.65 – 7.70 (m, 1H), 7.78 (dd, *J*=7.2, 1.2, 1H), 7.82 – 7.91 (m, 2H), 8.32 – 8.41 (m, 1H).

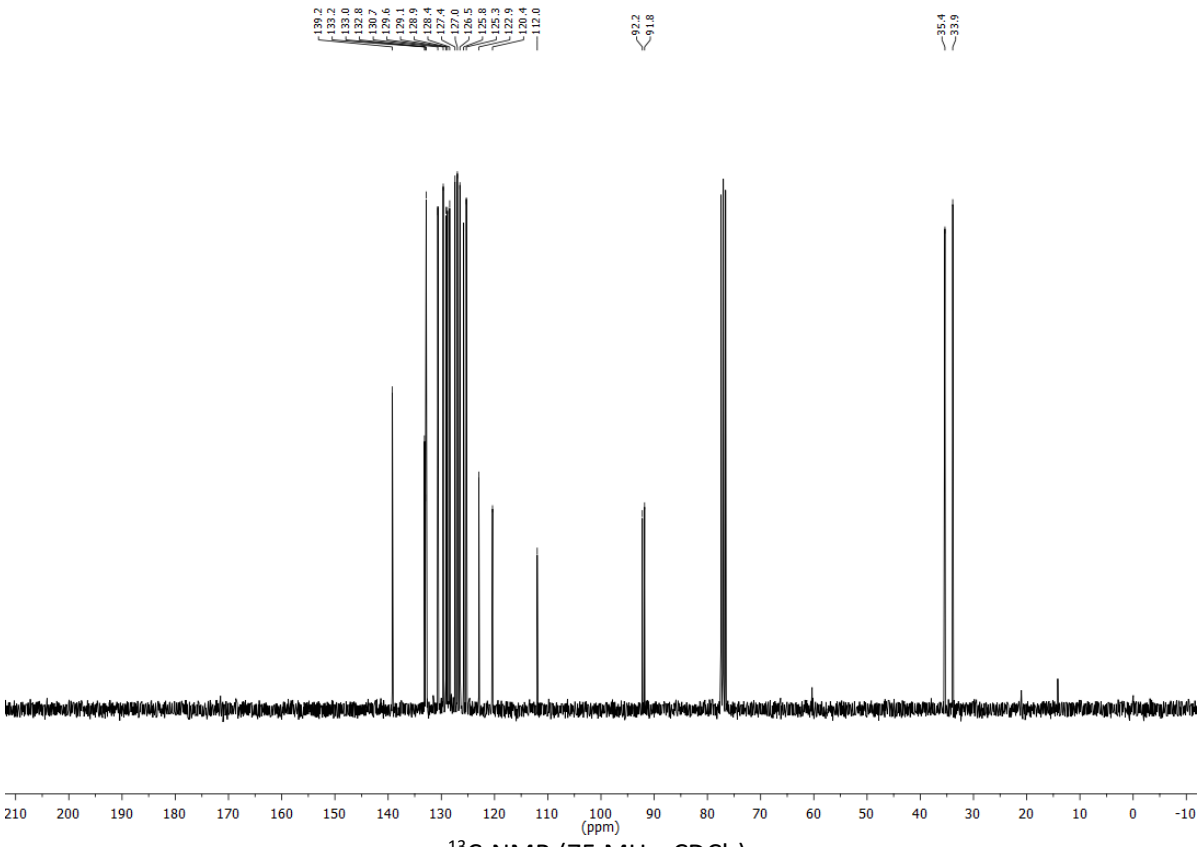
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 33.9, 35.4, 91.8, 92.2, 112.0, 120.4, 122.9, 125.3, 125.8, 126.5, 127.0, 127.4, 128.4, 128.9, 129.1, 129.6, 130.7, 132.8, 133.0, 133.2, 139.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2936, 2850, 2152, 1583, 1484, 1442, 1395.

$C_{21}H_{15}NS$ calcd.: 313.0925, found: 313.0917 (GC-HRMS).

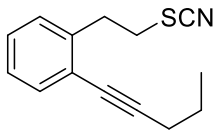


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Pent-1-yn-1-yl)-2-(2-thiocyanatoethyl)benzene (3e)



1-(2-Bromoethyl)-2-(pent-1-yn-1-yl)benzene (**13.1e**, 100 mg, 0.40 mmol) was converted via the aforementioned general procedure (GP 6) to afford the title compound **3e** as a colorless oil (89 mg, 0.39 mmol, 97%).

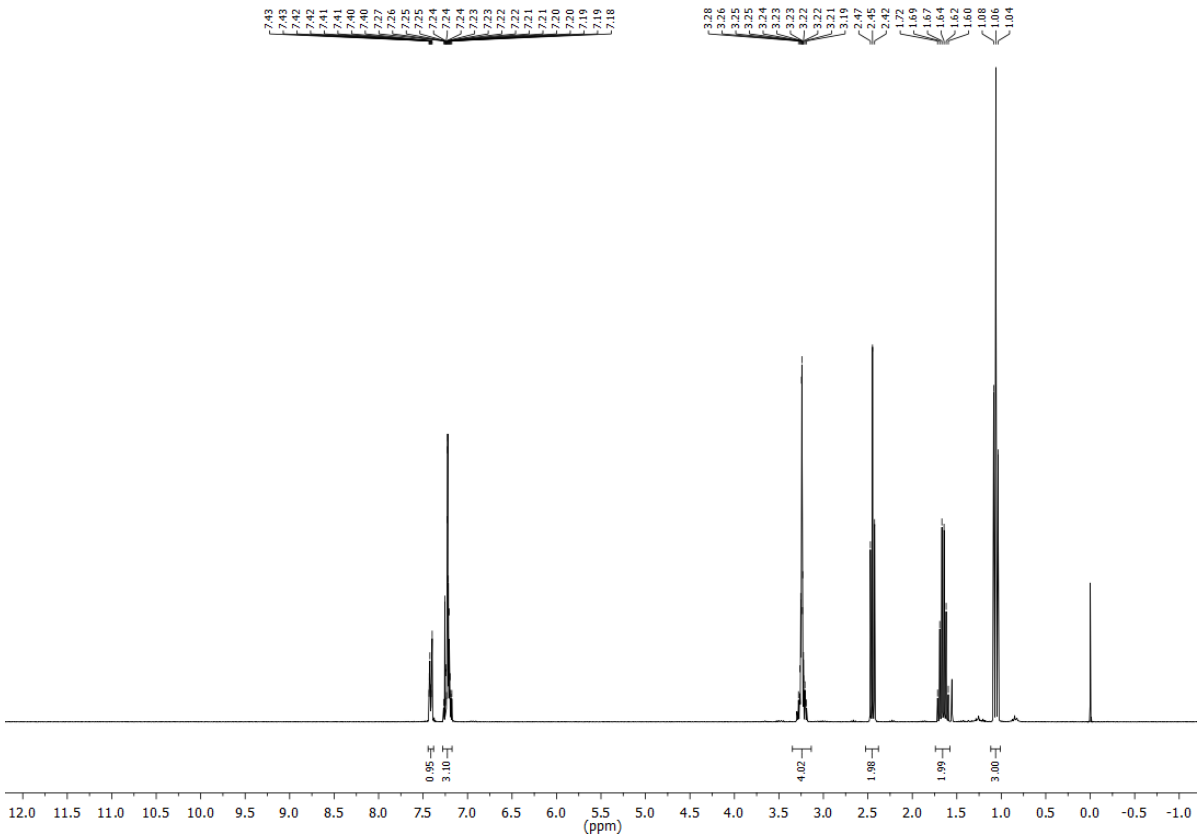
R_f = 0.62 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.44-7.39 (m, 1H), 7.30-7.14 (m, 3H), 3.31-3.18 (m, 4H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.66 (s, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H).

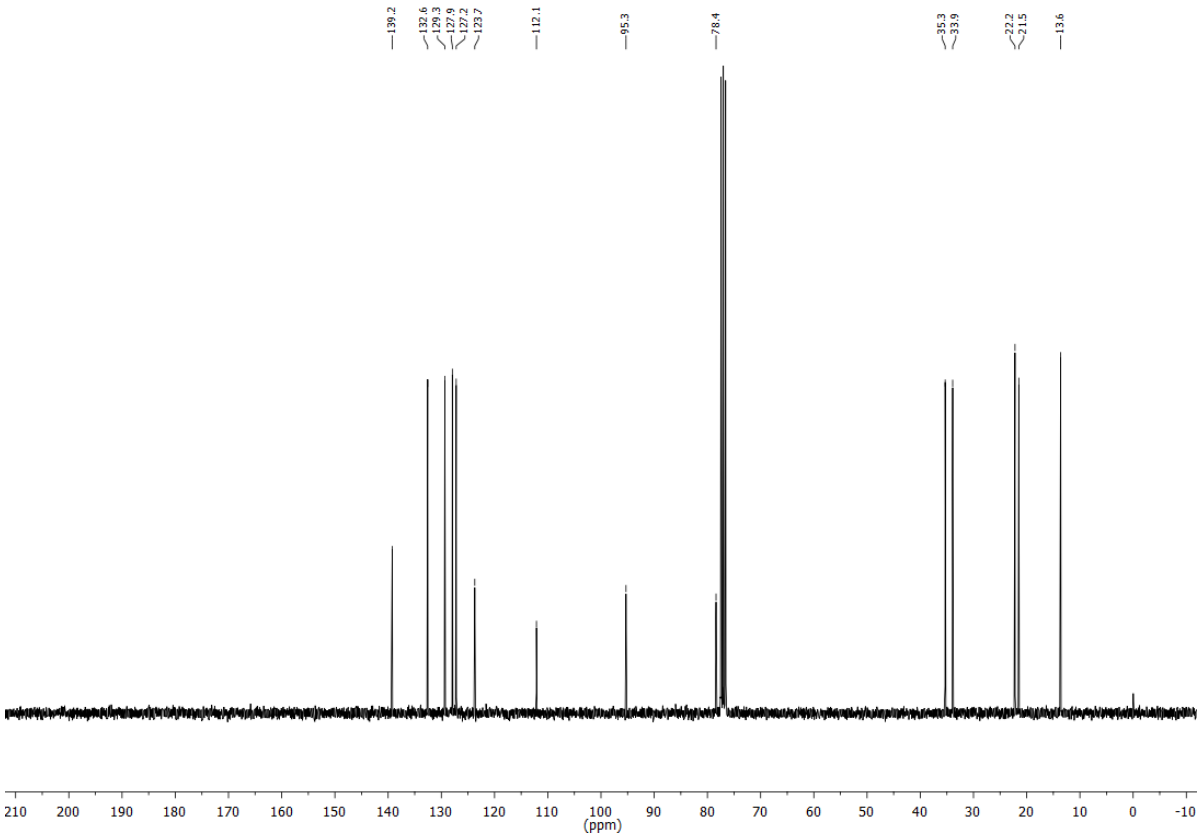
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 139.2, 132.6, 129.3, 127.9, 127.2, 123.7, 112.1, 95.3, 78.4, 35.3, 33.9, 22.2, 21.5, 13.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3065, 3023, 2963, 2933, 2871, 2232, 2154, 1484, 1447.

$C_{14}H_{15}NS$ calcd.: 229.0925, found: 229.0909 (GC-HRMS).

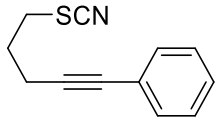


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(5-Thiocyanatopent-1-yn-1-yl)benzene (3f)



(5-Bromopent-1-yn-1-yl)benzene (prepared via GP 4, used crude) was converted via the aforementioned general procedure (GP 6) to afford the title compound **3f** as a pale yellow oil (1.44 g, 7.15 mmol, 40% over two steps).

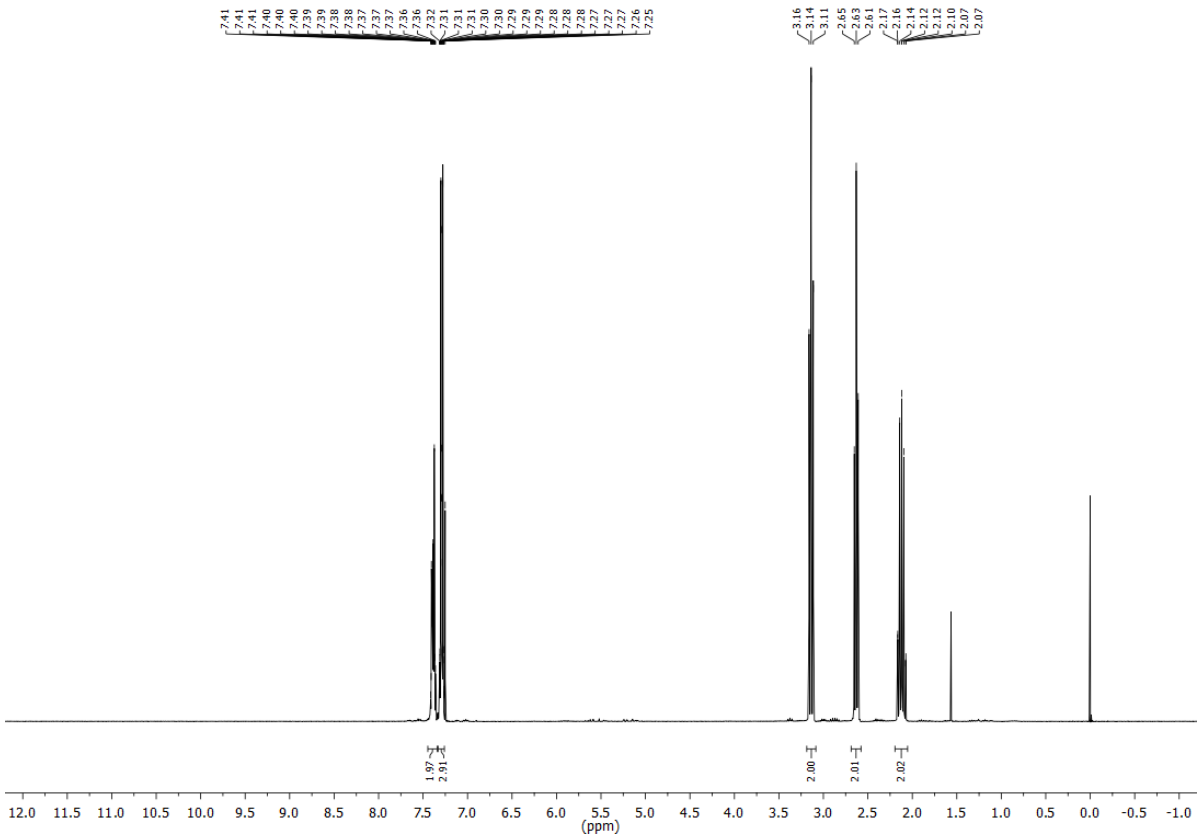
$\mathbf{R_f}$ = 0.48 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.04 – 2.16 (m, 2H), 2.61 (t, *J* = 6.6 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 7.26 – 7.32 (m, 3H), 7.36 – 7.42 (m, 2H).

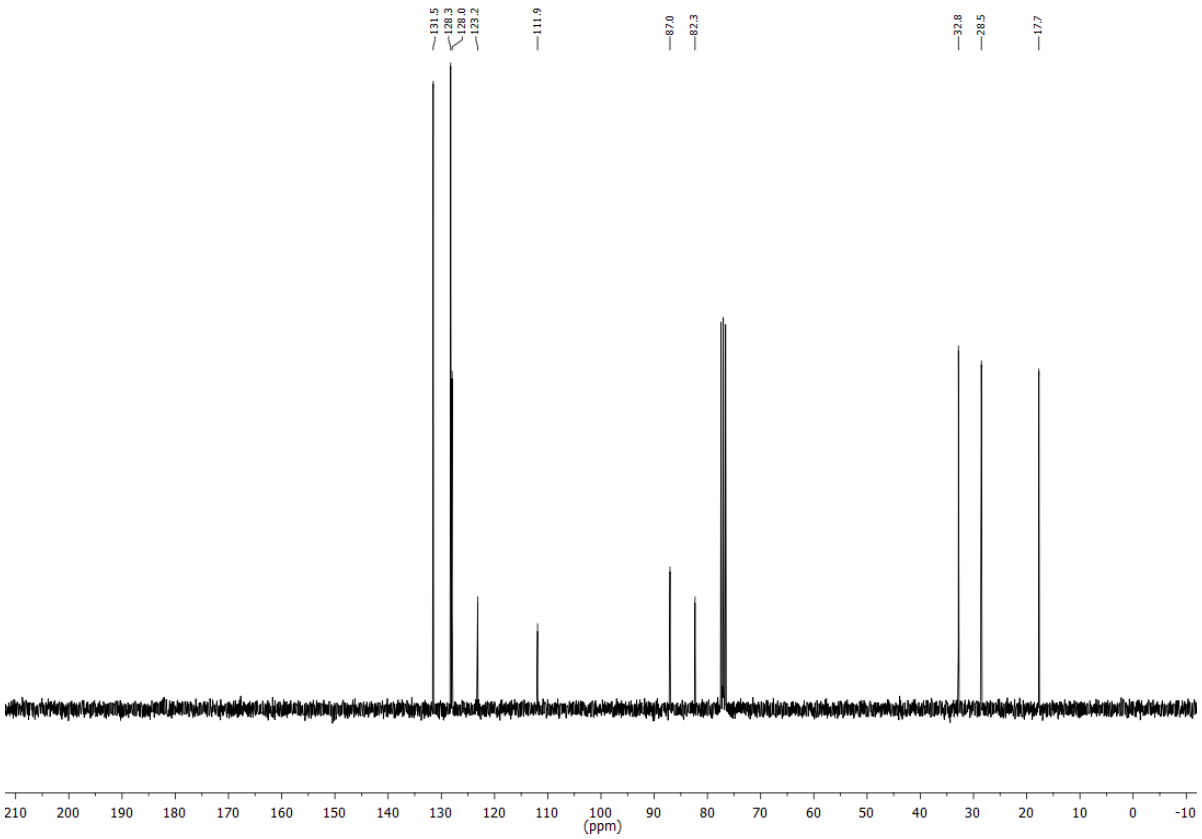
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.6, 28.4, 32.7, 82.2, 87.0, 111.9, 123.1, 127.9, 128.2, 131.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3078, 2939, 2838, 2153, 1598, 1489, 1439, 1332, 1283, 1069.

$C_{12}H_{11}NS$ calcd.: 201.0612, found: 201.0615 (GC-HRMS).

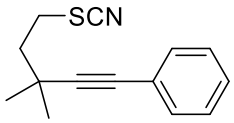


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(3,3-Dimethyl-5-thiocyanatopent-1-yn-1-yl)benzene (3f')



Compound **3f'** was synthesized from 3,3-dimethyl-5-phenylpent-4-yn-1-ol, which was obtained in a 4-step procedure[35]. Before reduction of the ester, the phenyl substituent was introduced by a Sonogashira reaction.

3,3-dimethyl-5-phenylpent-4-yn-1-ol (257 mg, 1.52 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **3f'** as a yellow oil (258 mg, 1.12 mmol, 74%).

R_f = 0.31 (*n*-pentane:EtOAc = 20:1).

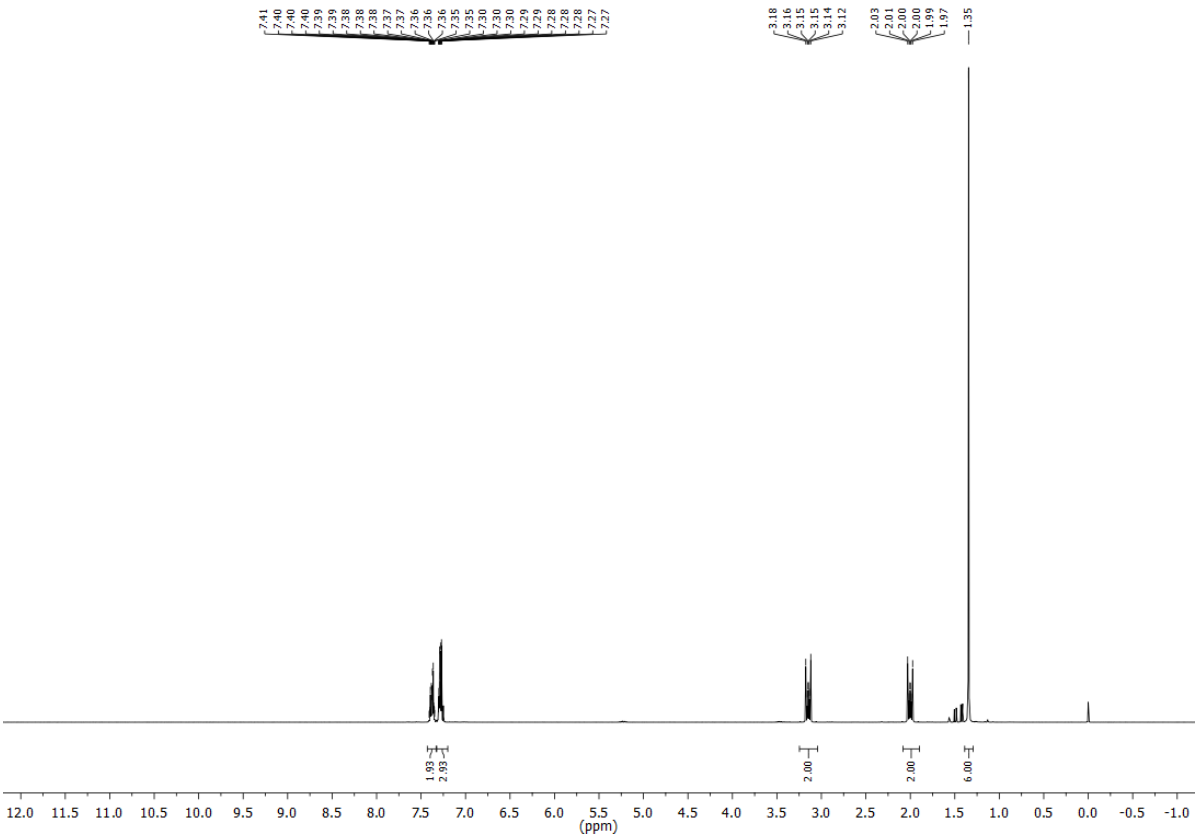
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 6H), 1.92 – 2.07 (m, 2H), 3.11 – 3.21 (m, 2H), 7.25 – 7.31 (m, 3H), 7.34 – 7.43 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 29.1 (2 C), 30.4, 31.8, 43.5, 82.0, 94.4, 112.2, 123.1, 127.9, 128.2 (2 C), 131.5 (2 C).

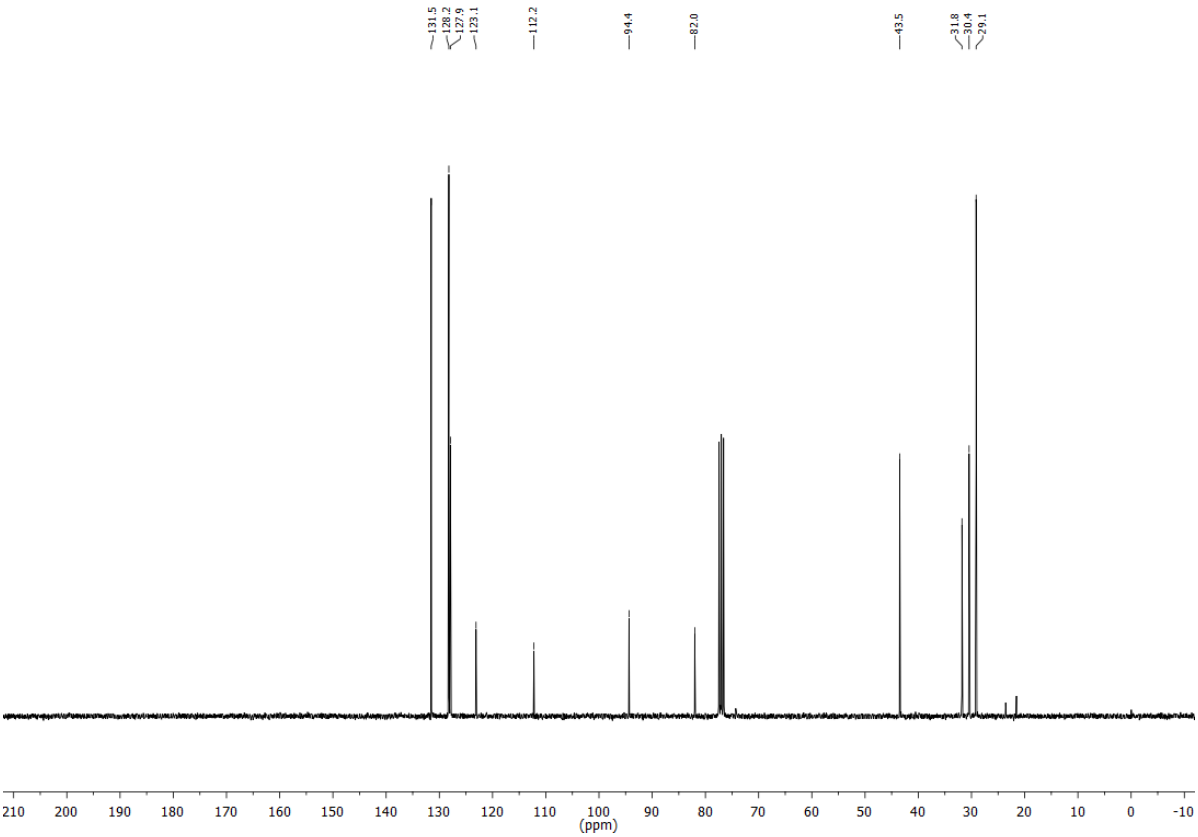
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2972, 2932, 2869, 2154, 1598, 1483, 1446, 1315, 1242, 1199.

$C_{14}H_{15}NS$ calcd.: 229.0925, found: 299.0938 (GC-HRMS).

[35] E. Rank and R. Brückner, *Eur. J. Org. Chem.*, 1998, **1998**, 1045.

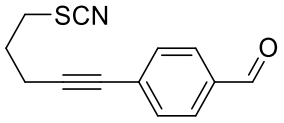


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

4-(5-Thiocyanatopent-1-yn-1-yl)benzaldehyde (3g)



4-(5-Hydroxypent-1-yn-1-yl)benzaldehyde[36] (377 mg, 2.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **3g** as a yellow solid (93 mg, 0.41 mmol, 20%).

m.p.: 41 °C.

$\mathbf{R_f}$ = 0.37 (*n*-pentane:EtOAc = 4:1).

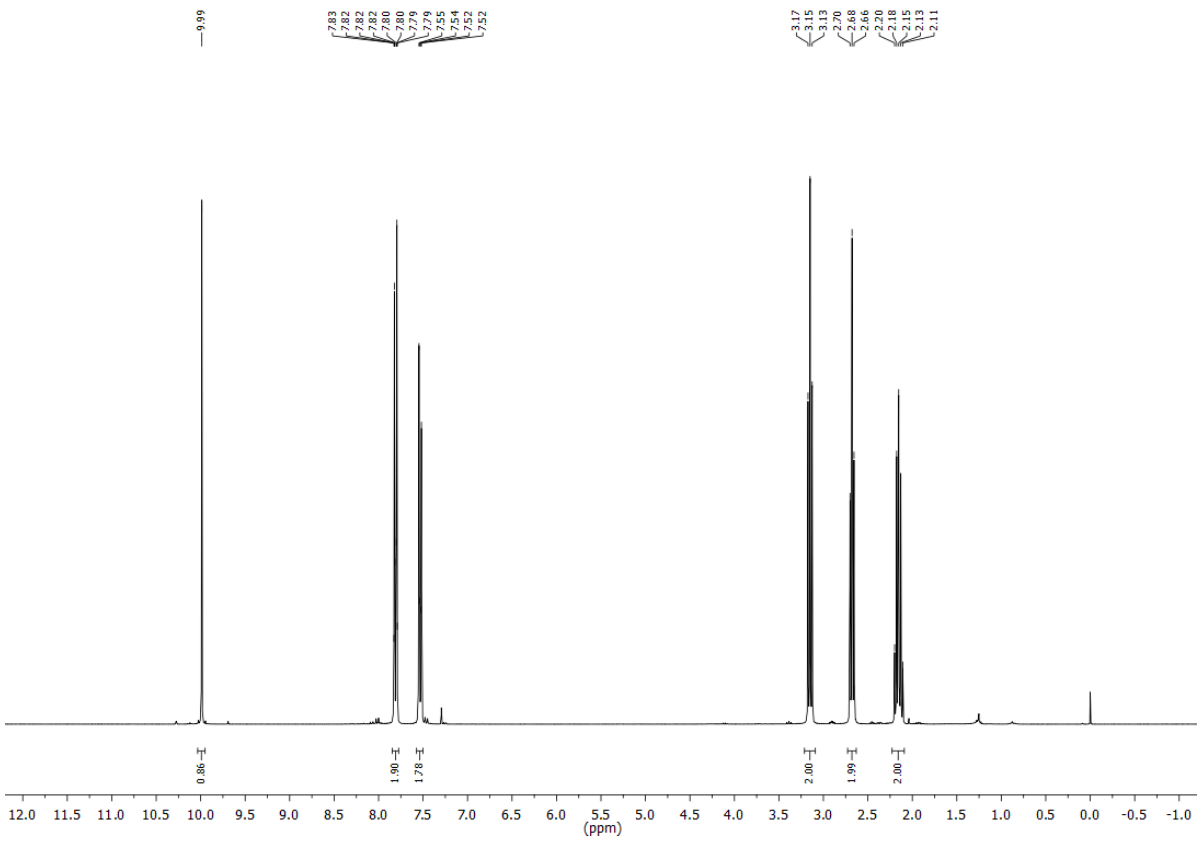
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.15 (p, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 6.7 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H), 7.51 – 7.56 (m, 2H), 7.78 – 7.83 (m, 2H), 9.99 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.7, 28.3, 32.7, 81.5, 91.6, 111.7, 129.4, 129.4, 132.0, 135.1, 191.3.

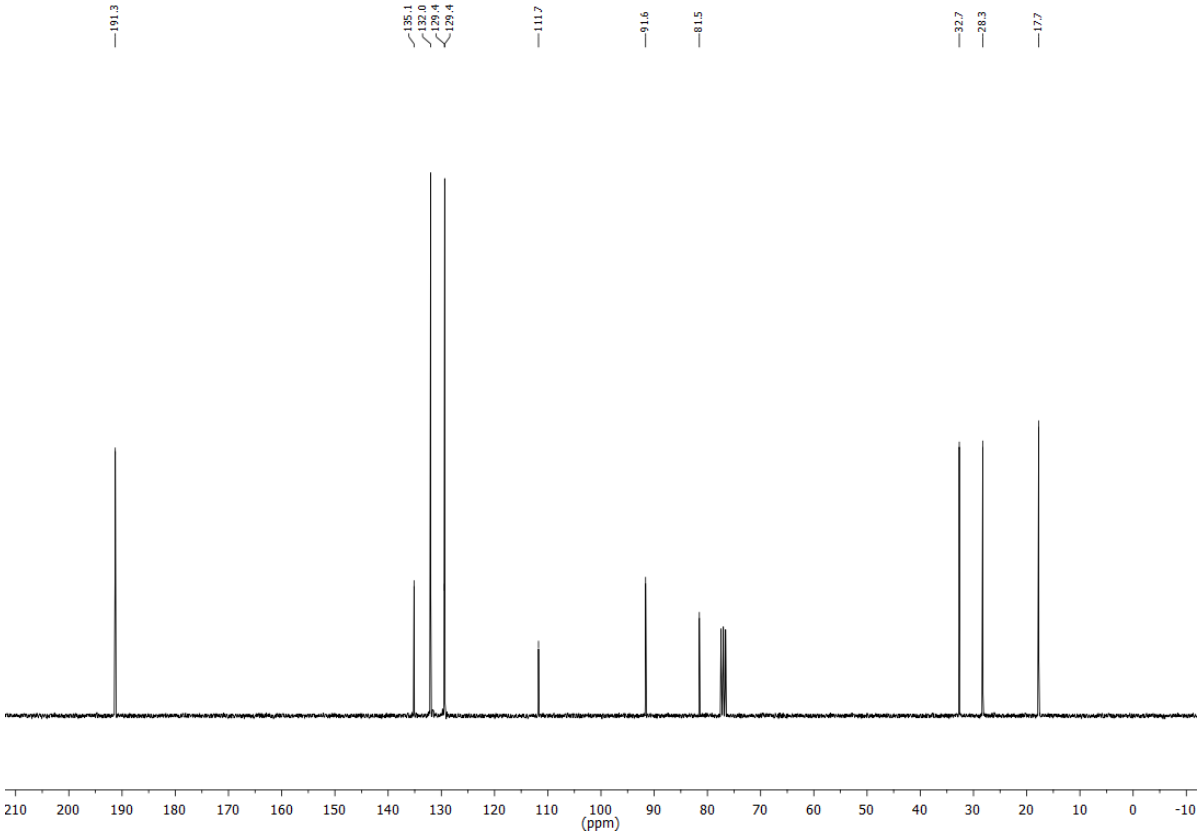
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3068, 2946, 2843, 2744, 2222, 2147, 1932, 1687, 1599, 1423, 1204, 1162.

$C_{13}H_{11}NOS$ calcd.: 229.0561, found: 229.0573 (GC-HRMS).

[36] B. H. Lipshutz, M. Hageman, J. C. Fennewald, R. Linstadt, E. Slack and K. Voigtritter, *Chem. Commun.*, 2014, **50**, 11378.

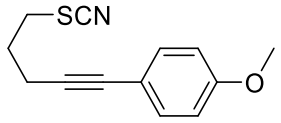


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-Methoxy-4-(5-thiocyanatopent-1-yn-1-yl)benzene (3h)



5-(4-Methoxyphenyl)pent-4-yn-1-ol[37] (190 mg, 1.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **3h** as a colorless oil (183 mg, 0.79 mmol, 79%).

R_f = 0.23 (*n*-pentane:EtOAc = 20:1).

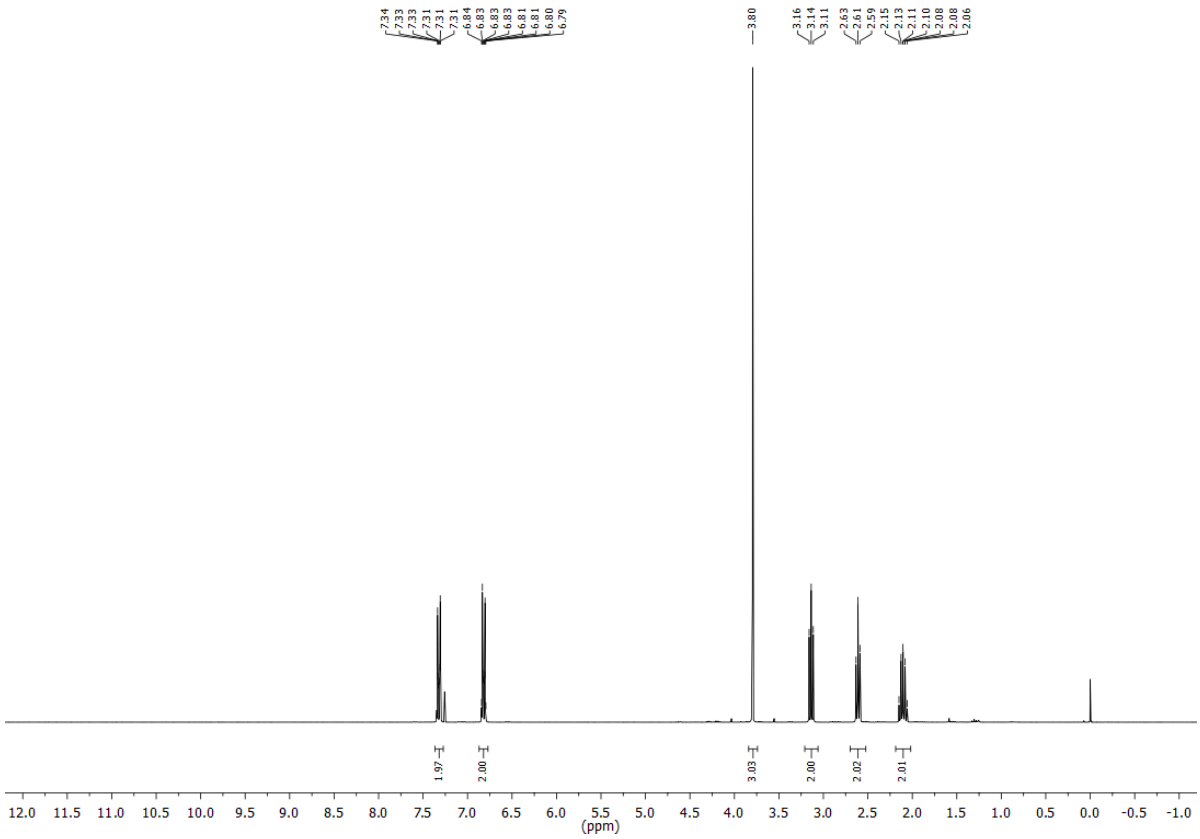
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.05 – 2.15 (m, 2H), 2.61 (t, *J* = 6.6 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 6.78 – 6.86 (m, 2H), 7.29 – 7.36 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.7, 28.6, 32.9, 55.2, 82.1, 85.4, 112.0, 113.9, 115.3, 132.9, 159.3.

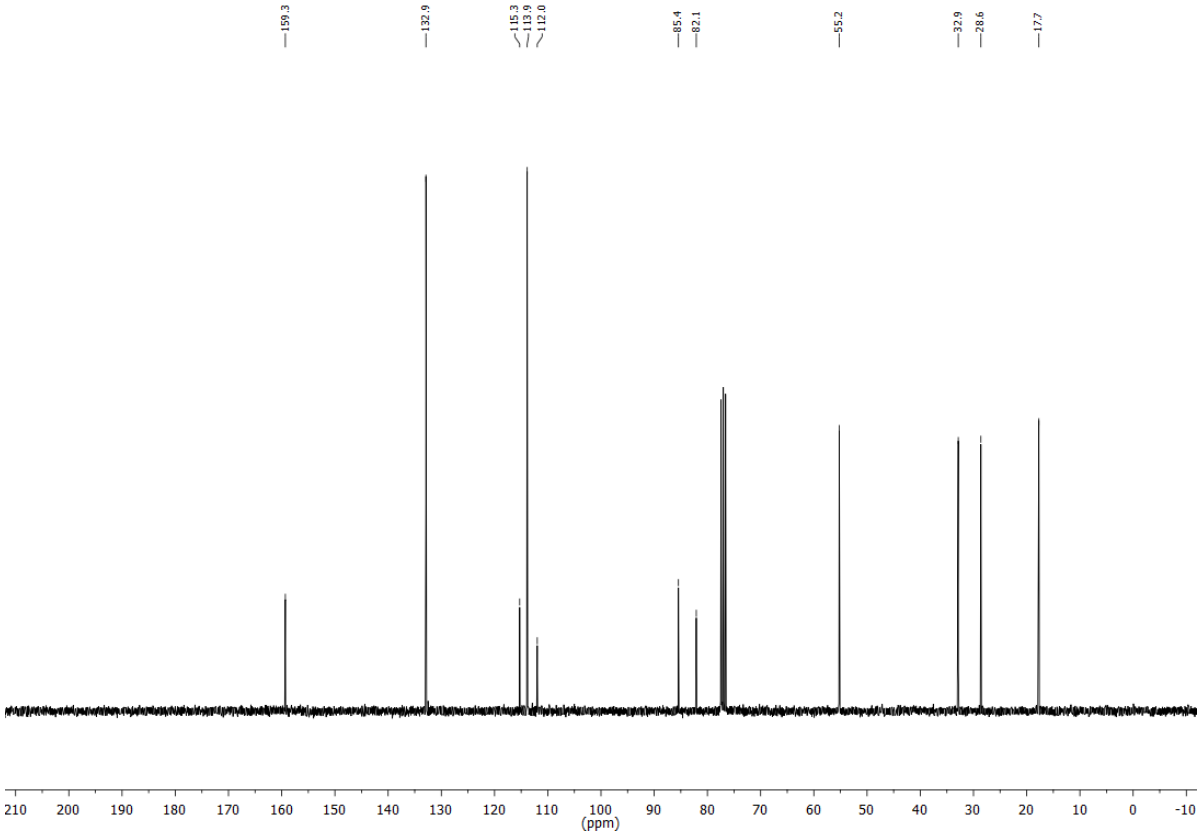
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3043, 3003, 2939, 2838, 2153, 1604, 1506, 1453, 1287, 1243, 1174, 1029.

$C_{13}H_{13}NOS$ calcd.: 231.0718, found: 231.0725 (GC-HRMS).

[37] D. M. Barber, H. J. Sanganee and D. J. Dixon, *Org. Lett.*, 2012, **14**, 5290.

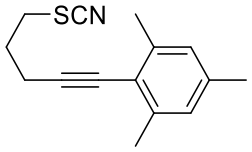


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1,3,5-Trimethyl-2-(5-thiocyanatopent-1-yn-1-yl)benzene (3i)



5-Mesitylpent-4-yn-1-ol[38] (405 mg, 2.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **3i** as a colorless oil (332 mg, 1.36 mmol, 68%).

R_f = 0.51 (*n*-pentane:EtOAc = 20:1).

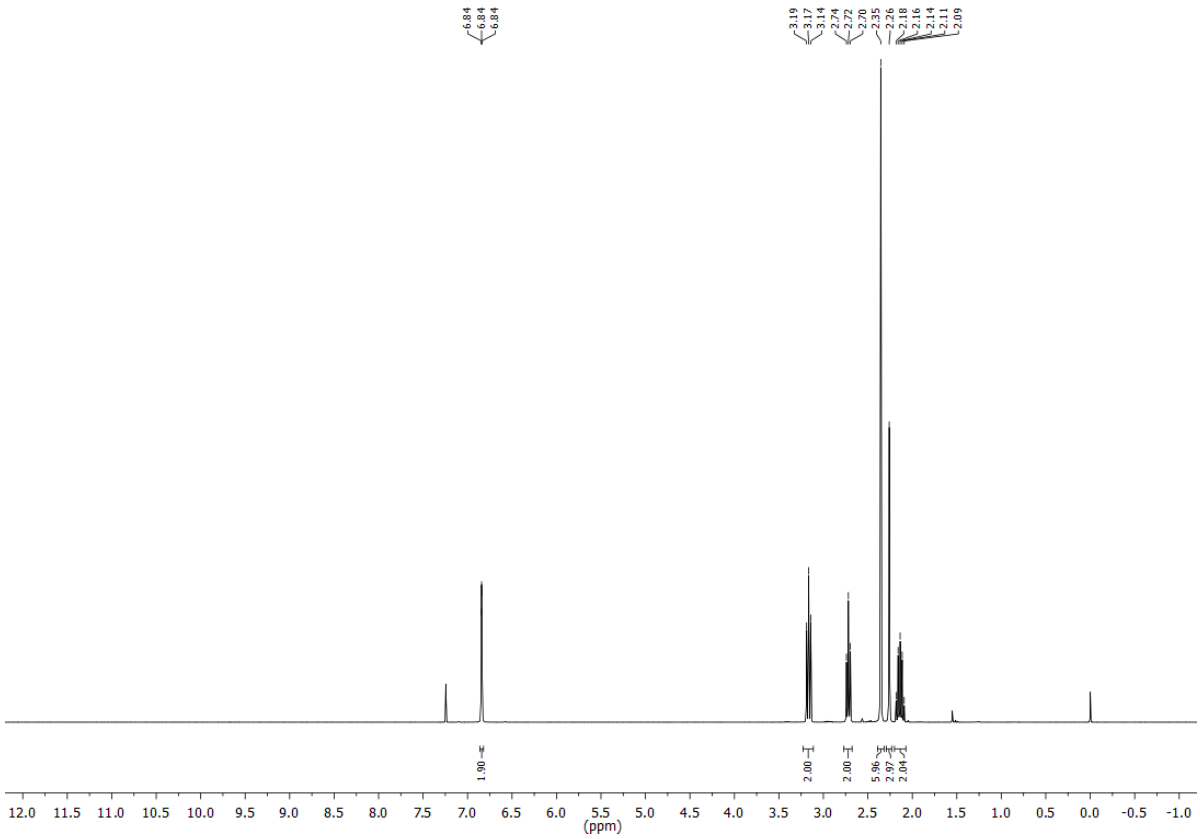
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.14 (p, *J* = 6.8 Hz, 2H), 2.26 (s, 3H), 2.35 (s, 6H), 2.72 (t, *J* = 6.6 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 6.83 – 6.85 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 18.0, 21.0, 21.2, 28.8, 32.9, 80.0, 94.5, 111.9, 119.9, 127.5, 137.3, 139.9.

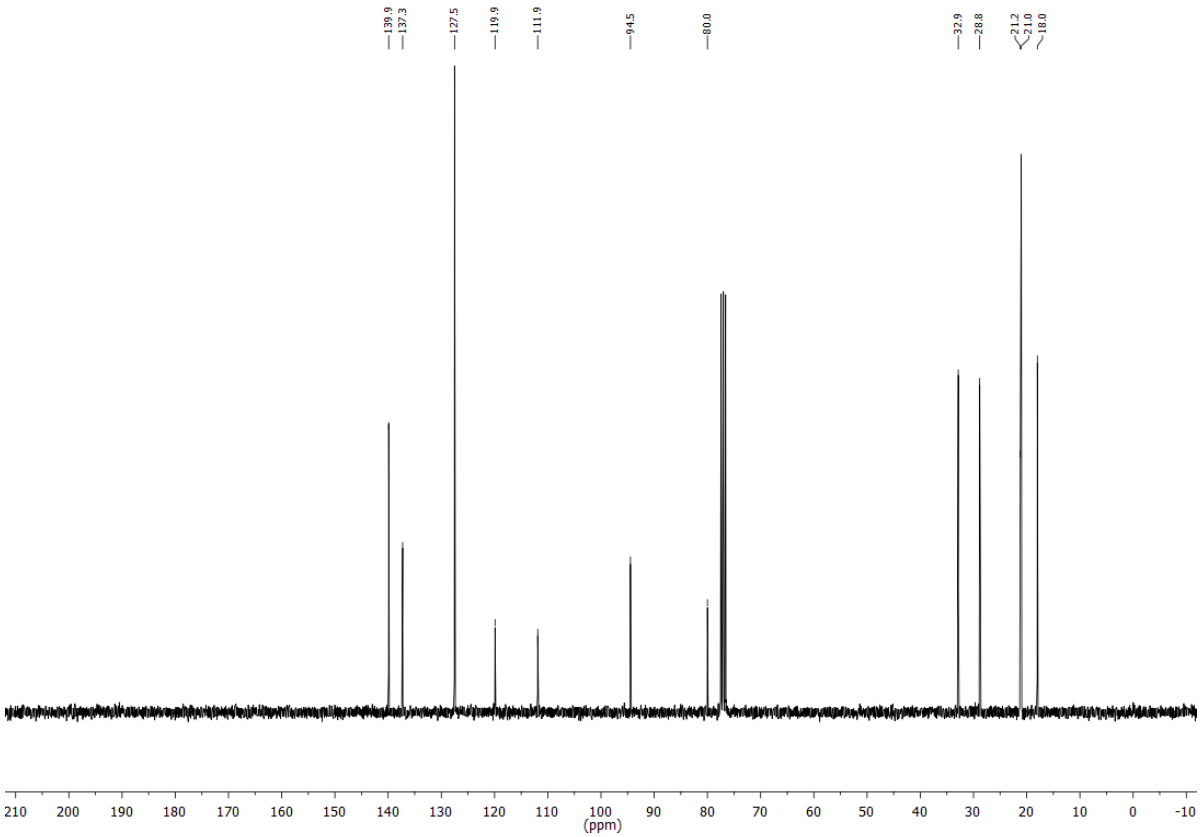
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2917, 2854, 2154, 1609, 1475, 1435, 1341, 1283, 1031.

$C_{15}H_{17}NS$ calcd.: 243.1082, found: 243.1100 (GC-HRMS).

[38] P. Wessig, G. Müller, R. Herre and A. Kühn, *Helv. Chim. Acta*, 2006, **89**, 2694.

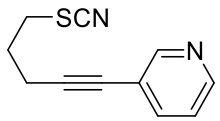


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

3-(5-Thiocyanatopent-1-yn-1-yl)pyridine (3j)



5-(Pyridin-3-yl)pent-4-yn-1-ol[39] (322 mg, 2.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **3j** as a yellow oil (247 mg, 1.22 mmol, 61%).

R_f = 0.09 (*n*-pentane:EtOAc = 4:1).

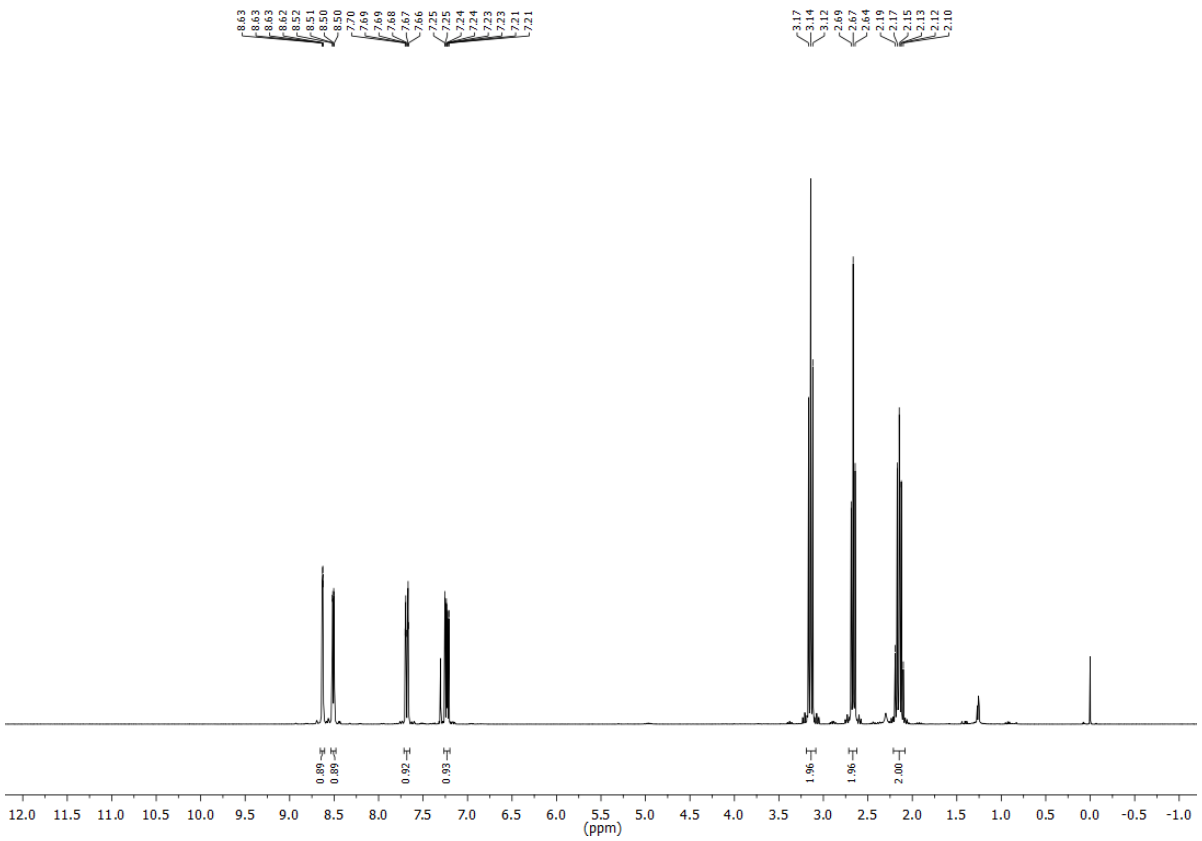
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.15 (p, *J* = 6.8 Hz, 2H), 2.67 (t, *J* = 6.7 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 7.23 (ddd, *J* = 7.8, 4.9, 0.9 Hz, 1H), 7.68 (dt, *J* = 7.9, 1.9 Hz, 1H), 8.51 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.63 (dd, *J* = 2.2, 0.9 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.6, 28.3, 32.7, 78.9, 90.7, 111.7, 120.2, 122.8, 138.4, 148.2, 152.1.

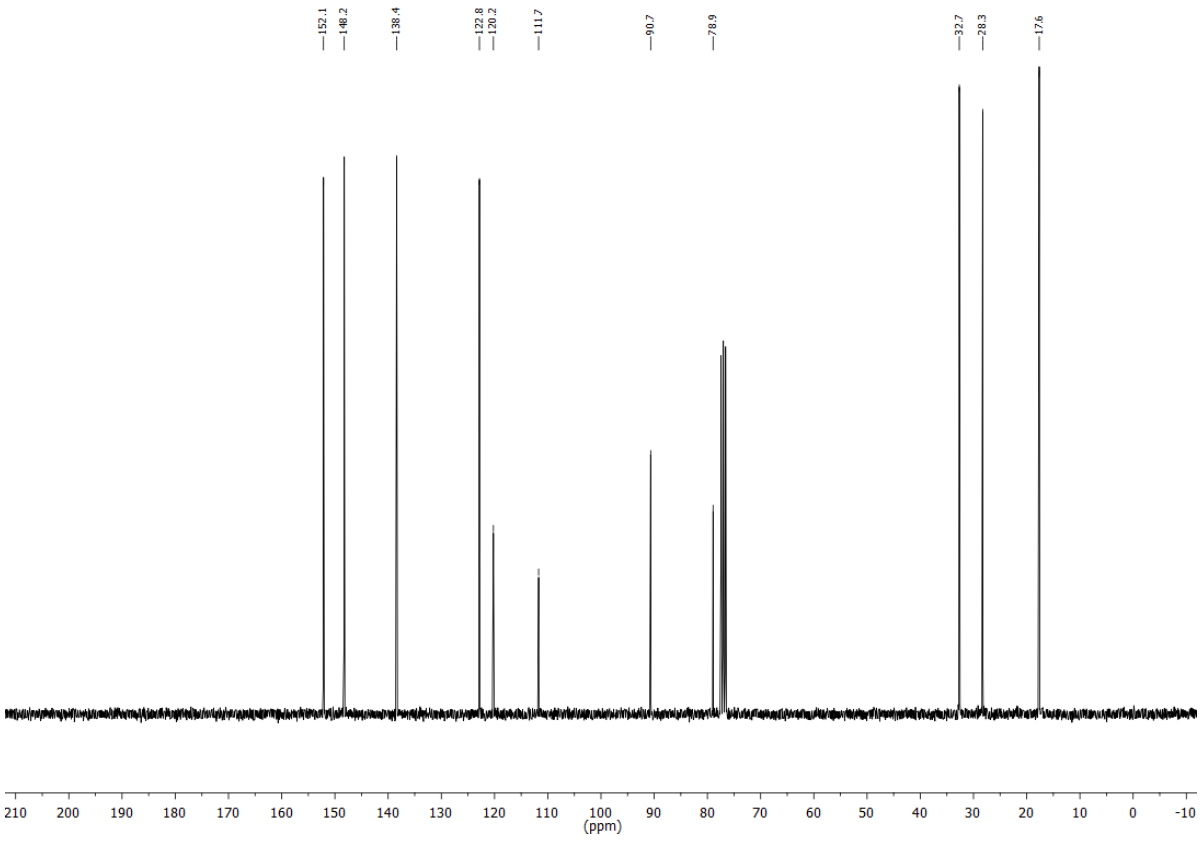
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3034, 2939, 2843, 2231, 2153, 1560, 1475, 1408, 1262, 1020.

$C_{13}H_{10}N_2S$ calcd.: 202.0565, found: 202.0579 (GC-HRMS).

[39] D. M. Barber, H. J. Sanganee and D. J. Dixon, *Org. Lett.*, 2012, **14**, 5290.

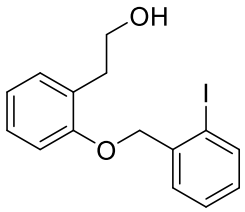


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

2-(2-((2-Iodobenzyl)oxy)phenyl)ethan-1-ol (13.1k)



According to a reported procedure[40], to a mixture of 2-(2-hydroxyethyl)phenol (2.24 g, 16.2 mmol, 1.0 equiv.) and K_2CO_3 (3.36 g, 24.3 mmol, 1.5 equiv.) in acetone (162 ml) was added 1-(bromomethyl)-2-iodobenzene (4.81 g, 16.2 mmol, 1.0 equiv.). The reaction mixture was refluxed for 4 h. After cooling, it was diluted with H_2O, extracted with EtOAc (3 x 100 ml), washed with brine and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the product was purified by flash column chromatography (*n*-pentane:EtOAc = 20:1 → 10:1) to afford a colorless solid (4.73 g, 13.4 mmol, 82%).

m.p.: 98 °C.

R_f = 0.25 (*n*-pentane:EtOAc = 4:1).

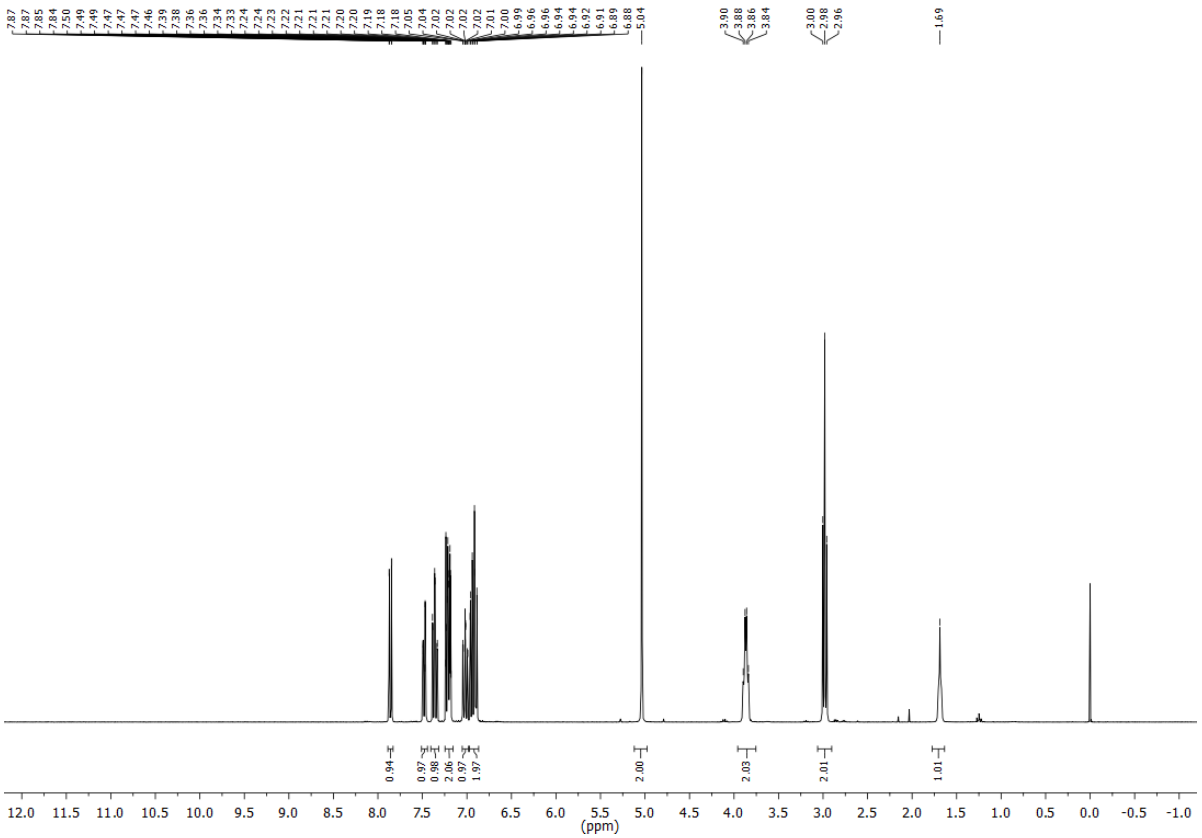
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.69 (s, 1H), 2.98 (t, *J*=6.5, 2H), 3.87 (q, *J*=6.1, 2H), 5.04 (s, 2H), 6.88 – 6.98 (m, 2H), 6.99 – 7.06 (m, 1H), 7.16 – 7.25 (m, 2H), 7.36 (td, *J*=7.5, 1.3, 1H), 7.45 – 7.51 (m, 1H), 7.86 (dd, *J*=7.9, 1.2, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 34.1, 62.7, 74.0, 97.2, 111.8, 121.1, 127.2, 127.8, 128.4, 128.4, 129.5, 131.0, 139.1, 139.3, 156.4.

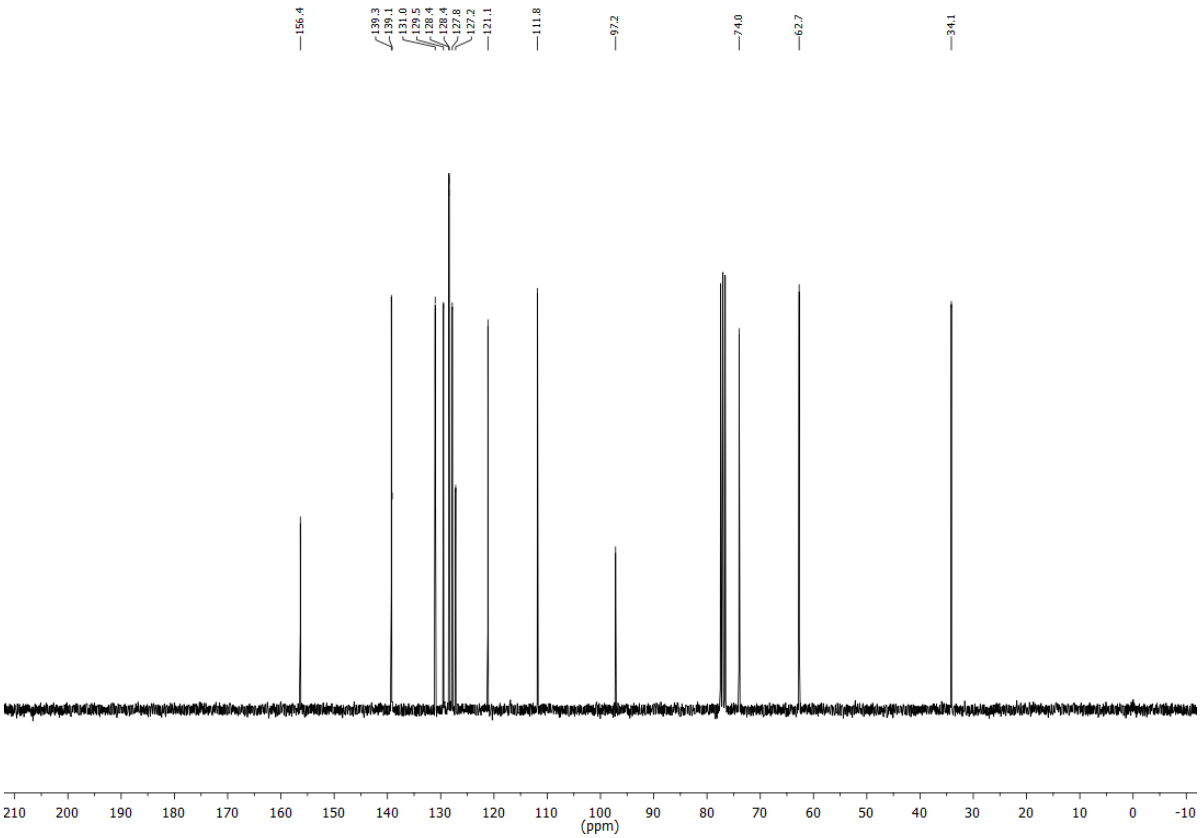
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3304, 3066, 2928, 2861, 1593, 1489, 1440, 1374, 1240, 1044, 1012.

$C_{15}H_{15}IO_2$ calcd.: 354.0117, found: 354.0100 (GC-HRMS).

[40] J. Lee, J.-H. Lee, S. Y. Kim, N. A. Perry, N. E. Lewin, J. A. Ayres and P. M. Blumberg, *Bioorg. Med. Chem.*, 2006, **14**, 2022.

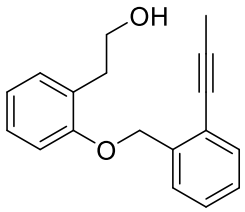


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

2-(2-((2-(Prop-1-yn-1-yl)benzyl)oxy)phenyl)ethan-1-ol (13.2k)



Similar to the synthesis of **11s**, compound **13.1k** (3.54 g, 10.0 mmol, 1.00 equiv.), $PdCl_2(PPh_3)_2$ (142 mg, 2 mol%) and CuI (78 mg, 4 mol%) were dissolved in triethylamine (30 ml). Afterwards, propyne (10.0 ml, 10.0 mmol, 1.0 M in THF, 1.00 equiv.) was added via syringe. After stirring overnight, saturated NH_4Cl solution was added and the mixture was extracted with Et_2O (3 x 100 ml). The combined organic phases were washed with brine, dried over Na_2SO_4, filtrated and evaporated. Silica gel column chromatography (*n*-pentane:EtOAc = 4:1) gave the desired product **13.2k** (2.42 g, 9.09 mmol, 91%) as brownish solid.

m.p.: 75 °C.

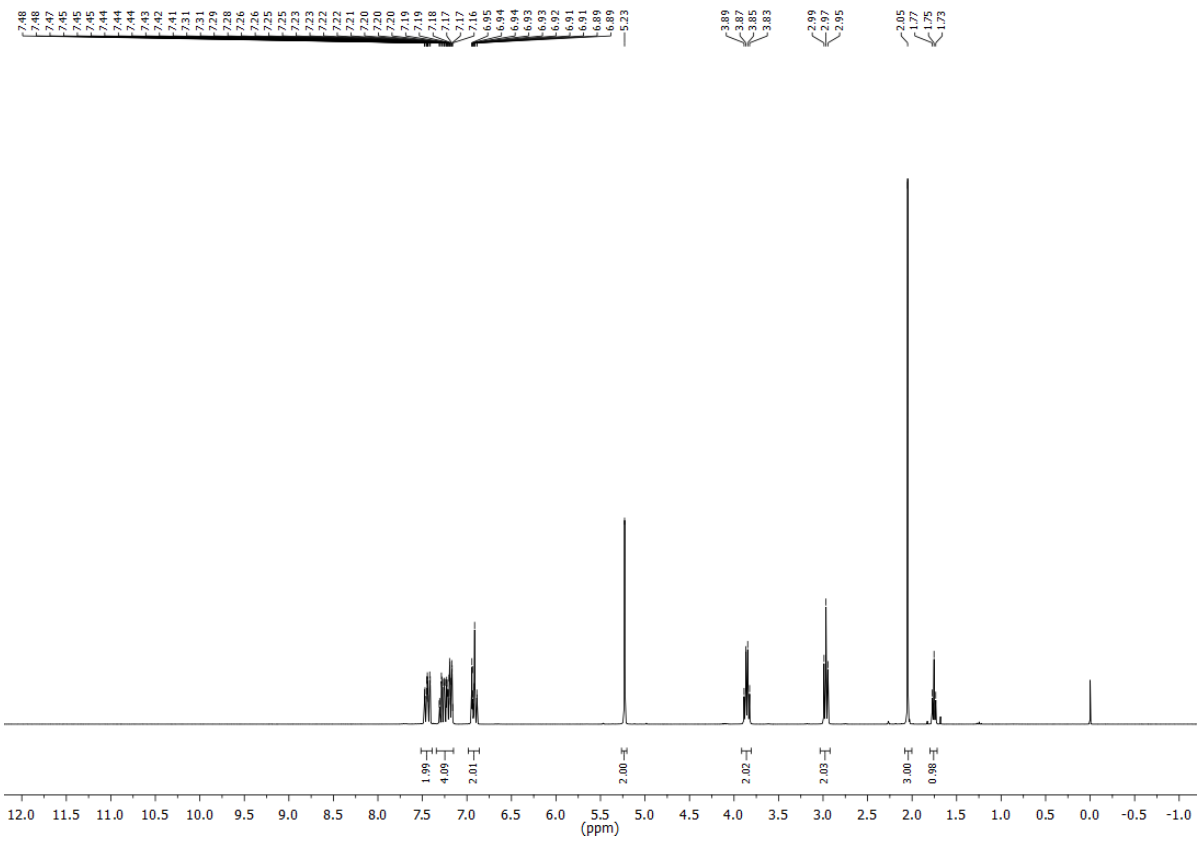
$\mathbf{R_f}$ = 0.09 (*n*-pentane:EtOAc =10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.75 (t, *J*=5.8, 1H), 2.05 (s, 3H), 2.97 (t, *J*=6.5, 2H), 3.86 (q, *J*=6.3, 2H), 5.23 (s, 2H), 6.86 – 6.97 (m, 2H), 7.14 – 7.33 (m, 4H), 7.40 – 7.49 (m, 2H).

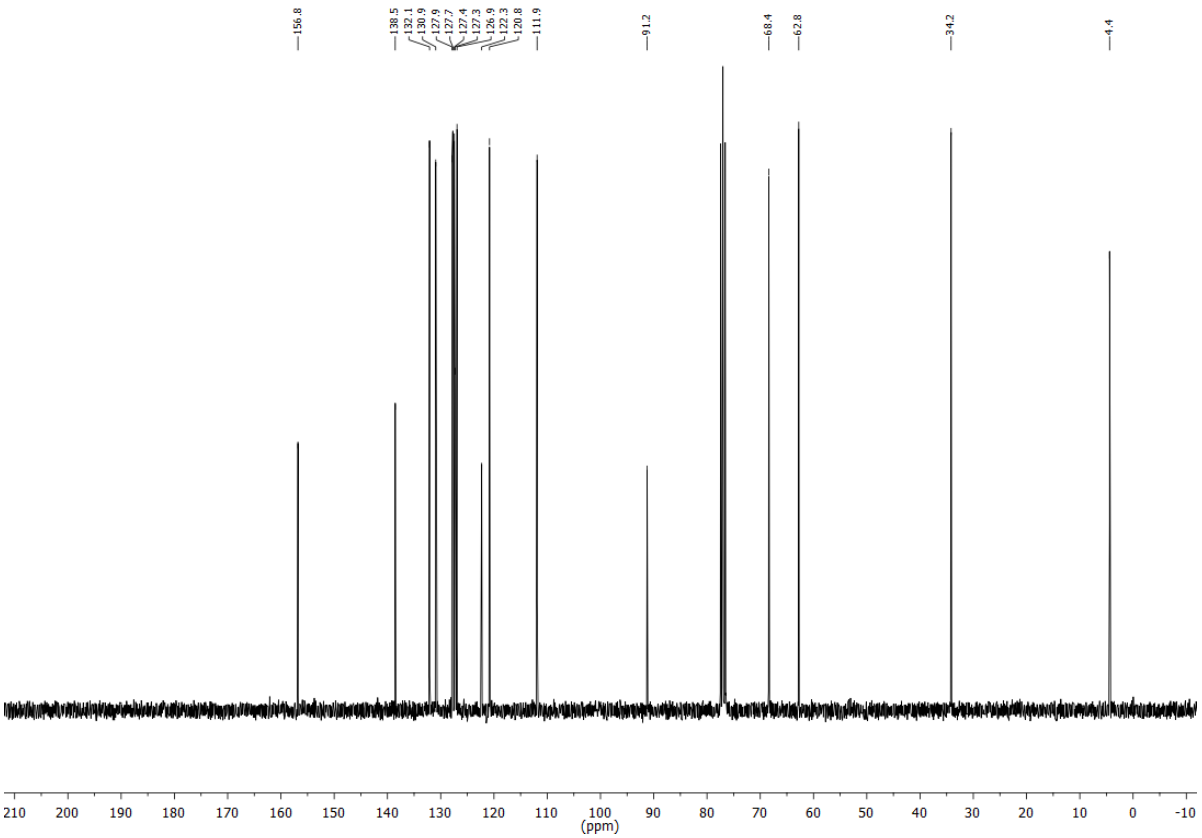
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.4, 34.2, 62.8, 68.4, 91.2, 111.9, 120.8, 122.3, 126.9, 127.3, 127.4, 127.7, 127.9, 130.9, 132.1, 138.5, 156.8, 1 C (alkyne) covered by $CDCl_3$.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3343, 3067, 3032, 2920, 2874, 1592, 1492, 1445, 1379, 1241, 1041, 1016.

$C_{18}H_{18}O_2$ calcd.: 266.1307, found: 266.1286 (GC-HRMS).

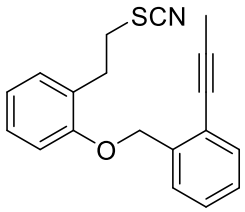


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

1-(Prop-1-yn-1-yl)-2-((2-(2-thiocyanatoethyl)phenoxy)methyl)benzene (3k)



Alcohol **13.2k** (1.33 g, 5.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **3k** as a colorless oil (391.0 mg, 1.27 mmol, 25%).

$\mathbf{R_f}$ = 0.24 (*n*-pentane:EtOAc = 20:1).

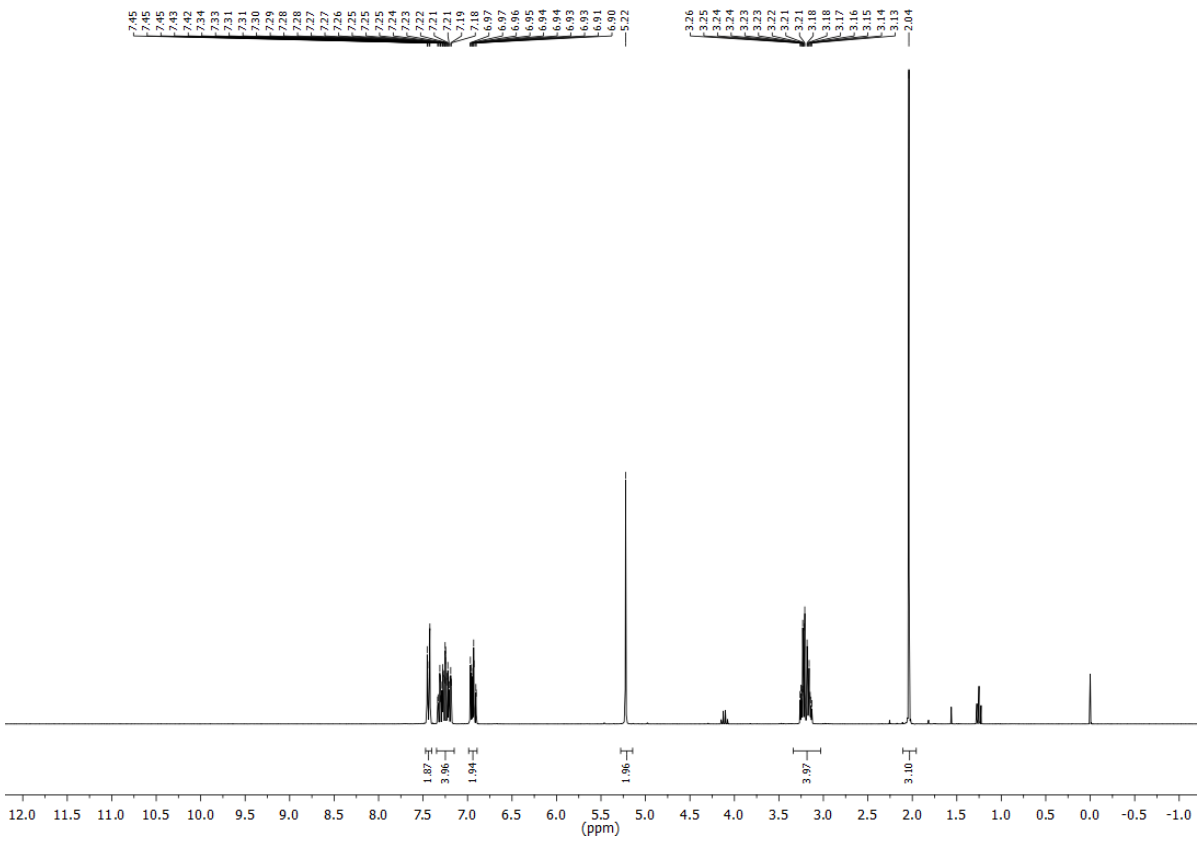
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.04 (s, 3H), 2.99 – 3.37 (m, 4H), 5.22 (s, 2H), 6.89 – 6.99 (m, 2H), 7.15 – 7.35 (m, 4H), 7.38 – 7.51 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 4.4, 31.7, 33.6, 68.4, 77.1, 91.2, 111.9, 112.4, 120.8, 122.5, 126.1, 127.1, 127.7, 127.9, 128.7, 130.9, 132.2, 138.2, 156.7.

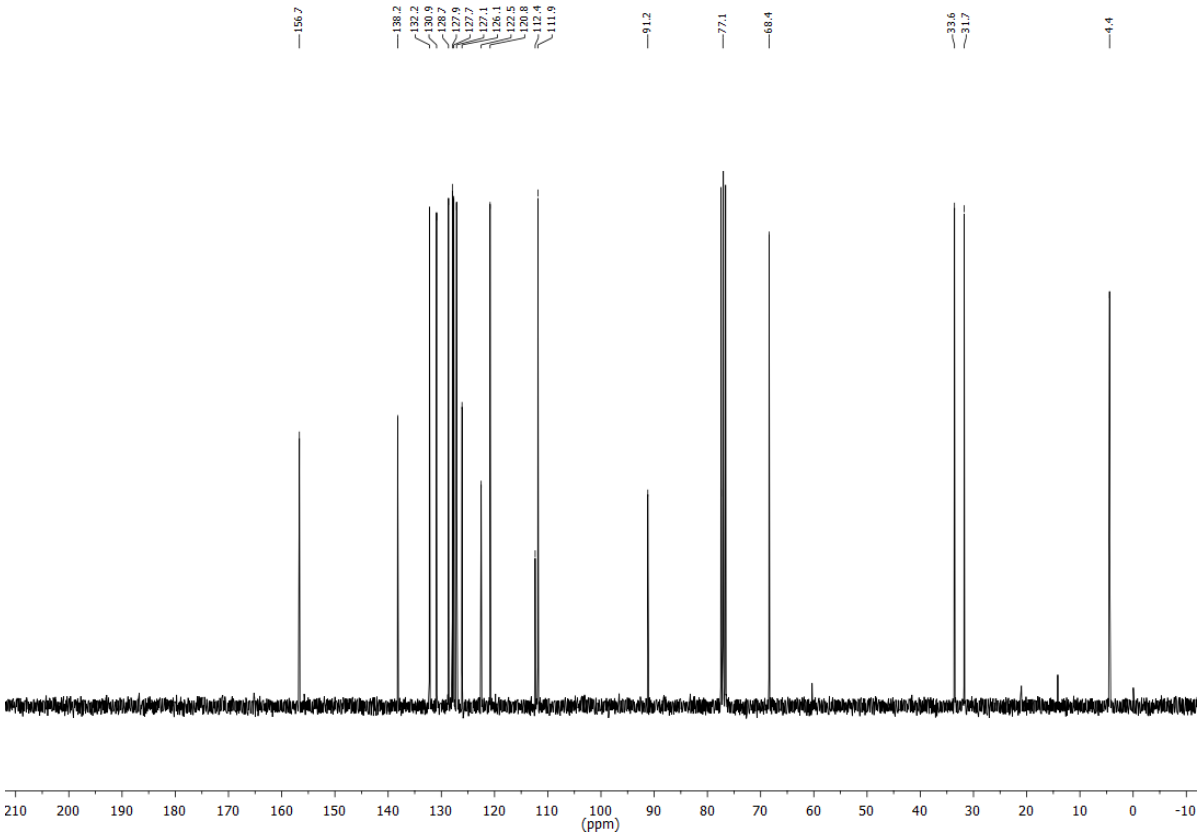
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3067, 3032, 2920, 2852, 2153, 1595, 1491, 1449, 1236, 1012.

$C_{19}H_{17}NOS$ calcd.: 307.1031, found: 307.1016 (GC-HRMS).

Compound **3k** was synthesized to obtain a ten-membered ring. Unfortunately, the synthesis of such a product was not possible.

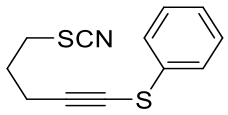


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

((5-Thiocyanatopent-1-yn-1-yl)thio)benzene (5e)



((5-Hydroxypent-1-yn-1-yl)thio)benzene[41] (193 mg, 1.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **5e** as a colorless oil (94 mg, 0.40 mmol, 40%).

R_f = 0.26 (*n*-pentane:EtOAc = 20:1).

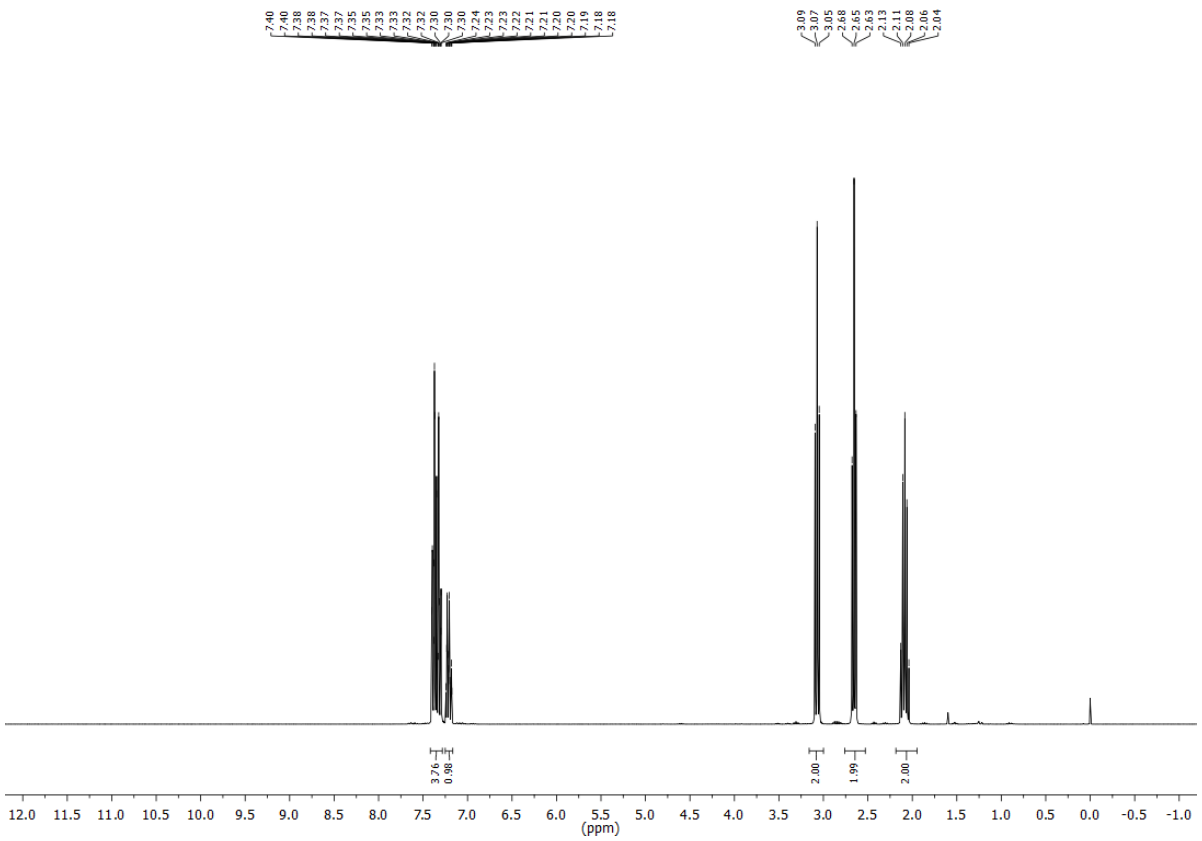
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.08 (p, *J* = 6.8 Hz, 2H), 2.65 (t, *J* = 6.7 Hz, 2H), 3.07 (t, *J* = 7.0 Hz, 2H), 7.17 – 7.25 (m, 1H), 7.29 – 7.41 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 18.5, 28.3, 32.6, 67.3, 96.5, 111.7, 125.9, 126.4, 129.1, 132.7.

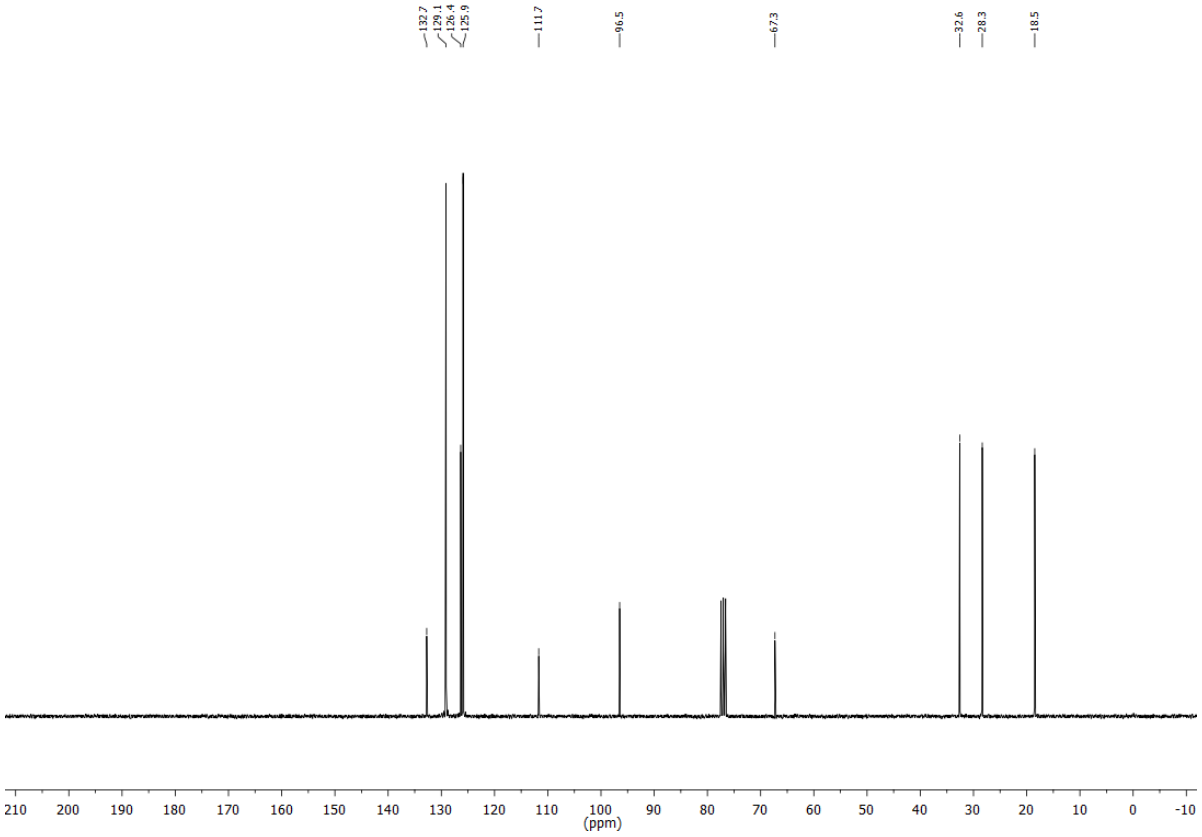
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2937, 2841, 2152, 1581, 1476, 1436, 1281, 1080, 1022.

$C_{12}H_{11}NS_2$ calcd.: 233.0333, found: 233.0350 (GC-HRMS).

[41] Y. Tokimizu, S. Oishi, N. Fujii and H. Ohno, *Angew. Chem. Int. Ed.*, 2015, **54**, 7862.

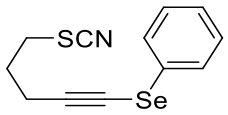


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

((5-Thiocyanatopent-1-yn-1-yl)selanyl)benzene (5f)



((5-Hydroxypent-1-yn-1-yl)selanyl)benzene (prepared similar to 3-hydroxy-1-propynyl phenyl sulfide,[42] 239 mg, 1.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **5f** as a colorless oil (95 mg, 0.34 mmol, 34%).

R_f = 0.28 (*n*-pentane:EtOAc = 20:1).

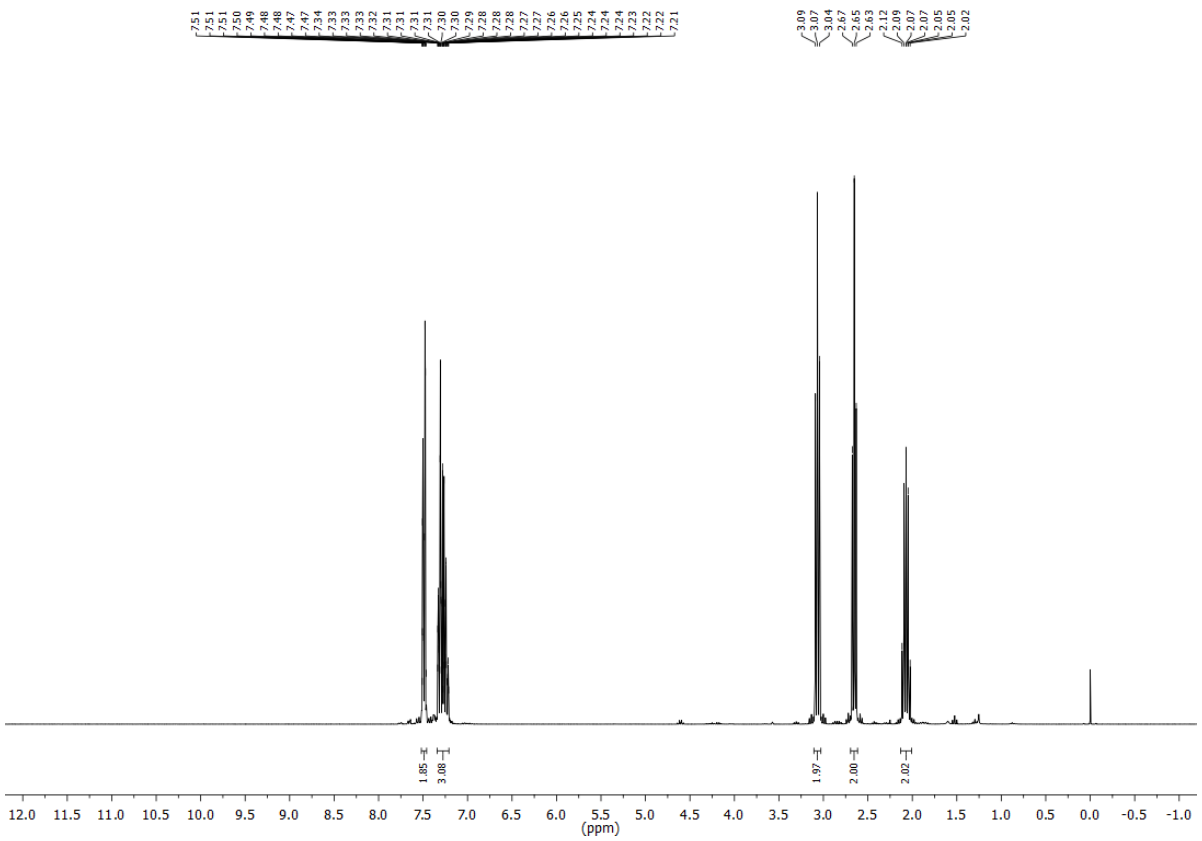
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.02 – 2.12 (m, 2H), 2.65 (t, *J* = 6.6 Hz, 2H), 3.04 – 3.09 (m, 2H), 7.21 – 7.35 (m, 3H), 7.45 – 7.52 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 18.7, 28.4, 32.6, 60.3, 101.1, 111.7, 127.0, 128.5, 128.8, 129.4.

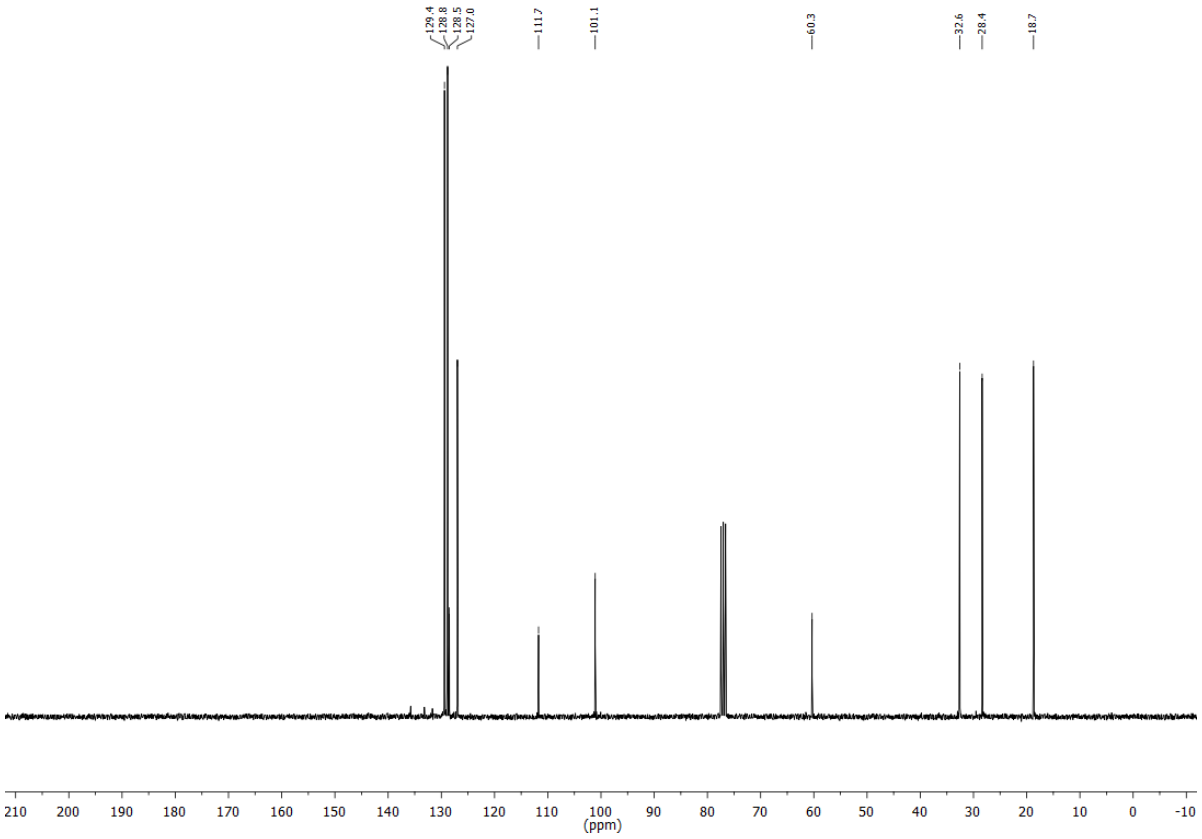
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2933, 2844, 2152, 1576, 1475, 1436, 1279, 1020.

$C_{12}H_{11}NSSe$ calcd.: 280.9777, found: 280.9791 (GC-HRMS).

[42] S. T. Kabanyane and D. I. MaGee, *Can. J. Chem.*, 1992, **70**, 2758.

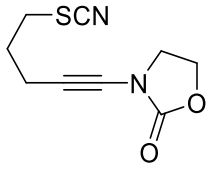


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

3-(5-Thiocyanatopent-1-yn-1-yl)oxazolidin-2-one (5g)



Tosylate **15g** (130 mg, 0.40 mmol, 1.00 equiv.) was dissolved in anhydrous DMF (5 ml) in a sealable tube. After addition of KSCN (300 mg, 3.1 mmol, 7.75 equiv.), the tube was capped and the mixture heated at 100 °C for 5 h. The reaction mixture was cooled to RT and water was added (50 ml). The aqueous phase was extracted with DCM (2 x 50 ml) and the combined organic layers were dried over Na_2SO_4. The solvent was removed *in vacuo*. After flash column chromatography (*n*-pentane:EtOAc = 1:1) the title compound was afforded as an orange solid (70 mg, 0.33 mmol, 83%).

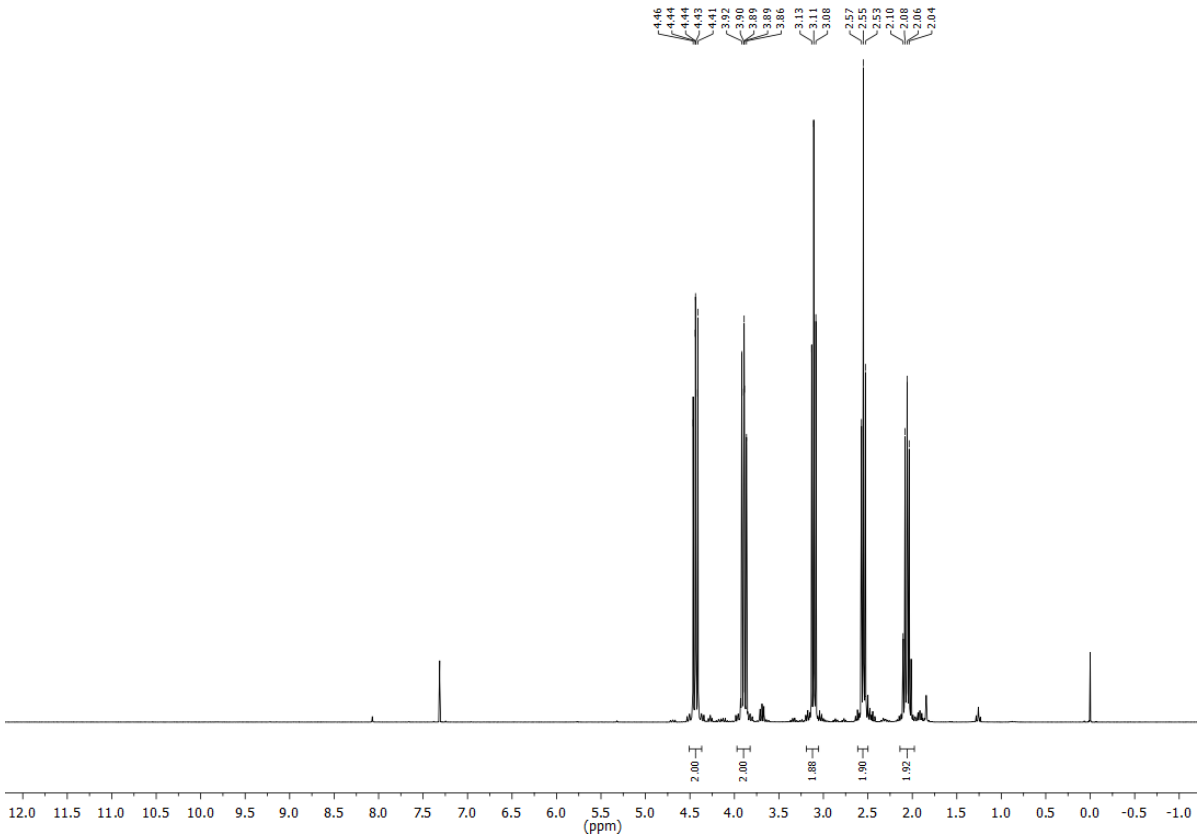
R_f = 0.11 (*n*-pentane:EtOAc = 2:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.06 (p, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 6.7 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 3.80 – 3.97 (m, 2H), 4.35 – 4.50 (m, 2H).

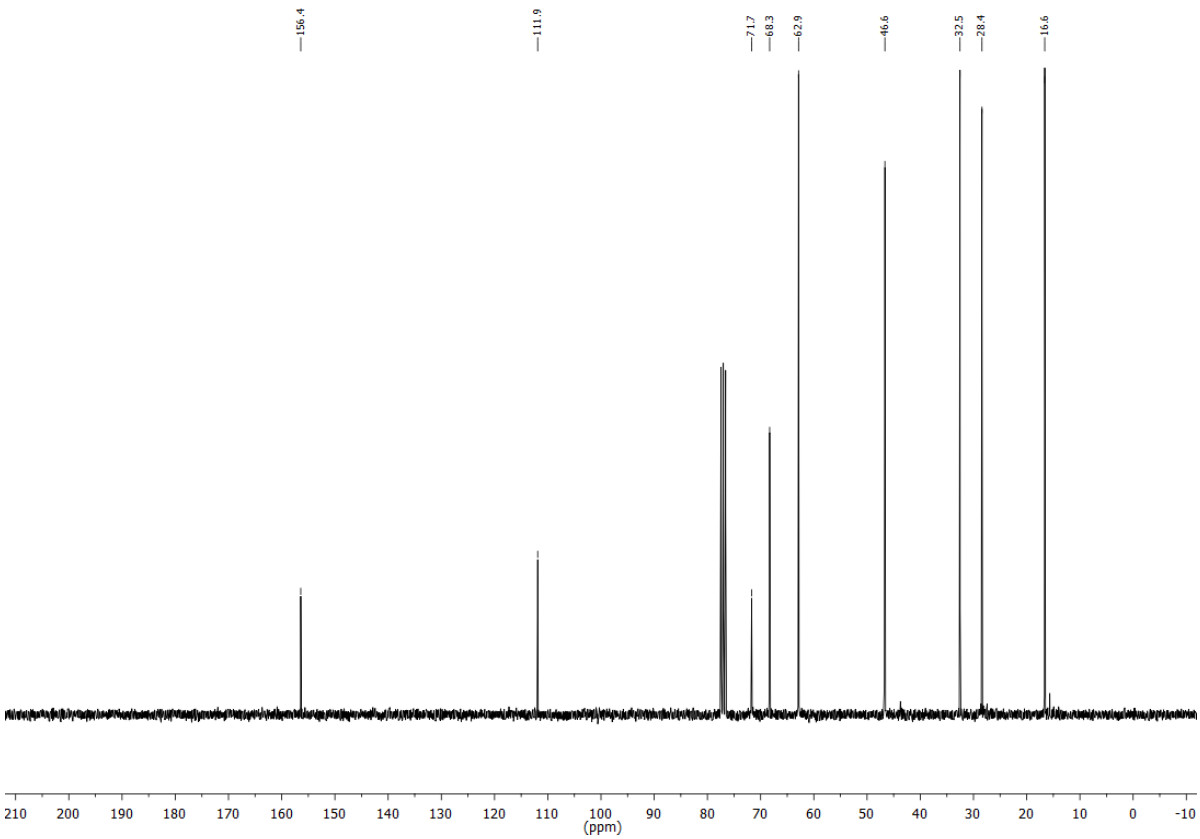
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.6, 28.4, 32.5, 46.6, 62.9, 68.3, 71.7, 111.9, 156.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3519, 2987, 2951, 2929, 2270, 2150, 1759, 1486, 1415, 1303, 1198, 1113, 1030, 965.

$C_9H_{10}N_2O_2S_2$ calcd.: 210.0463, found: 210.0480 (GC-HRMS).

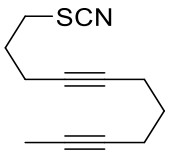


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

11-Thiocyanatoundeca-2,7-diyne (9c)



Undeca-4,9-diyn-1-ol (130 mg, 0.80 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **9c** as a colorless oil (36 mg, 0.18 mmol, 22%).

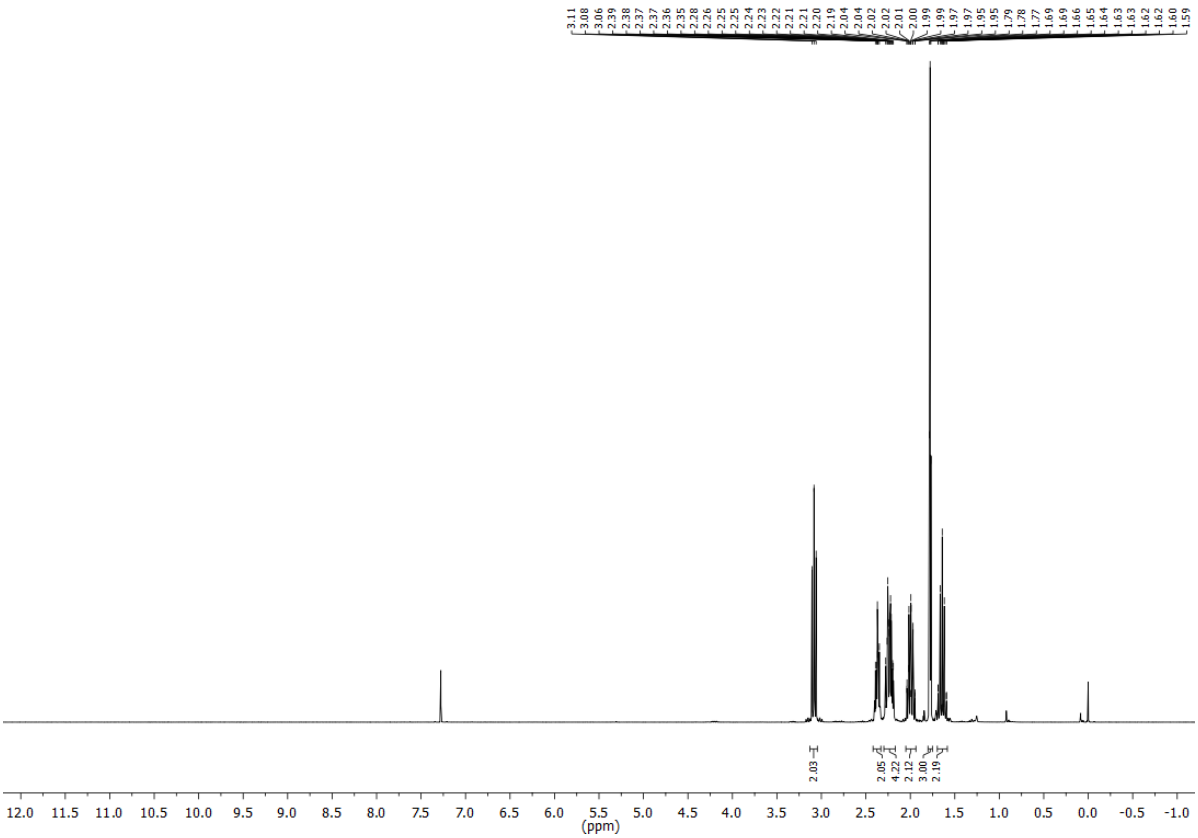
R_f = 0.22 (*n*-pentane:EtOAc = 50:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.58 – 1.70 (m, 2H), 1.78 (t, *J* = 2.6 Hz, 3H), 1.99 (pd, *J* = 6.7, 0.5 Hz, 2H), 2.18 – 2.29 (m, 4H), 2.34 – 2.41 (m, 2H), 3.04 – 3.12 (m, 2H).

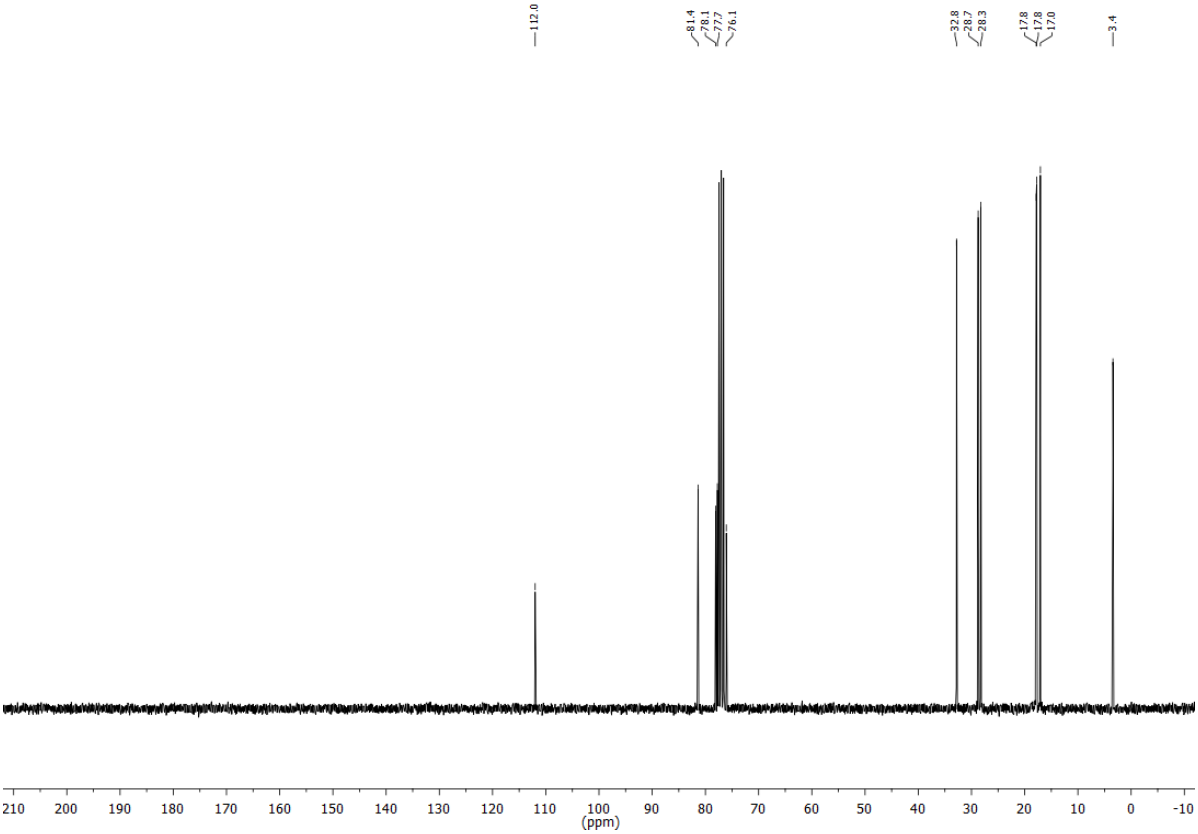
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 3.4, 17.0, 17.8, 17.8, 28.3, 28.7, 32.8, 76.1, 77.7, 78.1, 81.4, 112.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2936, 2919, 2858, 2843, 2154, 1433, 1347, 1283, 1259.

$C_{12}H_{15}NS$ calcd.: 205.0925, found: 205.0910 (GC-HRMS).

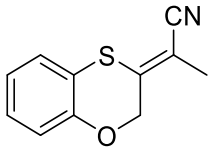


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)propanenitrile (2a)



Compound **1a** (20.3 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain product **2a** after flash column chromatography (*n*-pentane:EtOAc = 50:1 → 20:1) as a colorless solid (18.9 mg, 93 µmol, 93%). The reaction time was 4h.

m.p.: 95 °C.

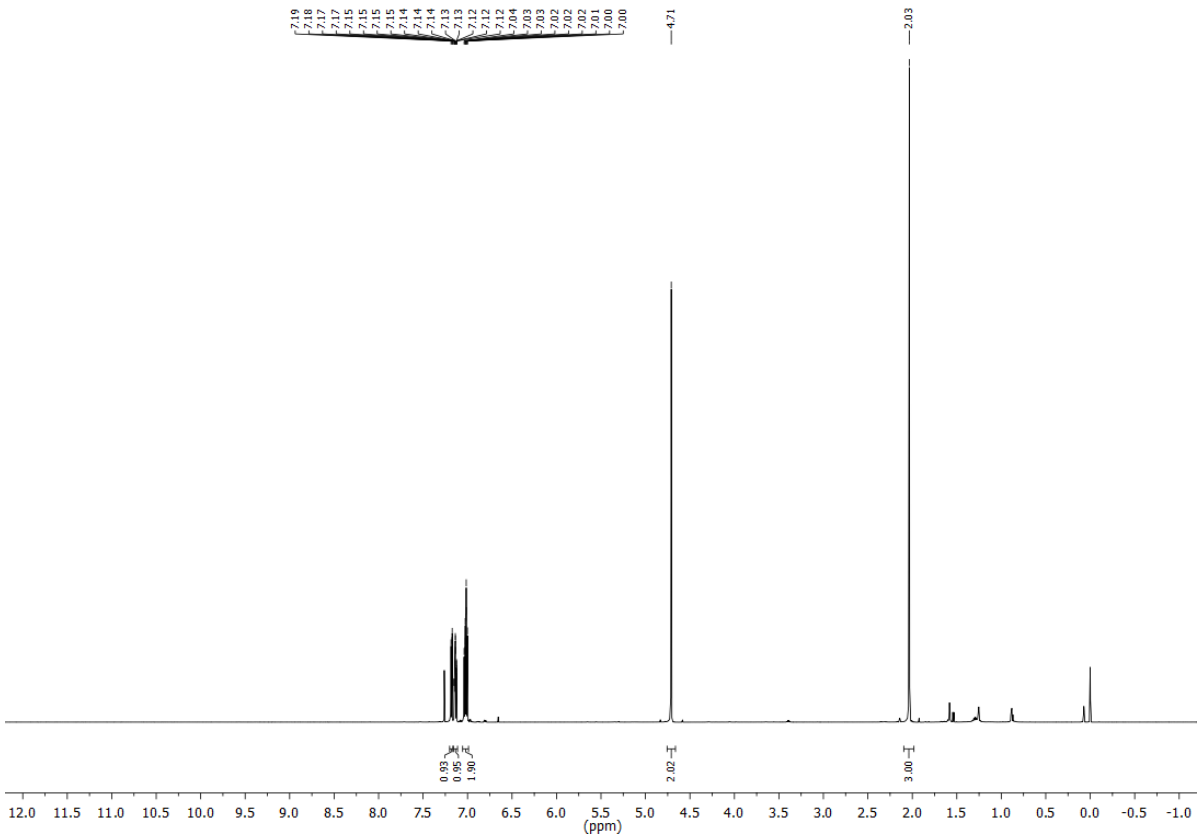
$\mathbf{R_f}$ = 0.14 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 2.03 (s, 3H), 4.71 (s, 2H), 6.99 – 7.05 (m, 2H), 7.14 (tdd, *J* = 8.0, 1.6, 0.8 Hz, 1H), 7.17 – 7.19 (m, 1H).

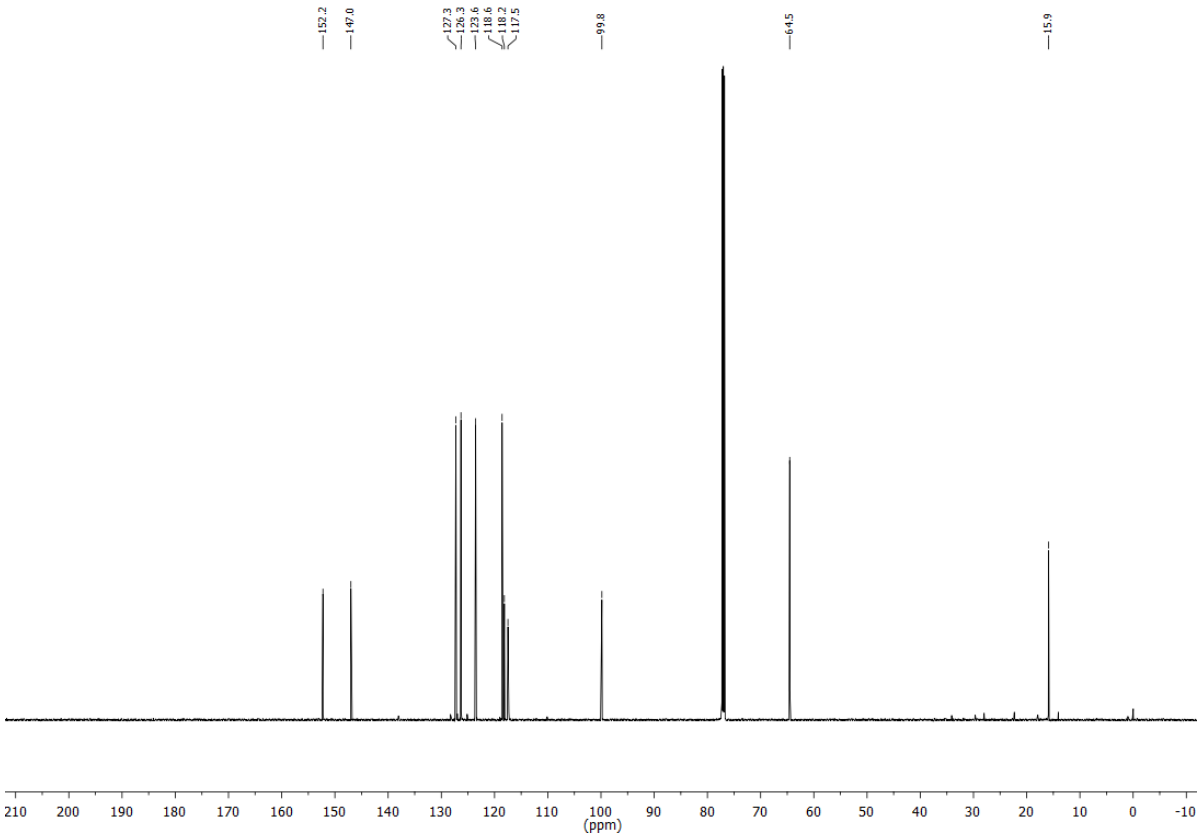
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 15.9, 64.5, 99.8, 117.5, 118.2, 118.6, 123.6, 126.3, 127.3, 147.0, 152.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3078, 3013, 2922, 2855, 2202, 1597, 1572, 1472, 1442, 1260, 1215, 1117, 1033, 1006.

$C_{11}H_9NOS$ calcd.: 203.0405, found: 203.0415 (GC-HRMS).

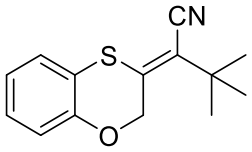


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-3,3-dimethylbutanenitrile (2b)



Compound **1b** (25.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain product **2b** after flash column chromatography (*n*-pentane:EtOAc = 40:1) as a colorless solid (23.4 mg, 96 µmol, 94%).

m.p.: 97 °C.

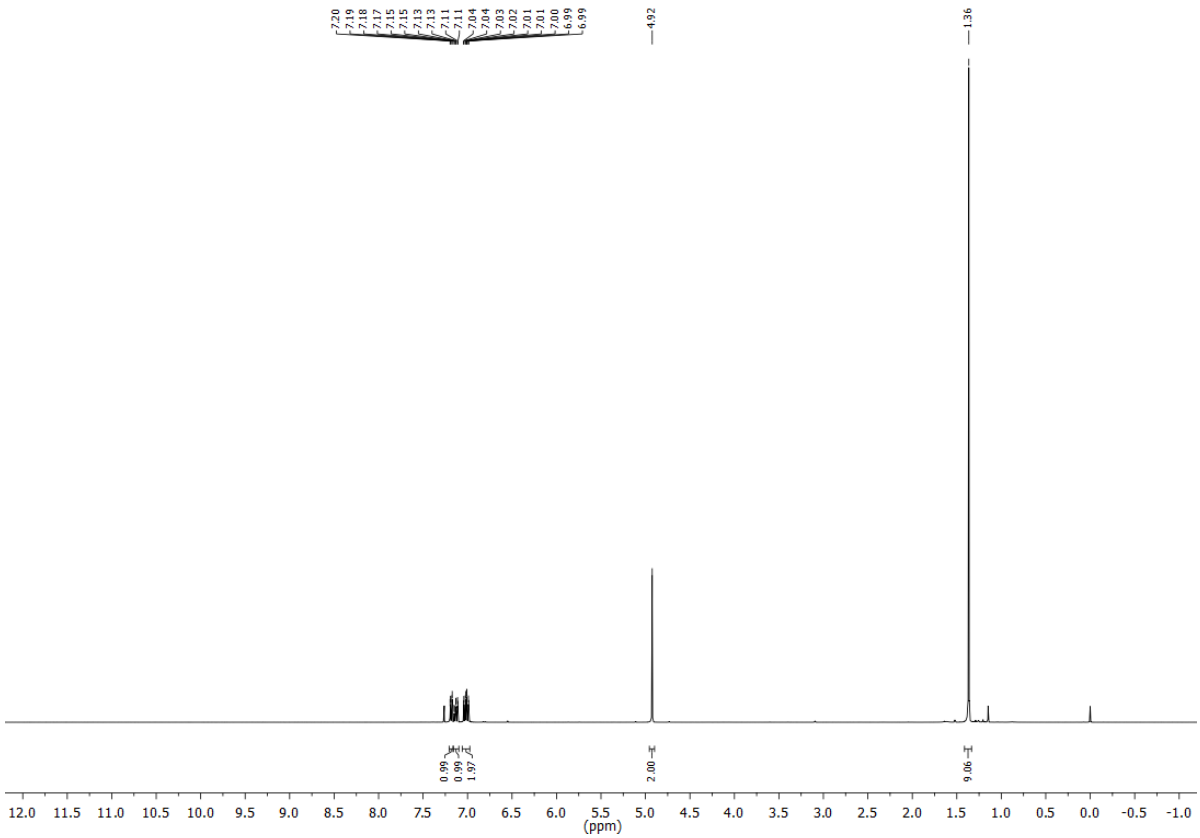
$\mathbf{R_f}$ = 0.33 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.36 (s, 9H), 4.92 (s, 2H), 6.98 – 7.06 (m, 2H), 7.10 – 7.16 (m, 1H), 7.18 (dd, *J* = 7.7, 1.7 Hz, 1H).

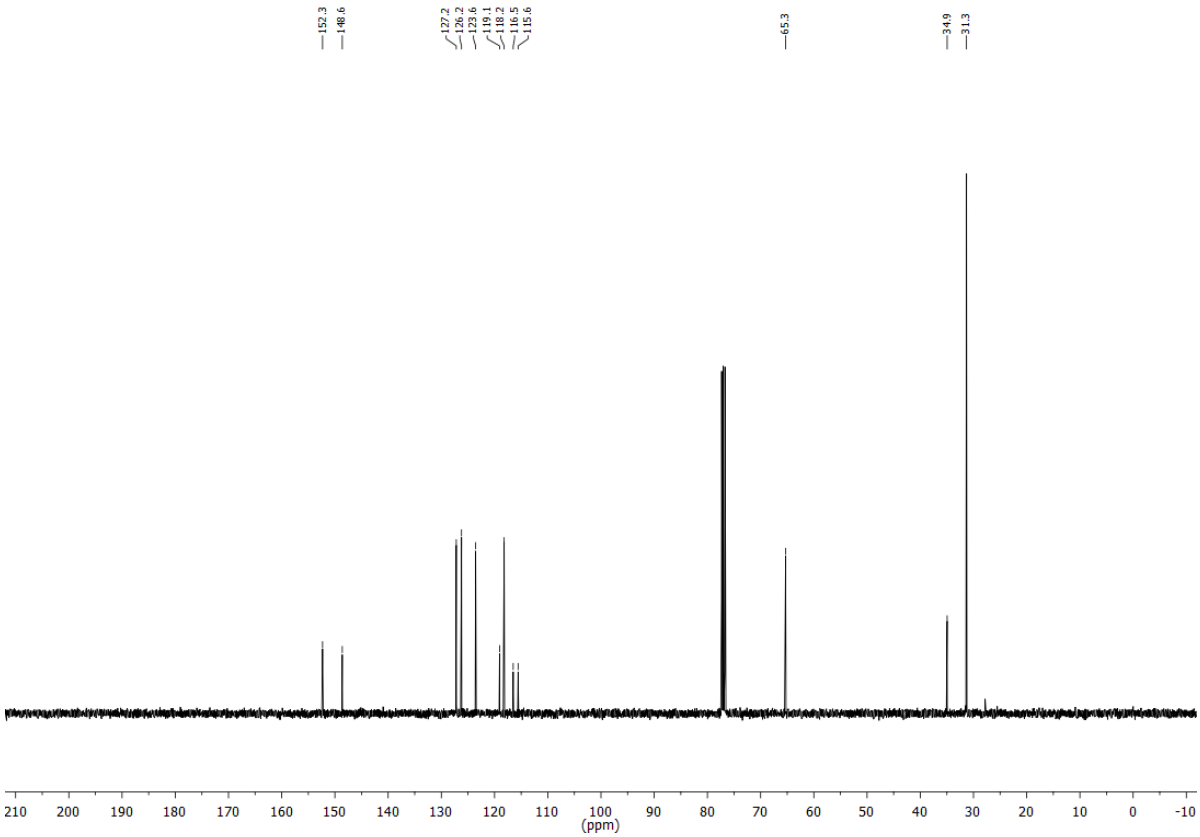
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 31.3, 34.9, 65.3, 115.6, 116.5, 118.2, 119.1, 123.6, 126.2, 127.2, 148.6, 152.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3057, 2973, 2938, 2872, 2199, 1579, 1555, 1473, 1443, 1364, 1262, 1225, 1071.

$C_{14}H_{15}NOS$ calcd.: 245.0874, found: 245.0884 (GC-HRMS).

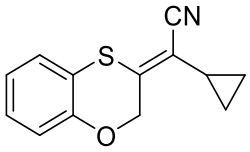


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-2-cyclopropylacetonitrile (2c)



Compound **1c** (24.0 mg, 105 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain product **2c** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as an off-colorless solid (17.0 mg, 74 µmol, 71%).

m.p.: 68 °C.

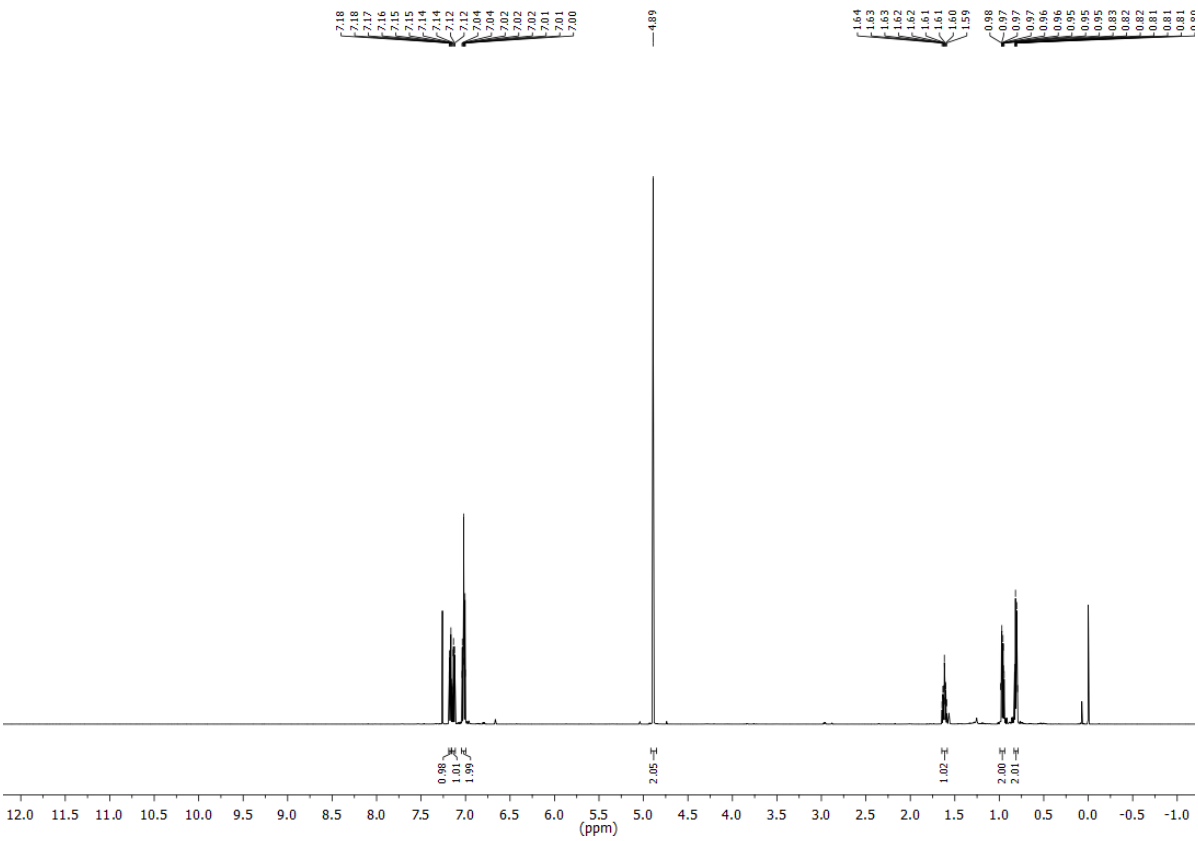
$\mathbf{R_f}$ = 0.22 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.78 – 0.83 (m, 2H), 0.94 – 0.99 (m, 2H), 1.62 (tt, *J* = 8.2, 5.0 Hz, 1H), 4.89 (s, 2H), 7.00 – 7.04 (m, 2H), 7.14 (td, *J* = 7.7, 1.6 Hz, 1H), 7.17 (m, 1H).

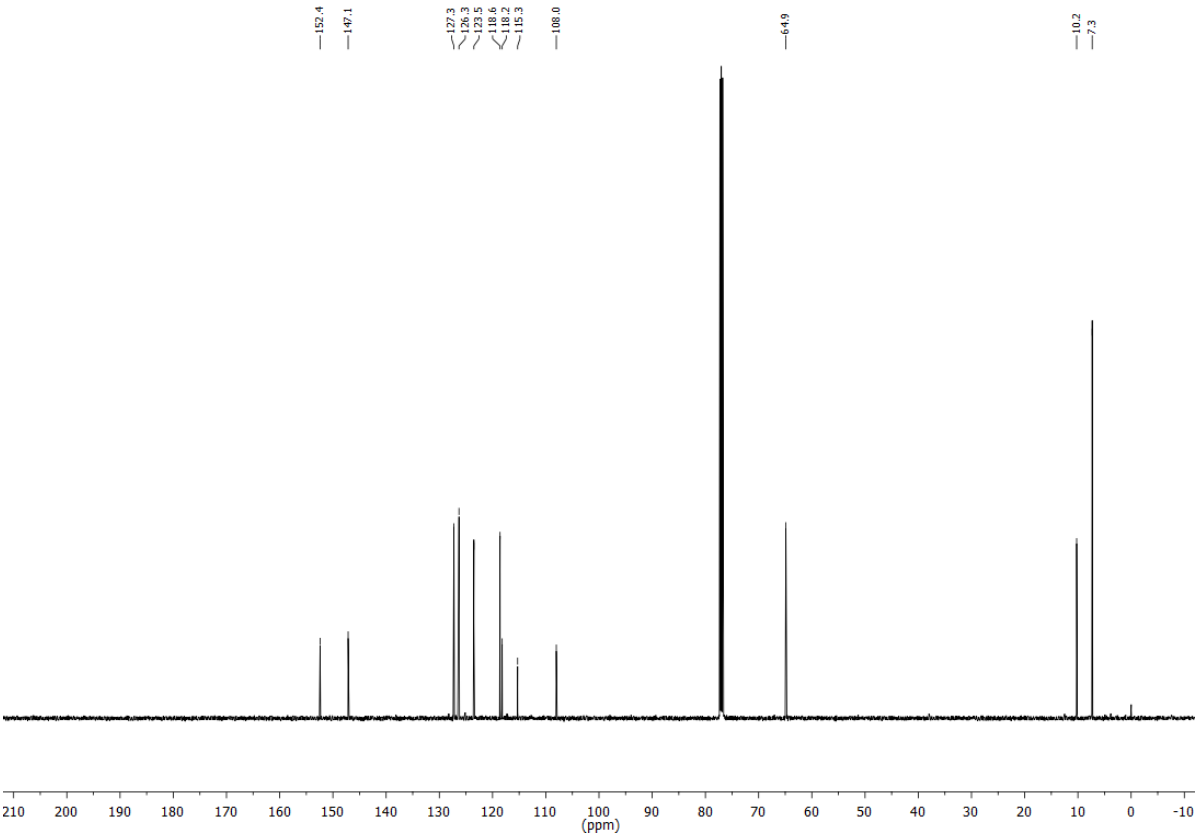
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 7.3, 10.2, 64.9, 108.0, 115.3, 118.2, 118.6, 123.5, 126.3, 127.3, 147.1, 152.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3080, 3004, 2921, 2865, 2203, 1594, 1571, 1468, 1443, 1253, 1216, 122, 1034, 1000.

$C_{13}H_{11}NOS$ calcd.: 229.0561, found: 229.0564 (GC-HRMS).

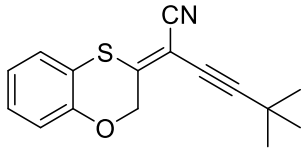


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-5,5-dimethylhex-3-ynenitrile (2d)



Compound **1d** (39.0 mg, 145 µmol, 1.00 equiv.) was transformed according to GP CAT2 to obtain product **2d** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a brownish solid (18.0 mg, 67 µmol, 46%).

m.p.: 79 °C.

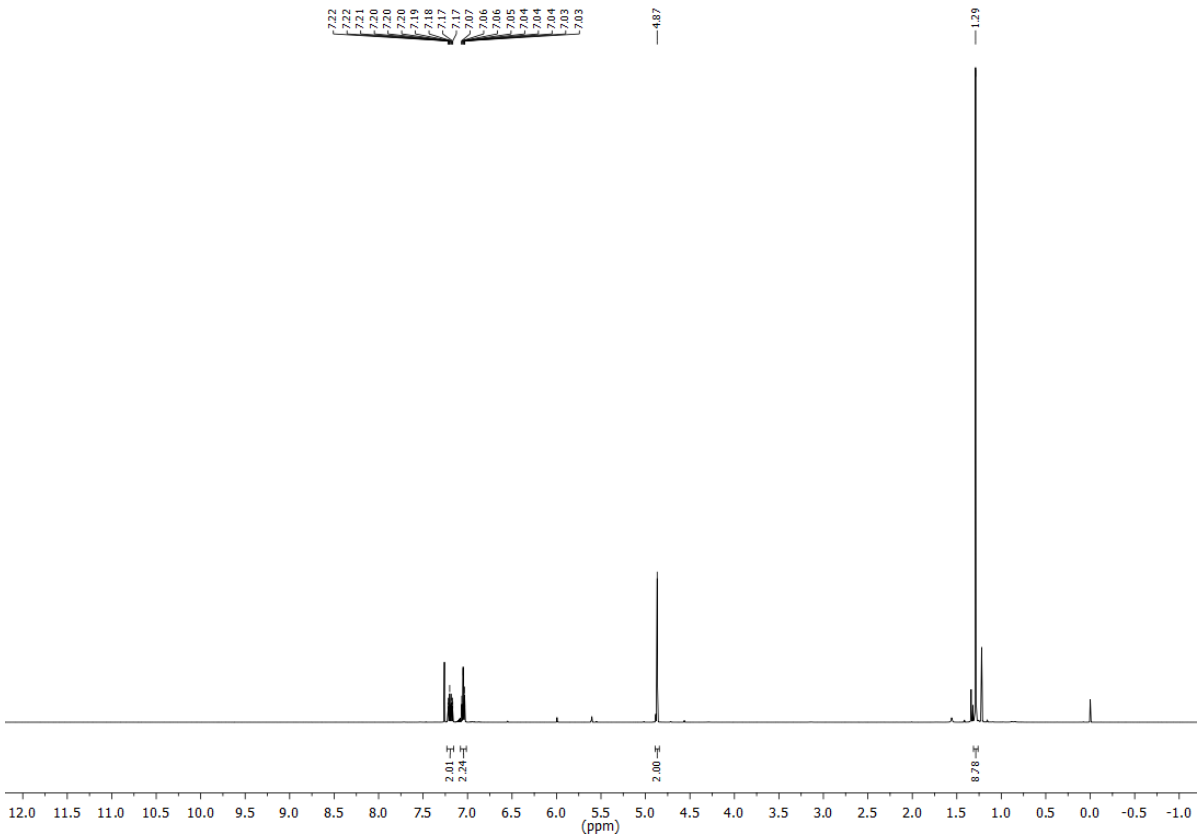
$\mathbf{R_f}$ = 0.65 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.29 (s, 9H), 4.87 (s, 2H), 7.03 – 7.08 (m, 2H), 7.16 – 7.23 (m, 2H).

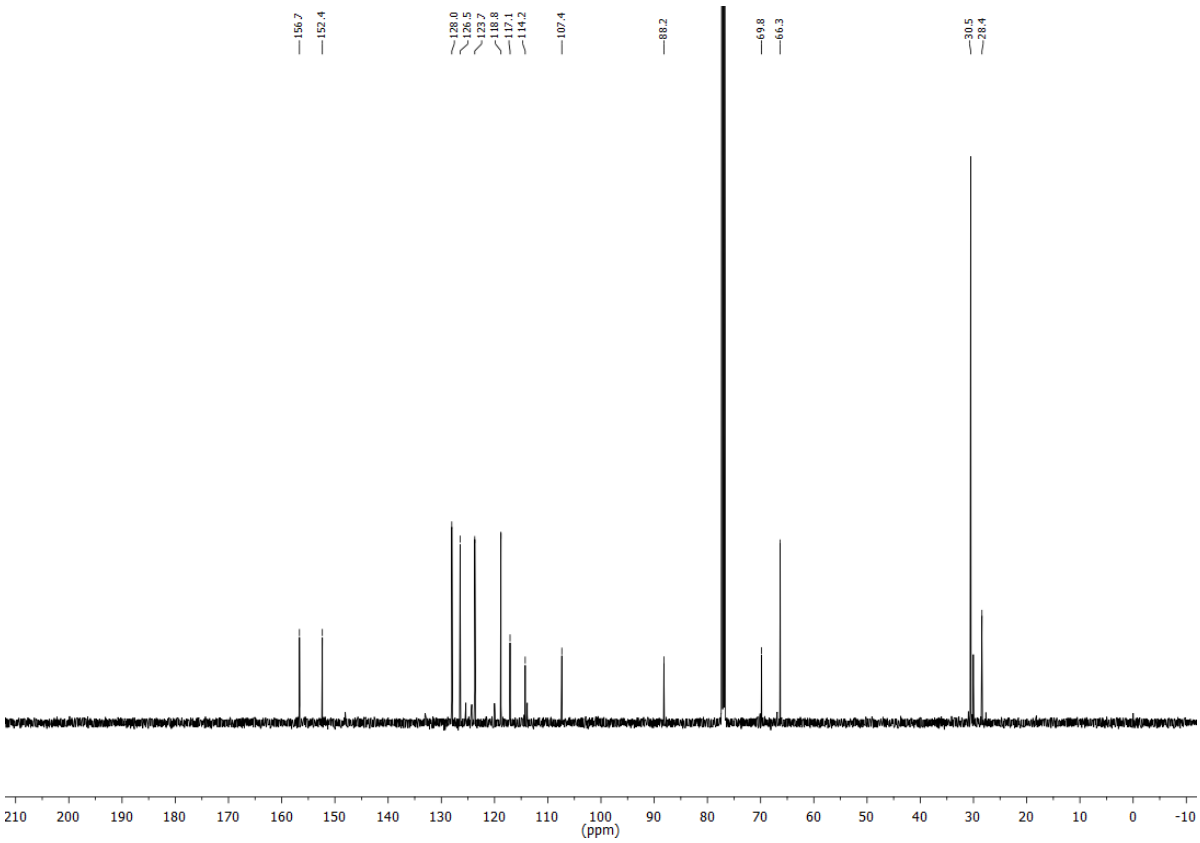
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 28.4, 30.5, 66.3, 69.8, 88.2, 107.4, 114.2, 117.1, 118.8, 123.7, 126.5, 128.0, 152.4, 156.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 2969, 2927, 2866, 2242, 1726, 1579, 1542, 1468, 1448, 1214, 1122, 1040.

$C_{16}H_{15}NOS$ calcd.: 269.0874, found: 269.0897 (GC-HRMS).

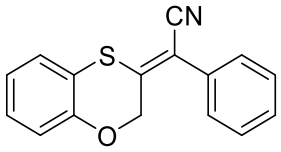


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-2-phenylacetonitrile (*syn*-2e)



Compound **1e** (27.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds ***syn*-2e** and ***anti*-2e** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a mixture (24.5 mg, 92 µmol, 90%). The isomers were separated by HPLC and the ratio of *syn*/*anti* (1.0/2.0) was determined by ^{1}H-NMR.

Compound ***syn*-2e** was isolated as a colorless solid.

m.p.: 116 °C.

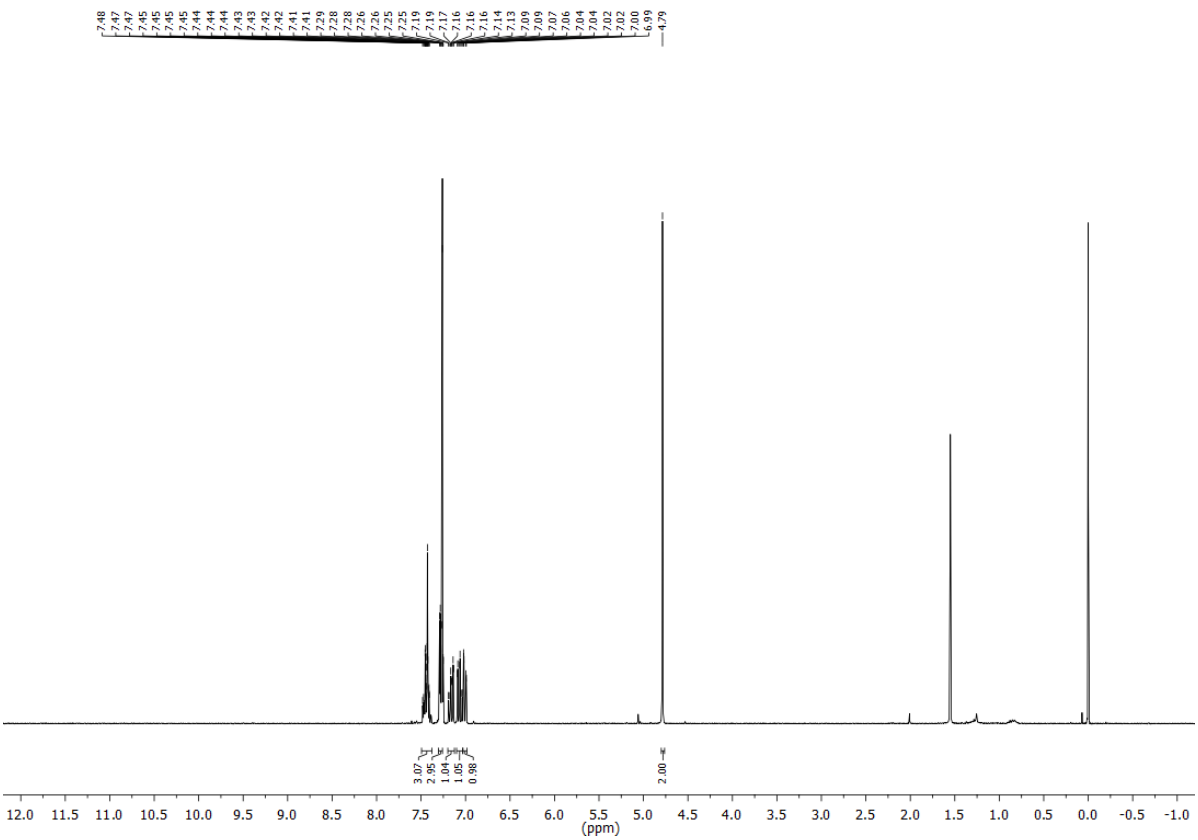
R_f = 0.27 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.79 (s, 2H), 7.01 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.03 – 7.10 (m, 1H), 7.16 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 7.25 – 7.30 (m, 3H), 7.40 – 7.49 (m, 3H).

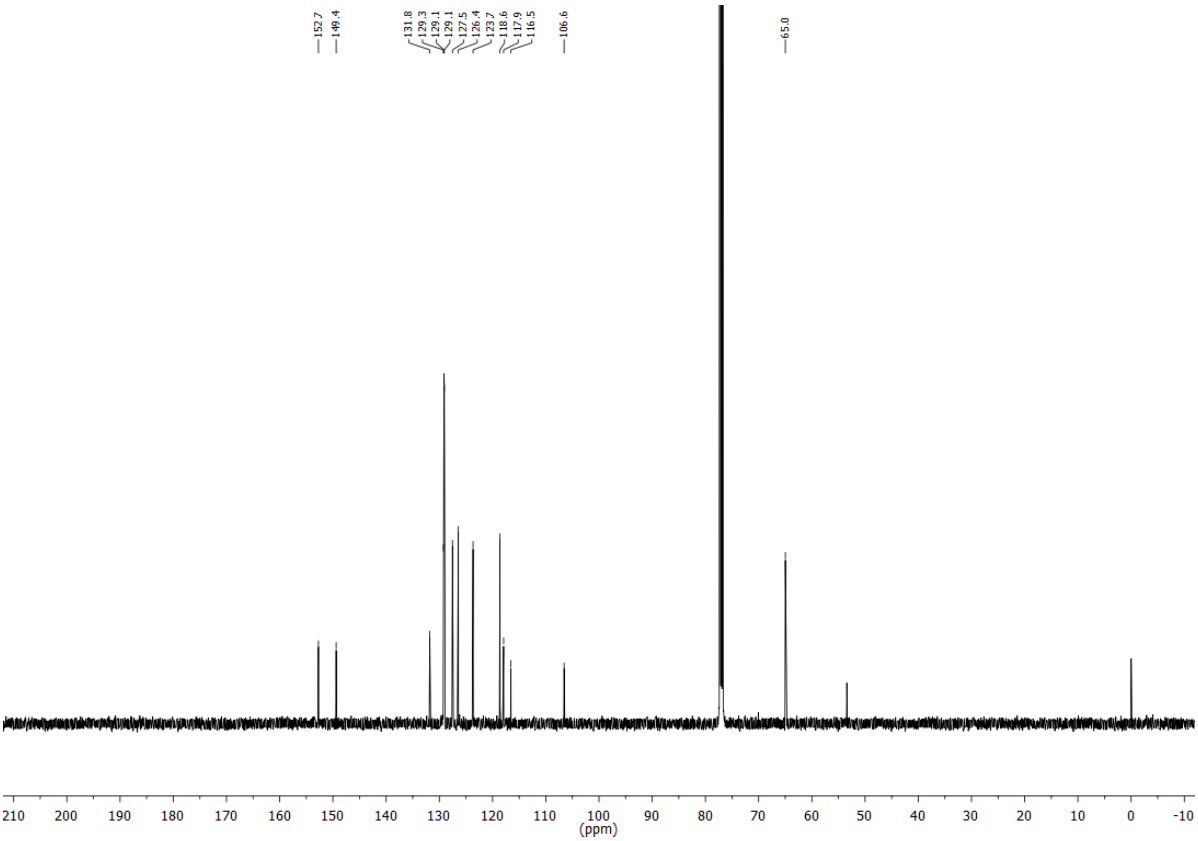
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 65.0, 106.6, 116.5, 117.9, 118.6, 123.7, 126.4, 127.5, 129.1, 129.1, 129.3, 131.8, 149.4, 152.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2956, 2920, 2852, 2199, 1580, 1557, 1470, 1440, 1258, 1221, 1143, 1047, 998.

$C_{16}H_{11}NOS$ calcd.: 265.0561, found: 265.0574 (GC-HRMS).

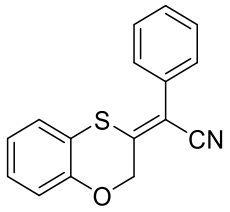


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*E*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-2-phenylacetonitrile (*anti*-2e)



Compound ***anti*-2e** was isolated as an off-white solid.

m.p.: 115 °C.

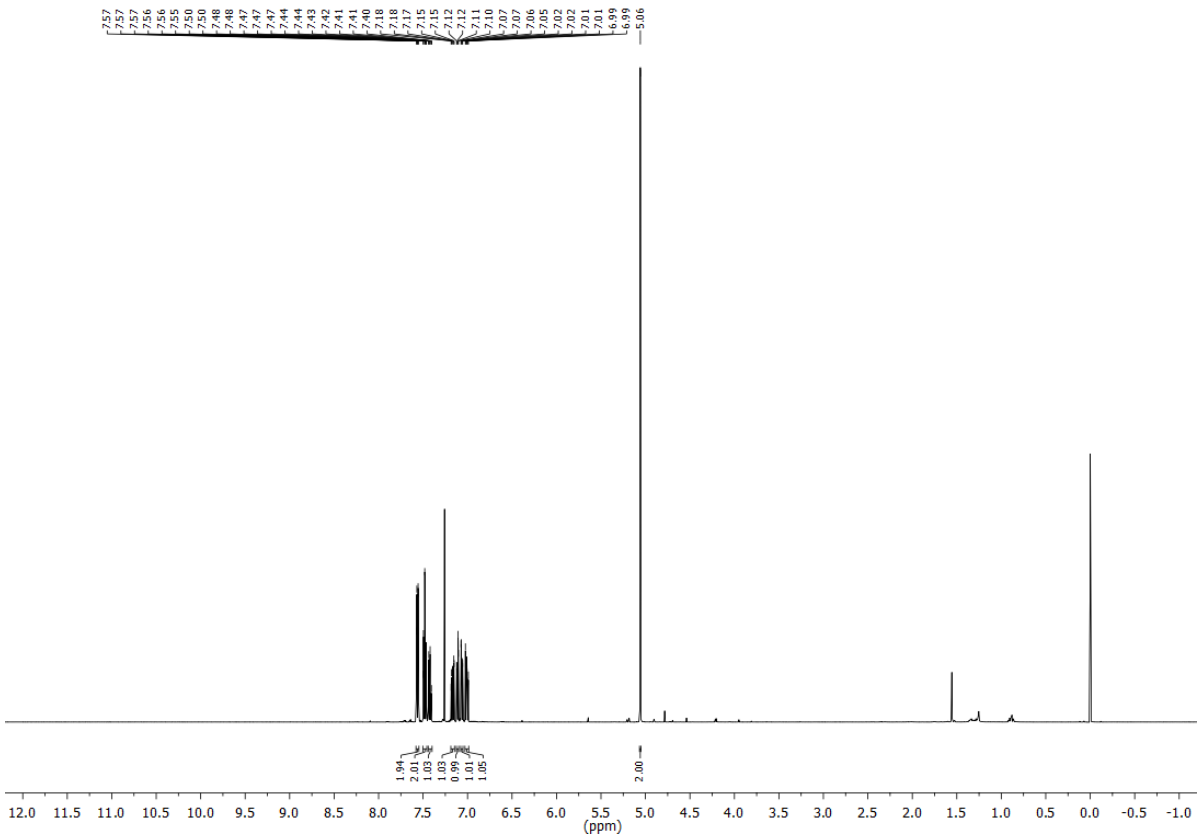
R_f = 0.35 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 5.06 (s, 2H), 6.99 – 7.03 (m, 1H), 7.06 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.15 – 7.19 (m, 1H), 7.40 – 7.44 (m, 1H), 7.46 – 7.50 (m, 2H), 7.54 – 7.58 (m, 2H).

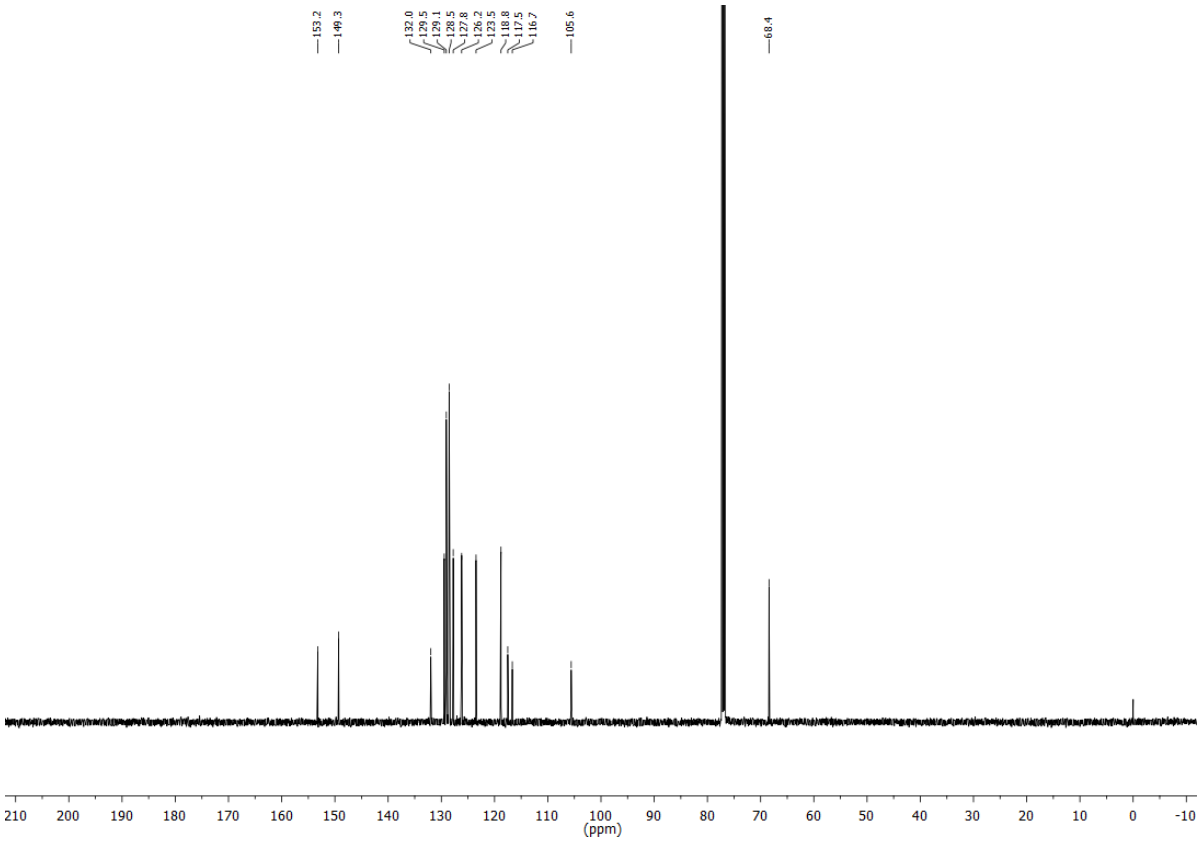
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 68.4, 105.6, 116.7, 117.5, 118.8, 123.5, 126.2, 127.8, 128.5, 129.1, 129.5, 132.0, 149.3, 153.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3057, 2923, 2901, 2850, 2198, 1586, 1469, 1441, 1259, 1214, 1157, 1034.

$C_{16}H_{11}NOS$ calcd.: 265.0561, found: 265.0574 (GC-HRMS).

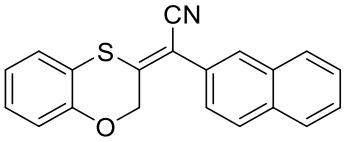


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-2-(naphthalen-2-yl)acetonitrile (*syn*-2f)



Compound **1f** (32.0 mg, 101 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds ***syn*-2f** and ***anti*-2f** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a mixture (24.0 mg, 76 µmol, 75%). The isomers were separated by HPLC and the ratio of *syn*/*anti* (1.0/2.0) was determined by ^{1}H-NMR.

Compound ***syn*-2f** was isolated as a colorless solid.

m.p.: 160 °C.

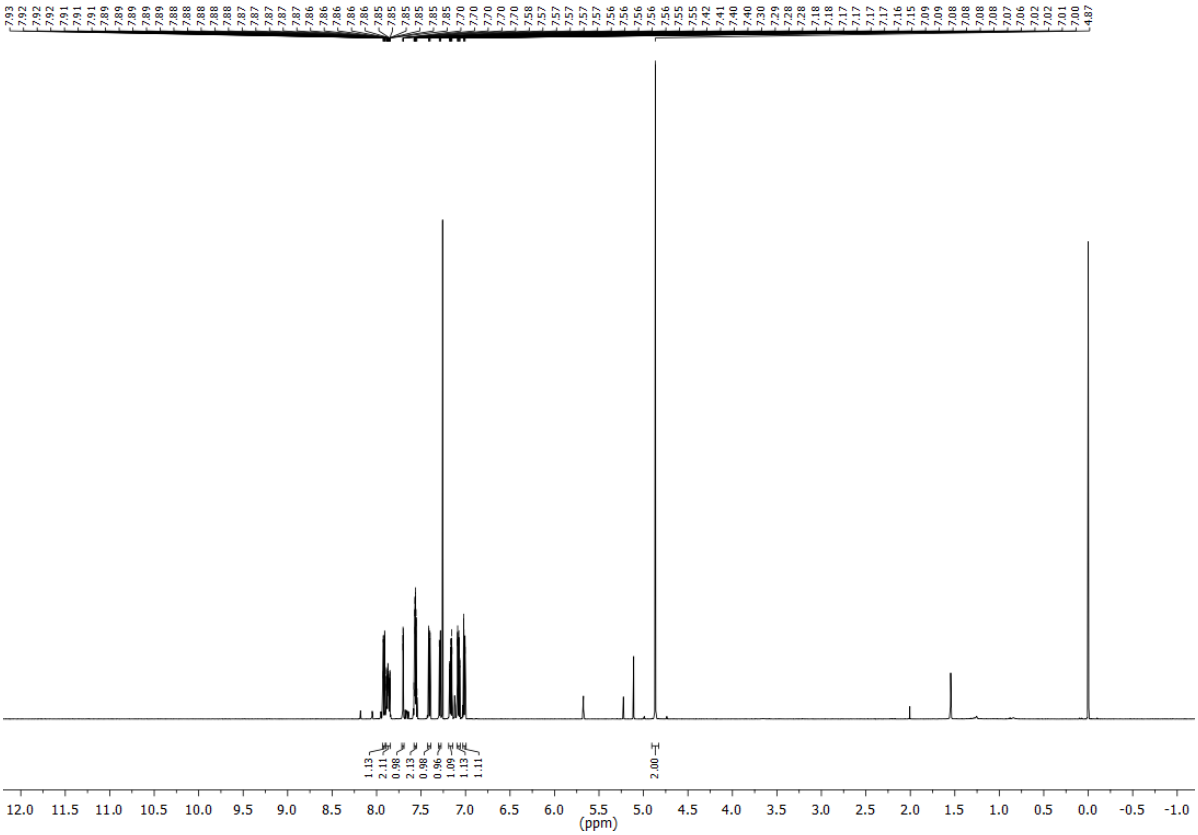
R_f = 0.33 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 4.87 (s, 2H), 7.01 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.08 (ddd, *J* = 7.9, 7.4, 1.3 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.41 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.54 – 7.59 (m, 2H), 7.69 – 7.71 (m, 1H), 7.84 – 7.90 (m, 2H), 7.90 – 7.93 (m, 1H).

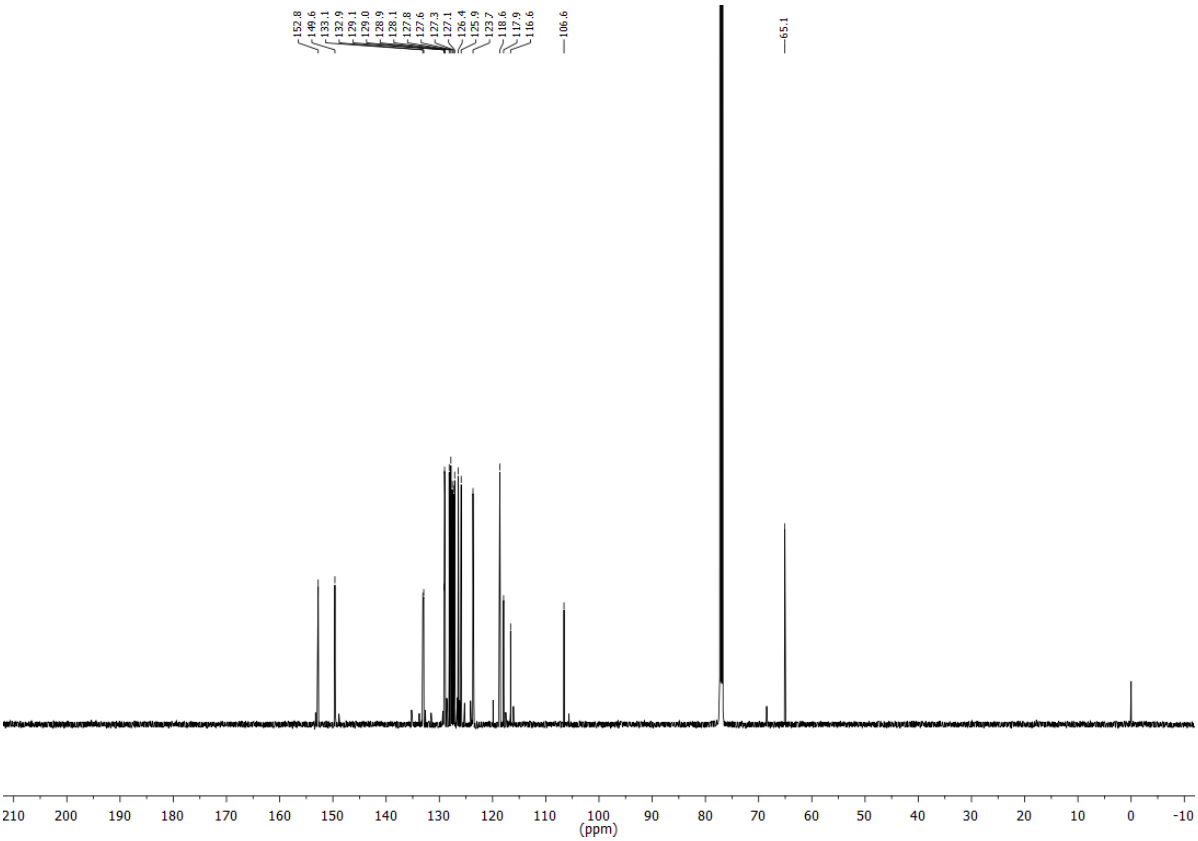
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 65.1, 106.6, 116.6, 117.9, 118.6, 123.7, 125.9, 126.4, 127.1, 127.3, 127.6, 127.8, 128.1, 128.9, 129.0, 129.1, 132.9, 133.1, 149.6, 152.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3054, 2921, 2852, 2208, 1579, 1552, 1469, 1441, 1263, 1214, 1119, 1048, 1000.

$C_{20}H_{13}NOS$ calcd.: 315.0718, found: 315.0745 (GC-HRMS).

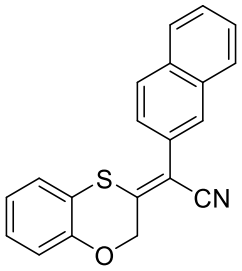


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*E*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-2-(naphthalen-2-yl)acetonitrile (*anti*-2f)



Compound ***anti*-2f** was isolated as an off-white solid.

m.p.: 106 °C.

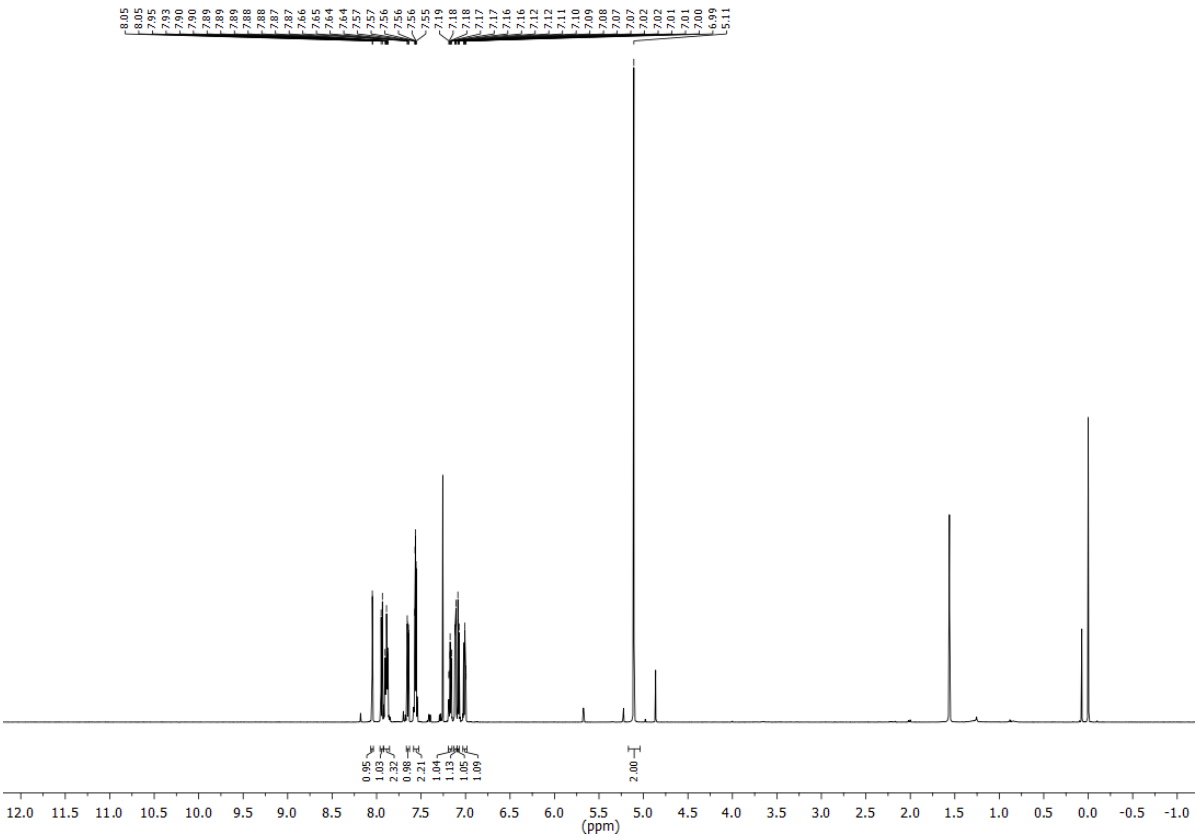
R_f = 0.42 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 5.11 (s, 2H), 7.01 (td, *J* = 7.5, 1.3 Hz, 1H), 7.08 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.11 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.17 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.54 – 7.59 (m, 2H), 7.65 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.86 – 7.91 (m, 2H), 7.94 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 1.8 Hz, 1H).

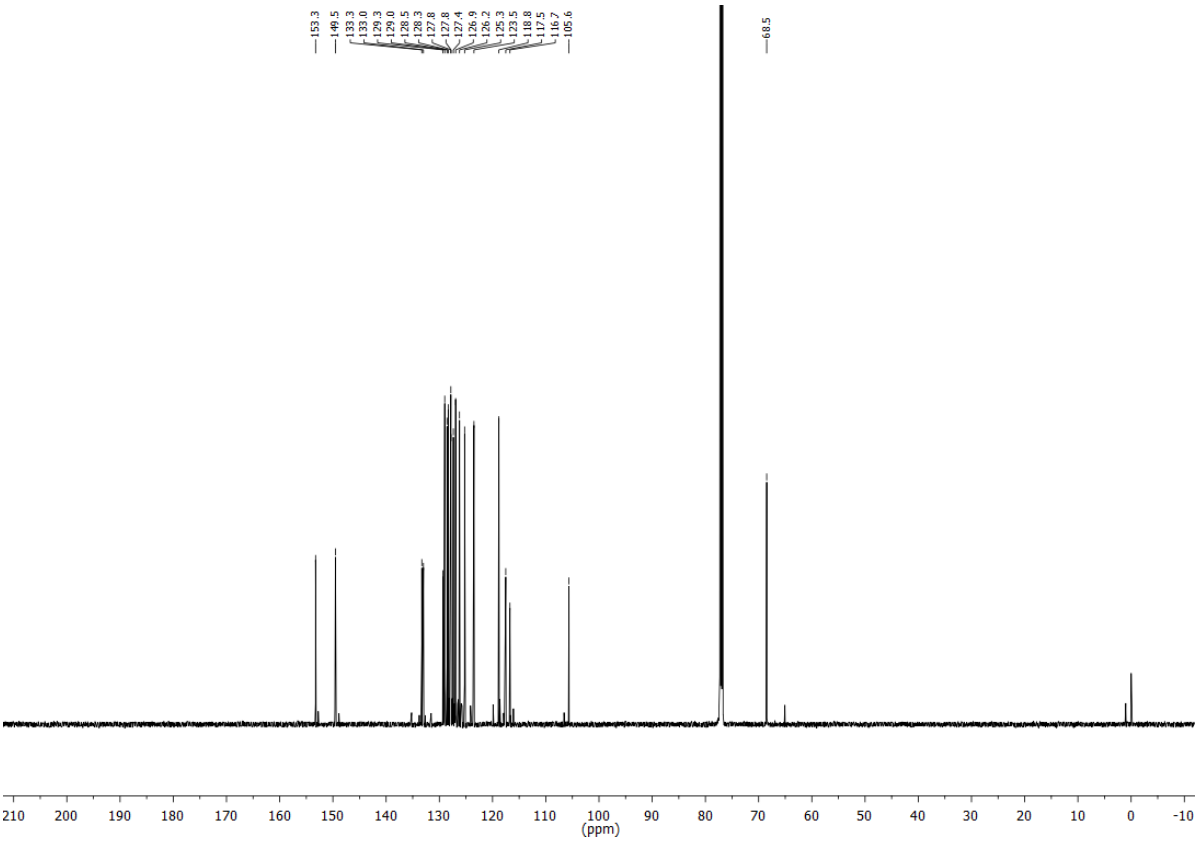
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 68.5, 105.6, 116.7, 117.5, 118.8, 123.5, 125.3, 126.2, 126.9, 127.4, 127.8, 127.8, 128.3, 128.5, 129.0, 129.3, 133.0, 133.3, 149.5, 153.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3051, 3019, 2923, 2900, 2851, 2203, 1579, 1551, 1469, 1439, 1266, 1210, 1145, 1015.

$C_{20}H_{13}NOS$ calcd.: 315.0718, found: 315.0740 (GC-HRMS).

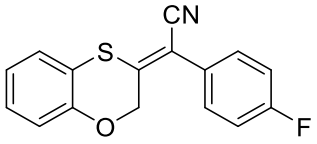


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-2-(4-fluorophenyl)acetonitrile (*syn*-2g)



Compound **1g** (29.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds ***syn*-2g** and ***anti*-2g** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a mixture (22.3 mg, 79 µmol, 77%). The isomers were separated by HPLC and the ratio of *syn*/*anti* (1.0/1.5) was determined by ^{1}H-NMR.

Compound ***syn*-2g** was isolated as an off-white solid.

m.p.: 108 °C.

R_f = 0.29 (*n*-pentane:EtOAc = 20:1).

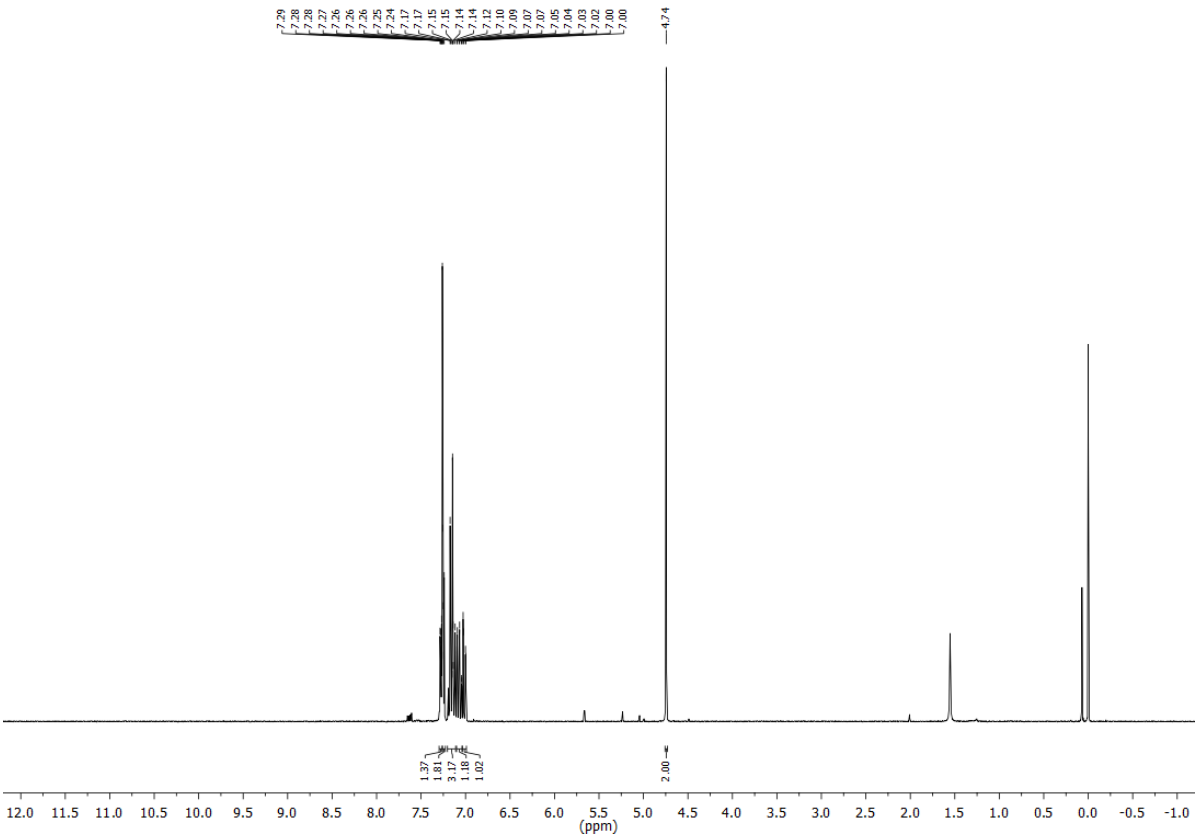
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.74 (s, 2H), 7.01 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.04 – 7.10 (m, 1H), 7.11 – 7.20 (m, 3H), 7.23 – 7.30 (m, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 64.88, 105.33, 116.29 (d, *J* = 22.0 Hz), 117.75, 118.63, 123.74, 126.43, 127.63, 127.79, 127.82, 131.04 (d, *J* = 8.5 Hz), 149.75, 152.64, 163.00 (d, *J* = 250.8 Hz).

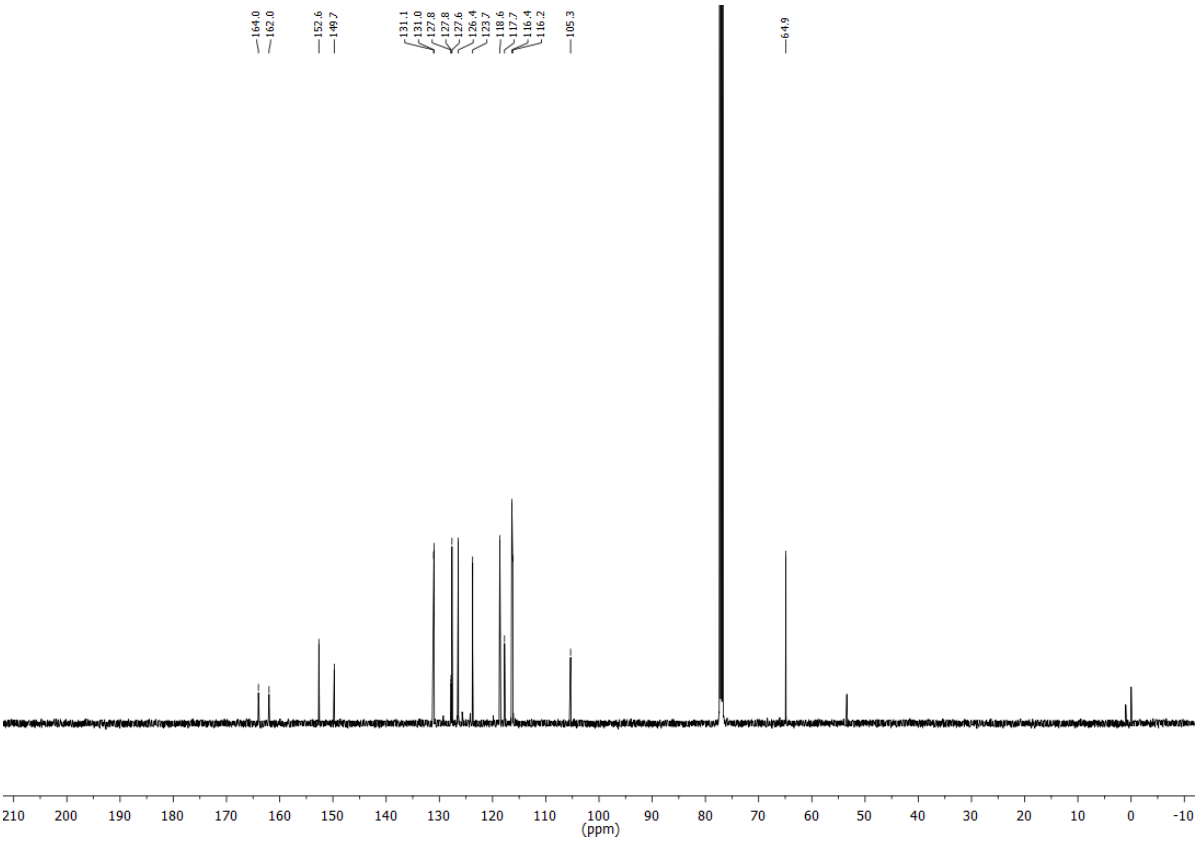
^{19}F NMR (377 MHz, $CDCl_3$) δ = -111.15.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 2956, 2920, 2853, 2197, 1589, 1555, 1502, 1474, 1444, 1222, 1141, 1042, 1002.

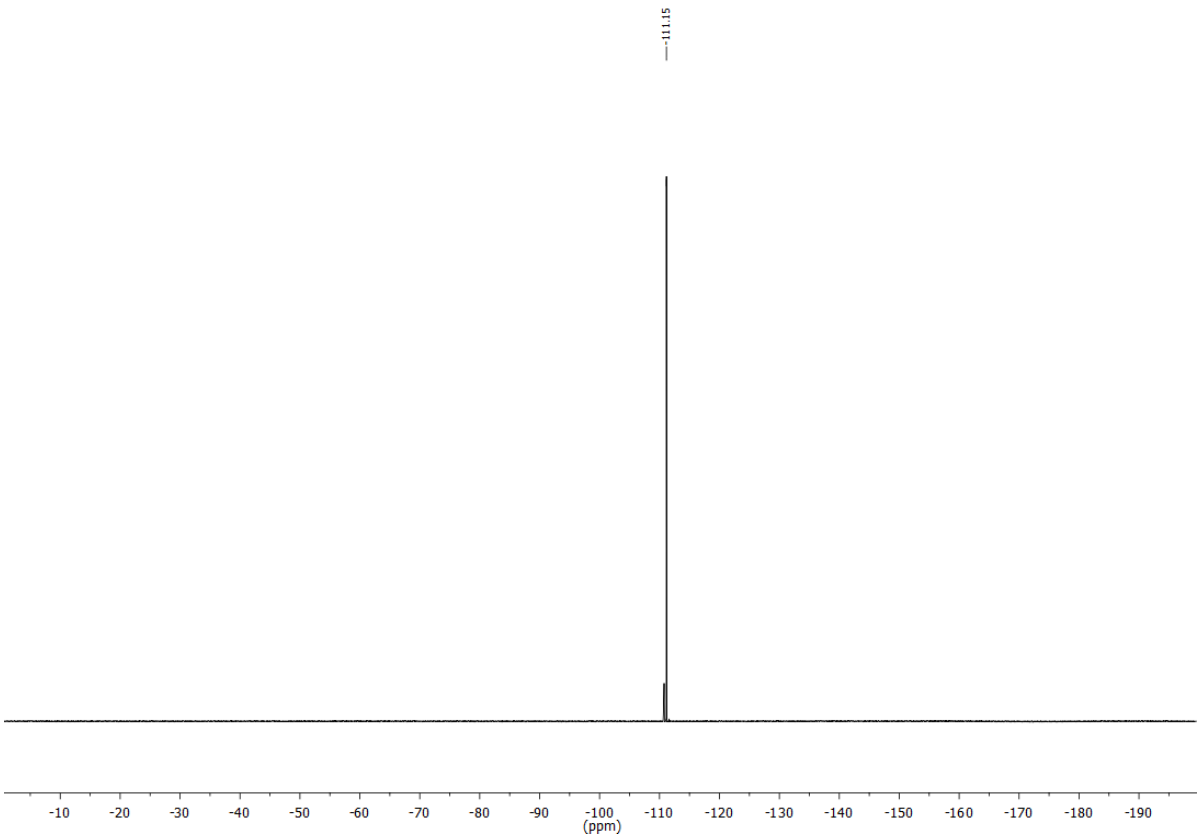
$C_{16}H_{10}FNOS$ calcd.: 283.0467, found: 283.0486 (GC-HRMS).



^{1}H-NMR (500 MHz, $CDCl_3$).

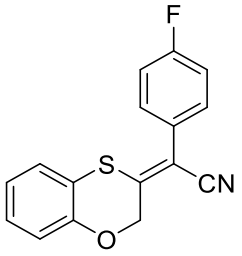


^{13}C-NMR (126 MHz, $CDCl_3$).



^{19}F-NMR (377 MHz, $CDCl_3$).

(*E*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-2-(4-fluorophenyl)acetonitrile (*anti*-2g)



Compound ***anti*-2g** was isolated as an off-white solid.

m.p.: 110 °C.

R_f = 0.39 (*n*-pentane:EtOAc = 20:1).

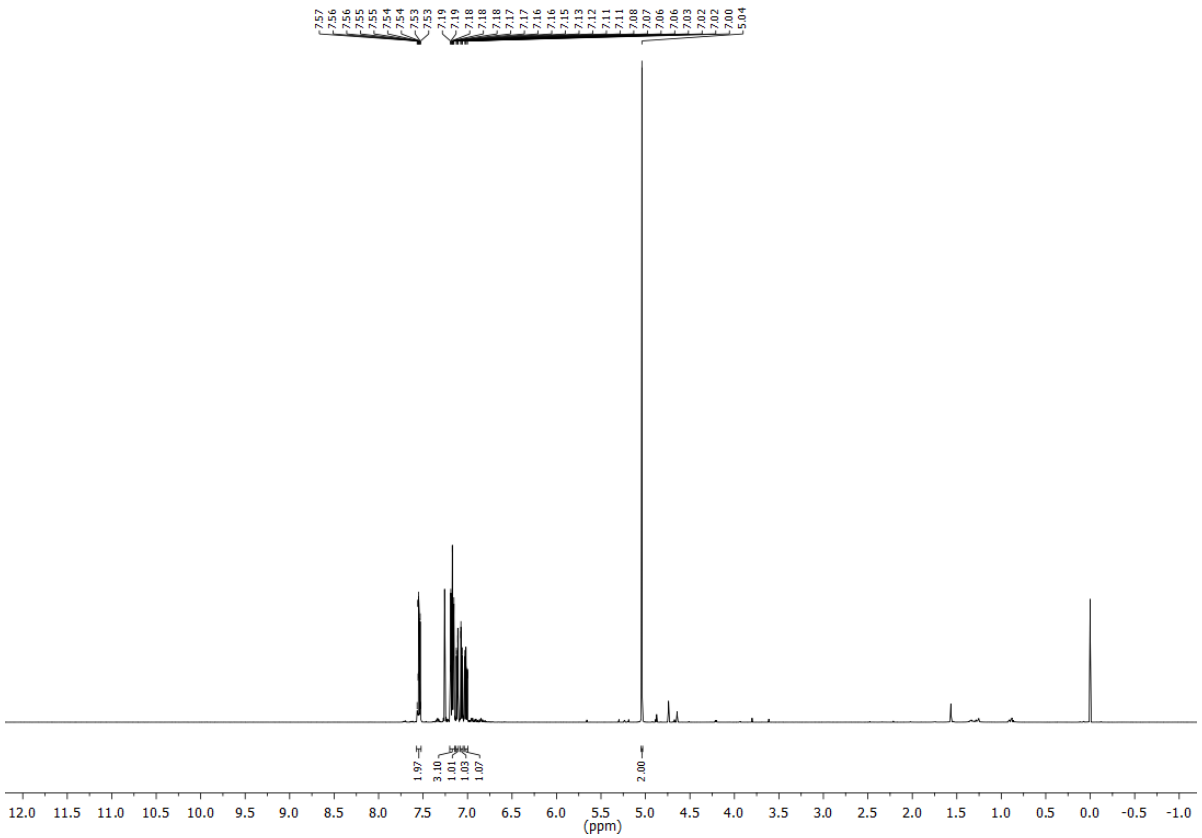
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.04 (s, 2H), 7.00 – 7.03 (m, 1H), 7.07 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.15 – 7.20 (m, 3H), 7.52 – 7.57 (m, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 68.33, 104.49, 116.26 (d, *J* = 22.1 Hz), 116.50, 117.24, 118.83, 123.55, 126.19, 127.89, 127.93 (d, *J* = 3.4 Hz), 130.62 (d, *J* = 8.6 Hz), 149.67, 153.14, 162.88 (d, *J* = 250.8 Hz).

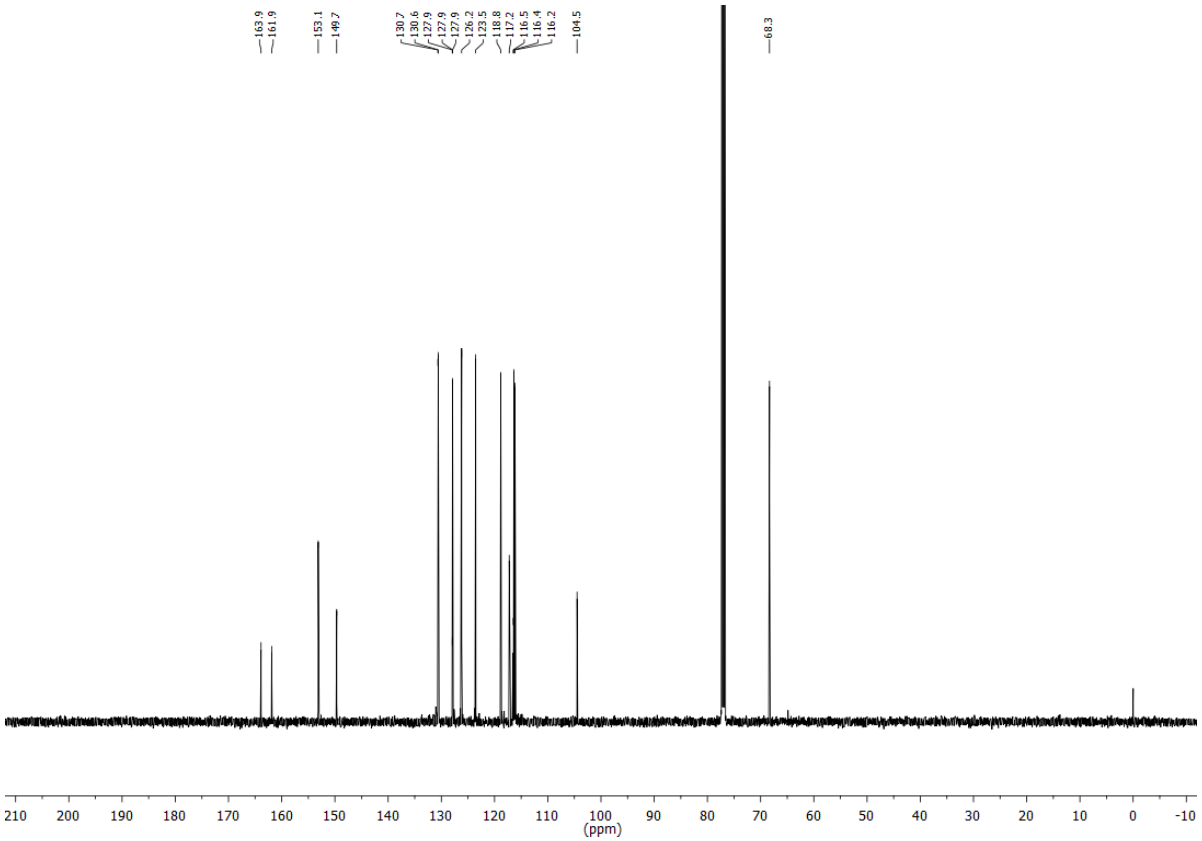
^{19}F NMR (471 MHz, $CDCl_3$) δ = -110.66.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3078, 2915, 2852, 2205, 1583, 1553, 1502, 1470, 1441, 1216, 1147, 1039, 1019.

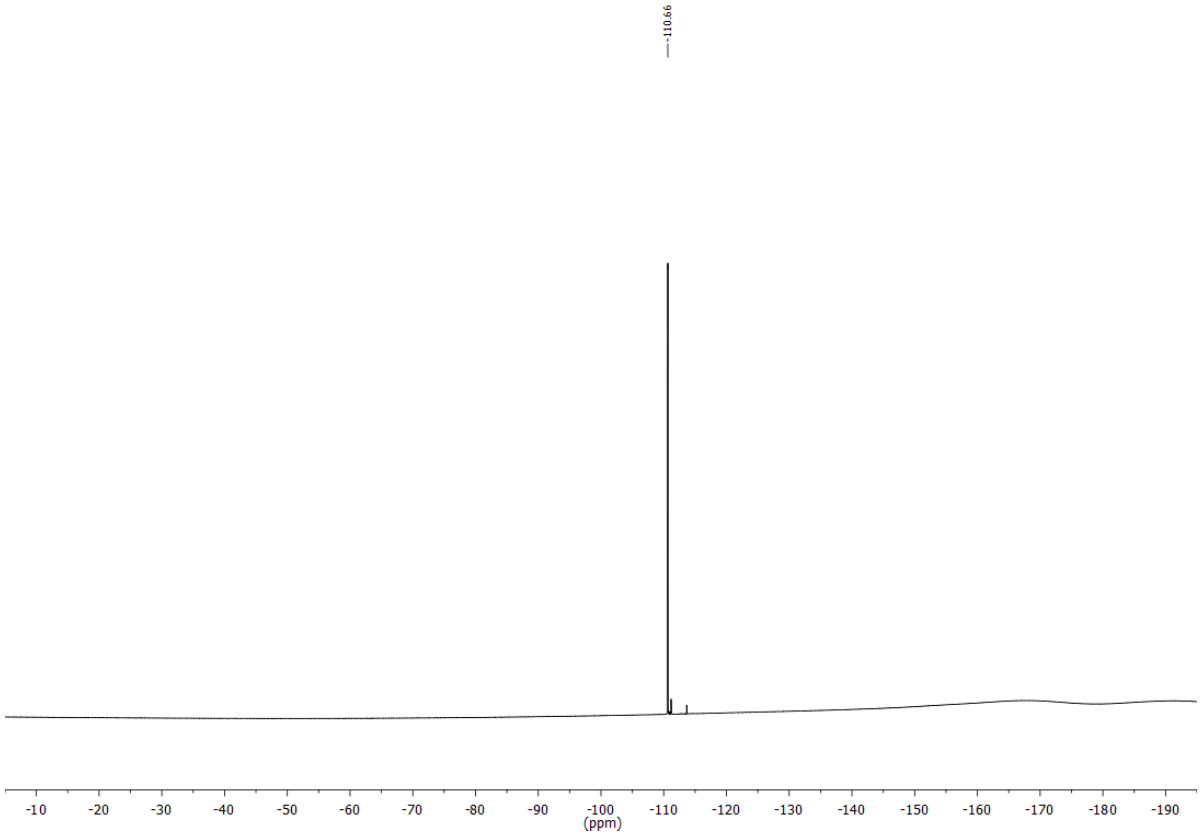
$C_{16}H_{10}FNOS$ calcd.: 283.0467, found: 283.0488 (GC-HRMS).



^{1}H-NMR (500 MHz, $CDCl_3$).

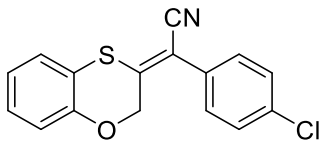


^{13}C-NMR (126 MHz, $CDCl_3$).



^{19}F-NMR (471 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-2-(4-chlorophenyl)acetonitrile (*syn*-2h)



Compound **1h** (31.0 mg, 103 µmol, 1.00 equiv.) was transformed according to GP CAT1. Purification by flash column chromatography (1st: *n*-pentane:EtOAc = 60:1, 2nd: *n*-pentane:DCM 3:1, 1st and 2nd fcc with reversed elution of isomers) lead to compounds ***syn*-2h** and ***anti*-2h** with a ratio of 1.0/2.0 (Σ = 28.1 mg, 94 µmol, 91%).

Compound ***syn*-2h** was isolated as a colorless solid.

m.p.: 122 °C.

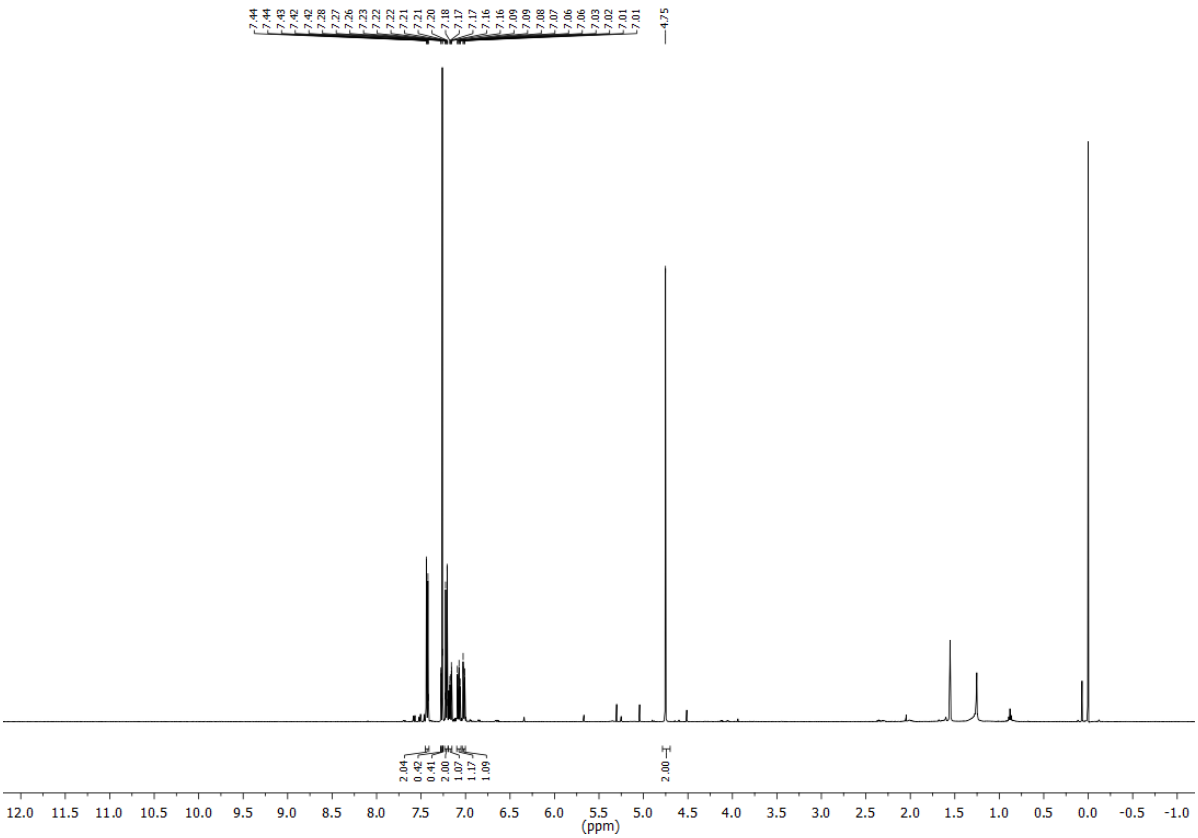
R_f = 0.32 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.75 (s, 2H), 7.01 – 7.03 (m, 1H), 7.06 – 7.10 (m, 1H), 7.15 – 7.19 (m, 1H), 7.20 – 7.23 (m, 2H), 7.25 – 7.28 (m, 1H), 7.41 – 7.45 (m, 2H).

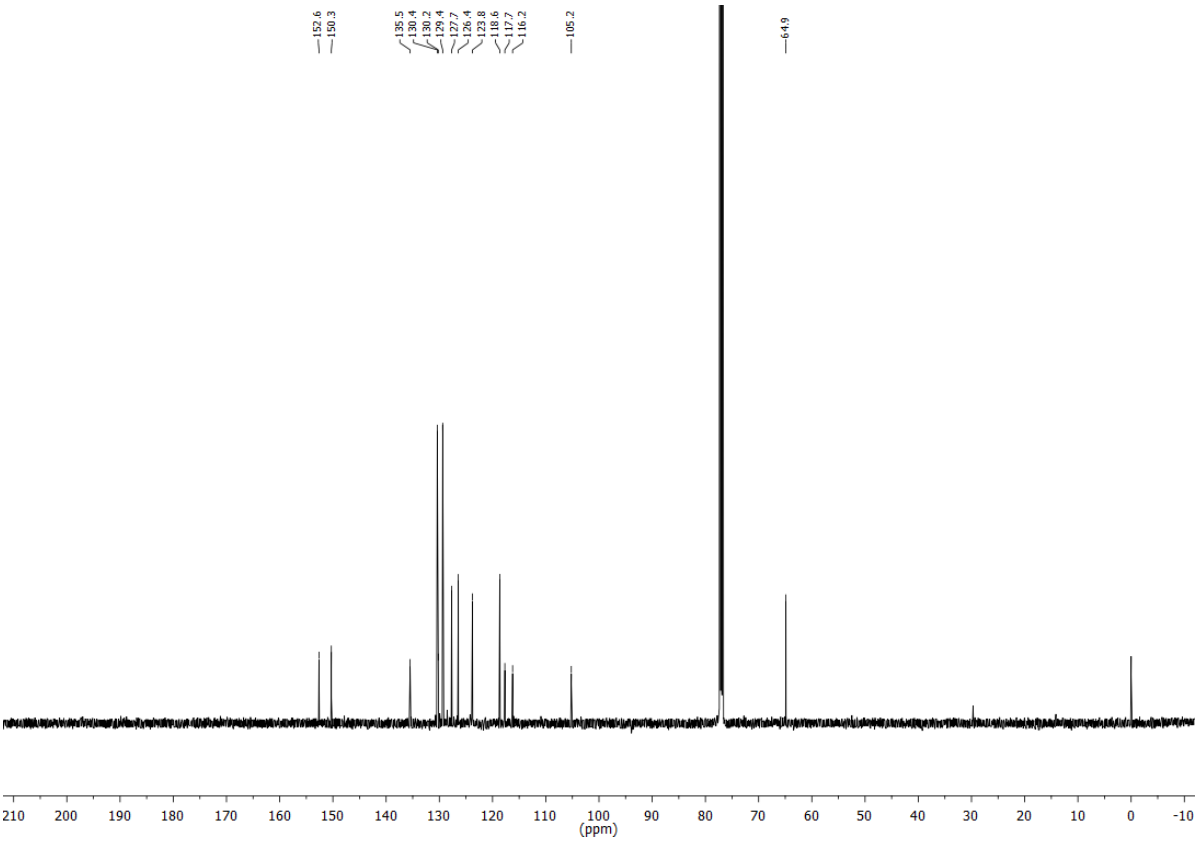
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 64.9, 105.2, 116.2, 117.7, 118.6, 123.8, 126.4, 127.7, 129.4, 130.2, 130.4, 135.5, 150.3, 152.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3060, 2921, 2851, 2202, 1580, 1551, 1470, 1262, 1218, 1092, 1045, 1008.

$C_{16}H_{10}ClNOS$ calcd.: 299.0172, found: 299.0180 (GC-HRMS).

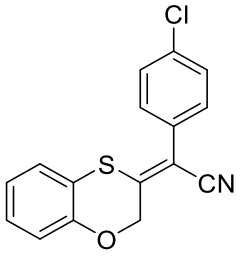


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-2-(4-chlorophenyl)acetonitrile (*anti*-2h)



Compound ***anti*-2h** was isolated as an off-white solid.

m.p.: 125 °C.

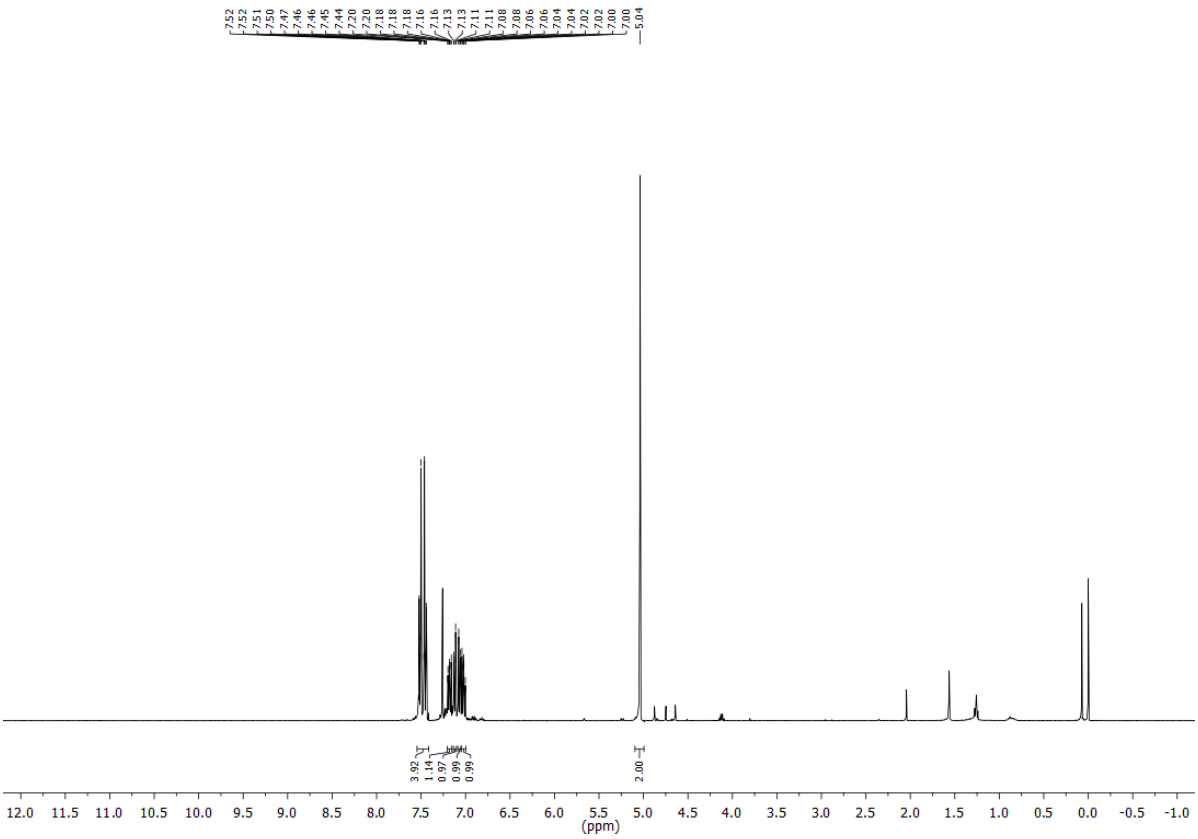
R_f = 0.36 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.04 (s, 2H), 6.99 – 7.05 (m, 1H), 7.07 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.12 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.15 – 7.21 (m, 1H), 7.43 – 7.54 (m, 4H).

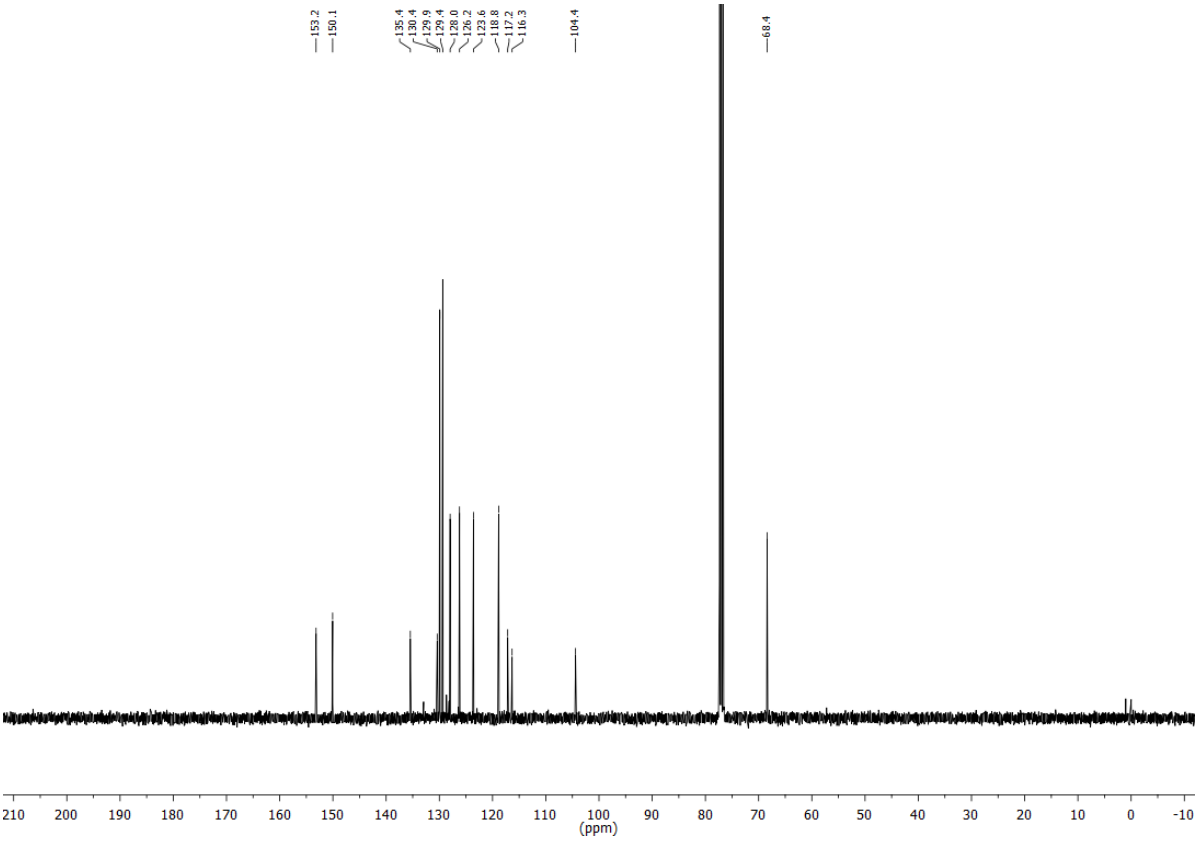
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 68.4, 104.4, 116.3, 117.2, 118.8, 123.6, 126.2, 128.0, 129.4, 129.9, 130.4, 135.4, 150.1, 153.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3078, 2956, 2920, 2852, 2204, 1583, 1549, 1470, 1439, 1260, 1214, 1149, 1093, 1015.

$C_{16}H_{10}ClNOS$ calcd.: 299.0172, found: 299.0185 (GC-HRMS).

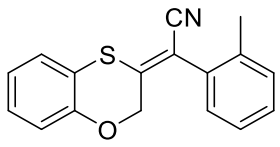


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-2-(*o*-tolyl)acetonitrile (*syn*-2i)



Compound **1i** (22.0 mg, 79 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds ***syn*-2i** and ***anti*-2i** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a mixture (19.0 mg, 68 µmol, 86%). The isomers were separated by HPLC and the ratio of *syn*/*anti* (2.0/1.0) was determined by ^{1}H-NMR.

Compound ***syn*-2i** was isolated as a colorless oil.

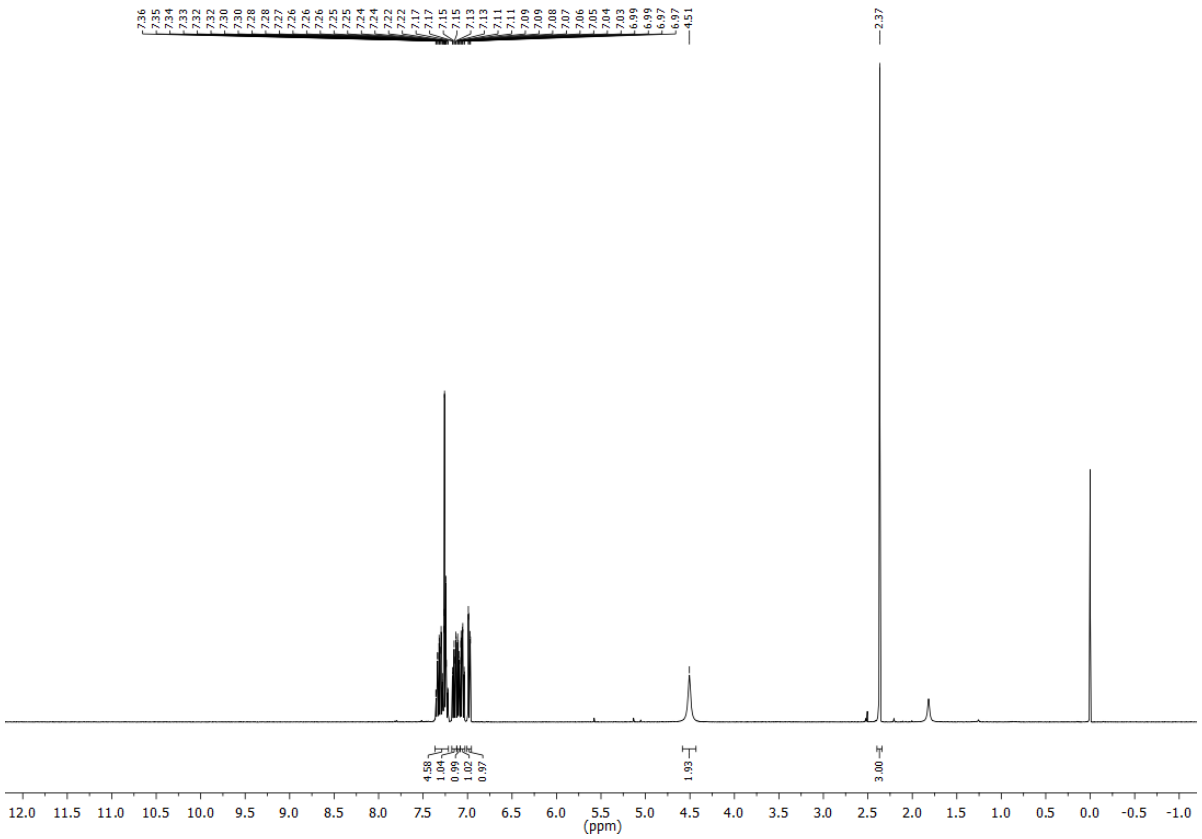
R_f = 0.38 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 4.51 (s, 2H), 6.98 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.06 (td, *J* = 7.6, 1.4 Hz, 1H), 7.10 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.12 – 7.17 (m, 1H), 7.22 – 7.36 (m, 4H).

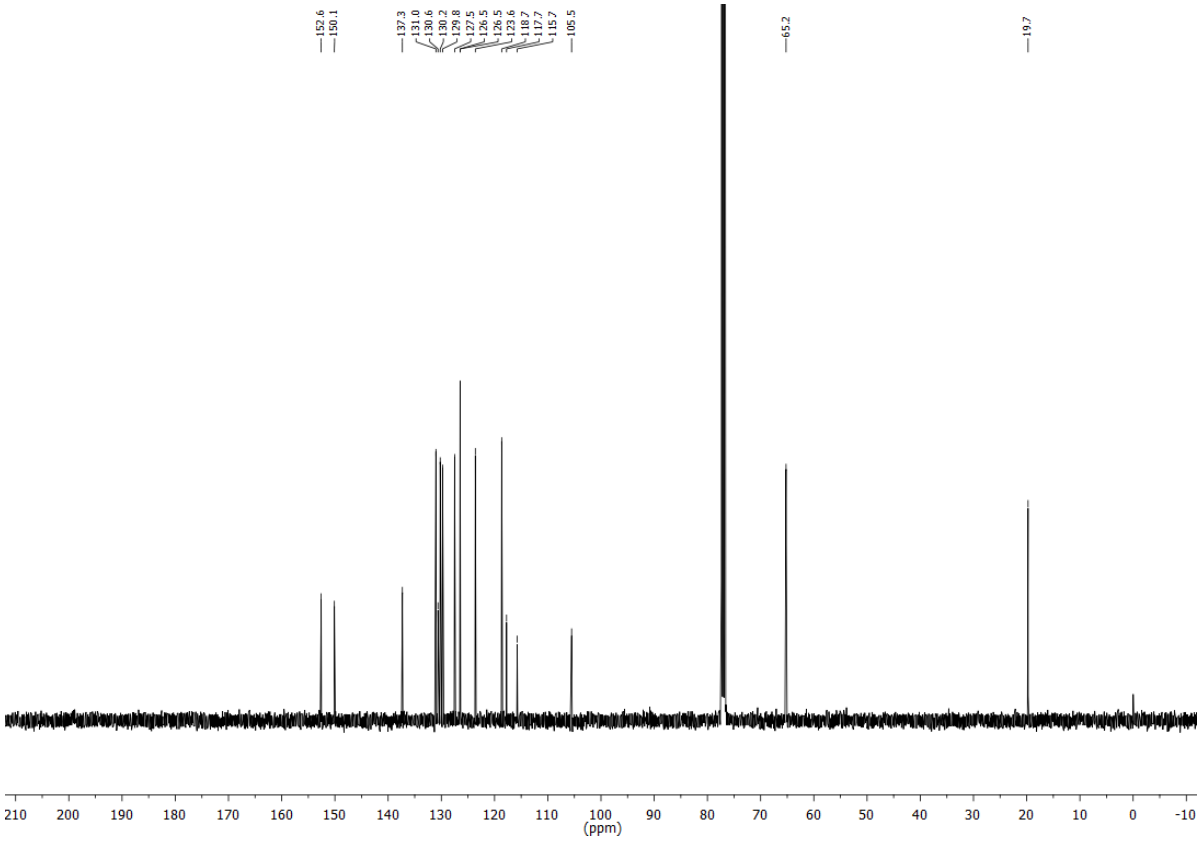
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 19.7, 65.2, 105.5, 115.7, 117.7, 118.7, 123.6, 126.5, 126.5, 127.5, 129.8, 130.2, 130.6, 131.0, 137.3, 150.1, 152.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 3018, 2917, 2856, 2202, 1583, 1471, 1444, 1261, 1215, 1148, 1045, 1001.

$C_{17}H_{13}NOS$ calcd.: 279.0718, found: 279.0741 (GC-HRMS).

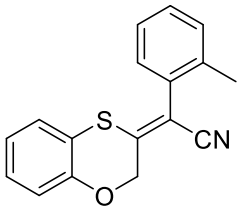


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*E*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-2-(*o*-tolyl)acetonitrile (*anti*-2i)



Compound ***anti*-2i** was isolated as a colorless oil.

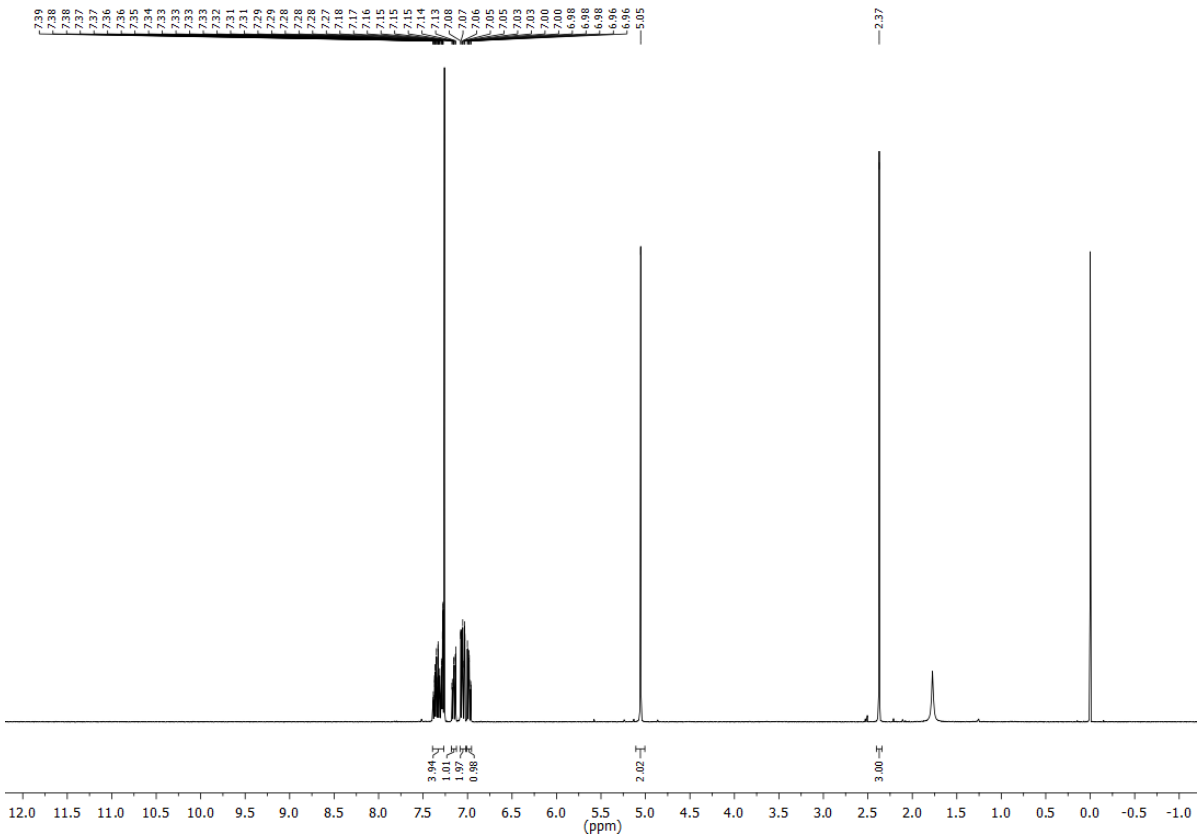
R_f = 0.40 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 5.05 (s, 2H), 6.96 – 7.01 (m, 1H), 7.02 – 7.09 (m, 2H), 7.15 (ddd, *J* = 8.2, 7.1, 1.8 Hz, 1H), 7.27 – 7.40 (m, 4H).

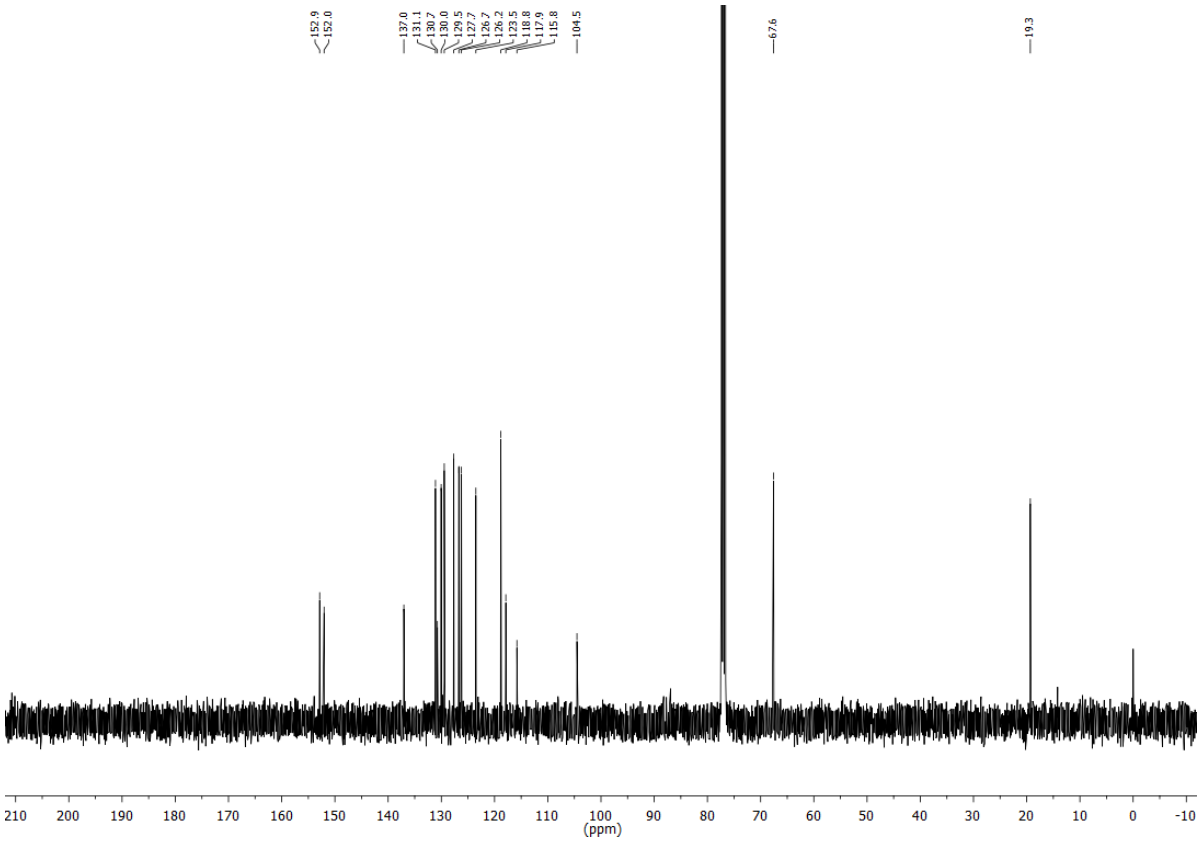
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 19.3, 67.6, 104.5, 115.8, 117.9, 118.8, 123.5, 126.2, 126.7, 127.7, 129.5, 130.0, 130.7, 131.1, 137.0, 152.0, 152.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063, 3020, 2916, 2855, 2201, 1587, 1474, 1444, 1266, 1217, 1154, 1034.

$C_{17}H_{13}NOS$ calcd.: 279.0718, found: 279.0739 (GC-HRMS).

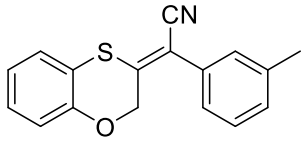


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-2-(*m*-tolyl)acetonitrile (*syn*-2j)



Compound **1j** (28.0 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT1. Purification by flash column chromatography (*n*-pentane:EtOAc = 60:1) lead to compounds ***syn*-2j** and ***anti*-2j** with a ratio of 1.0/1.0 (Σ = 23.6 mg, 84 µmol, 84%).

Compound ***syn*-2j** was isolated as a colorless solid.

m.p.: 108 °C.

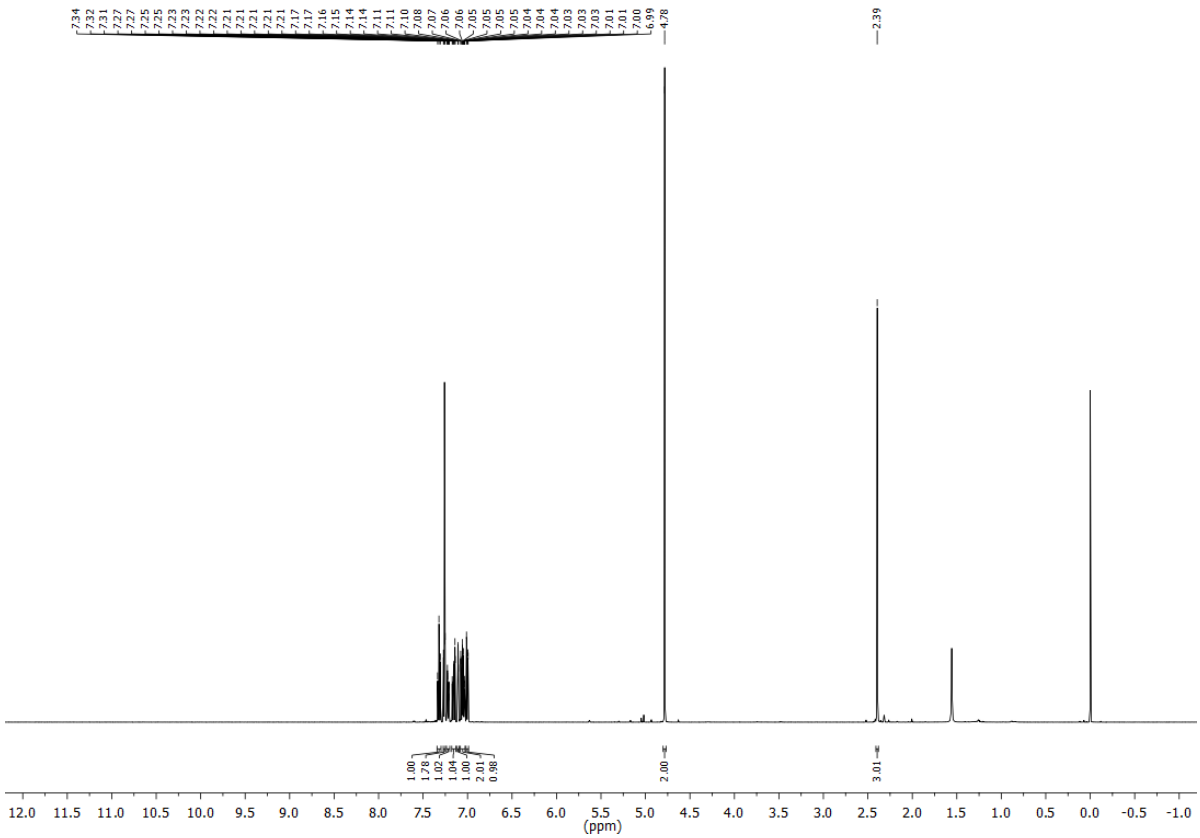
R_f = 0.36 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 4.78 (s, 2H), 7.00 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.03 – 7.08 (m, 2H), 7.09 – 7.12 (m, 1H), 7.13 – 7.18 (m, 1H), 7.21 – 7.23 (m, 1H), 7.26 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H).

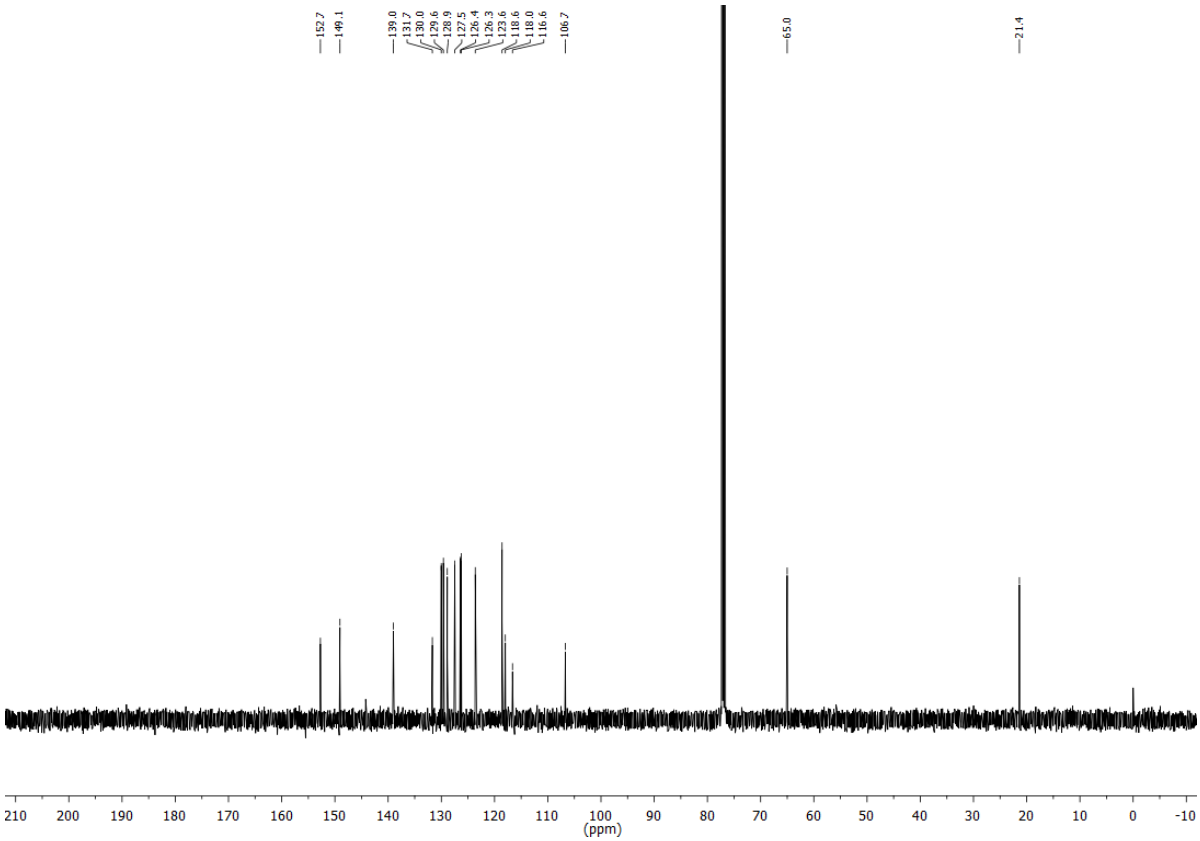
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 65.0, 106.7, 116.6, 118.0, 118.6, 123.6, 126.3, 126.4, 127.5, 128.9, 129.6, 130.0, 131.7, 139.0, 149.1, 152.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2953, 2919, 2856, 2199, 1582, 1556, 1471, 1443, 1261, 1219, 1138, 1059, 998.

$C_{17}H_{13}NOS$ calcd.: 279.0718, found: 279.0734 (GC-HRMS).

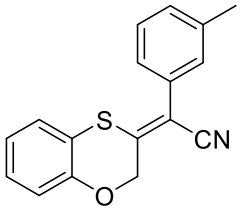


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-2-(Benzo[b][1,4]oxathiin-3(2*H*)-ylidene)-2-(*m*-tolyl)acetonitrile (*anti*-2j)



Compound ***anti*-2j** was isolated as a colorless oil.

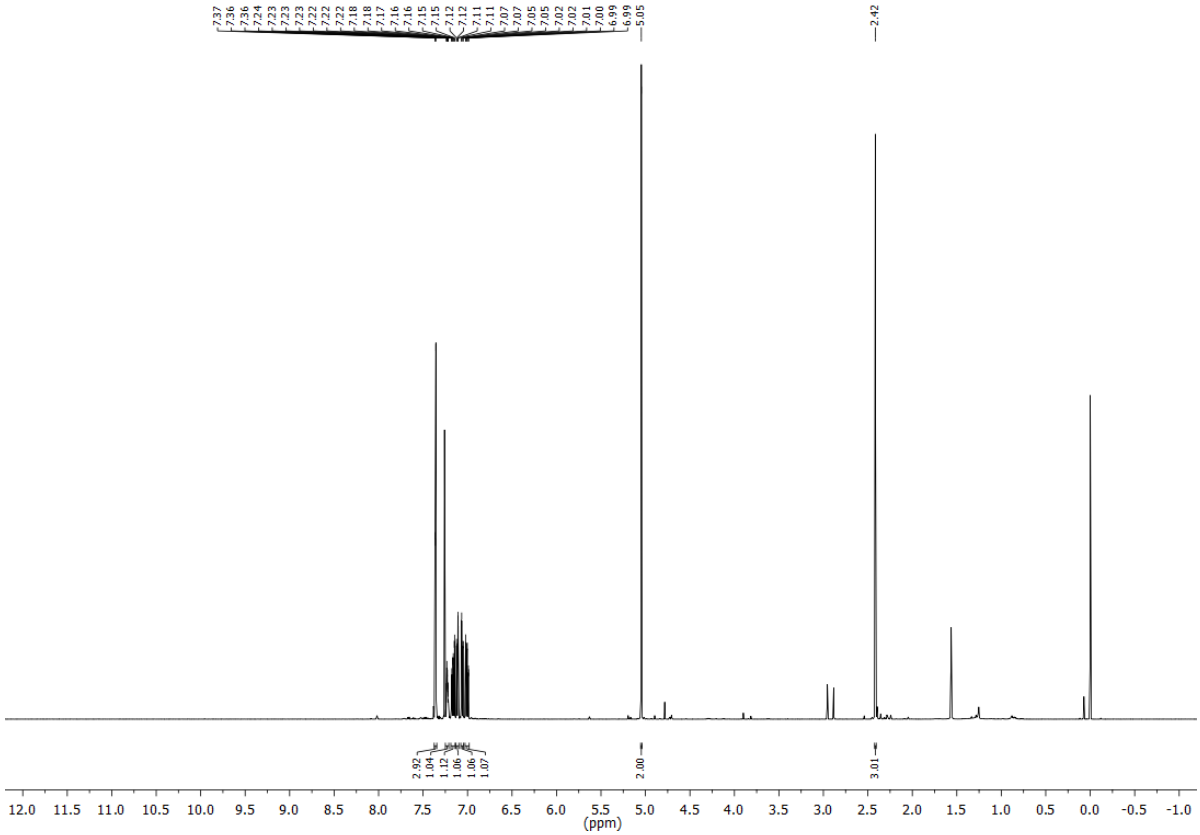
R_f = 0.45 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 5.05 (s, 2H), 6.98 – 7.03 (m, 1H), 7.06 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.11 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.14 – 7.18 (m, 1H), 7.21 – 7.25 (m, 1H), 7.34 – 7.38 (m, 3H).

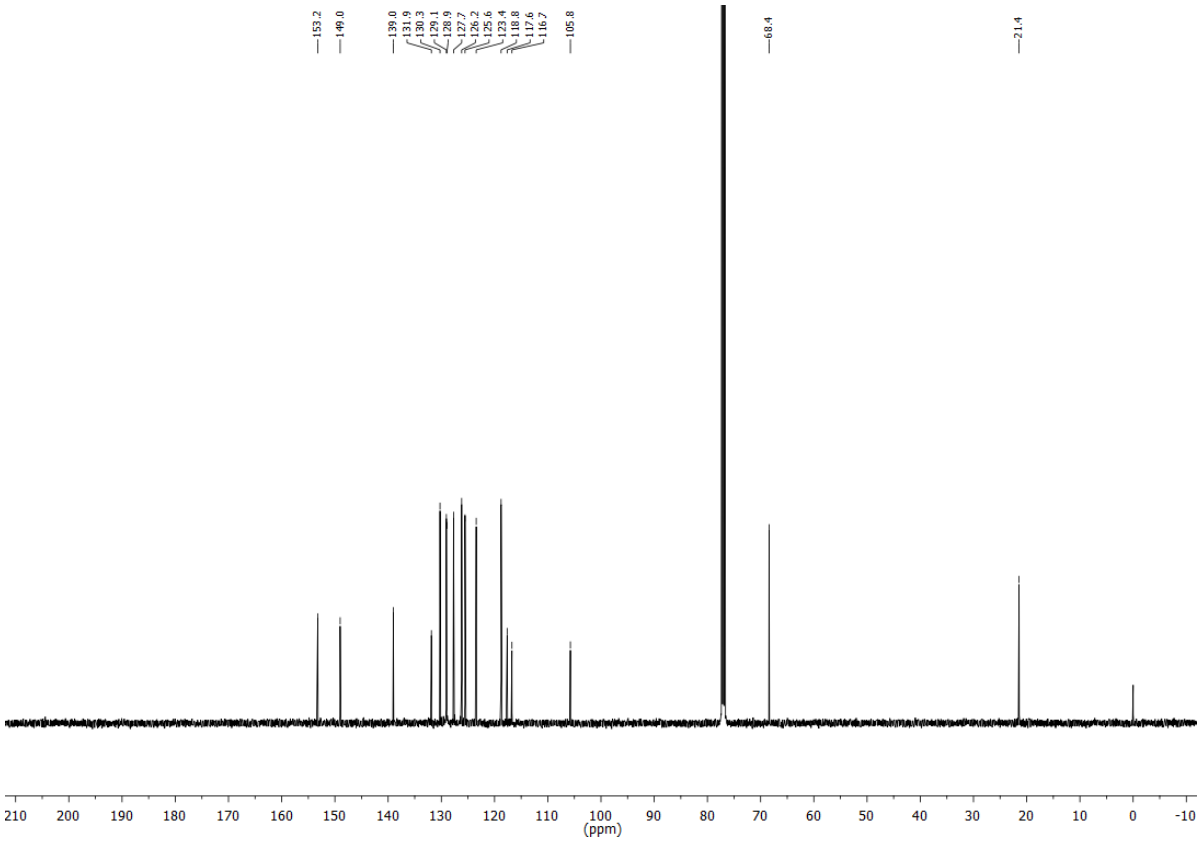
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 68.4, 105.8, 116.7, 117.6, 118.8, 123.4, 125.6, 126.2, 127.7, 128.9, 129.1, 130.3, 131.9, 139.0, 149.0, 153.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3059, 2918, 2857, 2205, 1584, 1473, 1444, 1262, 1219, 1143, 1038.

$C_{17}H_{13}NOS$ calcd.: 279.0718, found: 279.0722 (GC-HRMS).

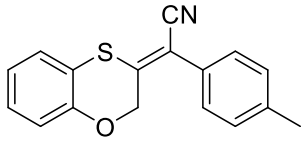


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-2-(*p*-tolyl)acetonitrile (*syn*-2k)



Compound **1k** (9.0 mg, 32 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds ***syn*-2k** and ***anti*-2k** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a mixture (6.5 mg, 23 µmol, 72%). The isomers were separated by HPLC and the ratio of *syn*/*anti* (1.0/1.7) was determined by ^{1}H-NMR.

Compound ***syn*-2k** was isolated as a colorless solid.

m.p.: 150 °C.

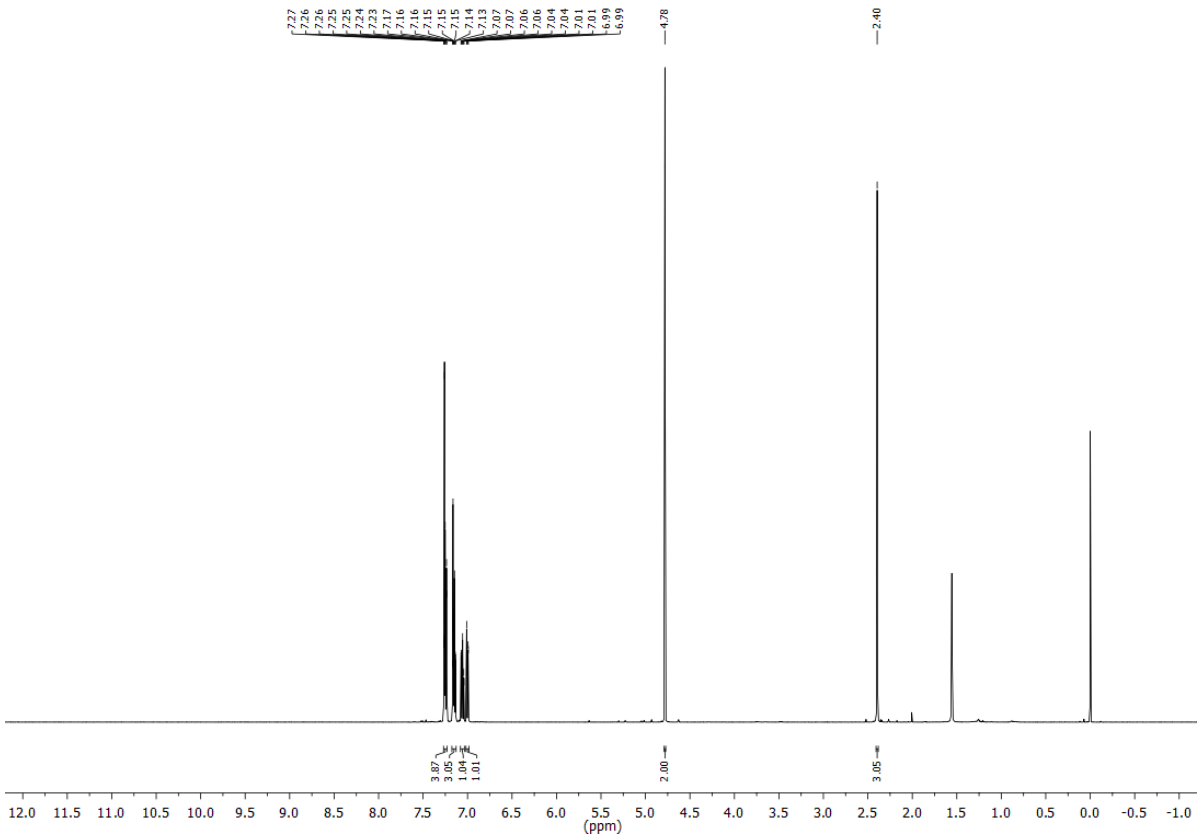
R_f = 0.34 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 4.78 (s, 2H), 7.00 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.06 (td, *J* = 7.6, 1.4 Hz, 1H), 7.13 – 7.17 (m, 3H), 7.23 – 7.27 (m, 3H).

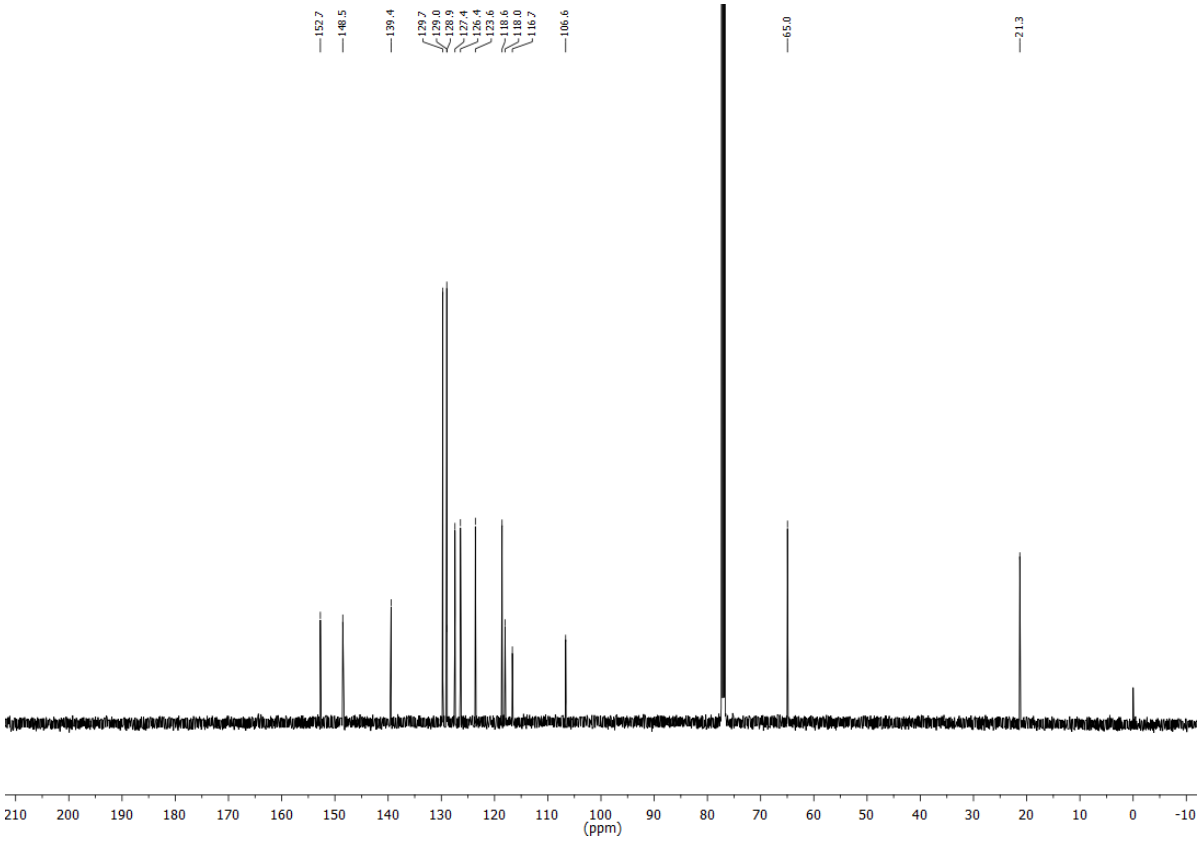
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.3, 65.0, 106.6, 116.7, 118.0, 118.6, 123.6, 126.4, 127.4, 128.9, 129.0, 129.7, 139.4, 148.5, 152.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2952, 2920, 2851, 2208, 1580, 1555, 1469, 1443, 1262, 1215, 1141, 1118, 1052, 1003.

$C_{17}H_{13}NOS$ calcd.: 279.0718, found: 279.07280 (GC-HRMS).

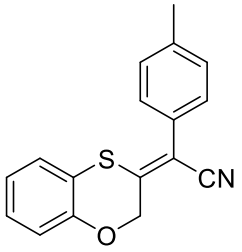


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-2-(*p*-tolyl)acetonitrile (*anti*-2k)



Compound ***anti*-2k** was isolated as a colorless solid.

m.p.: 88 °C.

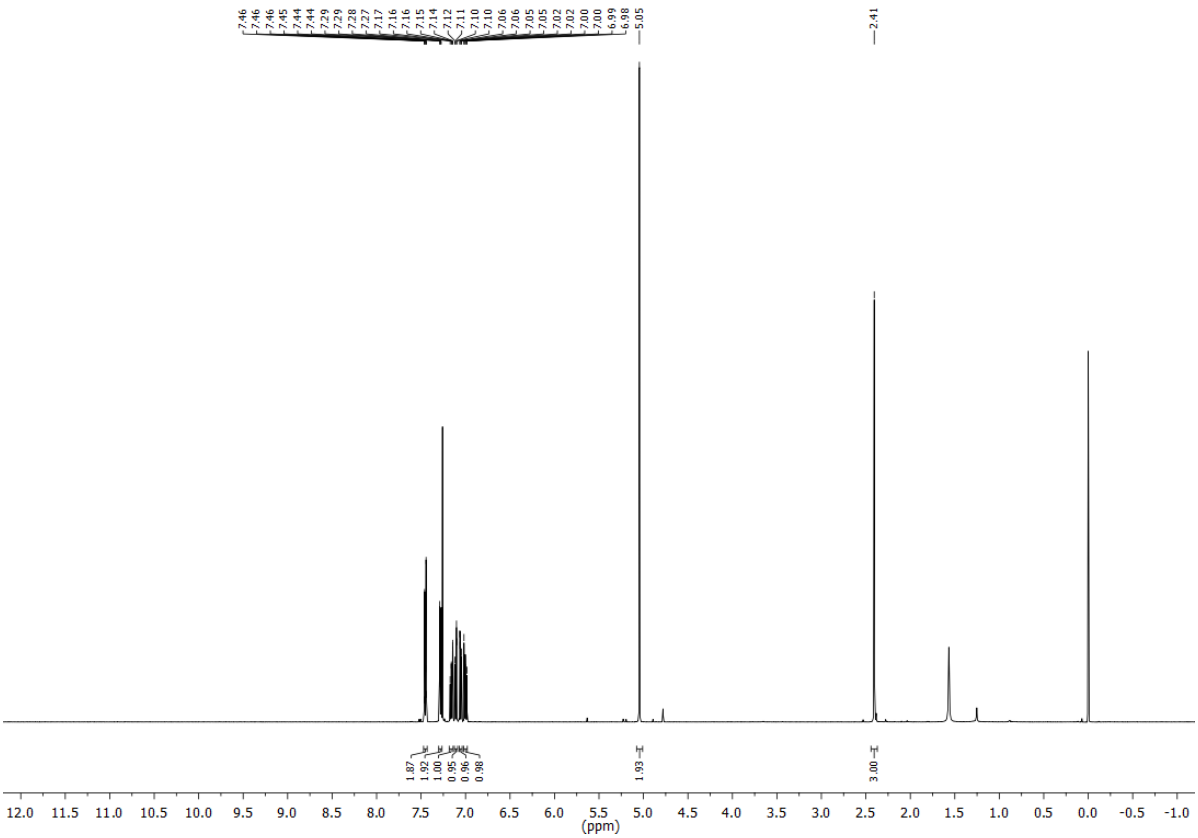
R_f = 0.42 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 5.05 (s, 2H), 6.98 – 7.03 (m, 1H), 7.04 – 7.07 (m, 1H), 7.11 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.14 – 7.18 (m, 1H), 7.26 – 7.30 (m, 2H), 7.43 – 7.47 (m, 2H).

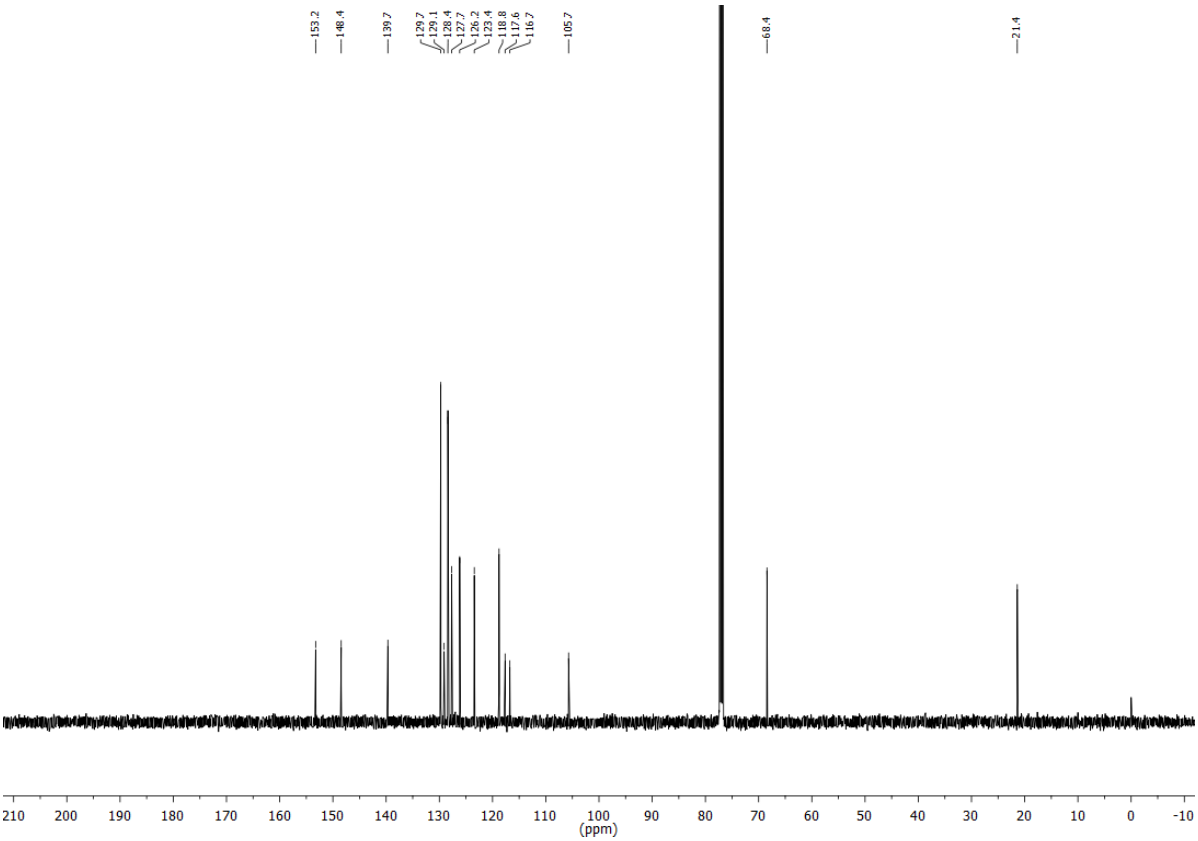
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 68.4, 105.7, 116.7, 117.6, 118.8, 123.4, 126.2, 127.7, 128.4, 129.1, 129.7, 139.7, 148.4, 153.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 3022, 2916, 2857, 2203, 1579, 1505, 1469, 1438, 1263, 1209, 1142, 1027.

$C_{17}H_{13}NOS$ calcd.: 279.0718, found: 279.0742 (GC-HRMS).

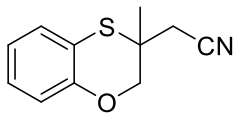


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

2-(3-Methyl-2,3-dihydrobenzo[*b*][1,4]oxathiin-3-yl)acetonitrile (2l)



Compound **1l** (20.5 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT2 (160 °C, DMF, 6 h) to obtain product **2l** after flash column chromatography (*n*-pentane:EtOAc = 20:1→10:1) as an off-colorless oil (2.1 mg, 10.0 µmol, 10%).

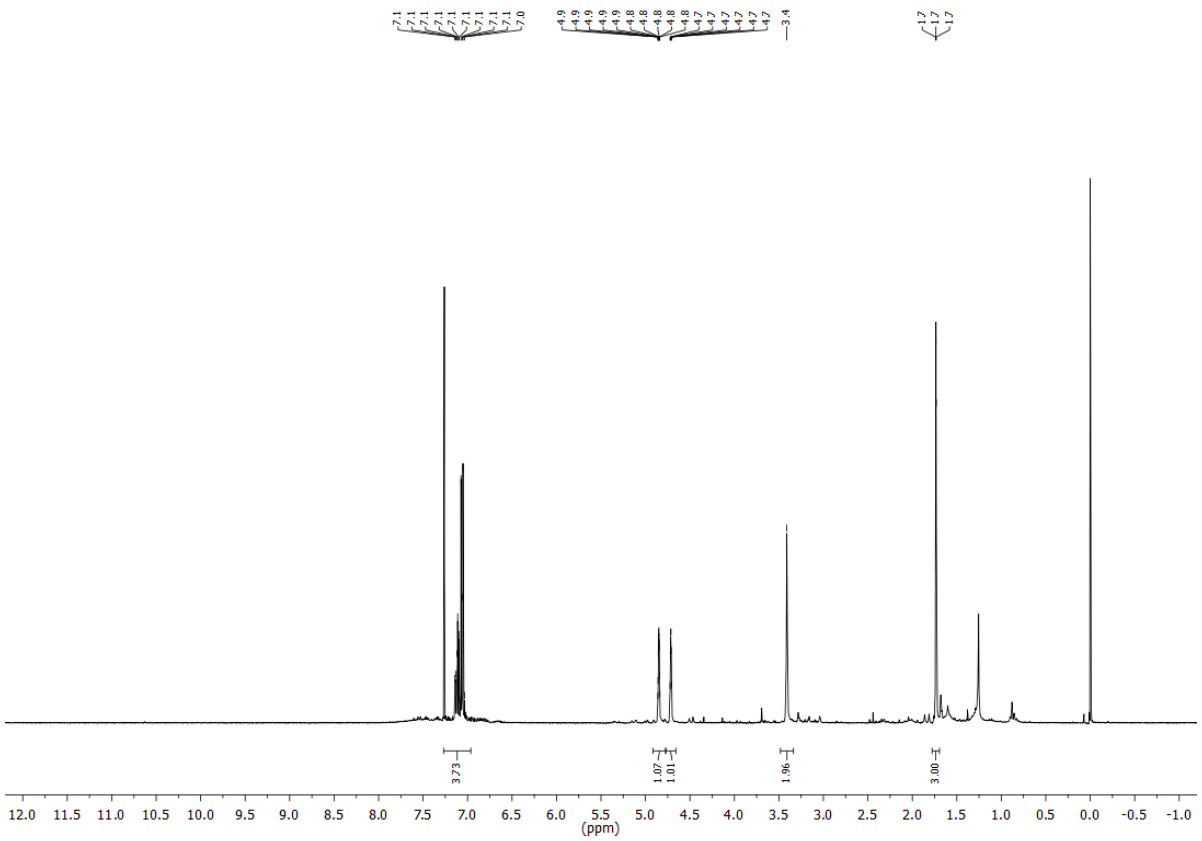
R_f = 0.05 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.7 (t, *J*=1.1, 3H), 3.4 (s, 2H), 4.7 – 4.8 (m, 1H), 4.8 – 4.9 (m, 1H), 7.0 – 7.2 (m, 4H).

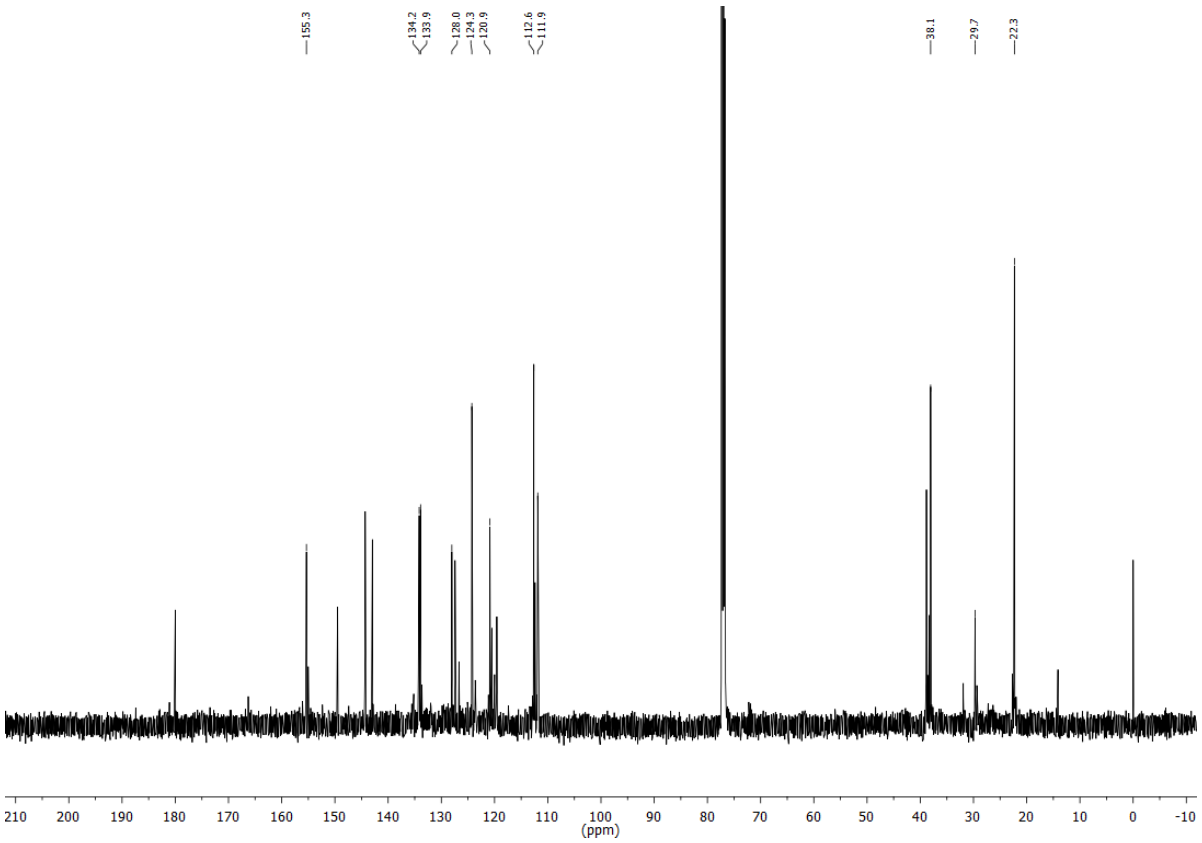
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 22.3, 29.7, 38.1, 111.9, 112.6, 120.9, 124.3, 128.0, 133.9, 134.2, 155.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3186, 3075, 2924, 2854, 2207, 1651, 1600, 1471, 1442, 1344, 1253, 1205, 1135.

$C_{11}H_{11}NOS$ calcd.: 205.0561, found: 205.0558 (GC-HRMS).

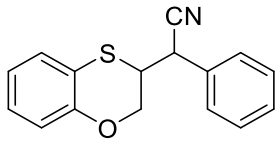


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

2-(2,3-Dihydrobenzo[*b*][1,4]oxathiin-3-yl)-2-phenylacetonitrile (2m)



Compound **1l** (244 mg, 0.91 mmol, 1.00 equiv.) was transformed according to GP CAT2 (160 °C, DMF, 6 h) to obtain product **2m** after flash column chromatography (*n*-pentane:EtOAc = 10:1) as a colorless oil (67.0 mg, 0.25 mmol, 27%).

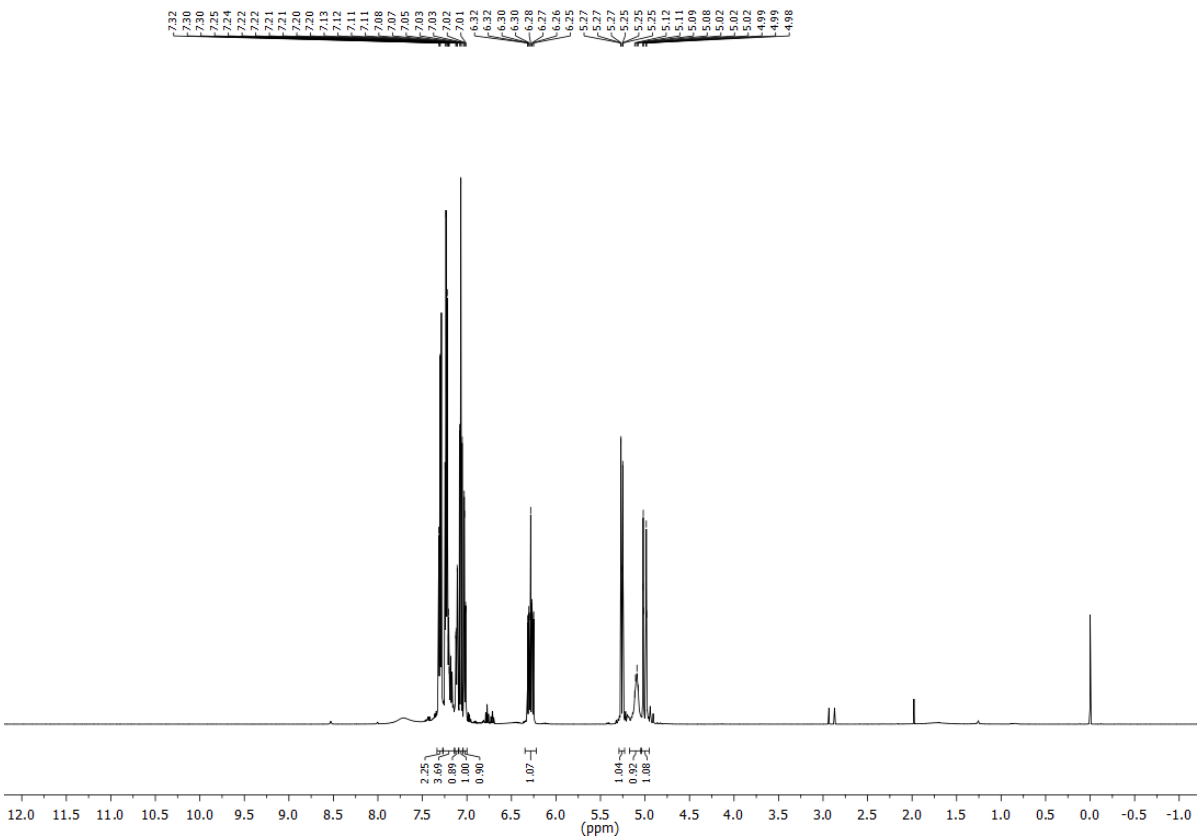
R_f = 0.23 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.00 (dt, *J*=17.1, 1.5, 1H), 5.09 (m, 1H), 5.26 (dt, *J*=10.3, 1.4, 1H), 6.28 (ddd, *J*=17.0, 10.2, 6.7, 1H), 7.02 (dd, *J*=7.7, 1.6, 1H), 7.07 (t, *J*=7.6, 1H), 7.12 (dd, *J*=7.7, 1.5, 1H), 7.19 – 7.26 (m, 4H), 7.28 – 7.33 (m, 2H).

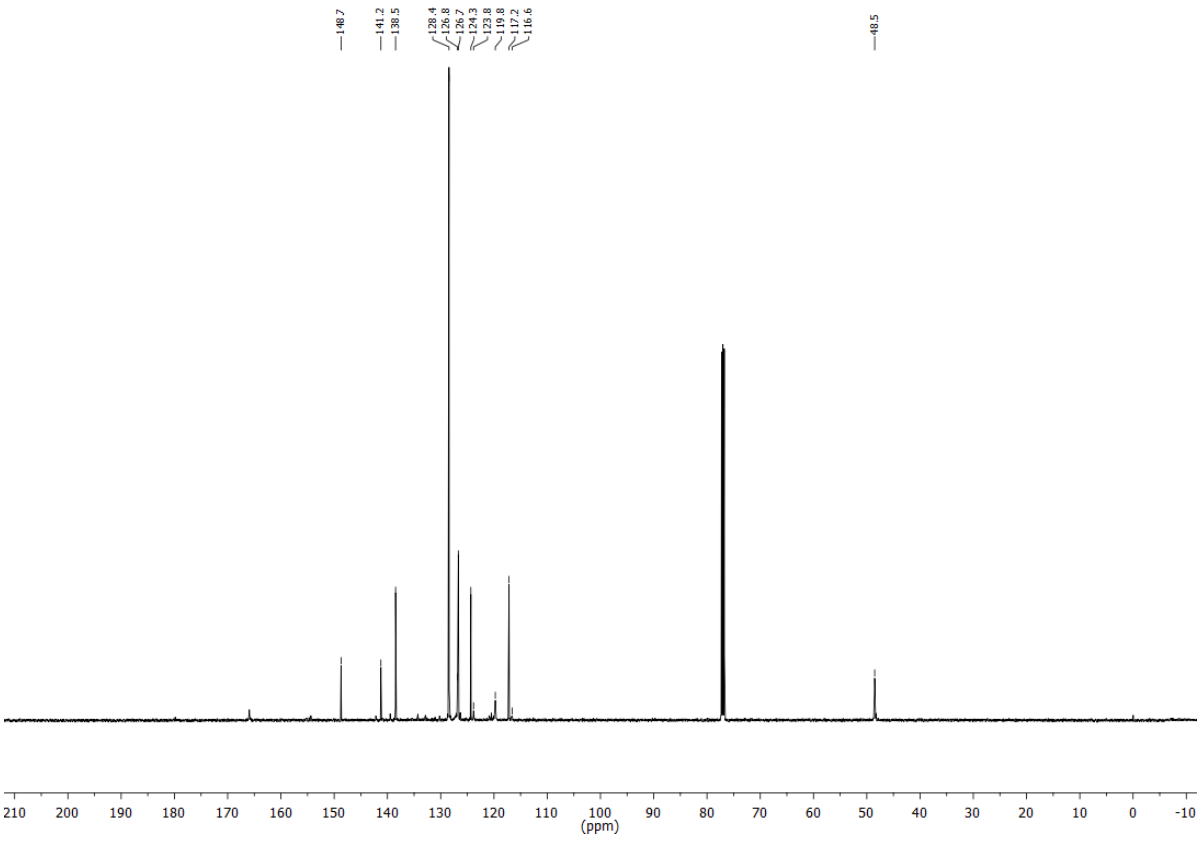
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 48.5, 116.6, 117.2, 119.8, 123.8, 124.3, 126.7, 126.8, 128.4, 138.5, 141.2, 148.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 3027, 2979, 1643, 1469, 1436, 1252, 1233, 997.

$C_{16}H_{13}NOS$ calcd.: 267.0718, found: 267.0734 (GC-HRMS).

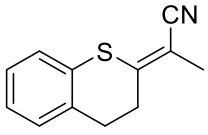


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(Thiochroman-2-ylidene)propanenitrile (2n)



Compound **1n** (29.0 mg, 144 µmol, 1.00 equiv.) was transformed according to GP CAT2 (3 h reaction time) to obtain product **2m** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a yellow solid (25.0 mg, 124 µmol, 86%).

m.p.: 80 °C.

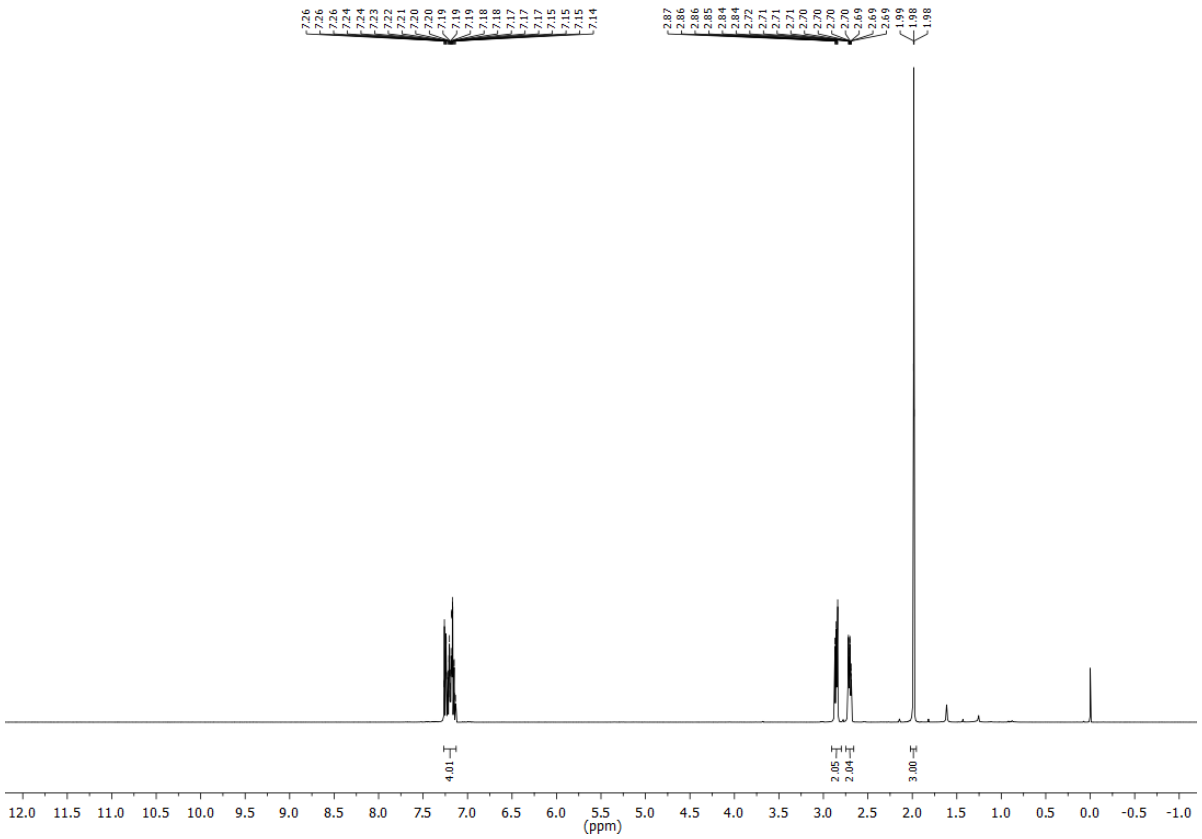
R_f = 0.26 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.98 (t, *J* = 1.1 Hz, 3H), 2.68 – 2.72 (m, 2H), 2.83 – 2.88 (m, 2H), 7.12 – 7.27 (m, 4H).

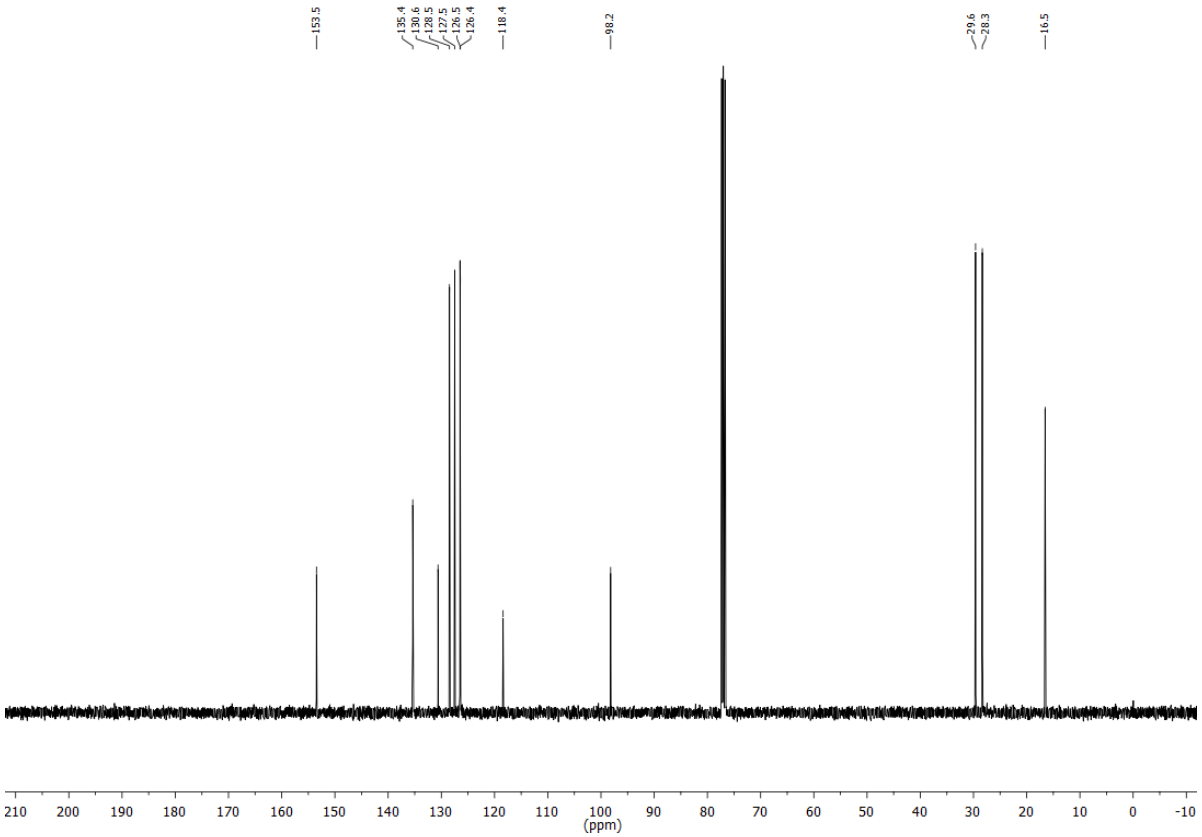
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 16.5, 28.3, 29.6, 98.2, 118.4, 126.4, 126.5, 127.5, 128.5, 130.6, 135.4, 153.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2960, 2919, 2850, 2196, 1581, 1471, 1438, 1065, 1034, 1004.

$C_{12}H_{11}NS$ calcd.: 201.0612, found: 201.0624 (GC-HRMS).

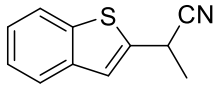


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

2-(Benzo[*b*]thien-2-yl)propanenitrile (2o)



Compound **1o** (19.0 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT2 (3 h reaction time) to obtain product **2l** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a pale yellow solid (14.0 mg, 75 µmol, 75%).

m.p.: 63 °C.

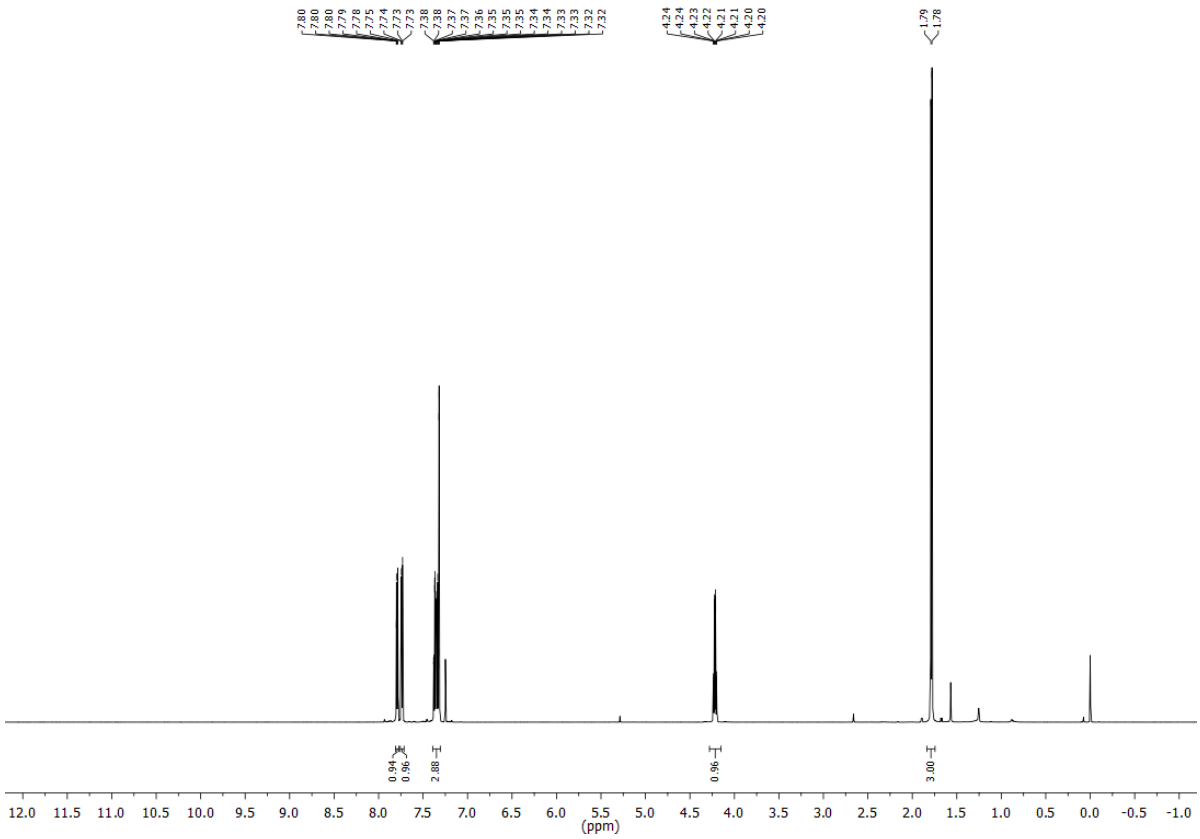
R_f = 0.42 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.79 (d, *J* = 7.3 Hz, 3H), 4.22 (qd, *J* = 7.2, 1.1 Hz, 1H), 7.31 – 7.39 (m, 3H), 7.74 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.77 – 7.81 (m, 1H).

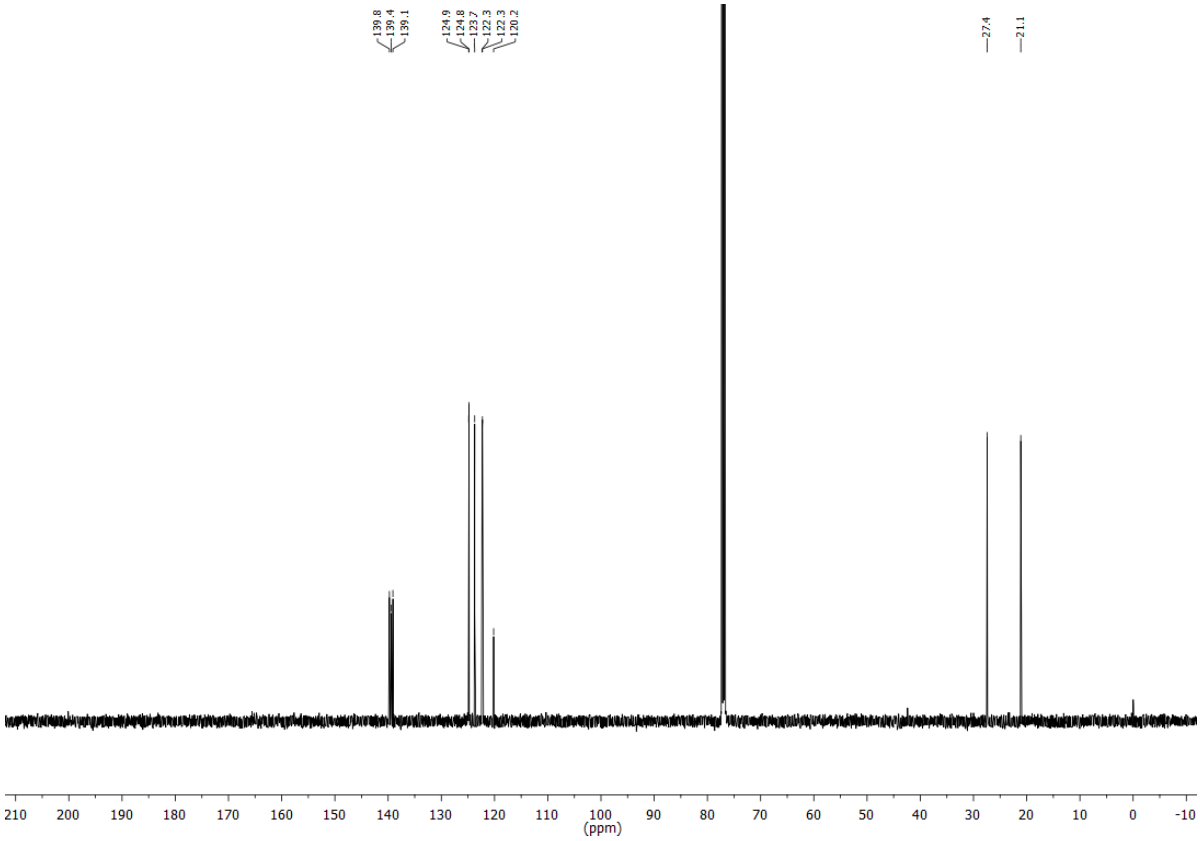
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 21.1, 27.4, 120.2, 122.3, 122.3, 123.7, 124.8, 124.9, 139.1, 139.4, 139.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3055, 2990, 2932, 2241, 1436, 1136, 1058, 967.

$C_{11}H_9NS$ calcd.: 187.0456, found: 187.0456 (GC-HRMS).

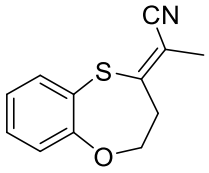


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*Z*)-2-(2,3-Dihydro-4*H*-benzo[*b*][1,4]oxathiepin-4-ylidene)propanenitrile (2p)



Compound **1p** (22.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (12 h reaction time) to furnish product **2p** after flash column chromatography (*n*-pentane:EtOAc = 20:1) as an off-white solid (12.8 mg, 59 µmol, 59%).

m.p.: 89 °C.

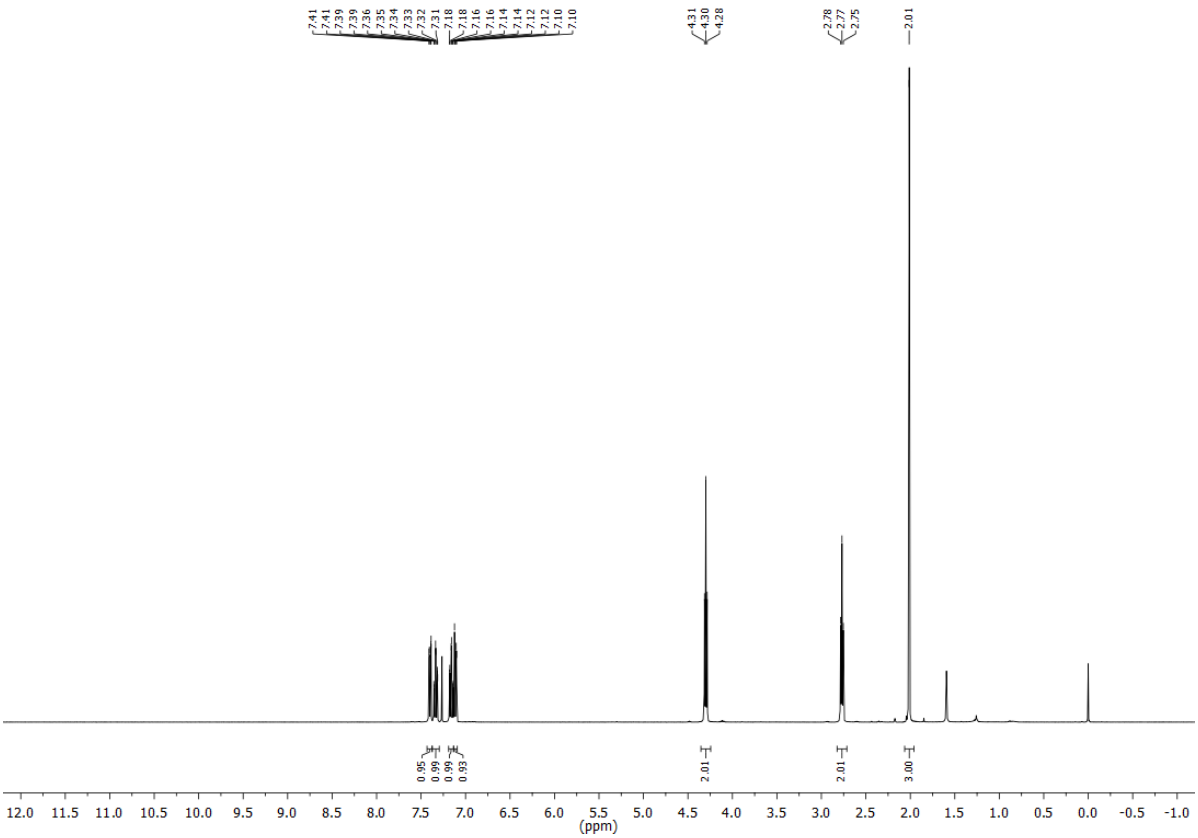
R_f = 0.06 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.01 (s, 3H), 2.77 (t, *J* = 6.1 Hz, 2H), 4.30 (t, *J* = 6.1 Hz, 2H), 7.11 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.16 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (td, *J* = 7.7, 1.7 Hz, 1H), 7.40 (dd, *J* = 7.7, 1.7 Hz, 1H).

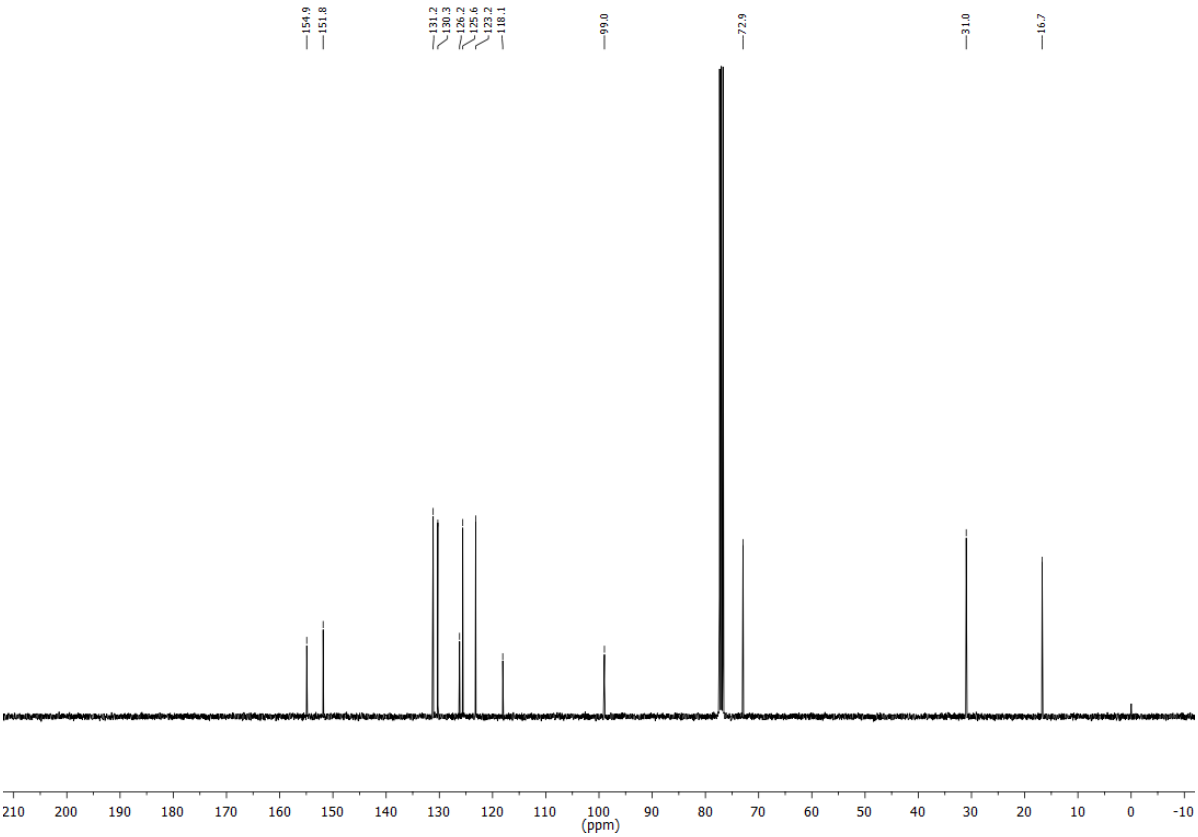
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 16.7, 31.0, 72.9, 99.0, 118.1, 123.2, 125.6, 126.2, 130.3, 131.2, 151.8, 154.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3055, 2925, 2876, 2203, 1588, 1473, 1440, 1254, 1222, 1032.

$C_{12}H_{11}NOS$ calcd.: 201.0612, found: 201.0624 (GC-HRMS).

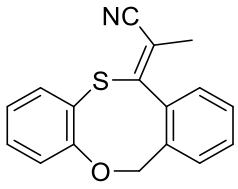


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Dibenzo[*b,f*][1,4]oxathiocin-11(6*H*)-ylidene)propanenitrile (2q)



Compound **1q** (28.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT2 (alternative B, 6 h reaction time) to furnish product **2q** after flash column chromatography (*n*-pentane:EtOAc = 20:1) as a colorless solid (27.0 mg, 96 µmol, 96%).

m.p.: 141 °C.

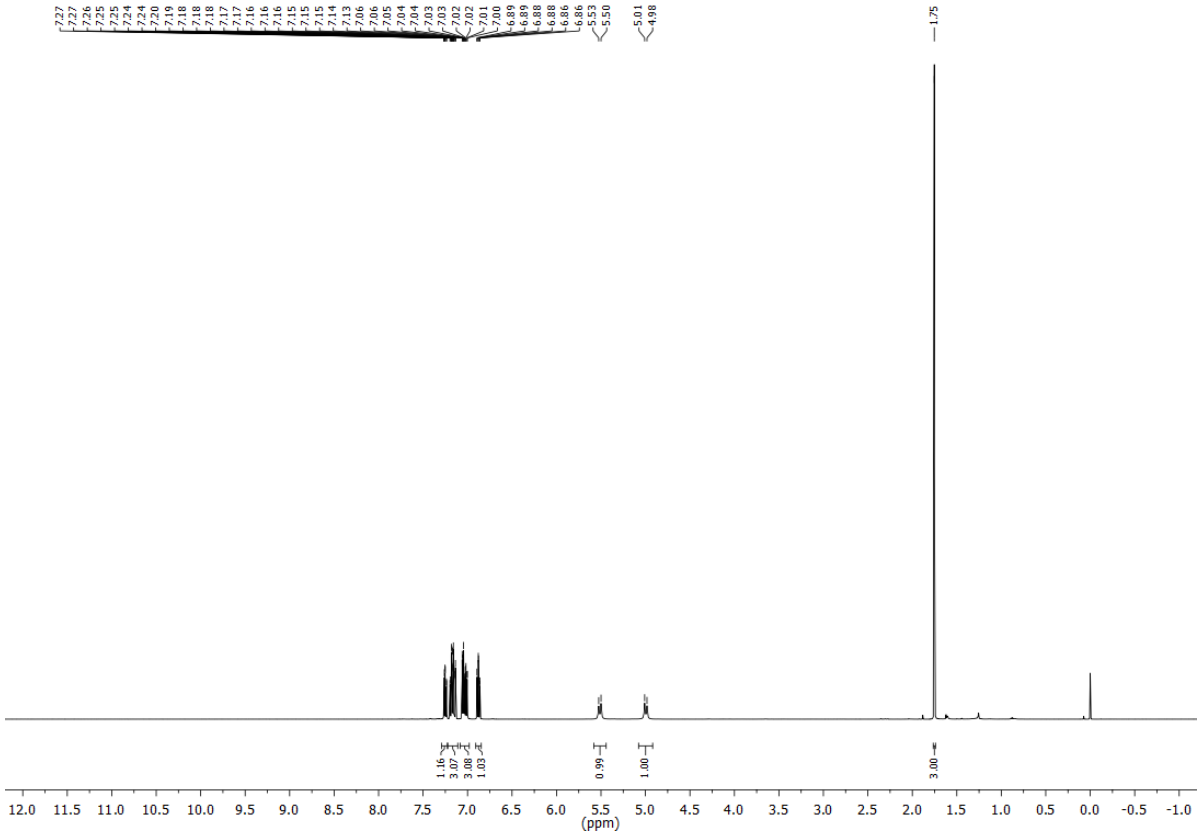
R_f = 0.19 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.75 (s, 3H), 5.00 (d, *J*=13.0, 1H), 5.51 (d, *J*=13.0, 1H), 6.88 (td, *J*=7.6, 1.4, 1H), 6.99 – 7.08 (m, 3H), 7.12 – 7.21 (m, 3H), 7.22 – 7.28 (m, 1H).

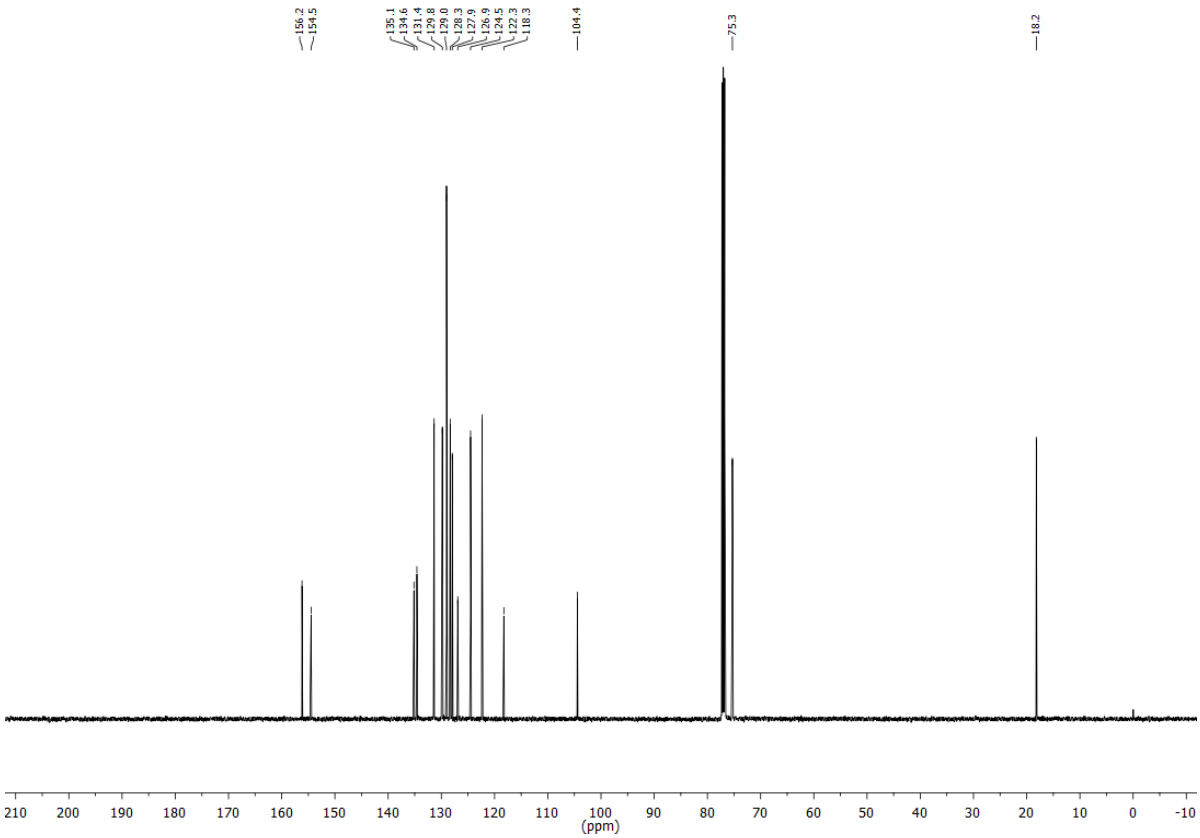
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 18.2, 75.3, 104.4, 118.3, 122.3, 124.5, 126.9, 127.9, 128.3, 129.0 (2 C), 129.8, 131.4, 134.6, 135.1, 154.5, 156.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3060, 3005, 2923, 2862, 2202, 1579, 1467, 1441, 1208, 1005.

$C_{17}H_{13}NOS$ calcd.: 279.0718, found: 279.0727 (GC-HRMS).

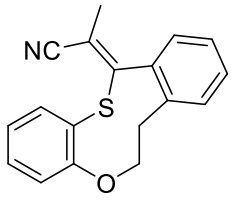


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(6,7-Dihydro-12*H*-dibenzo[*b,f*][1,4]oxathionin-12-ylidene)propanenitrile (2r)



Compound **1r** (28.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT2 (alternative B, 6 h reaction time) to furnish product **2r** after flash column chromatography (*n*-pentane:EtOAc = 20:1 → 10:1) as a colorless solid (27.0 mg, 92 µmol, 92%).

m.p.: 207 °C.

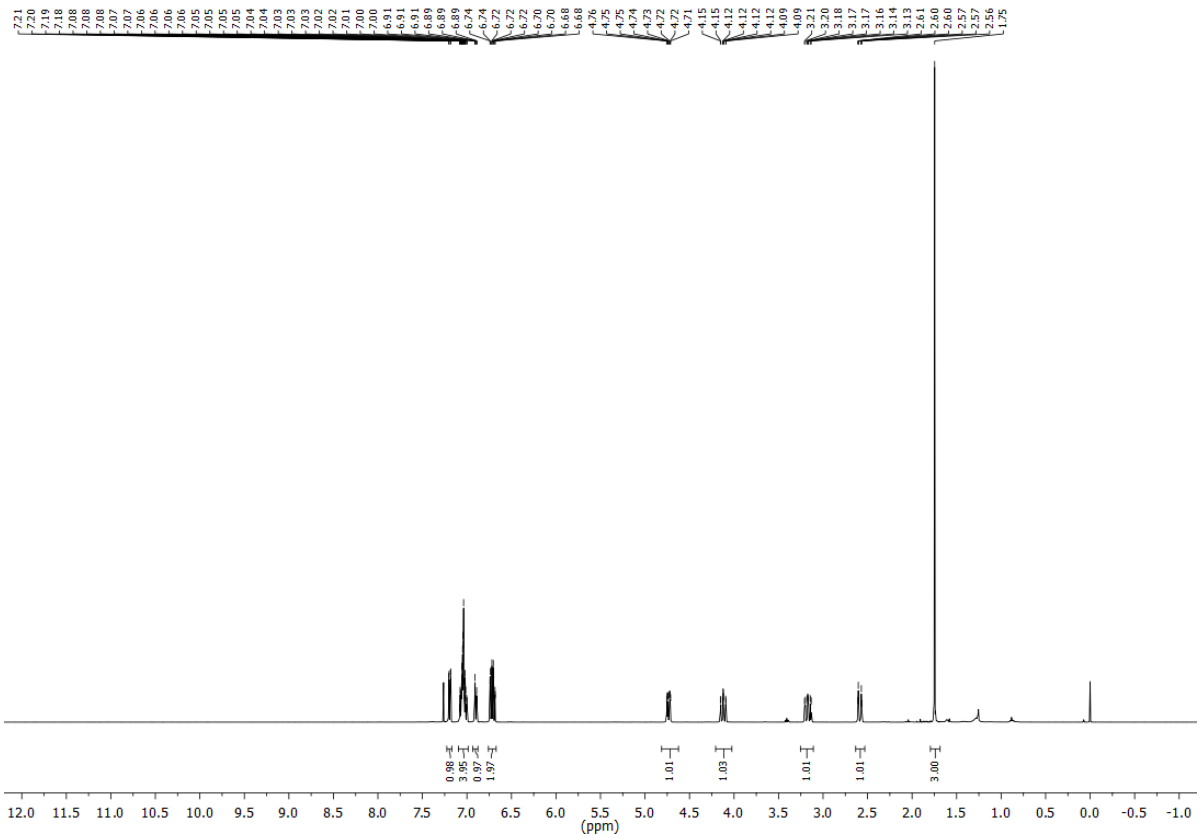
R_f = 0.15 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.75 (s, 3H), 2.59 (dt, *J*=13.8, 2.0, 1H), 3.17 (ddd, *J*=13.7, 12.2, 4.3, 1H), 4.12 (ddd, *J*=12.0, 11.2, 1.9, 1H), 4.73 (ddd, *J*=11.2, 4.3, 2.1, 1H), 6.68 – 6.75 (m, 2H), 6.90 (dt, *J*=7.0, 1.3, 1H), 6.99 – 7.10 (m, 4H), 7.19 (dd, *J*=7.7, 1.7, 1H).

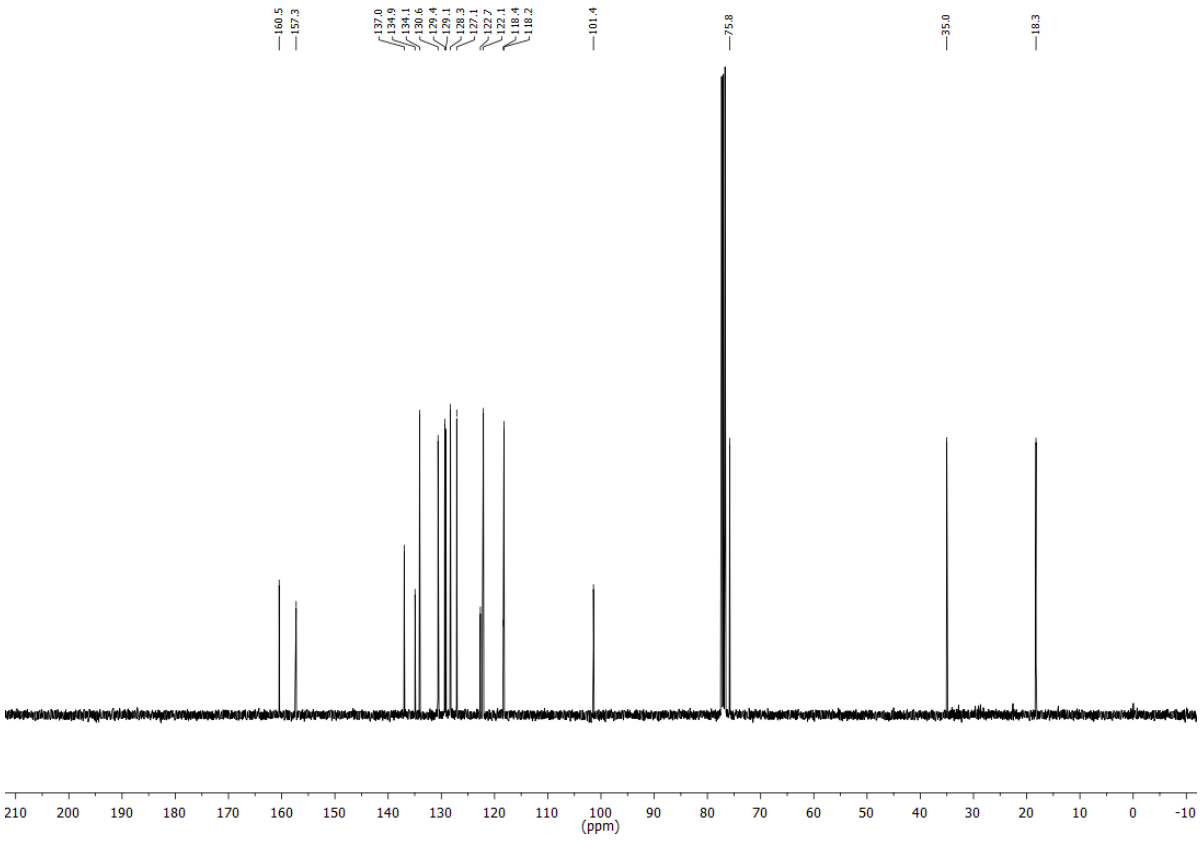
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 18.3, 35.0, 75.8, 101.4, 118.2, 118.4, 122.1, 122.7, 127.1, 128.3, 129.1, 129.4, 130.6, 134.1, 134.9, 137.0, 157.3, 160.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3065, 3018, 2963, 2950, 2923, 2854, 2210, 1586, 1466, 1442, 1274, 1220, 1030, 995.

$C_{18}H_{15}NOS$ calcd.: 293.0874, found: 293.0893 (GC-HRMS).

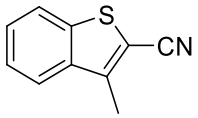


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

3-Methylbenzo[b]thiophene-2-carbonitrile (2s)



Compound **1s** (17.3 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT1 (31 h reaction time) to obtain product **2s** after flash column chromatography (*n*-pentane:EtOAc = 50:1→20:1) as a colorless solid (3.0 mg, 17 µmol, 17%).

m.p.: 84 °C.

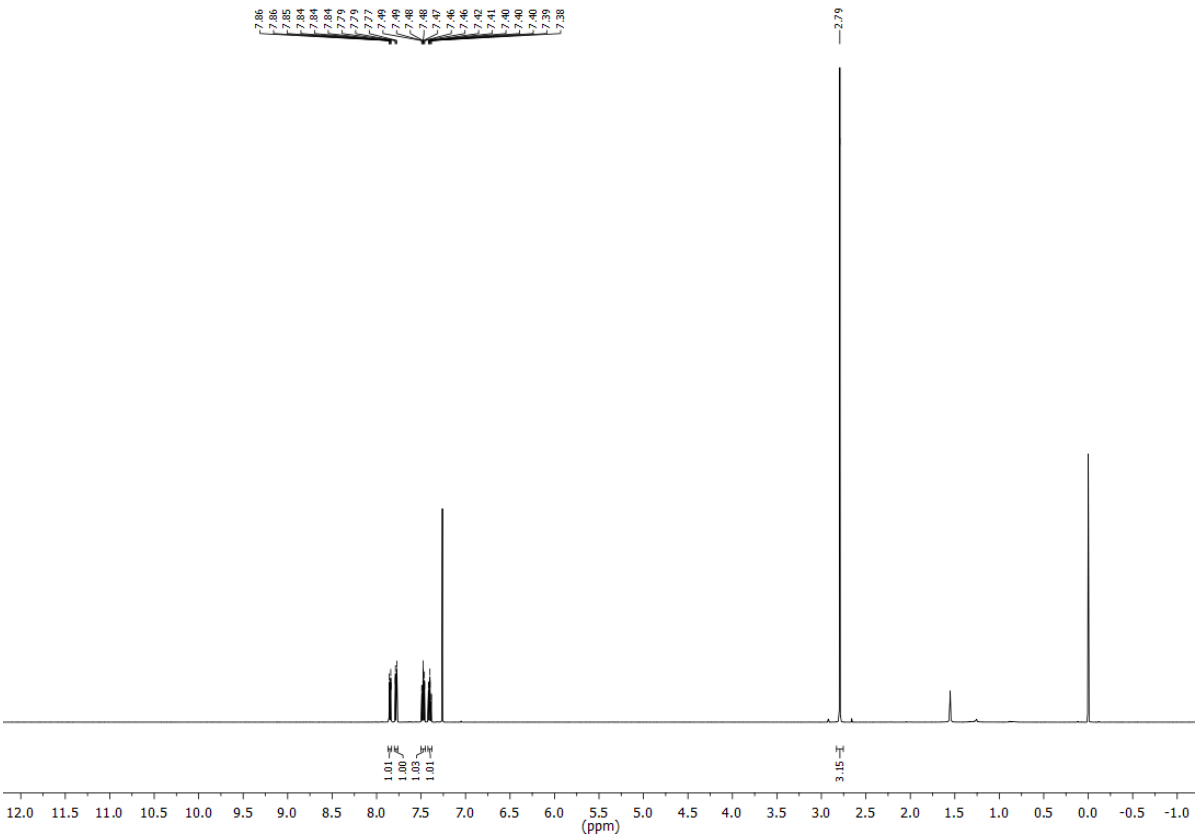
$\mathbf{R_f}$ = 0.58 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.79 (s, 3H), 7.40 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.48 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1H), 7.77 – 7.79 (m, 1H), 7.85 (dt, *J* = 8.1, 1.0 Hz, 1H).

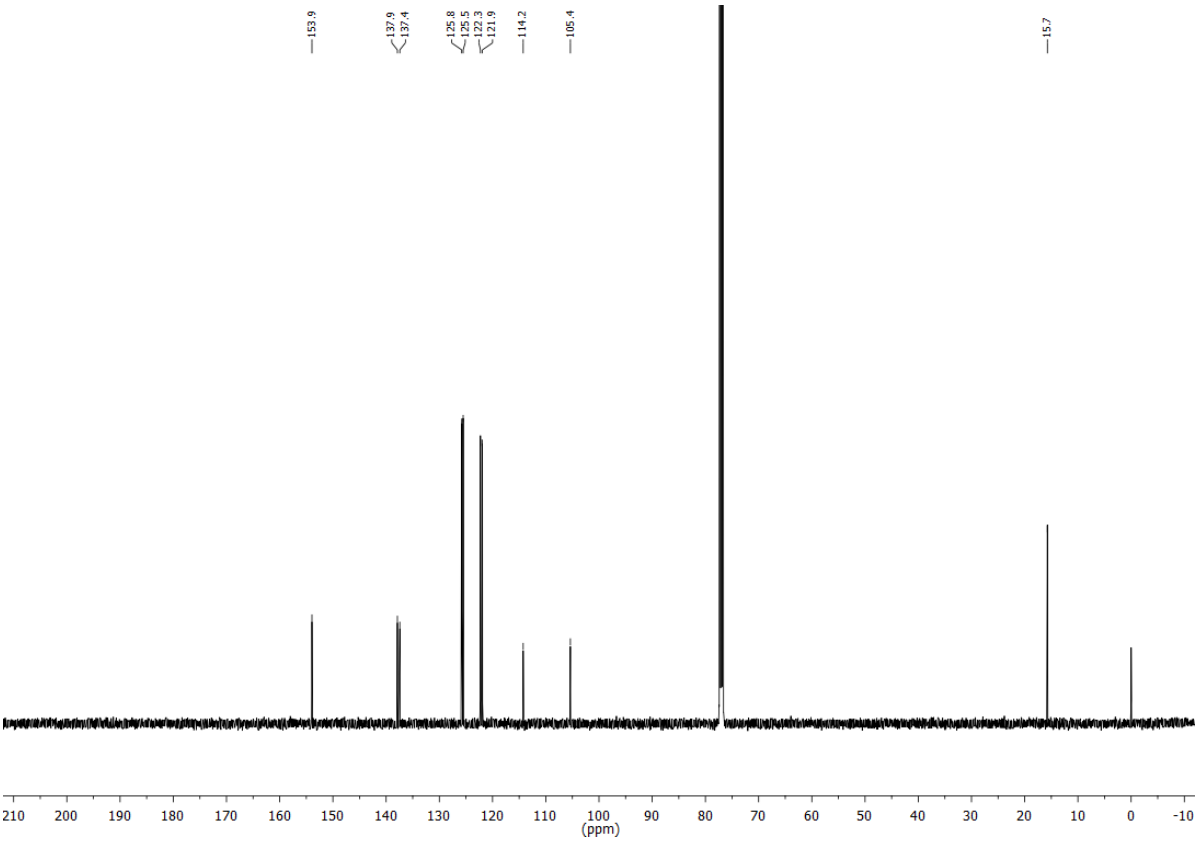
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 15.7, 105.4, 114.2, 121.9, 122.3, 125.5, 125.8, 137.4, 137.9, 153.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2921, 2853, 2217, 1527, 1431, 1380, 1181, 1019.

$C_{10}H_7NS$ calcd.: 173.0299, found: 173.0298 (GC-HRMS).

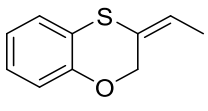


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-3-Ethylidene-2,3-dihydrobenzo[*b*][1,4]oxathiine (2t)



Compound **1a** (20.3 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT1 (ligand: $[Me_3PH][BF_4]$, 1.0 equiv.) to obtain product **2t** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a colorless oil (8.0 mg, 45 µmol, 45%).

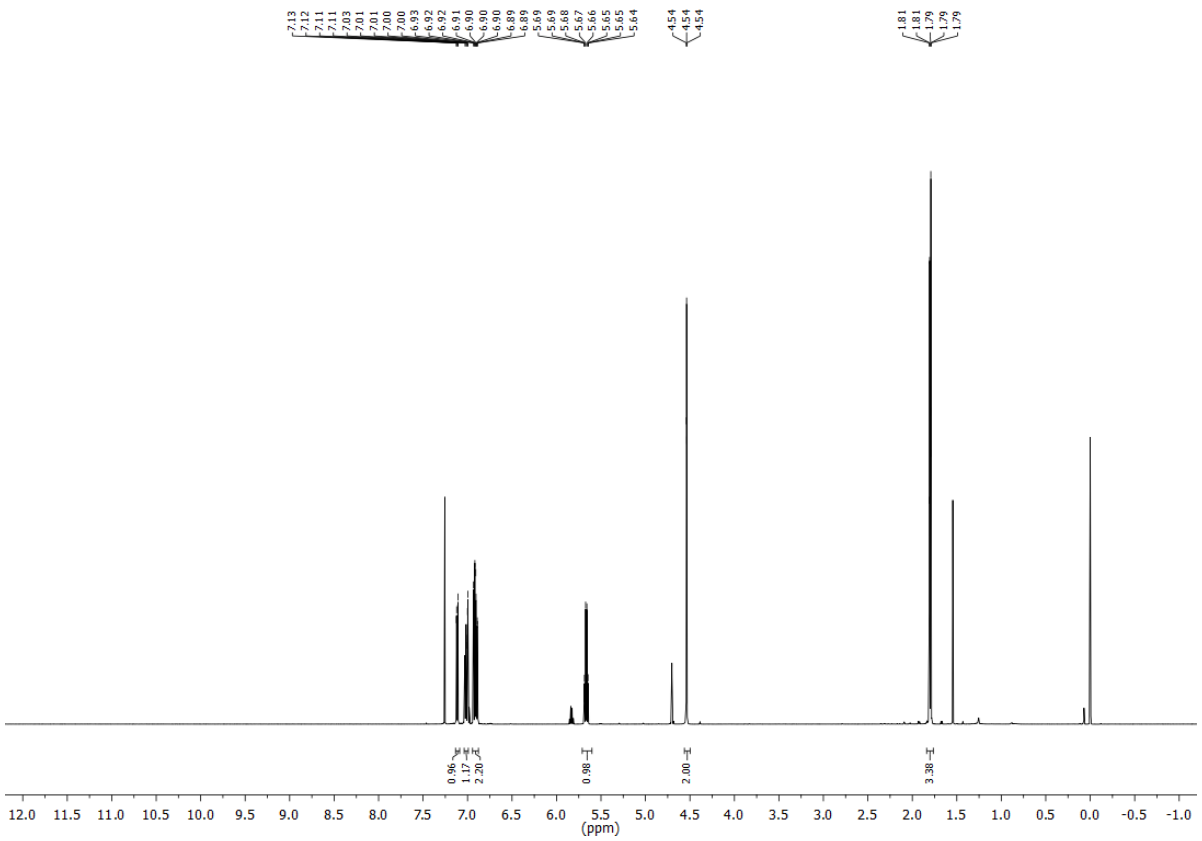
R_f = 0.79 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.79 – 1.82 (m, 3H), 4.54 (t, *J* = 1.0 Hz, 2H), 5.64 – 5.69 (m, 1H), 6.88 – 6.94 (m, 2H), 6.99 – 7.03 (m, 1H), 7.12 (dd, *J* = 7.6, 1.6 Hz, 1H).

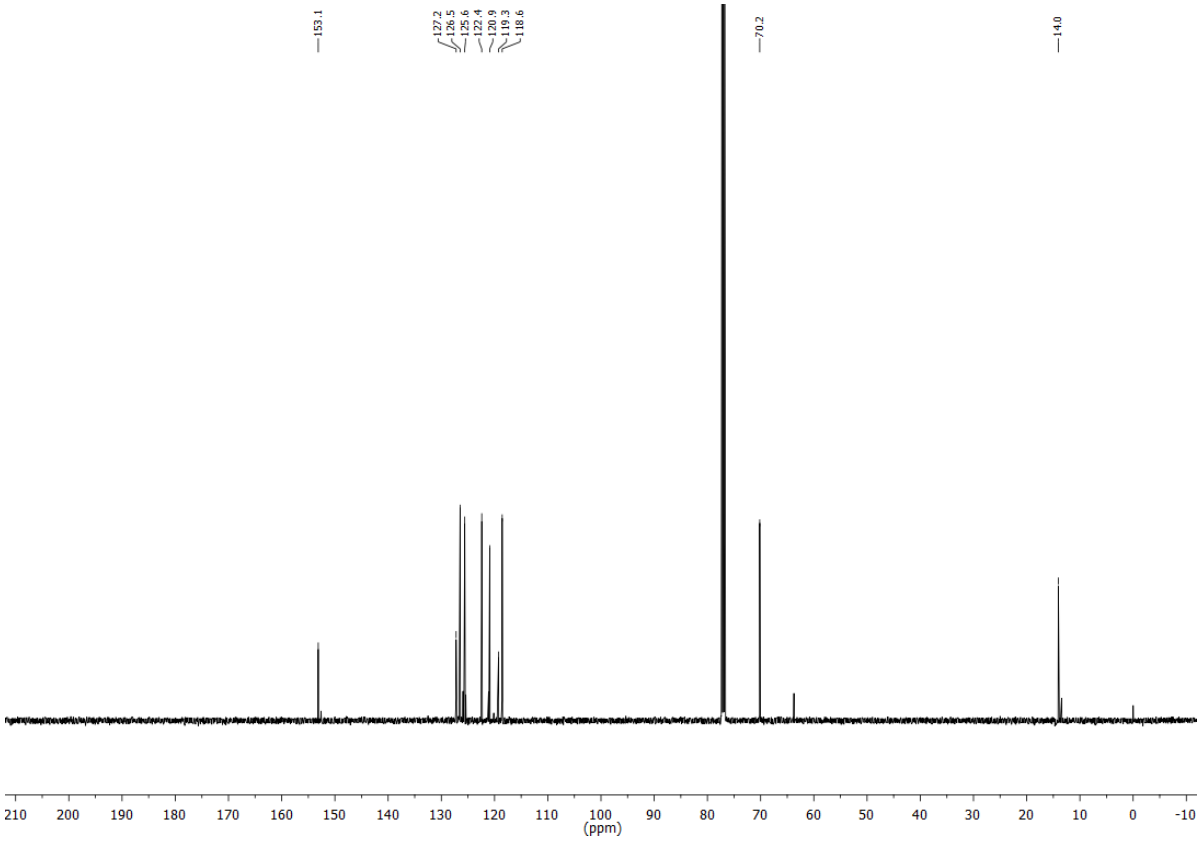
^{13}C-NMR (126 MHz, CD_2Cl_2): δ = 14.0, 70.2, 118.6, 119.3, 120.9, 122.4, 125.6, 126.5, 127.2, 153.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3064, 2970, 2908, 2853, 1727, 1648, 1472, 1439, 1212, 1033, 994.

$C_{10}H_{10}OS$ calcd.: 178.0452, found: 178.0451 (GC-HRMS).

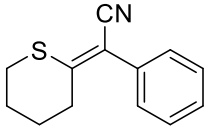


^{1}H-NMR (500 MHz, $CDCl_3$).



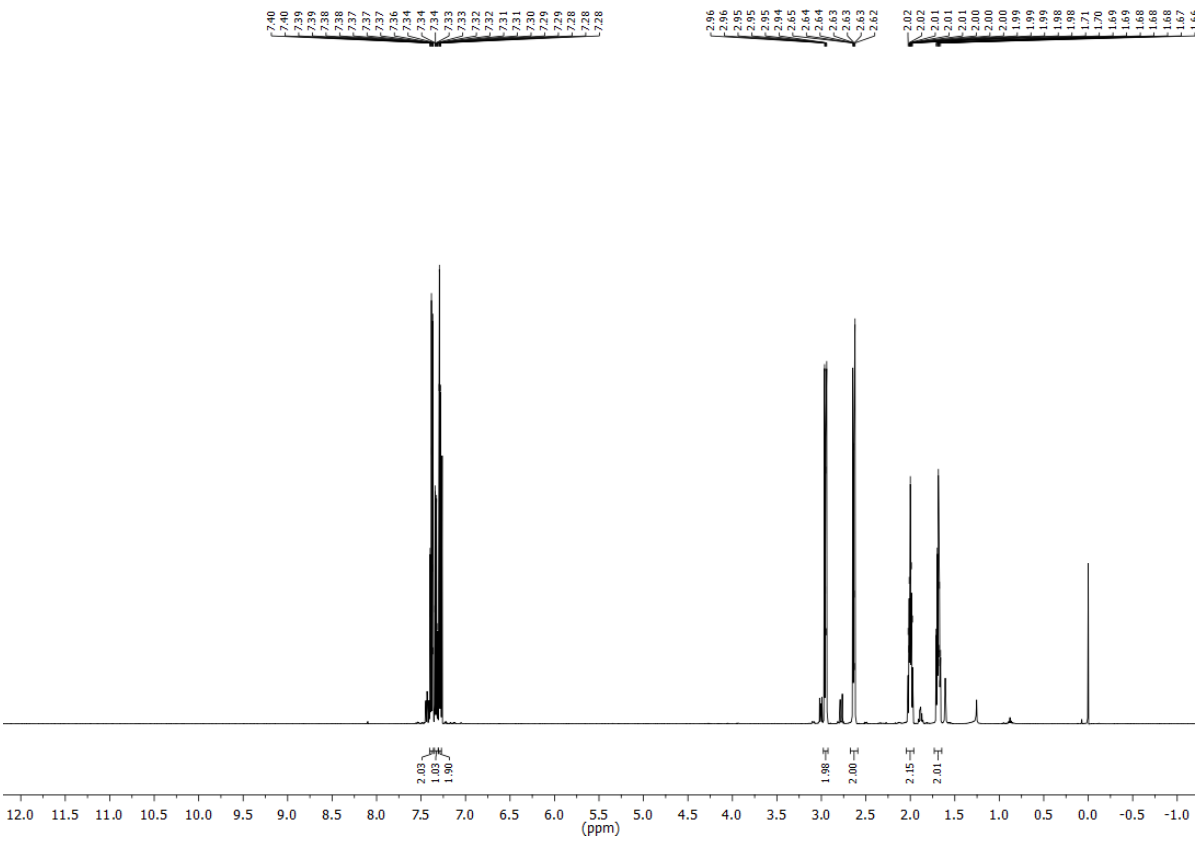
^{13}C-NMR (126 MHz, $CDCl_3$)

(*Z*)-2-Phenyl-2-(tetrahydro-2*H*-thiopyran-2-ylidene)acetonitrile (*syn*-4a)

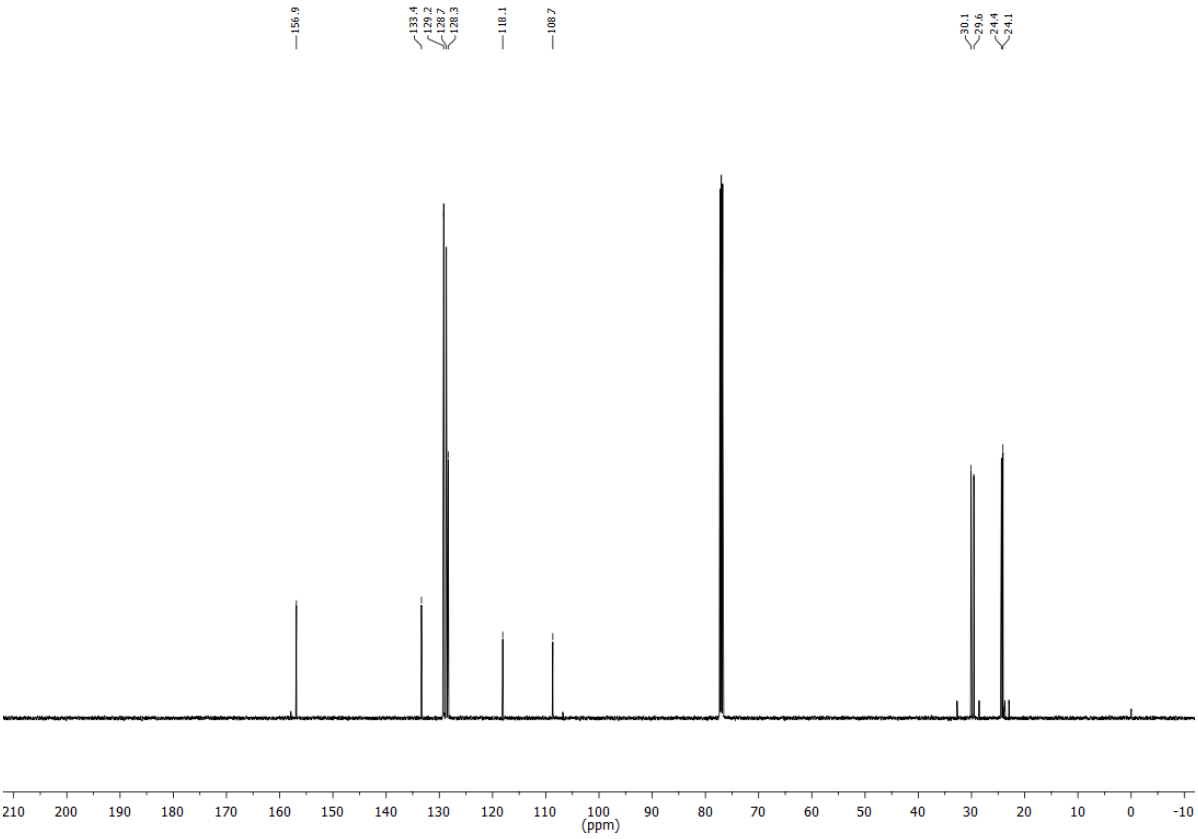


Compound **4a** (21.5 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (14 h reaction time) to furnish product ***syn*-4a** and ***anti*-4a** (Σ = 19.1 mg, 89 µmol, 89%, ratio 8.0/1.0) which were separated by flash column chromatography (*n*-pentane:EtOAc = 100:1).
Product ***syn*-4a** was obtained as a colorless oil.

R_f = 0.28 (*n*-pentane:EtOAc = 20:1).
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.65 – 1.72 (m, 1H), 1.95 – 2.03 (m, 1H), 2.60 – 2.65 (m, 1H), 2.93 – 2.98 (m, 1H), 7.27 – 7.30 (m, 1H), 7.31 – 7.35 (m, 1H), 7.36 – 7.40 (m, 1H).
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 24.1, 24.4, 29.6, 30.1, 108.7, 118.1, 128.3, 128.7, 129.2, 133.4, 156.9.
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2933, 2857, 2200, 1551, 1440, 1238, 1101, 963.
$C_{13}H_{13}NS$ calcd.: 215.0769, found: 215.0797 (GC-HRMS).

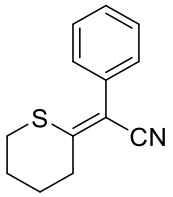


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-2-Phenyl-2-(tetrahydro-2*H*-thiopyran-2-ylidene)acetonitrile (*anti*-4a)



Product ***anti*-4a** was obtained as a colorless oil.

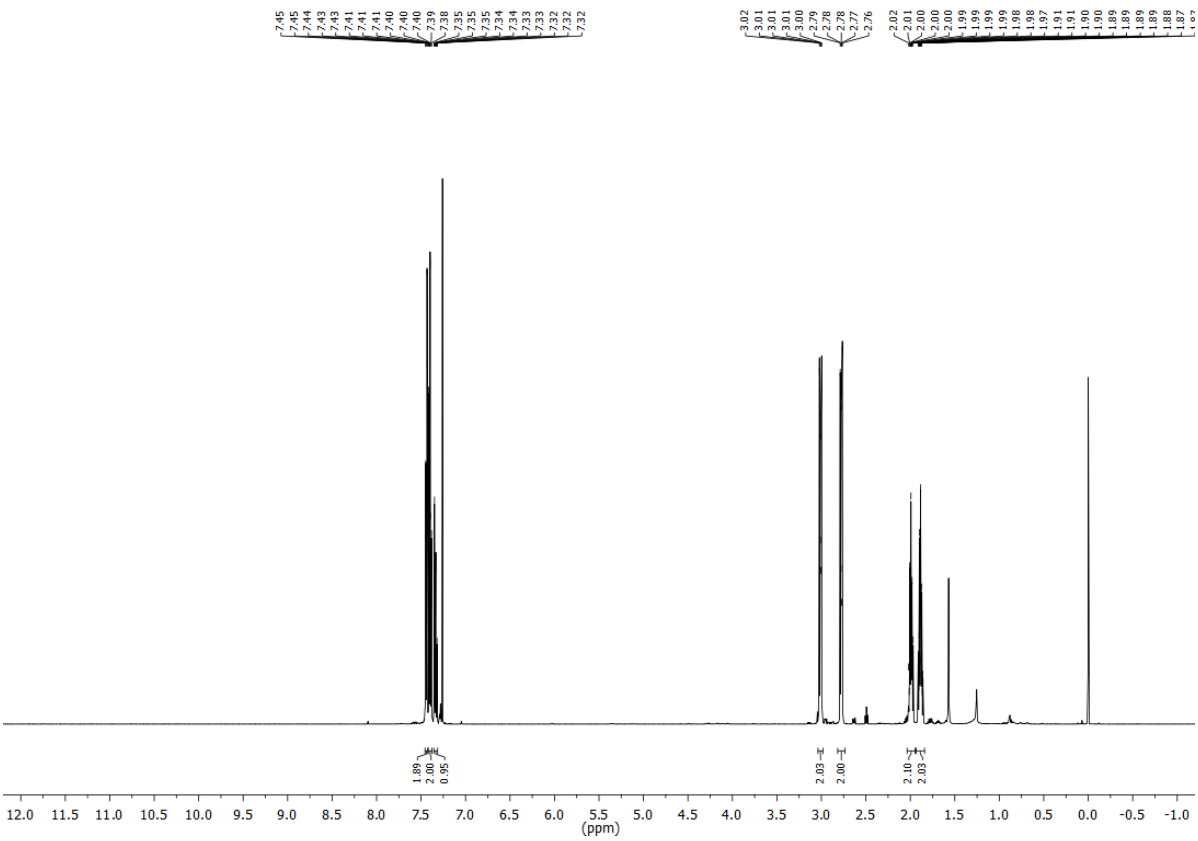
R_f = 0.22 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.85 – 1.92 (m, 2H), 1.97 – 2.02 (m, 2H), 2.74 – 2.80 (m, 2H), 2.97 – 3.04 (m, 2H), 7.31 – 7.36 (m, 1H), 7.37 – 7.42 (m, 2H), 7.43 – 7.45 (m, 2H).

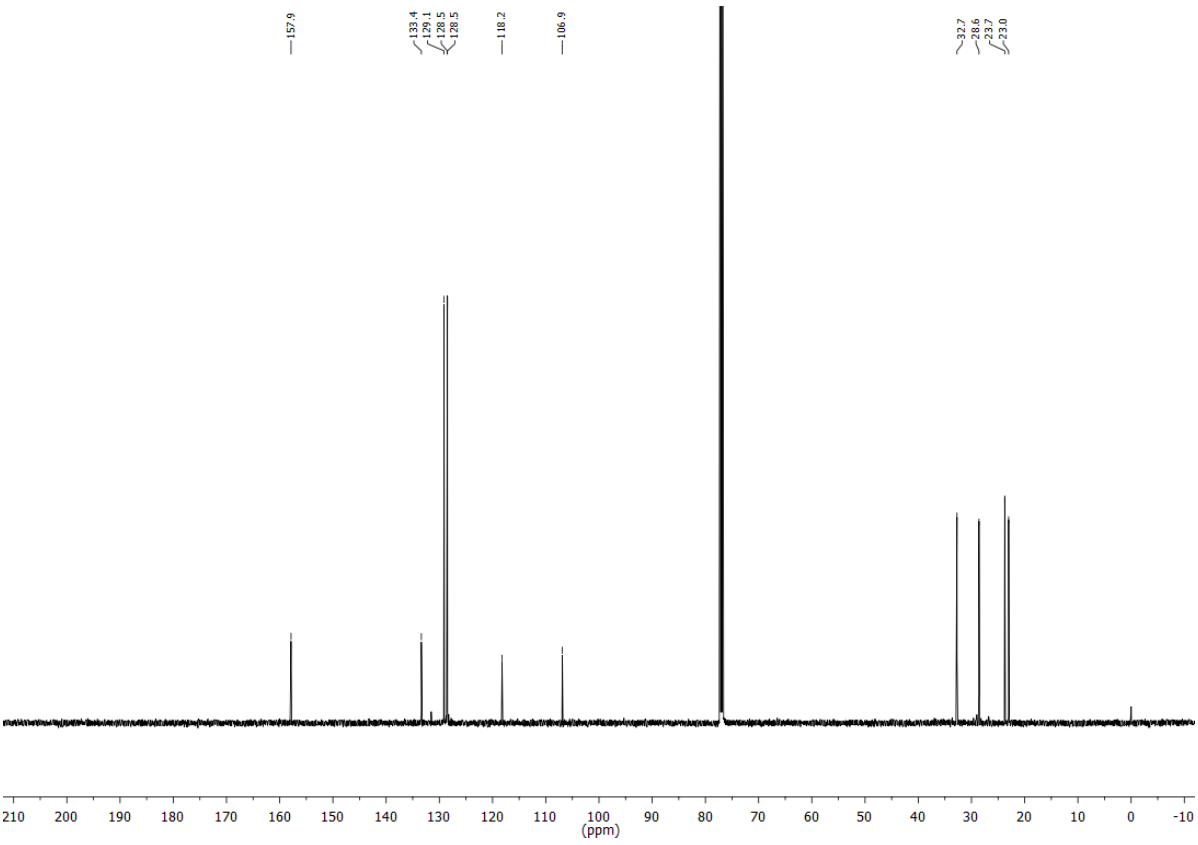
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 23.0, 23.7, 28.6, 32.7, 106.9, 118.2, 128.5, 128.5, 129.1, 133.4, 157.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2934, 2859, 2198, 1551, 1442, 1269, 1121, 965.

$C_{13}H_{13}NS$ calcd.: 215.0769, found: 215.0787 (GC-HRMS).

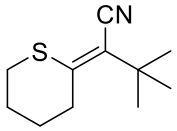


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-3,3-Dimethyl-2-(tetrahydro-2*H*-thiopyran-2-ylidene)butanenitrile (4b)



Compound **3b** (20.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT2 (3 h reaction time) to obtain product **4b** after flash column chromatography (*n*-pentane:EtOAc = 50:1) as a slight yellow oil (19.8 mg, 101 µmol, 99%).

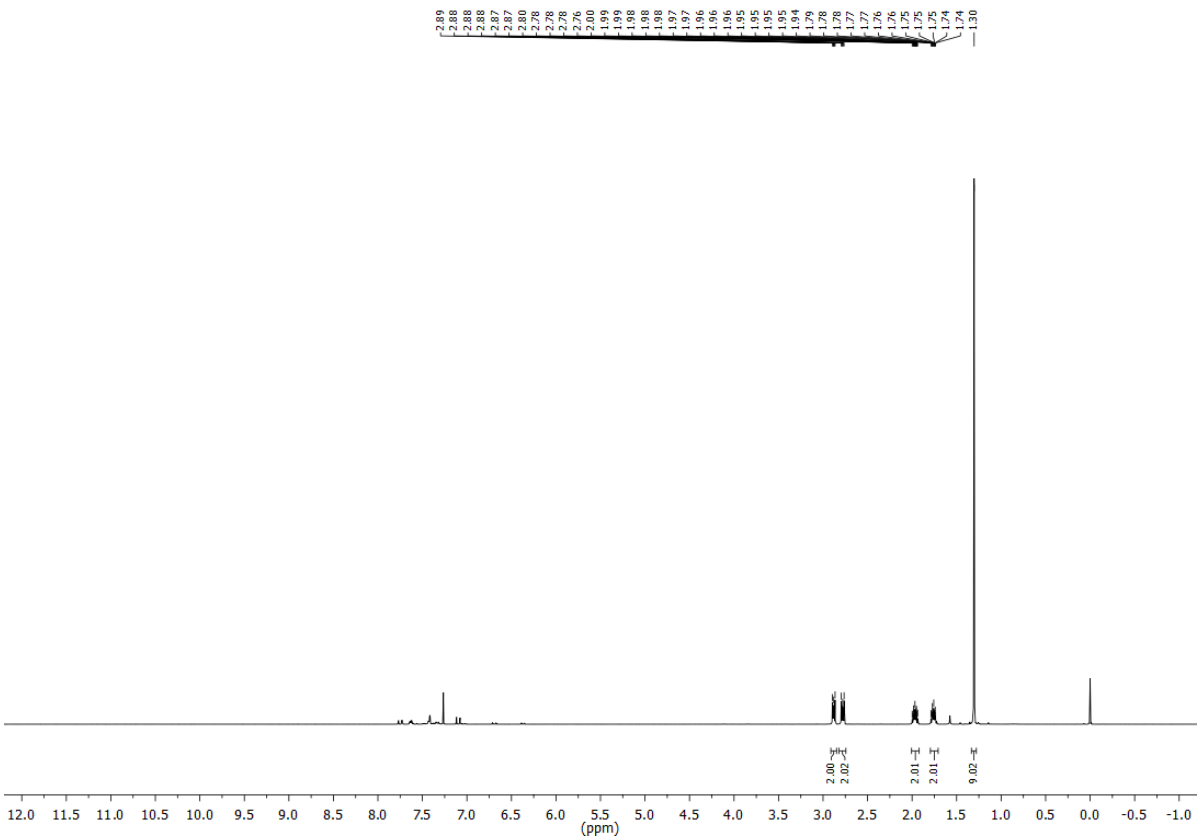
R_f = 0.62 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 9H), 1.74 – 1.80 (m, 2H), 1.91 – 2.02 (m, 2H), 2.75 – 2.81 (m, 2H), 2.84 – 2.92 (m, 2H).

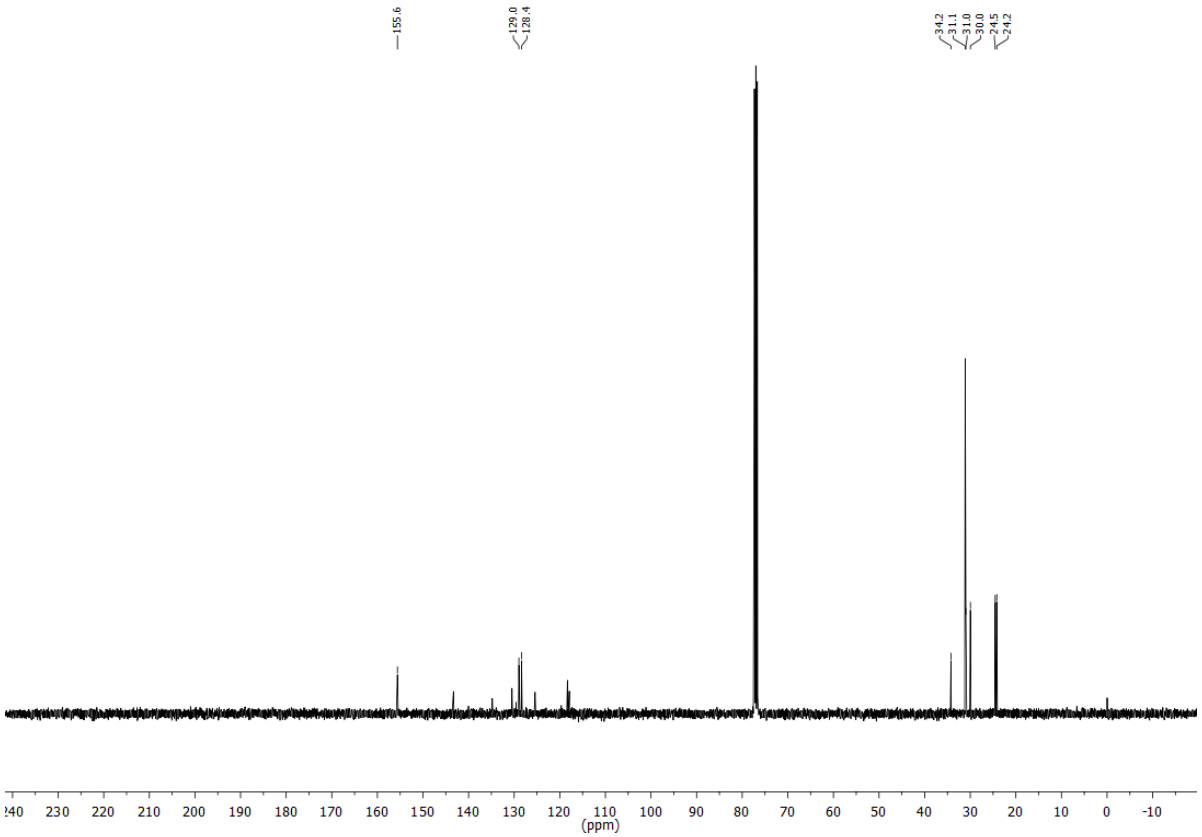
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 24.2, 24.5, 30.0, 31.0, 31.1, 34.2, 128.4, 129.0, 155.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2967, 2935, 2869, 2197, 1617, 1550, 1450, 1248, 1189, 1093, 964.

$C_{11}H_{17}NS$ calcd.: 195.1082, found: 195.1089 (GC-HRMS).

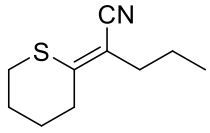


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Tetrahydro-2*H*-thiopyran-2-ylidene)pentanenitrile (4c)



Compound **3c** (30.0 mg, 165 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (14 h reaction time) to furnish product **4c** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a colorless oil (14.1 mg, 78 µmol, 47%).

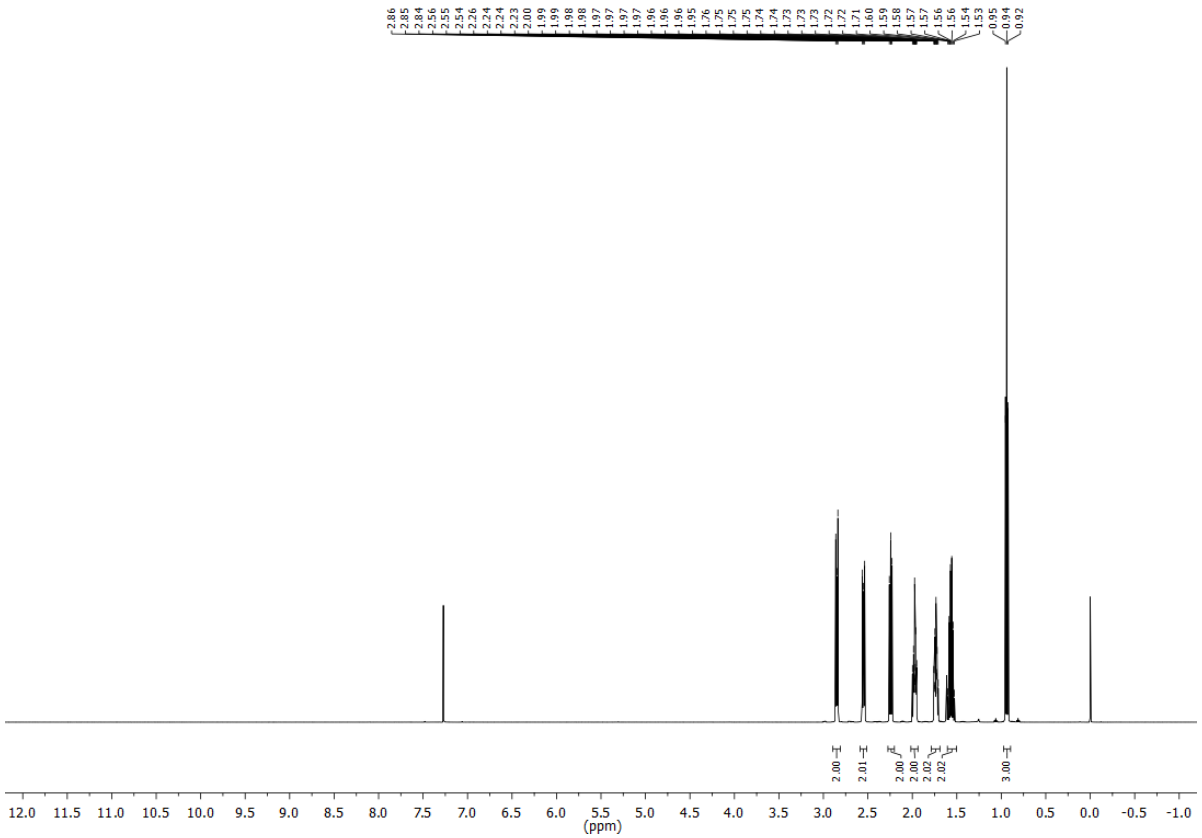
R_f = 0.60 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.4 Hz, 3H), 1.56 (h, *J* = 7.4 Hz, 2H), 1.69 – 1.77 (m, 2H), 1.92 – 2.01 (m, 2H), 2.21 – 2.28 (m, 2H), 2.53 – 2.57 (m, 2H), 2.81 – 2.87 (m, 2H).

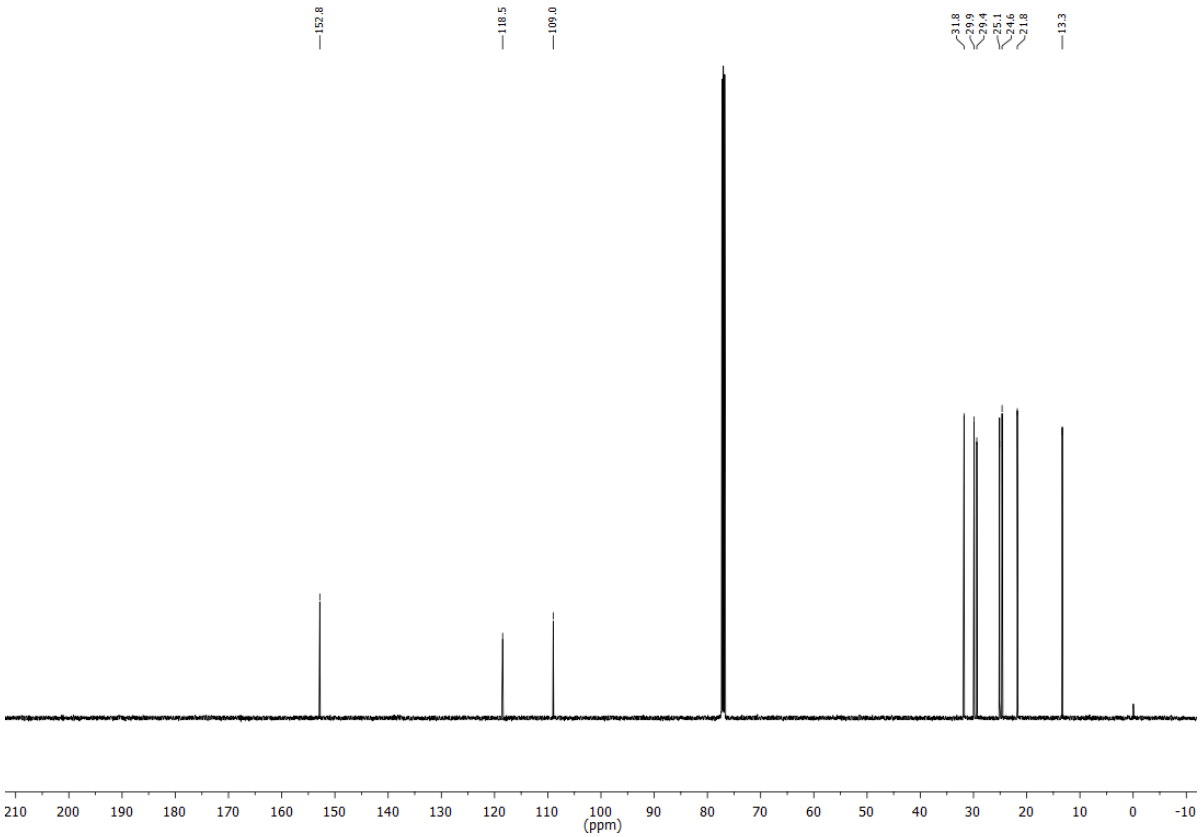
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.3, 21.8, 24.6, 25.1, 29.4, 29.9, 31.8, 109.0, 118.5, 152.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2959, 2932, 2869, 2202, 1577, 1456, 1293, 1257, 1239, 1063, 969.

$C_{10}H_{15}NS$ calcd.: 181.0925, found: 181.0926 (GC-HRMS).

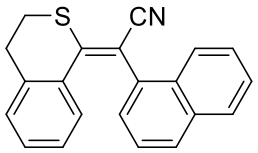


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(Isothiochroman-1-ylidene)-2-(naphthalen-1-yl)acetonitrile (4d)



Compound **3d** (31.3 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product **4d** after flash column chromatography (*n*-pentane:EtOAc = 10:1) as a yellow solid (20.0 mg, 64 µmol, 64%).

m.p.: 152 °C.

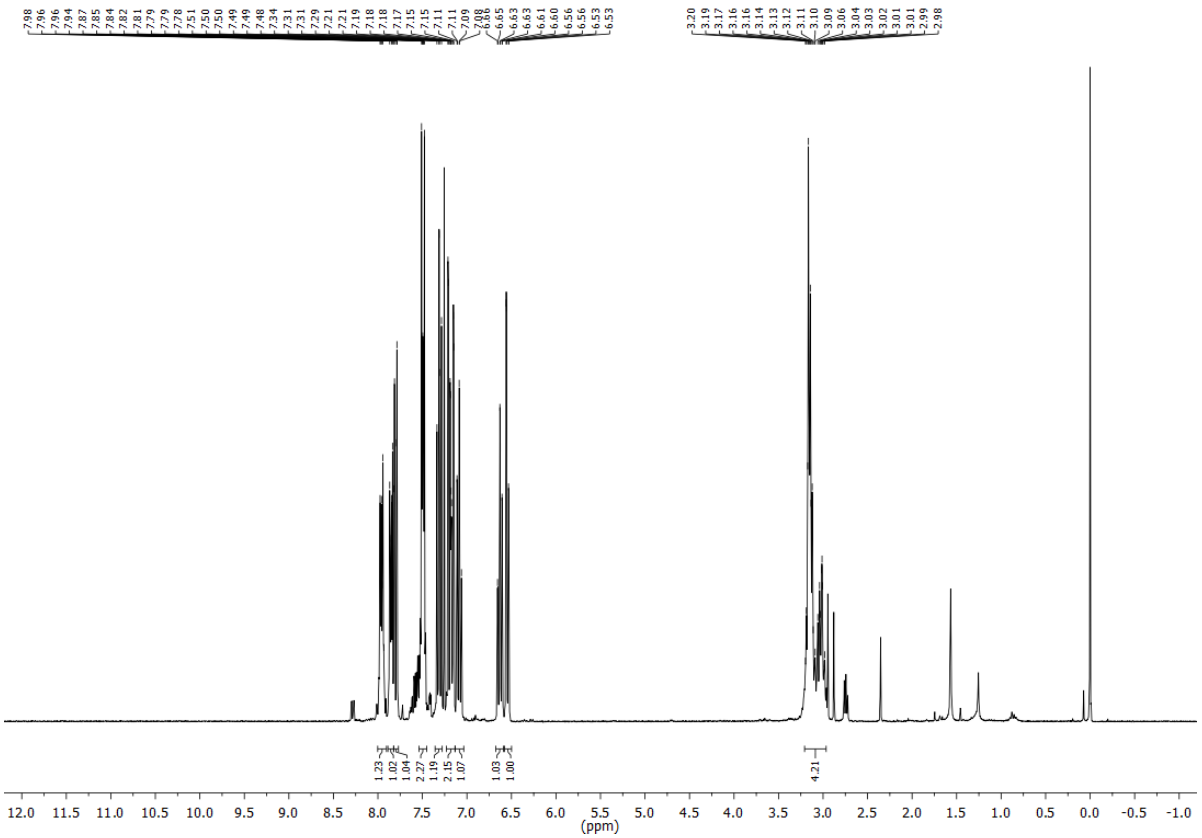
R_f = 0.15 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.98 – 3.20 (m, 4H), 6.54 (dd, *J*=8.0, 1.3, 1H), 6.63 (td, *J*=7.6, 1.4, 1H), 7.08 (td, *J*=7.4, 1.4, 1H), 7.14 – 7.23 (m, 2H), 7.31 (dd, *J*=8.2, 7.2, 1H), 7.44 – 7.53 (m, 2H), 7.75 – 7.82 (m, 1H), 7.83 – 7.89 (m, 1H), 7.92 – 8.00 (m, 1H).

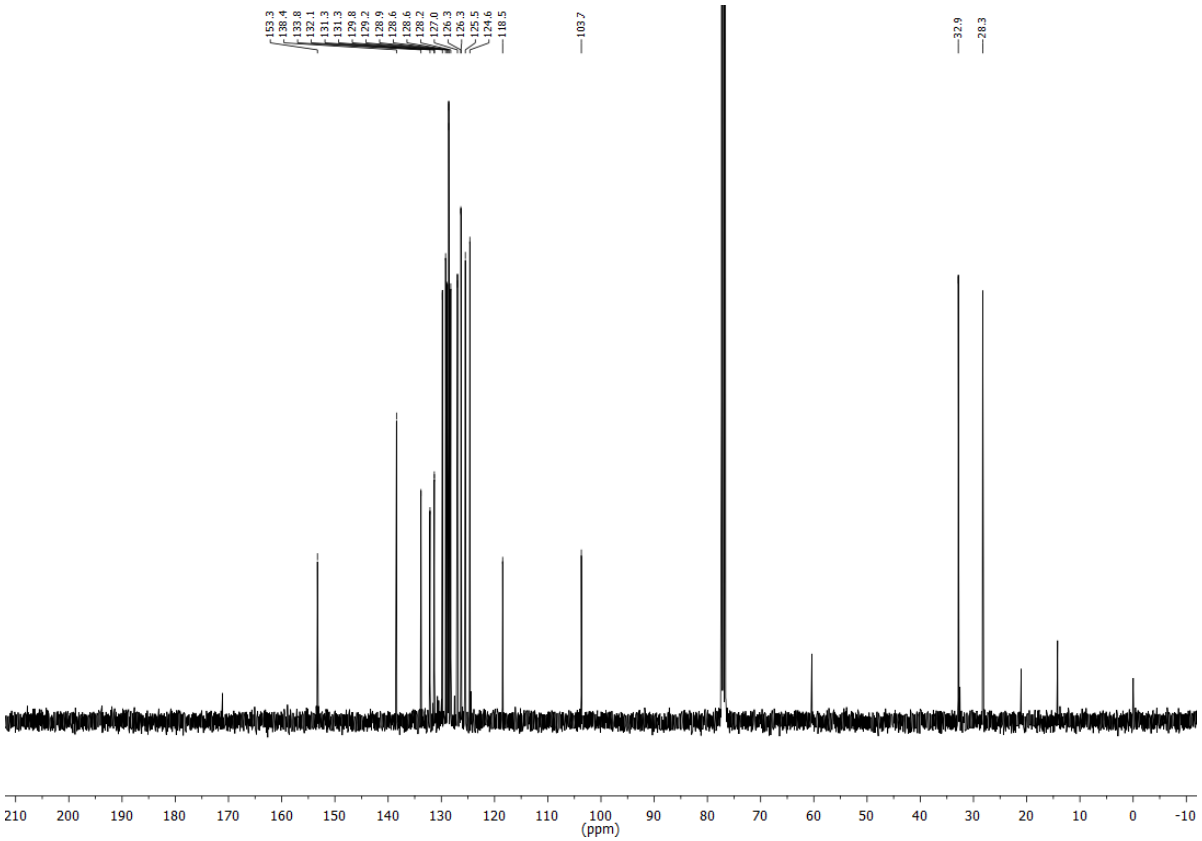
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 28.3, 32.9, 103.7, 118.5, 124.6, 125.5, 126.3, 126.3, 127.0, 128.2, 128.6, 128.6, 128.9, 129.2, 129.8, 131.3, 131.3, 132.1, 133.8, 138.4, 153.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 3025, 2930, 2902, 2841, 2196, 1593, 1542, 1504, 1473, 1430.

$C_{21}H_{15}NS$ calcd.: 313.0925, found: 313.0915 (GC-HRMS).

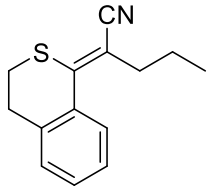


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Isothiochroman-1-ylidene)pentanenitrile (4e)



Compound **3e** (30.0 mg, 131 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (14 h reaction time) to furnish product **4e** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a colorless oil (21.3 mg, 93 µmol, 71%).

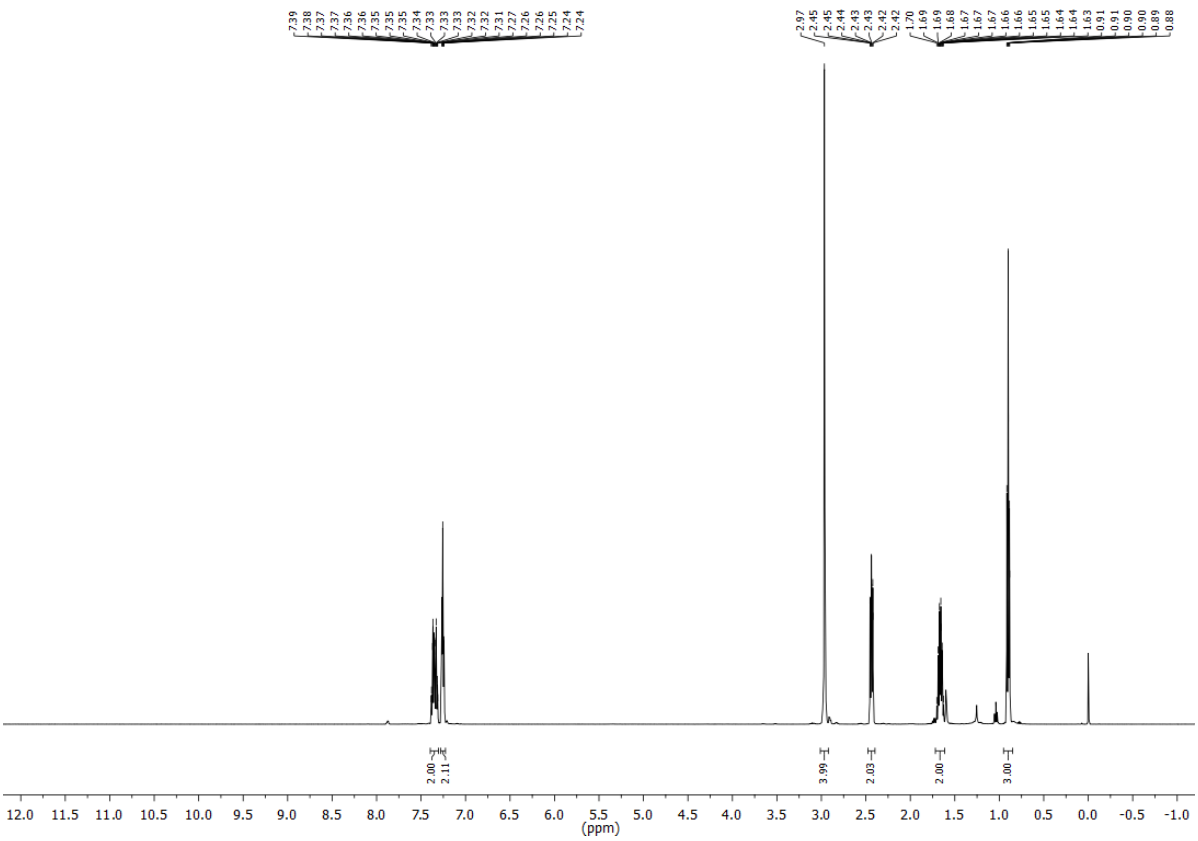
R_f = 0.32 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.90 (td, *J* = 7.3, 1.1 Hz, 3H), 1.62 – 1.72 (m, 2H), 2.41 – 2.46 (m, 2H), 2.97 (s, 4H), 7.23 – 7.27 (m, 2H), 7.31 – 7.39 (m, 2H).

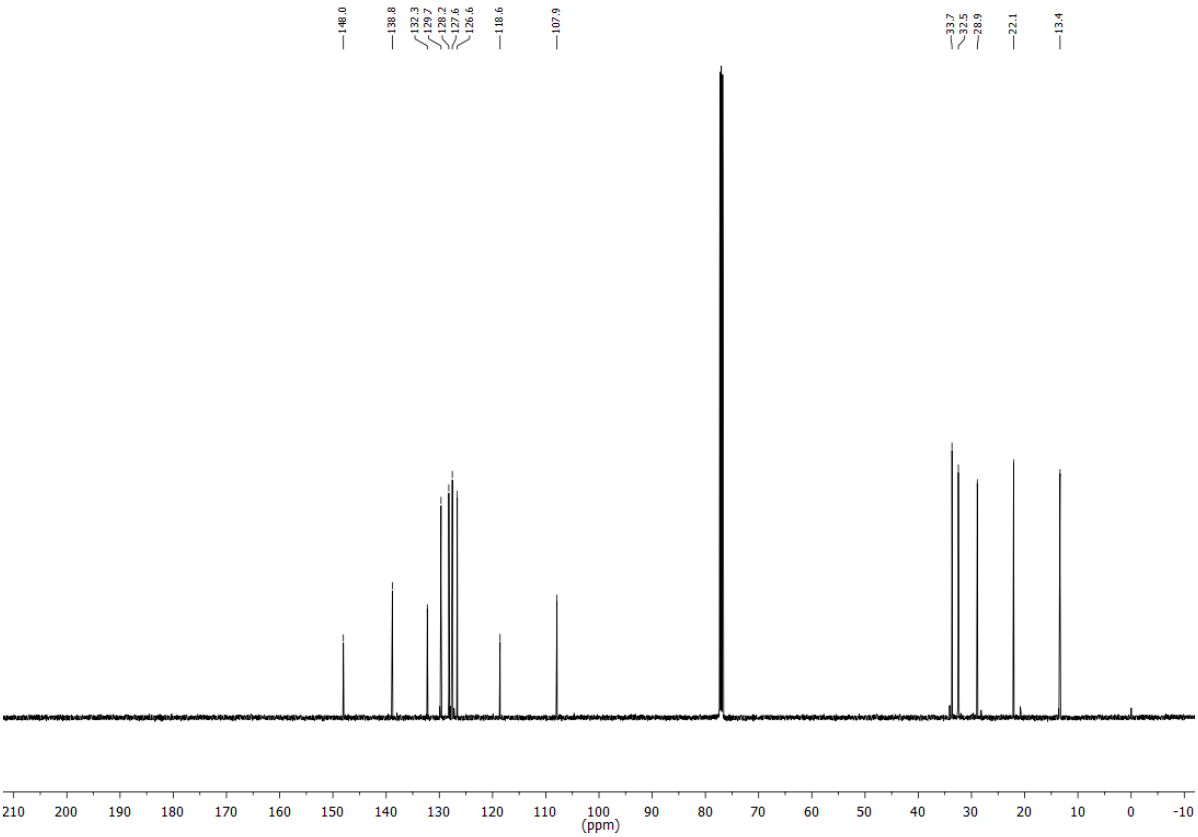
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.4, 22.1, 28.9, 32.5, 33.7, 107.9, 118.6, 126.6, 127.6, 128.2, 129.7, 132.3, 138.8, 148.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2964, 2932, 2870, 2198, 1561, 1446, 1281, 1236, 1069, 931.

$C_{14}H_{15}NS$ calcd.: 229.0925, found: 229.0950 (GC-HRMS).

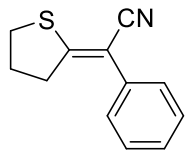


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(Dihydrothiophen-2(3*H*)-ylidene)-2-phenylacetonitrile (4f)



Compound **3f** (30.0 mg, 149 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (14 h reaction time) to furnish product **4f** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a slightly yellow oil (27.2 mg, 135 µmol, 91%).

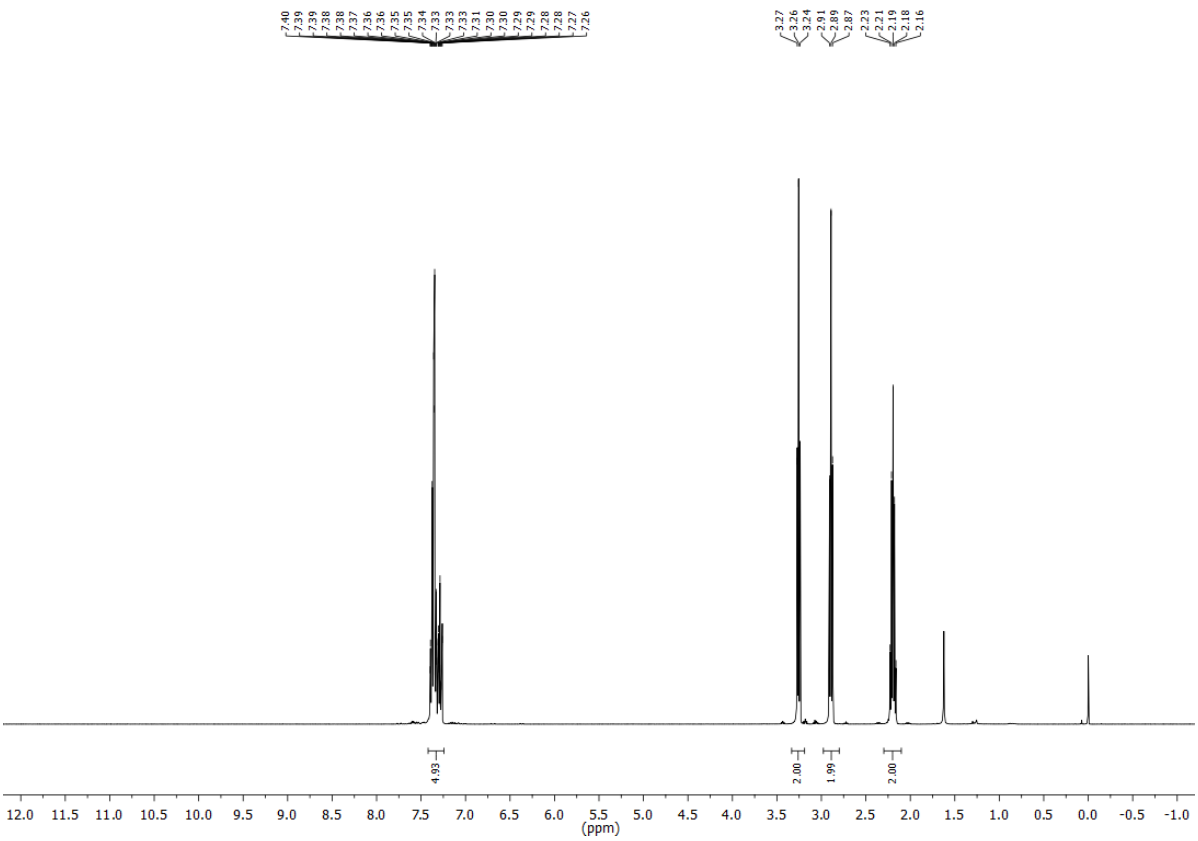
R_f = 0.43 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.19 (p, *J* = 6.6 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 3.26 (t, *J* = 6.4 Hz, 2H), 7.26 – 7.41 (m, 5H).

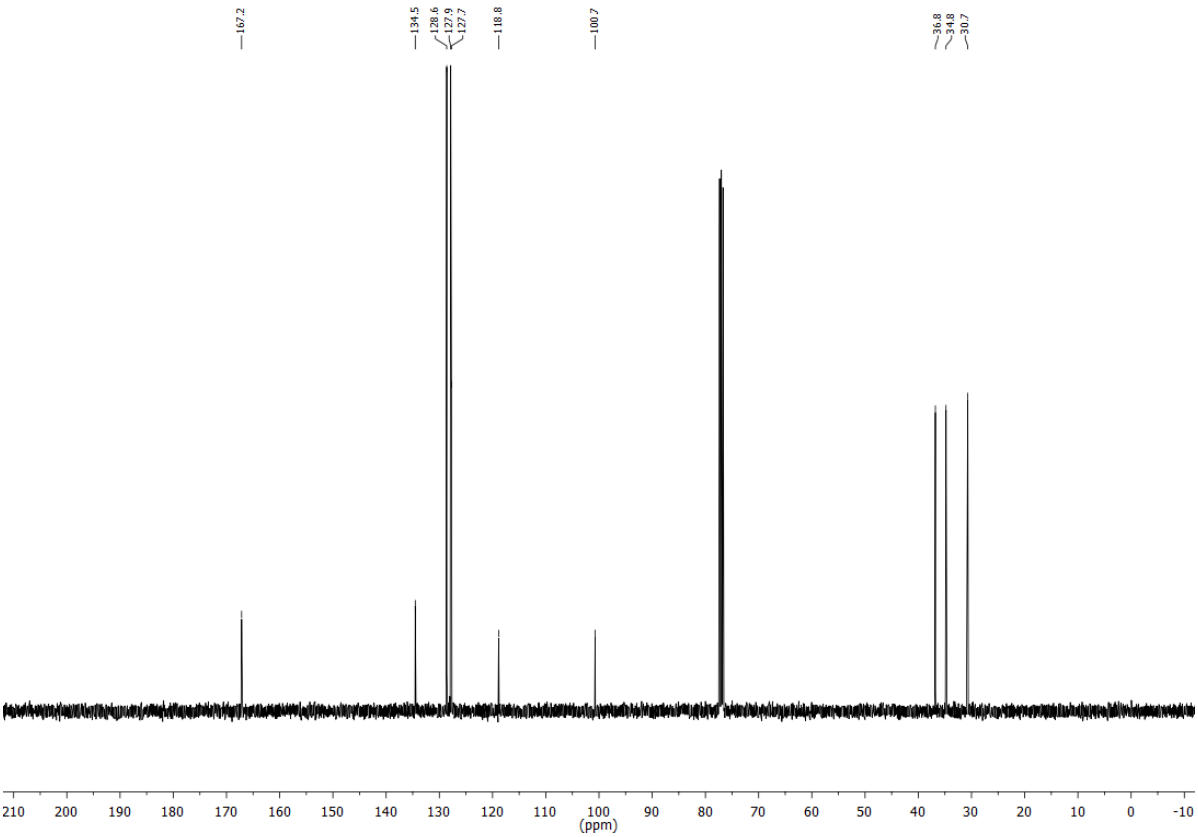
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 30.7, 34.8, 36.8, 100.7, 118.8, 127.7, 127.9, 128.6, 134.5, 167.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2967, 2937, 2864, 2195, 1557, 1489, 1437, 1156, 1082, 993.

$C_{12}H_{11}NS$ calcd.: 201.0612, found: 201.0616 (GC-HRMS).

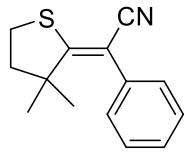


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(3,3-Dimethyldihydrothiophen-2(3*H*)-ylidene)-2-phenylacetonitrile (4f')



Compound **3f'** (23.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (1 h reaction time, 120 °C) to furnish product **4f'** after flash column chromatography (*n*-pentane:EtOAc = 10:1) as an off-colorless solid (22.0 mg, 96 µmol, 96%).

m.p.: 119 °C.

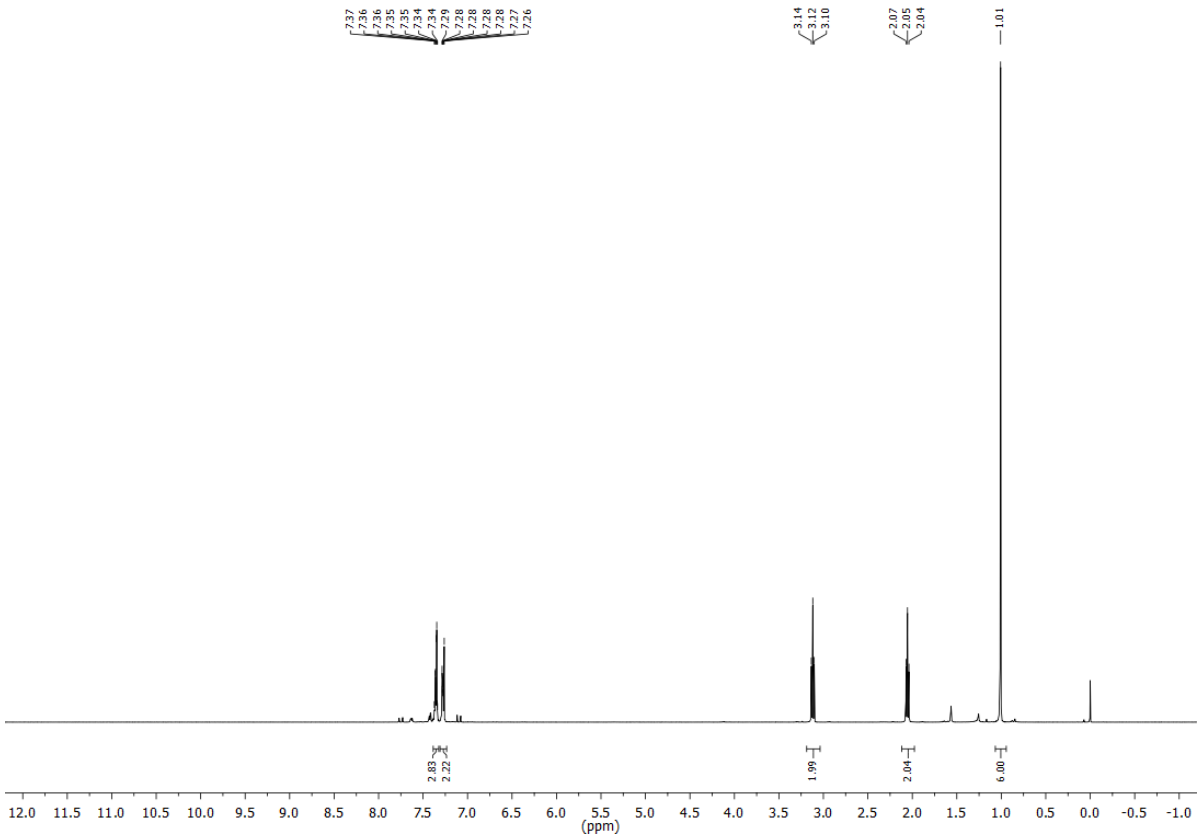
R_f = 0.16 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.01 (s, 6H), 2.05 (t, *J*=6.5, 2H), 3.12 (t, *J*=6.5, 2H), 7.25 – 7.30 (m, 2H), 7.36 (dd, *J*=5.0, 1.9, 3H).

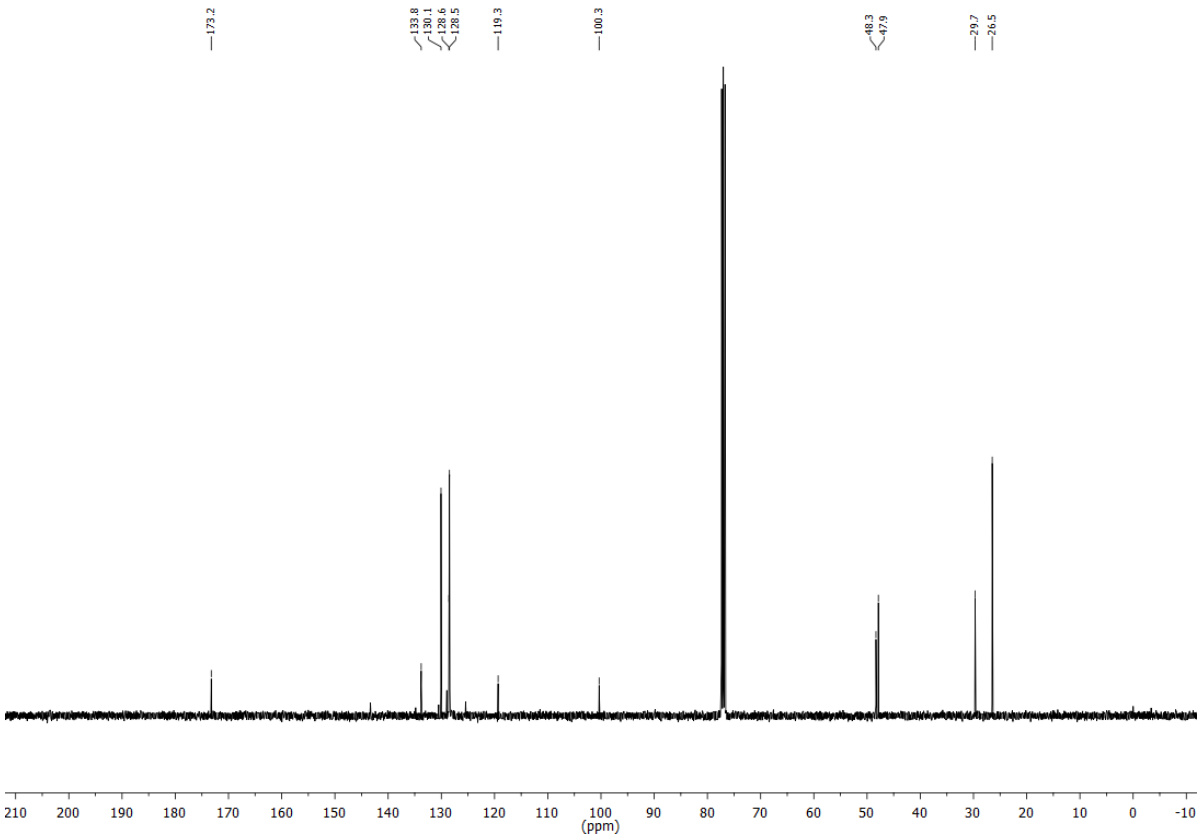
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 26.5 (2 C), 29.7, 47.9, 48.3, 100.3, 119.3, 128.5 (2 C), 128.6, 130.1 (2 C), 133.8, 173.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3055, 2965, 2926, 2864, 2187, 1562, 1446, 1231, 1150, 989.

$C_{14}H_{15}NS$ calcd.: 229.0925, found: 229.0900 (GC-HRMS).

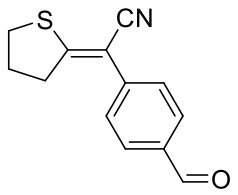


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Dihydrothiophen-2(3*H*)-ylidene)-2-(4-formylphenyl)acetonitrile (4g)



Compound **3g** (23.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product **4g** after flash column chromatography (*n*-pentane:EtOAc = 10:1→5:1) as an orange solid (13.0 mg, 57 µmol, 57%).

m.p.: 96 °C.

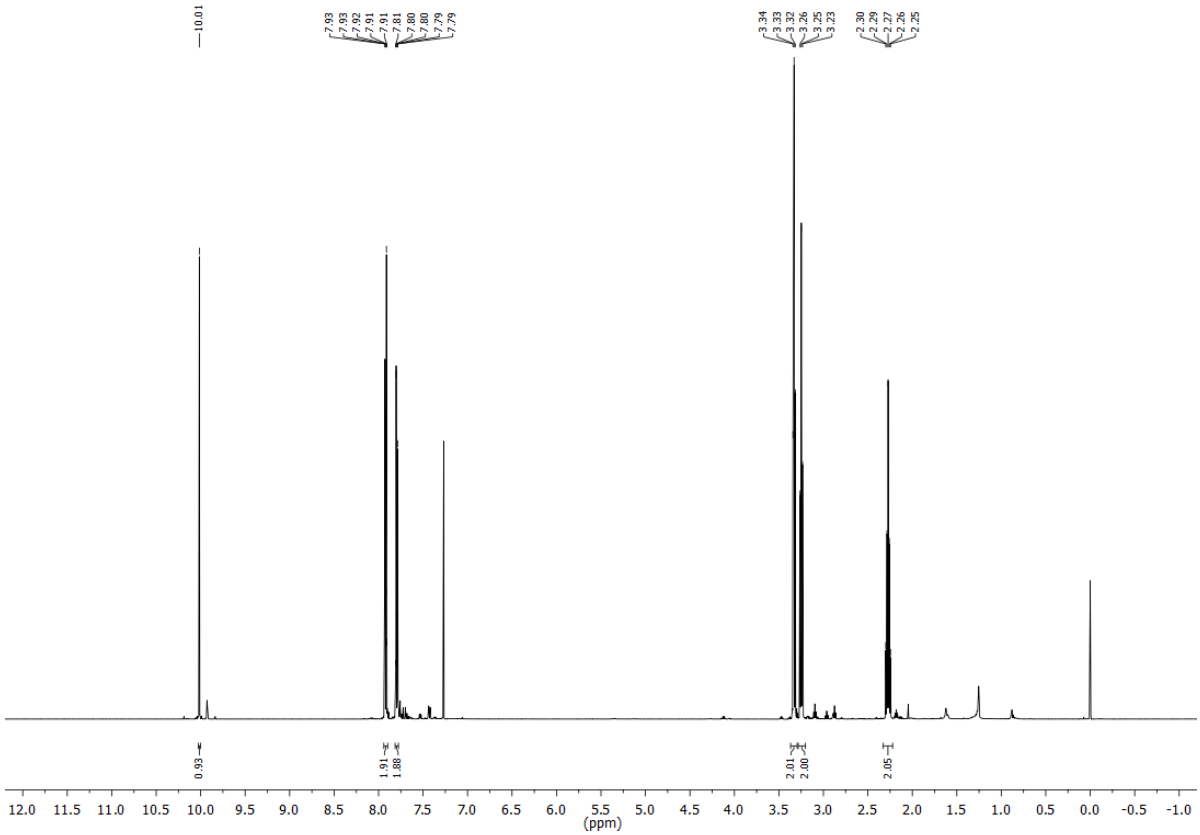
R_f = 0.63 (*n*-pentane:EtOAc = 1:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.27 (p, *J* = 6.7 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 3.33 (t, *J* = 6.4 Hz, 2H), 7.78 – 7.81 (m, 2H), 7.90 – 7.94 (m, 2H), 10.01 (s, 1H).

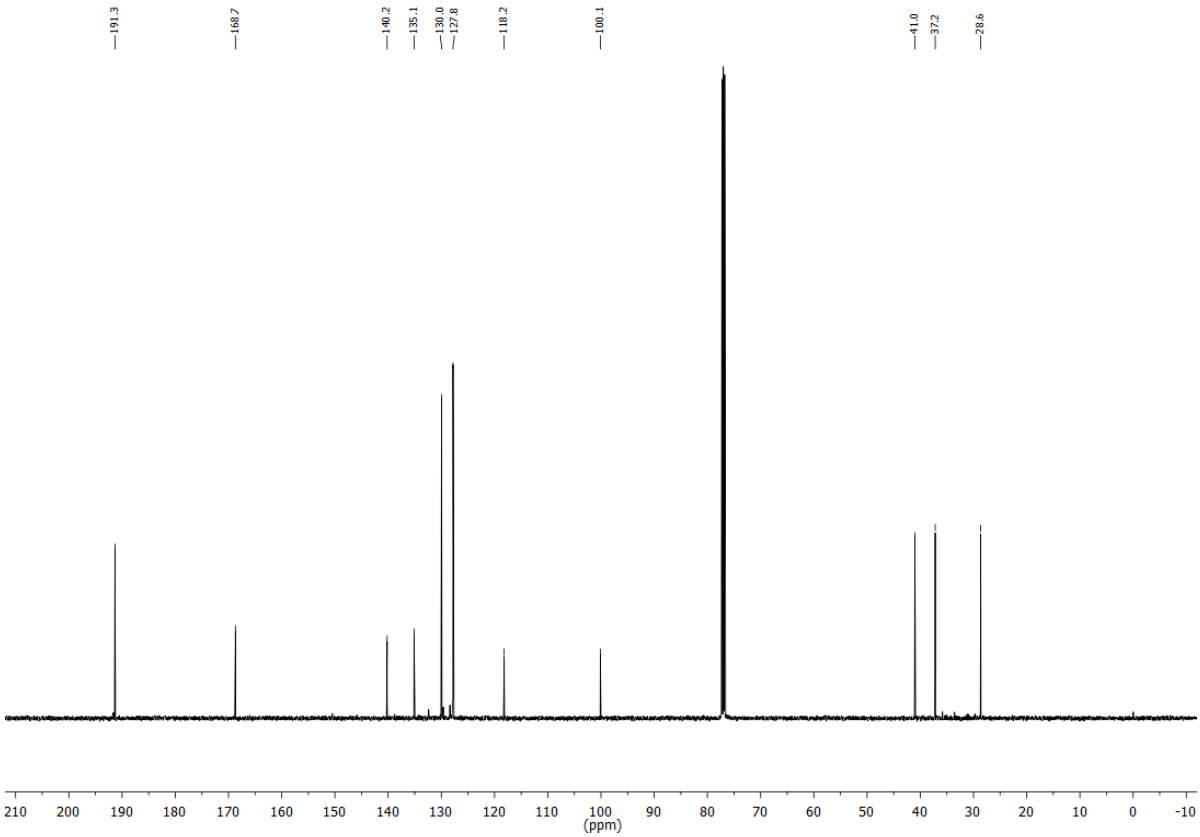
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 28.6, 37.2, 41.0, 100.1, 118.2, 127.8, 130.0, 135.1, 140.2, 168.7, 191.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2921, 2868, 2774, 2200, 1690, 1599, 1540, 1393, 1304, 1249, 1212, 1167, 1006.

$C_{13}H_{11}NOS$ calcd.: 229.0561, found: 229.0559 (GC-HRMS).

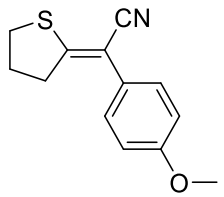


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(Dihydrothiophen-2(3*H*)-ylidene)-2-(4-methoxyphenyl)acetonitrile (4h)



Compound **3h** (23.2 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product **4h** after flash column chromatography (*n*-pentane:EtOAc = 20:1→5:1) as an orange oil (18.0 mg, 76 µmol, 76%).

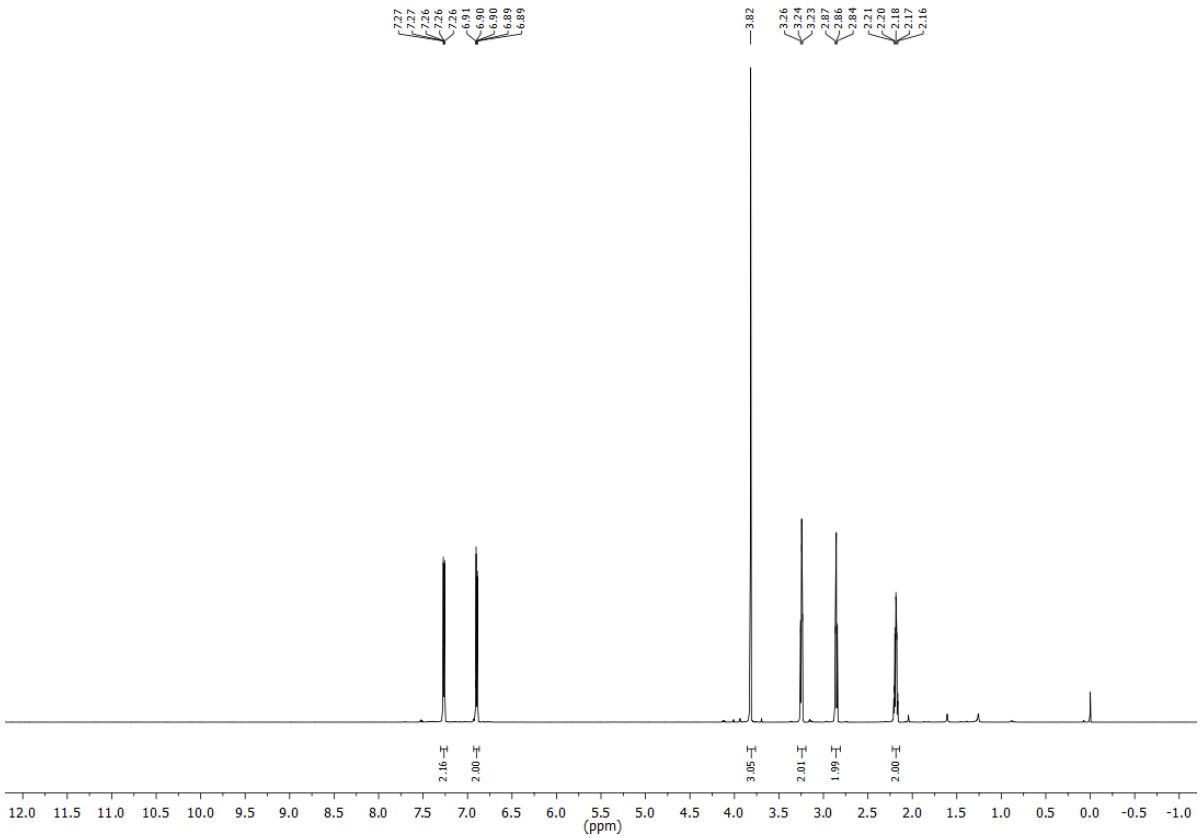
R_f = 0.67 (*n*-pentane:EtOAc = 1:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 2.18 (p, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 6.9 Hz, 2H), 3.24 (t, *J* = 6.5 Hz, 2H), 3.82 (s, 3H), 6.87 – 6.92 (m, 2H), 7.24 – 7.29 (m, 2H).

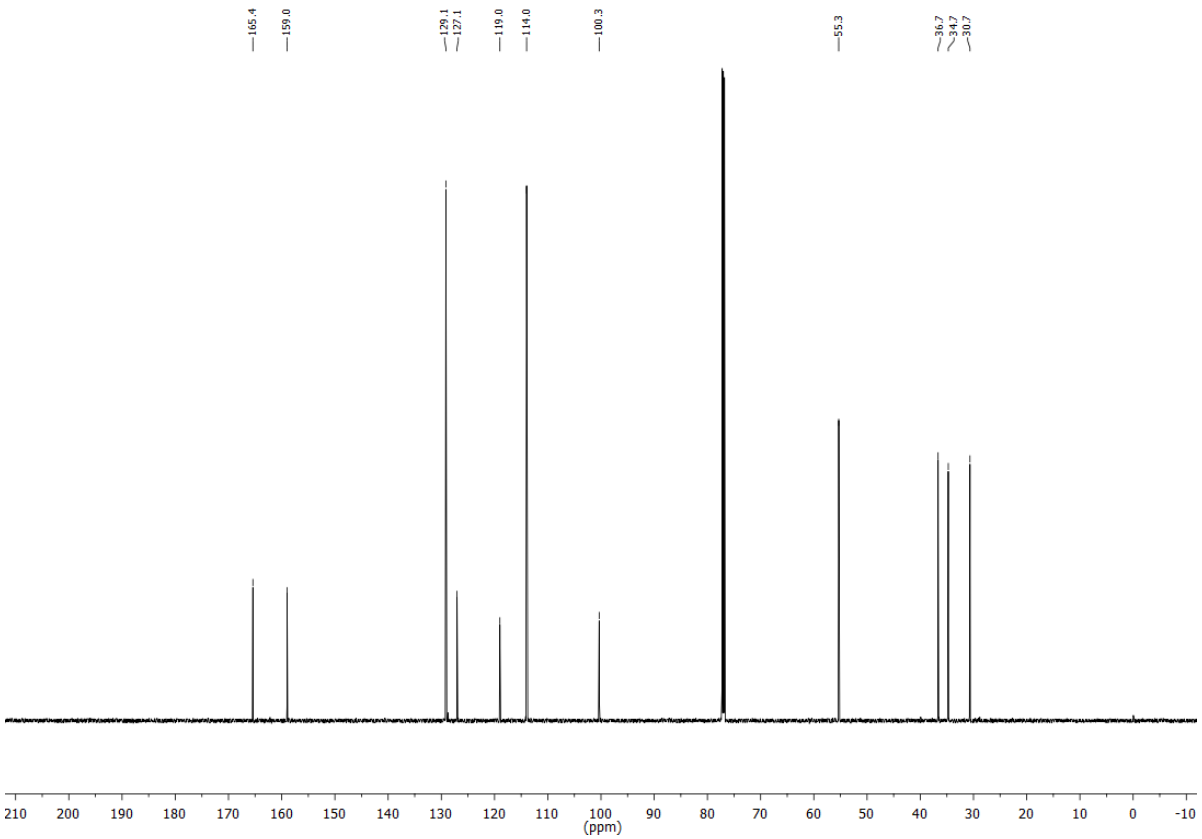
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 30.7, 34.7, 36.7, 55.3, 100.3, 114.0, 119.0, 127.1, 129.1, 159.0, 165.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2935, 2837, 2199, 1571, 1506, 1460, 1246, 1176, 1027, 995.

$C_{13}H_{13}NOS$ calcd.: 231.0718, found: 231.0734 (GC-HRMS).

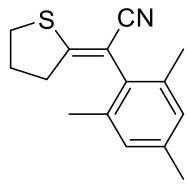


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*Z*)-2-(Dihydrothiophen-2(3*H*)-ylidene)-2-mesitylacetonitrile (4i)



Compound **3i** (24.4 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product **4i** after flash column chromatography (*n*-pentane:EtOAc = 10:1) as a colorless solid (16.5 mg, 68 µmol, 68%).

m.p.: 95 °C.

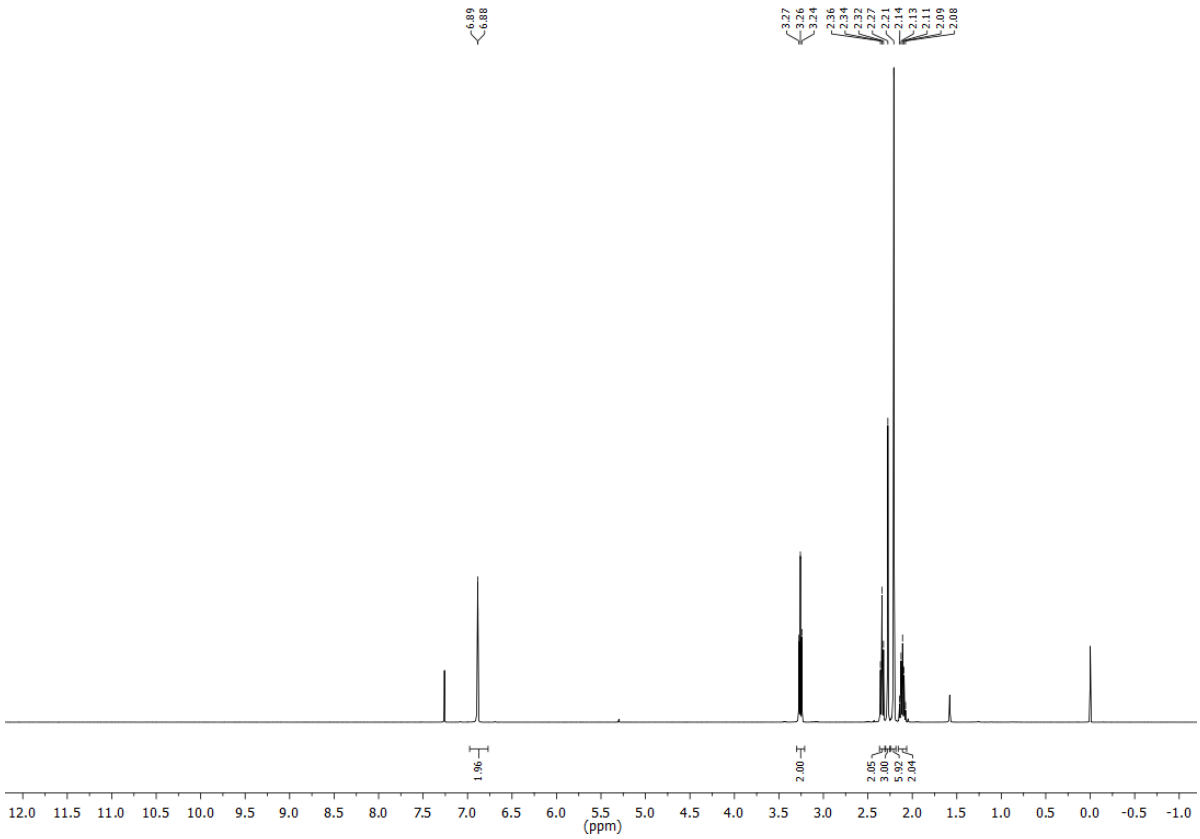
R_f = 0.23 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.11 (p, *J* = 6.6 Hz, 2H), 2.21 (s, 6H), 2.27 (s, 3H), 2.34 (t, *J* = 6.9 Hz, 2H), 3.26 (t, *J* = 6.4 Hz, 2H), 6.89 (d, *J* = 1.1 Hz, 2H).

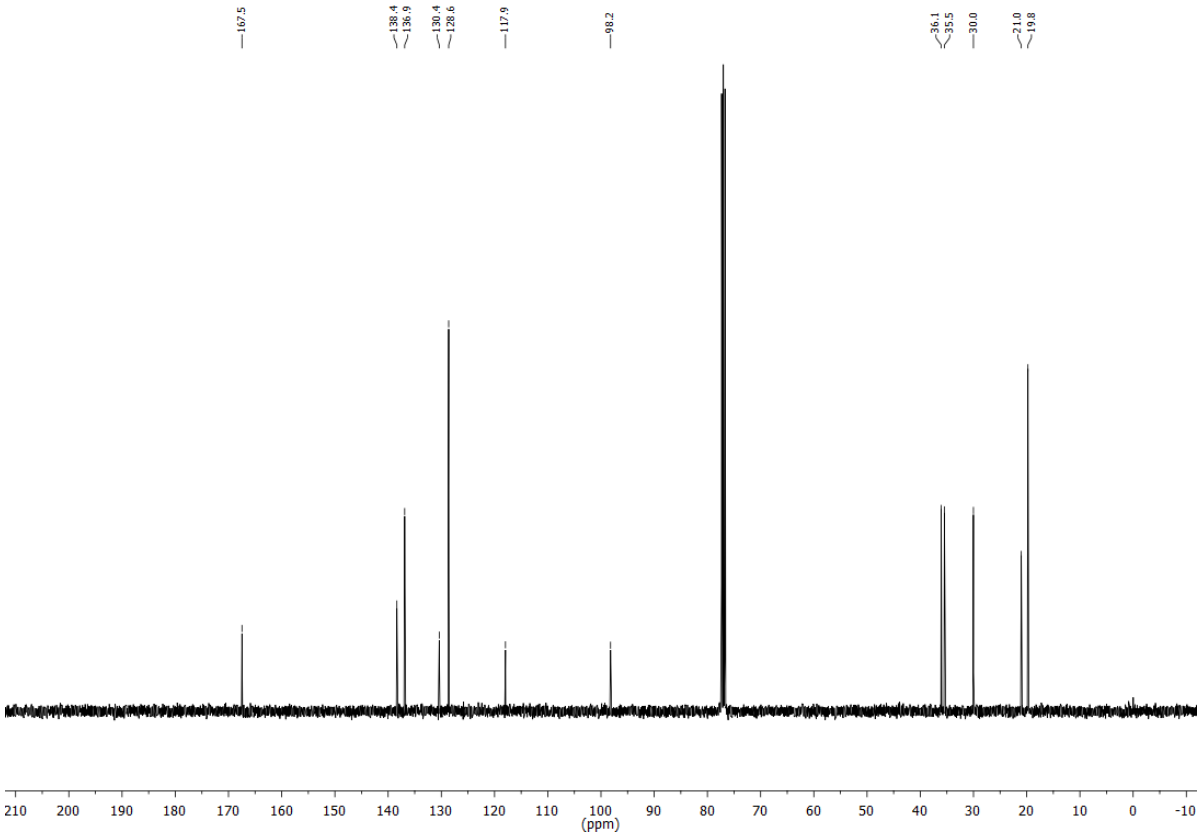
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 19.8, 21.0, 30.0, 35.5, 36.1, 98.2, 117.9, 128.6, 130.4, 136.9, 138.4, 167.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2969, 2919, 2857, 2193, 1580, 1440, 1375, 1088, 1000.

$C_{15}H_{17}NS$ calcd.: 243.1082, found: 243.1096 (GC-HRMS).

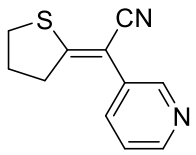


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Dihydrothiophen-2(3*H*)-ylidene)-2-(pyridin-3-yl)acetonitrile (4j)



Compound **3j** (20.3 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product **4j** after flash column chromatography (*n*-pentane:EtOAc = 4:1→1:1) as a colorless solid (16.5 mg, 68 µmol, 68%).

m.p.: 26 °C.

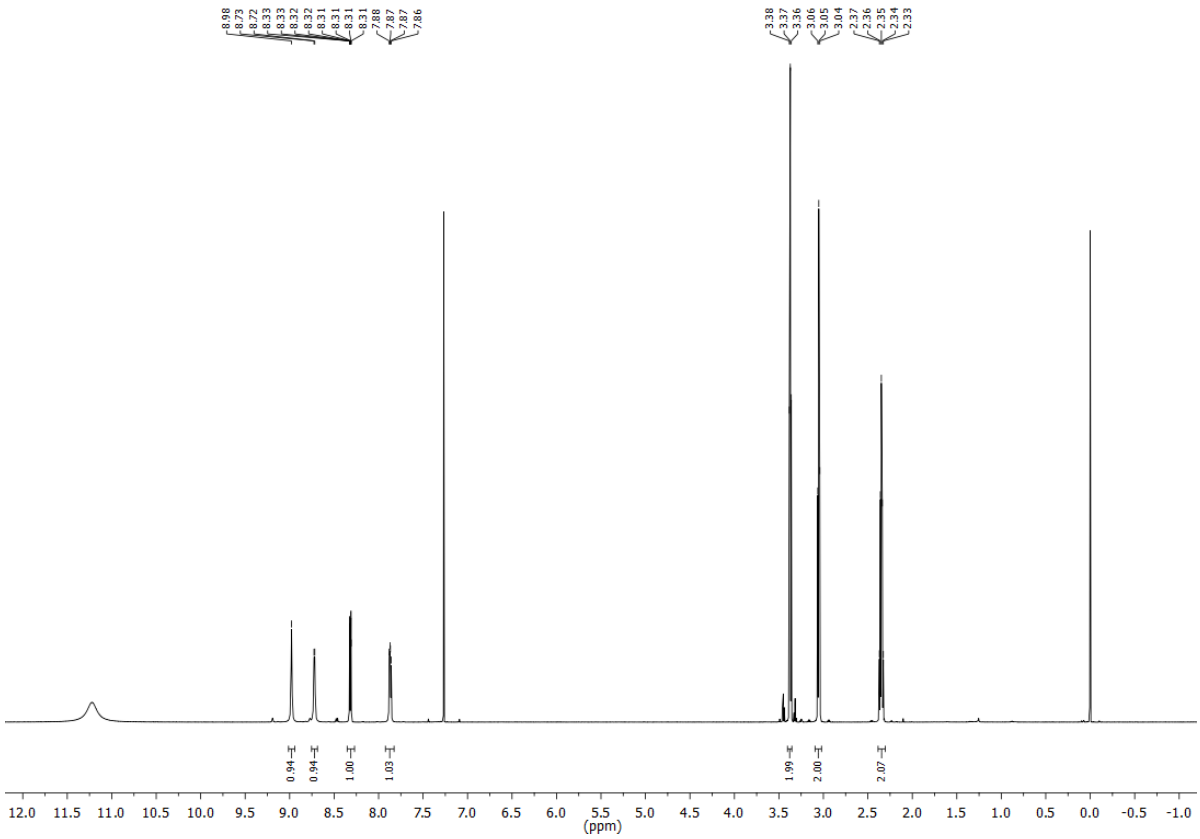
$\mathbf{R_f}$ = 0.08 (*n*-pentane:EtOAc = 1:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 2.35 (p, *J* = 6.7 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H), 3.37 (t, *J* = 6.5 Hz, 2H), 7.87 (dd, *J* = 8.2, 5.4 Hz, 1H), 8.32 (ddd, *J* = 8.3, 2.2, 1.2 Hz, 1H), 8.72 (d, *J* = 5.4 Hz, 1H), 8.98 (s, 1H).

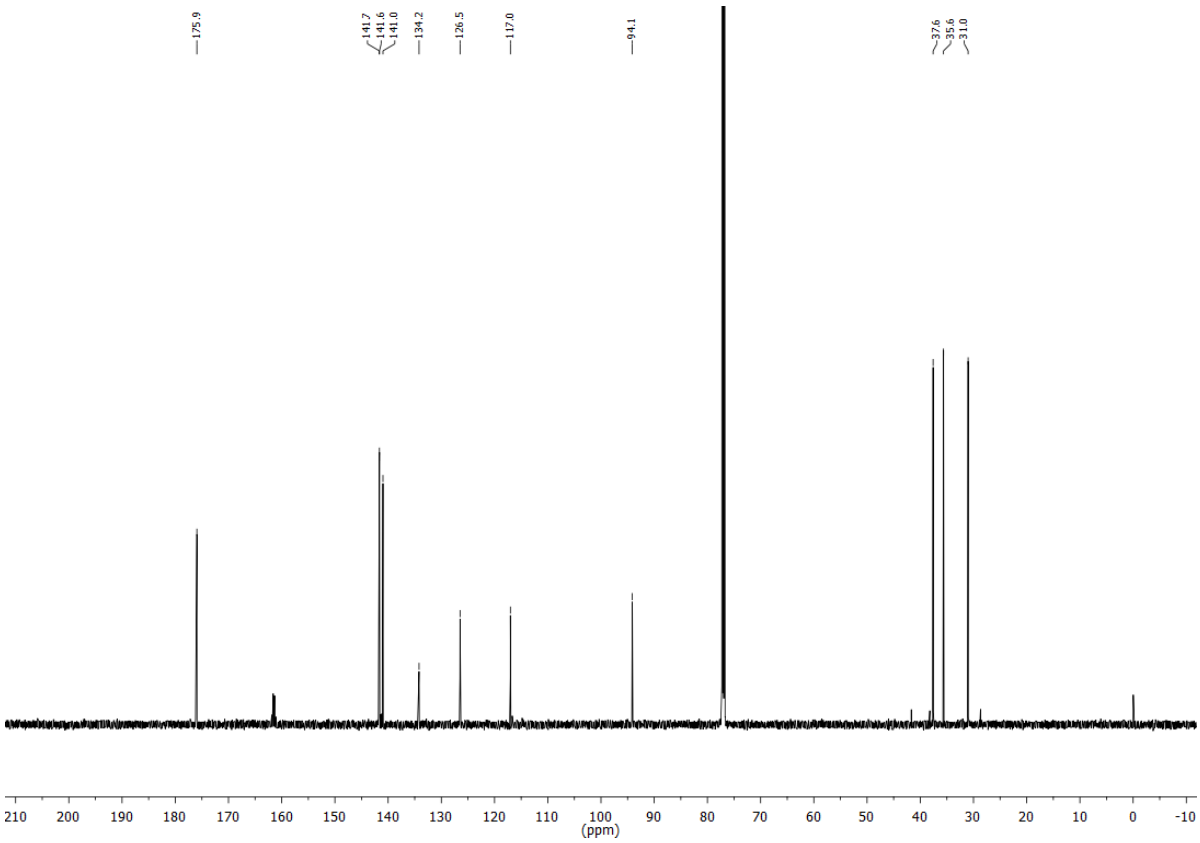
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 31.0, 35.6, 37.6, 94.1, 117.0, 126.5, 134.2, 141.0, 141.6, 141.7, 175.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3076, 3042, 2948, 2208, 1776, 1670, 1554, 1471, 1121.

$C_{11}H_{10}N_2S$ calcd.: 202.0565, found: 202.0589 (GC-HRMS).

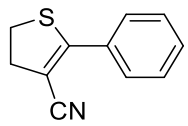


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

2-Phenyl-4,5-dihydrothiophene-3-carbonitrile (4k)



Compound **3j** (30.0 mg, 160 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (120 h reaction time) to furnish product **4j** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a slightly yellow oil (10.0 mg, 53 µmol, 33%).

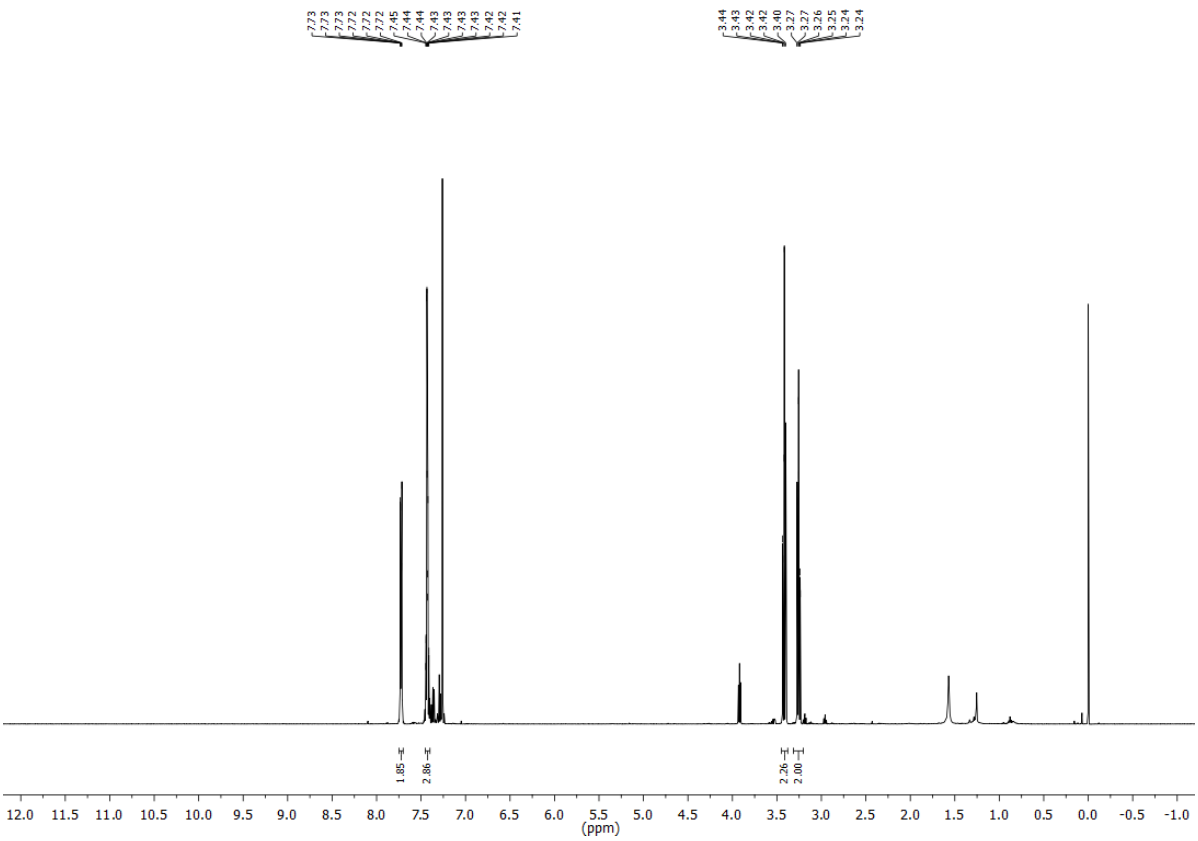
R_f = 0.40 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.26 (td, *J* = 8.7, 1.0 Hz, 2H), 3.39 – 3.44 (m, 2H), 7.40 – 7.46 (m, 3H), 7.71 – 7.74 (m, 2H).

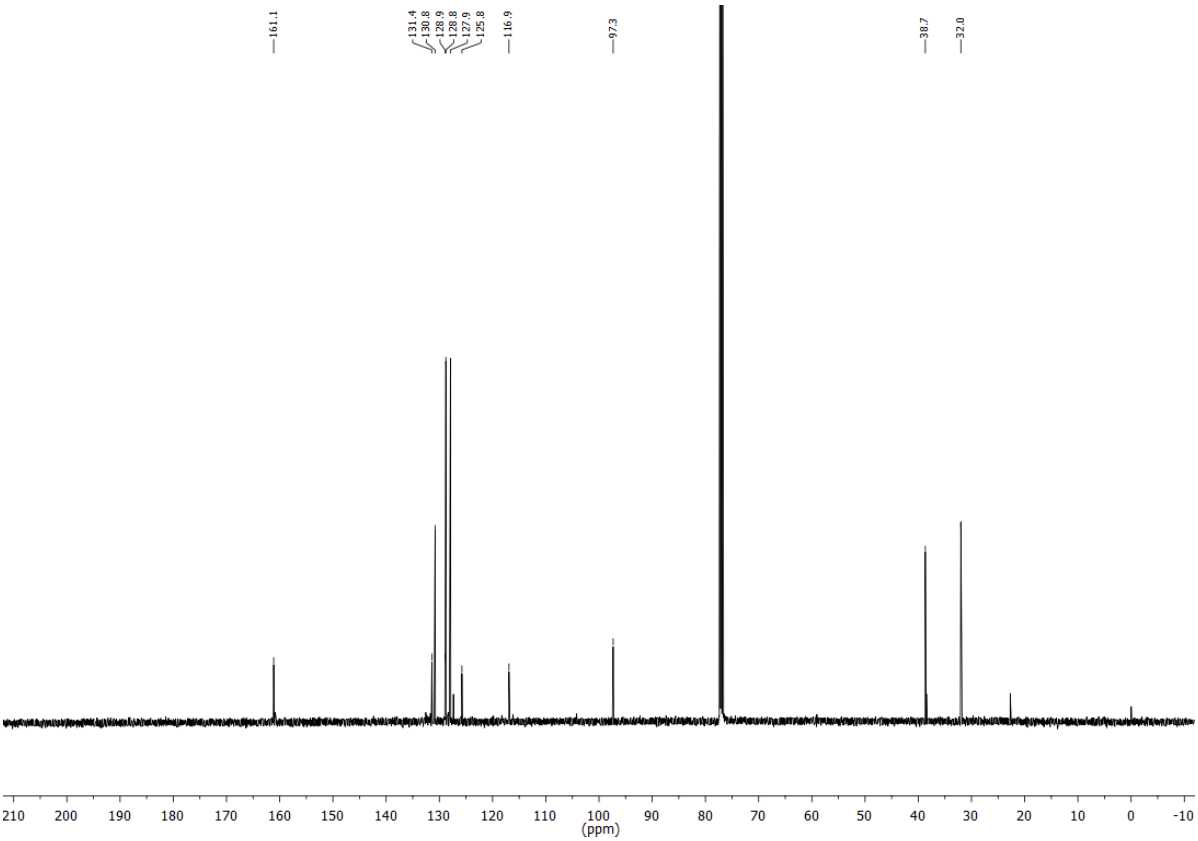
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 32.0, 38.7, 97.3, 116.9, 125.8, 127.9, 128.8, 128.9, 130.8, 131.4, 161.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3057, 2926, 2846, 2199, 1592, 1567, 1489, 1443, 1244, 1172, 1077.

$C_{11}H_9NS$ calcd.: 187.0456, found: 187.0453 (GC-HRMS).

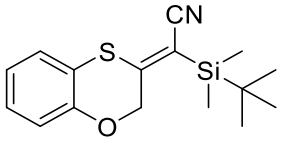


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-2-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-2-(*tert*-butyldimethylsilyl)acetonitrile (6a)



Compound **5a** (35.0 mg, 119 µmol, 1.00 equiv.) was transformed according to GP CAT2 (3 h reaction time) to obtain product **6a** after flash column chromatography (*n*-pentane:DCM = 4:1) as a colorless solid (19.0 mg, 62 µmol, 54%).

m.p.: 57 °C.

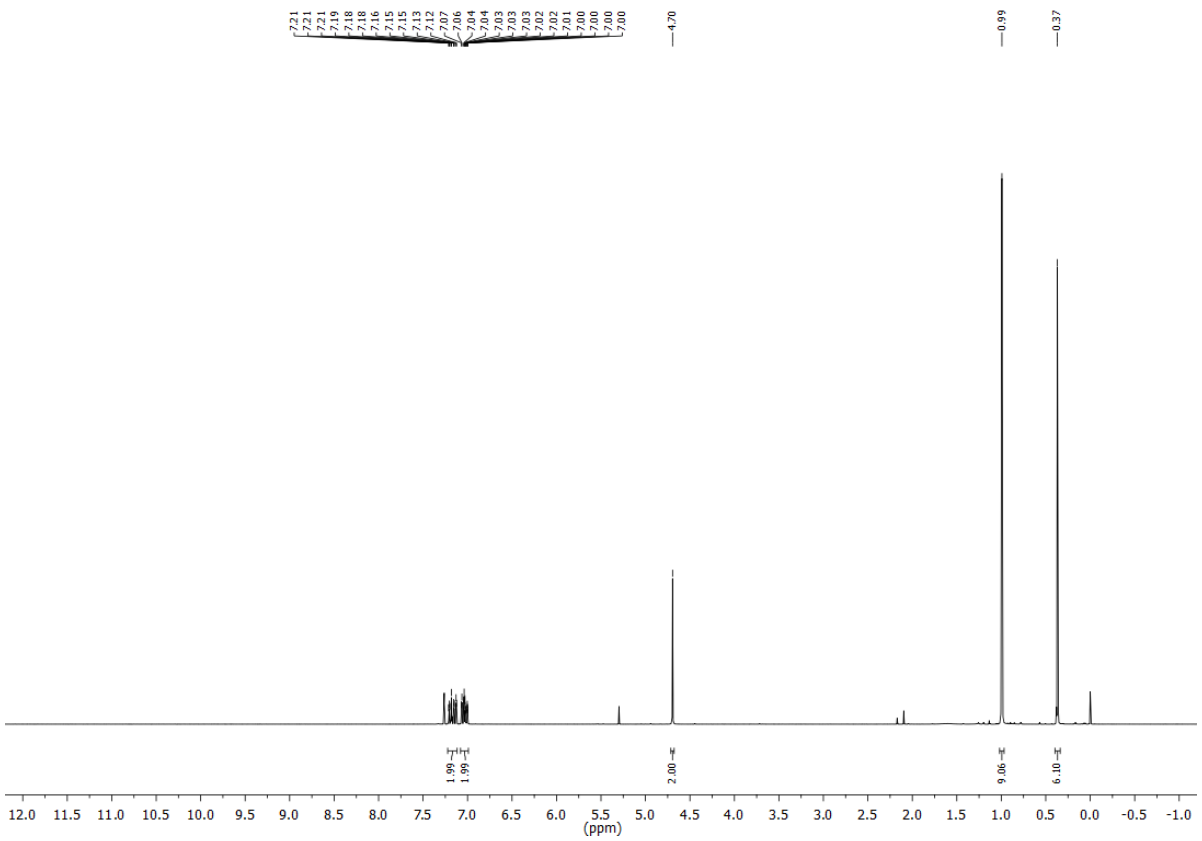
R_f = 0.41 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.37 (s, 6H), 0.99 (s, 9H), 4.70 (s, 2H), 6.99 – 7.07 (m, 2H), 7.12 – 7.22 (m, 2H).

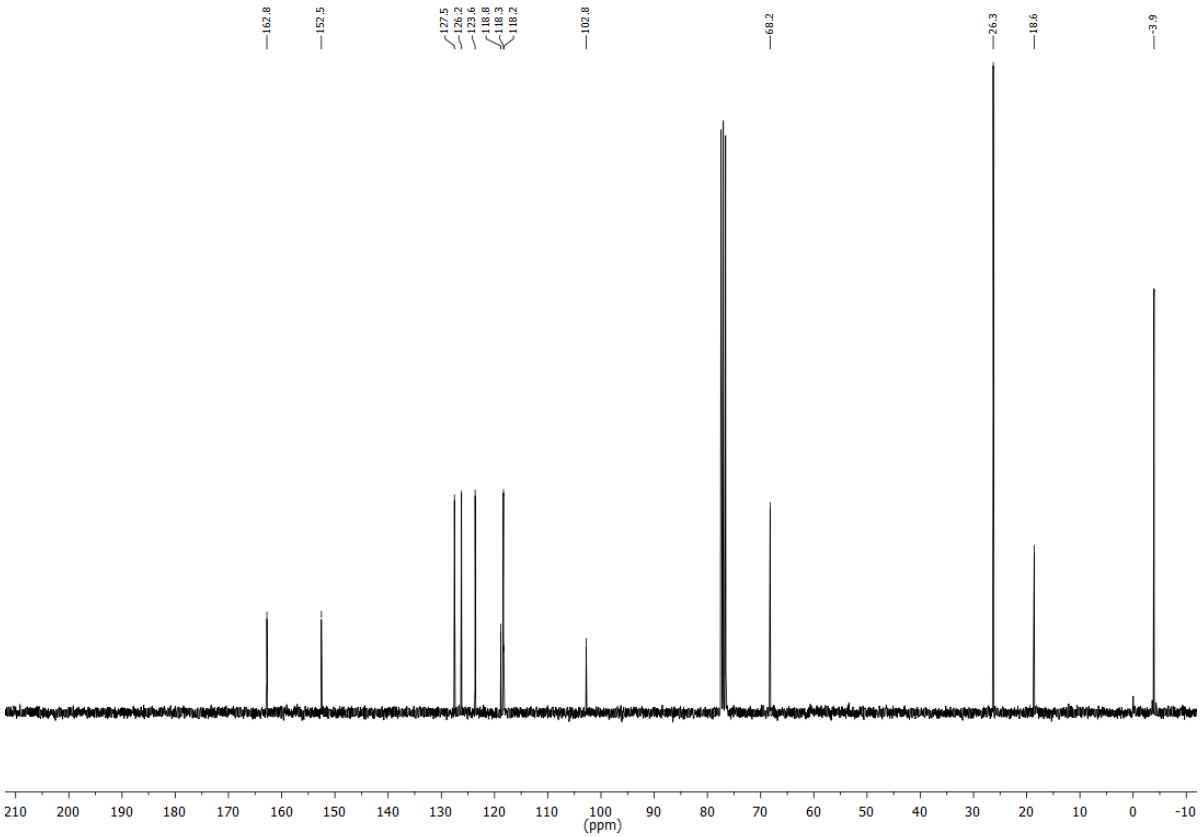
^{13}C-NMR (76 MHz, $CDCl_3$): δ = -3.9, 18.6, 26.3, 68.2, 102.8, 118.2, 118.3, 118.8, 123.6, 126.2, 127.5, 152.5, 162.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2959, 2929, 2883, 2856, 2187, 1533, 1469, 1258, 1216, 1157, 1044, 1003.

$C_{16}H_{21}NOSSi$ calcd.: 303.1113, found: 303.1130 (GC-HRMS).

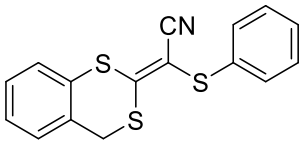


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (76 MHz, $CDCl_3$).

(*E*)-2-(4*H*-Benzo[*d*][1,3]dithiin-2-ylidene)-2-(phenylthio)acetonitrile (6b)



Compound **5b** (32.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 (3 h reaction time) to obtain product **6b** after flash column chromatography (*n*-pentane:EtOAc = 50:1) as a yellow oil (26.0 mg, 83 µmol, 81%).

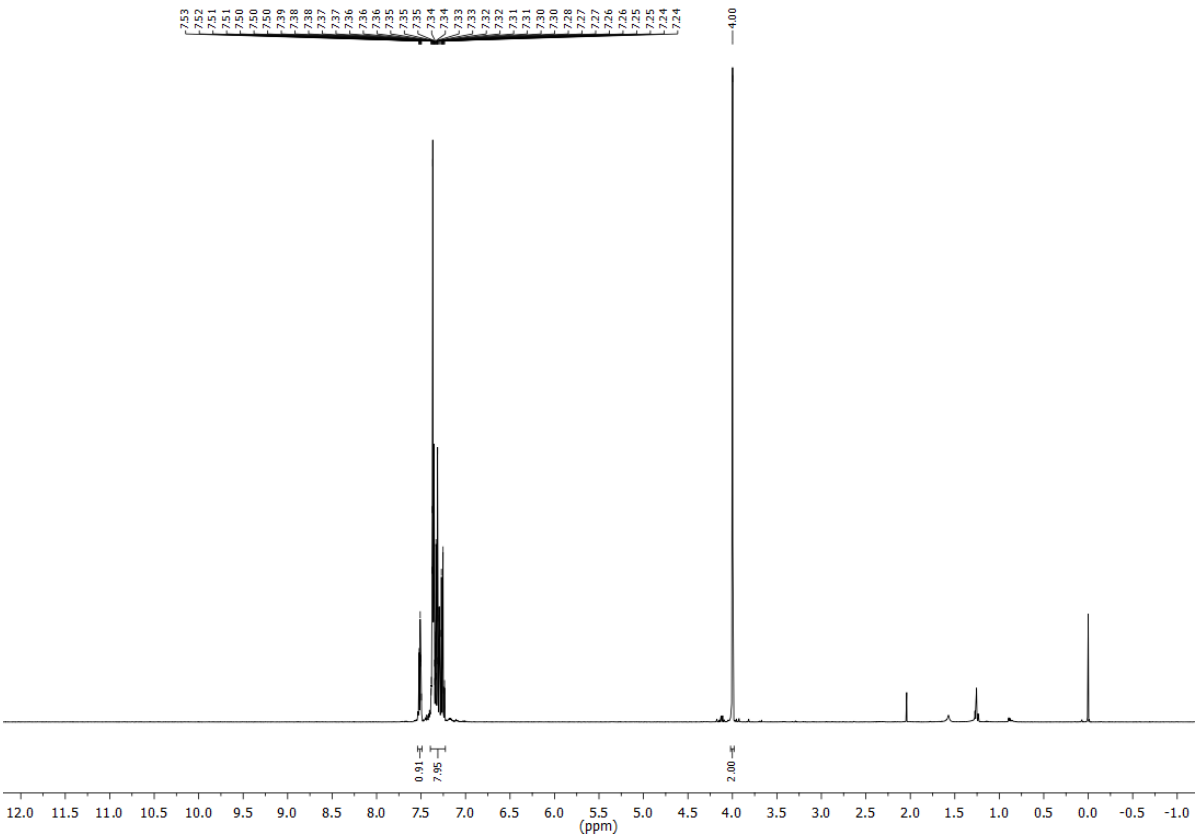
R_f = 0.12 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.00 (s, 2H), 7.23 – 7.40 (m, 8H), 7.49 – 7.54 (m, 1H).

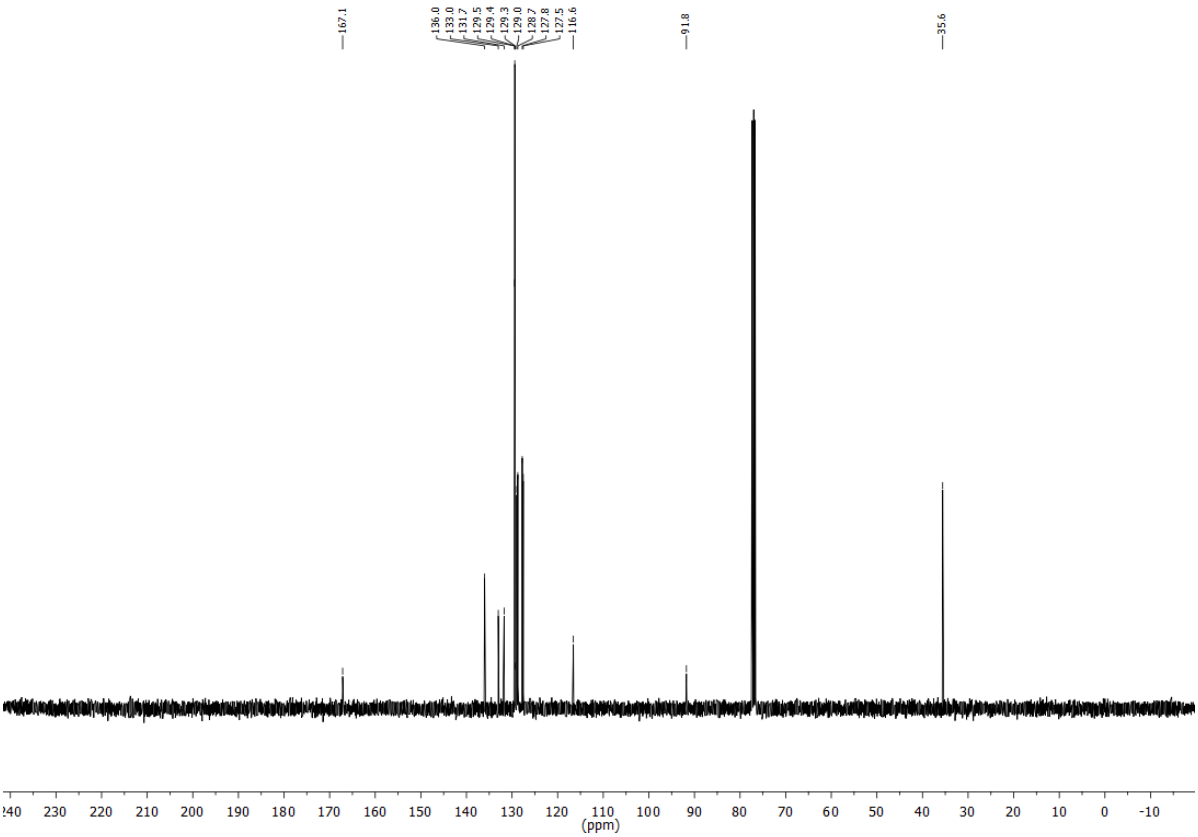
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 35.6, 91.8, 116.6, 127.5, 127.8, 128.7, 129.0, 129.3, 129.4, 129.5, 131.7, 133.0, 136.0, 167.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2919, 2852, 2193, 1576, 1467, 1446, 1410, 1070, 1022, 941.

$C_{16}H_{11}NS_3$ calcd.: 313.0054, found: 313.0042 (GC-HRMS).

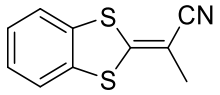


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

2-(Benzo[*d*][1,3]dithiol-2-ylidene)propanenitrile (6c)



Compound **5c** (21.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 (3 h reaction time) to obtain product **6c** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as an off-white solid (13.0 mg, 63 µmol, 62%).

m.p.: 71 °C.

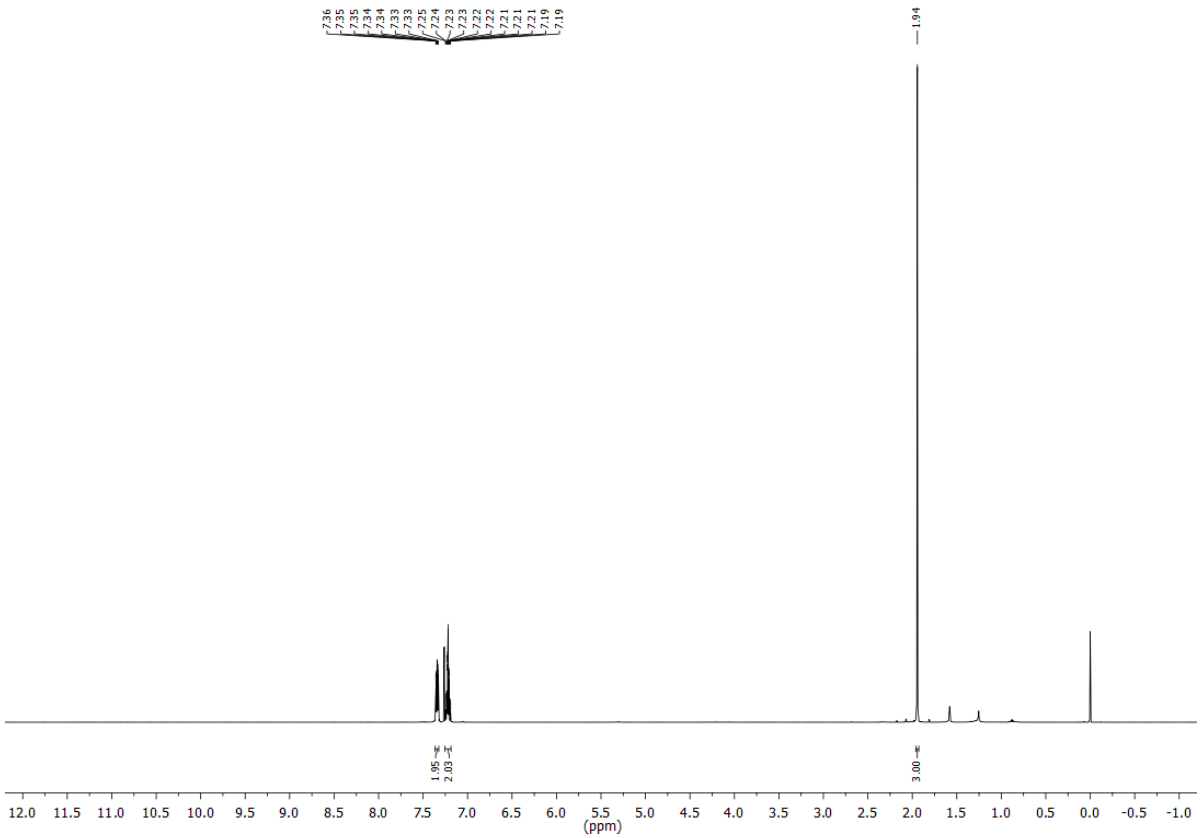
R_f = 0.22 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 7.19 – 7.25 (m, 2H), 7.33 – 7.36 (m, 2H).

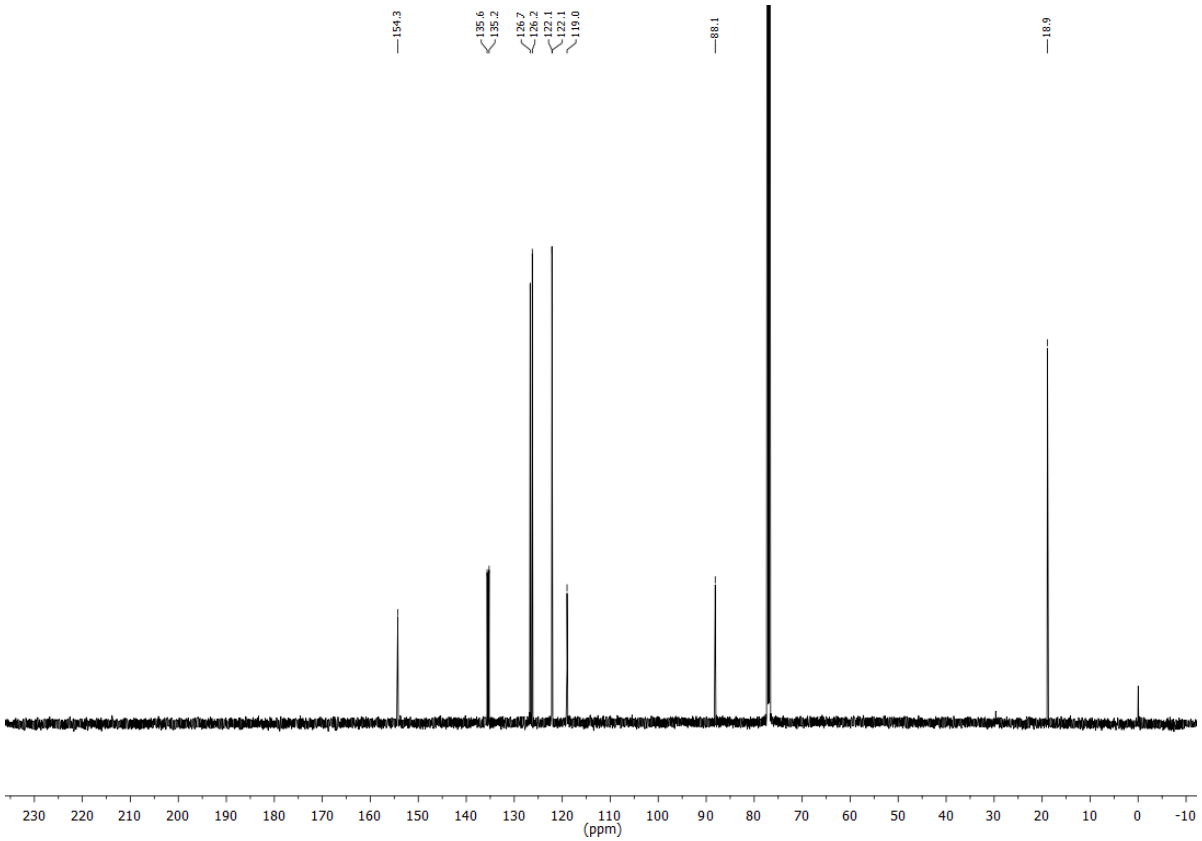
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 18.9, 88.1, 119.0, 122.1, 122.1, 126.2, 126.7, 135.2, 135.6, 154.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3057, 2921, 2851, 2193, 1571, 1542, 1436, 1232, 1120, 1034, 945.

$C_{10}H_7NS_2$ calcd.: 205.0020, found: 205.0025 (GC-HRMS).

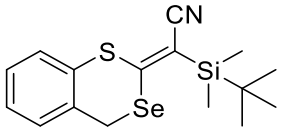


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(4*H*-benzo[*e*][1,3]thiaselenin-2-ylidene)-2-(*tert*-butyldimethylsilyl)acetonitrile (6d)



Compound **5d** (26.0 mg, 70 µmol, 1.00 equiv.) was transformed according to GP CAT1 (5 h reaction time) to obtain product **6d** after flash column chromatography (*n*-pentane:EtOAc = 100:1) as a colorless solid (17.3 mg, 47 µmol, 67%).

m.p.: 134 °C.

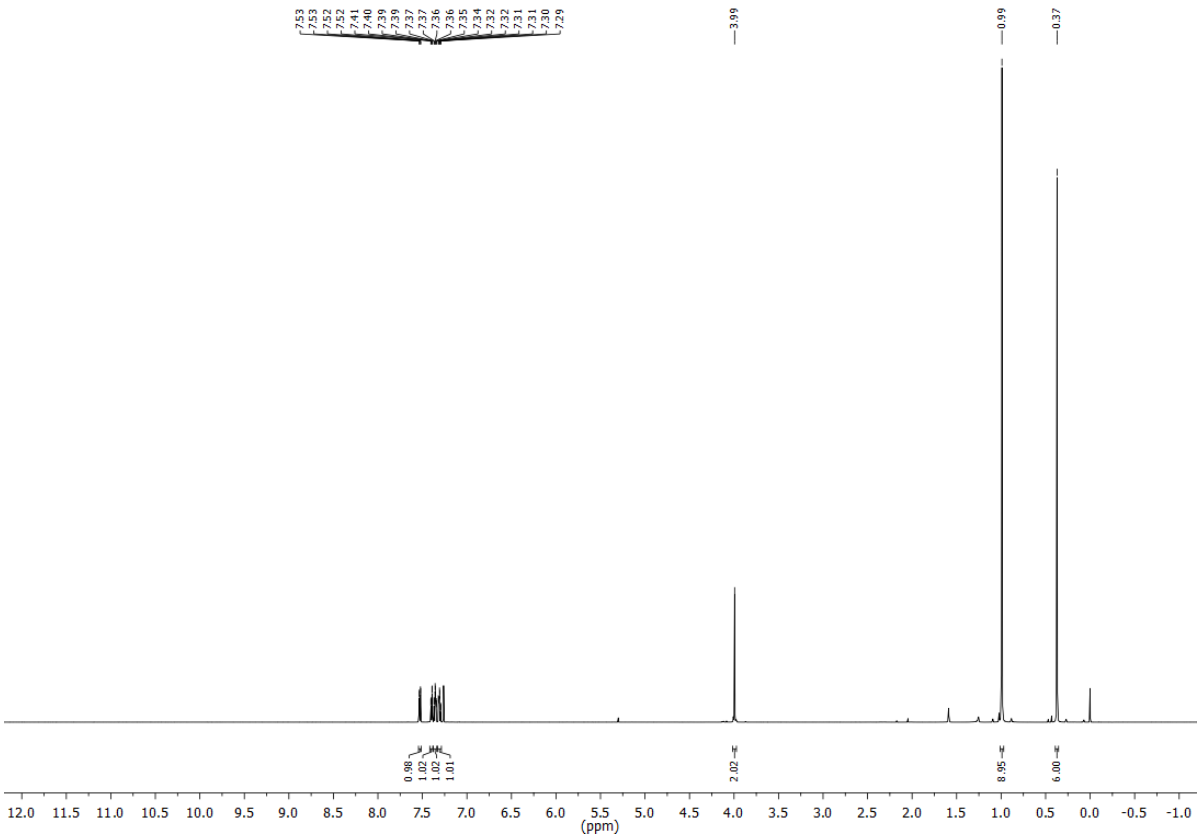
R_f = 0.31 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.37 (s, 6H), 0.99 (s, 9H), 3.99 (s, 2H), 7.31 (td, *J* = 7.5, 1.6 Hz, 1H), 7.36 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.3 Hz, 1H).

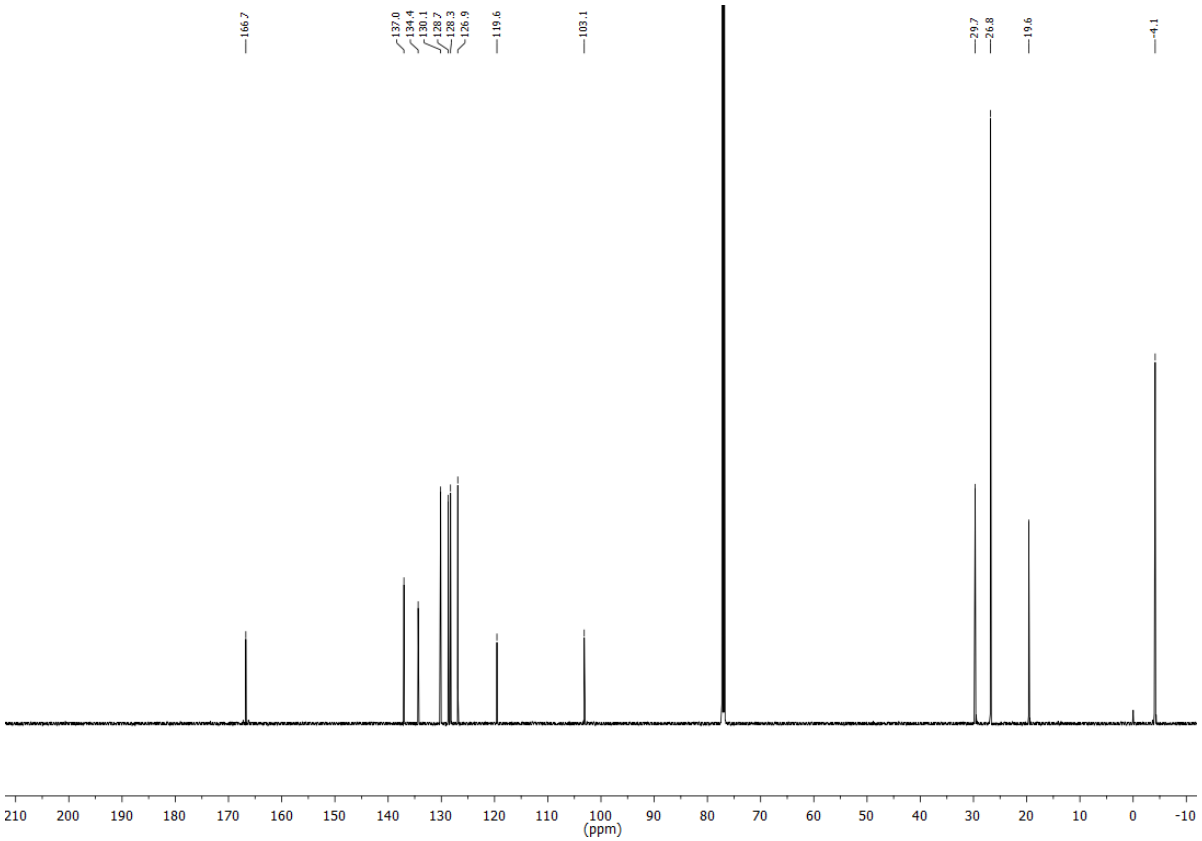
^{13}C-NMR (151 MHz, $CDCl_3$): δ = -4.1, 19.6, 26.8, 29.7, 103.1, 119.6, 126.9, 128.3, 128.7, 130.1, 134.4, 137.0, 166.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2933, 2886, 2854, 2184, 1455, 1245, 1134, 1062.

$C_{16}H_{21}NSSeSi$ calcd.: 367.0329, found: 367.0341 (GC-HRMS).

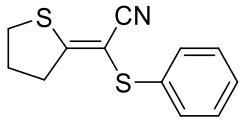


^{1}H-NMR (600 MHz, $CDCl_3$).



^{13}C-NMR (151 MHz, $CDCl_3$).

(*E*)-2-(Dihydrothiophen-2(3*H*)-ylidene)-2-(phenylthio)acetonitrile (6e)



Compound **5e** (23.4 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product **6e** after flash column chromatography (*n*-pentane:EtOAc = 20:1→10:1) as an orange-brown oil (16.7 mg, 71 µmol, 71%).

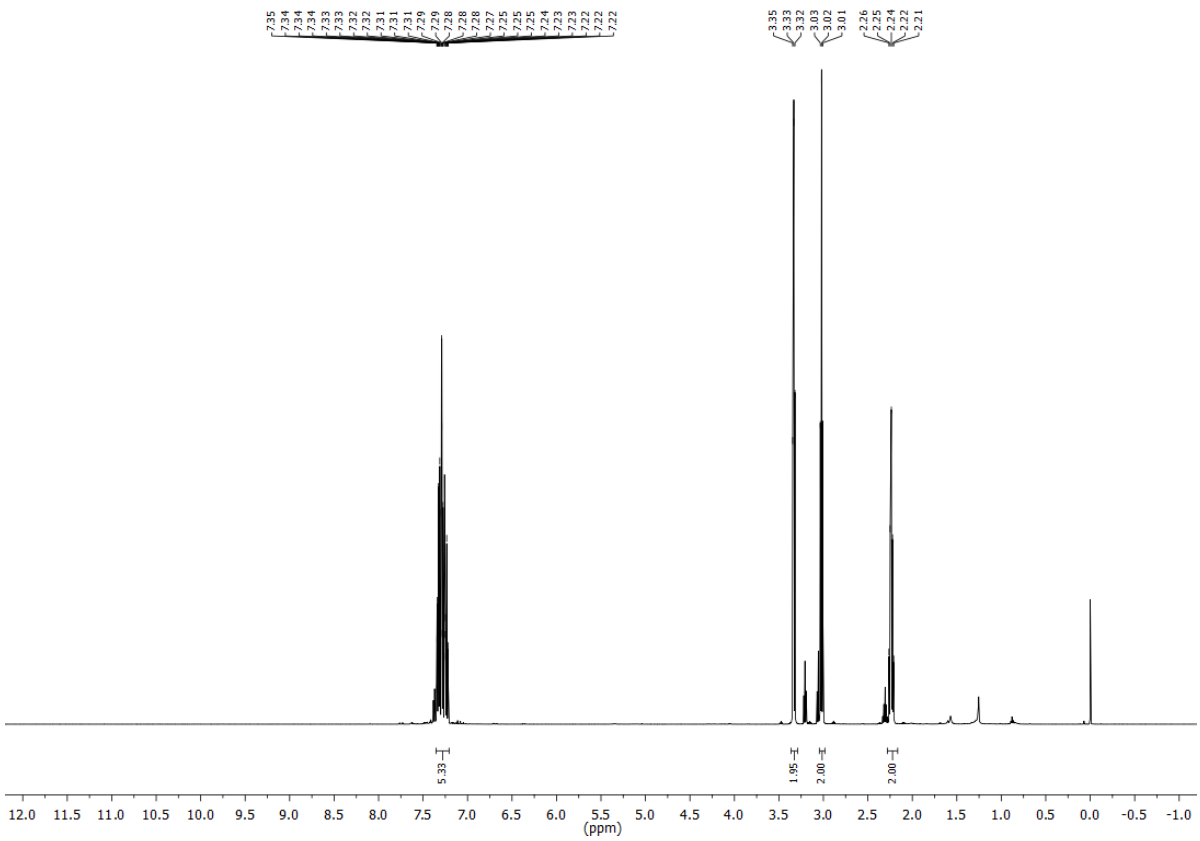
R_f = 0.13 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.24 (p, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 7.0 Hz, 2H), 3.33 (t, *J* = 6.4 Hz, 2H), 7.21 – 7.35 (m, 5H).

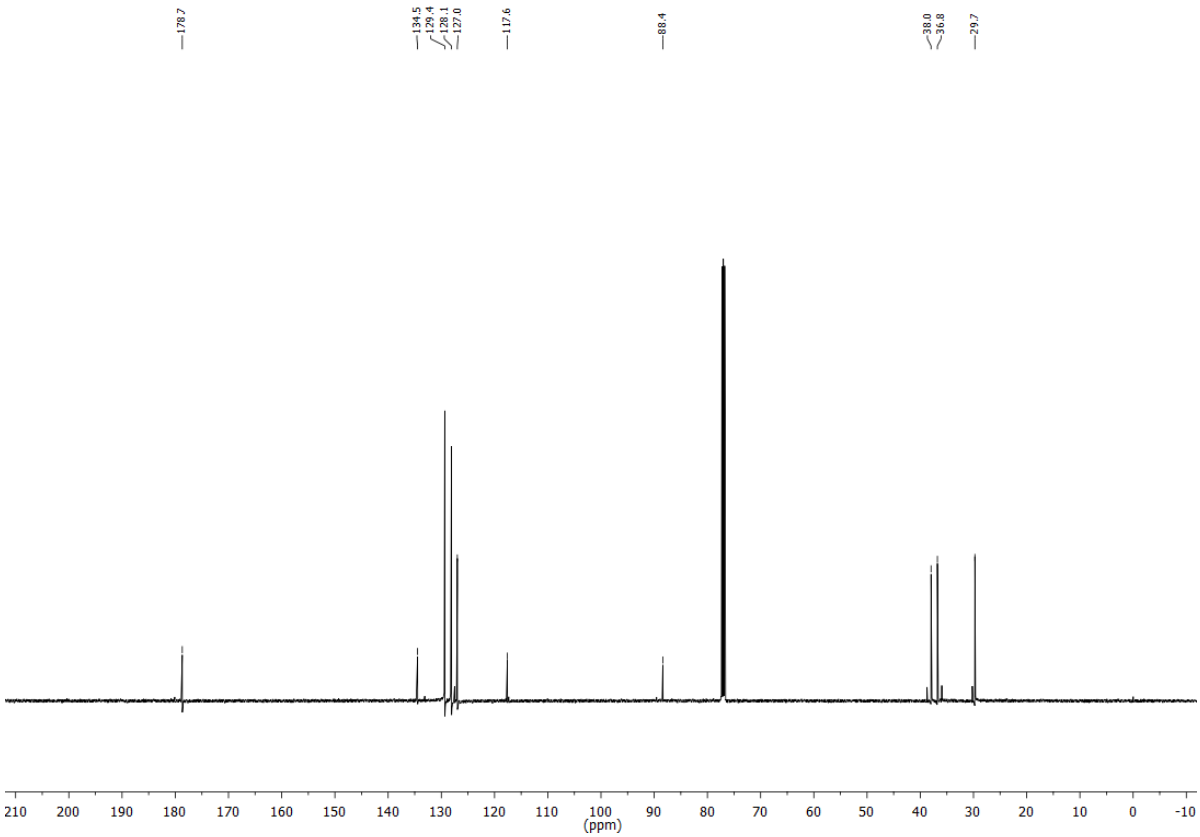
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 29.7, 36.8, 38.0, 88.4, 117.6, 127.0, 128.1, 129.4, 134.5, 178.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2933, 2859, 2201, 1539, 1475, 1437, 1266, 1131, 1073, 1001.

$C_{12}H_{11}NS_2$ calcd.: 233.0333, found: 233.0347 (GC-HRMS).

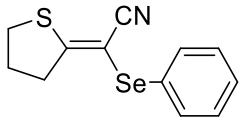


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-2-(Dihydrothiophen-2(3*H*)-ylidene)-2-(phenylselanyl)acetonitrile (6f)



Compound **5f** (30.0 mg, 107 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product **6f** after flash column chromatography (*n*-pentane:EtOAc = 50:1→20:1) as a yellow oil (13.0 mg, 46 µmol, 43%).

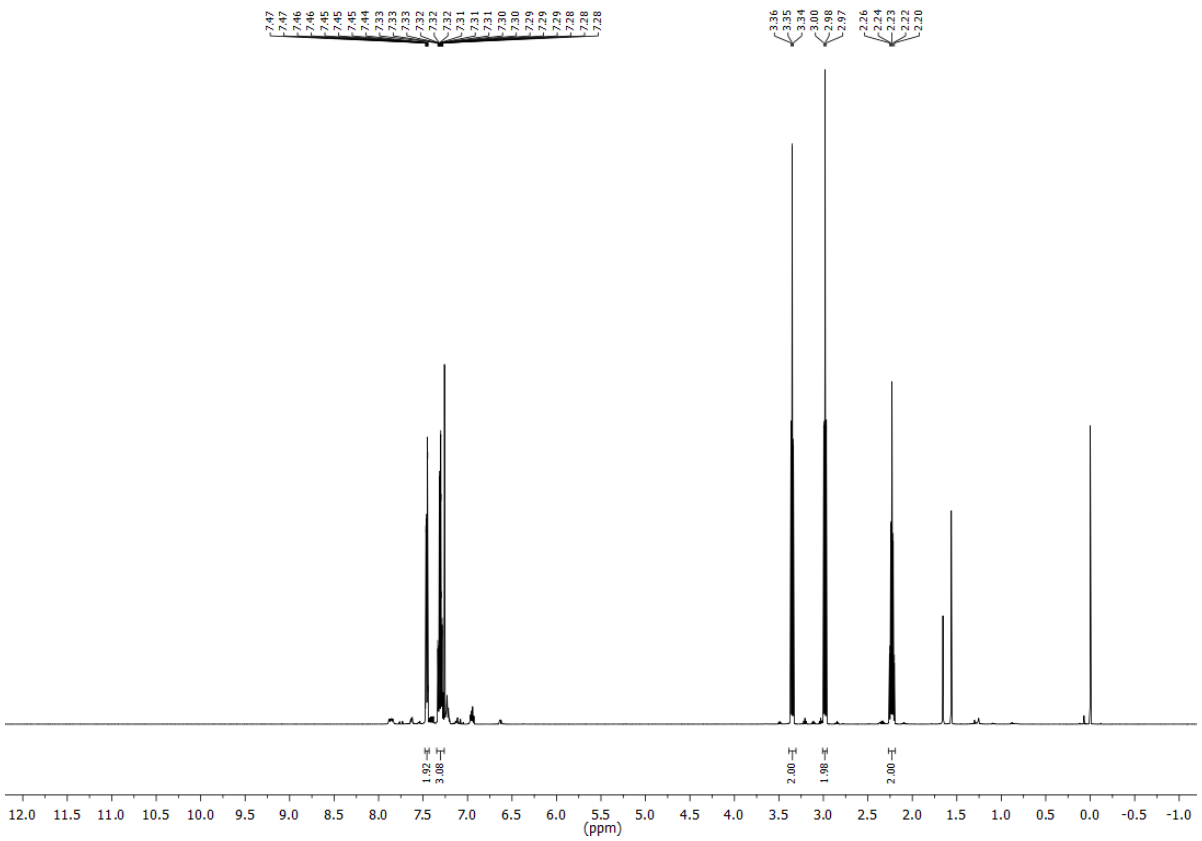
R_f = 0.10 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.23 (p, *J* = 6.7 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H), 3.35 (t, *J* = 6.5 Hz, 2H), 7.27 – 7.34 (m, 3H), 7.43 – 7.47 (m, 2H).

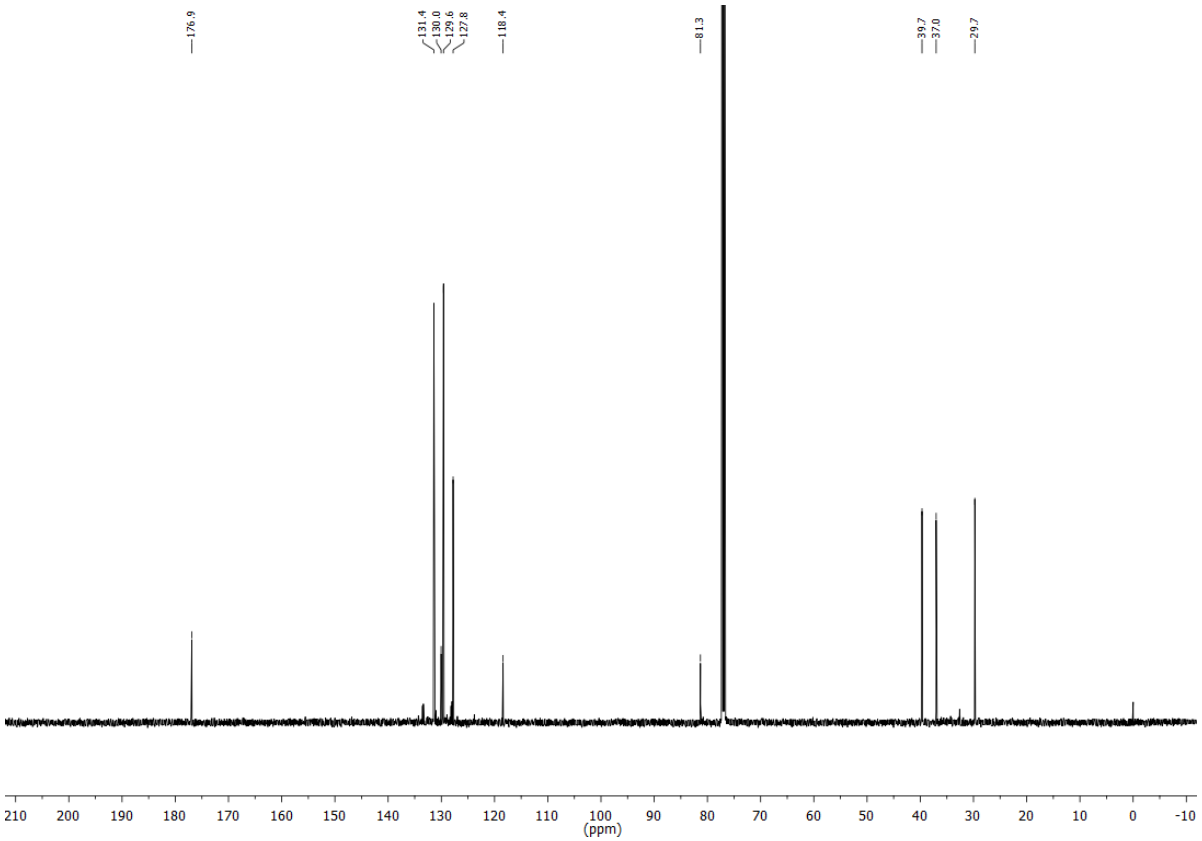
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 29.7, 37.0, 39.7, 81.3, 118.4, 127.8, 129.6, 130.0, 131.4, 176.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3056, 2934, 2860, 2195, 1543, 1472, 1432, 1403, 1263, 1226, 1117, 1094, 1009.

$C_{12}H_{11}NSSe$ calcd.: 280.9777, found: 280.9789 (GC-HRMS).

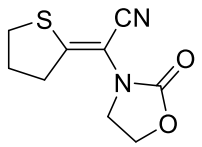


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-2-(dihydrothiophen-2(3*H*)-ylidene)-2-(2-oxooxazolidin-3-yl)acetonitrile (6g)



Compound **5g** (21.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product **6g** after flash column chromatography (*n*-pentane:EtOAc = 1:1) as a pale red solid (17 mg, 81 µmol, 81%).

m.p.: 110 °C.

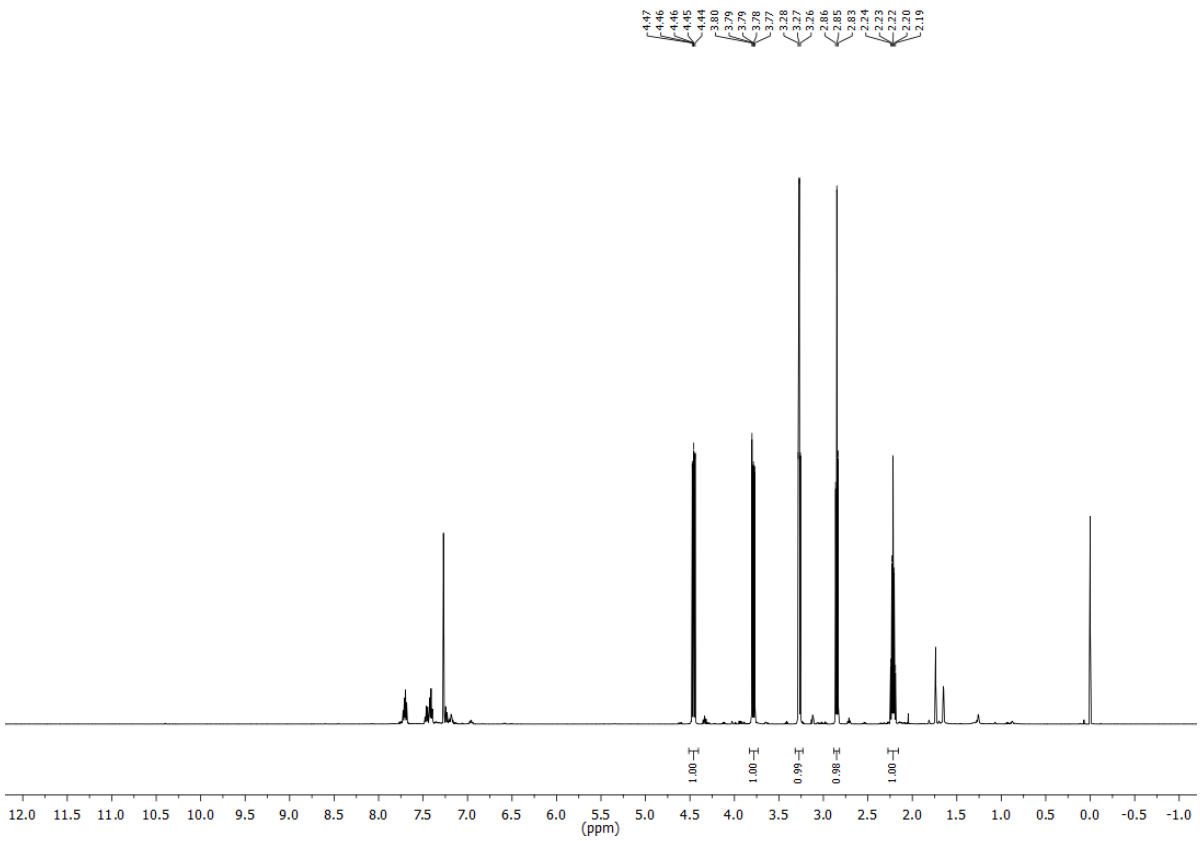
R_f = 0.14 (*n*-pentane:EtOAc = 1:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.22 (p, *J* = 6.8 Hz, 2H), 2.85 (t, *J* = 7.0 Hz, 2H), 3.27 (t, *J* = 6.4 Hz, 2H), 3.75 – 3.82 (m, 2H), 4.42 – 4.49 (m, 2H).

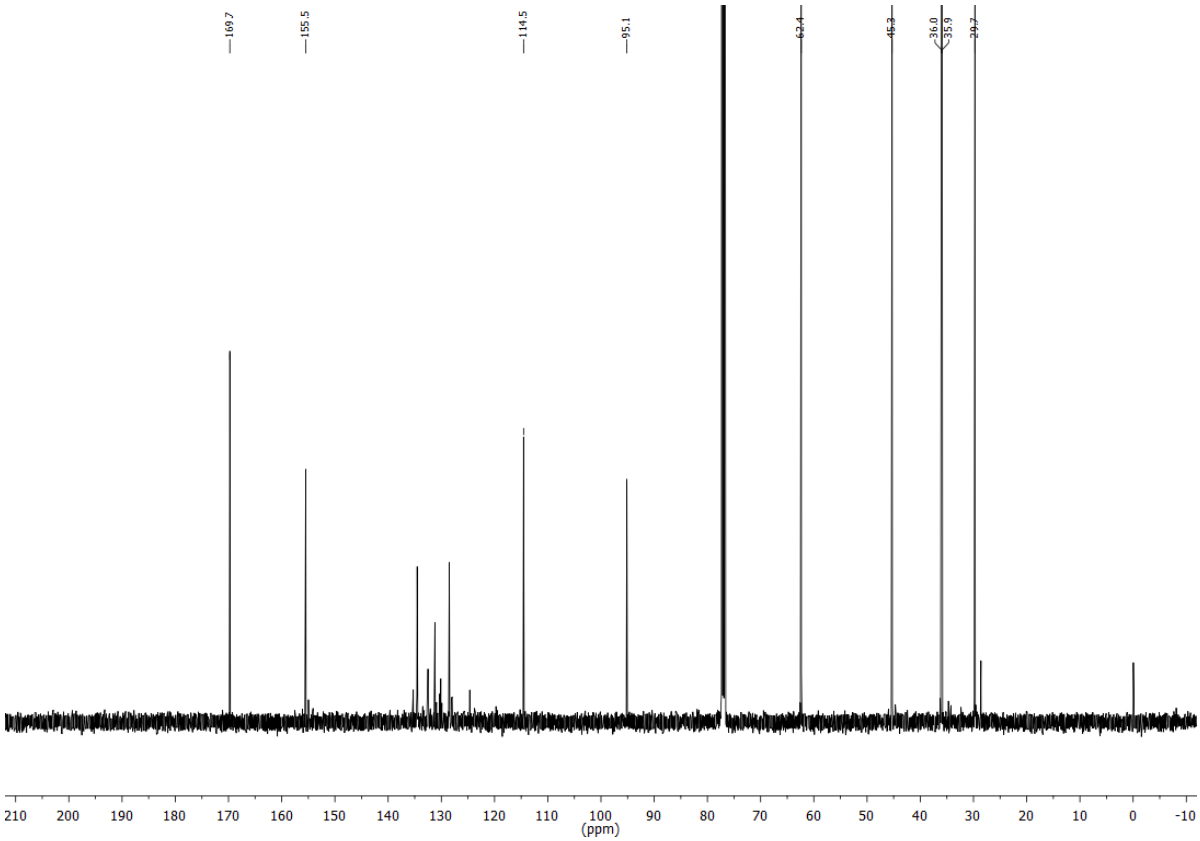
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 29.7, 35.9, 36.0, 45.3, 62.4, 95.1, 114.5, 155.5, 169.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3055, 2984, 2949, 2913, 2201, 1749, 1594, 1405, 1278, 1212, 1148, 1035, 982.

$C_9H_{10}N_2O_2S$ calcd.: 210.0463, found: 210.0488 (GC-HRMS).

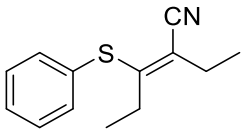


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-Ethyl-3-(phenylthio)pent-2-enenitrile (*syn*-8a)



Phenyl thiocyanate[43] (68.0 mg, 500 µmol, 1.00 equiv.) and 3-hexyne (82.0 mg, 114 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish the products ***syn*-8a** and ***anti*-8a** after flash column chromatography (*n*-pentane:EtOAc = 100:1) in a combined yield of 80%. ***syn*-8a** was obtained as a yellow oil (46.5 mg, 214 µmol).

R_f = 0.32 (*n*-pentane:EtOAc = 20:1).

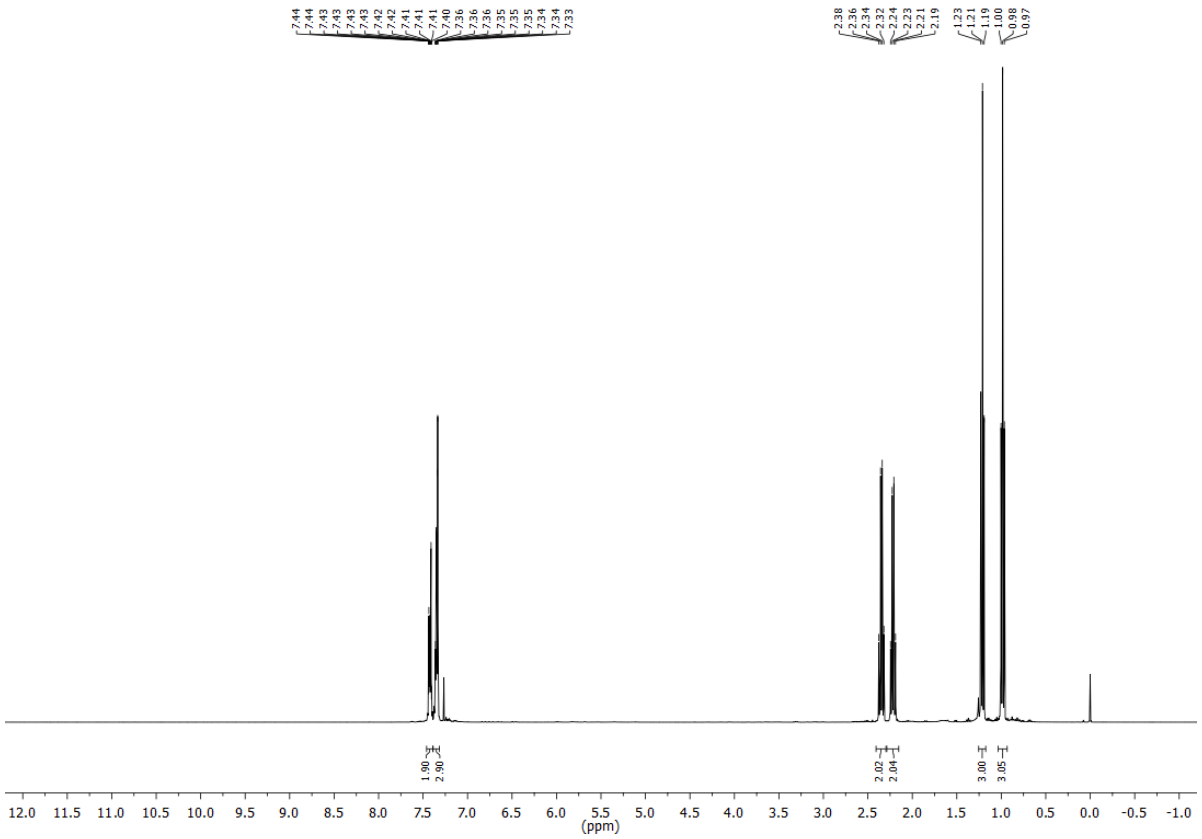
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, *J*=7.5, 3H), 1.21 (t, *J*=7.5, 3H), 2.22 (q, *J*=7.5, 2H), 2.35 (q, *J*=7.5, 2H), 7.31 – 7.37 (m, 3H), 7.39 – 7.45 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 13.1, 13.2, 24.5, 24.9, 114.7, 118.1, 128.5, 129.2 (2 C), 131.5, 133.2 (2 C), 155.6.

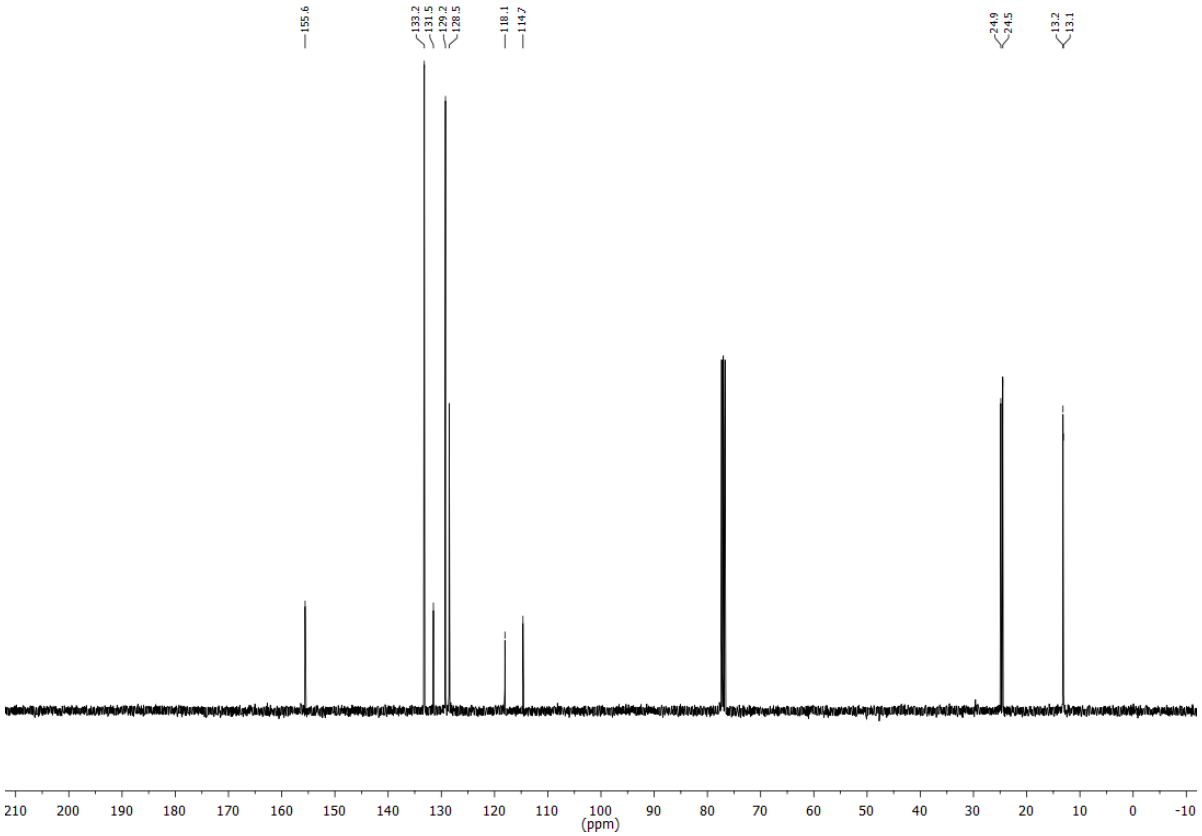
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2974, 2933, 2877, 2206, 1577, 1466, 1450, 1058, 1025.

$C_{13}H_{15}NS$ calcd.: 217.0925, found: 217.0937 (GC-HRMS).

[43] I. W. J. Still and I. D. G. Watson, *Synth. Commun.*, 2001, **31**, 1355.

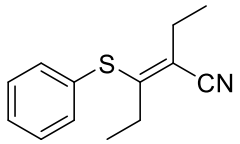


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*E*)-2-Ethyl-3-(phenylthio)pent-2-enenitrile (*anti*-8a)



***anti*-8a** was obtained as a yellow oil (40.5 mg, 186 µmol).

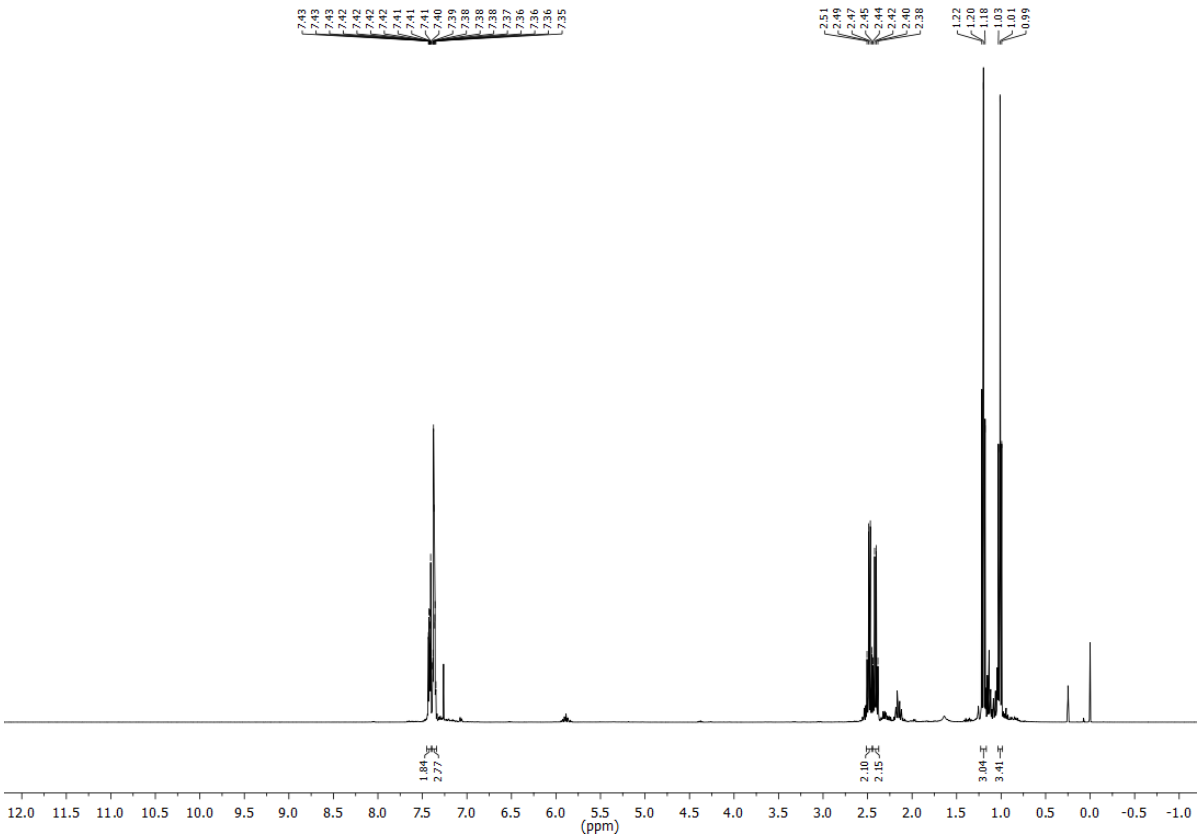
R_f = 0.50 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, *J*=7.4, 3H), 1.20 (t, *J*=7.5, 3H), 2.41 (q, *J*=7.4, 2H), 2.48 (q, *J*=7.5, 2H), 7.35 – 7.39 (m, 3H), 7.40 – 7.44 (m, 2H).

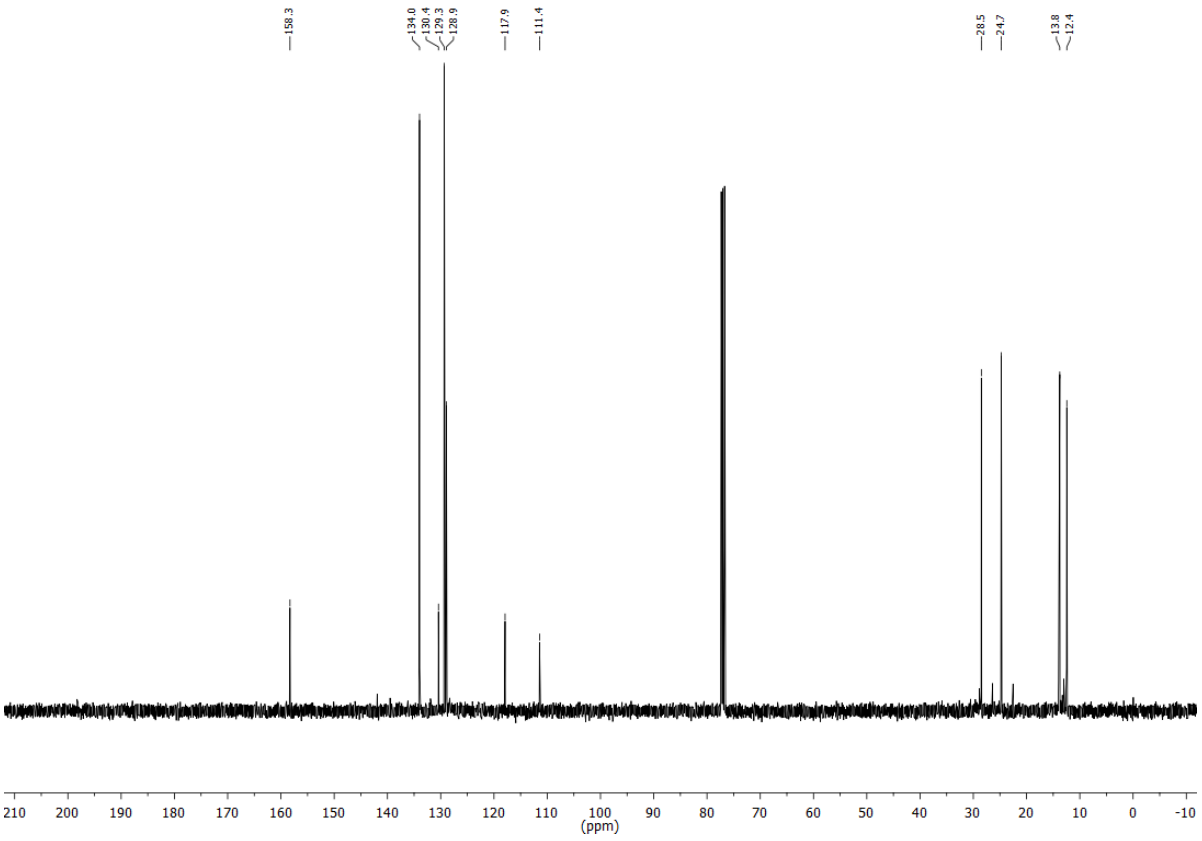
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 12.4, 13.8, 24.7, 28.5, 111.4, 117.9, 128.9, 129.3 (2 C), 130.4, 134.0 (2 C), 158.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2972, 2933, 2875, 2204, 1575, 1450, 1058, 1025.

$C_{13}H_{15}NS$ calcd.: 217.0925, found: 217.0939 (GC-HRMS).

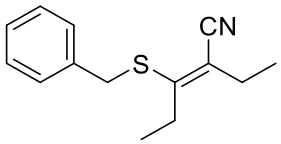


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-3-(Benzylthio)-2-ethylpent-2-enenitrile (8b)



Benzyl thiocyanate (75.0 mg, 500 µmol, 1.00 equiv.) and 3-hexyne (82.0 mg, 114 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish **8b** after flash column chromatography (*n*-pentane:EtOAc = 100:1 → 50:1) as a yellow oil (50.0 mg, 220 µmol, 44%).

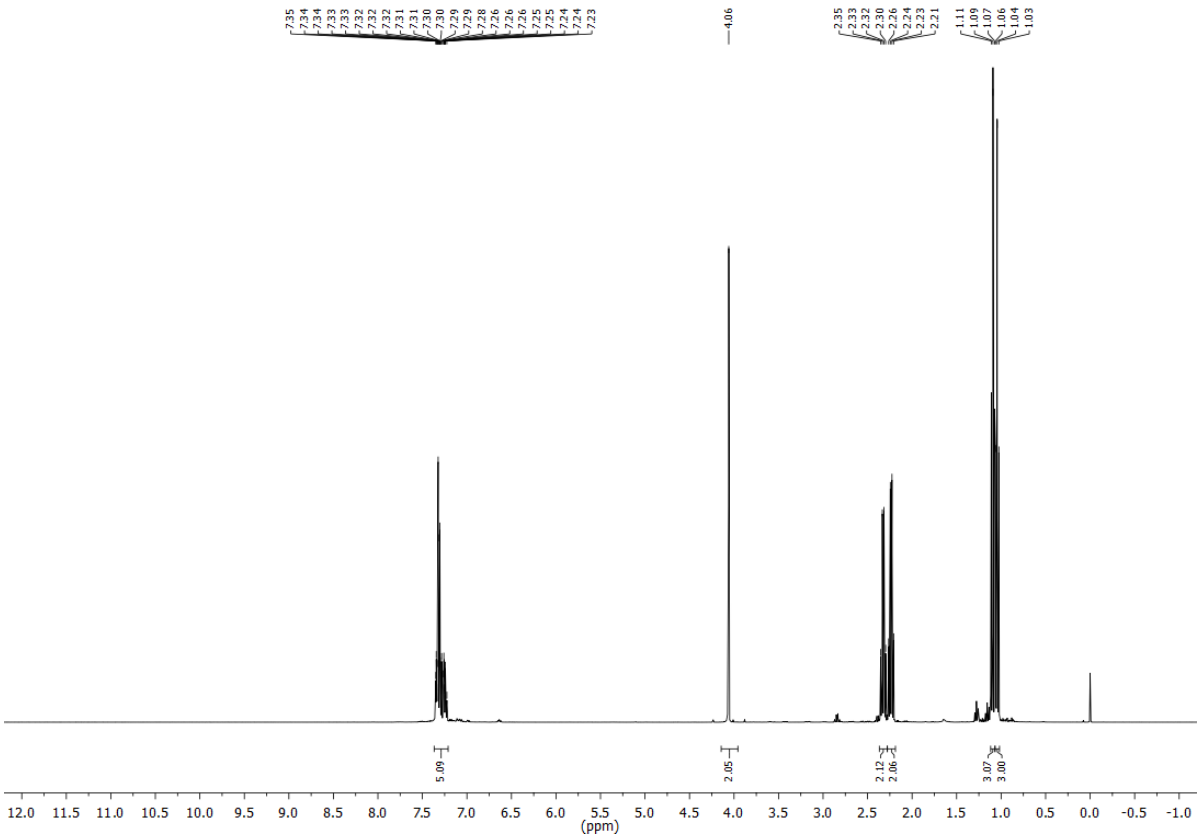
R_f = 0.26 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, *J*=7.5, 3H), 1.09 (t, *J*=7.5, 3H), 2.24 (q, *J*=7.5, 2H), 2.33 (q, *J*=7.5, 2H), 4.06 (s, 2H), 7.20 – 7.36 (m, 5H).

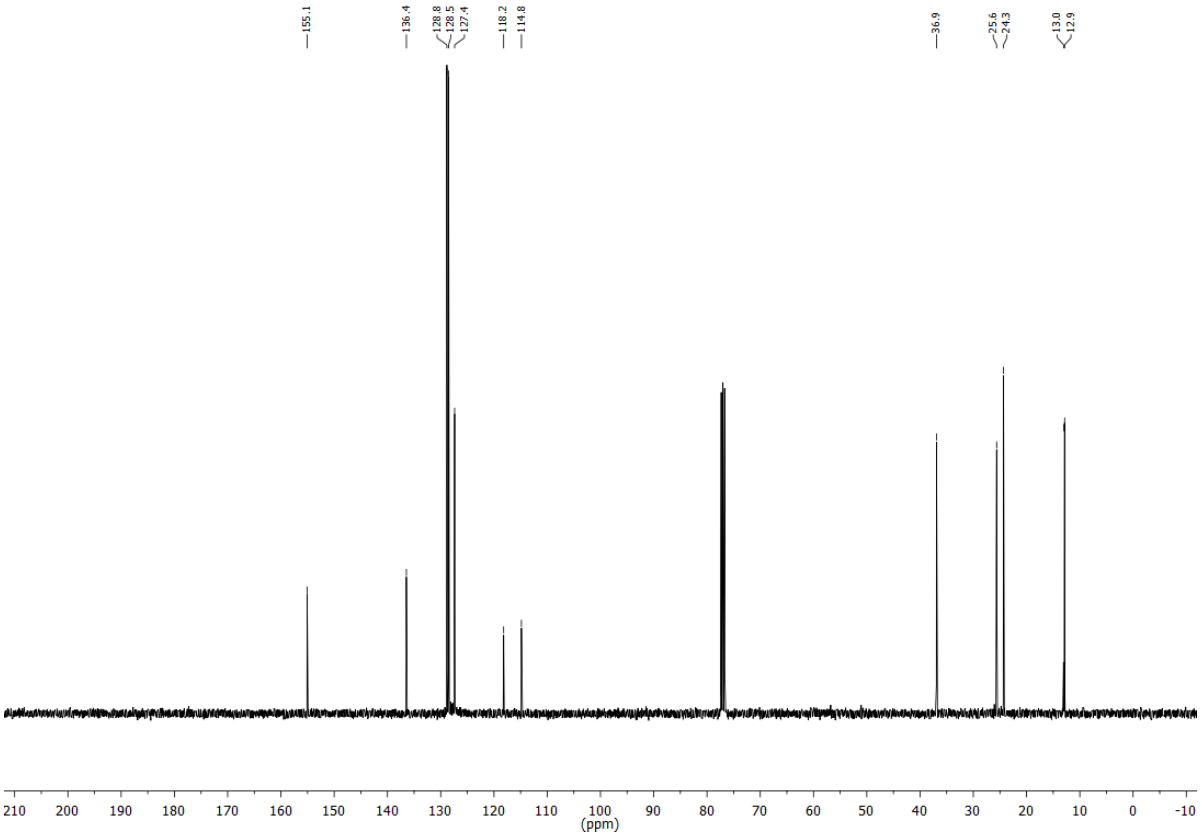
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 12.9, 13.0, 24.3, 25.6, 36.9, 114.8, 118.2, 127.4, 128.5 (2 C), 128.8 (2 C), 136.4, 155.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 3029, 2973, 2933, 2877, 2204, 1574, 1454, 1059, 1038.

$C_{14}H_{17}NS$ calcd.: 231.1082, found: 231.1094 (GC-HRMS).

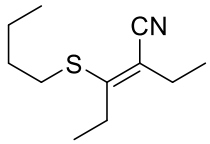


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-3-(Butylthio)-2-ethylpent-2-enenitrile (8c)



n-Butyl thiocyanate (58.0 mg, 61.0 µl, 500 µmol, 1.00 equiv.) and 3-hexyne (82.0 mg, 114 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish **8c** after flash column chromatography (*n*-pentane:EtOAc = 50:1) as a colorless oil (89.0 mg, 450 µmol, 90%).

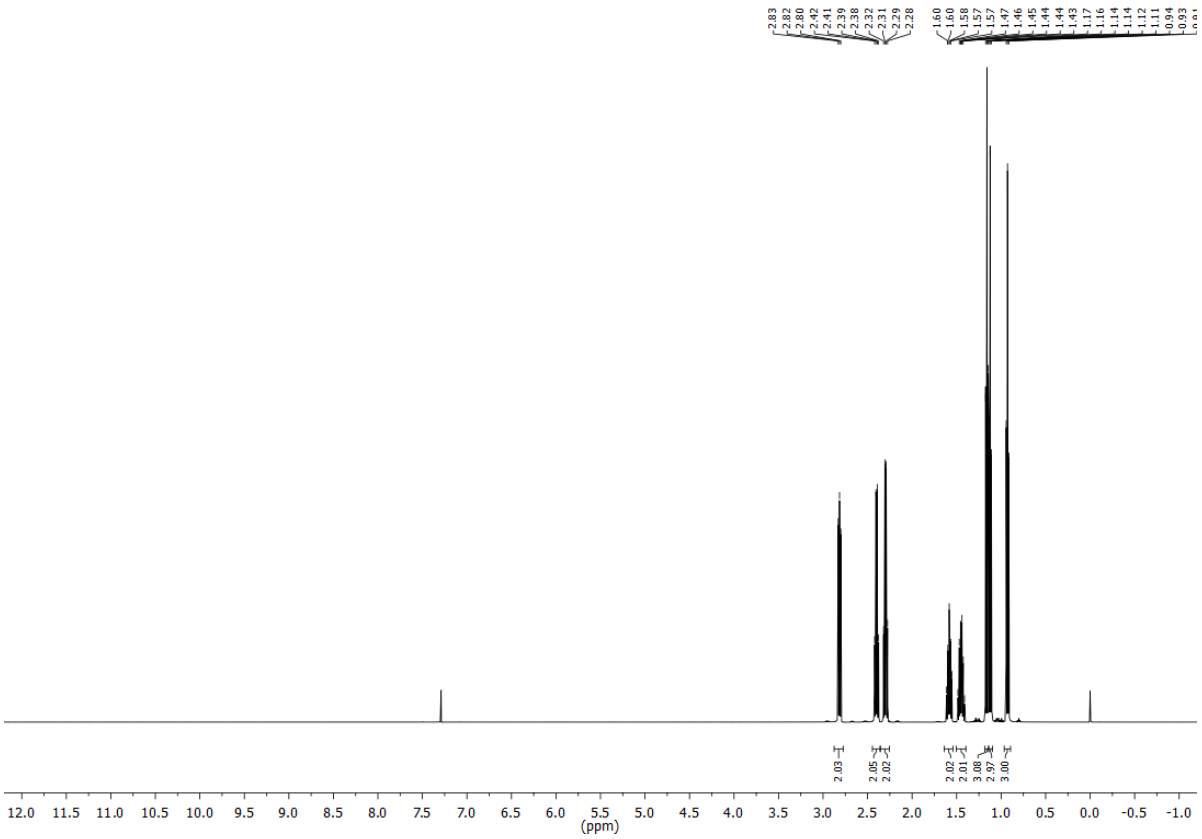
R_f = 0.35 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J*=7.4, 3H), 1.12 (t, *J*=7.5, 3H), 1.16 (t, *J*=7.5, 3H), 1.39 – 1.48 (m, 2H), 1.52 – 1.67 (m, 2H), 2.30 (q, *J*=7.6, 2H), 2.40 (q, *J*=7.6, 2H), 2.74 – 2.85 (m, 2H).

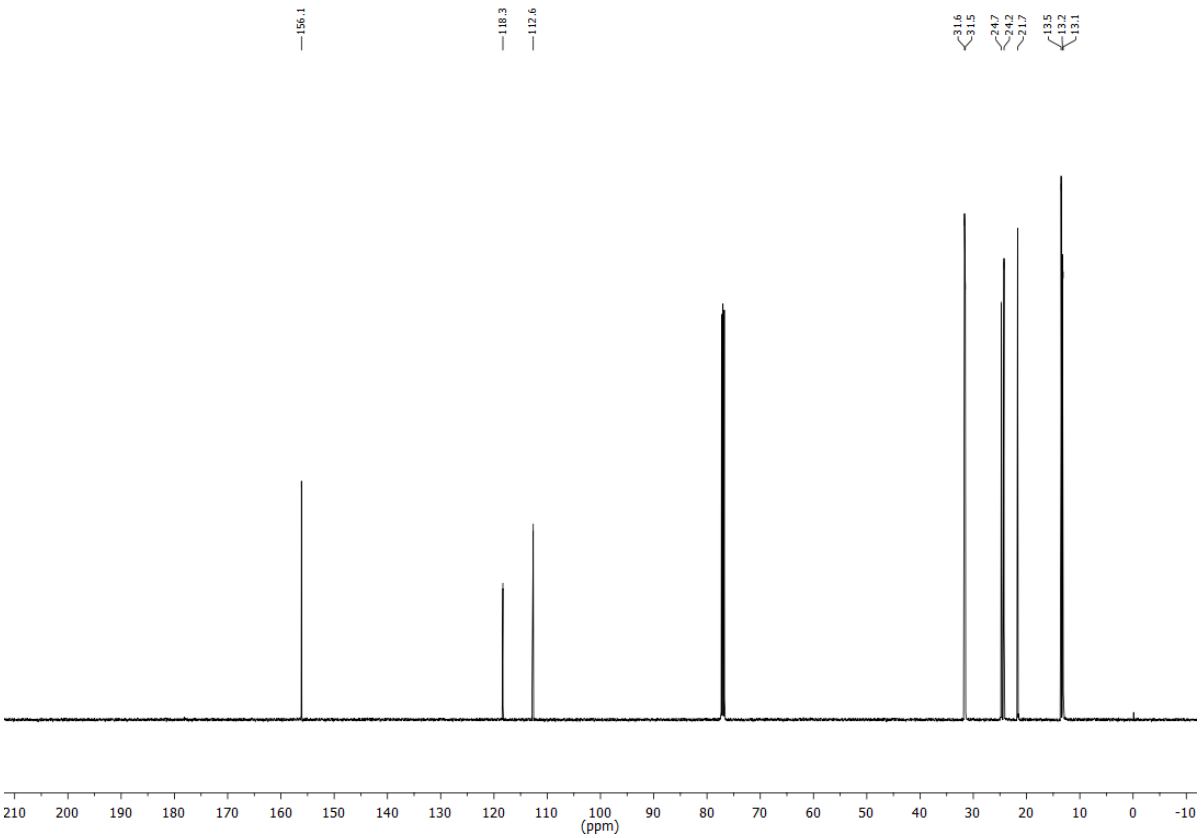
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.1, 13.2, 13.5, 21.7, 24.2, 24.7, 31.5, 31.6, 112.6, 118.3, 156.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2966, 2932, 2872, 2204, 1574, 1459, 1376, 1217, 1054.

$C_{11}H_{19}NS$ calcd.: 197.1238, found: 197.1242 (GC-HRMS).

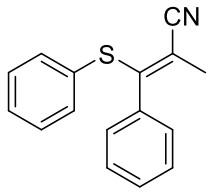


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-Methyl-3-phenyl-3-(phenylthio)acrylonitrile (α-Ph-8d)



Phenyl thiocyanate (68.0 mg, 500 µmol, 1.00 equiv.) and 1-phenyl-1-propyne (116.0 mg, 124 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish the products **α-Ph-8d** and **β-Ph-8d** after flash column chromatography (*n*-pentane:EtOAc = 100:1) in a combined yield of 88%. **α-Ph-8d** was obtained as a colorless oil (82.5 mg, 330 µmol).

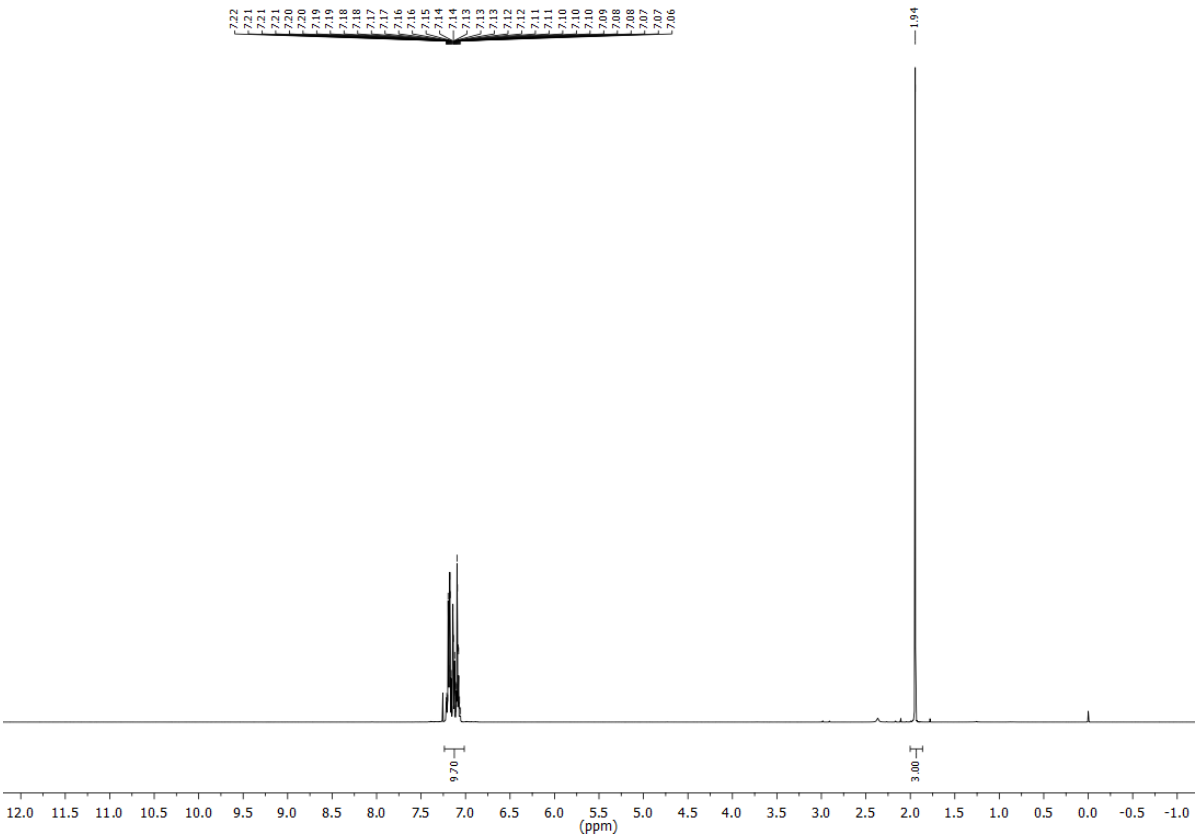
R_f = 0.29 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 6.98 – 7.24 (m, 10H).

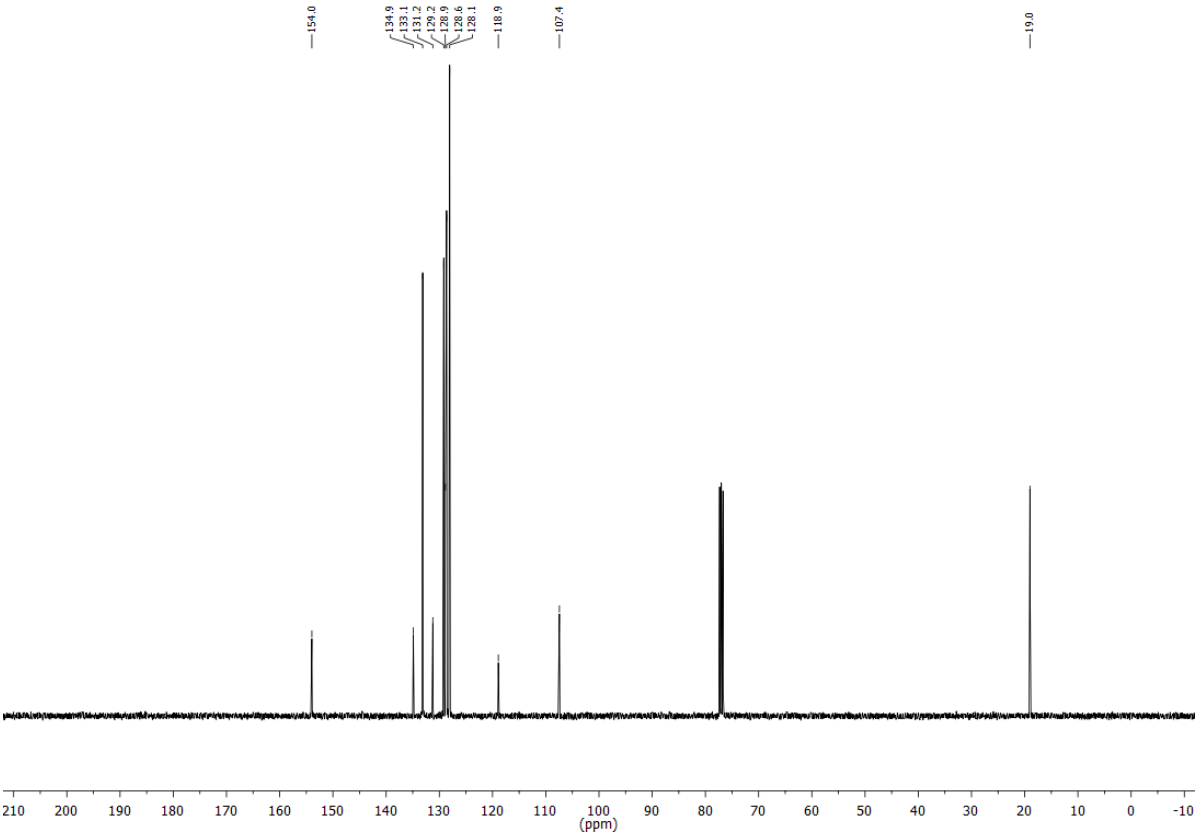
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 19.0, 107.4, 118.9, 128.1 (3 C), 128.6 (2 C), 128.9, 129.2 (2 C), 131.2, 133.1 (2 C), 134.9, 154.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058, 2954, 2921, 2857, 2206, 1575, 1479, 1439, 1074, 911.

$C_{16}H_{13}NS$ calcd.: 251.0769, found: 251.0789 (GC-HRMS).

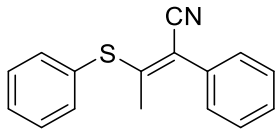


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-Phenyl-3-(phenylthio)but-2-enenitrile (β-Ph-8d)



β-Ph-8d was obtained as a colorless oil (27.5 mg, 110 µmol).

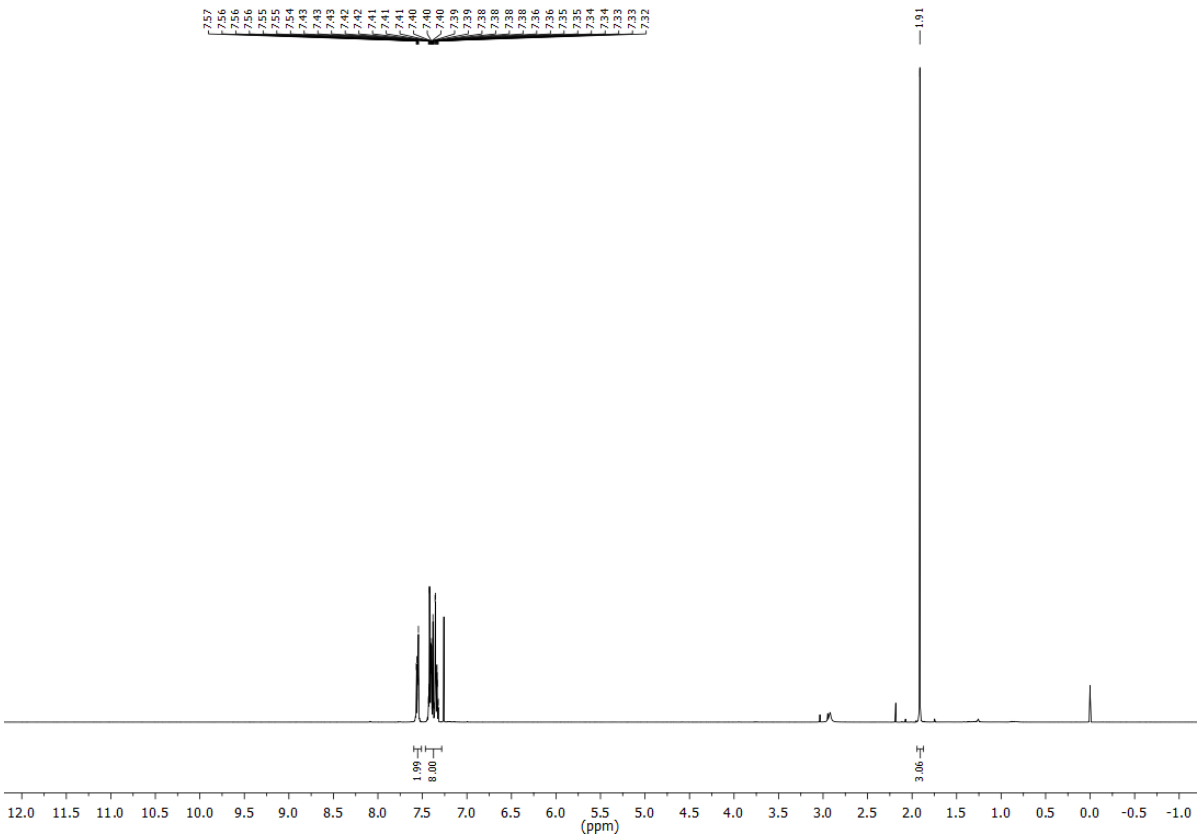
R_f = 0.30 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3H), 7.31 – 7.45 (m, 8H), 7.53 – 7.59 (m, 2H).

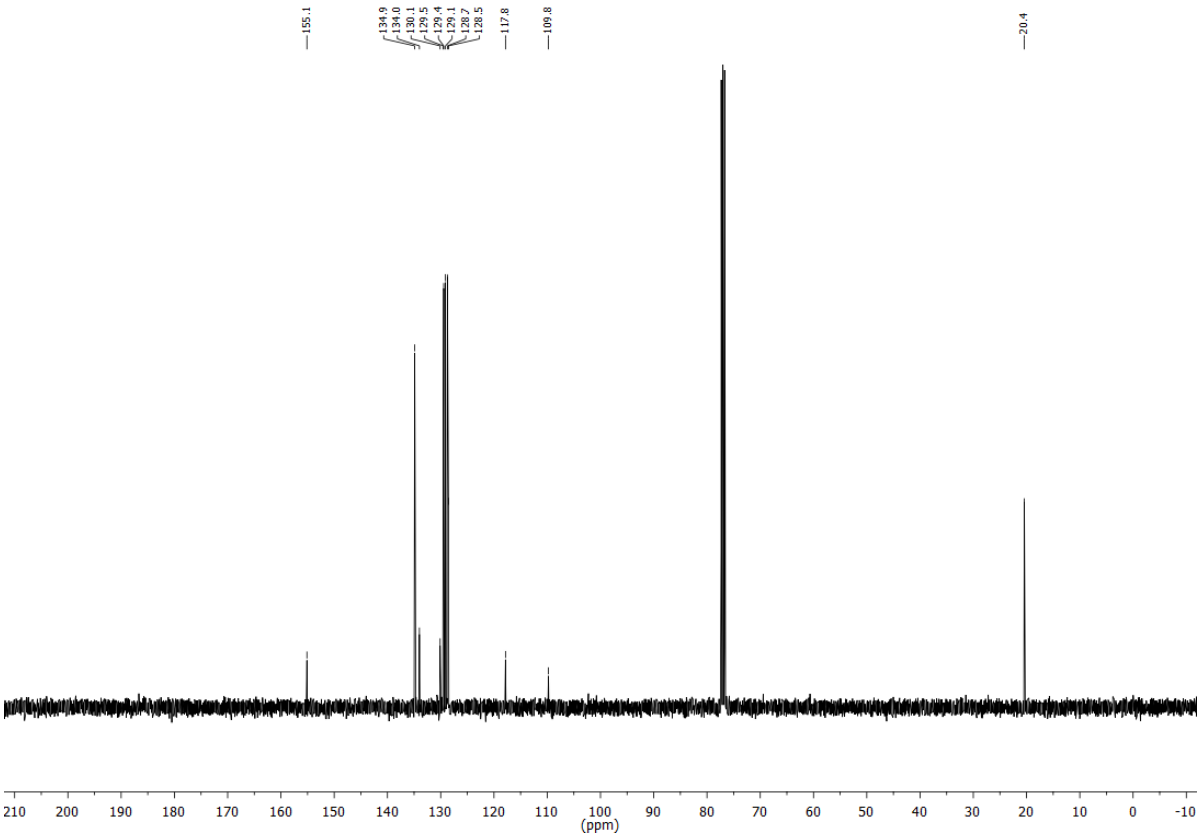
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 20.4, 109.8, 117.8, 128.5, 128.7 (2 C), 129.1 (2 C), 129.4 (2 C), 129.5, 130.1, 134.0, 134.9 (2 C), 155.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3059, 2921, 2851, 2204, 1560, 1478, 1436, 1137.

$C_{16}H_{13}NS$ calcd.: 251.0769, found: 251.0781 (GC-HRMS).

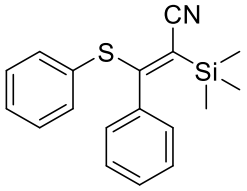


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*E*)-3-Phenyl-3-(phenylthio)-2-(trimethylsilyl)acrylonitrile (8e)



Phenyl thiocyanate (68.0 mg, 500 µmol, 1.00 equiv.) and 1-(trimethylsilyl)-1-propyne (174.0 mg, 195 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish the products **8e** and **8e'** after flash column chromatography (*n*-pentane:EtOAc = 100:1). **8e** was obtained as a yellow solid (28.0 mg, 90 µmol).

m.p.: 82 °C.

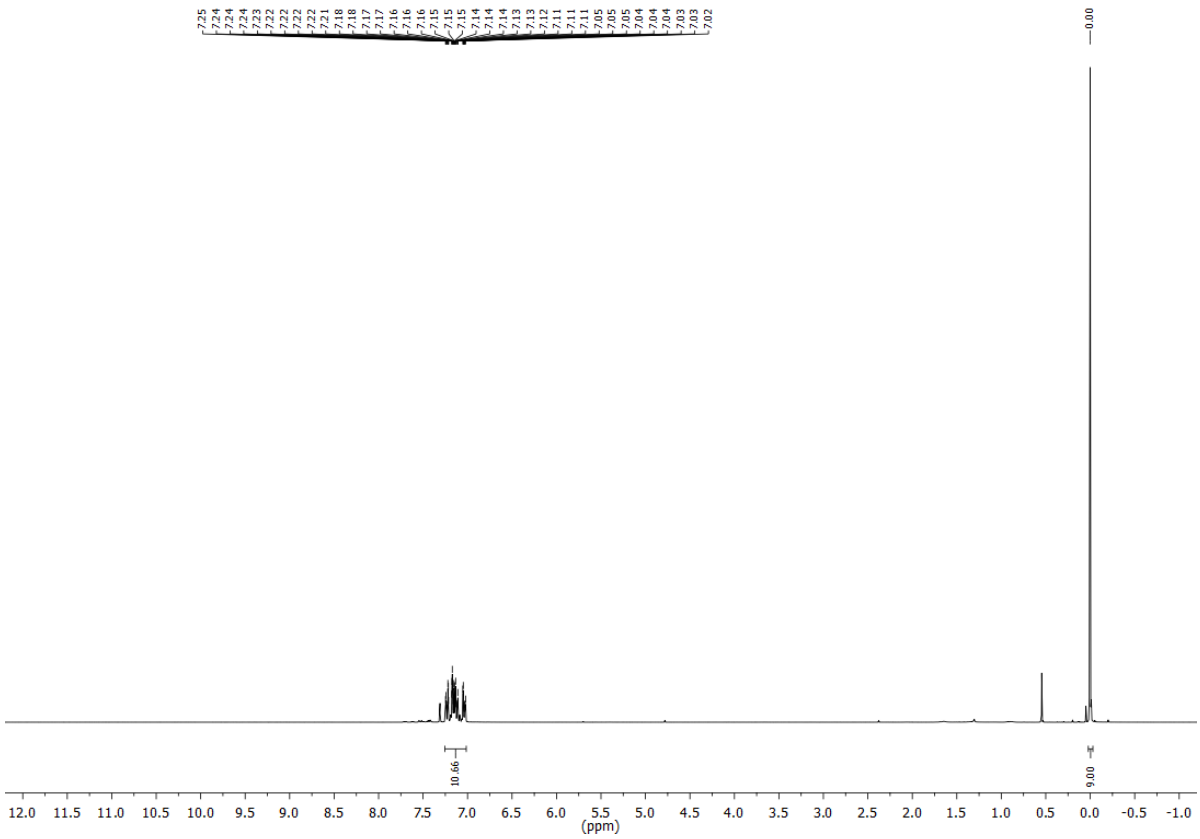
R_f = 0.34 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 7.01 – 7.26 (m, 10H).

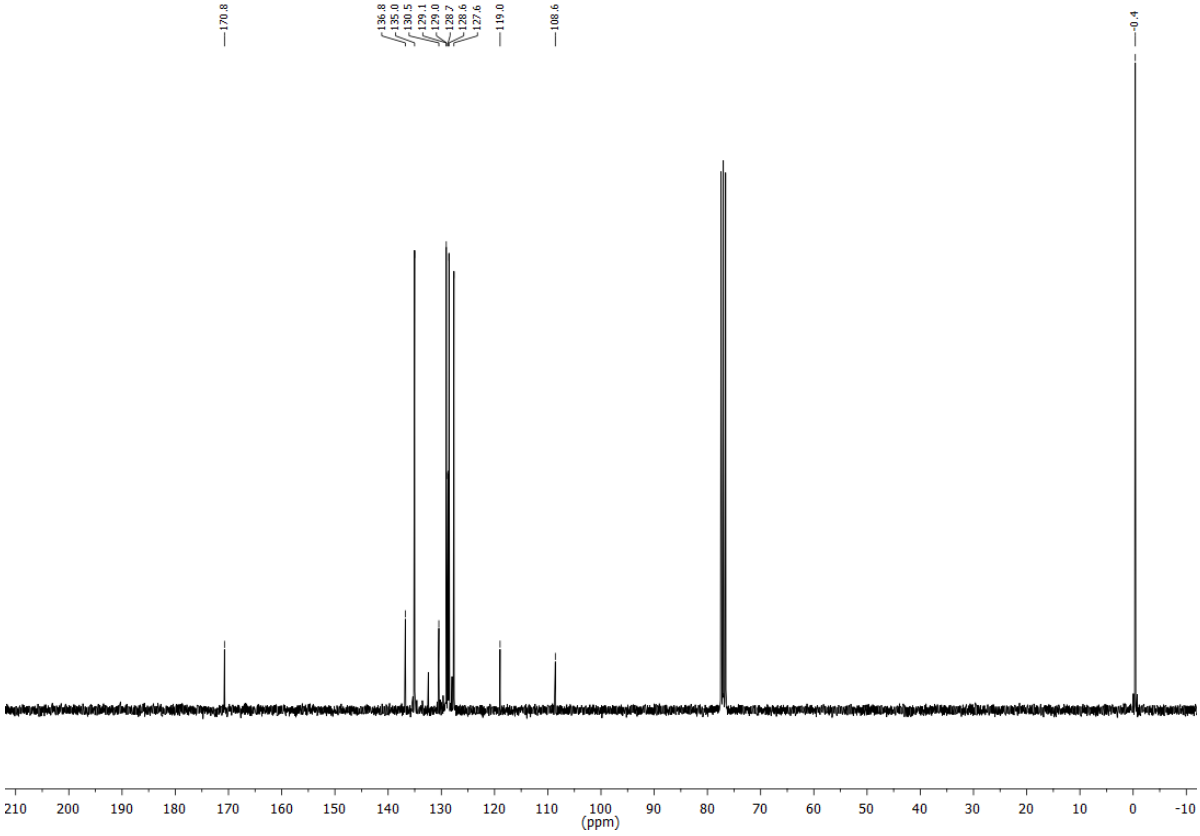
^{13}C-NMR (75 MHz, $CDCl_3$): δ = -0.4 (3 C), 108.6, 119.0, 127.6 (2 C), 128.6 (2 C), 128.7, 129.0, 129.1 (2 C), 130.5, 135.0 (2 C), 136.8, 170.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061, 2973, 2956, 2898, 2192, 1523, 1476, 1442, 1251, 1225, 1070.

$C_{18}H_{19}NSSi$ calcd.: 309.1008, found: 309.1027 (GC-HRMS).

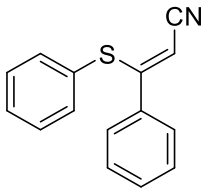


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(*Z*)-3-Phenyl-3-(phenylthio)acrylonitrile (8e')



8e' was obtained as a yellow oil (95.5 mg, 400 µmol).

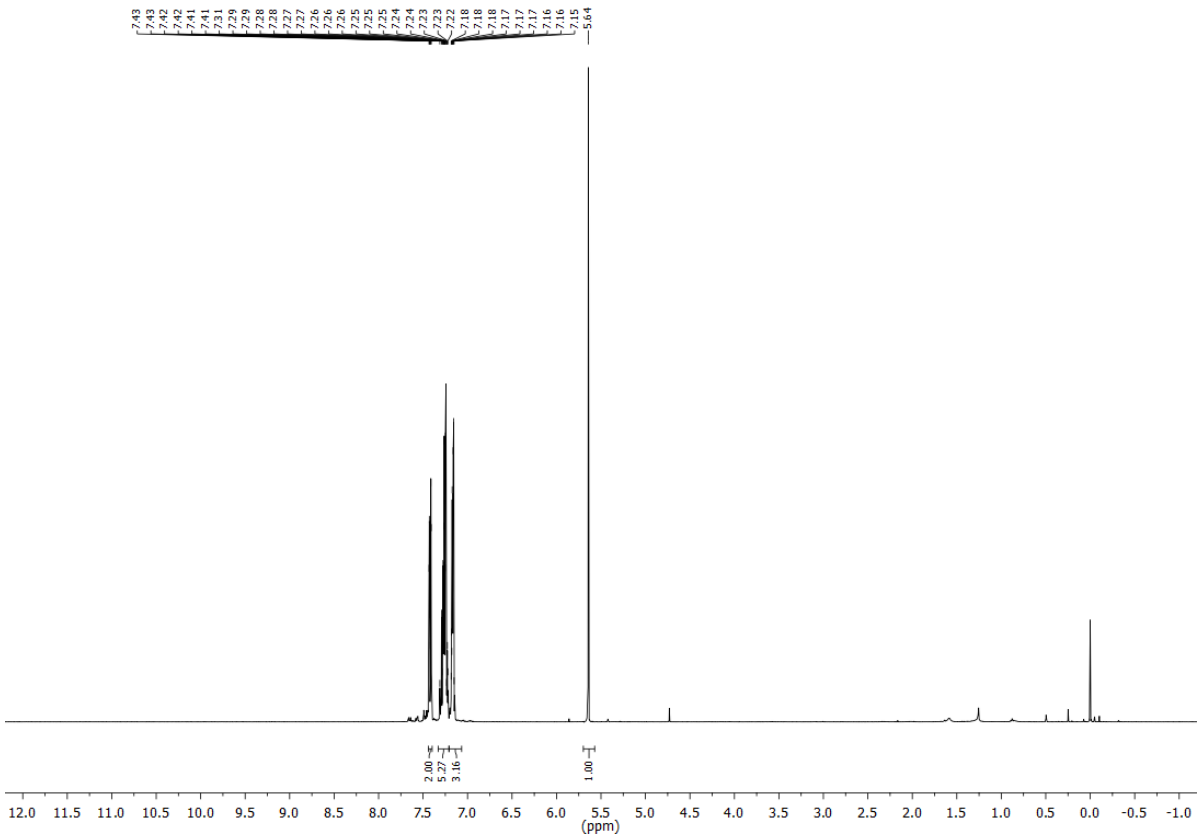
R_f = 0.20 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.64 (s, 1H), 7.08 – 7.20 (m, 3H), 7.20 – 7.33 (m, 5H), 7.39 – 7.49 (m, 2H).

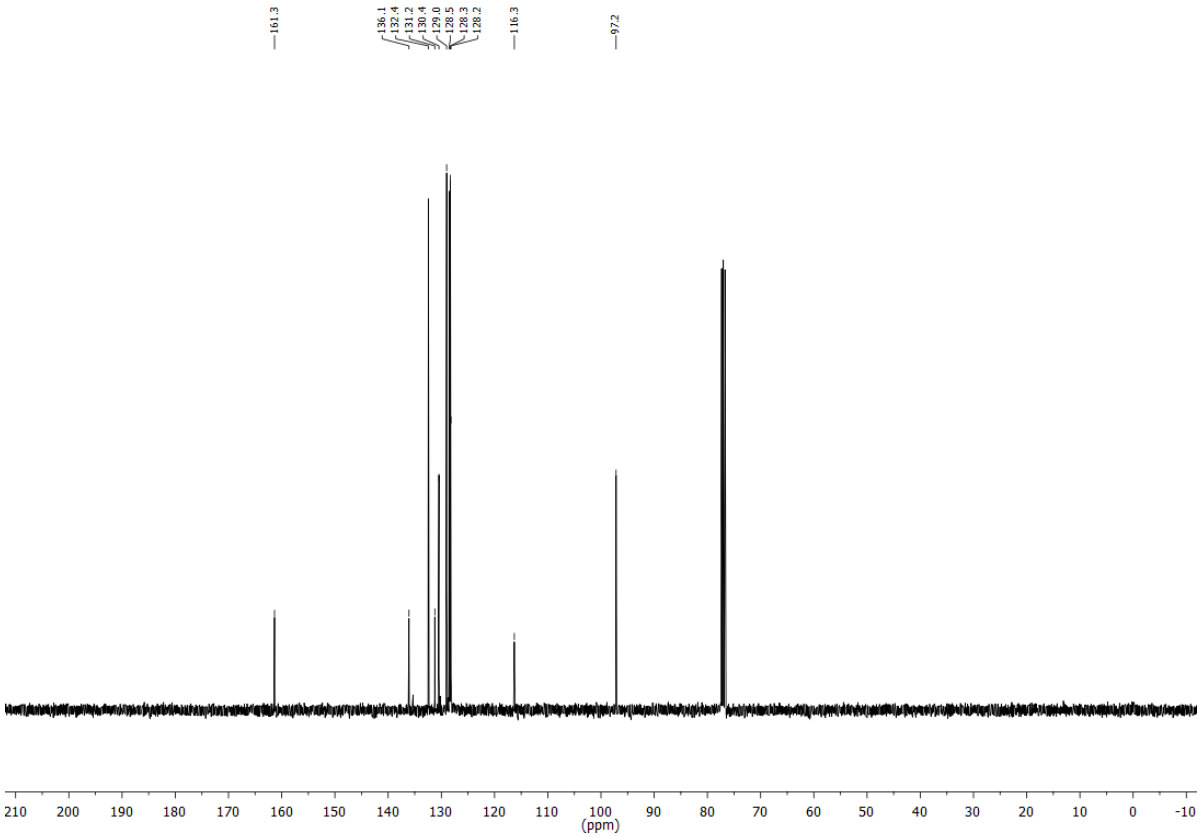
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 97.2, 116.3, 128.2, 128.3 (2 C), 128.5 (2 C), 129.0 (2 C), 130.4, 131.2, 132.4 (2 C), 136.1, 161.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3053, 2923, 2853, 2209, 1557, 1478, 1440, 1180.

$C_{15}H_{11}NS$ calcd.: 237.0612, found: 237.0620 (GC-HRMS).

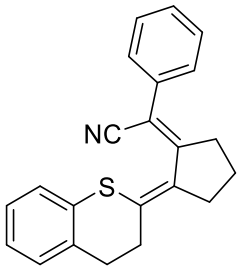


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-Phenyl-2-(2-((*Z*)-thiochroman-2-ylidene)cyclopentylidene)acetonitrile (10a)



Compound **9a** (20.0 mg, 61 µmol, 1.00 equiv.) was transformed according to GP CAT2 (110 °C, DMF, 3 h) to obtain product **10a** after flash column chromatography (*n*-pentane:Et_2O = 10:1) as a yellow solid (19.0 mg, 43 µmol, 70%).

m.p.: 60-70 °C.

R_f = 0.20 (*n*-pentane:EtOAc = 20:1).

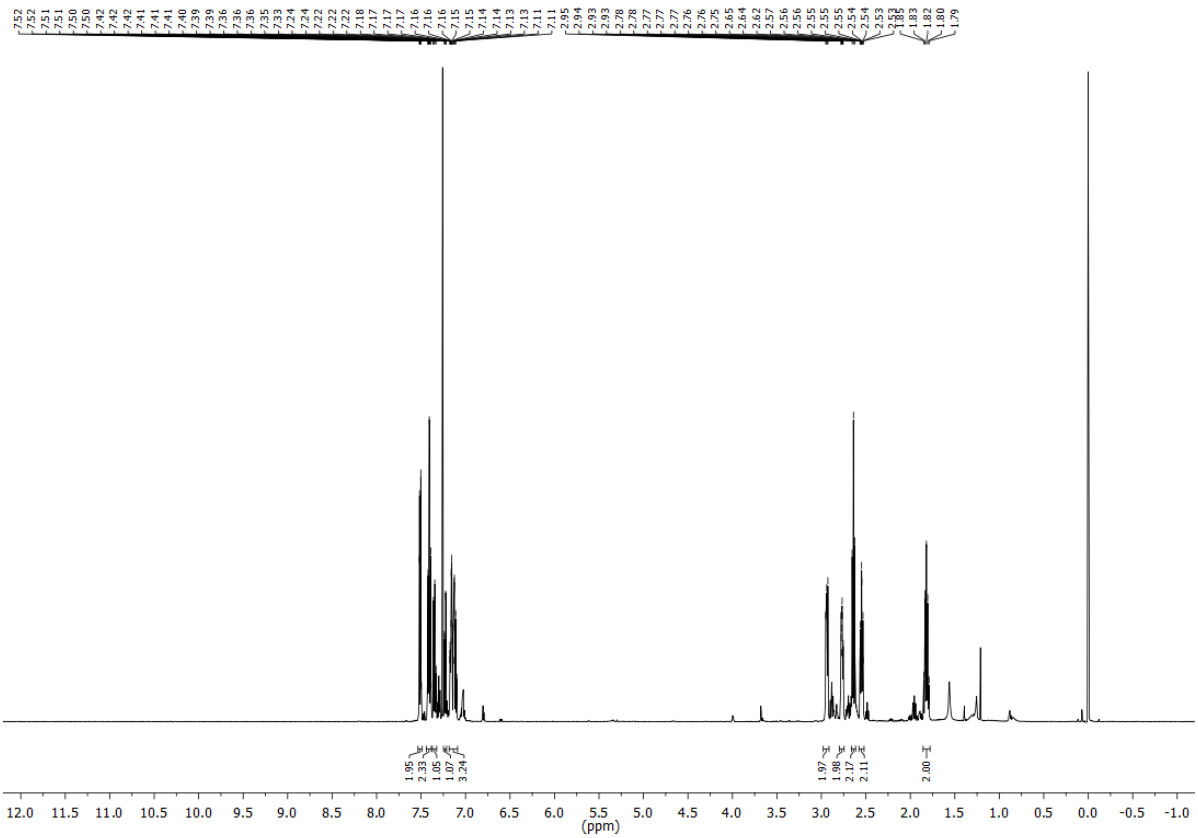
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.82 (p, *J* = 7.5 Hz, 2H), 2.55 (ddt, *J* = 8.2, 7.0, 1.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.75 – 2.78 (m, 2H), 2.92 – 2.96 (m, 2H), 7.09 – 7.19 (m, 3H), 7.21 – 7.24 (m, 1H), 7.32 – 7.37 (m, 1H), 7.38 – 7.44 (m, 2H), 7.49 – 7.52 (m, 2H).

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.81 (p, *J* = 7.5 Hz, 2H), 2.55 (ddt, *J* = 8.1, 6.8, 1.4 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.75 – 2.79 (m, 2H), 2.91 – 2.95 (m, 2H), 7.09 – 7.17 (m, 2H), 7.18 – 7.23 (m, 2H), 7.33 – 7.39 (m, 1H), 7.39 – 7.45 (m, 2H), 7.47 – 7.52 (m, 2H).

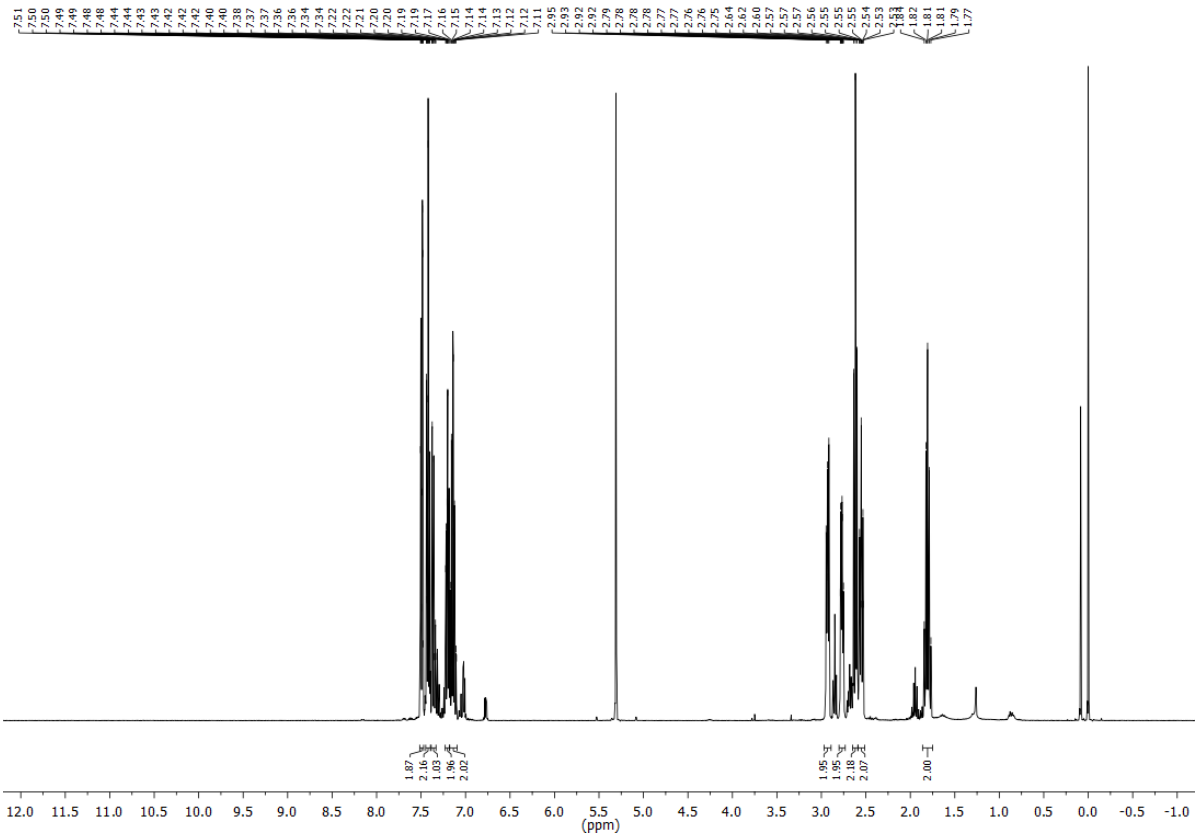
^{13}C-NMR (101 MHz, CD_2Cl_2): δ = 22.7, 30.5, 30.6, 32.1, 34.9, 108.9, 119.2, 126.2, 127.0, 127.4, 128.7, 128.7, 128.8, 129.3, 133.8, 133.9, 135.4, 135.6, 137.4, 159.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3057, 2953, 2905, 2843, 2200, 1549, 1473, 1437, 1264, 1123, 1064, 1008, 956.

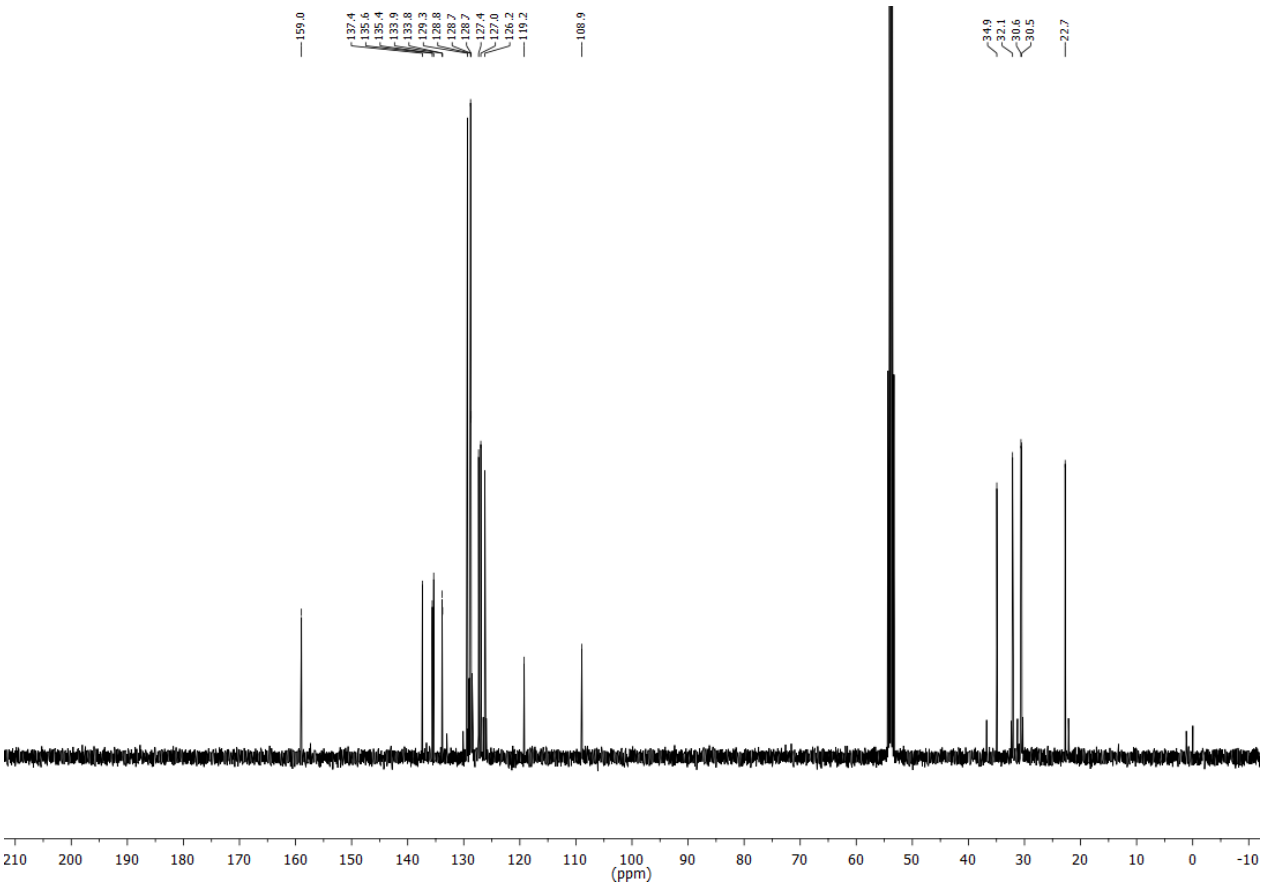
$C_{22}H_{19}NS$ calcd.: 329.1238, found: 329.1224 (GC-HRMS).



^{1}H-NMR (500 MHz, $CDCl_3$).

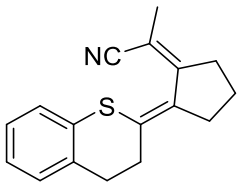


^{1}H-NMR (400 MHz, CD_2Cl_2).



^{13}C-NMR (101 MHz, CD_2Cl_2).

(*Z*)-2-(2-((*Z*)-Thiochroman-2-ylidene)cyclopentylidene)propanenitrile (10b)



Compound **9b** (14.0 mg, 52 µmol, 1.00 equiv.) was transformed according to GP CAT2 (160 °C, PhMe, 3 h) to obtain product **10b** after flash column chromatography (*n*-pentane:EtOAc = 50:1→20:1) as a pale yellow solid (9.3 mg, 34.5 µmol, 66%).

m.p.: 103 °C.

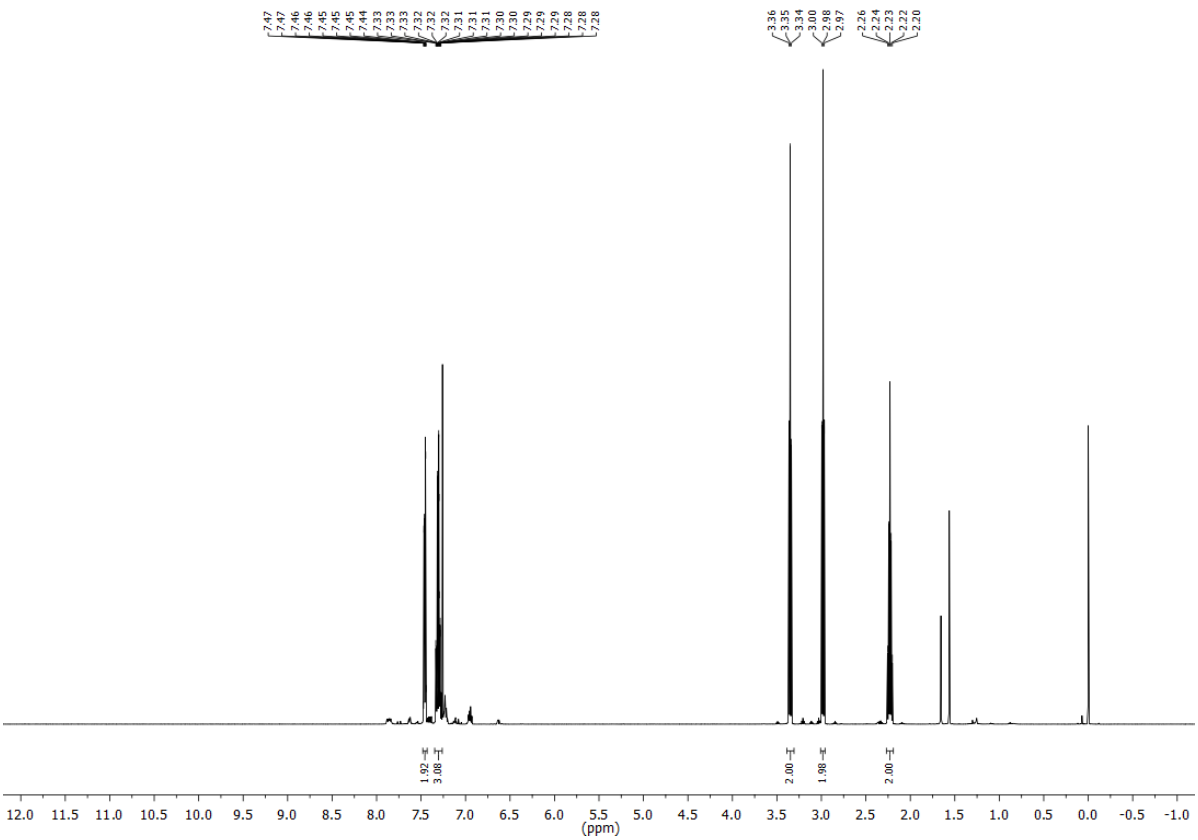
R_f = 0.21 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.80 (p, *J* = 7.6 Hz, 2H), 2.06 (s, 3H), 2.44 – 2.52 (m, 4H), 2.71 – 2.75 (m, 2H), 2.88 – 2.91 (m, 2H), 7.07 – 7.11 (m, 1H), 7.12 – 7.16 (m, 2H), 7.23 – 7.25 (m, 1H).

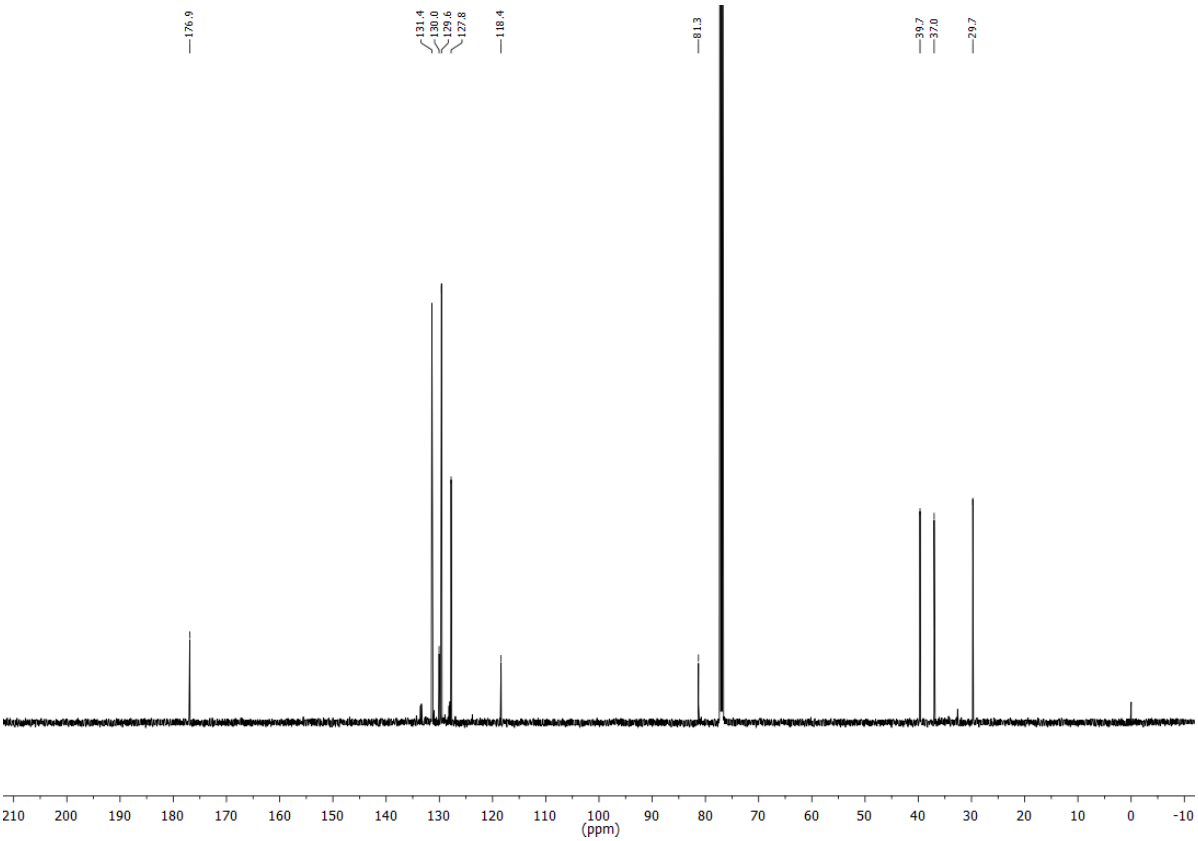
^{13}C-NMR (126 MHz, CD_2Cl_2): δ = 18.8, 21.6, 30.3, 31.5, 31.6, 31.8, 101.6, 120.3, 125.7, 126.8, 126.9, 128.2, 132.6, 132.8, 133.5, 136.8, 157.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3067, 2968, 2913, 2886, 2850, 2195, 1572, 1466, 1433, 1059, 1022.

$C_{17}H_{17}NS$ calcd.: 267.1082, found: 267.1092 (GC-HRMS).

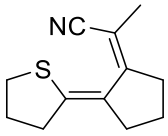


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-((*Z*)-2-(Dihydrothiophen-2(3*H*)-ylidene)cyclopentylidene)propanenitrile (10c)



Compound **9c** (26.0 mg, 126 µmol, 1.00 equiv.) was transformed according to GP CAT2 (160 °C, PhMe, 3 h) to obtain product **10c** after flash column chromatography (*n*-pentane:EtOAc = 50:1→20:1) as a colorless oil (3.9 mg, 19.0 µmol, 15%).

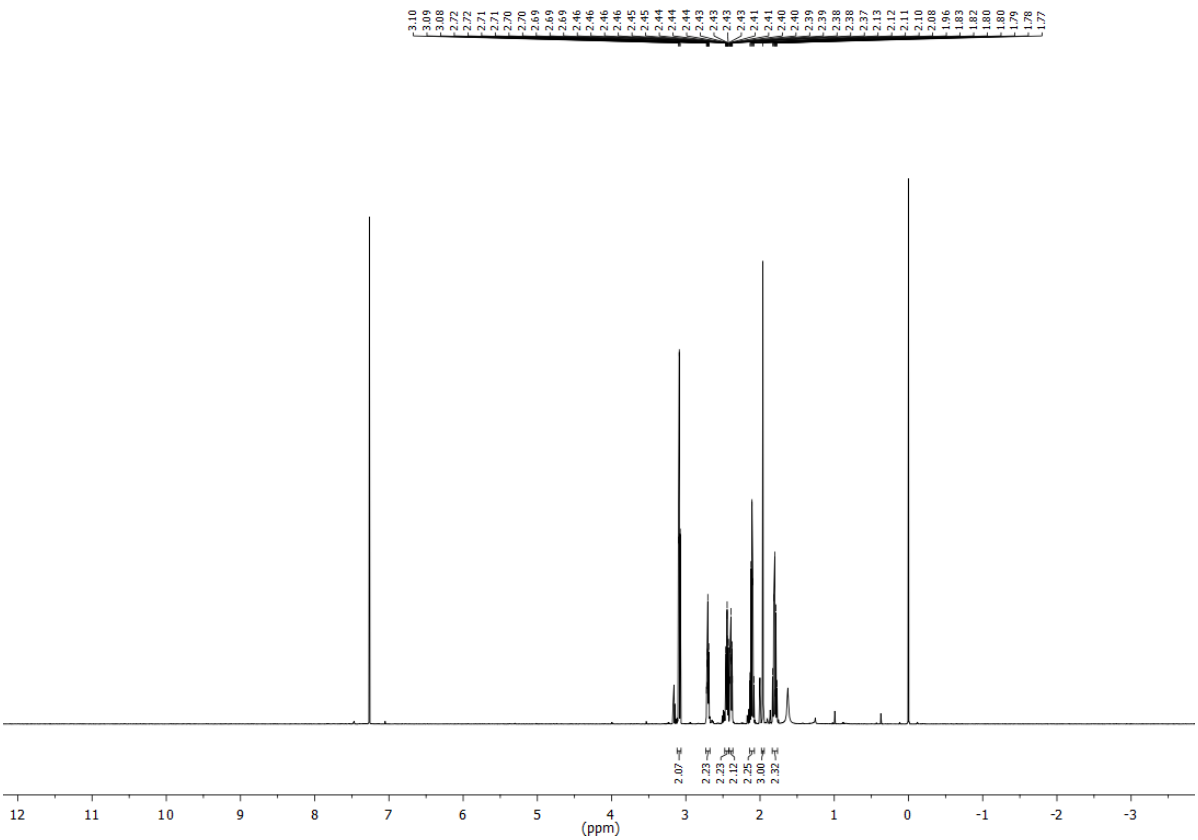
R_f = 0.37 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.76 – 1.84 (m, 2H), 1.96 (s, 3H), 2.11 (p, *J* = 6.6 Hz, 2H), 2.39 (tt, *J* = 7.6, 2.1 Hz, 2H), 2.44 (ddq, *J* = 8.2, 7.3, 1.2 Hz, 2H), 2.70 (tt, *J* = 6.8, 2.1 Hz, 2H), 3.09 (t, *J* = 6.4 Hz, 2H).

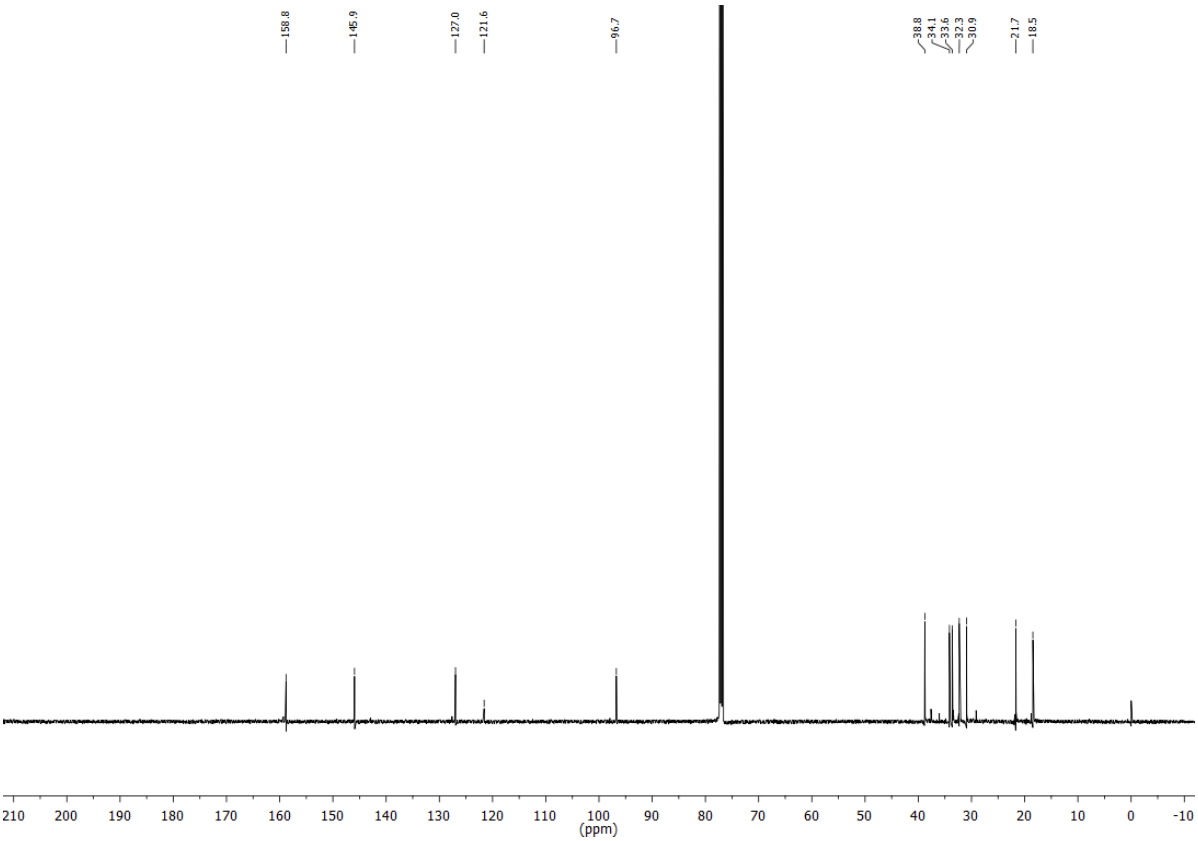
^{13}C-NMR (126 MHz, CD_2Cl_2): δ = 18.5, 21.7, 30.9, 32.3, 33.6, 34.1, 38.8, 96.7, 121.6, 127.0, 145.9, 158.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2947, 2861, 2198, 1587, 1434, 1197, 1018, 988.

$C_{12}H_{15}NS$ calcd.: 205.0925, found: 205.0930 (GC-HRMS).

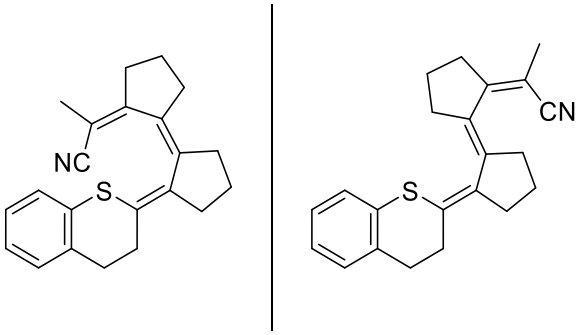


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-((*Z*)-2'-((*Z*)-thiochroman-2-ylidene)-[1,1'-bi(cyclopentylidene)]-2-ylidene)propanenitrile (*Z,Z,Z*-10d) and (*Z*)-2-((*E*)-2'-((*Z*)-thiochroman-2-ylidene)-[1,1'-bi(cyclopentylidene)]-2-ylidene)propanenitrile (Z,*E,Z*-10d)



Compound **9d** (36.0 mg, 108 µmol, 1.00 equiv.) was transformed according to GP CAT2 (110 °C, DMF, 5 h) to obtain products ***Z,Z,Z*-10d** and **Z,*E,Z*-10d** as isomeric mixture after flash column chromatography (*n*-pentane:EtOAc = 100:1→50:1) as a sticky mass (18.3 mg, 55.0 µmol, 51%).

Compound **Z,*E,Z*-10d** was crystallized as yellow solid.

m.p.: 119-126 °C.

R_f = 0.41/0.52 (*n*-pentane:EtOAc = 20:1).

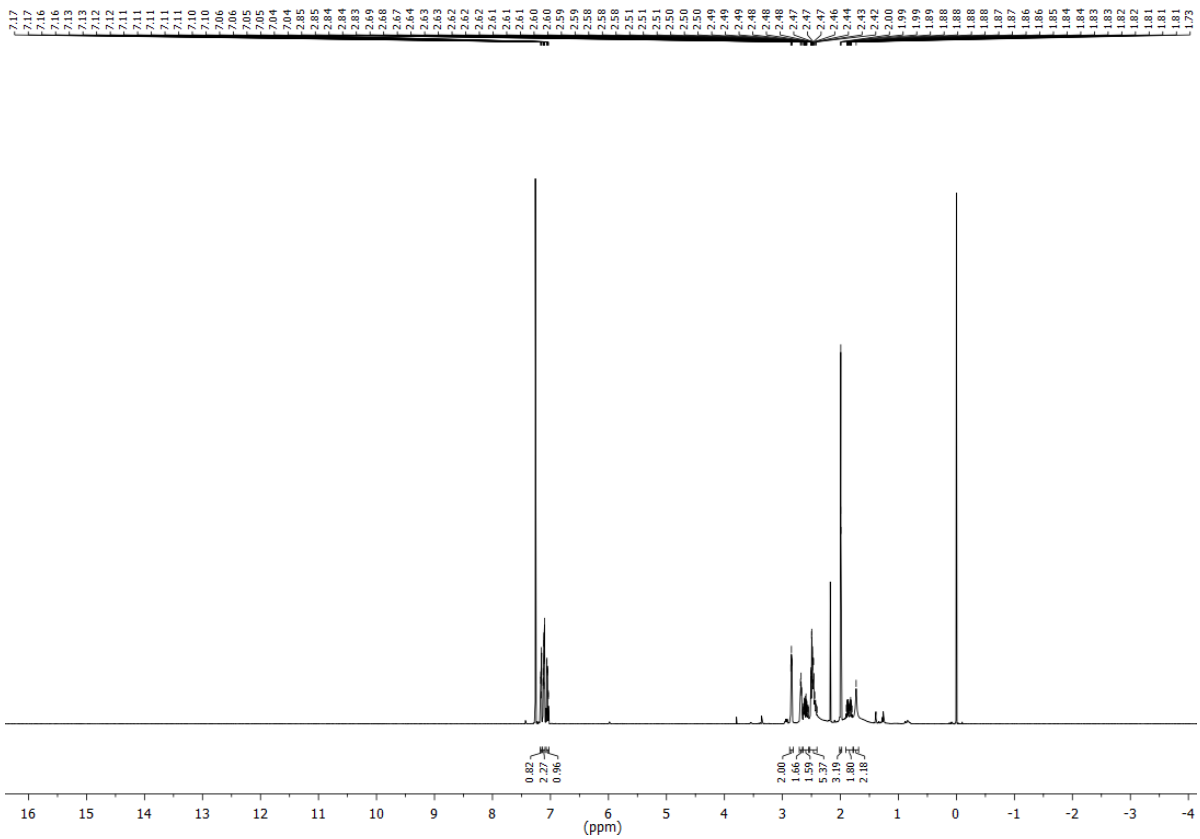
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.73 (s, 2H), 1.78 – 1.91 (m, 2H), 1.99 (t, *J* = 1.5 Hz, 3H), 2.38 – 2.52 (m, 6H), 2.54 – 2.66 (m, 2H), 2.68 (t, *J* = 6.2 Hz, 2H), 2.83 – 2.86 (m, 2H), 7.03 – 7.07 (m, 1H), 7.10 – 7.13 (m, 2H), 7.15 – 7.17 (m, 1H).

^{13}C-NMR (Isomer 1, 151 MHz, $CDCl_3$): δ = 18.4, 21.9, 22.2, 30.2, 30.9, 31.8, 31.9, 33.2, 34.1, 98.3, 119.9, 125.2, 125.4, 126.5, 126.6, 128.3, 133.5, 134.2, 135.2, 137.1, 139.2, 158.6.

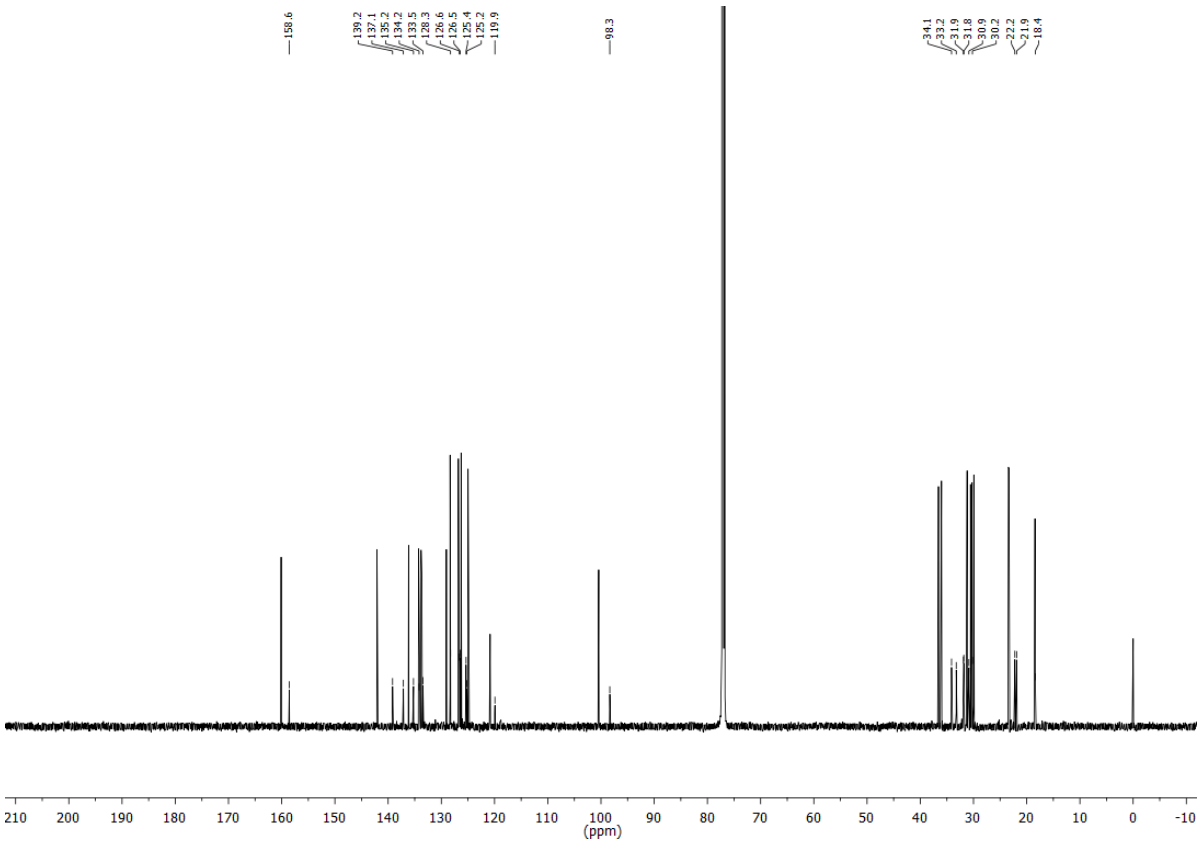
^{13}C-NMR (Isomer 2, 151 MHz, $CDCl_3$): δ = 18.4, 23.3, 23.4, 29.9, 30.3, 30.6, 31.2, 36.0, 36.6, 100.4, 120.8, 125.0, 126.3, 126.8, 128.4, 129.1, 133.7, 133.8, 134.3, 136.2, 142.1, 160.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3060, 2924, 2850, 2199, 1559, 1469, 1432, 1204, 1119, 1065, 965.

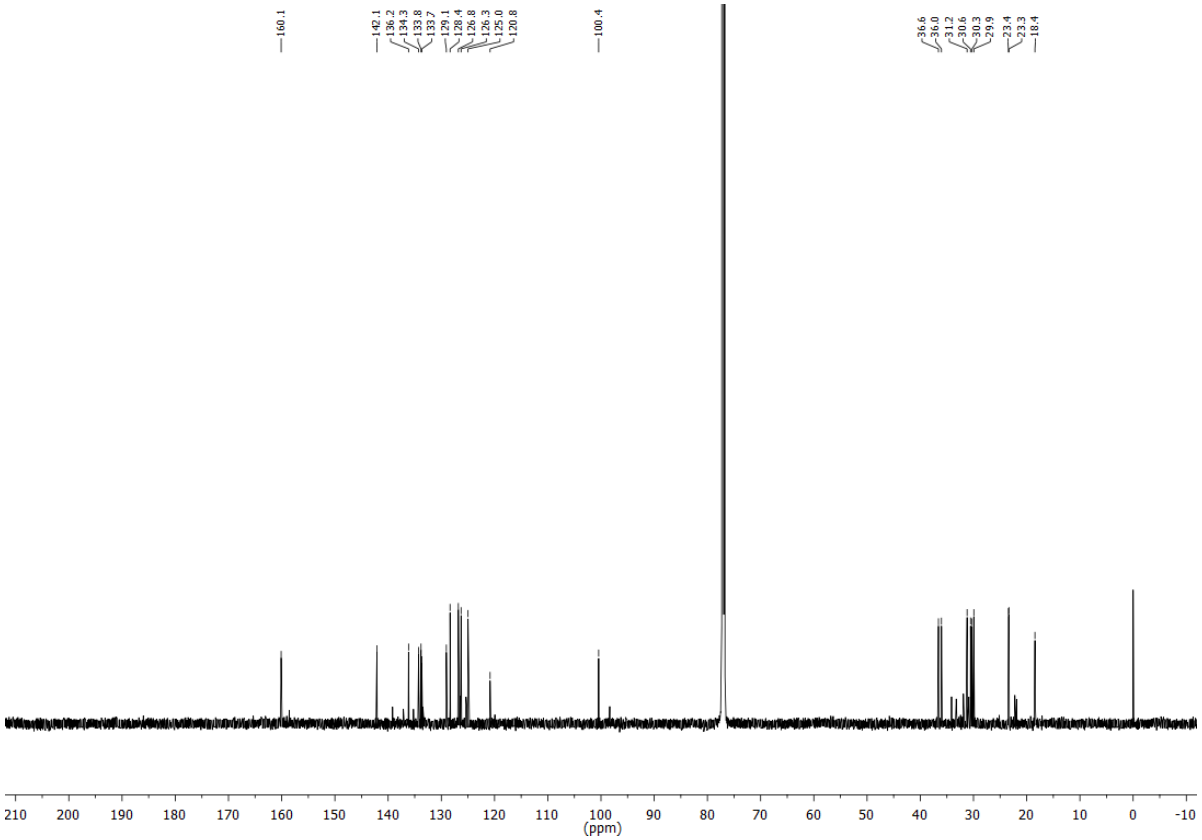
$C_{22}H_{23}NS$ calcd.: 333.1551, found: 333.1576 (GC-HRMS).



^{1}H-NMR (600 MHz, $CDCl_3$).

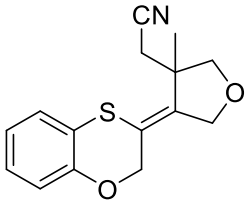


^{13}C-NMR (126 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*E*)-2-(4-(Benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)-3-methyltetrahydrofuran-3-yl)acetonitrile (11)



Compound **9e** (32.0 mg, 117 µmol, 1.00 equiv.) was transformed according to GP CAT2 (6.5 h reaction time, DMF, 110 °C) to obtain product **11** after flash column chromatography (*n*-pentane:EtOAc = 20:1→10:1) as a yellow oil (7.2 mg, 26.7 µmol, 23%).

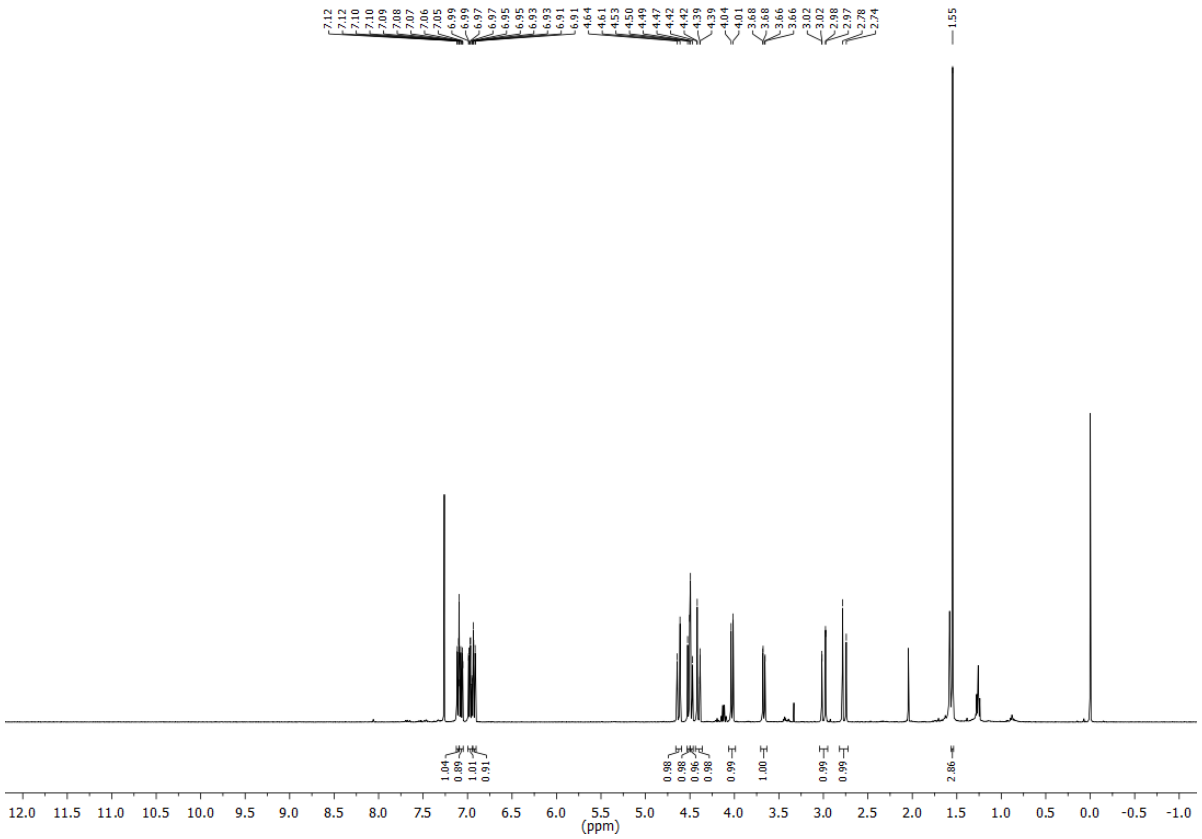
R_f = 0.75 (*n*-pentane:EtOAc = 1:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 3H), 2.76 (d, *J* = 16.9 Hz, 1H), 3.00 (dd, *J* = 16.8, 1.3 Hz, 1H), 3.67 (dd, *J* = 9.2, 1.1 Hz, 1H), 4.03 (d, *J* = 9.2 Hz, 1H), 4.38 – 4.43 (m, 1H), 4.48 (d, *J* = 9.4 Hz, 1H), 4.51 (d, *J* = 8.8 Hz, 1H), 4.63 (d, *J* = 13.3 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.97 (td, *J* = 7.5, 1.4 Hz, 1H), 7.05 – 7.09 (m, 1H), 7.11 (dd, *J* = 7.7, 1.7 Hz, 1H).

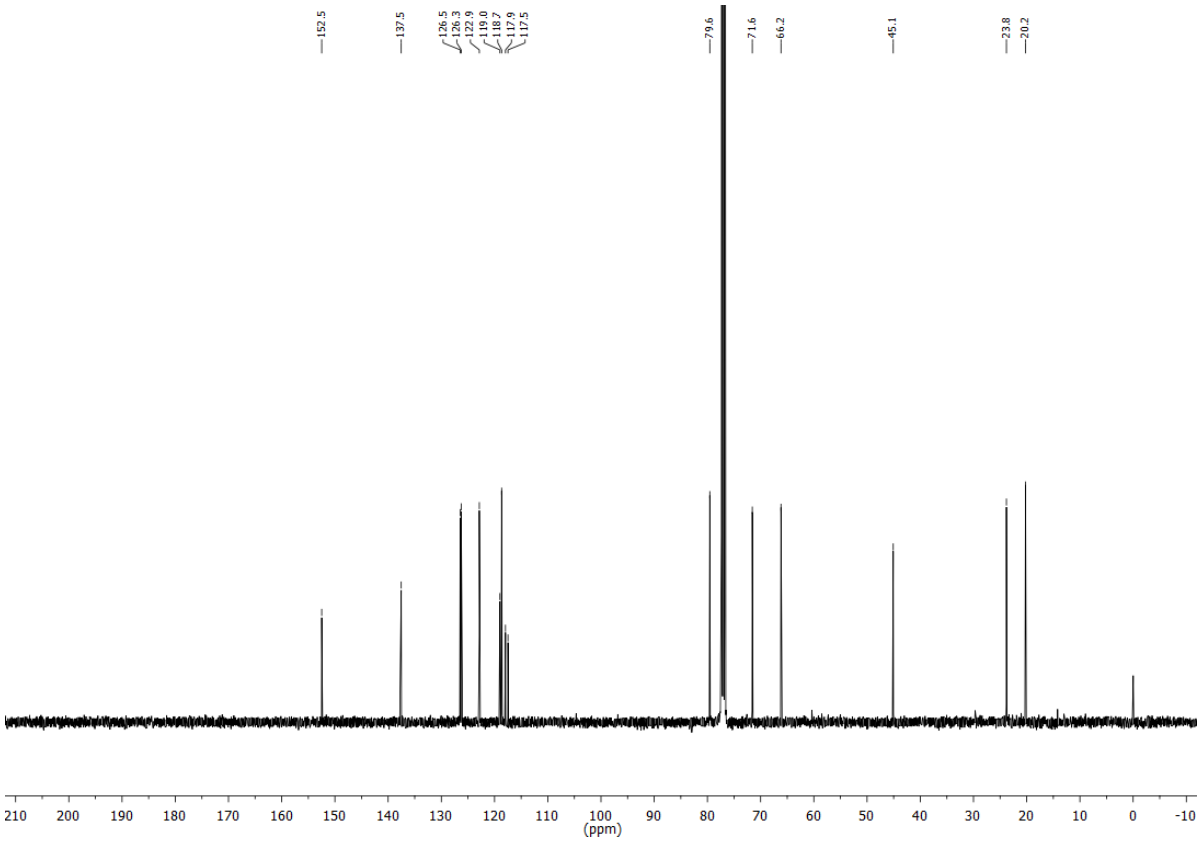
^{13}C-NMR (101 MHz, CD_2Cl_2): δ = 20.2, 23.8, 45.1, 66.2, 71.6, 79.6, 117.5, 117.9, 118.7, 119.0, 122.9, 126.3, 126.5, 137.5, 152.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3065, 2966, 2927, 2855, 2249, 1725, 1472, 1447, 1261, 1217, 1071, 990, 941.

$C_{15}H_{15}NO_2S$ calcd.: 273.0824, found: 273.0845 (GC-HRMS).

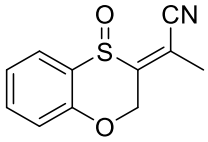


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(4-Oxidobenzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)propanenitrile (12a)



Following a reported procedure,[44] compound **2a** (20.0mg, 100µmol, 1.00 equiv.) was dissolved in DCM (2 ml). After addition of *m*-CPBA (17.3mg, 100µmol, 1.00 equiv.) the mixture was stirred overnight. The solution was then diluted with DCM (8 ml), washed with NaOH solution (2.0 M, 2 × 10 ml) and brine. The organic phase was dried over Na_2SO_4 and the solvent was evaporated. Flash column chromatography (*n*-pentane:EtOAc = 10:1→5:1) afforded the desired product as a colorless solid (13.5 mg, 61.5 µmol, 62%).

m.p.: 163 °C.

R_f = 0.07 (*n*-pentane:EtOAc = 4:1).

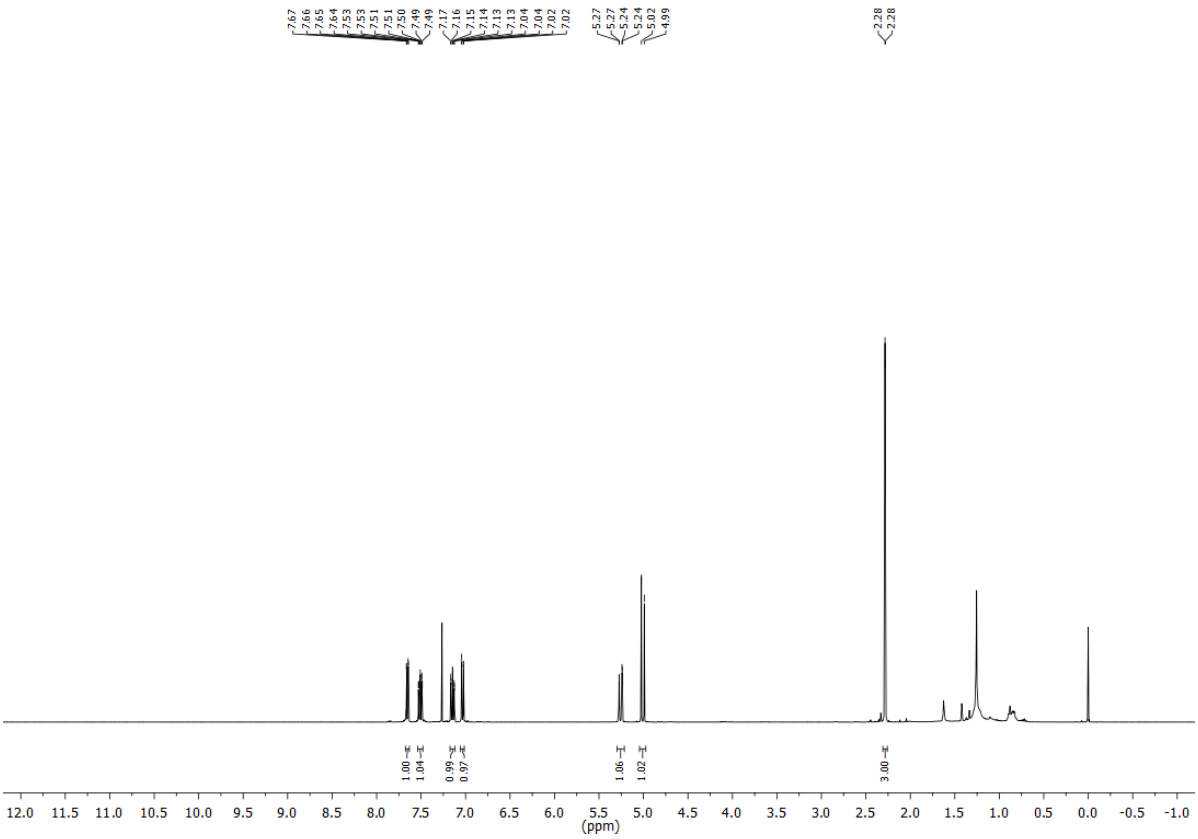
^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.28 (d, *J* = 1.3 Hz, 3H), 5.01 (d, *J* = 13.1 Hz, 1H), 5.26 (dd, *J* = 13.1, 1.3 Hz, 1H), 7.03 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.12 – 7.17 (m, 1H), 7.51 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.7 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 17.6, 56.0, 114.9, 117.8, 119.1, 122.4, 124.8, 132.6, 135.0, 149.6, 152.3.

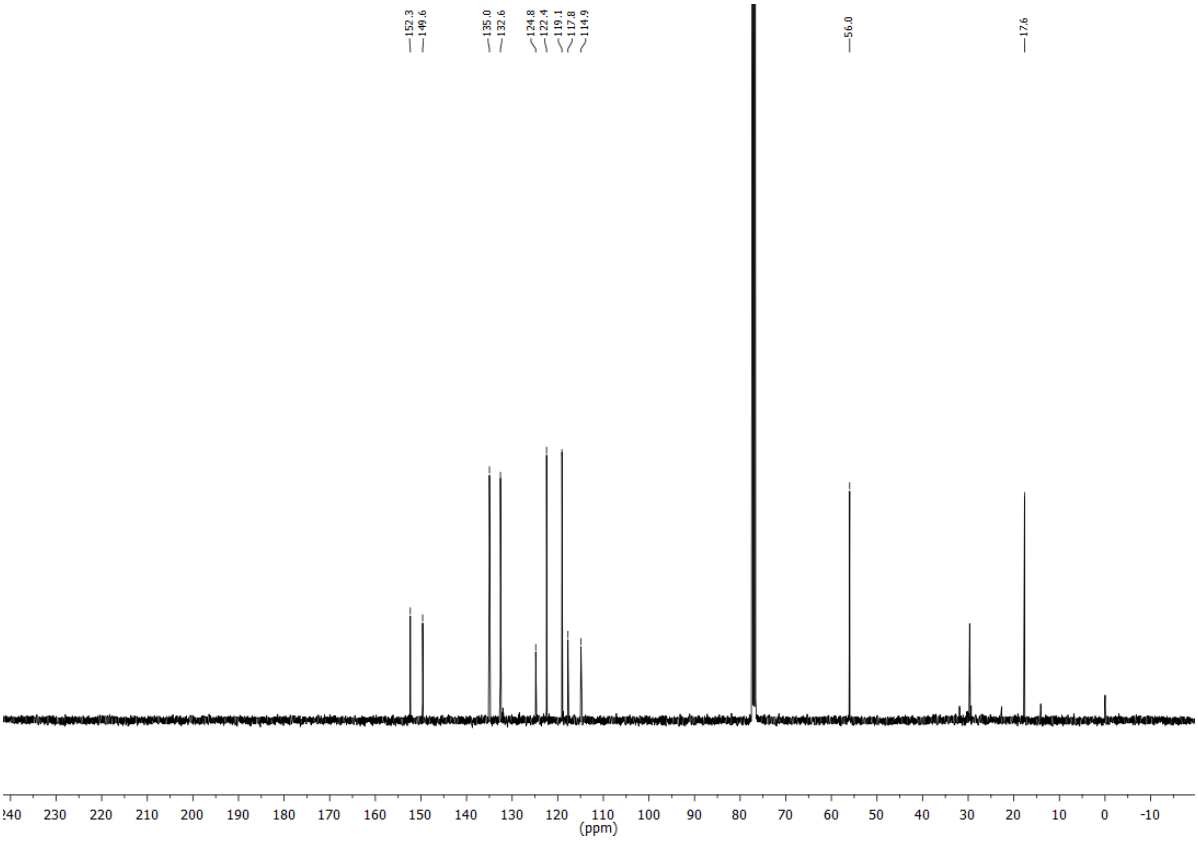
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3076, 3012, 2922, 2854, 2217, 1591, 1565, 1468, 1437, 1377, 1267, 1214, 1030, 993.

$C_{11}H_9NO_2S$ calcd.: 219.0354, found: 219.0367 (GC-HRMS).

[44] A. U. Augustin, M. Busse, P. G. Jones and D. B. Werz, *Org. Lett.*, 2018, **20**, 820.

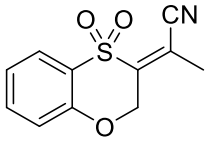


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(4,4-Dioxidobenzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)propanenitrile (12b)



Following a reported procedure,[36] compound **2a** (20.0mg, 100µmol, 1.00 equiv.) was dissolved in DCM (2 ml). After addition of *m*-CPBA (51.9mg, 300µmol, 3.00 equiv.) the mixture was stirred overnight. The solution was then diluted with DCM (8 ml), washed with NaOH solution (2.0 M, 2 × 10 ml) and brine. The organic phase was dried over Na_2SO_4 and the solvent was evaporated. Flash column chromatography (*n*-pentane:EtOAc = 10:1) afforded the desired product as an off-white solid (22.0 mg, 93.5 µmol, 94%).

m.p.: 183 °C.

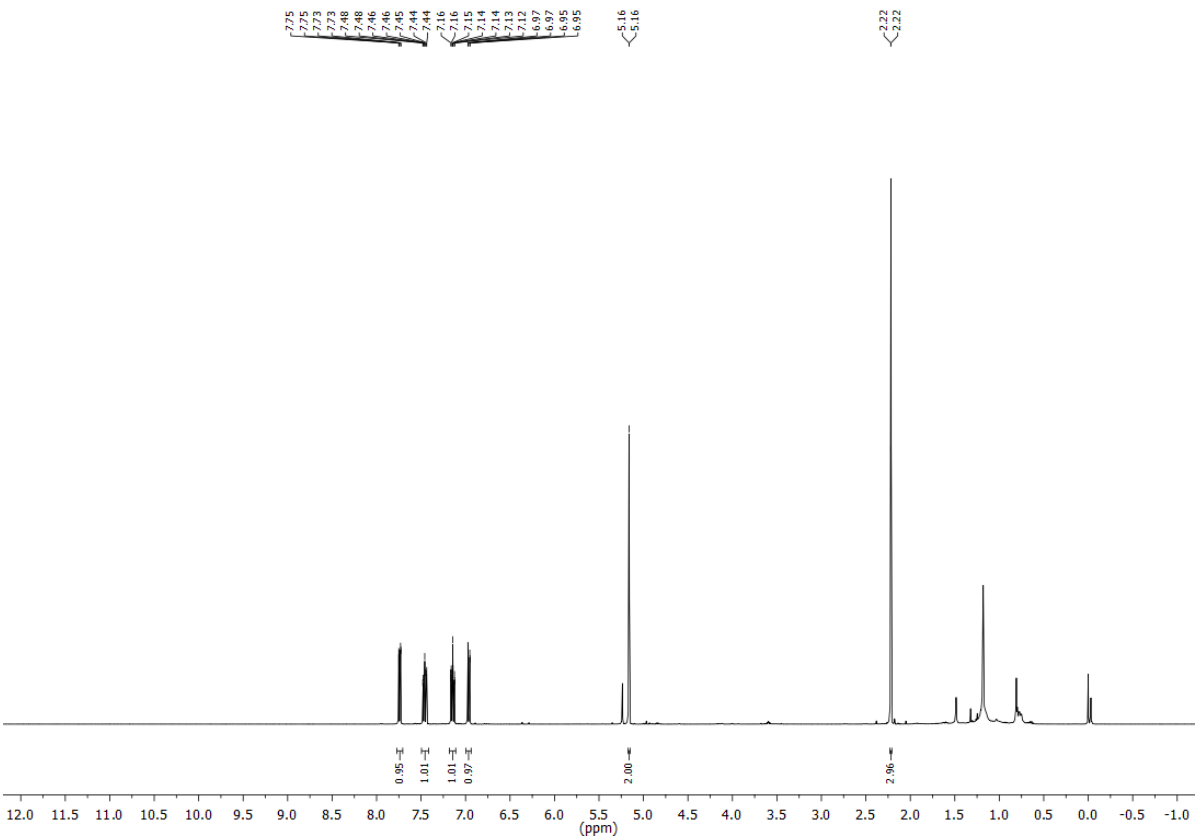
R_f = 0.12 (*n*-pentane:EtOAc = 4:1).

^{1}H-NMR (400 MHz, CD_2Cl_2) δ 2.22 (s, 3H), 5.16 (d, *J* = 0.9 Hz, 2H), 6.96 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.14 (ddd, *J* = 8.3, 7.3, 1.1 Hz, 1H), 7.46 (ddd, *J* = 8.8, 7.3, 1.7 Hz, 1H), 7.74 (dd, *J* = 8.0, 1.7 Hz, 1H).

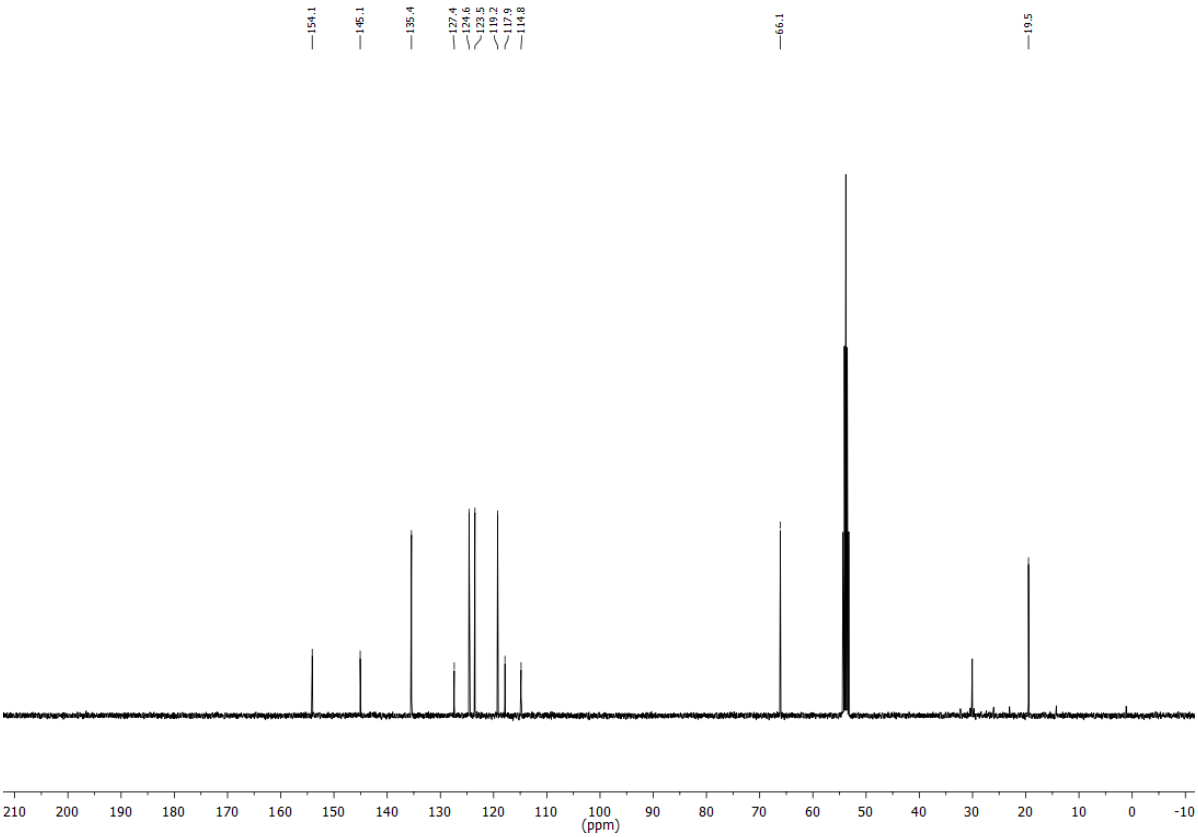
^{13}C-NMR (101 MHz, CD_2Cl_2) δ 19.5, 66.1, 114.8, 117.9, 119.2, 123.5, 124.6, 127.4, 135.4, 145.1, 154.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3045, 2926, 2856, 2221, 1595, 1568, 1472, 1442, 1304, 1268, 1217, 1141, 1039, 1003.

$C_{11}H_9NO_3S$ calcd.: 235.0303, found: 235.0324 (GC-HRMS).

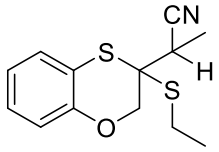


^{1}H-NMR (400 MHz, CD_2Cl_2).



^{13}C-NMR (101 MHz, CD_2Cl_2).

2-(3-(Ethylthio)-2,3-dihydrobenzo[*b*][1,4]oxathiin-3-yl)propanenitrile, Diastereomer 1 (12c)



Following a reported procedure,[45] compound **2a** (20.0mg, 100µmol, 1.00 equiv.) was dissolved in DMSO (0.6 ml). Ethanethiol (74.0 µl, 62.0 mg, 1.0 mmol, 10.00 equiv.) and subsequently piperidine (40.0 µl, 34.4 mg, 0.4 mmol, 4.00 equiv.) were added. The solution was stirred for 1 h at RT and then diluted with water. After extraction with Et_2O (3 x 10 ml), washing with brine and drying over Na_2SO_4 the crude mixture was subjected to flash column chromatography (*n*-pentane:EtOAc = 50:1) to obtain **12c** and **12c'** in an overall yield of 83% (22.0 mg, 83.0 µmol, *d.r.* 50:50)

Compound **12c** was obtained as a colorless oil.

R_f = 0.42 (*n*-pentane:EtOAc = 20:1).

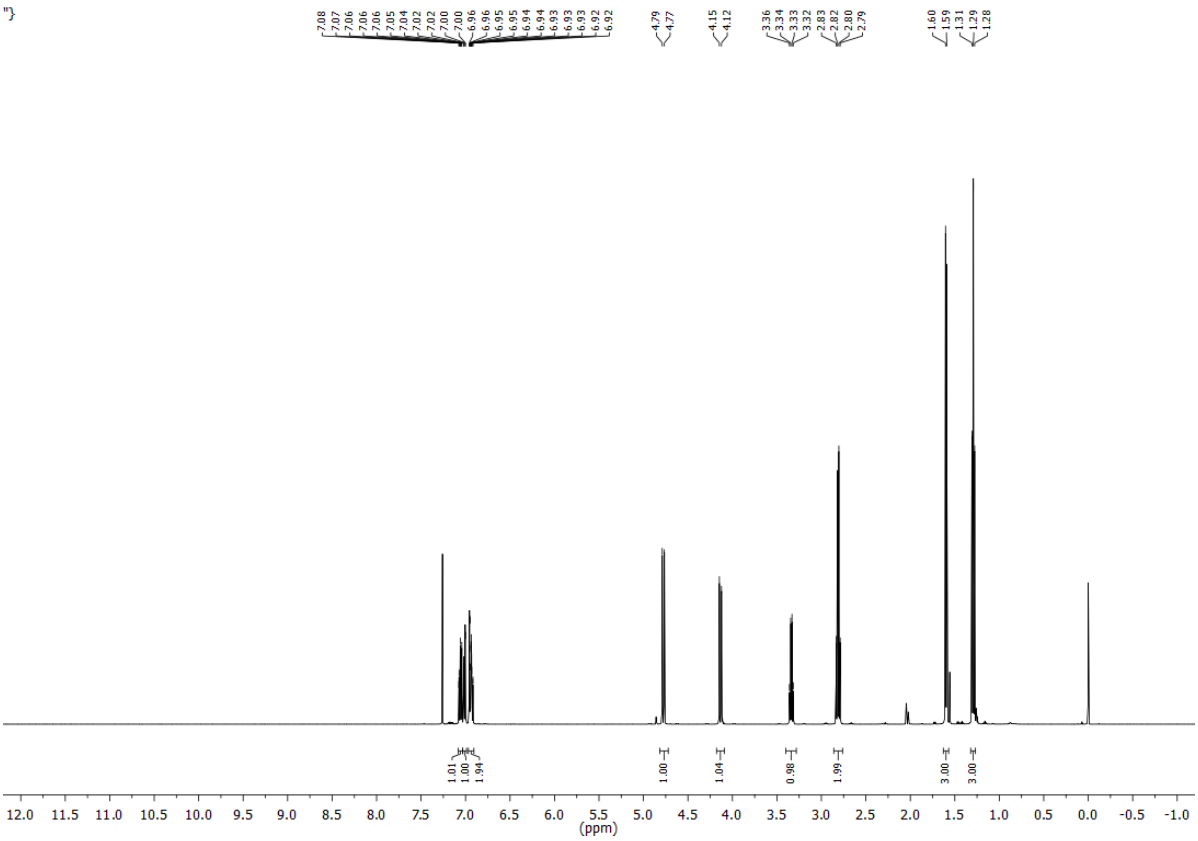
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.5 Hz, 3H), 1.60 (d, *J* = 7.2 Hz, 3H), 2.81 (q, *J* = 7.5 Hz, 2H), 3.34 (q, *J* = 7.3 Hz, 1H), 4.13 (d, *J* = 11.8 Hz, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 6.91 – 6.97 (m, 2H), 7.01 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.06 (ddd, *J* = 8.3, 7.0, 1.6 Hz, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.6, 14.6, 23.3, 33.5, 56.0, 71.5, 118.2, 118.7, 119.1, 122.7, 126.2, 126.5, 149.9.

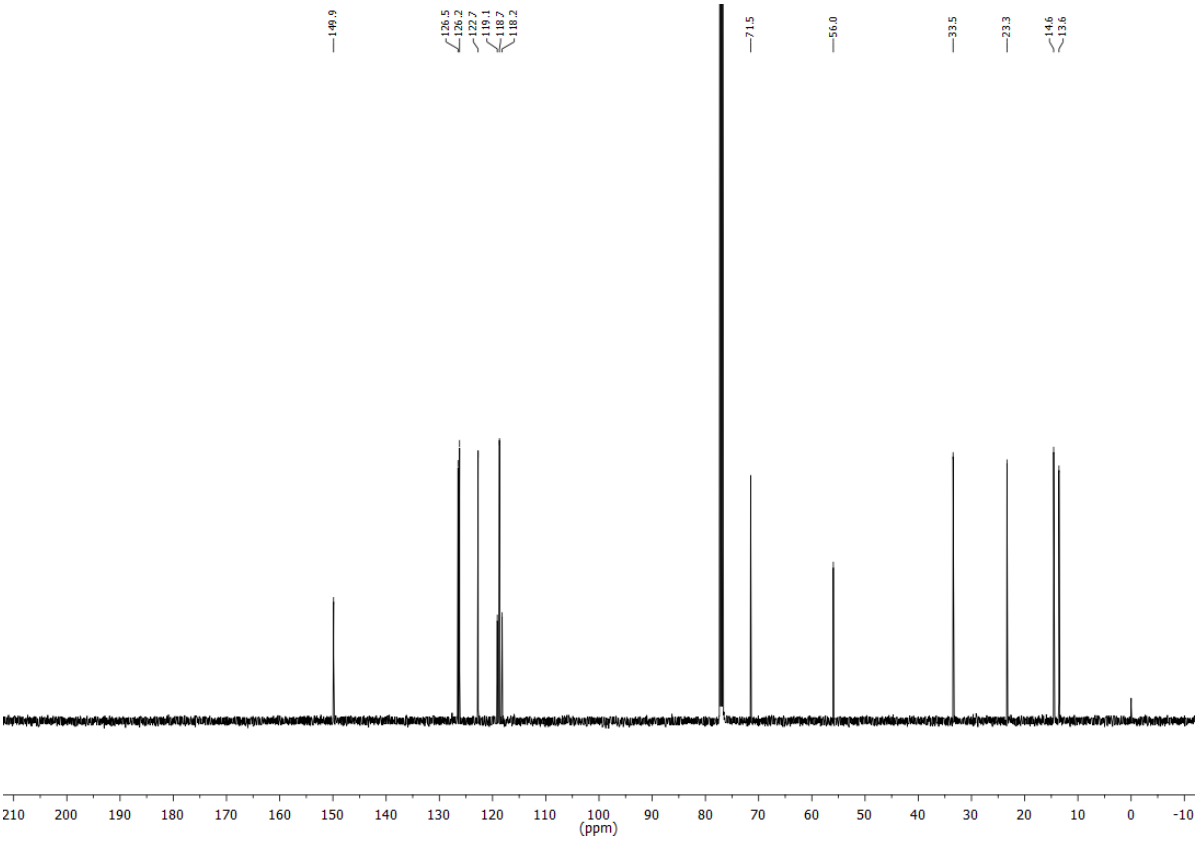
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3065, 2977, 2933, 2874, 2241, 1573, 1472, 1445, 1301, 1264, 1211, 1123, 1042.

$C_{13}H_{15}NOS_2$ calcd.: 265.0595, found: 265.0599 (GC-HRMS).

[45] P. Demin, O. Rounova, T. Grunberger, L. Cimpean, N. Sharfe and C. M. Roifman, *Bioorg. Med. Chem.*, 2004, **12**, 3019.

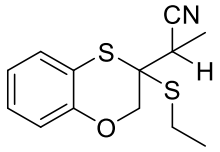


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

2-(3-(Ethylthio)-2,3-dihydrobenzo[*b*][1,4]oxathiin-3-yl)propanenitrile, Diastereomer 2 (12c')



Compound **12c'** was obtained as a colorless oil.

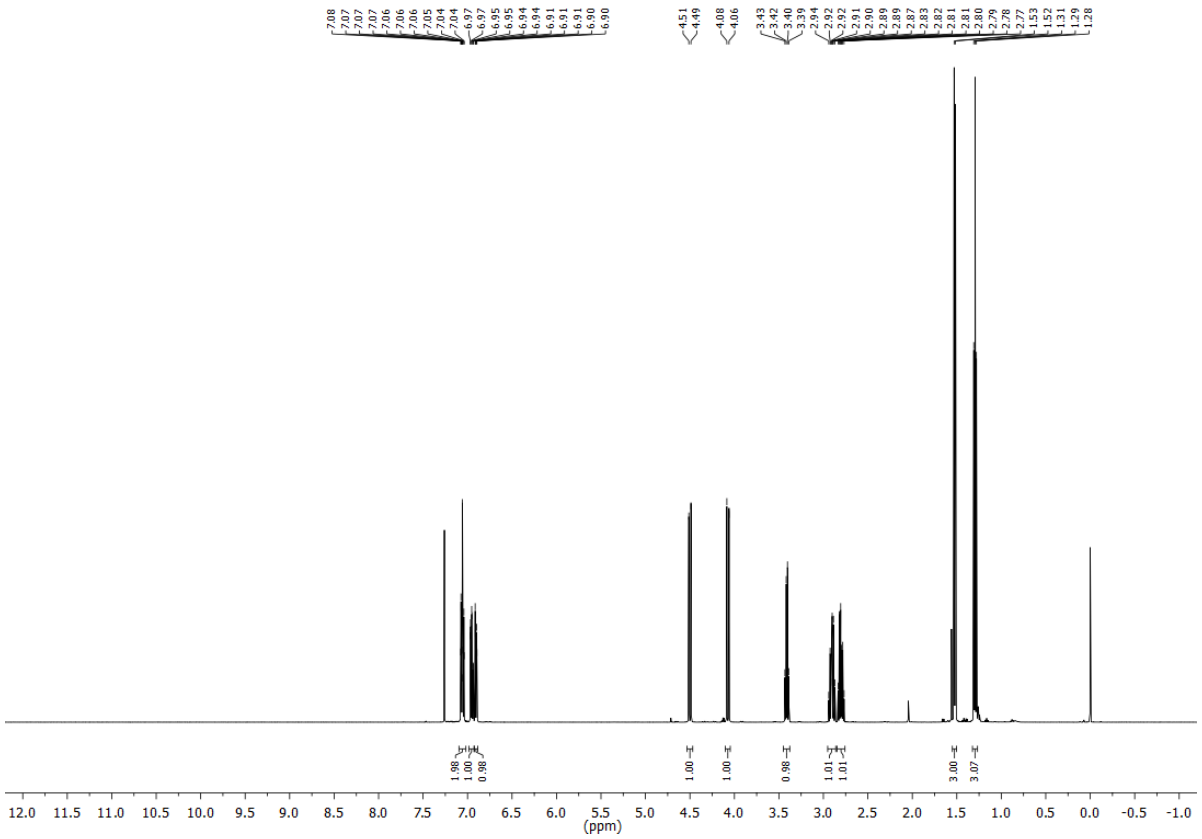
R_f = 0.27 (*n*-pentane:EtOAc = 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.5 Hz, 3H), 1.52 (d, *J* = 7.1 Hz, 3H), 2.80 (dq, *J* = 11.6, 7.3 Hz, 1H), 2.91 (dq, *J* = 11.6, 7.6 Hz, 1H), 3.41 (q, *J* = 7.1 Hz, 1H), 4.07 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 6.89 – 6.92 (m, 1H), 6.93 – 6.97 (m, 1H), 7.03 – 7.08 (m, 2H).

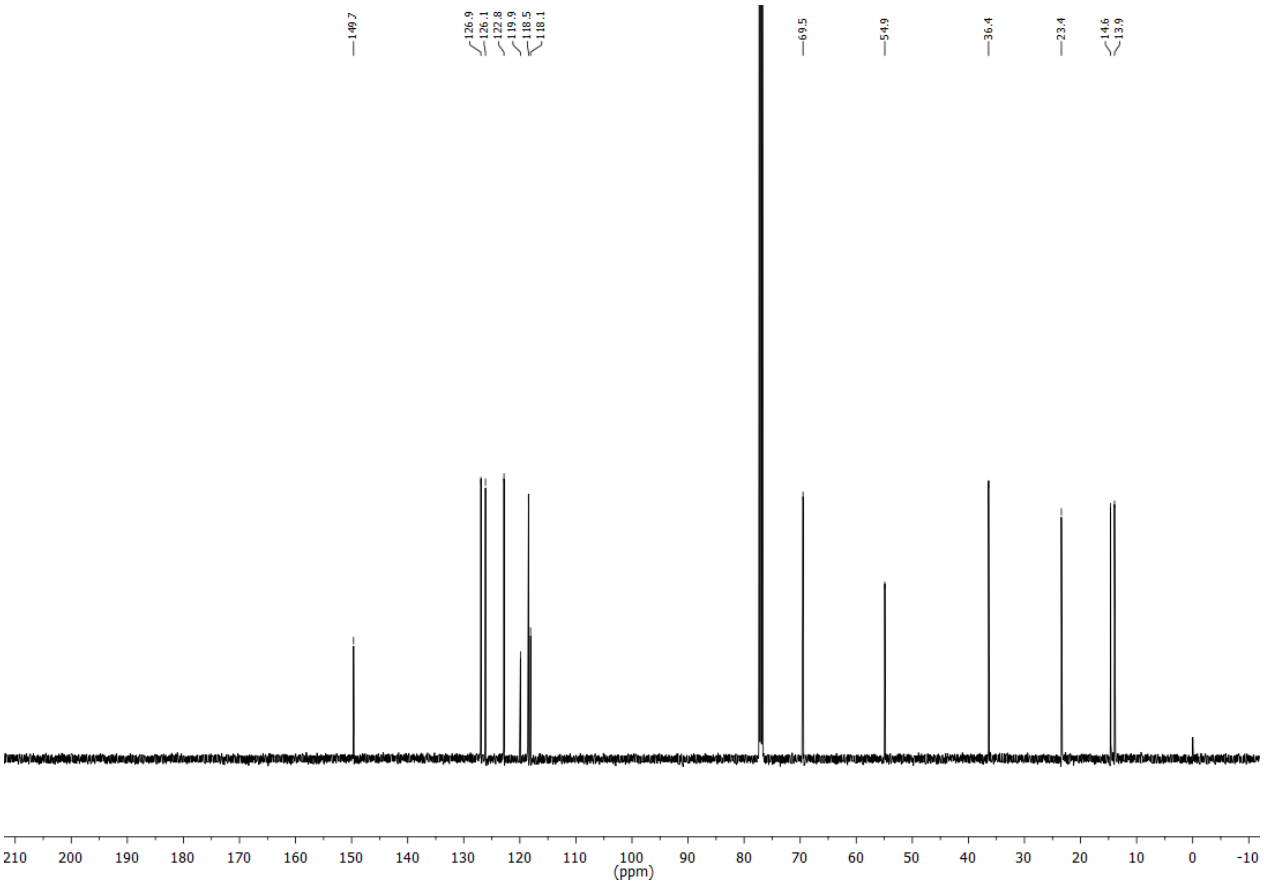
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.9, 14.6, 23.4, 36.4, 54.9, 69.5, 118.1, 118.5, 119.9, 122.8, 126.1, 126.9, 149.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3065, 2976, 2930, 2243, 1573, 1471, 1445, 1301, 1263, 1211, 1130, 1065, 1040, 1011.

$C_{13}H_{15}NOS_2$ calcd.: 265.0595, found: 265.0609 (GC-HRMS).

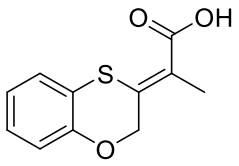


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[*b*][1,4]oxathiin-3(*2H*)-ylidene)propanoic acid (*exo*-12d)



According to a reported procedure,[46] compound **2a** (51.0mg, 250µmol, 1.00 equiv.) was weighed into a sealable tube EtOH (2 mL) and KOH (2 mL, 34% aq. solution) were added via syringe. The resulting reaction mixture was heated at 80 °C overnight. The reaction mixture was then quenched and acidified with HCl (2 M), diluted with EtOAc (5 mL). The aqueous phase was extracted with EtOAc (3 x 10 ml), the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (*n*-pentane:Et_2O:AcOH = 20:1:0.1) to provide ***exo*-12d** and ***endo*-12d** as a 1:3 mixture in an overall yield of 61% (34.0 mg, 153.0 µmol).

Compound ***exo*-12d** was obtained as a colorless solid.

m.p.: 168 °C.

R_f = 0.20 (*n*-pentane:Et_2O:AcOH = 10:1:0.1).

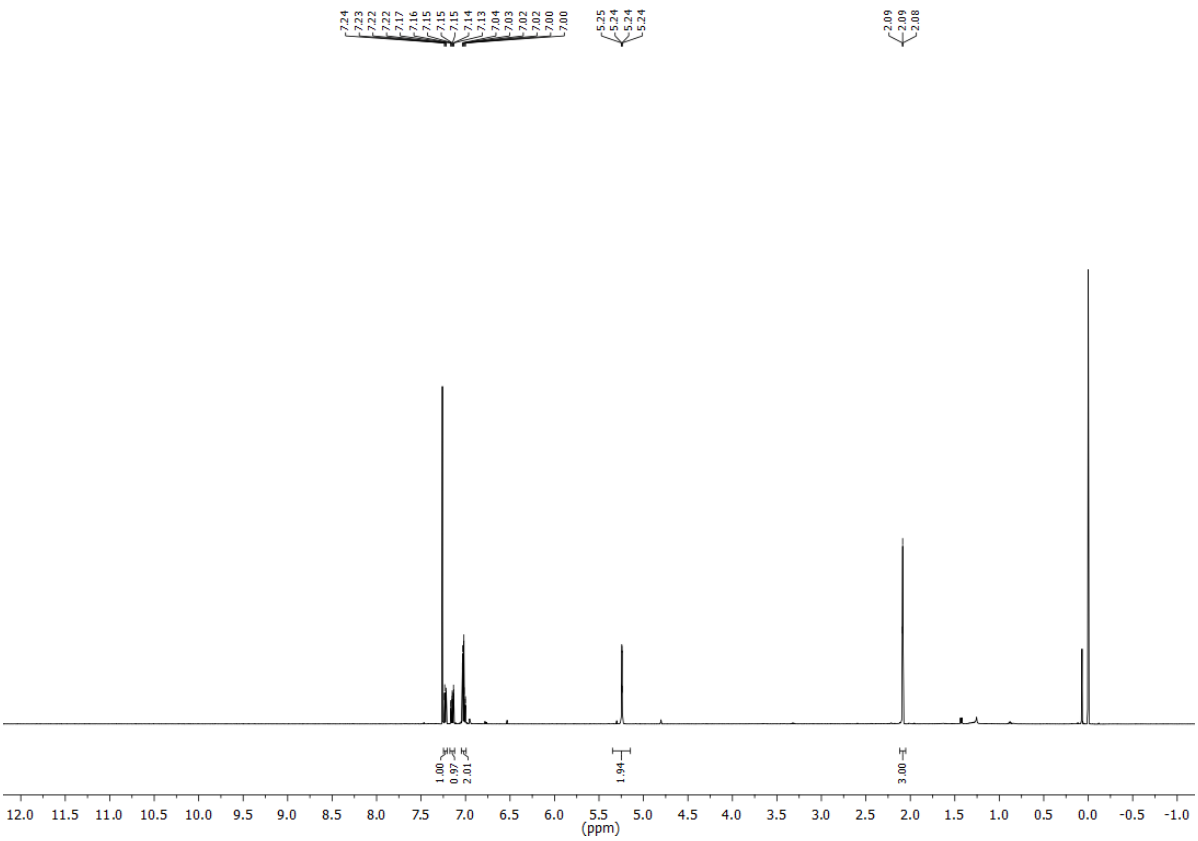
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.09 (t, *J* = 1.2 Hz, 3H), 5.24 (q, *J* = 1.3 Hz, 2H), 7.00 – 7.04 (m, 2H), 7.13 – 7.17 (m, 1H), 7.21 – 7.24 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 16.1, 66.5, 117.9, 118.4, 119.5, 123.2, 126.4, 127.4, 149.6, 153.5, 170.2.

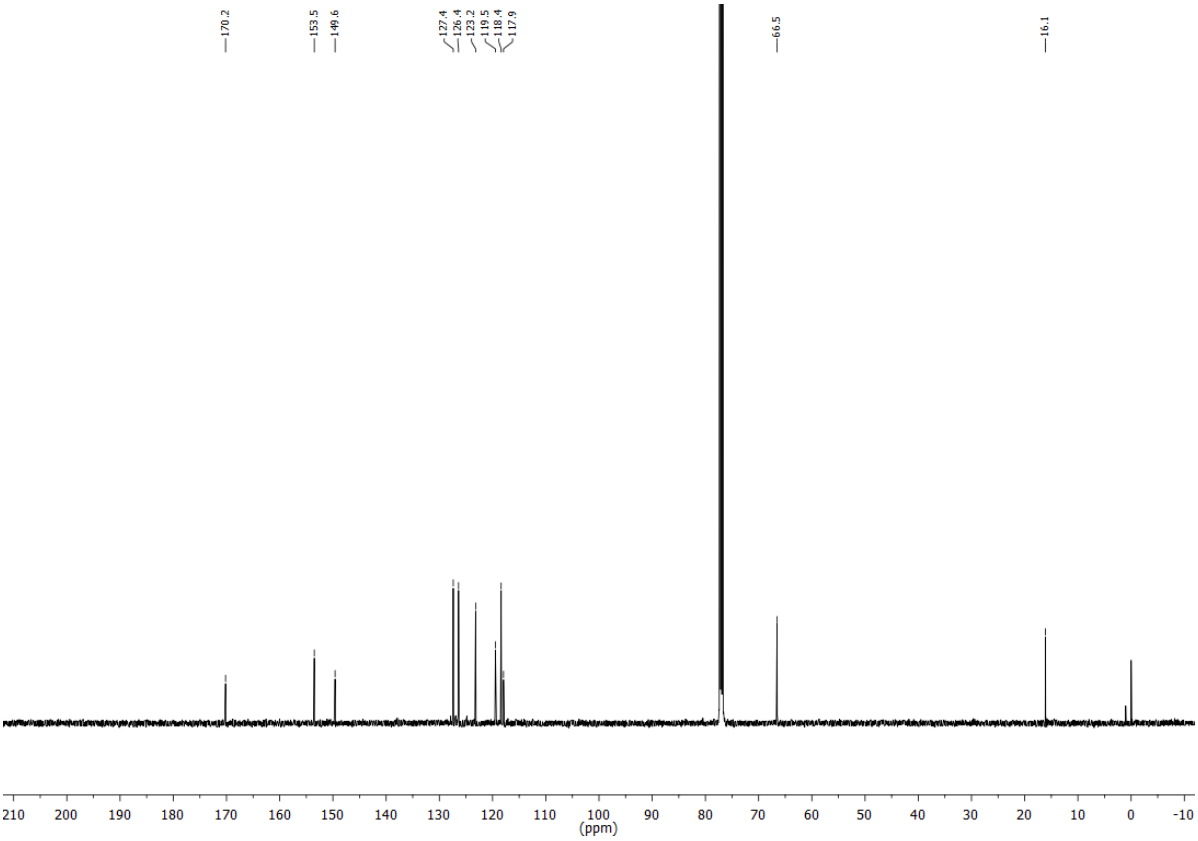
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3085, 2914, 2853, 2690, 2638, 2536, 1649, 1586, 1558, 1433, 1285, 1255, 1188, 1069.

$C_{11}H_{10}O_3S$ calcd.: 245.0243, found: 245.02 $[M+Na]^+$ (ESI-HRMS).

[46] X. Wang, Y. Tang, C.-Y. Long, W.-K. Dong, C. Li, X. Xu, W. Zhao and X.-Q. Wang, *Org. Lett.*, 2018, **20**, 4749.

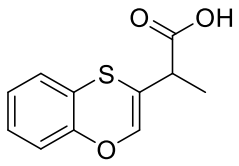


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

2-(Benzo[*b*][1,4]oxathiin-3-yl)propanoic acid (*endo*-12d)



***endo*-12d** was obtained as a yellow sticky compound.

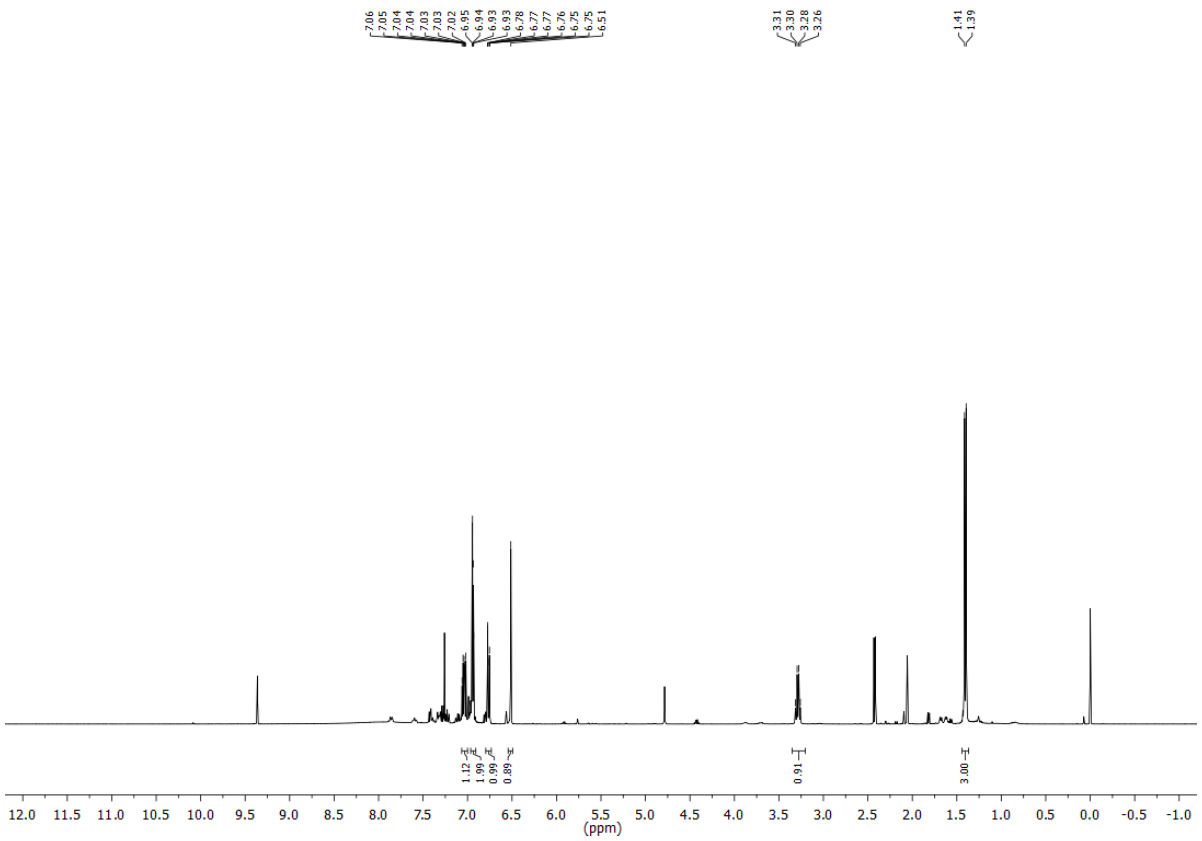
R_f = 0.20 (*n*-pentane:Et_2O:AcOH = 10:1:0.1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.40 (d, *J* = 7.2 Hz, 3H), 3.29 (q, *J* = 7.1 Hz, 1H), 6.51 (s, 1H), 6.74 – 6.79 (m, 1H), 6.92 – 6.96 (m, 2H), 7.01 – 7.07 (m, 1H).

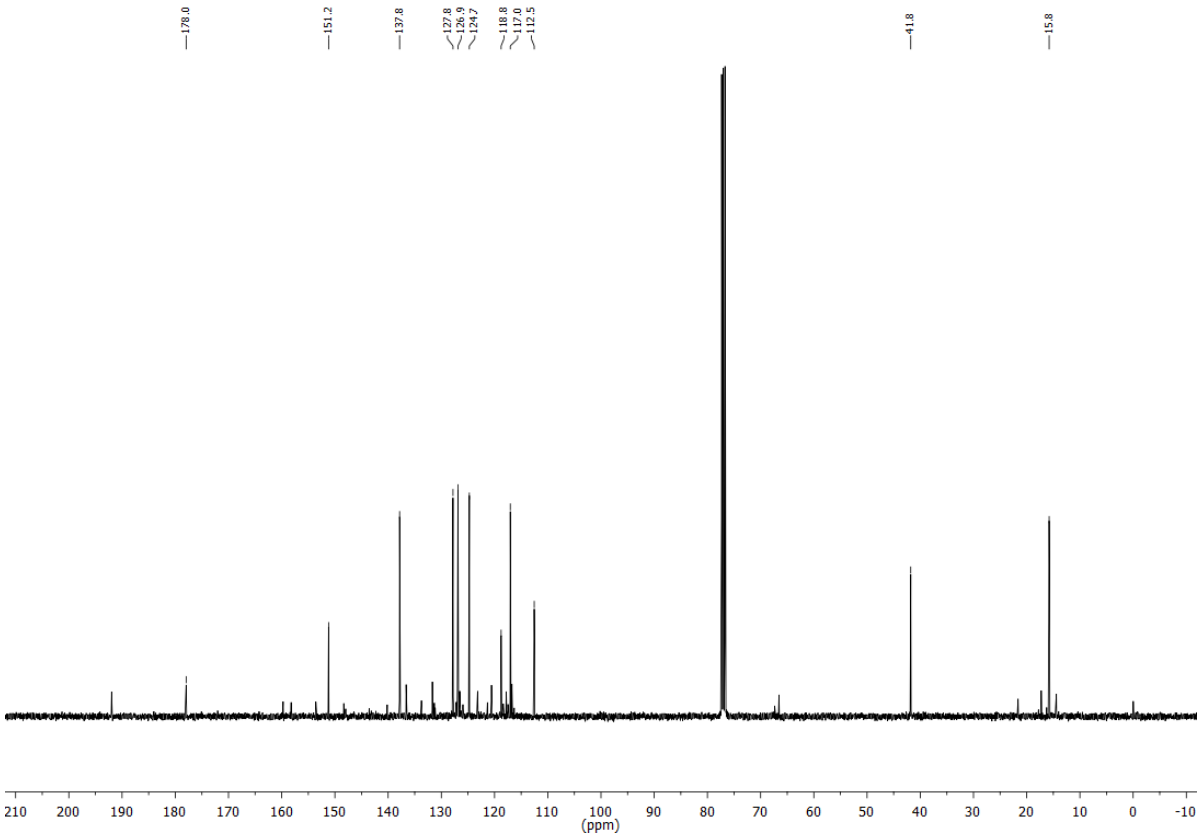
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 15.8, 41.8, 112.5, 117.0, 118.8, 124.7, 126.9, 127.8, 137.8, 151.2, 178.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3258, 3066, 2980, 2933, 1724, 1637, 1578, 1468, 1277, 1200, 973.

$C_{11}H_{10}O_3S$ calcd.: 245.0243, found: 245.0245 $[M+Na]^+$ (ESI-HRMS).

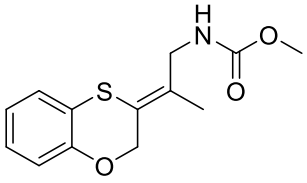


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

Methyl (*Z*)-(2-(benzo[*b*][1,4]oxathiin-3(2*H*)-ylidene)propyl)carbamate (12e)



Compound **2a** was subjected to a reported procedure[47] to obtain carbamate **12e** after flash column chromatography (*n*-pentane:EtOAc = 10:1→4:1) as a colorless solid (39.0 mg, 0.15 mmol, 75%).

m.p.: 88 °C.

$\mathbf{R_f}$ = 0.31 (*n*-pentane:EtOAc = 20:1).

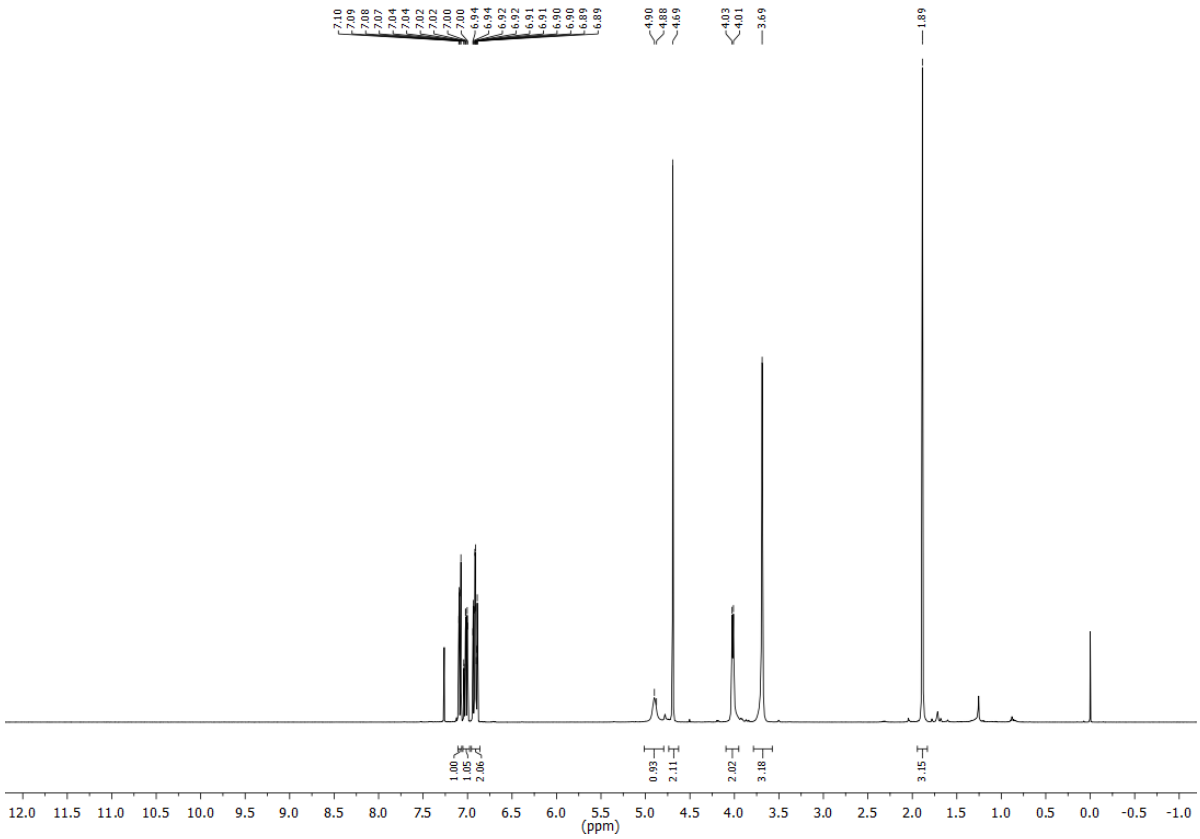
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.89 (s, 3H), 3.69 (s, 3H), 4.02 (d, *J*=6.2, 2H), 4.69 (s, 2H), 4.89 (s, 1H), 6.86 – 6.95 (m, 2H), 6.99 – 7.05 (m, 1H), 7.09 (dd, *J*=7.7, 1.7, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 16.4, 44.3, 52.3, 65.3, 118.3, 119.4, 122.5, 123.2, 125.8, 126.2, 128.4, 152.8, 157.3.

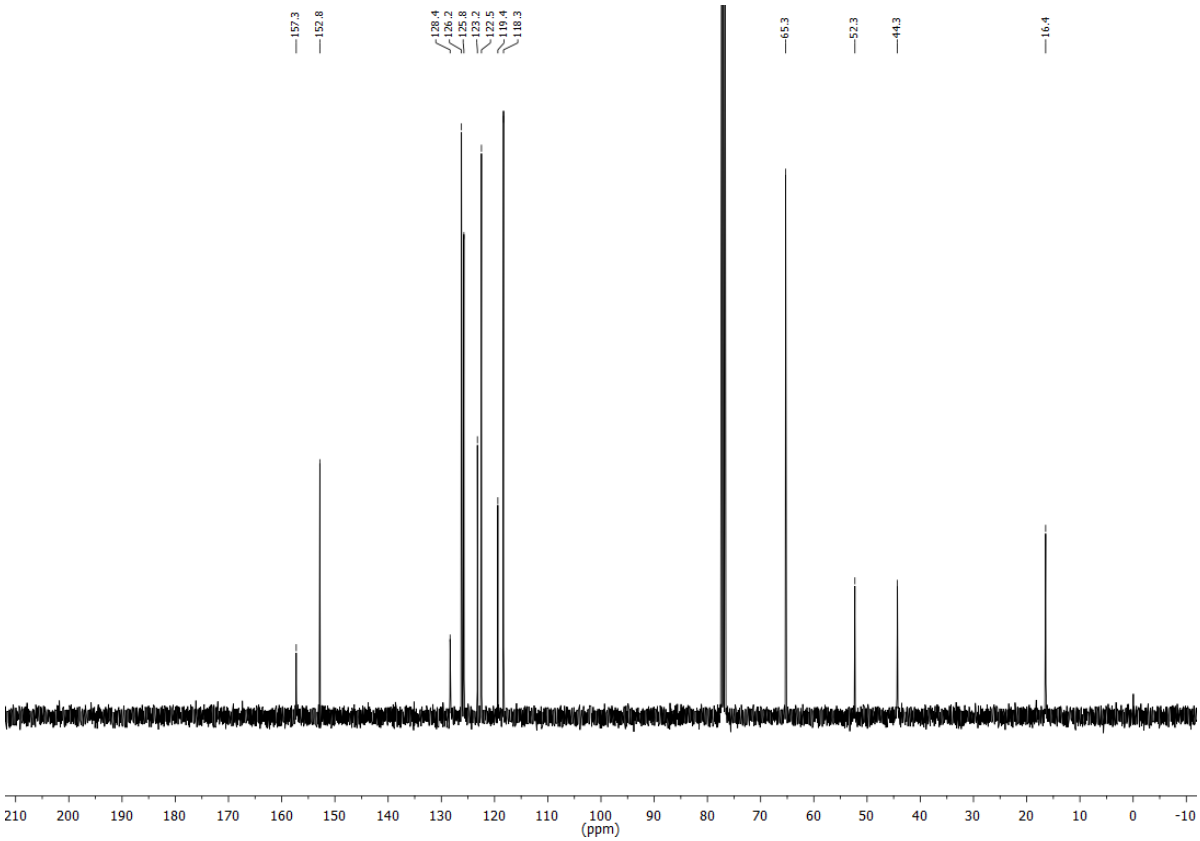
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3311, 3069, 2988, 2918, 2852, 1692. 1543, 1471, 1438, 1261, 1073, 988.

$C_{13}H_{15}NO_3S$ calcd.: 288.0665 [M+Na^+], found: 288.0668 [M+Na^+] (ESI-HRMS).

[47] M. Skvorcova, L. T. Lukasevics and A. Jirgensons, *J. Org. Chem.*, 2019, **84**, 3780.

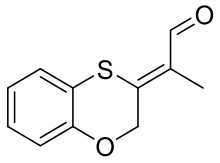


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(*Z*)-2-(Benzo[*b*][1,4]oxathiin-3(*2H*)-ylidene)propanal (12f)



According to a reported procedure,[38] compound **2a** (20.0 mg, 100 µmol, 1.00 equiv.) was weighed into a sealable tube. Dry toluene (0.50 mL) was added via and the solution was cooled to -78 °C. DIBAL-H (0.11 ml, 0.11 mmol, 1 M in hexane) was subsequently added and the tube was sealed. The resulting reaction mixture was taken from the cooling bath and stirred under ambient temperature for 30 min while warming. Afterwards, the mixture was directly transferred into a flask, diluted with further toluene. Silica gel was added to adsorb the reaction products. Immediate flash column chromatography (*n*-pentane:EtOAc 30:1→20:1) provided compound **12f** as a yellow solid (9.0 mg, 44 µmol, 44%).

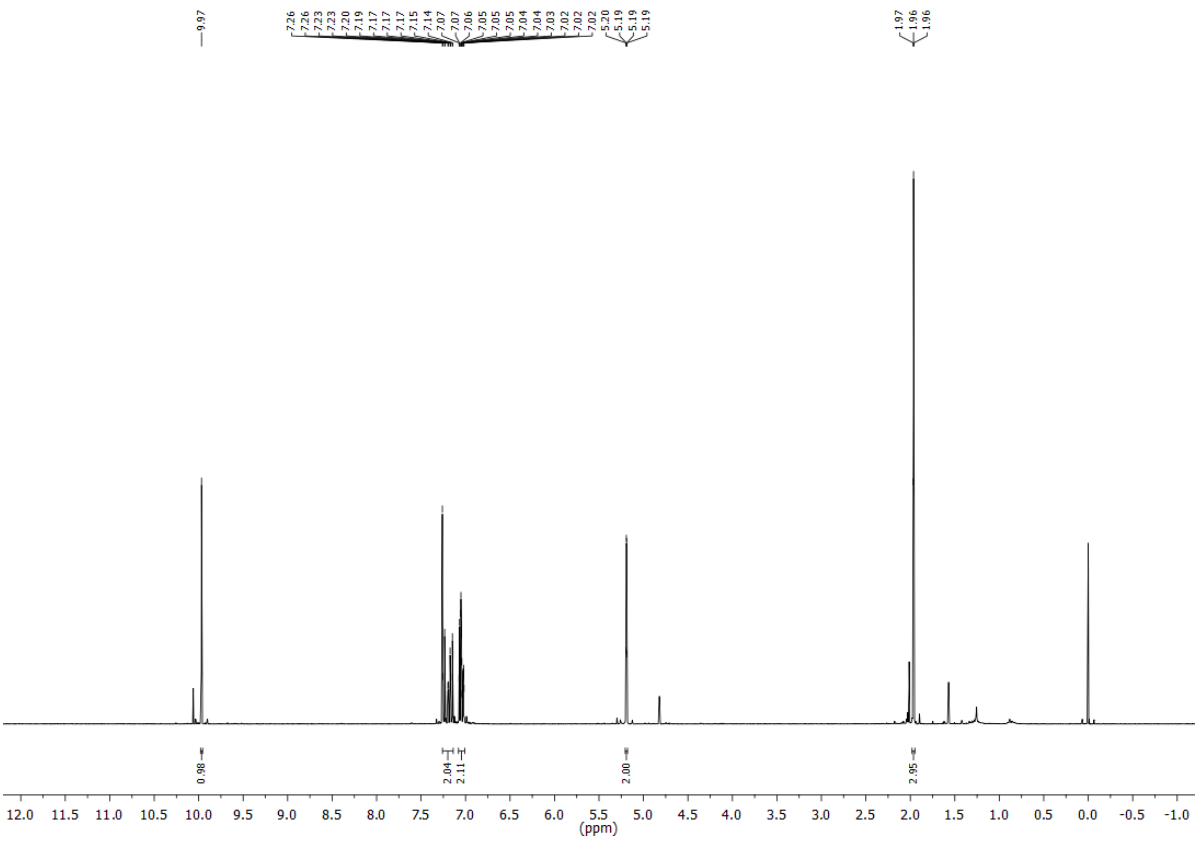
R_f = 0.46 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.96 (t, *J* = 1.0 Hz, 3H), 5.19 (q, *J* = 1.0 Hz, 2H), 7.01 – 7.08 (m, 2H), 7.14 – 7.27 (m, 2H), 9.97 (s, 1H).

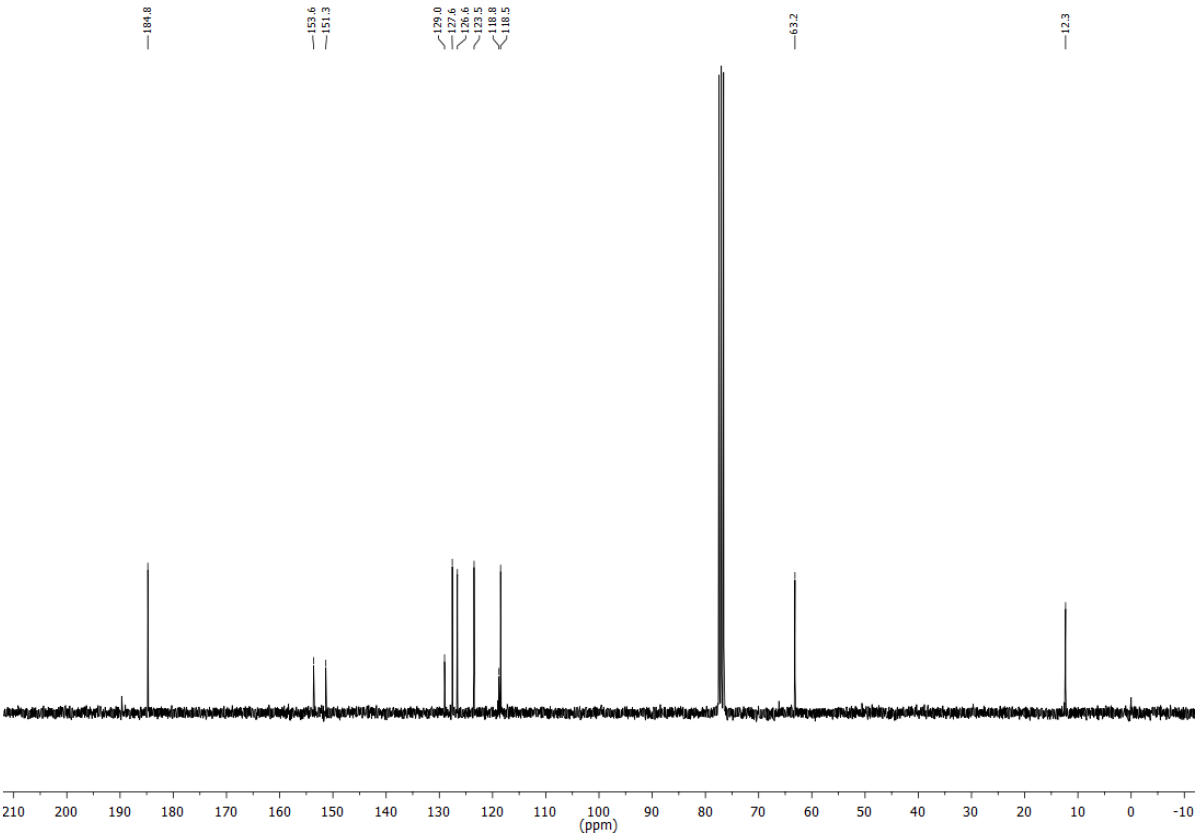
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 12.3, 63.2, 118.5, 118.8, 123.5, 126.6, 127.6, 129.0, 151.3, 153.6, 184.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3069, 2917, 2853, 1646, 1583, 1468, 1437, 1373, 1266, 1001.

$C_{11}H_{10}O_2S$ calcd.: 206.0402, found: 206.0409 (GC-HRMS).

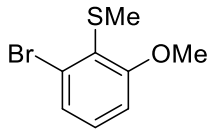


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(2-Bromo-6-methoxyphenyl)(methyl)sulfane (20a)



Compound **20a** was synthesized via a reported procedure[48] for methylation from 3-bromo-2-(methylthio)phenol and obtained as a colorless oil (9.5 g, 40.8 mmol, 91%).

The starting material, 3-bromo-2-(methylthio)phenol, was afforded via a 3-step procedure from 3-bromophenol (introduction of carbamate as directing group[49], lithiation in ortho-position and substitution with dimethyl disulfide[50], removal of the directing group[51]).

R_f = 0.69 (*n*-pentane:EtOAc = 20:1).

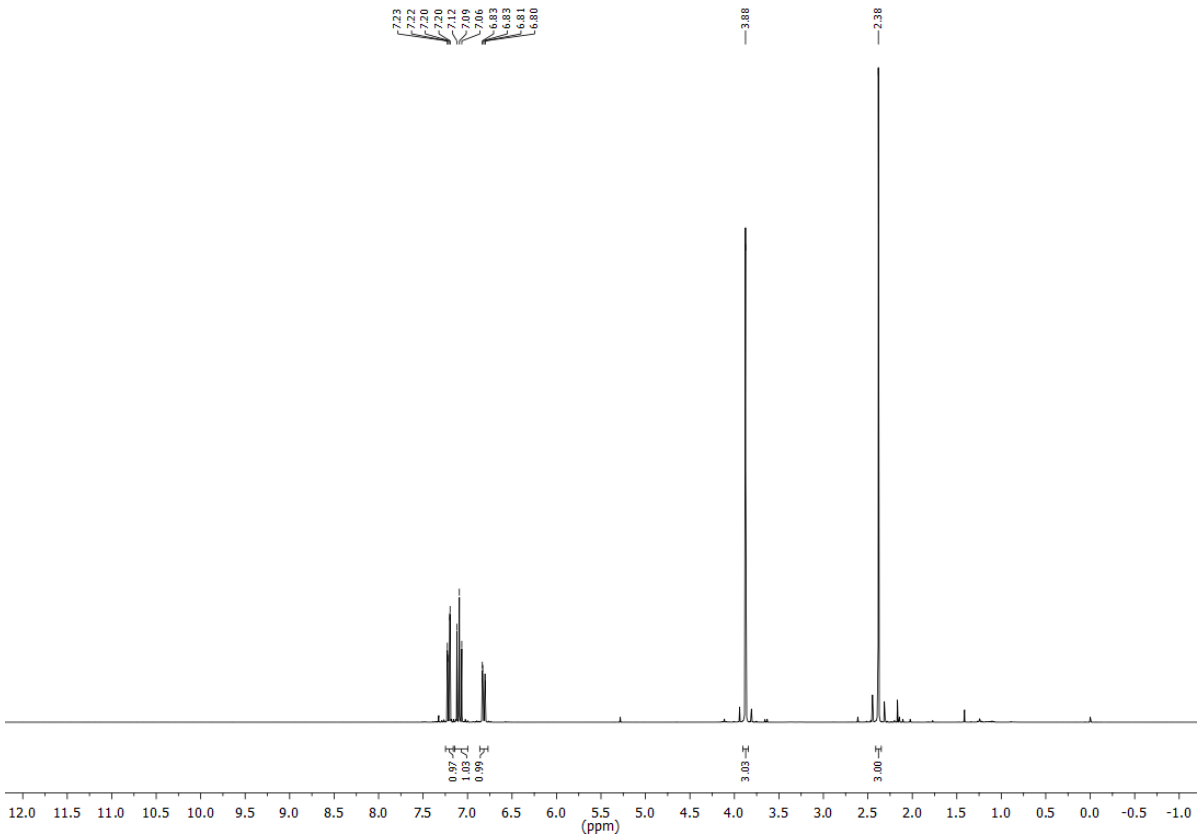
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.4 (s, 3H), 3.9 (s, 3H), 6.8 (dd, *J*=8.3, 1.3, 1H), 7.0 – 7.1 (m, 1H), 7.2 (dd, *J*=8.0, 1.2, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.9, 56.0, 109.8, 124.9, 125.2, 129.6, 130.2, 160.6.

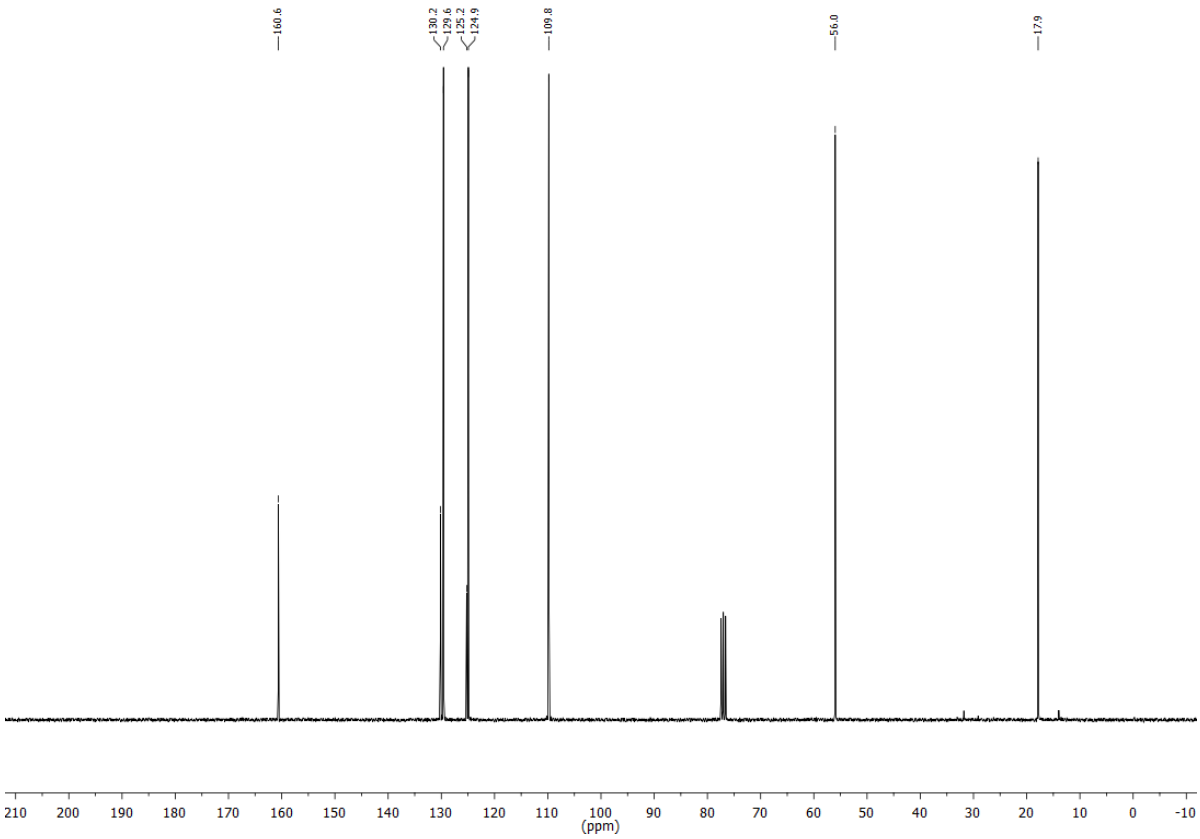
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2926, 2843, 1693, 1565, 1455, 1422, 1258, 1026.

C_8H_9BrOS calcd.: 231.9558, found: 231.9557 (GC-HRMS).

[48] A. Blencowe, N. Caiulo, K. Cosstick, W. Fagour, P. Heath and W. Hayes, *Macromolecules*, 2007, **40**, 939.
[49] X. Deng, Y.-Q. Guan, N.-N. Huo, Y.-J. Wang, H. Lv and X.-M. Zhang, *Synthesis*, 2017, **49**, 3726.
[50] R. Sanz, V. Guilarte, E. Hernando and A. M. Sanjuán, *J. Org. Chem.*, 2010, **75**, 7443.
[51] R. Sanz, M. P. Castroviejo, Y. Fernández and F. J. Fañanás, *J. Org. Chem.*, 2005, **70**, 6548.

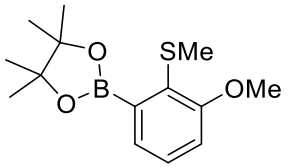


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

2-(3-Methoxy-2-(methylthio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20b)



Compound **20a** was subjected to a reported procedure[52] to obtain borolane **20b** after flash column chromatography (*n*-pentane:EtOAc = 20:1) as a colorless solid (4.8 g, 17.1 mmol, 47%).

m.p.: 38 °C.

R_f = 0.79 (*n*-pentane:EtOAc = 4:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.4 (s, 12H), 2.4 (s, 3H), 3.9 (s, 3H), 6.9 (dd, *J*=8.2, 1.3, 1H), 7.0 (dd, *J*=7.4, 1.3, 1H), 7.2 – 7.3 (m, 1H).

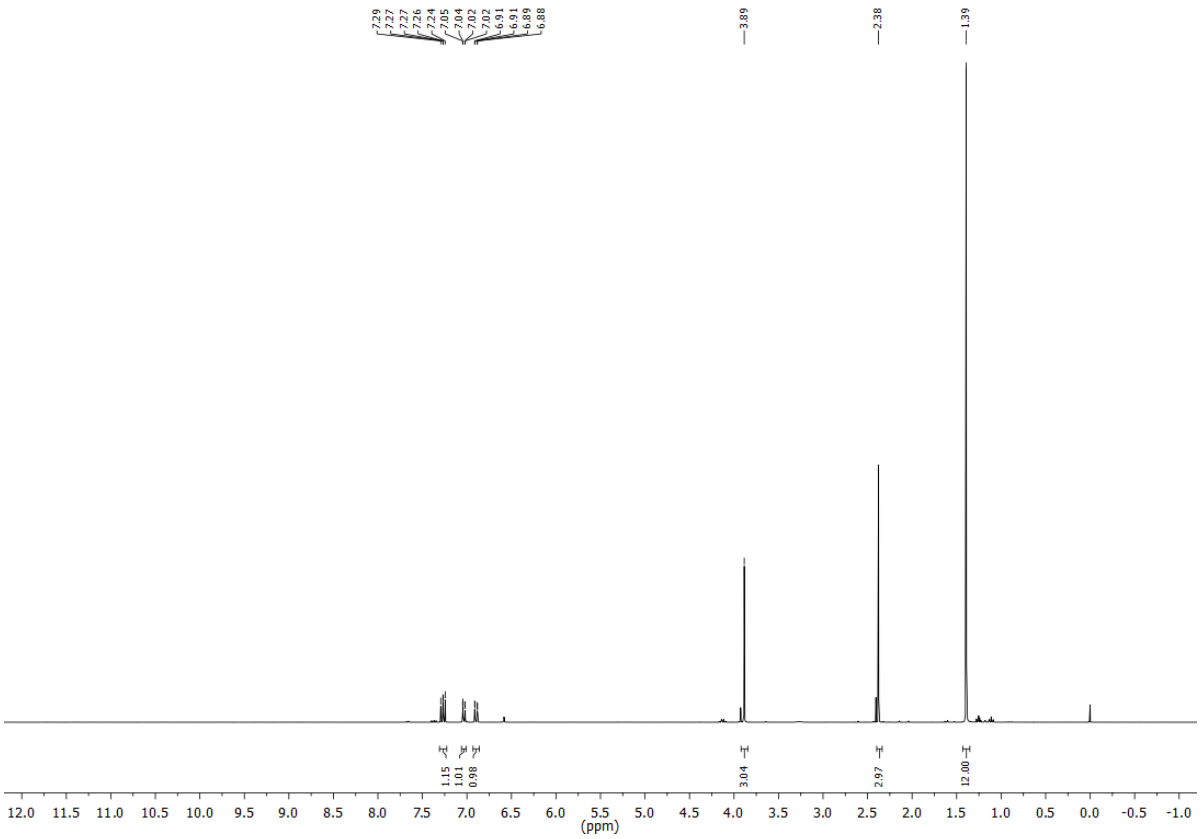
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 19.1, 24.8 (4 C), 55.8, 84.1 (2 C), 112.3, 113.7, 125.0, 127.6, 129.2, 159.5.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 30.7.

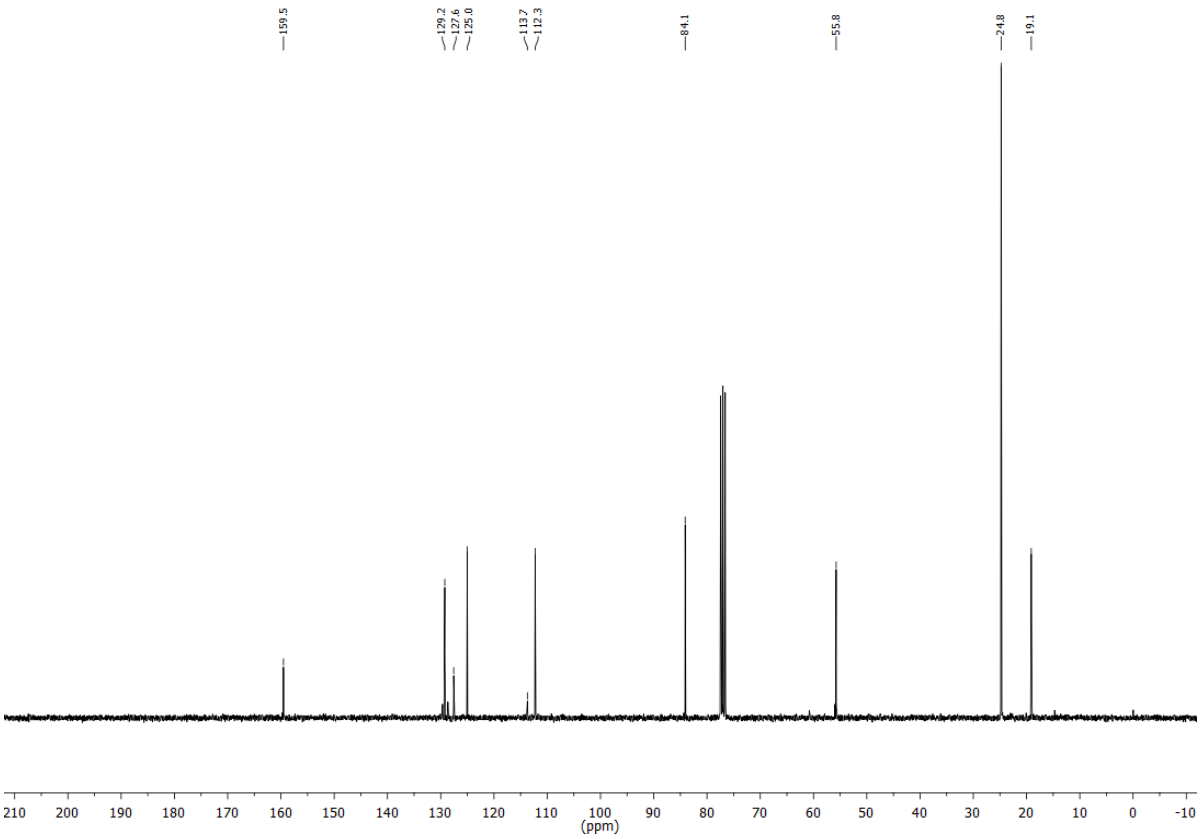
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2981, 2928, 2838, 1561, 1346, 1312, 1138, 1039.

$C_{14}H_{21}BO_3S$ calcd.: 280.1305, found: 280.1322 (GC-HRMS).

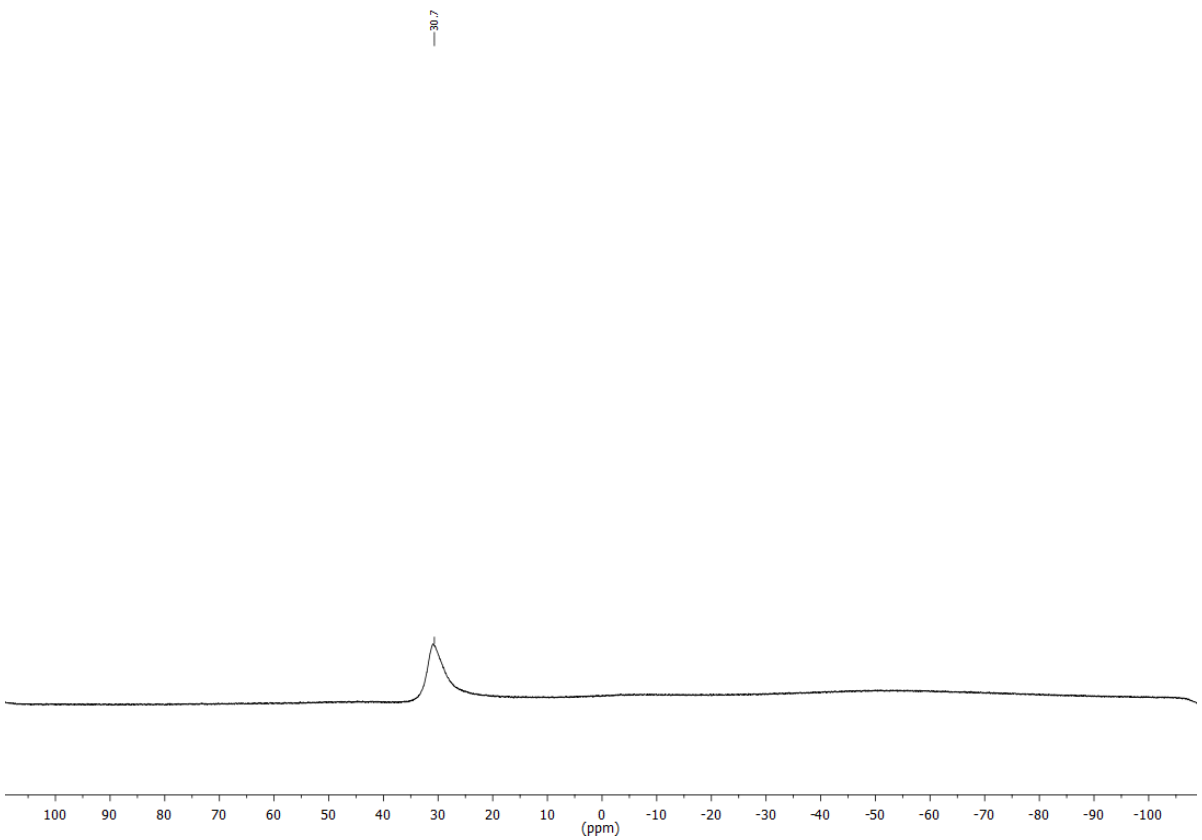
[52] S. O. Mihigo, W. Mammo, M. Bezabih, K. Andrae-Marobela and B. M. Abegaz, *Bioorg. Med. Chem.*, 2010, **18**, 2464.



^{1}H-NMR (300 MHz, $CDCl_3$).

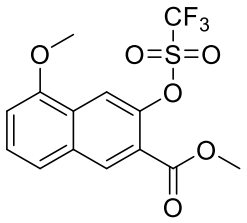


^{13}C-NMR (75 MHz, $CDCl_3$).



^{11}B-NMR (96 MHz, $CDCl_3$).

Methyl 5-methoxy-3-(((trifluoromethyl)sulfonyl)oxy)-2-naphthoate (21a)



Compound **21a** was synthesized via a reported procedure[53] from methyl 3-hydroxy-5-methoxy-2-naphthoate[54] and obtained as a colorless solid (3.9 g, 10.8 mmol, 95%).

m.p.: 105 °C.

R_f = 0.26 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.99 (s, 3H), 4.01 (s, 3H), 6.94 (p, *J*=4.7, 1H), 7.46 – 7.52 (m, 2H), 8.09 – 8.14 (m, 1H), 8.54 (d, *J*=0.4, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 52.6, 55.7, 107.1, 116.1 (d, *J*=1.5), 118.8 (q, *J*=320.8), 120.7, 122.3, 127.1, 128.3, 132.3, 134.1, 144.3, 155.0, 164.4.

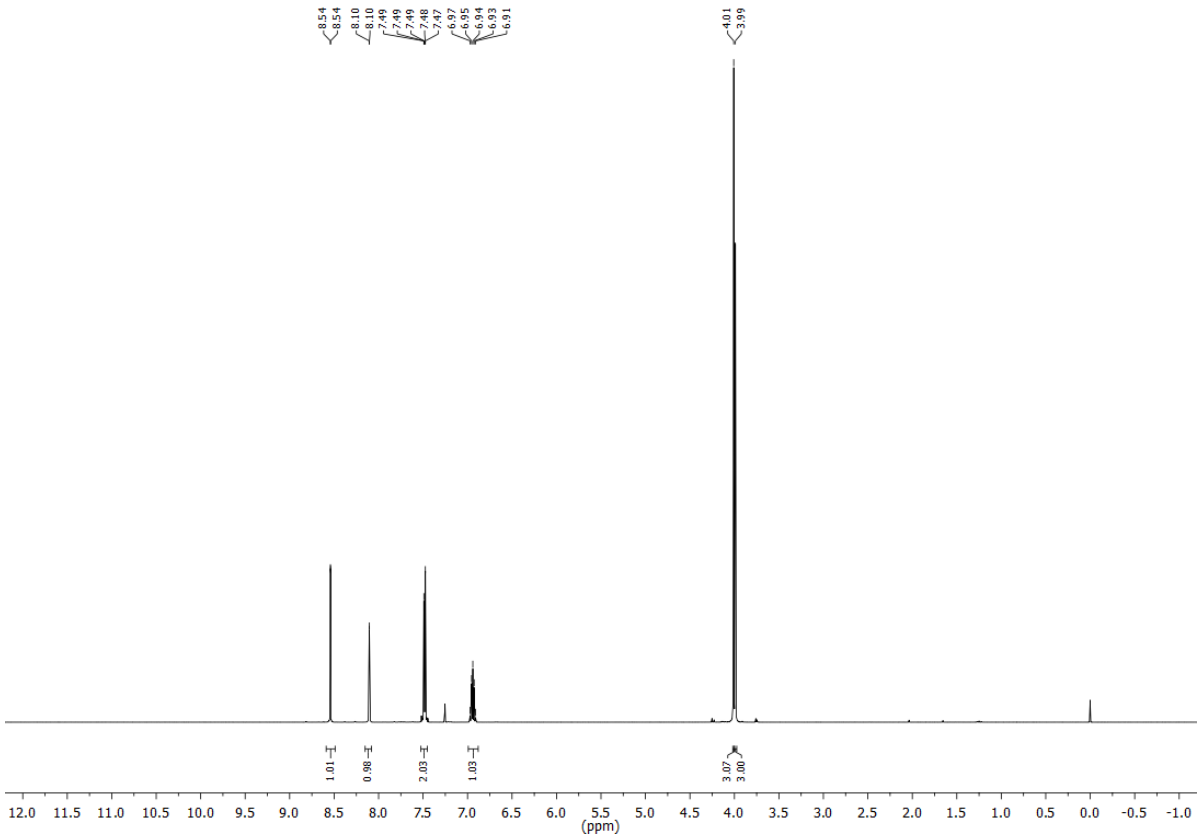
^{19}F NMR (283 MHz, $CDCl_3$): δ = -73.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3082, 3010, 2953, 2848, 1723, 1426, 1276, 1197, 1141, 1108, 1046.

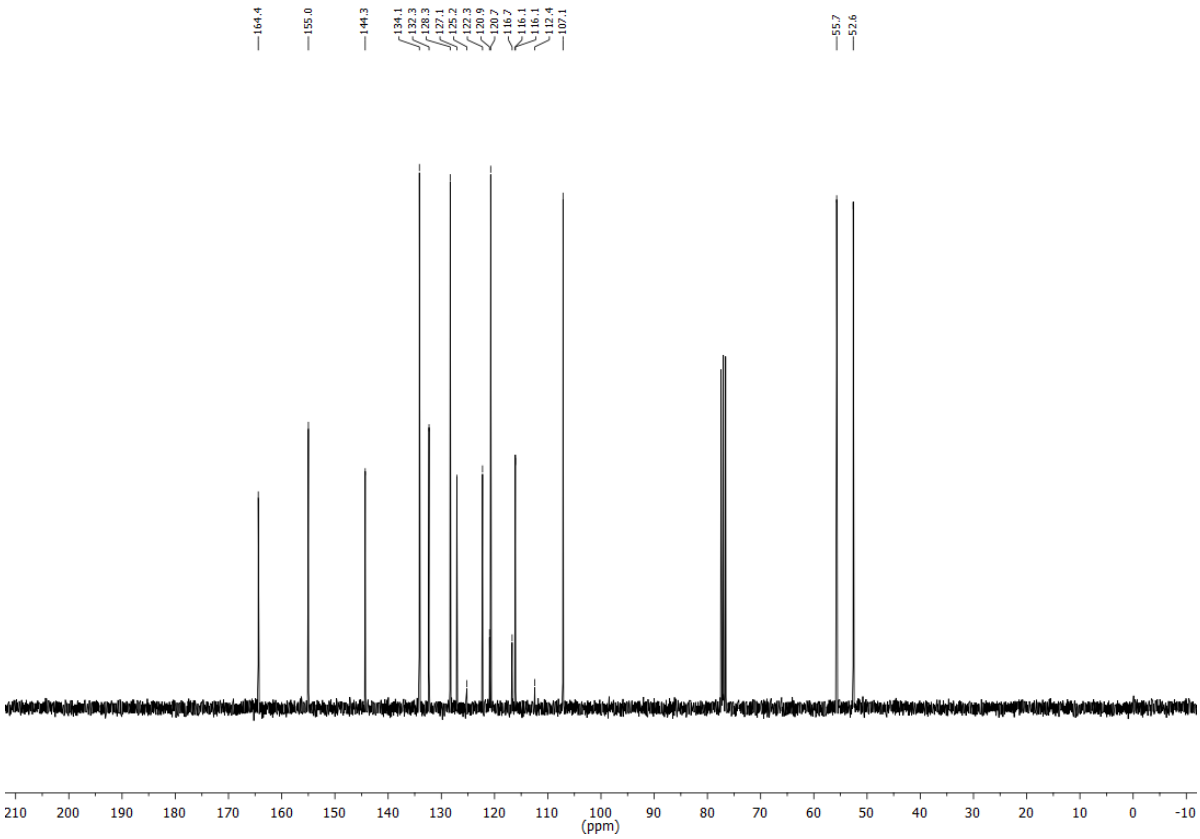
$C_{14}H_{11}F_3O_6S$ calcd.: 364.0228, found: 364.0232 (GC-HRMS).

[53] Y. Shi, Y. Ji, K. Xin and S. Gao, *Org. Lett.*, 2018, **20**, 732.

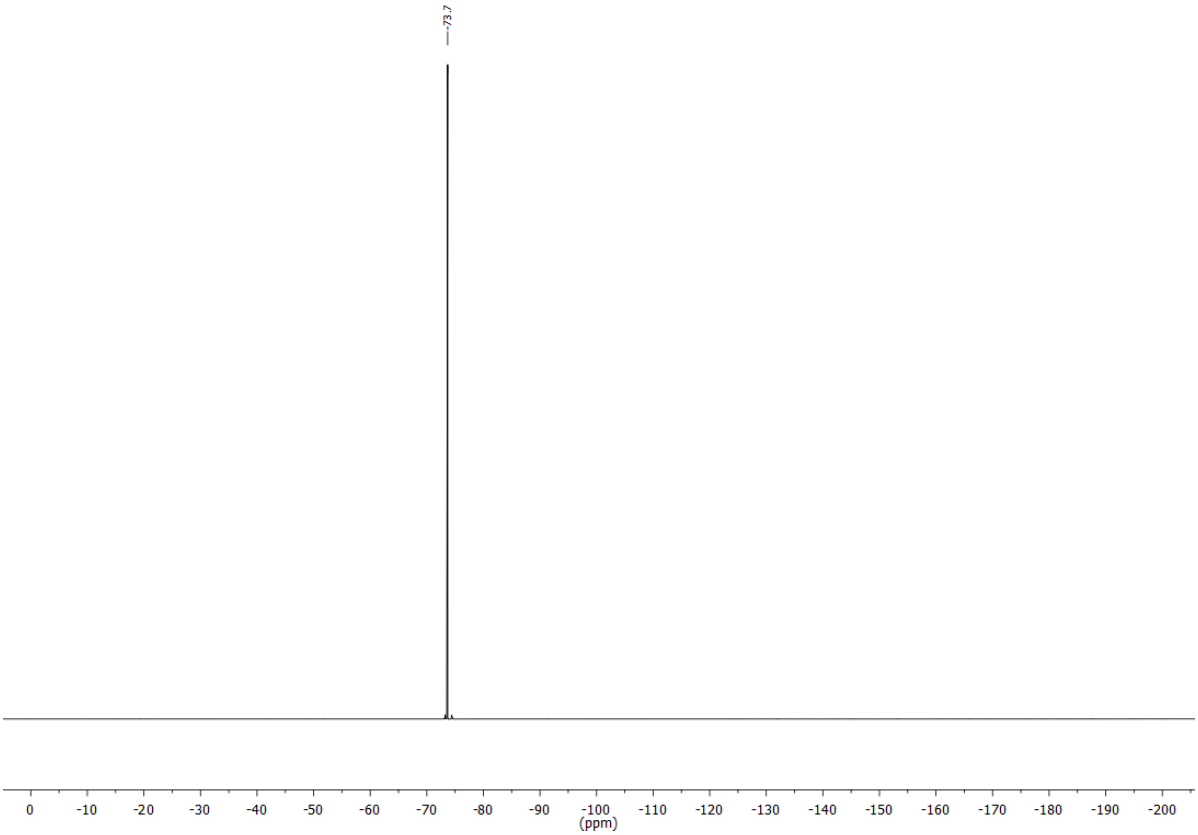
[54] E. E. Podlesny and M. C. Kozlowski, *J. Org. Chem.*, 2013, **78**, 466.



^{1}H-NMR (300 MHz, $CDCl_3$).

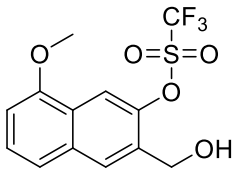


^{13}C-NMR (75 MHz, $CDCl_3$).



^{19}F-NMR (283 MHz, $CDCl_3$).

3-(Hydroxymethyl)-8-methoxynaphthalen-2-yl trifluoromethanesulfonate (21b)



The reduction of **21a** in accordance to a reported procedure[55] furnished compound **21b** as a white solid (7.9 g, 23.4 mmol, 87%)

m.p.: 84 °C.

R_f = 0.42 (*n*-pentane:EtOAc = 4:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.2 (s, 1H), 4.0 (s, 3H), 4.9 – 5.0 (m, 2H), 6.9 (dd, *J*=6.8, 1.8, 1H), 7.4 – 7.5 (m, 2H), 7.9 (s, 1H), 8.1 (s, 1H).

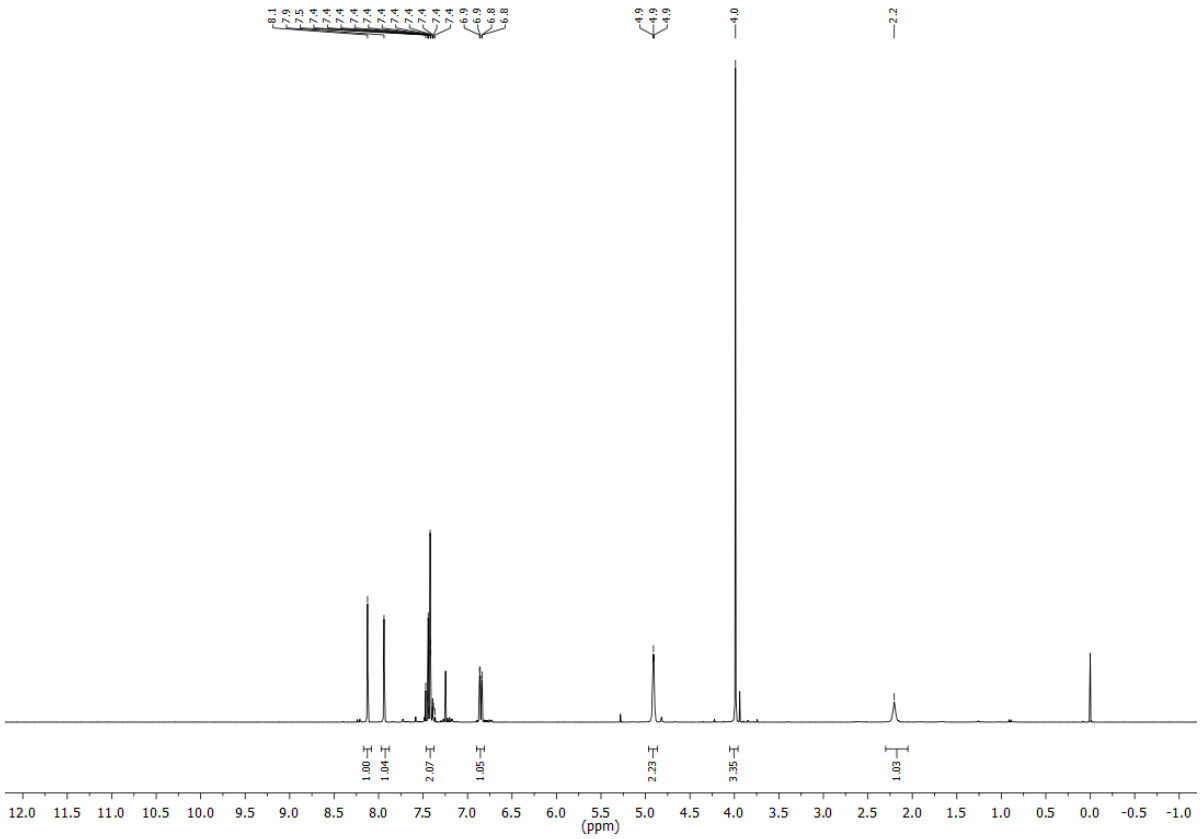
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 55.6, 60.2, 105.0, 114.5 (d), 119.8, 120.5 (q), 125.0, 127.6, 128.7, 131.9, 133.5, 144.8, 155.2.

^{19}F NMR (283 MHz, $CDCl_3$): δ = -73.9.

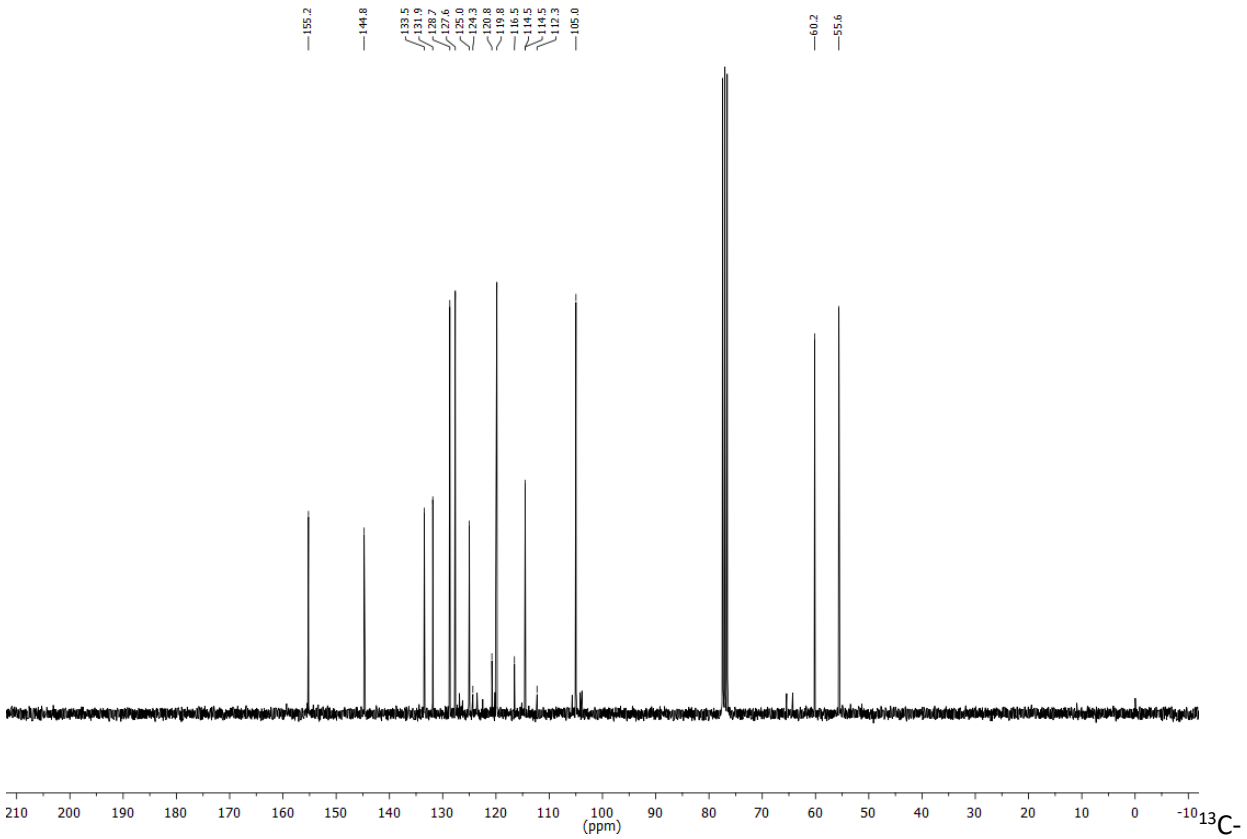
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3381, 3307, 3014, 2945, 2847, 1605, 1416, 1197, 1139, 1060.

$C_{13}H_{11}F_3O_5S$ calcd.: 336.0279, found: 336.0272 (GC-HRMS).

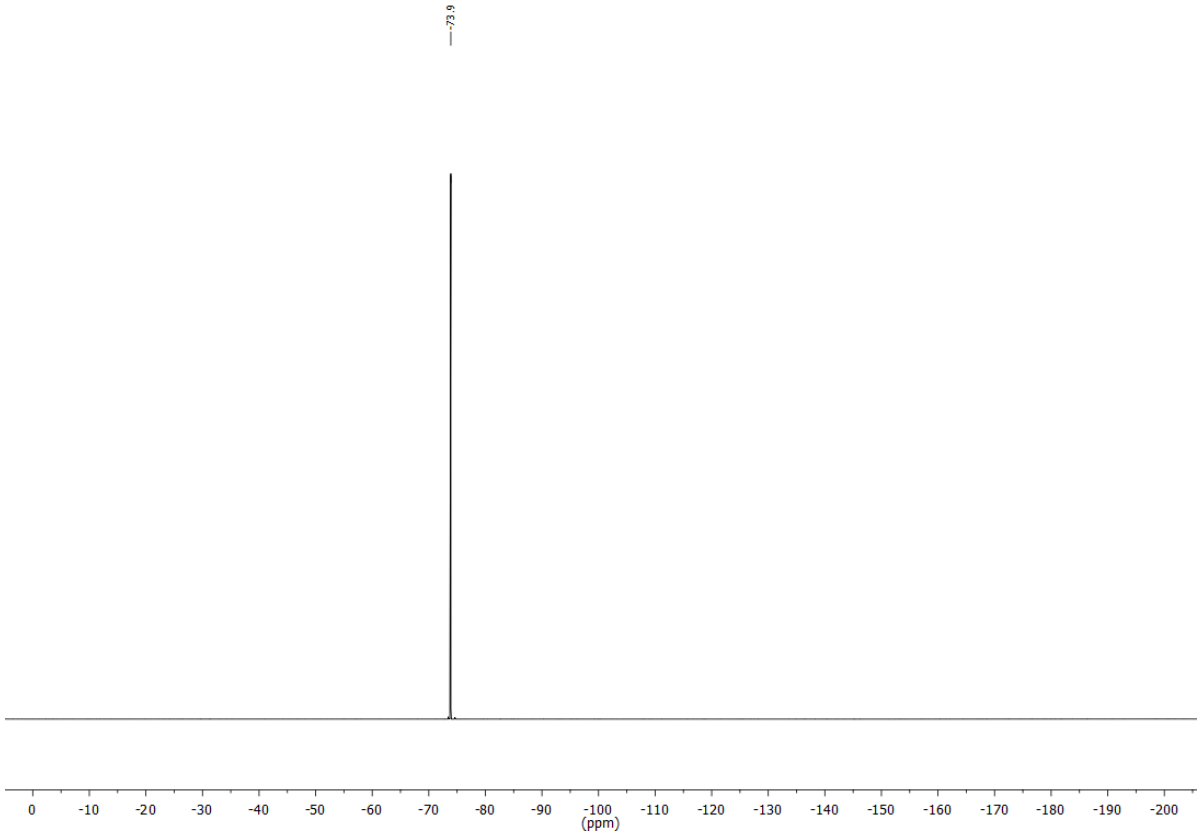
[55] A. M. Echavarren and J. K. Stille, *J. Org. Chem.*, 1988, **110**, 1557.



^{1}H-NMR (300 MHz, $CDCl_3$).

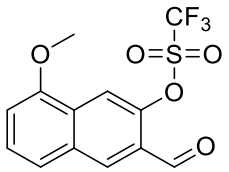


^{13}C-NMR (75 MHz, $CDCl_3$).



^{19}F-NMR (283 MHz, $CDCl_3$).

3-Formyl-8-methoxynaphthalen-2-yl trifluoromethanesulfonate (21c)



Compound **21c** was obtained as a pale yellow solid (6.2 g, 18.5 mmol, 79%) by oxidation of **21b** with DMP following a reported procedure.[56]

m.p.: 76 °C.

R_f = 0.20 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.0 (s, 3H), 7.0 (dd, *J*=6.7, 2.0, 1H), 7.5 – 7.7 (m, 2H), 8.2 (s, 1H), 8.4 (s, 1H), 10.3 (s, 1H).

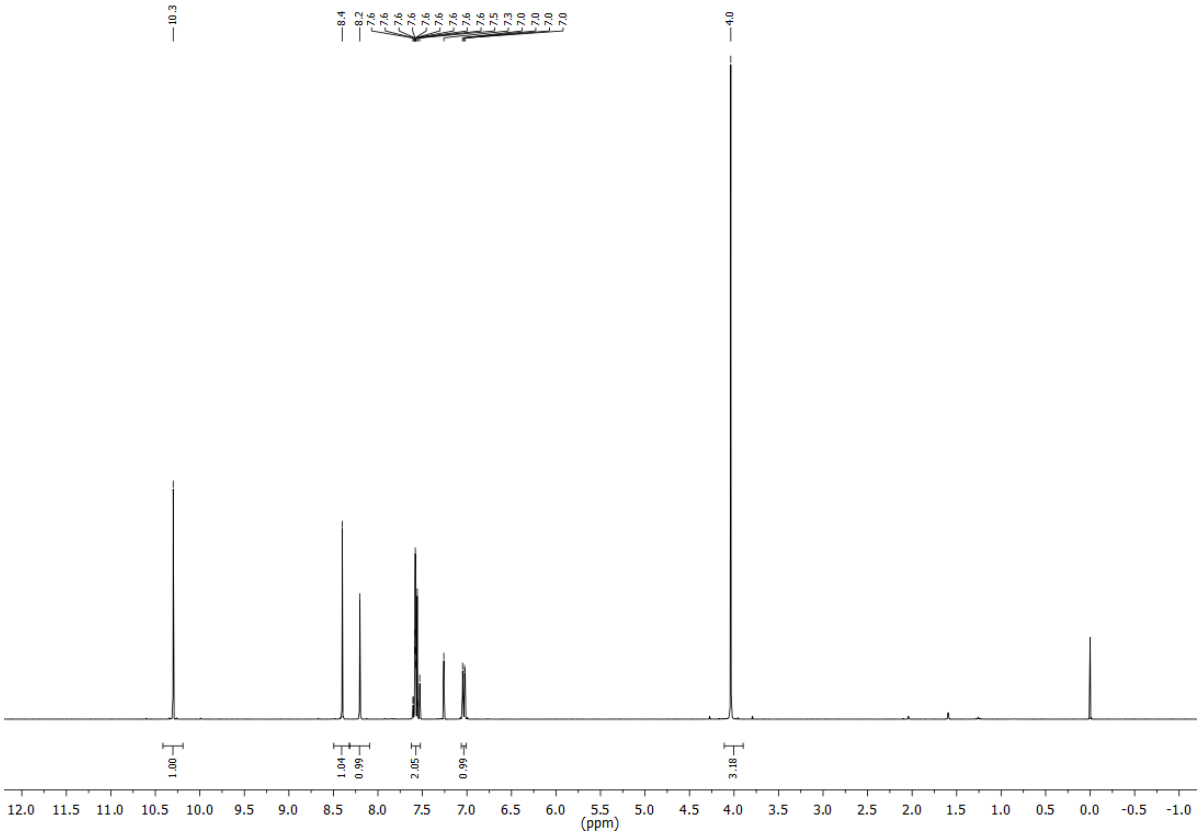
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 55.9, 108.0, 116.1 (d), 118.8 (q, *J*=320.8), 121.4, 126.9, 127.8, 128.7, 132.5, 134.4, 144.7, 155.2, 187.3.

^{19}F NMR (283 MHz, $CDCl_3$): δ = -73.3.

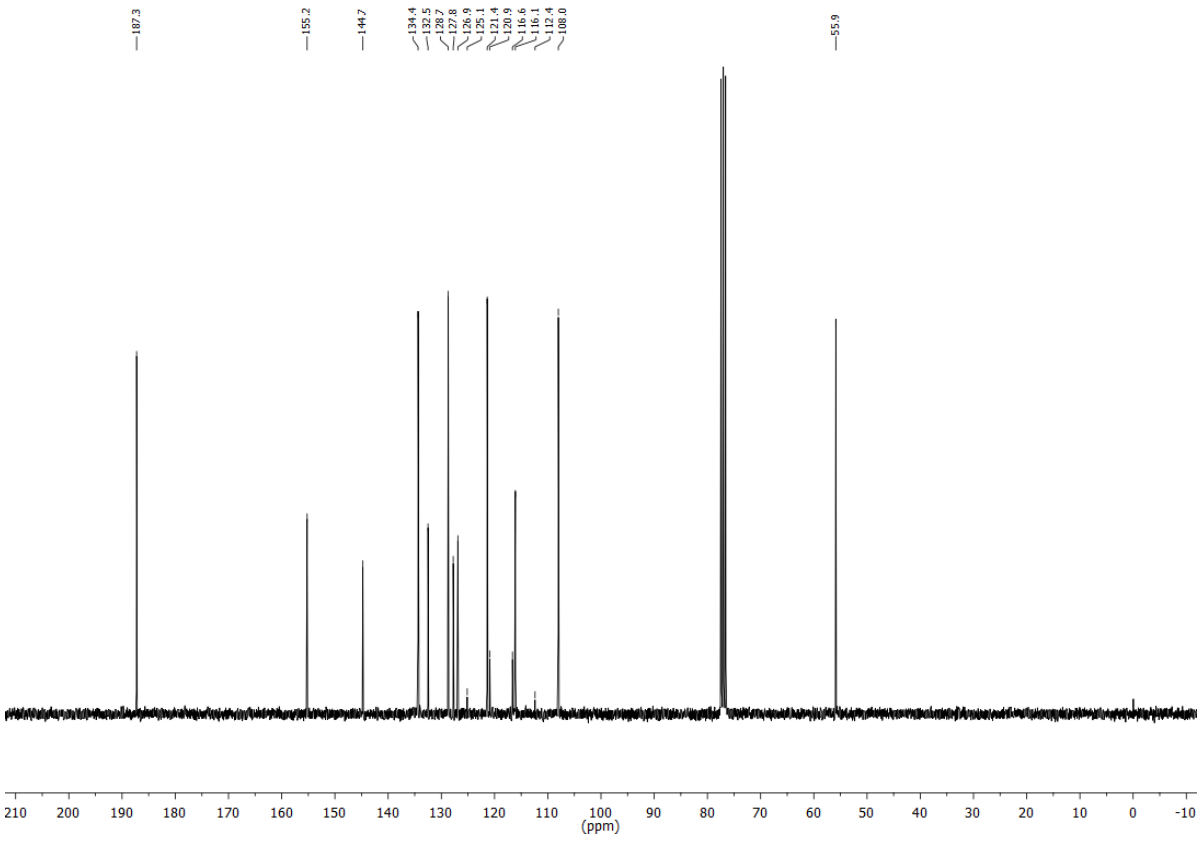
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3071, 3023, 2978, 2948, 2848, 1696, 1418, 1199, 1129, 1054.

$C_{13}H_9F_3O_5S$ calcd.: 334.0123, found: 334.0145 (GC-HRMS).

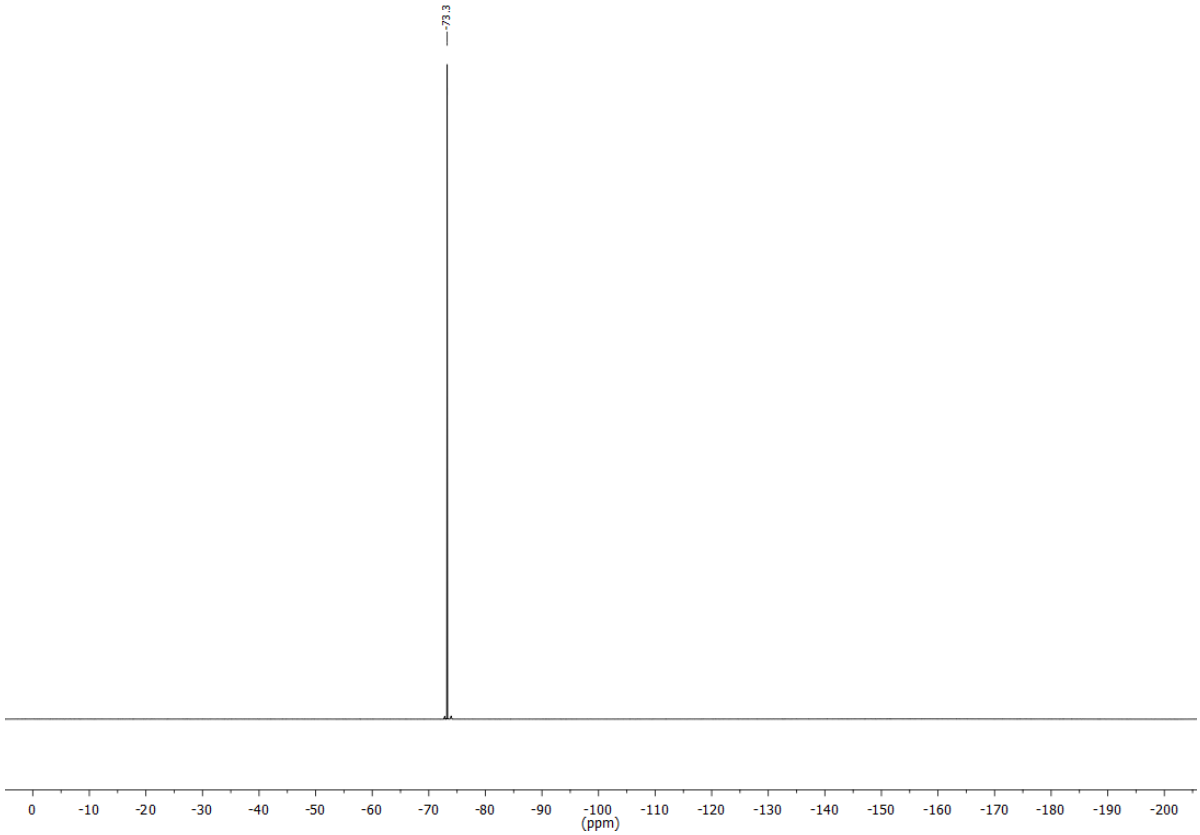
[56] C. C. Nawrat, L. I. Palmer, A. J. Blake and C. J. Moody, *J. Org. Chem.*, 2013, **78**, 5587.



^{1}H-NMR (300 MHz, $CDCl_3$).

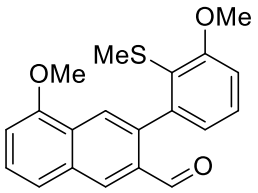


^{13}C-NMR (75 MHz, $CDCl_3$).



^{19}F-NMR (283 MHz, $CDCl_3$).

5-Methoxy-3-(3-methoxy-2-(methylthio)phenyl)-2-naphthaldehyde (22a)



Following a reported procedure[57], compound **22a** was afforded by Suzuki cross-coupling. Under an argon atmosphere, triflate **21c** (486 mg, 1.4 mmol, 1.0 equiv.) was added to a suspension of borolane **20b** (432 mg, 1.54 mmol, 1.1 equiv.), $Pd_2(dba)_3$ (64.1 mg, 5 mol%), SPhos (115.0 mg, 20 mol%) and K_2CO_3 (387 mg, 2.8 mmol, 2.0 equiv.) in degassed PhMe (7 ml) and degassed H_2O (7 ml) was added to the sealable vial. The reaction mixture was stirred at 140 °C for 18 h. After cooling, the phases were separated and the aq. phase was extracted with Et_2O (2 x 50 ml). The combined organic phases were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. After flash column chromatography (*n*-pentane:EtOAc = 20:1→10:1→5:1) the desired product was yielded as a yellow solid (420 mg, 1.24 mmol, 89%).

m.p.: 104 °C.

R_f = 0.19 (*n*-pentane:EtOAc = 10:1).

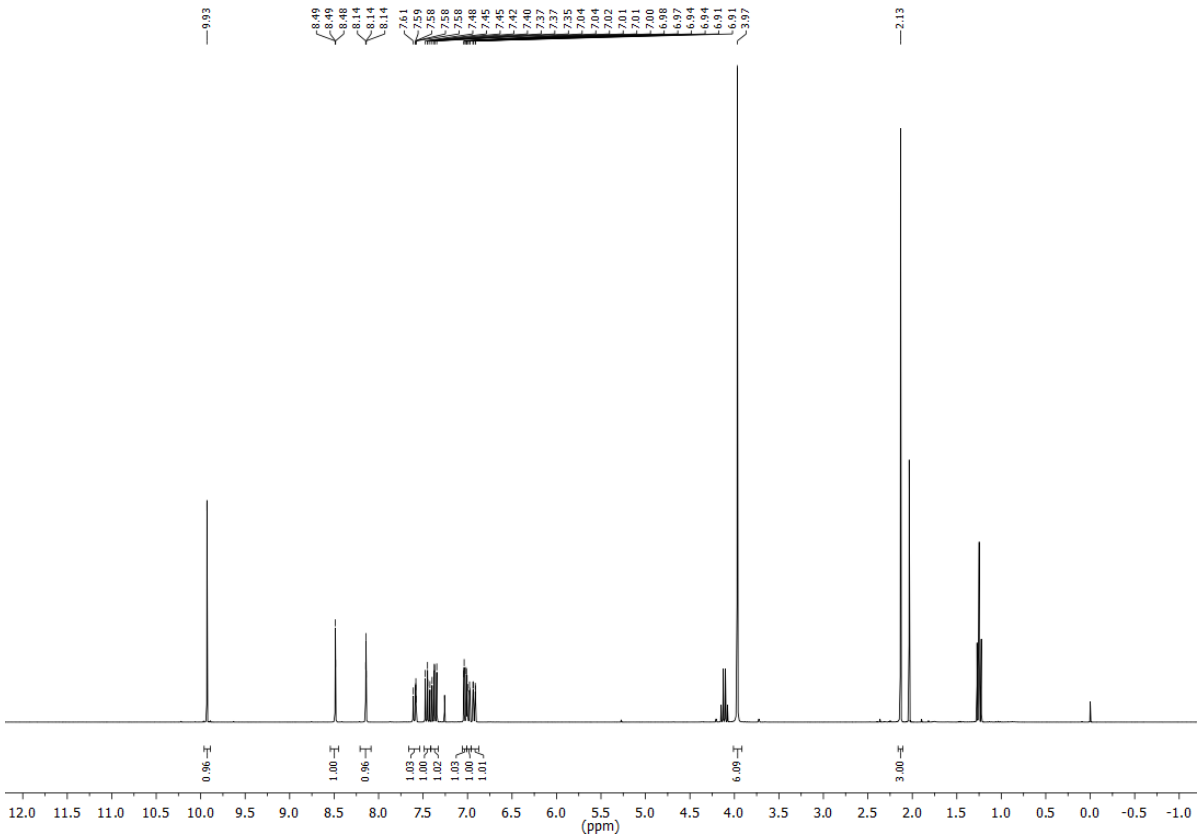
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3H), 3.97 (s, 6H), 6.92 (dd, *J*=7.8, 0.9, 1H), 6.99 (dd, *J*=8.3, 1.3, 1H), 7.03 (dd, *J*=7.6, 1.2, 1H), 7.37 (dd, *J*=8.3, 7.6, 1H), 7.45 (dd, *J*=8.3, 7.7, 1H), 7.57 – 7.62 (m, 1H), 8.14 (t, *J*=0.7, 1H), 8.49 (t, *J*=0.6, 1H), 9.93 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.8, 55.5, 56.0, 106.5, 110.7, 121.7, 123.4, 124.1, 124.2, 127.0, 127.5, 128.4, 128.8, 132.2, 132.9, 138.9, 143.7, 155.2, 159.7, 191.9.

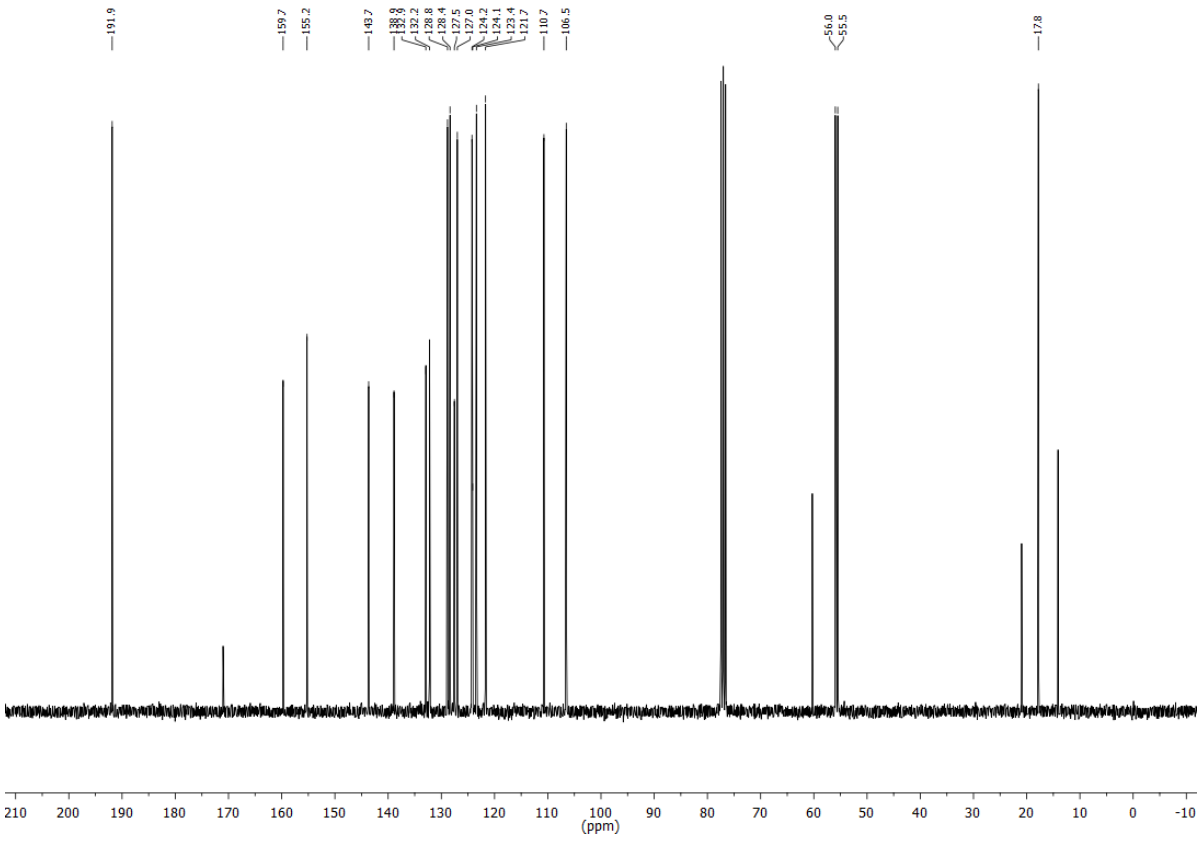
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3057, 3010, 2930, 2836, 1689, 1566, 1455, 1256, 1067, 1007.

$C_{20}H_{18}O_3S$ calcd.: 338.0977, found: 338.0976 (GC-HRMS).

[57] C. Kahrs, M. S. Wickleder and J. Christoffers, *Eur. J. Org. Chem.*, 2018, **2018**, 5754.

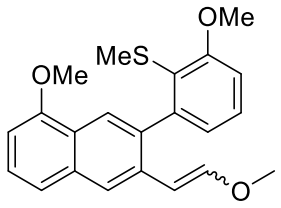


^{1}H-NMR (300 MHz, $CDCl_3$).



^{13}C-NMR (75 MHz, $CDCl_3$).

(2-Methoxy-6-(8-methoxy-3-(2-methoxyvinyl)naphthalen-2-yl)phenyl)(methyl)sulfane (22b)



Compound **22a** (677 mg, 2.0 mmol) was transformed to an *E*/Z-mixture of **22b** following a reported procedure.[58] After flash column chromatography (*n*-pentane:DCM = 1:1) a colorless foam (680 mg, 1.86 mmol, 93%) was obtained and used as isomeric mixture in the next step.

m.p.: 81 °C.

$\mathbf{R_f}$ = 0.26 and $\mathbf{R_f}$ = 0.22 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (500 MHz, $CDCl_3$, Isomer 1): δ = 2.16 (s, 3H), 3.79 (s, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 4.95 (d, *J*=7.2, 1H), 6.09 (d, *J*=7.1, 1H), 6.74 (d, *J*=7.3, 1H), 6.89 – 6.95 (m, 2H), 7.29 – 7.35 (m, 2H), 7.44 (d, *J*=8.3, 1H), 7.98 (s, 1H), 8.55 (s, 1H).

^{1}H-NMR (500 MHz, $CDCl_3$, Isomer 2): δ = 2.18 (s, 3H), 3.51 (s, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 5.59 (d, *J*=12.8, 1H), 6.73 (d, *J*=7.5, 1H), 6.89 – 6.95 (m, 2H), 6.97 (d, *J*=12.8, 1H), 7.29 – 7.36 (m, 2H), 7.37 – 7.40 (m, 1H), 7.78 (s, 1H), 7.99 (s,1H).

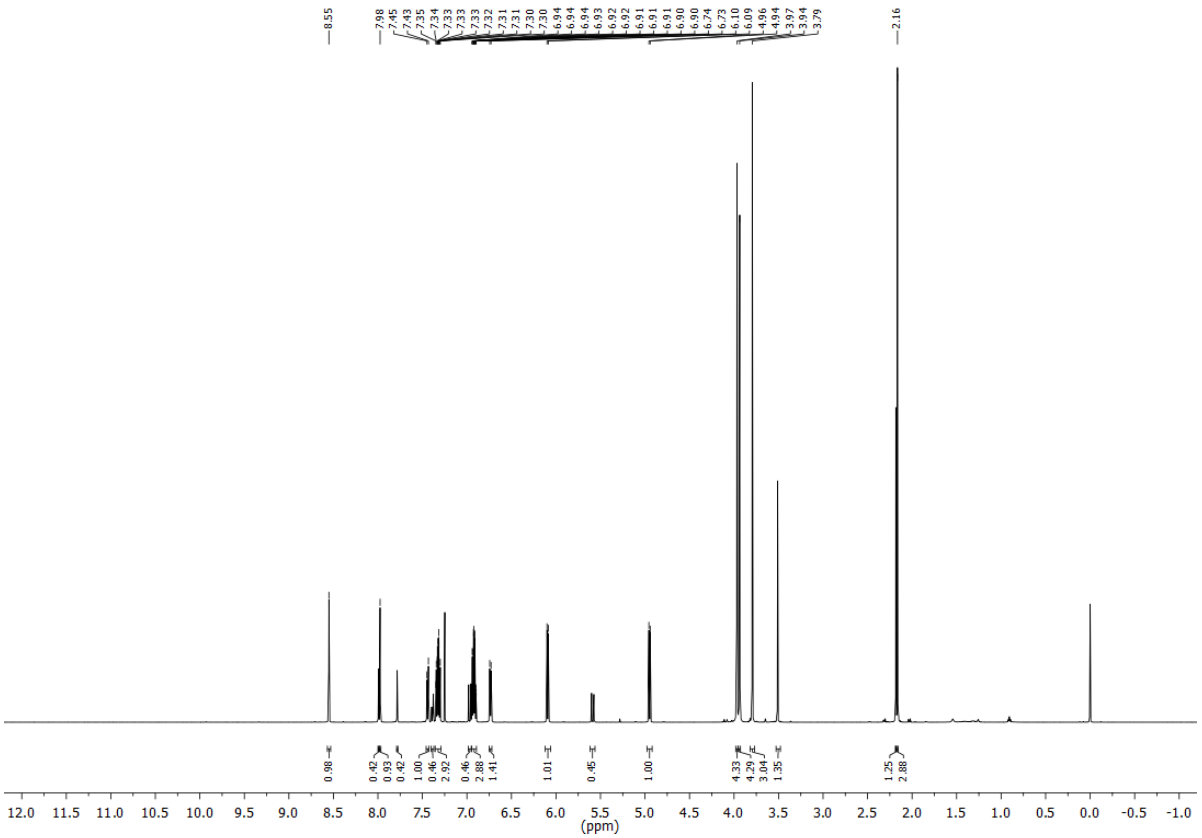
^{13}C-NMR (126 MHz, $CDCl_3$, Isomer 1): δ = 18.2, 55.4, 55.9, 60.8, 103.3, 103.4, 109.8, 120.4, 121.9, 123.2, 123.3, 123.3, 125.6, 126.7, 128.5, 132.6, 134.2, 138.3, 147.3, 148.5, 155.3, 159.8.

^{13}C-NMR (126 MHz, $CDCl_3$, Isomer 1): δ = 18.1, 55.4, 56.0, 56.7, 103.3, 104.2, 110.0, 119.8, 121.6, 122.6, 123.6, 124.0, 124.3, 126.0, 128.5, 133.8, 134.1, 138.2, 146.9, 149.5, 155.5, 159.9.

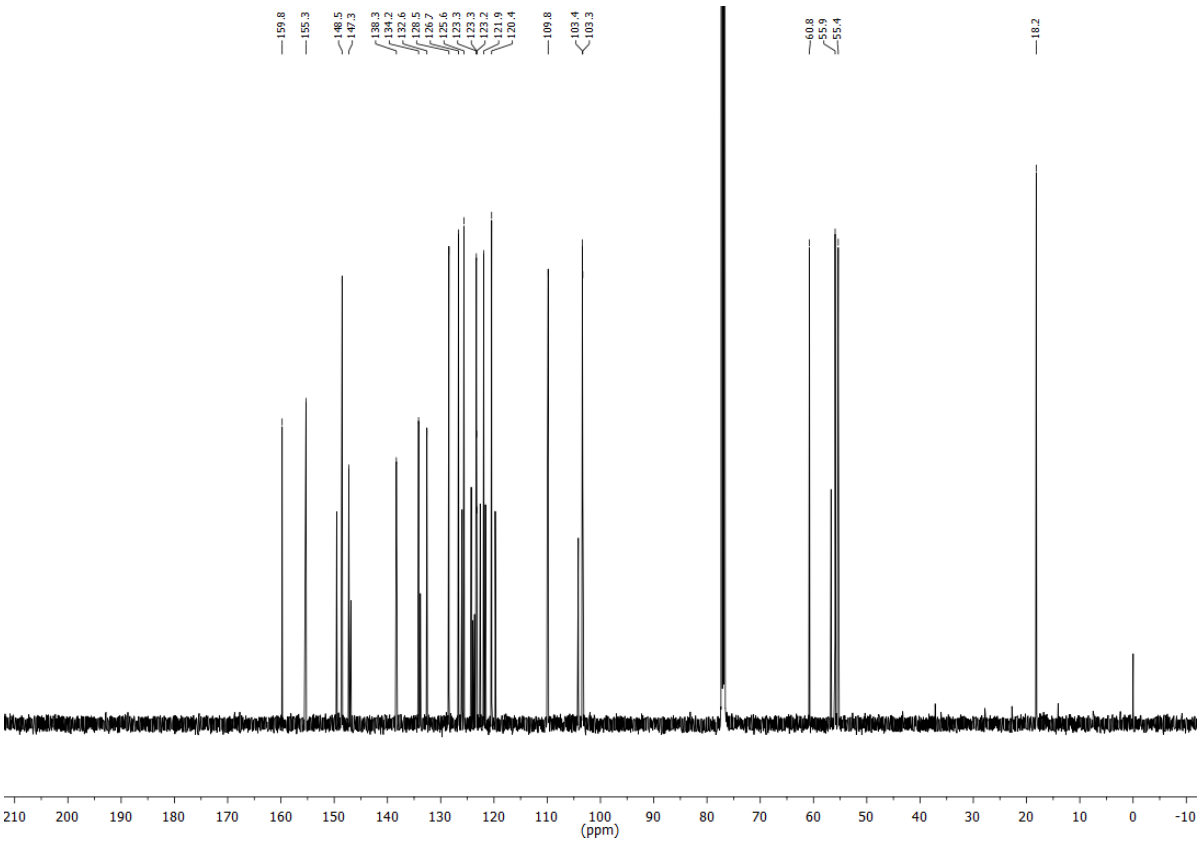
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3051, 3002, 2929, 2832, 1740, 1643, 1565, 1456, 1426, 1091.

$C_{22}H_{22}O_3S$ calcd.: 366.1290, found: 366.1283 (GC-HRMS).

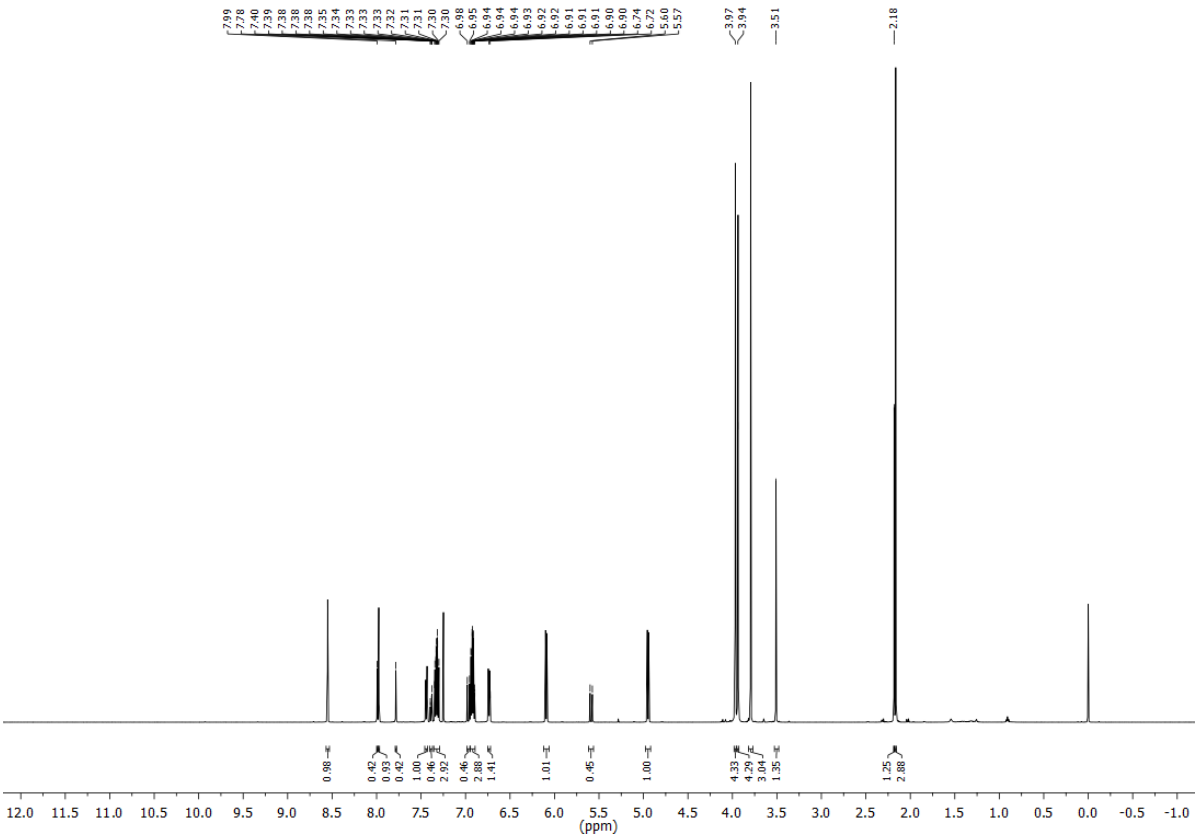
[58] N. Khunnawutmanotham, P. Sahakitpichan, N. Chimnoi and S. Techasakul, *Eur. J. Org. Chem.*, 2017, **2017**, 6434.



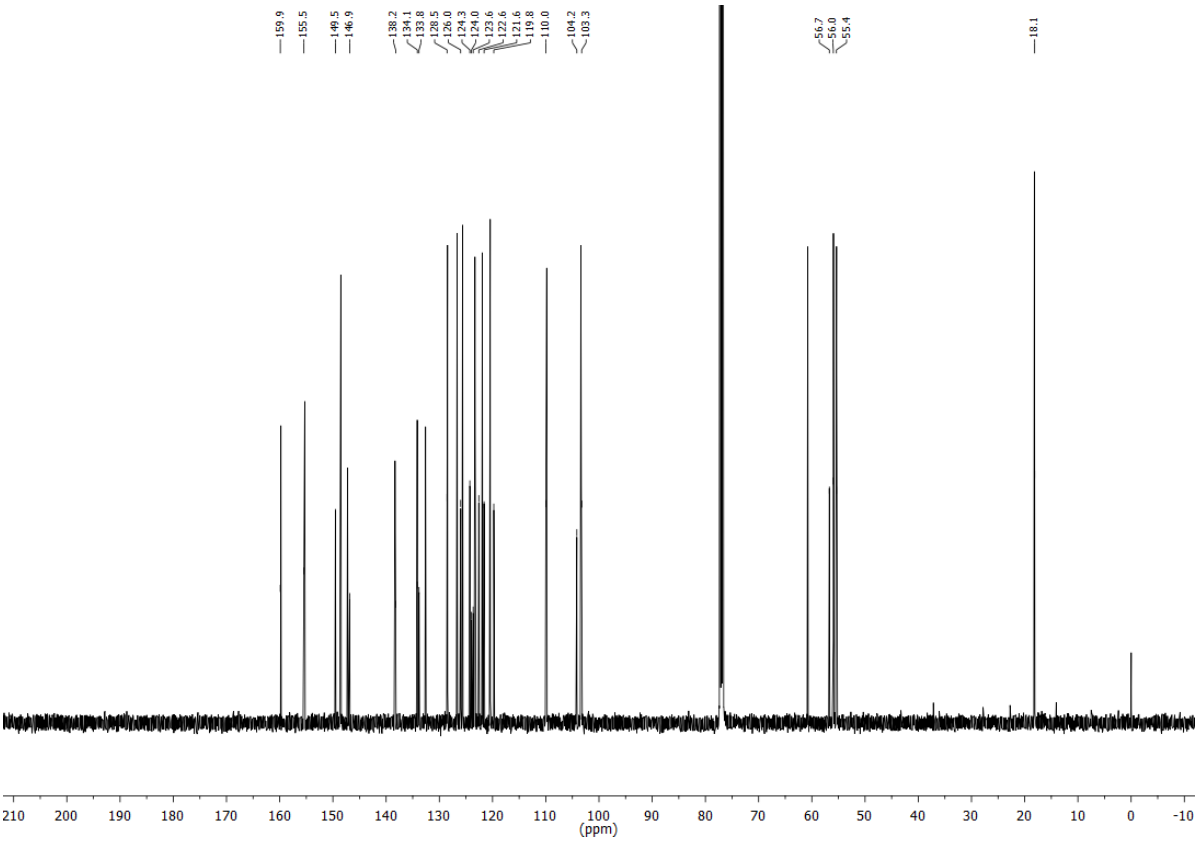
^{1}H-NMR (500 MHz, $CDCl_3$, Isomer 1).



^{13}C-NMR (126 MHz, $CDCl_3$, Isomer 1).

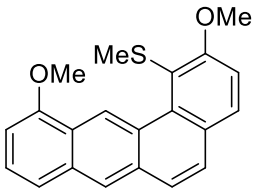


^{1}H-NMR (500 MHz, $CDCl_3$, Isomer 2).



^{13}C-NMR (126 MHz, $CDCl_3$, Isomer 2).

(2,11-Dimethoxytetraphen-1-yl)(methyl)sulfane (22c)



Following a reported procedure[59], compound **22c** was synthesized from the *E/Z*-mixture of **22b**. Prior to use DCE was degassed and $Bi(OTf)_3$ was dried under vacuum. To a suspension of $Bi(OTf)_3$ (61 mg, 5 mol%) in DCE (3 ml) was added a solution of substrate **22b** (680 mg, 1.86 mmol) in DCE (10 ml). The flask was rinsed with additional 2 ml of DCE. The reaction progress was followed by TLC. After 20 min the reaction was stopped and the mixture was added directly to a silica gel column (*n*-pentane:DCM = 2:1) because a previous experiment showed decomposition of the product when the solvent was evaporated. Finally, the desired product was obtained as a yellow solid (438 mg, 1.31 mmol, 70%).

m.p.: 165 °C.

$\mathbf{R_f}$ = 0.26 (*n*-pentane:EtOAc = 10:1).

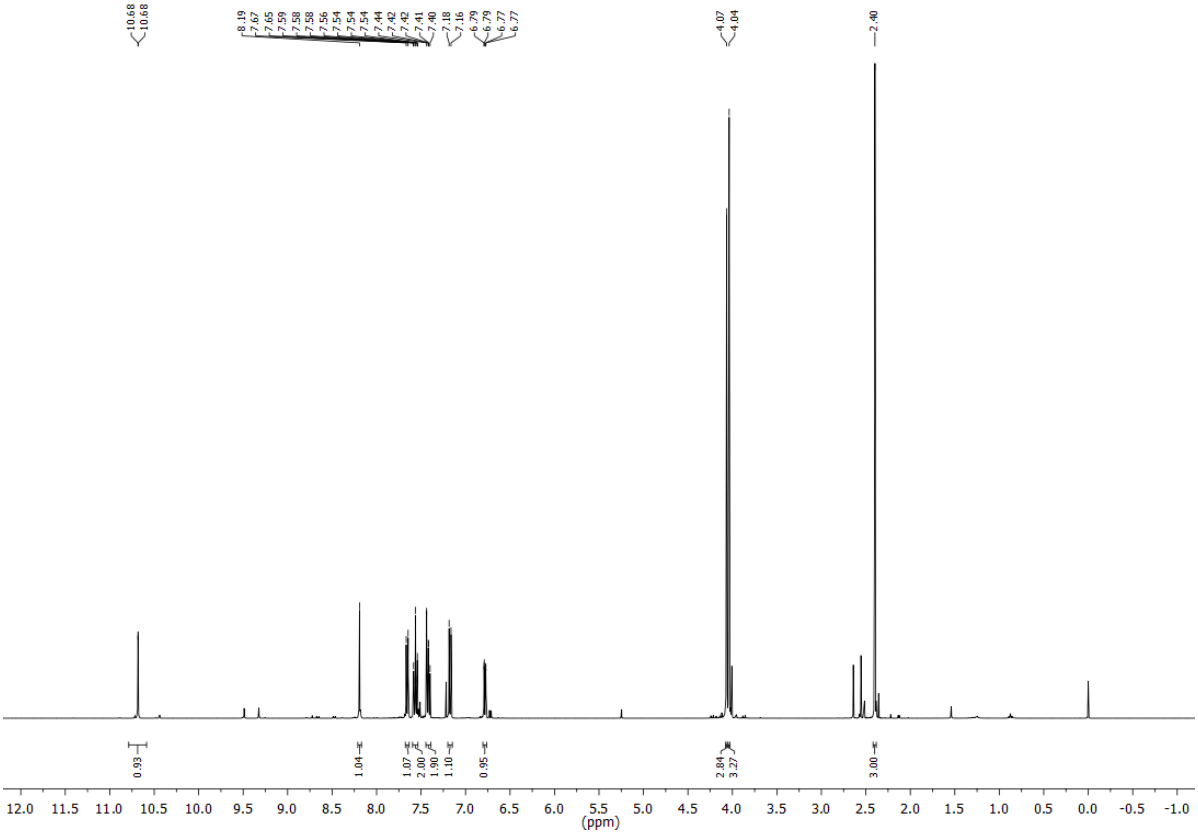
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 4.04 (s, 3H), 4.07 (s, 3H), 6.78 (dd, *J*=7.5, 0.9, 1H), 7.17 (d, *J*=8.6, 1H), 7.39 – 7.46 (m, 2H), 7.54 – 7.61 (m, 2H), 7.66 (d, *J*=8.7, 1H), 8.19 (s, 1H), 10.68 (d, *J*=1.0, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 19.5, 55.8, 56.6, 102.5, 111.1, 119.4, 122.2, 123.4, 123.8, 125.0, 125.6, 126.4, 127.1, 127.5, 127.9, 129.2, 132.4, 132.8, 133.8, 156.3, 159.4.

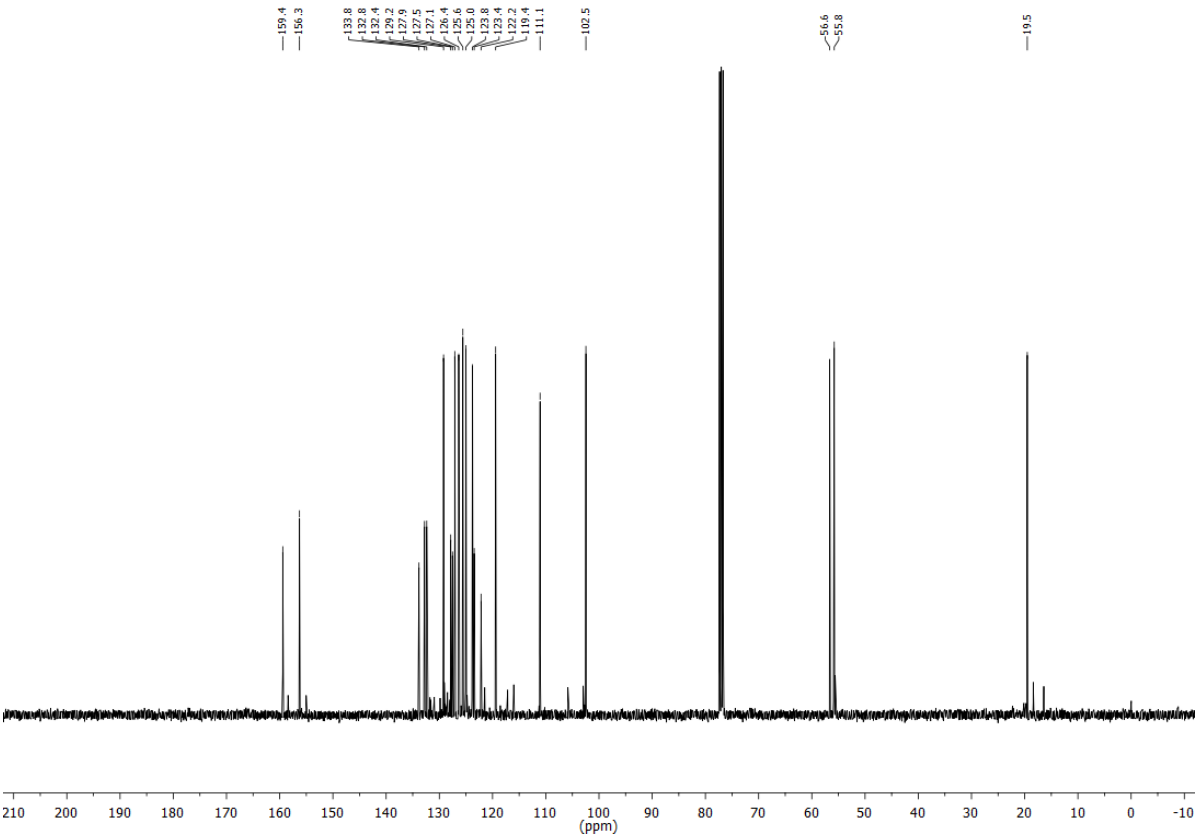
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3036, 2997, 2967, 2918, 2832, 1625, 1589, 1558, 1453, 1266, 1236, 1069.

$C_{21}H_{18}O_2S$ calcd.: 334.1028, found: 334.1020 (GC-HRMS).

[59] M. Murai, N. Hosokawa, D. Roy and K. Takai, *Org. Lett.*, 2014, **16**, 4134.

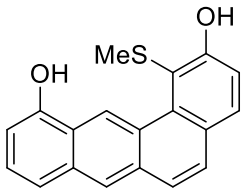


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

1-(Methylthio)tetraphene-2,11-diol (22d)



Compound **22c** (488 mg, 1.46 mmol, 1.0 equiv.) was dissolved in DCM (10 ml) and cooled to -83 °C. BBr_3 (3.6 ml of 1M solution in DCM, 3.6 mmol, 2.5 equiv.) was added dropwise to the solution. The reaction mixture was warmed to RT and quenched after 2 h carefully with cooled water. The phases were separated and the aq. phase was extracted with DCM (2 x 50 ml). The combined organic phases were washed with brine, dried over Na_2SO_4 and the solvent was evaporated. Purification by flash column chromatography (*n*-pentane:EtOAc = 10:1→4:1) afforded the product **22d** as a brown, sticky mass (263 mg, 0.54 mmol, 37%).

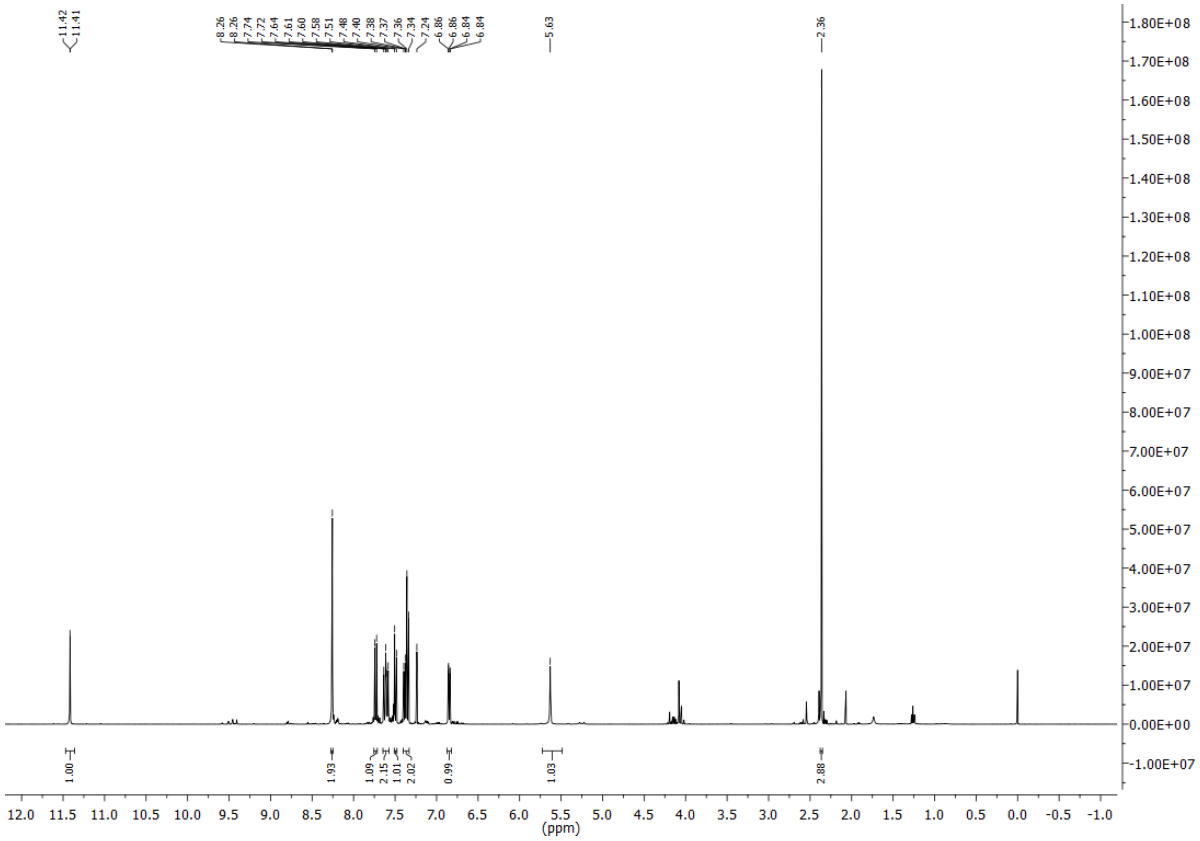
R_f = 0.16 (*n*-pentane:EtOAc = 10:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 5.63 (s, 1H), 6.85 (dd, *J*=7.3, 0.9, 1H), 7.31 – 7.43 (m, 2H), 7.49 (d, *J*=8.9, 1H), 7.61 (dd, *J*=12.5, 8.6, 2H), 7.73 (d, *J*=8.5, 1H), 8.26 (d, *J*=1.5, 2H), 11.42 (d, *J*=1.0, 1H).

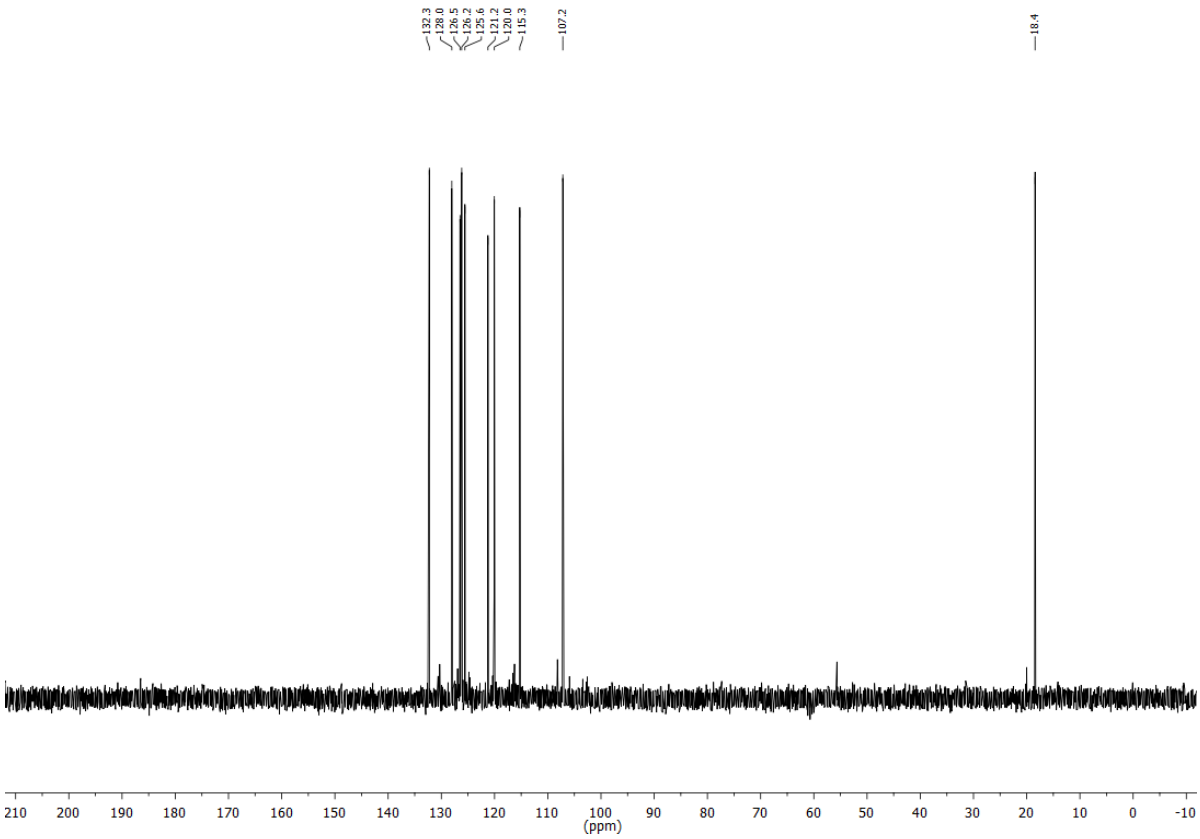
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 18.3, 107.1, 115.2, 115.8, 119.9, 121.1, 123.1, 125.5, 126.1, 126.4, 127.9, 127.9, 128.0, 132.2 (2 C), 132.6, 132.8, 152.3, 157.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3399, 3285, 3042, 2918, 2850, 1701, 1593, 1491, 1406, 1233, 1188, 1142.

$C_{19}H_{14}O_2S$ calcd.: 329.0607 [$M+Na^+$], found: 329.0607 [$M+Na^+$] (ESI-HRMS).

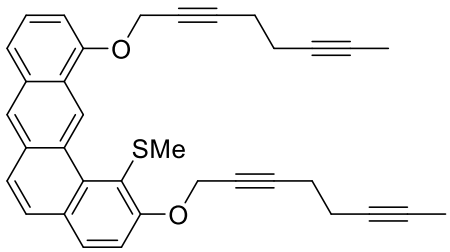


^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (101 MHz, $CDCl_3$).

(2,11-Bis(octa-2,6-diyn-1-yloxy)tetraphen-1-yl)(methyl)sulfane (22e)



Compound **22e** was synthesized according GP1.

A solution of **22d** (138.0 mg, 0.45 mmol, 1.00 equiv.), PPh_3 (472 mg, 1.80 mmol, 4.00 equiv.) and octa-2,6-diyn-1-ol[60] (220 mg, 1.80 mmol, 4.00 equiv.) in dry toluene (14 ml) was cooled to 0 °C. DIAD (364 mg, 354 µl, 1.80 mmol, 4.00 equiv.) in dry toluene (11 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (*n*-pentane:EtOAc = 20:1→10:1) gave the desired product (134 mg, 0.26 mmol, 58%) as an orange-brown oil.

R_f = 0.40 (*n*-pentane:EtOAc = 10:1).

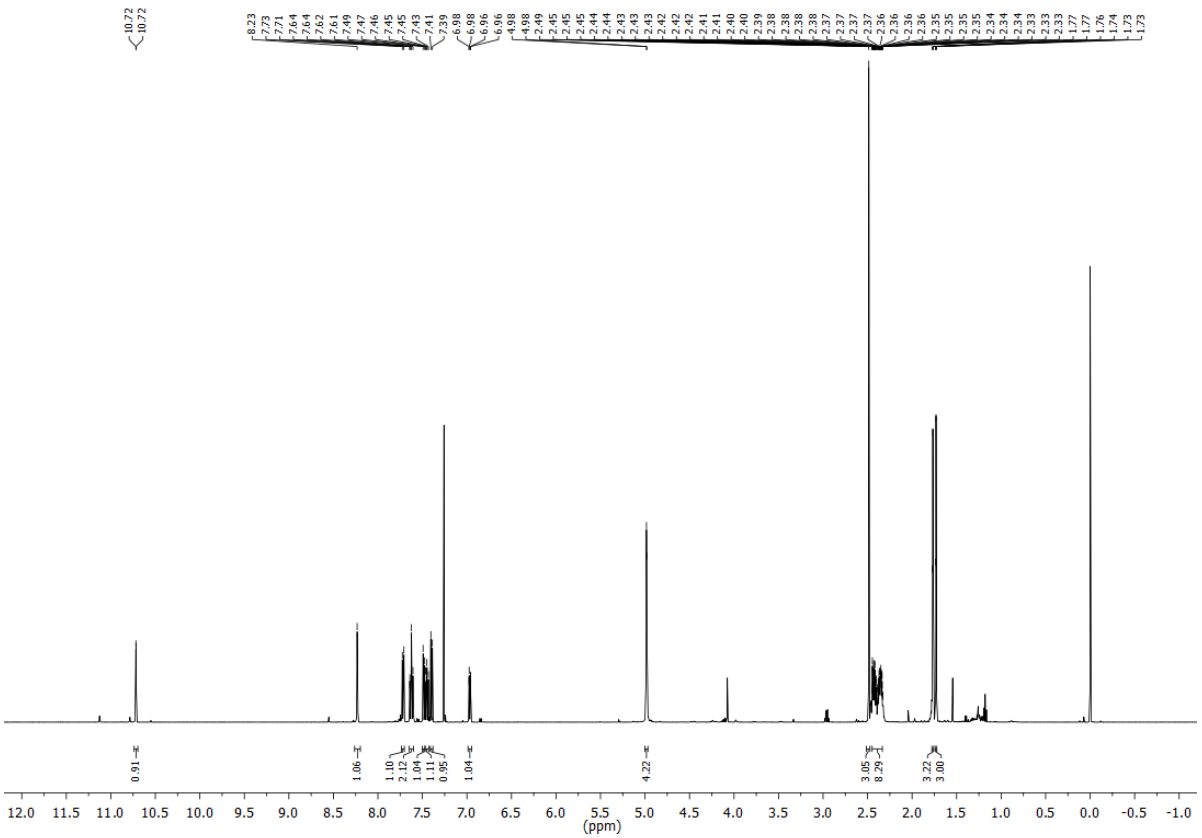
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.73 (t, *J*=2.4, 3H), 1.77 (t, *J*=2.5, 3H), 2.31 – 2.46 (m, 8H), 2.49 (s, 3H), 4.98 (d, *J*=1.6, 4H), 6.97 (dd, *J*=7.7, 0.9, 1H), 7.40 (d, *J*=8.5, 1H), 7.45 (dd, *J*=8.4, 7.5, 1H), 7.48 (d, *J*=8.9, 1H), 7.62 (t, *J*=8.6, 2H), 7.72 (d, *J*=8.7, 1H), 8.23 (s, 1H), 10.72 (d, *J*=0.9, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 3.7, 3.8, 19.1, 19.1, 19.7, 19.7, 20.0, 57.4, 58.2, 76.1, 76.2, 77.6, 77.7, 86.9, 87.3, 104.7, 113.9, 120.4, 123.8, 123.9, 124.1, 125.3, 126.2, 126.5, 127.4, 128.0, 128.7, 129.3, 132.6, 133.1, 134.2, 154.7, 158.2, 2 C (alkynes) are covered by $CDCl_3$.

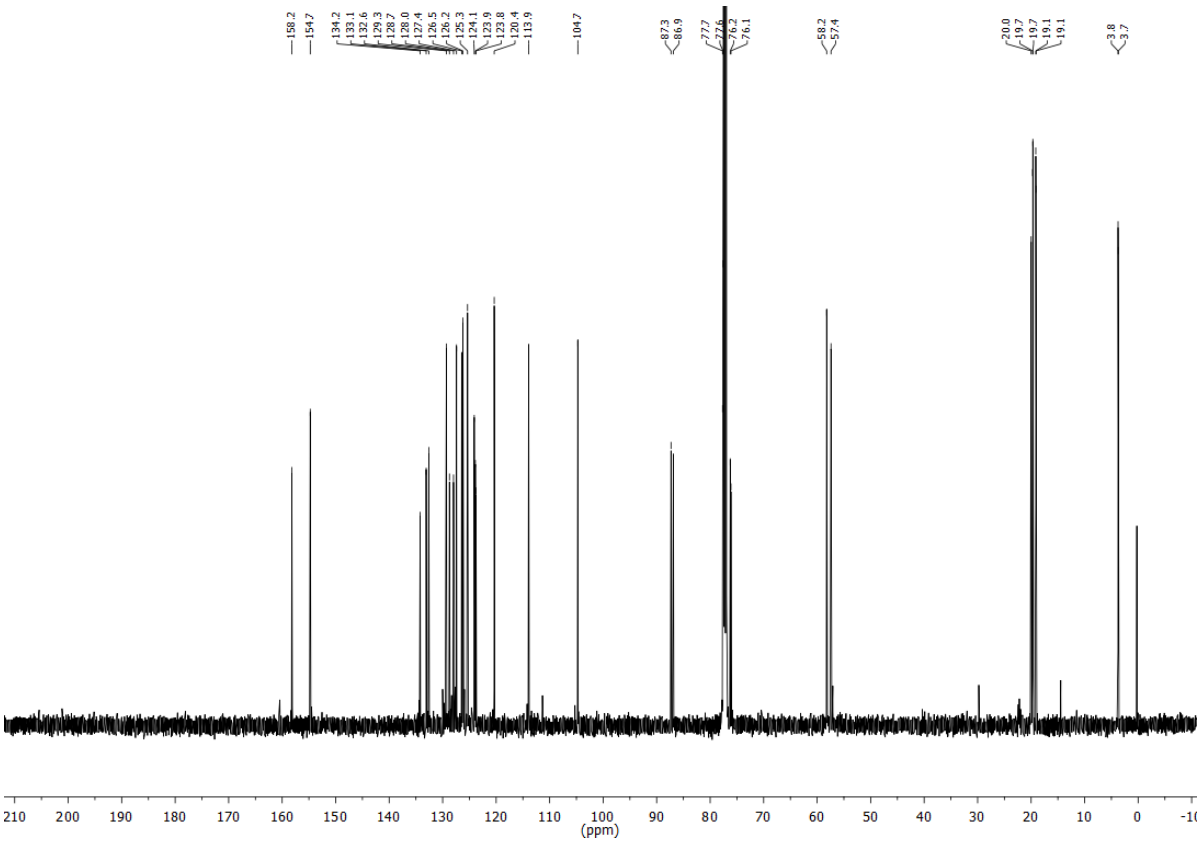
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3034, 2916, 2852, 1591, 1562, 1490, 1436, 1263, 1236, 1058, 990.

$C_{35}H_{30}O_2S$ calcd.: 514.1957 [M^+], found: 514.1961 [M^+] (EI-HRMS).

[60] J.-F. Devaux, S. V. O'Neil and N. Guill, *Collect. Czech. Chem. Commun.*, 2000, **65**, 490.

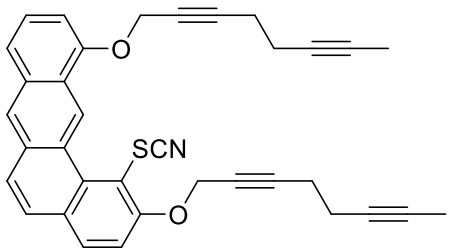


^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$).

2,11-Bis(octa-2,6-diyn-1-yloxy)-1-thiocyanatotetraphene (22f)



Compound **22e** (134 mg, 0.26 mmol, 1.0 equiv.) was dissolved in CH_3CN/THF (1:1, 2 ml) and added to a flask containing X-CN (161 mg, 0.312 mmol, 1.2 equiv.) The mixture was stirred for 30 min and the solvent was evaporated subsequently. Silica gel column chromatography (*n*-pentane:DCM = 1:3) gave the desired product **22f** (17 mg, 32 µmol, 12%) as a yellow solid.

m.p.: 184 °C.

R_f = 0.17 (*n*-pentane:EtOAc = 10:1).

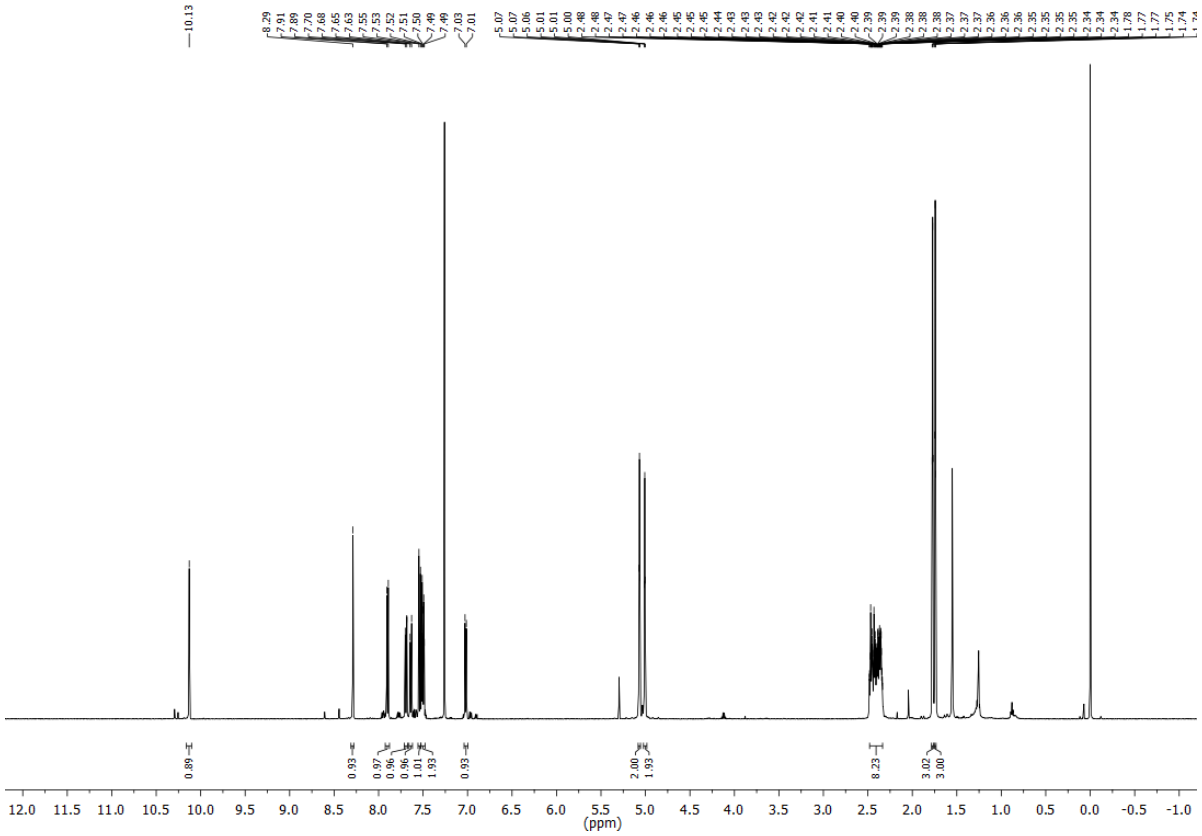
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.74 (t, *J*=2.5, 3H), 1.77 (t, *J*=2.5, 3H), 2.31 – 2.55 (m, 8H), 5.01 (t, *J*=2.0, 2H), 5.07 (t, *J*=2.1, 2H), 7.02 (d, *J*=7.5, 1H), 7.48 – 7.52 (m, 2H), 7.54 (d, *J*=8.6, 1H), 7.64 (d, *J*=8.4, 1H), 7.69 (d, *J*=8.6, 1H), 7.90 (d, *J*=8.7, 1H), 8.29 (s, 1H), 10.13 (s, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 3.5, 3.5, 18.7, 18.8, 19.4, 19.5, 57.2, 58.3, 75.1, 75.7, 76.8, 77.5, 87.0, 88.0, 104.9, 108.5, 111.3, 113.5, 120.1, 123.3, 123.7, 125.9, 126.2, 126.4, 126.7, 126.9, 128.8, 132.2, 132.3, 133.1, 133.9, 154.3, 157.8, 2 C (alkynes) are covered by $CDCl_3$.

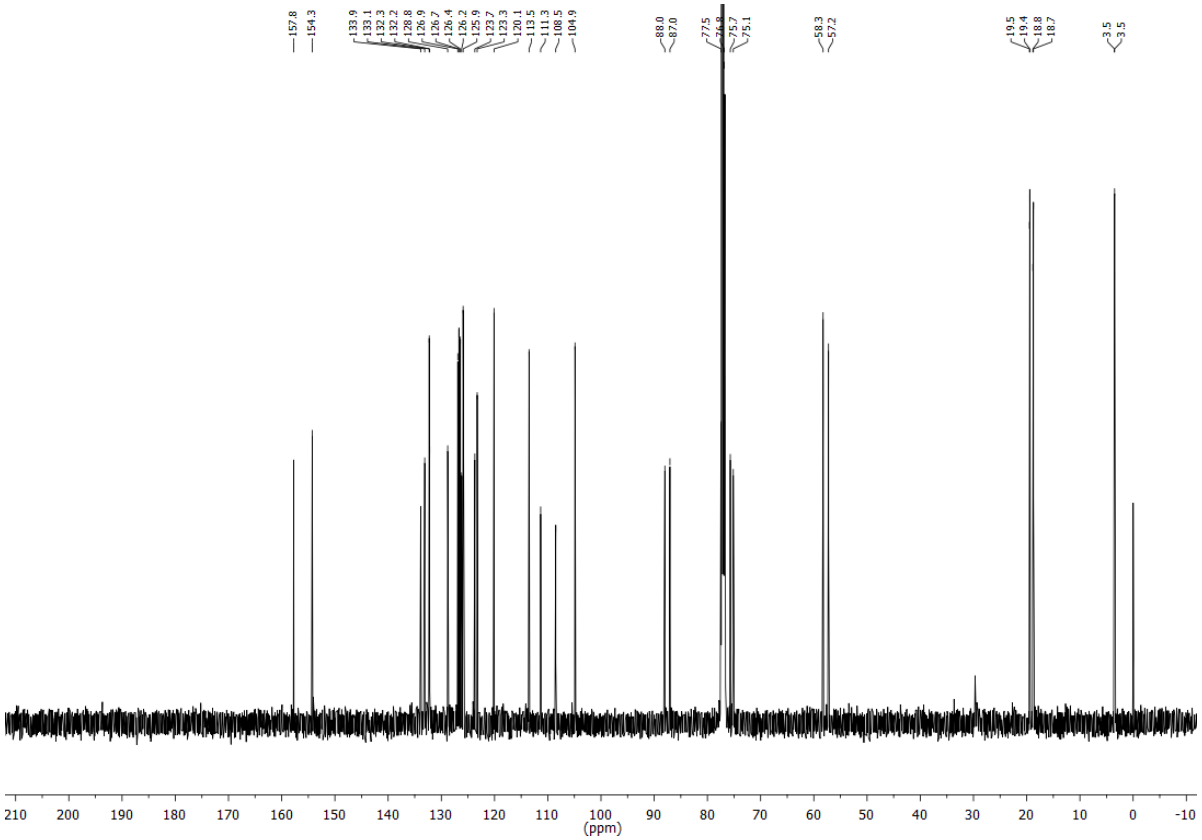
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3052, 2918, 2851, 2147, 1597, 1562, 1492, 1439, 1416, 1265, 1059.

$C_{35}H_{27}NO_2S$ calcd.: 525.1752 [M^+], found: 525.1757 [M^+] (EI-HRMS).

Compound **22f** was synthesized to obtain a twelve-membered ring formed in a “zipper”-type cascade reaction. Unfortunately, this synthesis was not possible.



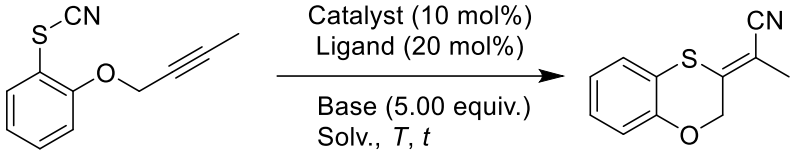
^{1}H-NMR (500 MHz, $CDCl_3$).



^{13}C-NMR (126 MHz, $CDCl_3$)

Screening of Reaction Conditions

Table S1: Optimization Table.



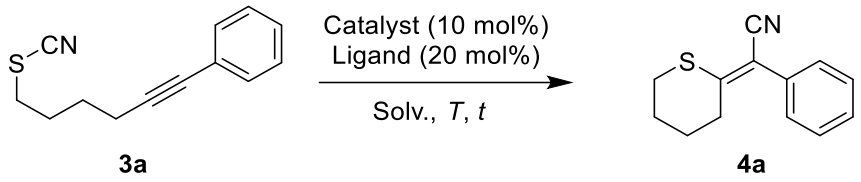
1a **2a**

Entry	Catalyst	Ligand	Base	Solv.	*T* [°C]	*t*	A [%]
1[a]	$PdCl_2(PhCN)_2$[b]	Fu' s salt	NEt_3	DMF	100	4 h	35
2[a]	$PdCl_2(PhCN)_2$	DTBPF	NEt_3	DMF	100	4 h	0
3[a]	$PdCl_2(PhCN)_2$	dppe	NEt_3	DMF	100	4 h	0
4[a]	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	DMF	100	4 h	76
5[c]	**$PdCl_2(PhCN)_2$**	**XantPhos**	**NEt_3**	**DMF**	**100**	**4 h**	**93**
6	$PdCl_2(PhCN)_2$[d]	XantPhos	NEt_3	DMF	100	4 h	41
7	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	DMA	100	4 h	43
8	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	PhMe	100	4 h	59[f]
9	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	CH_3CN	100	4 h	60[f]
10	$Pd(OAc)_2$	XantPhos	NEt_3	DMF	100	4 h	65[f]
11	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	DMF	80	4 h	45[f]
12	$PdCl_2(PhCN)_2$	XantPhos	-	DMF	100	4 h	0
13	$PdCl_2(PhCN)_2$	XantPhos	-	DMF	100	30 h	47
14	-	XantPhos	NEt_3	DMF	100	4 h	0
15	$PdCl_2(PhCN)_2$	-	NEt_3	DMF	100	4 h	0

Reaction conditions: **1a** (1.00 equiv.), Catalyst (10 mol%), Ligand (20 mol%), Base (5.00 equiv.), Solv. (20 mM); [a] solvent not degassed; [b] 18 mol% of catalyst; [c] from that entry all solvents (DMF, DMA, Ch_3CN, PhMe) were degassed; [d] 20 mol% of catalyst; [f] NMR yield;

Fu' s salt = [*t*Bu_3PH][BF_4]; DTBPF = 1,1'-Bis(di-*tert*-butylphosphino)ferrocene; dppe = 1,2-Bis(diphenylphosphino)ethane; Solv.. = Solvent, A = Yield.

Table S2: Optimization Table.



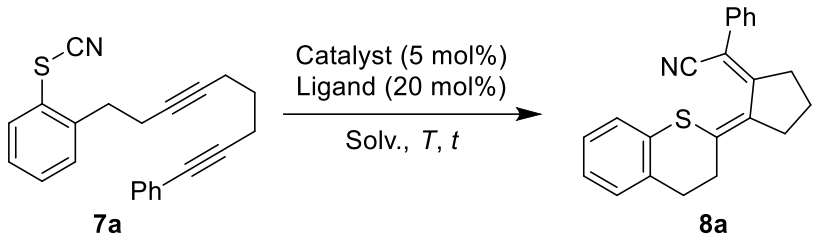
3a **4a**

Entry	Catalyst	Ligand	Base	Solv.	*T* [°C]	*t*	A [%]
1	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	DMF	[a]	[a]	61
2	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	DMF	120	96 h	n.d.[b]
3	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	DMF	140	21 h	42
4	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	DMF	160	14 h	59
5	$PdCl_2(PhCN)_2$	phenanthroline	NEt_3	DMF	140	14 h	0
6	$PdCl_2(PhCN)_2$	Fu' s salt	NEt_3	DMF	140	14 h	0
7	$PdCl_2(PhCN)_2$	BrettPhos	NEt_3	DMF	160	14 h	37
8	$PdCl_2(PhCN)_2$	MeOBiPHEP	NEt_3	DMF	160	14 h	33
9	$PdCl_2(PhCN)_2$	SPhos	NEt_3	PhMe	160	14 h	48
10	$Pd(OAc)_2$	XantPhos	NEt_3	DMF	140	14 h	39
11	$PdCl_2(PhCN)_2$	XantPhos	NEt_3	PhMe	160	14 h	53
12	$PdCl_2(PhCN)_2$	XantPhos	-	PhMe	160	14 h	0
13	**$Pd_2(dba)_3$**	**XantPhos**	**-**	**PhMe**	**160**	**14 h**	**89**
14	$Pd_2(dba)_3$	XantPhos	NEt_3	PhMe	160	14 h	85
15	$Pd_2(dba)_3$	XantPhos[c]	-	PhMe	160	19 h	n.d.[b]
16	$Pd_2(dba)_3$[d]	XantPhos[d]	-	PhMe	160	19 h	n.d.[b]

Reaction conditions: **3a** (1.00 equiv.), Catalyst (10 mol%), Ligand (20 mol%), Base (5.00 equiv.), Solv. (20 mM); [a] almost no conversion after 4 h at 100 °C, temperature the raised to 140 °C for 18 h; [b] significant amount of starting material left; [c] 10 mol%; [d] 5 mol%

Fu-Salt = [*t*Bu_3PH][BF_4]; MeOBiPHEP = 2,2′-Bis(diphenylphosphino)-6,6′-dimethoxy-1,1′-biphenyl; Solv.. = Solvent, A = Yield.

Table S3: Optimization Table.



7a **8a**

Entry	Catalyst	mol%	Ligand	mol%	Base	Solv.	*T* [°C]	*t*	A [%]
1	$PdCl_2(PhCN)_2$	20	XantPhos	20	NEt_3	DMF	100	6 h	(66)[a]
2	$PdCl_2(PhCN)_2$	20	Fu' s salt	20	NEt_3	DMF	100	6 h	(17)[a]
3	$PdCl_2(PhCN)_2$	10	XantPhos	20	NEt_3	DMF	140	12 h	n.d.[a]
4	$Pd_2(dba)_3$	10	XantPhos	20	NEt_3	PhMe	140	12 h	n.d.[a]
5	$PdCl_2(PhCN)_2$	10	XantPhos	20	NEt_3	DMI[b]	180	12 h	dec.
6	$PdCl_2(PhCN)_2$	10	XantPhos	20	NEt_3	Xylene	140	12 h	n.d.[a]
7	$PdCl_2(PhCN)_2$	10	Trisisopropyl phosphite	100	NEt_3	DMF	110	12 h	dec.
8	$PdCl_2(PhCN)_2$	10	Trimethyl phosphite	100	NEt_3	DMF	110	12 h	dec.
9	$PdCl_2(PhCN)_2$	10	$[Me_3PH][BF_4]$	100	NEt_3	DMF	110	12 h	[c]
10	$Pd(dba)_2$	10	$[Me_3PH][BF_4]$	20	NEt_3	DMF	120	12 h	[c]
11	$Pd(dba)_2$	10	$[Et_3PH][BF_4]$	20	NEt_3	DMF	120	12 h	[c]
12	$Pd(dba)_2$	10	$[Et_3PH][BF_4]$	100	NEt_3	DMF	120	12 h	[c]
13	$Pd(PPh_3)_4$	10	-	-	-	PhH	120[d]	1 h	n.d.[a]
14	$PdCl_2(PhCN)_2$	10	dppp	20	NEt_3	DMF	110	12 h	dec.
15	$PdCl_2(PhCN)_2$	10	dppp	100	NEt_3	DMF	110	12 h	n.d.[a]
16	$PdCl_2(PhCN)_2$	10	dppp	100	NEt_3	DMF	110	12 h	n.d.[a]

Entry	Catalyst	mol%	Ligand	mol%	Base	Solv.	*T* [°C]	*t*	A [%]
17	$Pd(PPh_3)_4$	10	SPhos	20	-	DMF	110	12 h	50[e]
18	$Pd(PPh_3)_4$	5	SPhos	10	-	DMF	110	12 h	n.d.[f]
19	$Pd(PPh_3)_4$	10	SPhos	20	-	DMF	140	12 h	n.d.[f]
20	$Pd(PPh_3)_4$	10	XPhos	20	-	DMF	110	12 h	n.d.[f]
21	$Pd(PPh_3)_4$	10	SPhos	20	-	DMF/ PhMe	110	12 h	n.d.[f]
22	$Pd(PPh_3)_4$	10	SPhos	20	-	DMF/ Dioxane	110	12 h	n.d.[f]
23[g]	$Pd(PPh_3)_4$	10	SPhos	40	-	DMF	110	12 h	60[e]
24	$Pd(PPh_3)_4$	10	SPhos	25	-	DMF	110	12 h	65[e]
25	SPhos Pd G4	5	-	-	KOAc	DMF	110	12 h	n.d.[f]
26	$Pd(PPh_3)_4$	10	SPhos	25	-	CH_3CN	110	3 h	n.d.[f]
27	$Pd(PPh_3)_4$	10	SPhos	25	-	PhMe	110	19 h	n.d.[f]
28	$Pd(PPh_3)_4$	10	SPhos	25	-	NMP	110	4 h	60[e]
29	$Pd(PPh_3)_4$	10	DavePhos	25	-	DMF	110	3 h	n.d.[f]
30	$Pd(PPh_3)_4$	10	tBuXPhos	25	-	DMF	110	19 h	n.d.[f]
31	$Pd(PPh_3)_4$	10	RuPhos	25	-	DMF	110	12 h	63[e]
32	$Pd(PPh_3)_4$	10	AdJohnPhos	25	-	DMF	110	12 h	n.d.[f]
33	$Pd(PPh_3)_4$	10	JohnPhos	45	-	DMF	110	2 h	n.d.[f]
34	$Pd(PPh_3)_4$	10	CyJohnPhos	45	-	DMF	110	12 h	n.d.[f]
35	**$Pd(PPh_3)_4$**	**5**	**SPhos**	**20**	**-**	**DMF**	**110**	**3 h**	**70**

Reaction conditions: **3a** (1.00 equiv.), Catalyst (10 mol%), Ligand (20 mol%), Base (5.00 equiv.), Solv. (20 mM); [a] single palladation product; [b] DMI = ; [c] protodepalladation product; [d] reaction in microwave; [e] NMR yield; [f] no improvement (TLC) [g] from that entry the catalyst and ligand were prestirred for 30 – 45 min

Fu-Salt = [*t*Bu_3PH][BF_4]; MeOBiPHEP = 2,2'-Bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl; Solv.. = Solvent, A = Yield.

Experiments with Lewis acid as co-catalyst

As the catalytic system with $PdCl_2(PhCN)_2$/XantPhos is not suitable for such experiments due to the use of NEt_3 as base, we first investigated the reaction of **1a** to **2a** with the adjusted conditions of GP CAT2 (100 µmol, PhMe, 80 °C). We followed the reaction progress by GC-MS measurements and took samples after 1, 3, 5, 10, 15 and 30 min from the reaction vial.

The figure shows, that the starting material (retention time 6.552) was consumed after 30 min and seems to be fully converted to the product **2a** (retention time 7.153). The other peak shows PPh_3 from the catalyst.

Next, we tested the influence of two Lewis acids. The first figure shows the tracking of the reaction in presence of 20 mol% BPh_3.

After an initially fast formation of the product the conversion stopped and stayed at a ratio of 1:2 (**1a**/**2a**).

The following figure shows the tracking of the reaction in presence of 20 mol% $AlCl_3$.

Until the measurement after 30 min the reaction showed almost no conversion of the starting material **1a** to the product **2a**. After 30 min there was a sharp increase to a ratio of 1:2 (**1a**/**2a**). However, also side products are visible.

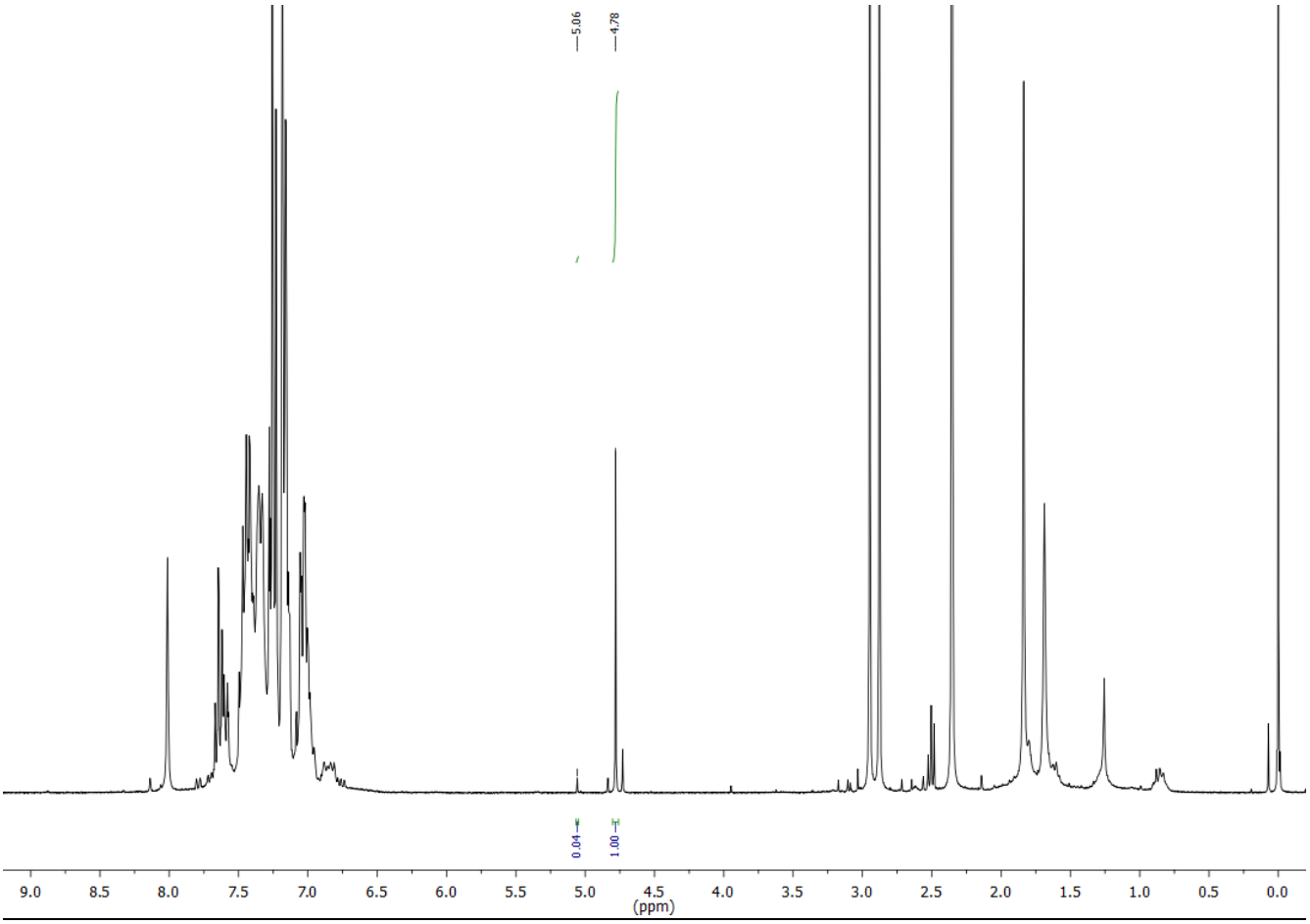
In summary, the use of a Lewis acid as co-catalyst for the cyanosulfenylation offers no benefit compared to the established catalytic system.

Configurational experiments (interconversion of *E* and *Z* isomers)

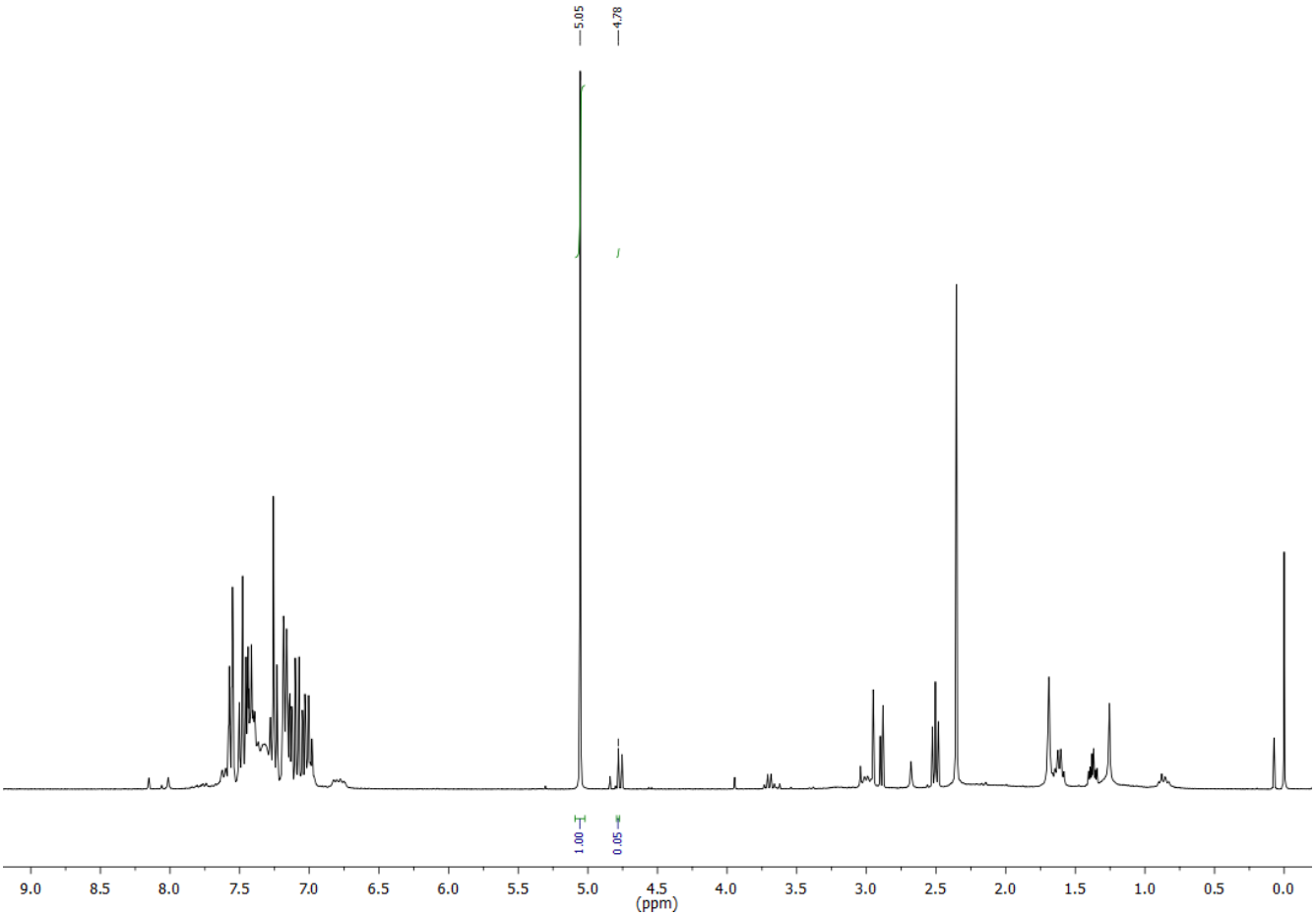
We investigated the configurational stability of the separated *E*- and *Z*-isomer of **2e**, respectively. Therefore, each of the pure isomers was subjected again to reaction conditions used for the transformation of **1e** into **2e**.

The crude reaction mixtures (after co-evaporation of the DMF with PhMe) were measured by ^{1}H-NMR spectroscopy. In both cases the other isomer arises in the spectrum. For determination, we used the chemical shift of the CH_2-signal.

For the *syn*-isomer it is 4.78 ppm and for the *anti*-isomer it is 5.05 ppm. In both cases a ratio of approximately 20:1 from one isomer (the one used for the experiment) to the other (the one that is formed in the experiment) results after 7 h.



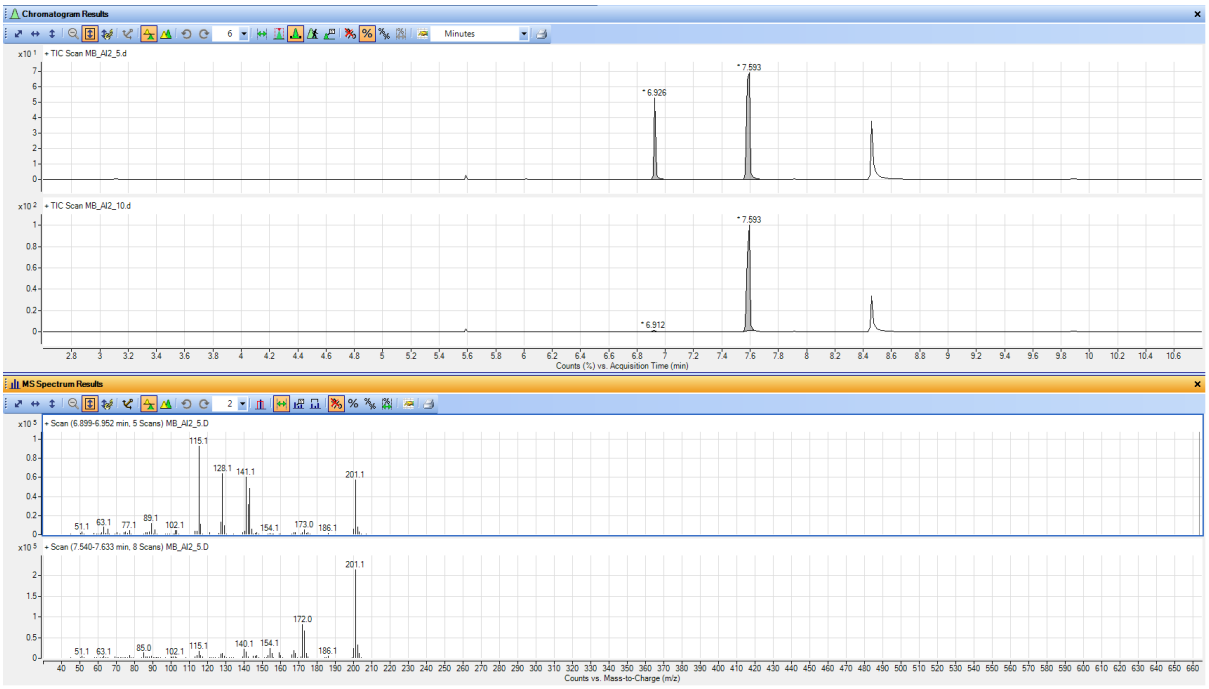
Scheme: Conversion of the syn-isomer to the anti-isomer.

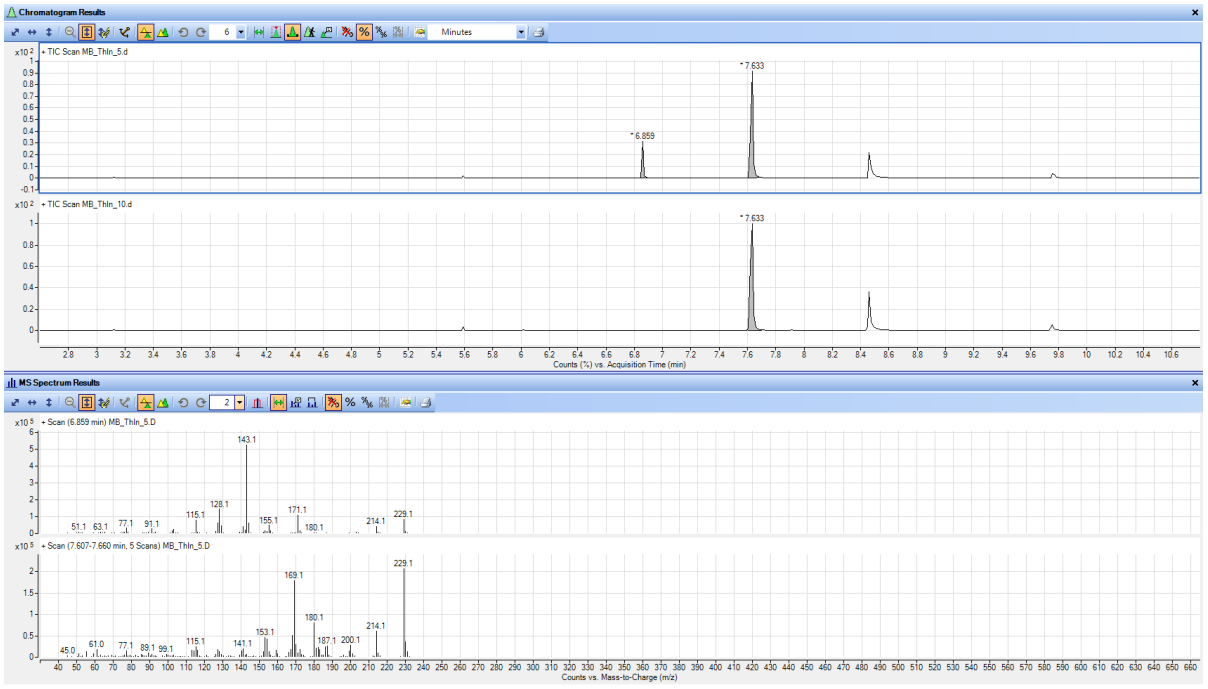


Scheme: Conversion of the anti-isomer to the syn-isomer.

Investigation of Thorpe-Ingold effect

Under optimized conditions of GP CAT3, we synthesized compound **4f** and **4f'** under the same conditions and tracked the reactions by GC-MS. As we assumed that a Thorpe-Ingold effect in substrate **3f'** may facilitate the reaction we decreased the temperature of the reaction to 120 °C.





The first figure shows the reaction of **3f** (retention time 6.296) to **4f** (retention time 7.593). In general, the substrates for the five-membered form the corresponding product apparently much faster than we observed it for the formation of the six-membered ring during the screening for the cyanosulfenylation of aliphatic thiocyanates (cf. Table S2).

The conversion of **3f** was almost complete after 10 minutes (see first figure). After 5 minutes, we determined a ratio of starting material to product of 4:10 (**3f**/**4f**).

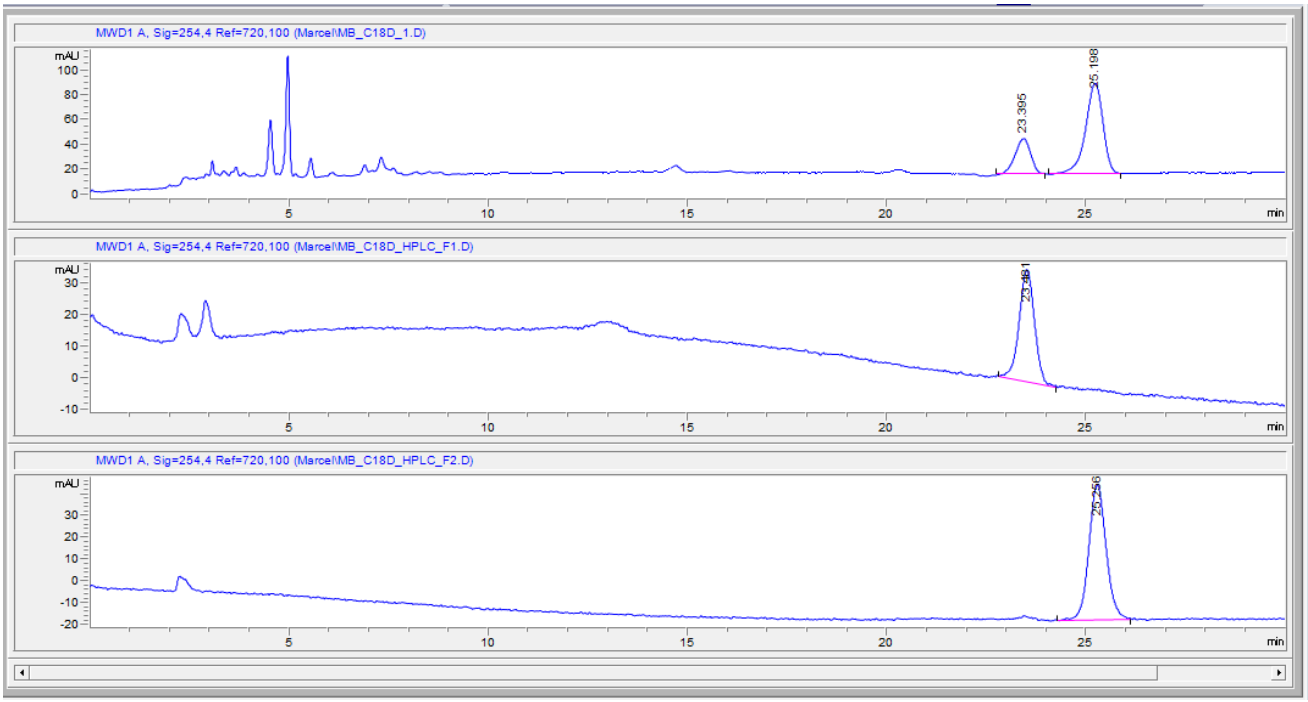
The second figure shows the reaction of **3f'** (retention time 6.859) to **4f'** (retention time 7.633). The conversion of **3f'** was complete after 10 minutes. After 5 minutes, we determined a ratio of starting material to product of 2.5:10 (**3f'**/**4f'**).

In conclusion, only a very small Thorpe-Ingold effect can be assumed as the reaction itself is fast for these simple substrates at the chosen reaction conditions.

Photochemical and thermal experiments with compound 10d

As we assumed an isomerization after formation of compound **10d** between the ***(Z,Z,Z)***- and ***(Z,E,Z)***-isomer (proved by X-ray) we investigated whether this effect may be caused thermally or photochemically. After the reaction we purified the isomeric mixture via a short silica gel column and subjected it to an HPLC experiment (eluent CH_3CN/H_2O 80:20).

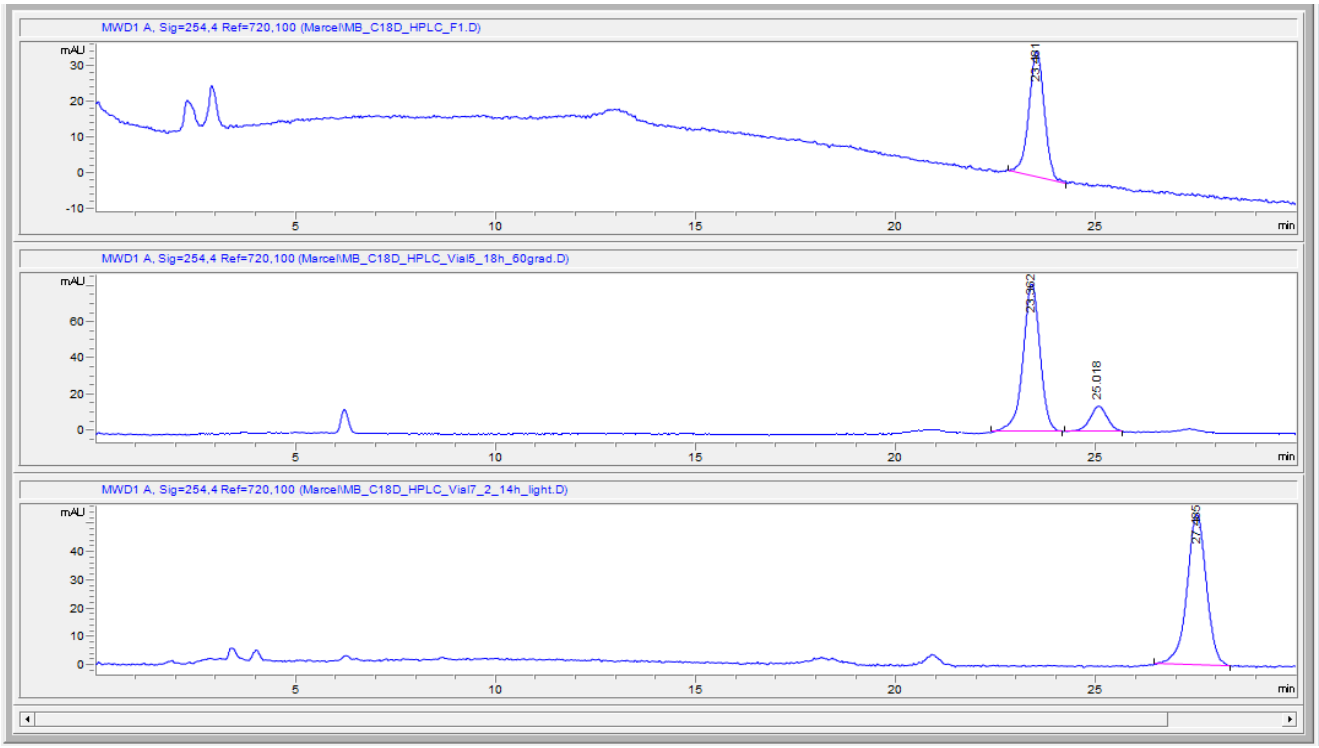
The first figure shows the chromatogram of the mixture and the separated fractions (F1 at 23.4 min and F2 at 25.2 min). Both were identified as one product isomer by LC-MS.



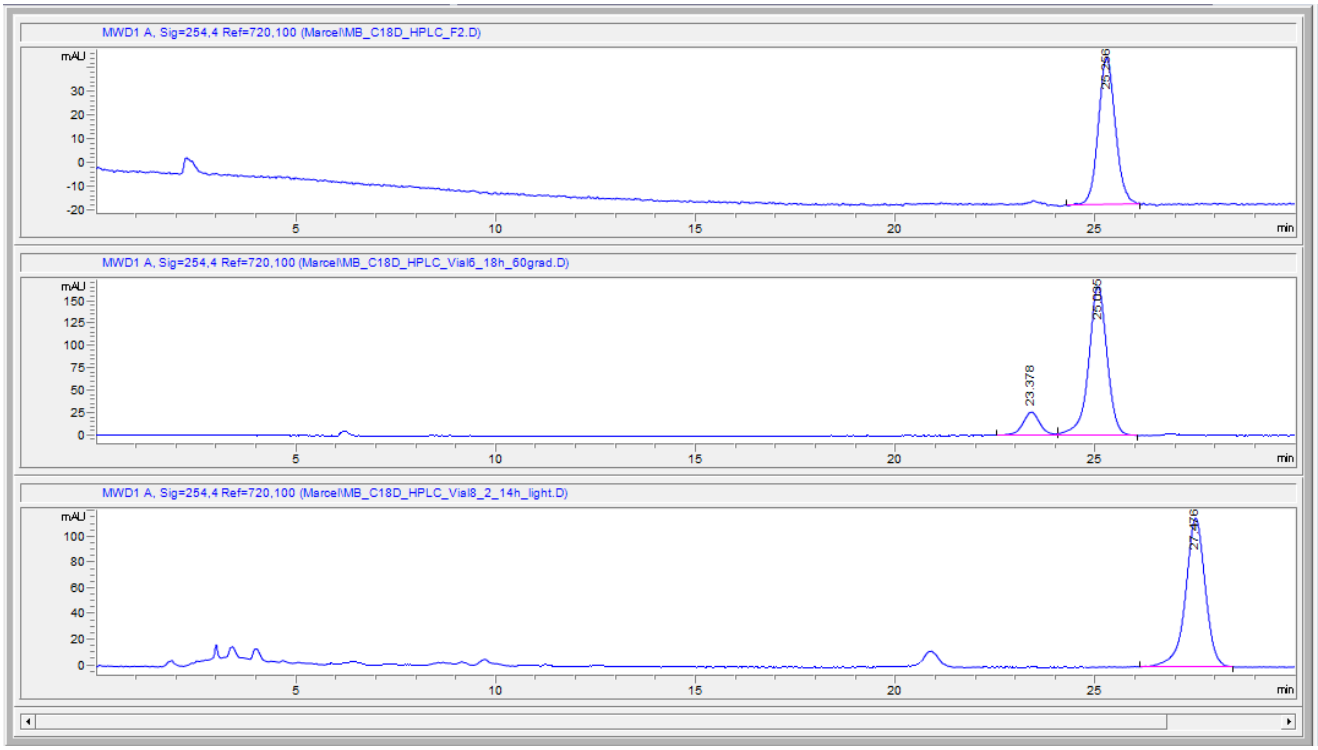
Both separated isomers were then either heated to 60 °C for 18 h or irradiated with white light for 14 h. The results are shown in the following figures.

For both isomers F1 and and F2 the thermal experiments showed that the other isomer F2 or F1, resp., was formed again (middle chromatogram in both figures).

Moreover, for both isomers F1 and and F2 the irradiation experiments (lower chromatogram in both figures) showed that a new compound was formed from both isomers F1 and F2 with a retention time of 27.5 minutes. In LC-MS the same mass as for the isomers F1 and F2 was found. A further characterization was not done and should be the considered for further studies.



Thermal (middle) and photochemical (bottom) reaction with isomer F1



Thermal (middle) and photochemical (bottom) reaction with isomer F2

Crystal Structure Determinations

Crystals were mounted in inert oil and transferred to the cold gas stream of the diffractometer; various Rigaku/Oxford instruments using monochromated Mo Kα (**6d**, **10b**, **10d**, **2s**, **10a'**), mirror-focussed Mo Kα (**2q, 2r, 8e**) or mirror-focussed Cu Kα (**2a**, **2e**) radiation were employed. Absorption corrections were implemented on the basis of multi-scans. The structures were refined anisotropically on F^2 using the program SHELXL-97[1] or SHELXL-2017[2]. Hydrogen atoms were included using rigid methyl groups or a riding model starting from calculated positions. *Special features*: For compound **8b**, the atom C12 is disordered over two positions with relative occupancy 0.81:0.19. Appropriate restraints were employed, but the dimensions of disordered groups should be interpreted with caution. Compound **8e** was a non-merohedral twin (by 180° rotation about the *a* axis). The structure was refined using the "HKLF 5" method;[2] the relative volume of the smaller twin component refined to 0.4553(6). The dataset comprised non-overlapped reflections from both components as well as overlapped reflections. For such refinements, the number of reflections and the *R*(int) value may not be well-defined.

Crystallographic data are summarized in Table S1. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC 1948156-1948162 and 1969696-1969698. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

References:

1. G. M. Sheldrick, *Acta Cryst*. **A64**, 112–122 (2008).

2. G. M. Sheldrick, *Acta Cryst*. **C71**, 3–8 (2015).

Table S1a: Crystallographic data and structure refinement details for compounds **2a**, **2e**, **6d** and **10b**.

Compound	**2a**	**2e**	**6d**	**10b**
CCDC number	1948156	1948157	1948158	1948159
Formula	$C_{11}H_9NOS$	$C_{16}H_{11}NOS$	$C_{16}H_{21}NSSeSi$	$C_{17}H_{17}NS$
M_r	203.25	265.32	366.45	267.38
Cryst. size (mm)	0.2 x 0.2 x 0.15	0.2 x 0.15 x 0.08	0.45 x 0.4 x 0.2	0.4 x 0.35 x 0.10
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/c$	$P2_1/c$
Temperature (°C)	-173	-173	-173	-173
a (Å)	10.9143(2)	12.2557(2)	10.6588(4)	11.1885(7)
b (Å)	7.26579(18)	9.5626(2)	8.0663(3)	11.2630(4)
c (Å)	12.4737(2)	21.5616(4)	20.1272(8)	12.1884(7)
α (°)	90	90	90	90
β (°)	104.425(2)	90	95.886(3)	116.756(8)
γ (°)	90	90	90	90
V (Å^3)	957.99	2526.94	1721.35	1371.50
Z	4	8	4	4
D_x (Mg m^{-3})	1.409	1.395	1.414	1.295
λ (Å)	1.54184	1.54184	0.71073	0.71073
μ (mm^{-1})	2.7	2.2	2.4	0.22
Transmissions	0.791 – 1.000	0.608 – 1.000	0.788 – 1.000	0.970 – 1.000
F(000)	424	1104	752	568
$2\theta_{max}$	151.7	152	62.2	58.2
Refl. measured	20246	49411	88854	31457
Refl. indep.	1990	2638	5310	3577
R_{int}	0.050	0.049	0.049	0.047
Parameters	128	172	186	178
$wR(F^2$, all refl.)	0.085	0.082	0.072	0.092
$R(F, >4\sigma(F))$	0.031	0.030	0.032	0.039
S	1.06	1.06	1.08	1.04
Max. Δp (e Å^{-3})	0.28, –0.30	0.23, –0.32	1.4, –0.6	0.49, –0.25

Table S1b: Crystallographic data and structure refinement details for compounds **10d**, **2s** and **10a'**.

Compound	**10d**	**2s**	**10a'**
CCDC number	1948160	1948161	1948162
Formula	$C_{22}H_{23}NS$	$C_{10}H_7NS$	$C_{21}H_{20}S$
M_r	333.47	173.23	304.43
Cryst. size (mm)	0.4 x 0.25 x 0.2	0.35 x 0.25 x 0.2	0.35 x 0.2 x 0.2
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P(-1)$	$P2_1/n$
Temperature (°C)	-173	-173	-171
a (Å)	13.9373(6)	6.9027(6)	7.5133(2)
b (Å)	7.7203(3)	7.3743(6)	25.6215(7)
c (Å)	17.0136(7)	9.3503(7)	8.2645(3)
α (°)	90	68.861(8)	90
β (°)	105.984(5)	73.292(8)	100.591(3)
γ (°)	90	84.246(6)	90
V (Å^3)	1759.90	425.18	1563.84
Z	4	2	4
D_x (Mg m^{-3})	1.259	1.353	1.293
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.19	0.32	0.20
Transmissions	0.954 – 1.000	0.976 – 1.000	0.955 – 1.000
F(000)	712	180	648
$2\theta_{max}$	60	62	62
Refl. measured	53738	22785	82578
Refl. indep.	5123	2532	4812
R_{int}	0.054	0.037	0.039
Parameters	218	110	199
$wR(F^2$, all refl.)	0.100	0.081	0.092
$R(F, >4\sigma(F))$	0.042	0.033	0.037
S	1.05	1.05	1.08
Max. Δp (e Å^{-3})	0.43, –0.21	0.43, –0.21	0.46, –0.28

Table S1c: Crystallographic data and structure refinement details for compounds **8e**, **2q** and **2r**.

Compound	**8e**	**2q**	**2r**
CCDC number	1996969	1969697	1969698
Formula	$C_{18}H_{19}NSSi$	$C_{17}H_{13}NOS$	$C_{18}H_{15}NOS$
M_r	309.49	279.34	293.37
Cryst. size (mm)	0.25 x 0.2 x 0.05	0.25 x 0.2 x 0.2	0.2 x 0.2 x 0.1
Crystal system	triclinic	monoclinic	orthorhombic
Space group	*P*(-1)	*C*2/*c*	*Pbca*
Temperature (°C)	-173	-173	-173
a (Å)	8.52831(11)	20.6204(8)	13.1964(2)
b (Å)	10.39109(14)	9.4103(3)	13.3812(2)
c (Å)	11.21545(16)	16.7239(6)	16.7048(3)
α (°)	117.5842(14)	90	90
β (°)	92.3119(11)	120.205	90
γ (°)	95.1854(11)	90	90
V (Å^3)	873.50	2804.6	2949.80
Z	2	8	8
D_x (Mg m^{-3})	1.177	1.323	1.321
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.25	0.23	0.22
Transmissions	0.930 – 1.000	0.790 – 1.000	0.933 – 1.000
F(000)	328	1168	1232
$2\theta_{max}$	68	72	72
Refl. measured	12628	70418	221112
Refl. indep.	12628	6266	6774
R_{int}	n/a	0.031	0.041
Parameters	194	182	191
wR(*F*^{2}, all refl.)	0.098	0.090	0.088
R(*F*, >4σ(*F*))	0.034	0.031	0.037
S	1.07	1.06	1.06
Max. Δ*p* (e Å^{-3})	0.49, –0.23	0.53, –0.26	0.53, –0.31

Thermal ellipsoid plots (all at the 50% probability level):

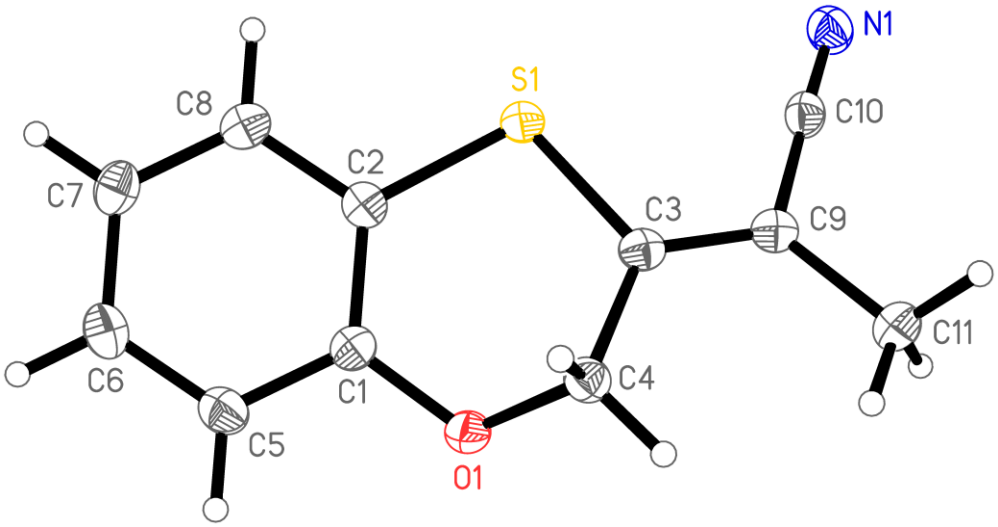


Fig. S1. Structure of compound **2a** in the crystal.

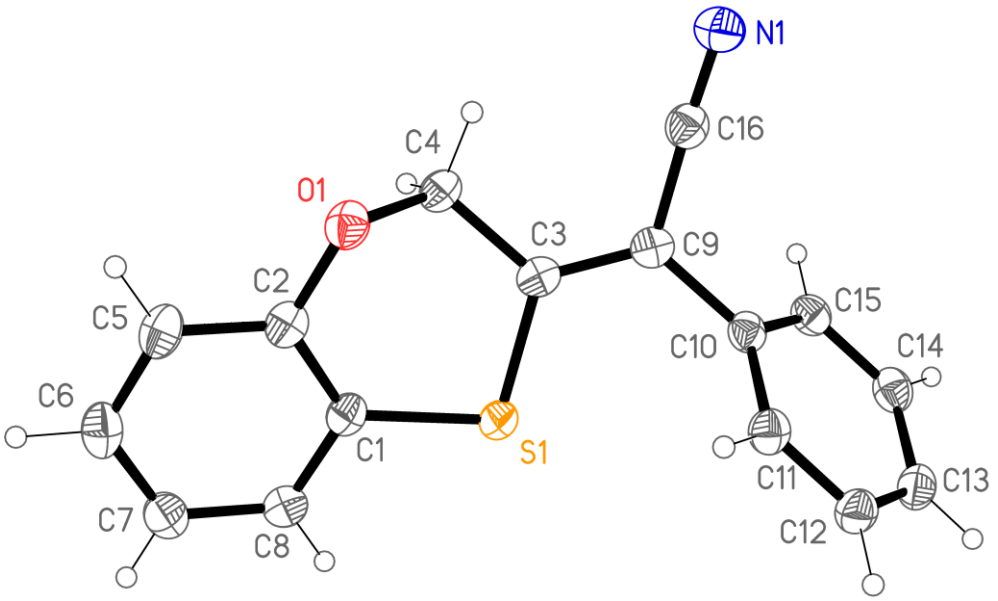


Fig. S2. Structure of compound **2e** in the crystal.

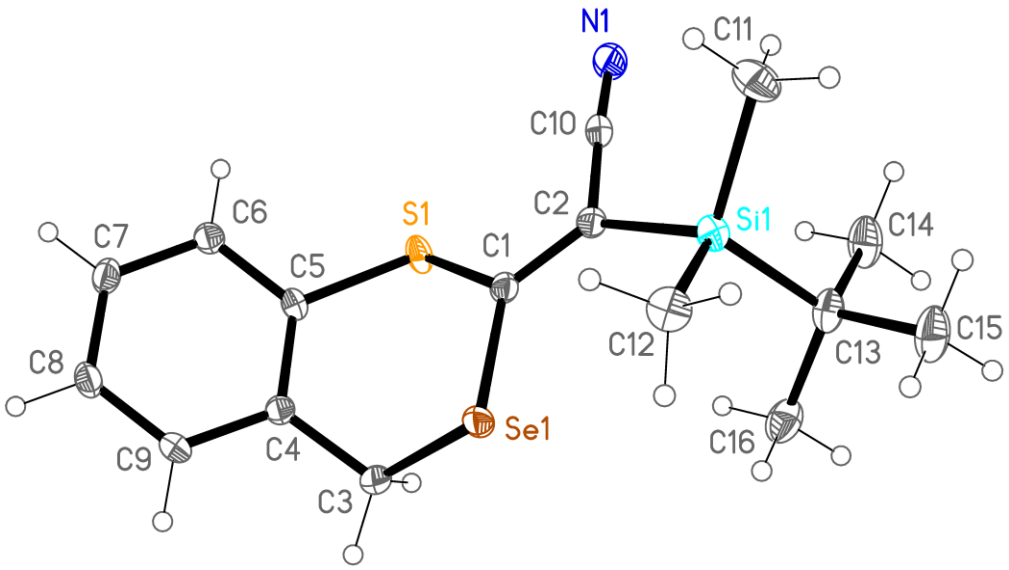


Fig. S3. Structure of compound **6d** in the crystal.

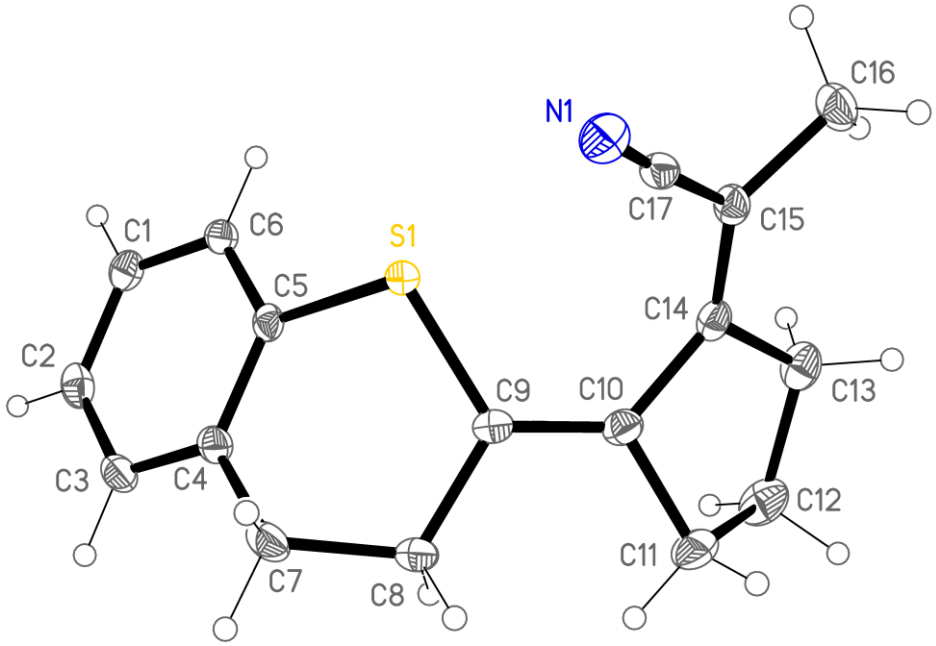


Fig. S4. Structure of compound **10b** in the crystal.

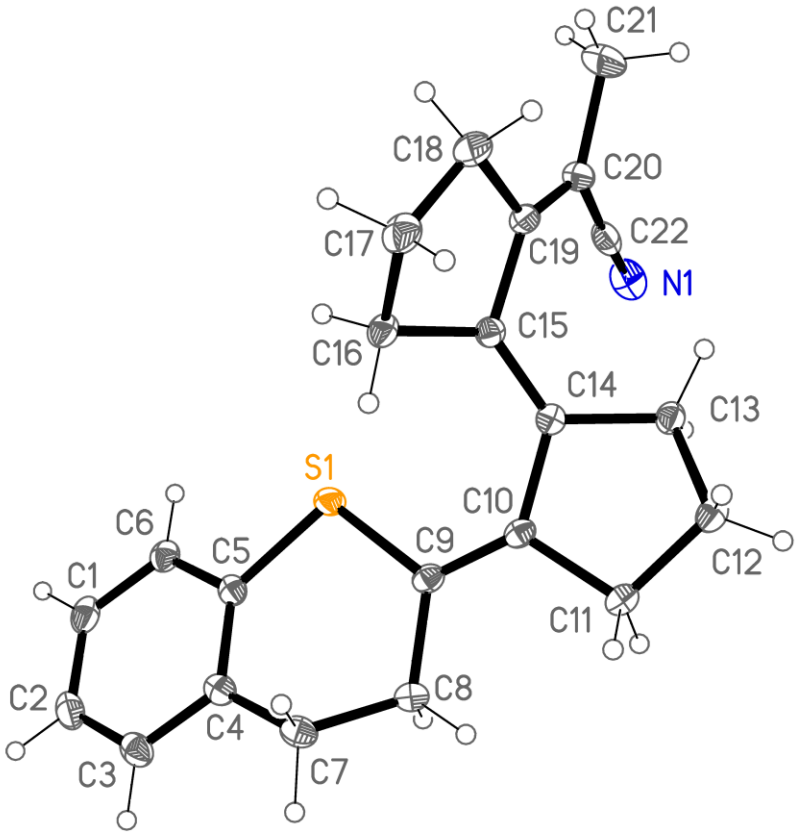


Fig. S5. Structure of compound **10d** in the crystal.

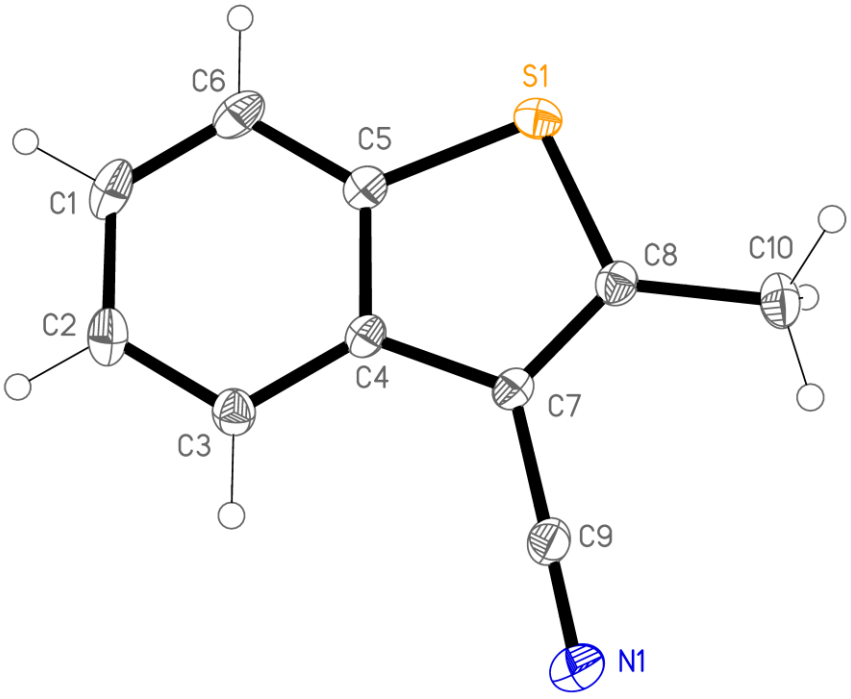


Fig. S6. Structure of compound **2s** in the crystal.

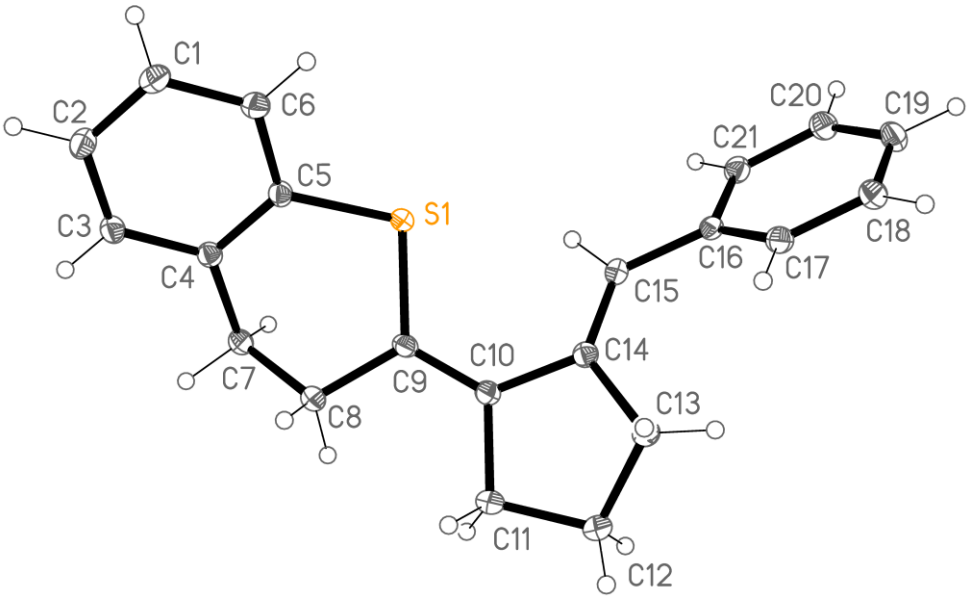


Fig. S7. Structure of compound **10a'** in the crystal.

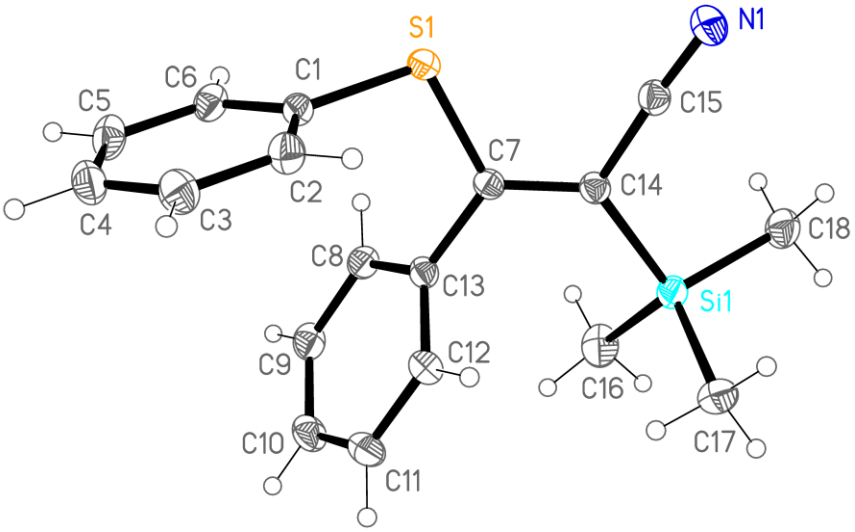


Fig. S8. Structure of compound **8e** in the crystal.

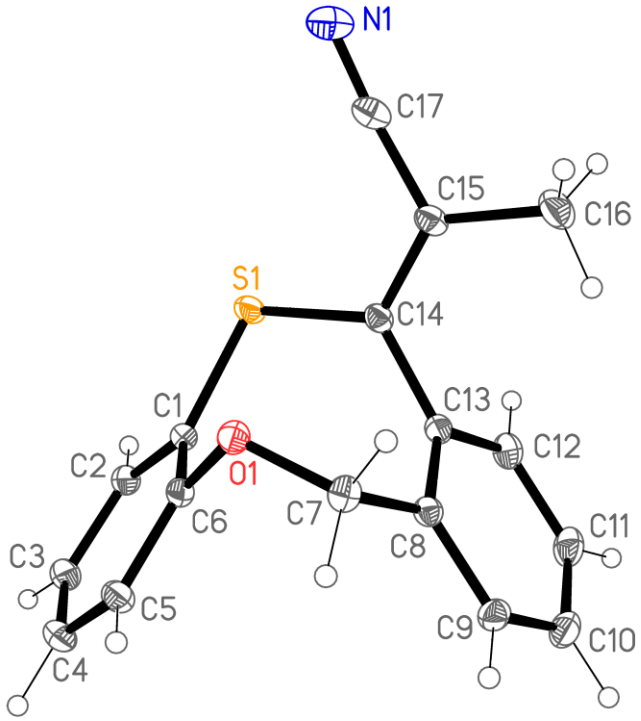


Fig. S9. Structure of compound **2q** in the crystal.

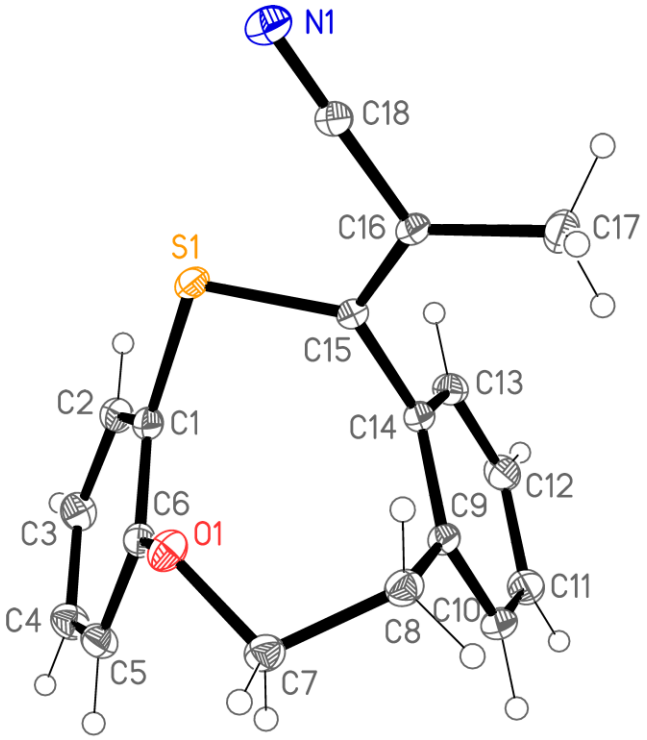


Fig. S10. Structure of compound **2r** in the crystal.