C-H Functionalization

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Direct Alkynylation of Thiophenes: Cooperative Activation of TIPS-Ethynyl-Benziodoxolone with Gold and Brønsted Acids. **

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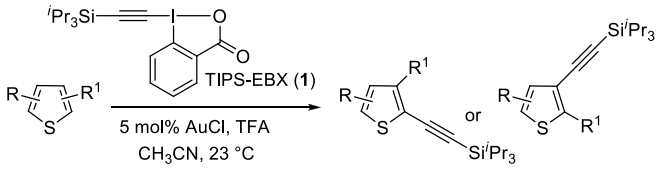
((Dedication----optional))

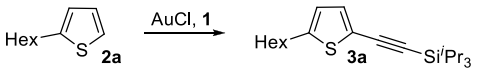
Thiophene is a ubiquitous heterocycle in both medicinal chemistry and material sciences.[1] Oligo and polythiophenes play a crucial role in organic electronic materials.[2] For most applications, extended systems of π electrons are required, which are usually prepared using cross-coupling methods.[3] Direct arylation has recently emerged as a more step- and atom- economic alternative.[4] In contrast, no direct alkynylation of thiophenes has been reported, even though oligo and poly(arylene ethynylene) are an important class of organic materials.[5] Consequently, more direct methods to access ethynyl thiophenes in particular would be highly desirable.

The direct alkynylation of (hetero)aromatics has recently become an active research area.[6,7]. The direct alkynylation of thiophenes, however, remains elusive. In fact, extending known alkynylation methodologies to thiophene is not easy, due to its low reactivity.[4,8] Herein, we wish to report the alkynylation of thiophenes using 1-[(tri*iso*propylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) (**1**). The reaction proceeded at room temperature under open flask conditions (Equation 1). The discovery of a cooperative effect between a gold catalyst and a Brønsted acid allowed the development of the direct silylethynylation of thiophenes.



Equation 1.

Recently, our group reported the direct alkynylation of indoles and pyrroles using AuCl and TIPS-EBX (**1**).[7,9] Unfortunately, only traces of product **3a** were observed under the previously developed reaction conditions (Table 1, Entry 1). Increased concentration, acetonitrile as solvent and higher temperature led to only slightly better results (Entry 2), demonstrating the challenges associated with the less reactive thiophenes. Inspired by recent examples about the activation of benziodoxole reagents,[9g-h] we then tried the reaction in presence of Lewis or Brønsted acids (Entries 3-8). The best result (84% yield) was obtained with trifluoro acetic acid (TFA) (1 equivalent compared to **1**). A correlation between yield and acid strength was observed, but no product was obtained with acids stronger than TFA and the starting material was decomposed in this case (Entry 8). TFA could also be used catalytically, but the yield was lower (Entry 9). No alkynylation occurred in the absence of AuCl. To the best of our knowledge, this is the first example of the cooperative activation of a benziodoxolone reagent with a gold catalyst and a Brønsted acid.[10] In contrast to most direct arylation methods, the alkynylation did not require heating. More diluted conditions (0.2 M) gave the product in 94% yield (83% isolated) (Entry 10). Other solvents or gold catalysts gave lower yields.[11] Alkynyliodonium salts and bromo or iodoalkynes did not afford any product, showing the unique properties of TIPS-EBX (**1**).[12] On a 2 mmol scale, **3a** was obtained in 84% yield using only 1 mol % AuCl and not dry solvents under air.[13] 2-Iodobenzoic acid could be recovered via a simple basic work-up in 86 % yield and could be recycled for the synthesis of TIPS-EBX (**1**).[14] ***Table 1.*** Reaction optimization and discovery of the Brønsted acid activation.



entry	solvent	[M]	Additive[b]	yield[a]
1	Et_2O	0.05	–	2%
2	CH_3CN	0.4	–	14%[c]
3	CH_3CN	0.4	$Zn(OTf)_2$	62%
4	CH_3CN	0.4	CH_3CO_2H	18%
5	CH_3CN	0.4	$ClCH_2CO_2H$	53%
6	CH_3CN	0.4	Cl_3CCO_2H	73%
7	CH_3CN	0.4	TFA	84%
8	CH_3CN	0.4	TsOH	0%
9	CH_3CN	0.4	TFA[d]	50%
10	CH_3CN	0.2	TFA	94% (83%)[e]

[a] Reaction conditions: 0.20 mmol **2a**, 0.24 mmol **1** and 0.01 mmol AuCl under N_2 for 12-15 h. GC yields using pentadecane as reference. [b] 1.2 equiv additive. [c] Reaction run at 60 °C. [d] 0.1 equiv TFA. [e] Isolated yield. Hex = Hexyl. Ts = *para*-toluene sulfonyl.

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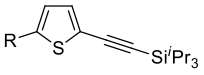
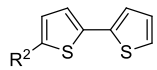
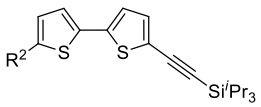
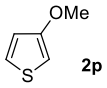
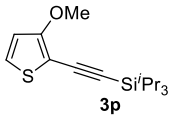
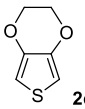
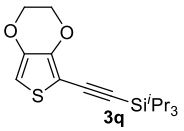
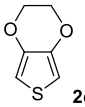
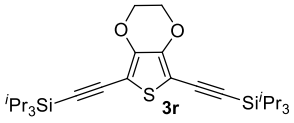
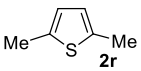
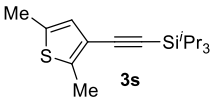
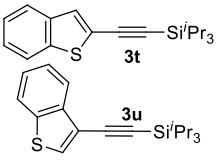
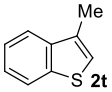
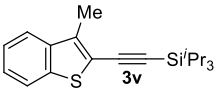
Table 2. Scope of the Ethynylation of Thiophenes

Entry	Substrate	Product	Yield[a]
			
1	R = Hexyl **2a**	**3a**	83%
2	R = Methyl **2b**	**3b**	80%
3[b,c]	R = H **2c**	**3c**	73%
4[c]	R = OMe **2d**	**3d**	68%
5	R = CH_2OH **2e**	**3e**	50%
6	R = CH_2CH_2OH **2f**	**3f**	65%
7[d]	R = CH_2NHCbz **2g**	**3g**	81%
8[d]	R = CH_2CO_2Et **2h**	**3h**	55%
9[d]	R = $C_2H_4NH(CbzVal)$ **2i**	**3i**	62%
10[d]	R = Phenyl **2j**	**3j**	70%
11[d]	R = 4-BrPhenyl **2k**	**3k**	67%
12	R = 4-MeOPhenyl **2l**	**3l**	67%
			
13	R^2 = Hexyl **2m**	**3m**	68%
14[e]	R^2 = Methyl **2n**	**3n**	73%
15[d]	R^2 = Bromo **2o**	**3o**	61%
16	 **2p**	 **3p**	63%
17[f]	 **2q**	 **3q**	70%
18[g]	 **2q**	 **3r**	71%
19	 **2r**	 **3s**	48%
20[h]	 **2s**	 **3t** **3u**	65%
21[h]	 **2t**	 **3v**	73%

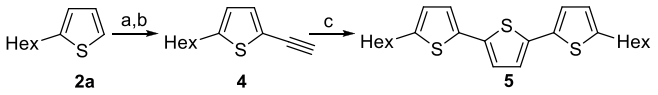
[a] Reaction conditions: 0.40 mmol **2**, 0.48 mmol **1**, 5 mol % AuCl, 0.48 mmol TFA, 0.2 M, rt, 12-60 h. Isolated yields are given.[b] Thiophene used as solvent. [c] Without TFA. [d] 2 equiv **1** and TFA, 10 mol% AuCl, 0.4 M. [e] 85% pure by NMR. [f] Without TFA, 1 equiv **1**, 3 equiv **2q**. [g] 2.2 equiv **1** and TFA. [h]1.5 equiv **1** and TFA.

The scope of the reaction was then examined. 2-Alkyl substituted thiophenes were alkynylated in good yields (Table 2, Entries 1-2). Monoalkynylation of thiophene (**2c**) was achieved using **2c** as solvent without TFA (Entry 3). 2-Methoxythiophene (**2d**) was also alkynylated without TFA (Entry 4).[15] The reaction was tolerant towards functional groups such as alcohols, carbamates, esters and amides, including a protected amino acid (Entries 5-9). The reaction was slower in the presence of protected amines or esters and full conversion could not be achieved under standard conditions. Fortunately, the use of 10% catalyst, two equivalents of **1** and TFA at higher concentration afforded the desired products in moderate to good yields (Entries 7-9). Only traces of product were observed for less nucleophilic substrates with electron-withdrawing groups directly attached to thiophene. [16]

We then turned to 2-aryl thiophenes, as substrates with extended π systems are more useful for application in materials science (Entries 10-12). Gratifyingly, full conversion could be achieved (Entries 10-11). 4-Bromophenylthiophene (**2k**) could be successfully alkynylated, demonstrating the orthogonality of the method to classical cross-coupling reactions (Entry 11). The alkynylation of 2,2'-bithiophenes gave useful building blocks for the elaboration of oligothiophenes (Entries 13-15).[2] 3-Methoxythiophene was selectively alkynylated in 2-position (Entry 16). 3,4-Ethylene-dioxythiophene (EDOT, **2q**), could be either mono- or bis-alkynylated depending on the reaction stoichiometry (Entries 17-18). 2,5-Methylthiophene (**2r**) furnished the 3-substituted alkynylated product **3s** in 48% yield (Entry 19). Less reactive benzothiophenes were then investigated. Gratifyingly, full conversion was obtained with 5 mol % AuCl for benzothiophene (**2s**), but no regioselectivity was observed (Entry 20).[17] Finally, 3-methylbenzothiophene (**2t**) afforded **3v** in 73% yield (Entry 21).

Our methodology allowed a rapid access to oligothiophenes (Scheme 1). 2-Hexylthiophene (**2a**) was alkynylated under standard conditions and deprotected to afford acetylene **4** in 78% yield. Instead of the reported two steps sequence,[18] we developed a one pot procedure involving copper-mediated dimerization and cyclization with Na_2S to give terthiophene **5** in 86% yield.

We[7] and others[6k] have proposed that the Au-catalyzed alkynylation could proceed either via a Au(III) acetylide complex or via π-activation of the triple bond. A mechanism involving reaction on the iodine atom or SET electron-transfer[19] appeared less probable, as it would be difficult to rationalize the role of the metal catalyst. However, it cannot be excluded yet at this stage. The cooperative effect observed here with Brønsted acids is particularly intriguing. TFA could promote the 2-auration of thiophene.[20] However, no product was obtained when **2**-[(triphenylphosphine)gold]thiophene[21] was treated with **1** with or without TFA. TFA could also activate TIPS-EBX (**1**).[9g-h] No product was observed when using the TfOH adduct of TIPS-EBX (**1**), but 54% GC yield was obtained when using the TFA adduct.[22]. At this point, it is not sure yet if the latter represented an activated form of the reagent, or just served as a source of TFA during the reaction. Stoichiometric mixtures of AuCl and **1** gave 2-iodobenzoic acid and 1,4-bis(tri*iso*propylsilyl)buta-1,3-diyne, and no strong effect of TFA was observed.[23] No Au-bond intermediate could be detected. These results did not allow us to discriminate with certitude between an oxidative or a π-activation mechanism. More investigation will be needed to understand the mechanism and the Brønsted acid effect.



Scheme 1. Straightforward synthesis of terthiophene **5**. Reaction conditions: a) 1.2 equiv **1**, 1.2 equiv TFA, 5 mol % AuCl, CH_3CN, RT; b) 1.2 equiv TBAF, THF, 0 °C, 78% over 2 steps; c) 2 equiv $Cu(OAc)_2$, CH_3CN, 80 °C, then 4 equiv $Na_2S•3H_2O$, 80 °C, 18 h, 86%.

In summary, we have reported the first direct alkynylation of thiophenes mediated by gold and TFA at room temperature. The unique reactivity of TIPS-EBX (**1**) was crucial for the success of the reaction. Activation by both the gold catalyst and the Brønsted acid was required, and the discovery of this cooperative effect is expected to significantly expand the scope of benziodoxolone-based alkynylation reactions. The scope included deactivated conjugated systems, such as aryl thiophenes, bithiophenes and benzothiophenes, which are important for organic materials. Mechanism investigation and extension of the scope are currently ongoing in our laboratory.

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[10] The effect of the Brønsted acid described here is different from the reported acceleration of a proto-deauration step. See: A. S. K. Hashmi, *Catal. Today* **2007**, *122*, 211.

[11] See supporting information.

[12] The success of TIPS-EBX (**1**) is probably due to steric shielding, which prevents side reactions.

[13] For comparison, the corresponding TMS-acetylene was obtained in two steps and 72% yield from 2-hexyl thiophene (**2a**) using a bromination-Sonogashira sequence: A. van Breemen, P. T. Herwig, C. H. T. Chlon, J. Sweelssen, H. F. M. Schoo, S. Setayesh, W. M. Hardeman, C. A. Martin, D. M. de Leeuw, J. J. P. Valeton, C. W. M. Bastiaansen, D. J. Broer, A. R. Popa-Merticaru, S. C. J. Meskers, *J. Am. Chem. Soc.* **2006**, *128*, 2336.

[14] V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz, A. J. Simonsen, *J. Org. Chem.* **1996**, *61*, 6547. The synthesis of **1** proceeded in 79% yield over 2 steps from 2-iodobenzoic acid on a 30 g scale. This compound will soon be commercially available.

[15] For electron-rich thiophenes, the higher reactivity observed in presence of TFA is sometimes counterbalanced by acid-mediated decomposition. In some cases, better yields are obtained without TFA. The best conditions are given in Table 2.

[16] 2-bromo-3-hexyl-, 2-formyl- and 3-acetyl- thiophenes were tested.

[17] The low regioselectivity observed for benzothiophene could not yet be rationalized at this stage.

[18] J. Kagan, S. K. Arora, *J. Org. Chem.* **1983**, *48*, 4317.

[19] a) V. V. Grushin, *Acc. Chem. Res.* **1992**, *25*, 529. b) T. Dohi, M. Ito, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Angew. Chem.* **2010**, *122*, 3406; *Angew. Chem., Int. Ed.* **2010**, *49*, 3334. When the reaction was run in the presence of BHT (3,5-di-*tert*-butyl-4-hydroxytoluol), full conversion was obtained, but the reaction was prevented by the addition of TEMPO. However, the result with TEMPO could also be due to oxidative degradation of the catalyst.

[20] For selected examples of auration of aromatic C-H bonds, see: a) Z. G. Li, D. A. Capretto, R. O. Rahaman, C. He, *J. Am. Chem. Soc.* **2007**, *129*, 12058; b) P. F. Lu, T. C. Boorman, A. M. Z. Slawin, I. Larrosa, *J. Am. Chem. Soc.* **2010**, *132*, 5580. For examples of reactions of organogold intermediates with oxidants, see: c) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592-597. For a selected review on gold catalysis, see: e) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180.

[21] F. Bonati, A. Burini, B. R. Pietroni, R. Galassi, *Gazz. Chim. Ital.* **1993**, *123*, 691. $AuPPh_3Cl$ itself was a viable catalyst for the reaction, although less efficient than AuCl (see supporting information).

[22] The TfOH adduct of **1** is a well-behaved solid compound that could be fully characterized (see supporting information). In contrast, the TFA adduct gave an oil upon evaporation of the solvent, and further studies are ongoing to determine its structure.

[23] 1,4-bis(tri*iso*propylsilyl)buta-1,3-diyne and 2-iodo benzoic acid were detected as the major products by ^{1}H-NMR and GC-MS, but could not be separated from other impurities formed during the reaction.

C-H Functionalization

Jonathan P. Brand and Jérôme Waser
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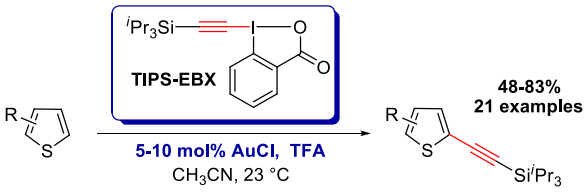
Direct Alkynylation of Thiophenes: Cooperative Activation of TIPS-Ethynyl-Benziodoxolone with Gold and Brønsted Acids.



Together stronger! Cooperative activation of the hypervalent iodine reagent TIPS-EBX with a gold catalyst and a Brønsted acid allowed the first direct ethynylation of thiophenes at room temperature. The obtained ethynyl thiophenes are important building blocks for organic dyes and electronic materials.

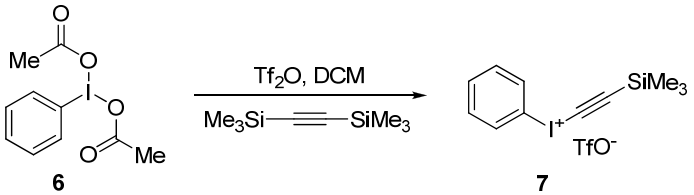
Table of content

1. General Methods

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et_2O, CH_3CN, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 10 ppm, *Karl-Fischer* titration). NEt_3 and pyridine were distilled under nitrogen from KOH. Gold chloride was purchased from Aldrich and kept in desiccator under anhydrous condition (decrease of reactivity has been observed for catalyst if prolonged exposition to air (*ca* 1 month). All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure.TLC was performed on Merck silica gel 60 F_{254} TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation).^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a Brucker DPX-400 100 MHz spectrometer in chloroform-d, DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm^{-1} (w = weak, m = medium, s = strong, br = broad). Gas chromatographic and low resolution mass spectrometric measurements were performed on a Perkin-Elmer Clarus 600 gas chromatographer and mass spectrometer using a Perkin-Elemer Elite fused silica column (length: 30 m, diameter: 0.32 mm) and Helium as carrier gas. High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. HPLC measurement were done on a JASCO HPLC system with an AS2055 Autosampler, a PU 2089 Pump, a UV 2075 detector and a SEDEX 85 (SEDERE) detector using a CHIRALPAK IC column from DAICEL Chemical Industries Ltd. HPLC grade solvents from Sigma-Aldrich were used.

2. Preparation of Reagents

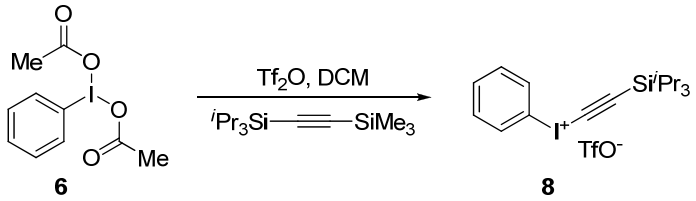
Phenyl(trimethylsilylethynyl)iodonium triflate (7).



6 **7**

Following a reported procedure,[1] phenyliodonium diacetate (**6**) (3.22 g, 10.0 mmol, 1.00 equiv) was diluted with CH_2Cl_2 (10 mL) and the mixture was stirred for 5 minutes. Tf_2O (0.67 mL, 5.0 mmol, 0.50 equiv.) was added dropwise at 0 °C and the resulting yellow mixture was stirred 30 min. Bis(trimethylsilyl)acetylene (2.28 mL, 10.0 mmol, 1.00 equiv) was added. The mixture was then stirred 2 h and diethyl ether was added to precipitate the product. Filtration afforded **7** (2.11 g, 4.67 mmol, 47% yield) as a colorless solid. Mp (Dec.) 139-145°C; Lit.:[1] 143-146°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 2 H, ArH), 7.66 (s, 1 H, ArH), 7.55 (m, 2 H, ArH), 0.24 (s, 9 H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 132.4, 132.2, 119.7 (q, ^1J(C,F) = 319 Hz), 119.1, 116.2, 43.3, -1.1. IR ν 1448 (w), 1286 (m), 1253 (m), 1236 (s), 1222 (s), 1161 (m), 1026 (s), 988 (w), 863 (m), 847 (s), 742 (w), 714 (m), 678 (w), 637 (s). Characterization data of **11** corresponded to the literature values. [1]

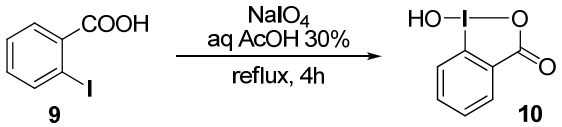
Phenyl(tri*iso*propylsilyl)iodonium triflate (8)



6 **8**

Following a slight modification of the reported procedure, [1] phenyliodonium diacetate (**6**) (2.53 g, 7.85 mmol, 1.00 equiv) was diluted with CH_2Cl_2 (7 mL) and the mixture was stirred for 5 minutes. Tf_2O (0.60 mL, 3.9 mmol, 0.50 equiv.) was added dropwise at 0 °C and the resulting yellow mixture was stirred 30 min. (Trimethylsilyl)(tri*iso*propylsilyl)acetylene (2.00 g, 7.86 mmol, 1.00 equiv) was added and the mixture was then stirred 2 h. Water was then added (30 mL) followed by extraction of the aqueous layer with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The resulting solid was triturated in hexane (10 mL). Filtration and removal of solvent in vacuo afforded phenyl(tri*iso*propylsilyl)iodonium triflate (**8**) (2.90 g, 11.2 mmol, 70% yield) as a colorless solid. Mp 109-114°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (m, 2 H, Ar*H*), 7.65 (m, 1 H, Ar*H*), 7.52 (m, 2 H, Ar*H*), 1.15-1.01 (m, 21 H, TIPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 132.5, 132.4, 119.7, 117.6, 117.6, 44.9, 18.3, 11.1. IR ν 3288 (w), 3088 (m), 2949 (m), 2894 (m), 2869 (w), 1563 (m), 1467 (w), 1451 (w), 1388 (w), 1281 (s), 1236 (s), 1221 (s), 1174 (s), 1068 (w), 1028 (s), 988 (m), 916 (m), 884 (m), 736 (s), 679 (m), 639 (s). HRMS (ESI) calcd for $C_{17}H_{26}ISi^+$ (M-OTf) 385.0843; found 385.0812.

1-Hydroxy-1,2-benziodoxol-3(*1H*)-one (**13**)



9 **10**

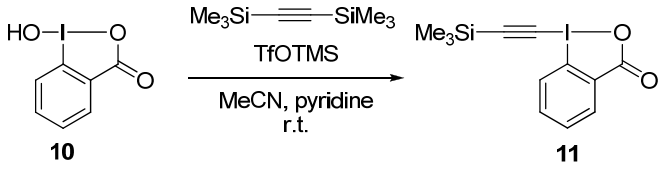
Following a reported procedure,[2] $NaIO_4$ (6.7 g, 31 mmol; 1.0 equiv) and 2-iodobenzoic acid (**9**) (7.4 g, 30 mmol, 1.0 equiv) were suspended in 30% (v:v) aq. AcOH (45 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (120 mL) and allowed to cool to room temperature, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 30 mL) and acetone (3 x 30 mL), and air-dried in the dark to give the pure

[1] T. Kitamura, M. Kotani, Y. Fujiwara, *Synthesis* **1998**, *10*, 1416. HRMS data were not reported, as the compound is too unstable for detection of the molecule ion.

[2] L. Kraszkiewicz, L. Skulski, *Arkivoc* **2003**, *6*, 120.

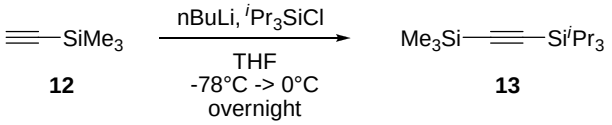
product **10** (7.3 g, 19 mmol, 92% yield) as a colorless solid. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.02 (dd, *J* = 7.7, 1.4 Hz, 1 H, Ar*H*), 7.97 (m, 1 H, Ar*H*), 7.85 (dd, *J* = 8.2, 0.7 Hz, 1 H, Ar*H*), 7.71 (td, *J* = 7.6, 1.2 Hz, 1 H, Ar*H*). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4. IR ν 3083 (w), 3060 (w), 2867 (w), 2402 (w), 1601 (m), 1585 (m), 1564 (m), 1440 (m), 1338 (s), 1302 (m), 1148 (m), 1018 (w), 834 (m), 798 (w), 740 (s), 694 (s), 674 (m), 649 (m).

1-[(Trimethylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TMS-EBX, 11)



Following a slight modification of the reported procedure,[3] trimethylsilyl triflate (5.54 mL, 30.7 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (**10**) (7.36 g, 28.0 mmol, 1 equiv) in CH_2Cl_2 (85 mL) at RT. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of bis(trimethylsilyl)acetylene (6.98 mL, 30.7 mmol, 1.1 equiv). The resulting suspension was stirred for 6 h at RT, during this time a white solid was formed. A saturated solution of $NaHCO_3$ was then added and the mixture was stirred vigorously until completely solubilization of the white solid. The two layers were separated and the combined organic extracts were washed with sat. $NaHCO_3$, dried over $MgSO_4$, filtered and evaporated under reduced pressure. Recrystallization from acetonitrile (5 mL) afforded **11** (7.17 g, 20.8 mmol, 74%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.42 (dd, *J* = 6.4, 1.9 Hz, 1 H, Ar*H*), 8.19 (m, 1 H, Ar*H*), 7.78 (m, 2 H, Ar*H*), 0.32 (s, 9 H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) 166.4, 134.9, 132.6, 131.7, 131.4, 126.1, 117.2, 115.4, 64.2, -0.5. IR ν 3389 (w), 2967 (w), 1617 (s), 1609 (s), 1562 (m), 1440 (w), 1350 (m), 1304 (w), 1254 (w), 1246 (w), 1112 (w), 1008 (w), 852 (s), 746 (m), 698 (m), 639 (m). The characterization data for compounds **11** corresponded to the reported values. [3]

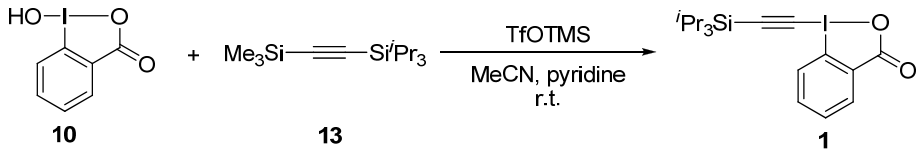
Tri*iso*propylsilyl trimethylsilylacetylene (13)



Following a reported procedure,[4] *n*-butyllithium (2.5 M in hexanes, 12.0 mL, 29.9 mmol, 0.98 equiv) was added dropwise to a stirred solution of ethynyltrimethylsilane (**12**) (3.0 g, 30 mmol, 1.0 equiv) in THF (48 mL) at -78 °C. The mixture was then warmed to 0 °C and stirred for 5 min. The mixture was then cooled back to -78 °C and chlorotri*iso*propylsilane (6.4 mL, 30 mmol, 1.0 equiv) was added dropwise. The mixture was then allowed to warm to room temperature and stirred overnight. A saturated solution of ammonium chloride (40 mL) was added, and the reaction mixture was extracted with diethyl ether (2 x 60 mL). The organic layer was washed with water and brine, then dried over $MgSO_4$, filtered and concentrated under reduced pressure to obtain a colorless liquid which was further purified by Kugelrohr distillation (56-57°C/0.25 mmHg) to yield **13** (7.16 g, 28.0 mmol, 92% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.08 (m, 21 H, TIPS), 0.18 (s, 9 H, TMS). IR ν 2959 (m), 2944 (m), 2896 (w), 2867 (m), 1464 (w), 1385 (w), 1250 (m), 996 (w), 842 (s), 764 (s), 675 (m), 660 (m). Characterization data of **13** corresponded to the literature values. [4]

[3] V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz, A. J. Simonsen, *J. Org. Chem.* **1996**, *61*, 6547.
[4] C J. Helal, P. A Magriotis, E. J. Corey, *J. Am. Chem. Soc.* **1996**, *118*, 10938.

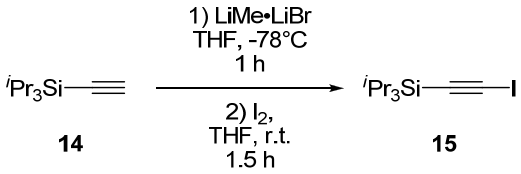
1-[(Tri*iso*propyllsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX, 1)



10 **13** **1**

Following a reported procedure, [3] 2-iodosylbenzoic acid (**10**) (21.7 g, 82.0 mmol, 1.0 equiv) was charged in oven-dried three-neck 1L flask equipped with a magnetic stirred. After 3 vacuum/nitrogen cycles, anhydrous acetonitrile (500 mL) was added via canula and cooled to 4 °C. Trimethylsilyltriflate (16.4 mL, 90.0 mmol, 1.1 equiv) was added dropwise via a dropping funnel over 30 min (no temperature increase was observed). After 15 min, (trimethylsilyl)(tri*iso*propylsilyl)acetylene (**13**) (23.0 g, 90.0 mmol, 1.1 equiv) was added via canula over 15 min (no temperature increase was observed). After 30 min, the suspension became an orange solution. After 10 min, pyridine (7.0 mL, 90 mmol, 1.1 equiv) was added via syringe. After 15 min, the reaction mixture was transferred in a one-neck 1L flask and reduced under vacuum until a solid was obtained. The solid was dissolved in DCM (200 mL) and transferred in a 1L separatory funnel. The organic layer was added and washed with 1 M HCl (200 mL) and the aqueous layer was extracted with CH_2Cl_2 (200 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (2 x 200 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (*ca* 120 mL) afforded **1** (30.1 g, 70.2 mmol, 86%) as colorless cristals.[5] Mp (Dec.) 170-176°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (m, 1 H, Ar*H*), 8.29 (m, 1 H, Ar*H*), 7.77 (m, 2 H, Ar*H*), 1.16 (m, 21 H, TIPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 134.6, 132.3, 131.4, 131.4, 126.1, 115.6, 114.1, 64.6, 18.4, 11.1. IR ν 2943 (m), 2865 (m), 1716 (m), 1618 (m), 1604 (s), 1584 (m), 1557 (m), 1465 (m), 1439 (w), 1349 (m), 1291 (m), 1270 (w), 1244 (m), 1140 (m), 1016 (m), 999 (m), 883 (m), 833 (m), 742 (m), 702 (s), 636 (m). Characterization data of **1** corresponded to the literature values. [3]

(Iodoethynyl)tri*iso*propylsilane (15)



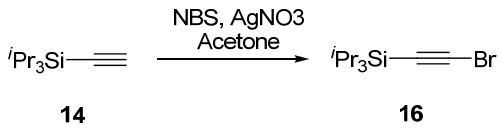
14 **15**

Following a reported procedure,[6] MeLi·LiBr (1.5 M in diethyl ether, 1.1.mL, 1.6 mmol, 1.0 equiv) was added to a stirred solution of tri*iso*propylsilylacetylene (**14**) (0.36 mL, 1.6 mmol, 1.0 equiv) in dry THF (1.8 mL), cooled at -78 °C, and the mixture was allowed to react for 1 h at that temperature. A solution of I_2 (457 mg, 1.80 mmol, 1.25 equiv) in dry THF (2.7 mL) was then added dropwise and the mixture was stirred for 1.5 h at -78°C. The mixture was then diluted with brine (6 mL) and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic layers were washed with a saturated aqueous solution of $Na_2S_2O_3$ (3 x 20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (SiO_2, hexane) afforded 2-iodo-1-tri*iso*propylsilyl acetylene (**15**) (470 mg, 1.52 mmol, 94% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10–1.04 (m, 21 H, TIPS). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 100.8, 18.5, 11.4 (one acetylene carbon was not resolved). Characterization data of **15** corresponded to the literature values. [6]

[5] TIPS-EBX (1) will soon be commercially available from Sigma-Aldrich (catalog number: **Aldrich 728365**).

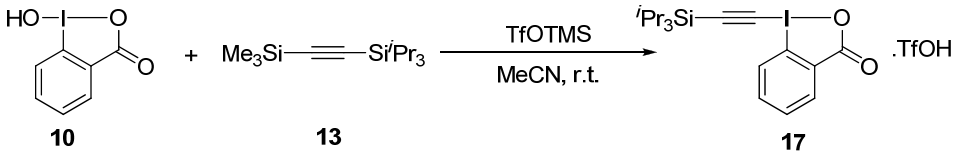
[6] S. López, F. Fernández-Trillo, P. Midón, L. Castedo, L. Saá, *J. Org. Chem.*, **2005**, *70*, 6346.

(Bromoethynyl)tri*iso*propylsilane (16)



Following a reported procedure,[7] NBS (0.62 g, 3.5 mmol, 1.0 equiv) was added in one portion to a solution of tri*iso*propylsilylacetylene (**14**) (0.68 mL, 3.0 mmol, 1.0 equiv) in wet acetone (20 mL). $AgNO_3$ (50 mg, 0.30 mmol, 0.1 equiv) was then added. The reaction was stirred for 2.5 h and then poured in ice-water. The mixture was then extracted twice with pentane (2 x 30 mL). The organic layers were combined, washed with water (30 mL), brine (30 mL), dried over $MgSO_4$ and concentrated under vacuum. The oil was dried overnight under high vacuum to afford **16** (0.70 g, 2.7 mmol, 89%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 21 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.5, 61.7, 18.5, 11.3. Characterization data of **16** corresponded to the literature values. [7]

2-[(Tri*iso*propylsilylethynyl)(trifluoromethanesulfonyloxy)iodo]benzoic acid (17)

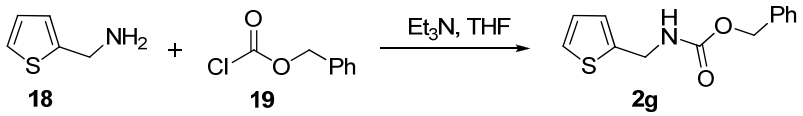


Following a reported procedure, [3] trimethylsilyltriflate (2.8 mL, 15 mmol, 1.4 equiv, freshly distilled) was added dropwise to a stirred solution of 2-iodosylbenzoic acid (**10**) (3.00 g, 11.4 mmol, 1.00 equiv) in DCM (85 mL). After 1 h, (trimethylsilyl)(tri*iso*propylsilyl)acetylene (**13**) (2.76 g, 10.8 mmol, 0.950 equiv) was added dropwise. The mixture was stirred 5 h. The solvent was then removed under reduced pressure and the yellow crude oil was crystallized in Et_2O/hexanes 1/1 to give **17**.[8] An analytical pure sample was obtained by recristallization of a saturated solution in DCM by addition of Et_2O/hexanes 1/1. Mp (Dec.) 156-158°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, 1 H, J = 7.5, 1.7 Hz, ArH), 8.35 (dd, 1 H, J = 8.3, 1.0 Hz, ArH), 7.92 (ddd, J = 8.1, 7.4, 1.7 Hz, ArH), 7.87 (td, 1 H, J = 7.4, 1.1 Hz, ArH), 1.20 (m, 3 H, CH), 1.13 (m, 18 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 137.7, 133.6, 132.3, 128.8, 125.9, 121.9, 120.0 (q, J = 319 Hz), 114.5, 48.2, 18.4, 11.1. IR 3476 (w), 3086 (w), 2947 (m), 2868 (m), 2509 (w), 2255 (w), 1645 (m), 1590 (w), 1464 (w), 1440 (w), 1285 (s), 1226 (s), 1169 (s), 1072 (w), 1026 (s), 999 (m), 912 (m), 883 (m), 804 (w), 713 (s), 680 (s), 641 (s). HRMS(ESI) calcd for $C_{18}H_{26}O_2ISi^+$ (M-OTf) 429.0747, found 429.0736.

3. Starting materials

Substrates **2g**, **2i**, **2l**, **2n** and **2o** were synthesized using the procedures indicated below. The other substrates are commercially available.

Benzyl thiophen-2-ylmethylcarbamate (2g)

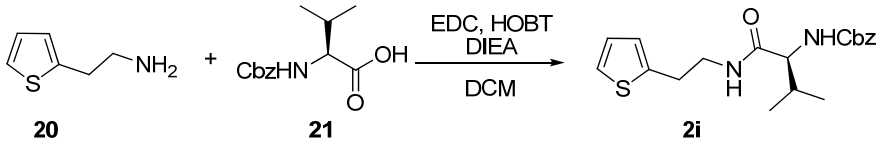


[7] M. X. W. Jiang, M. Rawat, W. D. Wulff, *J. Am. Chem. Soc.* **2004,** 126, 5970

[8] The exact structure of benziodoxolone TfOH adduct has not yet been absolutely defined. See: V. V. Zhdankin, P. J. Stang, *Tetrahedron* **1998**, *54*, 10927.

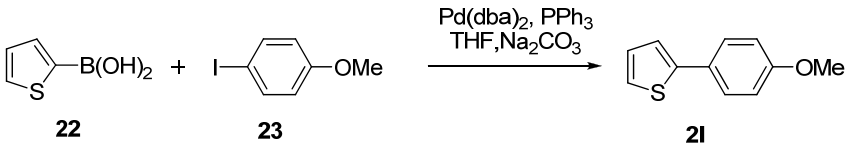
Benzyl chloroformate (**19**) (313 µL, 2.20 mmol, 1.1 equiv) was added to a stirring solution of 2-thiophenemethylamine (**18**) (206 µL, 2.00 mmol, 1 equiv) and Et_3N (306 µL, 2.20 mmol, 1.1 equiv) in THF (10 mL) at 0 °C. The reaction was stirred for one hour and then quenched with 0.1 M HCl (20 mL). The mixture was extracted twice with CH_2Cl_2 (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$, brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting oil was then dried under high vacuum overnight to afford **2g** (500 mg, 2.02 mmol, quant.) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 5 H, ArH), 7.25 (m, 1 H, ArH), 6.98 (m, 2 H, ArH), 5.17 (m, 3 H, CH_2 + NH), 4.58 (d, 2 H, *J* = 5.7 Hz, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 141.5, 136.3, 128.5, 128.2, 128.1, 126.9, 125.8, 125.1, 66.9, 39.9. IR 3416 (w), 3323 (w), 3068 (w), 3032 (w), 2936 (w), 1703 (s), 1515 (s), 1456 (w), 1369 (w), 1329 (w), 1157 (w), 1127 (w), 1045 (w), 975 (w), 910 (w), 853 (w), 836 (w), 777 (w), 735 (m), 698 (s). ^{1}H and ^{13}C NMR are consistent with the reported data.[9]

(*S*)-Benzyl 3-methyl-1-oxo-1-(2-(thiophen-2-yl)ethylamino)butan-2-ylcarbamate (2i)



Diisopropylethylamine (1 mL, 6 mmol, 3 equiv) was added to a stirring solution of Cbz-L-Valine (**21**) (503 mg, 2.00 mmol, 1 equiv) in DCM (15 mL). The reaction was cooled to 0 °C and EDC (421 mg, 2.20 mmol, 1.1 equiv), HOBT (306 mg, 2.20 mmol, 1.1 equiv) and thiophene **20** (436 mg, 2.40 mmol, 1.2 equiv) were added. The reaction was warmed to RT and stirred for 20 h. DCM (10 mL) was then added, the organic layer was washed three times with 5% $KHSO_4$ (30 mL), once with 5% $NaHCO_3$ (30 mL), once with water (30 mL), brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure to afford **2i** (685 mg, 1.90 mmol, 95%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.32 (m, 5 H, ArH), 7.17 (dd, 1 H, *J* = 5.1, 1.1 Hz, thiophene H), 6.95 (dd, 1 H, *J* = 5.1, 3.4 Hz, thiophene H), 6.84 (d, 1 H, *J* = 1.8 Hz, thiophene H), 6.03 (br s, 1 H, NH), 5.32 (br s, 1 H, NH), 5.12 (s, 2 H, OCH_2), 3.93 (dd, 1 H, *J* = 8.8, 6.2 Hz, C*H*CH$(CH_3)_2$), 3.67-3.46 (m, 2 H, CH_2CH_2NH), 3.05 (t, 2 H, *J* = 6.5 Hz, CH_2CH_2NH), 2.14 (m, 1 H, CHC*H*$(CH_3)_2$), 0.96 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.91 (d, 3 H, *J* = 6.8 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 156.4, 140.9, 136.2, 128.6, 128.2, 128.1, 127.1, 125.5, 124.0, 67.1, 60.6, 40.8, 30.9, 29.9, 19.3, 17.7. IR 3294 (m), 3109 (w), 2959 (w), 2872 (w), 1688 (s), 1647 (s), 1539 (s), 1456 (w), 1388 (w), 1340 (w), 1297 (m), 1248 (s), 1139 (w), 1039 (m), 968 (w), 913 (w), 846 (w), 744 (m), 698 (s). HRMS(ESI) calcd for $C_{19}H_{25}N_2O_3Si^+$ (M+H) 361.1586, found 361.1570.

2-(4-Methoxyphenyl)thiophene (2l)

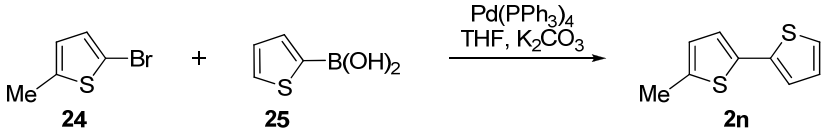


Following a reported procedure,[10] $Pd(dba)_2$ (10 mg, 0.020 mmol, 0.05 equiv), thiophen-2-ylboronic acid (**22**) (128 mg, 1.00 mmol, 2.5 equiv), 4-iodoanisole (**23**) (93 mg, 0.40 mmol, 1 equiv) and PPh_3 (21 mg, 0.04 mmol, 0.1 equiv) were charged in a oven-dried Schlenk tube. The reaction vessel was purged three times with Argon. Na_2CO_3 aq. 20% (3 mL) and THF (3 mL) were added and the reaction refluxed overnight under Ar. The reaction mixture was then diluted in EtOAc (25 mL), washed with water (20 mL), dried over $MgSO_4$ and reduced under vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O

[9] R. N. Salvatore, F. X. Chu, A. S. Nagle, E. A. Kapxhiu, R. M. Cross, K. W. Jung, *Tetrahedron* **2002**, *58*, 3329.
[10] M. Bossi, V. Belov, S. Polyakova, S. W. Hell, *Angew. Chem., Int. Ed.* **2006**, *45*, 7462.

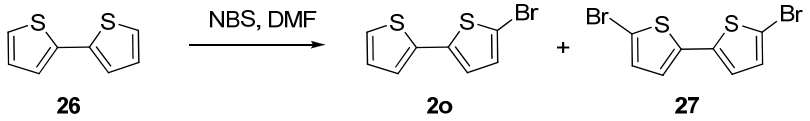
9/1) to afford **2l** (67 mg, 0.35 mmol, 88%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.9 Hz, 1 H, benzene H), 7.21 (m, 2 H, thiophene H), 7.05 (dd, J = 5.1, 3.6 Hz, 1 H, thiophene H), 6.92 (d, J = 8.9 Hz, 2 H, benzene H), 3.84 (s, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 144.4, 128.0, 127.4, 127.3, 123.9, 122.1, 114.3, 55.4. Characterization data of **2l** corresponded to the literature values.[11]

5-Methyl-2,2'-bithiophene (2n)



Following a reported procedure,[12] $Pd(PPh_3)_4$ (50 mg, 0.040 mmol, 0.03 equiv) was charged in a oven-dried two-neck flask. The reaction vessel was purged twice with N_2. THF (10 mL), K_2CO_3 aq. (2.5 M, 3 mL) and 2-bromo-5-methylthiophene (**24**) (165 µL, 2.00 mmol, 1 equiv) were then added. After 5 min stirring, thiophen-2-ylboronic acid (**25**) (256 mg, 2.00 mmol, 1 equiv) was added in one portion. The solution was degassed by three freeze-pump-thaw cycles. The reaction was refluxed overnight. Cold water (20 mL) was added and the water layer was extracted three times with Et_2O (20 mL). The organic layers were combined, washed with water (30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by column chromatography (pentane) to afford **2n** (246 mg, 1.37 mmol, 68%) as a colorless oil. R*f* 0.5 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 5.1 Hz, 1 H, ArH), 7.15 (d, J = 3.2 Hz, 1 H, ArH), 7.07-7.01 (m, 2 H, ArH), 6.71 (dd, J = 2.4, 0.8 Hz, 1 H, ArH), 2.53 (s, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.0, 135.3, 127.8, 126.1, 123.9, 123.8, 123.2, 15.5. IR 3106 (w), 3068 (w), 2946 (w), 2917 (w), 2858 (w), 1796 (w), 1734 (w), 1588 (w), 1520 (m), 1473 (w), 1427 (m), 1380 (w), 1354 (w), 1231 (m), 1205 (m), 1163 (w), 1080 (w), 1050 (m), 909 (w), 886 (w), 837 (s), 793 (s), 740 (w), 690 (s). ^{1}H and ^{13}C NMR are consistent with the reported data. [10]

5-Bromo-2,2'-bithiophene (2o)



Following a reported procedure, [12] N-Bromosuccinimide (660 mg, 3.15 mmol, 1.05 eq) dissolved in DMF (5 mL) was added to a stirring solution of 2,2'-bithiophene (**26**) (0.5 g, 3 mmol, 1 eq) in DMF (10 mL). After 4 h, the reaction was poured into HCl (0.25 M, 300 mL) and stirred for 30 min. The suspension was filtered, the solid was dissolved in DCM (50 mL), washed three times with brine (3 x 40 mL), dried over $MgSO_4$, and the solvent was removed under vacuum. The resulting oil was purified by column chromatography (pentane) to afford **2o** (275 mg, 1.12 mmol, 37%) as a slightly green solid. The product obtained from the remaining mixed fractions was recristallized from MeOH to obtain **27** (83 mg, 0.26 mmol, 9%) as a slightly green solid.

2o

R*f* 0.7 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, 1 H, J = 5.1 Hz), 7.11 (d, 1 H, J = 3.6 Hz), 7.01 (dd, 1 H, J = 5.0, 3.7 Hz), 6.97 (m, 1 H), 6.92 (d, 1 H, J = 3.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ

[11] S. E. Denmark, J. D. Baird, *Org. Lett.* **2006**, *8*, 793.
[12] N. Xie, Y. Chen, *New J. Chem.* **2006**, *30*, 1595.

138.9, 136.4, 130.5, 127.8, 124.8, 124.0, 123.8, 110.9. ^{1}H NMR and ^{13}C NMR are consistent with the reported data.[13]

27

R*f* 0.6 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, 1 H, *J* = 3.8 Hz), 6.85 (d, 1 H, *J* = 3.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 130.7, 124.1, 111.5. ^{1}H NMR is consistent with the reported data.[14]

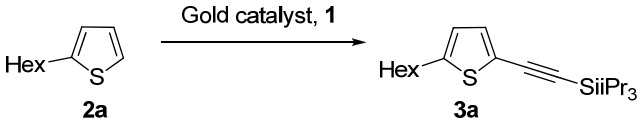
4. Alkynylation reaction

Optimization procedure:

TFA (18 µL, 0.24 mmol, 1.2 equiv) and **1** (103 mg, 0.240 mmol, 1.2 equiv) were added to a stirring solution of catalyst (0.010 mmol, 0.05 equiv) and 2-hexylthiophene (**2a**) (36 µL, 0.20 mmol, 1.0 equiv) in the indicated solvent (0.5 mL) under N_2 (see Table S1). The reaction was sealed and stirred at room temperature for 12-15 h. The reaction mixture was concentrated *in vacuo*. The residue was diluted with dichloromethane (1 mL, solution **A**). 0.1 mL of a solution of pentadecane 0.07 M in dichloromethane and 0.8 mL of dichloromethane were added to 0.1 mL of solution **A**. The resulting solution was injected into GC-MS and the following oven program was followed: Initial temperature: 50°C, Ramp: 10.0 °C/min to 250 °C, hold 25 min at 250 °C. Retention times: 2-hexylthiophene (**2a**): 13.80 min, pentadecance: 16.80min, ((5-Hexylthiophen-2-yl)ethynyl)tri*iso*propylsilane (**3a**) : 31.77 min.

[13] M. Frigoli, C. Moustrou, A. Samat, R. Guglielmetti, *Helv. Chim. Acta* **2000**, *83*, 3043.
[14] U. Dahlmann, R. Neidlein, *Helv. Chim. Acta* **1996**, *79*, 755.

Table S1. Reaction optimization: Catalyst and Solvent Effects

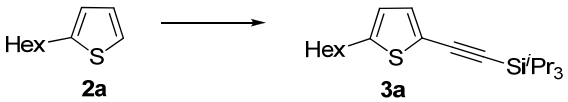


entry	Catalyst	Solvent	[M]	Additive	T (°C)	Yield (%)[a]
1	AuCl	CH_3CN	0.2	TFA	r.t.	94
2	AuCl	THF	0.2	TFA	r.t.	55
3	AuCl	DCM	0.2	TFA	r.t.	65
4	AuCl	^{i}PrOH	0.2	TFA	r.t.	61
5	AuCl	Et_2O	0.2	TFA	r.t.	63
6	$AuCl_3$	CH_3CN	0.2	TFA	r.t.	17
6	$NaAuCl_4$	CH_3CN	0.2	TFA	r.t.	0
7	PPh_3AuCl	CH_3CN	0.2	TFA	r.t.	55
8	NHCAuCl [b]	CH_3CN	0.2	TFA	r.t.	0
9	$PPh_3AuCl+AgBF_4$	CH_3CN	0.2	TFA	r.t.	67

[a]Reaction conditions: 0.20 mmol **2a**, 0.24 mmol **1** and 0.01 mmol catalyst under N_2 for 12-15 h. GC Yields using pentadecane as reference. [b]Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold(I)

Reagents **11, 12, 13, 18, 19** did not afford any product under standard conditions.

((5-Hexylthiophen-2-yl)ethynyl)tri*iso*propylsilane (3a)



To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN [15] (2 mL) was added 2-hexylthiophene (**2a**) (72 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **3a** (116 mg, 0.333 mmol, 83 %) as slightly yellow oil.

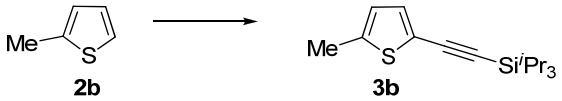
Large scale procedure:

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.01 equiv) in CH_3CN (10 mL) was added 2-hexylthiophene (**2a**) (360 µL, 2.00 mmol, 1 equiv) under air. After 2 min, TFA (0.18 mL, 2.4 mmol, 1.2 equiv) and **1** (1.03 g, 2.40 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 4 days. Et_2O (50 mL) was added, the organic layer was washed twice with 0.1 M NaOH (75 mL). The aqueous layers were combined and extracted with Et_2O (100 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (100 mL), brine (100 mL), dried with $MgSO_4$ and concentrated under

[15] Commercially available solvent was used without drying or purification.

reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **3a** (588 mg, 1.69 mmol, 84 %) as slightly yellow oil. 2-Iodobenzoic acid was recovered by adjusting the pH of the NaOH fraction to 2 with 1 M HCl and extracting with Et_2O (2x100 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure to afford 2-iodobenzoic acid (**9**) (513 mg, 2.07 mmol, 86% recovered) as a colorless solid. R*f* 0.6 (pentane, UV). ^{1}H NMR δ 7.08 (d, *J* = 3.5 Hz, 1 H, ArH), 6.65 (d, *J* = 3.5 Hz, 1 H, ArH), 2.80 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.68 (m, CH_2), 1.44-1.30 (m, 6 H, CH_2), 1.15 (m, 21 H, TIPS), 0.93 (t, *J* = 6.1 Hz, 3 H, CH_3). ^{13}C NMR δ 148.1, 132.4, 123.9, 121.0, 99.8, 94.3, 31.7, 31.6, 30.2, 28.7, 22.6, 18.7, 14.1, 11.4. IR (cm^{-1}): 2958 (s), 2928 (s), 2865 (s), 2143 (s), 1535 (w), 1463 (s), 1382 (w), 1367 (w), 1243 (w), 1167 (m), 1074 (w), 1018 (m), 997 (m), 920 (w), 883 (s), 800 (s), 757 (s), 736 (s), 678 (s), 658 (s), 633 (s). HRMS(ESI) calcd for $C_{21}H_{37}SSi^+$ (M+H) 349.2385, found 349.2381.

Tri*iso*propyl((5-methylthiophen-2-yl)ethynyl)silane (3b)



2b **3b**

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2-methylthiophene (**2b**) (39 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane) afforded **3b** (89 mg, 0.32 mmol, 80 %) as colorless oil. R*f* 0.5 (pentane, UV). ^{1}H NMR δ 7.06 (d, *J* = 3.5 Hz, 1 H, ArH), 6.63 (qd, *J* = 3.5 Hz, 1.0 Hz, ArH), 2.48 (d, *J* = 1.0 Hz, 3 H, CH_3), 1.15 (m, 21 H, TIPS). ^{13}C NMR δ 141.4, 132.2, 124.7, 120.9, 99.5, 93.9, 18.3, 15.0, 11.0. IR (cm^{-1}): 2943 (s), 2923 (m), 2865 (s), 2143 (s), 1537 (w), 1462 (m), 1383 (w), 1243 (w), 1179 (m), 1154 (m), 1073 (w), 1017 (w), 996 (m), 919 (w), 883 (s), 797 (s), 754 (s), 735 (m), 676 (s), 653 (s). HRMS(ESI) calcd for $C_{16}H_{26}SSiNa^+$ (M+Na) 301.1422, found 301.1411.

Tri*iso*propyl(thiophen-2-ylethynyl)silane (3c)

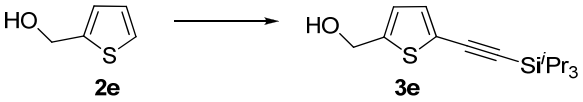
2c **3c**

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in thiophene (**2c**) (500 µL) under air, **1** (171 mg, 0.400 mmol, 1.0 equiv) was added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **3c** (76 mg, 0.29 mmol, 73 %) as colorless oil. R*f* 0.8 (pentane, UV).^{1}H NMR *δ* 7.26 (m, 2 H, ArH), 6.98 (ddd, *J* = 5.0 Hz, 3.6 Hz, 1.0 Hz, 1 H, ArH), 1.17 (m,21 H, TIPS). ^{13}C NMR *δ* 132.4, 127.0, 126.8, 123.7, 99.4, 95.4, 18.7, 11.3. IR (cm^{-1}): 3730 (s), 2943 (s), 2866 (s), 2145 (s), 1463 (m), 1422 (w), 1384 (w), 1233 (w), 1165 (m), 1139 (w), 1076 (m), 997 (m), 920 (m), 883 (s), 854 (m), 830 (m), 758 (s), 737 (s), 699 (s), 676 (s), 660 (s), 634 (s). HRMS(ESI) calcd for $C_{15}H_{25}SSi^+$ (M+H) 265.1446, found 265.1455.

Tri*iso*propyl((5-methoxythiophen-2-yl)ethynyl)silane (3d)

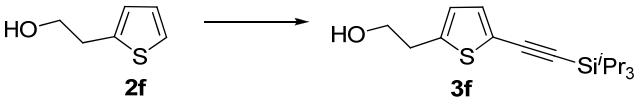
To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2-methoxythiophene (**2d**) (40 µL, 0.40 mmol, 1 equiv) under air. After 2 min, **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/DCM 9/1) afforded **3d** (80 mg, 0.27 mmol, 68 %) as yellow oil. R*f* 0.3 (pentane/DCM 9/1, UV). ^{1}H NMR δ 6.90 (d, J = 4.0 Hz, 1 H, ArH), 6.05 (d, J = 4.0 Hz, 1 H, ArH), 3.88 (s, 3 H, OMe), 1.12 (m, 21 H, TIPS). ^{13}C NMR δ 166.6, 131.1, 110.0, 103.9, 100.2, 92.9, 60.2, 18.7, 11.4. IR (cm^{-1}): 2942 (s), 2865 (s), 2138 (s), 1543 (s), 1486 (s), 1462 (s), 1426 (s), 1384 (w), 1240 (s), 1210 (s), 1165 (m), 1073 (w), 1043 (m), 996 (s), 919 (w), 883 (s), 769 (m), 754 (s), 735 (s), 675 (s), 661 (s). HRMS(ESI) calcd for $C_{16}H_{27}OSSi^+$ (M+H) 295.1552, found 295.1541.

(5-((Tri*iso*propylsilyl)ethynyl)thiophen-2-yl)methanol (3e)



To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added thiophen-2-ylmethanol (**2e**) (51 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **3e** (59 mg, 0.20 mmol, 50 %) as orange oil. R*f* 0.4 (pentane/Et_2O 6/4, UV). ^{1}H NMR δ 7.08 (d, J = 3.6 Hz, 1 H, ArH), 6.83 (dt, J = 3.6 Hz, 0.9 Hz, ArH), 4.75 (d, J = 0.5 Hz, 2 H, CH_2), 2.06 (br s, 1 H, OH), 1.12 (m, 21 H, TIPS). ^{13}C NMR δ 145.6, 132.3, 125.0, 123.7, 99.4, 95.7, 60.1, 18.7, 11.3. IR (cm^{-1}): 3309 (br s), 2943 (s), 2865 (s), 2144 (s), 1463 (s), 1383 (w), 1367 (w), 1243 (w), 1157 (m), 1073 (w), 1013 (s), 998 (s), 920 (w), 883 (s), 805 (s), 761 (s), 736 (s), 677 (s), 634 (s). HRMS(ESI) calcd for $C_{16}H_{27}OSSi^+$ (M+H) 295.1552, found 295.1540.

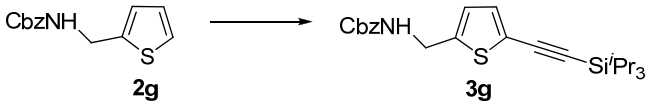
2-(5-((Tri*iso*propylsilyl)ethynyl)thiophen-2-yl)ethanol (3f)



To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added 2-(thiophen-2-yl)ethanol (**2f**) (44 µL, 0.40 mmol, 1 equiv) in CH_3CN (2 mL) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 15 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et_2O 6/4) afforded **3f** (80 mg, 0.26 mmol, 65 %) as yellow oil. R*f* 0.4 (pentane/Et_2O 6/4, UV),^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, 1 H, J = 3.6 Hz, ArH), 6.74 (d, 1 H, J = 3.5 Hz, ArH), 3.86 (t, 2 H, J = 6.3 Hz, C*H*$_2$OH), 3.04 (t, 2 H, J = 6.2 Hz, CH_2), 1.12 (m, 21 H, TIPS). ^{13}C NMR

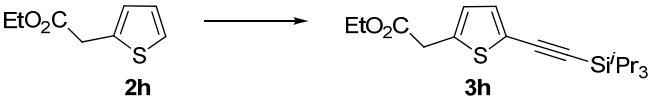
(101 MHz, $CDCl_3$) δ 142.8, 132.4, 125.4, 122.2, 99.5, 94.9, 63.2, 33.5, 18.6, 11.3. IR 3353 (w), 2943 (s), 2865 (s), 2143 (s), 1535 (w), 1463 (m), 1384 (w), 1233 (w), 1165 (m), 1045 (m), 997 (m), 994 (m), 920 (w), 883 (s), 803 (m), 756 (s), 736 (m), 677 (s), 660 (s), 600 (w). HRMS(ESI) calcd for $C_{17}H_{29}OSSi^+$ (M+H) 309.1708, found 309.1698.

Benzyl (5-((tri*iso*propylsilyl)ethynyl)thiophen-2-yl)methylcarbamate (3g)



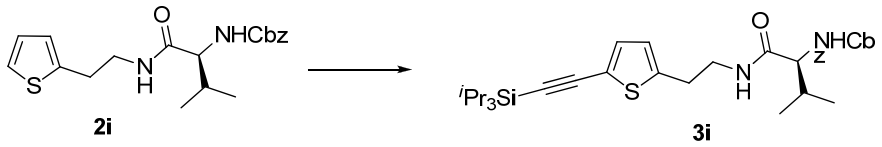
To a stirring solution of AuCl (9.2 mg, 0.040 mmol, 0.1 equiv) was added benzyl thiophen-2-ylmethylcarbamate (**2g**) (100 mg, 0.400 mmol, 1 equiv) in CH_3CN (1 mL) under air. After 2 min, TFA (60 µL, 0.80 mmol, 2.0 equiv) and **1** (342 mg, 0.800 mmol, 2.0 equiv) were added. The reaction was sealed and stirred at RT for 36 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et_2O 6/4) afforded **3g** (139 mg, 0.325 mmol, 81 %, 95% pure by ^{1}H NMR) as orange oil. R*f* 0.3 (pentane/Et_2O 6/4, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 5 H, ArH), 7.05 (d, 1 H, *J* = 3.6 Hz, ArH), 6.80 (m, 1 H, ArH), 5.12 (m, 3 H, CH_2+NH), 4.49 (d, 2 H, *J* = 5.9 Hz, CH_2), 1.09 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 143.1, 136.3, 132.2, 128.6, 128.2, 128.2, 125.4, 123.4, 99.3, 95.6, 67.1, 40.1, 18.7, 11.3. IR 3341 (w), 3033 (w), 2943 (s), 2891 (m), 2865 (s), 2144 (m), 1795 (w), 1702 (s), 1517 (s), 1462 (m), 1366 (w), 1244 (s), 1169 (m), 1129 (m), 1073 (w), 1046 (m), 1017 (m), 991 (m), 920 (w), 883 (s), 806 (w), 736 (s), 697 (s), 677 (s), 660 (s). HRMS(ESI) calcd for $C_{24}H_{34}NO_2SSi$+ (M+H) 428.2079, found 428.2072.

Ethyl 2-(5-((tri*iso*propylsilyl)ethynyl)thiophen-2-yl)acetate (3h)



To a stirring solution of AuCl (9.2 mg, 0.040 mmol, 0.1 equiv) was added ethyl 2-(thiophen-2-yl)acetate (**2h**) (60 µL, 0.40 mmol, 1 equiv) in CH_3CN (1 mL) under air. After 2 min, TFA (60 µL, 0.80 mmol, 2.0 equiv) and **1** (342 mg, 0.800 mmol, 2.0 equiv) were added. The reaction was sealed and stirred at RT for 20 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et_2O 9/1) afforded **3h** (78 mg, 0.22 mmol, 55 %) as orange oil. R*f* 0.3 (pentane/Et_2O 9/1, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, 1 H, *J* = 3.6 Hz, ArH), 6.77 (dt, 1 H, *J* = 3.6, 0.9 Hz, ArH), 4.18 (q, 2 H, *J* = 7.1 Hz, OCH_2), 3.77 (d, 2 H, *J* = 0.8 Hz, CH_2), 1.28 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.11 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 136.8, 132.1, 126.5, 123.3, 99.3, 95.3, 61.3, 35.7, 18.6, 14.1, 11.3. IR 2943 (s), 2866 (s), 2144 (m), 1742 (s), 1536 (w), 1463 (m), 1385 (w), 1369 (w), 1309 (w), 1265 (w), 1226 (m), 1178 (s), 1164 (s), 1113 (w), 1028 (m), 997 (m), 920 (w), 883 (s), 804 (m), 754 (m), 738 (s), 676 (s). HRMS(ESI) calcd for $C_{19}H_{31}O_2SSi^+$ (M+H) 351.1814, found 351.1799.

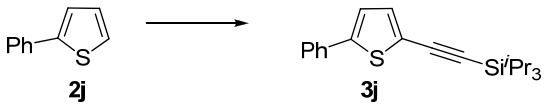
(*S*)-Benzyl-3-methyl-1-oxo-1-(2-(5-((triisopropylsilyl)ethynyl)thiophen-2-yl)ethylamino)butan-2-ylcarbamate (3i)



2i **3i**

To a stirring solution of AuCl (9.2 mg, 0.040 mmol, 0.1 equiv) was added **2i** (144 mg, 0.40 mmol, 1 equiv) in CH_3CN (1 mL) under air. After 2 min, TFA (60 µL, 0.80 mmol, 2.0 equiv) and **1** (342 mg, 0.800 mmol, 2.0 equiv) were added. The reaction was sealed and stirred at RT for 36 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et_2O 6/4) afforded **3i** (133 mg, 0.25 mmol, 62 %, 95% pure by ^{1}H NMR) as yellow oil. R*f* 0.3 (pentane/Et_2O 6/4, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5 H, ArH), 7.03 (d, 1 H, *J* = 3.6 Hz, thiophene H), 6.64 (d, 1 H, *J* = 3.1 Hz, thiophene H), 6.38 (br m, 1 H, NH), 5.49 (br d, 1 H, *J* = 8.5 Hz, NH), 5.07 (m, 2 H, OCH_2), 3.94 (dd, 1 H, *J* = 8.5, 6.8 Hz, C*H*CH$(CH_3)_2$), 3.63-3.35 (m, 2 H, CH_2CH_2NH), 2.94 (t, 2 H, *J* = 6.4 Hz, CH_2CH_2NH), 2.09 (m, 1 H, CHC*H*$(CH_3)_2$), 1.11 (s, 21 H, TIPS), 0.93 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.89 (d, 3 H, *J* = 6.7 Hz, CH_3).^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 156.4, 142.9, 136.1, 132.5, 128.5, 128.1, 128.0, 125.3, 122.2, 99.4, 95.1, 67.0, 60.6, 40.6, 30.8, 30.1, 19.3, 18.6, 17.8, 11.3. IR 3289 (m), 3069 (w), 2943 (m), 2866 (m), 2247 (w), 2143 (m), 1690 (s), 1645 (s), 1542 (s), 1467 (m), 1388 (m), 1369 (w), 1296 (m), 1248 (s), 1168 (w), 1138 (w), 1074 (w), 1039 (m), 997 (w), 909 (m), 883 (m), 845 (w), 804 (w), 756 (m), 735 (s), 696 (s), 678 (s). HRMS(ESI) calcd for $C_{33}H_{45}N_2O_3SSi^+$ (M+H) 541.2920, found 541.2914.

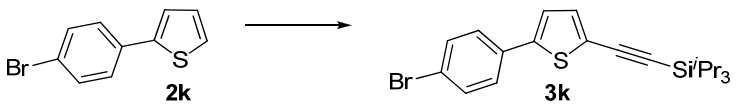
Tri*iso*propyl((5-phenylthiophen-2-yl)ethynyl)silane (3j)



2j **3j**

To a stirring solution of AuCl (9.2 mg, 0.040 mmol, 0.01 equiv) in CH_3CN (1 mL) was added 2-phenylthiophene (**2j**) (64 mg, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (60 µL, 2.0 mmol, 2.0 equiv) and **1** (342 mg, 0.800 mmol, 2.0 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane) afforded **3j** (95 mg, 0.28 mmol, 70 %) as pale yellow oil. R*f* 0.5 (pentane, UV). ^{1}H NMR *δ* 7.62 (m, 2 H, PhH), 7.42 (m, 2 H, PhH), 7.35 (m, 1 H, PhH), 7.24 (d, *J* = 3.8 Hz, 1 H, thiophene H), 7.20 (d, *J* = 3.8 Hz, 1 H, thiophene H), 1.20 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 133.7, 133.4, 128.9, 127.9, 125.8, 123.0, 122.7, 99.5, 96.3, 18.7, 11.4. IR (cm^{-1}): 3064 (w), 2942 (m), 2864 (m), 2141 (m), 2046 (w), 1600 (m), 1494 (m), 1462 (m), 1384 (w), 1245 (w), 1164 (m), 1073 (m), 997 (m), 908 (m), 886 (m), 804 (m), 754 (s), 749 (s), 677 (s), 635 (s). HRMS(ESI) calcd for $C_{21}H_{29}SSi^+$ (M+H) 341.1759, found 341.1755.

((5-(4-Bromophenyl)thiophen-2-yl)ethynyl)tri*iso*propylsilane (3k)



2k **3k**

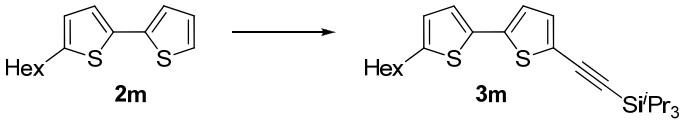
To a stirring solution of AuCl (9.2 mg, 0.040 mmol, 0.01 equiv) in CH_3CN (1 mL) was added 2-(4-bromophenyl)thiophene (**2k**) (96 mg, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (60 µL, 2.0 mmol,

2.0 equiv) and **1** (342 mg, 0.800 mmol, 2.0 equiv) were added. The reaction was sealed and stirred at RT for 48 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane) afforded **3k** (112 mg, 0.267 mmol, 67 %) as yellow oil. R*f* 0.6 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2 H, benzene H), 7.42 (m, 2 H, benzene H), 7.19 (d, 1 H, *J* = 3.8 Hz, thiophene H), 7.13 (d, 1 H, *J* = 3.7 Hz, thiophene H), 1.12 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 133.4, 132.6, 132.0, 127.2, 123.2, 123.1, 121.8, 99.2, 96.8, 18.7, 11.3. IR (cm^{-1}): 2941 (s), 2864 (s), 2141 (m), 1519 (w), 1463 (m), 1382 (w), 1366 (w), 1244 (w), 1161 (w), 1073 (w), 1049 (w), 1017 (w), 997 (m), 920 (w), 883 (s), 794 (s), 755 (s), 734 (s), 677 (s). HRMS(ESI) calcd for $C_{21}H_{28}BrSSi^+$ (M+H) 419.0864, found 419.0877.

Tri*iso*propyl((5-(4-methoxyphenyl)thiophen-2-yl)ethynyl)silane (3l)

To a stirring solution of AuCl (3.1 mg, 0.013 mmol, 0.05 equiv) was added 2-(4-methoxyphenyl)thiophene (**2l**) (52 mg, 0.27 mmol, 1 equiv) in wet CH_3CN (1.4 mL) under air. After 2 min, TFA (24 µL, 0.33 mmol, 1.2 equiv) and **1** (140 mg, 0.330 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 15 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/CH_2Cl_2 8/2) afforded **3l** (66 mg, 0.18 mmol, 67 %) as yellow oil. R*f* 0.6 (pentane/CH_2Cl_2 8/2, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dt, 2 H, *J* = 5.1, 3.1 Hz, benzene H), 7.20 (d, 1 H, *J* = 3.8 Hz, thiophene H), 7.07 (d, 1 H, *J* = 3.8 Hz, thiophene H), 6.94 (td, 2H, *J* = 5.1, 3.1 Hz, benzene H), 3.86 (s, 3 H, OMe), 1.17 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 145.5, 133.4, 127.1, 126.6, 121.9, 121.7, 114.3, 99.7, 95.8, 55.3, 18.7, 11.3. IR (cm^{-1}): 2943 (m), 2865 (m), 2140 (m), 1609 (m), 1573 (w), 1536 (w), 1506 (s), 1463 (m), 1384 (w), 1291 (m), 1251 (s), 1179 (m), 1113 (w), 1073 (w), 1035 (m), 997 (w), 910 (w), 883 (m), 830 (m), 799 (s), 758 (s), 736 (m), 634 (m). HRMS(ESI) calcd for $C_{22}H_{31}OSSi^+$ (M+H) 371.1865, found 371.1878.

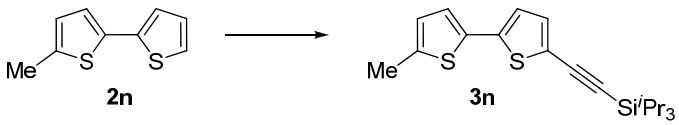
((5'-Hexyl-2,2'-bithiophen-5-yl)ethynyl)tri*iso*propylsilane (3m)



To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added 5-hexyl-2,2'-bithiophene (**2m**) (100 mg, 0.400 mmol, 1 equiv) in CH_3CN (1 mL) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 36 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane) afforded **3m** (117 mg, 0.272 mmol, 68 %) as yellow oil. R*f* 0.6 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 1 H, *J* = 3.8 Hz, ArH), 7.00 (d, 1 H, *J* = 3.6 Hz, ArH), 6.94 (d, 1 H, *J* = 3.8 Hz, ArH), 6.69 (dt, 1 H, *J* = 3.5, 0.9 Hz, ArH), 2.81 (t, 2 H, *J* = 7.5 Hz, CH_2), 1.70 (m, 2 H, CH_2), 1.46-1.26 (m, 6 H, CH_2), 1.16 (m, 21 H, TIPS), 0.93 (t, *J* = 6.9 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 139.2, 134.1, 133.1, 124.8, 123.8, 122.4, 121.5, 99.4, 96.3, 31.6, 31.5,

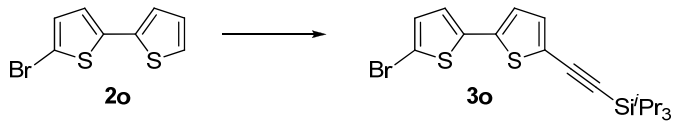
30.2, 28.8, 22.6, 18.7, 14.1, 11.3. IR 3068 (w), 2941 (s), 2864 (s), 2141 (m), 1558 (w), 1519 (w), 1463 (m), 1382 (w), 1366 (w), 1245 (w), 1163 (w), 1073 (w), 1049 (w), 1018 (w), 997 (m), 920 (w), 883 (s), 794 (s), 756 (s), 734 (m), 678 (s). HRMS(ESI) calcd for $C_{25}H_{39}S_2Si^+$ (M+H) 431.2263, found 431.2282.

((5'-Methyl-2,2'-bithiophen-5-yl)ethynyl)tri*iso*propylsilane (3n)



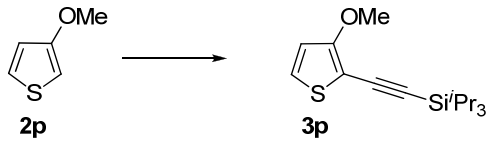
To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added 5-methyl-2,2'-bithiophene (**2n**) (72 mg, 0.40 mmol, 1 equiv) in CH_3CN (2 mL) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 36 h. Et_2O (10 mL) was added, the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane) afforded **3n** (105 mg, 0.291 mmol, 73 %) as yellow oil. The product was obtained in 85% purity together with inseparable impurities. R*f* 0.5 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, 1 H, *J* = 3.8 Hz, ArH), 6.97 (d, 1 H, *J* = 3.4 Hz, ArH), 6.93 (d, 1 H, *J* = 3.8 Hz, ArH), 6.67 (m, 1 H, ArH), 2.49 (s, 3 H, CH_3), 1.15 (m, 21 H, TIPS). 139.8, 139.1, 134.4, 133.1, 126.0, 124.0, 122.4, 121.5, 99.4, 96.3, 18.6, 15.3, 11.3. IR 3070 (w), 2942 (s), 2864 (s), 2140 (s), 1747 (w), 1521 (m), 1463 (m), 1383 (w), 1366 (w), 1246 (w), 1162 (m), 1074 (w), 1017 (w), 997 (m), 919 (w), 883 (s), 838 (w), 794 (s), 755 (s), 734 (s), 679 (s). HRMS(ESI) calcd for $C_{20}H_{29}S_2Si^+$ (M+H) 361.1480, found 361.1487.

((5'-Bromo-2,2'-bithiophen-5-yl)ethynyl)triisopropylsilane (3o)



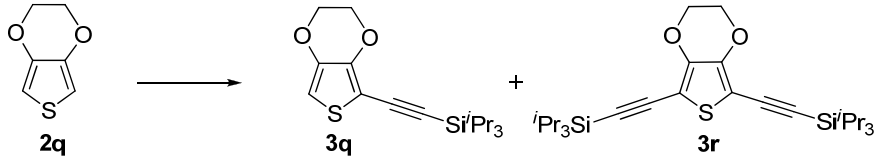
To a stirring solution of AuCl (9.2 mg, 0.040 mmol, 0.1 equiv) was added 5-bromo-2,2'-bithiophene (**2o**) (98 mg, 0.40 mmol, 1 equiv) in CH_3CN (1 mL) under air. After 2 min, TFA (60 µL, 0.80 mmol, 2.0 equiv) and **1** (342 mg, 0.800 mmol, 2.0 equiv) were added. The reaction was sealed and stirred at RT for 48 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane) afforded **3o** (103 mg, 0.242 mmol, 61 %) as yellow oil. R*f* 0.7 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, 1 H, *J* = 4.0 Hz, ArH), 6.97 (d, 1 H, *J* = 4.1 Hz, ArH), 6.94 (d, 1 H, *J* = 4.0 Hz, ArH), 6.90 (d, 1 H, *J* = 3.8 Hz, ArH), 1.12 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.3, 133.1, 130.7, 124.2, 123.4, 122.7, 111.6, 98.9, 97.2, 18.6, 11.3. IR 2942 (m), 2864 (m), 2141 (m), 1732 (w), 1508 (w), 1462 (m), 1426 (w), 1384 (w), 1366 (w), 1240 (w), 1218 (w), 1162 (w), 1073 (w), 1017 (w), 997 (w), 910 (w), 883 (m), 789 (s), 755 (s), 734 (s), 680 (s), 633 (s). HRMS(ESI) calcd for $C_{19}H_{26}BrS_2Si^+$ (M+H) 425.0428, found 425.0424.

Tri*iso*propyl((3-methoxythiophen-2-yl)ethynyl)silane (3p)



To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 3-methoxythiophene (**2p**) (40 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **3p** (73 mg, 0.25 mmol, 63 %) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 5.5 Hz, 1 H, ArH), 6.69 (d, J = 5.5 Hz, 1 H, ArH), 4.04 (s, 3 H, OMe), 1.15 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 125.2, 117.5, 116.0, 101.1, 97.7, 59.0, 18.7, 11.4. IR (cm^{-1}): 2942 (s), 2864 (s), 2139 (s), 1543 (s), 1462 (m), 1445 (w), 1384 (s), 1259 (s), 1195 (w), 1105 (w), 1073 (s), 1045 (m), 997 (m), 925 (m), 883 (s), 842 (m), 767 (s), 734 (m), 677 (s). HRMS(ESI) calcd for $C_{16}H_{27}OSSi^+$ (M+H) 295.1552, found 295.1566. HSQC and HMBC are in agreement with the regioselectivity proposed.

((2,3-Dihydrothieno[3,4-b][1,4]dioxin-5-yl)ethynyl)tri*iso*propylsilane (3q) and 5,7-bis((tri*iso*propylsilyl)ethynyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (3r)



Standard conditions:

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2,3-dihydrothieno[3,4-b][1,4]dioxine (**2q**) (42 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/DCM 8/2) afforded **3q** (55 mg, 0.17 mmol, 43 %) as yellow oil and **3r** (24 mg, 0.048 mmol, 12 %) as slightly yellow oil.

Monoaddition procedure:

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2,3-dihydrothieno[3,4-b][1,4]dioxine (**2q**) (128 µL, 1.20 mmol, 3 equiv) under air. After 2 min, **1** (171 mg, 0.400 mmol, 1.00 equiv) was added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/DCM 8/2) afforded **3q** (90 mg, 0.28 mmol, 70 %) as slightly yellow oil.

Diaddition procedure:

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2,3-dihydrothieno[3,4-b][1,4]dioxine (**2q**) (42 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (66 µL, 0.88 mmol, 2.2 equiv) and **1** (376 mg, 0.880 mmol, 2.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL).

The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/DCM 8/2) afforded **3r** (142 mg, 0.282 mmol, 71 %) as slightly yellow oil.

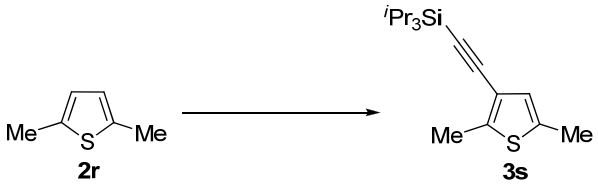
3q:

R*f* 0.3 (pentane/DCM 8/2, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (s, 1 H, ArH), 4.29 (m, 2 H, CH_2), 4.19 (m, 2 H, CH_2), 1.15 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.8, 100.7, 99.2, 98.1, 96.9, 64.9, 64.4, 18.7, 11.3. IR (cm^{-1}): 3113 (m), 2943 (s), 2865 (s), 2168 (s), 2141 (s), 1493 (s), 1462 (m), 1434 (s), 1365 (s), 1253 (w), 1224 (m), 1167 (s), 1119 m), 1072 (s), 1010 (s), 969 (m), 908 (s), 883 (s), 732 (s), 681 (s), 639 (s). HRMS(ESI) calcd for $C_{17}H_{27}O_2SSi^+$ (M+H) 323.1501, found 323.1500.

3r:

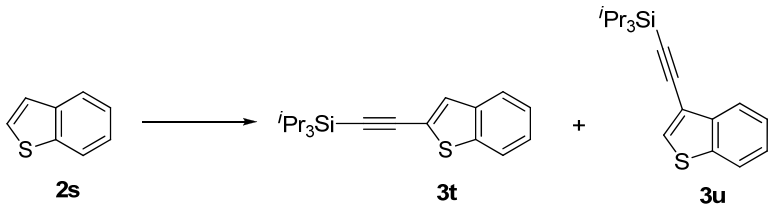
R*f* 0.2 (pentane/DCM 8/2, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (s, 4 H, CH_2), 1.11 (m, 42 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 99.6, 99.3, 96.4, 64.7, 18.7, 11.3. IR (cm^{-1}): 2943 (s), 2866 (s), 2140 (m), 1496 (m), 1442 (s), 1384 (w), 1362 (s), 1239 (w), 1155 (w), 1113 (w), 1086 (s), 1017 (w), 997 (m), 967 (m), 909 (m), 883 (s), 834 (w), 737 (m), 675 (s). HRMS(ESI) calcd for $C_{28}H_{47}O_2SSi_2^+$ (M+H) 503.2835, found 503.2829.

((2,5-Dimethylthiophen-3-yl)ethynyl)tri*iso*propylsilane (3s)



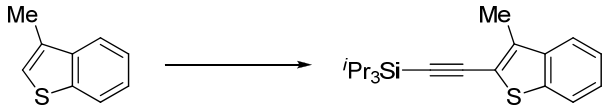
To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2,5-dimethylthiophene (**2r**) (40 µL, 0.40mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **3s** (56 mg, 0.19 mmol, 48 %) as colorless oil. R*f* 0.6 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1 H, ArH), 2.49 (s, 3 H, Me), 2.40 (s, 3 H, Me), 1.15 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 135.5, 127.4, 119.9, 101.8, 91.9, 18.7, 15.1, 14.4, 11.3. IR (cm^{-1}): 2942 (s), 2921 (s), 2864 (s), 2148 (s), 1463 (m), 1383 (w), 1365 (w), 1244 (w), 1222 (w), 1164 (w), 1074 (w), 1017 (w), 997 (m), 920 (m), 884 (s), 827 (m), 712 (s), 675 (s). HRMS(ESI) calcd for $C_{17}H_{29}SSi^+$ (M+H) 293.1759, found 293.1747.

(Benzo[b]thiophen-2-ylethynyl)tri*iso*propylsilane (3t) and (benzo[b]thiophen-3-ylethynyl)tri*iso*propylsilane (3u)



To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in wet CH_3CN (2 mL) was added benzo[b]thiophene (**2s**) (54 mg, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (45 µL, 0.60 mmol, 1.5 equiv) and **1** (257 mg, 0.600 mmol, 1.5 equiv) were added. The reaction was sealed and stirred at RT for 60 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **3t** and **3u** (81 mg, 0.26 mmol, 65 %) as colorless oil. **3t** and **3u** were obtained as a ca 1/1 unseparable mixture. Both regiosomers could not be fully distinguished by NMR. R*f* 0.5 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (ddd, 1 H, *J* = 7.8, 1.2, 0.6 Hz, A), 7.85 (m, 1 H, B), 7.79-7.70 (m, 2 H, A+B), 7.65 (s, 1 H, B), 7.51-7.44 (m, 2 H, A), 7.43-7.32 (m, 3 H A+B), 1.20 (m, 21 H), 1.16 (m, 21 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.5, 139.0, 138.8, 130.5, 129.2, 125.5, 125.0, 124.8, 124.7, 123.8, 123.5, 123.1, 122.6, 122.0, 118.9, 100.2, 99.7, 97.9, 93.4, 18.8, 18.7, 11.4, 11.3. IR 2942 (m), 2864 (m), 2145 (m), 1462 (m), 1462 (m), 1432 (w), 1384 (w), 1336 (w), 1254 (w), 1185 (w), 1156 (w), 1093 (w), 1069 (w), 1017 (w), 997 (w), 918 (w), 883 (m), 853 (m), 849 (m), 763 (w), 759 (m), 745 (m), 732 (s), 674 (s). HRMS(ESI) calcd for $C_{19}H_{27}SSi^+$ (M+H) 315.1603, found 315.1591.

Tri*iso*propyl((3-methylbenzo[b]thiophen-2-yl)ethynyl)silane (3v)



To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 3-methylbenzo[b]thiophene (**2t**) (54 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (45 µL, 0.60 mmol, 1.5 equiv) and **1** (257 mg, 0.600 mmol, 1.5 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **3v** (96 mg, 0.29 mmol, 73 %) as colorless oil. R*f* 0.5 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 1 H, ArH), 7.70 (m, 1 H, ArH), 7.40 (m, 2 H, ArH), 2.54 (d, 3 H, *J* = 0.7 Hz, CH_3), 1.19 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 139.1, 137.9, 125.6, 124.3, 122.3, 122.2, 118.8, 99.9, 99.4, 18.7, 13.2, 11.3. IR 3062 (w), 2942 (m), 2864 (m), 2142 (m), 1462 (m), 1435 (m), 1383 (w), 1320 (w), 1266 (w), 1243 (w), 1187 (w), 1161 (w), 1078 (w), 1000 (m), 996 (m), 919 (w), 883 (s), 833 (w), 753 (s), 729 (s), 701 (s), 677 (s), 620 (s), 600 (m). HRMS(ESI) calcd for $C_{20}H_{29}SSi^+$ (M+H) 329.1759, found 329.1780.

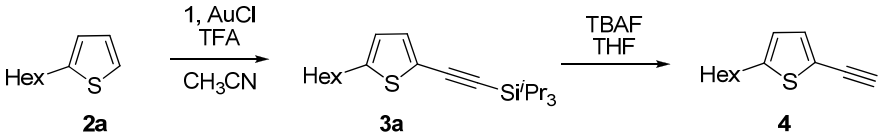
5. Deprotection procedures

2-Ethynyl-5-hexylthiophene (4)

From ((5-hexylthiophen-2-yl)ethynyl)tri*iso*propylsilane (3a)

TBAF (1M in THF, 0.98 mL, 0.98 mmol, 1.1 equiv) was added to a stirring solution of ((5-hexylthiophen-2-yl)ethynyl)tri*iso*propylsilane **3a** (311 mg, 0.890 mmol, 1 equiv) in THF (10 mL) at 0 °C. After 1 h, a saturated solution of NH_4Cl (20 mL) was added. The mixture was extracted three times with Et_2O (3 x 20 mL). The organic layers were then combined, washed twice with saturated NH_4Cl, brine, dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **4** (157 mg, 0.816 mmol, 92 %) as colorless oil. R*f* 0.5 (pentane, UV). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 3.6 Hz, 1 H, ArH), 6.64 (td, J = 3.6 Hz, 0.8 Hz, 1 H, ArH), 3.30 (s, 1 H, CH), 2.78 (t, J = 7.6 Hz, 2 H, CH_2), 1.66 (m, 2 H, CH_2), 1.33 (m, 6 H, CH_2), 0.90 (m, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 133.1, 124.0, 119.2, 80.4, 77.5, 31.5, 31.5, 30.2, 28.7, 22.6, 14.1. IR (cm^{-1}): 3309 (m), 2957 (m), 2929 (s), 2856 (m), 2103 (m), 1534 (w), 1462 (m), 1379 (w), 1141 (m), 1028 (m), 802 (s), 733 (w), 654 (s). HRMS(ESI) calcd for $C_{12}H_{17}S^+$ (M+H) 193.1051, found 193.1060.

From 2-hexylthiophene (2a)

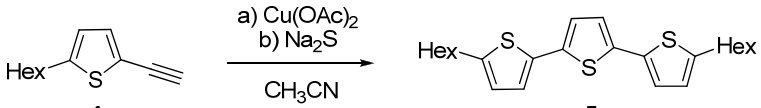


2a **3a** **4**

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2-hexylthiophene (**2a**) (72 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. Et_2O (10 mL) was added and the organic layer was washed twice with 0.1 M NaOH (15 mL). The aqueous layers were combined and extracted with Et_2O (20 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was dissolved in THF (5 mL) at 0 °C and TBAF (1 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv) was added. After 1 h, a saturated solution of NH_4Cl (20 mL) was added. The mixture was extracted three times with Et_2O (3 x 20 mL). The organic layers were then combined, washed twice with saturated NH_4Cl, brine, dried with $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (pentane) to afford **4** (59 mg, 0.31 mmol, 78 %) as colorless oil.

6. Synthesis of terthiophene 5

5,5''-Bis(n-hexyl)-2,2':5',2''-terthiophene (5)



4 **5**

A mixture of 2-ethynyl-5-hexylthiophene (**4**) (20 mg, 0.10 mmol, 1 equiv) and $Cu(OAc)_2$ (42 mg, 0.21 mmol, 2 equiv) were stirred at 80 °C for 5 h in CH_3CN (1 mL) under air. The reaction was cooled down and Na_2S•$3H_2O$ (59 mg, 0.42 mmol, 4 equiv) was added. The reaction was stirred at 80 °C for 18 h. The suspension was filtered and the solid was washed with DCM (10 mL). The organic layer was then washed twice with 0.1 M NaOH (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting oil was filtered over silica gel (pentane) to afford **5** (18 mg, 0.043 mmol, 86 %) as slightly yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 2 H, ArH), 6.96 (d, 2 H, J = 3.6 Hz, ArH), 6.67 (dt, 2 H, J = 3.4, 0.7 Hz, ArH), 2.79 (t, 4 H, J = 7.4 Hz, CH_2), 1.68 (m, 4 H, CH_2), 1.44-1.19 (m, 12 H, CH_2), 0.90 (m, 6

H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 136.1, 134.6, 124.7, 123.4, 123.1, 31.6, 30.2, 29.7, 28.7, 22.6, 14.1. Characterization data of **5** corresponded to the literature values.[16]

7. Mechanism investigation

Procedure using radical scavengers:

BHT:

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2-hexylthiophene (**2a**) (72 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv), BHT (0.10 g, 0.40 mmol, 1.0 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. GC/MS and ^{1}H NMR showed full conversion.

TEMPO:

To a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) in CH_3CN (2 mL) was added 2-hexylthiophene (**2a**) (72 µL, 0.40 mmol, 1 equiv) under air. After 2 min, TFA (36 µL, 0.48 mmol, 1.2 equiv), TEMPO (75 mg, 0.40 mmol, 1 equiv) and **1** (206 mg, 0.480 mmol, 1.2 equiv) were added. The reaction was sealed and stirred at RT for 14 h. No product could be detected by GC/MS or ^{1}H NMR (after TEMPO removal).

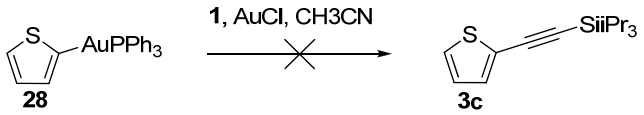
Thiophene gold triphenylphopshine (28)

2c **28**

Following a reported procedure,[17] *n*BuLi (2.5 M in hexanes, 0.16 mL, 0.4 mmol, 1 equiv) was added to a stirring solution of thiophene (**2c**) (34 µL, 0.40 mmol, 1 equiv) in THF (2 mL) at 0 °C. After 30 min, the reaction was warmed to RT and stirred for 1 h. PPh_3AuCl (0.20 g, 0.40 mmol, 1 equiv) was added in one portion. After 3 h, the reaction was quenched by adding MeOH (200 µL). Solvents were removed under vacuum. DCM (20 mL) was added, the organic layer was washed three times with water (15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting gum was stirred overnight in hexanes (5 mL). The resulting suspension was filtered. The solid was recrystallized from DCM/hexanes to afford **28** (150 mg, 0.277 mmol, 69%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 7 H, ArH), 7.55-7.39 (m, 10 H, ArH), 7.20 (t, 1 H, J = 3.0 Hz, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4 (d, J = 14 Hz), 133.2 (d, J = 3 Hz), 131.3 (d, J = 2 Hz), 130.5 (d, J = 52 Hz), 129.1 (d, J = 11 Hz), 127.0 (d, J = 4 Hz), 127.0 (d, J = 7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.7. Characterization data of **28** corresponded to the literature values. [17]

Mechanism investigation using thiophene gold triphenylphosphine

[16] G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, L. Antolini, O. Pudova, A. Bongini, *J. Org. Chem.* **1998**, *63*, 5497
[17] F. Bonati, A. Burini, B. R. Pietroni, R. Galassi, *Gazz. Chim. Ital.* **1993**, *123*, 691.



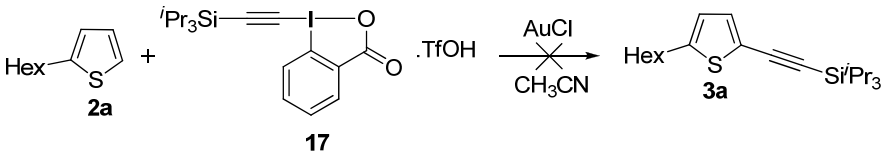
Procedure without TFA:

A mixture of **1** (24 mg, 0.055 mmol, 1 equiv) and thiophene gold triphenylphopshine (**28**) (30 mg, 0.055 mmol, 1 equiv) was stirred for 15 h under air in CH_3CN (275 µL). No product was detected by GC/MS and ^1H NMR. Starting materials were still present.

Procedure with TFA:

TFA (4 µL, 0.06 mmol, 1 equiv) was added to a mixture of **1** (24 mg, 0.055 mmol, 1 equiv) and thiophene gold triphenylphosphine (**28**) (30 mg, 0.055 mmol, 1 equiv) and the mixture was stirred for 15 h under air in CH_3CN (275 µL). No product was detected by GC/MS and ^1H NMR. Starting materials were decomposed to several unidentified side-products.

Mechanism investigation using 17



Procedure without TFA:

2-Hexylthiophene (**2a**) (36µL, 0.20 mmol, 1 equiv) was added to AuCl (2 mg, 0.04 mmol, 0.05 equiv) in CH_3CN (1 mL) under air. Then **17** (139 mg, 0.240 mmol, 1.2 equiv) was added. The reaction was stirred at RT for 15 h. Only traces of product **3a** were observed by GC-MS. Only few decomposition was observed.

Procedure with TFA:

2-Hexylthiophene (**2a**) (36 µL, 0.20 mmol, 1 equiv) was added to AuCl (2 mg, 0.04 mmol, 0.05 equiv) in CH_3CN (1 mL) under air. Then TFA (18 µL, 0.24 mmol, 1.2 equiv) and **17** (139 mg, 0.240 mmol, 1.2 equiv) were added. The reaction was stirred at RT for 15 h. Only traces of product **3a** were observed by GC-MS. **7** was still present but 2-hexylthiophene (**2a**) was degraded to several unidentified side-products.

Investigation using the TFA adduct of TIPS-EBX (1):

TFA (18 µL, 0.24 mmol, 1.2 equiv) was added to a suspension of **1** (103 mg, 0.240 mmol, 1.2 equiv) in CH_3CN (1 mL). After 15 min, the solvent was removed under vacuum. The resulting viscous colorless oil was then dissolved in CH_3CN (1 mL) and AuCl (2.3 mg, 0.010 mmol, 0.05 equiv) and 2-hexylthiophene **2a** (36 µL, 0.20 mmol, 1 equiv) were added. The reaction was stirred under air at RT for 15 h. GC/MS indicated 54% yield.

Stoechiometric mixture if AuCl and TIPS-EBX 1:

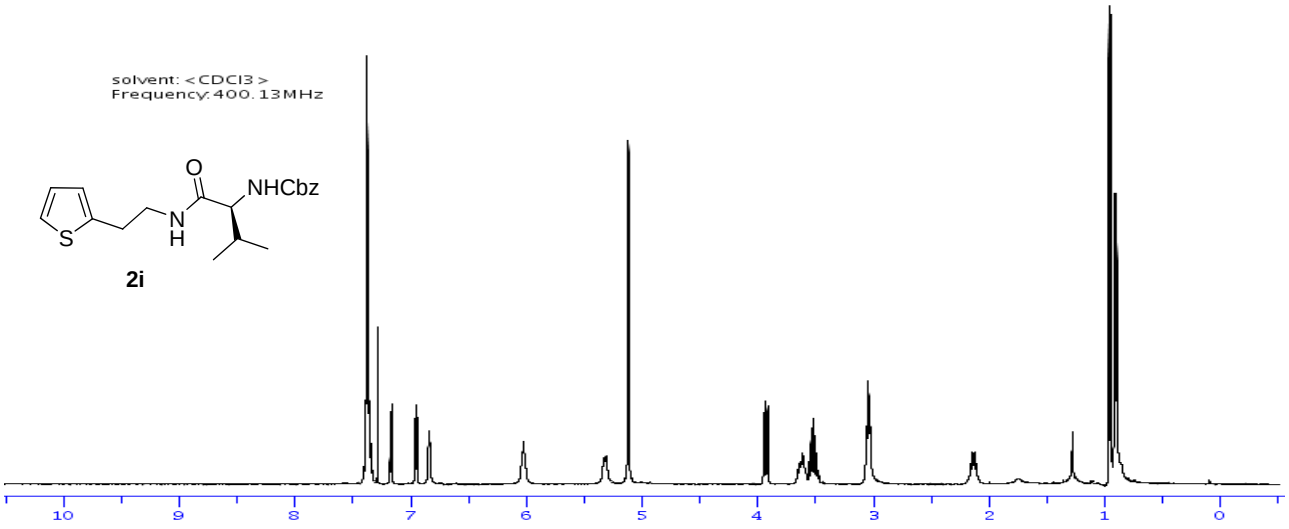
Procedure without TFA:

AuCl (10mg, 0.047mmol, 1 equiv) and **1** (18 mg, 0.047mmol, 1 equiv) were dissolved in CD_3CN (0.7 mL). ^1H NMR and GC/MS indicated the formation of 2-iodobenzoic acid (**9**) and 1,4-bis(tri*iso*propylsilyl)buta-1,3-diyne as major products, which were not separable from unidentified impurities.

Procedure with TFA:

AuCl (10 mg, 0.047 mmol, 1 equiv), **1** (18 mg, 0.047 mmol, 1 equiv) and TFA (4 µL, 0.05 mmol, 1 equiv) were dissolved in CD_3CN (0.7 mL). ^1H NMR and GC/MS indicated the formation of 2-iodobenzoic acid (**9**) and 1,4-bis(tri*iso*propylsilyl)buta-1,3-diyne as major products, which were not separable from unidentified impurities.

8. Spectra of new compounds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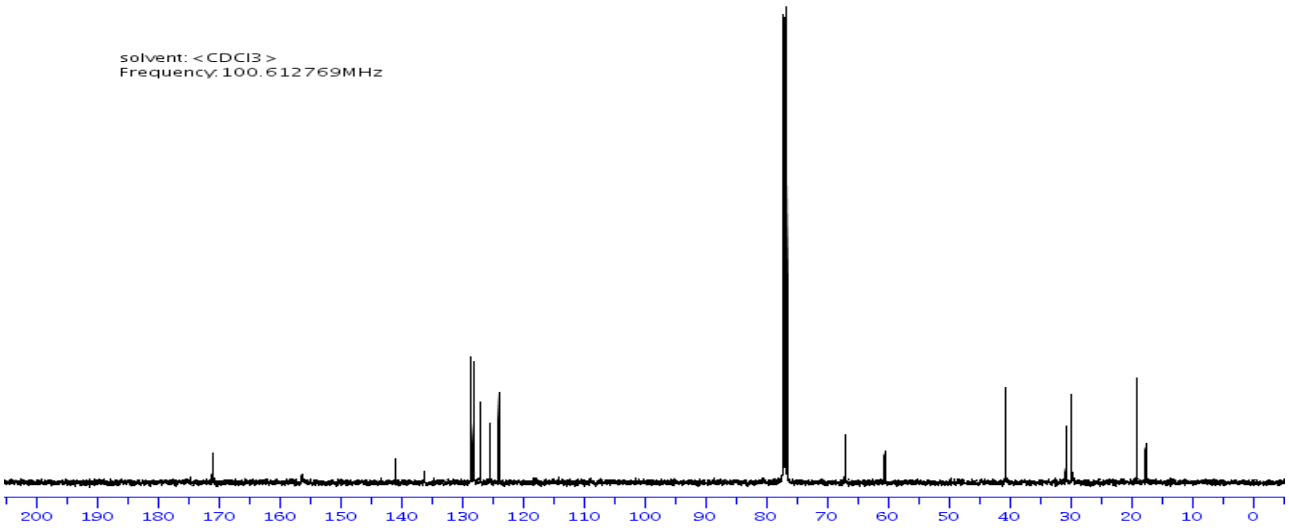
2i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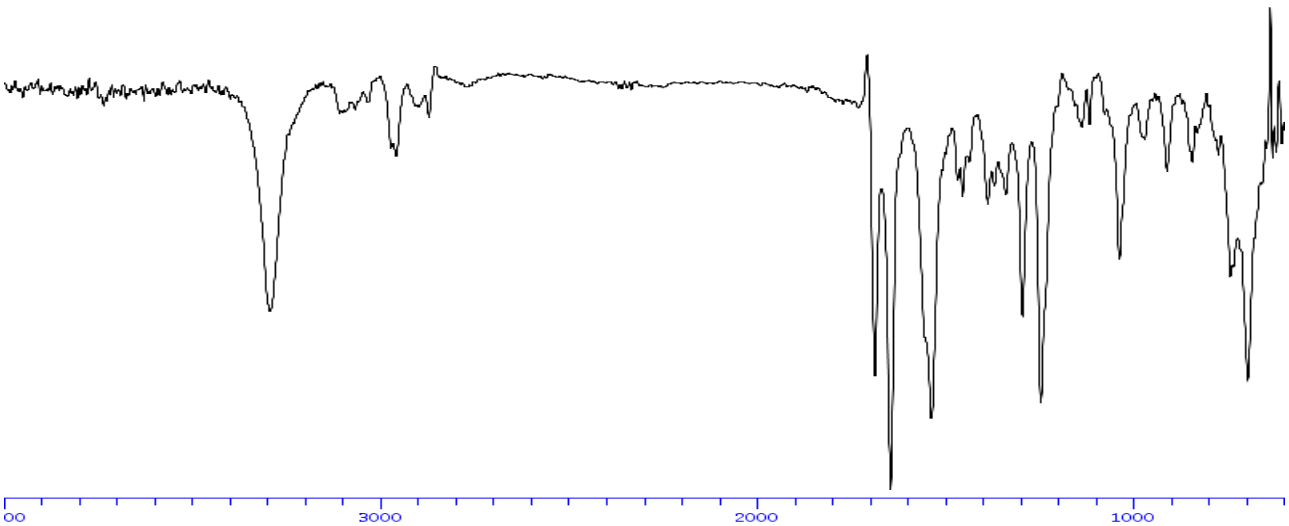
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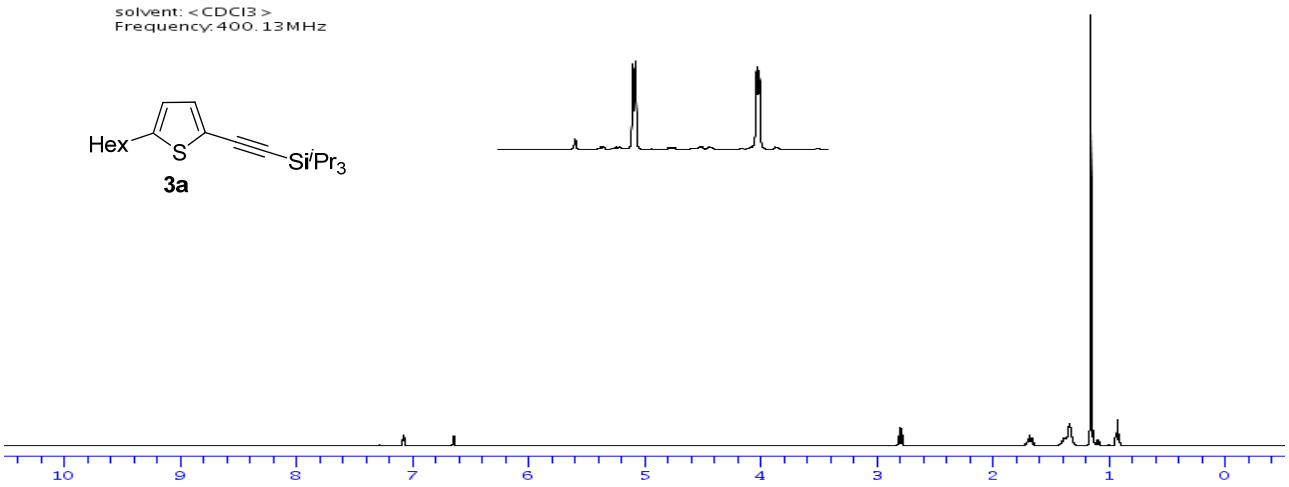
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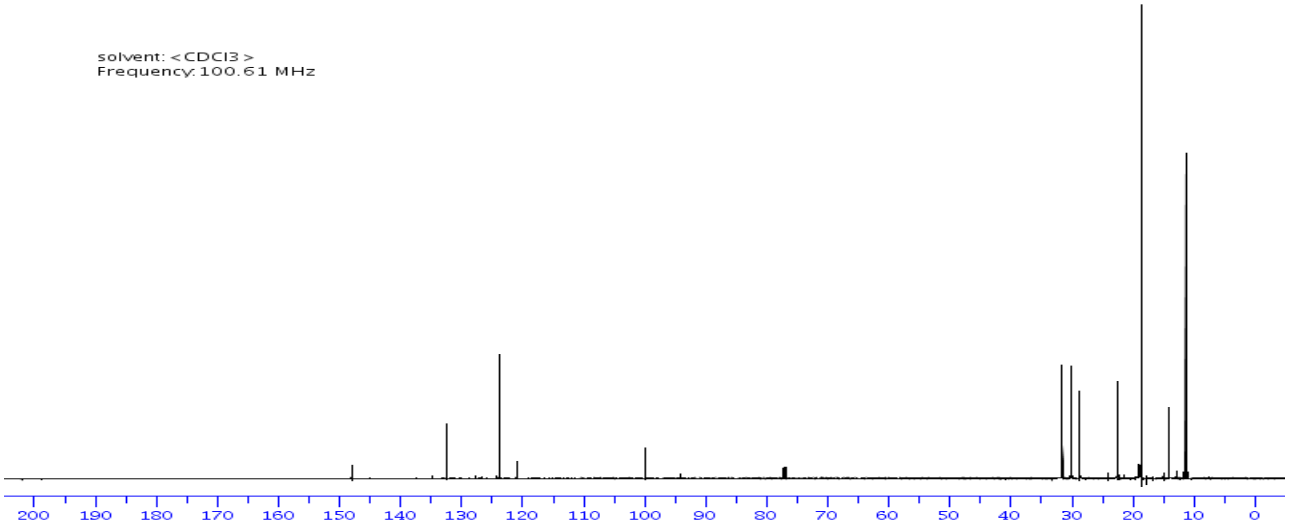
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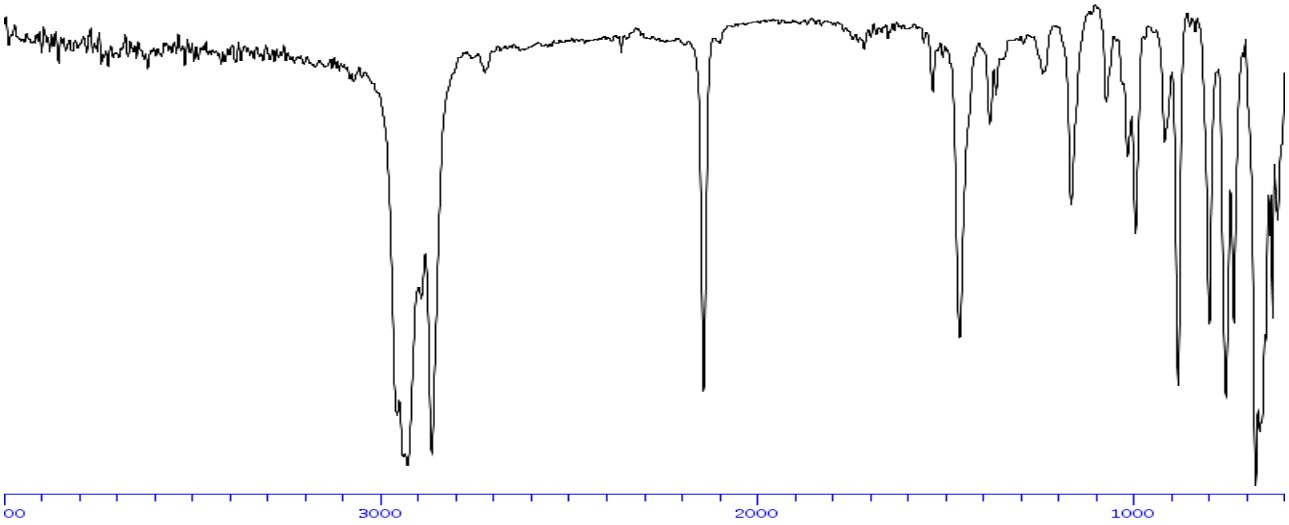
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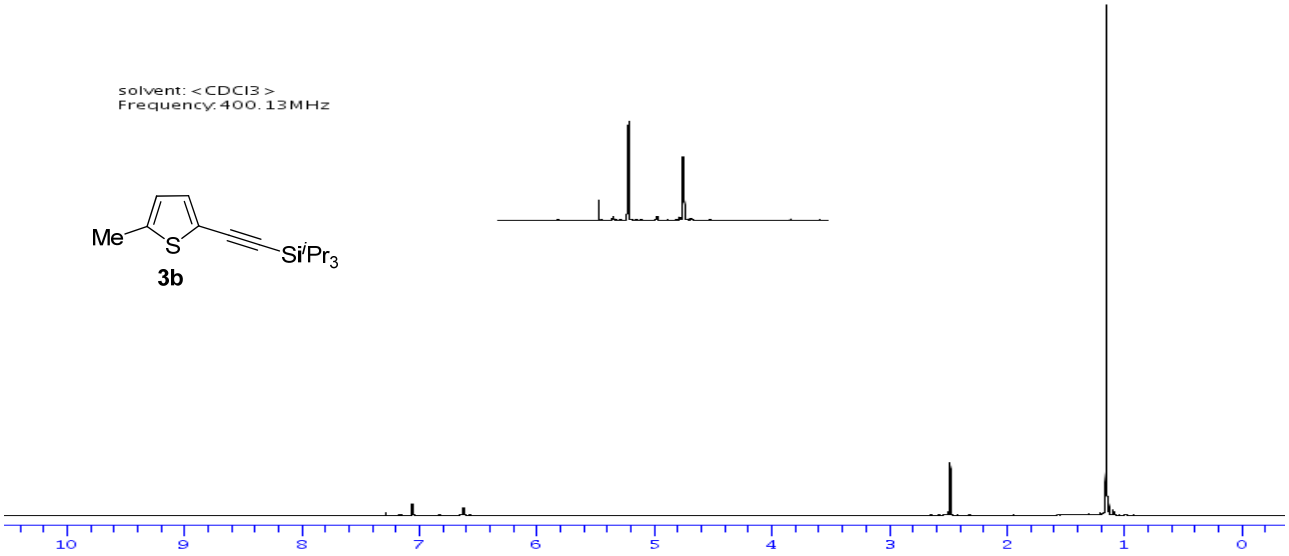
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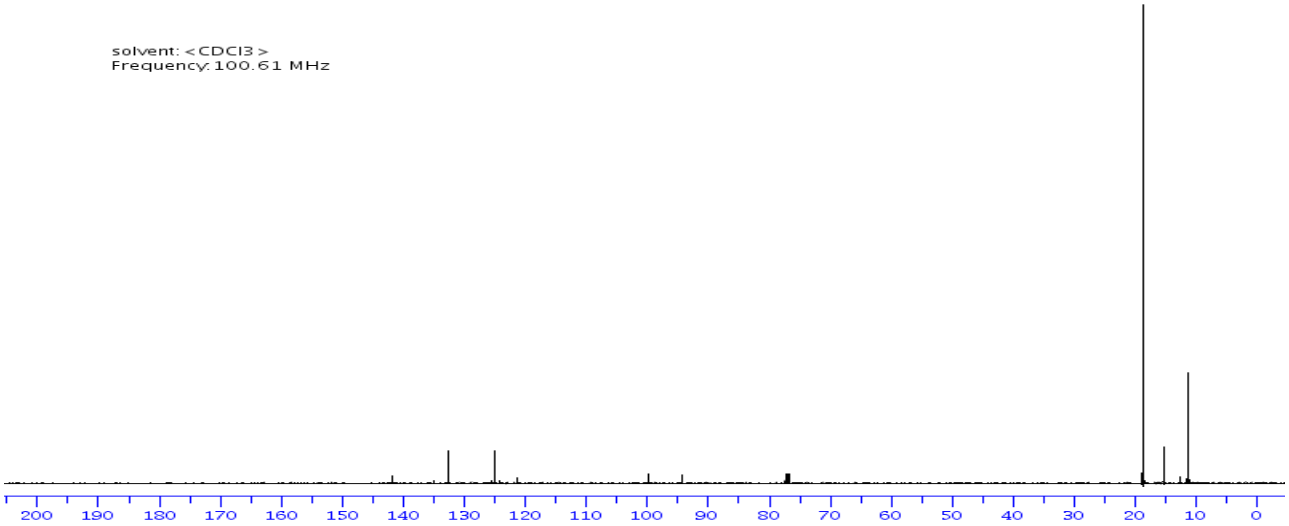
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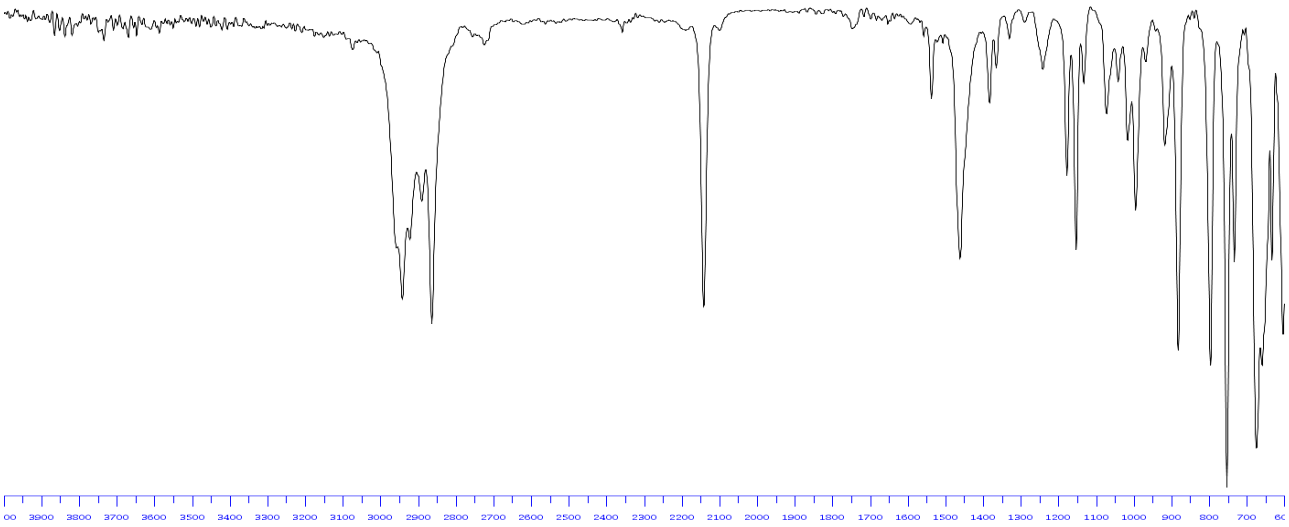

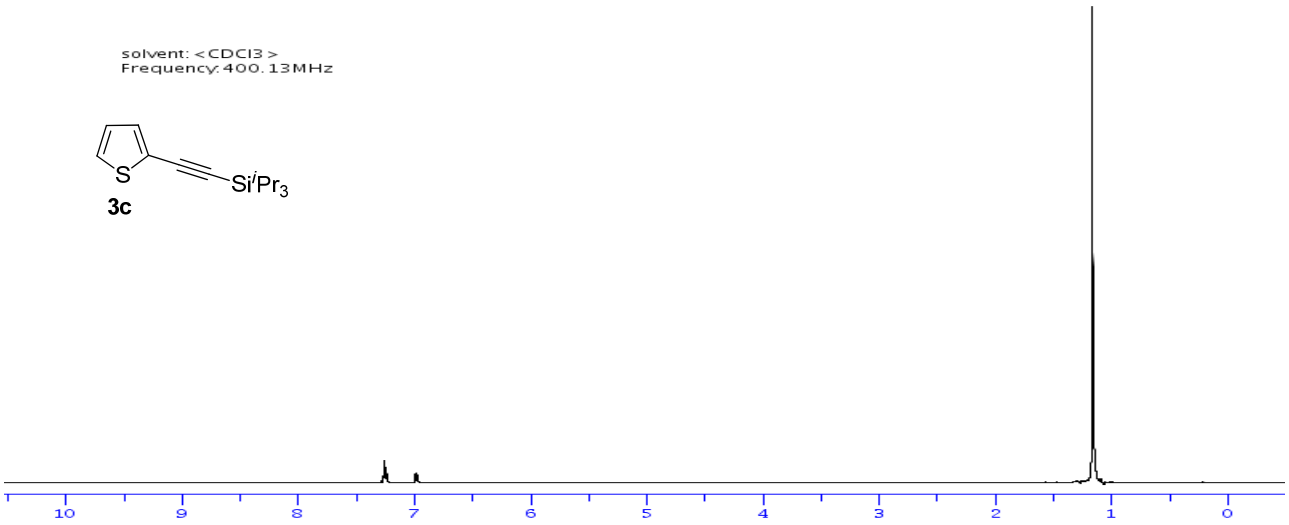
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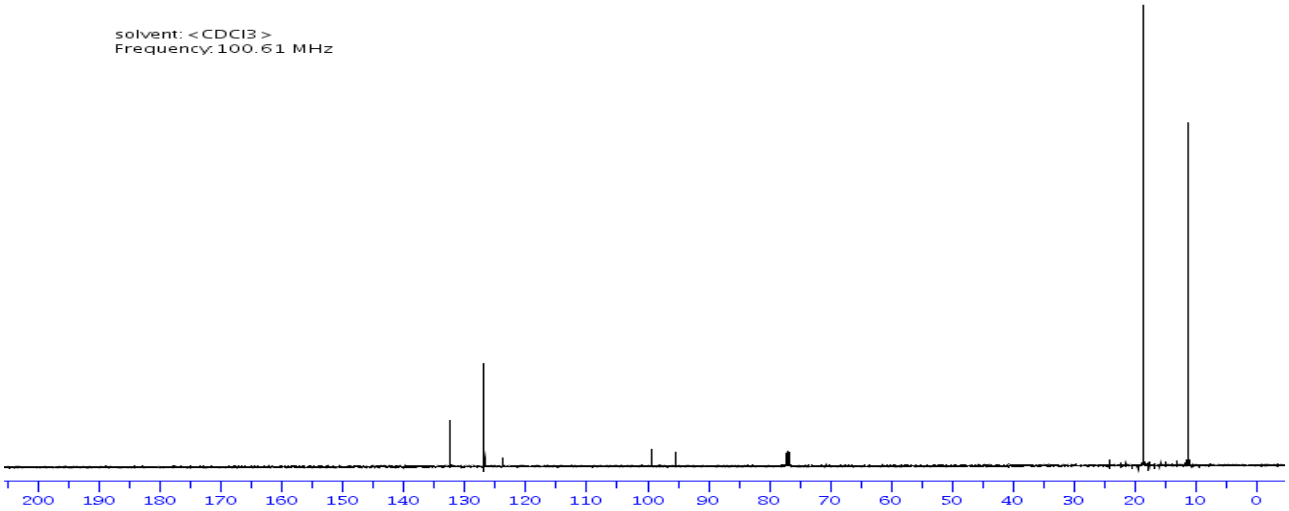
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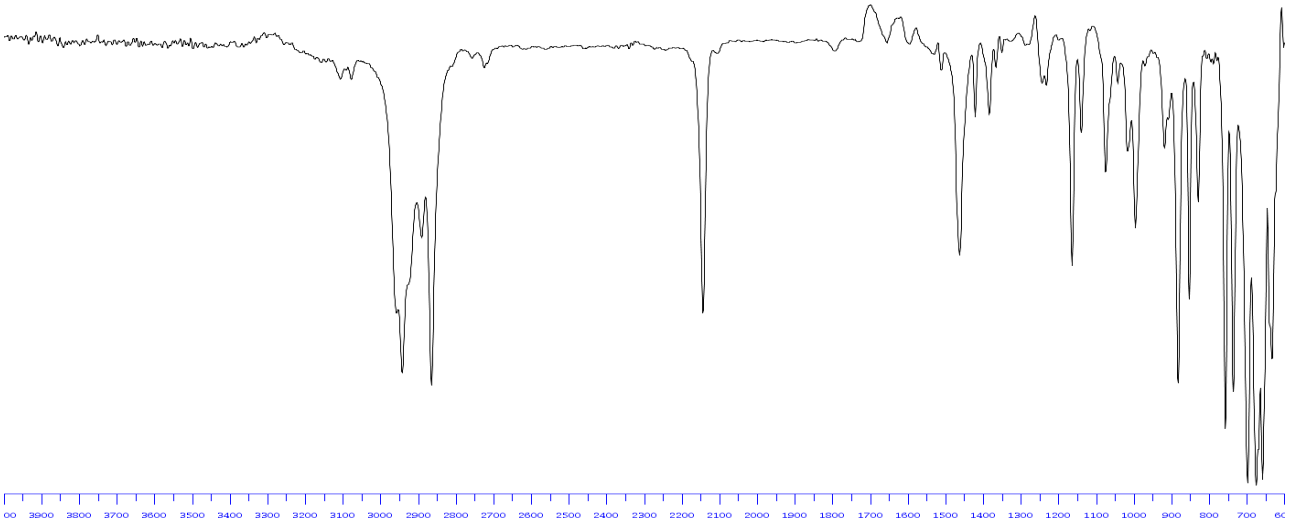

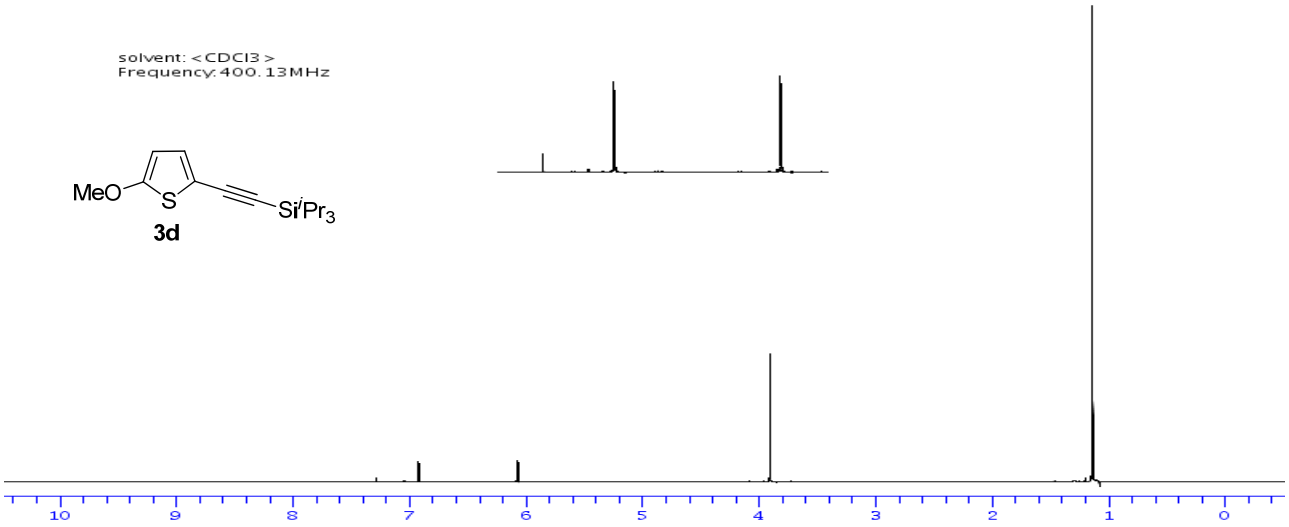
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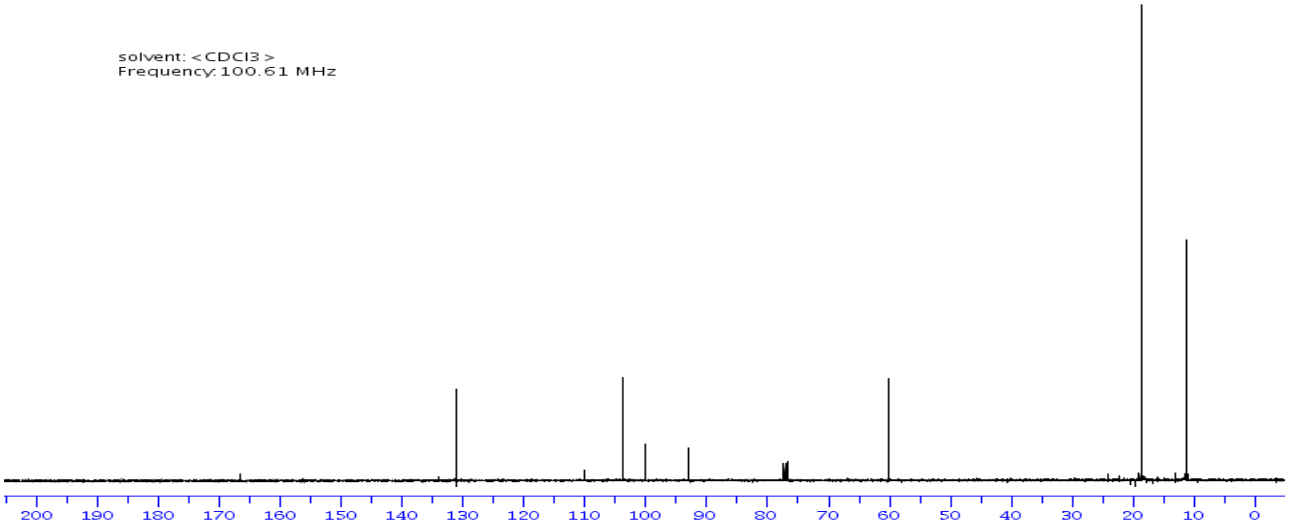
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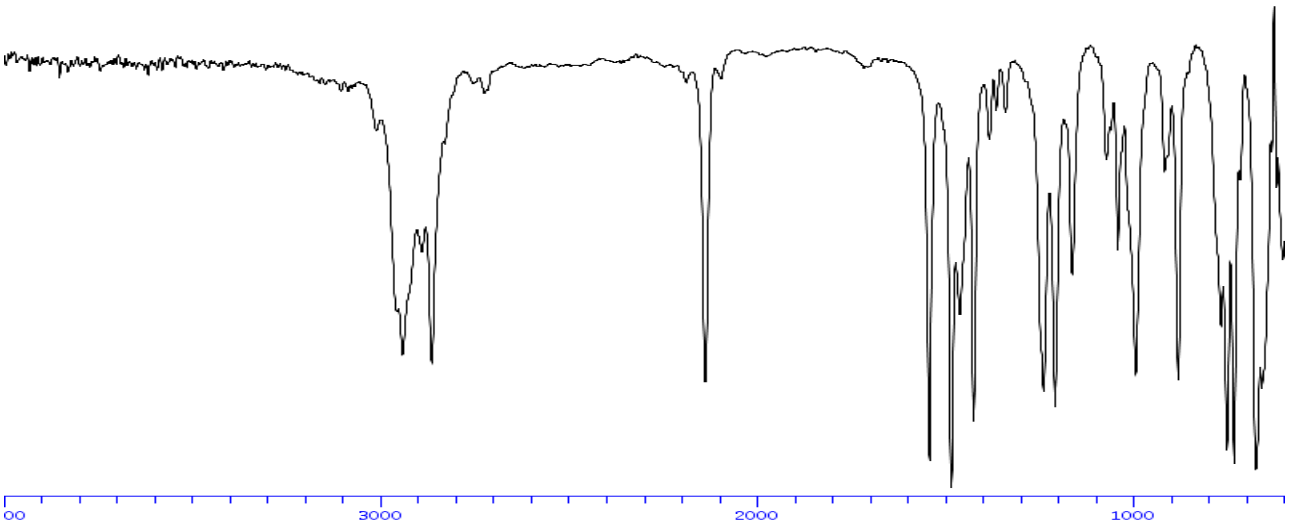
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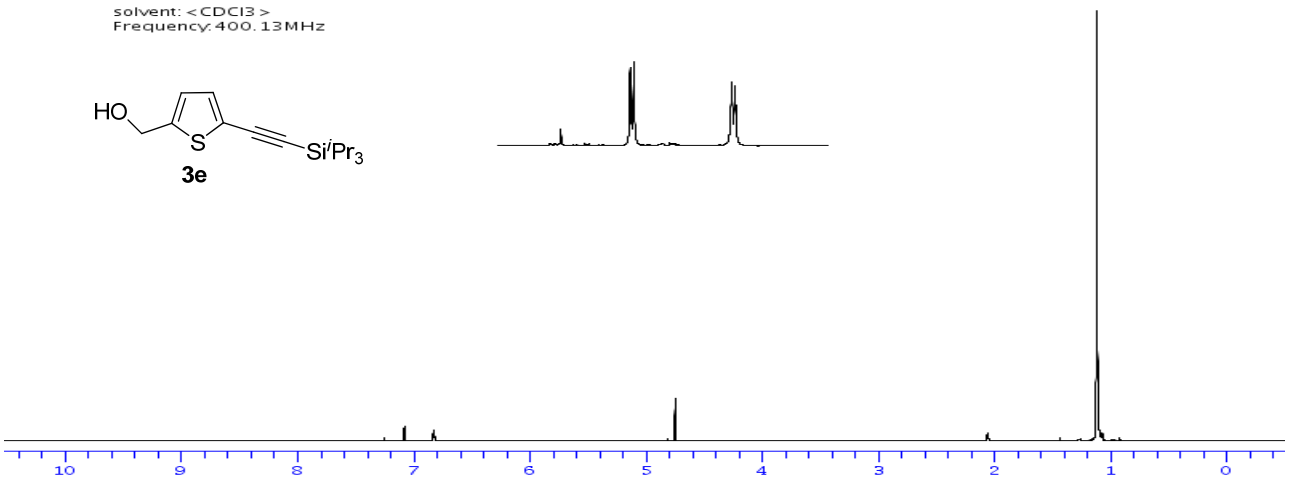
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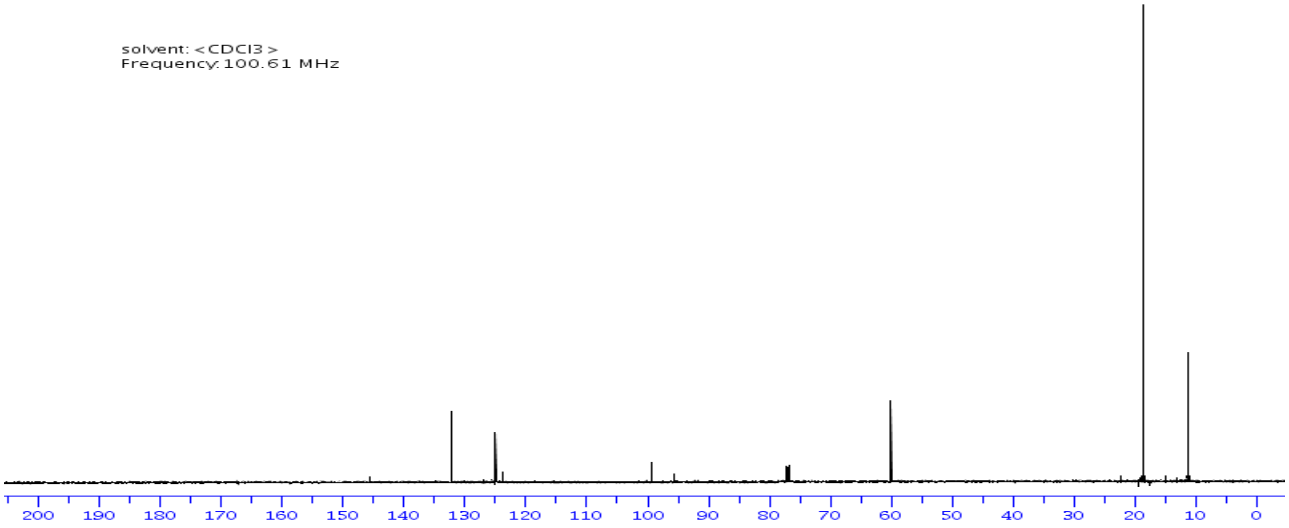
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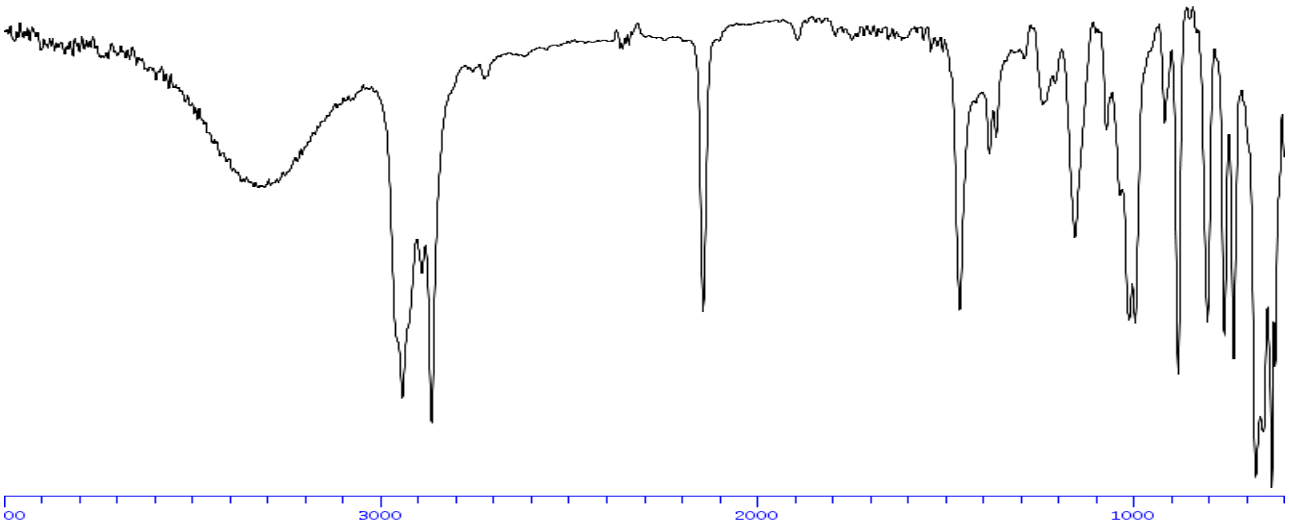
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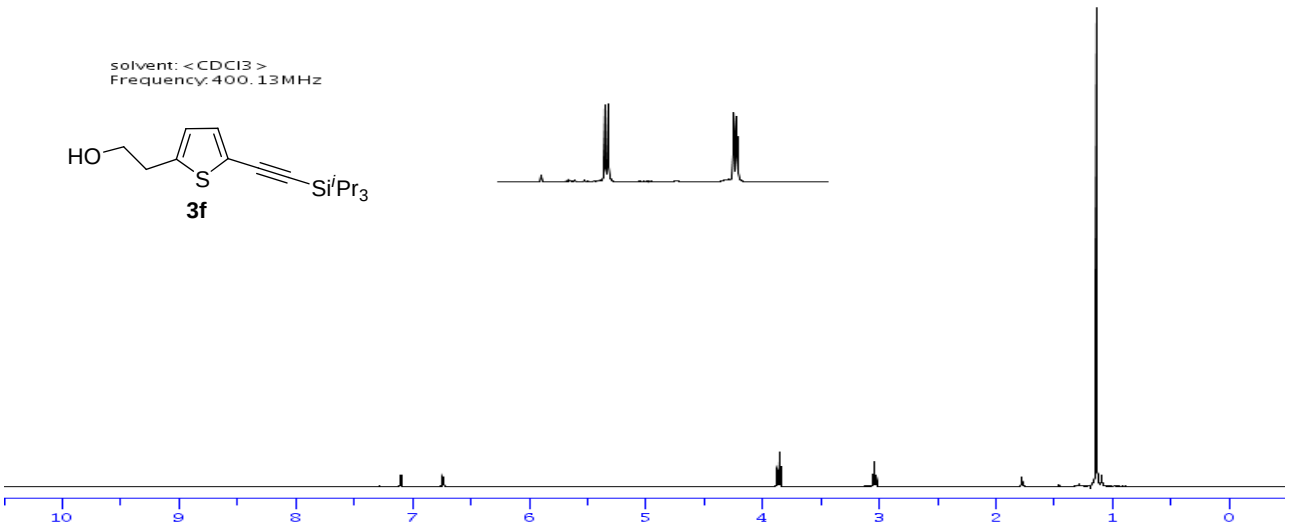
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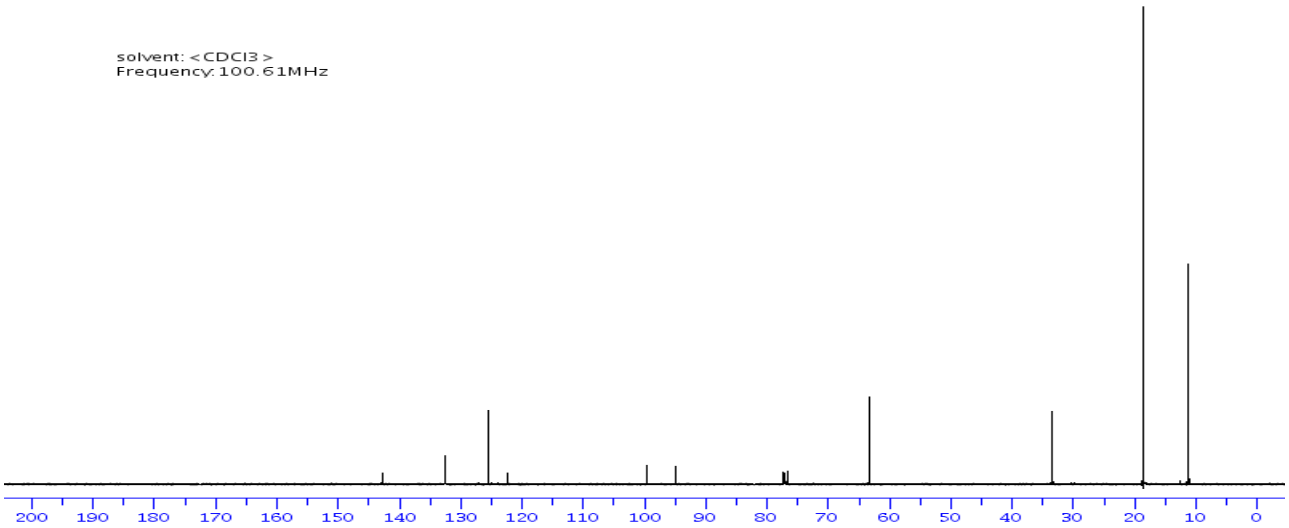
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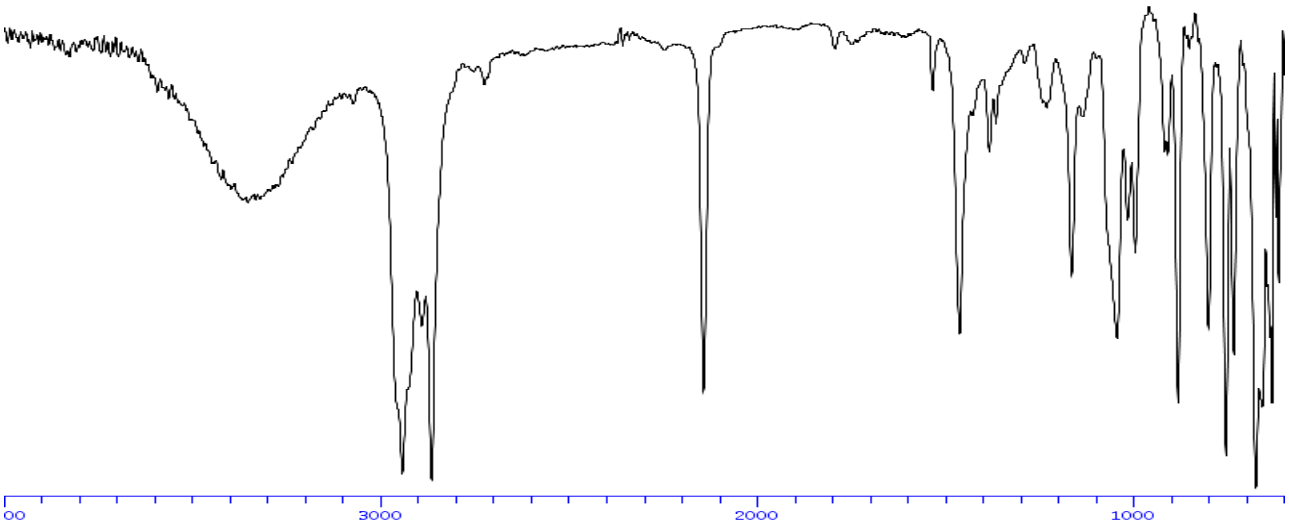
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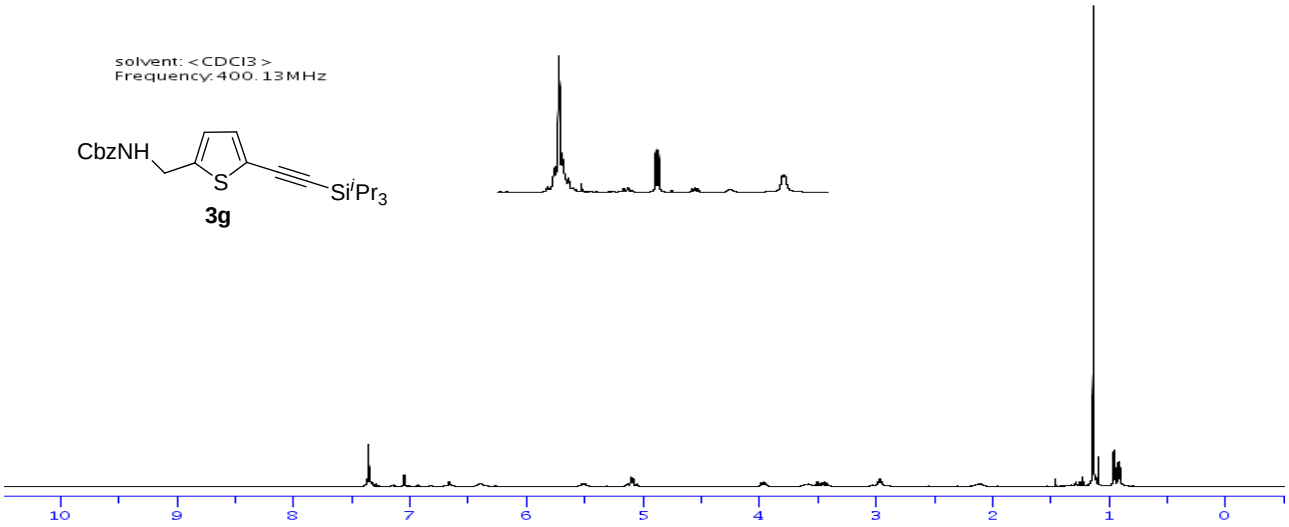
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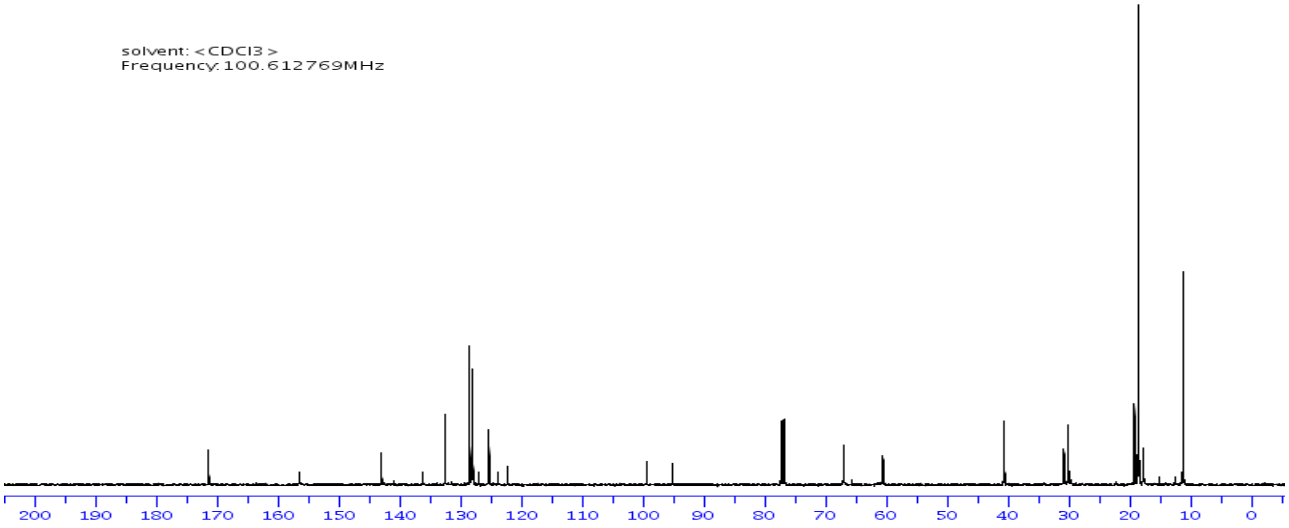
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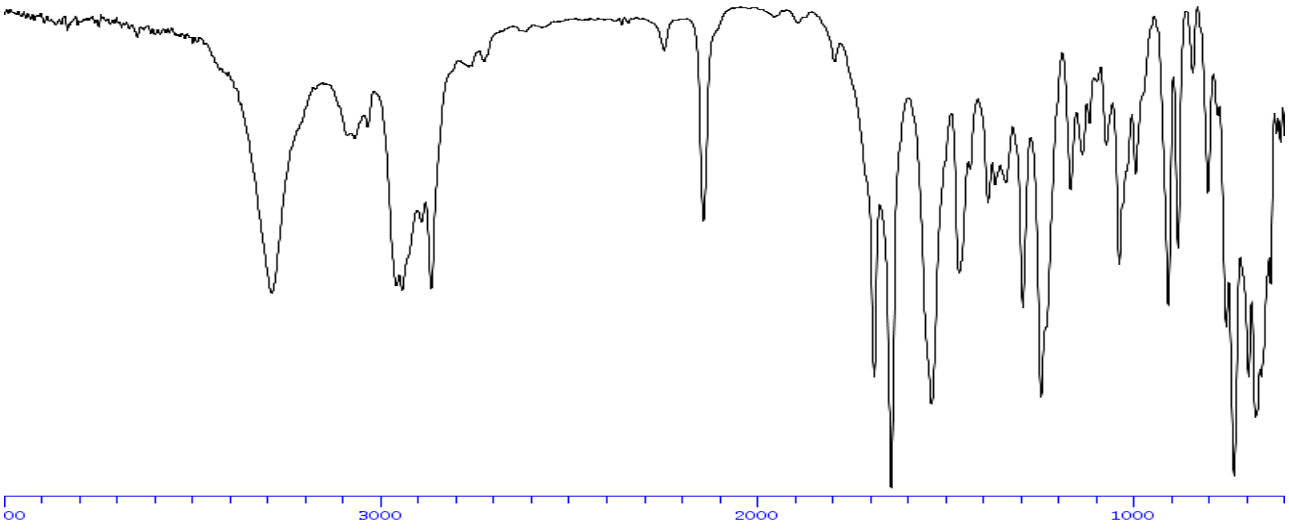
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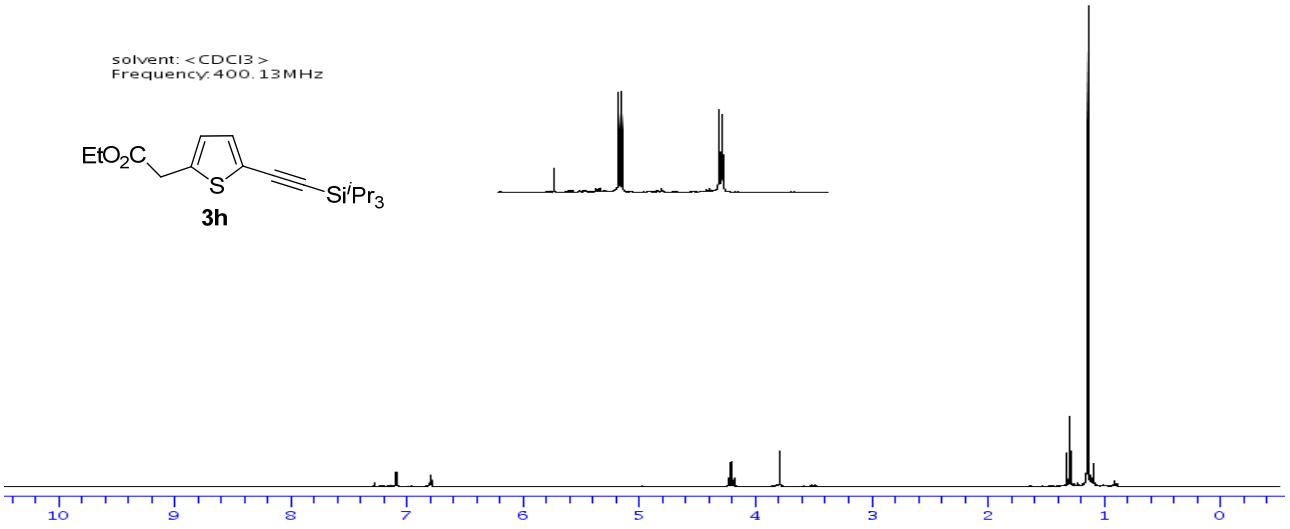
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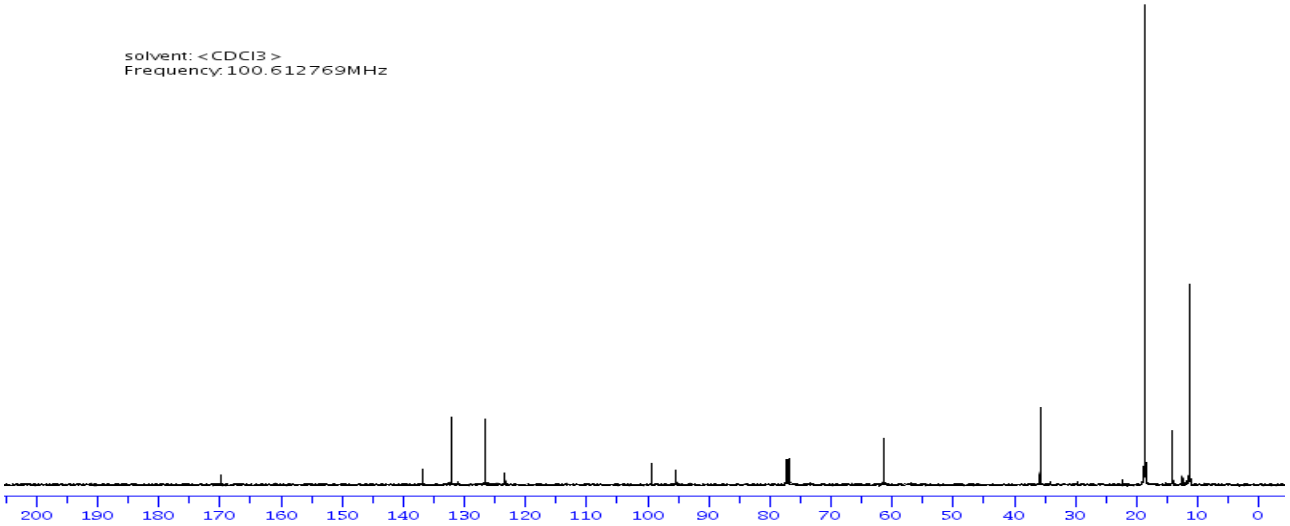
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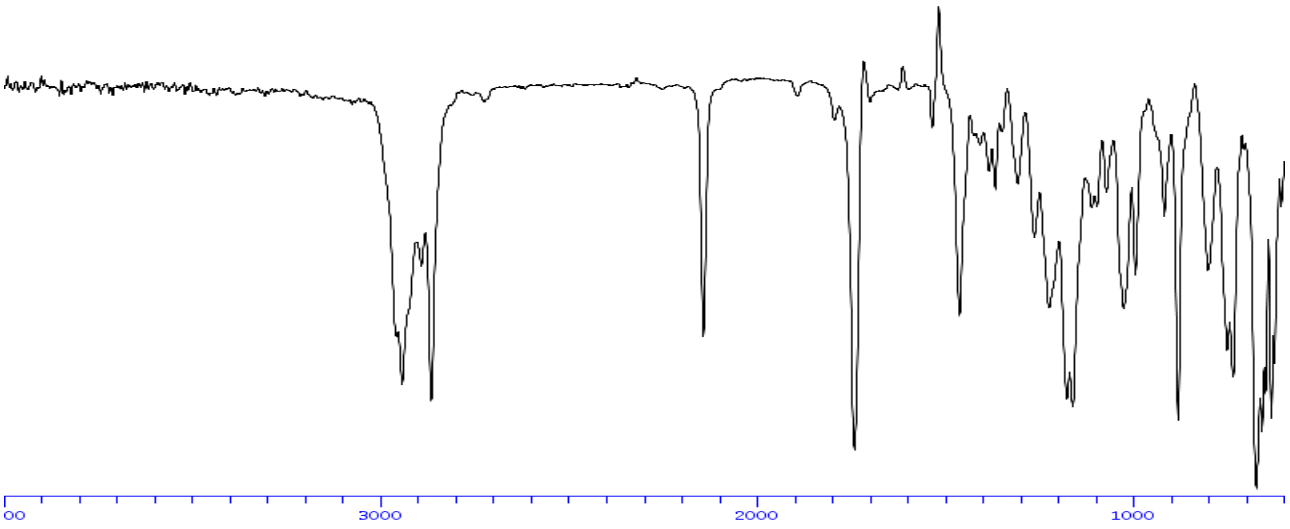
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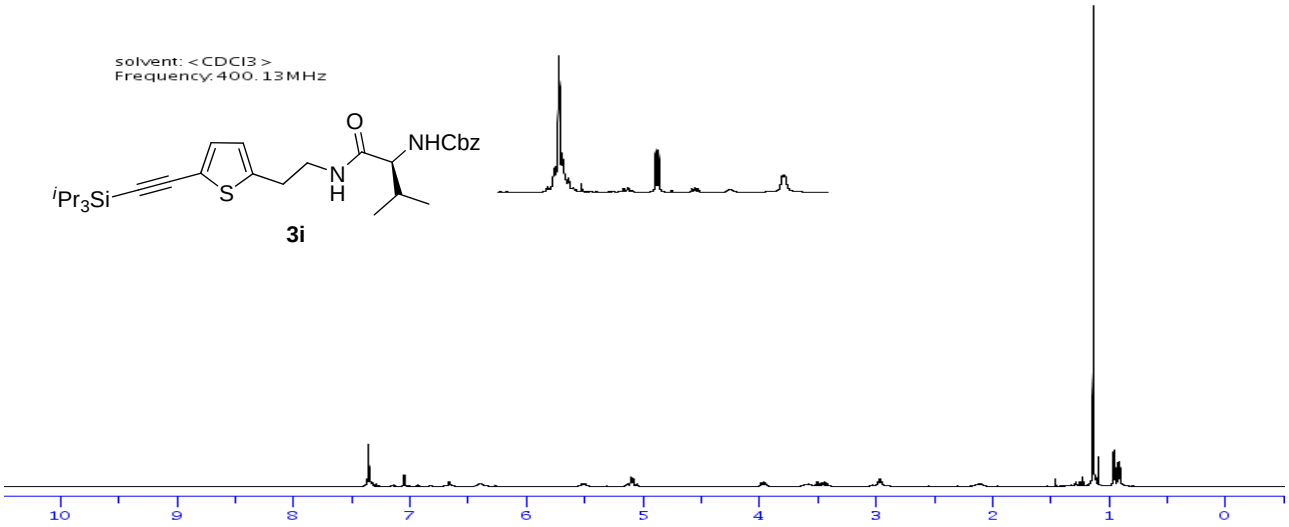
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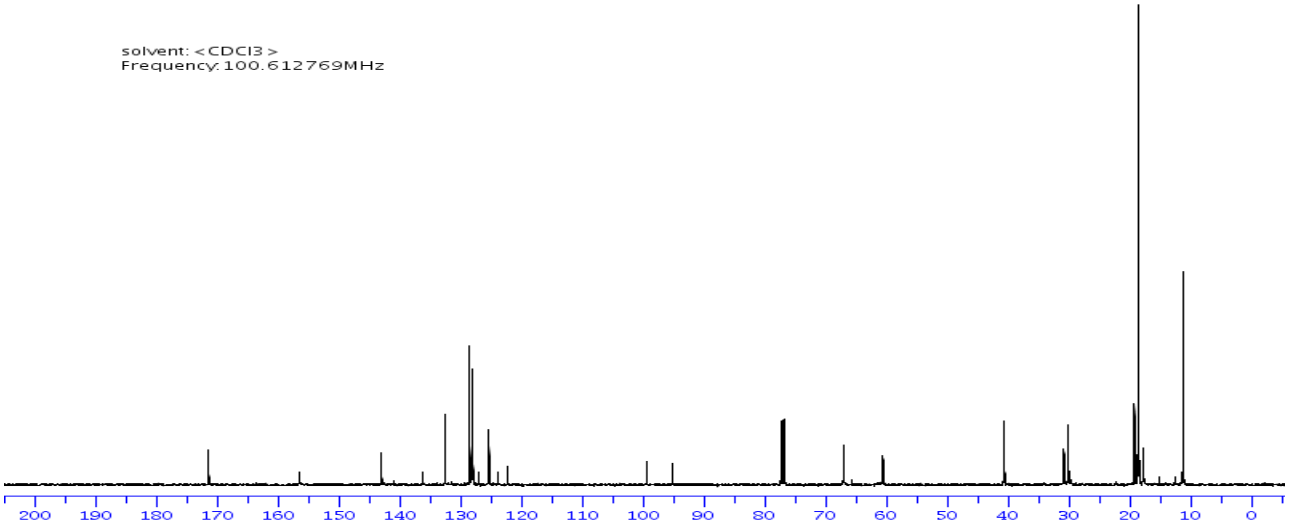
3i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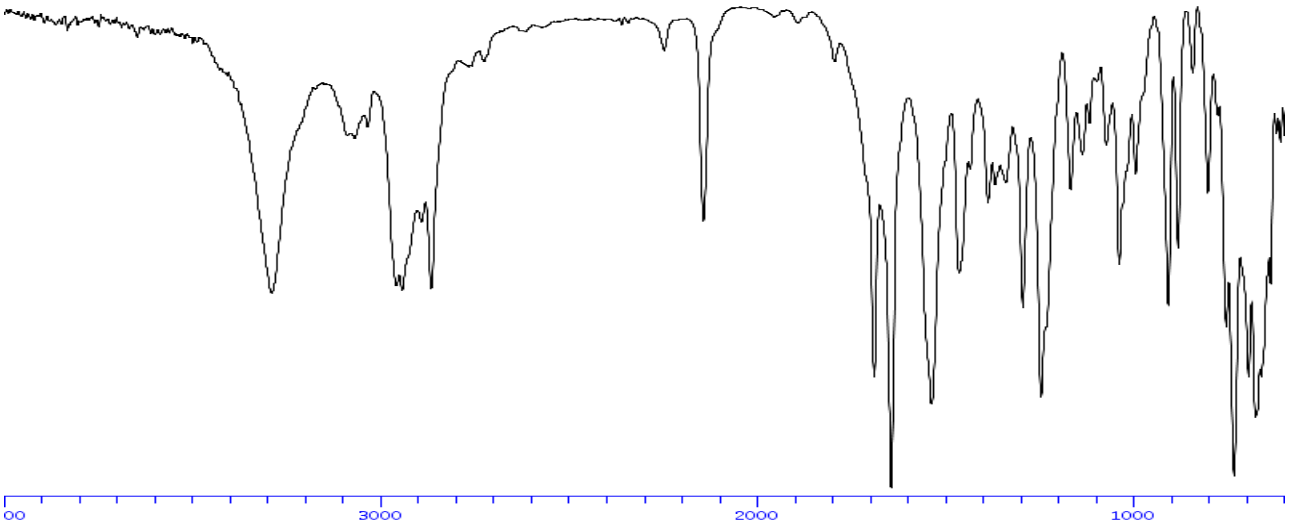
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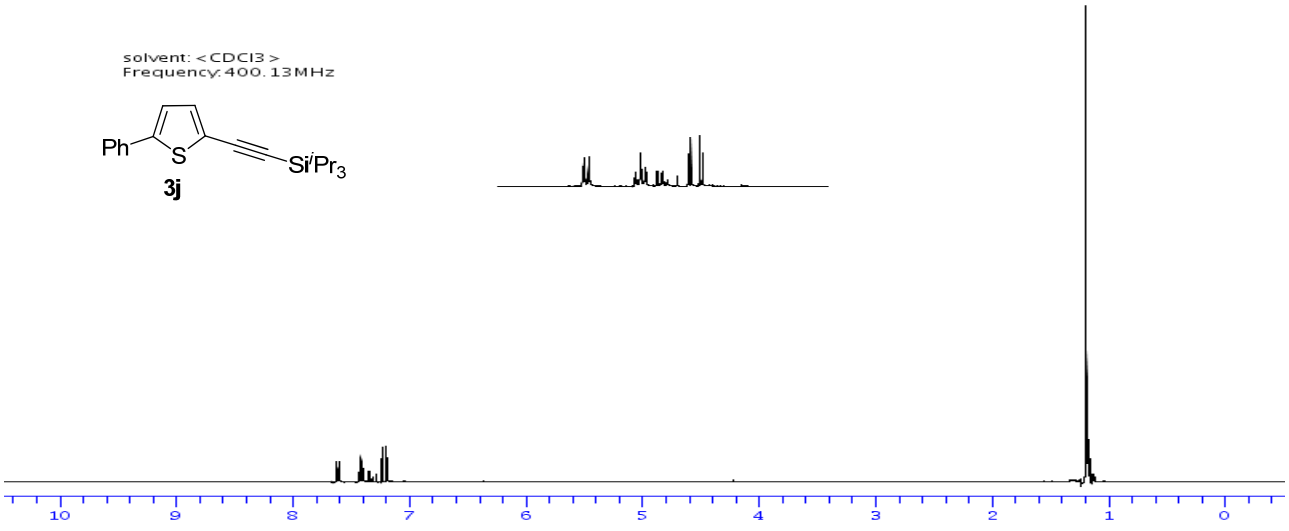
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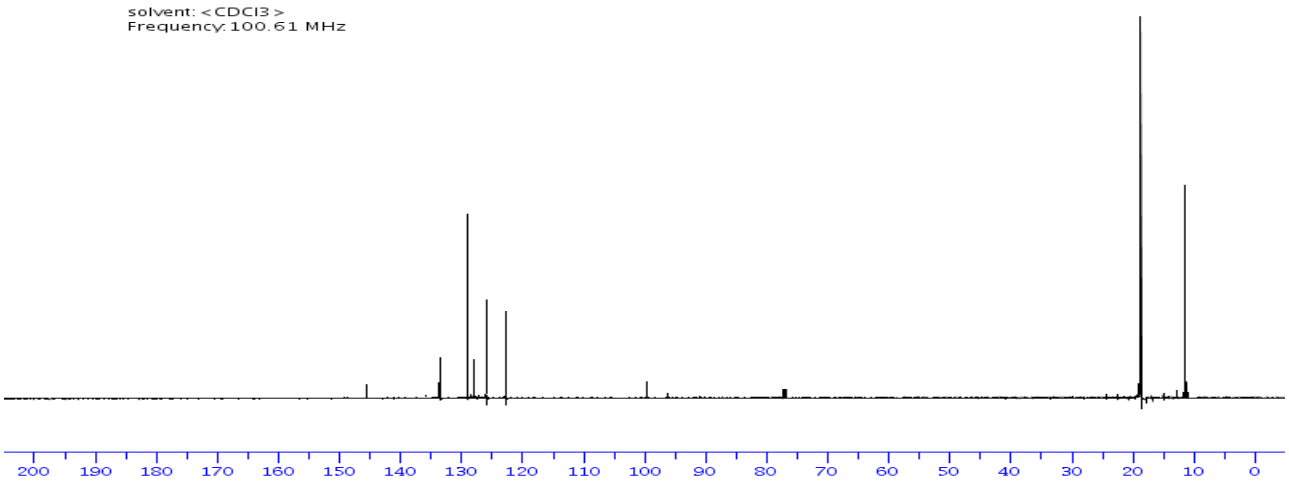
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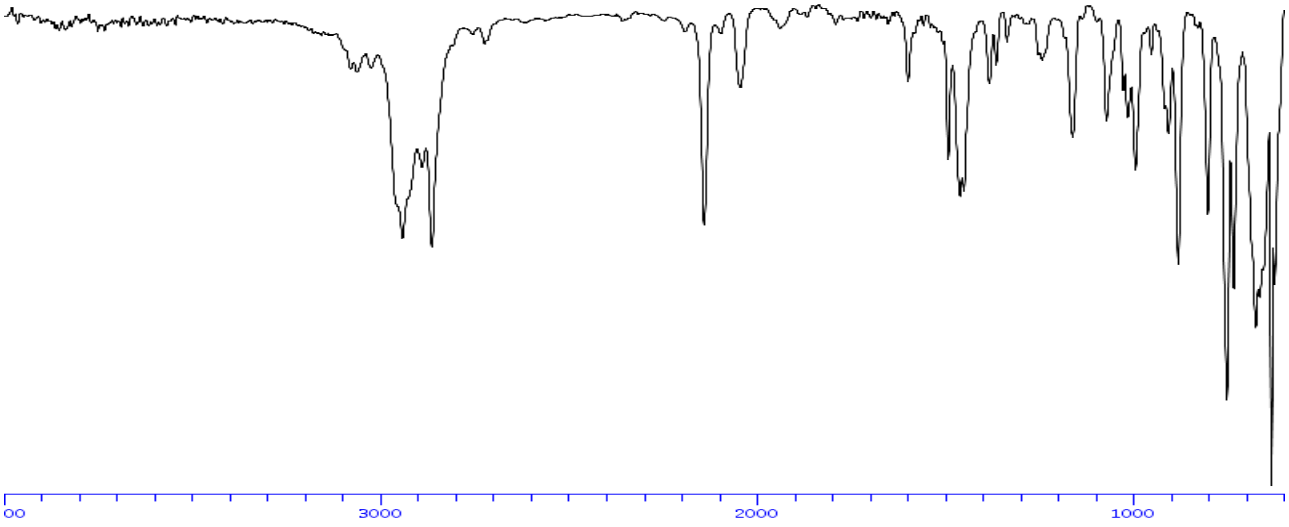
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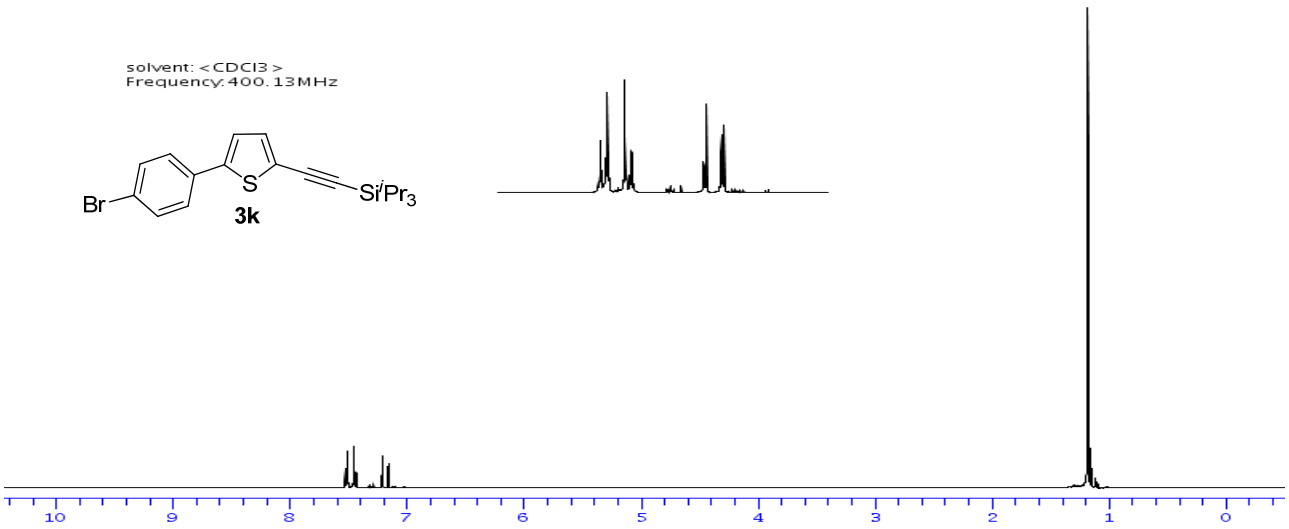
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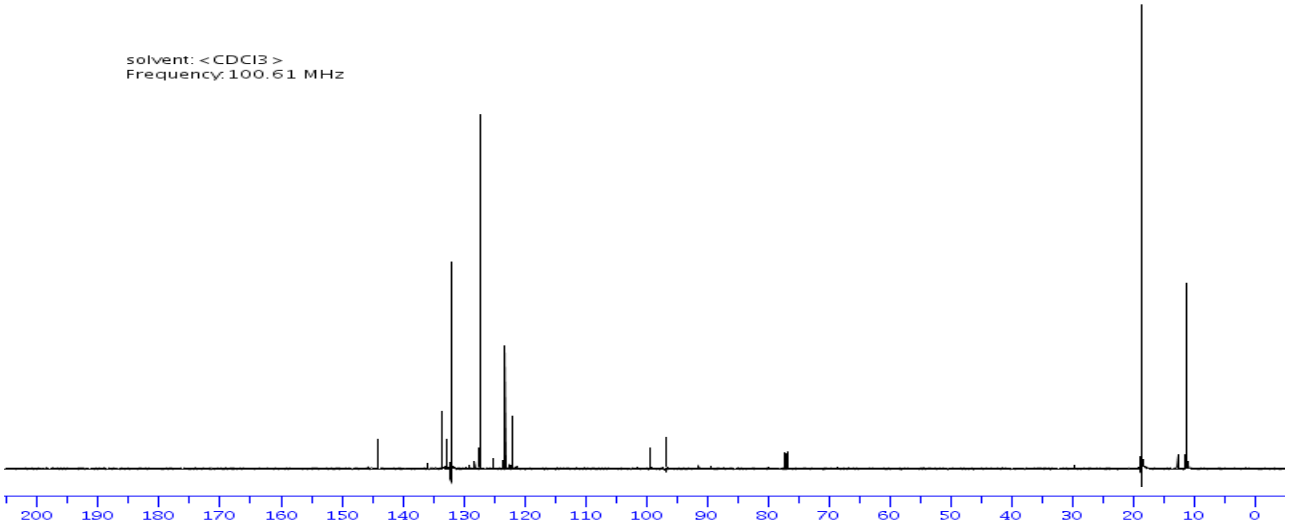
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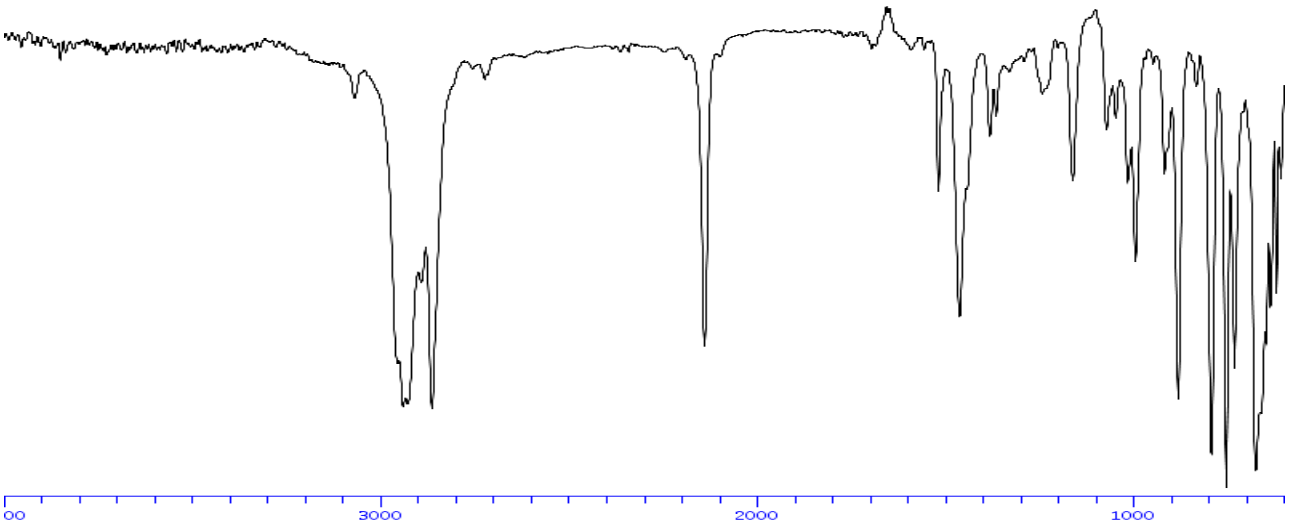
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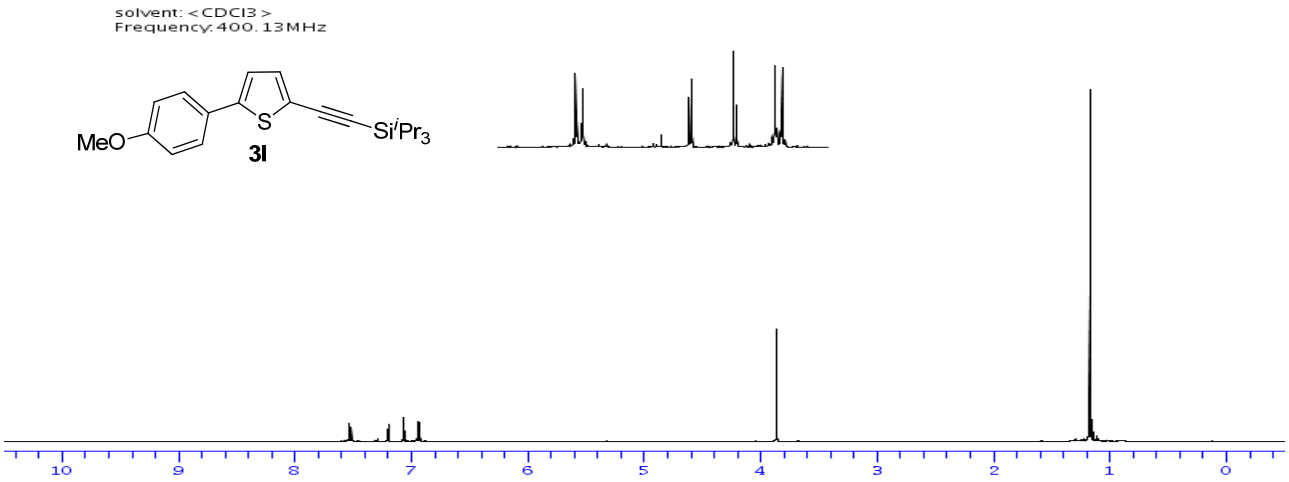
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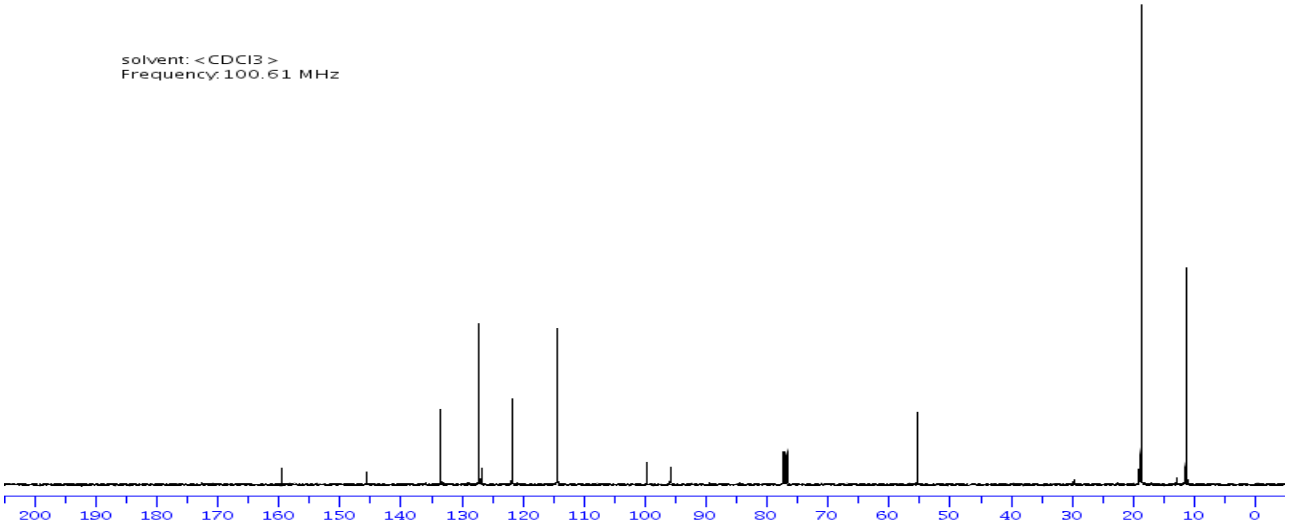
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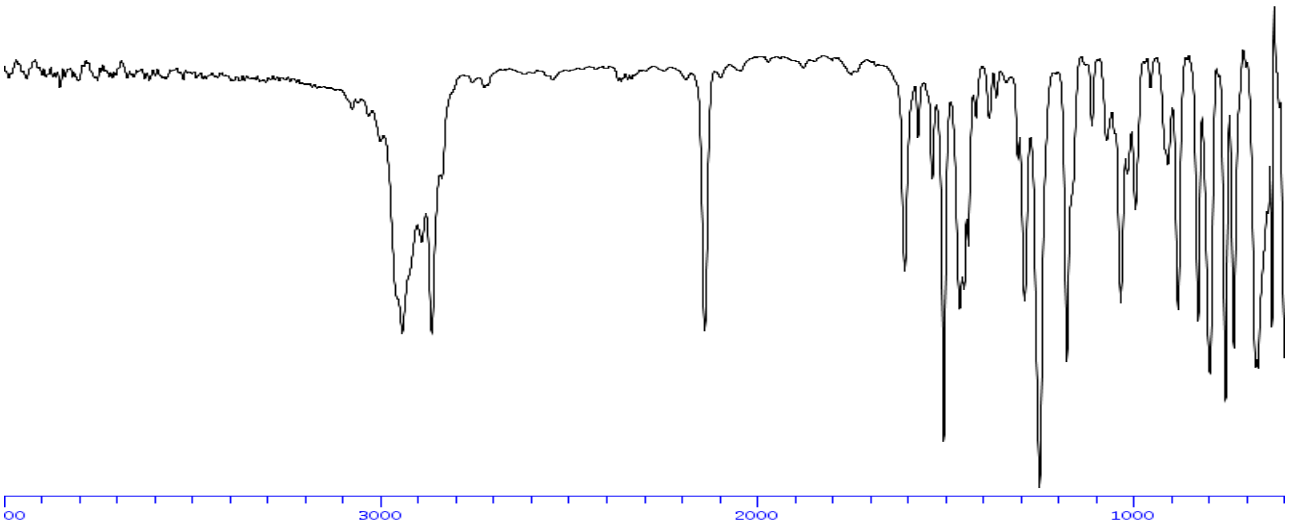
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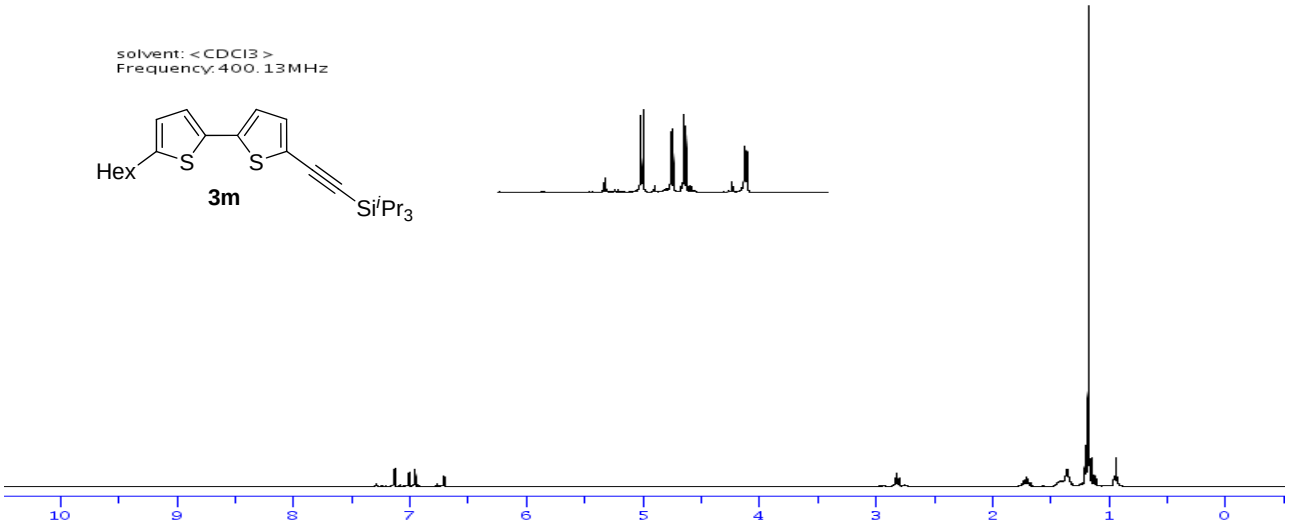
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Frequency: 400.13MHz
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S
Si^{i}Pr$_3$
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6
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4
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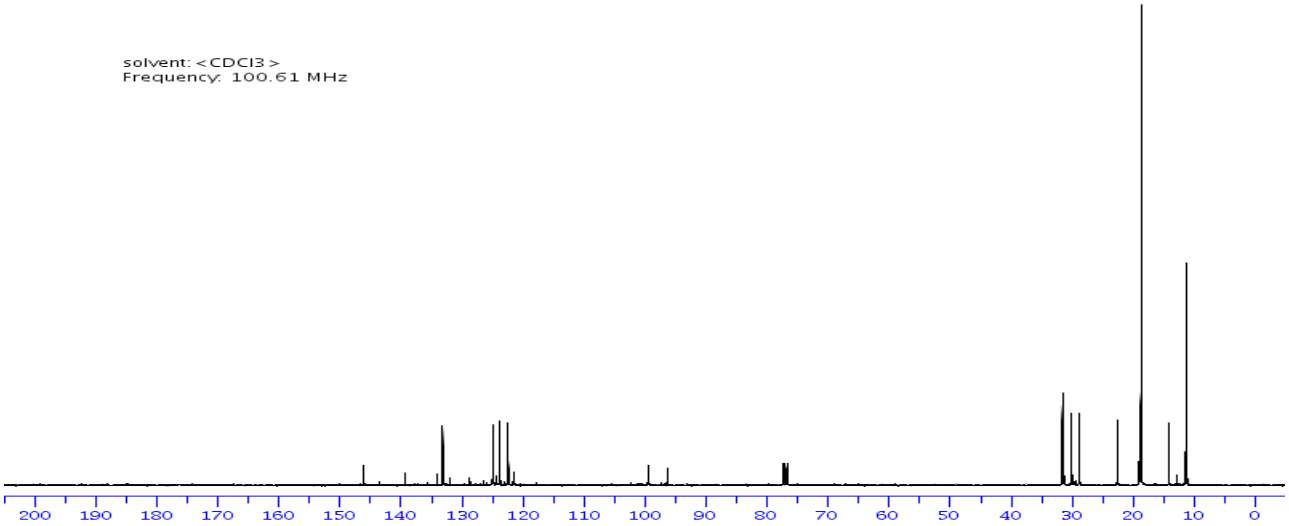
2
1
0

3m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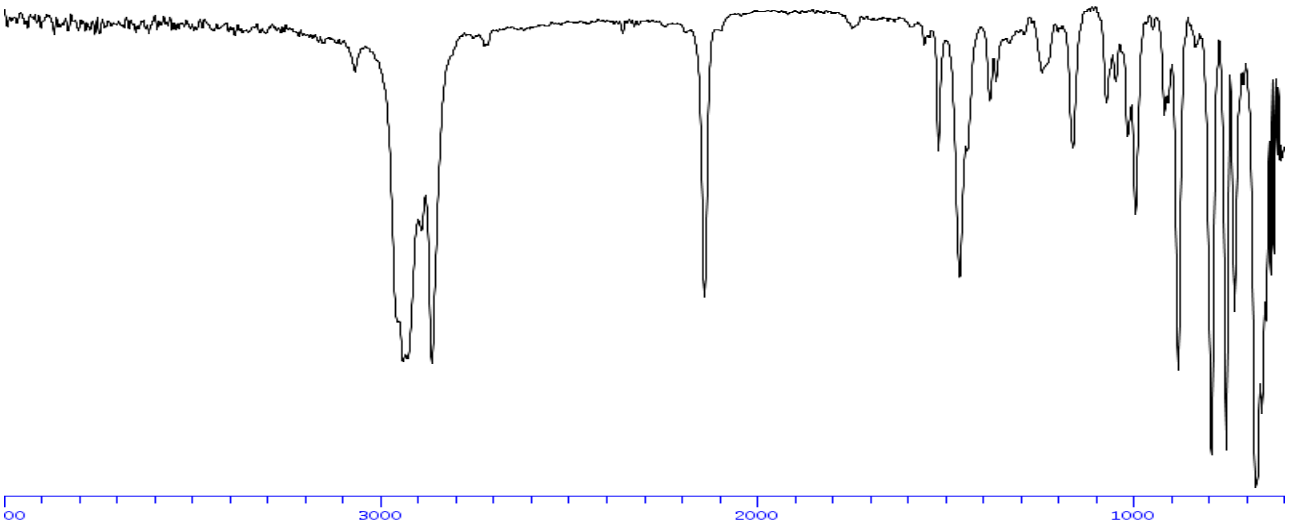
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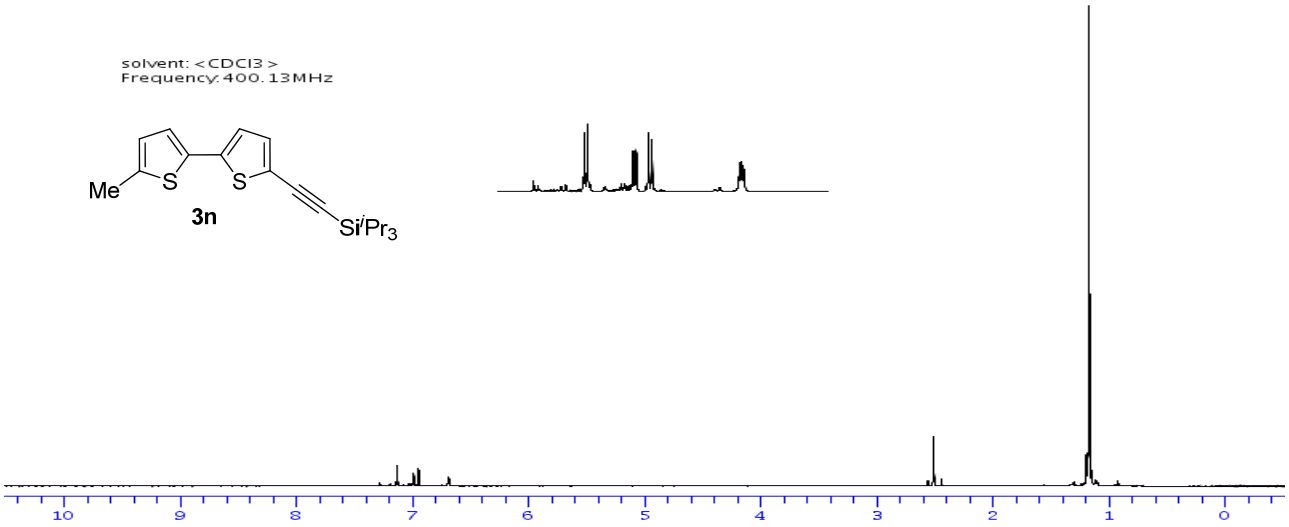
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S
3n
Si^{i}Pr$_3$
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3
2
1
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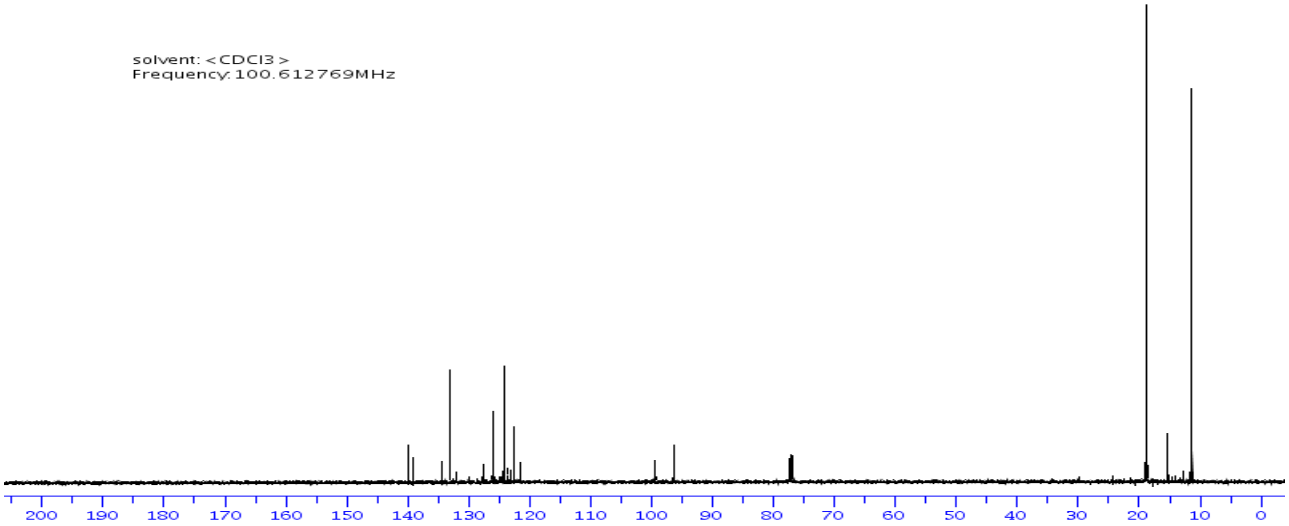
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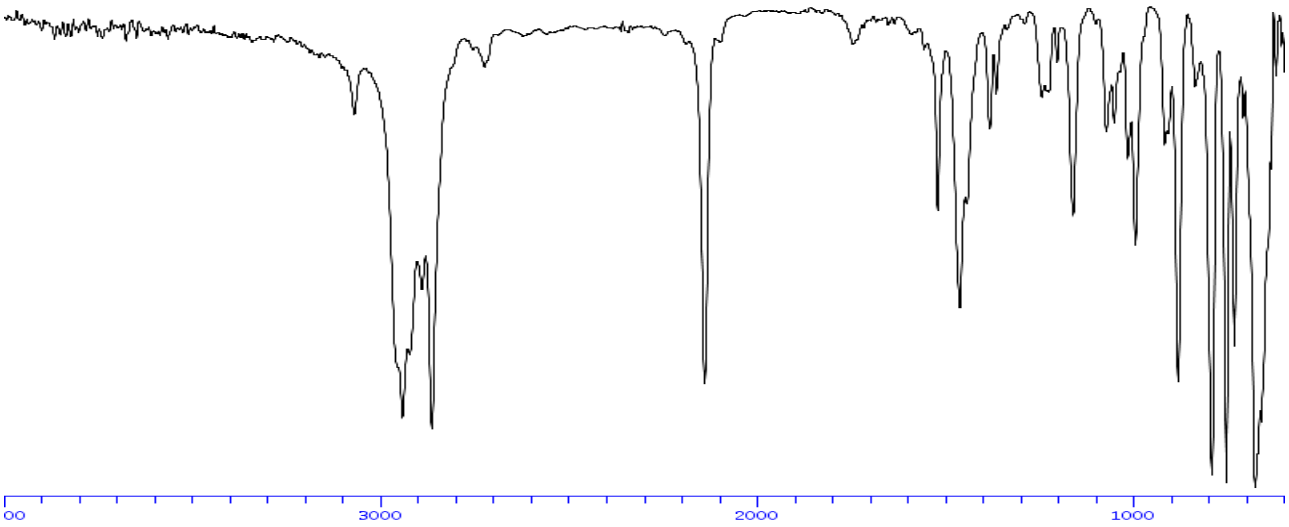
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2000
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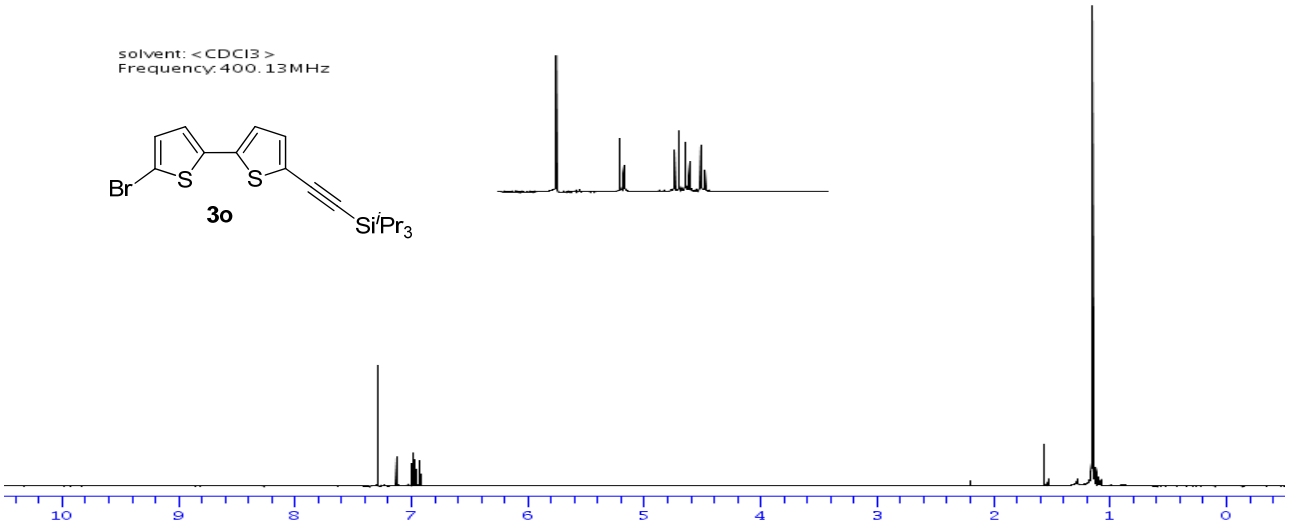
solvent: <CDCl3 >
Frequency: 400.13MHz
Br
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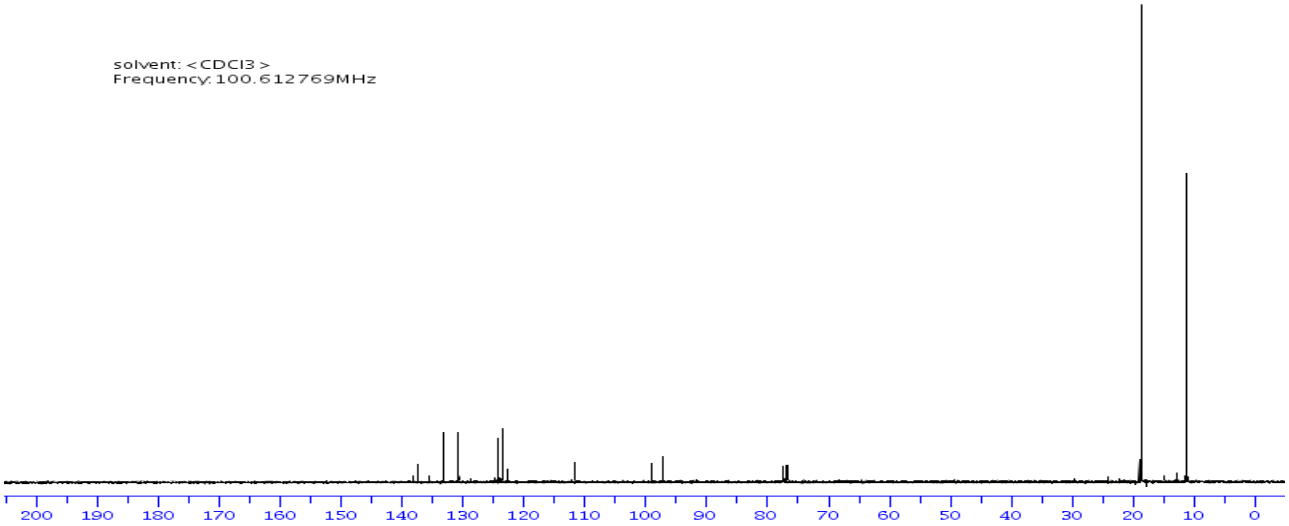
S
3o
SiiPr3
10
9
8
7
6
5
4
3
2
1
0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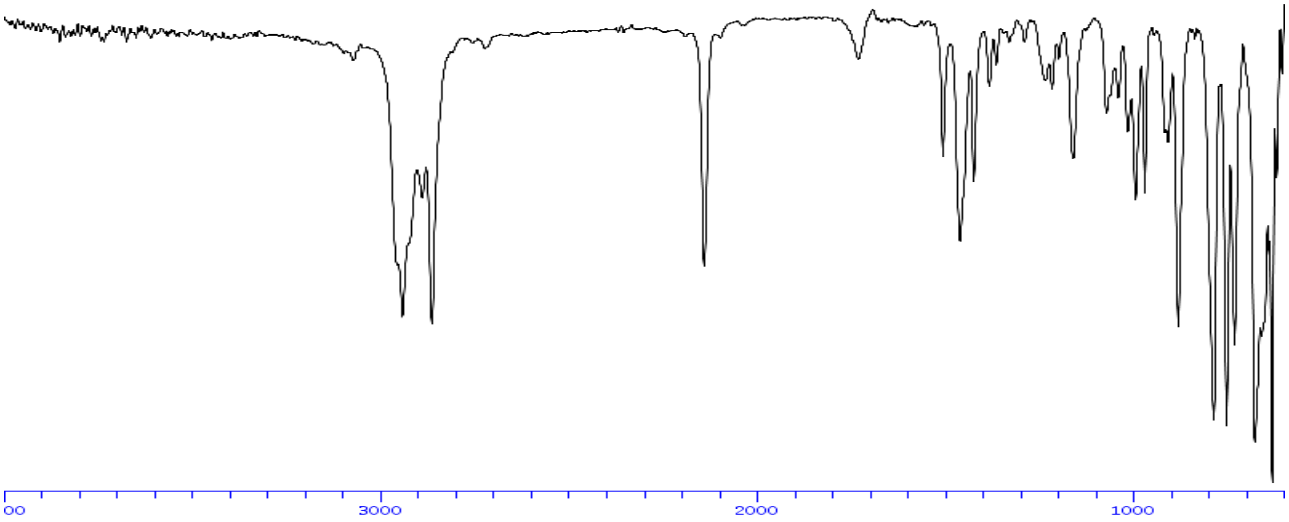
10
0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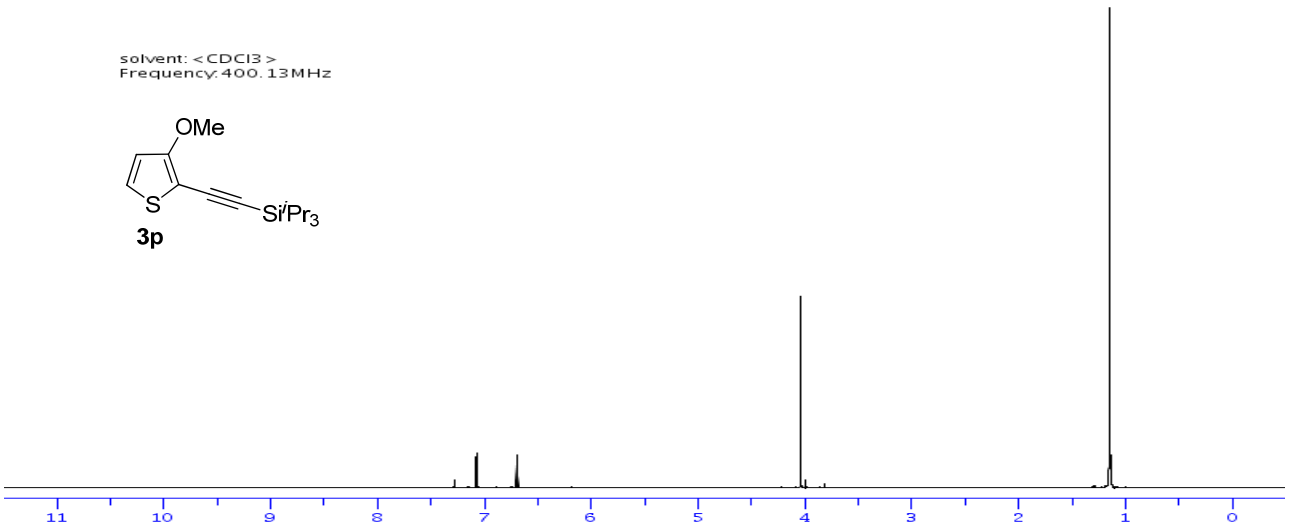
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Frequency: 400.13MHz
OMe
S
SiiPr3
3p
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7
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5
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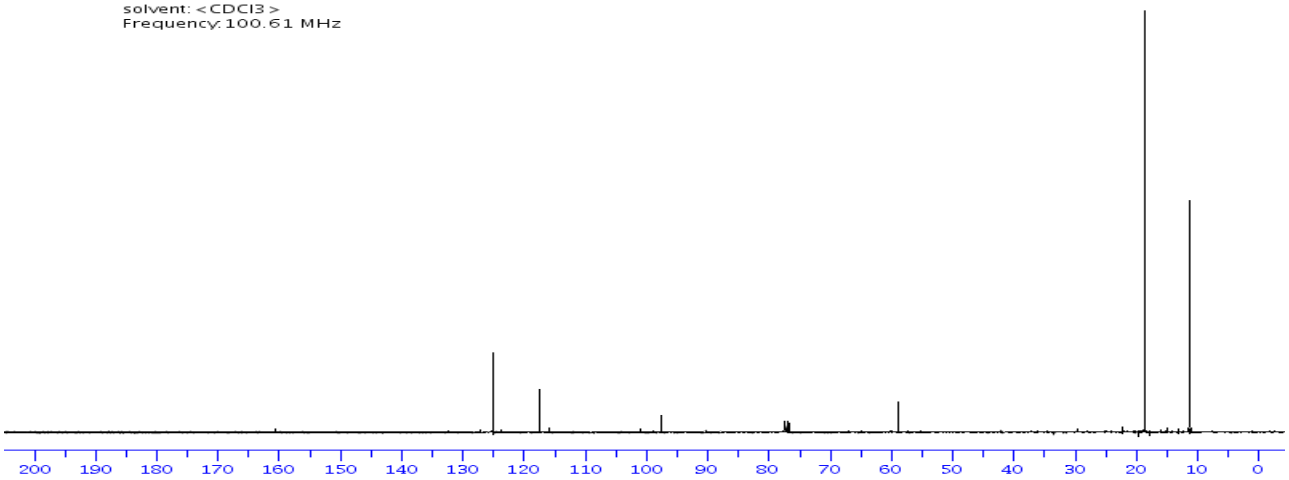
3
2
1
0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Frequency: 100.61 MHz
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50
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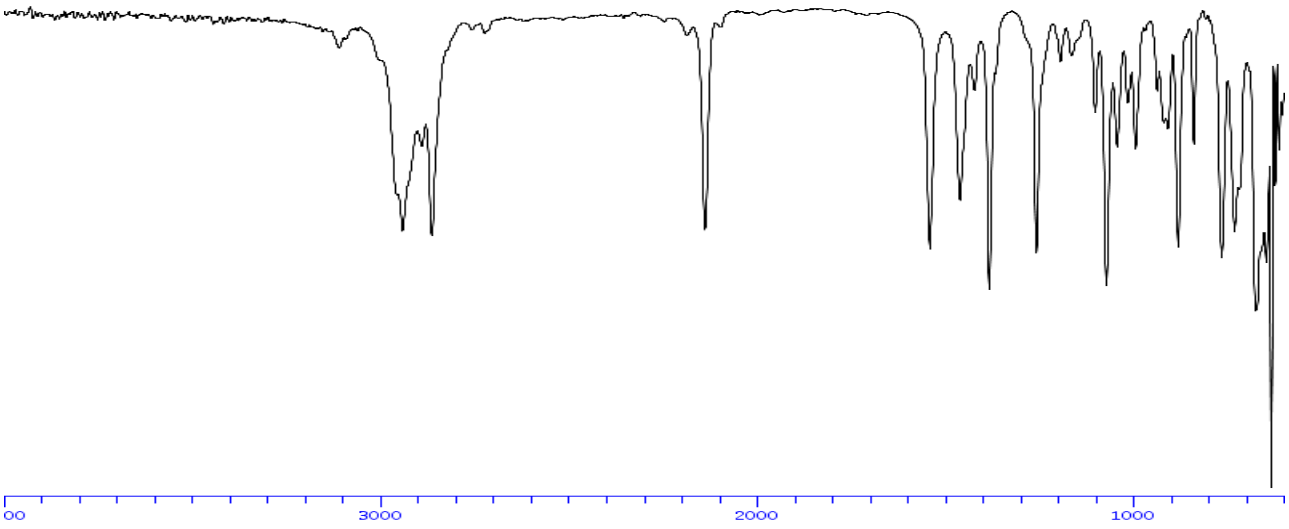
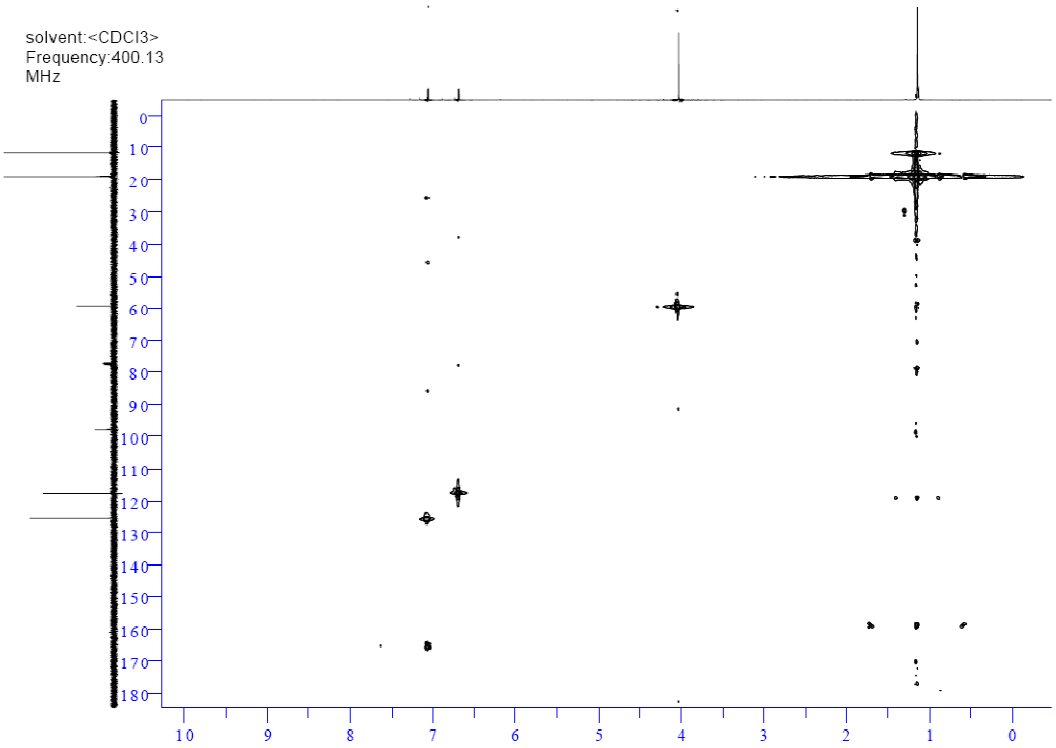
30
20
10
0


00
3000
2000
1000

HSQC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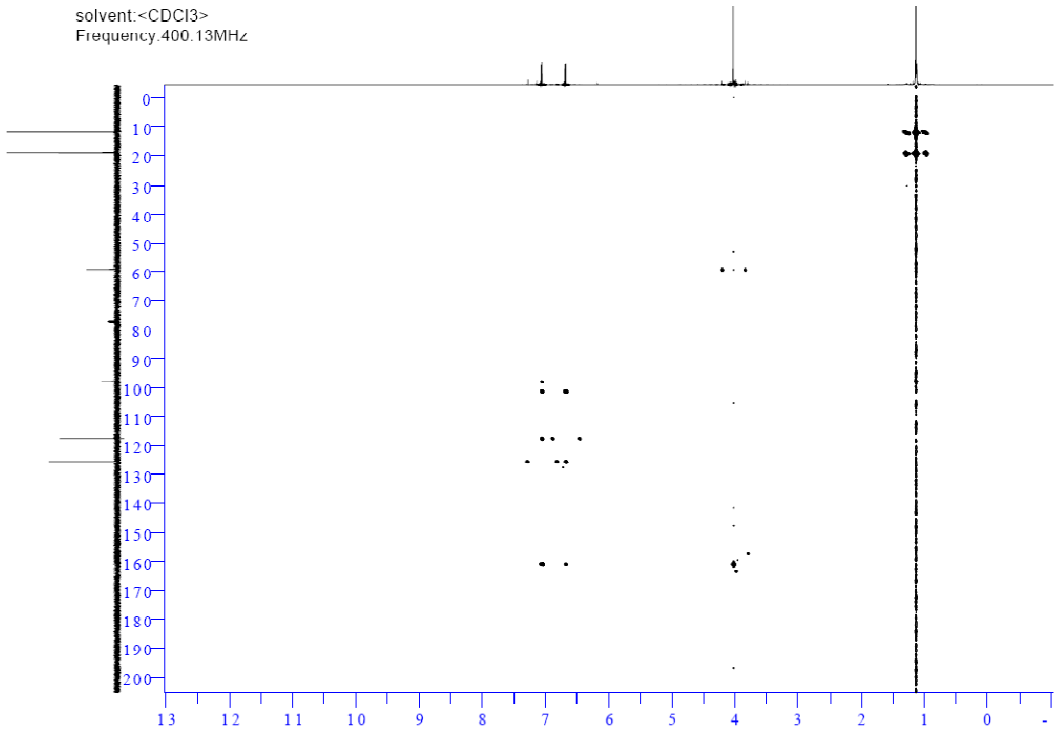
MHz

HMBC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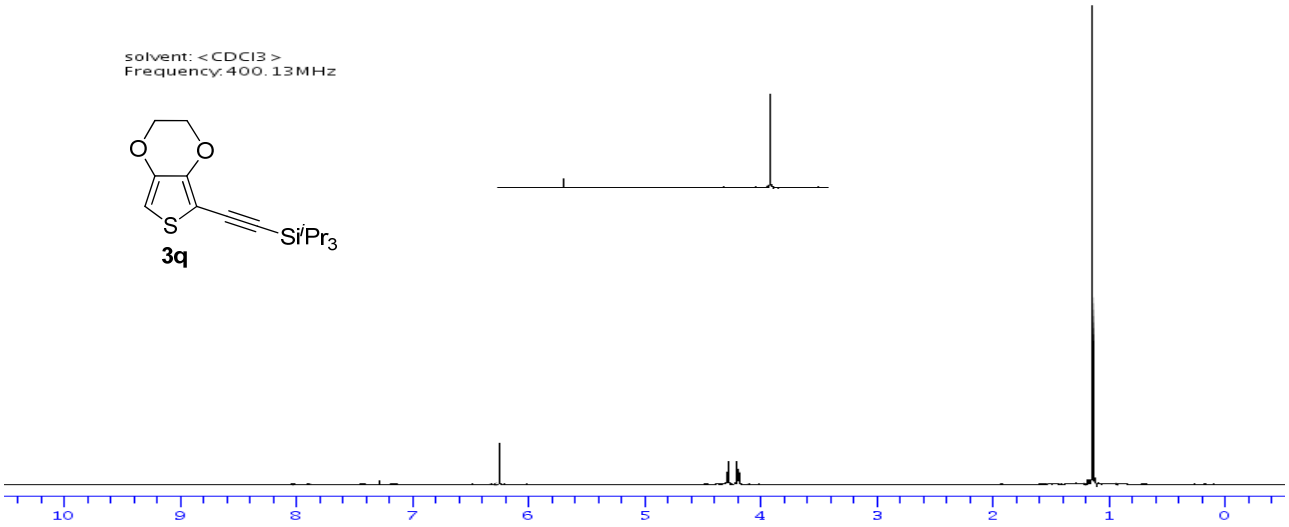
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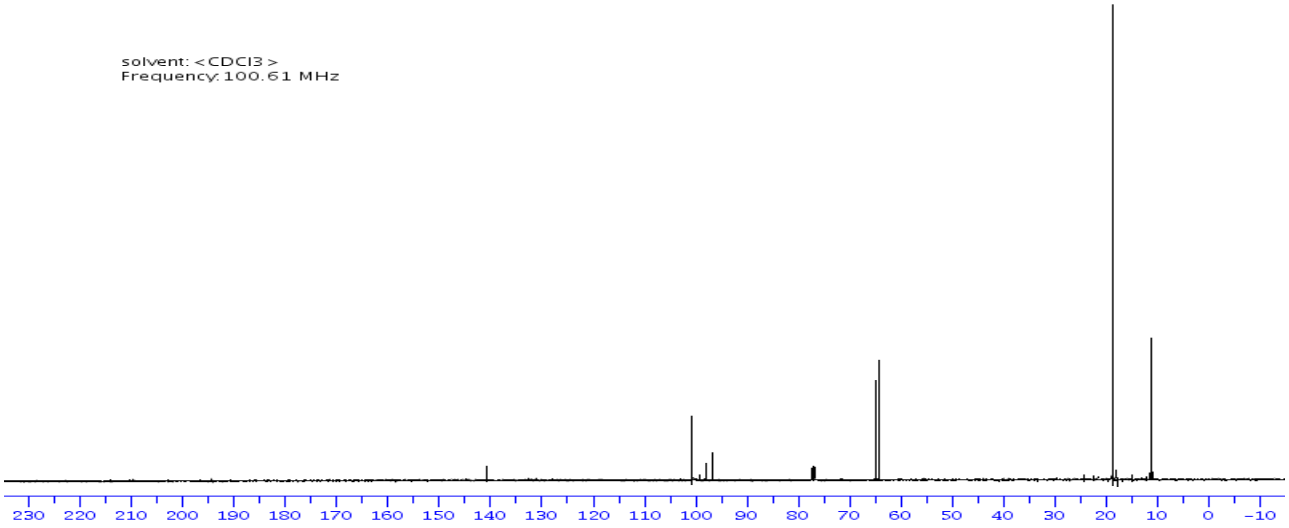
Frequency: 400.13MHz
O
O
S
SiiPr3
3q
10
9
8
7
6
5
4
3
2
1
0


solvent: <CDCl3>
Frequency: 100.61 MHz
230
220
210
200
190
180
170
160
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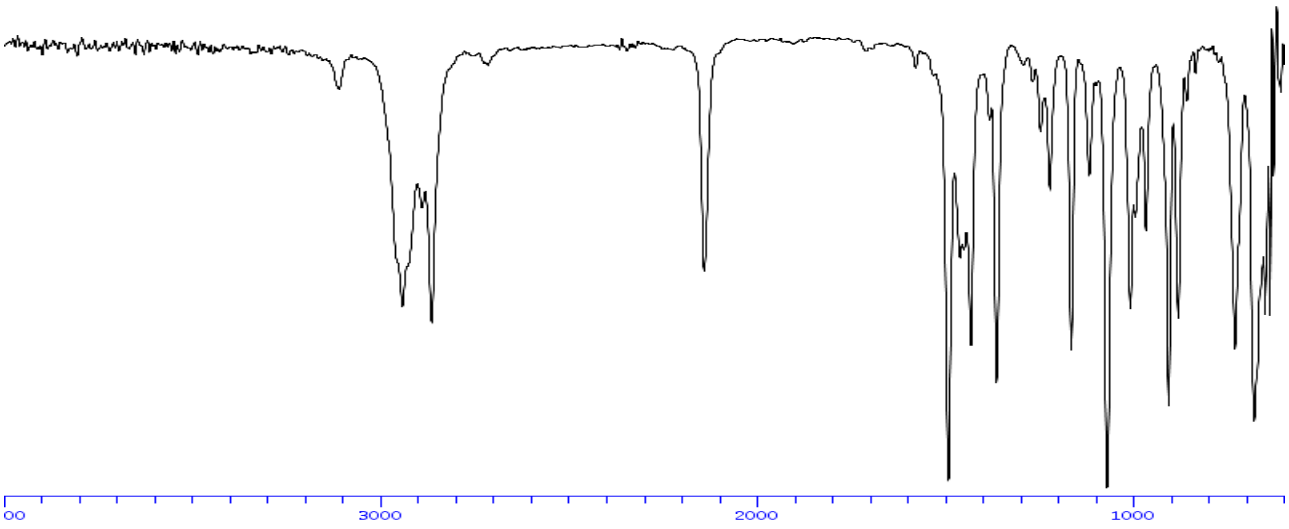
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


00
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2000
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solvent: <CDCl3>
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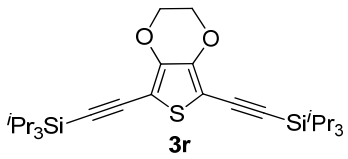

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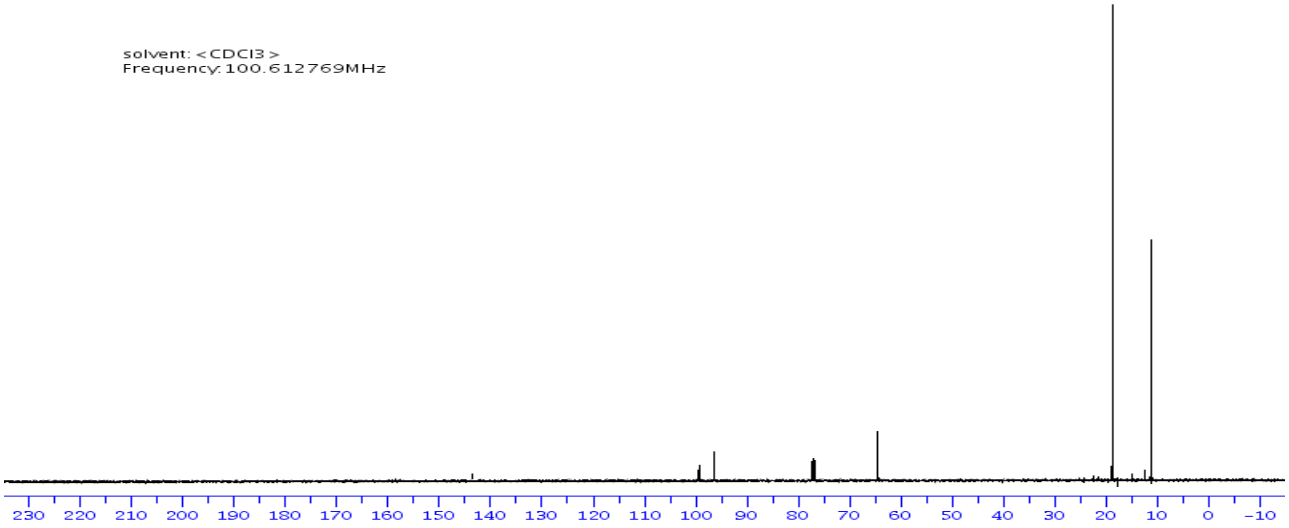
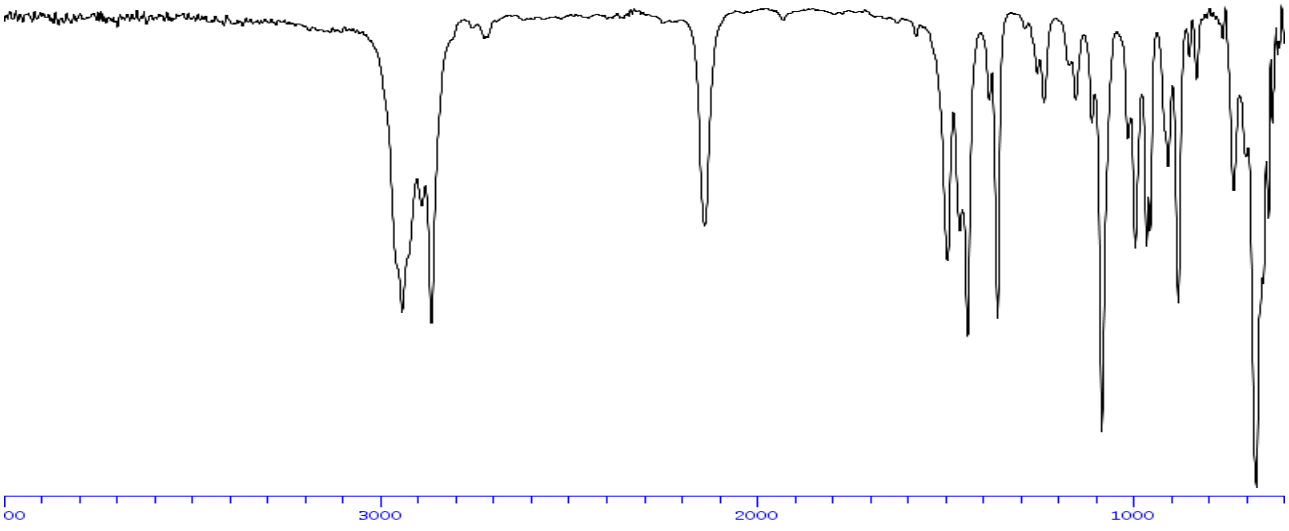
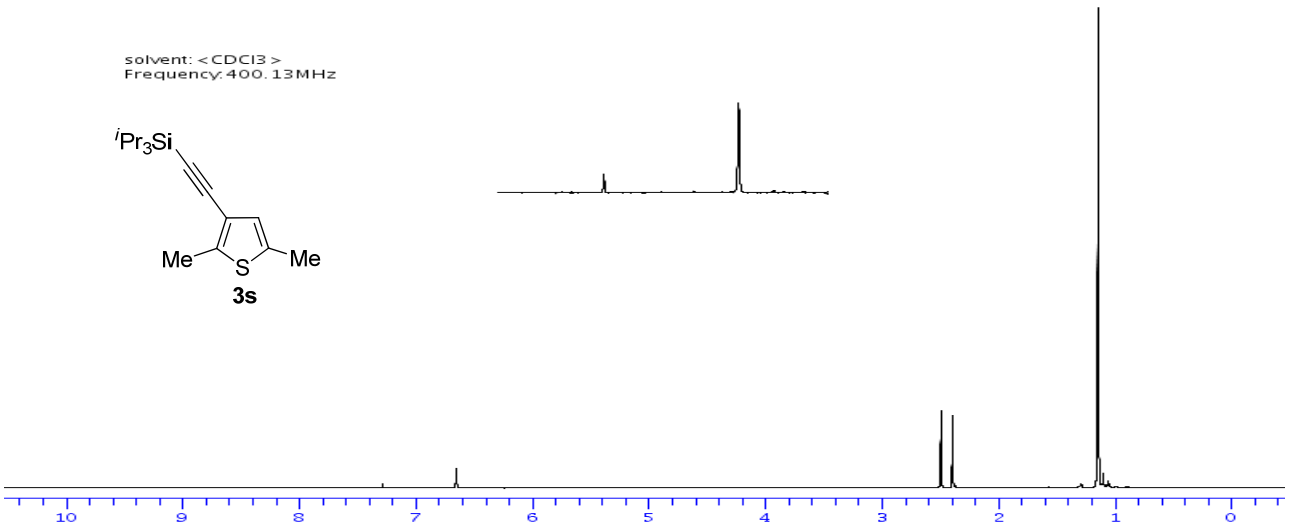
solvent: <CDCl3>
Frequency: 100.612769MHz



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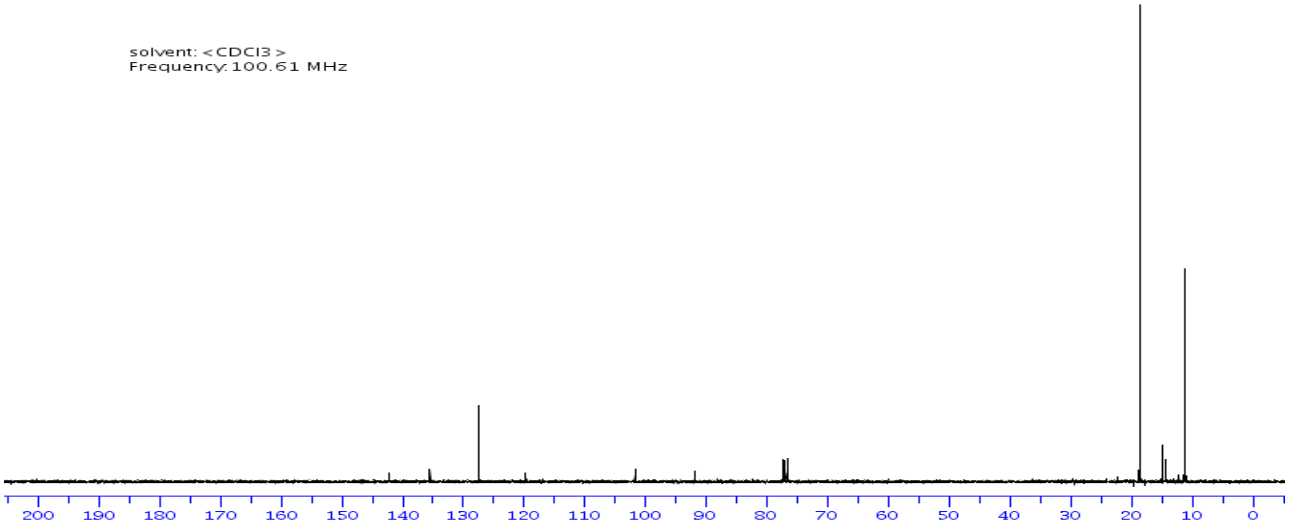
Frequency: 400.13MHz
$^{i}Pr_3Si$
Me
S
Me
3s
10
9
8
7
6
5
4
3
2
1
0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Frequency: 100.61 MHz
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120
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30
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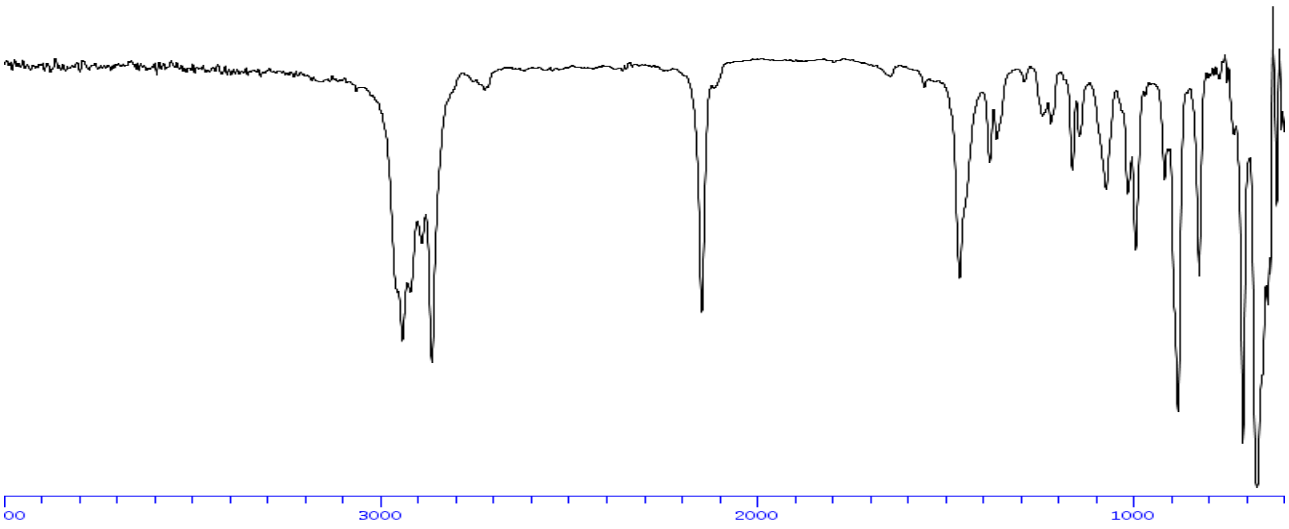
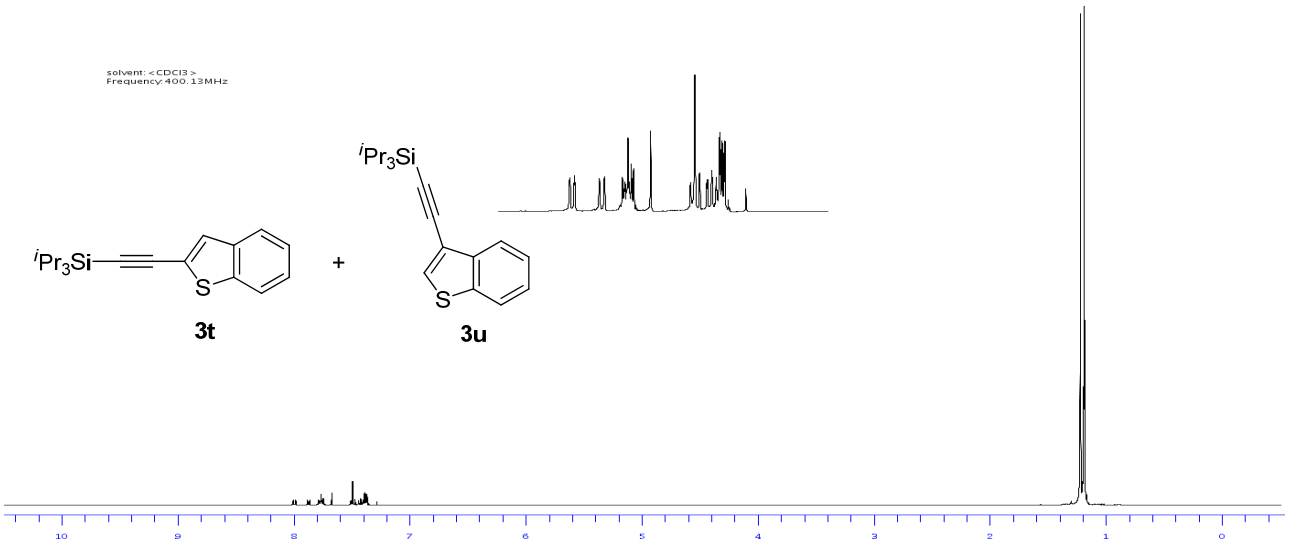
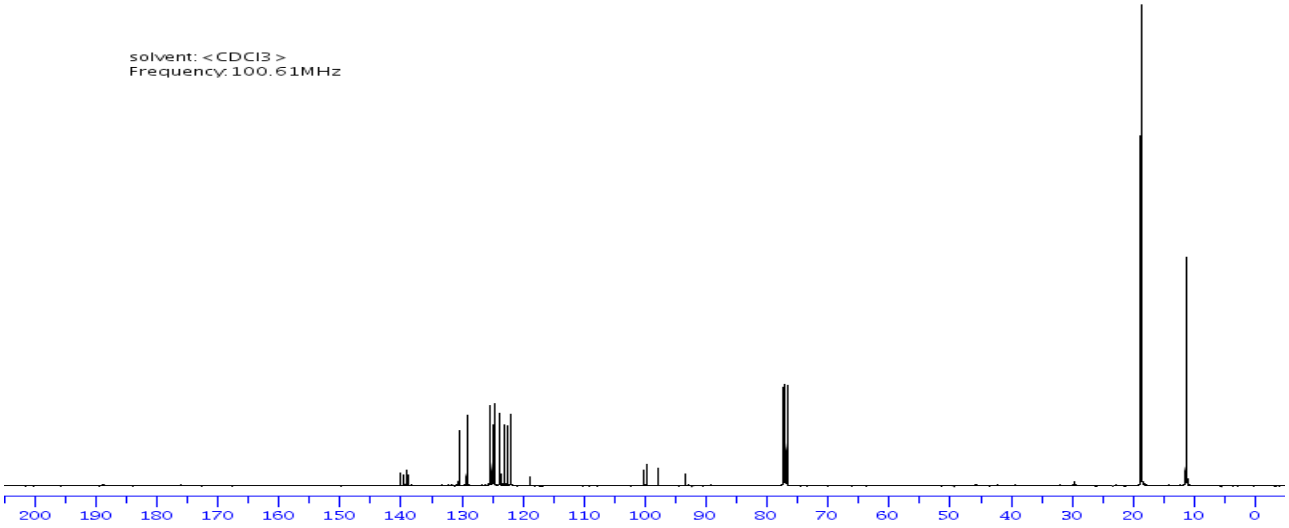
10
0


00
3000
2000
1000


solvent: <CDCl3 >
Frequency: 400.13MHz
$^{i}Pr_3Si$
S
3t
+
$^{i}Pr_3Si$
S
3u
10
9
8
7
6
5
4
3
2
1
0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Frequency: 100.61MHz
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120
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100
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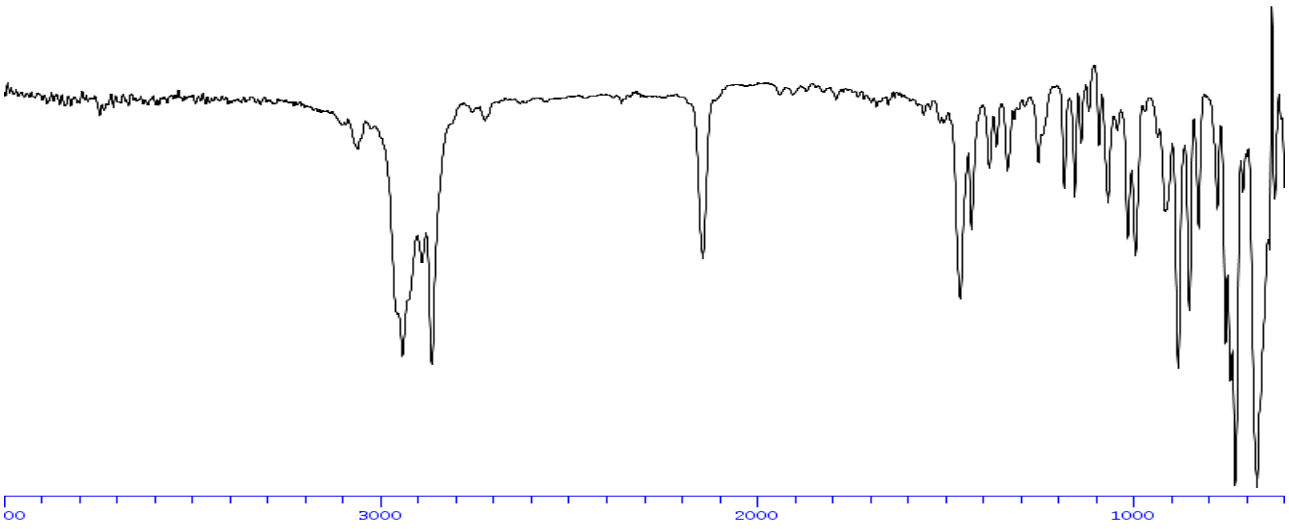
10
0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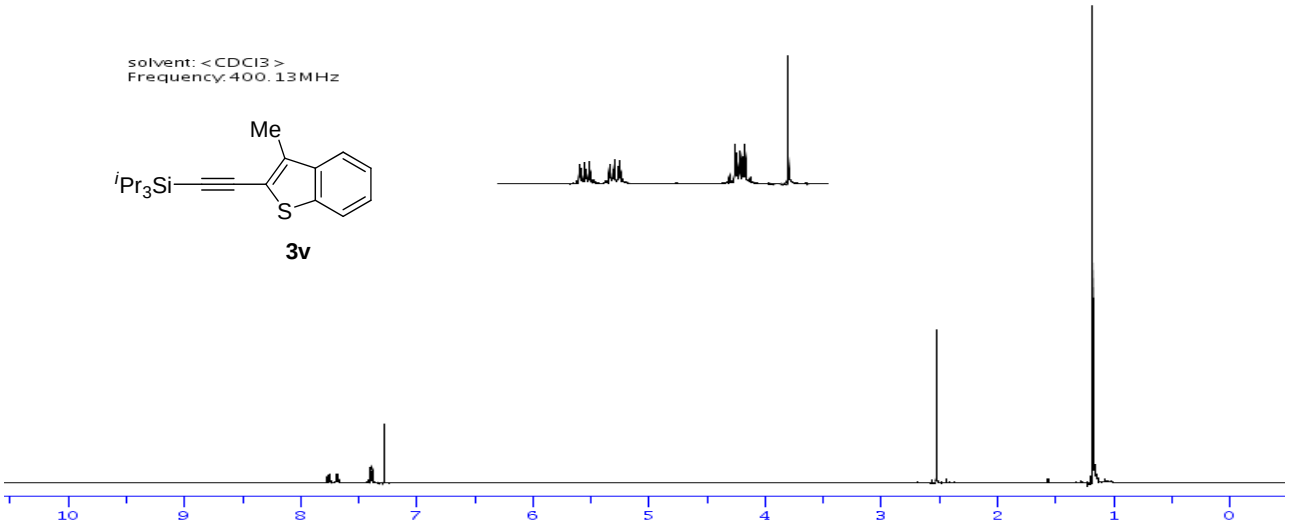
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8
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6
5
4
3
2
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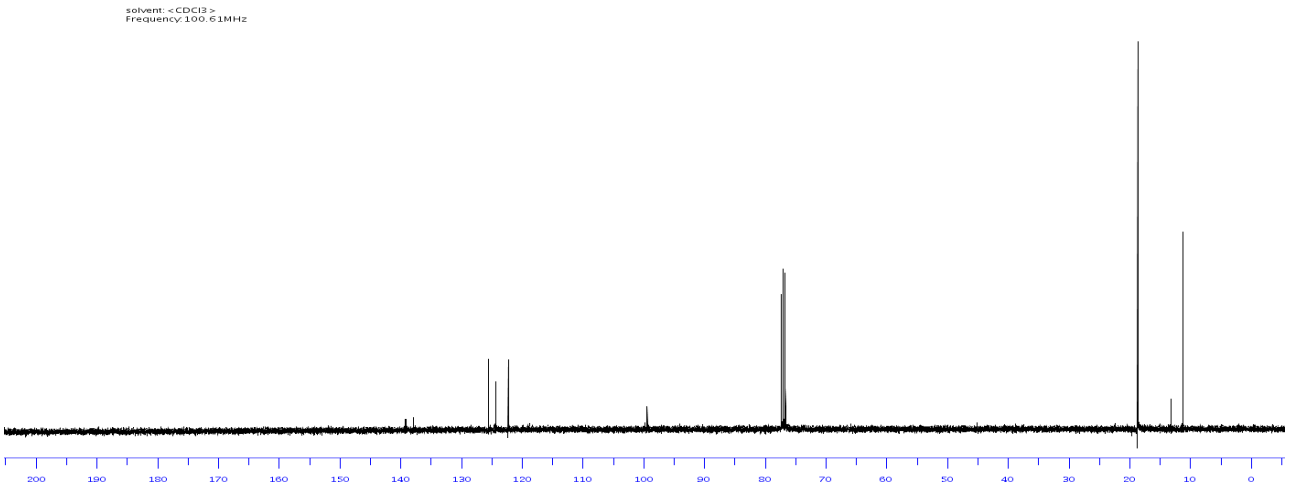
0

3v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10
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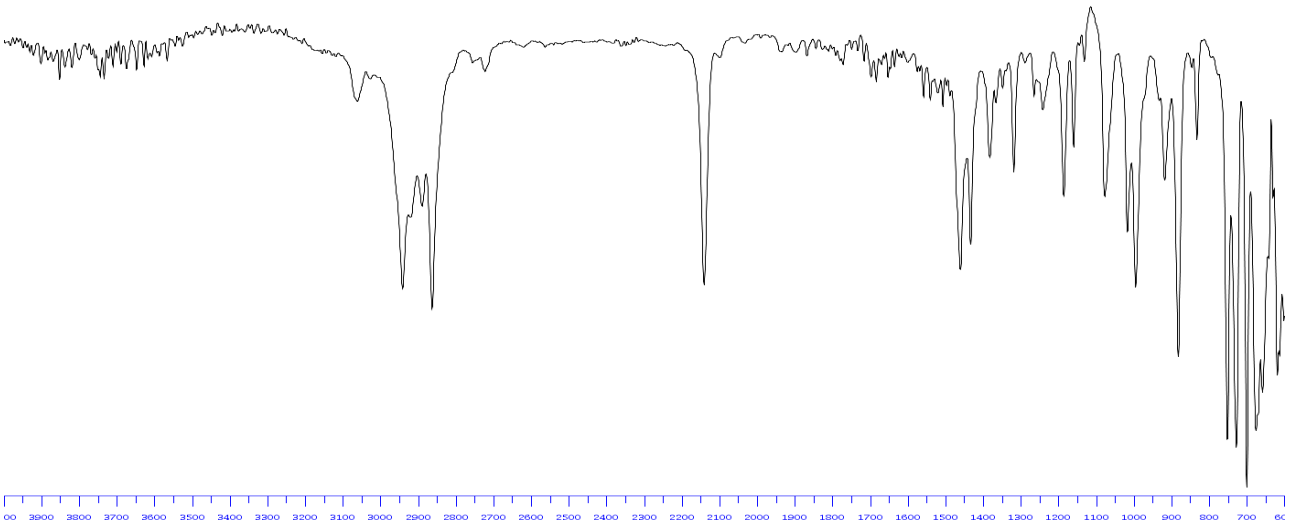
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3200
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2800
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2600
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1000
900
800
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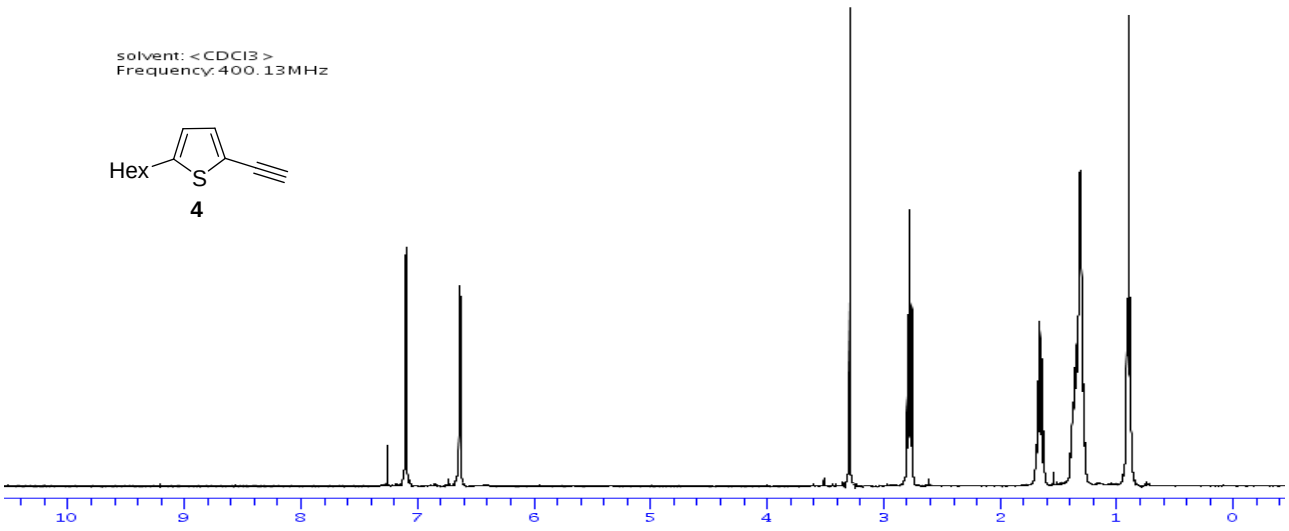
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Hex
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2
1
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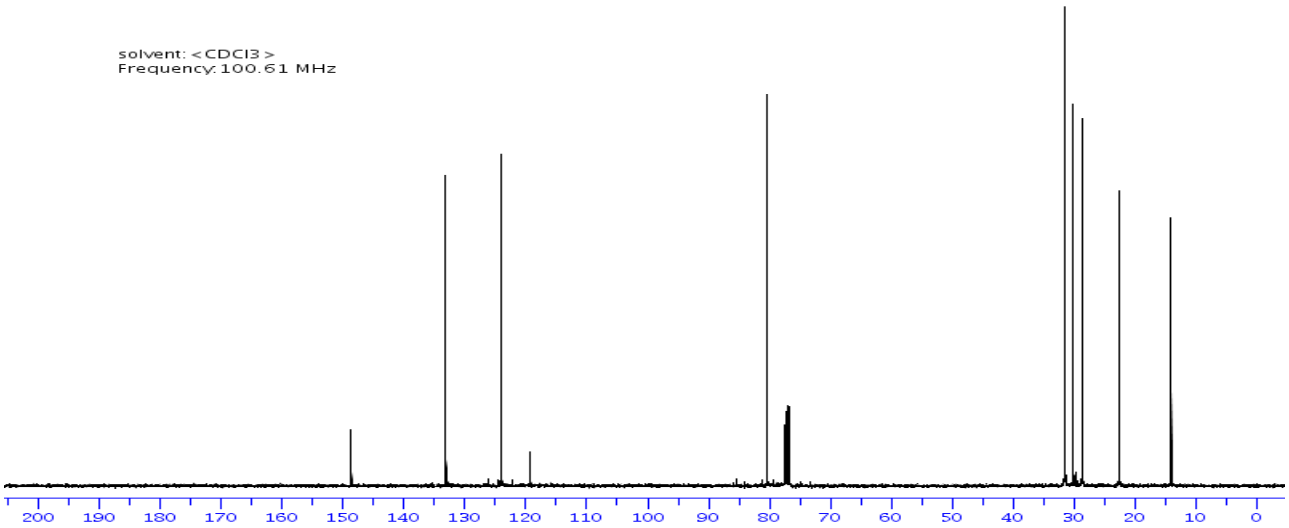
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Frequency: 100.61 MHz
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10
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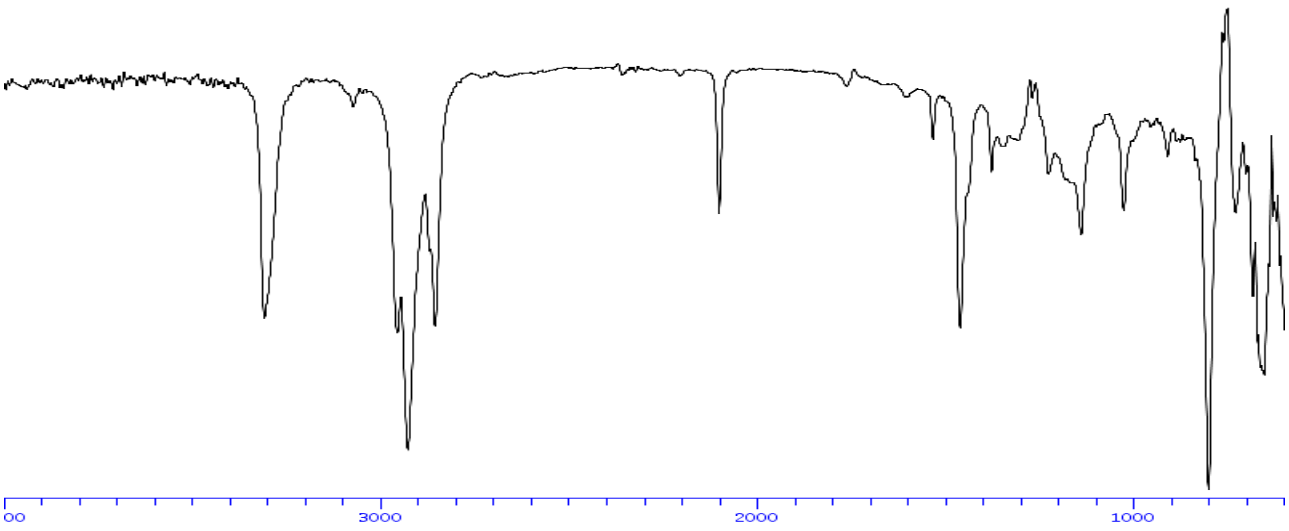
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solvent: <CDCl3 >
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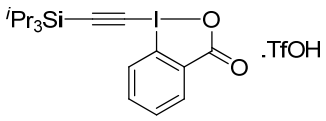
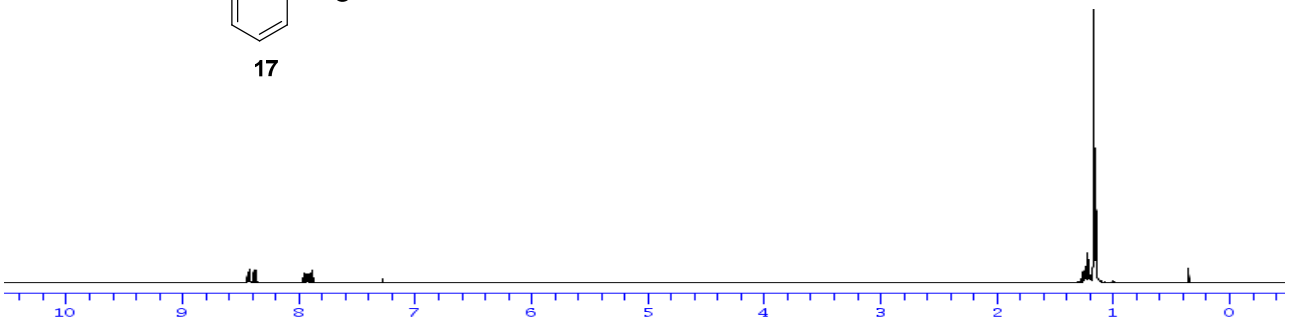


17



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