Para-Selective Gold-Catalyzed Direct Alkynylation of Anilines

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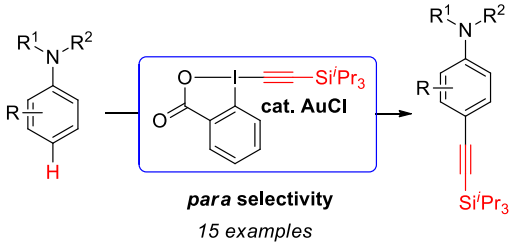
ABSTRACT



A method for the *para* selective alkynylation of anilines is reported using AuCl as catalyst and tri*iso*propylsilylethynyl-1,2-benziodoxol-3(*1H*)-one (TIPS-EBX) as an electrophilic acetylene equivalent. *Para*-alkynyl anilines substituted at positions 2 or 3 were obtained in one step from simple anilines under mild conditions (room temperature to 60 °C) under air. The methodology could also be extended to the alkynylation of trimethoxybenzenes.

Heteroarylacetylenes are important structures in both organic synthesis and material sciences.[1] They are versatile building blocks thanks to the large number of transformations available based on the functionalization of the triple bond. In addition, both aromatics and acetylenes have been successfully used in extended π systems for organic electronic materials.[2] In order to access heteroarylacetylenes, the Sonogashira reaction is one of the most popular methods for sp^2-sp bond formation.[3] However, the main drawback of this method is the required prefunctionnalization of the sp^2 carbon. Numerous methods have been developed in the field of C-H arylation in order to avoid this prefunctionalization of aromatics.[4] Surprinsingly, reports of direct alkynylations were scarce up to 2009.[5] Since then, important breakthroughs have been realized and several groups reported new C-H alkynylation methods.[6] Our

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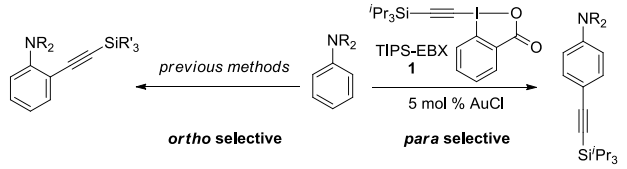
(6) Reviews: (a) Dudnik, A. S.; Gevorgyan, V. *Angew. Chem. Int., Ed.* **2010**, *49*, 2096. (b) Messaoudi, S.; Brion, J. D.; Alami, M. *Eur. J. Org. Chem.* **2010**, 6495. Selected examples: (c) Matsuyama, N.; Hirano,

group especially focused on the functionalization of electron-rich heterocycles such as indoles, pyrroles and thiophenes using tri*iso*propylsilylethynyl-1,2-benziodoxol-3(*1H*)-one (TIPS-EBX (**1**)) as electrophilic alkynylation reagent and AuCl as catalyst.[7] The focus on the synthesis of silylated acetylenes is motivated by their simple deprotection to access the synthetically highly versatile terminal alkynes.

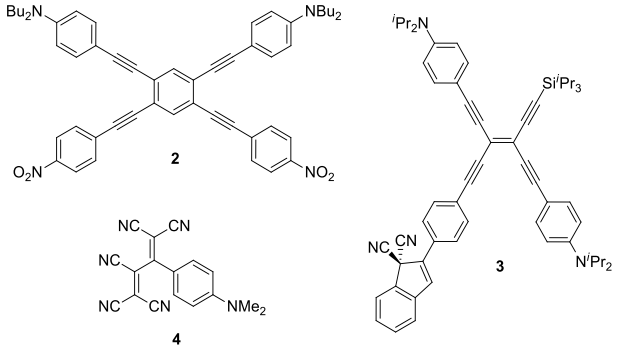
Presently, there are only two reports for the alkynylation of anilines by Yamaguchi and Chatani,[5b,6j] with both methods affording exclusively *ortho* alkynylated products. This selectivity was rationalized by a mechanism involving a directing effect of the nitrogen functional group. As the gold–catalyzed alkynylation did not require a directing group, we hypothesized that *para* selective functionalization could be realized (Scheme 1). Herein, we report the development of the first *para*-selective alkynylation of anilines using TIPS-EBX (**1**) as acetylene-transfer reagent, which proceeds under mild conditions (room temperature to 60 °C, ambient atmosphere).

Scheme 1. Direct Alkynylation of Anilines



Para-alkynyl anilines are widely used in material sciences, especially as strong electron donors in push-pull chromophores for applications in optoelectronic devices (Figure 1).[8] For example, tetraalkyne **2** has shown easily tunable photochromic properties.[8f] The tetraethynylene **3** (TEES) has molecular photoswitch properties.[8d] Furthermore, ethynylanilines are used as starting materials for the synthesis of chromophores based on core structure **4** via [2+2]-cycloaddition with tetracyanoethene followed by retro-electrocyclization.[8e] Consequently, an efficient access to *para* alkynylated anilines would lead to a more straightforward synthesis of electronic organic materials.

Figure 1. *Para*-Alkynyl Anilines in Material Sciences.



Gold catalysis has recently been investigated for the direct functionalization of benzene rings via amination,[9] alkylation,[10] hydroarylation[11] and arylation.[12] Only one example of the catalytic use of gold for the alkynylation of benzene rings has been reported, but no anilines were used in that work.[6l,13] Moreover, there are only two single examples of gold-catalyzed direct functionalization of anilines for amination[9b] and hydroarylation.[11d] Consequently, the extension of the alkynylation reaction to anilines would constitute an important advance, not only in the field of acetylene chemistry, but also for gold catalysis in general, especially in light of nitrogen-containing groups being reported to deactivate gold catalysts in several cases.[14]

In order to investigate the alkynylation of protected anilines with TIPS-EBX (**1**),[15] we decided to use *N*,*N*-

K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 4156. (d) Kawano, T.; Matsuyama, N.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2010**, *75*, 1764. (e) Kitahara, M.; Hirano, K.; Tsurugi, H.; Satoh, T.; Miura, M. *Chem. Eur. J.* **2010**, *16*, 1772. (f) Matsuyama, N.; Kitahara, M.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2010**, *12*, 2358. (g) Besselievre, F.; Piguel, S. *Angew. Chem., Int. Ed*. **2009**, 48, 9553. (h) Berciano, B. P.; Lebrequier, S.; Besselievre, F.; Piguel, S. *Org. Lett.* **2010**, *12*, 4038. (i) Kim, S. H.; Chang, S. *Org. Lett.* **2010**, *12*, 1868. (j) Tobisu, M.; Ano, Y.; Chatani, N. *Org. Lett.* **2009**, *11*, 3250. (k) Gu, Y. H.; Wang, X. M. *Tetrahedron Lett.* **2009**, *50*, 763. (l) de Haro, T.; Nevado, C. *J. Am. Chem. Soc.* **2010**, *132*, 1512. (m) Yang, L.; Zhao, L. A.; Li, C. J. *Chem. Commun.* **2010**, *46*, 4184

(7) (a) Brand, J. P.; Charpentier, J.; Waser, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 9346. (b) Brand, J. P.; Waser, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 7304. (c) Brand, J. P.; Chevalley, C.; Waser, J. *Beilstein J. Org. Chem.* **2011**, *7*, 565. First synthesis of TIPS-EBX (**1**): (d) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Simonsen, A. J. *J. Org. Chem.* **1996**, *61*, 6547.

(8) Selected examples: (a) Kivala, M.; Diederich, F. *Acc. Chem. Res.* **2009**, *42*, 235. (b) Gobbi, L.; Elmaci, N.; Luthi, H. P.; Diederich, F. *ChemPhysChem* **2001**, *2*, 423. (c) Bosshard, C.; Spreiter, R.; Gunter, P.; Tykwinski, R. R.; Schreiber, M.; Diederich, F. *Adv. Mater.* **1996**, *8*, 231. (d) Gobbi, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 674. (e) Reutenauer, P.; Kivala, M.; Jarowski, P. D.; Boudon, C.; Gisselbrecht, J. P.; Gross, M.; Diederich, F. *Chem. Commun.* **2007**, 4898. (f) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464.

(9) (a) Li, Z. G.; Capretto, D. A.; Rahaman, R. O.; He, C. *J. Am. Chem. Soc.* **2007**, *129*, 12058. (b) Gu, L.; Neo, B. S.; Zhang, Y. *Org. Lett.* **2011**, *13*, 1872.

(10) Shi, Z. J.; He, C. *J. Am. Chem. Soc.* **2004**, *126*, 13596

(11) Selected examples: (a) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485. (b) Shi, Z. J.; He, C. *J. Org. Chem.* **2004**, *69*, 3669. (c) Reich, N. W.; Yang, C. G.; Shi, Z. J.; He, C. *Synlett* **2006**, 1278. (d) Jean, M.; van de Weghe, P. **2011**, *52*, 3509.

(12) Kar, A.; Mangu, N.; Kaiser, H. M.; Beller, M.; Tse, M. K. *Chem. Commun.* **2008**, 386.

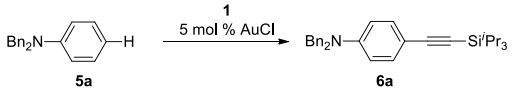
(13) For the stoichiometric use of gold, see: Fuchita, Y.; Utsunomiya, Y.; Yasutake, M. *J. Chem. Soc. Dalton Trans.* **2001**, 2330.

(14) (a) Belot, S.; Vogt, K. A.; Besnard, C.; Krause, N.; Alexakis, A., *Angew. Chem., Int. Ed.* **2009**, *48*, 8923. (b) Monge, D.; Jensen, K. L.; Franke, P. T.; Lykke, L.; Jorgensen, K. A., *Chem. Eur. J.* **2010**, *16*, 9478. (c) Loh, C. C. J.; Badorrek, J.; Raabe, G.; Enders, D. *Chem. Eur. J.* **2011**, *17*, 13409.

(15) Our work has been focused on TIPS-EBX (**1**) to afford easy to deprotect silyl acetylenes. Furthermore, a bulky silyl group was shown to be essential for the success of the reaction. See reference 7. Indeed, no product was obtained using phenylethynyl-1,2-benziodoxol-3(*1H*)-one as acetylene transfer reagent.

benzylaniline (**5a**) as model compound since it is more nucleophilic than the corresponding carbamate and the benzyl groups are easily removed by hydrogenation. Unfortunately, the reaction conditions previously optimized for indoles[7a] only afforded a 14% yield employing *N*,*N*-dibenzylaniline (**5a**) as substrate (Table 1, entry 1) due to low conversion. The outcome of the reaction was highly dependent on the solvent, with ^{i}PrOH giving the best result (entries 2-4). No *ortho* alkynylation was observed for aniline **5a**. The use of 1.4 equivalent of TIPS-EBX (**1**) was optimal (entries 4-6). The use of a higher concentration did not improve the yield (entry 7). Best results were obtained when the reaction was not pushed to full conversion in order to prevent the formation of side products. In this case, the starting material could easily be recovered. The obtained yields are in the same range as those obtained in the current state-of-the-art direct *para*-functionalizations of anilines.[16]

Table 1. Optimization of the *para*-Alkynylation of Anilines.



5a **6a**

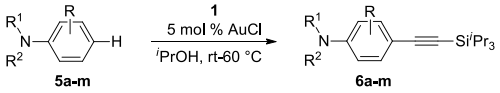
entry	solvent	TIPS-EBX (**1**) equivalents	yield[a]
1	Et_2O	1.2	14%
2	CH_2Cl_2	1.2	49%
3	CH_3CN	1.2	51%
4	^{i}PrOH	1.2	58%
5	^{i}PrOH	1.4	73% (84%)[b]
6	^{i}PrOH	1.6	55%
7[c]	^{i}PrOH	1.4	68% (81%)[b]

[a] Reaction conditions: 0.20 mmol *N*,*N*-dibenzylaniline (**5a**), 0.01 mmol AuCl in 4 mL ^{i}PrOH at 23 °C under air. Isolated yield after column chromatography. [b] Yield based on recovered starting material (brsm). [c] 2 mL ^{i}PrOH.

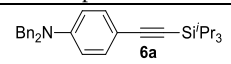
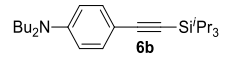
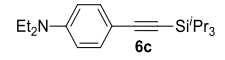
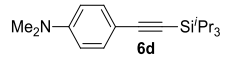
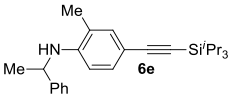
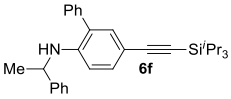
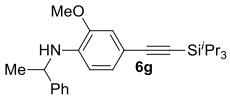
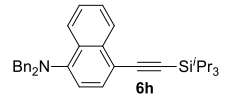
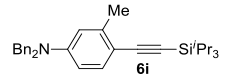
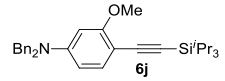
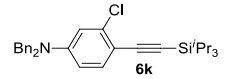
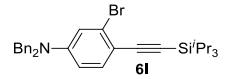
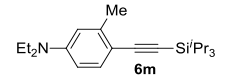
We then focused our attention on the scope of the reaction (Table 2). In addition to benzyl (entry 1), butyl, ethyl and methyl groups were tolerated as nitrogen substituents, but led to lower yields (entries 2-4). Smaller alkyl groups led to a complex mixture of side products, including 8% of the *ortho-para* disubstituted product for R = Me (entry 4). These results indicate that the process has the regioselectivity of an aromatic electrophilic substitution. It is in line with our previous highly SEAr regioselective methodologies for the alkynylation of indoles, pyrroles and thiophenes.[7a,b]

O*rtho* methyl, phenyl and methoxy groups were tolerated for monoprotected anilines (entries 5-7).[17] This result also demonstrated that the method was tolerant towards a free NH bond on the aniline. The alkynylation reaction was even successful in the case of the less reactive dibenzyl 2-aminonaphthalene (**5h**), although full conversion could not be achieved in this case (entry 8).

Table 2. Scope of the *para*-Alkynylation of Anilines.



5a-m **6a-m**

entry	product	yield (%)[a]
1	 **6a**	73% (84%)[b]
2	 **6b**	63%
3	 **6c**	44%
4[c]	 **6d**	46% (8%)[d]
5	 **6e**	64%
6[c]	 **6f**	65%
7[c]	 **6g**	42% (70%)[b]
8[c]	 **6h**	35% (65%)[b]
9[c]	 **6i**	73%
10[c]	 **6j**	85%
11[c]	 **6k**	41% (72%)[b]
12[c]	 **6l**	35% (61%)[b]
13[c]	 **6m**	75%

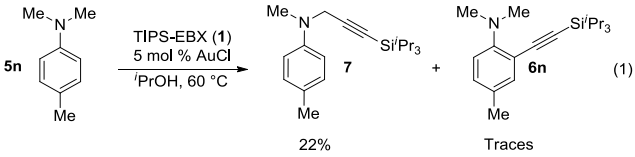
Reaction conditions: 0.40 mmol **5**, 0.56 mmol **1**, 0.02 mmol AuCl in 8 mL ^{i}PrOH at 23 °C under air. Isolated yields. [b]Yields based on recovered starting materials. [c]at 60 °C in 2 mL ^{i}PrOH. [d]*ortho-para* disubstituted product.

Importantly, alkynylation was also possible for alkyl, methoxy, chloro and bromo groups in the *meta* position, giving more sterically hindered 1,3,4-substituted anilines (entries 9-13). In addition, the tolerance to chloro and bromo substituents demonstrated the orthogonality of the method to classical Pd cross-couplings. Low yields of *ortho* alkynylated products were obtained using *para*

(16) Ciana, C. L.; Phipps, R. J.; Brandt, J. R.; Meyer, F. M.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 458.

(17) Ortho substituted *N*,*N*-disubstituted anilines were not reactive, probably because of the deconjugation of the nitrogen for steric reasons.

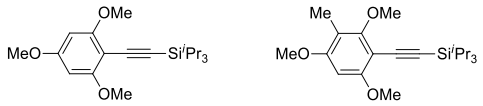
substituted anilines.[18] In the case of 4-methyl-*N,N*-dimethyl aniline (**5n**), one of the main products obtained was the sp^3 coupling product on the methyl substituent of the nitrogen (eq 1). It is interesting to note that this reaction can easily be achieved with free acetylenes and metal catalysts under oxidative conditions.[19] Consequently, it could indicate that this product results from the relatively high oxidation capacity of TIPS-EBX (**1**).



(1)

In addition to anilines, the reaction could also be applied towards the alkynylation of trimethoxybenzenes (Figure 2). Up to now, the only report for the alkynylation of this class of substrates was limited to the use of more electron-deficient propiolic acid derivatives.[6l] The use of TIPS-EBX (**1**) allowed access to an easily deprotectible non electron-deficient acetylene.

Figure 2. Alkynylation of trimethoxybenzenes[a]



[a]Reaction conditions: 0.40 mmol trimethoxybenzene, 0.56 mmol **1**, 0.02 mmol AuCl in 2 mL ^{i}PrOH at 60 °C under air. Isolated yields. Yields based on recovered starting materials under parenthesis.

In conclusion, we have developed the first *para*-selective direct alkynylation of anilines using gold chloride as catalyst and TIPS-EBX (**1**) as acetylene-transfer reagent. The method allowed a new and efficient access to important building blocks in synthetic chemistry and material sciences under mild reaction conditions and at ambient atmosphere. We demonstrated that a wide range of anilines could be alkynylated regioselectively using the developed methodology. Investigations towards the elucidation of the reaction mechanism are currently ongoing in our laboratory.

Supporting Information. Experimental procedures, analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) 4-Methyl-*N,N*-dibenzylaniline was *ortho* alkynylated in 18% yield.

(19) For sp^3 alkynylation of dimethylaniline (**5d**), see: (a) Li, Z. P.; Li, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 11810. (b) Volla, C. M. R.; Vogel, P. *Org. Lett.* **2009**, *11*, 1701. (c) Liu, P.; Zhou, C. Y.; Xiang, S.; Che, C. M. *Chem. Commun.* **2010**, *46*, 2739. For cyanation of dimethylaniline (**5d**) using hypervalent iodine, see: (d) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Mismash, B.; Woodward, J. K.; Simonsen, A. J. *Tetrahedron Lett.* **1995**, *36*, 7975. For sp^3 cyanation of dimethylaniline (**5d**) using a gold complexe, see: (e) Zhang, Y.; Peng, H.; Zhang, M.; Cheng, Y. X.; Zhu, C. J. *Chem. Commun.* **2011**, *47*, 2354.

Supporting Information

Para-Selective Gold-Catalyzed Direct Alkynylation of Anilines

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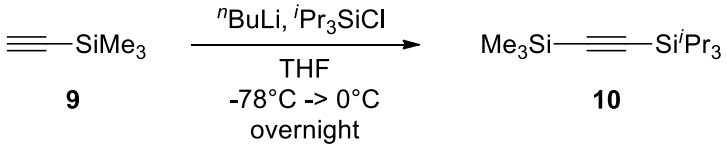
38 pages

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 or Alfa Aesar 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 calibrated Büchi B-540 melting point apparatus using open glass capillaries. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, C_6D_6 DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal C_6D_6 signal at 7.16 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. Some benziodoxol(on)es NMRs in $CDCl_3$ showed a small dependence to the concentration. As a result, the concentration of the corresponding NMR samples is indicated. 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.

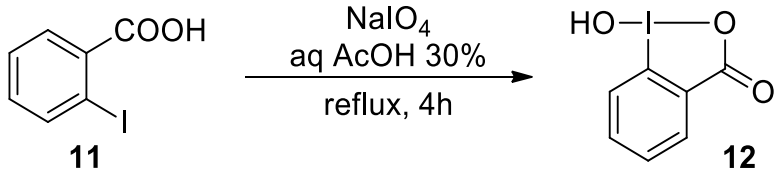
TIPS-EBX Synthesis

Tri*iso*propylsilyl trimethylsilylacetylene (10)



Following a reported procedure,[1] *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 (**9**) (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 **10** (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 **10** corresponded to the literature values. [1]

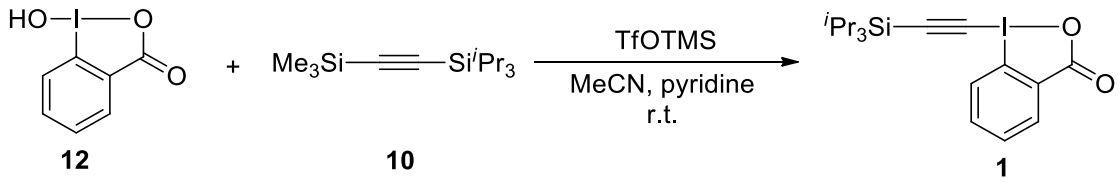
1-Hydroxy-1,2-benziodoxol-3(*1H*)-one (12)



Following a reported procedure,[2] $NaIO_4$ (6.7 g, 31 mmol; 1.0 equiv) and 2-iodobenzoic acid (**11**) (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 product **12** (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). The characterization data for compounds **12** corresponded to the reported values.[2]

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

(1) Helal, C J.; Magriotis, P. A; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 10938.
(2) Kraszkiewicz, L.; Skulski, L. *Arkivoc* **2003**, *6*, 120.



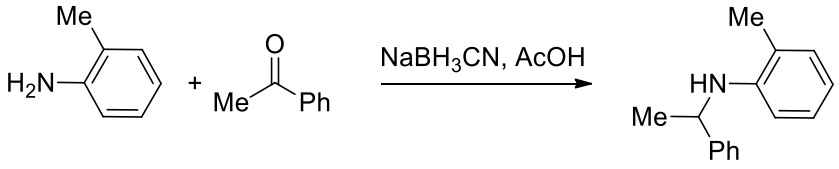
12 10 1

2-iodosylbenzoic acid (**12**) (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 (**10**) (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 CH_2Cl_2 (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. 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] A X-ray structure is available as a separate cif file.

Aniline synthesis

Anilines **5a-d** and **5n** are commercially available. The other anilines were synthesized following known procedures as indicated below. The used trimethoxybenzenes were all commercially available.

2-Methyl-*N*-(1-phenylethyl)aniline (5e)



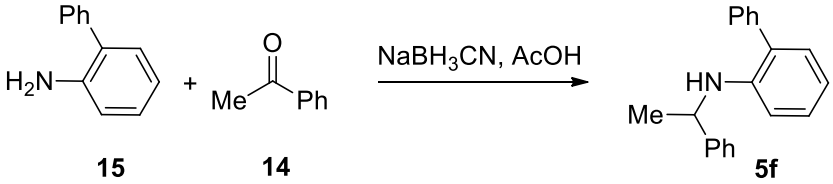
13 14 5e

Following a reported procedure,[4] acetophenone (**13**) (0.82 mL, 7.0 mmol, 1 equiv) was added to a stirring solution of *ortho*-toluidine (**13**) (0.75 mL, 7.0 mmol, 1 equiv) in AcOH (11.7 mL) and MeOH (2.3 mL). After 1h30, $NaBH_3CN$ (480 mg, 7.70 mmol, 1.1 equiv) was added. The reaction was stirred at RT for 20 h. The reaction was quenched with a saturated solution of Na_2CO_3 (10 mL) and extracted twice with CH_2Cl_2 (20 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under vacuum. Purification by column chromatography (Pentane/Et_2O 99/1) afforded **5e** (699 mg, 3.31 mmol, 47%) as a colorless oil. R_f (Pentane/Et_2O 99/1): 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 4 H, ArH), 7.23 (tm, 1 H,

(3) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Simonsen, A. J. **1996,** *61*, 6547.
(4) Ciana, C. L.; Phipps, R. J.; Brandt, J. R.; Meyer, F. M.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 458.

J = 7.0 Hz, ArH), 7.05 (d, 1 H, *J* = 6.9 Hz, ArH), 6.96 (t, 1 H, *J* = 7.2 Hz, ArH), 6.60 (td, 1 H, *J* = 7.4, 0.8 Hz, ArH), 6.36 (d, 1 H, *J* = 8.1 Hz, ArH), 4.54 (m, 1 H, CH), 3.85 (br s, 1 H, *J* = 2.3, 0.5 Hz, NH), 2.23 (s, 3 H, CH_3), 1.56 (d, 3 H, *J* = 6.7 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 145.1, 129.9, 128.6, 127.0, 126.8, 125.7, 121.5, 116.8, 111.0, 53.3, 25.3, 17.6. In accordance with reported data.[4]

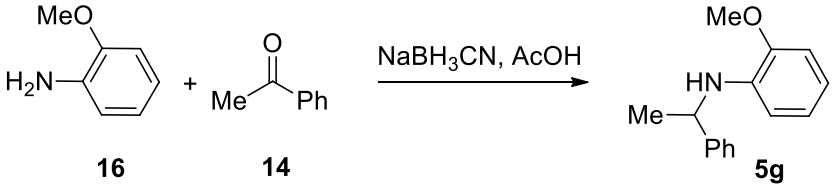
_N_-(1-phenylethyl)-[1,1'-biphenyl]-2-amine (5f)



15 **14** **5f**

Following a reported procedure,[4] acetophenone (**14**) (0.82 mL, 7.0 mmol, 1 equiv) was added to a stirring solution of 2-aminodiphenyl (**15**) (1.25 g, 7.00 mmol, 1 equiv) in AcOH (2.3 mL) and MeOH (11.7 mL). After 1 h, $NaBH_3CN$ (480 mg, 7.70 mmol, 1.1 equiv) was added. The reaction was stirred at RT for 20 h. The reaction was quenched with a saturated solution of Na_2CO_3 and extracted twice with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under vacuum. Purification by column chromatography (Hexane/EtOAc 99/1 to 9/1) afforded **5f** (534 mg, 2.35 mmol, 34%) as a colorless oil. R_f (Hexane/EtOAc 95/5): 0.3. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 4 H, ArH), 7.39 (m, 1 H, ArH), 7.32 (m, 4 H, ArH), 7.22 (m, 1 H, ArH), 7.06 (m, 2H, ArH), 6.71 (td, 1 H, *J* = 7.4, 1.1 Hz, ArH), 6.45 (d, 1 H, *J* = 8.1 Hz, ArH), 4.48 (q, 1 H, *J* = 6.7 Hz, CH), 4.31 (br s, 1 H, NH), 1.40 (d, 3 H, *J* = 6.7 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 143.9, 139.6, 130.1, 129.3, 129.0, 128.6, 128.5, 127.5, 127.2, 126.8, 125.7, 116.9, 111.7, 53.6, 25.0. Consistent with reported values.[5]

2-Methoxy-_N_-(1-phenylethyl)aniline (5g)



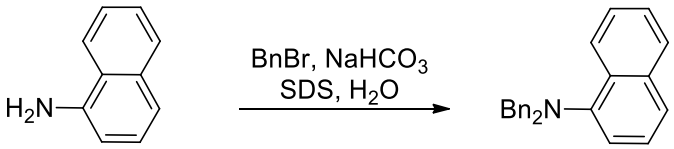
16 **14** **5g**

Following a reported procedure,[4] acetophenone (**14**) (0.59 mL, 5.0 mmol, 1 equiv) was added to a stirring solution of *ortho*-anisidine (**16**) (0.54 mL, 5.0 mmol, 1 equiv) in AcOH (1.6 mL) and MeOH (8.4 mL). After 45 min, $NaBH_3CN$ (344 mg, 5.50 mmol, 1.1 equiv) was added. The reaction was stirred at RT for 20 h. The reaction was quenched with saturated solution of Na_2CO_3 and extracted twice with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under vacuum. Purification by column chromatography (Pentane/Et_2O 98/2) afforded **5g** (432 mg, 1.91 mmol, 38%) as a colorless solid. R_f (Pentane/Et_2O 98/2): 0.25. Mp: 56-57°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 2 H, ArH), 7.34 (t, 2 H, *J* = 7.3 Hz, ArH), 7.25 (m, 1 H , ArH), 6.80 (d, 1 H, *J* = 7.8 Hz , ArH), 6.73 (m, 1 H, ArH), 6.64 (m, 1 H, ArH), 6.38 (d, 1 H, *J* = 7.8 Hz, ArH), 4.66 (s, 1 H, NH), 4.51 (q, 1 H, *J* = 6.2 Hz, CH), 3.91 (s, 3 H, CH_3), 1.58 (m, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 145.4, 137.2, 128.5, 126.7, 125.8, 121.1, 116.3, 111.0, 109.2, 55.4, 53.3, 25.1. IR 3426 (w), 3065 (w), 3027 (w), 2965 (w), 2954 (w), 2866 (w), 2834 (w), 1603 (m), 1511 (s), 1456 (m), 1447 (m), 1373 (w), 1346 (w), 1279 (w), 1252 (s), 1223 (s), 1177 (w), 1144

(5) R. E. Meadows, S. Woodward, *Tetrahedron* **2008**, *64*, 1218.

(m), 1110 (w), 1058 (w), 1029 (s), 910 (w), 764 (m), 735 (s), 701 (s). HRMS (ESI) calcd for $C_{15}H_{18}NO^+$ $[M+H]^+$ 228.1383; found 228.1380.

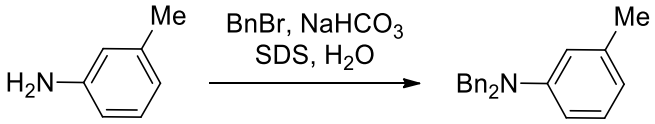
_N,N_-Dibenzylnaphthalen-1-amine (5h)



17 **5h**

Following a reported procedure,[6] benzyl bromide (1.83 mL, 15.4 mmol, 2.2 equiv) was added to a stirring solution of 2-aminonaphthalene (**17**) (1.0 g, 7.0 mmol, 1 equiv), $NaHCO_3$ (1.29 g, 15.4 mmol, 2.2 equiv) and sodium dodecyl sulfate (14 mg, 0.49 mmol, 0.007 equiv) in water (15 mL) and stirred at 80 °C for 1 h. The reaction was cooled and extracted twice with CH_2Cl_2 (20 mL). The organic layers were dried on $MgSO_4$ and concentrated under vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O 99/1) to afford **5h** (1.93 g, 5.98 mmol, 85%) as a colorless oil. R_f (pentane/Et_2O 99/1): 0.25. ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, 1 H, *J* = 8.2 Hz, ArH), 7.91 (d, 1 H, *J* = 8.0 Hz, ArH), 7.51-7.64 (m, 3 H, ArH), 7.25-7.39 (m, 11 H, ArH), 7.00 (d, 1 H, *J* = 7.4 Hz, ArH), 4.38 (s, 4 H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 138.2, 134.9, 129.7, 128.5, 128.4, 128.2, 126.9, 125.7, 125.5, 125.4, 123.7, 123.5, 118.4, 57.1. IR 3085 (w), 3061 (w), 3028 (w), 2920 (w), 2841 (w), 1949 (w), 1812 (w), 1594 (w), 1575 (m), 1509 (w), 1495 (m), 1454 (m), 1401 (m), 1363 (w), 1259 (w), 1223 (w), 1155 (w), 1100 (w), 1077 (w), 1029 (w), 1001 (w), 951 (w), 909 (m), 798 (m), 775 (s), 735 (s), 698 (s). HRMS (ESI) calcd for $C_{24}H_{22}N^+$ $[M+H]^+$ 324.1747; found 324.1737.

2-Methyl-_N_-(1-phenylethyl)aniline (5i)

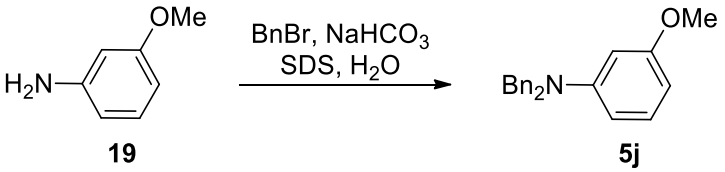


18 **5i**

Following a reported procedure, [6] benzyl bromide (1.32 mL, 11.0 mmol, 2.2 equiv) was added to a stirring solution of *m*-toluidine (**18**) (535 mg, 5.00 mmol, 1 equiv), $NaHCO_3$ (924 mg, 11.0 mmol, 1 equiv) and sodium dodecyl sulfate (20 mg, 0.069 mmol, 0.14 equiv) in water (20 mL) at 80 °C. After 1 h, the reaction was cooled and extracted twice with CH_2Cl_2 (20 mL). The organic layers were dried on $MgSO_4$ and concentrated under vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O 99/1) to afford **5i** (1.3 g, 4.6 mmol, 92%) as a colorless solid. R_f (pentane/Et_2O 99/1): 0.2. Mp: 77-78°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 10 H, ArH), 7.11 (m, 1 H, ArH), 6.61 (m, 3 H, ArH), 4.67 (s, 4 H, CH_2), 2.29 (s, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 138.9, 138.7, 129.1, 128.6, 126.8, 126.7, 117.7, 113.0, 109.7, 54.0, 21.9. IR 3085 (w), 3028 (w), 2912 (w), 2862 (w), 1949 (w), 1809 (w), 1602 (s), 1573 (m), 1495 (s), 1451 (s), 1390 (m), 1360 (m), 1328 (w), 1297 (w), 1249 (m), 1188 (m), 1181 (m), 1075 (w), 1029 (w), 991 (m), 961 (m), 911 (w), 838 (w), 767 (s), 736 (s), 695 (s). HRMS (ESI) calcd for $C_{21}H_{22}N^+$ $[M+H]^+$ 288.1747; found 288.1734.

(6) Singh, C. B.; Kavala, V.; Samal, A. K.; Patel, B. K. *Eur. J. Org. Chem.* **2007**, 1369

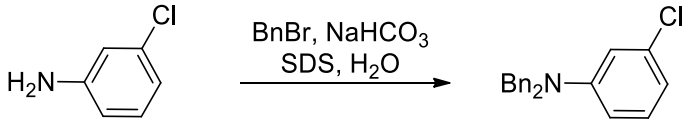
***N,N*-Dibenzyl-3-methoxyaniline (5j)**



19 **5j**

Following a reported procedure,[6] benzyl bromide (1.32 mL, 11.0 mmol, 2.2 equiv) was added to a stirring solution of *m*-anisidine (**19**) (559 μL, 5.00 mmol, 1 equiv), $NaHCO_3$ (924 mg, 11.0 mmol, 1 equiv) and sodium dodecyl sulfate (20 mg, 0.069 mmol, 0.14 equiv) in water (20 mL) and stirred at 80 °C for 1 h. The reaction was cooled and extracted twice with CH_2Cl_2 (20 mL). The organic layers were dried on $MgSO_4$ and concentrated under vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O 95/5) to afford **5j** (1.4 g, 4.6 mmol, 92%) as a colorless oil. R_f (pentane/Et_2O 95/5): 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 4 H, ArH), 7.25 (m, 6 H, ArH), 7.08 (t, 1 H, *J* = 8.1 Hz, ArH), 6.37 (m, 1 H, ArH), 6.28 (m, 2 H, ArH), 4.64 (s, 4 H, ArH, CH_2), 3.69 (m, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 150.5, 138.5, 129.8, 128.6, 126.8, 126.6, 105.6, 101.4, 99.0, 54.9, 54.2. IR 3063 (w), 3030 (w), 2907 (w), 2832 (w), 2140 (w), 1612 (s), 1576 (m), 1500 (s), 1453 (m), 1392 (w), 1361 (m), 1329 (w), 1266 (m), 1204 (s), 1168 (s), 1054 (w), 1043 (w), 989 (w), 962 (m), 911 (w), 827 (w), 751 (m), 735 (s), 697 (m). HRMS (ESI) calcd for $C_{21}H_{22}NO^+$ $[M+H]^+$ 304.1696; found 304.1690.

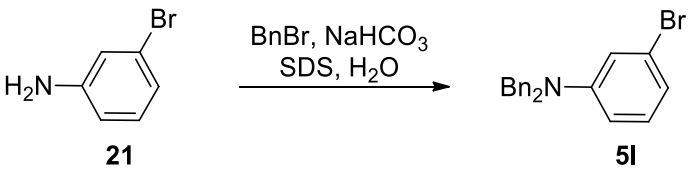
***N,N*-Dibenzyl-3-chloroaniline (5k)**



20 **5k**

Following a reported procedure,[6] benzyl bromide (1.32 mL, 11.0 mmol, 2.2 equiv) was added to a stirring solution of 3-chloroaniline (**20**) (532 μL, 5.00 mmol, 1 equiv), $NaHCO_3$ (924 mg, 11.0 mmol, 1 equiv) and sodium dodecyl sulfate (20 mg, 0.069 mmol, 0.14 equiv) in water (20 mL) and stirred at 80 °C for 1 h. The reaction was cooled and extracted twice with CH_2Cl_2 (20 mL). The organic layers were dried on $MgSO_4$ and concentrated under vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O 98/2) to afford **5k** (0.94 g, 3.1 mmol, 76%) as a colorless oil. R_f (pentane/Et_2O 98/2): 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.16 (m, 10 H, ArH), 7.06 (t, 1 H, *J* = 8.1 Hz, ArH), 6.72 (t, 1 H, *J* = 2.2 Hz, ArH), 6.66 (ddd, 1 H, *J* = 7.8, 1.8, 0.7 Hz, ArH), 6.59 (ddd, 1 H, *J* = 8.6, 2.7, 0.9 Hz, ArH), 4.63 (m, 4 H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 137.8, 130.1, 128.7, 127.1, 126.5, 116.6, 112.2, 110.6, 54.0. One carbon not resolved. Consistent with reported values.[6]

***N,N*-Dibenzyl-3-bromoaniline (5l)**

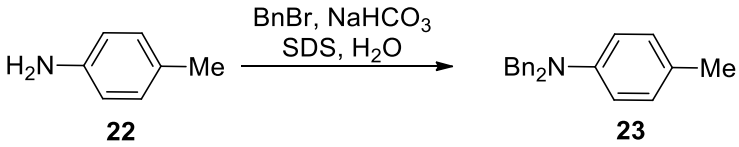


21 **5l**

Following a reported procedure,[6] benzyl bromide (1.32 mL, 11.0 mmol, 2.2 equiv) was added to a stirring solution of 3-bromoaniline (**21**) (544 μL, 5.00 mmol, 1 equiv), $NaHCO_3$ (924 mg, 11.0 mmol, 1 equiv) and sodium dodecyl sulfate (20 mg, 0.069 mmol, 0.14 equiv) in water (20 mL) and stirred at 80 °C for 2 h. The

reaction was cooled and extracted twice with CH_2Cl_2 (20 mL). The organic layers were dried on $MgSO_4$ and concentrated under vacuum. The resulting oil was purified by column chromatography (Hexane/EtOAc 99/1 to 9/1) and then purified by recrystallization in H_2O/EtOH to afford **5l** (708 mg, 1.93 mmol, 39%) as colorless needles. R_f (pentane/EtOAc 95/5): 0.5. Mp: 94-95°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 4 H, ArH), 7.30-7.19 (m, 6 H, ArH), 7.00 (m, 1 H, *J* = 7.9 Hz, ArH), 6.89 (t, 1 H, *J* = 1.8 Hz, ArH), 6.81 (d, 1H, *J* = 7.8 Hz, ArH), 6.63 (d, 1 H, *J* = 8.4 Hz, ArH), 4.63 (s, 4 H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 137.7, 130.4, 128.7, 127.1, 126.5, 123.5, 119.6, 115.0, 111.0, 54.0. Consistent with reported data.[7]

***N,N*-Dibenzyl-4-methylaniline (23)**

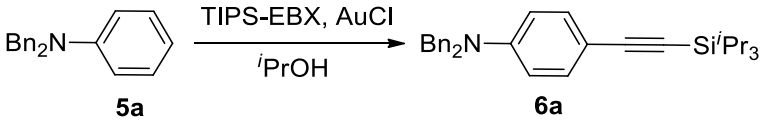


22 **23**

Following a reported procedure,[6] benzyl bromide (2.62 mL, 22.0 mmol, 2.2 equiv) was added to a stirring solution of *p*-toluidine (**22**) (1.07 g, 10.0 mmol, 1 equiv), $NaHCO_3$ (1.85 g, 22.0 mmol, 1 equiv) and sodium dodecyl sulfate (20 mg , 0.069 mmol, 0.14 equiv) in water (20 mL) and stirred at 80 °C for 1 h. The reaction was cooled and extracted twice with CH_2Cl_2 (20 mL). The organic layers were dried on $MgSO_4$ and concentrated under vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O 99/1 to 98/2) to afford **23** (2.04 g, 7.10 mmol, 71%) as a colorless solid. R_f (pentane/Et_2O 99/1): 0.15. Mp: 56-57°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 4 H, ArH), 7.38 (m, 6 H, ArH), 7.13 (d, 2 H, *J* = 8.7 Hz, ArH), 6.81 (d, 2 H, *J* = 8.6 Hz, ArH), 4.77 (s, 4H, CH_2), 2.38 (s, 3 H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 138.8, 129.7, 128.6, 126.8, 126.7, 125.8, 112.6, 54.4, 20.2. Consistent with reported data.[6]

Alkynylation

***N,N*-Dibenzyl-4-((tri*iso*propylsilyl)ethynyl)aniline (6a)**



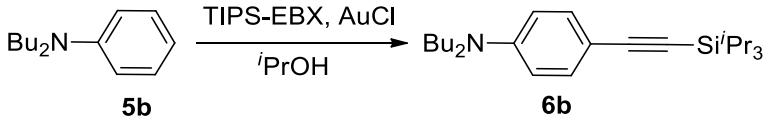
5a **6a**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of *N,N*-dibenzylaniline (**5a**) (109 mg, 0.400 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (8 mL) under air. The reaction was stirred at RT for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 9/1) to afford **6a** (126 mg, 0.278 mmol, 70%) as a colorless oil and a mixture of **5a** and **6a** (20 mg, 30w% product and 70w% *N,N*-dibenzylaniline, 3% product and 13% recovered starting material) as a colorless oil. Total yield = 73%. Yield based on recovered starting material = 84%. R_f (pentane/CH_2Cl_2 9/1) 0.15. ^{1}H NMR (400 MHz, C_6D_6) δ 7.37 (m, 2 H, ArH), 7.18-7.01 (m, 6 H, ArH), 6.95 (m, 4 H, ArH), 6.42 (m, 2 H, ArH), 4.15 (s, 4 H, CH_2), 1.21 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, C_6D_6) δ 149.3, 138.4, 133.9, 128.9, 127.3, 126.9, 112.4, 111.8, 109.6, 87.6, 53.9, 19.1, 11.9. IR 3051 (w), 2943 (w), 2865 (w), 2143 (w), 1606 (m), 1516 (m), 1495 (w), 1454 (w), 1398 (w), 1360 (w), 1266 (m),

(7) Feng, C.; Liu, Y.; Peng, S.; Shuai, Q.; Deng, G.; Li, C.-J. *Org. Lett.* **2010,** *12*, 4888.
(8) Commercial isopropanol was used without drying procedure.

1241 (w), 1188 (w), 1075 (w), 997 (w), 955 (w), 884 (w), 841 (w), 818 (w), 737 (s), 698 (m), 677 (m). HRMS (ESI) calcd for $C_{31}H_{40}NSi^+$ $[M+H]^+$ 454.2925; found 454.2913.

***N,N*-Dibutyl-4-((tri*iso*propylsilyl)ethynyl)aniline (6b)**



5b **6b**

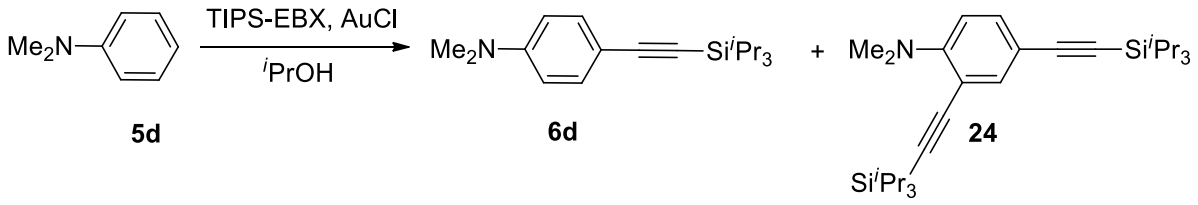
AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of *N*,*N*-dibutylaniline (**5b**) (91 mg, 0.40 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at RT for 20 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane) to afford **6b** (97 mg, 0.25 mmol, 63%) as a colorless oil. R_f (pentane) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2 H, ArH), 6.53 (m, 2 H, ArH), 3.27 (m, 4 H, CH_2), 1.56 (m, 4 H, CH_2), 1.35 (m, 4 H, CH_2), 1.13 (m, 21 H, TIPS), 0.95 (t, 6 H, J = 7.3 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 133.3, 111.1, 109.2, 108.6, 86.8, 50.7, 29.4, 20.3, 18.7, 14.0, 11.5. IR 2958 (m), 2942 (m), 2864 (s), 2142 (m), 1607 (s), 1514 (s), 1463 (m), 1401 (w), 1368 (m), 1288 (w), 1222 (w), 1187 (m), 1150 (w), 1111 (w), 1069 (w), 1017 (w), 996 (w), 923 (w), 883 (m), 839 (m), 814 (m), 734 (m), 676 (m), 634 (s). HRMS (ESI) calcd for $C_{25}H_{44}NSi^+$ $[M+H]^+$ 386.3238; found 386.3225.

***N,N*-Diethyl-4-((tri*iso*propylsilyl)ethynyl)aniline (6c)**

5c **6c**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of *N*,*N*-diethylaniline (**5c**) (64 μL, 0.40 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (8 mL) under air. The reaction was stirred at RT for 36 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 95/5) to afford **6c** (58 mg, 0.18 mmol, 44%) as a yellow oil. R_f (pentane/CH_2Cl_2 9/1) 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2 H, ArH), 6.56 (m, 2 H, ArH), 3.36 (q, 4 H, J = 7.1 Hz, CH_2), 1.19-1.10 (m, 27 H, CH_3 + TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 133.3, 111.0, 109.4, 108.6, 86.8, 44.3, 18.7, 12.5, 11.4. IR 2962 (m), 2941 (m), 2917 (w), 2864 (m), 2146 (m), 1607 (s), 1517 (s), 1464 (w), 1403 (w), 1356 (m), 1270 (m), 1197 (w), 1156 (w), 1076 (w), 997 (w), 920 (w), 883 (m), 839 (m), 817 (m), 789 (w), 710 (m), 675 (m). HRMS (ESI) calcd for $C_{21}H_{36}NSi^+$ $[M+H]^+$ 330.2612; found 330.2604.

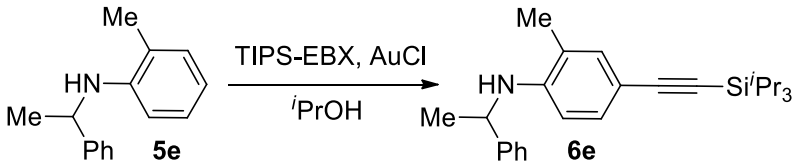
***N,N*-Dimethyl-4-((tri*iso*propylsilyl)ethynyl)aniline (6d) and *N,N*-dimethyl-2,4-bis((tri*iso*propylsilyl)ethynyl)aniline (24)**



5d **6d** **24**

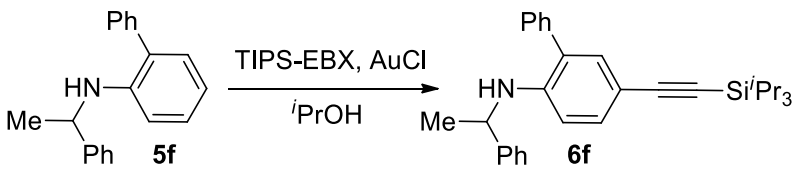
AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of *N*,*N*-dimethylaniline (**5d**) (51 μL, 0.40 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60°C for 20 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 95/5) to afford **24** (16 mg, 0.037 mmol, 8%) as a colorless oil and **6d** (55 mg, 0.18 mmol, 46%) as a yellow oil. **24**: R_f (pentane/CH_2Cl_2 95/5) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, 1 H, *J* = 2.1 Hz, ArH), 7.30 (dd, 1 H, *J* = 8.6, 2.1 Hz, ArH), 6.73 (d, 1 H, *J* = 8.6 Hz, ArH), 2.99 (s, 6 H, Me), 1.13 (m, 42 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 138.8, 133.0, 116.3, 114.4, 114.1, 106.8, 105.7, 96.4, 88.8, 43.1, 43.1, 18.7, 18.6, 11.4. IR 2943 (m), 2876 (w), 2865 (m), 2144 (m), 1597 (w), 1498 (m), 1462 (m), 1387 (w), 1335 (w), 1271 (w), 1245 (w), 1178 (w), 1138 (w), 1112 (w), 1072 (w), 1015 (w), 997 (w), 940 (m), 883 (m), 821 (w), 779 (w), 723 (m), 673 (s). HRMS (ESI) calcd for $C_{30}H_{52}NSi_2^+$ $[M+H]^+$ 482.3633; found 482.3628. **6d**: Rf (pentane/CH_2Cl_2 95/5) 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 2 H, ArH), 6.61 (d, 2 H, *J* = 8.9 Hz, ArH), 2.97 (s, 6 H, Me), 1.14 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 133.1, 111.6, 110.6, 108.3, 87.2, 40.2, 18.7, 11.4. IR 2941 (m), 2890 (m), 2864 (m), 2150 (m), 1713 (w), 1608 (s), 1519 (s), 1462 (m), 1360 (m), 1238 (m), 1186 (w), 1168 (w), 1070 (w), 996 (w), 949 (m), 909 (m), 883 (m), 839 (s), 817 (s), 724 (s), 676 (s). HRMS (ESI) calcd for $C_{19}H_{32}NSi^+$ $[M+H]^+$ 302.2299; found 302.2297.

2-Methyl-*N*-(1-phenylethyl)-4-((tri*iso*propylsilyl)ethynyl)aniline (6e)



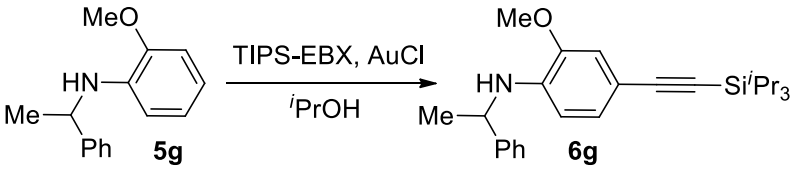
AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5e** (85 mg, 0.40 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60°C for 20 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 9/1) to afford **6e** (100 mg, 0.255 mmol, 64%) as a yellow oil. R_f (pentane/CH_2Cl_2 9/1): 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 4 H, ArH), 7.27 (m, 2 H, ArH), 7.15 (dd, 1 H, *J* = 8.3, 1.6 Hz, ArH), 6.30 (d, 1 H, *J* = 8.4 Hz, ArH), 4.60 (m, 1 H, CH), 4.07 (br d, 1 H, *J* = 4.6 Hz, NH), 2.24 (s, 3 H, Me), 1.60 (d, 3 H, *J* = 6.7 Hz, Me), 1.18 (m, 21H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 144.7, 133.7, 131.4, 128.8, 127.1, 125.7, 121.3, 111.2, 110.7, 108.5, 86.9, 53.1, 25.1, 18.8, 17.4, 11.5. IR 3442 (w), 2941 (m), 2864 (m), 2246 (w), 2144 (m), 1608 (m), 1574 (w), 1509 (s), 1454 (w), 1375 (w), 1321 (m), 1270 (w), 1235 (w), 1149 (w), 1068 (w), 1016 (w), 998 (m), 992 (w), 909 (s), 884 (m), 812 (m), 752 (s), 734 (s), 701 (s), 676 (s). HRMS (ESI) calcd for $C_{26}H_{38}NSi^+$ $[M+H]^+$ 392.2768; found 392.2765.

***N*-(1-phenylethyl)-5-((tri*iso*propylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (6f)**



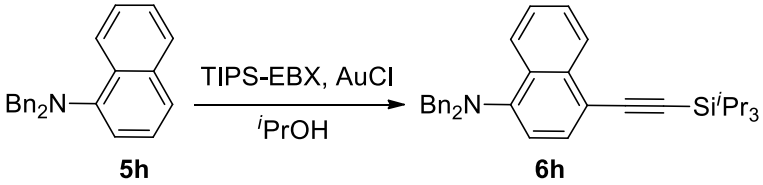
AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5f** (109 mg, 0.400 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60 °C for 20 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 9/5) to afford **6f** (117 mg, 0.258 mmol, 65%) as a yellow oil. R_f (pentane/CH_2Cl_2 9/5): 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.37 (m, 5 H, ArH), 7.35-7.17 (m, 7 H, ArH), 6.34 (d, 1 H, *J* = 8.4 Hz, ArH), 4.54-4.43 (m, 2 H, CH + NH), 1.40 (d, 3 H, *J* = 6.6 Hz, CH_3), 1.08 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 143.9, 141.5, 138.6, 133.8, 132.6, 129.3, 129.1, 128.7, 127.6, 127.3, 127.0, 125.6, 111.4, 108.0, 87.4, 53.2, 24.9, 18.7, 11.4. IR 2952 (w), 2859 (w), 2255 (w), 2146 (w), 1722 (s), 1607 (w), 1511 (w), 1455 (w), 1430 (w), 1349 (w), 1256 (m), 1201 (w), 1140 (w), 1121 (w), 1072 (m), 1013 (w), 994 (w), 973 (w), 928 (w), 908 (s), 873 (w), 813 (w). HRMS (ESI) calcd for $C_{31}H_{40}NSi^+$ $[M+H]^+$ 454.2925; found 454.2922.

2-Methoxy-*N*-(1-phenylethyl)-4-((tri*iso*propylsilyl)ethynyl)aniline (6g)



AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5g** (91 mg, 0.40 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60 °C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 98/2) to afford **6g** (62 mg, 0.15 mmol, 38%) as a yellow oil and a mixture of **6g** and **5g** (35 mg, 17 w% of product (0.015 mmol) and 83 w% of **5g** (0.13 mmol), 4% product and 32% starting material recovered) as well as some pure **5g** (7 mg, 0.030 mmol, 7%). Total yield: 42%. Yield brsm = 70%. R_f (pentane/CH_2Cl_2 98/2): 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4 H, ArH), 7.23 (m, 1 H, ArH), 6.89 (d, 1 H, *J* = 8.2 Hz, ArH), 6.84 (s, 1 H, ArH), 6.22 (d, 1 H, *J* = 8.0 Hz, ArH), 4.82 (br s, 1 H, NH), 4.51 (q, 1 H, *J* = 6.7 Hz, CH), 3.90 (s, 3 H, OMe), 1.56 (d, 3 H, *J* = 6.7 Hz, CH_3), 1.12 (m, 21H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 144.8, 137.6, 128.6, 126.9, 126.2, 125.7, 112.4, 110.5, 110.3, 108.5, 86.8, 55.5, 52.9, 24.9, 18.7, 11.4. IR 3435 (w), 3062 (w), 2941 (m), 2864 (m), 2144 (m), 1605 (m), 1542 (w), 1520 (s), 1462 (m), 1417 (w), 1353 (m), 1264 (m), 1236 (m), 1195 (w), 1146 (m), 1120 (w), 1073 (w), 1038 (m), 996 (w), 938 (m), 883 (m), 854 (w), 805 (m), 752 (m), 701 (m), 676 (s). HRMS (ESI) calcd for $C_{26}H_{38}NOSi^+$ $[M+H]^+$ 408.2717; found 408.2720.

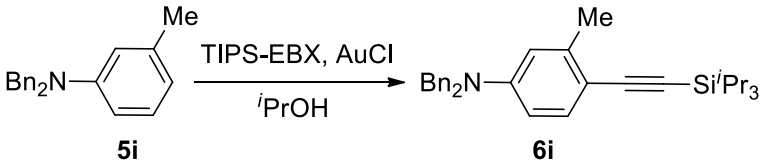
***N,N*-Dibenzyl-4-((tri*iso*propylsilyl)ethynyl)naphthalen-1-amine (6h)**



AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5h** (129 mg, 0.400 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60 °C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over

$MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 98/2 to 95/5) to afford **6h** (61 mg, 0.12 mmol, 30%) as a yellow oil and a mixture of **6h** and **5h** (25 mg, 42 w% product and 58 w% of starting material, 5% product and 11% recovered starting material) as well as **5h** (45 mg, 0.14 mmol, 35%). Total yield: 35%. Yield brsm= 65%. R_f pentane/CH_2Cl_2 98/2: 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (m, 1 H, ArH), 8.42 (m, 1 H, ArH), 7.63-7.51 (m, 3 H, ArH), 7.32-7.18 (m, 10 H, ArH), 6.84 (d, 1 H, *J* = 7.8 Hz, ArH), 4.33 (s, 4 H, CH_2), 1.19 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 137.8, 134.9, 131.0, 129.2, 128.4, 128.3, 127.0, 127.0, 126.7, 125.9, 124.0, 117.7, 116.1, 105.4, 94.5, 57.1, 18.8, 11.4. IR 3067 (w), 3028 (w), 2942 (m), 2872 (m), 2864 (m), 2247 (w), 2143 (m), 1574 (m), 1495 (w), 1455 (m), 1391 (m), 1363 (w), 1323 (w), 1272 (w), 1218 (w), 1155 (w), 1068 (m), 1030 (w), 992 (w), 908 (s), 884 (m), 832 (w), 767 (s), 734 (s), 698 (s), 673 (s). HRMS (ESI) calcd for $C_{35}H_{42}NSi^+$ $[M+H]^+$ 504.3081; found 504.3090.

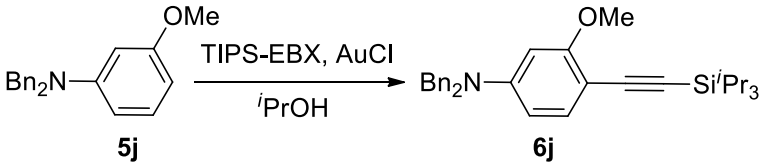
_N,N_-dibenzyl-3-methyl-4-((tri*iso*propylsilyl)ethynyl)aniline (6i)



5i **6i**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5i** (115 mg, 0.400 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60 °C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 98/2) to afford **6i** (136 mg, 0.291 mmol, 73%) as yellow oil. R_f pentane/CH_2Cl_2 98/2: 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.20 (m, 11 H, ArH), 6.61 (d, 1 H, *J* = 2.4 Hz, ArH), 6.52 (dd, 1 H, *J* = 8.6, 2.6 Hz, ArH), 4.67 (s, 4 H, CH_2), 2.38 (s, 3 H, Me), 1.14 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 141.9, 138.1, 133.6, 128.7, 127.0, 126.5, 112.8, 111.4, 109.6, 106.8, 91.3, 53.8, 21.5, 18.7, 11.4. IR 3063 (w), 3028 (w), 2942 (m), 2890 (w), 2864 (m), 2140 (m), 1606 (s), 1550 (w), 1506 (s), 1453 (m), 1366 (w), 1360 (m), 1297 (w), 1238 (m), 1202 (w), 1162 (w), 1075 (w), 1030 (w), 997 (w), 962 (w), 909 (m), 884 (m), 817 (w), 800 (s), 734 (s). HRMS (ESI) calcd for $C_{32}H_{42}NSi^+$ $[M+H]^+$ 468.3081; found 468.3076.

_N,N_-Dibenzyl-3-methoxy-4-((tri*iso*propylsilyl)ethynyl)aniline (6j)

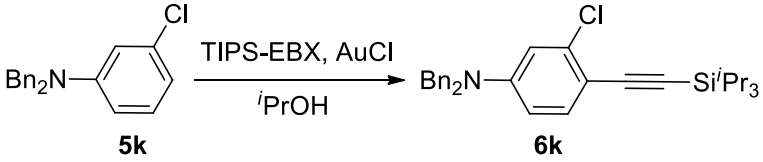


5j **6j**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5j** (121 mg, 0.400 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (8 mL) under air. The reaction was stirred at 60 °C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O 200/1 to 100/1) to afford **6j** (165 mg, 0.340 mmol, 85%) as a colorless oil. R_f pentane/Et_2O 200/1: 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.23 (m, 11 H, ArH), 6.32 (dd, 1 H, *J* = 8.6, 2.4 Hz, ArH), 6.22 (d, 1 H, *J* = 2.3 Hz, ArH), 4.70 (s, 4 H, CH_2), 3.69 (s, 3 H, OMe), 1.16 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 150.5, 138.0, 134.6, 128.7, 127.1, 126.6, 104.8, 104.3, 101.2, 96.3, 91.8, 55.7, 54.5, 18.7, 11.5. IR

3066 (w), 3062 (w), 3030 (w), 2940 (m), 2914 (m), 2863 (m), 2145 (m), 1716 (w), 1608 (s), 1552 (w), 1515 (s), 1453 (m), 1394 (w), 1360 (m), 1272 (m), 1268 (m), 1242 (m), 1205 (s), 1165 (m), 1134 (w), 1075 (w), 1031 (m), 996 (w), 965 (m), 909 (m), 883 (m), 812 (s), 733 (s), 697 (s), 677 (m). HRMS (ESI) calcd for $C_{32}H_{42}NOSi^+$ $[M+H]^+$ 484.3030; found 484.3030.

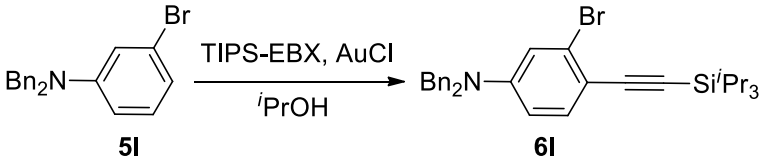
***N,N*-Dibenzyl-3-chloro-4-((tri*iso*propylsilyl)ethynyl)aniline (6k)**



5k **6k**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5k** (123 mg, 0.400 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60 °C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 98/2) to afford **6k** (32 mg, 0.066 mmol, 16%) as a yellow oil and a second batch (64 mg, 76w% of **6k** (0.010 mmol) and 24w% of **5k**(0.050 mmol), 25% of **6k** and 12% of **5k** recovered) as well as some pure **5k** (38 mg, 0.12 mmol, 31%). Total yield: 41%. Yield brsm = 72%. R_f pentane/CH_2Cl_2 98/2: 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 7 H, ArH), 7.19 (d, 4 H, *J* = 7.0 Hz, ArH), 6.74 (d, 1 H, *J* = 2.6 Hz, ArH), 6.53 (dd, 1 H, *J* = 8.8, 2.6 Hz, ArH), 4.64 (s, 4 H, CH_2), 1.11 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 137.5, 137.3, 134.4, 128.8, 127.2, 126.4, 112.4, 111.0, 110.5, 104.0, 93.1, 54.0, 17.9, 11.3. IR 2944 (w), 2875 (w), 2865 (m), 2154 (w), 1601 (s), 1530 (w), 1506 (s), 1455 (m), 1397 (w), 1355 (w), 1296 (w), 1231 (m), 1203 (w), 1146 (w), 997 (w), 959 (w), 910 (m), 883 (w), 831 (w), 785 (m), 734 (s). HRMS (ESI) calcd for $C_{31}ClH_{39}NSi^+$ $[M+H]^+$ 488.2535; found 488.2529.

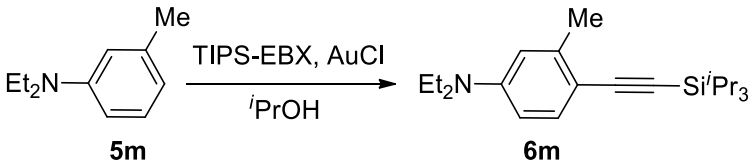
***N,N*-Dibenzyl-3-bromo-4-((tri*iso*propylsilyl)ethynyl)aniline (6l)**



5l **6l**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5l** (140 mg, 0.400 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60 °C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 99/1 to 95/5) to afford **6l** (75 mg, 0.14 mmol, 35%) as a yellow oil and **5l** (59 mg, 0.17 mmol, 41% recovered). Yield brsm = 61%. R_f pentane/CH_2Cl_2 99/1: 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 4 H, ArH), 7.28 (m, 3 H, ArH), 7.24-7.16 (m, 4 H, ArH), 6.95 (d, 1 H, *J* = 2.6 Hz, ArH), 6.57 (dd, 1 H, *J* = 8.7, 2.6 Hz, ArH), 4.63 (s, 4 H, CH_2), 1.13 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 137.3, 134.5, 128.8, 127.3, 127.1, 126.5, 115.5, 113.3, 111.1, 105.7, 92.5, 54.0, 18.7, 11.4. IR 2944 (w), 2865 (w), 2251 (w), 2153 (w), 1726 (w), 1598 (m), 1502 (m), 1454 (w), 1230 (w), 1140 (w), 1030 (w), 997 (w), 958 (w), 906 (s), 884 (w), 856 (w). HRMS (ESI) calcd for $C_{31}{}^{79}BrH_{39}NSi^+$ $[M+H]^+$ 532.2030; found 532.2019.

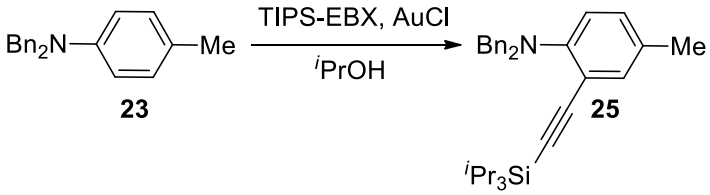
***N,N*-Diethyl-3-methyl-4-((tri*iso*propylsilyl)ethynyl)aniline (6m)**



5m **6m**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of **5m** (71 µL, 0.40 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60°C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 98/2 to 95/5) to afford **6m** (103 mg, 0.300 mmol, 75%, 95% pure) as a yellow oil. R_f pentane/CH_2Cl_2 98/2: 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, 1 H, *J* = 8.6 Hz, ArH), 6.50 (d, 1 H, *J* = 2.5 Hz, ArH), 6.45 (dd, 1 H, *J* = 8.6, 2.6 Hz, ArH), 3.38 (q, 4 H, *J* = 7.1 Hz, CH_2), 2.45 (s, 3 H, CH_3), 1.15 (m, 27 H, CH_3 + TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 141.8, 133.6, 112.1, 109.7, 108.8, 107.3, 90.6, 44.3, 21.6, 18.7, 12.6, 11.4. IR 2965 (m), 2941 (m), 2918 (m), 2864 (m), 2141 (m), 1713 (w), 1607 (s), 1548 (w), 1507 (m), 1464 (m), 1377 (w), 1256 (m), 1198 (w), 1113 (w), 1076 (w), 1017 (w), 996 (w), 909 (m), 881 (m), 860 (w), 840 (w), 793 (s), 735 (m), 695 (m), 677 (s). HRMS (ESI) calcd for $C_{22}H_{38}NSi^+$ $[M+H]^+$ 344.2768; found 344.2768.

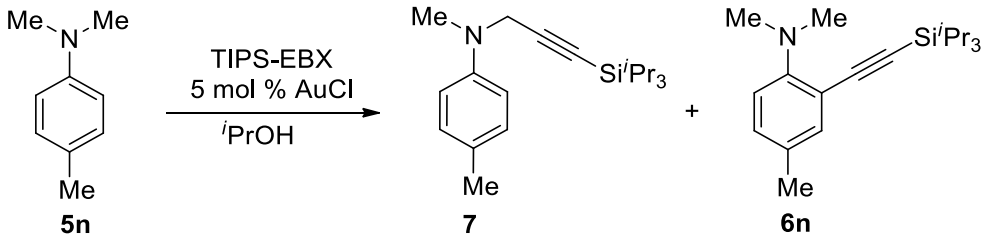
***N,N*-Dibenzyl-4-methyl-2-((tri*iso*propylsilyl)ethynyl)aniline (25)**



23 **25**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of aniline **23** (115 mg, 0.400 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under air. The reaction was stirred at 60 °C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 95/5) to afford **25** (34 mg, 0.073 mmol, 18%) as a colorless oil. Rf (pentane/CH_2Cl_2 95/5) 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, 1 H, *J* = 2.0 Hz, ArH), 7.31-7.21 (m, 10 H, ArH), 6.95 (ddd, 1 H, *J* = 8.3, 2.2, 0.6 Hz, ArH), 6.67 (d, 1 H, *J* = 8.3 Hz, ArH), 4.38 (s, 4 H, CH_2), 2.27 (s, 3 H, CH_3), 1.16 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 138.4, 135.4, 130.8, 129.7, 128.6, 128.1, 126.8, 121.3, 117.6, 106.3, 95.4, 55.6, 20.4, 18.8, 11.5. IR 3064 (w), 3027 (w), 2940 (m), 2863 (w), 2145 (w), 1602 (m), 1570 (w), 1496 (s), 1455 (m), 1344 (w), 1305 (m), 1278 (w), 1192 (w), 1154 (w), 1077 (w), 1021 (w), 883 (w), 779 (w), 742 (s), 700 (s), 646 (m). HRMS (ESI) calcd for $C_{32}H_{42}NSi^+$ $[M+H]^+$ 468.3081; found 468.3081.

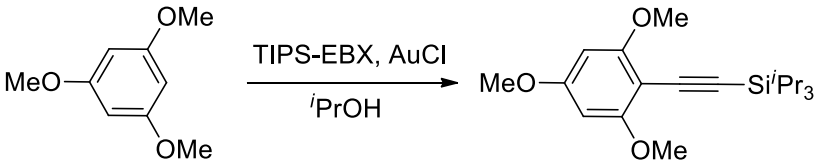
***N*,4-Dimethyl-*N*-(3-(tri*iso*propylsilyl)prop-2-yn-1-yl)aniline (7)**



5n **7** **6n**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of aniline **5n** (91 mg, 0.40 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (2 mL) under N_2. The reaction was stirred at 60 °C for 24 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/CH_2Cl_2 9/1 to 8/2) to afford **7** (28 mg, 0.089 mmol, 22%) as a yellow oil and traces of **6n** were identified by ^{1}H NMR. R_f (pentane/CH_2Cl_2 8/2) 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, 2 H, *J* = 8.7 Hz, ArH), 6.83 (d, 2 H, *J* = 8.5 Hz, ArH), 4.05 (s, 2 H, CH_2), 2.94 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 1.02 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 129.4, 127.7, 115.4, 103.2, 85.0, 44.2, 38.9, 20.3, 18.5, 11.1. IR 3012 (w), 2942 (s), 2865 (s), 2808 (w), 2166 (w), 1861 (w), 1619 (m), 1519 (s), 1463 (m), 1371 (w), 1363 (m), 1329 (m), 1238 (m), 1191 (m), 1109 (m), 1074 (w), 1000 (s), 976 (m), 923 (m), 883 (s), 807 (s), 738 (w), 665 (s), 643 (m). HRMS (ESI) calcd for $C_{20}H_{34}NSi^+$ $[M+H]^+$ 316.2455; found 316.2443.

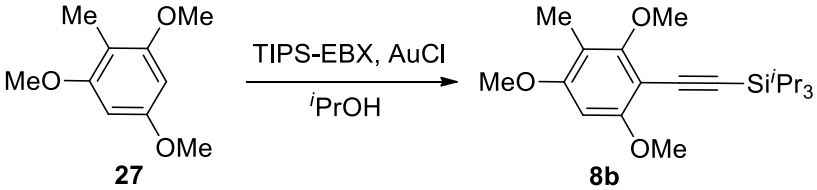
Tri*iso*propyl((2,4,6-trimethoxyphenyl)ethynyl)silane (8a)



26 **8a**

AuCl (2.3 mg, 0.010 mmol, 0.05 equiv) was added to a stirring solution of trimethoxybenzene (**26**) (34 mg, 0.20 mmol, 1 equiv) and TIPS-EBX (**1**) (120 mg, 0.280 mmol, 1.4 equiv) in ^{i}PrOH[8] (4 mL) under air. The reaction was stirred at RT for 20 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O 95/5) to afford **8a** (35 mg, 0.10 mmol, 51%) as a colorless oil and **26** (12 mg, 0.071mmol, 36% recovered). Yield brsm= 80%. R_f (pentane/Et_2O 95/5) 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 2 H, ArH), 3.85 (s, 6 H, OMe), 3.83 (s, 3 H, OMe), 1.17 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 161.3, 99.1, 97.5, 95.4, 90.6, 56.0, 55.3, 18.7, 11.5. IR 2944 (m), 2864 (m), 2147 (m), 1603 (s), 1463 (s), 1419 (w), 1340 (w), 1216 (s), 1132 (s), 1053 (w), 999 (w), 914 (w), 885 (w), 819 (s), 735 (w), 666 (m). HRMS (ESI) calcd for $C_{20}H_{33}O_3Si^+$ $[M+H]^+$ 349.2193; found 349.2191.

Tri*iso*propyl((2,4,6-trimethoxy-3-methylphenyl)ethynyl)silane (8b)

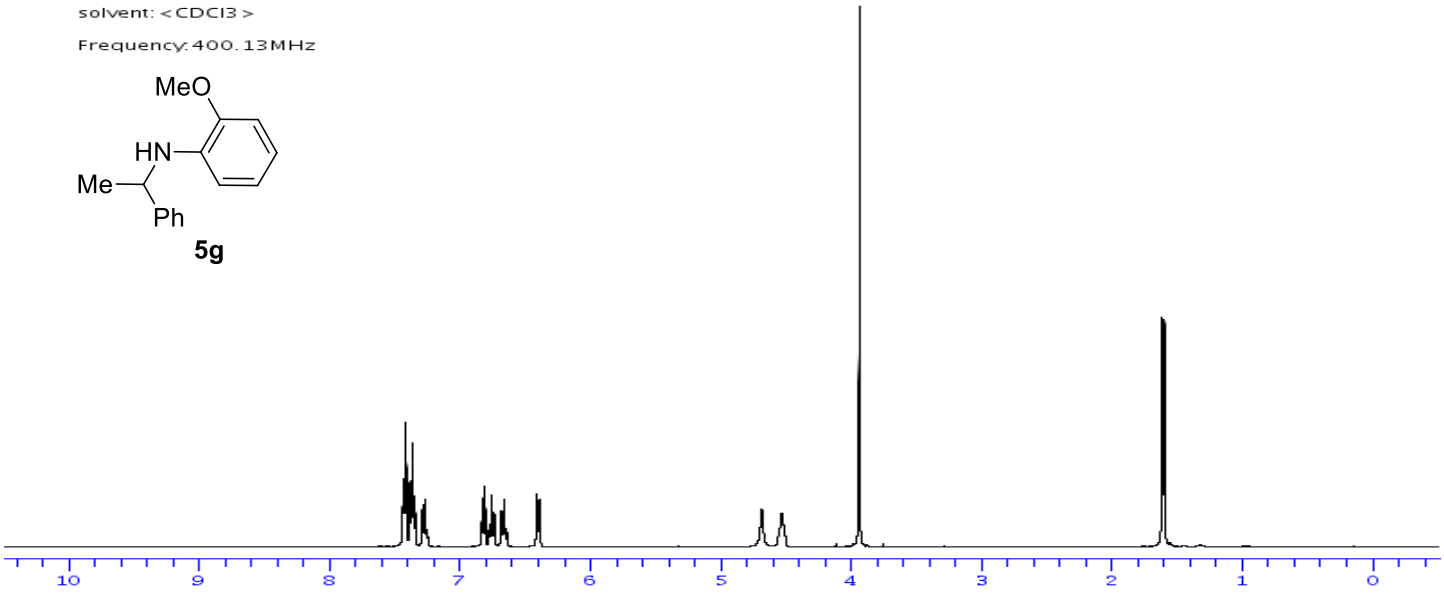


27 **8b**

AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) was added to a stirring solution of trimethoxytoluene (**7m**) (73 mg, 0.40 mmol, 1 equiv) and TIPS-EBX (**1**) (240 mg, 0.560 mmol, 1.4 equiv) in ^{i}PrOH[8] (8 mL) under air. The reaction was stirred at RT for 36 h. EtOAc (20 mL) was added to the reaction mixture. The organic mixture was then washed with 0.1 M NaOH (20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography (pentane/Et_2O 9/1) to afford a mixture of **8b** and **27** (99 mg, 72w% of **8b** (0.20 mmol) and 28w% of **27** (0.15 mmol), 50% of **8b** and 37% of **27** recovered) as a colorless oil. Yield brsm= 79%. Analytical pure compound was obtained by column chromatography. R_f (pentane/ Et_2O 9/1) 0.2. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 6.23 (s, 1 H, ArH), 3.91 (s, 3 H, OMe), 3.88 (s, 3 H, OMe), 3.85 (s, 3 H, OMe), 2.07 (s, 3 H, Me), 1.16 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 160.9, 159.1, 112.1, 99.7, 99.4, 97.6, 91.4, 60.6, 56.3, 55.6, 18.7, 11.5, 8.3. IR 2937 (m), 2864 (m), 2151 (w), 1729 (w), 1599 (m), 1579 (w), 1496 (w), 1463 (m), 1436 (w), 1399 (m), 1330 (m), 1291 (w), 1220 (m), 1191 (w), 1137 (s), 1120 (s), 1019 (m), 997 (w), 919 (m), 881 (m), 803 (m), 745 (m), 676 (m), 659 (m). HRMS (ESI) calcd for $C_{21}H_{34}AgO_3Si^+$ $[M+Ag]^+$ 469.1323; found 469.1312.

Spectra of New Compounds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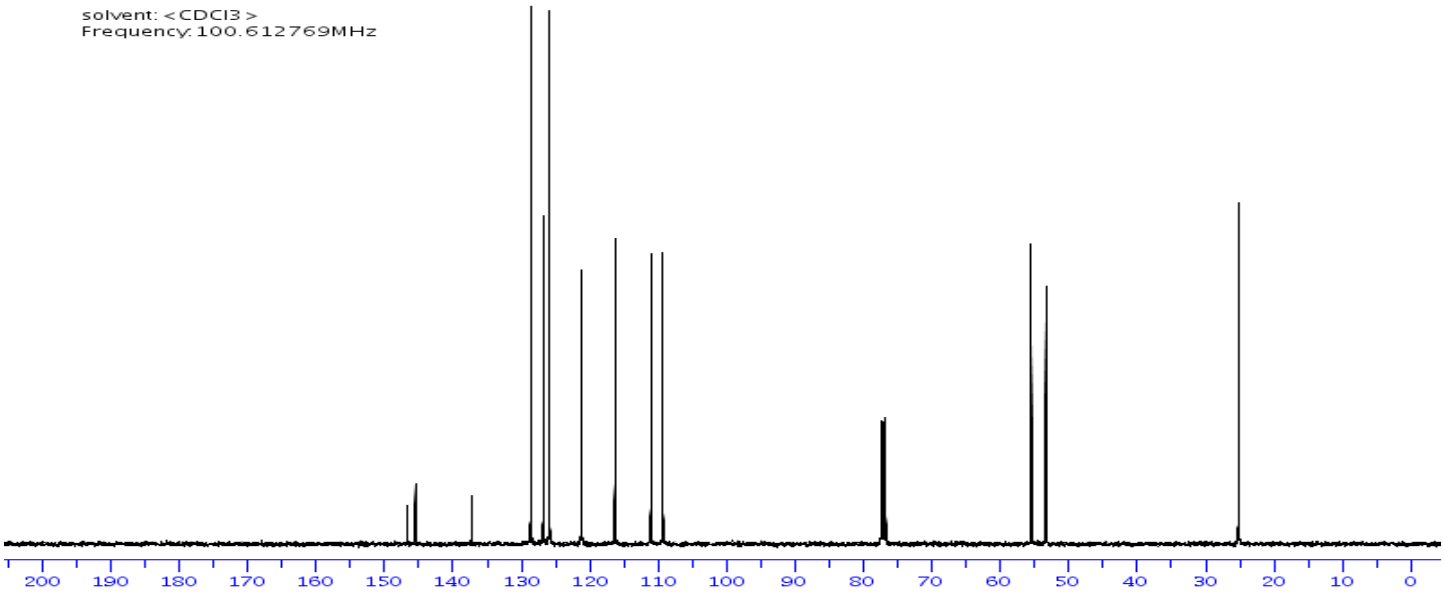
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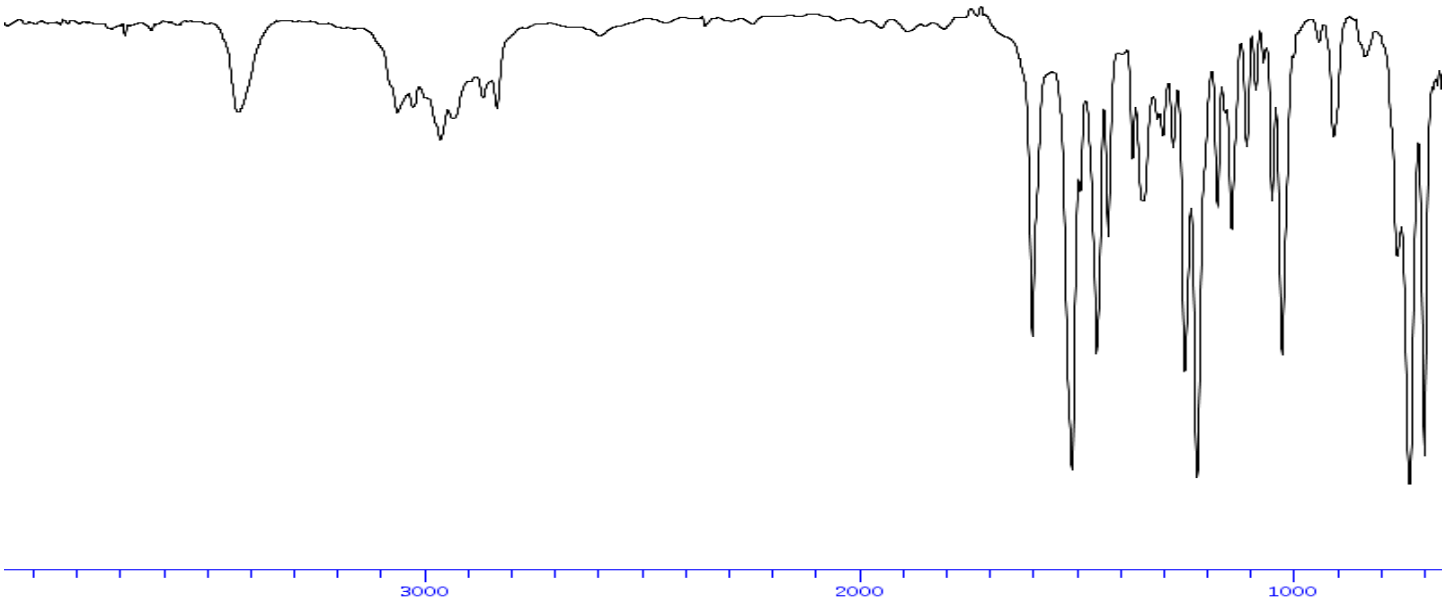
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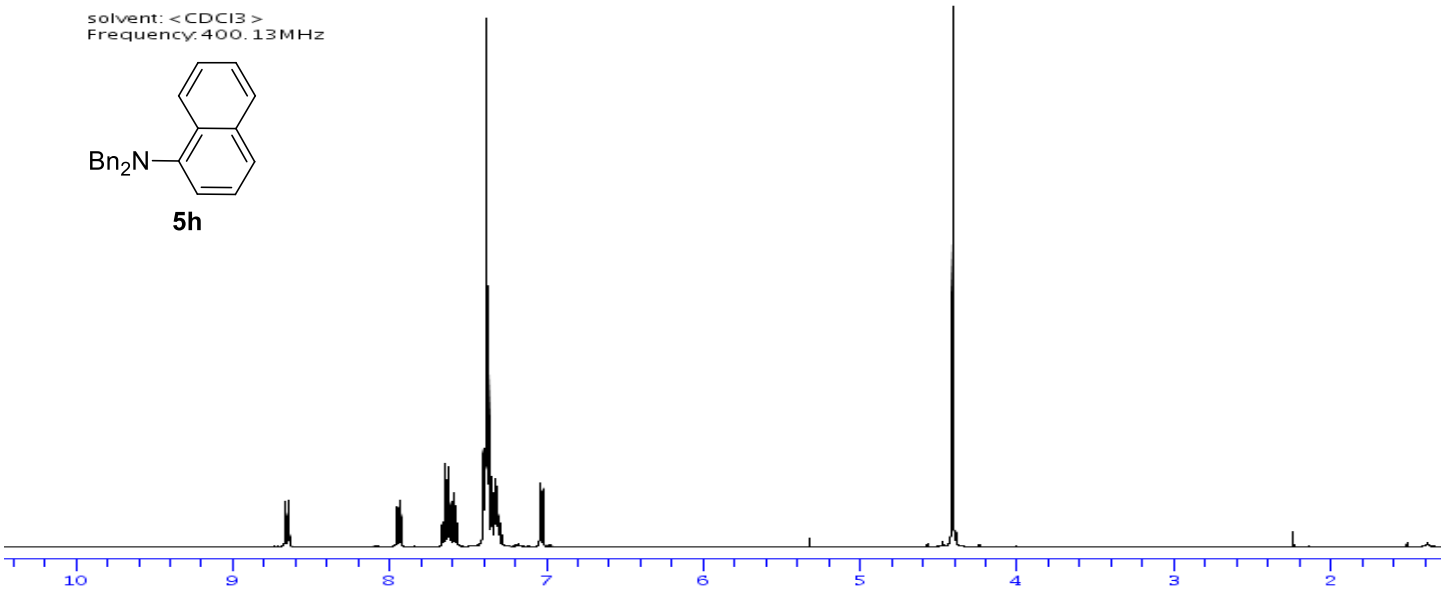
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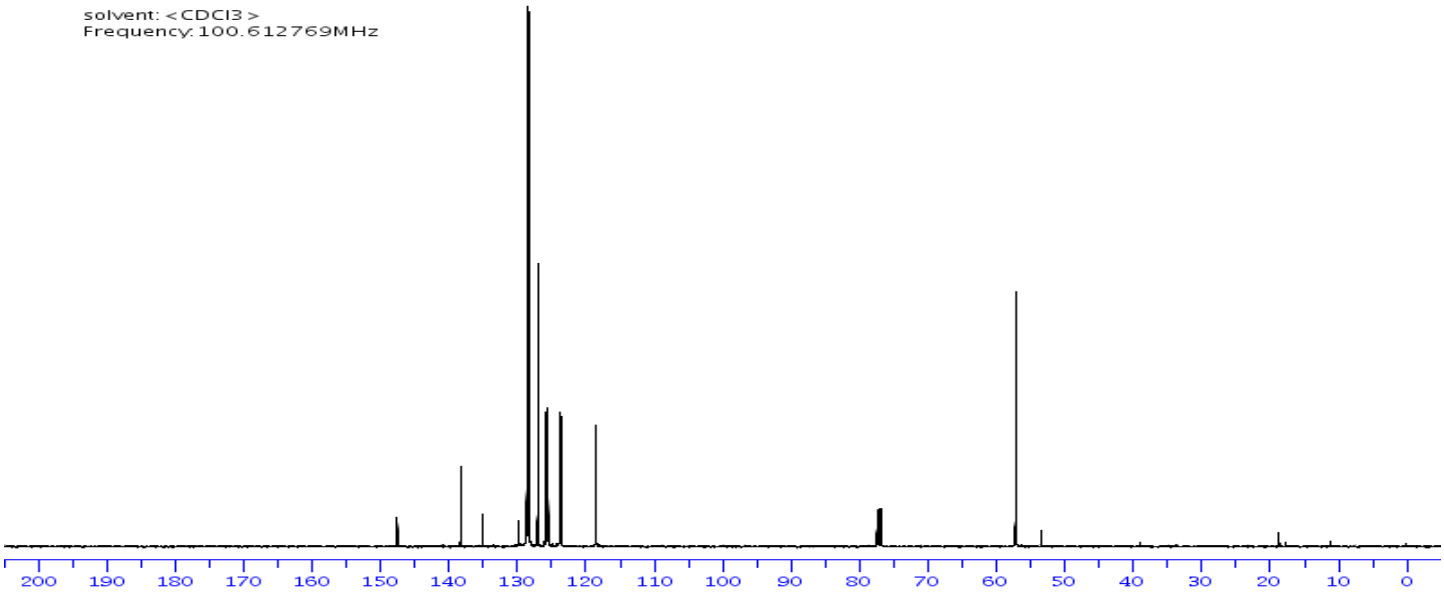
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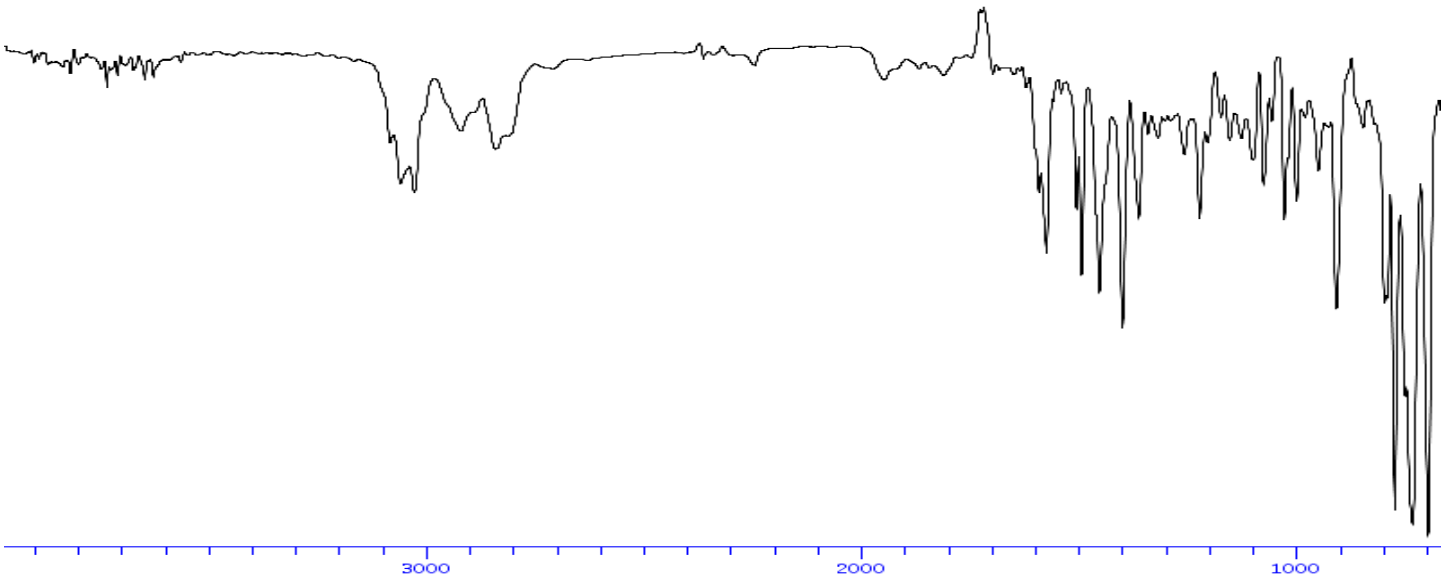
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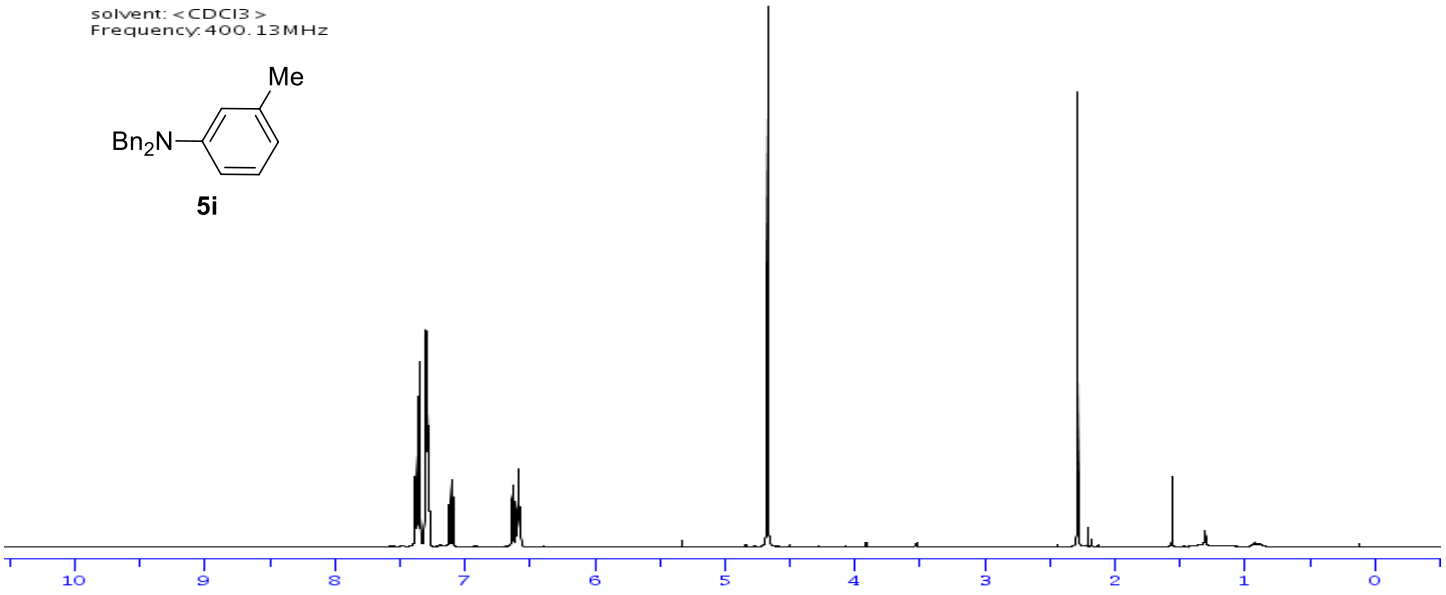
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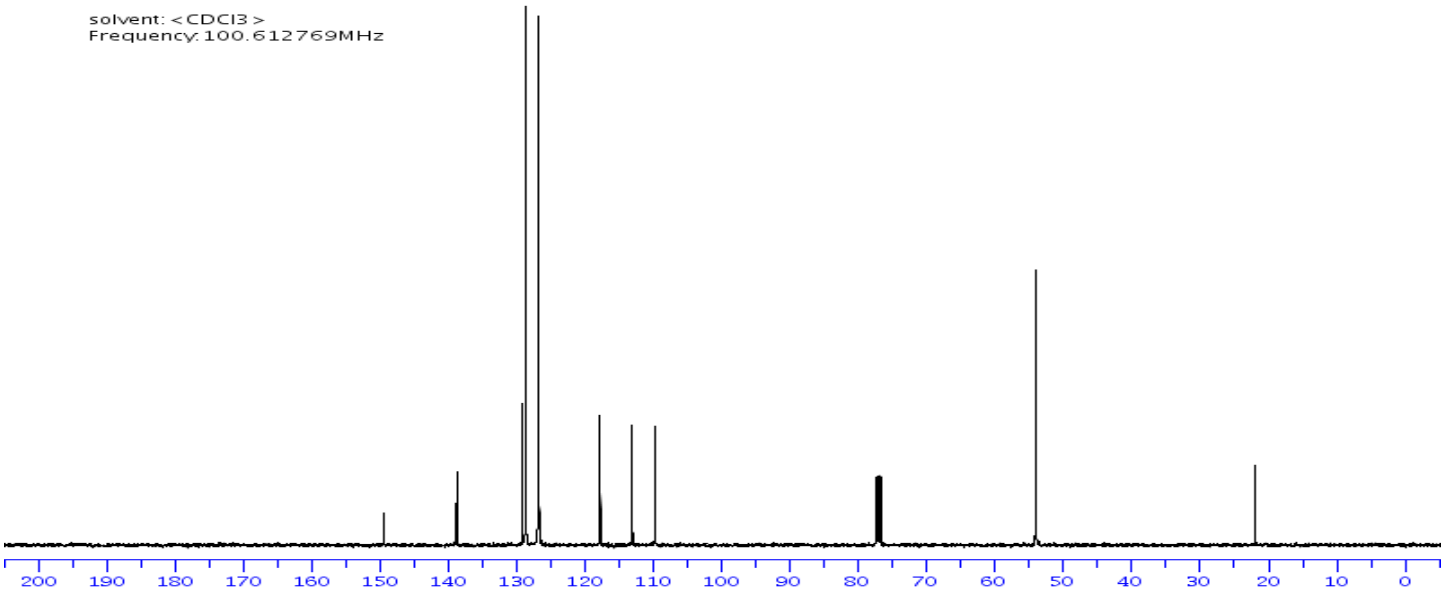
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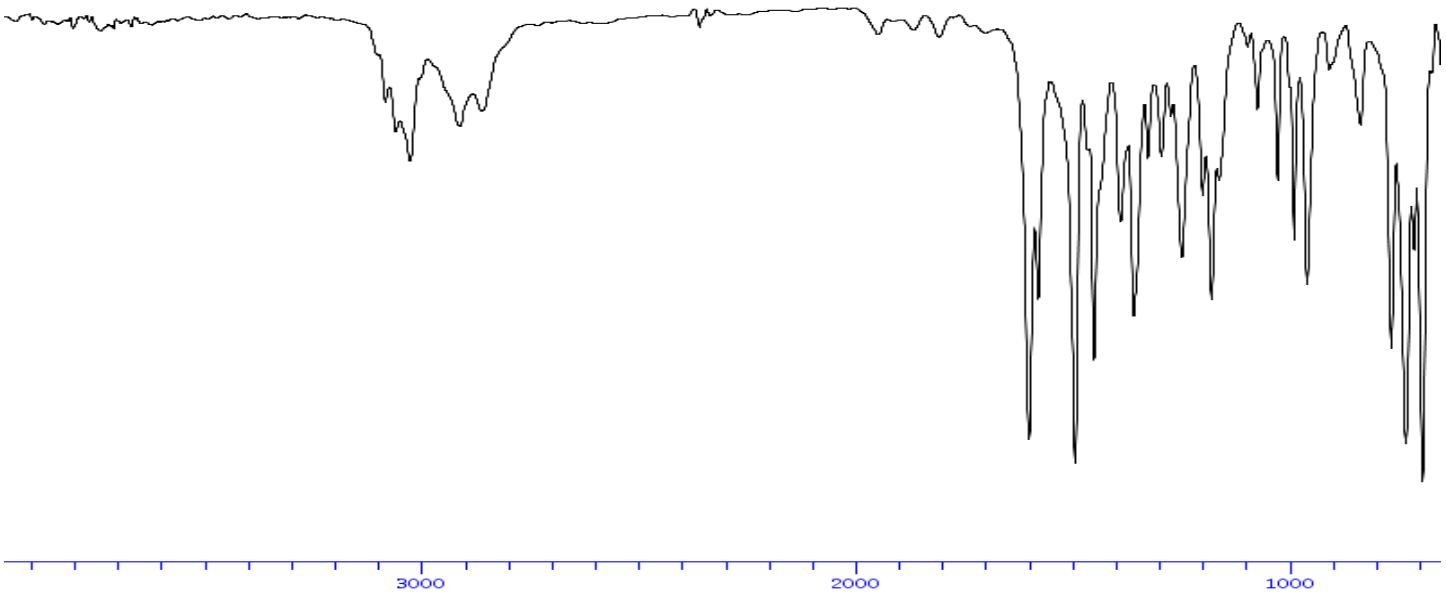
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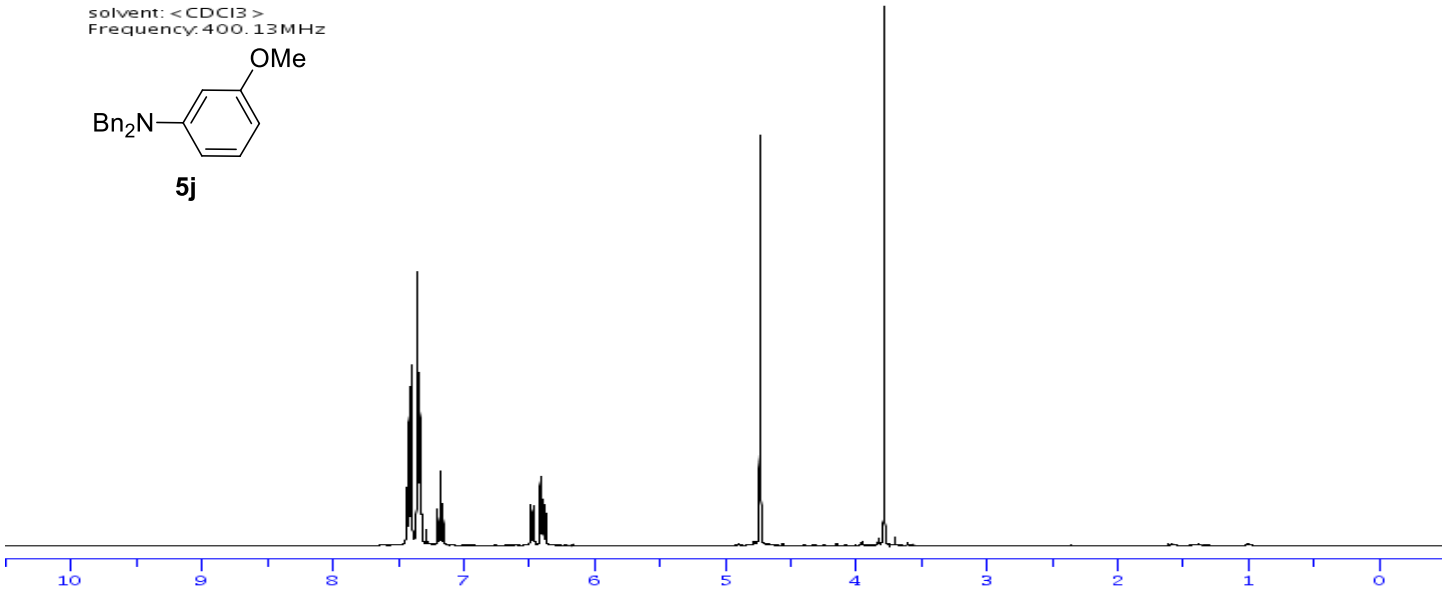
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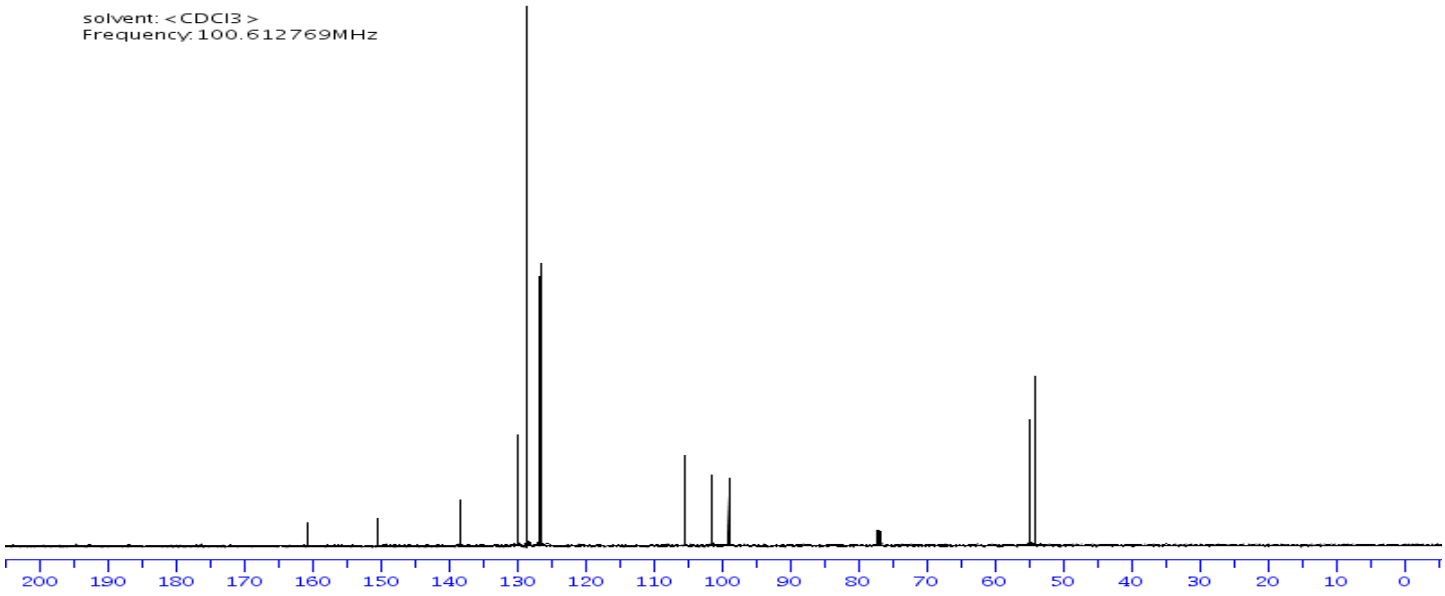
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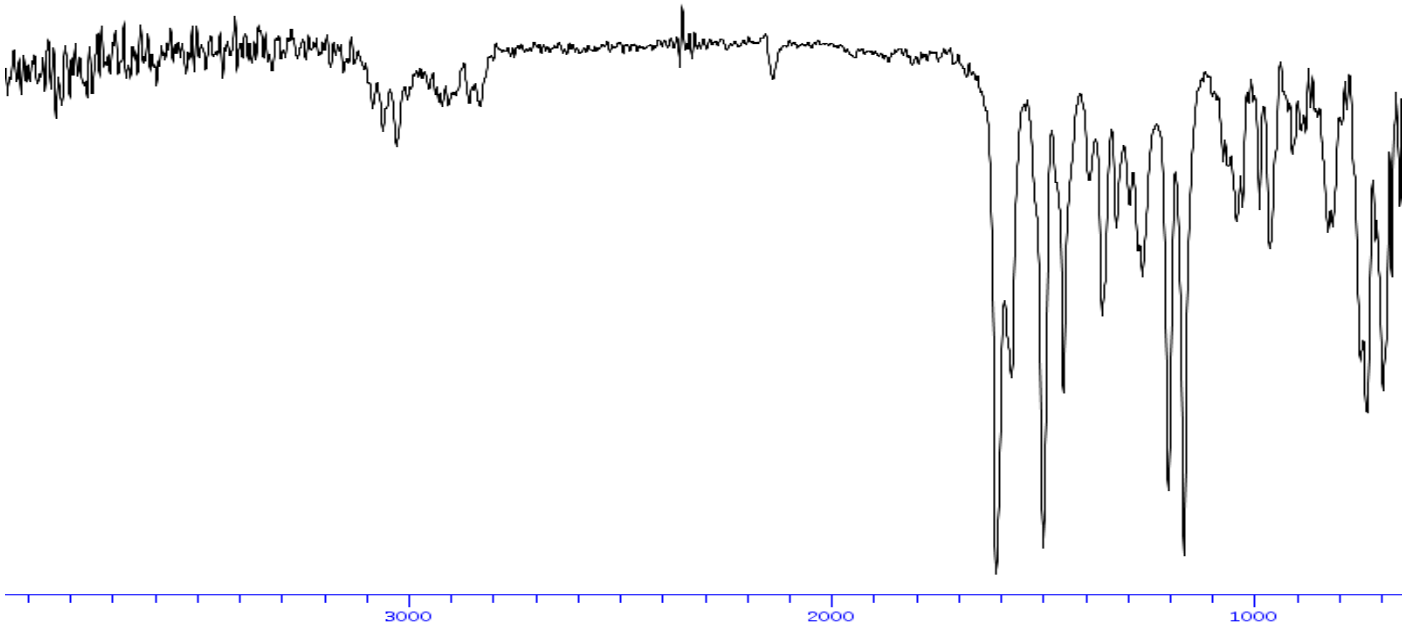
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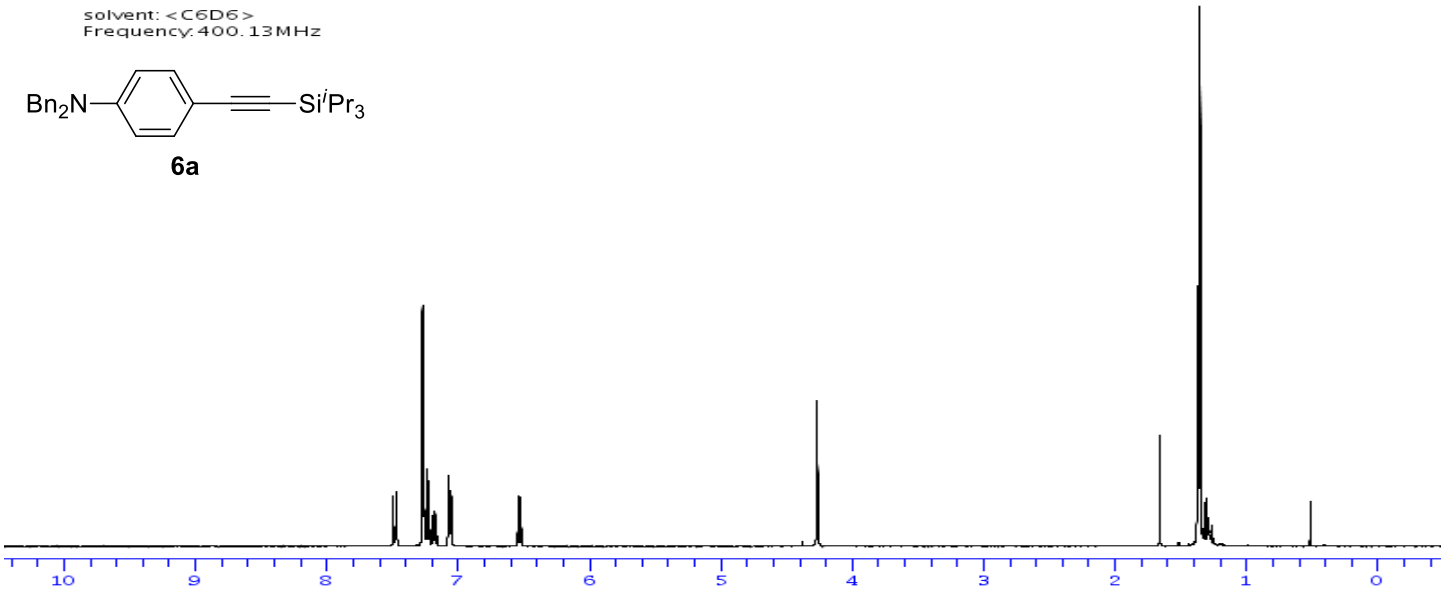
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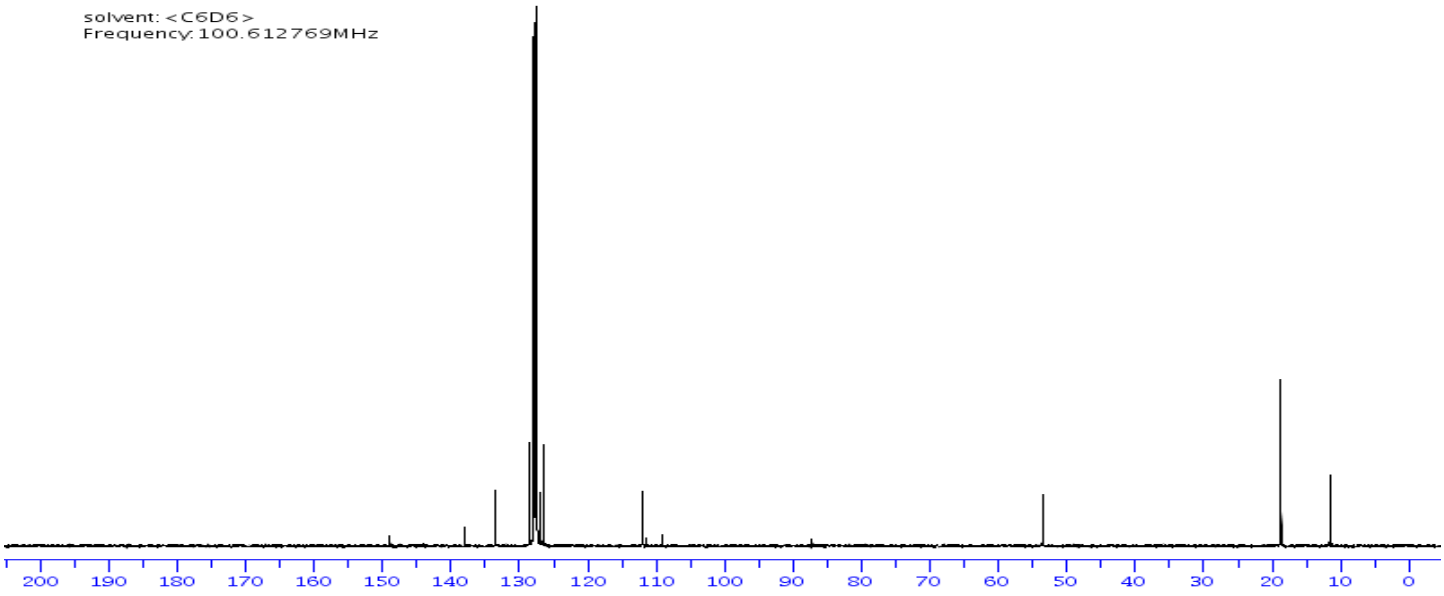
6a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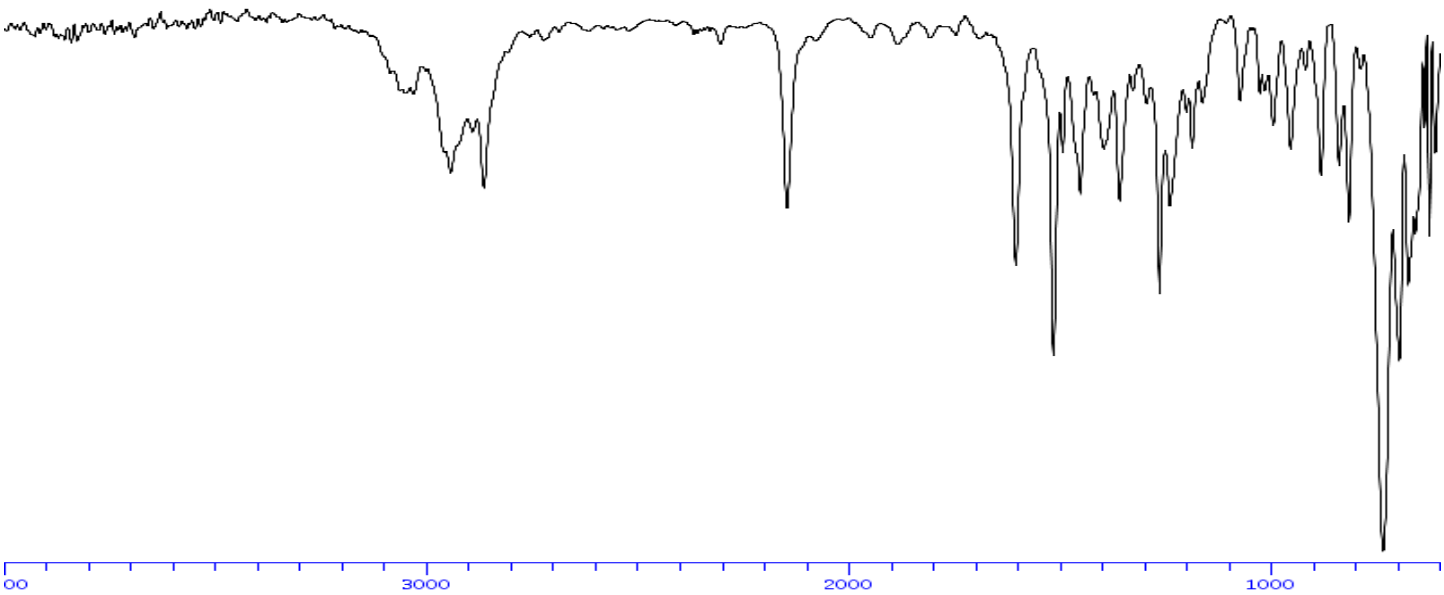
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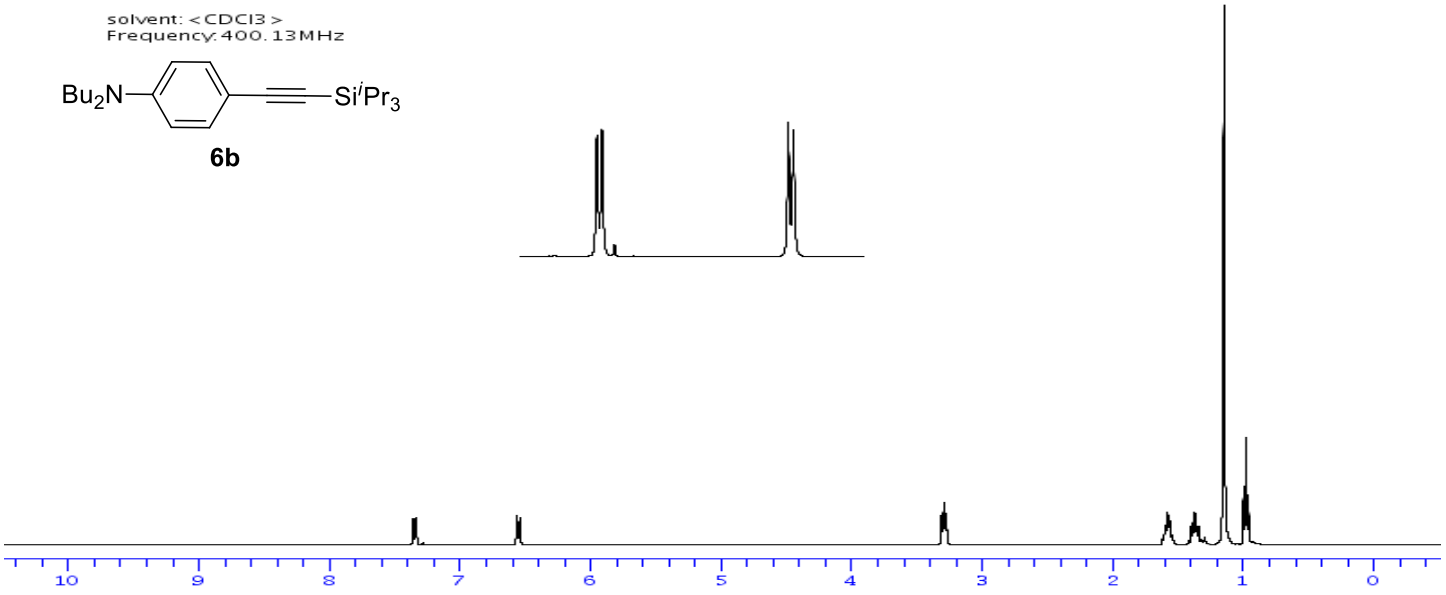
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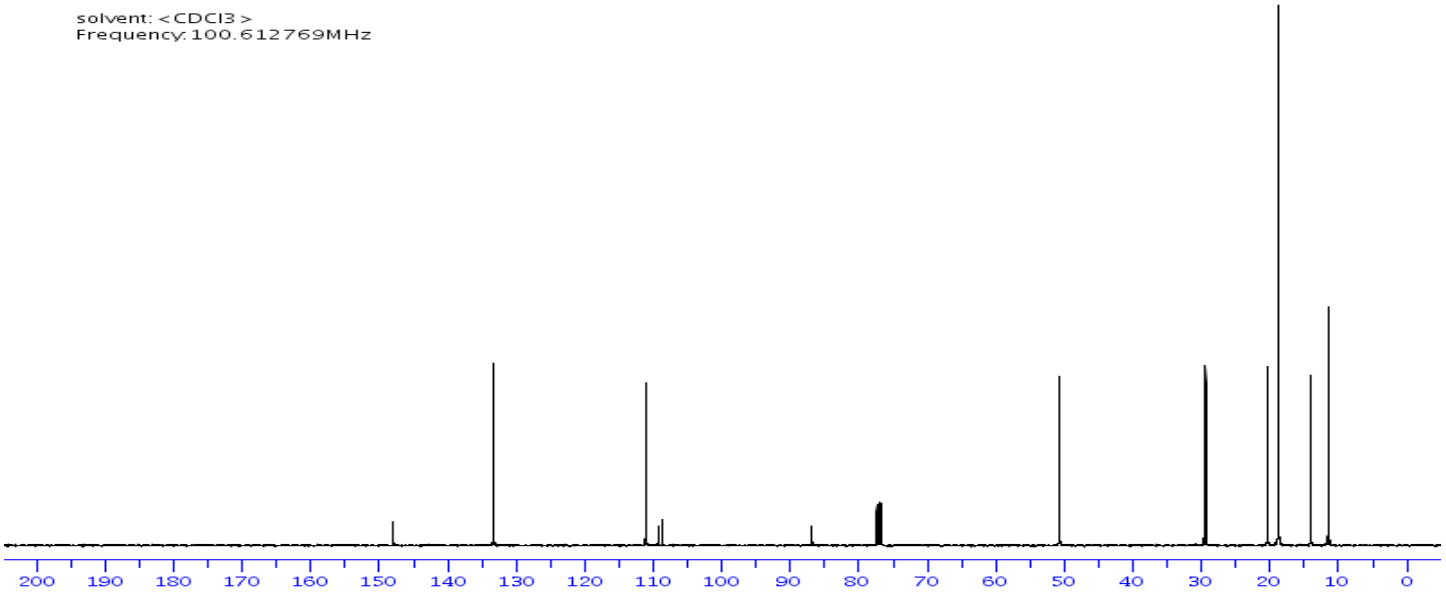
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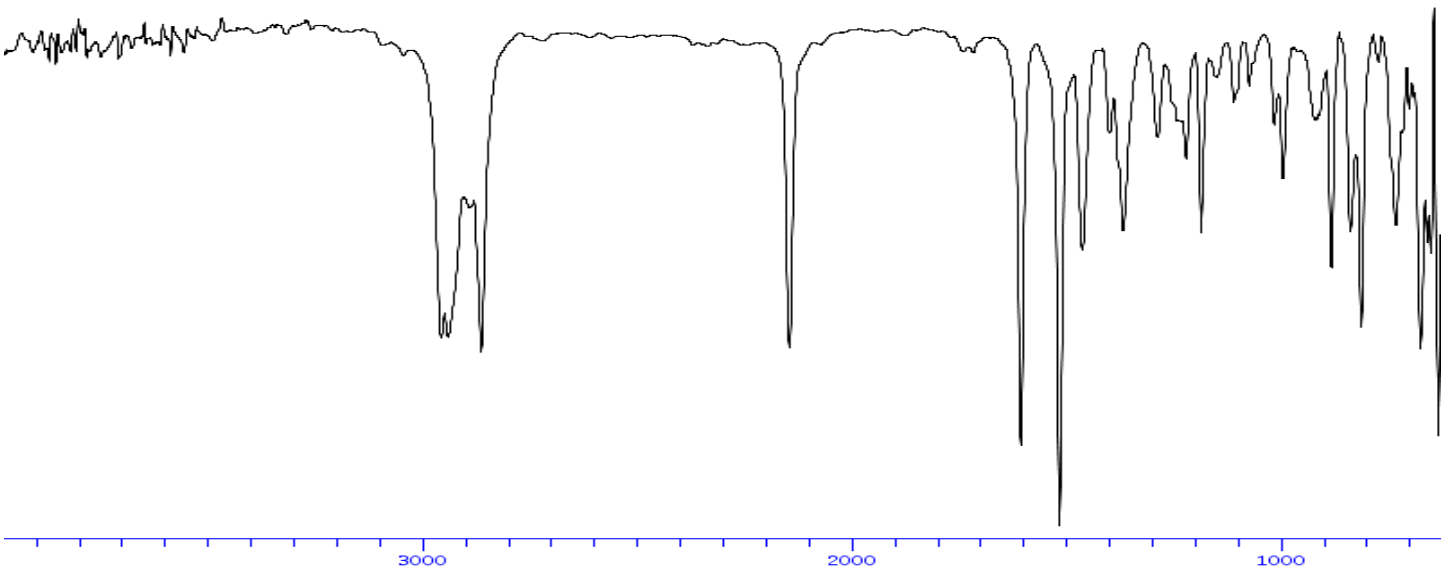
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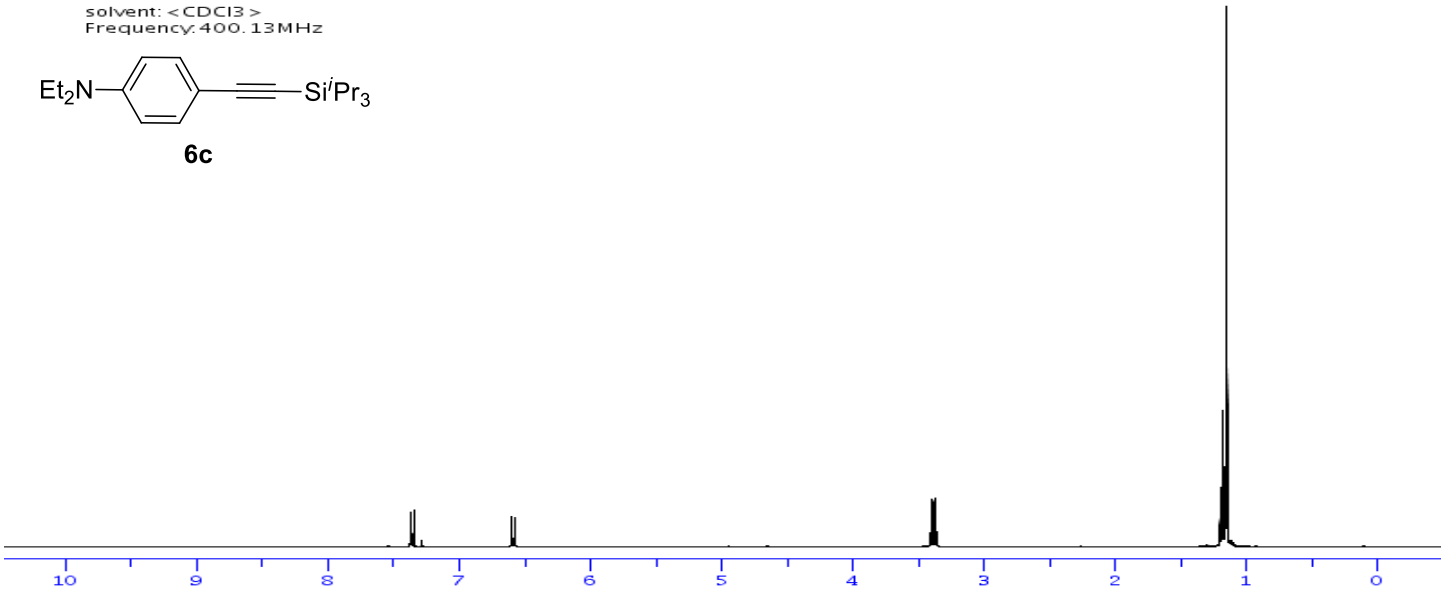
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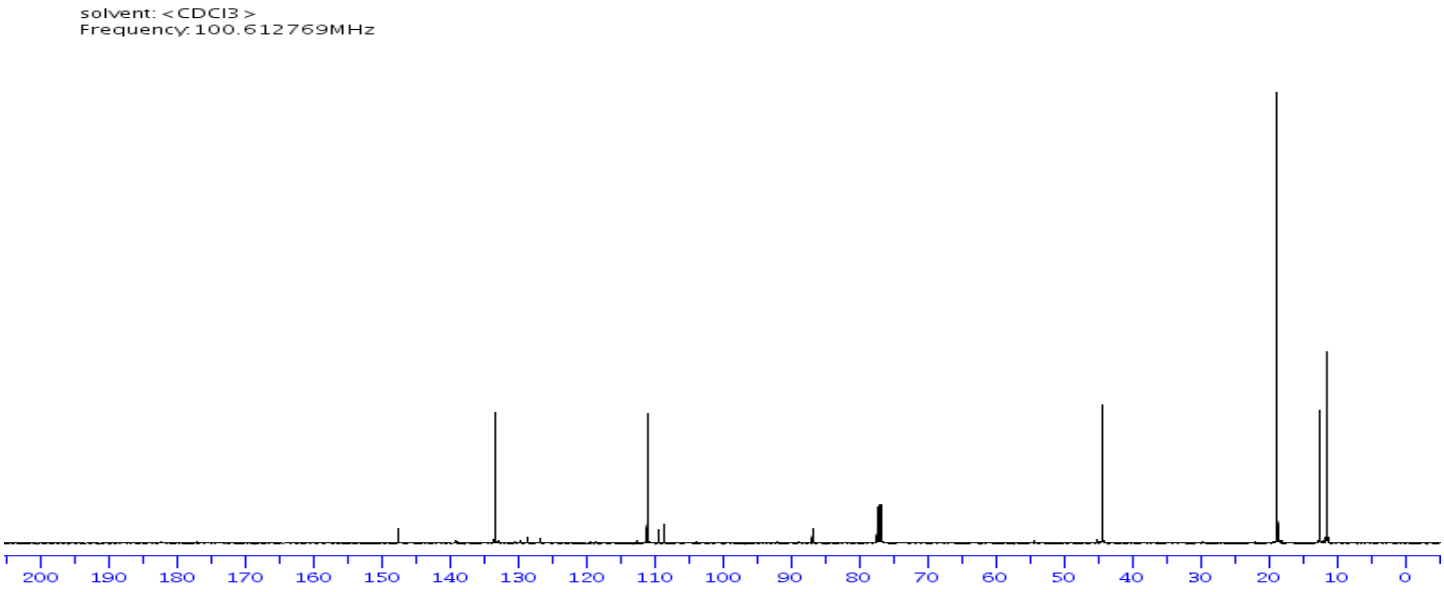
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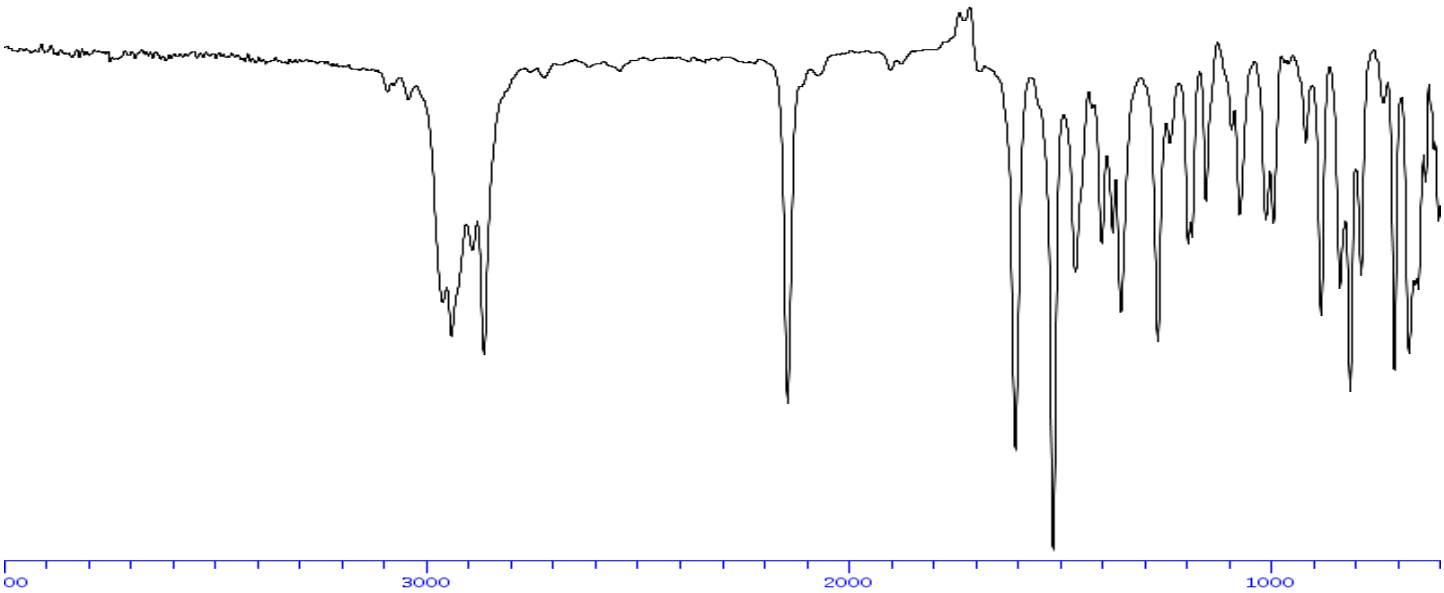
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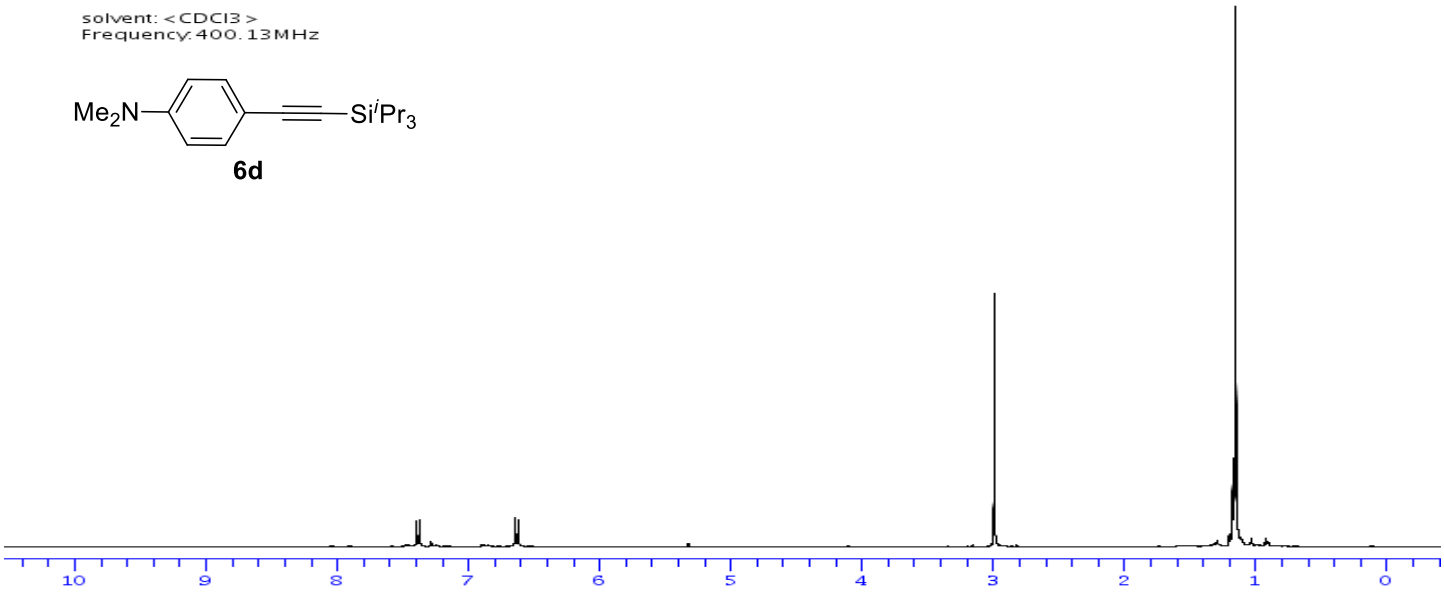
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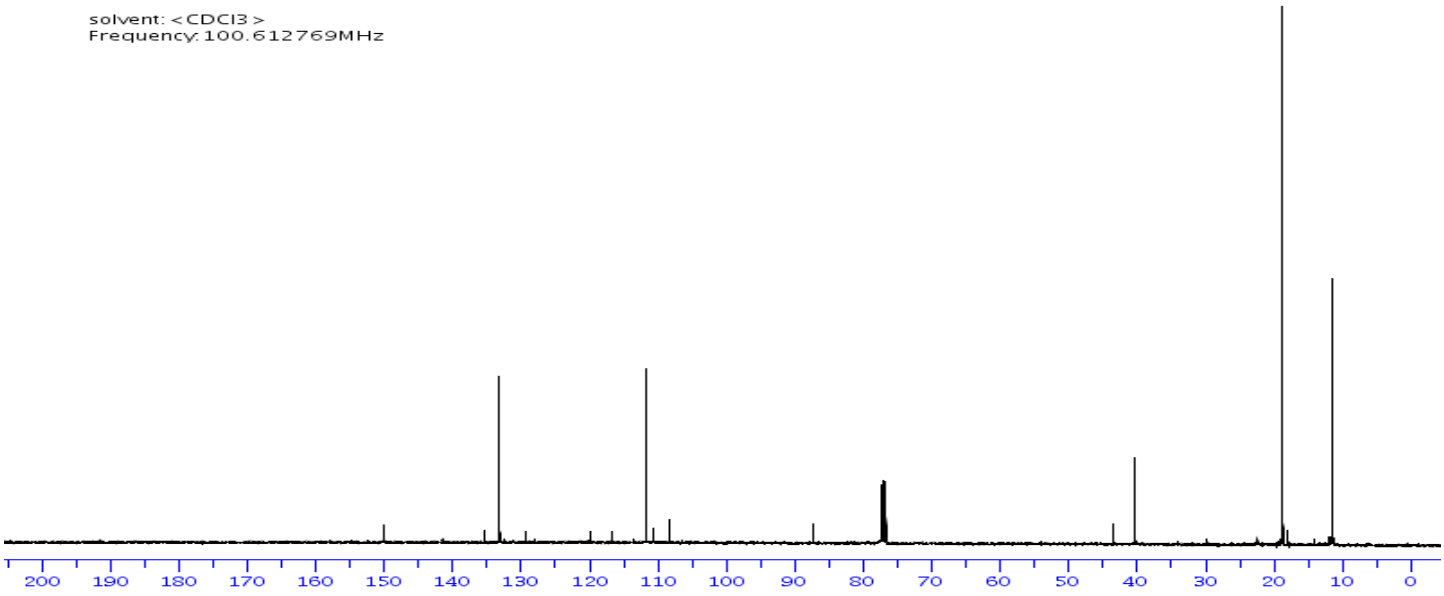
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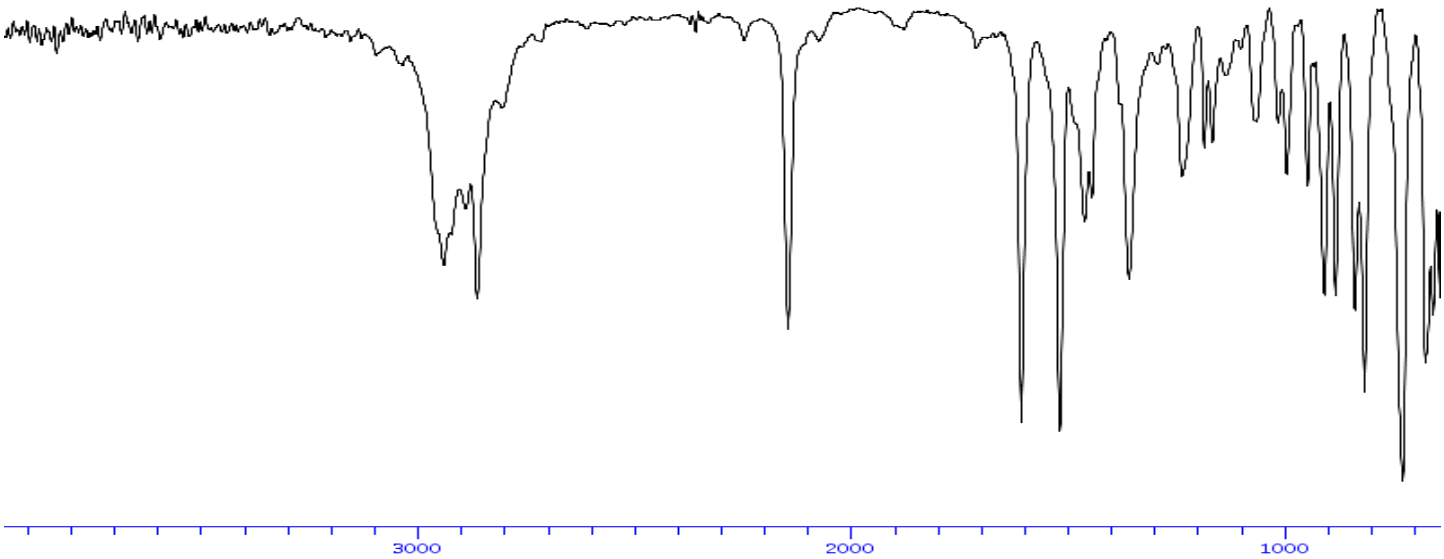
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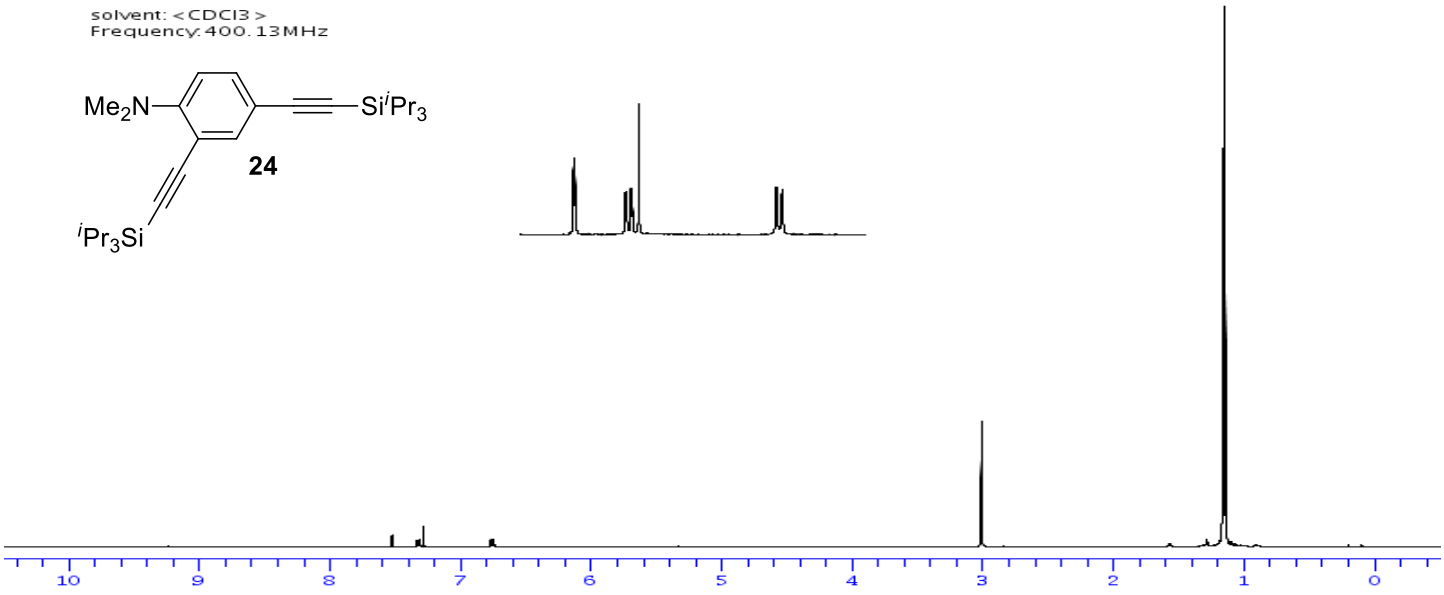
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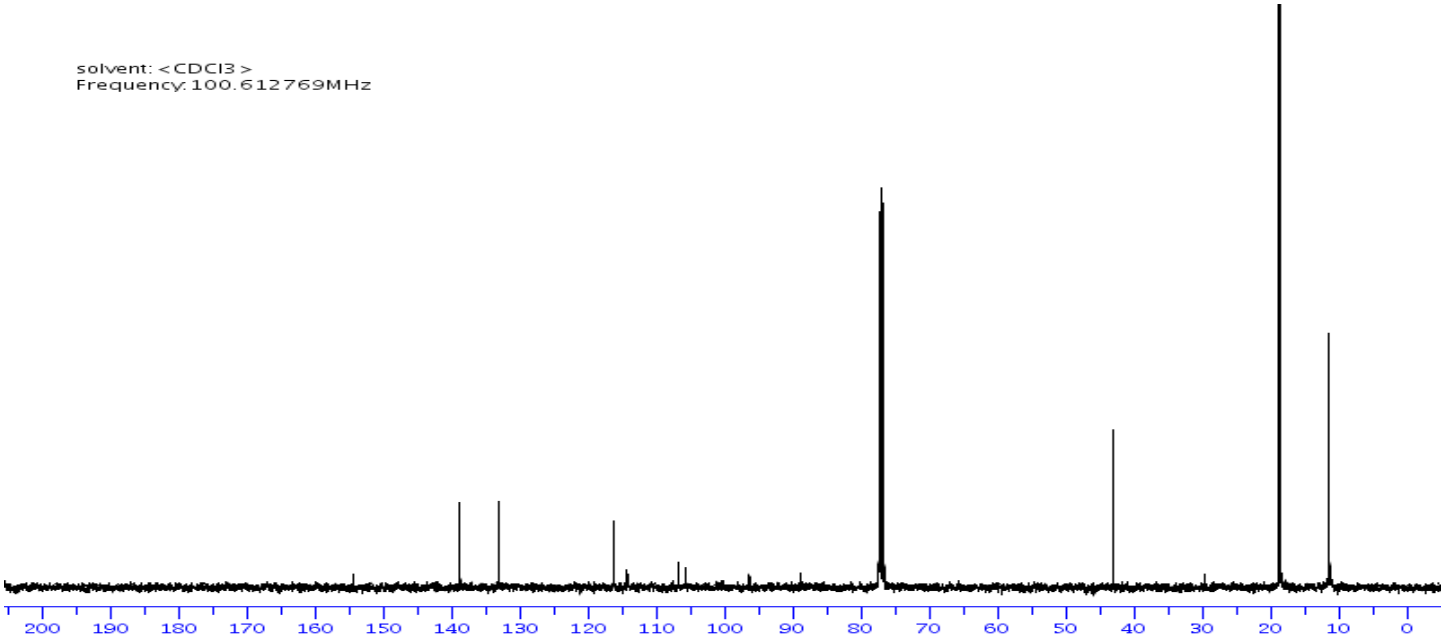
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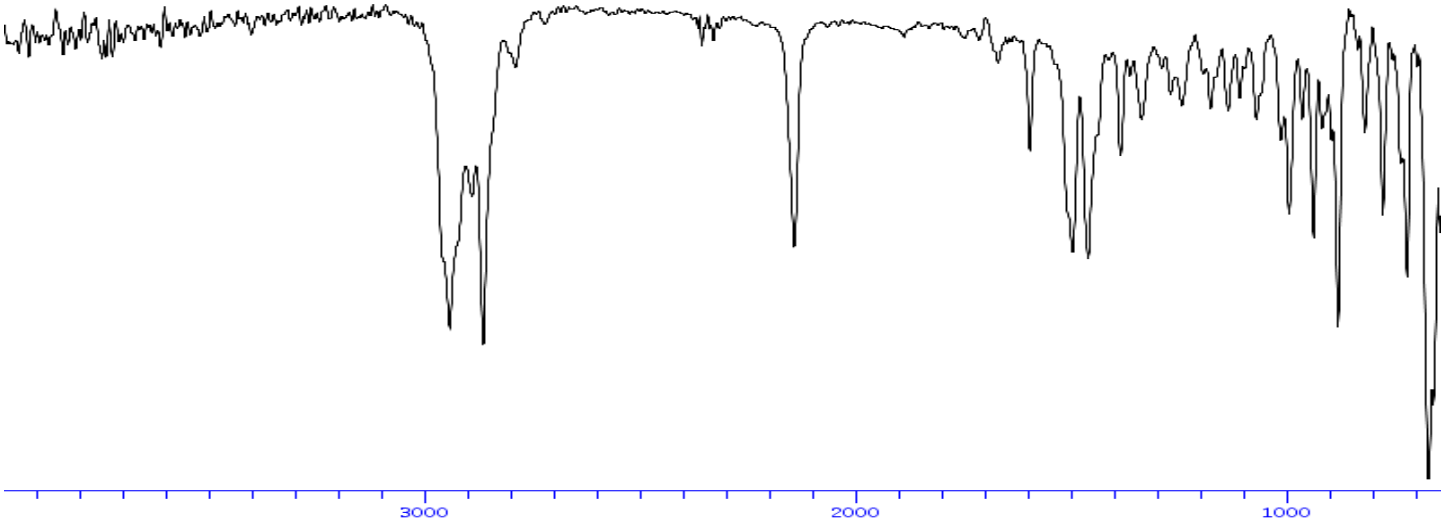
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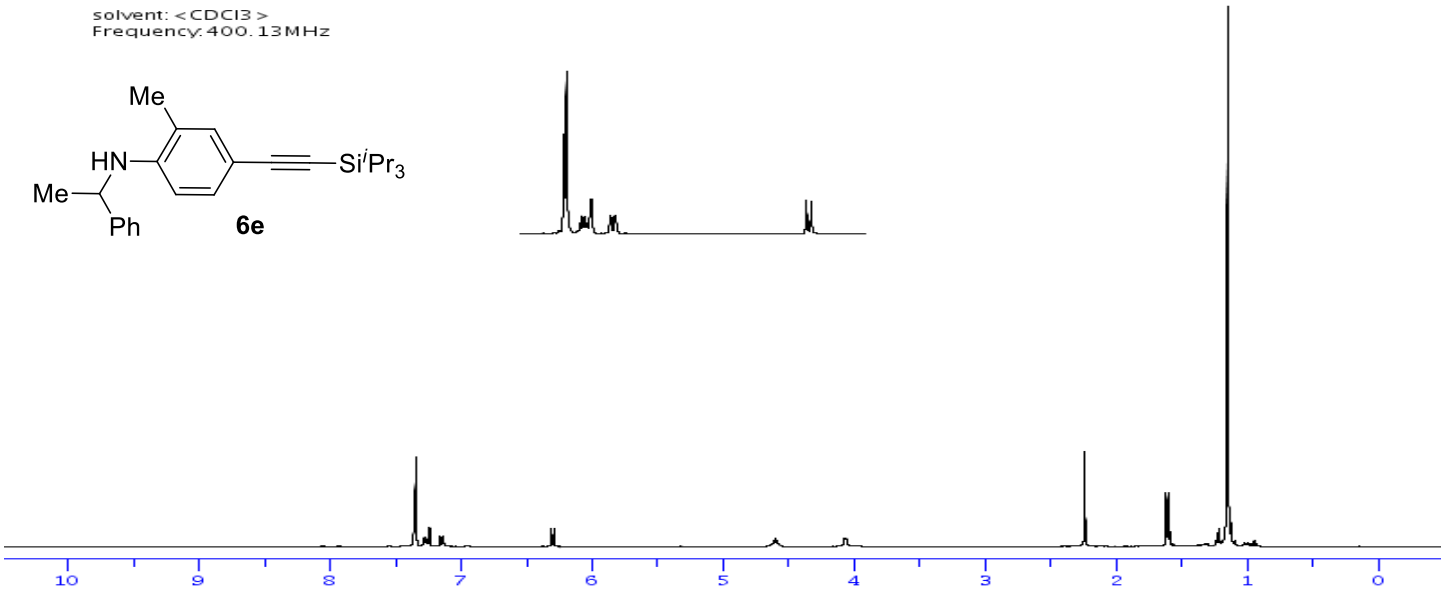
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Ph
Si^{i}Pr$_3$
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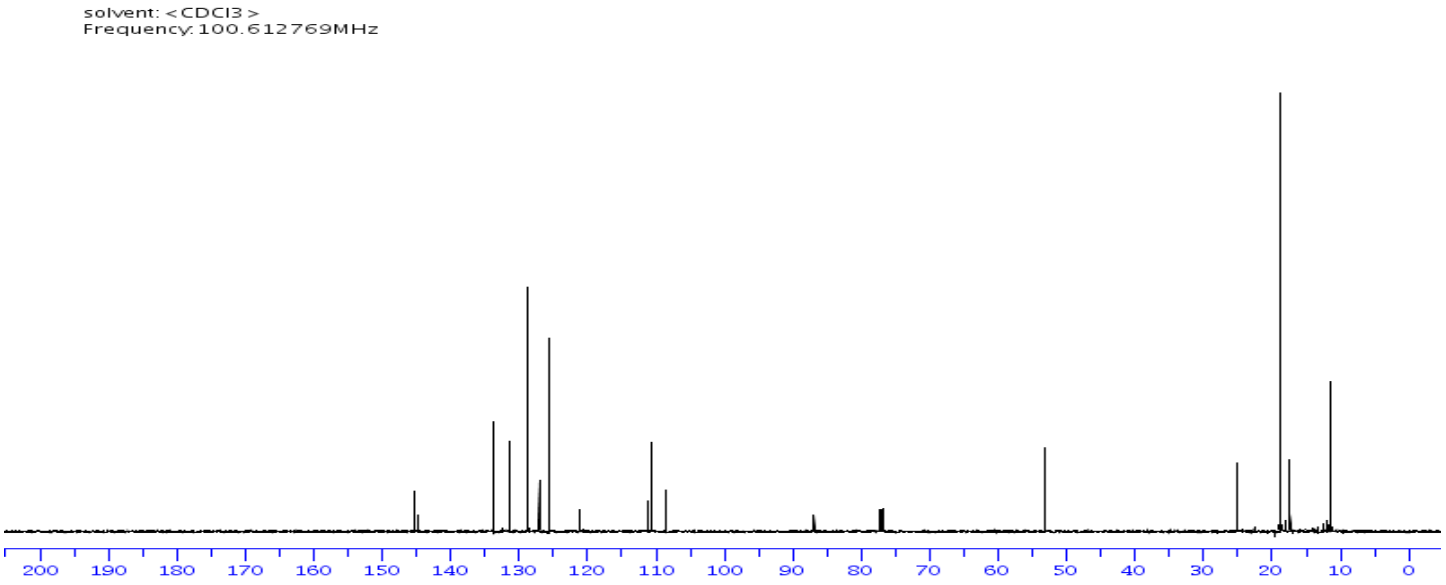
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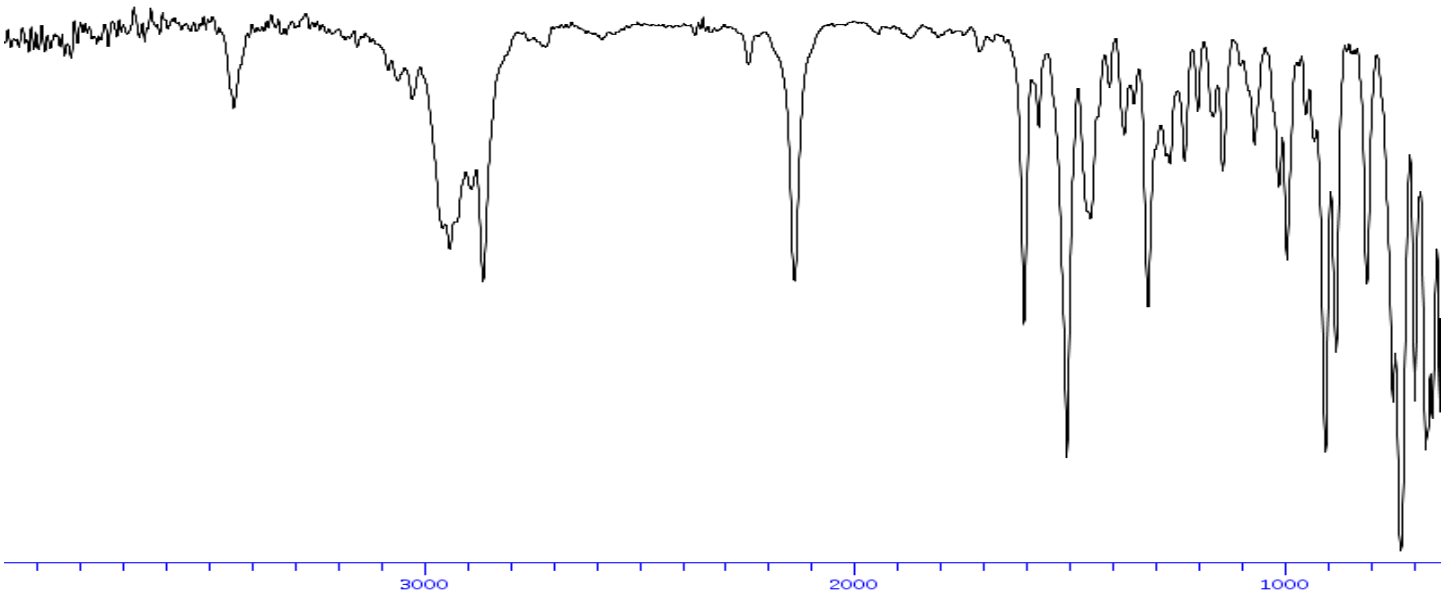
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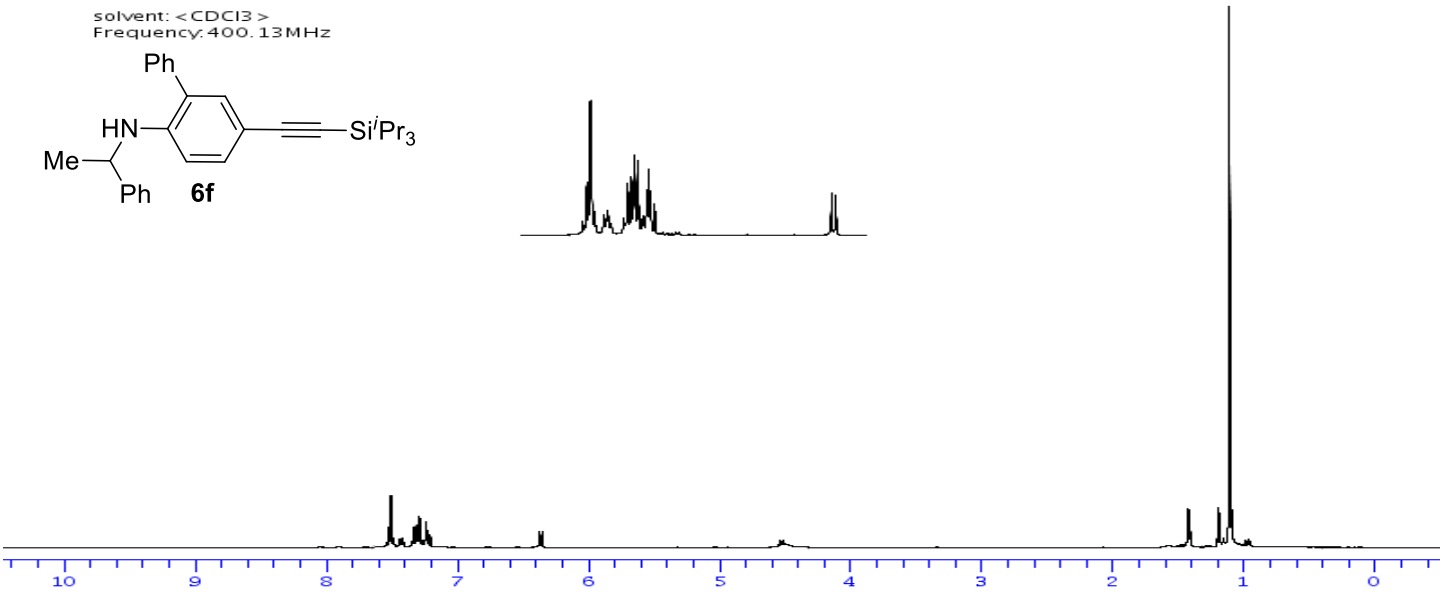
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Ph
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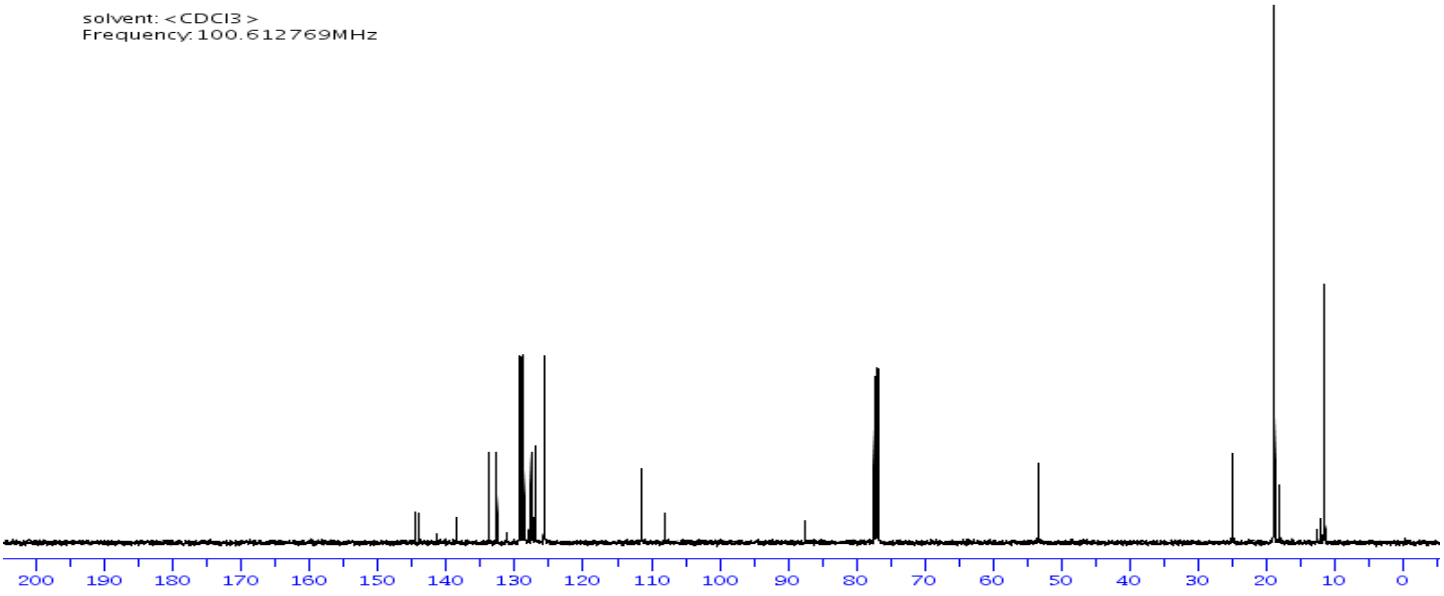
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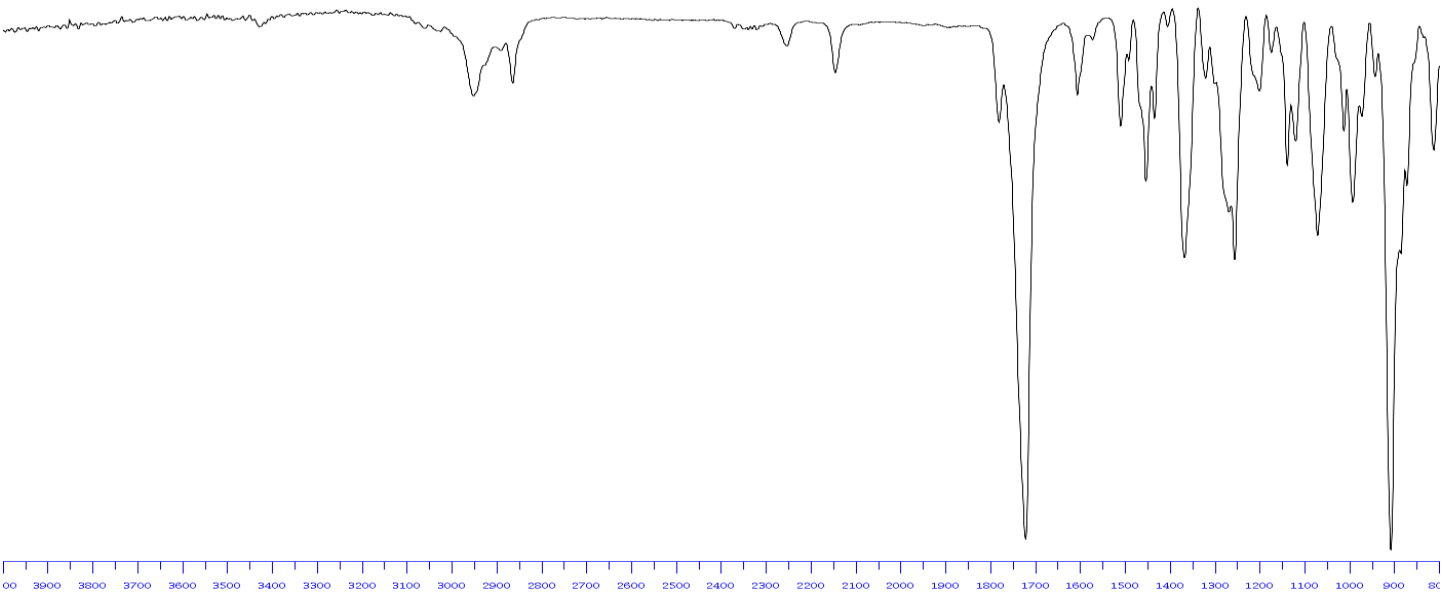

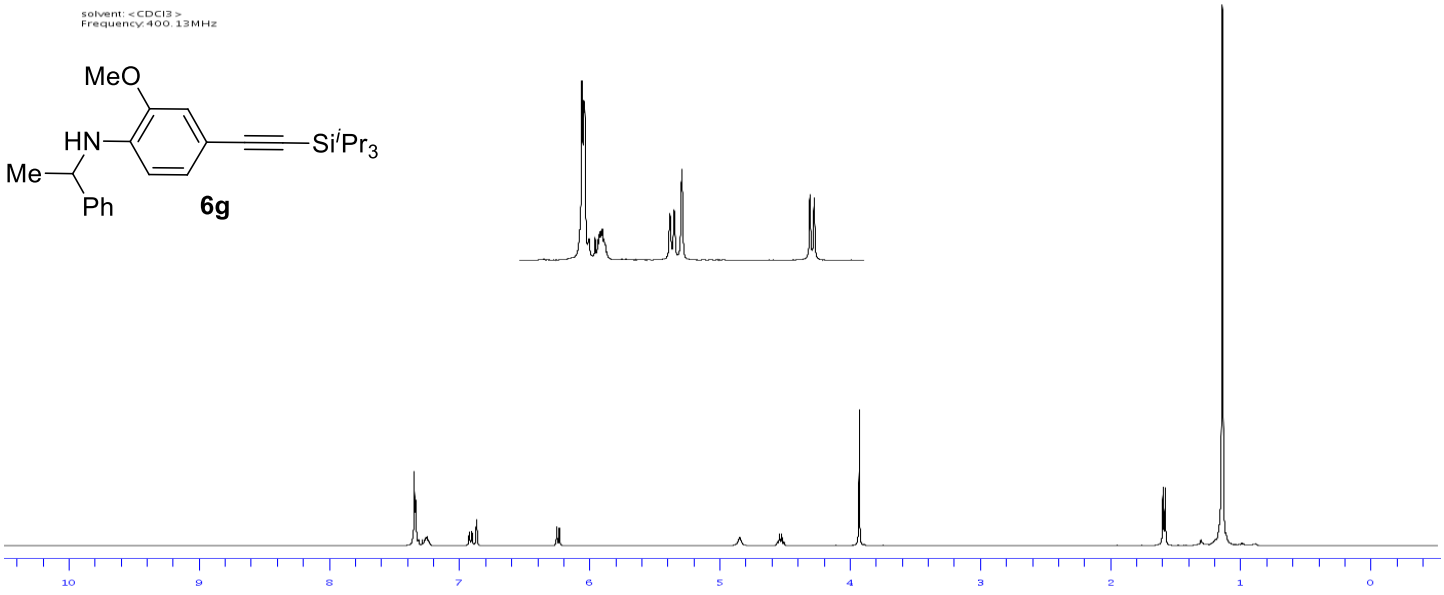
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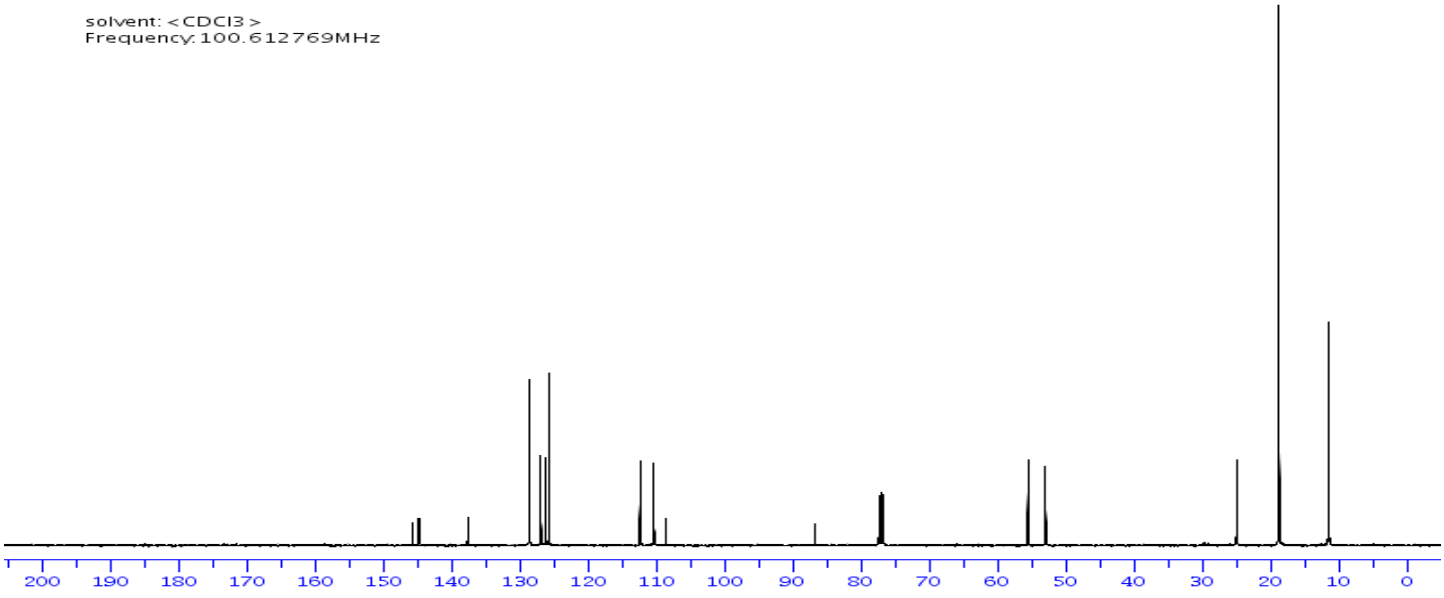
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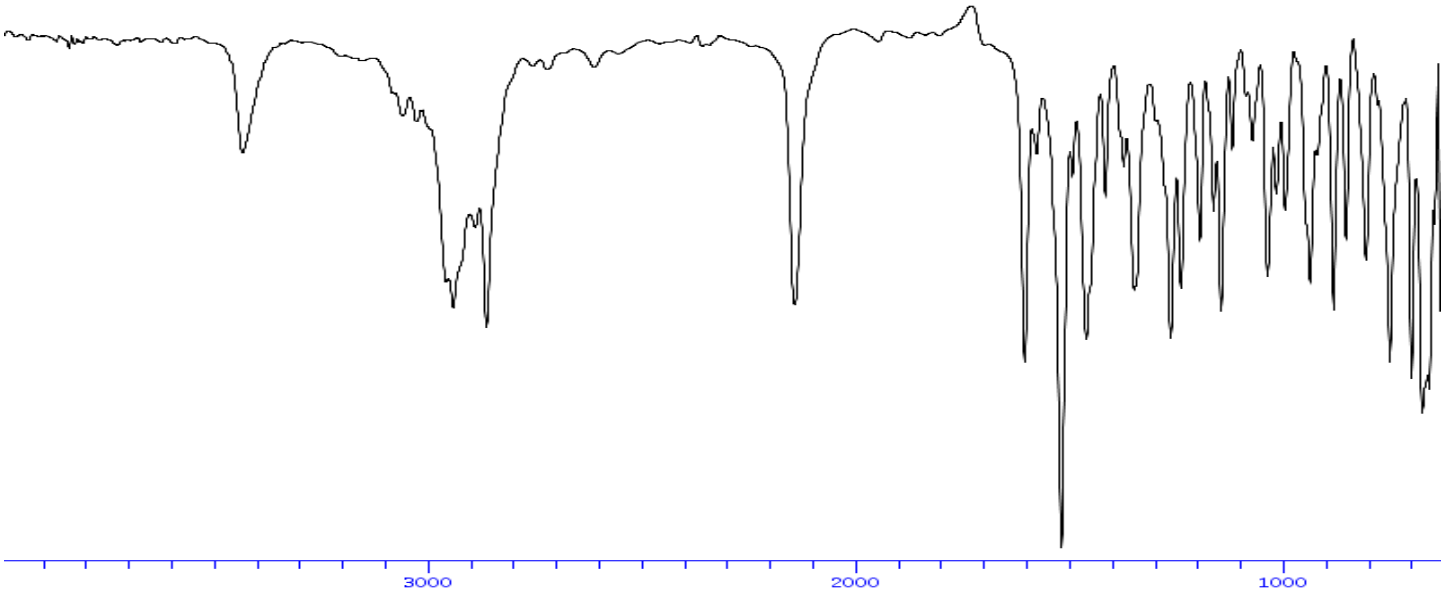
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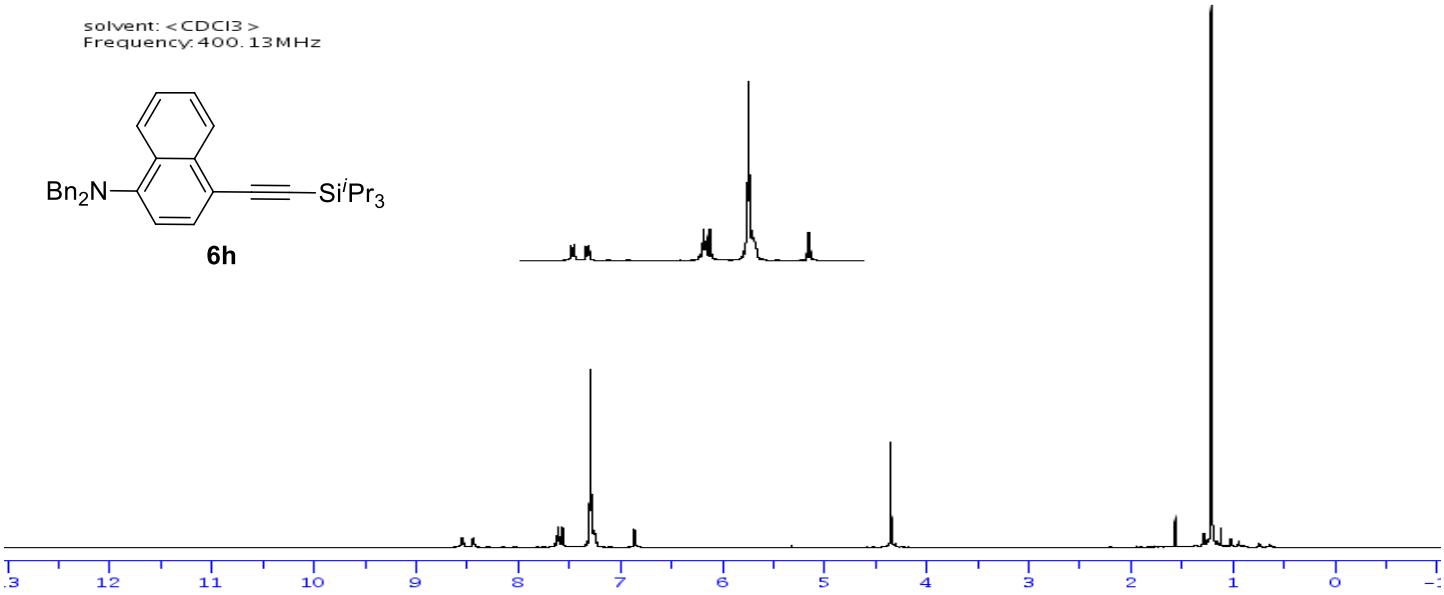
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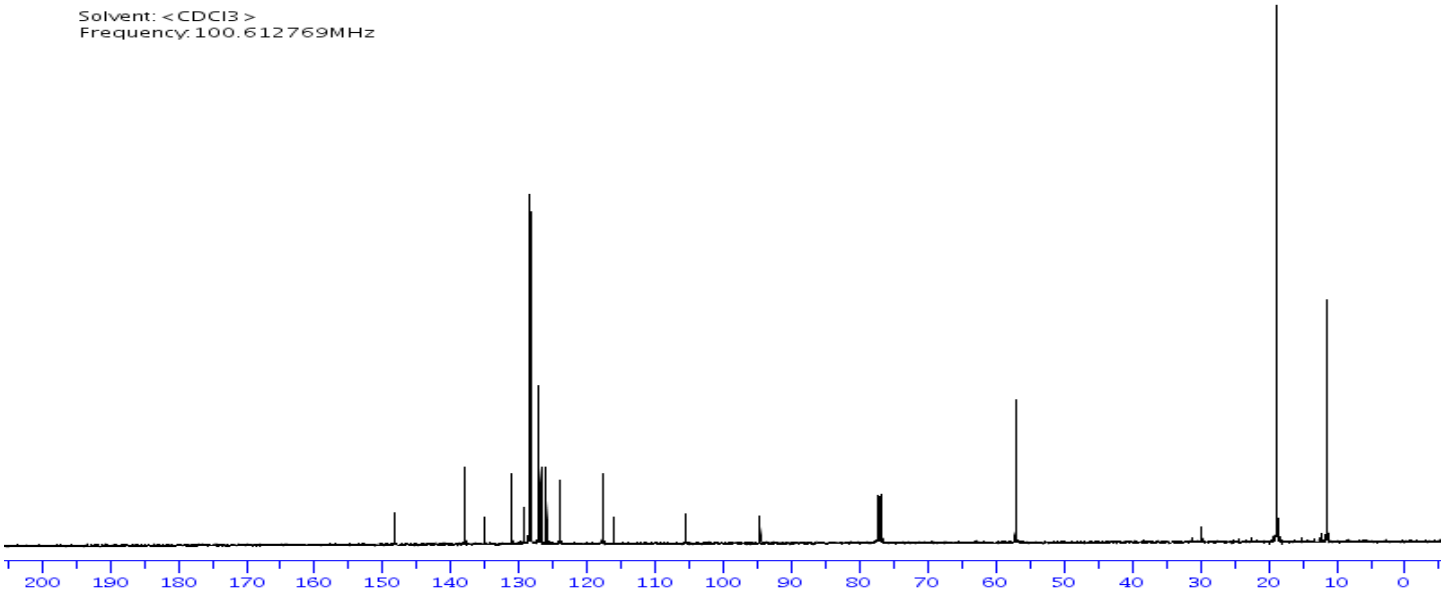
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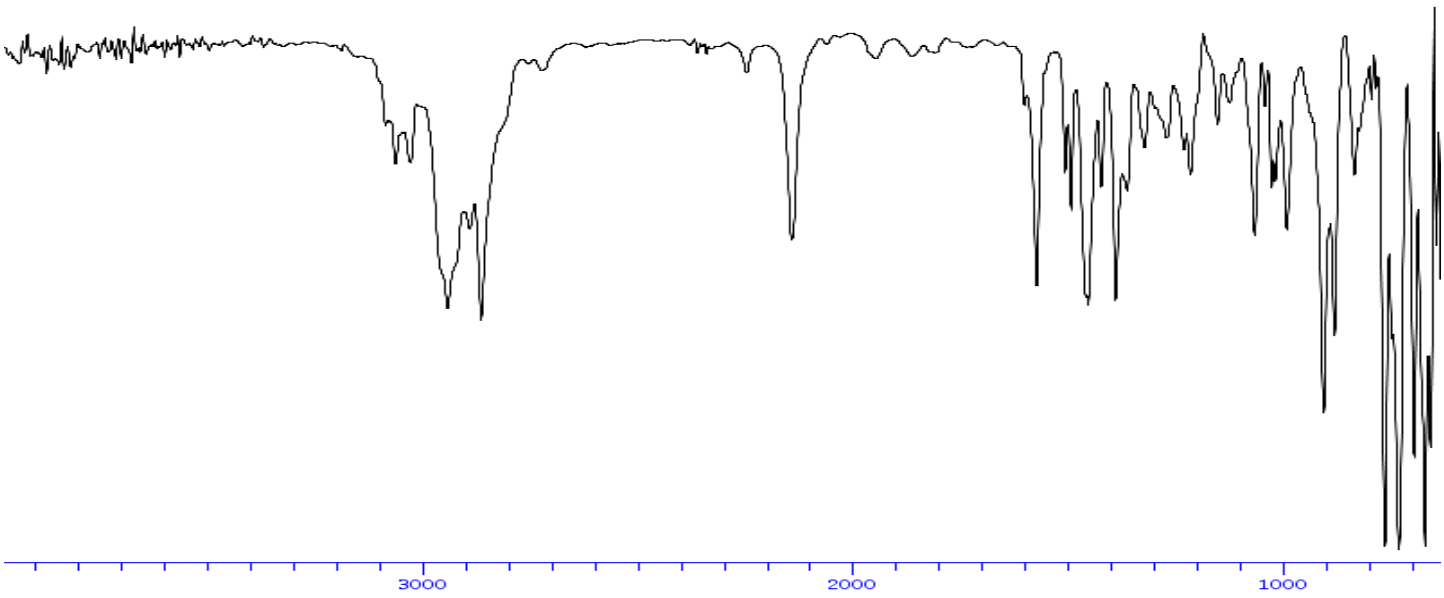
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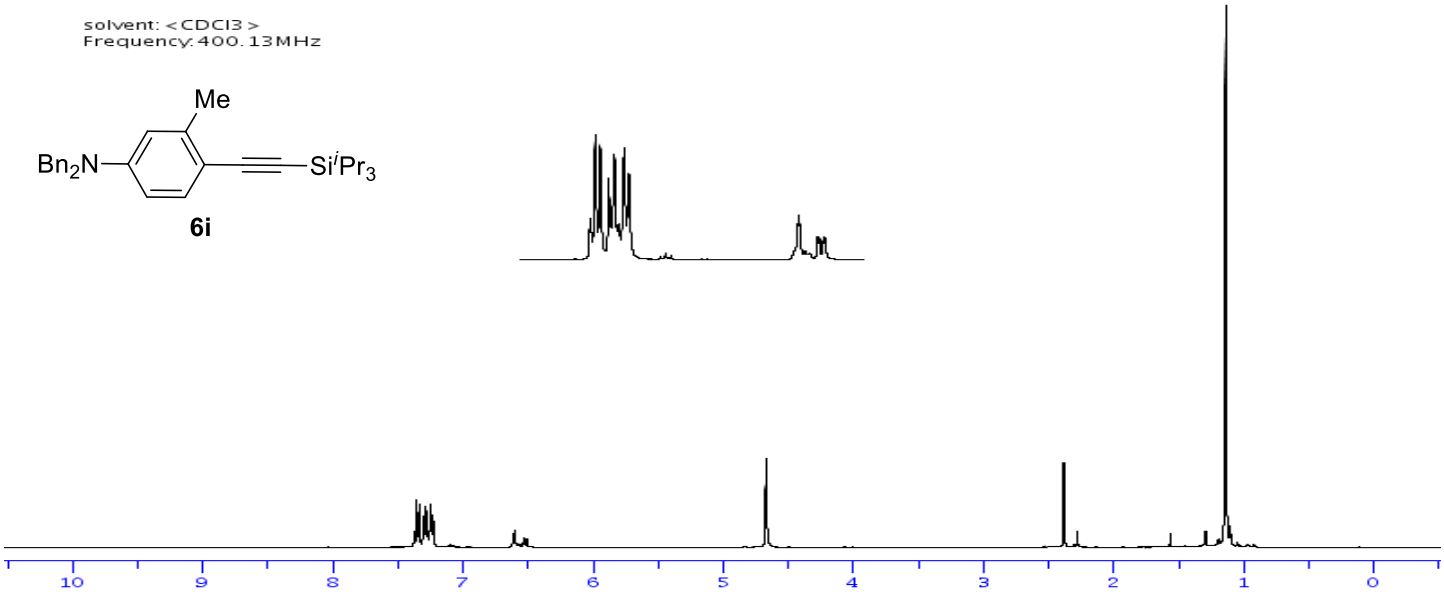
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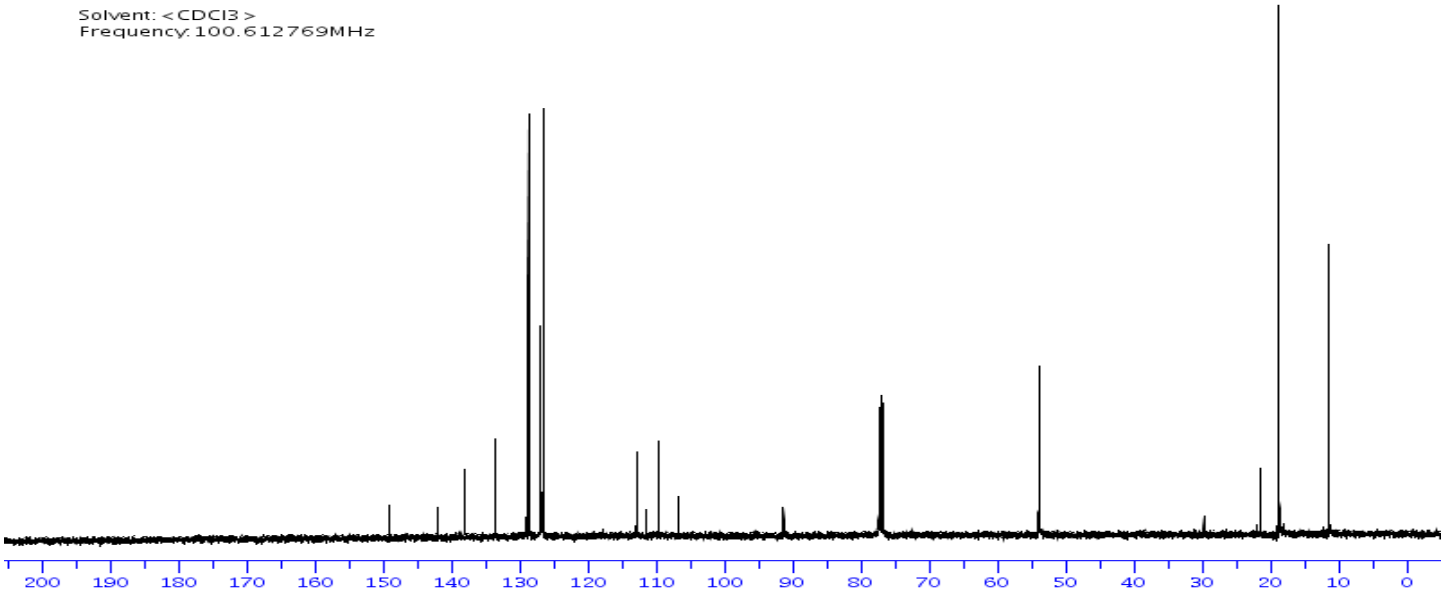
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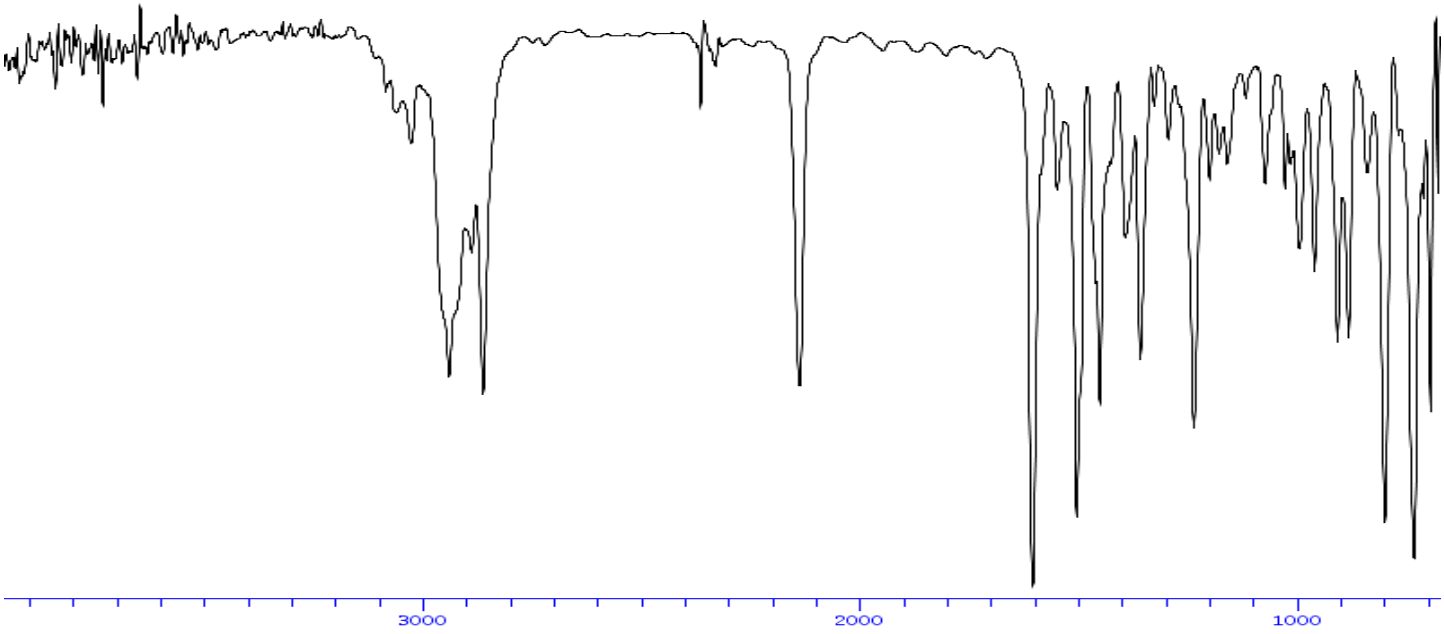
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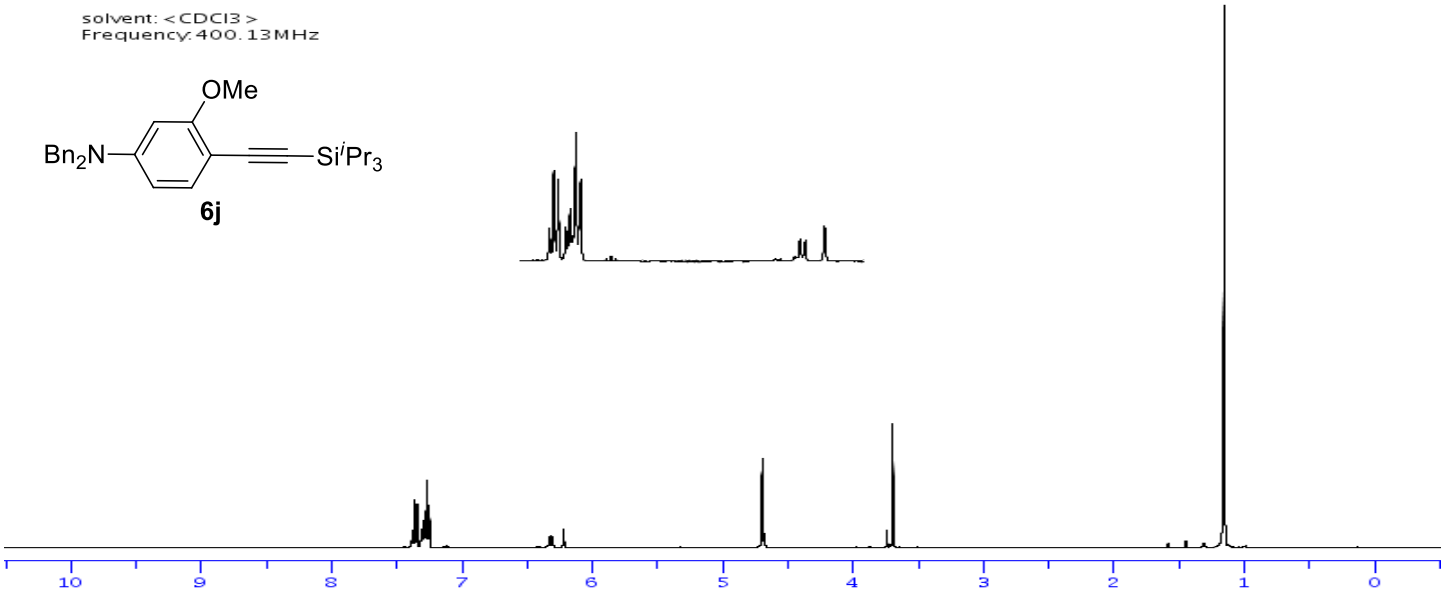
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OMe
Bn2N
SiiPr3
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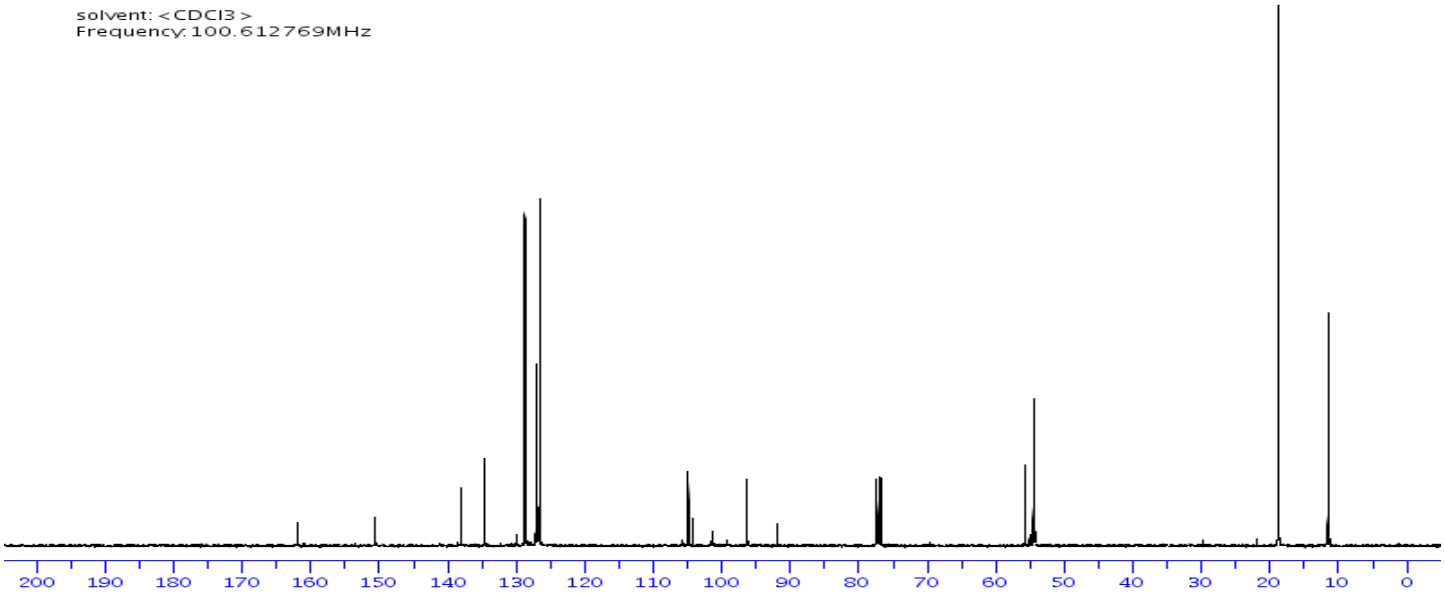
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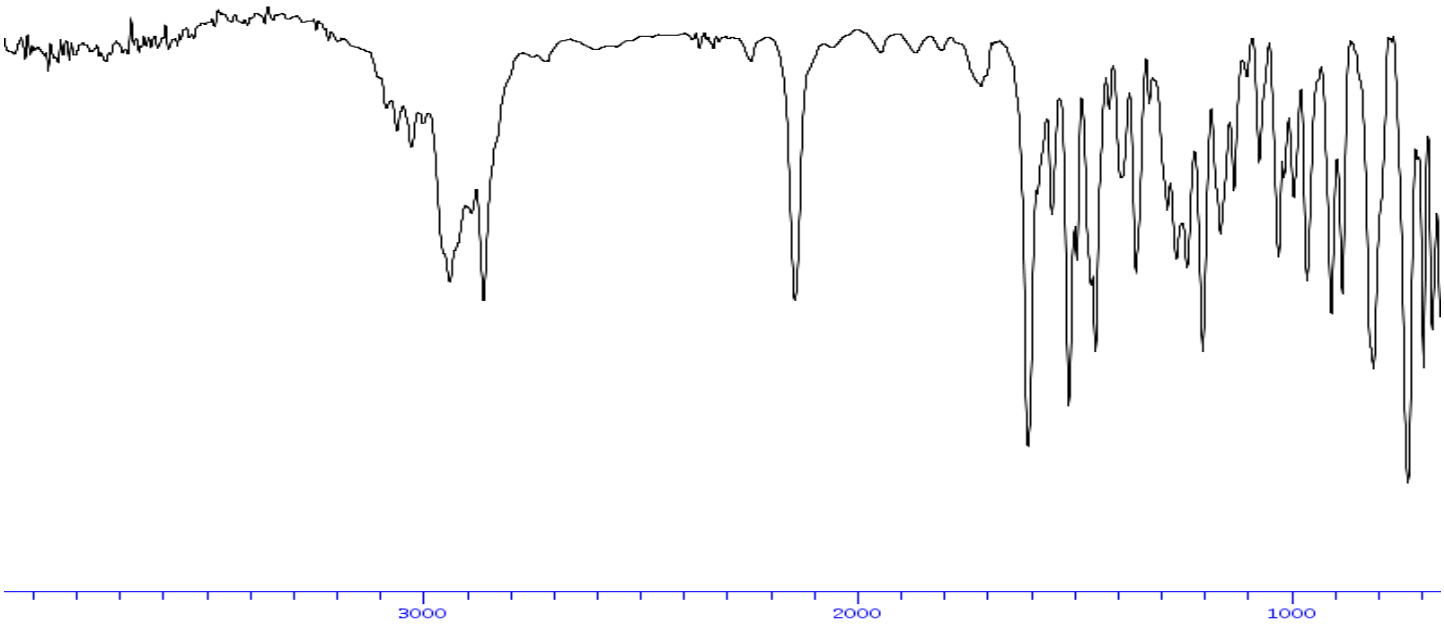
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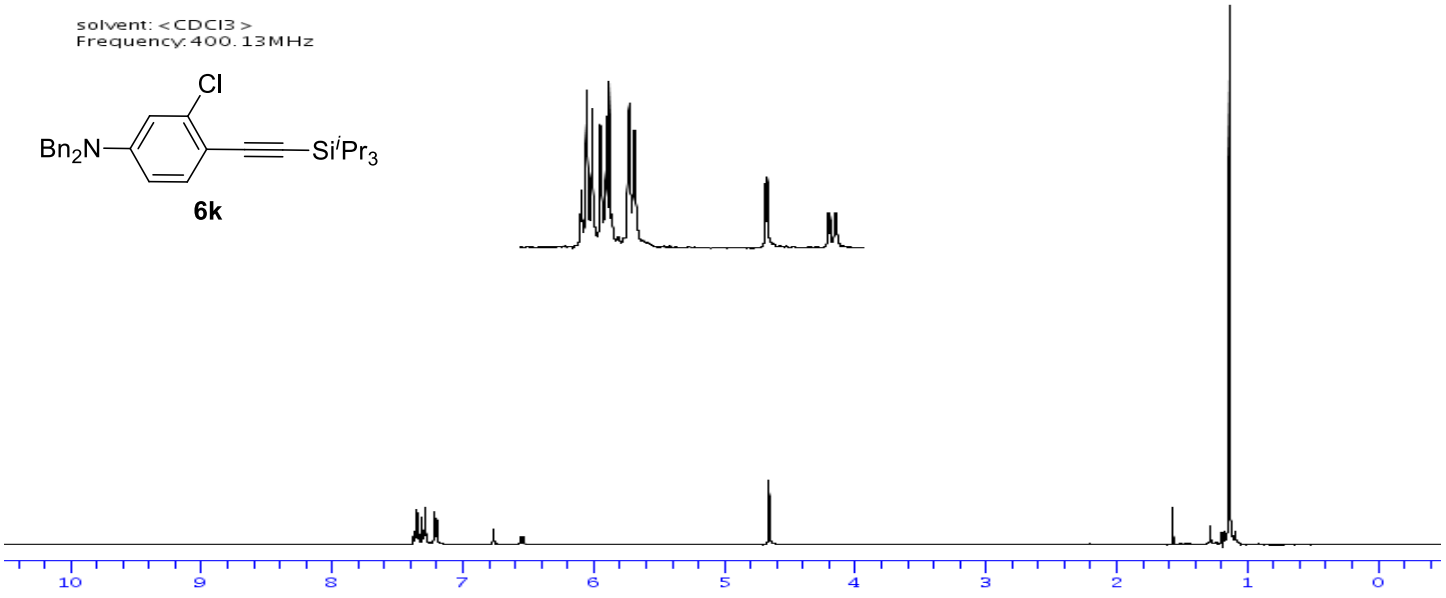
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SiiPr3
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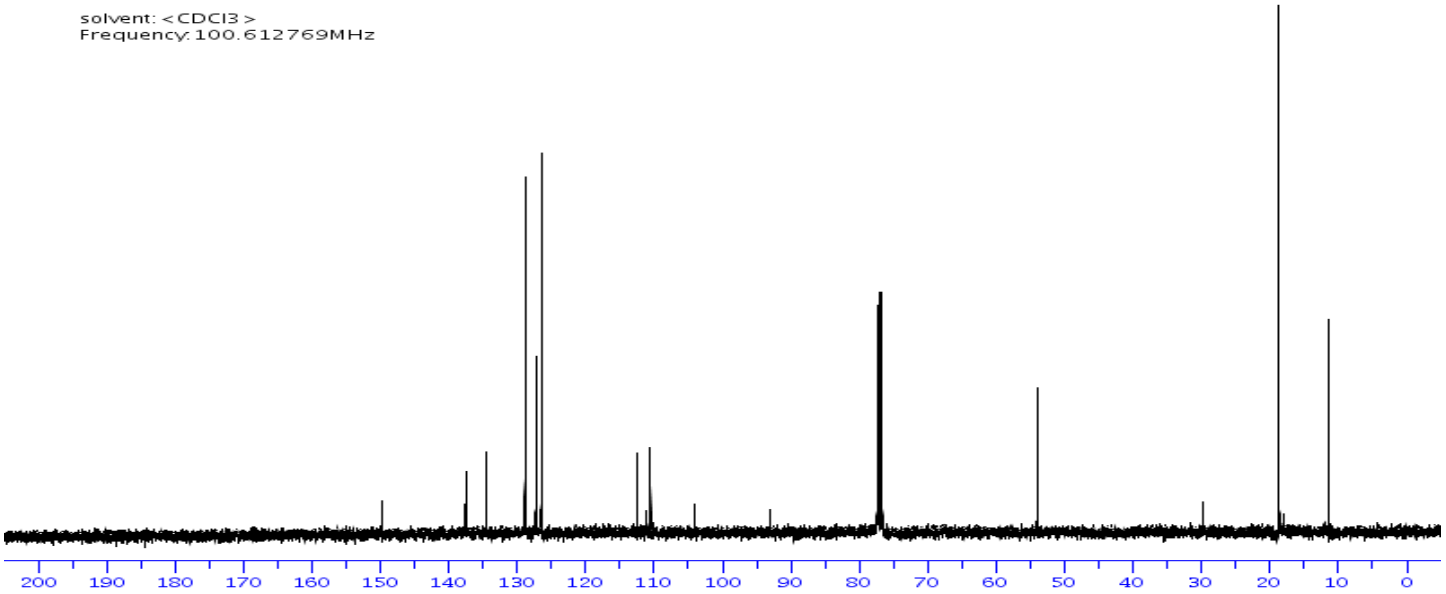
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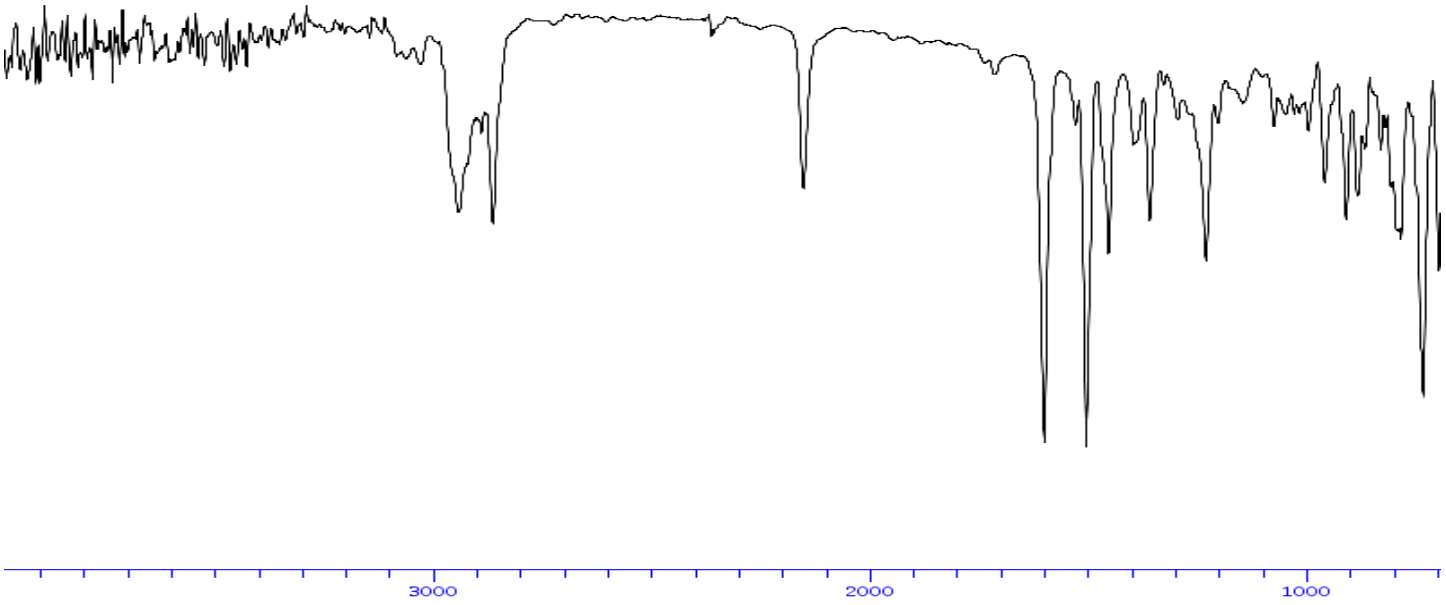
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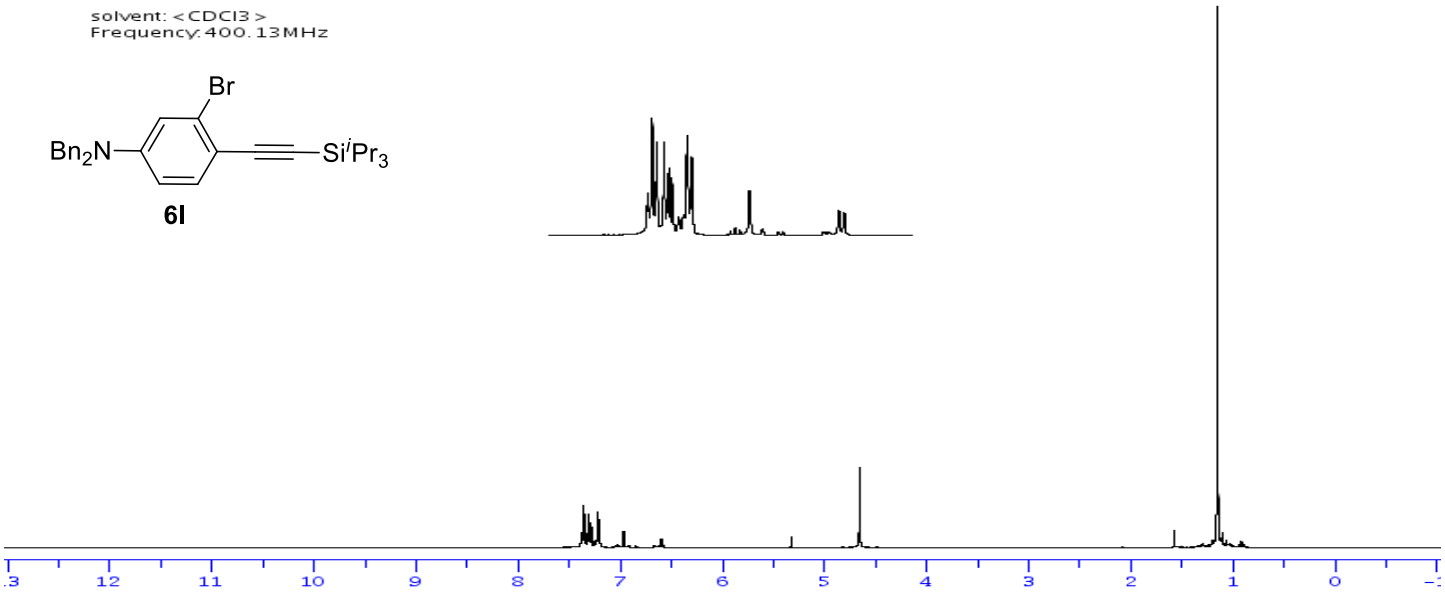
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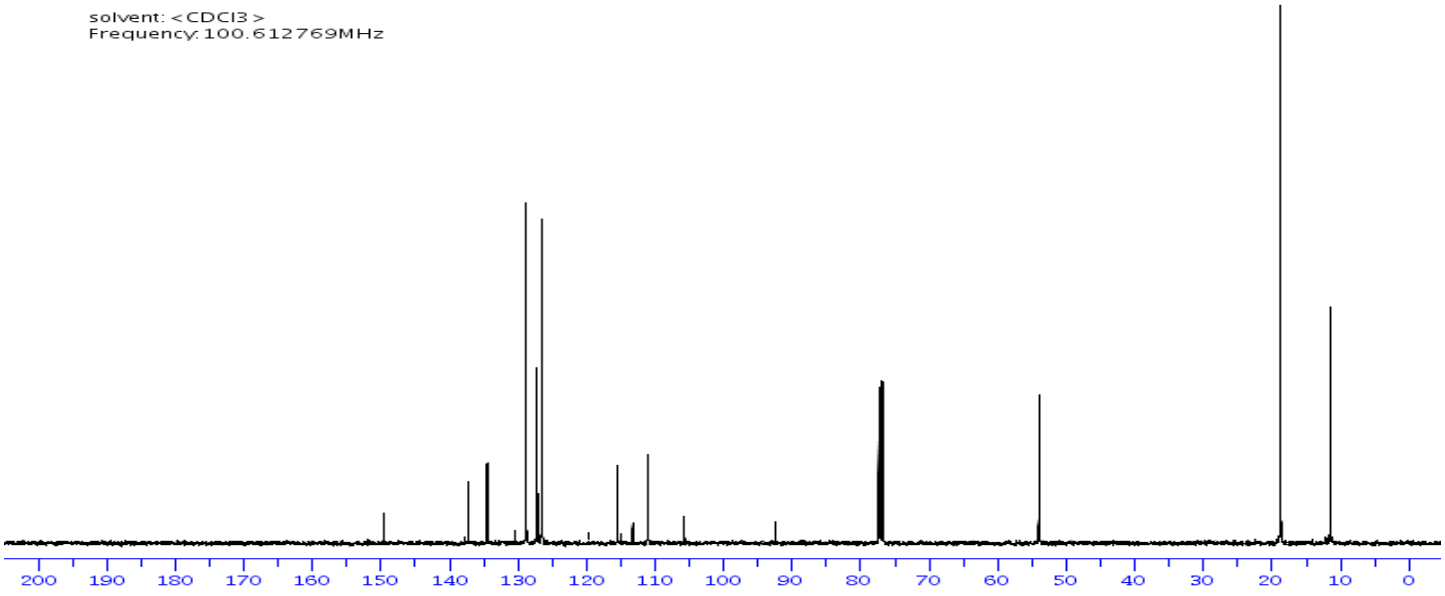
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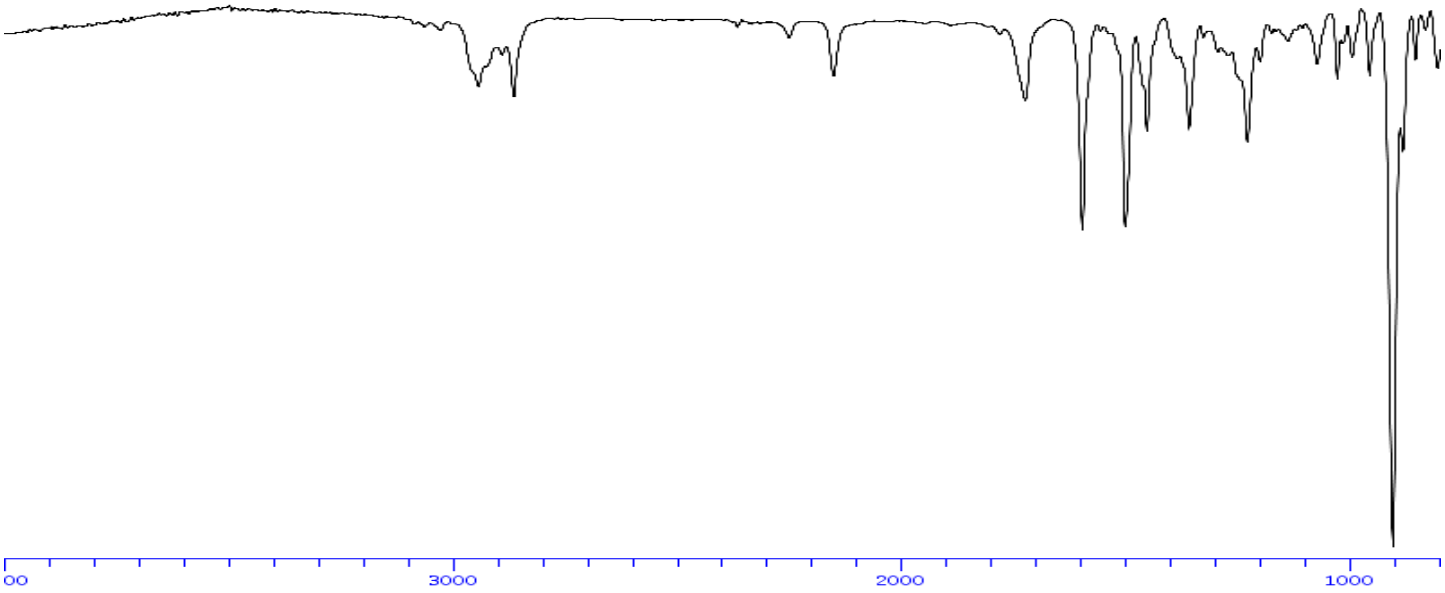
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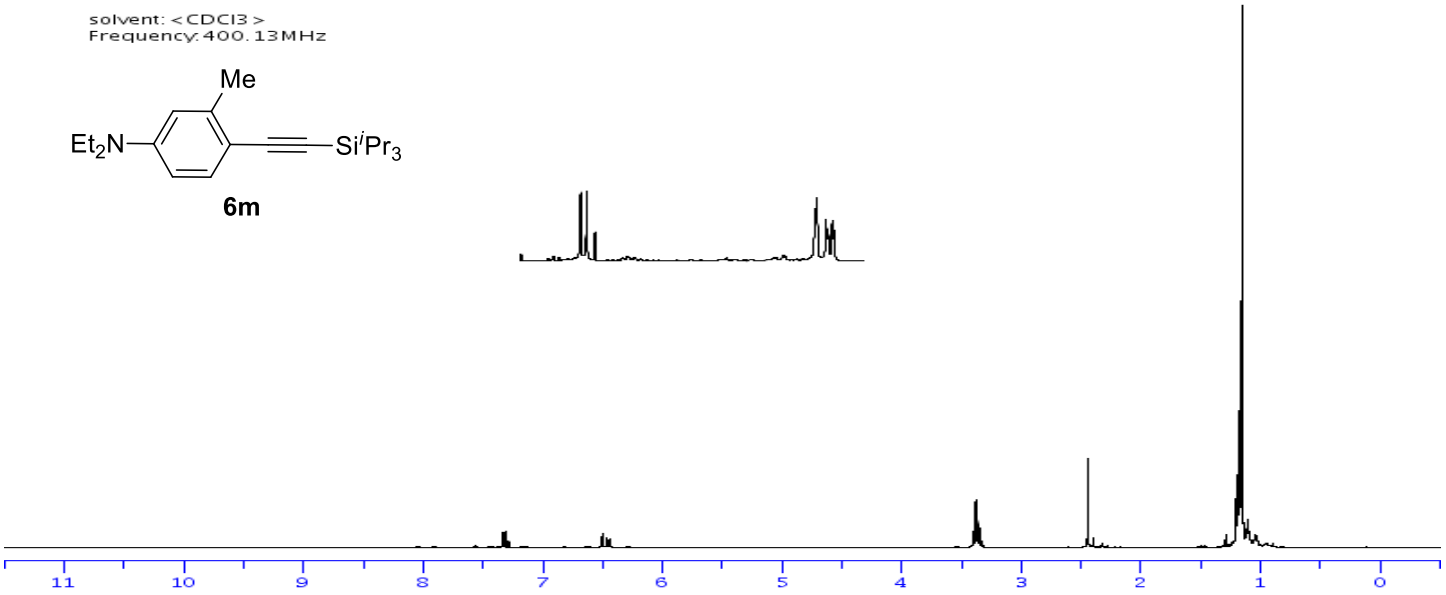
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Si iPr3
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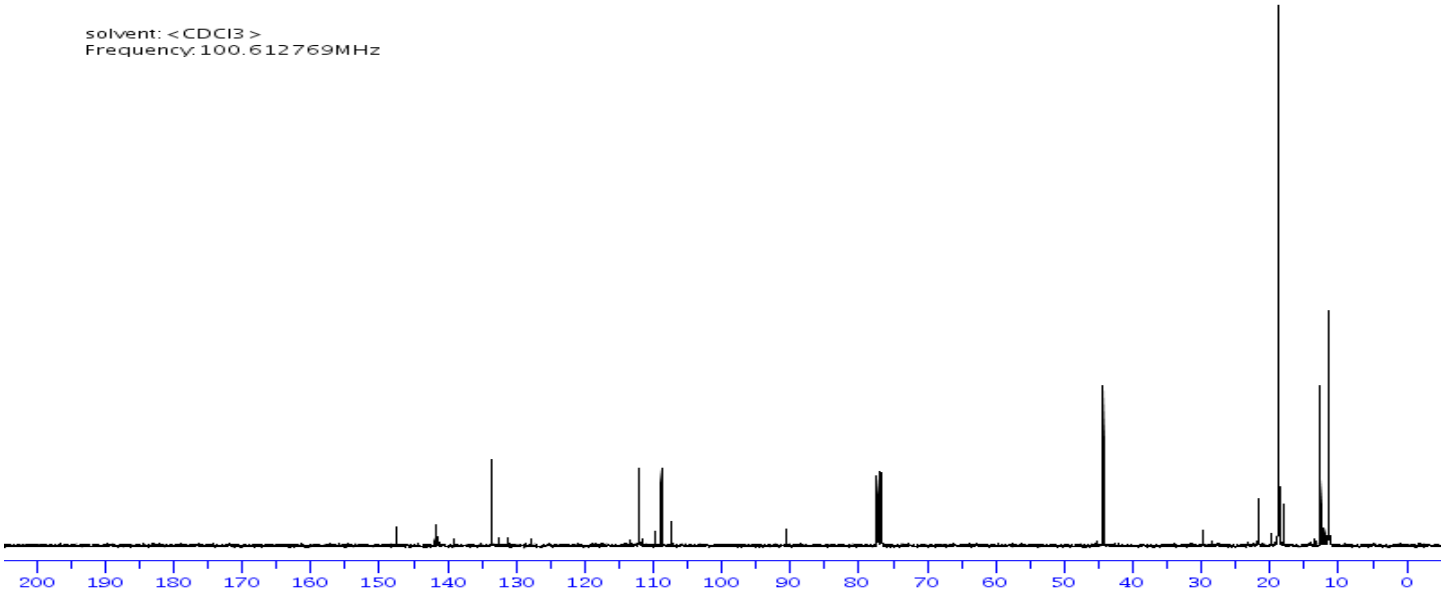
3
2
1
0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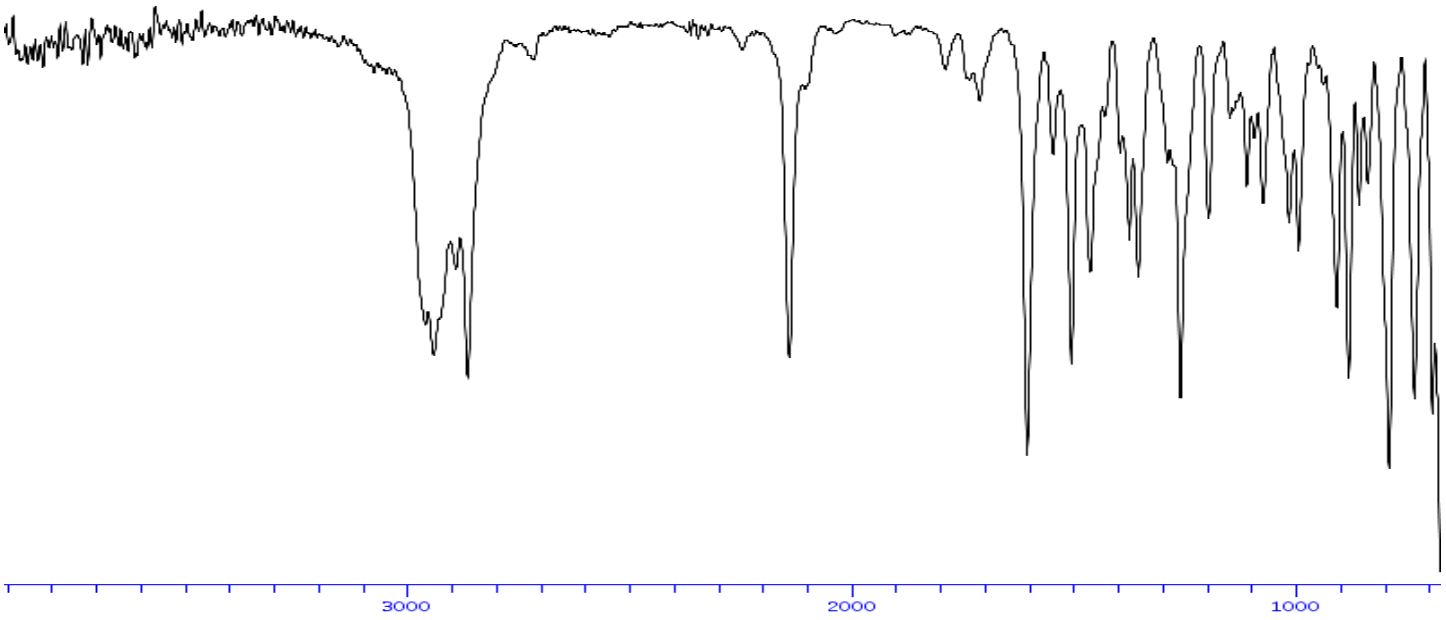
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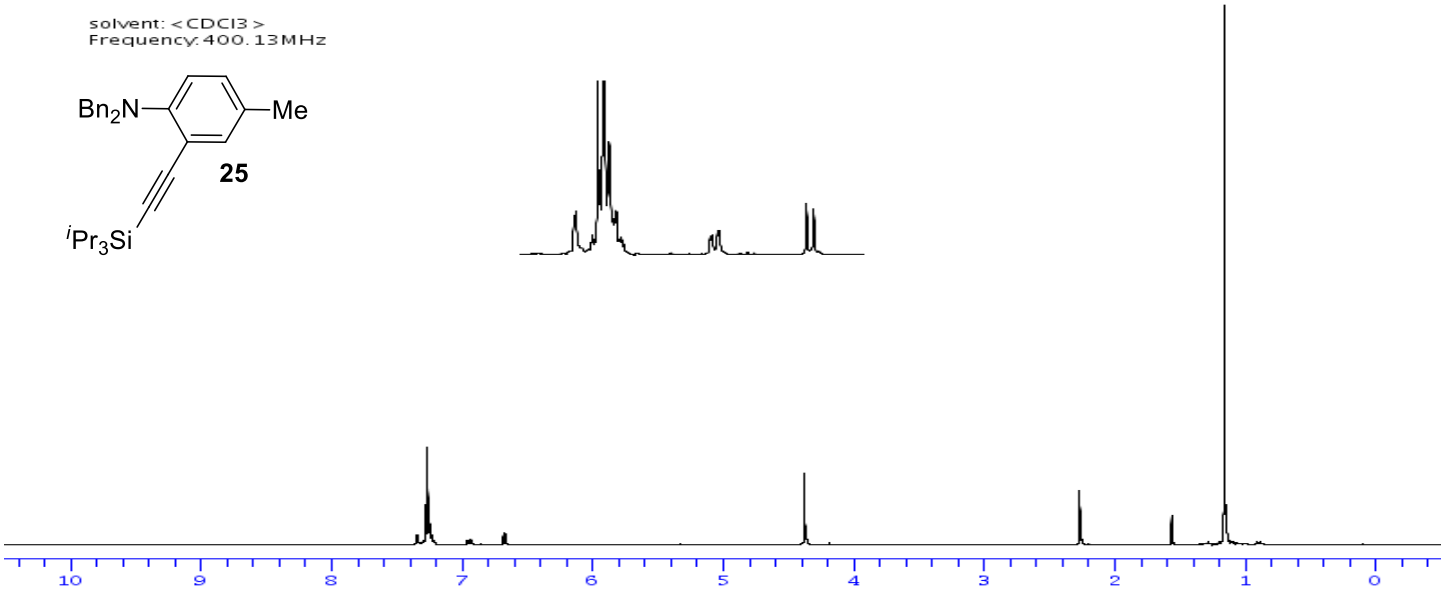
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2
1
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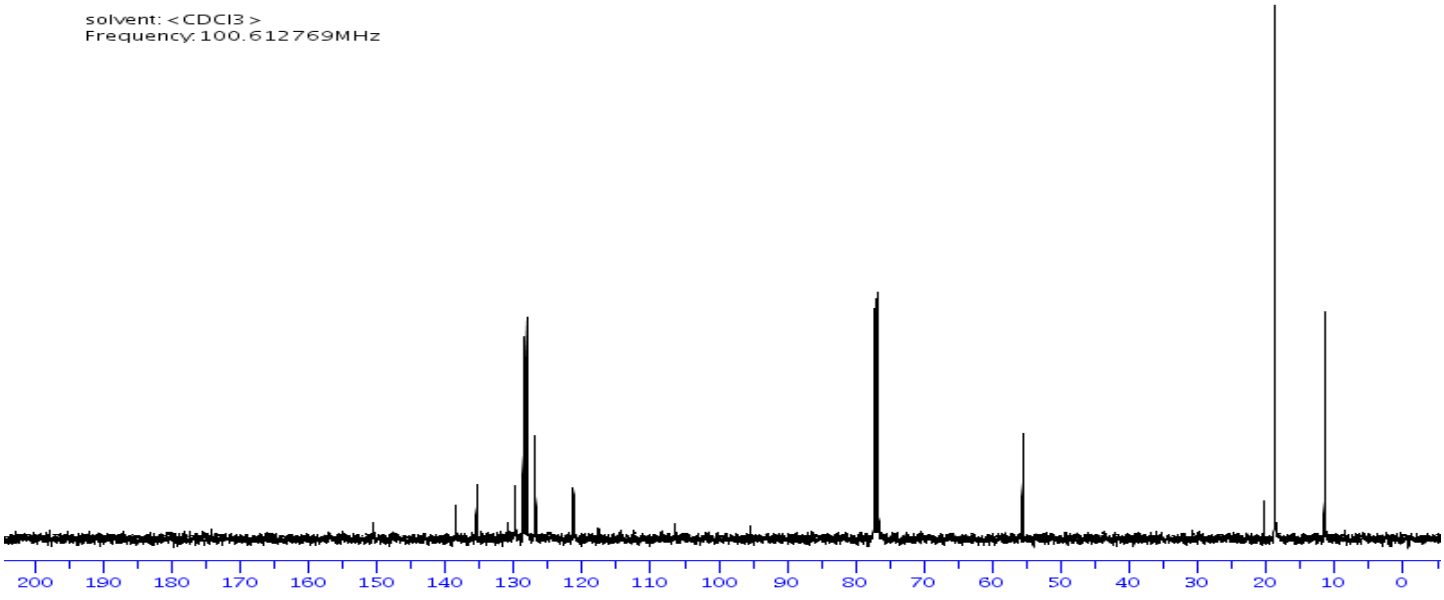
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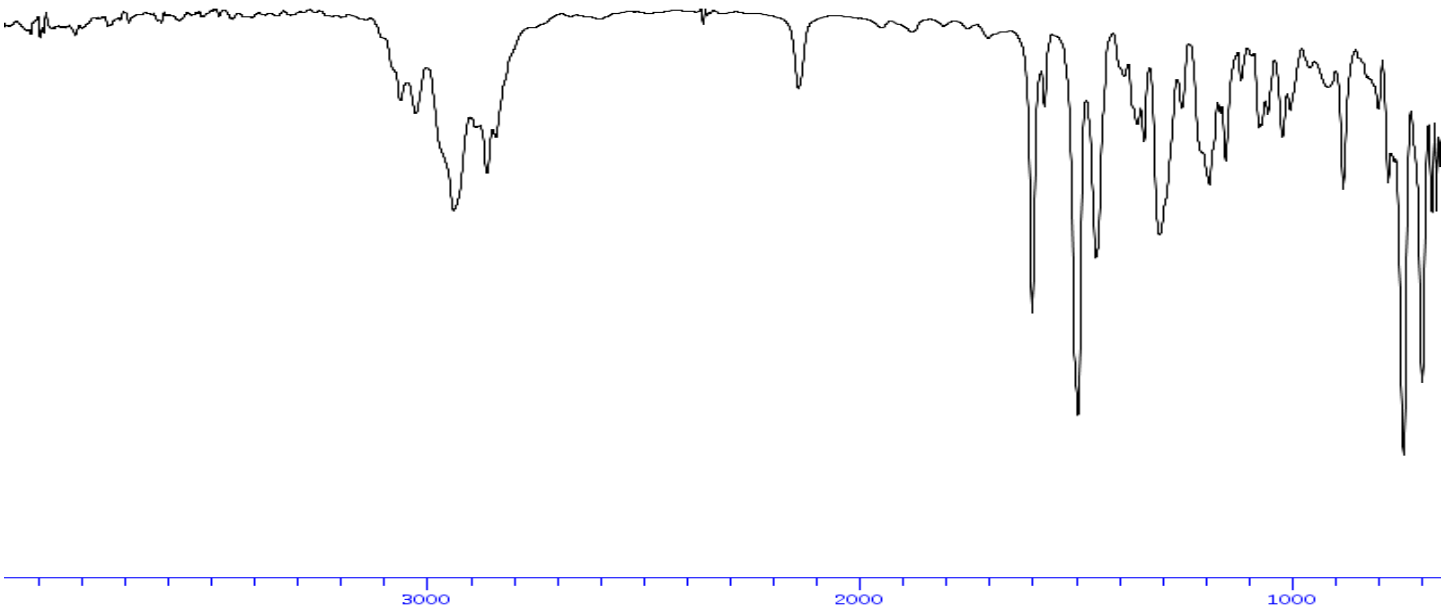
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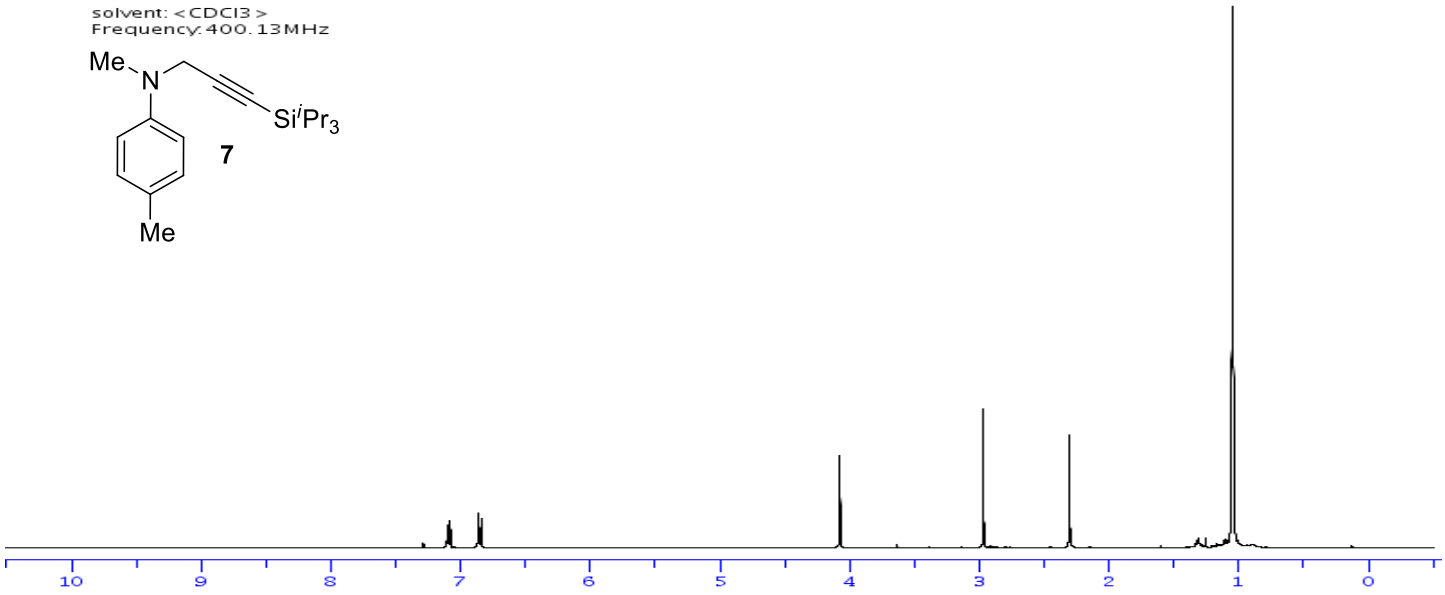
solvent: <CDCl3>
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N
Si^{i}Pr$_3$
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Me
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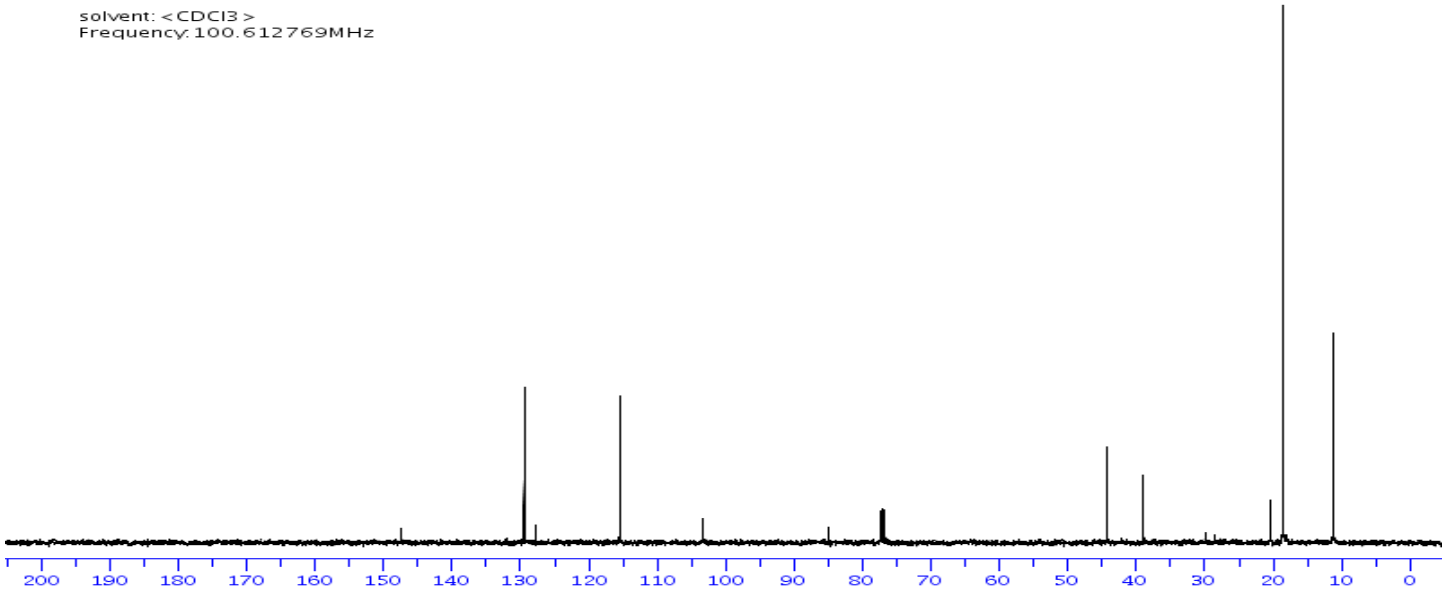
8
7
6
5
4
3
2
1
0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Frequency: 100.612769MHz
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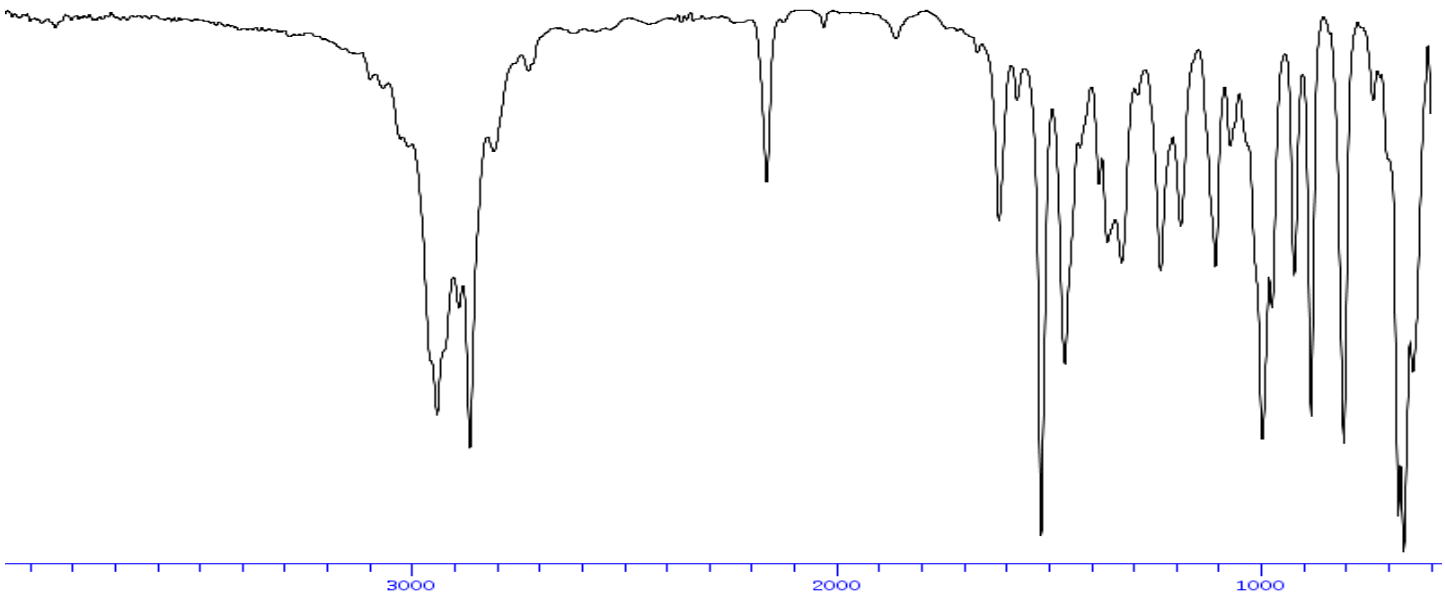
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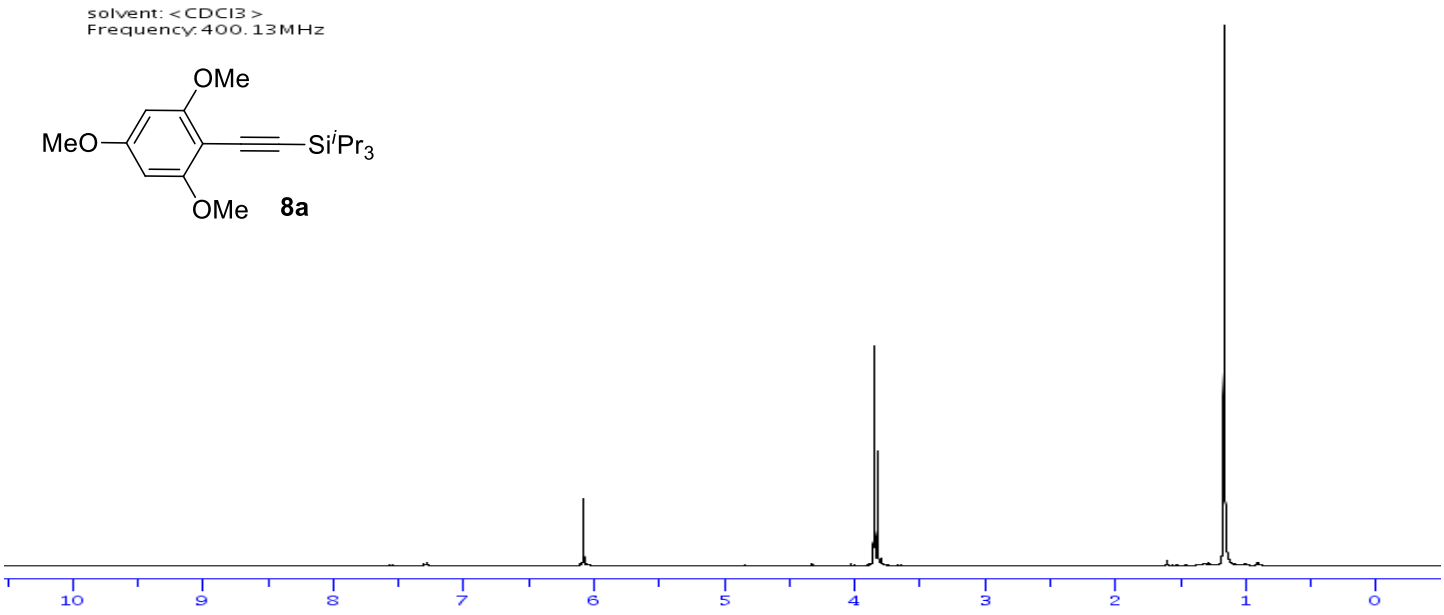
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Frequency: 400.13MHz
OMe
MeO
Si^{i}Pr$_3$
OMe
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9
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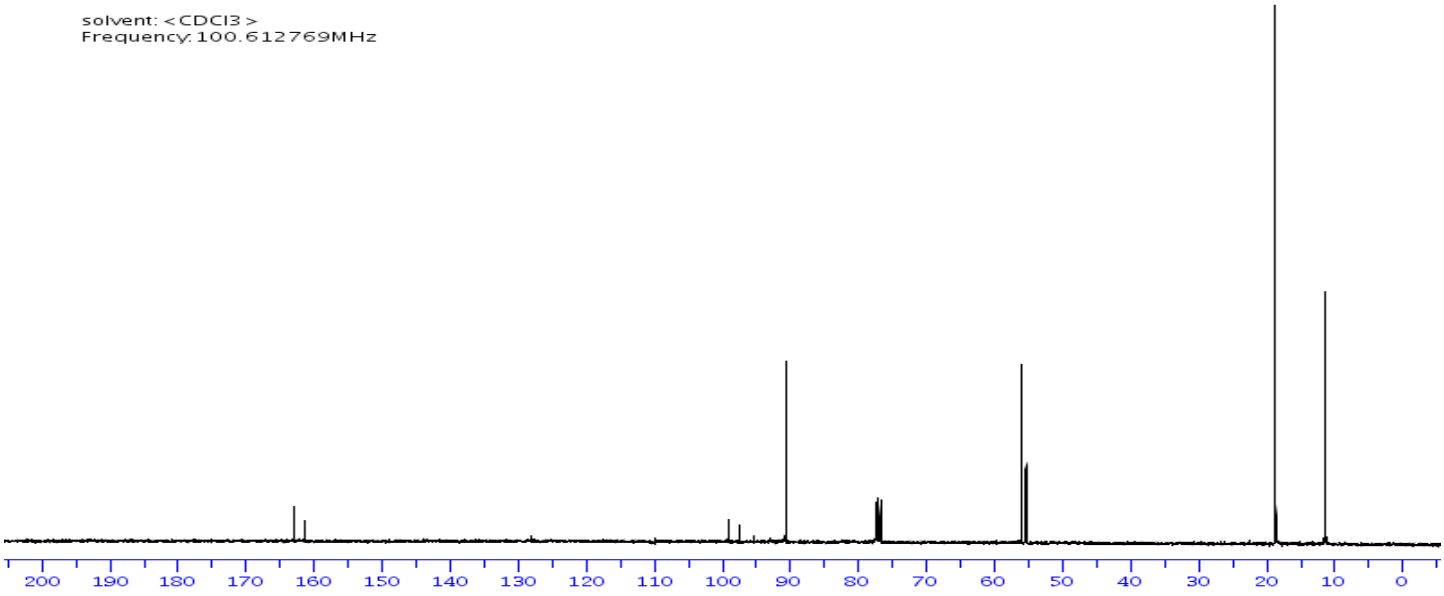
7
6
5
4
3
2
1
0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10
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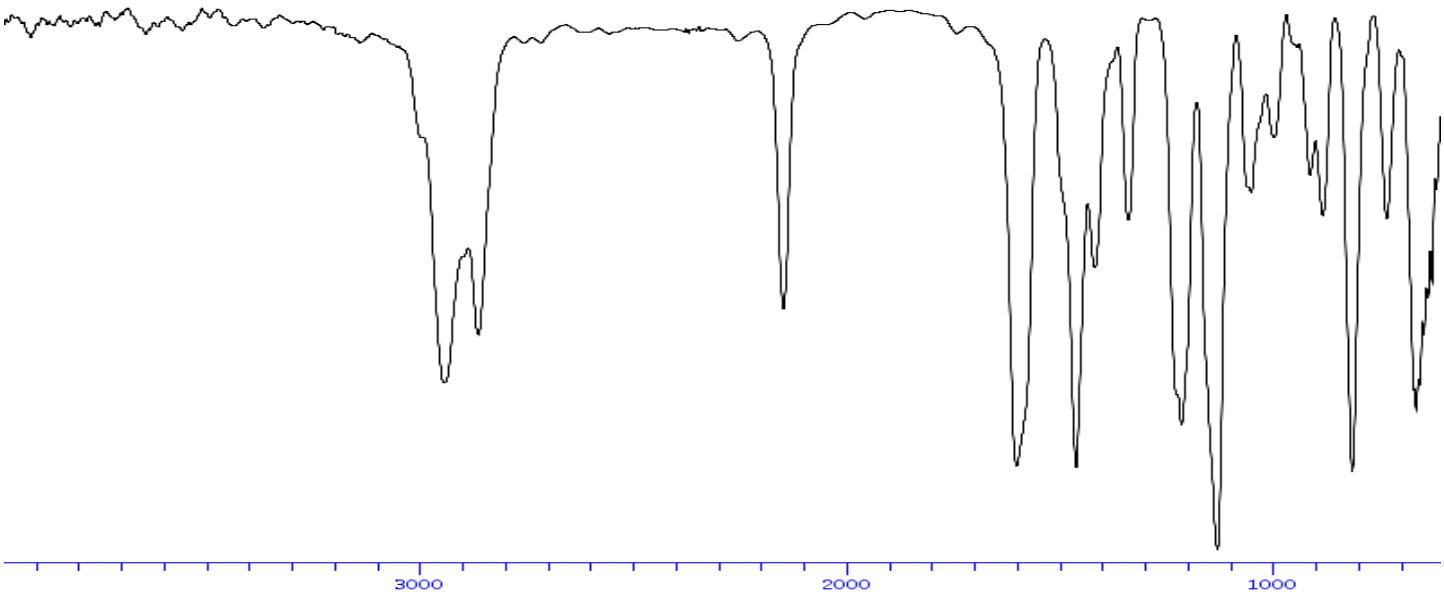
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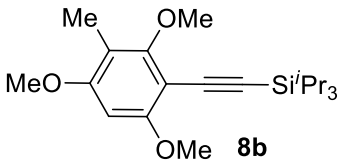
solvent: <CDCl3>
Frequency: 400.13MHz



8b

solvent: <CDCl3>
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