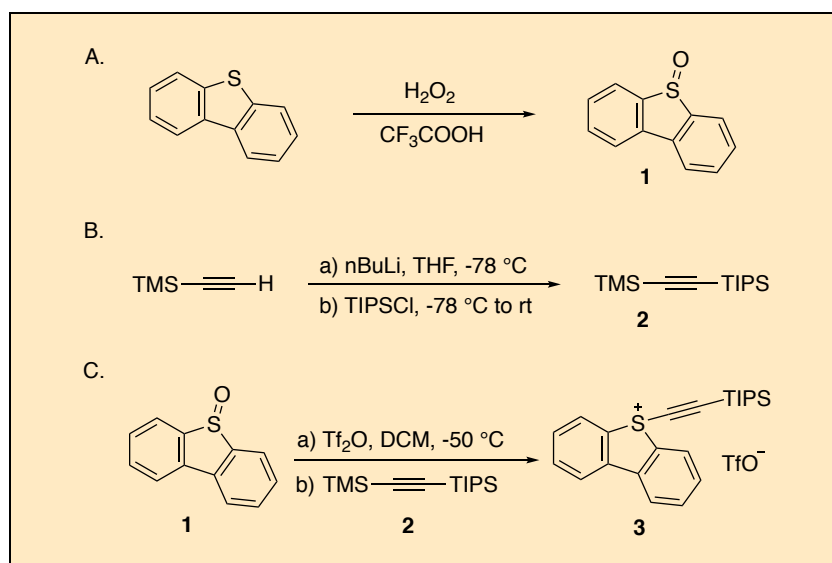


## Preparation of 5-(Triisopropylalkynyl) dibenzo[*b,d*]thiophenium triflate

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Checked by Christopher C. Nawrat, Chuck Orella, Donald Bachert, and Kevin Campos

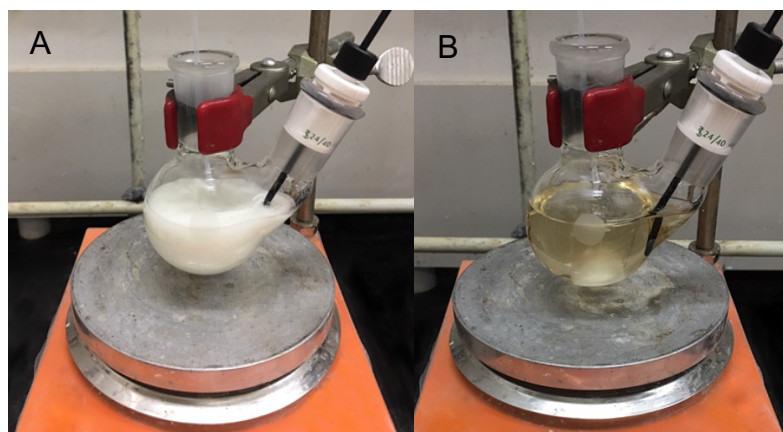


### Procedure (Note 1)

A. *Dibenzo[*b,d*]thiophene-5-oxide (1)*. A 100 mL two-necked flask is equipped with a thermocouple and 1.5 cm Teflon-coated magnetic oval stirrer and the second neck is left open. Dibenzo[*b,d*]thiophene (10.00 g, 54.3 mmol, 1.00 equiv) (Note 2) is added, followed by trifluoroacetic acid (40.0 mL)(Note 3), which forms a white suspension (Figure 1A). A 35% w/w

aqueous solution of  $\text{H}_2\text{O}_2$  (4.67 mL, 54.3 mmol, 1.00 equiv) is added dropwise by syringe pump to the white suspension over 2 h. Caution: the reaction is highly exothermic (Notes 4, 5 and 6). After the addition is completed, a clear solution is formed and the reaction mixture is stirred for an additional 10 min, after which starting material is no longer detectable (Figure 1B) (Note 7).

The reaction mixture is poured into an Erlenmeyer flask containing chilled water (350 mL) and the suspension thus obtained is filtered through a sintered glass frit (10  $\mu\text{M}$  pore size) and washed with ice-cold water (2 x 60 mL). The solid obtained is dried on the frit under passage of air for 2 h and then recrystallized from toluene (400 mL) (Notes 8 and 9) to afford pure **1** as white needles (9.03 g, 81% yield, 97 wt% purity) (Notes 10 and 11).<sup>2</sup>

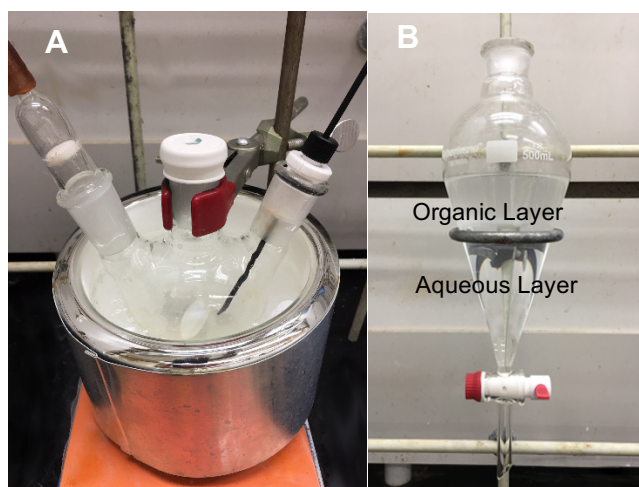


**Figure 1.** A. Initial suspension of dibenzo[*b,d*]thiophene in TFA prior to peroxide addition showing PTFE tubing for  $\text{H}_2\text{O}_2$  addition (center neck; see also Figure 5 in Note 5) and thermocouple (right neck); B. Solution formed after addition of  $\text{H}_2\text{O}_2$  is complete (Photos provided by Checkers)

B. *Triisopropyl(trimethylsilyl)ethynylsilane* (**2**). A 250 mL three-necked, round-bottomed flask equipped with nitrogen inlet (connected to Schlenk line and bubbler), rubber septum and thermocouple, containing a 1.5 cm teflon-coated magnetic stir bar, is placed under  $\text{N}_2$ . The flask is charged with TMS-acetylene (4.58 mL, 33.0 mmol, 1.08 equiv) (Note 12) and dry THF (50 mL) (Note 13). The resulting clear solution is cooled in an isopropanol-dry ice bath (internal temperature  $-70\text{ }^\circ\text{C}$ ) and *n*-BuLi (2.5 M in hexane; 13.2 mL, 33.0 mmol, 1.08 equiv) is added dropwise at a rate that keeps the internal temperature below  $-60\text{ }^\circ\text{C}$  (Note 14). Ten minutes after the addition

is finished, the cooling bath is removed and the solution is allowed to warm to 0 °C. Once this temperature is reached, the reaction flask is again cooled with an isopropanol-dry ice bath to an internal temperature of -60 °C and TIPSCl (6.55 mL, 30.6 mmol, 1.0 equiv) is added over 5 min (Note 15). After the addition has completed, the clear solution is allowed to slowly warm up to room temperature over 16 h (Figure 2A).

After this time, the reaction mixture is poured in a 500 mL separatory funnel, which already contains a saturated aqueous solution of ammonium chloride (150 mL). Addition of MTBE (50 mL) causes the formation of a biphasic mixture and the phases are separated (Figure 2B). The aqueous phase is extracted twice in the same manner (MTBE, 2 x 100 mL) and the combined organic phases are washed with brine (1 x 100 mL). The resulting colorless organic phase is dried over MgSO<sub>4</sub> (10 g) and the solvent evaporated under reduced pressure (40 °C, 375 to 75 mmHg) to afford the product as a colorless oil (7.42 g, 95% yield, 99 wt% purity) (Notes 16 and 17).<sup>3</sup>



**Figure 2. A. Reaction set-up after addition of TIPSCl showing nitrogen line (left neck), rubber septum (center neck) and thermocouple (right neck); B. Workup after dilution with ammonium chloride solution and MTBE (Photos provided by checkers).**

C. 5-(Triisopropylalkynyl) dibenzol[b,d]thiophenium triflate (**3**) A 250 mL three-necked, round-bottomed flask fitted with a nitrogen line, rubber septum and thermocouple is equipped with a 2.5 cm Teflon-coated magnetic stir bar and flame-dried under N<sub>2</sub>. Subsequently, the flask is charged with

dibenzo[*b,d*]thiophene 5-oxide **1** (5.0 g, 25.0 mmol, 1.0 equiv) and dry DCM (150 mL) (Note 18), and the clear solution is cooled to  $-50\text{ }^{\circ}\text{C}$  (internal temperature) using a cryocooler (Figure 3A). Triflic anhydride (4.20 mL, 25.0 mmol, 1.0 equiv) is slowly added over 5 min by syringe pump, causing an intense orange/red suspension to form (Figure 3B) (Note 19). The reaction mixture is stirred for 45 min at this temperature. After this time a solution of alkyne **2** (7.90 mL, 25.0 mmol, 1.0 equiv) in dry DCM (10 mL) is added to the reaction mixture over 5 min by syringe pump. No immediate change in the appearance of the suspension is observed. The reaction mixture is allowed to warm to  $-15\text{ }^{\circ}\text{C}$  over one hour during which time the orange-red suspension slowly becomes a clear light brown solution that is stirred at this temperature under  $\text{N}_2$  for another 12 h (Figure 3C).

The reaction mixture is quenched by addition of methanol (5 mL) and the resulting light brown solution is transferred to a 500 mL single-necked, round bottomed flask. Silica gel (50 mL) is added and the resulting slurry is concentrated to dryness, adsorbing the crude product onto silica gel (Note 20). This silica gel is dry-loaded onto a packed column prepared from a slurry of silica gel in  $\text{CH}_2\text{Cl}_2$  (95 g silica gel, 16.0 x 6.0 cm) and is covered with a layer of sand. The column is eluted first with DCM (500 mL) and later with a DCM:acetone mixture, 4:1 (2 L) (Notes 7, 21 and 22). The product-containing fractions are combined and the solvent partially evaporated ( $40\text{ }^{\circ}\text{C}$ , 600 to 375 mmHg) to leave approximately 15 mL of the colorless-to-pale-yellow solution eluent. Slow addition of  $\text{Et}_2\text{O}$  (100 mL) (Note 23) over 5 min causes the precipitation of **3** as a white microcrystalline powder (Figure 4). The resulting solution is cooled to  $0\text{ }^{\circ}\text{C}$  in an ice bath, and the solid is filtered and washed with  $\text{Et}_2\text{O}$  (50 mL) to afford pure **3** (7.50 g, 58% yield, 98 wt% purity) (Notes 24, 25, and 26).

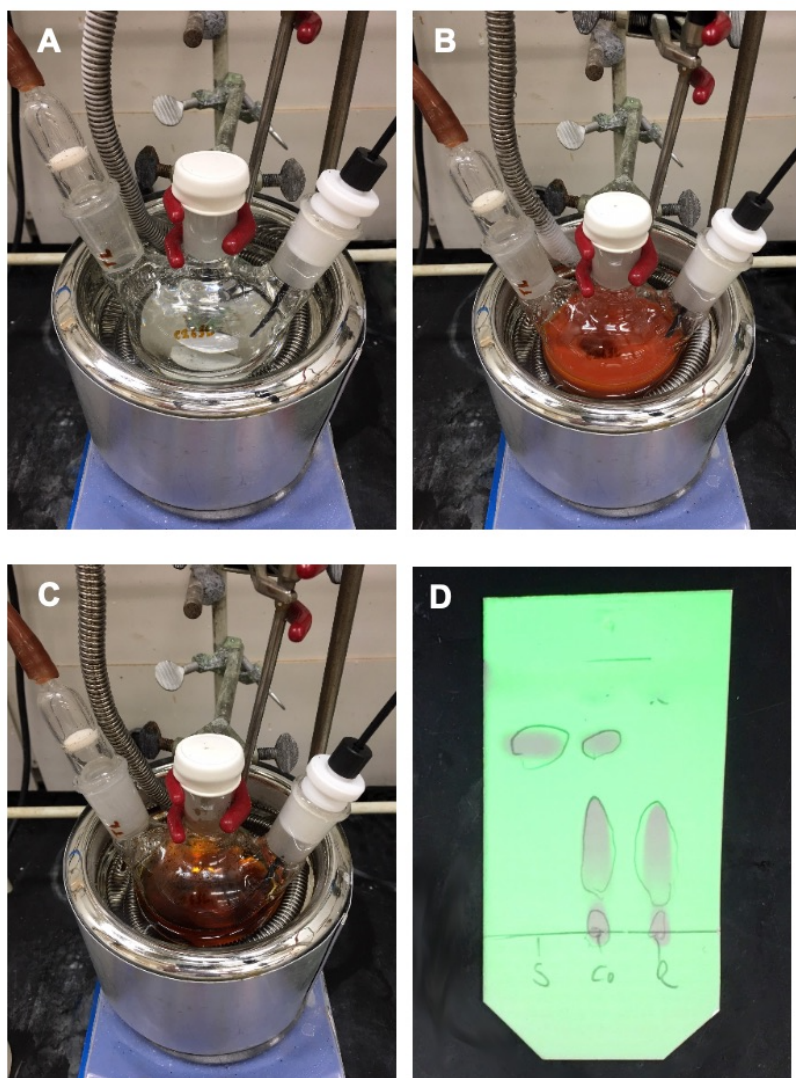


Figure 3. A. Reaction at  $-50\text{ }^{\circ}\text{C}$  before addition of  $\text{Tf}_2\text{O}$ ; B. Orange-red suspension after addition of  $\text{Tf}_2\text{O}$ ; C. Brown, clear reaction solution after warming to  $-15\text{ }^{\circ}\text{C}$ ; D. TLC before workup showing starting material (S, left,  $R_f$  0.72) versus reaction mixture (R, right,  $R_f$  0.34) with central co-spot (Co) using 20% acetone in  $\text{CH}_2\text{Cl}_2$  eluent and visualized under 254 nm UV lamp; (Photos provided by Checkers)

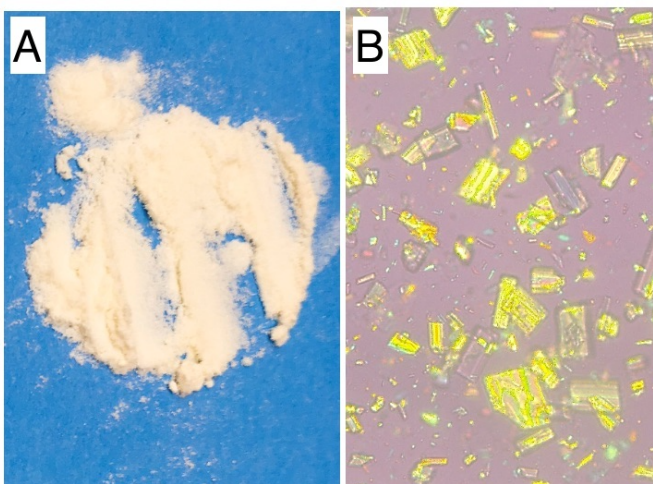


Figure 4. A. Solid 3 (on blue paper for clarity); B. Compound 3 viewed under a light microscope (x20 magnification); (Photos provided by Checkers)

## Notes

1. Prior to performing each reaction, a thorough hazard analysis and risk assessment should be carried out with regard to each chemical substance and experimental operation on the scale planned and in the context of the laboratory where the procedures will be carried out. Guidelines for carrying out risk assessments and for analyzing the hazards associated with chemicals can be found in references such as Chapter 4 of "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at <https://www.nap.edu/catalog/12654/prudent-practices-in-the-laboratory-handling-and-management-of-chemical>. See also "Identifying and Evaluating Hazards in Research Laboratories" (American Chemical Society, 2015) which is available via the associated website "Hazard Assessment in Research Laboratories" at <https://www.acs.org/content/acs/en/about/governance/committees/chemicalsafety/hazard-assessment.html>. In the case of this procedure, the risk assessment should include (but not necessarily be limited to) an evaluation of the potential hazards associated with dibenzothiophene,

hydrogen peroxide solution, trifluoroacetic acid, dichloromethane, methanol, trimethylsilylacetylene, tetrahydrofuran, *n*-butyllithium, tri(isopropyl)silyl chloride, ammonium chloride, methyl(*tert*-butyl)ether, magnesium sulfate, dibenzo[*b,d*]thiophene 5-oxide, triflic anhydride and diethylether.

2. Dibenzo[*b,d*]thiophene (98%) was purchased from J&K Scientific Ltd. or Sigma Aldrich (checkers) and used as received.
3. Trifluoroacetic acid ( $\geq 99.9\%$ ) was purchased from Carl Roth GmbH & Co. KG or Sigma Aldrich (checkers) and used as received.
4. Aqueous  $\text{H}_2\text{O}_2$  solution (35%) was purchased from Acros Organics and used as received.
5. For convenience and to avoid contact between hydrogen peroxide and metals, a 12-inch length of PTFE tubing with a Luer Lock fitting at one end is used with the syringe in place of a needle. Tubing with syringe fittings can be obtained from several scientific suppliers; in this case it was purchased from Hamilton Company (re-sold by Fisher Scientific).

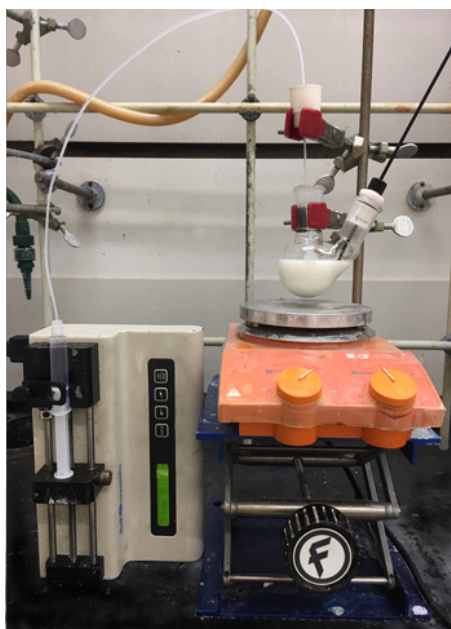


Figure 5. PTFE tubing with a Luer Lock fitting. (Photo below provided by the Checkers)

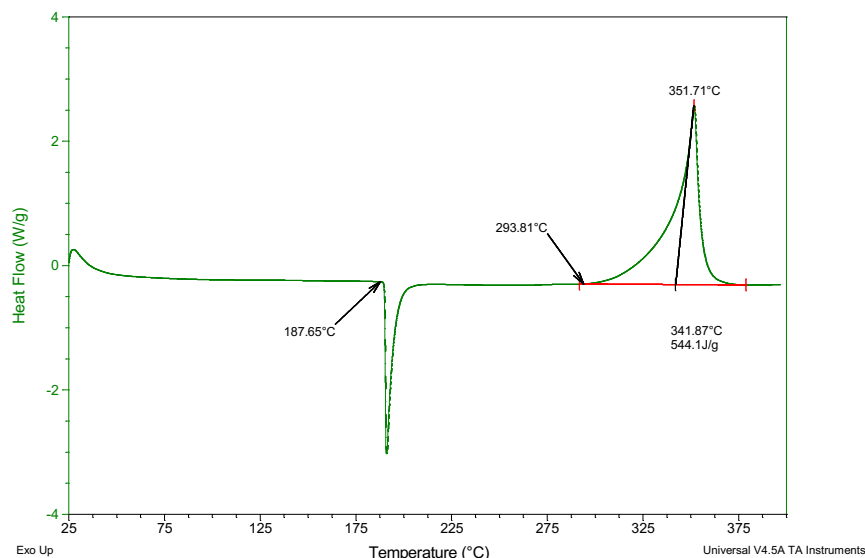
6. This reaction is highly exothermic and the exotherm may have a potentially dangerous delayed onset if the reaction is run at 0 °C. At room temperature, the reaction with hydrogen peroxide is rapid, such that no unexpectedly delayed exotherm is observed. If hydrogen peroxide is added over 2 h (as described), the internal temperature slowly increases from 21 °C at the start of addition to a maximum of 29 °C (around halfway through the addition), before decreasing to 27 °C by the time that addition has completed. Under this protocol, no cooling is necessary (assuming a lab air temperature of 20–25 °C). It was observed that if the reaction temperature is allowed to increase too far (>40 °C) a sulfone by-product starts to form, but this can be almost entirely avoided by keeping the internal temperature below 30 °C and carefully monitoring the conversion to ensure a timely quench (typically less than 0.1 area percent by HPLC at 254 nm of sulfone was observed by the checkers; it was near-invisible by TLC). No modification of the described oxidation conditions was required when the reaction was run at twice the described scale by the checkers and a comparable yield was obtained in a single experiment (18.2 g, 84% yield). However, it is likely that if further increase in reaction scale is desired, additional cooling and/or slower addition of peroxide would eventually be required due to the decreased surface area to volume ratio of larger glassware. If the reaction is ever run below room temperature, care should be taken to choose a temperature where the oxidation still occurs rapidly and without significantly delayed onset. This is easily checked if internal temperature monitoring is used (it is strongly recommended) by addition of a small portion of the hydrogen peroxide and waiting for a temperature increase. Otherwise, a runaway exotherm is possible.

It should be noted that this temperature rise is purely from the oxidation itself. Differential Scanning Calorimetry (DSC) shows that thermal decomposition of **1** is energetic (Figure 6), but this onset of this exotherm does not occur until almost 300 °C, making it unlikely to be a concern here.



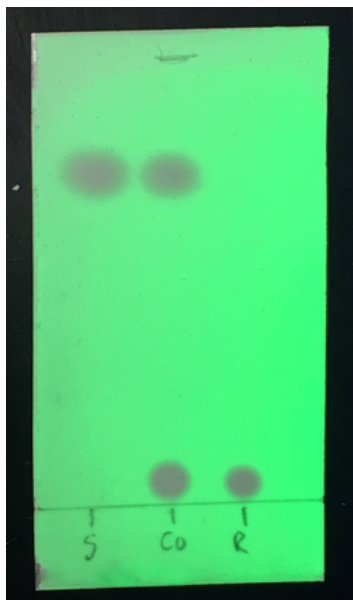
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Run Date: 26-Feb-2019 10:18  
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**Figure 6.** DSC for **1** shows rapid decomposition with exotherm (544 J/g) initiating at 294 °C. Also note endothermic melting at 188 °C.

- A TLC analysis is performed to be sure that the starting material is consumed. The plate is eluted with 1:4 ethyl acetate-hexanes and visualized under UV light at 254 nm. If present, the sulfone has  $R_f$  0.16 in this solvent system (i.e. it appears just above the product). For analysis of reaction progress, aliquots of reaction mixture were diluted with a few hundred microliters each of ethyl acetate-saturated aqueous sodium bicarbonate solution in a small vial and the top organic layer was spotted on the TLC plate. Spotting the TFA solution directly resulted in dramatically decreased resolution and did not give satisfactory results.

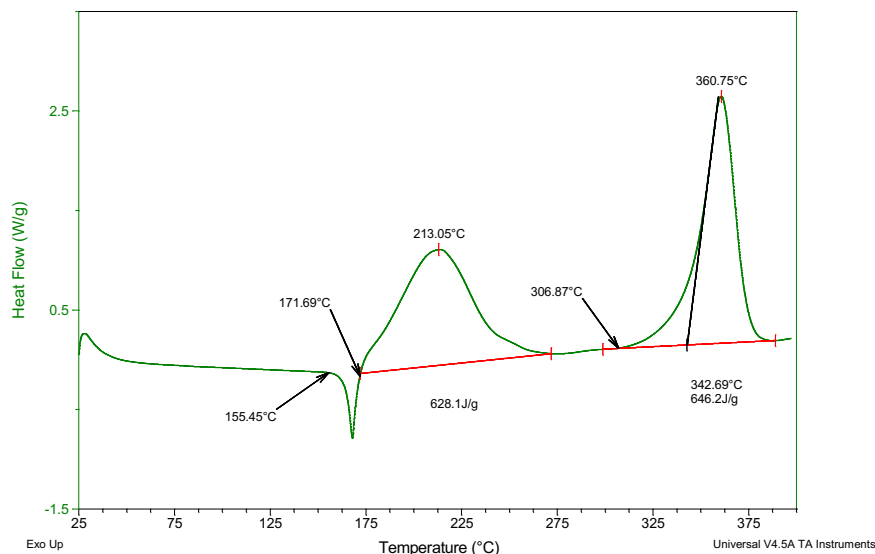


**Figure 7.** TLC of starting material (S, left,  $R_f$  0.75) versus reaction mixture at end of reaction (R, right, product  $R_f$  0.05). A central co-spot is also illustrated. (Photo provided by Checkers)

8. Toluene (99.5% ACS Reagent Grade) is purchased from Sigma-Aldrich. The crude dry solid (typically 10.5 g) is suspended in 400 mL toluene and heated until dissolved (around 90 °C; if it is not dissolved at this point then further toluene should be added). The solution is allowed to cool to room temperature unassisted, forming large white needles. The mixture is aged at room temperature for 2 h and the solids are collected by filtration, washed with ice-cold toluene (10 mL) and dried in vacuo. It should be noted that while unreacted dibenzo[*b,d*]thiophene is efficiently removed by recrystallization, the over-oxidized sulfone product is challenging to remove completely. As described, this procedure produces almost no detectable sulfone (by TLC), but if this by-product is formed then column chromatography is a more effective purification method for its removal – see following Note 9 for details.
9. Alternatively, **1** can be purified by flash column chromatography on silica gel as described by the submitters: Silica 60 was purchased from Macherey Nagel GmbH & Co. (0.04-0.063 mm) and used as received. Crude sulfoxide was directly charged into the pre-wetted silica gel

- column and purified by an eluent of DCM/MeOH 50:1 (1 L)-> 25:1 (0.5 L). ( $R_f = 0.55$ , DCM/MeOH = 25:1). Approximately, 2 L of the eluent was used in total. Small amounts of the sulfone and the starting thiophene could be also isolated.
- $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.50 (t,  $J = 7.5$  Hz, 1H), 7.60 (t,  $J = 7.5$  Hz, 1H), 7.81 (d,  $J = 7.5$  Hz, 1H), 7.99 (d,  $J = 7.5$  Hz, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 122.0, 127.7, 129.7, 132.7, 137.2, 145.3; IR (ATR): 3055, 1592, 1443, 1124, 1065, 1021, 762, 752, 713, 614  $\text{cm}^{-1}$ ; HRMS (ESI) for  $[\text{M}+\text{H}]^+$   $\text{C}_{12}\text{H}_9\text{OS}^+$  requires 201.0374, found: 201.0378. mp: 188 °C. The product was calculated to be 97% pure by QNMR using 1,3,5-trimethoxybenzene as an internal standard (4 scans, delay of 60 seconds).
  - Another reaction performed on identical scale provided 9.35 g (86%) of the product with 97% purity.
  - Trimethylsilylacetylene (98%) was purchased by Sigma Aldrich and used as received.
  - The submitters employed tetrahydrofuran (99.7%) was purchased from VWR Chemicals and dried using an MBraun SPS 7 solvent purification system. The checkers purchased dry tetrahydrofuran from Sigma-Aldrich (anhydrous,  $\geq 99.9\%$ , inhibitor-free).
  - n*-BuLi (2.5 M in hexanes) was purchased from Acros Organics and used as received without titration. Addition as described took approximately 5 minutes.
  - Triisopropylsilyl chloride (97%) was purchased from Fluorochem Ltd or Sigma-Aldrich (98%) (checkers) and was used as received.
  - $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.17 (s, 9H), 1.02–1.13 (m, 21H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.2, 11.2, 18.7, 110.3, 116.3; IR (ATR): 2943, 2895, 2866, 1463, 1383, 1249, 996, 883, 839, 760, 698, 974, 658  $\text{cm}^{-1}$ . The product was calculated to be 99% pure by QNMR using 1,3,5-trimethoxybenzene as internal standard.
  - Another reaction performed on identical scale provided 7.55 g (97%) of the product with 97% purity. In addition, the checkers obtained a similar yield when the reaction was run on ten times the described scale (73.8 g, 98% yield).
  - Dichloromethane was dried in a MBraun SPS 7 system or purchased as anhydrous from Sigma-Aldrich ( $\geq 99.8\%$ ) (checkers).
  - Trifluoromethanesulfonic anhydride (97%) was purchased from Fluorochem Ltd. or Sigma-Aldrich (99%) (checkers) and used as received.
  - Silica gel 230–400 mesh (grade 60) was purchased from Fisher Chemical and used as received.

21. Acetone (99.9%) was purchased from VWR Chemicals or Fisher Chemical (99.5% ACS Reagent Grade) (checkers) and used as received.
22. Large fractions can be collected due to the significant difference in  $R_f$  between the by-products (which are either non-polar or near-baseline) and the desired compound. The checkers collected the initial 500 mL (with pure  $\text{CH}_2\text{Cl}_2$  as eluent) as a single fraction, which can be discarded. Fractions of 100 mL and then 200 mL were then collected and analyzed by TLC.
23. Diethyl ether (99.5%) is purchased from VWR Chemicals and dried in a MBraun SPS 7 system or purchased as anhydrous from Sigma-Aldrich ( $\geq 99.8\%$ ) (checkers) and used as received.
24.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.99 (d,  $J = 7.3$  Hz, 18H), 1.06 – 1.13 (m, 3H), 7.73 (td,  $J = 7.8, 1.3$  Hz, 2H), 7.87 (td,  $J = 7.6, 1.1$  Hz, 2H), 8.14 (dd,  $J = 7.9, 1.3$  Hz, 2H), 8.34 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 11.0, 18.4, 78.9, 117.5, 121.6 (q,  $J_{\text{C-F}} = 320$  Hz), 124.5, 128.3, 131.0, 132.2, 134.9, 139.0;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$ : -78.21 ppm. IR (ATR): 3094, 2944, 2865, 2117 ( $\text{C}\equiv\text{C}$ ), 1461, 1448, 1269, 1248, 1227, 1152, 1029, 820, 767, 757,  $635\text{ cm}^{-1}$ ; HR-MS (ESI<sup>+</sup>) for  $\text{C}_{23}\text{H}_{29}\text{Si}^+$  requires 365.1754; found: 365.1754. The product was calculated to be 98% pure by QNMR using 1,3,5-trimethoxybenzene as internal standard mp: 155 °C (with decomposition; see DSC in Note 26).
25. Another reaction performed on identical scale provided 7.25 g (56%) of the product.
26. Differential Scanning Calorimetry for **3** shows decomposition on melting above 155 °C that leads to a large energy release of >600 J/g. Given this high energy, **3** was additionally subjected to drop weight testing on the BAM Fall Hammer. Three tests at 30 J impact energy did not lead to any observations of impact sensitivity. These results are consistent with the modified Yoshida correlation, and fall into the upper part of the Safe Zone. On the basis of these results, it is recommended that solid **3** should not be exposed to temperatures above 100 °C. Additionally, it is recommended that reactions with planned exposure of multigram quantities of **3** to temperatures above 80 °C should be examined by isothermal DSC.



**Figure 8.** DSC for 3 shows decomposition on melting above 155 °C that leads to a large energy release of >600 J/g

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out

that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

## Discussion

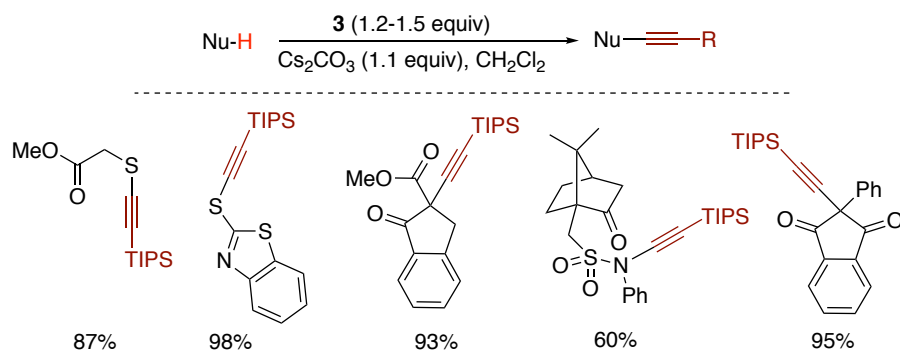
The chemical versatility of carbon-carbon triple bonds makes acetylene derivatives extremely useful precursors for the synthesis of fine chemicals. This justifies the enormous attention that has been paid to develop reactions that either allow their convenient installation in complex organic molecules,<sup>5,7</sup> or further broaden the chemical transformations that alkynes can accomplish.<sup>7</sup>

Specifically, terminal acetylenes depict a natural nucleophilic reactivity after deprotonation, which is often used to introduce alkyne moieties into elaborated organic skeletons. From a synthetic point of view, the availability of a complementary construction approach based on electrophilic acetylene synthons would be very useful; however, that alternative is often hampered by the lack of synthetic equivalents of the  $[R-C\equiv C]^+$  cation. Acetylene halides, being the most obvious candidates for this task, depict limited reactivity in this direction,<sup>8</sup> and only alkynyliodonium salts (EBX reagents) have demonstrated to be general transfer reagents for electrophilic alkynylation.<sup>9</sup> Unfortunately, the use of I(III) derivatives is not always straightforward. Most of these compounds show strong exothermic decompositions on heating and some of them are potentially explosive, which limits their use on industrial scale.<sup>10</sup> Moreover, their high reactivity often makes them unselective if several nucleophilic positions are present in the same substrate.

In an attempt to develop an alternative family of electrophilic acetylene synthons, our attention was attracted by the dibenzothiophenium platform, which was introduced by Umemoto for the preparation of S(IV)-based electrophilic trifluoromethylation reagents.<sup>11</sup> Interestingly, this scaffold had

never been explored in electrophilic alkylation reactions.<sup>12</sup> The detailed synthesis of one of these reagents, 5-(triisopropylalkynyl)dibenzothio-phenium triflate **3** is described in this article.

In the presence of bases such carbonates, compound **3** reacts in dichloromethane or dichloroethane with thiols, sulfonamides and doubly activated methylene groups to afford the desired S-, N-, or C-alkynylated products, respectively, in good to excellent yields. A selection of the compounds that can be obtained by electrophilic alkylation using **3** is shown in Figure 9; more examples can be found in reference 12.



**Figure 9.** Transfer of the alkyne moiety from **3** to different nucleophiles

Interestingly, reagent **3** can be purified by column chromatography and can be kept on the bench in a closed vial for weeks without apparent decomposition, making its handling relatively easy.

## References

1. Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstr 2, 37077 Göttingen, Germany. Email: [malcara@gwdg.de](mailto:malcara@gwdg.de). We thank the DFG for financial support.
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### Appendix

#### Chemical Abstracts Nomenclature (Registry Number)

Dibenzo[b,d]thiophene: Dibenzothiophene (132-65-0)

Trifluoroacetic acid: 2,2,2-Trifluoroacetic acid (76-05-1)

35%w/w aqueous solution of H<sub>2</sub>O<sub>2</sub>: aqueous solution of hydrogen peroxide (7722-84-1)

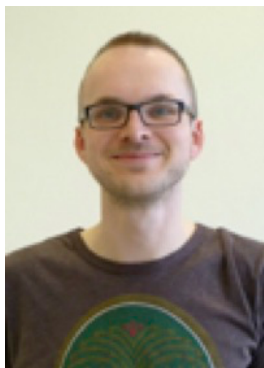
TMS-acetylene: Ethynyltrimethylsilane (1066-54-2)

*n*-BuLi: *n*-Butyllithium (109-72-8)

TIPSCl: Chlorotris(1-methylethyl)-silane (13154-24-0)

Tf<sub>2</sub>O: 1,1,1-Trifluoromethanesulfonic acid-1,1'-anhydride (358-23-6)

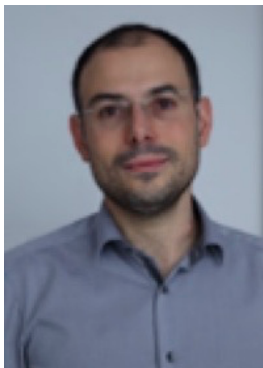




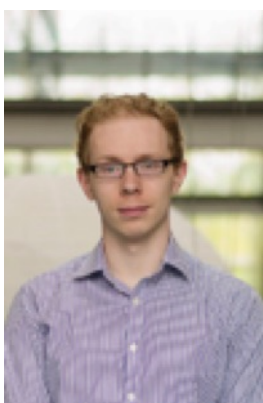
Bernd Waldecker was born in 1988 in Emden, Germany. He received his M. Sc. in 2014 from the University of Göttingen under supervision of Prof. Dr. Dr. h.c.mult. L. F. Tietze. In 2014/2015 he joined the BASF in Ludwigshafen for a research internship. He completed his Ph.D. studies at the University of Göttingen in 2019 working in the group of Professor Manuel Alcarazo on the synthesis of new sulfur-based transfer reagents.



Kevin Kafuta was born in 1990 in Bad Kreuznach, Germany. He received his B. Sc. title in chemistry from the University of Münster in 2014, under the supervision of Dr. Ulrich Hennecke. Afterwards he moved to the University of Göttingen, where he obtained a M. Sc. degree in 2017. Currently he is a doctoral candidate in the group of Prof. Manuel Alcarazo at the same university. His research interest focuses on sulfur and selenium-based transfer reagents.



Manuel Alcarazo was born in Alcalá de Guadaira, Spain in 1978. He obtained his Master (2002) and his Ph.D. (2005) from the University of Sevilla, after which he joined the group of Alois Fürstner as a postdoctoral fellow. He began his independent career at the Max Planck Institute for Coal Research in Mülheim an der Ruhr (Germany) supported by an ERC Starting Grant, focusing his research on the synthesis and applications of cationic phosphines. In 2015 he was promoted to the rank of full professor at the University of Göttingen (Germany), where he works on the development of new synthetic methodologies in organic chemistry either based on transition metal- or main group-promoted processes.



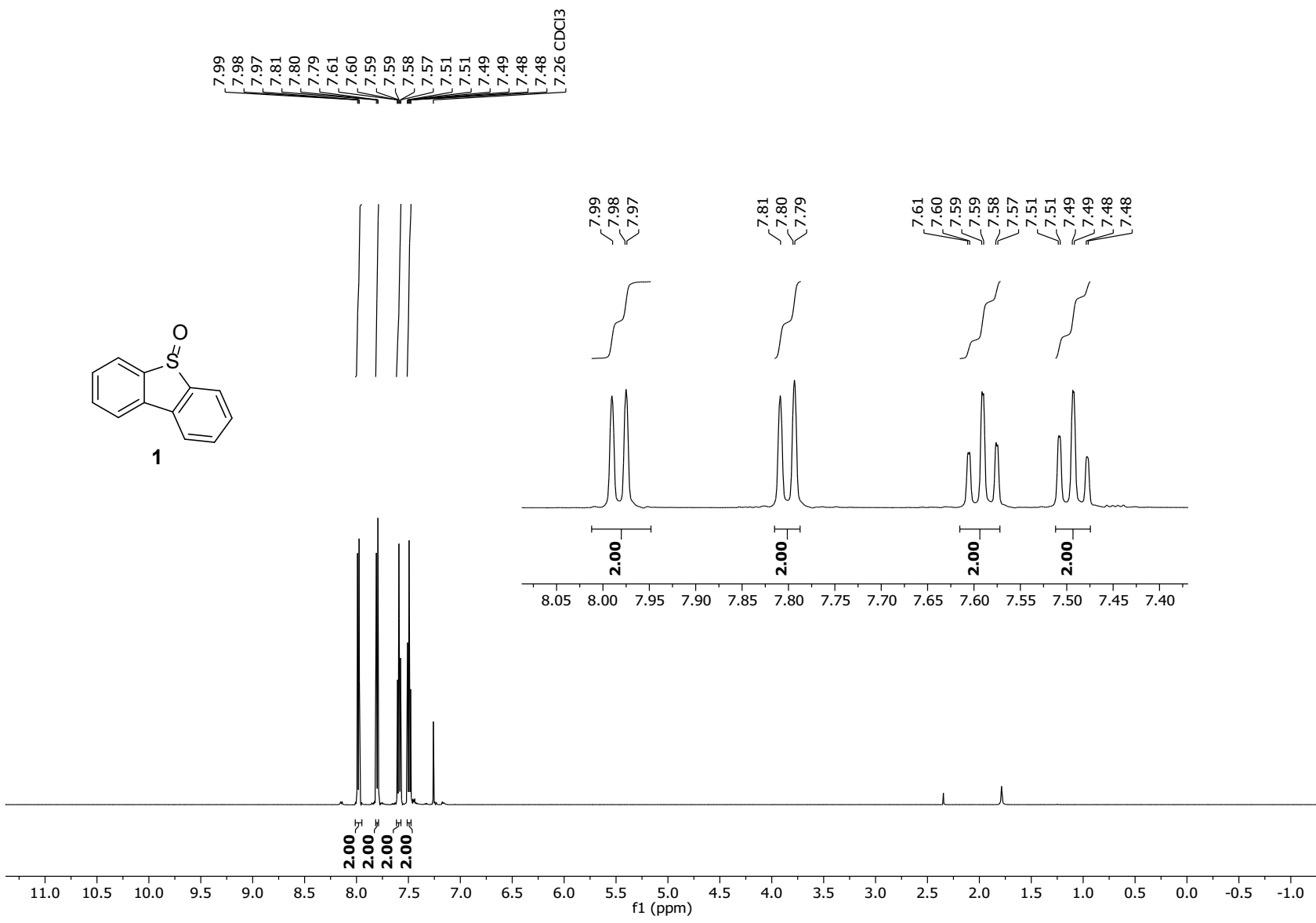
Chris Nawrat was born in Carshalton, near London in 1986. He completed his Ph.D. studies at the University of Nottingham in 2012 working with Professor Chris Moody on a number of total syntheses. In 2013 he undertook postdoctoral studies in the group of Dave MacMillan at Princeton University, where he gained expertise in photo- and organocatalysis. He joined the Process Chemistry Department at Merck and Co., Inc. in 2015 where he enjoys tackling challenging problems in drug development and has developed an interest in biocatalysis.



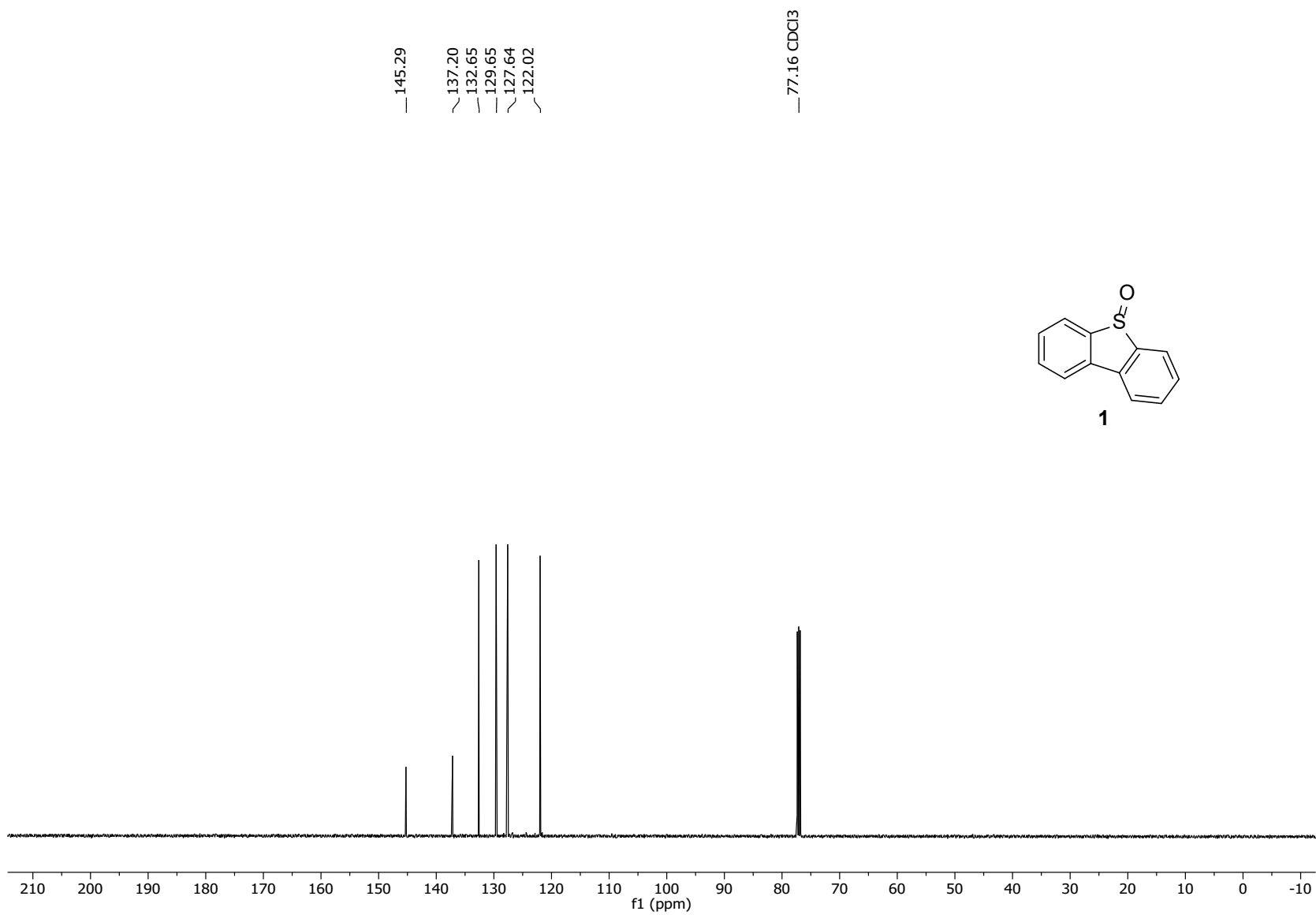
Chuck Orella received a B.S. from UC Santa Barbara, an MS from the University of Delaware, and a Ph.D. from the University of Virginia in Chemical Engineering. Chuck has over 30 years' experience in process development, characterization, scale up, and technology transfer at Merck & Co., Inc., where he led or made significant contributions to the commercial processes for two marketed vaccines and five marketed pharmaceuticals. Chuck has expertise and interests in reactions, separations, and in-situ analytical tools to enable more effective and rapid problem solving. His most recent responsibilities & interests have been in material & reactivity characterization for evaluating the process safety of new pharmaceutical candidates.



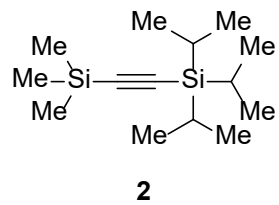
Don Bachert was born in Elizabeth, New Jersey and attended Kean University in Union, New Jersey. He has worked at Merck & Co., Inc for over 25 years in the Environmental Process safety Engineering laboratory (EPSE). Don has expertise in Thermal analysis including Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA), and Advanced Reactive Systems Screening Tool (ARSST) in regards to process safety for both piloting facilities and production scale processes. His other areas of interest include dust explosivity testing and material of construction evaluation.



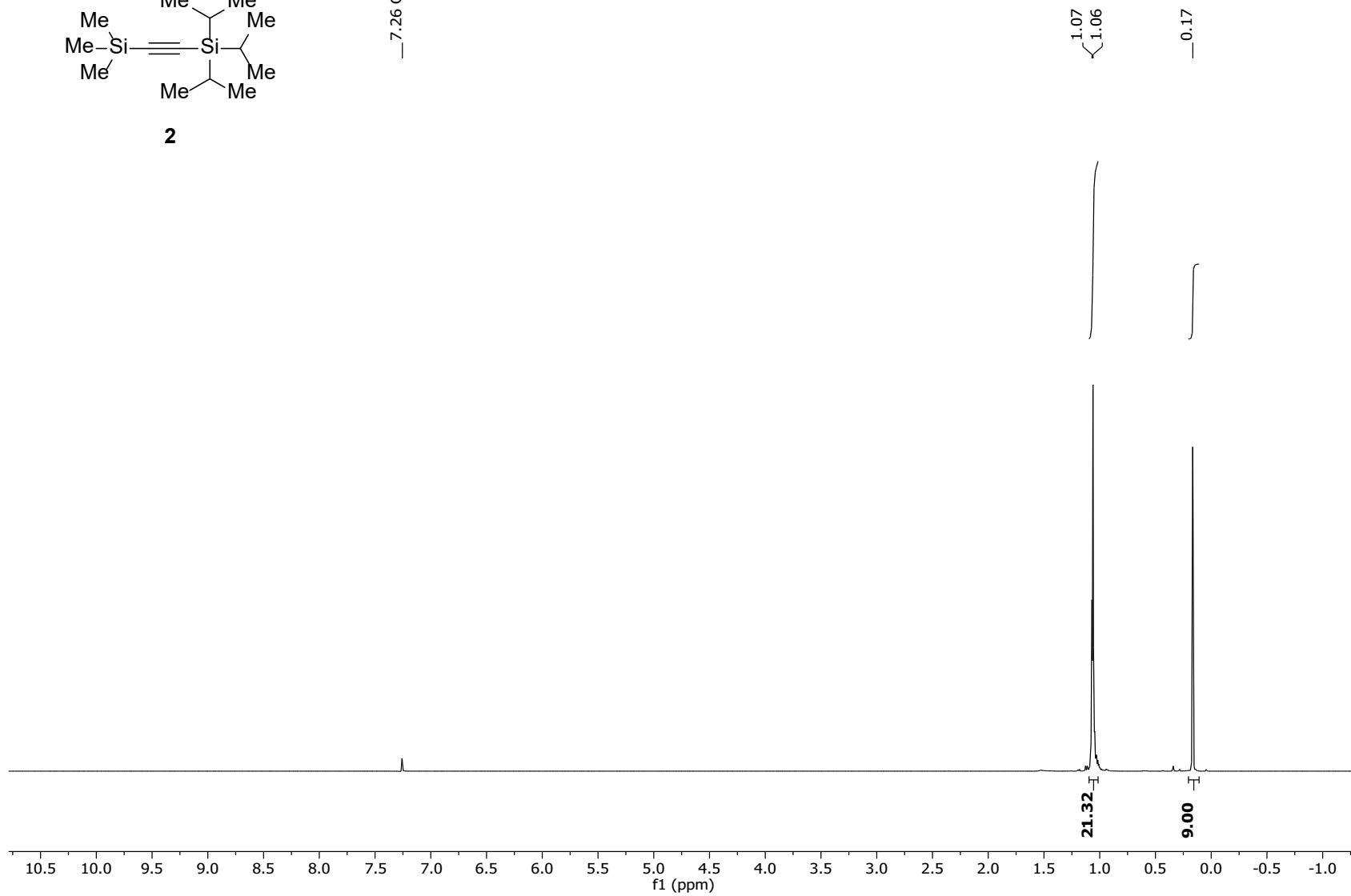
<sup>1</sup>H NMR spectrum of dibenzo[*b,d*]thiophene 5-oxide **1** in CDCl<sub>3</sub> at 500 MHz



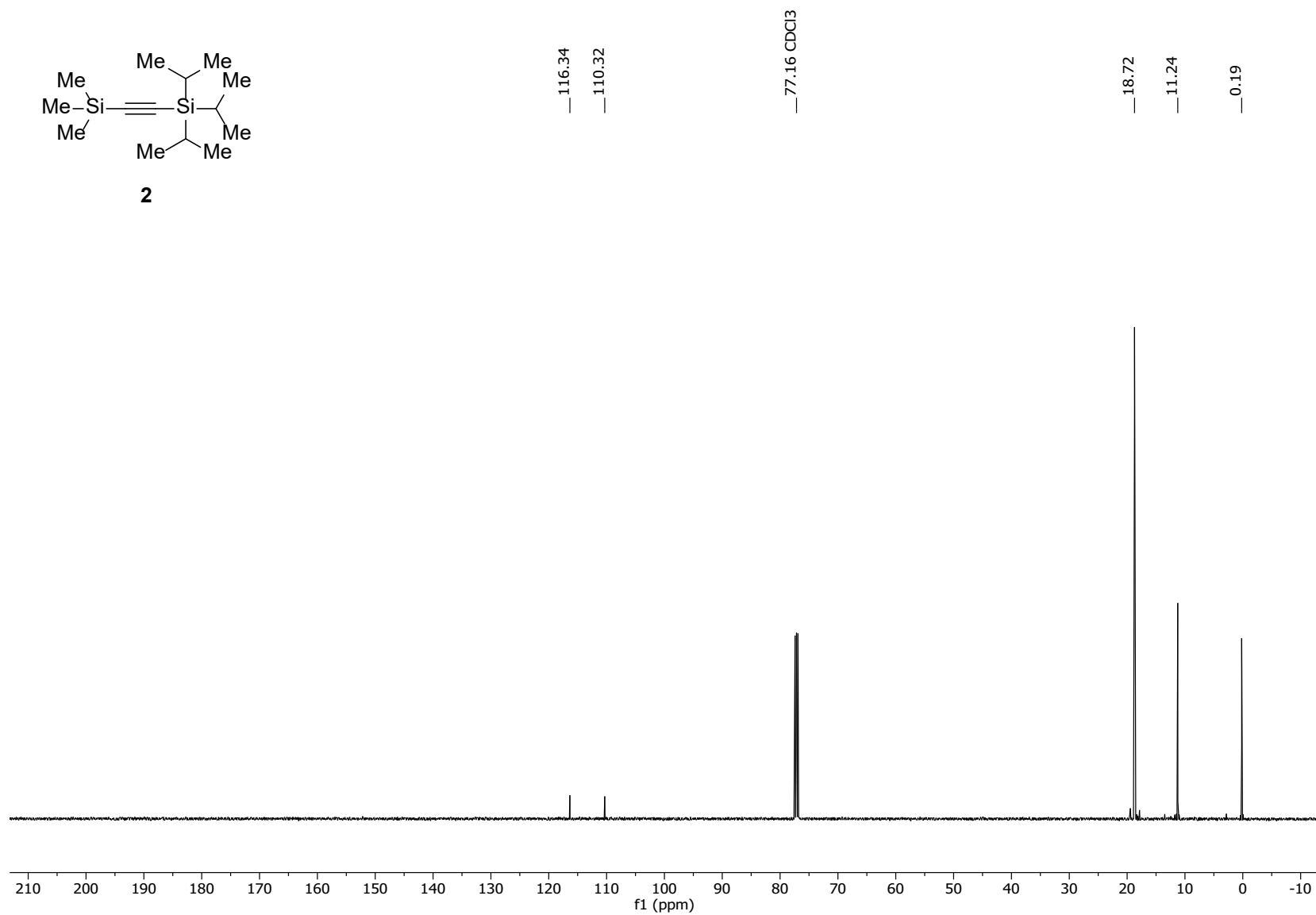
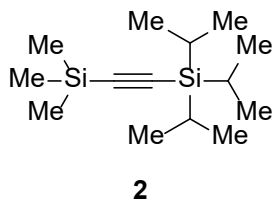
$^{13}\text{C}$  NMR spectrum of dibenzo[*b,d*]thiophene 5-oxide **1** in  $\text{CDCl}_3$  at 126 MHz



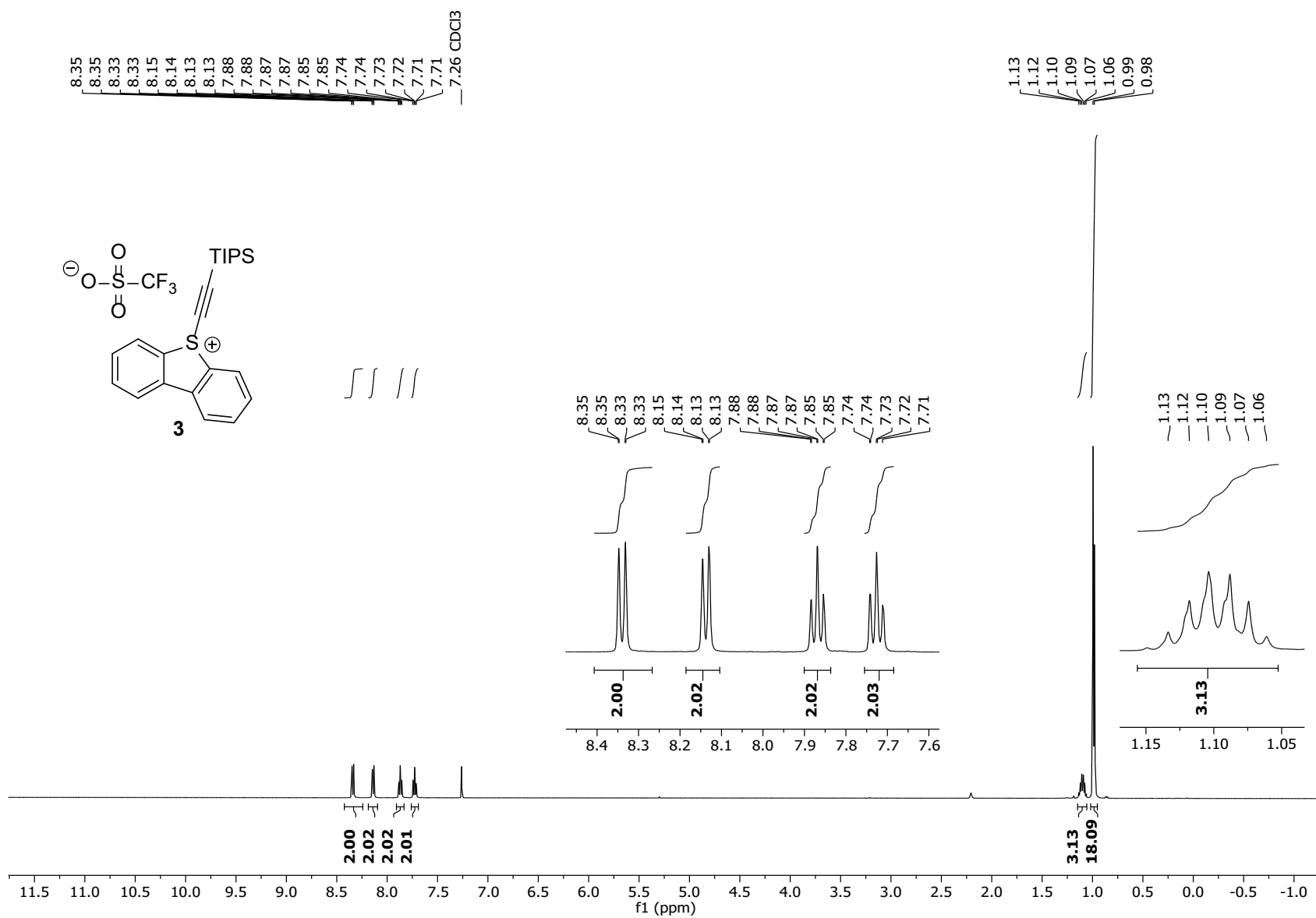
— 7.26 CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of trisopropyl((trimethylsilyl)ethynyl)silane **2** in CDCl<sub>3</sub> at 500 MHz

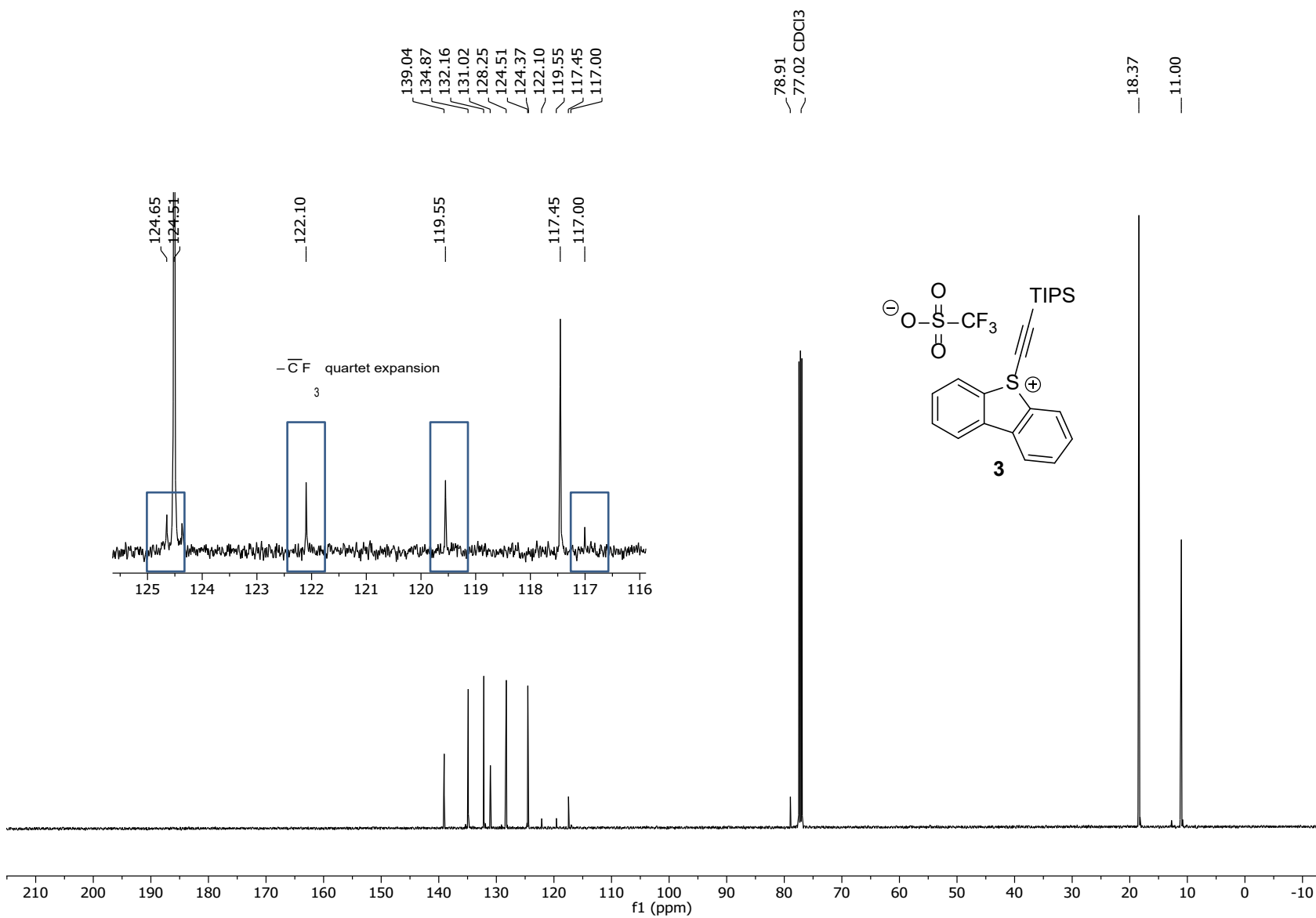


<sup>13</sup>C NMR spectrum of triisopropyl((trimethylsilyl)ethynyl)silane **2** in CDCl<sub>3</sub> at 126 MHz



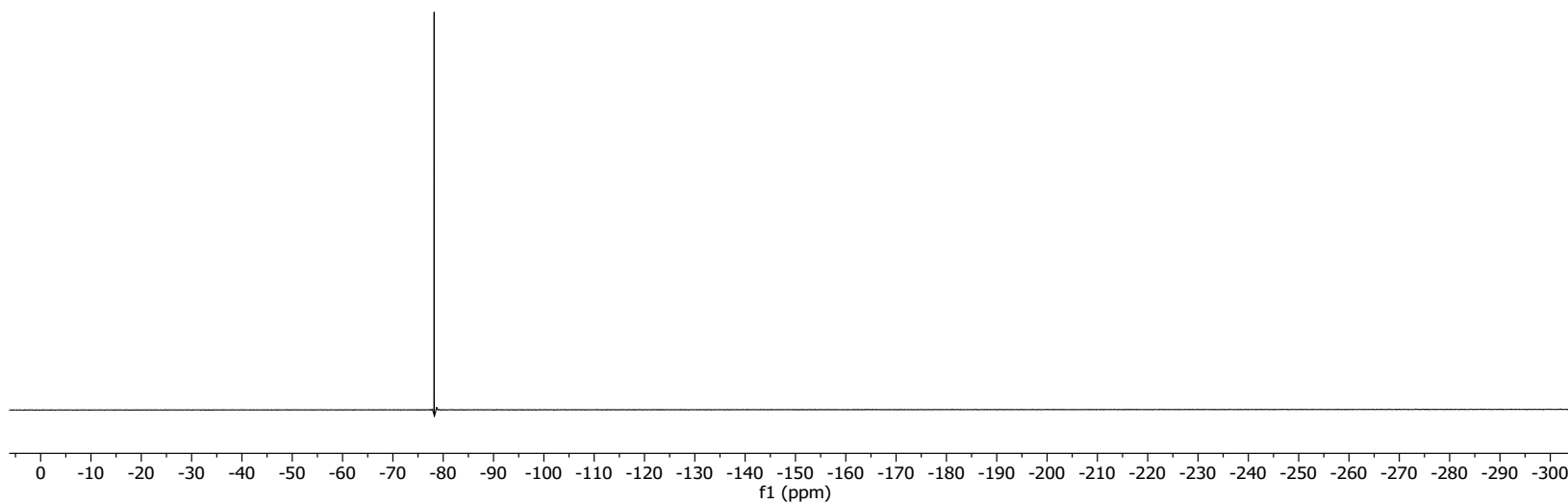
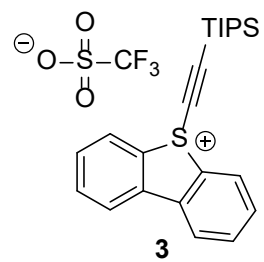
<sup>1</sup>H NMR spectrum of 5-(triisopropylalkynyl)-dibenzo[*b,d*]thiophenium triflate **3** in CDCl<sub>3</sub> at 500 MHz





<sup>13</sup>C NMR spectrum of 5-(triisopropylalkynyl)-dibenzo[*b,d*]thiophenium triflate **3** in CDCl<sub>3</sub> at 126 MHz

— -78.21



$^{19}\text{F}$  NMR spectrum of 5-(triisopropylalkynyl)-dibenzo[*b,d*]thiophenium triflate **3** in  $\text{CDCl}_3$  at 471 MHz