Supporting Information for:

Formation and *in situ* Reactions of Hypervalent Iodonium Alkynyl Triflates to Form Cyanocarbenes

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General Information:

WARNING: Azides and hypervalent iodine species are reported to be explosive when dried and made on larger scales. Use of a blast shield and small scale reactions are advised.

All anhydrous reactions were performed in oven dried glassware under a nitrogen atmosphere. Unless otherwise noted, all solvents and reagents were obtained from commercial sources and used without further purification. All azide solutions were prepared fresh for every reaction and were never stored for extended times. Silylation of alkynes used a modified procedure from literature.[1] The characterization for some compounds can be found in previous publications[2] and corresponding references.[3-8] NMR yields were obtained by using a $CDCl_3$ solution that had 1,2-dichloroethane (25.3 mM) as an internal standard. Chromatographic purification was performed using silica gel (60 Å, 32-63μm). NMR spectra were recorded in $CDCl_3$ using a JEOL ECA 400 spectrometer (400 MHz for 1H, 100 MHz for ^{13}C, and 376 MHz for ^{19}F), and JEOL ECA spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, and 470 MHz for ^{19}F). Coupling constants, *J*, are reported in hertz (Hz) and multiplicities are listed as singlet (s), doublet (d), triplet (t), doublet of doublets (dd), triplet of triplets (tt), quintet (quint), multiplet (m), etc. IR data was obtained with a Perkin Elmer FTIR spectrometer with ATR sampling accessory with frequencies reported in cm^{-1}. High Resolution Mass Spectra were acquired on a ThermoFisher Scientific LTQ Orbitrap XL MS system.

Experimental Procedures and Characterization

General Procedures for Table 2 entries

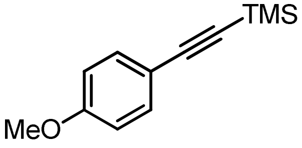
Method 1: Cyanocarbene O-H Insertion with DBU

Iodobenzene diacetate (0.11 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (0.055 mmol) was added to form Kitamura's reagent. The alkyne (0.11 mmol) was then added to form the HIAT. The consumption of the alkyne (5 min – 1 h) was monitored by TLC. When applicable, warming to room temperature was needed (as noted in Table 2). In a separate flask under argon, sodium azide (0.11 mmol) was dissolved at room temperature in methanol (5 mL). The azide solution was then slowly transferred to the HIAT solution. Once the addition was complete, DBU (0.33 mmol) was added, the cryogen was removed and the solution was allowed to warm to room temperature. After concentrating under reduced pressure, the entire crude mixture was dissolved in a 1 mL of $CDCl_3$ that had 1,2-dicholormethane (25.3 mM) as in internal standard. The NMR peak of 1,2-dichloroethane at 3.73 ppm was then integrated with respect to the cyanocarbene product (**9a**, R = Ph) singlet at 5.19 ppm[2] and a yield was calculated based on the molar ratio.

Method 2: Copper Catalyzed Cyanocarbene O-H Insertion

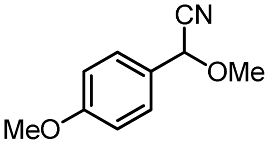
Note: It is important that a ligand is on the copper azide salts so that the complex does not precipitate. Reactions without ligands to solubilize the complex can result in detonation.

Iodobenzene diacetate (0.11 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (0.055 mmol) was added to form Kitamura's reagent. The alkyne (0.11 mmol) was then added to form the HIAT. The consumption of the alkyne (5 min – 1 h) was monitored by TLC. When applicable, warming to room temperature was needed but always cooled to -40 ℃ before azide addition. In a separate flask under argon, sodium azide (0.11 mmol) was dissolved at room temperature in methanol (5 mL). To this flask, $Cu(OAc)_2(dppe)$ (0.0275 mmol) was added and the solution turned a dark brown color. The copper solution was then slowly transferred to the HIAT solution. Once the addition was complete, the cryogen was removed and the solution was allowed to warm to room temperature. After concentrating under reduced pressure, the entire crude mixture was dissolved in a 1 mL of $CDCl_3$ that had 1,2-dicholormethane (25.3 mM) as in internal standard. The NMR peak of 1,2-dichloroethane at 3.73 ppm was then integrated with respect to the cyanocarbene product (**9a**, R = Ph) singlet at 5.19 ppm[2] and a yield was calculated based on the molar ratio.



20

((4-methoxyphenyl)ethynyl)trimethylsilane (20)[1]: Synthesized by following reference 1. Product matched spectral data.



9b

2-methoxy-2-(4-methoxyphenyl)acetonitrile (9b)[3]**:** Compound matched spectral data from reference 3.

Method 1: Cyanocarbene O-H Insertion with DBU

Iodobenzene diacetate (35.4 mg, 0.11 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (9.0 µL, 0.055 mmol) was added to form Kitamura's reagent. The alkyne **20** (22.4 mg, 0.11 mmol) was then added to form the HIAT. The solution was allowed to warm to room temperature, and the consumption of the alkyne was monitored by TLC. When the alkyne was consumed (20 min), the solution was then cooled back to 0 ℃. In a separate flask under argon, sodium azide (7.0 mg, 0.11 mmol) was dissolved at room temperature in methanol (5 mL). The azide solution was then slowly transferred to the HIAT solution. Once the addition was complete, DBU (49 µL, 0.33 mmol) was added, the cryogen was removed and the solution was allowed to warm to room temperature. The crude mixture was then evaporated and purified by column chromatography (R_f = 0.24 (9:1 Hexane/EtOAc), UV active). Yield: 2.7 mg, 12%

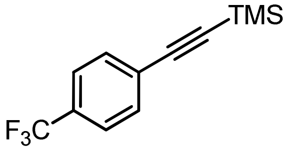
Method 2: Copper Catalyzed Cyanocarbene O-H Insertion

Note: It is important that a ligand is on the copper azide salts so that the complex does not precipitate. Reactions without ligands to solubilize the complex can result in detonation.

Iodobenzene diacetate (35.4 mg 0.11 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (9.0 µL, 0.055 mmol) was added to form Kitamura's reagent. The alkyne **20** (22.4 mg, 0.11 mmol) was then added to form the HIAT. The solution was allowed to warm to room temperature, and the consumption of the alkyne was monitored by TLC. When the alkyne was consumed, the solution was then cooled to -40 ℃. In a separate flask under argon, sodium azide (7.0 mg, 0.11 mmol) was dissolved at room temperature in methanol (5 mL). To this flask, $Cu(OAc)_2(dppe)$ (16 mg, 0.0275 mmol) was added and the solution turned a dark brown color. The copper solution was then slowly transferred to the HIAT solution. Once the addition was complete, the cryogen was removed and the solution was allowed to warm to room temperature. The crude mixture was then evaporated and purified by column chromatography (R_f = 0.24 (9:1 Hexane/EtOAc), UV active). Yield: 11.2 mg, 50%

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.51 (s, 3 H), 3.84 (s, 3 H), 5.15 (s, 1 H), 6.95 (d, *J*=8.2 Hz, 2 H), 7.42 (d, *J*=8.7 Hz, 2 H)

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 57.1, 72.0, 114.4 (2 C), 117.3, 125.4, 129.0 (2 C), 160.8



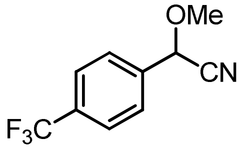
21

trimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane (21)[4]:

To a solution of 1-ethynyl-4-(trifluoromethyl)benzene (0.500 g, 2.93 mmol) in THF (10 mL) was added slowly nBuLi in hexanes (2.5 M, 1.28 mL, 3.22 mmol) at -78 ℃. After stirring for 5 mins at -78 ℃, to the reaction mixture was added chlorotrimethylsilane (0.41 mL, 3.22 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. A solution of aqueous ammonium chloride was then added to quench the reaction. The organic layer was extracted with ether, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Purification by silica-gel chromatography (R_f = 0.83 (9:1 Hexane/EtOAc), UV active) gave **21** (0.304 g, 42% yield). The product matched spectral data from reference 4.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (s, 4 H), 0.27 (s, 9 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.1, 130.2, 130.0, 126.9, 125.14, 125.11, 122.8, 103.4, 97.1, -0.2.



9c

2-methoxy-2-(4-(trifluoromethyl)phenyl)acetonitrile (9c)[7]:

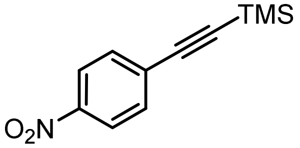
Method 1: Cyanocarbene O-H Insertion with DBU

Iodobenzene diacetate (40.0 mg, 0.124 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (10.5 µL, 0.062 mmol) was added to form Kitamura's reagent. The alkyne **21** (24.9 mg, 0.103 mmol) was then added to form the HIAT. The solution was heated to reflux, and the consumption of the alkyne was monitored by TLC. When the alkyne was consumed (1.5 hr), the solution was then cooled back to 0 ℃. In a separate flask under argon, sodium azide (8.0 mg, 0.124 mmol) was dissolved at room temperature in methanol (5 mL). The azide solution was then slowly transferred to the HIAT solution. Once the addition was complete, DBU (49 µL, 0.33 mmol) was added, the cryogen was removed and the solution was allowed to warm to room temperature. The crude mixture was then evaporated and purified by column chromatography (R_f = 0.5 (9:1 Hexane/EtOAc), UV active). Yield: 0.92 mg, 4%. The product matched spectral data from reference 7.

Method 2: Copper Catalyzed Cyanocarbene O-H Insertion

Note: It is important that a ligand is on the copper azide salts so that the complex does not precipitate. Reactions without ligands to solubilize the complex can result in detonation.

Iodobenzene diacetate (40.0 mg 0.124 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (10.5 µL, 0.062 mmol) was added to form Kitamura's reagent. The alkyne **21** (24.9 mg, 0.11 mmol) was then added to form the HIAT. The solution was heated to reflux, and the consumption of the alkyne was monitored by TLC. When the alkyne was consumed (1.5 hr), the solution was then cooled to -40 ℃. In a separate flask under argon, sodium azide (8.0 mg, 0.124 mmol) was dissolved at room temperature in methanol (5 mL). To this flask, $Cu(OAc)_2$(dppe) (15 mg, 0.026 mmol) was added and the solution turned a dark brown color. The copper solution was then slowly transferred to the HIAT solution. Once the addition was complete, the cryogen was removed and the solution was allowed to warm to room temperature. The crude mixture was then evaporated and purified by column chromatography (R_f = 0.5 (9:1 Hexane/EtOAc), UV active). Yield: 4.5 mg, 19%. The product matched spectral data from reference 7.

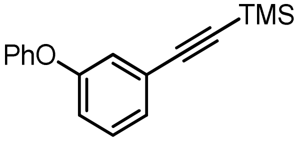


22

trimethyl((4-nitrophenyl)ethynyl)silane (22)[5]:

To a solution of 1-ethynyl-4-nitrobenzene (0.415 g, 2.82 mmol) in THF (10 mL) was added slowly nBuLi in hexanes (2.5 M, 1.13 mL, 2.82 mmol) at -78 ℃. After stirring for 5 mins at -78 ℃, to the reaction mixture was added chlorotrimethylsilane (0.36 mL, 2.82 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. A solution of aqueous ammonium chloride was then added to quench the reaction. The organic layer was extracted with ether, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Purification by silica-gel chromatography (R_f = 0.57 (9:1 Hexane/EtOAc), UV active) gave **22** (0.618 g, 64% yield). The product matched spectral data from reference 5.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.82 Hz, 2H), 7.57 -7.62 (m, 2H), 0.27 (s, 9H).



23

trimethyl((3-phenoxyphenyl)ethynyl)silane (23):

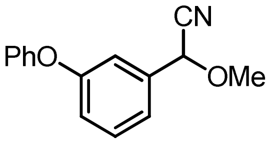
To a solution of 1-ethynyl-3-phenoxybenzene (0.46 g, 2.35 mmol) in THF (10 mL) was added slowly nBuLi in hexanes (2.5 M, 1.04 mL, 2.6 mmol) at -78 ℃. After stirring for 5 mins at -78 ℃, to the reaction mixture was added chlorotrimethylsilane (0.33 mL, 2.6 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. A solution of aqueous ammonium chloride was then added to quench the reaction.

The organic layer was extracted with ether, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Purification by silica-gel chromatography (R_f = 0.66 (9:1 Hexane/EtOAc), UV active) gave **23** (0.575 g, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.22 (m, 9 H), 6.98 (m, 3 H), 7.09 (m, 2 H), 7.21 (m, 2 H), 7.34 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 C), 94.8, 104.4, 119.2 (2 C), 119.5, 122.0, 123.6, 124.6, 127.0, 129.7, 129.9 (2 C), 156.9, 157.1.

HRMS (APCI): $C_{17}H_{18}OSi$ $[M]^+$, $C_{34}H_{36}O_2Si_2$ $[2M]^+$, calculated: 266.1127, 532.2254, found: 266.1118, 532.2249.



9e

2-methoxy-2-(3-phenoxyphenyl)acetonitrile (9e):

Method 1: Cyanocarbene O-H Insertion with DBU

Iodobenzene diacetate (35.4 mg, 0.11 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (9.0 µL, 0.055 mmol) was added to form Kitamura's reagent. The alkyne **23** (29.3 mg, 0.11 mmol) was then added to form the HIAT. The solution was allowed to warm to room temperature, and the consumption of the alkyne was monitored by TLC. When the alkyne was consumed (20 min), the solution was then cooled back to 0 ℃. In a separate flask under argon, sodium azide (7.0 mg, 0.11 mmol) was dissolved at room temperature in methanol (5 mL). The azide solution was then slowly transferred to the HIAT solution. Once the addition was complete, DBU (49 µL, 0.33 mmol) was added, the cryogen was removed and the solution was allowed to warm to room temperature. The crude mixture was then evaporated and purified by column chromatography (R_f = 0.25 (9:1 Hexane/EtOAc), UV active). Yield: 6.3 mg, 24%

Method 2: Copper Catalyzed Cyanocarbene O-H Insertion

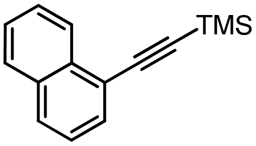
Note: It is important that a ligand is on the copper azide salts so that the complex does not precipitate. Reactions without ligands to solubilize the complex can result in detonation.

Iodobenzene diacetate (35.4 mg 0.11 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (9.0 µL, 0.055 mmol) was added to form Kitamura's reagent. The alkyne **23** (29.3 mg, 0.11 mmol) was then added to form the HIAT. The solution was allowed to warm to room temperature, and the consumption of the alkyne was monitored by TLC. When the alkyne was consumed, the solution was then cooled to -40 ℃. In a separate flask under argon, sodium azide (7.0 mg, 0.11 mmol) was dissolved at room temperature in methanol (5 mL). To this flask, $Cu(OAc)_2(dppe)$ (16 mg, 0.0275 mmol) was added and the solution turned a dark brown color. The copper solution was then slowly transferred to the HIAT solution. Once the addition was complete, the cryogen was removed and the solution was allowed to warm to room temperature. The crude mixture was then evaporated and purified by column chromatography (R_f = 0.25 (9:1 Hexane/EtOAc), UV active). Yield: 6.3 mg, 24%

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.55 (s, 3 H), 5.17 (s, 1 H), 7.05 (m, 3 H), 7.16 (m, 2 H), 7.23 (d, *J*=7.8 Hz, 1 H), 7.38 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 57.5, 72.0, 116.8, 117.4, 119.38 (2 C), 119.9, 121.8, 124.0, 130.0 (2 C), 130.5, 135.1, 156.5, 158.1.

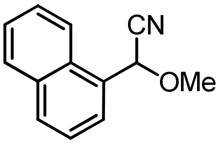
HRMS (APCI): $C_{15}H_{14}NO_2$ $[M+H]^+$, calculated: 240.1025, found: 240.1017.



24

trimethyl(naphthalen-1-ylethynyl)silane (24)[6]:

To a solution of 1-ethynylnaphthalene (0.700 g, 4.60 mmol) in THF (10 mL) was added slowly nBuLi in hexanes (2.5 M, 1.22 mL, 5.06 mmol) at -78 ℃. After stirring for 5 mins at -78 ℃, to the reaction mixture was added chloro trimethylsilane (0.546 g, 5.06 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. A solution of aqueous ammonium chloride was then added to quench the reaction. The organic layer was extracted with ether, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Purification by silica-gel chromatography (R_f = 0.7 (9:1 Hexane/EtOAc), UV active) gave **24** (0.423 g, 41% yield). The product matched spectral data from reference 6.



9f

2-methoxy-2-(naphthalene-1-yl)acetonitrile (9f):

Method 1: Cyanocarbene O-H Insertion with DBU

Iodobenzene diacetate (35.4 mg, 0.11 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (9.0 µL, 0.055 mmol) was added to form Kitamura's reagent. The alkyne **24** (24.7 mg, 0.11 mmol) was then added to form the HIAT. The solution was allowed to warm to room temperature, and the consumption of the alkyne was monitored by TLC. When the alkyne was consumed (20 min), the solution was then cooled back to 0 ℃. In a separate flask under argon, sodium azide (7.0 mg, 0.11 mmol) was dissolved at room temperature in methanol (5 mL). The azide solution was then slowly transferred to the HIAT solution. Once the addition was complete, DBU (49 µL, 0.33 mmol) was added, the cryogen was removed and the solution was allowed to warm to room temperature. The crude mixture was then evaporated and purified by column chromatography (R_f = 0.30 (9:1 Hexane/EtOAc), UV active). Yield: 3.4 mg, 16%

Method 2: Copper Catalyzed Cyanocarbene O-H Insertion

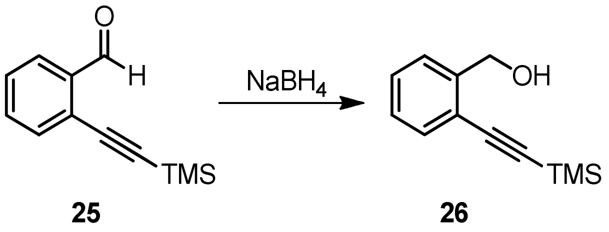
Note: It is important that a ligand is on the copper azide salts so that the complex does not precipitate. Reactions without ligands to solubilize the complex can result in detonation.

Iodobenzene diacetate (35.4 mg 0.11 mmol) was added to dichloromethane (1 mL) at room temperature in a round bottom flask and stirred under argon gas until dissolved. The solution was then submerged in an ice bath. To this solution, triflic anhydride (9.0 µL, 0.055 mmol) was added to form Kitamura's reagent. The alkyne **24** (24.7 mg, 0.11 mmol) was then added to form the HIAT. The solution was allowed to warm to room temperature, and the consumption of the alkyne was monitored by TLC. When the alkyne was consumed, the solution was then cooled to -40 ℃. In a separate flask under argon, sodium azide (7.0 mg, 0.11 mmol) was dissolved at room temperature in methanol (5 mL). To this flask, $Cu(OAc)_2(dppe)$ (16 mg, 0.0275 mmol) was added and the solution turned a dark brown color. The copper solution was then slowly transferred to the HIAT solution. Once the addition was complete, the cryogen was removed and the solution was allowed to warm to room temperature. The crude mixture was then evaporated and purified by column chromatography (R_f = 0.30 (9:1 Hexane/EtOAc), UV active). Yield: 13.9 mg, 64%

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.59 (s, 3 H), 5.86 (s, 1 H), 7.58 (m, 3 H), 7.80 (d, *J*=6.9 Hz, 1 H), 7.94 (t, *J*=8.7 Hz, 2 H), 8.09 (d, *J*=8.7 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 57.0, 71.1, 117.0, 123.1, 125.1, 126.6, 126.9, 127.4, 128.3, 129.1, 130.4, 131.1, 134.0.

HRMS (APCI): $C_{13}H_{12}ON$ $[M+H]^+$, calculated: 198.0919, found: 198.0913.

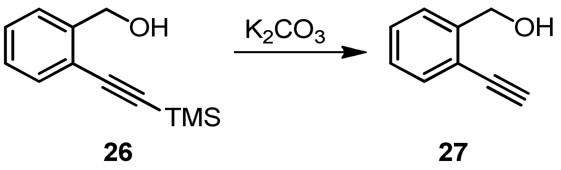


(2-((trimethylsilyl)ethynyl)phenyl)methanol (26)[8]:

Followed a literature procedure and matched spectral data of reference 8.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26 (s, 9 H), 2.23 (t, *J*=6.3 Hz, 1 H), 4.81 (d, *J*=6.3 Hz, 2 H), 7.23 (td, J_t=7.0, J_d=1.1 Hz, 1 H), 7.33 (td, J_t=7.4, J_d=1.7 Hz, 1 H), 7.40 (s, 1 H), 7.46 (dd, *J*=7.4, 1.1 Hz, 1 H).

TLC: R_f = 0.56 (5:1 Hexane/EtOAc), UV active.

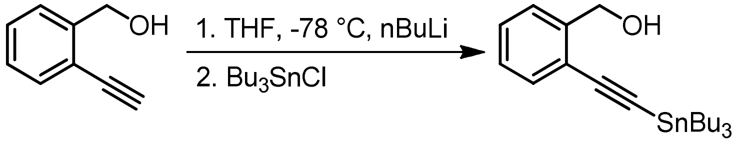


(2-ethynylphenyl)methanol (27)[8]:

Followed a literature procedure and matched spectral data of reference 8.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.04 (t, *J*=6.9 Hz, 1 H), 3.34 (s, 1 H), 4.84 (d, *J*=6.9 Hz, 2 H), 7.27 (td, J_t=7.1, J_d=1.4 Hz, 1 H), 7.37 (td, J_t=7.4, J_d=1.1 Hz, 1 H), 7.45 (d, *J*=6.9 Hz, 1 H), 7.51 (dd, *J*=7.4, 1.1 Hz, 1 H).

TLC: R_f = 0.37 (5:1 Hexane/EtOAc), UV active.



27 **15**

(2-((tributylstannyl)ethynyl)phenyl)methanol (13):

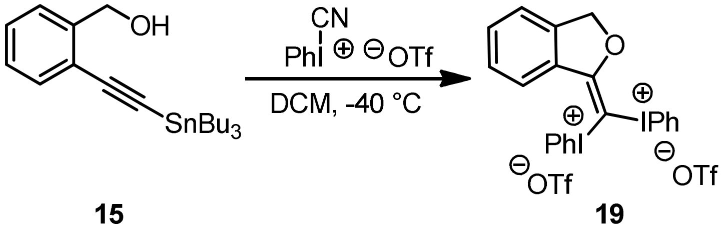
(2-ethynylphenyl)methanol (**27**) (0.100 g, 0.76 mmol) was dissolved in THF (5 mL) and cooled to -78 ℃. To this solution, nBuLi (0.61 mL, 1.52 mmol, 2.5 M in hexanes) was added and stirred for 5 minutes. Tributyltin chloride (0.21 mL, 0.76 mmol) was then added and the solution was slowly allowed to warm to room temperature. After an hour the solution was at room temperature and water was added to quench the reaction. The biphasic solution was then extracted using diethyl ether. The compound was used without further purification because chromatography caused rapid protodestannylation. Yield: 317 mg, 99%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J*=6.9 Hz, 9 H), 1.08 (m, 6 H), 1.38 (sxt, *J*=7.4 Hz, 6 H), 1.63 (m, 6 H), 2.54 (t, *J*=6.8 Hz, 1 H), 4.82 (d, *J*=6.9 Hz, 2 H), 7.24 (td, J_t=7.4, J_d=1.1 Hz, 1 H), 7.30 (td, J_t=7.6, J_d=1.4 Hz, 1 H), 7.37 (d, *J*=6.9 Hz, 1 H), 7.47 (dd, *J*=7.4, 1.1 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.2 (3C), 13.7 (3C), 26.9 (3C), 28.9 (3C), 64.3, 99.0, 107.4, 122.0, 127.1, 127.2, 128.2, 132.4, 142.9.

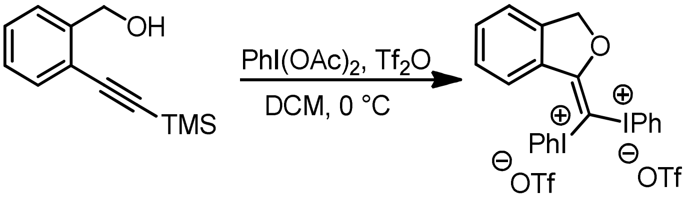
HRMS (ESI): C_9H_7 $[M+H\text{-}SnBu_3\text{-}OH]^+$, C_9H_8O $[M+2H\text{-}SnBu_3]^+$, $C_{12}H_{27}Sn$ $[SnBu_3\text{-}M]^+$, calculated: 115.0542, 133.0648, 291.1129, found: 115.0537, 133.0642, 291.1136.

(isobenzofuran-1(*3H*)-ylidenemethylene)bis(phenyliodonium) ditrifluoromethanesulfonate (17):



15 **19**

Using cyanophenyliodonium triflate[9]: A solution of dichloromethane (20 mL) and cyanophenyliodonium triflate[9] (0.303 g, 0.8 mmol) was cooled to -40 ℃. To this solution, (2-((tributylstannyl)ethynyl)phenyl)methanol (**15**) (0.053 g, 0.4 mmol) was added and the mixture was allowed to warm to room temperature. The solution was then cooled again to -40 ℃ and ether was added to precipitate the product. Yield: 0.151 g, 45%.



26 **19**

Using Kitamura's reagent: A solution of dichloromethane (1 mL) and iodobenzene diacetate (0.296 g, 0.78 mmol) was cooled to 0 ℃. Triflic anhydride (0.066 mL, 0.39 mmol) was then added to the solution and stirred for 5 minutes. To this solution, (2-((trimethylsilyl)ethynyl)phenyl)methanol (**26**) (0.051 g, 0.39 mmol) was added and the mixture was allowed to warm to room temperature. The solution was then cooled to -40 ℃ and ether was added to precipitate the product. Yield: 0.130 g, 39%.

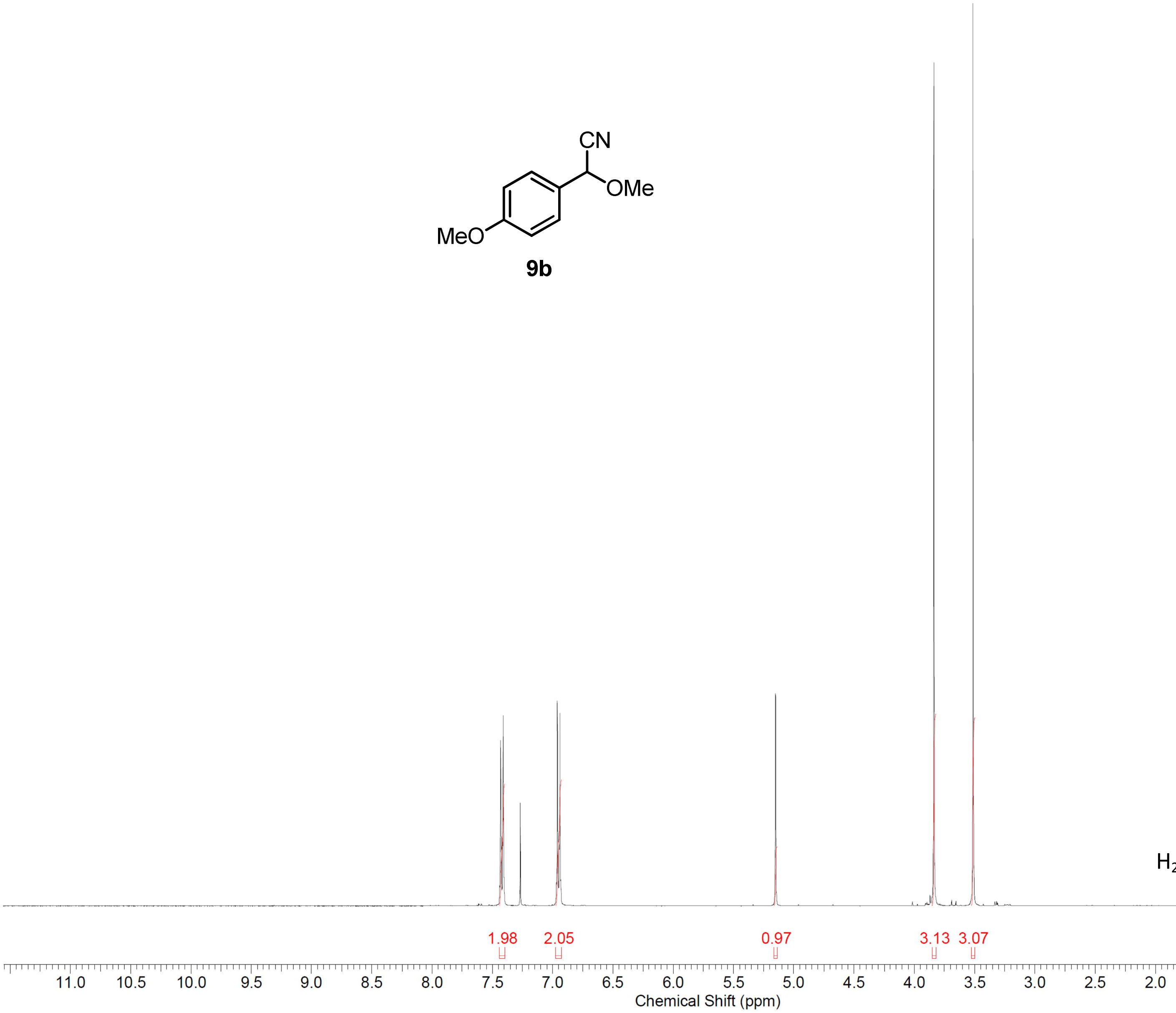
^{1}H NMR (500 MHz, CD_3CN): δ = 5.92 (s, 2 H), 7.34 (dt, *J*=13.7, 8.0 Hz, 4 H), 7.59 (m, 2 H), 7.72 (m, 2 H), 7.83 (m, 5 H), 8.52 (d, *J*=8.0 Hz, 1 H).

^{19}F NMR (470.6 MHz, CD_3CN): δ = -79.3.

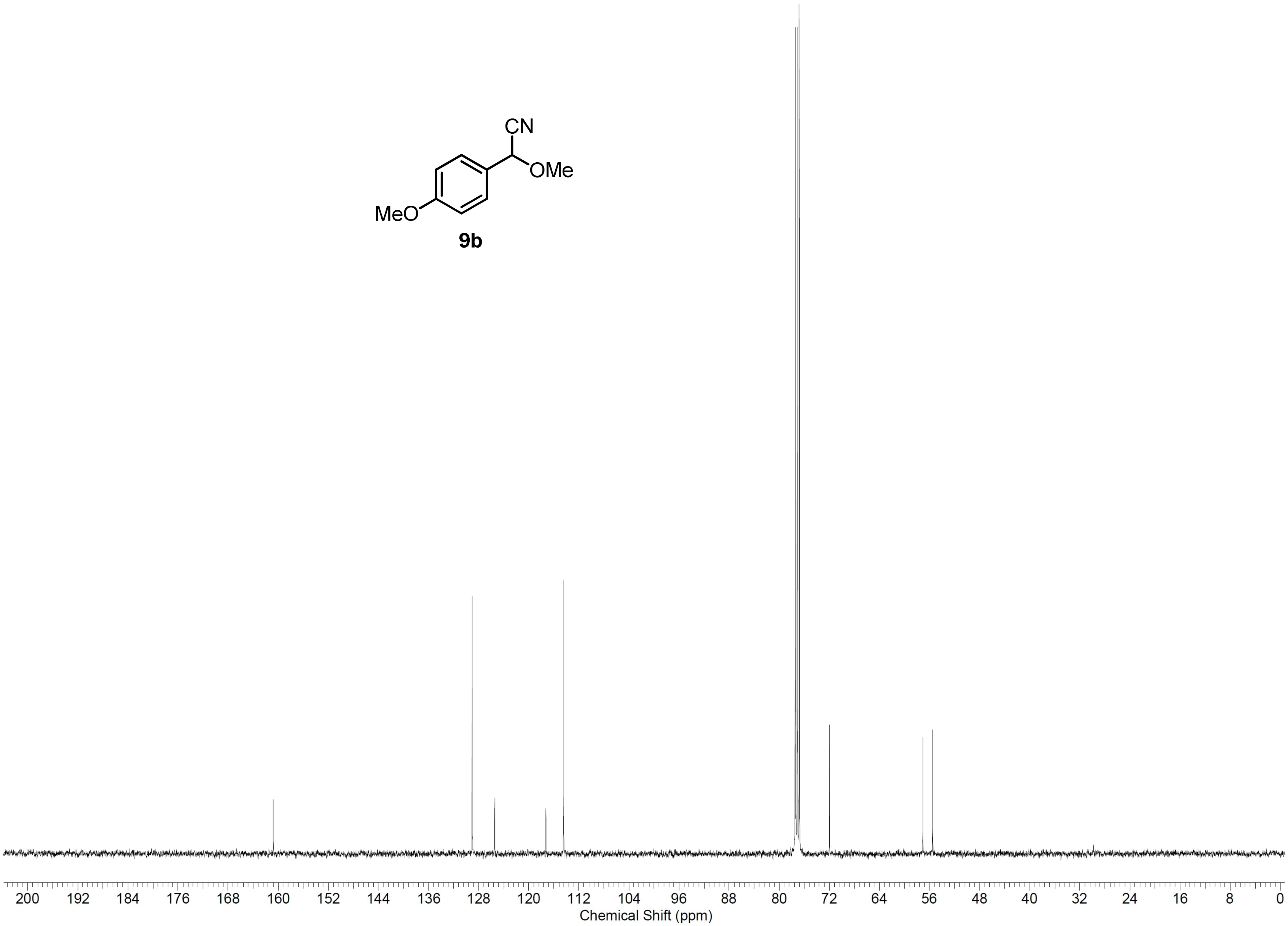
^{13}C NMR (125 MHz, CD_3CN): δ = 27.7, 78.5, 115.0, 116.7, 123.3, 126.4, 126.5, 129.6, 132.3 (2 C), 132.6 (2 C), 133.3, 133.5, 134.5 (2 C), 135.2, 135.8 (2 C), 148.9, 174.8. Triflate carbons could not be seen.

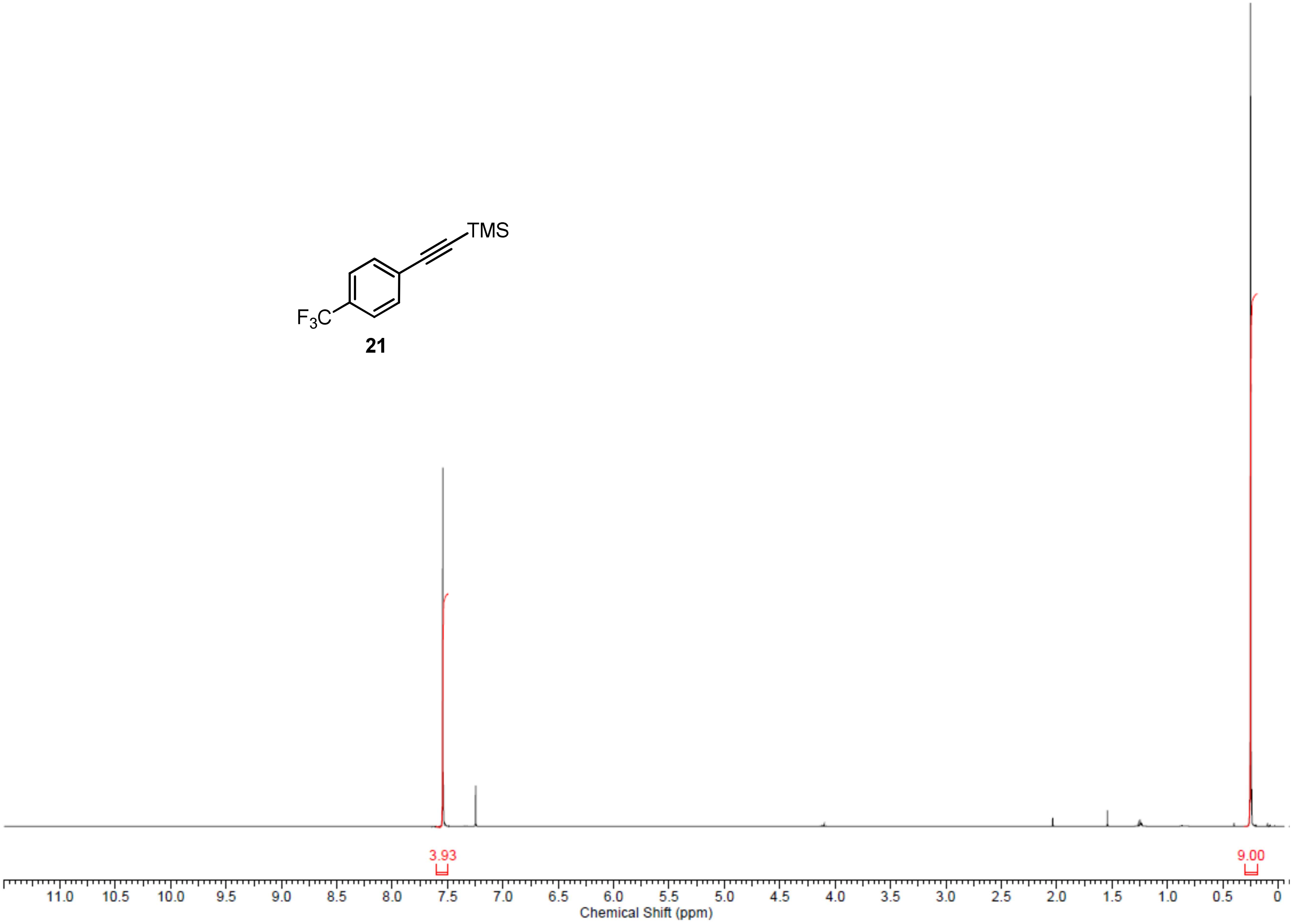
HRMS (ESI): $C_{22}H_{16}F_3I_2O_4S$ $[M\text{-}OTf]^+$, $C_{21}H_{16}I_2O$ $[M\text{-}OTf\text{-}OTf]^{2+}$, calculated: 686.8805, 537.9280/2 = 268.9640, found: 686.8799, 268.9639.

IR (neat): 3070 (w), 3060 (w), 1523 (s), 1469 (m), 1457 (m), 1443 (m), 1217 (s), 1015 (s), 733 (s), 627 (s).


CN
OMe
MeO
H2
1.98
2.05
0.97
3.13
3.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

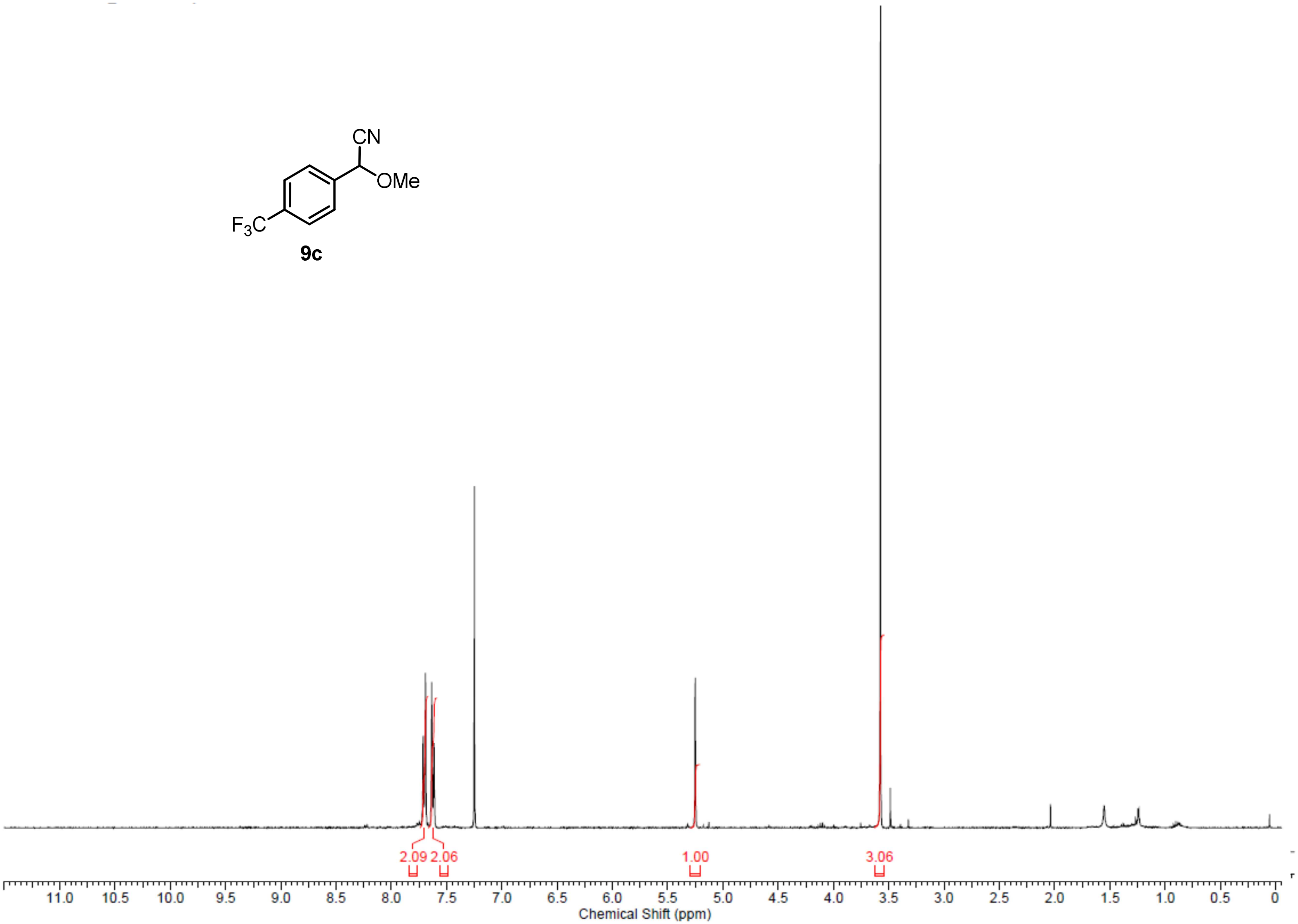
9b


CN
OMe
MeO
9b
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)



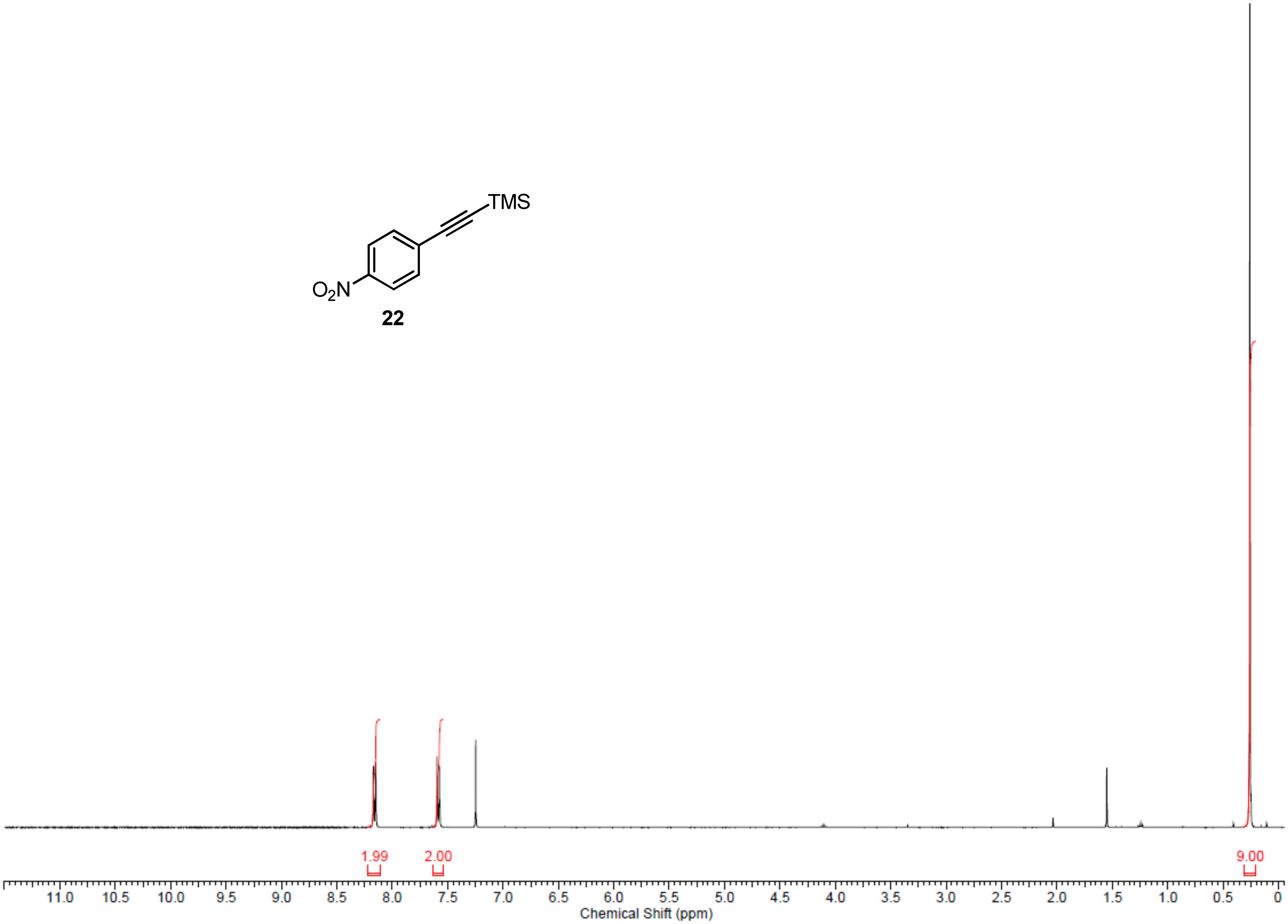
21

TMS
F3C
3.93
9.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

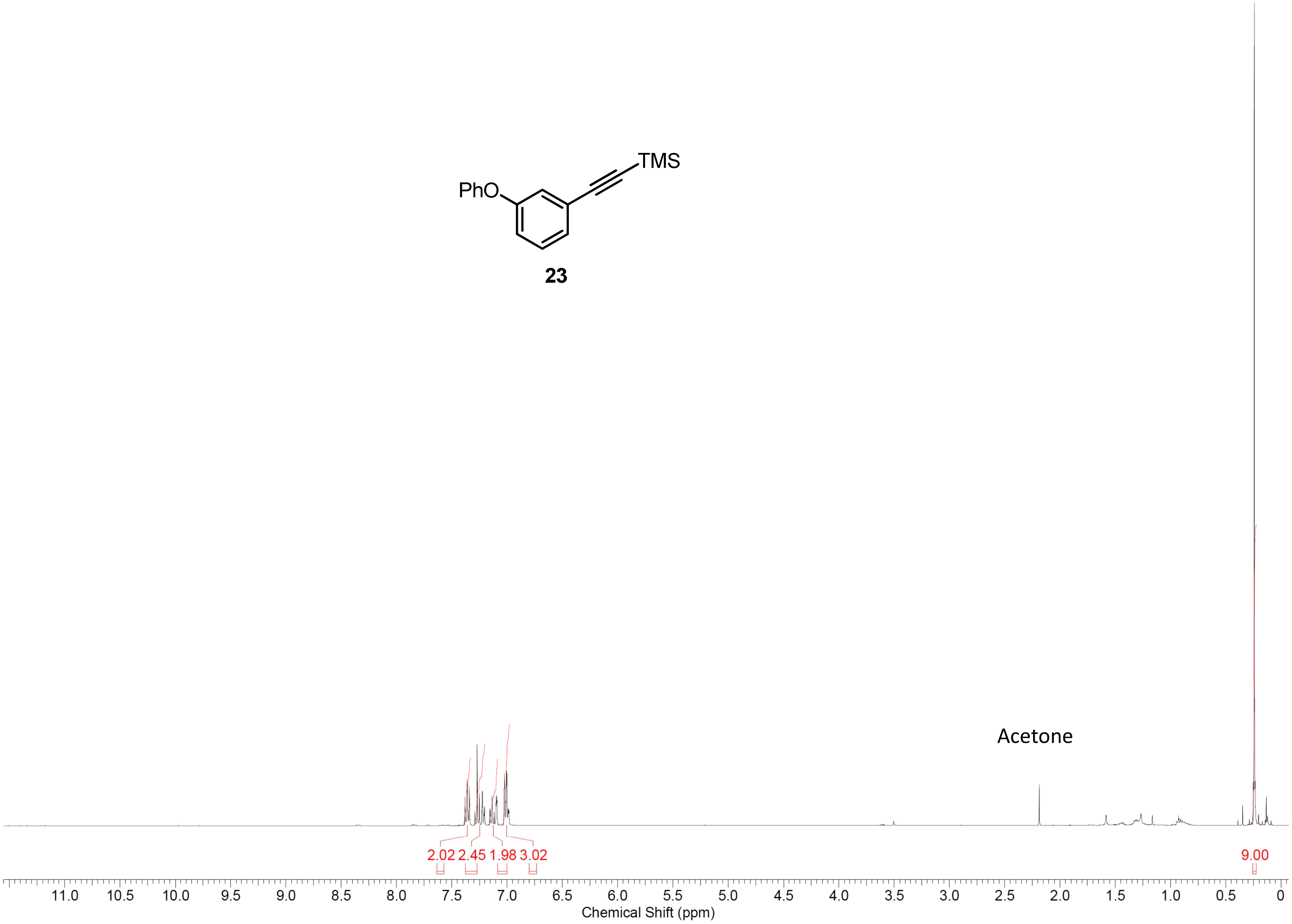


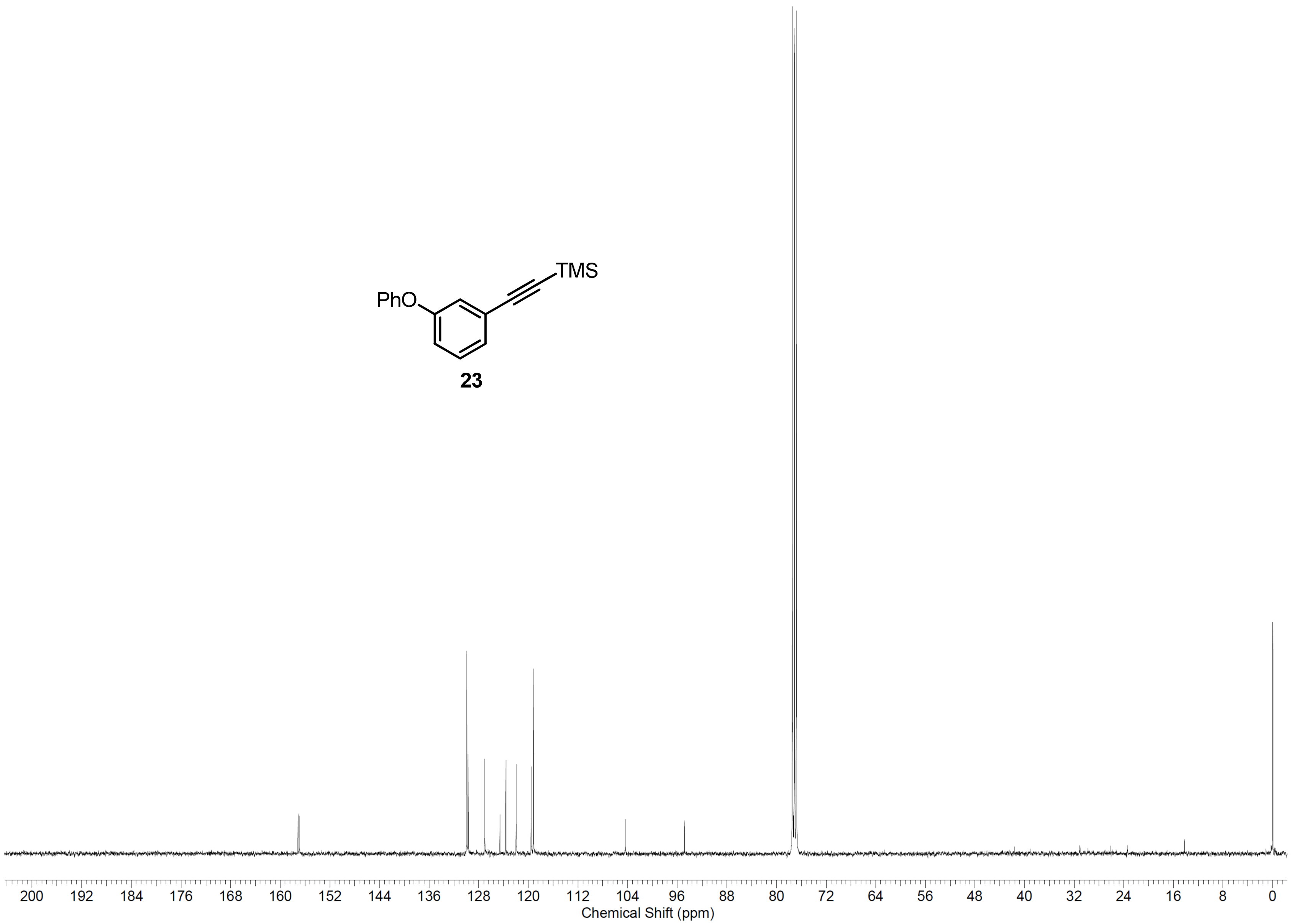
9c

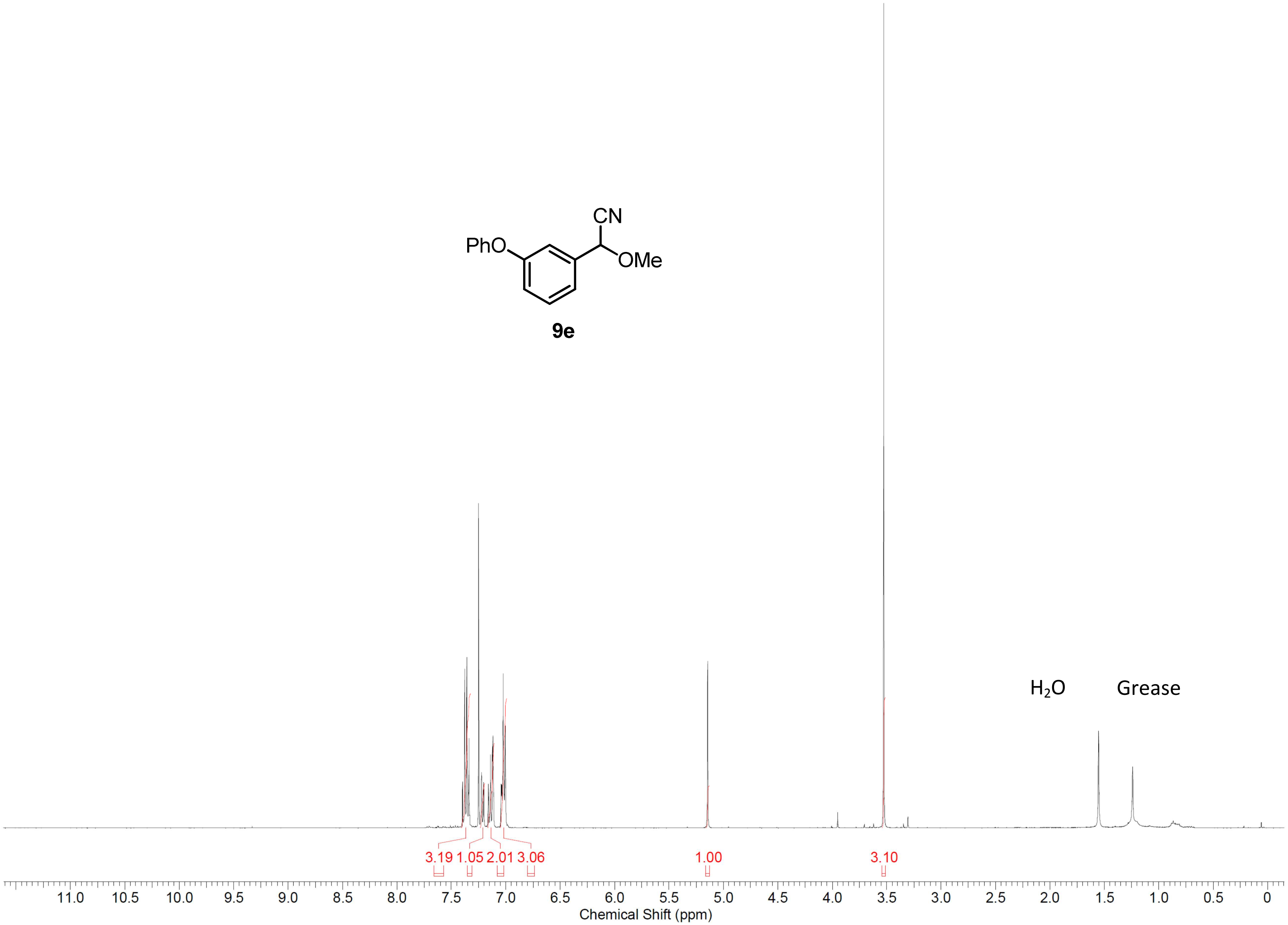
CN
OMe
F_3C
2.09
2.06
1.00
3.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


22
TMS
O2N
1.99
2.00
9.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

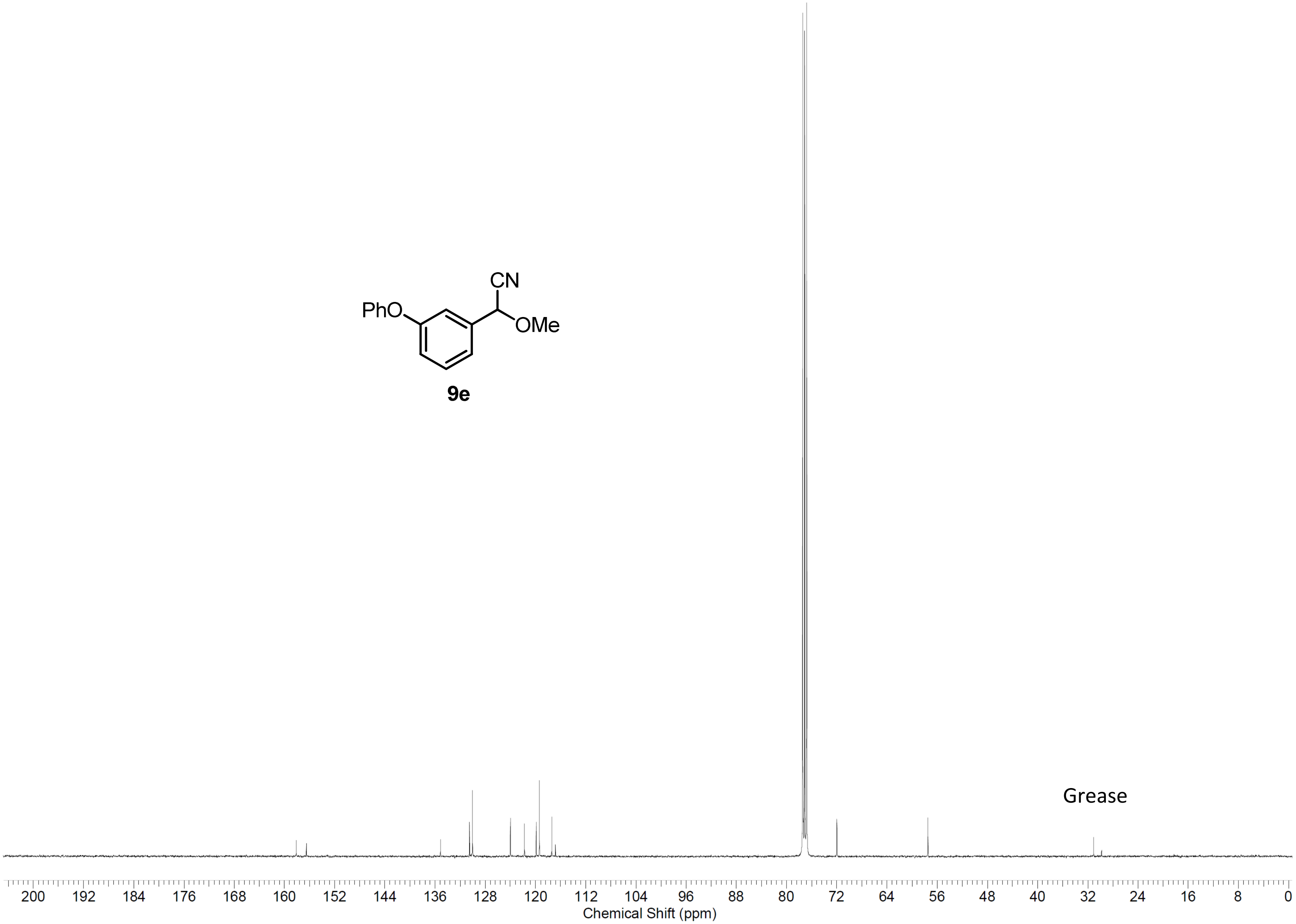
23


Acetone
2.02
2.45
1.98
3.02
9.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


PhO
TMS
23
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

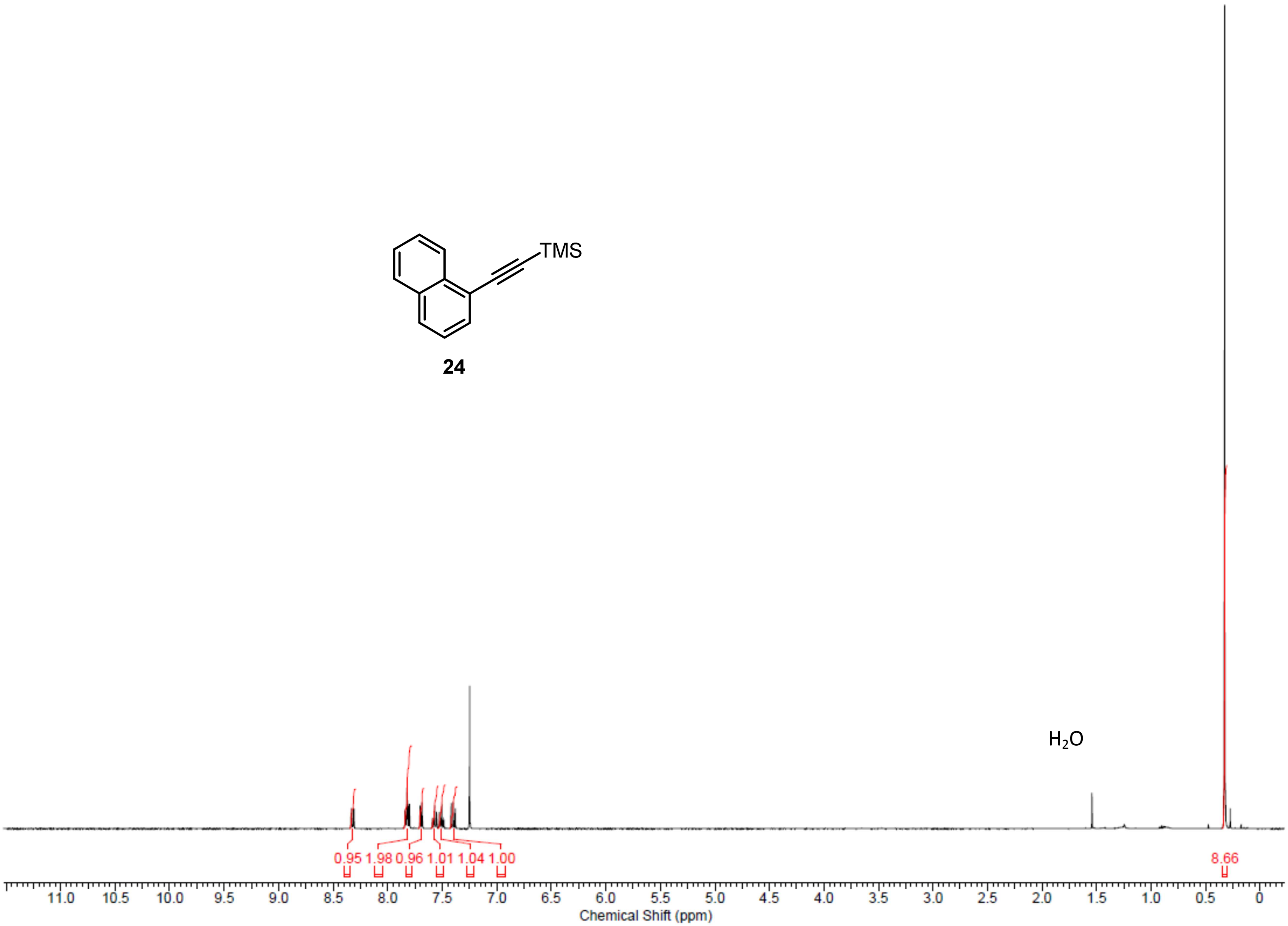


PhO
CN
OMe
9e
H$_2$O
Grease
3.19
1.05
2.01
3.06
1.00
3.10
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



9e

Grease
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

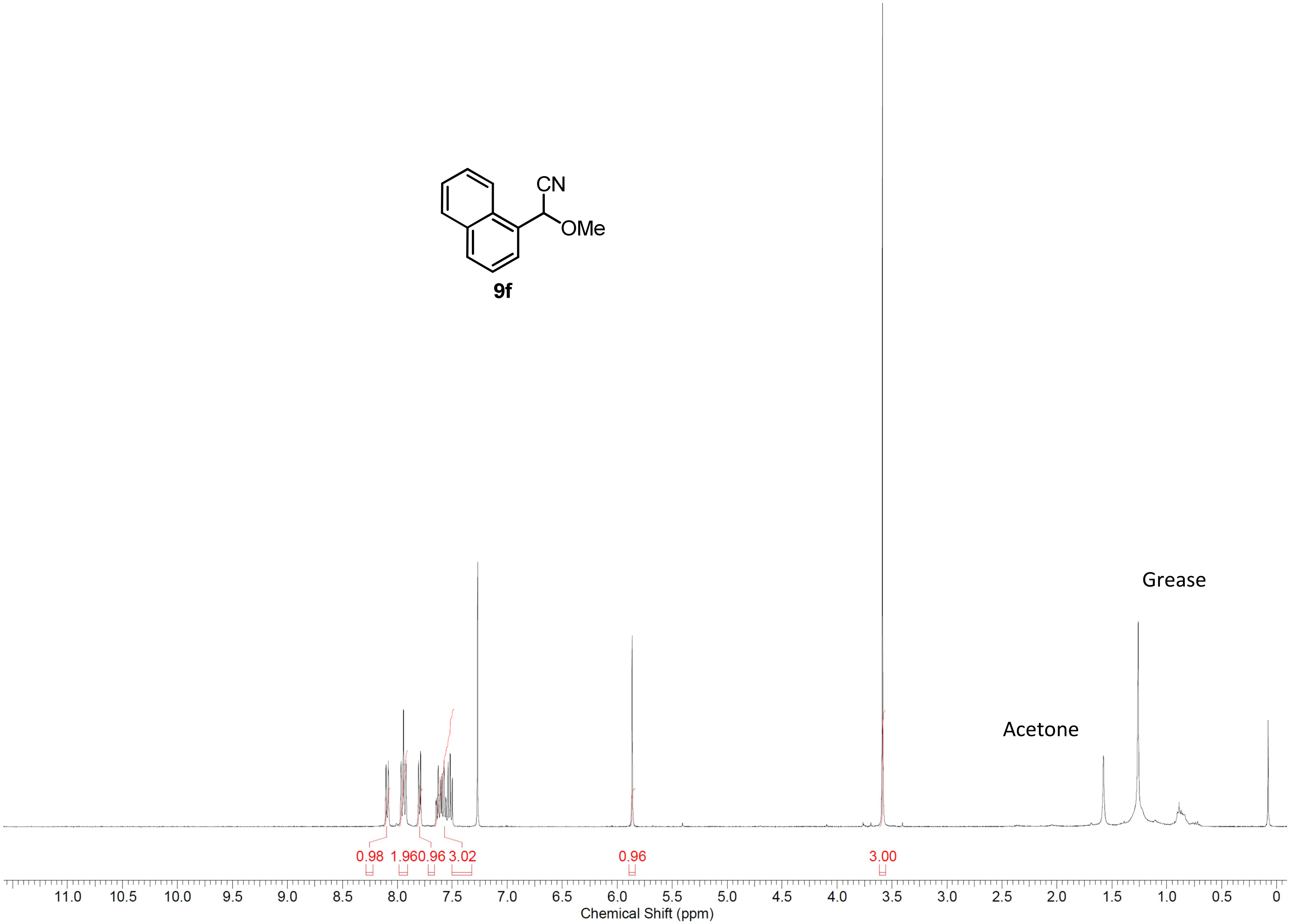

TMS

24

H$_2$O
0.95
1.98
0.96
1.01
1.04
1.00
8.66
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

CN
OMe

9f


Grease
Acetone
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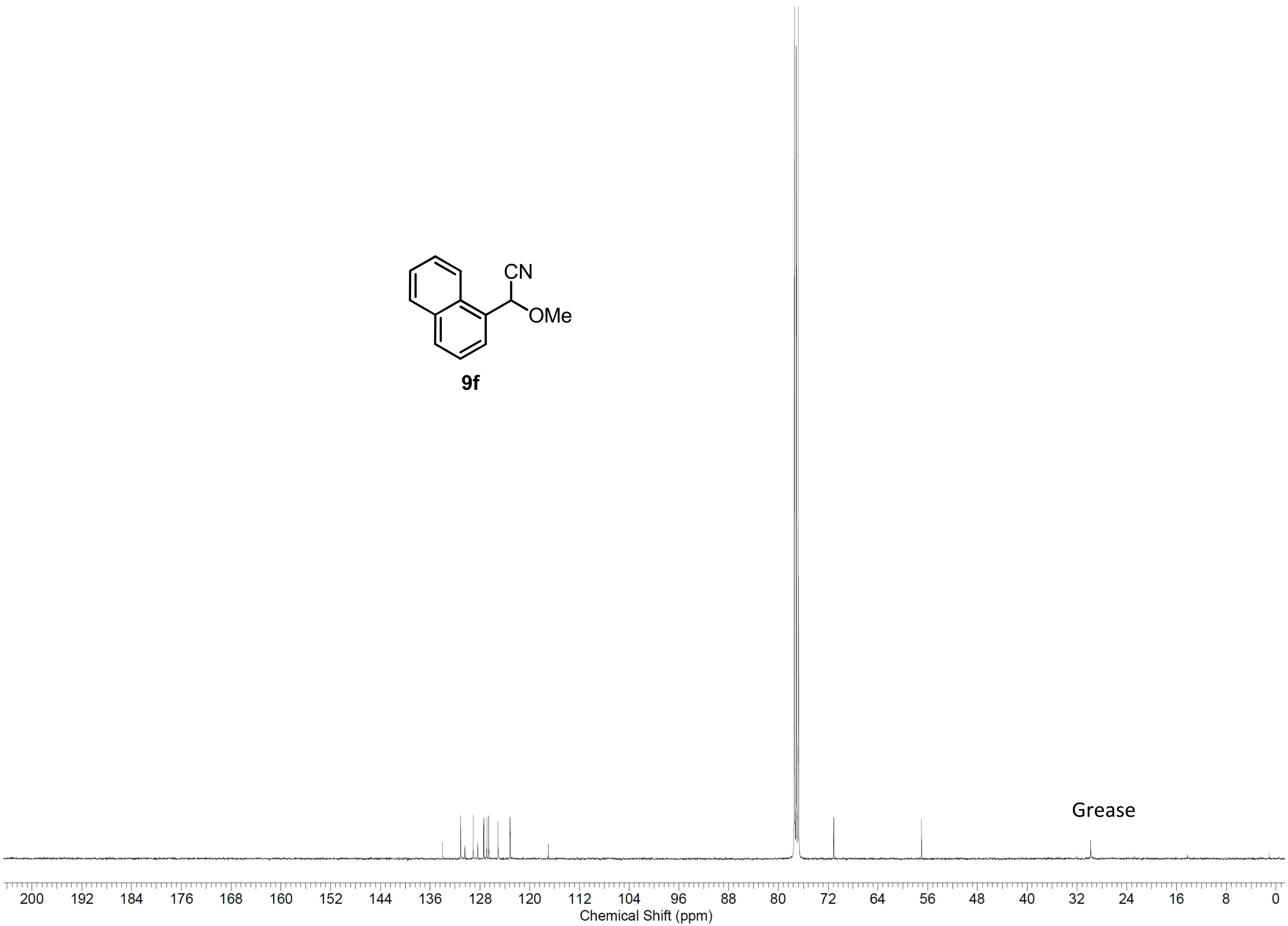
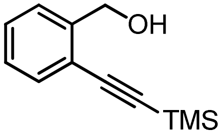
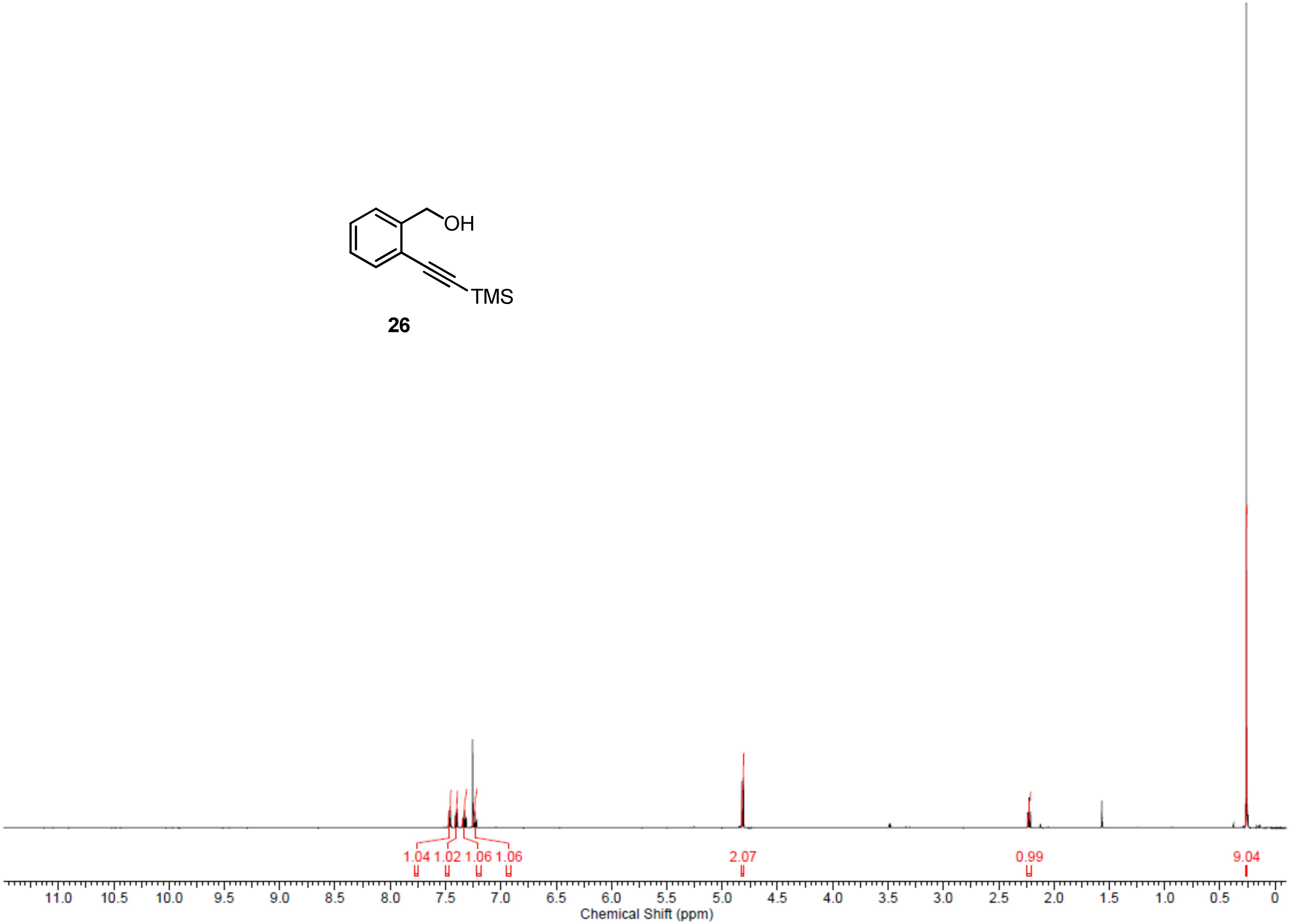
1.96
0.96
3.02
0.96
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CN
OMe
9f
Grease
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


OH
TMS

26


1.04
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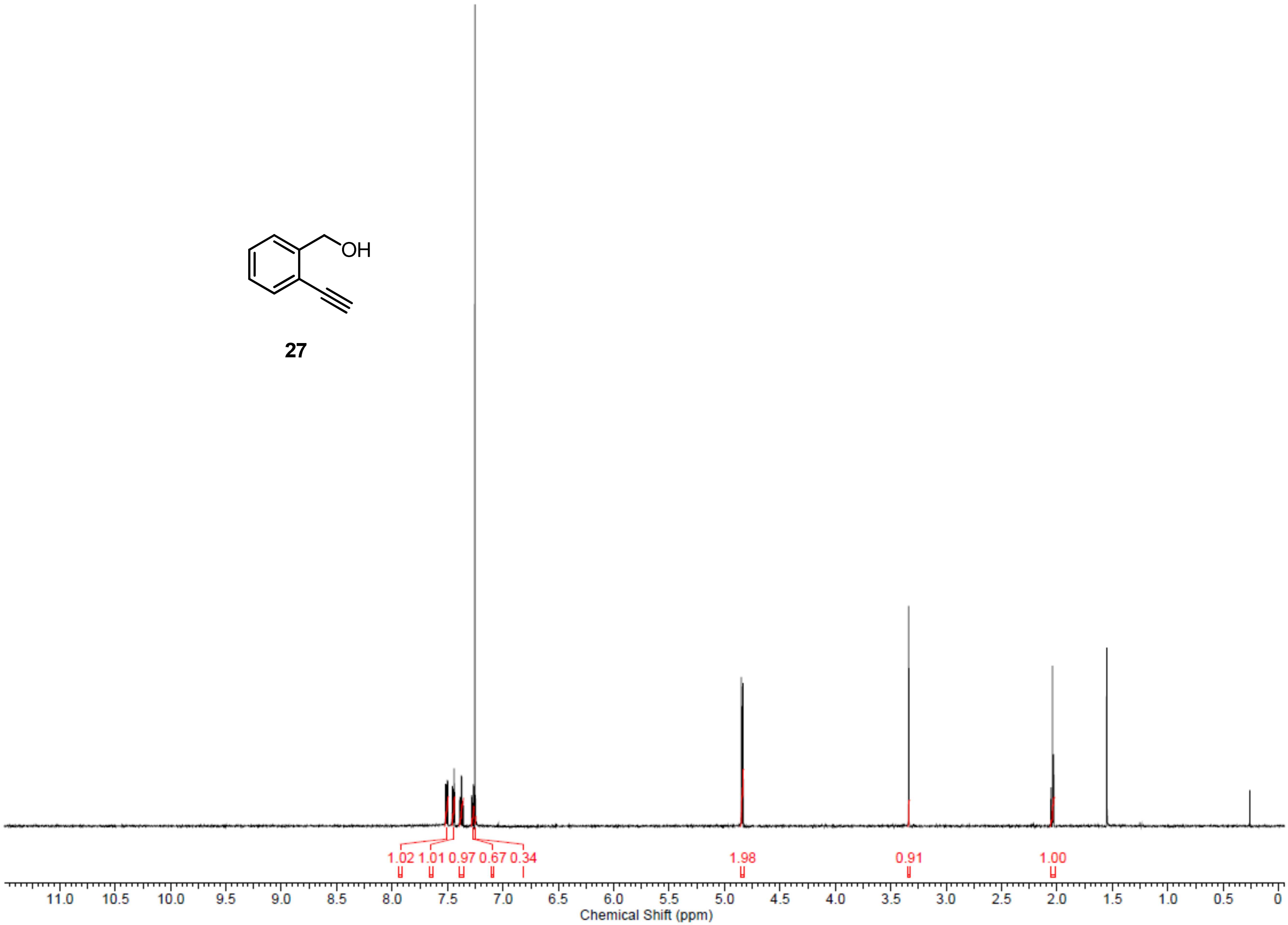
1.06
1.06
2.07
0.99
9.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

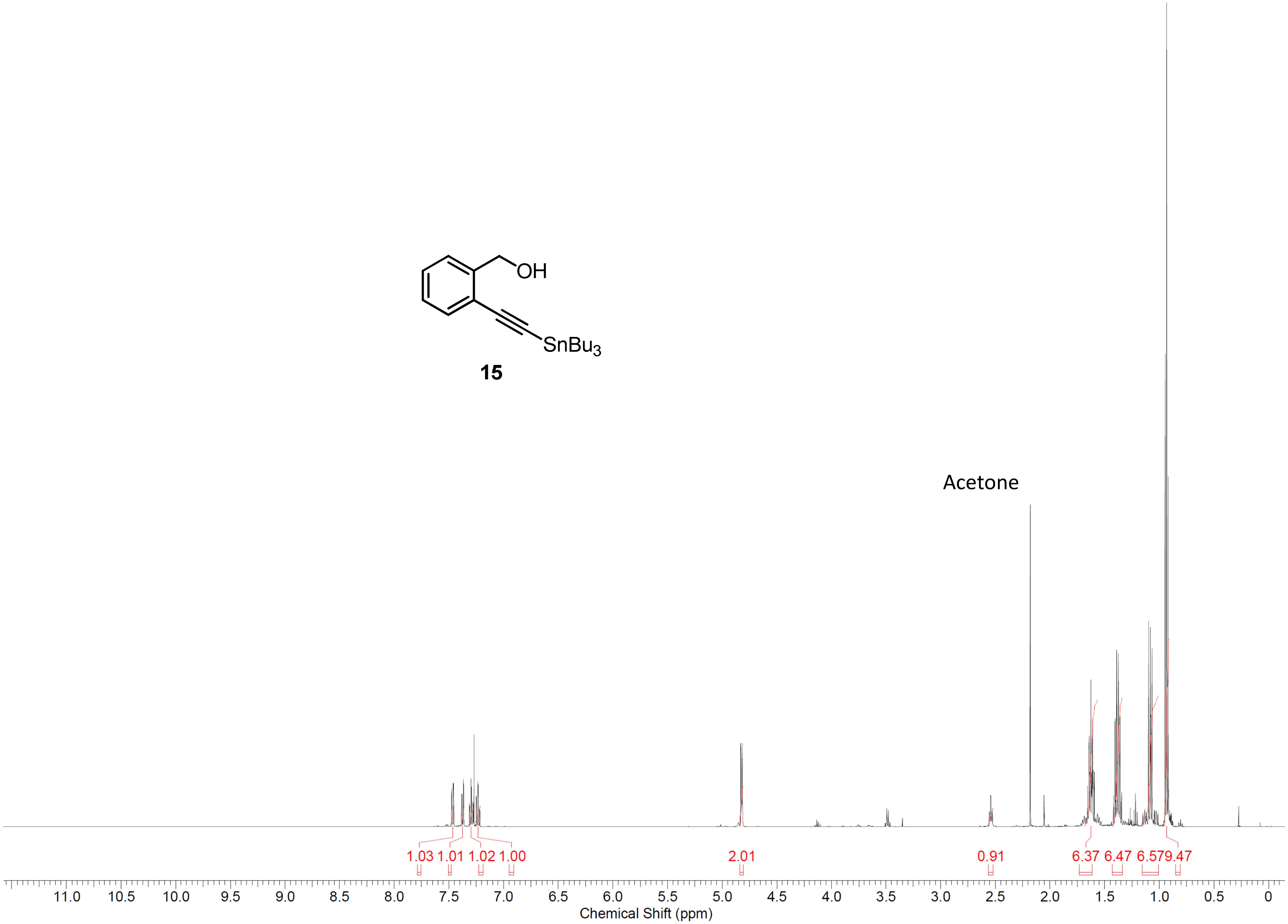
OH

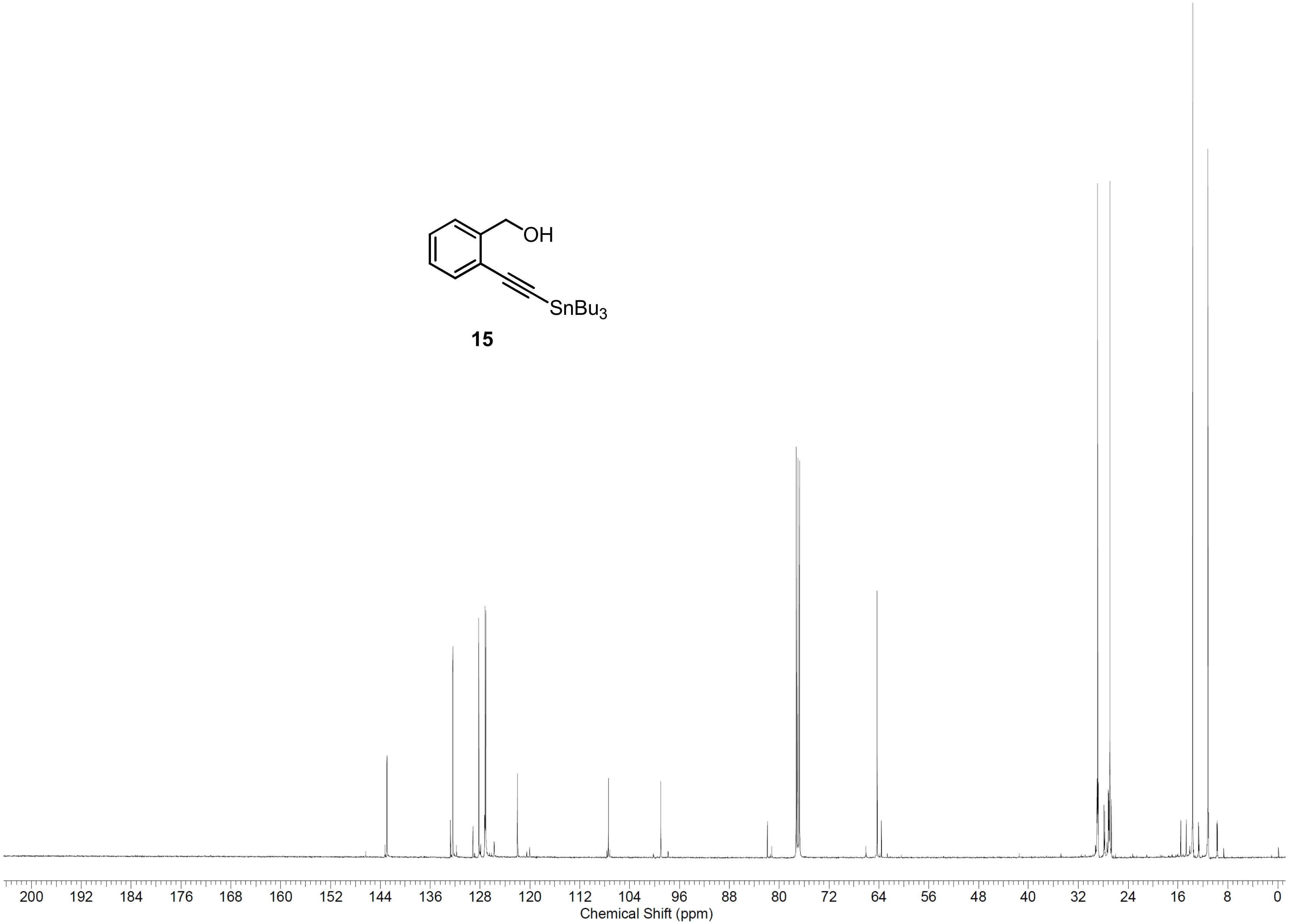
27


1.02
1.01
0.97
0.67
0.34
1.98
0.91
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

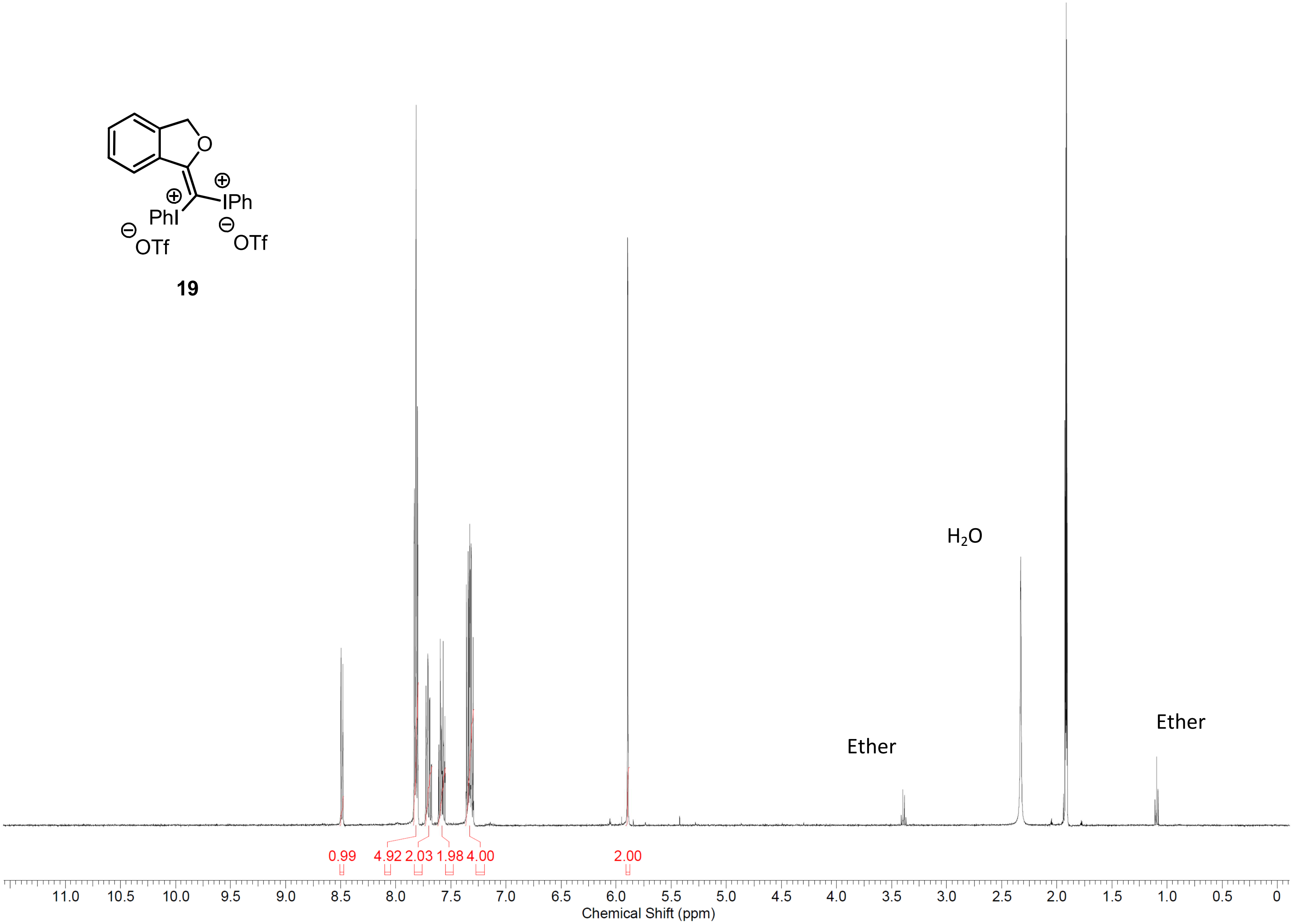
OH
$SnBu_3$

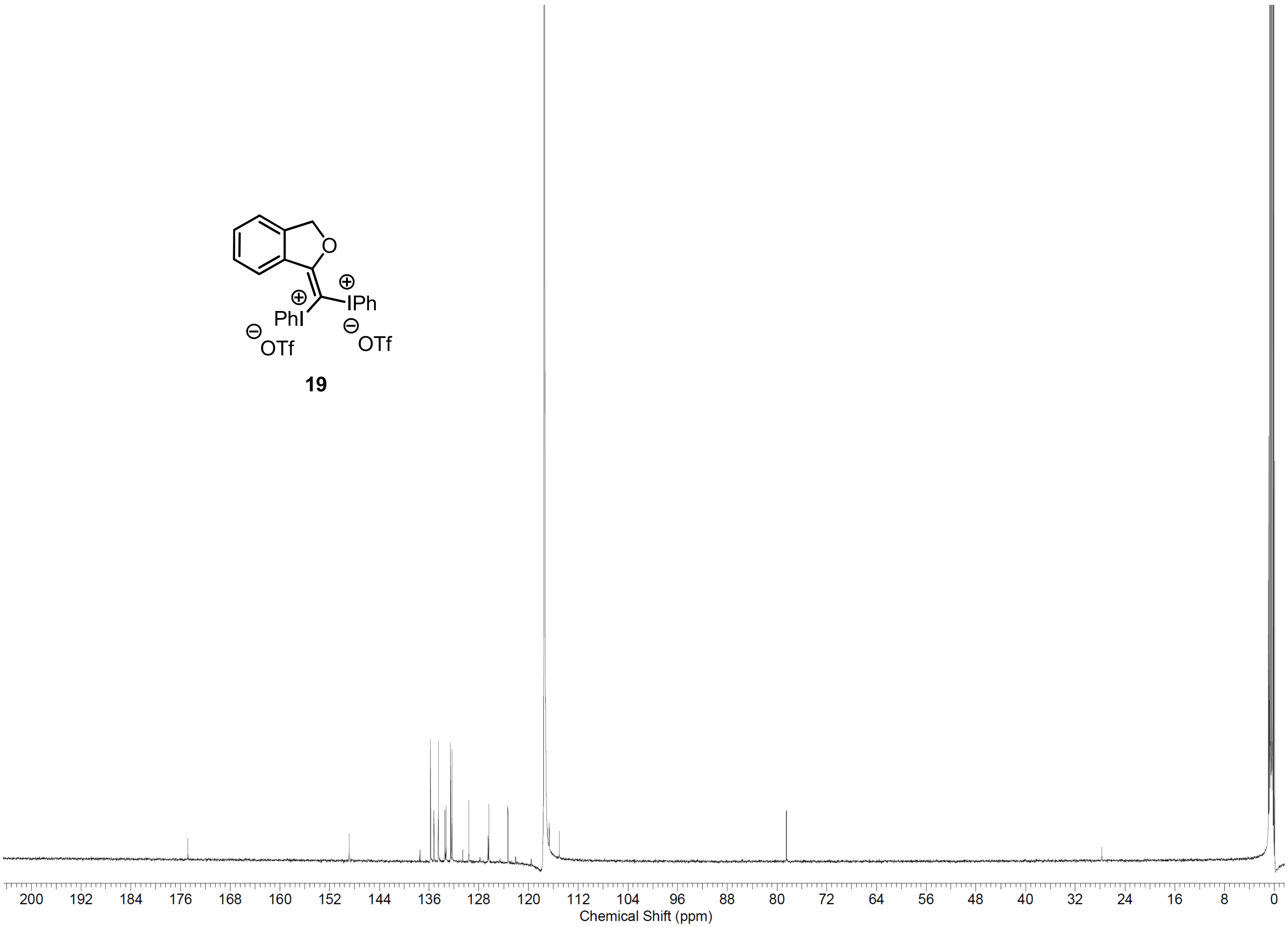
15


Acetone
1.03
1.01
1.02
1.00
2.01
0.91
6.37
6.47
6.57
9.47
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


OH
SnBu3
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

15


PhI
IPh
OTf
OTf
O
19
H2O
Ether
Ether
0.99
4.92
2.03
1.98
4.00
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


PhI
IPh
OTf
OTf
O
19
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

Experimental Details -Crystallography

A clear colourless irregular-shaped specimen of $C_{23}H_{16}F_6I_2O_7S_2$, approximate dimensions 0.120 mm x 0.140 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The crystal was cut from a larger crystal and contained a small crystallite. Of 10374 reflections harvested and processed with Cell_Now, 10243 could be assigned to the major crystal domain. Attempts to model the contribution to the scattering from the small fragment were unsuccessful and the crystal was treated as a single domain. The X-ray intensity data were measured on a Bruker APEX CCD system equipped with a graphite monochromator and a Mo Kα sealed x-ray tube (λ = 0.71073 Å).

The total exposure time was 14.12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 39120 reflections to a maximum θ angle of 30.05° (0.71 Å resolution), of which 8055 were independent (average redundancy 4.857, completeness = 99.8%, Rint = 3.20%, Rsig = 2.50%) and 6815 (84.61%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.5549(9) Å, b = 13.6694(12) Å, c = 19.1510(16) Å, β = 94.3100(10)°, volume = 2755.3(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9925 reflections above 20 $\sigma(I)$ with $7.061° < 2\theta < 61.77°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.845. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7040 and 0.7520.

Refinement

Structure showed minor disorder of 1 of the CF3 groups wherein 1 fluorine (F2) was disordered over 3 sites. Isotropic F atoms were included in the model at these sites with occupancies of 0.42/0.42/0.16, respectively. The final anisotropic full-matrix least-squares refinement on F^2 with 364 variables converged at R_1 = 5.52%, for the observed data and wR_2 = 14.83% for all data. The goodness-of-fit was 1.108. The largest peak in the final difference electron density synthesis was 6.709 $e^-/Å^3$ and the largest hole was -1.102 $e^-/Å^3$ with an RMS deviation of 0.194 e-/$Å^3$. The top 7 peaks in the final difference Fourier map (6.7 - 1.1 $e^-/Å^3$) were within 0.96 Å of an iodine or sulfur atom. There were no other peaks above the background level (0.96 $e^-/Å^3$). On the basis of the final model, the calculated density was 2.016 g/cm^3 and F(000), 1608 e^-. Crystal data, data collection and structure refinement details are summarized below.

Discussion

Short intermolecular contacts involving $I \cdots O$ (2.78 - 2.92 Å) are in agreement with similar contacts reported in the Cambridge Database (2.77 - 2.97 Å).

Computing details

Data collection: Bruker *SMART*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve and refine structure: *SHELXL2014* (Sheldrick 2014); molecular graphics: Bruker *APEX2*; software used to prepare material for publication: Bruker *APEX2*.

Acknowledgements

The WFU X-ray Facility thanks the National Science Foundation (grant CHE-0234489) for funds to purchase the X-ray instrument and computers.

References

Bruker (2014). *APEX2* (Version 2014.7). Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick (2014). *SHELXL* (Version 2014/3). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2002). *SMART* version 5.628. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2013). *SAINT* version 8. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2014). *SADABS*, Version 2014/3. University of Göttingen, Germany.

(a52t)

Crystal data

$C_{23}H_{16}F_6I_2O_7S_2$	$F(000) = 1608$
$M_r = 836.28$	$D_x = 2.016$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.5549$ (9) Å	Cell parameters from 9925 reflections
$b = 13.6694$ (12) Å	$\theta = 3.5$–$30.9°$
$c = 19.1510$ (16) Å	$\mu = 2.52$ mm^{-1}
$\beta = 94.310$ (1)°	$T = 193$ K
$V = 2755.3$ (4) Å^3	Irregular, colourless
$Z = 4$	0.15 × 0.14 × 0.12 mm

Data collection

Bruker APEX CCD diffractometer	6815 reflections with $I > 2\sigma(I)$
Radiation source: sealed x-ray tube	$R_{int} = 0.032$
Graphite monochromator	$\theta_{max} = 30.1°$, $\theta_{min} = 3.5°$

Absorption correction: multi-scan Data were corrected for absorption effects using the multi-scan technique (*SADABS*). The ratio of minimum to maximum apparent transmission was 0.845.	$h = -14 \rightarrow 14$
$T_{min} = 0.631$, $T_{max} = 0.746$	$k = -19 \rightarrow 19$
39120 measured reflections	$l = -26 \rightarrow 26$
8055 independent reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.055$	H-atom parameters constrained
$wR(F^2) = 0.148$	$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 13.577P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
8055 reflections	$\Delta\rangle_{max} = 6.71$ e Å^{-3}
364 parameters	$\Delta\rangle_{min} = -1.10$ e Å^{-3}

Special details

Experimental. Crystal was cut from a larger crystal and contained a small crystallite fragment.
Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
I1	0.59622 (3)	0.43244 (2)	-0.13869 (2)	0.02768 (10)	
I2	0.49259 (3)	0.24573 (2)	-0.25473 (2)	0.02969 (10)	
O1	0.3148 (4)	0.4525 (3)	-0.1251 (2)	0.0338 (8)	
C1	0.3265 (5)	0.3768 (4)	-0.1691 (3)	0.0276 (9)	
C2	0.2010 (5)	0.3443 (4)	-0.1971 (3)	0.0276 (9)	

C3	0.1592 (5)	0.2672 (4)	-0.2397 (3)	0.0312 (10)	
H3	0.2181	0.2224	-0.2571	0.037*	
C4	0.0299 (6)	0.2565 (4)	-0.2567 (3)	0.0390 (13)	
H4	-0.0003	0.2035	-0.2854	0.047*	
C5	-0.0557 (6)	0.3231 (5)	-0.2320 (3)	0.0402 (13)	
H5	-0.1437	0.3161	-0.2453	0.048*	
C6	-0.0152 (6)	0.3990 (5)	-0.1883 (4)	0.0434 (14)	
H6	-0.0745	0.4430	-0.1705	0.052*	
C7	0.1137 (6)	0.4094 (4)	-0.1712 (3)	0.0350 (11)	
C8	0.1832 (6)	0.4837 (5)	-0.1246 (4)	0.0397 (13)	
H8A	0.1714	0.5506	-0.1438	0.048*	
H8B	0.1541	0.4820	-0.0767	0.048*	
C9	0.4474 (5)	0.3457 (4)	-0.1805 (3)	0.0277 (9)	
C10	0.6326 (5)	0.3476 (4)	-0.0476 (3)	0.0337 (11)	
C11	0.5434 (7)	0.3472 (6)	0.0008 (3)	0.0495 (16)	
H11	0.4700	0.3875	-0.0054	0.059*	
C12	0.5623 (9)	0.2868 (8)	0.0592 (4)	0.067 (2)	
H12	0.5003	0.2839	0.0926	0.080*	
C13	0.6711 (8)	0.2315 (6)	0.0684 (4)	0.058 (2)	
H13	0.6860	0.1932	0.1096	0.070*	
C14	0.7595 (8)	0.2308 (7)	0.0180 (4)	0.059 (2)	
H14	0.8322	0.1898	0.0236	0.071*	
C15	0.7409 (6)	0.2909 (6)	-0.0408 (4)	0.0493 (16)	
H15	0.8011	0.2926	-0.0752	0.059*	
C16	0.5467 (5)	0.1305 (4)	-0.1850 (3)	0.0334 (11)	
C17	0.4571 (6)	0.0977 (6)	-0.1414 (4)	0.0522 (17)	
H17	0.3761	0.1278	-0.1411	0.063*	
C18	0.4904 (8)	0.0191 (7)	-0.0983 (5)	0.070 (3)	
H18	0.4318	-0.0045	-0.0669	0.084*	
C19	0.6082 (8)	-0.0257 (6)	-0.1003 (5)	0.061 (2)	
H19	0.6288	-0.0806	-0.0712	0.073*	
C20	0.6932 (7)	0.0084 (5)	-0.1434 (4)	0.0494 (16)	
H20	0.7741	-0.0221	-0.1434	0.059*	
C21	0.6650 (6)	0.0881 (4)	-0.1883 (3)	0.0369 (12)	
H21	0.7242	0.1116	-0.2194	0.044*	
S1	0.08510 (14)	-0.00441 (10)	-0.18312 (7)	0.0331 (3)	
O2	0.1898 (5)	0.0393 (4)	-0.2143 (3)	0.0545 (13)	

O3	0.1070 (6)	-0.1033 (4)	-0.1589 (3)	0.0548 (13)	
O4	-0.0358 (4)	0.0112 (4)	-0.2208 (2)	0.0485 (12)	
C22	0.0745 (7)	0.0628 (5)	-0.1014 (3)	0.0436 (14)	
F1	0.1771 (5)	0.0503 (5)	-0.0586 (3)	0.0772 (16)	
F2	0.0720 (12)	0.1594 (7)	-0.1113 (5)	0.0364 (19)*	0.42
F2'	0.0216 (12)	0.1503 (8)	-0.1147 (6)	0.050 (3)*	0.42
F2"	0.130 (3)	0.1561 (17)	-0.1077 (12)	0.038 (5)*	0.16
F3	-0.0210 (5)	0.0303 (5)	-0.0673 (2)	0.0841 (18)	
S2	-0.17384 (13)	0.63060 (10)	-0.10436 (7)	0.0328 (3)	
O5	-0.0527 (4)	0.6261 (3)	-0.1352 (2)	0.0407 (9)	
O6	-0.2089 (5)	0.5414 (3)	-0.0701 (2)	0.0450 (10)	
O7	-0.2745 (5)	0.6744 (4)	-0.1479 (3)	0.0546 (12)	
C23	-0.1443 (7)	0.7152 (5)	-0.0312 (4)	0.0464 (15)	
F4	-0.2477 (5)	0.7277 (5)	0.0033 (3)	0.0755 (16)	
F5	-0.0532 (5)	0.6822 (4)	0.0132 (2)	0.0693 (14)	
F6	-0.1109 (5)	0.8023 (3)	-0.0543 (3)	0.0688 (13)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02588 (16)	0.02957 (17)	0.02705 (16)	-0.00224 (12)	-0.00153 (11)	0.00068 (12)
I2	0.03150 (18)	0.02612 (17)	0.03095 (17)	0.00217 (12)	-0.00102 (12)	-0.00298 (12)
O1	0.0312 (19)	0.0315 (19)	0.038 (2)	0.0005 (15)	-0.0015 (15)	-0.0091 (16)
C1	0.033 (2)	0.024 (2)	0.026 (2)	-0.0028 (18)	0.0004 (18)	0.0004 (18)
C2	0.027 (2)	0.030 (2)	0.025 (2)	-0.0031 (19)	-0.0006 (17)	0.0015 (18)
C3	0.032 (3)	0.030 (2)	0.032 (2)	-0.003 (2)	0.003 (2)	-0.002 (2)
C4	0.043 (3)	0.036 (3)	0.036 (3)	-0.010 (2)	-0.007 (2)	0.000 (2)
C5	0.026 (3)	0.042 (3)	0.052 (3)	-0.002 (2)	-0.002 (2)	0.002 (3)
C6	0.031 (3)	0.037 (3)	0.062 (4)	0.003 (2)	0.002 (3)	-0.004 (3)
C7	0.033 (3)	0.031 (3)	0.040 (3)	-0.002 (2)	0.001 (2)	-0.001 (2)
C8	0.031 (3)	0.035 (3)	0.053 (3)	0.002 (2)	0.003 (2)	-0.011 (3)
C9	0.025 (2)	0.024 (2)	0.033 (2)	-0.0011 (17)	-0.0038 (18)	-0.0010 (18)
C10	0.032 (3)	0.038 (3)	0.030 (2)	-0.006 (2)	-0.002 (2)	0.004 (2)
C11	0.044 (4)	0.068 (5)	0.036 (3)	0.009 (3)	0.005 (3)	0.015 (3)
C12	0.067 (5)	0.096 (7)	0.040 (4)	0.016 (5)	0.014 (3)	0.028 (4)
C13	0.061 (5)	0.072 (5)	0.040 (3)	0.000 (4)	-0.003 (3)	0.025 (3)

C14	0.049 (4)	0.071 (5)	0.057 (4)	0.010 (4)	-0.003 (3)	0.025 (4)
C15	0.035 (3)	0.061 (4)	0.051 (4)	0.007 (3)	0.001 (3)	0.017 (3)
C16	0.028 (2)	0.033 (3)	0.039 (3)	-0.001 (2)	0.000 (2)	0.001 (2)
C17	0.034 (3)	0.048 (4)	0.075 (5)	0.004 (3)	0.008 (3)	0.020 (3)
C18	0.052 (4)	0.063 (5)	0.097 (7)	0.004 (4)	0.024 (4)	0.037 (5)
C19	0.060 (5)	0.052 (4)	0.069 (5)	0.012 (4)	-0.004 (4)	0.026 (4)
C20	0.045 (4)	0.048 (4)	0.054 (4)	0.016 (3)	-0.004 (3)	0.010 (3)
C21	0.032 (3)	0.038 (3)	0.040 (3)	0.004 (2)	0.002 (2)	0.001 (2)
S1	0.0405 (7)	0.0291 (6)	0.0289 (6)	-0.0001 (5)	-0.0034 (5)	-0.0027 (5)
O2	0.059 (3)	0.053 (3)	0.054 (3)	-0.016 (2)	0.018 (2)	-0.018 (2)
O3	0.078 (4)	0.039 (2)	0.045 (2)	-0.006 (2)	-0.016 (2)	0.009 (2)
O4	0.041 (2)	0.075 (3)	0.0279 (19)	0.015 (2)	-0.0049 (17)	-0.006 (2)
C22	0.059 (4)	0.045 (3)	0.027 (3)	-0.001 (3)	0.005 (2)	-0.001 (2)
F1	0.069 (3)	0.109 (4)	0.051 (3)	0.000 (3)	-0.017 (2)	-0.038 (3)
F3	0.075 (3)	0.147 (5)	0.031 (2)	-0.030 (4)	0.013 (2)	-0.007 (3)
S2	0.0340 (7)	0.0342 (6)	0.0293 (6)	-0.0048 (5)	-0.0024 (5)	-0.0012 (5)
O5	0.042 (2)	0.039 (2)	0.042 (2)	0.0006 (18)	0.0084 (18)	-0.0011 (18)
O6	0.051 (3)	0.046 (2)	0.038 (2)	-0.020 (2)	-0.0020 (19)	0.0019 (19)
O7	0.040 (2)	0.071 (3)	0.050 (3)	0.007 (2)	-0.008 (2)	0.007 (2)
C23	0.049 (4)	0.047 (4)	0.044 (3)	-0.012 (3)	0.010 (3)	-0.012 (3)
F4	0.067 (3)	0.089 (4)	0.074 (3)	-0.016 (3)	0.031 (3)	-0.036 (3)
F5	0.072 (3)	0.084 (3)	0.049 (2)	-0.017 (3)	-0.020 (2)	-0.013 (2)
F6	0.094 (4)	0.038 (2)	0.077 (3)	-0.016 (2)	0.020 (3)	-0.015 (2)

Geometric parameters (Å, º) for (a52t)

I1—C9	2.080 (5)	C14—H14	0.9500
I1—C10	2.106 (5)	C15—H15	0.9500
I2—C9	2.053 (5)	C16—C17	1.382 (9)
I2—C16	2.117 (6)	C16—C21	1.382 (8)
O1—C1	1.346 (6)	C17—C18	1.384 (10)
O1—C8	1.454 (7)	C17—H17	0.9500
C1—C9	1.378 (7)	C18—C19	1.389 (11)
C1—C2	1.460 (7)	C18—H18	0.9500
C2—C3	1.386 (7)	C19—C20	1.348 (11)
C2—C7	1.397 (8)	C19—H19	0.9500
C3—C4	1.386 (8)	C20—C21	1.406 (9)

C3—H3	0.9500	C20—H20	0.9500
C4—C5	1.391 (9)	C21—H21	0.9500
C4—H4	0.9500	S1—O2	1.426 (5)
C5—C6	1.380 (9)	S1—O4	1.434 (4)
C5—H5	0.9500	S1—O3	1.442 (5)
C6—C7	1.383 (8)	S1—C22	1.826 (6)
C6—H6	0.9500	C22—F3	1.318 (8)
C7—C8	1.507 (8)	C22—F1	1.319 (8)
C8—H8A	0.9900	C22—F2	1.335 (11)
C8—H8B	0.9900	C22—F2'	1.336 (13)
C10—C11	1.370 (9)	C22—F2"	1.41 (2)
C10—C15	1.380 (9)	F1—F2"	1.78 (2)
C11—C12	1.393 (10)	S2—O7	1.432 (5)
C11—H11	0.9500	S2—O6	1.446 (5)
C12—C13	1.375 (12)	S2—O5	1.450 (5)
C12—H12	0.9500	S2—C23	1.826 (7)
C13—C14	1.393 (11)	C23—F5	1.314 (9)
C13—H13	0.9500	C23—F6	1.328 (8)
C14—C15	1.395 (10)	C23—F4	1.328 (8)
C9—I1—C10	95.2 (2)	C17—C16—C21	123.6 (6)
C9—I2—C16	97.1 (2)	C17—C16—I2	117.3 (4)
C1—O1—C8	111.2 (4)	C21—C16—I2	119.0 (4)
O1—C1—C9	117.8 (4)	C16—C17—C18	117.2 (6)
O1—C1—C2	109.9 (4)	C16—C17—H17	121.4
C9—C1—C2	132.3 (5)	C18—C17—H17	121.4
C3—C2—C7	120.3 (5)	C17—C18—C19	120.9 (7)
C3—C2—C1	133.4 (5)	C17—C18—H18	119.6
C7—C2—C1	106.3 (5)	C19—C18—H18	119.6
C2—C3—C4	118.8 (5)	C20—C19—C18	120.2 (7)
C2—C3—H3	120.6	C20—C19—H19	119.9
C4—C3—H3	120.6	C18—C19—H19	119.9
C3—C4—C5	120.3 (5)	C19—C20—C21	121.5 (6)
C3—C4—H4	119.9	C19—C20—H20	119.2
C5—C4—H4	119.9	C21—C20—H20	119.2
C6—C5—C4	121.3 (5)	C16—C21—C20	116.5 (6)
C6—C5—H5	119.4	C16—C21—H21	121.7

C4—C5—H5	119.4	C20—C21—H21	121.7
C5—C6—C7	118.3 (6)	O2—S1—O4	114.5 (3)
C5—C6—H6	120.8	O2—S1—O3	114.6 (4)
C7—C6—H6	120.8	O4—S1—O3	114.6 (3)
C6—C7—C2	120.9 (5)	O2—S1—C22	104.4 (3)
C6—C7—C8	129.5 (6)	O4—S1—C22	104.3 (3)
C2—C7—C8	109.5 (5)	O3—S1—C22	102.4 (3)
O1—C8—C7	102.8 (4)	F3—C22—F1	105.7 (6)
O1—C8—H8A	111.2	F3—C22—F2	113.4 (8)
C7—C8—H8A	111.2	F1—C22—F2	102.9 (8)
O1—C8—H8B	111.2	F3—C22—F2'	94.2 (8)
C7—C8—H8B	111.2	F1—C22—F2'	123.1 (8)
H8A—C8—H8B	109.1	F3—C22—F2"	133.2 (12)
C1—C9—I2	125.5 (4)	F1—C22—F2"	81.0 (12)
C1—C9—I1	116.4 (4)	F3—C22—S1	110.7 (5)
I2—C9—I1	116.0 (2)	F1—C22—S1	111.5 (5)
C11—C10—C15	122.8 (6)	F2—C22—S1	112.2 (5)
C11—C10—I1	118.1 (4)	F2'—C22—S1	109.8 (6)
C15—C10—I1	119.1 (4)	F2"—C22—S1	109.1 (10)
C10—C11—C12	118.8 (7)	C22—F1—F2"	51.8 (9)
C10—C11—H11	120.6	C22—F2"—F1	47.2 (8)
C12—C11—H11	120.6	O7—S2—O6	114.4 (3)
C13—C12—C11	119.8 (7)	O7—S2—O5	114.8 (3)
C13—C12—H12	120.1	O6—S2—O5	114.4 (3)
C11—C12—H12	120.1	O7—S2—C23	105.0 (4)
C12—C13—C14	120.8 (7)	O6—S2—C23	102.7 (3)
C12—C13—H13	119.6	O5—S2—C23	103.5 (3)
C14—C13—H13	119.6	F5—C23—F6	108.9 (6)
C13—C14—C15	119.6 (7)	F5—C23—F4	108.2 (6)
C13—C14—H14	120.2	F6—C23—F4	107.4 (6)
C15—C14—H14	120.2	F5—C23—S2	110.7 (5)
C10—C15—C14	118.2 (7)	F6—C23—S2	110.2 (5)
C10—C15—H15	120.9	F4—C23—S2	111.3 (5)
C14—C15—H15	120.9		
C8—O1—C1—C9	173.5 (5)	C18—C19—C20—C21	-1.4 (14)

C8—O1—C1—C2	-5.5 (6)	C17—C16—C21—C20	-1.1 (10)
O1—C1—C2—C3	-175.1 (6)	I2—C16—C21—C20	-176.7 (5)
C9—C1—C2—C3	6.1 (10)	C19—C20—C21—C16	1.2 (11)
O1—C1—C2—C7	4.1 (6)	O2—S1—C22—F3	179.1 (5)
C9—C1—C2—C7	-174.7 (6)	O4—S1—C22—F3	58.6 (6)
C7—C2—C3—C4	0.6 (8)	O3—S1—C22—F3	-61.1 (6)
C1—C2—C3—C4	179.8 (5)	O2—S1—C22—F1	-63.5 (6)
C2—C3—C4—C5	0.8 (9)	O4—S1—C22—F1	176.1 (5)
C3—C4—C5—C6	-2.1 (10)	O3—S1—C22—F1	56.3 (6)
C4—C5—C6—C7	1.9 (10)	O2—S1—C22—F2	51.4 (8)
C5—C6—C7—C2	-0.4 (10)	O4—S1—C22—F2	-69.1 (8)
C5—C6—C7—C8	-179.1 (6)	O3—S1—C22—F2	171.2 (8)
C3—C2—C7—C6	-0.8 (9)	O2—S1—C22—F2'	76.5 (8)
C1—C2—C7—C6	179.8 (6)	O4—S1—C22—F2'	-44.0 (8)
C3—C2—C7—C8	178.1 (5)	O3—S1—C22—F2'	-163.7 (7)
C1—C2—C7—C8	-1.2 (6)	O2—S1—C22—F2"	24.2 (13)
C1—O1—C8—C7	4.4 (6)	O4—S1—C22—F2"	-96.3 (13)
C6—C7—C8—O1	177.1 (6)	O3—S1—C22—F2"	144.0 (13)
C2—C7—C8—O1	-1.8 (7)	F3—C22—F1—F2"	-132.5 (12)
O1—C1—C9—I2	-170.9 (4)	F2—C22—F1—F2"	-13.3 (11)
C2—C1—C9—I2	7.9 (8)	F2'—C22—F1—F2"	-26.6 (11)
O1—C1—C9—I1	-8.2 (6)	S1—C22—F1—F2"	107.1 (11)
C2—C1—C9—I1	170.6 (4)	F3—C22—F2"—F1	103.2 (13)
C15—C10—C11—C12	-0.3 (12)	F2—C22—F2"—F1	149 (3)
I1—C10—C11—C12	176.1 (7)	F2'—C22—F2"—F1	150.2 (11)
C10—C11—C12—C13	2.1 (14)	S1—C22—F2"—F1	-109.8 (7)
C11—C12—C13—C14	-3.6 (15)	O7—S2—C23—F5	179.6 (5)
C12—C13—C14—C15	3.3 (15)	O6—S2—C23—F5	59.7 (5)
C11—C10—C15—C14	0.0 (12)	O5—S2—C23—F5	-59.6 (5)
I1—C10—C15—C14	-176.3 (6)	O7—S2—C23—F6	-59.8 (6)
C13—C14—C15—C10	-1.5 (13)	O6—S2—C23—F6	-179.8 (5)
C21—C16—C17—	1.2 (12)	O5—S2—C23—F6	60.9 (6)

C18			
I2—C16—C17—C18	176.8 (7)	O7—S2—C23—F4	59.2 (6)
C16—C17—C18—C19	-1.4 (15)	O6—S2—C23—F4	-60.7 (6)
C17—C18—C19—C20	1.5 (16)	O5—S2—C23—F4	180.0 (6)

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Least-squares planes (x,y,z in crystal coordinates) and deviations
from them
 (* indicates atom used to define plane)

  4.7182 (0.0348) x + 10.3436 (0.0192) y + 8.4670 (0.0383) z = 6.1419
(0.0191)

 *   -0.0301 (0.0034)  I1
 *    0.0349 (0.0050)  C10
 *    0.0202 (0.0067)  C11
 *   -0.0209 (0.0071)  C12
 *   -0.0027 (0.0072)  C13
 *   -0.0182 (0.0067)  C14
 *    0.0168 (0.0067)  C15

 Rms deviation of fitted atoms =   0.0227


  3.3245 (0.0345) x + 8.7493 (0.0156) y + 12.9295 (0.0373) z = 0.5292
(0.0259)

 Angle to previous plane (with approximate esd) = 16.371 ( 0.330 )

 *   -0.0351 (0.0034)  I2
 *    0.0385 (0.0050)  C16
 *    0.0164 (0.0071)  C17
 *   -0.0031 (0.0074)  C18
 *   -0.0292 (0.0074)  C19
 *   -0.0050 (0.0056)  C20
 *    0.0175 (0.0052)  C21

 Rms deviation of fitted atoms =   0.0244


 - 0.3293 (0.0195) x + 9.0347 (0.0051) y - 14.2737 (0.0103) z = 5.6615
(0.0107)

 Angle to previous plane (with approximate esd) = 83.557 ( 0.105 )

 *    0.0487 (0.0019)  C1
 *   -0.1098 (0.0041)  C9
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 *    0.0288 (0.0011)  I1
 *    0.0323 (0.0012)  I2

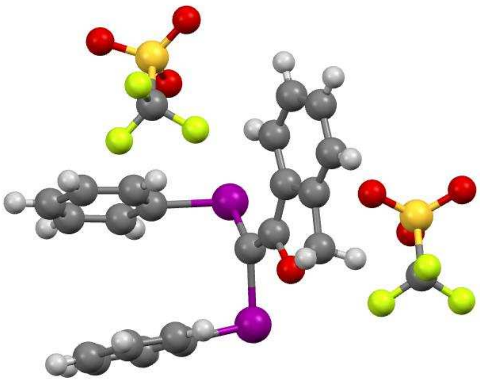
 Rms deviation of fitted atoms =   0.0639

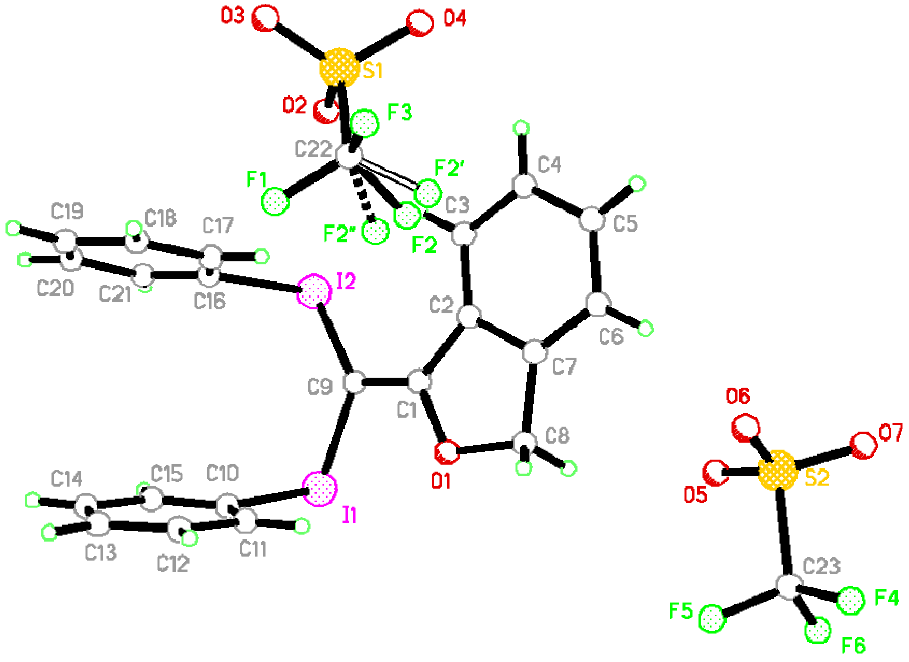

  1.2874 (0.0131) x + 8.1806 (0.0184) y - 15.2967 (0.0187) z = 6.0945
(0.0034)

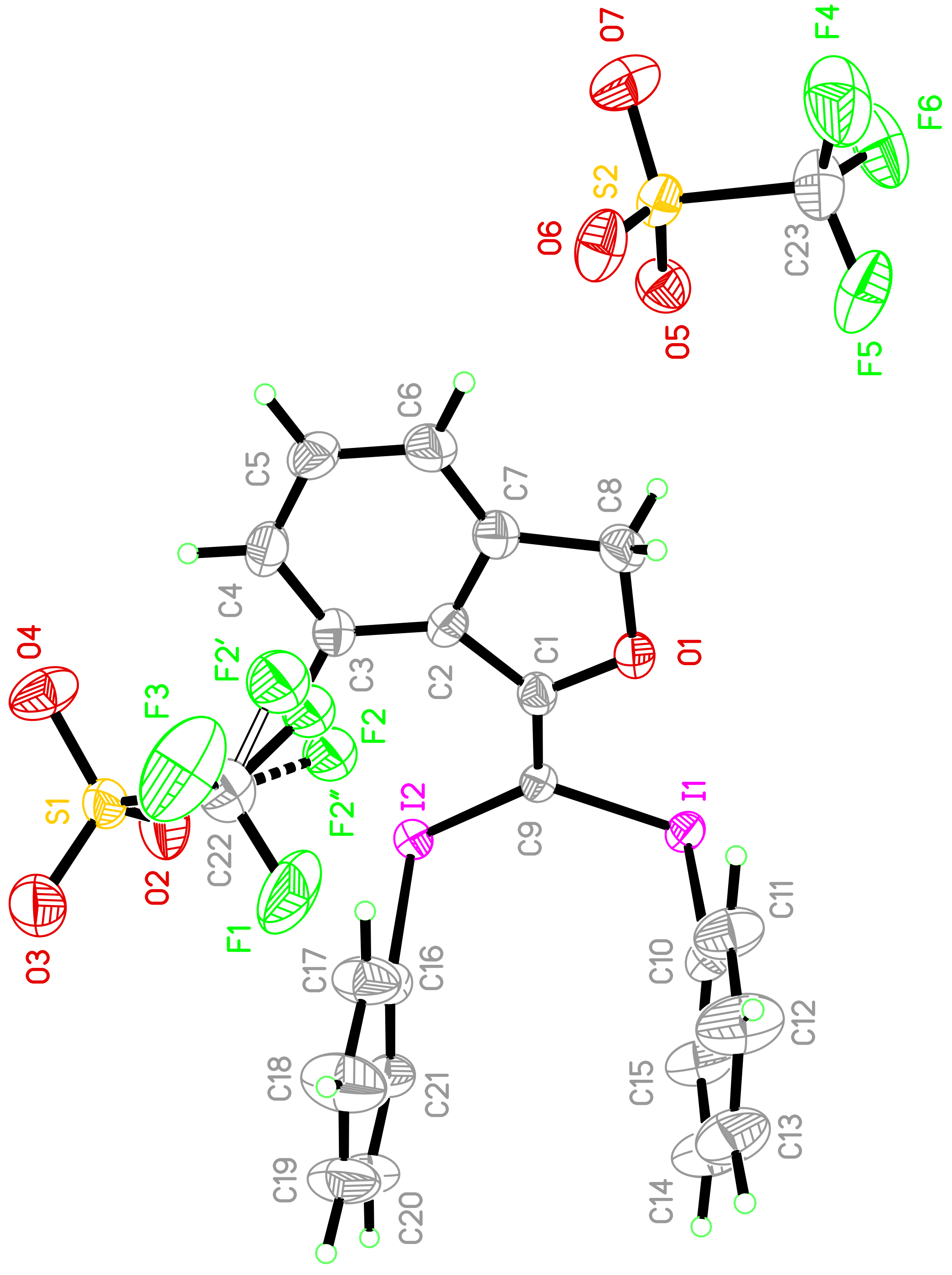
 Angle to previous plane (with approximate esd) =  9.791 ( 0.167 )

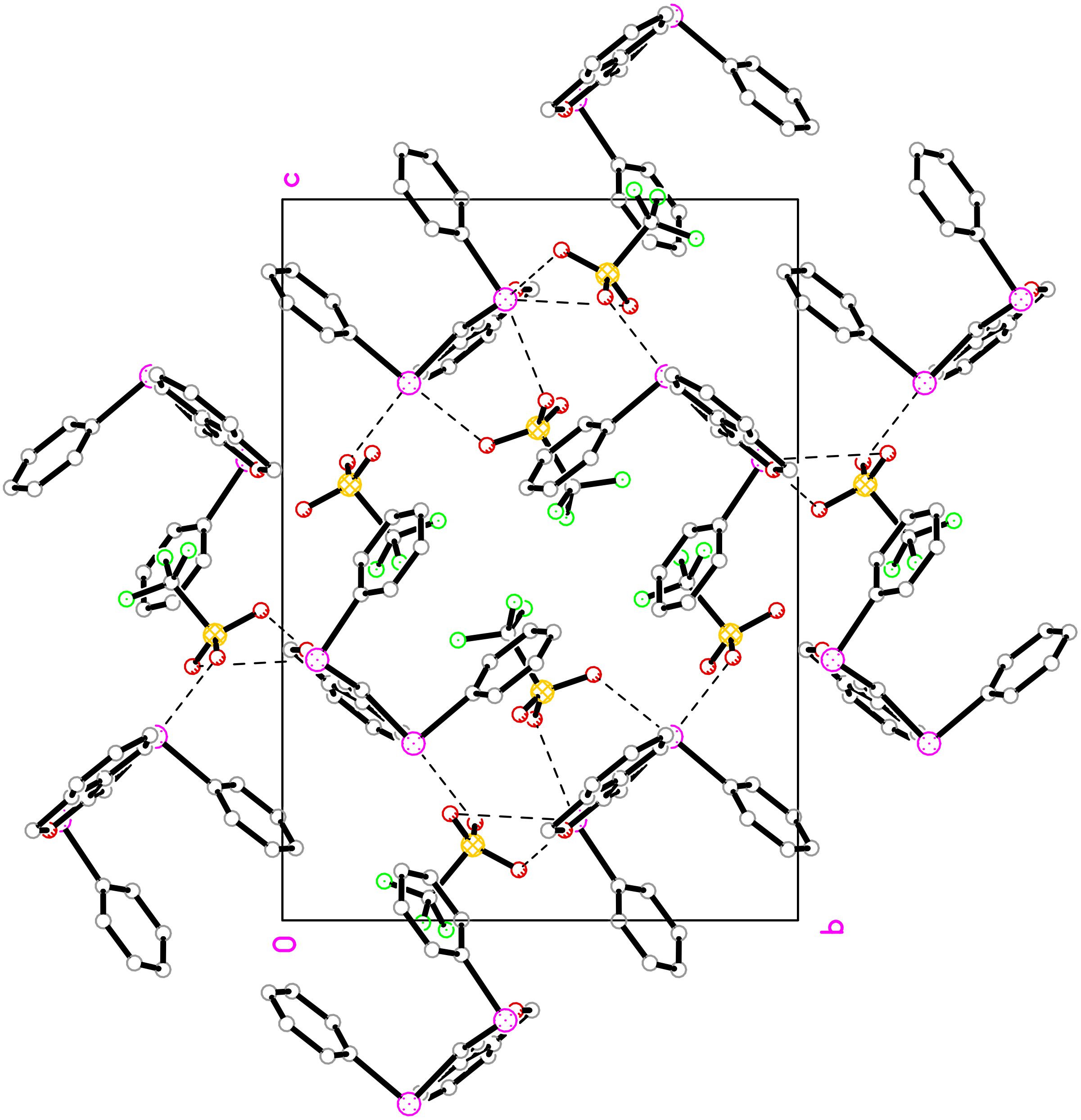
 *   -0.0731 (0.0041)  O1
 *   -0.0054 (0.0044)  C1
 *   -0.0049 (0.0047)  C2
 *   -0.0367 (0.0047)  C3
 *   -0.0303 (0.0048)  C4
 *    0.0250 (0.0053)  C5
 *    0.0306 (0.0057)  C6
 *    0.0198 (0.0055)  C7
 *    0.0051 (0.0051)  C8
 *    0.0699 (0.0038)  C9

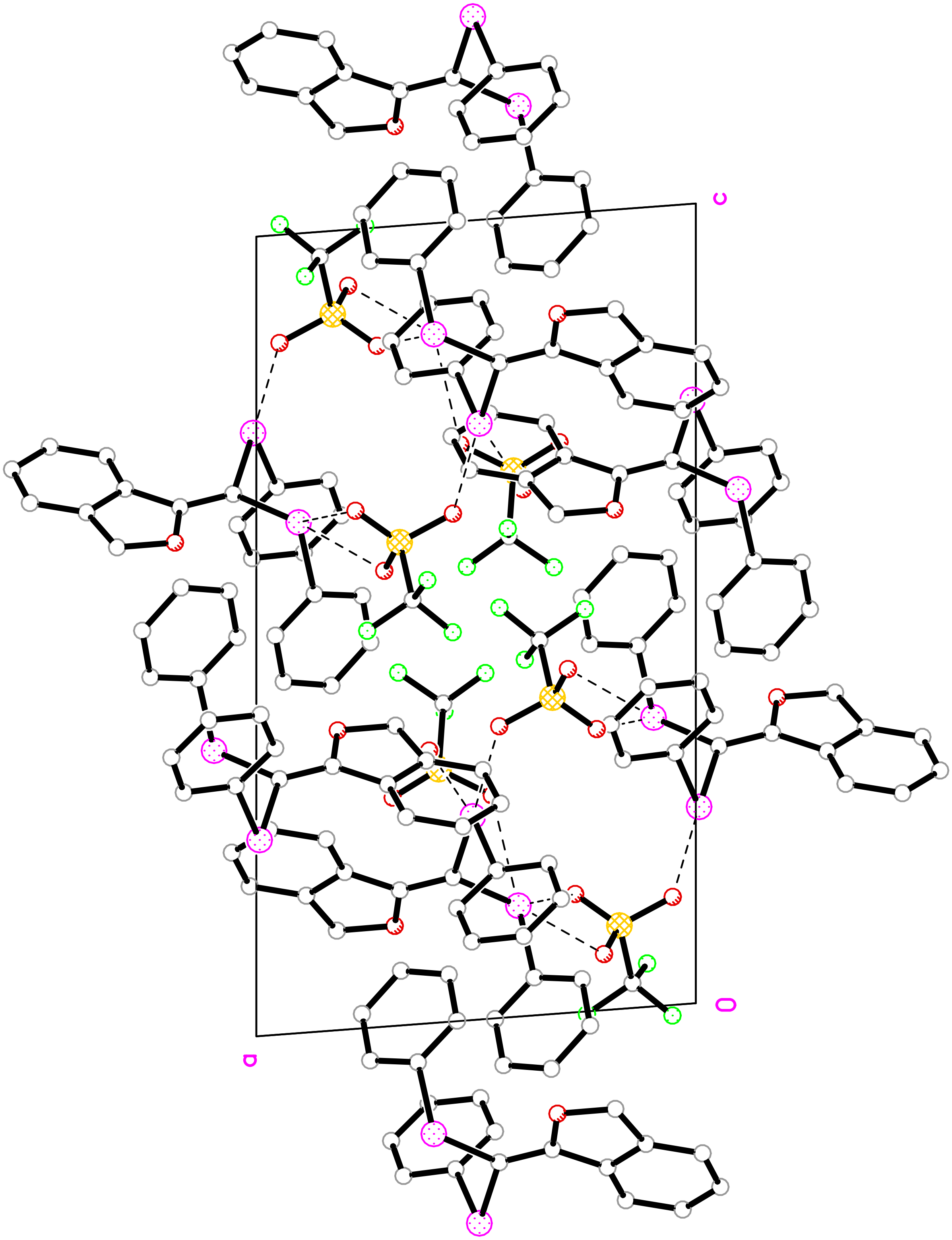
 Rms deviation of fitted atoms =   0.0381
```

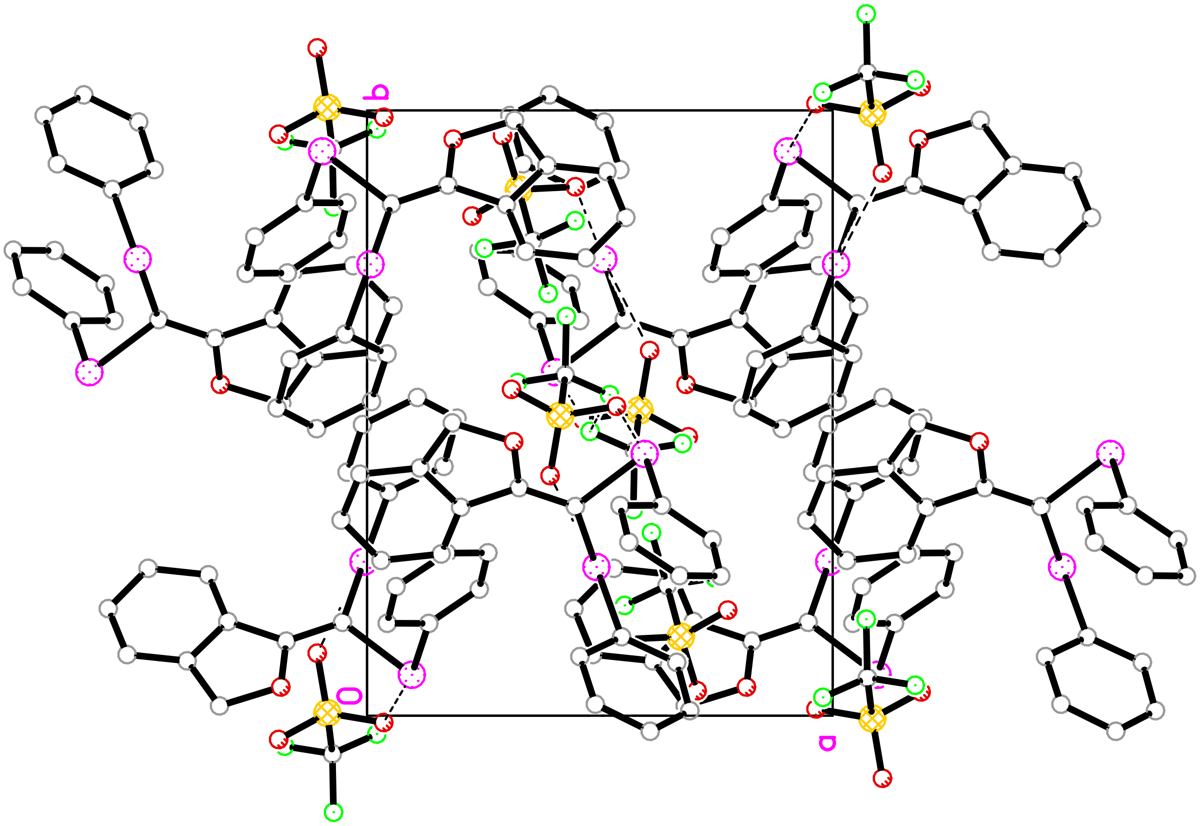



O3
O4
S1
O2
F3
C22
F1
F2'
C4
C3
C5
F2''
F2
C19
C18
C17
C20
C21
C16
I2
C2
C6
C7
C9
C1
C8
O6
O7
O1
O5
S2
C14
C15
C10
I1
C13
C12
C11
C23
F5
F4
F6


O7
F4
F6
S2
O6
C23
O5
F5
C6
C5
C7
C8
C4
O4
F2'
C3
C2
C1
O1
F3
F2
I2
I1
S1
F2''
C9
C22
O2
C11
O3
F1
C17
C16
C10
C12
C18
C21
C15
C13
C19
C20
C14


c
0
b


c
0
a


b
0
a

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