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One-Pot, Three-Component Arylalkynyl Sulfone Synthesis

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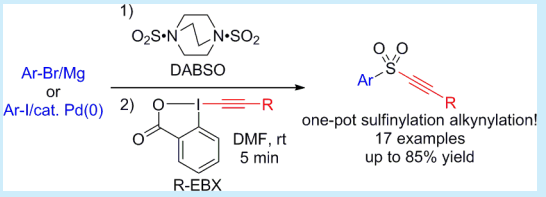
Supporting Information

ABSTRACT: A one-pot three-component protocol for the preparation of arylsulfonyl alkynes through the reaction of ethynyl-benziodoxolone (EBX) reagents, DABSO (DABCO·SO_2), and either organomagnesium reagents or aryl iodides with a palladium catalyst is reported. A broad range of aryl and heteroarylalkynyl sulfones were obtained in 46−85% overall yield.



Aryl sulfone-containing compounds display a variety of biological activities. Several of them are marketed drugs for treatment of human diseases. Examples include the antimigraine Vioxx (**1**),[1a] the antibacterial Dapsone (**2**)[1b] and the antiandrogen Casodex (**3**)[1c] (Figure 1).

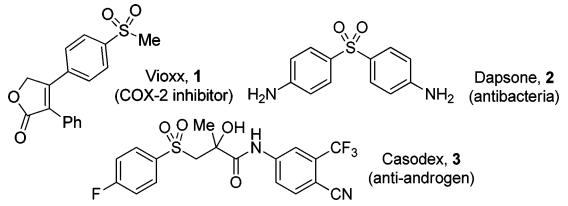
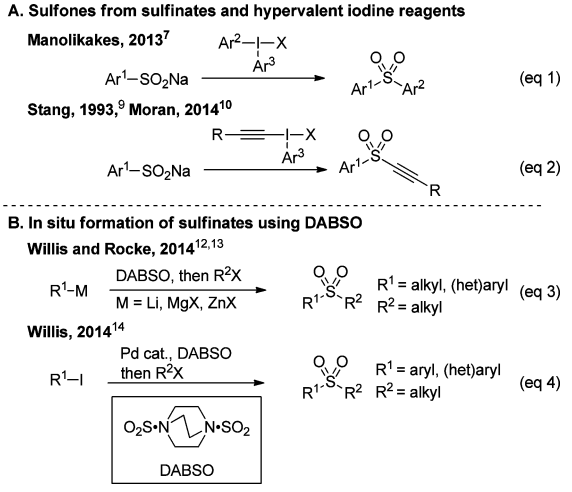


Figure 1. Biologically active aryl sulfones.

Among all sulfones, (aryl)alkynyl sulfones constitute an important class of building blocks due to their versatile reactivity. The sulfonyl unit has a strong electron-withdrawing character that enhances the reactivity of the triple bond.[2] Therefore, sulfonyl acetylenes are widely utilized in cycloadditions and conjugate additions reactions. They were also found to react in certain cases with organometallic reagents or radicals through 1,3-addition to generate anions or radical intermediates, followed by an elimination of the sulfonyl group to give disubstituted alkynes.[3]

Up to now, the preparation of sulfones could be achieved by numerous approaches, the most frequent one being the oxidation of the corresponding thiols.[4] Another convenient method is based on the reaction of sulfinate salts with electrophiles.[5] If the introduction of an aryl or an alkynyl group is desired on the sulfinate, hypervalent iodine reagents have emerged as reagents of choice, due to their exceptional reactivity.[6] For example, Manolikakes and co-workers reported that diaryl sulfones could be synthesized from arylsulfinate and diaryliodonium salts (Scheme 1A, eq 1).[7] Electrophilic alkynyl iodonium salts are also widely used in alkynylation reactions,[8] and their utilization for the preparation of alkynyl sulfones from sulfinate salts were reported by the groups of Stang[9] and Moran (Scheme 1A, eq 2).[10] However, the scope of arylsulfinate salts

Scheme 1. Recent Reports on Sulfone Synthesis



reported was limited (only $PhSO_2Na$ and *p*-$TolSO_2Na$), probably due to the low number of commercially available sulfinate salts. Recently, Willis and co-workers showed that DABSO (DABCO·SO_2, the combination of DABCO and sulfur dioxide) can serve as a surrogate of SO_2 for the in situ formation of sulfinate salts in the synthesis of sulfonamides.[11] More importantly, Willis and co-workers[12] and Rocke and co-workers[13] independently demonstrated a one-pot synthesis of sulfones from organolithium/magnesium and organozinc reagents, DABSO, and alkyl halides (Scheme 1B, eq 3). In addition, transition metal-catalyzed, e.g. palladium[14] (eq 4) and gold,[15] as well as metal-free[16] sulfinate salt formation with DABSO were also reported for sulfone synthesis. These recent breakthroughs have greatly simplified the synthesis of sulfones. However, a one-pot protocol for the preparation of arylalkynyl sulfones has still not been reported. The synthesis of this class

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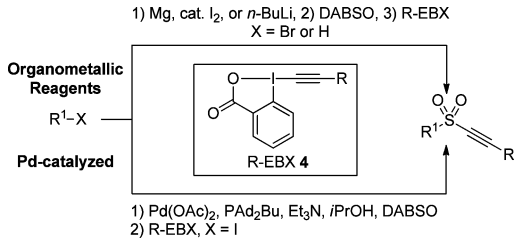
of compounds is especially challenging, as the products themselves are also highly reactive.

Our group is interested in alkyne synthesis using electrophilic alkynylation reagents, in particular ethynyl-benziodoxolones (EBX, **4**).[17,18] These cyclic hypervalent iodine reagents display high reactivity, but are more stable than the traditionally used alkynyliodonium salts. We therefore thought they would be well-suited to develop the first one-pot three-component synthesis of alkynyl sulfones. Herein we would like to present the successful implementation of this approach using EBX reagents **4**, DABSO, and organomagnesium/lithium reagents or aryl iodides with a palladium catalyst (Scheme 2).

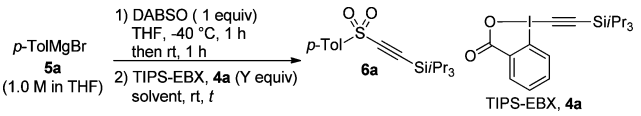
Scheme 2. Our Approach toward the Synthesis of Alkynyl Sulfones



The preparation of sulfonyl alkynes starting from tolyl magnesium bromide (**5a**) with TIPS-EBX (**4a**) and DABSO was examined first. Initially, the protocol developed by Willis for preparation of sulfonamides[11a] was utilized. Unfortunately, the desired product was not obtained when using THF only as solvent. To our delight, 16% yield of **6a** was observed when THF was removed and replaced by DMF (Table 1, entry 1).

Longer reaction time (14 h), and DMF/H_2O (v/v = 5/1) as a solvent system for the alkynylation did not give better results (Table 1, entries 2–4). On the other hand, we were pleased to observe an increased yield of **6a** (65%) when THF was not removed before adding DMF for the alkynylation step (Table 1, entry 5). In contrast, the addition of DMSO was not successful (Table 1, entry 6). A fast examination of TIPS-EBX **4a** loading and reaction time (Table 1, entries 6–12) showed that 1.2 equiv of **4a** and 5 min reaction time resulted in the production of **6a** in 80% yield (Table 1, entry 11). The lower yields observed with longer reaction times are probably due to the high reactivity of the formed alkynyl sulfone **6a**.

Table 1. Optimization of the Arylalkynyl Sulfone Synthesis



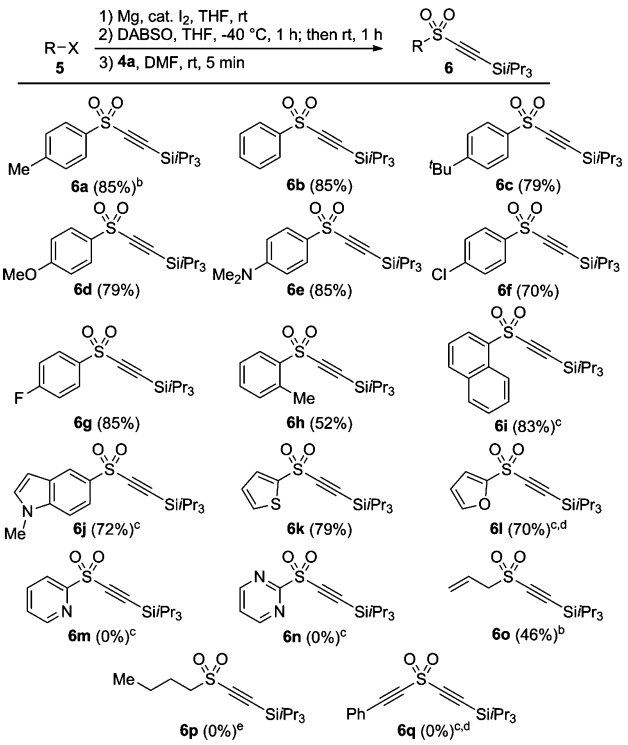
entry[a]	equiv of **4a**	solvent	t	yield (%)[d]
1	1.2	DMF[b]	2 h	16
2	1.2	DMF[b]	14 h	0
3	1.2	DMF/H_2O[b,c]	2 h	15
4	1.2	DMF/H_2O[b,c]	14 h	0
5	1.2	DMF	2 h	65
6	1.2	DMSO	2 h	0
7	1.5	DMF	2 h	50
8	1.5	DMF	1 h	50
9	1.5	DMF	30 min	75
10	1.5	DMF	5 min	78
11	1.2	DMF	5 min	80
12	1.1	DMF	5 min	75

[a]0.06 mmol *p*-tolylmagnesium bromide (**5a**) was used in 0.2 mL of THF. 0.2 mL of solvent was added for the second step (final concentration: 0.13 M). [b]THF was removed before adding 0.2 mL of solvent (final concentration: 0.3 M). [c]Ratio (v/v) = 5/1. [d]The yield was obtained based on ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal reference.

With optimized conditions in hand we examined the scope of the one-pot sulfinylation alkynylation from organometallic reagents with TIPS-EBX **4a** (Scheme 3). Acetylene **6a** was obtained in good yield on preparative scale (85%). We further expanded the utility of this protocol by preparing the organomagnesium/lithium reagents immediately before use. Phenylalkynyl sulfone **6b** could be synthesized in 85% overall yield starting from bromobenzene **5b**. Other electron-rich and electron-poor functional groups were well-tolerated. For example, *p*-*tert*-butyl, *p*-methoxy, and *p*-dimethylaminosulfonyl alkynes **6c**, **6d**, and **6e** were obtained in good yields (79, 79, and 85% respectively). *p*-Chloro and *p*-fluorophenylsulfonyl alkynes **6f**, and **6g** were also synthesized in 70 and 85% yield, respectively.

o-Tolyl sulfinate magnesium salt gave a lower yield of product **6h** (52%). In addition, alkyne **6i** was also obtained from 1-bromonaphthalene in 83% yield. The heteroaryl bromides 5-bromo-*N*-methylindole (**5j**) and 2-bromo-thiophene (**5k**) gave products **6j** and **6k** in 72 and 79% yield,

Scheme 3. Scope of the One-Pot Sulfinylation Alkynylation[a]



[a]Reaction conditions: 0.20 mmol of **5** (1.0 equiv), 0.20 mmol of Mg (1.0 equiv), 0.20 mmol of DABSO (1.0 equiv), and THF (0.65 mL) were used for the first step. 0.24 mmol of TIPS-EBX **4a** (1.2 equiv) and DMF (0.65 mL) were added for the second step. Isolated yield after purification on column chromatography is given. [b]Commercial Grignard reagent was used. [c]0.5 M organometallic reagent in THF. [d]R-Li was generated from the corresponding C–H bond with *n*-BuLi. [e]Commercial *n*-BuLi was used.

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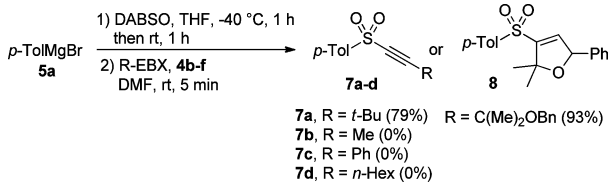
respectively. Sulfone **6l** was synthesized in 70% yield starting from furan **5l** using a selective lithiation at C2. However, 2-pyridinyl and 2-pyrimidinyl alkynyl sulfones **6m** and **6n** could not be synthesized using this one-pot protocol. Allylsulfonyl alkyne **6o** was obtained in 46% yield. Sulfones **6p** and **6q** could not be obtained when starting from the corresponding organolithium reagents.

Further extension of the scope of the one-pot sulfonyl alkynylation was focused on *p*-tolyl Grignard (**5a**) with R-EBX reagents (Scheme 4). Alkyne **7a** was made in 79% yield using *t*-Bu-EBX **4b**.[18f] Unfortunately, Me-EBX **4c**,[18k] Ph-EBX **4d**,[18f] and *n*-Hex-EBX **4e**[18f] were not able to react with the in situ formed *p*-tolyl sulfinate salt to deliver the desired alkynes **7b**, **7c**, and **7d** respectively. Interestingly, dihydrofuran **8** was obtained in 93% yield when the EBX reagent **4f** was utilized in the alkynylation.

Scheme 4. Iodine Reagent Scope of the One-Pot Sulfinylation Alkynylation[a]

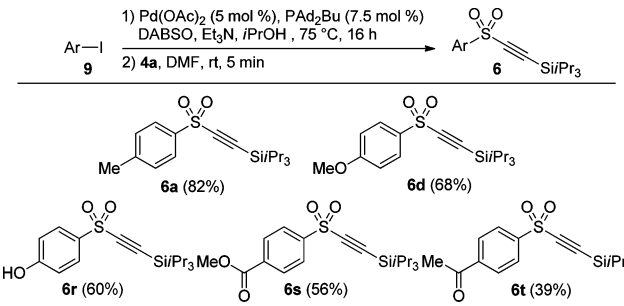


[a]Reaction conditions: 0.20 mmol of *p*-tolylMgBr (**5a**) (1.0 equiv), 0.20 mmol of DABSO (1.0 equiv) and THF (0.65 mL) were used for the first step. 0.24 mmol of R-EBX **4** (1.2 equiv) and DMF (0.65 mL) were added for the second step. Isolated yield after purification on column chromatography is given.

At least three different mechanisms could be considered for the alkynylation step in this one-pot protocol. A first possibility frequently occurring with hypervalent iodine reagents is direct nucleophilic attack of sulfinate onto the iodine atom of the benziodoxolone, followed by a C−S bond formation via a reductive elimination step.[6] Our group has recently discovered by computation an alternative mechanism for the alkynylation of thiols involving a concerted three-atom transition state including the iodine, the sulfur and the α-carbon atom of the alkyne.[18k] However, these two mechanisms are less likely to be involved in the alkynylation of sulfinates because (i) dihydrofuran **8** was obtained and this product most probably results from 1,5-C−H insertion of a carbene intermediate, and (ii) EBX reagents **4c**−**f** did not give the desired alkyne products, in contrast to the high yields observed with thiols.[18k] These facts suggest that the reaction mechanism is different for sulfinates and most probably involves a third alternative: a conjugate addition of the sulfinate onto the β-alkynyl carbon of ethynyl-benziodoxolone, followed by an α-elimination of the aryl iodide to give a carbene intermediate, and finally a 1,2-shift to form the alkyne.[10,19]

One disadvantage of the developed sulfonylation-alkynylation protocol involving organo-magnesium or -lithium reagents is that it cannot be applied to substrates sensitive to strong bases or nucleophiles. In order to further enhance the generality of the one-pot approach for the synthesis of alkynyl sulfones, we then examined a Pd-catalyzed ammonium sulfinate salt formation starting from aryl iodides which can proceed under much milder conditions (Scheme 1B, eq 4).[14] Alkynes **6a** (82%) and **6d** (68%) could be synthesized in comparable yields using the Pd-catalyzed sulfinylation in the first step (Scheme 5).

Scheme 5. Scope of the Pd-Catalyzed One-Pot Sulfinylation Alkynylation[a]



[a]Reaction conditions: 0.20 mmol of ArI **9** (1.0 equiv), 10 μmol of $Pd(OAc)_2$ (5 mol %), 15 μmol of PAd_2Bu (7.5 mol %), 0.20 mmol DABSO (1.0 equiv), Et_3N (3.0 equiv) and *i*PrOH (1.7 mL) were used for the first step. 0.24 mmol of TIPS-EBX **4a** (1.2 equiv) and DMF (0.65 mL) were used for the second step. Isolated yield after purification on column chromatography is given.

Gratifyingly, alkynes **6r**, **6s** and **6t** bearing potentially base- and nucleophile sensitive hydroxy, methyl ester, and methyl ketone groups were synthesized successfully in 39−60% yield.

In conclusion, we report a simple one-pot protocol for sulfonylation-alkynylation starting either from organomagnesium/lithium reagents or from aryl iodides with a palladium catalyst, DABSO, and EBX reagents, in up to 85% overall yield. The method from organomagnesium/lithium reagents gives an unprecedented efficient access to aryl-alkynyl sulfones bearing benzene rings with electron-poor or electron-rich substituents, as well as heterocycles. The complementary Pd-catalyzed protocol can be used for substrates sensitive to the use of strongly basic or nucleophilic organometallic reagents. Extension of the scope and investigations on the mechanism of the sulfonyl alkynylation are currently underway and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and 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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Notes

The authors declare no competing financial interest.

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Table of Content

1. General Method

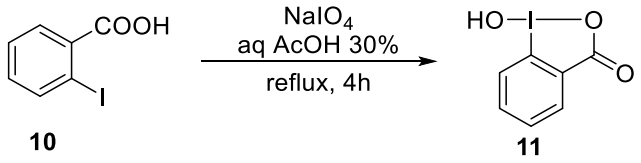
All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem, Maybrige, TCI or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F_{254} TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain.Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, all signals were reported in ppm with the internal chloroform signal at 7.26 ppm. 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 Bruker DPX-400 100 MHz spectrometer in chloroform-d, all signals were reported in ppm with the internal chloroform signal at 77.0 ppm. ^{19}F-NMR spectra were recorded on a Brucker DPX-400 376 MHz spectrometer in chloroform-d. No internal standard was used for ^{19}F-NMR spectra. 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). 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.

2. Synthesis of Reagents and Starting Materials

1-[(Tri*iso*propyllsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX, **4a**), [1] 3,3-dimethylbutynyl-1,2-benziodoxol-3(1*H*)-one (*t*Bu-EBX, **4b**), [2] and propynyl-1,2-benziodoxol-3(1*H*)-one (Me-EBX, **4c**), 1-[phenylethynyl]-1,2-benziodoxol-3(1*H*)-one (Ph-EBX, **4d**), octynyl-1,2-benziodoxol-3(1*H*)-one (Hex-EBX, **4e**), and 3-(benzyloxy)-3-methyl-but-1-yn-1-yl)-1,2-benziodoxol-3(1H)-one (**4f**), [3] were prepared by using our reported protocol. The reported experimental data are given again in order to give all the data to reproduce the results in a single file.

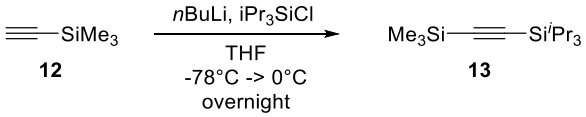
Preparation of 1-[(triisopropyllsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one (TIPS-EBX, 4a)[1]

1-Hydroxy-1,2-benziodoxol-3(*1H*)-one (11)



"Caution: reaction carried out behind a safety shield! $NaIO_4$ (77.2 g, 0.361 mol, 1.0 equiv) and 2-iodobenzoic acid (**10**) (89.5 g, 0.361 mmol, 1.0 equiv) were suspended in 30% (v:v) aq. AcOH (700 mL) under air in a 4-neck sulfonation flask equipped with a mechanic stirrer, a thermometer and a condenser. The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (500 mL) and allowed to cool to room temperature, protecting it from light. After 45 min, the suspension was added to water (1.5 L) and the crude product was collected by filtration, washed on the filter with ice water (3 x 300 mL) and cold acetone (3 x 300 mL), and air-dried in the dark overnight to give the pure product **11** (77.3 g, 0.292 mol, 81% 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*). The characterization data for trimethylsilyl(triisopropylsilyl)acetylene corresponded to the reported values.[1]

Trimethylsilyl(triisopropylsilyl)acetylene (13)

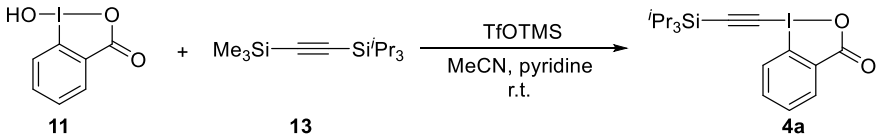


"Trimethylsilylacetylene (**12**) (30.3 ml, 213 mmol, 1 equiv) was charged in a 4-neck 500 mL flask equipped with a thermometer, a dropping funnel, an agitator magnetic and a nitrogen arrival. THF (330 mL) was added via a dropping funnel and the reaction was cooled to -78°C.

[1] Brand, J. P.; Waser, J. *Synthesis* **2012**, *44*, 1155.
[2] Brand, J. P.; Chevalley, C.; Scopelliti, R.; Waser, J. *Chem. Eur. J.* **2012**, *18*, 5655.
[3] Frei, R.; Wodrich, M. D.; Hari, D. P.; Borin, P. A.; Chauvier, C.; Waser, J. *J. Am. Chem. Soc.* **2014**, *136*, 16563.

^{n}BuLi (86 mL, 0.21 mmol, 0.98 equiv) was added and the reaction was stirred for 5 minutes at -78°C, then warmed to 0°C and stirred for 5 minutes. The reaction was then cooled back to -78°C and $^{i}Pr_3SiCl$ (45.5 mL, 213 mmol, 1 equiv) was added dropwise via a dropping funnel. The mixture was then allowed to warm to r.t. and stirred overnight. A saturated solution of NH_4Cl (300 mL) was added and the reaction was extracted with Et_2O (2x300 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. Distillation of the crude product (1.4 mbar, 55°C) afforded trimethylsilyl (triisopropylsilyl) acetylene (**13**) (51.4 g, 203 mmol, 95%) as a colorless liquid." ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (m, 21H, TIPS), 0.18 (s, 9H, TMS). The characterization data for trimethylsilyl(triisopropylsilyl)acetylene corresponded to the reported values.[1]

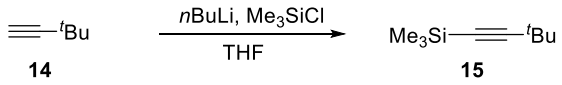
1-[(Tri*iso*propyllsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX, 4a)



"Caution: reaction carried out behind a safety shield! 2-iodosylbenzoic acid (**11**) (26.4 g, 100 mmol, 1.0 equiv) was charged in a four-neck flat-bottom flask equipped with a thermometer, a dropping funnel, a mechanic stirrer and a nitrogen arrival. The system was flushed with N_2 by three vacuum/N_2 cycles. Anhydrous acetonitrile (350 mL) was then canulated. The reaction mixture (white suspension) was cooled to 4 °C and then trimethylsilyltriflate (20.0 mL, 110 mol, 1.1 equiv) was added dropwise for 15 min via a dropping funnel. The dropping funnel was rinsed with anhydrous acetonitrile (10 mL). No increase of temperature was observed. The ice bath was removed and the reaction stirred for 15 min. Trimethylsilyl)(tri*iso*propylsilyl)acetylene (**13**) (28.0 g, 110 mmol, 1.1 equiv) was added dropwise via dropping funnel over 15 min (the colorless suspension was converted to a yellow solution). The dropping funnel was rinsed with anhydrous acetonitrile (10 mL) and the reaction was stirred for 30 min. Then pyridine (9.9 mL, 25 mmol, 1.1 equiv) was added dropwise via a dropping funnel over 5 min. After 15 min, the reaction mixture was transferred in a one-neck 1L flask and reduced under reduced pressure until a solid was obtained. The solid was dissolved in CH_2Cl_2 (250 mL) and transferred in a 2L separatory funnel. The organic layer was added and washed with 1 M HCl (150 mL) and the aqueous layer was extracted with CH_2Cl_2 (250 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (2x250 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The resulting solid (44.8 g) was then recristallized in CH_3CN (110 mL). The colorless solid obtained over cooling down was then filtered over Büchner, washed with hexanes (2x40 mL) and dried for 1 h at 40°C at 5 mbar. TIPS-EBX (**4a**) (36.2 g, 84.5 mmol, 85%) was obtained as white crystals. Mp (Dec.) 170-176°C." ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.44 (m, 1H, Ar-*H*), 8.29 (m, 1H, Ar-*H*), 7.77 (m, 2H, Ar-*H*), 1.16 (m, 21H, TIPS). The characterization data for trimethylsilyl(triisopropylsilyl)acetylene corresponded to the reported values.[1]

Preparation of 3,3-dimethylbutynyl-1,2-benziodoxol-3(1H)-one (tBu-EBX, 4b)[2]

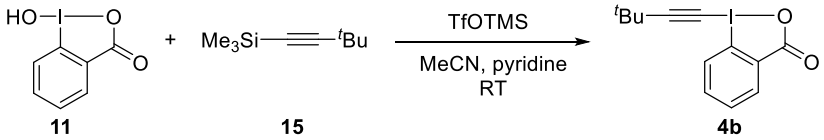
(3,3-dimethylbut-1-yn-1-yl)trimethylsilane



14 15

"n-butyllithium (2.5 M in hexanes, 8.3 mL, 21 mmol, 1.04 equiv) was added dropwise to a stirred solution of 3,3-dimethylbut-1-yne (**14**) (2.54 mL, 20.4 mmol, 1.02 equiv) in THF (70 mL) at –78 °C. The mixture was stirred for 2 h at -78°C. Trimethylsilylchloride (2.54 mL, 20.0 mmol, 1.0 equiv) dissolved in THF (10 mL) was added dropwise. The mixture was then allowed to warm to room temperature and stirred overnight. A saturated solution of ammonium chloride (100 mL) was added, and the reaction mixture was extracted with CH_2Cl_2 (2x100 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 (bp = 50°C, p = 0.5 mbar) to yield (3,3-dimethylbut-1-yn-1-yl)trimethylsilane (**15**) (1.35 g, 8.75 mmol, 44% yield) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H, ^{t}Bu), 0.13 (s, 9H, TMS)." The characterization data for (3,3-dimethylbut-1-yn-1-yl)trimethylsilane (**15**) corresponded to the reported values.[2]

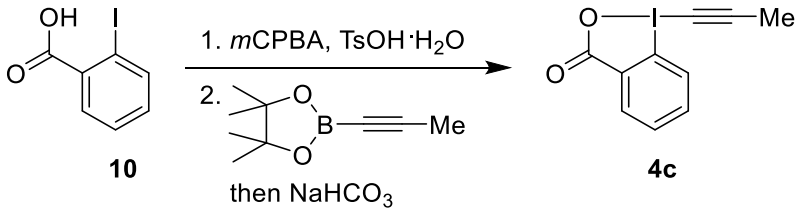
1-[3,3-Dimethylbutynyl]-1,2-benziodoxol-3(1*H*)-one (4b)



11 15 4b

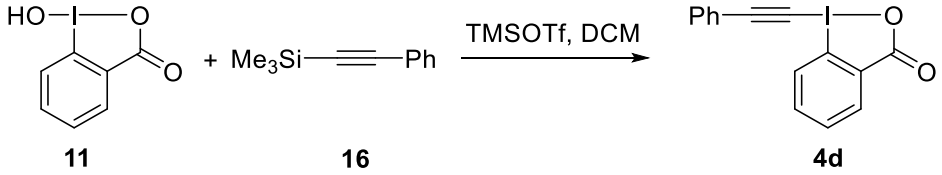
"Trimethylsilyltriflate (1.52 mL, 8.42 mmol, 1.0 equiv, freshly distilled) was added dropwise to a stirred solution of 2-iodosylbenzoic acid (**11**) (2.69 g, 10.1 mmol, 1.2 equiv) in acetonitrile (30 mL). 3,3-dimethylbut-1-yn-1-yl)trimethylsilane (**15**) (1.30 g, 8.42 mmol, 1.0 equiv) was then added dropwise, followed, after 15 min, by the addition of pyridine (680 µL, 8.42 mmol, 1.0 equiv). The mixture was stirred 10 min. The solvent was then removed under reduced pressure. CH_2Cl_2 and 1 M NaOH were added. The resulting suspension was filtered. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Two recrystallization (with hot filtration) from acetonitrile were necessary to afforded 1-[3,3-dimethylbutynyl]-1,2-benziodoxol-3(1*H*)-one (**4b**) (1.43g, 4.36 mmol, 57%) as a colorless solid." Mp (Dec.) 189 – 192°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.39 (m, 1H, Ar-*H*), 8.12 (m, 1H, Ar-*H*), 7.75 (m, 2H, Ar-*H*), 1.37 (s, 9H, ^{t}Bu). The characterization data for 1-[3,3-Dimethylbutynyl]-1,2-benziodoxol-3(1*H*)-one corresponded to the reported values.[2]

Propynyl-1,2-benziodoxol-3(1*H*)-one (4c)



Following a slightly modified procedure,[4] 2-iodobenzoic acid (**10**) (1.07 g, 4.30 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$, 818 mg, 4.30 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 1.17 g, 4.73 mmol, 1.10 eq.) were dissolved in dichloromethane (7 mL) and 2,2,2-trifluoroethanol (7 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which propynyl-1-boronic acid pinacol ester (4.85 g, 21.2 mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 2.5 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (30 mL) and under vigorous stirring, saturated aq. $NaHCO_3$ (30 mL) was added. The mixture was stirred for 15 minutes, the two layers were separated and the aqueous phase was extracted with additional portions of dichloromethane (3 x 25 mL). The combined organic layers were washed with brine (25 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford **4c** (1.03 g, 3.60 mmol, 84%) as a white solid. R_f (EtOAc) = 0.10. Mp 124-150 °C (decomposition). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41-8.35 (m, 1 H, Ar*H*), 8.22-8.14 (m, 1 H, Ar*H*), 7.79-7.68 (m, 2 H, Ar*H*), 2.27 (s, 3 H, CCC*H*$_3$). The characterization data corresponded to the reported values.[3]

1-[Phenylethynyl]-1,2-benziodoxol-3(1*H*)-one (Ph-EBX, 4d)

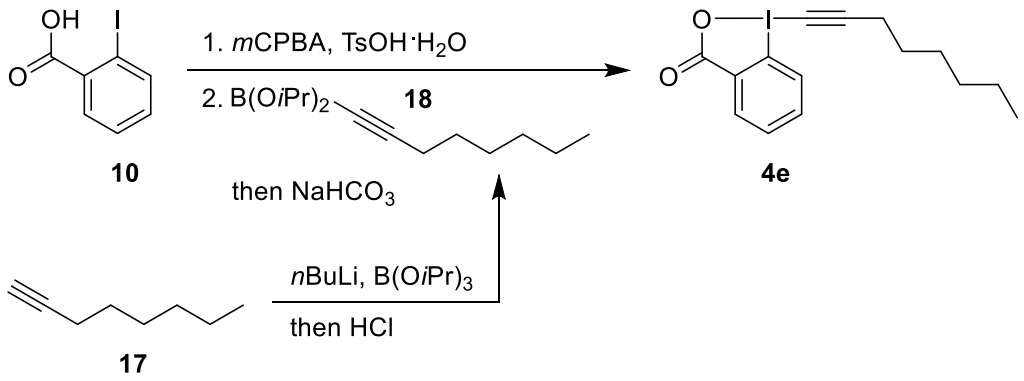


Following a reported procedure,[2] trimethylsilyltriflate (1.60 mL, 8.56 mmol, 1.1 eq.) was added dropwise to a stirred solution of 2-iodosylbenzoic Trimethylsilyl triflate (7.50 mL, 41.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (**11**) (10.0 g, 37.7 mmol, 1 equiv) in CH_2Cl_2 (100 mL) at RT. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of trimethyl(phenylethynyl)silane (**16**) (8.10 mL, 41.5 mmol, 1.1 equiv) (slightly exothermic). The resulting suspension was stirred for 6 h at RT, during this time a white solid was formed. A saturated solution of $NaHCO_3$ (100 mL) was then added and the mixture was

[4] Bouma, M. J.; Olofsson, B. *Chem. Eur. J.* **2012**, *18*, 14242.

stirred vigorously. The resulting suspension was filtered on a glass filter of porosity 4. The two layers of the mother liquors were separated and the organic layer was washed with sat. $NaHCO_3$ (100 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting mixture was combined with the solid obtained by filtration and boiled in CH_3CN (300 mL). The mixture was cooled down, filtered and dried under high vacuum to afford **4d** (6.08 g, 17.4 mmol, 46 %) as a colorless solid. Mp (Dec.) 155 – 160°C (lit 153-155°C). ^{1}H NMR (400 MHz, $CDCl_3$) (*ca* 0.03 mmol/ml) δ 8.46 (m, 1 H, ArH), 8.28 (m, 1 H, ArH), 7.80 (m, 2 H, ArH), 7.63 (m, 2 H, ArH), 7.48 (m, 3 H, ArH). Consistent with reported data.[2]

Octynyl-1,2-benziodoxol-3(1*H*)-one (4e)



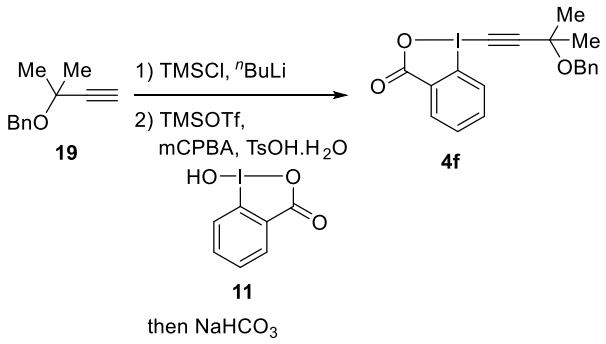
Following a slightly modified procedure,[5] a solution of 1-octyne (**17**) (747 mg, 6.78 mmol, 1.00 eq.) and dry diethyl ether (7.0 mL) was cooled to -78 °C, at which temperature 1.6 M *n*BuLi in hexanes (4.24 mL, 6.78 mmol, 1.00 eq.) was added dropwise. The mixture was stirred at -78 °C for 90 minutes and then canullated into a to -78 °C pre-cooled solution consisting of triisopropyl borate (1.56 mL, 6.78 mmol, 1.00 eq.) and dry diethyl ether (7.0 mL). The reaction mixture was stirred at -78 °C for 2 hours, after which 2.0 M HCl in diethyl ether (3.73 mL, 7.46 mmol, 1.10 eq.) was added. The cooling bath was removed and the mixture was stirred for an additional 60 minutes. After filtration and solvent removal, Kugelrohr distillation (75 °C at 0.6 mbar) furnished pure diisopropyloct-1-ynylboronate (**18**, 940 mg, 3.95 mmol, 58% yield) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.55 (sept, 2 H, *J* = 6.2 Hz, ^{i}Pr-CH), 2.27 (t, 2 H, *J* = 7.0 Hz, propargyl CH_2), 1.60-1.48 (m, 2 H, CH_2), 1.45-1.24 (m, 6 H, CH_2), 1.19 (d, 12 H, *J* = 6.2 Hz, ^{i}Pr-

[5] Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett.* **1988**, *29*, 2631.

CH_3), 0.89 (t, 3 H, J = 6.9 Hz, alkyl CH_3). The values of the ^{1}H NMR spectrum are in accordance with reported literature data.[6]

Following a slightly modified procedure,[4] 2-iodobenzoic acid (**10**) (692 mg, 2.79 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$, 531 mg, 2.79 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 756 mg, 3.07 mmol, 1.10 eq.) were dissolved in dichloromethane (4.5 mL) and 2,2,2-trifluoroethanol (4.5 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which diisopropyloct-1-ynylboronate (**18**, 930 mg, 3.90 mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 2 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (30 mL) and under vigorous stirring, saturated aq. $NaHCO_3$ (30 mL) was added. The mixture was stirred for 15 minutes, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford **4e** (940 mg, 2.64 mmol, 95%) as a white solid. R_f (EtOAc) = 0.25. Mp 50-63 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42-8.35 (m, 1 H, Ar*H*), 8.20-8.13 (m, 1 H, Ar*H*), 7.78-7.69 (m, 2 H, Ar*H*), 2.59 (t, 2 H, J = 7.1 Hz, CCC*H*$_2$), 1.70-1.58 (m, 2 H), 1.51-1.39 (m, 2 H), 1.38-1.26 (m, 4 H), 0.94-0.86 (m, 3 H, CH_2CH_3). Consistent with reported data.[3]

3-(benzyloxy)-3-methyl-but-1-yn-1-yl)-1,2-benziodoxol-3(1H)-one(4f)[3]



"(((2-methylbut-3-yn-2-yl)oxy)methyl)benzene (**19**) (850 mg, 4.90 mmol, 1.00 eq.) was dissolved in 10 mL of dry THF. Next, ^{n}BuLi (2.5 M in hexane, 5.1 mL, 13 mmol, 2.6 eq.) was added through syringe dropwise over 10 minutes and the reaction mixture was stirred for another

[6] Morita, R.; Shirakawa, E.; Tsuchimoto, T.; Kawakami, Y. *Org. Biomol. Chem.* **2005**, *3*, 1263.

10 minutes to get a brownish-red solution. Next, TMSCl (0.70 mL, 5.5 mmol, 1.1 eq.) was added dropwise to get a clear solution and the reaction mixture was stirred for 1.5 h at 0 °C. The resulting reaction mixture was continuously stirred at room temperature for 2.5 h until a white solid precipitated. It was then diluted with hexane (30 mL), washed with water (3 x 20 mL), brine (20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography using EtOAc:Pentane 1:20 as mobile phase to afford (3-(benzyloxy)-3-methylbut-1-yn-1-yl)trimethylsilane in 33% (362 mg, 1.47 mmol) yield, which was used directly in the next step."

"Trimethylsilyltriflate (1.60 mL, 8.56 mmol, 1.1 eq.) was added dropwise to a stirred solution of 2-iodosylbenzoic acid (**11**) (2.12 g, 7.99 mmol, 1.0 eq.) in acetonitrile (40 mL) at 0 °C. After 15 minutes, (3-(benzyloxy)-3-methylbut-1-yn-1-yl)trimethylsilane (2.07 g, 8.89 mmol, 1.05 eq.) was added dropwise, followed, after 30 min, by the addition of pyridine (6 mL). The mixture was stirred for 20 minutes. The solvent was then removed under reduced pressure and the crude oil was dissolved in dichloromethane (100 mL). The organic layer was washed with 0.5 M HCl (100 mL) and the aqueous layer was extracted with CH_2Cl_2 (100 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (2 x 100 mL), brine (100 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Recrystallization from hot EtOAc afforded 3-(benzyloxy)-3-methyl-but-1-yn-1-yl)-1,2-benziodoxol-3(1H)-one (**4f**) (770 mg, 0.183 mmol, 23%) as a light yellow solid." Mp 146.6-148.0 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.39 (dd, 1H, *J* = 7.3, 1.8 Hz, Ar-*H*), 8.11 (dd, 1H, *J* = 8.2, 1.1 Hz, Ar-*H*), 7.78-7.62 (m, 2H, Ar-*H*), 7.39-7.31 (m, 4H, Ar-*H*), 7.31-7.27 (m, 1H, Ar-*H*), 4.70 (s, 2H, ArCH_2), 1.69 (s, 6H, 2 x CH_3). The characterization data for 3-(benzyloxy)-3-methyl-but-1-yn-1-yl)-1,2-benziodoxol-3(1H)-one corresponded to the reported values.[3]

General procedure I*: preparation of non-commercially available magnesium or lithium reagents*

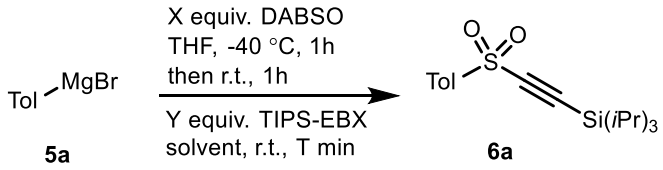
p-Tolylmagnesium bromide (1.0 M solution in THF) and allylmagnesium bromide (1.0 M solution in THF) were used as received from Sigma-Aldrich. Other Grignard or lithium reagents were prepared using the procedures described below.

For magnesium reagents: magnesium turnings (24 mg, 1.0 mmol) and a stirring bar were placed in a 7.5 mL microwave tube with a cap (not sealed at this moment). The tube was flamed dry under high vacuum for 1 min. After cooling down to r.t., and filled with nitrogen, a catalytic amount of iodine was added, and the tube was sealed; evacuated and filled with nitrogen three times. Anhydrous THF was added (1 mL), and the resulting solution was stirred for 5 min before adding the corresponding aryl bromide (1.00 mmol). The resulting mixture was stirred for 2 h at r.t. The Grignard reagent (0.20 mL, <0.20 mmol) was used directly for reactions.

For lithium reagents: a 7.5 mL microwave tube was charged with a stirring bar with a sealed cap. The tube was flamed dry under high vacuum for 1 min. After cooling down to r.t., and filled with nitrogen, anhydrous THF (1 mL) and the corresponding heteroarene (1.00 mmol) were added and placed in a -78 ^{0}C (acetone + dry ice) bath. *n*BuLi (2.5 M in hexane, 0.40 mL, 1.0 mmol) was added, and the resulting mixture was stirred for 30 min at -78 ^{0}C. The lithium reagent (0.28 mL, 0.20 mmol) was used directly for next step reactions.

3. Sulfinylation-Alkynylation Reaction

Optimization procedure:

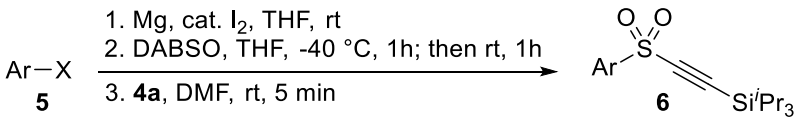


A stirring bar was placed in a 7.5 mL microwave tube with a cap (not sealed at this moment), and flamed dry under high vacuum. After cooling down to r.t. and filled with nitrogen, DABSO (15 mg, 0.060 mmol) as added in to the microwave tube. The tube was sealed, evacuated and filled with nitrogen four times. Anhydrous THF (0.2 mL) was added, and the tube was replaced in a -40 ^{0}C (MeCN + dry ice) bath for 10 min. *p*-tolylmagnesium bromide (**5a**) (1.0 M solution in THF, 64 μL, 0.060 mmol) was added, and the reaction mixture stirred for 1 h. The cooling bath was then removed, and the resulting solution was stirred at r.t. for another 1 h.

The sealed cap was removed; the solvent (0.2 mL) and TIPS-EBX (**4a**) were subsequently added to the resulting solution and stirred for further 5 min. The reaction was quenched by adding 1 M HCl (1 mL). The resulting layers were separated, and the aqueous layer was extracted with EtOAc (3x3 mL). All of the organic layers were combined, washed with (sat.) $NaHCO_3$, dried over $MgSO_4$, and filtrated. The organic solvent was removed under reduced pressure to give the crude adduct. 1,3,5-trimethoxybenzene was used as the internal standard for the calculation of ^{1}H-NMR yields.

Entry	X	Y	solvent	T (min)	Yield (%)
1	1	1.2	THF removed before adding DMF	120	16
2	1	1.2	THF removed before adding DMF	14 h	0
3	1	1.2	THF removed before adding DMF/H_2O (5/1)	120	0
4	1	1.2	THF removed before adding DMF/H_2O (5/1)	14 h	15
5	1	1.2	DMSO	120	0
6	1	1.2	DMF	120	65
7	1	1.5	DMF	120	50
8	1	1.5	DMF	60	50
9	1	1.5	DMF	30	75
10	1	1.5	DMF	5	78
11	1	1.2	DMF	5	80
12	1	1.1	DMF	5	75

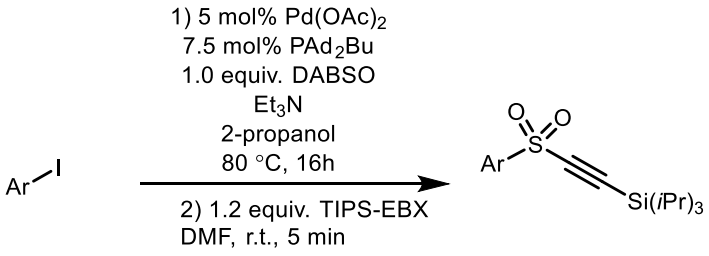
General procedure* II *for one-pot preparation of alkynyl sulfones using Grignard reagents.



Following a slightly modified reported procedure,[7] a stirring bar was placed in a 7.5 mL microwave tube with a cap (not sealed at this moment), and flamed dry under high vacuum. After cooling down to r.t. and filled with nitrogen, DABSO (48 mg, 0.20 mmol) was added in to the microwave tube. The tube was sealed, evacuated and filled with nitrogen four times. Anhydrous THF (0.65 mL) was added, and the tube was replaced in a -40 ^{0}C (MeCN + dry ice) bath for 10 min. The corresponding Grignard reagent (0.20 mL, 0.20 mmol) was added, and the reaction mixture was stirred for 1 h. The cooling bath was then removed, and the resulting solution was stirred at r.t. for another 1 h.

The sealed cap was removed, and DMF 0.65 mL and TIPS-EBX (**4a**) ((103 mg, 0.240 mmol) or other R-EBX **4** (0.24 mmol) were subsequently added to the resulting solution and stirred for further 5 min. The reaction was quenched by adding 1 M HCl (2 mL). The resulting layers were separated and the aqueous layer was extracted with EtOAc (3x5 mL). All of the organic layers were combined, washed with (sat.) $NaHCO_3$, dried over $MgSO_4$, and filtrated. The organic solvent was removed under reduced pressure to give the crude product. The crude product was purified by column chromatography to afford the desired product. The yields given are based on the indicated concentration for commercial Grignard reagents and on the used bromide starting material for self-made Grignard reagents.

General procedure* III *for one-pot preparation of alkynyl sulfones using palladium catalysis.



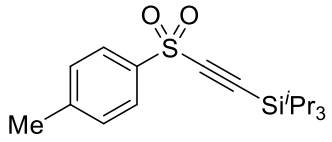
Scope-3

Following a slightly modified reported procedure,[8] a 7.5 mL microwave tube was charged with a stirring bar, $Pd(OAc)_2$ (2.2 mg, 10 μmol), CataCXium A (5.4 mg, 15 μmol), DABSO (48 mg, 0.20 mmol), and aryl iodide (0.20 mmol), sealed with a cap and evacuated and filled with nitrogen three times. Anhydrous triethylamine (84 μL, 0.60 mmol) and anhydrous 2-propanol (1.7 mL) were added and the resulting solution stirred in a steel tube holder at 75 ^{0}C for 16 h.

[7] Deeming, A. S.; Russell, C. J.; Hennessy, A. J.; Willis, M. C. *Org. Lett*. **2014**, *16*, 150.
[8] Emmett, E. J.; Hayter, B. R.; Willis, M. C. *Angew. Chem. Int. Ed*. **2014**, *53*, 10204.

After cooling to r.t., anhydrous DMF (0.65 mL) and TIPS-EBX **4a** (103 mg, 0.240 mmol) were subsequently added to the resulting solution and stirred for further 5 min. The reaction was quenched by adding 1 M HCl (2 mL). The resulting layers were separated and the aqueous layer was extracted with EtOAc (3x5 mL). All of the organic layers were combined, washed with (sat.) $NaHCO_3$, dried over $MgSO_4$, and filtrated. The organic solvent was removed under reduced pressure to give the crude product. The crude product was purified by column chromatography to afford the desired product.

Triisopropyl(tosylethynyl)silane (6a)[9]



p-Tolylmagnesium bromide (0.20 mL, 1.0M in THF, 0.20 mmol) was used in this reaction. **6a** was obtained as a colorless gel (57 mg, 0.17 mmol, 85% yield) by using the general procedure II. Alternatively, the title compound was obtained as a colorless gel (55 mg, 0.16 mmol, 82% yield) by using the general procedure III.

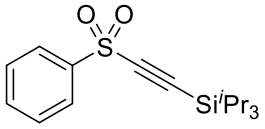
R*f* 0.7 (pentane/EtOAc 3/1, $KMnO_4$, UV); pentane/EtOAc 6/1 was used as the eluting solvents for purification.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 8.1 Hz, 2H Ar-*H*), 2.39 (s, 3H, C*H*$_3$), 0.96 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 145.2, 139.1, 129.8, 127.2, 100.8, 100.1, 21.7, 18.3, 10.8.

The analytic data are in accordance with reported literature data.[9]

Triisopropyl((phenylsulfonyl)ethynyl)silane (6b)



Bromobenzene (21μL, 0.20 mmol) was used in this reaction. **6b** was obtained as a colorless gel (55 mg, 0.17 mmol, 85% yield)[10] by using the general procedure I and II.

R*f* 0.5 (pentane/EtOAc 5/1, $KMnO_4$); pentane/EtOAc 5/1 was used as the eluting solvents for purification.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H, Ar-*H*), 7.70 – 7.61 (m, 1H, Ar-*H*), 7.57 (ddd, *J* = 8.2, 6.6, 1.3 Hz, 2H, Ar-*H*), 1.19 – 0.95 (m, 21H, Si*i*Pr$_3$).

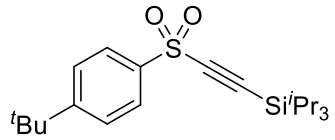
^{13}C-NMR (101 MHz, $CDCl_3$) δ 142.1, 134.0, 129.2, 127.2, 100.9, 100.6, 18.3, 10.8.

[9] Tykwinski, R. R.; Williamson, B. L.; Fisher, D. R.; Stang, P. J.; Arif, A. M. *J. Org. Chem*. **1993**, *58*, 5235.
[10] The corresponding compound contains ca. 5% grease. Rucker, C.; Fritz, H. *Magn. Reson. Chem.* **1988,** *26*, 1103.

IR 4352(w), 3853(w), 3661(s), 3227(w), 2939(br), 2124(w), 1934(w), 1452(m), 1407(s), 1407(s), 1251(s), 1055(s), 893(s), 795(m).

HRMS (ESI) calcd for $C_{17}H_{27}O_2SSi^+$ $[M+H]^+$ 323.1496, found 323.1497.

(((4-(Tert-butyl)phenyl)sulfonyl)ethynyl)triisopropylsilane (6c)



1-Bromo-4-*tert*-butylbenzene (35 μL, 0.20 mmol) was used in this reaction. **6c** was obtained as a colorless solid (60 mg, 0.16 mmol, 79% yield) by using the general procedure I and II.

R*f* 0.8 (pentane/EtOAc 4/1, $KMnO_4$, UV); pentane/EtOAc 10/1 was used as the eluting solvents for purification.

Mp 103-104 °C.

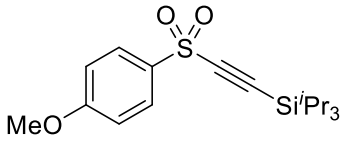
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.57 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 1.35 (s, 9H, *t*Bu), 1.02 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 158.1, 139.0, 127.0, 126.2, 100.9, 100.4, 35.3, 31.0, 18.3, 10.8.

IR 3674(m), 2971(br), 2122(w), 1934(w), 1592(w), 1394(s), 1331(m), 1251(m), 1158(m), 1058(s), 893(m), 790(m), 751(m).

HRMS (ESI) calcd for $C_{21}H_{35}O_2SSi^+$ $[M+H]^+$ 379.2122, found 379.2124.

Triisopropyl(((4-methoxyphenyl)sulfonyl)ethynyl)silane (6d)



4-Bromoanisole (25 μL, 0.20 mmol) was used in this reaction. **6d** was obtained as a colorless gel (56 mg, 0.16 mmol, 79% yield) by using the general procedure I and II. Alternatively, the title compound was obtained as a colorless gel (48 mg, 0.13 mmol, 68% yield) by using the general procedure III.

R*f* 0.7 (pentane/EtOAc 4/1, $KMnO_4$, UV); pentane/EtOAc 10/1 was used as the eluting solvents for purification.

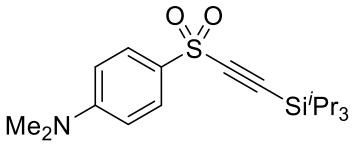
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.86 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.09 – 6.93 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 3.89 (s, 3H, OC*H*$_3$), 1.15 – 0.96 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.0, 133.6, 129.6, 114.4, 101.1, 99.4, 55.7, 18.3, 10.8.

IR 3853(w), 3674(s), 3224(w), 2970(br), 2270(w), 2124(w), 1934(w), 1597(w), 1408(s), 1251(s), 1078(s), 893(s), 810(m), 787(m).

HRMS (ESI) calcd for $C_{18}H_{29}O_3SSi^+$ $[M+H]^+$ 353.1601, found 353.1601.

<u>*N*,*N*-Dimethyl-4-(((triisopropylsilyl)ethynyl)sulfonyl)aniline (6e)</u>



4-Bromo-*N*,*N*-dimethylaniline (40 mg, 0.20 mmol) was used in this reaction. **6e** was obtained as a colorless solid (58 mg, 0.16 mmol, 79% yield) by using the general procedure I and II.

R*f* 0.65 (pentane/EtOAc 3/1, $KMnO_4$, UV); pentane/EtOAc 5/1 was used as the eluting solvents for purification.

Mp 114 °C.

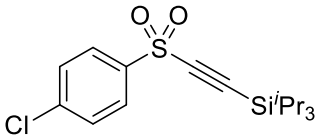
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 9.1 Hz, 2H, Ar-*H*), 6.68 (d, *J* = 9.1 Hz, 2H, Ar-*H*), 3.07 (s, 6H, N(C*H*$_3$)$_2$), 1.02 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.6, 129.3, 127.0, 110.9, 102.0, 97.4, 40.1, 18.3, 10.8.

IR 3674(s), 2973(br), 2113(w), 1934(w), 1595(w), 1407(s), 1251(s), 1089(s), 893(m), 782(m), 762(m).

HRMS (ESI) calcd for $C_{19}H_{32}NO_2SSi^+$ $[M+H]^+$ 366.1918, found 366.1922.

<u>(((4-Chlorophenyl)sulfonyl)ethynyl)triisopropylsilane (6f)</u>



1-Bromo-4-chlorobenzene (39 mg, 0.20 mmol) was used in this reaction. **6f** obtained as a colorless solid (50 mg, 0.14 mmol, 70% yield) by using the general procedure I and II.

R*f* 0.7 (pentane/EtOAc 4/1, $KMnO_4$, UV); pentane/EtOAc 10/1 was used as the eluting solvents for purification.

Mp 86 °C.

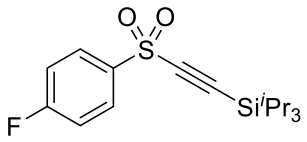
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.19 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 1.15 – 1.10 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 140.8, 140.5, 129.6, 128.7, 101.6, 100.2, 18.3, 10.8.

IR 3674(m), 2907(br), 2123(w), 1925(w), 1584(w), 1407(s), 1251(s), 1083(s), 882(m), 792(m), 751(m).

HRMS (ESI) calcd for $C_{17}H_{26}ClO_2SSi^+$ $[M+H]^+$ 357.1106, found 357.1111.

(((4-Fluorophenyl)sulfonyl)ethynyl)triisopropylsilane (6g)



1-Bromo-4-fluorobenzene (22 μL, 0.20 mmol) was used in this reaction. **6g** was obtained as a colorless solid (58 mg, 0.17 mmol, 85% yield) by using the general procedure I and II.

R*f* 0.7 (pentane/EtOAc 5/1, $KMnO_4$, UV); pentane/EtOAc 10/1 was used as the eluting solvents for purification.

Mp 77-78 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 2H, Ar-*H*), 7.18 (m, 2H, Ar-*H*), 1.14 – 0.86 (m, 21H, Si*i*Pr$_3$).

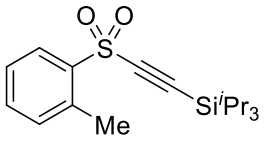
^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.9 (d, *J* = 257.3 Hz), 138.1 (d, *J* = 3.1 Hz), 130.2 (d, *J* = 9.8 Hz), 116.6 (d, *J* = 22.8 Hz), 101.2, 100.4, 18.3, 10.8.

^{19}F-NMR (376 MHz, $CDCl_3$) δ -102.5.

IR 3853(w), 3663(s), 3226(w), 2921(br), 2124(w), 1932(w), 1408(s), 1251(s), 1055(s), 893(s), 789(m).

HRMS (ESI) calcd for $C_{17}H_{26}FO_2SSi^+$ $[M+H]^+$ 341.1401, found 341.1402.

Triisopropyl((o-tolylsulfonyl)ethynyl)silane (6h)



2-Bromotoluene (24 μL, 0.20 mmol) was used in this reaction. **6h** was obtained as a colorless gel (35 mg, 0.10 mmol, 52% yield) by using the general procedure I and II.

R*f* 0.6 (pentane/EtOAc 4/1, $KMnO_4$, UV); pentane/EtOAc 6/1 was used as the eluting solvents for purification.

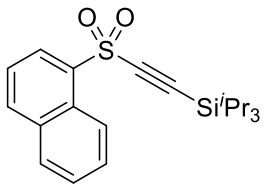
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0, 1.4 Hz, 1H, Ar-*H*), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H, Ar-*H*), 7.35 – 7.25 (m, 2H, Ar-*H*), 2.71 (s, 3H, C*H*$_3$), 1.25 – 0.88 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 139.7, 138.3, 134.0, 132.6, 128.6, 126.4, 100.4, 98.8, 19.9, 18.3, 10.8.

IR 4339(w), 3859(w), 3674(m), 2971(br), 2122(w), 1454(m), 1407(m), 1328(m), 1160(m), 1058(s), 883(m), 783(m).

HRMS (ESI) calcd for $C_{18}H_{29}O_2SSi^+$ $[M+H]^+$ 337.1652, found 337.1653.

Triisopropyl((naphthalen-1-ylsulfonyl)ethynyl)silane (6i)



1-Bromonaphthalene (28 μL, 0.20 mmol) was used in this reaction. **6i** was obtained as a colorless solid (62 mg, 0.17 mmol, 83% yield) by using the general procedure I and II.

R*f* 0.75 (pentane/EtOAc 5/1, $KMnO_4$, UV); pentane was used as the eluting solvents for purification.

Mp 73 °C.

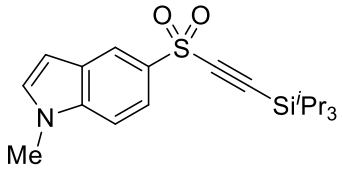
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 8.7, 1.1 Hz, 1H, Ar-*H*), 8.37 (dd, *J* = 7.4, 1.2 Hz, 1H, Ar-*H*), 8.14 (dt, *J* = 8.2, 1.1 Hz, 1H, Ar-*H*), 8.01 – 7.91 (m, 1H, Ar-*H*), 7.69 (ddd, *J* = 8.7, 6.9, 1.4 Hz, 1H, Ar-*H*), 7.65 – 7.56 (m, 2H, Ar-*H*), 1.10 – 0.89 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 136.5, 135.6, 134.1, 128.9, 128.9, 128.4, 128.3, 127.1, 124.5, 124.2, 100.9, 100.1, 18.2, 10.8.

IR (3674m), 2971(br), 2125(w), 1454(m), 1394(m), 1319(m), 1250(m), 1129(m), 1067(s), 882(m), 786(m).

HRMS (ESI) calcd for $C_{21}H_{29}O_2SSi^+$ $[M+H]^+$ 373.1652, found 373.1652.

1-Methyl-5-(((triisopropylsilyl)ethynyl)sulfonyl)-1*H*-indole (6j)



5-Bromo-1-methyl-1*H*-indole (43 mg, 0.20 mmol) was used in this reaction. **6j** was obtained as a pale brown solid (54 mg, 0.14 mmol, 72% yield) by using the general procedure I and II.

R*f* 0.6 (pentane/EtOAc 3/1, $KMnO_4$, UV); pentane/EtOAc 6/1 was used as the eluting solvents for purification.

Mp 109 °C.

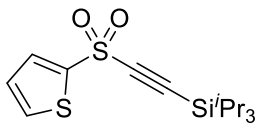
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 1.8 Hz, 1H, Ar-*H*), 7.82 (dd, *J* = 8.8, 1.8 Hz, 1H, Ar-*H*), 7.43 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.21 (d, *J* = 3.2 Hz, 1H, Ar-*H*), 6.65 (dd, *J* = 3.2, 0.9 Hz, 1H, Ar-*H*), 3.86 (s, 3H, NC*H*$_3$), 1.01 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 139.0, 132.5, 131.5, 127.8, 121.9, 120.1, 109.8, 103.2, 101.6, 98.6, 33.2, 18.3, 10.8.

IR 3675(w), 2942(m), 2119(w), 1601(w), 1449(w), 1326(m), 1281(m), 1147(s), 1058(s), 882(m), 787(s), 754(m).

HRMS (ESI) calcd for $C_{20}H_{30}NO_2SSi^+$ $[M+H]^+$ 376.1760, found 376.1760.

Triisopropyl((thiophen-2-ylsulfonyl)ethynyl)silane (6k)



2-Bromothiophene (19 μL, 0.20 mmol) was used in this reaction. **6k** was obtained as a colorless solid (56 mg, 0.16 mmol, 79% yield) by using the general procedure I and II.

R*f* 0.8 (pentane/EtOAc 5/1, $KMnO_4$); pentane/EtOAc 10/1 was used as the eluting solvents for purification.

Mp 43 °C.

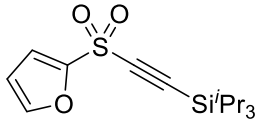
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 3.8, 1.4 Hz, 1H, Ar-*H*), 7.68 (dd, *J* = 5.0, 1.4 Hz, 1H, Ar-*H*), 7.08 (dd, *J* = 5.0, 3.8 Hz, 1H, Ar-*H*), 1.08 – 0.92 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 143.2, 134.7, 134.0, 127.8, 100.7, 100.7, 18.3, 10.8.

IR 3674(m), 2908(br), 2116(w), 1934(w), 1455(m), 1331(m), 1229(s), 1151(s), 1072(s), 889(m), 787(s), 744(m).

HRMS (ESI) calcd for $C_{15}H_{25}O_2S_2Si^+$ $[M+H]^+$ 329.1060, found 329.1062.

((Furan-2-ylsulfonyl)ethynyl)triisopropylsilane (6l)



Furan (15 μL, 0.2 mmol) was used in this reaction. **6l** was obtained as a colorless gel (44 mg, 0.14 mmol, 70% yield) by using the general procedure I and II.

R*f* 0.8 (pentane/EtOAc 2/1, $KMnO_4$); pentane/EtOAc 3/1 was used as the eluting solvents for purification.

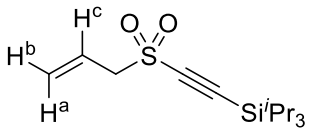
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 1.9, 0.9 Hz, 1H, Ar-*H*), 7.17 (dd, *J* = 3.6, 0.9 Hz, 1H, Ar-*H*), 6.52 (dd, *J* = 3.6, 1.7 Hz, 1H, Ar-*H*), 1.10 – 0.93 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.9, 147.8, 118.3, 111.9, 101.9, 99.1, 18.3, 10.8.

IR 3662(s), 3474(w), 3226(w), 2914(br), 2272(w), 2124(w), 1934(w), 1407(s), 1251(s), 1071(s), 893(s), 795(m).

HRMS (ESI) calcd for $C_{15}H_{25}O_3SSi^+$ $[M+H]^+$ 313.1288, found 313.1287.

((Allylsulfonyl)ethynyl)triisopropylsilane (6o)



Allylmagnesium bromide (0.2 mL, 1M in THF, 0.2 mmol) was used in this reaction. **6o** was obtained as a colorless gel (26 mg, 0.10 mmol, 46% yield)[11] by using the general procedure II.

R*f* 0.6 (pentane/EtOAc 4/1, $KMnO_4$); pentane/EtOAc 10/1 was used as the eluting solvents for purification.

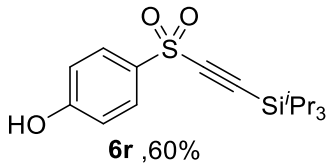
^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.94 (ddt, *J* = 17.0, 10.2, 7.3 Hz, 1H, Hc), 5.54 (dt, *J* = 10.2, 1.0 Hz, 1H, Hb), 5.48 (dd, *J* = 17.0, 1.0 Hz, 1H, Ha), 3.88 (dt, *J* = 7.3, 1.0 Hz, 2H, CH_2), 1.25 – 0.97 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 125.7, 124.0, 100.0, 97.6, 62.6, 18.4, 10.8.

IR 3674(s), 3475(w), 3227(w), 2969(br), 2272(w), 2126(w), 1407(s), 1251(s), 1071(s), 893(s), 803(m).

HRMS (ESI) calcd for $C_{14}H_{26}NaO_2SSi^+$ $[M+Na]^+$ 309.1315, found 309.1315.

4-(((Triisopropylsilyl)ethynyl)sulfonyl)phenol (6r)



6r ,60%

4-Iodophenol (44 mg, 0.20 mmol) was used in this reaction. **6r** was obtained as a colorless solid (40 mg, 0.12 mmol, 60% yield) by using the general procedure III.

R*f* 0.75 (pentane/EtOAc 3/1, $KMnO_4$); pentane/EtOAc 20/1 to 4/1 was used as the eluting solvents for purification.

Mp 65 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.97 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 5.87 (br, 1H, O*H*), 1.02 (m, 21H, Si*i*Pr$_3$).

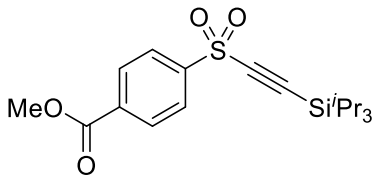
^{13}C-NMR (101 MHz, $CDCl_3$) δ 160.7, 133.7, 129.9, 116.1, 100.9, 99.9, 18.3, 10.8.

IR 3661(s), 2980(br), 2123(w), 1933(w), 1584(m), 1407(s), 1316(s), 1251(s), 1078(s), 882(s), 841(m), 788(m).

[11] The corresponding compound contains ca. 5% grease.

HRMS (ESI) calcd for $C_{17}H_{27}O_3SSi^+$ $[M+H]^+$ 339.1445, found 339.1445.

Methyl 4-(((triisopropylsilyl)ethynyl)sulfonyl)benzoate (6s)



Methyl-4-iodobenzoate (53 mg, 0.20 mmol) was used in this reaction. **6s** was obtained as a colorless gel (43.0 mg, 0.11 mmol, 56% yield) by using the general procedure III.

R*f* 0.55 (pentane/EtOAc 10/1, $KMnO_4$); pentane/EtOAc 10/1 was used as the eluting solvents for purification.

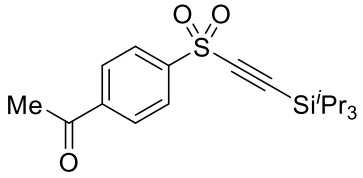
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 8.09 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 3.97 (s, 3H, C*H*$_3$), 1.14 – 0.97 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.4, 145.7, 135.0, 130.4, 127.2, 102.4, 99.9, 52.8, 18.3, 10.8.

IR 3674(s), 3416(w), 3225(w), 2975(br), 2124(w), 1934(w), 1734(br), 1408(s), 1230(s), 1076(s), 894(s), 795(w).

HRMS (ESI) calcd for $C_{19}H_{29}O_4SSi^+$ $[M+H]^+$ 381.1550, found 381.1561.

1-(4-(((Triisopropylsilyl)ethynyl)sulfonyl)phenyl)ethanone (6t)



4-Iodoacetophenone (50 mg, 0.20 mmol) was used in this reaction. **6t** was obtained as a colorless gel (29 mg, 0.080 mmol, 39%) by using the general procedure III.

R*f* 0.8 (pentane/EtOAc 3/1, $KMnO_4$); pentane/EtOAc 10/1 to 4/1 was used as the eluting solvents for purification.

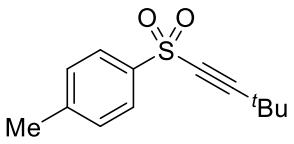
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 4H, Ar-*H*), 2.68 (s, 3H, C*H*$_3$), 1.32 – 0.82 (m, 21H, Si*i*Pr$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.6, 145.6, 141.0, 129.0, 127.5, 102.5, 99.9, 27.0, 18.3, 10.8.

IR 3674(s), 3416(w), 3226(w), 2927(br), 2124(w), 1932(w), 1698(w), 1408(s), 1251(s), 1088(s), 894(s), 800(m).

HRMS (ESI) calcd for $C_{19}H_{29}O_3SSi^+$ $[M+H]^+$ 365.1601, found 365.1599.

1-((3,3-Dimethylbut-1-yn-1-yl)sulfonyl)-4-methylbenzene (7a)[12]



3,3-Dimethylbutynyl-1,2-benziodoxol-3(1*H*)-one[9b] (79 mg, 0.24 mmol) was used in this reaction. **7a** was obtained as a colorless solid (60 mg, 0.16 mmol, 79% yield) by using the general procedure II.

R*f* 0.8 (pentane/EtOAc 4/1, $KMnO_4$, UV); pentane/EtOAc 10/1 was used as the eluting solvents for purification.

Mp 100-101 °C.

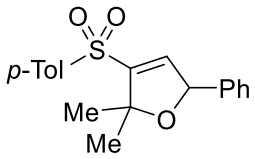
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.35 (d, *J* = 8.3, 2H, Ar-*H*), 2.45 (s, 3H, C*H*$_3$), 1.23 (s, 9H, *t*Bu).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 145.0, 139.3, 129.9, 127.2, 103.6, 29.4, 27.9, 21.7.[13]

IR 3674(m), 2971(br), 2213(w), 2170(w), 1933(w), 1723(w), 1597(w), 1407(s), 1317(s), 1252(s), 1148(m), 1074(s), 893(m), 818(m), 779(m).

HRMS (ESI) calcd for $C_{13}H_{17}O_2S^+$ $[M+H]^+$ 237.0944, found 237.0946.

2,2-Dimethyl-5-phenyl-3-tosyl-2,5-dihydrofuran (8)



3-(Benzyloxy)-3-methyl-but-1-yn-1-yl)-1,2-benziodoxol-3(1H)-one (101 mg, 0.240 mmol) was used in this reaction. **8** was obtained as a colorless solid (61 mg, 0.19 mmol, 93% yield) by using the general procedure II.

R*f* 0.75 (pentane/EtOAc 2/1, $KMnO_4$, UV); pentane/EtOAc 6/1 was used as the eluting solvents for purification.

Mp 87-88 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2, 2H, Ar-*H*), 7.32 – 7.22 (m, 5H, Ar-*H*), 7.22 – 7.16 (m, 2H, Ar-*H*), 6.55 (d, *J* = 1.5 Hz, 1H, SO_2CC*H*), 5.73 (d, *J* = 1.5 Hz, 1H, C*H*Ph), 2.38 (s, 3H, CH_3), 1.40 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 148.6, 145.0, 140.6, 138.9, 137.2, 129.9, 128.7, 128.4, 128.2, 126.6, 88.2, 83.5, 28.2, 27.7, 21.7.

[12] (a) Truce, W. E.; Wolf, G. C. *J. Org. Chem*. **1971**, *36*, 1727; (b) Tykwinski, R. R.; Williamson, B. L.; Fisher, D. R.; Stang, P. J.; Arif, A. M. *J. Org. Chem*. **1993**, *58*, 5235.

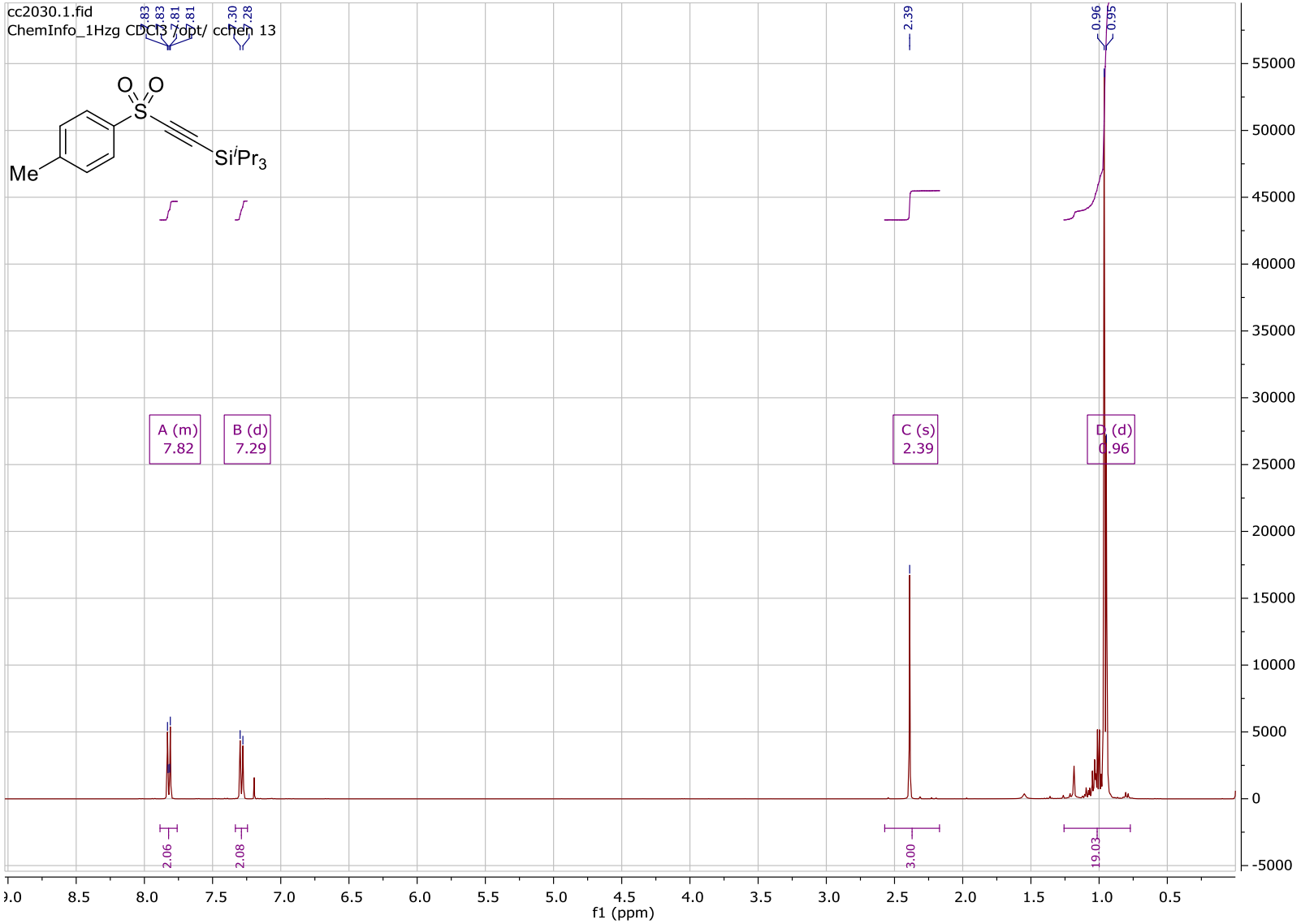
[13] Not all acetylene signals were resolved.

IR 3673(s), 2953(br), 2113(w), 1934(w), 1596(m), 1452(s), 1408(s), 1318(s), 1251(s), 1149(s), 1086(s), 893(s), 782(m).

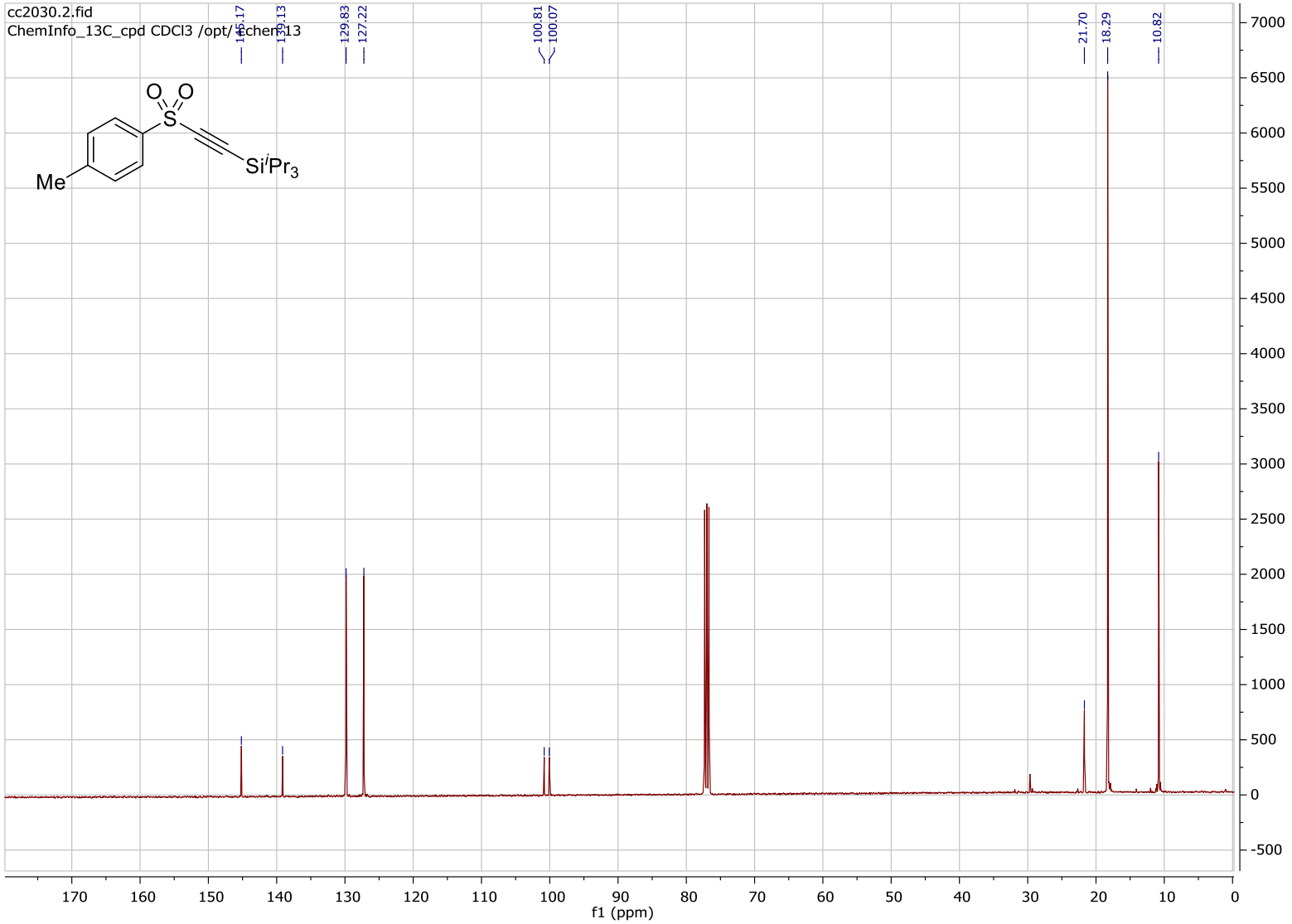
HRMS (ESI) calcd for $C_{19}H_{21}O_3S^+$ $[M+H]^+$ 329.1206, found 329.1204.

4. Spectra of New Compounds

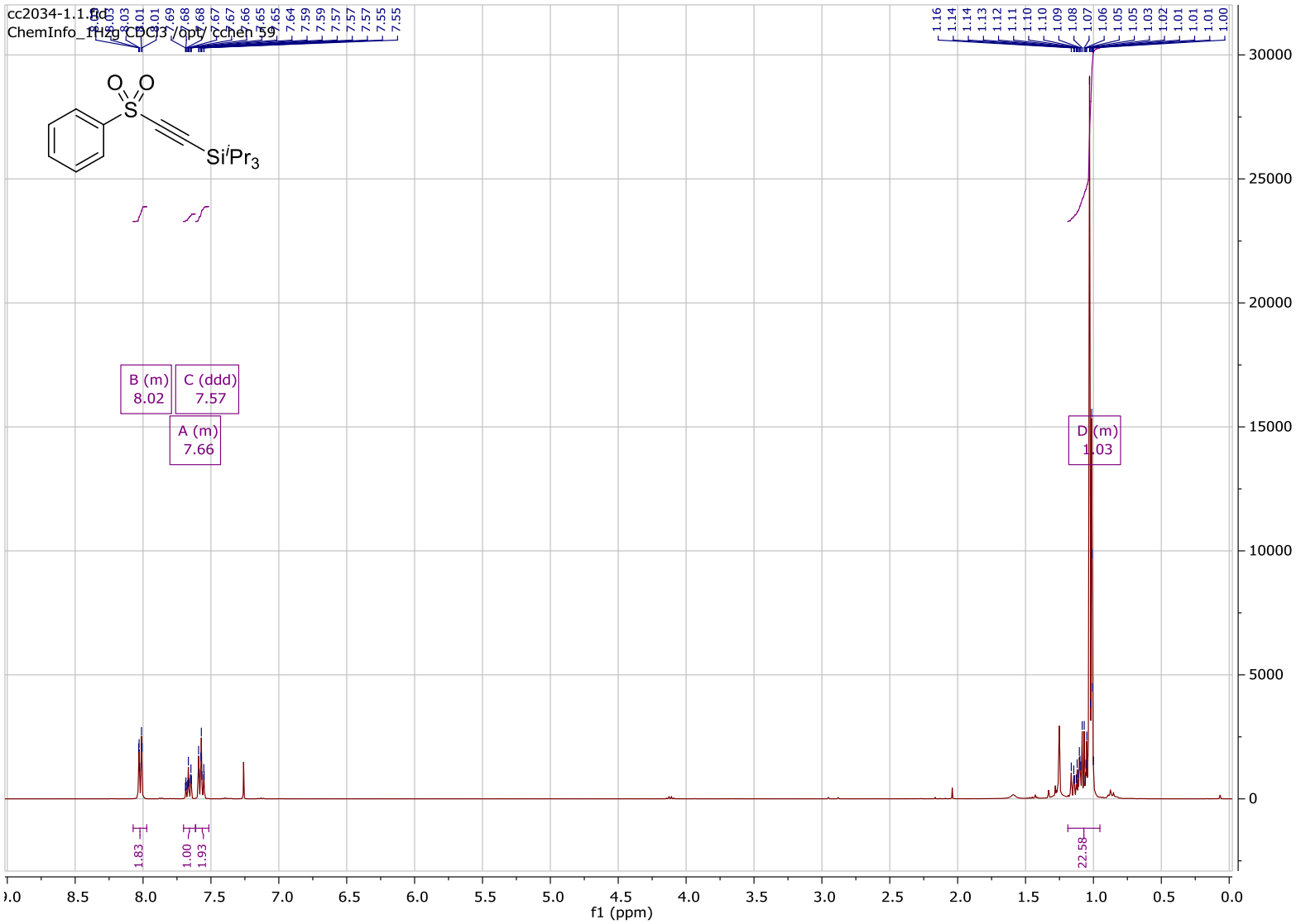
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6a**



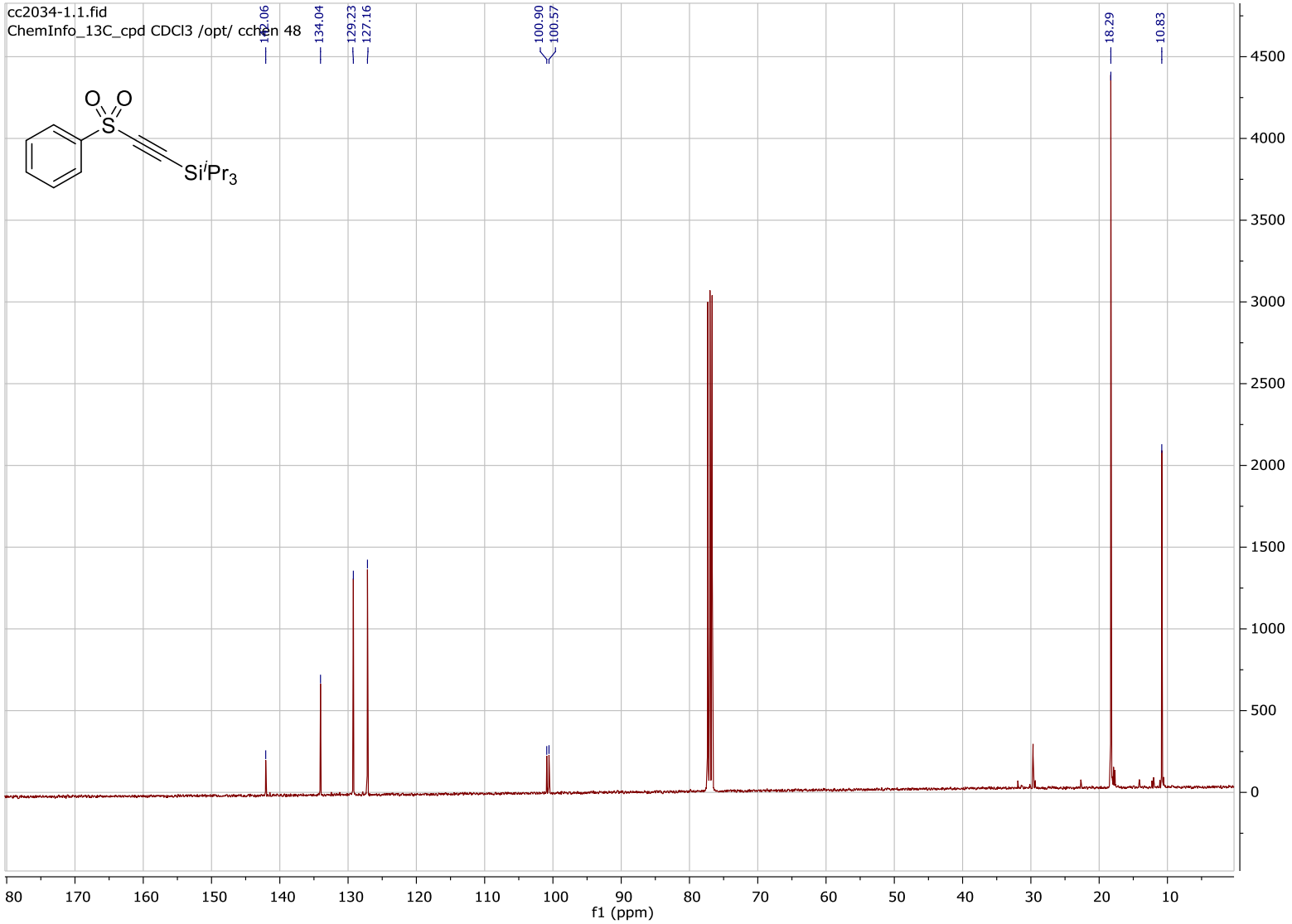
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6a**



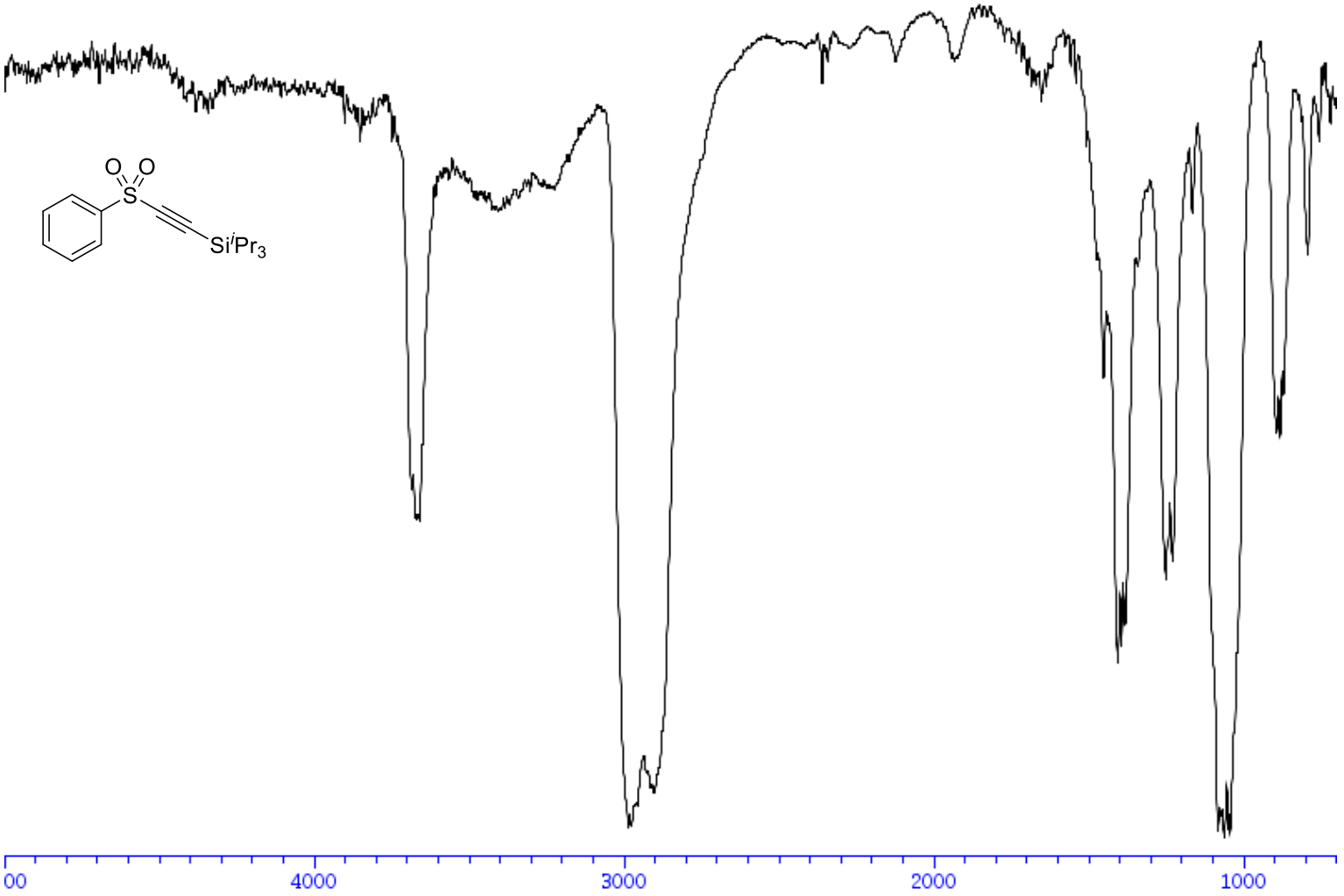
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6b**



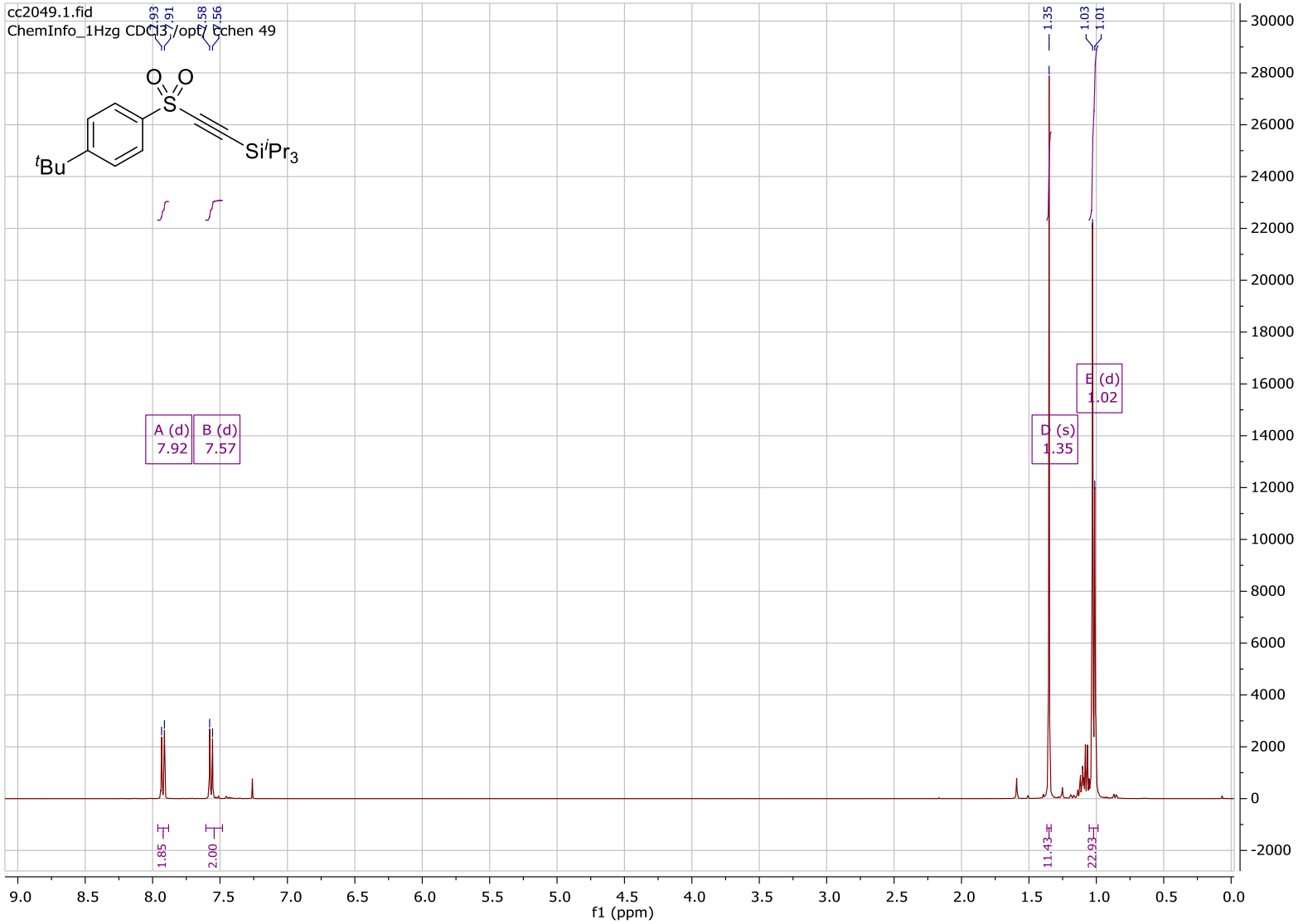
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6b**



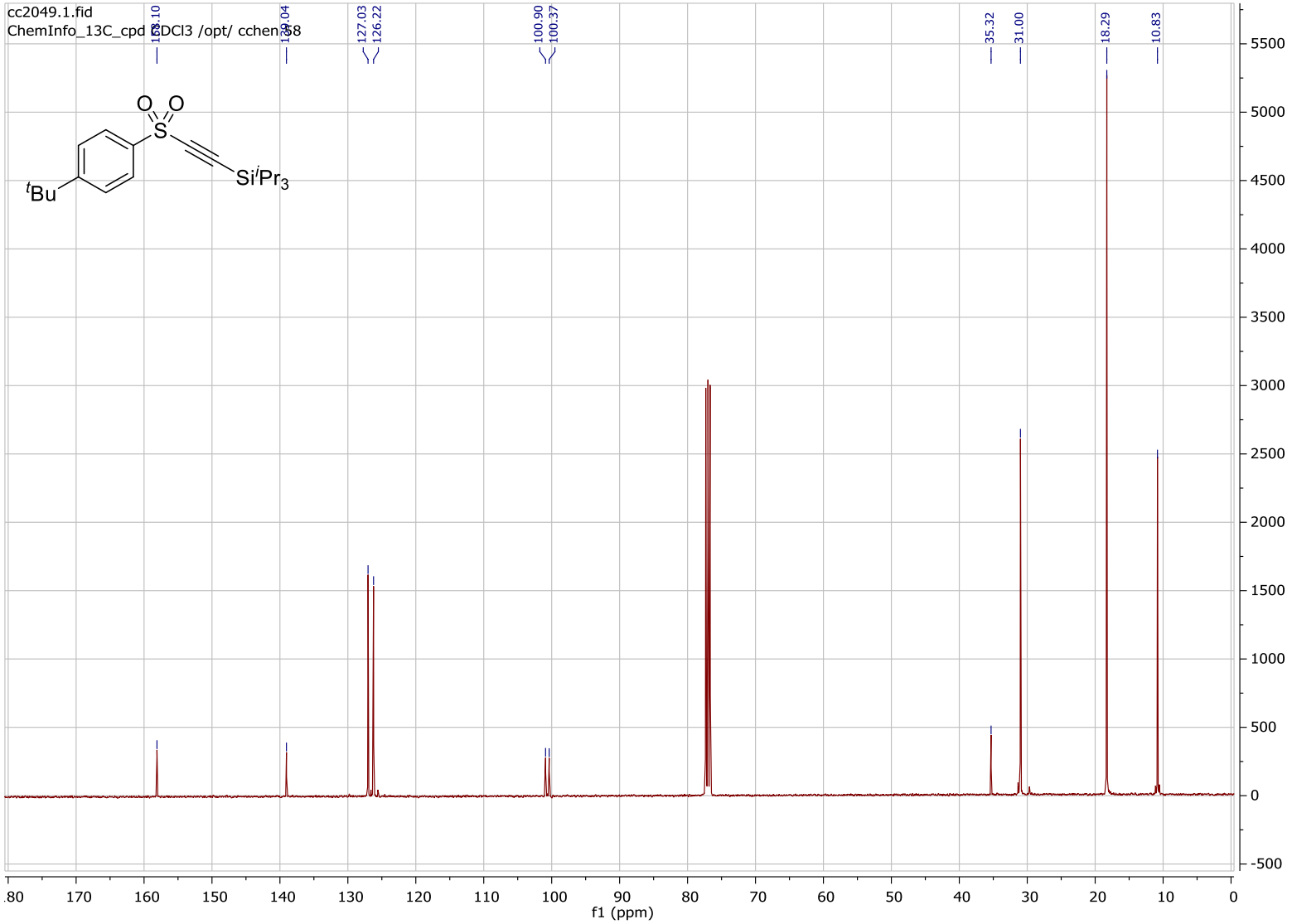
IR of compound **6b**



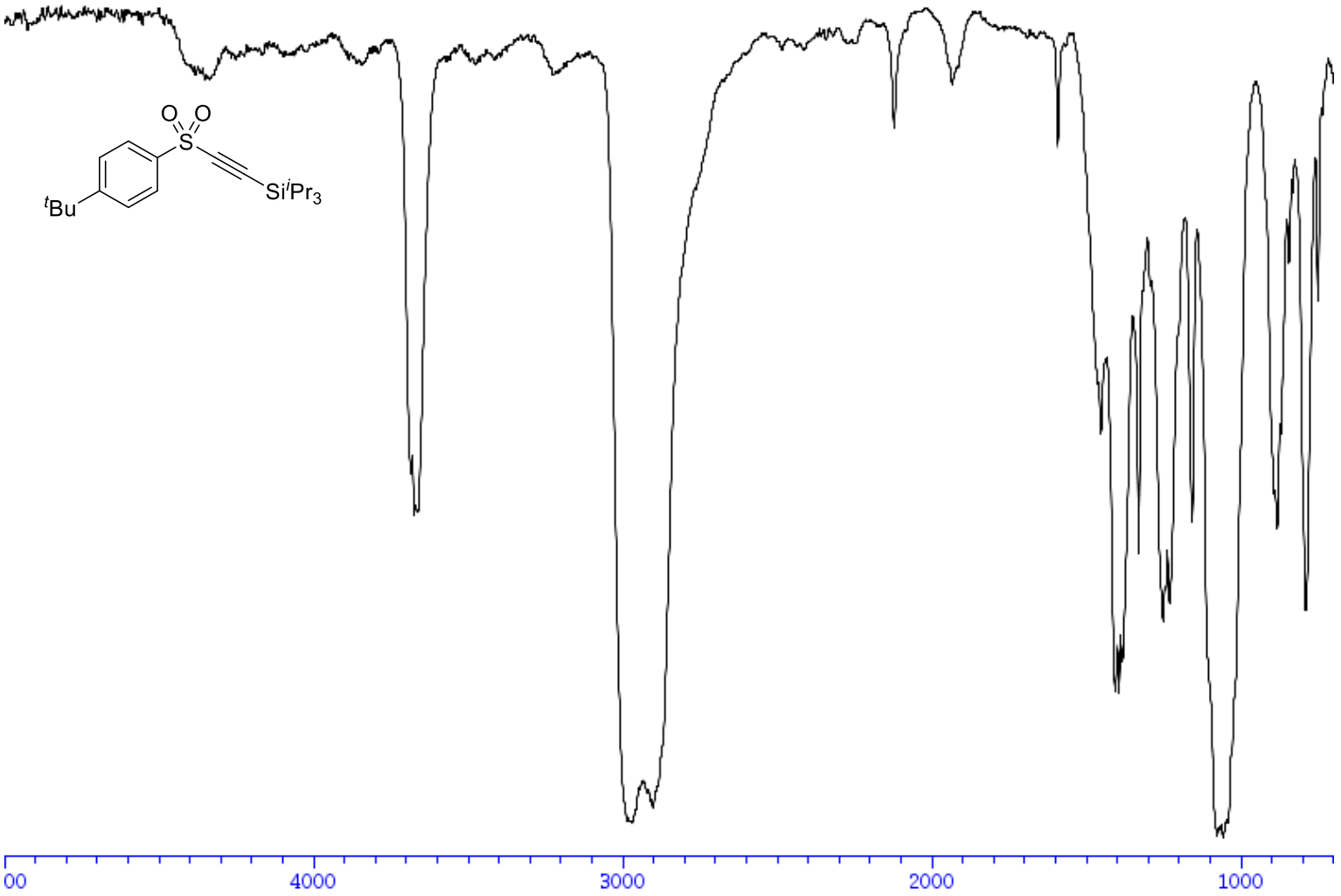
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6c**



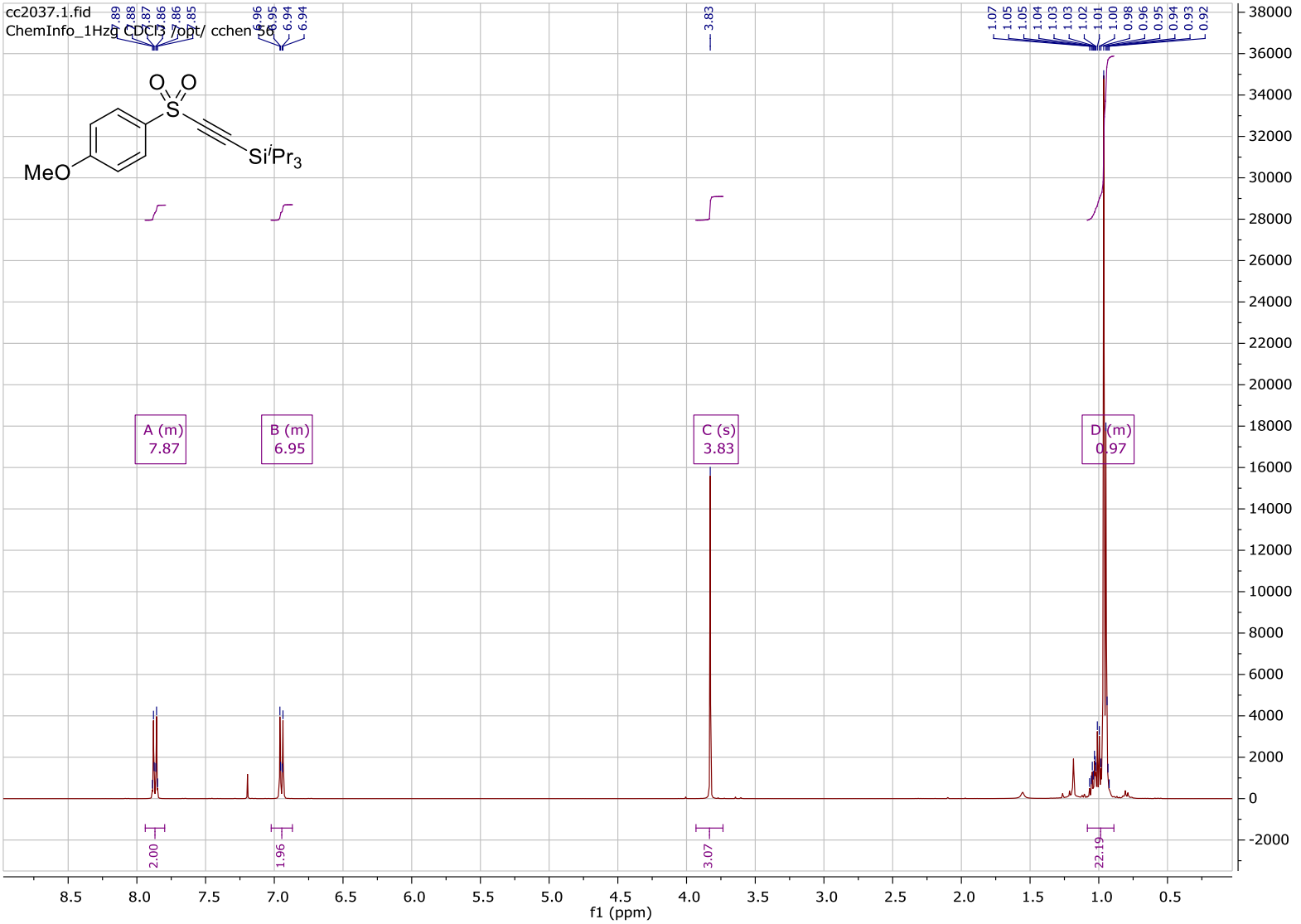
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6c**



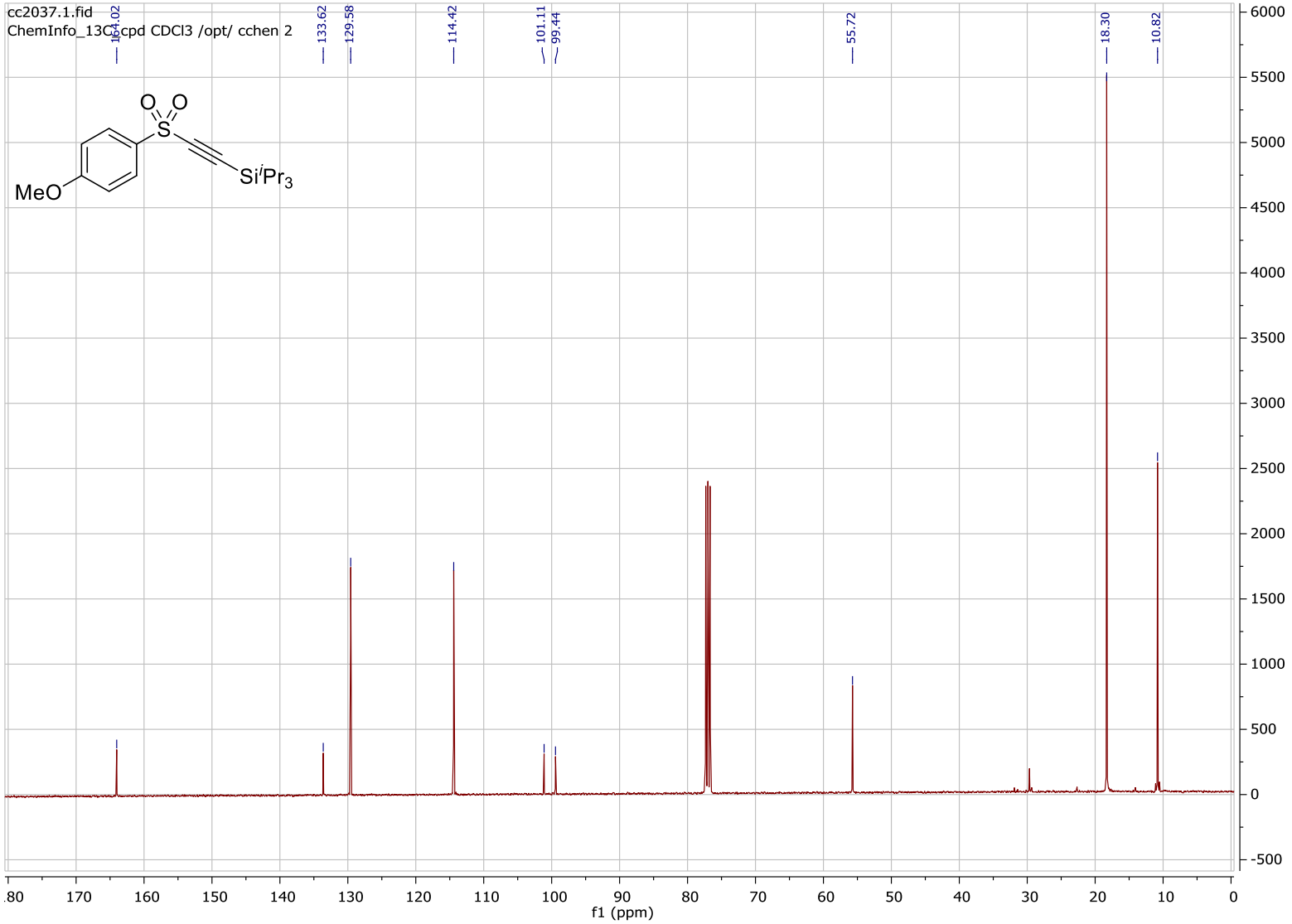
IR of compound **6c**



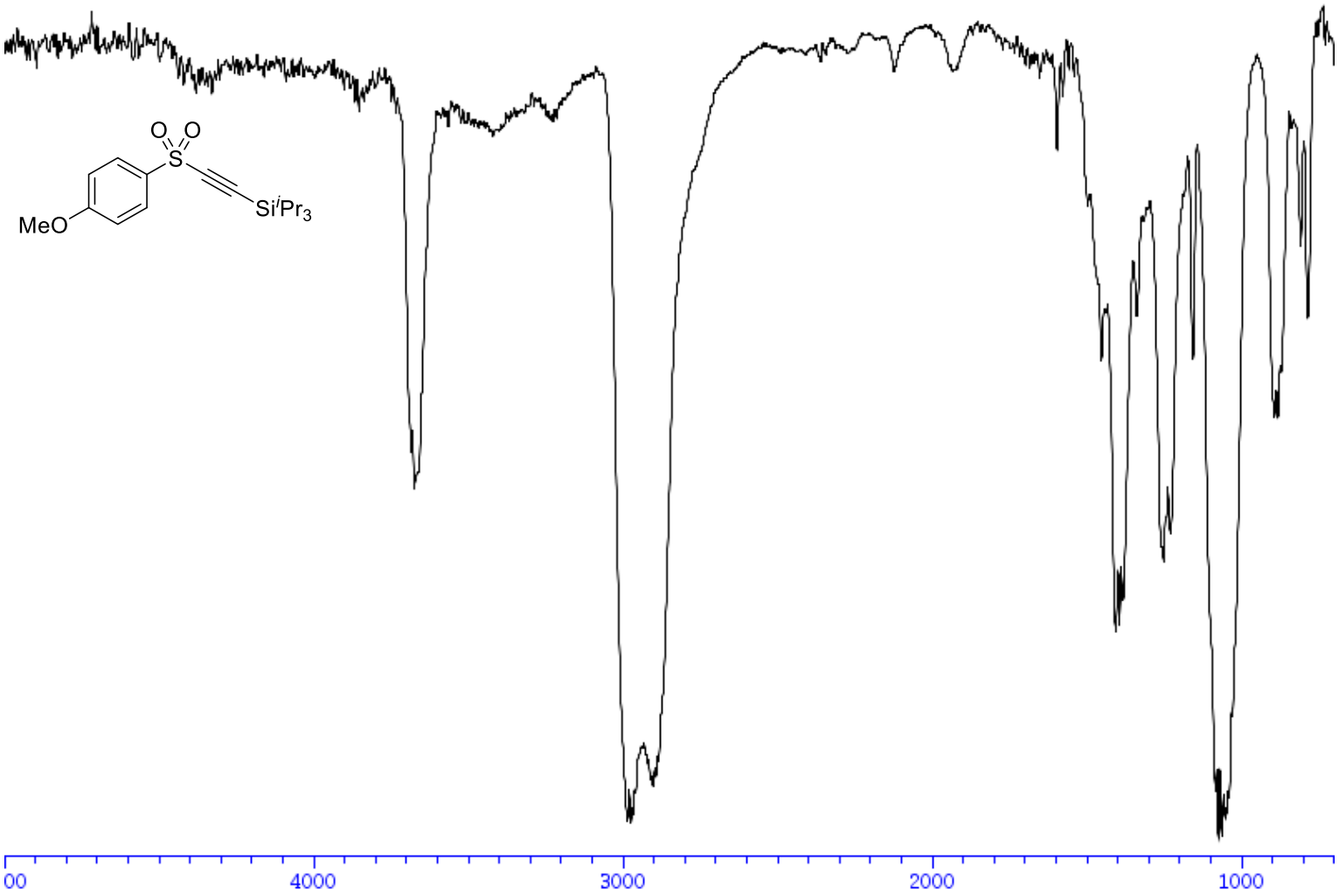
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6d**



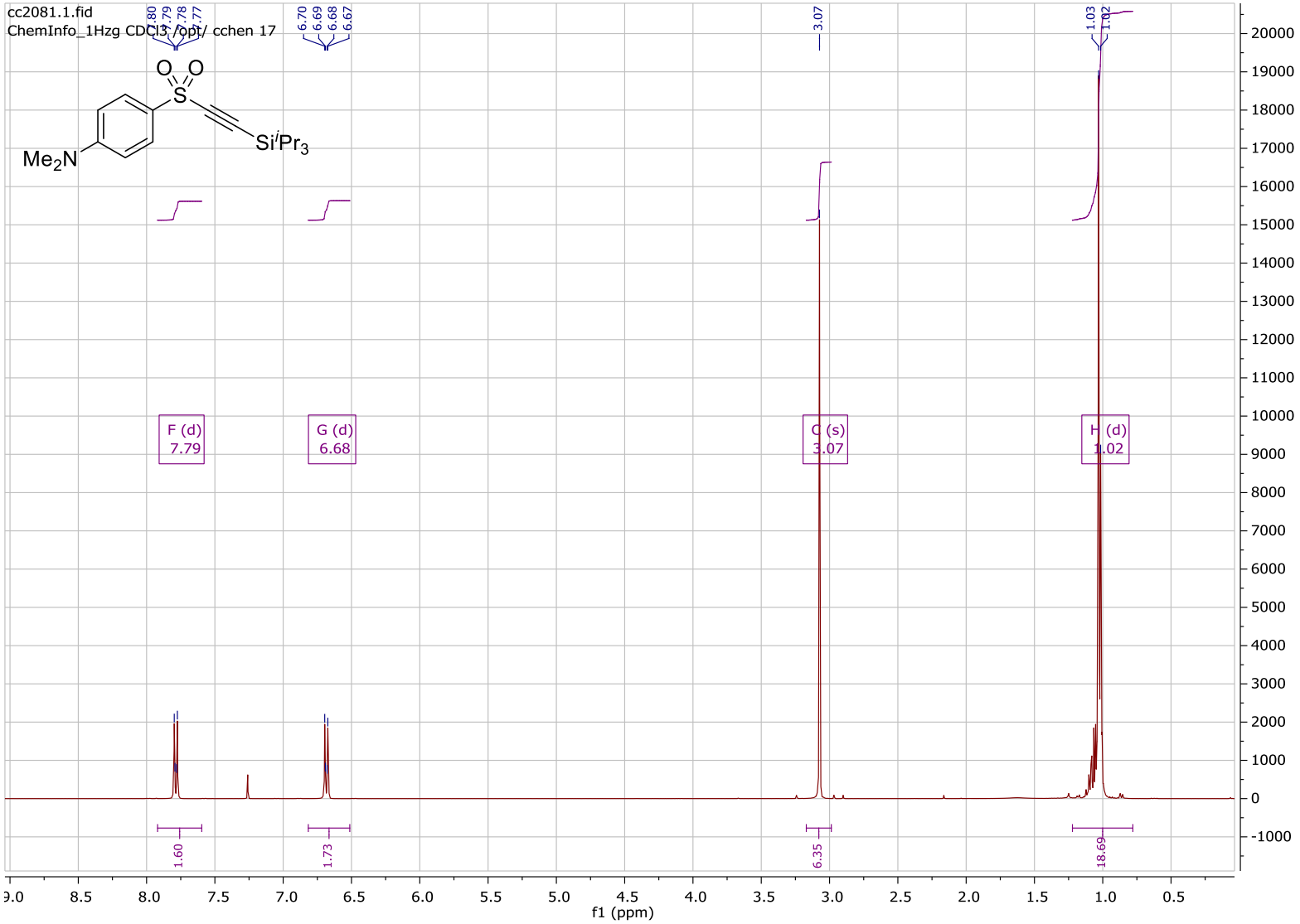
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6d**



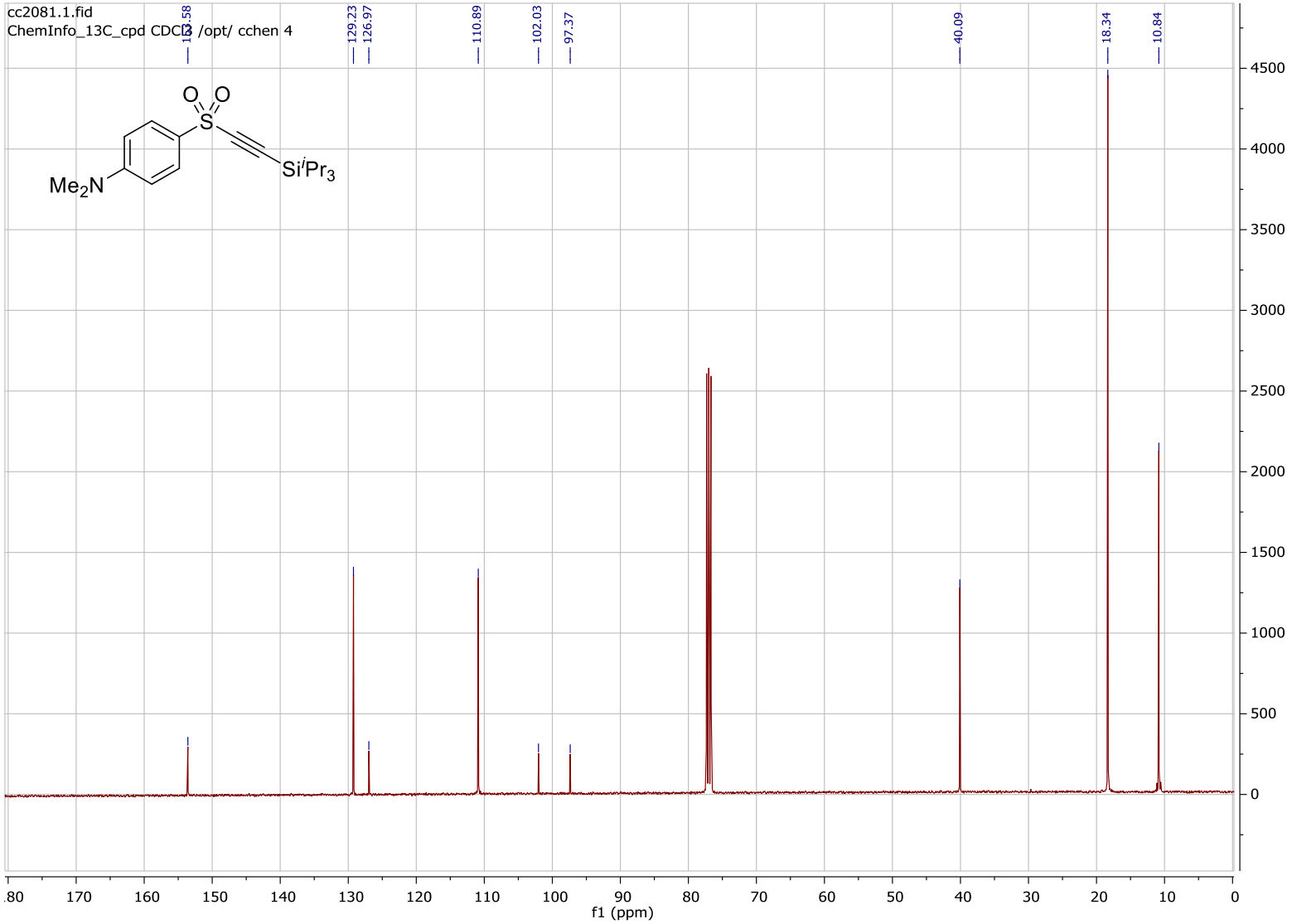
IR of compound **6d**



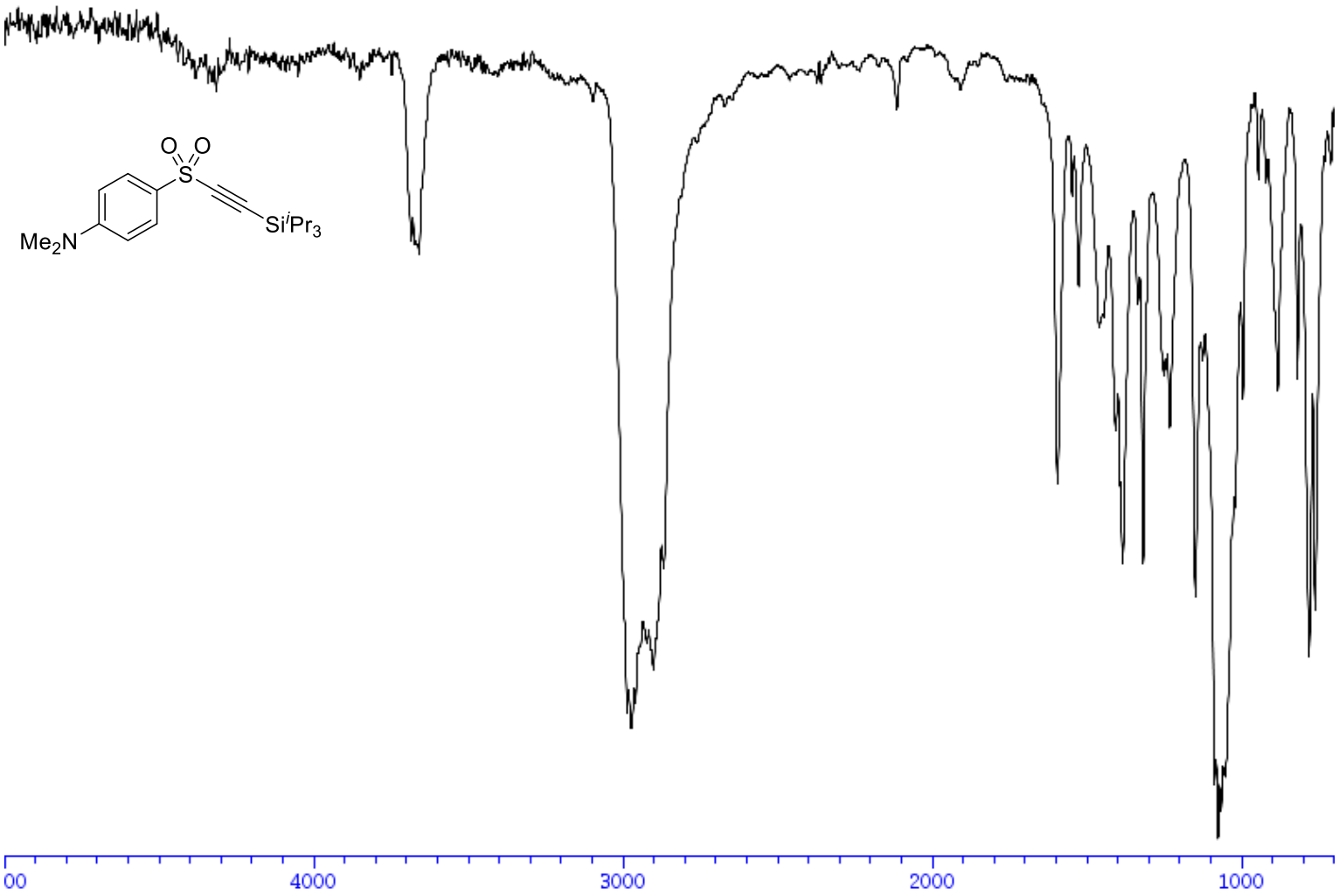
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6e**



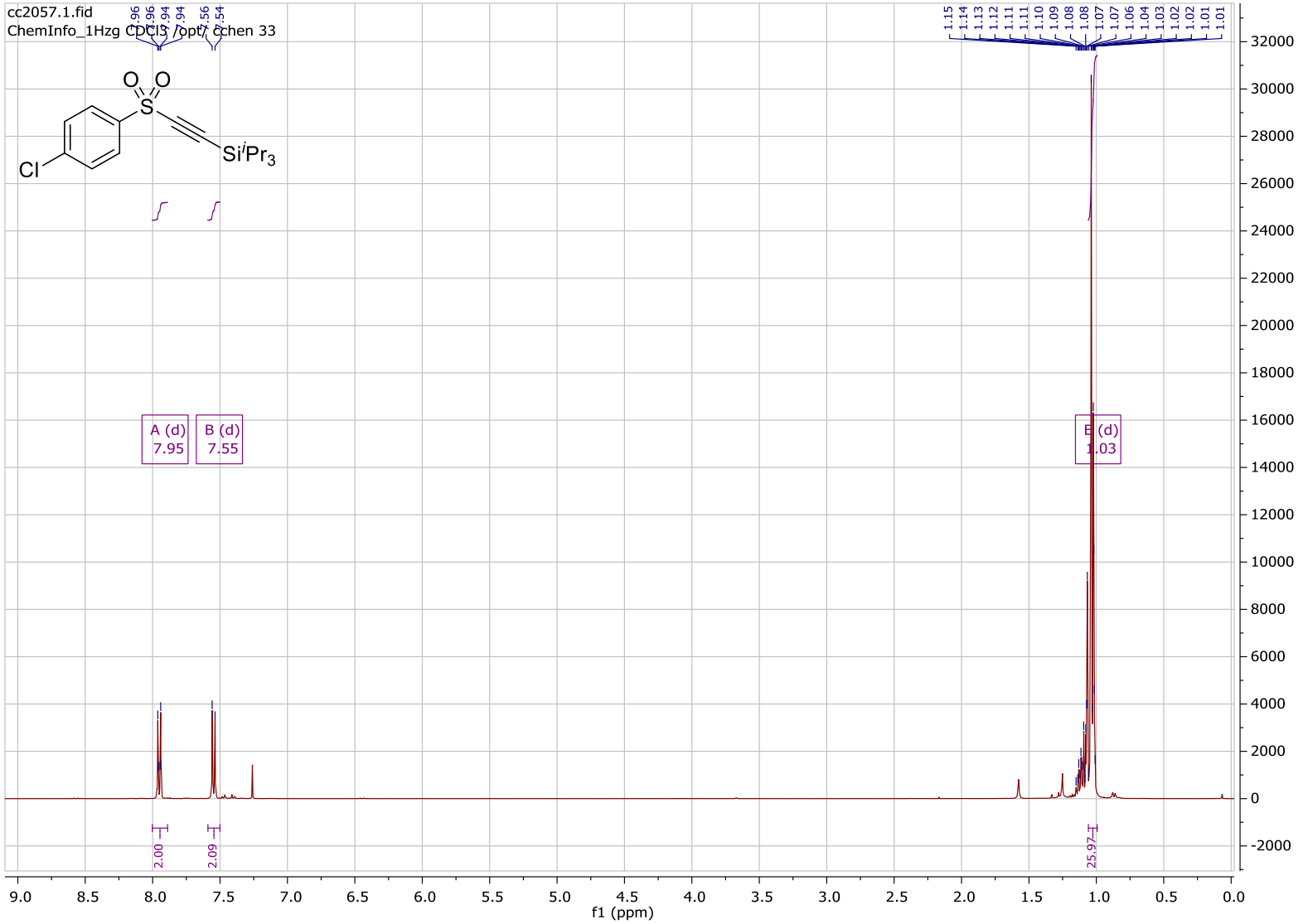
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6e**



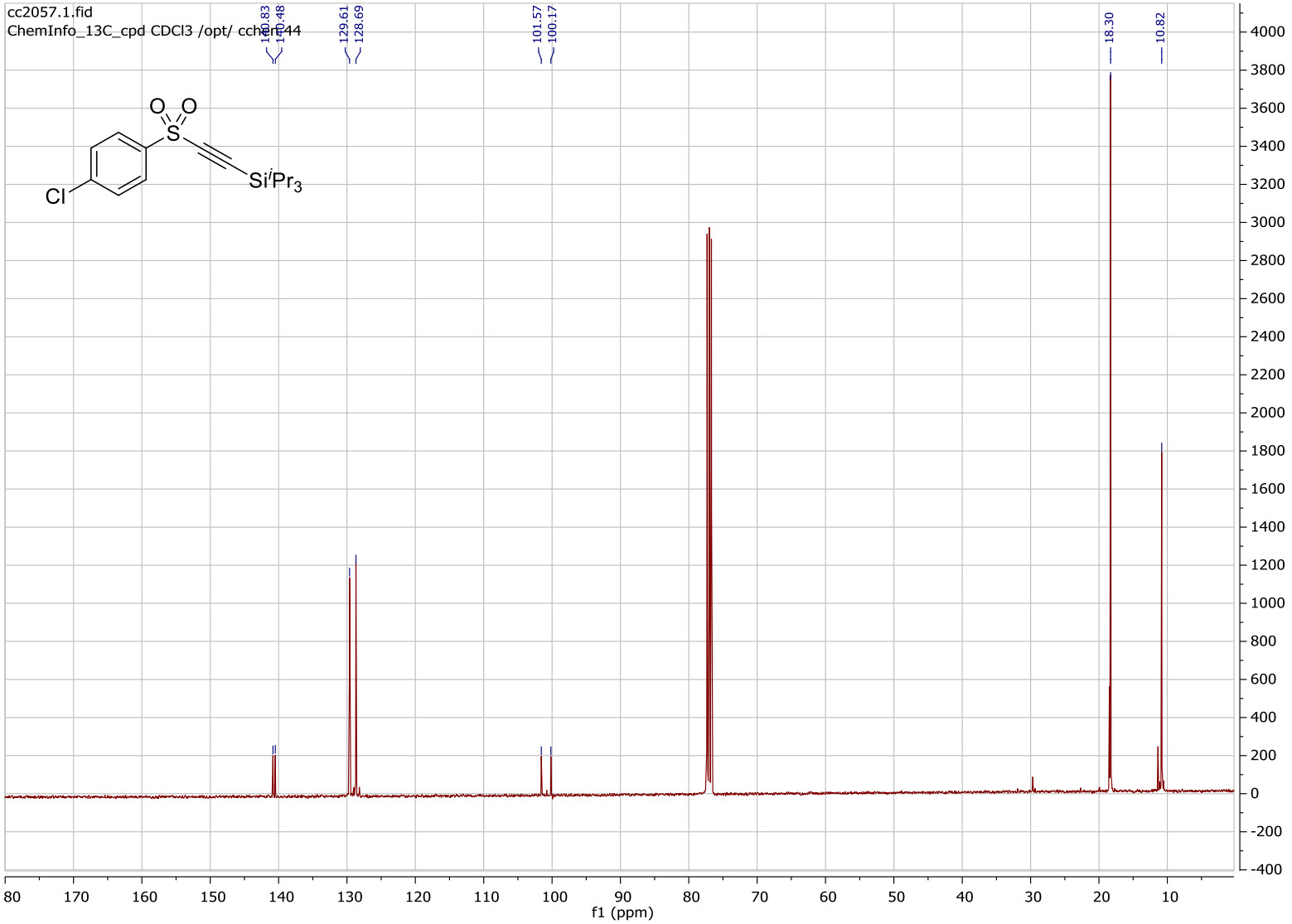
IR of compound **6e**



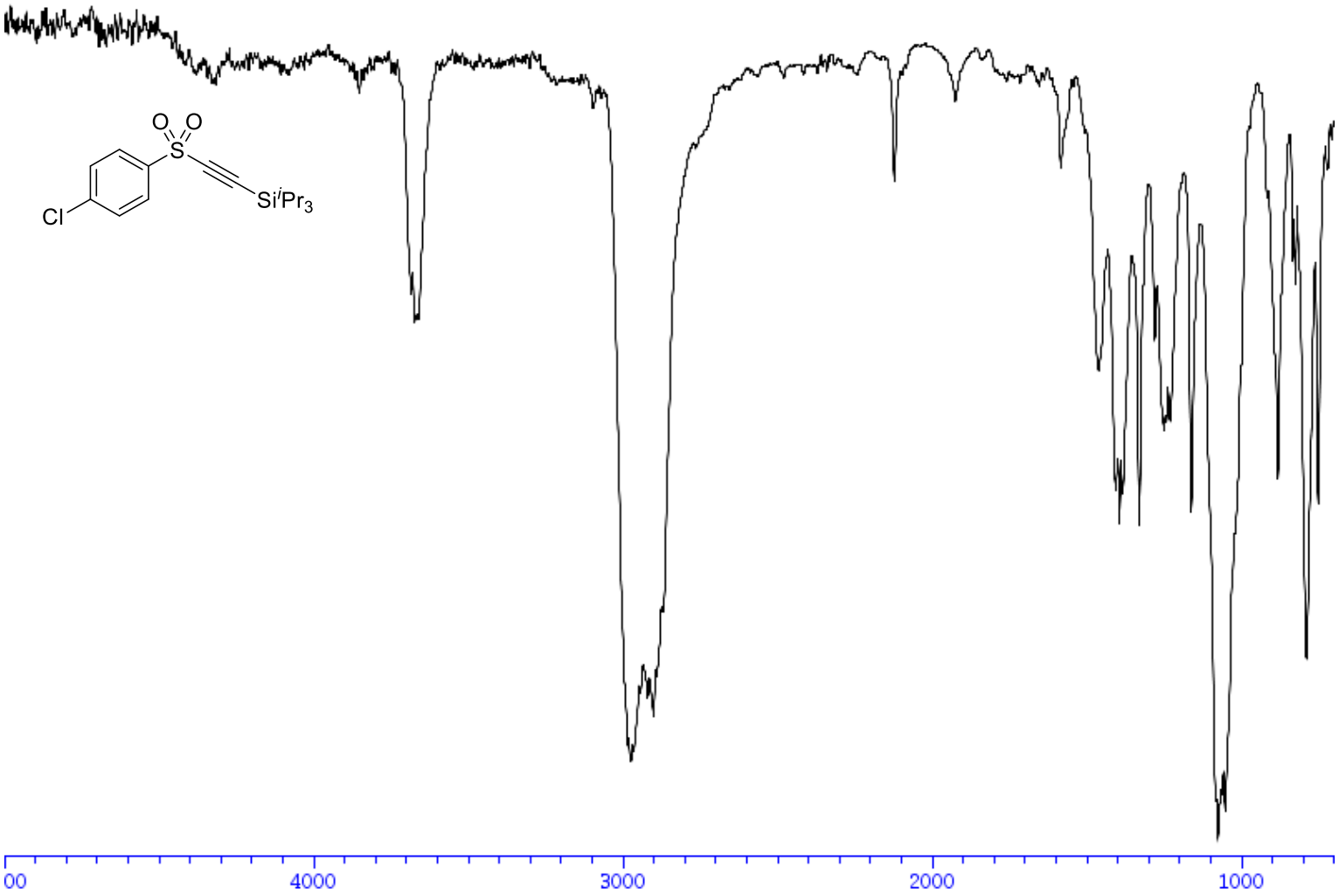
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6f**



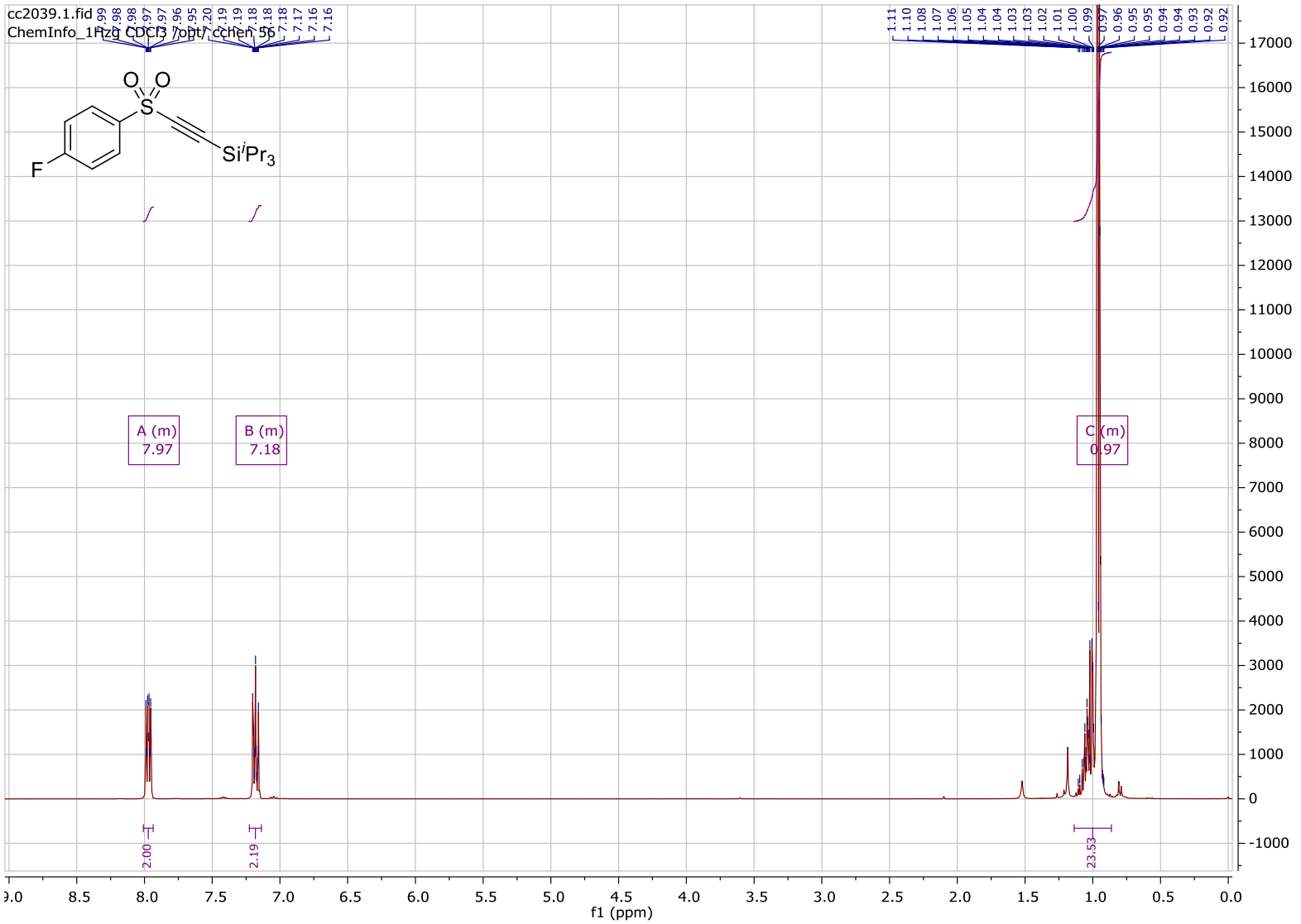
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6f**



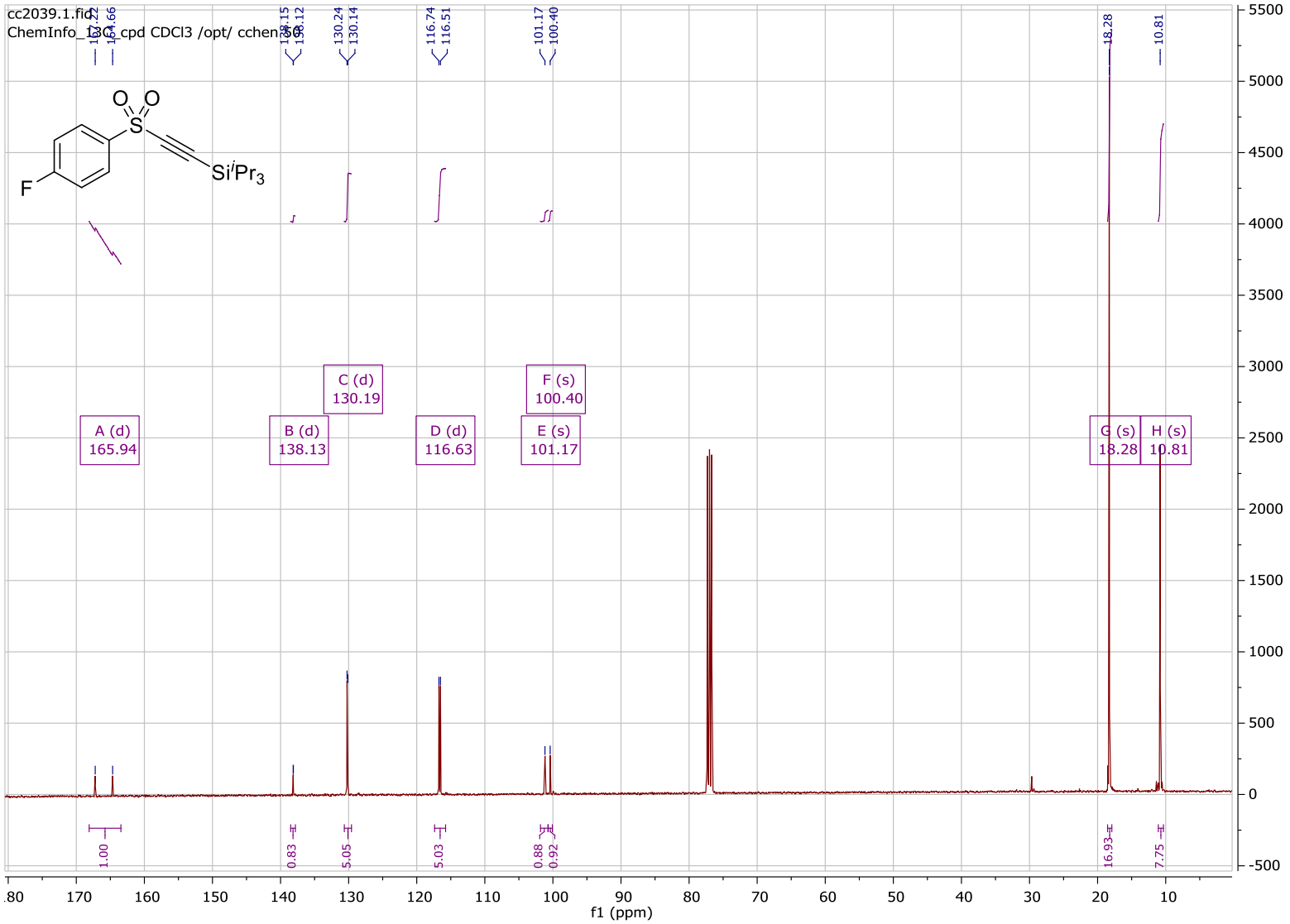
IR of compound **6f**



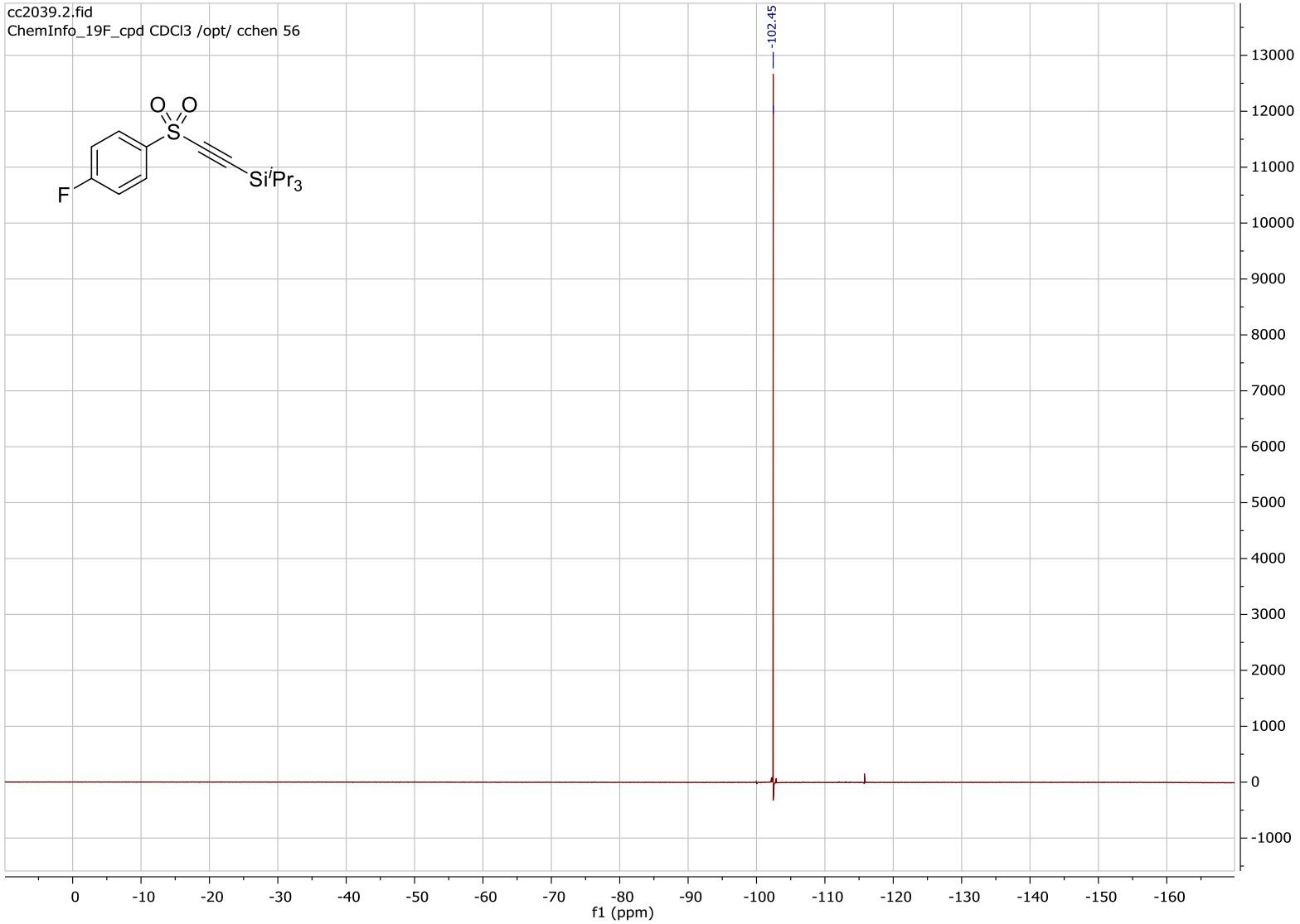
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6g**



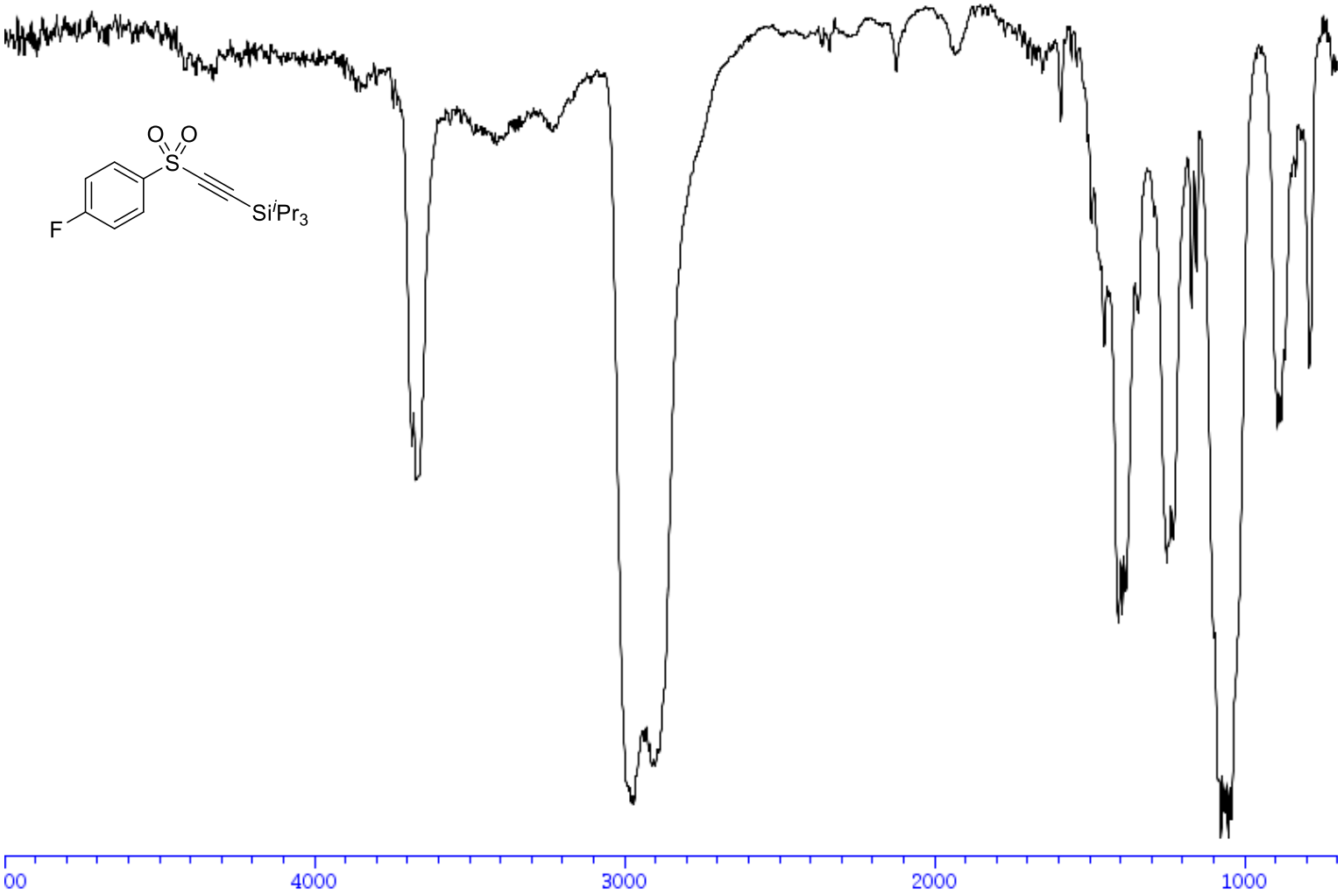
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6g**



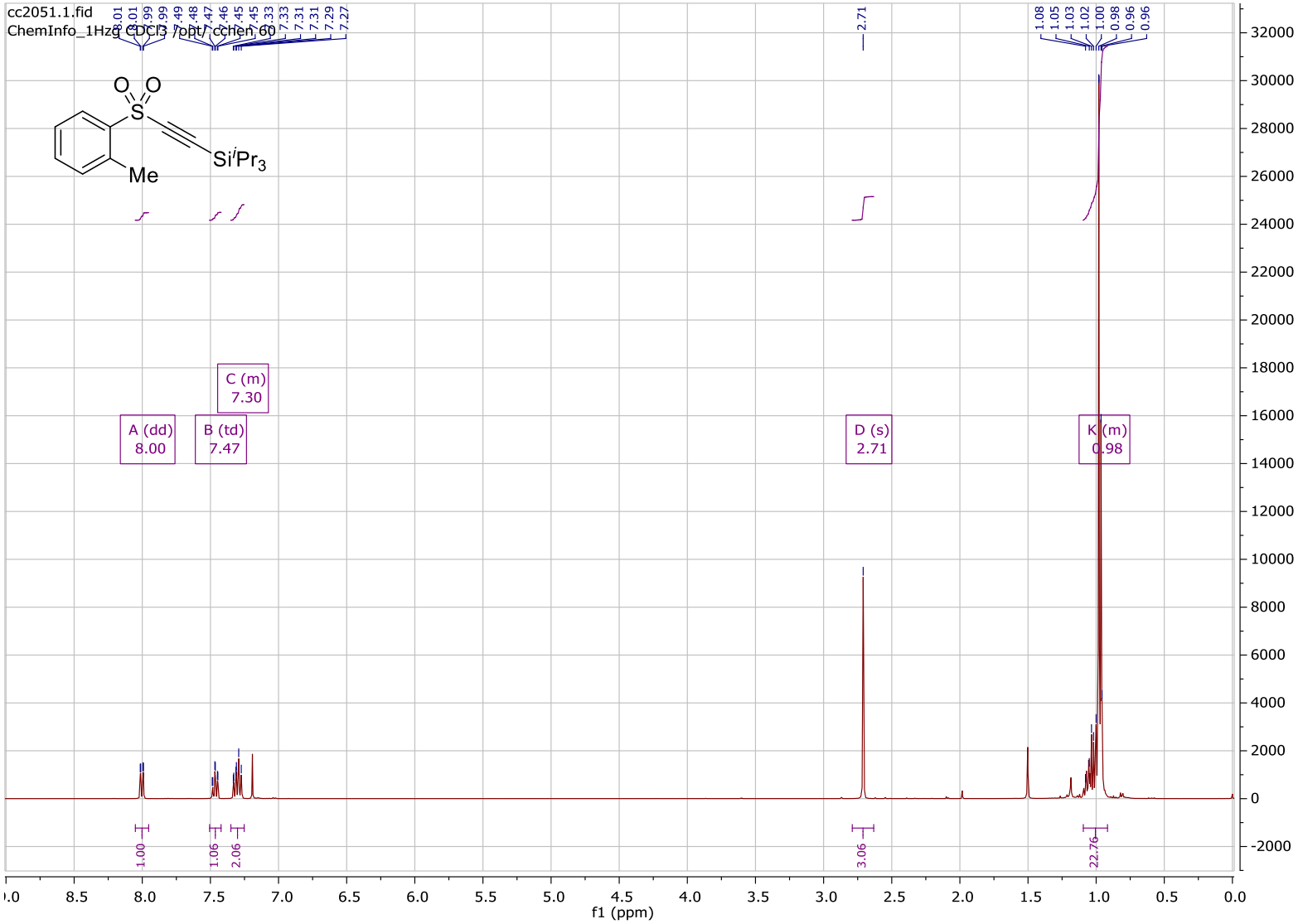
^{19}F-NMR (376 MHz, $CDCl_3$) of compound **6g**



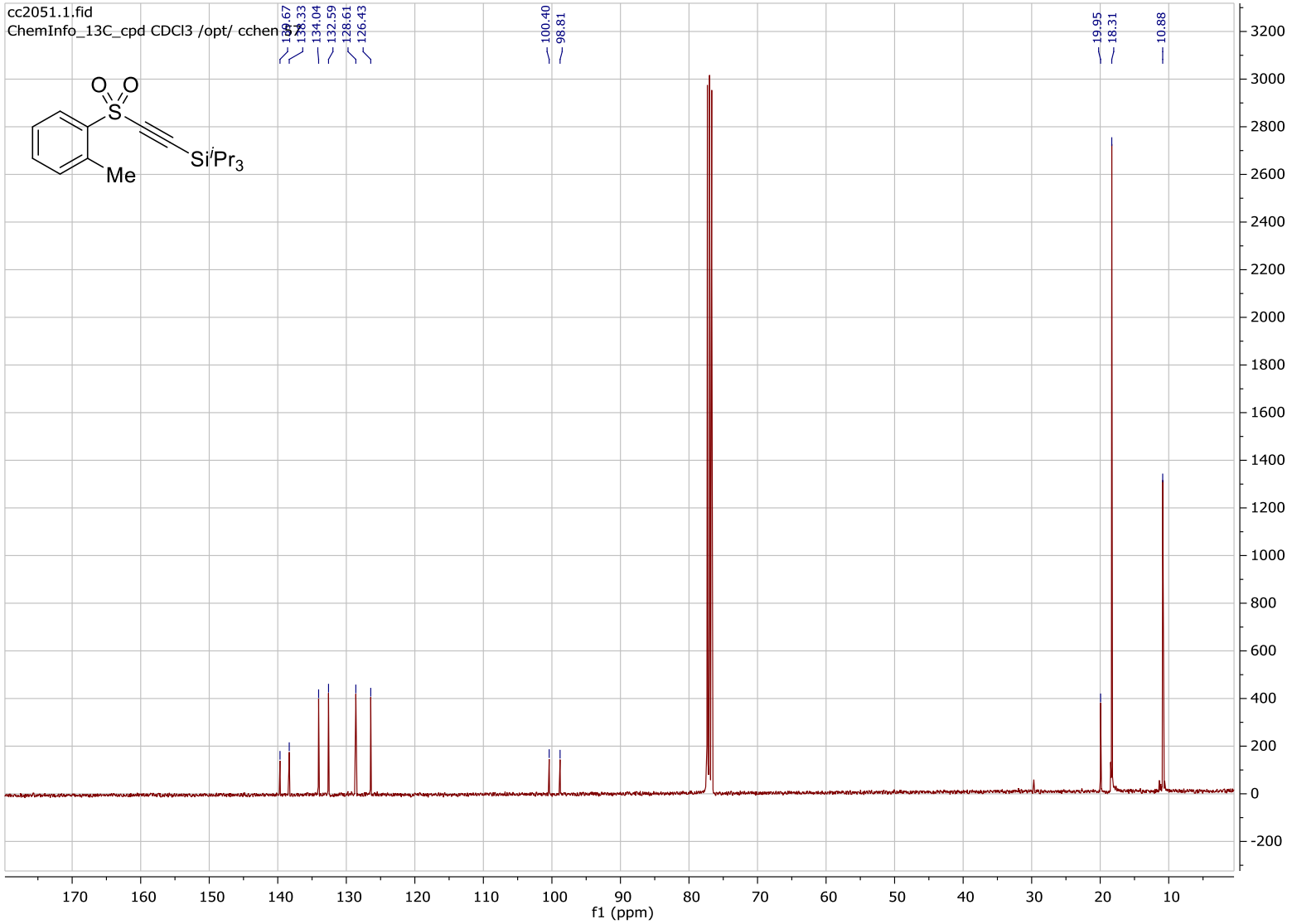
IR of compound **6g**



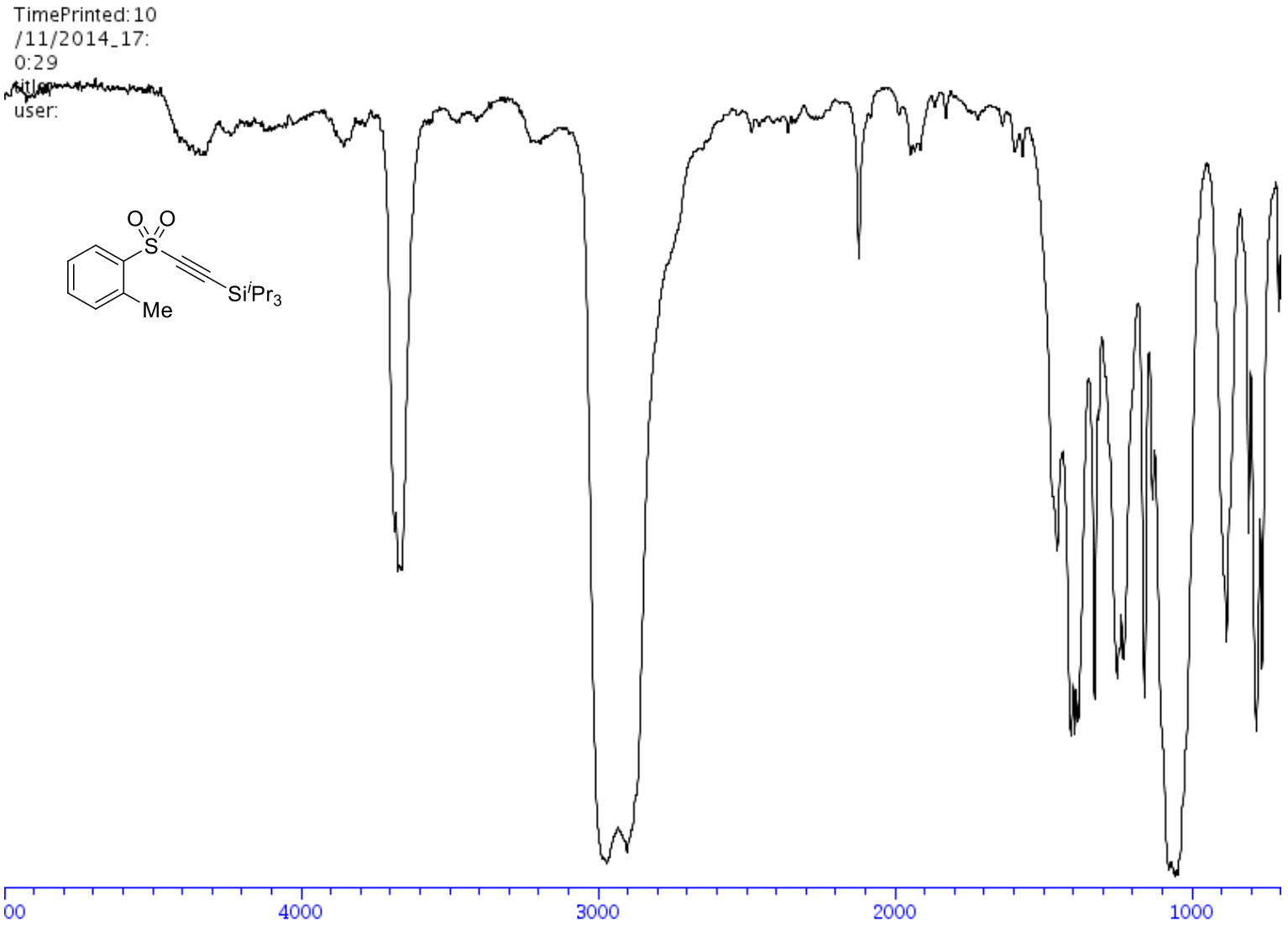
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6h**



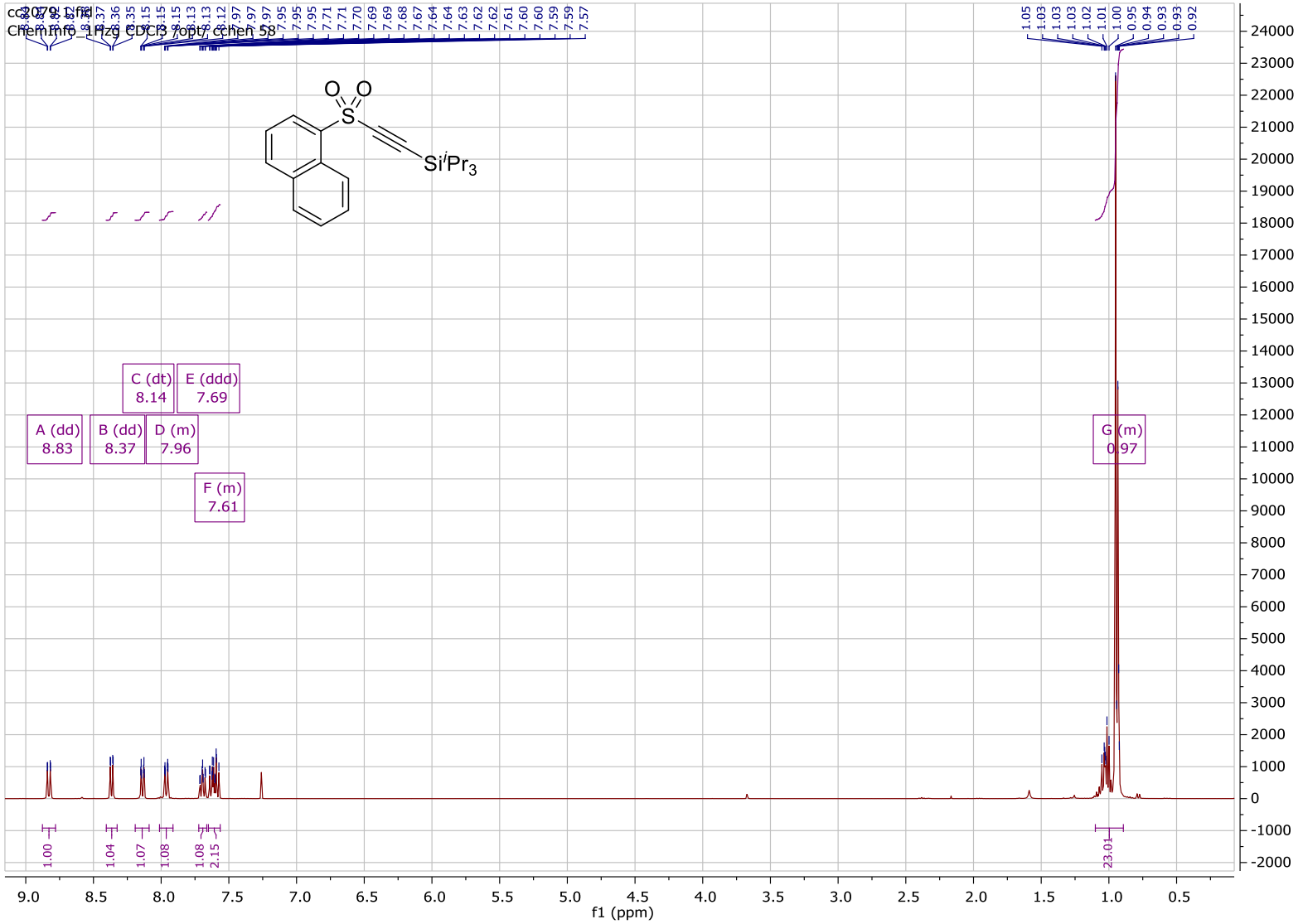
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6h**



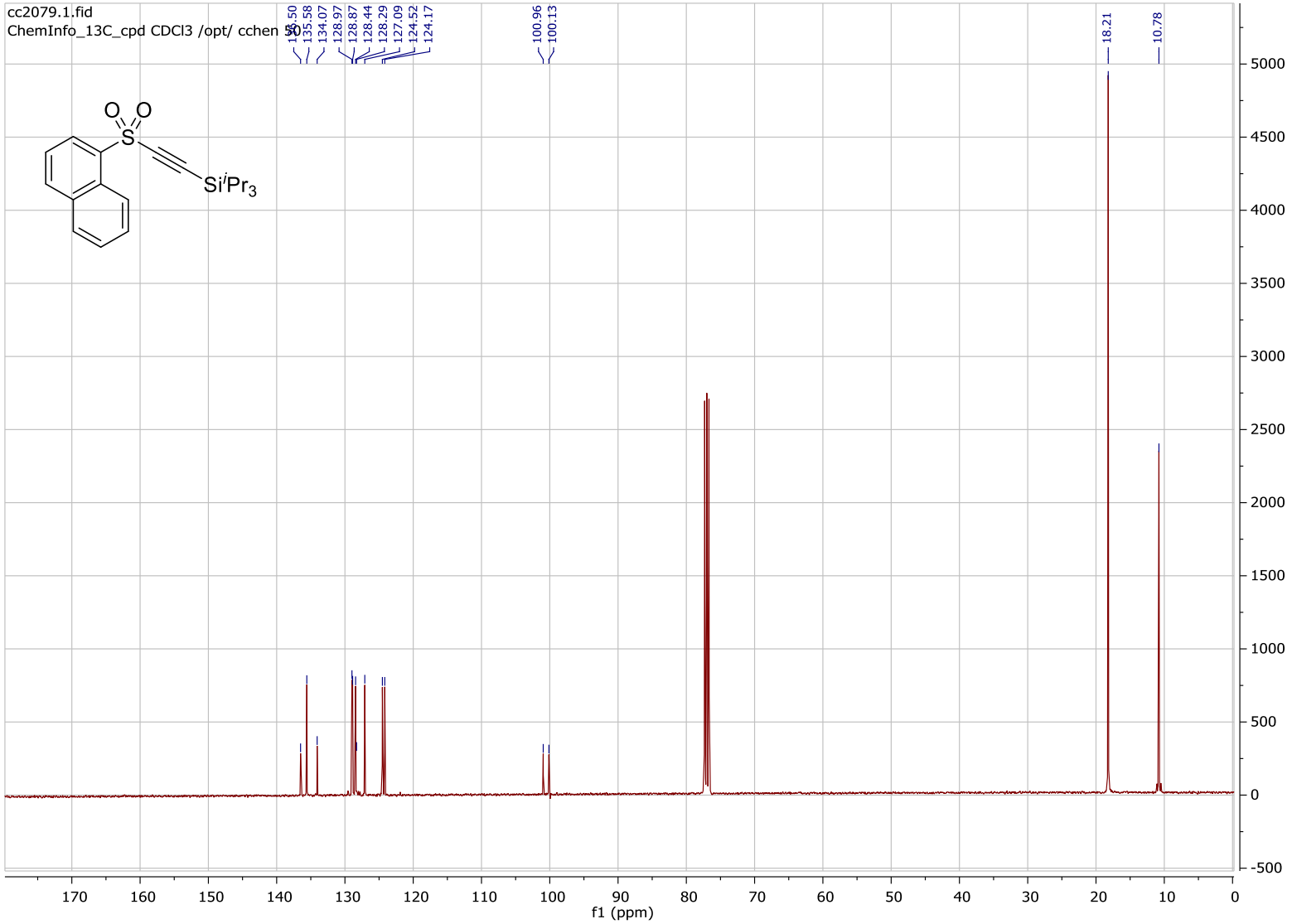
IR of compound **6h**



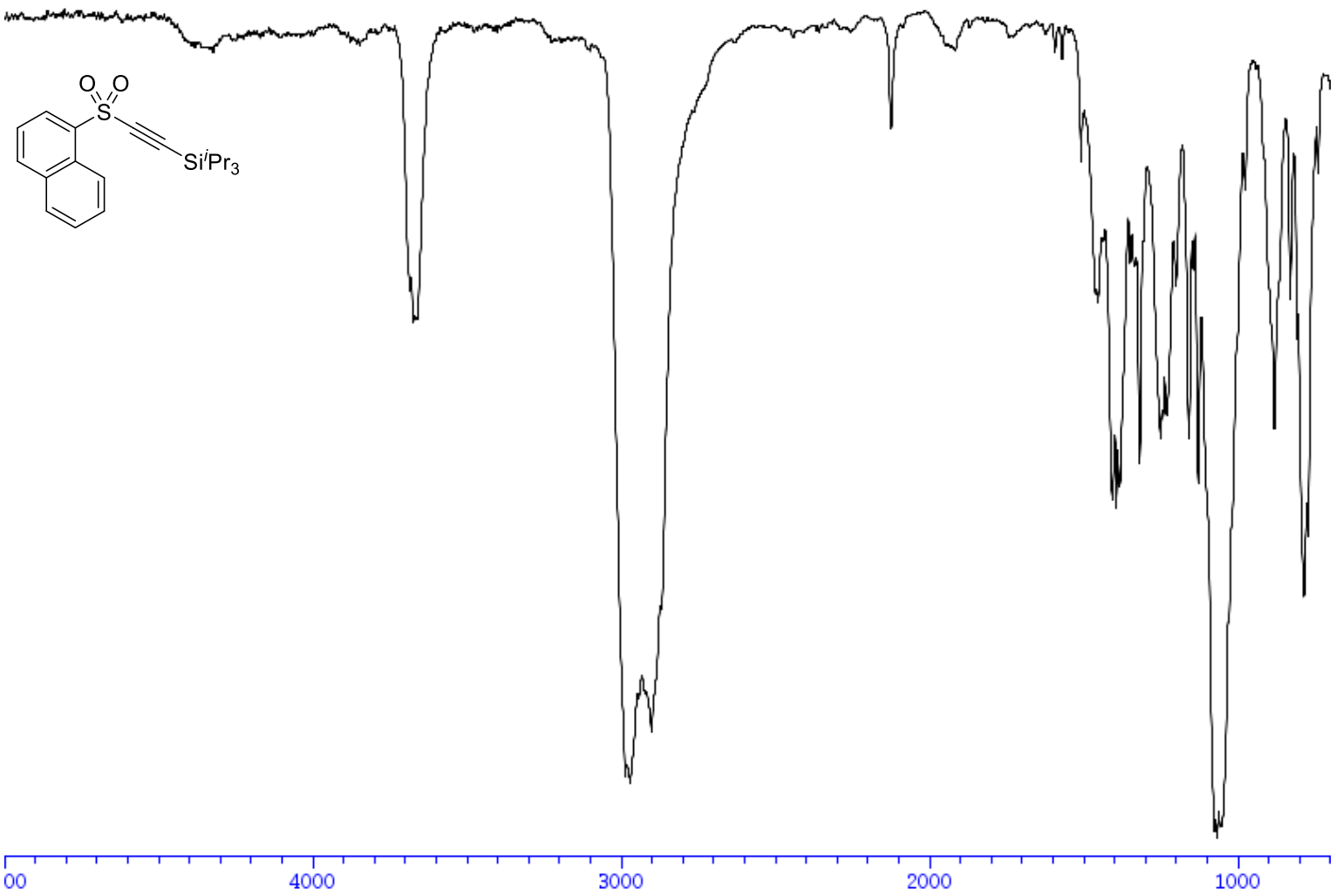
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6i**



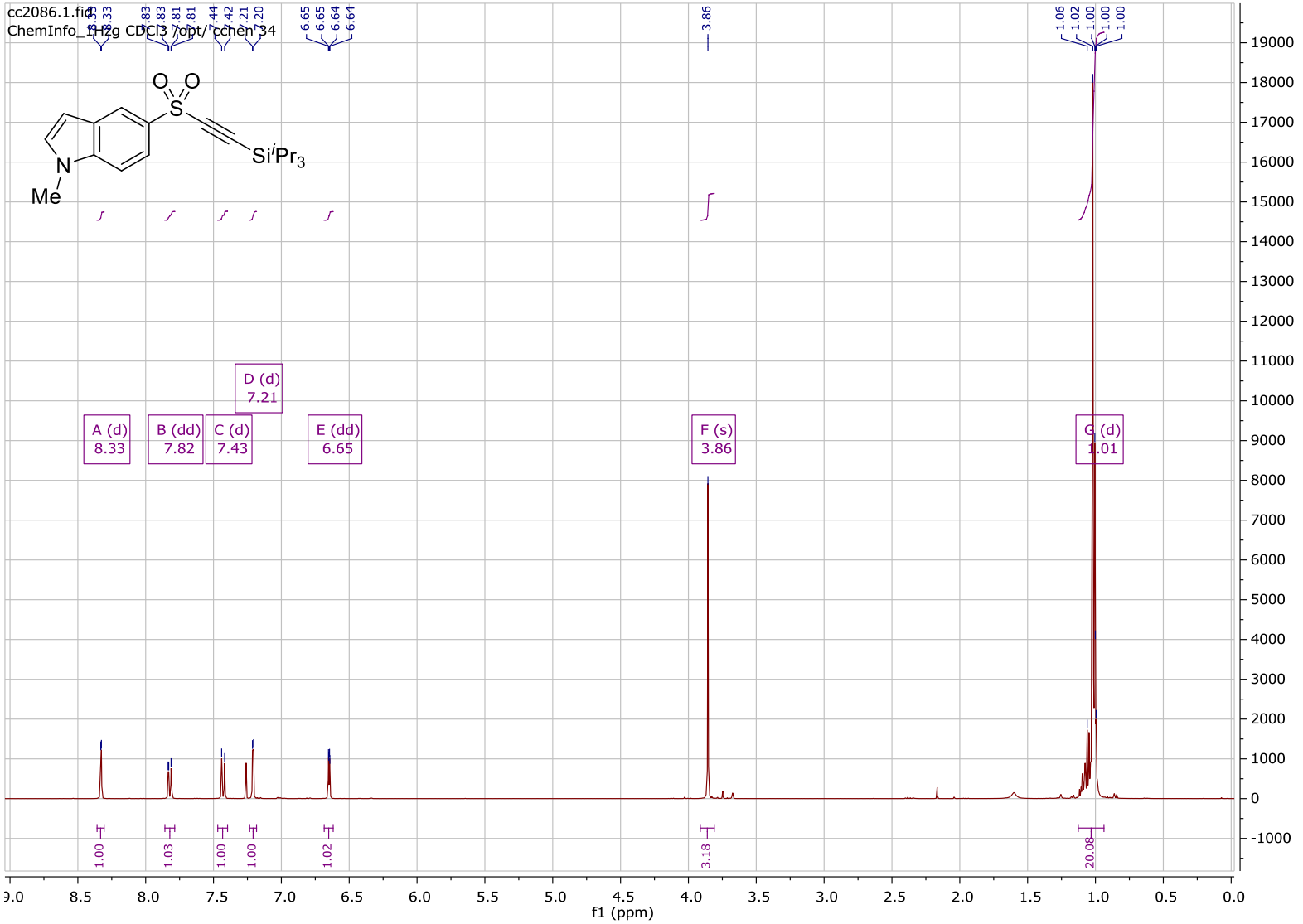
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6i**



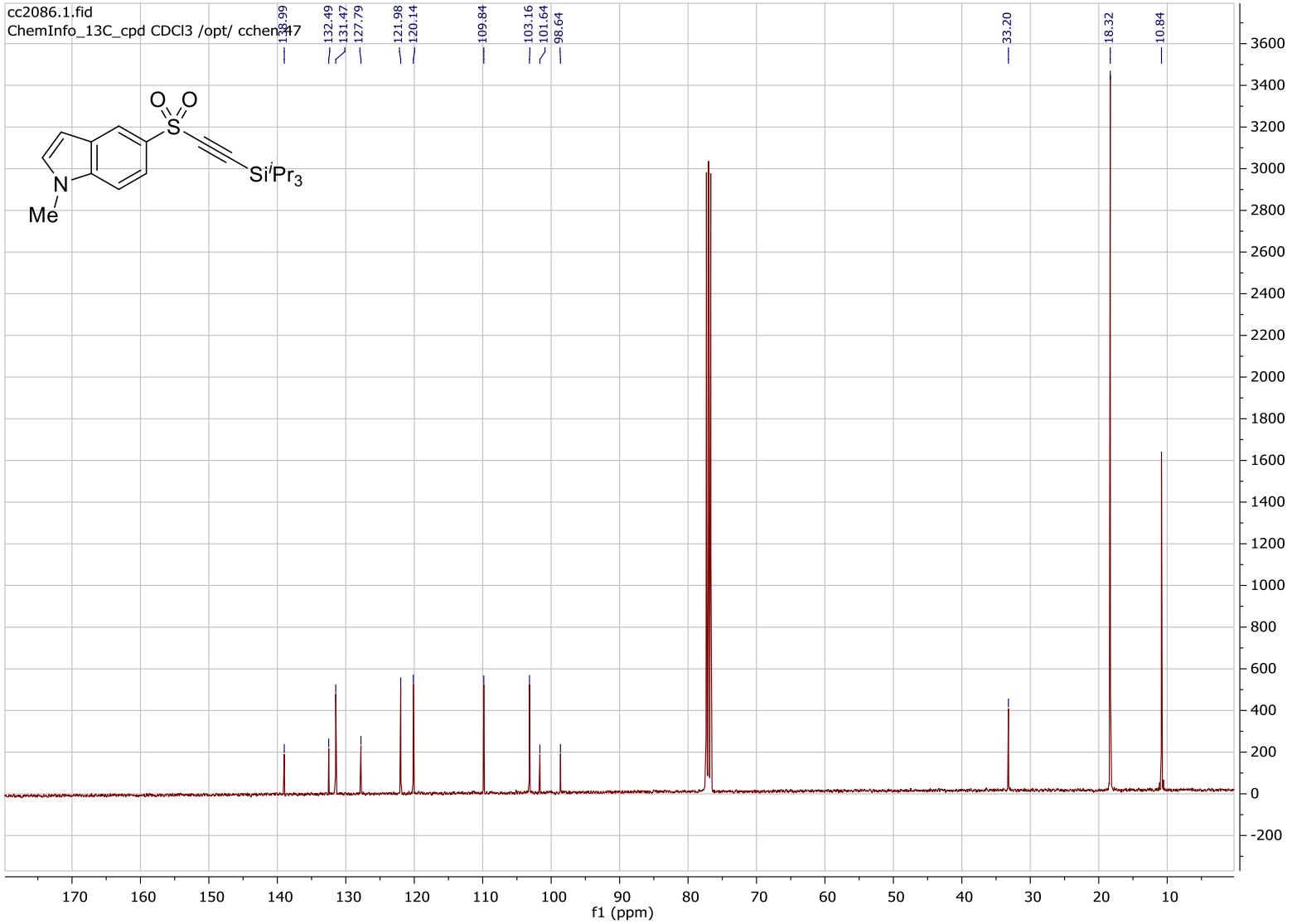
IR of compound **6i**



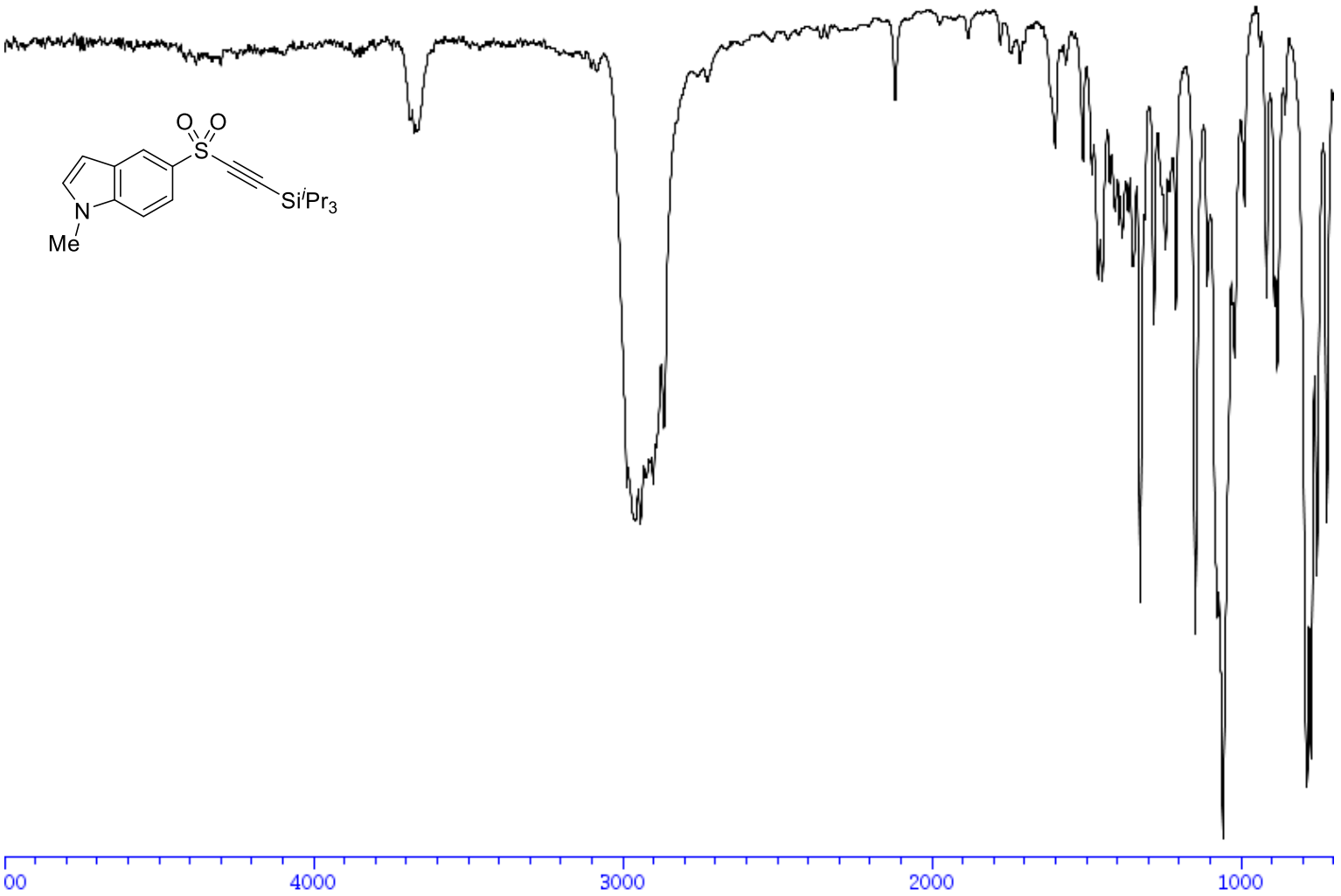
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6j**



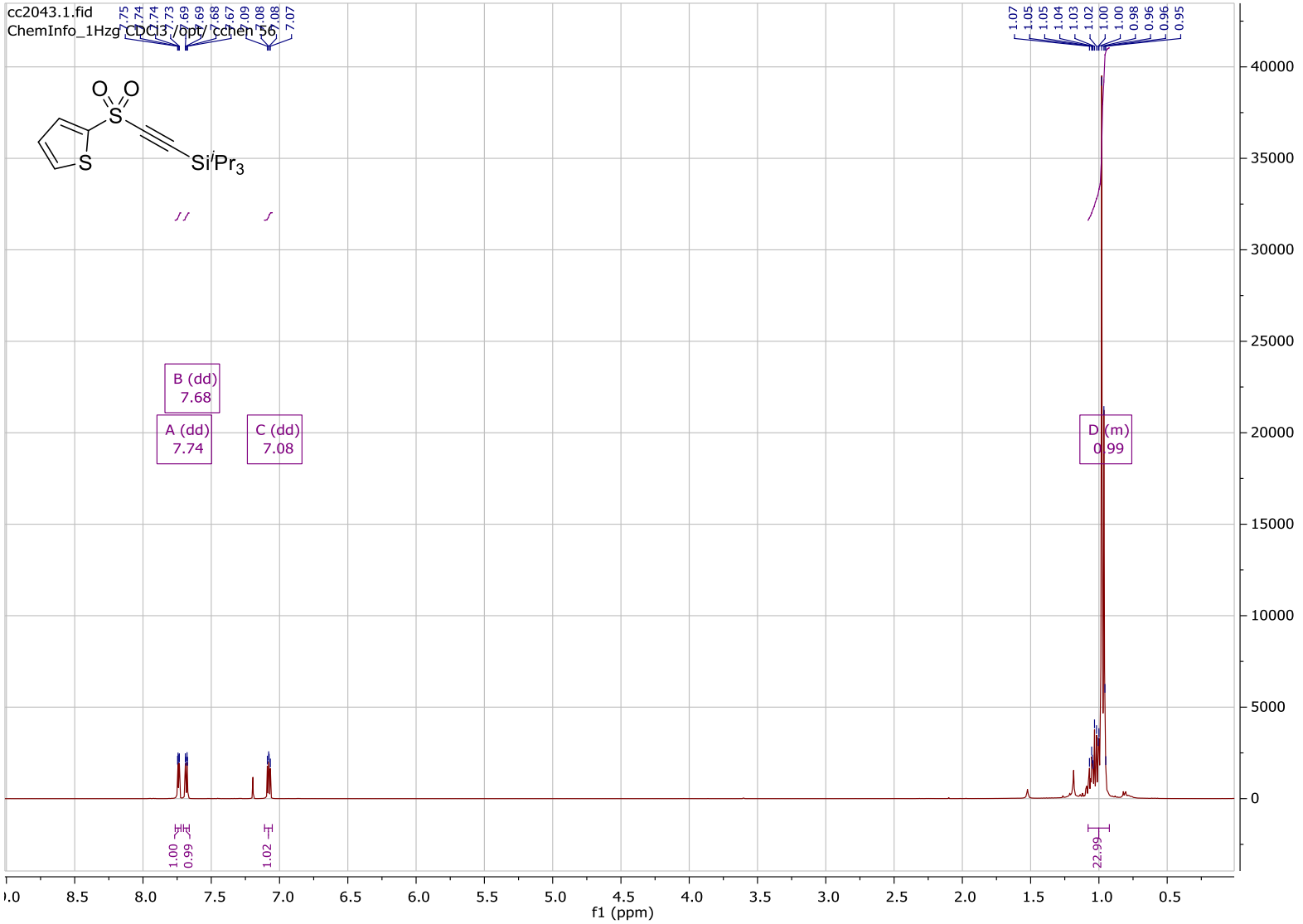
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6j**



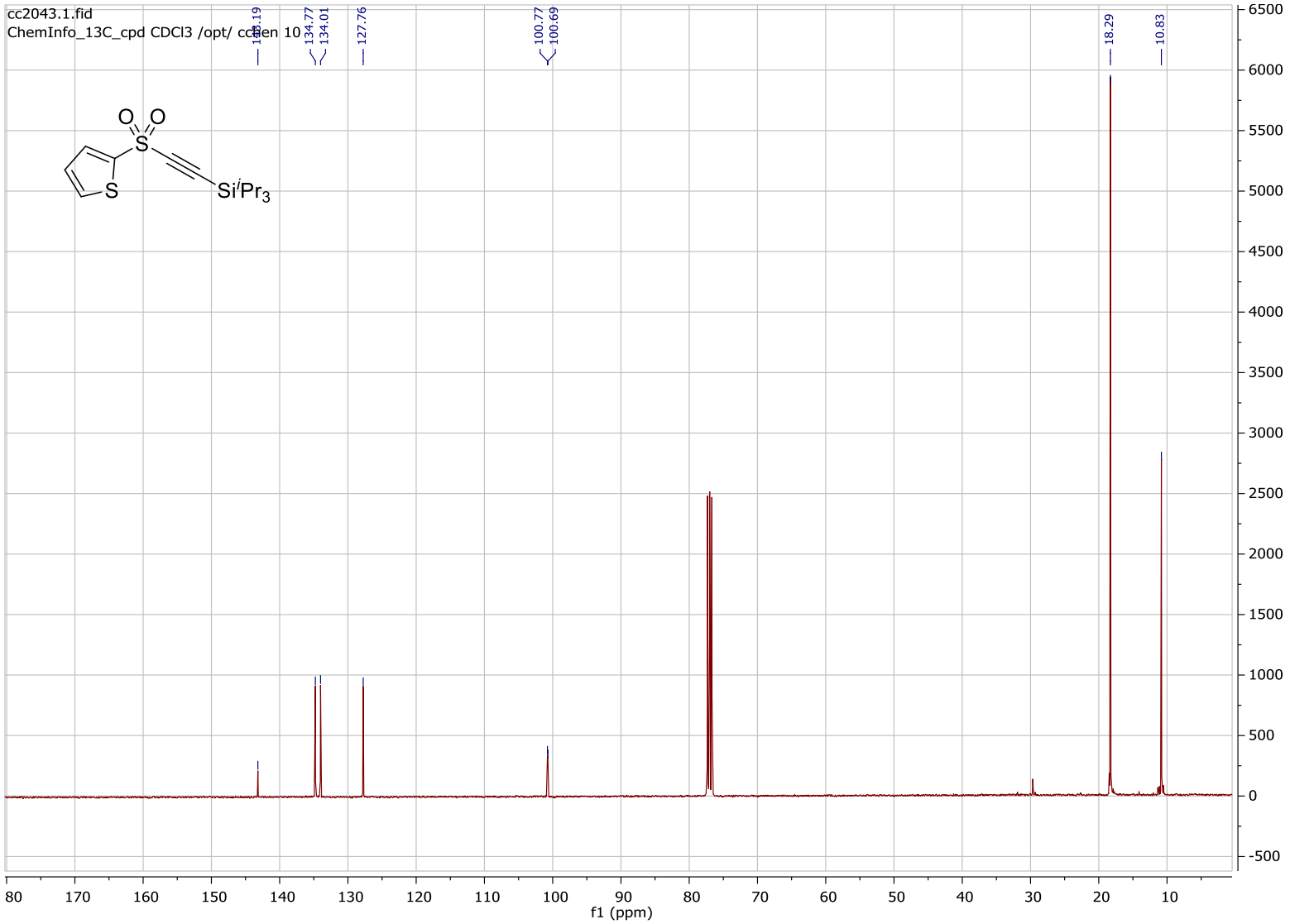
IR of compound **6j**



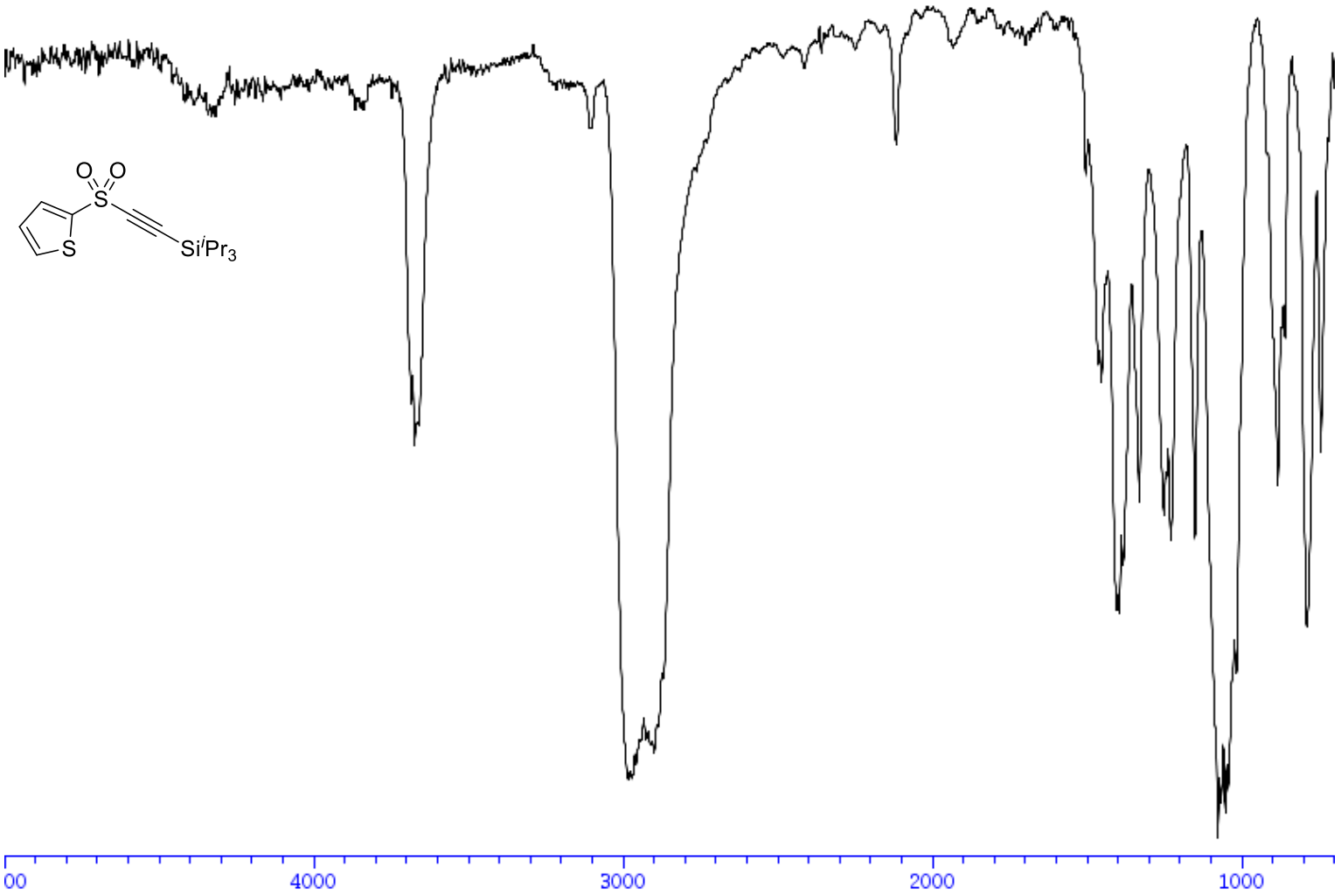
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6k**



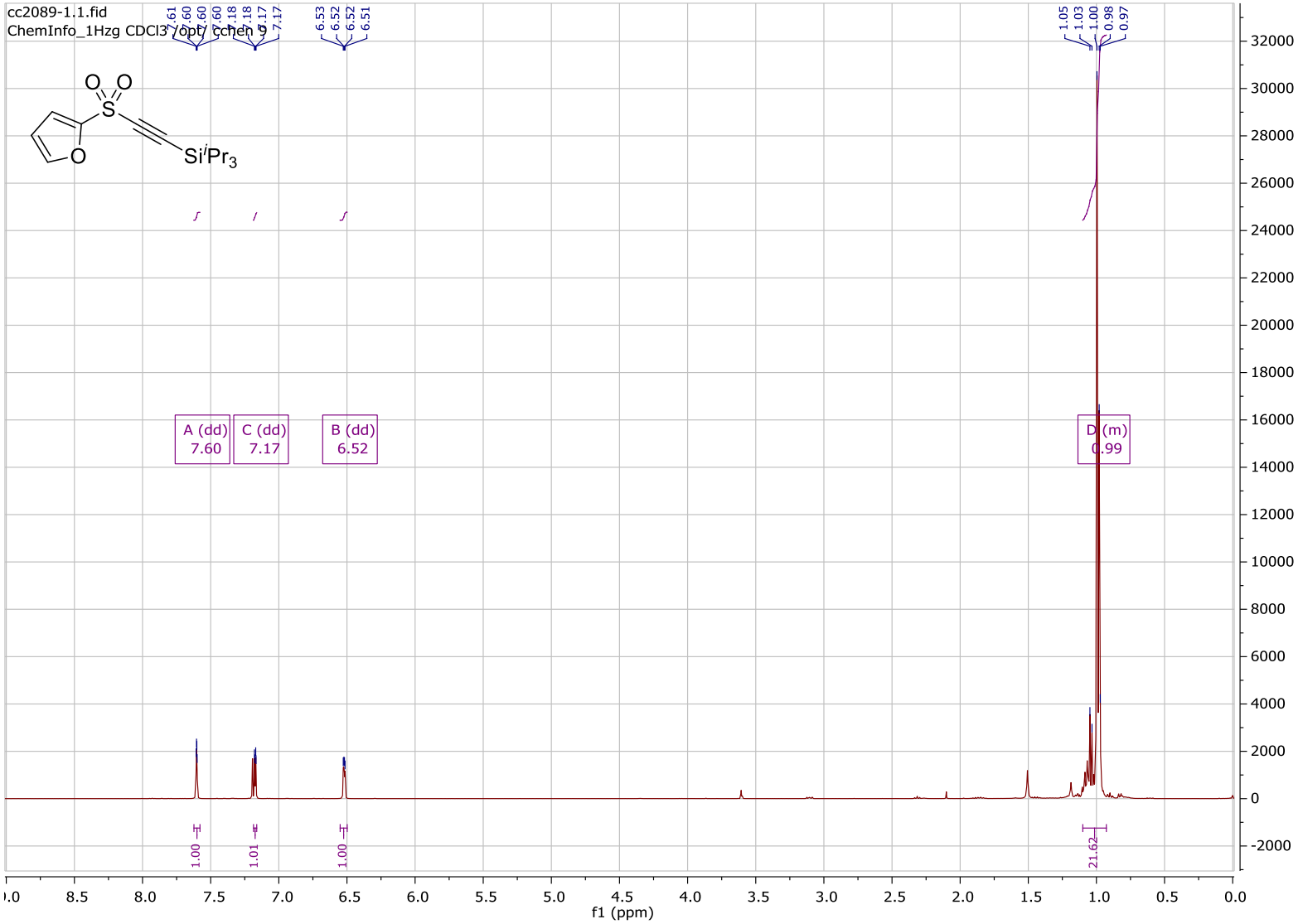
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6k**



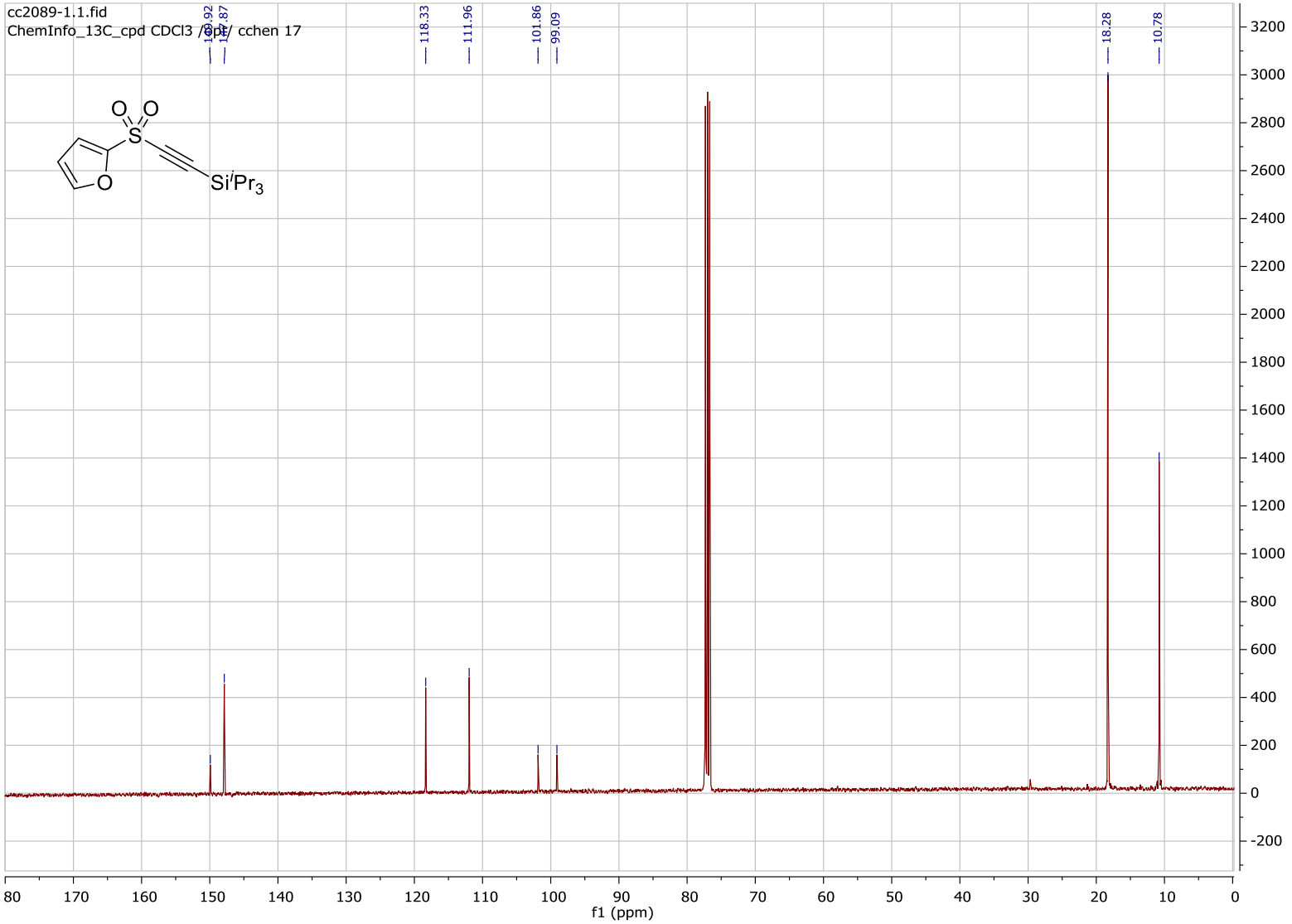
IR of compound **6k**



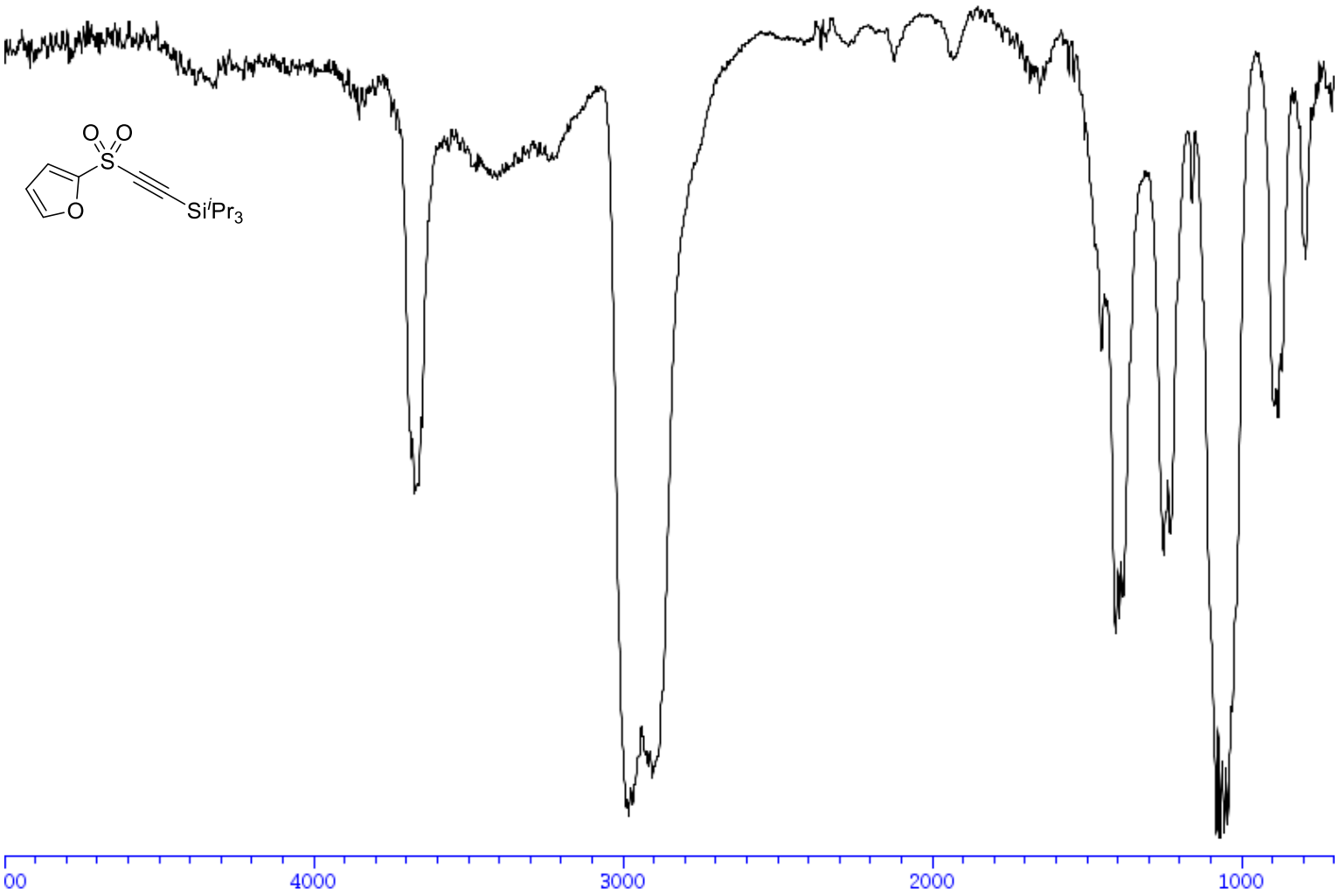
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6l**



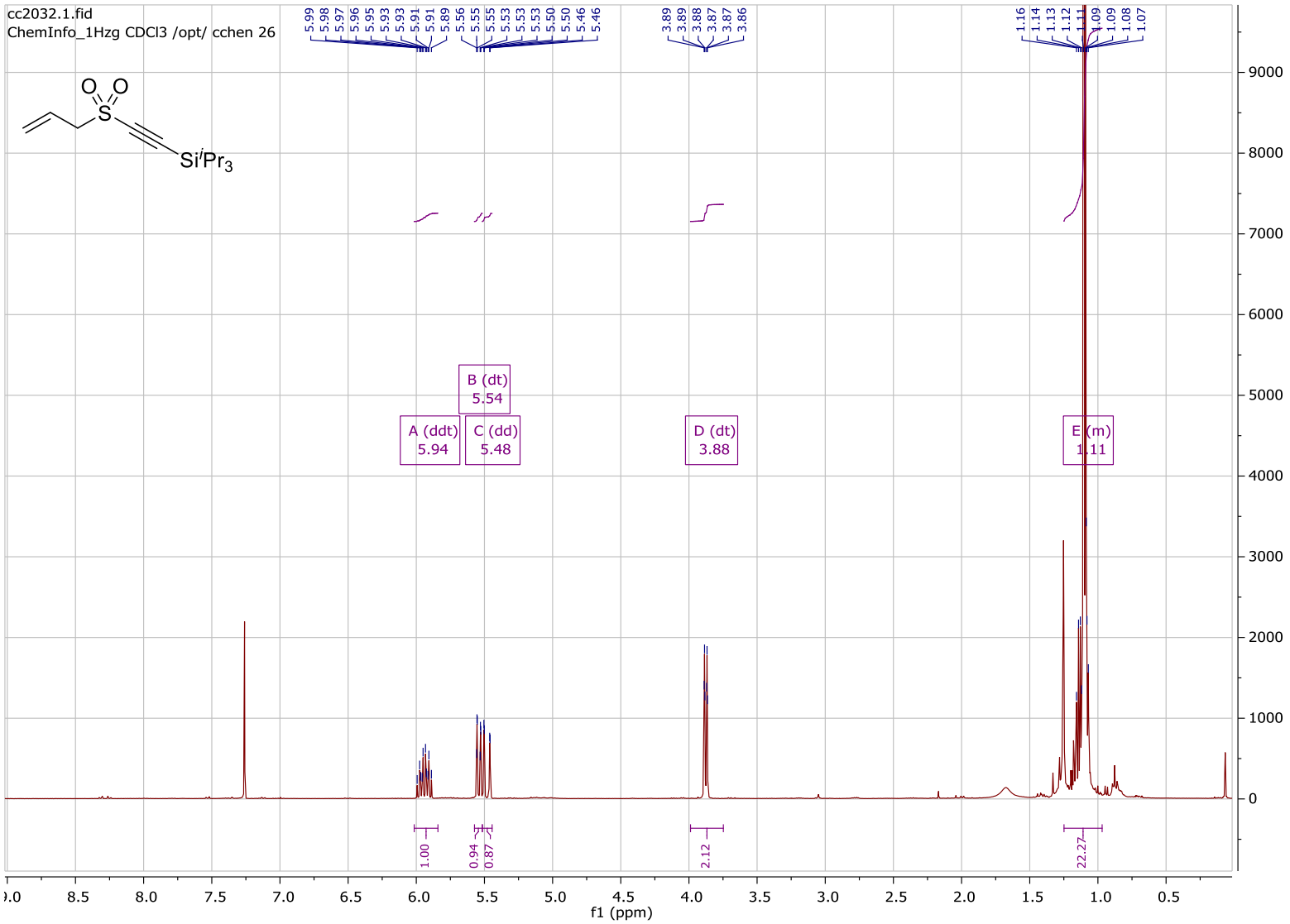
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6l**



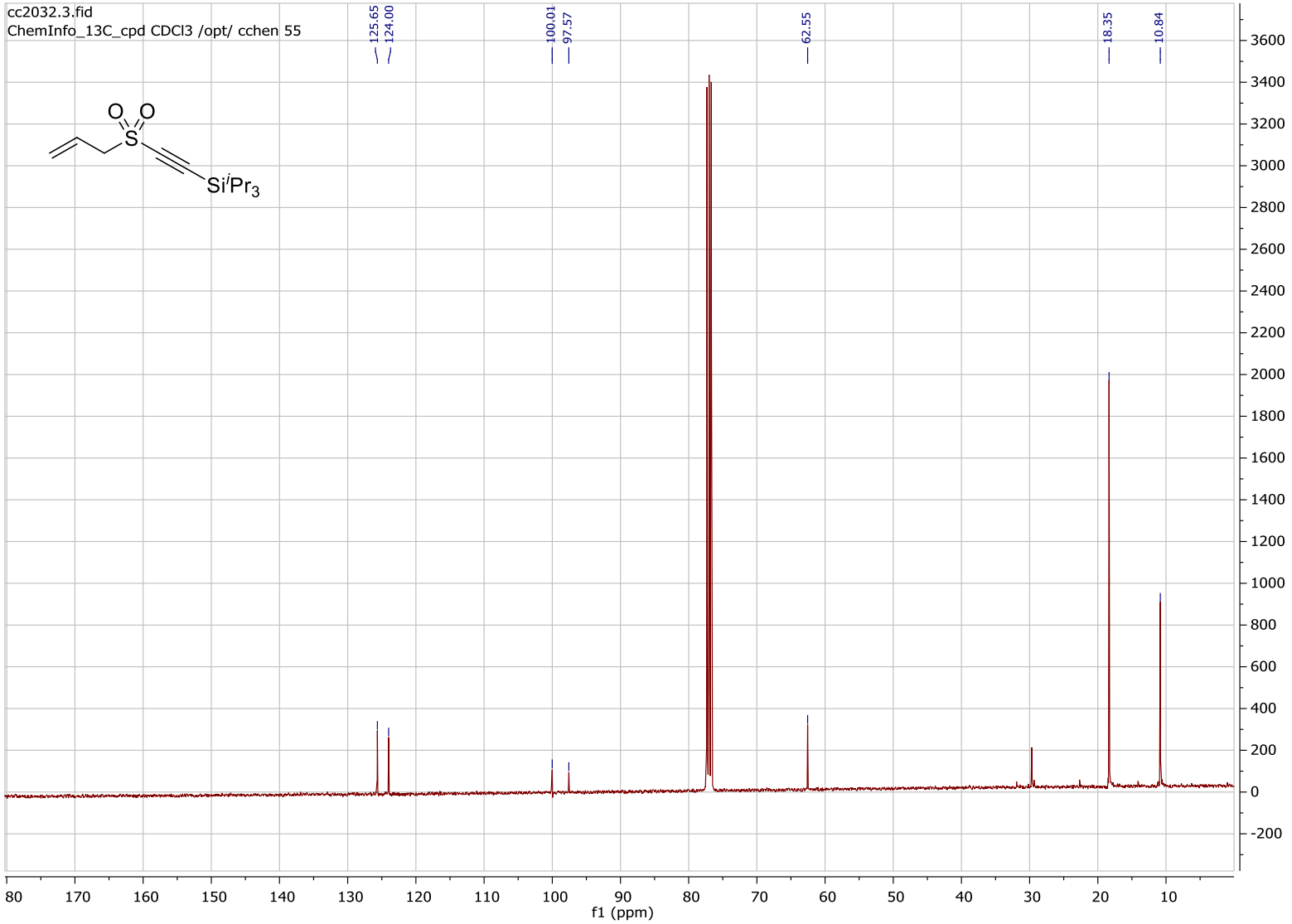
IR of compound **6l**



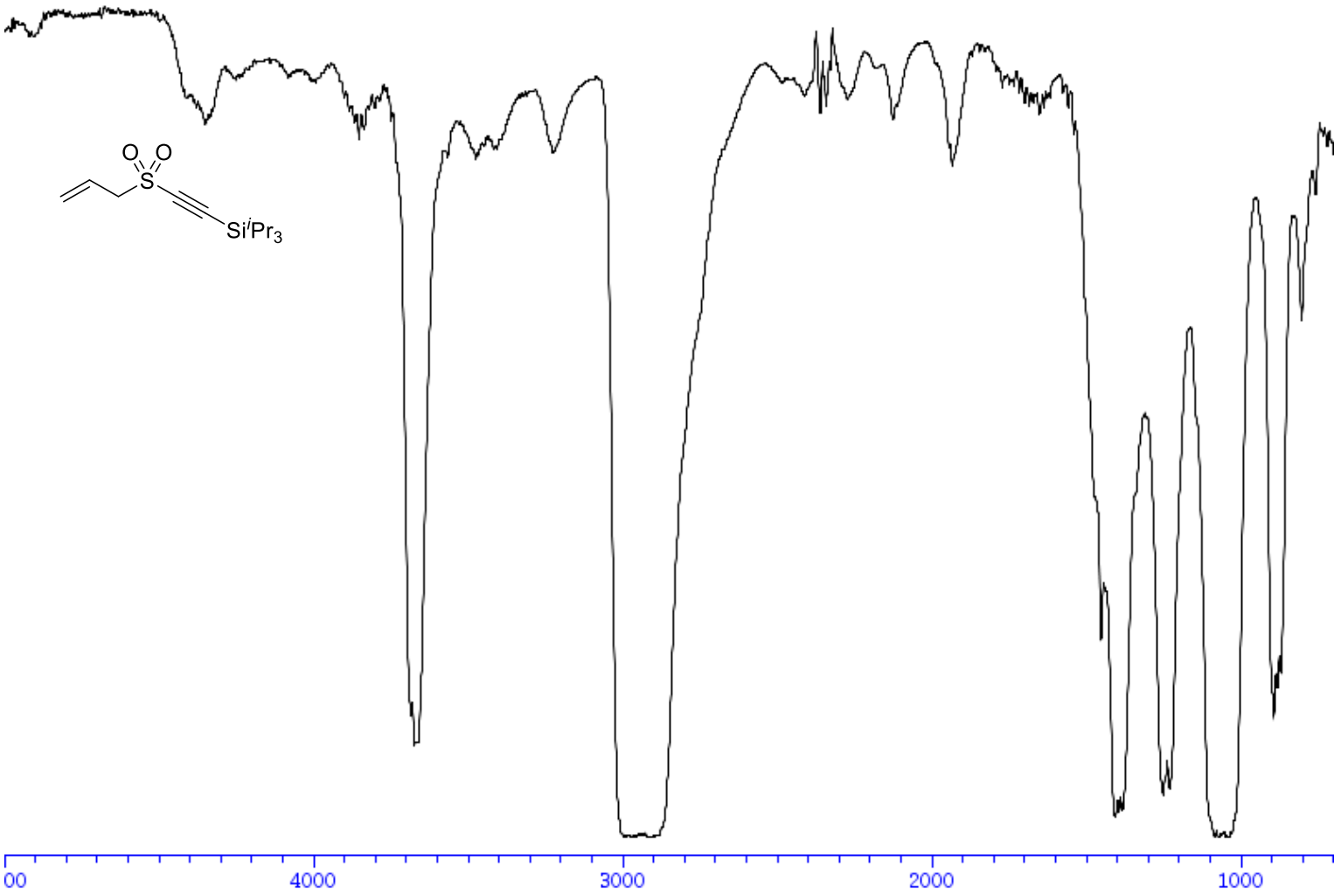
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6o**



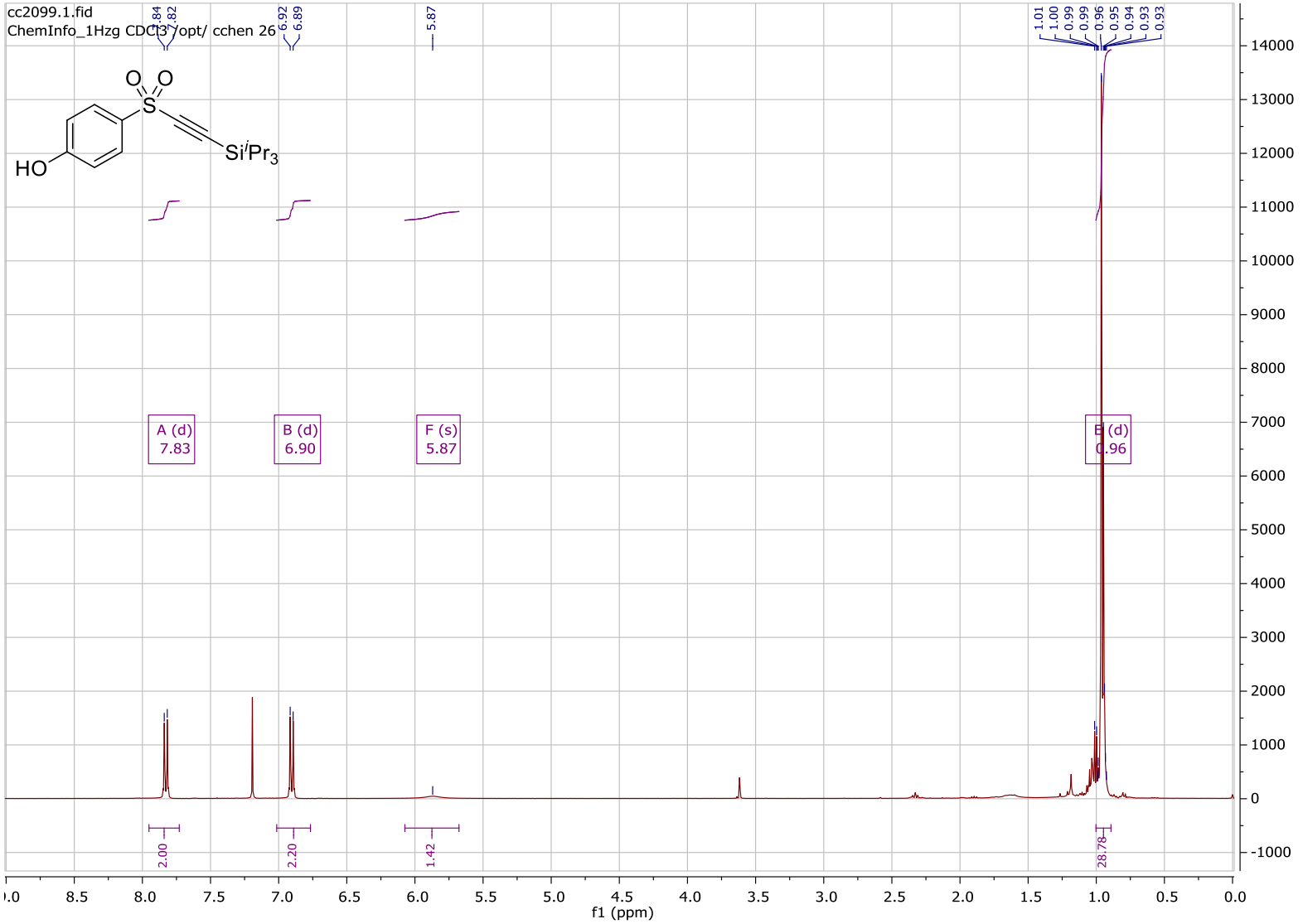
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6o**



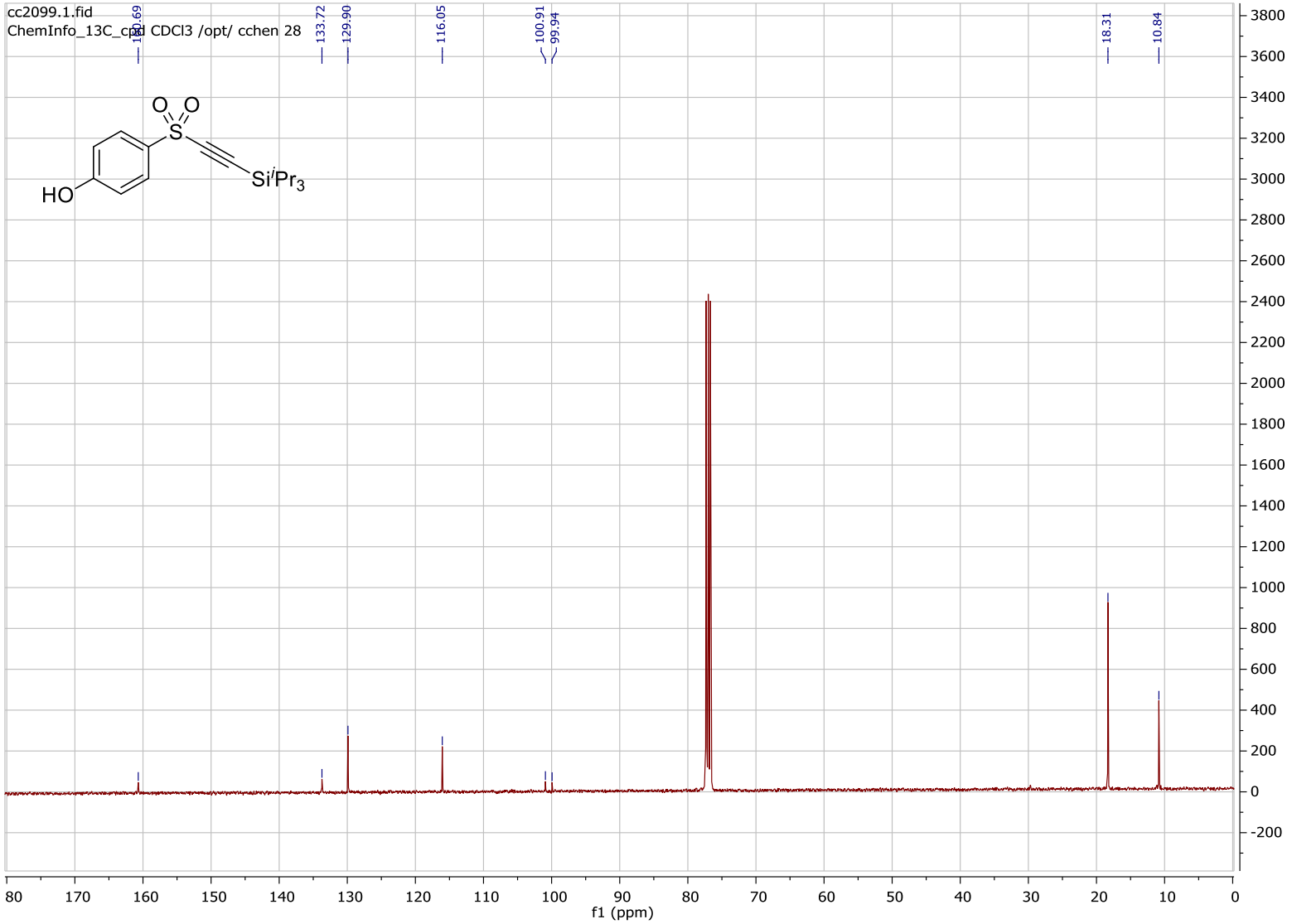
IR of compound **6o**



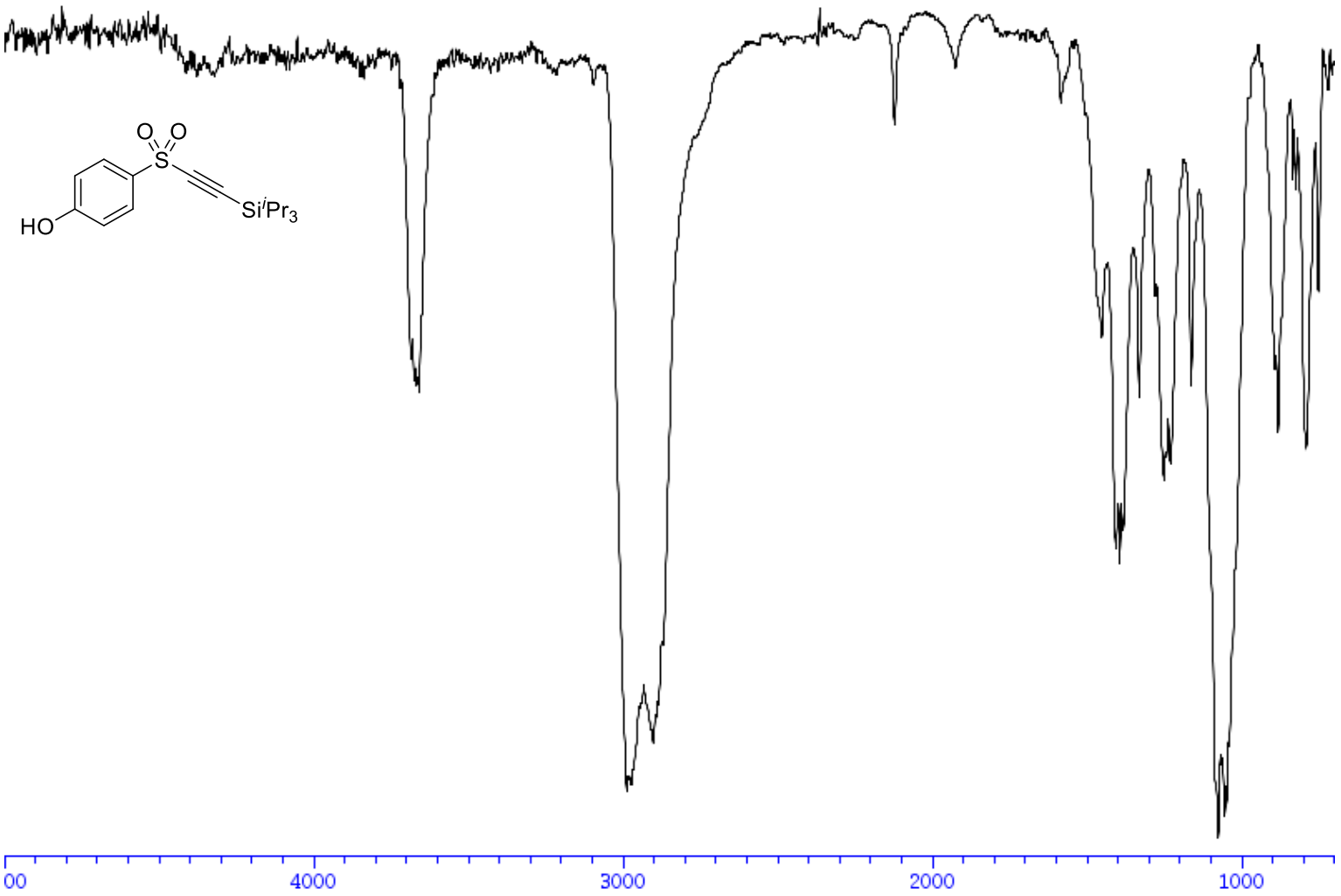
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6r**



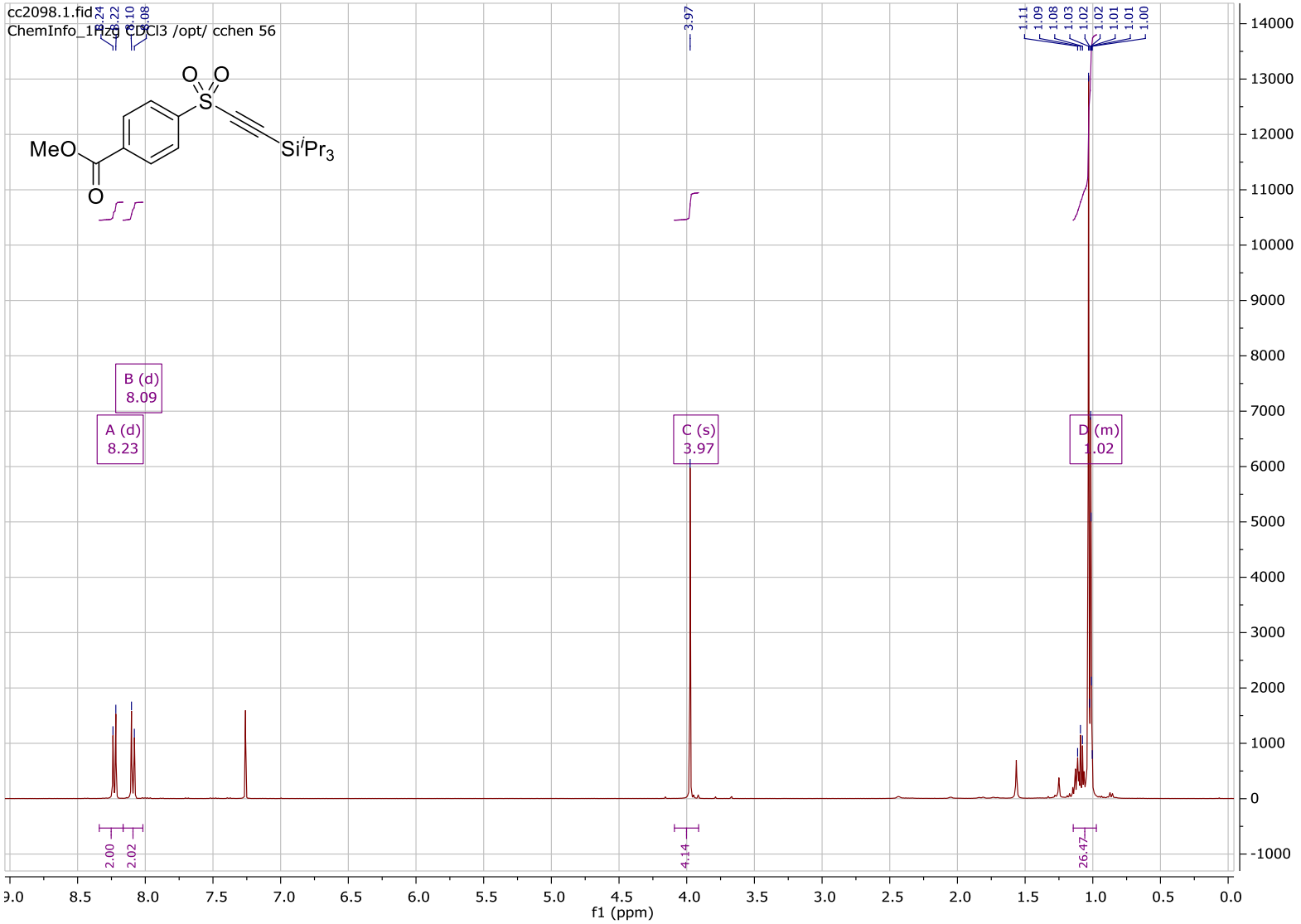
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6r**



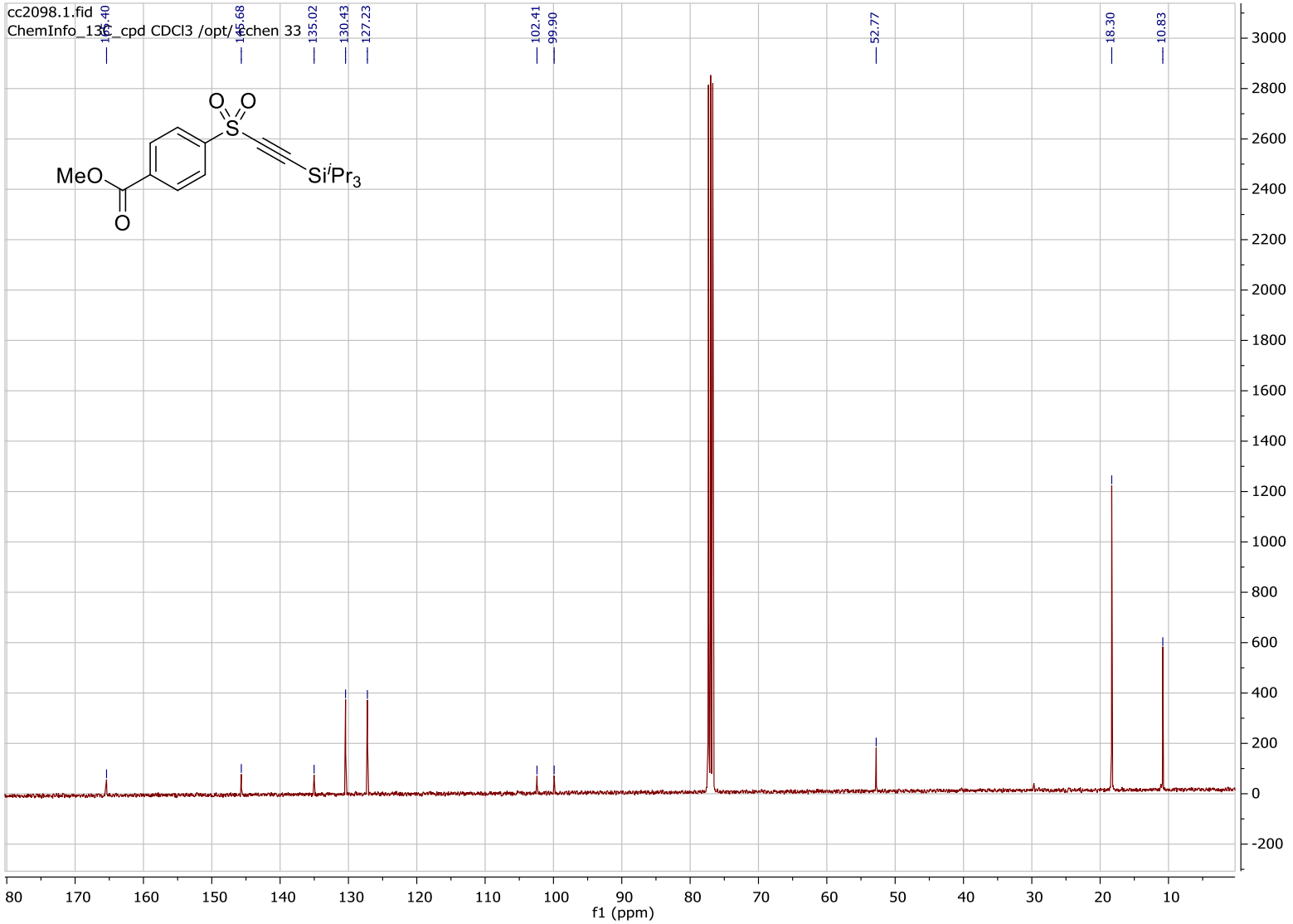
IR of compound **6r**



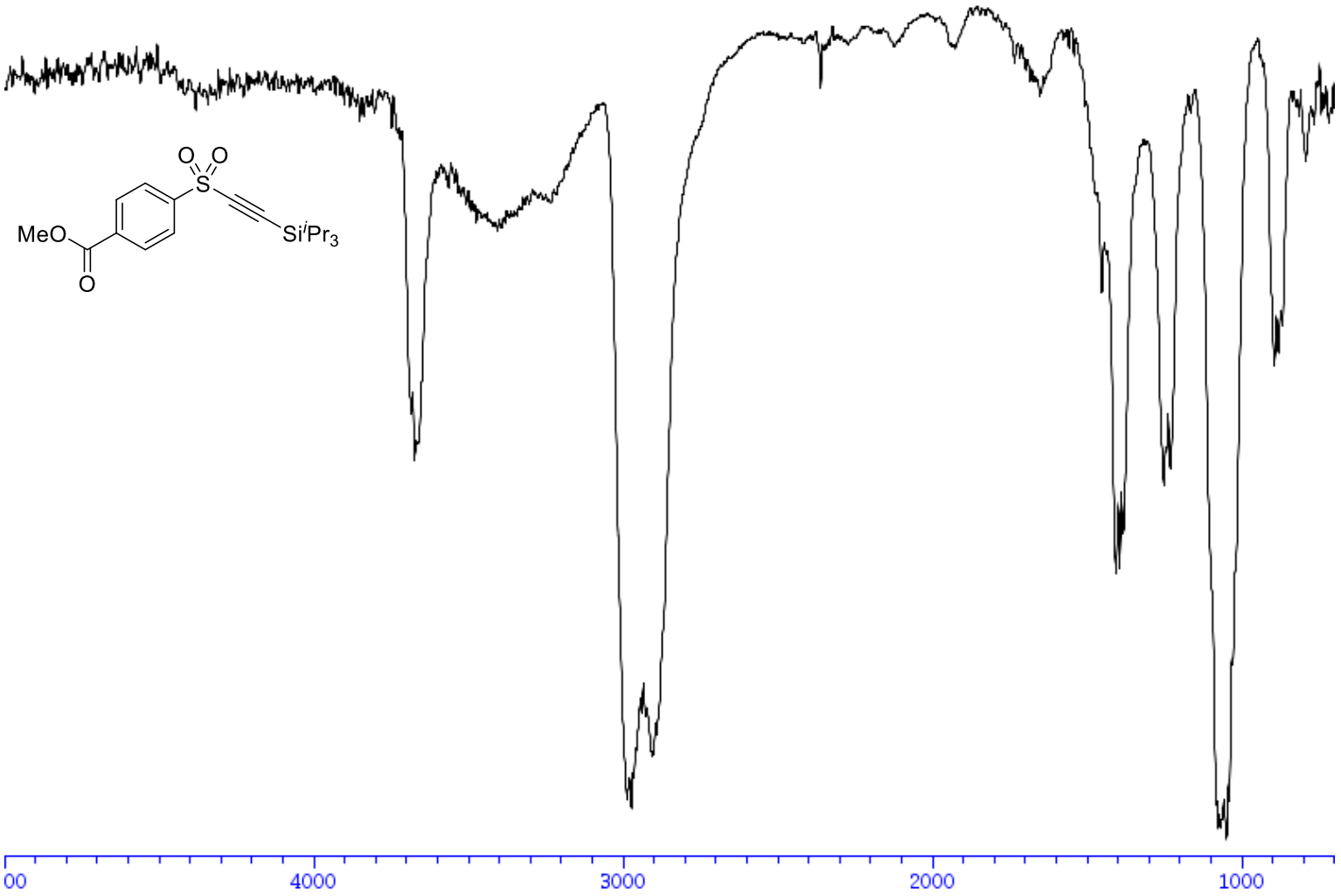
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6s**



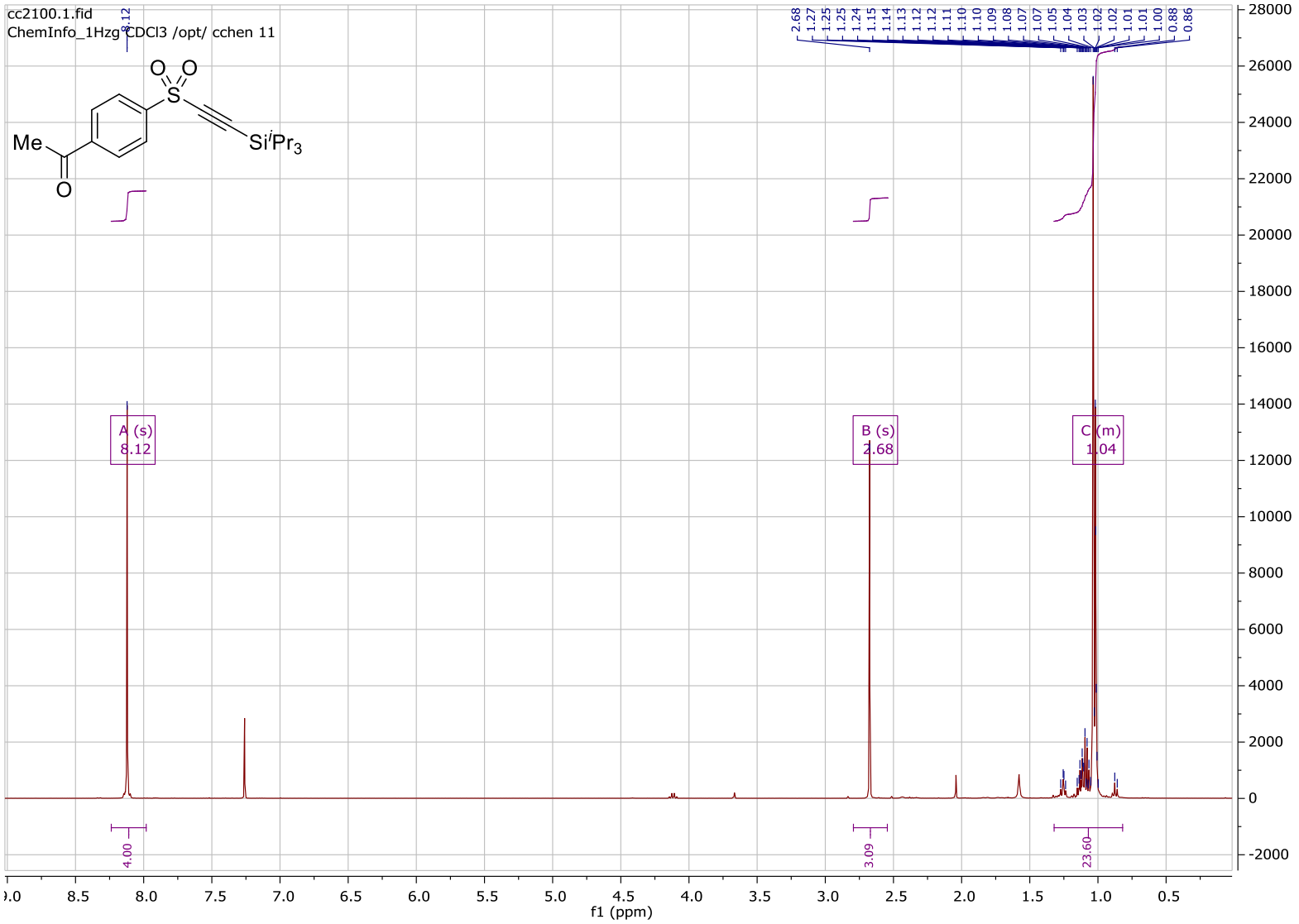
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6s**



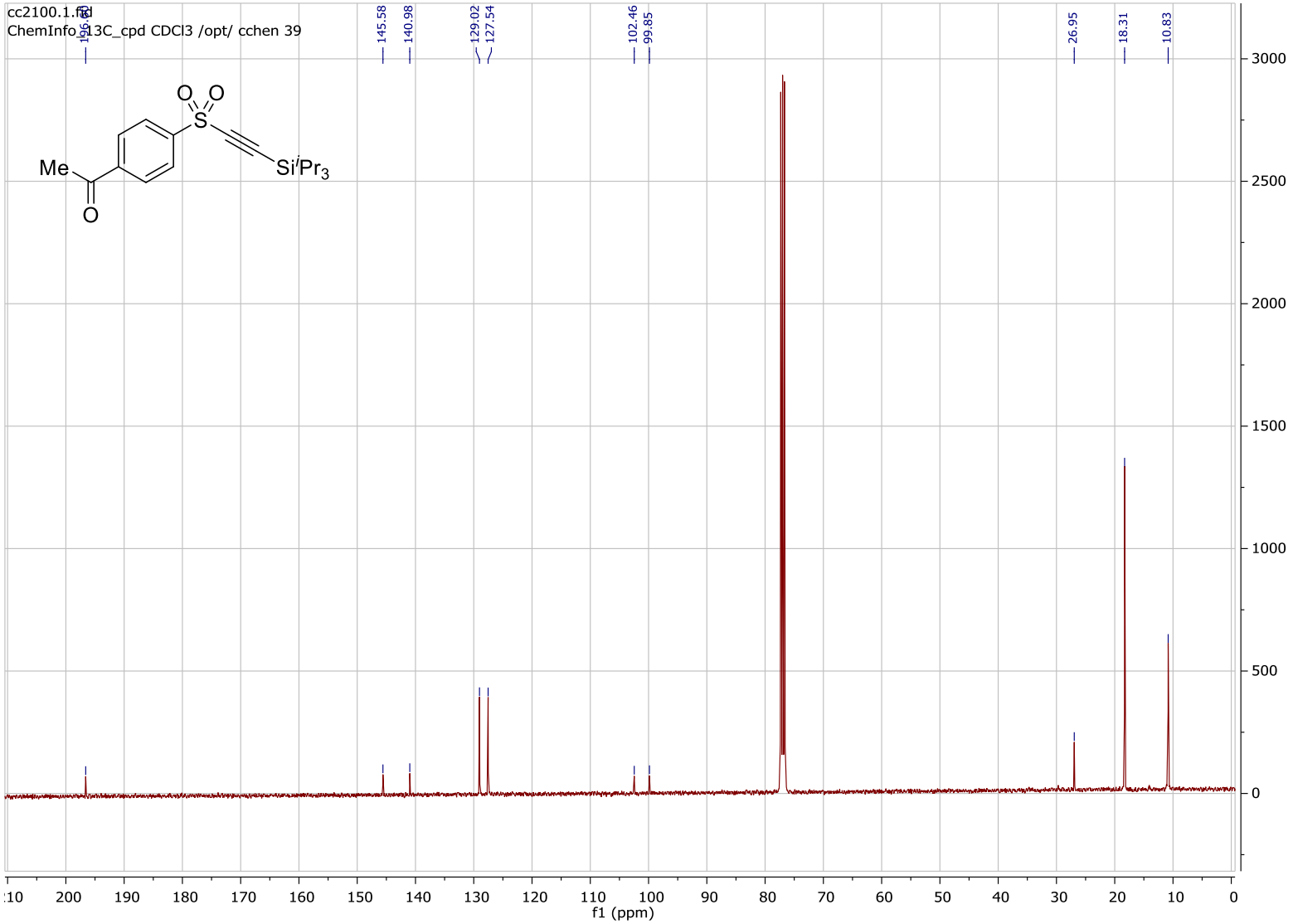
IR of compound **6s**



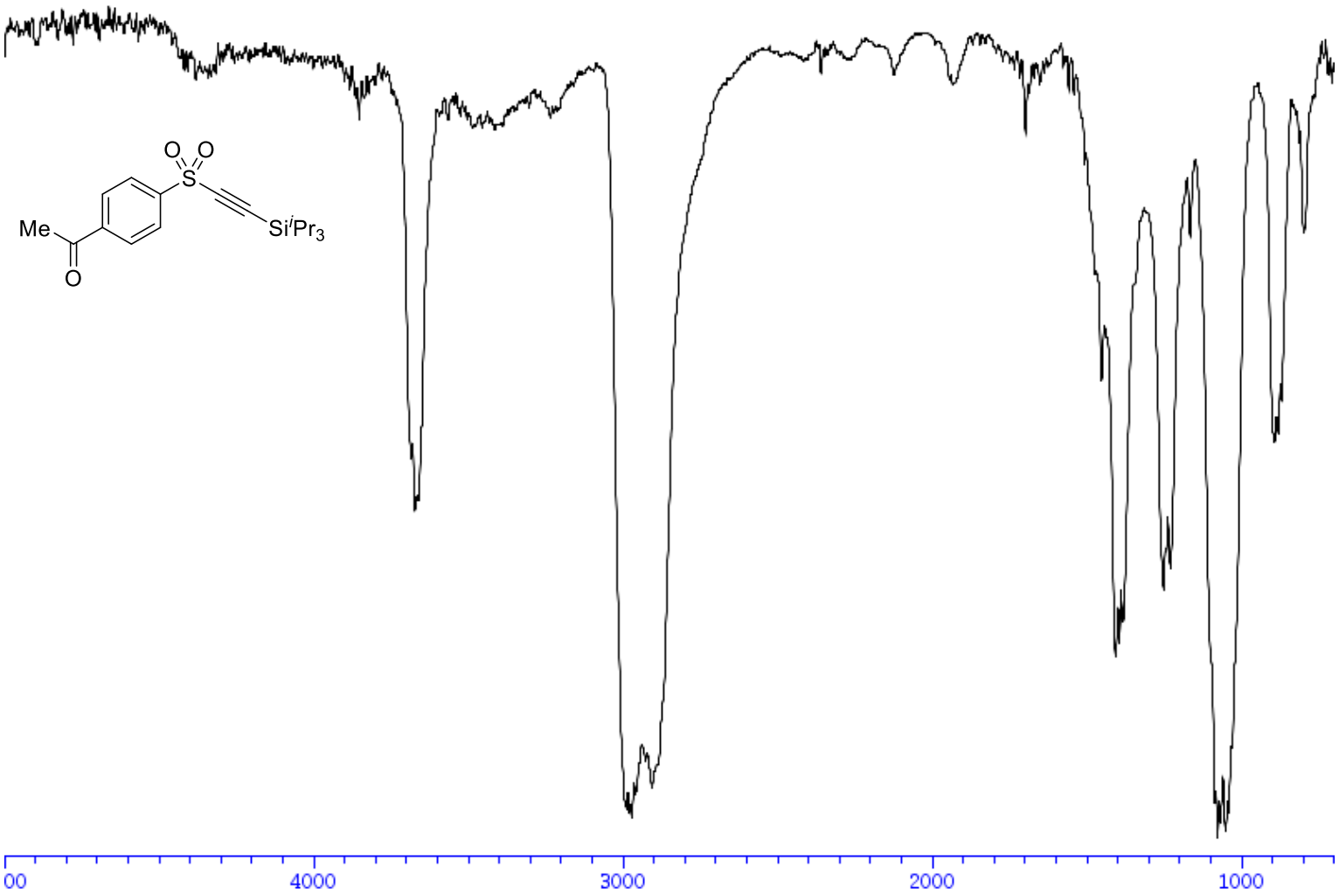
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6t**



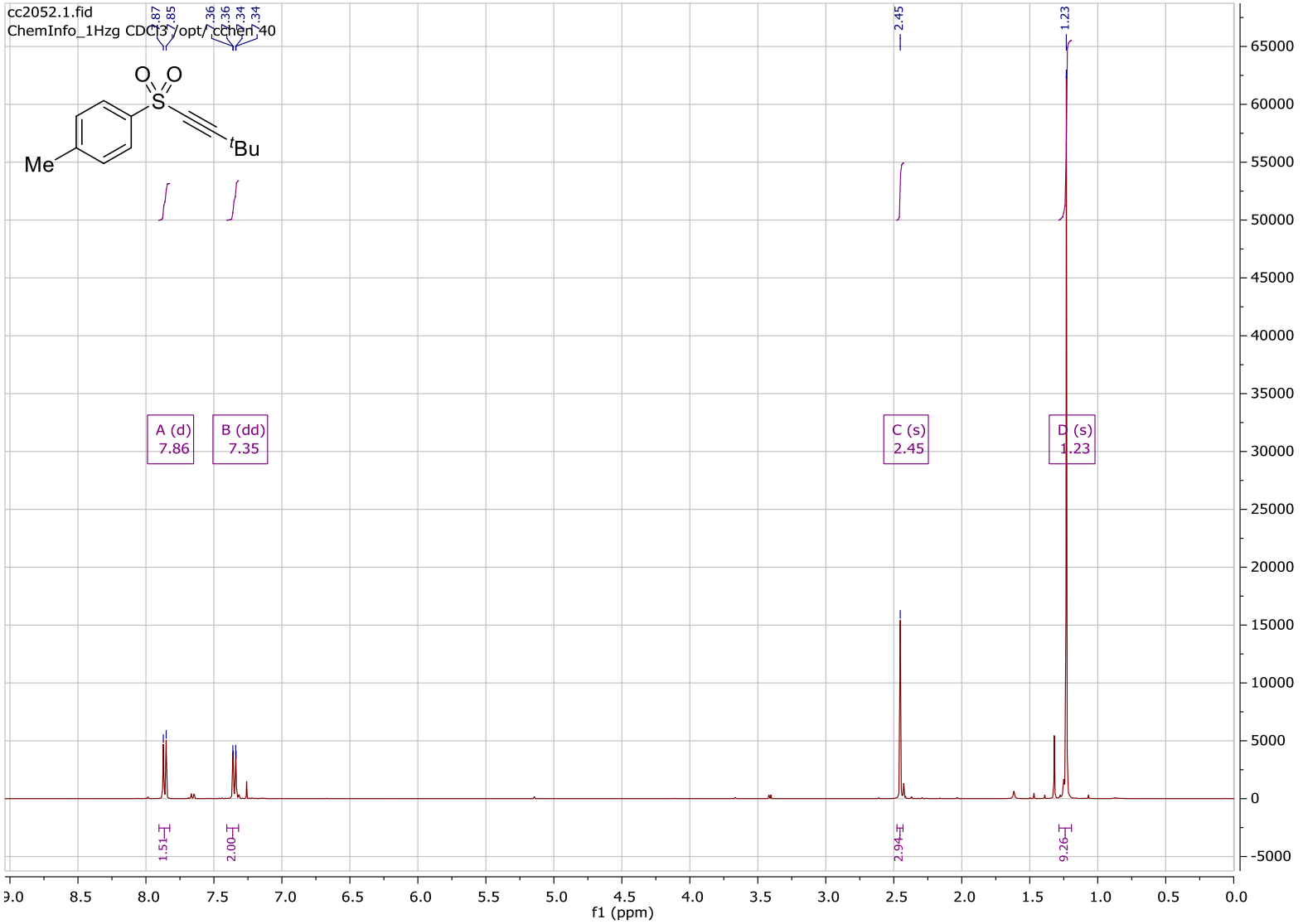
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6t**



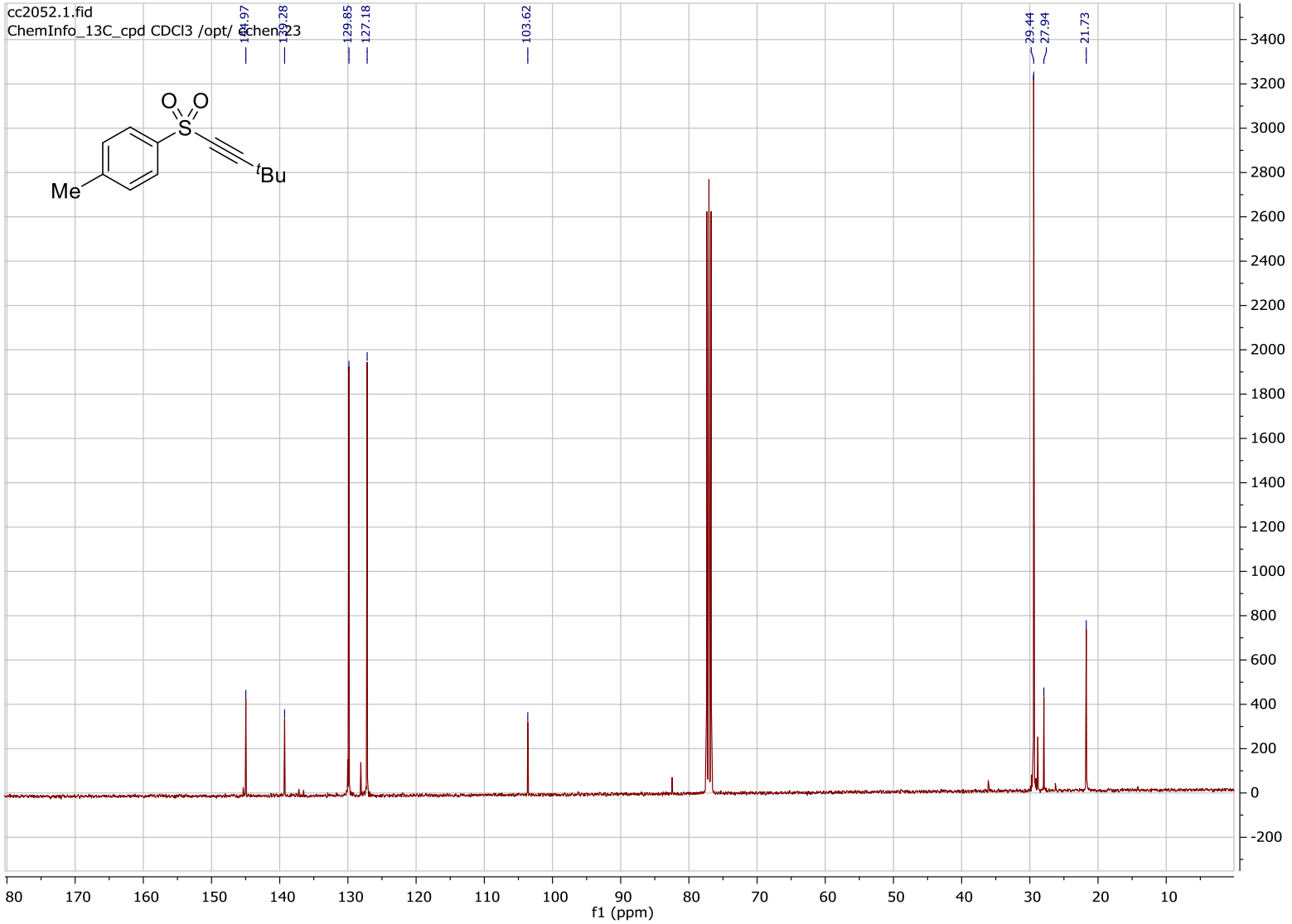
IR of compound **6t**



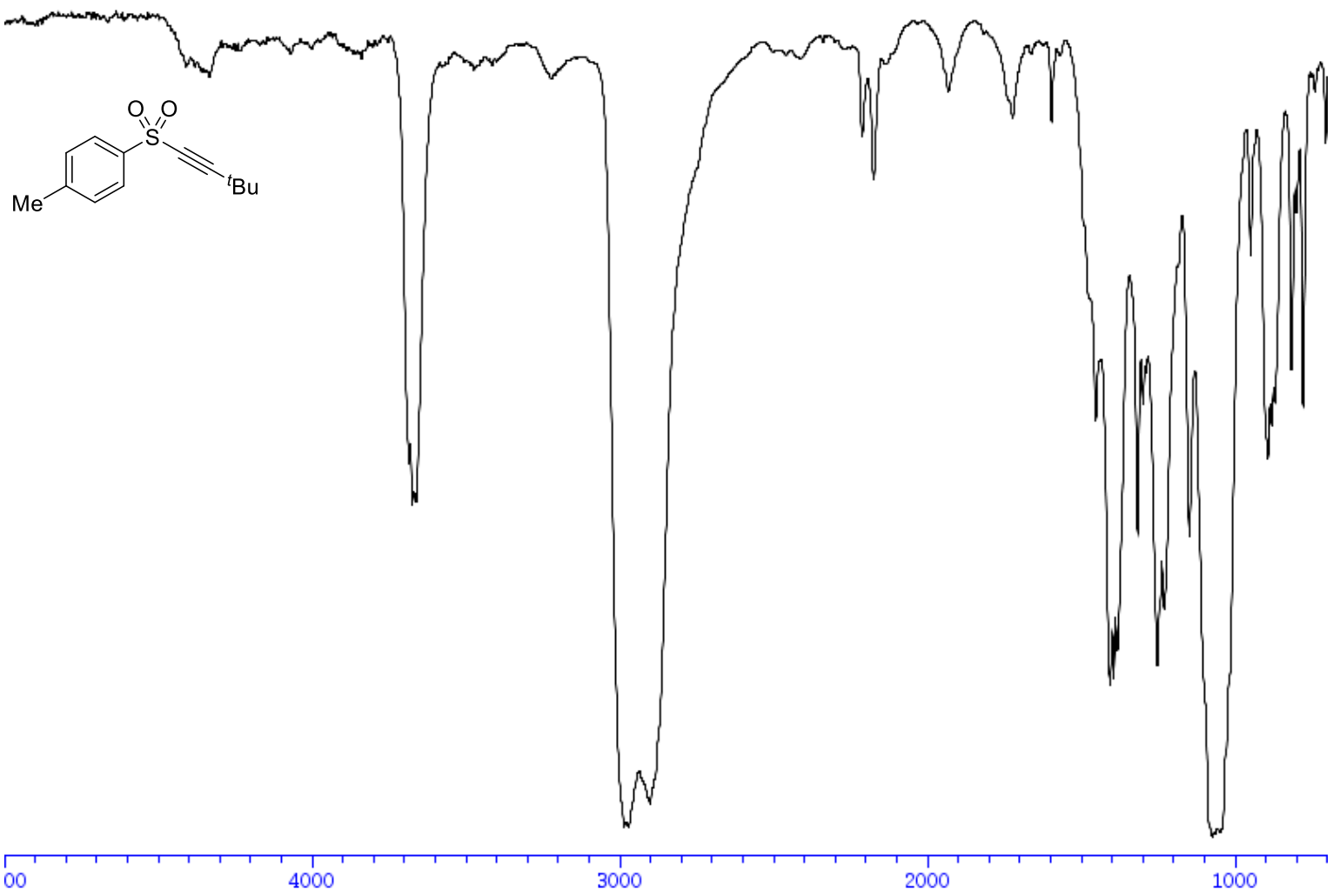
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7a**



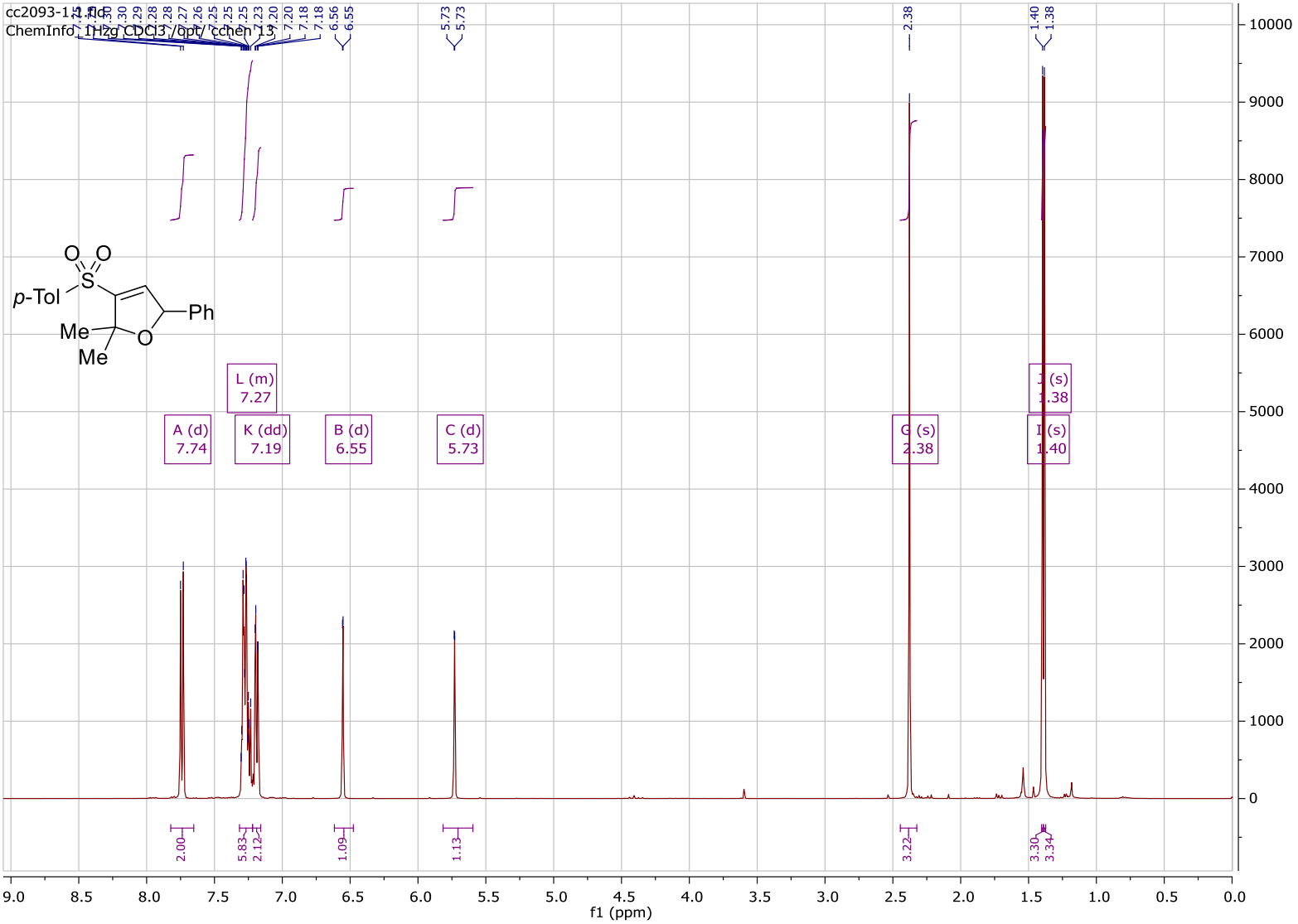
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7a**



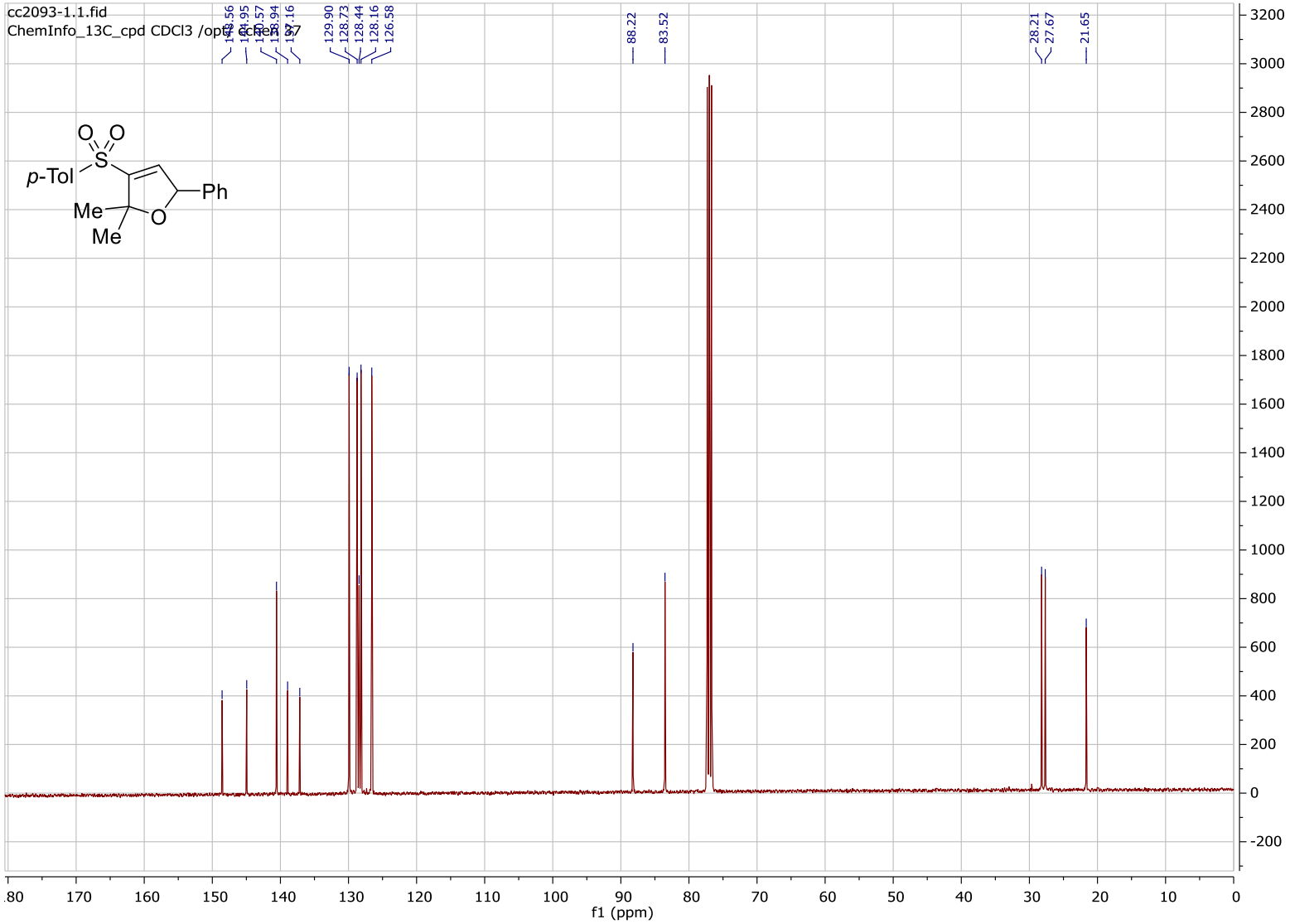
IR of compound **7a**



^{1}H-NMR (400 MHz, $CDCl_3$) of compound **8**



^{13}C-NMR (101 MHz, $CDCl_3$) of compound **8**



IR of compound **8**