Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Isoxazole as nitrile synthon: En routes to *ortho*-alkenylated isoxazole and benzonitrile with allyl sulfone catalyzed by Ru(II)

Pritishree Panigrahi, Subhendu Ghosh, Tamanna Khandelia, Raju Mandal, Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology Guwahati, Assam, India

E-mail: patel@iitg.ac.in

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1. General Information:

All the reagents were commercial grade and purified according to the established procedures. All the reactions were carried out in oven-dried glassware. The highest commercial quality reagents were purchased and were used without further purification unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) on a 0.25 mm silica gel plates ($60F_{254}$) visualized under UV illumination at 254 nm. Organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4). Solvents were removed using a rotary evaporator under reduced pressure. Column chromatography was performed to purify the crude product on silica gel 60–120 mesh using a mixture of hexane and ethyl acetate as eluent. All the isolated compounds were characterized by ^1H, $^{13}C\{^1H\}$ NMR and IR spectroscopic (HRMS-spectrometric) techniques. NMR spectra for all the samples were recorded in deuterochloroform ($CDCl_3$). ^1H, $^{13}C\{^1H\}$ were recorded in 600 (151), 500 (126) or 400 (101) MHz spectrometer and were calibrated using tetramethylsilane for ^1H NMR, deuterochloroform for ^{13}C NMR as an internal reference {$Si(CH_3)_4$: 0.00 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR. The chemical shifts are quoted in δ units, parts per million (ppm). ^1H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, integration and coupling constant(s) *J* in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflection experiments. FT-IR spectra were recorded as neat and reported in the frequency of absorption (cm^{-1}). The (allylsulfonyl)benzene (**2**) was purchased from commercial sources.

2. Representative Biologically Active Isoxazole:

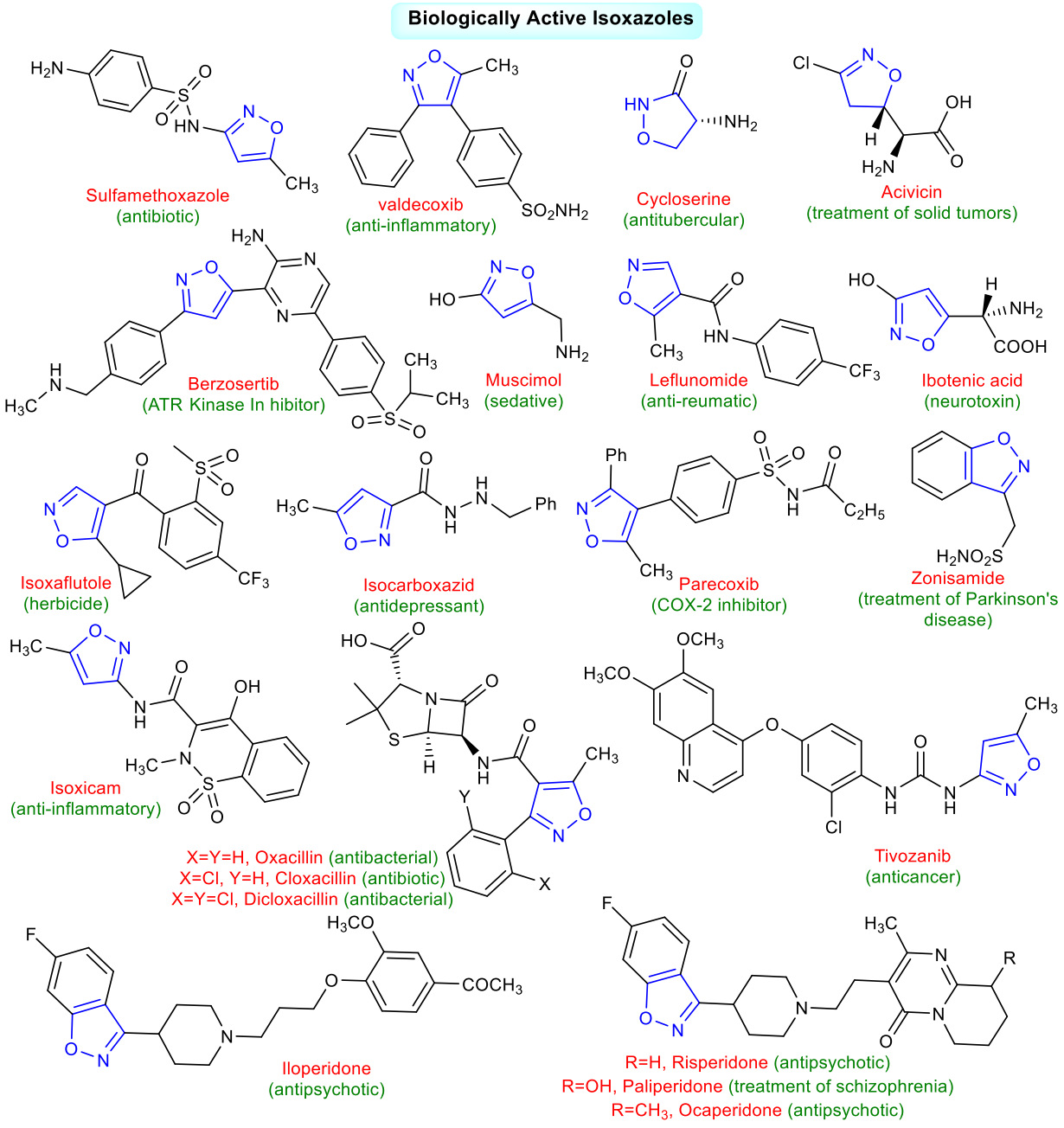
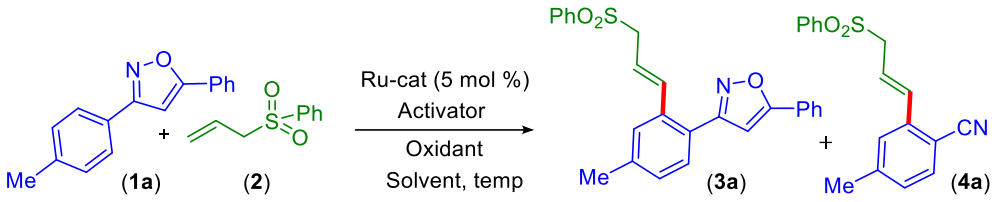


Fig S1. Biologically active isoxazoles.

3. Optimization of the Reaction Condition:

Table S1. Optimization of Reaction Conditions.[a,b]



Entry	Activator (mol%)	Oxidant (equiv)	Solvent	Temp	Yield%[b] (3a/4a)
1.	$AgSbF_6$ (0.2)	$Cu(OAc)_2$ (1.0)	DCM	65 °C	50/n.d.
2.	AgOTf (0.2)	$Cu(OAc)_2$ (1.0)	DCM	65 °C	52/n.d.
3.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (1.0)	DCM	65 °C	59/n.d.
4.	$AgNTf_2$ (0.2)	$Cu(OAc)_2$ (1.0)	DCM	65 °C	49/n.d.
5.	$AgBF_4$ (0.5)	$Cu(OAc)_2$ (1.0)	DCM	65 °C	55/n.d.
6.	AgBF4 (0.2)	---	DCM	65 °C	n.d./n.d.
7.	$AgBF_4$ (0.5)	$Cu(OAc)_2.H_2O$ (1.0)	DCM	65 °C	45/n.d.
8.	$AgBF_4$ (0.2)	$CuCl_2$ (1.0)	DCM	65 °C	31/n.d.
9.	$AgBF_4$ (0.2)	CuO (1.0)	DCM	65 °C	43/n.d.
10.	$AgBF_4$ (0.2)	$Cu(OTf)_2$ (1.0)	DCM	65 °C	45/n.d.
11.	$AgBF_4$ (0.2)	AgOAc (1.0)	DCM	65 °C	14/n.d.
12.	$AgBF_4$ (0.2)	Ag_2CO_3 (1.0)	DCM	65 °C	n.d./n.d.
13.	**$AgBF_4$ (0.2)**	**$Cu(OAc)_2$ (2.0)**	**DCM**	**65 °C**	**70/n.d.**
14.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.5)	DCM	65 °C	72/n.d.
15.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.0)	DCM	75 °C	68/n.d.
16.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.0)	THF	65 °C	n.d./n.d.
17.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.0)	MeCN	65 °C	n.d./n.d.
18.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.0)	DMSO	65 °C	n.d./n.d.
19.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.0)	$CHCl_3$	65 °C	16/n.d.

20.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.0)	1,2-DCE	65 °C	12/38
21.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.0)	PhCl	65 °C	<10/22
22.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (2.0)	1,2-DCB	65 °C	traces/25
23.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (1.0)	1,2-DCE	65 °C	<8/41
24.	$AgBF_4$ (0.2)	$Cu(OAc)_2$ (0.5)	1,2-DCE	65 °C	traces/35
25.	$AgBF_4$ (0.2)	---	1,2-DCE	65 °C	n.d./n.d.
26.	---	$Cu(OAc)_2$ (1.0)	1,2-DCE	65 °C	n.d./traces
27.	$AgBF_4$ (0.2)	$Cu(OAc)_2.H_2O$ (1.0)	1,2-DCE	65 °C	15/47
28.	$AgBF_4$ (0.2)	$Cu(OAc)_2.H_2O$ (1.0)	1,2-DCE	95 °C	traces/64
29.	**$AgBF_4$ (0.2)**	**$Cu(OAc)_2.H_2O$ (1.0)**	**1,2-DCE**	**110 °C**	**n.d./75**
30.	$AgBF_4$ (0.2)	$Cu(OAc)_2.H_2O$ (1.0)	1,2-DCE	120 °C	n.d./70

[a]Reaction Conditions unless specified otherwise: **1a** (0.3 mmol), **2** (0.39 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), additives, oxidants, solvent (2 ml) for 18 h. [b]Isolated yield. n.d. = not detected.

Now to optimize the initial finding, various reaction parameters were altered keeping **1a** and **2** as the model coupling partners. At first a series of silver salts *viz.* $AgSbF_6$, AgOTf, $AgBF_4$, $AgNTf_2$ were screened, among which $AgBF_4$ gave a better yield (59 %) of **3a** (Table S1, entries 1-4). Notably, when the loading of $AgBF_4$ was enhanced from 20 mol% to 50 mol%, it was found counterproductive providing a reduced yield of 55% (Table S1, entry 5). In the absence of $Cu(OAc)_2$ no trace of *o*-olefinated adduct **3a** was observed (Table S1, entry 6). Thus, a series of other oxidants such as $Cu(OAc)_2.H_2O$, $CuCl_2$, CuO, $Cu(OTf)_2$, AgOAc and Ag_2CO_3 were examined in lieu of $Cu(OAc)_2$. Unfortunately, all the Cu-salts provided lower yields of **3a** compared to the original oxidant $Cu(OAc)_2$ (Table S1, entries 7-12). Interestingly, when the loading of $Cu(OAc)_2$ was enhanced from 1 to 2 equivalent, the yield of **3a** improved to 70% (Table S1, entry 13). However, any further enhancement of $Cu(OAc)_2$ loading to 2.5 equivalent failed to improve the yield (Table S1, entry 14). Further, enhancement in the reaction temperature to 75 °C, was found not so effective for this protocol (Table S1, entry 15). Now various solvents such as THF, MeCN, DMSO, $CHCl_3$, 1,2-DCE, PhCl, 1,2-DCB were screened (Table S1, entries

16-22). ***Although the yield of 3a was not enhanced, but surprisingly in the chlorinated solvents like 1,2-DCE, PhCl, 1,2-DCB, a new product was isolated. From the single-crystal X-ray analysis the structure of the new compound was found to be (E)-4-methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4a). This is a unique illustration of isoxazole serving as a nitrile surrogate and route to ortho-alkenylated benzonitriles which is unprecedented.*** Since 1,2-DCE was found to be the ideal solvent for the formation of **4a** (Table S1, entry 20), the remaining optimization was continued using the same. Meanwhile, when the $Cu(OAc)_2$ loading was decreased to 1 equivalent, the yield of **4a** improved to 41% (Table S1, entry 23). A further decrease in the loading to 50 mol%, gave inferior yield of **4a** (Table S1, entry 24). Notably, the presence of $Cu(OAc)_2$ and $AgBF_4$ in this protocol was found to be crucial (Table S1, entries 25 and 26). Now the use of $Cu(OAc)_2.H_2O$ gave a slightly better yield of **4a** (Table S1, entry 27). The increment in the reaction temperature from 65 to 95 to 110 °C was found to enhance the yield to 75% (Table S1, entries 28 and 29). Further enhancement came out be unproductive (Table S1, entry 30).

Thus, it can be concluded that:

(i) A definite solvent dependent selectivity is observed.

(ii) From entry 13 it was observed that nitrile is not forming at all in DCM, which also supports our solvent-dependent selectivity.

(iii) At 65 °C in DCE (entry 20), nitrile product **4a** starts forming.

(iv) At a higher temperature 95 °C, the nitrile product **4a** is forming even using 1 equivalent of oxidant $Cu(OAc)_2.H_2O$.

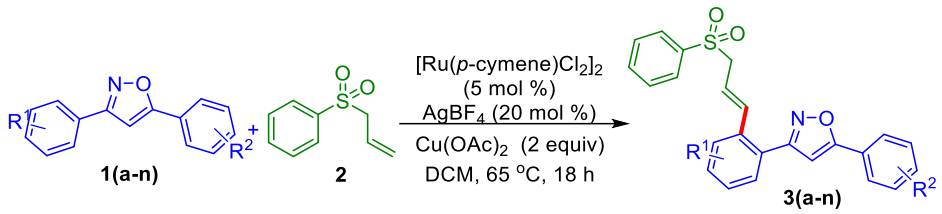
(v) The best yield of **4a** (75%) is obtained at 110 °C.

4. General Procedure:

(**A**) General Procedure for the Synthesis of Isoxazoles:

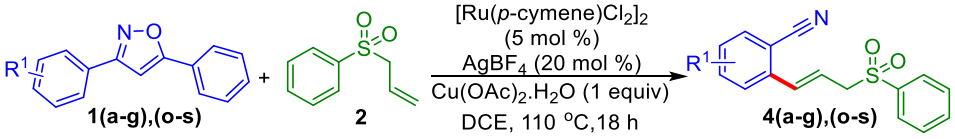
All isoxazole derivatives (**1a**-**1w**) were synthesized by following the previous reported procedure.[1]

(**B**) General Procedure for the Synthesis of 3a–3n:



To an oven-dried round bottom flask (25 mL) containing a magnetic bar was added 3,5-diarylisoxazole [**1**(**a-n**), 0.3 mmol, 1 equiv], (allylsulfonyl)benzene (**2**, 0.39 mmol, 71.0 mg), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol, 9.1 mg), silver tetrafluoroborate (0.06 mmol, 11.7 mg,), copper acetate (0.6 mmol, 109.0 mg) and DCM (2 mL). After that, the reaction mixture was stirred at 65 °C in a preheated oil bath for 18 h. After completion of the reaction (monitored by TLC), the solvent (DCM) was evaporated under reduced pressure. After evaporation the reaction mixture was mixed with water (10 mL) and extracted with ethyl acetate (2 × 15 mL). Then the organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Then the crude mixture was purified over column chromatography (60-120 mesh silica) by eluting it with hexane/EtOAc mixtures to afford the desired products **3**(**a–n**). The identity and purity of the product was confirmed by spectroscopic analysis.

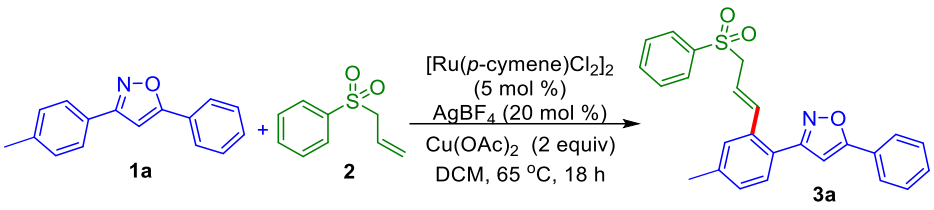
(C) General Procedure for the Synthesis of 4a-4g, 4o-4s:



To an oven-dried pressure tube (20.3 cm x 19 mm, 21 mL) containing a magnetic bar was added 3-aryl-5-phenylisoxazole **1**(**a-g**), (**o-s**) (0.3 mmol, 1 equiv), (allylsulfonyl)benzene (**2**, 0.39 mmol, 71.0 mg), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol, 9.1 mg), silver tetrafluoroborate (0.06 mmol, 11.7 mg), copper acetate monohydrate (0.3 mmol, 59.9 mg) and DCE (1 mL). After that, the reaction mixture was stirred at 110 °C in a preheated oil bath for 18 h. After completion of the reaction (monitored by TLC), the solvent (DCE) was evaporated under reduced pressure. After evaporation, the reaction mixture was mixed with water (10 mL) and extracted with ethyl acetate (2 × 15 mL). Then the organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Then the crude mixture was purified over column chromatography (60-120 mesh silica) by eluting it with hexane/EtOAc mixtures to afford the

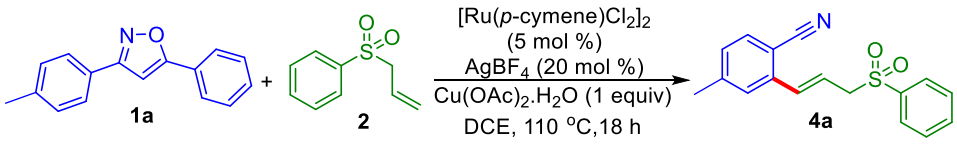
desired products **4**(**a-g**), **4**(**o-s**). The identity and purity of the product was confirmed by spectroscopic analysis.

(**D**) **Procedure for 1 mmol scale synthesis of 3a:**



To an oven-dried round bottom flask (25 mL) containing a magnetic bar was added 5-phenyl-3-(*p*-tolyl)isoxazole (**1a**, 1 mmol, 236 mg), (allylsulfonyl)benzene (**2**, 1.3 mmol, 236.9 mg), [$RuCl_2$(*p*-cymene)]$_2$ (0.05 mmol, 30.6 mg), silver tetrafluoroborate (0.2 mmol, 38.9 mg), copper acetate (2 mmol, 363.3 mg) and DCM (3 mL). After that, the reaction mixture was stirred at 65 ^oC in a preheated oil bath for 18 h. After completion of the reaction (monitored by TLC), the solvent (DCM) was evaporated under reduced pressure. After evaporation, the reaction mixture was mixed with water (10 mL) and extracted with ethyl acetate (2 × 15 mL). Then the organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 10% ethyl acetate in hexane to give pure (*E*)-3-(4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (**3a**) as brown gummy compound with 65% yield (81 mg).

(**E**) **Procedure for 1 mmol scale synthesis of 4a:**



To an oven-dried pressure tube (20.3 cm x 19 mm, 21 mL) containing a magnetic bar was added 5-phenyl-3-(*p*-tolyl**)**isoxazole (**1a**, 0.3 mmol, 236 mg), (allylsulfonyl)benzene (**2**, 1.3 mmol, 236.9 mg), [$RuCl_2$(p-cymene)]$_2$ (0.05 mmol, 30.6 mg), silver tetrafluoroborate (0.2 mmol, 38.9 mg), copper acetate monohydrate (1 mmol, 199.6 mg) and DCE (2 mL). After that, the reaction mixture was stirred at 110 ^oC in a preheated oil bath for 18 h. After completion of the reaction (monitored by TLC), the solvent (DCE) was evaporated under reduced pressure. After evaporation the reaction mixture was mixed with water (10 mL) and extracted with ethyl acetate (2 × 15 mL). Then the organic layer was dried over anhydrous

Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give pure (*E*)-4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4a**) as brown gummy liquid with 68% yield (62 mg).

5. Crystallographic Information:

Crystal data were collected with Bruker Smart Apex-II CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 296 K. Cell parameters were retrieved using SMART [a] software and refined with SAINT[a] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS[b]. The structure was solved by direct methods implemented in SHELX-2014[c] program and refined by full-matrix least-squares methods on F2. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. yellow crystals of **4c** were isolated from DMF solvent at room temperature.

a. SMART V 4.043 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 2008.

b. SAINT Plus (v 6.14) Bruker AXS Inc., Madison, WI, 2008.

c. Sheldrick, G. M. SHELXL-2014, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen (Germany), 1997

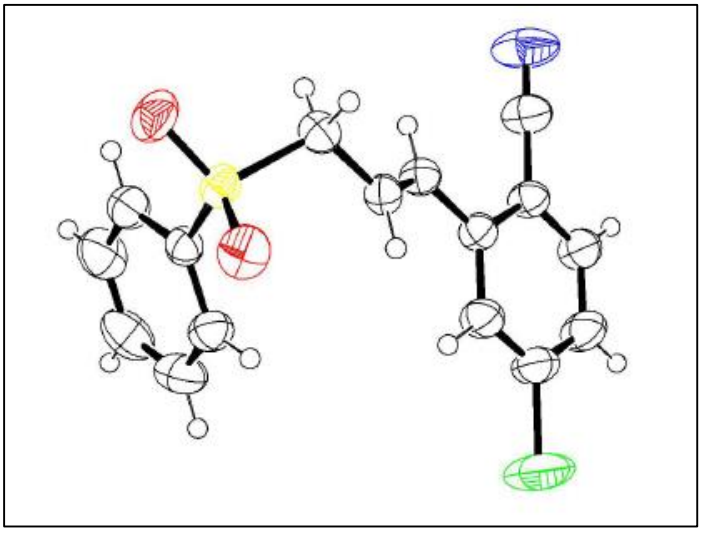
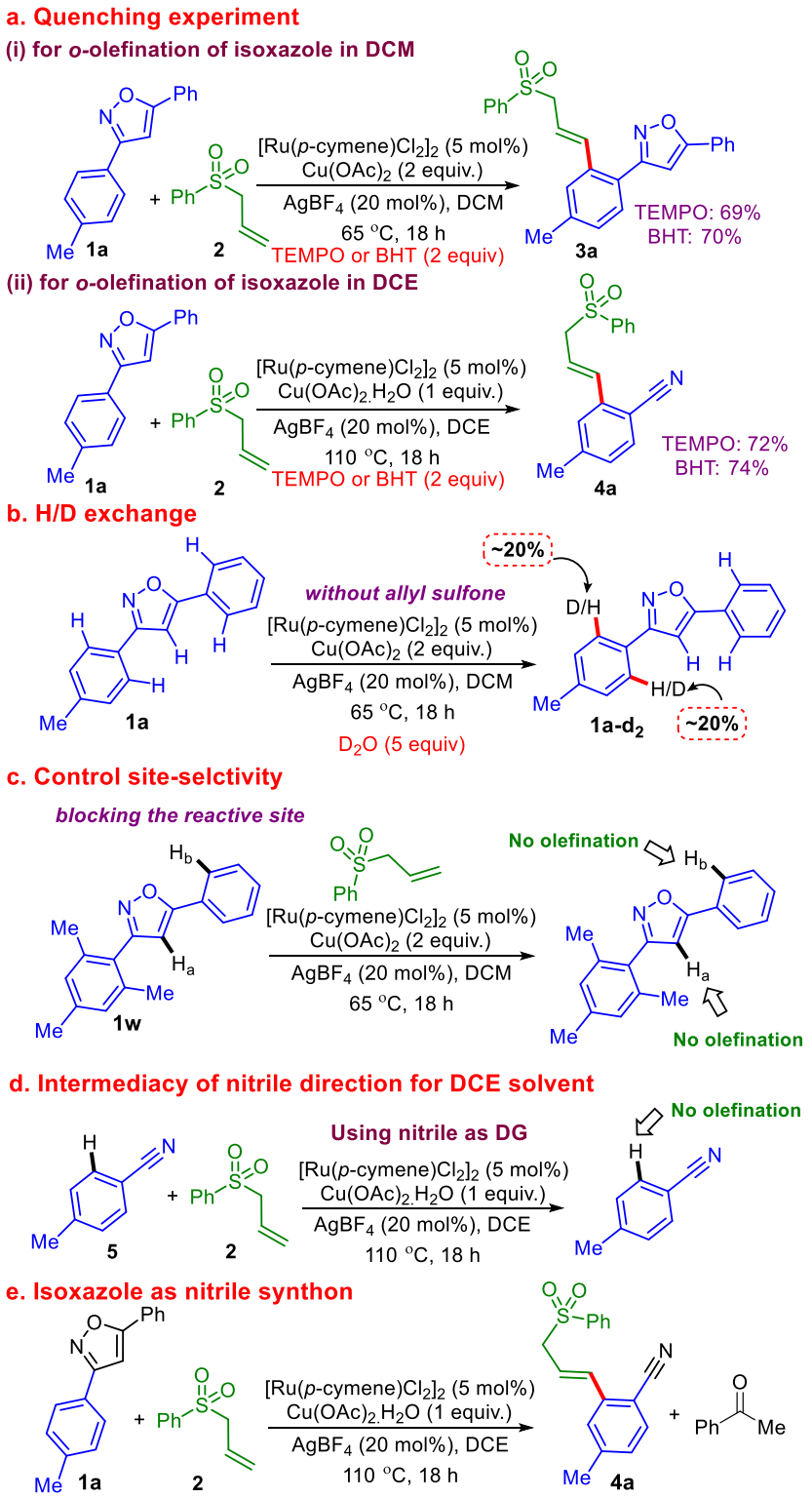


Figure S2. ORTEP diagram of **4c** with the thermal ellipsoids set at 50% probability.

Table S2. Crystal Data table for 4c

Empirical formula	$C_{16}H_{12}ClNO_2S$
CCDC number	2263865
Formula weight	318.78
Temperature	297(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 13.756(8) Å, b = 8.641(5) Å, c = 14.081(8) Å $\alpha = 90^o$, $\beta = 113.558(14)^o$, $\gamma = 90^o$
Volume	1534.3(15) $Å^3$
Z	4
Density (calculated)	1.380 g/cm^{-3}
Absorption coefficient	0.388
F(000)	660
Theta range for data collection	1.749 to 24.999^o
Index ranges	-16 < = h < = 16, -10 < = k < = 10, -16< = l < = 16
Reflections collected	33602
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	2688/ 0/ 190
Goodness-of-fit on F2	1.028
Final R indices [I>2sigma(I)]	0.0376, wR2 = 0.1028
R indices (all data)	0.0421, wR2 = 0.1091

6. Control Experiments for Elucidation of Mechanisms:



Scheme S1. Control reactions.

Discussion on control reactions:

The formation of *o*-olefinated isoxazole (**3a**) and *o*-olefinated benzonitrile (**4a**) was unaffected in the presence of radical scavengers such as 2,2,6,6-tetramethyl piperidin-1-yl-oxidanyl (TEMPO) and 2,6-di-tert-butyl-4-methylphenol (BHT), which rules out the non-involvement of a radical pathway [Scheme S1a]. Now to confirm the reversibility of *o*-C–H metallation, a standard reaction without (**2**), was subjected to reaction condition-A in the presence of D_2O (5 equiv.) (Scheme S1b). It was observed that both the *o*-C–H's of the C-3 tolyl-ring in (**1a**) were deuterated (39% D) without any deuteration at other C–H bonds, suggesting a reversible metal binding. An isoxazole (**1t**) having 2,4,6-trimethyl substituents on the C3-phenyl ring was subjected to the standard condition A in DCM, but this reaction failed to provide any olefination at the other available C–H sites suggesting exclusive *N*-directed *o*-olefination (Scheme S1c). Now to check the nitrile intermediacy as DG for the *o*-olefination in DCE, *p*-methyl benzonitrile (**5**) was reacted under the standardized condition B in DCE (Scheme S1d). But the reaction failed to provide any *o*-olefination, suggesting non-involvement of benzonitriles as directing group. The nitrile group may be forming via the cleavage of isoxazole after *o*-olefination under the reaction condition.

a. Quenching Experiment:

(i) Procedure of quenching experiment for 3a:

An oven-dried 25 mL round-bottom flask containing a magnetic bead was charged with 5-phenyl-3-(*p*-tolyl)isoxazole (**1a**, 0.3 mmol, 70.8 mg), (allylsulfonyl)benzene (**2**, 0.39 mmol, 71.0 mg), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol, 9.1 mg), silver tetrafluoroborate (0.06 mmol, 11.7 mg), copper acetate (0.6 mmol, 109.0 mg) TEMPO (0.6 mmol, 94 mg,) or BHT (0.6 mmol, 132 mg) and DCM (2 mL) under an open atmosphere and was refluxed in an oil bath at 65 °C for 18 h. After completion of the reaction, the reaction mixture was then mixed with water (5 mL) and extracted with ethyl acetate (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate and was evaporated under reduced pressure. Then the crude reaction mixture was purified over column chromatography (60-120 mesh silica) by eluting it with hexane/EtOAc (90:10) mixture to afford the desired products **3a** in 69% (86 mg) (for TEMPO) and 70% (87 mg) (for BHT). This observation suggests the non-involvement of any radical pathway.

(ii) Procedure of quenching experiment for 4a:

An oven-dried pressure tube (20.3 cm x 19 mm, 21 mL) containing a magnetic bead was charged with 5-phenyl-3-(*p*-tolyl)isoxazole (**1a**, 0.3 mmol, 70.8 mg), (allylsulfonyl)benzene (**2**, 0.39 mmol, 71 mg), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol, 9.1 mg), silver tetrafluoroborate (0.06 mmol, 11.7 mg), copper acetate monohydrate (0.3 mmol, 59.9 mg), TEMPO (0.6 mmol, 94 mg) or BHT (0.6 mmol, 132 mg) and DCE (1 mL). After that, the reaction mixture was stirred at 110 °C in a preheated oil bath for 18 h. After completion of the reaction, the reaction mixture was then mixed with water (5 mL) and extracted with ethyl acetate (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate and was evaporated under reduced pressure. Then the crude reaction mixture was purified over column chromatography (60-120 mesh silica) by eluting it with hexane/EtOAc (85:15) mixture to afford the desired products **4a** in 72% (64 mg) (for TEMPO) and 74% (66 mg) (for BHT). This observation suggests the non-involvement of any radical pathway.

b. Procedure of H/D exchange without allyl phenyl sulfone (2):

An oven-dried 25 mL round-bottom flask containing a magnetic bead was charged with 5-phenyl-3-(*p*-tolyl)isoxazole (**1a**, 0.3 mmol, 70.8 mg), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol, 9.1 mg), silver tetrafluoroborate (0.06 mmol, 11.7 mg), copper acetate (0.6 mmol, 109.0 mg), deuterium oxide (D_2O) (1.5 mmol, 30 mg) and DCM (2 mL) under an open atmosphere and was refluxed in an oil bath at 65 °C for 18 h. After completion of the reaction, the reaction mixture was then mixed with water (5 mL) and extracted with ethyl acetate (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate and was evaporated under reduced pressure. Then the crude mixture was purified over column chromatography (60-120 mesh silica) by eluting it with hexane/EtOAc (95:5) mixture to afford the deuterated products **1a-d$_2$**. The extent of H/D exchange was determined by comparing the ^{1}H NMR of deuterated **1a-d$_2$** to that of undeuterated **1a.** The singlet peak at δ 6.79 ppm for **1a** and 6.63 ppm for **1a-d$_2$** which has an integral value of 1.00 was considered as the reference in both spectra. Integrating accordingly in both of them, it was found that upon deuteration the characteristic peak for two *ortho*-H of C-3 phenyl ring of isoxazole which appears at 7.75 ppm was reduced to an integral value 1.61 from 2.00. Thus, there was 39% deuteration (2.00-1.61= 0.39 i.e. 39% D) for two *ortho* protons of C-3 phenyl ring of isoxazole observed without affecting other proton [Scheme S1(b)].

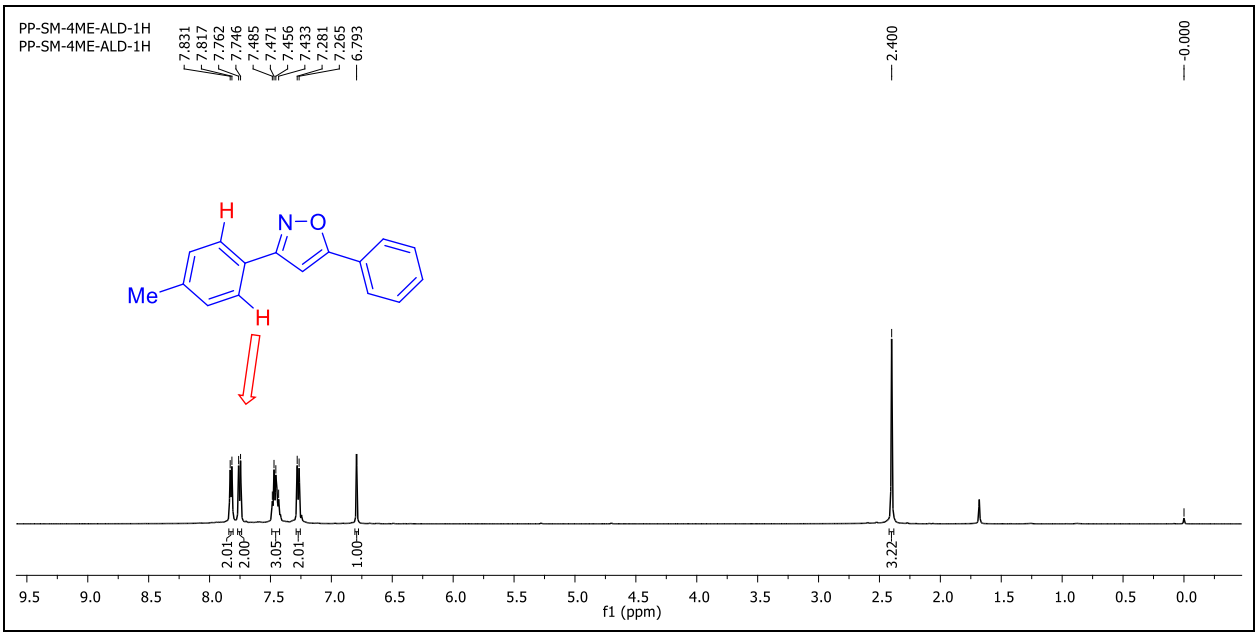


Figure S3. ^{1}H NMR spectra of **1a**.

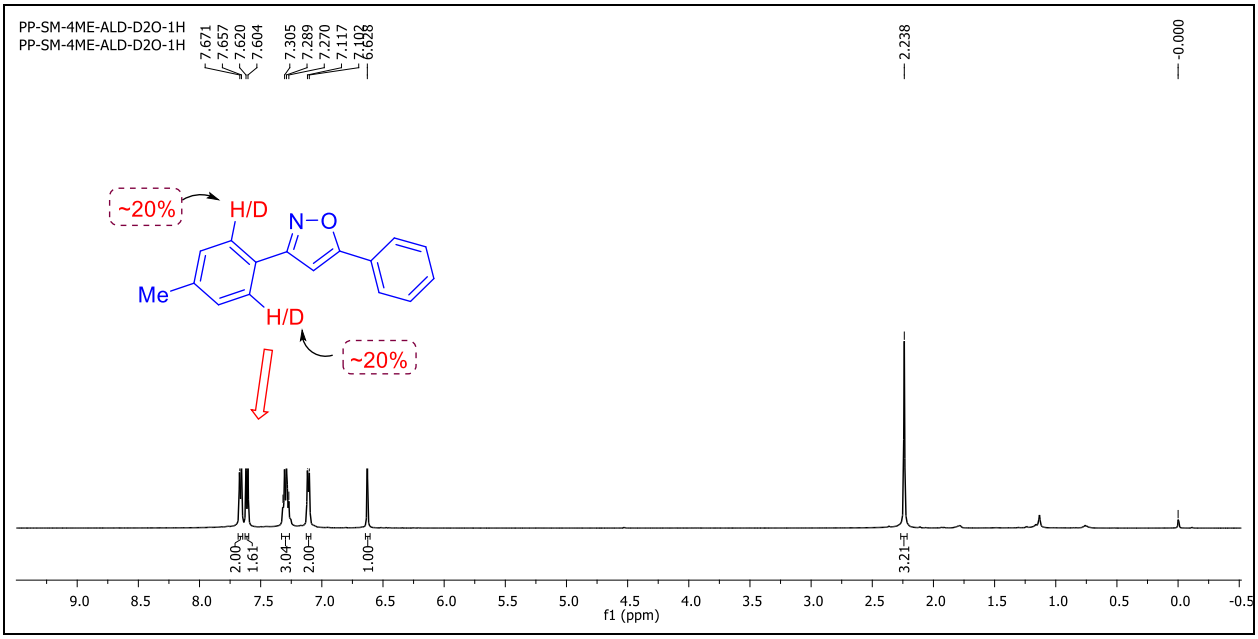


Figure S4. ^{1}H NMR spectra of Deuterated **1a-d$_2$**.

c. Procedure of exclusive site selectivity experiment for DCM solvent:

An oven-dried 25 mL round-bottom flask containing a magnetic bead was charged with 3-mesityl-5-phenylisoxazole (**1w**, 0.3 mmol, 79 mg), (allylsulfonyl)benzene (**2**, 0.39 mmol, 71 mg), [$RuCl_2$(*p*-

cymene)]$_2$ (0.015 mmol, 9.1 mg), silver tetrafluoroborate (0.06 mmol, 11.7 mg), copper acetate (0.6 mmol, 109.0 mg) and DCM (2 mL) under an open atmosphere and was refluxed in an oil bath at 65 °C for 18 h. Neither desired product nor any other product was obtained. This observation suggests that the olefination takes place only at the *ortho* position of the C3-phenyl ring of isoxazole.

d. Procedure of Intermediacy of nitrile direction for DCE solvent:

An oven-dried pressure tube (20.3 cm x 19 mm, 21 mL) containing a magnetic bead was charged with 4-methylbenzonitrile (**5**, 0.3 mmol, 35 mg), (allylsulfonyl)benzene (**2**, 0.39 mmol, 71 mg), [$RuCl_2$(*p*-cymene)]$_2$ (0.015 mmol, 9.1 mg), silver tetrafluoroborate (0.06 mmol, 11.7 mg), copper acetate monohydrate (0.3 mmol, 59.8 mg), and DCE (1 mL). After that, the reaction mixture was stirred at 110 °C in a preheated oil bath for 18 h. After 18 h of reaction, TLC was checked and no product was formed. This observation suggests that the nitrile group is not the intermediate and it is formed after the olefination reaction.

e. Isoxazole as nitrile synthon:

An oven-dried pressure tube (20.3 cm x 19 mm, 21 mL) containing a magnetic bead was charged with 5-phenyl-3-(*p*-tolyl**)**isoxazole (**1a**, 0.3 mmol, 70.8 mg), (allylsulfonyl)benzene (**2**, 1.3 mmol, 71.1 mg), [$RuCl_2$(p-cymene)]$_2$ (0.05 mmol, 9.1 mg), silver tetrafluoroborate (0.2 mmol, 11.7 mg), copper acetate monohydrate (1 mmol, 59.9 mg) and DCE (1 mL). After that, the reaction mixture was stirred at 110 ^oC in a preheated oil bath for 18 h. After completion of the reaction (monitored by TLC), the solvent (DCE) was evaporated under reduced pressure. After evaporation, the reaction mixture was mixed with water (10 mL) and extracted with ethyl acetate (2 × 15 mL). Then the organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give pure (*E*)-4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4a**) as brown gummy liquid with 75% yield (67 mg) and acetophenone as a byproduct.

f. Elucidation of acetophenone elimination in the formation of 4 by ^{19}F analysis:

In order to confirm the elimination of acetophenone during the reaction pathway for the formation of **4**, ^{19}F NMR of the standard reaction (with **1l** as the starting material) aliquot was analyzed at a different

time interval**.** It was observed that after 4 hours, a peak for acetophenone starts appearing at 105.5 ppm which is comparable to the standard 4'-Fluoroacetophenone (105.4 ppm). The peak intensity increases with time as observed in 7 hours.

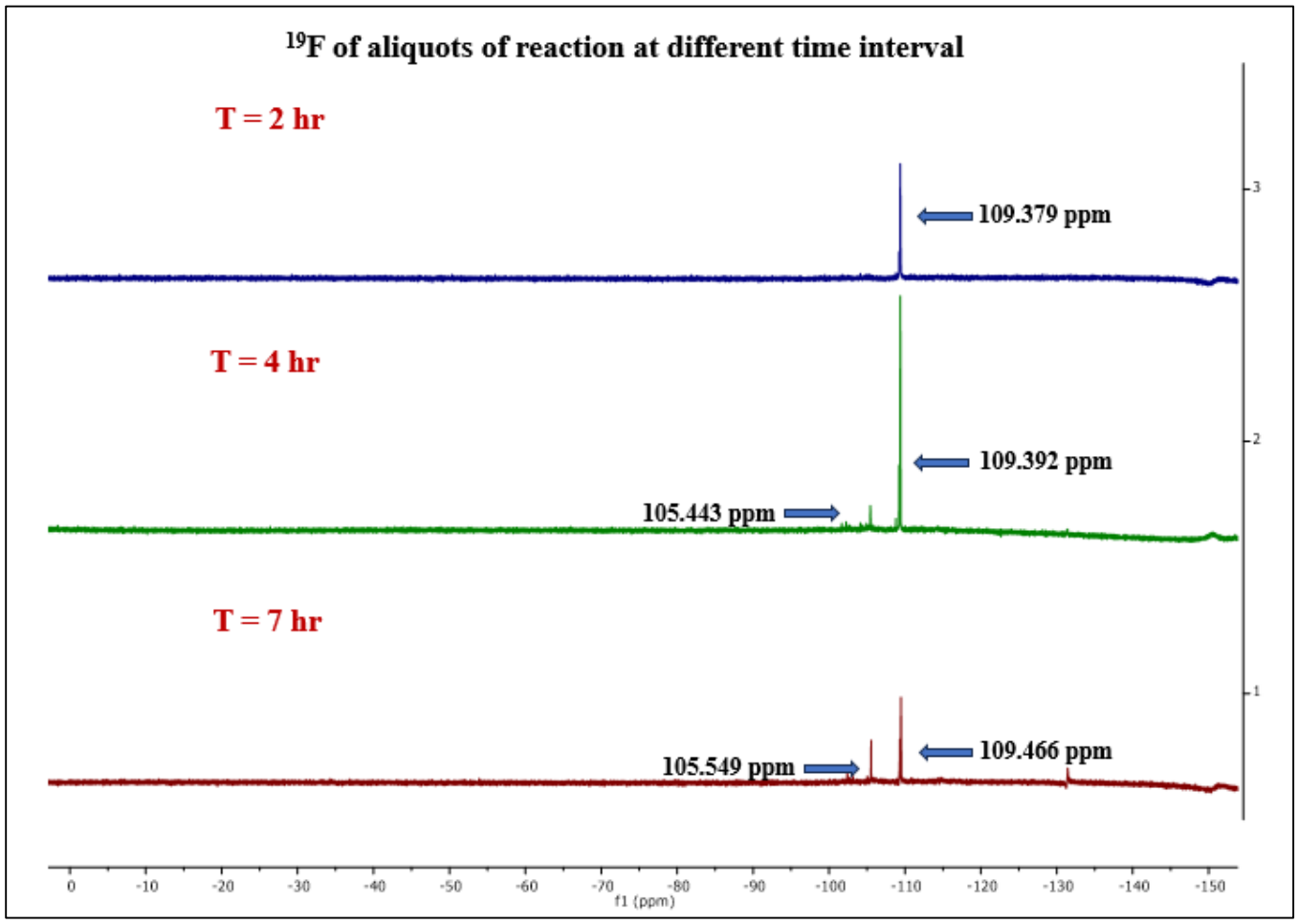


Figure S5.[19]F NMR of aliquots of reaction at different time interval.

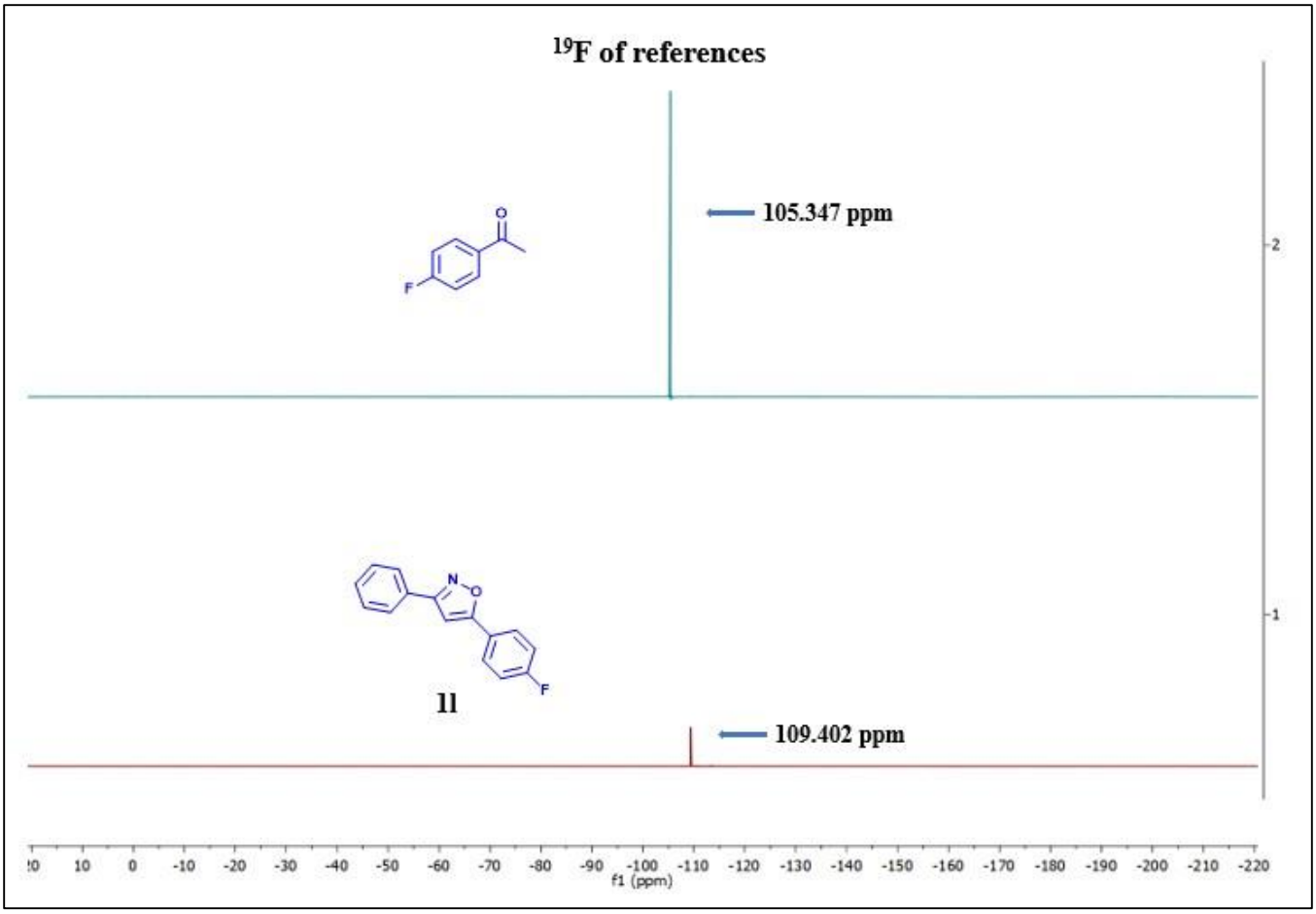


Figure S6.[19]F NMR of 4'-Fluoroacetophenone and **1l**.

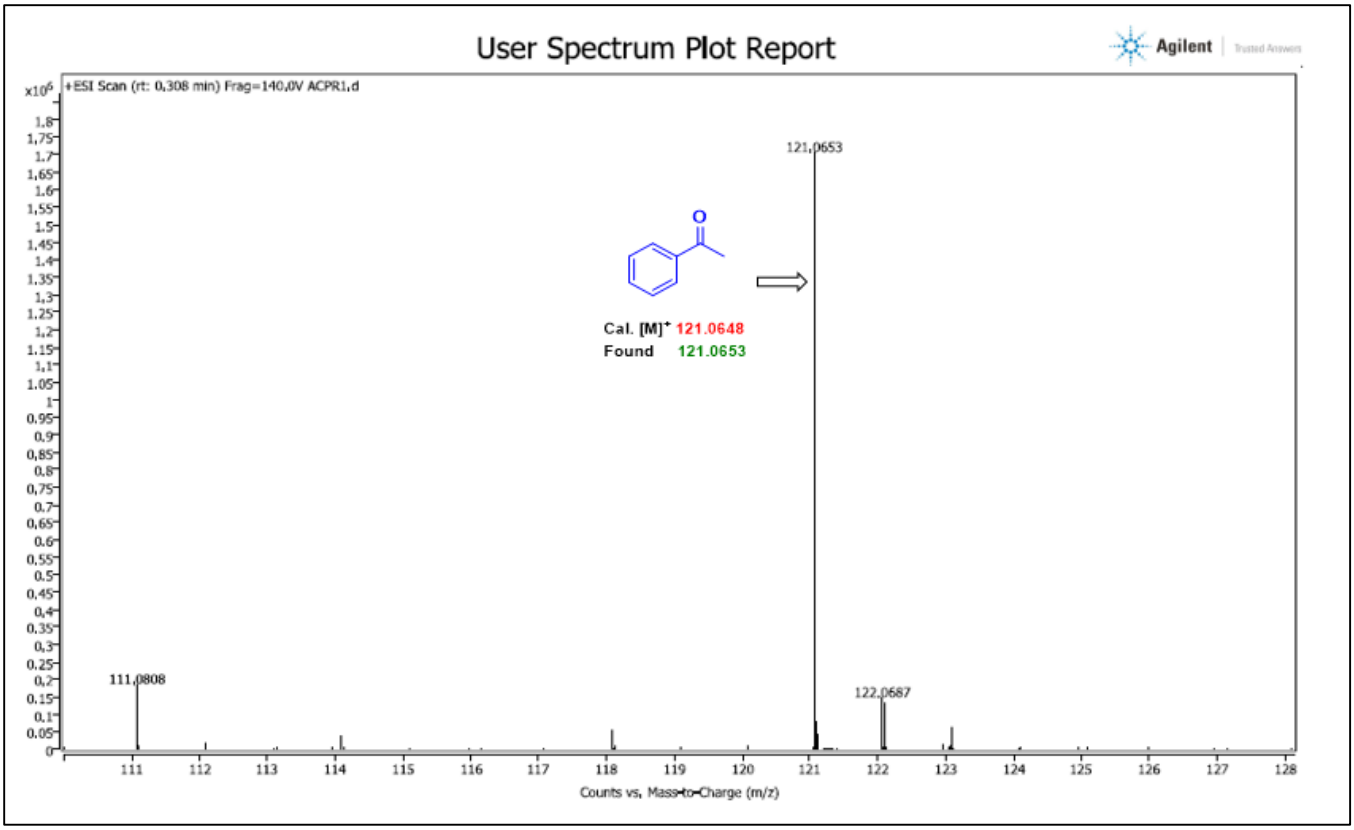


Figure S7. HRMS spectra of the crude reaction mixture for *o*-olefination in DCE (detection of acetophenone).

7. HRMS analysis of crude reaction mixture:

(a) For *o*-olefination in DCM solvent:

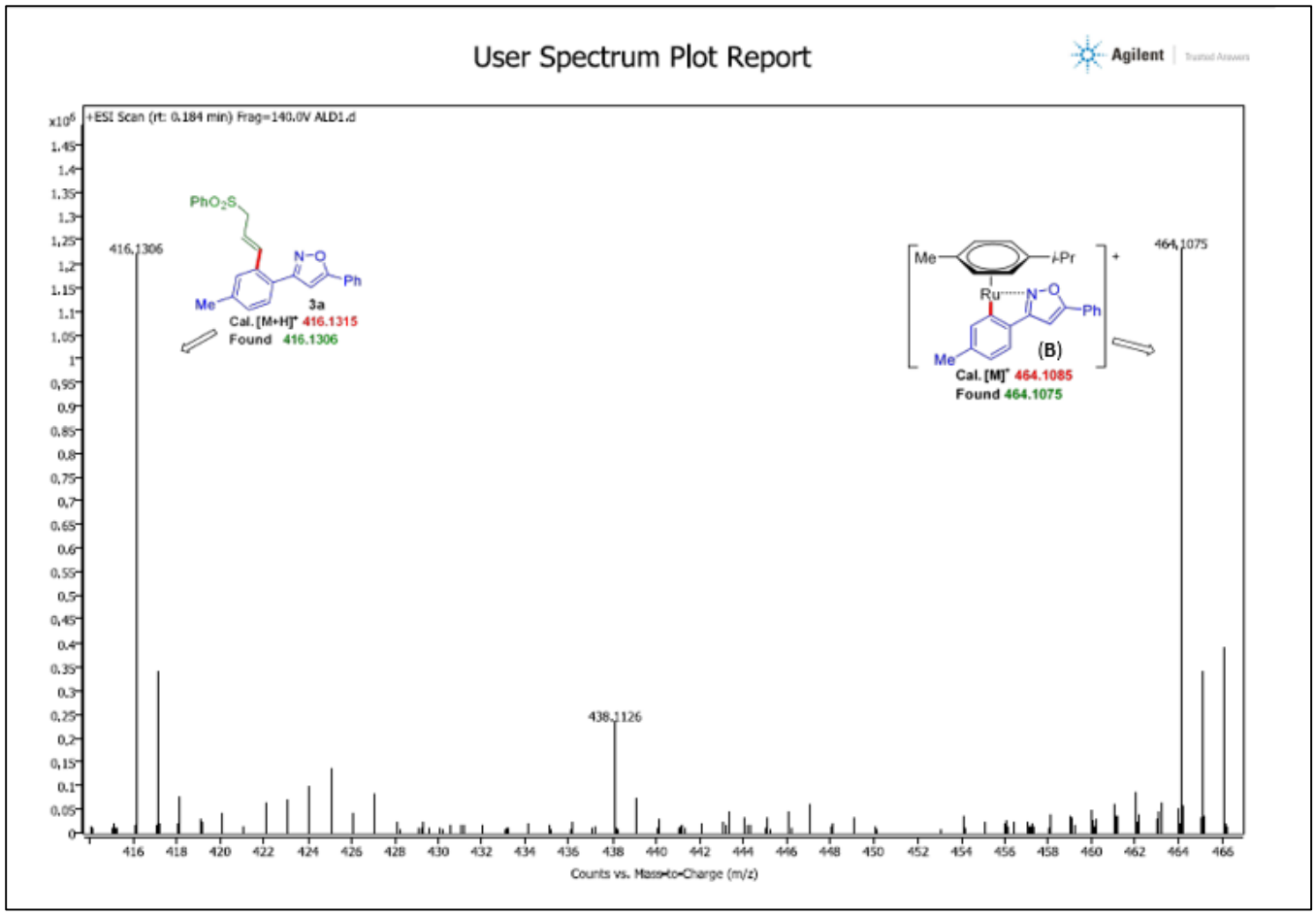


Figure S8. HRMS spectra of the crude reaction mixture for *o*-olefination in DCM (Int. **B** and **3a**).

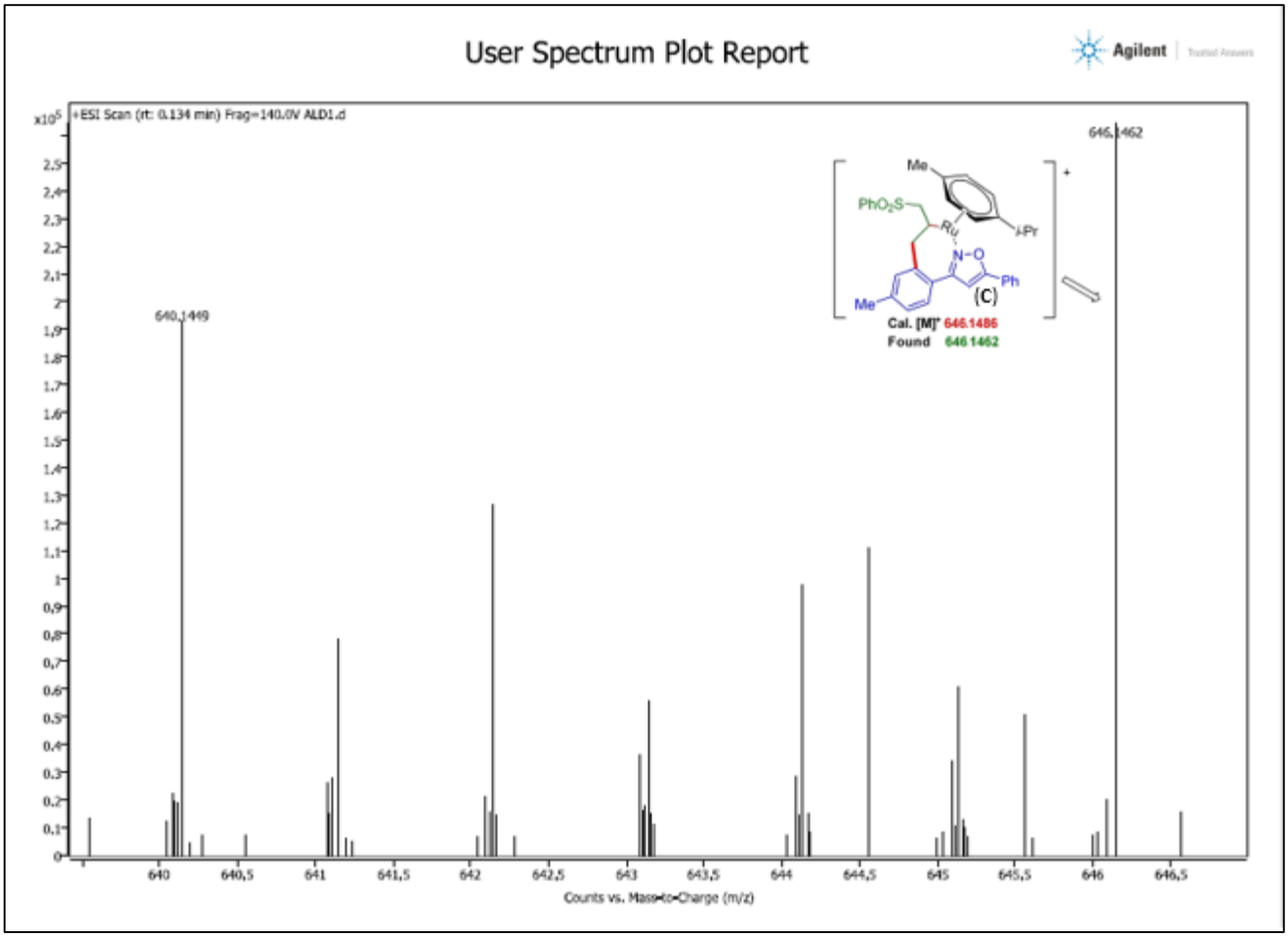


Figure S9. HRMS spectra of the crude reaction mixture for *o*-olefination in DCM (Int. **C**).

(b) For *o*-olefination in DCE solvent:

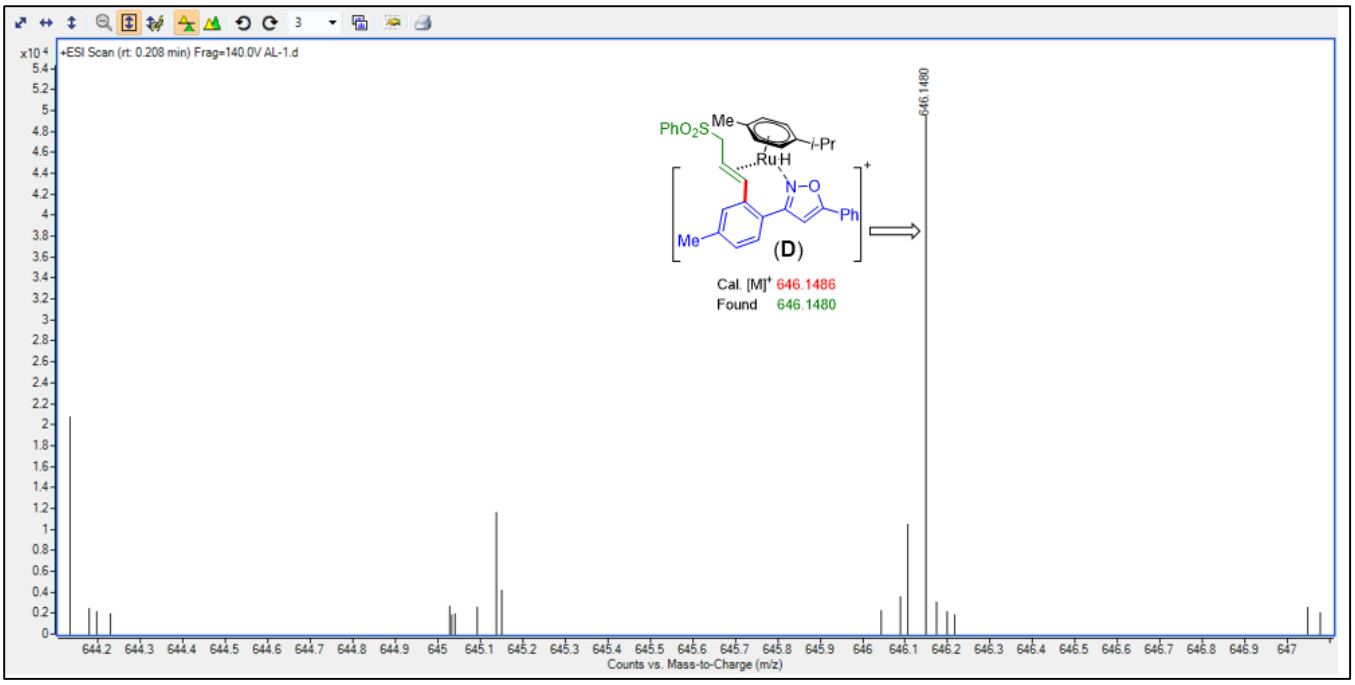


Figure S10. HRMS spectra of the crude reaction mixture for *o*-olefination in DCE (Int. **D**).

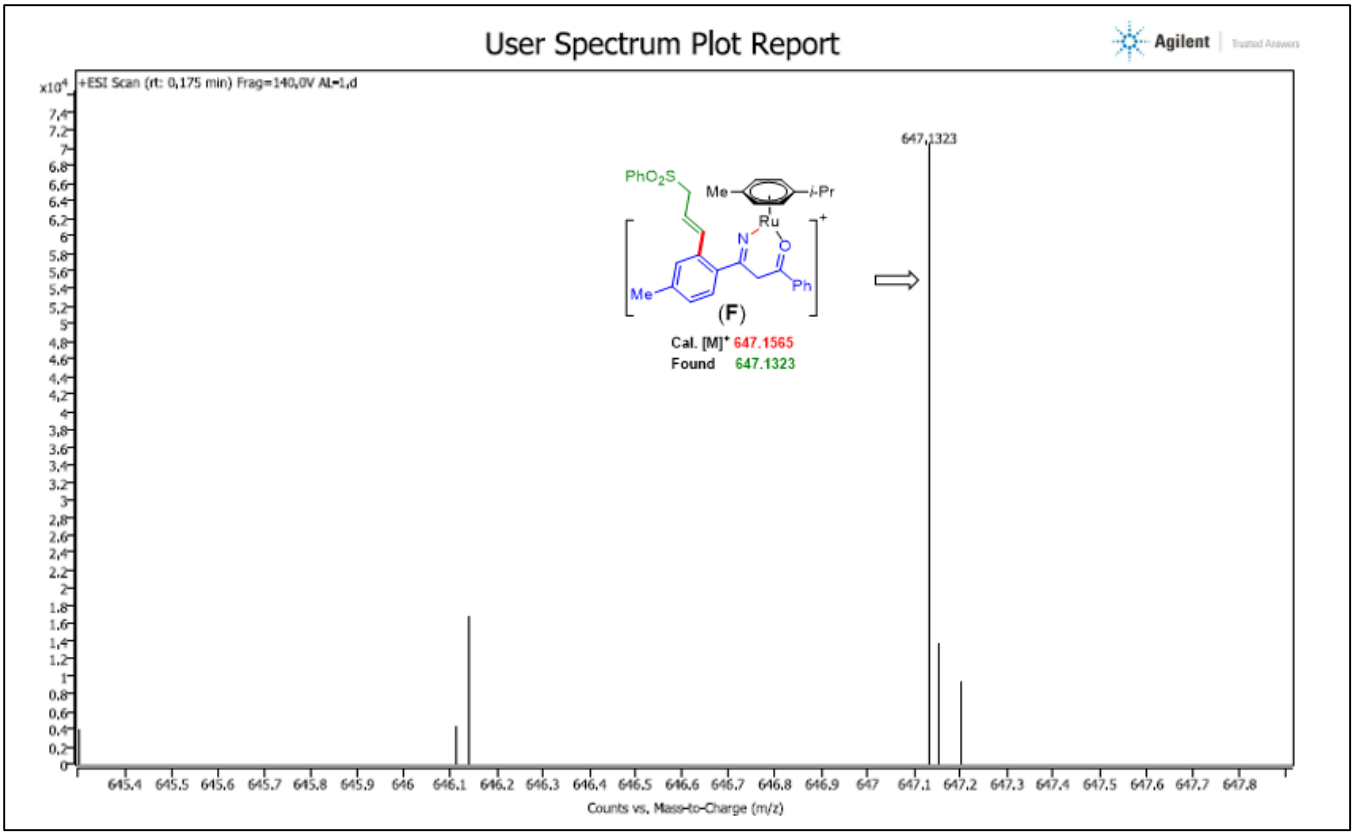


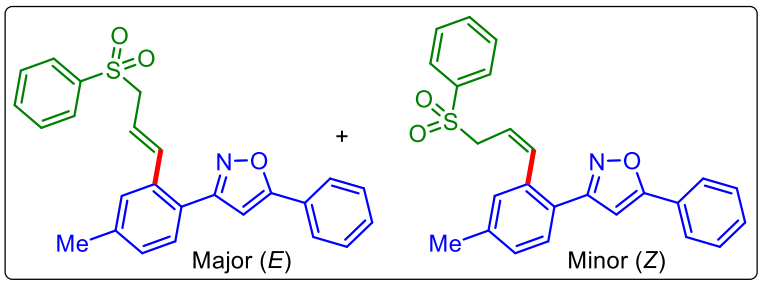
Figure S11. HRMS spectra of the crude reaction mixture for *o*-olefination in DCE (Int. **F**).

8. References:

1. P. Kumar and M. Kapur, *Org. Lett.*, 2019, **21**, 2134.

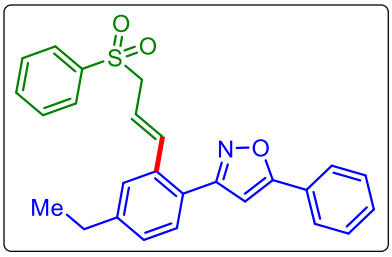
9. Spectral Data:

(*E*)-3-(4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (**3a**):



A brown gummy compound (87 mg, 70% yield, *E*/*Z* 1:0.43); purified over a column of silica gel (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 4H), 7.79 (d, *J* = 6.8 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.53 – 7.43 (m, 8H), 7.37 (s, 1H), 7.21 (t, *J* = 7.0 Hz, 1H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.69 (s, 1H), 6.13 – 6.05 (m, 1H), 3.97 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 169.6, 162.7, 162.6, 140.1, 139.8, 139.0, 138.8, 138.3, 137.3, 135.1, 134.0, 133.90, 133.86, 130.4, 130.3, 129.7, 129.6, 129.5, 129.33, 129.28, 129.25, 129.17, 128.5, 128.4, 127.7, 127.53, 127.51, 126.04, 125.95, 125.6, 125.4, 118.3, 117.4, 101.1, 100.4, 60.7, 56.2, 22.8, 21.5; IR (neat, cm^{-1}): 2924, 1574, 1448, 1307, 1265, 1151, 1085, 731, 689, 530; HRMS (ESI-TOF) calcd for $C_{25}H_{21}NO_3S$ $[M + H]^+$ 416.1315, found 416.1315.

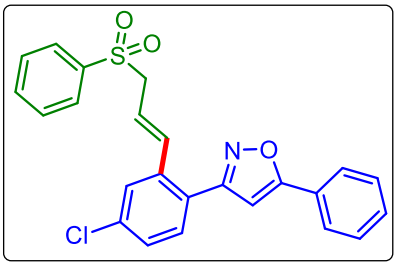
(*E*)-3-(4-Ethyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (**3b**) :



A brown gummy compound (86 mg, 67% yield, *E*/*Z* 1:0.11); purified over a column of silica gel (10% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.54–7.46 (m, 5H), 7.38 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 6.5 Hz, 1H), 6.90 (d, *J* = 15.5 Hz, 1H), 6.69 (s, 1H), 6.13-6.07 (m, 1H), 3.98 (d, *J* = 7.5 Hz, 2H), 2.71 (q, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 169.9, 162.7, 146.4, 138.5, 135.2, 133.9, 130.4, 129.8, 129.3, 129.2, 128.53, 128.46, 128.3, 127.6, 126.6, 126.1, 125.6,

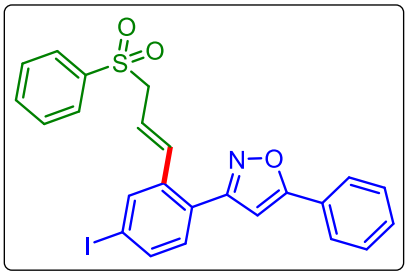
117.4, 101.1, 60.7, 28.9, 15.5; IR (neat, cm^{-1}): 2927, 1688, 1447, 1308, 1265, 1138, 1085, 730, 688, 531; HRMS (ESI-TOF) calcd for $C_{26}H_{23}NO_3S$ $[M + H]^+$ 430.1471, found 430.1474.

(*E*)-3-(4-Chloro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (**3c**):



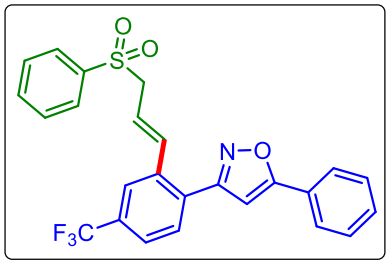
A yellow gummy compound (78 mg, 60% yield, *E*/*Z* 1:0.05); purified over a column of silica gel (11% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91–7.86 (m, 4H), 7.62–7.59 (m, 2H), 7.57 (d, J = 3.2 Hz, 1H), 7.54 (s, 1H), 7.52–7.47 (m, 4H), 7.38 (dd, J = 8.4, 1.6 Hz, 1H), 6.88 (d, J = 15.6 Hz, 1H), 6.76 (s, 1H), 6.13-6.05 (m, 1H), 3.98 (d, J = 7.6 Hz, 2H). ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 170.4, 161.8, 138.8, 137.2, 136.9, 136.1, 134.1, 131.1, 130.6, 129.4, 129.2, 128.8, 128.5, 127.3, 127.1, 126.6, 126.1, 119.1, 101.0, 60.4; IR (neat, cm^{-1}): 2928, 1689, 1446, 1309, 1263, 1140, 1086, 731, 689, 530; HRMS (ESI-TOF) calcd for $C_{24}H_{18}ClNO_3S$ $[M + H]^+$ 436.0769, found 436.0774.

(*E*)-3-(4-Iodo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (**3d**):



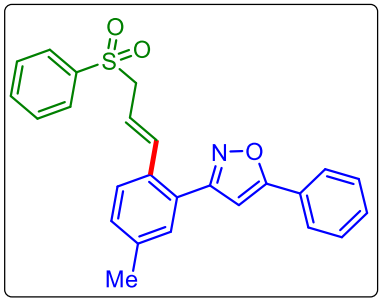
A light orange liquid compound (87 mg, 55% yield); purified over a column of silica gel (12% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91–7.85 (m, 5H), 7.73 (dd, J = 8.2, 1.8 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.49 (s, 1H), 7.36 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 16.0 Hz, 1H), 6.76 (s, 1H), 6.11-6.03 (m, 1H), 3.97 (d, J = 7.6 Hz, 2H). ^{13}C{^1H} NMR (126 MHz, $CDCl_3$) δ 170.4, 162.0, 138.8, 137.7, 137.2, 137.0, 136.1, 134.1, 131.2, 130.6, 129.5, 129.4, 129.2, 128.5, 127.6, 126.1, 119.1, 100.9, 96.2, 60.5; IR (neat, cm^{-1}): 2946, 1634, 1489, 1316, 1263, 1104, 1086, 784, 689, 534; HRMS (ESI-TOF) calcd for $C_{24}H_{18}INO_3S$ $[M + H]^+$ 528.0125, found 528.0131.

(*E*)-5-Phenyl-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-4-(trifluoromethyl)phenyl)isoxazole (**3e**):



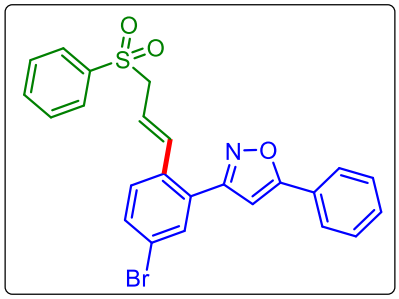
A light yellow liquid compound (81 mg, 58% yield, *E*/*Z* 1:0.13); purified over a column of silica gel (11% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (t, *J* = 8.0 Hz, 4H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.56–7.48 (m, 5H), 6.96 (d, *J* = 16 Hz, 1H), 6.83 (s, 1H), 6.18-6.12 (m, 1H), 4.00 (d, *J* = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 161.7, 138.9, 137.2, 136.1, 134.1, 131.5, 130.7, 130.4, 129.5, 129.3, 128.5, 128.3, 127.2, 126.1, 126.0, 125.3 (q, *J* = 3.5 Hz), 124.1 (q, *J* = 3.6 Hz), 119.7, 101.1, 60.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9; IR (neat, cm^{-1}): 2930, 1650, 1456, 1320, 1270, 1134, 1088, 792, 689, 531; HRMS (ESI-TOF) calcd for $C_{25}H_{18}F_3NO_3S$ $[M + H]^+$ 470.1032, found 470.1029.

(*E*)-3-(5-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (**3f**):



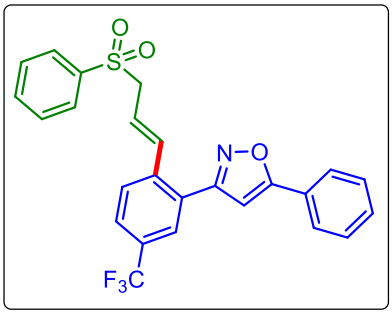
A brown gummy compound (86 mg, 69% yield, E/*Z* 1:0.13); purified over a column of silica gel (10% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (t, *J* = 9.0 Hz, 4H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.52–7.43 (m, 7H), 7.25 (d, *J* = 7 Hz, 1H), 6.84 (d, *J* = 15.5 Hz, 1H), 6.69 (s, 1H), 6.08-6.01 (m, 1H), 3.96 (d, *J* = 7.5 Hz, 2H), 2.40 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.0, 162.8, 138.9, 138.8, 138.0, 133.9, 132.5, 130.9, 130.4, 130.3, 129.3, 129.2, 128.5, 128.0, 127.5, 127.0, 126.1, 116.8, 101.2, 60.7, 21.2; IR (neat, cm^{-1}): 2925, 1572, 1447, 1309, 1269, 1156, 1089, 730, 688, 530; HRMS (ESI-TOF) calcd for $C_{25}H_{21}NO_3S$ $[M + H]^+$ 416.1315, found 416.1315.

(*E*)-3-(5-Bromo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (**3g**):



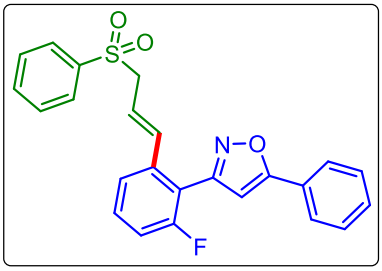
A dark brown gummy compound (83 mg, 58% yield, *E*/*Z* 1:0.09); purified over a column of silica gel (11% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.86 (m, 4H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.56 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.54–7.48 (m, 5H), 7.42 (d, *J* = 8.5 Hz, 1H), 6.84 (d, *J* = 15.5 Hz, 1H), 6.74 (s, 1H), 6.12-6.06 (m, 1H), 3.96 (d, *J* = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.5, 161.5, 138.8, 137.3, 134.2, 134.0, 133.1, 132.6, 130.7, 129.90, 129.86, 129.4, 129.3, 128.6, 128.5, 127.3, 126.1, 122.7, 118.4, 101.0, 60.6; IR (neat, cm^{-1}): 2925, 1688, 1442, 1315, 1276, 1145, 1088, 730, 685, 531; HRMS (ESI-TOF) calcd for $C_{24}H_{18}BrNO_3S$ $[M + H]^+$ 480.0264, found 480.0279.

***(E)*-5-Phenyl-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-5-(trifluoromethyl)phenyl)isoxazole** (**3h**):



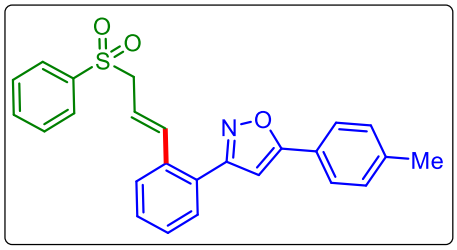
A light yellow liquid compound (77 mg, 55% yield, *E*/*Z* 1:0.10); purified over a column of silica gel (11% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 5H), 7.68 (q, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.48 (m, 5H), 6.95 (d, *J* = 16 Hz, 1H), 6.80 (s, 1H), 6.22 – 6.15 (m, 1H), 4.00 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 161.7, 138.8, 138.7, 137.1, 134.1, 130.7, 129.4, 129.3, 128.8, 128.5, 127.7, 127.2, 126.9 (d, *J* = 3.5 Hz), 126.7 (q, *J* = 3.4 Hz), 126.1, 120.2, 101.0, 60.5.^{19}F NMR (471 MHz, $CDCl_3$) δ -62.7; IR (neat, cm^{-1}): 2931, 1651, 1458, 1323, 1271, 1132, 1086, 791, 689, 530; HRMS (ESI-TOF) calcd for $C_{25}H_{18}F_3NO_3S$ $[M + H]^+$ 470.1032, found 470.1029.

(*E*)-3-(2-Fluoro-6-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (**3i**):



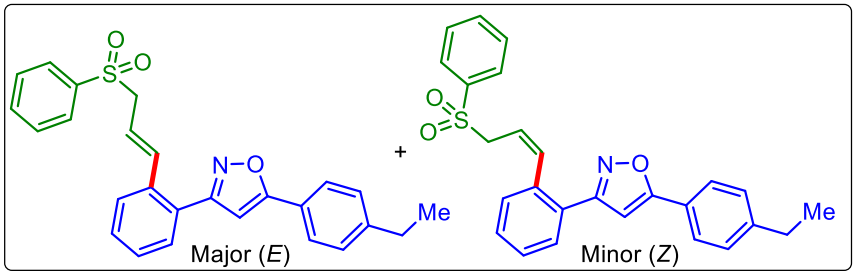
A light yellow liquid compound (68 mg, 54% yield, *E*/*Z* 1:0.13); purified over a column of silica gel (12% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 - 7.83 (m, 4H), 7.57 – 7.54 (m, 1H), 7.53 – 7.48 (m, 5H), 7.42 – 7.38 (m, 2H), 7.16 – 7.12 (m, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.64 (d, *J* = 2.0 Hz, 1H), 6.18-6.12 (m, 1H), 3.95 (d, *J* = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.1, 161.7, 157.1, 138.6, 137.9 (d, *J* = 2.1 Hz), 136.6 (d, *J* = 2.9 Hz), 133.9, 131.2 (d, *J* = 9.1 Hz), 130.6, 129.2 (d, *J* = 2.6 Hz), 128.5, 127.3, 126.0, 122.4 (d, *J* = 3.2 Hz), 119.0, 116.5 (d, *J* = 14.7 Hz), 115.8, 115.6, 102.0 (d, *J* = 3.7 Hz), 60.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.7; IR (neat, cm^{-1}): 2934, 1659, 1467, 1312, 1269, 1131, 1085, 789, 681, 531; HRMS (ESI-TOF) calcd for $C_{24}H_{18}FNO_3S$ $[M + H]^+$ 420.1064, found 420.1070.

(*E*)-3-(2-(3-(Phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-(p-tolyl)isoxazole (**3j**):



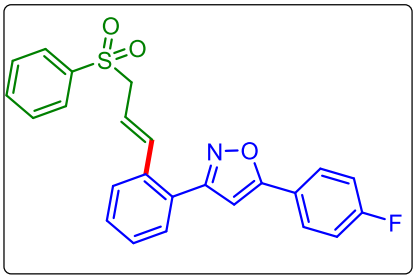
A brown gummy compound (84 mg, 68% yield, *E*/*Z* 1:0.20); purified over a column of silica gel (10% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.49 (m, 5H), 7.43-7.39 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.64 (s, 1H), 6.12-6.06 (m, 1H), 3.97 (d, *J* = 7.5 Hz, 2H), 2.42 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.2, 162.7, 140.8, 138.8, 138.2, 135.3, 133.9, 130.3, 130.0, 129.9, 129.3, 128.7, 128.5, 128.3, 127.0, 126.0, 124.8, 117.7, 100.5, 60.7, 21.6; IR (neat, cm^{-1}): 2926, 1573, 1448, 1308, 1268, 1158, 1085, 731, 689, 530; HRMS (ESI-TOF) calcd for $C_{25}H_{21}NO_3S$ $[M + H]^+$ 416.1315, found 416.1315.

(*E*)-5-(4-Ethylphenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (**3k**):



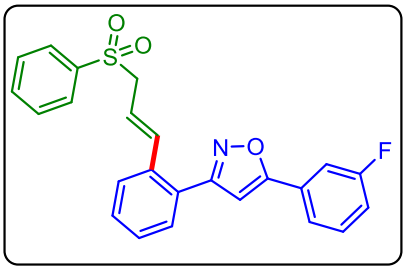
A brown gummy compound (89 mg, 69% yield, *E*/*Z* 1:0.21); purified over a column of silica gel (10% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.62–7.58 (m, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.44–7.39 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 16 Hz, 1H), 6.65 (s, 1H), 6.12-6.06 (m, 1H), 3.98 (d, *J* = 7.5 Hz, 2H), 2.72 (q, *J* = 7.7 Hz, 2H), 1.28 (t, J = 7.8 Hz 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.3, 162.7, 147.1, 138.8, 138.2, 135.3, 133.9, 130.5, 130.0, 129.8, 129.3, 128.7, 128.5, 128.2, 127.0, 126.1, 125.0, 117.7, 100.6, 60.7, 29.0, 15.5; IR (neat, cm^{-1}): 2926, 1687, 1447, 1308, 1265, 1138, 1086, 730, 688, 531; HRMS (ESI-TOF) calcd for $C_{26}H_{23}NO_3S$ $[M + H]^+$ 430.1471, found 430.1474.

(*E*)-5-(4-Fluorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (**3l**):



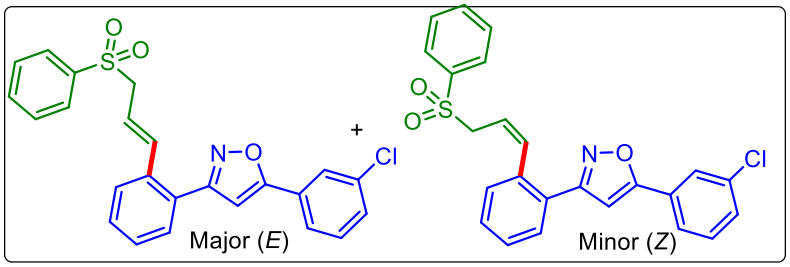
A light yellow liquid compound (67 mg, 53% yield, *E*/*Z* 1:0.20); purified over a column of silica gel (12% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.86 (m, 4H), 7.65–7.60 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 3H), 7.46 – 7.39 (m, 2H), 7.19 (t, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 15.6 Hz, 1H), 6.77 (s, 1H), 6.11-6.03 (m, 1H), 3.98 (d, *J* = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 169.1, 163.9 (d, *J* = 251.6 Hz), 162.8, 139.0, 138.5, 135.4, 134.0, 129.9 (d, *J* = 45.8 Hz), 129.4, 128.8, 128.5, 128.3, 128.2 (d, *J* = 8.6 Hz), 128.0, 127.2, 123.9 (d, *J* = 3.4 Hz), 117.7, 116.4 (d, *J* = 22.2 Hz), 101.1, 60.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.3; IR (neat, cm^{-1}): 2924, 1613, 1447, 1394, 1264, 1138, 1085, 765, 688, 530; HRMS (ESI-TOF) calcd for $C_{24}H_{18}FNO_3S$ $[M + H]^+$ 420.1064, found 420.1070.

(*E*)-5-(3-Fluorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (**3m**):



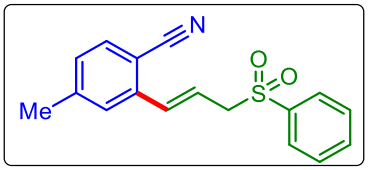
A light yellow liquid compound (65 mg, 52% yield, *E*/*Z* 1:0.19); purified over a column of silica gel (12% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.3 Hz, 2H), 7.58–7.52 (m, 4H), 7.49–7.41 (m, 3H), 7.18-7.15 (m, 1H), 6.90 (d, *J* = 15.5 Hz, 1H), 6.80 (s, 1H), 6.13-6.06 (m, 1H), 3.98 (d, *J* = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.8 (d, *J* = 2.8 Hz), 163.2 (d, *J* = 247.6 Hz), 162.8, 138.9, 138.3, 135.4, 134.0, 131.0 (d, *J* = 8.2 Hz), 130.2, 129.8, 129.4, 128.8, 128.5, 128.3, 127.9, 127.2, 121.9 (d, *J* = 2.9 Hz), 117.9, 117.4 (d, *J* = 21.3 Hz), 113.1 (d, *J* = 23.8 Hz), 102.1, 60.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.6; IR (neat, cm^{-1}): 2925, 1621, 1445, 1365, 1268, 1135, 1086, 786, 689, 531; HRMS (ESI-TOF) calcd for $C_{24}H_{18}FNO_3S$ $[M + H]^+$ 420.1064, found 420.1070.

(*E*)-5-(3-Chlorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (**3n**):



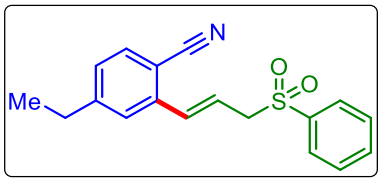
A light brown liquid compound (71 mg, 54% yield, *E*/*Z* 1:0.25); purified over a column of silica gel (12% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.86 (s, 1H), 7.77 (t, *J* = 3.6 Hz, 1H), 7.62 (dd, *J* = 7.2, 5.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 3H), 7.47 – 7.39 (m, 4H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.79 (s, 1H), 6.14 – 6.07 (m, 1H), 3.98 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 168.3, 162.8, 139.0, 138.9, 138.3, 137.1, 135.34, 135.26, 134.2, 134.0, 130.7, 130.4, 130.2, 129.92, 129.89, 129.8, 129.6, 129.39, 129.36, 129.1, 129.0, 128.8, 128.6, 128.5, 128.3, 127.9, 127.2, 126.1, 126.0, 124.2, 124.1, 118.6, 117.9, 102.1, 101.4, 60.6, 56.1; IR (neat, cm^{-1}): 2939, 1664, 1469, 1343, 1265, 1141, 1089, 793, 688, 530; HRMS (ESI-TOF) calcd for $C_{24}H_{18}ClNO_3S$ $[M + H]^+$ 436.0769, found 436.0774.

(*E*)-4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4a**):



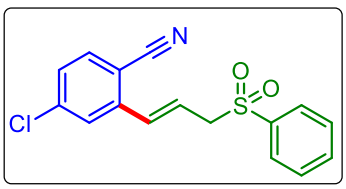
A light brown gummy compound (67 mg, 75% yield, *E*/*Z* 1:0.14); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.7 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (s, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 15.6 Hz, 1H), 6.41-6.33 (m, 1H), 4.02 (dd, *J* = 7.6, 0.8 Hz, 2H), 2.43 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.0, 138.7, 138.4, 134.9, 134.3, 133.1, 129.8, 129.5, 129.4, 128.5, 126.6, 120.4, 108.6, 60.6, 22.0; IR (neat, cm^{-1}): 2923, 2224, 1673, 1446, 1305, 1139, 1084, 967, 733, 689, 527; HRMS (ESI-TOF) calcd for $C_{17}H_{15}NO_2S$ $[M + Na]^+$ 320.0716, found 320.0712.

(*E*)-4-Ethyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4b**):



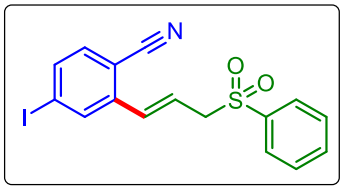
A light brown liquid compound (67 mg, 72% yield, *E*/*Z* 1:0.15); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.0 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 16 Hz, 1H), 6.41-6.35 (m, 1H), 4.03 (d, *J* = 7.5 Hz, 2H), 2.71 (q, *J* = 7.7 Hz, 2H), 1.27 (t, *J* = 7.7 Hz, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.8, 138.8, 138.4, 135.0, 134.3, 133.2, 129.4, 128.6, 128.5, 125.5, 120.4, 117.7, 108.7, 60.6, 29.3, 15.1; IR (neat, cm^{-1}): 2930, 2222, 1602, 1447, 1307, 1140, 1085, 967, 730, 688, 529; HRMS (ESI-TOF) calcd for $C_{18}H_{17}NO_2S$ $[M + Na]^+$ 334.0872, found 334.0870.

(*E*)-4-Chloro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4c**):



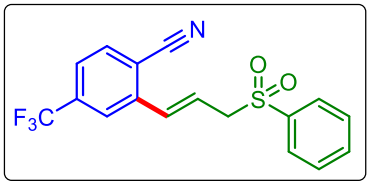
A light yellow solid compound (65 mg, 68% yield); purified over a column of silica gel (16% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.60-7.57 (m, 3H), 7.54 (d, J = 8 Hz, 1H), 7.35 (dd, J = 8.3, 1.8 Hz, 1H), 6.64 (d, J = 16 Hz, 1H), 6.42-6.36 (m, 1H), 4.04 (d, J = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.4, 139.9, 138.4, 134.4, 134.3, 133.6, 129.5, 129.2, 128.5, 126.4, 122.4, 116.7, 109.8, 60.4; IR (neat, cm^{-1}): 2923, 2224, 1577, 1446, 1307, 1139, 1085, 966, 732, 688, 530; HRMS (ESI-TOF) calcd for $C_{16}H_{12}ClNO_2S$ [M + Na]$^{+}$ 340.0169, found 340.0164.

(*E*)-4-Iodo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4d**):



A light brown liquid compound (80 mg, 65% yield, *E*/*Z* 1:0.08); purified over a column of silica gel (17% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 8 Hz, 1H), 6.59 (d, J = 15.5 Hz, 1H), 6.41-6.35 (m, 1H), 4.03 (d, J = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.1, 138.4, 137.9, 135.3, 134.4, 133.9, 133.4, 129.5, 128.5, 122.3, 116.9, 110.7, 100.6, 60.4; IR (neat, cm^{-1}): 2923, 2224, 1577, 1446, 1305, 1139, 1084, 966, 732, 688, 529; HRMS (ESI-TOF) calcd for $C_{16}H_{12}INO_2S$ [M + H]$^{+}$ 409.9706, found 409.9714.

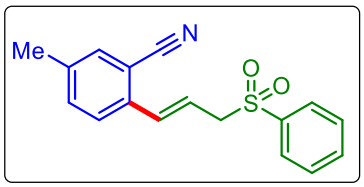
(*E*)-2-(3-(Phenylsulfonyl)prop-1-en-1-yl)-4-(trifluoromethyl)benzonitrile (**4e**):



A light yellow liquid compound (66 mg, 63% yield); purified over a column of silica gel (16% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 2H), 7.83 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.3 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.5 Hz, 2H), 6.75 (d, J = 15.5 Hz, 1H), 6.51-6.45 (m, 1H), 4.07 (d, J = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.8, 138.3, 134.5, 133.9, 133.5, 129.5, 128.5, 127.9, 125.4 (q, J = 3.6 Hz), 123.1, 123.0, 116.2, 114.6, 114.1, 60.4. ^{19}F NMR (471

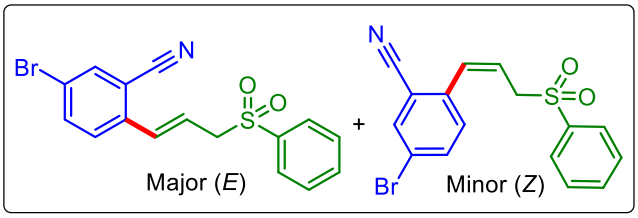
MHz, $CDCl_3$) δ -63.6; IR (neat, cm^{-1}): 2926, 2230, 1585, 1425, 1323, 1134, 1083, 968, 731, 689, 529; HRMS (ESI-TOF) calcd for $C_{17}H_{12}F_3NO_2S$ $[M + Na]^+$ 374.0433, found 374.0427.

(*E*)-5-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4f**):



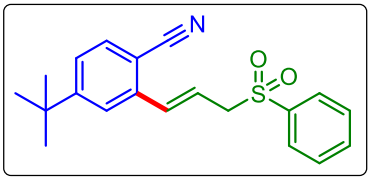
A light brown gummy compound (66 mg, 74% yield, *E*/*Z* 1:0.10); purified over a column of silica gel (15% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 16 Hz, 1H), 6.35-6.29 (m, 1H), 4.02 (d, *J* = 7.5 Hz, 2H), 2.37 (s, 3H). ^{13}C $\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.3, 138.3, 136.1, 134.7, 134.2, 134.1, 133.3, 129.4, 128.5, 125.9, 119.7, 117.6, 111.3, 60.6, 21.0; IR (neat, cm^{-1}): 2923, 2224, 1673, 1446, 1305, 1139, 1084, 967, 733, 689, 527; HRMS (ESI-TOF) calcd for $C_{17}H_{15}NO_2S$ $[M + Na]^+$ 320.0716, found 320.0712.

(*E*)-5-Bromo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4g**):



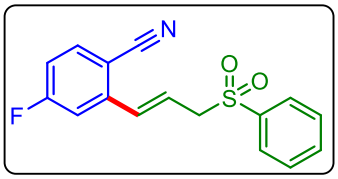
A dark brown liquid compound (73 mg, 67% yield, *E*/*Z* 1:0.09); purified over a column of silica gel (16% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.50 – 7.47 (m, 2H), 6.62 (d, *J* = 15.5 Hz, 1H), 6.42-6.35 (m, 1H), 4.02 (d, *J* = 8.0 Hz, 2H). ^{13}C $\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.4, 135.5, 134.4, 133.8, 133.7, 130.3, 129.5, 128.6, 128.5, 127.4, 121.6, 116.0, 113.0, 60.5; IR (neat, cm^{-1}): 2924, 2224, 1603, 1446, 1305, 1136, 1085, 969, 732, 688, 531; HRMS (ESI-TOF) calcd for $C_{16}H_{12}BrNO_2S$ $[M + Na]^+$ 383.9664, found 383.9667.

(*E*)-4-(*tert*-Butyl)-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4o**):



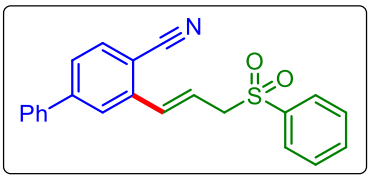
A brown liquid compound (70 mg, 69% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.39 (d, J = 7 Hz, 1H), 6.68 (d, J = 16 Hz, 1H), 6.39-6.33 (m, 1H), 4.03 (d, J = 7.5 Hz, 2H), 1.34 (s, 9H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.0, 138.6, 138.5, 135.4, 134.3, 133.0, 129.4, 128.6, 126.3, 123.1, 120.3, 117.7, 108.5, 60.6, 35.5, 31.1; IR (neat, cm^{-1}): 2961, 2222, 1600, 1465, 1308, 1142, 1085, 968, 729, 688, 530; HRMS (ESI-TOF) calcd for $C_{20}H_{21}NO_2S$ [M + Na]$^{+}$ 362.1185, found 362.1184.

(*E*)-4-Fluoro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4p**):



A light yellow solid compound (60 mg, 66% yield, *E*/*Z* 1:0.12); purified over a column of silica gel (16% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 2H), 7.71-7.67 (m, 1H), 7.64 – 7.56 (m, 3H), 7.29 (dd, J = 9.6, 2.4 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.68 (dd, J = 15.8, 1 Hz, 1H), 6.42 – 6.34 (m, 1H), 4.04 (dd, J = 7.6, 0.8 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.9 (d, J = 10.1 Hz), 138.4, 135.6 (d, J = 10.1 Hz), 134.4, 133.8, 129.6, 129.5, 128.5, 122.4, 116.7 (d, J = 6.3 Hz), 116.6, 113.3 (d, J = 22.7 Hz), 107.6, 60.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.2; IR (neat, cm^{-1}): 2893, 2225, 1603, 1446, 1285, 1138, 1084, 976, 738, 688, 528; HRMS (ESI-TOF) calcd for $C_{16}H_{12}FNO_2S$ [M + Na]$^{+}$ 324.0465, found 324.0466.

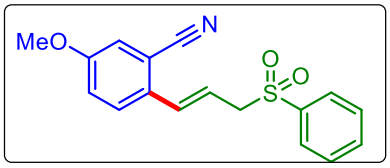
(*E*)-3-(3-(Phenylsulfonyl)prop-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile (**4q**):



A yellow liquid compound (74 mg, 69% yield, *E*/*Z* 1:0.15); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.79 (s, 1H), 7.67 (d, J = 8.4 Hz,

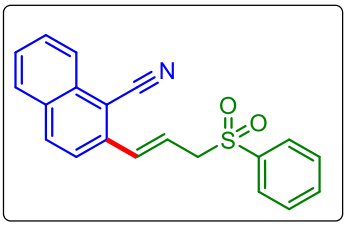
2H), 7.61-7.56 (m, 5H), 7.53-7.49 (m, 2H), 7.48-7.46 (m, 1H), 6.73 (d, *J* = 16 Hz, 1H), 6.51-6.43 (m, 1H), 4.06 (d, *J* = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.2, 139.2, 139.1, 138.4, 134.9, 134.3, 133.6, 129.5, 129.3, 129.1, 128.8, 128.6, 127.6, 127.4, 124.7, 121.0, 117.6, 109.9, 60.6; IR (neat, cm^{-1}): 2923, 2221, 1600, 1447, 1307, 1139, 1084, 999, 730, 690, 526; HRMS (ESI-TOF) calcd for $C_{22}H_{17}NO_2S$ $[M + Na]^+$ 382.0872, found 382.0878.

(*E*)-5-Methoxy-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (**4r**):



A light brown liquid compound (66 mg, 71% yield); purified over a column of silica gel (17% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.55 (q, *J* = 8.5 Hz, 4H), 7.11 – 7.08 (m, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.60 (d, *J* = 15.5 Hz, 1H), 6.26-6.20 (m, 1H), 4.00 (d, *J* = 7.0 Hz, 2H), 3.83 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.4, 134.3, 134.2, 131.9, 131.6, 129.4, 128.6, 127.7, 127.4, 120.2, 118.3, 116.9, 112.3, 60.6, 55.9; IR (neat, cm^{-1}): 2925, 2226, 1602, 1448, 1306, 1144, 1085, 968, 737, 689, 530; HRMS (ESI-TOF) calcd for $C_{17}H_{15}NO_3S$ $[M + Na]^+$ 336.0665, found 336.0663.

(*E*)-2-(3-(Phenylsulfonyl)prop-1-en-1-yl)-1-naphthonitrile (**4s**):

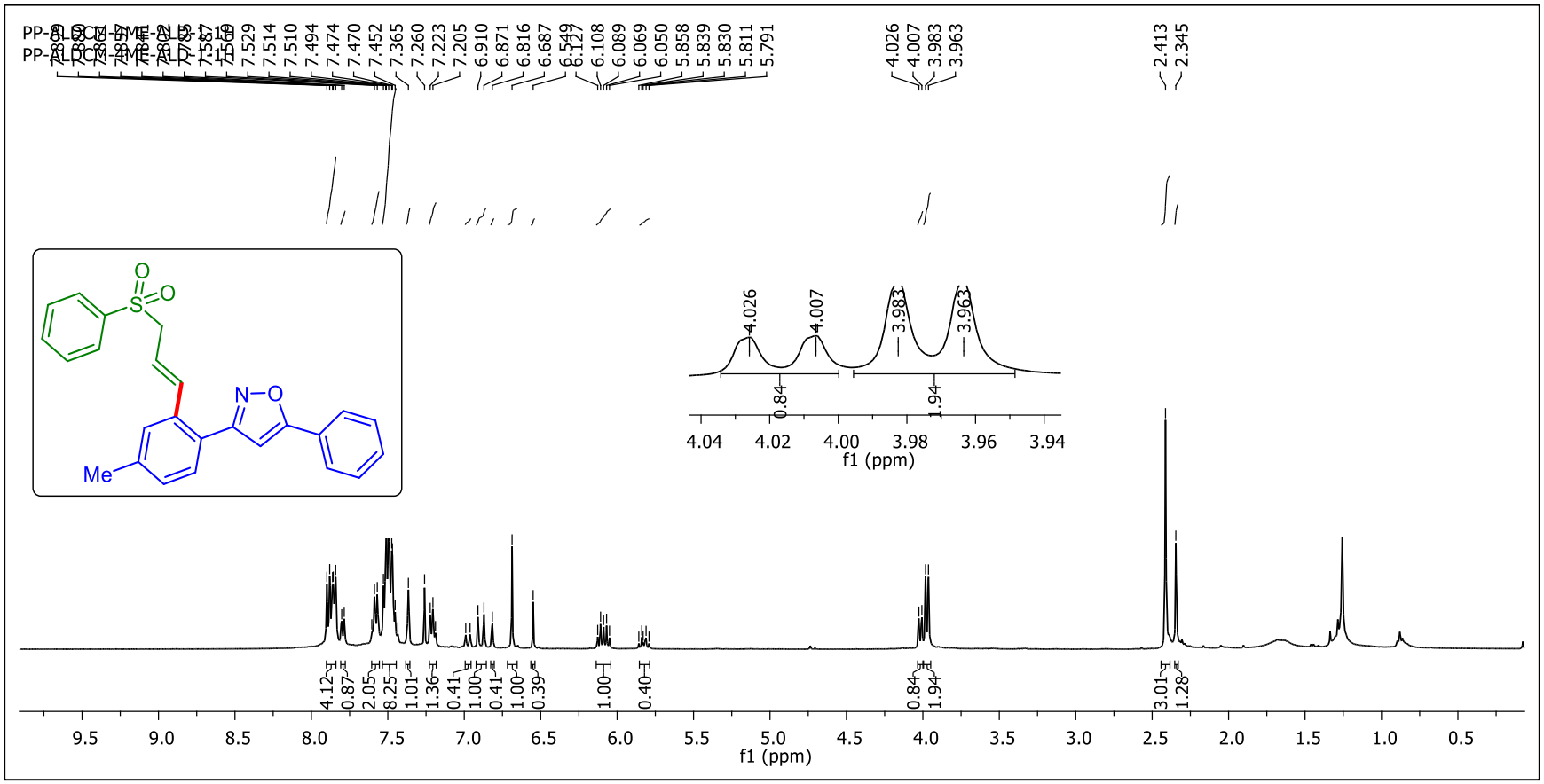


A light brown solid compound (70 mg, 70% yield); purified over a column of silica gel (16% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 8 Hz, 1H), 7.71 – 7.66 (m, 3H), 7.62 – 7.55 (m, 3H), 6.92 (d, *J* = 16 Hz, 1H), 6.57-6.50 (m, 1H), 4.11 (d, *J* = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.8, 138.3, 135.3, 134.3, 133.2, 132.7, 132.6, 129.4, 129.3, 128.59, 128.56, 128.0, 125.8, 122.1, 121.7, 116.3, 108.9, 60.7;

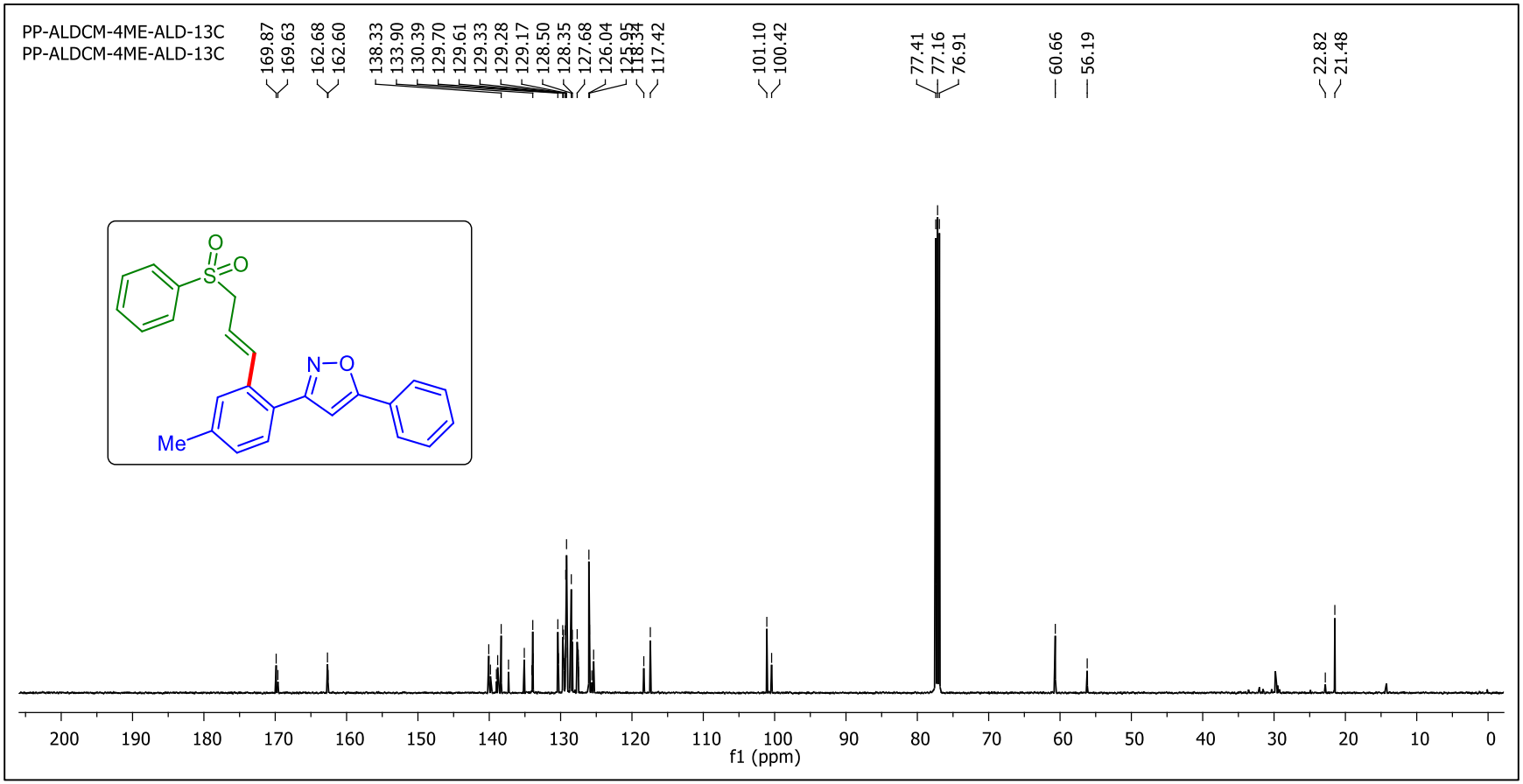
IR (neat, cm^{-1}): 2920, 2216, 1577, 1446, 1268, 1136, 1084, 963, 730, 688, 529; HRMS (ESI-TOF) calcd for $C_{20}H_{15}NO_2S$ $[M + Na]^+$ 356.0716, found 356.0709.

10. NMR Spectra

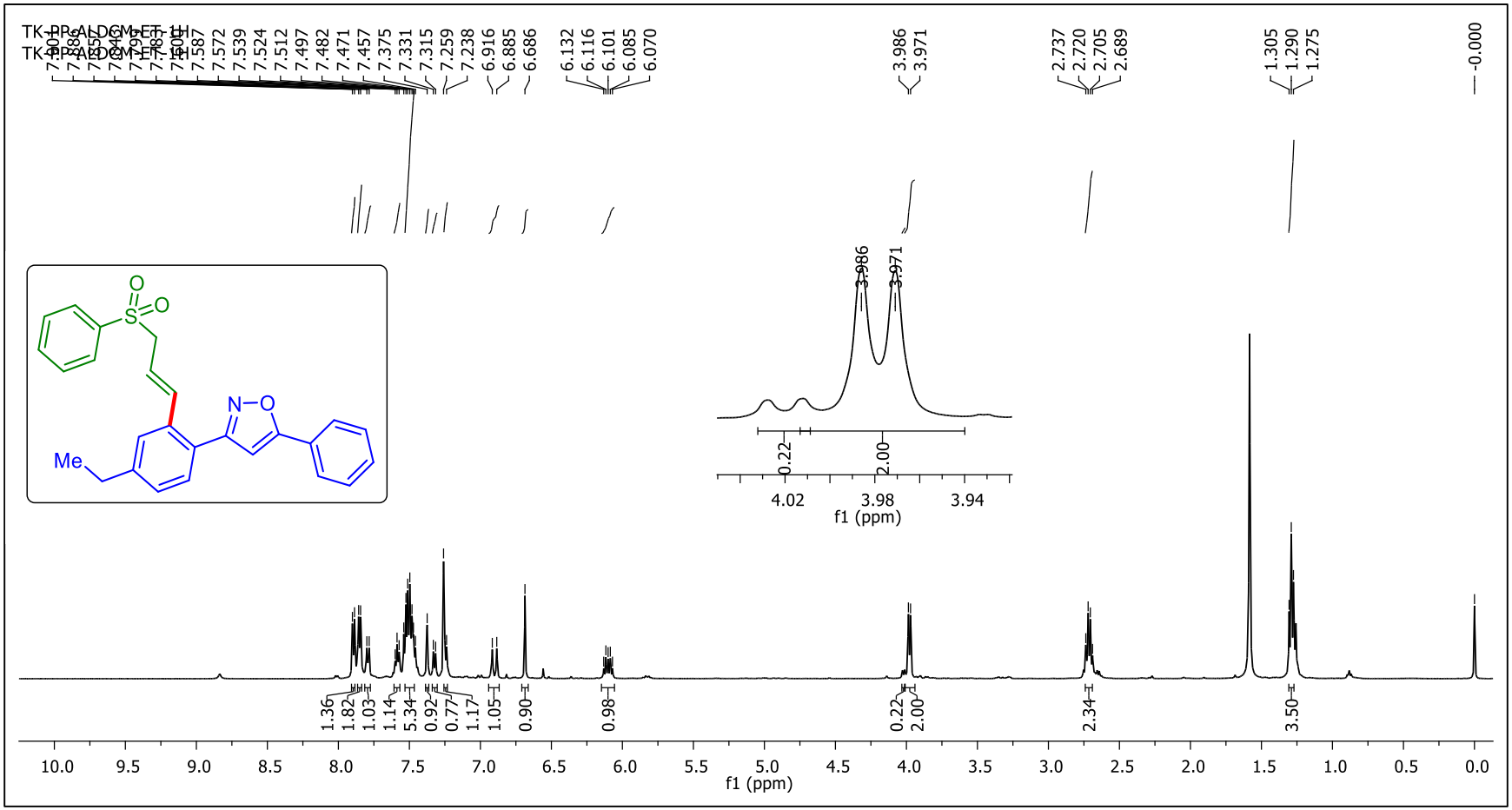
^{1}H NMR of (*E*)-3-(4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3a) ($CDCl_3$, 500 MHz)



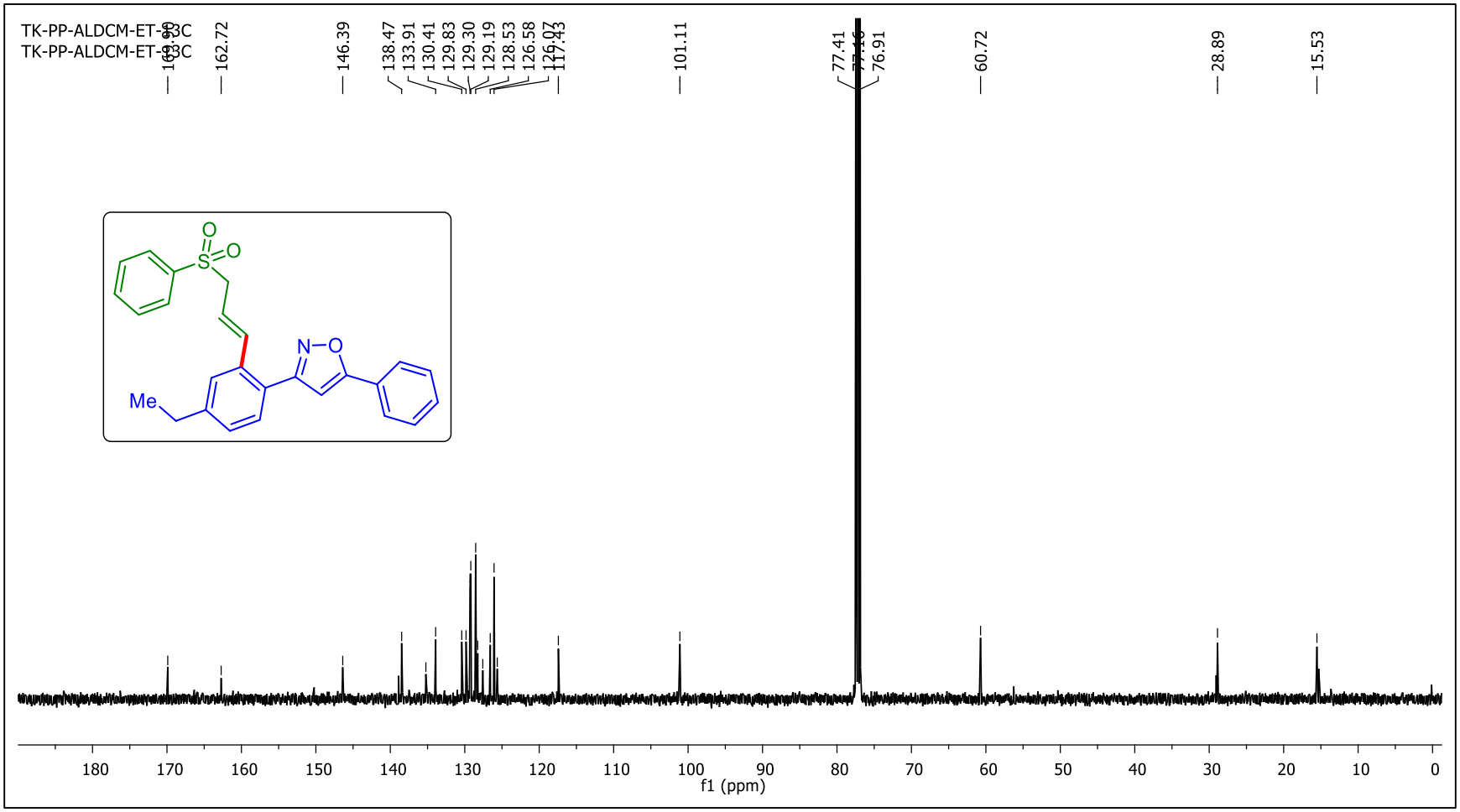
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3a) ($CDCl_3$, 126 MHz)



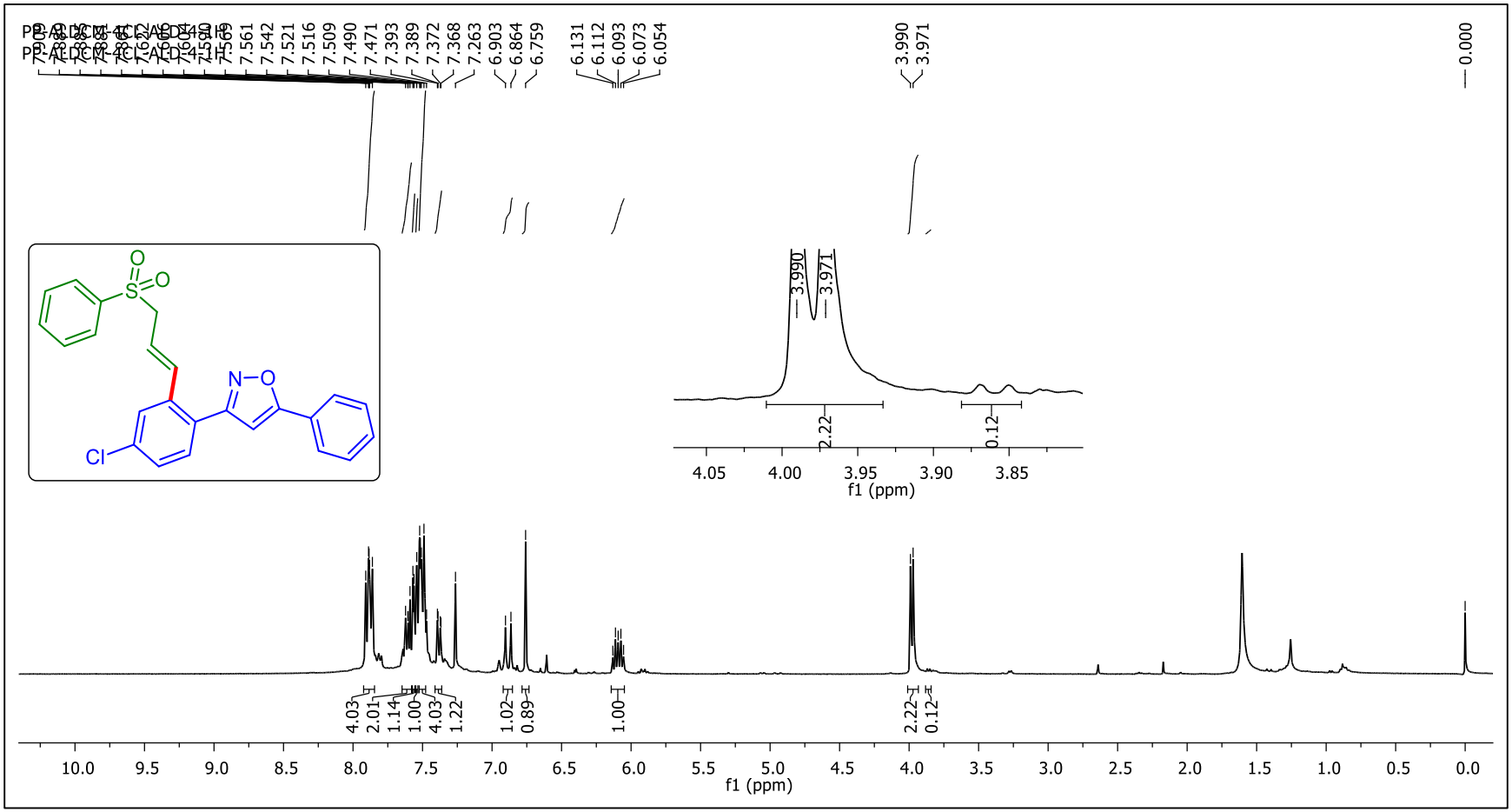
^{1}H NMR of (*E*)-3-(4-Ethyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3b) ($CDCl_3$, 500 MHz)



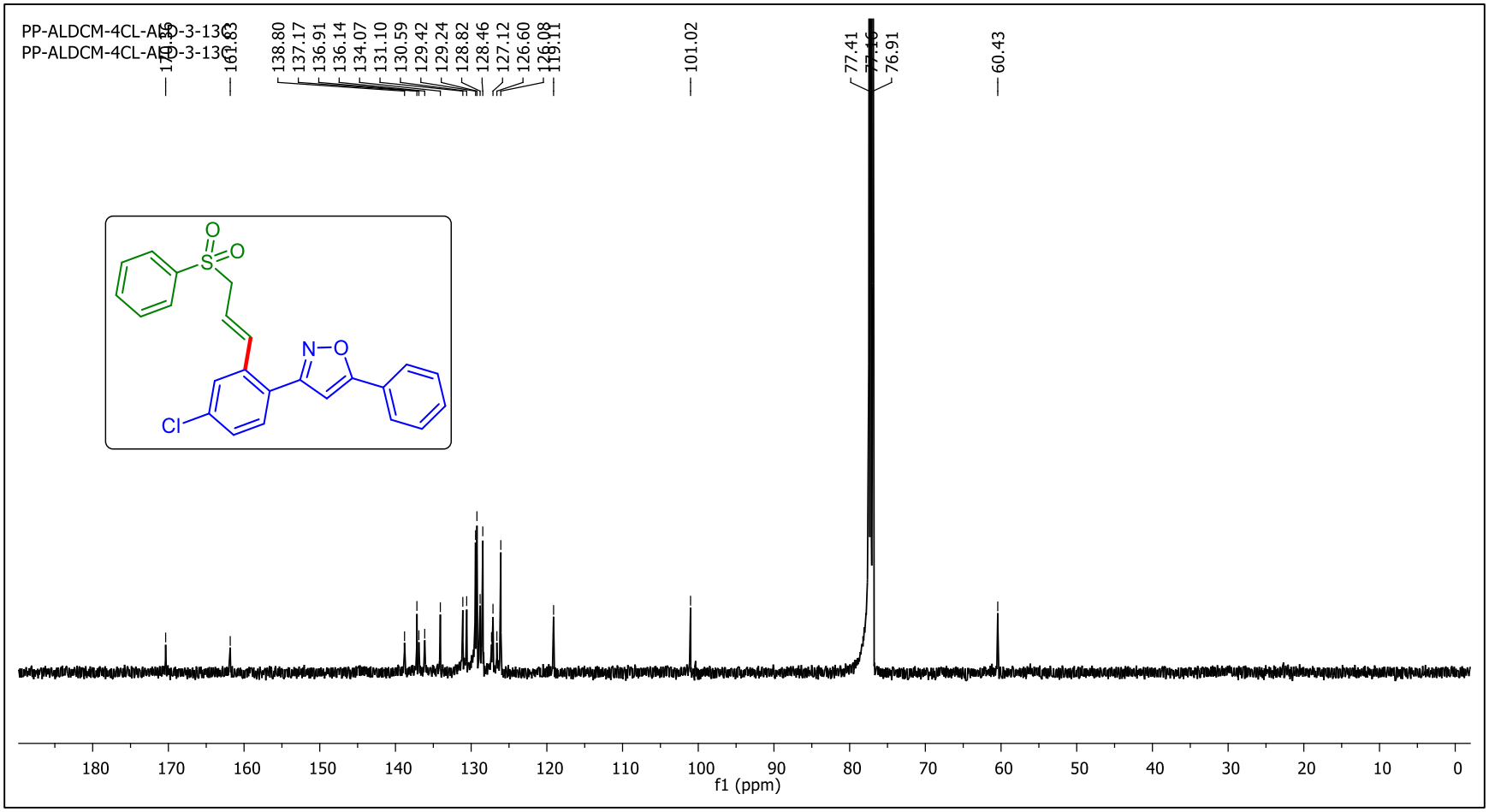
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(4-Ethyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3b) ($CDCl_3$, 126 MHz)



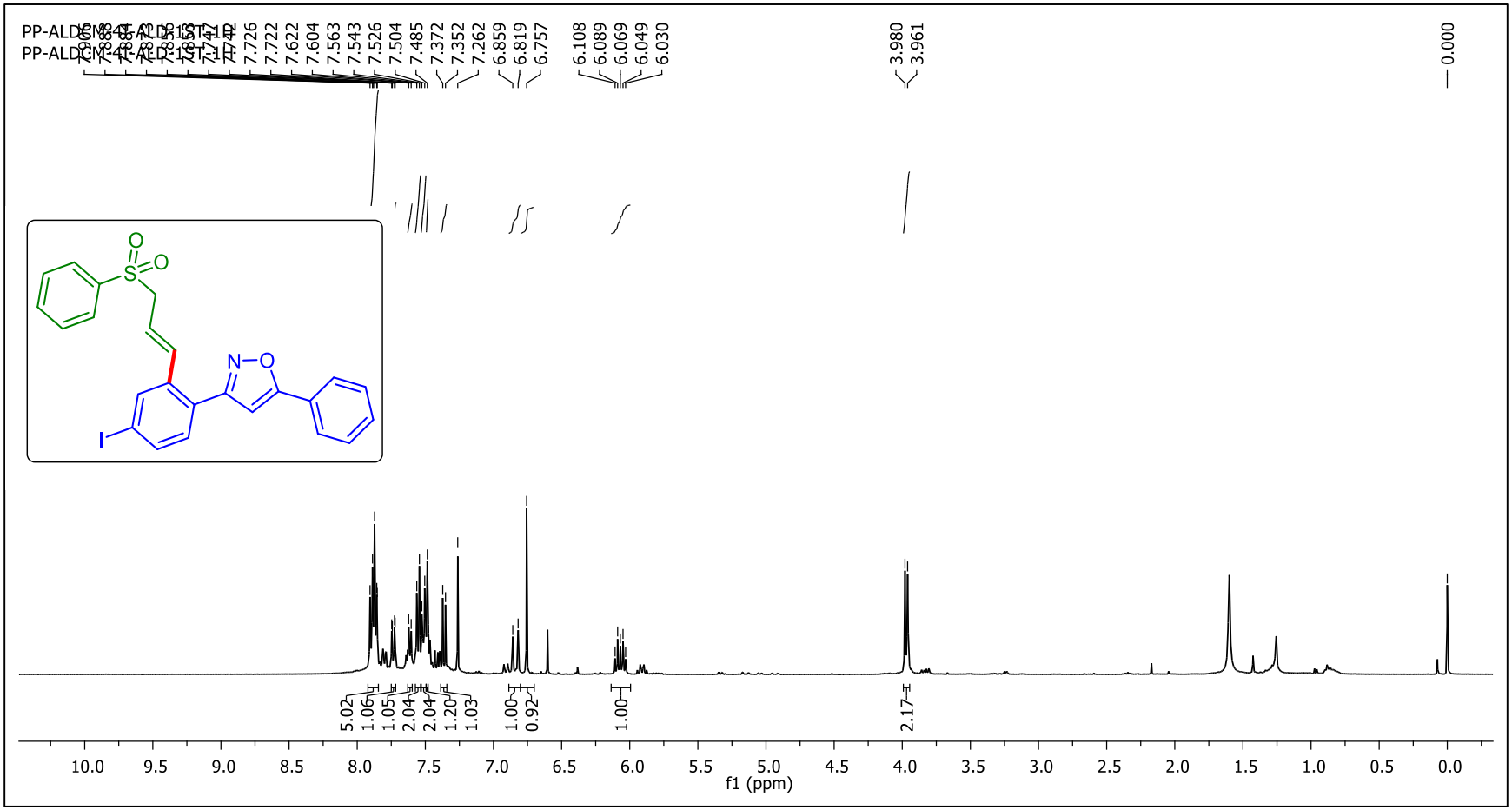
^{1}H NMR of (*E*)-3-(4-Chloro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3c) ($CDCl_3$, 400 MHz)



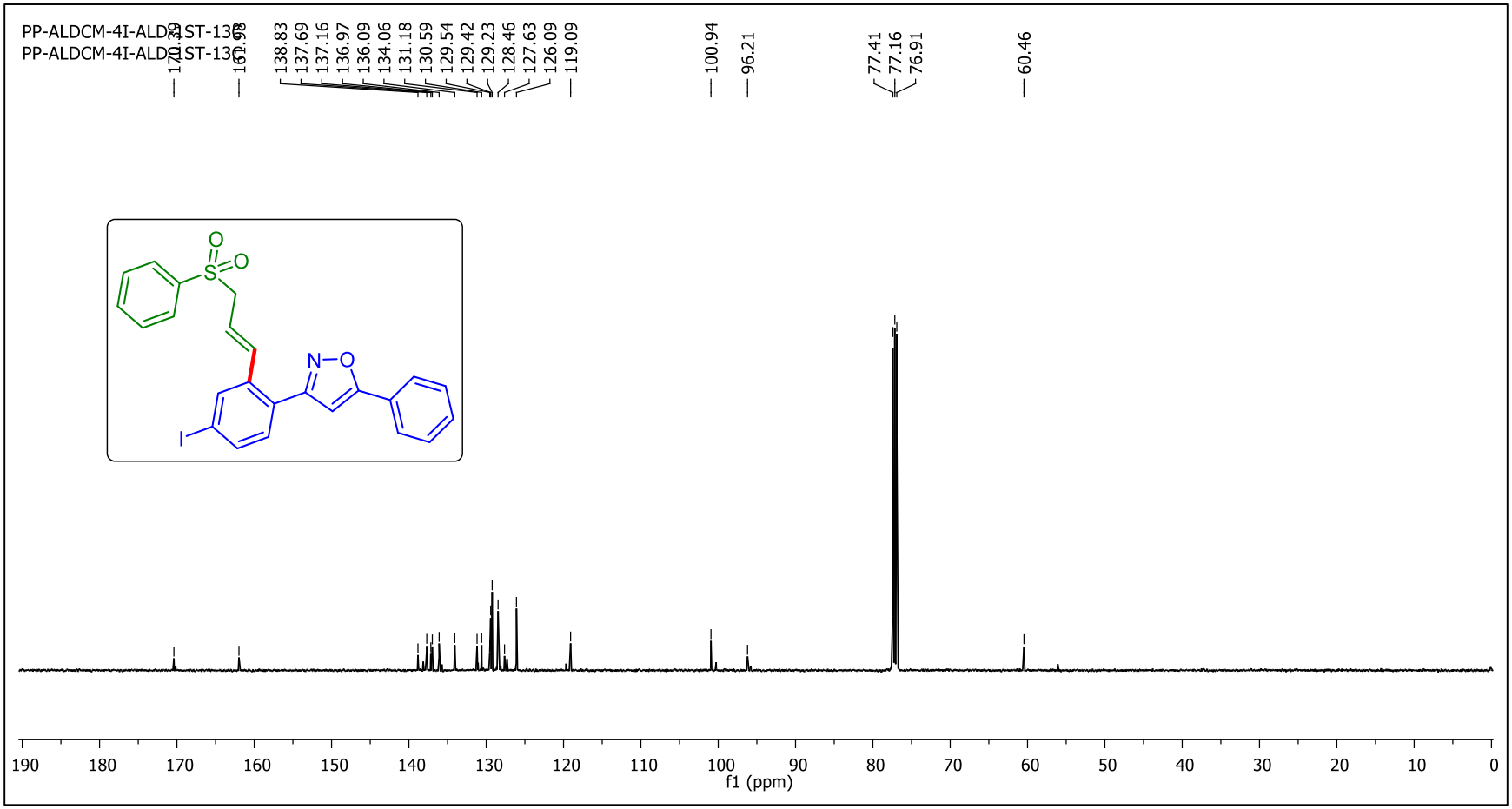
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(4-Chloro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3c) ($CDCl_3$, 126 MHz)



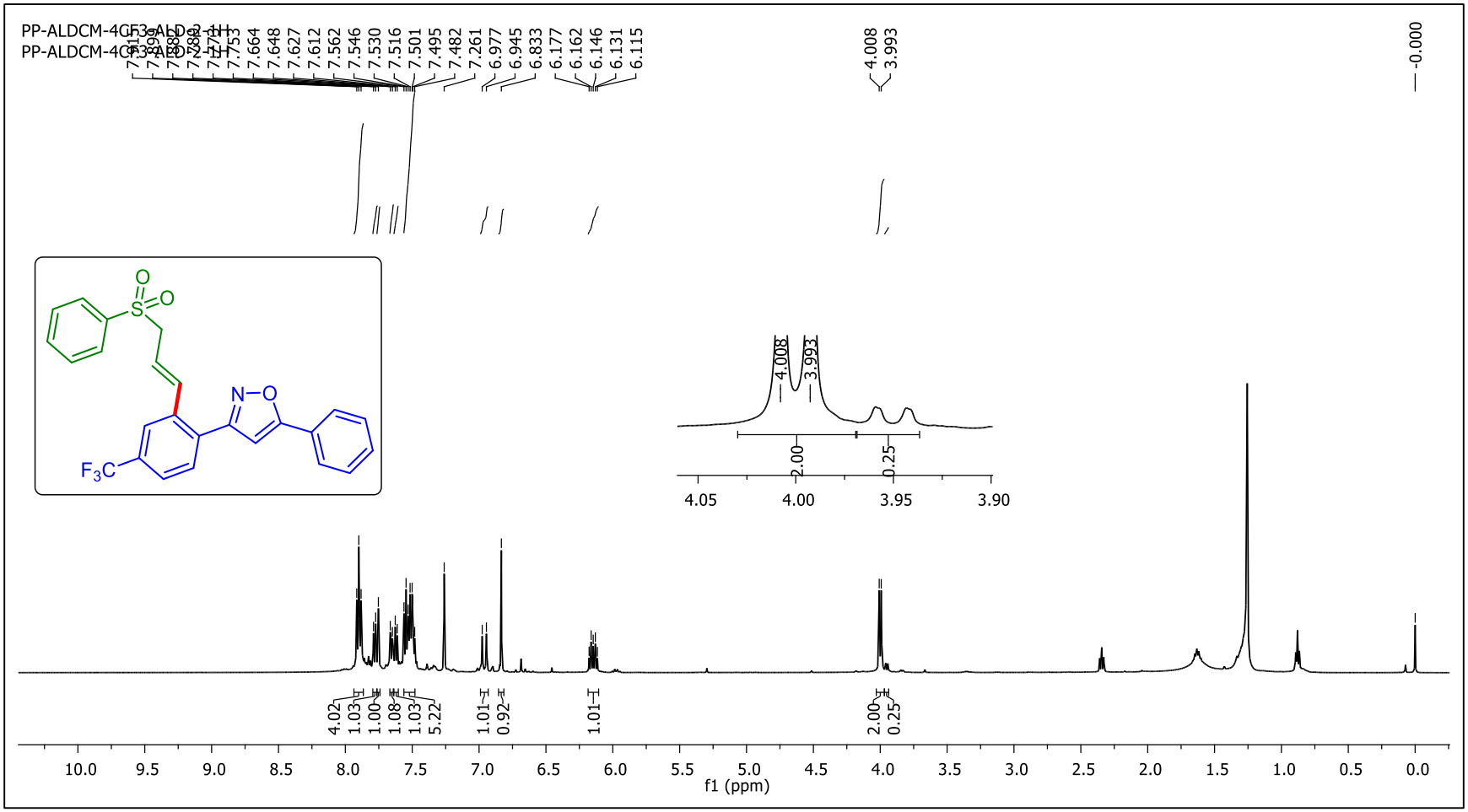
^{1}H NMR of (*E*)-3-(4-Iodo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3d) ($CDCl_3$, 400 MHz)



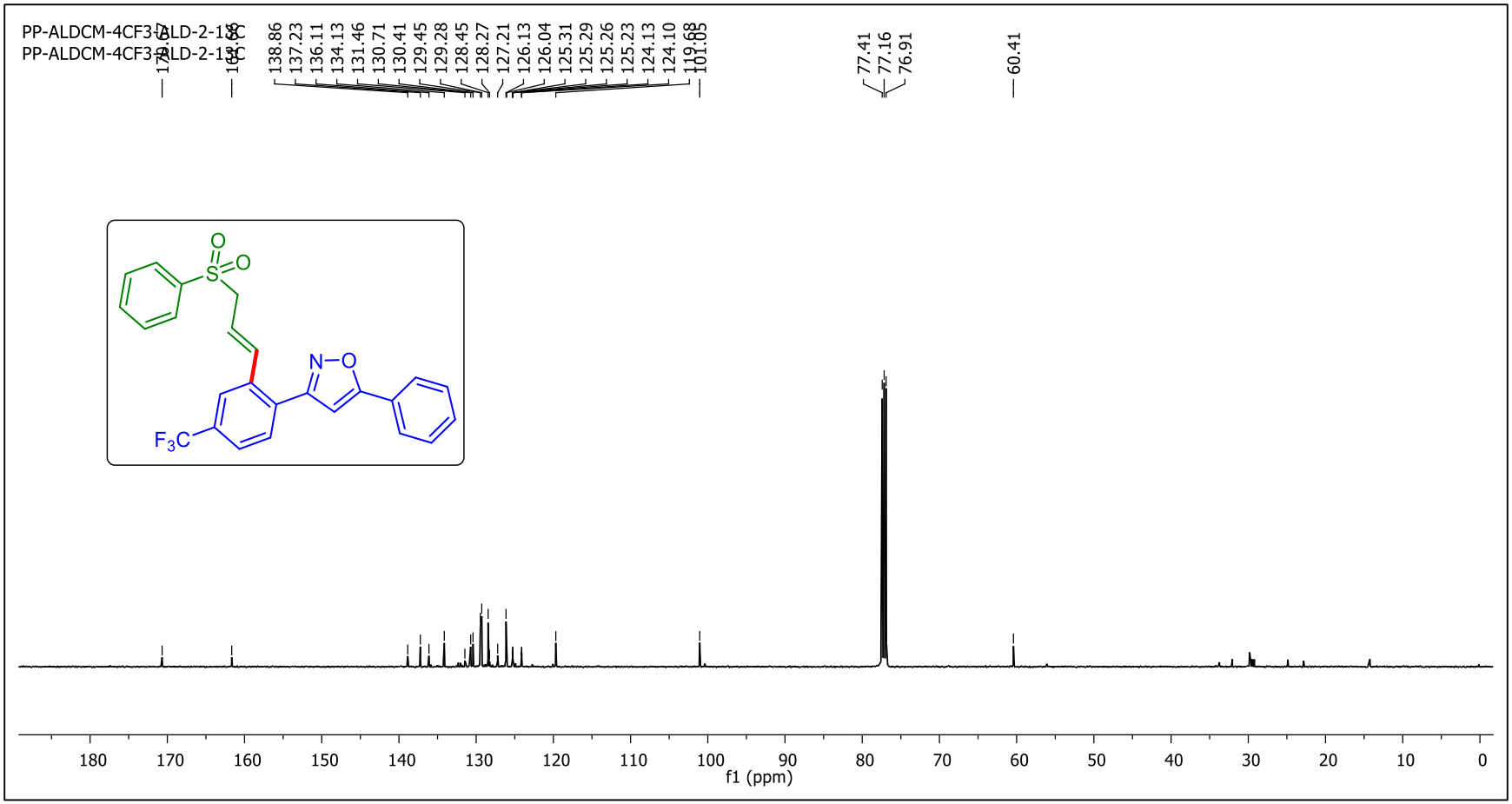
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(4-Iodo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3d) ($CDCl_3$, 126 MHz)



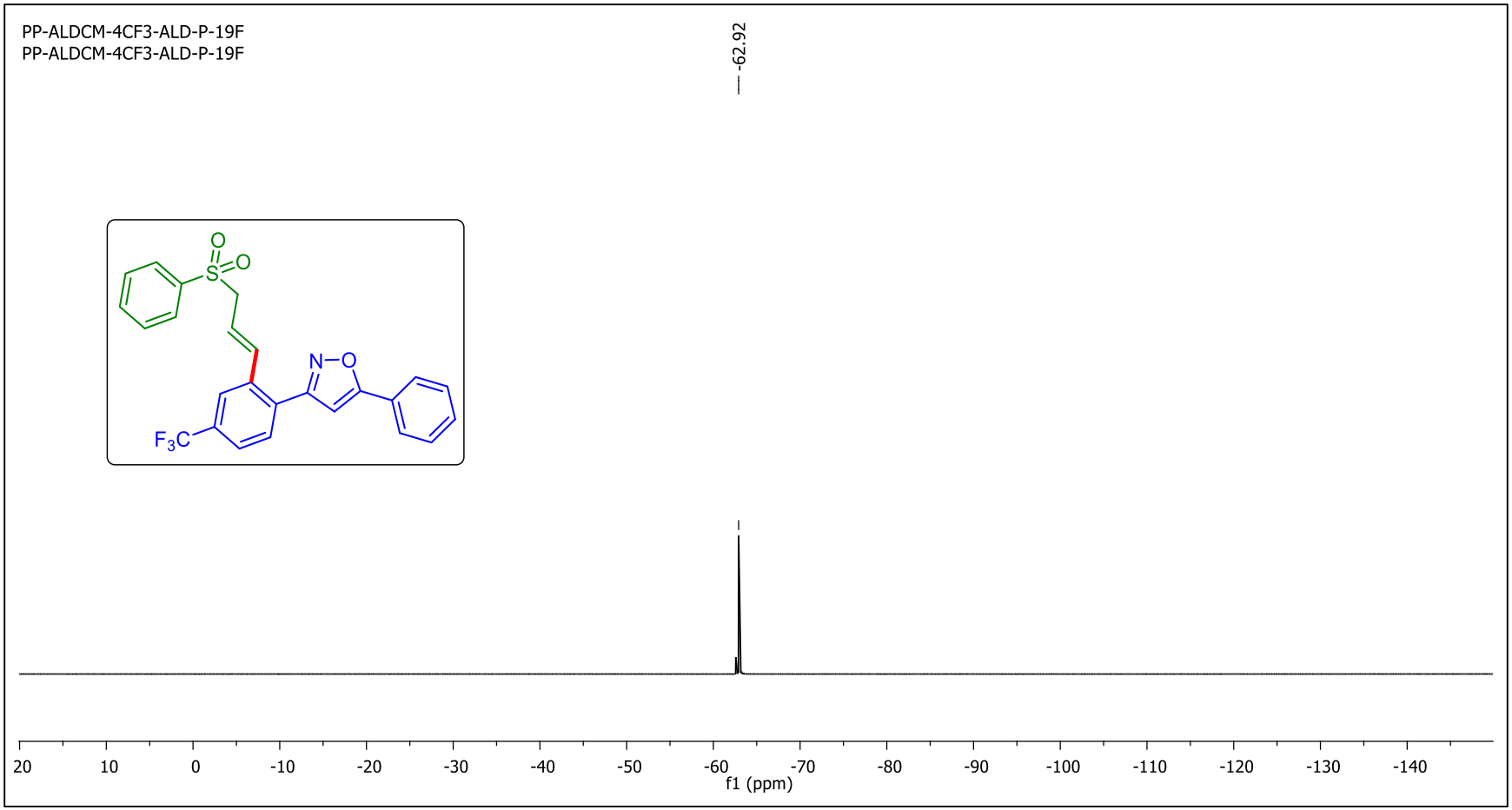
^{1}H NMR of (*E*)-5-Phenyl-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-4-(trifluoromethyl)phenyl)isoxazole (3e) ($CDCl_3$, 500 MHz)



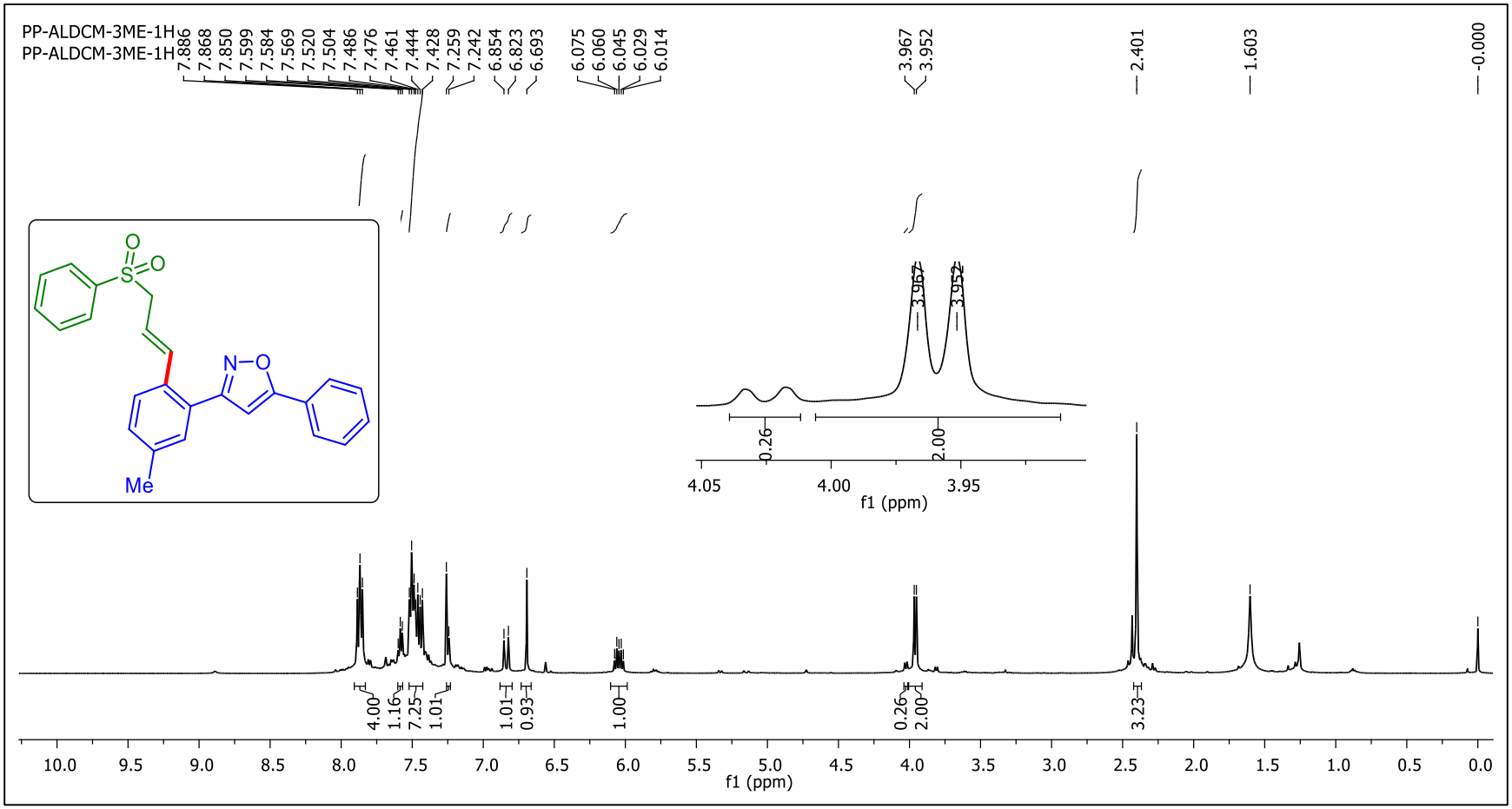
$^{13}C\{^{1}H\}$ NMR of (*E*)-5-Phenyl-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-4-(trifluoromethyl)phenyl)isoxazole (3e) ($CDCl_3$, 126 MHz)



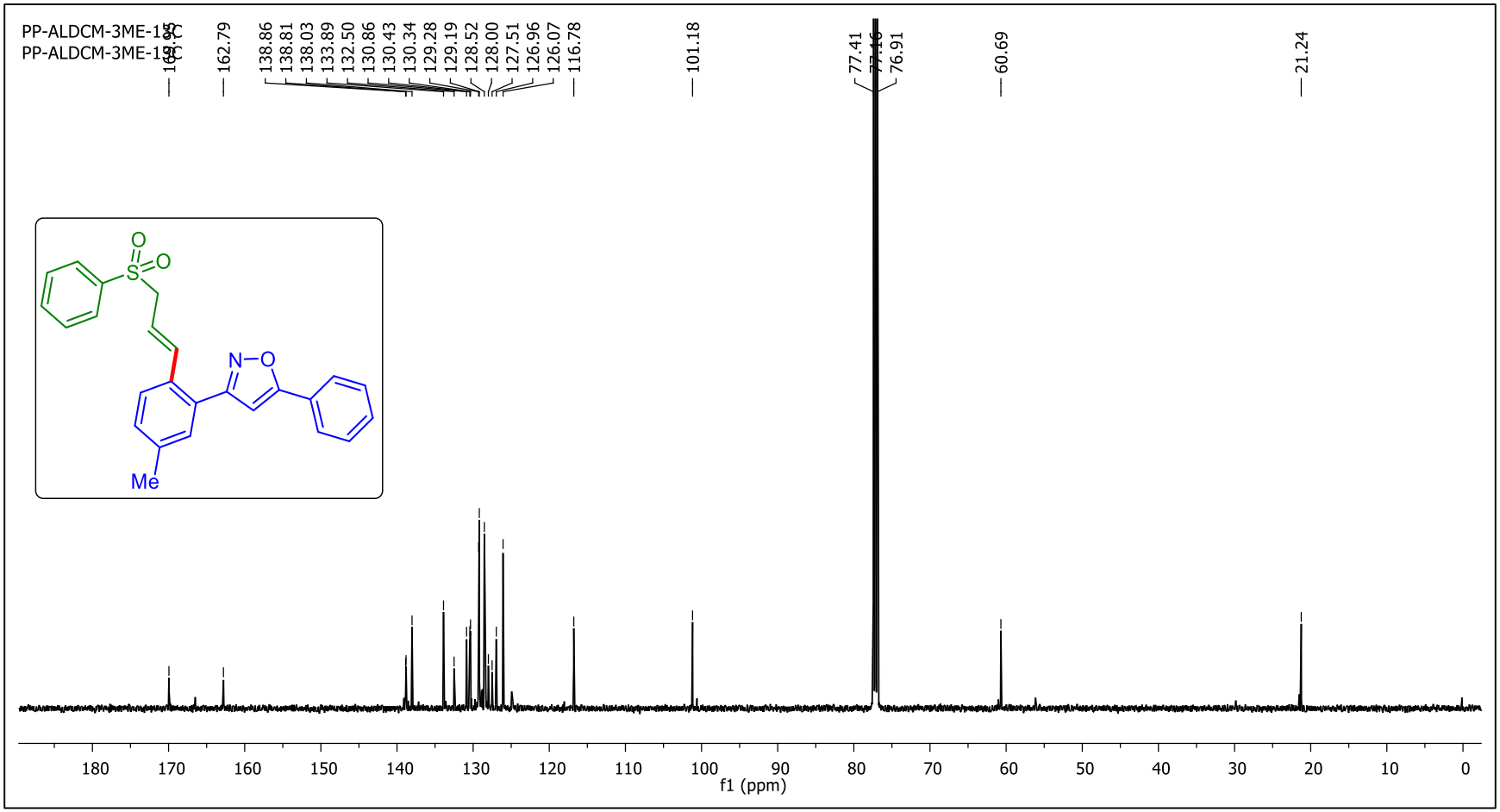
^{19}F NMR of (*E*)-5-Phenyl-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-4-(trifluoromethyl)phenyl)isoxazole (3e) ($CDCl_3$, 471 MHz)



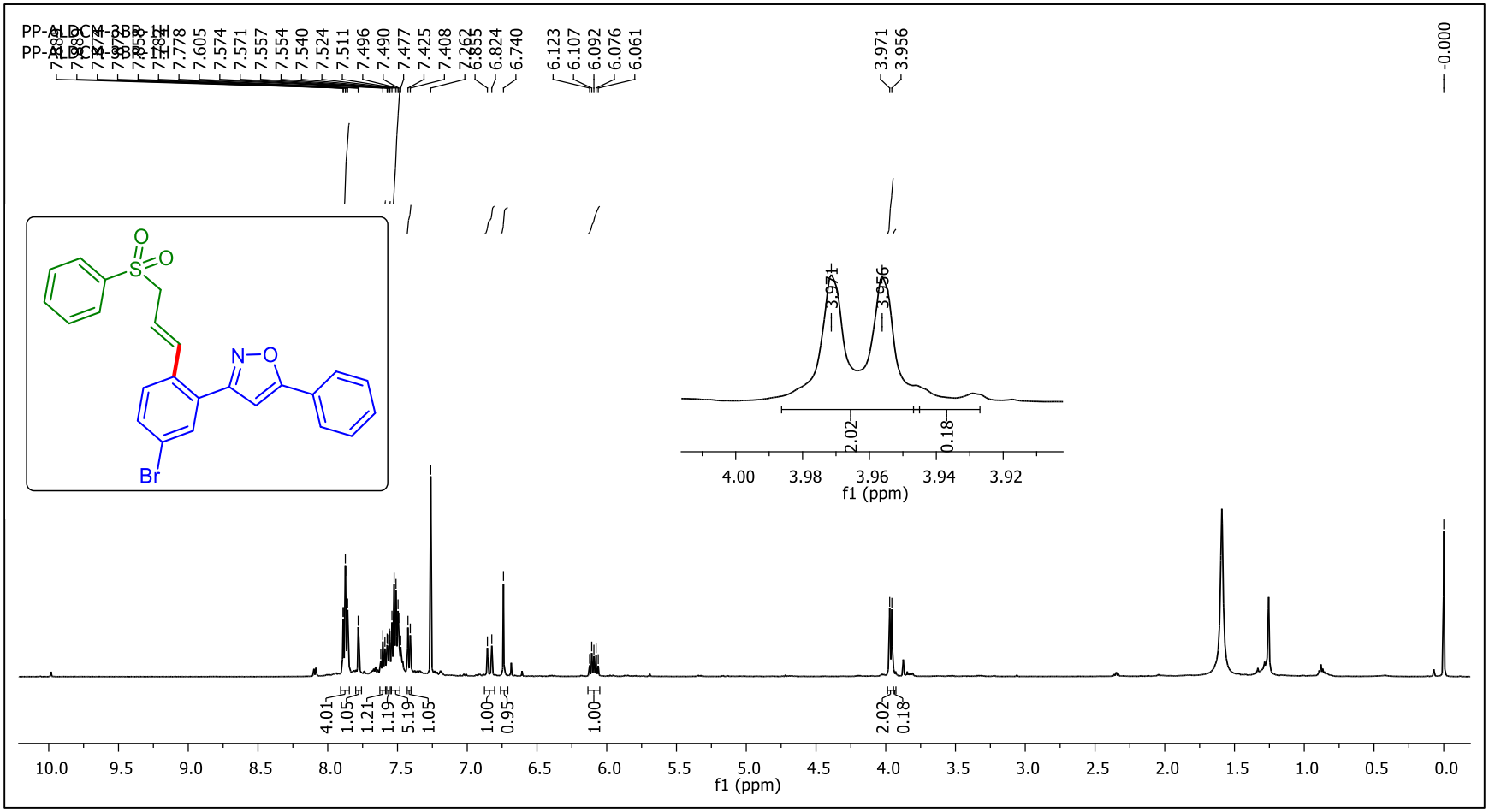
^{1}H NMR of (*E*)-3-(5-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3f) ($CDCl_3$, 500 MHz)



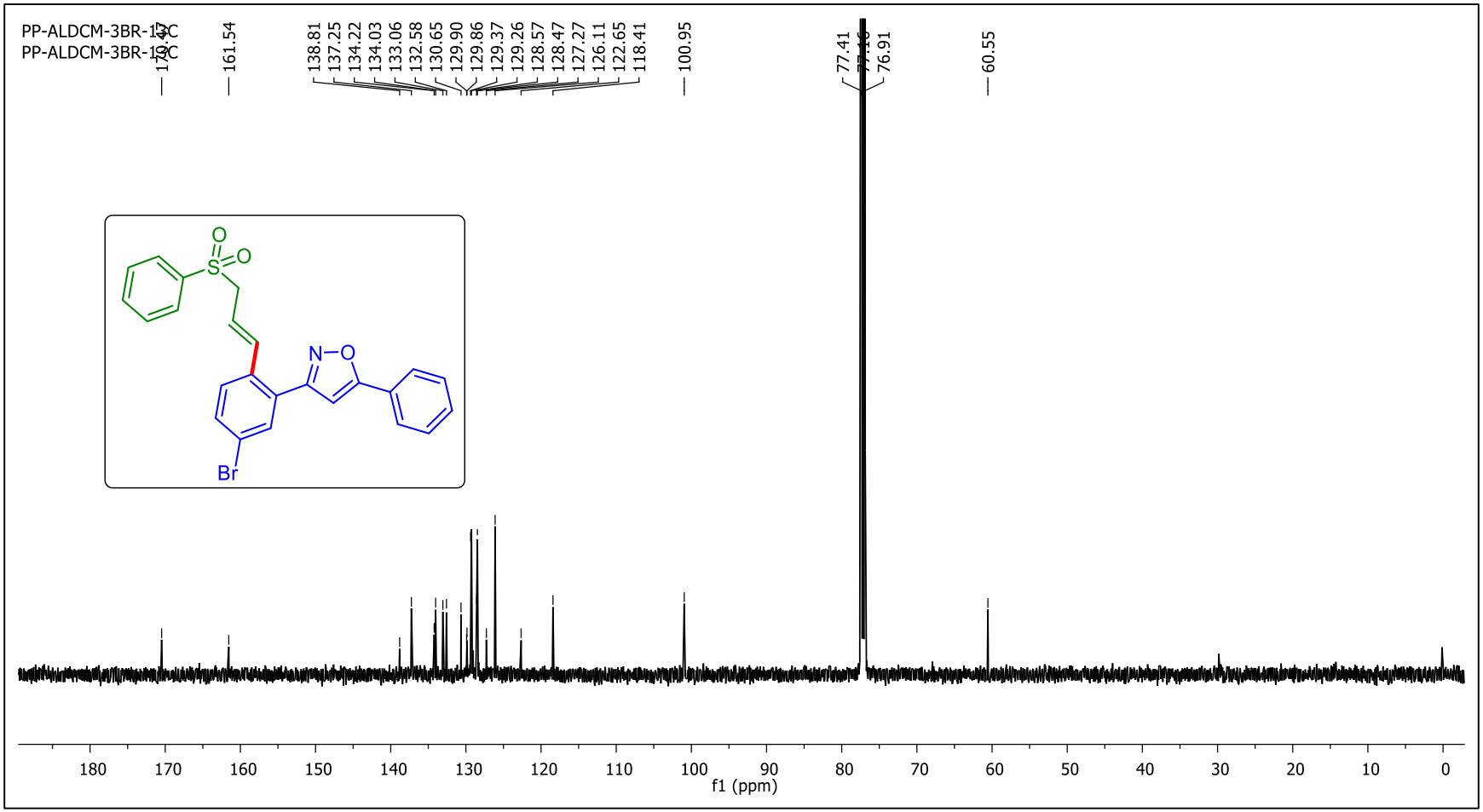
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(5-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3f) ($CDCl_3$, 126 MHz)



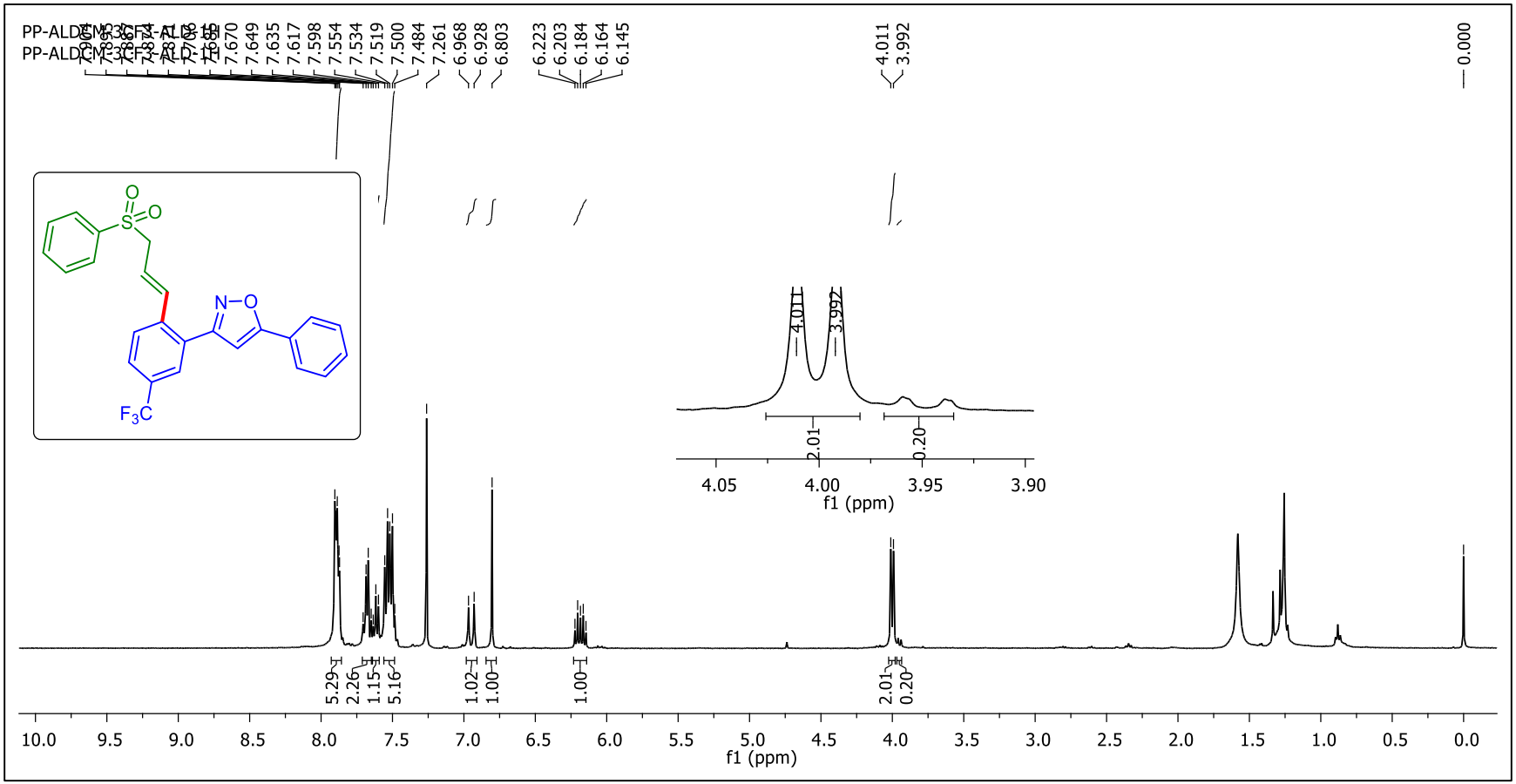
^{1}H NMR of (*E*)-3-(5-Bromo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3g) ($CDCl_3$, 500 MHz)



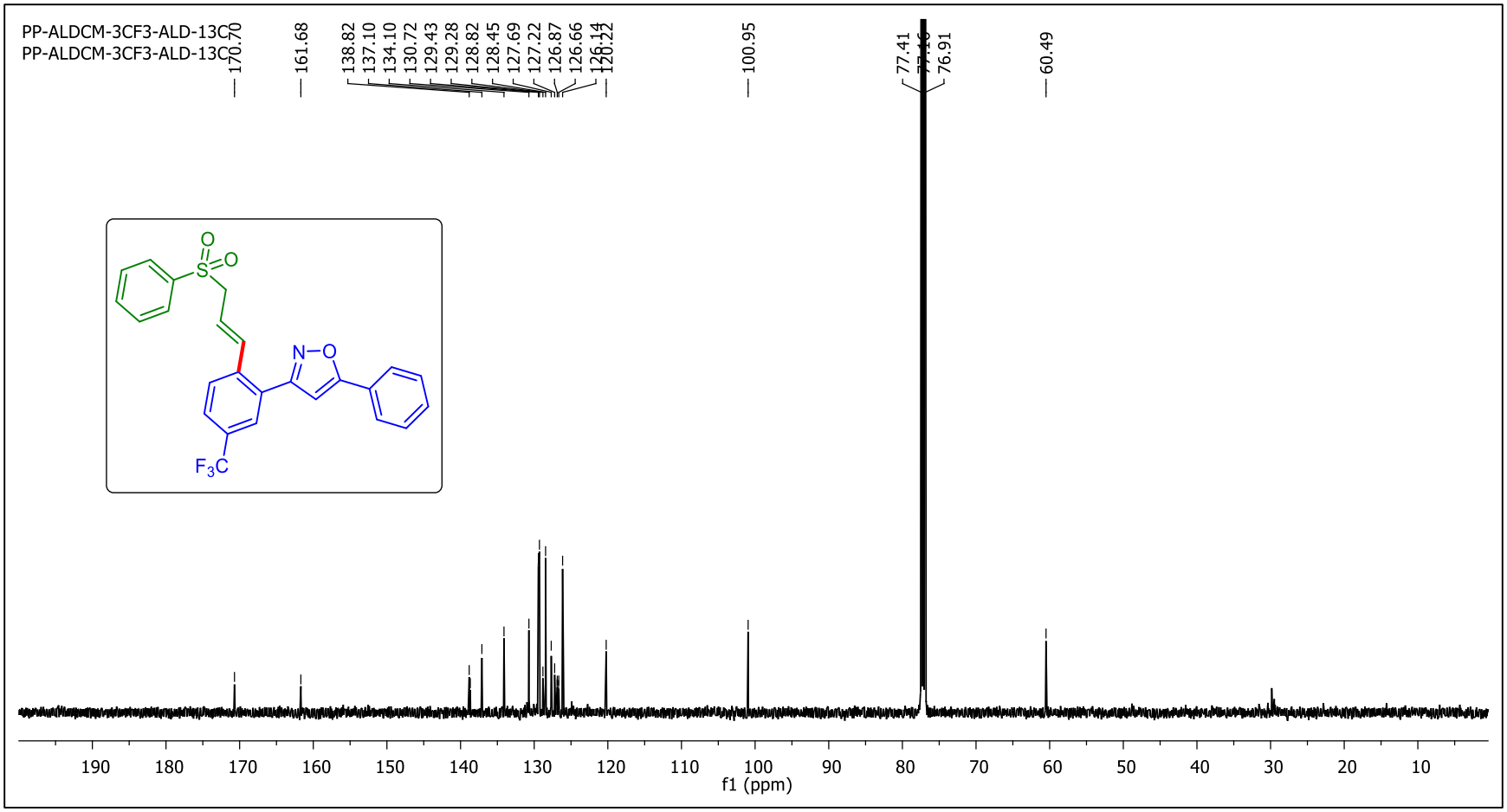
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(5-Bromo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3g) ($CDCl_3$, 126 MHz)



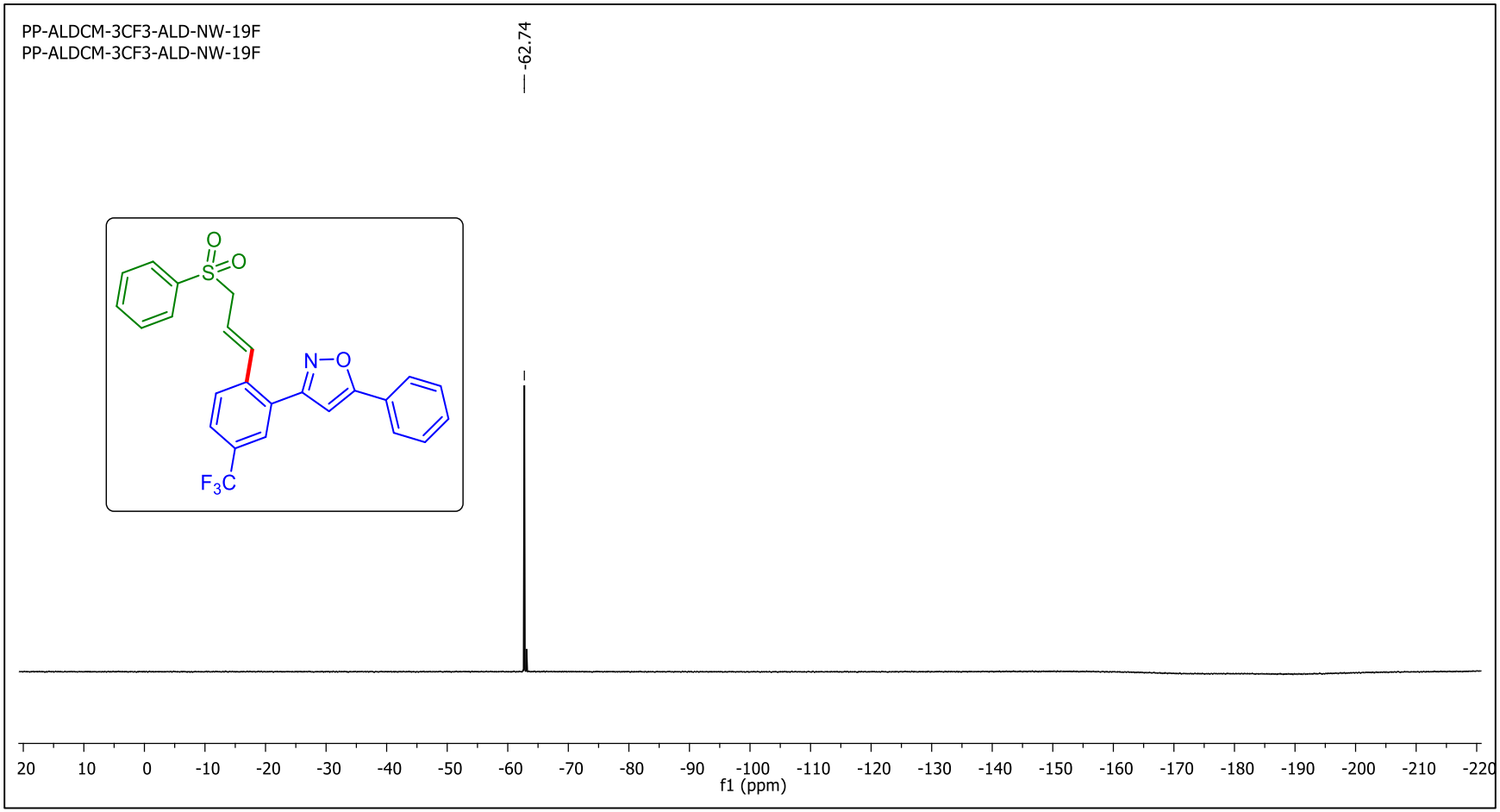
^{1}H NMR of (*E*)-5-Phenyl-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-5-(trifluoromethyl)phenyl)isoxazole (3h) ($CDCl_3$, 400 MHz)



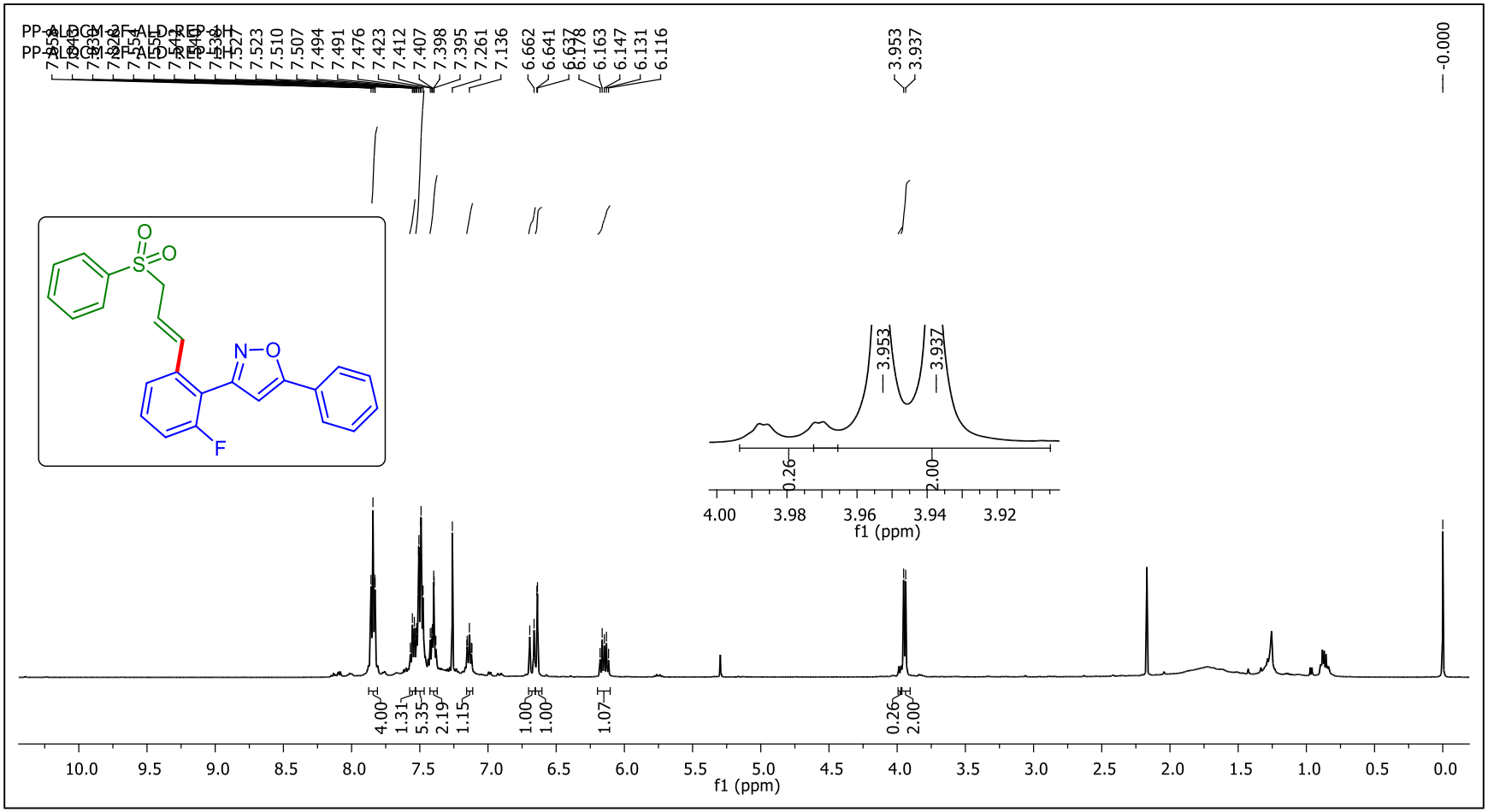
$^{13}C\{^{1}H\}$ NMR of (*E*)-5-Phenyl-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-5-(trifluoromethyl)phenyl)isoxazole (3h) ($CDCl_3$, 126 MHz)



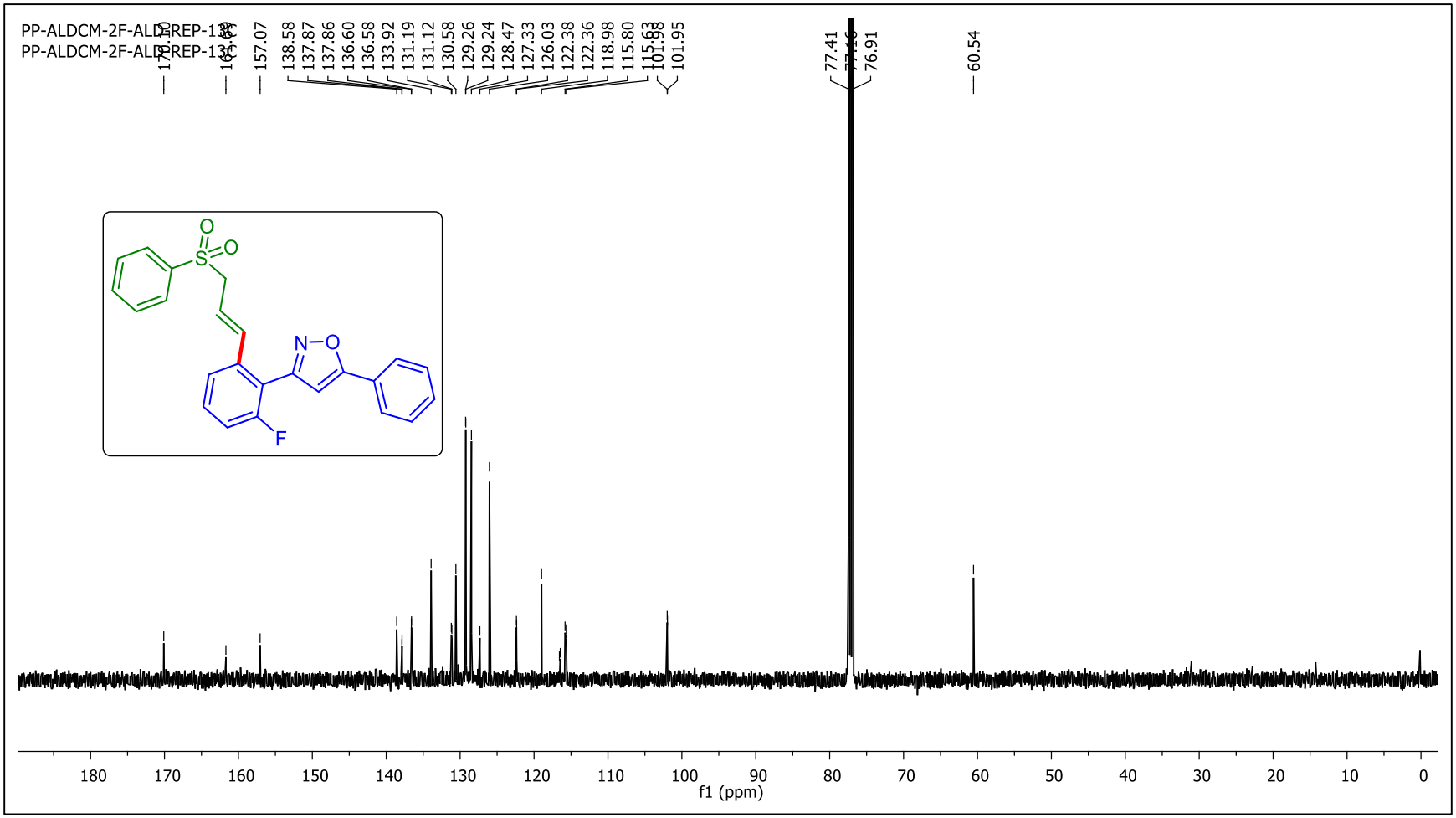
^{19}F NMR of (*E*)-5-Phenyl-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-5-(trifluoromethyl)phenyl)isoxazole (3h) ($CDCl_3$, 471 MHz)



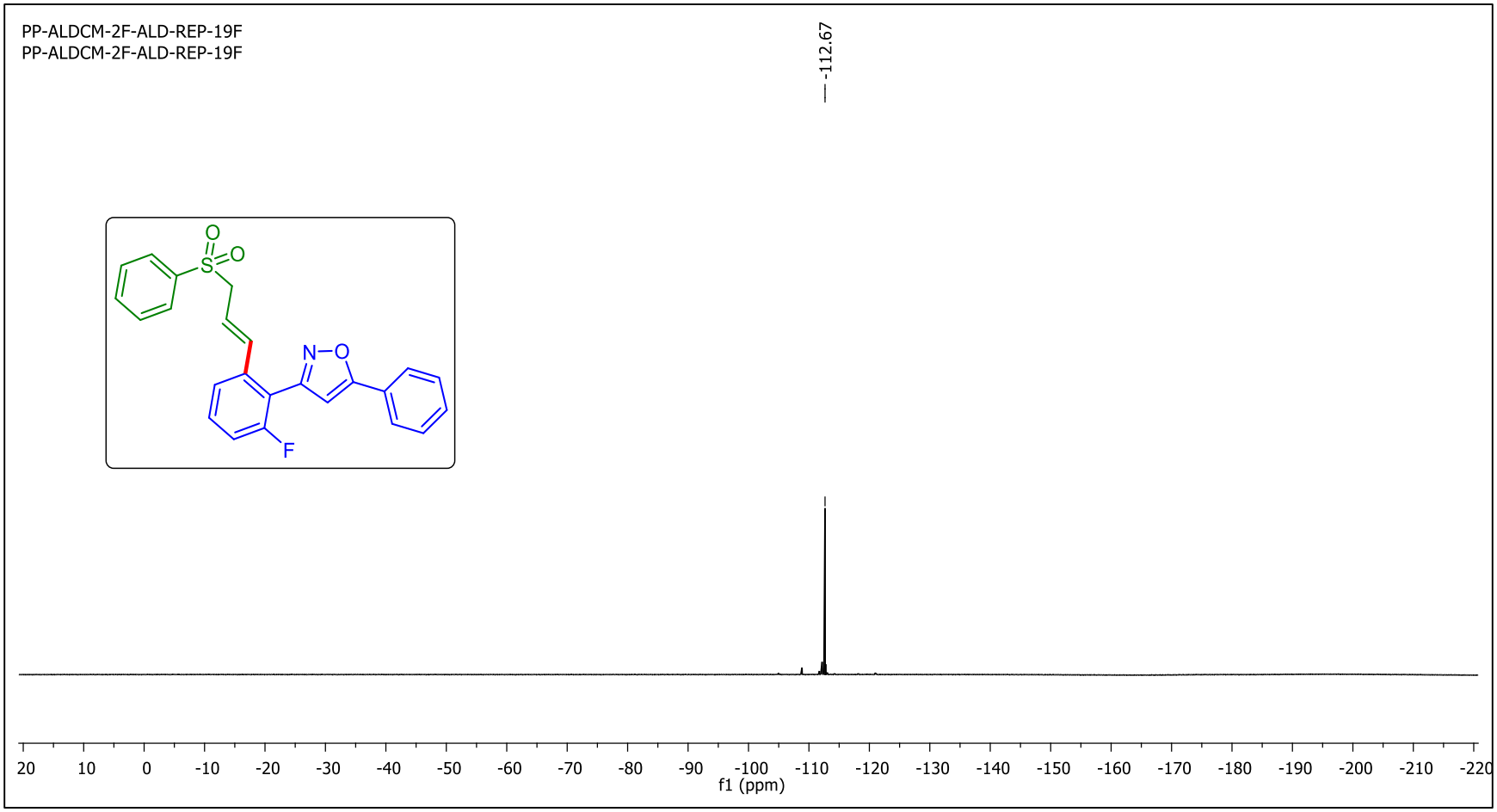
^{1}H NMR of (*E*)-3-(2-Fluoro-6-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3i) ($CDCl_3$, 500 MHz)



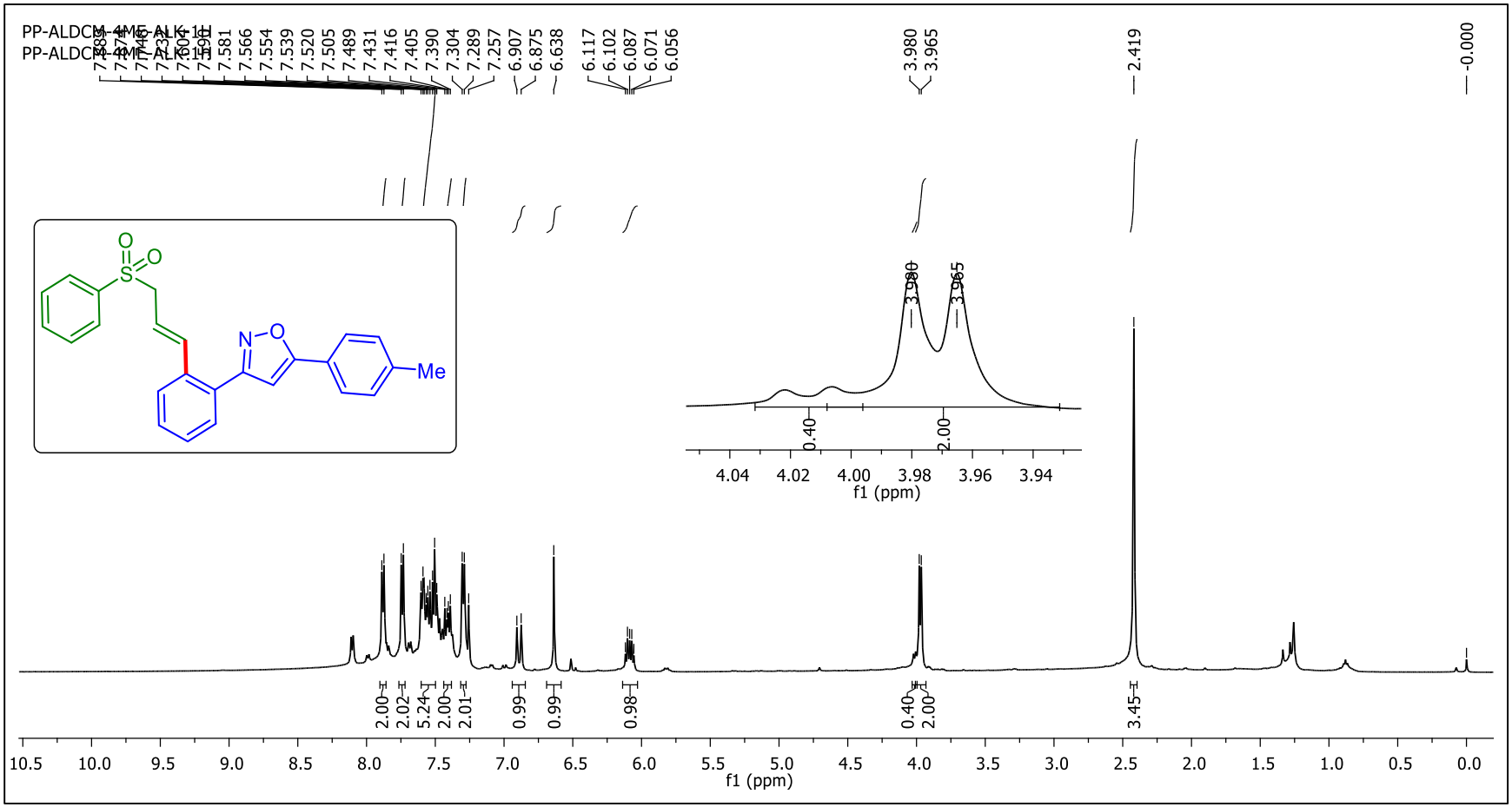
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(2-Fluoro-6-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3i) ($CDCl_3$, 126 MHz)



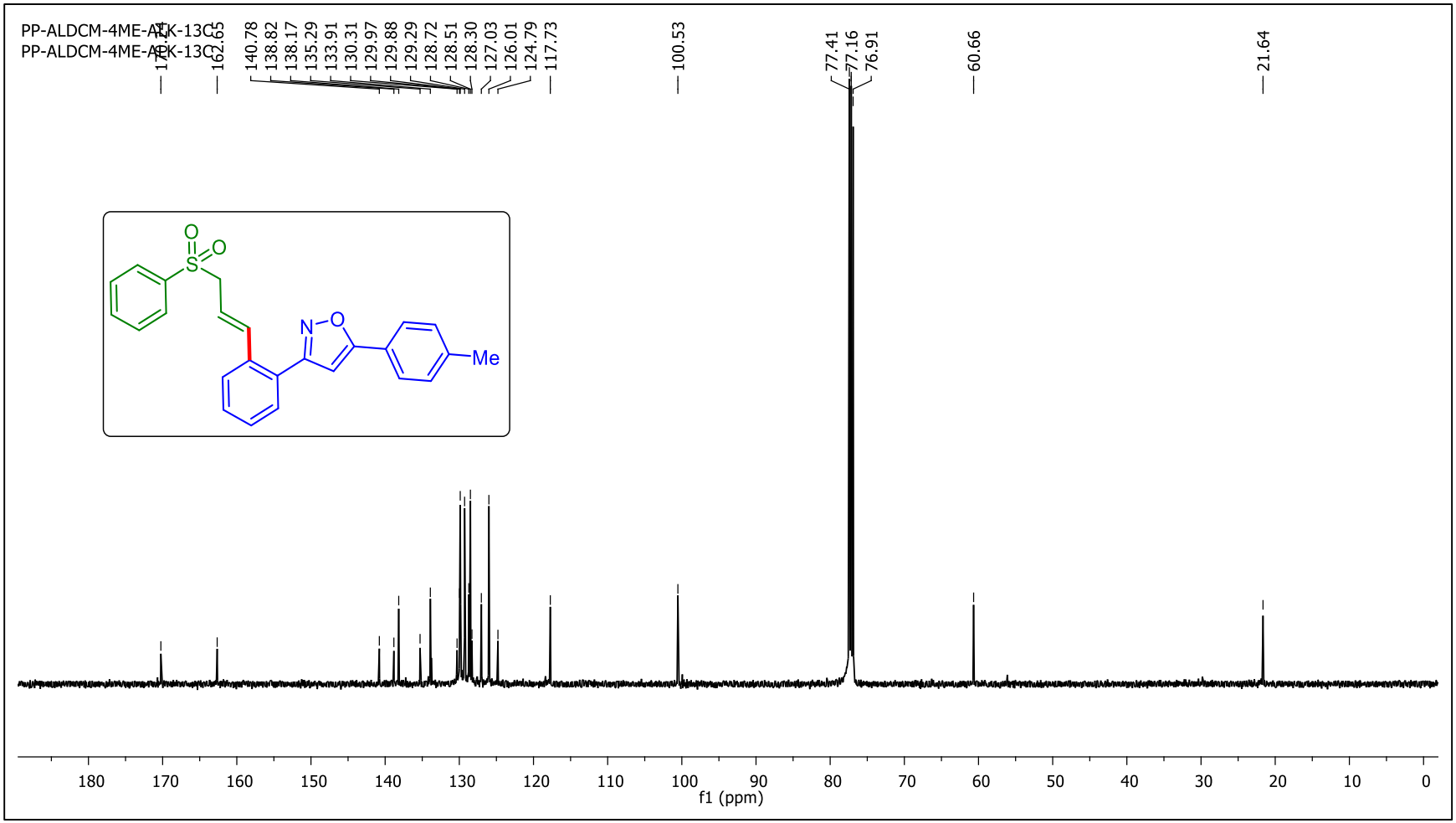
^{19}F NMR of (*E*)-3-(2-Fluoro-6-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-phenylisoxazole (3i) ($CDCl_3$, 471 MHz)



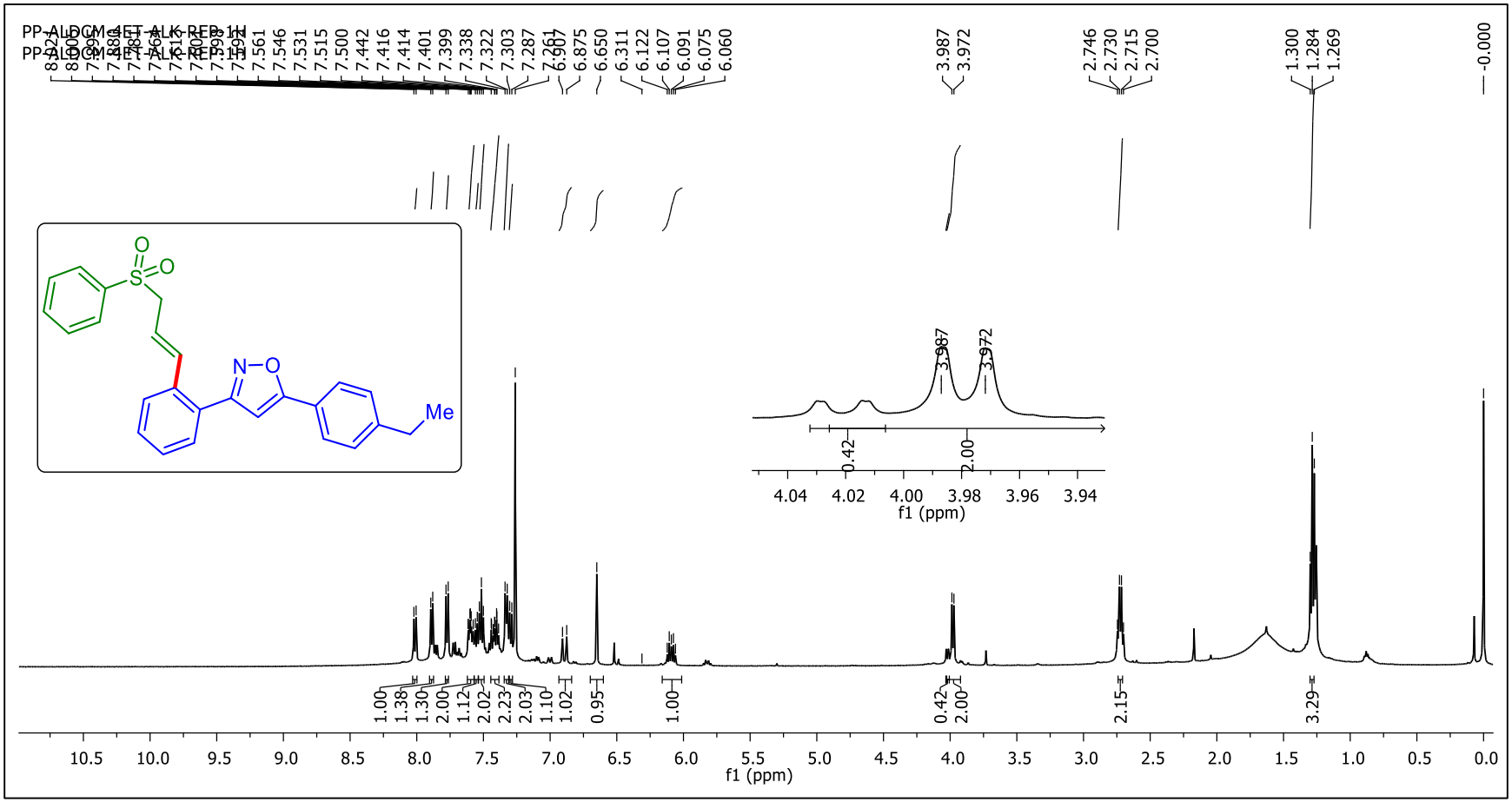
^{1}H NMR of (*E*)-3-(2-(3-(Phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-(p-tolyl)isoxazole (3j) ($CDCl_3$, 500 MHz)



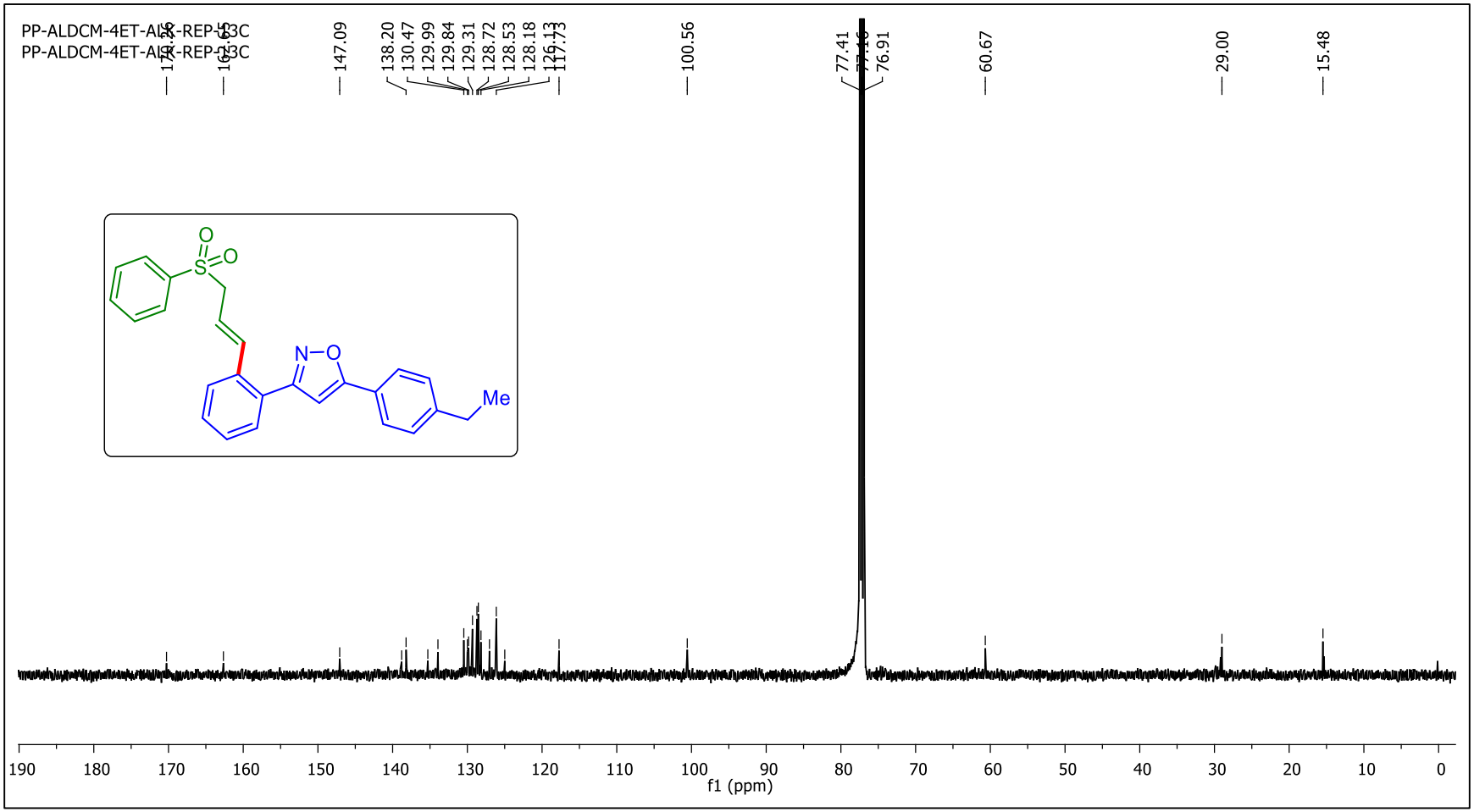
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(2-(3-(Phenylsulfonyl)prop-1-en-1-yl)phenyl)-5-(p-tolyl)isoxazole (3j) ($CDCl_3$, 126 MHz)



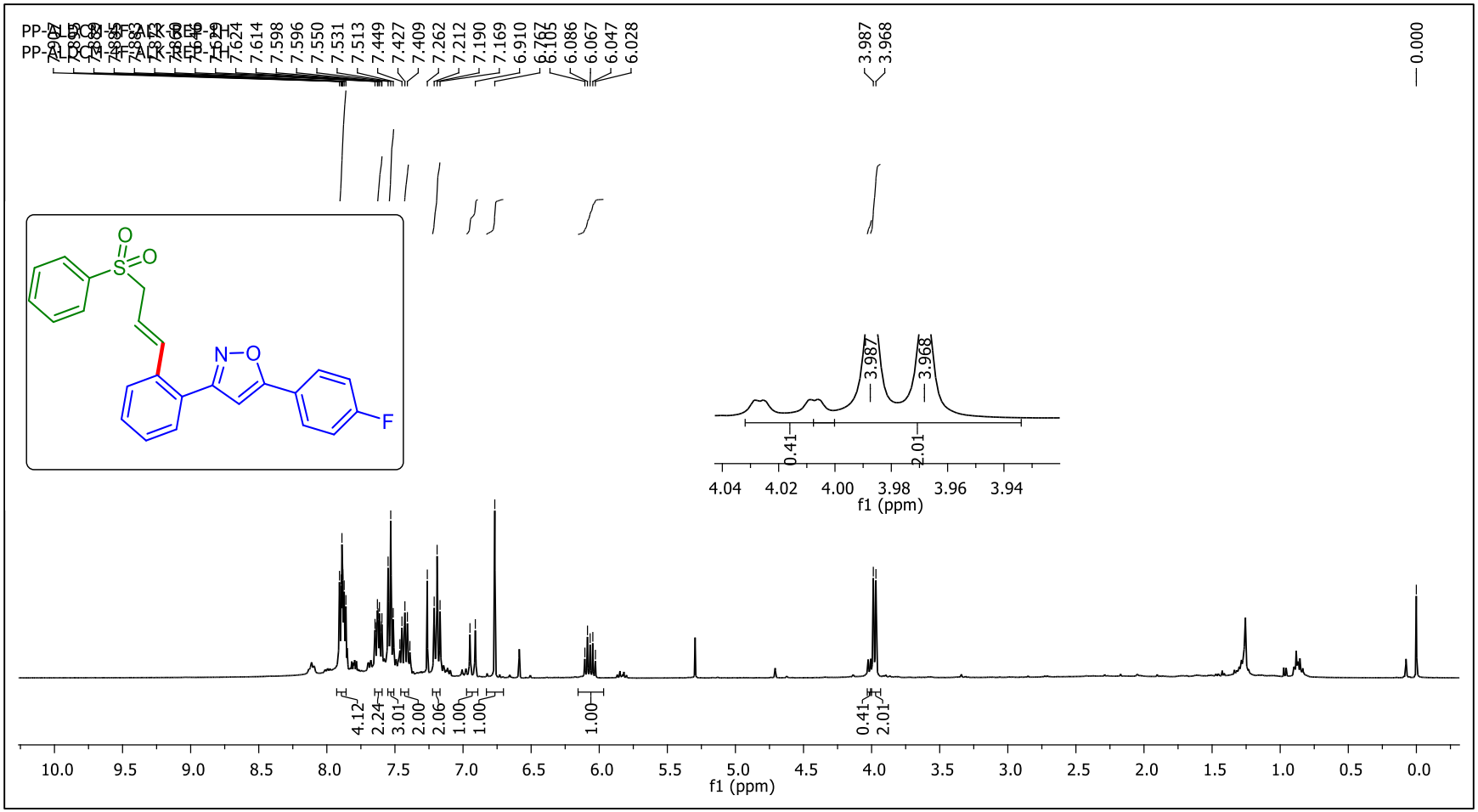
^{1}H NMR of (*E*)-5-(4-Ethylphenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3k) ($CDCl_3$, 500 MHz)



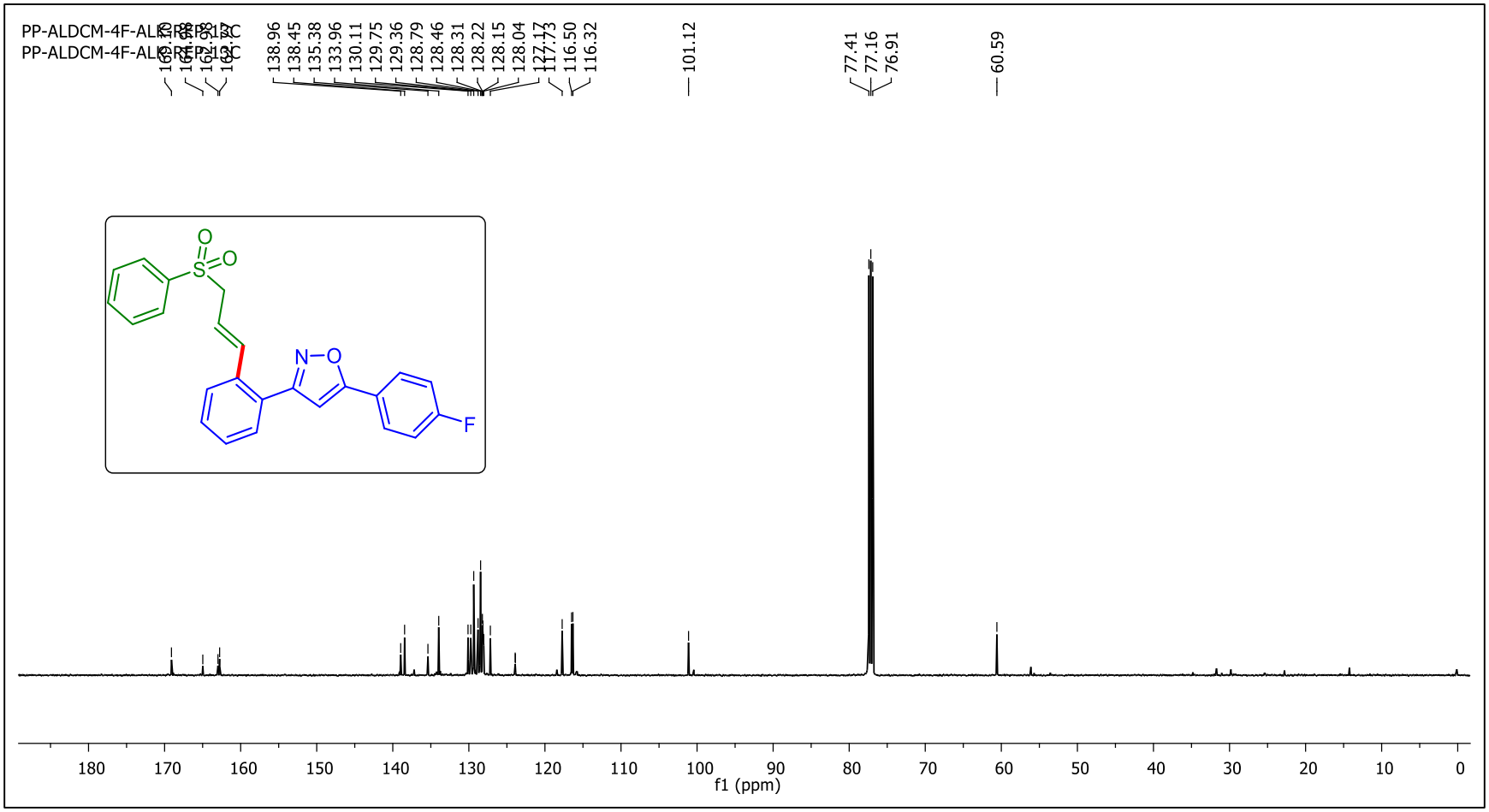
$^{13}C\{^{1}H\}$ NMR of (*E*)-5-(4-Ethylphenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3k) ($CDCl_3$, 126 MHz)



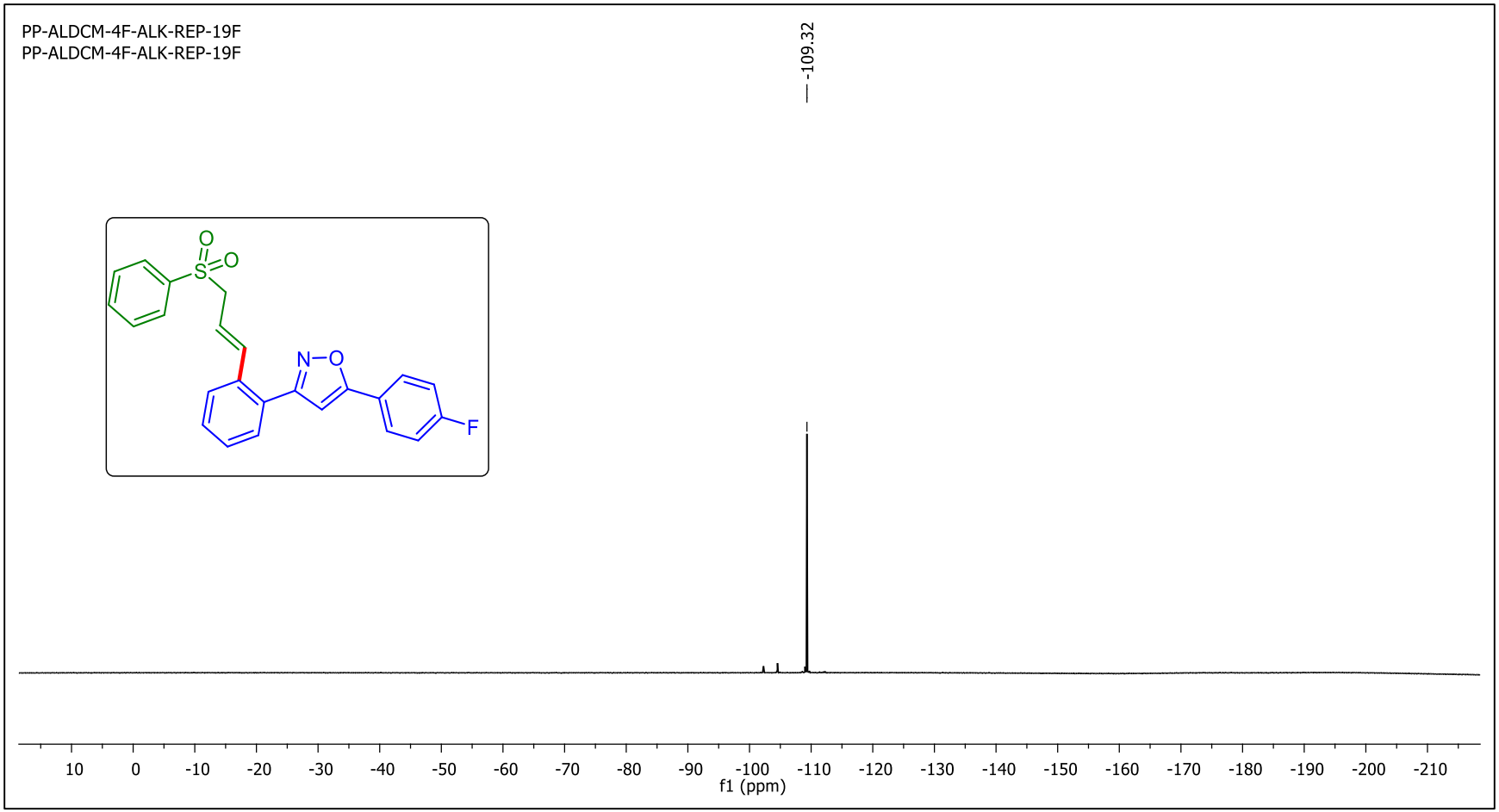
^{1}H NMR of (*E*)-5-(4-Fluorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3l) ($CDCl_3$, 400 MHz)



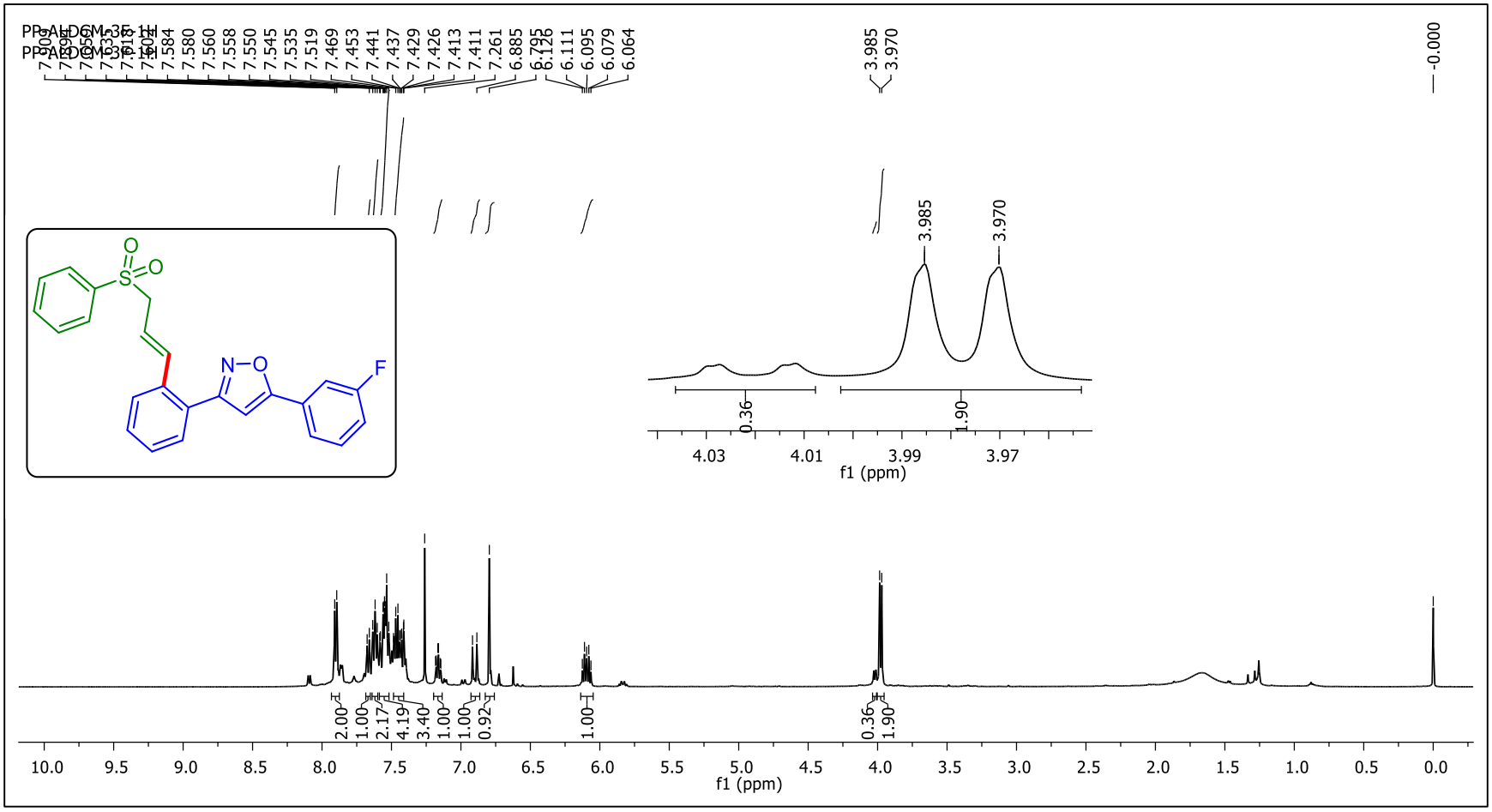
$^{13}C\{^{1}H\}$ NMR of (*E*)-5-(4-Fluorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3l) ($CDCl_3$, 126 MHz)



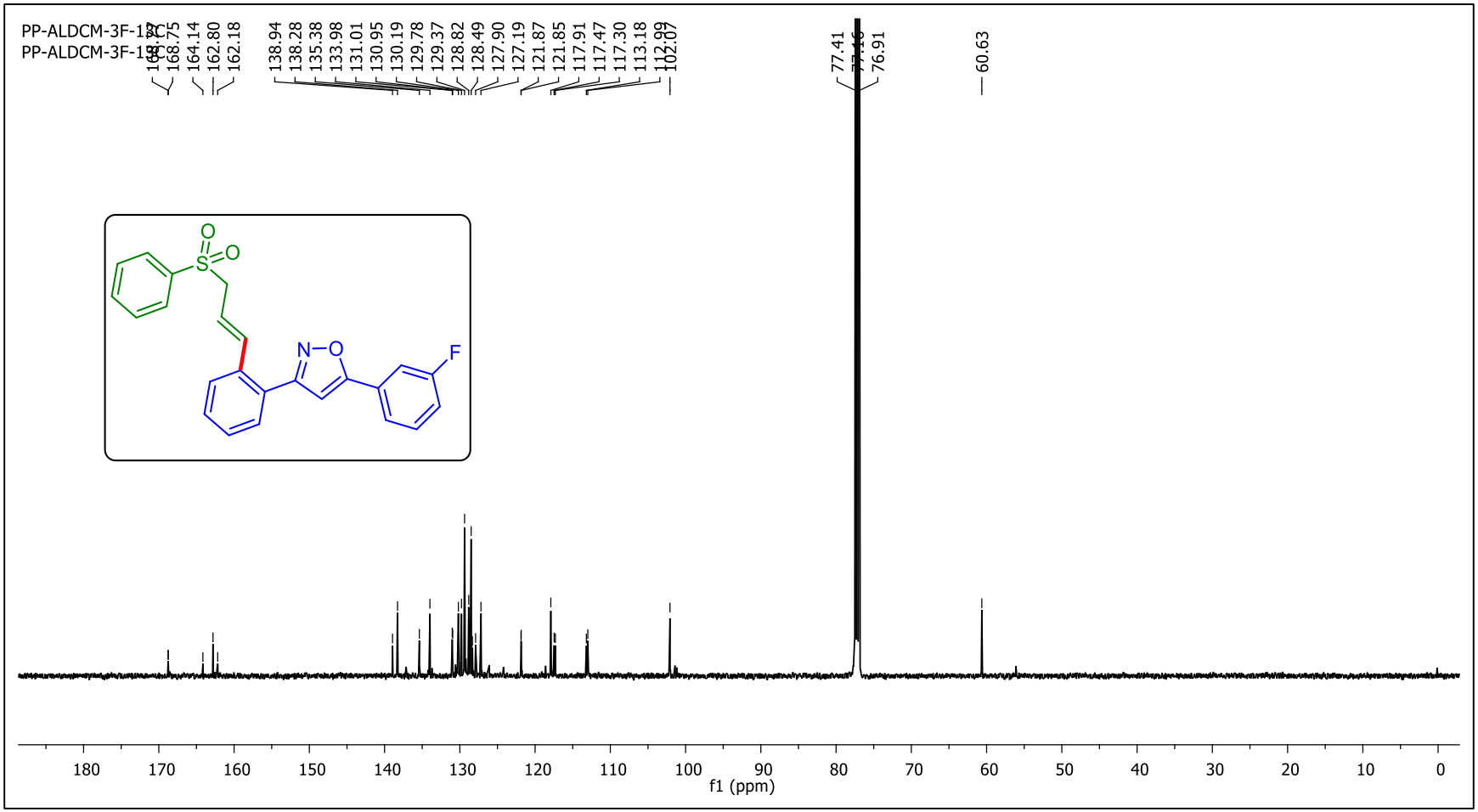
^{19}F NMR of (*E*)-5-(4-Fluorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3l) ($CDCl_3$, 377 MHz)



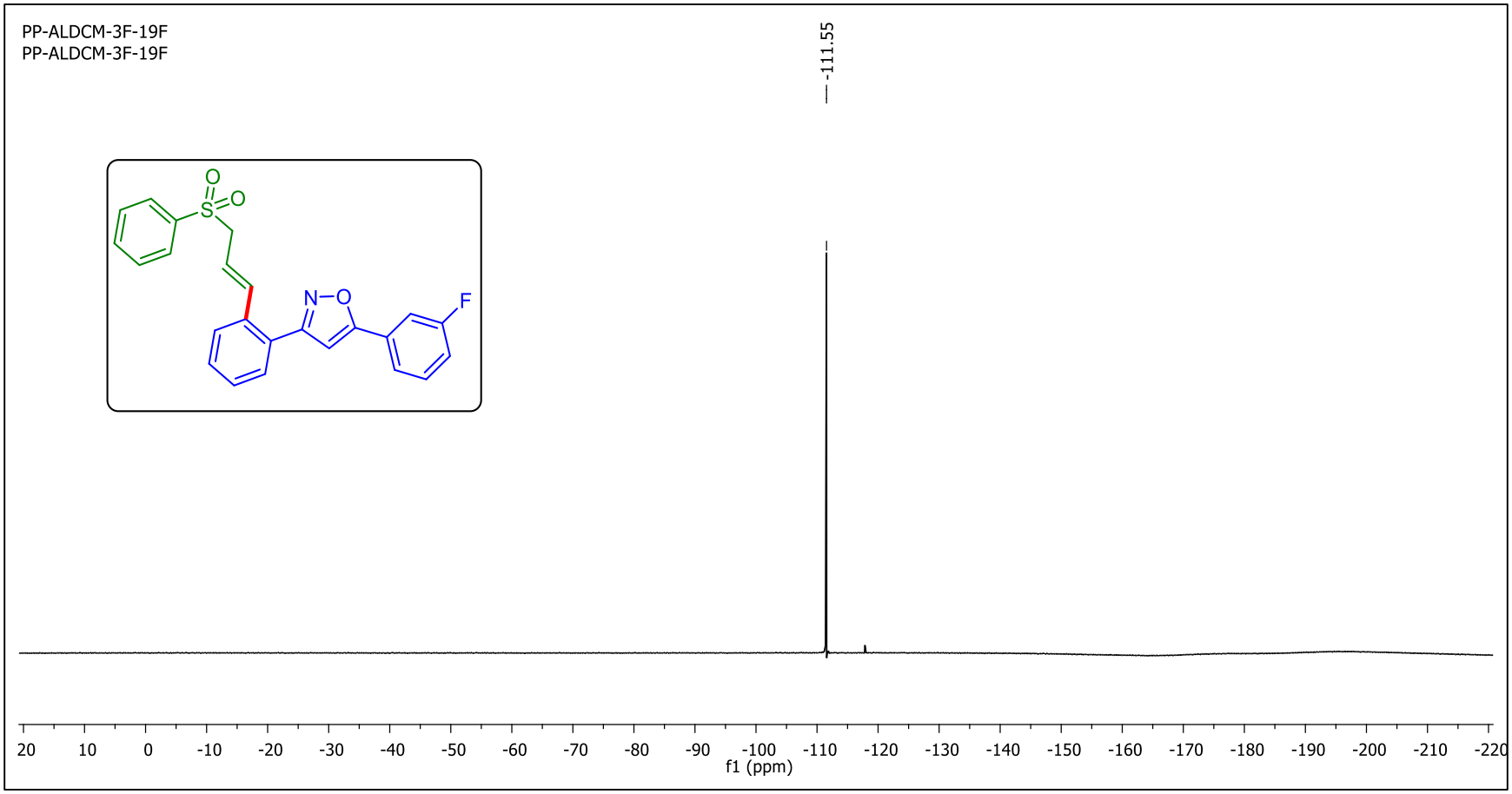
^{1}H NMR of (*E*)-5-(3-Fluorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3m) ($CDCl_3$, 500 MHz)



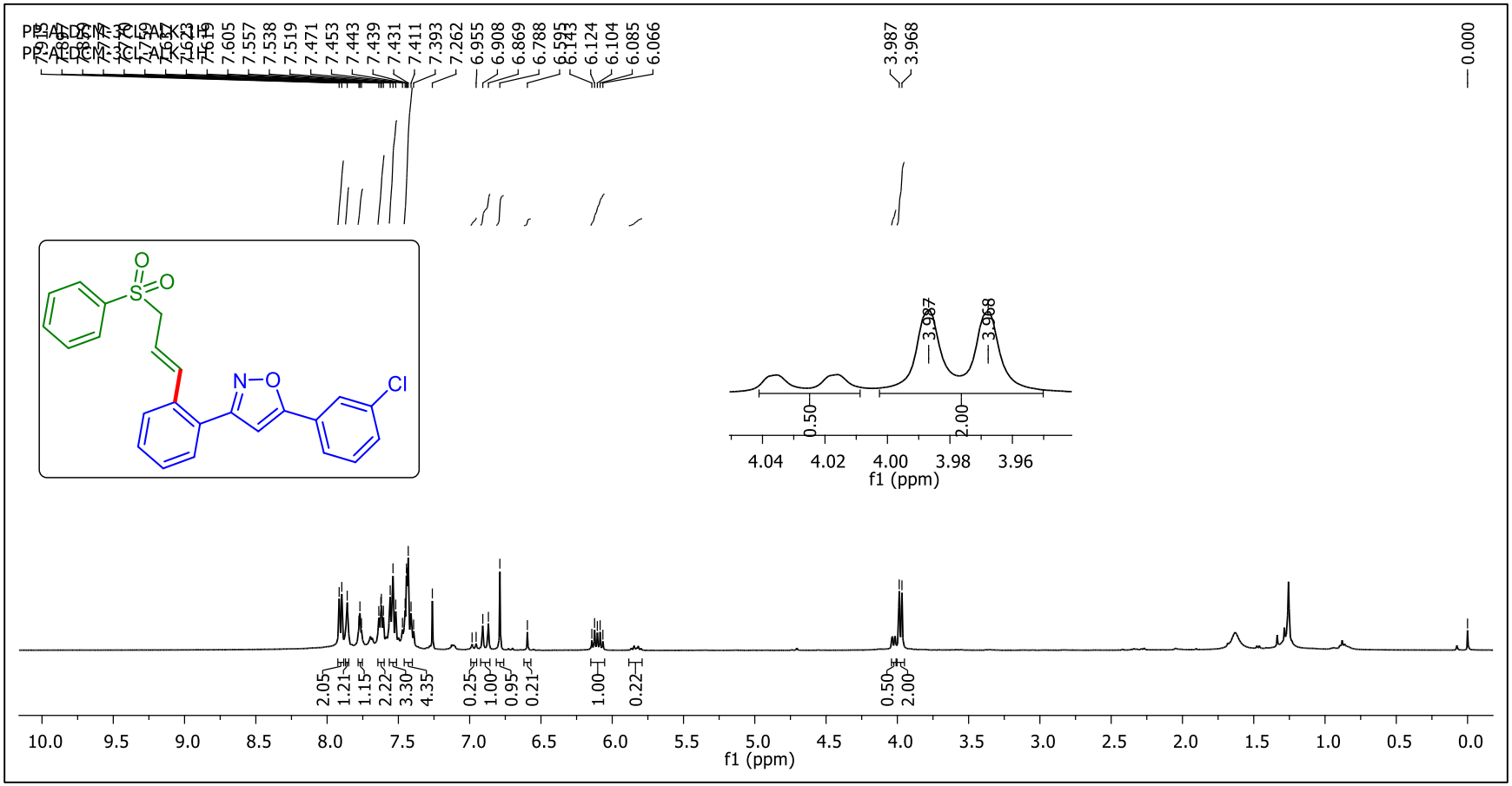
$^{13}C\{^{1}H\}$ NMR of (*E*)-5-(3-Fluorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3m) ($CDCl_3$, 126 MHz)



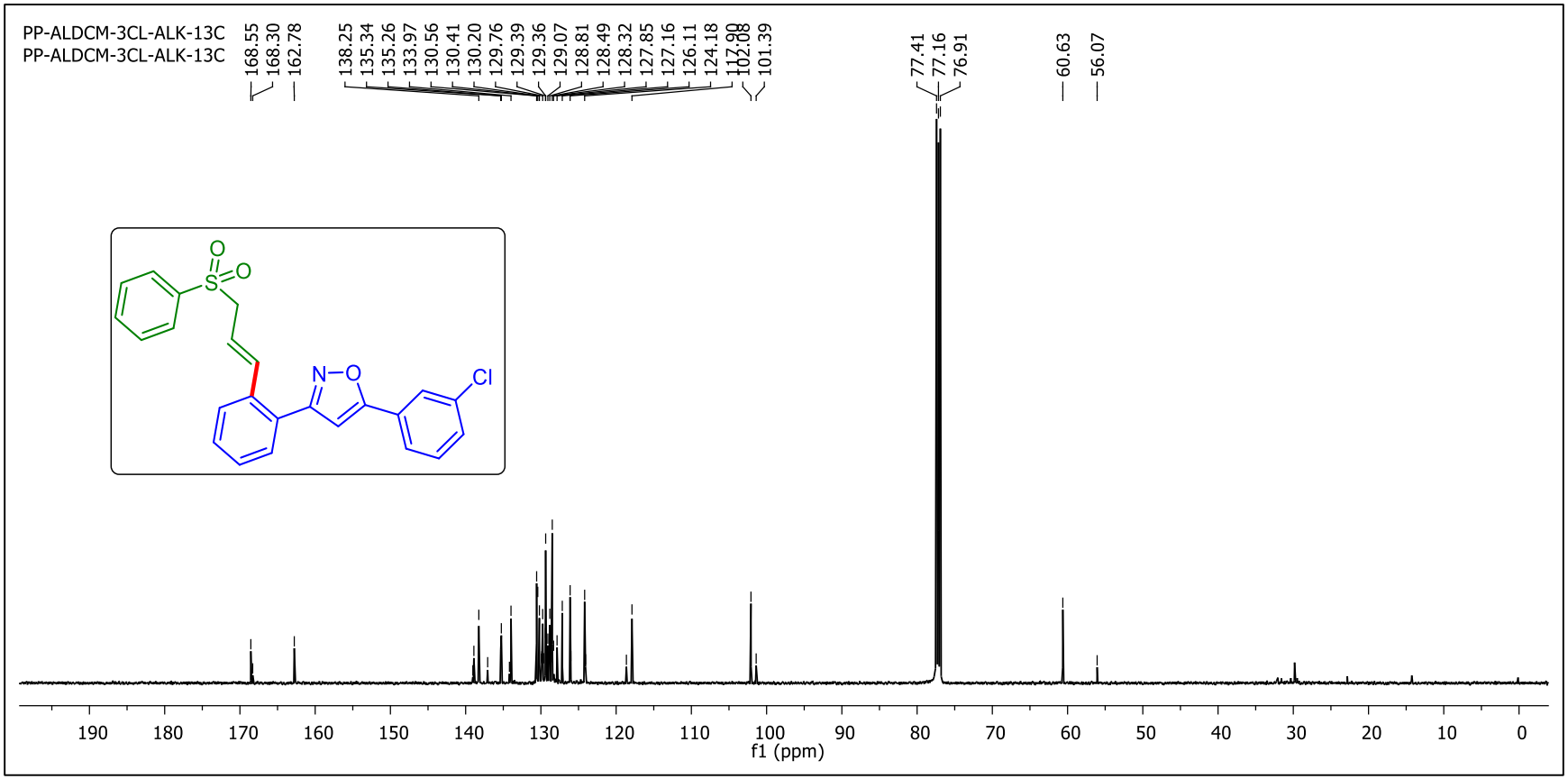
^{19}F NMR of (*E*)-5-(3-Fluorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3m) ($CDCl_3$, 471 MHz)



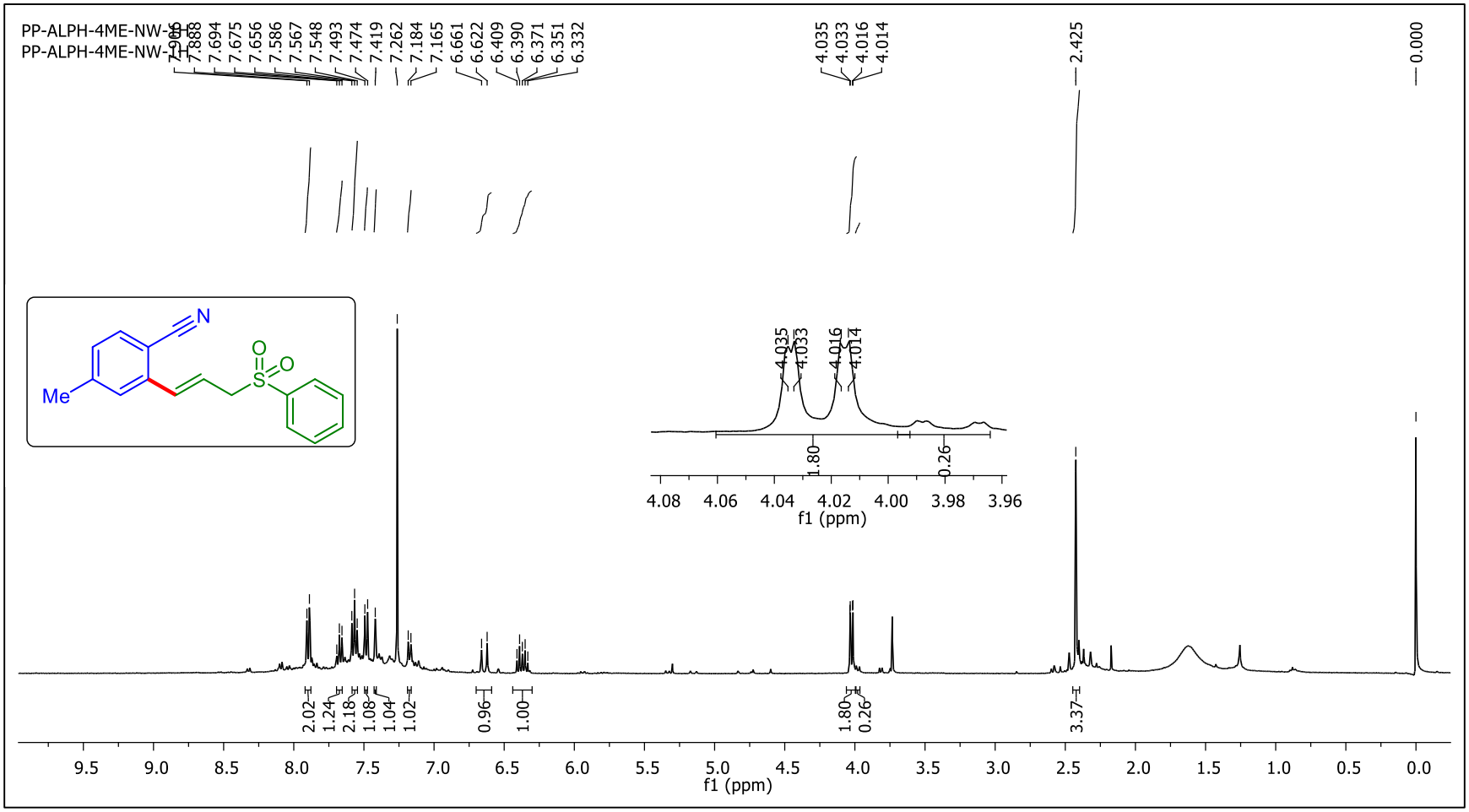
^{1}H NMR of (*E*)-5-(3-Chlorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3n) ($CDCl_3$, 400 MHz)



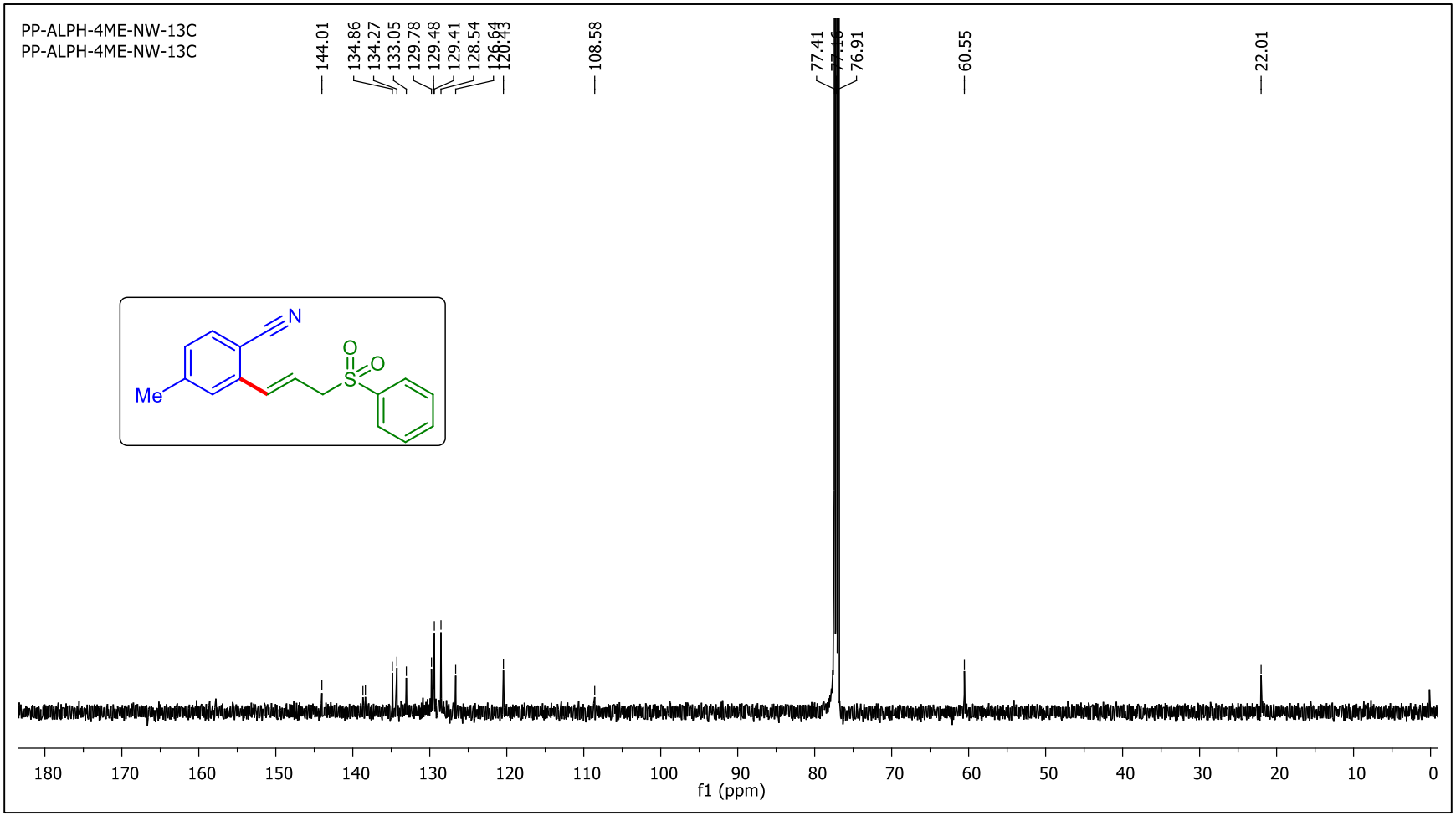
$^{13}C\{^{1}H\}$ NMR of (*E*)-5-(3-Chlorophenyl)-3-(2-(3-(phenylsulfonyl)prop-1-en-1-yl)phenyl)isoxazole (3n) ($CDCl_3$, 126 MHz)



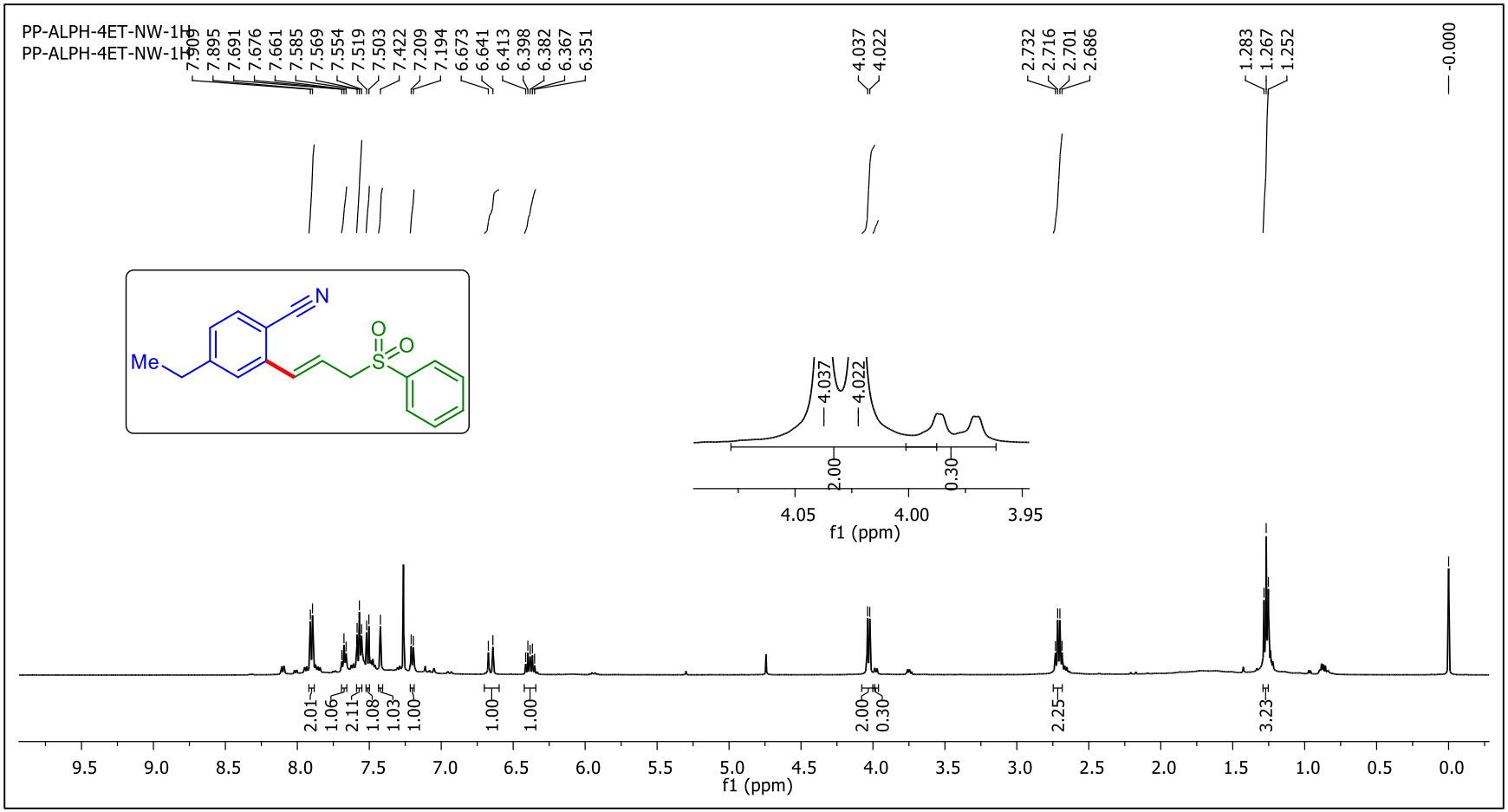
^{1}H NMR of (*E*)-4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4a) ($CDCl_3$, 400 MHz)



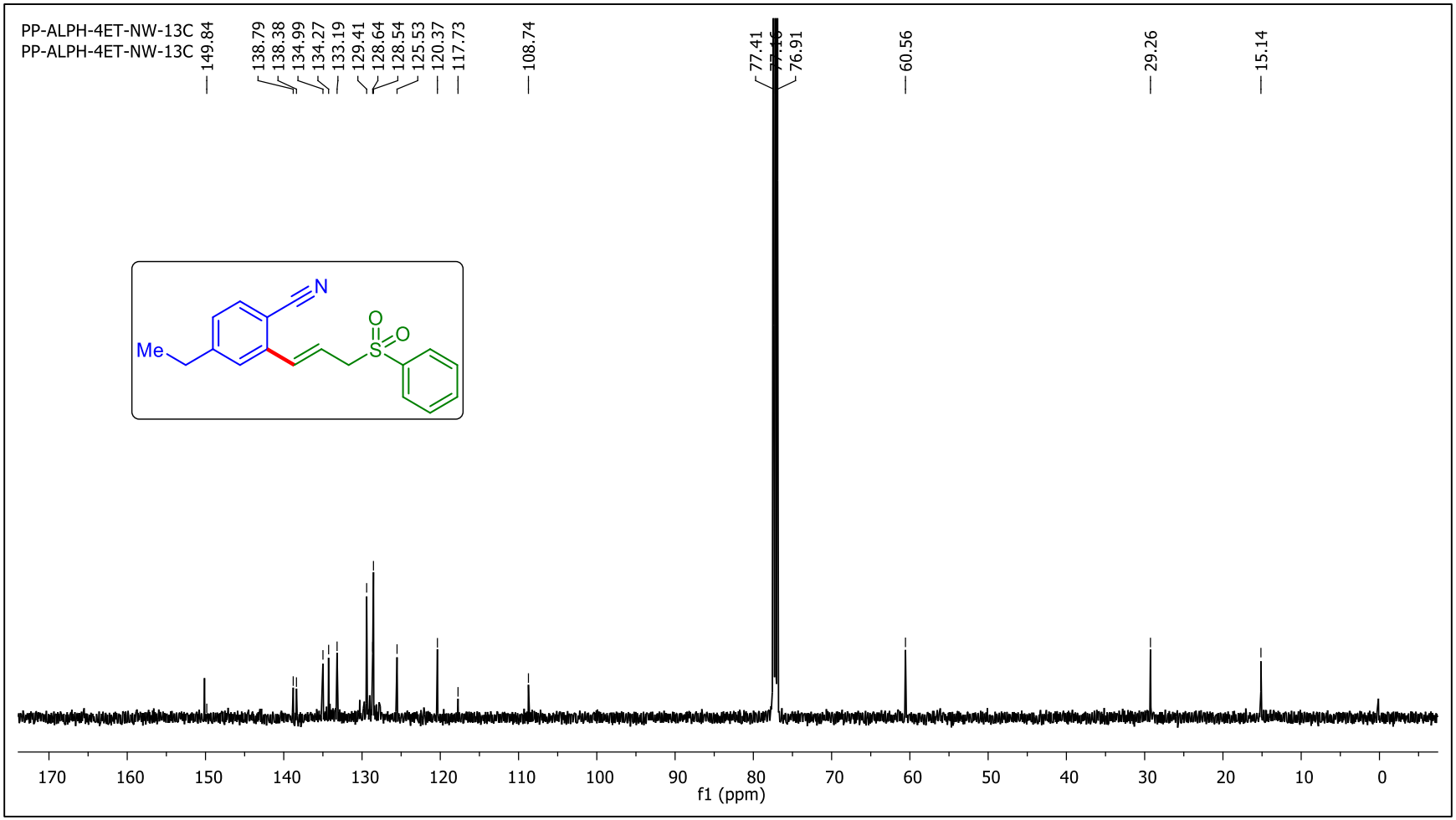
$^{13}C\{^{1}H\}$ NMR of (*E*)-4-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4a) ($CDCl_3$, 126 MHz)



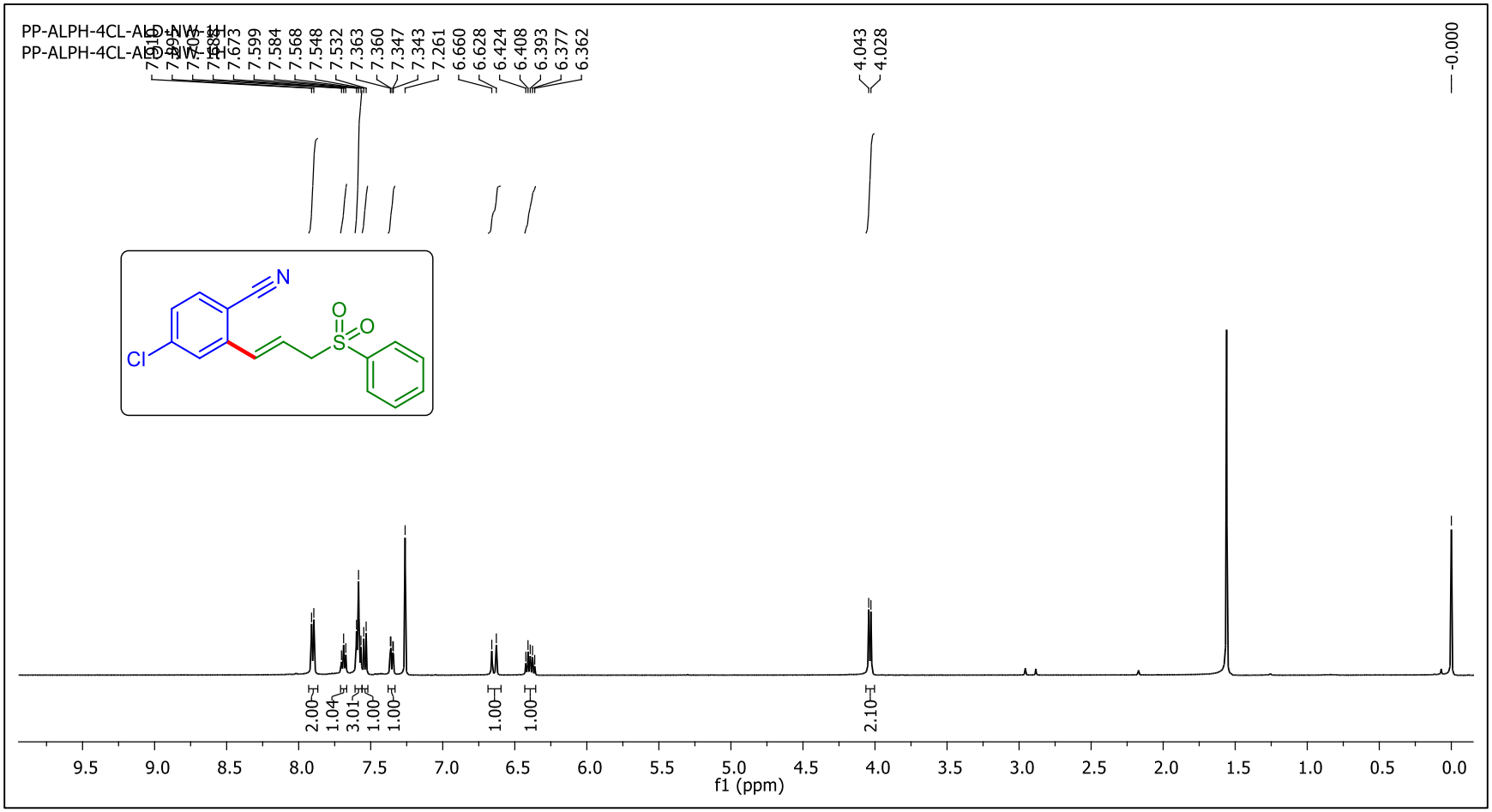
^{1}H NMR of (*E*)-4-Ethyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4b) ($CDCl_3$, 500 MHz)



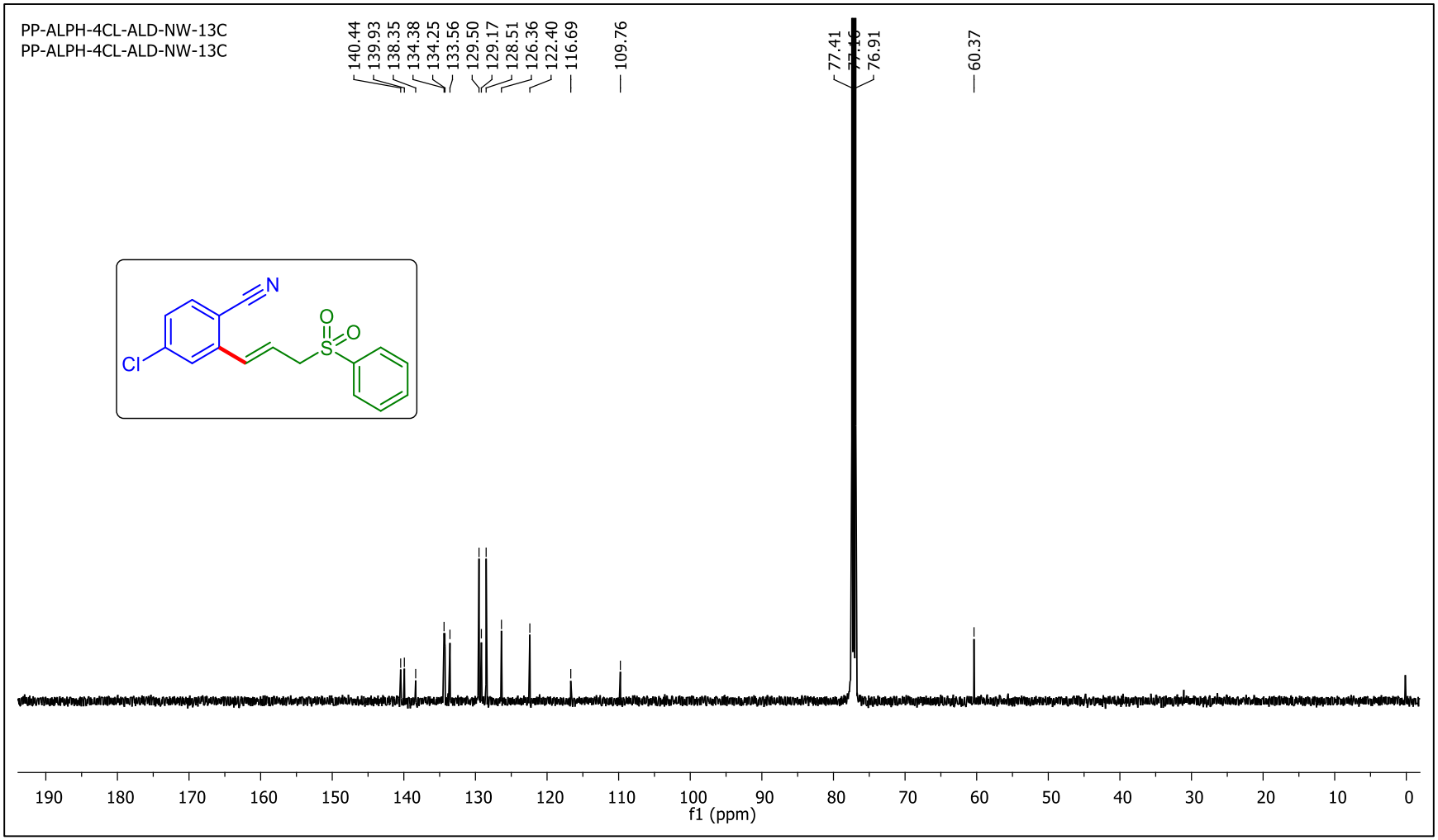
$^{13}C\{^{1}H\}$ NMR of (*E*)-4-Ethyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4b) ($CDCl_3$, 126 MHz)



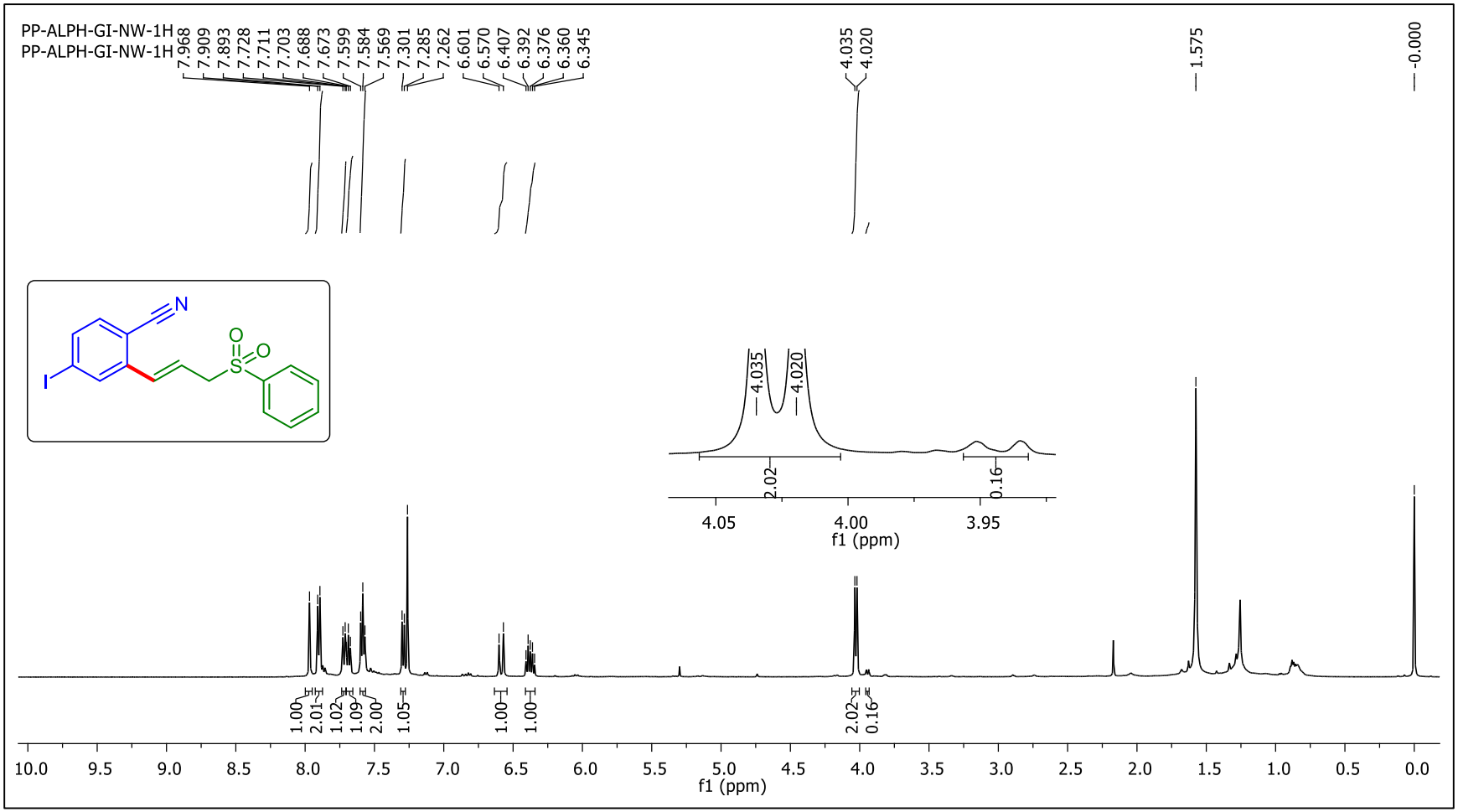
^{1}H NMR of (*E*)-4-Chloro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4c) ($CDCl_3$, 500 MHz)



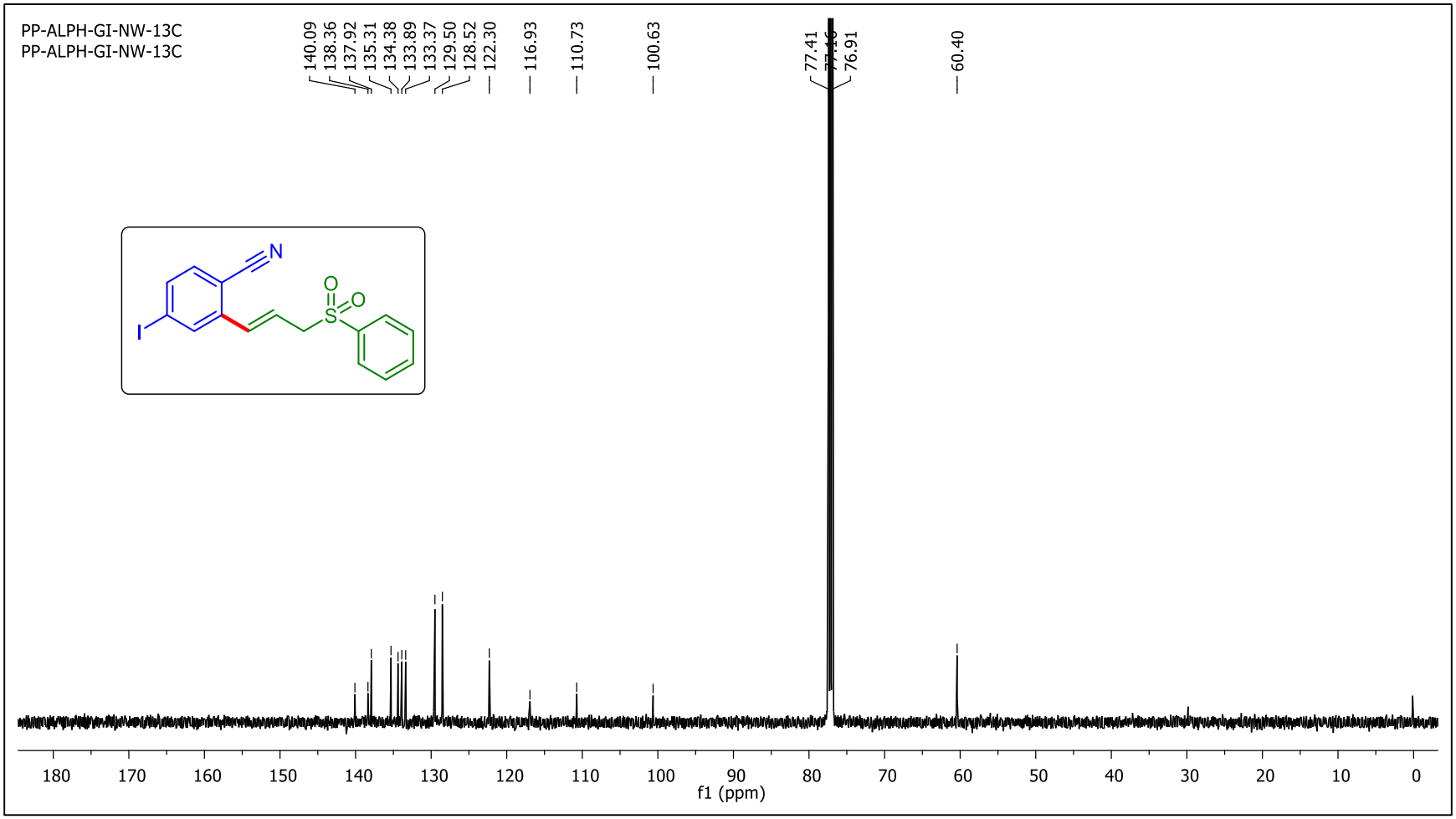
$^{13}C\{^{1}H\}$ NMR of (*E*)-4-Chloro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4c) ($CDCl_3$, 126 MHz)



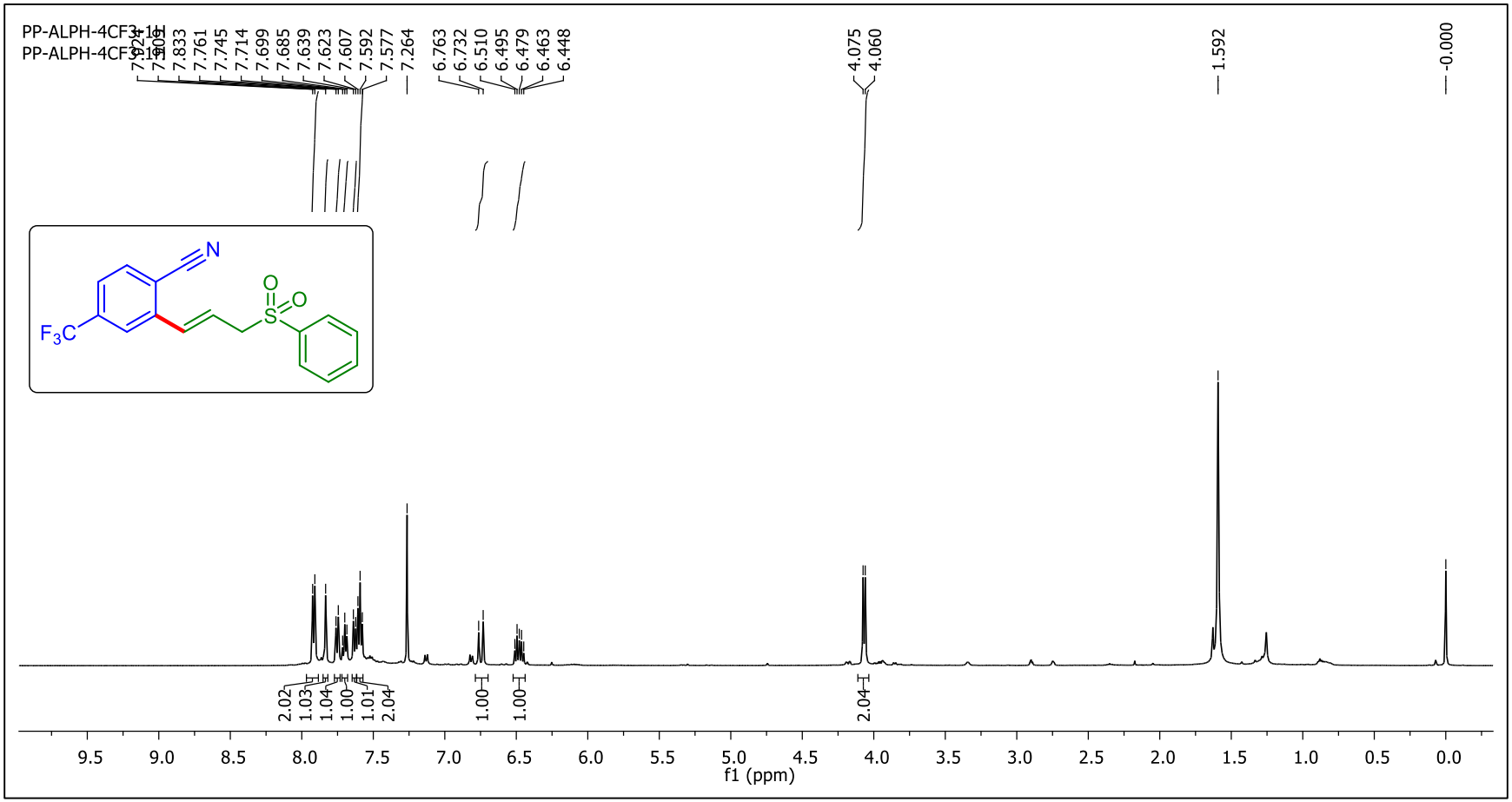
^{1}H NMR of (*E*)-4-Iodo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4d) ($CDCl_3$, 500 MHz)



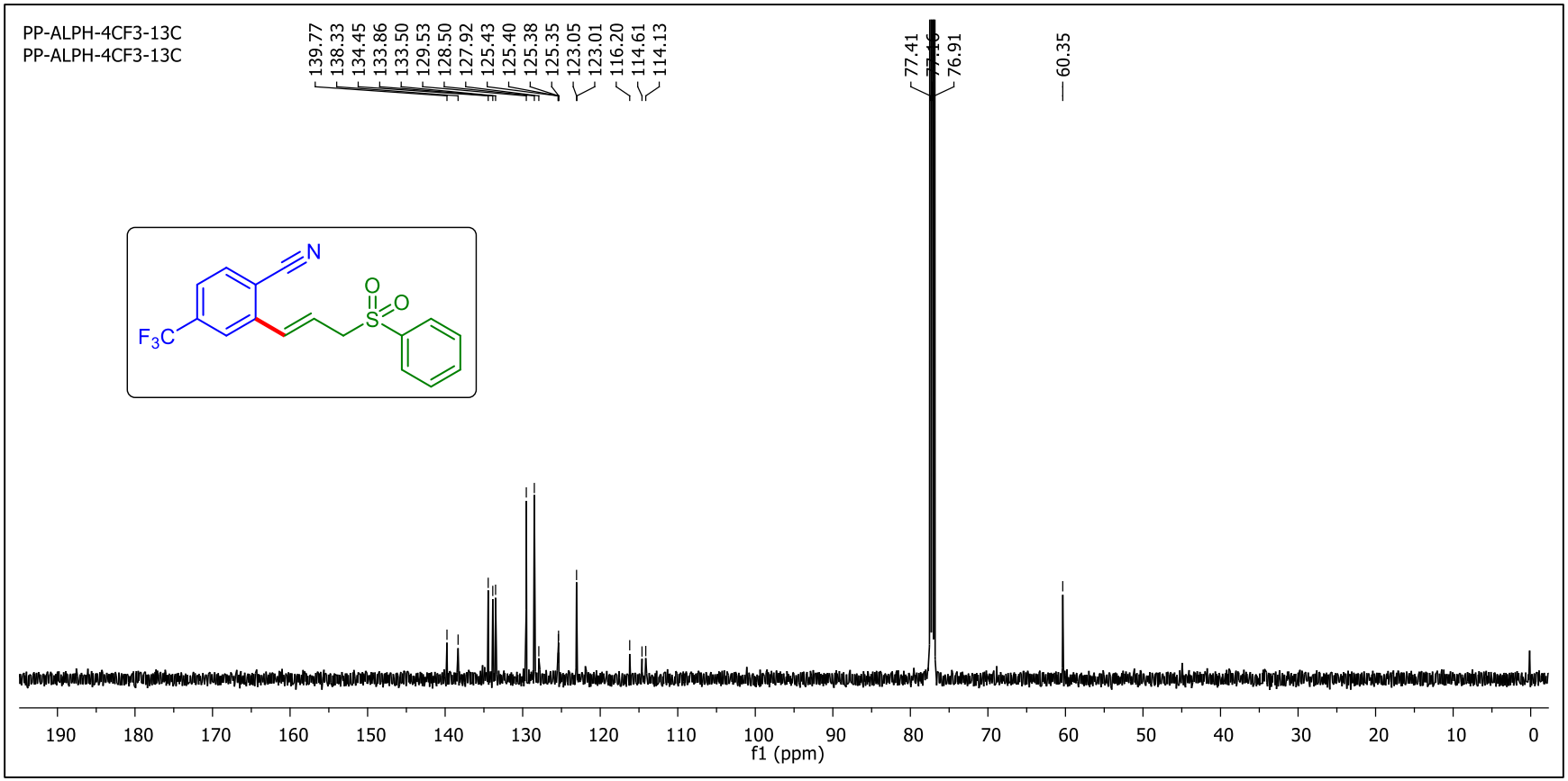
$^{13}C\{^{1}H\}$ NMR of (*E*)-4-Iodo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4d) ($CDCl_3$, 126 MHz)



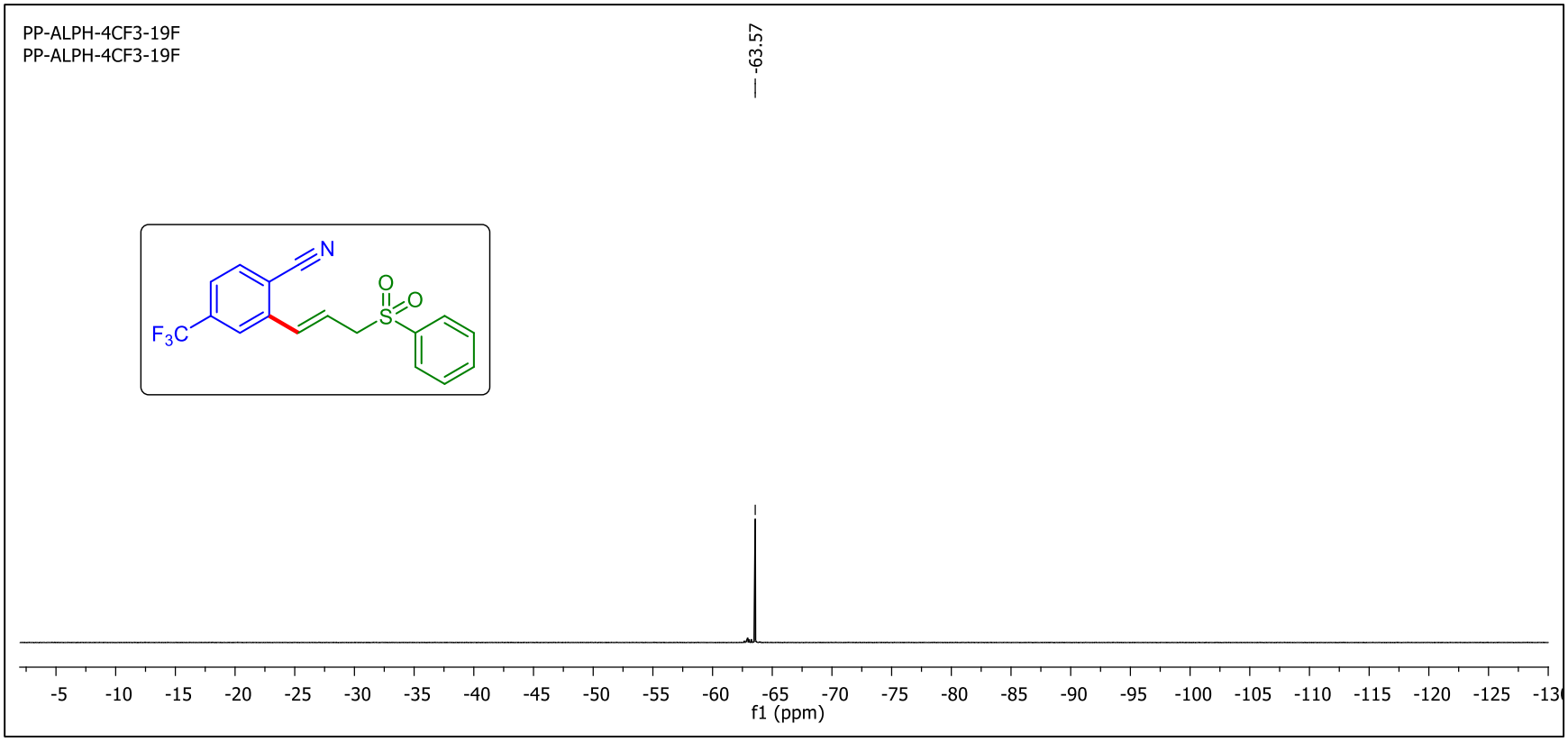
^{1}H NMR of (*E*)-2-(3-(Phenylsulfonyl)prop-1-en-1-yl)-4-(trifluoromethyl)benzonitrile (4e) ($CDCl_3$, 500 MHz)



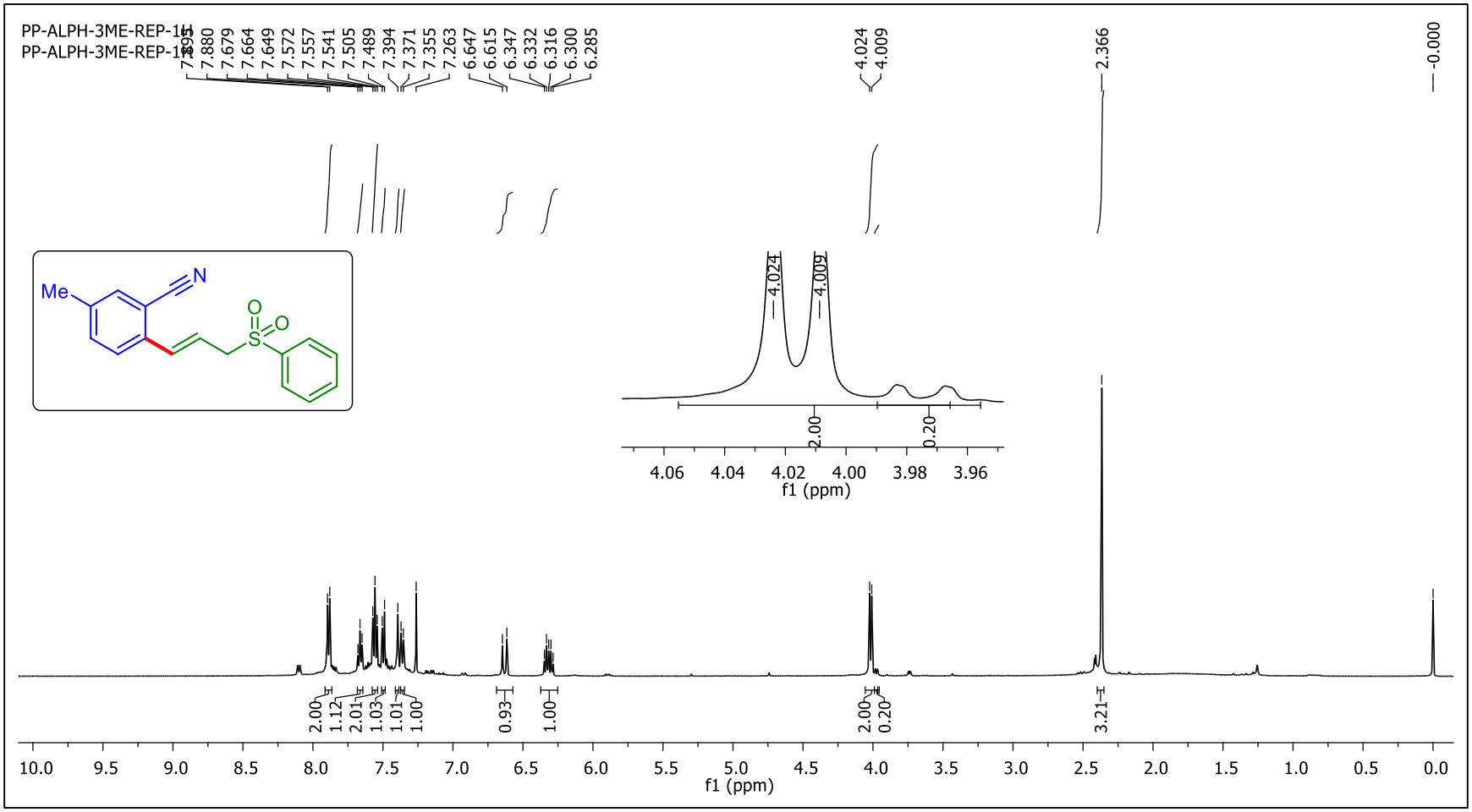
$^{13}C\{^{1}H\}$ NMR of (*E*)-2-(3-(Phenylsulfonyl)prop-1-en-1-yl)-4-(trifluoromethyl)benzonitrile (4e) ($CDCl_3$, 126 MHz)



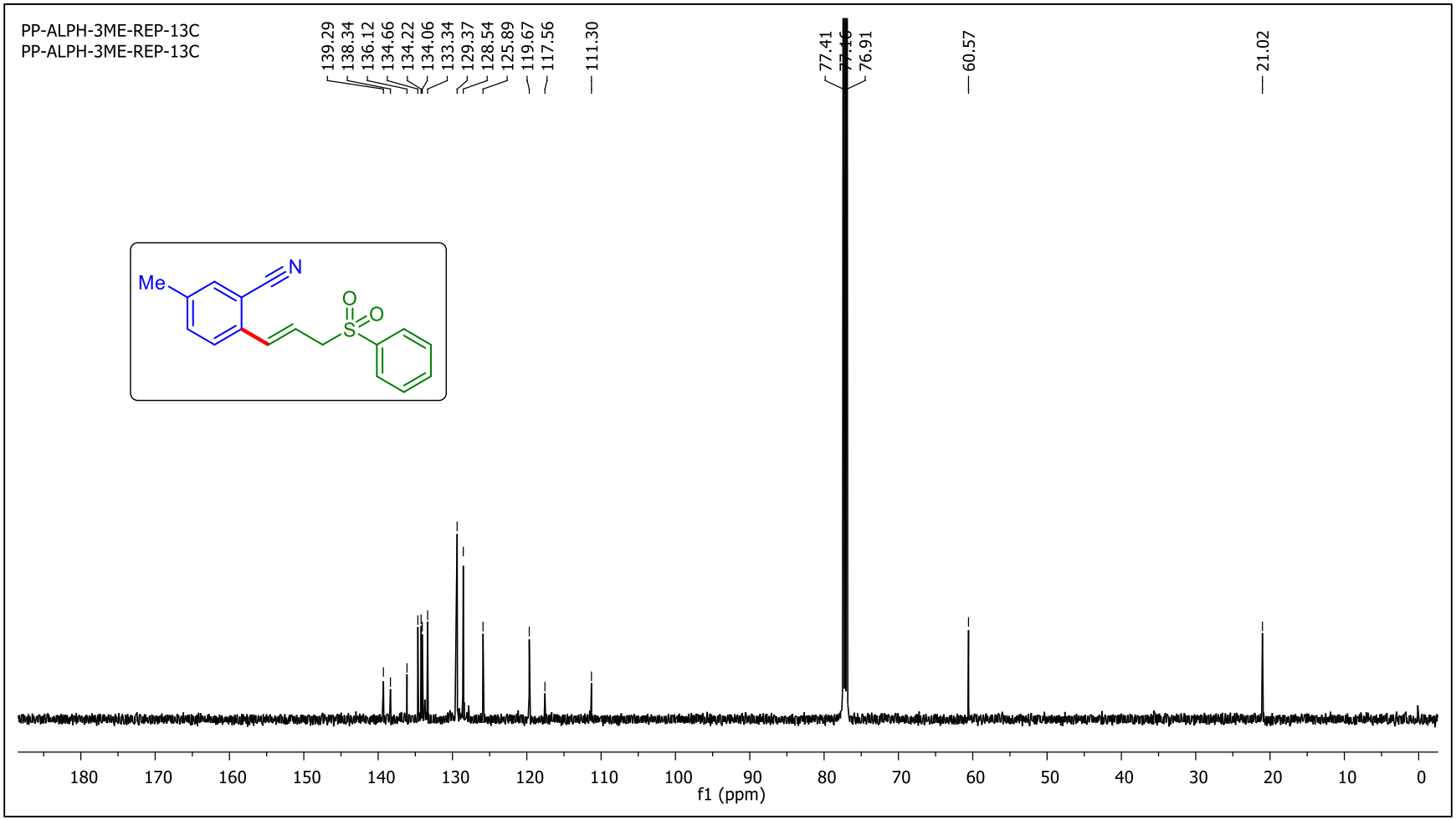
^{19}F NMR of (*E*)-2-(3-(Phenylsulfonyl)prop-1-en-1-yl)-4-(trifluoromethyl)benzonitrile (4e) ($CDCl_3$,471 MHz)



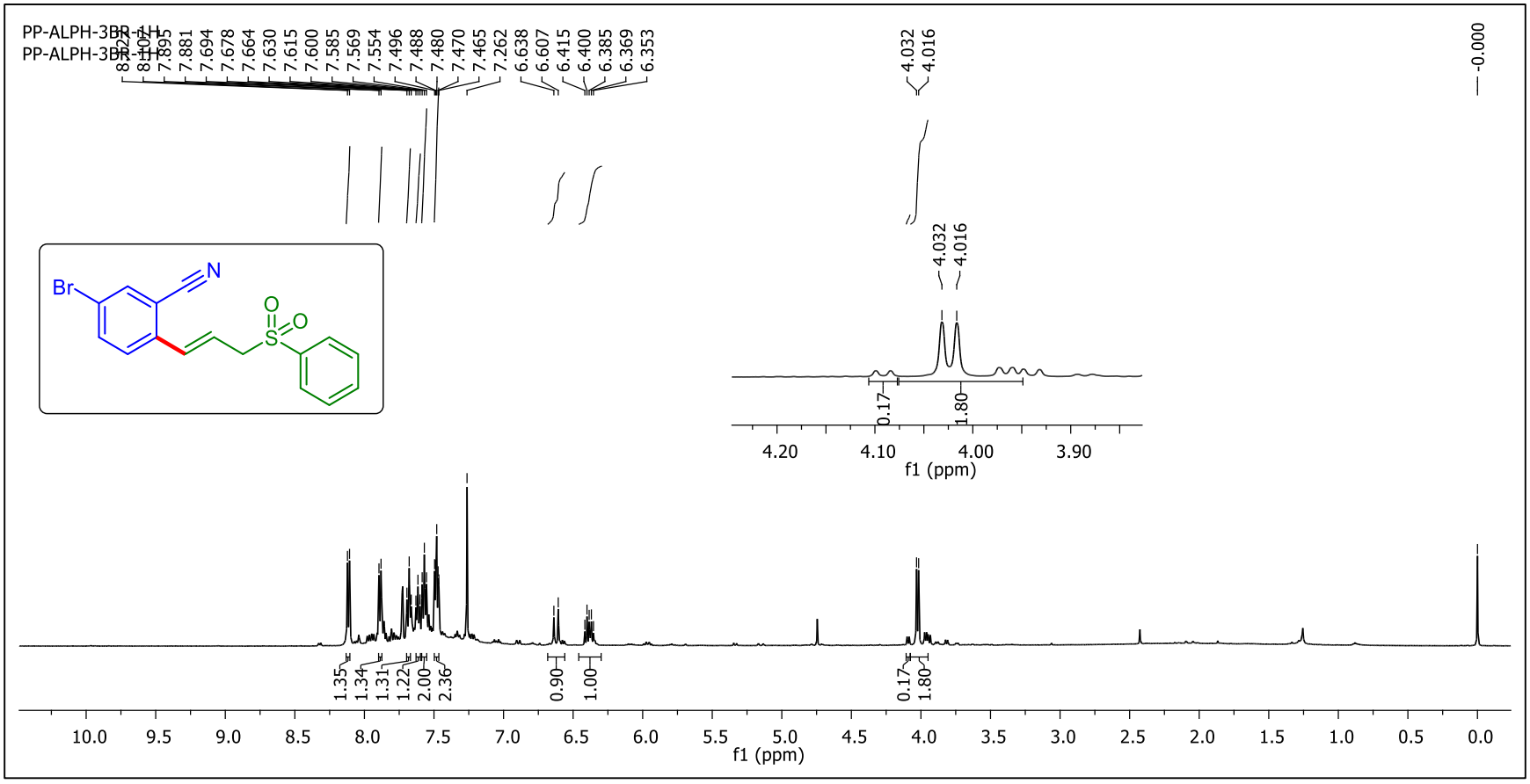
^{1}H NMR of (E)-5-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4f) ($CDCl_3$, 500 MHz)



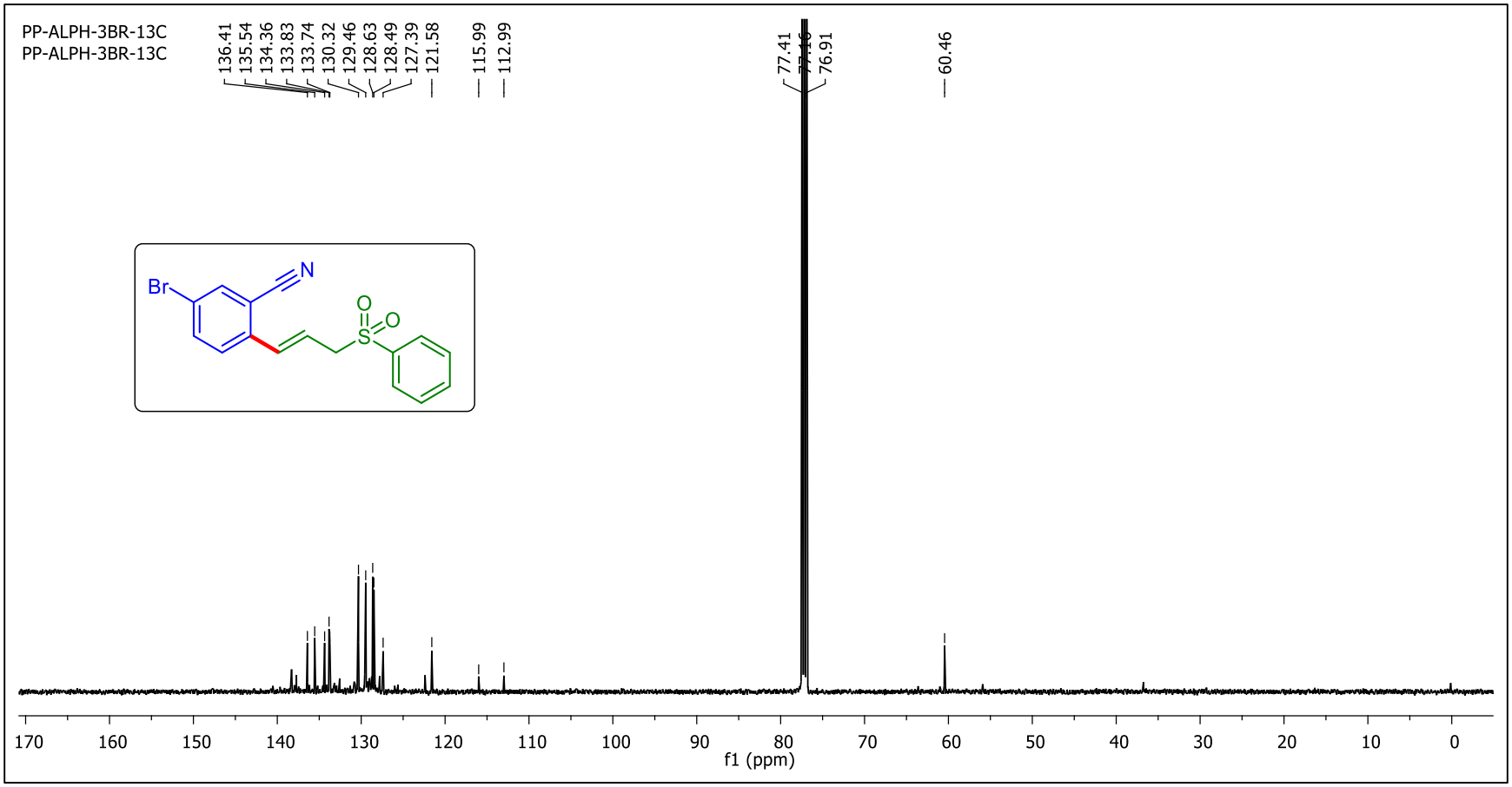
$^{13}C\{^{1}H\}$ NMR of (E)-5-Methyl-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4f) ($CDCl_3$, 126 MHz)



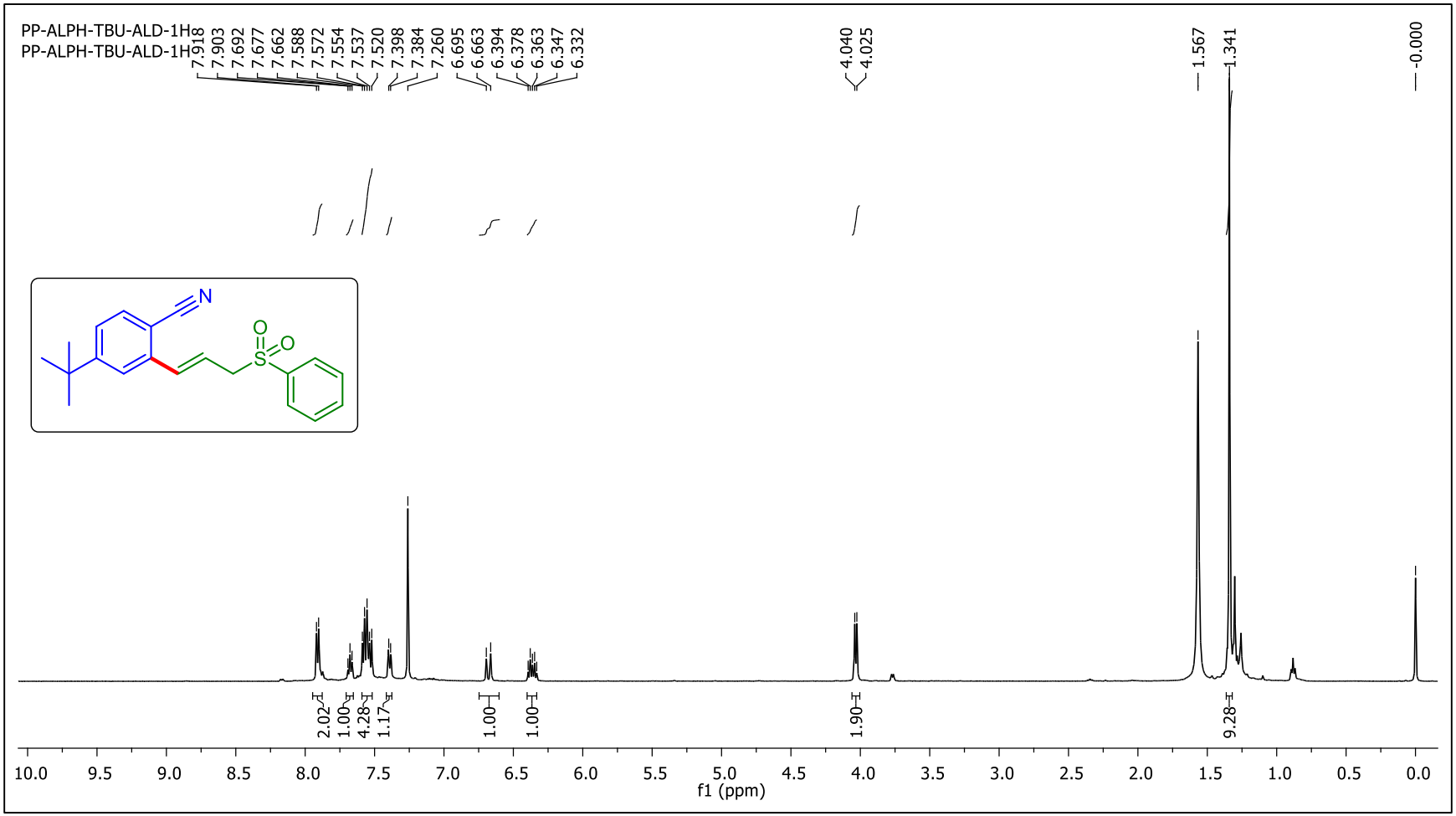
^{1}H NMR of (*E*)-5-Bromo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4g) ($CDCl_3$, 500 MHz)



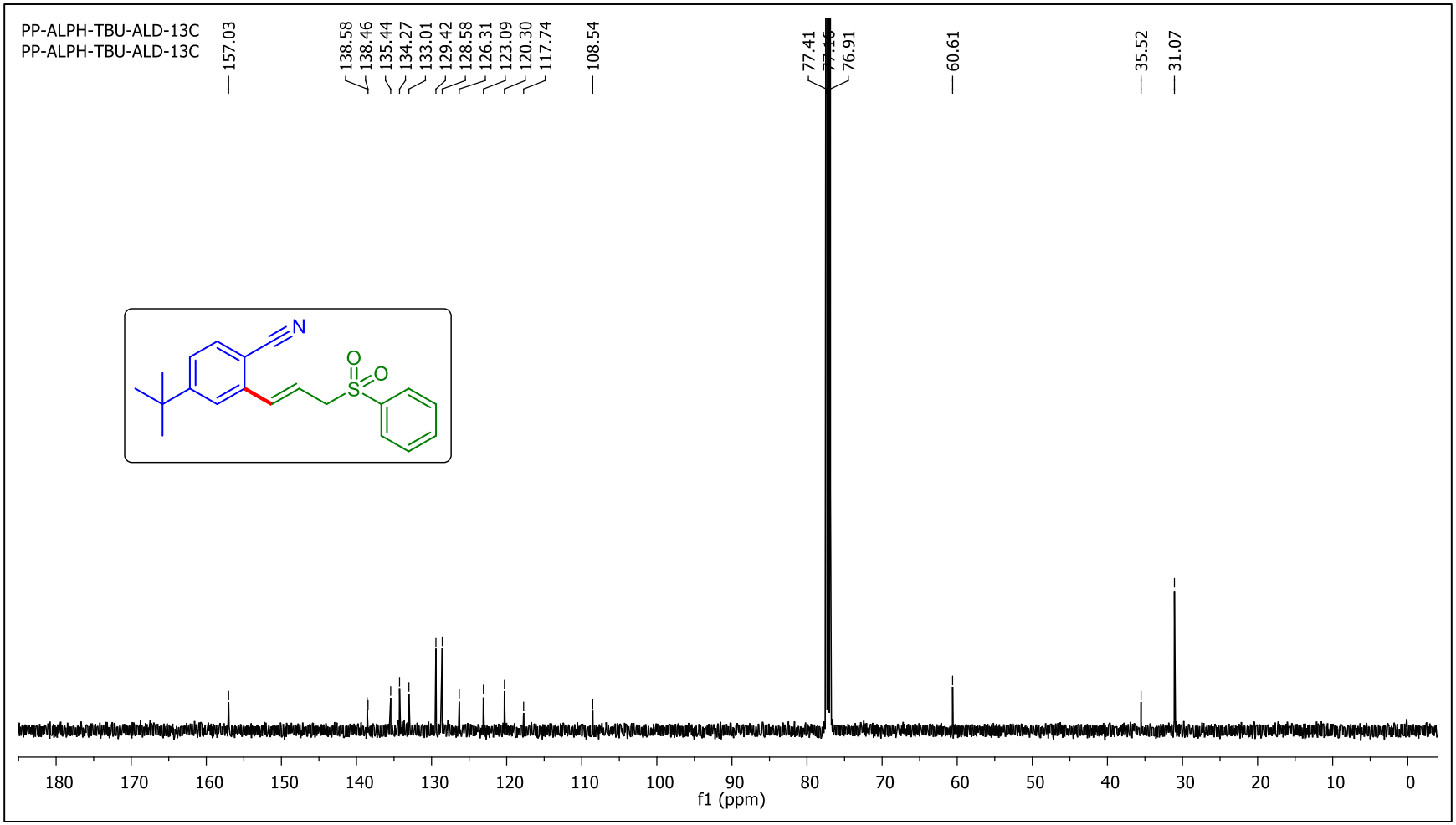
$^{13}C\{^{1}H\}$ NMR of (*E*)-5-Bromo-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4g) ($CDCl_3$, 126 MHz)



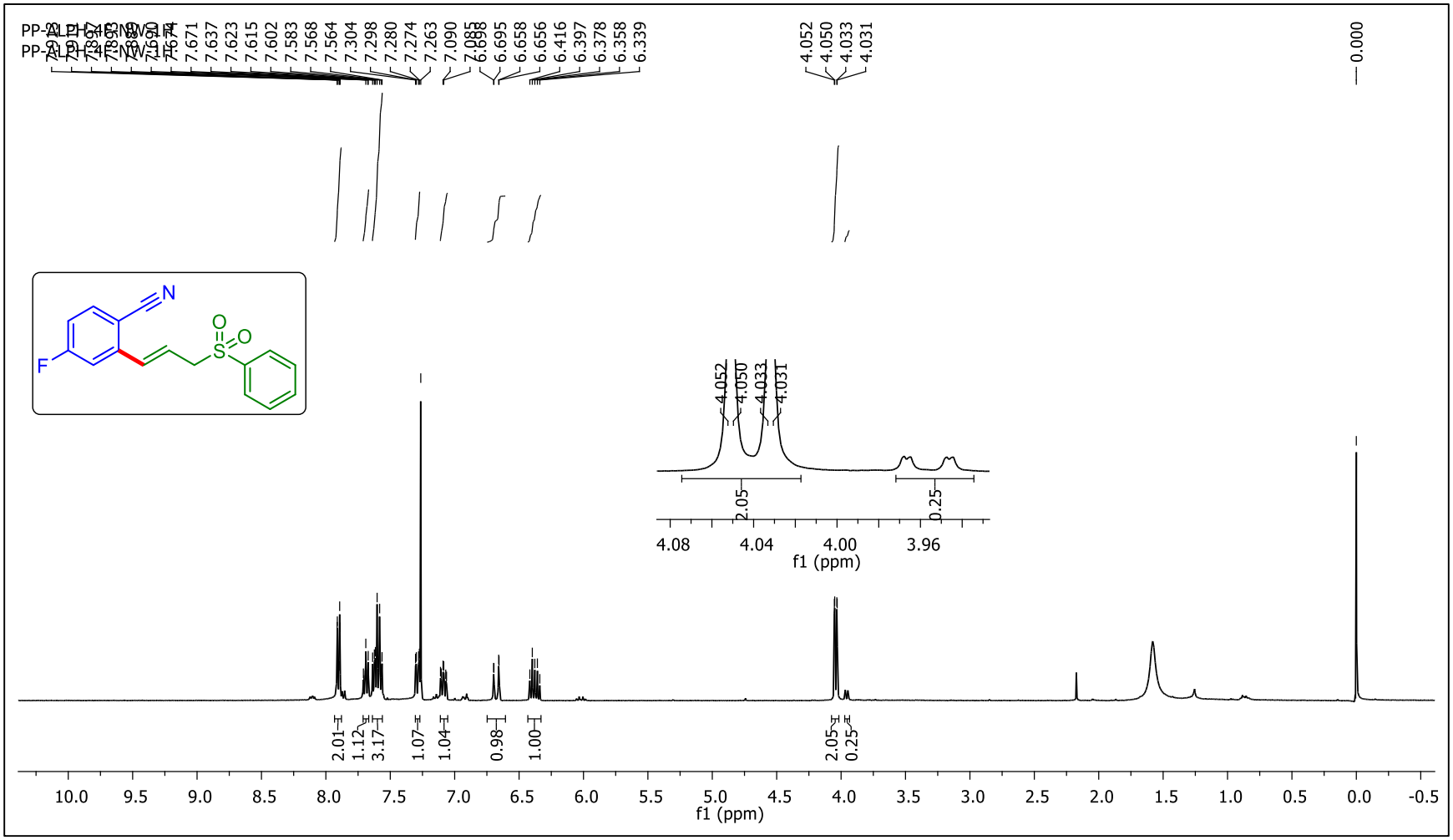
^{1}H NMR of (*E*)-4-(*tert*-Butyl)-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4o) ($CDCl_3$, 500 MHz)



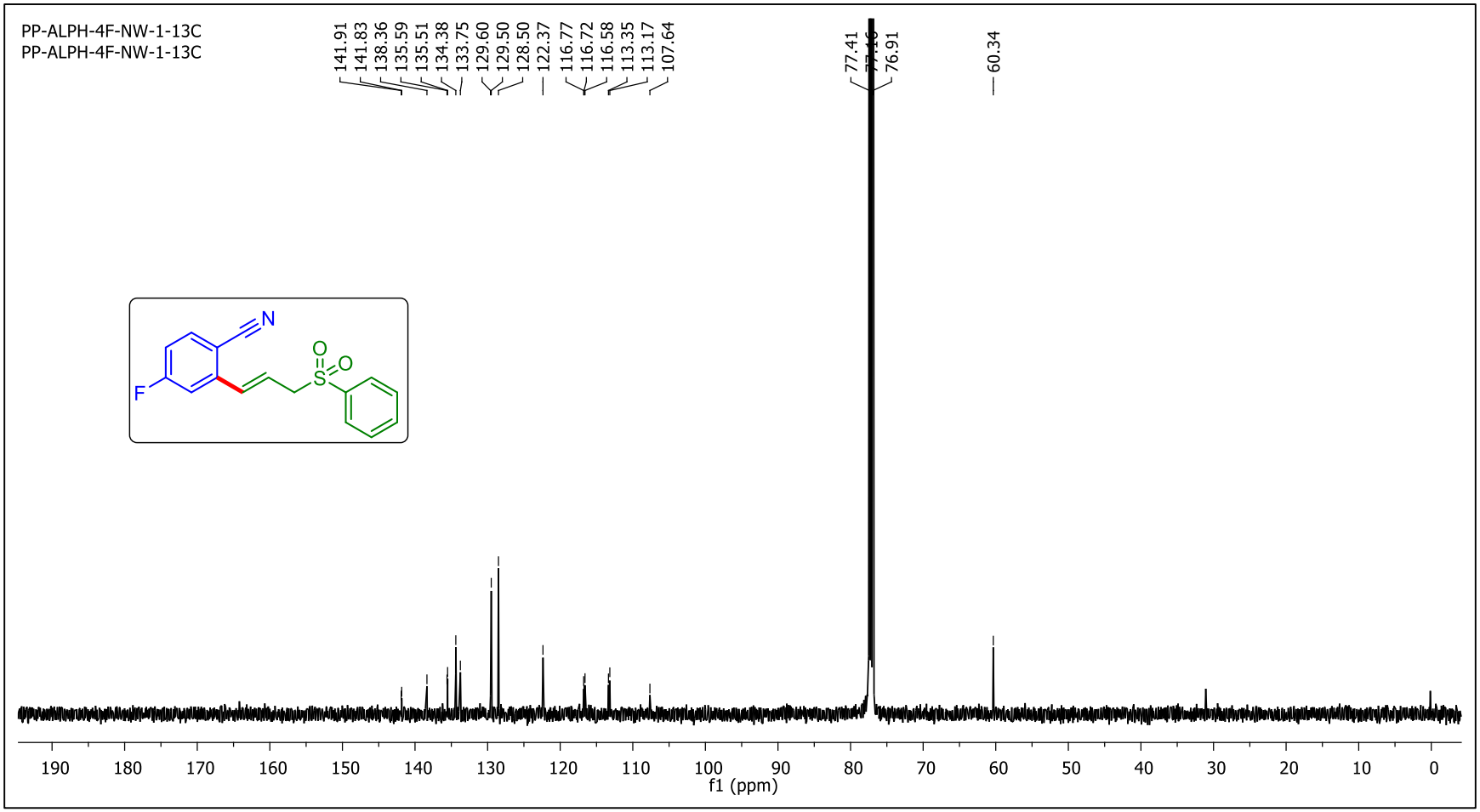
$^{13}C\{^{1}H\}$ NMR of (*E*)-4-(*tert*-Butyl)-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4o) ($CDCl_3$, 126 MHz)



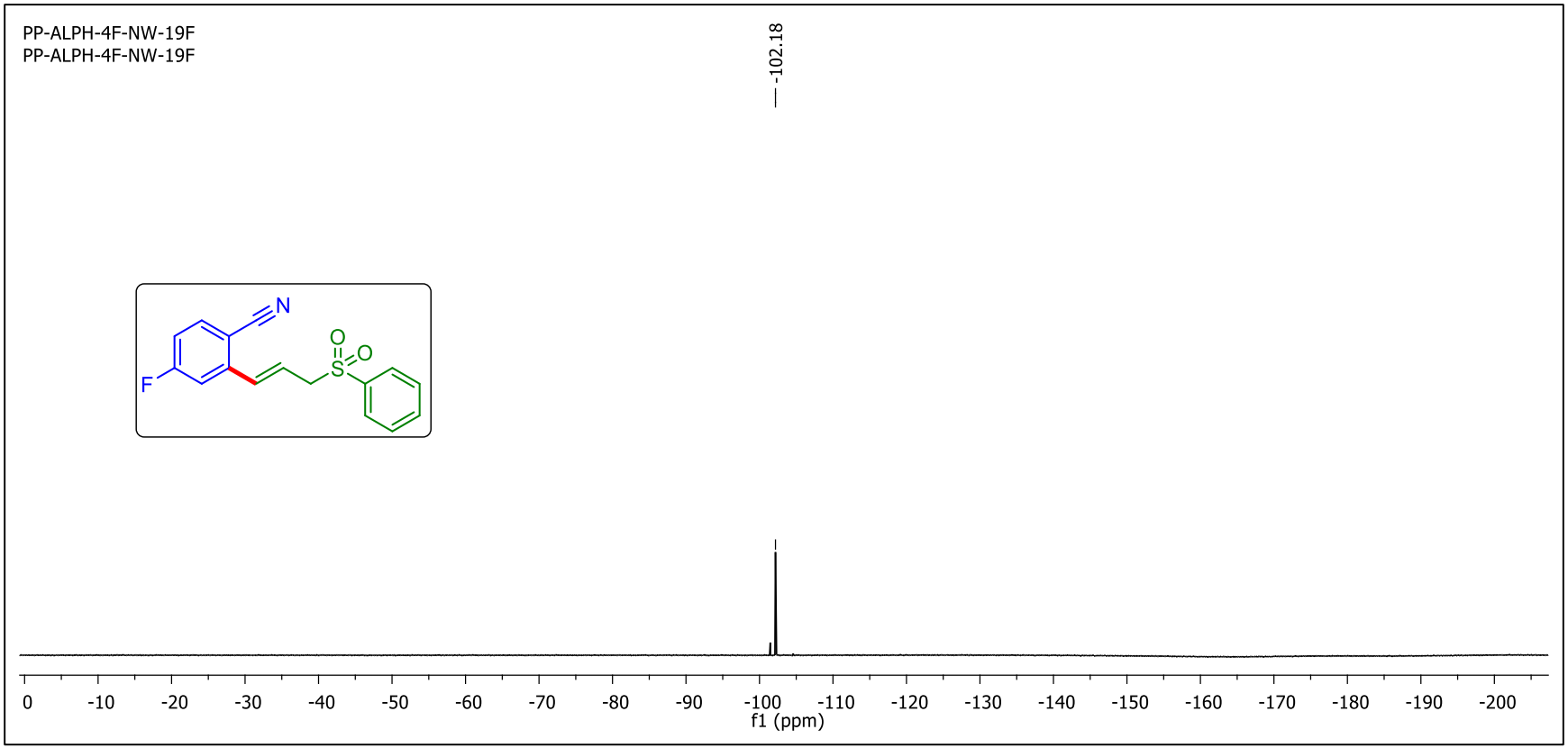
^{1}H NMR of (*E*)-4-Fluoro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4p) ($CDCl_3$, 400 MHz)



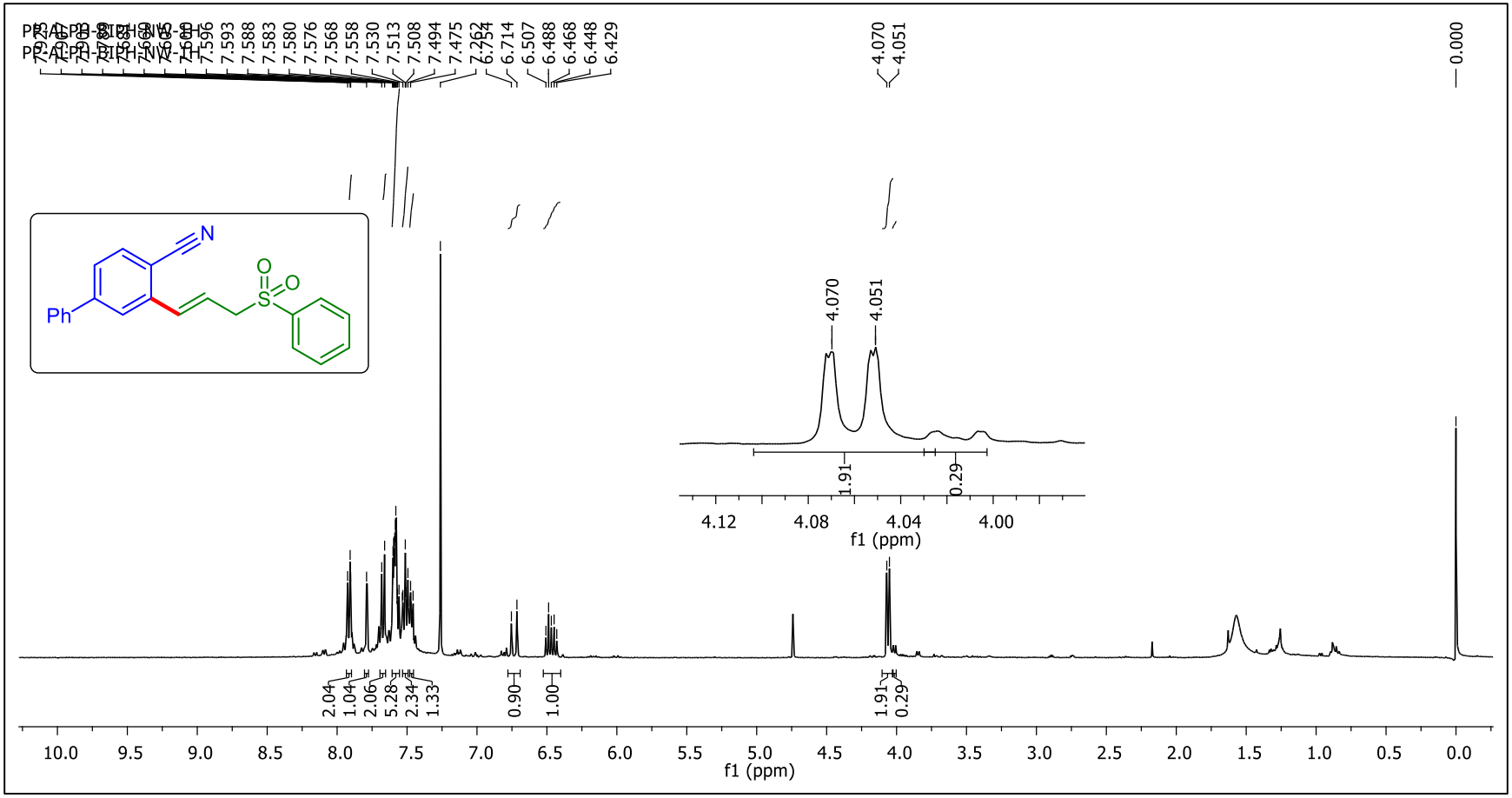
$^{13}C\{^{1}H\}$ NMR of (*E*)-4-Fluoro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4p) ($CDCl_3$, 126 MHz)



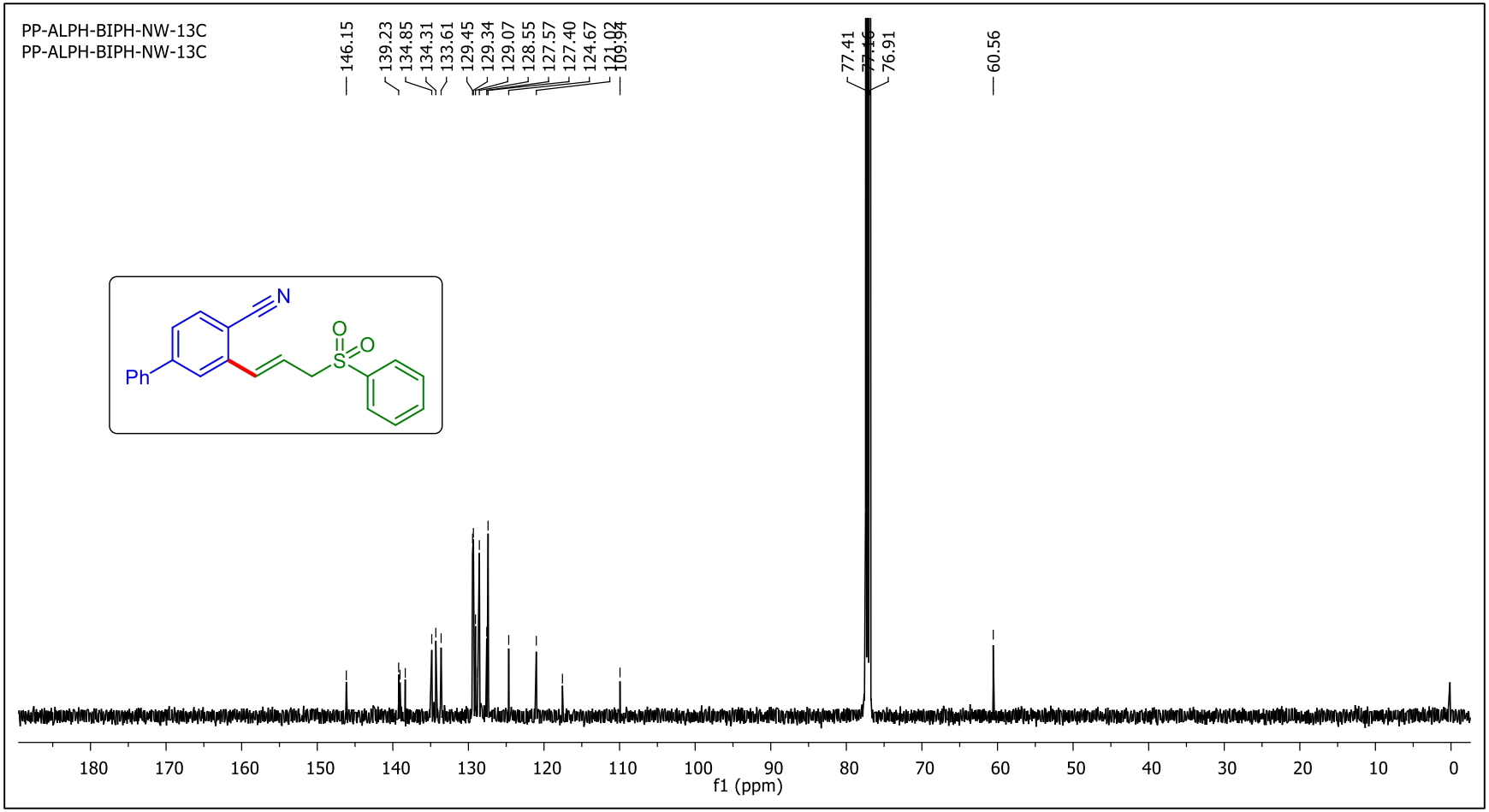
^{19}F NMR of (*E*)-4-Fluoro-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4p) ($CDCl_3$, 377 MHz)



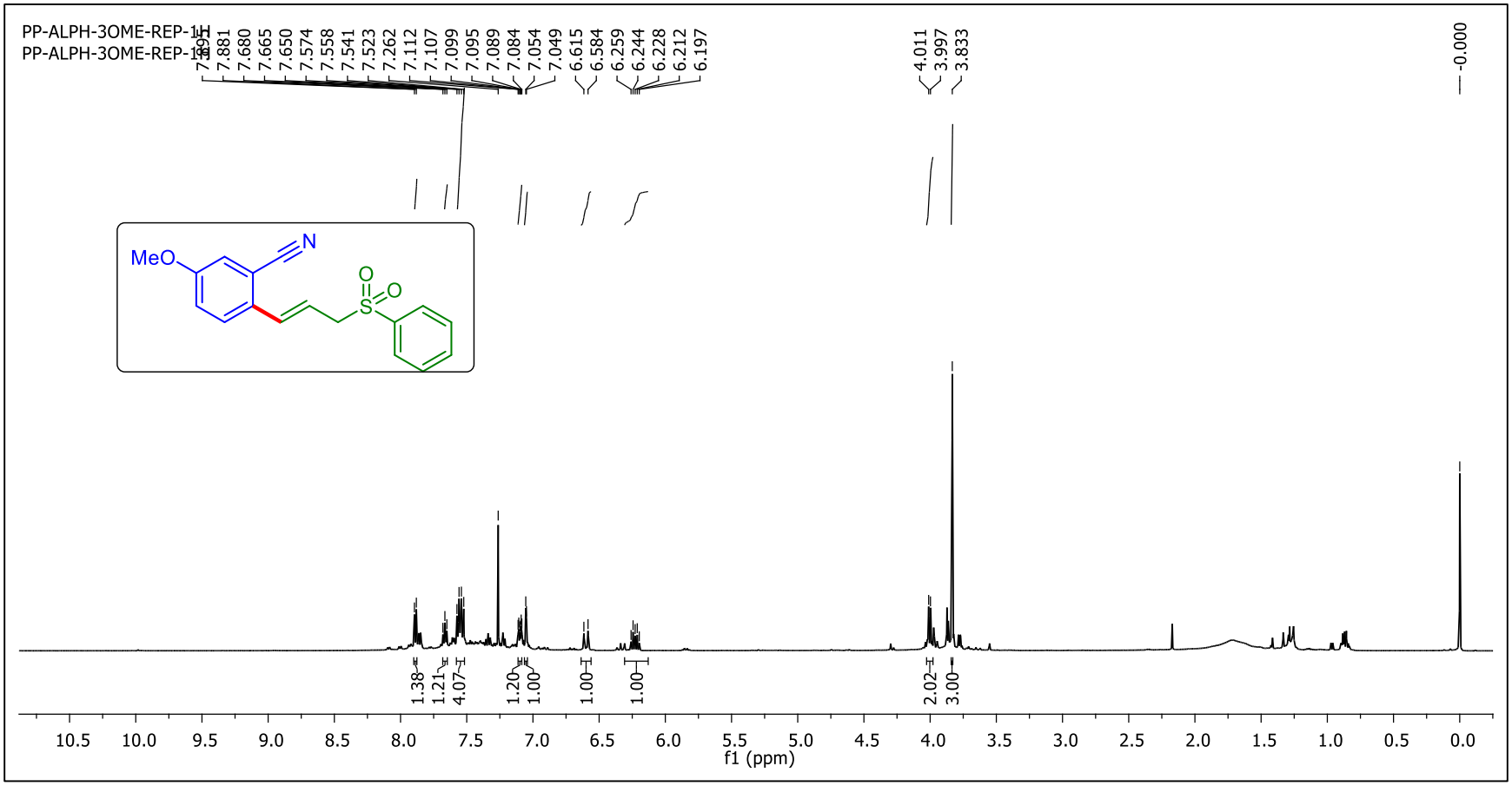
^{1}H NMR of (*E*)-3-(3-(Phenylsulfonyl)prop-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile (4q) ($CDCl_3$, 400 MHz)



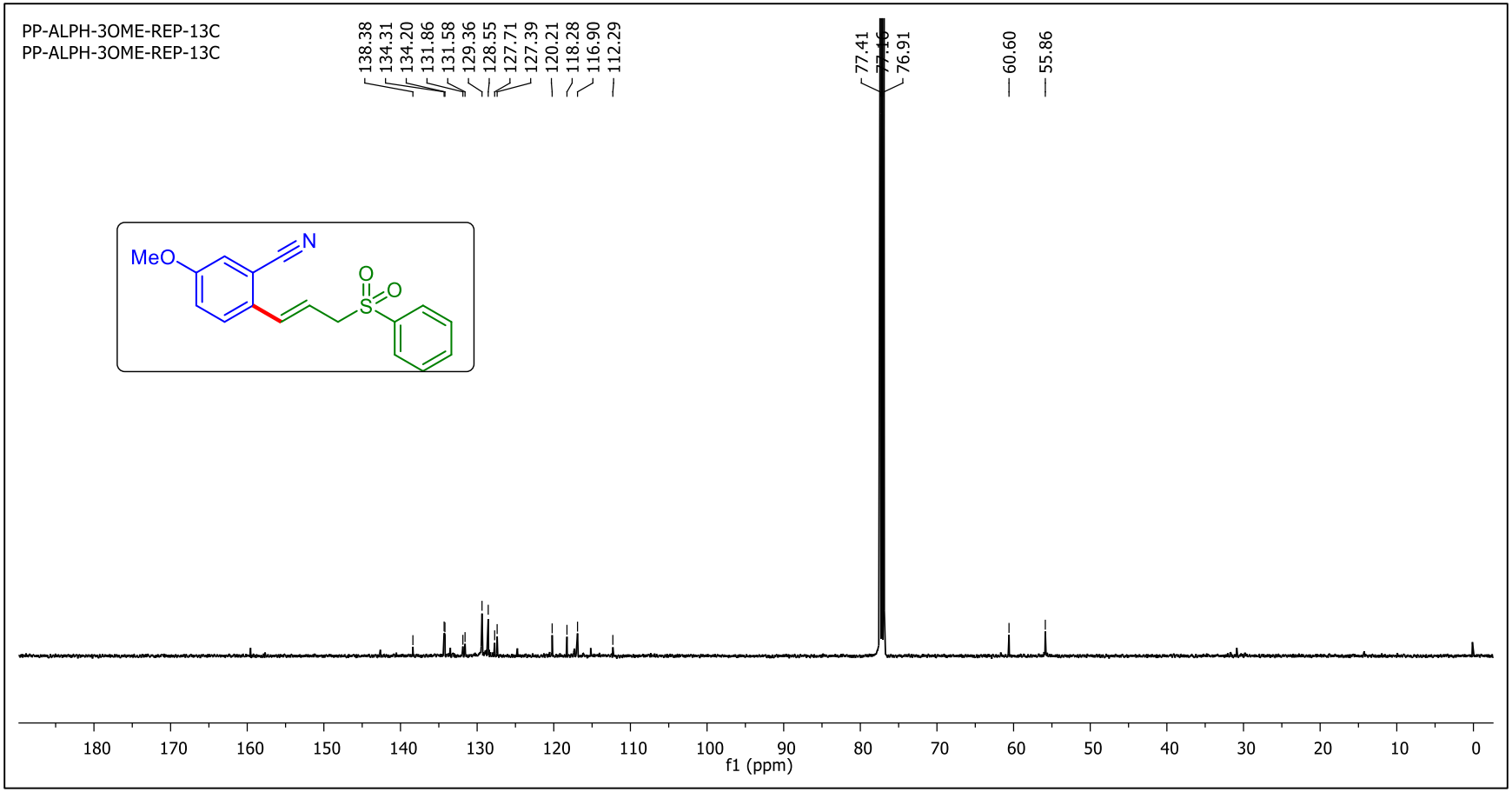
$^{13}C\{^{1}H\}$ NMR of (*E*)-3-(3-(Phenylsulfonyl)prop-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile (4q) ($CDCl_3$, 126 MHz)



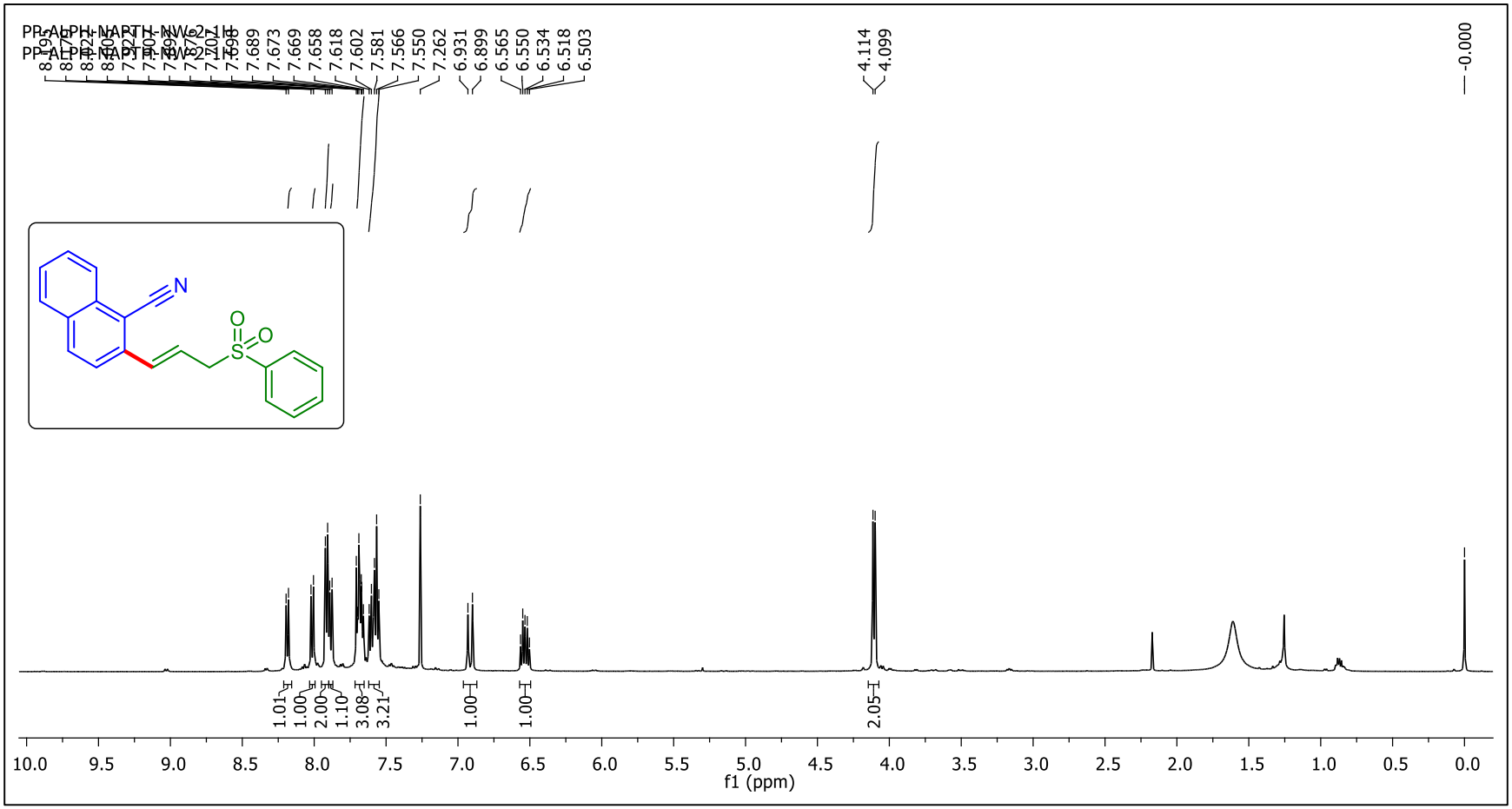
^{1}H NMR of (*E*)-5-Methoxy-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4r) ($CDCl_3$, 500 MHz)



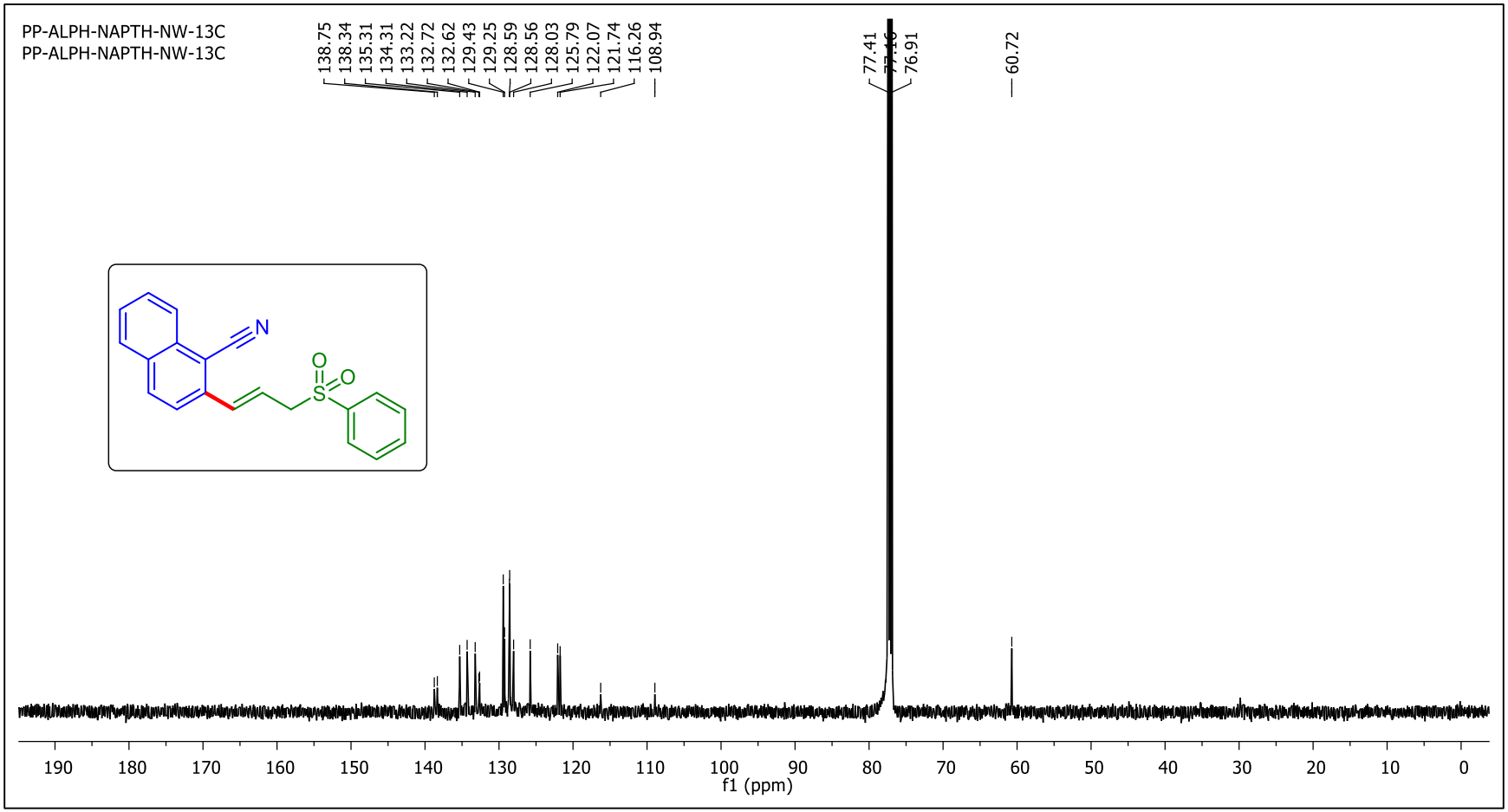
$^{13}C\{^{1}H\}$ NMR of (*E*)-5-Methoxy-2-(3-(phenylsulfonyl)prop-1-en-1-yl)benzonitrile (4r) ($CDCl_3$, 126 MHz)



^{1}H NMR of (*E*)-2-(3-(Phenylsulfonyl)prop-1-en-1-yl)-1-naphthonitrile (4s) ($CDCl_3$, 500 MHz)

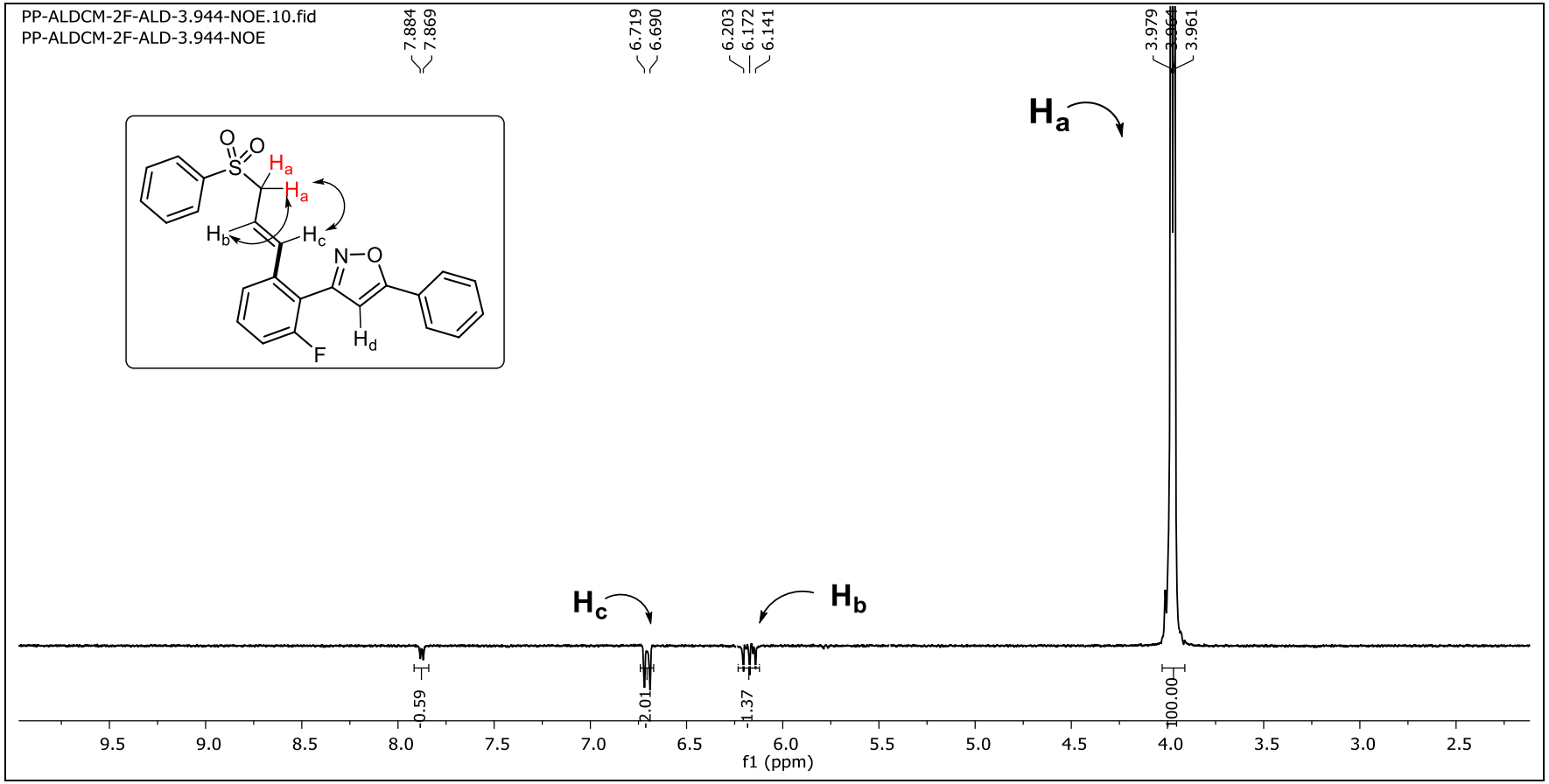


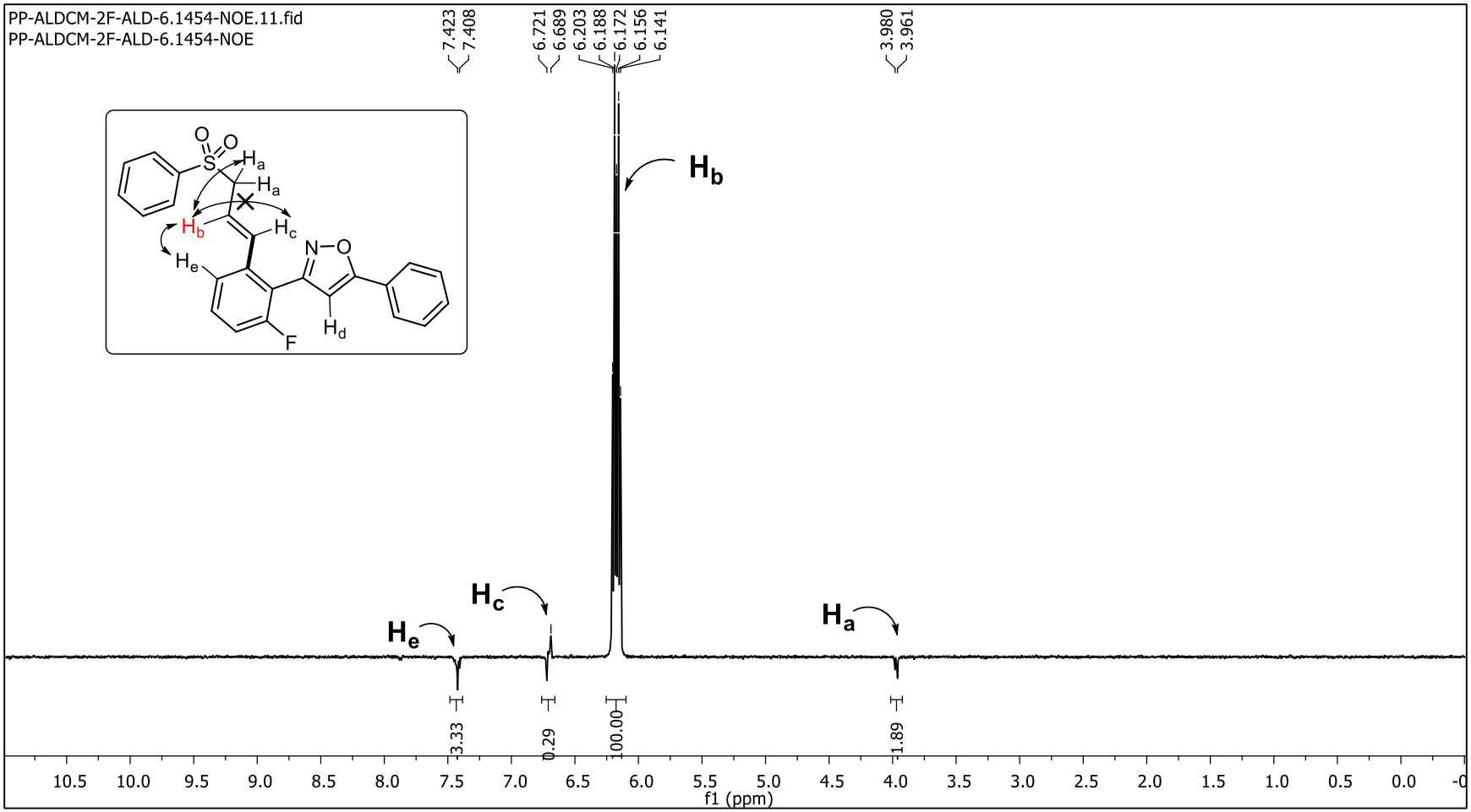
$^{13}C\{^{1}H\}$ NMR of (*E*)-2-(3-(Phenylsulfonyl)prop-1-en-1-yl)-1-naphthonitrile (4s) ($CDCl_3$, 126 MHz)

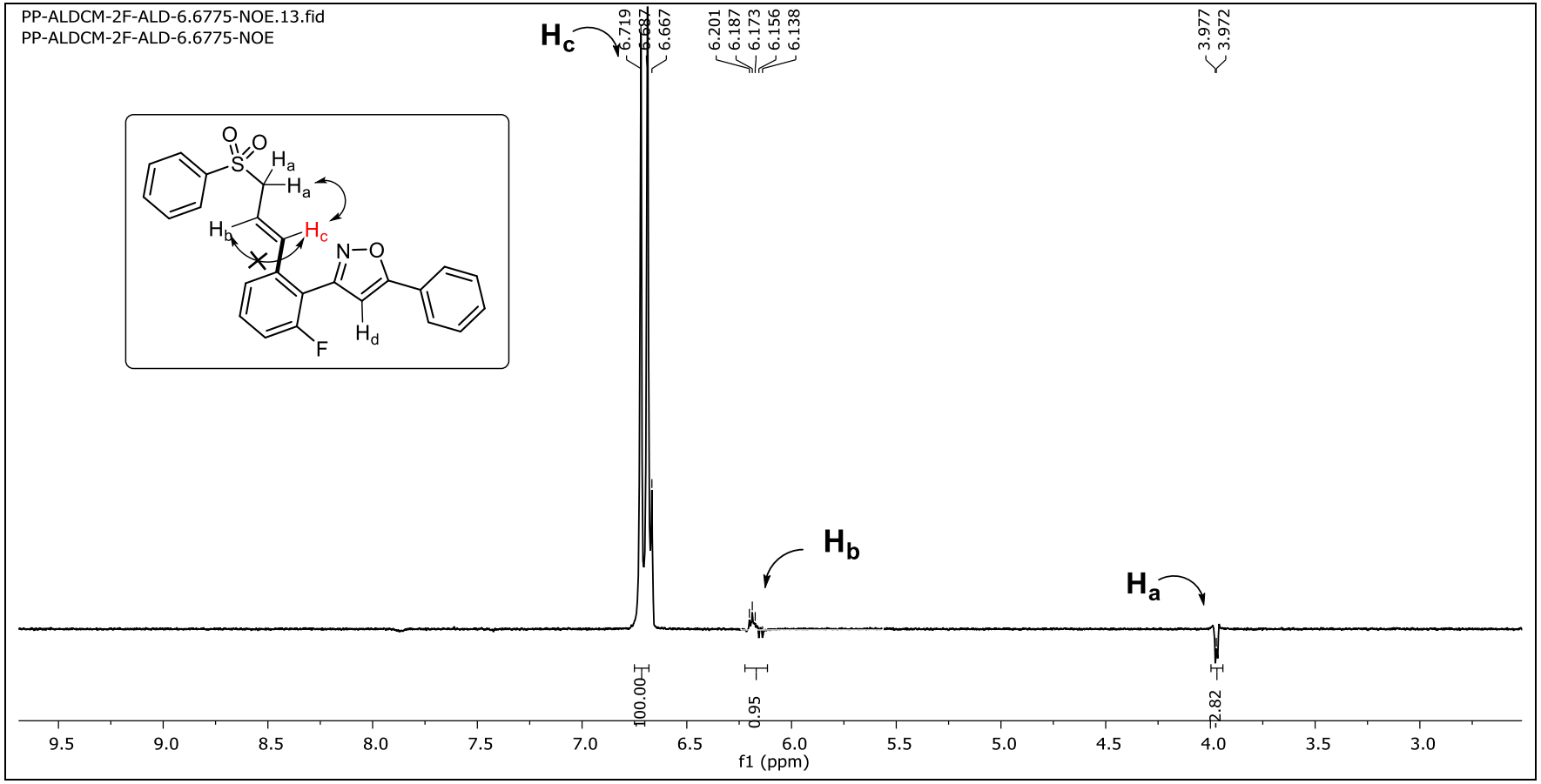


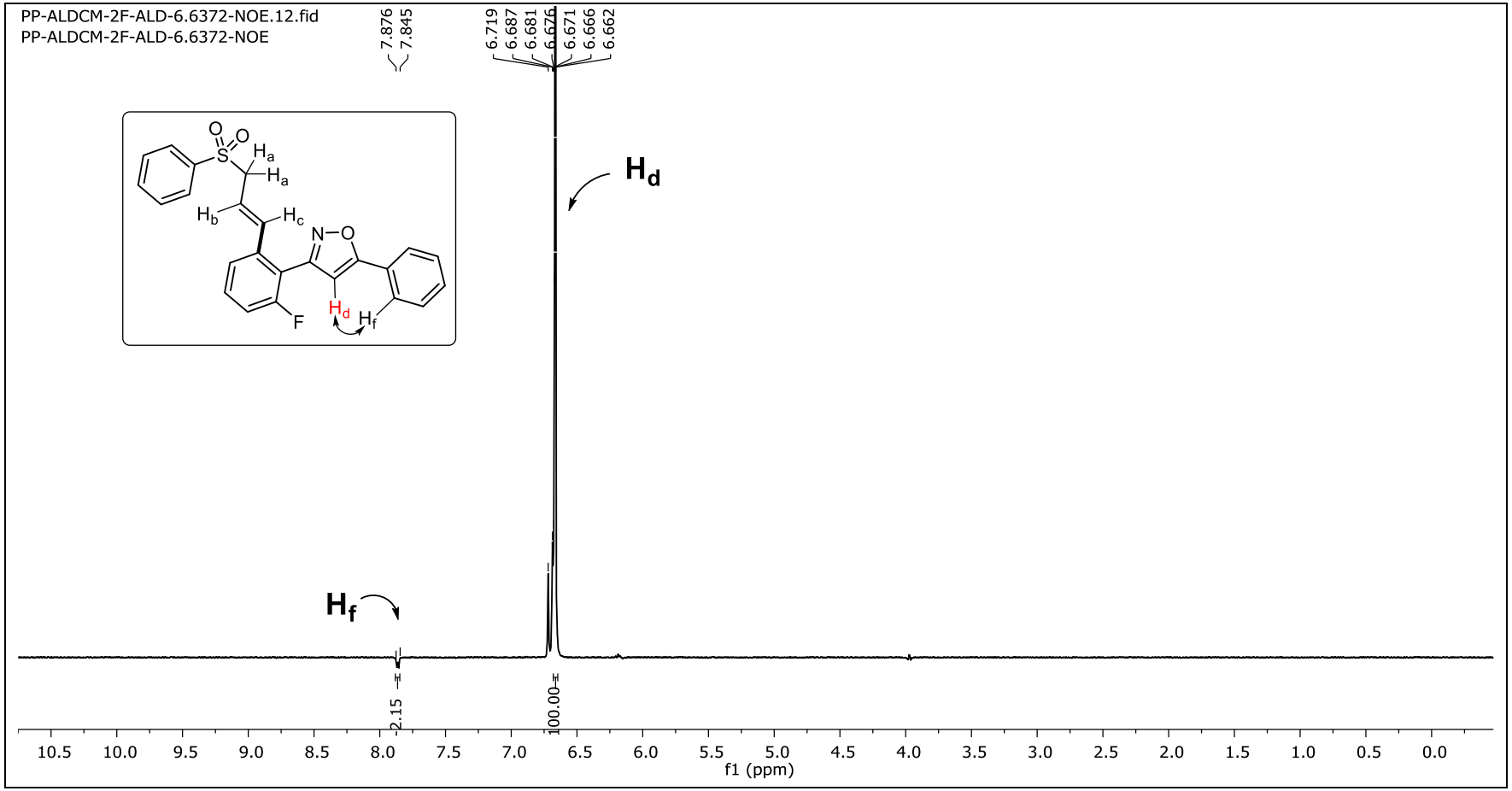
11. NOE experiment of 3i

Upon irradiation of H_a, enhancement was observed in the signals corresponding to H_b (1.37% w.r.t. H_a), H_c (2.01% w.r.t. H_a), which indicates that H_a is in *cis* relation with H_b and H_c. Similarly, upon irradiation of H_b, enhancement was observed for H_e (3.33% w.r.t. H_b), H_c (0.29% w.r.t. H_b), H_a (1.89% w.r.t. H_b), which indicates that H_b is in *cis* relation with H_e and H_a. Further, upon irradiation of H_c, enhancement was observed for H_a (2.82% w.r.t. H_c), H_b (0.95% w.r.t. H_c), which indicates that H_c is in *cis* relation with H_a and in *trans* relation to H_b. Next, upon irradiation of H_d, enhancement was observed for H_f (2.15% w.r.t. H_d), which indicates that H_d is in *cis* relation with H_f.


PP-ALDCM-2F-ALD-3.944-NOE.10.fid
PP-ALDCM-2F-ALD-3.944-NOE
7.884
7.869
6.719
6.690
6.203
6.172
6.141
3.979
3.964
3.961
Ha
Hc
Hb
0.59
2.01
1.37
100.00
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
f1 (ppm)


PP-ALDCM-2F-ALD-6.1454-NOE.11.fid
PP-ALDCM-2F-ALD-6.1454-NOE
7.423
7.408
6.721
6.689
6.203
6.188
6.172
6.156
6.141
3.980
3.961
Hb
Hc
He
Ha
3.33
0.29
100.00
1.89
f1 (ppm)


PP-ALDCM-2F-ALD-6.6775-NOE.13.fid
PP-ALDCM-2F-ALD-6.6775-NOE
Hc
6.719
6.687
6.667
6.201
6.187
6.173
6.156
6.138
3.977
3.972
Hb
Ha
100.00
0.95
2.82
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
f1 (ppm)


PP-ALDCM-2F-ALD-6.6372-NOE.12.fid
PP-ALDCM-2F-ALD-6.6372-NOE
7.876
7.845
6.719
6.687
6.681
6.676
6.671
6.666
6.662
Hd
Hf
2.15
100.00
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
0.0
f1 (ppm)