Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Experimental Section, Materials, and Methods

For

Metallaphotoredox Catalysis Enables Facile (Trifluoromethyl)thiolation of Alkenyl Iodides

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General Information

Reagents were purchased from commercial sources and were used as received unless otherwise stated. (*Z*)-(2-iodovinyl)benzene[1] and (*E*)-(2-bromovinyl)benzene[2] were synthesized as previously reported. All reactions were performed using borosilicate glass vials of appropriate sizes. Chromatographic purification of products was accomplished by silica gel chromatography using a Teledyne ISCO CombiFlash Companion. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator with an isopropanol/dry-ice cooling trap for volatile compounds. Thin layer chromatography (TLC) was performed on silica gel 60 F254 plates. Visualization of the developed chromatogram was performed with a compact UV-lamp (254/365 nm). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on either a BRUKER UltrashieldTM 500 MHz spectrometer or BRUKER UltrashieldTM 600 MHz spectrometer and were internally referenced to residual protio-solvent signals or an internal standard as specified. Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, q = quartet, m = multiplet, b = broad), integration, and coupling constant (Hz). Data for ^{13}C and ^{19}F NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent nuclei. Product *E*:*Z* ratios derived from crude ^{19}F NMR, *E* and *Z* product peaks were integrated relative to internal hexafluorobenzene standard (equimolar with alkenyl-iodide substrate) added after completion of the reaction. HRMS were obtained using a hybrid quadrupole time-of-flight mass spectrometer in ESI^{+} and ESI^{-} mode. FTIR spectra were collected on a Nicolet iS50 FT-IR and data were reported as follows: wavenumber (cm^{-1}) and intensity (vw = very weak, w = weak, m = medium, s = strong, vs = very strong). A 34W Kessil H150 blue LED lamp was used as the light source in a HepatoChem EvoluChemTM PhotoRedOx reaction apparatus. $AgSCF_3$ was sourced from TCI America.

Photocatalyst Structures and Properties

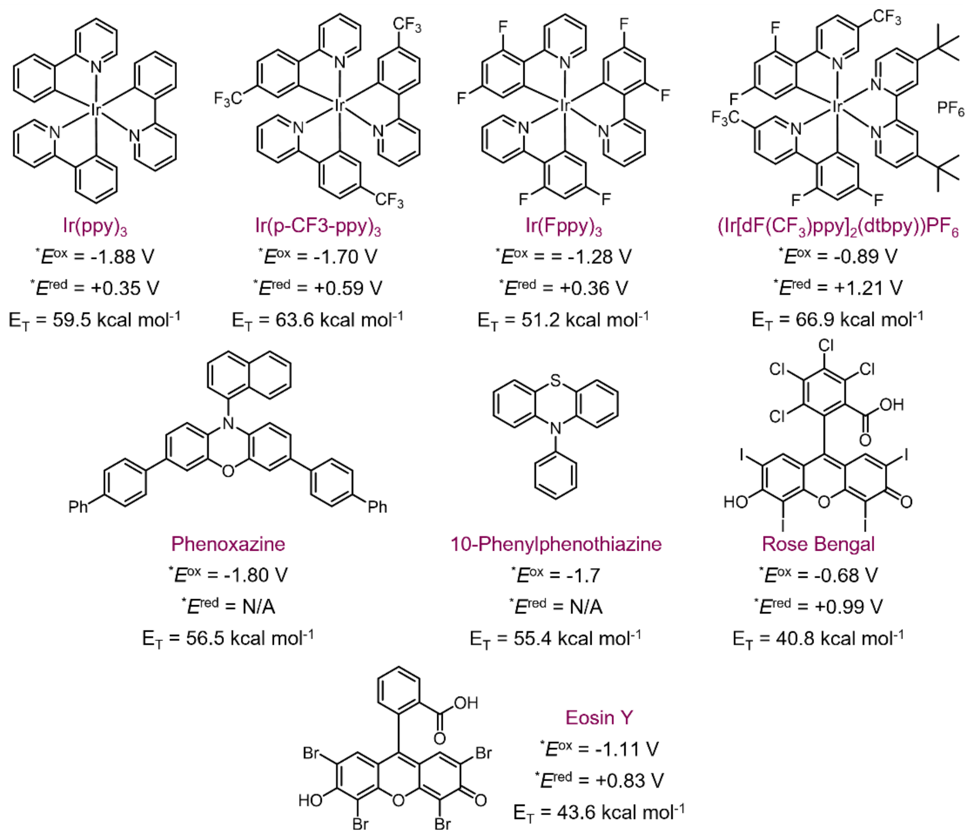


Figure S1. Structures, excited state redox properties, and triplet energies (E_T) of photocatalysts investigated in this study.[3]

Density Functional Theory (DFT) Results and Analysis

Computational Details

All quantum mechanical calculations were performed with the TURBOMOLE v.7 software. All calculations were performed in the COSMO solvation model. Ground state free energies were obtained employing the following procedure: 1) the molecular geometry was optimized using the settings describe below, 2) the electronic energy of the converged geometry was calculated at a higher level of theory using the settings described below. For the purpose of calculating ground state free energy, thermal and entropy contributions (RRHO approximation) were added to the final electronic energy. To this effect, the electronic Hessian was calculated via numerical frequency calculations as implemented in the NumForce function of Turbomole. Triplet energies (E_T), defined as the vertical electronic energy gap between the ground electronic singlet state (S^0) and the excited triplet state (T^1), were obtained using the following procedure: 1) the molecular geometry (S^0) was optimized using the settings describe below, 2) The electronic energy of the converged singlet geometry in its singlet ground state was calculated at a higher level of theory using the settings described below, 3) The electronic energy converged singlet geometry in *its triplet state* was calculated at the same level of theory.

Geometry optimization was performed using default geometry and self-consistent field (SCF) convergence settings, with the grid setting m3. Energy was estimated using the functional BP86 in conjunction with the Def2-SVP basis set.[4-6] Single-point final energies were performed using default SCF convergence settings and the grid level m5. The functional PW6B95 was used in conjunction with the Def2-TZVPD basis set.[7] To get a reliable estimation of the present model to calculate the triplet energy (E_T), E_T of 20 molecules (18 organic molecules and 2 iridium-based photocatalysts) were calculated and compared to the experimental values.[3, 8-12] Because the reported experimental values correspond to 0-0 energy, the E_T was calculated using the following methodologies. 1) the geometry was optimized in the singlet state and 2) in the triplet state, 3) one final single-point energy calculation was performed on the singlet optimal geometry, and 4) one final single-point energy calculation was performed on the triplet optimal geometry. The E_T is taken as the difference between the triplet and singlet single-point energies. The result show an adequate correlation between calculated and experimental E_T (**Figure S2**), with an RMSD of 5.4 kcal mol^{-1}. In the following study, a similar distribution is assumed for the error on E_T.

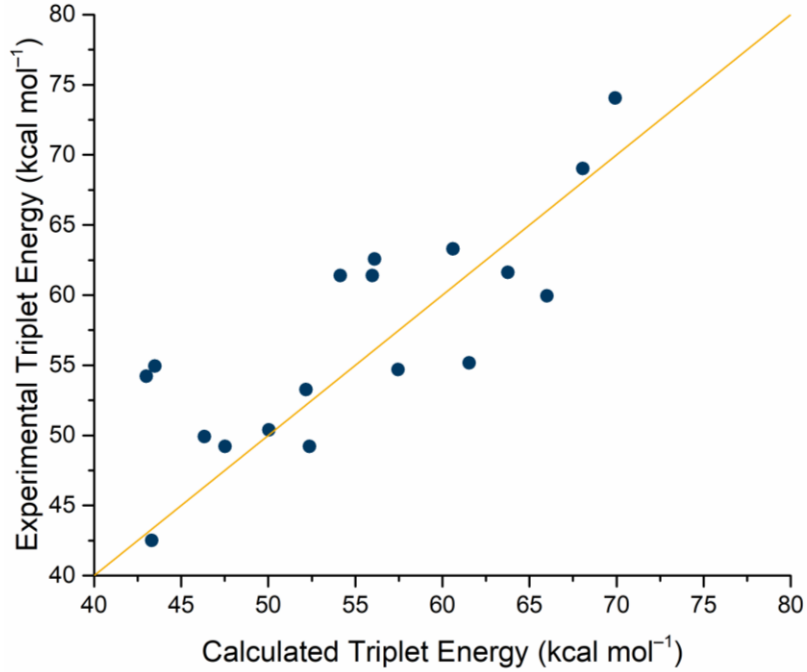


Figure S2. Calculated vs experimental E_T for all benchmarked molecules (blue dot). Parity line (orange line).

Results and Analysis

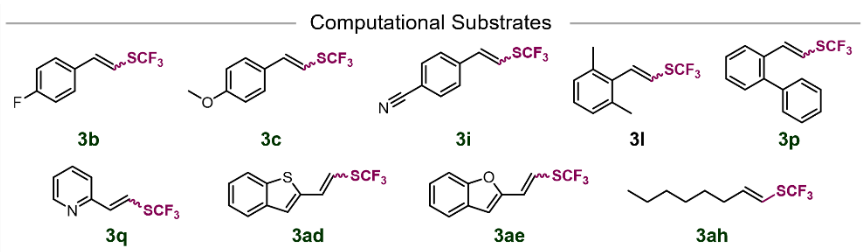


Figure S3. Substrates assessed computationally in this study.

To ensure the *E*/*Z* ratio is not driven by ground state thermodynamics of the product, the difference of free energy of the *E* and *Z* isomer for products **3b**, **3c**, **3i**, **3l,** **3p**, **3q**, **3ad**, and **3ae** (see below for product **3ah**) was compared to the *E*/*Z* isomer ratio. Indeed, were the isomerization driven by simple thermodynamics, a correlation would be observed, as in equation (S1):

$$G_E - G_Z = -k_B T ln\left(\frac{E}{Z}\right) \quad \text{(S1)}$$

Results are summarized in **Figure S4**. Clearly, there is no visible correlation between free energy of the ground state and the isomer ratio. Moreover, the results are qualitatively contradicting what would be observed if the isomerization was driven by ground state thermodynamics. For all compound investigated, the *E* isomer more stable than the Z isomer, whereas all products show a higher concentration of the *Z* isomer over that of the *E* isomer. These results imply that the isomerization is not driven by ground-state thermodynamics.

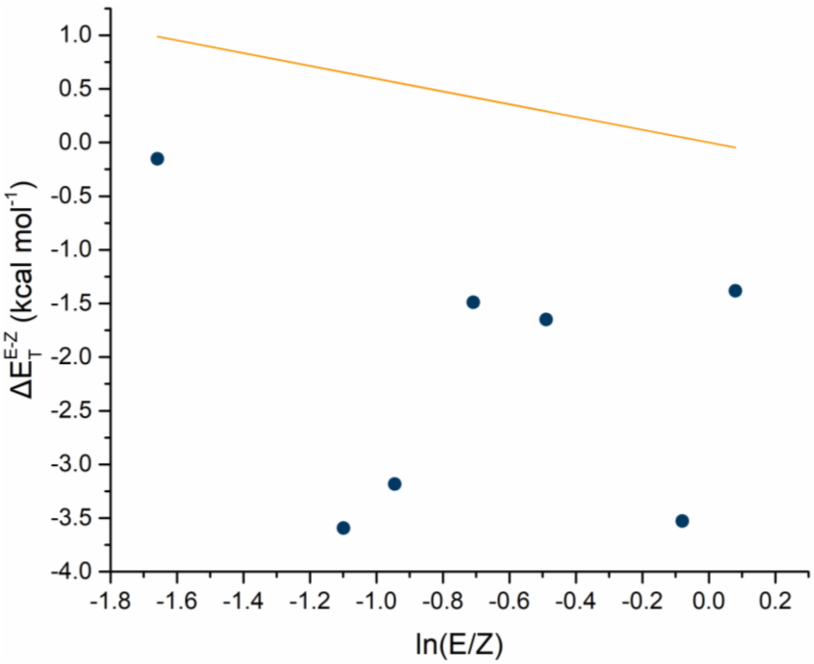


Figure S4. logarithmic isomer ratio plot against the calculated free energy difference between the E and Z isomer (G_E-G_Z). Expected free energy associated with an isomer ratio difference if associated with ground state thermodynamics (orange line). Substrate **3l** is omitted as ln(E/Z) is undefined (i.e., ln(0)).

Next, the photochemically-induced isomerization was investigated in the alkenyl-SCF_3 products. It is assumed in the following discussion that product isomerization, over that of the substrates, drives the ultimate *E*/*Z* ratio. This assumption is based on three arguments: 1) the isomer ratio suggests that photochemically-induced isomerization is a reversible process, 2) the reaction conversion is close to total, and 3) the illumination time is long enough for a steady-state *E*/*Z* ratio to be reached. The absolute value of E_T of the products relative to that of the photosensitizer determines the regime of the energy transfer. E_T gaps of **3b**, **3c**, **3i**, **3l**, **3p**, **3q**, **3ad**, **3ae,** and **3ah** in *E* and *Z* configurations are tabulated in **Table S1** and visually depicted in **Figure S5**. The experimental E_T of the photosensitizer ($Ir(ppy)_3$) is 55.8 kcal mol^{-1}. All substrates and products except **3ad** and **3ae** calculated E_T higher than that of $Ir(ppy)_3$, meaning that isomerization is limited by the energy transfer step between the photosensitizer and the substrate/product.[9] In this regime, the kinetic constant is given by equation S2:[8, 9]

$$k \propto e^{-\frac{E_{ST}-E_{ST,PS}}{k_B T}} \quad \text{(S2)}$$

On the other hand, for products **3ad** and **3ae** it is impossible to predict whether the E_T of $Ir(ppy)_3$ is inferior or superior to the E_T of the product, and both regimes could in principle be observed.

Table S1. Calculated E_T for select products.

Entry	Product	E/Z	Ln(E/Z)	E_T^E (kcal mol^{-1})	E_T^Z (kcal mol^{-1})	ΔE_T^{E-Z} (kcal mol^{-1})
1	**3b**	0.333	-1.099	69.37959	71.53458	-2.15499
2	**3c**	0.389	-0.944	66.38015	67.56071	-1.18056
3	**3i**	0.613	-0.490	63.10501	64.05321	-0.94820
4	**3l**	0.00	—	73.68754	85.77545	-12.08791
5	**3p**	0.190	-1.658	72.05703	75.98745	-3.93042
6	**3q**	0.493	-0.708	68.52923	70.44758	-1.91836
7	**3ad**	1.083	0.080	58.36361	58.50001	-0.1364
8	**3ae**	0.923	-0.080	58.42802	58.27706	0.15096
9	**3ah**	—	—	92.49419	94.27229	-1.7781

For **3b**, **3c**, **3i**, **3l**, **3p**, and **3q** the *E* and *Z* isomers comprise E_T above that of the Ir(ppy)$_3$, the directionality of the isomerization is dictated by **eq. S2**. Moreover, the energy difference between the E_T of the *E* and *Z* isomers (ΔE_T^{E-Z}, **Table S1**) translates in a difference in *E*-to-*Z* and *Z*-to-*E* rate constants, and eventually into the isomer ratio in the steady-state. As shown in **Figure S5**, products **3b**, **3c**, **3i**, **3l, 3p**, and **3q** all have a lower E_T in the *E* configuration, which translates in a higher *E*-to-*Z* rate constant. This is consistent with the observed isomer ratio driven towards the generation of *Z*. For products **3ad** and **3ae**, the model is inconclusive with regards to the limiting step, because within the error range of the model it is impossible to accurately determine the regime of the energy transfer. However, two cases may appear: 1) the regime is limited by diffusion. In this case, the diffusion of the photosensitizer does not depend on the configuration of the product or substrate, which explains the lack of selectivity, and 2) the regime is limited by the energy transfer step. In this case, the selectivity is driven by the difference in E_T of the *E* and *Z* configuration, as explained above. However, unlike **3b**, **3c**, **3i**, **3l, 3p**, and **3q**, products **3ad** and **3ae** exhibit no significant difference in the E_T of the *E* and *Z* configuration (**Figure S5**). Hence, the forward and backward rate constants are similar, which explains the lack of selectivity. Notably, the calculations mistakenly predict an *E*-to-*Z* isomerization for **3ah**. This is because the excitation energy of **3ah** (92-94 kcal mol^{-1}) is much higher than the excitation energy of all other products (58.4-71.5 kcal mol^{-1}), making the energy transfer with the photocatalyst slow (see **eq. S2**). Hence the isomerization does not occur, despite the favorable difference in E_T of the *E* and *Z* configuration. This high excitation energy in **3ah** correlates with the absence of aromatic moiety in the alkenyl-SCF_3 motif, as has been previously observed.[8-10]

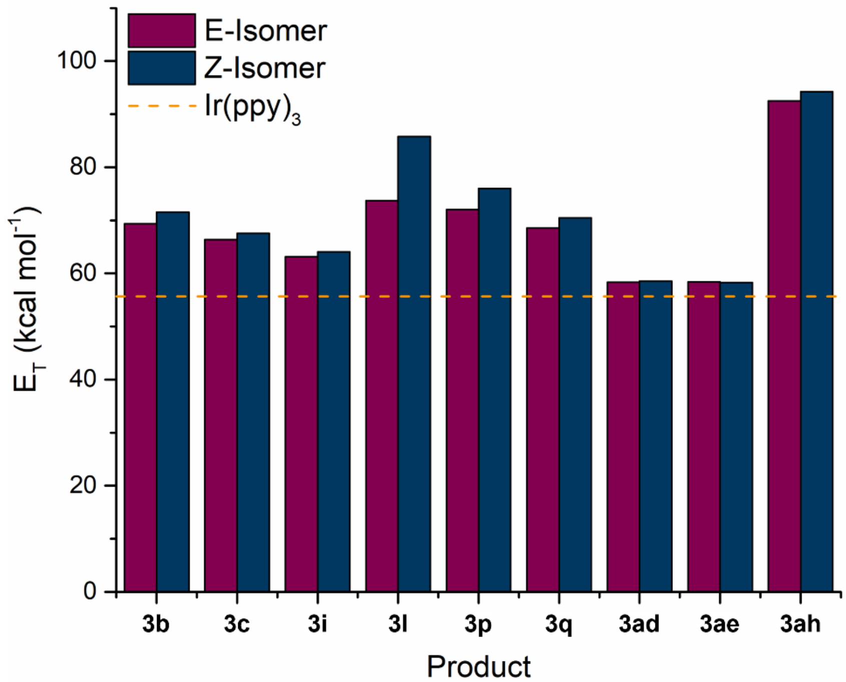


Figure S5. E_T of the investigated products in E (maroon) and Z (blue) configurations. The orange dashed line corresponds to the experimental E_T of the $Ir(ppy)_3$ (55.8 kcal mol^{-1})

Next, we sought to rationalize the observed *E*:*Z* isomer ratios. Clearly, the isomerization is not total, but instead reaches a photo-stationary state, wherein the rate of *E*-to-*Z* isomerization is equal to that of the *Z*-to-*E* isomerization. From a simplistic view, this can be modelled in accordance with equation S3:

$$k_{E-Z}[E] = k_{Z-E}[Z] \tag{S3}$$

In cases where the rate of reaction is dictated by the energy transfer step, this rearranges to the following expression, where the singlet-triplet gap of the photocatalyst vanishes, as demonstrated in equation S4:

$$\frac{[E]}{[Z]} = e^{-\frac{(E_{ST}^{Z}-E_{ST}^{E})}{k_B T}} \tag{S4}$$

As shown in **Figure S6**, the linear dependence of the logarithmic *E*:*Z* isomer ratio with respect to E_T is observed, confirming the importance of this physical value in the isomer ratio. However, the exact relationship expected in **eq. S4** is not observed, suggesting that the kinetics are more complex, as has been observed in previous studies.[8, 9] Elaborating a quantitative kinetic model to predict the isomer ratios of the photo stationary states is beyond the scope of this study. Instead, the following section focuses on explaining the trend based on chemical structure.

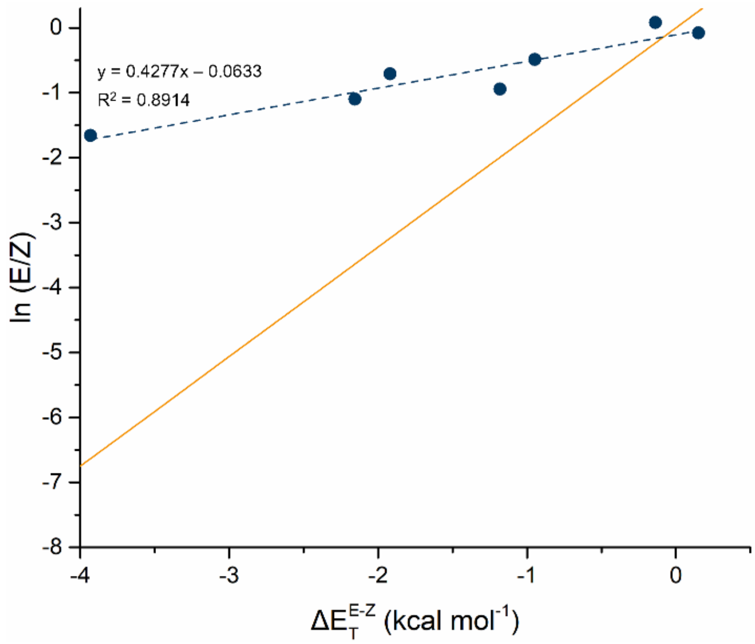


Figure S6. S-T gaps of the products plotted against the logarithmic isomer ratios (blue dots), linear regression (blue dotted line), and expected relationship between E_T and isomer ratios in **eq. S4** (orange line). Substrate **3l** and **3ah** are omitted as ln(E/Z) is undefined (i.e., ln(0)) and no isomerization is observed, respectively.

Differences in E_T between the *E* and *Z* configuration appears to drive the ultimate *E*:*Z* isomer ratios, so we sought to determine how chemical structure influences this phenomena. The steric hinderance between the *Z* isomer and the nearby aromatic ring is key in regulating the resultant isomer ratio. Indeed, these unfavourable interaction forces rotation of the bond connecting the ring to the double bond (θ, **Figure S7**). Consequently, this reduces the electronic delocalization of π electrons towards the arene. A known consequence of this phenomenon is to increase $\pi \rightarrow \pi^*$ excitation energy.[8] Because this is an effect particularly strong in the *Z* isomer, this means sterically bulky aromatic rings increase E_T which in turn leads to an asymmetric E:Z isomer distribution. This trend is highlighted in **Figure S7** and tabulated in **Table S2**. Five-membered ring are less bulky than their six-membered counterparts, and these are all much less sterically hindering than biphenyl; consequently, the dihedral increases along the series **3ad**, **3ae** < **3b**, **3c**, **3i** < **3o** < **3l**. A similar trend has been previously observed in the literature.[8, 9]

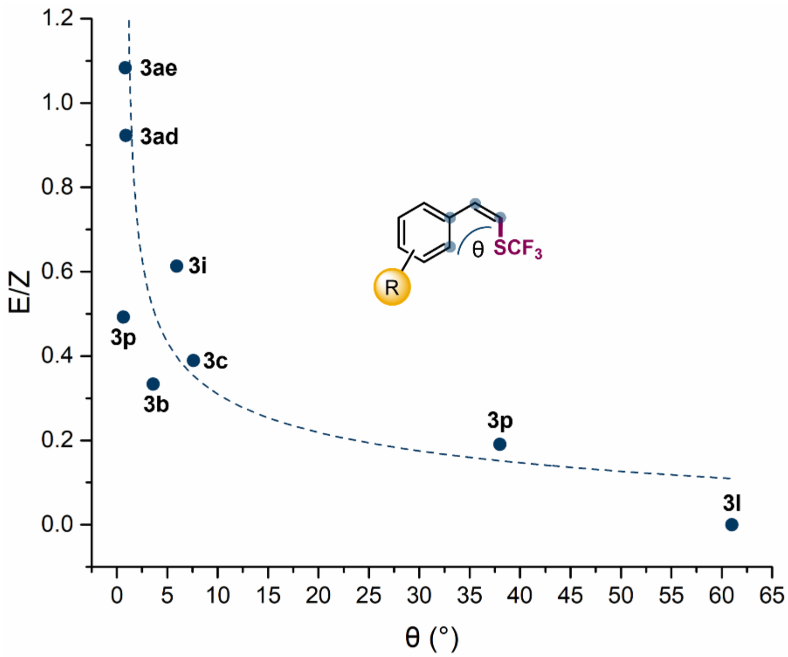


Figure S7. Evolution of the isomer ratio with the *Z* isomer dihedral angle (θ) in the studied products and logarithmic fit (dashed line).

Table S2. Calculated *θ* for select product *Z* isomers

Entry	Product	E/Z	Ln(E/Z)	*θ* (°)[a]
1	**3b**	0.333	-1.099	3.6
2	**3c**	0.389	-0.944	7.6
3	**3i**	0.613	-0.490	5.96
4	**3l**	0.00	—	61.0
5	**3p**	0.190	-1.658	38
6	**3q**	0.493	-0.708	0.67
7	**3ad**	1.083	0.080	0.83
8	**3ae**	0.923	-0.080	0.91

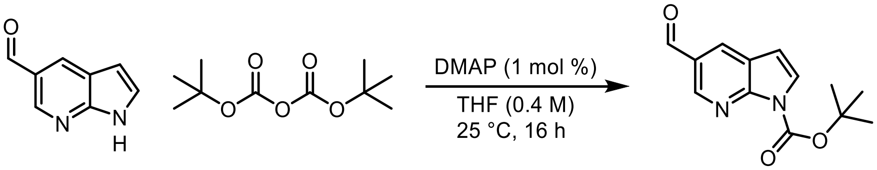
[a]Dihedral angle between (hetero)arene and alkene of product *Z* isomers

In conclusion, the computational study confirms that isomerization is driven by a photochemical effect rather than ground state thermodynamics. Due to the nature of the photochemical process and experimental conditions, this study assumes that the directionality of the isomerization is driven by the product rather than the substrate. Moreover, the difference in E_T of the *E* and *Z* isomer likely drives the reaction, except for **3ah**, which lacks a low-lying acceptor state for the energy transfer. Increasing steric hinderance between the aromatic ring and the alkenyl-SCF_3 increases the E_T of the *Z* isomer, thus driving the reaction towards generation of the *Z* isomer.

Experimental Data

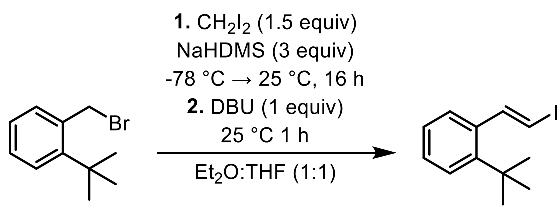
Alkenyl Iodides and Precursors

***Tert*-butyl 5-formyl-1H-pyrrolo[2,3-b]pyridine-1-carboxylate**



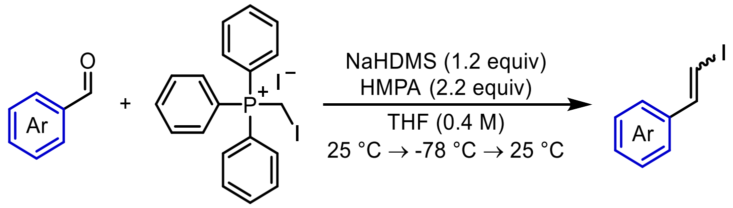
An oven dried 40 mL vial was charged with 1*H*-pyrrolo[2,3-*b*]pyridine-5-carbaldehyde (1.00 g, 6.84 mmol, 1.00 equiv), N,N-dimethylpyridin-4-amine (DMAP, 8.36 mg, 0.07 mmol, 0.01 equiv), and tetrahydrofuran (0.4 M). The solution was degassed and di-*tert*-butyl decarbonate (2M in THF, 3.76 ml, 7.53 mmol, 1.1 equiv) was added dropwise. The solution was stirred overnight and concentrated in vacuo. The resulting residue was purified by flash silica chromatography, elution gradient 0 to 100% EtOAc in hexanes. Product fractions were evaporated to dryness to afford *tert*-butyl 5-formyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (1.419 g, 84 %) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 10.16 (s, 1 H), 8.97 (d, *J* = 1.98 Hz, 1 H), 8.38 (d, *J* = 1.98 Hz, 1 H), 7.75 (d, *J* = 3.97 Hz, 1 H), 6.64 (d, *J* = 4.12 Hz, 1 H), 1.68 (s, 1 H)**.** **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 190.65, 150.88, 148.53, 147.42, 129.46, 128.77, 127.51, 123.19, 105.23, 85.10, 28.05. **HRMS (ESI-TOF) m/z:** $[M+H]^+$- *t*Bu$^+$ Calcd for $C_9H_7N_2O_3$ 191.0457; found 191.0460 (Δ = 1.6 ppm).

(*E*)-1-(*tert*-butyl)-2-(2-iodovinyl)benzene:



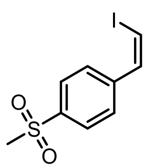
A solution of diiodomethane (CH_2I_2, 0.442 g, 1.65 mmol, 1.5 equiv) in THF (3.7 mL) and Et_2O (3.7 mL) was added dropwise to sodium bis(trimethylsilyl)amide (NaHDMS, 1M in THF, 3302 µl, 3.30 mmol, 3 equiv) at -78 °C. After 30 min, a solution of the 1-(bromomethyl)-2-(tert-butyl)benzene (250 mg, 1.10 mmol, 1 equiv) in THF (0.5 mL) was added in dropwise fashion. The reaction mixture was stirred at-78 °C and allowed to warm to room temperature slowly over 16 h. 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine (DBU, 0.168 g, 1.10 mmol) was added dropwise and stirred further for 1 h before DCM (15 mL) was added. The mixture was filtered through a plug of celite and the solvent removed under reduced pressure. The resulting residue was purified by flash silica chromatography, elution gradient 0 to 20% DCM in hexanes. Product fractions were evaporated to dryness to afford (*E*)-1-(*tert*-butyl)-2-(2-iodovinyl)benzene (222 mg, 70.5 %, *E*:*Z* = 1:0) as a clear oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.07 (d, J = 14.34 Hz, 1 H), 7.40 (d, J = 7.78 Hz, 1 H), 7.25 - 7.30 (m, 2 H), 7.13 - 7.23 (m, 1 H), 6.49 (d, J = 14.50 Hz, 1 H), 1.44 (s, 10 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 147.60, 146.79, 137.97, 129.47, 128.29, 126.30, 125.92, 77.23, 35.64, 31.32. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3099.34 (vw), 3058 (vw), 2965.19 (w), 2954.46 (w), 2906.73 (w), 2869.49 (w), 1597.04 (vw), 1583.3 (w), 1562.93 (vw), 1476.15 (w), 1457.58 (w), 1438.9 (w), 1395.75 (w), 1364.77 (w), 1270.04 (w), 1250.75 (w), 1196.39 (w), 1169.39 (m), 1126.12 (w), 1083.7 (w), 1052.84 (w), 950.15 (m), 927.73 (w), 756.09 (vs), 704.38 (m), 667.14 (w), 579.63 (w), 558.06 (w), 540.22 (w), 495.02 (w), 484.54 (w).

General Procedure A – Wittig Synthesis of Alkenyl Iodides:

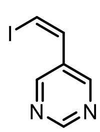


To a degassed solution of (iodomethyl)triphenylphosphonium iodide (1.0 mmol, 1 equiv) in THF (1 M), a 1 M solution of sodium bis(trimethylsilyl)amide in THF (NaHDMS, 1.1 mmol, 1.1 equiv) was added dropwise. The solution was cooled to -78 °C and hexamethylphosphoramide (HMPA, 2.2 mmol, 2.2 equiv) was added, the solution allowed to for 20 min, and a solution of (hetero)aromatic aldehyde (1.0 mmol, 1 equiv) in THF (0.5 mL) was added dropwise. The mixture was stirred at -78 °C for 5 min, and allowed to warm to room temperature with stirring for 1 h. The solution was diluted with DCM (25 mL), filtered over a pad of celite, concentrated in vacuo, and purified via silica gel flash chromatography to provide pure (hetero)aromatic alkenyl iodides.

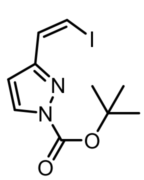
Alkenyl Iodide Data



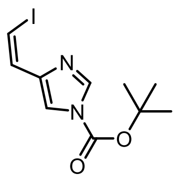
(*Z*)-1-(2-Iodovinyl)-4-(methylsulfonyl)benzene: Following general procedure A using 4-(methylsulfonyl)benzaldehyde (0.25 g, 1.36 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate) yielded (*Z*)-1-(2-iodovinyl)-4-(methylsulfonyl)benzene (305 mg, 73%, *E*:*Z* = 1:11.5) as a yellow waxy solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.84 - 7.89 (m, 2 H), 7.81 (t, *J* = 8.39 Hz, 1 H), 7.71 (d, *J* = 8.24 Hz, 2 H), 7.53 - 7.59 (m, 1 H), 7.50 (d, *J* = 8.39 Hz, 1 H), 7.40 (d, *J* = 8.70 Hz, 1 H), 7.32 (d, *J* = 8.70 Hz, 1 H), 7.08 (d, *J* = 15.11 Hz, 1 H), 6.74 (d, *J* = 8.85 Hz, 1 H), 3.01 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 148.62, 144.15, 142.79, 141.95, 141.71, 139.98, 139.51, 139.41, 139.32, 136.79, 132.69, 132.50, 128.76, 128.25, 127.48, 127.39, 127.13, 126.97, 126.90, 126.59, 126.34, 83.37, 81.98, 81.49, 81.36, 44.07, 44.00. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_9H_9IO_2S$ 308.9446; found 308.9444 (Δ = 0.6 ppm).



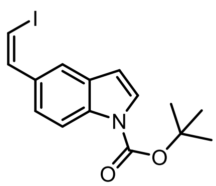
(*Z*)-5-(2-iodovinyl)pyrimidine: Following general procedure A using pyrimidine-5-carbaldehyde (1.50 g, 13.9 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (*Z*)-5-(2-iodovinyl)pyrimidine (1.98 g, 62%, *E*:*Z* = 1:32.3) as a yellow solid. **^{1}H NMR** (600 MHz, $CDCl_3$): δ ppm 9.15 (s, 1 H), 8.98 (s, 2 H), 7.30 (d, *J* = 8.85 Hz, 1 H), 6.92 (d, *J* = 8.85 Hz, 1 H). **^{13}C NMR** (151 MHz, $CDCl_3$): 157.75, 155.89, 132.49, 130.97, 85.34. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_6N_2IH_5$ 232.9575; found 232.9580 (Δ = 2.1 ppm).



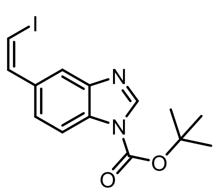
***Tert*-butyl (*Z*)-3-(2-iodovinyl)-1*H*-pyrazole-1-carboxylate**: Following general procedure A using *tert*-butyl 3-formyl-1*H*-pyrazole-1-carboxylate (1.50 g, 7.65 mmol), synthesized as previously reported,[13] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *tert*-butyl (*Z*)-3-(2-iodovinyl)-1*H*-pyrazole-1-carboxylate (2.12 g, 68%, *E*:*Z* = 1:5.7) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.05 (d, *J* = 2.90 Hz, 1 H), 7.98 (d, *J* = 2.44 Hz, 1 H), 7.55 (d, *J* = 9.00 Hz, 1 H), 7.48 (d, *J* = 15.11 Hz, 1 H), 7.31 (d, *J* = 2.90 Hz, 1 H), 7.04 (d, *J* = 15.11 Hz, 1 H), 6.74 (d, *J* = 9.00 Hz, 1 H), 1.64 (s, 8 H), 1.63 (d, *J* = 2.14 Hz, 4 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 153.25, 147.39, 136.62, 131.64, 131.64, 131.11, 130.44, 112.26, 107.69, 105.67, 85.79, 81.92, 81.89, 80.08, 27.91, 27.88. **HRMS (ESI-TOF) m/z:** $[M+H]^+$–Boc Calcd for $C_5H_5IN_2$ 220.9576; found 220.9586 (Δ = 4.5 ppm). **FT-IR (ATR)**: ν_{max} cm^{-1} 3134.53 (vw), 3069.08 (vw), 2980.49 (vw), 2933.97 (vw), 1747.46 (m), 1619.46 (vw), 1515.32 (w), 1476.27 (w), 1458.07 (vw), 1438.18 (w), 1394.43 (m), 1368.75 (m), 1355.73 (m), 1340.19 (w), 1293.78 (s), 1280.16 (s), 1256.18 (m), 1233.88 (m), 1139.62 (vs), 1054.41 (m), 967.87 (s), 838.41 (m), 779.11 (m), 765.01 (s), 647.13 (w), 581.44 (w), 543.23 (w), 528.17 (w), 498.28 (w), 435.12 (m).



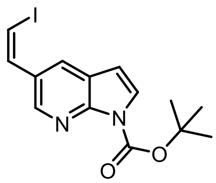
***Tert*-butyl (*Z*)-4-(2-iodovinyl)-1*H*-imidazole-1-carboxylate**: Following general procedure A using *tert*-butyl 4-formyl-1*H*-imidazole-1-carboxylate (1.50 g, 7.65 mmol), synthesized as previously reported,[14] as the substrate. Purification via flash chromatography (Hexane:DCM gradient) yielded *tert*-butyl (*Z*)-4-(2-iodovinyl)-1*H*-imidazole-1-carboxylate (2.13 g, 87%, *E*:*Z* = 0:1) as a yellow solid. ^{1}**H NMR** (600 MHz, DMSO-d_6): δ ppm 8.24 (s, 1 H), 8.15 (s, 1 H), 7.43 (d, *J* = 8.85 Hz, 1 H), 6.74 (d, *J* = 8.85 Hz, 1 H), 1.57 (s, 9 H). ^{13}**C NMR** (151 MHz, DMSO-d_6): δ ppm 146.40, 139.58, 136.68, 131.82, 114.89, 85.79, 80.47, 27.32. **HRMS (ESI-TOF) m/z:** $[M-H]^-$ Calcd for $C_{10}N_2O_2IH_{12}$ 318.9943; found 318.9946 (Δ = 0.9 ppm).



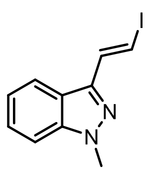
***Tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-indole-1-carboxylate**: Following general procedure A using *tert*-butyl 5-formyl-1*H*-indole-1-carboxylate (1.50 g, 6.12 mmol), synthesized as previously reported,[15] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-indole-1-carboxylate (1.38 g, 61%, *E*:*Z* = 1:24) as a yellow oil. ^{1}**H NMR** (500 MHz, $CDCl_3$): δ ppm 8.14 (br d, *J* = 8.24 Hz, 1 H), 7.90 (s, 1 H), 7.62 (br d, *J* = 3.51 Hz, 1 H), 7.56 (d, *J* = 8.54 Hz, 1 H), 7.42 (d, *J* = 8.54 Hz, 1 H), 6.61 (d, *J* = 3.81 Hz, 1 H), 6.54 (d, *J* = 8.54 Hz, 1 H), 1.70 (s, 9 H), 1.69 (br s, 2 H). ^{13}**C NMR** (126 MHz, $CDCl_3$): δ ppm 149.60, 138.87, 134.91, 131.27, 130.33, 128.10, 126.55, 125.05, 124.92, 120.83, 115.12, 114.81, 107.46, 106.99, 83.86, 78.09, 28.18, 28.15. **HRMS (ESI-TOF) m/z:** $[M+H]^+$–Boc Calcd for $C_{10}H_8IN$ 269.9780; found 269.9764 (Δ = 5.9 ppm). **FT-IR (ATR)**: ν_{max} cm^{-1} 3152.01 (vw), 3115.73 (vw), 3063.3 (vw), 2977.36 (w), 2931.44 (w), 1728.3 (vs), 1599.81 (vw), 1574.86 (vw), 1535.69 (w), 1462.16 (m), 1436.37 (w), 1366.58 (vs), 1344.4 (s), 1334.04 (s), 1320.66 (vs), 1250.99 (s), 1220.62 (m), 1215.07 (m), 1193.38 (m), 1157.7 (vs), 1136.61 (vs), 1116.48 (s), 1078.75 (s), 1039.94 (m), 1021.14 (s), 886.87 (w), 852.52 (w), 840.34 (m), 822.75 (m), 762.12 (s), 728.25 (m), 704.63 (m), 658.94 (w), 599.76 (m), 572.16 (w), 528.05 (w), 490.08 (w), 448.86 (w), 415.23 (w)



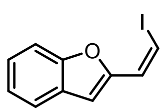
***Tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-benzo[*d*]imidazole-1-carboxylate**: Following general procedure A using *tert*-butyl 5-formyl-1*H*-benzo[*d*]imidazole-1-carboxylate (1.50 g, 6.09 mmol), synthesized as previously reported,[16] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-benzo[*d*]imidazole-1-carboxylate (1.56 g, 69%, *E*:*Z* = 0:1) as a colorless oil which solidified on standing. ^{1}**H NMR** (500 MHz, $CDCl_3$): δ ppm 8.46 (d, *J* = 11.60 Hz, 1 H), 8.33 (s, 1 H), 8.10 (s, 1 H), 7.98 (br d, *J* = 8.39 Hz, 1 H), 7.77 (d, *J* = 8.39 Hz, 1 H), 7.62 (br d, *J* = 8.39 Hz, 1 H), 7.56 (br d, *J* = 8.39 Hz, 1 H), 7.44 (d, *J* = 4.58 Hz, 1 H), 7.42 (d, *J* = 4.58 Hz, 1 H), 6.62 (t, *J* = 8.16 Hz, 1 H), 1.71 (s, 9 H). ^{13}**C NMR** (126 MHz, $CDCl_3$): δ ppm 147.95 147.85, 144.03, 143.97, 142.91, 142.64, 138.74, 138.39, 133.90, 133.12, 131.17, 125.86, 125.06, 120.35, 120.25, 114.08, 113.98, 85.83, 85.76, 79.65, 79.49, 28.14, 28.03. **HRMS (ESI-TOF) m/z:** $[M+H]^+$–*t*Bu Calcd for $C_{10}H_7IN_2O_2$ 314.9631; found 314.9635 (Δ = 1.3 ppm). **FT-IR (ATR)**: ν_{max} cm^{-1} 3108.62 (vw), 3061.13 (vw), 2983.87 (w), 2976.64 (w), 2933.97 (vw), 1739.75 (vs), 1618.13 (w), 1511.7 (w), 1485.43 (w), 1477.47 (w), 1438.06 (w), 1428.41 (m), 1364.41 (vs), 1349.47 (m), 1323.79 (m), 1310.17 (s), 1287.03 (m), 1278.59 (m), 1255.21 (s), 1245.33 (s), 1205.07 (m), 1153.48 (vs), 1138.54 (vs), 1127.21 (s), 1107.08 (m), 1061.4 (s), 1033.68 (m), 945.08 (m), 880.24 (m), 842.03 (s), 832.51 (s), 826.96 (s), 812.5 (m), 764.05 (vs), 749.22 (m), 715.83 (m), 664.97 (m), 621.7 (s), 593.5 (m), 583.61 (m), 529.98 (m), 452.84 (m), 411.25 (m).



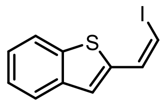
***Tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate**: Following general procedure A using *tert*-butyl 5-formyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (1.00 g, 4.06 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (872 mg, 58%, *E*:*Z* = 1:24) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.63 (d, *J* = 1.98 Hz, 1 H), 8.32 (d, *J* = 1.98 Hz, 1 H), 7.66 (d, *J* = 4.12 Hz, 1 H), 7.43 (d, *J* = 8.54 Hz, 1 H), 6.89 (d, *J* = 14.95 Hz, 1 H), 6.68 (d, *J* = 8.70 Hz, 1 H), 6.55 (d, *J* = 3.97 Hz, 1 H), 1.68 (s, 9 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 147.77, 147.74, 145.94, 136.01, 132.38, 127.89, 127.78, 127.28, 122.29, 104.68, 104.22, 84.23, 80.65, 28.08. **HRMS (ESI-TOF) m/z:** $[M+H]^+$–*t*Bu Calcd for $C_{10}H_7IN_2O_2$ 314.9631; found 314.9624 (Δ = 2.2 ppm). **FT-IR (ATR)**: ν_{max} cm^{-1} 3223.85 (vw), 3194.8 (vw), 3164.3 (vw), 3111.99 (vw), 3042.09 (w), 2977.48 (w), 2930.84 (vw), 1744.57 (s), 1599.09 (w), 1588.24 (vw), 1530.5 (w), 1474.46 (m), 1385.51 (s), 1368.15 (m), 1318.25 (s), 1310.17 (s), 1250.39 (s), 1204.11 (m), 1193.62 (m), 1152.76 (vs), 1125.88 (s), 1092.49 (s), 1044.64 (m), 1027.41 (s), 969.79 (m), 907.24 (s), 755.01 (s), 717.64 (vs), 669.31 (m), 641.59 (m), 607.12 (s).



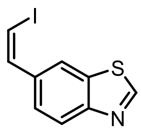
(*Z*)-3-(2-iodovinyl)-1-methyl-1*H*-indazole: Following general procedure A using 1-methyl-1*H*-indazole-3-carbaldehyde (1.00 g, 6.24 mmol), as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (*E*)-3-(2-iodovinyl)-1-methyl-1*H*-indazole (1.28 mg, 72%, *E*:*Z* = 1:0) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.82 (d, *J* = 8.09 Hz, 1 H), 7.75 (d, *J* = 15.11 Hz, 1 H), 7.36 - 7.44 (m, 2 H), 7.22 (d, *J* = 7.63 Hz, 1 H), 7.19 (d, *J* = 14.95 Hz, 1 H), 4.05 (s, 2 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 142.02, 140.95, 136.46, 126.58, 121.38, 121.30, 120.32, 109.26, 77.93, 35.58. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_9IN_2$ 284.9889; found 284.9892 (Δ = 1.1 pm).



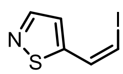
(*Z*)-2-(2-iodovinyl)benzofuran: Following general procedure A using benzofuran-2-carbaldehyde (1.00 g, 6.84 mmol) as the substrate. Purification via flash chromatography (Hexane:DCM gradient) yielded (*Z*)-2-(2-iodovinyl)benzofuran (1.39 g, 75%, *E*:*Z* = 1:2.3) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.65 (d, *J* = 7.78 Hz, 2 H), 7.54 - 7.58 (m, 3 H), 7.47 - 7.54 (m, 5 H), 7.45 (d, *J* = 8.24 Hz, 1 H), 7.30 - 7.39 (m, 5 H), 7.19 - 7.30 (m, 4 H), 7.12 (d, *J* = 14.80 Hz, 1 H), 6.76 (d, *J* = 9.16 Hz, 2 H), 6.59 (s, 1 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 154.85, 154.20, 153.95, 153.29, 132.99, 128.50, 128.19, 127.85, 125.28, 125.19, 123.09, 123.09, 121.52, 121.36, 111.20, 111.02, 106.81, 104.85, 79.69, 78.74. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_7IO$ 270.9620; found 270.9622 (Δ = 0.7 ppm).



(*Z*)-2-(2-iodovinyl)benzo[*b*]thiophene: Following general procedure A using benzo[*b*]thiophene-2-carbaldehyde (1.00 g, 6.16 mmol) as the substrate. Purification via flash chromatography (Hexane:DCM gradient) yielded (*Z*)-2-(2-iodovinyl)benzo[*b*]thiophene (1.23 g, 70%, *E*/*Z* = 1:2.2) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.86 (dd, *J* = 7.48, 0.61 Hz, 1 H), 7.75 - 7.82 (m, 2 H), 7.70 - 7.74 (m, 1 H), 7.62 (s, 1 H), 7.59 (s, 1 H), 7.29 - 7.44 (m, 3 H), 7.15 (s, 1 H), 6.80 (d, *J* = 14.65 Hz, 1 H), 6.64 (d, *J* = 8.70 Hz, 1 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 142.35, 139.78, 139.44, 139.22, 139.01, 138.42, 138.24, 133.13, 127.38, 125.21, 124.70, 124.60, 123.97, 123.75, 122.87, 122.25, 122.22, 78.43, 77.65. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_7IS$ 286.9391; found 286.9390 (Δ = 0.3 ppm).

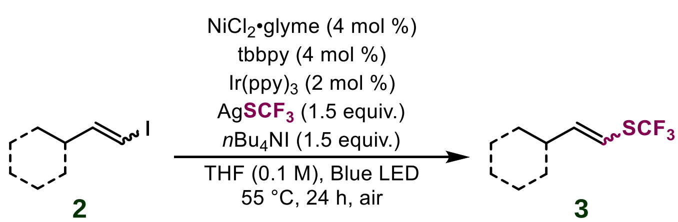


(*Z*)-6-(2-iodovinyl)benzo[*d*]thiazole: Following general procedure A using benzo[*d*]thiazole-6-carbaldehyde (1.00 g, 6.13 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (*Z*)-6-(2-iodovinyl)benzo[*d*]thiazole (1.55 g, 73%, *E*:*Z* = 1/19) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 9.03 (s, 1 H), 8.31 (s, 1 H), 8.14 (d, *J* = 8.54 Hz, 1 H), 7.73 (d, *J* = 8.54 Hz, 1 H), 7.46 (d, *J* = 8.70 Hz, 1 H), 6.70 (d, *J* = 8.54 Hz, 1 H).**^{13}C NMR** (151 MHz, DMSO-d_6): **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 154.78, 152.98, 137.99, 134.37, 133.77, 127.05, 123.50, 123.28, 78.13. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for C_9H_6INS 287.9344; found 287.9350 (Δ = 2.1 ppm).



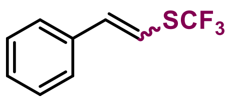
(*Z*)-5-(2-iodovinyl)isothiazole: Following general procedure A using isothiazole-5-carbaldehyde (0.250 g, 2.21 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (*Z*)-5-(2-iodovinyl)isothiazole (251 mg, 48%, *E*:*Z* = 1:7.3) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.62 (s, 1 H), 8.47 (s, 1 H), 8.39 (d, *J* = 0.92 Hz, 1 H), 7.85 (d, *J* = 8.54 Hz, 1 H), 7.39 (s, 1 H), 7.31 (d, *J* = 0.61 Hz, 1 H), 6.99 (d, *J* = 8.54 Hz, 1 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 163.81, 161.76, 155.97, 155.83, 142.55, 131.05, 125.92, 125.44, 85.46. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for C_5H_4INS 237.9187; found 237.9188 (Δ = 0.4 ppm).

Trifluoromethylthiolation of Alkenyl Iodides

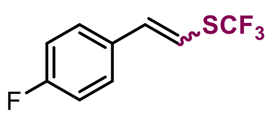


General Procedure B – Trifluoromethylthiolation Examples with NMR Yields: To a vial containing ((trifluoromethyl)thio)silver ($AgSCF_3$, 94.0 mg, 0.45 mmol), tetrabutylammonium iodide ($n Bu_4NI$, 166 mg, 0.45 mmol), tris(2-(pyridin-2-yl)phenyl)iridium ($Ir(ppy)_3$, 3.93 mg, 6.00 µmol), $NiCl_2$ • glyme (2.64 mg, 12.0 µmol), 4,4'-di-*tert*-butyl-2,2'-bipyridine (tbbpy, 3.22 mg, 12.0 µmol) and alkenyl iodide (0.30 mmol) was added 3.0 mL of THF and the reaction irradiated at 440 nm with a blue kessil LED stirring in a EvoluChem™ PhotoRedOx Box for 24 h with no cooling fan (55°C). 0.3 mmol, 34.62 µL of hexafluorobenzene referenced to –163.0 ppm was added as an internal standard and an aliquot was filtered and analyzed by ^{19}F NMR in DMSO-d_6.

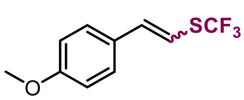
General Procedure C – Trifluoromethylthiolation Examples with Isolated Yields: To a vial containing ((trifluoromethyl)thio)silver ($AgSCF_3$, 94.0 mg, 0.45 mmol), tetrabutylammonium iodide (nBu_4NI, 166 mg, 0.45 mmol), tris(2-(pyridin-2-yl)phenyl)iridium ($Ir(ppy)_3$, 3.93 mg, 6.00 µmol), $NiCl_2$ • glyme (2.64 mg, 12.0 µmol), 4,4'-di-*tert*-butyl-2,2'-bipyridine (tbbpy, 3.22 mg, 12.0 µmol) and alkenyl iodide (0.30 mmol) was added 3.0 mL of THF and the reaction irradiated at 440 nm with a blue kessil LED stirring in a EvoluChem™ PhotoRedOx Box for 24 h with no cooling fan (55°C). After completion the reaction was concentrated in vacuo to approximately 1 mL and diluted with pentane, or ethyl acetate for more polar compounds. The reaction was then filtered to remove solids, concentrated, and purified via silica gel flash chromatography to provide the final product.



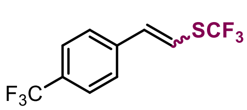
Styryl(trifluoromethyl)sulfane (3a): Following general procedure B using (*E*)-(2-iodovinyl)benzene (69 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 82% NMR yield of styryl(trifluoromethyl)sulfane (*E*:*Z* = 1:2.7). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -42.24, -42.73. The NMR data accords with the reference.[18]



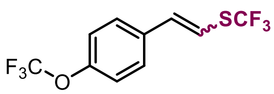
(4-Fluorostyryl)(trifluoromethyl)sulfane (3b): Following general procedure B using (*E*)-(2-iodovinyl)benzene (69 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 88% NMR yield of (4-fluorostyryl)(trifluoromethyl)sulfane (*E*:*Z* = 1:3). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -42.23, -42.62, -111.69, -112.43. The NMR data accords with the reference.[19]



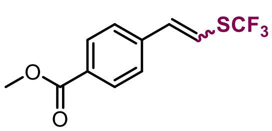
(4-Methoxystyryl)(trifluoromethyl)sulfane (3c): Following general procedure C using (*E*)-1-(2-iodovinyl)-4-methoxybenzene (78 mg, 0.3 mmol), synthesized as previously reported,[20] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (4-methoxystyryl)(trifluoromethyl)sulfane (51 mg, 73%, *E*:*Z* = 1:2.6) as a pale yellow oil. **^1H NMR** (500 MHz, $CDCl_3$): δ ppm 7.37 (d, *J*=8.70 Hz, 1 H), 7.34 (d, *J* = 8.70 Hz, 2 H), 7.02 (d, *J* = 15.11 Hz, 1 H), 6.94 - 6.98 (m, 2 H), 6.92 (d, *J* = 8.85 Hz, 1 H), 6.82 (d, *J* = 10.38 Hz, 1 H), 6.61 (d, *J* = 15.26 Hz, 1 H), 6.30 (d, *J*=10.38 Hz, 1 H), 3.84 - 3.87 (m, 4 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -43.15, -43.28. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 160.54, 159.51, 142.19, 142.19, 132.30, 132.30, 130.94, 130.21, 130.13, 128.49, 128.32, 127.87, 127.71, 129.62, 114.23, 114.15, 113.94, 111.16, 108.37, 55.23, 55.20. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_{10}F_3OS$ 235.0404; found 235.0403 (Δ = 0.4 ppm).



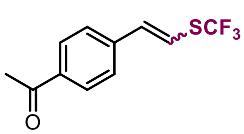
(Trifluoromethyl)(4-(trifluoromethyl)styryl)sulfane (3d): Following general procedure C using (*E*)-1-(2-iodovinyl)-4-(trifluoromethyl)benzene (89 mg, 0.3 mmol), synthesized as previously reported,[20] as the substrate. Purification via flash chromatography (Hexane) yielded (trifluoromethyl)(4-(trifluoromethyl)styryl)sulfane (62 mg, 76%, *E*:*Z* = 1:2.1) as a pale yellow oil. **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.65 (m, 3 H), 7.50 (br d, *J* = 7.93 Hz, 1 H), 7.45 (br d, *J* = 7.93 Hz, 2 H), 6.99 (m, 1 H), 6.89 (br d, *J* = 5.80 Hz, 1 H), 6.86 (s, 1 H), 6.56 (br d, *J* = 10.53 Hz, 1 H) **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.44, -43.05, -62.83, -62.84. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 138.42, 138.39, 137.81, 130.93, 130.66, 130.62, 130.53, 130.20, 129.94, 128.83, 128.21, 128.08, 126.88, 125.85, 125.63, 125.55, 125.45, 125.00, 122.84, 116.75, 116.72, 116.69, 115.40, 115.37.



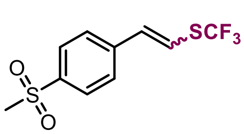
(4-(trifluoromethoxy)styryl)(trifluoromethyl)sulfanesulfane (3e): Following general procedure C using (*E*)-1-(2-iodovinyl)-4-(trifluoromethoxy)benzene (94 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (4-(trifluoromethoxy)styryl)(trifluoromethyl)sulfane (71 mg, 82%, *E*/*Z* = 1:2.7) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.43 (d, *J* = 8.54 Hz, 1 H), 7.39 (d, *J* = 8.54 Hz, 2 H), 7.25 (m, 3 H), 6.99 (d, *J* =1 5.41 Hz, 1 H), 6.83 (d, *J* = 10.53 Hz, 1 H), 6.76 (d, *J* = 15.41 Hz, 1 H), 6.47 (d, *J* = 10.68 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.76, -43.17, -57.95, -57.98. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 148.81, 138.93, 133.78, 133.67, 130.84, 130.84, 130.14, 128.15, 127.86, 121.51, 121.26, 121.26, 120.94, 119.46, 114.97, 113.17.



Methyl 4-(2-((trifluoromethyl)thio)vinyl)benzoate (3f): Following general procedure C using methyl (*E*)-4-(2-iodovinyl)benzoate (86 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded methyl 4-(2-((trifluoromethyl)thio)vinyl)benzoate (40 mg, 51%, *E*:*Z* = 1:1.7) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.05 - 8.08 (m, 2 H), 8.03 (d, *J* = 8.39 Hz, 1 H), 7.43 - 7.49 (m, 2 H), 7.40 (d, *J* = 8.24 Hz, 2 H), 6.96 - 7.02 (m, 1 H), 6.89 (s, 1 H), 6.84 - 6.89 (m, 1 H), 6.53 (d, *J* = 10.68 Hz, 1 H), 3.94 (s, 5 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.37, -43.05. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 166.49, 166.49, 139.32, 139.20, 138.26, 138.26, 130.86, 130.34, 130.13, 129.82, 128.51, 126.56, 116.49, 116.46, 116.43, 115.17, 115.14, 52.19.

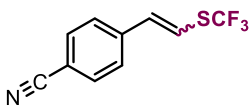


1-(4-(2-((trifluoromethyl)thio)vinyl)phenyl)ethan-1-one (3g): Following general procedure C using (E)-1-(4-(2-iodovinyl)phenyl)ethan-1-one (82 mg, 0.3 mmol), synthesized as previously reported,[21] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 1-(4-(2-((trifluoromethyl)thio)vinyl)phenyl)ethan-1-one (35 mg, 47%, *E*:*Z* = 1:1.6) as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.97 (d, *J* = 8.24 Hz, 2 H), 7.94 (d, *J* = 8.24 Hz, 2 H), 7.46 (d, *J* = 8.24 Hz, 2 H), 7.41 (d, *J* = 8.24 Hz, 2 H), 6.94 - 7.00 (m, 1 H), 6.88 (d, *J* = 15.41 Hz, 1 H), 6.85 (s, 1 H), 6.53 (d, *J* = 10.68 Hz, 1 H), 2.60 (s, 3 H), 2.60 (s, 2 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.36, -43.06. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 197.17, 197.17, 139.41, 139.26, 137.98, 137.98, 137.04, 136.29, 130.75, 128.84, 128.69, 128.52, 128.45, 126.72, 116.58, 115.33, 26.50. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_9F_3OS$ 247.0404; found 247.0408 (Δ = 0.6 ppm).

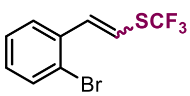


(4-(methylsulfonyl)styryl)(trifluoromethyl)sulfane (3h): Following general procedure C using (*E*)-1-(2-iodovinyl)-4-(methylsulfonyl)benzene (92 mg, 0.3 mmol), synthesized as previously reported,[22] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (4-(methylsulfonyl)styryl)(trifluoromethyl)sulfane (50 mg, 59%, *E*:*Z* = 1:2) as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.84 - 7.96 (m, 3 H), 7.63 (d, *J* = 8.54 Hz, 1 H), 7.54 (d, *J* = 8.39 Hz, 1 H), 7.49 (d, *J* = 8.24 Hz, 2 H), 6.94 (d, *J* = 5.34 Hz, 1 H), 6.87 (d, *J* = 10.68

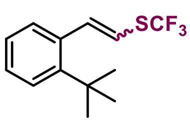
Hz, 1 H), 6.59 (d, *J* = 10.68 Hz, 1 H), 3.05 (s, 3 H), 3.04 (s, 2 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.16, -42.87. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 142.74, 140.28, 140.25, 140.13, 140.02, 139.63, 136.34, 135.07, 132.77, 130.25, 129.97, 129.97, 129.20, 127.96, 127.55, 126.82, 117.83, 116.99, 44.30. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_9F_3O_2S_2$ 283.0074; found 283.0081 (Δ = 2.5 ppm).



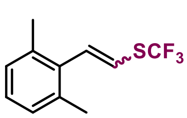
4-(2-((Trifluoromethyl)thio)vinyl)benzonitrile (3i): Following general procedure B using methyl (*E*)-4-(2-iodovinyl)benzonitrile (77 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 80% NMR yield of 4-(2-((trifluoromethyl)thio)vinyl)benzonitrile (*E*:*Z* = 1:1.6). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -41.66, -42.51. The NMR data accords with the reference.[18]



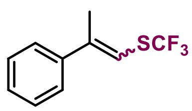
(2-Bromostyryl)(trifluoromethyl)sulfane (3j): Following general procedure C using (*E*)-1-bromo-2-(2-iodovinyl)benzene (93 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. Purification via flash chromatography (Hexane) yielded (2-bromostyryl)(trifluoromethyl)sulfane (65 mg, 77%, *E*:*Z* = 1:5.3) as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.64 (d, *J*=8.24 Hz, 1 H), 7.60 (d, *J*=8.09 Hz, 1 H), 7.52 (dd, *J*=7.78, 1.53 Hz, 1 H), 7.29 - 7.39 (m, 2 H), 7.16 - 7.24 (m, 1 H), 7.02 (br d, *J*=10.22 Hz, 1 H), 6.76 (d, *J*=15.26 Hz, 1 H), 6.52 - 6.58 (m, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.43, -42.72. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 138.11, 135.10, 134.98, 133.23, 133.01, 132.04, 132.04, 130.69, 130.17, 129.78, 129.51, 128.24, 127.70, 127.25, 127.22, 123.79, 123.61, 116.60, 115.30.



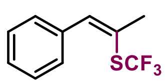
(2-(*Tert*-butyl)styryl)(trifluoromethyl)sulfane (3k): Following general procedure C using (*E*)-1-(tert-butyl)-2-(2-iodovinyl)benzene (86 mg, 0.3 mmol) as the substrate. Purification via flash chromatography (Hexane) yielded (2-bromostyryl)(trifluoromethyl)sulfane (42.2 mg, 54%, *E*:*Z* = 1:24) as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.75 (d, *J* = 7.93 Hz, 1 H), 7.48 (td, *J* = 8.24, 1.07 Hz, 2 H), 7.42 (d, *J* = 9.77 Hz, 1 H), 7.29 - 7.37 (m, 2 H), 7.17- 7.28 (m, 2 H), 7.09 (d, *J* = 7.32 Hz, 1 H), 6.68 (d, *J* = 8.09 Hz, 1 H), 6.46 (d, *J* = 9.77 Hz, 1 H), 1.42 (s, 9 H), 1.41 (s, 5 H). **^{19}F NMR** (471 MHz, $CDCl_3$ ppm -42.43, -42.50. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 148.26, 147.83, 143.50, 137.83, 136.80, 134.43, 131.43, 130.85, 128.65, 128.15, 126.31, 125.99, 125.99, 125.85, 115.37, 84.56, 35.83, 35.83, 30.78, 30.66. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3101.27 (vw), 3059.68 (vw), 2966.03 (w), 2908.78 (vw), 2871.17 (vw), 1598.12 (vw), 1478.56 (w), 1462.65 (vw), 1439.5 (vw), 1395.03 (vw), 1364.29 (w), 1298.12 (w), 1254.37 (vw), 1153.72 (w), 1110.09 (vs), 1083.21 (m), 1052.12 (w), 947.98 (vw), 880.12 (vw), 853.96 (vw), 836.49 (vw), 818.77 (vw), 756.69 (m), 715.11 (w), 640.38 (vw), 554.56 (vw), 532.39 (vw), 515.63 (w), 478.03 (w).



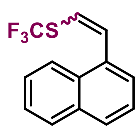
(2,6-dimethylstyryl)(trifluoromethyl)sulfane (3l): Following general procedure B using 2-(2-iodovinyl)-1,3-dimethylbenzene (73 mg, 0.3 mmol), synthesized as previously reported,[23] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 40% NMR yield of 2-(2-iodovinyl)-1,3-dimethylbenzene (*E*:*Z* = 0:1). **^{19}F NMR** (471 MHz, DMSO-d_6): δ ppm -41.35. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 2951.57 (w), 2930.72 (m), 2867.92 (w), 2853.58 (w), 1709.86 (m), 1607.52 (w), 1467.23 (w), 1437.7 (w), 1408.77 (w), 1383.58 (w), 1379.48 (w), 1369.72 (w), 1319.45 (w), 1279.08 (m), 1255.09 (w), 1177.11 (m), 1160.96 (m), 1145.41 (m), 1106.48 (vs), 1027.53 (w), 1016.44 (w), 996.07 (w), 979.68 (w), 958.58 (w), 948.22 (w), 938.94 (w), 906.64 (m), 853 (w), 838.05 (w), 807.8 (w), 778.27 (w), 769.23 (w), 753.44 (w), 733.43 (s), 668.95 (w), 649.9 (w), 625.8 (vw), 524.79 (w).



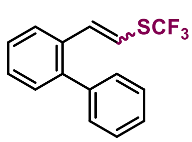
(2-Phenylprop-1-en-1-yl)(trifluoromethyl)sulfane (3m): Following general procedure B using (*E*)-(1-iodoprop-1-en-2-yl)benzene (77 mg, 0.3 mmol), synthesized as previously reported,[24] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 81% NMR yield of (2-phenylprop-1-en-1-yl)(trifluoromethyl)sulfane (*E*:*Z* = 1/13.3). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -41.90 (s, 3F), -42.63 (s, 3F). The NMR data accords with the reference.[18]



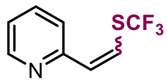
(1-Phenylprop-1-en-2-yl)(trifluoromethyl)sulfane (3n): Following general procedure B using (*Z*)-(2-iodoprop-1-en-1-yl)benzene (73 mg, 0.3 mmol), synthesized as previously reported,[25] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 82% NMR yield of (1-phenylprop-1-en-2-yl)(trifluoromethyl)sulfane (E:Z = 1:1.5). **^{19}F NMR** (471 MHz, DMSO-d_6): δ ppm -37.96, -40.58. The NMR data accords with the reference.[18]



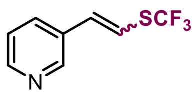
(2-(naphthalen-1-yl)vinyl)(trifluoromethyl)sulfane (3o): Following general procedure C using (*Z*)-1-(2-iodovinyl)naphthalene (84 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. Purification via flash chromatography (Hexane) yielded (2-(naphthalen-1-yl)vinyl)(trifluoromethyl)sulfane (69 mg, 90%, *E*:*Z* = 1:2.9) as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.09 (d, *J* = 8.39 Hz, 1 H), 7.84 - 7.99 (m, 4 H), 7.80 (d, *J* = 15.11 Hz, 1 H), 7.37 - 7.66 (m, 7 H), 6.84 (d, *J* = 15.11 Hz, 1 H), 6.72 (d, *J* = 10.07 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.55, -42.75. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 138.37, 133.55, 133.55, 133.35, 132.72, 132.06, 131.02, 130.90, 130.87, 130.79, 130.73, 129.53, 129.01, 128.66, 128.61, 126.71, 126.52, 126.26, 126.19, 126.20, 125.47, 125.08, 124.56, 124.10, 123.35, 117.26, 114.55.



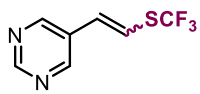
(2-([1,1'-biphenyl]-2-yl)vinyl)(trifluoromethyl)sulfane (3p): Following general procedure C using (E)-2-(2-iodovinyl)-1,1'-biphenyl (92 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. Purification via flash chromatography (Hexane) yielded (2-([1,1'-biphenyl]-2-yl)vinyl)(trifluoromethyl)sulfane (66 mg, 79%, *E*:*Z* = 1:5.3) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.65 (dd, *J* = 7.32, 1.68 Hz, 1 H), 7.37 - 7.54 (m, 11 H), 7.10 (d, *J* = 15.26 Hz, 1 H), 6.82 (dd, *J* = 10.22, 0.92 Hz, 1 H), 6.75 (d, *J* = 15.26 Hz, 1 H), 6.43 (d, *J* = 10.22 Hz, 1 H), **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.63, -42.80. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 141.60, 141.37, 140.81, 140.81, 140.26, 140.00, 133.30, 133.30, 132.95, 130.40, 130.18, 129.72, 129.60, 128.98, 128.67, 128.58, 128.33, 128.29, 128.16, 127.67, 127.49, 127.41, 127.15, 126.39, 129.74, 114.58, 112.35. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3083.67 (vw), 3061.61 (vw), 3025.57 (vw), 2956.87 (vw), 2924.69 (vw), 1596.8 (vw), 1473.25 (w), 1450.83 (vw), 1436.25 (vw), 1154.45 (w), 1102.14 (vs), 1008.85 (w), 950.03 (vw), 916.16 (vw), 880 (vw), 849.74 (vw), 773.57 (w), 754.77 (w), 741.51 (m), 699.32 (m), 648.22 (vw), 614.95 (w), 555.89 (vw), 541.06 (vw), 513.94 (w), 487.43 (vw), 455.61 (w).



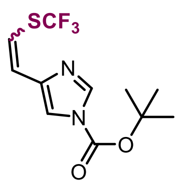
2-(2-((Trifluoromethyl)thio)vinyl)pyridine (3q): Following general procedure B using (*Z*)-2-(2-iodovinyl)pyridine (69 mg, 0.3 mmol), synthesized as previously reported,[21] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 85% NMR yield of 2-(2-((trifluoromethyl)thio)vinyl)pyridine (*E*:*Z* = 1:2). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -41.94, -42.53. The NMR data accords with the reference.[19]



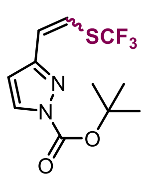
3-(2-((Trifluoromethyl)thio)vinyl)pyridine (3r): Following general procedure B using (*Z*)-3-(2-iodovinyl)pyridine (69 mg, 0.3 mmol), synthesized as previously reported,[26] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 86% NMR yield of 3-(2-((trifluoromethyl)thio)vinyl)pyridine (*E*:*Z* = 1:2.1). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -41.89, -42.49. The NMR data accords with the reference.[18]



5-(2-((trifluoromethyl)thio)vinyl)pyrimidine (3s): Following general procedure B using (*Z*)-5-(2-iodovinyl)pyrimidine (70 mg, 0.3 mmol) as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 71% NMR yield of 5-(2-((trifluoromethyl)thio)vinyl)pyrimidine (*E*:*Z* = 1:1.7). **^{19}F NMR** (471 MHz, DMSO-d_6): δ = -41.58, -42.28. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_7H_6F_3N_2S$ 207.0204; found 207.0206 (Δ = 1.0 ppm).

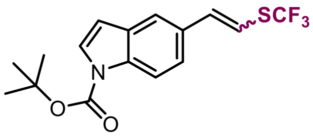


***Tert*-butyl 4-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole-1-carboxylate (3t)**: Following general procedure C using *tert*-butyl (*Z*)-4-(2-iodovinyl)-1*H*-imidazole-1-carboxylate (96 mg, 0.3 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *tert*-butyl 4-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole-1-carboxylate (66 mg, 75%, *E*:*Z* = 1:1.3) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.02 - 8.12 (m, 2 H), 7.31 - 7.40 (m, 2 H), 6.99 (d, *J* = 14.95 Hz, 1 H), 6.80 (d, *J* = 15.11 Hz, 1 H), 6.57 (d, *J* = 10.53 Hz, 1 H), 6.36 (d, *J* = 10.38 Hz, 1 H), 1.63 (s, 16 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.71, -44.35 **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 146.70, 146.58, 139.34, 139.17, 137.62, 137.29, 136.71, 135.36, 131.10, 130.73, 130.73, 130.69, 128.65, 128.24, 119.74, 115.65, 115.38, 114.99, 112.75, 86.15, 86.11, 27.76. **HRMS (ESI-TOF) m/z:** $[M–H]^–$ Calcd for $C_{11}H_{12}F_3N_2O_2S$ 293.0572; found 293.0575 (Δ = 1.0 ppm).

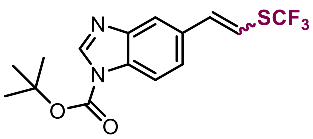


***T*ert-butyl 3-(2-((trifluoromethyl)thio)vinyl)-1*H*-pyrazole-1-carboxylate (3u)**: Following general procedure C using *tert*-butyl (*Z*)-3-(2-iodovinyl)-1*H*-pyrazole-1-carboxylate (96 mg, 0.3 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *tert*-butyl 3-(2-((trifluoromethyl)thio)vinyl)-1*H*-pyrazole-1-carboxylate (53 mg, 60%, *E*:*Z* = 1:2.1) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.05 (d, *J* = 2.75 Hz, 1 H), 8.03 (d, *J* = 2.90 Hz, 1 H), 6.95 - 7.03 (m, 1 H), 6.88 - 6.94 (m, 1 H), 6.67 - 6.72 (m, 1 H), 6.60 - 6.65 (m, 1 H), 6.49 (d, *J* = 2.90 Hz, 1 H), 6.44 (d, *J* = 2.90 Hz, 1 H), 1.66 (s, 4 H), 1.65 (s, 9 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.31, -44.08**. ^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 152.02, 151.40, 147.27, 131.82, 131.37, 130.51, 130.20, 130.20, 128.06, 119.67, 119.27, 119.24, 117.41, 108.64, 106.22, 85.90, 85.60, 27.84. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3110.19 (vw), 3048.23 (vw), 2983.63 (vw), 2936.38 (vw), 1747.94 (w), 1612.83 (vw), 1532.67 (vw), 1478.56 (vw), 1407.32 (w), 1397.44 (w), 1370.56 (m), 1355.13 (w), 1296.55 (m), 1281.61

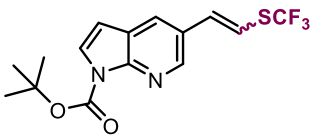
(m), 1243.4 (w), 1141.31 (m), 1105.51 (vs), 1053.92 (m), 968.11 (m), 841.91 (m), 765.61 (m), 756.94 (m), 729.33 (w), 651.23 (vw), 542.15 (vw), 474.29 (vw), 458.62 (vw).



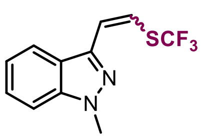
***Tert*-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1*H*-indole-1-carboxylate (3v)**: Following general procedure C using *tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-indole-1-carboxylate (111 mg, 0.3 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *tert*-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1*H*-indole-1-carboxylate (80 mg, 78%, *E*:*Z* = 1:3) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.17 (br d, *J* = 7.02 Hz, 1 H), 7.60 - 7.69 (m, 1 H), 7.59 (d, *J* = 1.22 Hz, 1 H), 7.55 (d, *J* = 1.37 Hz, 1 H), 7.40 (dd, *J* = 8.62, 1.60 Hz, 1 H), 7.31 (dd, *J* = 8.62, 1.60 Hz, 1 H), 7.13 (d, *J* = 15.26 Hz, 1 H), 6.96 (d, *J* = 10.38 Hz, 1 H), 6.74 (d, *J* = 15.26 Hz, 1 H), 6.60 (d, *J* = 3.66 Hz, 1 H), 6.58 (d, *J* = 3.66 Hz, 1 H), 6.37 (d, *J* = 10.38 Hz, 1 H), 1.71 (s, 12 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.95, -43.19. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 149.50, 149.43, 142.62, 134.67, 133.31, 132.83, 130.92, 130.86, 130.65, 129.78, 129.66, 128.47, 128.42, 126.88, 126.79, 125.07, 122.89, 121.14, 119.81, 115.45, 115.15, 112.32, 109.53, 107.31, 107.31, 84.03, 83.97, 28.26, 28.11. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3152.49 (vw)., 3119.35 (vw), 3065.47 (vw), 2990.02 (vw), 2939.63 (vw), 1733.48 (s), 1470.96 (w), 1441.31 (w), 1370.68 (m), 1336.21 (m), 1291.49 (w), 1258.22 (w), 1212.54 (w), 1193.62 (w), 1116.84 (vs), 1084.06 (m), 1043.56 (m), 1024.39 (m), 950.51 (w), 884.1 (w), 869.39 (w), 842.51 (w), 828.17 (m), 779.6 (m), 764.05 (m), 757.42 (m), 728.49 (m), 724.75 (m), 700.41 (m), 655.21 (m), 622.54 (w), 601.09 (m), 573.61 (w), 531.78 (m), 466.46 (w), 417.4 (w), 404.02 (w).



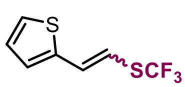
***Tert*-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1*H*-benzo[*d*]imidazole-1-carboxylate (3w)**: Following general procedure C using *tert*-butyl 5-(2-iodovinyl)-1*H*-benzo[*d*]imidazole-1-carboxylate (111 mg, 0.3 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *Tert*-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1*H*-benzo[*d*]imidazole-1-carboxylate (87 mg, 84%, *E*:*Z* = 1:2) as a yellow oil. Spectra exhibit multiple peaks associated with *Boc* rotamers. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.45 (d, *J* = 7.93 Hz, 2 H), 8.42 (d, *J* = 4.73 Hz, 1 H), 8.05 - 8.11 (m, 1 H), 7.92 - 8.04 (m, 3 H), 7.69 - 7.81 (m, 3 H), 7.43 (dd, *J* = 8.47, 1.45 Hz, 1 H), 7.39 (dd, *J* = 8.32, 1.60 Hz, 1 H), 7.35 (dd, *J* = 8.39, 1.53 Hz, 1 H), 7.30 (dd, *J* = 8.39, 1.53 Hz, 1 H), 7.10 (d, *J* = 15.26 Hz, 1 H), 6.96 (dd, *J* = 10.53, 1.68 Hz, 2 H), 6.78 (d, *J* = 10.53 Hz, 1 H), 6.75 (d, *J* = 10.68 Hz, 1 H), 6.59 (d, *J* = 8.54 Hz, 1 H), 6.42 (d, *J* = 7.02 Hz, 1 H), 6.40 (d, *J* = 6.87 Hz, 1 H), 1.71 (s, 10 H), 1.70 (s, 19 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.78 (d, *J* = 13.87 Hz), -43.13 (d, *J* = 8.67 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 147.85, 147.73, 147.69, 147.66, 144.69, 144.49, 144.25, 143.87, 143.05, 142.90, 142.82, 141.23, 138.35, 132.38, 132.26, 132.21, 132.15, 131.54, 131.46, 131.36, 131.01, 130.71, 125.98, 125.34, 123.90, 123.23, 120.80, 120.58, 120.58, 120.31, 119.04, 114.61, 114.32, 114.25, 113.95, 113.70, 113.59, 112.83, 111.55, 111.10, 85.98, 85.95, 85.92, 85.86, 79.36, 28.10, 28.02, 27.95, 27.96**. HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3120.43 (vw), 3054.86 (vw), 2982.54 (vw), 2933.73 (vw), 1747.1 (w), 1617.53 (vw), 1505.07 (vw), 1478.19 (vw), 1440.71 (w), 1429.74 (vw), 1362.73 (m), 1302.94 (w), 1287.27 (w), 1252.8 (w), 1204.47 (w), 1102.38 (vs), 1058.99 (m), 1035.12 (w), 945.93 (vw), 844.68 (w), 834.92 (w), 818.29 (w), 800.09 (w), 792.73 (w), 768.27 (w), 755.85 (w), 734.4 (w), 630.02 (vw).



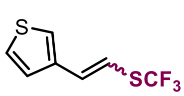
***Tert*-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (3x)**: Following general procedure C using *tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-pyrrolo[2,3-b]pyridine-1-carboxylate (111 mg, 0.3 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded *tert*-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (82 mg, 79%, *E*:*Z* = 1:2.9) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.61 (d, *J* = 1.53 Hz, 1 H), 8.43 - 8.51 (m, 1 H), 7.97 (d, *J* = 1.83 Hz, 1 H), 7.88 - 7.95 (m, 1 H), 7.67 (d, *J* = 3.81 Hz, 1 H), 7.10 (d, *J* = 15.41 Hz, 1 H), 6.94 (d, *J* = 10.53 Hz, 1 H), 6.78 (d, *J* = 15.26 Hz, 1 H), 6.50 - 6.55 (m, 1 H), 6.48 (d, *J* = 10.38 Hz, 1 H), 1.67 (s, 5 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ = -42.68, -42.93. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 148.40, 148.33, 147.71, 147.67, 147.50, 145.90, 144.51, 138.34, 132.40, 130.61, 130.12, 128.35, 128.16, 127.89, 127.72, 127.64, 126.16, 126.09, 126.05, 123.10, 122.70, 114.72, 114.69, 114.66, 112.04, 104.58, 104.51, 84.51, 84.47, 84.40, 78.74, 28.08. **HRMS (ESI-TOF) m/z:** $[M+H]^+$–*t*Bu Calcd for $C_{11}H_7F_3N_2O_2S$ 289.0259; found 289.0256 (Δ = 1.0 ppm). **FT-IR (ATR)**: ν_{max} cm^{-1} 3156.35 (vw) ,3118.26 (vw) ,3048.72 (vw) ,3006.65 (vw) ,2983.63 (vw) ,2934.57 (vw) ,1745.89 (m) ,1604.87 (vw) ,1529.78 (w) ,1476.27 (w) ,1387.07 (m) ,1370.32 (m) ,1354.77 (w) ,1316.2 (s) ,1252.92 (m) ,1196.51 (w) ,1151.8 (m) ,1105.63 (vs) ,1086.59 (vs) ,1042.11 (m) ,1026.2 (m) ,971.84 (w) ,913.02 (w) ,847.09 (w) ,781.64 (m) ,767.3 (w) ,754.77 (m) ,723.67 (m) ,661.48 (w) ,637.01 (w) ,601.69 (w) ,592.29 (w) ,535.88 (w), 462.36 (w).



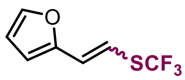
1-methyl-3-(2-((trifluoromethyl)thio)vinyl)-1*H*-indazole (3y): Following general procedure C using *tert*-butyl (*Z*)-3-(2-iodovinyl)-1-methyl-1*H*-indazole (85 mg, 0.3 mmol) as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 1-methyl-3-(2-((trifluoromethyl)thio)vinyl)-1*H*-indazole (60 mg, 78%, *E*:*Z* = 1:1) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.74 (d, *J* = 8.09 Hz, 1 H), 7.36 - 7.46 (m, 2 H), 7.18 - 7.24 (m, 1 H), 7.03 (dd, *J* = 10.38, 0.92 Hz, 1 H), 6.62 (d, *J* = 10.22 Hz, 1 H), 4.12 (s, 3 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -44.36. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 140.45, 140.04, 126.63, 130.05, 122.67, 120.95, 119.57, 116.81, 116.81, 115.90, 109.03, 35.85. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_9F_3N_2S$ 259.0517; found 259.0516 (Δ = 0.4 ppm).



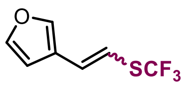
2-(2-((Trifluoromethyl)thio)vinyl)thiophene (3z): Following general procedure B using (*Z*)-2-(2-iodovinyl)thiophene (71 mg, 0.3 mmol), synthesized as previously reported,[27] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 80% NMR yield of 2-(2-((trifluoromethyl)thio)vinyl)thiophene (*E*:*Z* = 1.2:1). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -42.12, -42.70. The NMR data accords with the reference.[18]



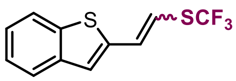
3-(2-((trifluoromethyl)thio)vinyl)thiophene (3aa): Following general procedure C using (*Z*)-3-(2-iodovinyl)thiophene (71 mg, 0.3 mmol), synthesized as previously reported,[28] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 76% NMR yield of 3-(2-((trifluoromethyl)thio)vinyl)thiophene (*E*:*Z* = 1.5:1). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -42.38, -42.51. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_7H_5F_3S_2$ 210.9863; found 210.9866 (Δ = 1.4 ppm).



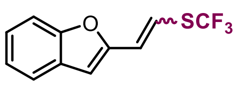
2-(2-((trifluoromethyl)thio)vinyl)furan (3ab): Following general procedure C using (*Z*)-2-(2-iodovinyl)furan (66 mg, 0.3 mmol), synthesized as previously reported,[29] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 41% NMR yield of 2-(2-((trifluoromethyl)thio)vinyl)furan (*E*:*Z* = 1:1.3). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -42.75, -42.96. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_7H_5F_3OS$ 195.0091; found 195.0094 (Δ = 1.5 ppm).



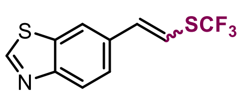
3-(2-((trifluoromethyl)thio)vinyl)furan (3ac): Following general procedure C using (*Z*)-3-(2-iodovinyl)furan (66 mg, 0.3 mmol), synthesized as previously reported,[30] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 41% NMR yield of 3-(2-((trifluoromethyl)thio)vinyl)furan (*E*:*Z* = 1.6/1). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -42.26, -42.68. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_7H_5F_3OS$ 195.0091; found 195.0093 (Δ = 1.0 ppm).



2-(2-((trifluoromethyl)thio)vinyl)benzo[*b*]thiophene (3ad): Following general procedure C using (*Z*)-2-(2-iodovinyl)benzo[*b*]thiophene (86 mg, 0.3 mmol), as the substrate. Purification via flash chromatography (Hexane) yielded 2-(2-((trifluoromethyl)thio)vinyl)benzo[*b*]thiophene (65 mg, 83%, *E*:*Z* = 1.1:1) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.82 - 7.87 (m, 1 H), 7.77 - 7.81 (m, 2 H), 7.72 - 7.77 (m, 1 H), 7.32 - 7.43 (m, 5 H), 7.25 (s, 1 H), 7.20 (d, *J* = 15.11 Hz, 1 H), 7.09 (d, *J* = 10.22 Hz, 1 H), 6.66 (d, *J* = 15.11 Hz, 1 H), 6.42 (d, *J* = 10.22 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.51, -42.57. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 140.80, 139.48, 139.48, 139.37, 138.76, 138.03, 134.47, 134.47, 133.03, 132.99, 130.58, 130.53, 128.13, 128.08, 127.38, 127.38, 126.69, 125.65, 125.30, 125.22, 124.81, 124.76, 124.11, 123.96, 122.31, 122.23, 113.19, 113.09

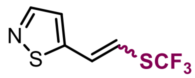


2-(2-((trifluoromethyl)thio)vinyl)benzofuran (3ae): Following general procedure C using (*Z*)-2-(2-iodovinyl)benzofuran (81 mg, 0.3 mmol), as the substrate. Purification via flash chromatography (Hexane:DCM gradient) yielded 2-(2-((trifluoromethyl)thio)vinyl)benzofuran (53 mg, 72%, *E*:*Z* = 1:1.1) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.10 (d, *J* = 7.78 Hz, 1 H), 8.03 (d, *J* = 8.24 Hz, 1 H), 7.84 (t, *J* = 7.25 Hz, 1 H), 7.71 - 7.80 (m, 1 H), 7.21 (d, *J* = 10.83 Hz, 1 H), 7.00 (d, *J* = 10.83 Hz, 1 H). ^{19}F NMR (471 MHz, $CDCl_3$): δ ppm -42.44, -43.39. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 154.87, 152.45, 130.84, 128.39, 128.25, 125.22, 123.28, 121.33, 118.05, 115.70, 111.33, 107.39. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3122.6 (vw), 3107.9 (vw), 3080.29 (vw), 3048.59 (vw), 1640.79 (vw), 1620.66 (vw), 1548.1 (vw), 1471.32 (vw), 1448.54 (w), 1426.12 (vw), 1353.44 (w), 1341.75 (vw), 1288.36 (vw), 1137.57 (m), 1126.73 (m), 1092.86 (vs), 1004.63 (m), 942.67 (m), 919.41 (m), 887.47 (m), 848.54 (w), 817.68 (m), 785.14 (m), 746.21 (vs), 721.14 (m), 683.41 (w), 628.09 (m), 620.25 (m), 608.68 (m), 542.27 (w), 485.02 (m), 467.66 (w), 423.43 (w), 406.91 (m).

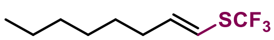


6-(2-((trifluoromethyl)thio)vinyl)benzo[*d*]thiazole (3af): Following general procedure C using (*Z*)-6-(2-iodovinyl)benzo[*d*]thiazole (86 mg, 0.3 mmol), as the substrate. Purification via flash chromatography (Hexane:DCM gradient) yielded 6-(2-((trifluoromethyl)thio)vinyl)benzo[*d*]thiazole (66 mg, 84%, *E*:*Z* = 1:1.7) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.98 - 9.07 (m, 2 H), 8.04 - 8.19 (m, 2 H), 7.94 (br d, *J* = 4.12 Hz, 2 H), 7.58 (dd, *J* = 8.54, 1.37 Hz, 1 H), 7.50 (dd, *J* = 8.54, 1.37 Hz, 1 H), 7.10

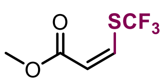
(d, *J* = 15.26 Hz, 1 H), 6.97 (br d, *J* = 10.53 Hz, 1 H), 6.84 (d, *J* = 15.41 Hz, 1 H), 6.50 (d, *J* = 10.53 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.57, -42.96. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 155.23, 154.97, 154.92, 154.72, 153.56, 152.73, 139.77, 137.89, 134.51, 134.21, 133.04, 132.71, 132.61, 131.48, 130.70, 130.59, 130.04, 128.26, 128.14, 127.03, 126.98, 125.78, 124.70, 123.83, 123.53, 123.41, 123.18, 121.75, 121.36, 120.40, 114.82, 112.84. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_6F_3NS_2$ 261.9972; found 261.9977 (Δ = 1.9 ppm).



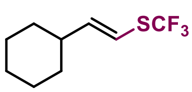
5-(2-((trifluoromethyl)thio)vinyl)isothiazole (3ag): Following general procedure B using (*Z*)-5-(2-iodovinyl)isothiazole (71 mg, 0.3 mmol), as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 43% NMR yield of 5-(2-((trifluoromethyl)thio)vinyl)isothiazole (*E*:*Z* = 1.2:1). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -41.36, -41.65. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_6H_4F_3NS_2$ 211.9816; found 211.9820 (Δ = 1.9 ppm).



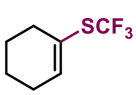
(*E*)-oct-1-en-1-yl(trifluoromethyl)sulfane (3ah): Following general procedure B using (*E*)-1-iodooct-1-ene (71 mg, 0.3 mmol), as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 85% NMR yield of (*E*)-oct-1-en-1-yl(trifluoromethyl)sulfane (*E*:*Z* = 1:0). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -42.91. The NMR data accords with the reference.[31]



Methyl (*Z*)-3-((trifluoromethyl)thio)acrylate (3ai): Following general procedure B using methyl (*Z*)-3-iodoacrylate (71 mg, 0.3 mmol), synthesized as previously reported,[17] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 69% NMR yield of methyl (*Z*)-3-((trifluoromethyl)thio)acrylate (*E*:*Z* = 0:1). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -44.31. The NMR data accords with the reference.[32]

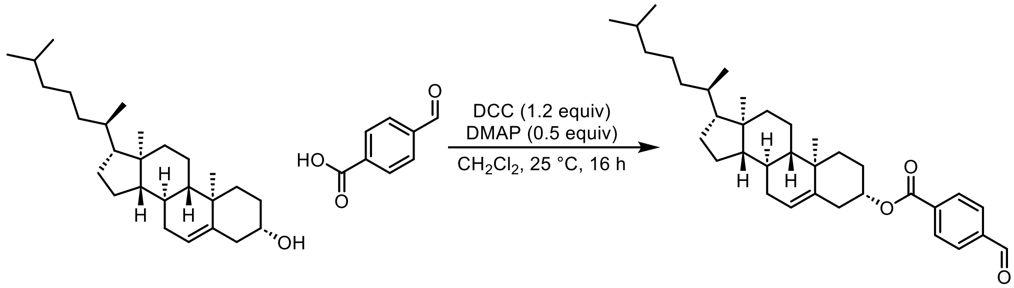


(*E*)-(2-cyclohexylvinyl)(trifluoromethyl)sulfane (3aj): Following general procedure B using (*E*)-(2-iodovinyl)cyclohexane (71 mg, 0.3 mmol), synthesized as previously reported,[33] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 89% NMR yield of (*E*)-(2-cyclohexylvinyl)(trifluoromethyl)sulfane (*E*:*Z* = 1:0). **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -42.92. The NMR data accords with the reference.[34]

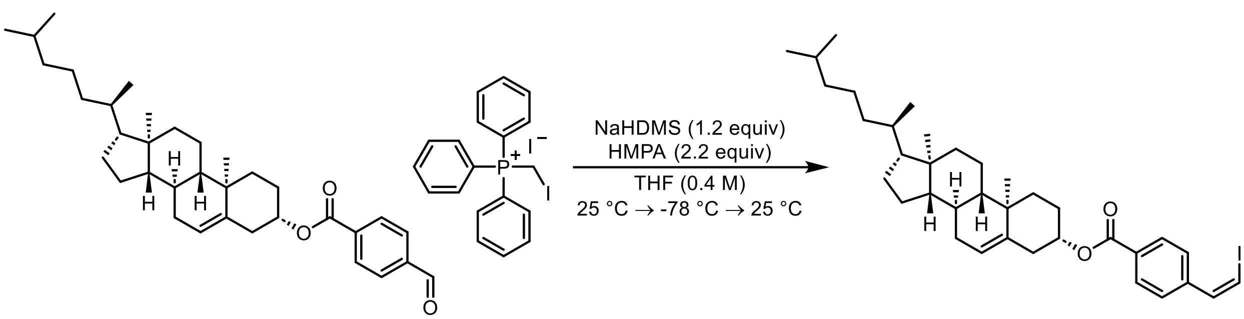


Cyclohex-1-en-1-yl(trifluoromethyl)sulfane (3ak): Following general procedure B using 1-iodocyclohex-1-ene (62 mg, 0.3 mmol), synthesized as previously reported,[35] as the substrate. ^{19}F NMR analysis employing hexafluorobenzene as an internal standard gave a 93% NMR yield of cyclohex-1-en-1-yl(trifluoromethyl)sulfane. **^{19}F NMR** (377 MHz, DMSO-d_6): δ = -40.89. The NMR data accords with the reference.[36]

Synthesis and Trifluoromethylthiolation of Biologically Relevant Substrates

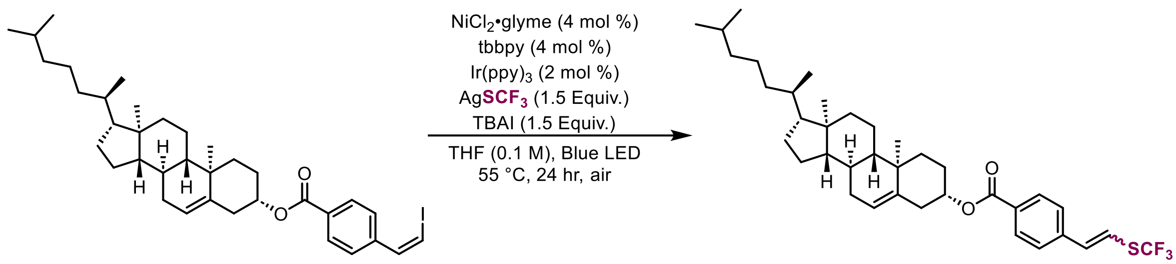


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-formylbenzoate: Adapting from the precedented literature procedure,[37] an oven dried 20 mL vial was charged with (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (cholesterol, 500 mg, 1.29 mmol), 4-formylbenzoic acid (233 mg, 1.55 mmol), *N*,*N*-dimethylpyridin-4-amine (DMAP, 79 mg, 0.65 mmol), and dicyclohexylmethanediimine (DCC, 320 mg, 1.55 mmol); the solids were dissolved in CH_2Cl_2 (12.5 ml) and the reaction was degassed and allowed to stir at 25 °C overnight. The reaction was concentrated in vacuo and the resulting residue was purified by flash silica chromatography, elution gradient 0 to 25% EtOAc in hexanes. Product fractions were evaporated to dryness to afford (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-formylbenzoate (623 mg, 93 %) as a white solid. The NMR data accords with the reference.[37]

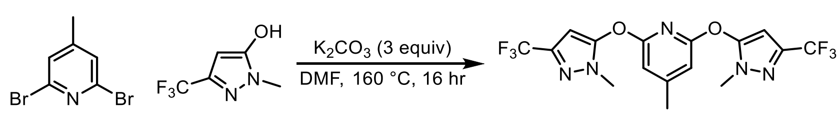


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*Z*)-2-iodovinyl)benzoate: Following general procedure A using (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-formylbenzoate (0.600 g, 1.16 mmol), synthesized as previously reported,[37] as the substrate. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-3-yl 4-((*Z*)-2-iodovinyl)benzoate (432 mg, 58%, *E*:*Z* = 1:7.3) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.06 (d, *J* = 8.24 Hz, 2 H), 8.00 (d, *J* = 8.39 Hz, 1 H), 7.68 (d, *J* = 8.24 Hz, 2 H), 7.55 (d, *J* = 8.39 Hz, 1 H), 7.38 (d, *J* = 8.85 Hz, 1 H), 6.73 (d, *J* = 8.70 Hz, 1 H), 5.43 (br d, *J* = 3.51 Hz, 2 H), 4.80 - 4.95 (m, 2 H), 2.48 (br d, *J* = 7.32 Hz, 3 H), 1.96 - 2.07 (m, 5 H), 1.90 - 1.96 (m, 2 H), 1.68 - 1.89 (m, 3 H), 1.43 - 1.66 (m, 11 H), 0.96 - 1.42 (m, 29 H), 0.93 (d, *J*

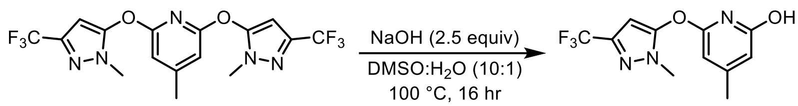
= 6.56 Hz, 5 H), 0.84 - 0.90 (m, 10 H), 0.70 (s, 5 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 165.61, 141.02, 139.62, 139.55, 137.99, 131.98, 130.45, 129.46, 129.41, 128.20, 122.87, 122.82, 82.90, 81.69, 79.85, 74.89, 74.70, 56.71, 56.16, 50.06, 42.33, 39.75, 39.52, 38.22, 38.18, 37.03, 37.03, 36.66, 36.66, 36.19, 35.79, 31.94, 31.89, 28.23, 28.01, 27.89, 27.86, 27.86, 24.29, 23.84, 22.81, 22.56, 21.06, 19.37, 18.72, 11.87. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 2931.44 (m), 2904.44 (w), 2891.54 (w), 2865.63 (w), 2851.77 (w), 1712.27 (s), 1609.09 (w), 1587.27 (vw), 1567.03 (vw), 1504.59 (vw), 1465.9 (w), 1436.49 (w), 1409.13 (w), 1382.01 (w), 1369.84 (w), 1353.93 (w), 1303.54 (w), 1273.65 (vs), 1256.78 (m), 1197.48 (w), 1179.64 (w), 1107.56 (s), 1085.62 (w), 1027.17 (w), 1017.16 (m), 1010.77 (w), 997.03 (m), 978.35 (w), 948.82 (w), 925.32 (w), 888.44 (vw), 859.27 (m), 843.96 (w), 799 (w), 777.31 (m), 770.68 (m), 714.99 (w), 695.46 (w), 670.15 (w), 644.96 (w), 638.33 (w), 623.15 (w), 592.41 (w), 522.86 (w), 503.46 (w), 487.07 (w).



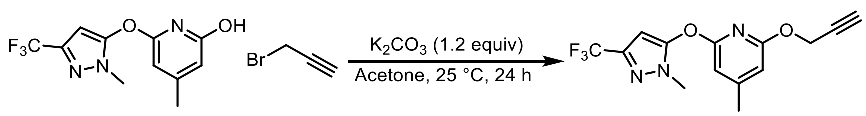
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(2-((trifluoromethyl)thio)vinyl)benzoate (3al): Following general procedure C using (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(2-iodovinyl)benzoate as the substrate. Purification via flash chromatography (Hexane:Ethyl acetate gradient) (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(2-((trifluoromethyl)thio)vinyl)benzoate (120 mg, 35%, *E*:*Z* = 1:1.8) as a waxy yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.95 - 8.12 (m, 5 H), 7.55 (br d, *J* = 8.09 Hz, 1 H), 7.35 - 7.49 (m, 2 H), 6.95 - 7.03 (m, 1 H), 6.82 - 6.92 (m, 2 H), 6.52 (br d, *J* = 10.68 Hz, 1 H), 5.43 (br s, 2 H), 4.79 - 4.95 (m, 2 H), 2.48 (br d, *J* = 7.48 Hz, 5 H), 1.68 - 2.13 (m, 16 H), 1.44 - 1.67 (m, 17 H), 0.77 - 1.44 (m, 78 H), 0.71 (s, 7 H). ^{19}F NMR (471 MHz, $CDCl_3$): δ ppm -42.34, -43.03. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 165.34, 165.24, 139.56, 139.11, 138.98, 138.45, 131.96, 131.07, 130.96, 130.85, 130.54, 130.29, 130.09, 129.78, 129.40, 128.42, 126.51, 126.47, 122.84, 116.33, 116.31, 116.28, 116.25, 114.91, 114.89, 74.88, 74.82, 74.78, 56.69, 56.16, 50.05, 42.32, 39.74, 39.52, 38.20, 37.03, 36.64, 36.19, 35.80, 31.93, 31.88, 28.23, 28.00, 27.88, 24.29, 23.85, 22.80, 22.67, 22.55, 21.06, 19.36, 18.72, 11.85. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3061.13 (w), 3017.5 (w), 2954.58 (m), 2927.82 (m), 2867.32 (m), 2854.42 (m), 1710.1 (m), 1606.92 (w), 1465.18 (m), 1437.82 (m), 1408.77 (w), 1377.07 (w), 1288.48 (s), 1163.73 (m), 1115.15 (vs), 1028.13 (w), 1016.44 (w), 996.31 (w), 979.32 (w), 853 (w), 830.82 (m), 768.87 (vs), 703.06 (s), 539.74 (m).



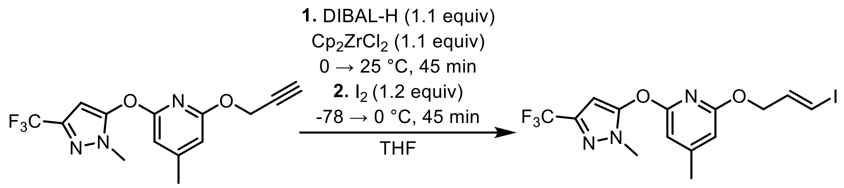
4-methyl-2,6-bis((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)pyridine: Adapting from the precedented literature procedure,[38] an oven dried 40 mL vial was charged with 2,6-dibromo-4-methylpyridine (300 mg, 1.20 mmol), 1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (417 mg, 2.51 mmol), potassium carbonate (496 mg, 3.59 mmol), and DMF (5978 µl), the reaction was degassed, heated to 160 °C, and allowed to stir overnight. The reaction was then cooled, quenched with 5N HCl, extracted into DCM, washed with H_2O (3 x 50 mL), dried with $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by flash silica chromatography, elution gradient 0 to 100% EtOAc in hexanes. Product fractions were concentrated under reduced pressure to afford 4-methyl-2,6-bis((1-methyl-3-(trifluoromethyl)-1H-pyrazol-5-yl)oxy)pyridine (474 mg, 94 %) as a white waxy solid. The NMR data accords with the reference.[38]



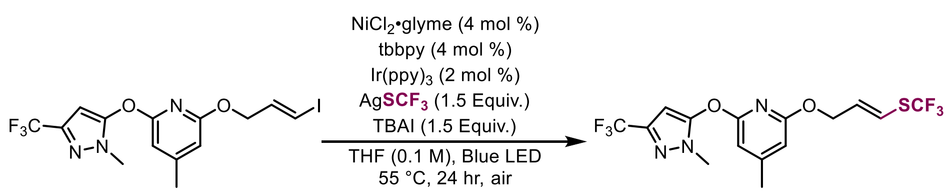
4-methyl-6-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)pyridin-2-ol: Adapting from the precedented literature procedure,[38] a 40 mL reaction vial was charged with 4-methyl-2,6-bis((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)pyridine (500 mg, 1.19 mmol), sodium hydroxide (119 mg, 2.97 mmol), DMSO (5395 µl), water (539 µl), and degassed. The reaction was heated to 100 °C and allowed to stir overnight, after which the reaction was quenched with 5N HCl, extracted into ethyl acetate, washed with H_2O (3 x 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by flash silica chromatography, elution gradient 0 to 75% EtOAc in hexanes. Product fractions were evaporated to dryness to afford 4-methyl-6-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)pyridin-2-ol (212 mg, 65 %) as a white solid. The NMR data accords with the reference.[38]



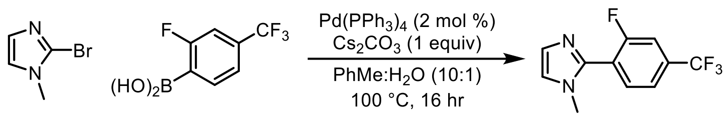
4-methyl-2-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)-6-(prop-2-yn-1-yloxy) pyridine: Adapting from the precedented literature procedure,[38] an oven dried 20 mL vial was charged with 4-methyl-6-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)pyridin-2-ol (296.5 mg, 1.09 mmol, 1 equiv), potassium carbonate. (180 mg, 1.30 mmol, 1.2 equiv), and acetone (0.1 M), the reaction was degassed and allowed to stir at 25 °C for 30 min, after which 3-bromoprop-1-yne (80 wt % in toluene, 363 µl, 3.26 mmol, 3 equiv) was added dropwise. The reaction was shielded from light and allowed to stir at 25 °C overnight. The reaction was then concentrated in vacuo and the resulting residue was purified by flash silica chromatography, elution gradient 0 to 100% ethyl acetate in hexanes. Product fractions were evaporated to dryness to afford 4-methyl-2-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)-6-(prop-2-yn-1-yloxy)pyridine (262 mg, 77 %) as a pale yellow oil which solidified on standing. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 6.46 (s, 1 H), 6.44 (s, 1 H), 6.38 (s, 1 H), 4.75 (d, *J*=2.29 Hz, 2 H), 3.79 (s, 3 H), 2.41 (t, *J*=2.37 Hz, 1 H), 2.34 (s, 3 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -62.90 (s, 3 F). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 161.41, 159.08, 154.48, 148.24, 140.35 (q, *J*=38.53 Hz,), 121.10 (q, *J*=268.41 Hz), 106.93, 103.72, 92.12 (d, *J*=2.07 Hz), 78.77, 74.31, 53.63, 35.13, 21.05. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{12}F_3N_3O_2$ 312.0960; found 312.0958 (Δ = 0.6 ppm).



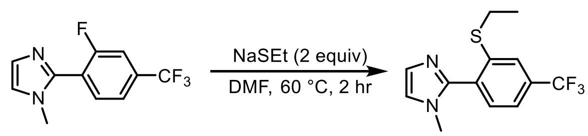
(*E*)-2-((3-iodoallyl)oxy)-4-methyl-6-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy) pyridine: Adapting from the precedented literature procedure,[33] an oven dried round bottom flask was charged with Cp_2ZrCl_2 (172 mg, 0.59 mmol, 1.1 equiv) followed by tetrahydrofuran (4749 µl) and cooled to 0 ºC. diisobutylaluminum hydride (DIBAL-H, 1.0 M in *n*-hexane, 587 µl, 0.59 mmol, 1.1 equiv) was added dropwise. After stirring for 30 min at 0 °C, 4-methyl-2-((1-methyl-3-(trifluoromethyl)-1H-pyrazol-5-yl)oxy)-6-(prop-2-yn-1-yloxy)pyridine (166.1 mg, 0.53 mmol, 1.0 equiv) was added as a solution in THF (1.0 M). The reaction mixture was warmed to room temperature and stirred for 45 min, at which time the solution was homogenous. The reaction mixture was then cooled to –78 ºC and a solution of I_2 (176 mg, 0.69 mmol, 1.3 equiv) in THF (1.0 M) was added dropwise. The resulting solution was stirred at –78 ºC for 45 min before warming to 0 ºC within 45 min. A Schlenk-flask filled with hexanes (0.2 M) and HCl (2.8 equiv) was cooled to 0 °C and the reaction mixture was carefully transferred into it via cannula with vigorous stirring. The resulting biphasic solution was separated and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layer was washed with, $Na_2S_2O_3$ (sat. aq. sol., 50 mL) and brine (50 mL). The resulting residue was purified by flash silica chromatography, elution gradient 0 to 100% ethyl acetate in hexanes. Product fractions were evaporated to dryness to afford (*E*)-2-((3-iodoallyl)oxy)-4-methyl-6-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)pyridine (136 mg, 58 %, *E*:*Z* = 1:0) as a viscous pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 6.63 (dt, *J* = 14.50, 5.80 Hz, 1 H), 6.41 (d, *J* = 16.02 Hz, 2 H), 6.35 (dt, *J* = 14.57, 1.41 Hz, 1 H), 6.22 (s, 1 H), 4.54 (dd, *J* = 5.80, 1.37 Hz, 2 H), 3.77 (s, 3 H), 2.33 (s, 3 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -62.80. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 161.88, 159.31, 154.37, 148.26, 140.53, 140.44, 140.22, 122.04, 119.91, 106.72, 103.09, 92.20, 92.19, 92.18, 80.06, 67.26, 35.17, 21.04. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{13}F_3IN_3O_2$ 440.0083; found 440.0085 (Δ = 0.5 ppm).



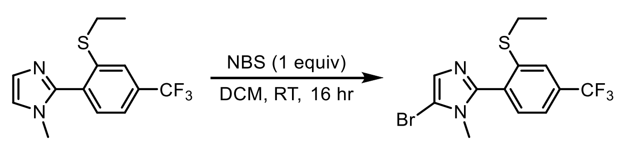
(*E*)-4-methyl-2-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)-6-((3-((trifluoro-methyl)thio)allyl)oxy)pyridine (1a): Following general procedure C using (*E*)-2-((3-iodoallyl)oxy)-4-methyl-6-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)pyridine (132 mg, 0.3 mmol), as the substrate. Purification via flash chromatography (Hexane:Ethyl acetate gradient) yielded (*E*)-4-methyl-2-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)-6-((3-((trifluoromethyl)thio)allyl)oxy)pyridine (102 mg, 82%, *E*:*Z* = 1:0) as a waxy yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 6.44 (s, 1 H), 6.31 - 6.38 (m, 1 H), 6.25 (t, J=5.11 Hz, 1 H), 6.22 (s, 1 H), 4.71 (d, J=5.04 Hz, 1 H), 3.77 (s, 2H), 2.35 (s, 2 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.66, -62.97. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 161.84, 159.32, 154.53, 148.30, 140.58, 140.27, 136.25, 130.62, 128.18, 122.07, 119.93, 116.06, 116.06, 106.80, 103.29, 92.07, 92.07, 92.06, 64.89, 35.12, 21.05, 21.05, 21.04. The NMR data accords with the reference.[38]



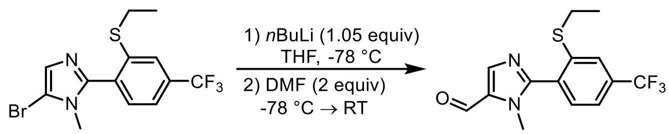
2-(2-fluoro-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole: Adapting from the precedented literature procedure,[39] an oven dried 100 mL round bottom flask was charged with 2-bromo-1-methyl-1*H*-imidazole (1 g, 6.21 mmol), (2-fluoro-4-(trifluoromethyl)phenyl)boronic acid (1.937 g, 9.32 mmol), cesium carbonate (2.024 g, 6.21 mmol), tetrakis(triphenylphosphine)palladium(0) (0.144 g, 0.12 mmol), toluene (28.2 ml), and water (2.82 ml), the solution was degassed and the reaction vessel heated to 100 °C overnight, the reaction was cooled to room temperature, extracted into ethyl acetate, washed with DI H_2O (3 x 50 mL), brine (3 x 50 mL), dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by flash silica chromatography, elution gradient 0 to 100% EtOAc in hexanes. Product fractions were evaporated to dryness to afford 2-(2-fluoro-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole (0.941 g, 62 %) as a yellow oil which solidified on standing. The NMR data accords with the reference.[39]



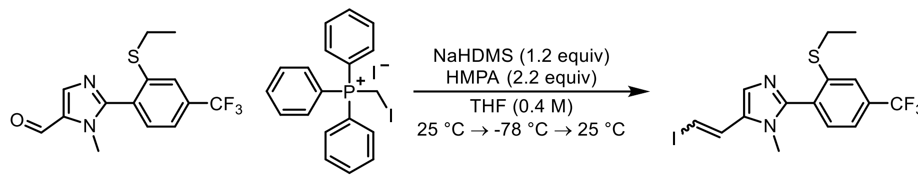
2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole: Adapting from the precedented literature procedure,[39] an oven dried 40 mL vial was charged with 2-(2-fluoro-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole (900.5 mg, 3.69 mmol), sodium ethanethiolate (689 mg, 7.38 mmol), and DMF (3.7 ml); the reaction was degassed and heated to 60 °C overnight. The reaction was cooled, diluted with ethyl acetate, washed with H_2O (3 x 30 mL), brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by flash silica chromatography, elution gradient 0 to 100% EtOAc in hexanes. Product fractions were evaporated to dryness to afford 2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole (751 mg, 71 %) as a yellow oil which solidified on standing. The NMR data accords with the reference.[39]



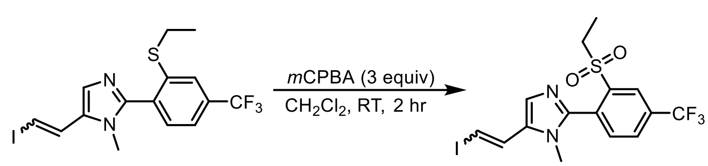
5-bromo-2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole: Adapting from the precedented literature procedure,[39] an oven dried 40 mL vial was charged with 2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole (751.3 mg, 2.62 mmol), 1-bromopyrrolidine-2,5-dione (467 mg, 2.62 mmol), and DCM (26.2 ml); the solution was immediately degassed, shielded from light, and allowed to stir at 25 °C overnight. The reaction was then concentrated in vacuo. The resulting residue was purified by flash silica chromatography, elution gradient 0 to 100% EtOAc in hexanes. Product fractions were evaporated to dryness to afford 5-bromo-2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole (575 mg, 60 %) as a colorless oil which solidified on standing. The NMR data accords with the reference.[39]



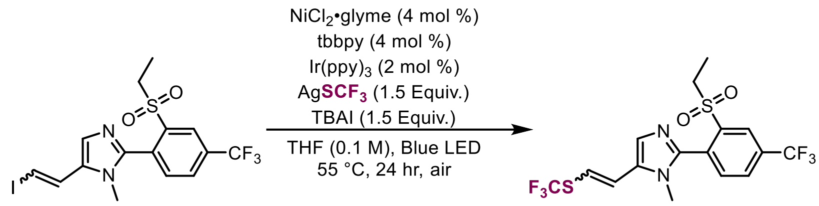
2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole-5-carbaldehyde: Adapting from the precedented literature procedure,[39] an oven dried 100 mL roundbottom was charged with 5-bromo-2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole (317.4 mg, 0.87 mmol) and THF (17 ml), the reaction was degassed and cooled to -78 °C for 30 min. *n*-butyllithium (365 µl, 0.91 mmol) was added dropwise over 5 min, the solution was stirred at -78 °C for 30 min, after which *N*,*N*-dimethylformamide (135 µl, 1.74 mmol) was added dropwise, the solution was stirred at -78 °C for 30 min, and warmed to room temperature over 45 min. The solution was concentrated in vacuo, and the resulting residue was purified by flash silica chromatography, elution gradient 0 to 100% EtOAc in hexanes. Product fractions were evaporated to dryness to afford 2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole-5-carbaldehyde (115 mg, 42 %) as a pale yellow oil which solidified on standing. The NMR data accords with the reference.[39]



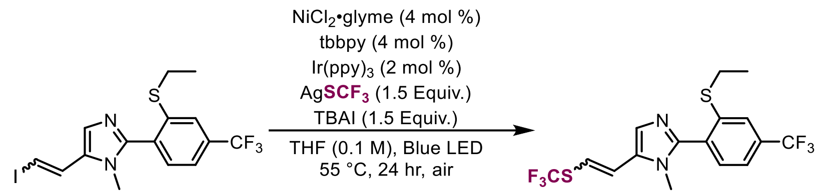
2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-5-(2-iodovinyl)-1-methyl-1*H*-imidazole: Adapting from the precedented literature procedure[39] and following general procedure A using 2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole-5-carbaldehyde (70.8 mg, 0.23 mmol) as the substrate, purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (*Z*)-2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-5-(2-iodovinyl)-1-methyl-1*H*-imidazole (80 mg, 81 %, *E*:*Z* = 1:2.1) as a pale yellow oil. The NMR data accords with the reference.[39]



2-(2-(ethylsulfonyl)-4-(trifluoromethyl)phenyl)-5-(2-iodovinyl)-1-methyl-1*H*-imidazole: Adapting from the precedented literature procedure,[39] an oven dried 1 dram vial was charged with 2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-5-(2-iodovinyl)-1-methyl-1*H*-imidazole (75 mg, 0.17 mmol) and 3-chlorobenzoperoxoic acid (97 mg, 0.56 mmol), and DCM (1.2 ml), the reaction was degassed, shielded from light, and allowed to stir at room temperature for 2 hrs. The solution was concentrated in vacuo and the resulting residue was purified by flash silica chromatography, elution gradient 0 to 75% EtOAc in hexanes. Product fractions were evaporated to dryness to afford 2-(2-(ethylsulfonyl)-4-(trifluoromethyl)phenyl)-5-(2-iodovinyl)-1-methyl-1*H*-imidazole (50 mg, 63 %, *E*:*Z* = 1:2.1) as a yellow solid. The NMR data accords with the reference.[39]

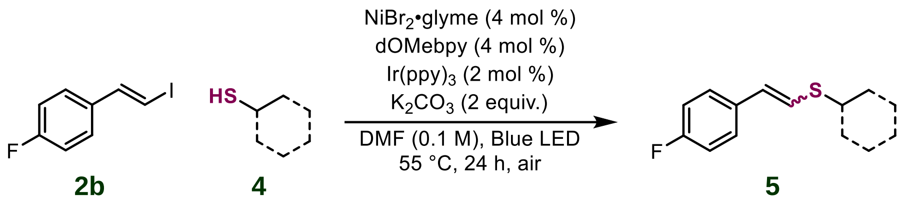


2-(2-(ethylsulfonyl)-4-(trifluoromethyl)phenyl)-1-methyl-5-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole (1b): Following general procedure C using 2-(2-(ethylsulfonyl)-4-(trifluoromethyl)phenyl)-5-(2-iodovinyl)-1-methyl-1*H*-imidazole (141 mg, 0.3 mmol), synthesized as previously reported,[39] as the substrate. Purification via preparative LCMS (XSelect CSH C18 column, 5µm silica, 30 mm diameter, 100 mm length), using decreasingly polar mixtures of water (containing 0.2% NH_4OH) and MeCN as eluents yielded 2-(2-(ethylsulfonyl)-4-(trifluoromethyl)phenyl)-1-methyl-5-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole (80 mg, 60%, *E*:*Z* = 1.2:1) as a waxy white solid. **^{1}H NMR** (500 MHz, DCM-d_2): δ ppm 8.42 (s, 2 H), 8.02 (d, *J* = 7.93 Hz, 2 H), 7.63 (dd, *J* = 7.86, 3.59 Hz, 2 H), 7.31 - 7.42 (m, 2 H), 6.92 (d, *J* = 15.26 Hz, 1 H), 6.66 - 6.75 (m, 2 H), 6.50 (d, *J* = 10.38 Hz, 1 H), 3.45 (q, *J* = 7.32 Hz, 4 H), 3.41 (s, 3 H), 3.38 (s, 3 H), 1.21 (td, *J* = 7.44, 1.45 Hz, 6 H). **^{19}F NMR** (471 MHz, DCM-d_2): δ ppm -43.02, -43.32, -63.32. **^{13}C NMR** (126 MHz, DCM-d_2): δ ppm 145.21, 144.47, 141.29, 141.29, 135.46, 134.19, 134.15, 132.96, 131.35, 131.22, 130.91, 130.83, 130.73, 130.70, 130.70, 130.66, 130.63, 129.52, 129.10, 128.61, 128.55, 128.48, 128.29, 124.78, 124.78, 122.62, 118.34, 114.49, 112.10, 112.08, 51.98, 51.98, 32.53, 32.25, 30.27, 7.34, 7.34. The NMR data accords with the reference.[39]

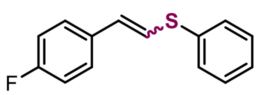


2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-5-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole (1c): Following general procedure C using 2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-5-(2-iodovinyl)-1-methyl-1*H*-imidazole (131 mg, 0.3 mmol), synthesized as previously reported,[39] as the substrate. Purification via flash chromatography (Hexane:Ethyl acetate gradient) yielded 2-(2-(ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-5-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole (71 mg, 57%, *E*:*Z* = 1:1.4) as a yellow solid. **^{1}H NMR** (500 MHz, DCM-d_2): δ ppm 7.62 (s, 2 H), 7.48 - 7.54 (m, 2 H), 7.40 - 7.48 (m, 3 H), 7.36 (s, 1 H), 6.94 (d, *J* = 15.11 Hz, 1 H), 6.64 - 6.73 (m, 2 H), 6.47 (d, *J* = 10.38 Hz, 1 H), 3.46 (s, 3 H), 3.42 (s, 3 H), 2.92 (q, *J* = 7.32 Hz, 2 H), 1.28 (t, *J* = 7.32 Hz, 3 H). **^{19}F NMR** (471 MHz, DCM-d_2): δ ppm -43.10, -43.46, -63.29, -63.30. **^{13}C NMR** (126 MHz, DCM-d_2): δ ppm 147.75, 146.93, 141.34, 134.41, 134.24, 132.43, 132.43, 131.20, 130.53, 129.60, 129.15, 129.07, 128.94, 128.82, 125.53, 124.33, 124.30, 124.27, 124.23, 124.20, 122.41, 118.69, 113.88, 113.85, 111.08, 111.08, 32.27, 31.94, 27.41, 14.04, 14.04. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{16}H_{14}F_6N_2S_2$ 413.0581; found 413.0586 (Δ = 1.2 ppm).

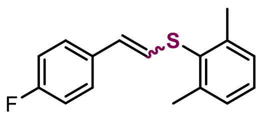
Thiolation of Alkenyl Iodides



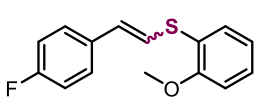
General Procedure D – Thiolation of Alkenyl Iodides: To a vial containing (*E*)-1-fluoro-4-(2-iodovinyl)benzene (74.4 mg, 0.30 mmol), potassium carbonate (82.9 mg, 0.60 mmol), tris(2-(pyridin-2-yl)phenyl)iridium (Ir(ppy)$_3$, 3.93 mg, 6.0 µmol), $NiBr_2$ • glyme (3.70 mg, 12.0 µmol), 4,4'-dimethoxy -2,2'-bipyridine (dOMebpy, 2.59 mg, 12.0 µmol) and thiol (0.45 mmol) was added 3.0 mL of DMF and the reaction irradiated at 440 nm with a blue kessil LED stirring in a EvoluChem™ PhotoRedOx Box for 24 h with no cooling fan (55°C). After completion the reaction was diluted with DCM (20 mL), washed with DI H_2O (3 x 10 mL) and brine (3 x 10 mL). The reaction was dried with $MgSO_4$, filtered, concentrated in vacuo, and purified via silica gel flash chromatography to provide the final product.



(4-Fluorostyryl)(phenyl)sulfane (5a): Following general procedure D using benzenethiol (50 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane) yielded (4-fluorostyryl)(phenyl)sulfane (58 mg, 84%, *E*:*Z* = 1:1.6) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.43 - 7.60 (m, 6 H), 7.25 - 7.42 (m, 6 H), 7.12 (br t, *J* = 8.70 Hz, 2 H), 7.04 (br t, *J* = 8.62 Hz, 2 H), 6.80 - 6.87 (m, 1 H), 6.70 - 6.77 (m, 1 H), 6.56 - 6.62 (m, 1 H), 6.49 - 6.54 (m, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -114.00. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 163.22, 162.62, 161.26, 160.65, 135.90, 135.07, 132.68, 130.95, 130.54, 130.43, 130.37, 130.03, 129.84, 129.16, 129.16, 127.53, 127.23, 126.16, 125.57, 125.57, 123.12, 123.12, 115.40.

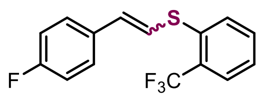


(2,6-Dimethylphenyl)(4-fluorostyryl)sulfane (5b): Following general procedure D using 2,6-dimethylbenzenethiol (62 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane) yielded (4-fluorostyryl)(phenyl)sulfane (58 mg, 91%, *E*:*Z* = 1:2.1) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.62 (dd, *J* = 8.54, 5.49 Hz, 1 H), 7.17 - 7.30 (m, 4 H), 7.14 (t, *J* = 8.70 Hz, 1 H), 6.97 (t, *J* = 8.70 Hz, 1 H), 6.61 (d, *J* = 15.26 Hz, 1 H), 6.46 (d, *J* = 10.83 Hz, 1 H), 6.01 (d, *J* = 10.99 Hz, 1 H), 2.56 (br s, 2 H), 2.55 (s, 4 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -114.57, -115.49. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 162.66, 162.34, 160.71, 160.37, 143.29, 142.39, 133.57, 133.22, 133.20, 133.11, 133.08, 130.35, 130.29, 129.77, 129.23, 128.89, 128.39, 128.32, 127.96, 127.96, 126.86, 126.80, 124.29, 124.26, 124.05, 115.47, 115.29, 115.27, 115.10, 22.07, 21.68.

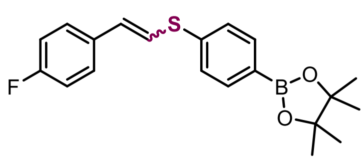


(4-Fluorostyryl)(2-methoxyphenyl)sulfane (5c): Following general procedure D using 2-methoxybenzenethiol (63 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:DCM gradient) yielded (4-fluorostyryl)(2-methoxyphenyl)sulfane (71 mg, 89%, *E*:*Z* = 1:1.5) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.56 - 7.63 (m, 2 H), 7.44 (dd, *J* = 7.71, 1.60 Hz, 1 H), 7.38 (dd, *J* = 7.63, 1.68 Hz, 1 H), 7.23 - 7.36 (m, 3 H), 7.07 - 7.13 (m, 2 H), 6.97 - 7.06 (m, 3 H), 6.93 (dd,

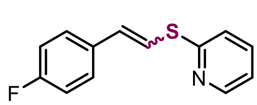
J = 8.16, 0.84 Hz, 2 H), 6.81 (d, J = 15.56 Hz, 1 H), 6.74 (d, J = 15.56 Hz, 1 H), 6.61 (d, J=10.83 Hz, 1 H), 6.47 (d, J=10.68 Hz, 1 H), 3.92 (s, 5 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -114.16, -114.21. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 163.12, 162.51, 161.16, 160.54, 157.18, 157.02, 132.74, 130.80, 130.50, 130.44, 130.33, 128.51, 128.18, 127.50, 127.43, 126.54, 124.84, 124.84, 123.81, 123.25, 122.11, 122.11, 121.27, 121.27, 115.28, 110.88, 110.80, 55.80, 55.80. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{13}FOS$ 261.0749; found 261.0753 (Δ = 1.5 ppm).



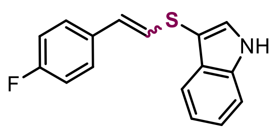
(4-Fluorostyryl)(2-(trifluoromethyl)phenyl)sulfane (5d): Following general procedure D using 2-(trifluoromethyl)benzenethiol (80 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane) yielded (4-fluorostyryl)(2-(trifluoromethyl)phenyl)sulfane (79 mg, 88%, E:Z = 1:1.6) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.85 (d, J = 7.93 Hz, 1 H), 7.70 (d, J = 7.78 Hz, 1 H), 7.66 (d, J = 7.78 Hz, 1 H), 7.46 - 7.59 (m, 2 H), 7.32 - 7.41 (m, 3 H), 7.01 - 7.07 (m, 2 H), 6.86 (d, J = 15.41 Hz, 1 H), 6.74 (d, J = 15.26 Hz, 1 H), 6.69 (d, J = 10.68 Hz, 1 H), 6.39 (d, J = 10.53 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -60.53, -61.02, -113.26 - -113.14, -113.55 - -113.44. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 163.60, 161.63, 135.48, 133.93, 132.49, 132.37, 132.34, 132.15, 131.34, 129.31, 129.07, 127.93, 127.86, 126.86, 126.68, 126.64, 126.46, 127.15, 122.61, 121.05, 115.83, 115.66. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 442.71 (w), 514.07 (m), 530.82 (w), 596.03 (w), 646.17 (m), 701.01 (m), 731.38 (w), 760.19 (s), 799.36 (w), 838.17 (m), 932.67 (w), 948.46 (w), 1032.71 (s), 1044.16 (w), 1093.82 (m), 1112.5 (s), 1125.16 (s), 1158.18 (m), 1172.41 (m), 1228.69 (m), 1258.1 (m), 1310.05 (vs), 1443.48 (w), 1471.44 (w), 1506.88 (m), 1571.36 (w), 1593.54 (w), 1601.26 (w), 2865.15 (vw), 2927.34 (vw), 3034.49 (vw), 3070.53 (vw).



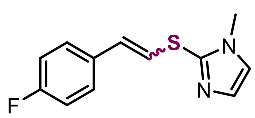
2-(4-((4-Fluorostyryl)thio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e): Following general procedure D using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenethiol (106 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 2-(4-((4-fluorostyryl)thio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67 mg, 63%, E:Z = 1:1.6) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.79 (t, J = 8.09 Hz, 3 H), 7.72 - 7.76 (m, 1 H), 7.53 (dd, J = 8.62, 5.42 Hz, 2 H), 7.49 (d, J = 8.39 Hz, 1 H), 7.44 (d, J = 8.24 Hz, 2 H), 7.39 (d, J = 8.24 Hz, 1 H), 7.31 - 7.37 (m, 2 H), 7.06 - 7.12 (m, 2 H), 7.00 - 7.06 (m, 1 H), 6.80 - 6.86 (m, 1 H), 6.75 - 6.80 (m, 1 H), 6.59 - 6.65 (m, 1 H), 6.49 - 6.55 (m, 1 H), 1.36 (s, 21 H), 1.35 (s, 7 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm –113.81, -113.92. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 163.35, 162.70, 161.38, 160.73, 139.54, 139.24, 135.63, 135.44, 135.39, 135.33, 132.58, 131.73, 130.51, 130.44, 129.01, 128.31, 128.00, 127.68, 127.61, 127.10, 125.94, 124.26, 124.26, 121.90, 121.90, 115.44, 83.90, 26.64, 24.84, 24.66. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 3069.21 (vw) ,3034.73 (vw) ,2977.6 (w) ,2930.96 (vw) ,1595.23 (m) ,1581.25 (w) ,1506.4 (m) ,1466.5 (w) ,1389.84 (m) ,1355.98 (vs) ,1321.38 (m) ,1298 (w) ,1271.36 (w) ,1258.71 (w) ,1228.69 (m) ,1214.35 (w) ,1158.43 (w) ,1142.03 (m) ,1097.56 (s) ,1075.86 (w) ,1016.08 (m) ,961.48 (w) ,857.22 (m) ,835.76 (m) ,819.37 (m) ,728.37 (w) ,695.95 (w) ,667.74 (w) ,651.23 (s) ,577.71 (vw) ,529.61 (w), 438.49 (w).



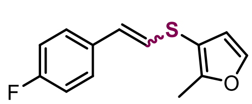
2-((4-Fluorostyryl)thio)pyridine (5f): Following general procedure D using pyridine-2-thiol (50 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 2-((4-fluorostyryl)thio)pyridine (47 mg, 68%, *E*:*Z* = 1:4.9) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.52 - 8.55 (m, 1 H), 8.48 - 8.51 (m, 1 H), 7.53 - 7.59 (m, 1 H), 7.48 - 7.53 (m, 2 H), 7.44 (s, 1 H), 7.38 - 7.43 (m, 1 H), 7.36 (d, *J*=10.83 Hz, 1 H), 7.27 - 7.31 (m, 1 H), 7.21 - 7.26 (m, 1 H), 7.05 - 7.12 (m, 3 H), 7.00 - 7.05 (m, 1 H), 6.84 (d, *J*=15.87 Hz, 1 H), 6.71 (d, *J*=10.83 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -118.80 - -118.72 (m, 1 F), -118.93 - -118.84 (m, 1 F). ^{13}C NMR (126 MHz, DMSO-d_6): δ ppm 163.31, 162.62, 161.35, 160.65, 157.77, 156.20, 149.80, 149.75, 136.53, 136.42, 132.85, 132.82, 132.82, 130.56, 130.43, 130.37, 127.80, 127.73, 126.30, 122.82, 122.06, 120.64, 120.24, 119.84, 119.84, 119.44, 119.44, 115.64, 115.47, 115.33, 115.16, 77.25, 77.00, 76.75. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{10}FNS$ 232.0596; found 232.0599 (Δ = 1.3 ppm).



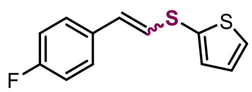
3-((4-Fluorostyryl)thio)-1*H*-indole (5g): Following general procedure D using 1*H*-indole-3-thiol (67 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 3-((4-fluorostyryl)thio)-1*H*-indole (75 mg, 93%, *E*:*Z* = 1:2.2) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.33 (br s, 1 H), 8.26 (br s, 4 H), 7.81 (d, *J* = 7.93 Hz, 4 H), 7.78 (s, 1 H), 7.59 - 7.66 (m, 8 H), 7.47 (s, 1 H), 7.42 - 7.46 (m, 5 H), 7.41 (d, *J* = 2.59 Hz, 4 H), 7.33 (td, *J* = 7.51, 1.14 Hz, 5 H), 7.24 - 7.31 (m, 5 H), 7.12 - 7.20 (m, 10 H), 6.92 - 6.99 (m, 2 H), 6.72 (d, *J* = 15.41 Hz, 1 H), 6.39 - 6.43 (m, 4 H), 6.33 - 6.37 (m, 4 H), 6.31 (d, *J* = 15.41 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -114.63, -115.51. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 162.67, 162.37, 160.72, 160.41, 136.29, 136.09, 133.12, 133.10, 133.06, 133.04, 130.33, 130.27, 130.08, 130.08, 129.44, 128.76, 128.62, 128.47, 126.99, 126.93, 126.32, 126.32, 125.03, 123.60, 123.06, 120.87, 120.80, 119.48, 119.27, 115.43, 115.30, 115.26, 115.13, 111.60, 111.55, 105.88, 102.69. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{16}H_{12}FNS$ 270.0753; found 270.0748 (Δ = 1.9 ppm).



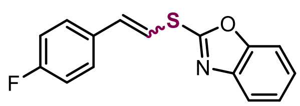
2-((4-Fluorostyryl)thio)-1-methyl-1*H*-imidazole (5h): Following general procedure D using 1-methyl-1*H*-imidazole-2-thiol (51 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 2-((4-fluorostyryl)thio)-1-methyl-1*H*-imidazole (29 mg, 41%, *E*:*Z* = 1:2.1) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.40 - 7.46 (m, 6 H), 7.21 - 7.27 (m, 2 H), 7.12 (d, *J* = 1.07 Hz, 1 H), 7.03 - 7.11 (m, 9 H), 7.01 (d, *J* = 1.22 Hz, 1 H), 6.93 - 6.98 (m, 5 H), 6.76 (d, *J* = 15.56 Hz, 1 H), 6.63 (d, *J* = 10.53 Hz, 3 H), 6.58 (d, *J* = 10.68 Hz, 3 H), 6.50 (d, *J* = 15.56 Hz, 1 H), 3.65 (s, 3 H), 3.61 (s, 9 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -113.72, -113.99. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 163.14, 162.62, 161.17, 160.65, 139.58, 138.34, 132.30, 132.27, 132.18, 132.15, 130.28, 130.22, 129.86, 129.62, 129.46, 127.56, 127.49, 126.61, 123.16, 122.88, 122.08, 122.08, 120.71, 120.71, 115.51, 115.32, 115.32, 115.14, 33.41, 33.27. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{11}FN_2S$ 235.0705; found 235.0706 (Δ = 0.4 ppm).



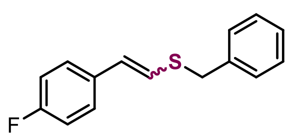
3-((4-Fluorostyryl)thio)-2-methylfuran (5i): Following general procedure D using 2-methylfuran-3-thiol (51 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:DCM gradient) yielded 3-((4-fluorostyryl)thio)-2-methylfuran (48 mg, 69%, *E*:*Z* = 1:1.9) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.46 - 7.55 (m, 2 H), 7.38 (d, *J* = 1.83 Hz, 1 H), 7.33 (d, *J* = 1.83 Hz, 1 H), 7.25 - 7.30 (m, 1 H), 7.18 - 7.24 (m, 1 H), 7.06 - 7.14 (m, 2 H), 6.98 (t, *J* = 8.70 Hz, 1 H), 6.57 (d, *J* = 15.26 Hz, 1 H), 6.38 - 6.45 (m, 3 H), 6.28 (d, *J* = 15.41 Hz, 1 H), 6.18 (d, *J* = 10.83 Hz, 1 H), 2.43 (s, 1 H), 2.35 - 2.40 (m, 4 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -114.43, -115.18. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 162.86, 162.47, 160.90, 160.51, 155.66, 154.45, 141.09, 140.88, 140.80, 140.80, 132.97, 132.95, 132.77, 132.75, 130.29, 130.22, 128.18, 128.18, 127.09, 127.02, 125.54, 124.81, 124.81, 124.30, 115.57, 115.40, 115.32, 115.19, 115.15, 114.92, 114.73, 114.29, 110.71, 107.44, 11.82, 11.38. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{11}FOS$ 235.0593; found 235.0591 (Δ = 0.9 ppm).



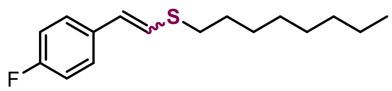
2-((4-Fluorostyryl)thio)thiophene (5j): Following general procedure D using thiophene-2-thiol (52 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:DCM gradient) yielded 2-((4-fluorostyryl)thio)thiophene (38 mg, 54%, *E*:*Z* = 1.9:1) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.44 - 7.51 (m, 2 H), 7.42 (dd, *J* = 5.34, 1.22 Hz, 1 H), 7.23 (dd, *J* = 3.51, 1.22 Hz, 1 H), 7.06 - 7.13 (m, 2 H), 7.04 (dd, *J* = 5.34, 3.66 Hz, 1 H), 6.70 (d, *J* = 15.26 Hz, 1 H), 6.42 - 6.46 (m, 1 H), 6.34 - 6.38 (m, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm –113.95, -114.40. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 162.67, 160.69, 133.32, 133.23, 132.40, 132.37, 130.37, 130.31, 129.76, 128.57, 128.57, 127.85, 127.70, 127.64, 127.59, 124.81, 115.40, 115.22. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_9FS_2$ 237.0208; found 237.0209 (Δ = 0.4 ppm).



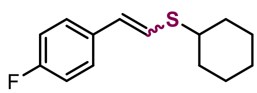
2-((4-Fluorostyryl)thio)benzo[*d*]oxazole (5k): Following general procedure D using benzo[*d*]oxazole-2-thiol (68 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 2-((4-fluorostyryl)thio)benzo[*d*]oxazole (69 mg, 85%, *E*:*Z* = 1:2.2) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.82 - 7.87 (m, 1 H), 7.77 - 7.81 (m, 2 H), 7.72 - 7.77 (m, 1 H), 7.32 - 7.43 (m, 5 H), 7.25 (s, 1 H), 7.20 (d, *J* = 15.11 Hz, 1 H), 7.09 (d, *J* = 10.22 Hz, 1 H), 6.66 (d, *J* = 15.11 Hz, 1 H), 6.42 (d, *J* = 10.22 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -42.51, -42.57. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 140.80, 139.48, 139.48, 139.37, 138.76, 138.03, 134.47, 134.47, 133.03, 132.99, 130.58, 130.53, 128.13, 128.08, 127.38, 127.38, 126.69, 125.65, 125.30, 125.22, 124.81, 124.76, 124.11, 123.96, 122.31, 122.23, 113.19, 113.09. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{10}FNOS$ 272.0545; found 272.0551 (Δ = 2.2 ppm).



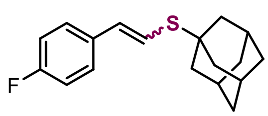
Benzyl(4-fluorostyryl)sulfane (5l): Following general procedure D using phenylmethanethiol (56 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane) yielded benzyl(4-fluorostyryl)sulfane (53 mg, 72%, *E*:*Z* = 1:2) as a clear oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.41 - 7.48 (m, 2 H), 7.33 - 7.41 (m, 5 H), 7.26 - 7.33 (m, 2 H), 7.18 - 7.25 (m, 1 H), 7.01 - 7.07 (m, 2 H), 6.95 - 7.01 (m, 1 H), 6.59 - 6.67 (m, 1 H), 6.48 - 6.54 (m, 1 H), 6.40 (d, *J* = 10.99 Hz, 1 H), 6.24 (d, *J* = 10.83 Hz, 1 H), 4.02 (s, 1 H), 4.01 (s, 2 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -114.69, -115.08. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 162.91, 162.35, 160.95, 160.39, 137.27, 137.16, 133.16, 133.14, 133.05, 133.03, 130.31, 130.25, 128.95, 128.80, 128.70, 128.66, 127.44, 127.35, 127.07, 127.01, 126.95, 125.52, 125.52, 124.80, 124.00, 124.00, 115.59, 115.41, 115.19, 115.02, 39.41, 37.41.



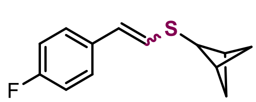
(4-Fluorostyryl)(octyl)sulfane (5m): Following general procedure D using octane-1-thiol (66 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane) yielded (4-fluorostyryl)(octyl)sulfane (64 mg, 80%, *E*/*Z* = 1:1.9) as a dark red oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.45 - 7.53 (m, 2 H), 7.24 - 7.31 (m, 1 H), 7.07 (t, *J*=8.70 Hz, 2 H), 7.01 (t, *J* = 8.70 Hz, 1 H), 6.67 (d, *J* = 15.56 Hz, 1 H), 6.46 (d, *J* = 15.56 Hz, 1 H), 6.42 (d, *J* = 10.83 Hz, 1 H), 6.25 (d, *J* = 10.99 Hz, 1 H), 2.77 - 2.85 (m, 3 H), 1.72 (quin, *J* = 7.44 Hz, 3 H), 1.41 - 1.51 (m, 3 H), 1.25 - 1.39 (m, 13 H), 0.92 (t, *J* = 6.87 Hz, 5 H). **^{19}F NMR** (471 MHz, CDl_3): δ ppm -114.96, -115.51. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 162.76, 162.24, 160.80, 160.27, 133.42, 133.39, 133.26, 133.23, 130.21, 130.14, 127.20, 127.20, 126.86, 126.80, 125.55, 125.09, 125.09, 124.11, 115.54, 115.37, 115.13, 114.96, 35.80, 32.66, 31.77, 30.20, 29.43, 29.13, 29.13, 28.79, 28.56, 22.61, 14.05. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{16}H_{23}FS$ 267.1583; found 267.1582 (Δ = 0.4 ppm).



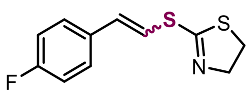
Cyclohexyl(4-fluorostyryl)sulfane (5n): Following general procedure D using cyclohexanethiol (52 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane) yielded cyclohexyl(4-fluorostyryl)sulfane (62 mg, 88%, *E*:*Z* = 1:1.6) as a dark red oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.41 - 7.52 (m, 2 H), 7.21 - 7.31 (m, 1 H), 6.92 - 7.12 (m, 3 H), 6.64 - 6.71 (m, 1 H), 6.51 - 6.57 (m, 1 H), 6.36 - 6.42 (m, 1 H), 6.28 - 6.34 (m, 1 H), 2.84 - 3.01 (m, 2 H), 2.00 - 2.14 (m, 3 H), 1.81 (br dd, *J* = 8.99, 3.61 Hz, 3 H), 1.56 - 1.71 (m, 2 H), 1.21 - 1.53 (m, 9 H). **^{19}F NMR** (377 MHz, $CDCl_3$): δ ppm -115.12, -115.33. **^{13}C NMR** (101 MHz, $CDCl_3$): δ ppm 163.09, 162.46, 160.64, 160.00, 133.38, 133.36, 133.35, 133.30, 130.24, 130.16, 127.53, 127.02, 126.94, 125.40, 125.40, 123.91, 123.72, 123.72, 115.56, 115.34, 115.13, 114.92, 47.69, 45.33, 33.63, 33.58, 25.98, 25.93, 25.63, 25.55.



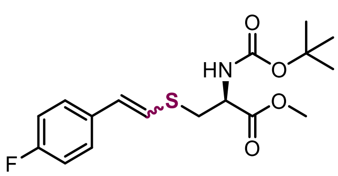
Adamantan-1-yl(4-fluorostyryl)sulfane (5o): Following general procedure D using adamantane-1-thiol (76 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane) yielded adamantan-1-yl(4-fluorostyryl)sulfane (85 mg, 98%, *E*:*Z* = 1:1.3) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.48 (dd, *J* = 8.62, 5.56 Hz, 2 H), 7.30 (dd, *J* = 8.50, 5.56 Hz, 2 H), 7.02 (dt, *J* = 13.79, 8.70 Hz, 4 H), 6.81 - 6.87 (m, 1 H), 6.64 - 6.71 (m, 1 H), 6.46 - 6.52 (m, 1 H), 6.41 - 6.46 (m, 1 H), 2.10 (br d, *J* = 3.06 Hz, 8 H), 1.98 (dd, *J* = 9.78, 2.45 Hz, 11 H), 1.84 (d, *J* = 2.45 Hz, 5 H), 1.63 - 1.78 (m, 16 H). **^{19}F NMR** (377 MHz, $CDCl_3$): δ ppm -114.84, -115.19. **^{13}C NMR** (101 MHz, $CDCl_3$): δ ppm 163.23, 162.41, 160.78, 159.96, 133.37, 130.67, 130.32, 130.25, 127.31, 127.23, 124.11, 120.31, 115.18, 47.54, 47.27, 46.63, 46.46, 43.63, 43.56, 43.23, 43.06, 36.36, 36.29, 36.15, 36.14, 36.13, 35.78, 30.09, 30.02, 29.78, 29.72. **HRMS (ESI-TOF)**: Sample failed to ionize. **FT-IR (ATR)**: ν_{max} cm^{-1} 2901.43 (s), 2848.27 (m), 1600.9 (w), 1576.19 (w), 1504.59 (vs), 1448.3 (w), 1342.11 (w), 1299.45 (m), 1227.97 (s), 1157.58 (m), 1101.05 (w), 1039.1 (m), 976.91 (w), 944.6 (w), 929.66 (w), 857.46 (m), 834.08 (s), 812.14 (w), 799.97 (w), 765.01 (w), 731.87 (w), 699.92 (m), 685.1 (w), 660.63 (w), 616.16 (w), 528.41 (s), 512.62 (m), 439.22 (w), 410.77 (w).



Bicyclo[1.1.1]pentan-2-yl(4-fluorostyryl)sulfane (5p): Following general procedure D using bicyclo[1.1.1]pentane-2-thiol (45 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane) yielded bicyclo[1.1.1]pentan-2-yl(4-fluorostyryl)sulfane (30 mg, 45%, *E*:*Z* = 1.9:1) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.38 - 7.45 (m, 2 H), 7.25 - 7.31 (m, 1 H), 6.93 - 7.10 (m, 4 H), 6.63 (s, 1 H), 6.58 - 6.62 (m, 1 H), 6.45 (d, *J* = 10.83 Hz, 1 H), 6.31 (d, *J* = 10.83 Hz, 1 H), 2.81 - 2.84 (m, 1 H), 2.09 - 2.12 (m, 9 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -119.59, -119.71. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 162.99, 162.33, 161.02, 160.36, 133.24, 133.21, 133.12, 133.10, 130.43, 130.26, 130.21, 130.15, 128.51, 127.20, 127.14, 124.37, 123.61, 123.61, 122.49, 122.49, 115.77, 115.59, 115.42, 115.17, 115.00, 53.90, 53.54, 44.29, 43.97, 29.03, 28.59. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{13}FS$ 221.0800; found 221.0802 (Δ = 0.9 ppm).



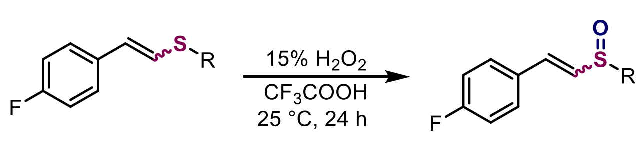
2-((4-Fluorostyryl)thio)-4,5-dihydrothiazole (5q): Following general procedure D using 4,5-dihydrothiazole-2-thiol (54 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:DCM gradient) yielded 2-((4-fluorostyryl)thio)-4,5-dihydrothiazole (32 mg, 45%, *E*:*Z* = 1:3.2) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.41 (dd, *J* = 8.62, 5.42 Hz, 2 H), 7.17 (d, *J* = 15.87 Hz, 1 H), 7.03 - 7.11 (m, 3 H), 6.79 (d, *J* = 15.87 Hz, 1 H), 6.66 (d, *J* = 10.83 Hz, 1 H), 4.29 (t, *J* = 8.01 Hz, 2 H), 3.44 (t, *J* = 8.01 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$): δ ppm -113.26, -113.01. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 163.56, 162.91, 160.93, 132.00, 131.98, 130.54, 130.47, 128.09, 127.96, 118.88, 118.88, 115.73, 115.48, 115.31, 64.10, 35.35. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_{10}FNS_2$ 240.0317; found 240.0317 (Δ = 0.0 ppm).



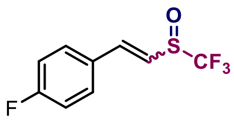
Methyl *N*-(*tert*-butoxycarbonyl)-*S*-(4-fluorostyryl)-*D*-cysteinate (5r): Following general procedure D using methyl (tert-butoxycarbonyl)-D-cysteinate (106 mg, 0.45 mmol) as the thiol reactant. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded methyl N-(tert-butoxycarbonyl)-S-(4-fluorostyryl)-D-cysteinate (80 mg, 75%, *E*:*Z* = 1:1.9) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.43 (dd, *J* = 8.56, 5.50 Hz, 2 H), 7.21 - 7.29 (m, 1 H), 6.95 - 7.08 (m, 3 H), 6.55 (d, *J* = 3.18 Hz, 1 H), 6.40 (d, *J*=10.76 Hz, 1 H), 6.14 (d, *J* = 10.88 Hz, 1 H), 5.39 (br d, *J* =7 .46 Hz, 1 H), 4.65 (br s, 1 H), 3.76 (s, 3 H), 3.71 (s, 2 H), 3.19 - 3.33 (m, 3 H), 1.45 (s, 9 H), 1.43 (s, 5 H). **^{19}F NMR** (377 MHz, $CDCl_3$): δ ppm -114.38, -114.58. **^{13}C NMR** (101 MHz, $CDCl_3$): δ ppm 170.89, 170.73, 163.29, 162.63, 160.83, 160.18, 154.93, 132.76, 132.76, 132.63, 132.63, 130.33, 130.25, 128.51, 127.21, 127.13, 125.90, 125.46, 123.63, 115.62, 115.41, 115.21, 115.00, 80.24, 80.18, 53.68, 53.50, 52.60, 52.60, 38.19, 35.72, 28.22. **HRMS (ESI-TOF) m/z:** $[M+Na]^+$ Calcd for $C_{17}H_{22}FNO_4S$ 378.1151; found 378.1157 (Δ = 1.6 ppm).

Post-functionalization of (Trifluoromethyl)thiolation Products

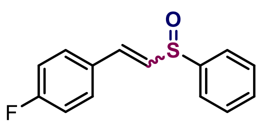
Product oxidation to sulfoxides and sulfones



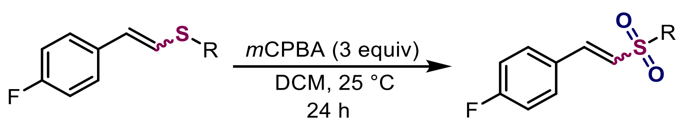
General Procedure E – Sulfoxide formation: Sulfoxide products were synthesized employing a procedure derived from existing literature.[40] An oven dried 1 dram vial was charged with alkenyl sulfide (0.15 mmol) and trifluoroacetic acid (1.5 ml). Hydrogen peroxide (15.73 µl, 0.15 mmol) and was added dropwise and the reaction was allowed to stir at room temperature overnight. The resulting mixture was poured into DI H_2O (2 mL), neutralized with aqueous $NaHCO_3$, and extracted into DCM (20 mL). The reaction was dried with $MgSO_4$, filtered, concentrated in vacuo, and purified via silica gel flash chromatography to provide the final product.



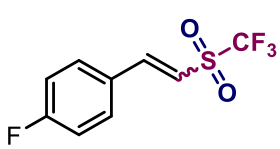
1-Fluoro-4-(2-((trifluoromethyl)sulfinyl)vinyl)benzene (6a): Following general procedure E using (4-fluorostyryl)(trifluoromethyl)sulfane (**3b**, 33.9 mg, 0.15 mmol) as the alkenyl sulfide. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 1-fluoro-4-(2 1-fluoro-4-(2-((trifluoromethyl)sulfinyl)vinyl)benzene (17 mg, 46%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.09 (t, *J* = 1.83 Hz, 1 H), 8.00 (dt, *J* = 7.78, 1.30 Hz, 1 H), 7.57 - 7.61 (m, 1 H), 7.52 (d, *J* = 10.68 Hz, 1 H), 7.43 (t, *J* = 7.86 Hz, 1 H), 7.35 - 7.40 (m, 2 H), 7.09 - 7.19 (m, 2 H), 6.62 (d, *J* = 10.68 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -72.60, -108.47. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 170.42, 164.98, 162.97, 145.54, 134.66, 133.77, 131.86, 131.79, 131.05, 130.19, 129.80, 128.85, 128.83, 128.25, 127.05, 126.64, 123.98, 121.32, 116.23, 116.06. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for C_9H_6F4OS 239.0154; found 239.0160 (Δ = 2.5 ppm).



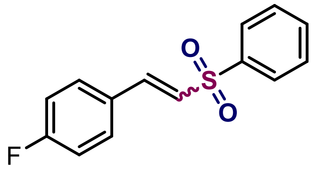
1-Fluoro-4-(2-(phenylsulfinyl)vinyl)benzene (6b): Following general procedure E using (4-Fluorostyryl)(phenyl)sulfane (**5a**, 34.5 mg, 0.15 mmol) as the alkenyl sulfide. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 1-fluoro-4-(2-(phenylsulfinyl)vinyl)benzene (20 mg, 53%) as a off white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.63 - 7.72 (m, 2 H), 7.47 - 7.57 (m, 3 H), 7.43 (dd, *J* = 8.54, 5.49 Hz, 2 H), 7.34 (d, *J* = 15.41 Hz, 1 H), 7.04 (t, *J* = 8.54 Hz, 2 H), 6.77 (d, *J* = 15.41 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -110.08. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 164.49, 162.50, 143.59, 135.24, 132.40, 132.40, 131.20, 129.90, 129.87, 129.62, 129.55, 129.44, 124.64, 116.04, 115.87.



General Procedure F – Sulfone formation: Sulfoxide products were synthesized employing a procedure derived from existing literature.[39, 40] An oven dried 1 dram vial was charged with alkenyl sulfide (0.15 mmol) and 3-chlorobenzoperoxoic acid (78 mg, 0.45 mmol), and DCM (1.5 mL), the reaction was degassed, shielded from light, and allowed to stir at room temperature for 2 h. The solution was concentrated in vacuo and purified via silica gel flash chromatography to provide the final product.

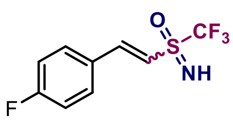


1-Fluoro-4-(2-((trifluoromethyl)sulfonyl)vinyl)benzene (6c): Following general procedure F using (4-fluorostyryl)(trifluoromethyl)sulfane (**3b**, 33.9 mg, 0.15 mmol) as the alkenyl sulfide. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 1-fluoro-4-(2-((trifluoromethyl)sulfonyl)vinyl)benzene (29 mg, 75%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.05 (t, *J* = 1.75 Hz, 1 H), 7.97 (dt, *J* = 7.78, 1.22 Hz, 1 H), 7.86 (d, *J* = 15.41 Hz, 1 H), 7.57 - 7.69 (m, 2 H), 7.48 (t, *J* = 7.93 Hz, 1 H), 7.13 - 7.24 (m, 2 H), 6.77 (d, *J*=15.56 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -78.72, -103.89. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 166.59, 164.55, 161.79, 152.32, 135.15, 134.48, 131.88, 131.81, 130.25, 129.77, 127.88, 127.53, 127.51, 127.08, 116.97, 116.79, 116.35, 119.67. **HRMS (ESI-TOF) m/z:** $[M–H]^–$ Calcd for $C_9H_6F_4O_2S$ 252.9946; found 252.9940 (Δ = 2.4 ppm).

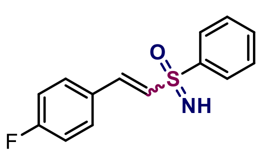


1-Fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (6d): Following general procedure F using (4-fluorostyryl)(phenyl)sulfane (**5a**, 34.5 mg, 0.15 mmol) as the alkenyl sulfide. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 1-fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (37 mg, 95%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.09 (s, 1 H), 8.00 (d, *J* = 7.78 Hz, 1 H), 7.79 - 7.87 (m, 2 H), 7.53 - 7.64 (m, 4 H), 7.45 - 7.50 (m, 2 H), 7.40 - 7.45 (m, 1 H), 6.96 - 7.11 (m, 3 H), 6.51 (d, *J* = 12.05 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -109.92. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 164.48, 162.48, 140.84, 140.12, 134.66, 133.78, 133.44, 132.45, 132.38, 131.08, 130.82, 130.82, 130.21, 129.81, 129.01, 128.36, 128.33, 128.27, 127.45, 115.31, 115.13.

Product derivatization to *N*H-sulfoximines via O- and N-transfer.

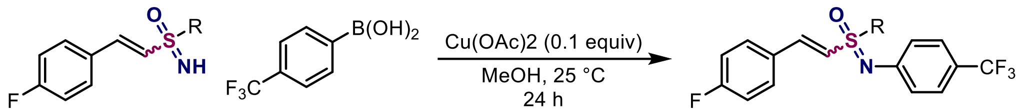


(4-Fluorostyryl)(imino)(trifluoromethyl)-λ^6-sulfanone (7a): *N*H-Sulfoximine products derived from alkenyl-SCF_3 products were synthesized employing a procedure derived from existing literature.[41] An oven dried 1 dram vial was charged with ((4-fluorostyryl)(trifluoromethyl)sulfane (**3b**, 33.9 mg, 0.15 mmol), ammonium carbamate (24 mg, 0.30 mmol), (diacetoxyiodo)benzene (121 mg, 0.38 mmol), and 2,2,2-trifluoroethanol (1.5 mL), the reaction was degassed, shielded from light, and allowed to stir at room temperature for 3 h. The reaction was concentrated in vacuo and the crude mixture was diluted with aqueous HCl (6M,300 µL) and MeCN (600 µL) and the reaction stirred overnight at room temperature. The reaction was quenched with aqueous $NaHCO_3$ and extracted into EtOAc, the organic phase was washed sequentially with DI H_2O (15 mL) and brine (2 x 15 mL), dried over $MgSO_4$, concentrated in vacuo, and purified via silica gel flash chromatography (Hexane:Ethyl Acetate gradient) yielding (4-fluorostyryl)(imino)(trifluoromethyl)-λ^6-sulfanone (19 mg, 49%) as an off white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.80 (d, *J* = 15.56 Hz, 1 H), 7.59 (br dd, *J* = 8.54, 5.34 Hz, 2 H), 7.14 (br t, *J* = 8.47 Hz, 2 H), 6.80 (d, *J* = 15.56 Hz, 1 H), 3.63 (br s, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -79.18, -105.40. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 166.08, 164.05, 150.04, 131.43, 131.36, 127.89, 122.10, 119.47, 117.46, 116.64, 116.47. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_9NOF_4SH_7$ 254.0263; found 254.0271 (Δ = 3.1 ppm).

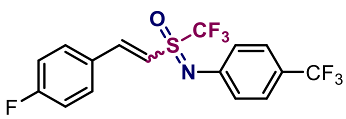


(4-Fluorostyryl)(imino)(phenyl)-λ^6-sulfanone (7b): NH-Sulfoximine products derived from alkenyl-sulfide products were synthesized employing a procedure derived from existing literature.[42, 43] An oven dried 1 dram vial was charged with (4-fluorostyryl)(phenyl)sulfane (**5a**, 34.5 mg, 0.15 mmol), ammonium carbamate (24 mg, 0.30 mmol), (diacetoxyiodo)benzene (121 mg, 0.38 mmol), and methanol (1.5 mL), the reaction was degassed, shielded from light, and allowed to stir at room temperature for 3 h. The solution was concentrated in vacuo and purified via silica gel flash chromatography (Hexane:Ethyl Acetate gradient) yielding (4-fluorostyryl)(imino)(phenyl)-λ^6-sulfanone (21 mg, 53%) as an off white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.02 (d, *J* = 7.48 Hz, 2 H), 7.54 - 7.62 (m, 2 H), 7.48 - 7.54 (m, 2 H), 7.45 (dd, *J* = 8.54, 5.34 Hz, 2 H), 7.05 (t, *J* = 8.54 Hz, 2 H), 6.87 (d, *J* = 15.26 Hz, 1 H), 2.54 - 3.24 (m, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -108.40. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 165.04, 163.03, 142.73, 140.12, 132.74, 130.39, 130.32, 129.19, 129.19, 129.14, 128.87, 128.84, 127.78, 116.20, 116.02. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}NOFSH_{12}$ 262.0702; found 262.0704 (Δ = 0.8 ppm).

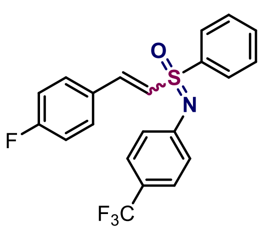
N-arylation of alkenyl-*N*H-sulfoximines.



General Procedure G – *N*H-Sulfoximine arylation: arylated *N*H-sulfoximine products were synthesized employing a procedure derived from existing literature.[44] An oven dried 1 dram vial was charged with alkenyl-*N*H-sulfoximine (0.15 mmol), $Cu(OAc)_2$ (0.015 mmol), and methanol (1.5 mL). The reaction was allowed to stir for 24 h at 25 °C, after which the solution was concentrated in vacuo and purified via silica gel flash chromatography to provide the final product.

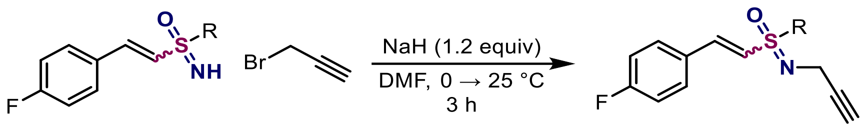


(4-Fluorostyryl)(trifluoromethyl)((4-(trifluoromethyl)phenyl)imino)- λ^6-sulfanone (8a): Following general procedure G (4-fluorostyryl)(imino)(trifluoromethyl)-λ^6-sulfanone (**7a**, 38.0 mg, 0.15 mmol) as the alkenyl sulfide. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded 4-fluorostyryl)(trifluoromethyl)((4-(trifluoromethyl)phenyl)imino)- λ^6-sulfanone (30 mg, 51%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.88 (d, *J* = 15.41 Hz, 1 H), 7.65 (dd, *J* = 8.47, 5.26 Hz, 2 H), 7.54 (br d, *J* = 8.39 Hz, 2 H), 7.26 - 7.33 (m, 2 H), 7.19 (t, *J* = 8.47 Hz, 2 H), 6.83 (d, *J* = 15.41 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -62.06, -72.56, -104.54. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 165.38, 150.46, 144.95, 131.62, 127.79, 126.37, 125.99, 125.74, 125.37, 123.94, 123.22, 122.74, 120.06, 117.25, 116.83.**HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{16}H_{11}F_7NOS$ 398.0450; found 398.0454 (Δ = 1.0 ppm).

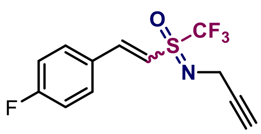


(4-Fluorostyryl)(phenyl)((4-(trifluoromethyl)phenyl)imino)- λ^6-sulfanone (8b): Following general procedure G (4-fluorostyryl)(imino)(phenyl)-λ^6-sulfanone (**7b**, 38.0 mg, 0.15 mmol) as the alkenyl sulfide. Purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (4-fluorostyryl)(phenyl)((4-(trifluoromethyl)phenyl)imino)- λ^6-sulfanone (41 mg, 68%) as an off white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.03 (br d, *J* = 7.48 Hz, 2 H), 7.69 (br d, *J* = 15.26 Hz, 1 H), 7.45 - 7.63 (m, 5 H), 7.41 (br d, *J* = 8.24 Hz, 2 H), 7.20 (br d, *J* = 8.09 Hz, 2 H), 7.08 (br t, *J* = 8.32 Hz, 2 H), 6.87 (br d, *J* = 15.26 Hz, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -61.63, -107.57. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 165.35, 163.34, 148.31, 148.31, 142.26, 139.46, 133.26, 130.65, 130.58, 129.59, 128.60, 128.57, 128.45, 126.81, 126.81, 126.14, 125.66, 123.13, 116.36, 116.19. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{21}H_{16}F_4NOS$ 406.0889; found 406.0893 (Δ = 1.0 ppm).

N-propargylation of alkenyl-*N*H-sulfoximines.

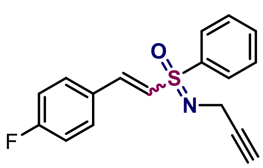


General Procedure H – *N*H-Sulfoximine propargylation: Propargylated NH-sulfoximine products were synthesized employing a procedure derived from existing literature.[42] An oven dried 1 dram vial was charged with alkenyl-*N*H-sulfoximine (0.15 mmol) and DMF (1.5 mL), the reaction was degassed and cooled to 0 °C. Sodium hydride (4.3 mg, 0.18 mmol) was added in one portion and the reaction allowed to stir for 30 min at 0 °C, after which propargyl bromide (80% in toluene, 25 µL, 0.23 mmol) was added and the reaction was allowed to warm to room temperature and stir for 3 h. The solution was concentrated in vacuo and purified via silica gel flash chromatography to provide the final product.



(4-Fluorostyryl)(prop-2-yn-1-ylimino)(trifluoromethyl)-λ^6-sulfanone (9a): Propargylated NH-sulfoximine products were synthesized employing a procedure derived from existing literature.[42] An oven dried 1 dram vial was charged with (4-fluorostyryl)(imino)(trifluoromethyl)-λ^6-sulfanone (**7a**, 38.0 mg, 0.15 mmol) and DMF (1.5 mL), the reaction was degassed and cooled to 0 °C. A solution of aqueous NaOH (1M, 180 µL, 0.18 mmol) was added in one portion and the reaction allowed to stir for 30 min at 0 °C, after which propargyl bromide (80% in toluene, 25 µL, 0.23 mmol) was added and the reaction was allowed to warm to room temperature and stir for 3 h. The solution was concentrated in vacuo and purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (4-fluorostyryl)(prop-2-yn-1-ylimino)(trifluoromethyl)-λ^6-sulfanone (27 mg, 62%) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.75 (d, *J* = 15.72 Hz, 1 H), 7.54 - 7.61 (m, 2 H), 7.12 - 7.20 (m, 2 H), 6.74 (d, *J* = 15.56 Hz, 1 H), 4.06 - 4.18 (m, 2 H), 2.32 (t, *J* = 2.52 Hz, 1 H). **^{19}F NMR** (471 MHz,$CDCl_3$): δ ppm -73.19, -105.26. **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 166.16, 164.13, 149.11, 131.39, 131.31, 127.93, 127.90, 122.84, 120.15, 117.63, 116.79, 116.61, 71.14, 32.33. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_9F_4NOS$ 292.0419; found 292.0424 (Δ = 2.5 ppm).

(4-Fluorostyryl)(phenyl)(prop-2-yn-1-ylimino)-λ^6-sulfanone (9b): Propargylated NH-sulfoximine products were synthesized employing a procedure derived from existing literature.[42] An oven dried 1 dram vial was charged with alkenyl-(4-fluorostyryl)(imino)(phenyl)-λ6-sulfanone (**7b**, 39.2 mg, 0.15 mmol) and DMF (1.5 mL), the reaction was degassed and cooled to 0 °C. Sodium hydride (4.3 mg, 0.18 mmol) was added in one portion and the reaction allowed to stir for 30 min at 0 °C, after which propargyl bromide (80% in toluene, 25 µL, 0.23 mmol) was added and the reaction was allowed to warm to room temperature and stir for 3 h. The solution was concentrated in vacuo and purification via flash chromatography (Hexane:Ethyl Acetate gradient) yielded (4-fluorostyryl)(phenyl)(prop-2-yn-1-ylimino)-λ^6-sulfanone (28 mg, 63%) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.00 (br d, *J* = 7.48 Hz, 2 H), 7.52 - 7.65 (m, 4 H), 7.47 (br dd, *J* = 8.24, 5.49 Hz, 2 H), 7.07 (t, *J* = 8.47 Hz, 2 H), 6.86 (br d, *J* = 15.26 Hz, 1 H), 3.80 - 3.97 (m, 2 H), 2.22 (s, 1 H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ ppm -108.20.**^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 165.20, 163.19, 141.61, 139.19, 139.19, 133.01, 130.46 (d,



J=8.73 Hz, 1 C), 129.41, 128.92, 128.63, 126.90, 116.22, 83.02, 70.52, 32.60. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}NOFSH_{14}$ 300.0858; found 300.0864 (Δ = 2.0 ppm).

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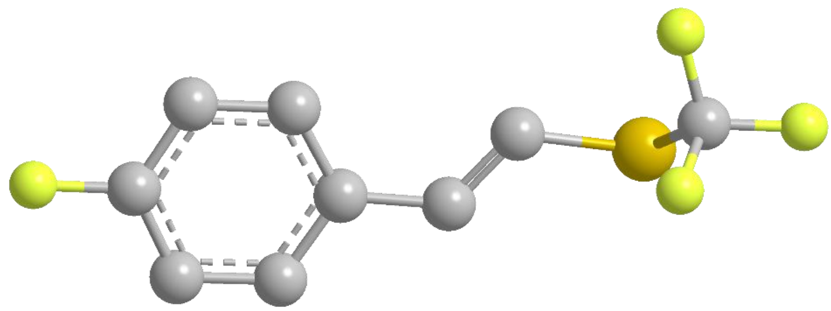
Optimized DFT Geometries and Coordinates

(*E*)-(4-fluorostyryl)(trifluoromethyl)sulfane (3b)



Atom (Number)	X (Å)	Y (Å)	Z (Å)
F	-3.84242	-0.32802	-0.11288
C	-2.49129	-0.34332	-0.2929
C	-1.73233	0.707481	0.238042
C	-0.34755	0.691938	0.047396
C	0.28253	-0.36338	-0.661
C	1.732265	-0.43239	-0.8682
C	2.653641	0.421225	-0.35787
S	4.35063	0.313932	-0.86397
C	5.158401	0.333288	0.780402
F	4.845582	1.433316	1.511914
F	4.836179	-0.74138	1.543526
F	6.498387	0.32351	0.591111
C	-0.52907	-1.40042	-1.18333
C	-1.91879	-1.40093	-1.00422
H	-2.22449	1.523079	0.783774
H	0.24919	1.519481	0.452816
H	2.084726	-1.26242	-1.50098
H	2.399015	1.270812	0.291649
H	-0.05873	-2.22405	-1.73897
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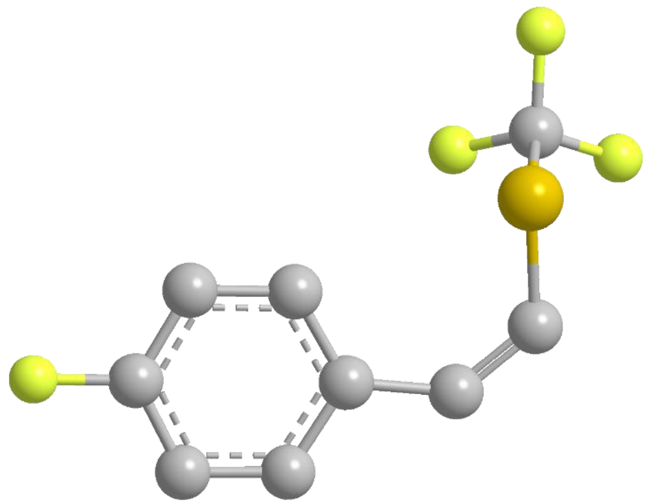
(*Z*)-(4-fluorostyryl)(trifluoromethyl)sulfane (3b)



Atom	X (Å)	Y (Å)	Z (Å)
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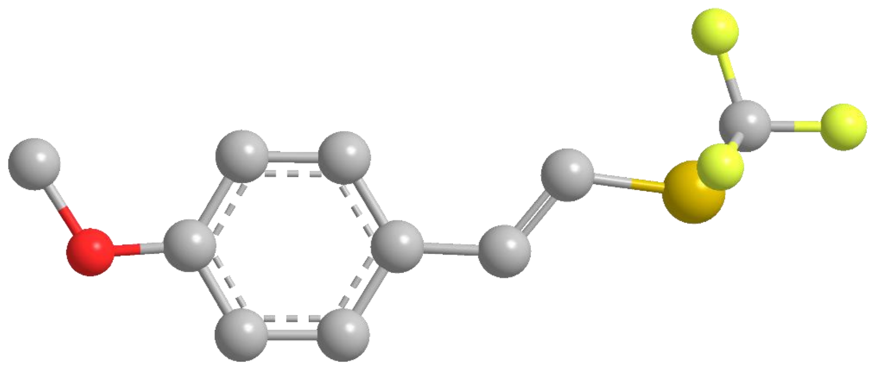
C	-0.4201	0.908489	-0.26874
C	0.370095	-0.2228	-0.60207
C	1.818625	-0.20575	-0.82976
C	2.773751	0.75566	-0.74246
S	2.550894	2.431096	-0.15697
C	2.537211	3.304129	-1.76642
F	3.646943	3.068107	-2.51321
F	1.4741	2.969873	-2.54212
F	2.471892	4.635612	-1.52575
C	-0.28525	-1.4737	-0.74522
C	-1.6659	-1.60755	-0.55934
H	-2.41404	1.668254	0.173752
H	0.050579	1.889892	-0.15552
H	2.218002	-1.18534	-1.14249
H	3.814605	0.494885	-0.97519
H	0.305815	-2.36187	-1.00931
H	-2.16836	-2.57719	-0.66943

(*E*)-(4-methoxystyryl)(trifluoromethyl)sulfane (3c)



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C	9.550849	-0.43623	-0.30332
C	10.32504	0.628773	0.216548
C	11.71189	0.637669	0.028466
C	12.37386	-0.40189	-0.66917
C	13.82245	-0.44412	-0.87141
C	14.7391	0.410404	-0.34736
S	16.43265	0.340529	-0.86139
C	17.24344	0.391309	0.783455
F	16.90272	1.490087	1.494819
F	16.93626	-0.67755	1.548499
F	18.57677	0.408568	0.592604
C	11.57675	-1.45699	-1.18713
C	10.19342	-1.48039	-1.00898
H	6.432359	0.217174	0.484538
H	7.630846	1.483529	0.012924
H	7.83177	0.57685	1.568752
H	9.852486	1.457141	0.760617
H	12.28819	1.484907	0.429897
H	14.18684	-1.2602	-1.51983
H	14.47264	1.242984	0.324018
H	12.06322	-2.27688	-1.73872
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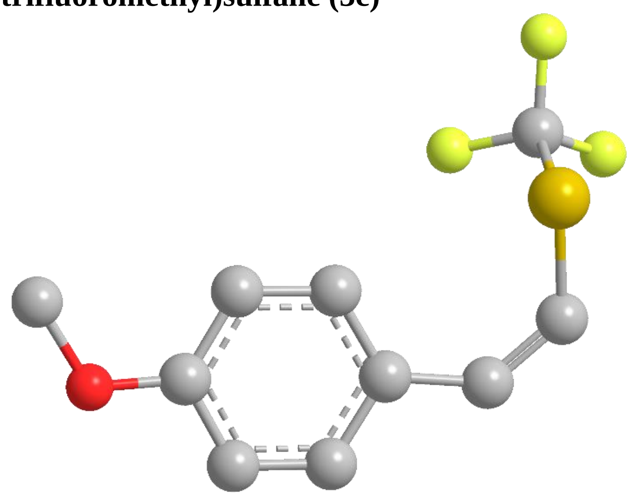
(*Z*)-(4-methoxystyryl)(trifluoromethyl)sulfane (3c)



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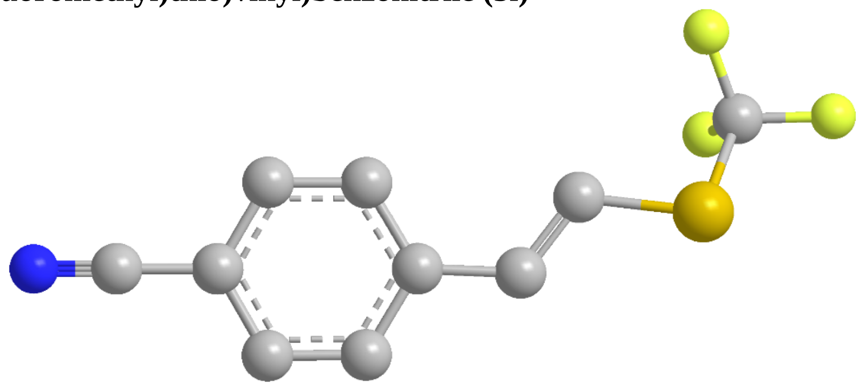
C	9.99953	0.546917	0.057504
C	11.34273	0.769724	-0.26237
C	12.21065	-0.29602	-0.61148
C	13.62185	-0.15811	-0.96776
C	14.50416	0.879087	-0.94923
S	14.20229	2.524039	-0.32366
C	13.76967	3.377463	-1.88981
F	14.7122	3.220688	-2.84385
F	12.60379	2.941612	-2.421
F	13.64267	4.694322	-1.63037
C	11.65664	-1.60673	-0.63418
C	10.32194	-1.84533	-0.314
H	6.314029	-0.51427	0.877799
H	7.174658	0.699125	-0.14751
H	7.623639	0.501745	1.596475
H	9.363775	1.403856	0.315944
H	11.72533	1.797048	-0.24806
H	14.07227	-1.10255	-1.32511
H	15.53999	0.702173	-1.27949
H	12.30233	-2.45541	-0.90948
H	9.903883	-2.86254	-0.33151

(*E*)-4-(2-((trifluoromethyl)thio)vinyl)benzonitrile (3i)



Atom	X (Å)	Y (Å)	Z (Å)
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F	4.440967	1.183389	-1.1384
S	3.512433	0.448311	1.255124
C	1.950409	0.393881	0.428818
C	0.86735	-0.1492	1.038013
C	-0.50215	-0.12346	0.520549
C	-0.87026	0.573344	-0.66039
C	-2.18465	0.55895	-1.12129
C	-3.17753	-0.1555	-0.40331
C	-2.82936	-0.85182	0.778623
C	-1.50793	-0.83036	1.22716
C	-4.53039	-0.16685	-0.86866
N	-5.64144	-0.17669	-1.24906
H	1.904739	0.903359	-0.54426
H	1.004232	-0.65812	2.005025
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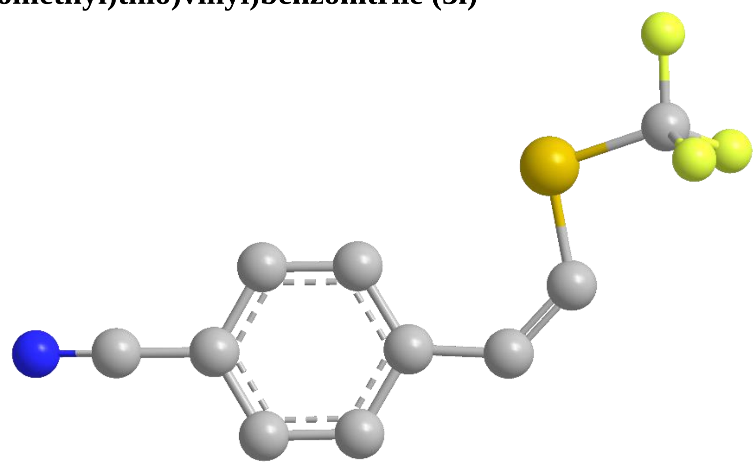
H	-2.45625	1.103316	-2.03485
H	-3.59629	-1.40412	1.336605
H	-1.241	-1.37236	2.144875

(*Z*)-4-(2-((trifluoromethyl)thio)vinyl)benzonitrile (3i)



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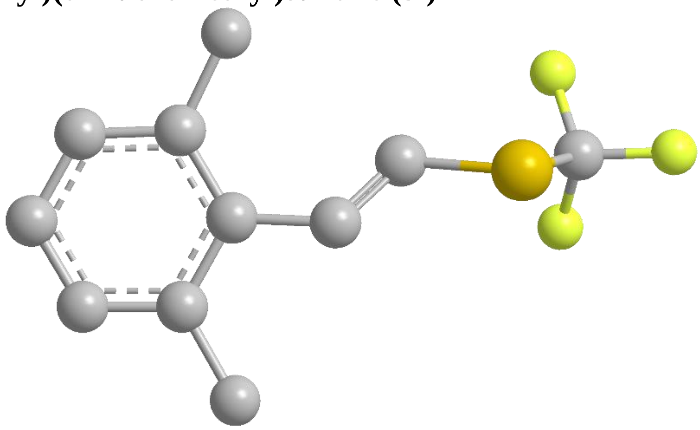
F	4.107402	2.546334	-0.65405
S	1.454014	2.361225	-0.91113
C	1.586707	1.283713	0.485114
C	0.654768	0.391973	0.915628
C	-0.67275	0.073075	0.396166
C	-1.20912	0.605031	-0.80739
C	-2.49155	0.267402	-1.23901
C	-3.28365	-0.62258	-0.47487
C	-2.76489	-1.17349	0.723211
C	-1.48138	-0.82735	1.141529
C	-4.60089	-0.96691	-0.9143
N	-5.68256	-1.24868	-1.27462
H	2.535108	1.363398	1.032895
H	0.951172	-0.17146	1.813931
H	-0.62339	1.284183	-1.4375
H	-2.88599	0.689322	-2.17201
H	-3.37323	-1.86809	1.316397
H	-1.08389	-1.25902	2.070293

(*E*)-(2,6-dimethylstyryl)(trifluoromethyl)sulfane (3l)



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C	-2.84626	-0.34978	-1.86047
C	-2.44141	-1.47518	-1.12733
C	-1.3812	-1.3929	-0.20905
C	-0.95995	-2.6242	0.557934
C	-0.69854	-0.14684	-0.03312
C	0.39246	-0.11902	0.952254
C	1.524018	0.62438	0.902423
S	2.614315	0.675735	2.303564
C	4.219736	0.488142	1.445408
F	5.204474	0.622847	2.363669
F	4.414863	1.42267	0.480443
F	4.370681	-0.72104	0.84746
H	-1.19276	3.152965	-0.94073
H	-0.2203	2.574658	0.452354
H	0.433348	2.479654	-1.20127
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H	-1.06407	-2.48276	1.653401
H	-1.57841	-3.49294	0.272368
H	0.277098	-0.78944	1.818417
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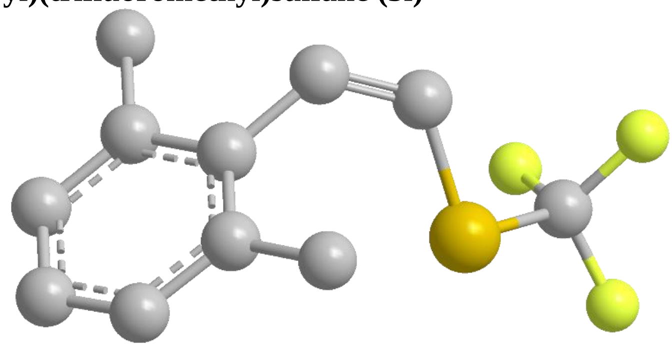
(*Z*)-(2,6-dimethylstyryl)(trifluoromethyl)sulfane (3l)



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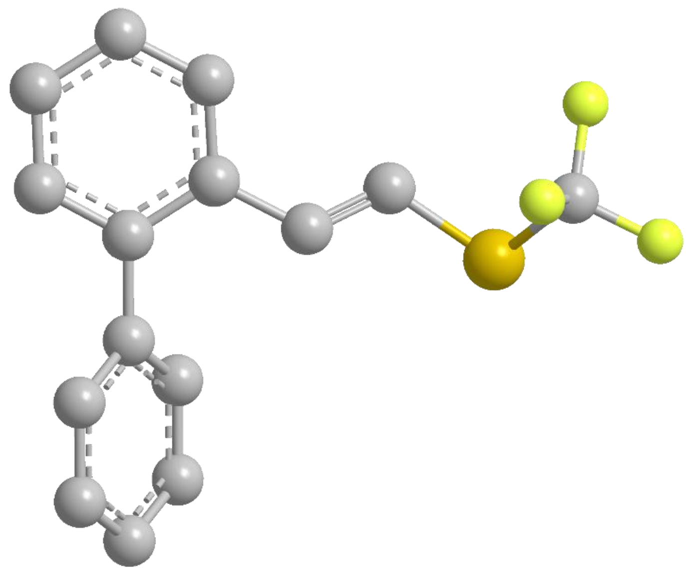
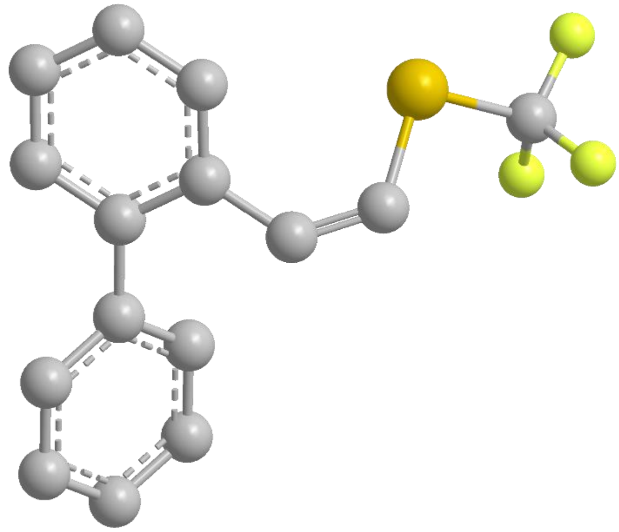
C	-2.4367	-1.24791	1.606722
C	-2.11579	-1.87383	0.390859
C	-1.27947	-1.24062	-0.54322
C	-0.92908	-1.92283	-1.84316
C	-0.74177	0.045246	-0.23732
C	0.16167	0.658712	-1.23488
C	1.451939	1.011174	-1.04687
S	2.269253	0.845688	0.525235
C	3.957165	0.486413	-0.07816
F	4.775255	0.436514	0.998309
F	4.437524	1.430221	-0.92702
F	4.052795	-0.70134	-0.72904
H	-1.42093	2.650294	1.835145
H	-0.30902	2.665081	0.429908
H	0.247026	2.07352	2.020921
H	-2.20149	0.524892	2.830994
H	-3.09453	-1.75183	2.329165
H	-2.51807	-2.87119	0.161584
H	0.166479	-2.05272	-1.94821
H	-1.26104	-1.32539	-2.71699
H	-1.40516	-2.91693	-1.9107
H	-0.2293	0.802607	-2.25568
H	2.052067	1.461003	-1.84989

(*E*)-(2-([1,1'-biphenyl]-2-yl)vinyl)(trifluoromethyl)sulfane (3p)



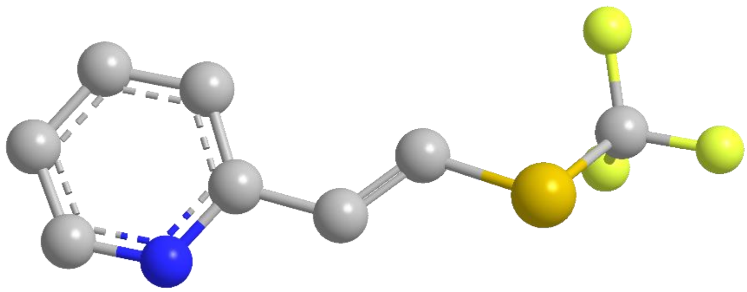
Atom	X (Å)	Y (Å)	Z (Å)
F	5.058838	-3.41269	0.532491
C	4.47115	-2.2047	0.362217
F	4.384749	-1.60898	1.579124
F	5.303538	-1.4352	-0.38559
S	2.838726	-2.46913	-0.42393
C	2.317262	-0.77885	-0.60982
C	1.185837	-0.35385	0.001208
C	0.581875	0.976731	-0.1392
C	1.369993	2.097487	-0.49564
C	0.820339	3.381505	-0.55584
C	-0.53928	3.574249	-0.24862
C	-1.33632	2.476792	0.101475
C	-0.80323	1.170521	0.149588
C	-1.6982	0.027467	0.466099
C	-2.54501	0.068028	1.596805
C	-3.39276	-1.00999	1.893699
C	-3.41404	-2.14407	1.062769
C	-2.58638	-2.18949	-0.07249
C	-1.73817	-1.11272	-0.3698
H	2.890191	-0.16858	-1.322
H	0.661995	-1.06153	0.660716
H	2.441641	1.96069	-0.69458
H	1.454181	4.23673	-0.82815
H	-0.97874	4.580798	-0.28848
H	-2.40467	2.622162	0.313847
H	-2.51897	0.944923	2.259278
H	-4.03571	-0.96815	2.784383
H	-4.07577	-2.98962	1.297684
H	-2.60344	-3.06668	-0.73463
H	-1.10963	-1.14386	-1.27032

(*Z*)-(2-([1,1'-biphenyl]-2-yl)vinyl)(trifluoromethyl)sulfane (3p)



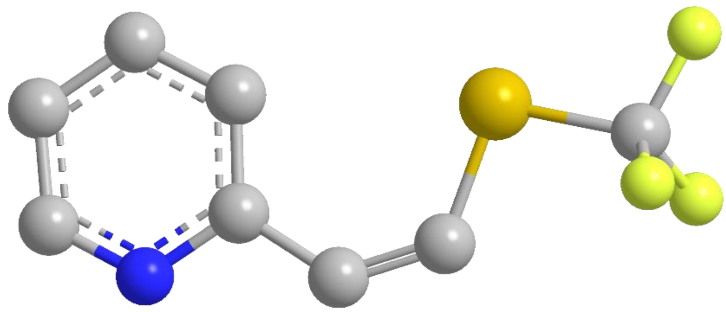
Atom	X (Å)	Y (Å)	X (Å)
F	3.564198	-0.02532	-4.77611
C	3.046151	-0.64148	-3.69011
F	1.957023	-1.34672	-4.08582
F	3.954664	-1.54868	-3.24929
S	2.656542	0.644457	-2.44501
C	2.049488	-0.43534	-1.16754
C	1.146355	-0.07285	-0.22612
C	0.532433	1.248173	-0.03439
C	1.286542	2.42947	-0.22463
C	0.731541	3.696171	0.002795
C	-0.5958	3.802681	0.450069
C	-1.35713	2.642011	0.652238
C	-0.8207	1.360844	0.408127
C	-1.68412	0.163194	0.573638
C	-2.44984	-0.01759	1.747811
C	-3.28772	-1.13408	1.890692
C	-3.37792	-2.08722	0.861104
C	-2.62705	-1.91421	-0.3148
C	-1.78719	-0.79993	-0.45672
H	2.474133	-1.44808	-1.17628
H	0.843945	-0.86876	0.471236
H	2.349847	2.356188	-0.49254
H	1.342165	4.596583	-0.15033
H	-1.04058	4.789713	0.638845
H	-2.40365	2.724641	0.97747
H	-2.37071	0.717265	2.561546
H	-3.86903	-1.26477	2.814805
H	-4.03437	-2.96152	0.97421
H	-2.69986	-2.64816	-1.13024
H	-1.21773	-0.65712	-1.38461

(*E*)-2-(2-((trifluoromethyl)thio)vinyl)pyridine (3q)



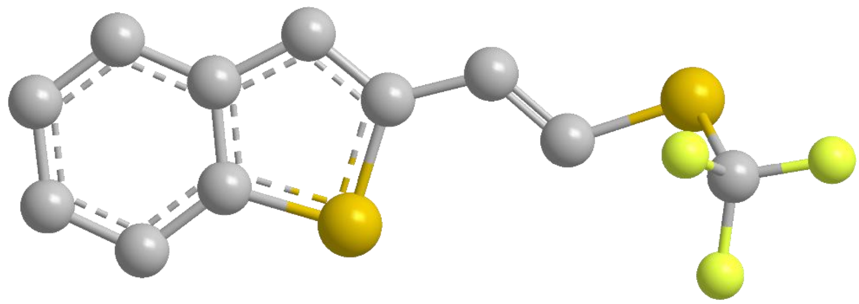
Atom	X (Å)	Y (Å)	Z (Å)
F	4.011413	1.56354	-0.55704
C	4.171052	0.224126	-0.69738
F	5.48342	-0.0619	-0.54839
F	3.8163	-0.07908	-1.97012
S	3.244747	-0.73994	0.555372
C	1.613348	-0.13108	0.24024
C	0.530268	-0.92298	0.427392
C	-0.87101	-0.49033	0.335916
C	-1.25763	0.850909	0.09822
C	-2.61733	1.163214	0.012578
C	-3.56355	0.13687	0.171798
C	-3.09387	-1.16458	0.411026
N	-1.79	-1.47802	0.492373
H	1.544038	0.936204	-0.01579
H	0.664988	-1.98754	0.67365
H	-0.50226	1.639729	-0.01286
H	-2.93701	2.198266	-0.17121
H	-4.64191	0.337713	0.117265
H	-3.80501	-1.99514	0.545114

(*Z*)-2-(2-((trifluoromethyl)thio)vinyl)pyridine (3q)



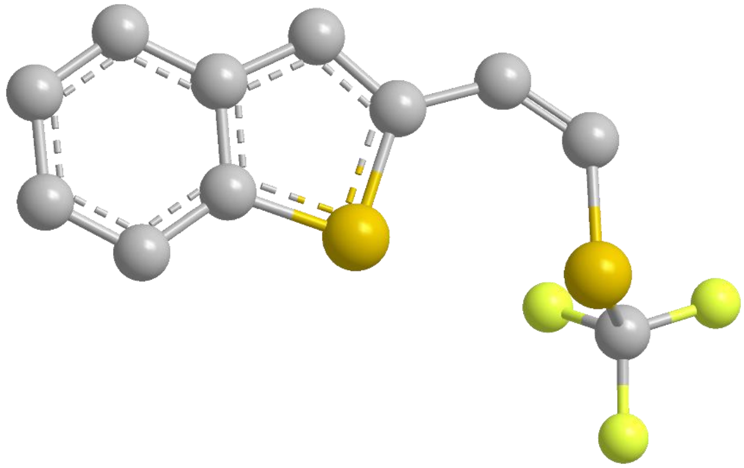
Atom	X (Å)	Y (Å)	Z (Å)
F	3.943395	1.861034	1.340312
C	2.947954	2.304089	2.144576
F	3.076419	3.640217	2.280423
F	3.137956	1.733169	3.357471
S	1.27671	1.982641	1.459059
C	1.361573	0.215588	1.384359
C	0.383499	-0.62578	0.961868
C	-0.96933	-0.3558	0.468805
C	-1.52921	0.937809	0.325471
C	-2.83634	1.073586	-0.15625
C	-3.5626	-0.07907	-0.48771
C	-2.93487	-1.32544	-0.31758
N	-1.68409	-1.4684	0.143414
H	2.318144	-0.20727	1.718715
H	0.637793	-1.69583	0.991659
H	-0.96093	1.839916	0.581667
H	-3.27953	2.072241	-0.27074
H	-4.59039	-0.02062	-0.8697
H	-3.47244	-2.254	-0.56748

(*E*)-2-(2-((trifluoromethyl)thio)vinyl)benzo[b]thiophene (3ad)



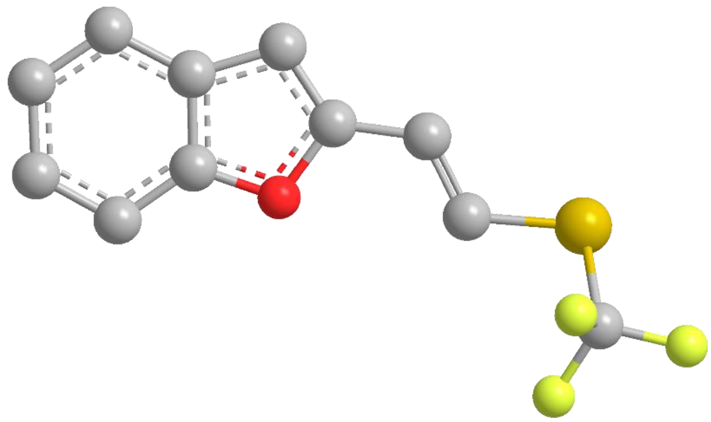
Atom	X (Å)	Y (Å)	Z (Å)
F	5.295791	-0.15131	1.344886
C	5.378418	0.368545	0.09408
F	5.00276	1.668579	0.188802
F	6.674601	0.335894	-0.29006
S	4.397257	-0.57398	-1.13577
C	2.809008	-0.48199	-0.361
C	1.705294	-0.12768	-1.06988
C	0.350233	-0.15656	-0.56762
C	-0.78667	0.25343	-1.24399
C	-1.98946	0.134359	-0.46972
C	-3.32244	0.458845	-0.82593
C	-4.34948	0.258748	0.0996
C	-4.0749	-0.26328	1.387021
C	-2.76746	-0.59348	1.769465
C	-1.73701	-0.39187	0.836578
S	-0.02598	-0.72633	1.071322
H	2.758012	-0.82306	0.68422
H	1.814092	0.210026	-2.11246
H	-0.75515	0.635566	-2.27218
H	-3.53612	0.865819	-1.82404
H	-5.38391	0.509647	-0.17279
H	-4.89769	-0.41254	2.100294
H	-2.55919	-0.99738	2.769153

(*Z*)-2-(2-((trifluoromethyl)thio)vinyl)benzo[b]thiophene (3ad)



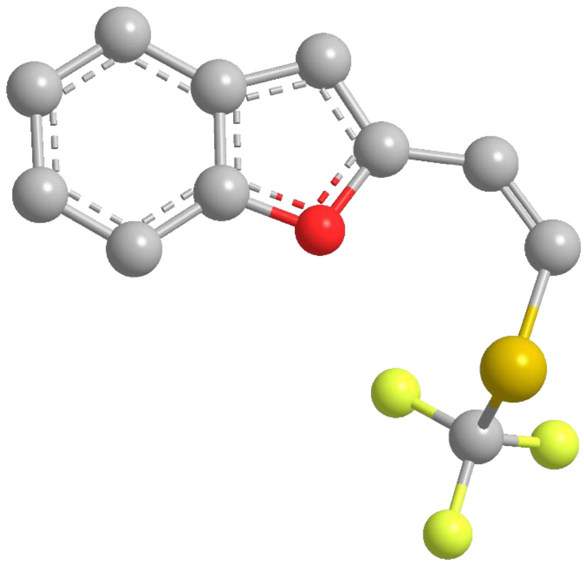
Atom	X (Å)	Y (Å)	Z (Å)
F	4.588987	-3.53589	0.079074
C	3.382052	-3.40907	0.68913
F	2.462349	-3.92777	-0.15868
F	3.401983	-4.17112	1.80737
S	3.001377	-1.68488	1.189246
C	2.907811	-0.92716	-0.41626
C	1.775487	-0.35974	-0.91148
C	0.425787	-0.30804	-0.39646
C	-0.62406	0.321566	-1.05046
C	-1.87896	0.223407	-0.36618
C	-3.14859	0.735574	-0.73658
C	-4.24608	0.515391	0.097955
C	-4.10571	-0.2128	1.305499
C	-2.86492	-0.73302	1.696104
C	-1.76041	-0.50888	0.856039
S	-0.10945	-1.05782	1.126507
H	3.850012	-0.86073	-0.97602
H	1.890084	0.150913	-1.88175
H	-0.4885	0.842677	-2.00684
H	-3.25882	1.298083	-1.67404
H	-5.2323	0.910158	-0.18271
H	-4.98313	-0.37319	1.947877
H	-2.76154	-1.29811	2.632219

(*E*)-2-(2-((trifluoromethyl)thio)vinyl)benzofuran (3ae)



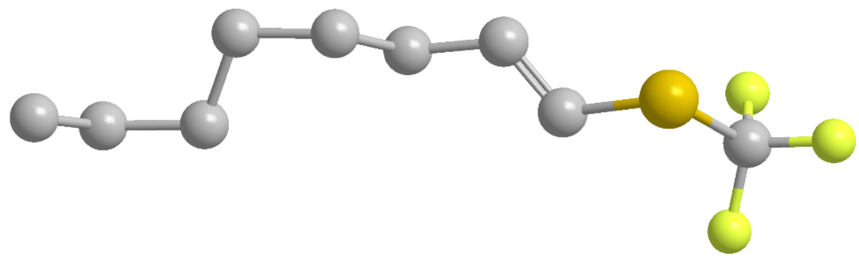
Atom	X (Å)	Y (Å)	Z (Å)
F	6.104173	-1.88884	1.169793
C	4.789689	-1.58012	1.229953
F	4.115905	-2.68289	1.644161
F	4.621911	-0.63888	2.19087
S	4.265656	-1.0111	-0.43077
C	2.547746	-0.74948	-0.10455
C	1.872588	0.270611	-0.6962
C	0.450862	0.461379	-0.59014
O	-0.27553	-0.4474	0.16769
C	-1.58691	-0.046	0.11679
C	-2.66285	-0.67675	0.74383
C	-3.92452	-0.08891	0.550047
C	-4.08459	1.077762	-0.23882
C	-2.99093	1.696094	-0.85821
C	-1.70994	1.125229	-0.67957
C	-0.37665	1.43293	-1.12364
H	2.042741	-1.50813	0.509331
H	2.400575	1.012809	-1.3122
H	-2.52714	-1.58021	1.352236
H	-4.8059	-0.54574	1.02127
H	-5.08968	1.503705	-0.36485
H	-3.12312	2.600711	-1.46703
H	-0.05409	2.263237	-1.75859

(*Z*)-2-(2-((trifluoromethyl)thio)vinyl)benzofuran (3ae)



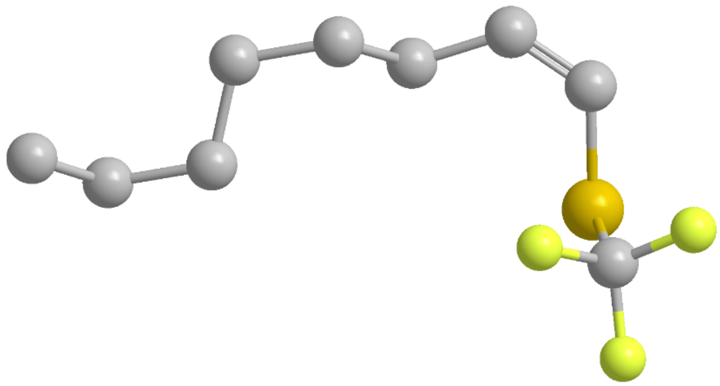
Atom	X (Å)	Y (Å)	Z (Å)
F	0.786387	-4.84576	-1.05725
C	1.273415	-3.62755	-1.40449
F	2.270244	-3.82161	-2.30946
F	0.292554	-2.95987	-2.0578
S	1.836199	-2.79949	0.128845
C	2.494043	-1.2835	-0.54767
C	1.798248	-0.12851	-0.73013
C	0.410825	0.191391	-0.53223
O	-0.48304	-0.77215	-0.09348
C	-1.7094	-0.16921	-0.02129
C	-2.90207	-0.7838	0.368328
C	-4.04618	0.029683	0.365608
C	-3.98659	1.396456	-0.01135
C	-2.78187	1.993712	-0.39878
C	-1.61351	1.195956	-0.40836
C	-0.23138	1.403361	-0.73421
H	3.570012	-1.30093	-0.76501
H	2.38063	0.727853	-1.10524
H	-2.93825	-1.84184	0.657492
H	-5.0114	-0.40384	0.66204
H	-4.9084	1.994318	0.00179
H	-2.7423	3.052496	-0.68796
H	0.24822	2.324968	-1.07703

(*E*)-oct-1-en-1-yl(trifluoromethyl)sulfane (3ah)



Atom	X (Å)	Y (Å)	Z (Å)
C	-4.59088	0.169784	0.45333
C	-3.58802	-0.94276	0.120679
C	-2.11375	-0.53081	0.27125
C	-1.65289	0.534574	-0.73425
C	-0.21027	1.01739	-0.52604
C	0.852579	-0.08736	-0.71738
C	2.245015	0.459435	-0.62875
C	3.10488	0.173677	0.369908
S	4.649476	1.049998	0.52426
C	5.800118	-0.36638	0.634728
F	5.799693	-1.14706	-0.47602
F	7.053482	0.121373	0.798076
F	5.533574	-1.1905	1.682271
H	-4.49561	1.03197	-0.23496
H	-5.63293	-0.19702	0.381705
H	-4.43474	0.545815	1.484864
H	-3.7816	-1.81363	0.779651
H	-3.75945	-1.30159	-0.91697
H	-1.48174	-1.4358	0.16698
H	-1.942	-0.15308	1.303512
H	-2.32078	1.417172	-0.67457
H	-1.76163	0.134056	-1.76574
H	-0.10409	1.442797	0.494185
H	0.002341	1.845412	-1.23262
H	0.715609	-0.88834	0.034276
H	0.708762	-0.54474	-1.7204
H	2.552528	1.17283	-1.41206
H	2.85232	-0.51722	1.188711

(*Z*)-oct-1-en-1-yl(trifluoromethyl)sulfane (3ah)

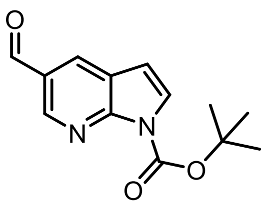


Atom (Number)	X (Å)	Y (Å)	Z (Å)
C	-4.88967	-0.01787	-0.44922
C	-3.78609	-1.0223	-0.0908
C	-2.42488	-0.38366	0.232703
C	-1.78955	0.370041	-0.94445
C	-0.41624	0.984021	-0.6363
C	0.673437	-0.06894	-0.34054
C	2.030529	0.548766	-0.22725
C	2.875556	0.512735	0.824342
S	2.536287	-0.44806	2.297404
C	2.326561	0.920348	3.489478
F	1.258972	1.711657	3.209506
F	2.133601	0.386145	4.720105
F	3.406138	1.744137	3.558939
H	-4.65857	0.533957	-1.38114
H	-5.86022	-0.52866	-0.60014
H	-5.02265	0.729324	0.359273
H	-4.1111	-1.62415	0.782437
H	-3.65477	-1.74316	-0.92594
H	-1.73618	-1.18148	0.577739
H	-2.53924	0.316219	1.089493
H	-2.46675	1.183648	-1.27334
H	-1.6923	-0.3201	-1.81102
H	-0.49969	1.672024	0.230984
H	-0.09399	1.604826	-1.49696
H	0.436613	-0.62847	0.583327
H	0.686075	-0.80496	-1.17489
H	2.381609	1.117336	-1.10613
H	3.854684	1.01025	0.799577

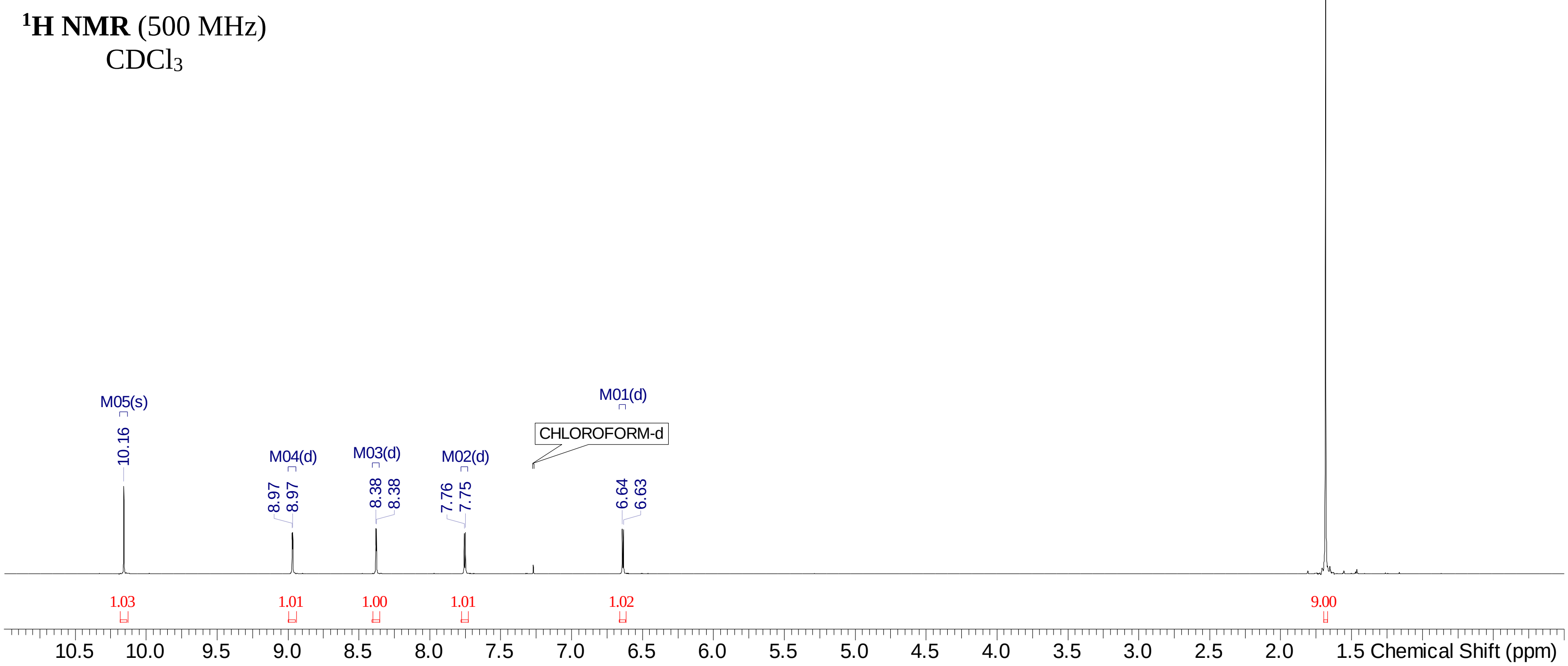
NMR Spectra

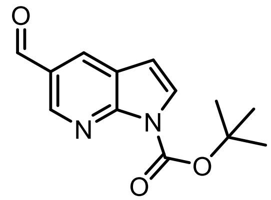
Alkenyl Iodides and Precursors

Tert-butyl 5-formyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate

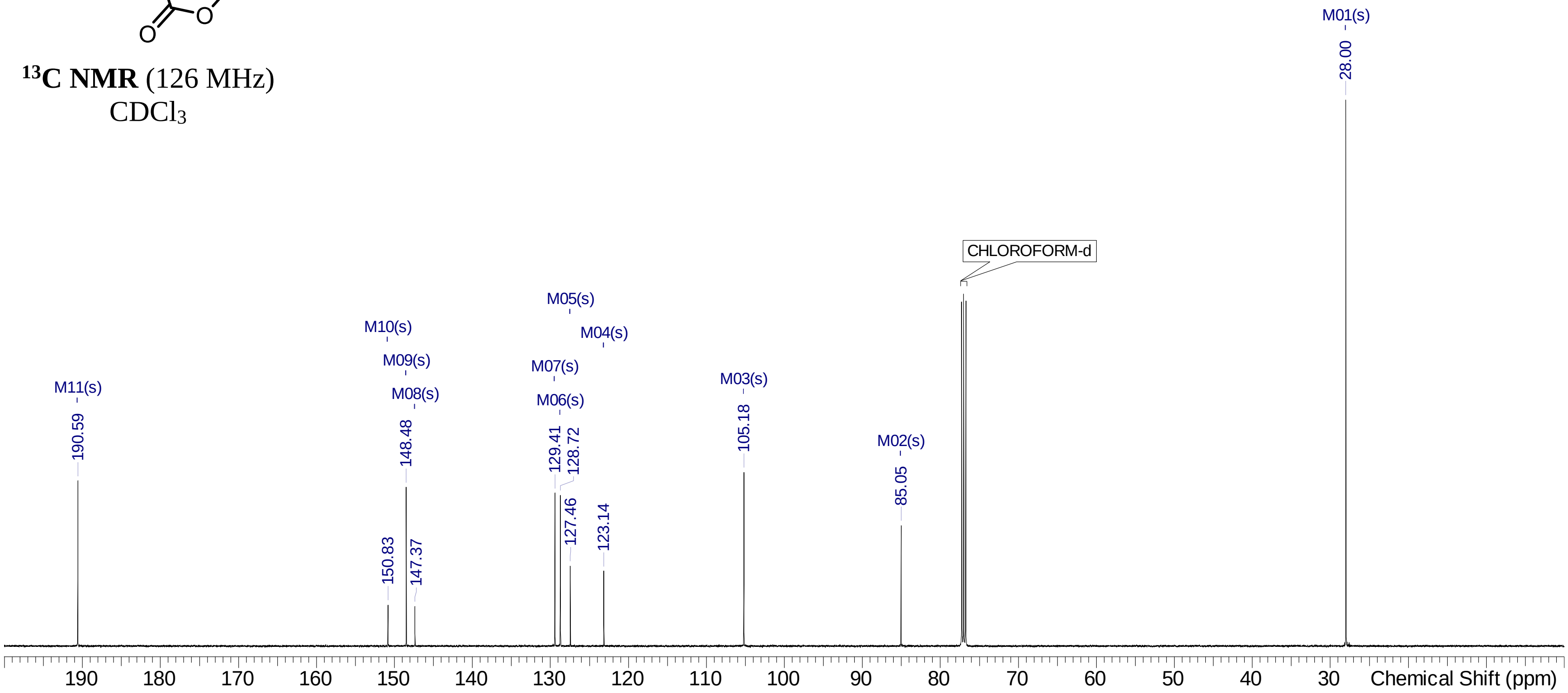


^{1}H NMR (500 MHz)
$CDCl_3$

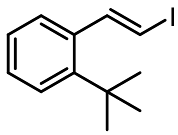




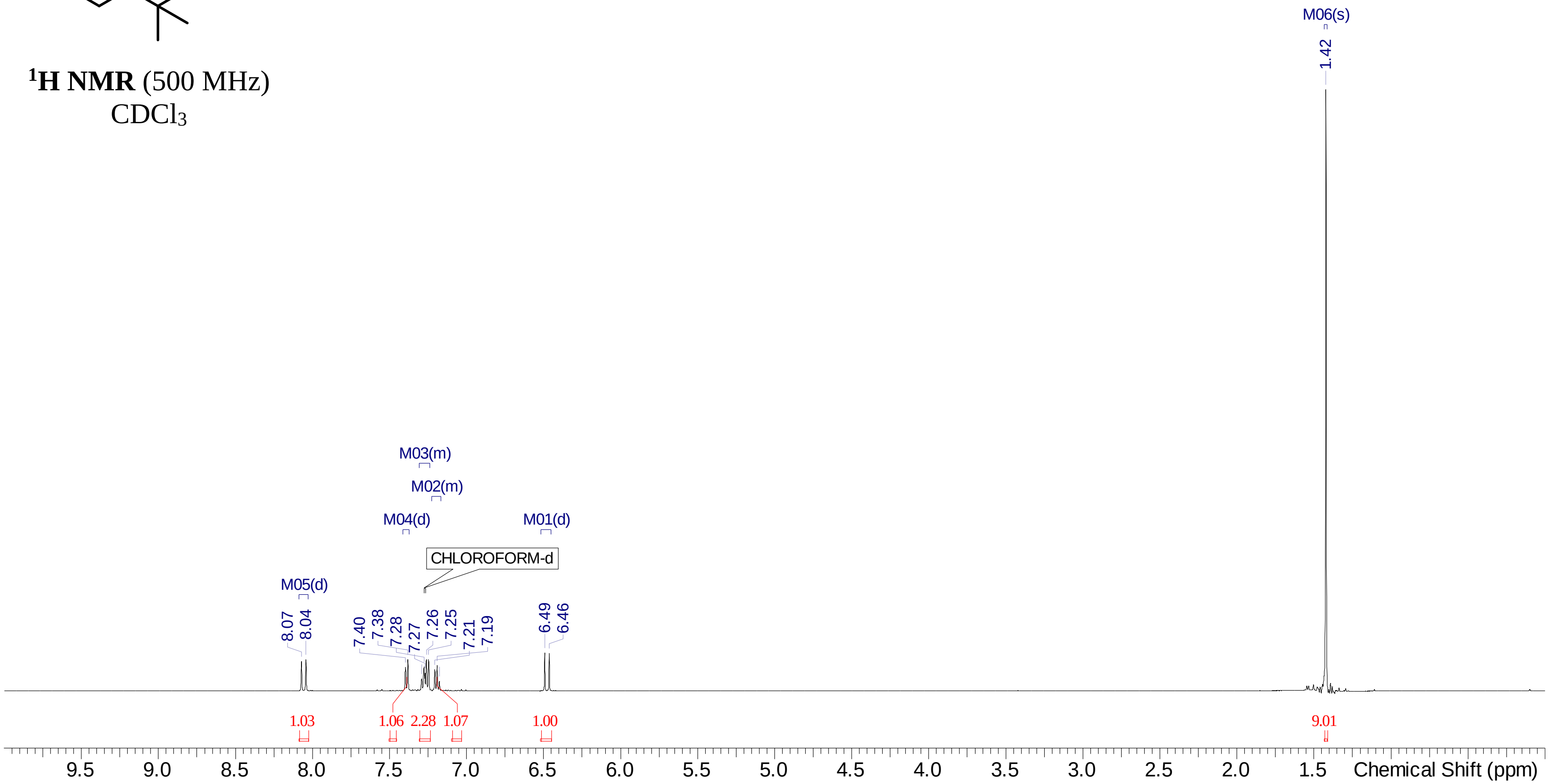
^{13}C **NMR** (126 MHz)
$CDCl_3$

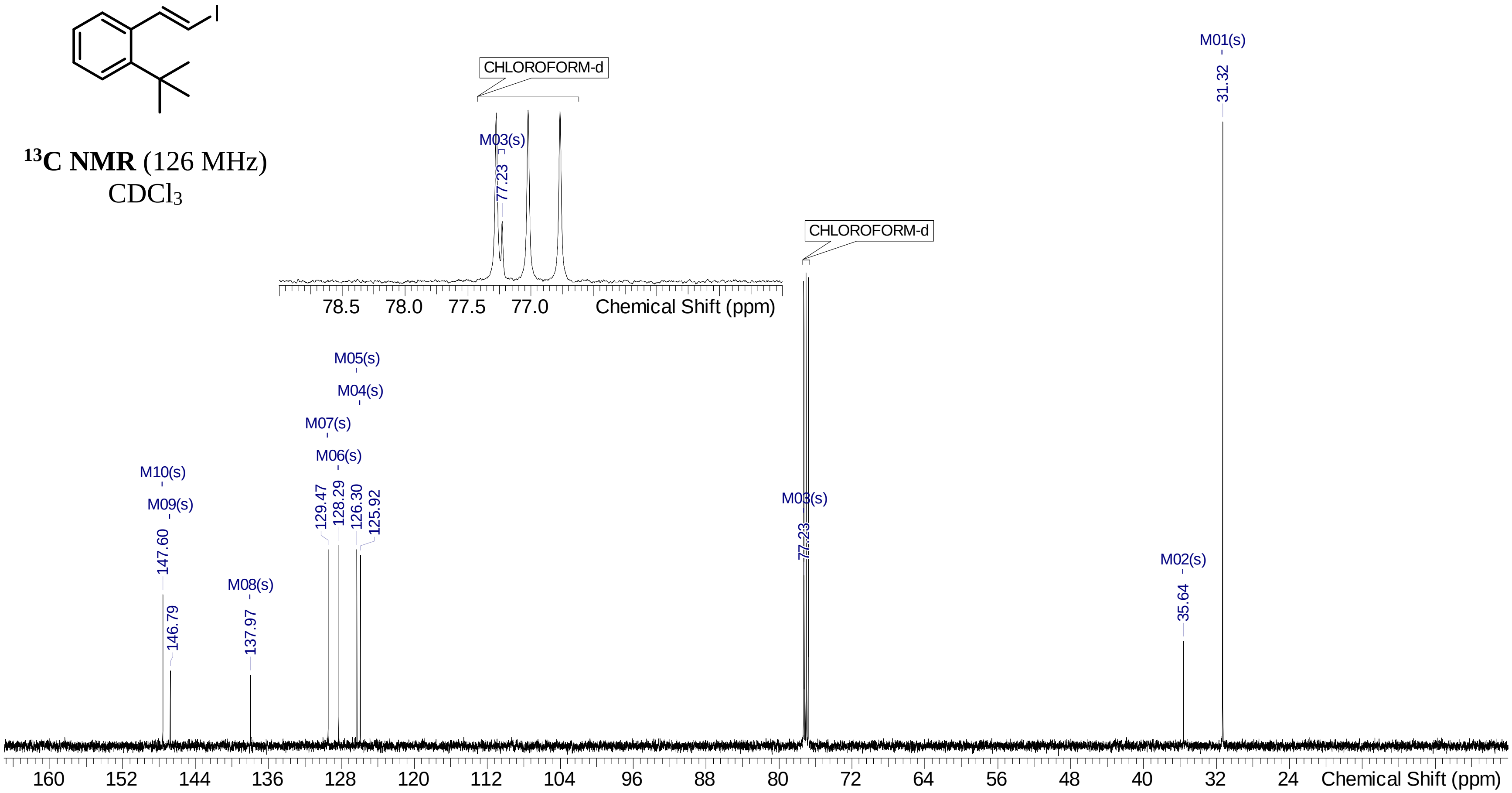


(*E*)-1-(*tert*-butyl)-2-(2-iodovinyl)benzene



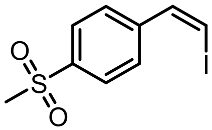
^{1}H NMR (500 MHz)
$CDCl_3$



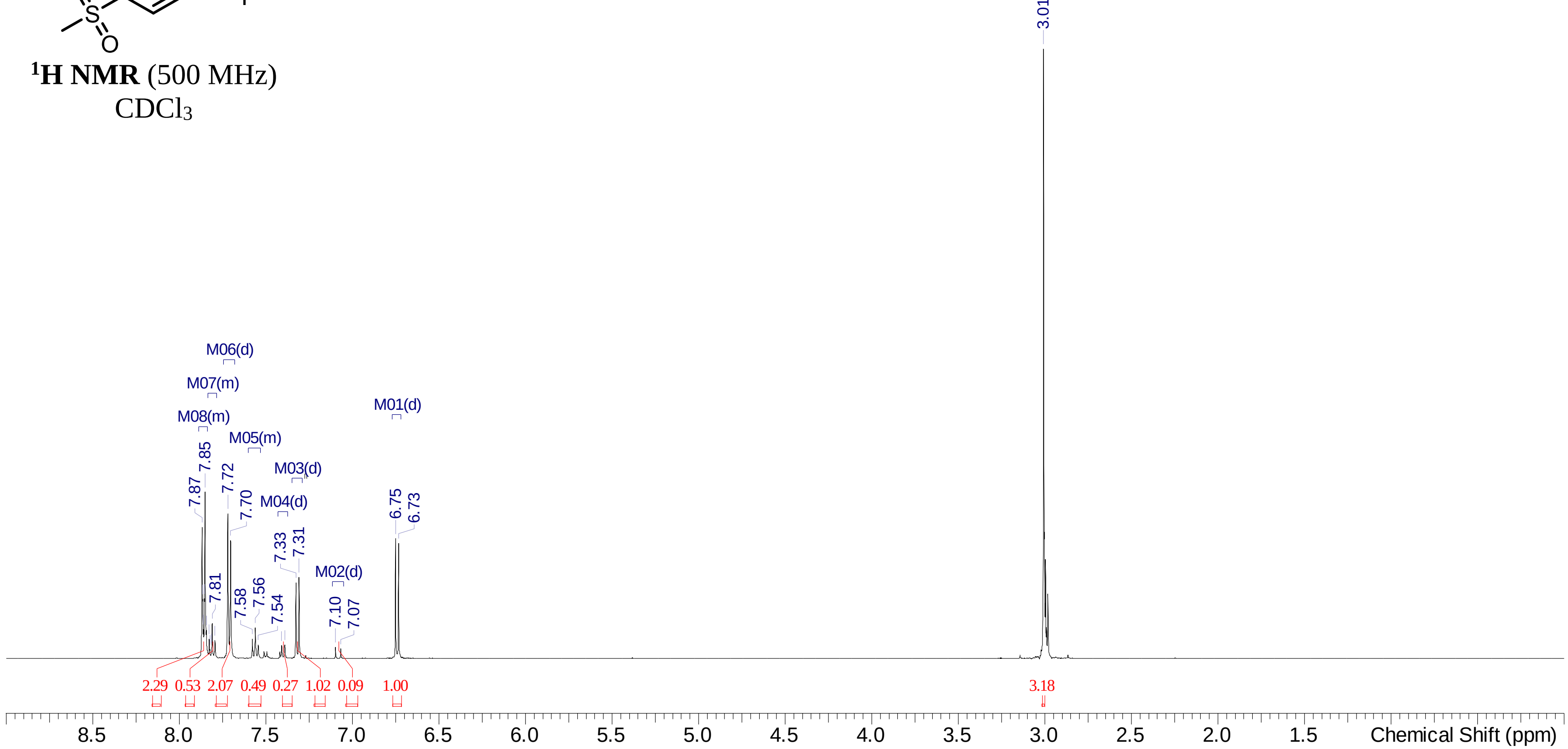


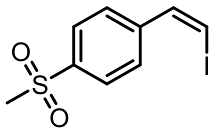
^{13}C NMR (126 MHz)
$CDCl_3$

(*Z*)-1-(2-iodovinyl)-4-(methylsulfonyl)benzene

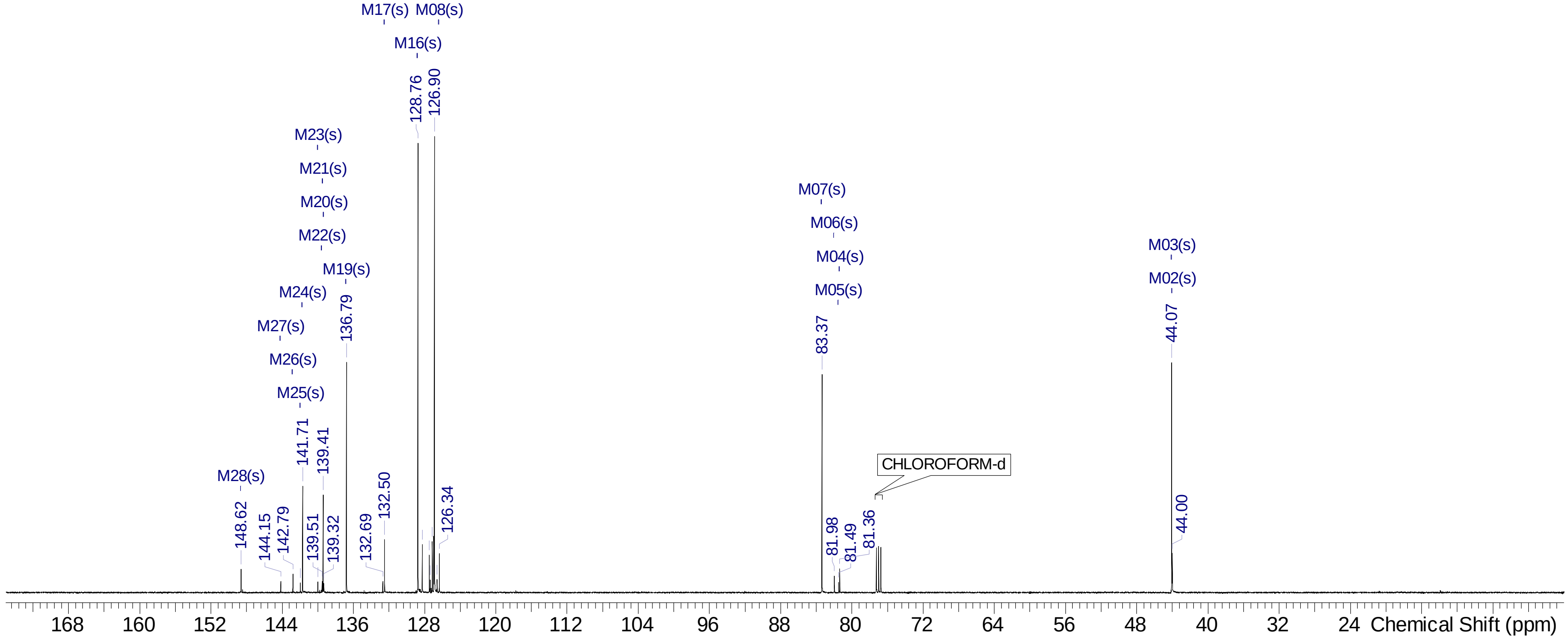


^{1}H NMR (500 MHz)
$CDCl_3$

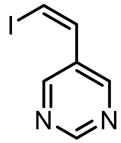




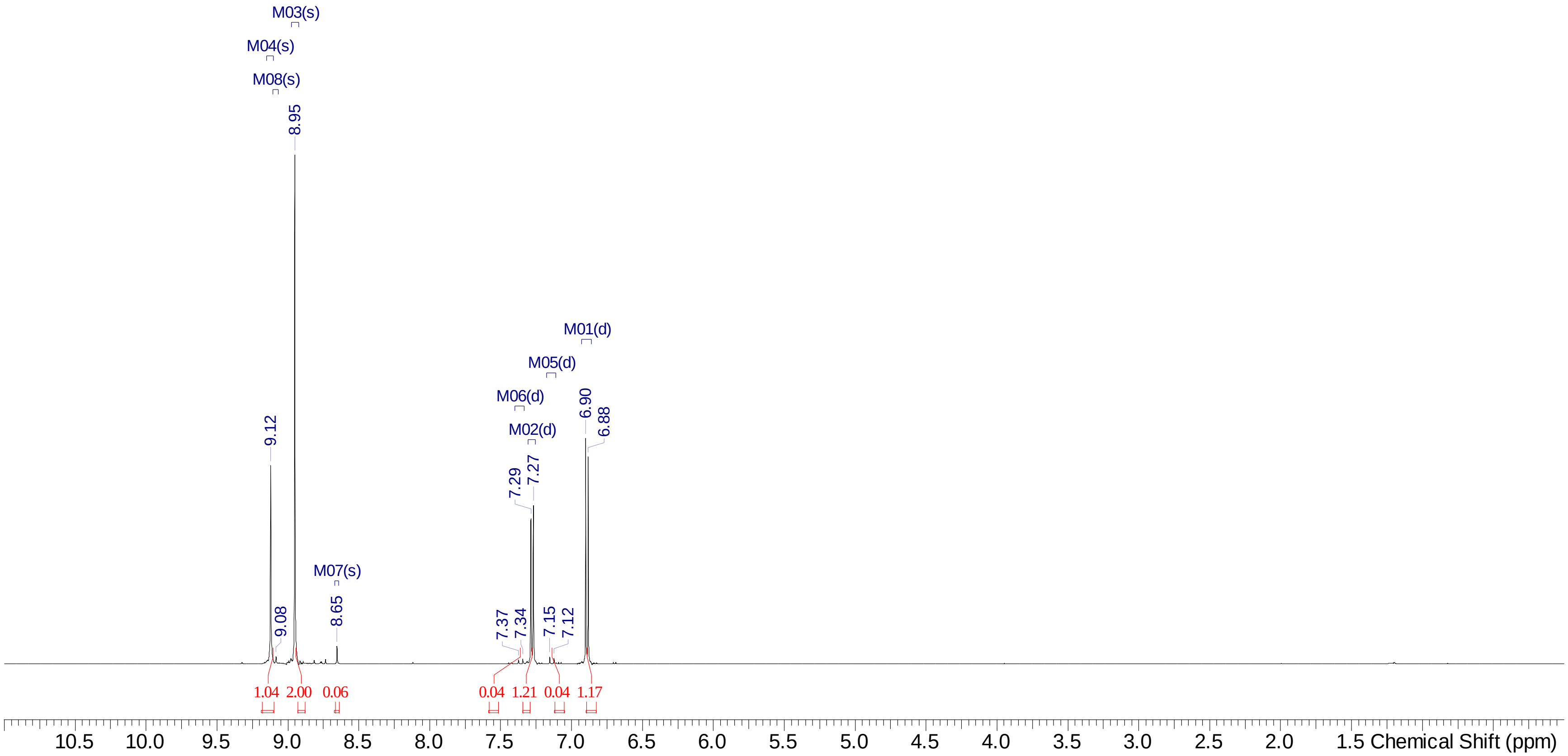
^{13}C NMR (126 MHz)
$CDCl_3$

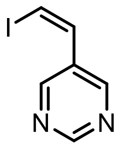


(*Z*)-5-(2-iodovinyl)pyrimidine

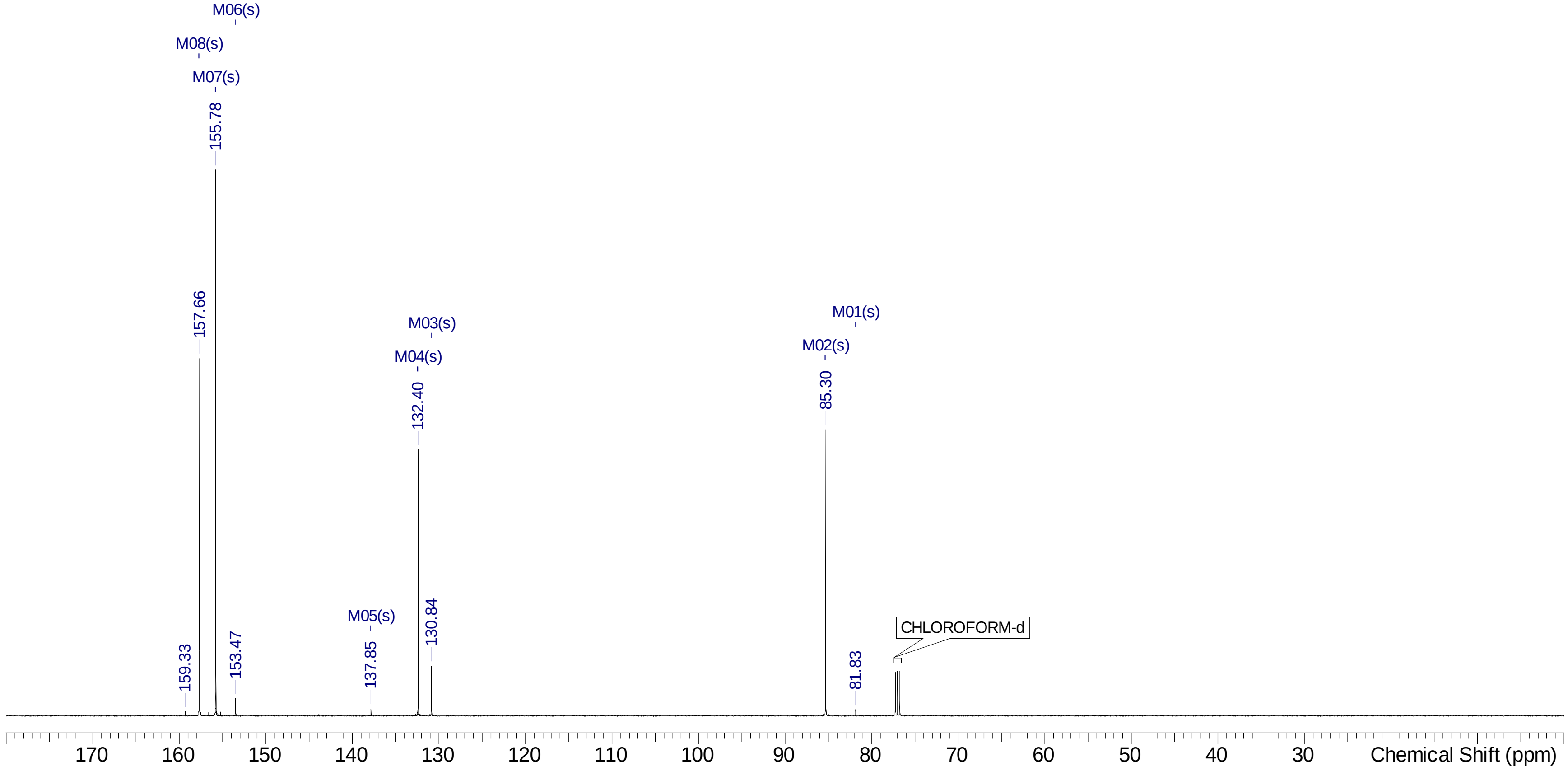


¹H NMR (500 MHz)
DMSO-d_6

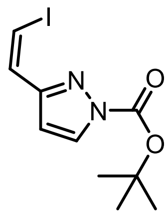




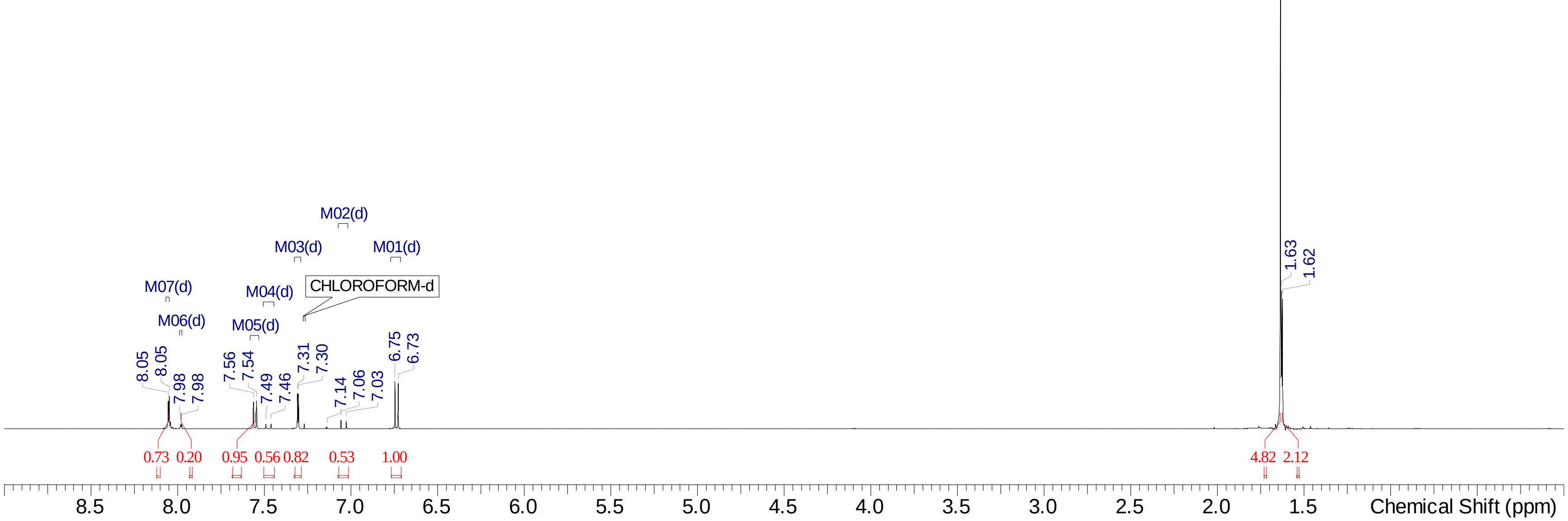
^{13}C NMR (126 MHz)
DMSO-d_6

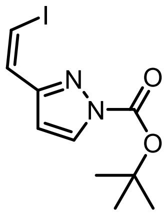


***Tert*-butyl (*Z*)-3-(2-iodovinyl)-1*H*-pyrazole-1-carboxylate**

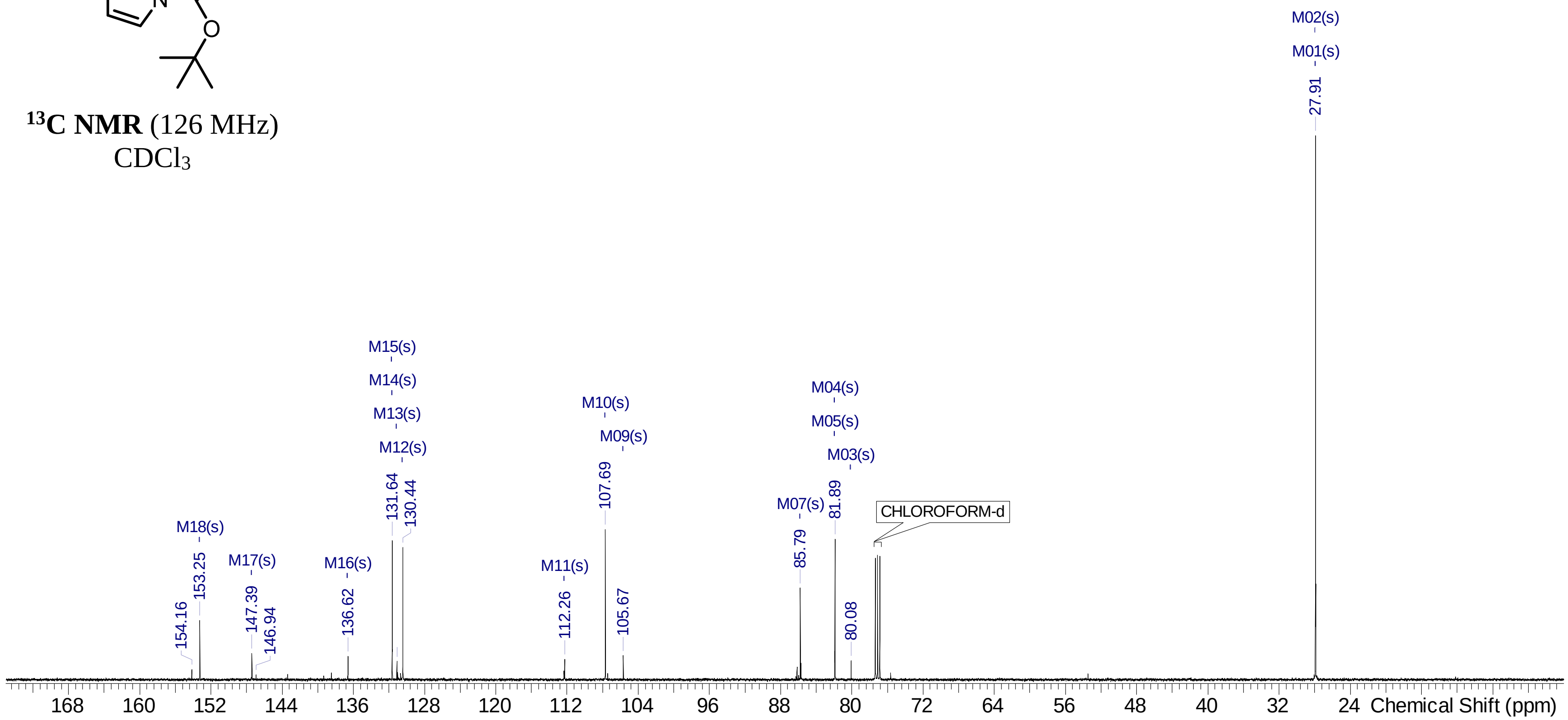


^{1}H NMR (500 MHz)
$CDCl_3$

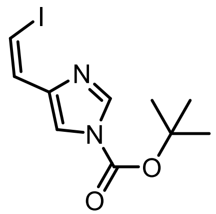




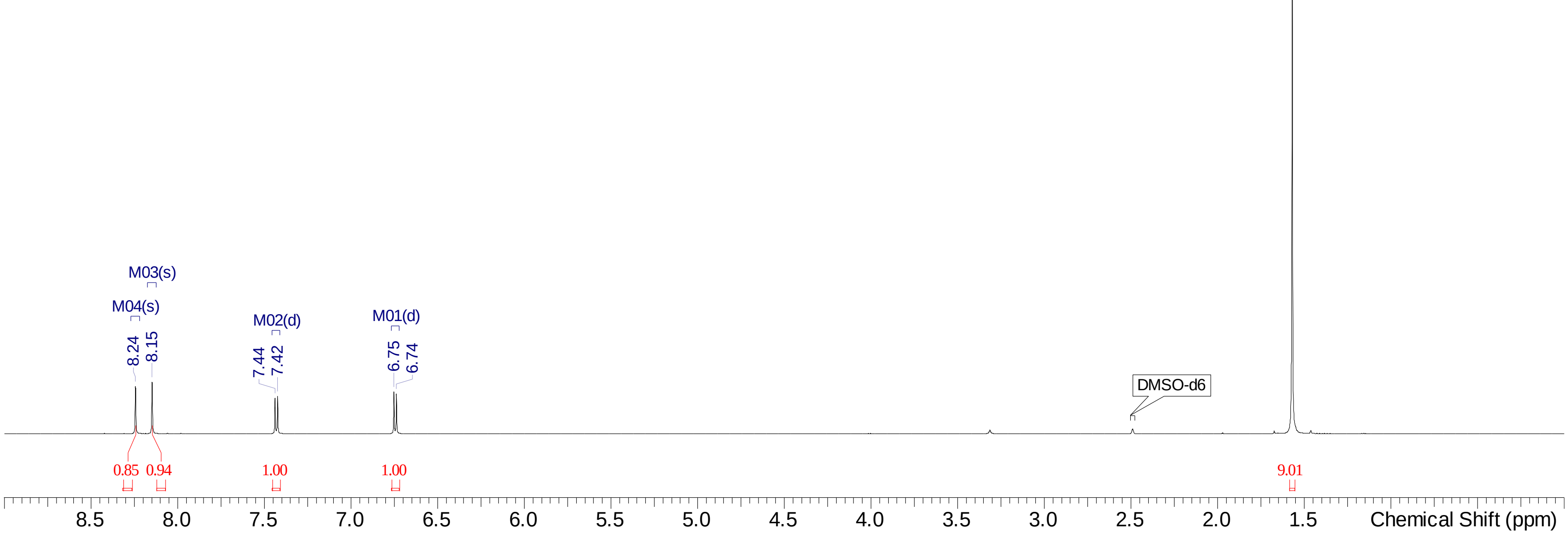
^{13}**C NMR** (126 MHz)
$CDCl_3$

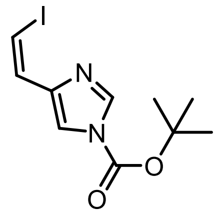


***Tert*-butyl (*Z*)-3-(2-iodovinyl)-1*H*-imidazole-1-carboxylate**

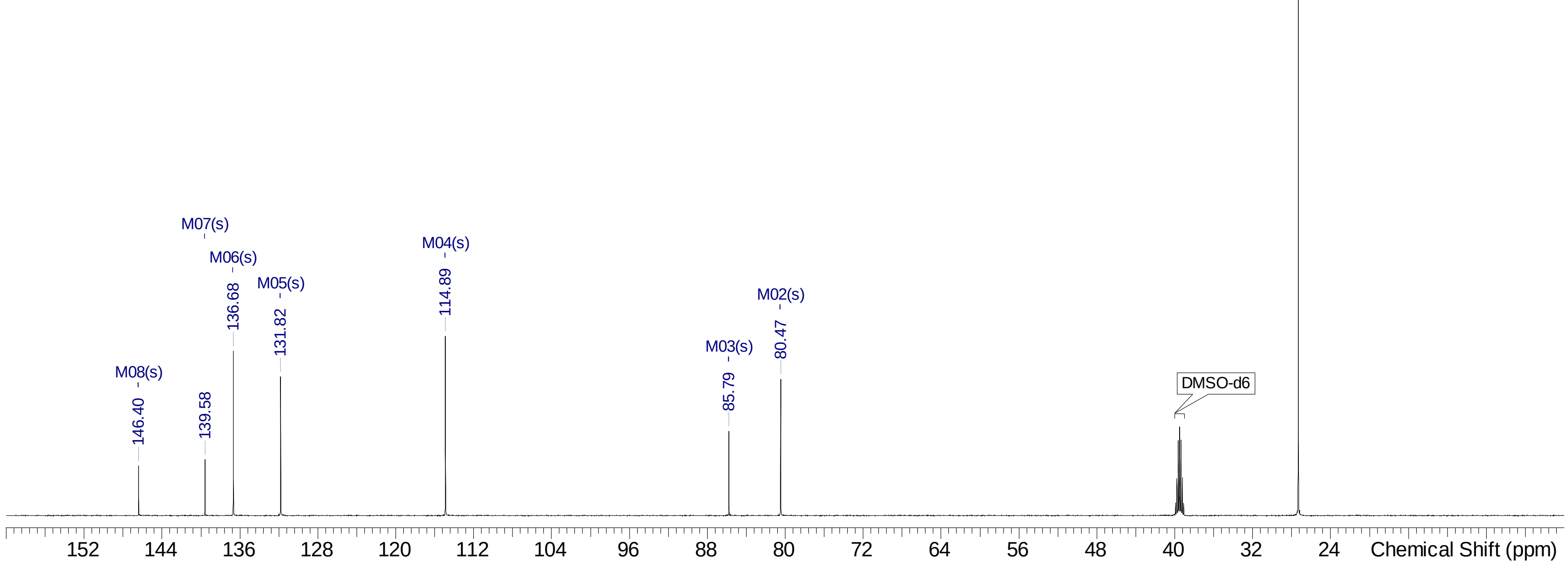


^{1}H NMR (600 MHz)
DMSO-d_6

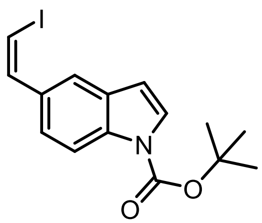




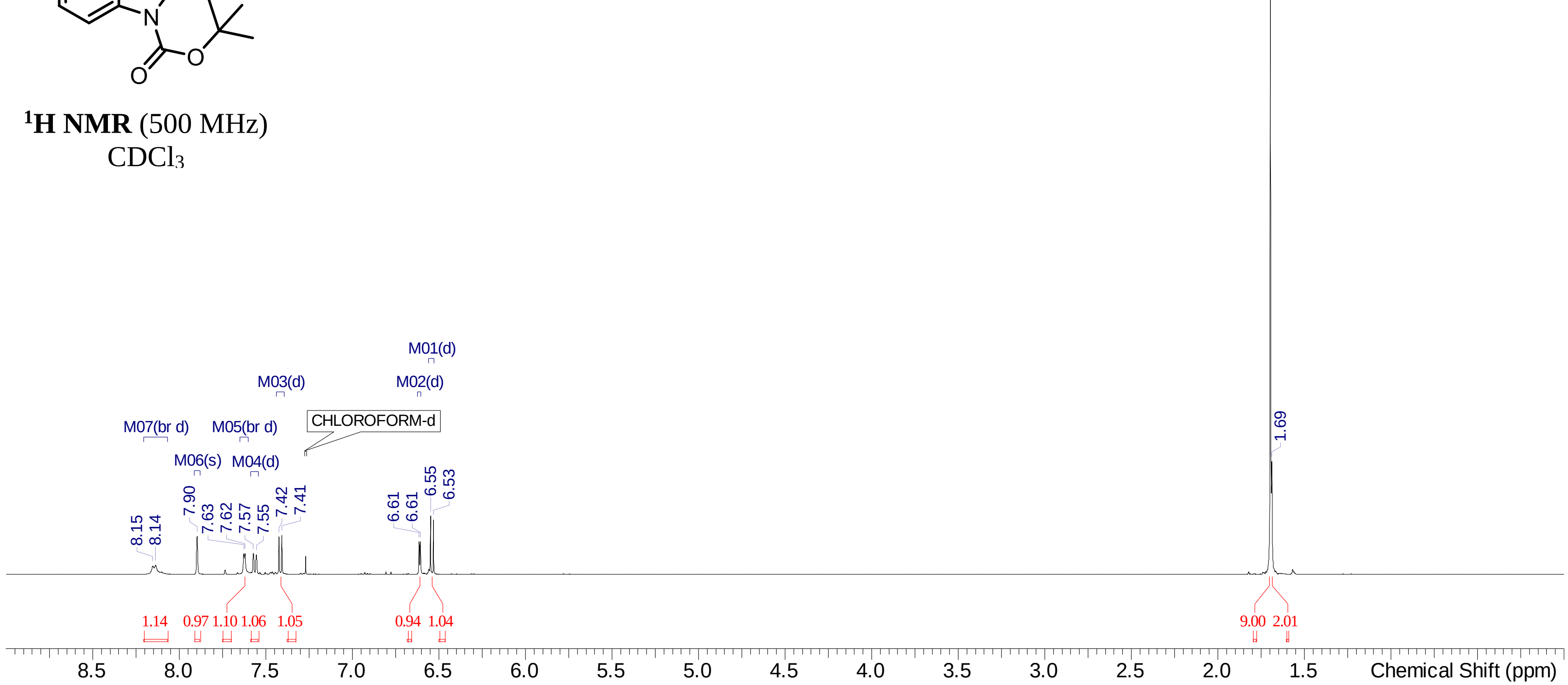
^{13}C NMR (151 MHz)
DMSO-d_6

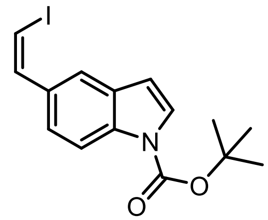


***Tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-indole-1-carboxylate**

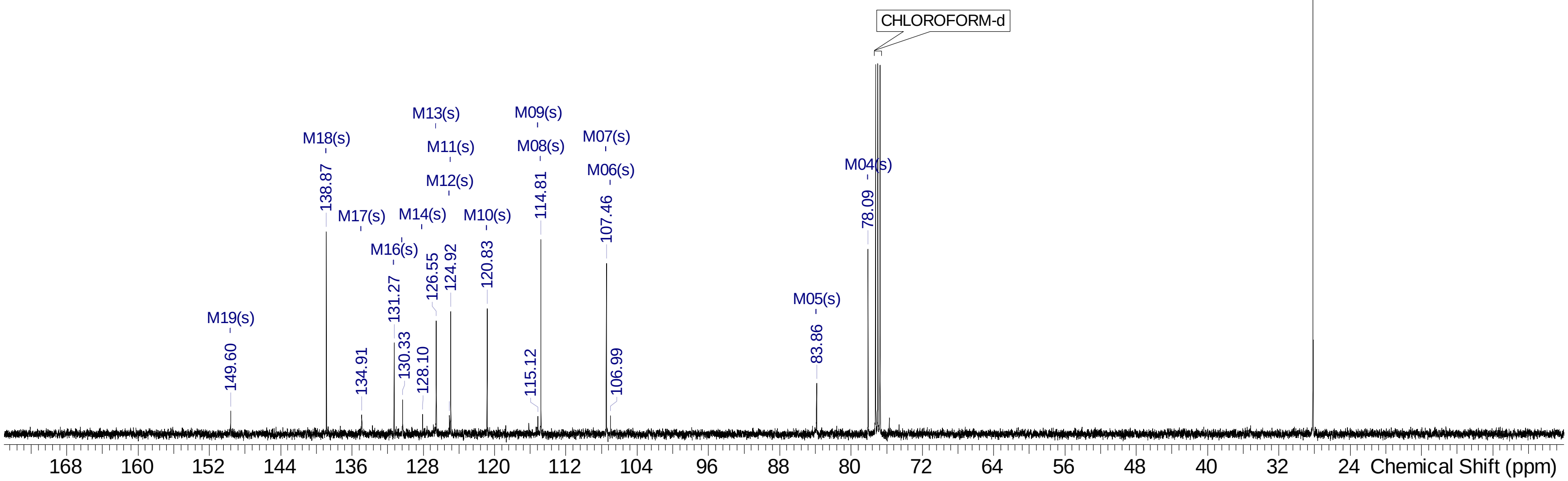


^{1}H NMR (500 MHz)
$CDCl_3$

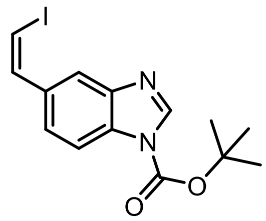




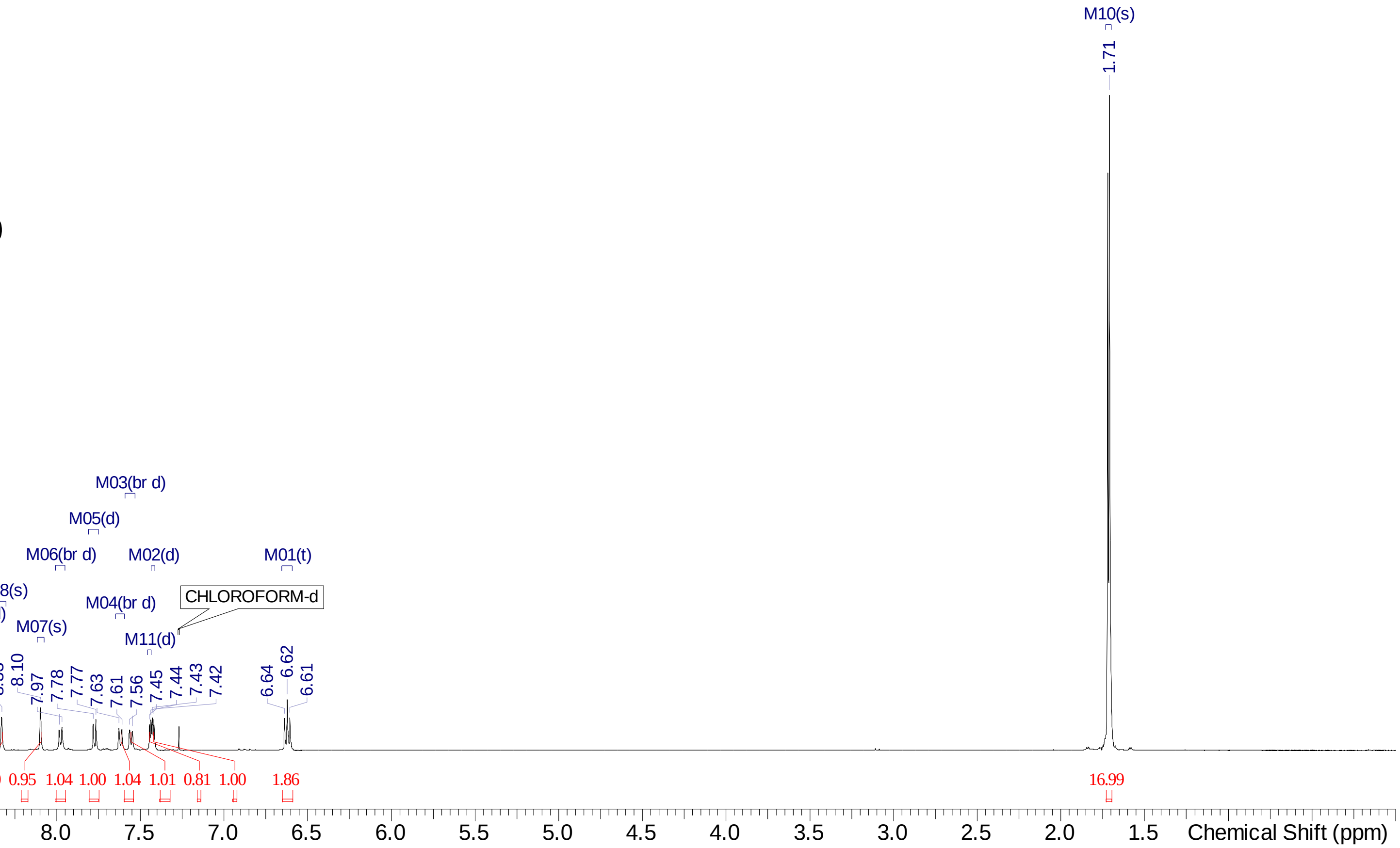
^{13}**C NMR** (126 MHz)
$CDCl_3$

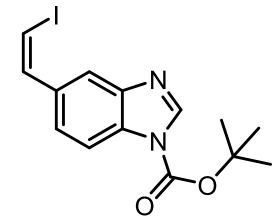


Tert-butyl (_Z_)-5-(2-iodovinyl)-1_H_-benzo[_d_]imidazole-1-carboxylate

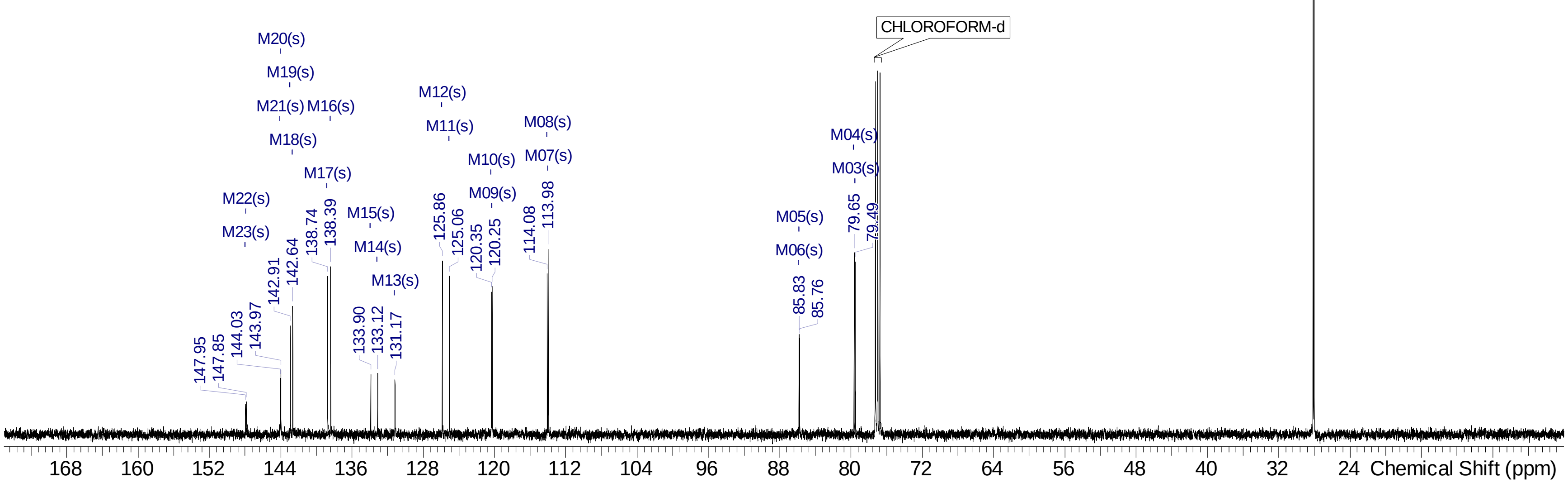


^{1}H NMR (500 MHz)
$CDCl_3$

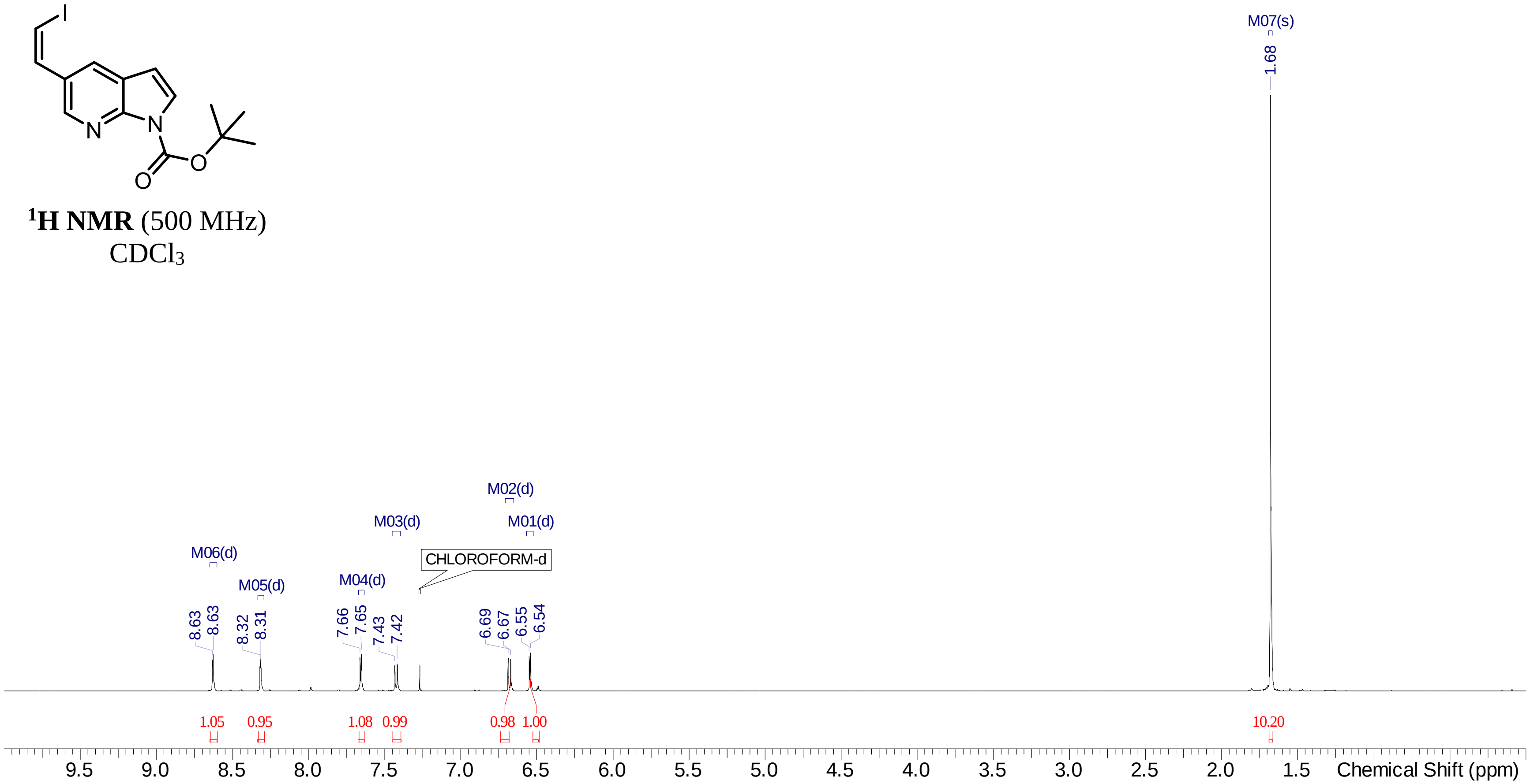




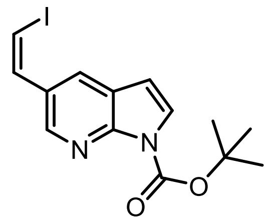
^{13}C NMR (126 MHz)
$CDCl_3$



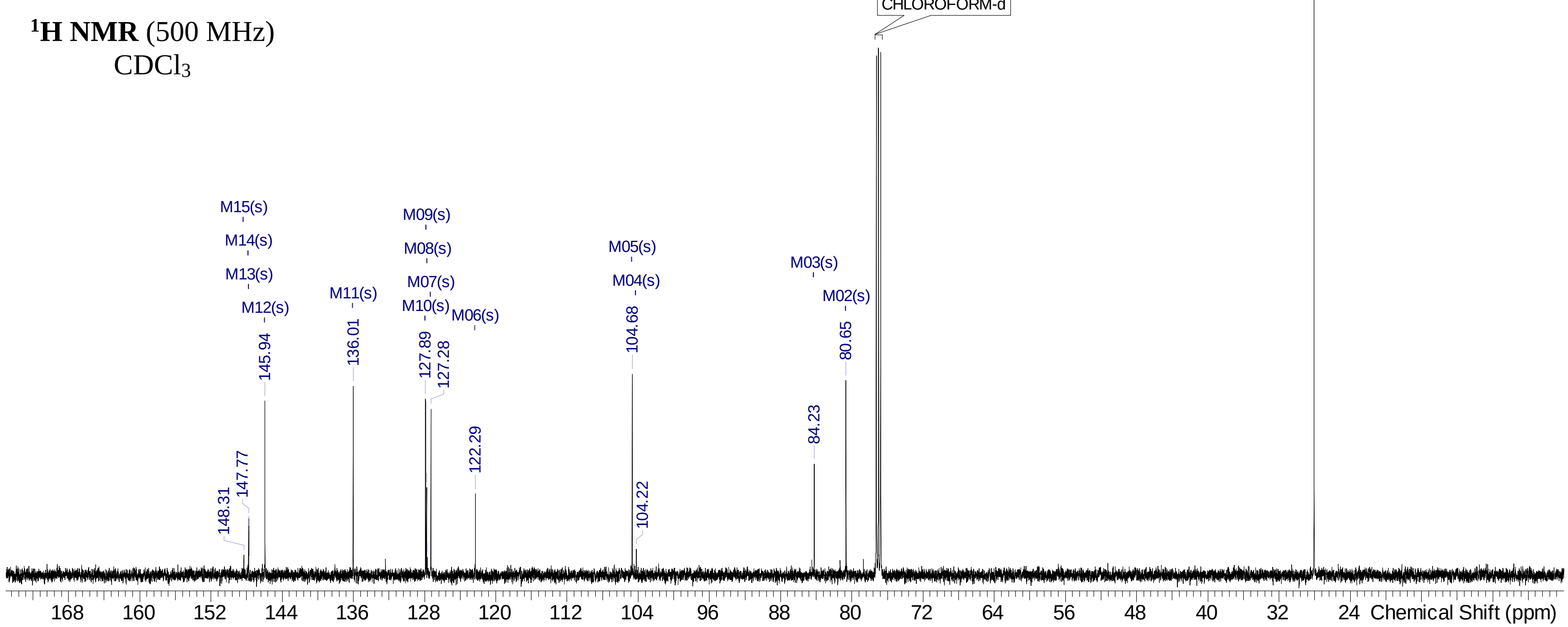
***Tert*-butyl (*Z*)-5-(2-iodovinyl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate**



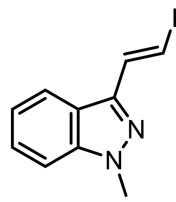
^{1}H NMR (500 MHz)
$CDCl_3$



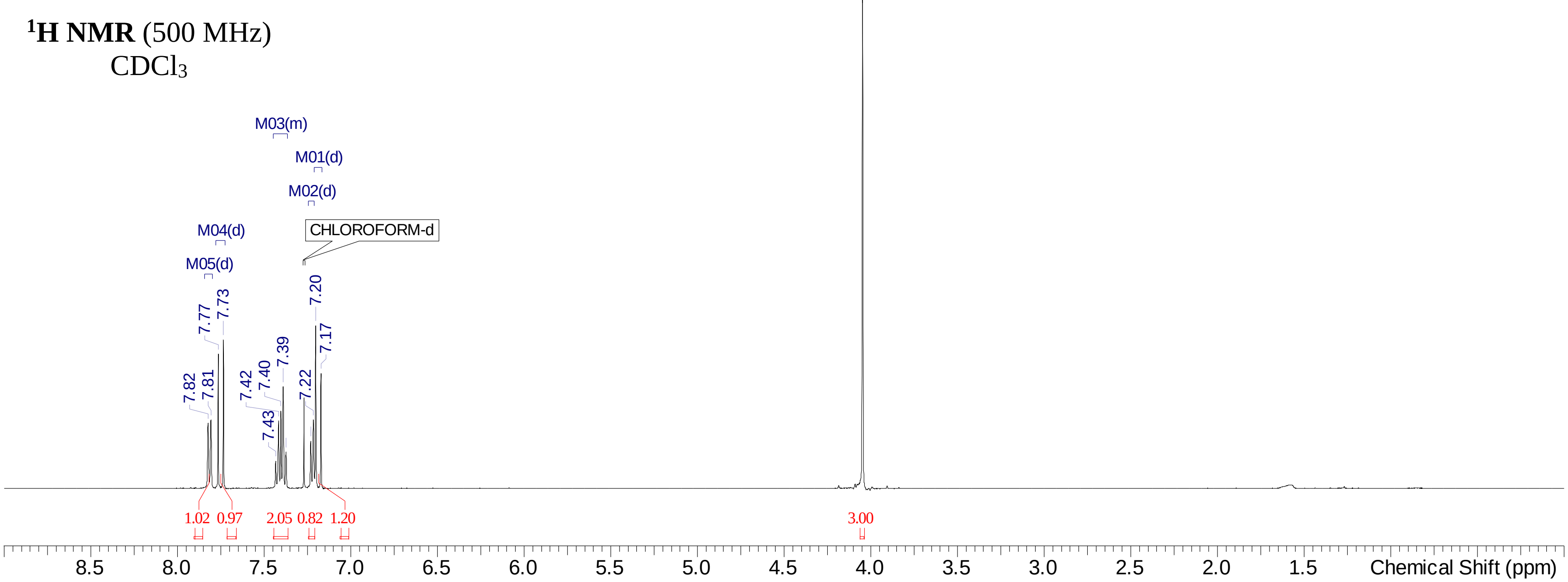
[1]H NMR (500 MHz)
$CDCl_3$

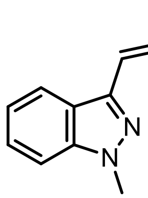


(*E*)-3-(2-iodovinyl)-1-methyl-1*H*-indazole

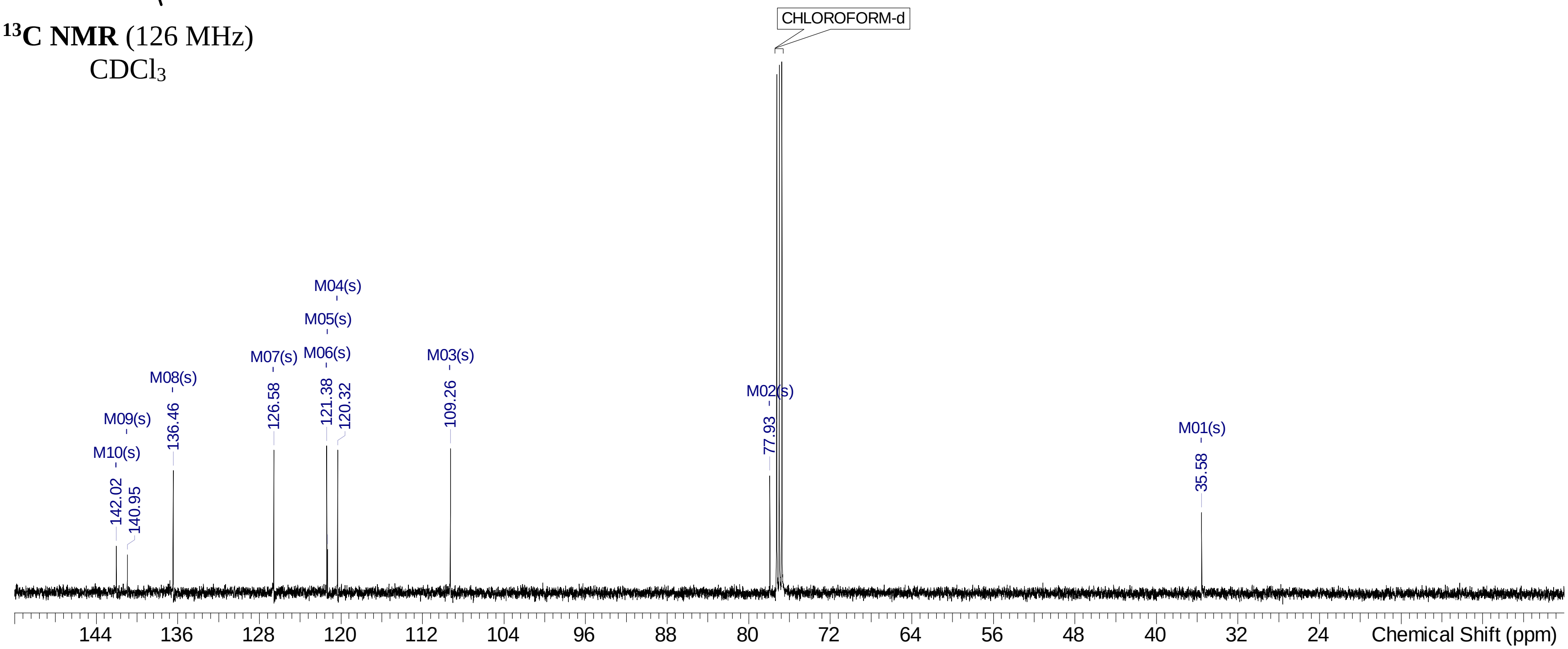


^{1}H NMR (500 MHz)
$CDCl_3$

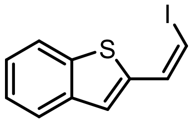




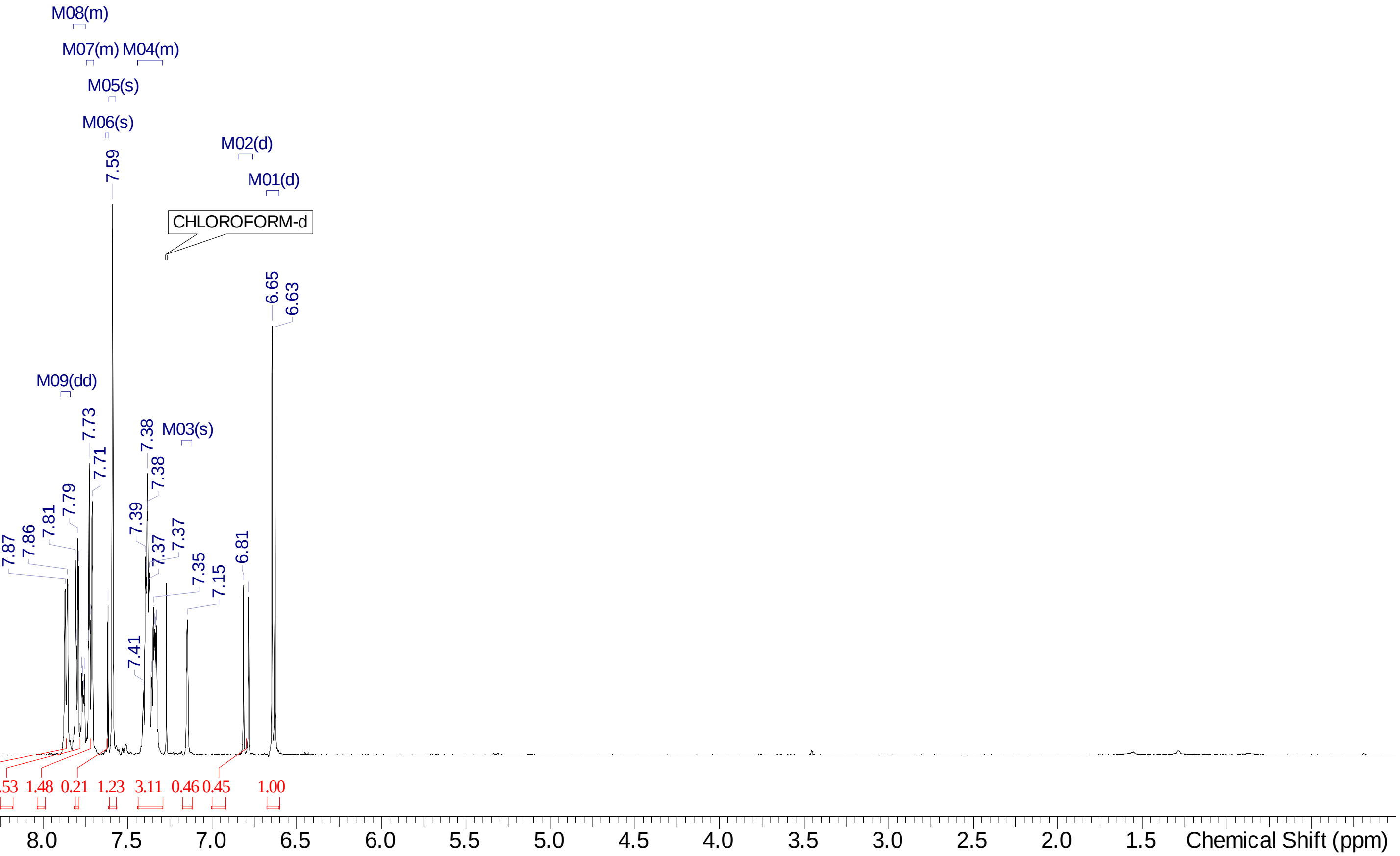
^{13}C NMR (126 MHz)
$CDCl_3$

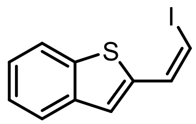


(*Z*)-2-(2-iodovinyl)benzo[*b*]thiophene

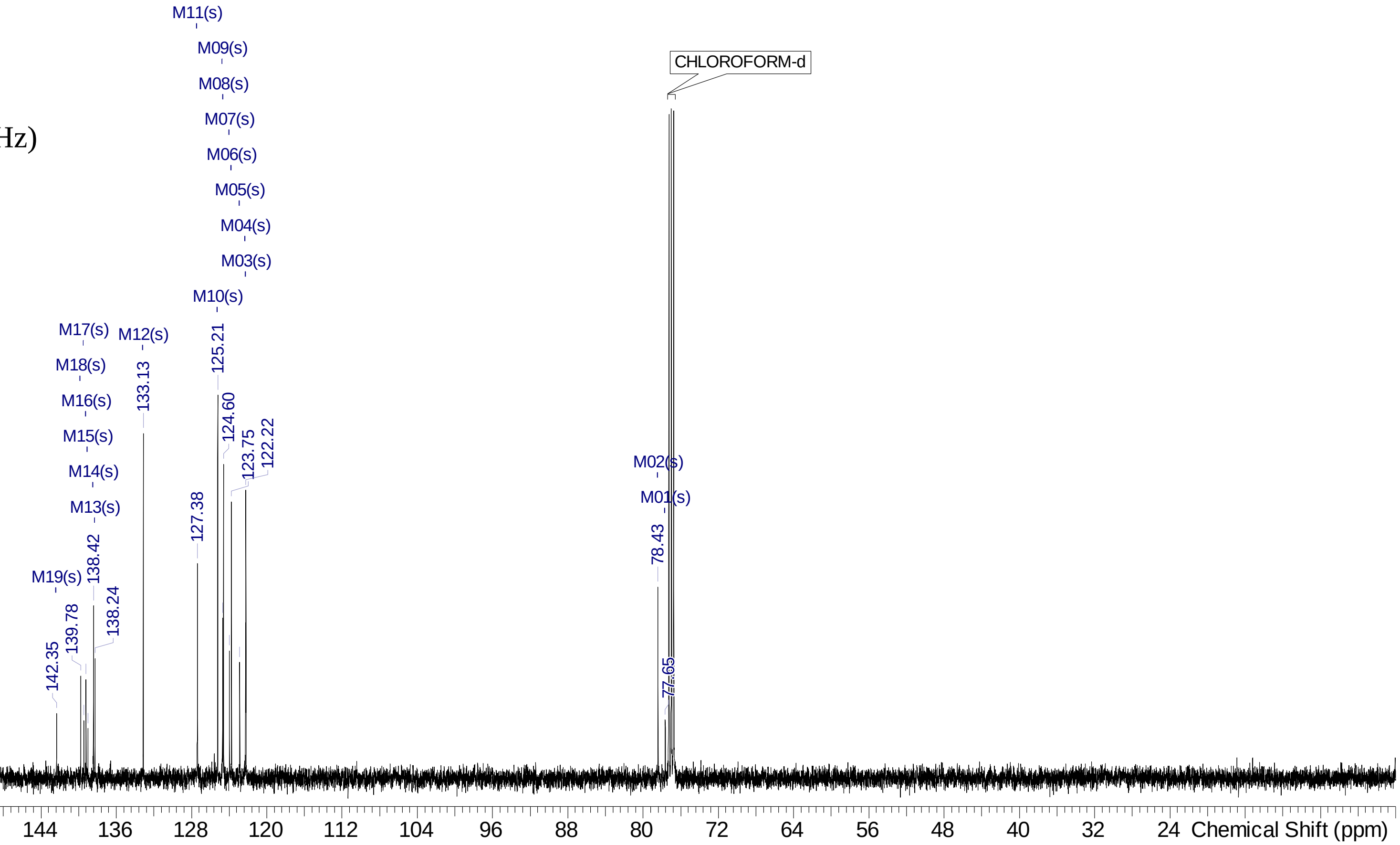


^{1}H NMR (500 MHz)
$CDCl_3$

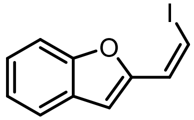




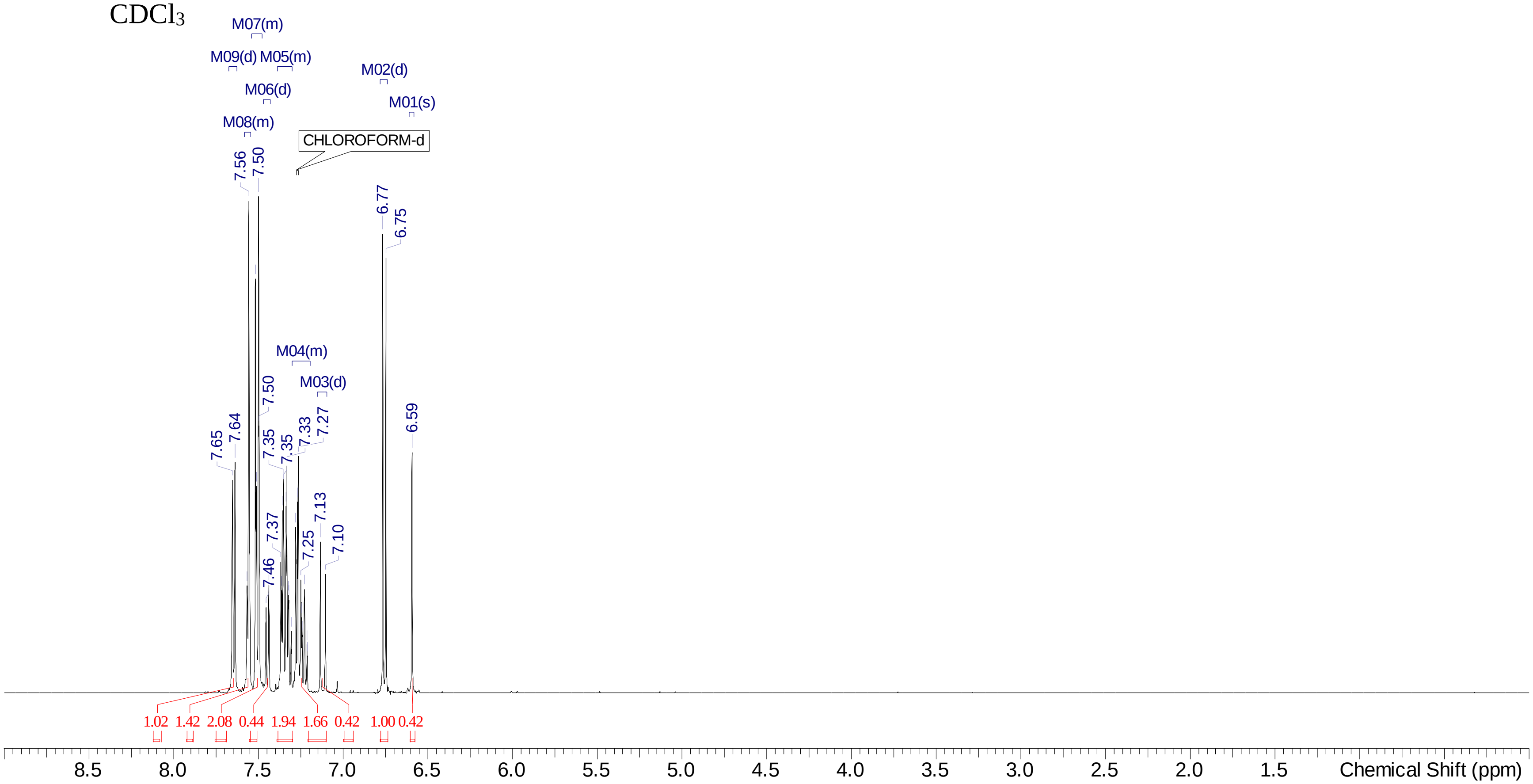
^{13}C NMR (126 MHz)
$CDCl_3$

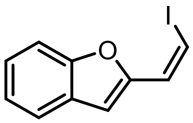


(*Z*)-2-(2-iodovinyl)benzofuran

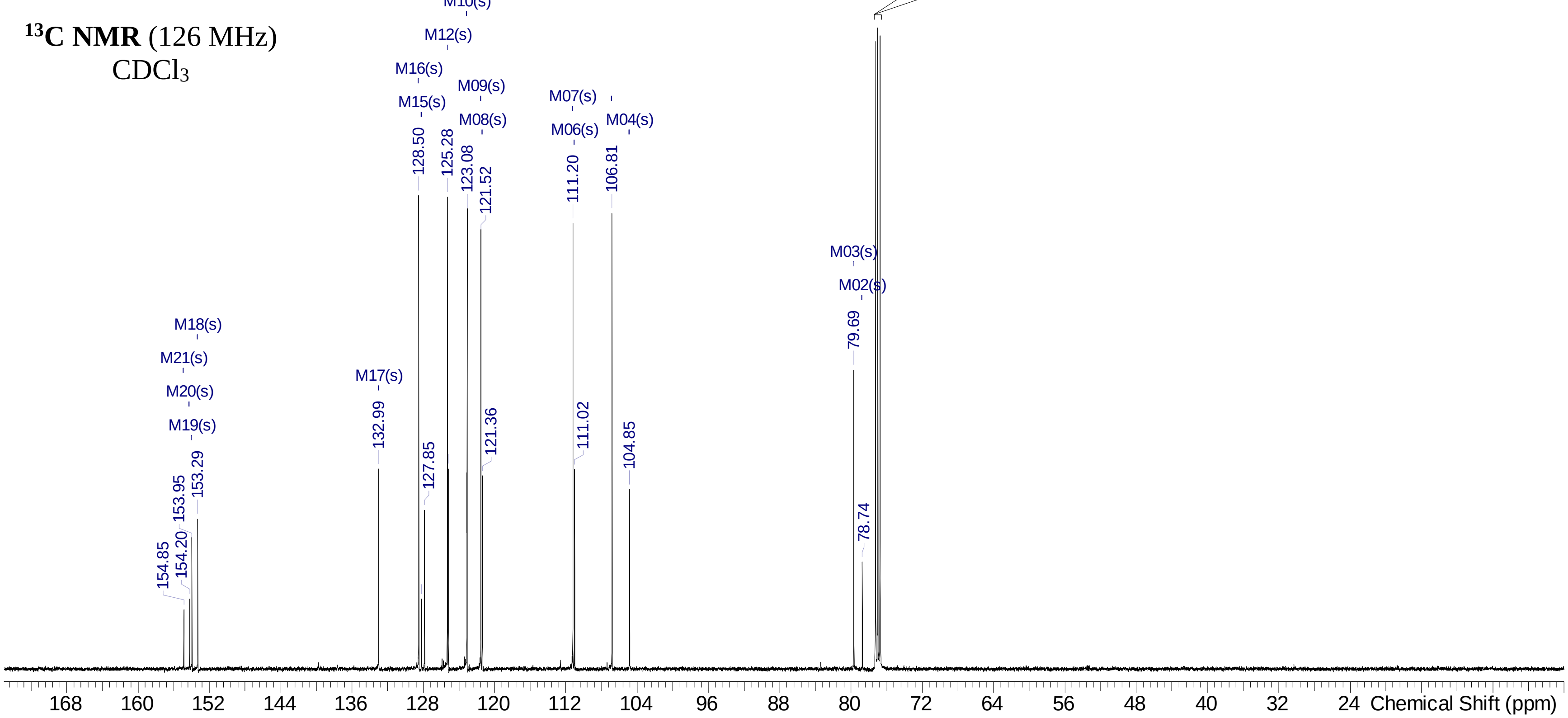


^{1}H NMR (500 MHz)
$CDCl_3$

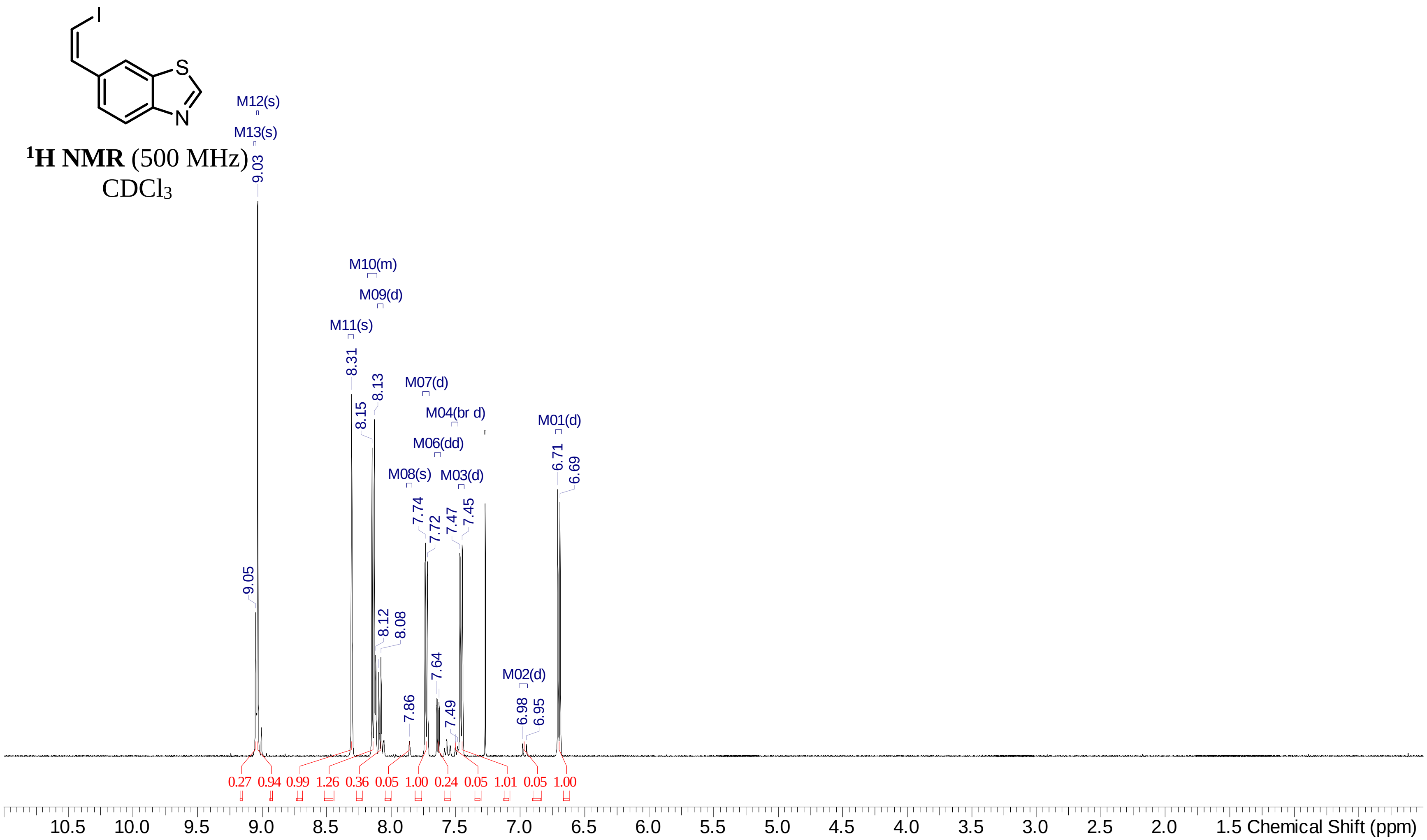


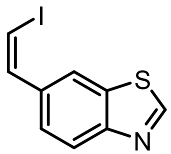


^{13}C NMR (126 MHz)
$CDCl_3$

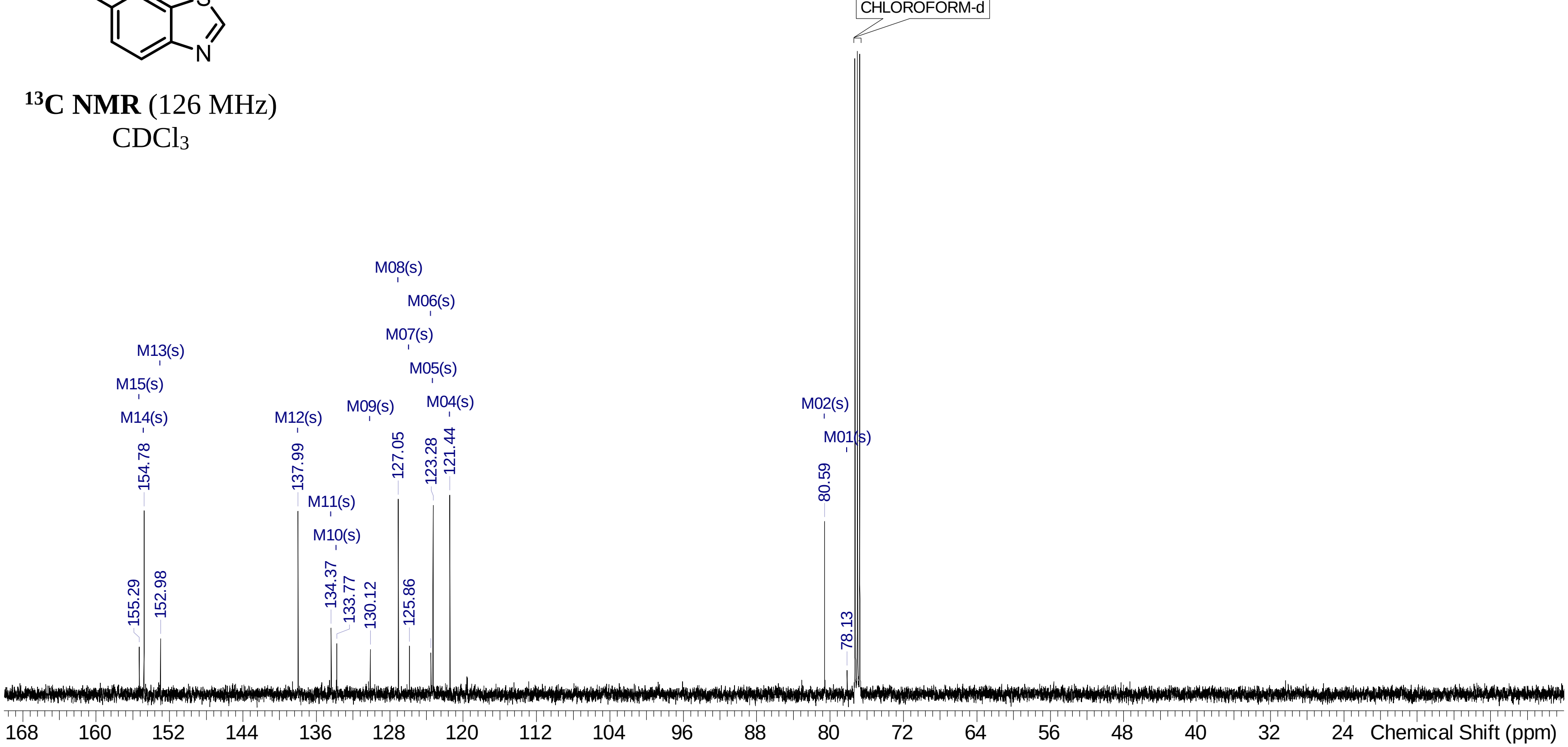


(*Z*)-6-(2-iodovinyl)benzo[*d*]thiazole

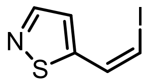


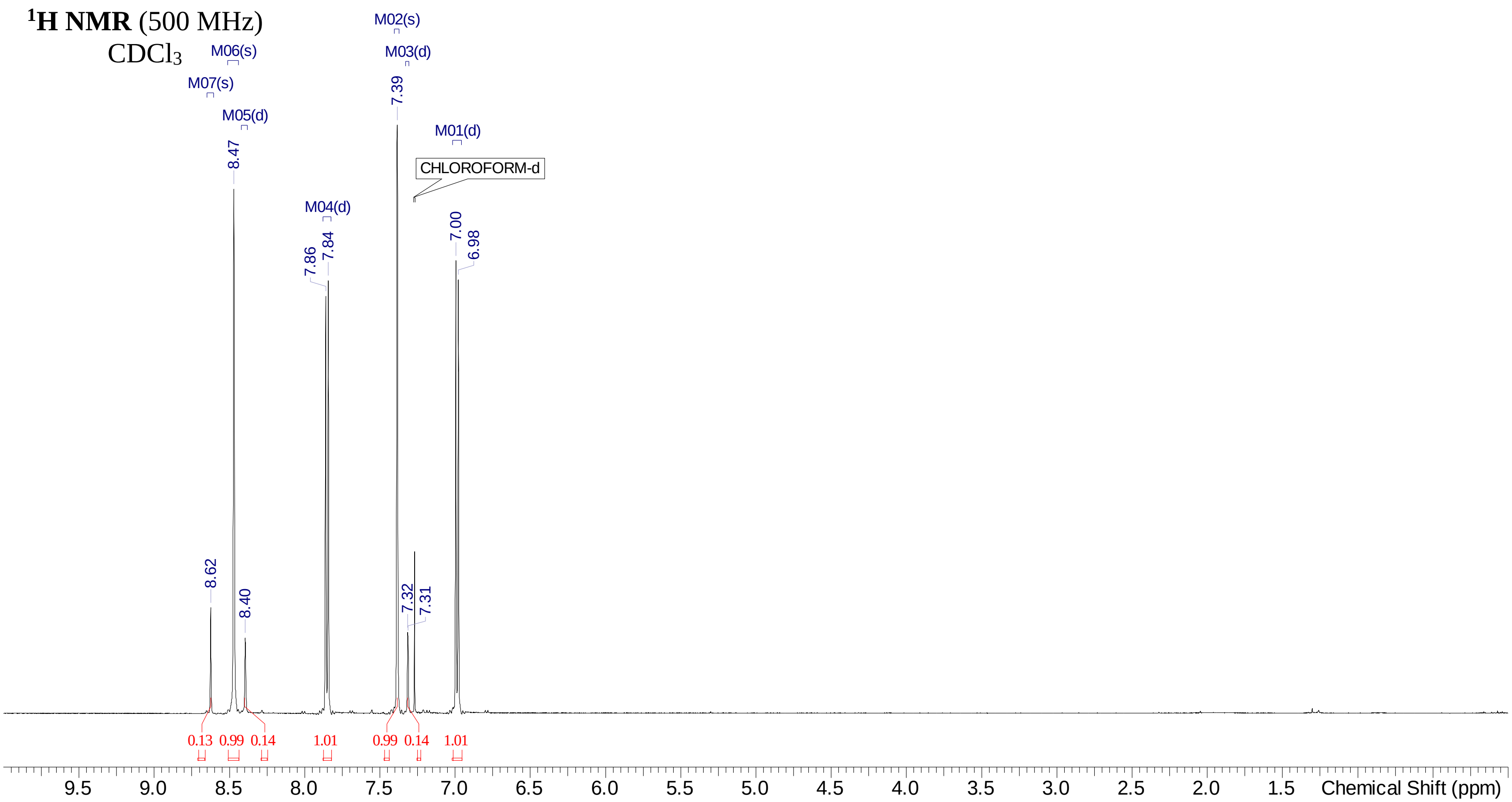


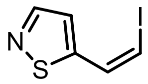
^{13}**C NMR** (126 MHz)
$CDCl_3$



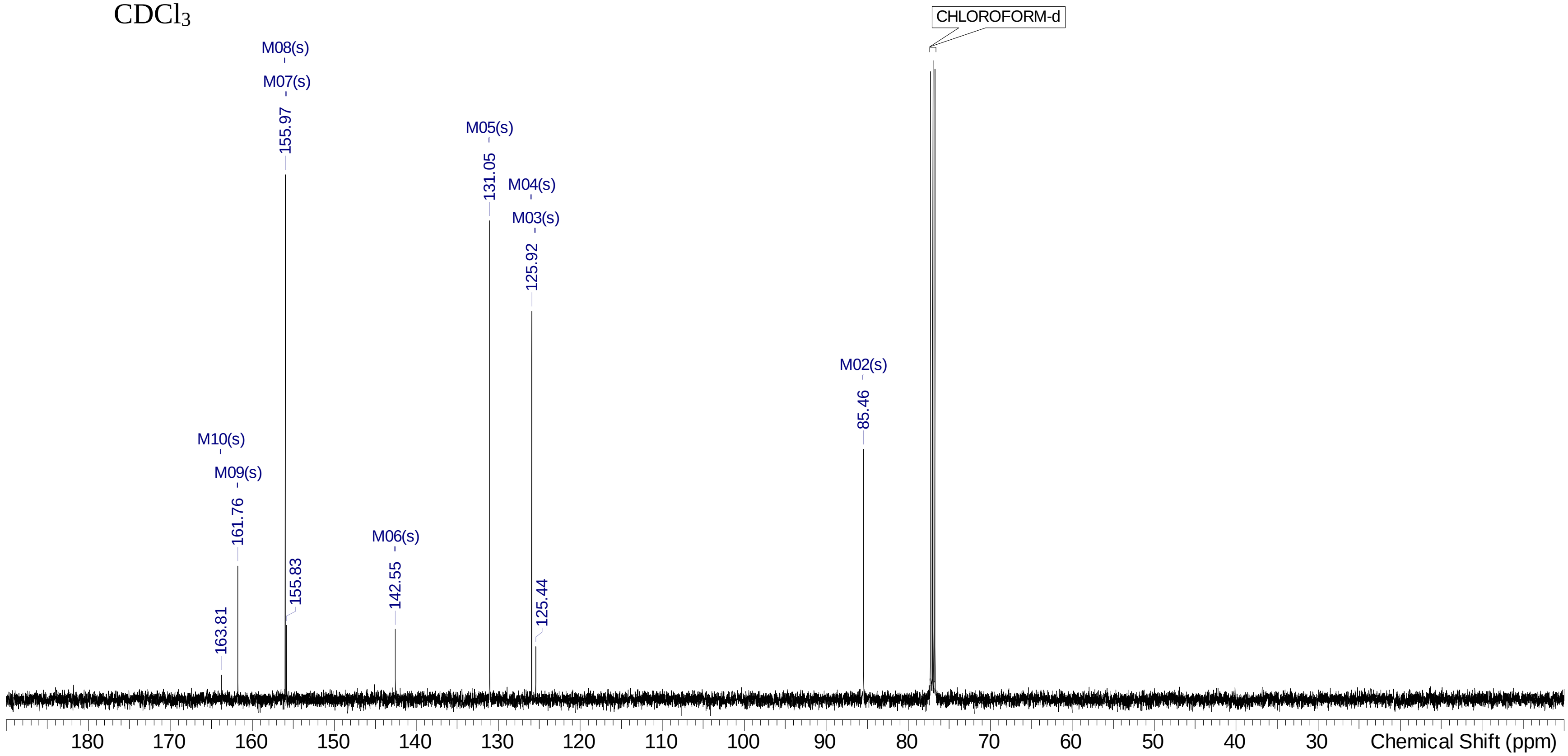
(*Z*)-5-(2-iodovinyl)isothiazole





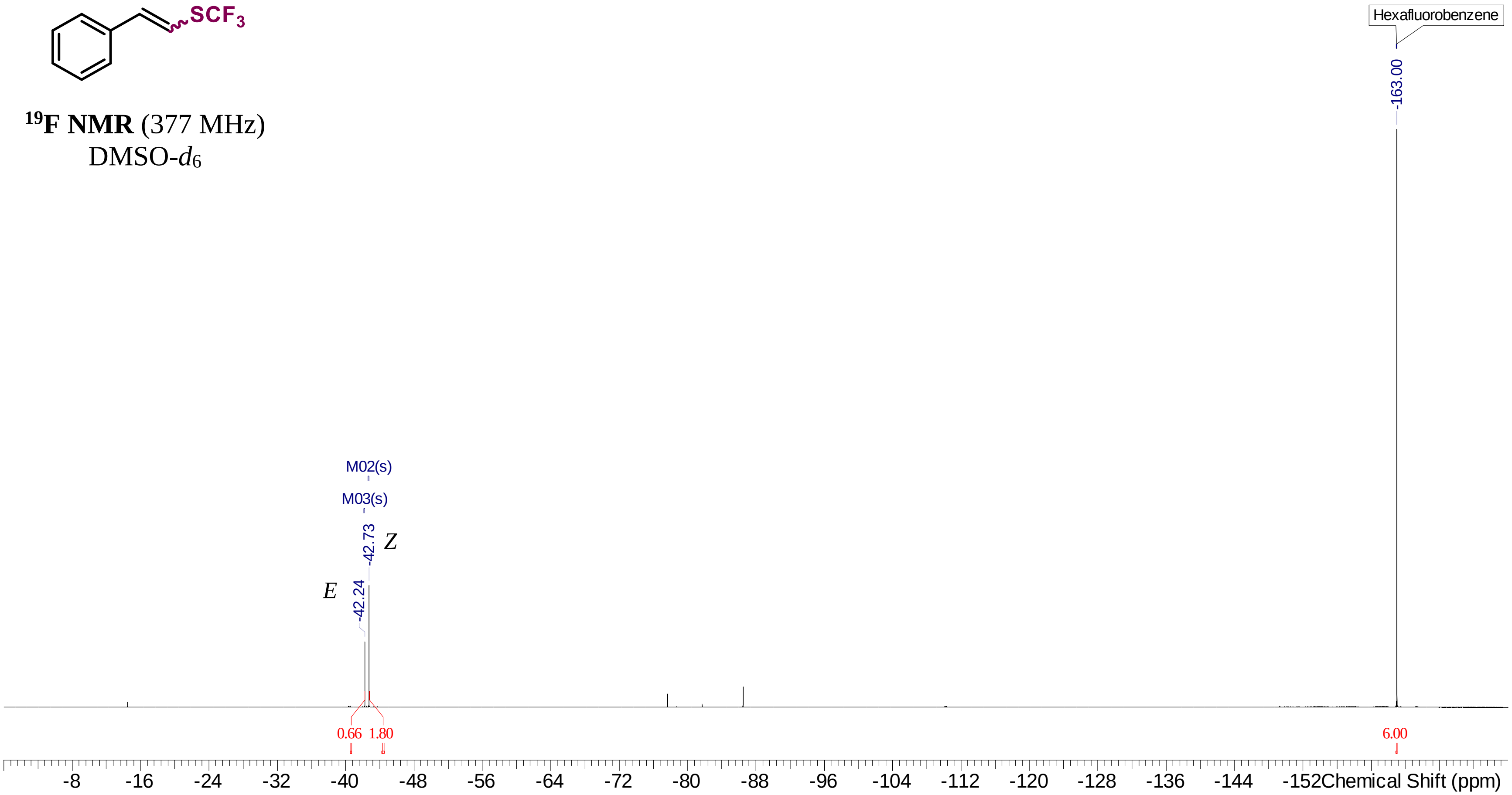


^{13}C NMR (126 MHz)
$CDCl_3$

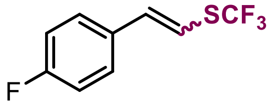


NMR Yields of Volatile Vinyl Trifluoromethylthioether Products

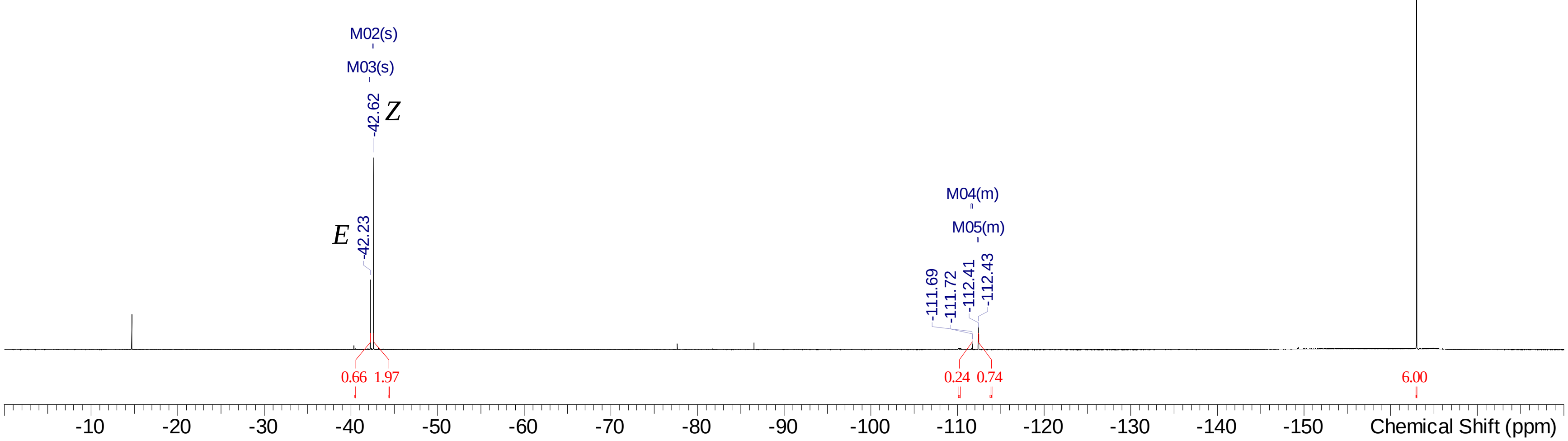
Styryl(trifluoromethyl)sulfane (3a)



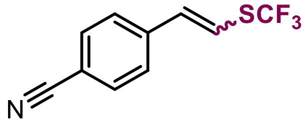
(4-Fluorostyryl)(trifluoromethyl)sulfane (3b)



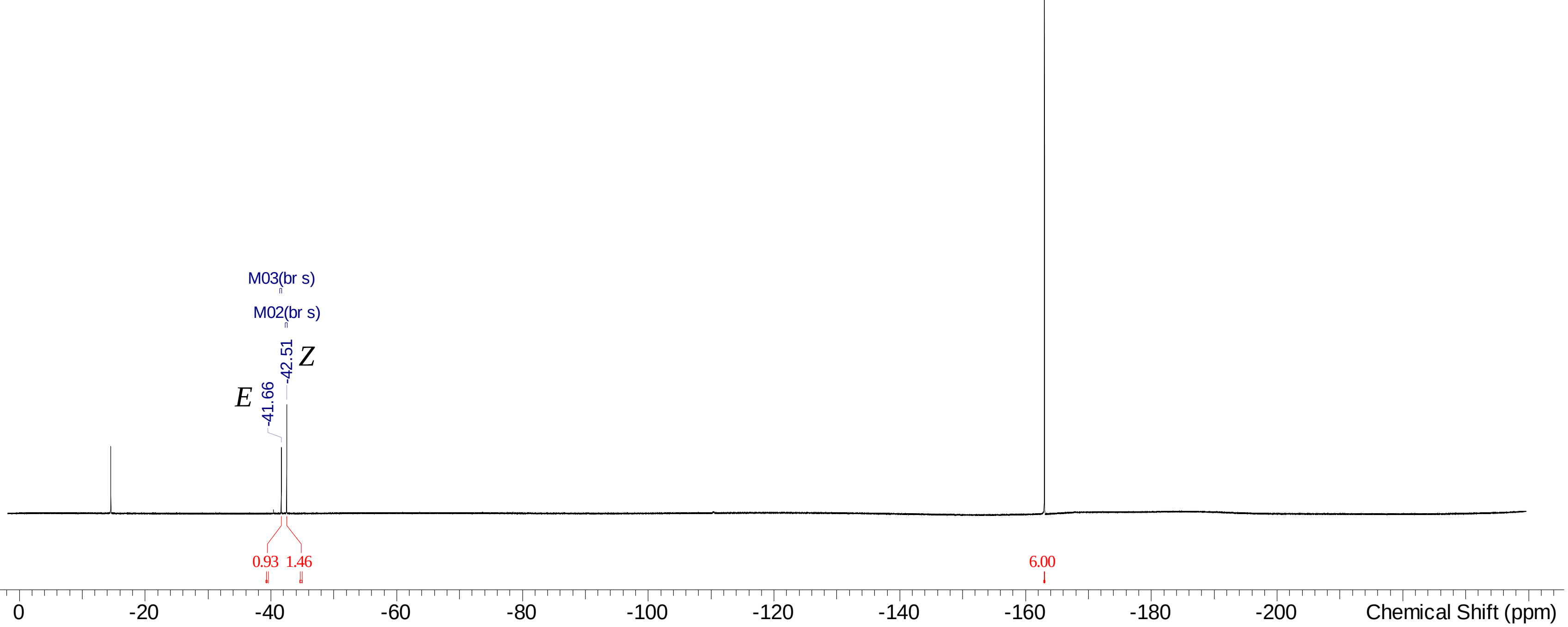
[19]F NMR (377 MHz)
DMSO-d_6



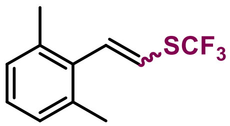
4-(2-((Trifluoromethyl)thio)vinyl)benzonitrile (3i)



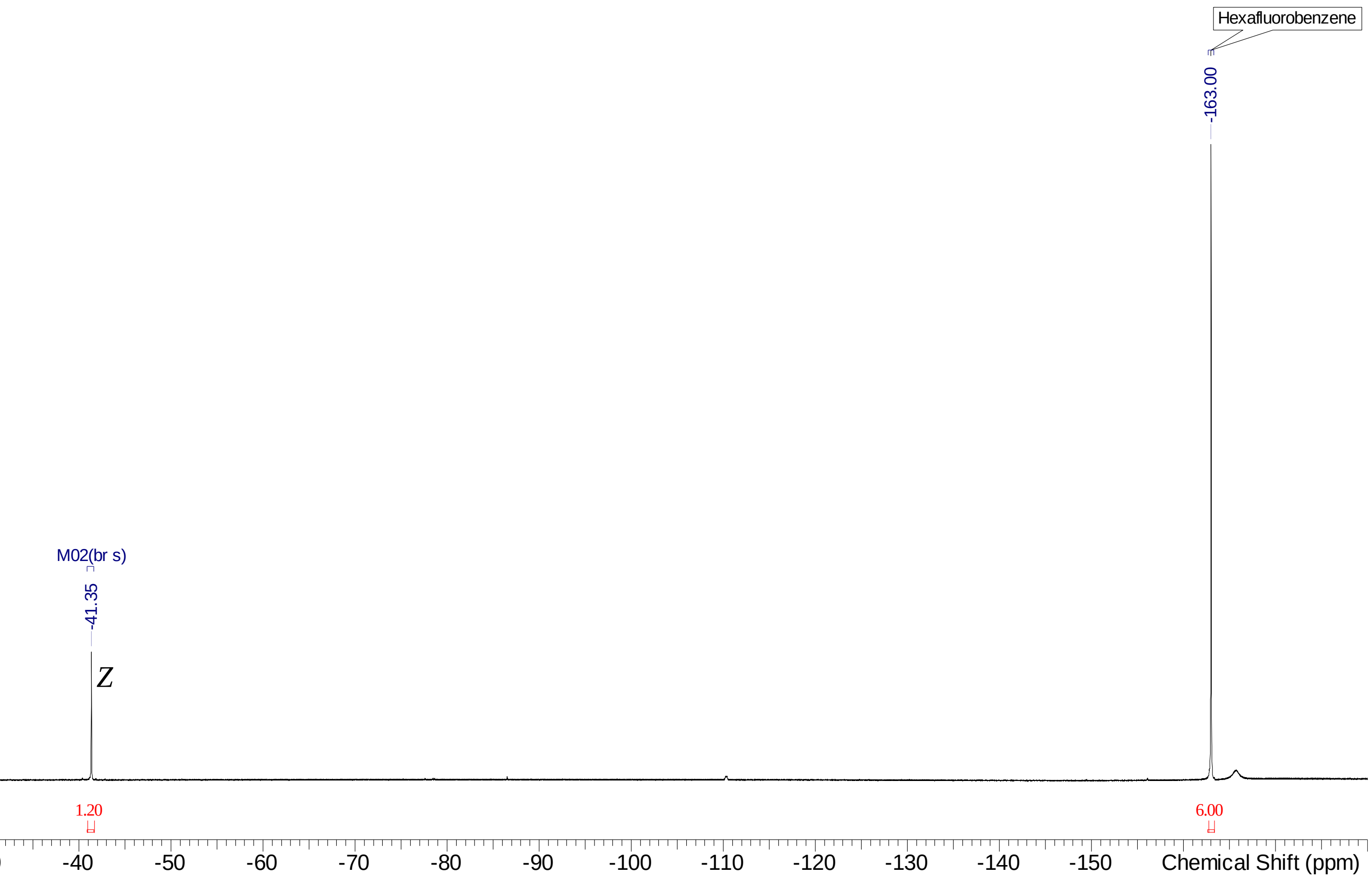
^{19}F NMR (471 MHz)
DMSO-d_6



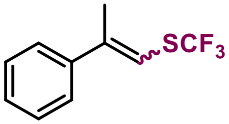
(2,6-dimethylstyryl)(trifluoromethyl)sulfane (3l)



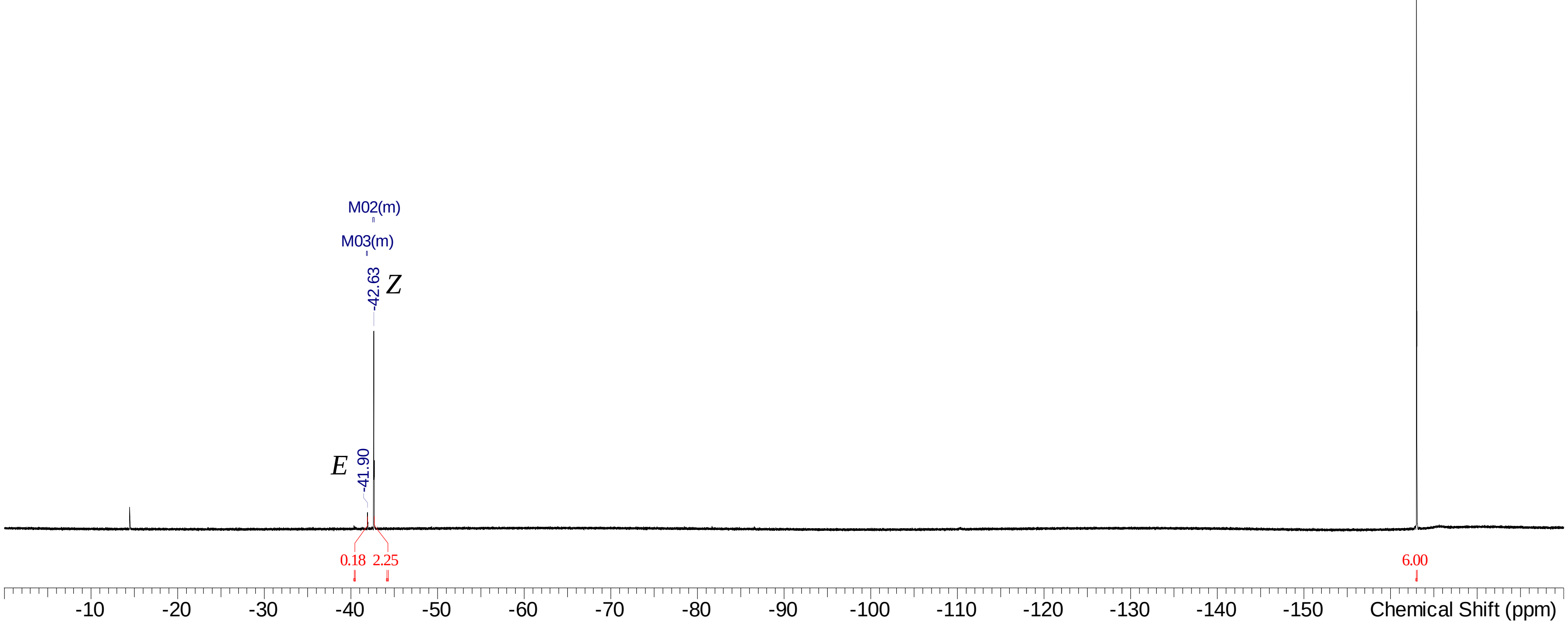
[19]F NMR (471 MHz)
DMSO-d_6



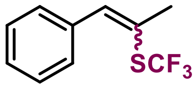
(2-Phenylprop-1-en-1-yl)(trifluoromethyl)sulfane (3m)



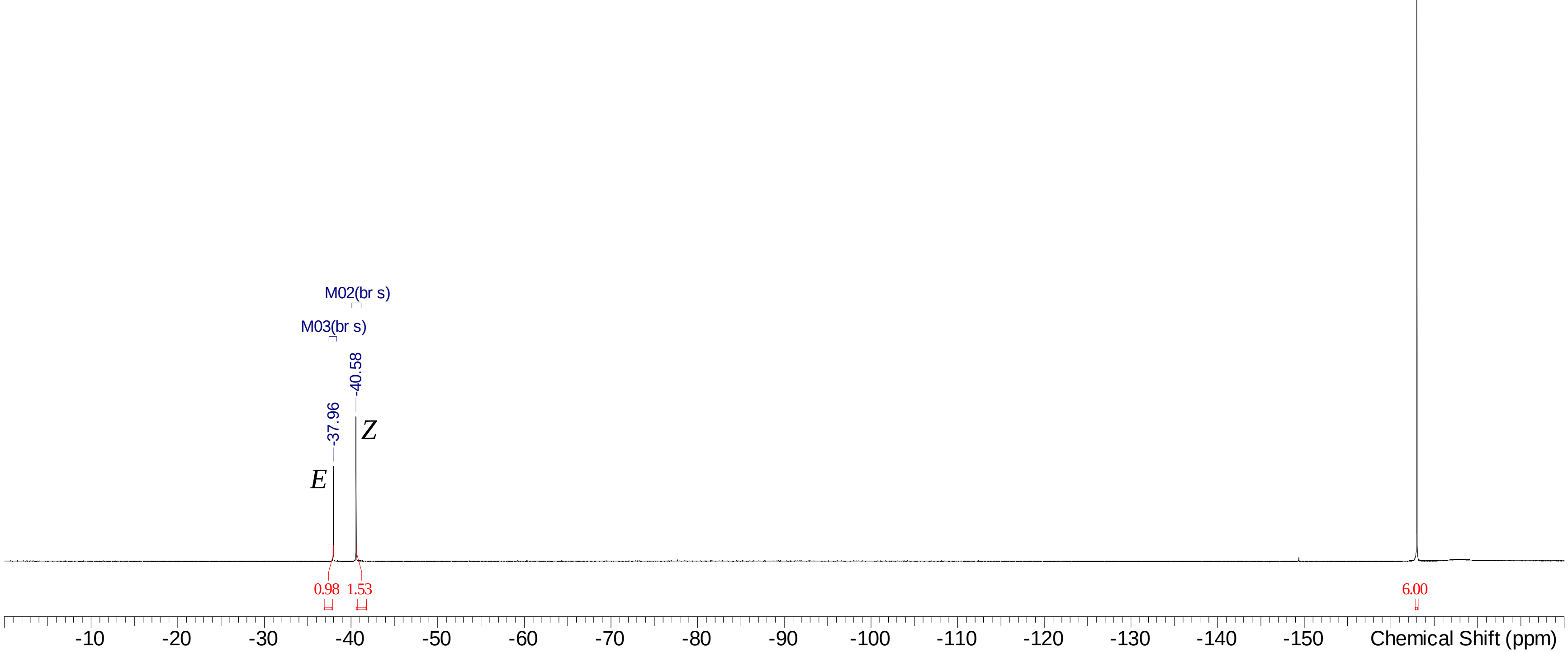
^{19}**F NMR** (471 MHz)
DMSO-d_6



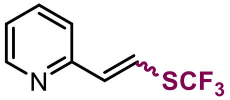
(1-phenylprop-1-en-2-yl)(trifluoromethyl)sulfane (3n)



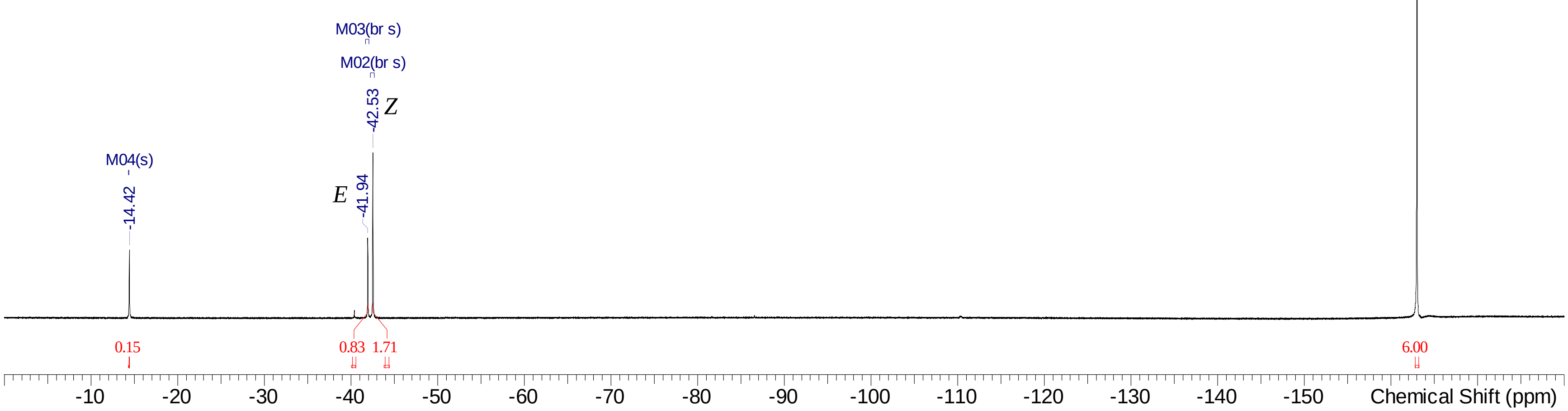
^{19}F NMR (471 MHz)
DMSO-d_6



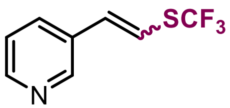
2-(2-((trifluoromethyl)thio)vinyl)pyridine (3q)



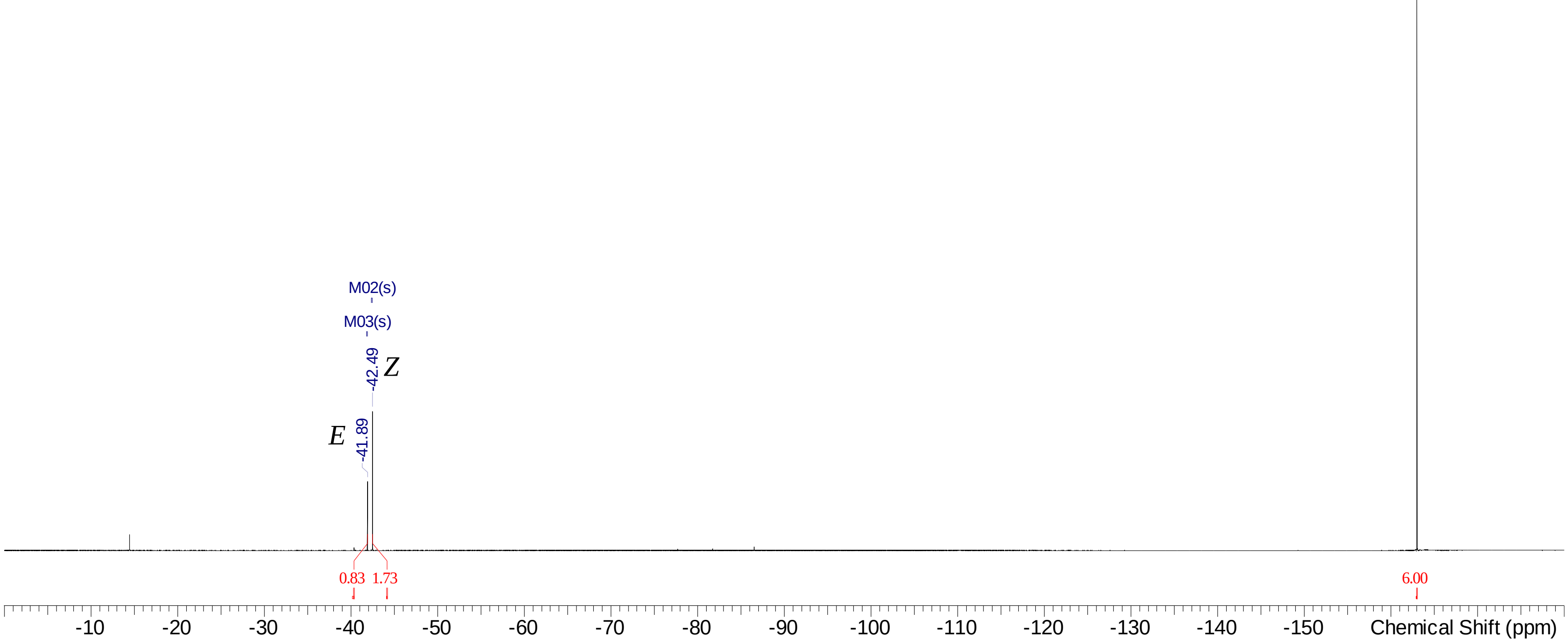
^{19}F NMR (471 MHz)
DMSO-d_6



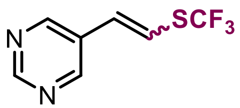
3-(2-((Trifluoromethyl)thio)vinyl)pyridine (3r)



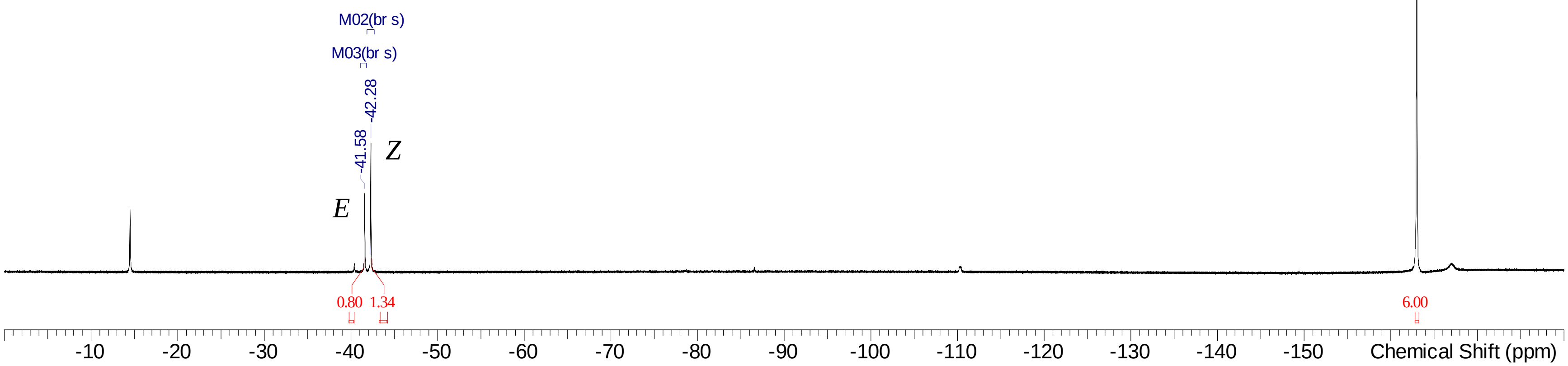
^{19}F NMR (471 MHz)
DMSO-d_6



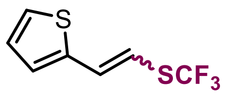
5-(2-((trifluoromethyl)thio)vinyl)pyrimidine (3s)



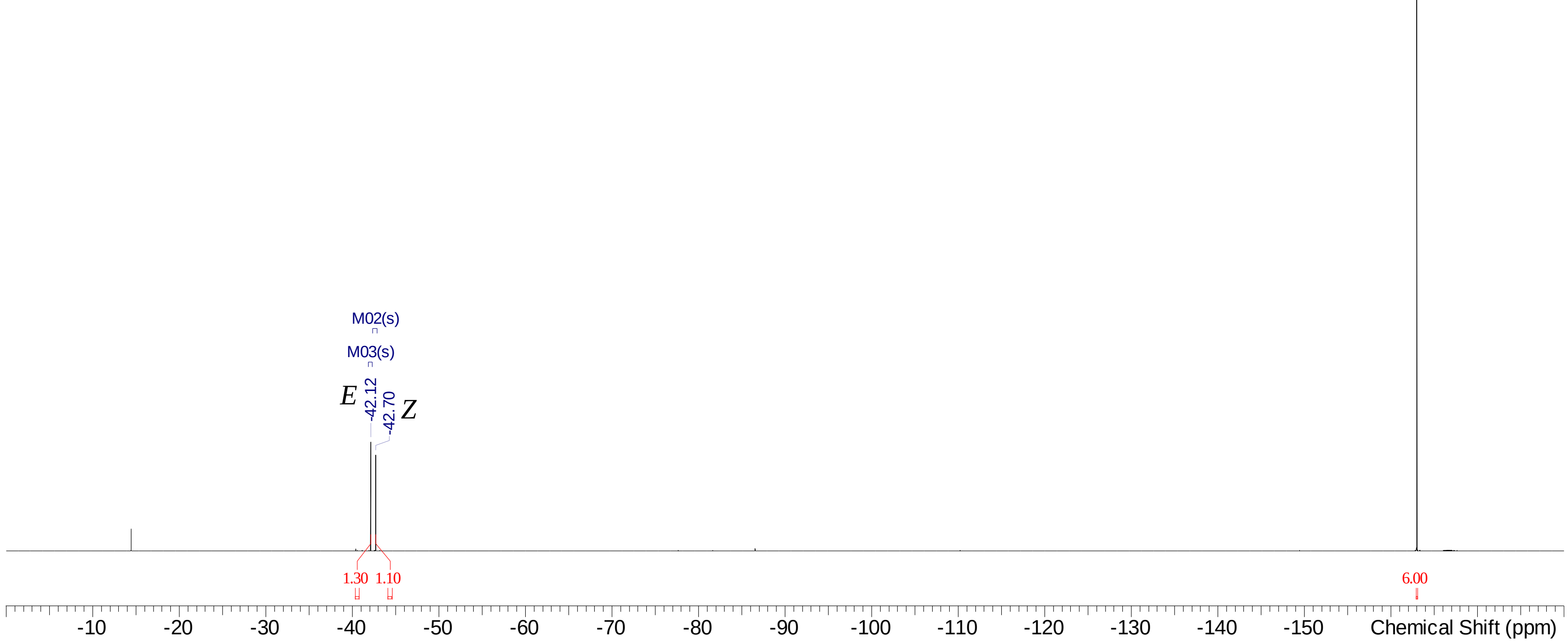
[19]F NMR (471 MHz)
DMSO-d_6



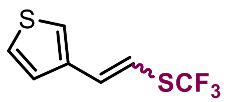
2-(2-((Trifluoromethyl)thio)vinyl)thiophene (3z)



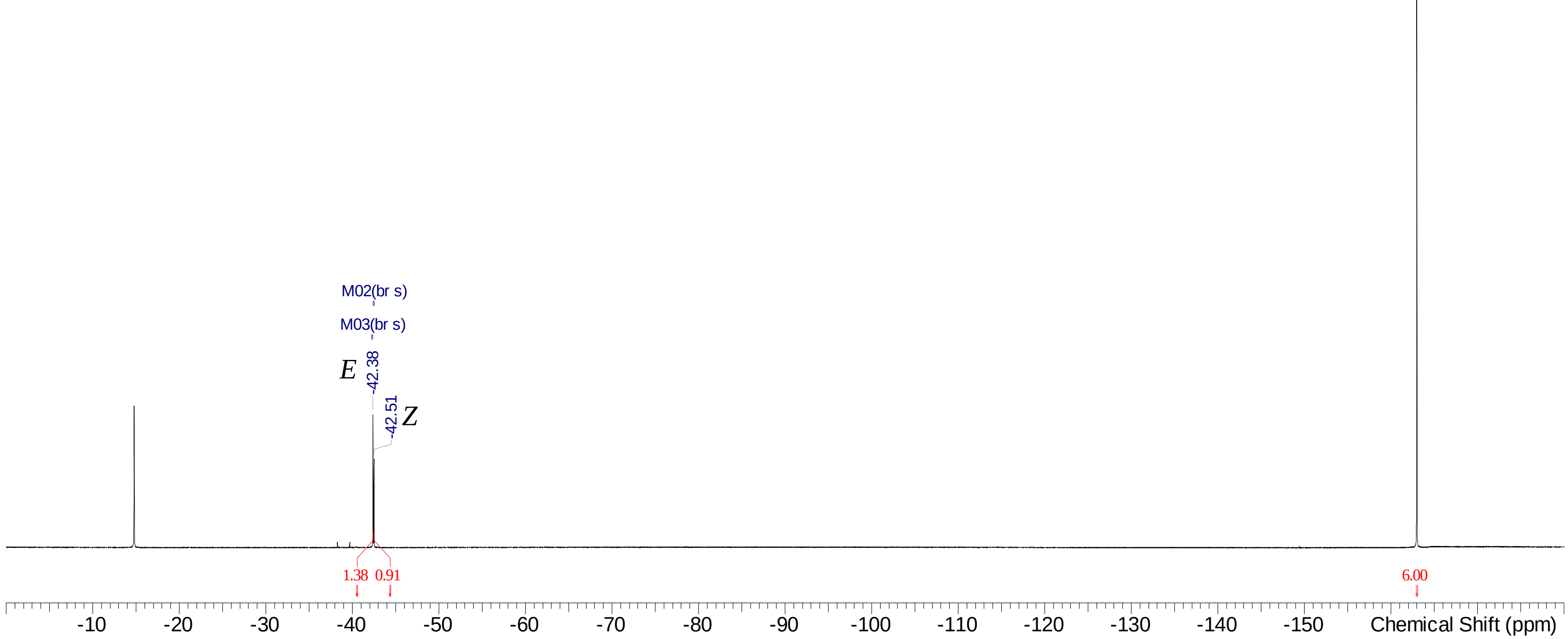
^{19}F NMR (471 MHz)
DMSO-d_6



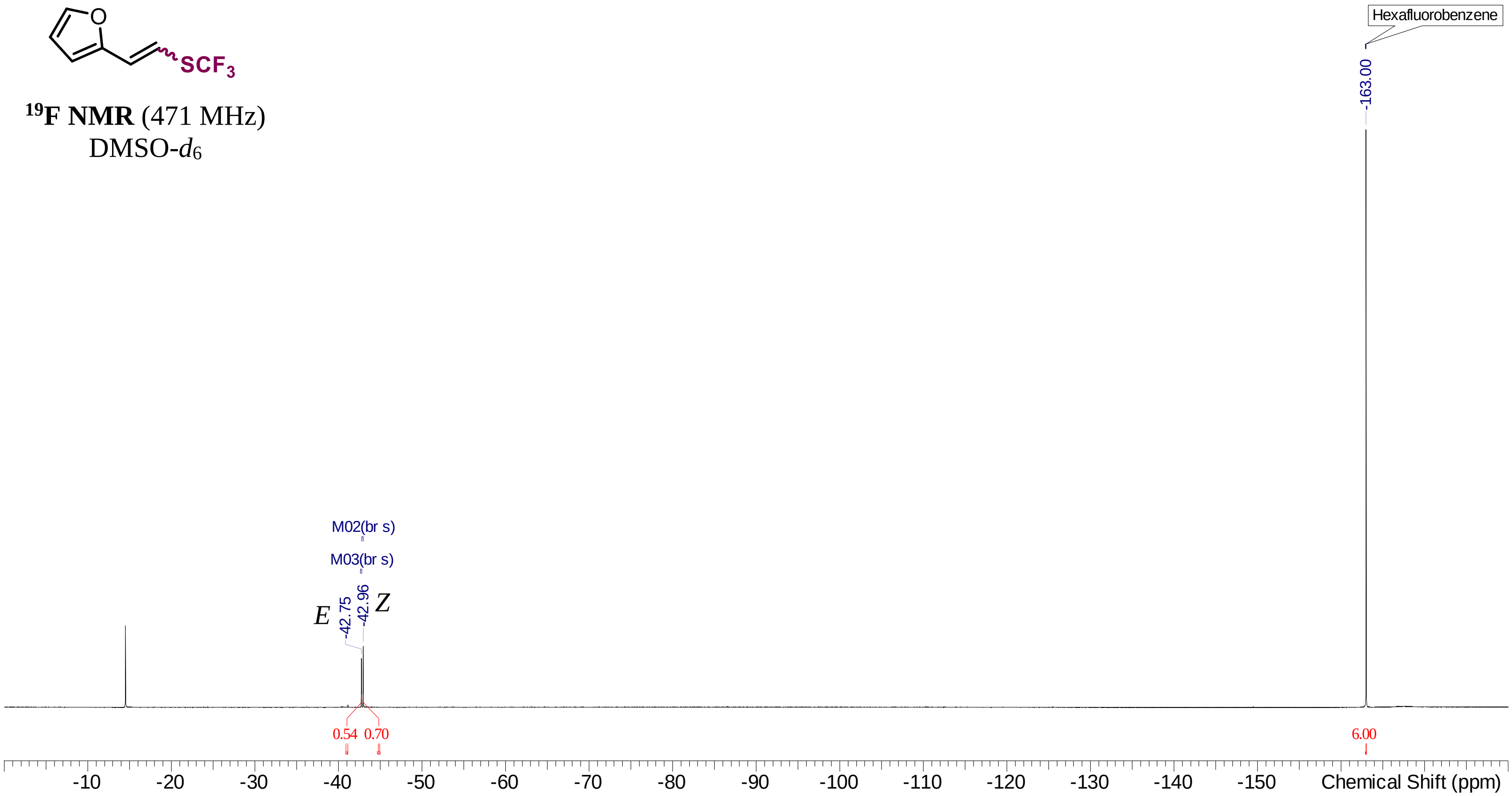
3-(2-((Trifluoromethyl)thio)vinyl)thiophene (3aa)



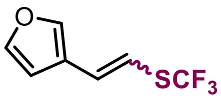
[19]F NMR (471 MHz)
DMSO-d_6



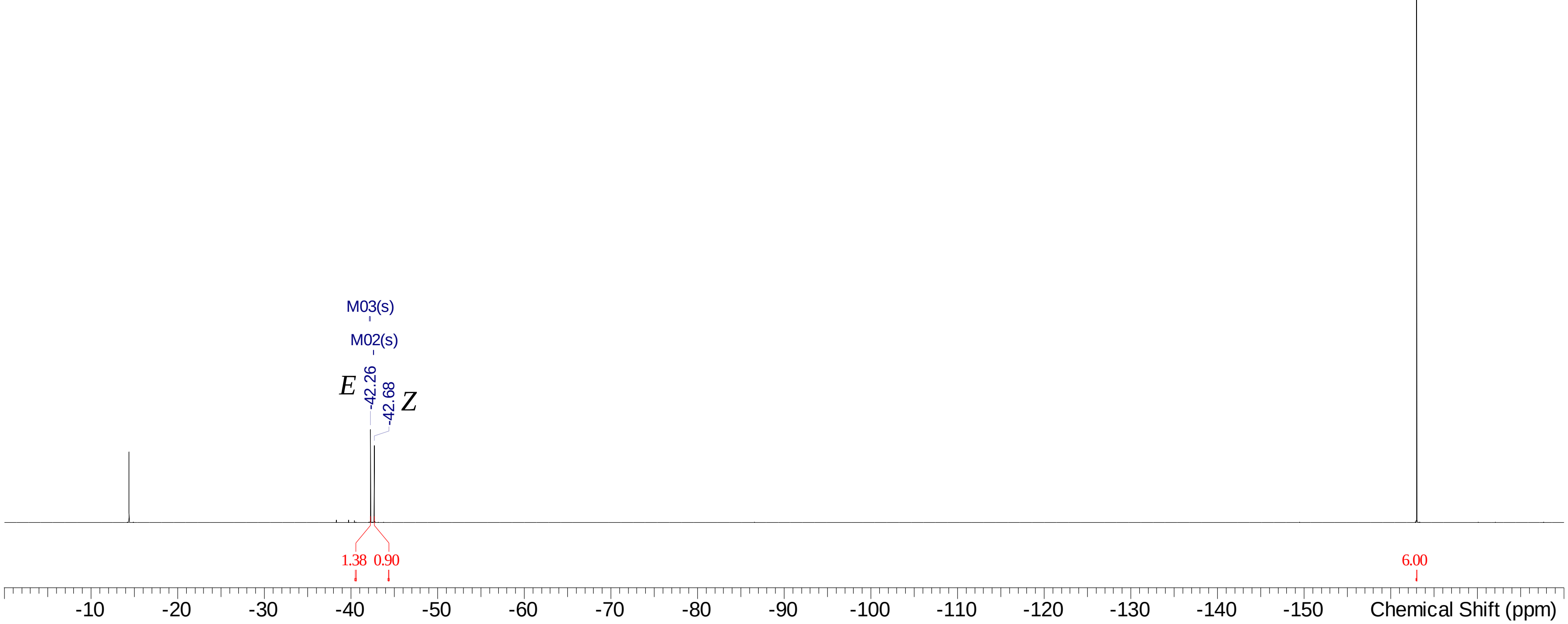
2-(2-((Trifluoromethyl)thio)vinyl)furan (3ab)



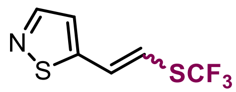
3-(2-((Trifluoromethyl)thio)vinyl)furan (3ac)



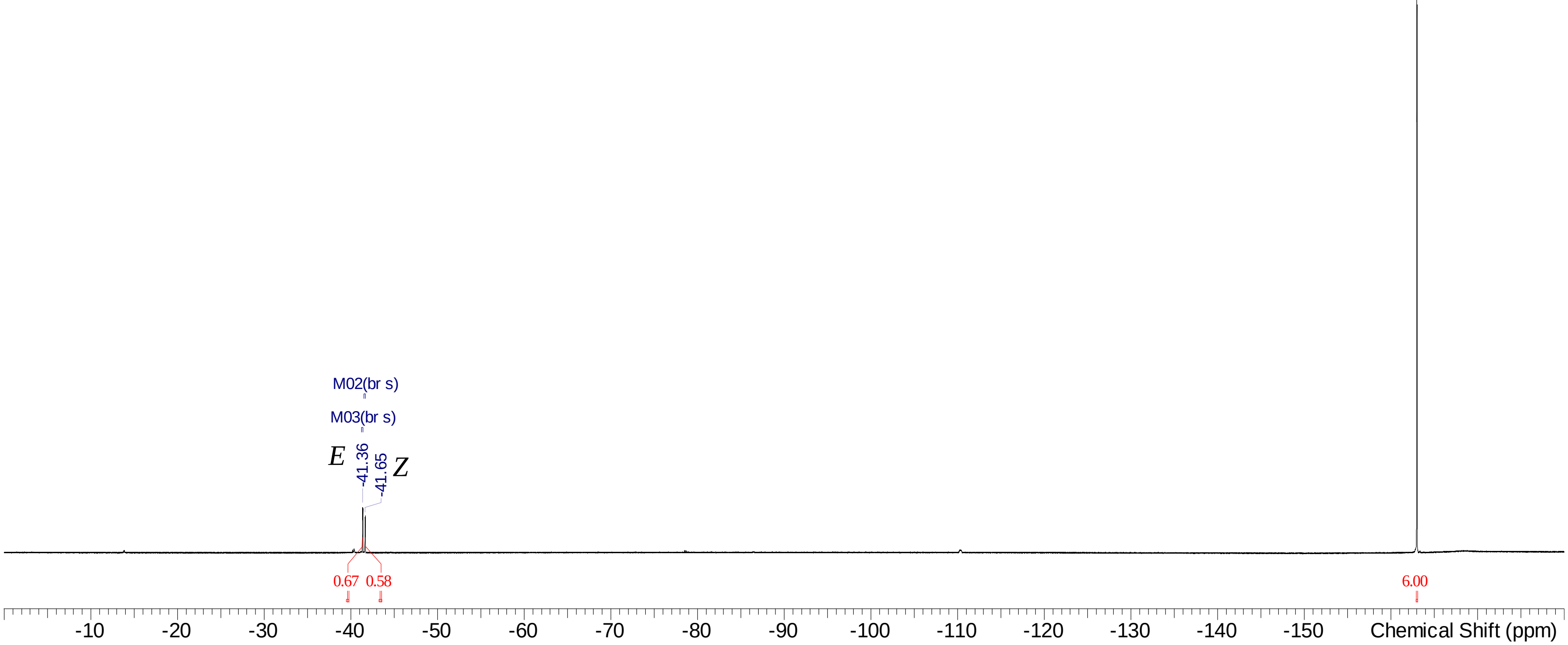
[19]F NMR (471 MHz)
DMSO-d_6



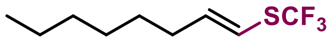
5-(2-((Trifluoromethyl)thio)vinyl)isothiazole (3ag)



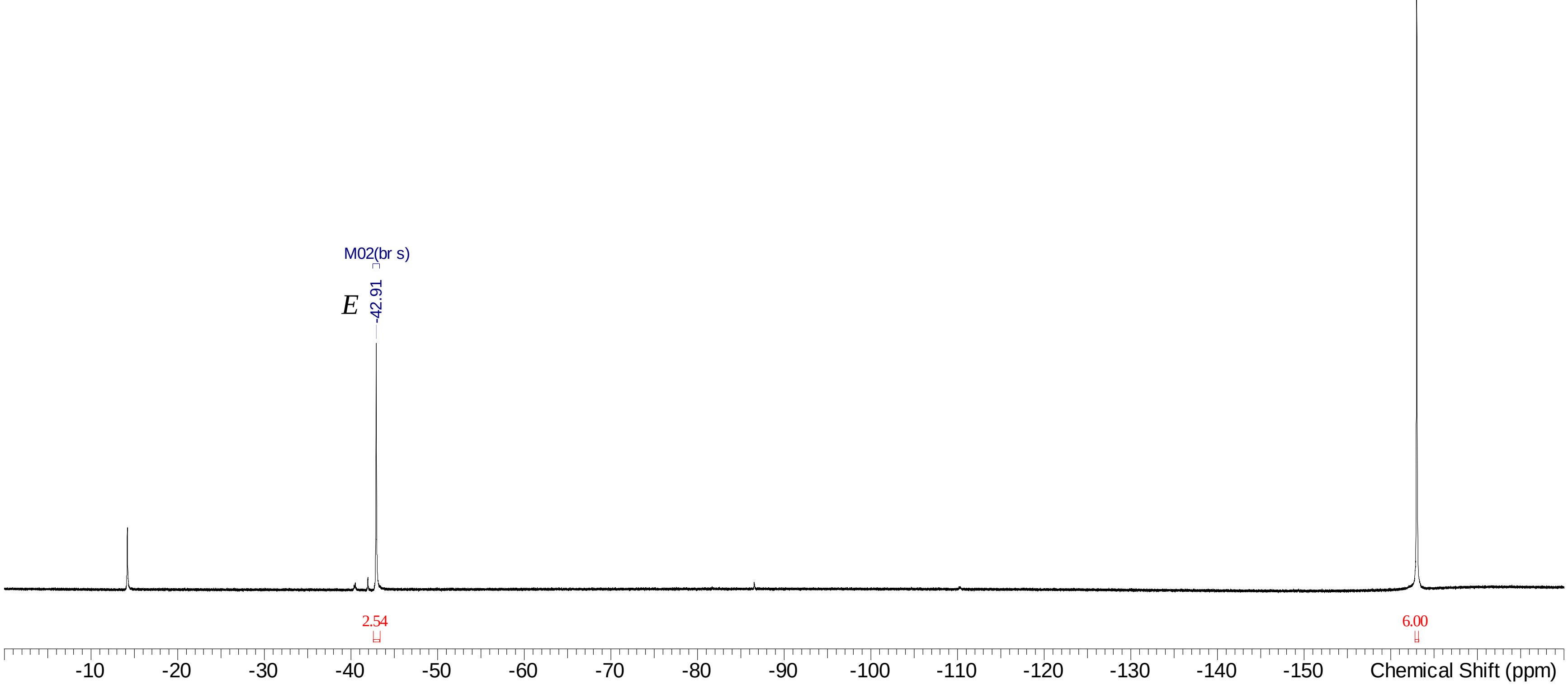
^{19}F NMR (471 MHz)
DMSO-d_6



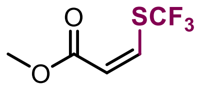
(*E*)-Oct-1-en-1-yl(trifluoromethyl)sulfane (3ah)



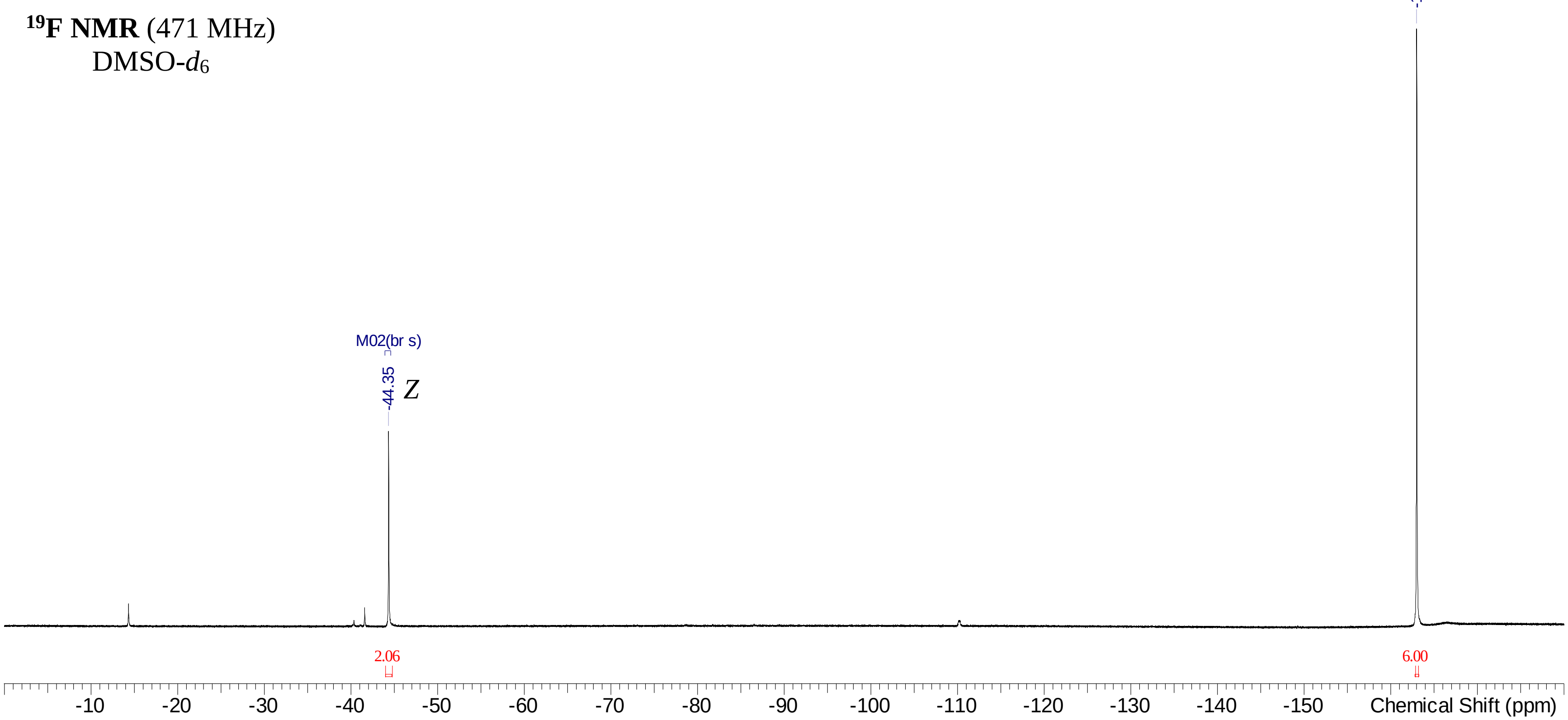
^{19}F NMR (471 MHz)
DMSO-d_6



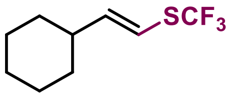
Methyl (*Z*)-3-((trifluoromethyl)thio)acrylate (3ai)



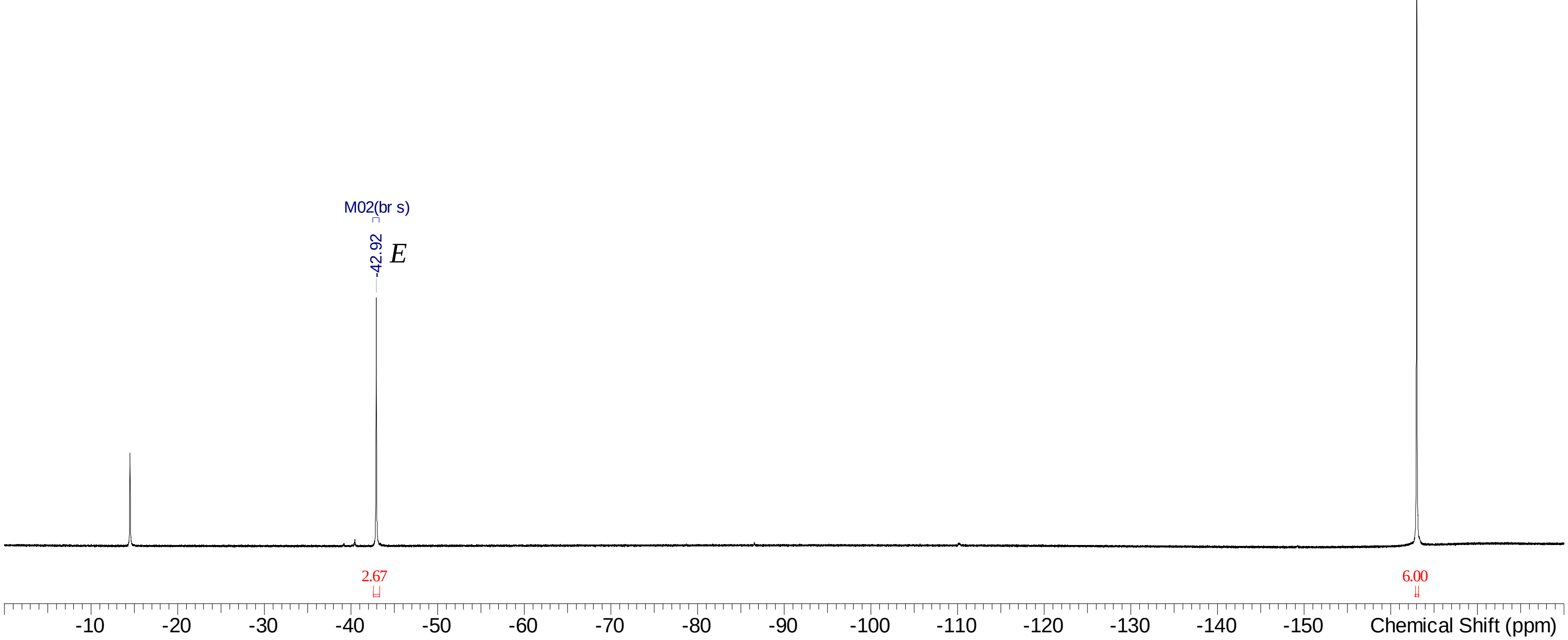
[19]F NMR (471 MHz)
DMSO-d_6



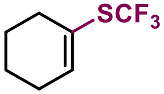
(*E*)-(2-Cyclohexylvinyl)(trifluoromethyl)sulfane (3aj)



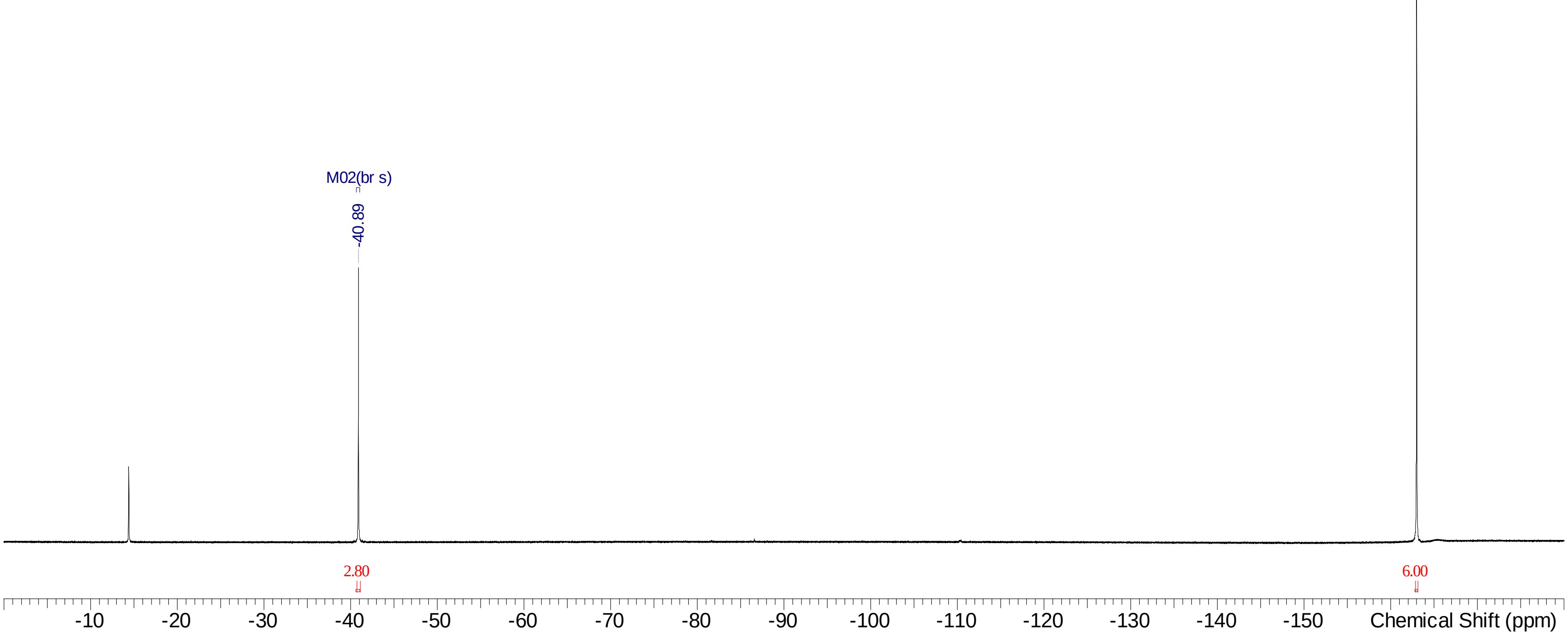
^{19}F NMR (471 MHz)
DMSO-d_6



Cyclohex-1-en-1-yl(trifluoromethyl)sulfane (3ak)

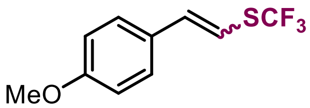


[19]F NMR (471 MHz)
DMSO-d_6

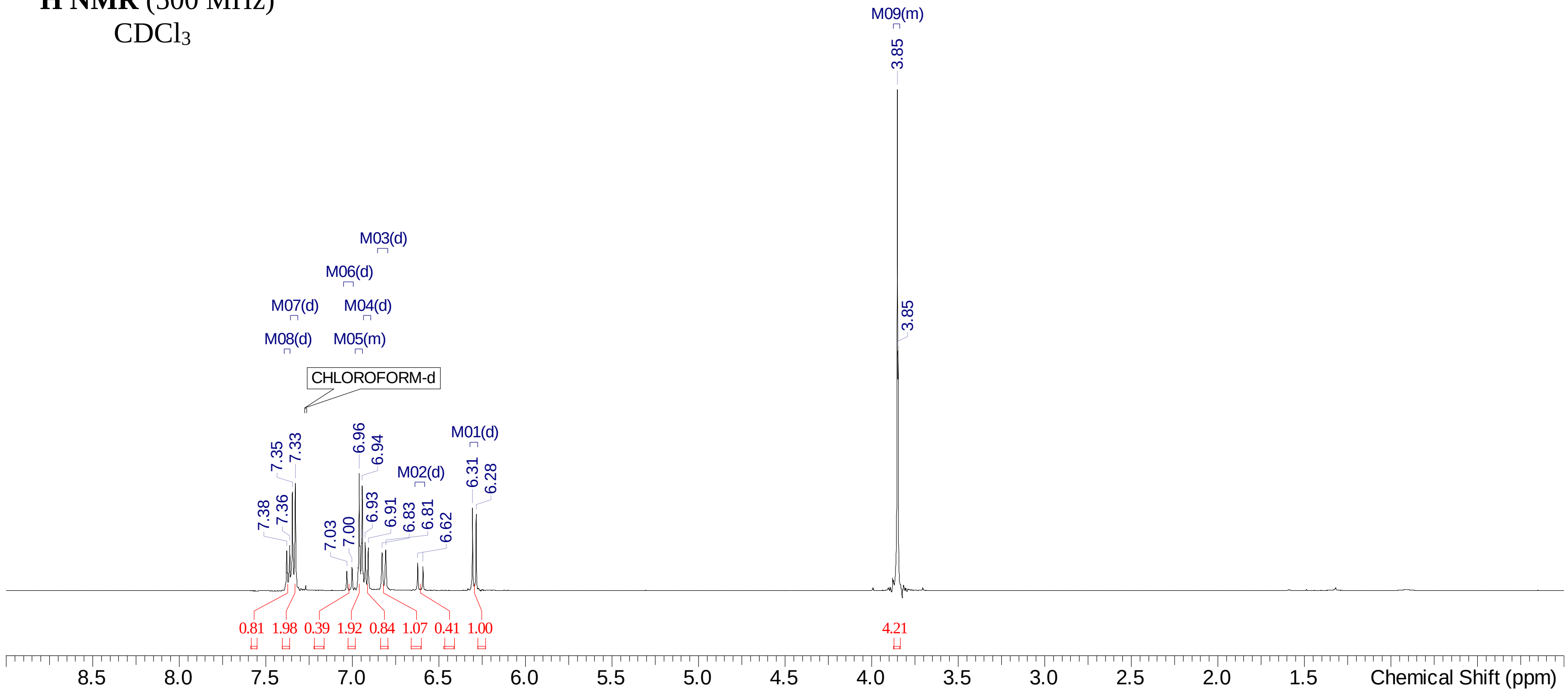


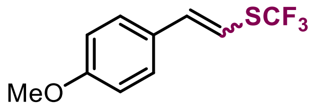
Alkenyl Trifluoromethylthioether Products

(4-Methoxystyryl)(trifluoromethyl)sulfane (3c)

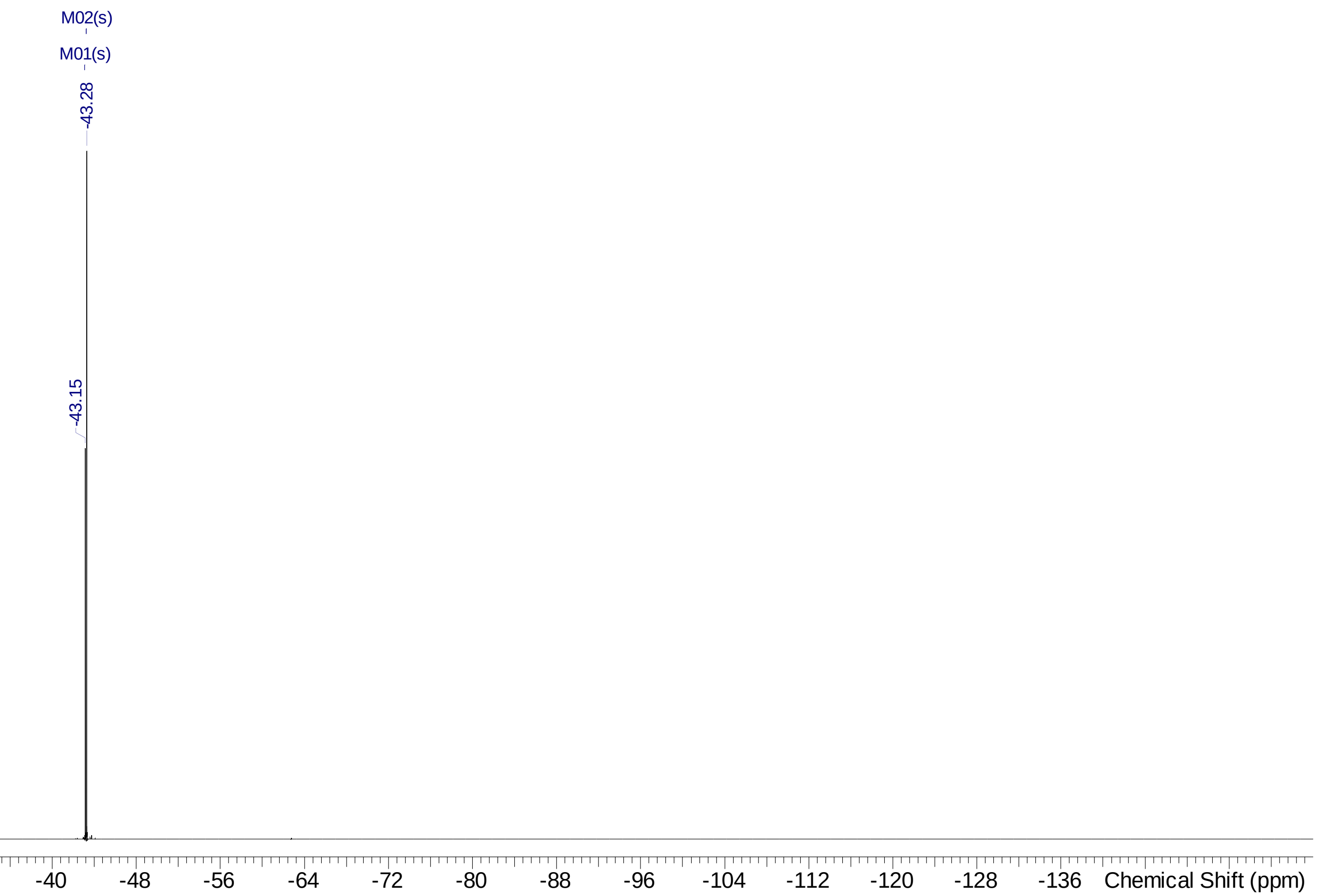


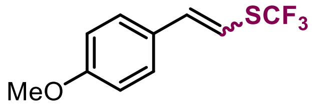
¹H NMR (500 MHz)
$CDCl_3$



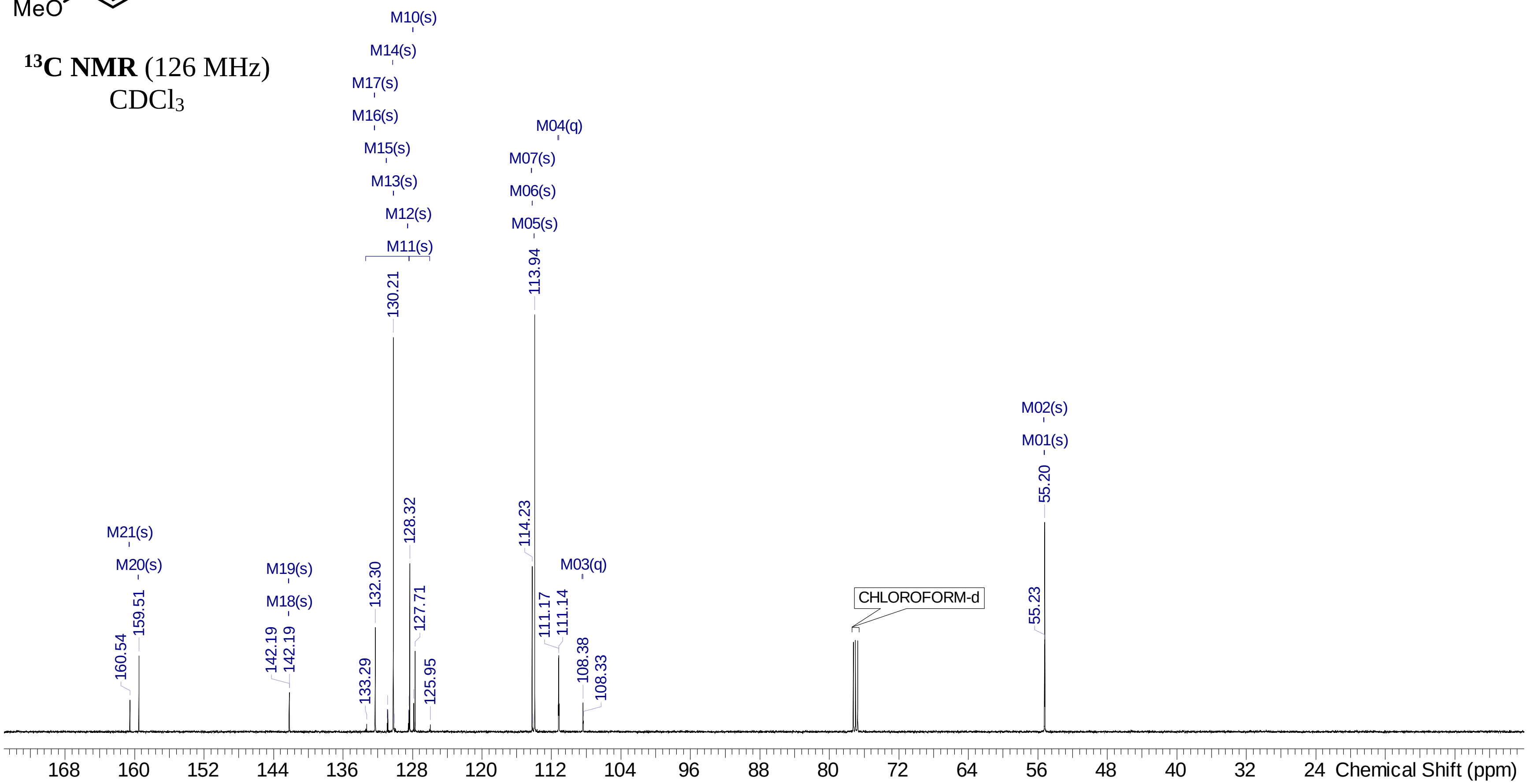


[19]F NMR (471 MHz)
$CDCl_3$

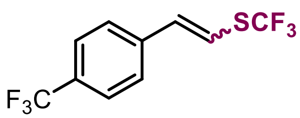




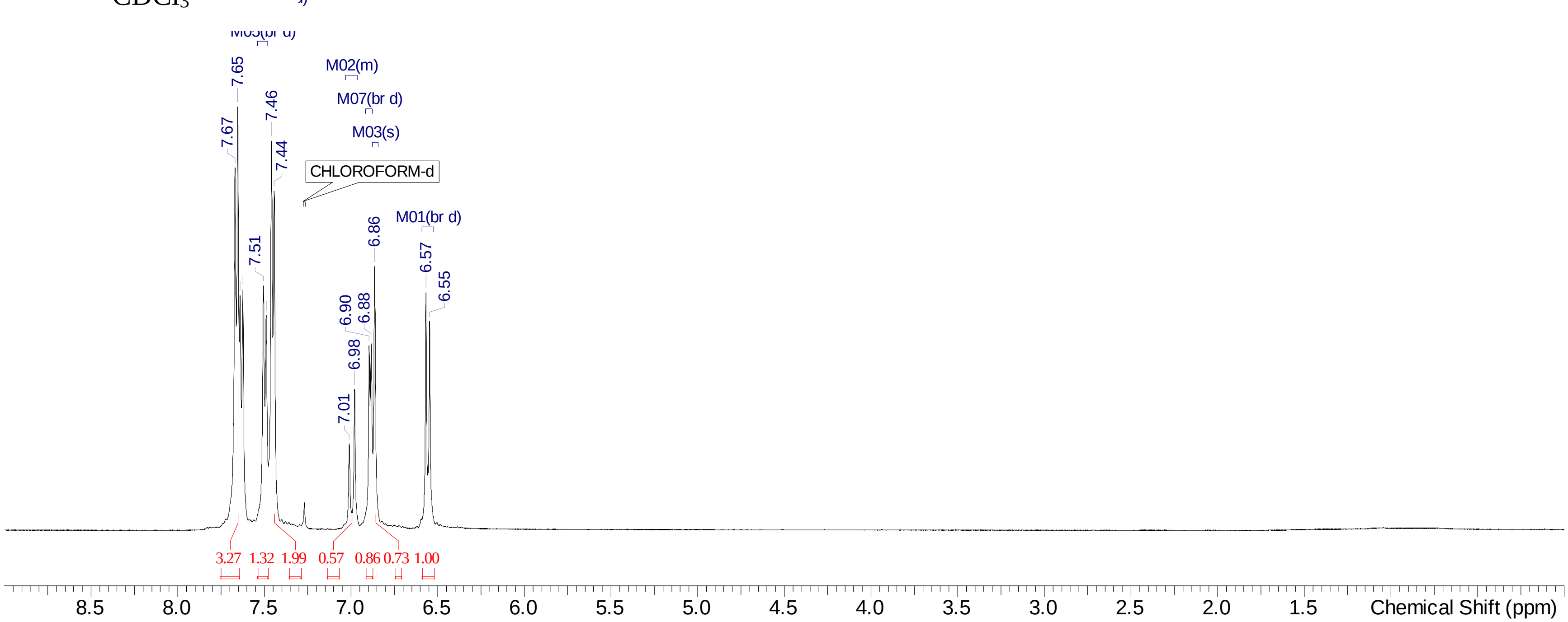
^{13}C **NMR** (126 MHz)
$CDCl_3$

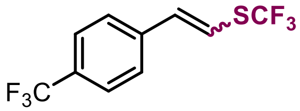


(Trifluoromethyl)(4-(trifluoromethyl)styryl)sulfane (3d)

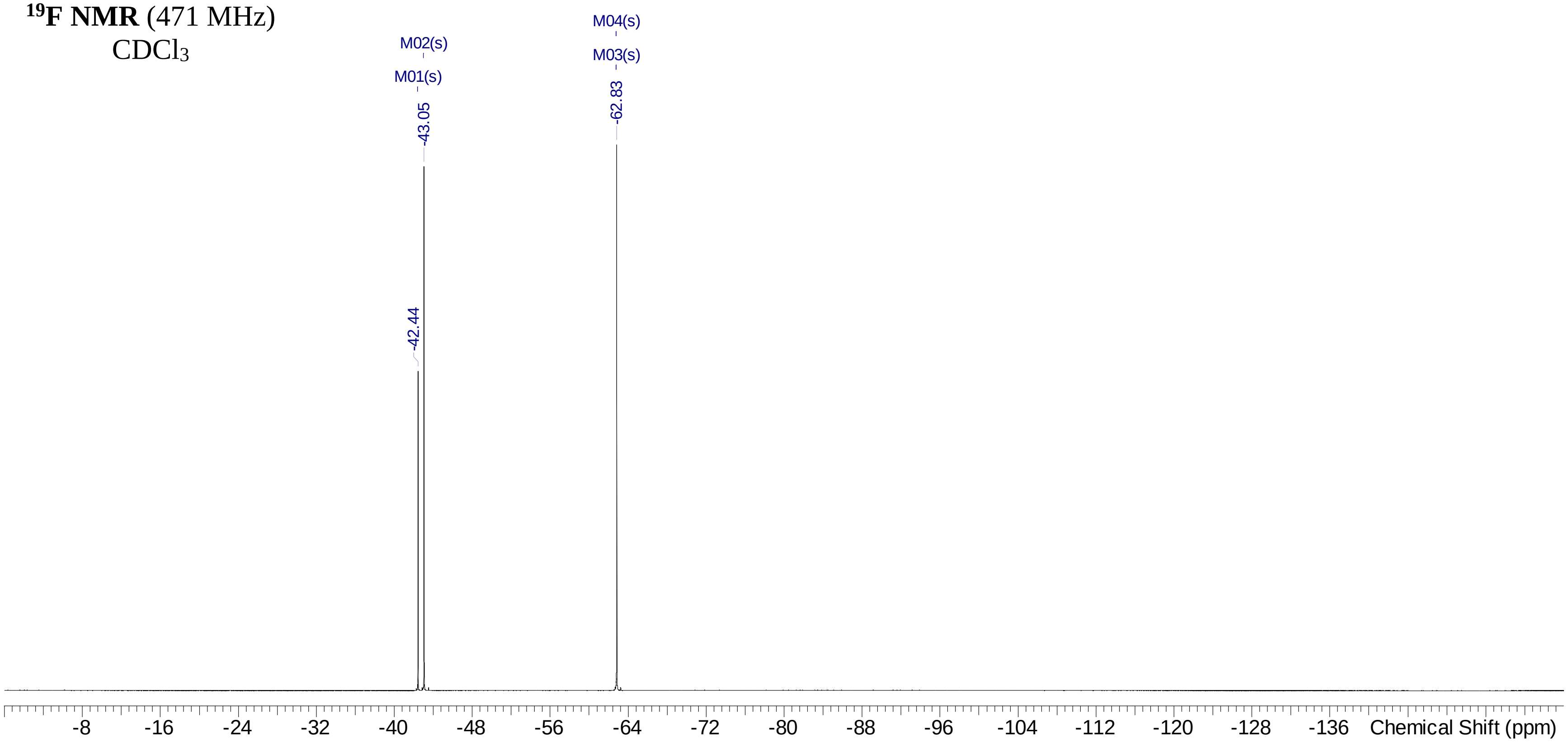


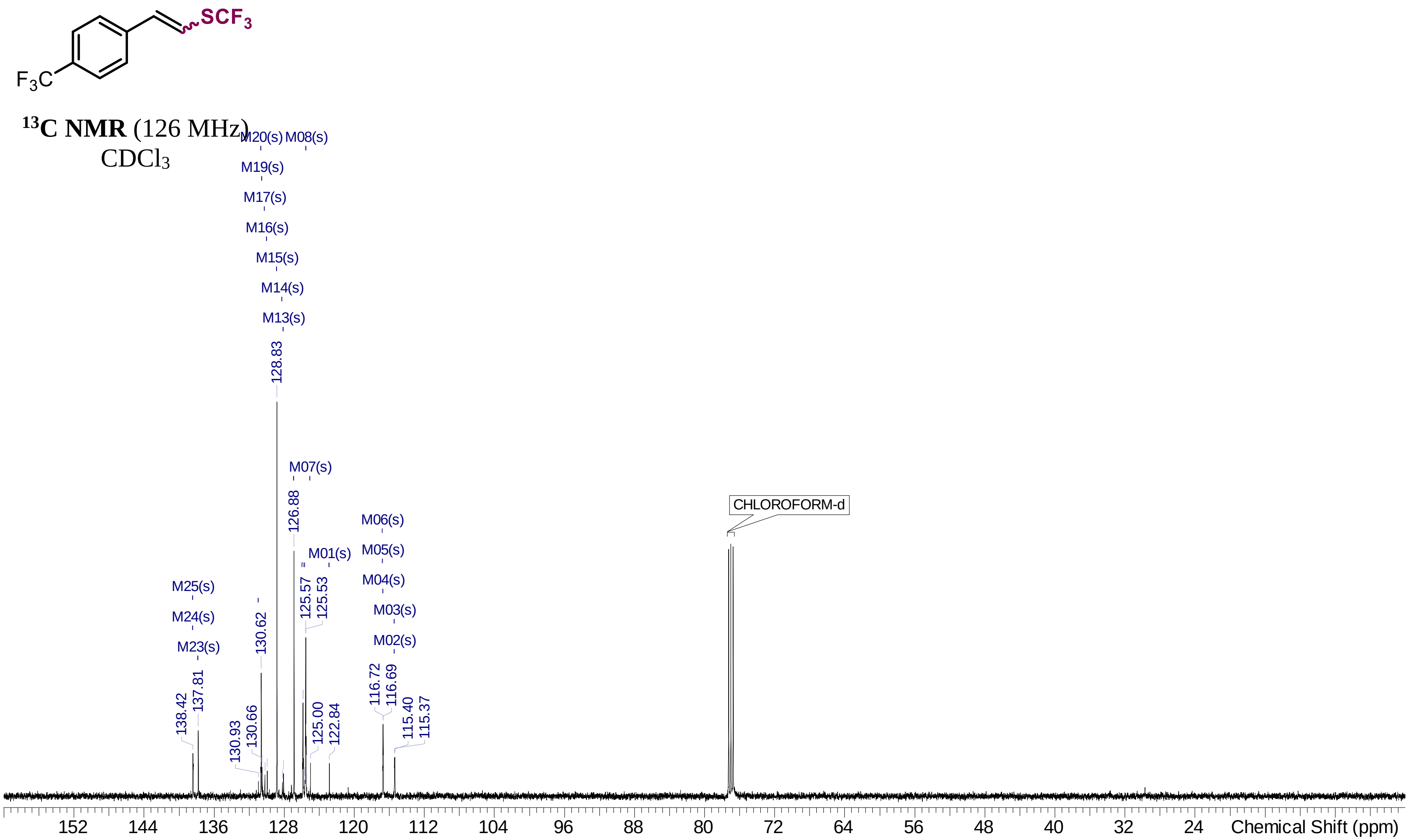
^{1}H NMR (500 MHz)
CDCl$_3$



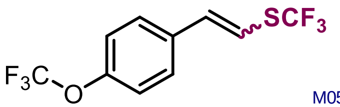


^{19}F NMR (471 MHz)
$CDCl_3$

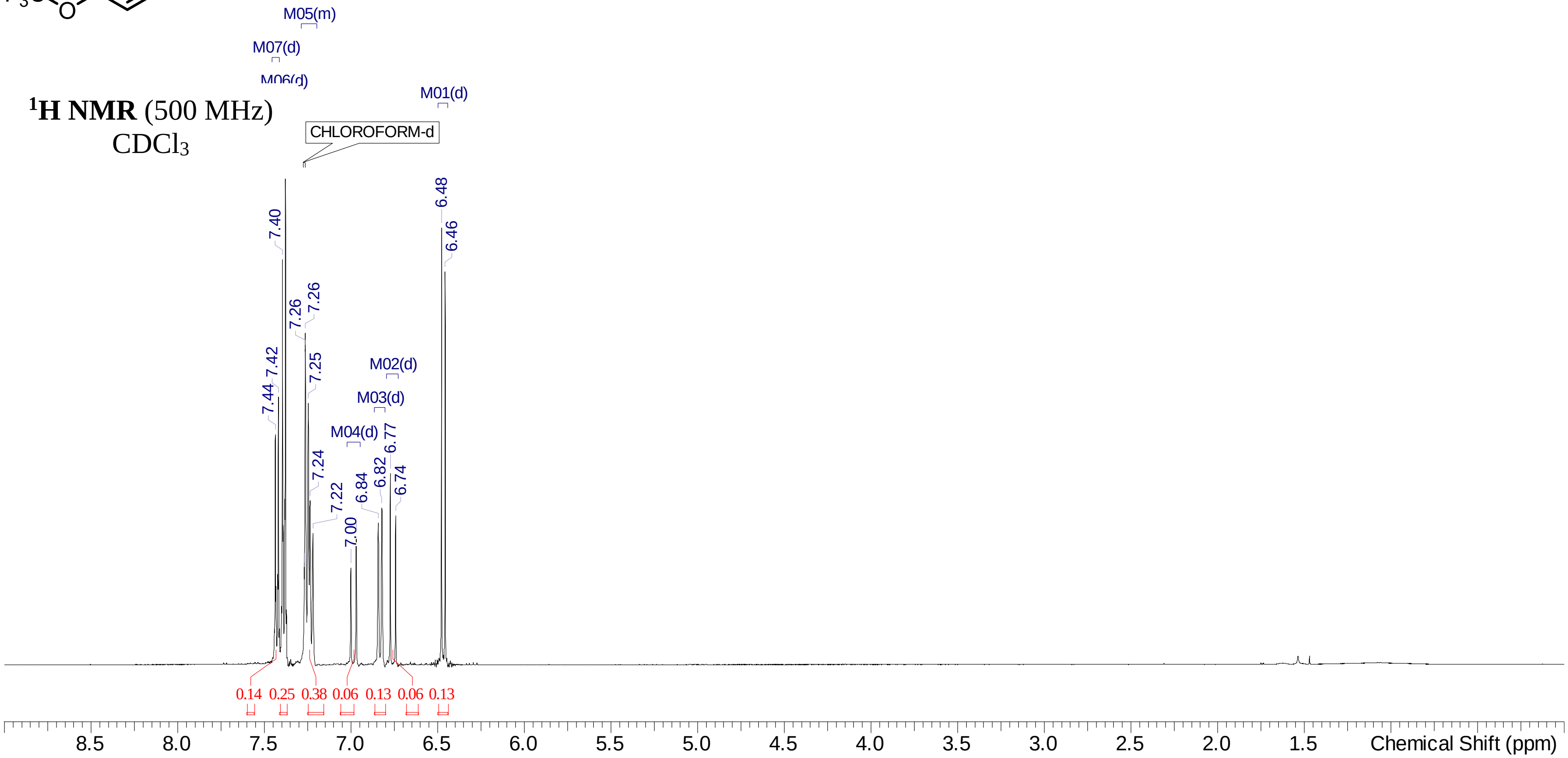


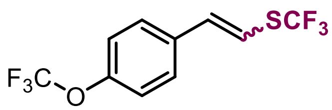

SCF3
F3C
13C NMR (126 MHz)
CDCl3
M20(s) M08(s)
M19(s)
M17(s)
M16(s)
M15(s)
M14(s)
M13(s)
128.83
M07(s)
126.88
M01(s)
125.57
125.53
M06(s)
M05(s)
M04(s)
M03(s)
M02(s)
M25(s)
M24(s)
M23(s)
130.62
138.42
137.81
130.93
130.66
125.00
122.84
116.72
116.69
115.40
115.37
CHLOROFORM-d
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

(4-(trifluoromethoxy)styryl)(trifluoromethyl)sulfane (3e)

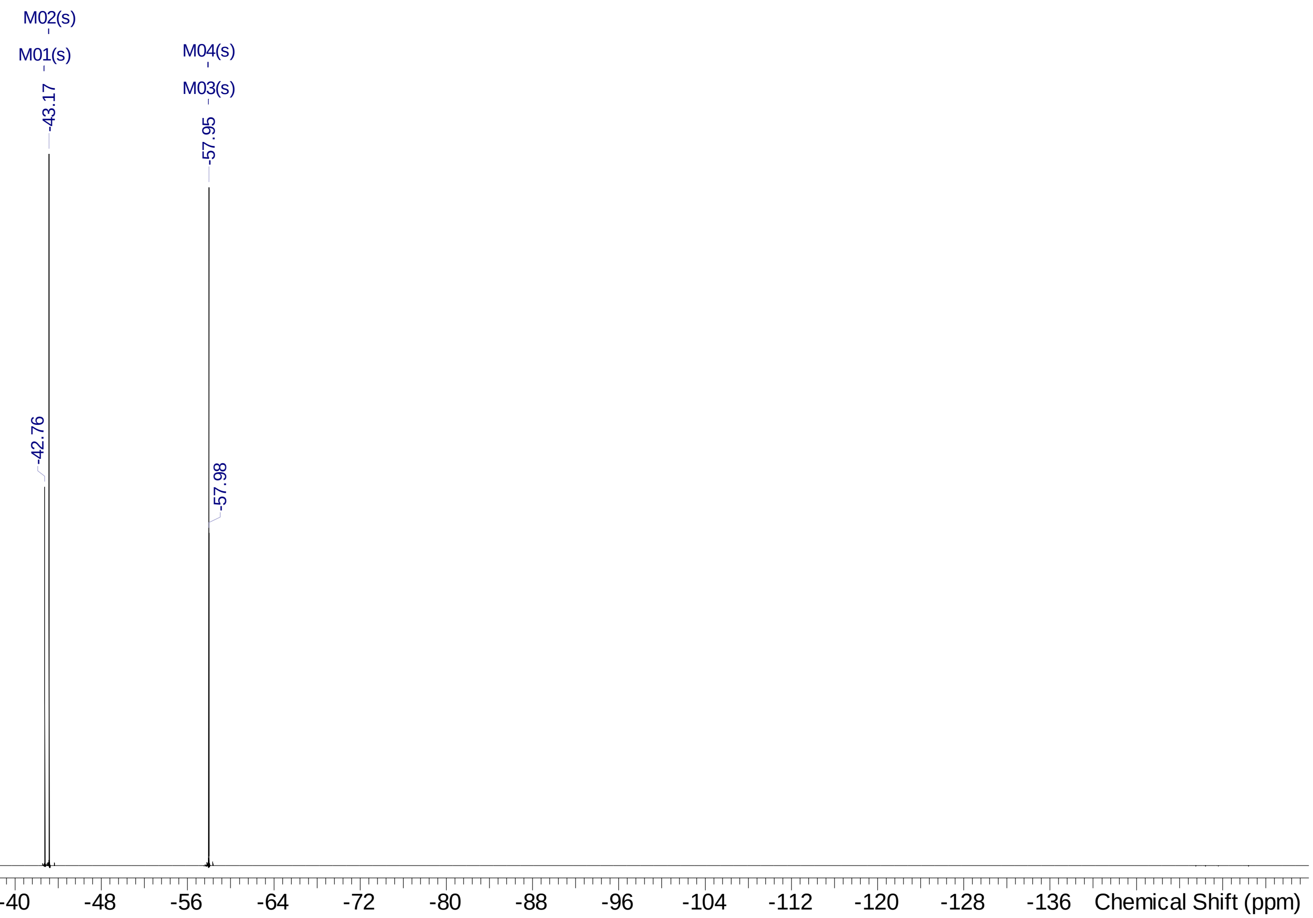


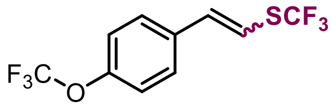
^{1}H NMR (500 MHz)
$CDCl_3$



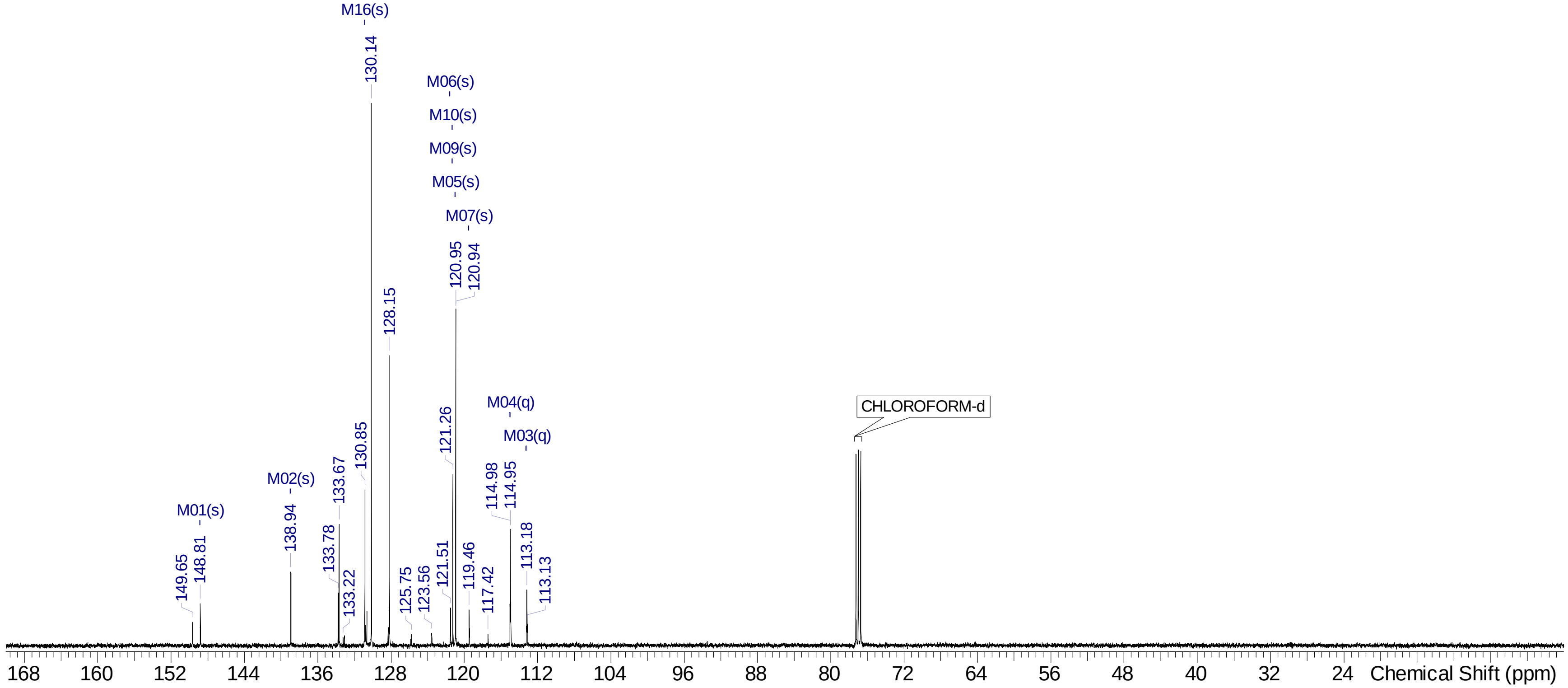


^{19}F NMR (471 MHz)
$CDCl_3$

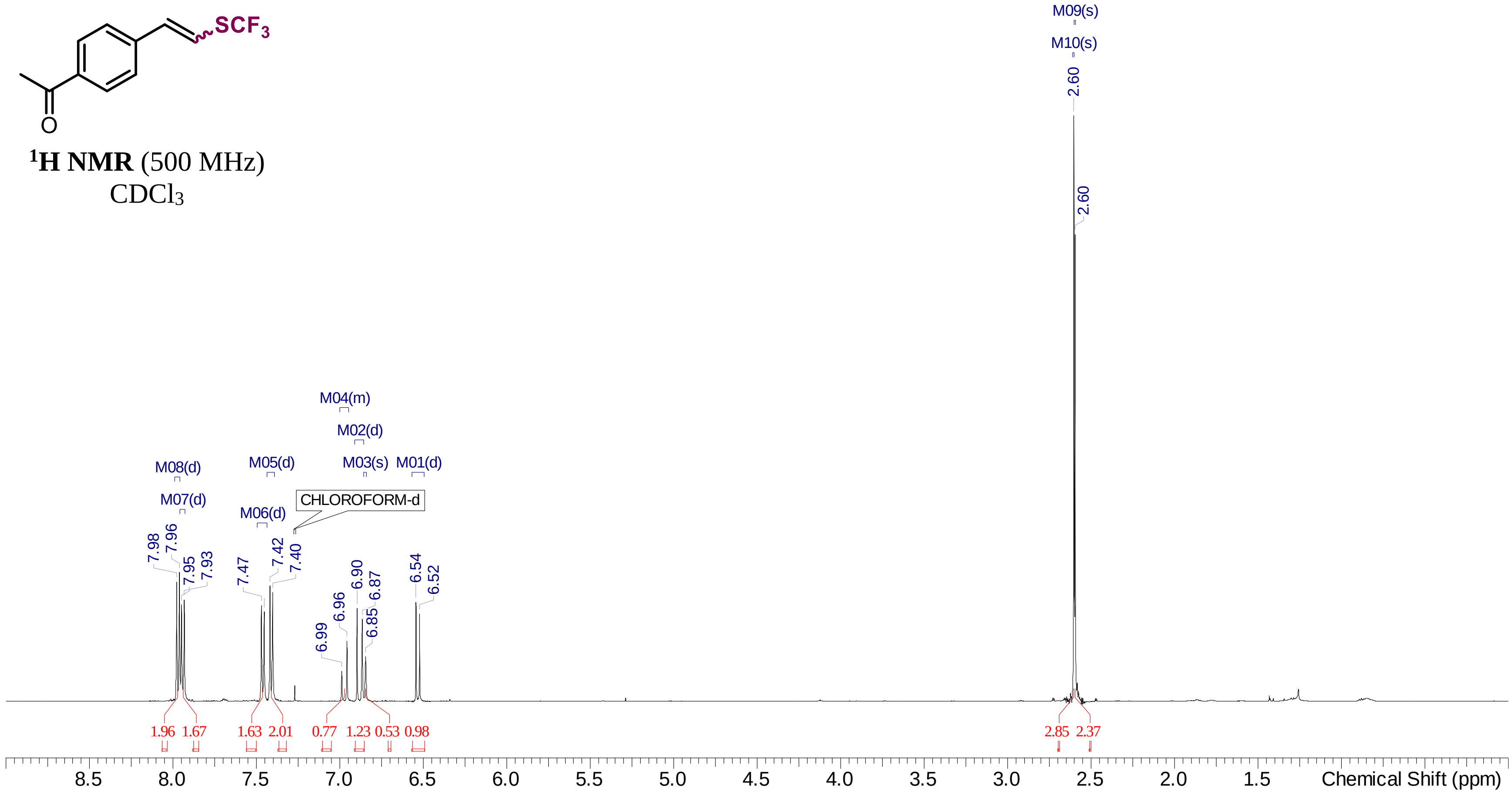


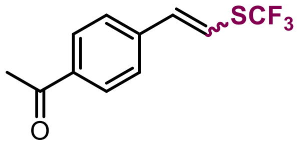


^{13}C NMR (126 MHz)
$CDCl_3$

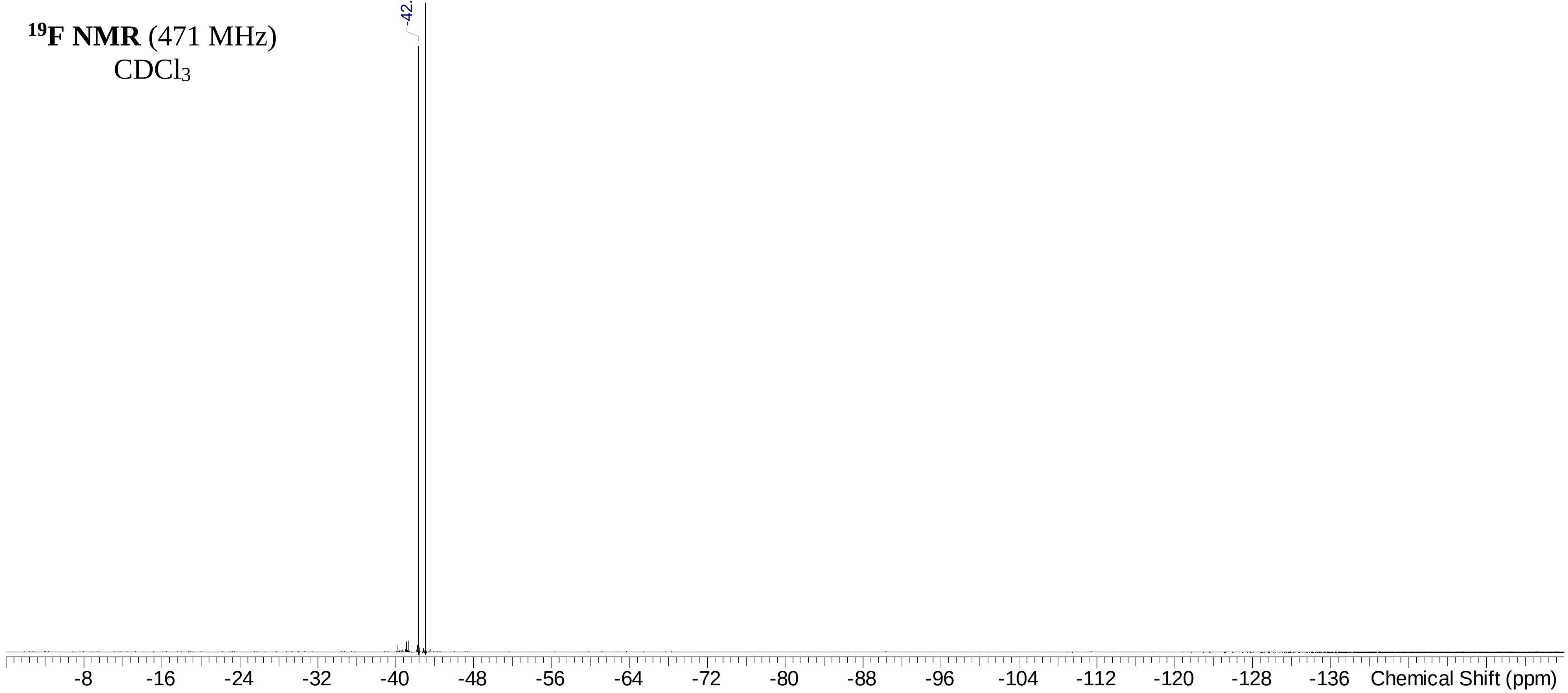


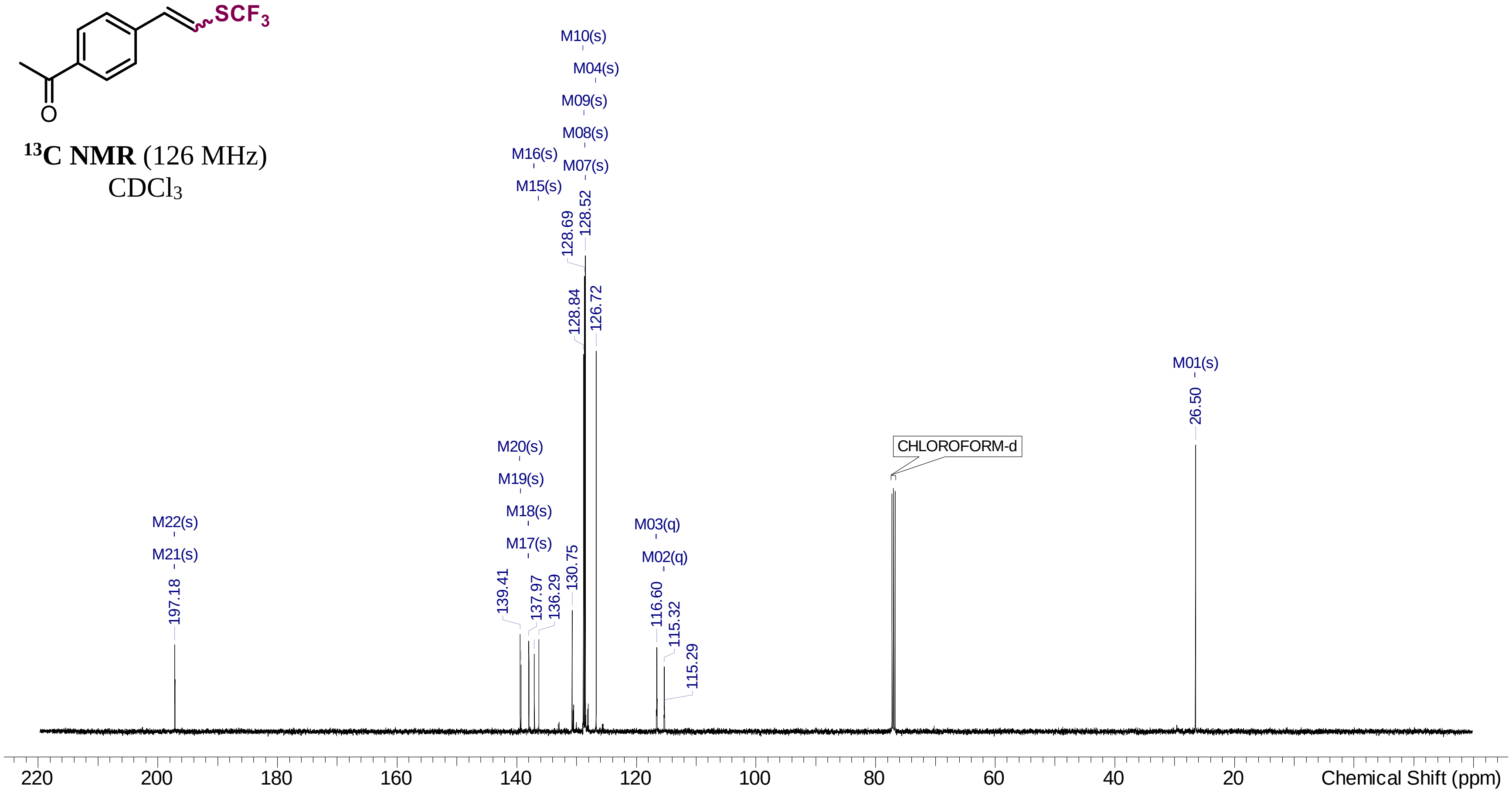
1-(4-(2-((Trifluoromethyl)thio)vinyl)phenyl)ethan-1-one (3g)



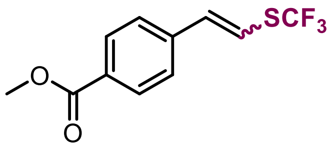


^{19}F NMR (471 MHz)
$CDCl_3$

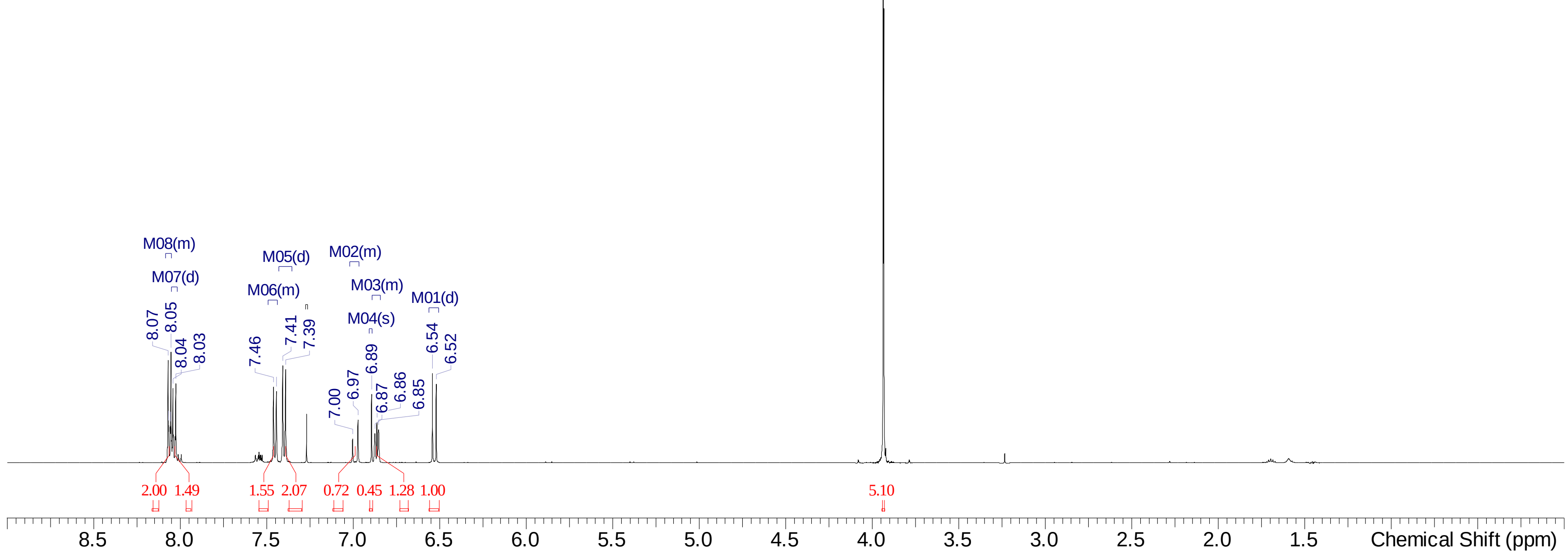


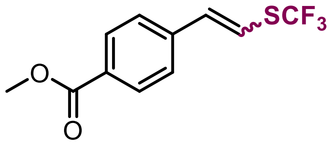

SCF3
O
13C NMR (126 MHz)
CDCl3
M10(s)
M04(s)
M09(s)
M08(s)
M16(s)
M07(s)
M15(s)
128.69
128.52
128.84
126.72
M01(s)
26.50
CHLOROFORM-d
M20(s)
M19(s)
M18(s)
M22(s)
M17(s)
M03(q)
M21(s)
M02(q)
130.75
197.18
139.41
137.97
136.29
116.60
115.32
115.29
220
200
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

Methyl 4-(2-((trifluoromethyl)thio)vinyl)benzoate (3f)

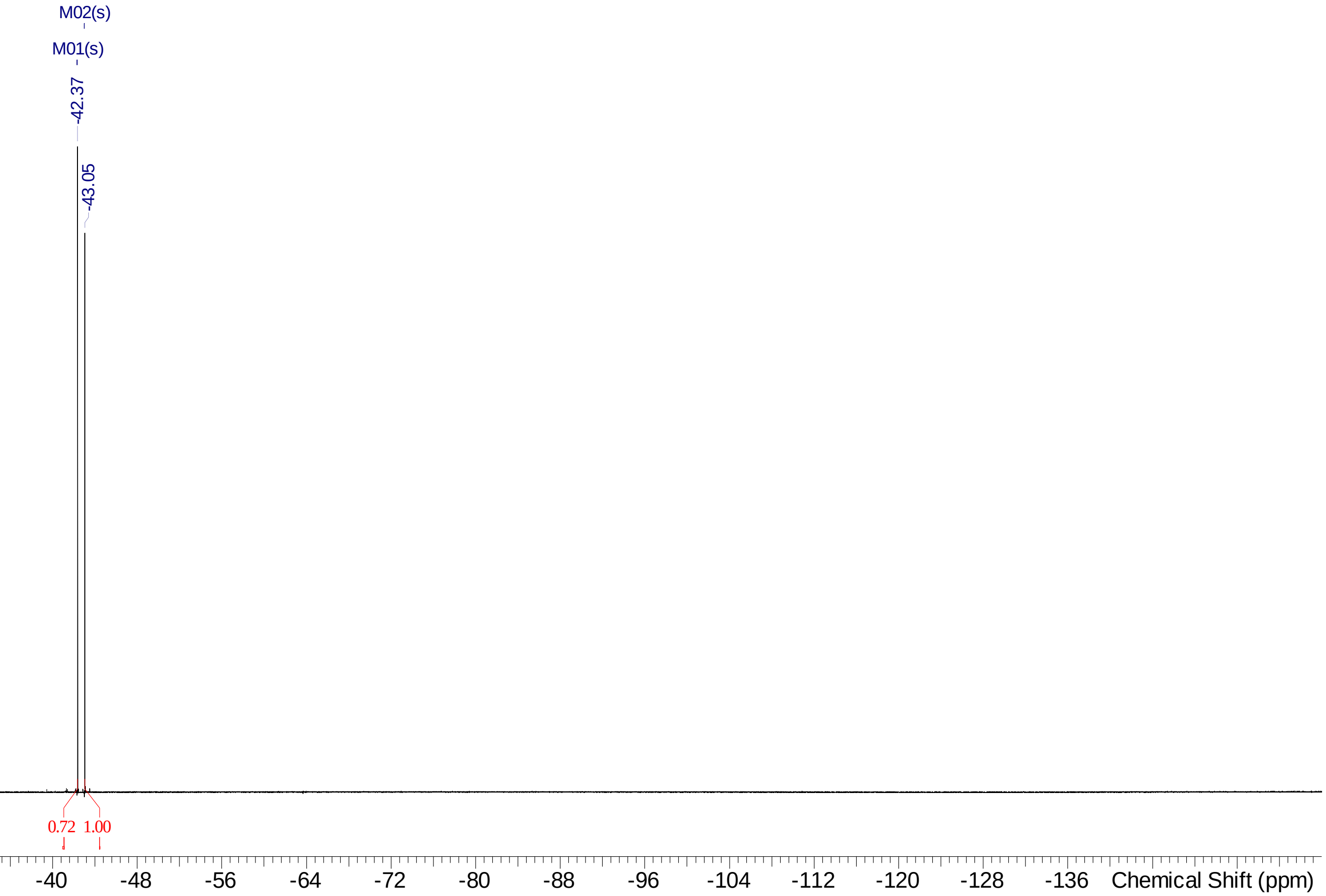


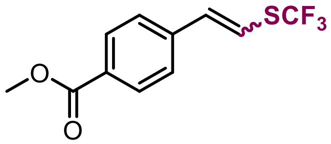
^{1}H NMR (500 MHz)
$CDCl_3$



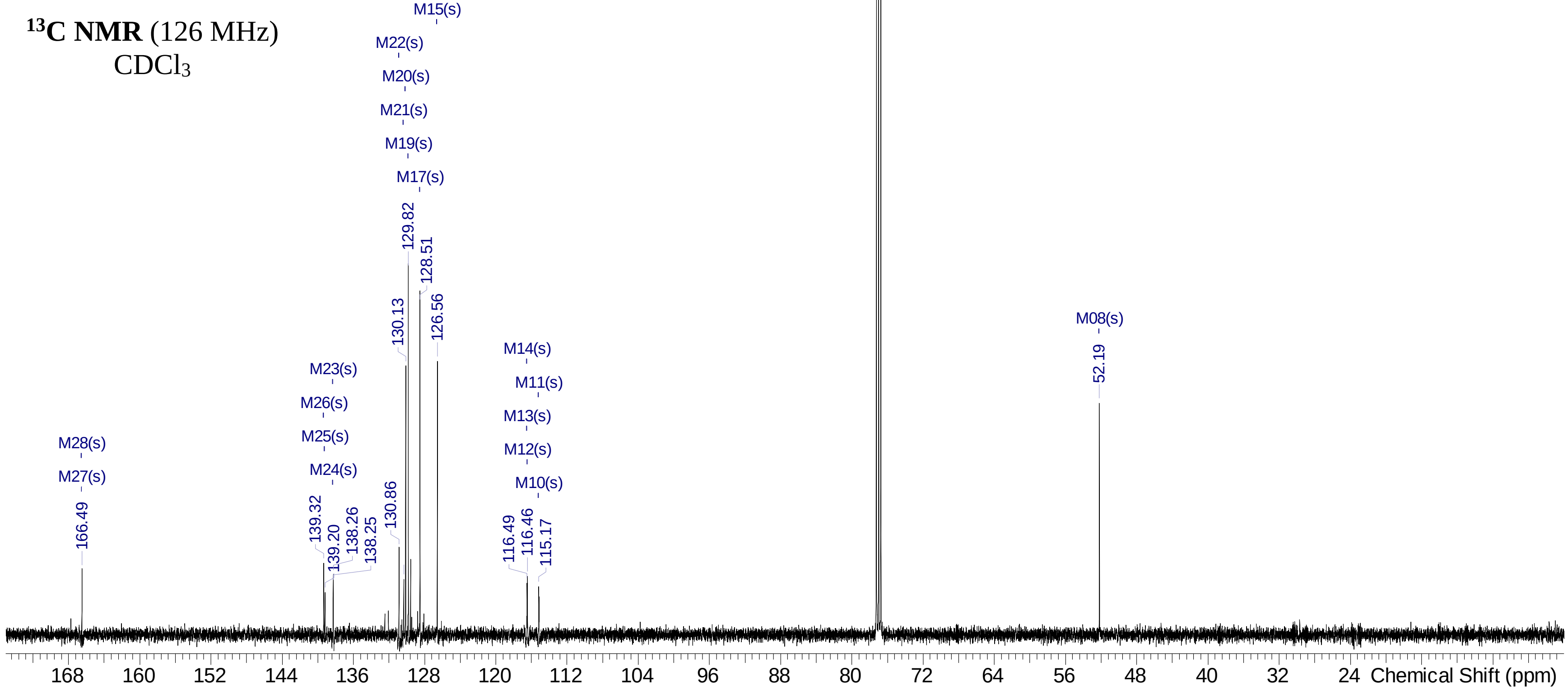


19F NMR (471 MHz)
$CDCl_3$

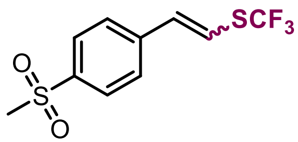




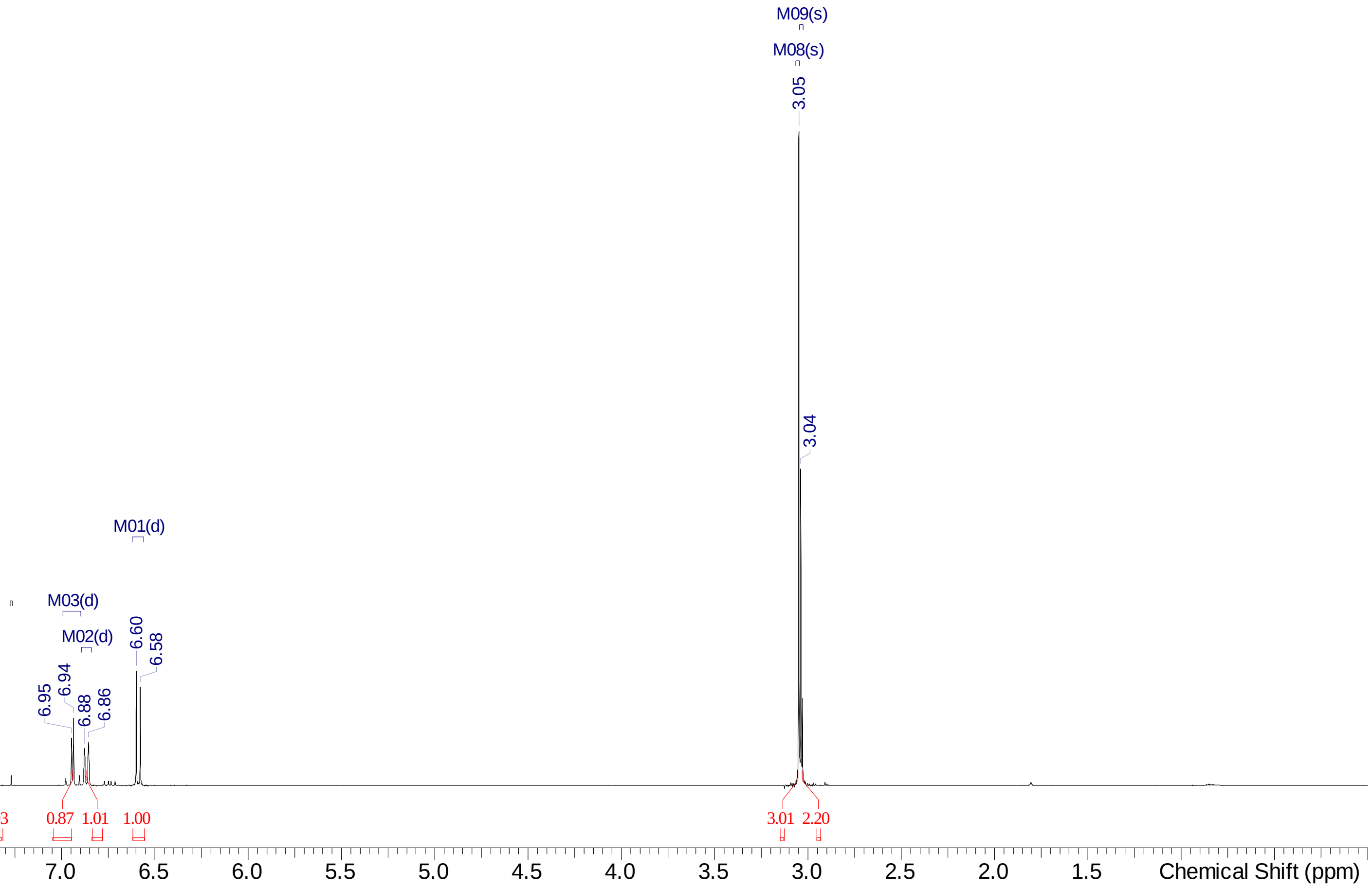
^{13}C NMR (126 MHz)
$CDCl_3$

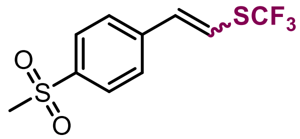


(4-(Methylsulfonyl)styryl)(trifluoromethyl)sulfane (3h)

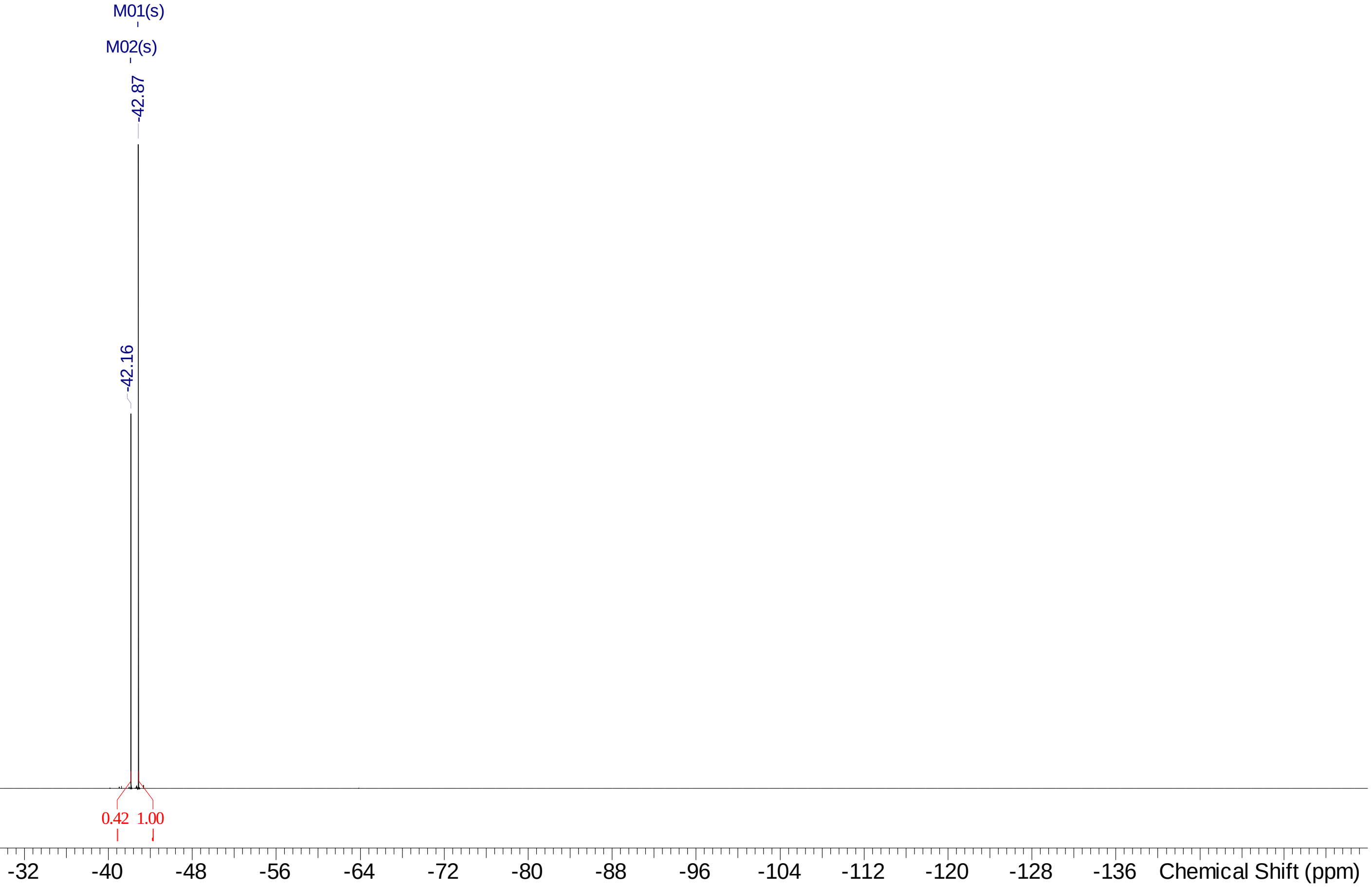


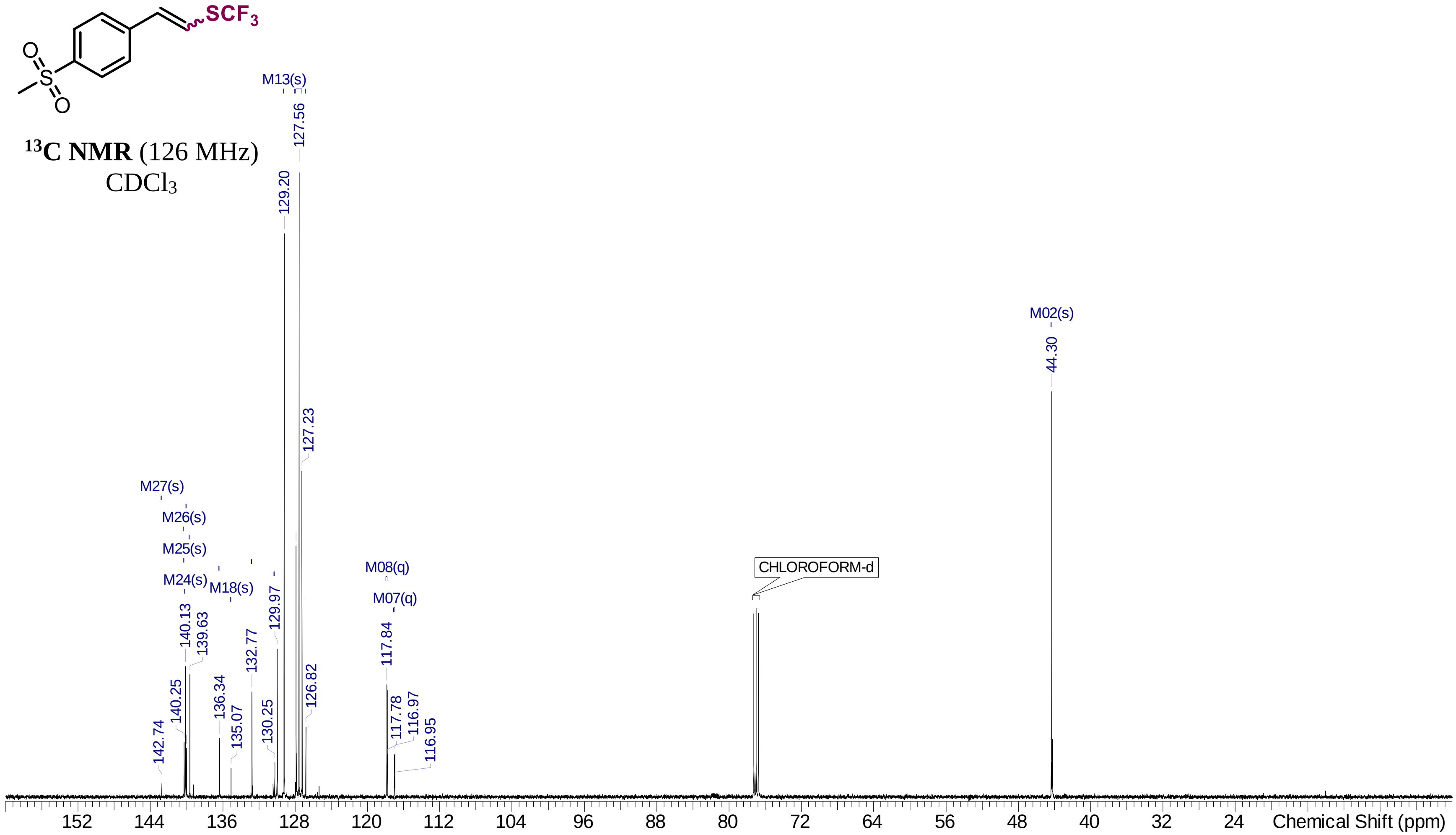
^{1}H NMR (500 MHz)
$CDCl_3$





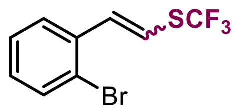
^{19}F NMR (471 MHz)
$CDCl_3$



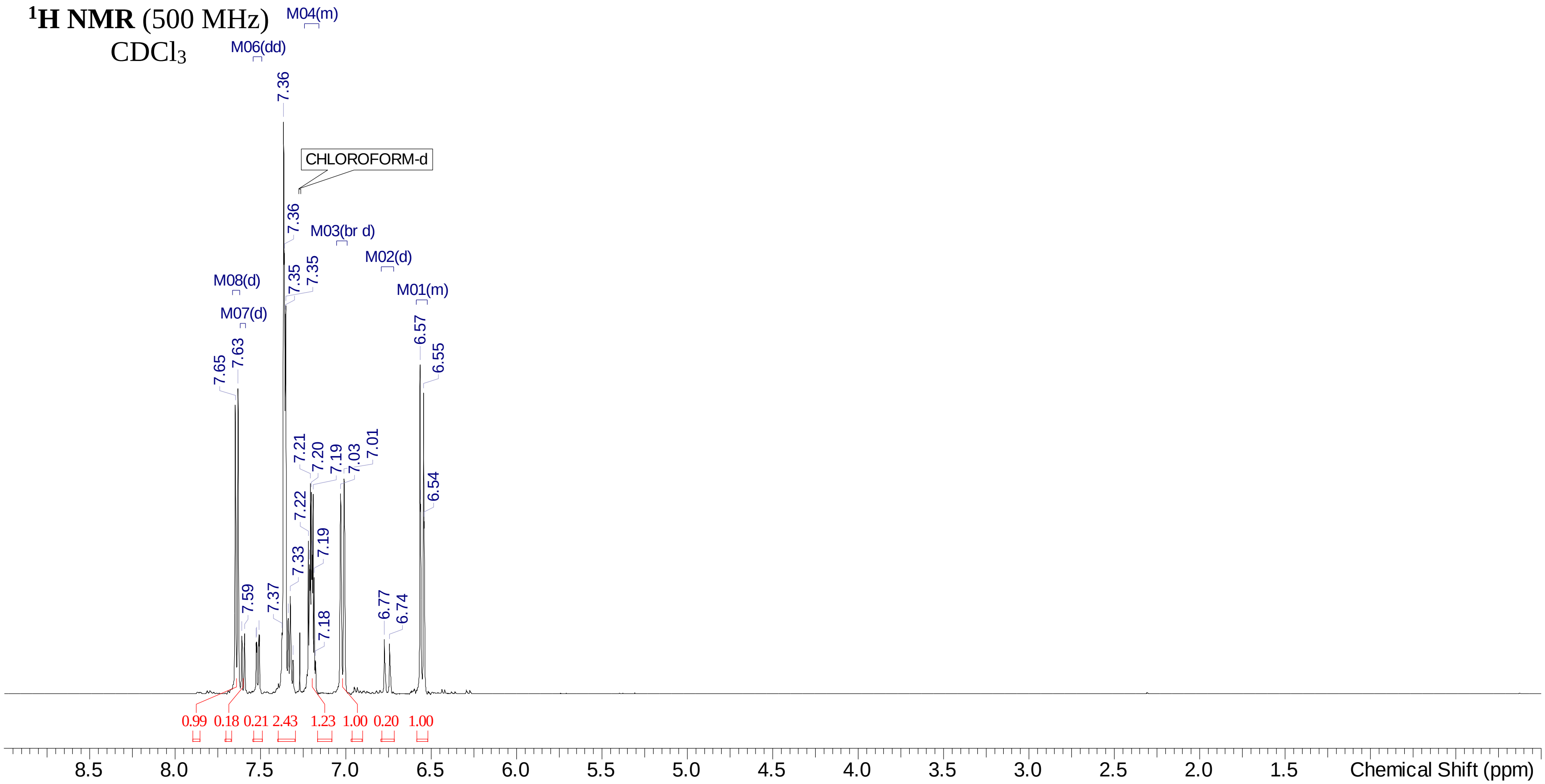


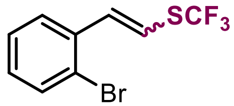
^{13}C NMR (126 MHz)
$CDCl_3$

(2-bromostyryl)(trifluoromethyl)sulfane (3j)

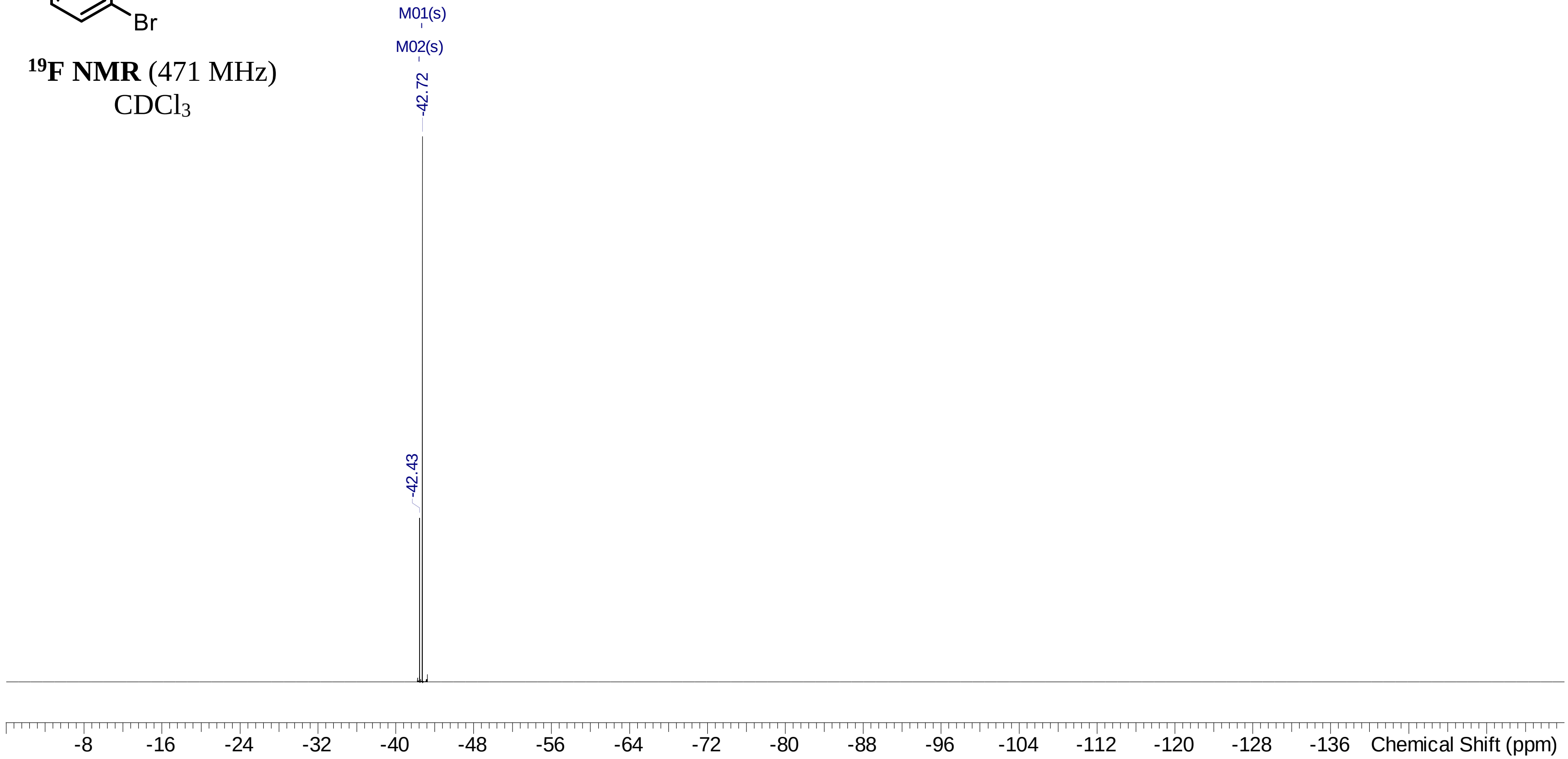


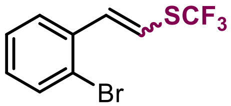
^{1}H NMR (500 MHz)
CDCl$_3$





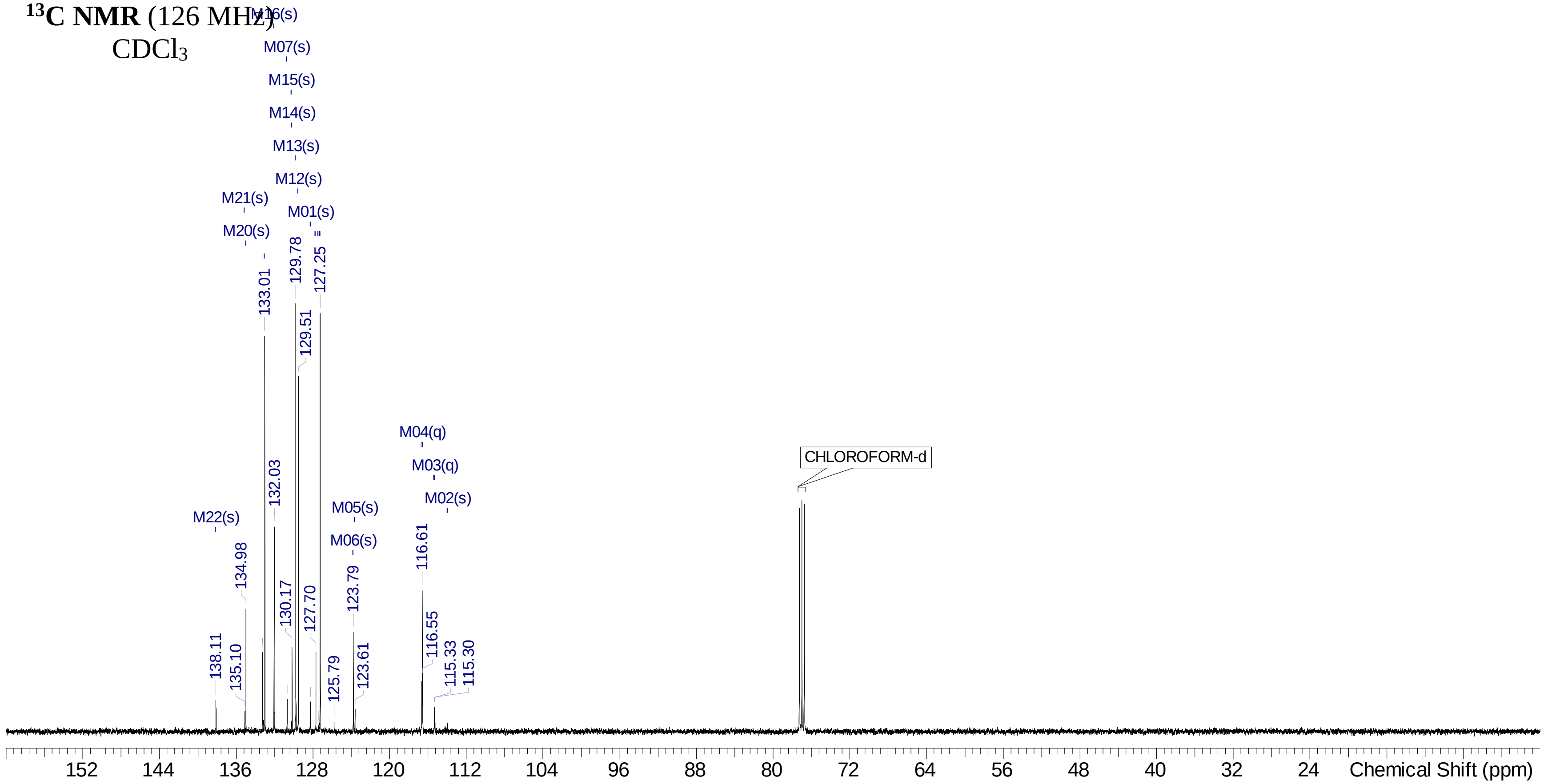
^{19}F NMR (471 MHz)
$CDCl_3$



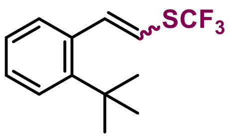


^{13}C NMR (126 MHz)

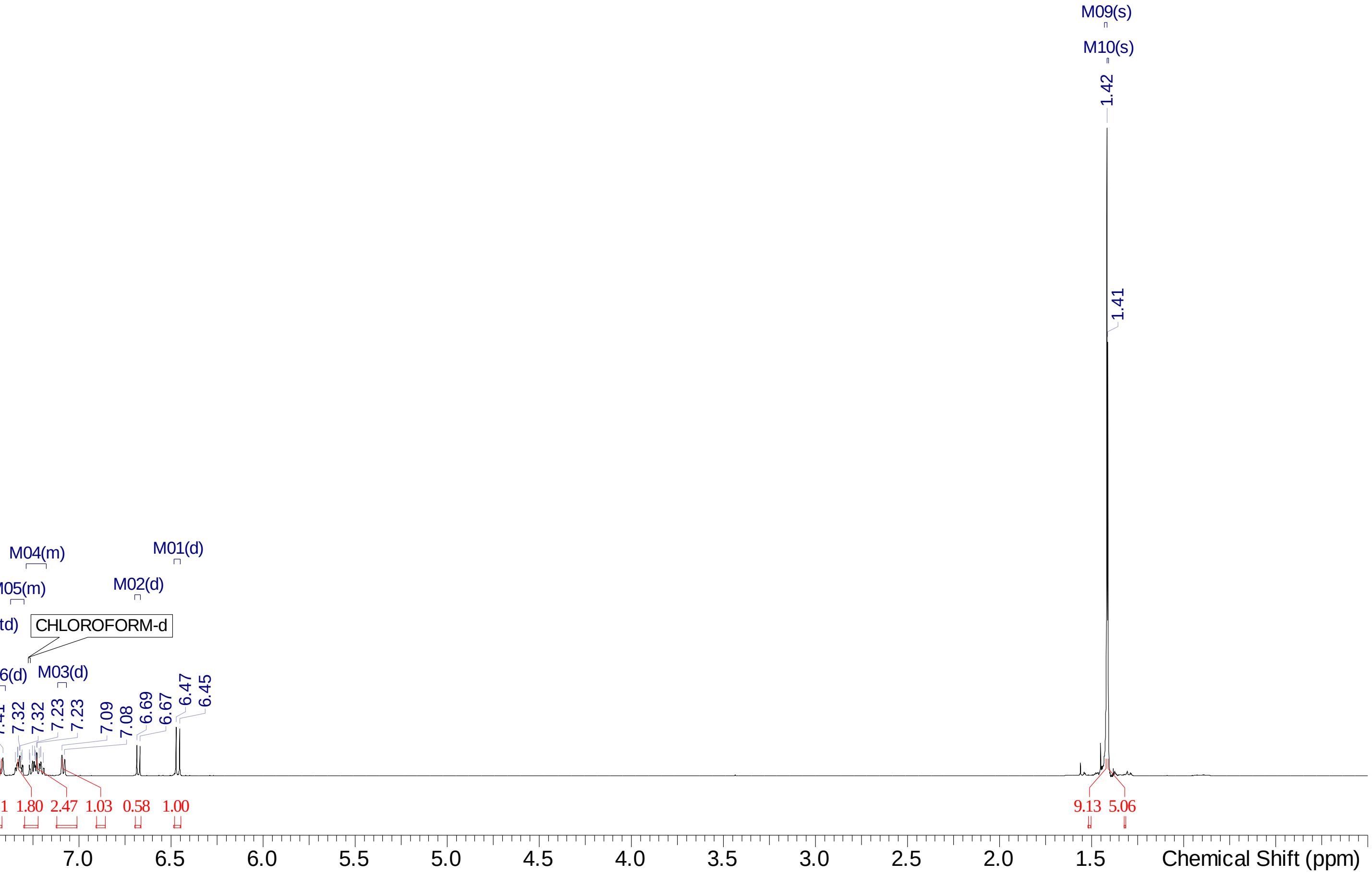
$CDCl_3$

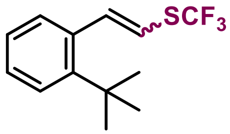


(2-(*Tert*-butyl)styryl)(trifluoromethyl)sulfane (3k)

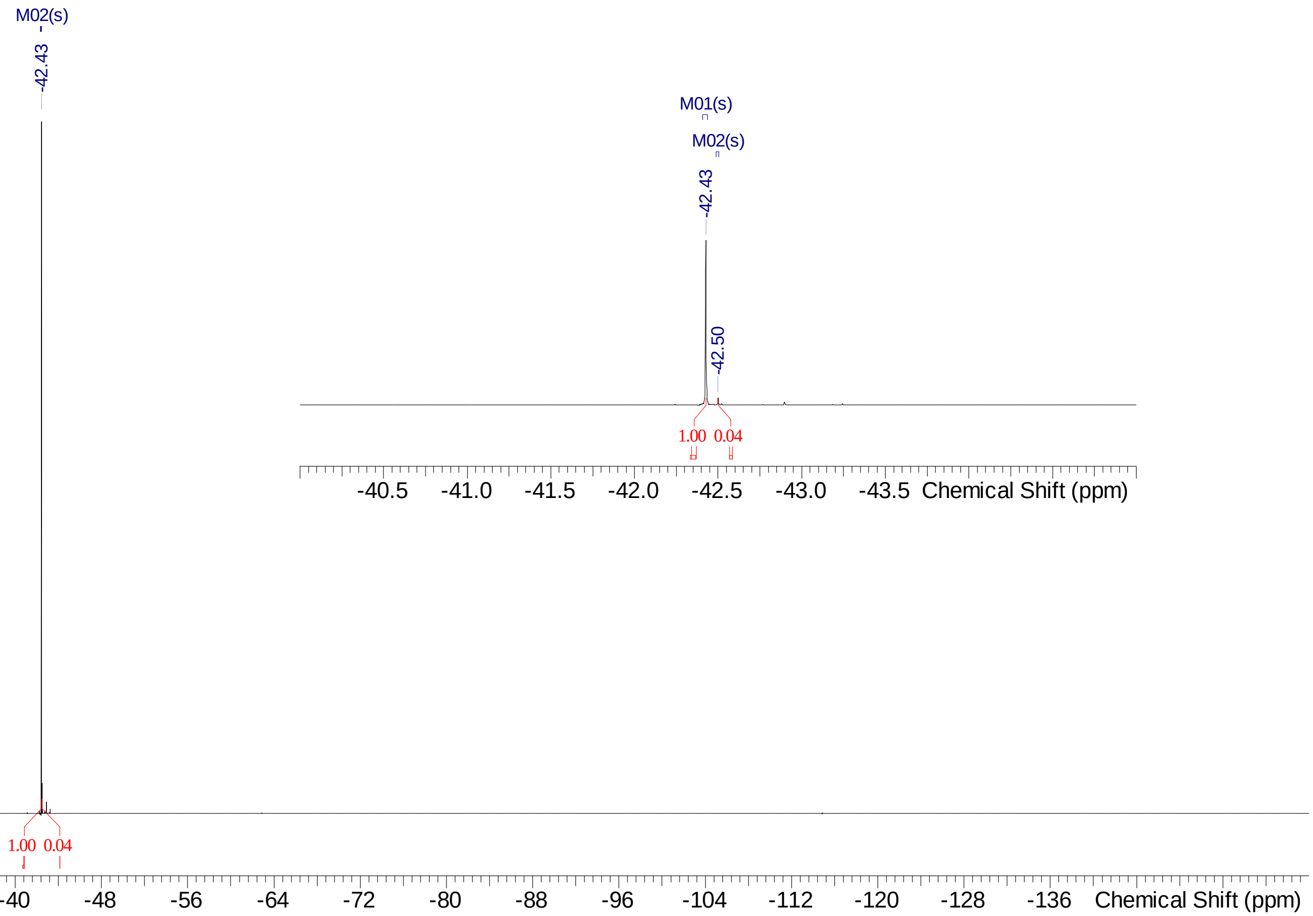


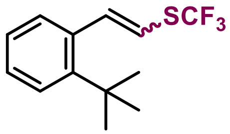
[1]H NMR (500 MHz)
$CDCl_3$



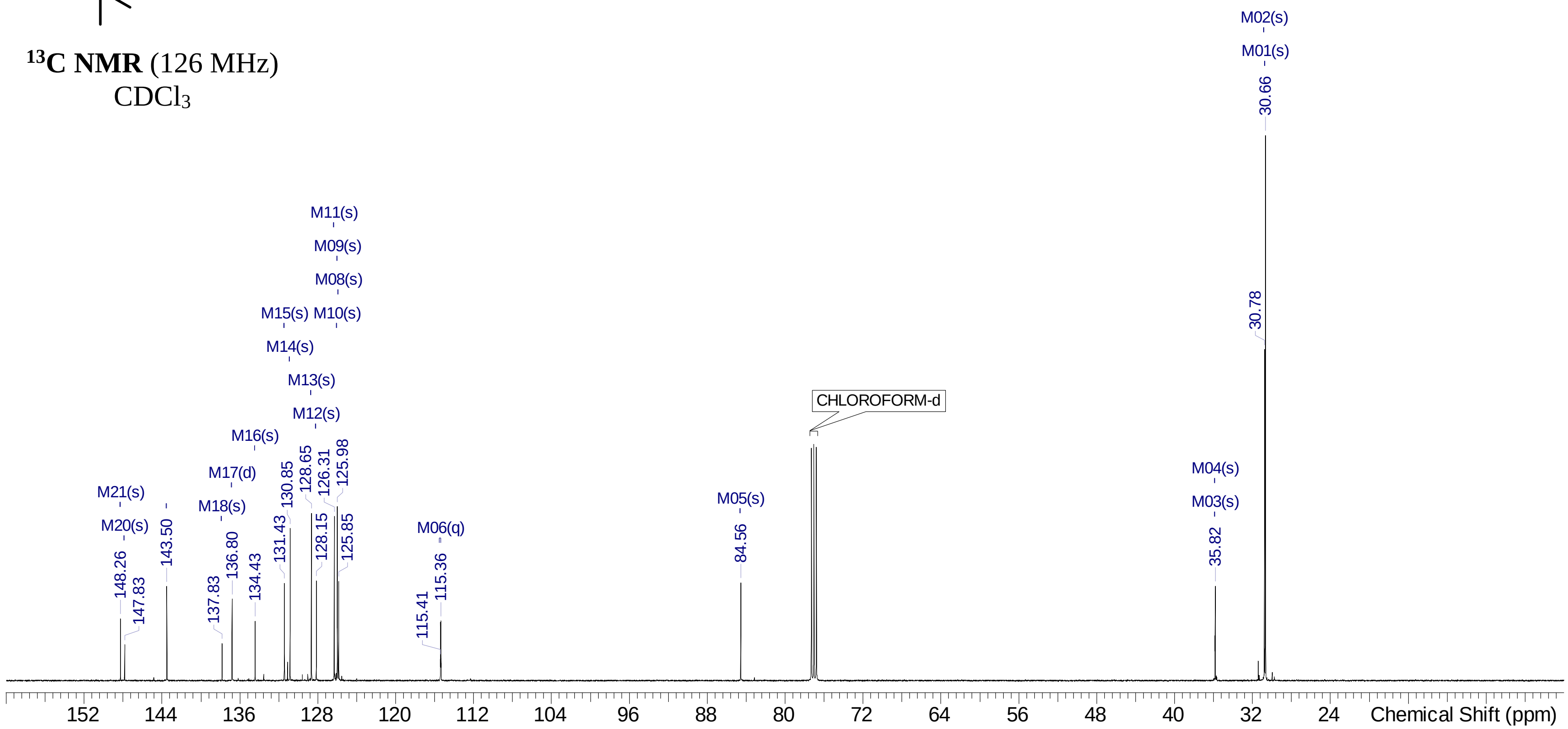


^{19}F NMR (471 MHz)
$CDCl_3$

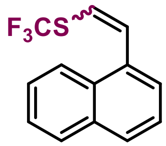




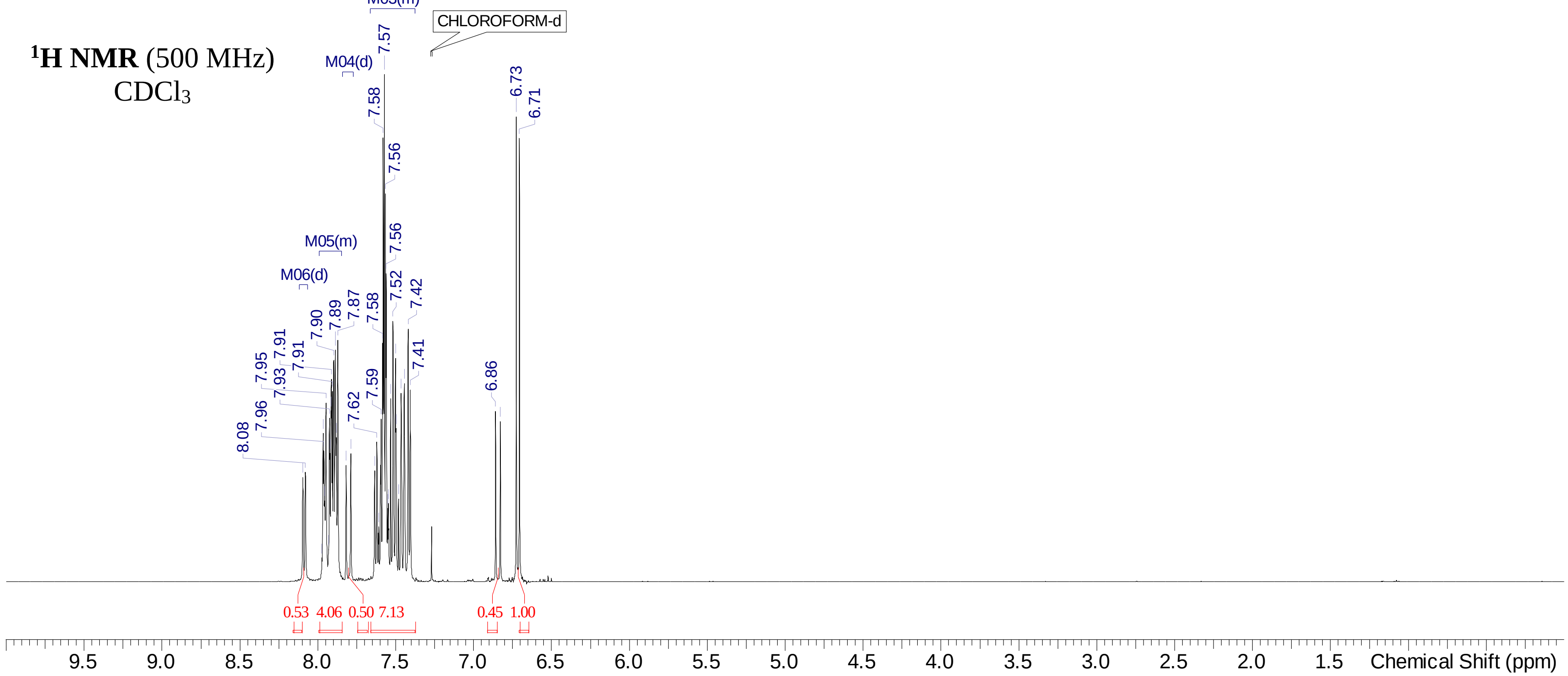
^{13}C NMR (126 MHz)
$CDCl_3$

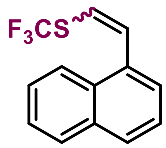


(2-(naphthalen-1-yl)vinyl)(trifluoromethyl)sulfane (3o)

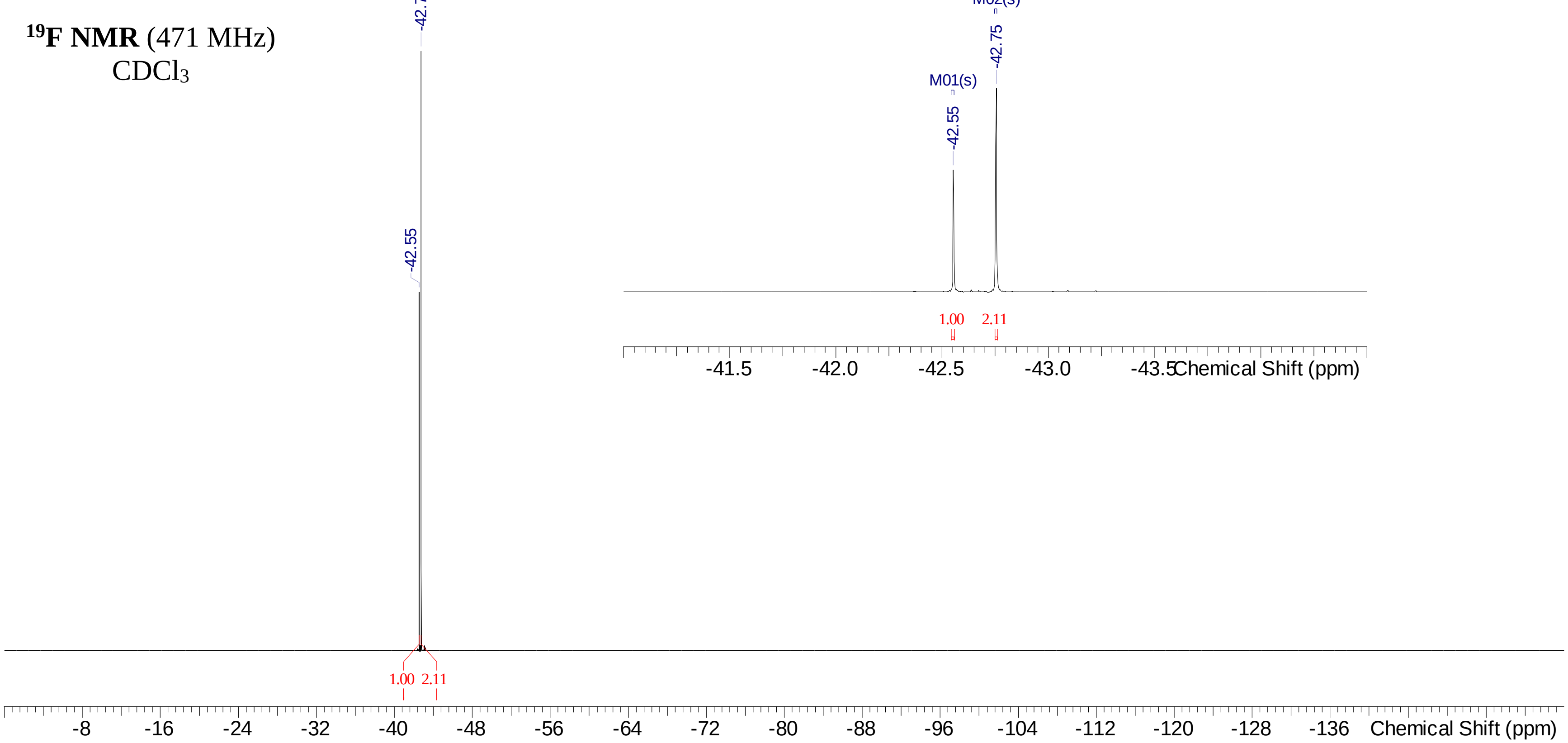


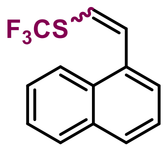
[1]H NMR (500 MHz)
$CDCl_3$



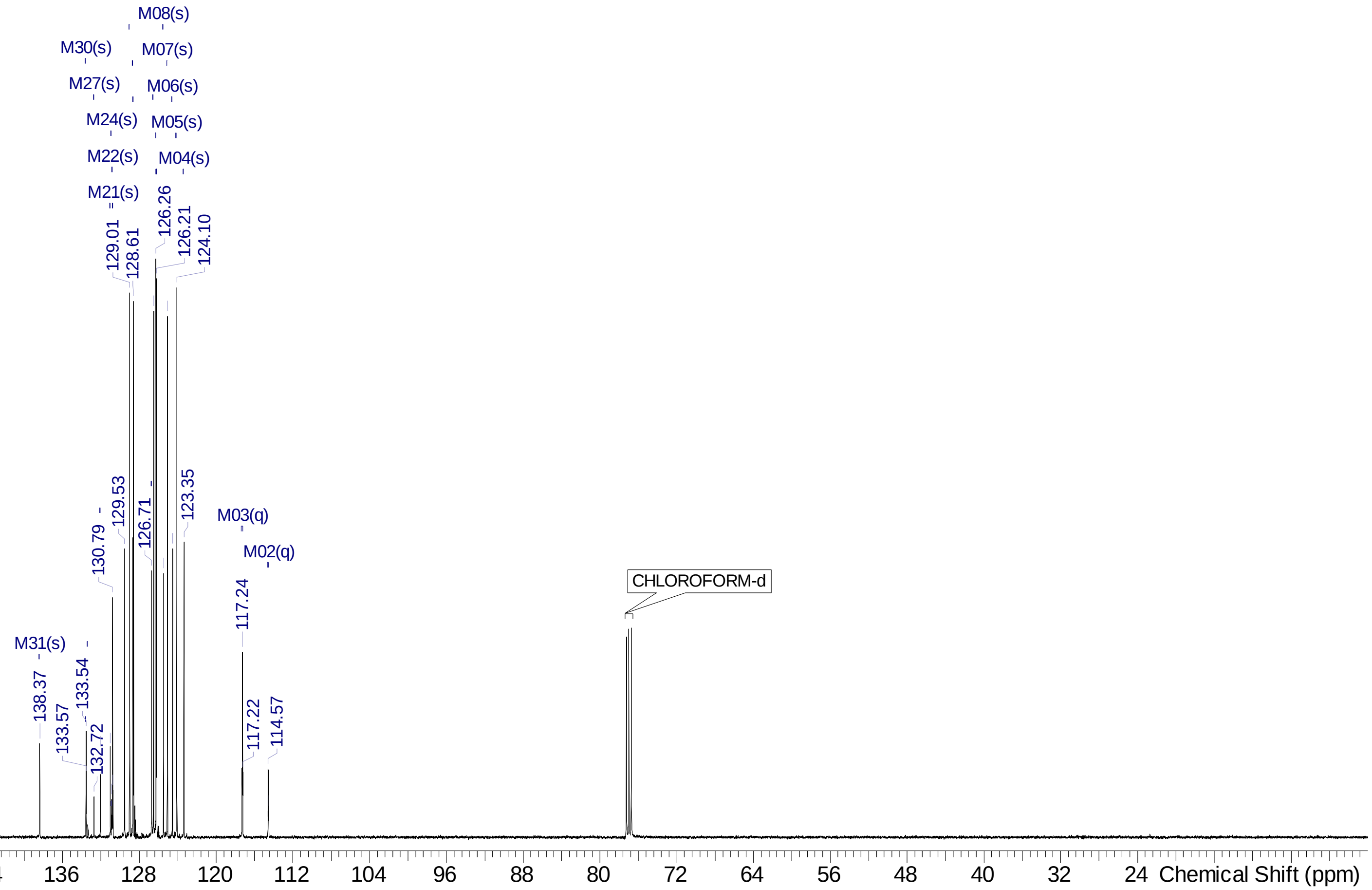


19F NMR (471 MHz)
CDCl3

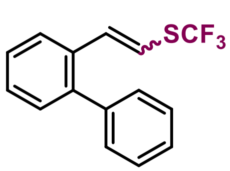




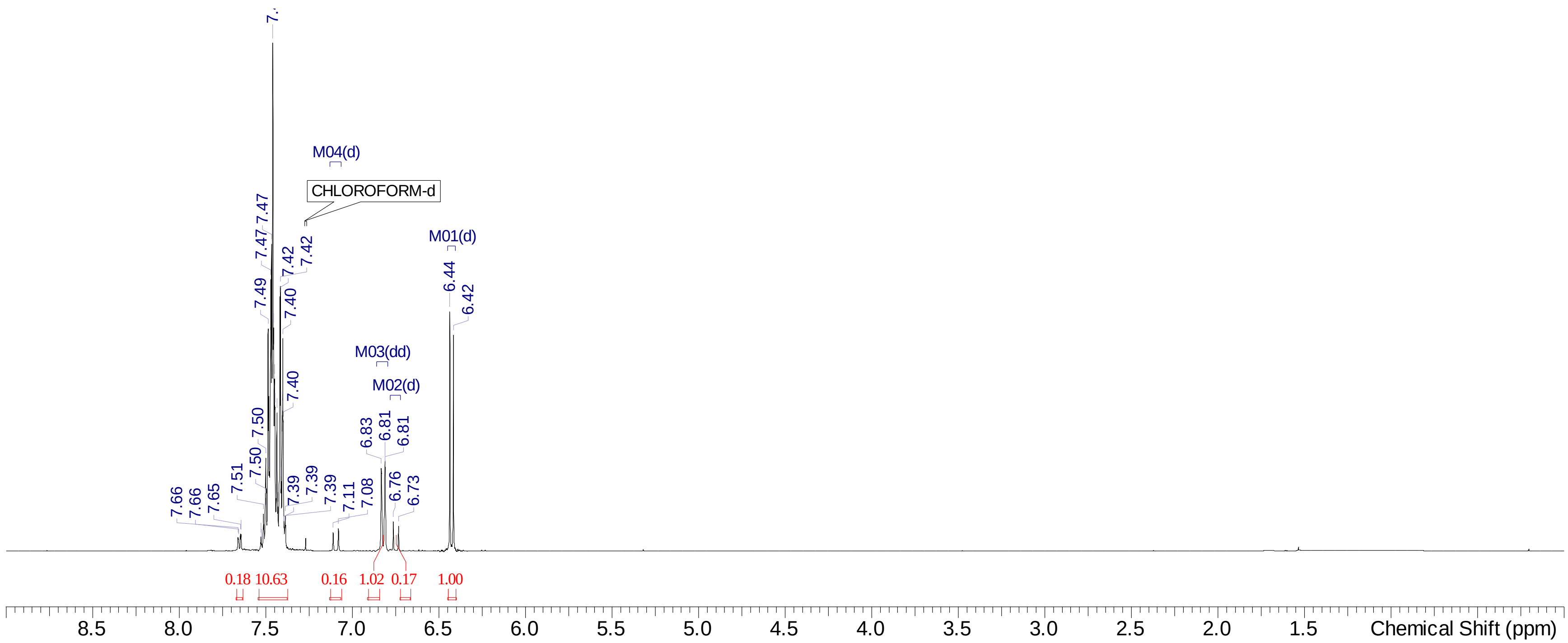
^{13}C NMR (126 MHz)
$CDCl_3$

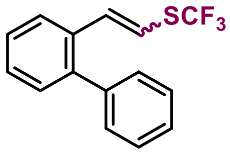


(2-([1,1'-biphenyl]-2-yl)vinyl)(trifluoromethyl)sulfane (3p)

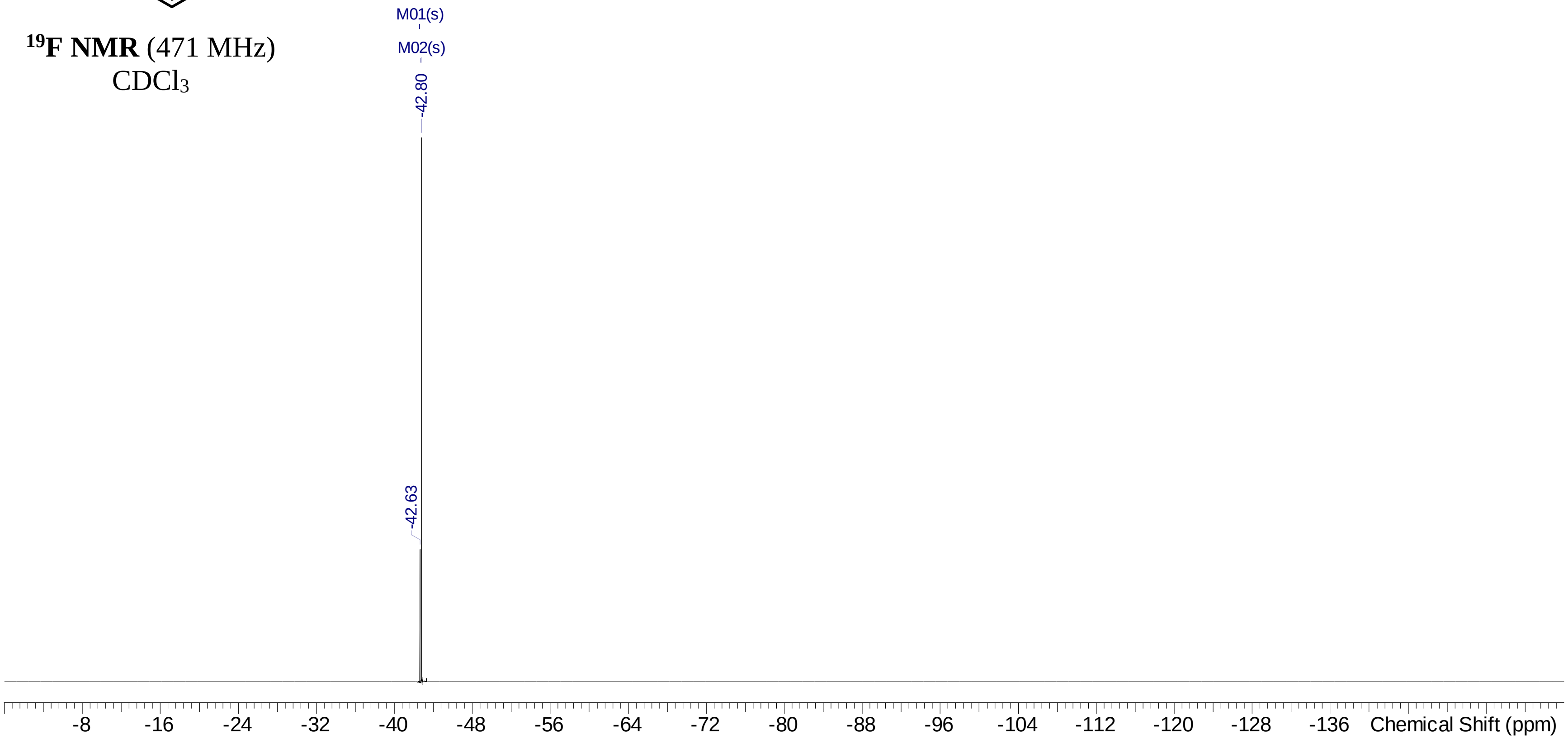


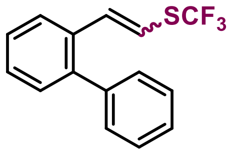
^{1}H NMR (500 MHz)
$CDCl_3$



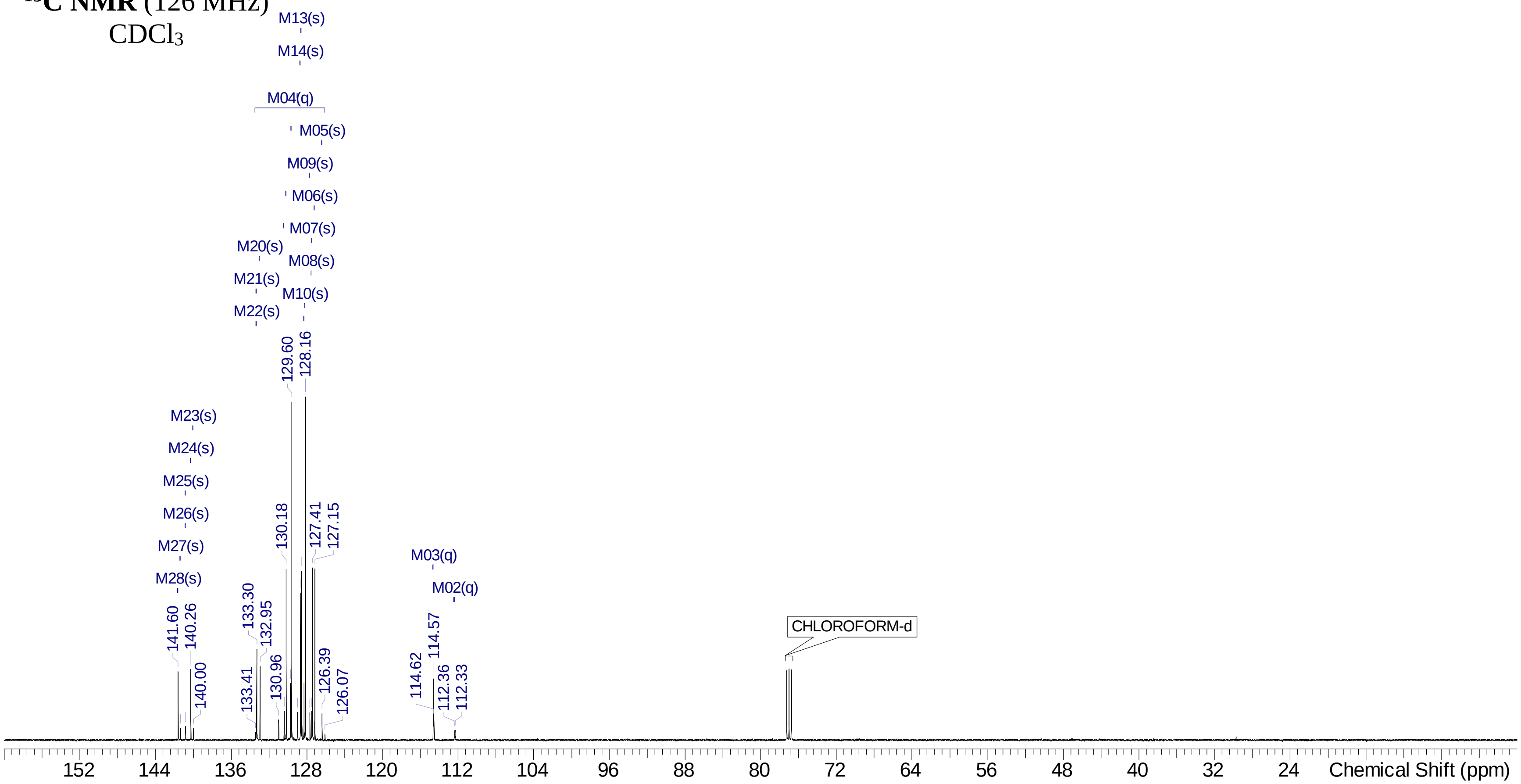


^{19}F NMR (471 MHz)
$CDCl_3$

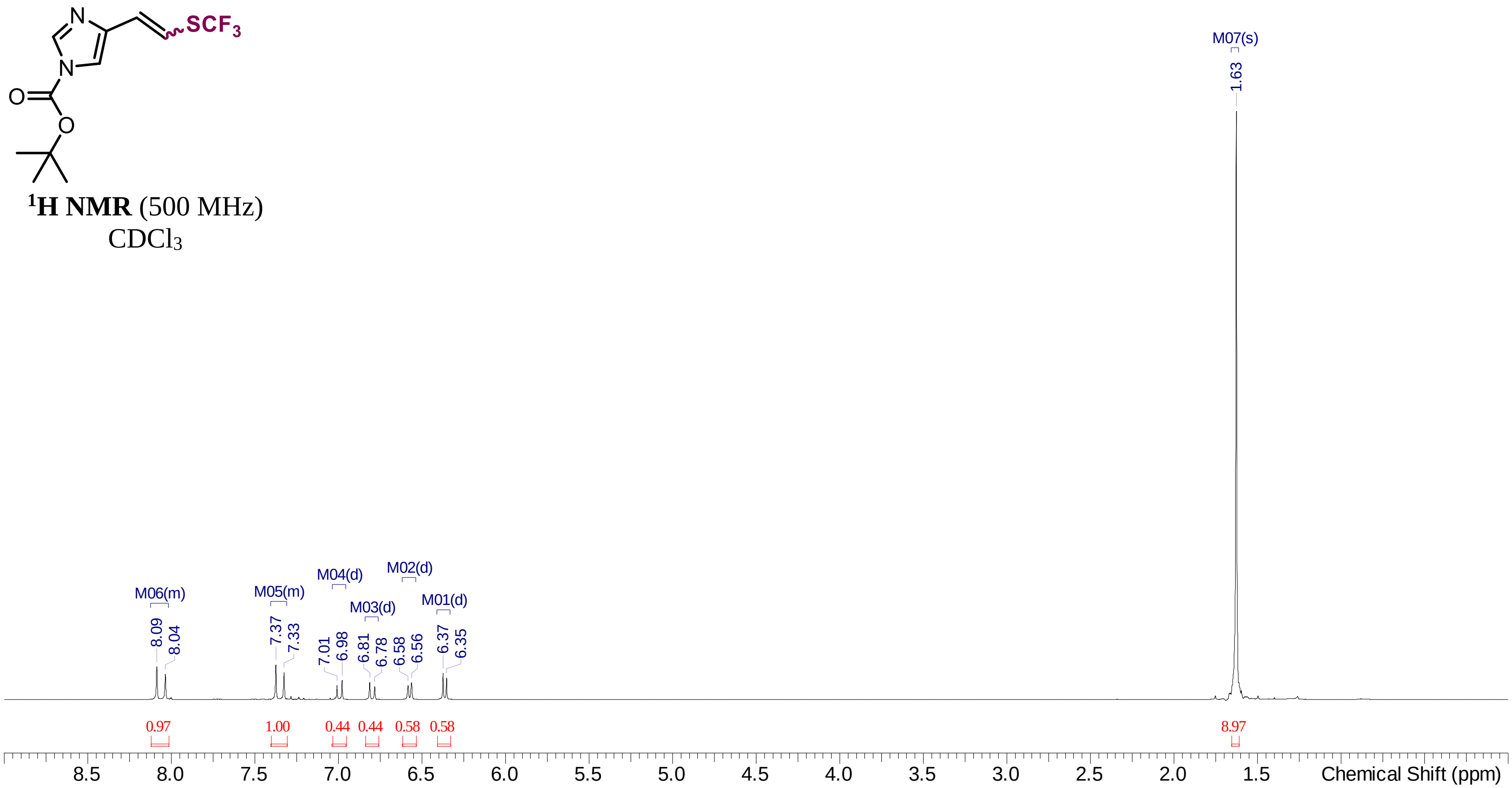




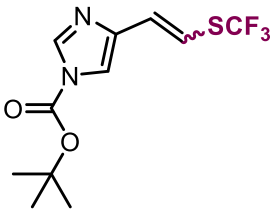
[13]C NMR (126 MHz)
$CDCl_3$



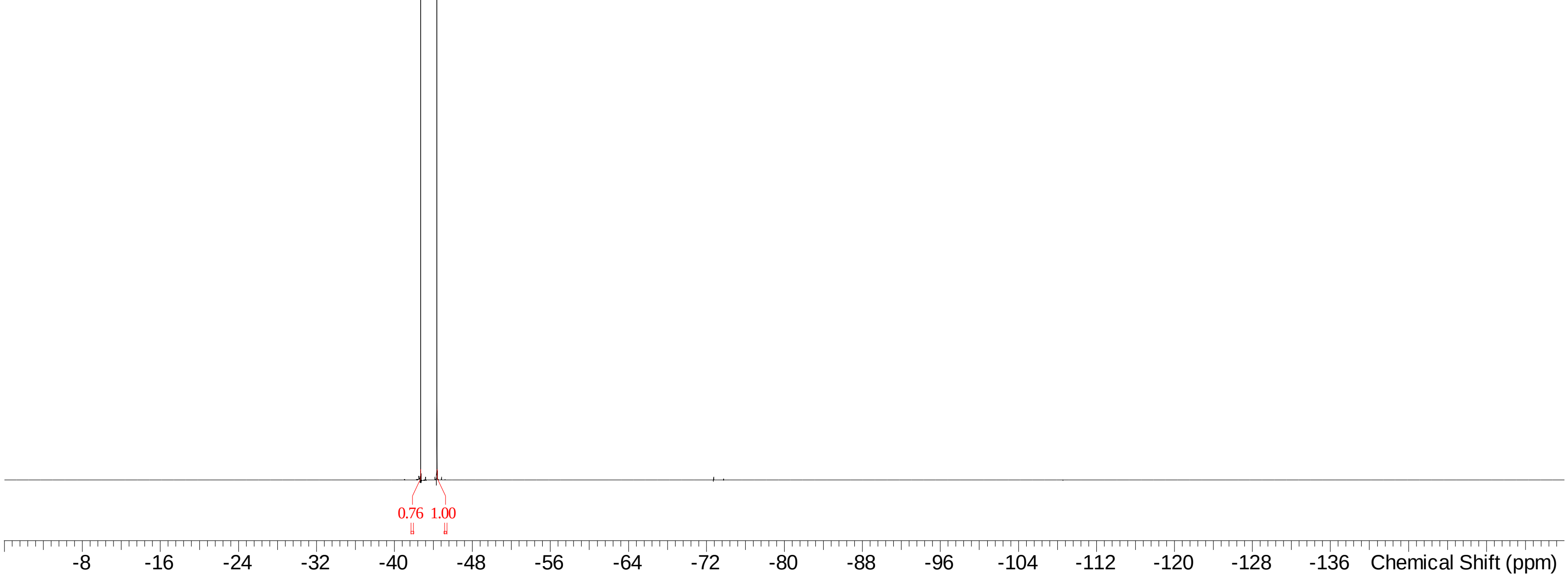
***Tert*-butyl 4-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole-1-carboxylate (3t)**

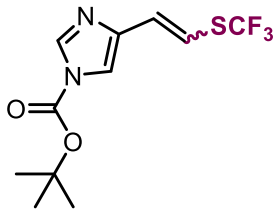


[1]H NMR (500 MHz)
$CDCl_3$

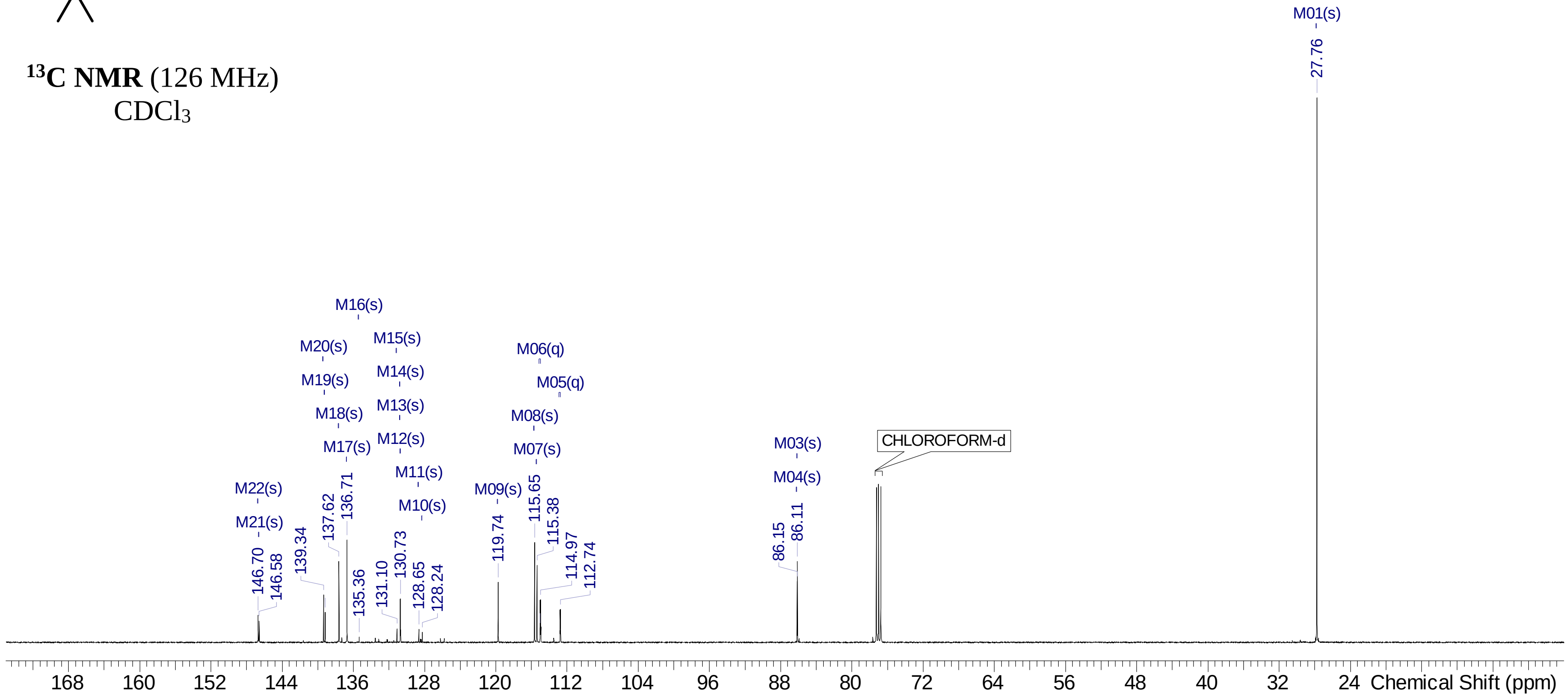


19F NMR (471 MHz)
$CDCl_3$

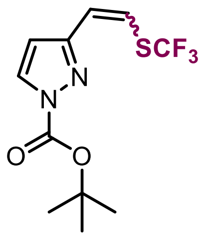




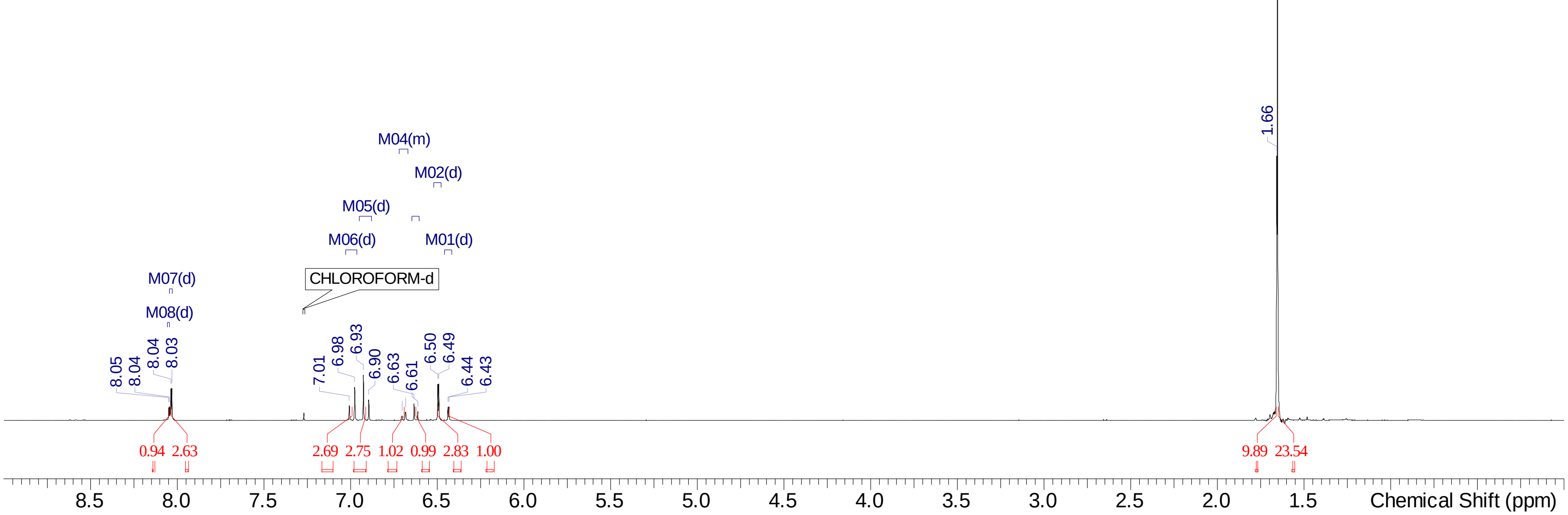
^{13}C **NMR** (126 MHz)
$CDCl_3$

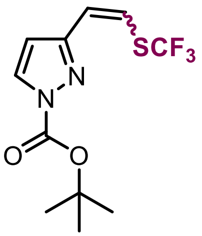


***Tert*-butyl 3-(2-((trifluoromethyl)thio)vinyl)-1*H*-pyrazole-1-carboxylate (3u)**

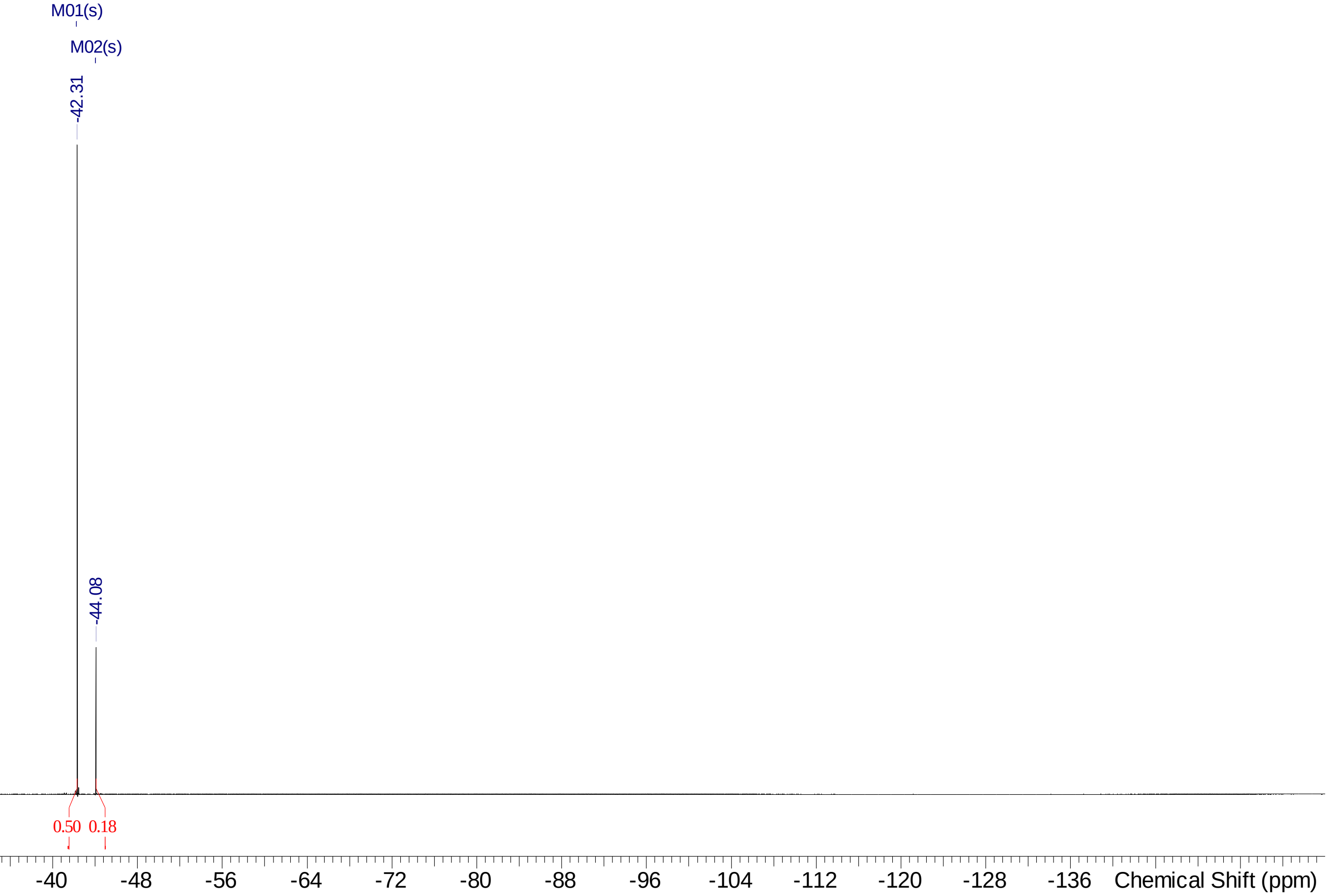


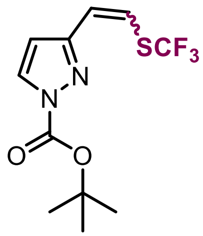
[1]H NMR (500 MHz)
$CDCl_3$



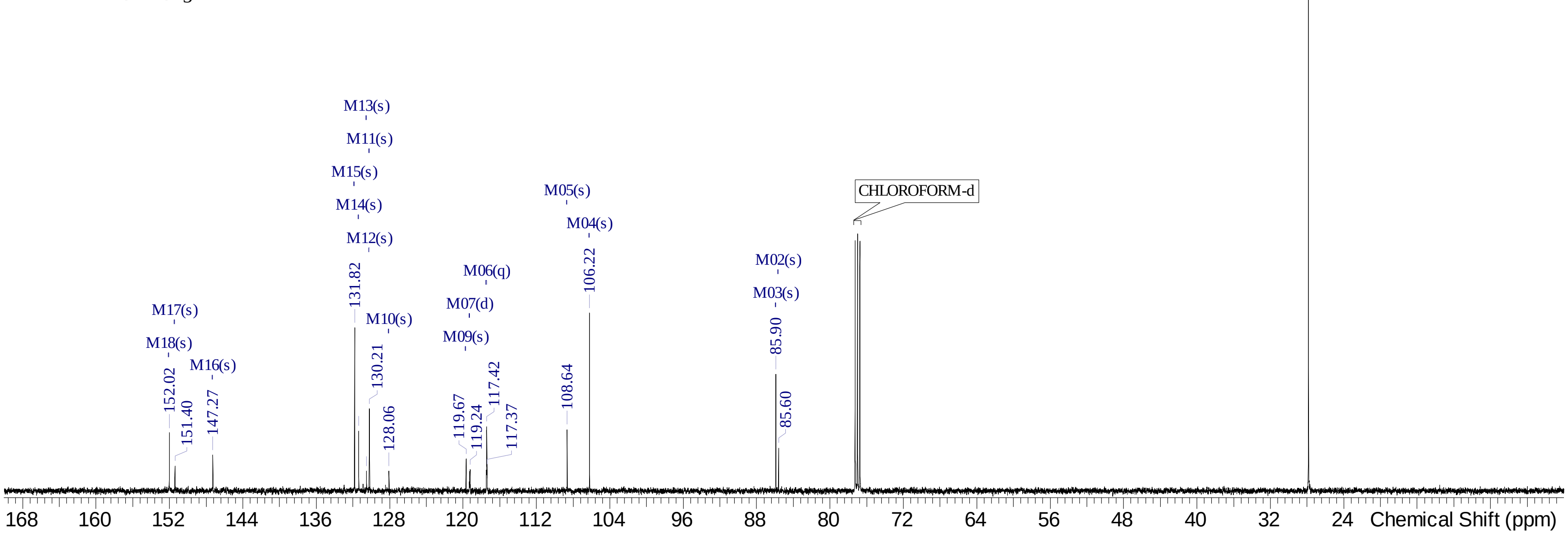


[19]F NMR (471 MHz)
$CDCl_3$

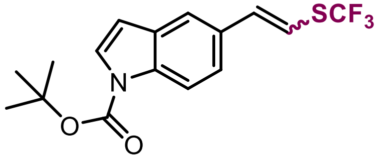




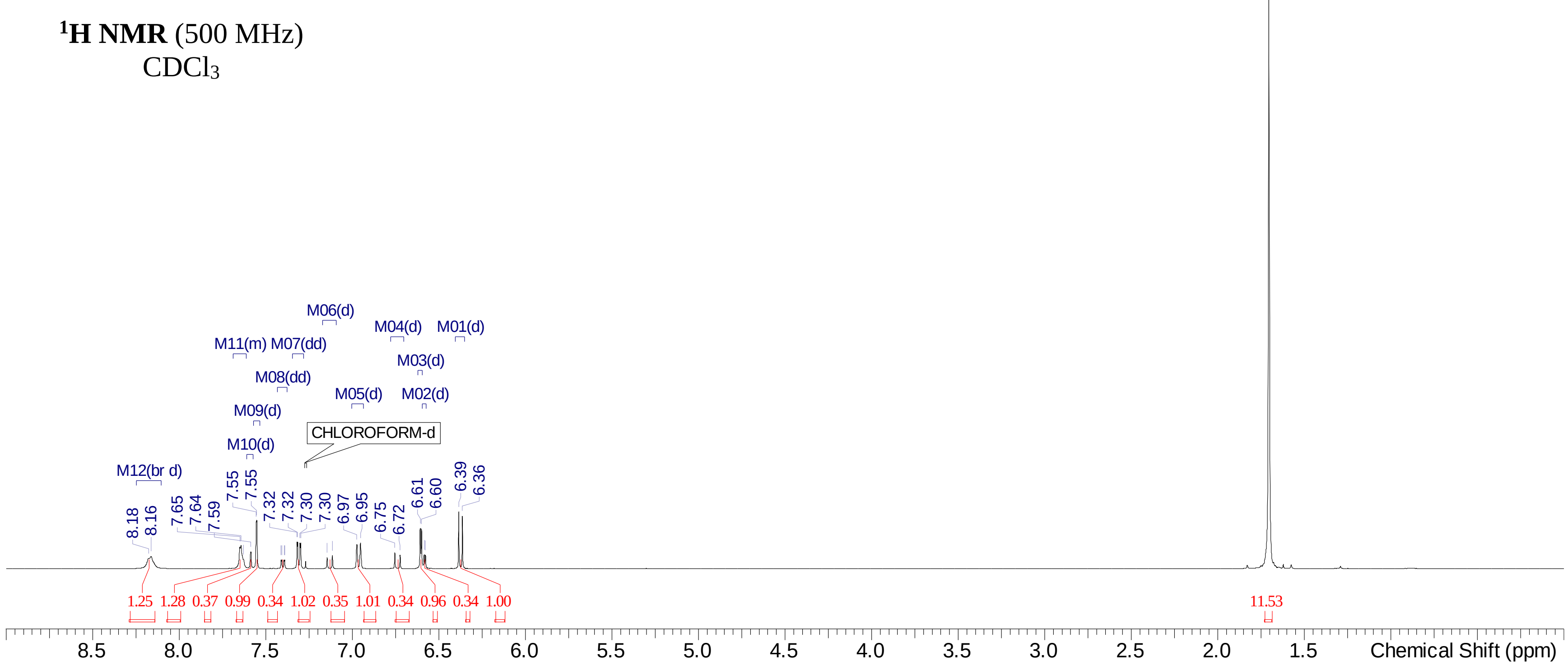
^{13}C NMR (126 MHz)
$CDCl_3$

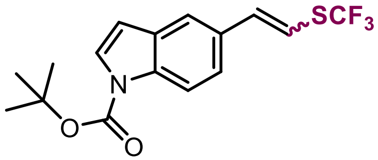


***Tert*-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1*H*-indole-1-carboxylate (3v)**

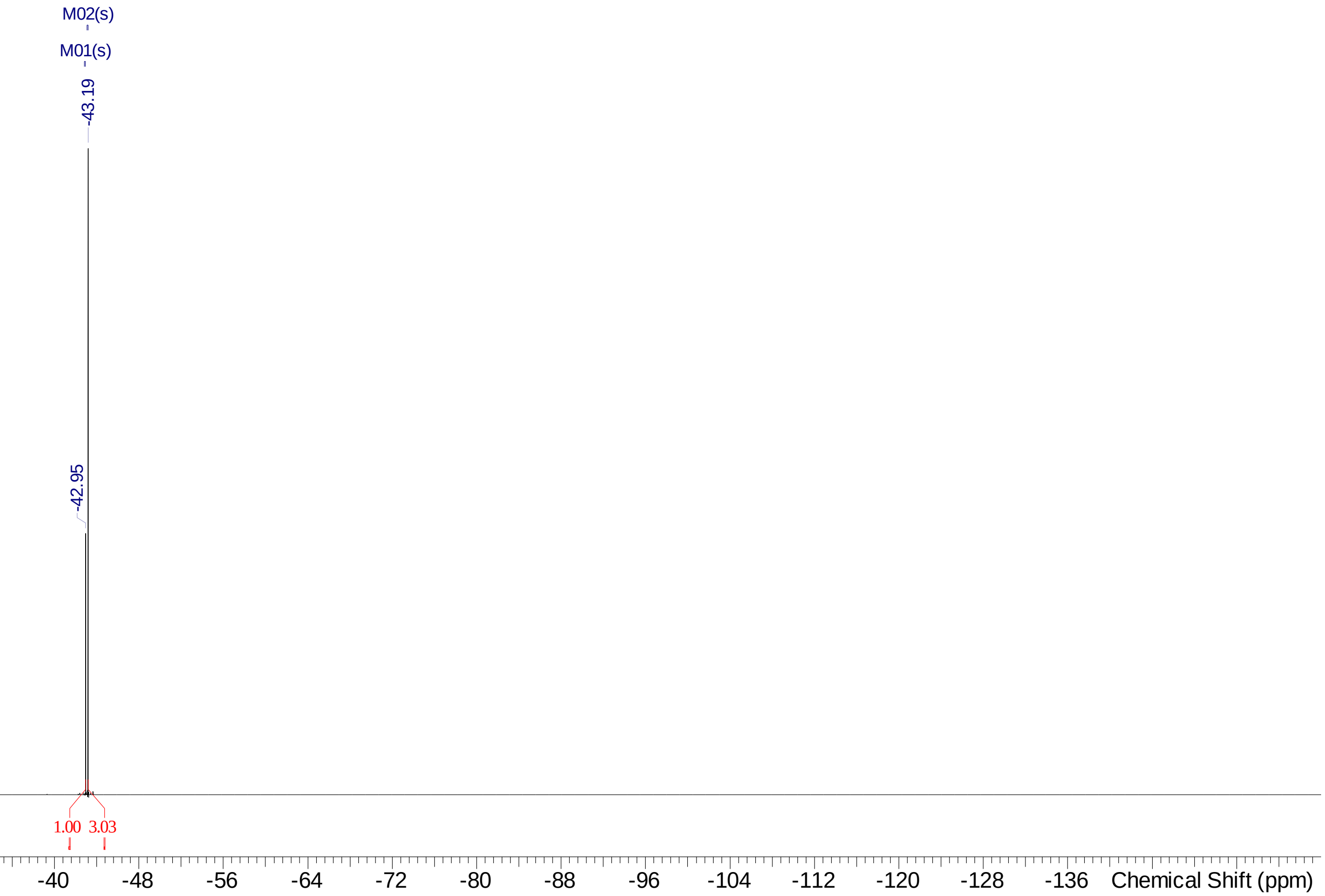


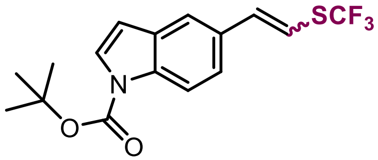
^{1}H NMR (500 MHz)
$CDCl_3$



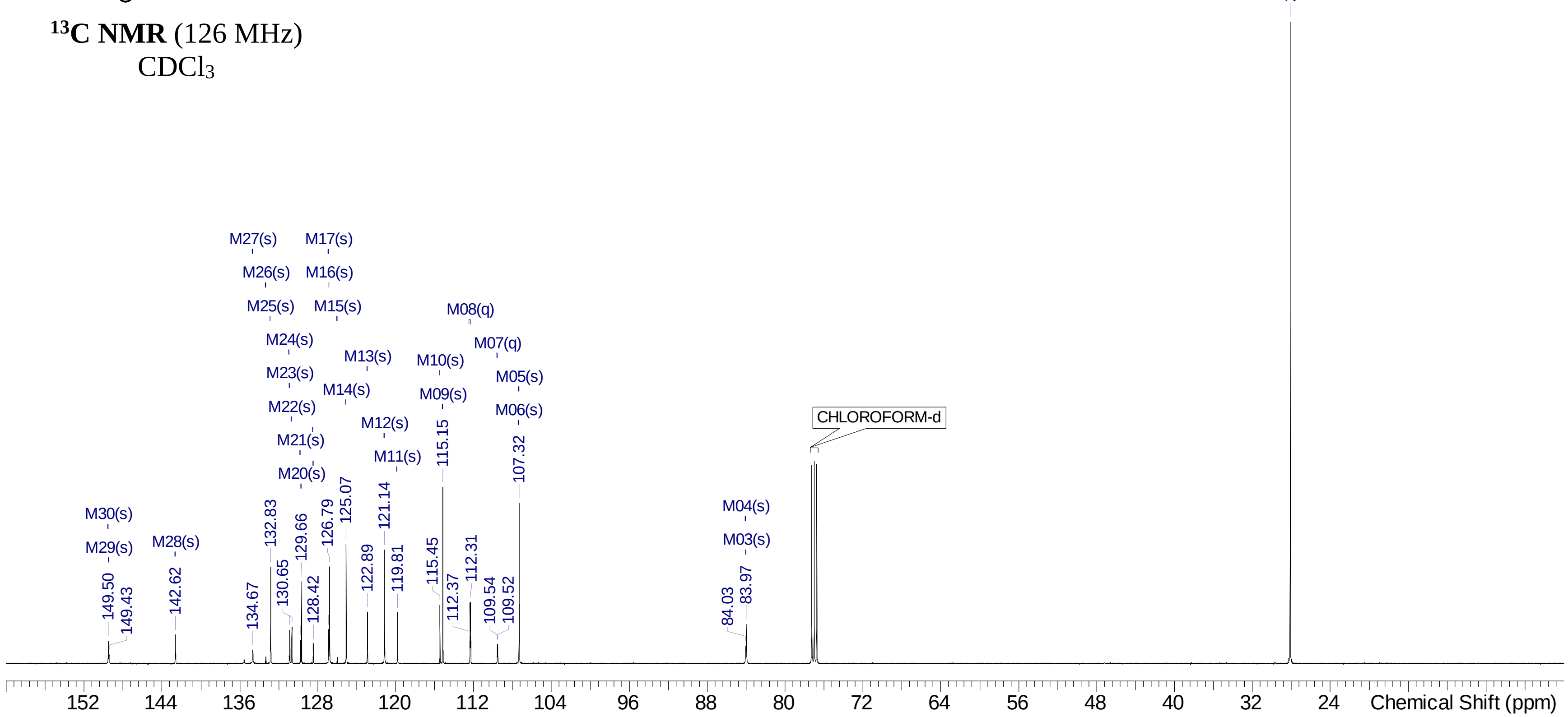


^{19}F NMR (471 MHz)
$CDCl_3$

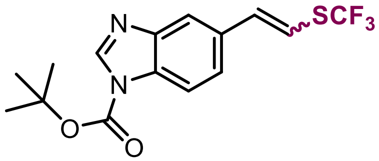




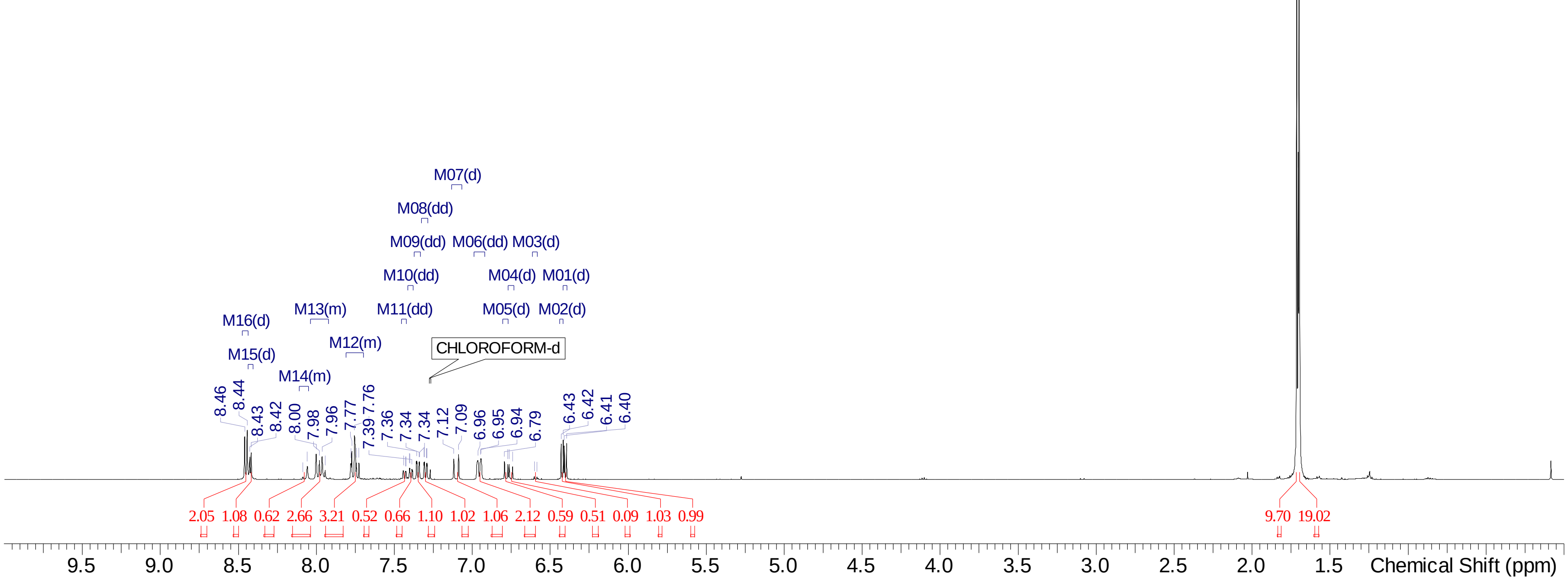
^{13}C NMR (126 MHz)
$CDCl_3$

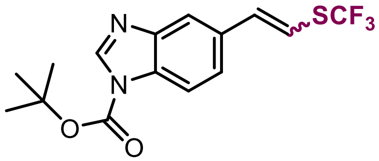


Tert-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1_H_-benzo[_d_]imidazole-1-carboxylate (3w)

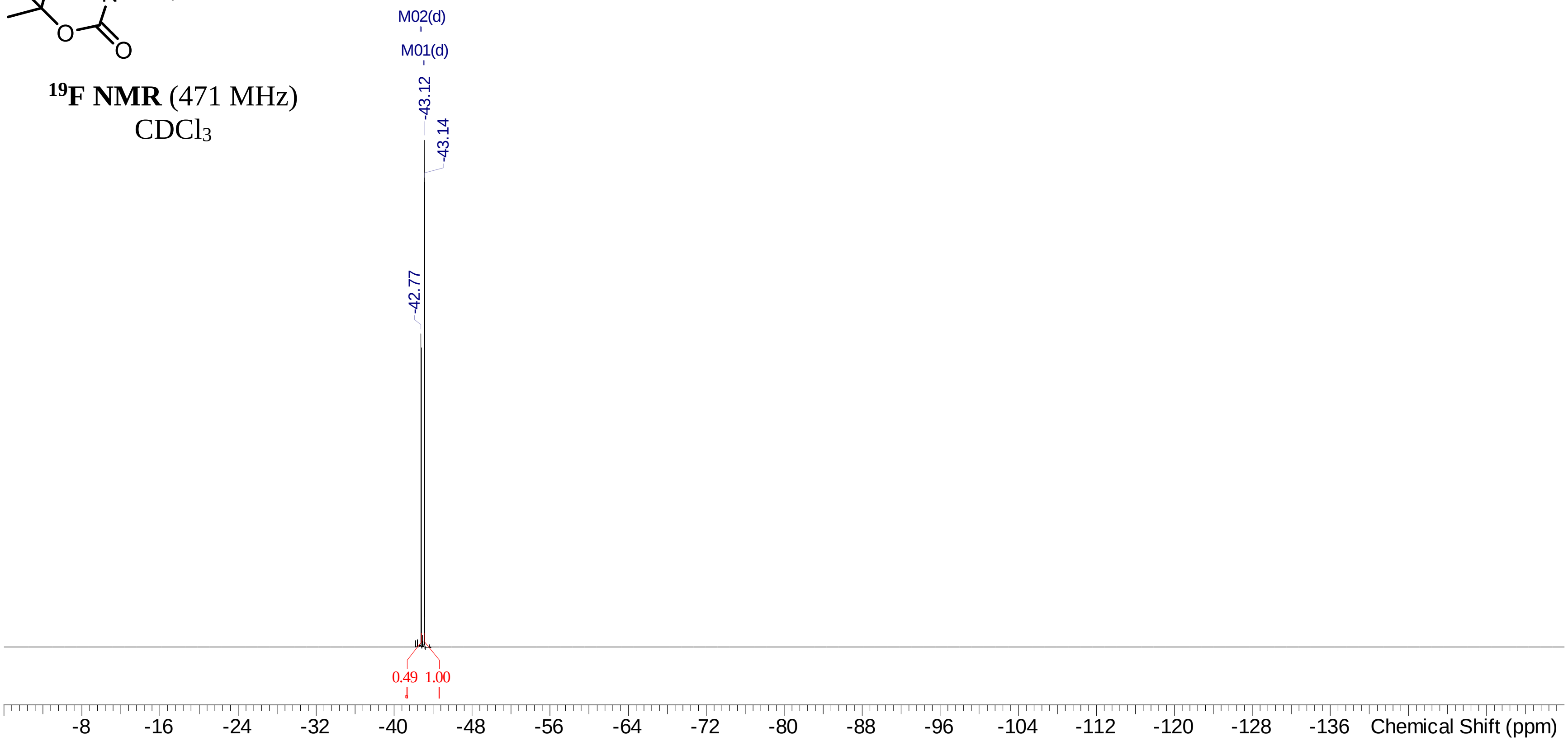


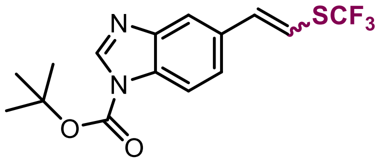
^{1}H NMR (500 MHz)
$CDCl_3$



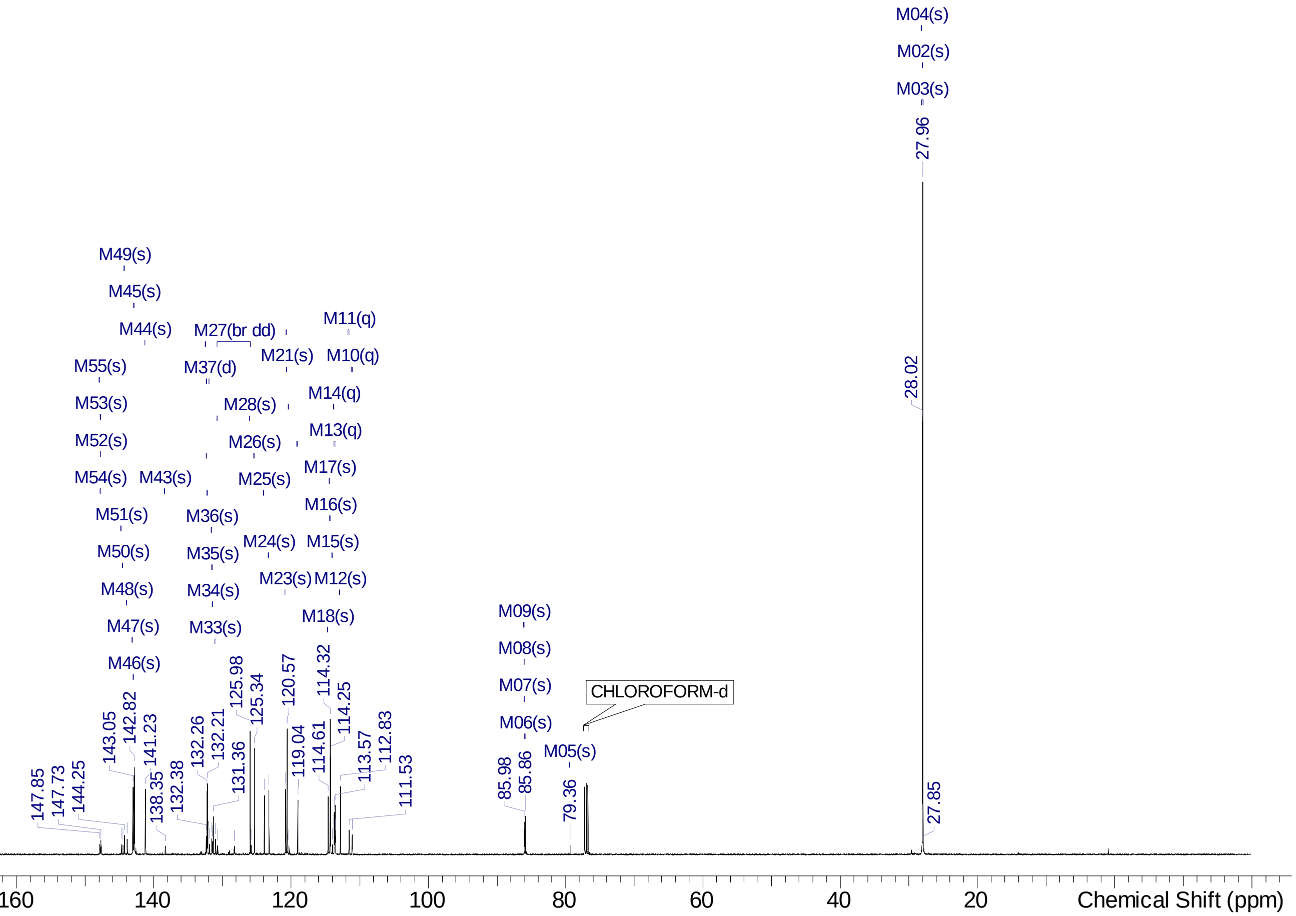


^{19}F NMR (471 MHz)
$CDCl_3$

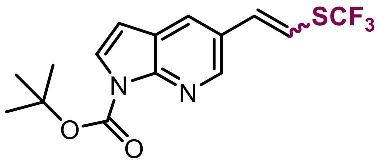




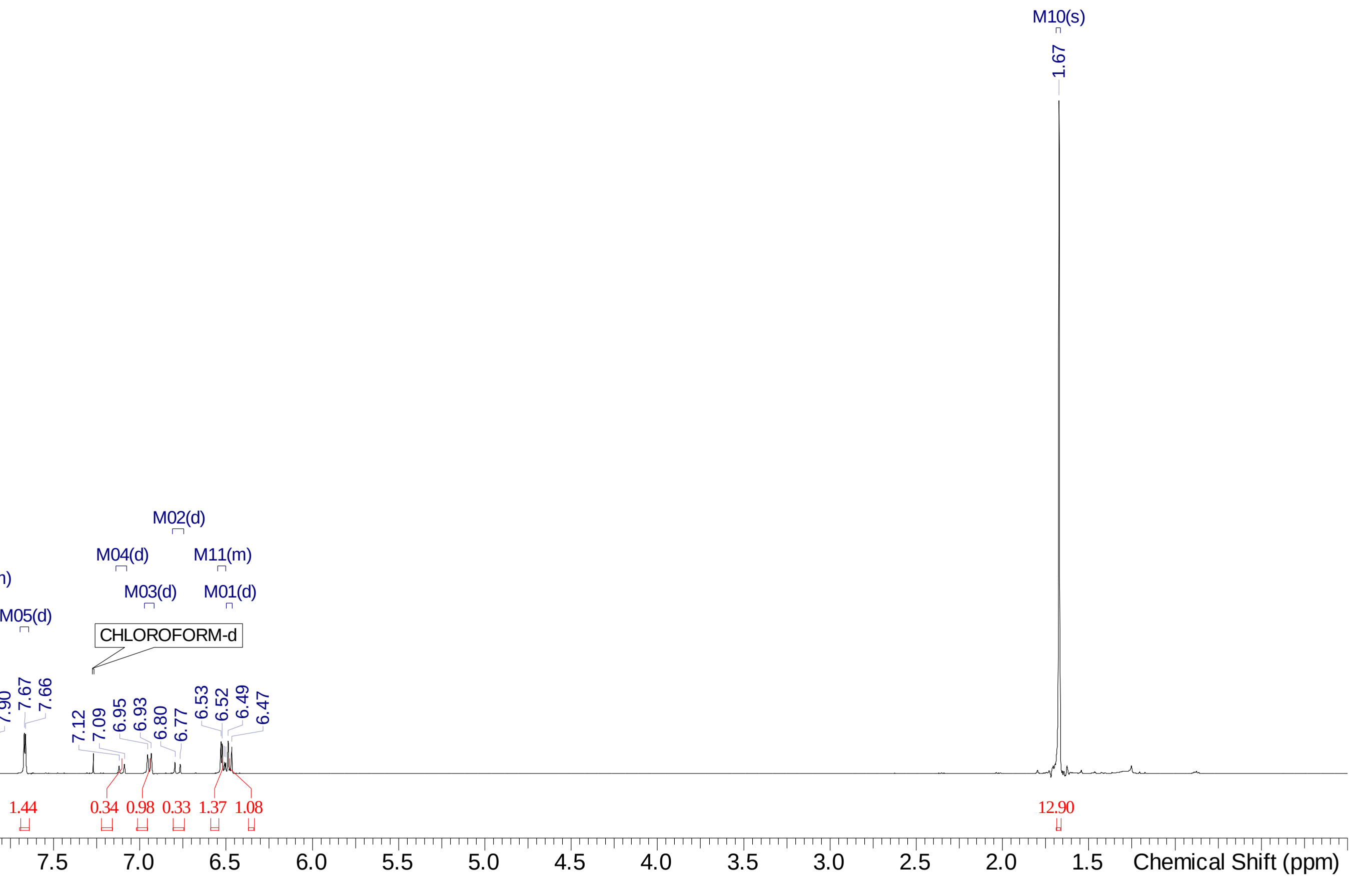
^{13}**C NMR** (126 MHz)
$CDCl_3$

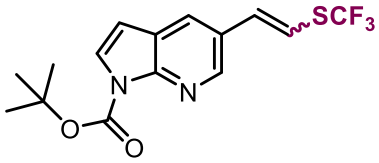


Tert-butyl 5-(2-((trifluoromethyl)thio)vinyl)-1_H_-pyrrolo[2,3-_b_]pyridine-1-carboxylate (3x)

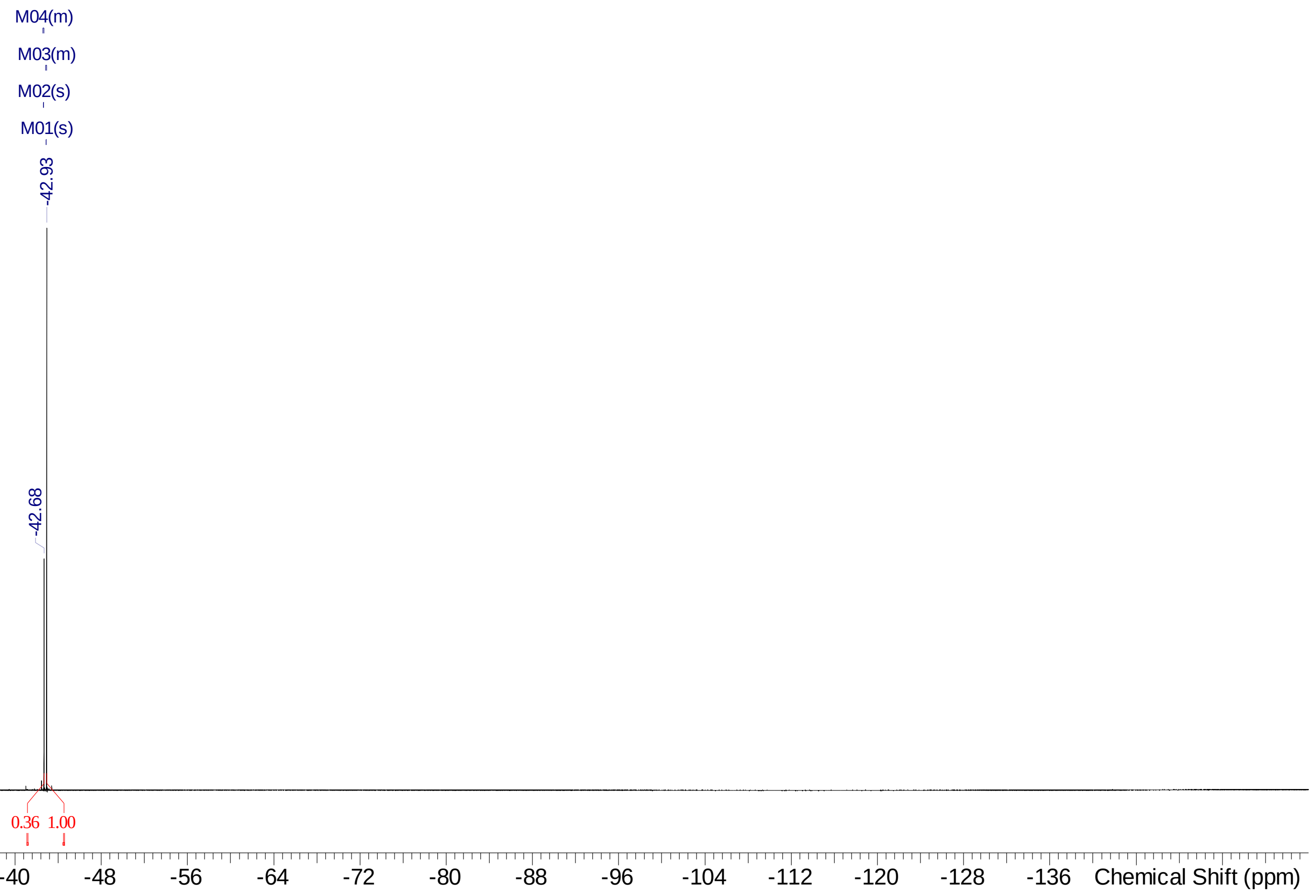


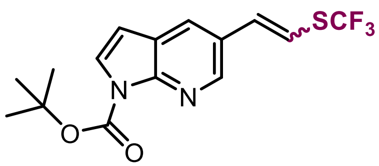
[1]H NMR (500 MHz)
$CDCl_3$



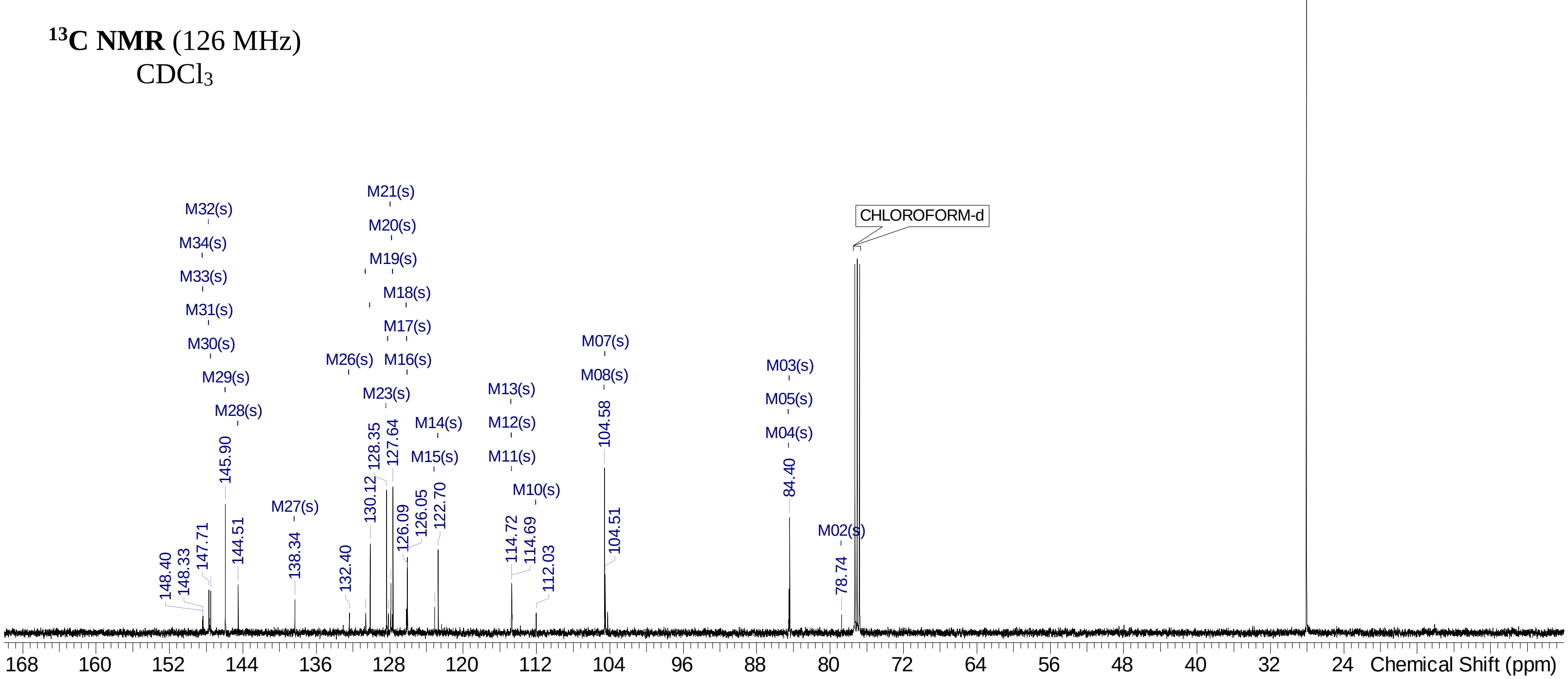


^{19}F NMR (471 MHz)
$CDCl_3$

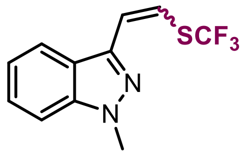




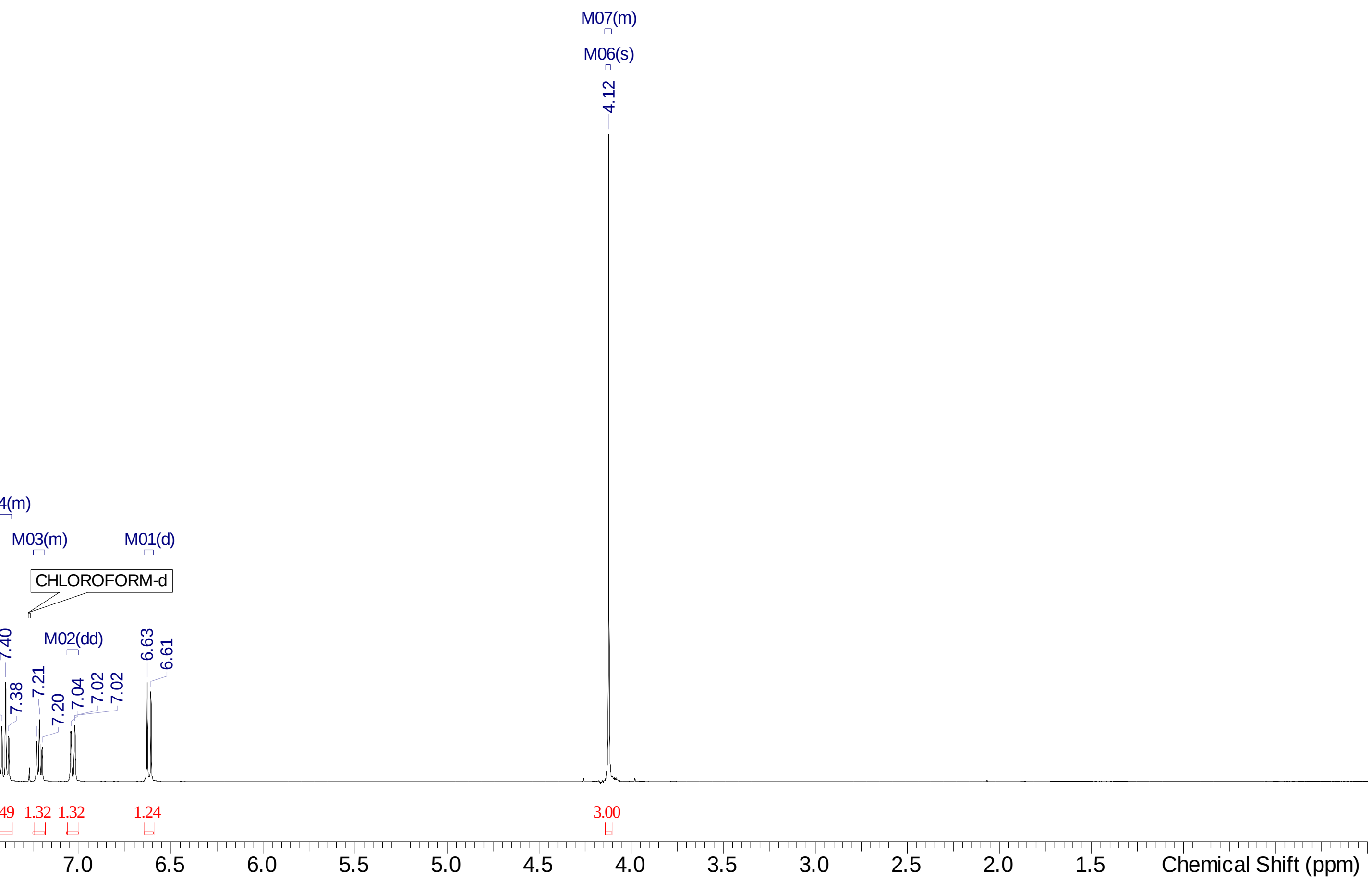
^{13}C NMR (126 MHz)
$CDCl_3$

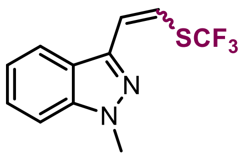


1-methyl-3-(2-((trifluoromethyl)thio)vinyl)-1H-indazole (3y)

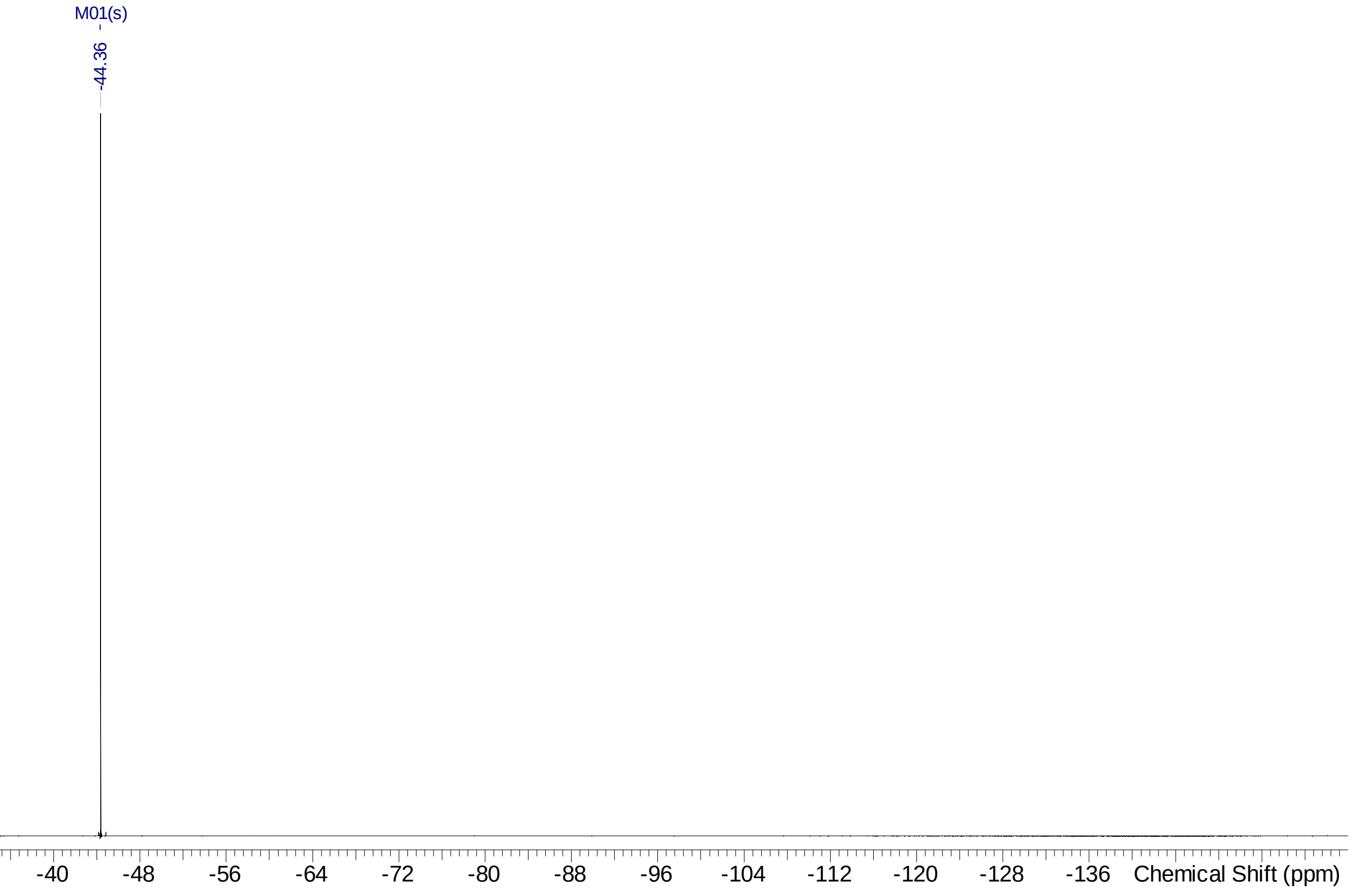


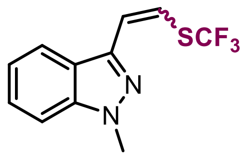
[1]H NMR (500 MHz)
$CDCl_3$



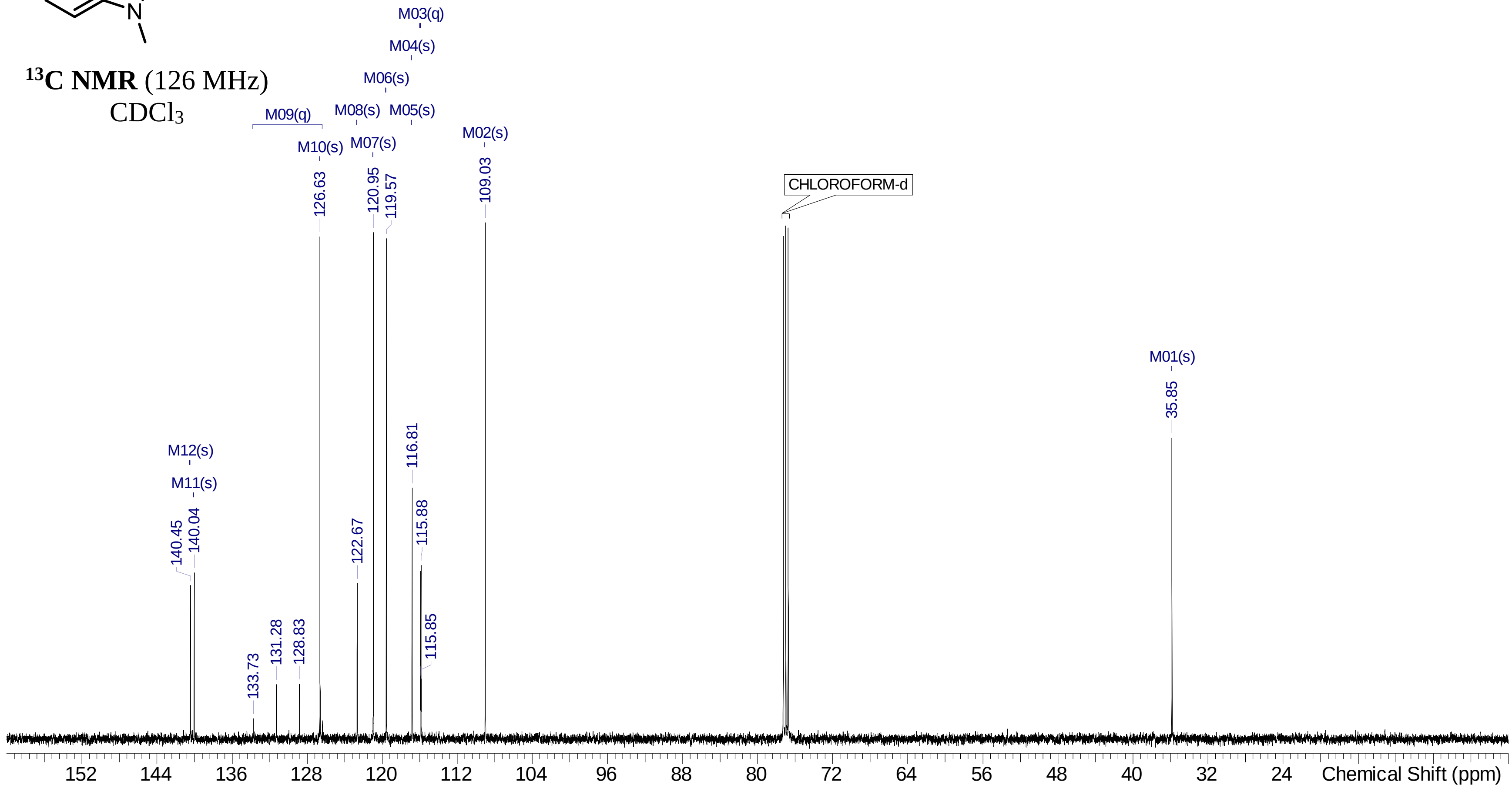


^{19}F NMR (471 MHz)
$CDCl_3$

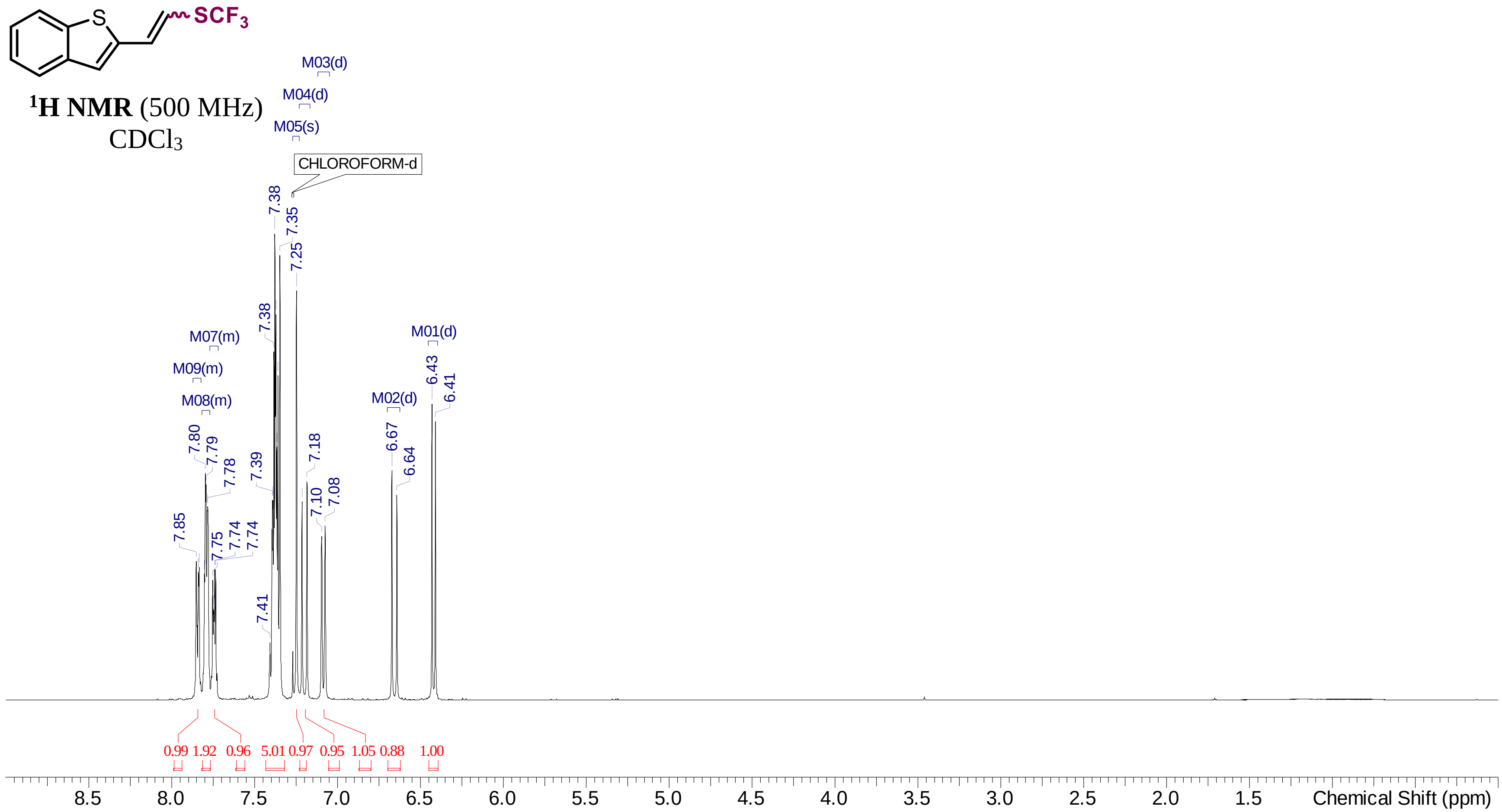




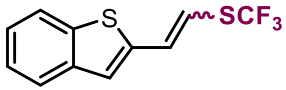
^{13}C NMR (126 MHz)
$CDCl_3$



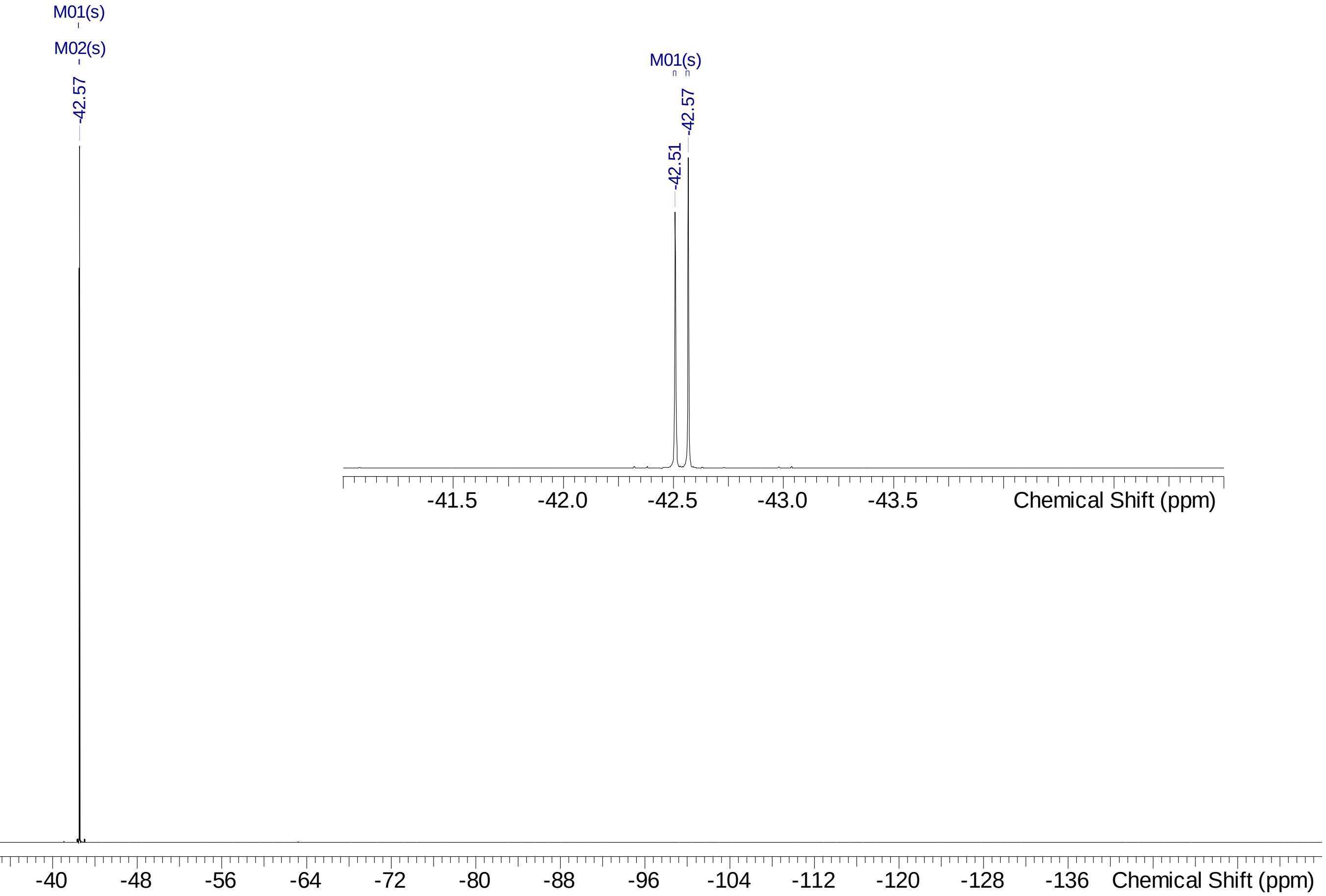
2-(2-((trifluoromethyl)thio)vinyl)benzo[b]thiophene (3ad)

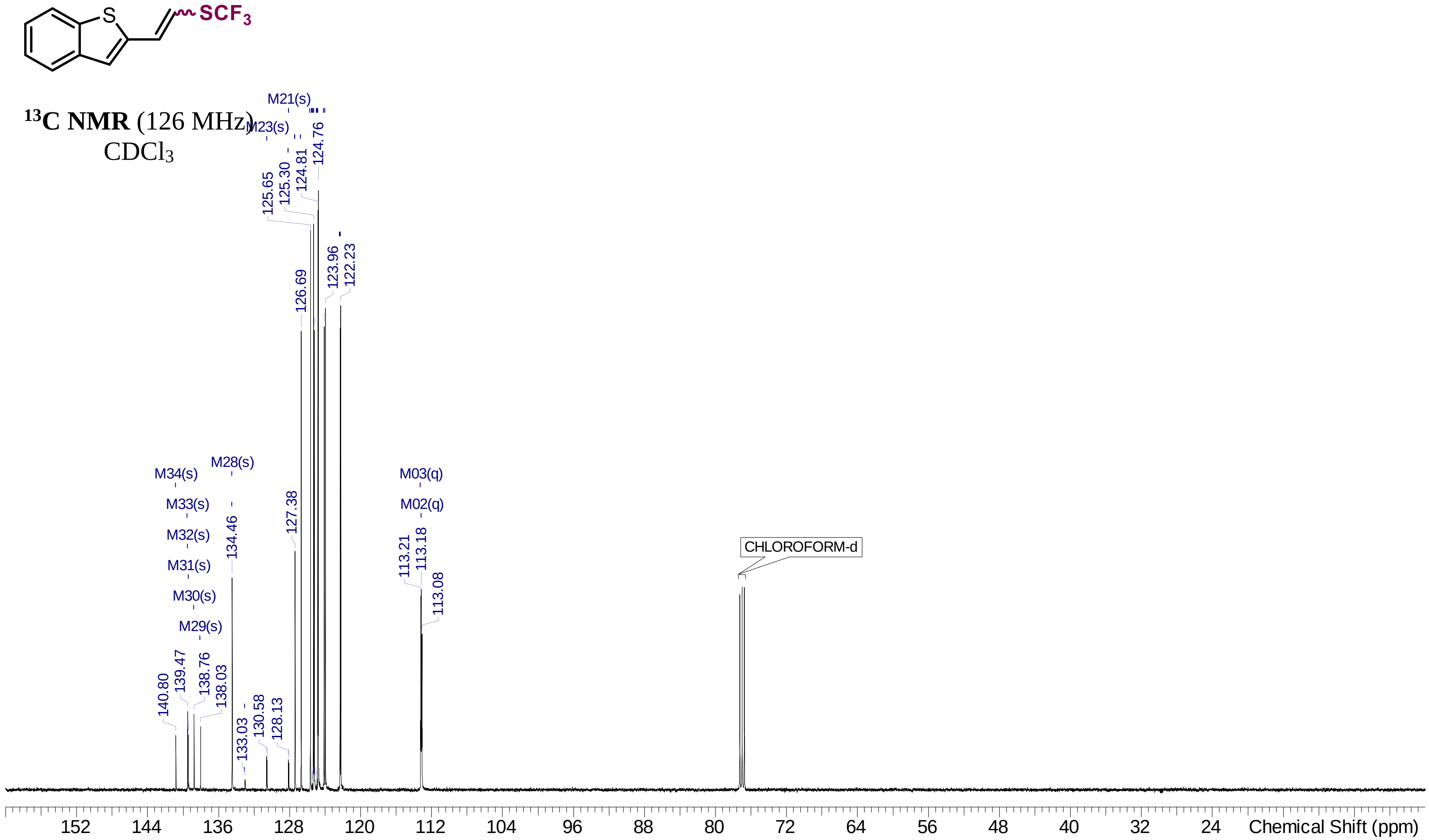


[1]H NMR (500 MHz)
$CDCl_3$

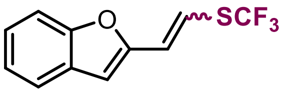


[19]F NMR (471 MHz)
$CDCl_3$

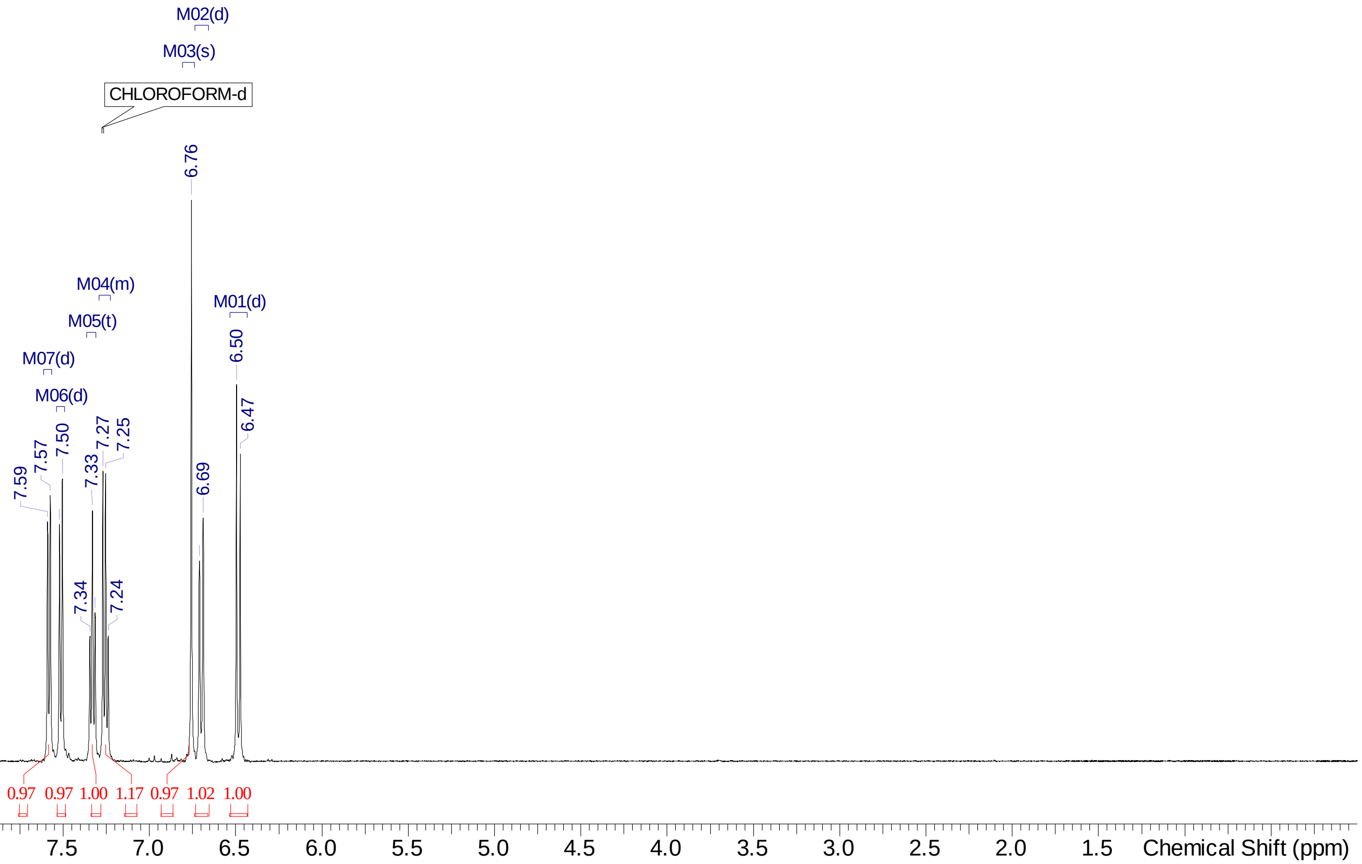


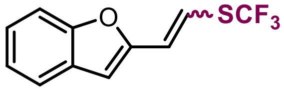

S
SCF3
13C NMR (126 MHz)
CDCl3
M21(s)
M23(s)
125.65
125.30
124.81
124.76
126.69
123.96
122.23
M34(s)
M28(s)
M33(s)
M32(s)
M31(s)
M30(s)
M29(s)
134.46
127.38
140.80
139.47
138.76
138.03
133.03
130.58
128.13
M03(q)
M02(q)
113.21
113.18
113.08
CHLOROFORM-d
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

2-(2-((Trifluoromethyl)thio)vinyl)benzofuran (3ae)

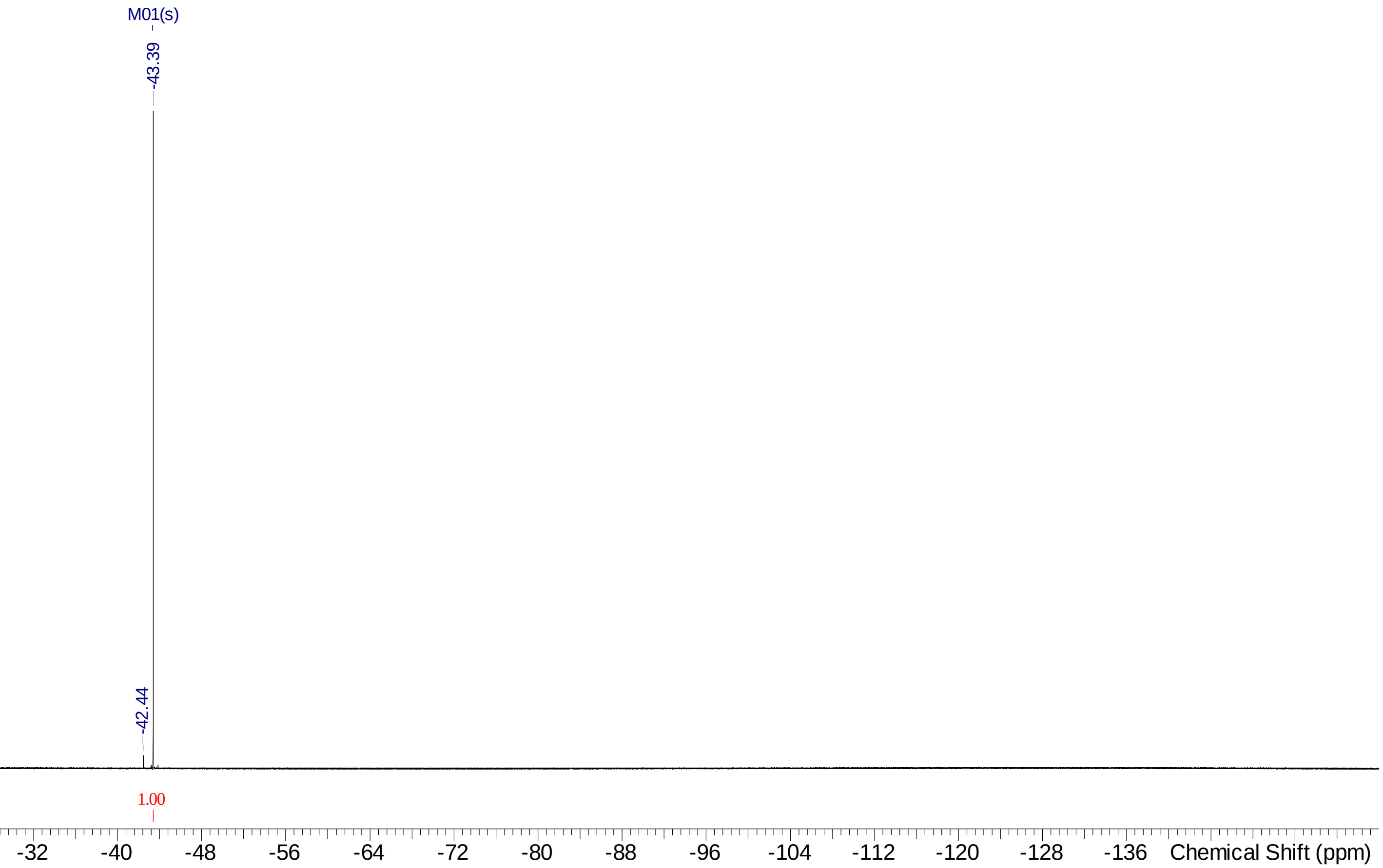


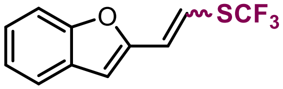
[1]H NMR (500 MHz)
$CDCl_3$



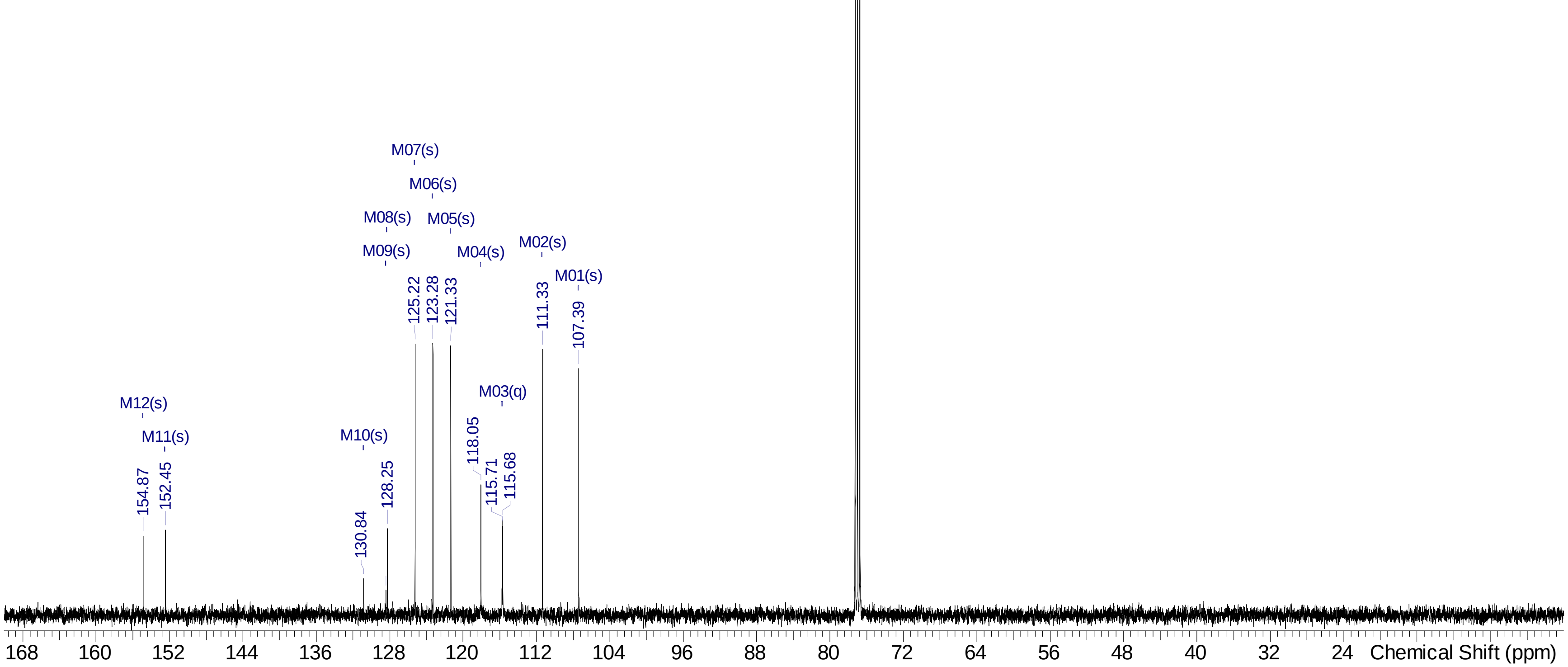


^{19}F NMR (471 MHz)
$CDCl_3$

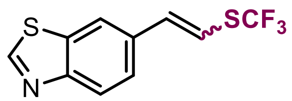




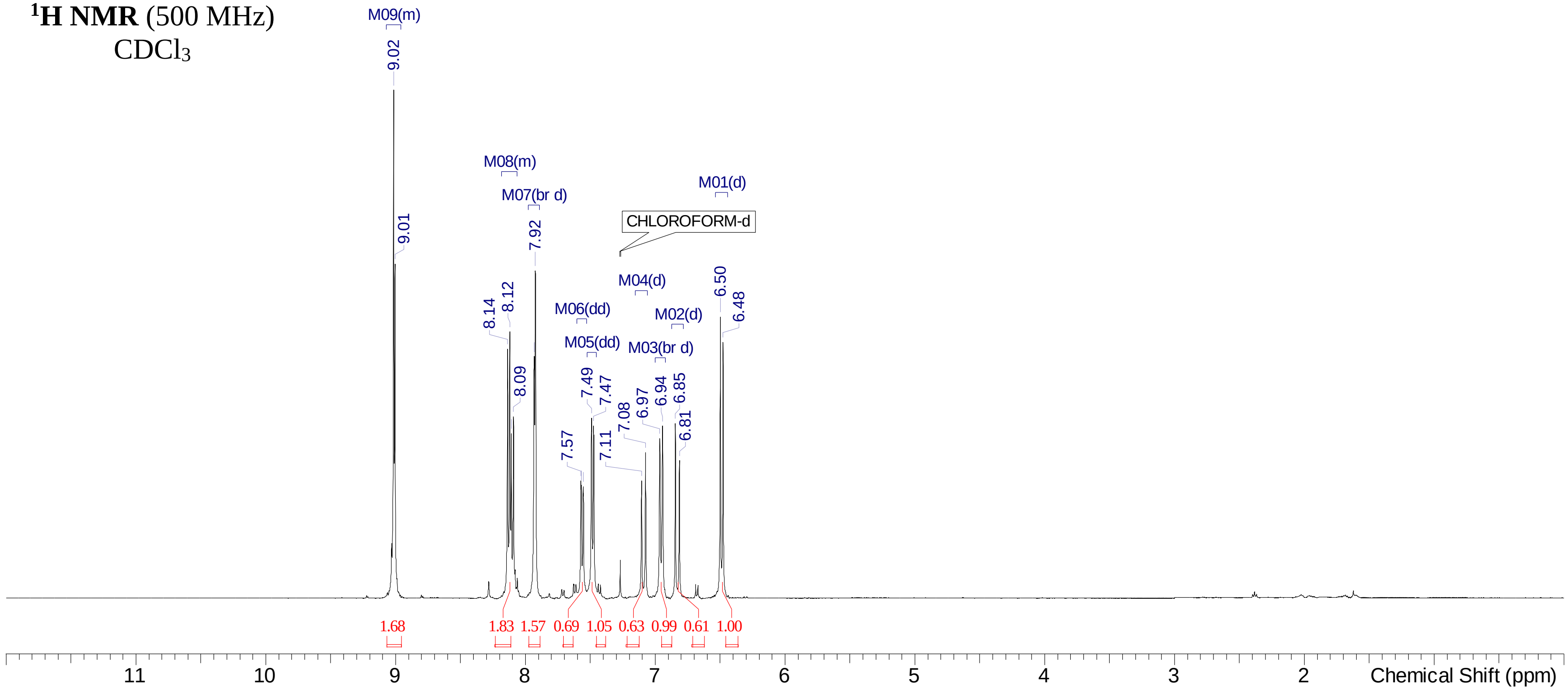
^{13}C NMR (126 MHz)
$CDCl_3$

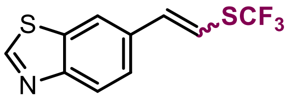


6-(2-((Trifluoromethyl)thio)vinyl)benzo[d]thiazole (3af)

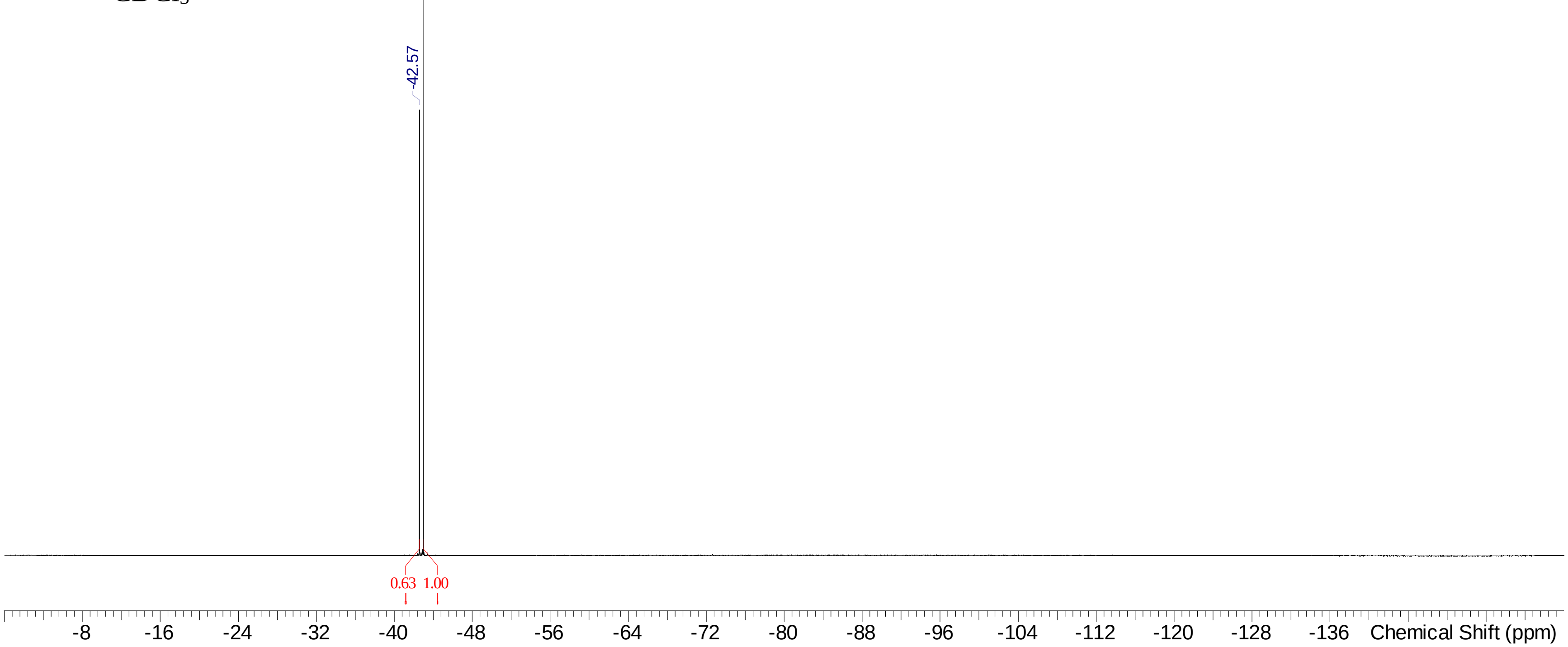


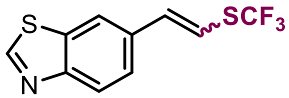
^{1}H NMR (500 MHz)
$CDCl_3$



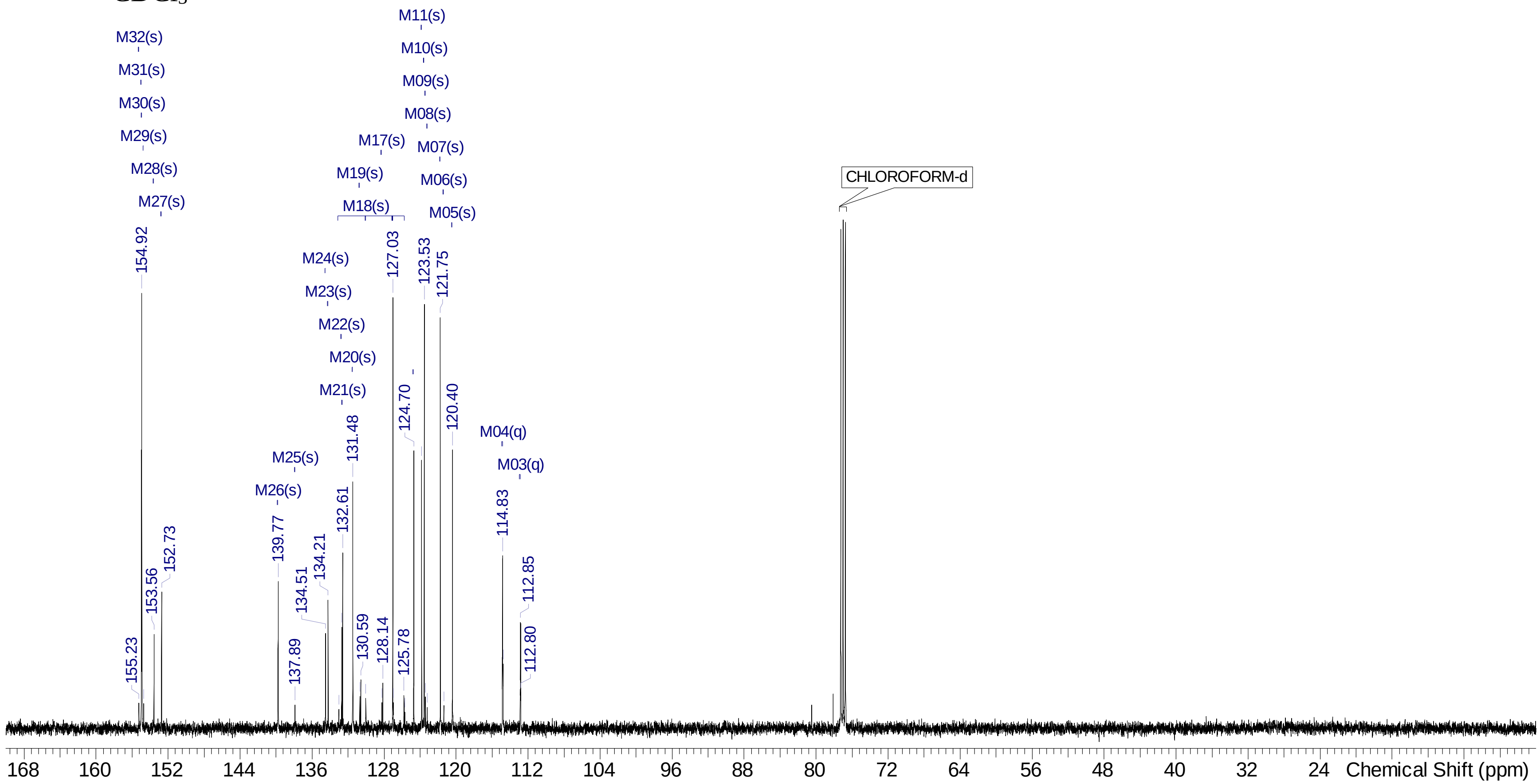


^{19}F NMR (471 MHz)
$CDCl_3$



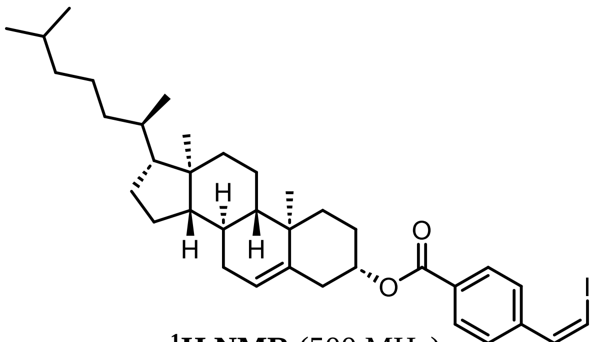


^{13}C NMR (126 MHz)
$CDCl_3$

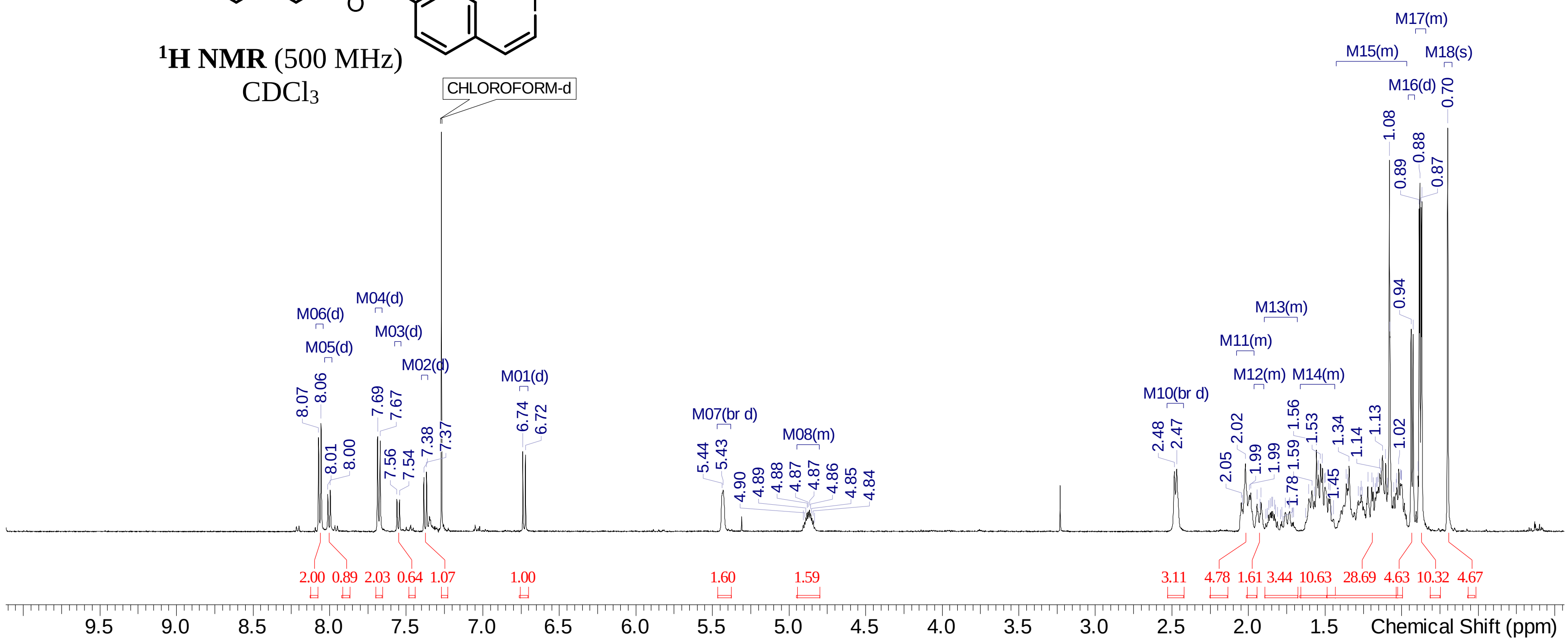


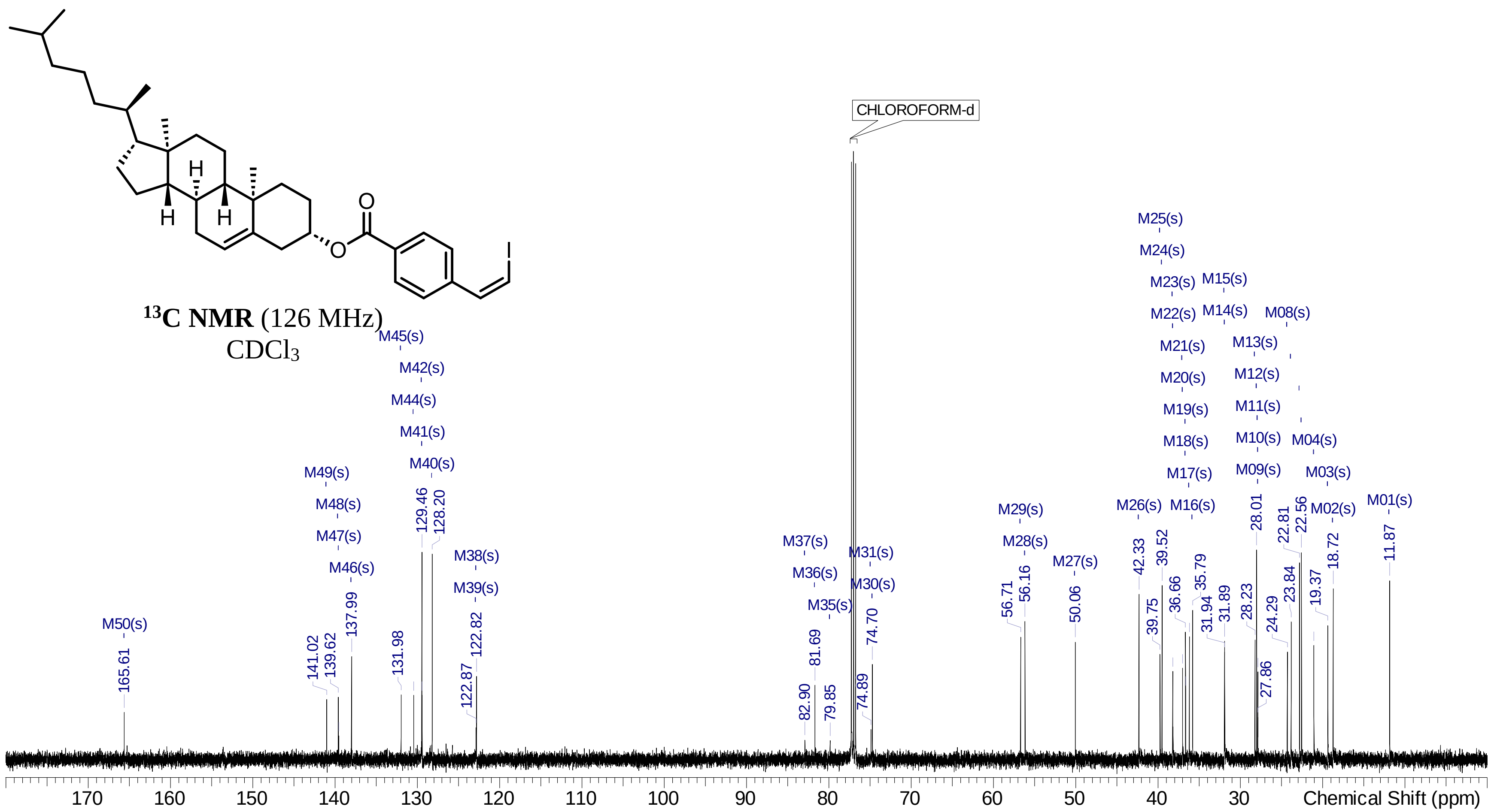
Biologically Active Substrates

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*Z*)-2-iodovinyl)benzoate



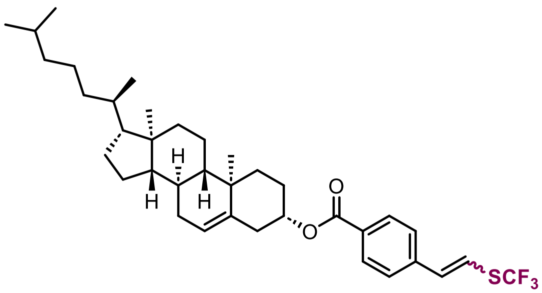
^{1}H NMR (500 MHz)
$CDCl_3$



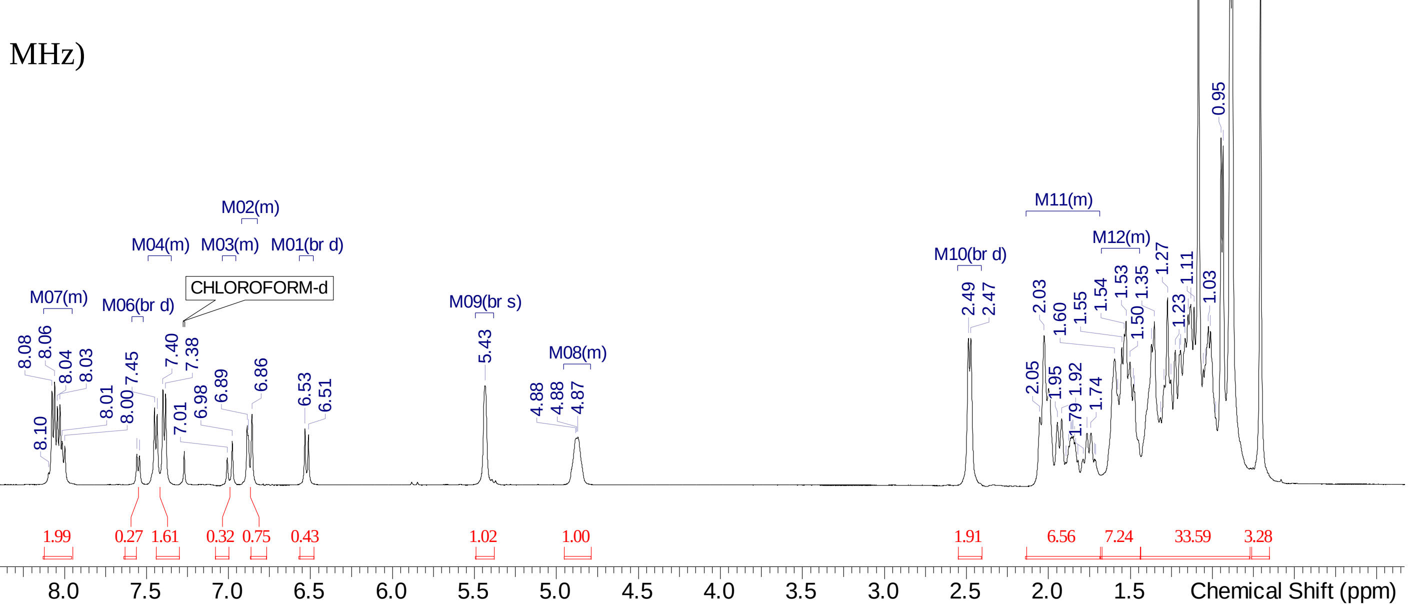


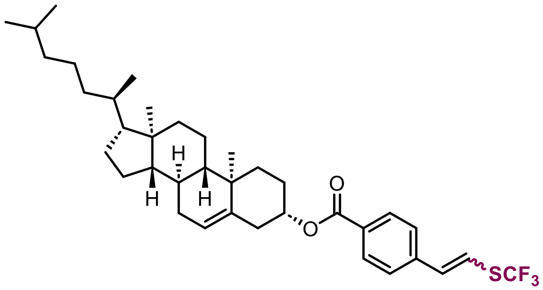
^{13}C NMR (126 MHz)
$CDCl_3$

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(2-((trifluoromethyl)thio)vinyl)benzoate (3al)

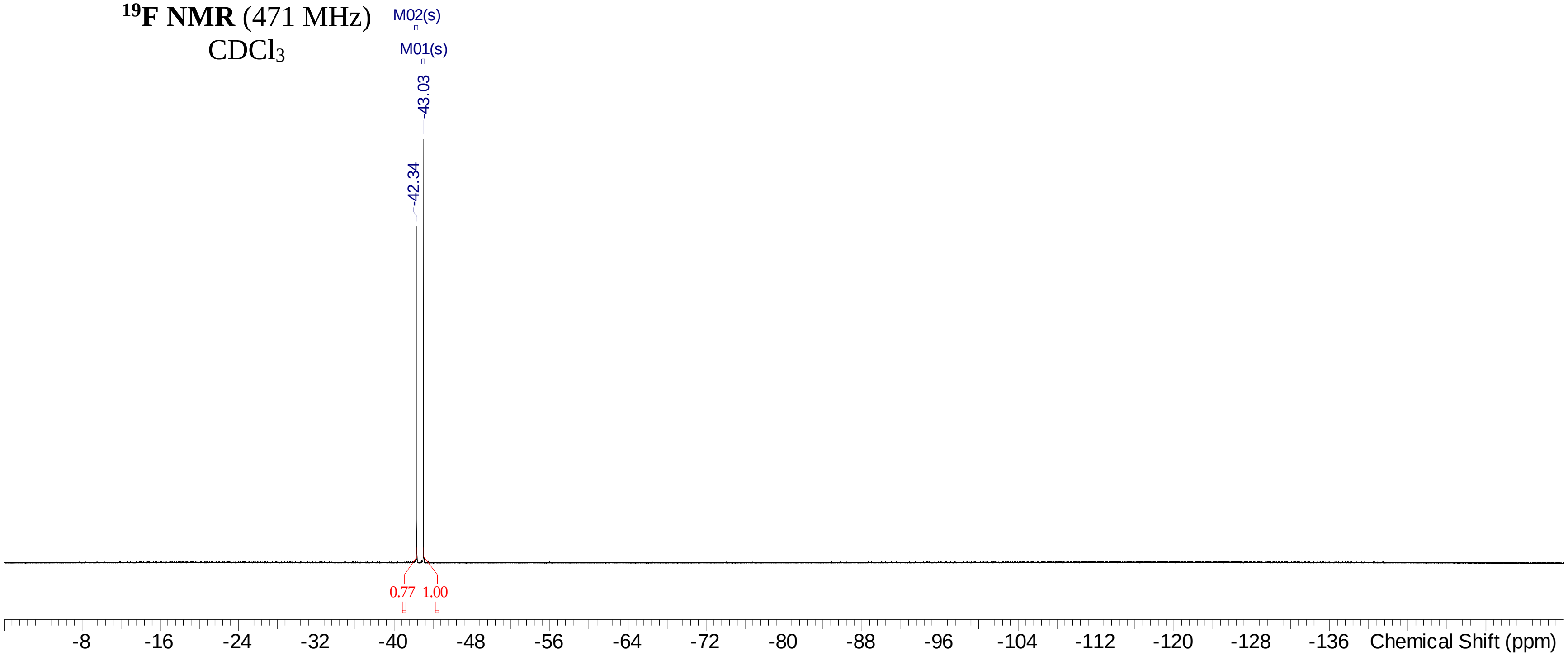


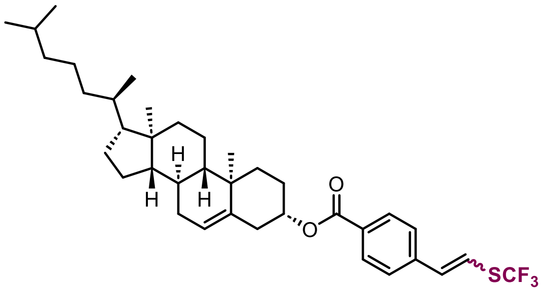
^{1}H NMR (500 MHz)
$CDCl_3$



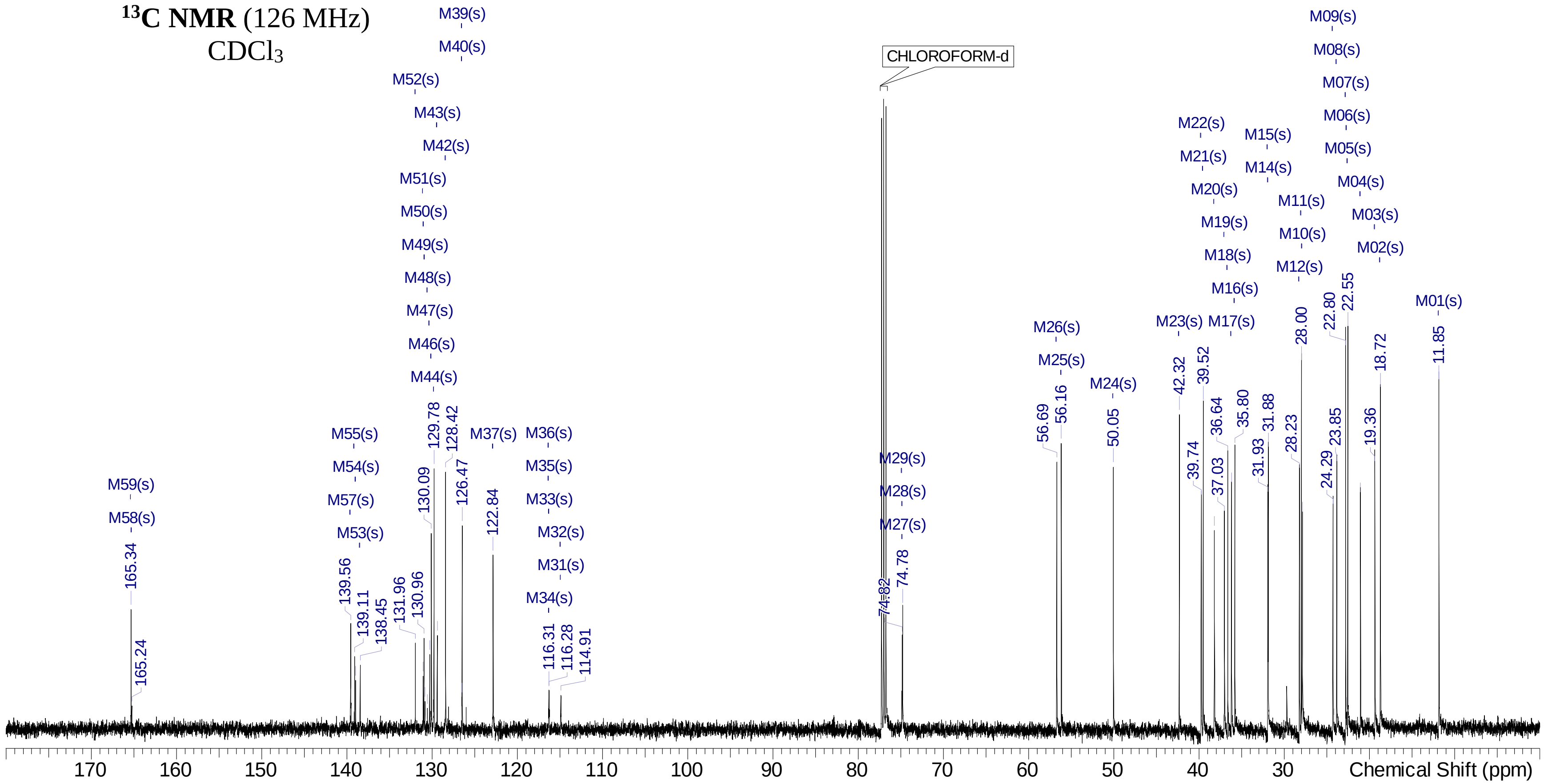


^{19}F NMR (471 MHz)
$CDCl_3$

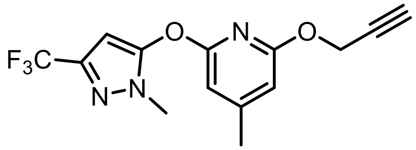




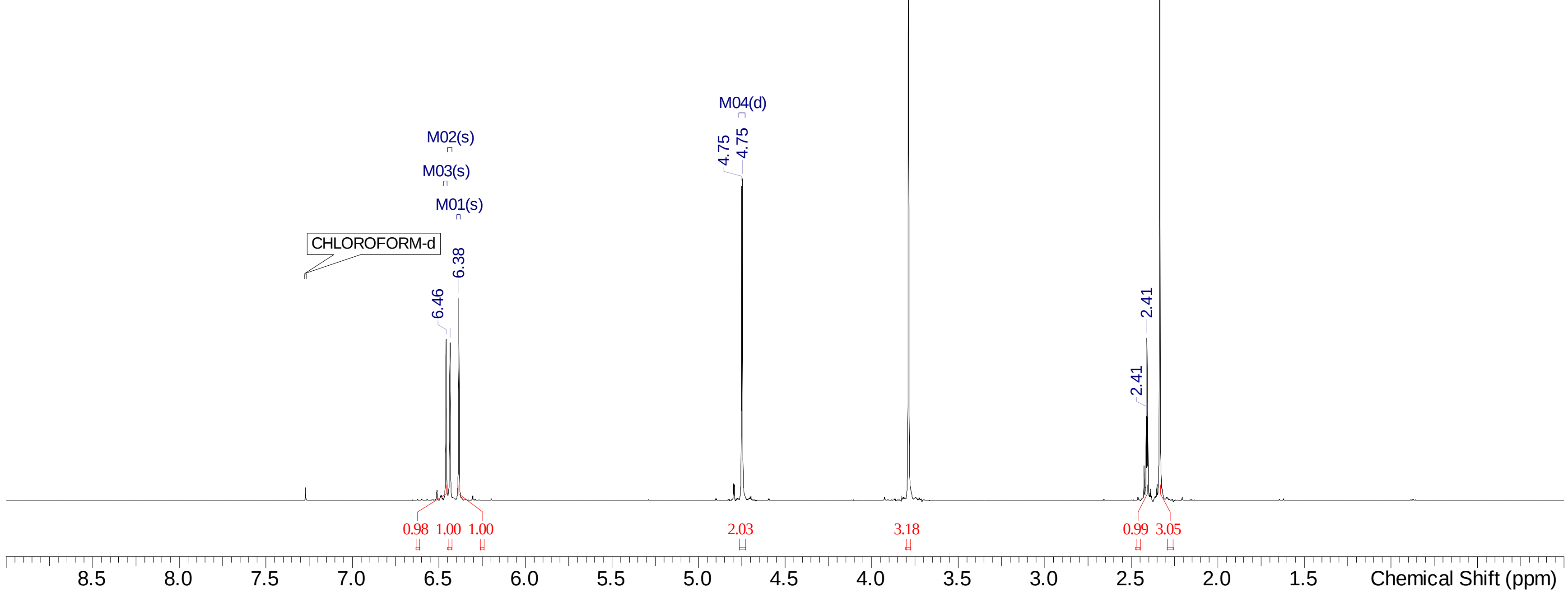
^{13}**C NMR** (126 MHz)
$CDCl_3$

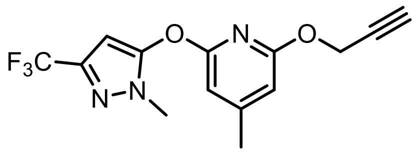


4-Methyl-2-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)-6-(prop-2-yn-1-yloxy)pyridine

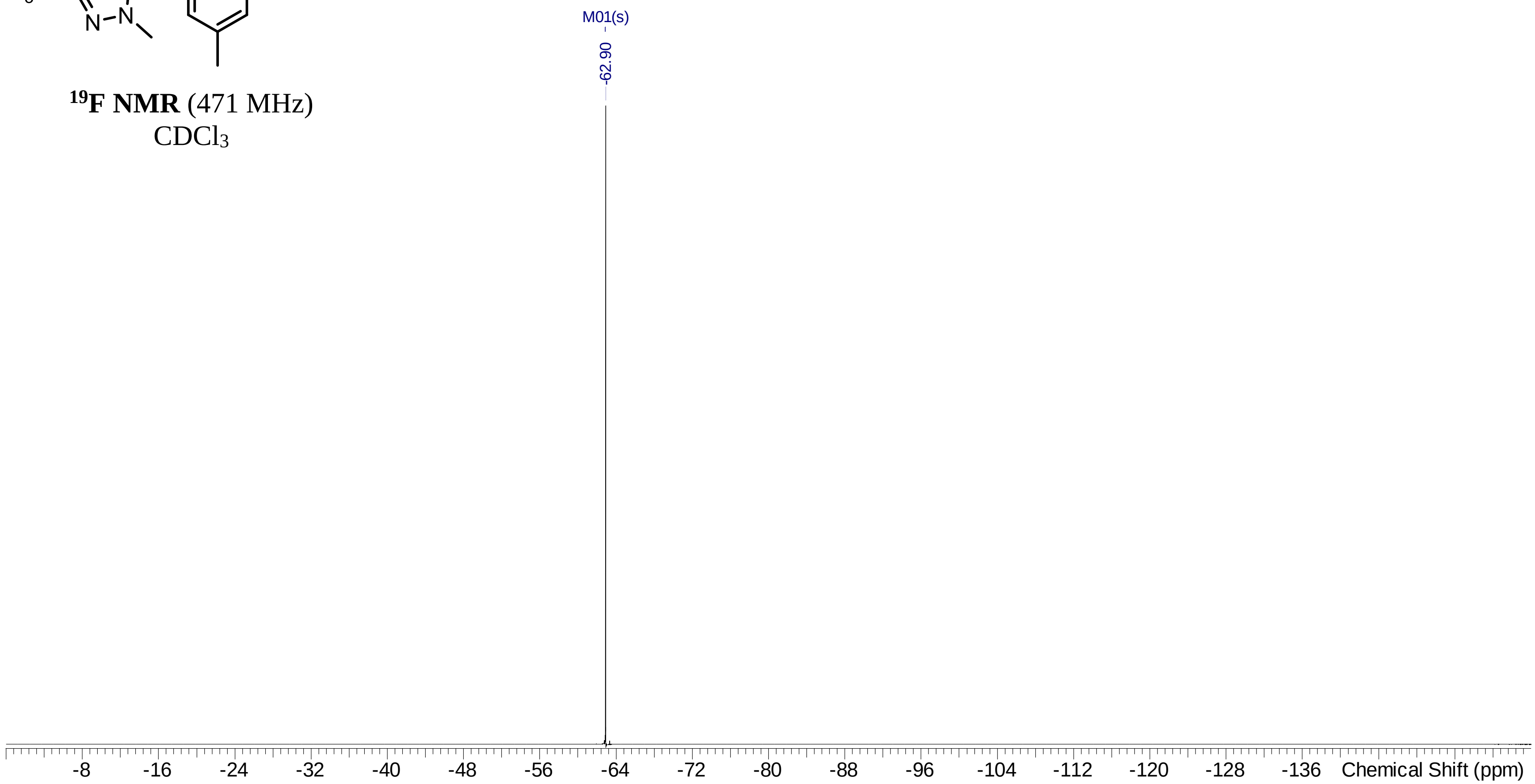


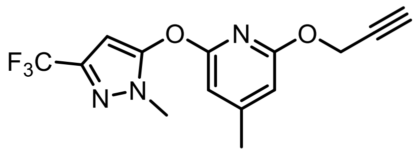
^{1}H NMR (500 MHz)
$CDCl_3$



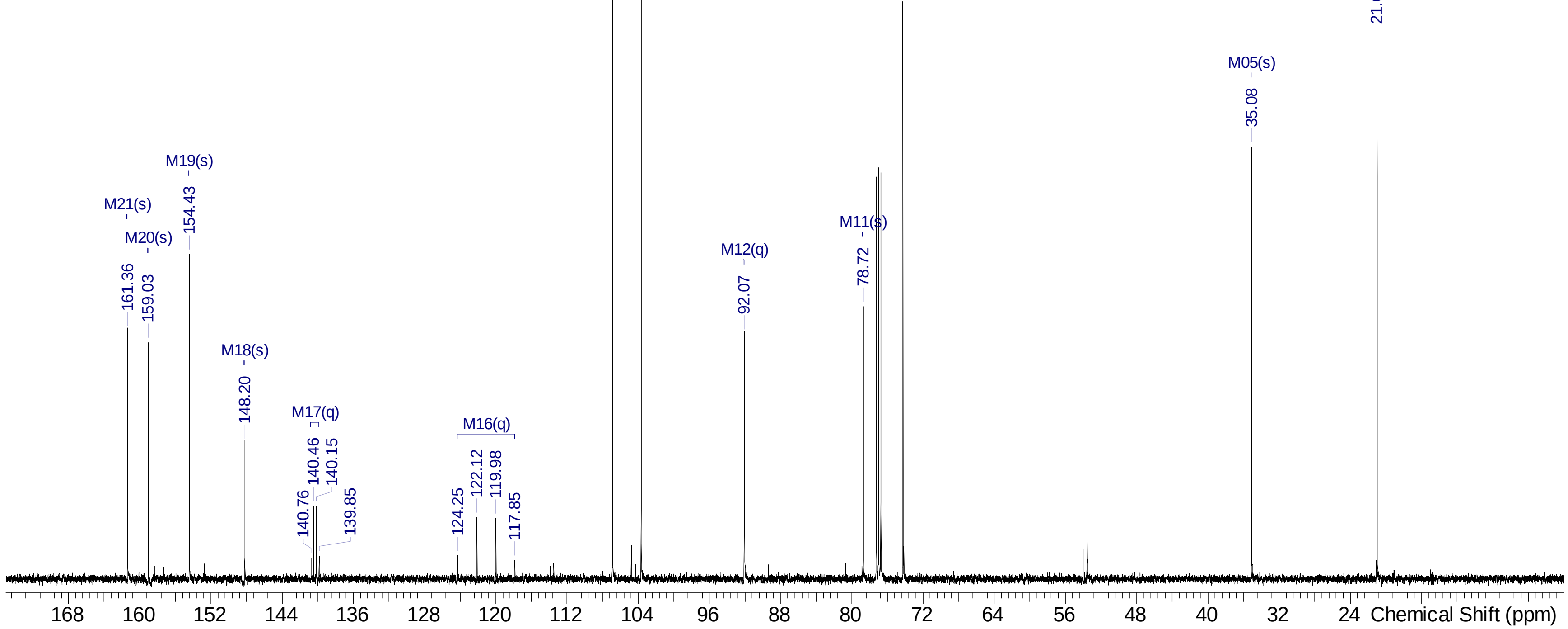


^{19}F NMR (471 MHz)
$CDCl_3$

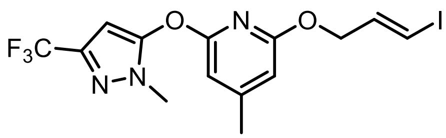




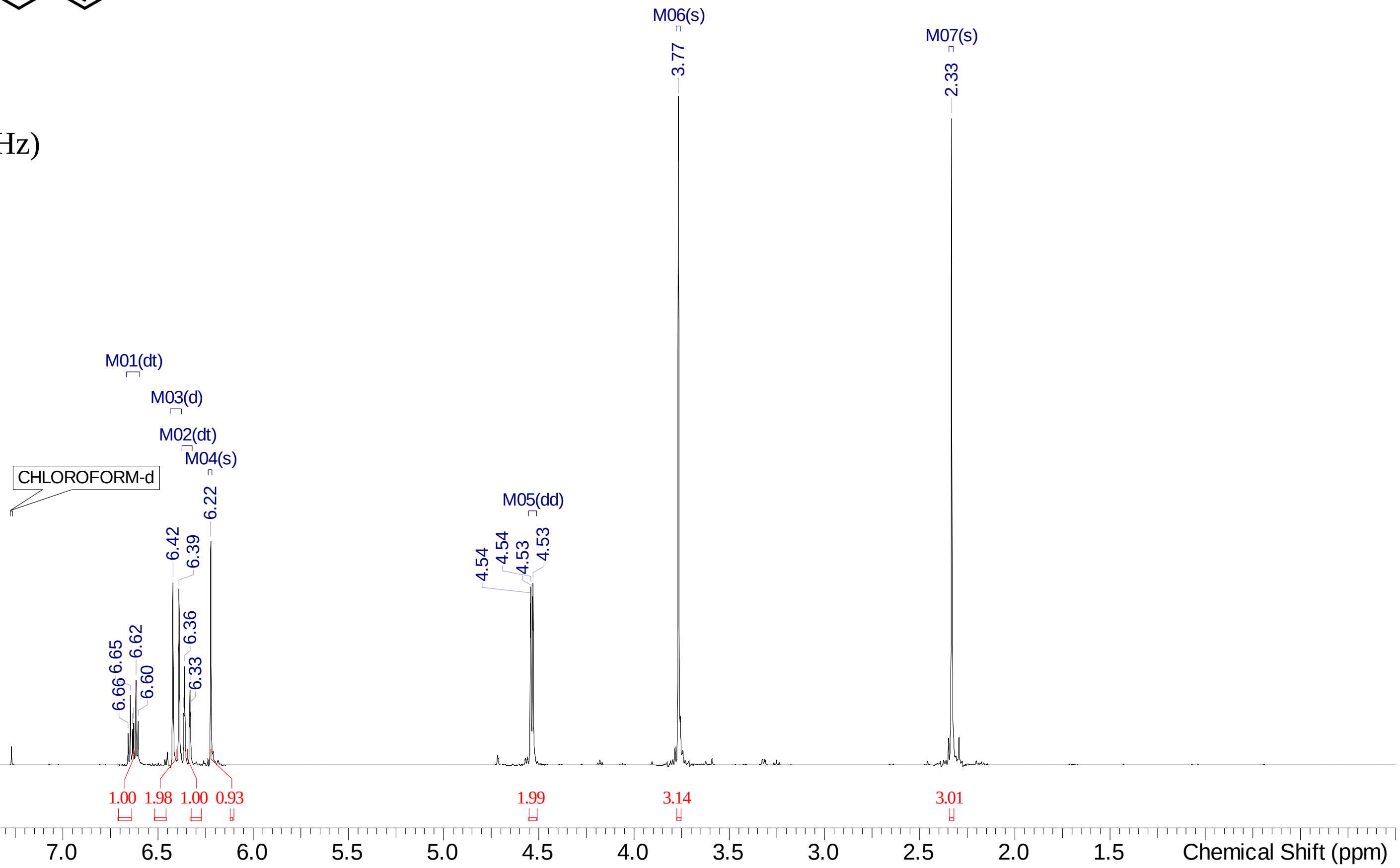
^{13}C NMR (126 MHz)
$CDCl_3$

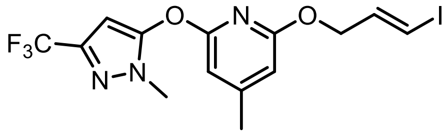


(*E*)-2-((3-iodoallyl)oxy)-4-methyl-6-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)pyridine

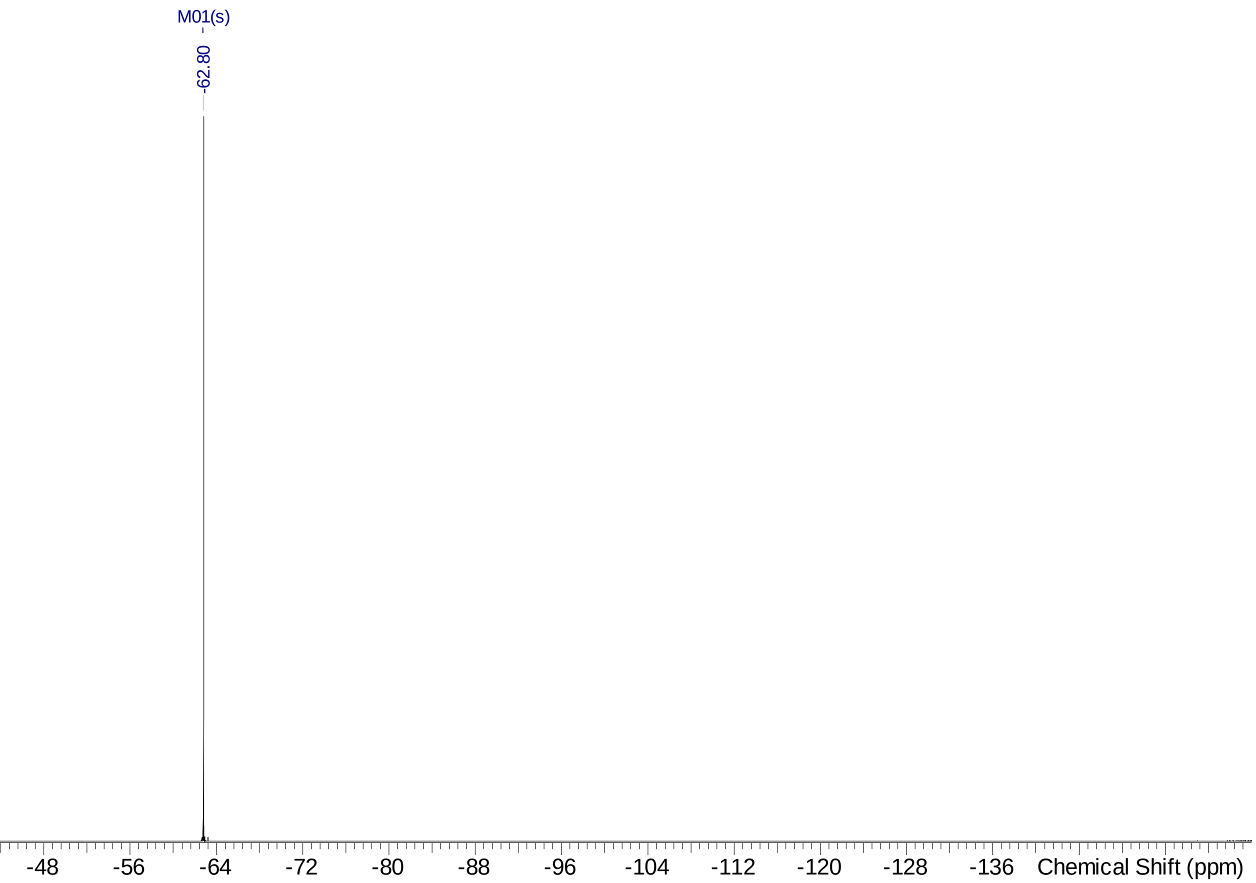


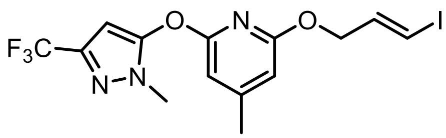
¹H NMR (500 MHz)
$CDCl_3$



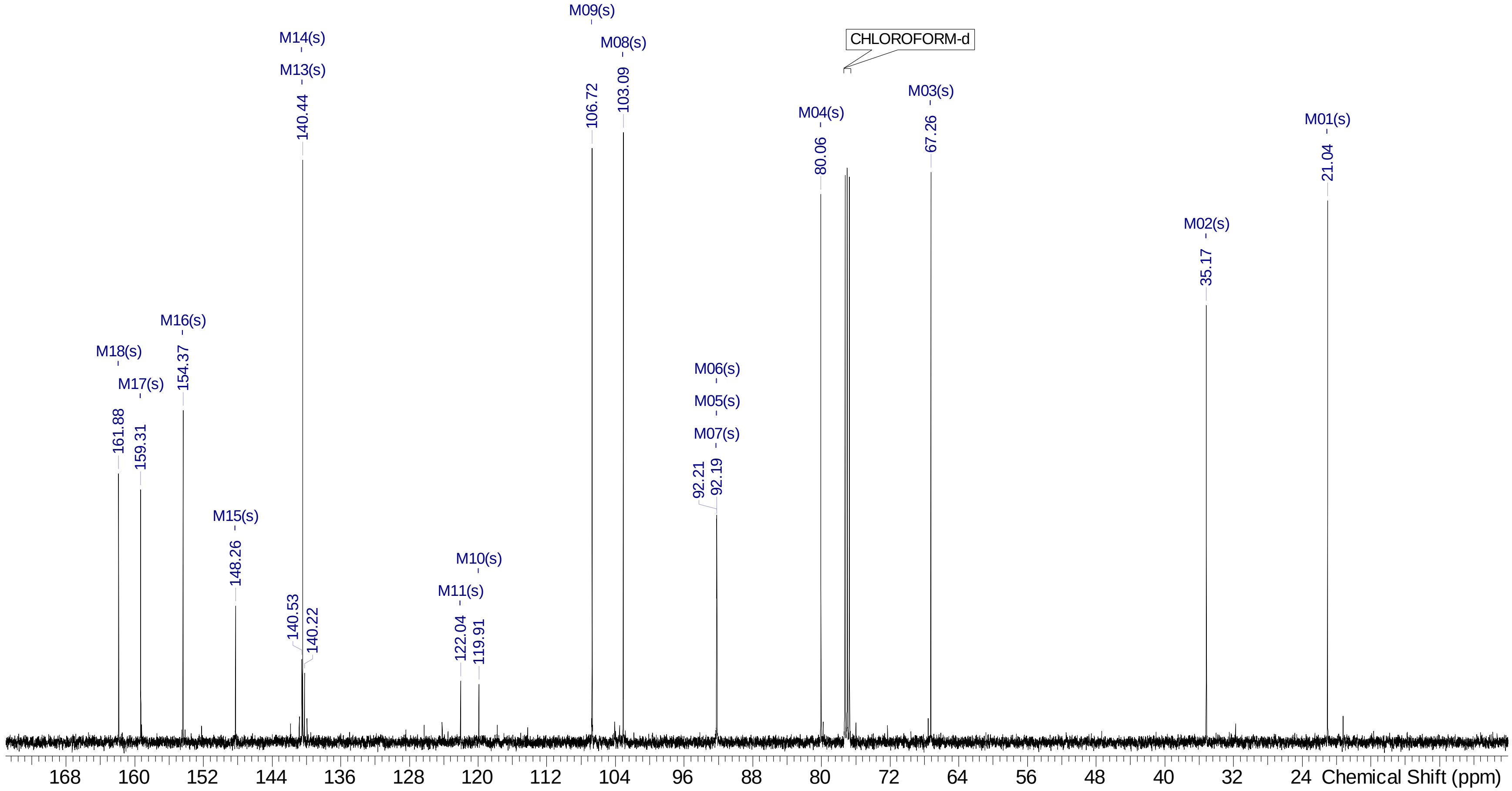


¹⁹F NMR (471 MHz)
$CDCl_3$

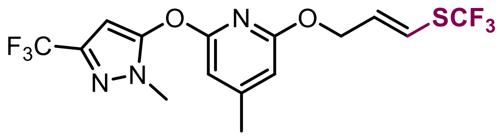




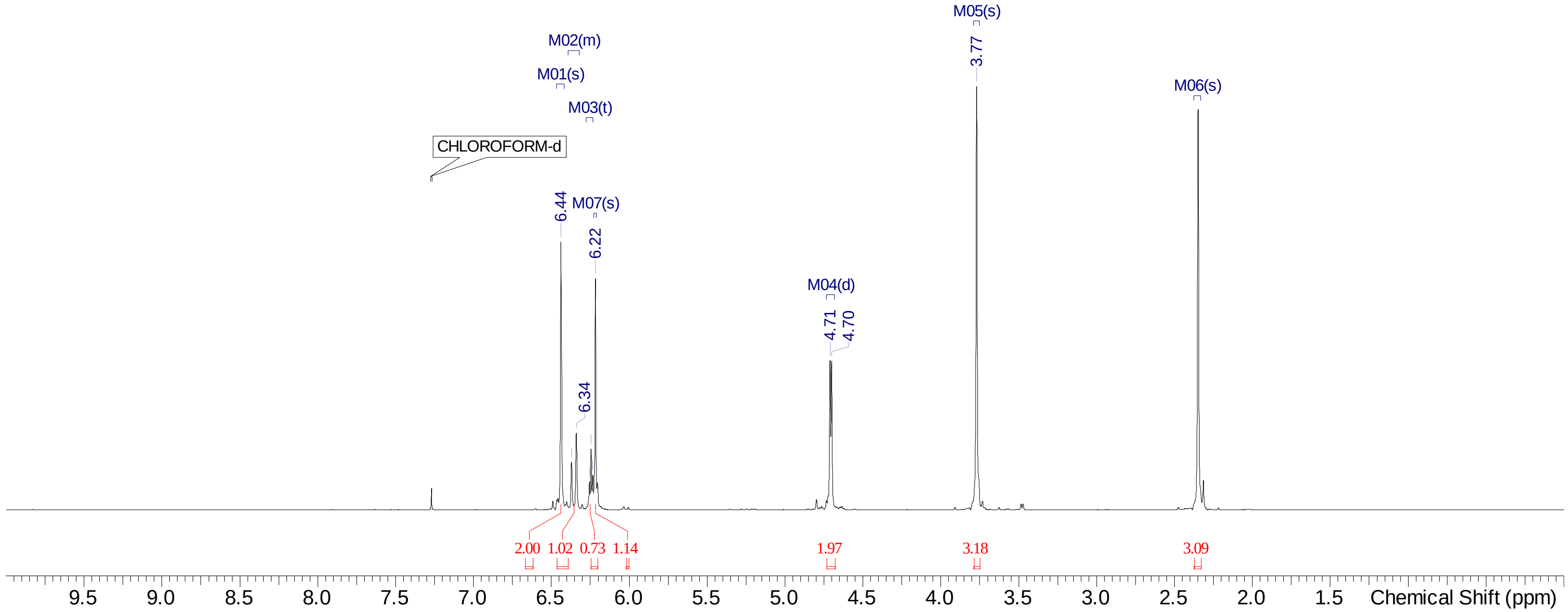
^{13}C NMR (126 MHz)
$CDCl_3$

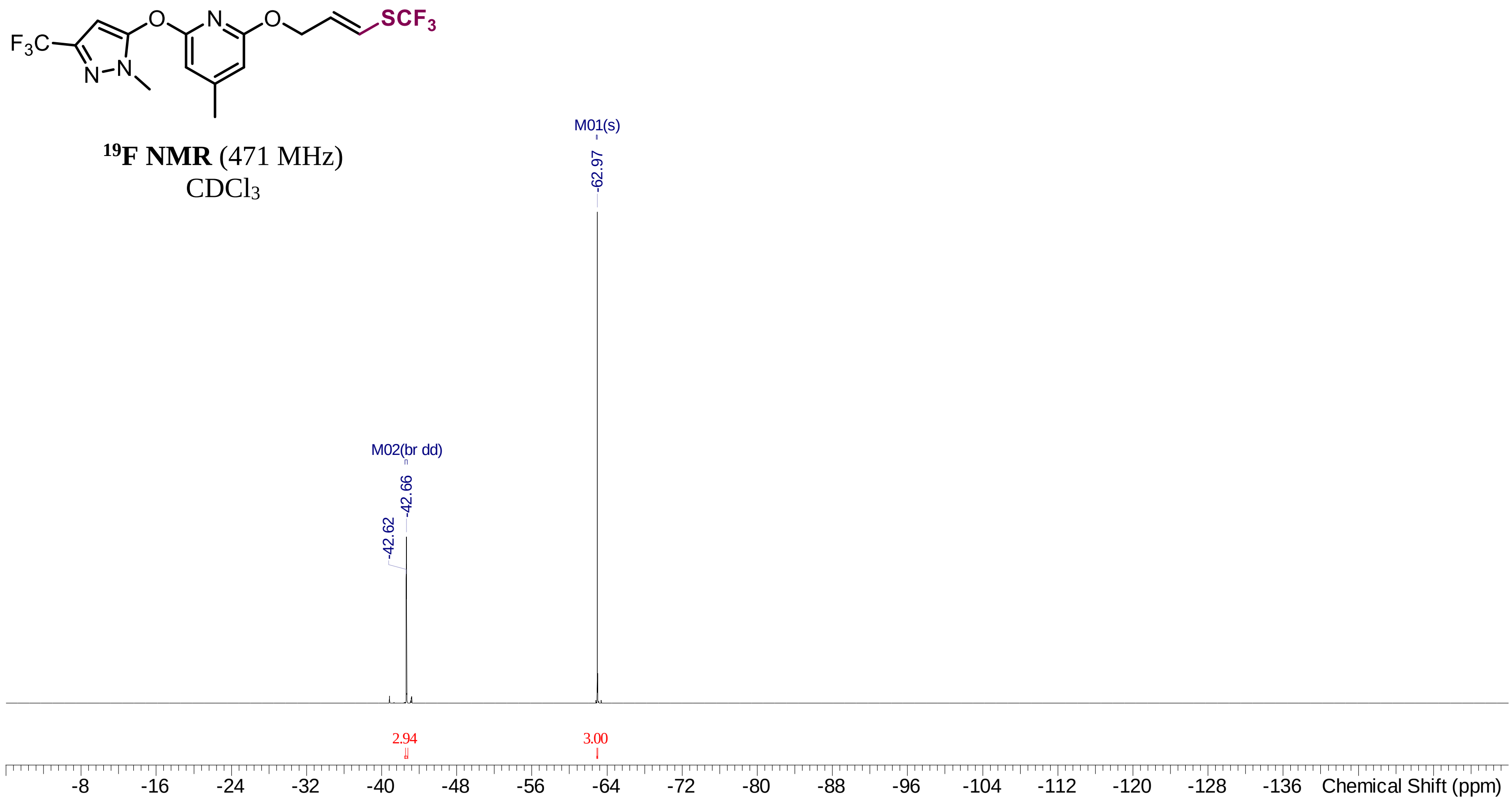


(*E*)-4-methyl-2-((1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)oxy)-6-((3-((trifluoromethyl)thio)allyl)oxy)pyridine (1a)

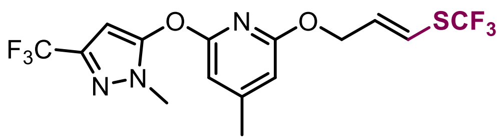


^{1}H NMR (500 MHz)
$CDCl_3$

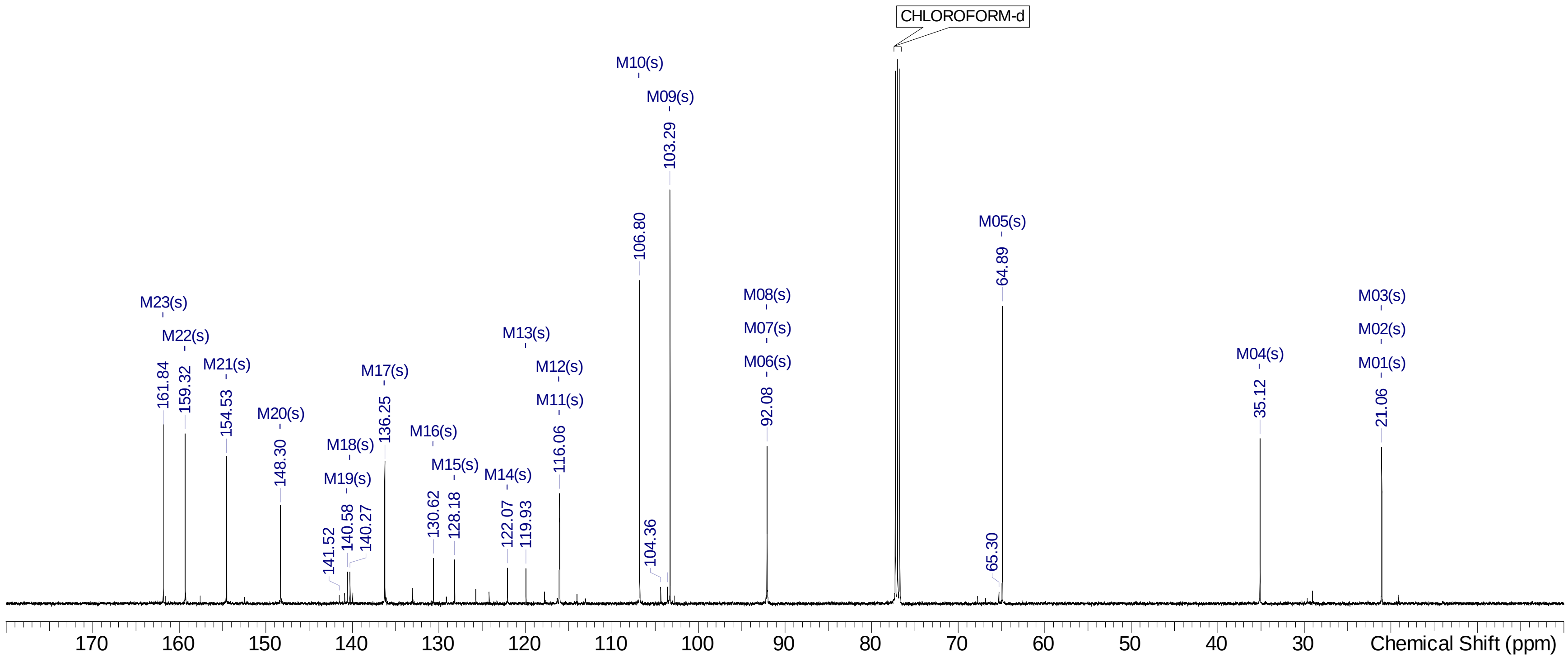




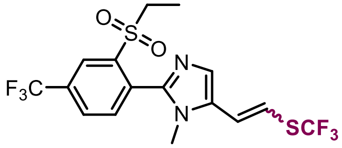
^{19}F NMR (471 MHz)
$CDCl_3$



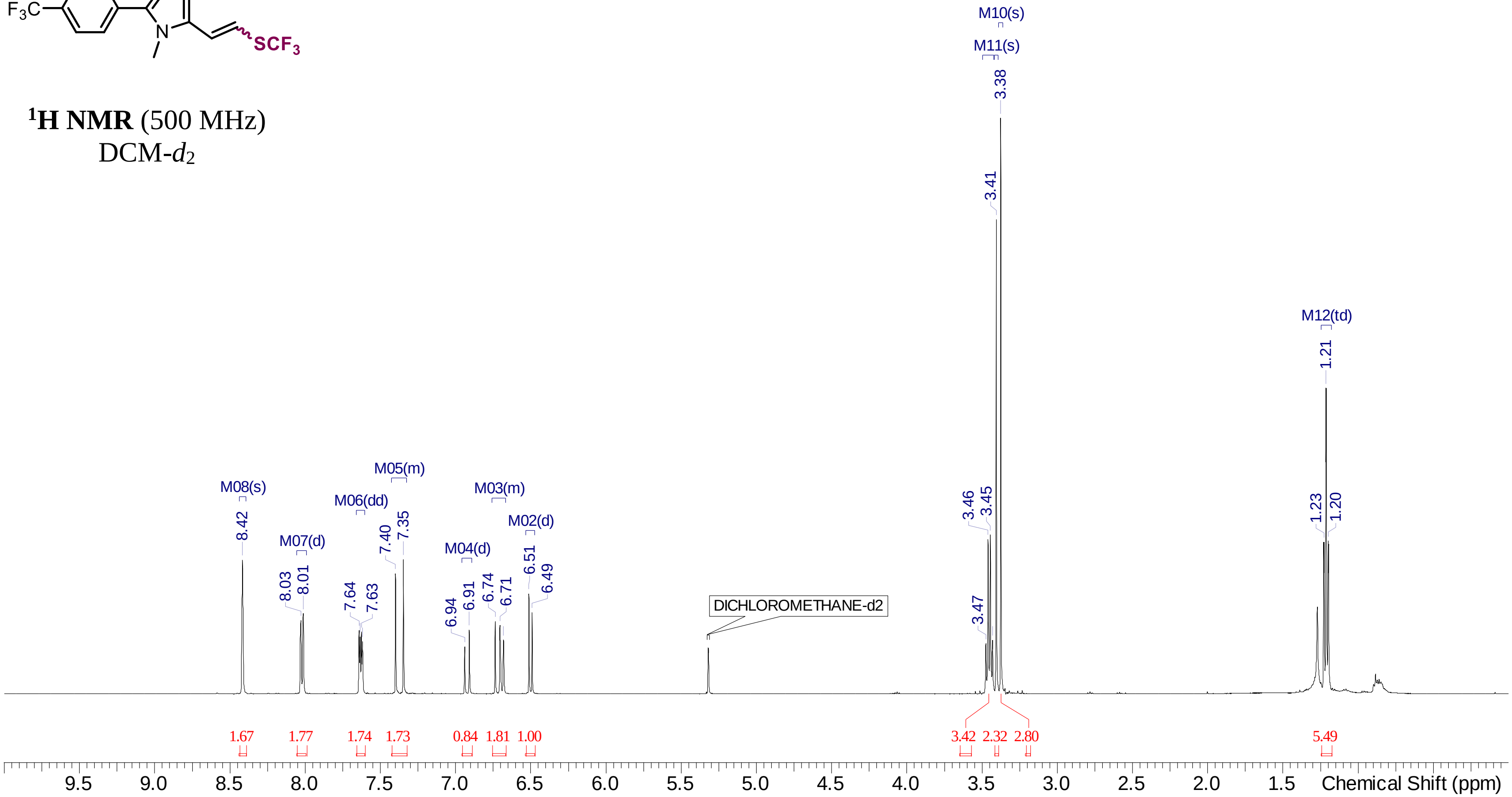
^{13}C NMR (126 MHz)
$CDCl_3$

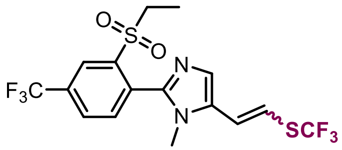


2-(2-(Ethylsulfonyl)-4-(trifluoromethyl)phenyl)-1-methyl-5-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole (1b)

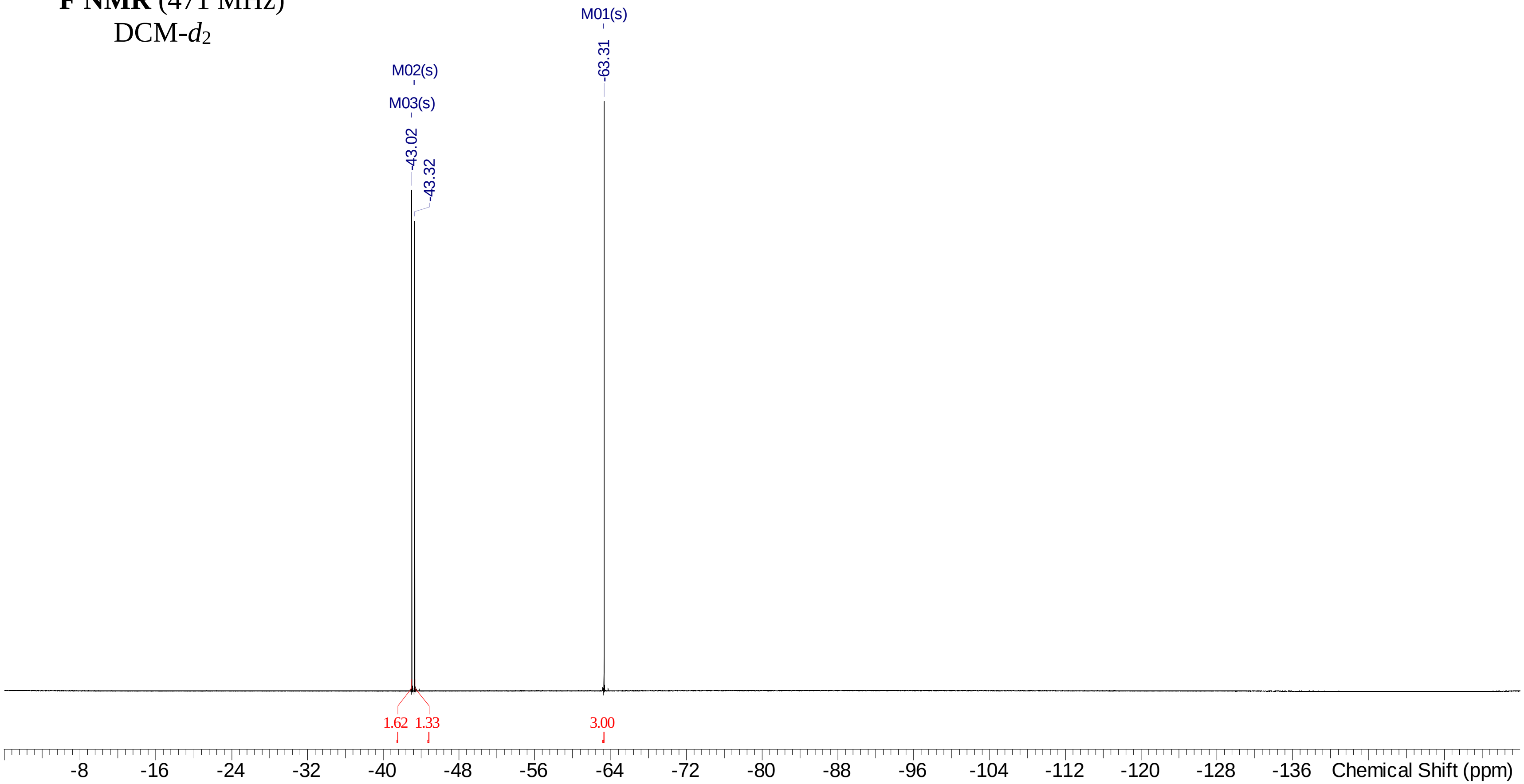


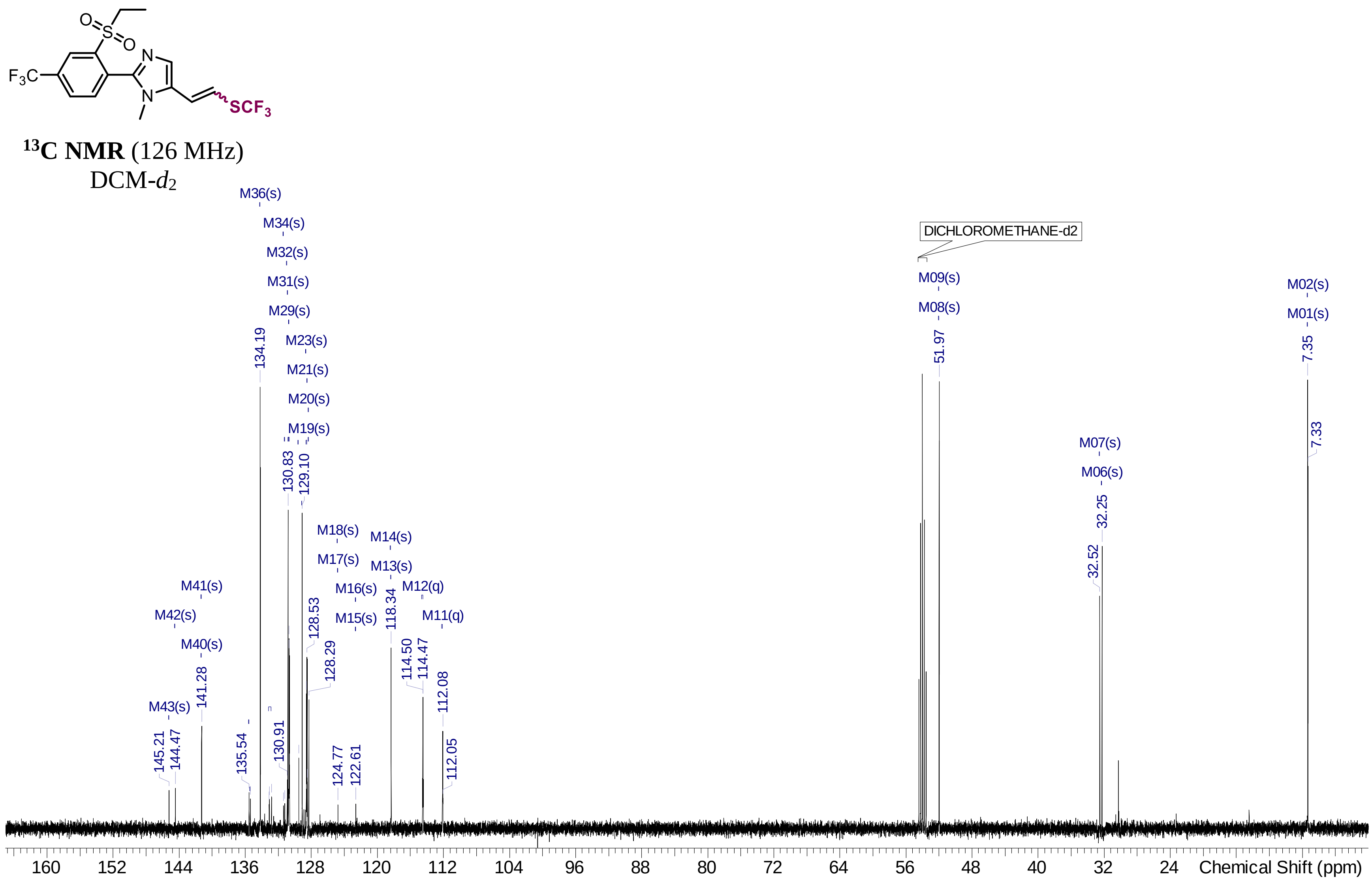
^{1}H NMR (500 MHz)
DCM-d_2



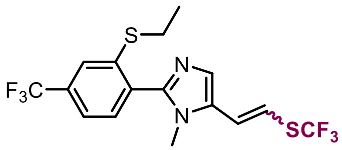


[19]F NMR (471 MHz)
DCM-d_2

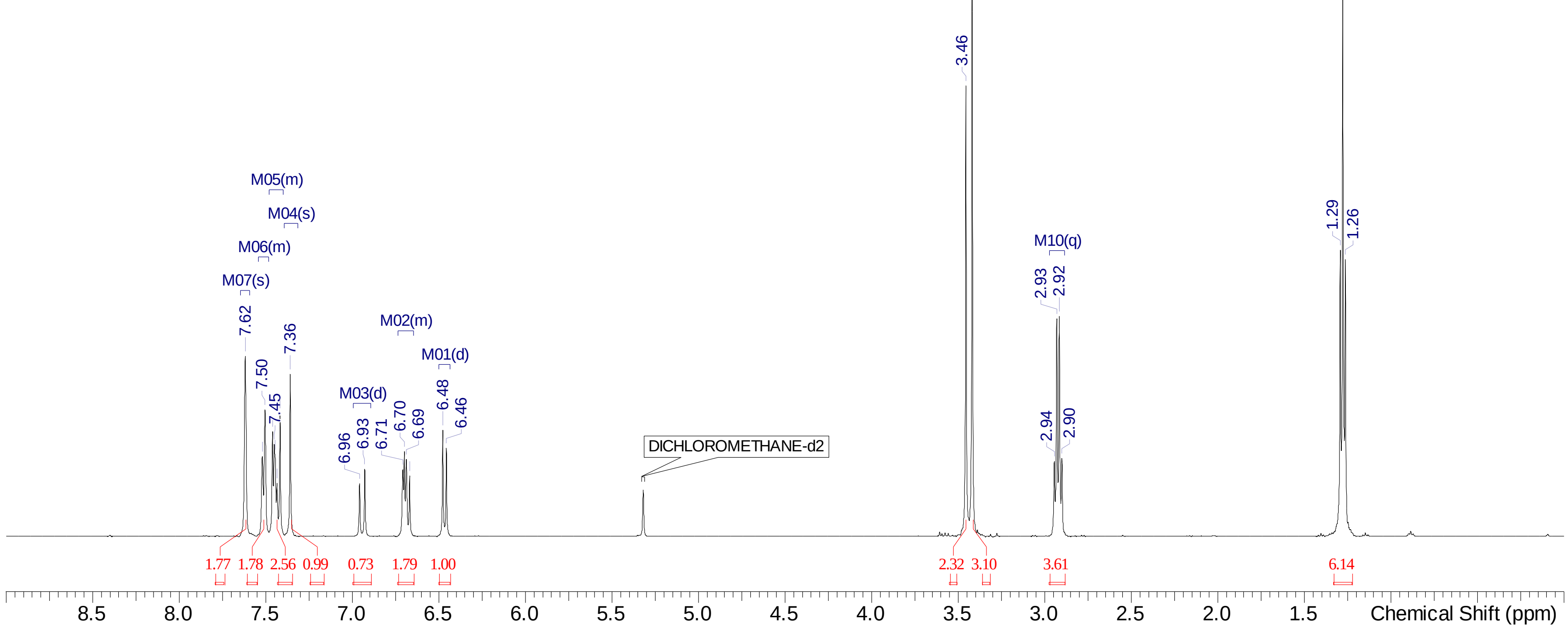


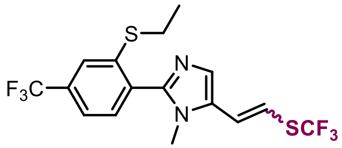

F3C
O
S
O
N
N
SCF3
13C NMR (126 MHz)
DCM-d2
DICHLOROMETHANE-d2
M36(s)
M34(s)
M32(s)
M31(s)
M29(s)
M23(s)
M21(s)
M20(s)
M19(s)
134.19
130.83
129.10
M18(s)
M17(s)
M16(s)
M15(s)
M14(s)
M13(s)
M12(q)
M11(q)
M41(s)
M42(s)
M40(s)
M43(s)
145.21
144.47
141.28
135.54
130.91
128.53
128.29
124.77
122.61
118.34
114.50
114.47
112.08
112.05
M09(s)
M08(s)
51.97
M07(s)
M06(s)
32.25
32.52
M02(s)
M01(s)
7.35
7.33
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

2-(2-(Ethylthio)-4-(trifluoromethyl)phenyl)-1-methyl-5-(2-((trifluoromethyl)thio)vinyl)-1*H*-imidazole (1c)

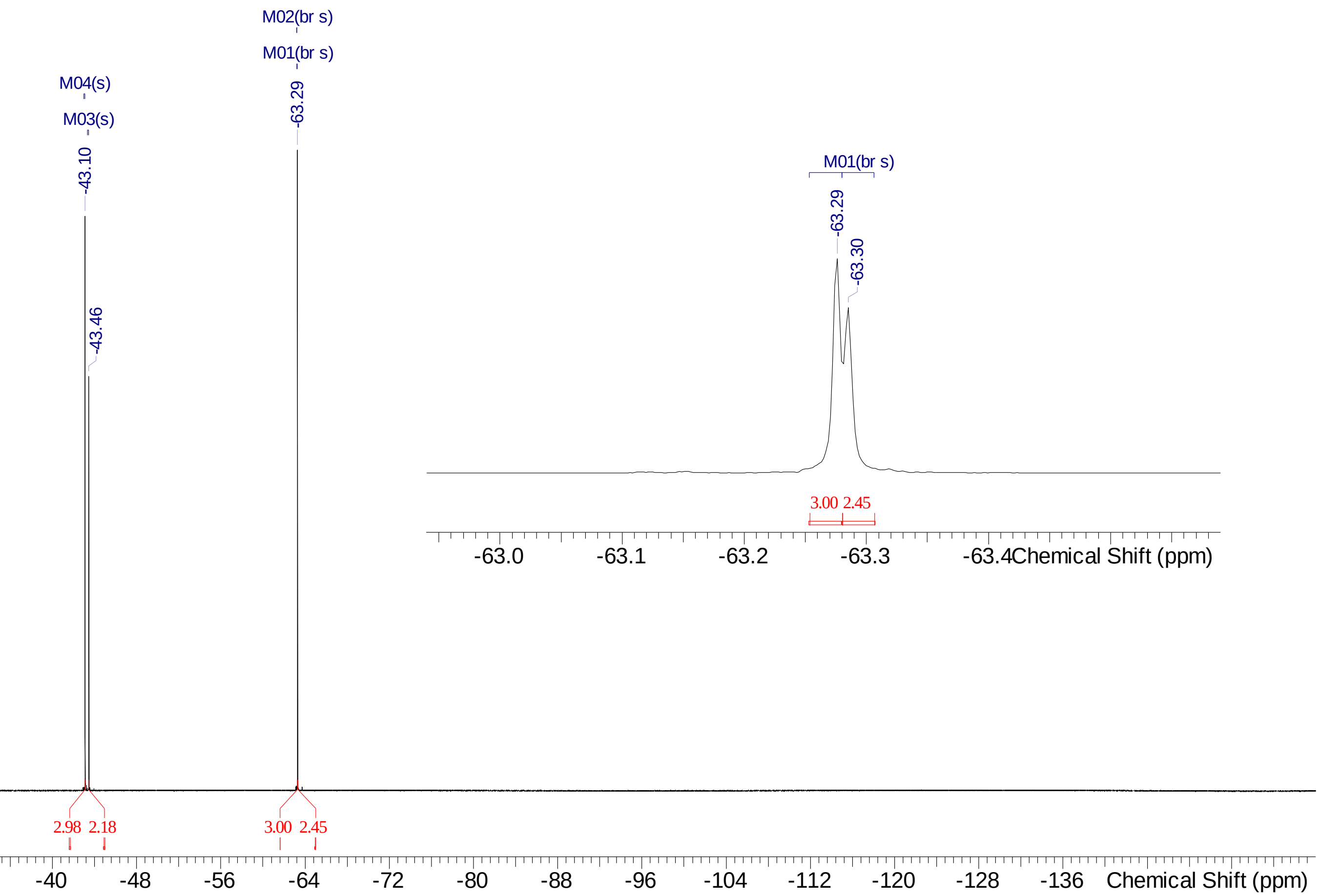


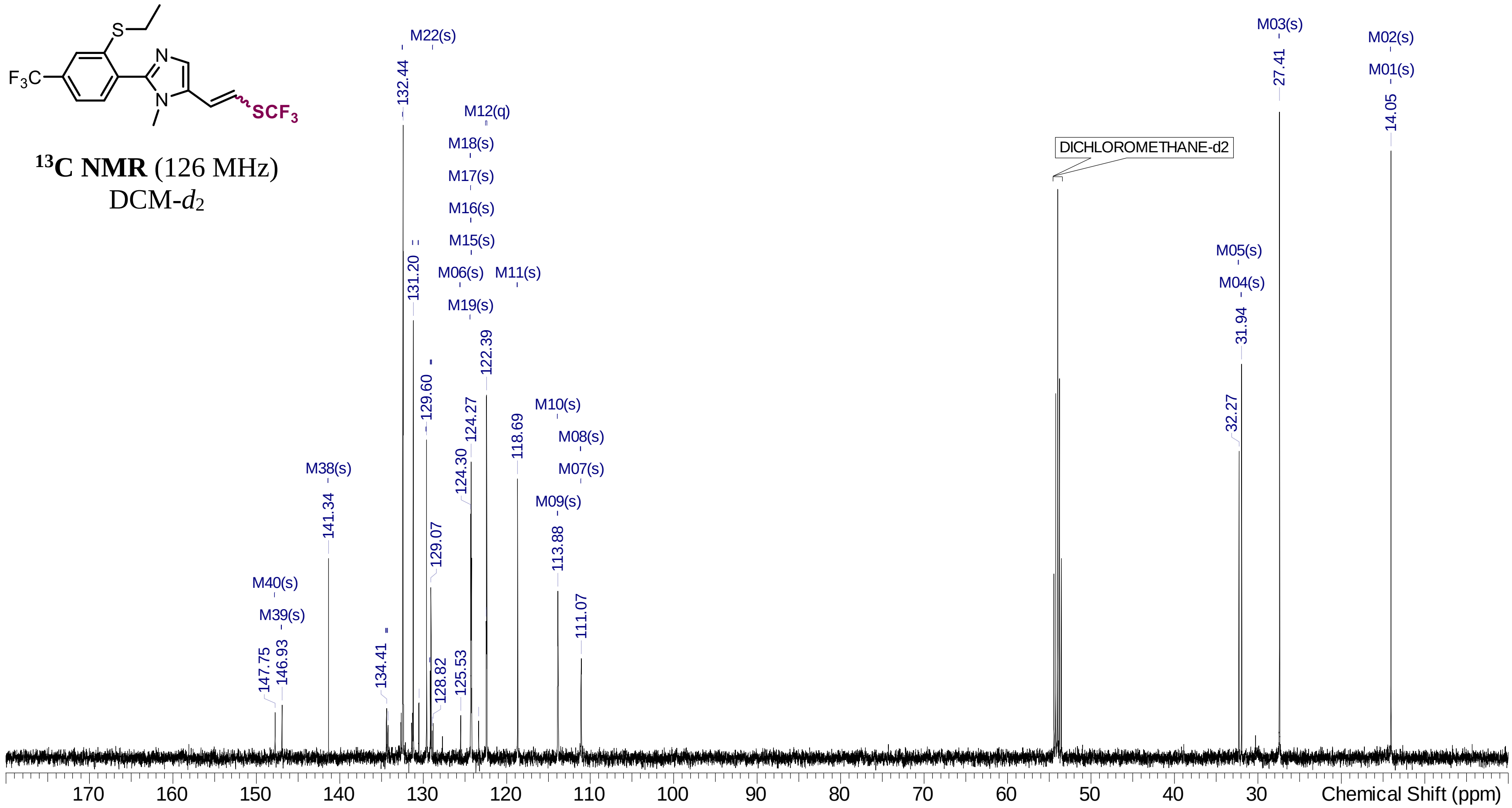
[1]H NMR (500 MHz)
DCM-d_2





^{19}F NMR (471 MHz)
DCM-d_2

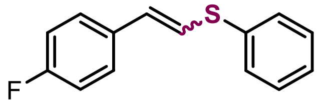




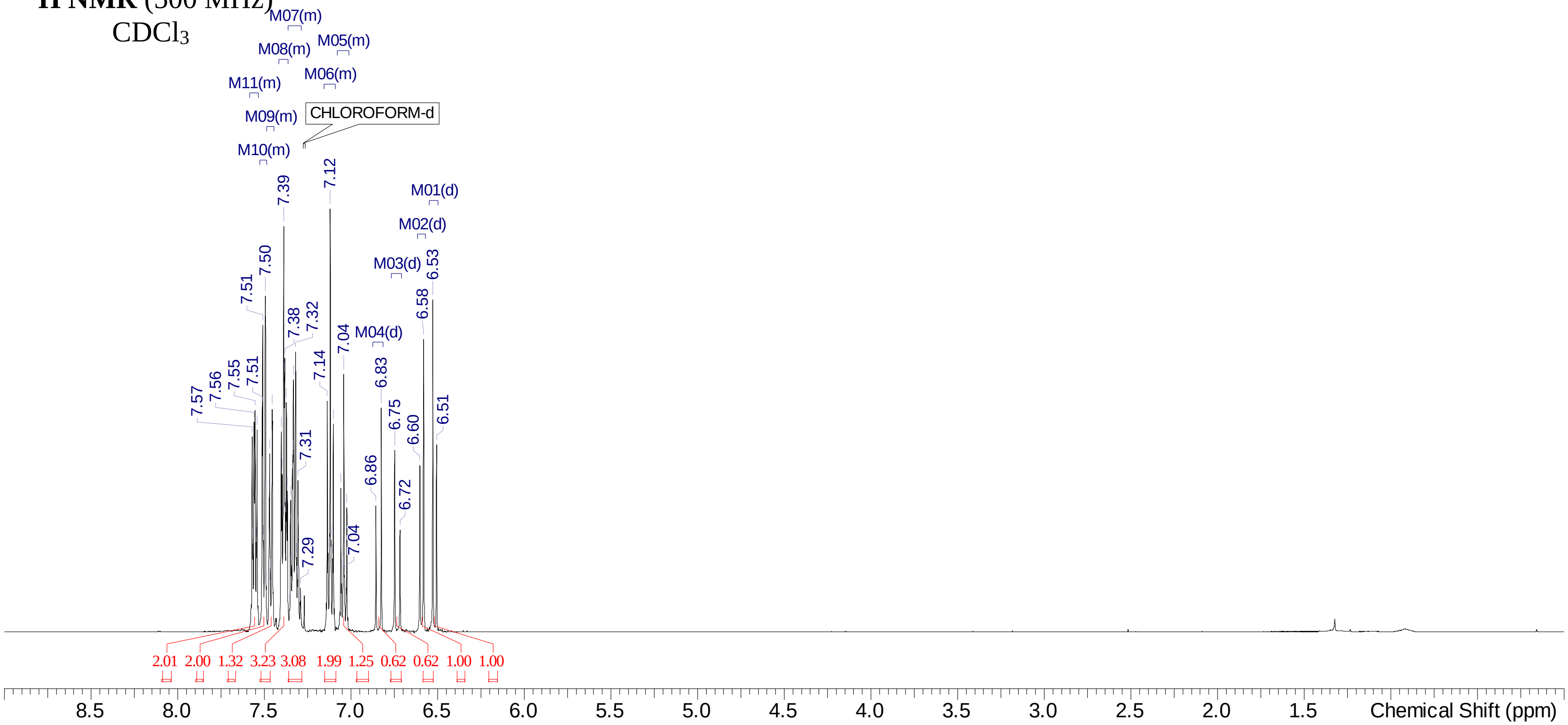
^{13}C NMR (126 MHz)
DCM-d_2

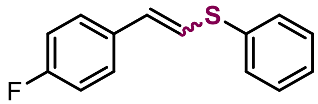
Alkenyl Sulfide Products

2-(2-((trifluoromethyl)thio)vinyl)benzo[b]thiophene (5a)

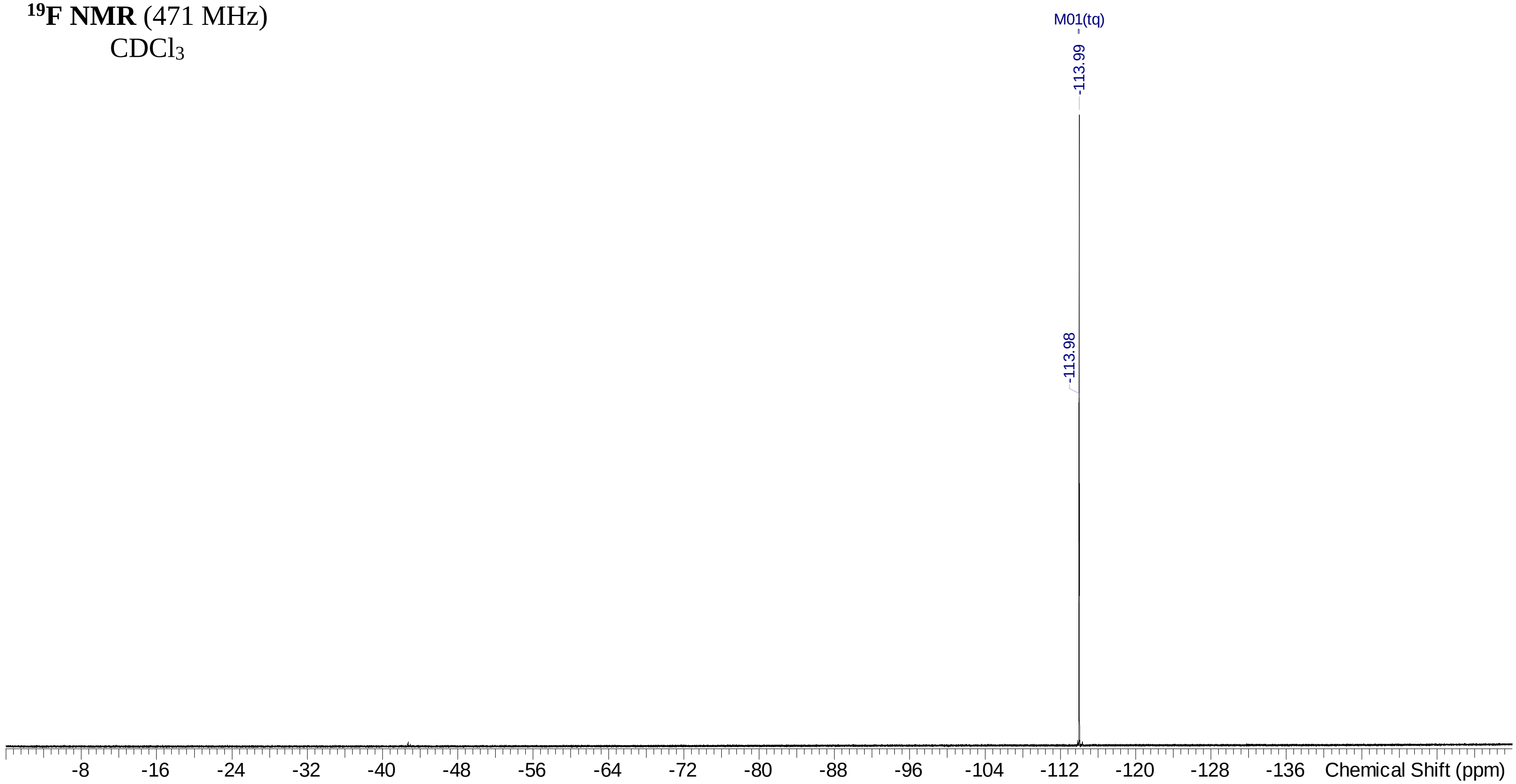


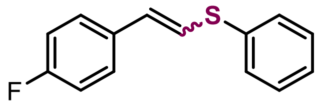
^{1}H NMR (500 MHz)
CDCl$_3$



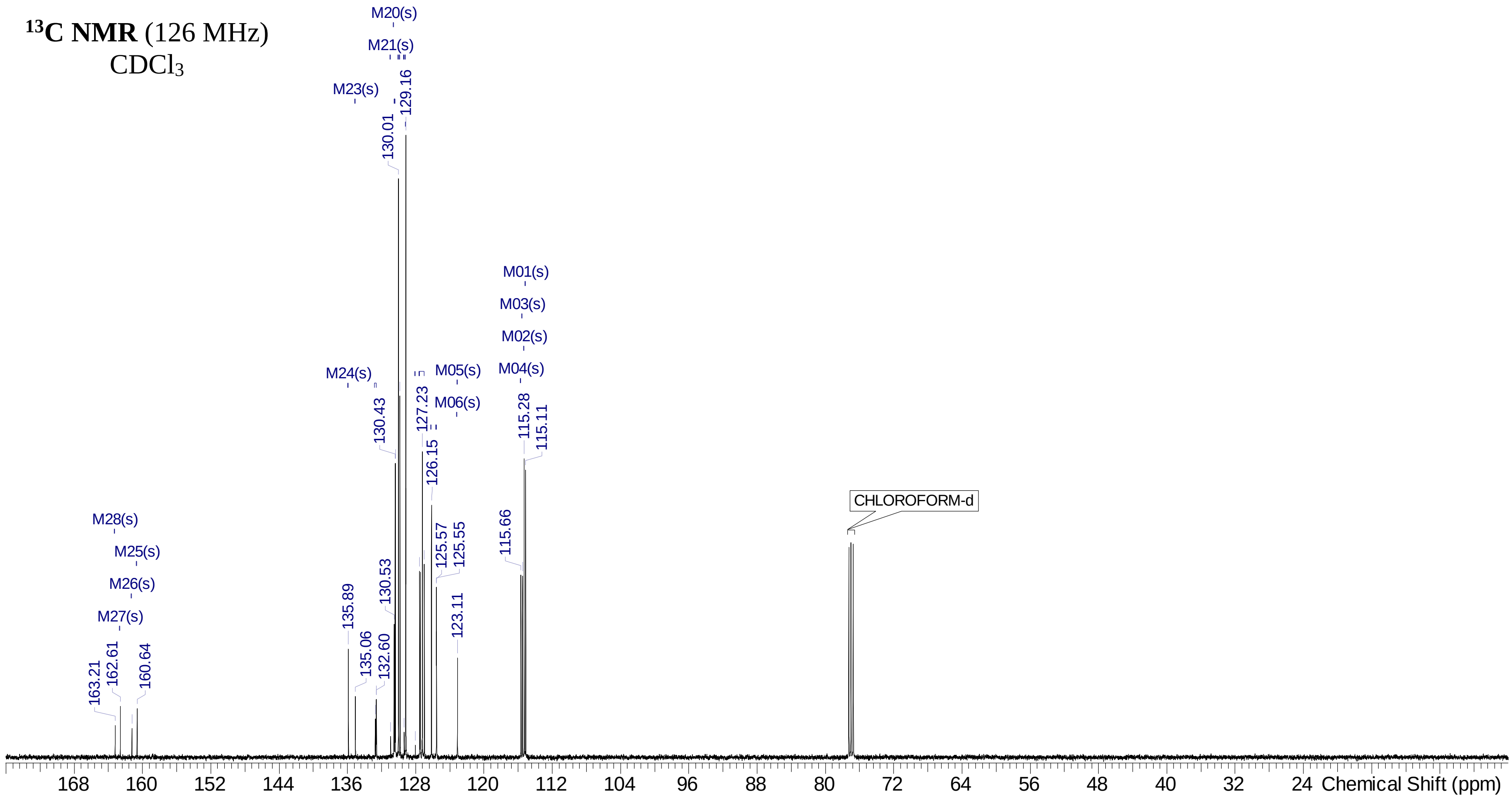


^{19}F NMR (471 MHz)
$CDCl_3$

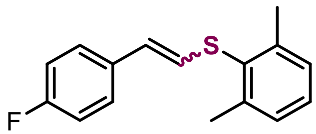




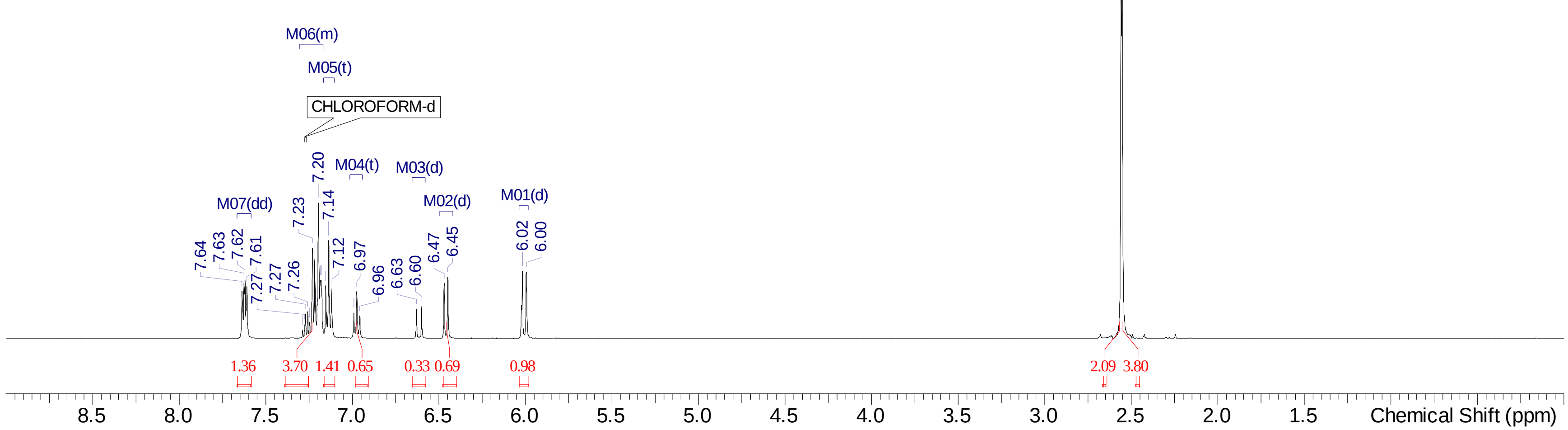
^{13}**C NMR** (126 MHz)
$CDCl_3$

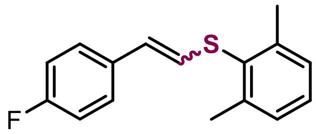


(2,6-Dimethylphenyl)(4-fluorostyryl)sulfane (5b)

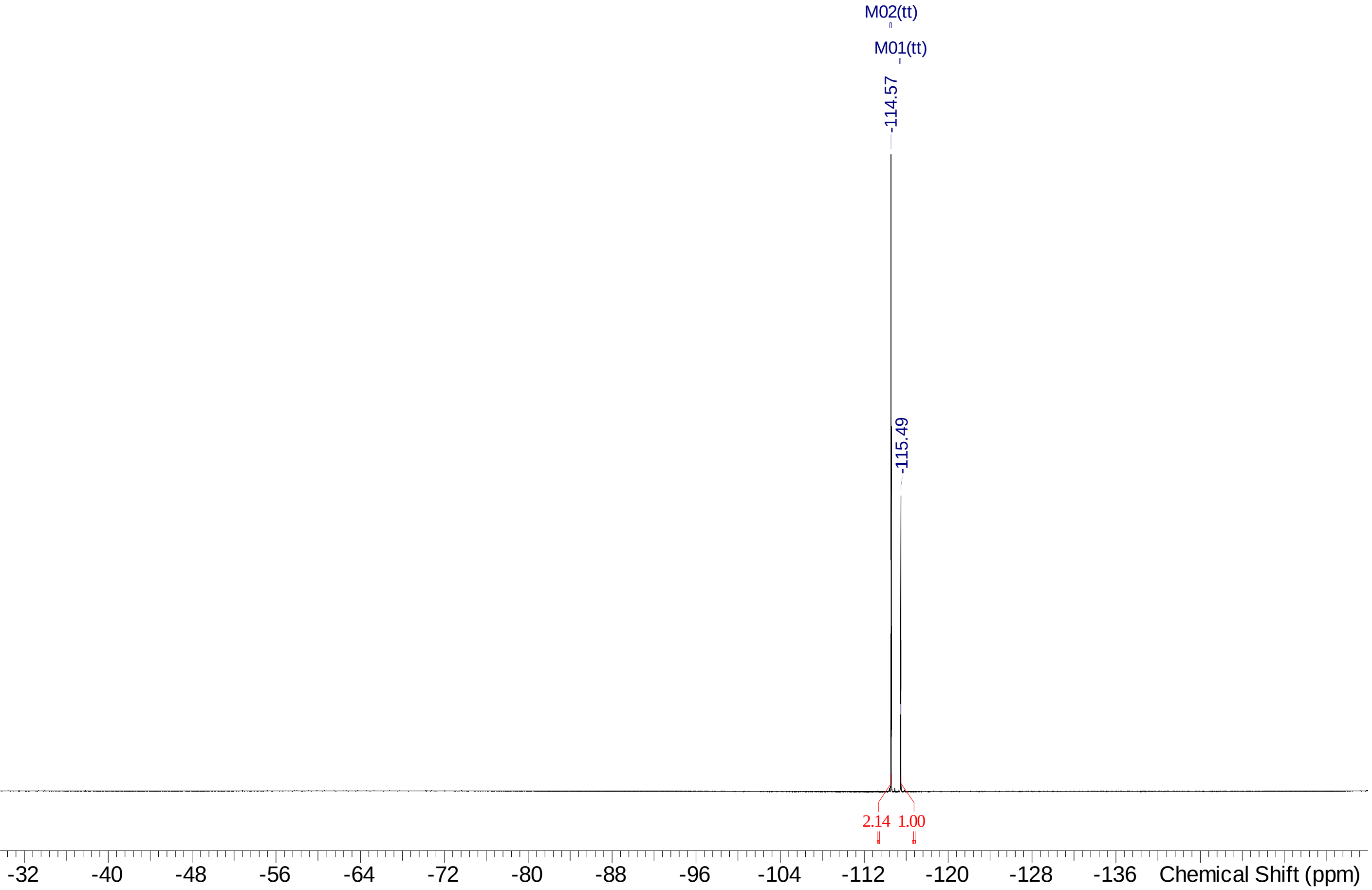


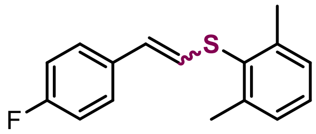
^{1}H NMR (500 MHz)
$CDCl_3$



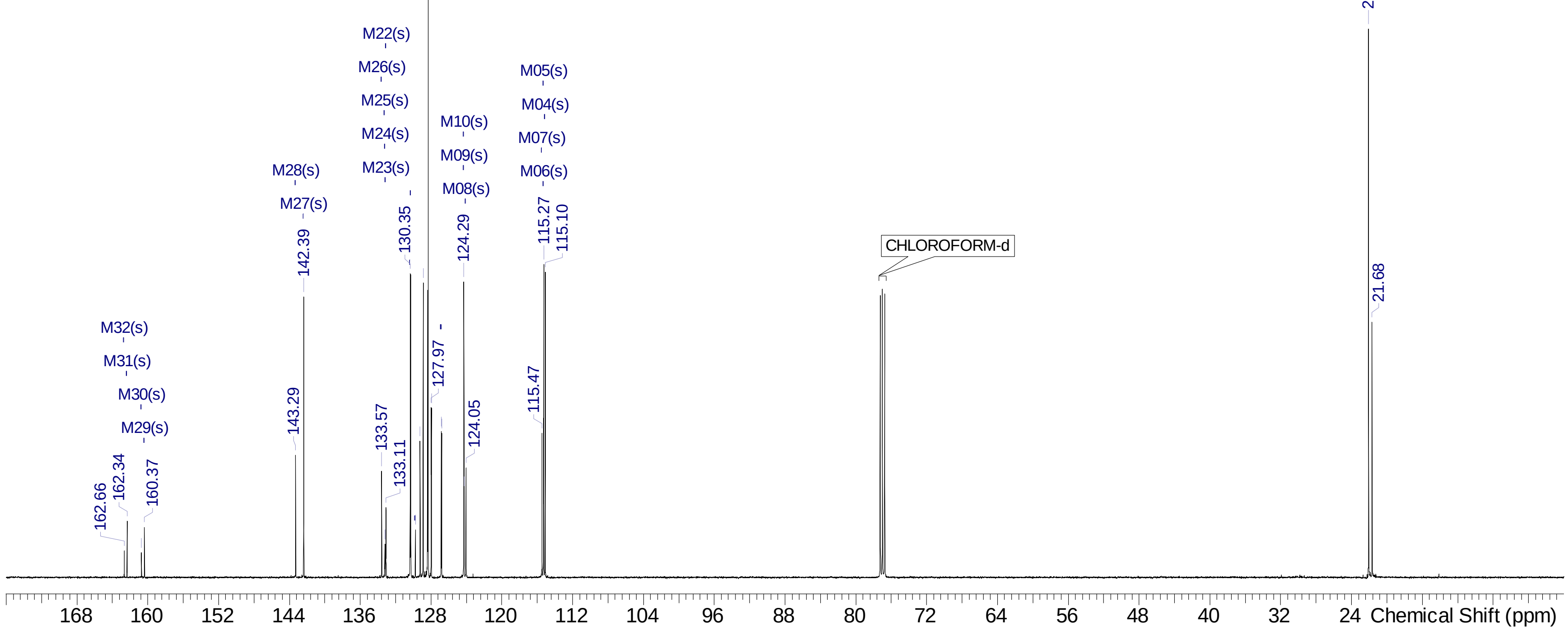


[19]F NMR (471 MHz)
$CDCl_3$

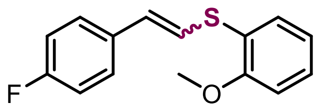




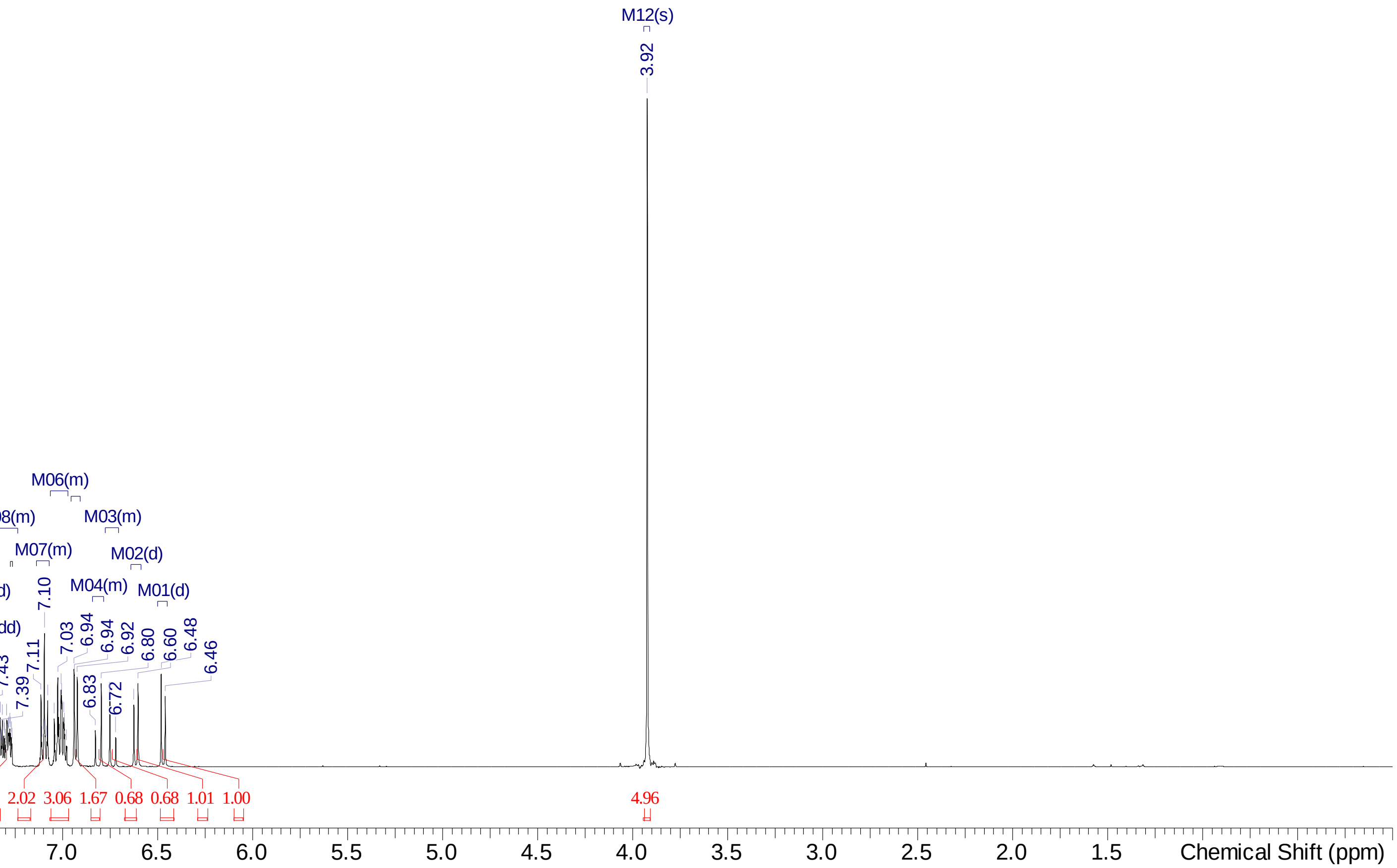
^{13}C NMR (126 MHz)
$CDCl_3$

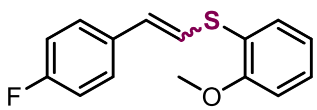


(4-Fluorostyryl)(2-methoxyphenyl)sulfane (5c)

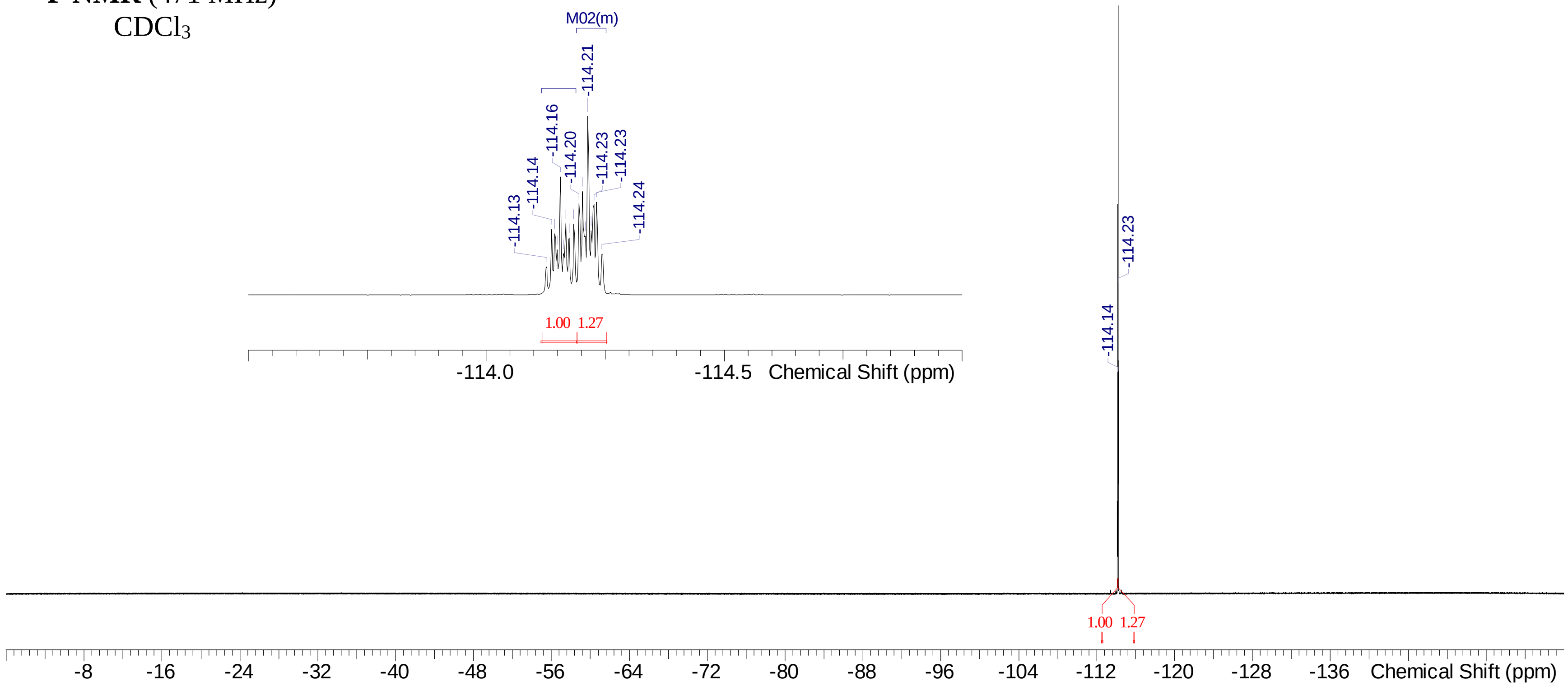


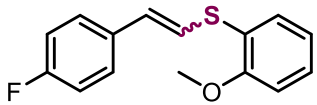
^{1}H NMR (500 MHz)
$CDCl_3$



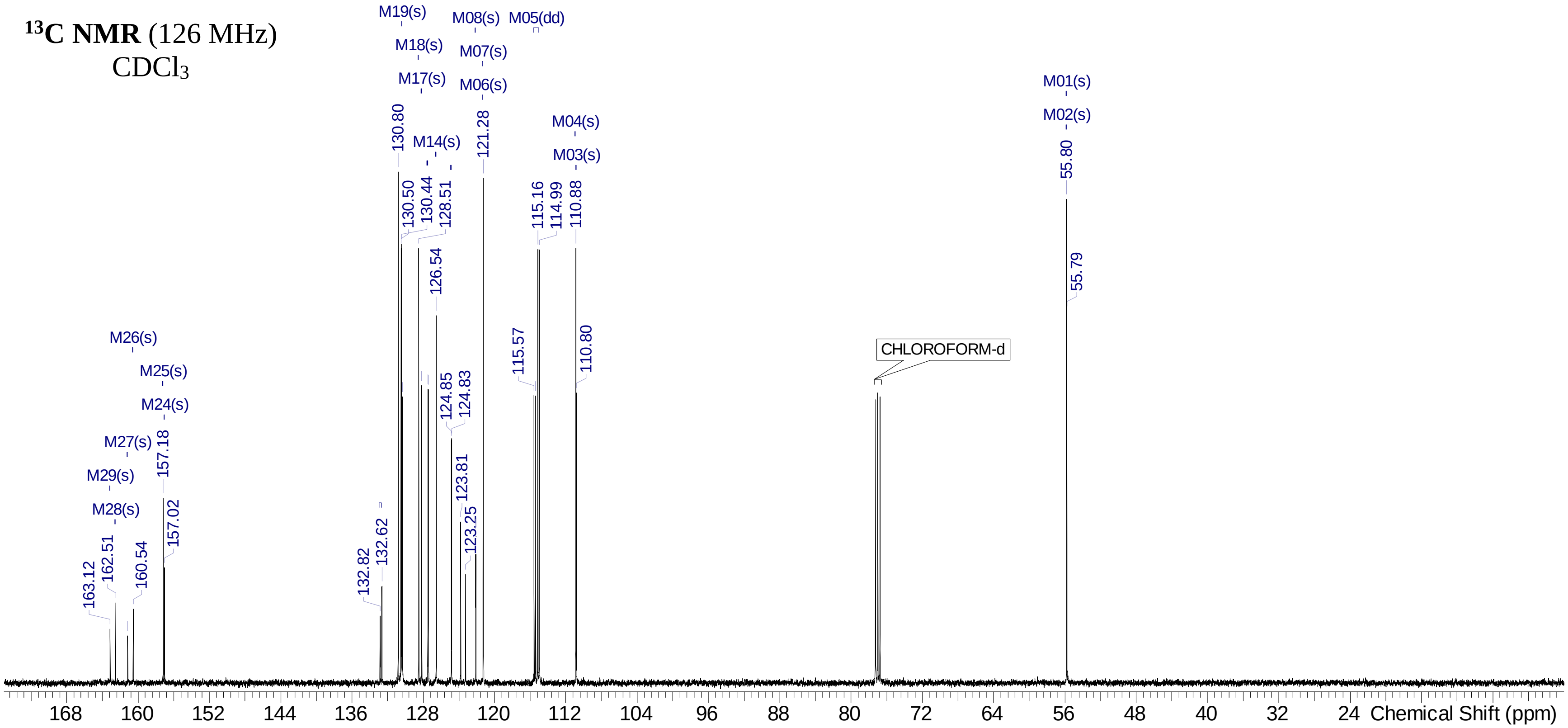


^{19}**F NMR** (471 MHz)
$CDCl_3$

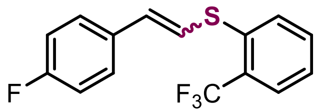




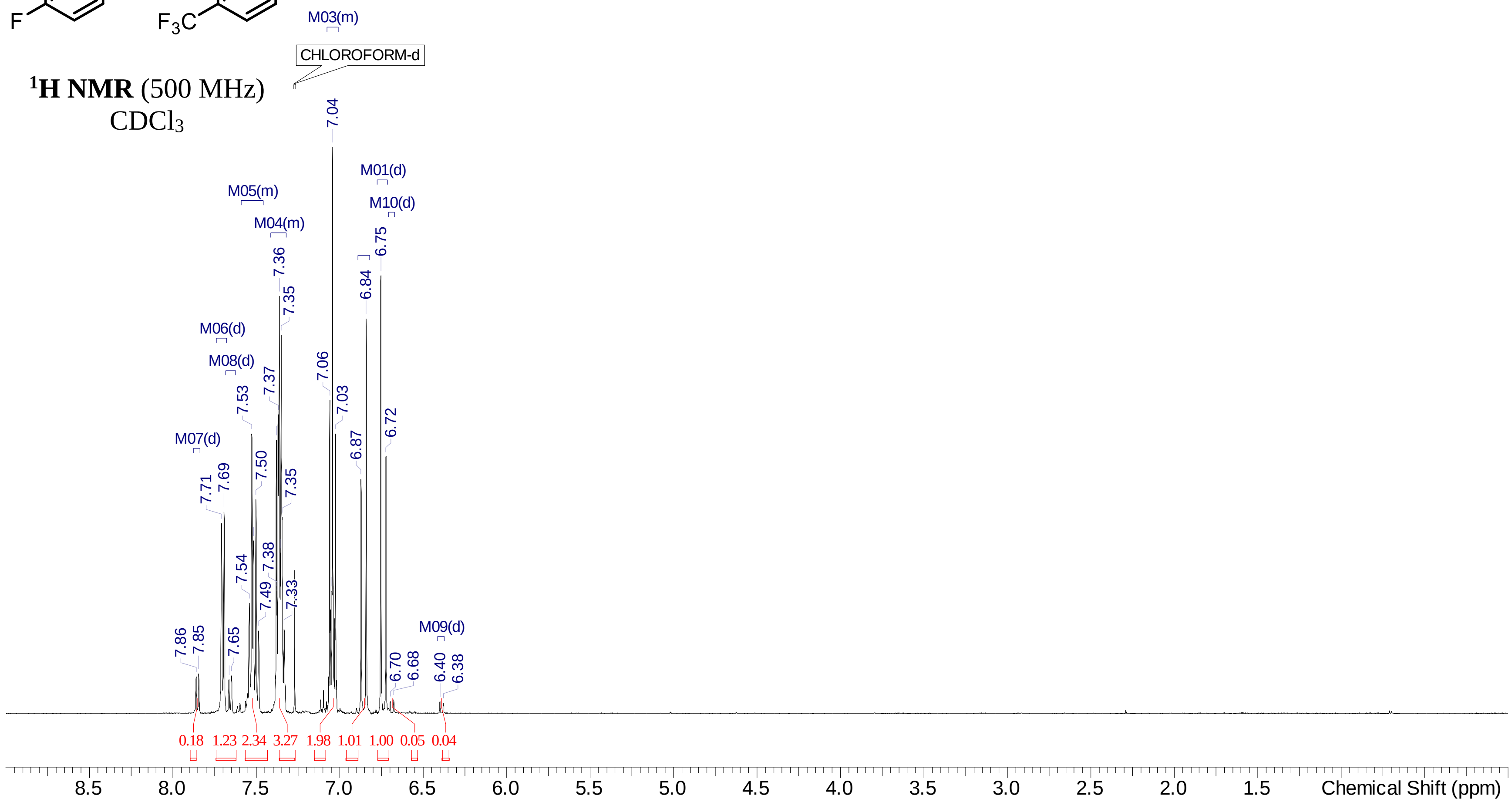
^{13}C NMR (126 MHz)
$CDCl_3$

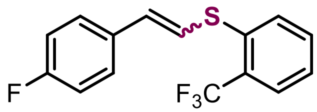


(4-Fluorostyryl)(2-(trifluoromethyl)phenyl)sulfane (5d)

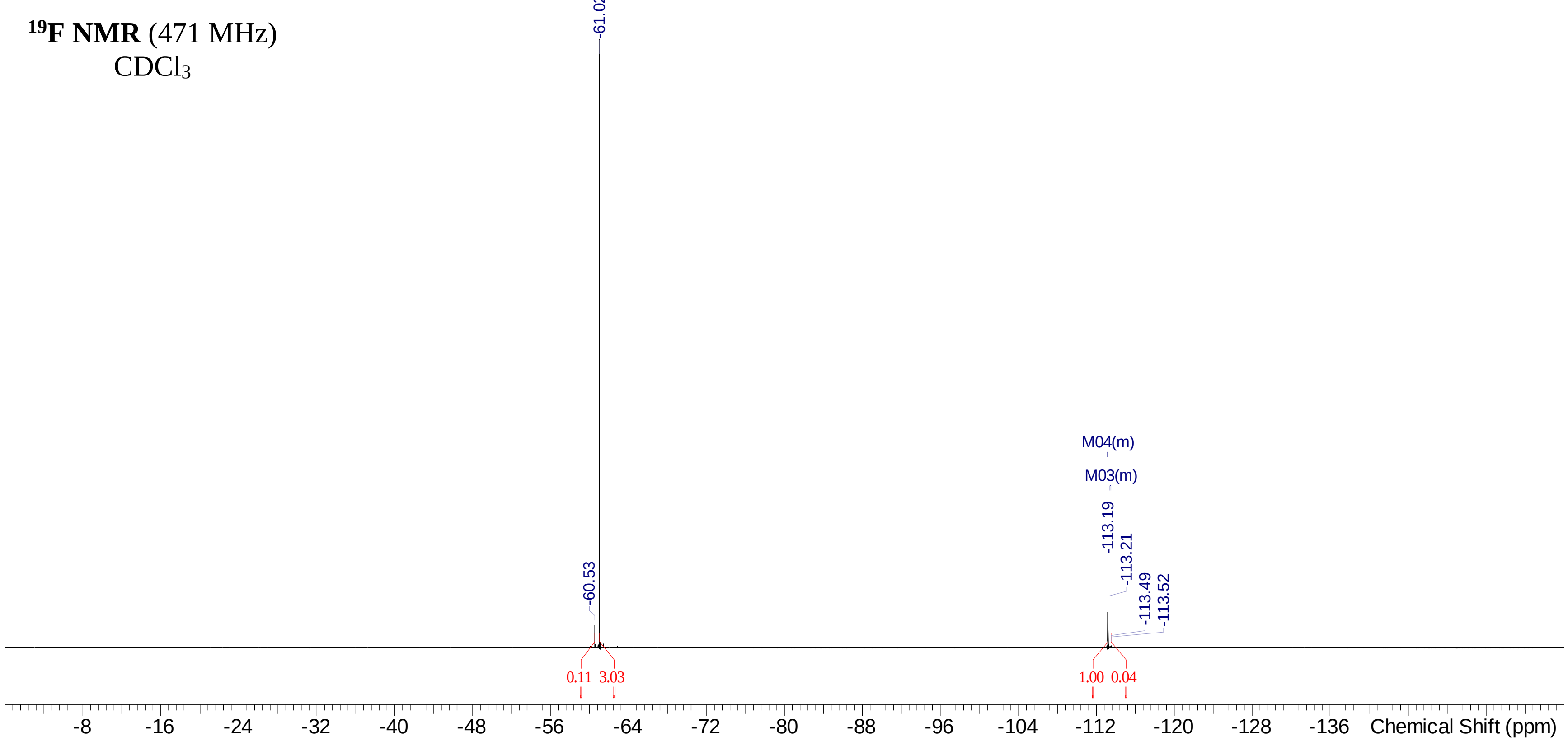


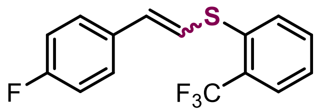
[1]H NMR (500 MHz)
$CDCl_3$



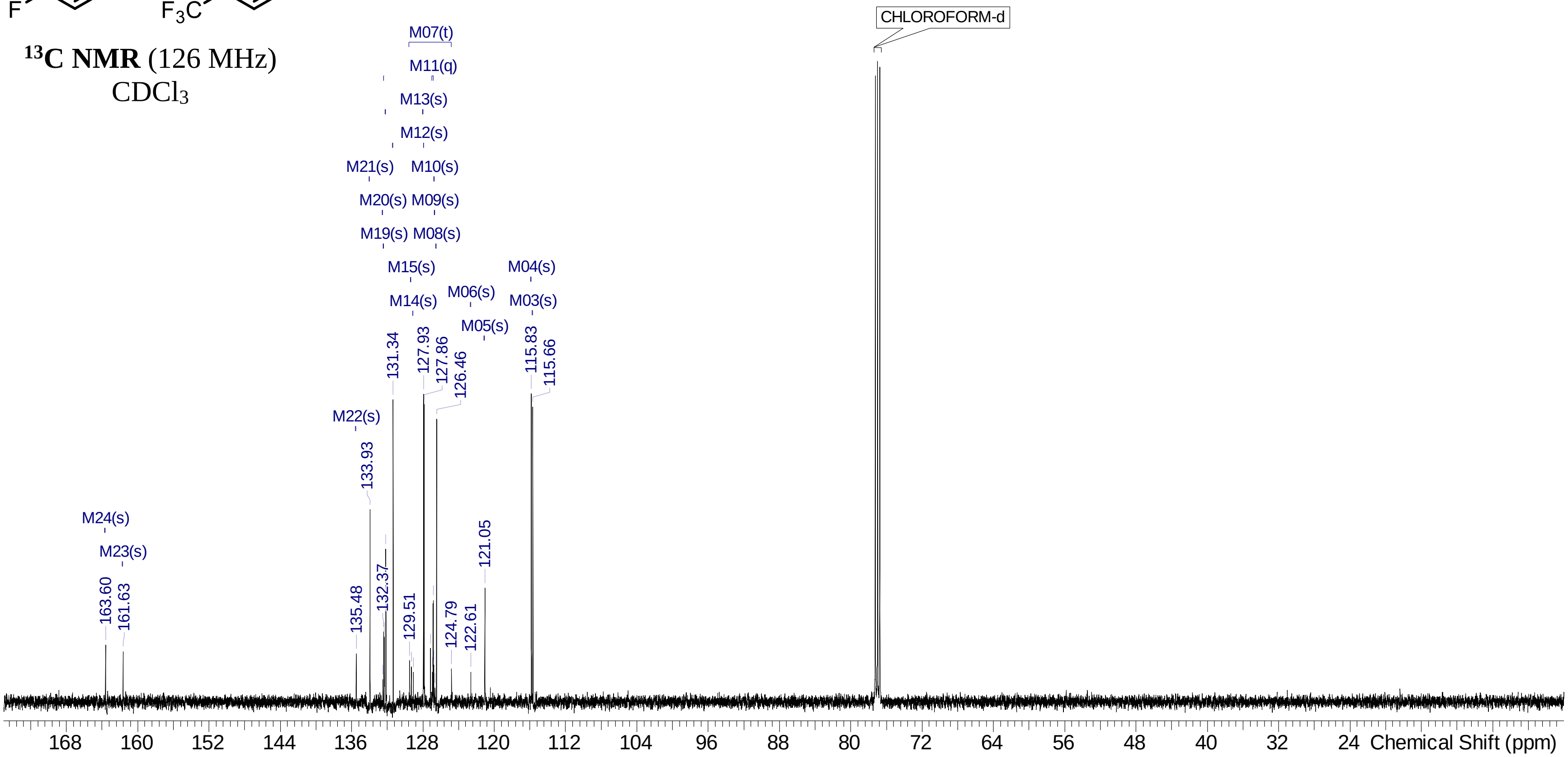


19F NMR (471 MHz)
$CDCl_3$

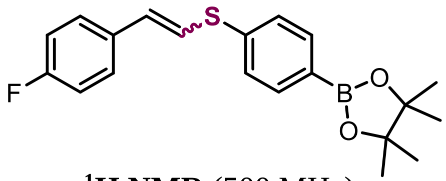




^{13}**C NMR** (126 MHz)
$CDCl_3$

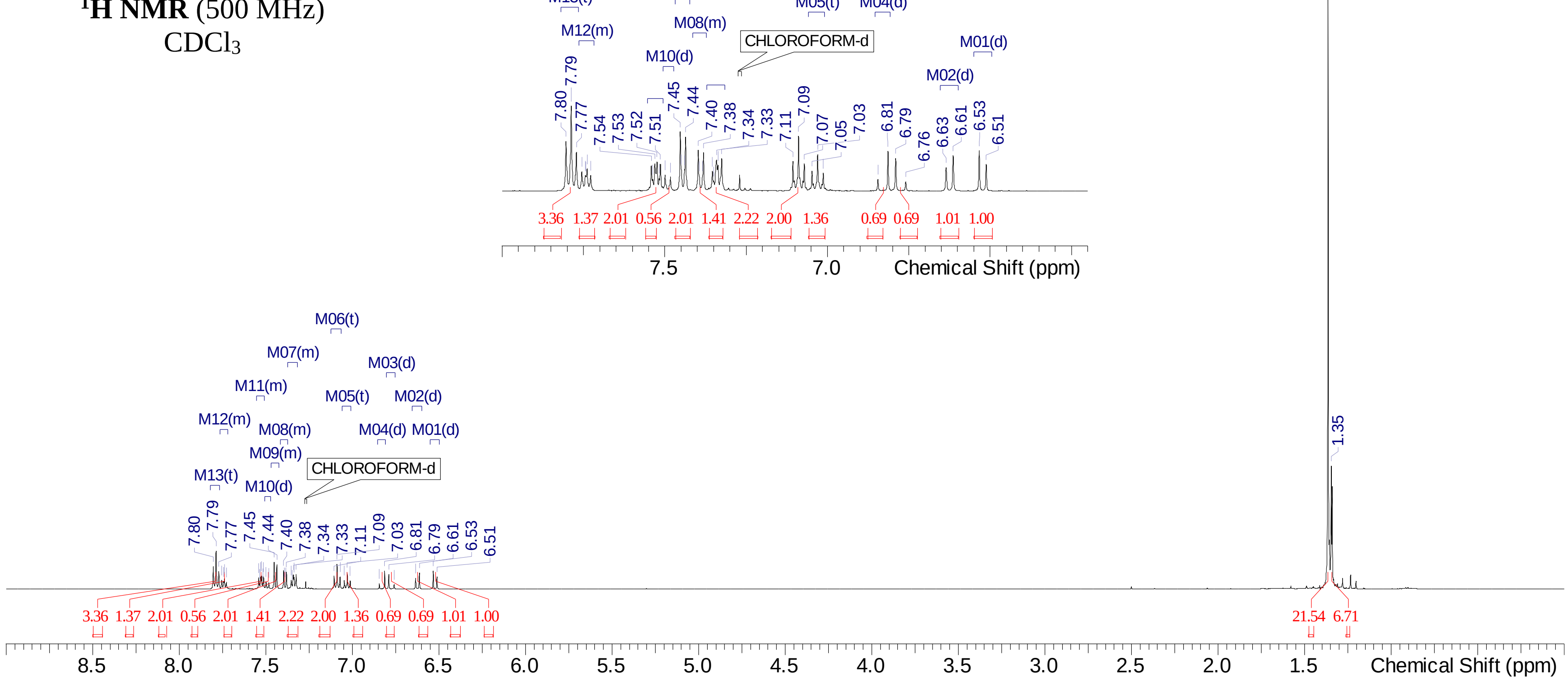


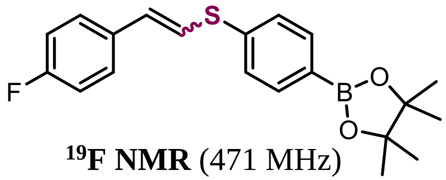
2-(4-((4-Fluorostyryl)thio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e)



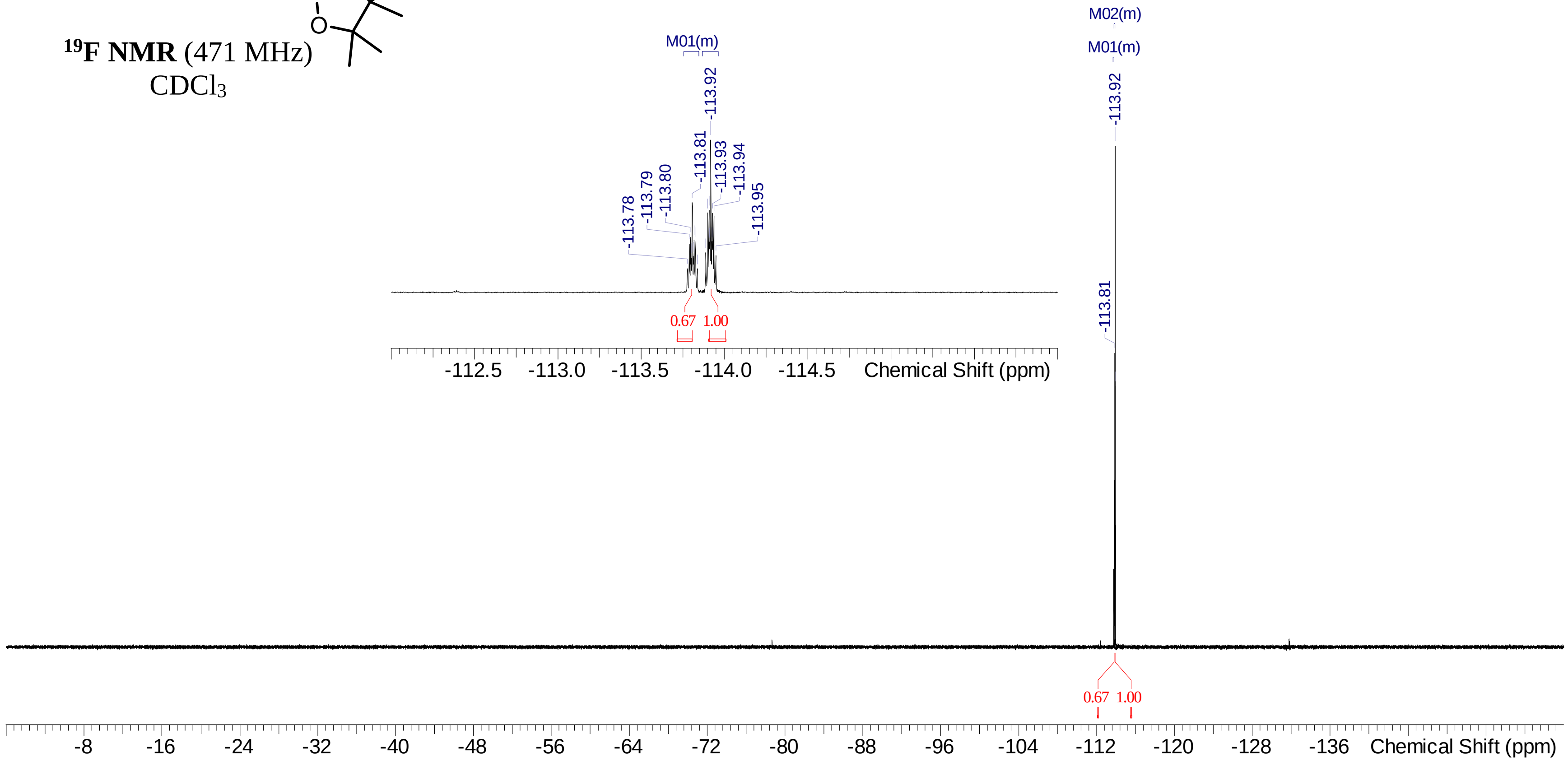
^{1}H NMR (500 MHz)

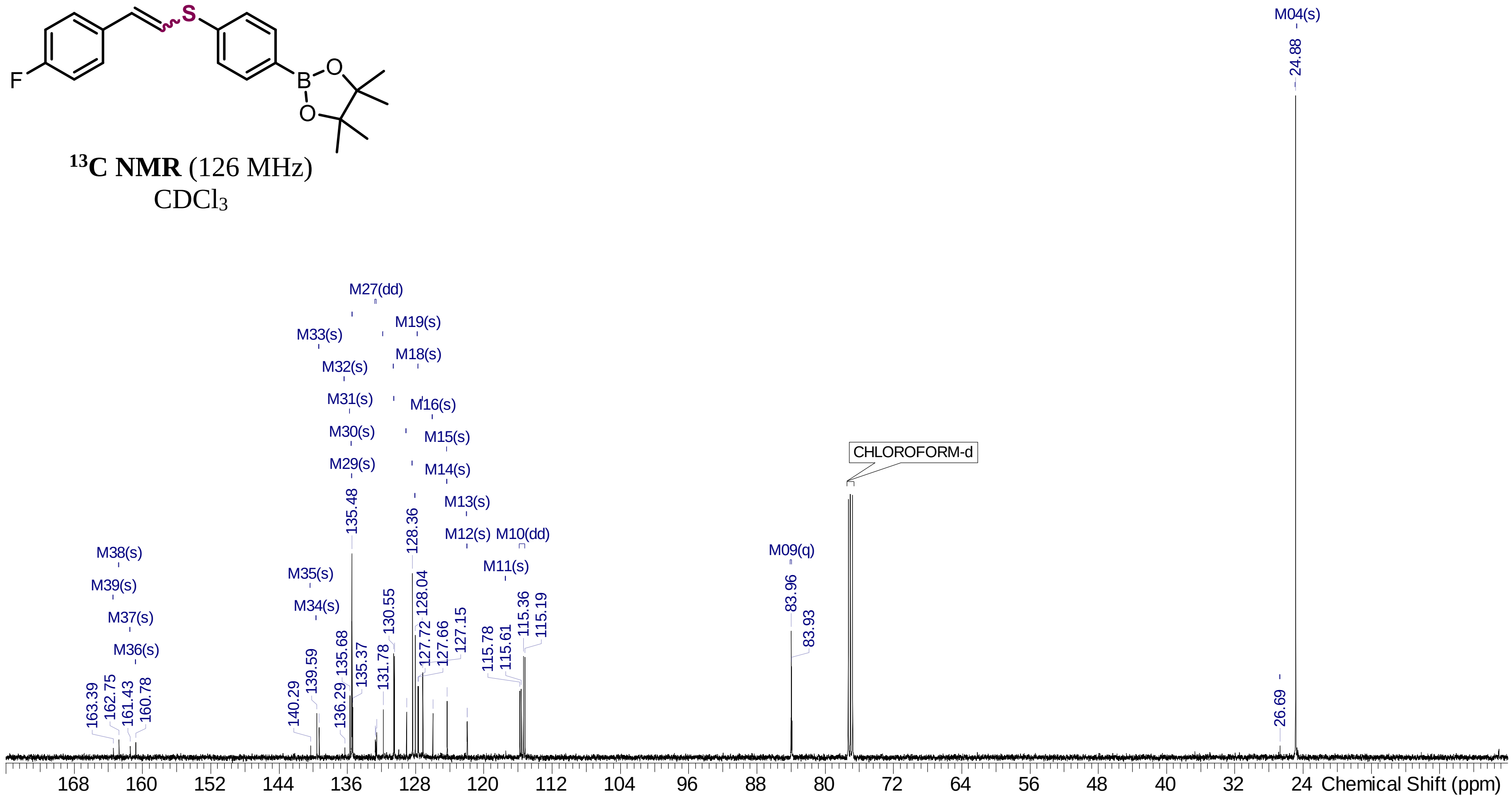
$CDCl_3$





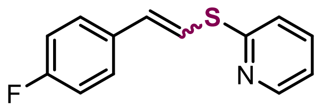
[19]F NMR (471 MHz)
$CDCl_3$



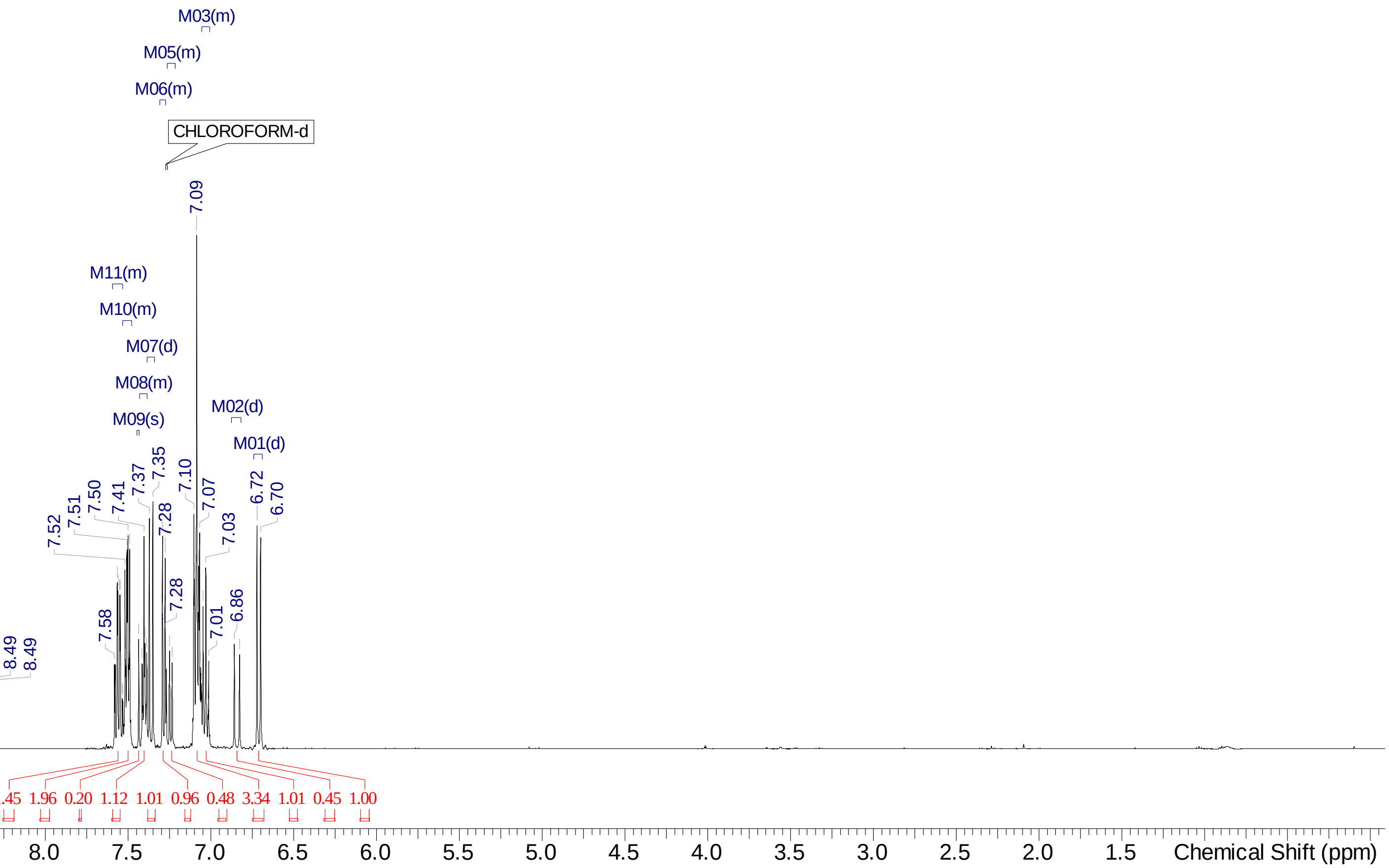


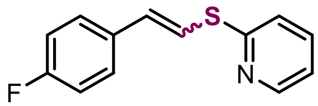
^{13}C NMR (126 MHz)
$CDCl_3$

2-((4-Fluorostyryl)thio)pyridine (5f)

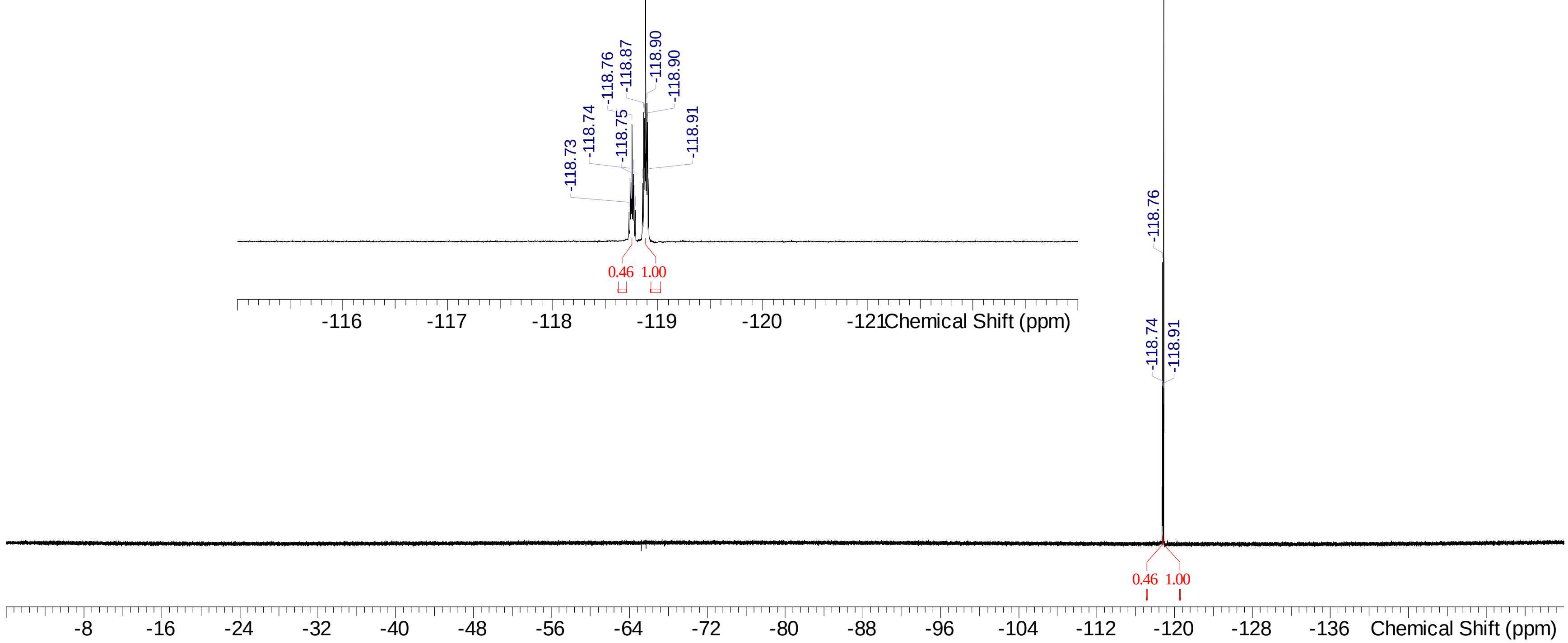


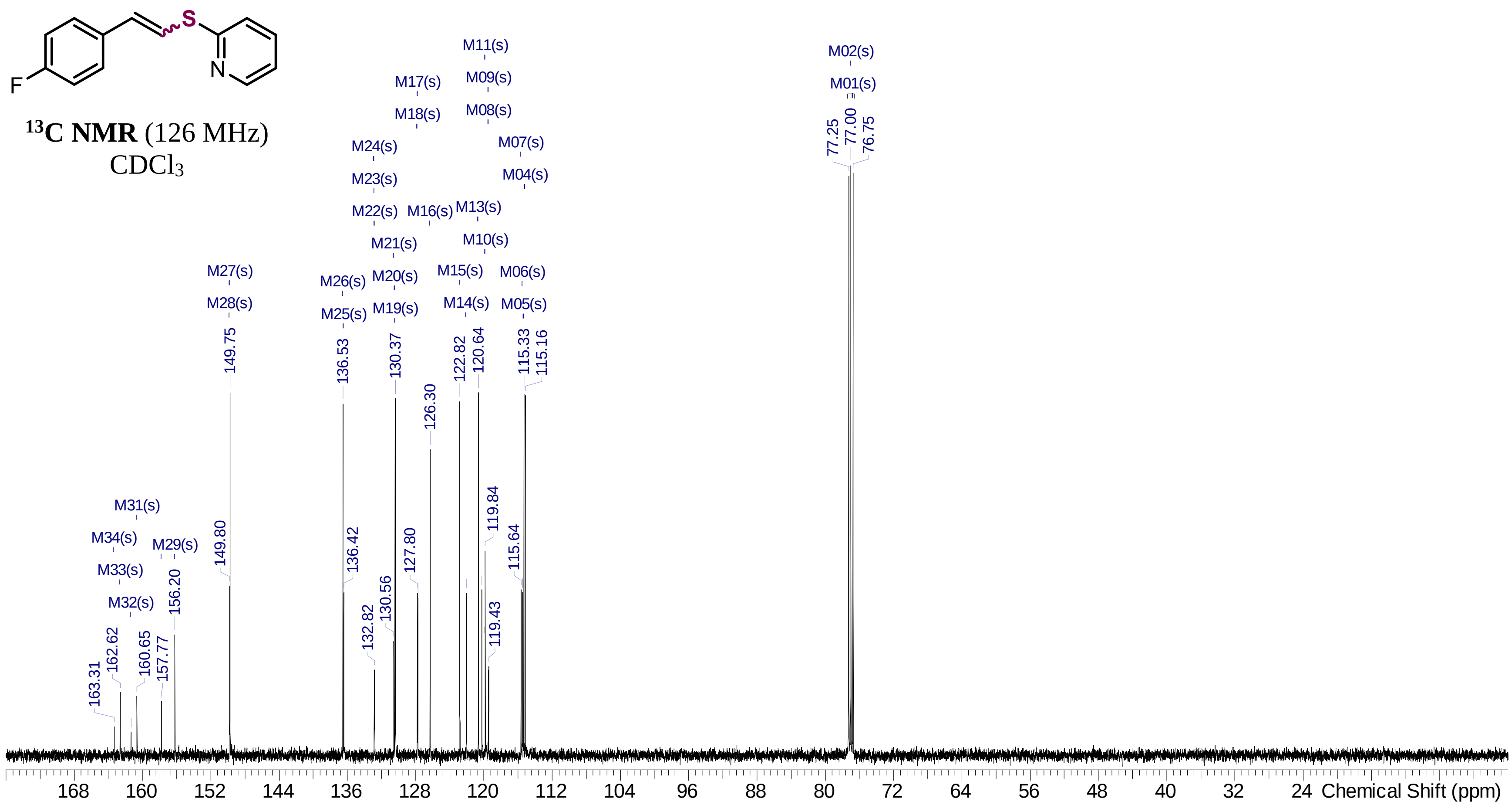
[1]H NMR (500 MHz)
CDCl3



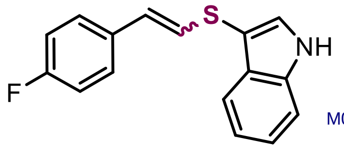


^{19}F NMR (471 MHz)
$CDCl_3$

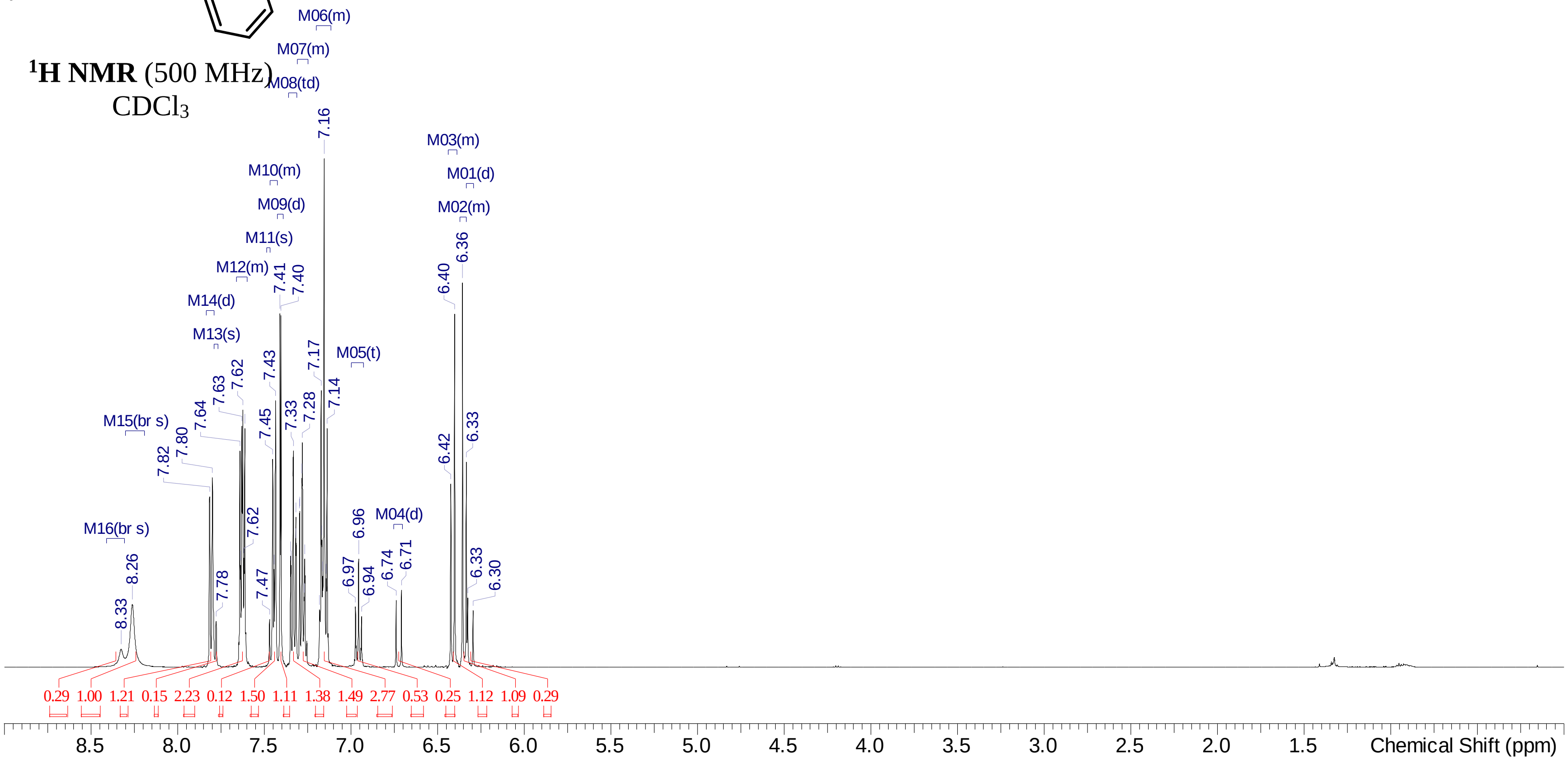


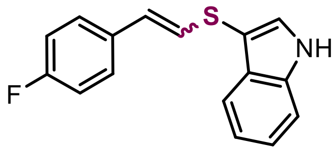

F
S
N
13C NMR (126 MHz)
CDCl3
163.31
162.62
160.65
157.77
156.20
149.80
149.75
136.53
136.42
132.82
130.56
130.37
127.80
126.30
122.82
120.64
119.84
119.43
115.64
115.33
115.16
77.25
77.00
76.75
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24
Chemical Shift (ppm)

3-((4-fluorostyryl)thio)-1*H*-indole (5g)

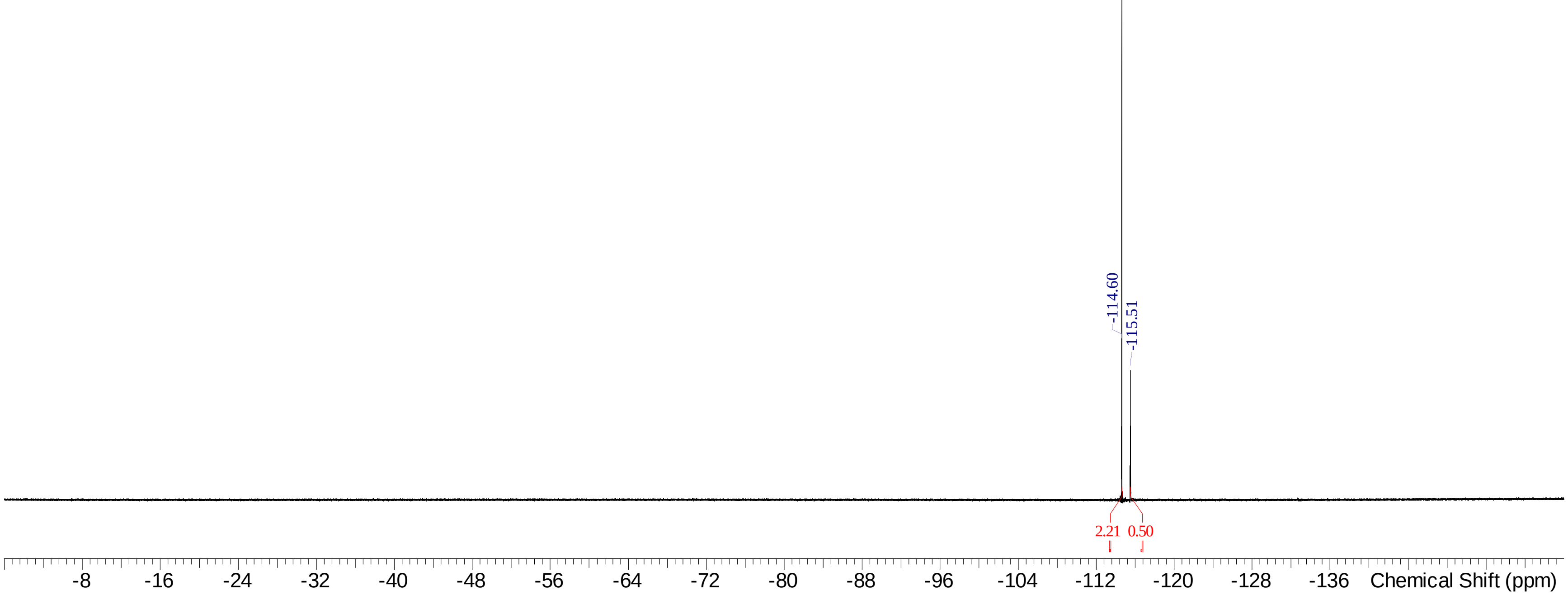


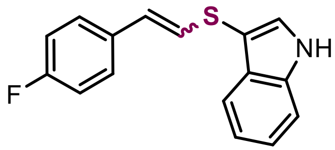
^{1}H NMR (500 MHz)
$CDCl_3$



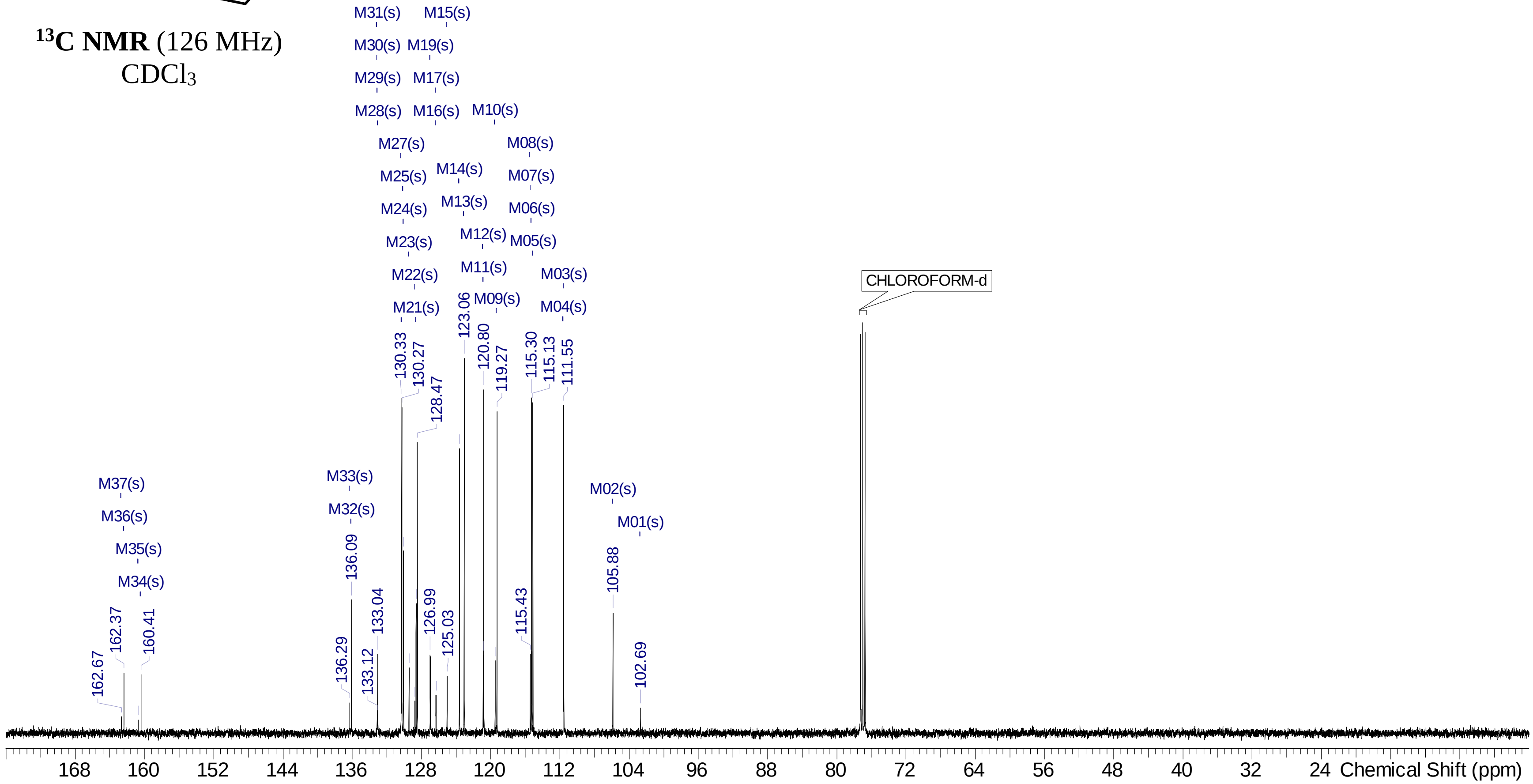


[19]F NMR (471 MHz)
$CDCl_3$

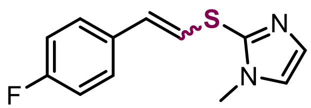




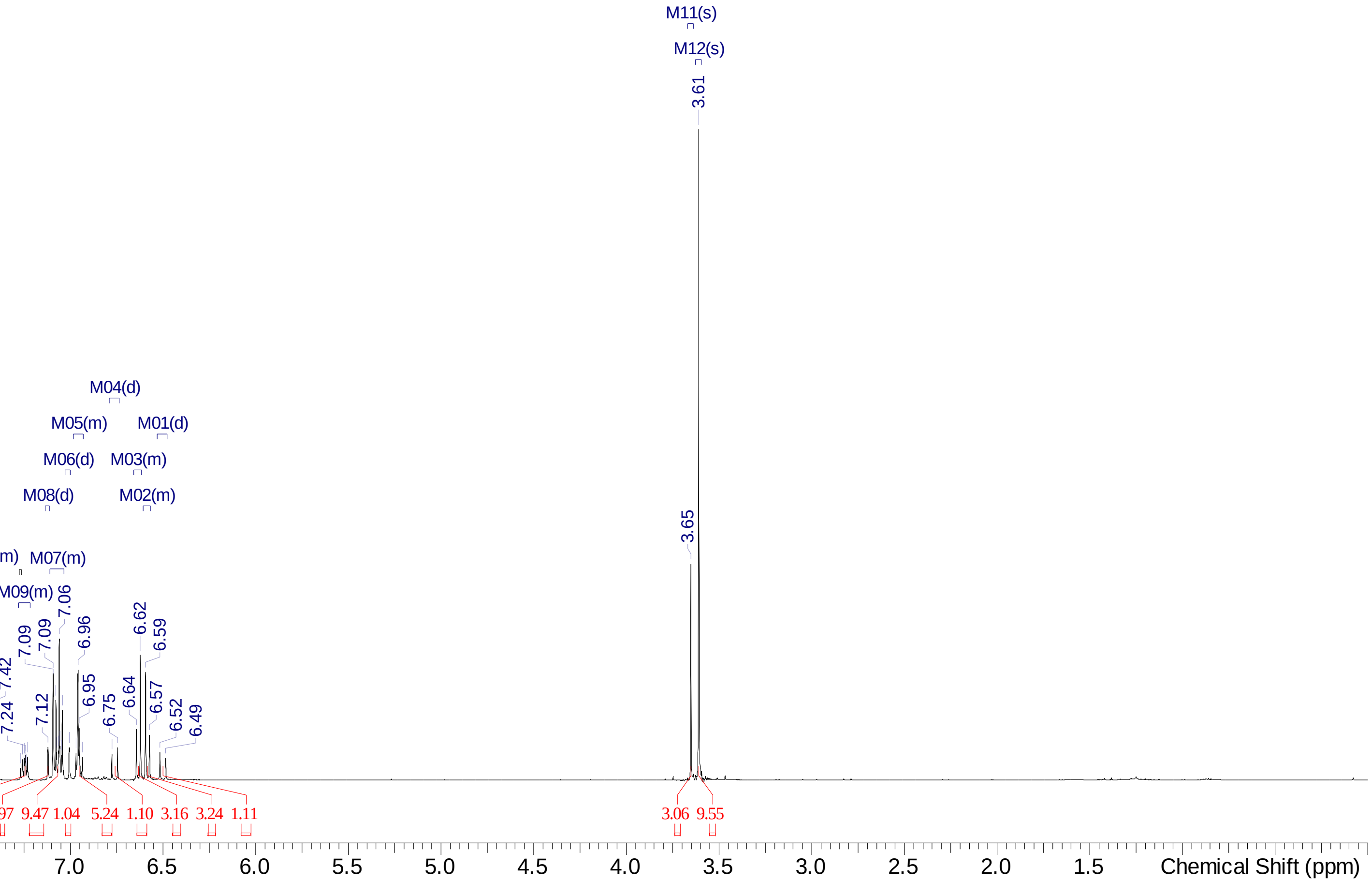
^{13}C NMR (126 MHz)
$CDCl_3$

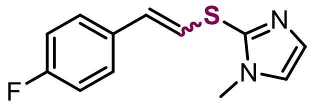


2-((4-fluorostyryl)thio)-1-methyl-1*H*-imidazole (5h)

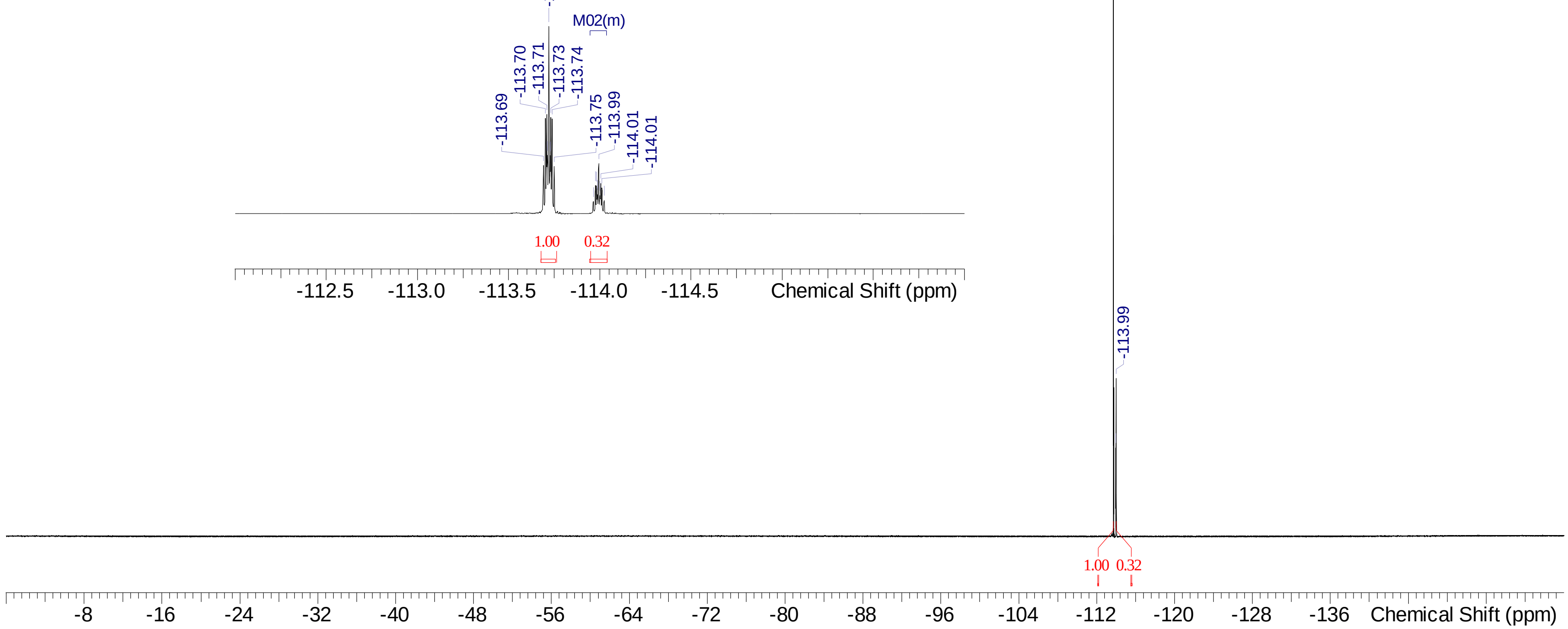


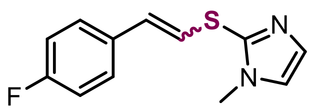
^{1}H NMR (500 MHz)
$CDCl_3$



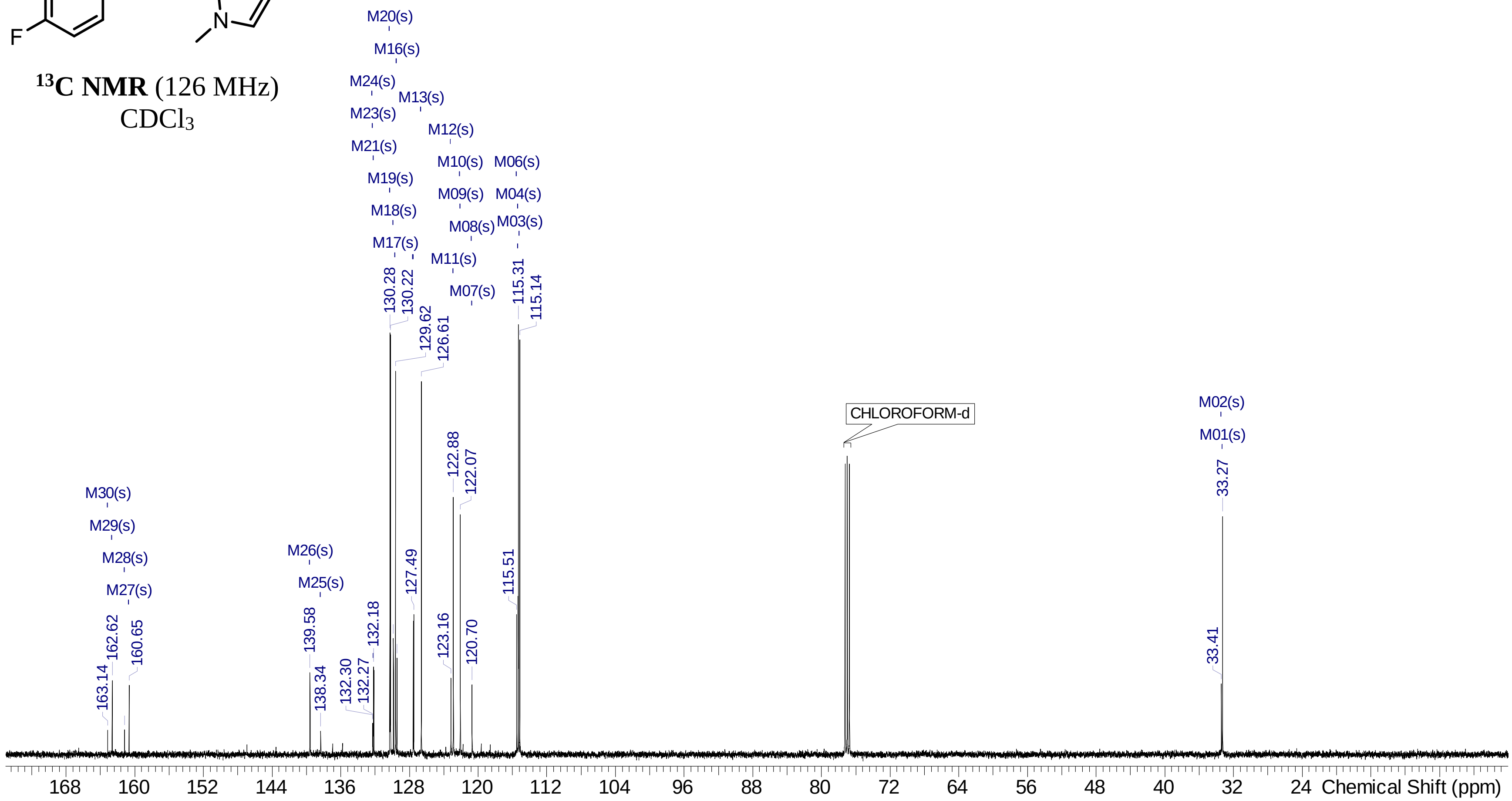


[19]F NMR (471 MHz)
$CDCl_3$

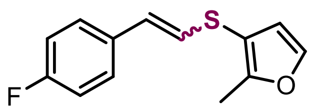




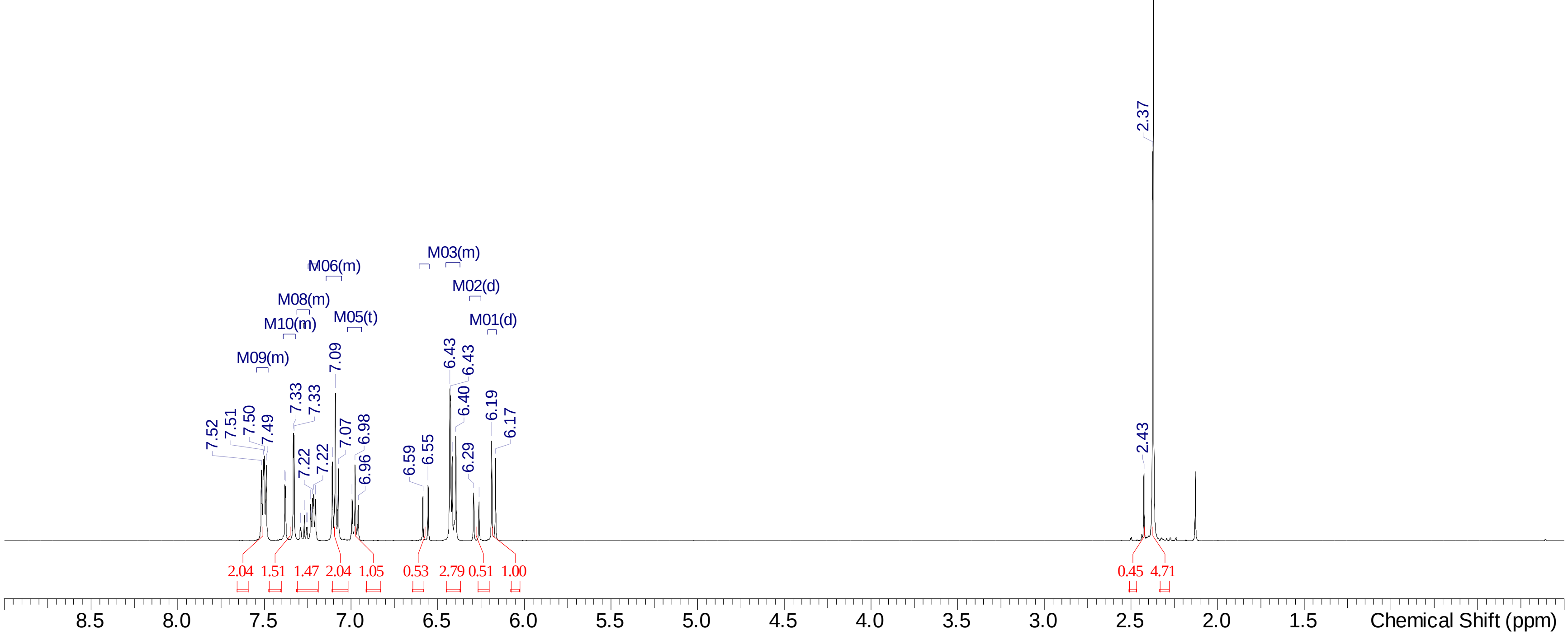
^{13}**C NMR** (126 MHz)
$CDCl_3$

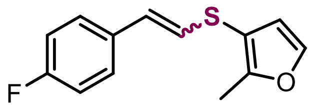


3-((4-Fluorostyryl)thio)-2-methylfuran (5i)

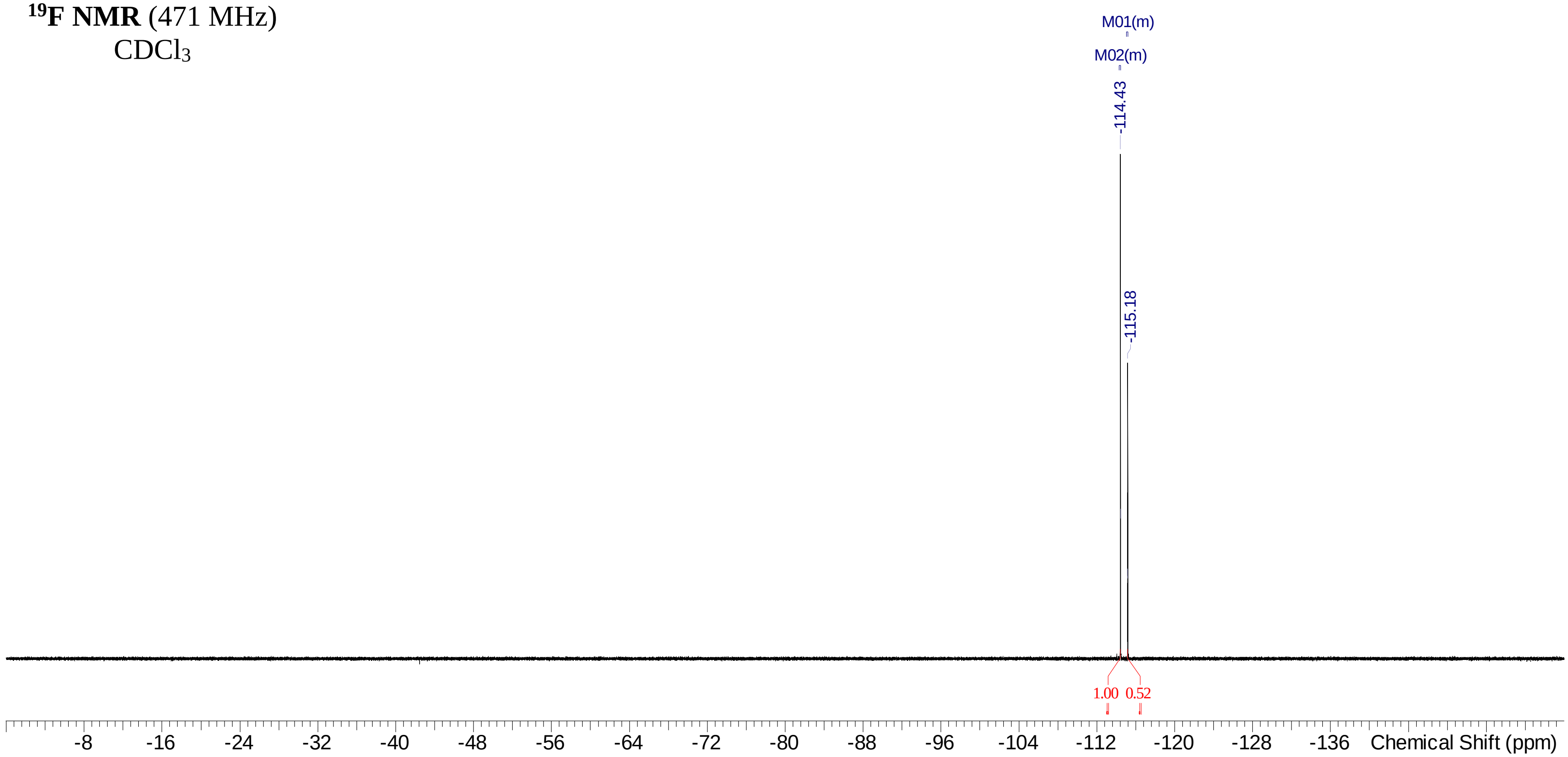


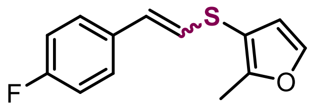
^{1}H NMR (500 MHz)
$CDCl_3$



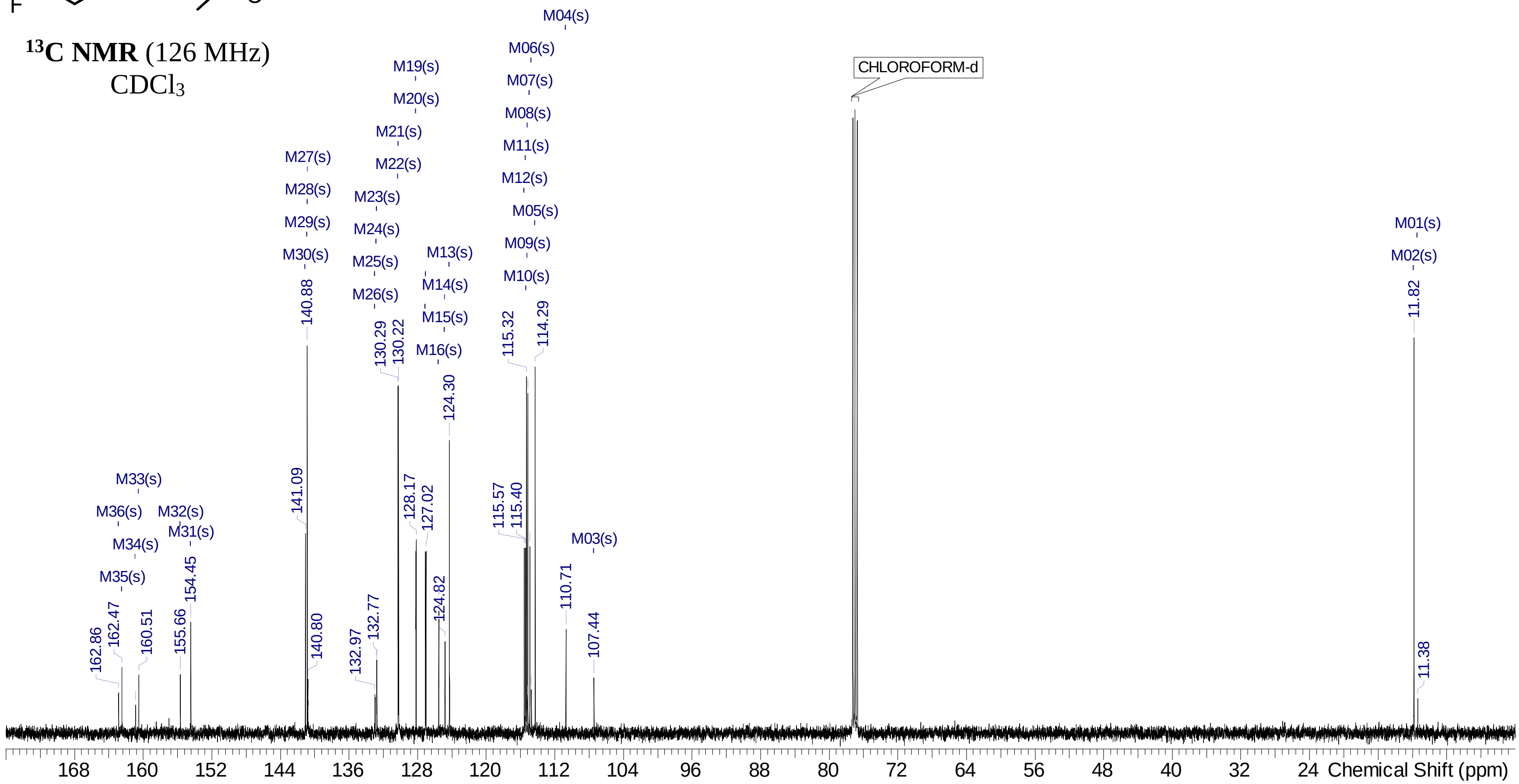


^{19}F NMR (471 MHz)
$CDCl_3$

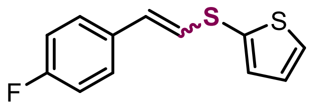




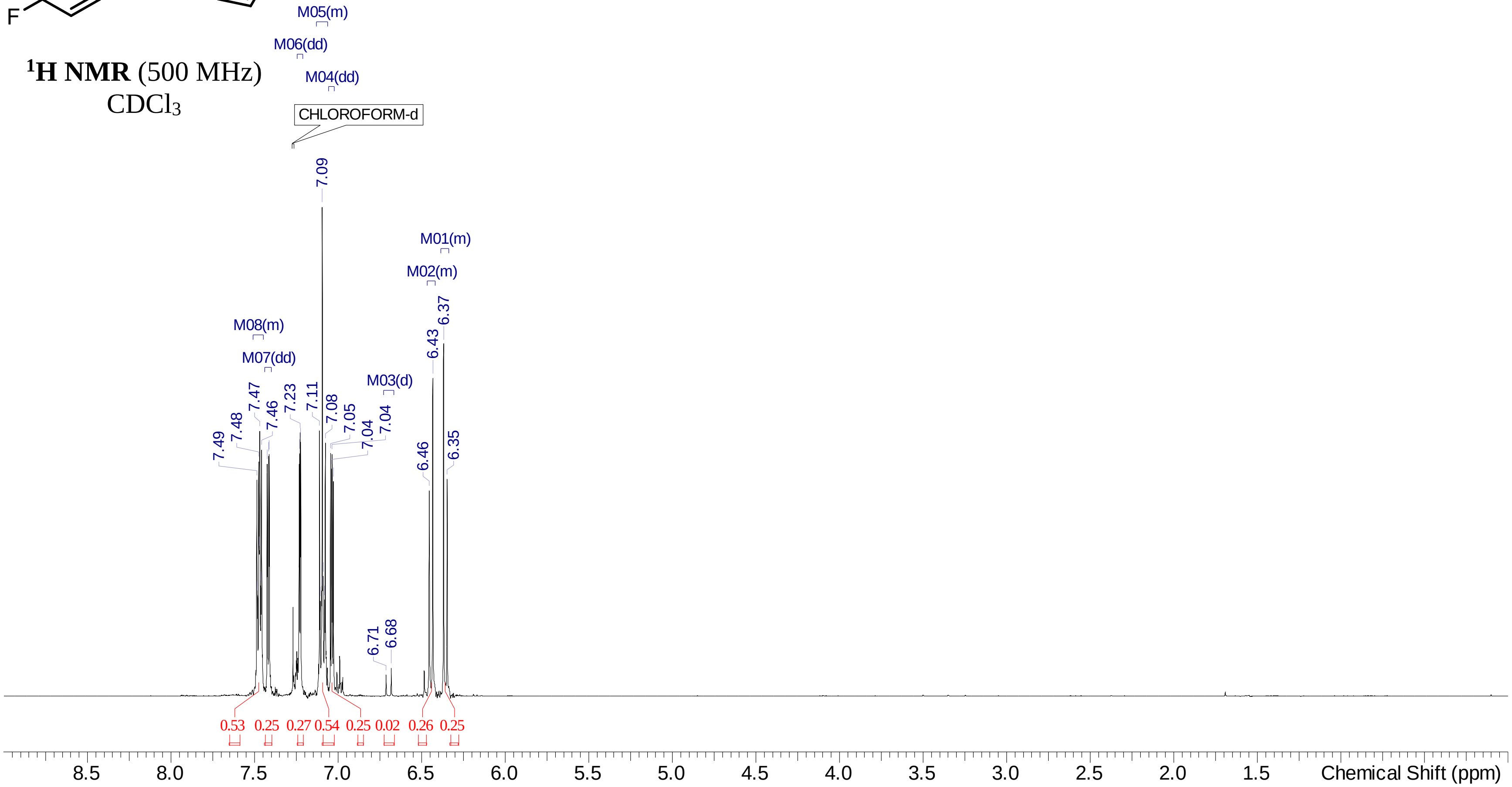
^{13}**C NMR** (126 MHz)
$CDCl_3$

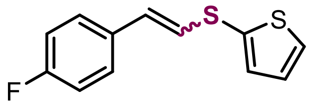


2-((4-Fluorostyryl)thio)thiophene (5j)

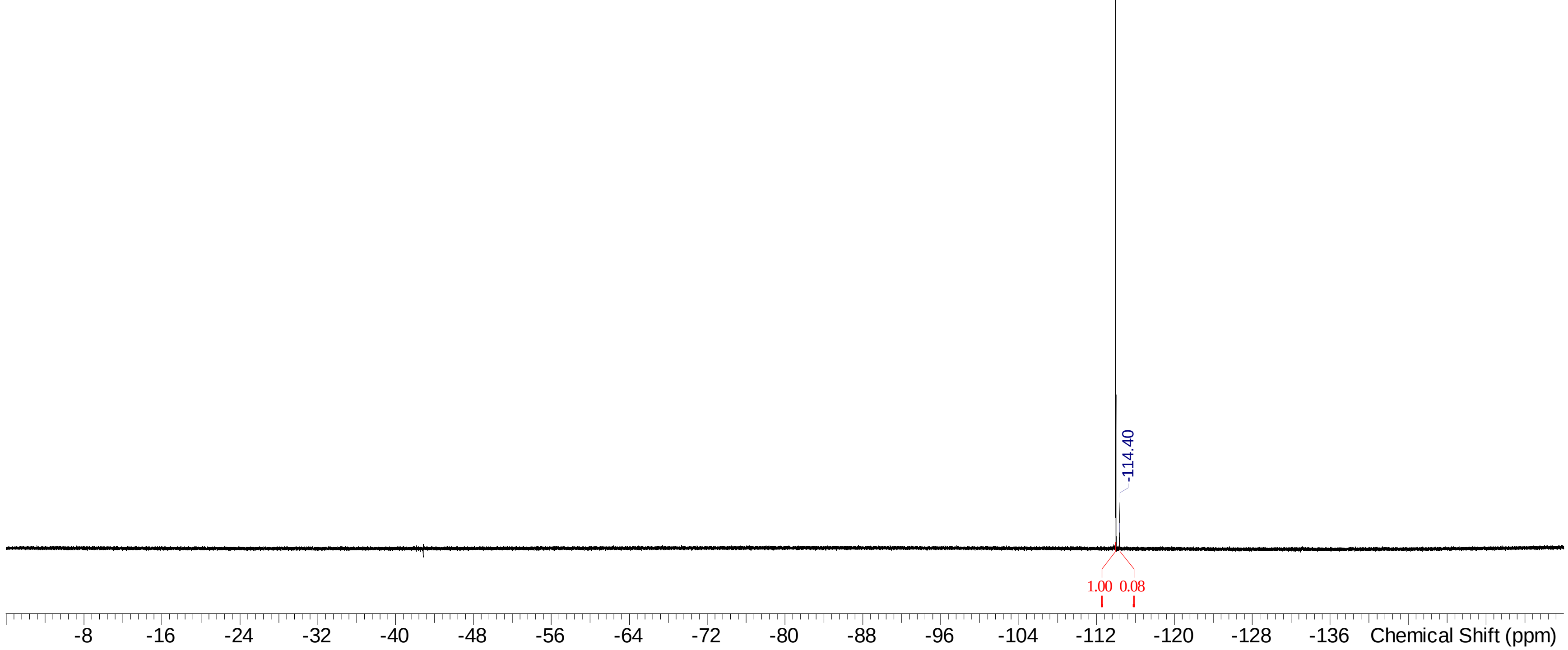


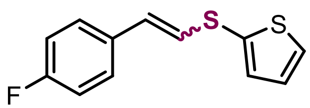
^{1}H NMR (500 MHz)
$CDCl_3$



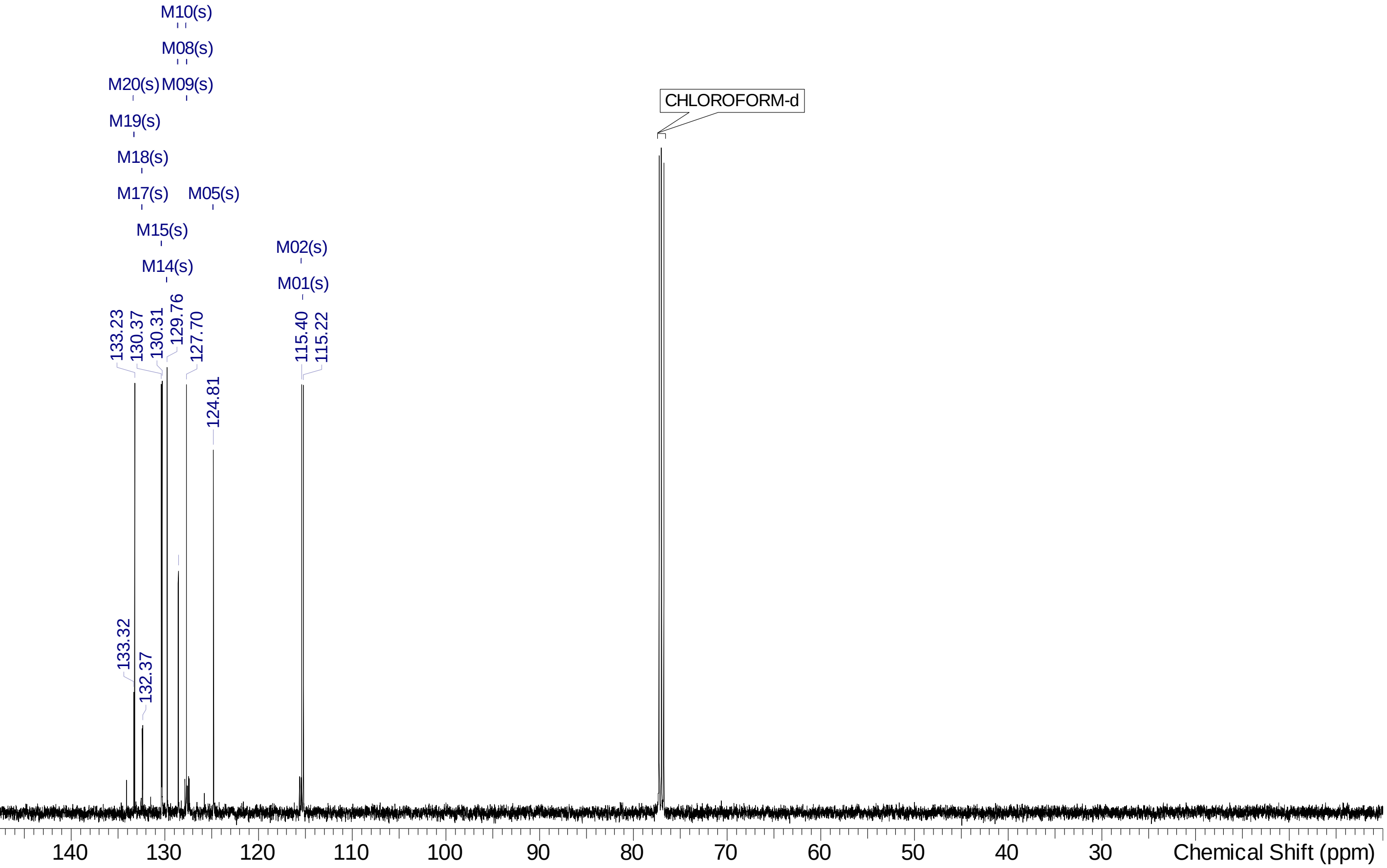


[19]F NMR (471 MHz)
$CDCl_3$

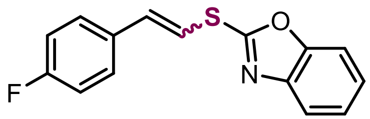




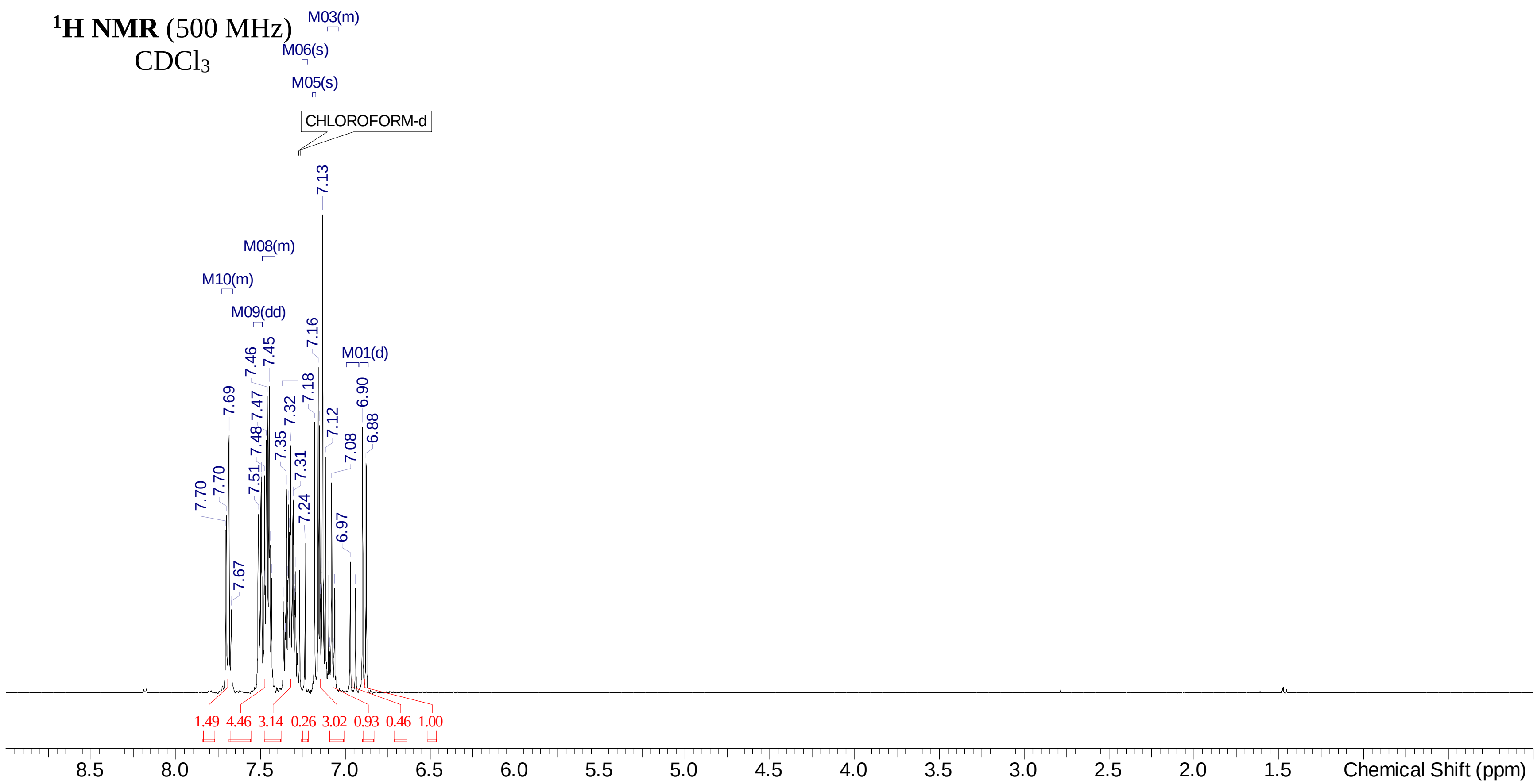
^{13}C NMR (126 MHz)
$CDCl_3$

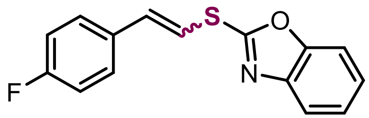


2-((4-Fluorostyryl)thio)benzo[d]oxazole (5k)

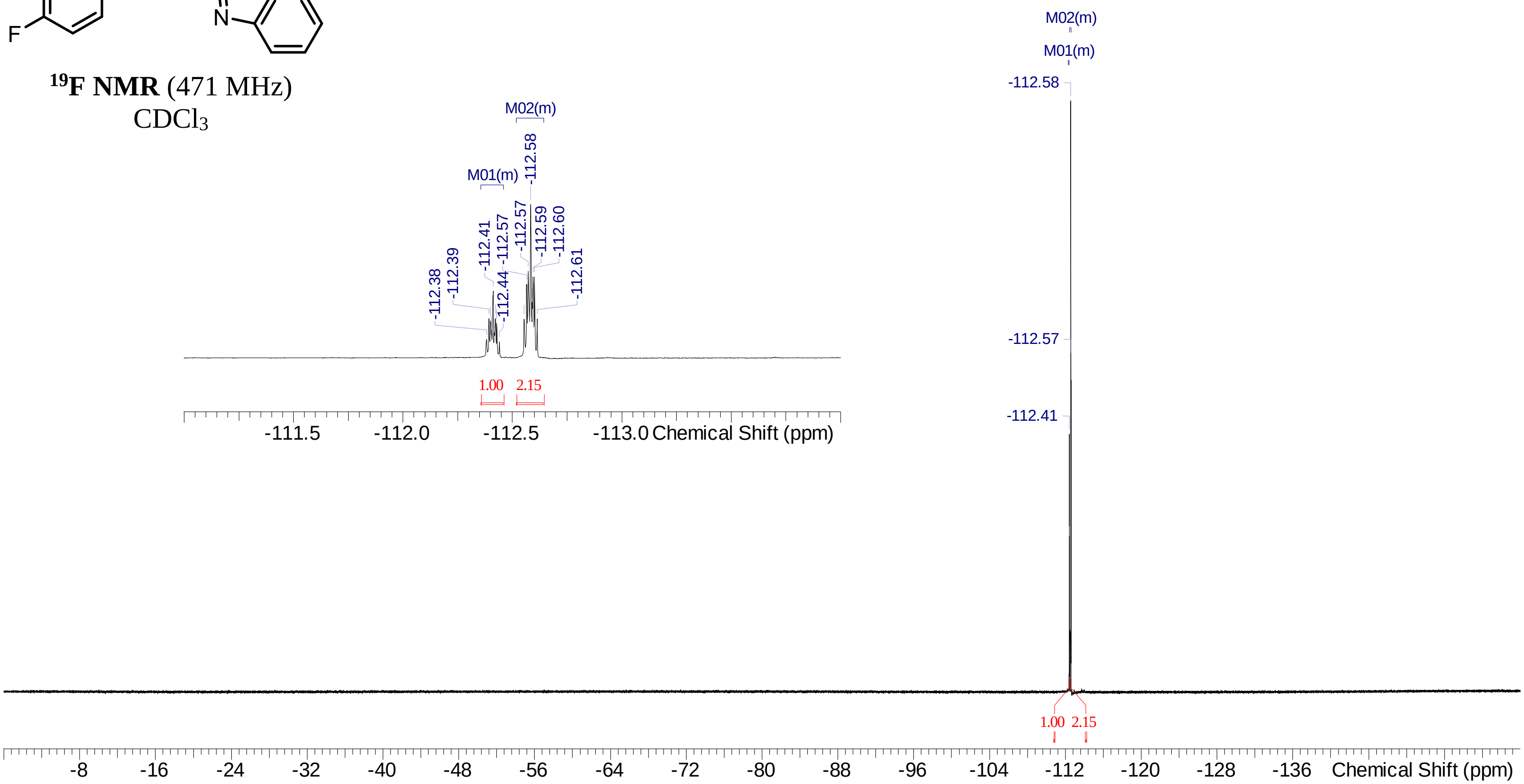


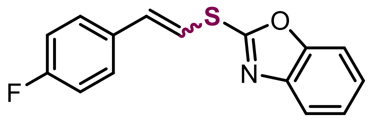
¹H NMR (500 MHz)
CDCl₃



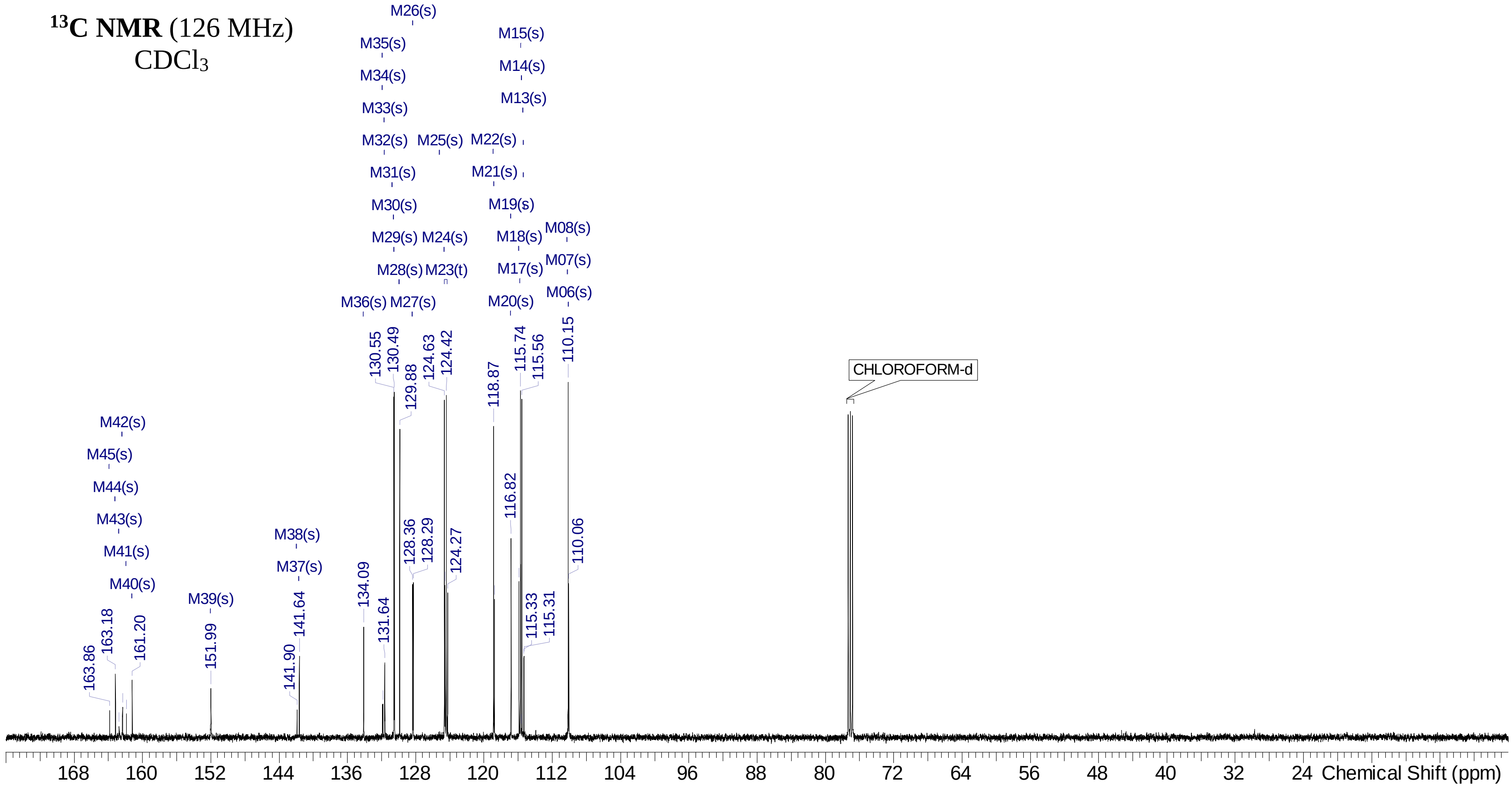


19F NMR (471 MHz)
$CDCl_3$

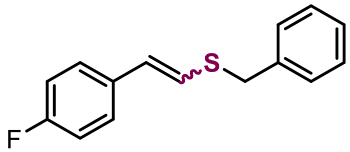




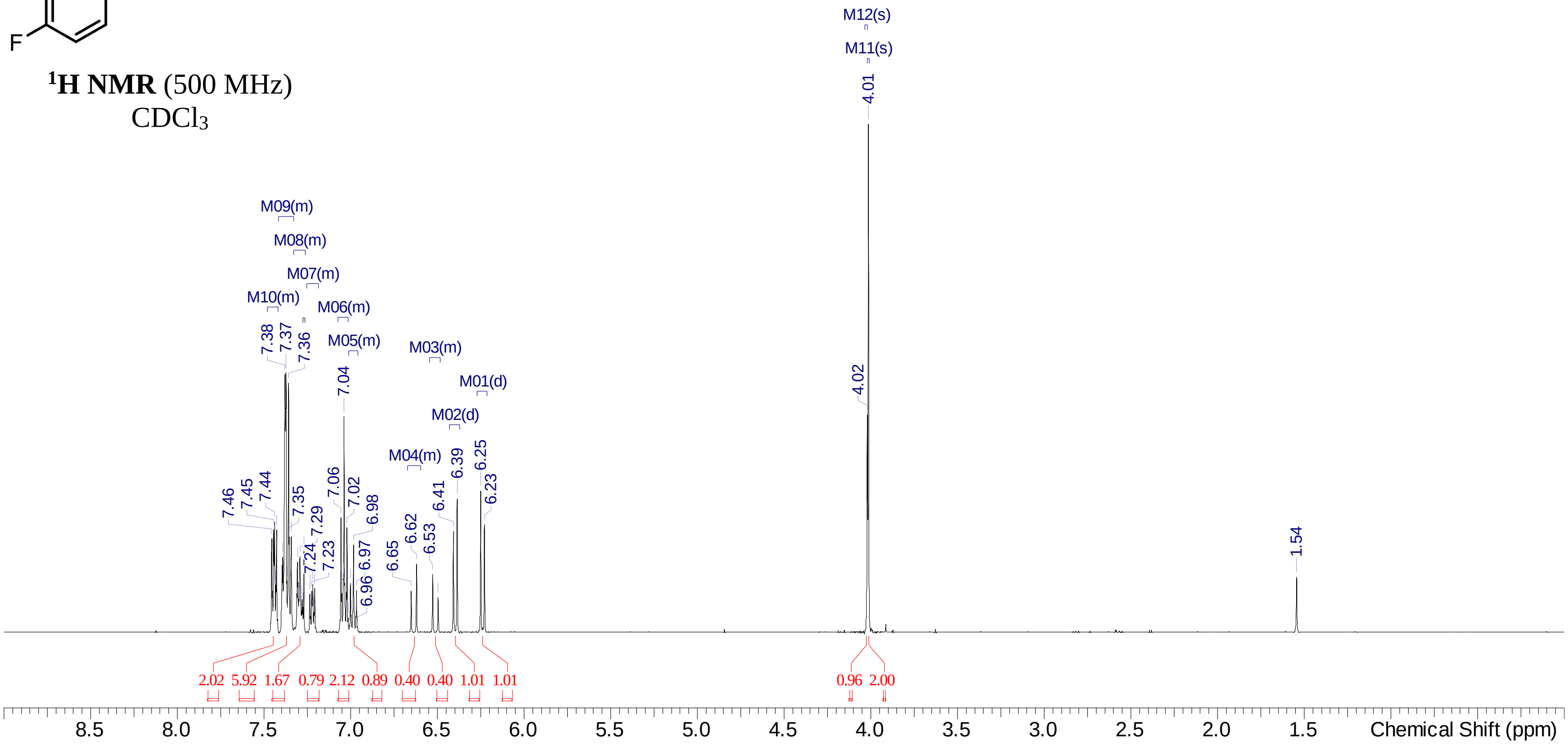
^{13}C NMR (126 MHz)
$CDCl_3$

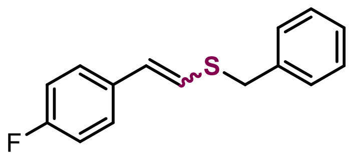


Benzyl(4-fluorostyryl)sulfane (5l)

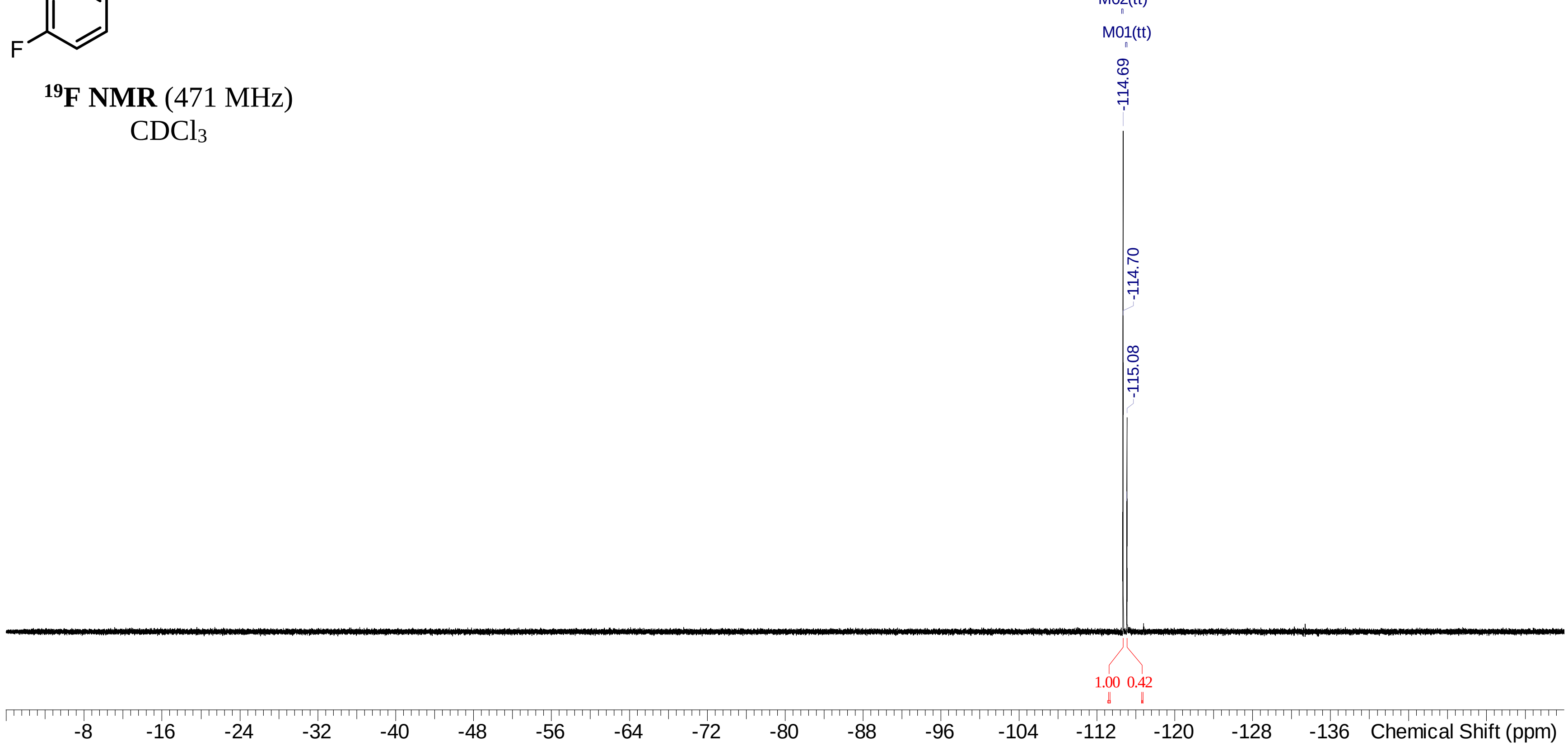


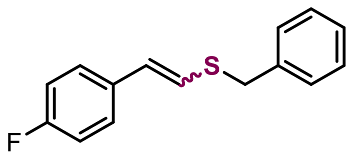
^{1}H NMR (500 MHz)
$CDCl_3$



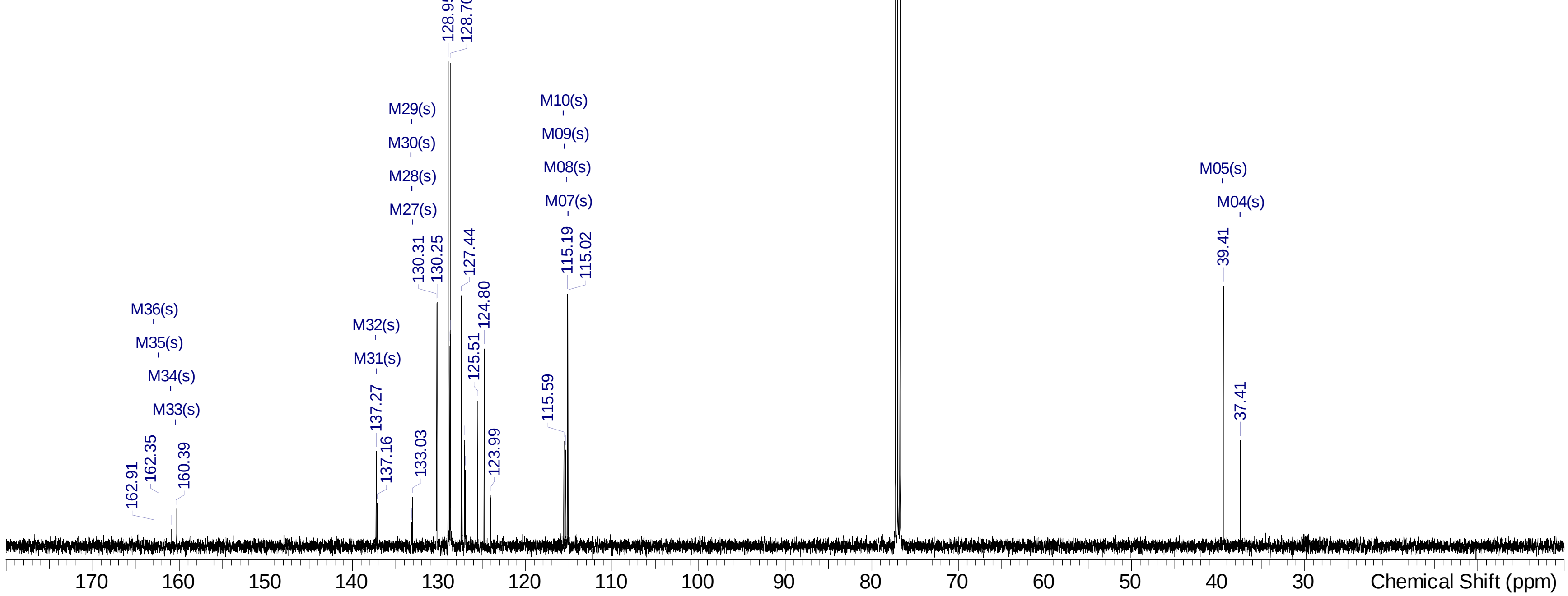


^{19}F NMR (471 MHz)
$CDCl_3$

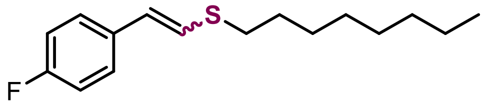




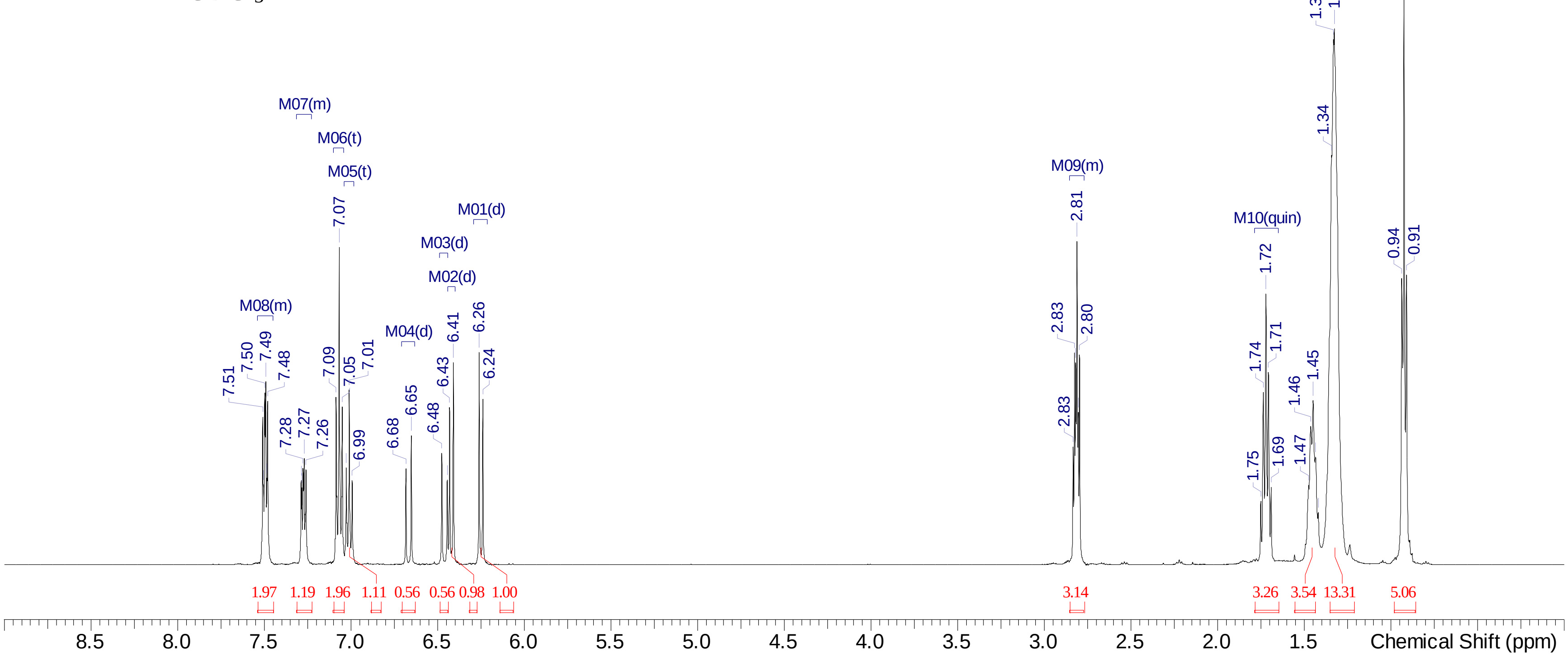
^{13}C NMR (126 MHz)
$CDCl_3$

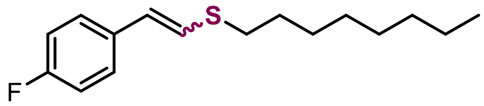


(4-Fluorostyryl)(octyl)sulfane (5m)

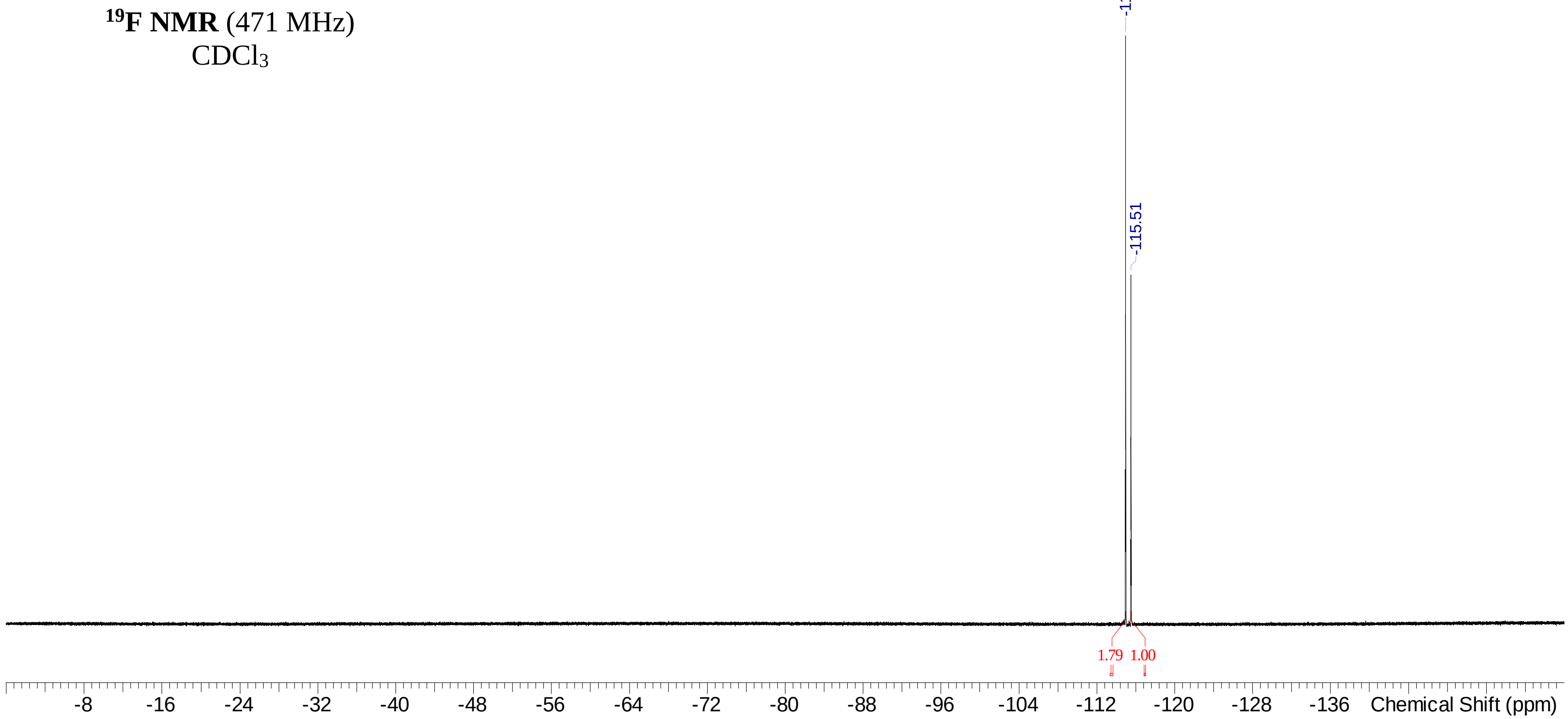


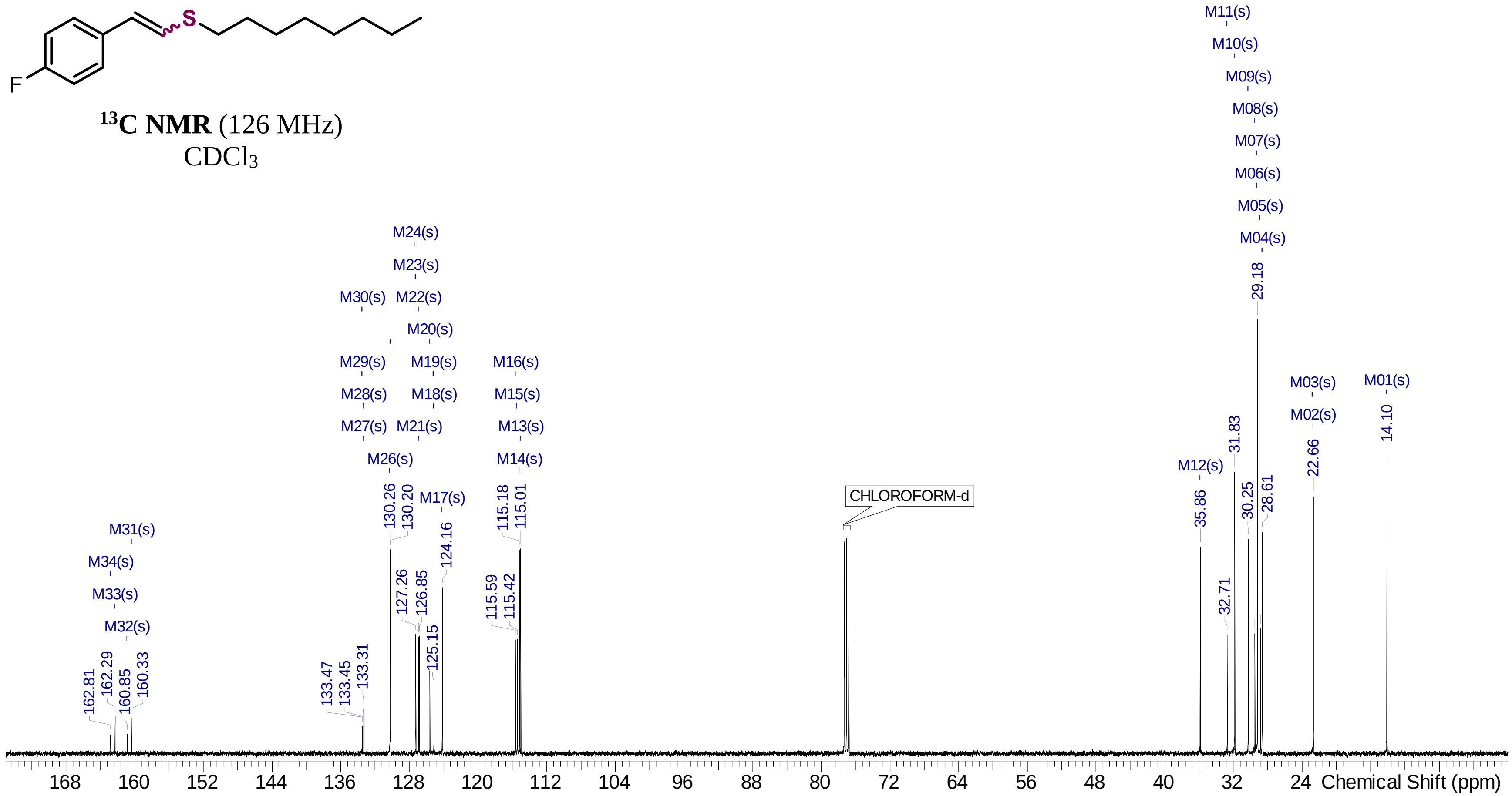
[1]**H NMR** (500 MHz)
$CDCl_3$





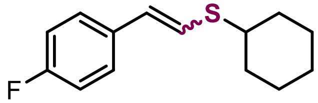
19F NMR (471 MHz)
$CDCl_3$



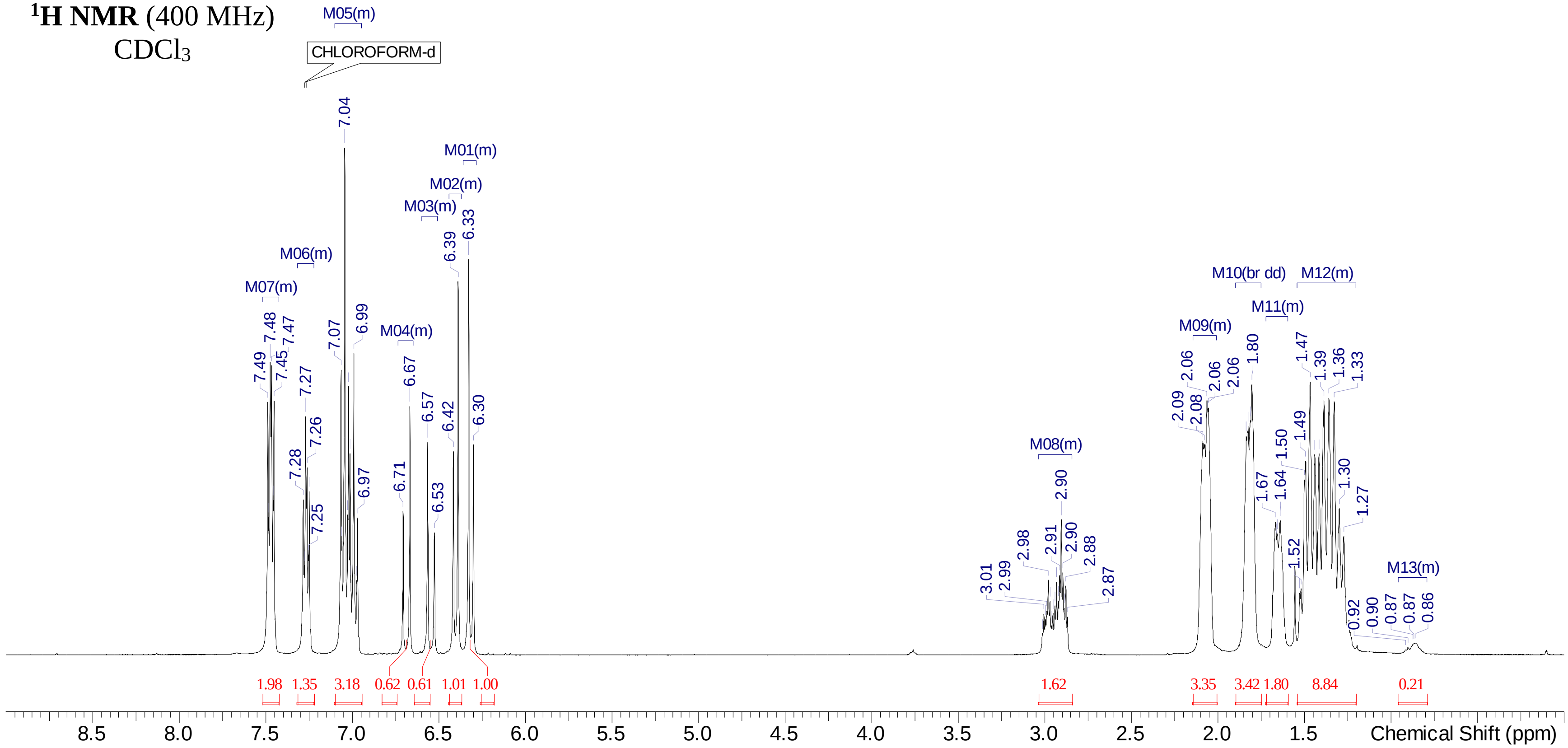


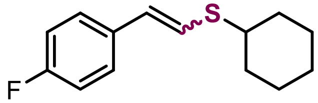
^13^C NMR (126 MHz)
$CDCl_3$

Cyclohexyl(4-fluorostyryl)sulfane (5n)

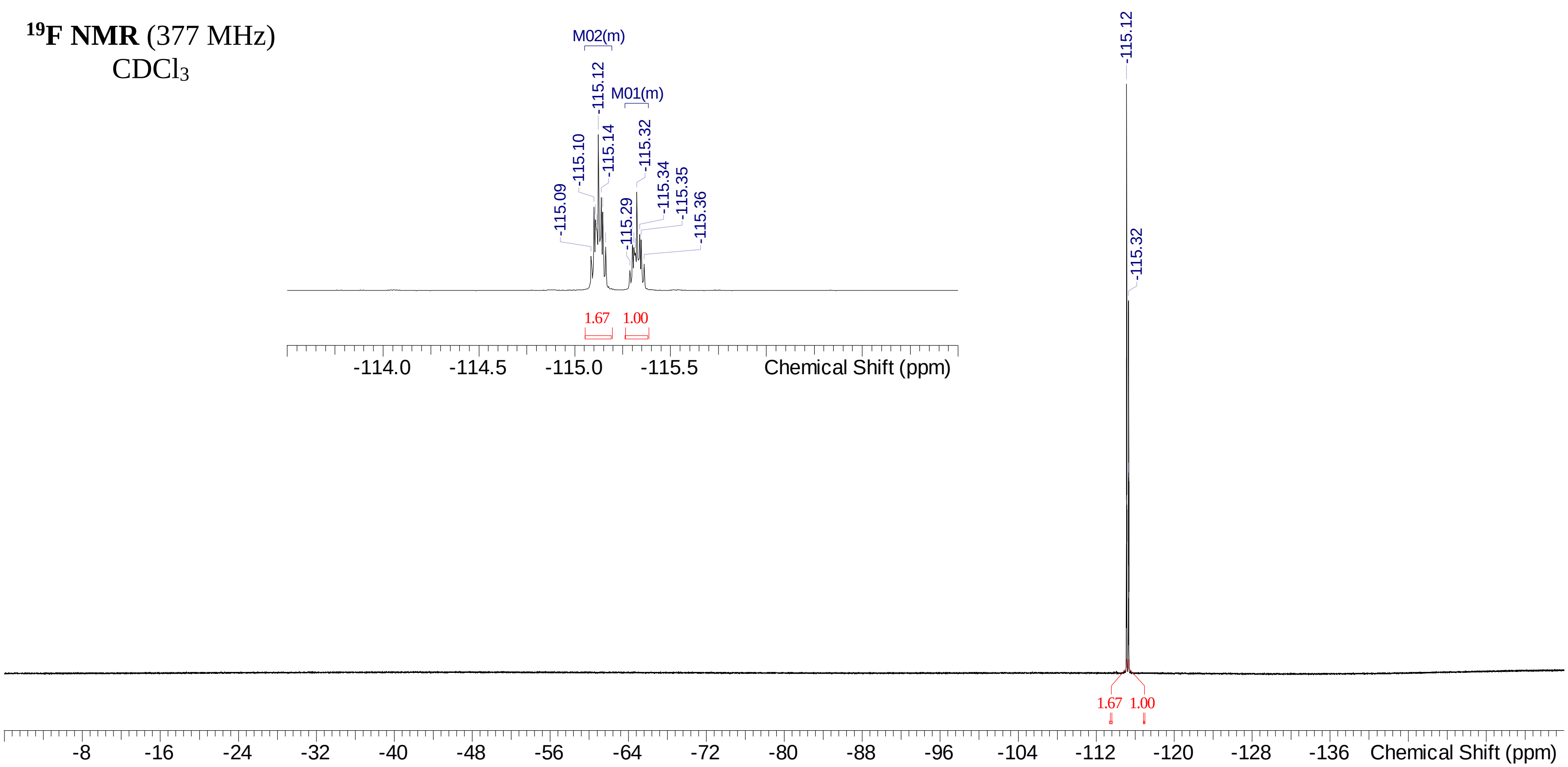


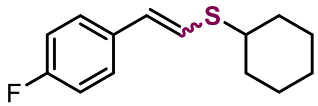
^{1}H NMR (400 MHz)
$CDCl_3$



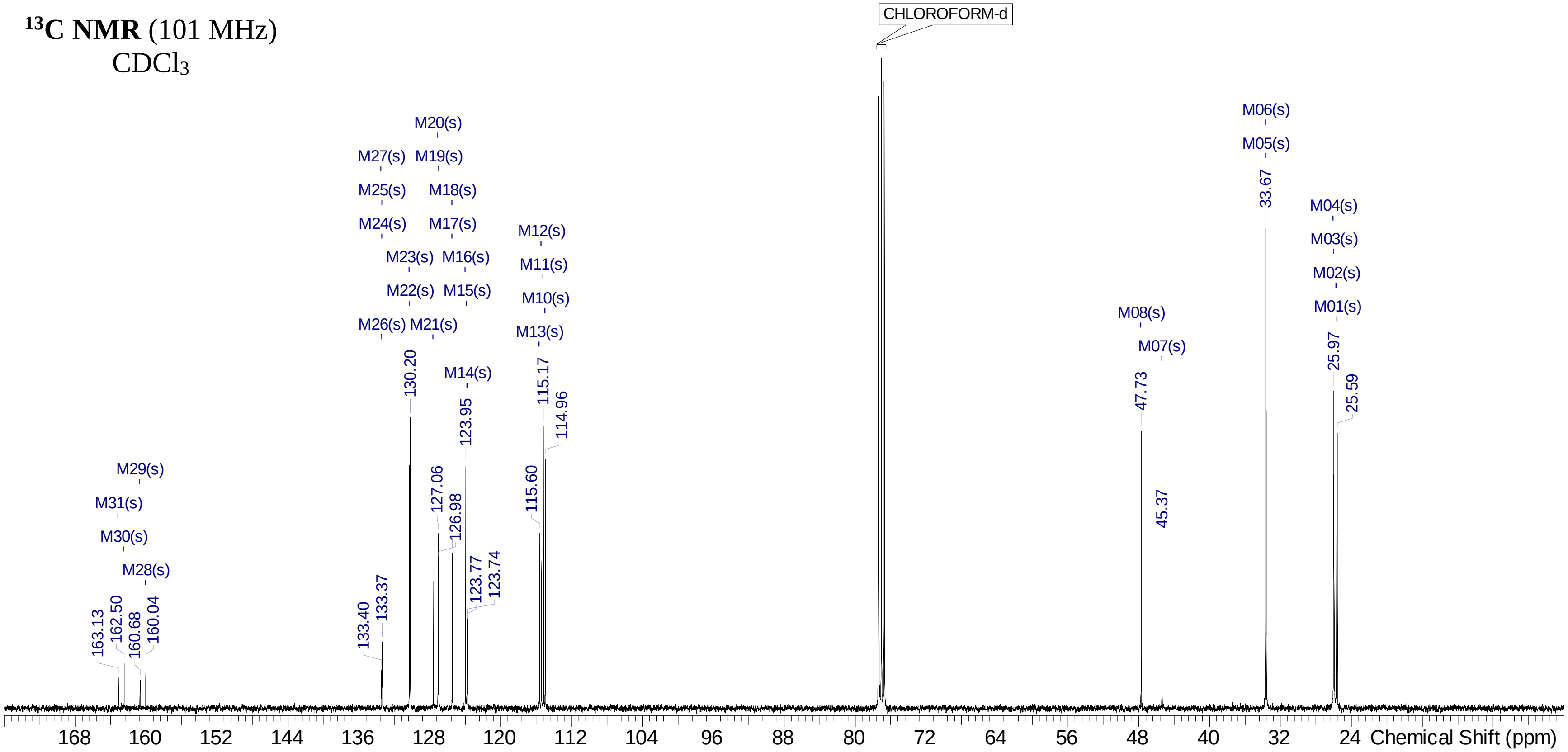


^{19}**F NMR** (377 MHz)
$CDCl_3$

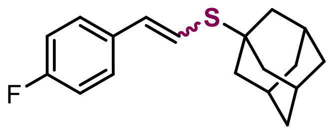




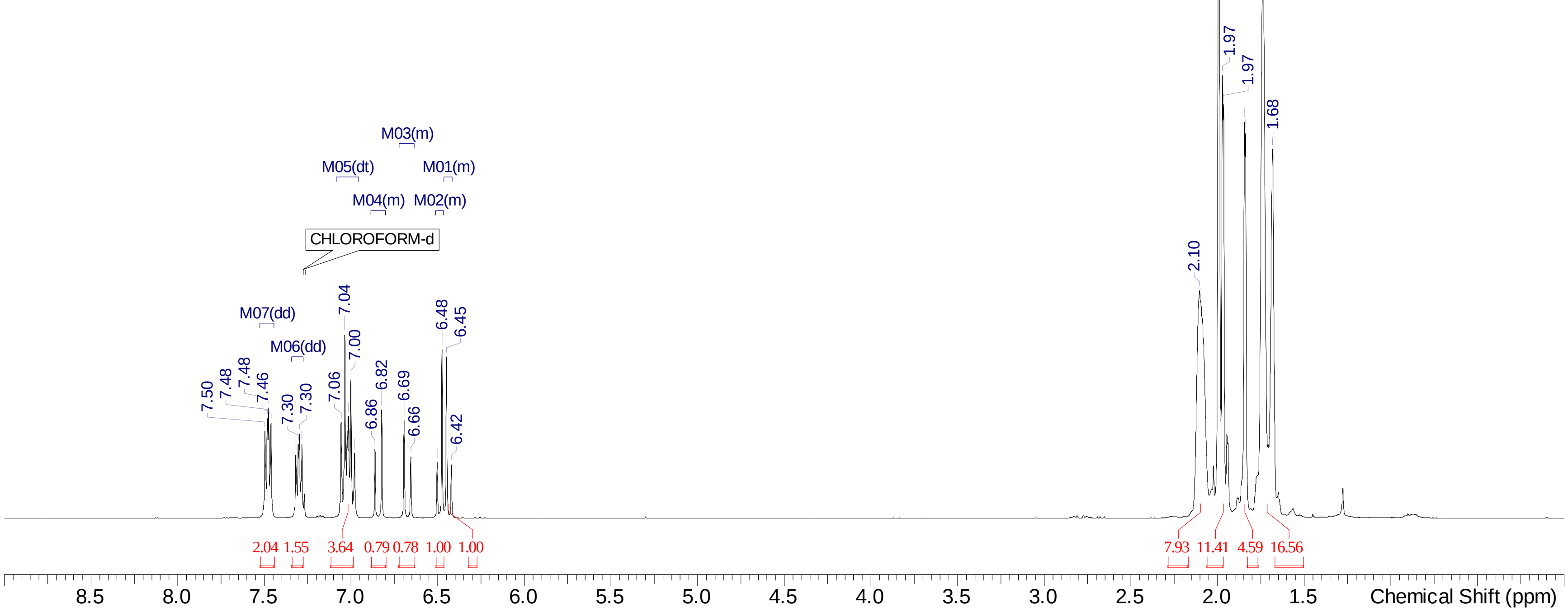
^{13}C NMR (101 MHz)
$CDCl_3$

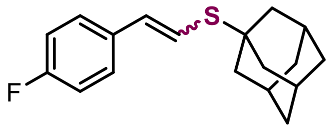


Adamantan-1-yl(4-fluorostyryl)sulfane (5o)

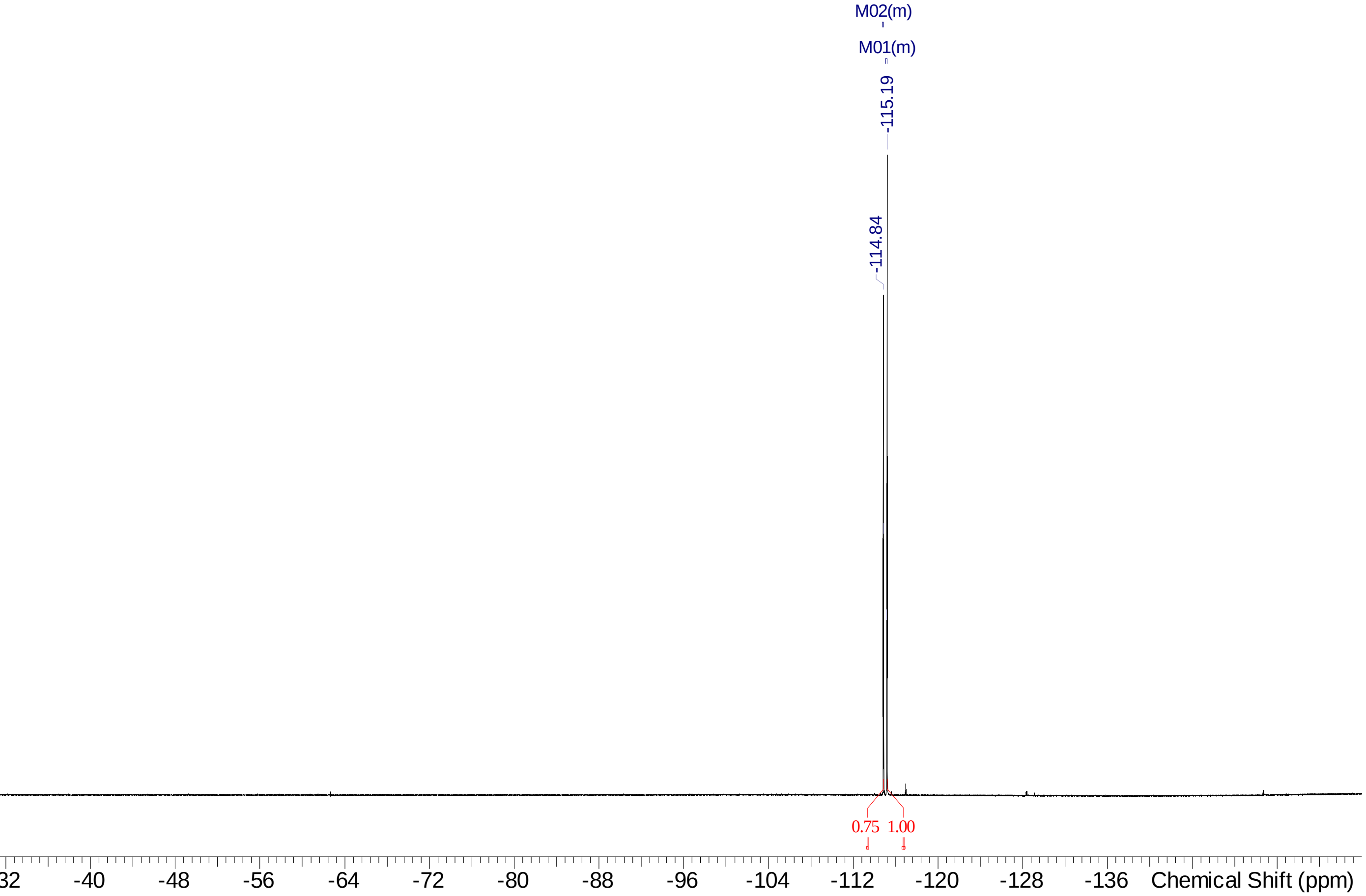


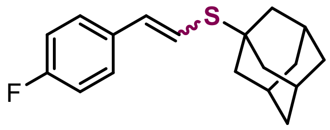
[1]H NMR (400 MHz)
$CDCl_3$



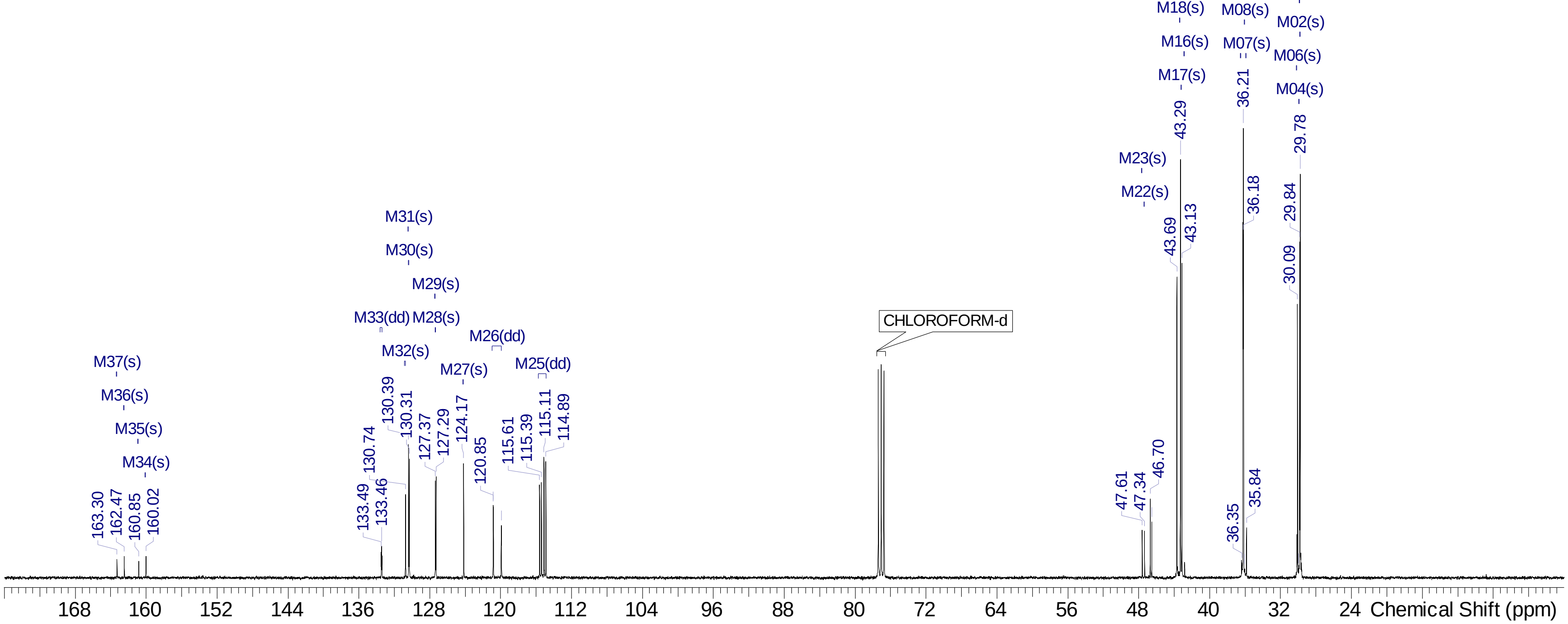


^{19}F NMR (377 MHz)
$CDCl_3$

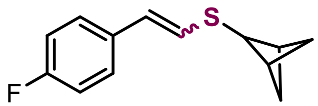




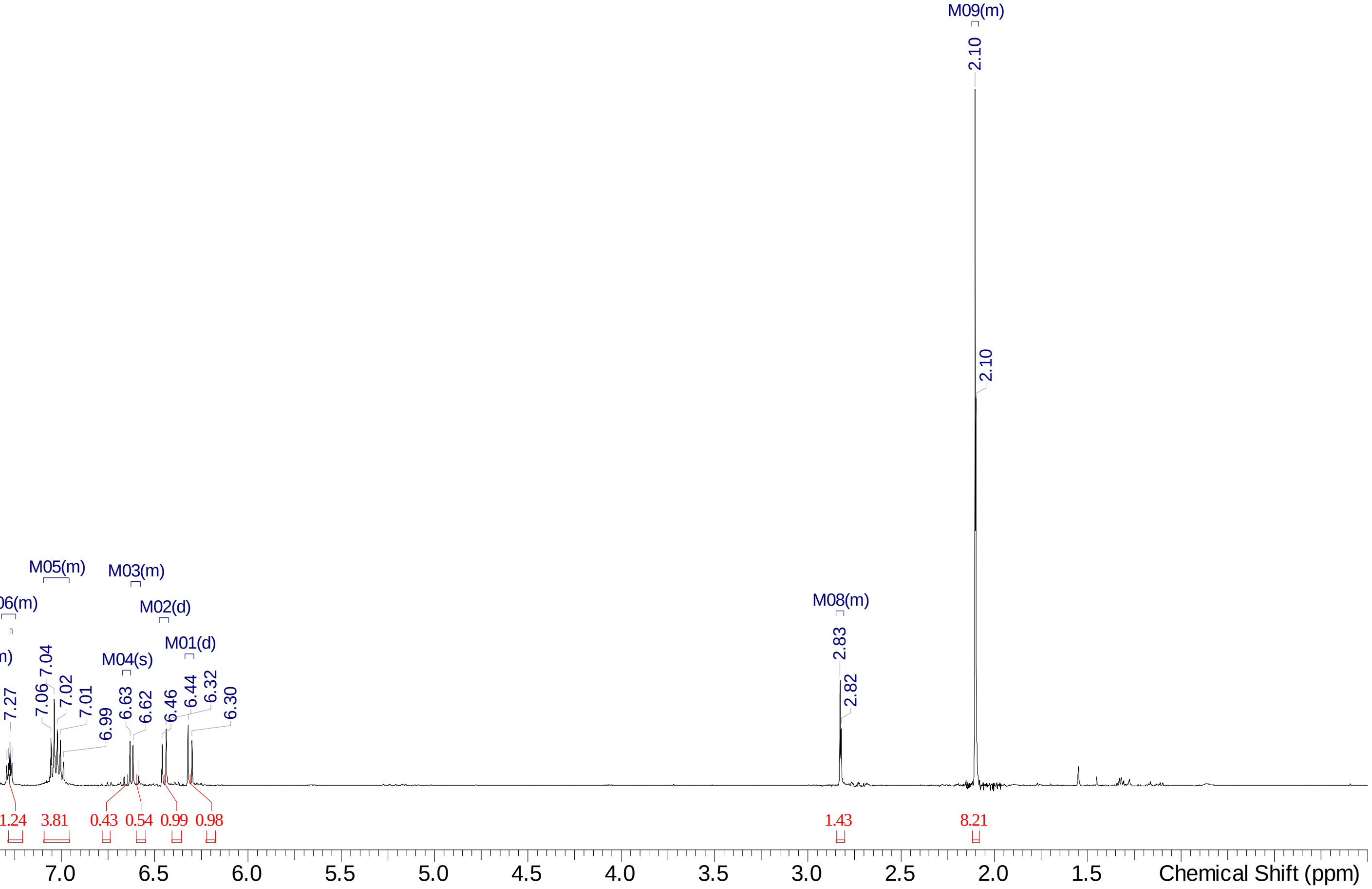
^{13}C NMR (101 MHz)
$CDCl_3$

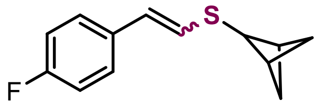


Bicyclo[1.1.1]pentan-2-yl(4-fluorostyryl)sulfane (5p)

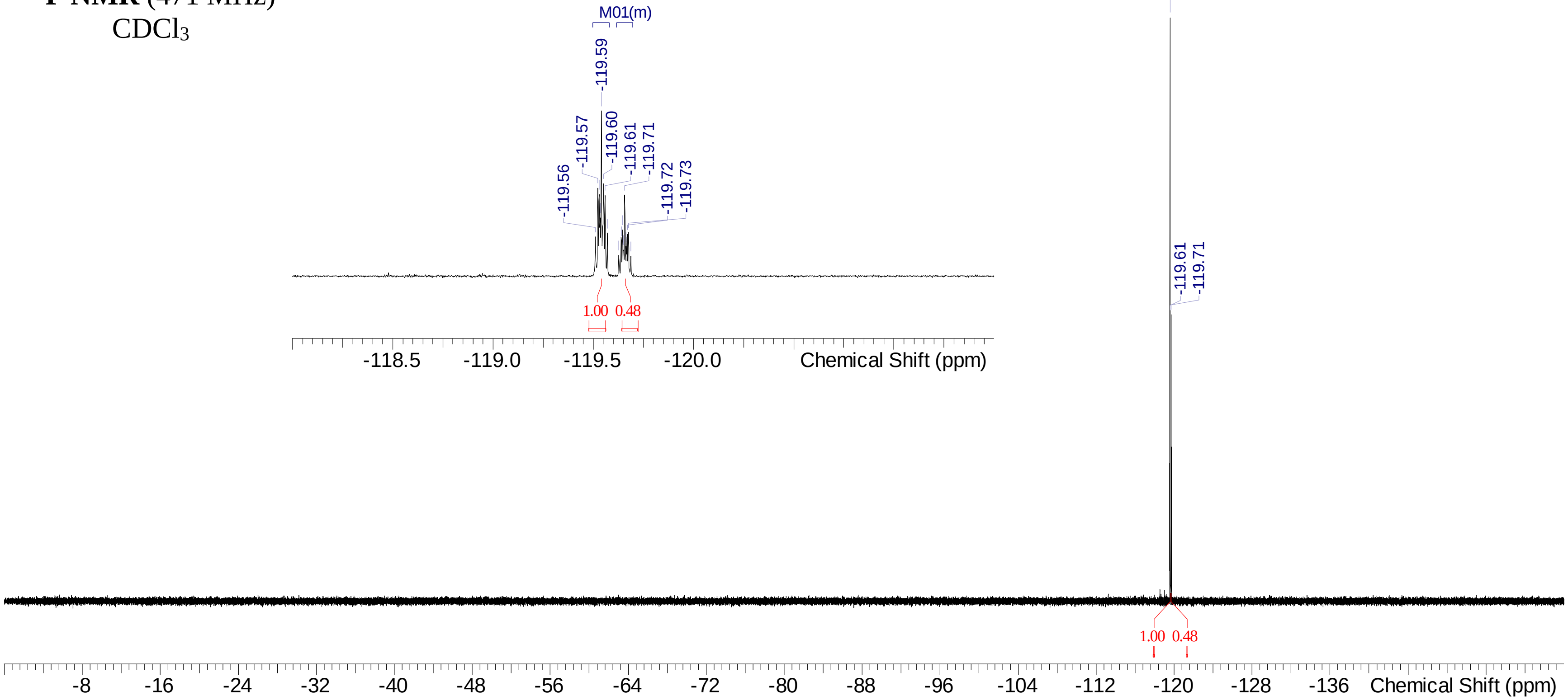


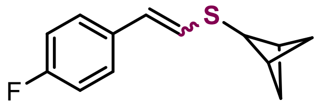
^{1}H NMR (500 MHz)
$CDCl_3$



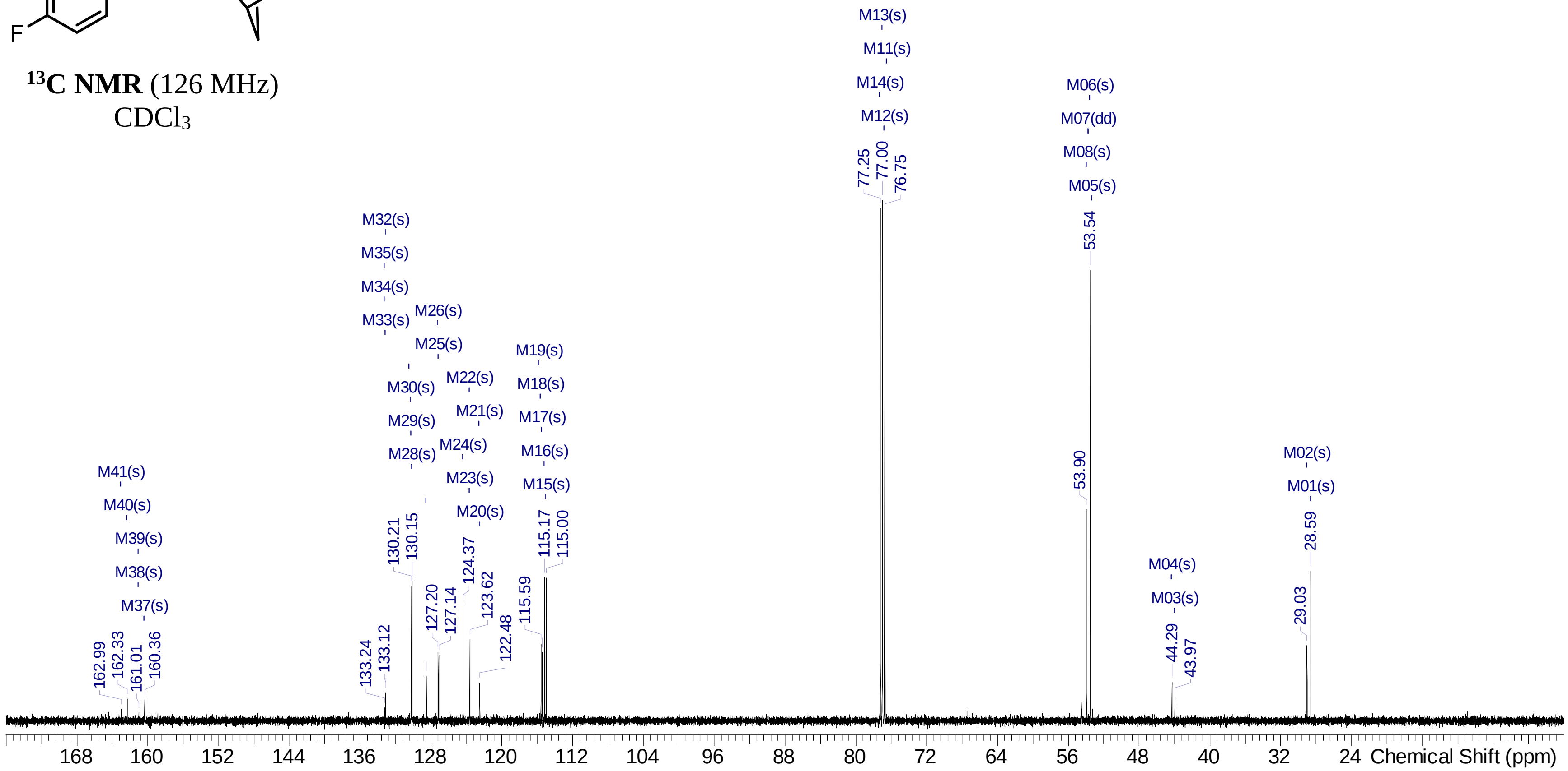


^{19}F NMR (471 MHz)
$CDCl_3$

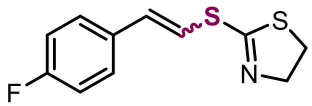




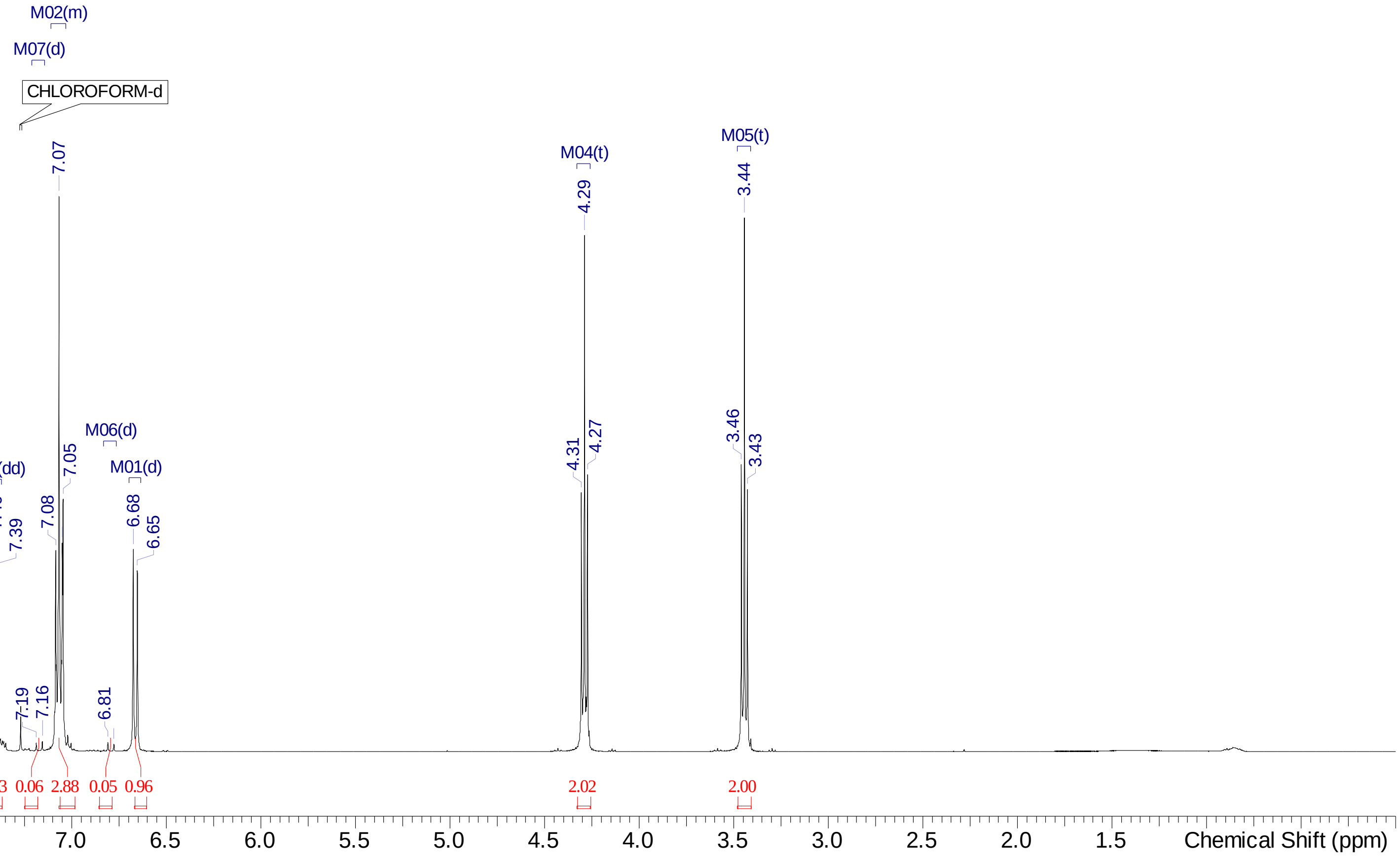
^{13}C NMR (126 MHz)
$CDCl_3$

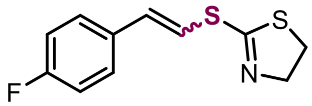


2-((4-Fluorostyryl)thio)-4,5-dihydrothiazole (5q)

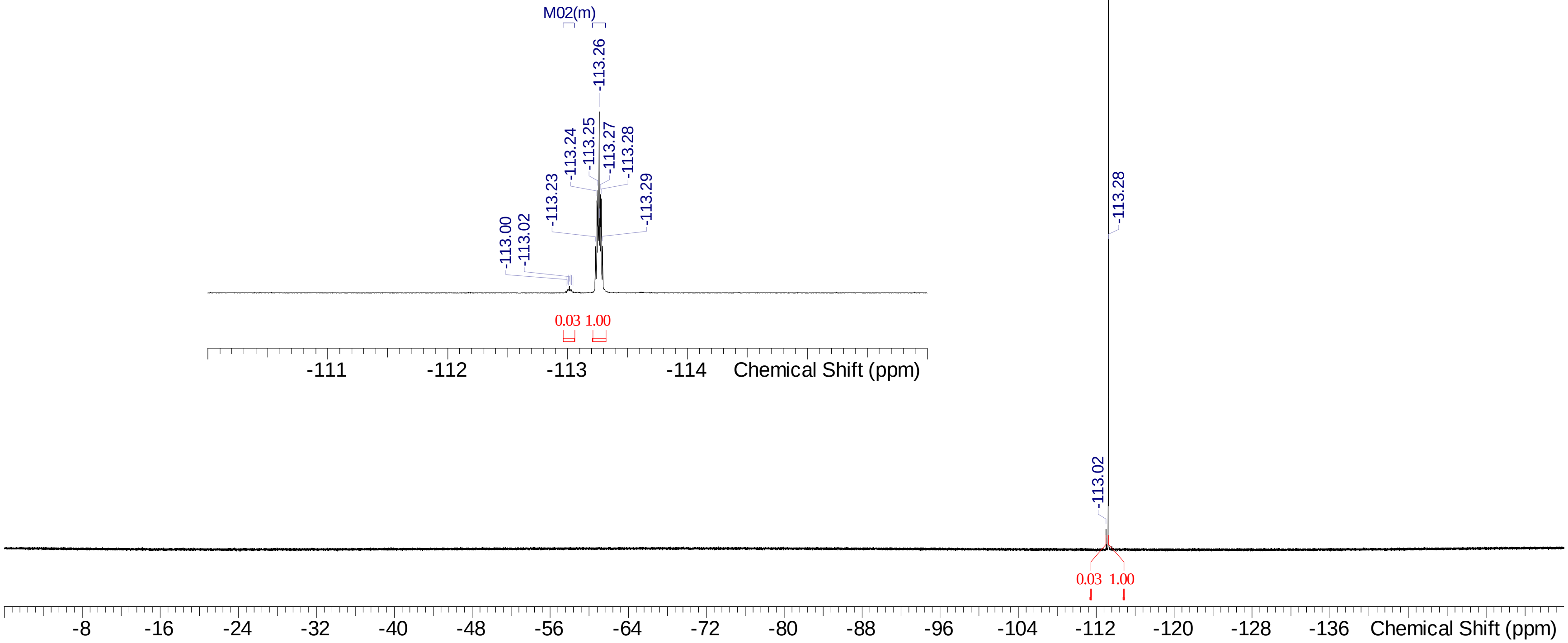


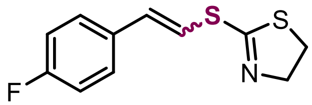
[1]H NMR (500 MHz)
$CDCl_3$



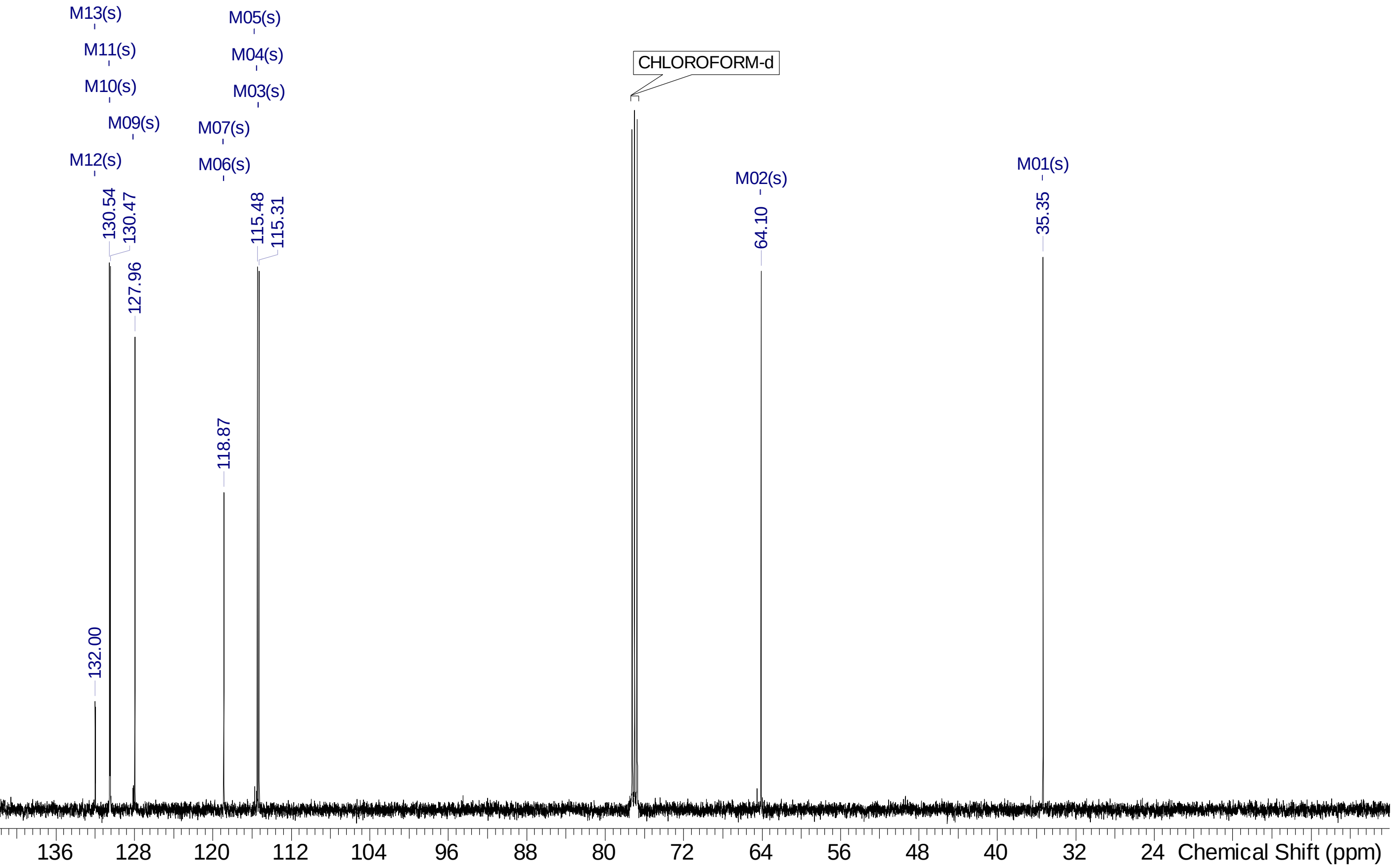


^{19}**F NMR** (471 MHz)
$CDCl_3$

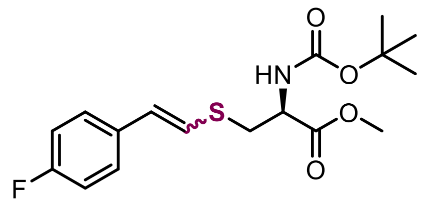




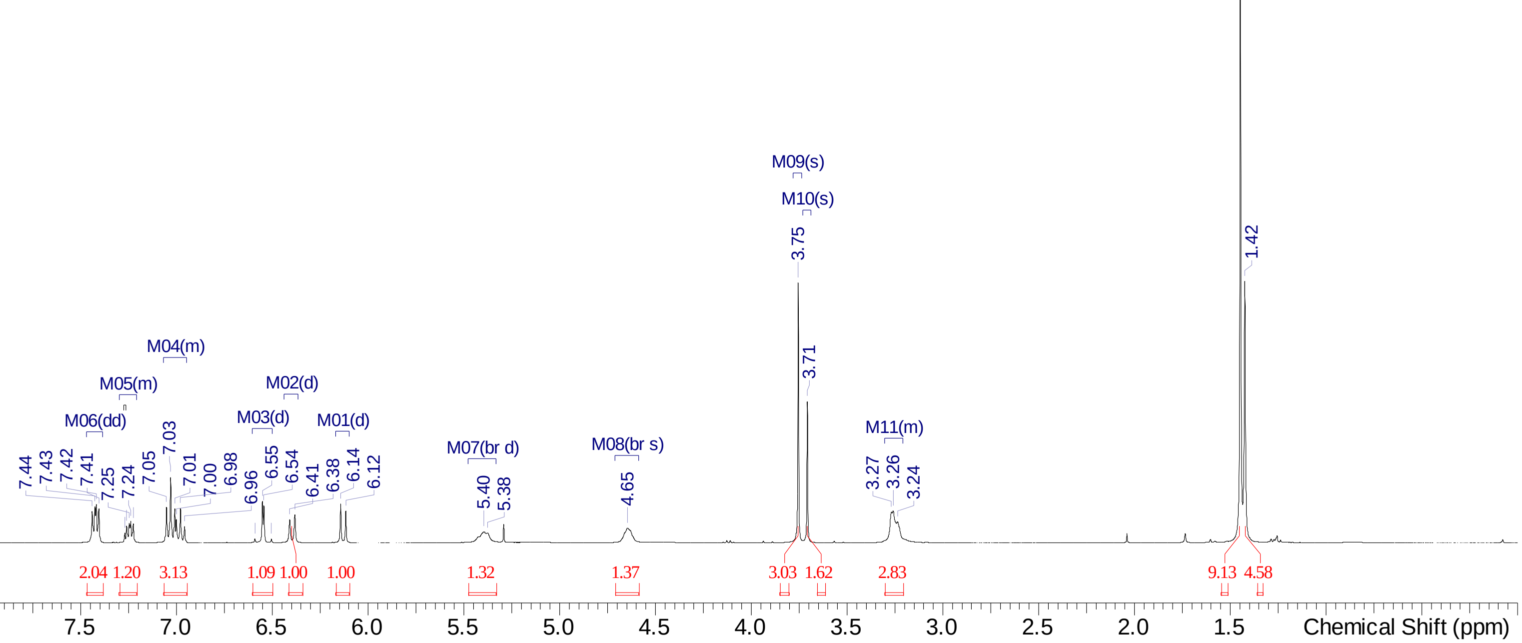
^{13}C NMR (126 MHz)
$CDCl_3$

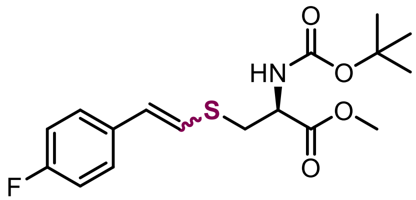


Methyl *N*-(3,3-dimethylbutanoyl)-*S*-(4-fluorostyryl)-*D*-cysteinate (5r)

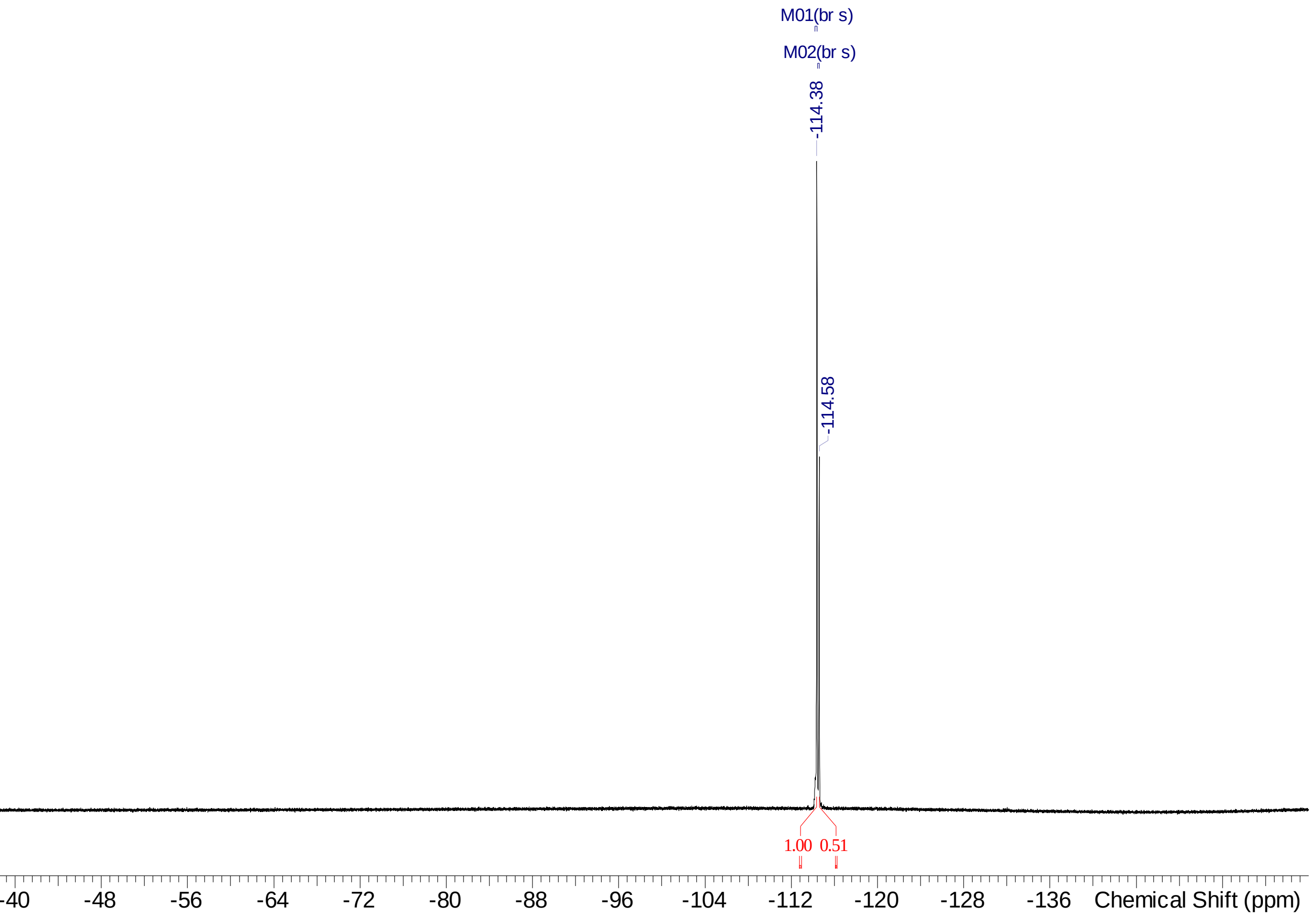


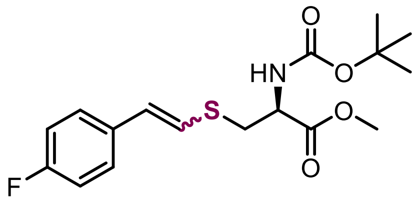
[1]H NMR (400 MHz)
$CDCl_3$



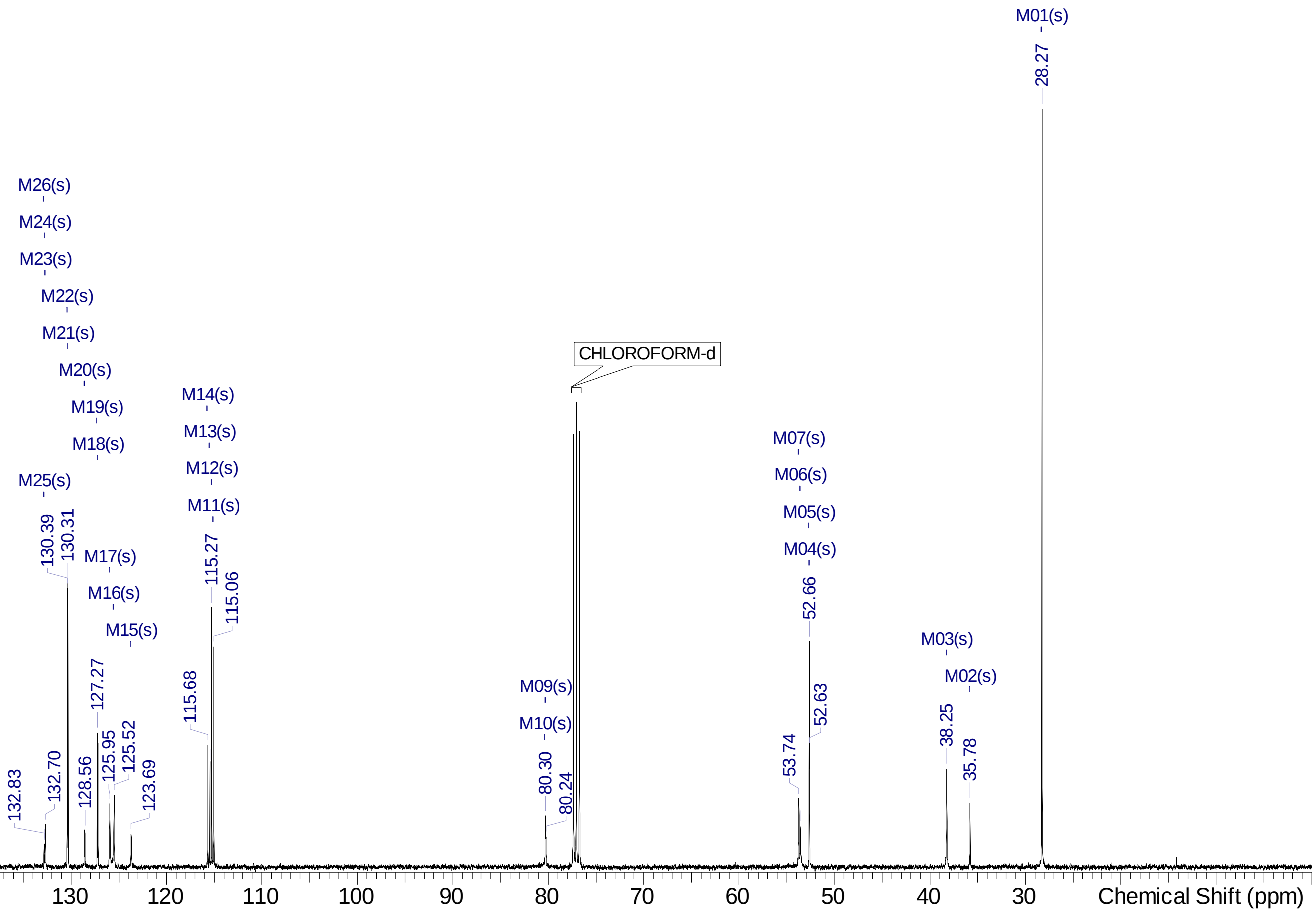


^{19}F NMR (377 MHz)
$CDCl_3$



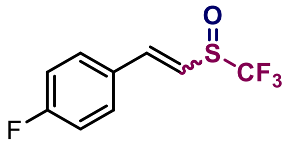


^{13}C NMR (101 MHz)
$CDCl_3$

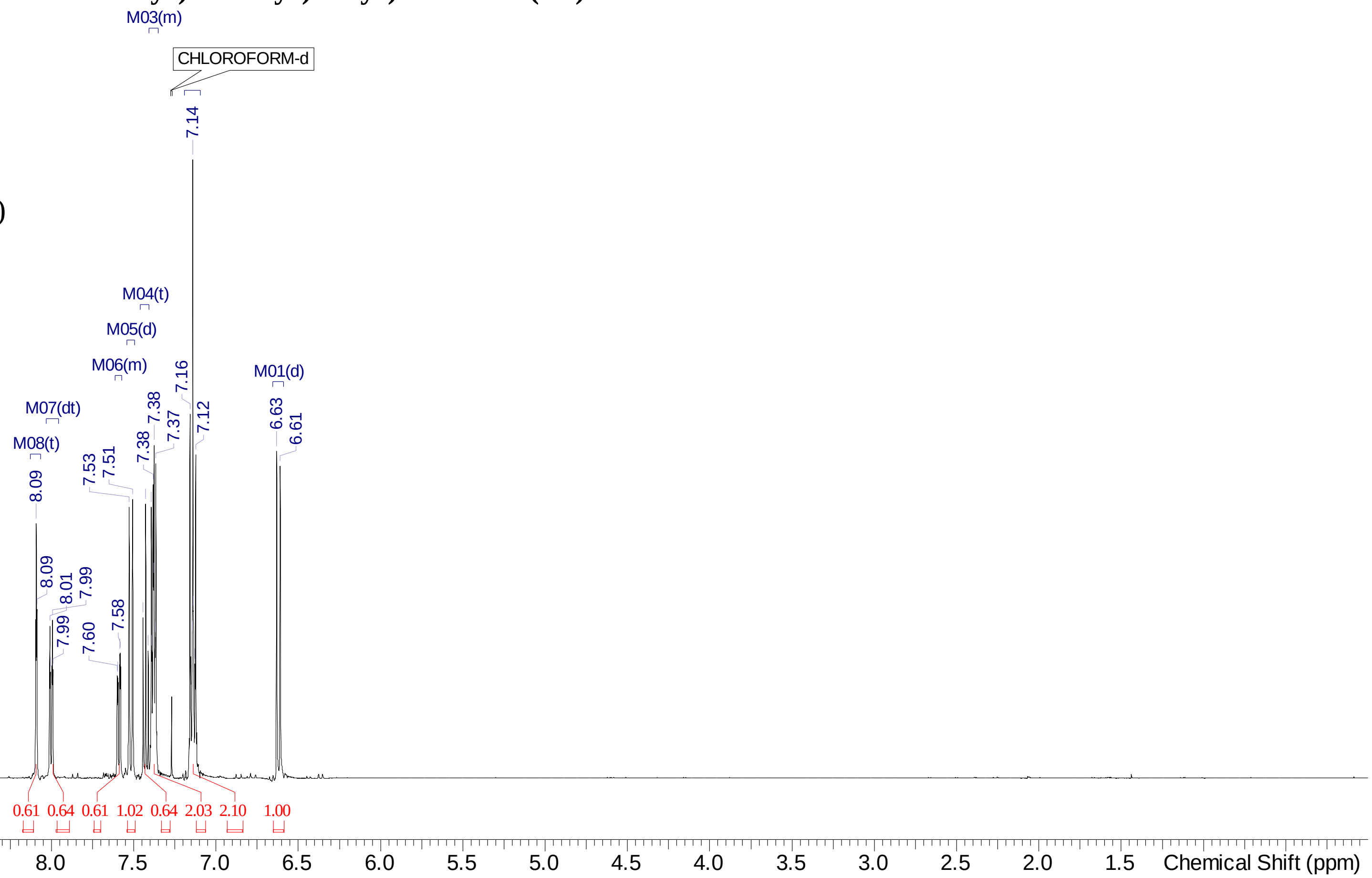


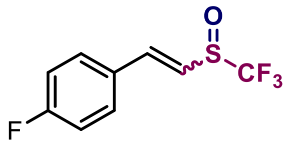
Post-Functionalized Products

1-fluoro-4-(2-((trifluoromethyl)sulfinyl)vinyl)benzene (6a)

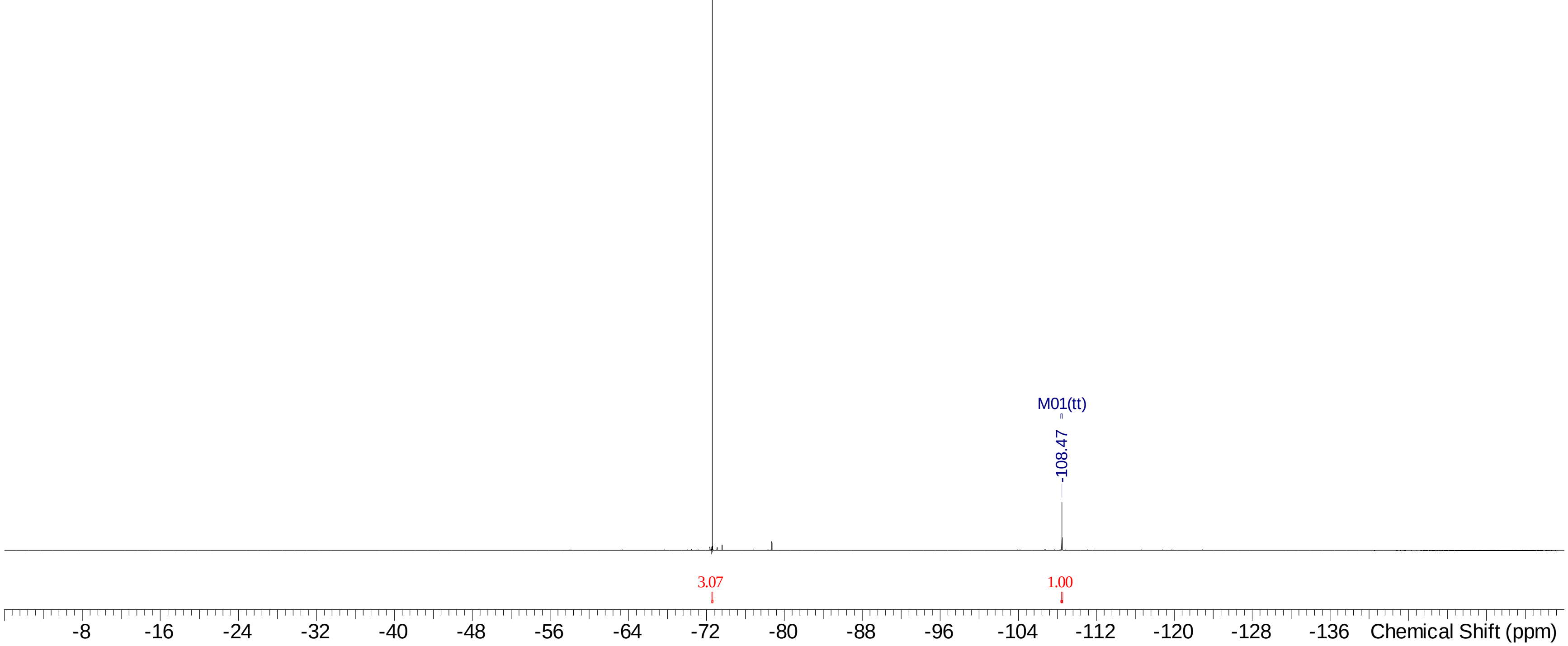


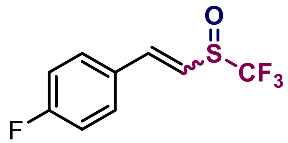
^{1}H NMR (500 MHz)
$CDCl_3$



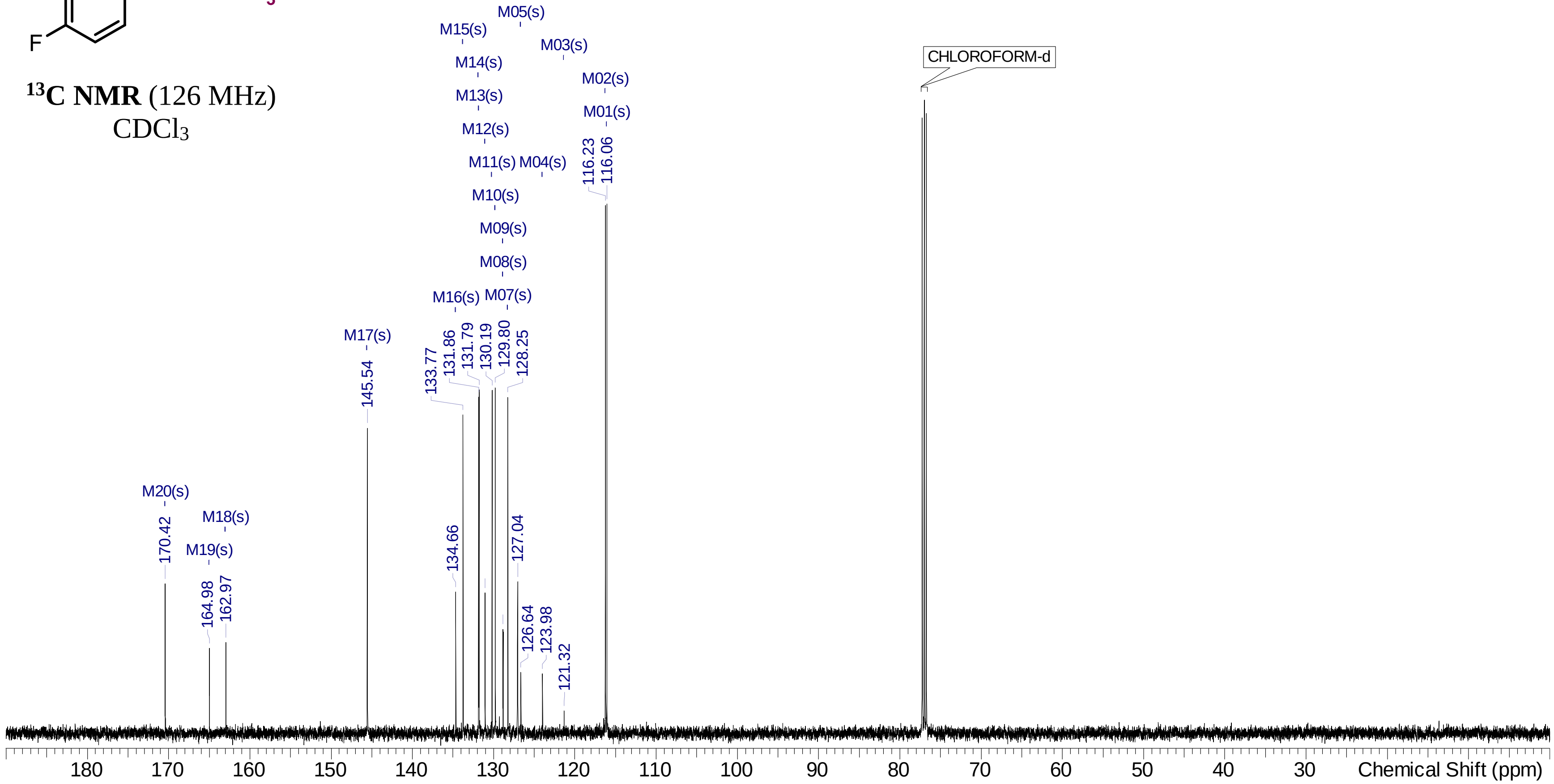


^{19}**F NMR** (471 MHz)
$CDCl_3$

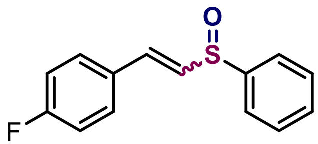




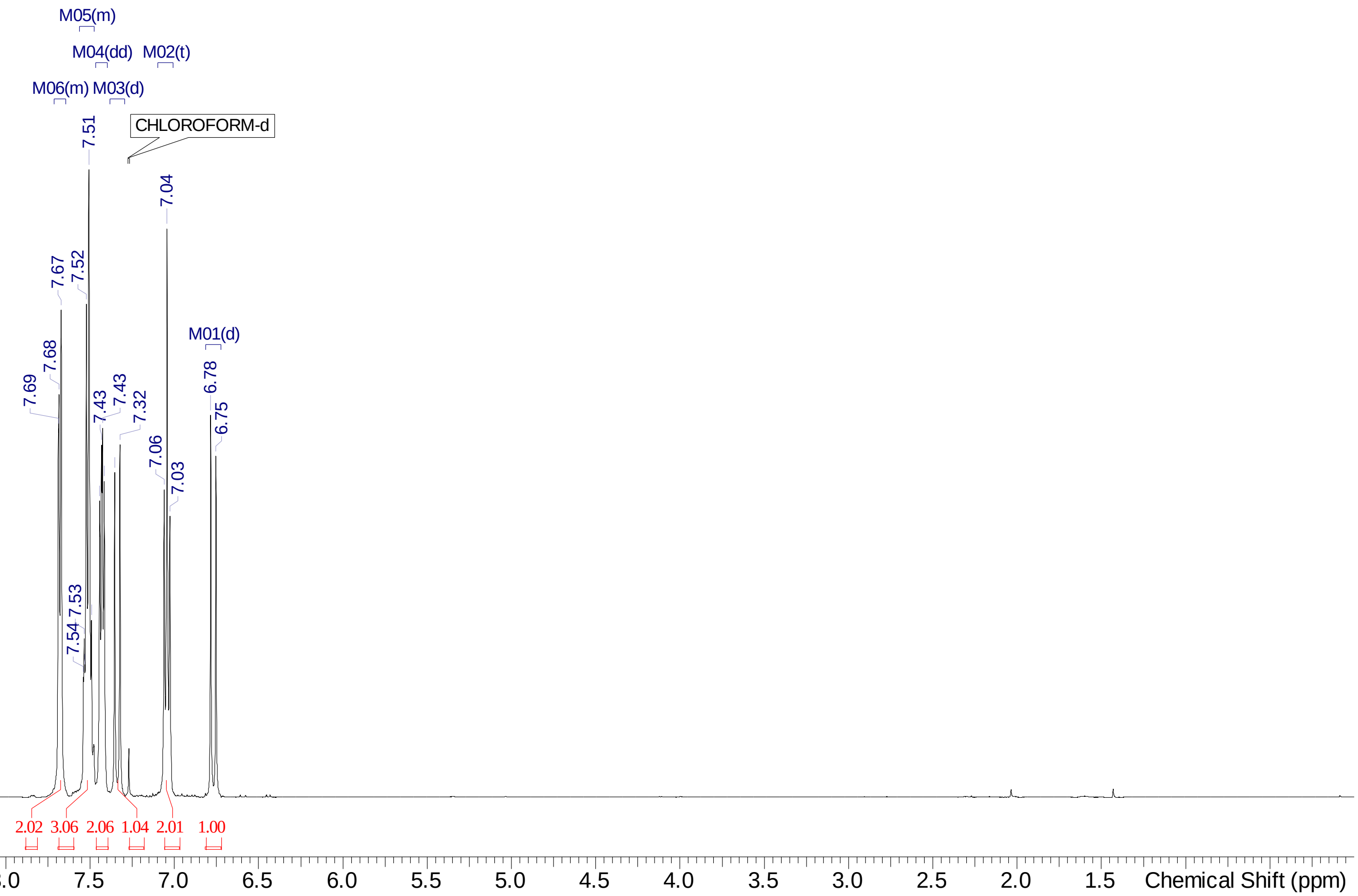
^{13}C **NMR** (126 MHz)
$CDCl_3$

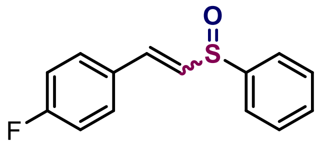


1-Fluoro-4-(2-(phenylsulfinyl)vinyl)benzene (6b)

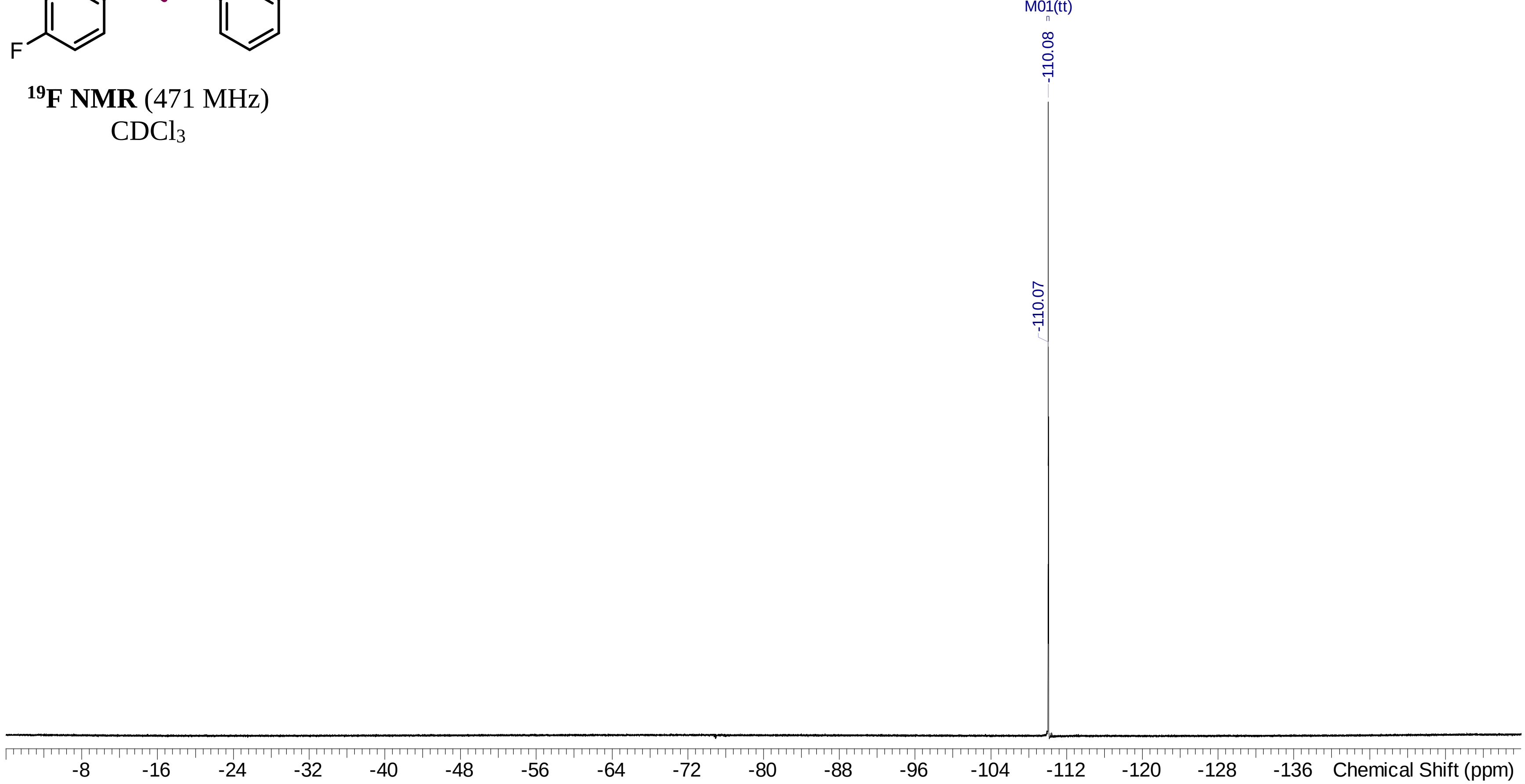


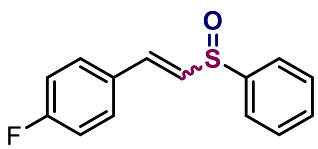
^{1}H NMR (500 MHz)
$CDCl_3$



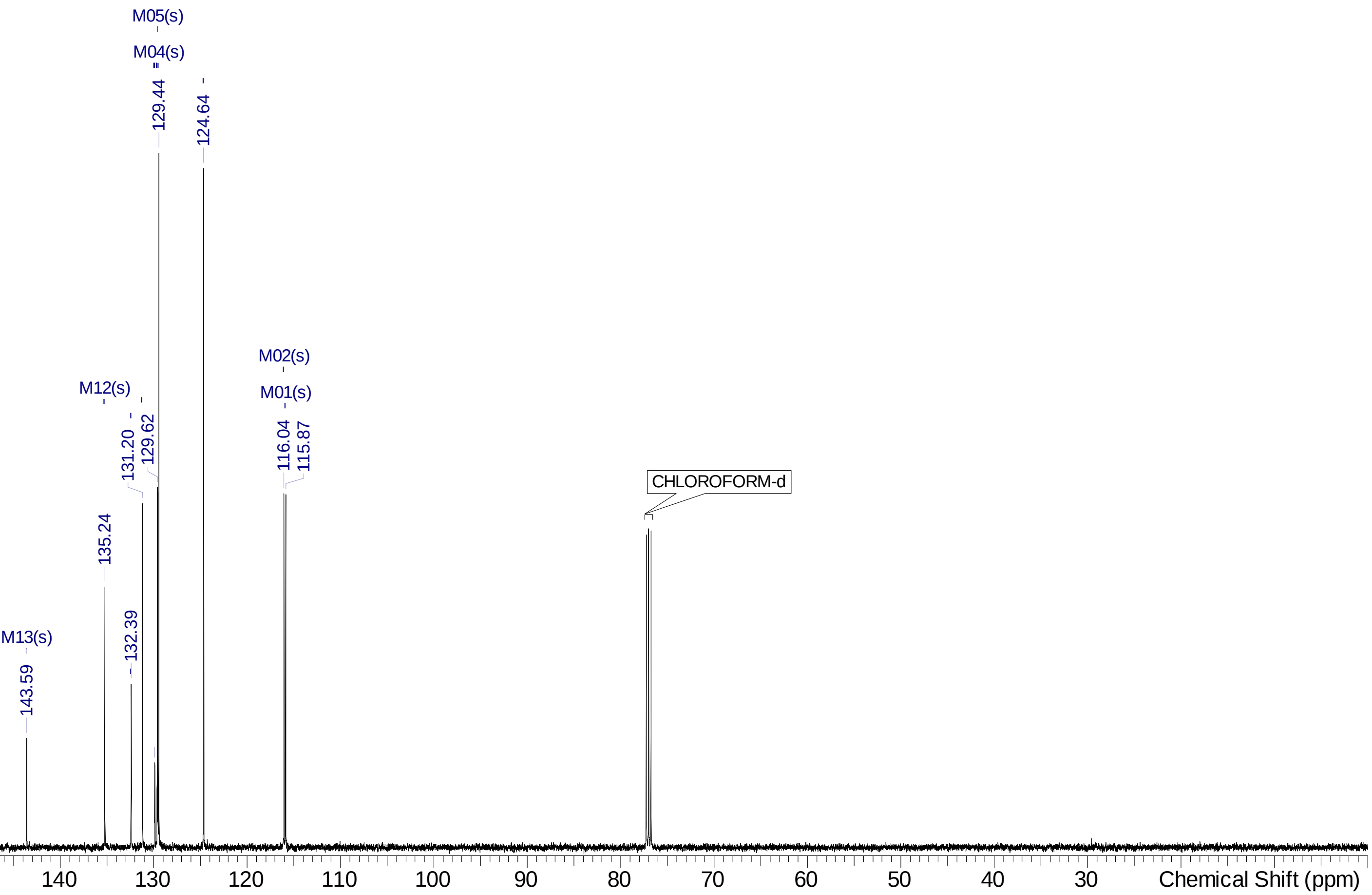


^{19}F NMR (471 MHz)
$CDCl_3$

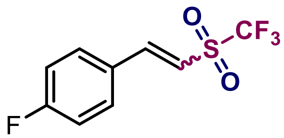




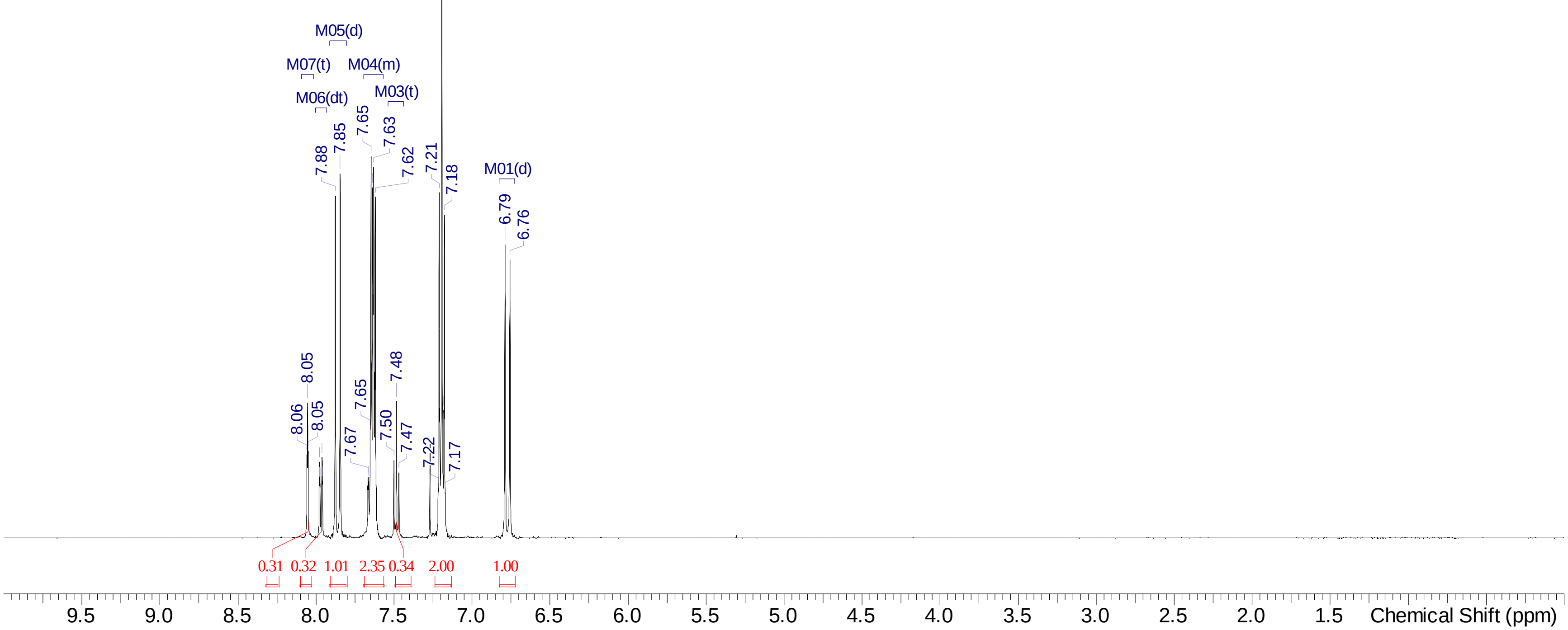
^{13}C NMR (126 MHz)
$CDCl_3$

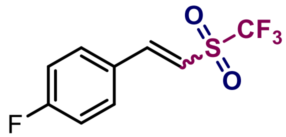


1-Fluoro-4-(2-((trifluoromethyl)sulfonyl)vinyl)benzene (6c)

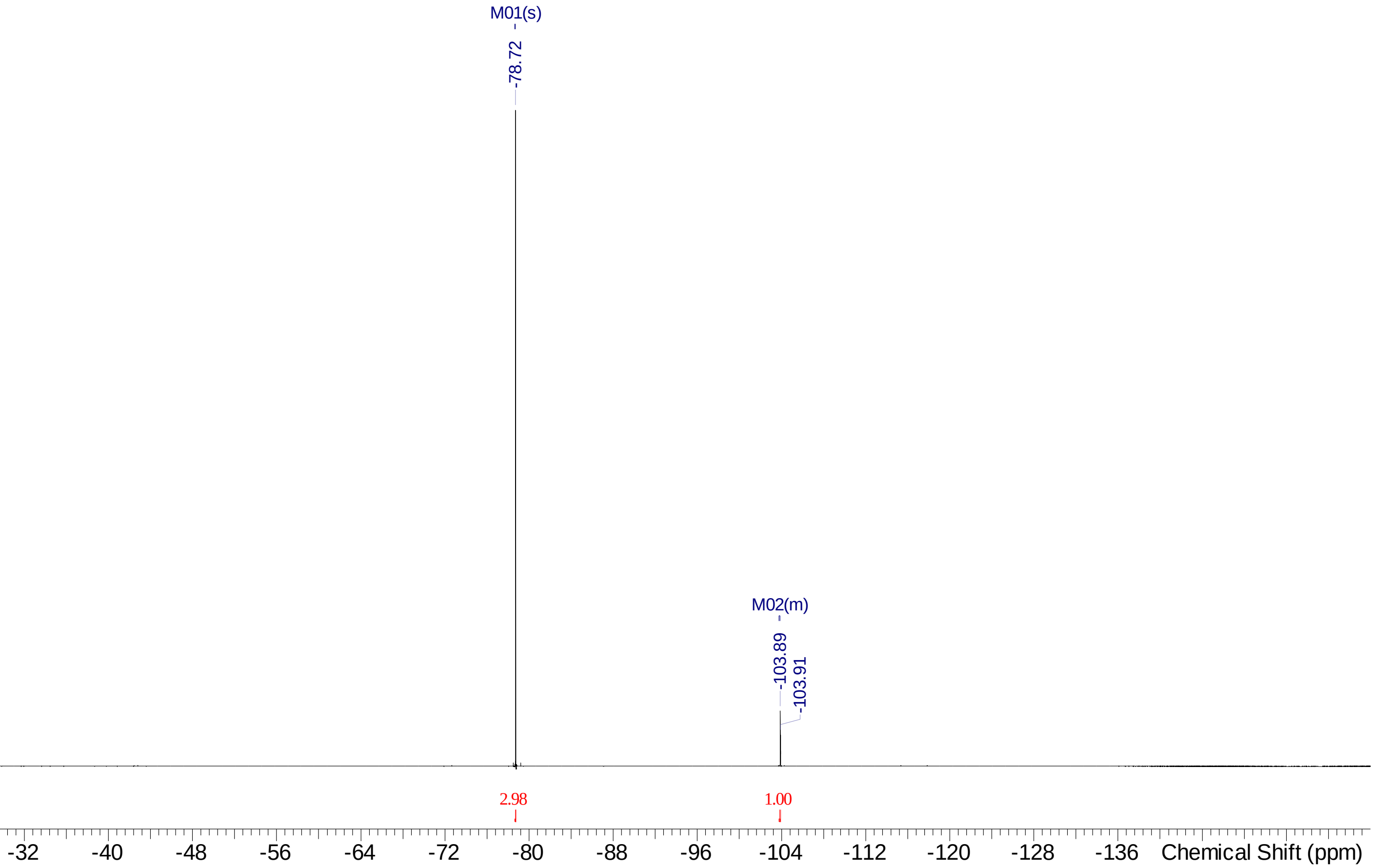


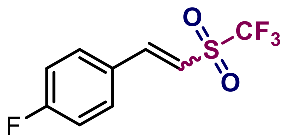
[1]H NMR (500 MHz)
$CDCl_3$



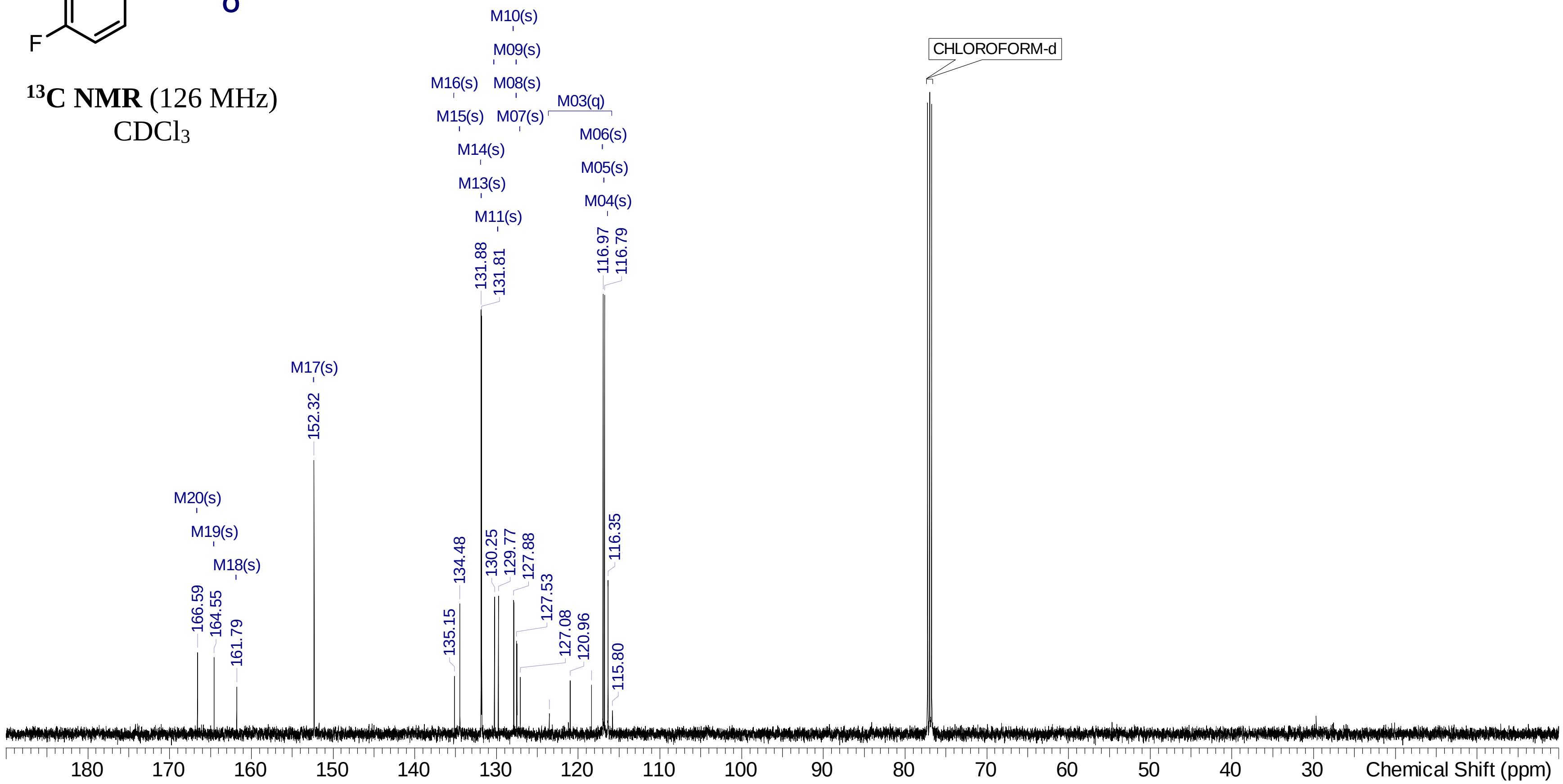


[19]F NMR (471 MHz)
$CDCl_3$

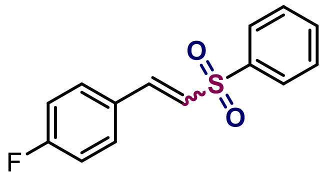




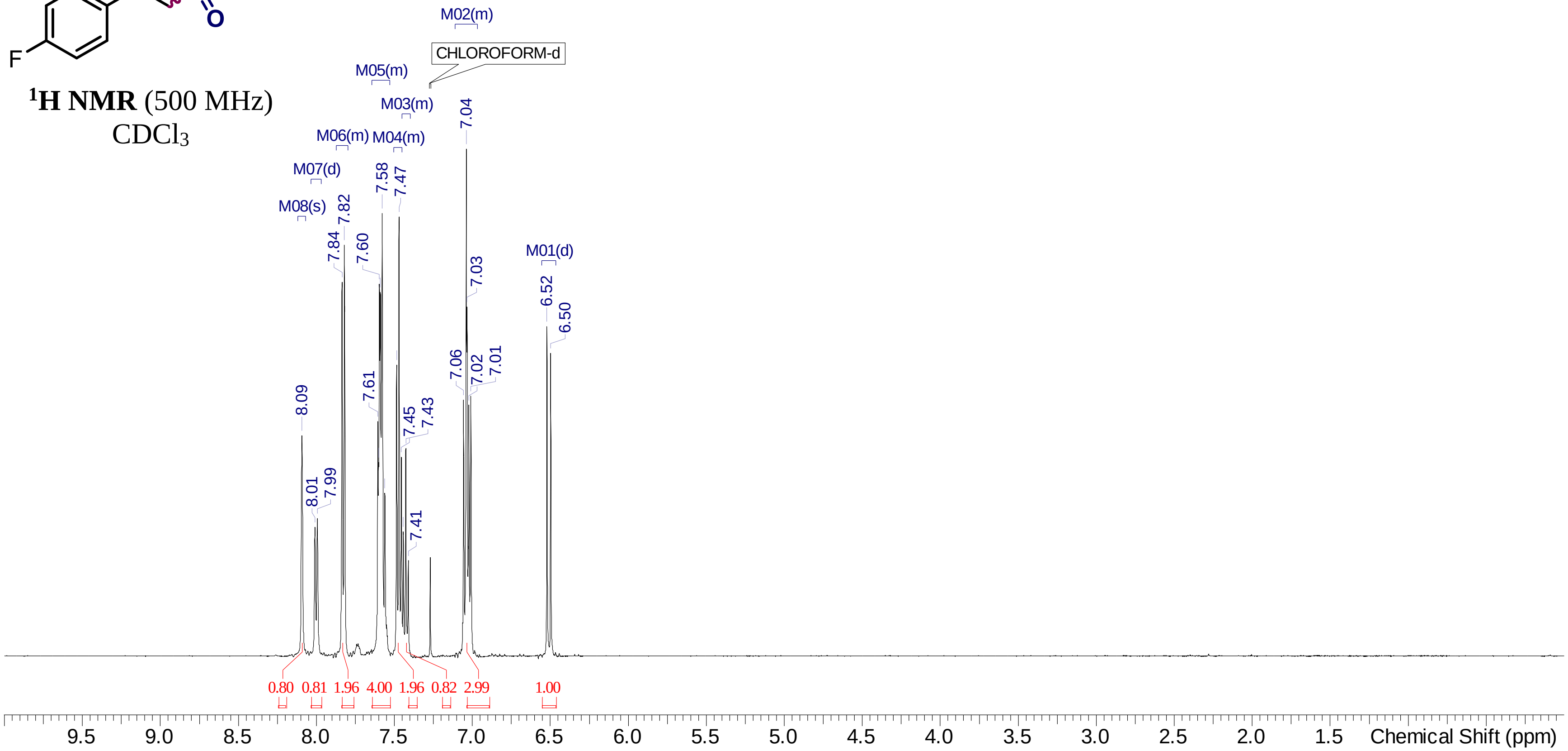
^{13}C NMR (126 MHz)
$CDCl_3$

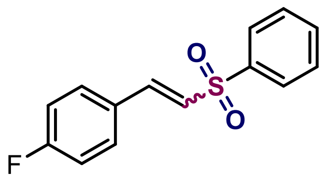


1-fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (6d)

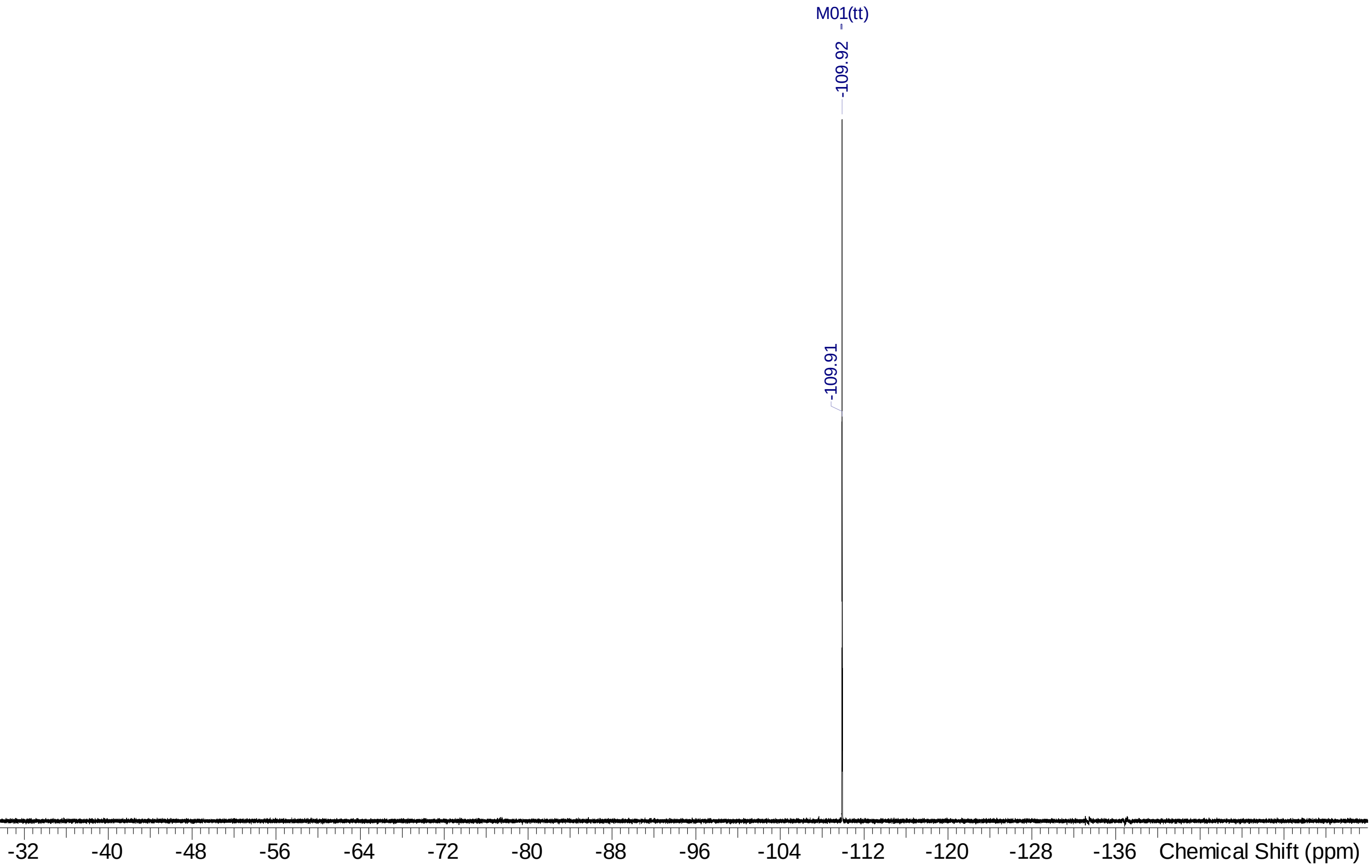


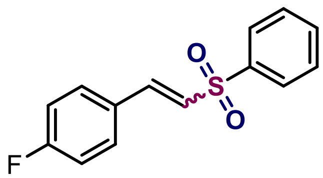
^{1}H NMR (500 MHz)
$CDCl_3$



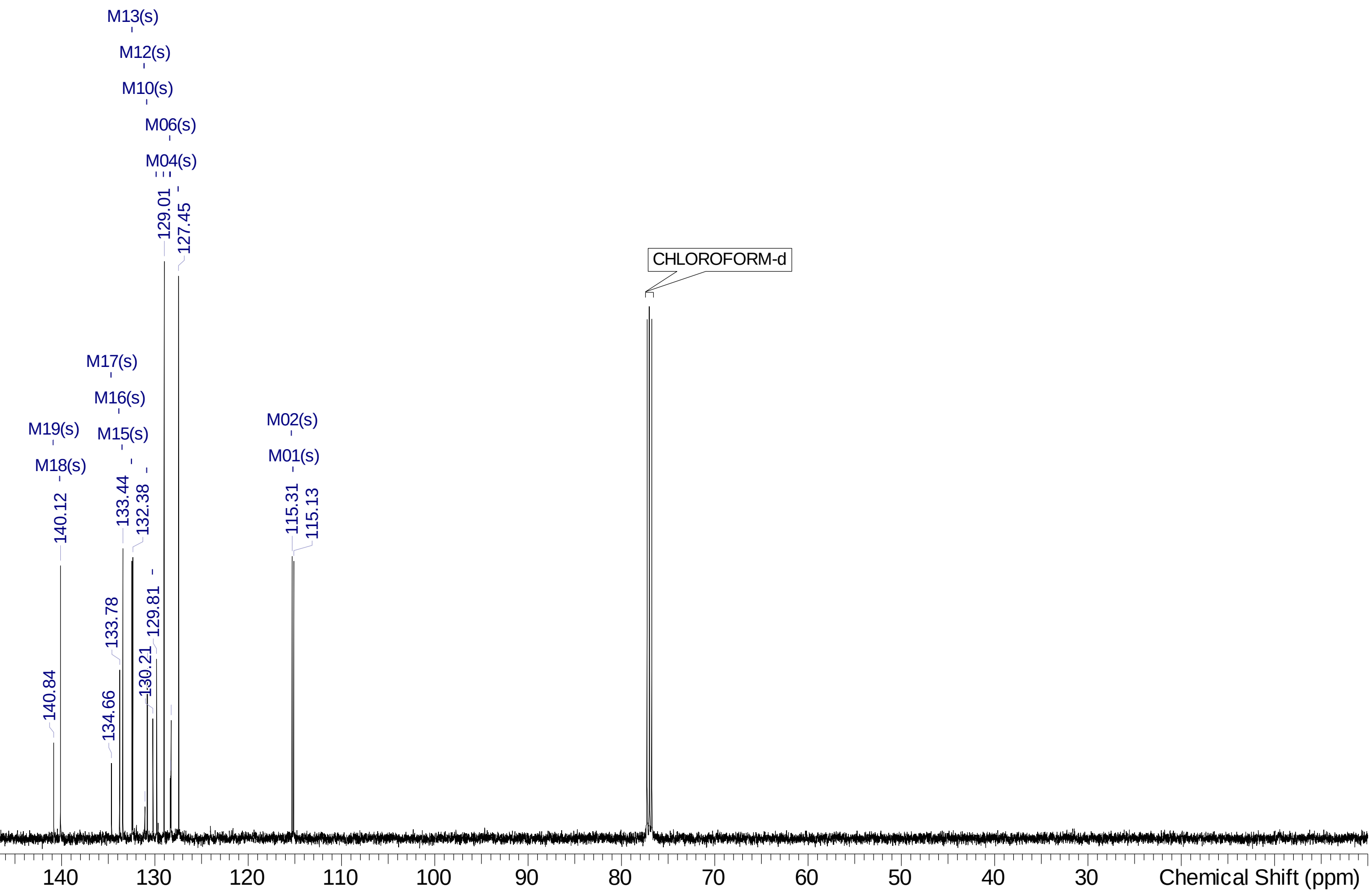


^{19}F NMR (471 MHz)
$CDCl_3$

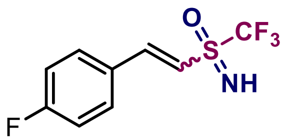




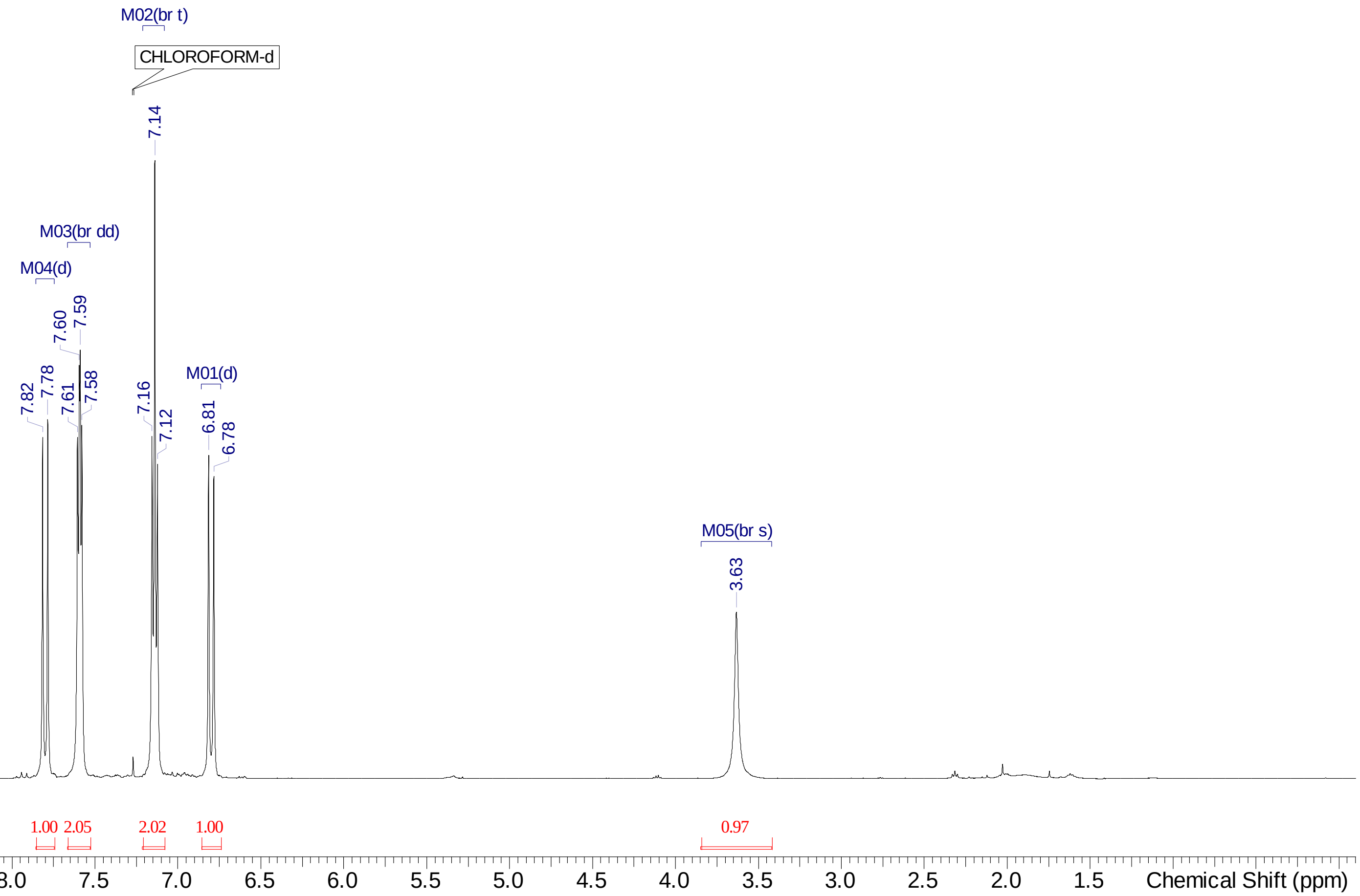
[13]C NMR (126 MHz)
$CDCl_3$

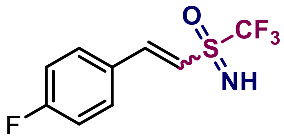


(4-Fluorostyryl)(imino)(trifluoromethyl)-λ^6-sulfanone (7a)

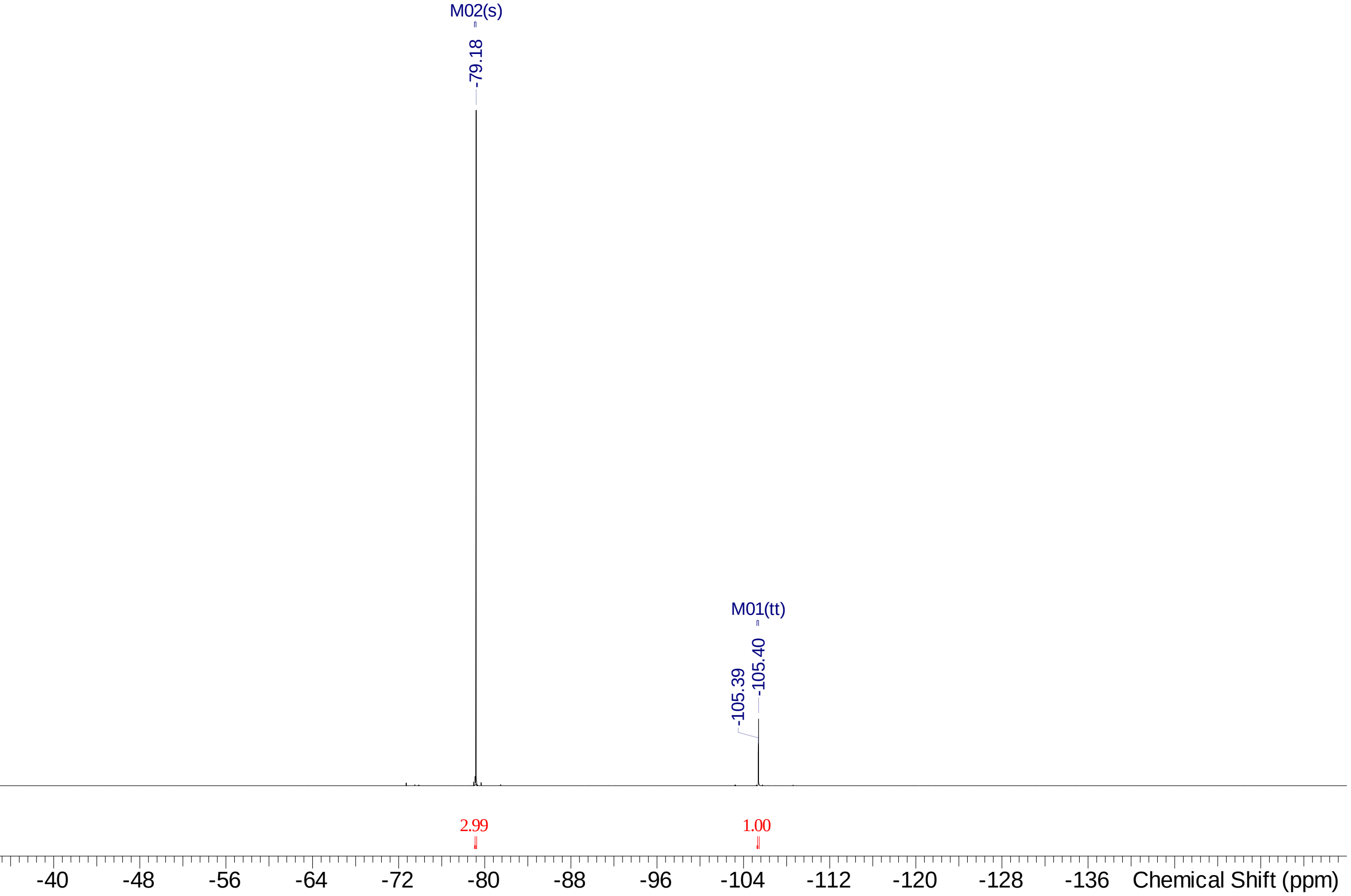


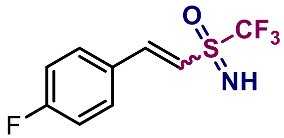
^{1}H NMR (500 MHz)
$CDCl_3$



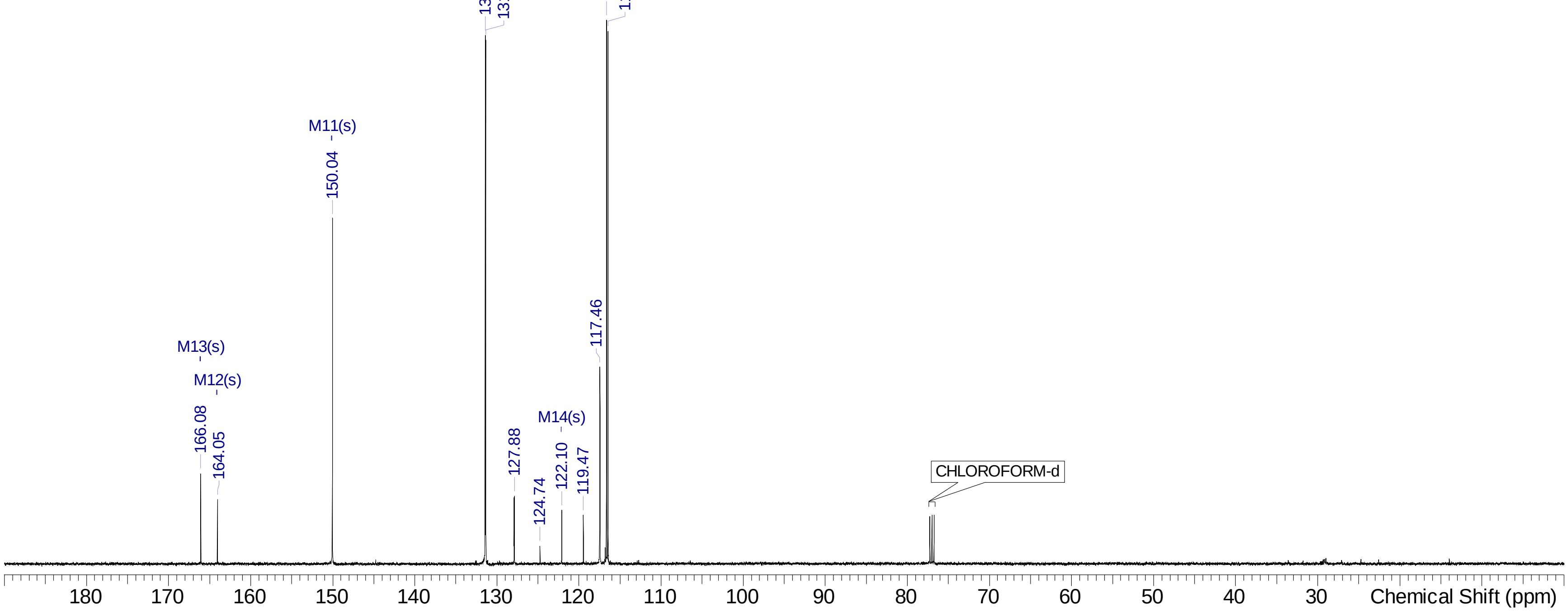


[19]F NMR (471 MHz)
$CDCl_3$

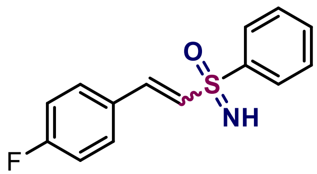


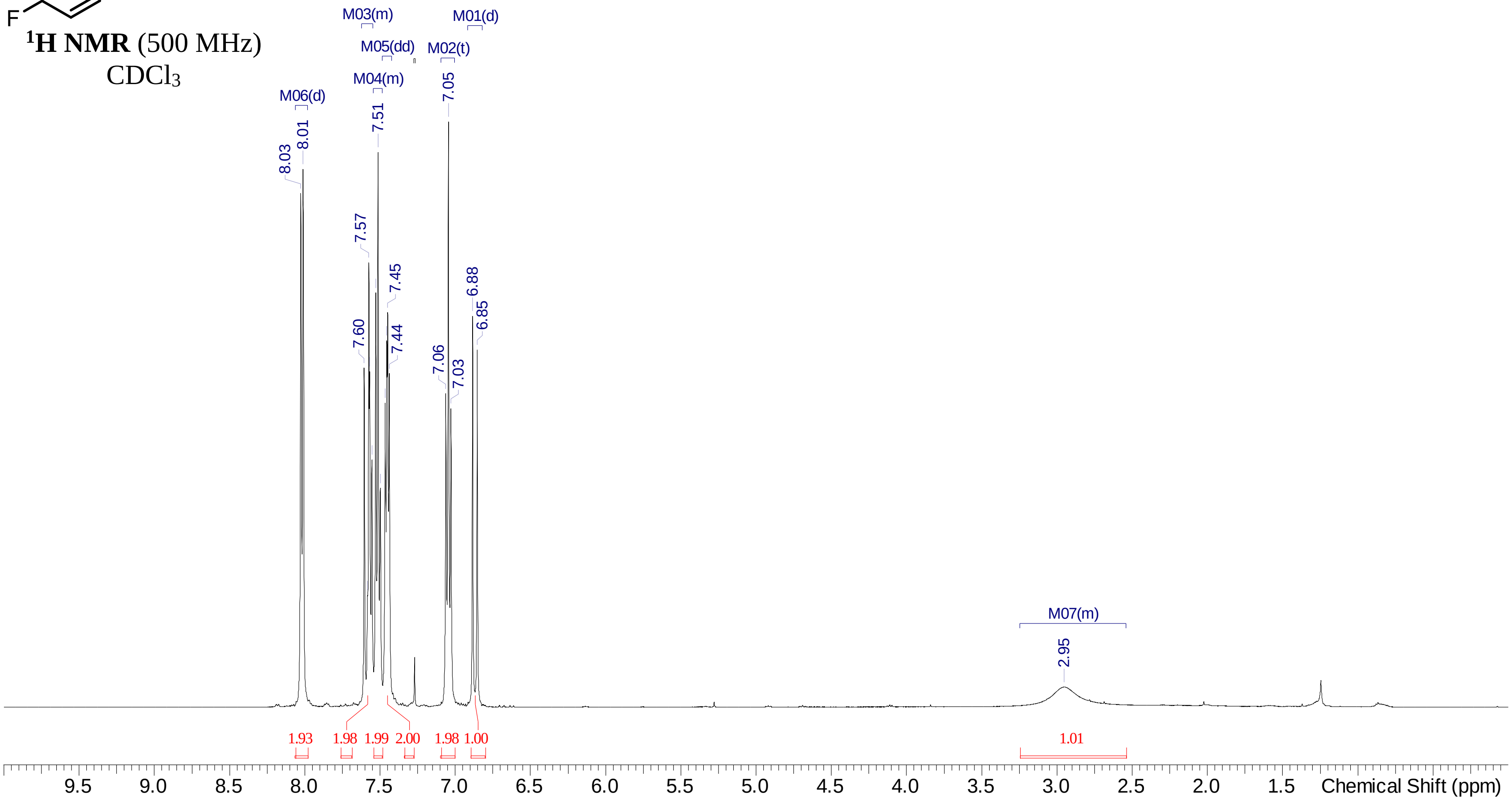


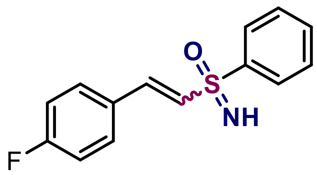
^{13}**C NMR** (126 MHz)
$CDCl_3$



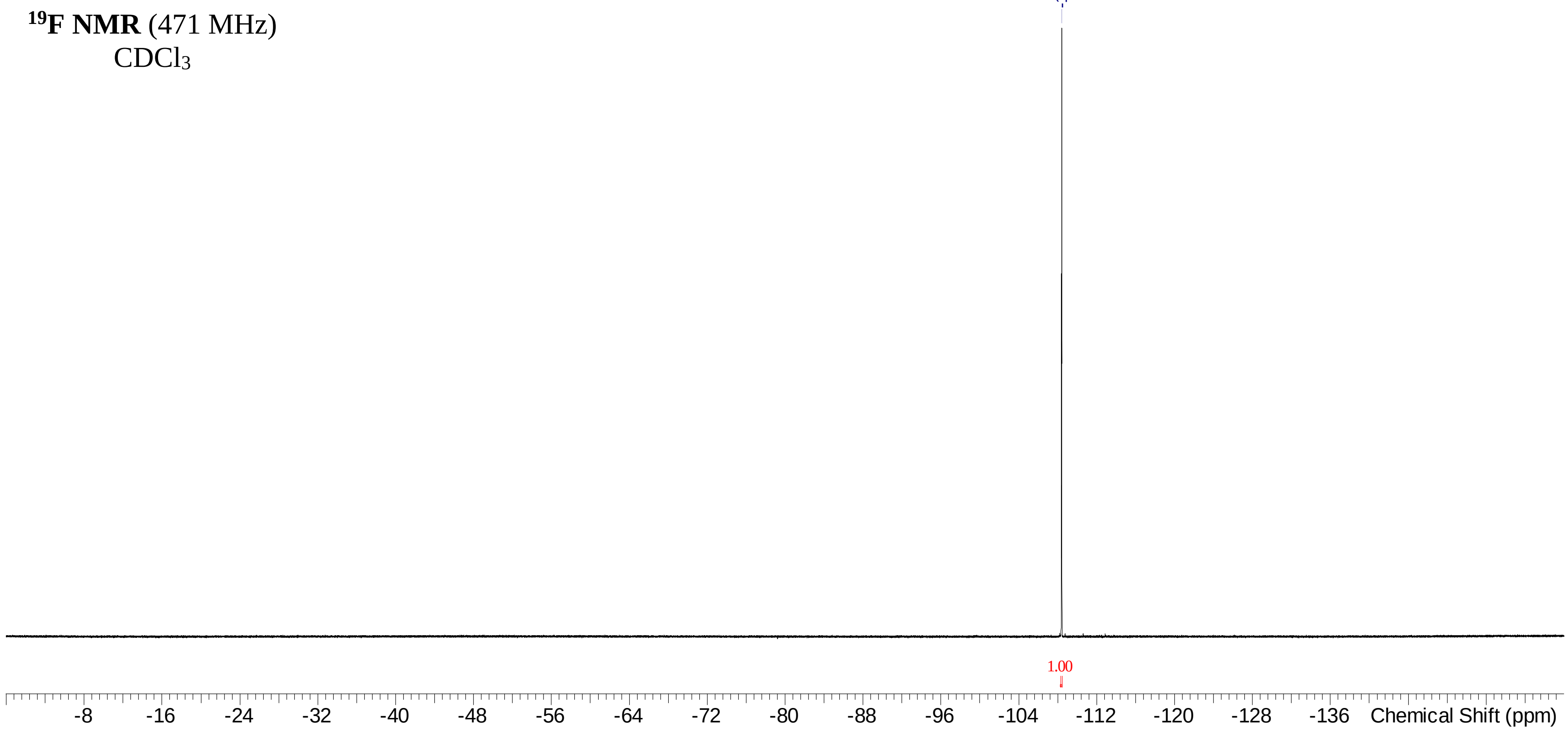
(4-Fluorostyryl)(imino)(phenyl)-λ^6-sulfanone (7b)

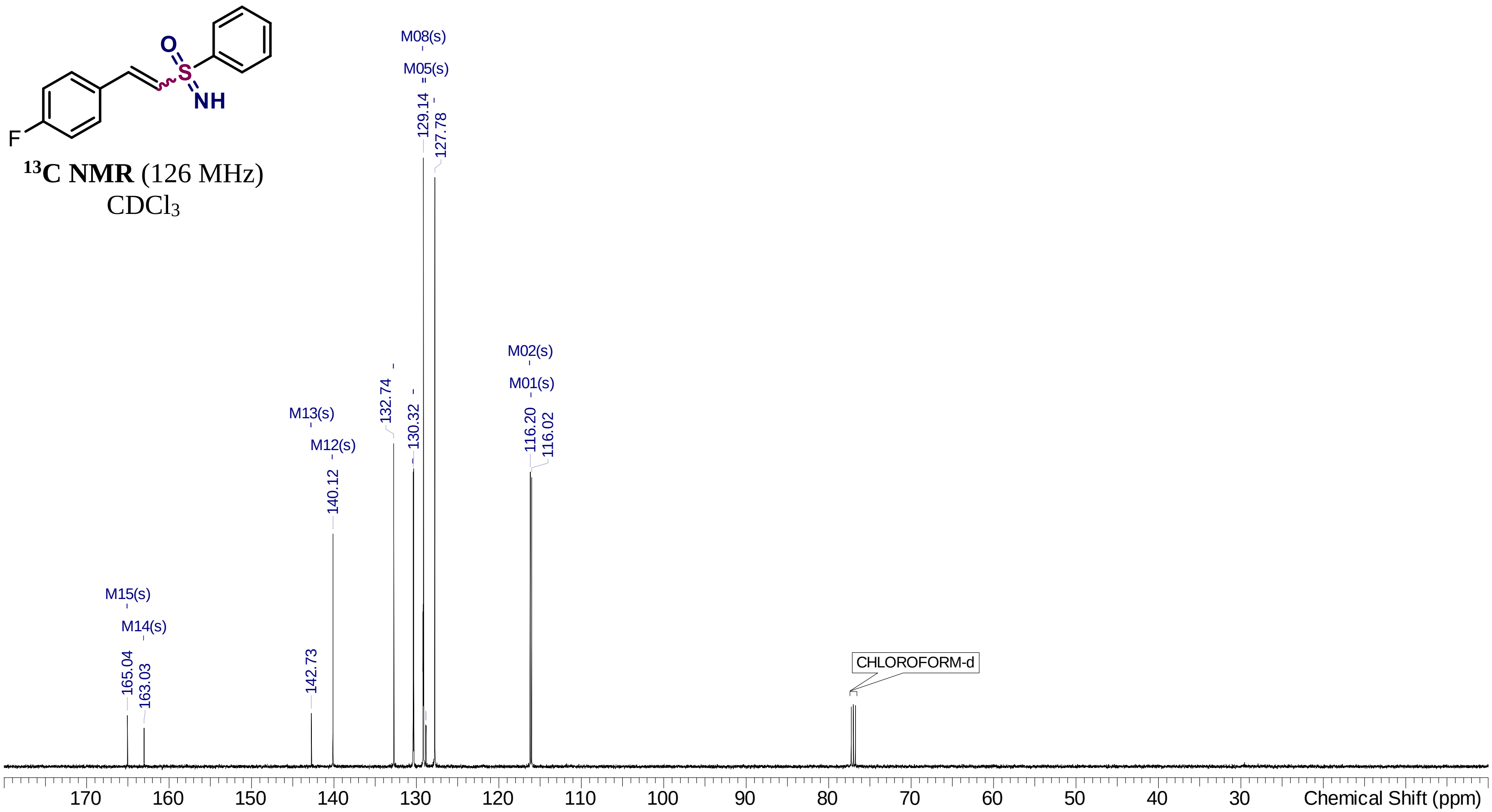




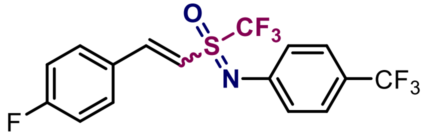


^{19}F NMR (471 MHz)
$CDCl_3$

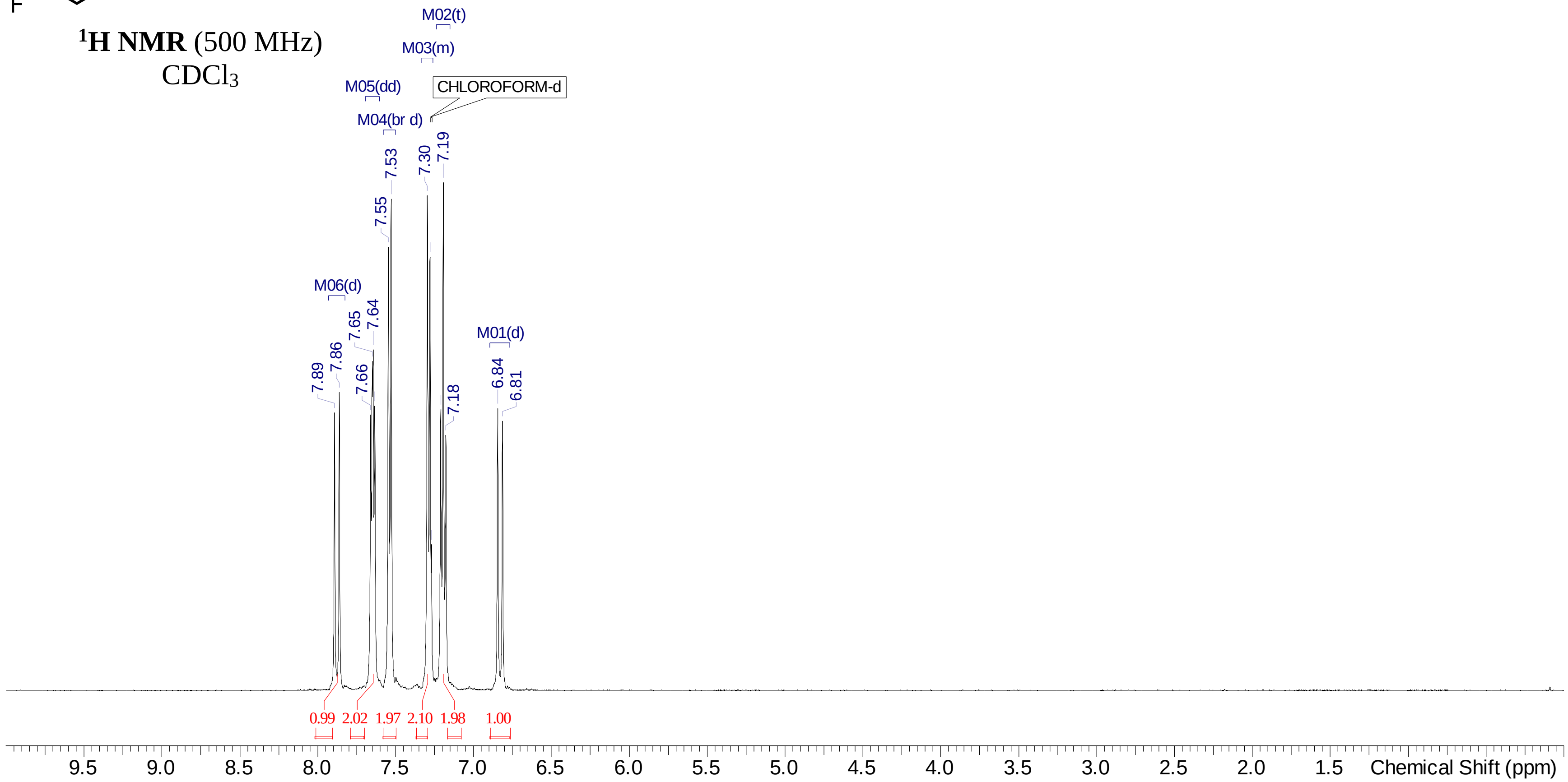


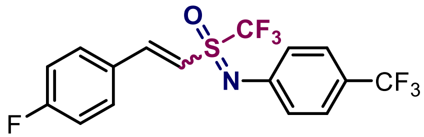

F
O
S
NH
13C NMR (126 MHz)
CDCl3
M08(s)
M05(s)
129.14
127.78
M02(s)
M01(s)
116.20
116.02
132.74
130.32
M13(s)
M12(s)
140.12
M15(s)
M14(s)
165.04
163.03
142.73
CHLOROFORM-d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
Chemical Shift (ppm)

(4-fluorostyryl)(trifluoromethyl)((4-(trifluoromethyl)phenyl)imino)-λ⁶-sulfanone (8a)

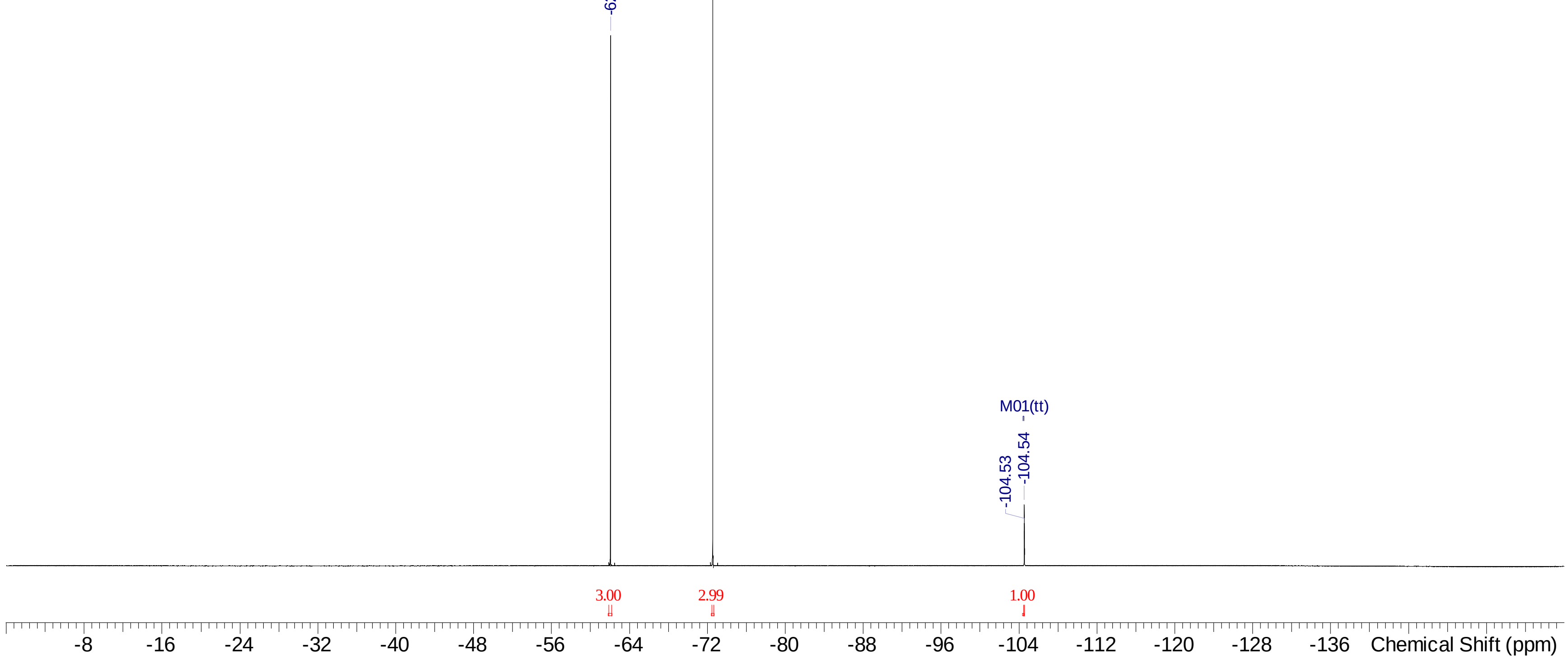


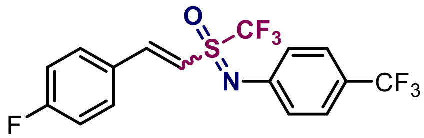
^{1}H NMR (500 MHz)
$CDCl_3$



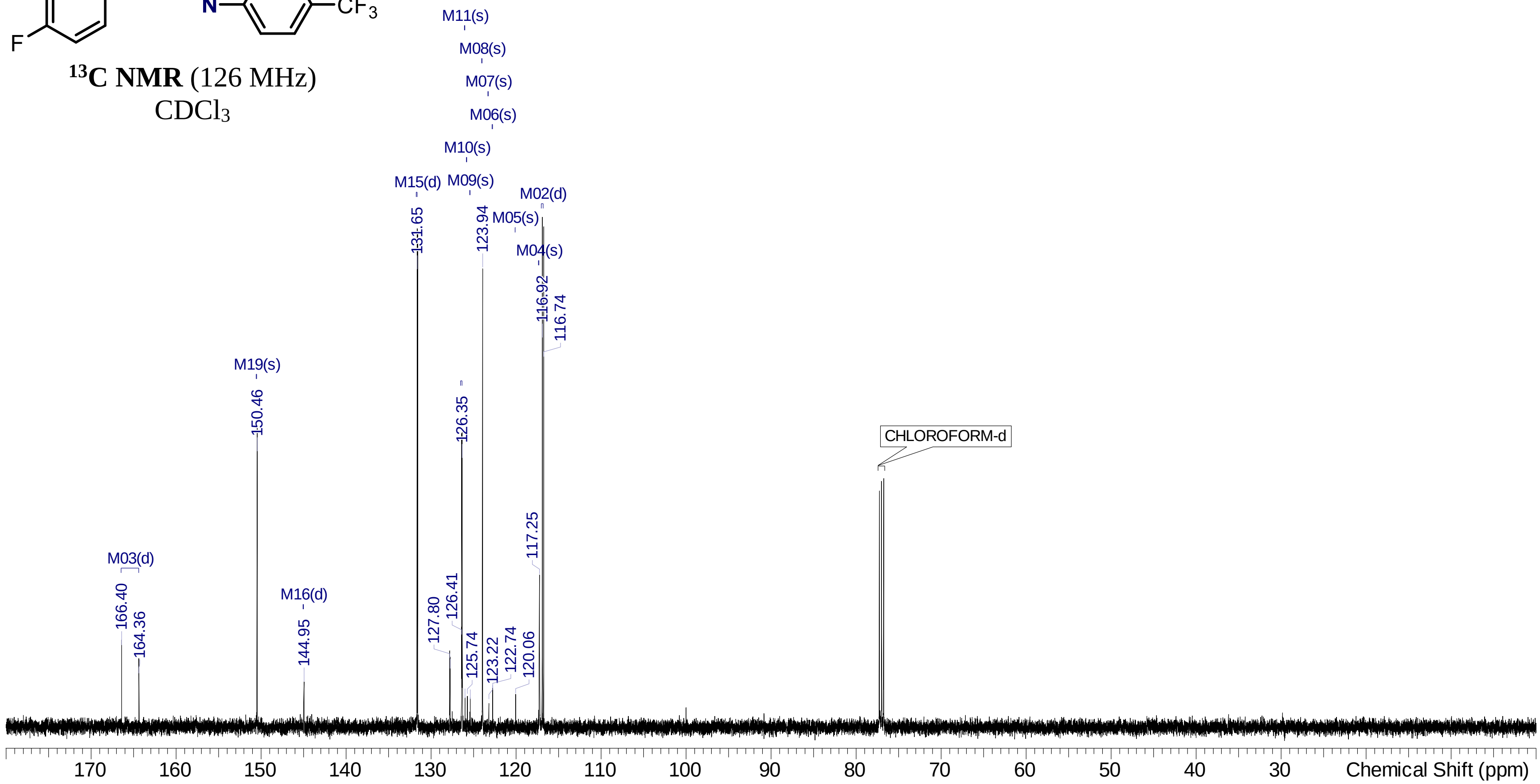


^{19}F NMR (471 MHz)
$CDCl_3$

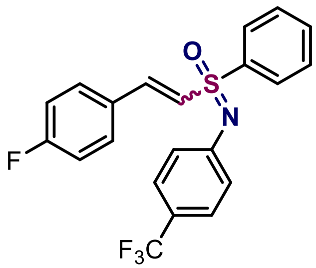




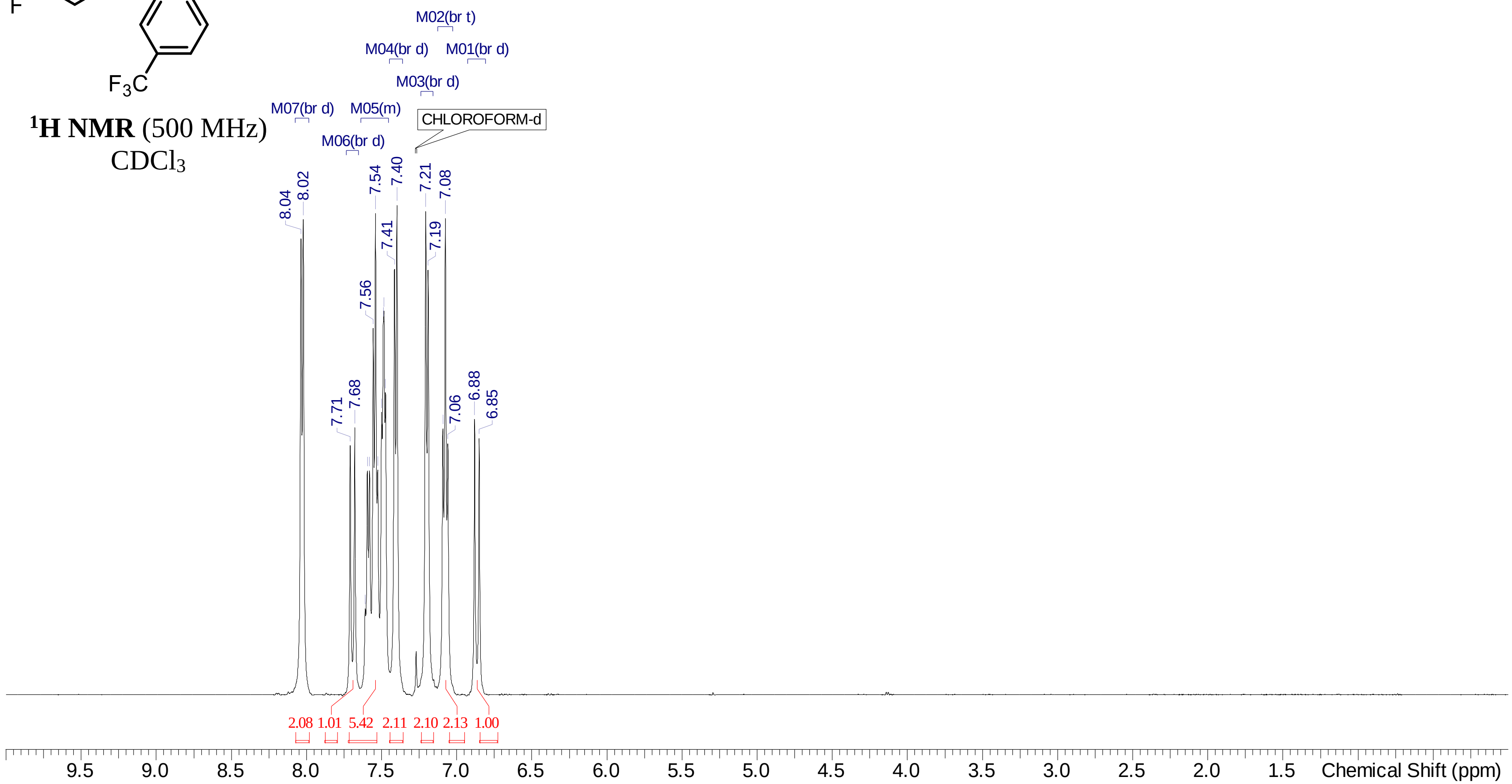
^{13}C NMR (126 MHz)
$CDCl_3$

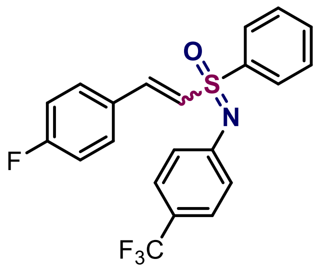


(4-fluorostyryl)(phenyl)((4-(trifluoromethyl)phenyl)imino)-λ⁶-sulfanone (8b)

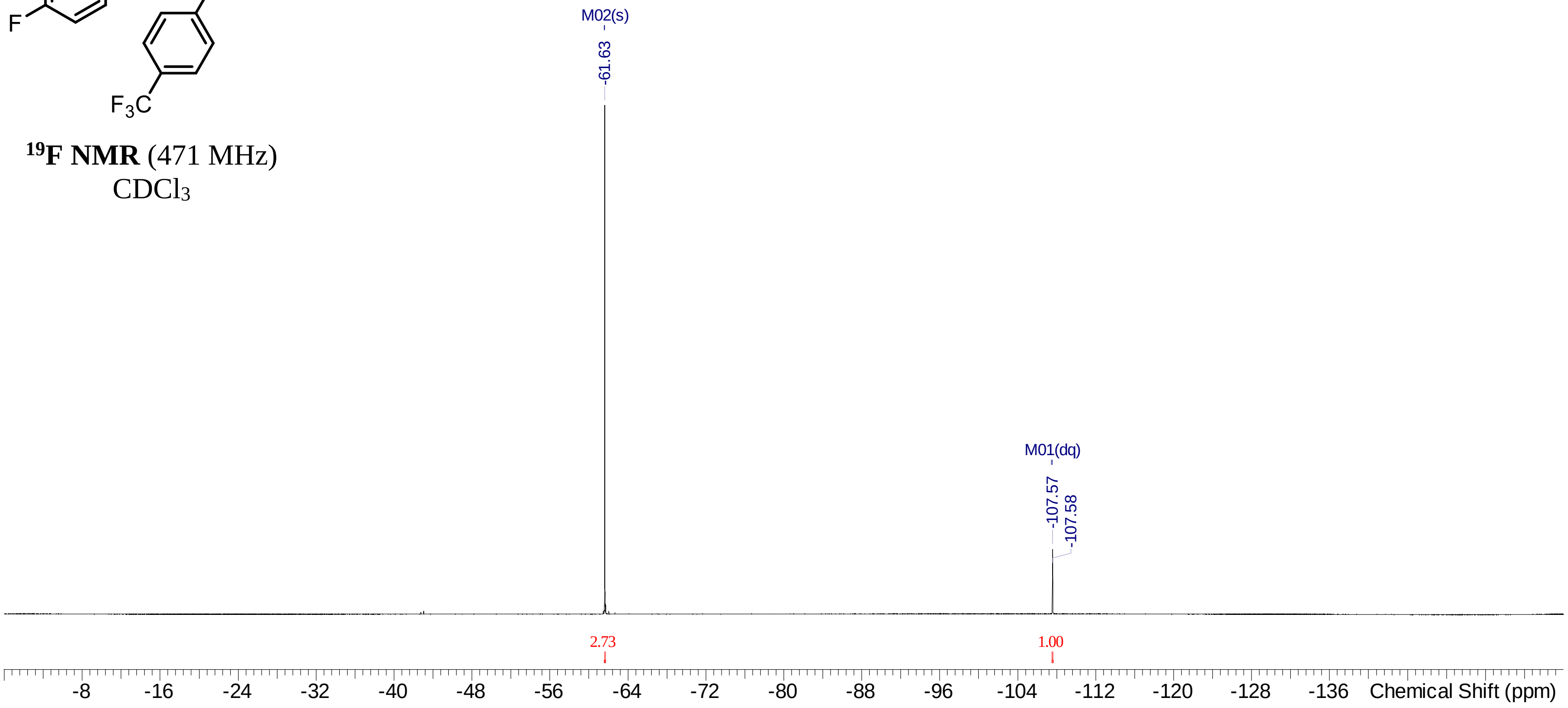


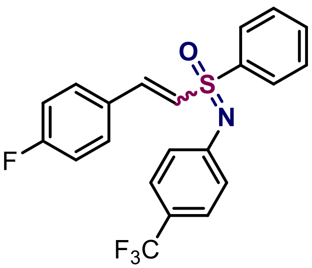
¹H NMR (500 MHz)
$CDCl_3$



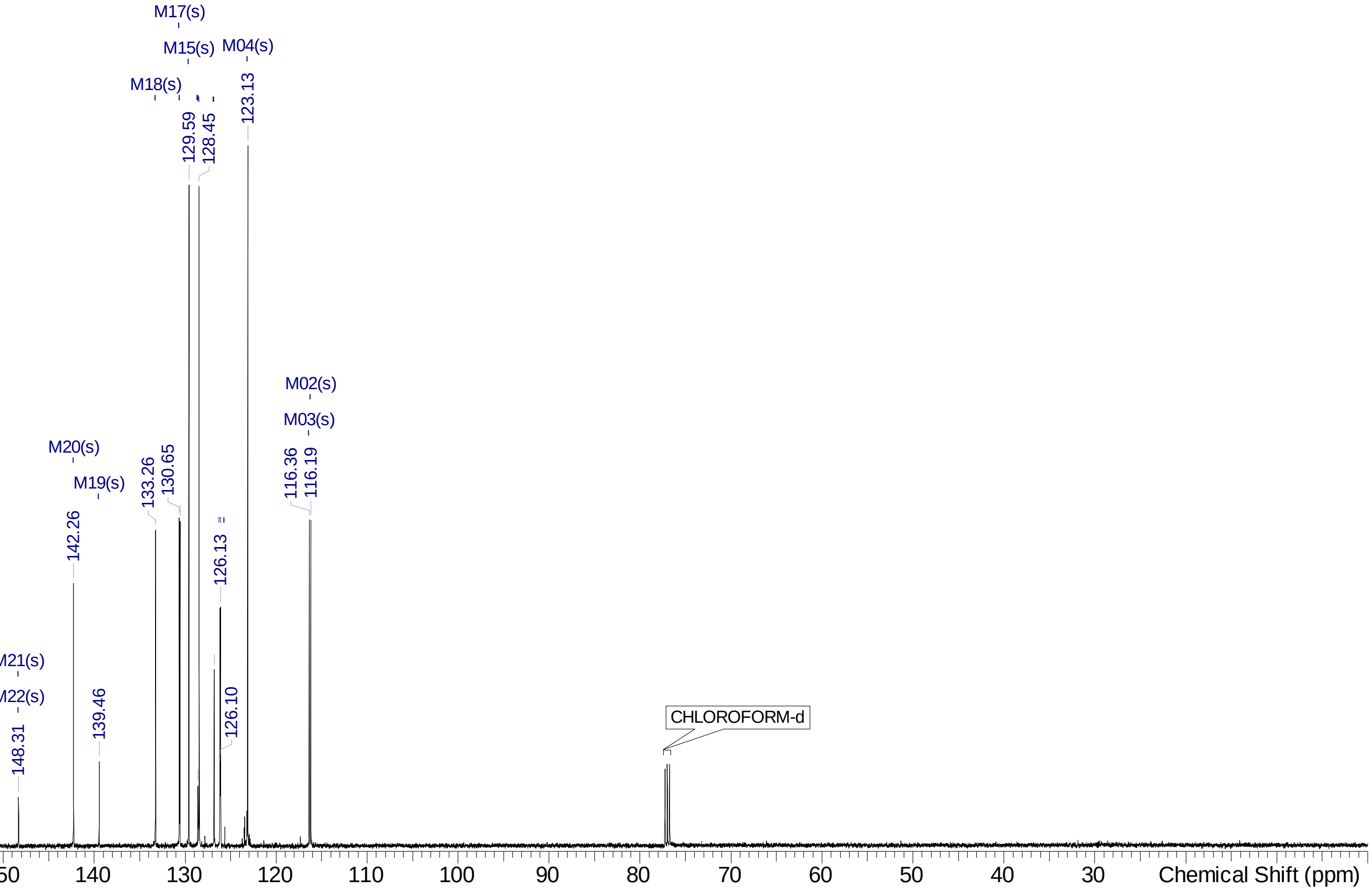


19F NMR (471 MHz)
$CDCl_3$

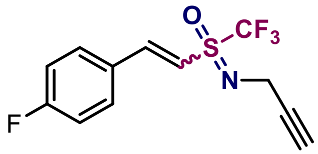




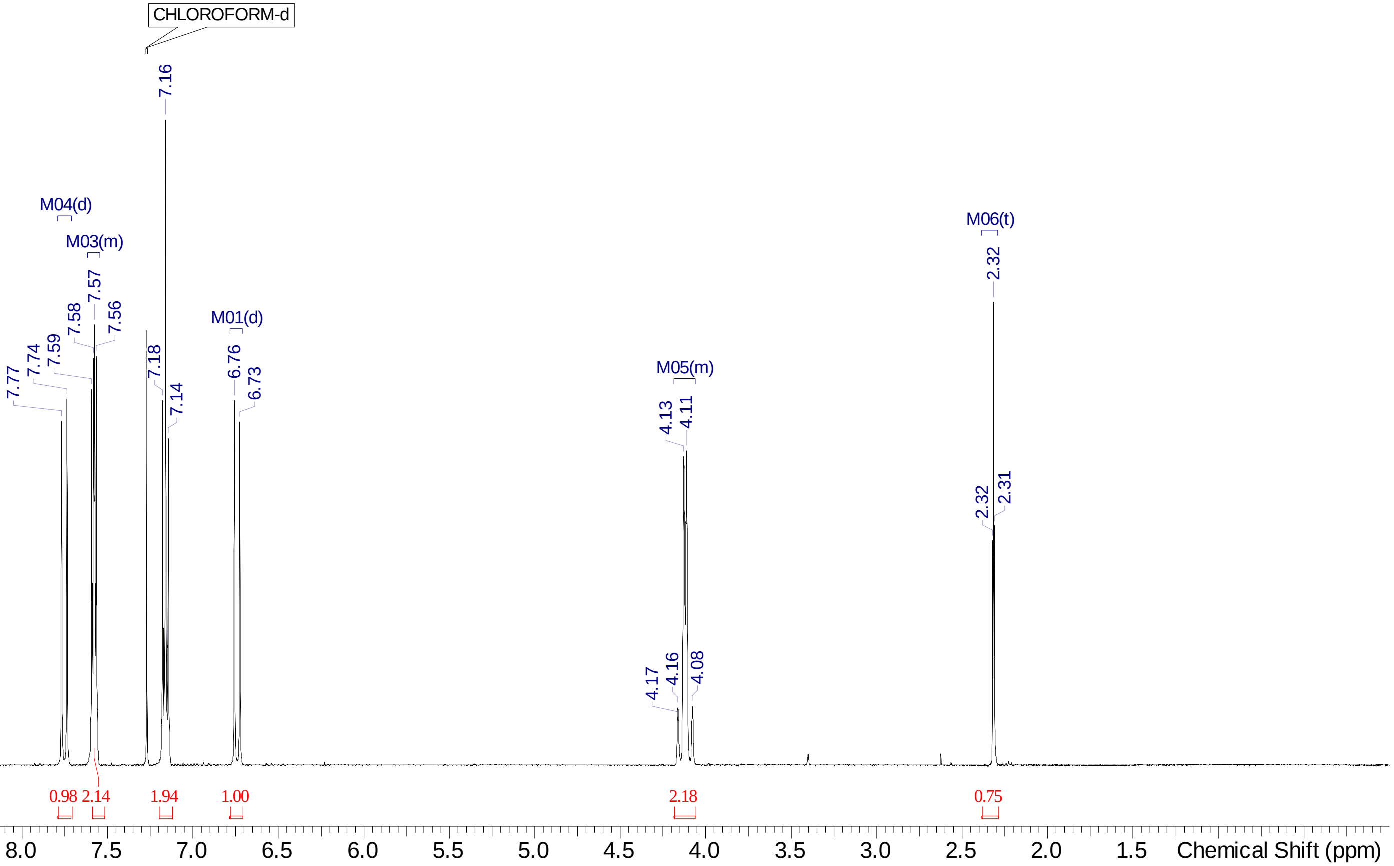
^{13}**C NMR** (126 MHz)
$CDCl_3$

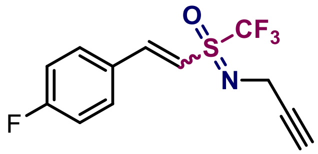


(4-Fluorostyryl)(prop-2-yn-1-ylimino)(trifluoromethyl)-λ^6-sulfanone (9a)

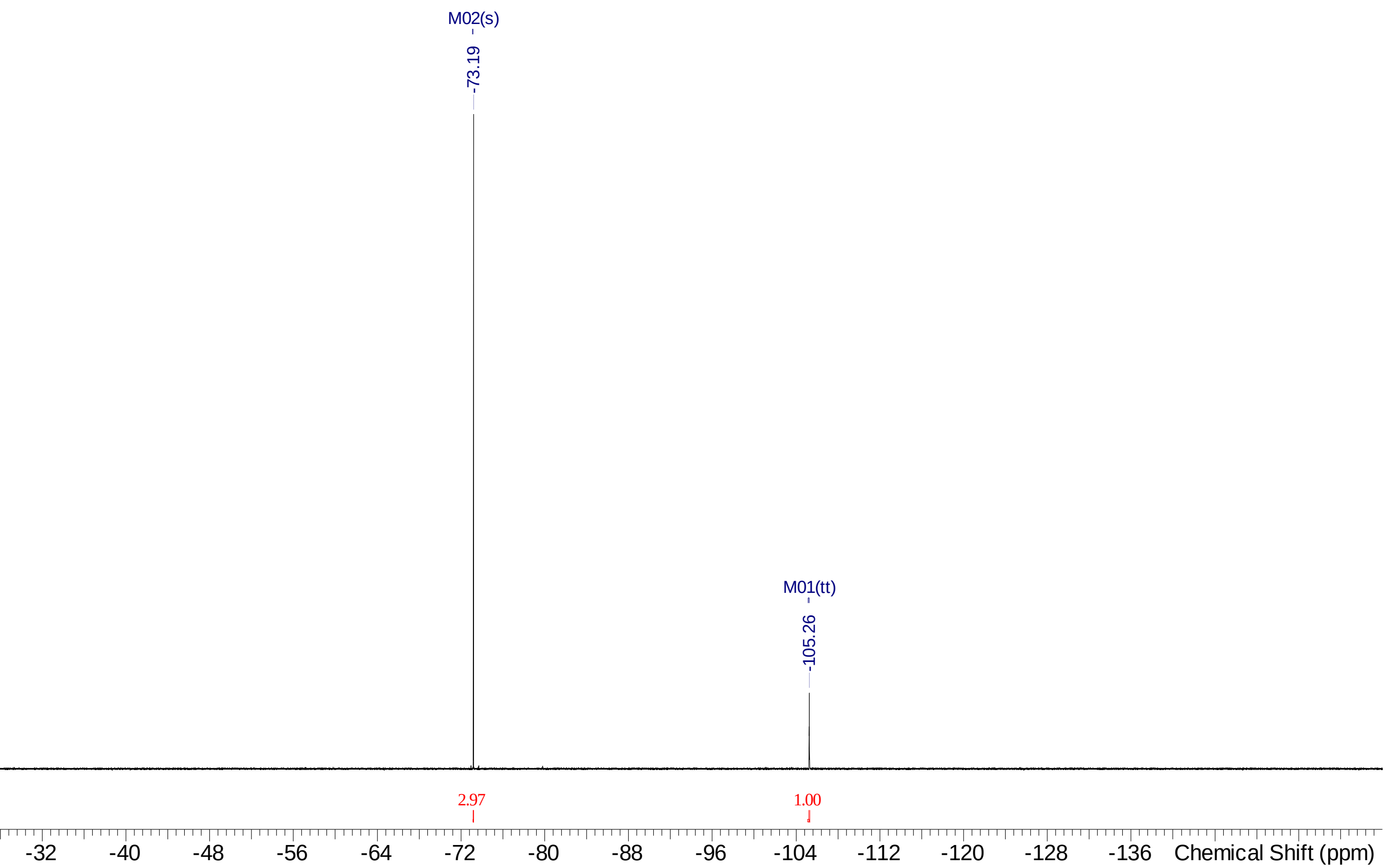


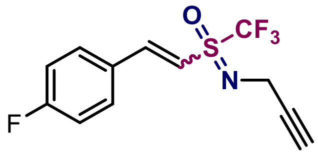
^{1}H NMR (500 MHz)
$CDCl_3$



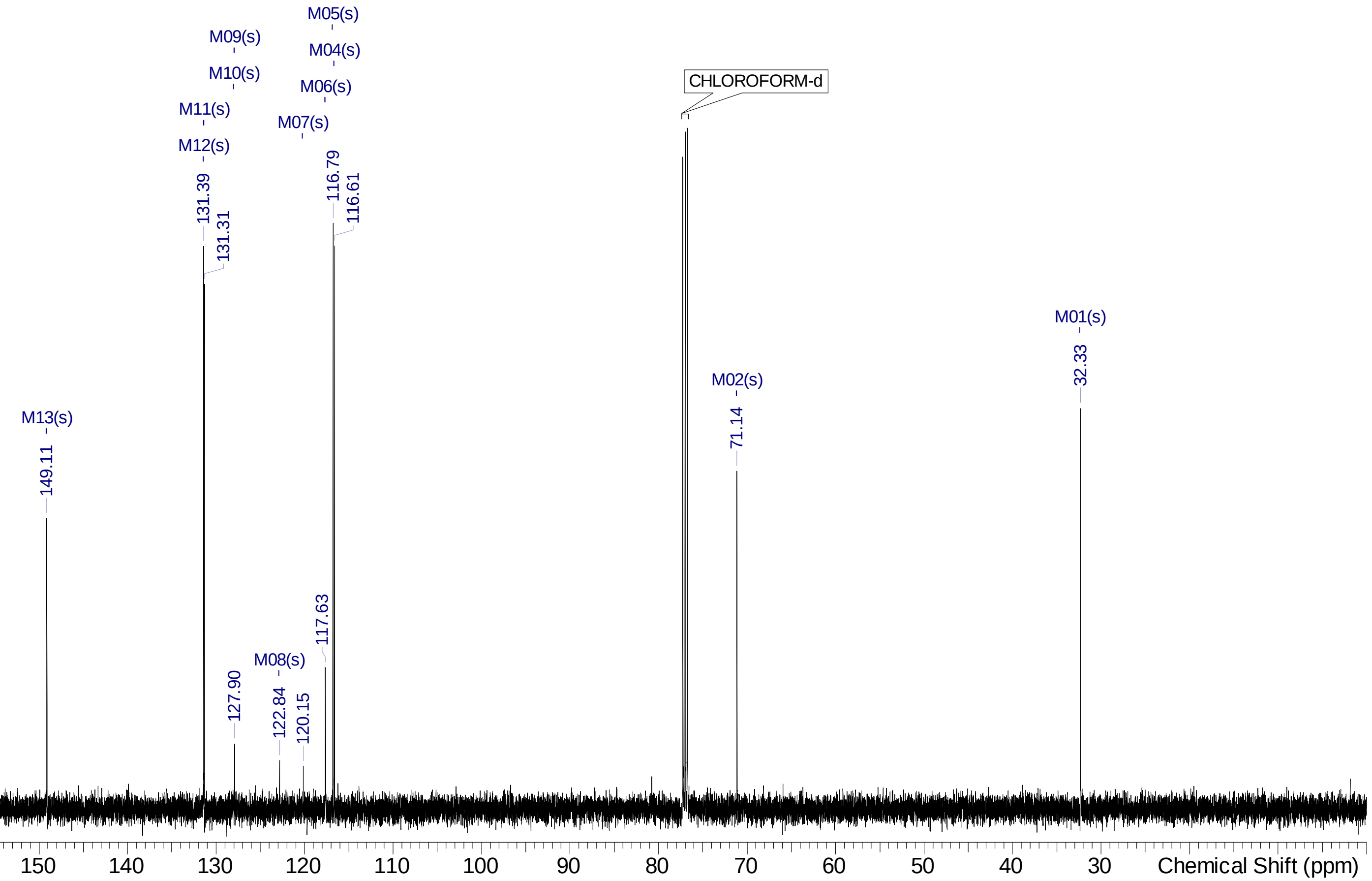


¹⁹F NMR (471 MHz)
$CDCl_3$

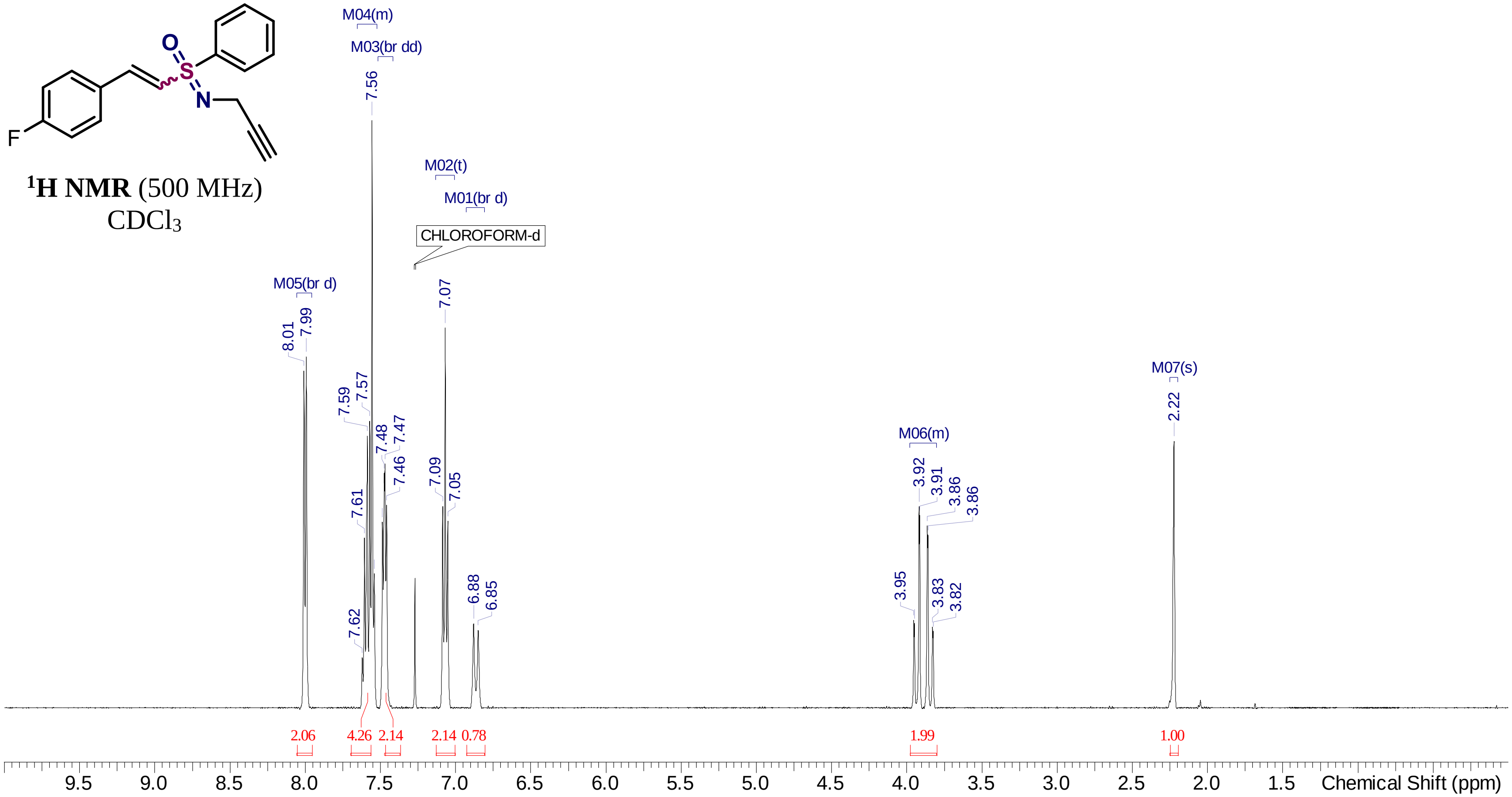




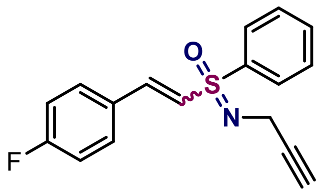
[13]C NMR (126 MHz)
$CDCl_3$



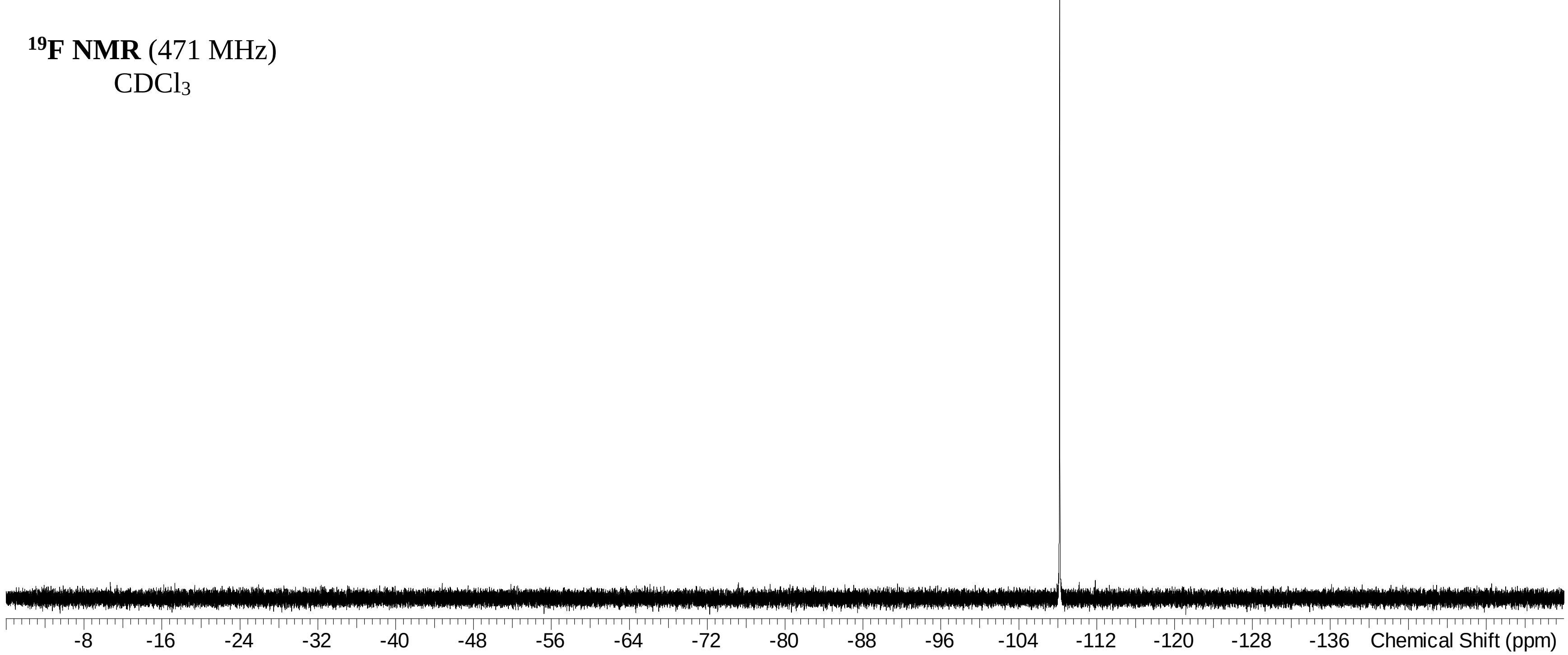
(4-Fluorostyryl)(phenyl)(prop-2-yn-1-ylimino)-λ^6-sulfanone (9b)

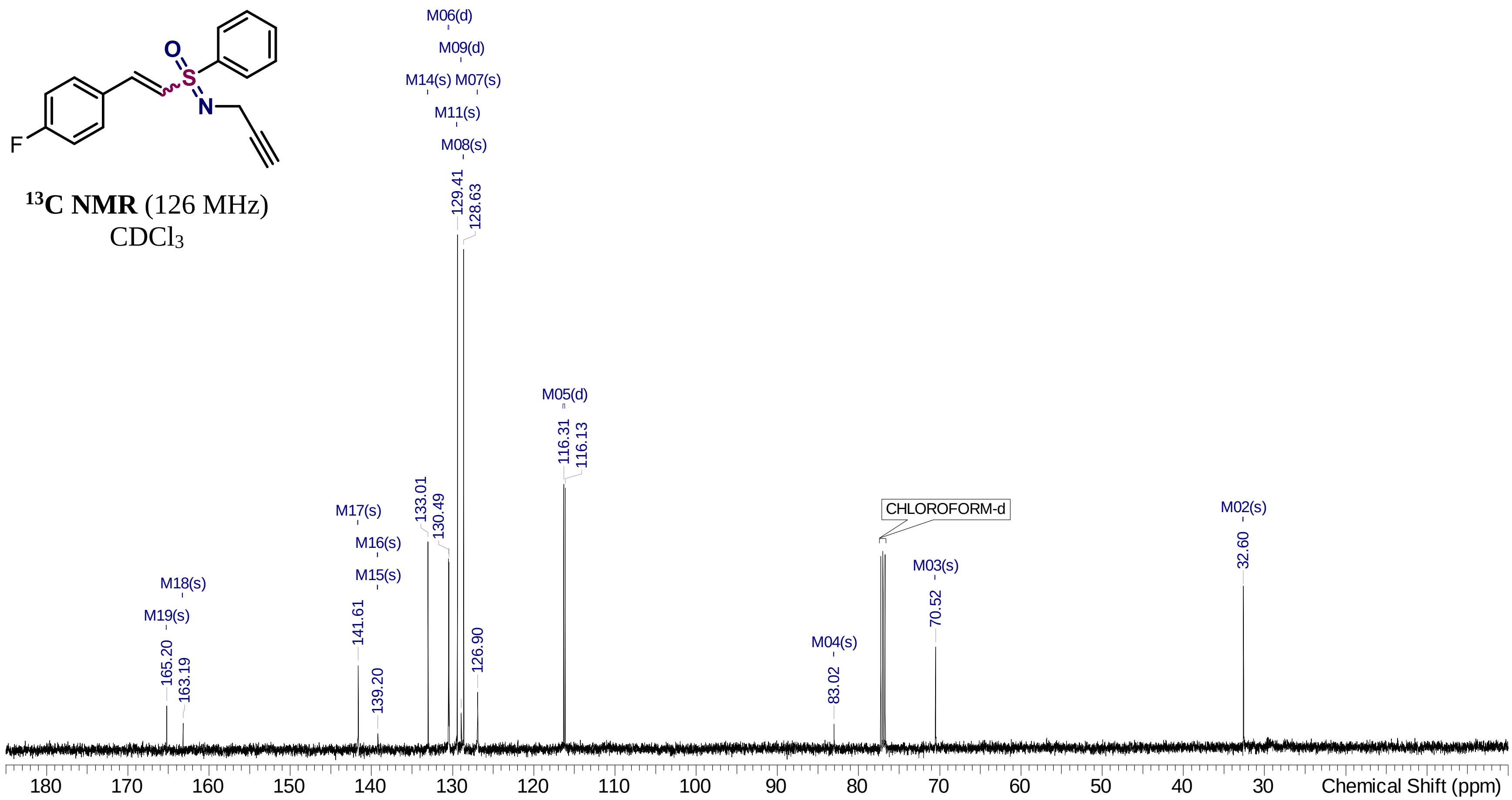


^{1}H NMR (500 MHz)
$CDCl_3$



^{19}F NMR (471 MHz)
$CDCl_3$




F
O
S
N
13C NMR (126 MHz)
CDCl3
M06(d)
M09(d)
M14(s) M07(s)
M11(s)
M08(s)
129.41
128.63
M05(d)
116.31
116.13
M17(s)
133.01
130.49
M16(s)
M15(s)
M18(s)
M19(s)
165.20
163.19
141.61
139.20
126.90
CHLOROFORM-d
M03(s)
70.52
M04(s)
83.02
M02(s)
32.60
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
Chemical Shift (ppm)