Mn- and Co-Catalyzed Aminocyclizations of Unsaturated Hydrazones Providing a Broad Range of Functionalized Pyrazolines

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Supporting Information

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General Information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in glassware dried with a heat gun (650 °C) under high vacuum (<1 mbar). Syringes which were used to transfer anhydrous solvents or reagents were purged thrice with nitrogen prior to use. All reagents were purchased from commercial suppliers (ABCR, ACROS, Sigma Aldrich, Fluka, TCI, Strem, Alfa, Combi-Blocks or Fluorochem) and used without further purification. Anhydrous solvents over molecular sieves were purchase from Acros and used as received.

Chromatography

Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 TLC glass plates and visualized with 254 nm light and potassium permanganate followed by heating. Organic solutions were concentrated by rotary evaporation at 40 °C. Purification of reaction products was carried out by flash chromatography using Brunschwig silica 32-63, 60Å under 0.3–0.5 bar overpressure. Neutral silica gel was obtained from NACALAI TESQUE, INC.: Silica Gel 60, spherical, neutral.

$KMnO_4$ solution: $KMnO_4$ (3.0 g), 5 drops of conc. H_2SO_4 in water (300 mL).

Analytical Data

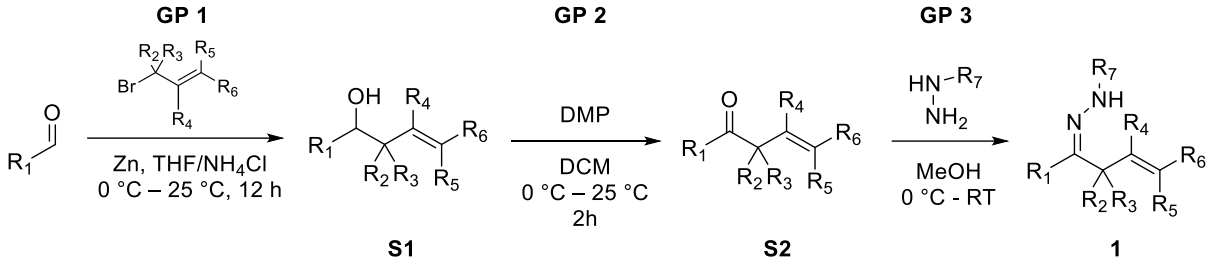
NMR: ^{1}H NMR spectra were recorded on a Bruker AVIII 600 MHz spectrometer with He or prodigy N_2 cryo-probes, Bruker AVIII HD 500 MHz and 400 spectrometers as well as Bruker Neo 500 MHz and 400 MHz spectrometers, and are reported in ppm with the solvent resonance as the reference unless noted otherwise ($CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm, CD_2Cl_2 at 5.32 ppm, DMSO-d_6 at 2.50 ppm, CD_3CN at 1.94 ppm). Peaks are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded with ^{1}H-decoupling on Bruker AVIII 150 MHz spectrometers with He or prodigy N_2 cryo-probes, Bruker AVIII HD 125 MHz and 100 MHz spectrometers as well as Bruker Neo 125 MHz and 100 MHz spectrometers, and are reported in ppm with the solvent resonance as the reference unless noted otherwise ($CDCl_3$ at 77.16 ppm, C_6D_6 at 128.06 ppm, CD_2Cl_2 at 54.00 ppm, DMSO-d_6 at 39.52 ppm, CD_3CN at 1.32 ppm).

Mass spectrometry: High resolution mass spectrometric data were obtained at the mass spectrometry service operated by the Laboratory of Organic Chemistry at the ETHZ on VG-TRIBRID for electron impact ionization (ESI), Varian IonSpec Spectrometer for electrospray ionization (ESI), or IonSpec Ultima Fourier Transform Mass Spectrometer for matrix-assisted laser desorption/ionization (MALDI) and are reported as (*m*/*z*). Molecular fragments are reported starting at a relative intensity of 10-20%.

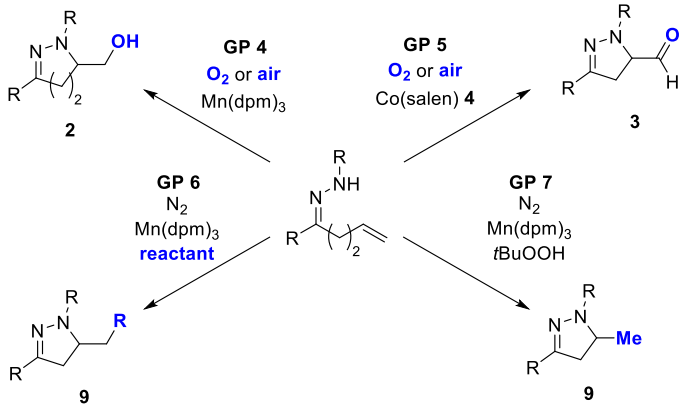
Infrared spectra (IR) were recorded neat on a Perkin-Elmer Spectrum Two FT-IR spectrometer. The main peaks are reported as absorption maxima (cm^{-1}).

Melting points (m.p.) were determined on a Büchi B545 Melting Point Apparatus.

General Procedures



Scheme 1: General Procedures **GP 1** – **GP 3**



Scheme 2: General Procedures **GP 4** – **GP 7**

General Procedure 1: Preparation of unsaturated alcohols **S1**

Under ambient atmosphere, the given aldehyde was dissolved in THF (2 mL/mmol aldehyde) and a sat. aq. NH_4Cl solution (2 mL/mmol aldehyde) and the given allylic bromide (2 equiv) was added. After cooling to 0 °C, zinc dust (2 equiv) was added portion wise to the reaction mixture and, after slow warming, stirring proceeded at 25 °C for 12 h. The reaction mixture was extracted with ethyl acetate (3 x 100 mL) and the organic phase was dried using Na_2SO_4, filtered and the solvents removed in vacuo. If purification was required, it was performed via flash column chromatography on silica gel using the appropriate eluent.

General Procedure 2: Preparation of unsaturated ketones **S2**

Under ambient atmosphere, DMP (1.2 – 1.5 equiv) was added to a solution of alcohol **S1** (1 equiv) in DCM (0.6 M) at 0 °C. After stirring at 25 °C until completion, the reaction was quenched by slow addition of a sat. aq. $NaHCO_3$ solution (2 mL/mmol alcohol) and a 40% aq. $NaHSO_3$ solution (0.5 mL/mmol alcohol) at 0 °C. After stirring for 20 min at the same temperature, the reaction mixture was extracted with DCM (3 x 100 mL), the organic phase

dried using Na_2SO_4, filtered and the solvents removed in vacuo. The crude product was purified by flash column chromatography on silica gel using the appropriate eluent.

General Procedure 3: Preparation of unsaturated hydrazones **1**

Ketone **S2** was dissolved in MeOH (1 M) and cooled to 0 °C. After addition of the corresponding hydrazide (1.0 – 1.5 equiv), the reaction was stirred at the given temperature for the given time. The reaction was monitored carefully by TLC as prolonged reaction times led to isomerization of the desired hydrazone. If the product precipitated from the reaction mixture, filtration gave the pure hydrazone. If further purification was required, the solvent was removed in vacuo, and the crude purified by flash column chromatography on silica gel using the appropriate eluent.[1]

General Procedure 4: Manganese-catalyzed aerobic cyclization of unsaturated hydrazones **1** to give pyrazoline alcohols **2**

Hydrazone **1** (1 equiv) and $Mn(dpm)_3$ (0.1 equiv) were added to a dry flask or crimp vial (5 mL) which was evacuated and set under O_2 atmosphere using a balloon. *i*PrOH (0.1 M) was added and the reaction mixture stirred at 55 °C for 2 h. After addition of water (10 mL), the mixture was extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using the appropriate eluent.

General Procedure 5: Cobalt-catalyzed cyclization of unsaturated hydrazones **1** to give pyrazoline aldehydes **3**

Hydrazone **1** (1 equiv) and Co(salen) **4** (0.1 equiv) were added to a dry flask or crimp vial (5 mL) which was evacuated and set under O_2 atmosphere using a balloon. *i*PrOH (0.1 M) was added and the reaction mixture stirred at 25 °C for 1 h. After addition of water (10 mL), the mixture was extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using the appropriate eluent.

General Procedure 6: Manganese-catalyzed cyclization of unsaturated hydrazones **1** to give pyrazolines **9a–e**

Hydrazone **1** (1 equiv) and $Mn(dpm)_3$ (0.1 equiv) were dissolved/suspended in the given solvent (0.1 M) and *t*BuOOH (2 equiv) and the respective reactant (1.2 – 4 equiv) was added and the reaction mixture stirred at 55 °C for the given time. After addition of water (10 mL), the mixture was extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over

[1] Depending on substituents, some hydrazones form *E*/*Z*-mixtures.

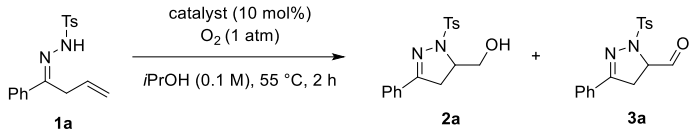
Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using the appropriate eluent.

General Procedure 7: Manganese-catalyzed cyclization of unsaturated hydrazones **1** to give pyrazolines **9f–h**

Hydrazone **1** (1 equiv) and $Mn(dpm)_3$ (0.1 equiv) were dissolved/suspended in the given solvent (0.1 M) and *t*BuOOH (2 equiv) was added and the reaction mixture stirred at 55 °C for the given time. After addition of water (10 mL), the mixture was extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using the appropriate eluent.

Optimization of Reaction Conditions

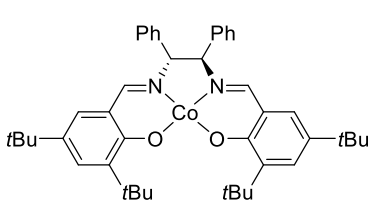
Table T1: Catalyst screening.



1a **2a** **3a**

entry	catalyst	yield **2a**[a]	yield **3a**[a]
1	$MnCl_2$	3%	-
2	$Mn(dpm)_3$	80% (78%)[b]	1.6%
3	$Mn(acac)_3$	31%	15%
4	$Mn(OAc)_2$	-	traces
5	Mn(salen) **5**	-	-
6	$CoCl_2$	-	-
7	$Co(modp)_2$	40%	4%
8	$Co(OAc)_2$	-	traces
9	$Co(dpm)_2$	31%	traces
10	Co(salen) **4**	24%[b]	70%[b]
11	$CuCl_2$	traces	4%
12	$Cu(acac)_2$	13%	12%
13	$Cu(dpm)_2$	-	-
14	$Fe(dpm)_3$	-	-
15	$PdCl_2$	-	-
16	$Pd(OAc)_2$	traces	-
17	$NiCl_2$	-	-
18	$Ni(acac)_2$	8%	-
19	$CrCl_3$	-	-

[a] NMR yield using 1,3,5-trimethoxybenzene as standard. [b] Isolated yield.



4

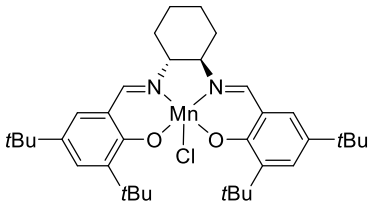


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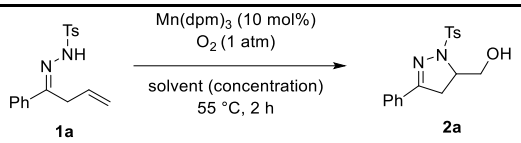
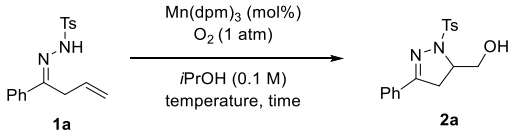
Table T2: Solvent and concentration screening



entry	solvent	catalyst	Concentration [M]	yield **2a**[a]
1	DCE	$Mn(dpm)_3$	0.1	17%
2	acetone	$Mn(dpm)_3$	0.1	20%
3	toluene	$Mn(dpm)_3$	0.1	30%
4	HFIP	$Mn(dpm)_3$	0.1	20%
5	*i*PrOH	$Mn(dpm)_3$	0.1	79% (78%)[b]
6	*i*PrOH	$Mn(dpm)_3$	0.02	73%
7	*i*PrOH	$Mn(dpm)_3$	0.5	71%

[a] NMR yield using 1,3,5-trimethoxybenzene as standard. [b] Isolated yield of **2a**.

Table T3: Catalyst loading and temperature screening

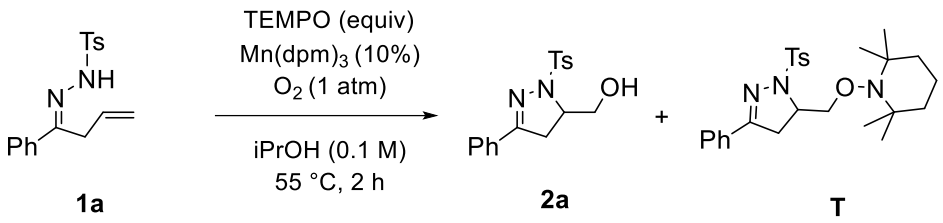


entry	catalyst loading	temperature	time	yield **2a**[a]
1	1%	55 °C	2 h	17%
2	2%	55 °C	2 h	16%
3	5%	55 °C	2 h	35%
4	10%	55 °C	2 h	79% (78%)[b]
5	30%	55 °C	2 h	30%
6	10%	25 °C	12 h	65%
7	10%	40 °C	2 h	76%
8	10%	70 °C	2 h	66%

[a] NMR yield using 1,3,5-trimethoxybenzene as standard. [b] Isolated yield of **2**.

TEMPO Trapping Experiments

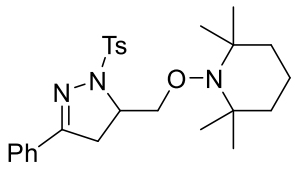
TEMPO trapping of General Procedure 4



entry	TEMPO	yield (**2a**)	yield (**T**)
1	0 equiv	79%	-
2	0.1 equiv	16%[a]	-
3	1.5 equiv	-	36%

[a] NMR yield using 1,3,5-trimethoxybenzene as standard.

2,2,6,6-Tetramethyl-1-((3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methoxy)-piperidine (T)



T

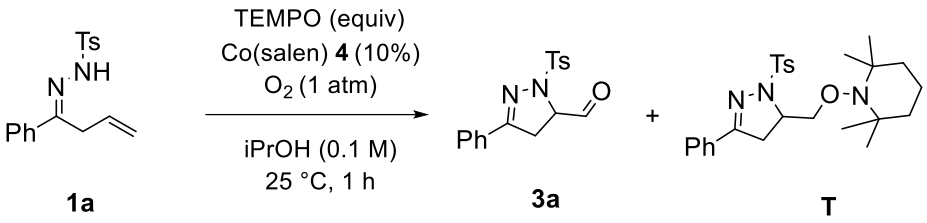
Pyrazoline **T** was prepared via **GP4**, using hydrazone **1a** (32 mg, 0.10 mmol), TEMPO (24 mg, 0.15 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1, R_f = 0.2) to give **T** (17 mg, 36 µmol, 36%) as a light yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.81 – 7.76 (m, 2H), 7.72 – 7.67 (m, 2H), 7.44 – 7.35 (m, 3H), 7.29 – 7.26 (m, 2H), 4.31 (dd, *J* = 9.2, 3.8 Hz, 1H), 4.12 (dd, *J* = 9.2, 7.4 Hz, 1H), 3.96 (dddd, *J* = 11.1, 8.8, 7.3, 3.8 Hz, 1H), 3.14 (qd, *J* = 17.2, 9.9 Hz, 2H), 2.38 (s, 3H), 1.55 – 1.33 (m, 6H), 1.32 – 1.15 (m, 6H), 1.15 – 1.00 (m, 6H).

The spectrum is in agreement with the literature.[2]

[2] Chen, S.; Chen, W.; Chen, X.; Chen, G.; Ackermann, L.; Tian, X. *Org. Lett.* **2019**, *21*, 7787-7790.

TEMPO trapping of General Procedure 5

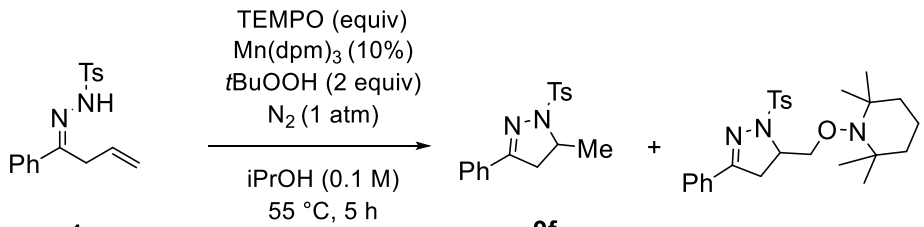


1a **3a** **T**

entry	TEMPO	yield (**3a**)	yield (**T**)
1	0 equiv	70%	-
2	0.1 equiv	41%[a]	-
3	1.5 equiv	26%[a]	25%[a]

[a] NMR yield using 1,3,5-trimethoxybenzene as standard.

TEMPO trapping of General Procedure 6



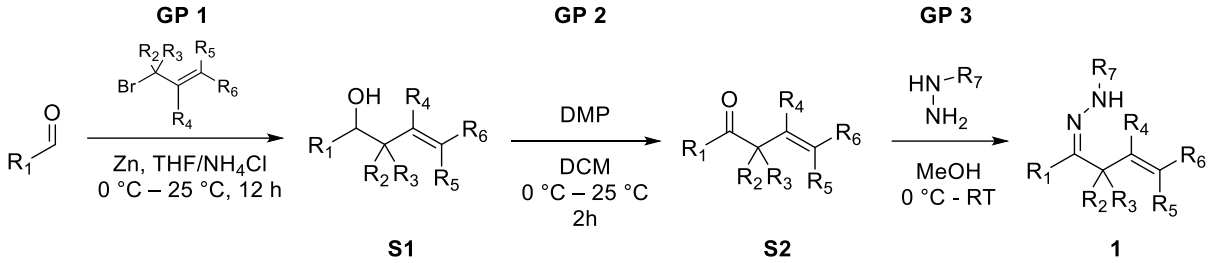
1a **9f** **T**

entry	TEMPO	yield (**9f**)	yield (**T**)
1	0 equiv	55%	-
2	0.1 equiv	43%[a]	-
3	1.5 equiv	-	65%[a]

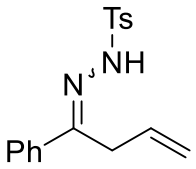
[a] NMR yield using 1,3,5-trimethoxybenzene as standard.

Preparation of Compounds 1 to 17

Starting Material Synthesis (1a–v)



4-Methyl-*N*'-(1-phenylbut-3-en-1-ylidene)benzenesulfonohydrazide (1a)



1a

Ketone **S2a** was prepared via **GP2**, using 1-Phenyl-3-buten-1-ol (1.80 g, 12.1 mmol) and DMP (7.68 g, 18.1 mmol) and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9.5:0.5) to give **S2a** (1.45 g, 9.92 mmol, 82%) as a colorless oil which was used directly in the next step.

Hydrazone **1a** was prepared via **GP3**, using ketone **S2a** (826 mg, 5.65 mmol), tosylhydrazide (1.16 g, 6.22 mmol) and the reaction was stirred for 4.5 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 9.5:0.5) and recrystallized from hexane/ethyl acetate to give **1a** (1.12 g, 3.56 mmol, 63%, d.r. = >20:1) as a colorless solid.

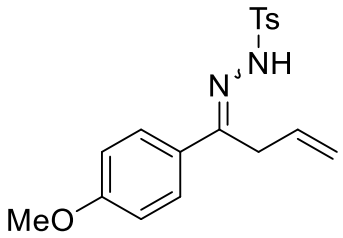
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.89 – 7.84 (m, 2H), 7.70 – 7.59 (m, 3H), 7.37 – 7.32 (m, 3H), 7.32 – 7.28 (m, 2H), 5.84 (ddt, *J* = 17.4, 10.2, 5.0 Hz, 1H), 5.07 (dtd, *J* = 10.3, 2.0, 0.9 Hz, 1H), 4.79 (dtd, *J* = 17.4, 2.1, 0.9 Hz, 1H), 3.39 (dt, *J* = 5.0, 2.0 Hz, 2H), 2.41 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 153.0, 144.3, 136.8, 135.4, 129.85, 129.78, 129.7, 128.6, 128.2, 126.5, 118.0, 31.9, 21.7.

The spectra are in agreement with the literature.[3]

[3] Hu, X.-Q.; Chen, J.-R.; Wei, Q.; Liu, F.-L.; Deng, Q.-H.; You-Quan, Z.; Xiao, W.-J. *Eur. J. Org. Chem.* **2014**, 3082-3086.

***N*'-(1-(4-Methoxyphenyl)but-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1b)**



1b

Alcohol **S1b** was prepared by dissolving 4-methoxybenzaldehyde (2.43 mL, 20.0 mmol) in dry Et_2O (10 mL) and cooling the mixture to 0 °C. Allylmagnesium bromide (1.0 M in Et_2O, 40.0 mL, 40.0 mmol) was added dropwise and the reaction was warmed slowly and stirred at 25 °C for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL) and extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (hexane:ethyl acetate = 8:2) to give **S1b** (2.57 g, 14.4 mmol, 72%) as a colorless oil which was used directly in the next step.

Ketone **S2b** was prepared via **GP2**, using **S1b** (2.21 g, 12.4 mmol) and DMP (5.36 g, 17.4 mmol) and the reaction was stirred for 20 min. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 8.5:1.5) to give **S2b** (1.27 g, 7.20 mmol, 58%) as a colorless oil which was used directly in the next step.

Hydrazone **1b** was prepared via **GP3**, using ketone **S2b** (176 mg, 1.00 mmol), tosylhydrazide (186 mg, 1.00 mmol) and the reaction was stirred for 4 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **1b** (200 mg, 581 µmol, 58%, d.r. = >20:1) as a colorless solid.

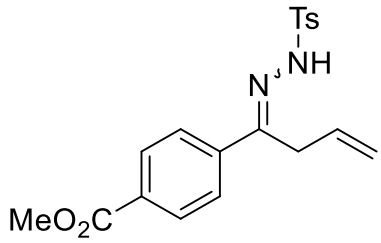
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.87 – 7.83 (m, 2H), 7.63 – 7.57 (m, 2H), 7.50 (s, 1H), 7.32 – 7.27 (m, 2H), 6.88 – 6.82 (m, 2H), 5.82 (ddt, *J* = 17.4, 10.2, 5.0 Hz, 1H), 5.05 (dtd, *J* = 10.3, 2.0, 0.9 Hz, 1H), 4.76 (dtd, *J* = 17.4, 2.1, 0.9 Hz, 1H), 3.81 (s, 3H), 3.36 (dt, *J* = 5.0, 2.0 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 161.1, 153.0, 144.2, 135.5, 130.0, 129.7, 129.3, 128.2, 128.0, 117.9, 113.9, 55.5, 31.8, 21.7.

The spectra are in agreement with the literature.[4]

[4] Xu, Z.-Q.; Wang, W.-B.; Zheng, L.-C.; Li, L.; Duan, L.; Li, Y.-M. *Org. Biomol. Chem.* **2019**, *17*, 9026-9038.

Methyl 4-(1-(2-tosylhydrazineylidene)but-3-en-1-yl)benzoate (1c)



1c

Alcohol **S1c** was prepared via **GP1**, using methyl 4-formylbenzoate (3.28 g, 20.0 mmol), allyl bromide (3.46 mL, 40.0 mmol) and zinc powder (2.62 g, 40.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1c** (3.42 g, 16.6 mmol, 83%) was obtained as a colorless oil which was used directly in the next step.

Ketone **S2c** was prepared via **GP2**, using **S1c** (4.12 g, 20.0 mmol) and DMP (10.2 g, 24.0 mmol) and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2c** (3.28 g, 16.0 mmol, 80%) as a colorless solid which was used directly in the next step.

Hydrazone **1c** was prepared via **GP3**, using ketone **S2c** (408 mg, 2.00 mmol) and tosylhydrazide (558 mg, 3.00 mmol) and the reaction was stirred for 2 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3) to give **1c** (438 mg, 1.18 mmol, 59%, d.r. = >20:1) as a colorless solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.12 – 7.95 (m, 5H), 7.57 – 7.45 (m, 2H), 6.80 – 6.69 (m, 2H), 5.16 (ddt, *J* = 17.3, 10.3, 5.1 Hz, 1H), 4.68 – 4.60 (m, 1H), 4.55 – 4.48 (m, 1H), 3.45 (s, 3H), 2.68 – 2.56 (m, 2H), 1.78 (s, 3H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 166.2, 150.9, 144.0, 141.2, 136.6, 131.4, 130.0, 129.8, 129.7, 128.5, 126.5, 117.3, 51.7, 31.1, 21.1.

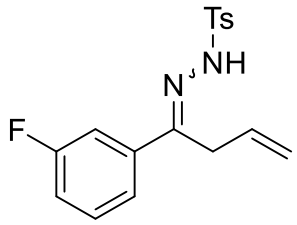
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3194 (broad), 2952, 1720, 1611, 1597, 1436, 1406, 1379, 1278, 1167, 1109, 1018, 814, 774, 733, 705, 670, 552, 501.

MS (ESI): m/z (%) = 373 (73), 371 (50), 223 (20), 217 (33), 194 (48), 159 (24).

HRMS (ESI) for $C_{18}H_{21}N_2O_3S$ (373.1217): 373.1209 (M^++H^+).

M.p. (°C): 100–105.

***N*'-(1-(3-Fluorophenyl)but-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1d)**



1d

Alcohol **S1d** was prepared via **GP1**, using 3-fluorobenzaldehyde (2.20 mL, 20.7 mmol), allyl bromide (3.46 mL, 40.0 mmol) and zinc powder (2.62 g, 40.0 mmol) and the reaction was stirred for 14 h. After work-up, the crude product **S1d** (3.36 g, 20.2 mmol, 97%) was obtained as a colorless oil which was used directly in the next step.

Ketone **S2d** was prepared via **GP2**, using **S1d** (3.20 g, 19.3 mmol) and DMP (12.2 g, 28.9 mmol) and the reaction was stirred for 30 min. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2d** (2.60 g, 15.8 mmol, 82%) as a light yellow oil which was used directly in the next step.

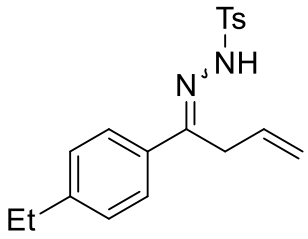
Hydrazone **1d** was prepared via **GP3**, using ketone **S2d** (493 mg, 3.00 mmol), tosylhydrazide (838 mg, 4.50 mmol) and the reaction was stirred for 4 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **1d** (752 mg, 2.26 mmol, 75%, d.r. = >20:1) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.89 – 7.83 (m, 3H), 7.41 – 7.27 (m, 5H), 7.04 (tdd, *J* = 8.2, 2.6, 1.1 Hz, 1H), 5.82 (ddt, *J* = 17.4, 10.2, 5.1 Hz, 1H), 5.07 (dtd, *J* = 10.3, 1.9, 0.8 Hz, 1H), 4.78 (dtd, *J* = 17.4, 2.1, 0.9 Hz, 1H), 3.36 (dt, *J* = 5.1, 2.0 Hz, 2H), 2.41 (s, 3H).

The spectrum is in agreement with the literature.[5]

[5] Hu, X.-Q.; Chen, J.-R.; Wei, Q.; Liu, F.-L.; Deng, Q.-H.; Beauchemin, A. M.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2014**, *53*, 12163-12167.

***N*'-(1-(4-Ethylphenyl)but-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1e)**



1e

Alcohol **S1e** was prepared via **GP1**, using 4-ethylbenzaldehyde (2.68 g, 20.0 mmol), allyl bromide (3.46 mL, 40.0 mmol) and zinc powder (2.62 g, 40.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1e** (2.35 g, 13.3 mmol, 67%) was obtained as a colorless oil which was used directly in the next step.

Ketone **S2e** was prepared via **GP2**, using **S1e** (2.30 g, 11.2 mmol) and DMP (5.72 g, 13.5 mmol) and the reaction was stirred for 10 min. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 10:0.3) to give **S2e** (1.52 g, 8.70 mmol, 78%) as a colorless oil which was used directly in the next step.

Hydrazone **1e** was prepared via **GP3**, using ketone **S2e** (350 mg, 2.00 mmol), tosylhydrazide (559 mg, 3.00 mmol) and the reaction was stirred for 12 h. After filtration **1e** (383 mg, 1.12 mmol, 56%, d.r. = >20:1) was obtained as a colorless solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.12 – 8.06 (m, 2H), 8.03 (s, 1H), 7.62 – 7.54 (m, 2H), 6.98 – 6.92 (m, 2H), 6.77 – 6.70 (m, 2H), 5.32 (ddt, *J* = 17.4, 10.3, 5.2 Hz, 1H), 4.74 – 4.57 (m, 2H), 2.82 (dt, *J* = 5.2, 2.0 Hz, 2H), 2.35 (q, *J* = 7.6 Hz, 2H), 1.79 (s, 3H), 1.00 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 152.6, 146.0, 143.7, 136.9, 135.0, 130.4, 129.6, 128.6, 128.2, 126.8, 117.1, 31.4, 28.9, 21.1, 15.6.

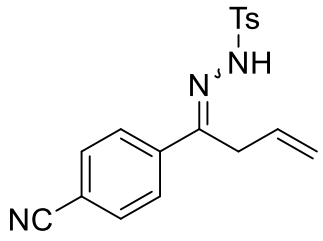
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3222, 2966, 2931, 273, 1598, 1392, 1330, 1306, 1167, 1084, 682, 589, 551.

MS (ESI): m/z (%) = 343 (100), 295 (52), 227 (14), 187 (28), 177 (30).

HRMS (ESI) for $C_{19}H_{23}N_2O_2S$ (343.1475): 343.1477 $(M+H)^+$.

M.p. (°C): 131–134.

***N*'-(1-(4-Cyanophenyl)but-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1f)**



1f

Alcohol **S1f** was prepared via **GP1**, using 4-cyanobenzaldehyde (1.31 g, 10.0 mmol), allyl bromide (1.73 mL, 20.0 mmol) and zinc powder (1.31 g, 20.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1f** was obtained as a colorless oil which was used directly in the next step.

Ketone **S2f** was prepared via **GP2**, using **S1f** and DMP (5.09 g, 12.0 mmol) and the reaction was stirred for 90 min. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2f** (1.29 g, 7.54 mmol, 75% over two steps) as a light yellow solid which was used directly in the next step.

Hydrazone **1f** was prepared via **GP3**, using ketone **S2f** (171 mg, 1.00 mmol), tosylhydrazide (279 mg, 1.50 mmol) and the reaction was stirred for 2 h at 0 °C. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3) using neutral silica to give **1f** (232 mg, 684 µmol, 68%, d.r. = >20:1) as a colorless solid.

^{1}H-NMR (400 MHz, DMSO-d_6): δ / ppm = 11.07 (s, 1H), 7.86 – 7.72 (m, 6H), 7.47 – 7.34 (m, 2H), 5.81 – 5.65 (m, 1H), 5.07 – 4.88 (m, 2H), 3.57 – 3.48 (m, 2H), 2.37 (s, 3H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ / ppm = 150.4, 143.6, 140.8, 136.0, 132.4, 131.1, 129.6, 127.4, 126.9, 118.6, 117.5, 111.5, 30.7, 21.0.

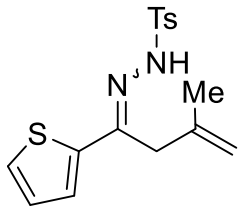
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3205, 1596, 1614, 1389, 1336, 1303, 1160, 1074, 990, 895, 661, 567, 549.

MS (ESI): m/z (%) = 362 (51), 340 (39), 185 (24), 184 (100), 169 (14).

HRMS (ESI) for $C_{18}H_{17}N_3NaO_2S$ (362.0934): 362.0936 $(M+Na)^+$.

M.p. (°C): 163–165.

4-Methyl-*N*'-(3-methyl-1-(thiophen-2-yl)but-3-en-1-ylidene)benzenesulfonohydrazide (1g)



1g

Alcohol **S1g** was prepared via **GP1**, using thiophene-2-carboxaldehyde (1.12 g, 10.0 mmol), allyl bromide (1.73 mL, 20.0 mmol) and zinc powder (1.31 g, 20.0 mmol) and the reaction was stirred for 20 h. After work-up, the crude product **S1g** was obtained as a colorless oil which was used directly in the next step.

Ketone **S2m** was prepared via **GP2**, using **S1g** and DMP (5.09 g, 12.0 mmol) and the reaction was stirred for 90 min. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2m** (1.44 g, 8.66 mmol, 87%) as a light yellow oil which was used directly in the next step.

Hydrazone **1g** was prepared via **GP3**, using ketone **S2m** (334 mg, 2.00 mmol), tosylhydrazide (558 mg, 3.00 mmol) and the reaction was stirred for 5 h. After filtration, hydrazone **1g** (374 mg, 1.12 mmol, 56%, d.r. = >20:1) was obtained as a light yellow solid.

^{1}H-NMR (400 MHz, DMSO-d_6): δ / ppm = 10.48 (s, 1H), 7.80 – 7.75 (m, 2H), 7.73 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.48 (dd, *J* = 5.1, 2.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 (dd, *J* = 5.1, 1.3 Hz, 1H), 4.69 (q, *J* = 1.6 Hz, 1H), 4.47 – 4.42 (m, 1H), 3.38 (s, 2H), 2.36 (s, 3H), 1.66 (s, 3H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ / ppm = 149.2, 143.3, 140.0, 139.4, 136.1, 129.4, 127.4, 126.5, 125.5, 125.3, 111.6, 35.4, 22.5, 21.0.

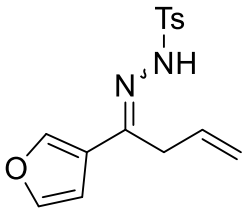
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3202, 3110, 1598, 1373, 1345, 1168, 1089, 860, 787, 656, 558.

MS (ESI): m/z (%) = 335 (100), 180 (83), 179 (16), 165 (34), 164 (18).

HRMS (ESI) for $C_{16}H_{19}N_2O_2S_2$ (335.0882): 335.0880 $(M+H)^+$.

M.p. (°C): 153–154.

***N*'-(1-(Furan-3-yl)but-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1h)**



1h

Alcohol **S1h** was prepared via **GP1**, using furan-3-carbaldehyde (1.73 g, 20.0 mmol), allyl bromide (3.46 mL, 40.0 mmol) and zinc powder (2.62 g, 40.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1h** (1.46 g, 10.5 mmol, 53%) was obtained as a colorless oil which was used directly in the next step.

Ketone **S2h** was prepared via **GP2**, using **S1h** (1.46 g, 10.5 mmol) and DMP (5.40 g, 12.7 mmol), K_2CO_3 (1.47 g, 10.6 mmol), DCM (10 mL) and the reaction was stirred for 3 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3) to give **S2h** (747 mg, 5.20 mmol, 52%) as a light yellow oil which was used directly in the next step.

Hydrazone **1h** was prepared via **GP3**, using ketone **S2h** (136 mg, 1.00 mmol), tosylhydrazide (279 mg, 1.50 mmol) and the reaction was stirred for 2 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3) to give **1h** (217 mg, 713 µmol, 71%, d.r. = 11:1) as a colorless solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.09 – 8.04 (m, 2H), 7.95 (s, 1H), 7.01 (dd, *J* = 1.5, 0.8 Hz, 1H), 6.88 (dd, *J* = 1.9, 1.4 Hz, 1H), 6.78 – 6.74 (m, 2H), 6.73 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.17 (ddt, *J* = 17.3, 10.3, 5.5 Hz, 1H), 4.66 (dtd, *J* = 10.2, 1.8, 1.2 Hz, 1H), 4.58 (dtd, *J* = 17.3, 1.9, 1.2 Hz, 1H), 2.51 (dt, *J* = 5.5, 1.9 Hz, 2H), 1.81 (p, *J* = 0.4 Hz, 3H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 147.0, 144.0, 143.8, 142.4, 136.7, 130.1, 129.6, 128.5, 126.1, 117.4, 108.5, 32.4, 21.1.

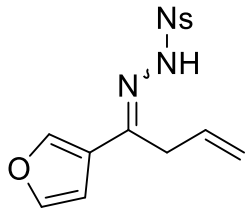
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3204 (broad), 2924, 1676, 1597, 1513, 1447, 1382, 1331, 1161, 1090, 1037, 923, 873, 812, 743, 706, 667, 596, 550.

MS (ESI): m/z (%) = 305 (100), 149 (25), 135 (12).

HRMS (ESI) for $C_{15}H_{17}N_2O_3S$ (305.0954): 305.0953 $(M+H)^+$.

M.p. (°C): 115–119.

***N*'-(1-(Furan-3-yl)but-3-en-1-ylidene)-4-nitrobenzenesulfonohydrazide (1i)**



1i

Hydrazone **1i** was prepared via **GP3**, using ketone **S2i** (136 mg, 1.00 mmol), nosylhydrazide (326 mg, 1.50 mmol) and the reaction was stirred for 3 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3) to give **1i** (175 mg, 522 µmol, 52%, d.r. = >20:1) as a colorless solid. **1i** dissolves poorly in C_6D_6 and decomposes rapidly in $CDCl_3$ and CD_2Cl_2.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 7.75 (d, *J* = 8.7 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.45 (s, 2H), 6.98 (d, *J* = 1.4 Hz, 1H), 6.89 (d, *J* = 1.7 Hz, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 5.02 (ddt, *J* = 16.2, 10.7, 5.5 Hz, 1H), 4.59 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.48 – 4.39 (m, 1H), 2.33 (dd, *J* = 5.0, 2.4 Hz, 2H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 148.3, 144.4, 144.1, 142.8, 129.9, 129.2, 123.9, 117.6, 108.1, 32.4.

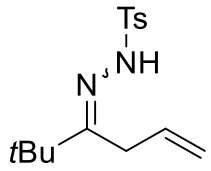
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3216, 2925, 1607, 1529, 1404, 1349, 1312, 1172, 1088, 1027, 873, 855, 811, 738, 684, 606, 596.

MS (ESI): m/z (%) = 322 (36), 223 (23), 194 (44), 159 (100).

HRMS (ESI) for $C_{14}H_{13}N_3NaO_5S$ (358.0468): 358.0471 $(M+Na)^+$.

M.p. (°C): 150–153 (decomposition).

***N*'-(2,2-Dimethylhex-5-en-3-ylidene)-4-methylbenzenesulfonohydrazide (1j)**



1j

Alcohol **S1j** was prepared via **GP1**, using pivaldehyde (2.42 g, 22.3 mmol), allyl bromide (3.46 mL, 40.0 mmol) and zinc powder (2.62 g, 40.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1j** (1.72 g, 13.4 mmol, 60%) was obtained as a colorless oil which was used directly in the next step.

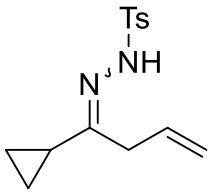
Ketone **S2j** was prepared via **GP2**, using **S1j** (1.72 g, 13.4 mmol) and DMP (8.5 g, 20.0 mmol) and the reaction was stirred for 90 min. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2j** (801 mg, 6.35 mmol, 47%) as a colorless oil which was used directly in the next step.

Hydrazone **1j** was prepared via **GP3**, using ketone **S2j** (252 mg, 2.00 mmol), tosylhydrazide (559 mg, 3.00 mmol) and the reaction was stirred for 5 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8.5:1.5) to give **1j** (152 mg, 516 µmol, 26%, d.r. = >20:1) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.83 – 7.77 (m, 2H), 7.37 (s, 1H), 7.32 – 7.27 (m, 2H), 5.66 (ddt, *J* = 17.5, 10.4, 5.2 Hz, 1H), 5.04 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.67 – 4.58 (m, 1H), 2.98 (dt, *J* = 5.2, 2.0 Hz, 2H), 2.43 (s, 3H), 1.04 (s, 9H).

The spectra are in agreement with the literature.[5]

***N*'-(1-Cyclopropylbut-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1k)**



1k

Alcohol **S1k** was prepared via **GP1**, using cyclopropylcarboxaldehyde (1.49 mL, 20.0 mmol), allyl bromide (3.46 mL, 40.0 mmol) and zinc powder (2.62 g, 40.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1k** (2.10 g, 18.7 mmol, 94%) was obtained as a colorless oil which was used directly in the next step.

Ketone **S2k** was prepared via **GP2**, using **S1k** (1.99 g, 17.7 mmol) and DMP (10.5 g, 24.8 mmol) and the reaction was stirred for 60 min. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **S2k** (850 mg, 7.72 mmol, 43%) as a colorless volatile liquid which was used directly in the next step.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 5.97 (ddtd, J = 17.2, 10.3, 6.9, 0.8 Hz, 1H), 5.15 (q, J = 1.6 Hz, 2H), 3.32 (dt, J = 6.9, 1.4 Hz, 2H), 1.97 (tdd, J = 7.8, 5.0, 4.2 Hz, 1H), 1.08 – 1.00 (m, 2H), 0.93 – 0.84 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 208.8, 130.9, 118.8, 48.5, 20.2, 11.1.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2931, 2840, 1727, 1295, 1250, 1045, 718.

MS (ESI): m/z (%) = 128 (5), 104 (100).

HRMS (ESI) for $C_7H_{14}NOS$ (128.1070): 128.1070 (M^++H^+).

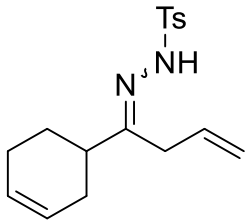
Hydrazone **1k** was prepared via **GP3**, using ketone **S2k** (165 mg, 1.50 mmol), tosylhydrazide (419 mg, 2.25 mmol) and the reaction was stirred for 3.5 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **1k** (186 mg, 668 µmol, 45%, d.r. = 10:1) as a colorless oil. Hydrazone **1k** decomposes rapidly and needs to be used directly for the cyclization reaction.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.01 – 7.96 (m, 2H), 7.26 (s, 1H), 6.78 – 6.72 (m, 2H), 5.14 (ddt, *J* = 17.4, 10.3, 5.7 Hz, 1H), 4.70 (dq, *J* = 10.2, 1.6 Hz, 1H), 4.58 (dq, *J* = 17.3, 1.8 Hz, 1H), 2.16 (dt, *J* = 5.8, 1.9 Hz, 2H), 1.82 (s, 3H), 1.11 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.60 – 0.52 (m, 2H), 0.36 – 0.28 (m, 2H).

MS (ESI): m/z (%) = 279 (100), 177 (24), 150 (30).

HRMS (ESI) for $C_{14}H_{19}N_2O_2S$ (279.1162): 279.1159 (M^++H^+).

***N*'-(1-(Cyclohex-3-en-1-yl)but-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1l)**



1l

Alcohol **S1l** was prepared via **GP1**, using cyclohex-3-ene-1-carbaldehyde (2.34 mL, 20.0 mmol), allyl bromide (3.46 mL, 40.0 mmol) and zinc powder (2.62 g, 40.0 mmol) and the reaction was stirred for 7.5 h. After work-up, the crude product **S1l** (2.64 g, 17.4 mmol, 87%) was obtained as a colorless oil which was used directly in the next step.

Ketone **S2l** was prepared via **GP2**, using **S1l** (2.64 g, 17.4 mmol) and DMP (8.85 g, 20.9 mmol) and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2l** (2.01 g, 13.4 mmol, 77%) as a light yellow oil which was used directly in the next step.

Hydrazone **1l** was prepared via **GP3**, using ketone **S2l** (600 mg, 4.00 mmol), tosylhydrazide (1.12 g, 6.00 mmol) and the reaction was stirred for 12 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) and recrystallized from hexane/ethyl acetate to give **1l** (754 mg, 2.96 mmol, 71%, d.r. = 7:1) as a colorless solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.04 (d, *J* = 8.3 Hz, 2H), 7.83 (s, 1H), 6.84 – 6.73 (m, 2H), 5.61 – 5.51 (m, 2H), 5.23 (ddt, *J* = 17.3, 10.2, 5.6 Hz, 1H), 4.74 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.58 (dq, *J* = 17.4, 1.8 Hz, 1H), 2.40 (dt, *J* = 5.6, 1.9 Hz, 2H), 2.16 – 1.94 (m, 2H), 1.91 – 1.75 (m, 6H), 1.60 (ddd, *J* = 12.9, 5.2, 2.4 Hz, 1H), 1.43 – 1.24 (m, 1H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 159.4, 143.5, 136.9, 130.5, 129.5, 128.7, 126.7, 126.1, 117.4, 42.0, 33.1, 28.8, 26.3, 25.5, 21.2.

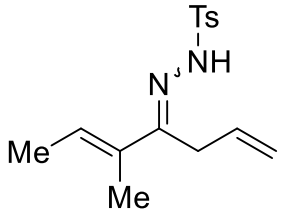
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3221, 3023, 2921, 2838, 1598, 1336, 1164, 859, 812, 665, 548.

MS (ESI): m/z (%) = 319 (100), 164 (10), 163 (25), 149 (12).

HRMS (ESI) for $C_{17}H_{23}N_2O_2S$ (319.1475): 319.1474 $(M+H)^+$.

M.p. (°C): 120–121.

4-Methyl-*N*'-((*E*)-5-methylhepta-1,5-dien-4-ylidene)benzenesulfonohydrazide (1m)



1m

Alcohol **S1m** was prepared via **GP1**, using tiglic aldehyde (1.93 g, 20.0 mmol), allyl bromide (3.46 mL, 40.0 mmol) and zinc powder (2.62 g, 40.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1m** was obtained as a colorless oil which was used directly in the next step.

Ketone **S2m** was prepared via **GP2**, using **S1m** and DMP (8.31 g, 19.6 mmol) and the reaction was stirred for 90 min. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2m** (334 mg, 2.67 mmol, 13%) as a colorless oil which was used directly in the next step.

Hydrazone **1m** was prepared via **GP3**, using ketone **S2m** (334 mg, 2.67 mmol), tosylhydrazide (745 mg, 4.00 mmol) and the reaction was stirred for 4.5 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **1m** (135 mg, 462 µmol, 18%, d.r. = 12:1) as a colorless solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.07 – 8.00 (m, 2H), 7.72 (s, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 5.50 (dddd, *J* = 8.3, 6.9, 5.6, 1.4 Hz, 1H), 5.23 (ddt, *J* = 17.4, 10.3, 5.2 Hz, 1H), 4.69 (dq, *J* = 10.3, 1.7 Hz, 1H), 4.51 (dq, *J* = 17.3, 1.8 Hz, 1H), 2.61 (dt, *J* = 5.2, 2.0 Hz, 2H), 1.88 – 1.85 (m, 3H), 1.82 (s, 3H), 1.37 (dd, *J* = 6.8, 1.2 Hz, 3H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 154.7, 143.6, 136.8, 135.3, 131.1, 129.5, 128.6, 127.8, 116.7, 29.8, 21.1, 14.2, 12.5.

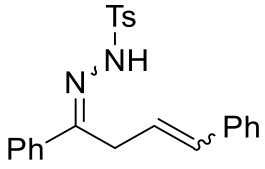
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3225, 2900, 1600, 1400, 1350, 1150, 1100, 1075, 925, 675, 550.

MS (ESI): m/z (%) = 293 (100), 227 (16), 212 (11), 177 (33), 138 (16), 137 (38), 123 (15).

HRMS (ESI) for $C_{15}H_{21}N_2O_2S$ (293.1318): 293.1318 $(M+H)^+$.

M.p. (°C): 97–99.

***N*'-(1,4-Diphenylbut-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1n)**



1n

Ketone **S2n** was prepared according to a literature protocol.[6] Acetophenone (1.17 mL, 10.0 mmol), phenylacetylene (1.10 mL, 10.0 mmol) and KO^{t}Bu (1.12 g, 10.0 mmol) were dissolved in DMSO (24 mL) and reaction stirred at 100 °C for 1 h. After cooling to 25 °C, the mixture was diluted with H_2O (25 mL) and a sat. aq. NH_4Cl solution (ca 200 mL) was added until a pH of 7 was reached. The mixture was extracted with ethyl acetate (3x100 mL) and the combined organic extracts were washed with H_2O (100 mL). After drying over $MgSO_4$, filtering and removal of solvent, the crude product was purified by flash column chromatography using silica gel (hexane:ethyl acetate = 95:5) to give **S2n** (1.10 g, 4.95 mmol, 50%, d.r. = 12:1) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.97 – 7.88 (m, 2H), 7.62 – 7.53 (m, 2H), 7.52 – 7.42 (m, 3H), 7.42 – 7.34 (m, 3H), 7.34 – 7.26 (m, 3H), 7.25 – 7.19 (m, 1H), 6.73 (dd, *J* = 11.6, 1.9 Hz, 1H), 6.60 – 6.44 (m, 1H), 6.07 (d, *J* = 11.6 Hz, 1H), 4.01 (dd, *J* = 7.1, 1.8 Hz, 2H), 3.92 (dd, *J* = 6.4, 0.9 Hz, 1H).

The spectrum is in agreement with the literature.[6]

Hydrazone **1n** was prepared via **GP3**, using ketone **S2n** (391 mg, 1.76 mmol), tosylhydrazide (491 mg, 2.64 mmol) and the reaction was stirred for 5 h. After filtration **1n** (425 mg, 1.09 mmol, 62%) was obtained as a colorless solid (d.r. = > 10.1).

[6] Trofimov, B. A.; Schmidt, E. Y.; Zorina, N. V.; Ivanova, E. V.; Ushakov, I. A. *J. Org. Chem.* **2012**, *77*, 6880-6886.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.38 (s, 1H), 8.04 – 7.95 (m, 2H), 7.72 – 7.64 (m, 2H), 7.13 – 6.96 (m, 6H), 6.88 – 6.81 (m, 2H), 6.63 – 6.55 (m, 2H), 5.97 (dt, J = 16.1, 2.0 Hz, 1H), 5.69 (dt, J = 16.2, 5.4 Hz, 1H), 2.96 (dd, J = 5.4, 2.0 Hz, 2H), 1.77 (s, 3H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 152.5, 143.6, 137.5, 136.8, 136.7, 132.0, 129.8, 129.7, 129.6, 129.5, 128.7, 128.6, 128.3, 126.7, 121.8, 30.5, 21.1.

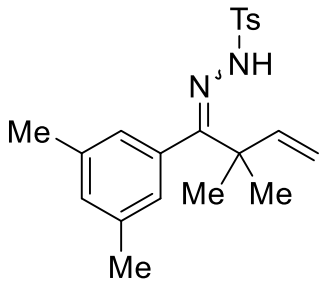
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3218, 3060, 1736, 1598, 1494, 1447, 1343, 1167, 1085, 903, 814, 760, 694, 669, 591, 550

MS (ESI): m/z (%) = 413 (55), 371 (75), 322 (53), 194 (65), 159 (25), 142 (53).

HRMS (ESI) for $C_{23}H_{22}N_2NaO_2S$ (413.1294): 413.1295 $(M+Na)^+$.

M.p. (°C): 142–144.

***N*'-(1-(3,5-Dimethylphenyl)-2,2-dimethylbut-3-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1o)**



1o

Alcohol **S1o** was prepared via **GP1**, using 3,5-dimethylbenzaldehyde (1.34 g, 10.0 mmol), 1-bromo-3-methylbut-2-ene (2.31 mL, 20.0 mmol) and zinc powder (1.31 g, 20.0 mmol) and the reaction was stirred for 22 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9.5:1) to give **S1o** (1.73 g, 8.50 mmol, 85%) as a colorless oil which was used directly in the next step.

Ketone **S2o** was prepared via **GP2**, using **S1o** (1.73 g, 8.50 mmol) and DMP (4.32 g, 10.2 mmol) and the reaction was stirred for 3 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2o** (1.48 g, 7.32 mmol, 86%) as a colorless oil which was used directly in the next step.

Hydrazone **1o** was prepared via **GP3**, using ketone **S2o** (174 mg, 1.00 mmol), tosylhydrazide (280 mg, 1.50 mmol), and *para*-toluenesulfonic acid (38 mg, 0.20 mmol) and the reaction was stirred for 9 h. After filtration and washing with cold MeOH, hydrazone **1o** (204 mg, 550 µmol, 55%, d.r. = >20:1) was obtained as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.81 – 7.73 (m, 2H), 7.37 – 7.29 (m, 2H), 7.02 – 6.95 (m, 2H), 6.35 (dt, *J* = 1.5, 0.7 Hz, 2H), 5.74 (dd, *J* = 17.4, 10.6 Hz, 1H), 4.95 (dd, *J* = 10.6, 1.0 Hz, 1H), 4.85 (dd, *J* = 17.4, 1.1 Hz, 1H), 2.46 (s, 3H), 2.27 (d, *J* = 0.8 Hz, 6H), 1.15 (s, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 163.9, 144.2, 144.0, 139.0, 135.6, 131.5, 131.1, 129.5, 128.1, 125.2, 113.0, 44.5, 25.4, 21.8, 21.5.

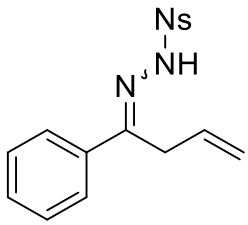
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3210, 2971, 2916, 1865, 1597, 1371, 1341, 1167, 1019, 809, 676, 548, 564.

MS (ESI): m/z (%) = 371 (100), 295 (36), 177 (37), 159 (12).

HRMS (ESI) for $C_{21}H_{27}N_2O_2S$ (371.1795): 371.1790 $(M+H)^+$.

M.p. (°C): 139–140.

4-Nitro-*N*'-(1-phenylbut-3-en-1-ylidene)benzenesulfonohydrazide (1p)



1p

Hydrazone **1p** was prepared via **GP3**, using ketone **S2a** (126 mg, 860 µmol), nosylhydrazide (280 mg, 1.50 mmol) and the reaction was stirred for 3 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **1p** (164 mg, 475 µmol, 55%, d.r. = >20:1) as a light yellow solid.

^{1}H-NMR (500 MHz, C_6D_6): δ / ppm = 7.79 – 7.75 (m, 2H), 7.71 – 7.65 (m, 1H), 7.52 – 7.46 (m, 4H), 7.10 – 7.02 (m, 3H), 5.17 (ddt, J = 17.4, 10.4, 5.2 Hz, 1H), 4.61 (dtd, J = 10.3, 1.9, 1.0 Hz, 1H), 4.46 (dtd, J = 17.4, 2.1, 1.0 Hz, 1H), 2.63 (dt, J = 5.2, 2.0 Hz, 2H).

^{13}C-NMR (126 MHz, C_6D_6): δ / ppm = 153.8, 150.3, 144.1, 136.8, 130.2, 130.0, 129.2, 128.8, 126.6, 124.0, 117.3, 31.5.

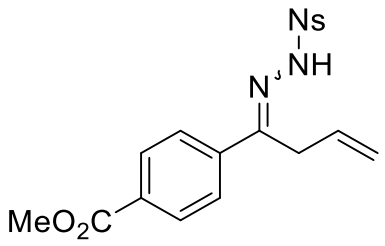
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3207, 3070, 2853, 1608, 131, 1349, 1178, 1008, 760, 595.

MS (ESI): m/z (%) = 368 (100), 346 (37), 173 (19).

HRMS (ESI) for $C_{16}H_{15}N_3O_4SNa$ (368.0675): 368.0675 $(M+Na)^+$.

M.p. (°C): 128–130.

Methyl 4-(1-(2-((4-nitrophenyl)sulfonyl)hydrazineylidene)but-3-en-1-yl)benzoate (1q)



1q

Hydrazone **1q** was prepared via **GP3**, using ketone **S2c** (204 mg, 1.00 mmol), nosylhydrazide (326 mg, 1.50 mmol) and the reaction was stirred for 2 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3) to give **1q** (191 mg, 473 µmol, 47%, d.r. = >20:1) as a light yellow solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.09 – 8.04 (m, 2H), 7.97 (s, 1H), 7.81 – 7.77 (m, 2H), 7.57 – 7.53 (m, 2H), 7.52 – 7.47 (m, 2H), 5.19 (ddt, *J* = 17.4, 10.3, 5.2 Hz, 1H), 4.67 – 4.63 (m, 1H), 4.47 (dtd, *J* = 17.3, 2.0, 0.9 Hz, 1H), 3.46 (s, 3H), 2.64 (dt, *J* = 5.2, 2.0 Hz, 2H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 166.1, 152.7, 150.4, 143.9, 140.6, 131.9, 130.1, 129.7, 129.2, 126.6, 124.1, 117.5, 51.9, 31.3.

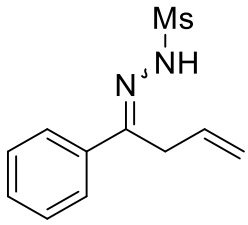
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3214, 3106, 2954, 1720, 1607, 1530, 1437, 1405, 1349, 1280, 1174, 1110, 1013, 855, 738, 684, 606.

MS (ESI): m/z (%) = 426 (20), 160 (10), 159 (100), 158 (10), 144 (12).

HRMS (ESI) for $C_{18}H_{17}N_3NaO_6S$ (426.0730): 426.0721 $(M+Na)^+$.

M.p. (°C): 92–95.

***N*'-(1-Phenylbut-3-en-1-ylidene)methanesulfonohydrazide (1r)**



1r

Hydrazone **1r** was prepared via **GP3**, using ketone **S2a** (161 mg, 1.10 mmol), mesylhydrazide (175 mg, 1.60 mmol) and the reaction was stirred for 2.25 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3) to give **1r** (176 mg, 739 µmol, 67%, d.r. = >20:1) as a light yellow solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 7.84 (s, 1H), 7.66 – 7.59 (m, 2H), 7.10 (dd, *J* = 5.1, 2.0 Hz, 3H), 5.40 (ddt, *J* = 17.4, 10.5, 5.4 Hz, 1H), 4.89 – 4.75 (m, 2H), 2.87 (dt, *J* = 5.4, 1.9 Hz, 2H), 2.59 (s, 3H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 152.8, 137.3, 130.4, 129.8, 128.7, 126.8, 117.5, 38.2, 31.7.

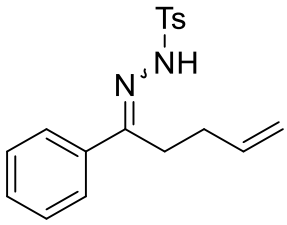
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3215, 3025, 2979, 2933, 1683, 1640, 1446, 1389, 1319, 1162, 974, 764, 695, 517.

MS (ESI): m/z (%) = 261 (100), 239 (34), 227 (11), 177 (38), 160 (12), 159 (22), 145 (14), 144 (23).

HRMS (ESI) for $C_{11}H_{14}N_2O_2SNa$ (261.0668): 261.0668 $(M+Na)^+$.

M.p. (°C): 95–97.

4-Methyl-*N*'-(1-phenylpent-4-en-1-ylidene)benzenesulfonohydrazide (1s)



1s

Ketone **S2s** was prepared following a literature procedure.[7]

Hydrazone **1s** was prepared via **GP3**, using ketone **S2s** (360 mg, 2.25 mmol), tosylhydrazide (629 mg, 3.38 mmol) and the reaction was stirred for 4 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **1s** (582 mg, 1.72 mmol, 76%, d.r. = 9:1) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.94 – 7.88 (m, 3H), 7.66 – 7.29 (m, 6H), 5.69 (ddt, *J* = 16.9, 10.1, 6.8 Hz, 1H), 5.05 – 4.85 (m, 2H), 2.73 – 2.53 (m, 2H), 2.44 (d, *J* = 11.8 Hz, 3H), 2.22 (tdt, *J* = 7.8, 6.6, 1.3 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 157.5, 155.3, 144.3, 144.1, 137.2, 136.3, 136.2, 135.5, 133.2, 130.1, 130.0, 129.8, 129.7, 128.7, 128.6, 128.4, 128.24, 128.17, 128.1, 126.8, 126.5, 117.1, 115.4, 37.5, 30.1, 29.8, 26.4, 21.7.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3217, 2978, 1598, 1575, 1334, 1292, 1166, 916, 668, 612.

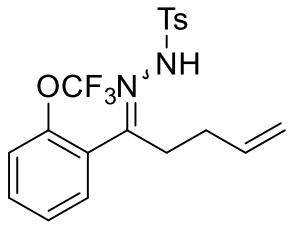
MS (ESI): m/z (%) = 329 (100), 296 (31), 251 (14), 223 (16), 194 (11).

HRMS (ESI) for $C_{18}H_{21}N_2O_2S$ (329.1318): 329.1315 $(M+H)^+$.

M.p. (°C): 118–120.

[7] Nicolai, S.; Waser, J. *Org. Lett.* **2011**, *13*, 6324-6327.

4-Methyl-*N*'-(1-(2-(trifluoromethoxy)phenyl)pent-4-en-1-ylidene)benzenesulfonohydrazide (1t)



1t

Alcohol **S1t** was prepared by dissolving 2-(trifluoromethoxy)benzaldehyde (1.37 mL, 9.50 mmol) in THF (15 mL) and cooling to –15 °C. Then, CuI (180 mg, 950 µmol) was added, followed by dropwise addition of 3-butenylmagnesium bromide (0.5 M in THF). After slow warming to 25 °C, the reaction mixture was stirred for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL) and extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (hexane:ethyl acetate = 9:1) to give **S1t** (1.54 g, 6.24 mmol, 66%) as a colorless oil which was used directly in the next step.

Ketone **S2t** was prepared via **GP2**, using **S1t** (740 g, 3.00 mmol) and DMP (1.91 g, 4.50 mmol) and the reaction was stirred for 4 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 10:0.4) to give **S2t** (692 mg, 2.83 mmol, 94%) as a colorless oil which was used directly in the next step.

Hydrazone **1t** was prepared via **GP3**, using ketone **S2t** (244 mg, 1.00 mmol), tosylhydrazide (279 mg, 1.50 mmol) and the reaction was stirred for 4 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **1t** (330 mg, 800 µmol, 80%, d.r. = 10:1) as a colorless solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 8.05 (s, 1H), 7.86 – 7.77 (m, 2H), 7.41 – 7.34 (m, 1H), 7.32 – 7.29 (m, 2H), 7.28 – 7.23 (m, 2H), 7.23 – 7.19 (m, 1H), 5.76 – 5.57 (m, 1H), 4.99 – 4.87 (m, 2H), 2.65 – 2.51 (m, 2H), 2.43 (s, *J* = 0.9 Hz, 3H), 2.10 (dtt, *J* = 9.2, 6.6, 1.3 Hz, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ / ppm = 155.0, 152.7, 146.78, 146.77, 144.3, 144.2, 137.1, 136.1, 135.4, 131.7, 131.34, 131.28, 130.5, 129.7, 129.6, 129.3, 128.11, 128.06, 128.0, 126.9, 121.5, 120.31, 120.30, 119.4, 116.7, 115.4, 36.8, 29.8, 29.2, 29.1, 21.7.

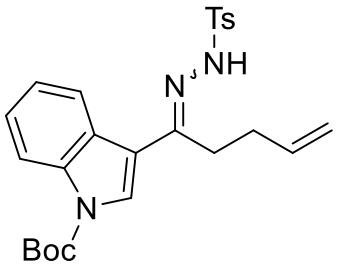
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3218, 3079, 2956, 1643, 1599, 1493, 1448, 1248, 1217, 1163, 1077, 917, 733, 667, 611.

MS (ESI): m/z (%) = 435 (100), 413 (70), 308 (11), 296 (19), 268 (67), 187 (52), 180 (11), 163 (12), 104 (80).

HRMS (ESI) for $C_{19}H_{19}F_3N_2NaO_3S$ (435.0961): 435.0959 $(M+H)^+$.

M.p. (°C): 105–107.

***tert*-Butyl 3-(1-(2-tosylhydrazineylidene)pent-4-en-1-yl)-1*H*-indole-1-carboxylate (1u)**



1u

Alcohol **S1u** was prepared by dissolving 1-Boc-3-formylindole (2.33 mL, 9.5 mmol) in THF (15 mL) and cooling to –15 °C. Then, CuI (180 mg, 0.95 mmol) was added, followed by dropwise addition of 3-butenylmagnesium bromide (0.5 M in THF). After slow warming to 25 °C, the reaction mixture was stirred for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL) and extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (hexane:ethyl acetate = 9:1) to give **S1u** (2.60 g, 8.63 mmol, 91%) as a colorless oil which was used directly in the next step.

Ketone **S2u** was prepared via **GP2**, using **S1u** (904 g, 3.00 mmol) and DMP (1.91 g, 4.50 mmol) and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 10:0.4) to give **S2u** (319 mg, 1.07 mmol, 36%) as a colorless oil which was used directly in the next step.

Hydrazone **1u** was prepared via **GP3**, using ketone **S2u** (160 mg, 534 µmol), tosylhydrazide (149 mg, 0.80 mmol) and the reaction was stirred for 4 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **1u** (78 mg, 167 µmol, 31%, d.r. = >20:1) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 8.30 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 1H), 8.09 – 8.04 (m, 2H), 7.99 – 7.93 (m, 2H), 7.76 (s, 1H), 7.37 – 7.27 (m, 4H), 5.76 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.05 – 4.96 (m, 2H), 2.71 – 2.64 (m, 2H), 2.38 (s, 3H), 2.32 (tdt, *J* = 8.0, 6.8, 1.3 Hz, 2H), 1.68 (s, 9H).

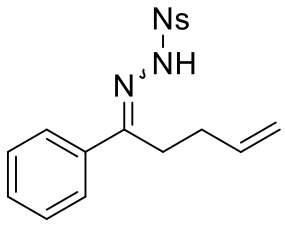
^{13}C-NMR (126 MHz, $CDCl_3$): δ / ppm = 152.4, 149.6, 144.3, 136.3, 135.9, 135.5, 129.8, 128.3, 127.7, 126.7, 125.3, 124.0, 123.7, 118.5, 117.1, 114.9, 84.8, 30.5, 28.3, 27.7, 21.7.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3217, 2979, 1734, 1598, 1558, 1450, 1370, 1336, 1152, 1061, 910, 730, 667.

MS (ESI): m/z (%) = 468 (100), 412 (69), 269 (82), 187 (64), 104 (98).

HRMS (ESI) for $C_{25}H_{30}N_3O_4S$ (468.1952): 468.1949 $(M+H)^+$.

4-Nitro-*N*'-(1-phenylpent-4-en-1-ylidene)benzenesulfonohydrazide (1v)



1v

Hydrazone **1v** was prepared via **GP3**, using ketone **S2s** (801 mg, 5.00 mmol), nosylhydrazide (1.63 mg, 7.50 mmol) and the reaction was stirred for 2 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **1v** (1.10 g, 3.10 mmol, 61%, d.r. = 3:1) as a yellow solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.02 (s, 1H), 7.89 – 7.82 (m, 2H), 7.60 – 7.45 (m, 4H), 7.14 – 7.02 (m, 3H), 5.38 (m, J = 1H), 4.76 – 4.66 (m, 2H), 2.13 (dd, J = 8.4, 6.8 Hz, 2H), 1.83 (q, J = 7.5, 7.1 Hz, 2H).

Note: Peaks of major diastereomer are given.

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 157.6, 156.6, 150.4, 150.3, 144.2, 144.1, 137.0, 136.4, 136.1, 132.6, 130.2, 130.0, 129.7, 129.29, 129.26, 128.8, 126.9, 126.7, 124.0, 123.9, 116.8, 115.7, 37.4, 30.1, 29.9, 26.1.

Note: Peaks of the diastereomeric mixture are given.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3225, 3106, 1529, 1349, 1172, 920, 854, 738, 530.

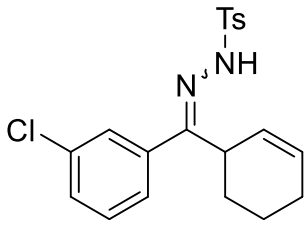
MS (ESI): m/z (%) = 382 (100), 360 (84), 338 (26), 329 (34), 309 (22), 251 (25), 223 (28).

HRMS (ESI) for $C_{17}H_{17}N_3NaO_4S$ (382.0832): 382.0830 $(M+Na)^+$.

M.p. (°C): 117–120.

Starting Material Synthesis (5a–c, 7a and 7b)

***N*'-((3-Chlorophenyl)(cyclohex-2-en-1-yl)methylene)-4-methylbenzenesulfonohydrazide (5a)**



5a

Alcohol **S1-5a** was prepared via **GP1**, using 3-chlorobenzaldehyde (1.13 mL, 10.0 mmol), 3-bromocyclohex-1-ene (2.30 mL, 20.0 mmol) and zinc powder (1.31 g, 20.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1-5a** (1.15 g, 5.21 mmol, 52%) was obtained as a colorless.

Ketone **S2-5a** was prepared via **GP2**, using **S1-5a** (1.15 g, 5.21 mmol) and DMP (2.21 g, 7.80 mmol) and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9.5:0.5) to give **S2-5a** (970 mg, 4.40 mmol, 84%) as a light yellow oil.

Hydrazone **5a** was prepared via **GP3**, using ketone **S2-5a** (224 mg, 1.00 mmol), tosylhydrazide (279 mg, 1.50 mmol) and the reaction was stirred for 5 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8.5:1.5) using neutral silica to give **5a** (135 mg, 347 µmol, 35%, d.r. = 3:1) as a colorless oil.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 9.13 (s, 1H), 8.07 – 8.00 (m, 2H), 7.60 (t, *J* = 1.9 Hz, 1H), 7.34 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.03 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 6.81 – 6.74 (m, 3H), 5.63 (ddt, *J* = 9.8, 4.0, 2.5 Hz, 1H), 5.22 – 5.11 (m, 1H), 3.22 (ddq, *J* = 9.6, 4.7, 2.6 Hz, 1H), 1.80 (s, 3H), 1.75 – 1.51 (m, 2H), 1.50 – 1.42 (m, 1H), 1.37 (dtd, *J* = 10.6, 6.6, 5.3, 2.7 Hz, 2H), 1.30 – 1.01 (m, 1H).

Note: Peaks of major diastereomer are given.

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 157.8, 154.0, 143.9, 143.8, 140.0, 136.70, 136.66, 135.6, 134.6, 134.3, 132.3, 130.8, 129.8, 129.7, 129.6, 129.2, 128.6, 128.5, 127.3, 127.2, 126.5, 125.9, 125.8, 125.2, 43.6, 38.2, 26.6, 25.1, 24.4, 23.7, 21.7, 21.2, 21.1.

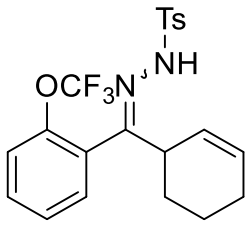
Note: All peaks are given.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3429, 3203, 2934, 1597, 1564, 1379, 1341, 1167, 1092, 890, 802, 667, 567, 549, 497

MS (ESI): m/z (%) = 389 (100), 295 (52), 233 (14), 219 (18), 203 (17), 177 (32).

HRMS (ESI) for $C_{20}H_{22}ClN_2O_2S$ (389.1085): 389.1084 $(M+H)^+$.

***N*'-(Cyclohex-2-en-1-yl(2-(trifluoromethoxy)phenyl)methylene)-4-methylbenzenesulfonohydrazide (5b)**



5b

Alcohol **S1-5b** was prepared via **GP1**, using 2-(trifluoromethoxy)benzaldehyde (1.43 mL, 10.0 mmol), 3-bromocyclohex-1-ene (2.30 mL, 20.0 mmol) and zinc powder (1.31 g, 20.0 mmol) and the reaction was stirred for 24 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **S1-5b** (1.54 g, 5.70 mmol, 57%) was obtained as a colorless.

Ketone **S2-5b** was prepared via **GP2**, using **S1-8b** (1.54 g, 5.66 mmol) and DMP (2.89 g, 6.81 mmol) and the reaction was stirred for 3 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) to give **S2-5b** (1.31 g, 4.85 mmol, 85%) as a colorless oil.

Hydrazone **5b** was prepared via **GP3**, using ketone **S2-5b** (270 mg, 1.00 mmol), tosylhydrazide (279 mg, 1.50 mmol) and the reaction was stirred for 28 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1) using neutral silica and recrystallized from hexane/ethyl acetate to give **5b** (50.0 mg, 114 µmol, 11%, d.r. = >20:1) as a colorless solid. **5b** decomposes rapidly and was used in the next step without further delay.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.01 (s, 1H), 7.98 – 7.89 (m, 2H), 7.22 – 7.17 (m, 1H), 6.87 (qq, *J* = 3.3, 1.8 Hz, 1H), 6.79 – 6.73 (m, 2H), 6.70 (dd, *J* = 8.3, 2.0 Hz, 2H), 5.73 – 5.64 (m, 1H), 5.55 (d, *J* = 10.1 Hz, 1H), 3.14 (s, 1H), 1.81 (s, 3H), 1.78 – 1.55 (m, 3H), 1.47 – 1.30 (m, 2H), 1.06 – 0.90 (m, 1H).

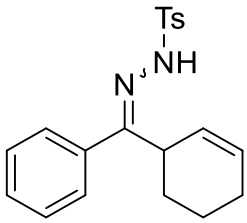
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3215, 2934, 1599, 1449, 1346, 1253, 1218, 1168, 1085, 924, 814, 765, 668, 556.

MS (ESI): m/z (%) = 439 (100), 283 (29), 269 (39), 268 (21), 253 (42).

HRMS (ESI) for $C_{21}H_{22}F_3N_2O_3S$ (439.1298): 439.1299 $(M+H)^+$.

M.p. (°C): 116–117.

***N*'-(Cyclohex-2-en-1-yl(phenyl)methylene)-4-methylbenzenesulfonohydrazide (5c)**



5c

Alcohol **S1-5c** was prepared via **GP1**, using benzaldehyde (1.01 mL, 10.0 mmol), 3-bromocyclohex-1-ene (2.30 mL, 20.0 mmol) and zinc powder (1.31 g, 20.0 mmol) and the reaction was stirred for 12 h. After work-up, the crude product **S1-5c** was obtained as a colorless oil which was used directly in the next step.

Ketone **S2-5c** was prepared via **GP2**, using **S1-5c** and DMP (4.58 g, 10.8 mmol) and the reaction was stirred for 3 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 10:0.5) to give **S2-5c** (1.32 g, 7.06 mmol, 71% over two steps) as a colorless oil which was used directly in the next step.

Hydrazone **5c** was prepared via **GP3**, using ketone **S2-5c** (558 mg, 3.00 mmol), tosylhydrazide (838 mg, 4.50 mmol) and the reaction was stirred for 4 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2) to give **5c** (481 mg, 1.36 mmol, 45%, d.r. = 1.2:1) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.84 (s, 0.5H), 7.88 – 7.75 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.27 (m, 5H), 7.23 (s, 0.5H), 7.03 – 6.94 (m, 1H), 6.11 – 5.70 (m, 1H), 5.53 (m, 1H), 3.80 – 3.20 (m, 1H), 2.45–2.41 (2 x s, *3*H), 2.29 – 2.11 (m, 1H), 2.00 –1.45 (m, 5H).

Note: Peaks of the diastereomeric mixture are given.

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 155.0, 152.7, 146.8, 146.8, 144.3, 144.2, 137.1, 136.1, 135.4, 131.7, 131.34, 131.28, 130.5, 129.7, 129.6, 129.3, 128.11, 128.06, 128.0, 126.9, 121.5, 120.31, 120.30, 119.4, 116.7, 115.4, 36.8, 29.8, 29.2, 29.1, 21.7.

Note: Peaks of the diastereomeric mixture are given.

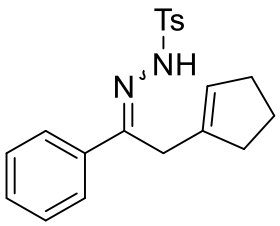
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3208, 2933, 2863, 1597, 1444, 1381, 1337, 1166, 1088, 909, 889, 829, 865, 665.

MS (ESI): m/z (%) = 355 (100), 251 (6), 223 (7), 194 (6), 105 (5).

HRMS (ESI) for $C_{20}H_{23}N_2O_2S$ (355.1475): 355.1470 (M^++H^+).

M.p. (°C): 89–91.

***N*'-(2-(Cyclopent-1-en-1-yl)-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (7a)**



7a

Ketone **S2-7a** was prepared according to a literature procedure:[8] 2-(Cyclopent-1-en-1-yl)acetonitrile (1.80 mL, 15 mmol) was dissolved in Et_2O (90 mL, 0.17 M) and PhMgBr (3.0 M in Et_2O, 10 mL, 30 mmol) was added dropwise at 25 °C followed stirring at 45 °C for 3 h. After cooling to 25 °C, THF (70 mL) was added and the mixture further cooled to 0 °C. The mixture was acidified by addition of 10% aq. HCl (40 mL) and stirred for 16 h at 25 °C. The mixture was extracted with EtOAc (40 mL) and washed with sat. aq. $NaHCO_3$ (2 x 50 mL) and brine (1 x 50 mL). After drying over Mg_2SO_4, filtration and concentrated in vacuo, the crude product was purified *via* silica gel flash chromatography (hexane:ethyl acetate = 97:3) to give **S2-7a** (500 mg, 2.70 mmol, 18%) as a yellow oil.

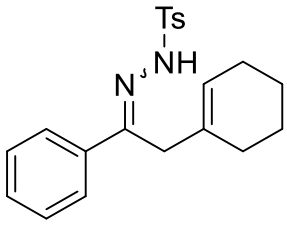
Hydrazone **7a** was prepared via **GP3**, using ketone **S2-7a** (460 mg, 2.47 mmol), tosylhydrazide (690 mg, 3.70 mmol) and the reaction was stirred for 9 h. After filtration, **7a** (413 mg, 1.16 mmol, 47%, d.r. = >20:1) was obtained as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.83 (d, J = 8.3 Hz, 2H), 7.68 (s, 1H), 7.64 – 7.59 (m, 2H), 7.39 – 7.32 (m, 3H), 7.30 (d, J = 8.1 Hz, 2H), 5.00 – 4.88 (m, 1H), 3.33 (s, 2H), 2.41 (s, 3H), 2.23 – 2.14 (m, 4H), 1.92 – 1.80 (m, 2H).

The spectrum is in agreement with the literature.[9]

[8] Crotti, P.; Badalassi, F.; Di Bussolo, V.; Favero, L.; Pineschi, M. *Tetrahedron*. **2001**, *57,* 8599-8572.
[9] Miyashi, T.; Nishizawa, Y.; Fujii, Y.; Yamakawa, K.; Kamata, M.; Akao, S.; Mukai, T. *J. Am. Chem. Soc.* **1986**, *108,* 1617-1632.

***N*'-(2-(Cyclohex-1-en-1-yl)-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (7b)**



7b

Ketone **S2-7b** was prepared according to a literature procedure:[10] 2-(cyclohex-1-en-1-yl)acetonitrile (2.10 mL, 15 mmol) was dissolved in Et_2O (90 mL, 0.17 M) and PhMgBr (3.0 M in Et_2O, 10 mL, 30 mmol) was added dropwise at 25 °C followed stirring at 45 °C for 3 h. After cooling to 25 °C, THF (70 mL) was added and the mixture further cooled to 0 °C. The mixture was acidified by addition of 10% aq. HCl (40 mL) and stirred for 16 h at 25 °C. The mixture was extracted with EtOAc (40 mL) and washed with sat. aq. $NaHCO_3$ (2 x 50 mL) and brine (1 x 50 mL). After drying over Mg_2SO_4, filtration and concentrated in vacuo, the crude product was purified *via* silica gel flash chromatography (hexane:ethyl acetate = 97:3) to give **S2-7b** (0.90 g, 4.50 mmol, 30%) as a yellow oil.

Hydrazone **7b** was prepared via **GP3**, using ketone **S2-7a** (460 mg, 2.30 mmol), tosylhydrazide (642 mg, 3.44 mmol) and the reaction was stirred for 16 h. After filtration, **7b** (335 mg, 909 µmol, 40%, d.r. = >20:1) was obtained as a colorless solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 8.34 (s, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 6.7 Hz, 2H), 7.13 – 6.99 (m, 3H), 6.73 (d, J = 8.0 Hz, 2H), 5.03 (s, 1H), 2.85 (s, 2H), 1.79 (s, 3H), 1.67 – 1.52 (m, 4H), 1.41 – 1.23 (m, 4H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 152.8, 143.6, 138.1, 137.0, 131.0, 129.6, 129.5, 128.6, 128.5, 126.7, 123.7, 36.1, 28.6, 25.3, 22.9, 22.2, 21.1.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3218, 2836, 1573, 1348, 1185, 1069, 813, 693, 550.

MS (ESI): m/z (%) = 369 (17), 329 (27), 251 (40), 237 (21), 223 (40), 217 (28), 214 (21), 209 (19), 195 (17), 194 (22), 158 (25).

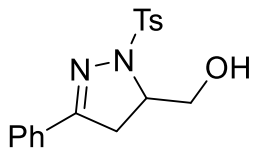
HRMS (ESI) for $C_{21}H_{25}N_2O_2S$ (369.1631): 369.1628 $(M+H)^+$.

M.p. (°C): 130–133.

[10] Crotti, P.; Badalassi, F.; Di Bussolo, V.; Favero, L.; Pineschi, M. *Tetrahedron*. **2001**, *57,* 8599-8572.

Preparation of Compounds 2a–v, 6a–c, 8a–b

(3-Phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2a)



2a

Pyrazoline **2a** was prepared via **GP4**, using hydrazone **1a** (97.0 mg, 308 µmol) and $Mn(dpm)_3$ (18 mg, 30 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **2a** (79.0 mg, 239 µmol, 78%) as a colorless oil.

4 mmol Scale Reaction:

Pyrazoline **2a** was prepared via **GP4**, using hydrazone **1a** (1.26 g, 4.00 mmol) and $Mn(dpm)_3$ (242 mg, 400 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4) to give **2a** (800 mg, 2.42 mmol, 61%) as a colorless oil.

Reaction under air:

Hydrazone **1a** (34.0 mg, 0.108 µmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol) were placed in a flask, dissolved in *i*PrOH (1 mL). Air was continuously introduced to the solution via needle and the reaction stirred at 55 °C for 2 h. When the solvent level was reduced by 0.5 mL, additional *i*PrOH (1 mL) was added. Water was added and the mixture extracted with EtOAc (3 x 30 mL). The organic phase was washed with water (3 x 30 mL) and brine (2 x 30 mL) and submitted to crude ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as standard which indicated formation of **2a** (24 mg, 73 µmol, 68%).

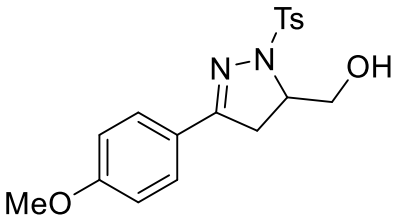
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.82 – 7.76 (m, 2H), 7.71 – 7.63 (m, 2H), 7.44 – 7.34 (m, 3H), 7.32 – 7.27 (m, 2H), 4.09 (dd, *J* = 11.9, 3.2 Hz, 1H), 3.98 (dddd, *J* = 11.0, 9.3, 4.1,

3.2 Hz, 1H), 3.88 (dd, *J* = 11.8, 4.1 Hz, 1H), 3.23 – 3.03 (m, 2H), 2.57 (d, *J* = 19.8 Hz, 1H), 2.39 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 158.6, 144.7, 131.7, 130.9, 130.7, 129.8, 128.81, 128.77, 127.1, 64.5, 63.8, 36.7, 21.7.

The spectra are in agreement with the literature.[11]

(3-(4-Methoxyphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2b)



2b

Pyrazoline **2b** was prepared via **GP4**, using hydrazone **1b** (20 mg, 58 µmol) and $Mn(dpm)_3$ (3.5 mg, 6.0 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **2b** (13 mg, 36 µmol, 62%) as a colorless oil.

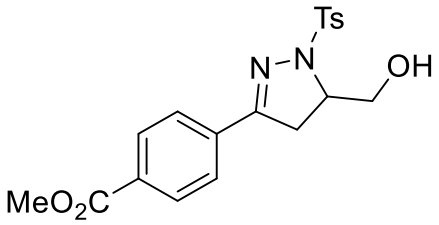
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.84 – 7.75 (m, 2H), 7.65 – 7.57 (m, 2H), 7.31 – 7.26 (m, 2H), 6.92 – 6.84 (m, 2H), 4.07 (dd, *J* = 11.8, 3.1 Hz, 1H), 3.95 (dddd, *J* = 10.8, 9.2, 4.2, 3.1 Hz, 1H), 3.86 (dd, *J* = 11.8, 4.3 Hz, 1H), 3.83 (s, 3H), 3.16 – 2.99 (m, 2H), 2.39 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 161.8, 158.3, 144.6, 131.7, 129.7, 128.9, 128.8, 123.3, 114.2, 64.6, 63.6, 55.5, 36.8, 21.7.

The spectra are in agreement with the literature.[11]

[11] Chen, S.; Chen, W.; Chen, X.; Chen, G.; Ackermann, L.; Tian, X. *Org. Lett.* **2019**, *21*, 7787-7790.

Methyl 4-(5-(hydroxymethyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-3-yl)benzoate (2c)



2c

Pyrazoline **2c** was prepared via **GP4**, using hydrazone **1c** (74 mg, 0.20 mmol) and $Mn(dpm)_3$ (12 mg, 20 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.25) to give **2c** (51 mg, 0.13 mmol, 66%) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.03 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.28 (m, 2H), 4.12 (dd, *J* = 11.9, 3.2 Hz, 1H), 4.08 – 3.97 (m, 1H), 3.93 (s, 3H), 3.89 (dd, *J* = 11.9, 3.9 Hz, 1H), 3.27 – 3.05 (m, 2H), 2.39 (s, 3H), 2.24 (d, *J* = 13.0 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 166.5, 157.4, 144.9, 134.7, 131.9, 131.8, 130.0, 129.9, 128.8, 127.0, 64.3, 64.0, 52.5, 36.5, 21.8.

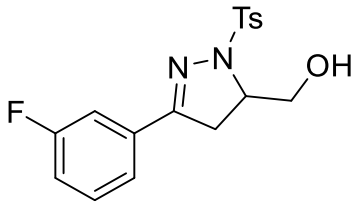
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3519 (broad), 2952, 1720, 1597, 1436, 1411, 1354, 1279, 1167, 1109, 1015, 911, 858, 815, 772, 732, 706, 666, 590, 548

MS (ESI): m/z (%) = 389 (100), 235 (12), 234 (93), 203 (49).

HRMS (ESI) for $C_{19}H_{21}N_2O_5S$ (389.1166): 389.1163 ($M+H^+$).

M.p. (°C): 117–119.

(3-(3-Fluorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2d)



2d

Pyrazoline **2d** was prepared via **GP4**, using hydrazone **1d** (66 mg, 0.20 mmol) and $Mn(dpm)_3$ (12 mg, 20 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **2d** (55.0 mg, 158 µmol, 79%) as a colorless oil.

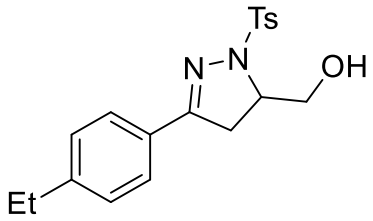
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.85 – 7.75 (m, 2H), 7.42 – 7.27 (m, 5H), 7.10 (tdd, *J* = 8.2, 2.5, 1.3 Hz, 1H), 4.10 (dd, *J* = 11.9, 3.3 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.88 (dd, *J* = 11.9, 4.0 Hz, 1H), 3.21 – 3.01 (m, 2H), 2.39 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 162.8 (d, *J* = 247.0 Hz), 157.4 (d, *J* = 3.0 Hz), 144.9, 132.9 (d, *J* = 8.0 Hz), 131.7, 130.4 (d, *J* = 8.2 Hz), 129.9, 128.76, 122.9 (d, *J* = 3.0 Hz), 117.8 (d, *J* = 21.5 Hz), 113.8 (d, *J* = 23.0 Hz), 64.3, 63.9, 36.6, 21.8.

^{19}F-NMR (376 MHz, $CDCl_3$): δ / ppm = -112.1.

The spectra are in agreement with the literature.[11]

(3-(4-Ethylphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2e)



2e

Pyrazoline **2e** was prepared via **GP4**, using hydrazone **1e** (34 mg, 0.10 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **2e** (23 mg, 64 µmol, 64%) as a light-brown solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 7.96 – 7.90 (m, 2H), 7.49 – 7.43 (m, 2H), 6.96 – 6.87 (m, 2H), 6.75 – 6.63 (m, 2H), 3.96 – 3.77 (m, 2H), 3.68 (dt, *J* = 10.5, 4.7 Hz, 1H), 2.67 – 2.53 (dd, *J* = 9.6 Hz, 17.3 Hz, 1 H), 2.40 – 2.26 (m, 4H), 1.75 (s, 3H), 1.00 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 158.1, 147.1, 143.9, 133.3, 129.6, 129.1, 129.0, 127.4, 64.6, 64.1, 36.4, 29.0, 21.1, 15.6.

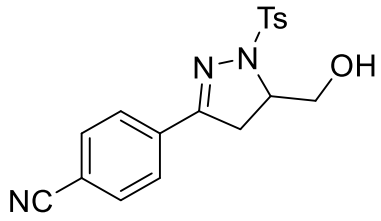
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3521, 2964, 2930, 1611, 1353, 1167, 1021, 666, 594, 552.

MS (ESI): m/z (%) = 381 (100), 360 (20), 359 (89), 295 (73), 204 (94), 177 (46).

HRMS (ESI) for $C_{19}H_{22}N_2NaO_3S$ (381.1243): 381.1239 $(M+Na)^+$.

M.p. (°C): 154–155.

4-(5-(Hydroxymethyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-3-yl)benzonitrile (2f)



2f

Pyrazoline **2f** was prepared via **GP4**, using hydrazone **1f** (34 mg, 0.10 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **2f** (28 mg, 80 µmol, 80%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.82 – 7.71 (m, 4H), 7.70 – 7.62 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.18 – 4.10 (m, 1H), 4.06 (ddt, *J* = 11.3, 9.4, 3.5 Hz, 1H), 3.88 (ddd, *J* = 11.2, 6.5, 3.5 Hz, 1H), 3.25 – 3.05 (m, 2H), 2.50 (t, *J* = 6.6 Hz, 1H), 2.40 (s, 3H).

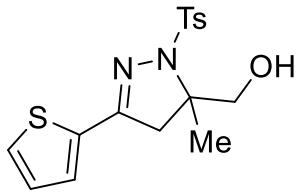
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 156.4, 145.1, 134.9, 132.5, 131.8, 129.9, 128.7, 127.5, 118.3, 114.1, 64.18, 64.15, 36.2, 21.8.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3513, 1596, 1354, 1167, 1093, 1012, 667, 590.

MS (ESI): m/z (%) = 356 (100), 201 (67), 184 (23), 170 (46).

HRMS (ESI) for $C_{18}H_{18}N_3O_3S$ (356.1063): 356.1060 $(M+H)^+$.

(5-Methyl-3-(thiophen-2-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2g)



2g

Pyrazoline **2g** was prepared via **GP4**, using hydrazone **1g** (34.0 mg, 102 µmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.35) to give **2g** (23.0 mg, 65.6 µmol, 64%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.94 – 7.89 (m, 2H), 7.48 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.42 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.34 – 7.27 (m, 3H), 4.15 (d, *J* = 12.1 Hz, 1H), 3.66 (d, *J* = 12.1 Hz, 1H), 3.47 (d, *J* = 16.6 Hz, 1H), 2.85 (d, *J* = 16.6 Hz, 1H), 2.41 (s, 3H), 1.37 (s, 3H).

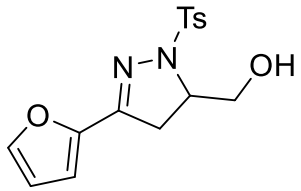
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 150.9, 144.1, 136.8, 133.9, 129.6, 128.2, 126.7, 125.9, 73.1, 68.0, 45.6, 21.7, 21.5.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3530, 2924, 1598, 1357, 1327, 1163, 1038, 784, 660, 593.

MS (ESI): m/z (%) = 351 (82), 333 (12), 197 (11), 196 (100), 165 (53).

HRMS (ESI) for $C_{16}H_{19}N_2O_3S_2$ (351.0832): 351.0830 $(M+H)^+$.

(3-(Furan-2-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2h)



2h

Pyrazoline **2h** was prepared via **GP4**, using hydrazone **1h** (61 mg, 0.20 mmol) and $Mn(dpm)_3$ (12 mg, 20 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.3) to give **2h** (37 mg, 0.12 µmol, 58%) as a light yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.79 – 7.72 (m, 2H), 7.58 (t, *J* = 1.2 Hz, 1H), 7.41 (t, *J* = 1.7 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.78 (dd, *J* = 1.9, 0.8 Hz, 1H), 4.04 (dd, *J* = 11.8, 3.3 Hz, 1H), 3.93 (ddt, *J* = 11.0, 8.9, 3.7 Hz, 1H), 3.84 (dd, *J* = 11.8, 4.1 Hz, 1H), 3.08 – 2.86 (m, 2H), 2.52 (s, *J* = 24.6 Hz, 1H), 2.39 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 152.8, 144.7, 144.3, 143.6, 131.6, 129.8, 128.8, 118.9, 108.4, 64.4, 63.1, 37.2, 21.7.

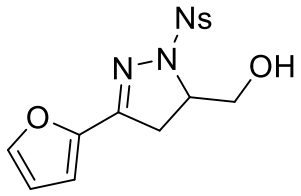
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3510, 3127, 2925, 2254, 1761, 1620, 1597, 1516, 1351, 1162, 1089, 1001, 909, 872, 813, 728, 665, 588, 549.

MS (ESI): m/z (%) = 343 (100), 321 (74), 166 (67), 159 (22), 135 (17).

HRMS (ESI) for $C_{15}H_{16}N_2NaO_4S$ (343.0723): 343.0722 $(M+Na)^+$.

M.p. (°C): 153–155.

(3-(Furan-2-yl)-1-((4-nitrophenyl)sulfonyl)-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2i)



2i

Pyrazoline **2i** was prepared via **GP4**, using hydrazone **1i** (67 mg, 0.20 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 3:2–1:1, R_f = 0.3) to give **2i** (50 mg, 0.14 mmol, 70%) as a light yellow oil.

^{1}H-NMR (400 MHz, DMSO-d_6): δ / ppm = 8.42 – 8.37 (m, 2H), 8.12 (dd, *J* = 1.5, 0.8 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.77 (t, *J* = 1.7 Hz, 1H), 6.77 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.14 (t, *J* = 5.4 Hz, 1H), 4.05 – 3.94 (m, 1H), 3.77 – 3.64 (m, 2H), 3.14 – 2.99 (m, 2H).

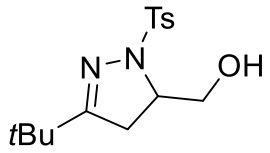
^{13}C-NMR (101 MHz, DMSO-d_6): δ / ppm = 154.4, 150.3, 145.3, 145.0, 140.2, 129.7, 124.4, 118.2, 107.8, 62.6, 62.3, 37.0.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3369, 3107, 2970, 1738, 1619, 1529, 1351, 1310, 1175, 1089, 1025, 1003, 834, 873, 856, 805, 738, 686, 647, 618, 593, 578, 464.

MS (ESI): m/z (%) = 374 (100), 352 (16), 173 (13), 166 (63), 142 (43), 135 (15).

HRMS (ESI) for $C_{14}H_{13}N_3NaO_6S$ (374.0417): 374.0417 $(M+Na)^+$.

(3-(*tert*-Butyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2j)



2j

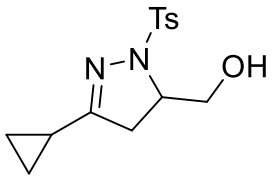
Pyrazoline **2j** was prepared via **GP4**, using hydrazone **1j** (31.0 mg, 105 µmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **2j** (21 mg, 68 µmol, 64%) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.76 – 7.69 (m, 2H), 7.34 – 7.27 (m, 2H), 3.99 – 3.89 (m, 1H), 3.82 – 3.69 (m, 2H), 2.76 – 2.55 (m, 2H), 2.42 (s, 3H), 2.5 – 2.3 (s, 1H), 1.06 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 171.3, 144.5, 131.3, 129.4, 129.0, 64.6, 63.4, 35.7, 34.4, 28.0, 21.7.

The spectra are in agreement with the literature.[11]

(3-Cyclopropyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2k)



2k

Pyrazoline **2k** was prepared via **GP4**, using hydrazone **1k** (28 mg, 0.10 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.25) to give **2k** (14 mg, 48 µmol, 48%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.77 – 7.69 (m, 2H), 7.36 – 7.29 (m, 2H), 3.95 (dd, *J* = 11.6, 3.0 Hz, 1H), 3.84 – 3.68 (m, 2H), 2.64 – 2.46 (m, 2H), 2.44 (s, 3H), 1.65 (tt, *J* = 8.3, 5.0 Hz, 1H), 0.92 – 0.75 (m, 3H), 0.73 – 0.62 (m, 1H).

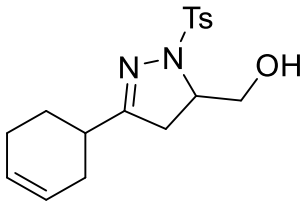
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 165.7, 144.5, 131.7, 129.6, 128.9, 64.5, 62.8, 37.2, 21.8, 11.2, 7.7, 7.3.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3412, 2924, 1617, 1497, 1351, 1165, 1092, 815, 667, 594.

MS (ESI): m/z (%) = 295 (100), 177 (32), 150 (15), 140 (60).

HRMS (ESI) for $C_{14}H_{19}N_2O_3S$ (295.1111): 295.1110 $(M+H)^+$.

(3-(Cyclohex-3-en-1-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2l)



2l

Pyrazoline **2l** was prepared via **GP4**, using hydrazone **1l** (62 mg, 0.20 mmol) and $Mn(dpm)_3$ (12 mg, 20 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **2l** (28 mg, 84 µmol, 42%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.73 (dq, *J* = 8.5, 2.1 Hz, 2H), 7.35 – 7.28 (m, 2H), 5.65 (q, *J* = 2.3 Hz, 2H), 3.97 (dd, *J* = 11.6, 2.9 Hz, 1H), 3.84 – 3.70 (m, 2H), 2.79 – 2.46 (m, 4H), 2.43 (s, 3H), 2.16 – 1.95 (m, 4H), 1.86 – 1.76 (m, 1H), 1.57 – 1.42 (m, 1H).

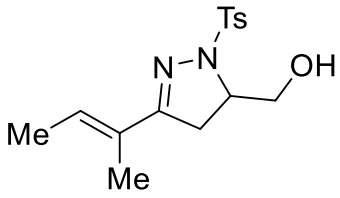
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 167.4, 167.2, 144.6, 144.5, 131.52, 131.48, 129.6, 129.0, 128.9, 127.0, 126.9, 125.3, 125.2, 64.5, 62.9, 62.8, 37.3, 37.2, 35.43, 35.35, 28.6, 28.5, 26.4, 26.0, 24.8, 24.5, 21.8.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3500, 2923, 2854, 1597, 1400, 1352, 1165, 1091, 707, 665, 923, 550.

MS (ESI): m/z (%) = 357 (100), 335 (80), 257 (40), 255 (40), 214 (30), 212 (33), 177 (25).

HRMS (ESI) for $C_{17}H_{22}N_2NaO_3S$ (357.1243): 357.1244 $(M+Na)^+$.

(*E*)-(3-(But-2-en-2-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2m)



2m

Pyrazoline **2m** was prepared via **GP4**, using hydrazone **1m** (27 mg, 92 µmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.3) to give **2m** (16 mg, 52 µmol, 57%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.83 – 7.74 (m, 2H), 7.35 – 7.29 (m, 2H), 5.81 (dddd, *J* = 8.3, 6.9, 5.6, 1.4 Hz, 1H), 4.02 (dd, *J* = 11.4, 2.7 Hz, 1H), 3.90 – 3.78 (m, 2H), 2.90 – 2.80 (m, 2H), 2.61 (s, 1H), 2.44 (s, 3H), 1.92 (q, *J* = 1.1 Hz, 3H), 1.78 (dq, *J* = 7.0, 1.1 Hz, 3H).

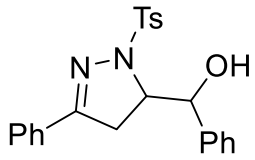
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 161.4, 144.5, 132.4, 131.6, 130.3, 129.6, 128.8, 64.5, 63.8, 36.0, 21.8, 14.4, 12.5.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3520, 2924, 2856, 1573, 1641, 1352, 1256, 1166, 949, 815, 670, 589, 547.

MS (ESI): m/z (%) = 331 (100), 309 (44), 295 (83), 227 (20), 177 (50), 154 (64).

HRMS (ESI) for $C_{15}H_{20}N_2NaO_3S$ (331.1087): 331.1083 $(M+Na)^+$.

Phenyl(3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2n)



2n

Pyrazoline **2n** was prepared via **GP4**, using hydrazone **1n** (77.0 mg, 197 µmol) and $Mn(dpm)_3$ (12 mg, 20 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 8.5:1.5) to give **2n** as a mix of diastereomers. Major (R_f = 0.35): 42.0 mg, 103 µmol, 52%, colorless solid. Minor (R_f = 0.2): 21 mg, 52 µmol, 26%, colorless oil. Combined: 63.0 mg, 155 µmol, 79%.

^{1}H-NMR (400 MHz, $CDCl_3$, minor diastereomer): δ / ppm = 7.86 – 7.81 (m, 2H), 7.58 – 7.53 (m, 2H), 7.47 – 7.42 (m, 2H), 7.41 – 7.27 (m, 8H), 4.96 (d, *J* = 7.4 Hz, 1H), 4.25 (dt, *J* = 10.9, 7.7 Hz, 1H), 2.85 – 2.66 (m, 2H), 2.39 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, minor diastereomer): δ / ppm = 159.4, 144.9, 139.7, 132.0, 131.0, 130.4, 129.9, 128.82, 128.81, 128.7, 128.6, 127.7, 127.2, 76.4, 67.1, 37.2, 21.8.

^{1}H-NMR (400 MHz, CD_2Cl_2, major diastereomer): δ / ppm = 7.83 (m, 2H), 7.60 (m, 2H), 7.37 (m, 10H), 5.55 (d, *J* = 2.2 Hz, 1H), 4.13 (ddd, *J* = 11.3, 9.0, 2.3 Hz, 1H), 3.29 (dd, *J* = 17.4, 9.1 Hz, 1H), 2.70 (s, 1H), 2.64 – 2.52 (m, 1H), 2.37 (s, 3H).

^{13}C-NMR (101 MHz, CD_2Cl_2, major diastereomer): δ / ppm = 159.5, 145.2, 140.1, 132.0, 131.1, 130.1, 129.0, 128.94, 128.92, 128.0, 127.3, 126.0, 72.9, 68.6, 33.2, 21.7.

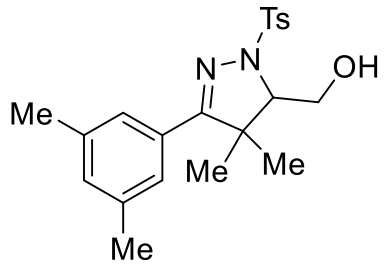
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3501, 3063, 2923, 2853, 1597, 1449, 1360, 1168, 1092, 1012, 814, 766, 747, 706, 693, 659, 592, 555

MS (ESI): m/z (%) = 429 (100), 371 (27), 322 (17), 194 (29), 159 (58).

HRMS (ESI) for $C_{23}H_{22}N_2NaO_3S$ (429.1243): 429.1244 $(M+Na)^+$.

M.p. (major diastereomer, °C): 220 °C (decomposition).

(3-(3,5-Dimethylphenyl)-4,4-dimethyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2o)



2o

Pyrazoline **2o** was prepared via **GP4**, using hydrazone **1o** (37 mg, 0.10 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.35) to give **2o** (25 mg, 65 µmol, 65%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.86 – 7.78 (m, 2H), 7.37 – 7.29 (m, 2H), 7.18 (dt, *J* = 1.6, 0.7 Hz, 2H), 7.03 (tq, *J* = 1.3, 0.7 Hz, 1H), 4.12 (dd, *J* = 12.7, 6.3 Hz, 1H), 3.89 (dd, *J* = 12.7, 2.5 Hz, 1H), 3.16 (dd, *J* = 6.3, 2.5 Hz, 1H), 2.43 (s, 3H), 2.31 (q, *J* = 0.7 Hz, 6H), 1.24 (s, 3H), 1.13 (s, 3H).

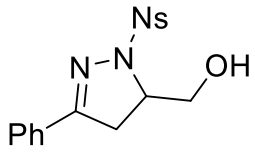
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 165.3, 144.8, 138.1, 131.9, 130.9, 130.3, 129.7, 129.1, 125.5, 74.7, 61.0, 51.4, 25.4, 21.8, 21.5, 19.4.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3531, 2969, 2923, 1598, 1465, 1356, 1168, 983, 882, 687, 586.

MS (ESI): m/z (%) = 387 (100), 295 (49), 232 (41), 177 (29).

HRMS (ESI) for $C_{21}H_{27}N_2O_3S$ (387.1737): 387.1737 $(M+H)^+$.

(1-((4-Nitrophenyl)sulfonyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2p)



2p

Pyrazoline **2p** was prepared via **GP4**, using hydrazone **1p** (35 mg, 0.10 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.35) to give **2p** (29 mg, 80 µmol, 80%) as a light yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.41 – 8.28 (m, 2H), 8.19 – 8.06 (m, 2H), 7.69 – 7.62 (m, 2H), 7.48 – 7.34 (m, 3H), 4.12 (dd, *J* = 11.8, 3.5 Hz, 1H), 4.05 (ddt, *J* = 11.0, 8.9, 3.6 Hz, 1H), 3.91 (dd, *J* = 11.8, 3.7 Hz, 1H), 3.32 – 3.09 (m, 2H), 2.13 (s, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 159.5, 150.6, 140.7, 131.2, 130.0, 129.9, 128.8, 127.0, 124.2, 64.1, 63.6, 36.6.

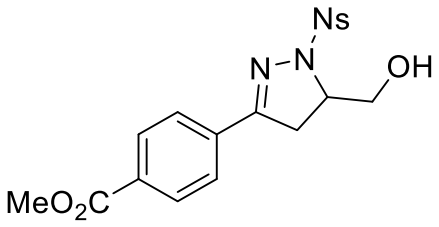
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3531, 3105, 3065, 2925, 1605, 1528, 1349, 1172, 1092, 1011, 907, 854, 734, 612.

MS (ESI): m/z (%) = 384 (73), 362 (19), 269 (31), 252 (40), 176 (64).

HRMS (ESI) for $C_{16}H_{15}N_3O_5SNa$ (384.0625): 384.0626 $(M+Na)^+$.

M.p. (°C): 140–141.

Methyl 4-(5-(hydroxymethyl)-1-((4-nitrophenyl)sulfonyl)-4,5-dihydro-1*H*-pyrazol-3-yl)benzoate (2q)



2q

Pyrazoline **2q** was prepared via **GP4**, using hydrazone **1q** (40 mg, 0.10 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 1:1, , R_f = 0.32) to give **2q** (31 mg, 74 µmol, 74%) as a light yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.36 – 8.30 (m, 2H), 8.14 – 8.06 (m, 2H), 8.04 – 7.97 (m, 2H), 7.72 – 7.65 (m, 2H), 4.19 – 4.04 (m, 2H), 3.92 (s, 4H), 3.39 – 3.13 (m, 2H), 2.44 (s, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 166.3, 158.5, 150.8, 140.8, 134.1, 132.3, 130.0, 129.9, 127.0, 124.4, 64.0, 63.9, 52.5, 36.5.

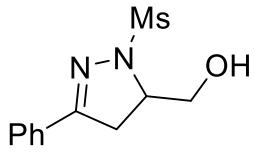
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3559, 3111, 2924, 1712, 1603, 1531, 1440, 1355, 1288, 1172, 1113, 1046, 1017, 860, 769, 739, 698, 683, 619, 594, 570, 553, 464.

MS (ESI): m/z (%) = 442 (5), 371 (25), 322 (15), 223 (11), 194 (15), 160 (10), 159 (100), 145 (12).

HRMS (ESI) for $C_{18}H_{17}N_3NaO_7S$ (442.0679): 442.0672 $(M+Na)^+$.

M.p. (°C): 176–179 (decomposition).

(1-(Methylsulfonyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (2r)



2r

Pyrazoline **2r** was prepared via **GP4**, using hydrazone **1r** (24 mg, 0.10 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **2r** (19 mg, 75 µmol, 75%) as a colorless solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.78 – 7.71 (m, 2H), 7.48 – 7.39 (m, 3H), 4.40 (dddd, *J* = 11.2, 9.0, 4.0, 3.4 Hz, 1H), 4.04 (dd, *J* = 11.9, 3.4 Hz, 1H), 3.84 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.49 (dd, *J* = 17.2, 11.2 Hz, 1H), 3.29 (dd, *J* = 17.3, 8.9 Hz, 1H), 3.13 (s, 3H), 2.35 (s, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 158.9, 131.1, 130.5, 128.9, 127.2, 64.4, 62.5, 37.0, 36.8.

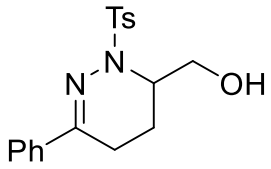
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3521, 2929, 1448, 1343, 1162, 1010, 961, 692, 569, 531, 508.

MS (ESI): m/z (%) = 277 (65), 269 (23), 177 (29), 173 (45), 167 (16).

HRMS (ESI) for $C_{11}H_{14}N_2O_3S$ (277.0614): 277.0617 $(M+Na)^+$.

M.p. (°C): 160–162.

(6-Phenyl-2-tosyl-2,3,4,5-tetrahydropyridazin-3-yl)methanol (2s)



2s

Tetrahydropyridazine **2s** was prepared via **GP4**, using hydrazone **1s** (41.0 mg, 125 µmol) and $Mn(dpm)_3$ (8.0 mg, 13 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 1:1 + 1% trimethylamine, R_f = 0.3) to give **2s** (23 mg, 67 µmol, 53%) as a light yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.91 – 7.83 (m, 2H), 7.73 – 7.63 (m, 2H), 7.39 – 7.32 (m, 3H), 7.32 – 7.27 (m, 2H), 4.45 – 4.36 (m, 1H), 3.84 (dd, *J* = 11.6, 5.7 Hz, 1H), 3.69 (t, *J* = 8.4 Hz, 1H), 2.61 (dddd, *J* = 18.0, 5.7, 2.1, 1.1 Hz, 1H), 2.50 – 2.42 (m, 1H), 2.40 (s, 3H), 2.23 (ddt, *J* = 13.7, 6.6, 2.1 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.63 – 1.50 (m, 1H).

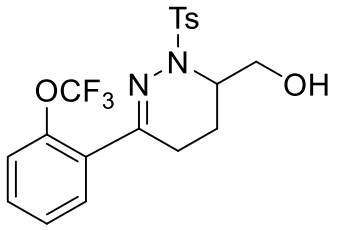
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = δ 148.2, 144.1, 137.0, 135.6, 129.7, 129.4, 128.5, 128.1, 125.4, 63.5, 53.3, 21.7, 19.1, 18.8.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3523, 3064, 2931, 1597, 1495, 1447, 1339, 1168, 990, 972.

MS (ESI): m/z (%) = 345 (84), 310 (43), 237 (87), 181 (57), 159 (35), 116 (24), 111 (100), 102 (24).

HRMS (ESI) for $C_{18}H_{21}N_2O_3S$ (345.1267): 345.1266 $(M+H)^+$.

(2-Tosyl-6-(2-(trifluoromethoxy)phenyl)-2,3,4,5-tetrahydropyridazin-3-yl)methanol (2t)



2t

Tetrahydropyridazine **2t** was prepared via **GP4**, using hydrazone **1t** (82 mg, 0.20 mmol) and $Mn(dpm)_3$ (12 mg, 20 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.25) to give **2t** (48.0 mg, 112 µmol, 56%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.94 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.51 – 7.44 (m, 1H), 6.97 – 6.73 (m, 5H), 4.40 (q, *J* = 7.0, 6.6 Hz, 1H), 3.88 – 3.71 (m, 1H), 3.52 (dq, *J* = 17.1, 10.4, 9.6 Hz, 1H), 2.40 – 2.24 (m, 1H), 2.19 – 1.72 (m, 6H), 1.07 (ddt, *J* = 16.9, 13.8, 5.6 Hz, 1H).

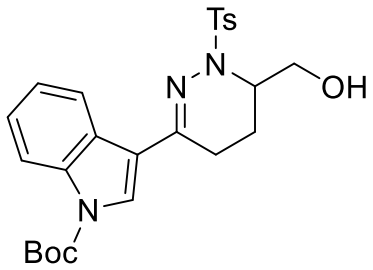
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 147.6, 147.0, 143.6, 136.6, 132.7, 130.7, 130.1, 129.6, 127.3, 122.3, 121.2, 119.8, 63.3, 53.9, 22.3, 21.1, 18.3.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3524, 2930, 2878, 1598, 1493, 1248, 1217, 1166, 1091, 830, 670.

MS (ESI): m/z (%) = 429 (100), 223 (6), 194 (8).

HRMS (ESI) for $C_{19}H_{20}F_3N_2O_4S$ (429.1090): 429.1085 $(M+H)^+$.

***tert*-Butyl 3-(6-(hydroxymethyl)-1-tosyl-1,4,5,6-tetrahydropyridazin-3-yl)-1*H*-indole-1-carboxylate (2u)**



2u

Tetrahydropyridazine **2u** was prepared via **GP4**, using hydrazone **1u** (63.0 mg, 135 µmol) and $Mn(dpm)_3$ (8.0 mg, 13 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 1:1, R_f = 0.3) to give **2u** (25 mg, 52 µmol, 39%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.41 – 8.37 (m, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.72 (s, 1H), 7.39 – 7.23 (m, 5H), 4.44 – 4.35 (m, 1H), 3.90 (dd, *J* = 11.4, 5.8 Hz, 1H), 3.77 (d, *J* = 8.3 Hz, 1H), 2.62 – 2.41 (m, 2H), 2.38 (s, 3H), 2.20 (ddt, *J* = 13.7, 6.1, 2.3 Hz, 1H), 2.06 (s, 1H), 1.67 (s, 9H), 1.59 (dtd, *J* = 13.8, 11.8, 6.1 Hz, 2H).

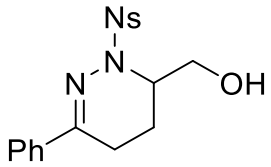
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 149.6, 145.9, 144.1, 136.2, 135.5, 129.8, 128.1, 127.4, 125.4, 125.3, 123.9, 123.8, 119.2, 114.9, 84.6, 63.8, 53.6, 28.3, 21.7, 19.3, 18.9.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3532, 1733, 1598, 1451, 1361, 1185, 728, 627.

MS (ESI): m/z (%) = 484 (100), 340 (59), 329 (30), 251 (47), 228 (67), 223 (52), 194 (51).

HRMS (ESI) for $C_{25}H_{30}N_3O_5S$ (484.1901): 484.1901 $(M+H)^+$.

(2-((4-Nitrophenyl)sulfonyl)-6-phenyl-2,3,4,5-tetrahydropyridazin-3-yl)methanol (2v)



2v

Tetrahydropyridazine **2v** was prepared via **GP4**, using hydrazone **1v** (180 mg, 500 µmol) and $Mn(dpm)_3$ (30 mg, 50 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 2:8, R_f = 0.17) to give **2v** (120 mg, 320 µmol, 64%) as a yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.43 – 7.36 (m, 2H), 7.28 – 7.21 (m, 2H), 6.74 – 6.67 (m, 2H), 6.46 – 6.39 (m, 3H), 3.59 – 3.51 (m, 1H), 2.88 (dd, *J* = 11.3, 6.2 Hz, 1H), 2.75 (dd, *J* = 11.3, 6.8 Hz, 1H), 1.72 (dddd, *J* = 18.2, 5.8, 1.8, 1.0 Hz, 1H), 1.53 (ddd, *J* = 18.2, 12.7, 6.8 Hz, 1H), 1.34 (ddt, *J* = 13.8, 6.8, 2.0 Hz, 1H), 1.07 (s, 1H), 0.80 – 0.68 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 150.3, 149.7, 144.4, 136.4, 129.9, 129.5, 128.7, 125.4, 124.2, 63.0, 53.2, 19.1, 18.9.

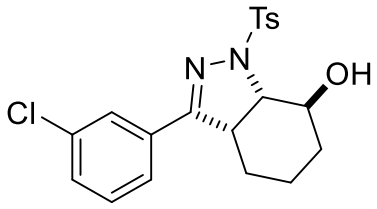
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3535, 3105, 2940, 1529, 1349, 1173, 1093, 854, 736, 605, 568.

MS (ESI): m/z (%) = 398 (77), 376 (100), 329 (40), 309 (29), 251 (29), 223 (33), 190 (100), 159 (43).

HRMS (ESI) for $C_{17}H_{18}N_3O_5S$ (376.0962): 376.0968 $(M+H)^+$.

M.p. (°C): 140–143.

3-(3-Chlorophenyl)-1-tosyl-3a,4,5,6,7,7a-hexahydro-1*H*-indazol-7-ol (6a)



6a

Pyrazoline **6a** was prepared via **GP4**, using hydrazone **5a** (39 mg, 0.10 mmol) and $Mn(dpm)_3$ (6.0 mg, 10 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.35) to give **6a** (27 mg, 67 µmol, 67%, d.r. = 10:1) as a light yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.83 – 7.76 (m, 2H), 7.66 (t, *J* = 2.0 Hz, 1H), 7.54 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.37 (ddd, *J* = 8.0, 2.1, 1.2 Hz, 1H), 7.34 – 7.28 (m, 3H), 4.57 (dt, *J* = 7.6, 3.8 Hz, 1H), 3.44 – 3.30 (m, 2H), 2.39 (s, 3H), 1.97 (ddd, *J* = 13.0, 6.6, 3.5 Hz, 1H), 1.82 (ddd, *J* = 12.4, 6.4, 3.2 Hz, 1H), 1.77 – 1.58 (m, 3H), 1.42 – 1.29 (m, 1H), 1.25 (dd, *J* = 5.2, 1.9 Hz, 1H).

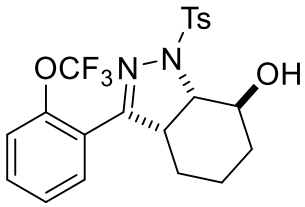
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 160.7, 144.9, 135.0, 131.9, 130.8, 130.7, 130.2, 129.8, 129.2, 127.2, 125.3, 69.4, 67.4, 44.2, 27.2, 23.5, 21.8, 17.1.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3526, 2939, 2867, 1596, 1560, 1433, 1356, 1168, 1091, 1029, 979, 966, 814, 735, 688, 667, 598, 552, 535.

MS (ESI): m/z (%) = 427 (100), 405 (52), 295 (51), 250 (53), 177 (32).

HRMS (ESI) for $C_{20}H_{21}ClN_2NaO_3S$ (427.0854): 427.0853 $(M+Na)^+$.

1-Tosyl-3-(2-(trifluoromethoxy)phenyl)-3a,4,5,6,7,7a-hexahydro-1*H*-indazol-7-ol (6b)



6b

Pyrazoline **6b** was prepared via **GP4**, using hydrazone **5b** (20 mg, 45 µmol), $Mn(dpm)_3$ (3 mg, 5 µmol) and *i*PrOH (0.5 mL), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3 R_f = 0.3) to give **6b** (13 mg, 29 µmol, 64%) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.83 – 7.71 (m, 3H), 7.50 – 7.41 (m, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.22 (m, 1H), 4.36 – 4.26 (m, 1H), 3.57 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.43 (td, *J* = 10.2, 5.2 Hz, 1H), 3.27 (s, 1H), 2.40 (s, 3H), 2.00 – 1.91 (m, 1H), 1.68 – 1.44 (m, 4H), 1.40 – 1.27 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 161.3, 147.0, 144.8, 131.8, 131.4, 131.2, 129.7, 128.8, 127.3, 124.1, 120.92, 120.90, 68.7, 68.5, 46.8, 27.4, 22.6, 21.7, 17.7.

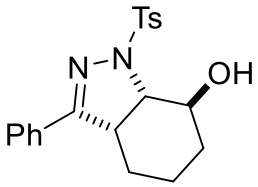
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3531, 2941, 2868, 1598, 1494, 1449, 1351, 1251, 1217, 1168, 1091, 1026, 993, 814, 767, 668, 598, 553.

MS (ESI): m/z (%) = 477 (77), 456 (63), 455 (100), 437 (29), 300 (24).

HRMS (ESI) for $C_{21}H_{21}F_3N_2NaO_4S$ (477.1066): 477.1062 $(M+Na)^+$.

M.p. (°C): 109–111.

3-Phenyl-1-tosyl-3a,4,5,6,7,7a-hexahydro-1*H*-indazol-7-ol (6c)



6c

Pyrazoline **6c** was prepared via **GP4**, using hydrazone **5c** (71.0 mg, 200 µmol) and $Mn(dpm)_3$ (12 mg, 20 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.28) to give **6c** (57.0 mg, 154 µmol, 77%) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.81 – 7.77 (m, 2H), 7.71 – 7.65 (m, 2H), 7.44 – 7.34 (m, 3H), 7.32 – 7.26 (m, 2H), 4.56 (dt, *J* = 7.3, 3.5 Hz, 1H), 3.45 – 3.31 (m, 2H), 3.19 (s, 1H), 2.39 (d, *J* = 4.2 Hz, 3H), 2.02 – 1.92 (m, 1H), 1.90 – 1.56 (m, 4H), 1.54 – 1.31 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 161.9, 144.7, 130.7, 129.7, 129.2, 128.89, 128.87, 127.29, 127.27, 69.3, 67.6, 44.4, 27.3, 23.6, 21.7, 17.3.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3554, 2958, 2941, 1349, 1167, 1091, 664, 596, 502.

MS (ESI): m/z (%) = 371 (20), 251 (34), 223 (35), 216 (21), 194 (19).

HRMS (ESI) for $C_{20}H_{23}N_2O_3S$ (371.1424): 371.1425 $(M+H)^+$.

M.p. (°C): 112–115.

For 1D NOE experiments, a diastereomeric mixture was prepared according to literature[11] and separated via column chromatography (hexane:ethyl acetate = 7:3).

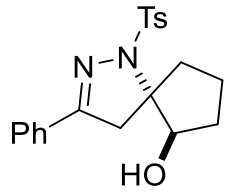
^{1}H-NMR (500 MHz, $CDCl_3$, minor diastereomer): δ / ppm = 7.84 – 7.79 (m, 2H), 7.69 – 7.66 (m, 2H), 7.44 – 7.36 (m, 3H), 7.32 – 7.28 (m, 2H), 4.12 (m, 1H), 4.09 – 4.03 (m, 1H), 3.67 (ddd, *J* = 8.6, 3.2, 0.9 Hz, 1H), 3.40 – 3.32 (m, 1H), 2.39 (s, 3H), 1.95 (dq, *J* = 9.4, 6.7, 6.1 Hz, 1H), 1.88 – 1.74 (m, 3H), 1.54 – 1.47 (m, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$, minor diastereomer): δ / ppm = 162.0, 144.9, 130.83, 130.79, 130.0, 129.8, 129.2, 128.9, 127.3, 68.18, 68.17, 47.0, 27.7, 23.5, 21.8, 20.3.

^{1}H-NMR (400 MHz, C_6D_6, major diastereomer): δ / ppm = 8.03 – 7.96 (m, 2H), 7.53 – 7.43 (m, 2H), 7.08 – 6.99 (m, 3H), 6.74 – 6.66 (m, 2H), 4.76 (dt, *J* = 7.1, 3.5 Hz, 1H), 3.48 (dd, *J* = 8.7, 4.0 Hz, 1H), 2.86 (ddd, *J* = 12.3, 8.8, 5.3 Hz, 2H), 1.86 (m, 1H), 1.73 (s, 3H), 1.51 – 1.27 (m, 3H), 1.13 (tdd, *J* = 11.5, 7.8, 5.7 Hz, 1H), 1.05 – 0.88 (m, 1H).

^{13}C-NMR (126 MHz, C_6D_6, major diastereomer): δ / ppm = 161.7, 144.1, 132.3, 130.7, 130.4, 129.58, 129.55, 128.8, 127.4, 69.3, 66.9, 43.7, 27.7, 24.1, 21.1, 17.0.

3-Phenyl-1-tosyl-1,2-diazaspiro[4.4]non-2-en-6-ol (8a)



8a

Pyrazoline **8a** was prepared via **GP4**, using hydrazone **7a** (89 mg, 0.25 mmol) and $Mn(dpm)_3$ (30 mg, 50 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 2:8, R_f = 0.35) to give **8a** (61 mg, 16 µmol, 64%) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.93 (d, J = 8.0 Hz, 2H), 7.72 – 7.64 (m, 2H), 7.43 – 7.33 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 4.92 (t, J = 9.0 Hz, 1H), 3.74 (d, J = 16.9 Hz, 1H), 2.77 (d, J = 16.9 Hz, 1H), 2.59 – 2.47 (m, 1H), 2.40 (s, 3H), 2.13 – 2.00 (m, 1H), 1.92 (s, 1H), 1.85 – 1.69 (m, 1H), 1.68 – 1.51 (m, 2H), 1.51 – 1.37 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 155.0, 143.9, 136.8, 131.3, 130.3, 129.6, 128.6, 128.1, 126.8, 79.4, 74.7, 40.5, 32.2, 27.6, 21.7, 17.2.

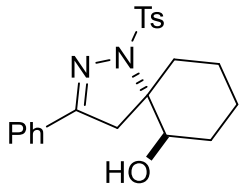
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3508, 2959, 1353, 1162, 1039, 730, 597, 543.

MS (ESI): m/z (%) = 763 (39), 393 (100), 371 (30), 251 (29), 237 (19), 223 (33), 209 (20).

HRMS (ESI) for $C_{20}H_{22}N_2NaO_3S$ (393.1243): 393.1239 $(M+H)^+$.

M.p. (°C): 183–185.

3-Phenyl-1-tosyl-1,2-diazaspiro[4.5]dec-2-en-6-ol (8b)



8b

Pyrazoline **8b** was prepared via **GP4**, using hydrazone **7b** (178 mg, 483 µmol) and $Mn(dpm)_3$ (30 mg, 50 µmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 2:8, R_f = 0.25) to give **8b** (139 mg, 362 µmol, 75%) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.93 (d, J = 8.1 Hz, 2H), 7.73 – 7.65 (m, 2H), 7.43 – 7.34 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 4.50 – 4.39 (m, 1H), 3.52 (d, J = 16.8 Hz, 1H), 2.88 (d, J = 16.8 Hz, 1H), 2.41 (s, 3H), 2.34 – 2.22 (m, 2H), 2.11 – 1.94 (m, 1H), 1.83 – 1.54 (m, 3H), 1.50 – 1.31 (m, 1H), 1.35 – 1.10 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 154.6, 144.0, 137.2, 131.3, 130.3, 129.6, 128.6, 128.1, 126.7, 78.8, 72.2, 38.9, 33.4, 31.2, 23.7, 23.0, 21.7.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3498, 2933, 2864, 1495, 1364, 1342, 1160, 1093, 1050, 1035, 670, 594, 569, 445.

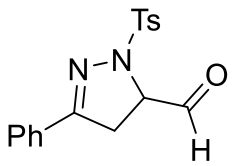
MS (ESI): m/z (%) = 385 (29), 329 (25), 322 (25), 251 (42), 237 (21), 230 (52), 223 (41), 217 (28), 209 (20), 194 (25), 158 (23).

HRMS (ESI) for $C_{21}H_{25}N_2O_3S$ (385.1580): 385.1583 $(M+H)^+$.

M.p. (°C): 180–183.

Preparation of Compounds 3a–j

3-Phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole-5-carbaldehyde (3a)



3a

Pyrazoline **3a** was prepared via **GP5**, using hydrazone **1a** (32 mg, 0.10 mmol) and Co(salen) **4**[12] (7.0 mg, 10 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.3) to give **3a** (23 mg, 70 µmol, 70%) as a light brown oil.

Reaction using air:

Hydrazone **1a** (62.0 mg, 197 µmol) and Co(salen) **4** (7.0 mg, 10 µmol) were added to a dry flask and dissolved in *i*PrOH (1 mL). Air was continuously introduced to the solution via needle and the reaction stirred at 25 °C for 1 h. After work-up according to **GP5** the crude product was purified via column chromatography (hexane:ethyl acetate = 7:3, R_f = 0.3) to give **3a** (37.0 mg, 113 µmol, 57%) as a light brown oil.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 9.67 (d, *J* = 2.5 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.35 – 7.28 (m, 2H), 7.07 – 6.95 (m, 3H), 6.68 (d, *J* = 8.0 Hz, 2H), 4.06 – 3.95 (m, 1H), 2.38 (dd, *J* = 17.2, 10.8 Hz, 1H), 2.12 (dd, *J* = 17.2, 11.8 Hz, 1H), 1.75 (s, 3H).

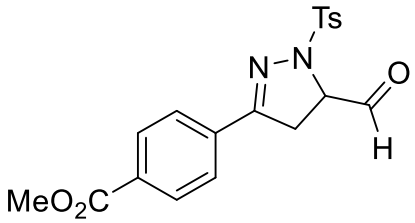
^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 196.1, 157.1, 144.5, 132.8, 130.8, 130.6, 129.8, 129.2, 128.7, 127.2, 68.4, 34.2, 21.1.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.90 (d, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.70 – 7.63 (m, 2H), 7.48 – 7.28 (m, 5H), 4.30 (ddd, *J* = 12.0, 9.9, 1.9 Hz, 1H), 3.37 (dd, *J* = 17.3, 10.1 Hz, 1H), 3.17 (dd, *J* = 17.3, 12.0 Hz, 1H), 2.41 (s, 3H).

The spectra are in accordance with the literature.[11]

[12] Co(salen) **4** was prepared according to: Chawner, S. J.; Cases-Thomas, M. J.; Bull, J. A. *Eur. J. Org. Chem.* **2017**, 5015-5024.

Methyl 4-(5-formyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-3-yl)benzoate (3b)



3b

Pyrazoline **3b** was prepared via **GP5**, using hydrazone **1c** (22 mg, 59 µmol) and Co(salen) **4** (4 mg, 6 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.25) to give **3b** (14 mg, 36 µmol, 61%) as a light brown oil.

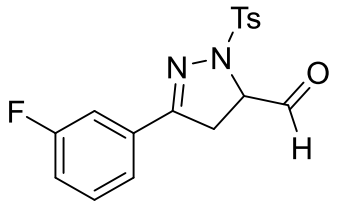
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.91 (d, *J* = 1.8 Hz, 1H), 8.09 – 8.01 (m, 2H), 7.85 – 7.80 (m, 2H), 7.72 (dq, *J* = 8.6, 1.7 Hz, 2H), 7.36 – 7.30 (m, 2H), 4.36 (ddd, *J* = 12.0, 10.0, 1.8 Hz, 1H), 3.93 (s, 3H), 3.40 (dd, *J* = 17.3, 10.1 Hz, 1H), 3.20 (dd, *J* = 17.3, 12.0 Hz, 1H), 2.41 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 196.4, 166.4, 156.8, 145.4, 134.1, 132.3, 131.6, 130.09, 130.06, 128.9, 127.1, 68.0, 52.6, 34.6, 21.8.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2954, 2925, 2853, 1721, 1597, 1436, 1356, 1280, 1168, 1110, 1015, 666, 601, 592.

HRMS (ESI) for $C_{19}H_{19}N_2O_5S$ (387.1009): 387.1015 $(M+H)^+$.

3-(3-Fluorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazole-5-carbaldehyde (3c)



3c

Pyrazoline **3c** was prepared via **GP5**, using hydrazone **1d** (66 mg, 0.20 mmol) and Co(salen) **4** (14 mg, 20 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography using neutral silica (hexane:ethyl acetate = 8:2–7:3, R_f (7:3) = 0.2) to give **3c** (32 mg, 92 µmol, 46%) as a light brown oil.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 9.66 (d, *J* = 2.4 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.05 (ddd, *J* = 9.6, 2.5, 1.5 Hz, 1H), 6.96 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.79 – 6.60 (m, 4H), 3.98 (ddd, *J* = 11.9, 10.9, 2.4 Hz, 1H), 2.25 (dd, *J* = 17.2, 10.9 Hz, 1H), 1.95 (dd, *J* = 17.2, 11.9 Hz, 1H), 1.74 (s, 3H).

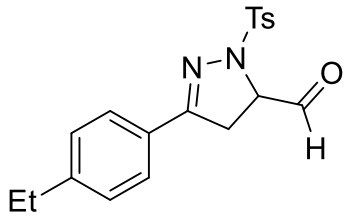
^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 195.8, 163.0 (d, *J* = 246.5 Hz), 155.9 (d, *J* = 3.0 Hz), 144.7, 132.76, 132.75, 130.4 (d, *J* = 8.1 Hz), 129.8, 129.2, 122.8 (d, *J* = 3.0 Hz), 117.6 (d, *J* = 21.2 Hz), 114.0 (d, *J* = 23.0 Hz), 68.4, 34.0, 21.1.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3484, 2924, 2853, 1735, 1494, 1359, 1147, 1019, 788, 672, 593.

MS (ESI): m/z (%) = 347 (76), 295 (26), 177 (18), 175 (24), 163 (18), 155 (18).

HRMS (ESI) for $C_{17}H_{16}FN_2O_3S$ (347.0860): 347.0859 $(M+H)^+$.

3-(4-Ethylphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazole-5-carbaldehyde (3d)



3d

Pyrazoline **3d** was prepared via **GP5**, using hydrazone **1e** (68 mg, 0.20 mmol) and Co(salen) **4** (14 mg, 20 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.2) to give **3d** (45 mg, 0.13 mmol, 65%) as a light brown oil.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 9.69 (d, *J* = 2.5 Hz, 1H), 7.92 – 7.81 (m, 2H), 7.38 – 7.31 (m, 2H), 6.96 – 6.88 (m, 2H), 6.73 – 6.66 (m, 2H), 4.02 (ddd, *J* = 11.8, 10.7, 2.5 Hz, 1H), 2.45 (dd, *J* = 17.1, 10.8 Hz, 1H), 2.34 (q, *J* = 7.6 Hz, 2H), 2.19 (dd, *J* = 17.2, 11.8 Hz, 1H), 1.76 (s, 3H), 1.00 (t, *J* = 7.6 Hz, 3H).

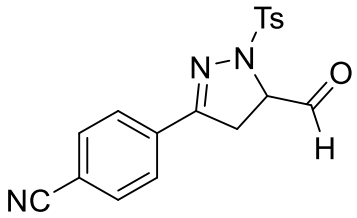
^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 196.2, 157.3, 147.5, 144.5, 132.8, 129.8, 129.2, 128.2, 127.4, 68.4, 34.4, 29.0, 21.1, 15.5.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3483, 2965, 2873, 1736, 1611, 1355, 1167,1020, 836, 860, 666, 591.

MS (ESI): m/z (%) = 357 (85), 295 (59), 227 (15), 185 (30), 177 (36), 173 (26).

HRMS (ESI) for $C_{19}H_{21}N_2O_3S$ (357.1267): 357.1264 $(M+H)^+$.

4-(5-Formyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-3-yl)benzonitrile (3e)



3e

Pyrazoline **3e** was prepared via **GP5**, using hydrazone **1f** (34 mg, 0.10 mmol) and Co(salen) **4** (7.0 mg, 10 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.25) to give **3e** (18 mg, 51 µmol, 51%) as a light brown oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.91 (d, *J* = 1.6 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.79 – 7.73 (m, 2H), 7.71 – 7.65 (m, 2H), 7.37 – 7.32 (m, 2H), 4.41 (ddd, *J* = 12.2, 10.0, 1.7 Hz, 1H), 3.40 (dd, *J* = 17.4, 10.0 Hz, 1H), 3.19 (dd, *J* = 17.4, 12.2 Hz, 1H), 2.42 (s, 3H).

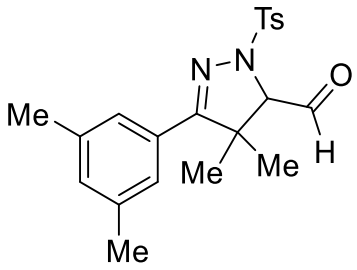
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 196.1, 155.8, 145.6, 134.2, 132.7, 131.6, 130.1, 128.9, 127.5, 118.2, 114.5, 68.1, 34.3, 21.8.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3491, 2925, 2229, 1736, 1596, 1508, 1357, 1167, 1056, 911, 841, 667, 587.

MS (ESI): m/z (%) = 354 (66), 336 (10), 212 (13), 182 (24), 170 (14), 155 (65).

HRMS (ESI) for $C_{18}H_{16}N_3O_3S$ (354.0907): 354.0910 $(M+H)^+$.

3-(3,5-Dimethylphenyl)-4,4-dimethyl-1-tosyl-4,5-dihydro-1*H*-pyrazole-5-carbaldehyde (3f)



3f

Pyrazoline **3f** was prepared via **GP5**, using hydrazone **1o** (37 mg, 0.10 mmol) and Co(salen) **4** (7 mg, 10 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1, R_f = 0.25) to give **3f** (32 mg, 83 µmol, 83%) as an off white solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 9.93 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 1.6 Hz, 2H), 7.07 – 7.03 (m, 1H), 3.37 (dd, *J* = 3.9, 1.1 Hz, 1H), 2.43 (s, 3H), 2.31 (s, 6H), 1.38 (s, 3H), 1.30 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ / ppm = 198.4, 164.4, 145.2, 138.4, 132.3, 130.6, 129.8, 129.4, 129.2, 125.5, 77.5, 54.2, 25.1, 21.8, 21.5, 20.5.

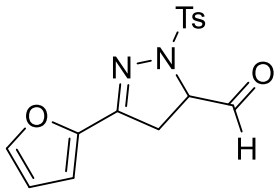
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2969, 2922, 2871, 1731, 1571, 1598, 1363, 1167, 1089, 994, 853, 670, 661, 587.

MS (ESI): m/z (%) = 385 (100), 371 (20), 213 (24).

HRMS (ESI) for $C_{21}H_{25}N_2O_3S$ (385.1580): 385.1579 $(M+H)^+$.

M.p. (°C): 163–165.

3-(Furan-2-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazole-5-carbaldehyde (3g)



3g

Pyrazoline **3g** was prepared via **GP5**, using hydrazone **1h** (24 mg, 79 µmol) and Co(salen) **4** (5.6 mg, 8.0 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.25) to give **3g** (16 mg, 50 µmol, 63%) as a light brown oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.87 (d, *J* = 1.8 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.61 (t, *J* = 1.2 Hz, 1H), 7.44 (t, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.78 (dd, *J* = 2.0, 0.8 Hz, 1H), 4.25 (ddd, *J* = 11.7, 9.7, 1.8 Hz, 1H), 3.25 (dd, *J* = 17.1, 9.8 Hz, 1H), 2.98 (dd, *J* = 17.1, 11.9 Hz, 1H), 2.42 (s, 3H).

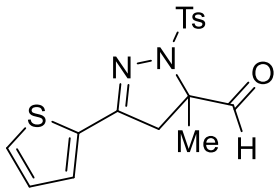
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 196.7, 151.9, 145.2, 144.6, 143.8, 131.4, 130.0, 129.0, 118.4, 108.4, 67.4, 35.2, 21.8.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3488, 2924, 1735, 1620, 1597, 1357, 1307, 1166, 846, 848, 667, 596.

MS (ESI): m/z (%) = 319 (34), 299 (16), 219 (12), 147 (12), 142 (14), 135 (12).

HRMS (ESI) for $C_{15}H_{15}N_2O_4S$ (319.0747): 319.0740 $(M+H)^+$.

5-Methyl-3-(thiophen-2-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazole-5-carbaldehyde (3h)



3h

Pyrazoline **3h** was prepared via **GP5**, using hydrazone **1g** (34.0 mg, 102 µmol) and Co(salen) **4** (7.0 mg, 10 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2, R_f = 0.3) to give **3h** (19.0 mg, 545 µmol, 53%) as a light brown oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.86 (s, 1H), 7.94 – 7.86 (m, 2H), 7.50 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.45 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.35 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.33 – 7.28 (m, 2H), 3.48 (d, *J* = 16.8 Hz, 1H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.42 (s, 3H), 1.47 (s, 3H).

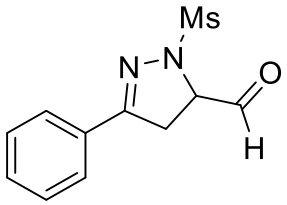
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 196.5, 150.1, 144.4, 136.5, 133.0, 129.7, 128.2, 127.1, 126.5, 125.9, 75.1, 43.9, 21.7, 18.9.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3106, 2824, 2854, 1737, 1597, 1352, 1320, 1163, 1091, 785, 731, 644, 599.

MS (ESI): m/z (%) = 349 (84), 331 (73), 177 (17), 165 (76), 155 (22).

HRMS (ESI) for $C_{16}H_{17}N_2O_3S_2$ (349.0675): 349.0673 $(M+H)^+$.

1-(Methylsulfonyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole-5-carbaldehyde (3i)



3i

Pyrazoline **3i** was prepared via **GP5**, using hydrazone **1r** (26 mg, 0.11 mmol) and Co(salen) **4** (7.0 mg, 10 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.35) to give **3i** (13 mg, 52 µmol, 47%) as a light yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.79 (d, *J* = 1.4 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.50 – 7.39 (m, 3H), 4.79 (td, *J* = 10.6, 1.4 Hz, 1H), 3.56 – 3.46 (m, 2H), 3.22 (s, 3H).

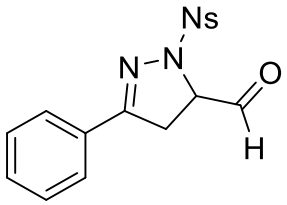
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 196.3, 158.2, 131.5, 129.9, 129.0, 127.3, 66.2, 37.5, 34.8.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3475, 3026, 2930, 2852, 1735, 1448, 1348, 1164, 1011, 757, 692, 561, 517.

MS (ESI): m/z (%) = 253 (27), 223 (10), 159 (31), 145 (9).

HRMS (ESI) for $C_{11}H_{13}N_2O_3S$ (253.0641): 253.0641 $(M+H)^+$.

1-((4-Nitrophenyl)sulfonyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole-5-carbaldehyde (3j)



3j

Pyrazoline **3j** was prepared via **GP5**, using hydrazone **1p** (38.0 mg, 110 µmol) and Co(salen) **4** (7.0 mg, 10 µmol), and the reaction was stirred for 1 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 6:4, R_f = 0.3) to give **3j** (18.5 mg, 515 µmol, 47%) as a light yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.89 (d, J = 1.8 Hz, 1H), 8.41 – 8.36 (m, 2H), 8.19 – 8.14 (m, 2H), 7.70 – 7.61 (m, 2H), 7.51 – 7.35 (m, 3H), 4.39 (ddd, J = 11.7, 9.7, 1.8 Hz, 1H), 3.44 (dd, J = 17.5, 9.7 Hz, 1H), 3.28 (dd, J = 17.5, 12.0 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 195.6, 158.7, 151.0, 140.7, 131.8, 130.2, 129.5, 129.1, 127.2, 124.5, 67.7, 34.9.

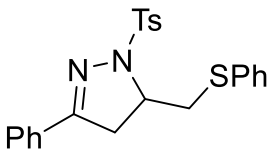
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3482, 3106, 926, 2854, 1737, 1688, 1530, 1349, 1175, 1108, 956, 910, 763, 737, 615, 585.

MS (ESI): m/z (%) = 360 (7), 322 (45), 251 (15), 223 (17), 194 (21), 173 (14), 159 (10), 142 (100).

HRMS (ESI) for $C_{16}H_{14}N_3O_5S$ (360.0649): 360.0647 $(M+H)^+$.

Preparation of Compounds 9a–g

3-Phenyl-5-((phenylthio)methyl)-1-tosyl-4,5-dihydro-1*H*-pyrazole (9a)



9a

Pyrazoline **9a** was prepared via **GP6**, using hydrazone **1a** (32 mg, 0.10 mmol), $Mn(dpm)_3$ (6.0 mg, 10 µmol), *t*BuOOH (5.5 M in decane, 40 µL, 0.20 mmol), and diphenyl disulfide (38 mg, 0.20 mmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1 + 1% trimethylamine, R_f = 0.2) to give **9a** (24.7 mg, 58 µmol, 58%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.66 – 7.59 (m, 4H), 7.51 – 7.46 (m, 2H), 7.43 – 7.27 (m, 6H), 7.21 – 7.16 (m, 2H), 4.02 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.91 (tdd, *J* = 10.6, 9.3, 3.2 Hz, 1H), 3.22 (dd, *J* = 17.5, 10.7 Hz, 1H), 3.09 – 2.98 (m, 2H), 2.35 (s, 3H).

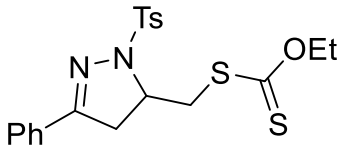
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 157.8, 144.4, 134.4, 131.7, 130.82, 130.78, 129.9, 129.6, 129.3, 128.8 (2C), 127.1, 126.8, 61.1, 39.9, 38.7, 21.7.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3059, 2924, 2854, 1597, 1401, 1358, 1167, 908, 760, 691, 591.

MS (ESI): m/z (%) = 423 (86), 371 (17), 299 (10), 145 (11).

HRMS (ESI) for $C_{23}H_{23}N_2O_2S_2$ (423.1195): 423.1194 $(M+H)^+$.

***O*-Ethyl S-((3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methyl) carbonodithioate (9b)**



9b

Pyrazoline **9b** was prepared via **GP6**, using hydrazone **1a** (32 mg, 0.10 mmol), $Mn(dpm)_3$ (6.0 mg, 10 µmol), *t*BuOOH (5.5 M in decane, 40 µL, 0.20 mmol), and *S*-benzyl *O*-ethyl carbonodithioate[13] (42 mg, 0.20 mmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1 + 1% trimethylamine, R_f = 0.2) to give **9b** (25 mg, 58 µmol, 58%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.86 – 7.79 (m, 2H), 7.68 – 7.61 (m, 2H), 7.44 – 7.33 (m, 3H), 7.31 – 7.27 (m, 2H), 4.68 (qd, *J* = 7.1, 1.4 Hz, 2H), 4.32 – 4.19 (m, 1H), 4.14 (dd, *J* = 14.1, 3.6 Hz, 1H), 3.54 (dd, *J* = 14.1, 8.4 Hz, 1H), 3.18 (dd, *J* = 17.3, 10.7 Hz, 1H), 3.05 (dd, *J* = 17.3, 9.3 Hz, 1H), 2.39 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 213.6, 157.7, 144.6, 132.1, 130.9, 130.7, 129.7, 128.9, 128.8, 127.1, 70.8, 60.6, 40.3, 39.0, 21.8, 13.9.

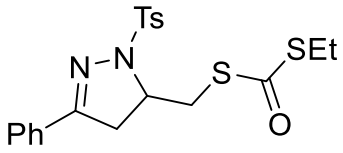
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2923, 2852, 1770, 1448, 1360, 1229, 1169, 1048, 853, 761, 676, 592.

MS (ESI): m/z (%) = 457 (100), 445 (31), 435 (85), 371 (33), 347 (23), 142 (69).

HRMS (ESI) for $C_{20}H_{22}N_2NaO_3S_3$ (457.0685): 457.0684 $(M+H)^+$.

[13] Chěnevert, R.; Paquin, R.; Rodrigue, A. *Synth. Comm.* **1981**, *11*, 817-821.

***S*-ethyl *S*-((3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methyl) carbonodithioate (9c)**



9c

Pyrazoline **9c** was prepared via **GP6**, using hydrazone **1a** (32 mg, 0.10 mmol), $Mn(dpm)_3$ (6.0 mg, 10 µmol), *t*BuOOH (5.5 M in decane, 40 µL, 0.20 mmol), and *O*-benzyl *S*-ethyl carbonodithioate[14] (42 mg, 0.20 mmol), and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1 + 1% trimethylamine, R_f = 0.2) to give **9c** (38 mg, 84 µmol, 84%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.85 – 7.79 (m, 2H), 7.66 – 7.61 (m, 2H), 7.44 – 7.33 (m, 3H), 7.31 – 7.27 (m, 2H), 4.11 (dddd, *J* = 10.9, 9.5, 8.1, 3.2 Hz, 1H), 3.90 (dd, *J* = 14.0, 3.2 Hz, 1H), 3.40 (dd, *J* = 14.0, 8.1 Hz, 1H), 3.16 (dd, *J* = 17.3, 10.8 Hz, 1H), 3.07 – 2.91 (m, 3H), 2.39 (s, 3H), 1.31 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 189.2, 157.7, 144.6, 131.9, 130.8, 130.7, 129.7, 128.9, 128.7, 127.1, 61.5, 38.9, 34.8, 25.7, 21.7, 15.0.

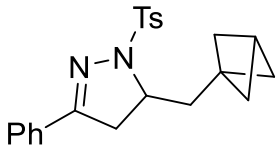
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3064, 2964, 2926, 1645, 1358, 1169, 872, 675, 592.

MS (ESI): m/z (%) = 457 (100), 445 (29), 435 (66), 371 (28), 299 (16), 142 (19).

HRMS (ESI) for $C_{20}H_{22}N_2NaO_3S_3$ (457.0685): 457.0692 $(M+Na)^+$.

[14] Lu, X.; Ni, Z. *Synthesis* **1987**, *1987*, 66-68.

5-(Bicyclo[1.1.1]pentan-1-ylmethyl)-3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (9d)



9d

Pyrazoline **9d** was prepared via **GP6**, using hydrazone **1a** (32 mg, 0.10 mmol), $Mn(dpm)_3$ (6.0 mg, 10 µmol), *t*BuOOH (5.5 M in decane, 20 µL, 0.10 mmol), and [1.1.1]propellane (0.57 M in Bu_2O, 0.185 mL, 0.105 mmol)[15], and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 10:0.5–9:1, R_f = 0.2) to give **9d** (22 mg, 58 µmol, 58%) as a colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.81 – 7.75 (m, 2H), 7.68 – 7.63 (m, 2H), 7.43 – 7.34 (m, 3H), 7.30 – 7.26 (m, 2H), 3.73 (tdd, *J* = 10.7, 9.7, 2.9 Hz, 1H), 3.15 (dd, *J* = 17.1, 10.8 Hz, 1H), 2.79 (dd, *J* = 17.1, 9.7 Hz, 1H), 2.52 (d, *J* = 12.2 Hz, 2H), 2.38 (s, 3H), 1.94 – 1.83 (m, 1H), 1.76 (s, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 157.7, 144.2, 132.3, 131.1, 130.6, 129.6, 128.8, 128.7, 127.0, 60.9, 51.3, 42.9, 40.0, 38.9, 29.0, 21.7.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2961, 2906, 2868, 1598, 1448, 1355, 1167, 1092, 851, 692, 669, 591.

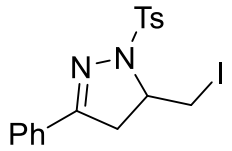
MS (ESI): m/z (%) = 381 (100), 226 (11), 142 (18).

HRMS (ESI) for $C_{22}H_{25}N_2O_2S$ (381.1631): 381.1627 $(M+H)^+$.

M.p. (°C): 153–155.

[15] Makarov, I. S.; Brocklehurst, C. E.; Karaghiosoff, K.; Koch, G.; Knochel, P. *Angew. Chem., Int. Ed.* **2017**, *56*, 12774-12777.

5-(Iodomethyl)-3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (9e)



9e

Pyrazoline **9e** was prepared via **GP6**, using hydrazone **1a** (34.0 mg, 108 µmol), $Mn(dpm)_3$ (6.0 mg, 10 µmol), *t*BuOOH (5.5 M in decane, 40 µL, 0.20 mmol), and allyl iodide (40 µL, 0.40 mmol), and the reaction was stirred for 1.5 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1, R_f = 0.25) to give **9e** (37.0 mg, 84.0 µmol, 78%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.84 – 7.77 (m, 2H), 7.70 – 7.63 (m, 2H), 7.46 – 7.34 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.04 (dtd, *J* = 10.7, 9.1, 3.2 Hz, 1H), 3.83 (dd, *J* = 9.9, 3.2 Hz, 1H), 3.45 (t, *J* = 9.7 Hz, 1H), 3.32 (dd, *J* = 17.5, 10.8 Hz, 1H), 3.00 (dd, *J* = 17.5, 8.8 Hz, 1H), 2.39 (s, 3H).

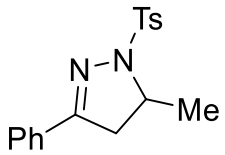
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 156.8, 144.7, 132.1, 130.9, 130.6, 129.8, 128.80, 128.75, 127.1, 62.3, 41.7, 21.8, 9.9.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3031, 2923, 2853, 1597, 1448, 1401, 1356, 1166, 1010, 908, 730, 691, 681, 583, 548.

MS (ESI): m/z (%) = 441 (100), 371 (8), 285 (21), 284 (9).

HRMS (ESI) for $C_{17}H_{18}IN_2O_2S$ (441.0128): 441.0119 $(M+H)^+$.

5-Methyl-3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (9f)



9f

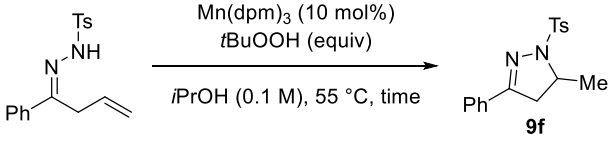
Pyrazoline **9f** was prepared via **GP6**, using hydrazone **1a** (64.0 mg, 200 µmol), $Mn(dpm)_3$ (12 mg, 20 µmol), and *t*BuOOH (5.5 M in decane, 70 µL, 0.40 mmol), and the reaction was stirred for 3 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2, R_f = 0.25) to give **9f** (35.0 mg, 111 µmol, 56%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.83 – 7.77 (m, 2H), 7.67 – 7.62 (m, 2H), 7.43 – 7.34 (m, 3H), 7.28 (m, 2H), 3.90 (ddq, *J* = 10.5, 9.7, 6.2 Hz, 1H), 3.18 (dd, *J* = 16.9, 10.6 Hz, 1H), 2.77 (dd, *J* = 16.9, 9.8 Hz, 1H), 2.38 (s, 3H), 1.64 (d, *J* = 6.2 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 157.3, 144.2, 132.5, 131.2, 130.6, 129.6, 128.8, 128.7, 127.0, 58.4, 41.7, 22.0, 21.7.

The spectra are in agreement with the literature.[3]

Control experiment:

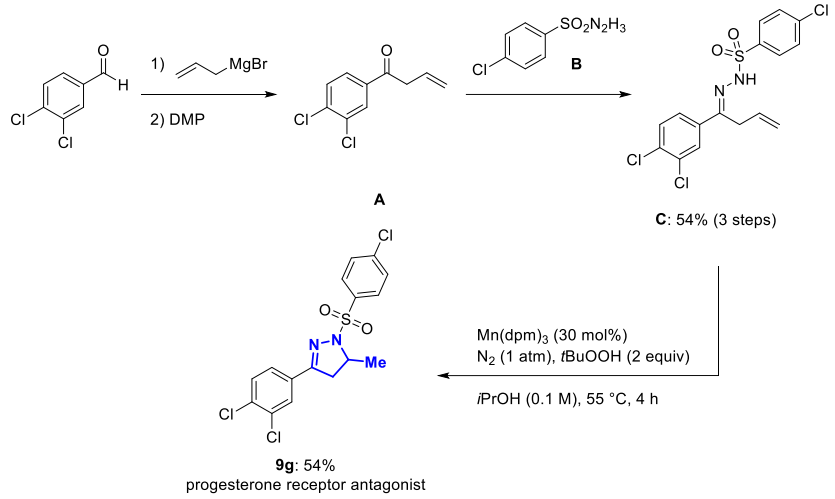


9f

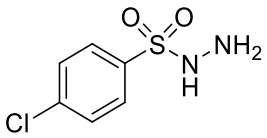
entry	*t*BuOOH	time	yield (**9f**)
1	-	14 h	<5%[a]
2	2 equiv	3 h	56%

[a] alongside starting material.

Preparation of Compounds A, B, C, 9g



4-chlorobenzenesulfonohydrazide (B)



B

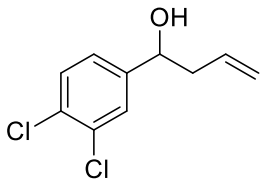
Hydrazide **B** was prepared according to a literature procedure:[16] 4-Chlorobenzenesulfonyl chloride (4.22 g, 20.0 mmol) was dissolved in THF (20 mL) and cooled to 0 °C. Then, hydrazine monohydrate (2.50 mL, 50.0 mmol) was added dropwise and the mixture stirred for additional 45 min. After dilution with THF (20 mL) at the same temperature, the mixture was washed with water (2 x 10 mL) and brine (20 mL), the organic phase separated, dried with Na_2SO_4, filtered and the solvents removed in vacuo, affording **B** (3.51 g, 16.9 mmol, 84%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.47 (s, 1H), 7.84 – 7.76 (m, 2H), 7.72 – 7.64 (m, 2H), 4.19 (s, 2H).

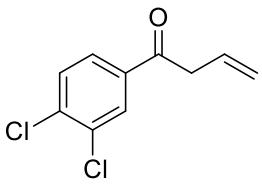
The spectra are in agreement with the literature.[17]

[16] Terent'ev, A. O.; Mulina, O. M.; Pirgach, D. A.; Demchuk, D. V.; Syroeshkin, M. A.; Nikishin, G. I. *RSC Adv.* **2016**, *6*, 93476-93485.
[17] Mulina, O. M.; Zhironkina, N. V.; Paveliev, S. A.; Demchuk, D. V.; Terent'ev, A. O. *Org. Lett.* **2020**, *22*, 1818-1824.

1-(3,4-Dichlorophenyl)but-3-en-1-one (A)



S-A



A

3,4-Dichlorobenzaldehyde (1.75 g, 10.0 mmol) was dissolved in Et_2O (100 mL) and cooled to 0 °C. Allylmagnesium bromide (12.0 mL, 1 M in Et_2O) was added dropwise over 30 min using a syringe pump and the rection stirred for additional 60 min, whilst slowly warming to 25 °C. The reaction mixture was quenched with aq. sat. NH_4Cl (20 mL) and extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 9:1, R_f = 0.3) to give **S-A** (1.66 g, 7.64 mmol, 76%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.47 (dd, *J* = 2.1, 0.7 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.19 (ddd, *J* = 8.2, 2.1, 0.6 Hz, 1H), 5.85 – 5.70 (m, 1H), 5.22 – 5.13 (m, 2H), 4.71 (ddd, *J* = 8.0, 4.2, 3.2 Hz, 1H), 2.57 – 2.37 (m, 2H), 2.09 (d, *J* = 3.3 Hz, 1H).

The spectra are in agreement with the literature.[18]

Ketone **A** was prepared via **GP2**, using **S-A** (722 mg, 3.33 mmol) and DMP (2.12 g, 5.00 mmol) and the reaction was stirred for 2 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 10:0.4, R_f = 0.35) to give **A** (652 g, 3.06 mmol, 92%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.04 (d, *J* = 2.1 Hz, 1H), 7.79 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 6.05 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.32 – 5.18 (m, 2H), 3.72 (dt, *J* = 6.7, 1.4 Hz, 2H).

[18] Lanfranchi, D. A.; Bour, C.; Boff, B.; Hanquet, G. *Eur. J. Org. Chem.* **2010**, *2010*, 5232-5247.

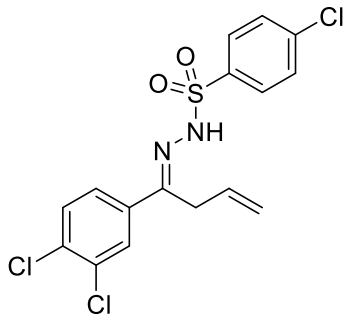
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 195.9, 137.9, 136.2, 133.5, 130.9, 130.45, 130.37, 127.5, 119.5, 43.5.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3082, 2983, 1688, 1583, 1375, 1199, 1030, 917, 815, 676, 613.

MS (ESI): m/z (%) = 236 (33), 203 (35), 117 (63), 173 (100).

HRMS (ESI) for $C_{10}H_8Cl_2NaO$ (236.9844): 236.9849 $(M+Na)^+$.

4-Chloro-*N*'-(1-(3,4-dichlorophenyl)but-3-en-1-ylidene)benzenesulfonohydrazide (C)



C

Hydrazone **C** was prepared via **GP3**, using ketone **A** (192 mg, 893 µmol), hydrazide **B** (273 g, 1.35 mmol) and the reaction was stirred for 1.5 h. After removal of solvents, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2, R_f = 0.25) to give **C** (285 g, 686 µmol, 77%) as a colorless solid.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 7.95 (s, 1H), 7.81 – 7.73 (m, 2H), 7.51 (d, *J* = 2.1 Hz, 1H), 7.05 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.88 – 6.81 (m, 2H), 5.11 (ddt, *J* = 17.4, 10.2, 5.1 Hz, 1H), 4.60 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.41 (dq, *J* = 17.4, 1.4 Hz, 1H), 2.49 (dt, *J* = 5.3, 2.0 Hz, 2H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 150.6, 139.9, 137.5, 136.9, 134.1, 133.2, 130.7, 129.8, 129.5, 129.4, 128.4, 125.7, 117.3, 31.0.

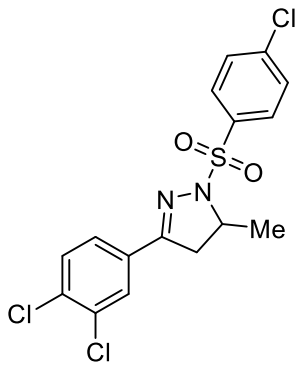
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3218, 3091, 2925, 1684, 1585, 1476, 1396, 1168, 1087, 1014, 825, 755.

MS (ESI): m/z (%) = 427 (100), 425 (98), 405 (57), 403 (56), 229 (25), 227 (36), 177 (50), 172 (20).

HRMS (ESI) for $C_{16}H_{13}Cl_3N_2NaO_2S$ (424.9656): 424.9653 $(M+Na)^+$.

M.p. (°C): 148–151.

1-((4-chlorophenyl)sulfonyl)-3-(3,4-dichlorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole (9g)



9g

Pyrazoline **9g** was prepared via **GP6**, using hydrazone **C** (41.0 mg, 102 µmol), $Mn(dpm)_3$ (18 mg, 30 µmol), and *t*BuOOH (40 µL, 0.20 mmol), and the reaction was stirred for 11.5 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 8:2, R_f = 0.25) to give **9g** (22.0 mg, 545 µmol, 53%) as a light yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.89 – 7.81 (m, 2H), 7.70 (dd, *J* = 1.9, 0.5 Hz, 1H), 7.52 – 7.42 (m, 4H), 3.97 (ddq, *J* = 10.6, 9.6, 6.2 Hz, 1H), 3.21 (dd, *J* = 17.0, 10.6 Hz, 1H), 2.76 (dd, *J* = 17.0, 9.7 Hz, 1H), 1.64 (d, *J* = 6.2 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 155.5, 140.3, 135.0, 134.0, 133.3, 130.9, 130.8, 130.1, 129.4, 128.7, 125.9, 58.8, 41.5, 21.9.

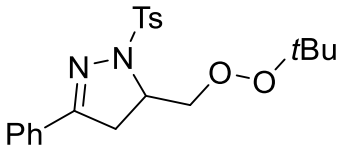
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3093, 2926, 2854, 1584, 1476, 1396, 1361, 1171, 1088, 1029, 759, 628.

MS (ESI): m/z (%) = 427 (100), 425 (99), 405 (74), 403 (73), 228 (47), 177 (82), 173 (30).

HRMS (ESI) for $C_{16}H_{13}Cl_3N_2NaO_2S$ (424.9656): 424.9652 $(M+Na)^+$.

M.p. (°C): 186–188.

5-((*tert*-Butylperoxy)methyl)-3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (9h)



9h

Pyrazoline **9h** was prepared via **GP6**, using hydrazone **1a** (32 mg, 0.10 mmol), $Mn(dpm)_3$ (6.0 mg, 10 µmol), and *t*BuOOH (5.5 M in decane, 40 µL, 0.20 mmol), in dichloroethane (1 mL), and the reaction was stirred for 2.5 h. After work-up, the crude product was purified via column chromatography (hexane:ethyl acetate = 9:1, R_f = 0.25) to give **9h** (35 mg, 87 µmol, 87%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.84 – 7.76 (m, 2H), 7.72 – 7.62 (m, 2H), 7.46 – 7.33 (m, 3H), 7.30 – 7.26 (m, 2H), 4.67 (dd, *J* = 11.5, 3.3 Hz, 1H), 4.22 – 4.03 (m, 2H), 3.18 (dd, *J* = 9.6, 1.6 Hz, 2H), 2.38 (s, 3H), 1.26 (s, 9H).

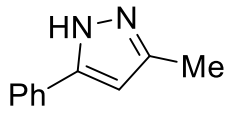
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 158.6, 144.4, 132.1, 130.9, 130.8, 129.7, 128.8, 128.7, 127.1, 81.1, 77.3, 60.1, 38.4, 26.4, 21.7.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2978, 2927, 2872, 1571, 1449, 1361, 1169, 1093, 1009, 692, 663, 595.

MS (ESI): m/z (%) = 425 (21), 403 (18), 371 (20), 348 (29), 347 (100), 167 (18).

HRMS (ESI) for $C_{21}H_{26}N_2NaO_4S$ (425.1505): 425.1500 $(M+Na)^+$.

5-Methyl-3-phenyl-1*H*-pyrazole (14)



14

Pyrazoline **14** (66 mg, 0.20 mmol) was dissolved in TBAF (1 M in THF, 1.2 mL, 1.2 mmol) and the reaction stirred at 80 °C for 12 h. The reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 x 30 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 1:1–3:7, R_f = 0.25) to give **14** (26.0 mg, 149 µmol, 75%) as a colorless solid.

^{1}H-NMR (400 MHz, Acetone-d_6): δ / ppm = 12.54 (s, 1H), 8.31 – 8.23 (m, 2H), 7.90 – 7.80 (m, 2H), 7.79 – 7.69 (m, 1H), 7.05 (d, *J* = 0.6 Hz, 1H), 5.13 (s, 2H), 4.76 (s, 1H).

^{13}C-NMR (101 MHz, Acetone-d_6): δ / ppm = 129.5, 128.2, 126.1, 101.1, 57.2. (Quatenary carbon signals not visible due to C-N quadrupole interaction). See attached HMBC spectrum and XRay structure.)

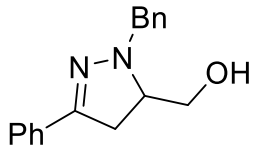
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3132, 3105, 2924, 2876, 1632, 1464, 1437, 1335, 1224, 1001, 693, 763.

MS (ESI): m/z (%) = 175 (69), 172 (58), 168 (17), 158 (11), 157 (100).

HRMS (ESI) for $C_{10}H_{11}N_2O$ (175.0866): 175.0865 $(M+H)^+$.

M.p. (°C): 143–145.

(1-Benzyl-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol (15)



15

Pyrazoline **2p** (36 mg, 0.10 mmol) and K_2CO_3 (42 mg, 0.30 mmol) were dissolved in DMF (1.5 mL). Thiophenol (14 µL, 0.14 mmol) was added and the reaction stirred at 25 °C for 1 h. After cooling to 0 °C, benzyl bromide (24 µL, 0.20 mmol) was added and stirring continued for additional 2 h. The reaction mixture was diluted with a 10% aq. LiCl solution (10 mL) and extracted with diethyl ether (4 x 25 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 6:4 + 1% trimethylamine, R_f = 0.35) to give **15** (15 mg, 56 µmol, 56%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.67 – 7.61 (m, 2H), 7.42 – 7.27 (m, 8H), 4.49 – 4.30 (m, 2H), 3.63 – 3.44 (m, 3H), 3.15 – 3.08 (m, 2H).

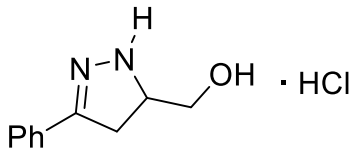
^{13}C-NMR (101 MHz, $CDCl_3$): δ / ppm = 151.1, 137.2, 132.9, 129.5, 128.9, 128.64, 128.60, 127.7, 126.1, 66.3, 61.2, 58.7, 35.8.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3379, 3084, 3060, 3058, 2924, 2852, 1560, 1453, 1447, 1361, 1203, 1039, 859, 692.

MS (ESI): m/z (%) = 267 (100), 239 (4), 177 (18).

HRMS (ESI) for $C_{17}H_{19}N_2O$ (267.1492): 267.1496 $(M+H)^+$.

(3-Phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)methanol hydrochloride (16)



16

Pyrazoline **2p** (26 mg, 72 µmol) and K_2CO_3 (30 mg, 0.22 mmol) were dissolved in DMF (1.1 mL). Thiophenol (10 µL, 0.10 mmol) was added and the reaction stirred at 25 °C for 1 h. The reaction mixture was diluted with a 10% aq. LiCl solution (10 mL) and extracted with diethyl ether (4 x 25 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude was dissolved in Et_2O (0.4 mL) and added dropwise to a solution of HCl in Et_2O (0.33 M, 0.65 mL, 0.22 mmol) and **16** (7.0 mg, 33 µmol, 46%) precipitated as a light yellow solid which was obtained via filtration.

NMR yield: Pyrazoline **2p** (36 mg, 0.10 mmol) and K_2CO_3 (42 mg, 0.30 mmol) was dissolved in DMF (1.5 mL). Thiophenol (15 µL, 0.15 mmol) was added and the reaction stirred at 25 °C for 1 h. The reaction mixture was diluted with water (10 mL) and extracted with diethyl ether (5 x 25 mL). The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude was dissolved in Et_2O (1 mL) and HCl (2 M in Et_2O, 60 µL, 1.2 mmol) was added. The solvent was removed in vacuo, trimethoxybenzene added as standard, the mixture dissolved in DMSO-d_6, and the yield of **16** (55 µmol, 55%) determined via NMR.

^{1}H-NMR (500 MHz, DMSO-d_6): δ / ppm = 7.86 – 7.83 (m, 2H), 7.61 (ddt, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.56 – 7.52 (m, 2H), 4.17 (dtd, *J* = 10.1, 6.2, 4.0 Hz, 1H), 3.72 (dd, *J* = 11.9, 4.0 Hz, 1H), 3.64 (dd, *J* = 11.9, 6.0 Hz, 1H), 3.58 (dd, *J* = 17.9, 9.8 Hz, 1H), 3.34 (dd, *J* = 17.9, 6.4 Hz, 1H).

^{13}C-NMR (126 MHz, DMSO-d_6): δ / ppm = 132.4, 129.1, 129.03, 128.99, 128.1, 60.1, 59.1, 37.1.

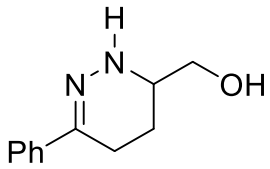
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3301, 3057, 2868, 2837, 2754, 2585, 1653, 1560, 1577, 1591, 1356, 1096, 922, 853, 762, 688.

MS (ESI): m/z (%) = 177 (100), 159 (14), 159 (58), 141 (11).

HRMS (ESI) for $C_{10}H_{13}N_2O$ (177.1022): 177.1022 $(M+H)^+$.

M.p. (°C): 97–99.

(6-Phenyl-2,3,4,5-tetrahydropyridazin-3-yl)methanol (17)



17

Pyrazoline **2v** (37.5 mg, 99.9 µmol) and K_2CO_3 (42 mg, 0.30 mmol) were dissolved in DMF (1.0 mL). Thiophenol (30 µL, 0.30 mmol) was added and the reaction stirred at 25 °C for 1 h. After cooling to 0 °C, benzyl bromide (24 µL, 0.20 mmol) was added and stirring continued for additional 2 h. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with 10% aq. LiCl solution (2 x 10 mL) and brine (15 mL). The organic phase was then dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (DCM:ethyl acetate=3:7, R_f = 0.3) to give **17** (12.3 mg, 64.7 µmol, 65%) as a colorless oil.

^{1}H-NMR (400 MHz, C_6D_6): δ / ppm = 7.83 – 7.78 (m, 2H), 7.27 – 7.20 (m, 2H), 7.16 – 7.10 (m, 1H), 3.19 (d, *J* = 5.8 Hz, 2H), 2.75 (p, *J* = 6.2 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.44 – 1.34 (m, 2H).

^{13}C-NMR (101 MHz, C_6D_6): δ / ppm = 142.5, 139.4, 128.4, 124.9, 64.8, 52.6, 22.1, 22.0.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3350, 2932, 1682, 1594, 1447, 1347, 1141, 1056, 1024, 756, 694.

MS (ESI): m/z (%) = 349 (49), 335 (88), 223 (30), 203 (40), 191 (100), 187 (29), 177 (40).

HRMS (ESI) for $C_{11}H_{15}N_2O$ (191.1179): 191.1180 $(M+H)^+$.

Single Crystal X-Ray Data

Single crystals of compound **6c** were obtained by slow evaporation of benzene-d_6 solution. Single crystals of compound **8a** and **8b** were obtained by slow evaporation of ethanol solutions. Single crystals of compound **9d** were obtained by slow evaporation of chloroform solution. **14** was dissolved in ethyl acetate in a small vial which was placed in a larger vial containing hexane which was then closed and left standing for several days to obtain single crystals.

CCDC 2078368 (**6c**), CCDC 2078369 (**8a**), CCDC 2078370 (**8b**), CCDC 2078371 (**9d**), and CCDC 2078372 (**14**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Structure Data of 6c (CCDC 2078368).

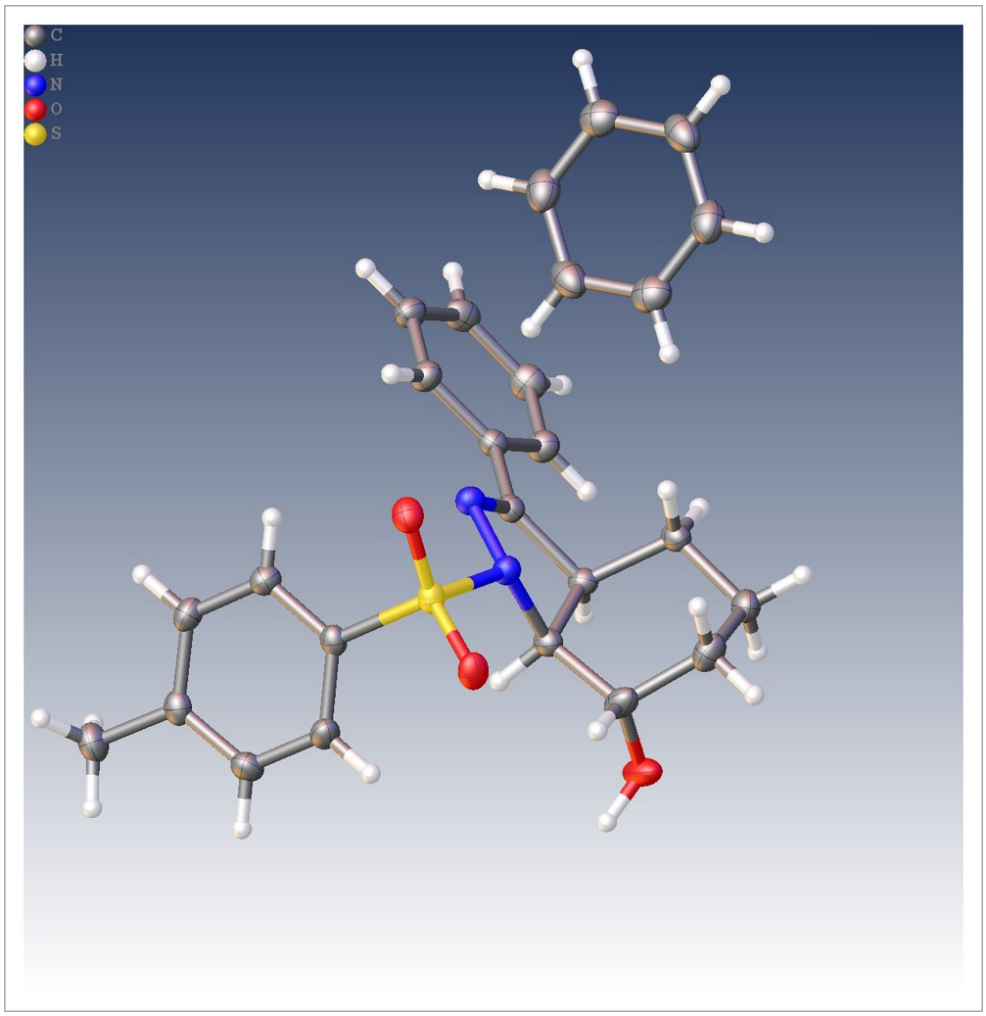


Table T4 Crystal data and structure refinement for **6c** (CCDC 2078368).

Identification code	ca061220_1_1
Empirical formula	$C_{23}H_{25}N_2O_3S$
Formula weight	409.51
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.68420(10)
b/Å	25.2973(2)

c/Å	8.78460(10)
α/°	90
β/°	109.0070(10)
γ/°	90
Volume/Å^3	2034.75(4)
Z	4
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	1.634
F(000)	868.0
Crystal size/mm^3	0.269 × 0.209 × 0.035
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.988 to 159.994
Index ranges	-12 ≤ h ≤ 12, -32 ≤ k ≤ 32, -11 ≤ l ≤ 10
Reflections collected	50821
Independent reflections	4378 [R_{int} = 0.0526, R_{sigma} = 0.0228]
Data/restraints/parameters	4378/1/266
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0928
Final R indexes [all data]	R_1 = 0.0403, wR_2 = 0.0948
Largest diff. peak/hole / e Å^{-3}	0.29/-0.47

Crystal Structure Data of 8a (CCDC 2078369)

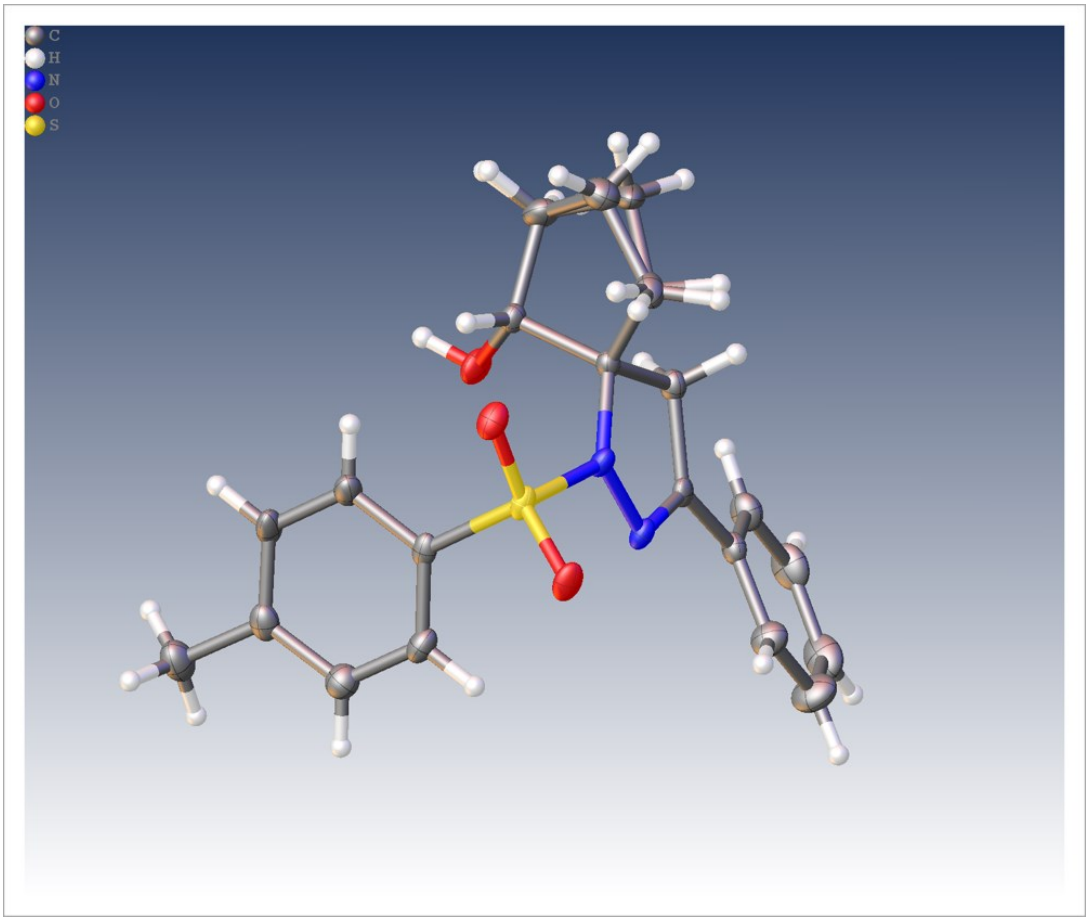


Table T5 Crystal data and structure refinement for **8a** (CCDC 2078369).

Identification code	ca050221_1_1
Empirical formula	$C_{20}H_{22}N_2O_3S$
Formula weight	370.45
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.5364(7)
b/Å	10.9885(16)
c/Å	25.521(4)
α/°	90

β/°	95.158(4)
γ/°	90
Volume/Å^3	1825.6(4)
Z	4
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.200
F(000)	784.0
Crystal size/mm^3	0.26 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.038 to 56.656
Index ranges	-8 ≤ h ≤ 8, -14 ≤ k ≤ 14, -33 ≤ l ≤ 31
Reflections collected	16584
Independent reflections	4525 [R_{int} = 0.0498, R_{sigma} = 0.0550]
Data/restraints/parameters	4525/18/249
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0449, wR_2 = 0.0988
Final R indexes [all data]	R_1 = 0.0725, wR_2 = 0.1107
Largest diff. peak/hole / e Å^{-3}	0.33/-0.45

Crystal Structure Data of 8b (CCDC 2078370)

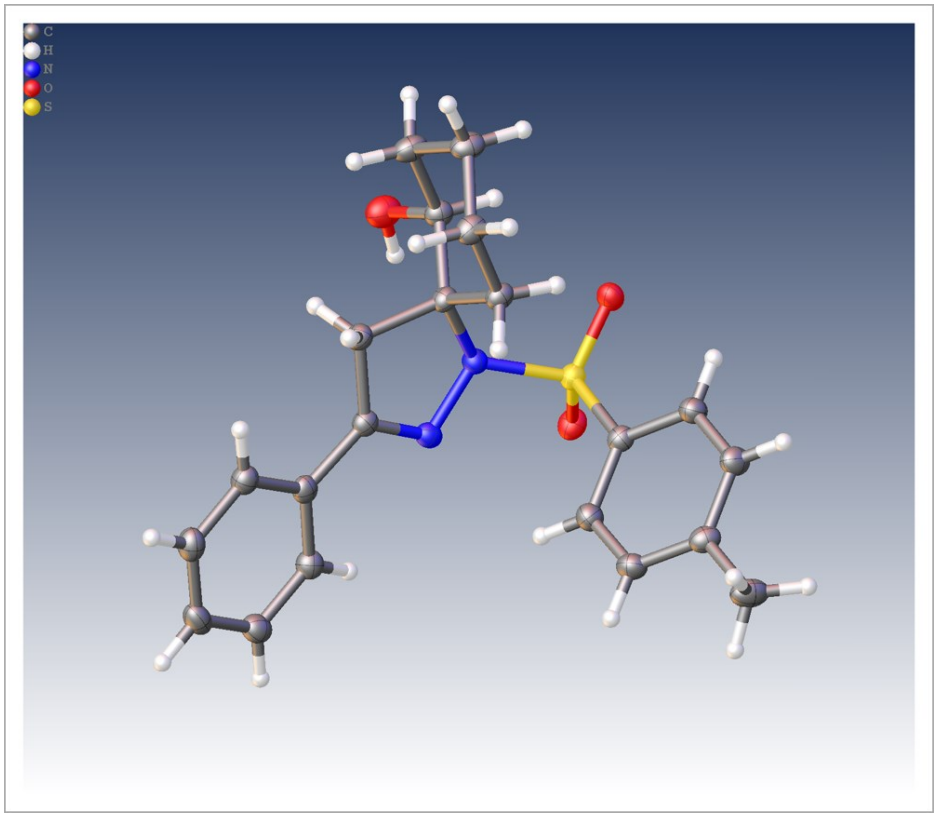


Table T6 Crystal data and structure refinement for **8b** (CCDC 2078370).

Identification code	ca110121_1_1
Empirical formula	$C_{21}H_{24}N_2O_3S$
Formula weight	384.48
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.2584(2)
b/Å	18.2306(2)
c/Å	10.24990(10)
α/°	90
β/°	116.215(2)

γ/°	90
Volume/Å^3	1887.38(5)
Z	4
ρ_{calc}g/cm^3	1.353
μ/mm^{-1}	1.723
F(000)	816.0
Crystal size/mm^3	0.191 × 0.119 × 0.056
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.754 to 160.596
Index ranges	-14 ≤ h ≤ 14, -23 ≤ k ≤ 23, -11 ≤ l ≤ 12
Reflections collected	49272
Independent reflections	4082 [R_{int} = 0.0677, R_{sigma} = 0.0244]
Data/restraints/parameters	4082/1/248
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.1267
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.1285
Largest diff. peak/hole / e Å^{-3}	1.39/-0.49

Crystal Structure Data of 9d (CCDC 2078371)

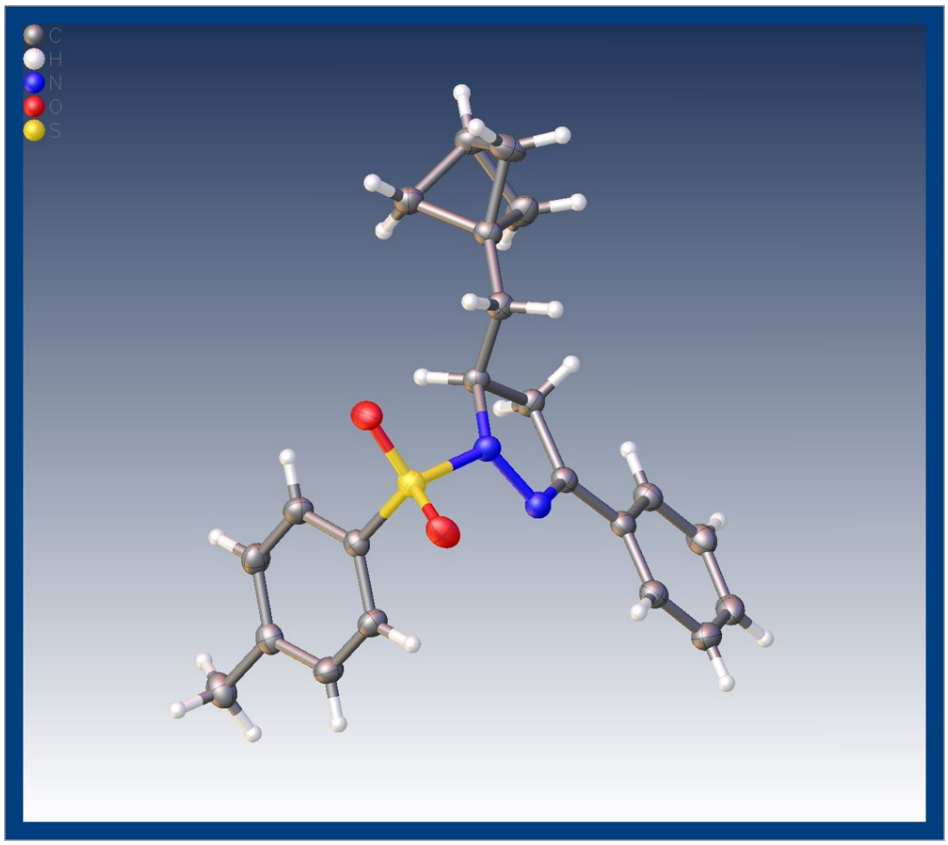


Table T7 Crystal data and structure refinement for **9d** (CCDC 2078371).

Identification code	ca150920_1_1
Empirical formula	$C_{22}H_{24}N_2O_2S$
Formula weight	380.49
Temperature/K	100.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	6.01790(10)
b/Å	8.8113(2)
c/Å	18.0991(2)
α/°	93.6700(10)

β/°	91.3400(10)
γ/°	91.3820(10)
Volume/Å^3	957.17(3)
Z	2
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	1.654
F(000)	404.0
Crystal size/mm^3	0.198 × 0.121 × 0.055
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.894 to 160.046
Index ranges	-7 ≤ h ≤ 7, -9 ≤ k ≤ 10, -23 ≤ l ≤ 23
Reflections collected	23188
Independent reflections	4054 [R_{int} = 0.0427, R_{sigma} = 0.0279]
Data/restraints/parameters	4054/0/245
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.0994
Final R indexes [all data]	R_1 = 0.0491, wR_2 = 0.1076
Largest diff. peak/hole / e Å^{-3}	0.43/-0.43

Crystal Structure Data of 14 (CCDC 2078372)

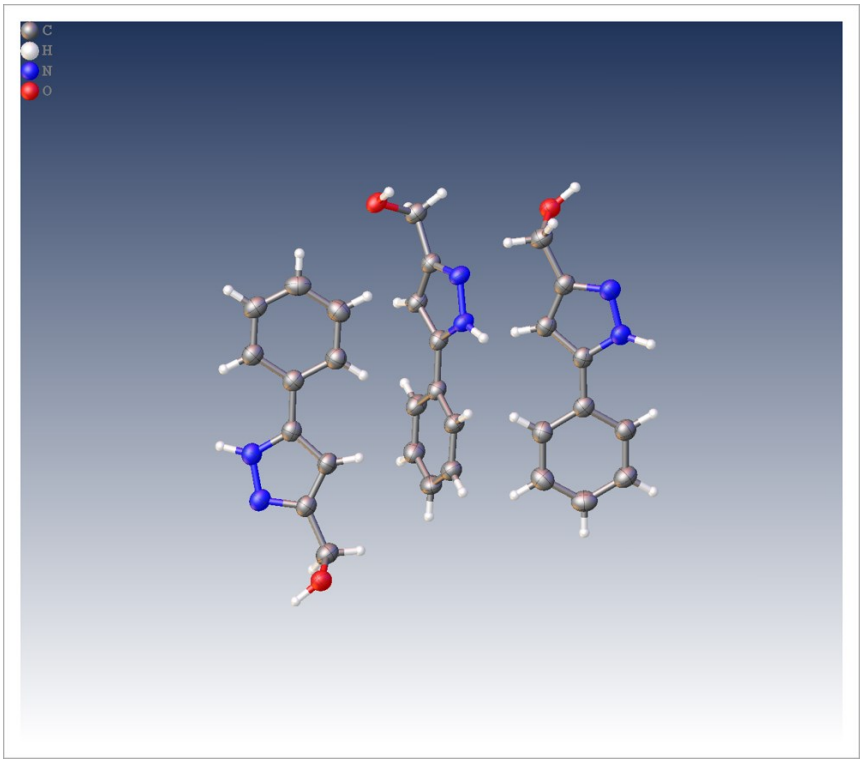


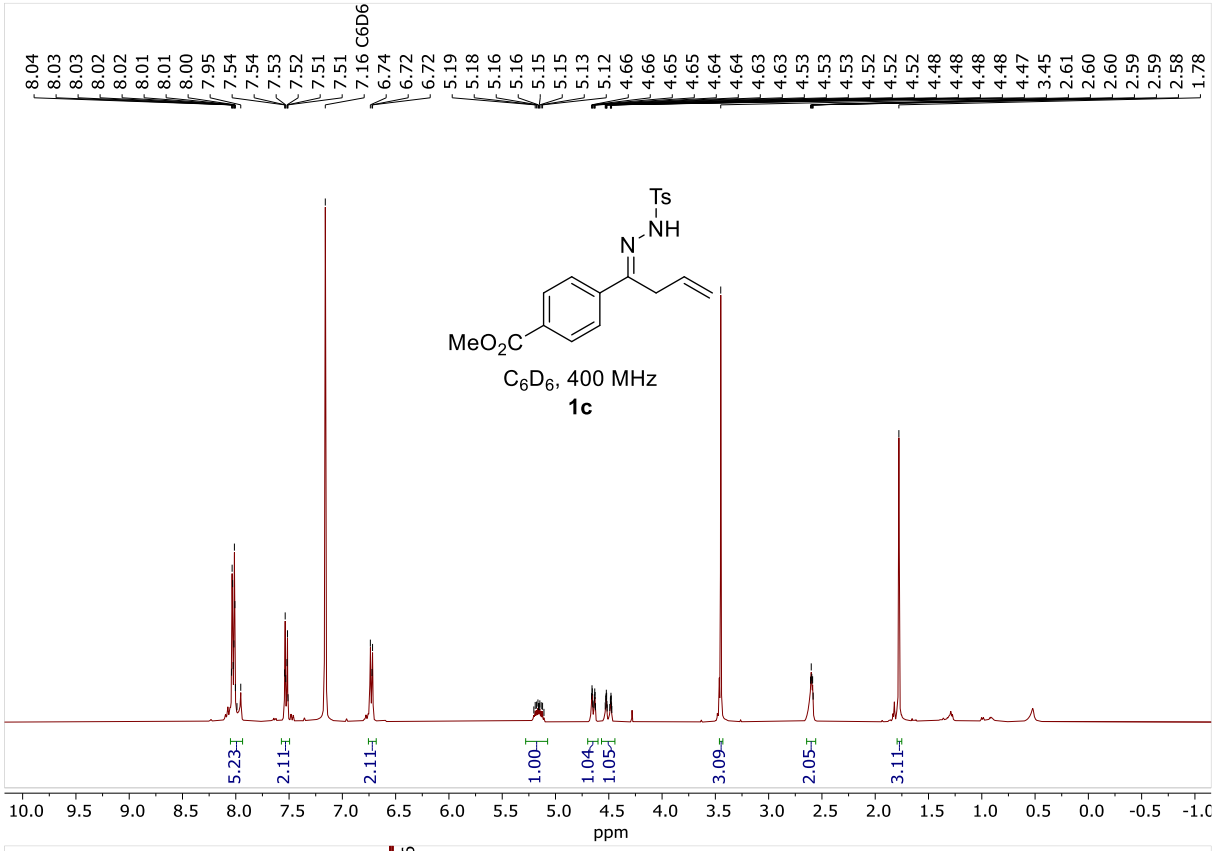
Table T8 Crystal data and structure refinement for **14** (CCDC 2078372).

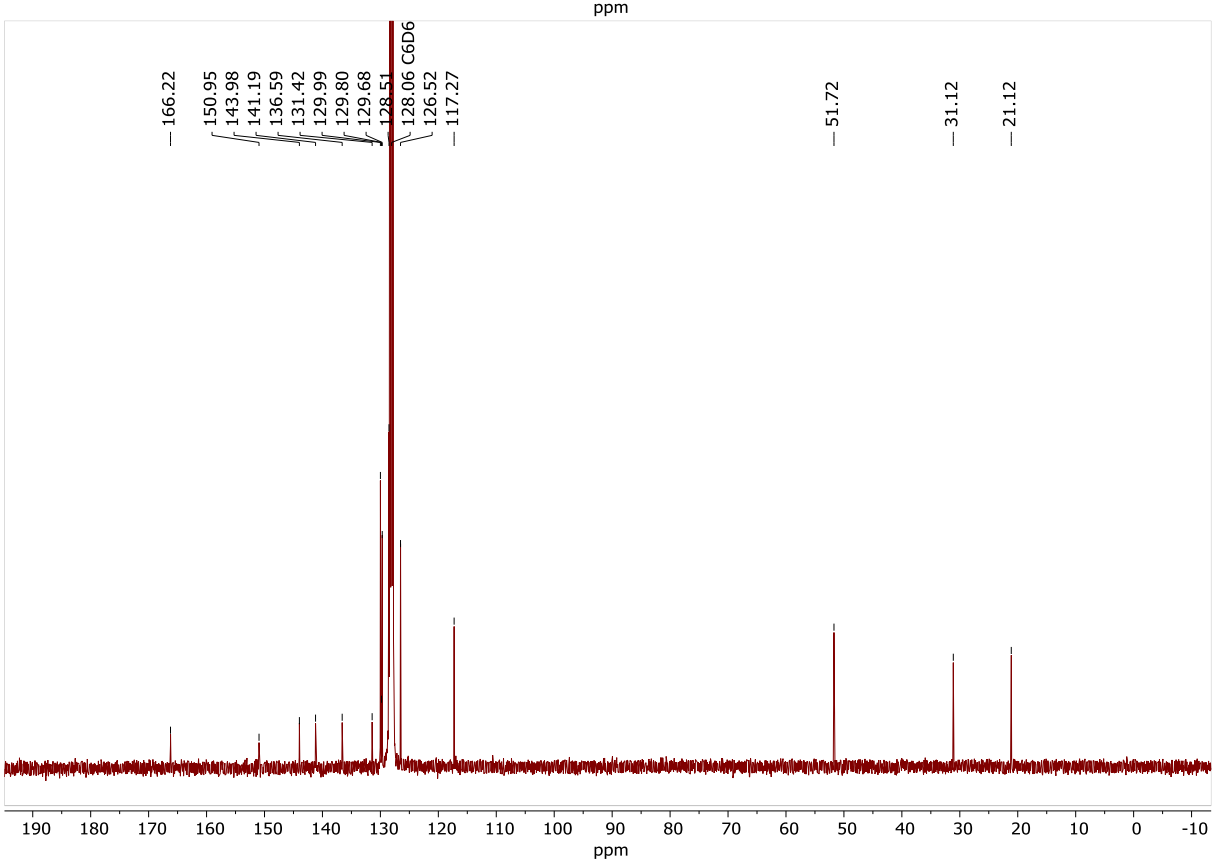
Identification code	ca230920_1_1
Empirical formula	$C_{10}H_{10}N_2O$
Formula weight	174.20
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.6322(2)
b/Å	27.6617(7)
c/Å	14.7131(5)
α/°	90
β/°	92.857(3)
γ/°	90

Volume/Å^3	2695.88(14)
Z	12
ρ_{calc}g/cm^3	1.288
μ/mm^{-1}	0.692
F(000)	1104.0
Crystal size/mm^3	0.194 × 0.094 × 0.022
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.39 to 160.184
Index ranges	-8 ≤ h ≤ 8, -34 ≤ k ≤ 34, -18 ≤ l ≤ 18
Reflections collected	42104
Independent reflections	5798 [R_{int} = 0.0957, R_{sigma} = 0.0441]
Data/restraints/parameters	5798/6/370
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0557, wR_2 = 0.1511
Final R indexes [all data]	R_1 = 0.0769, wR_2 = 0.1666
Largest diff. peak/hole / e Å^{-3}	0.31/-0.28

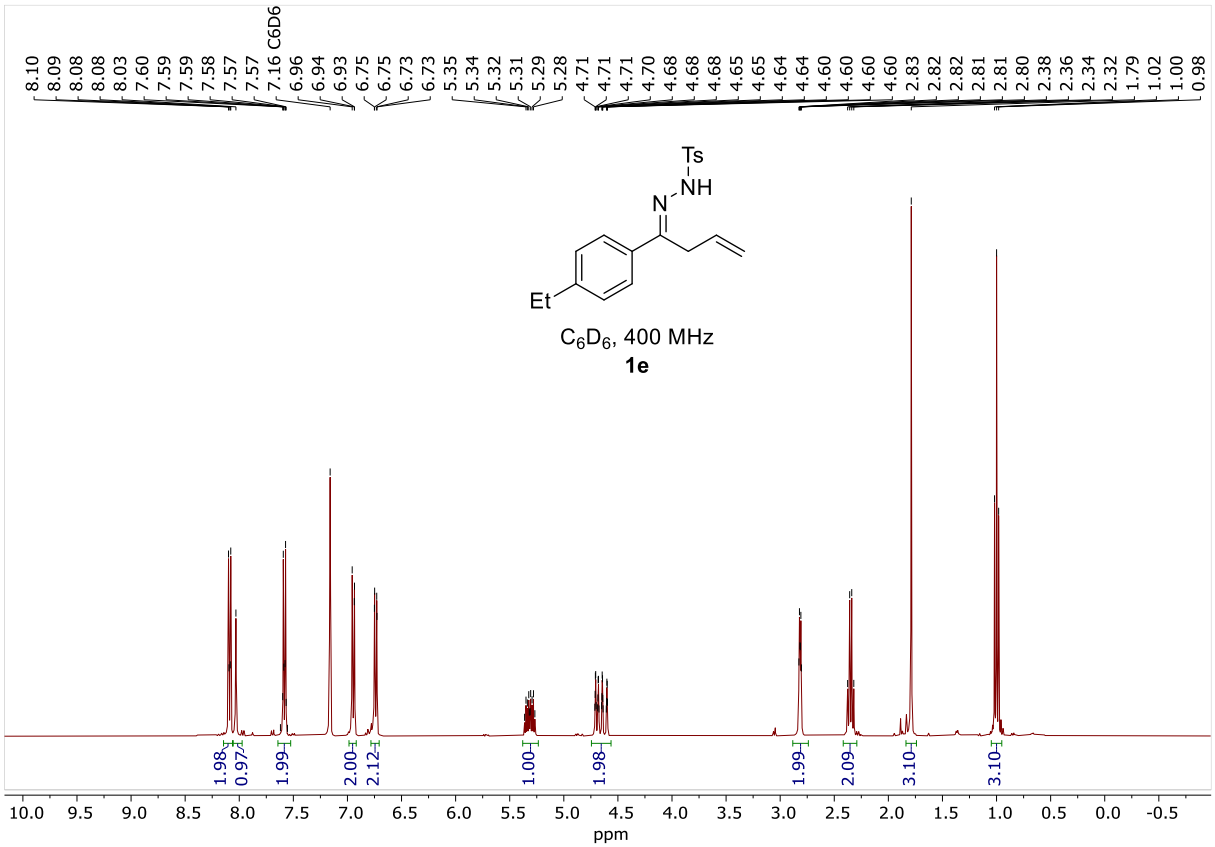
^{1}H and ^{13}C NMR spectra of compounds 1 - 17

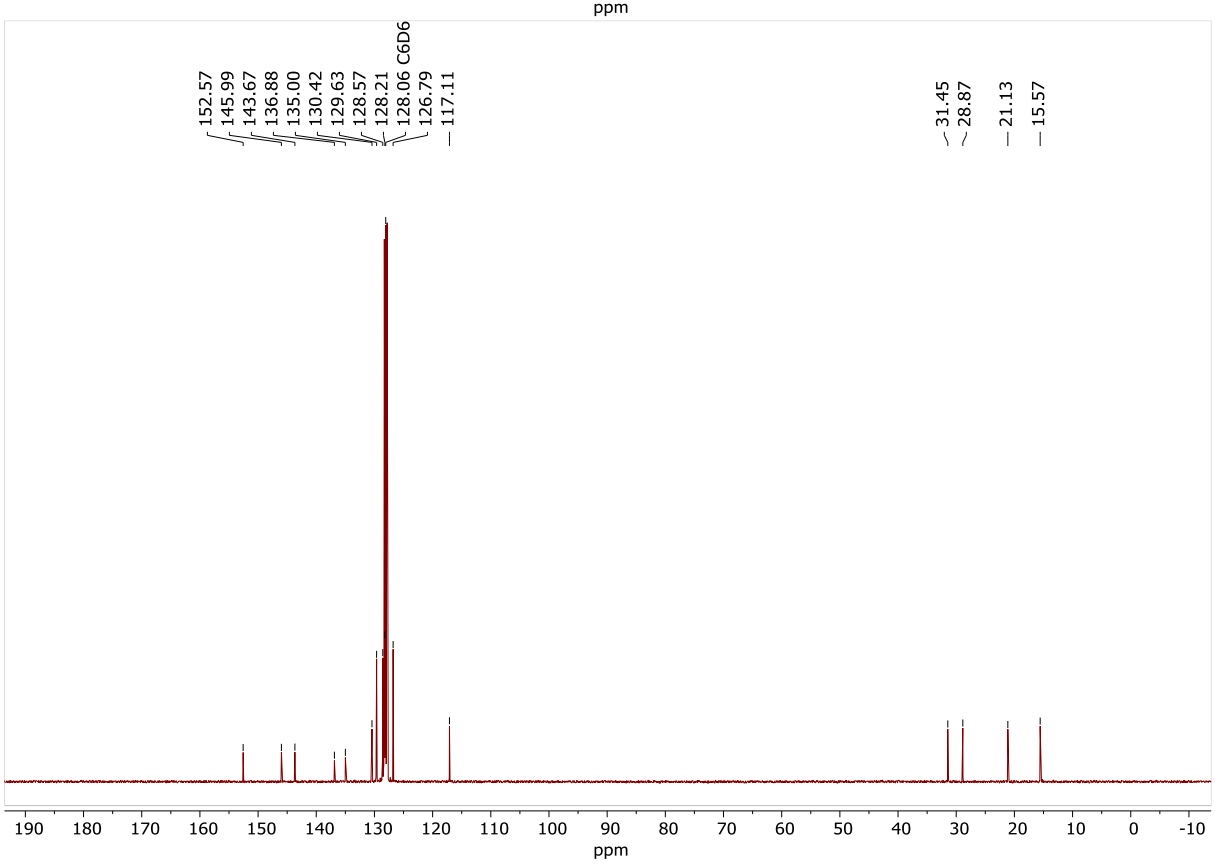
^{1}H NMR and ^{13}C NMR spectrum of compound **1c**



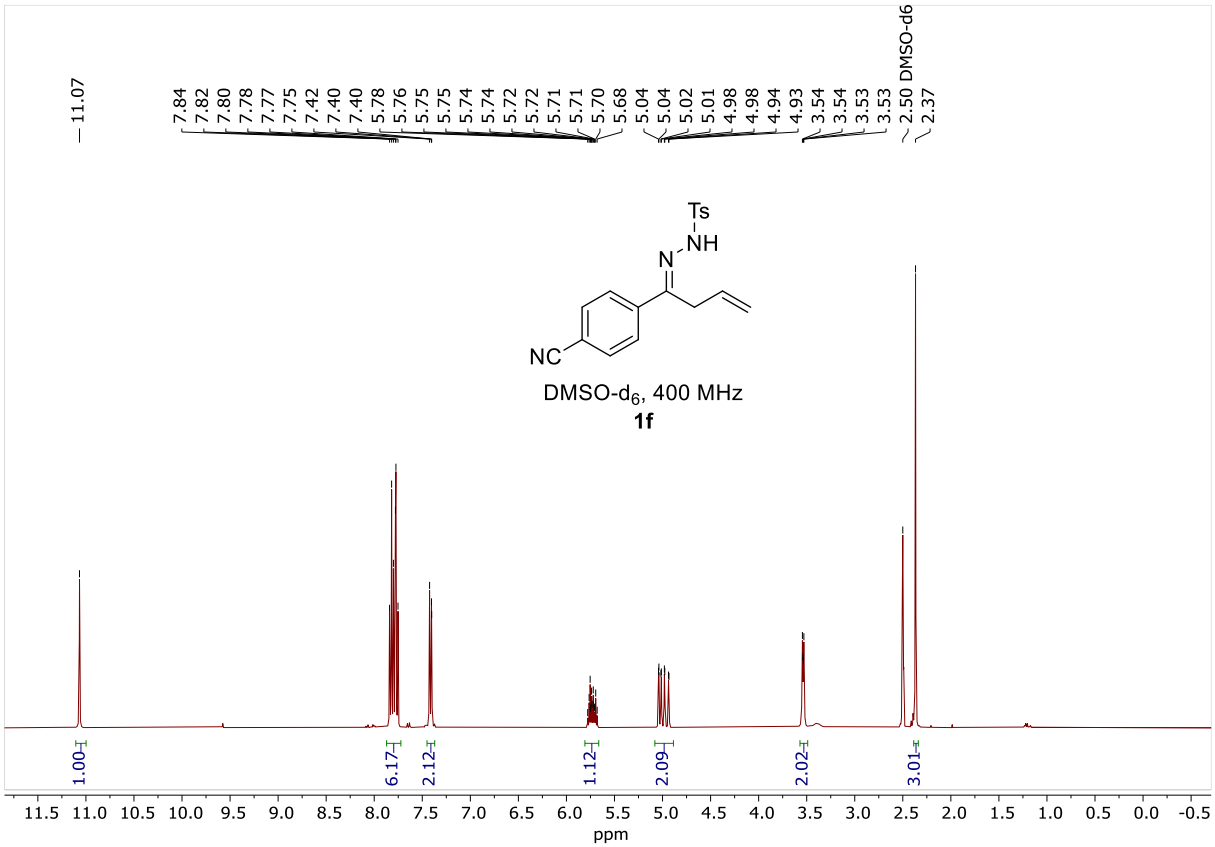


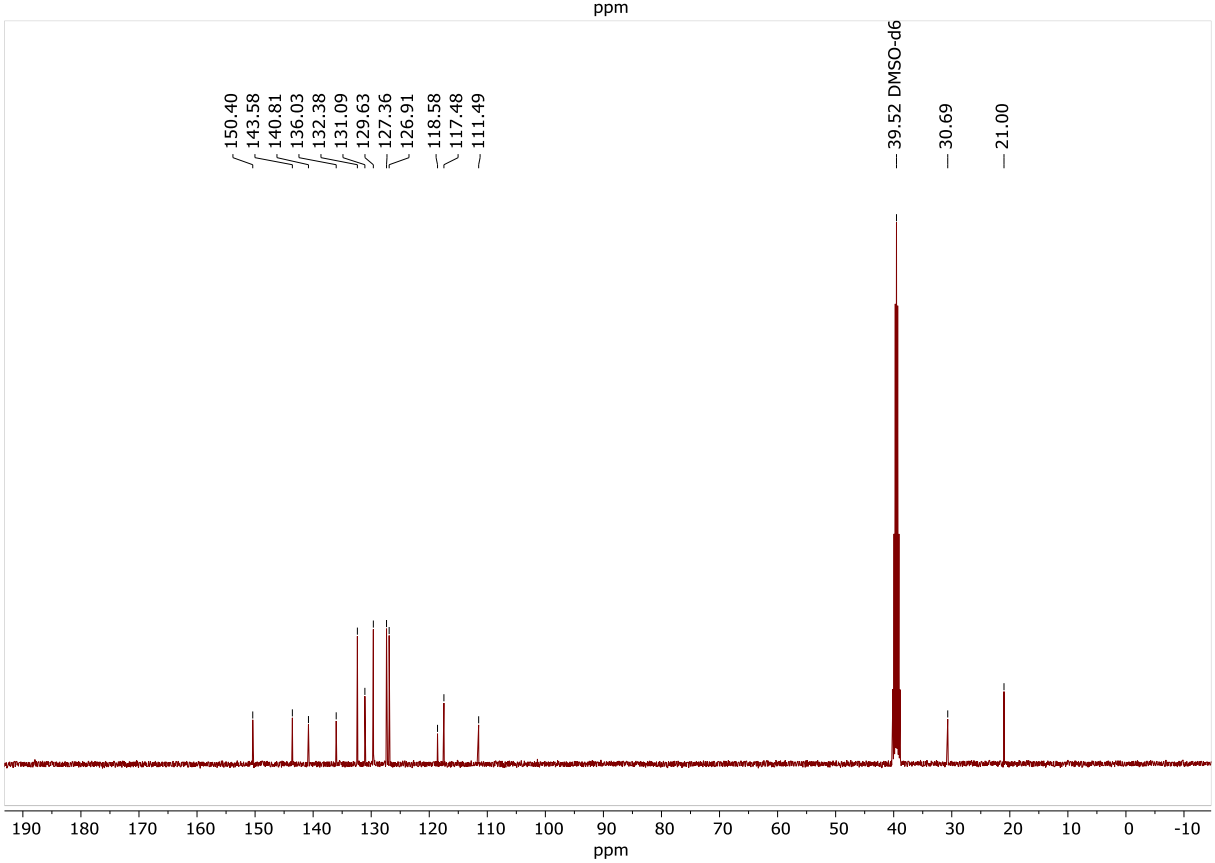
^{1}H NMR and ^{13}C NMR spectrum of compound **1e**



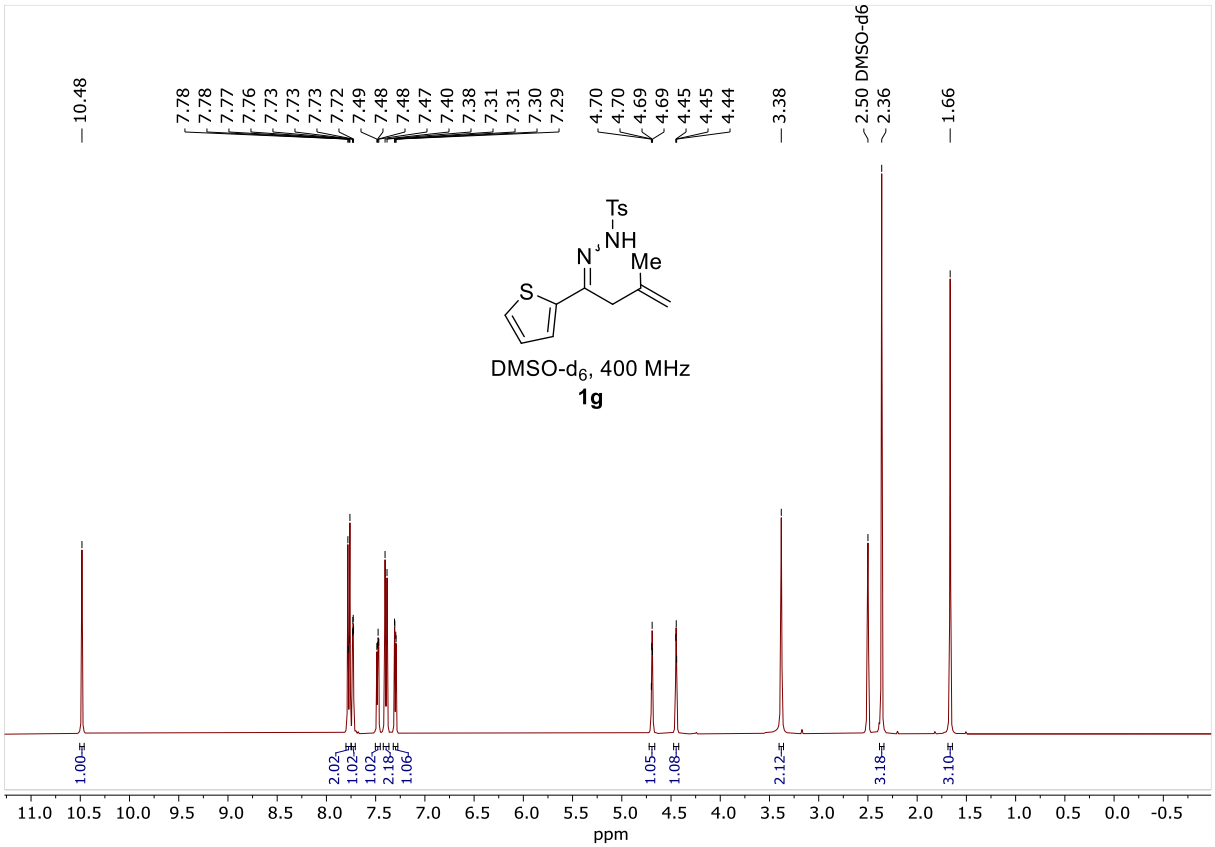


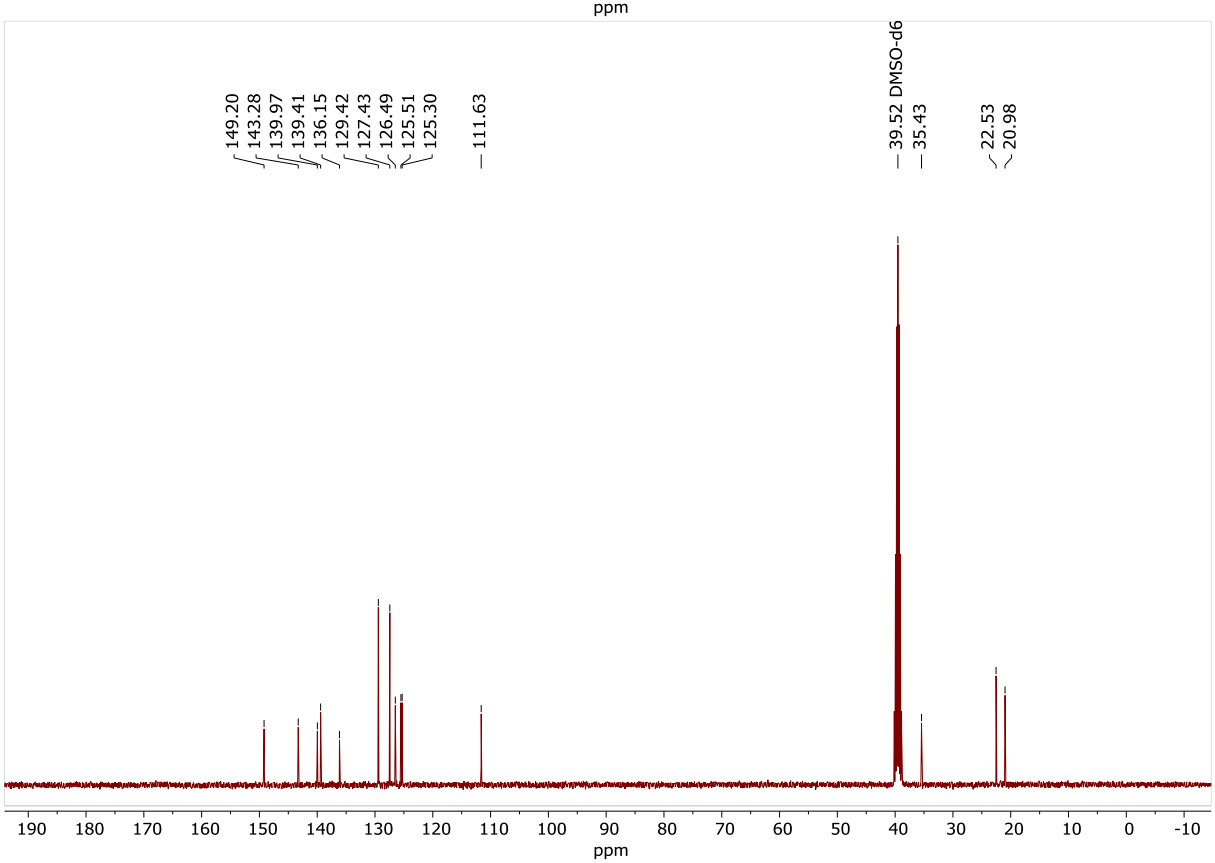
^{1}H NMR and ^{13}C NMR spectrum of compound **1f**



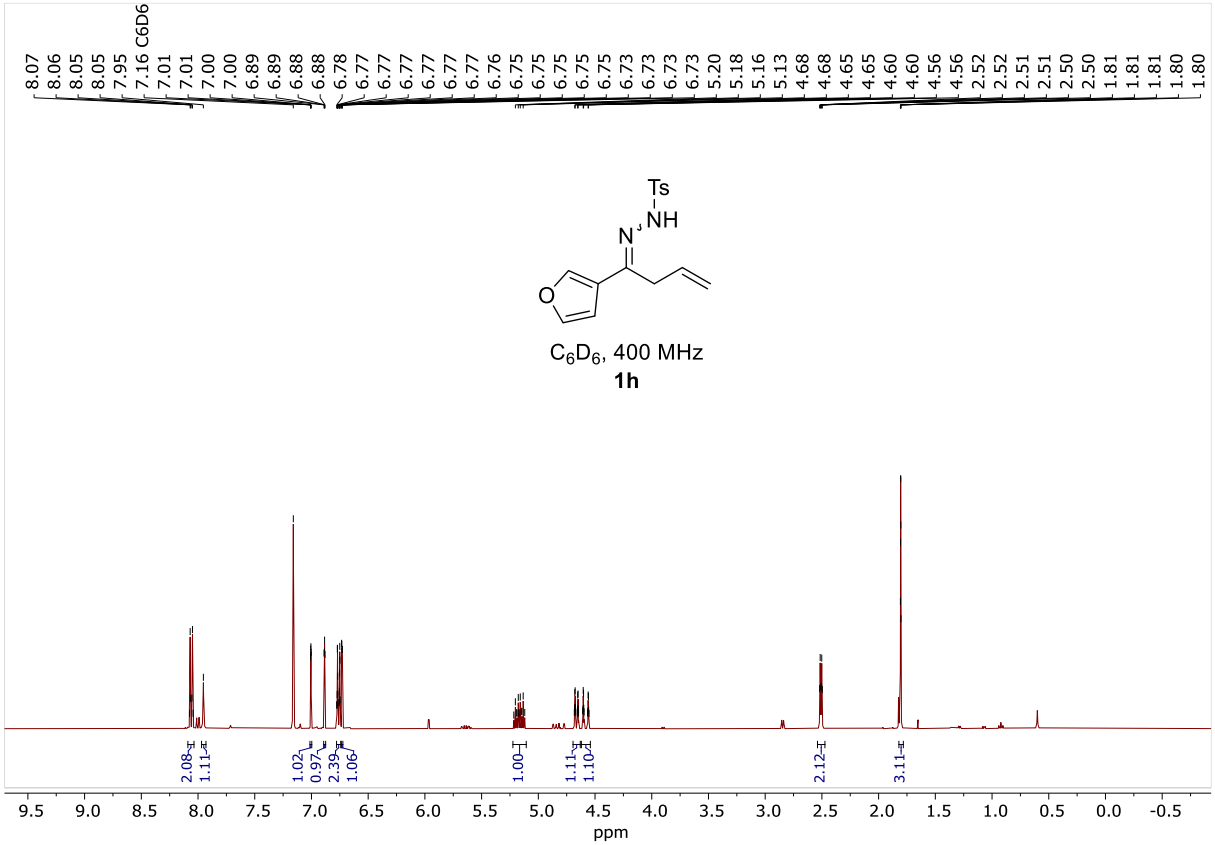


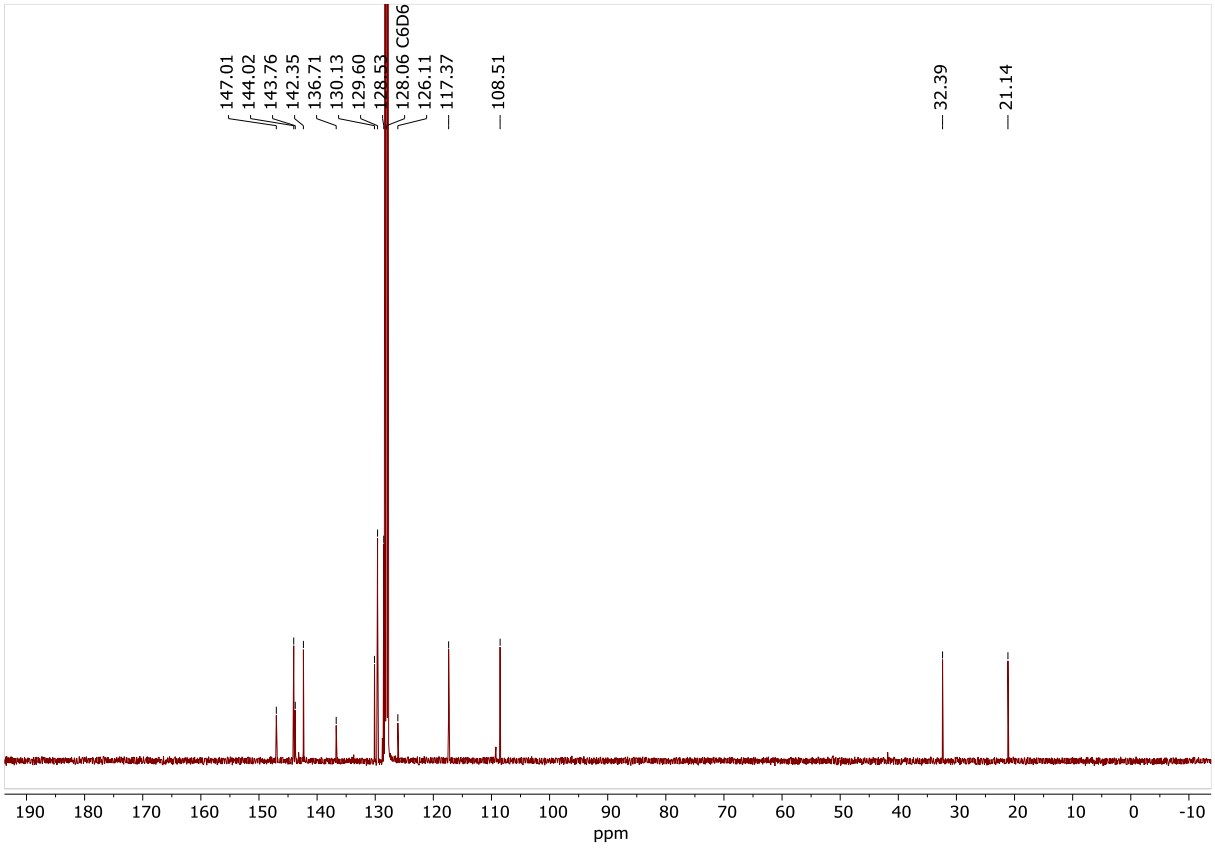
^{1}H NMR and ^{13}C NMR spectrum of compound **1g**



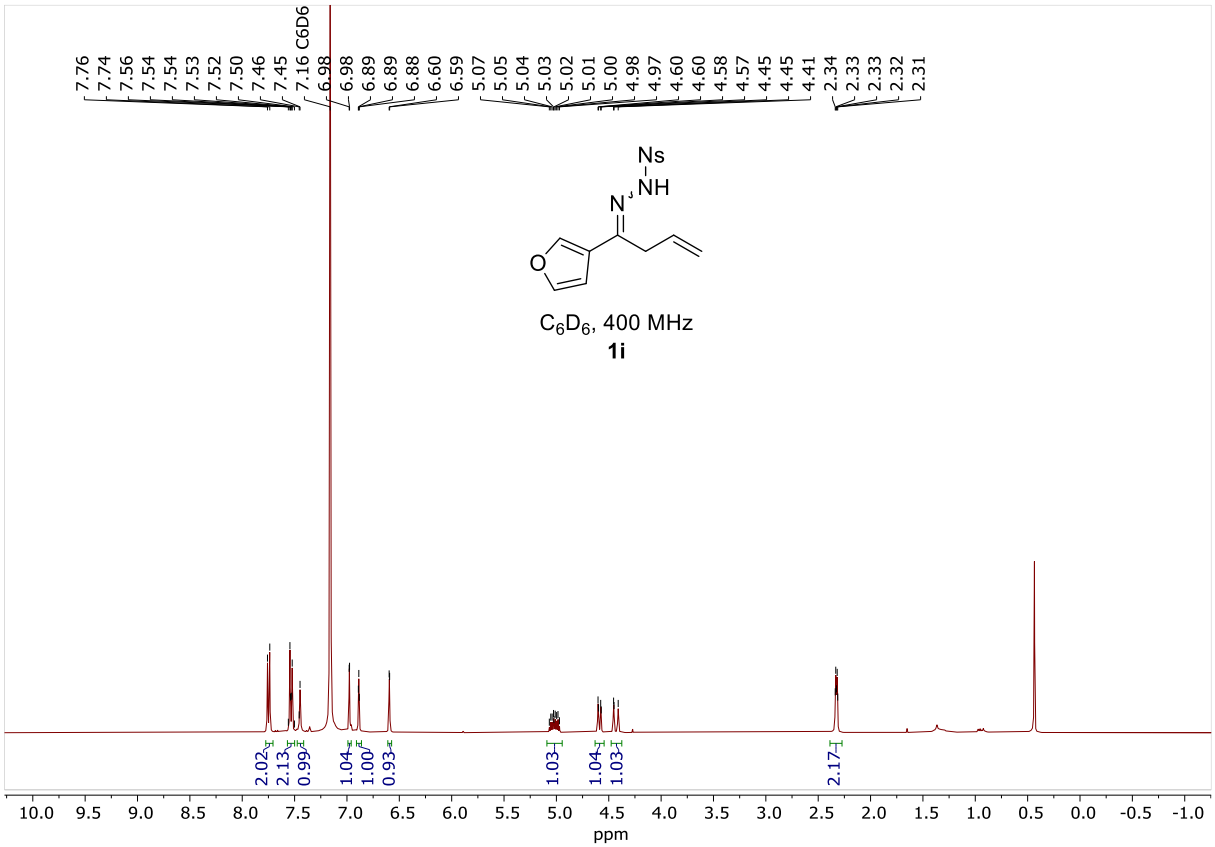


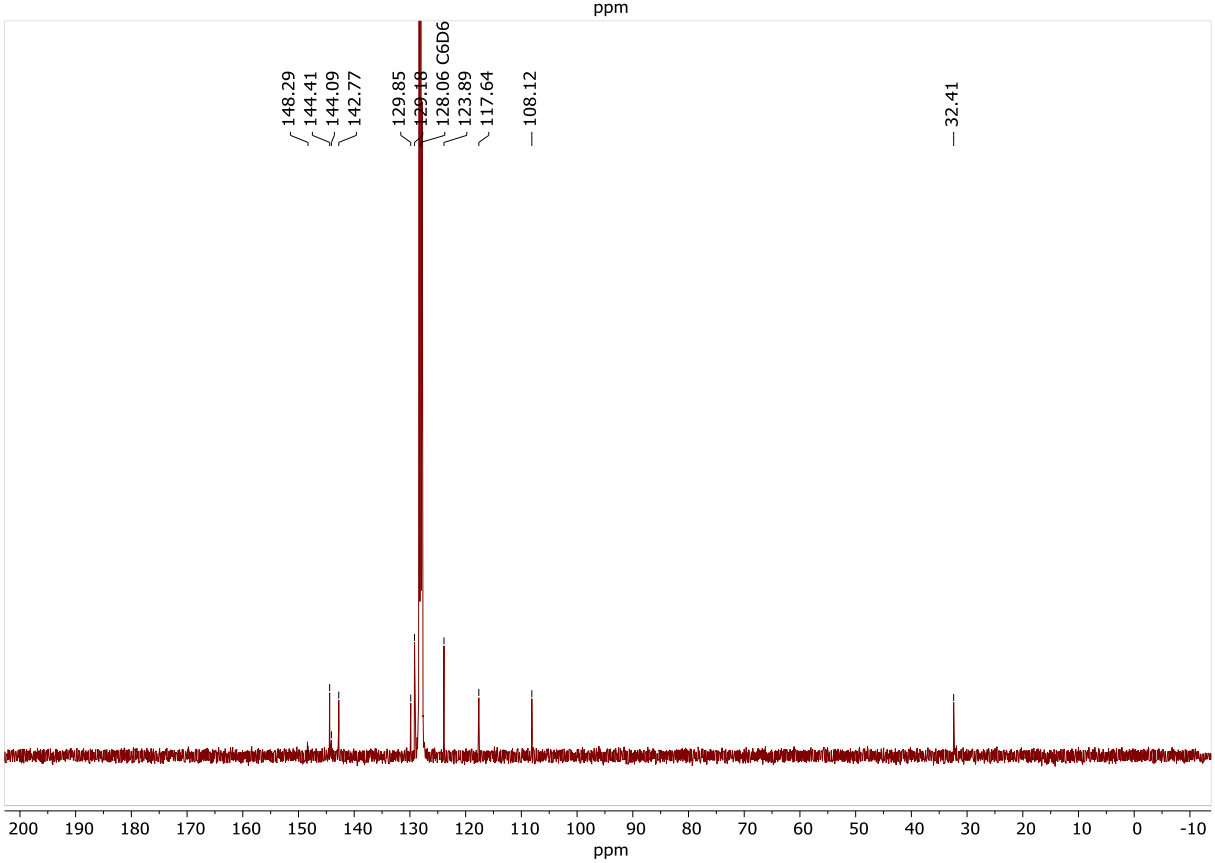
^{1}H NMR and ^{13}C NMR spectrum of compound **1h**



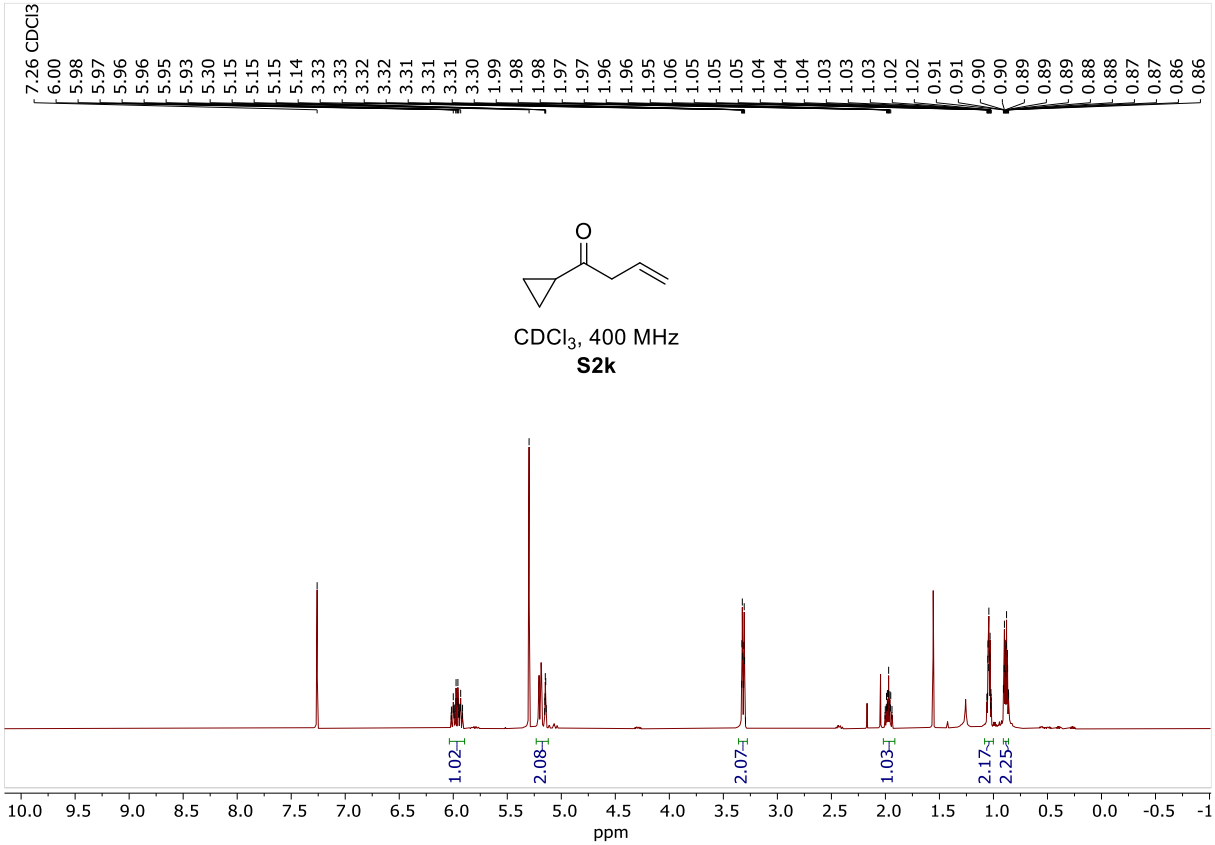


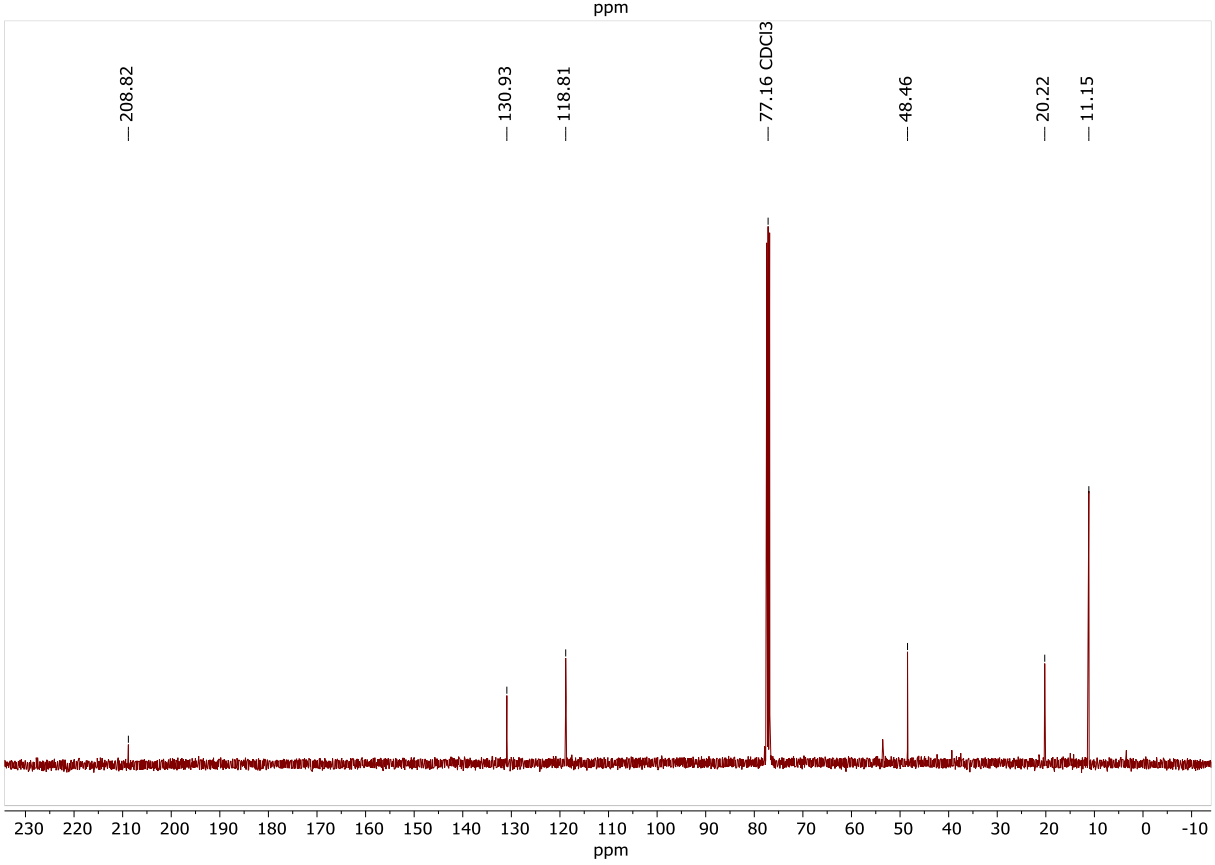
^{1}H NMR and ^{13}C NMR spectrum of compound **1i**



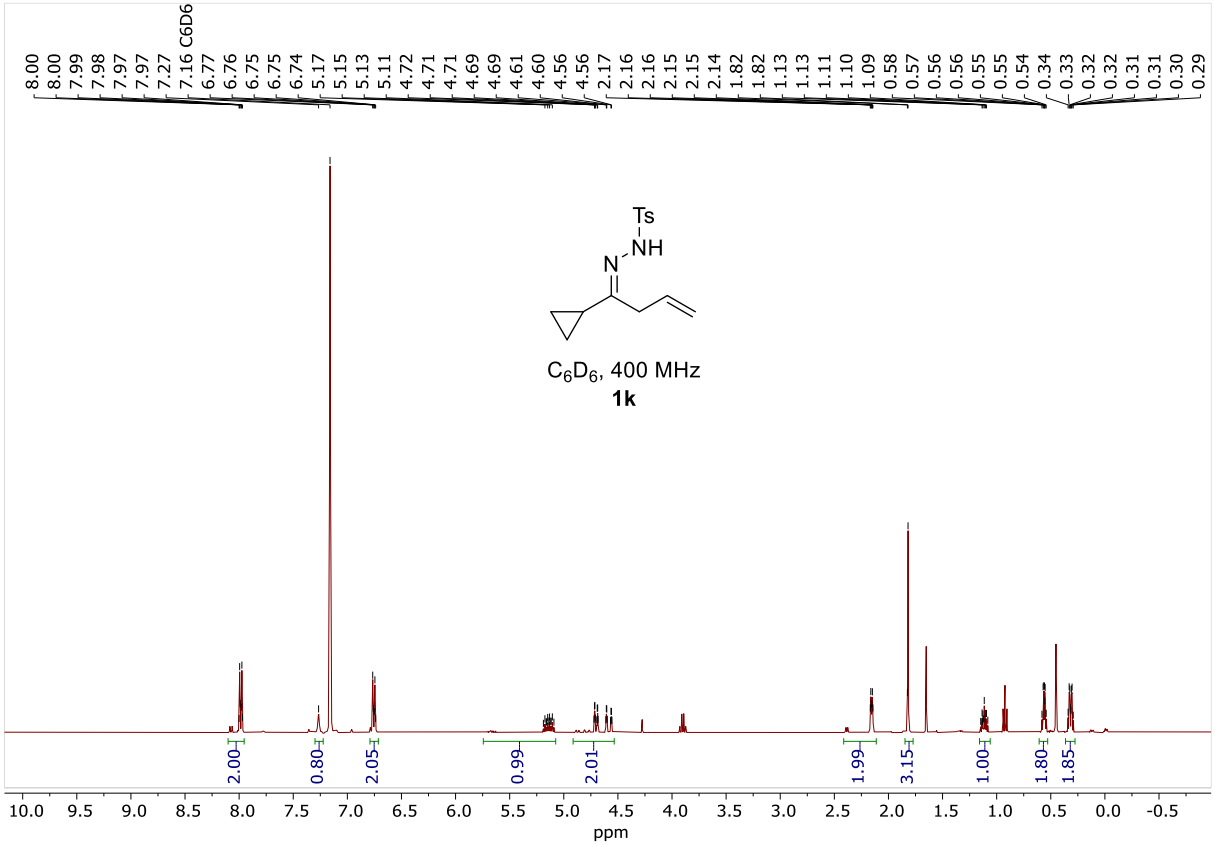


^{1}H NMR and ^{13}C NMR spectrum of compound **S2k**

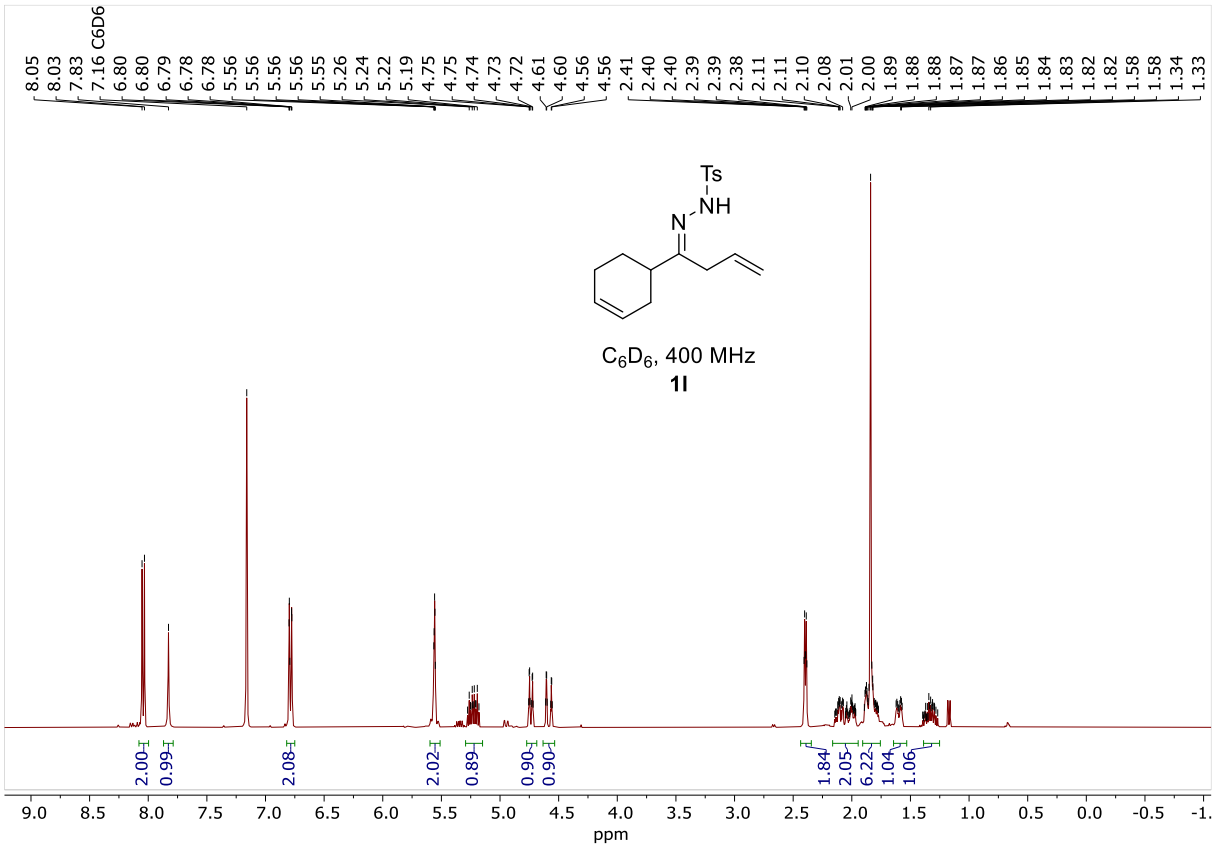


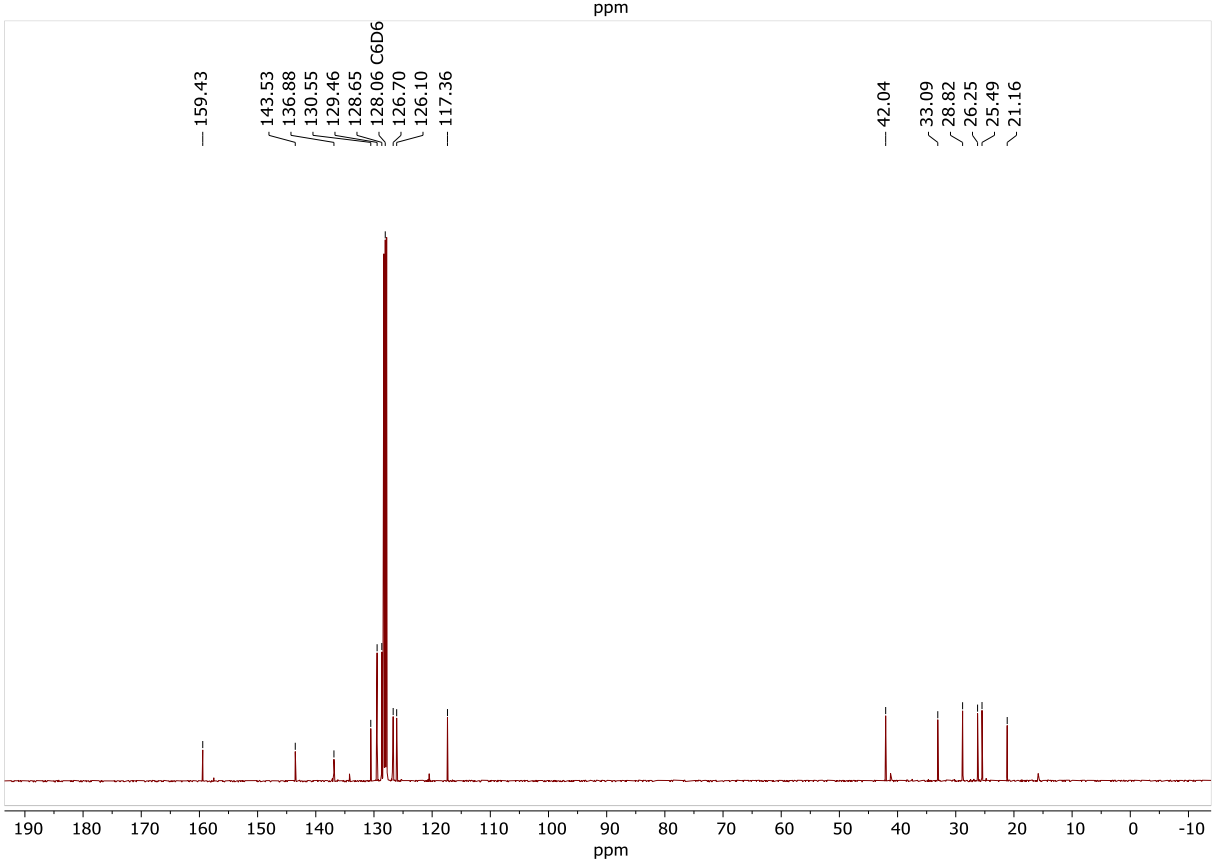


^{1}H NMR and ^{13}C NMR spectrum of compound **1k**

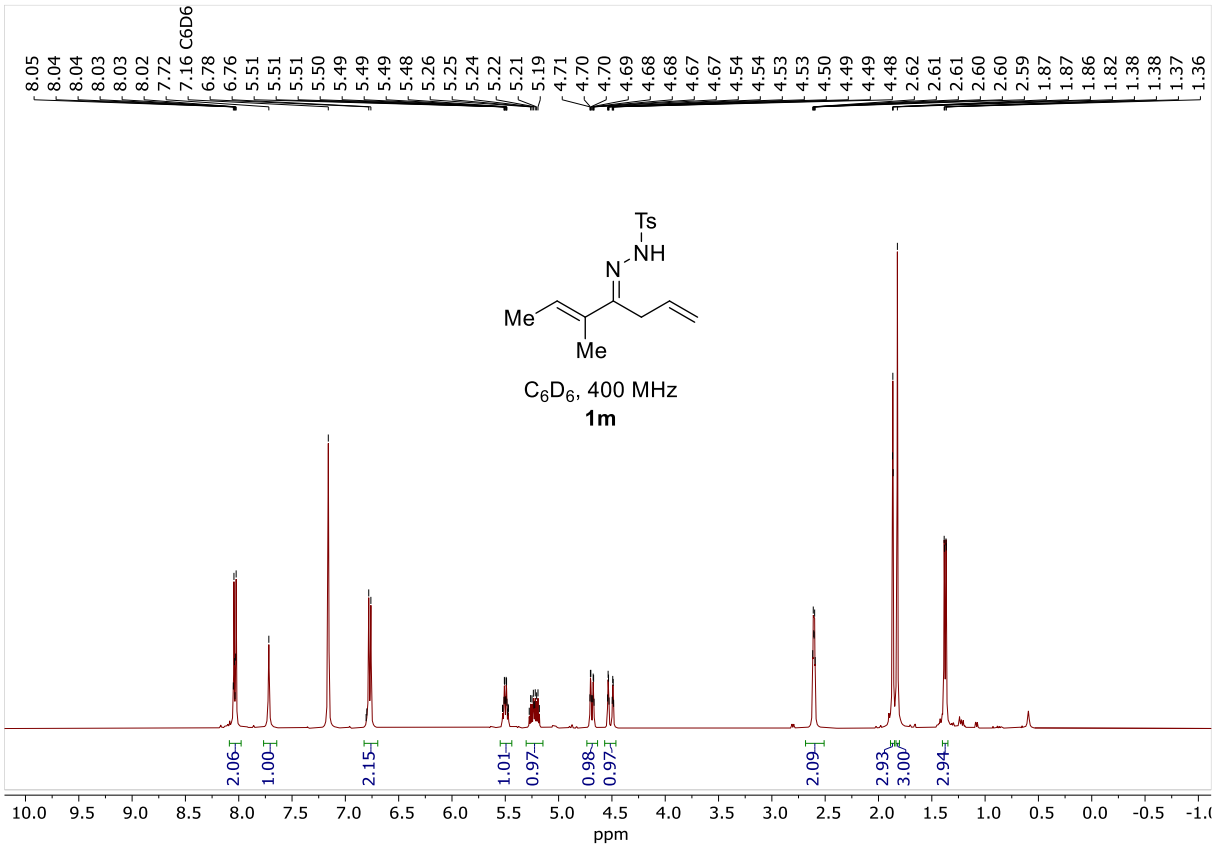


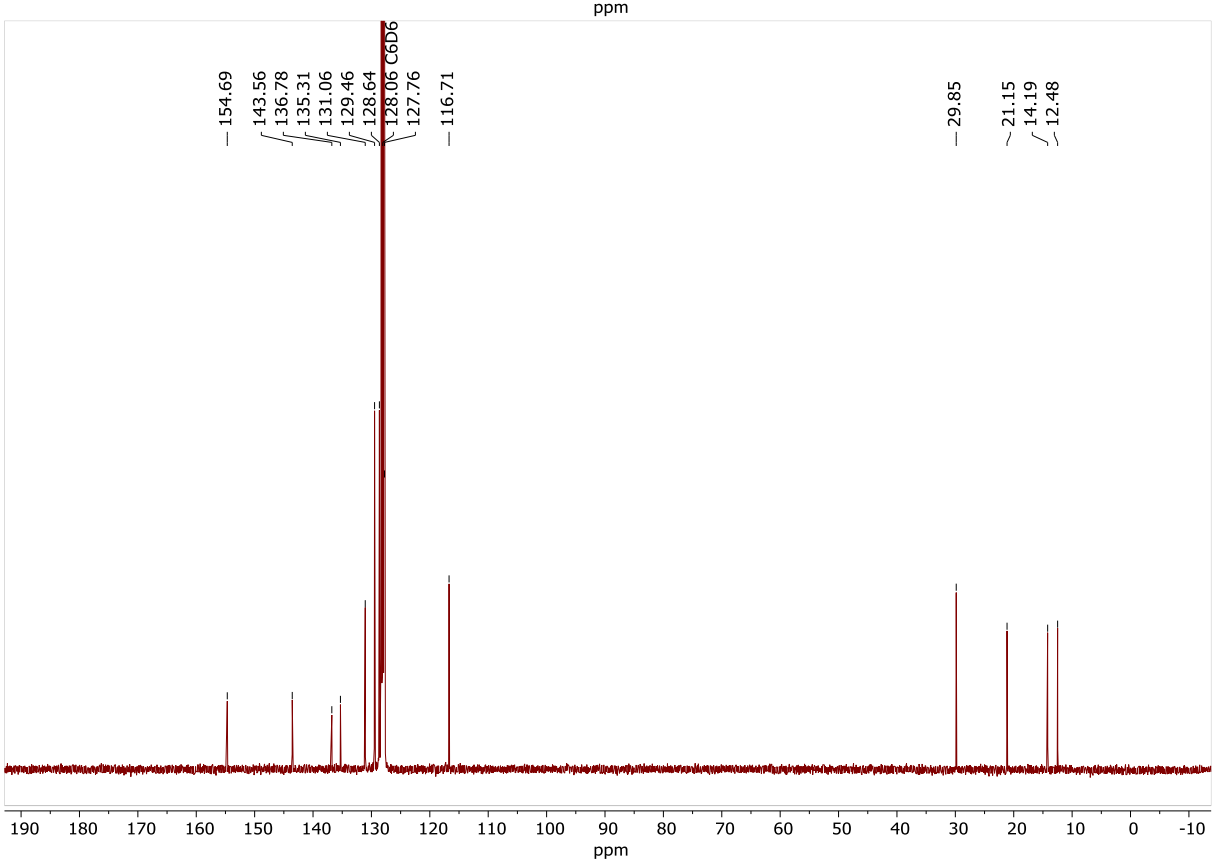
^{1}H NMR and ^{13}C NMR spectrum of compound **1l**



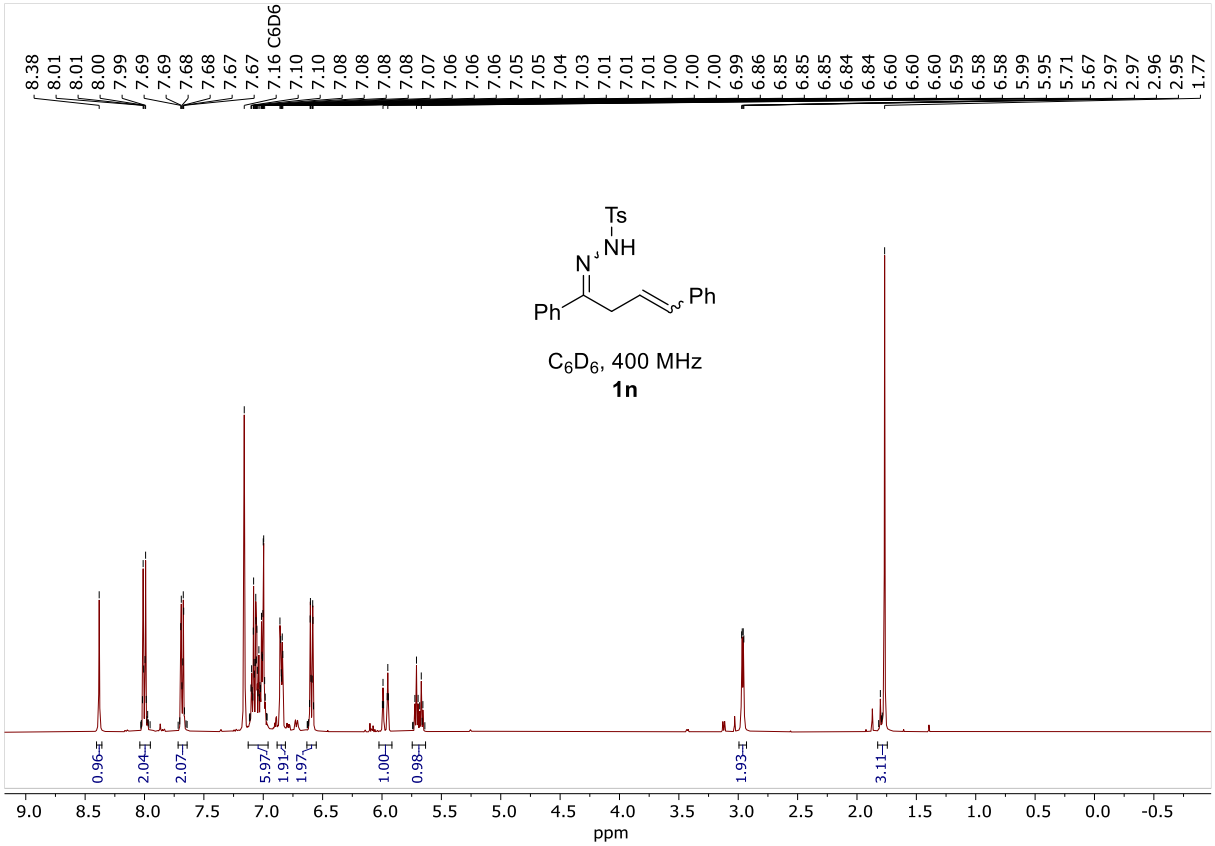


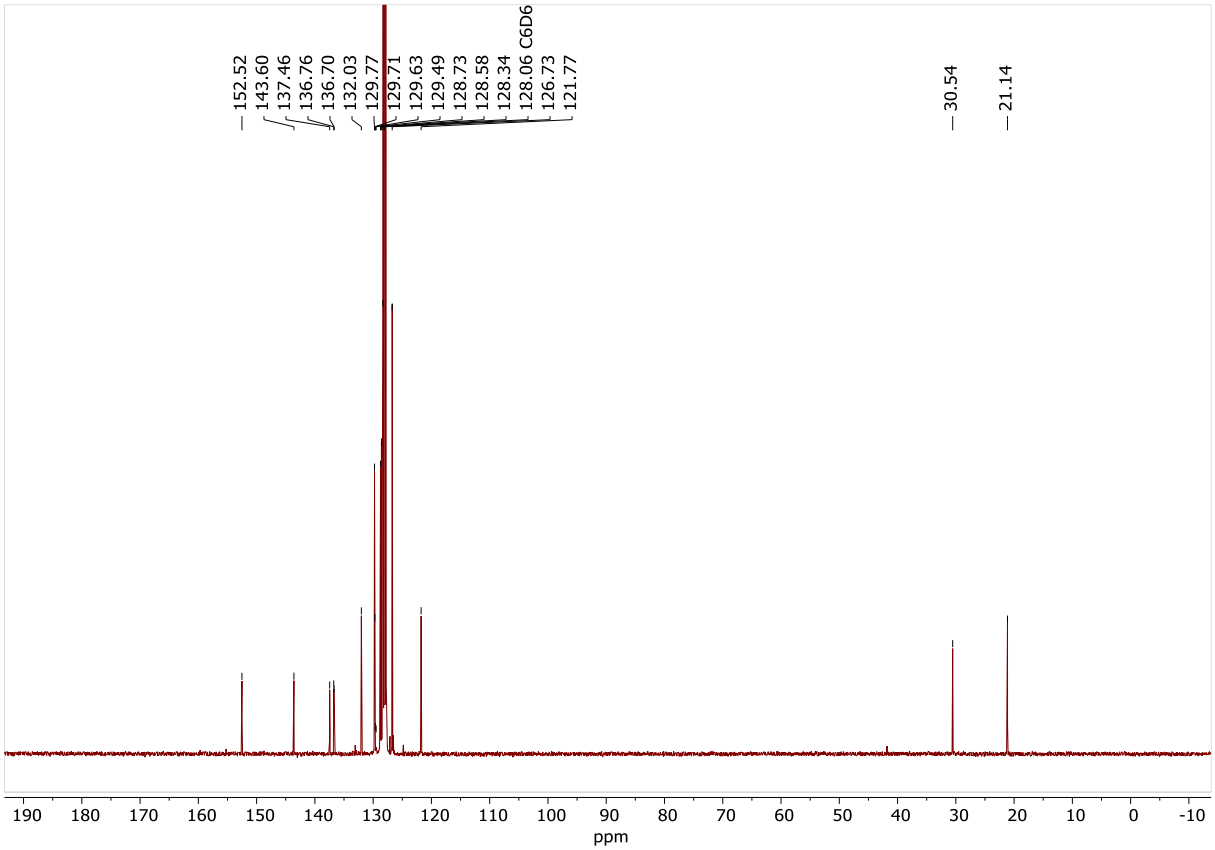
^{1}H NMR and ^{13}C NMR spectrum of compound **1m**



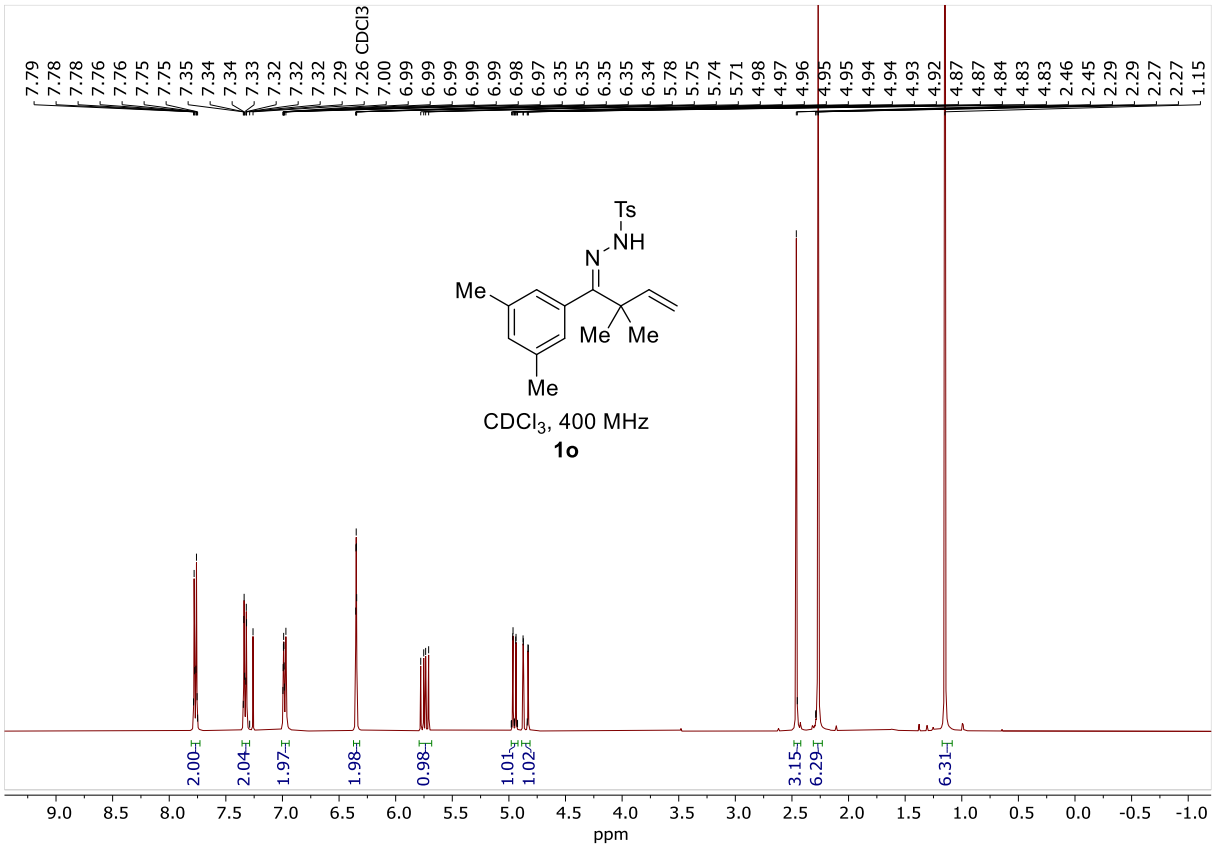


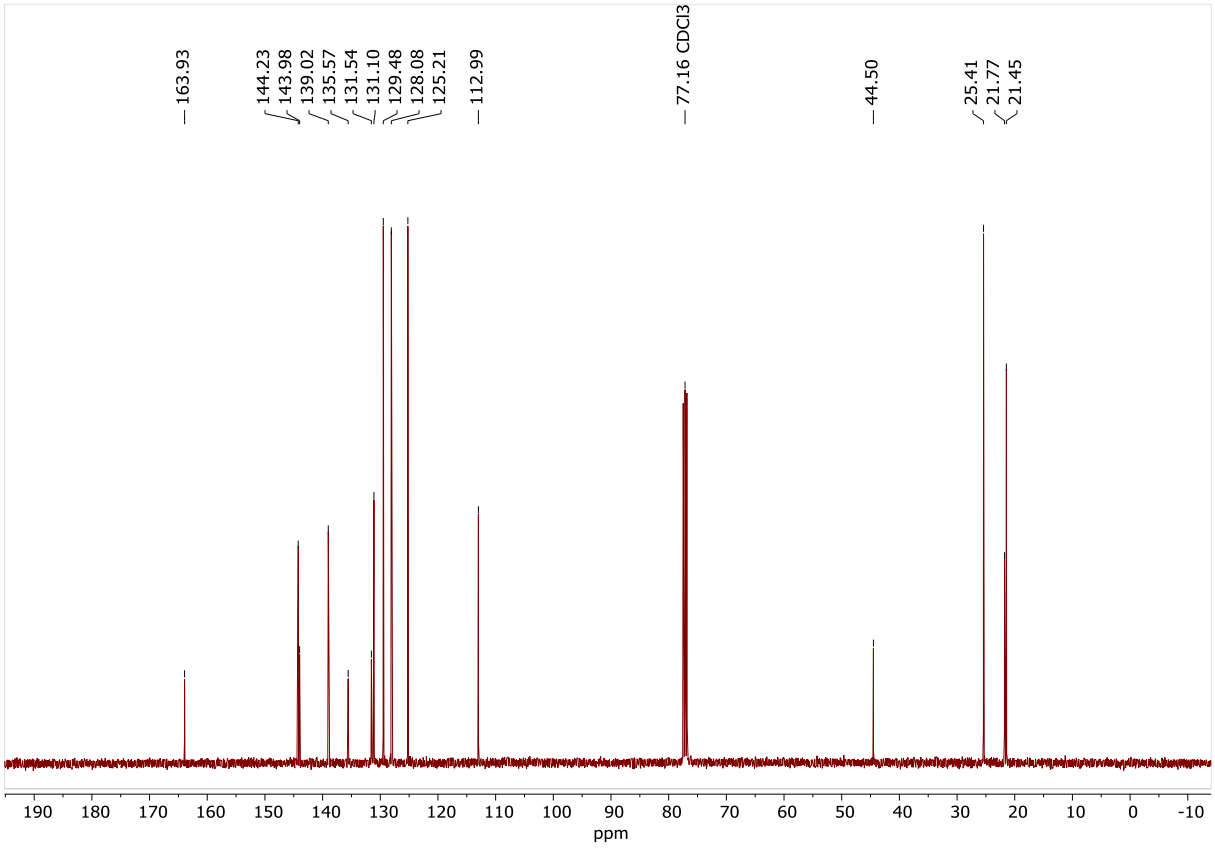
^{1}H NMR and ^{13}C NMR spectrum of compound **1n**



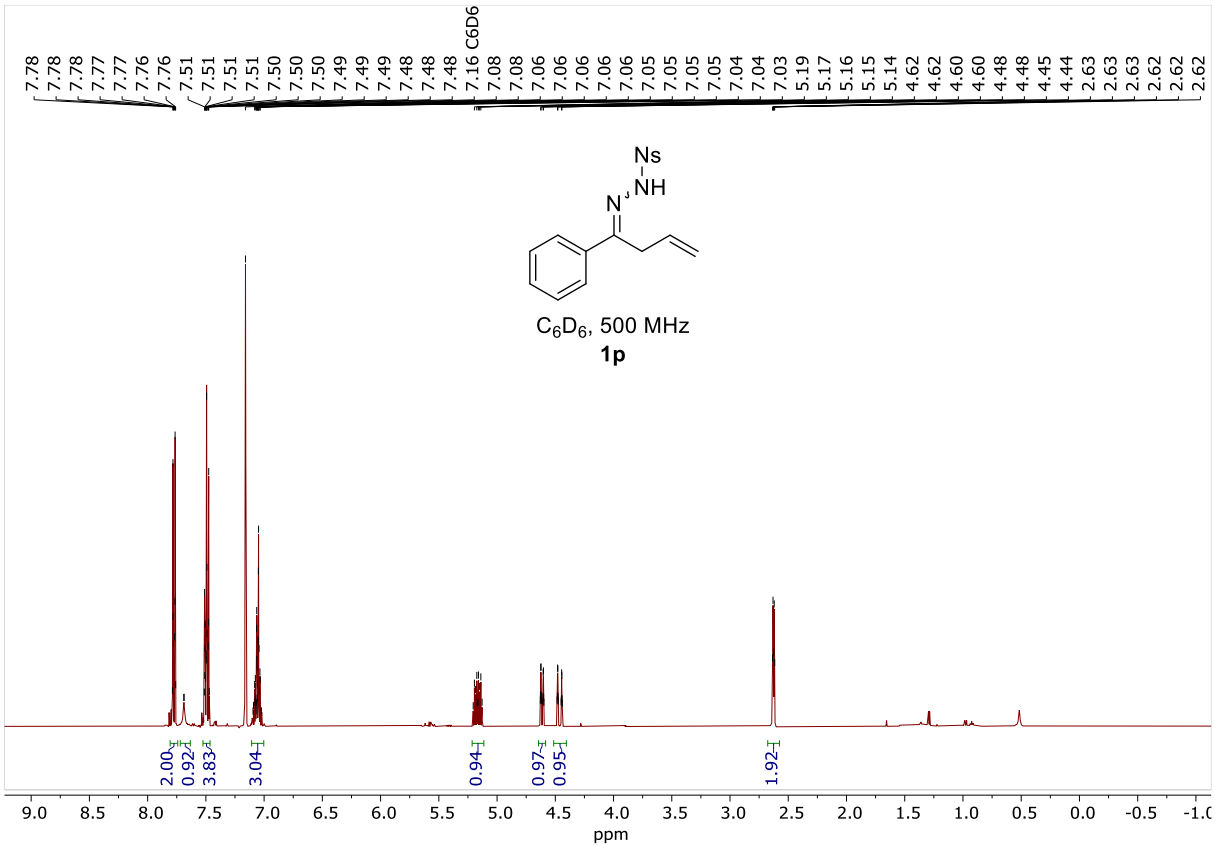


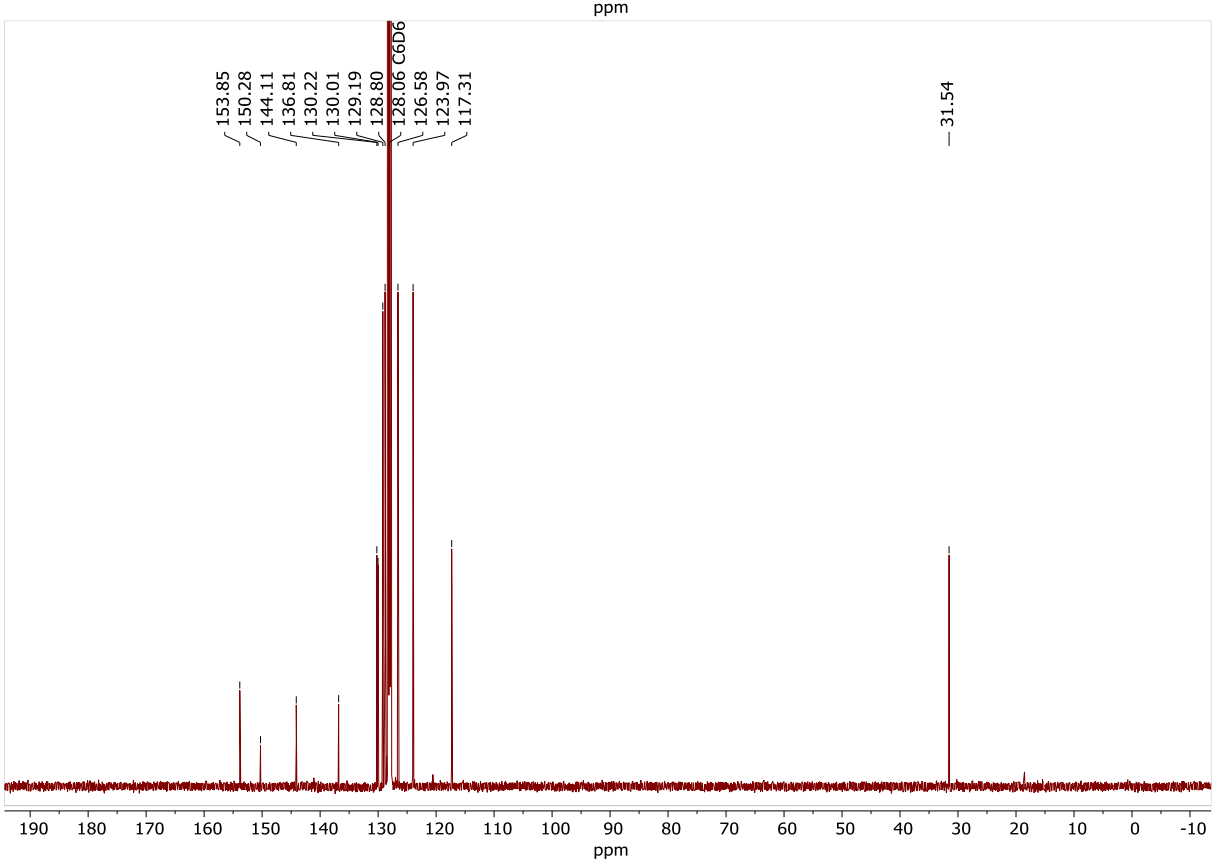
^{1}H NMR and ^{13}C NMR spectrum of compound **1o**



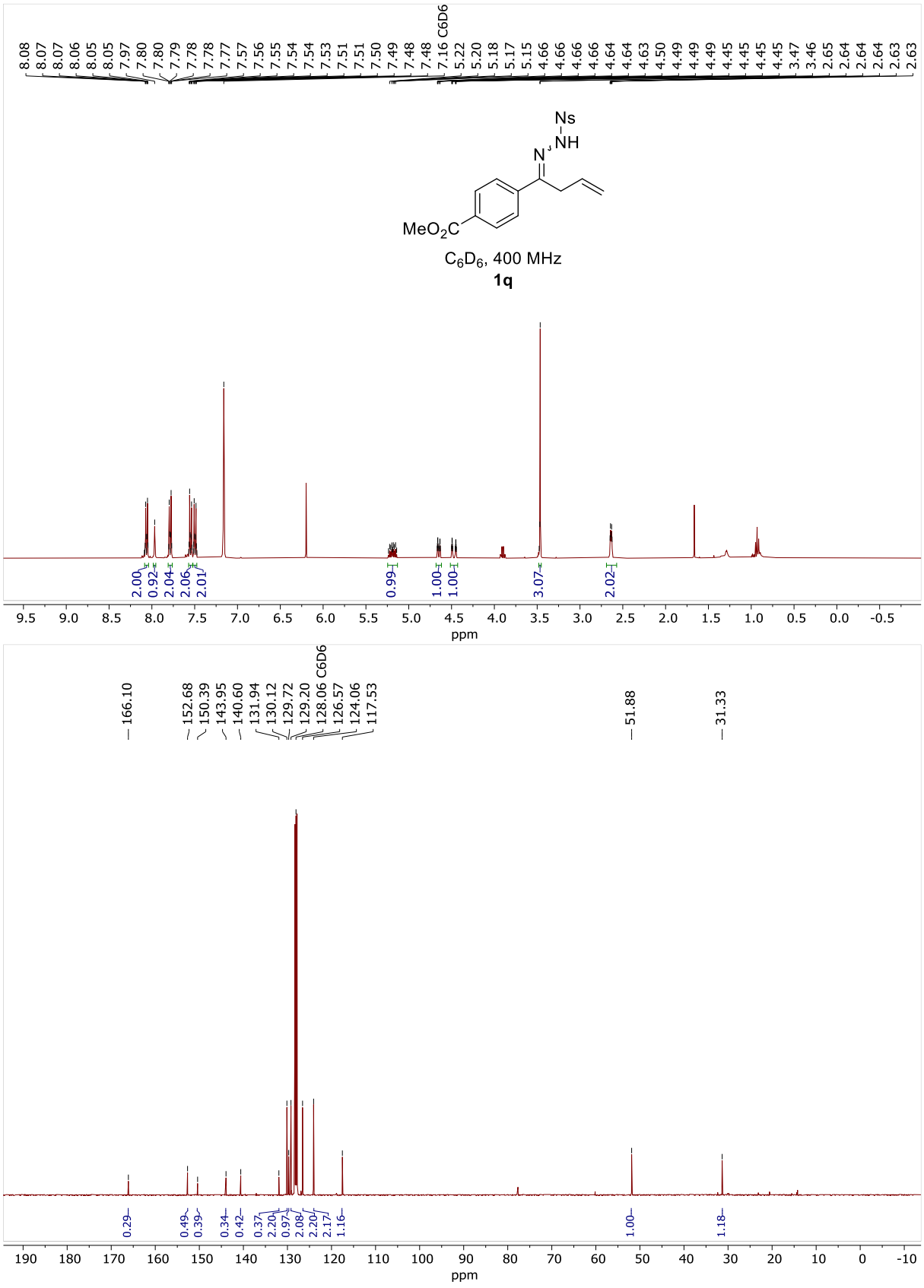


^{1}H NMR and ^{13}C NMR spectrum of compound **1p**

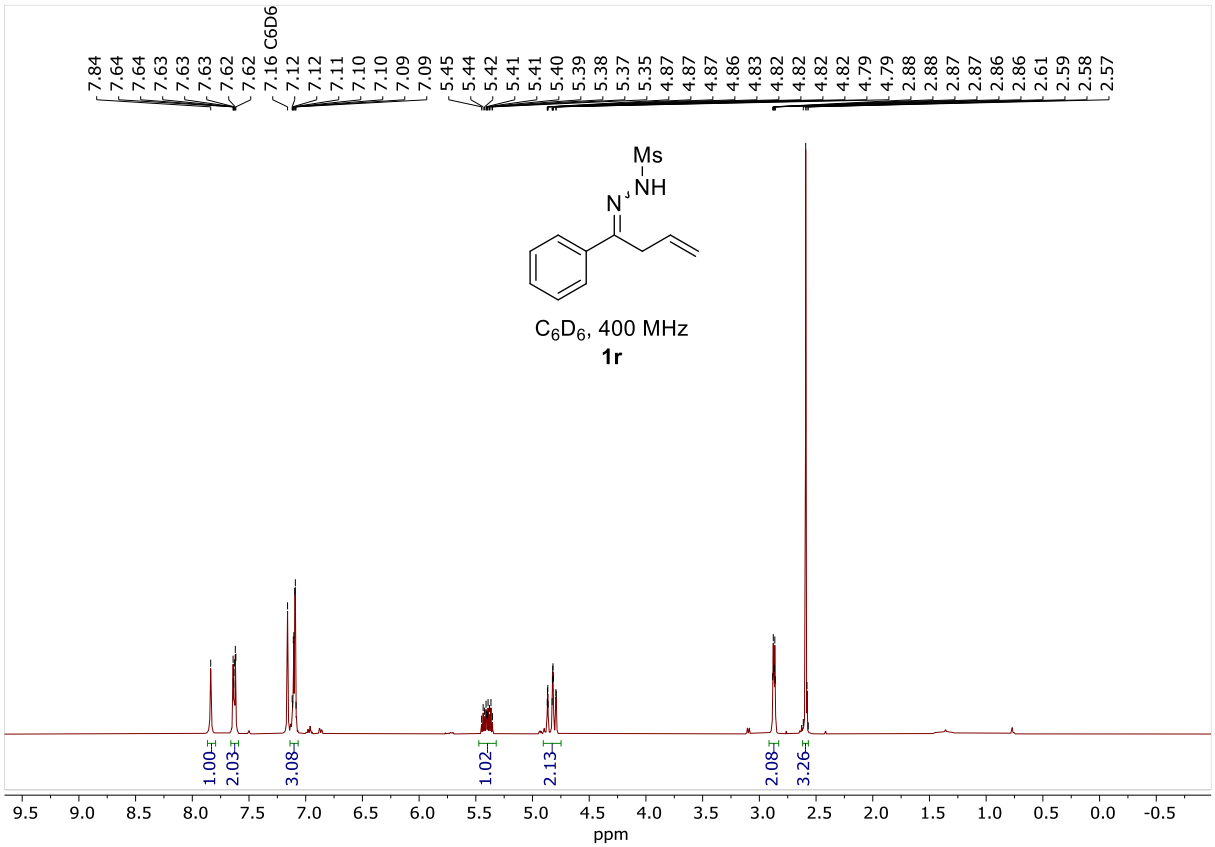


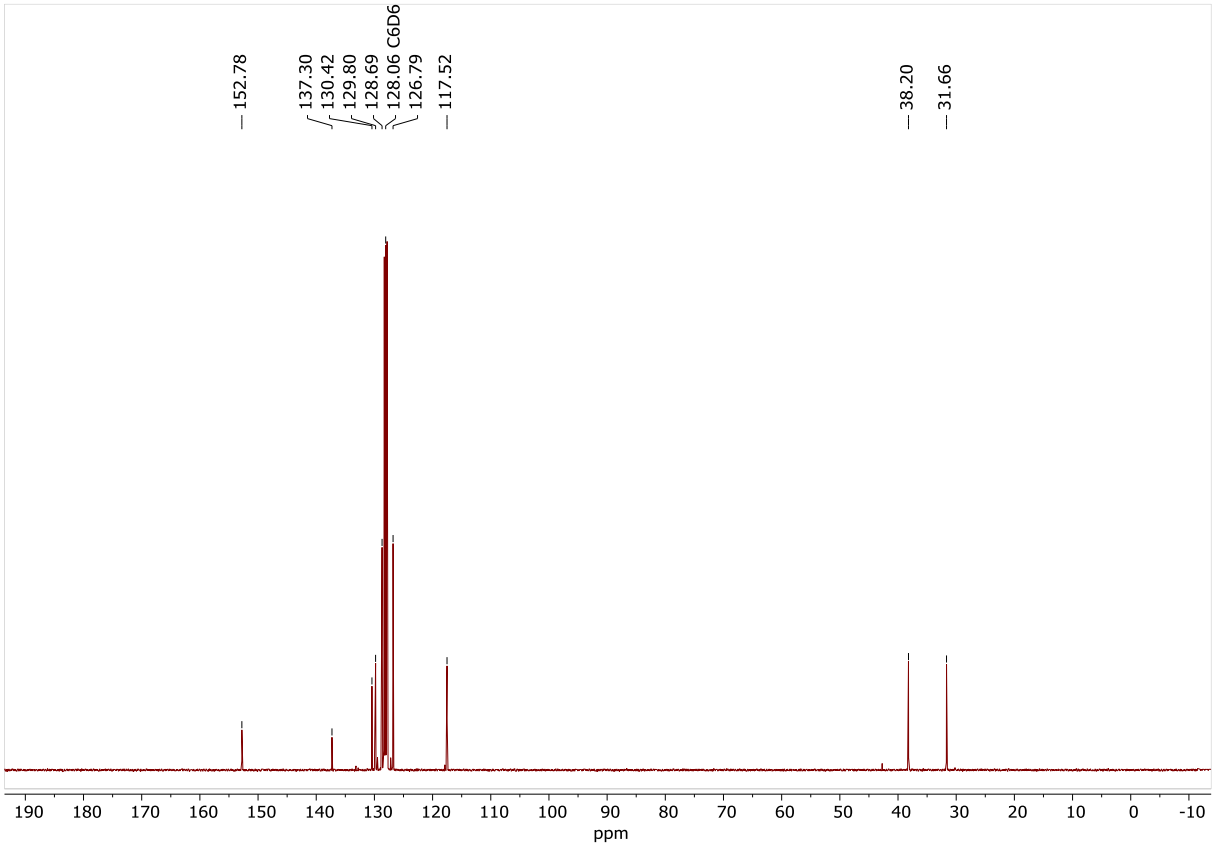


^{1}H NMR and ^{13}C NMR spectrum of compound **1q**

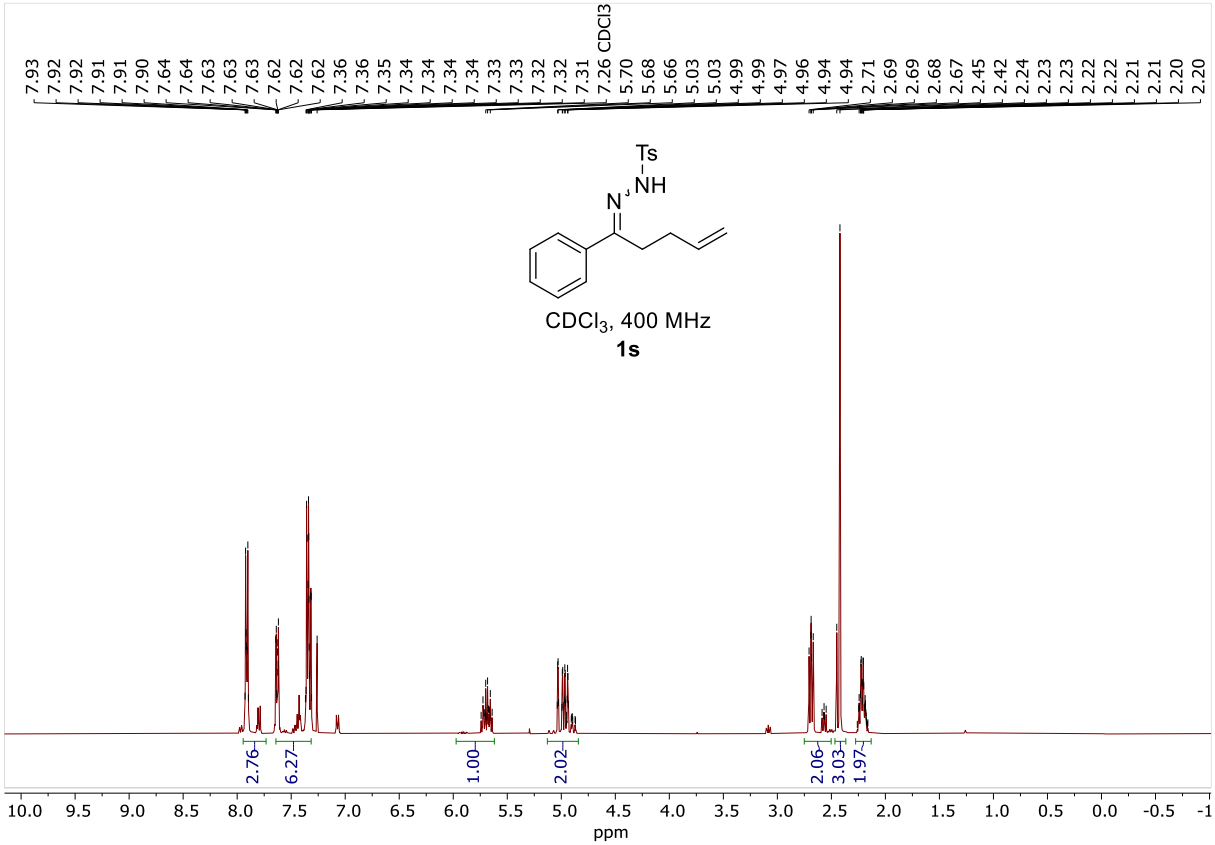


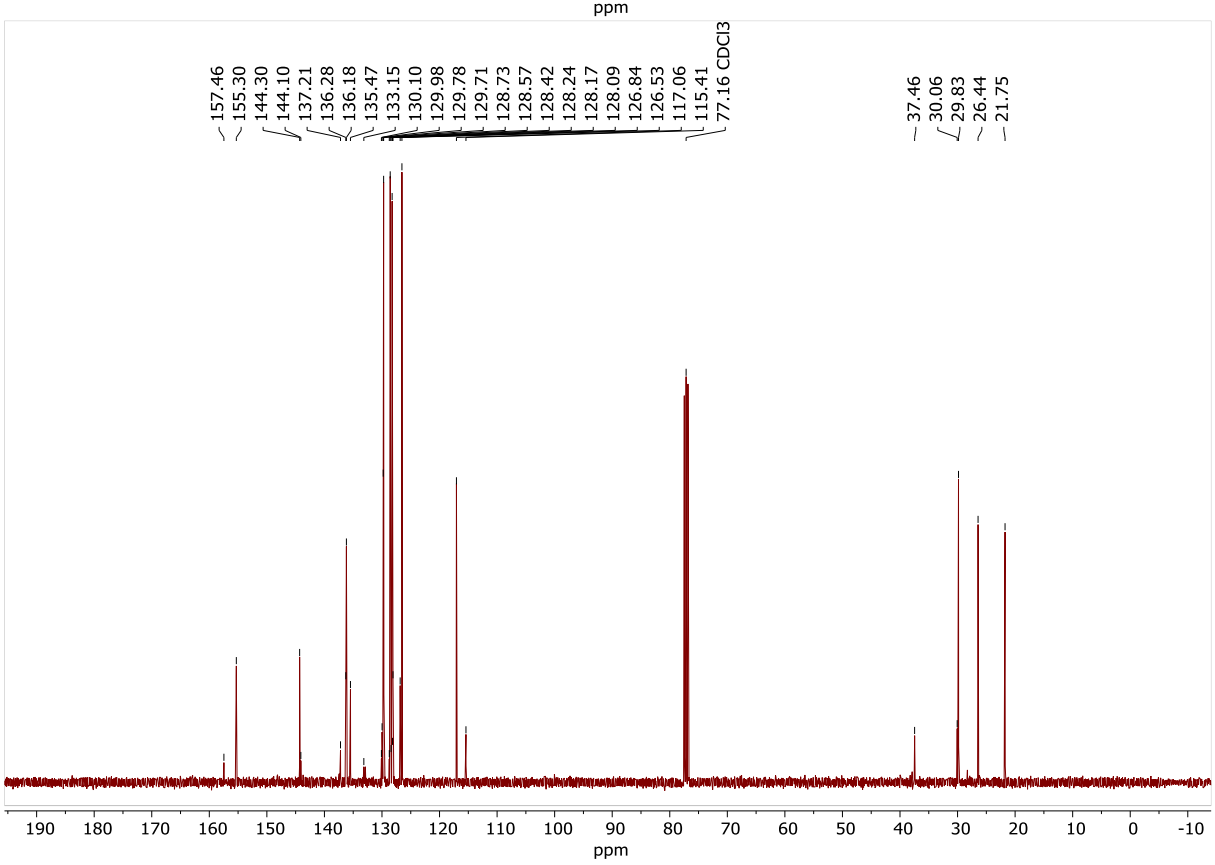
^{1}H NMR and ^{13}C NMR spectrum of compound **1r**



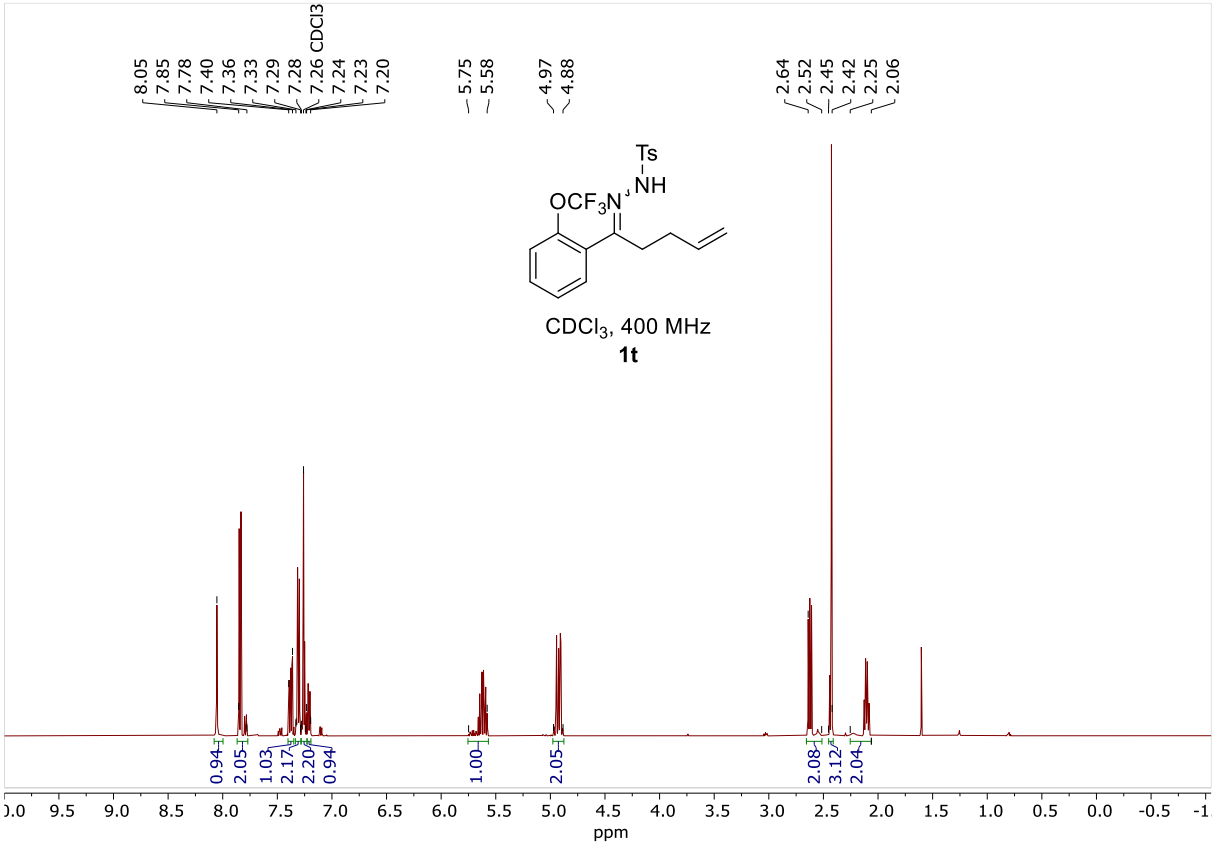


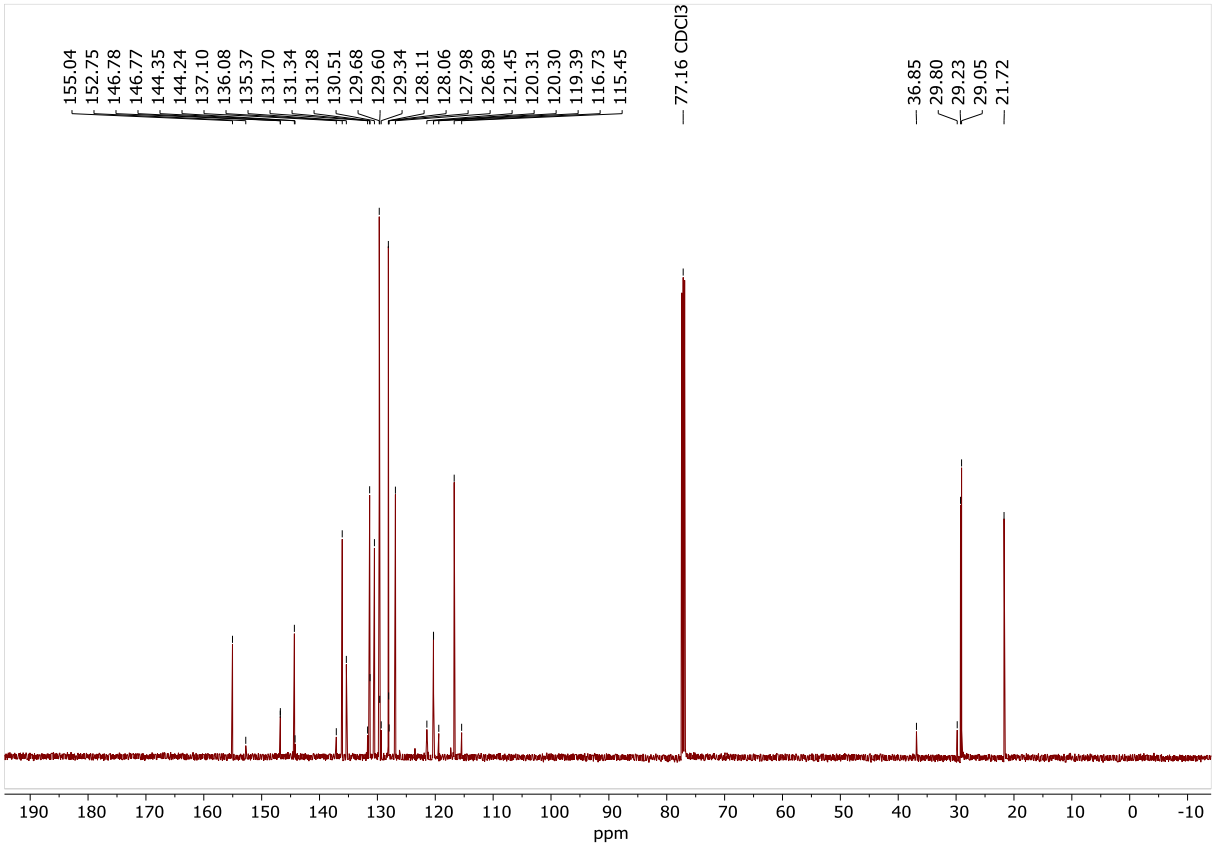
^{1}H NMR and ^{13}C NMR spectrum of compound **1s**



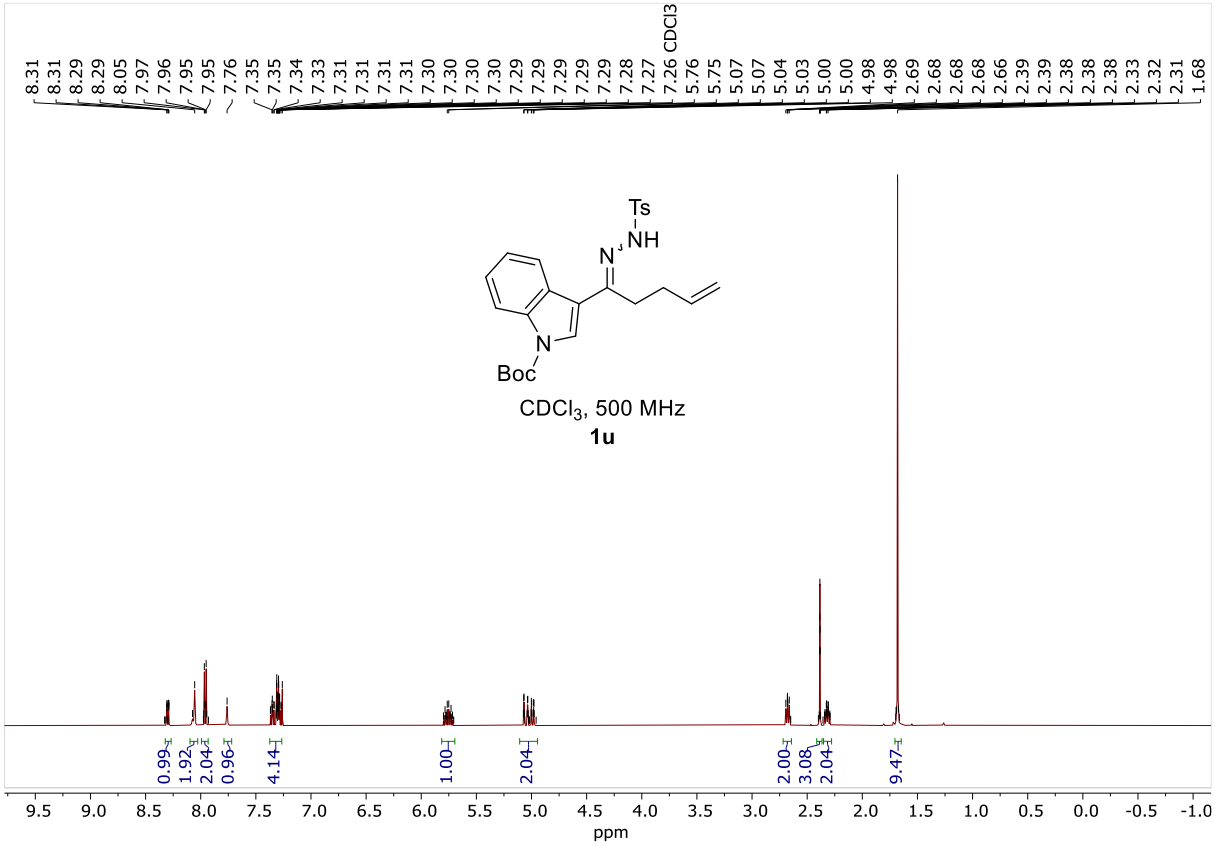


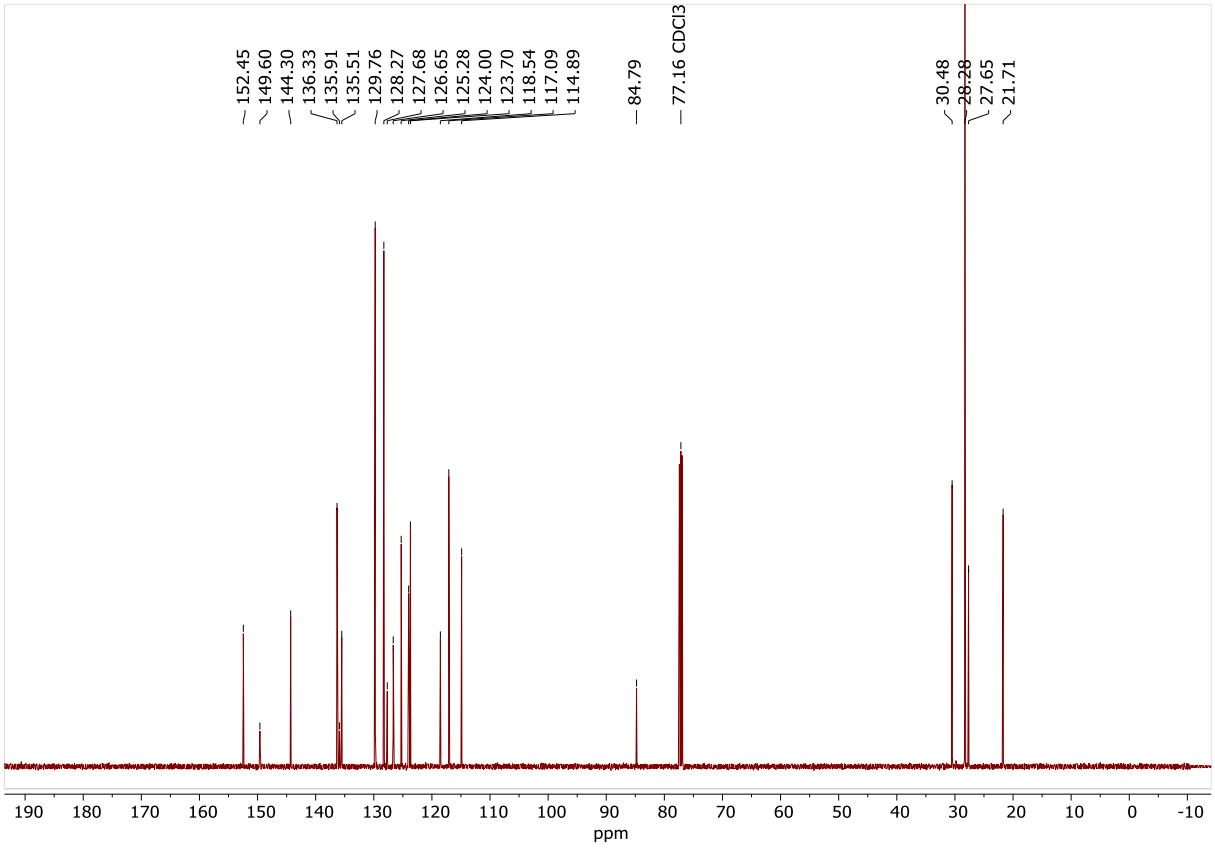
^{1}H NMR and ^{13}C NMR spectrum of compound **1t**



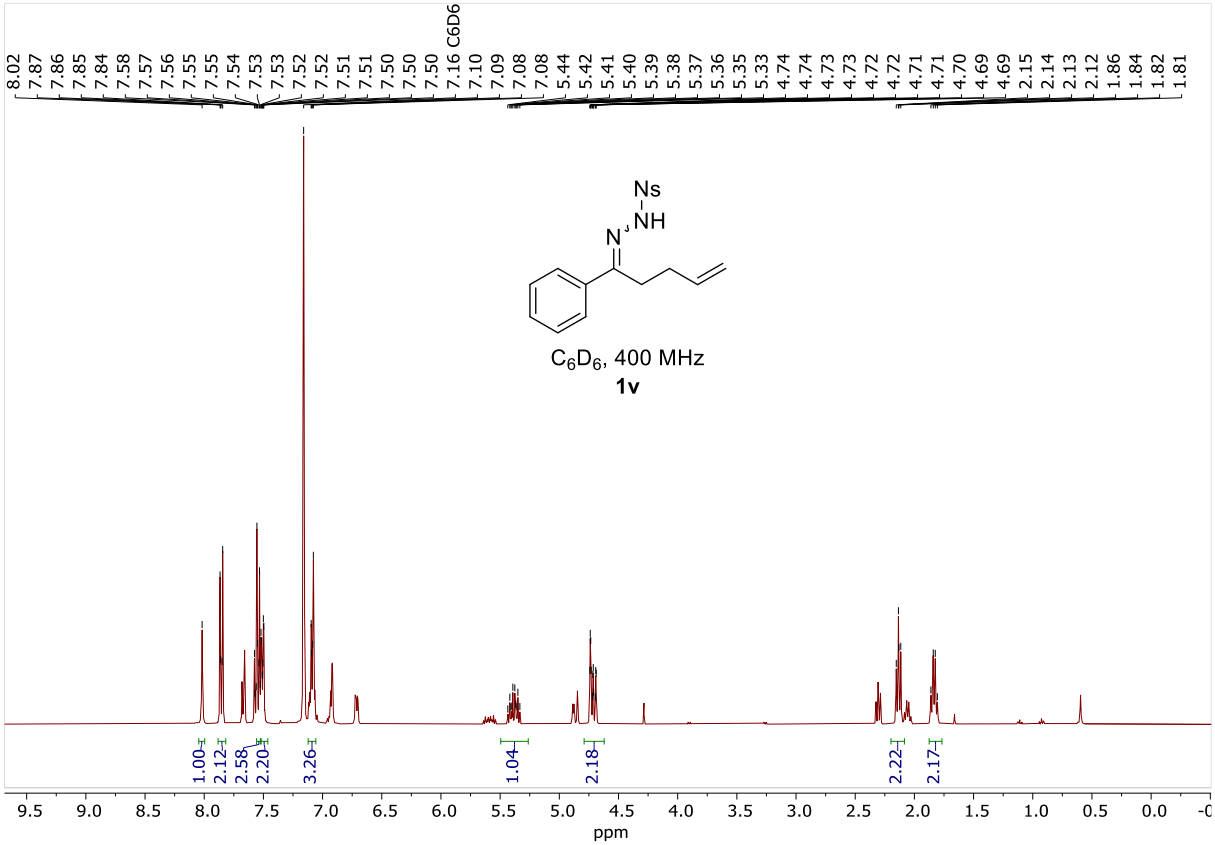


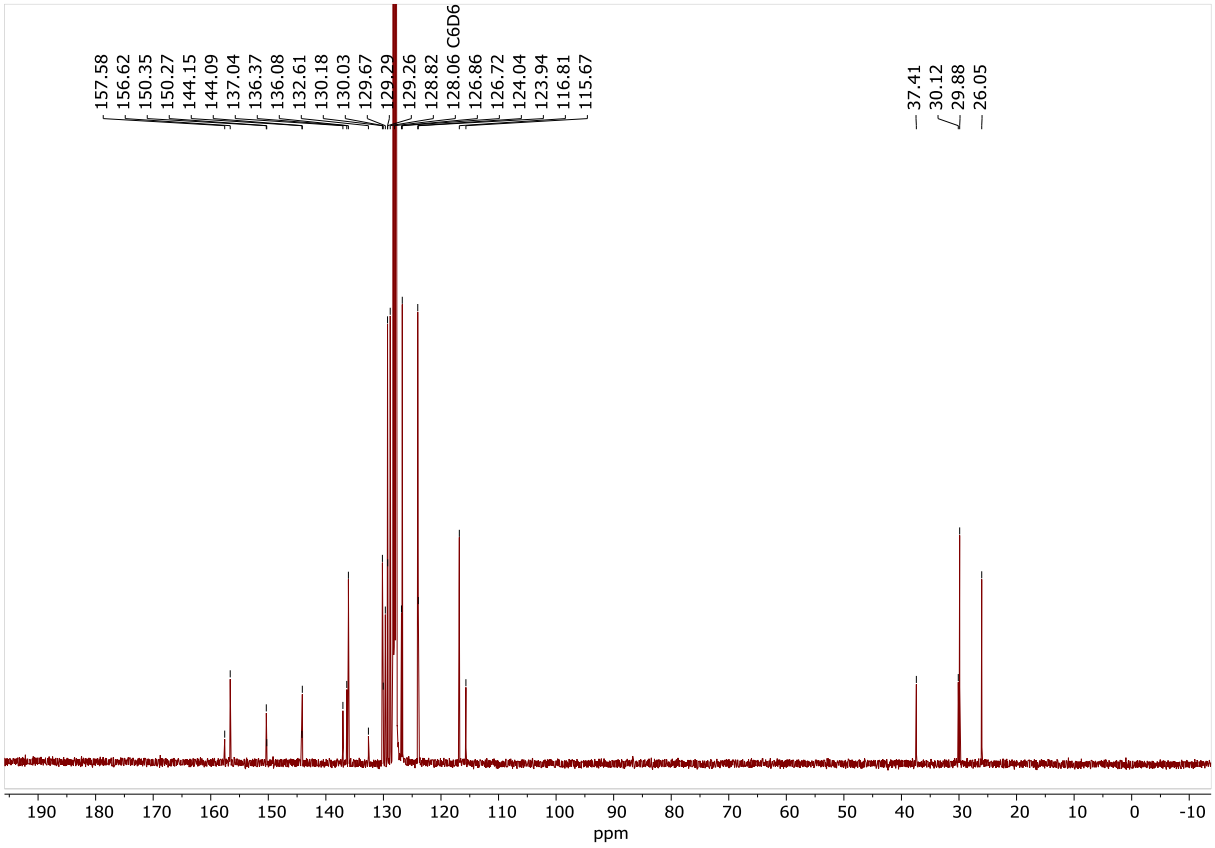
^{1}H NMR and ^{13}C NMR spectrum of compound **1u**



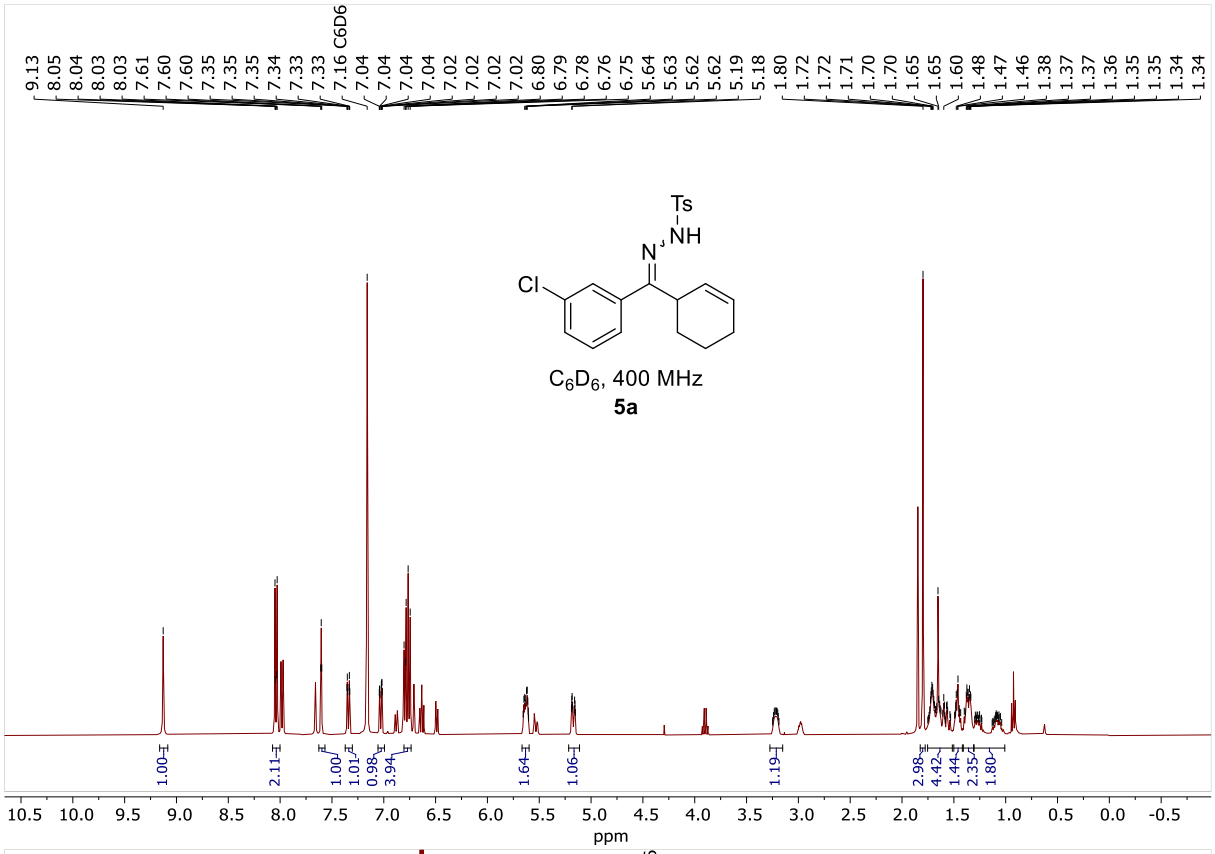


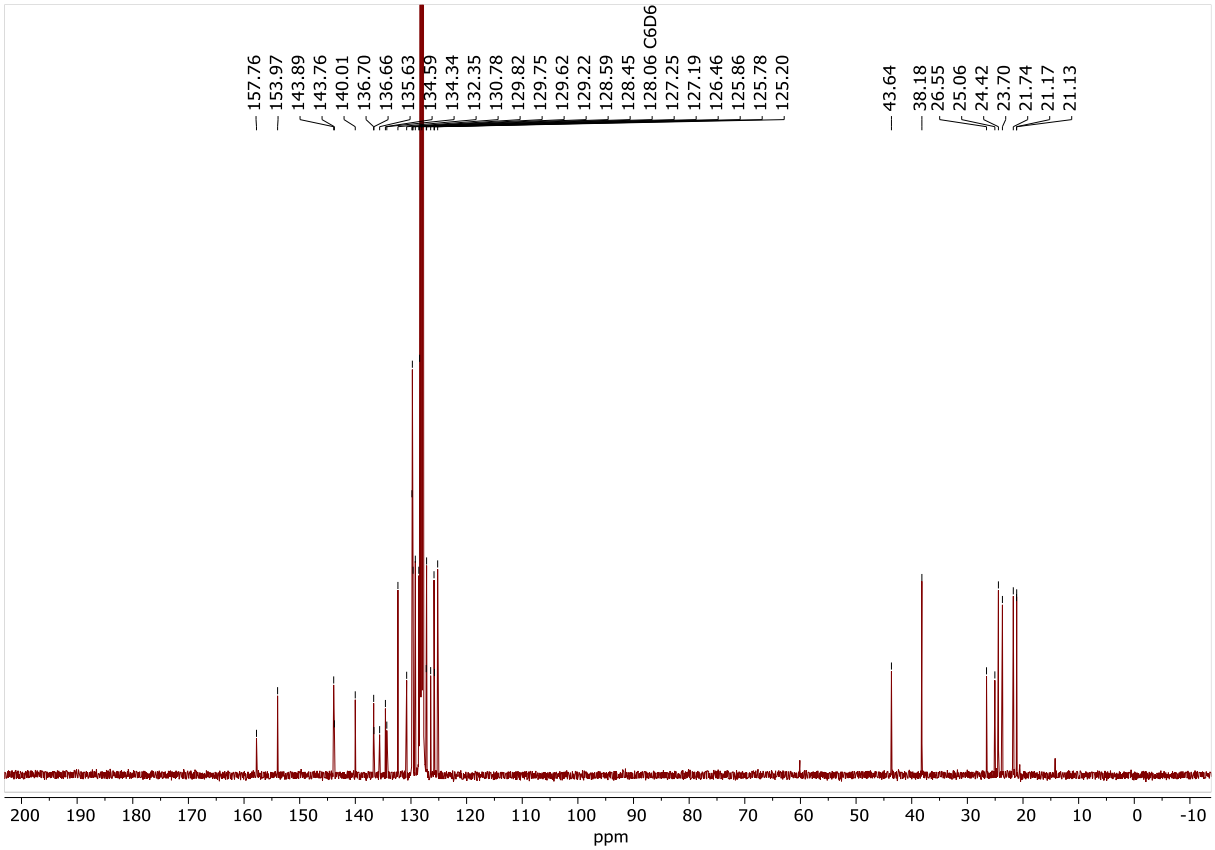
^{1}H NMR and ^{13}C NMR spectrum of compound **1v**



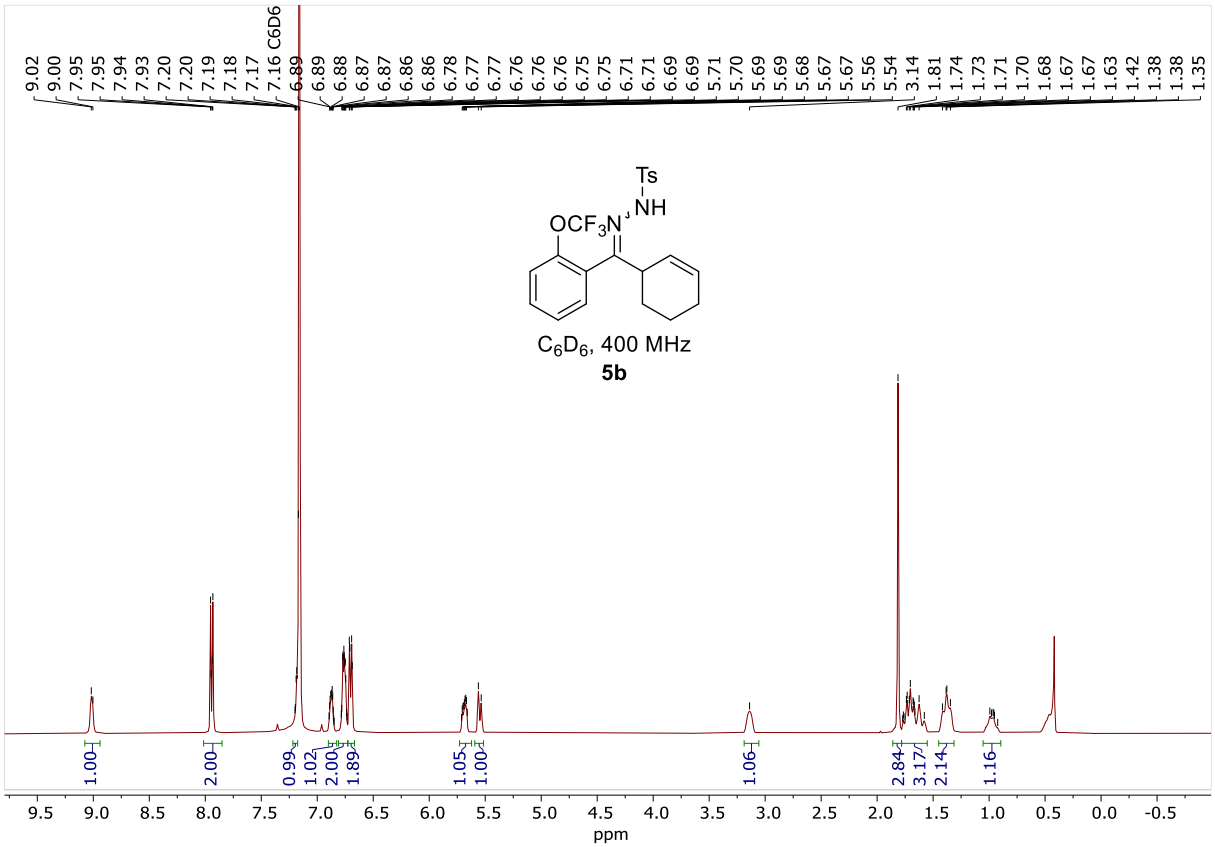


^{1}H NMR and ^{13}C NMR spectrum of compound **5a**

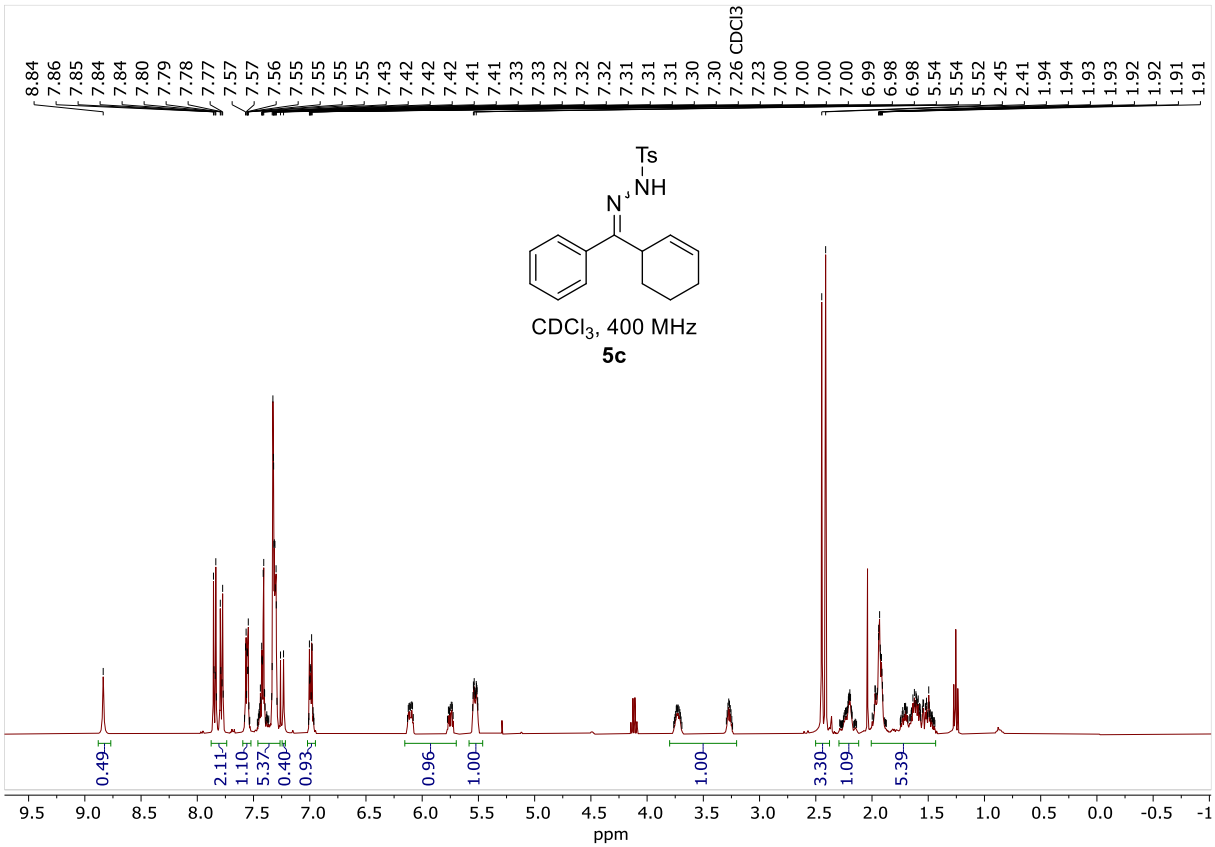


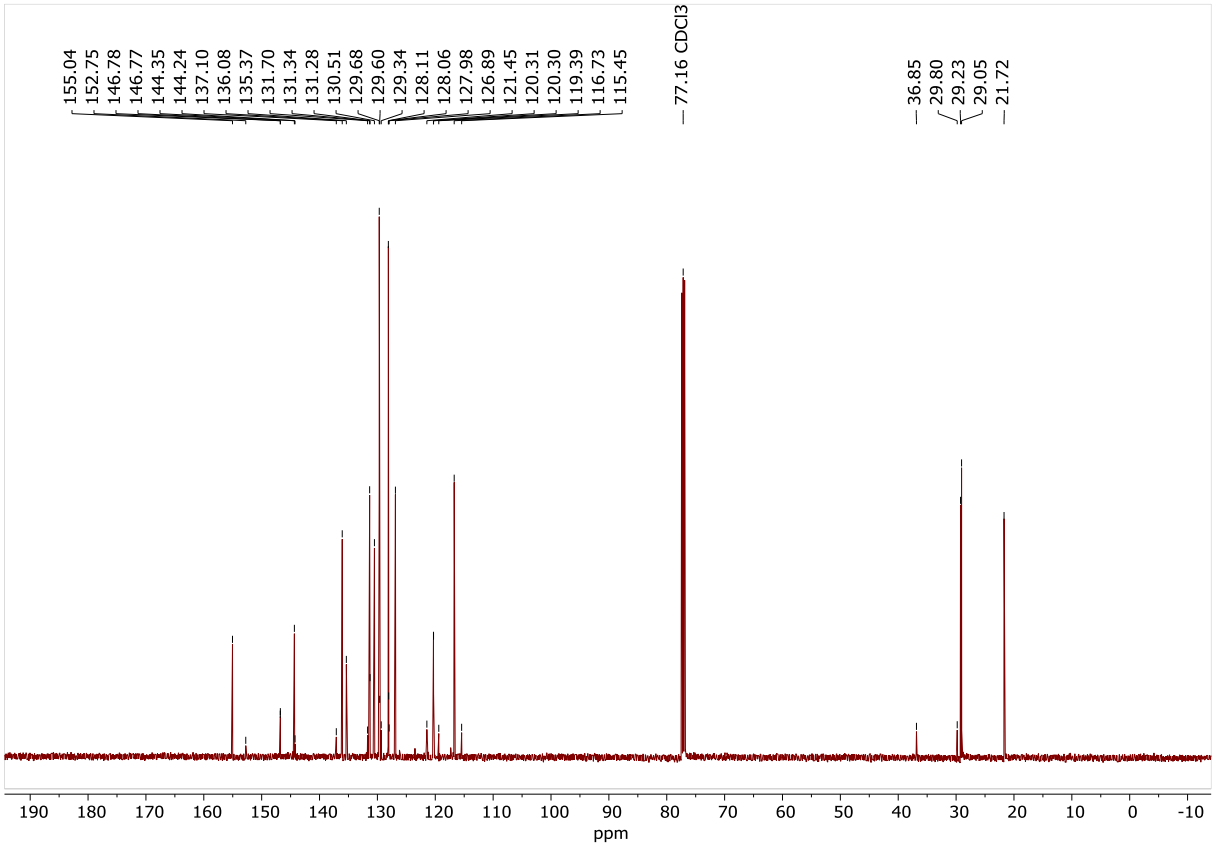


^{1}H NMR and ^{13}C NMR spectrum of compound **5b**

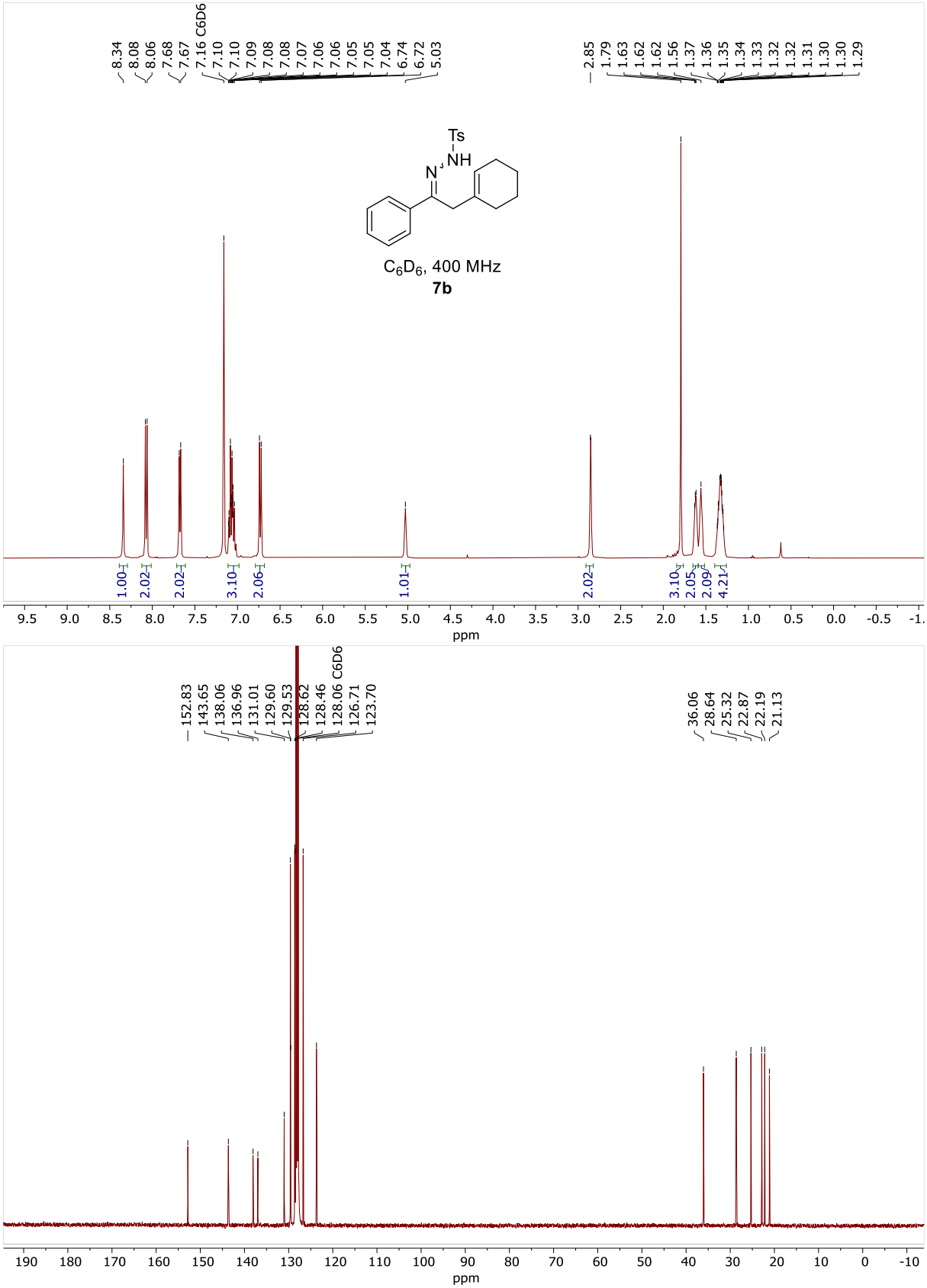


^{1}H NMR and ^{13}C NMR spectrum of compound **5c**

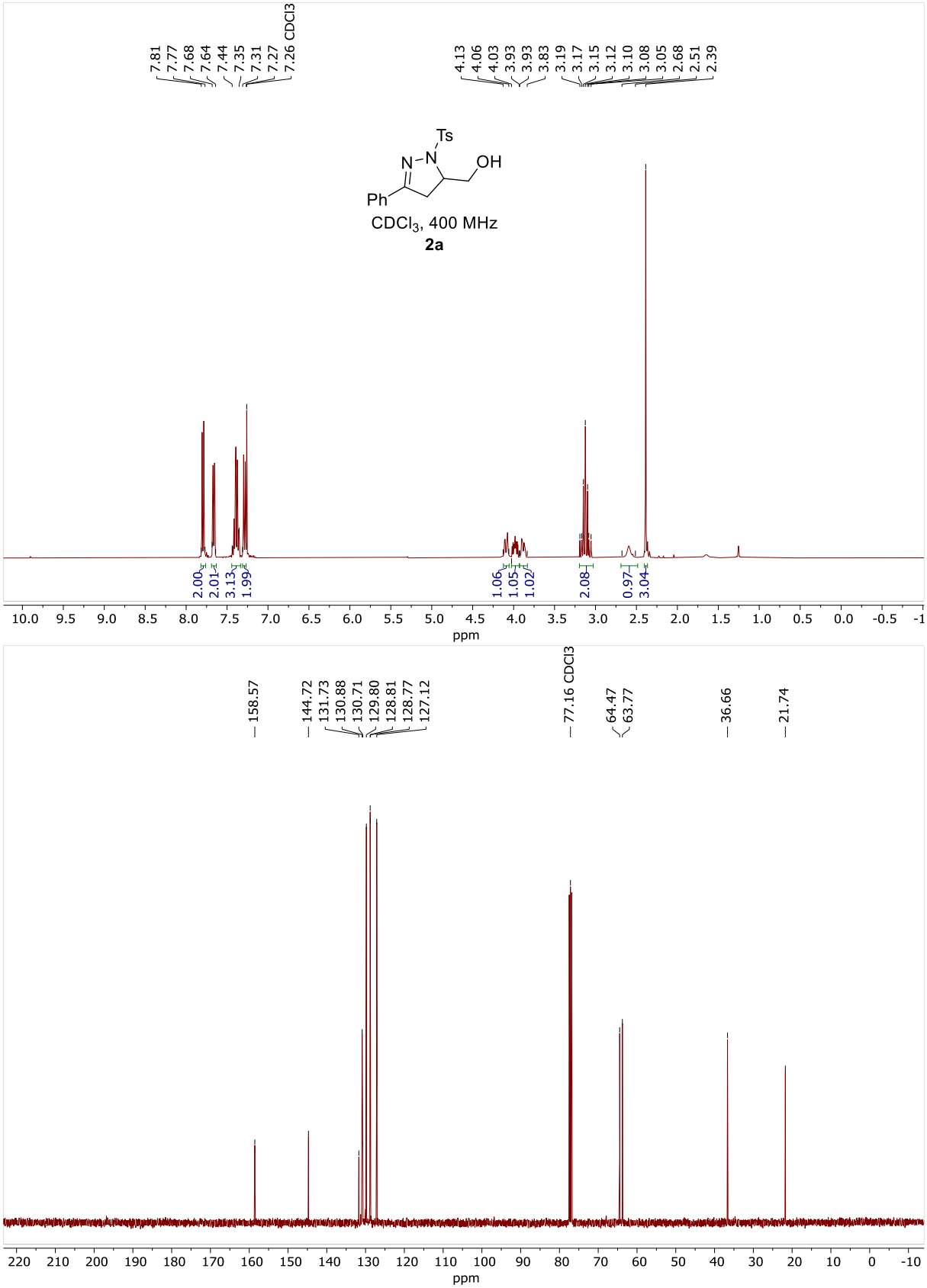




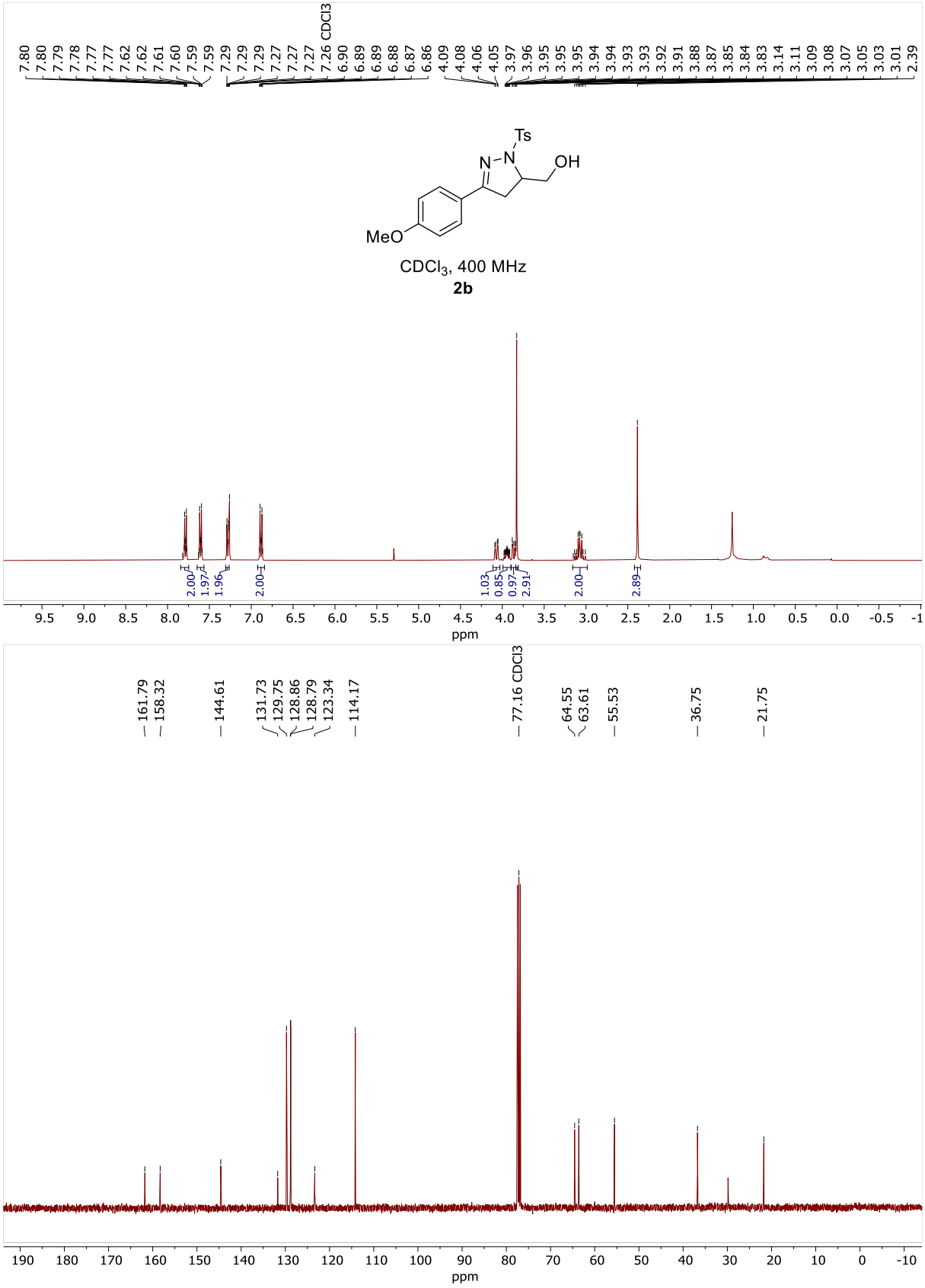
^{1}H NMR and ^{13}C NMR spectrum of compound **7b**



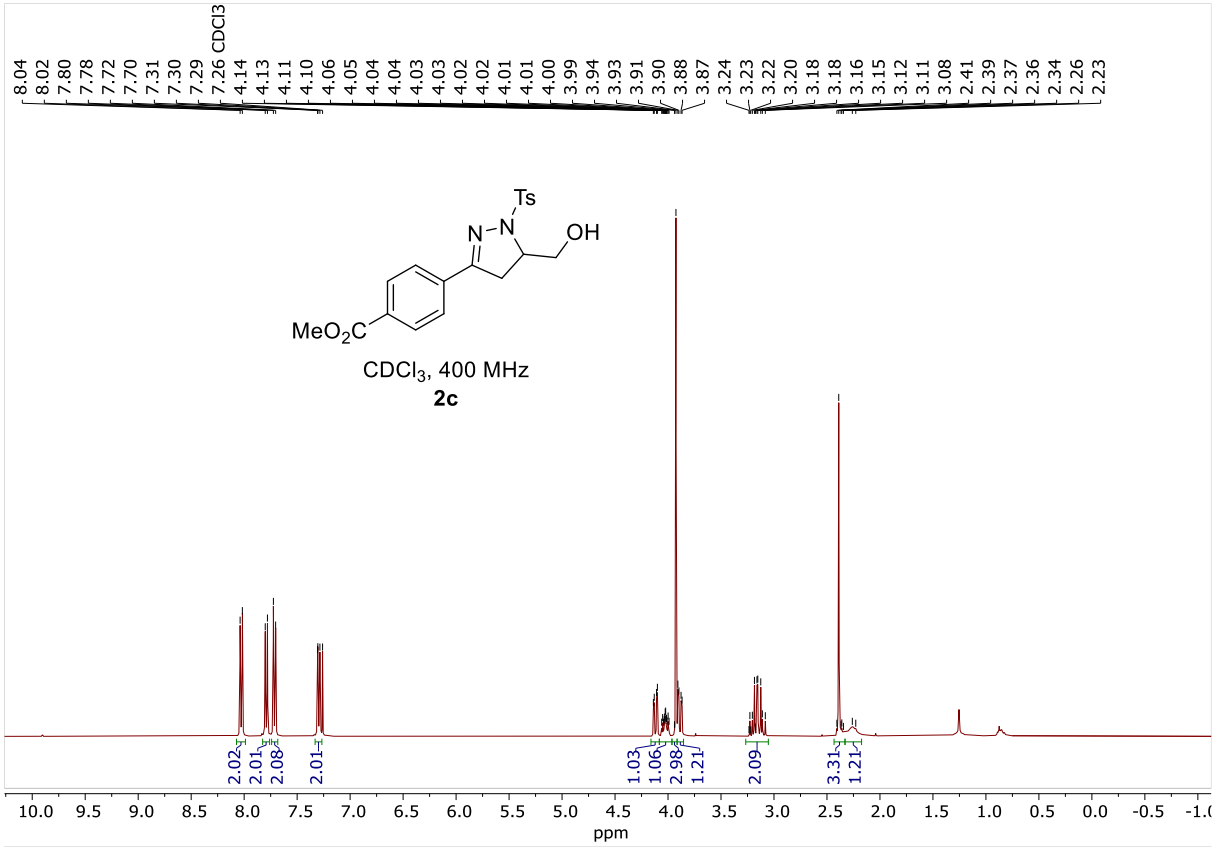
^{1}H NMR and ^{13}C NMR spectrum of compound **2a**

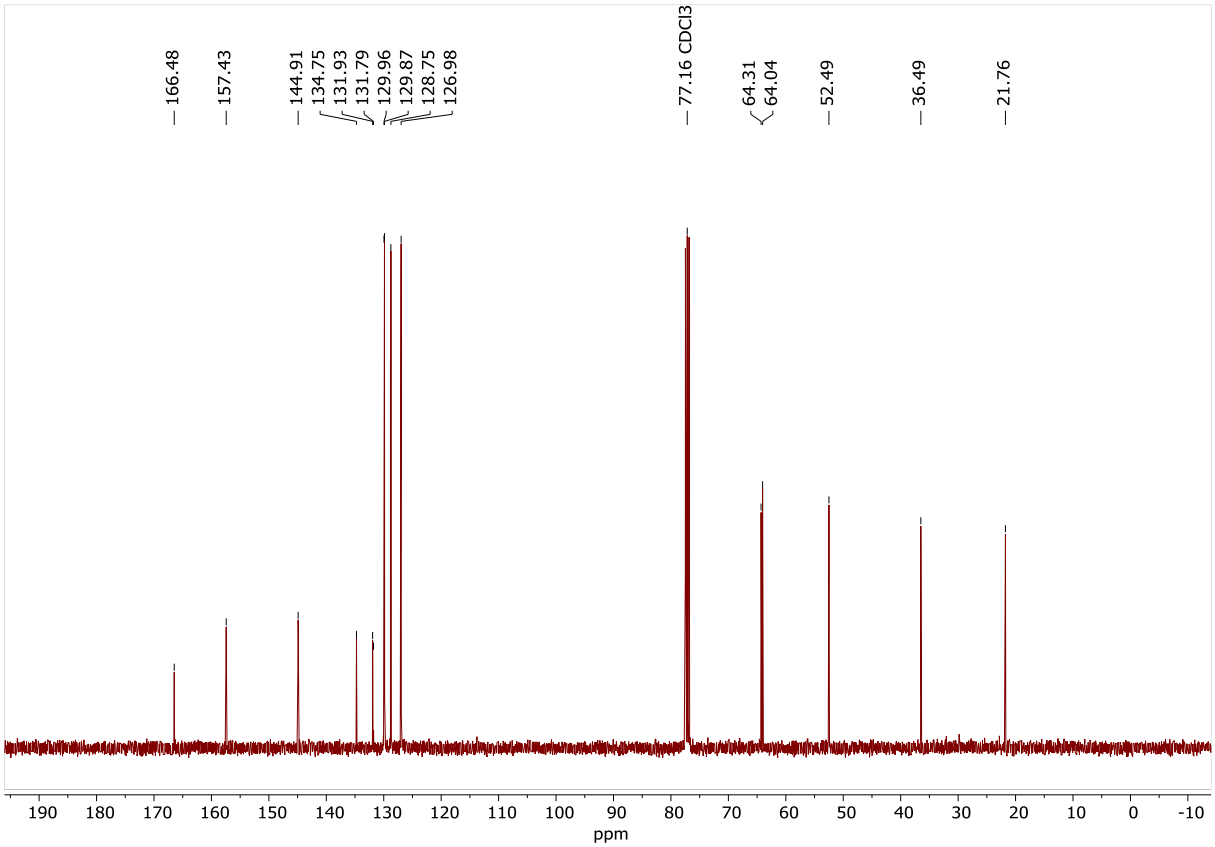


^{1}H NMR and ^{13}C NMR spectrum of compound **2b**

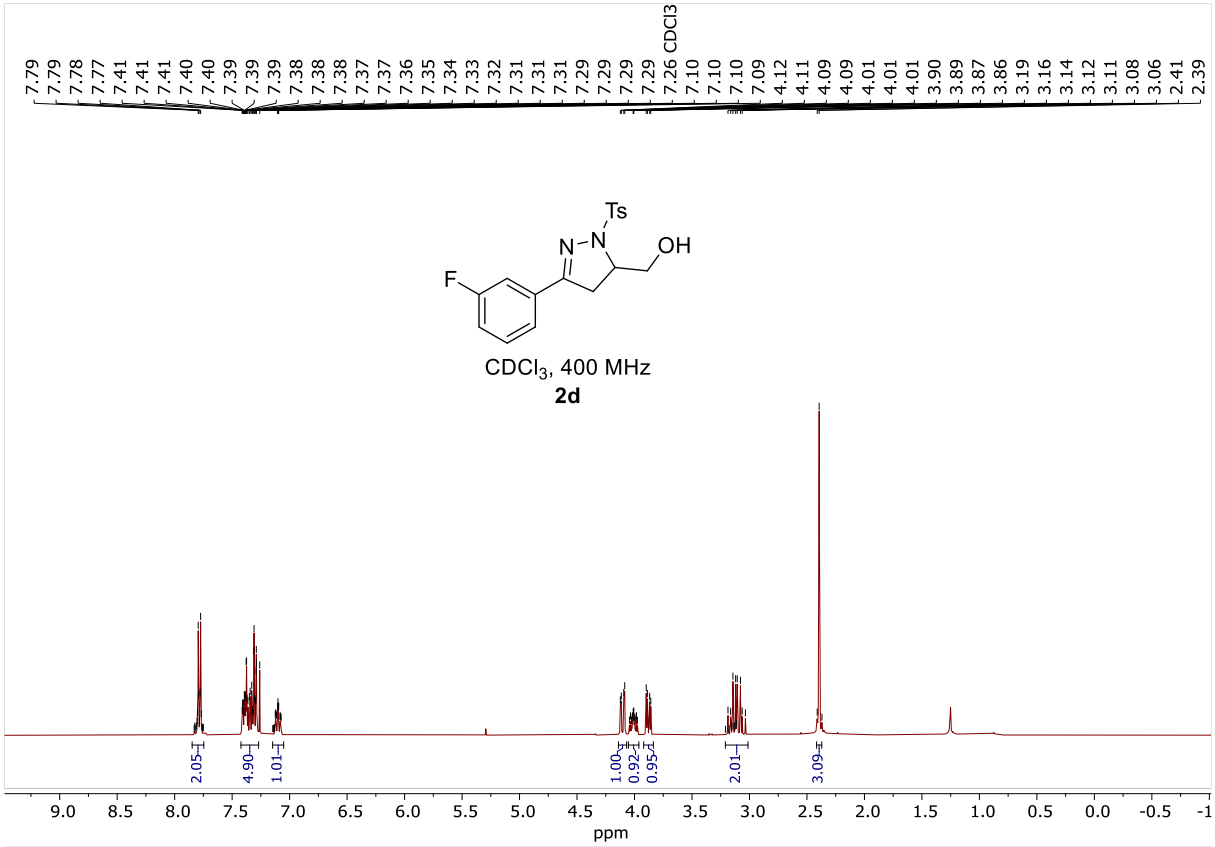


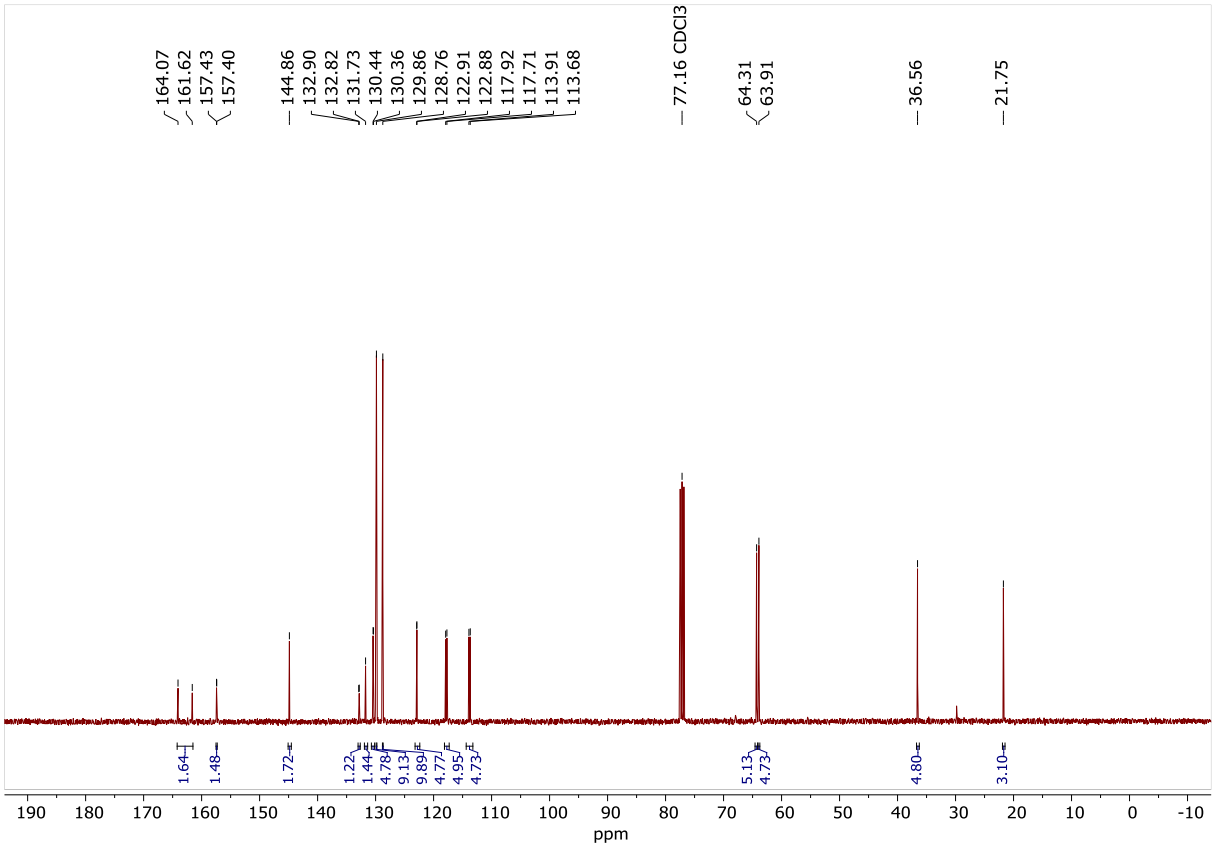
^{1}H NMR and ^{13}C NMR spectrum of compound **2c**



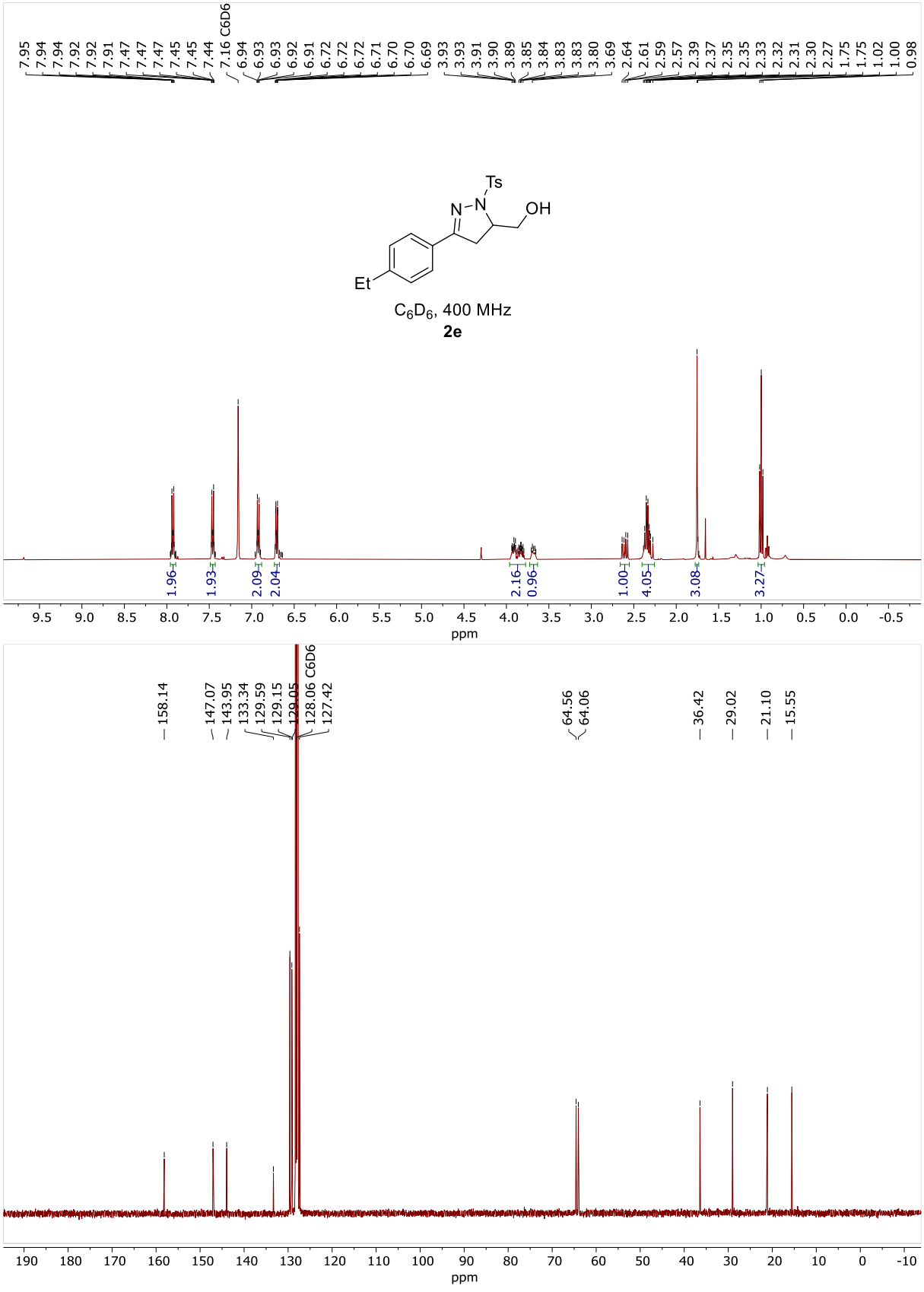


^{1}H NMR and ^{13}C NMR spectrum of compound **2d**

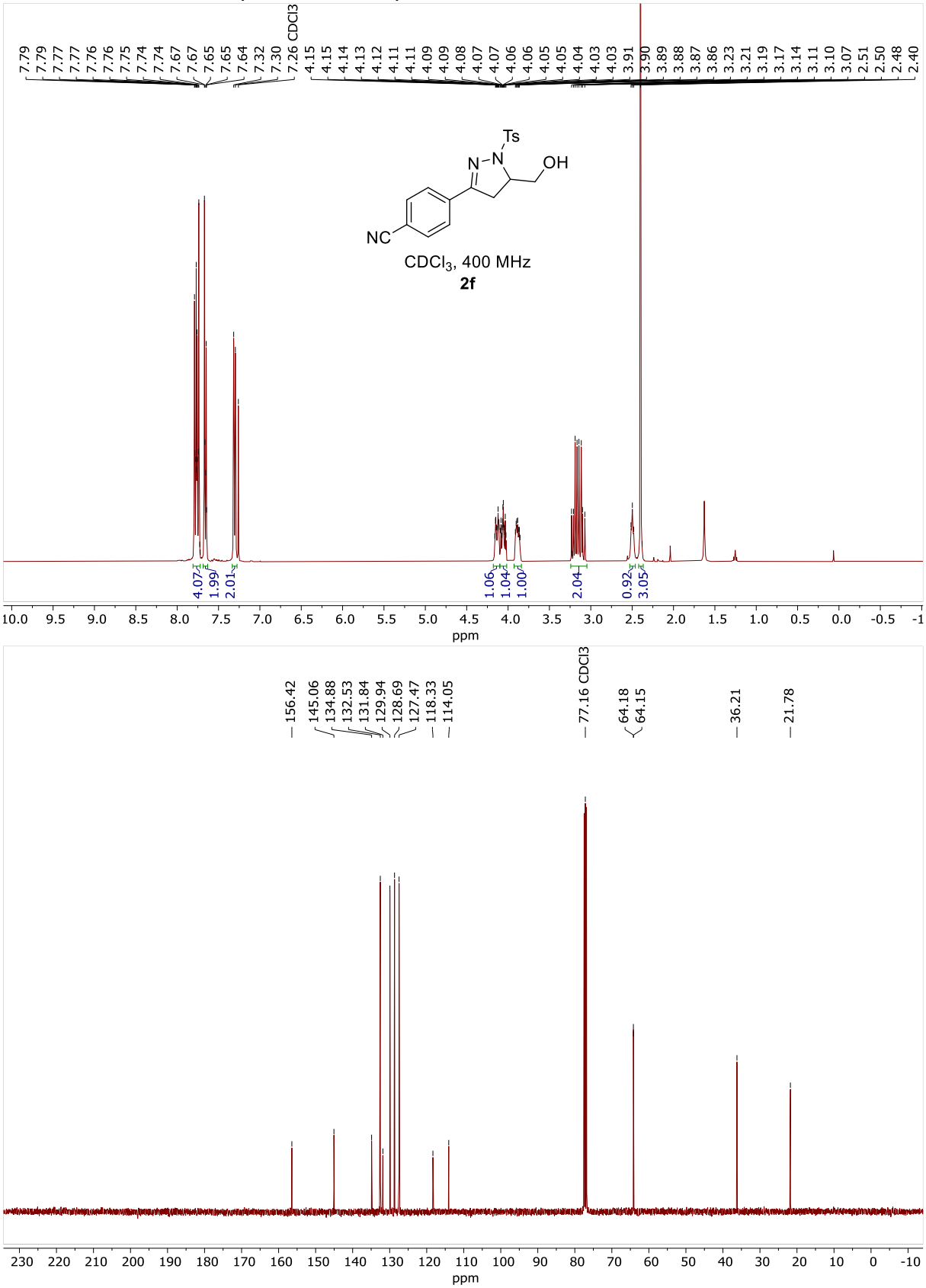




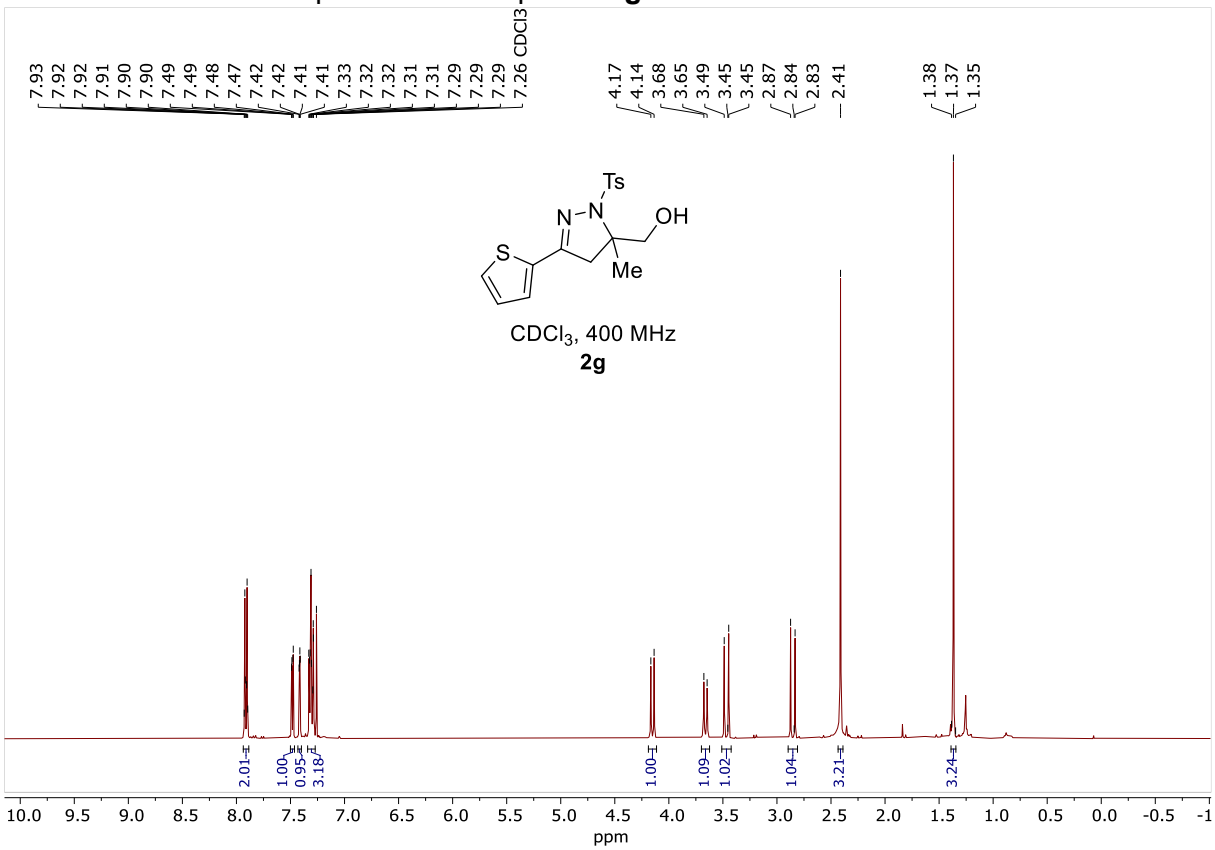
^{1}H NMR and ^{13}C NMR spectrum of compound **2e**

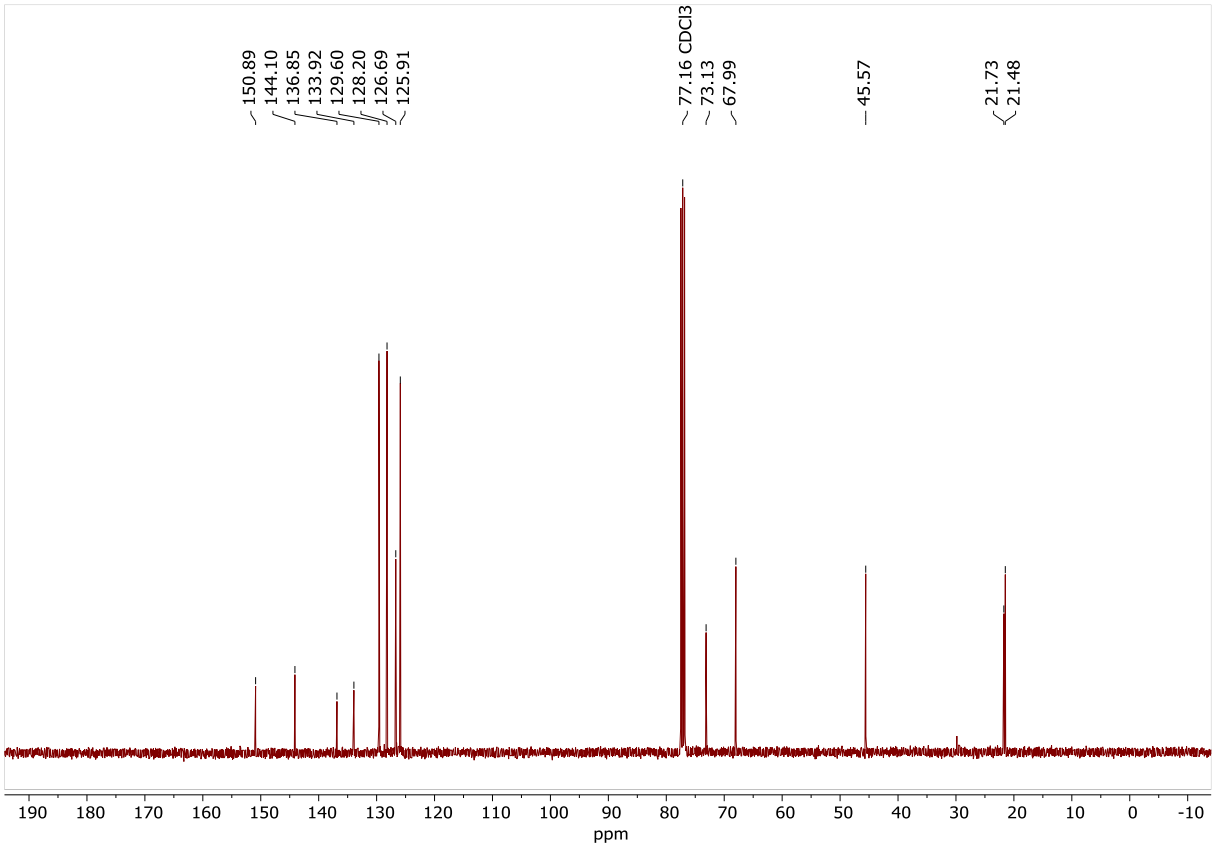


^{1}H NMR and ^{13}C NMR spectrum of compound **2f**

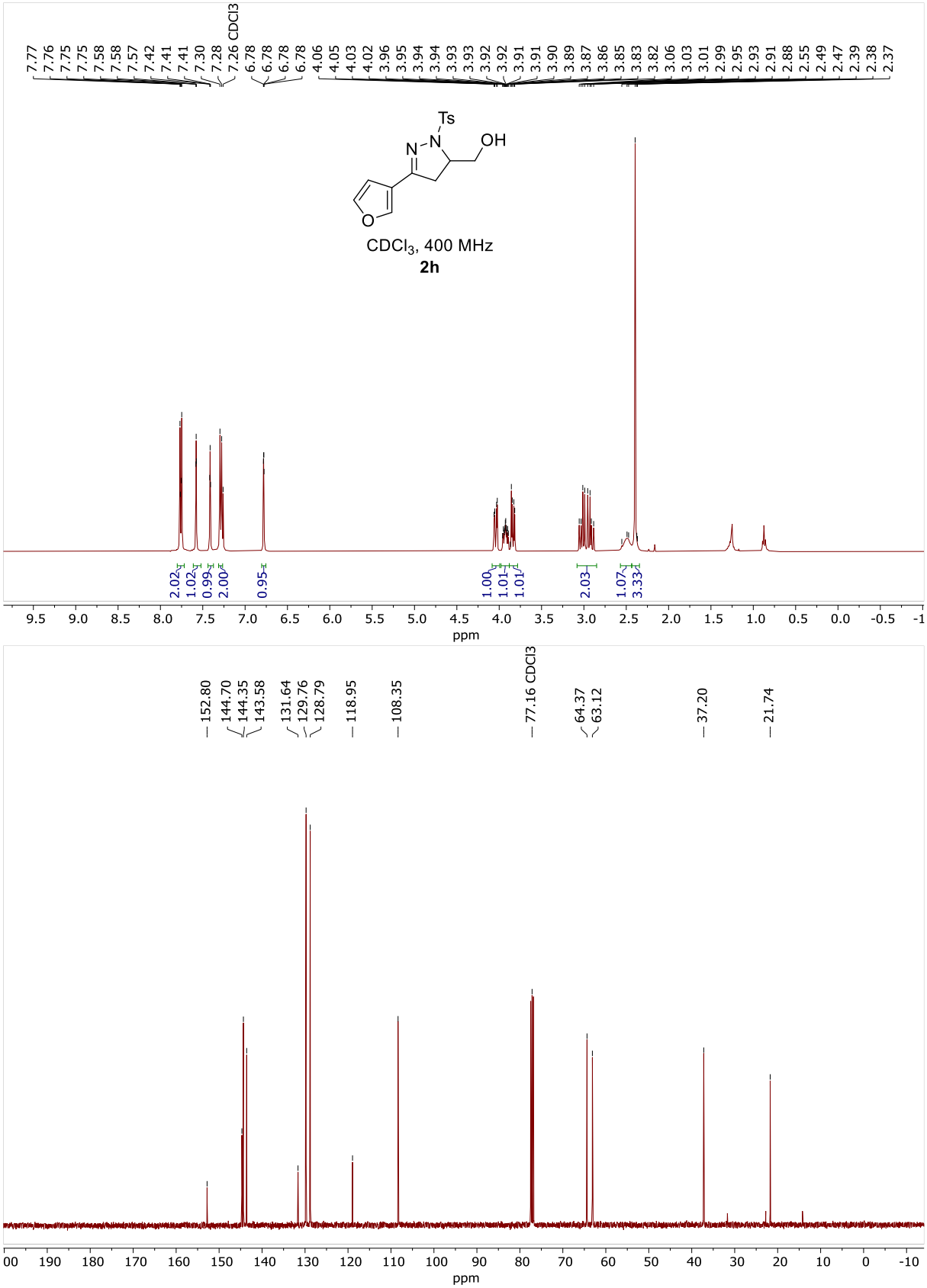


^{1}H NMR and ^{13}C NMR spectrum of compound **2g**

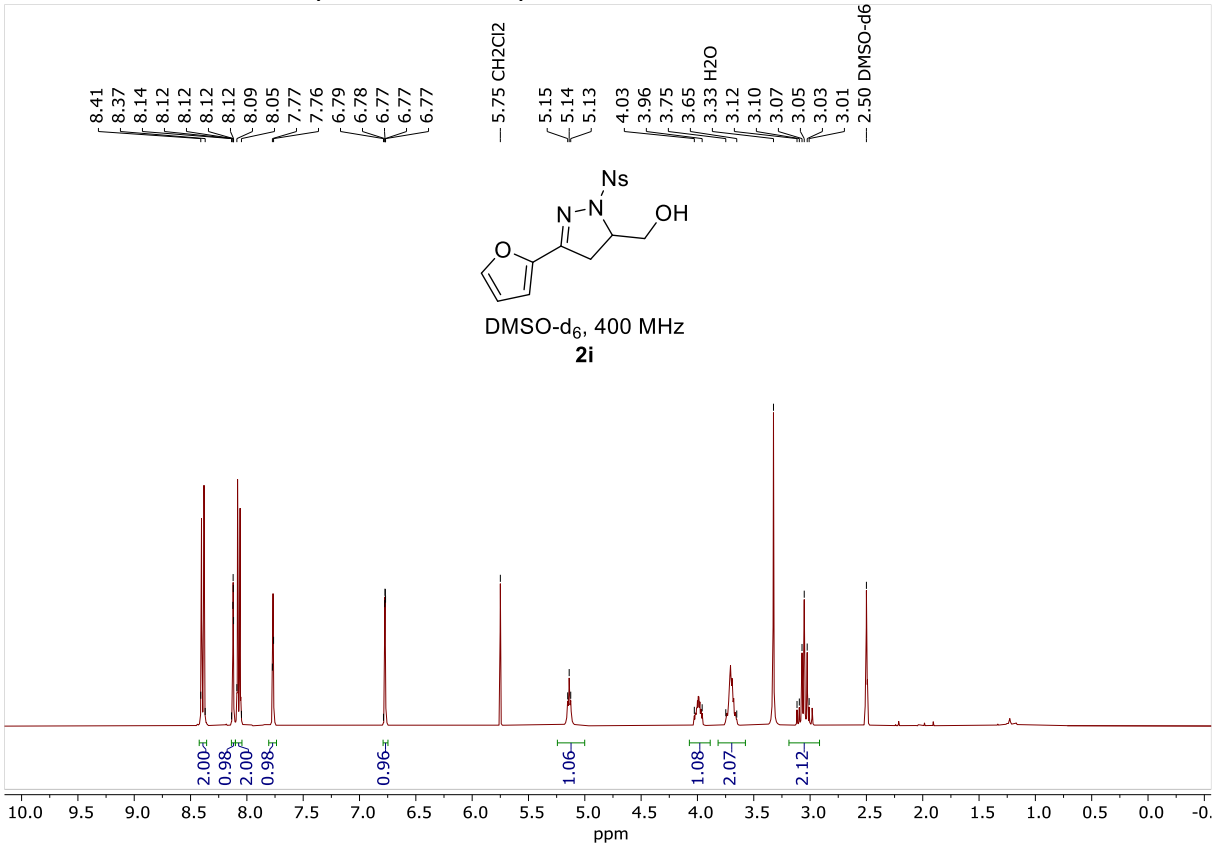


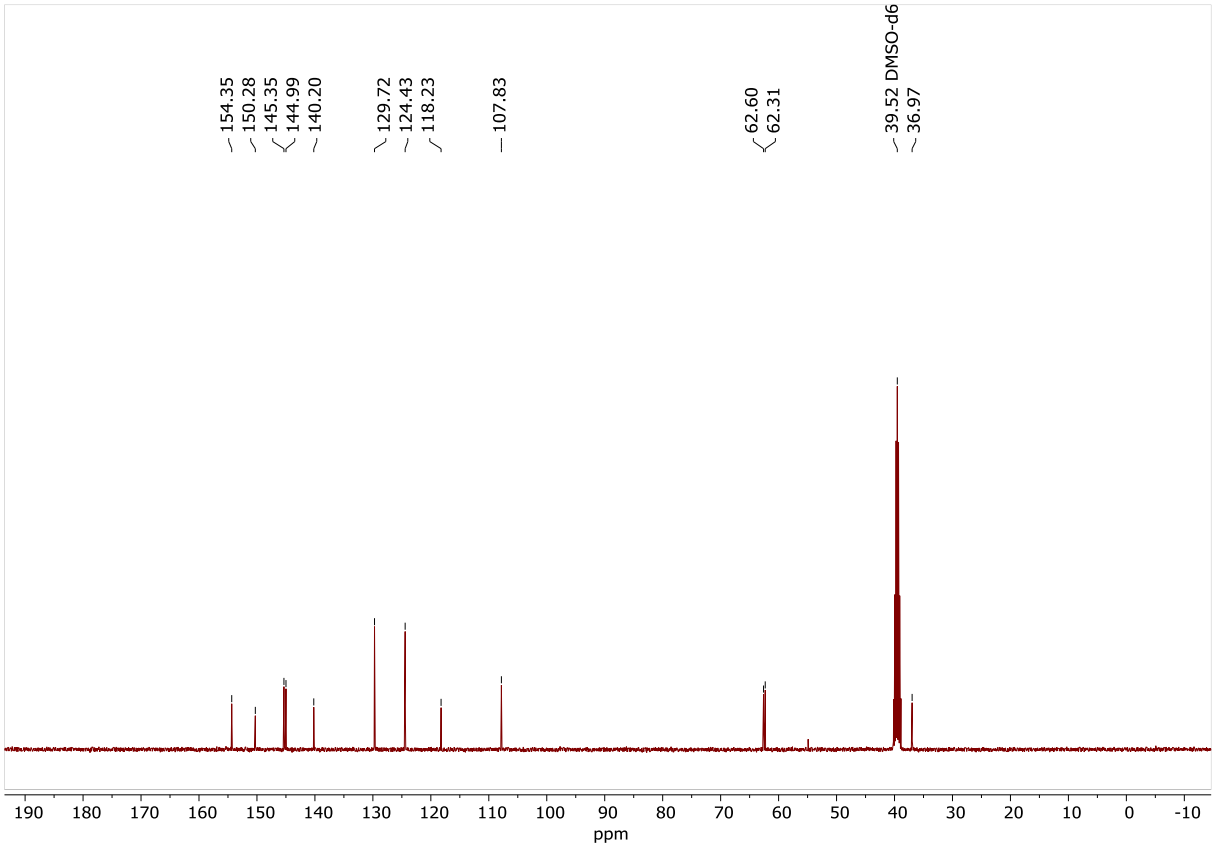


^{1}H NMR and ^{13}C NMR spectrum of compound **2h**

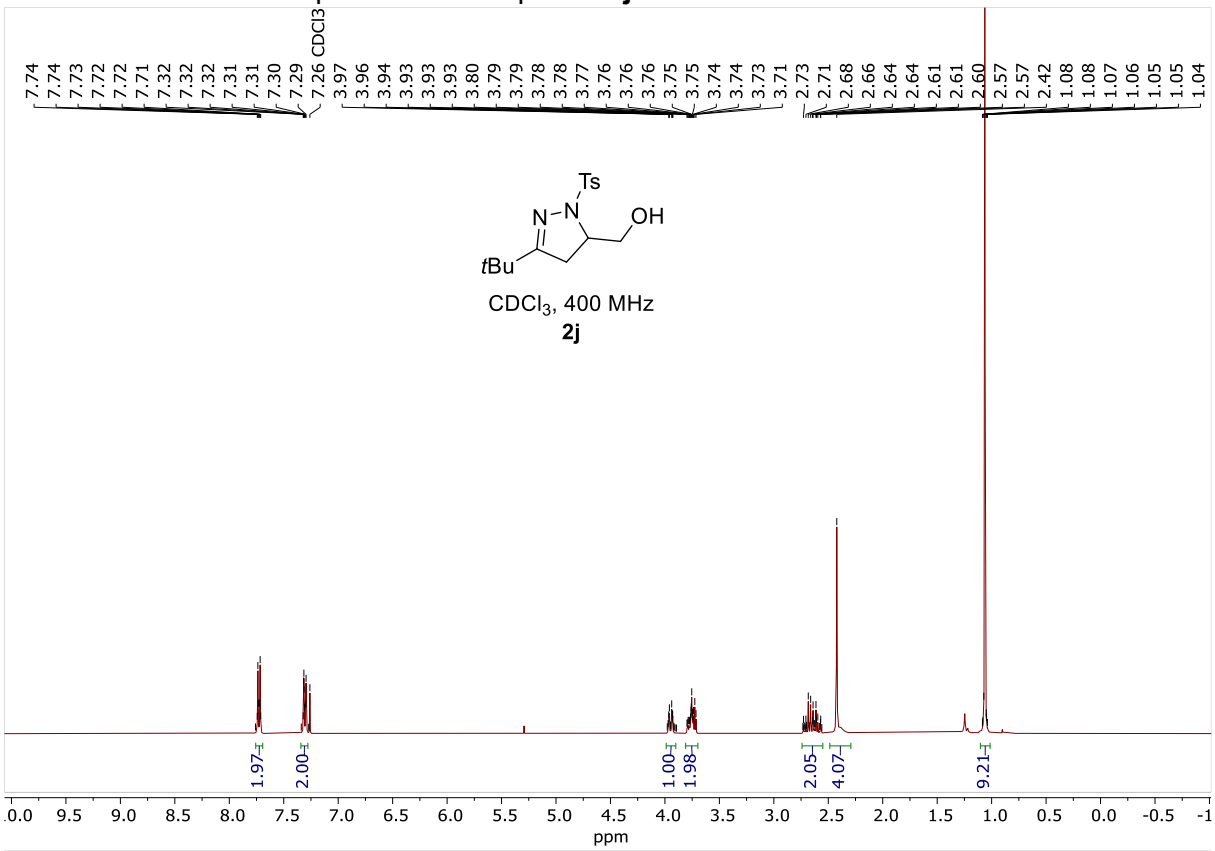


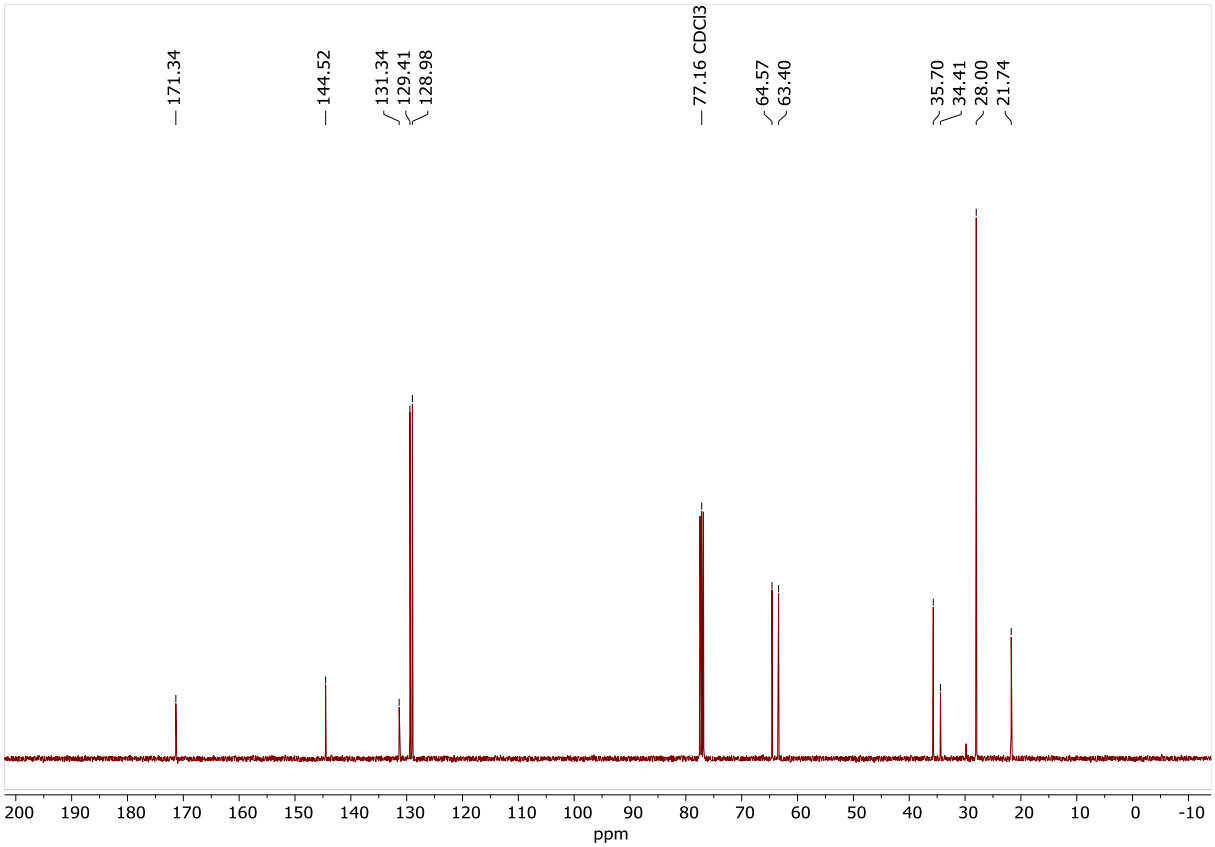
^{1}H NMR and ^{13}C NMR spectrum of compound **2i**



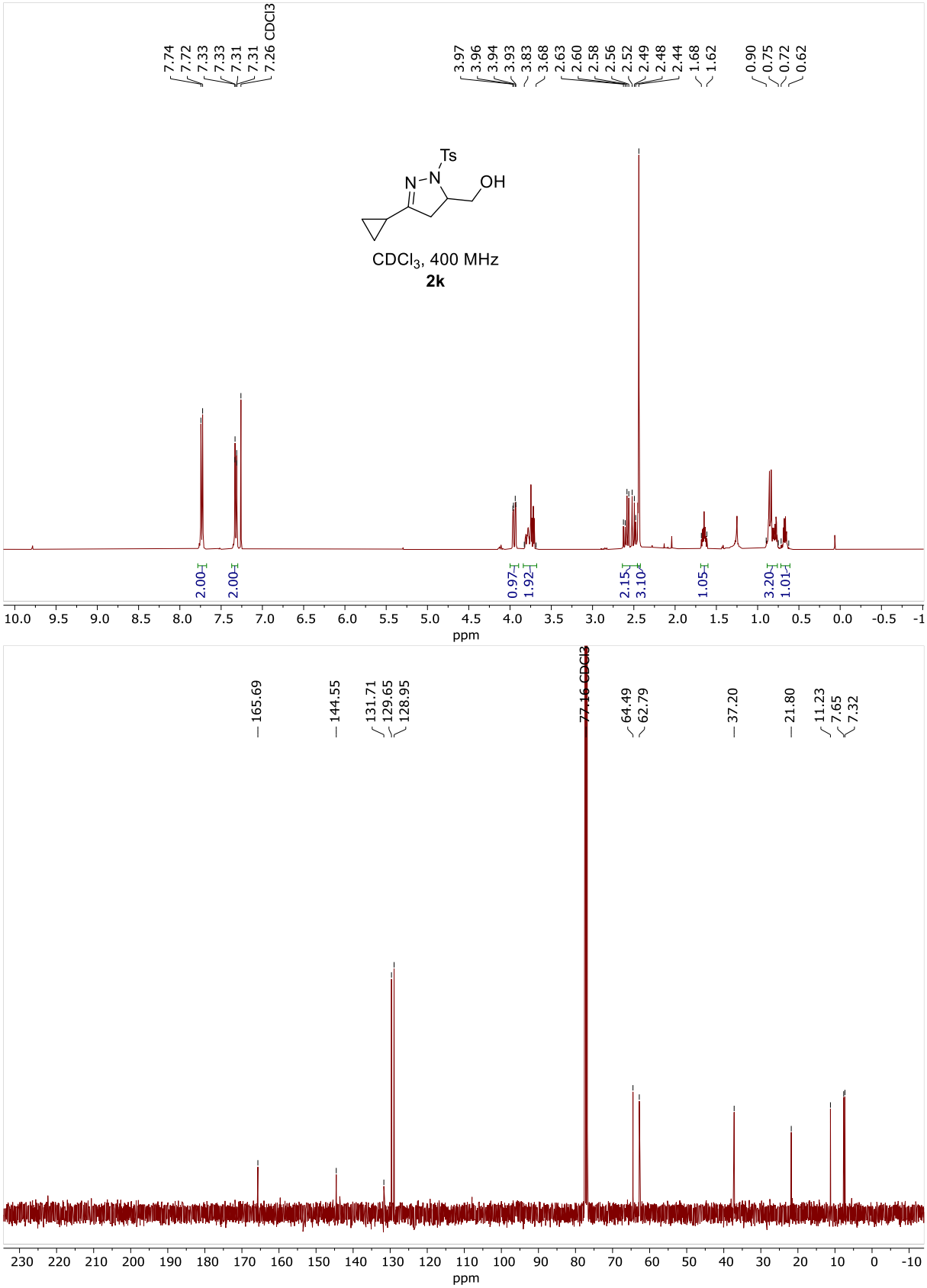


^{1}H NMR and ^{13}C NMR spectrum of compound **2j**

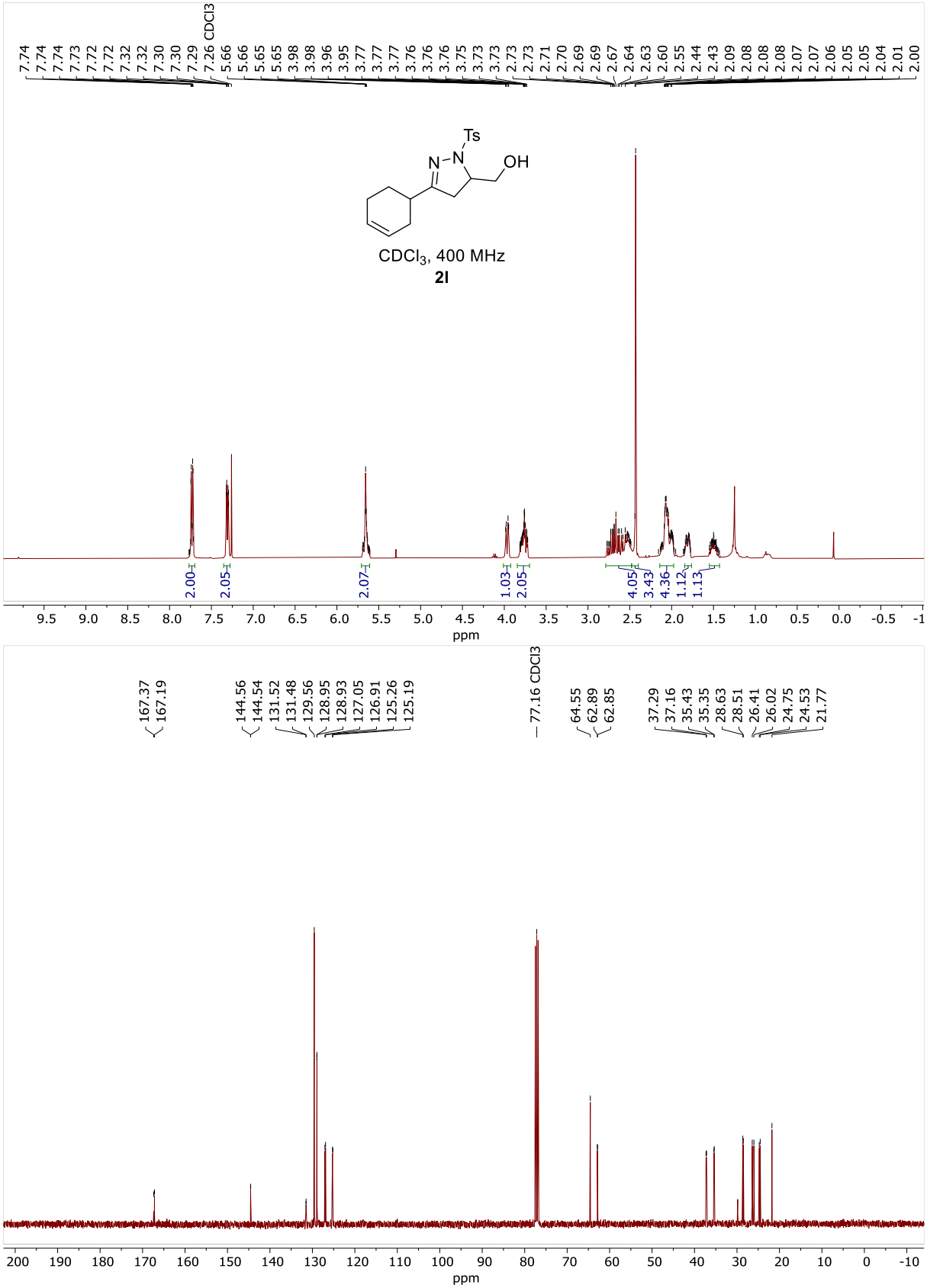




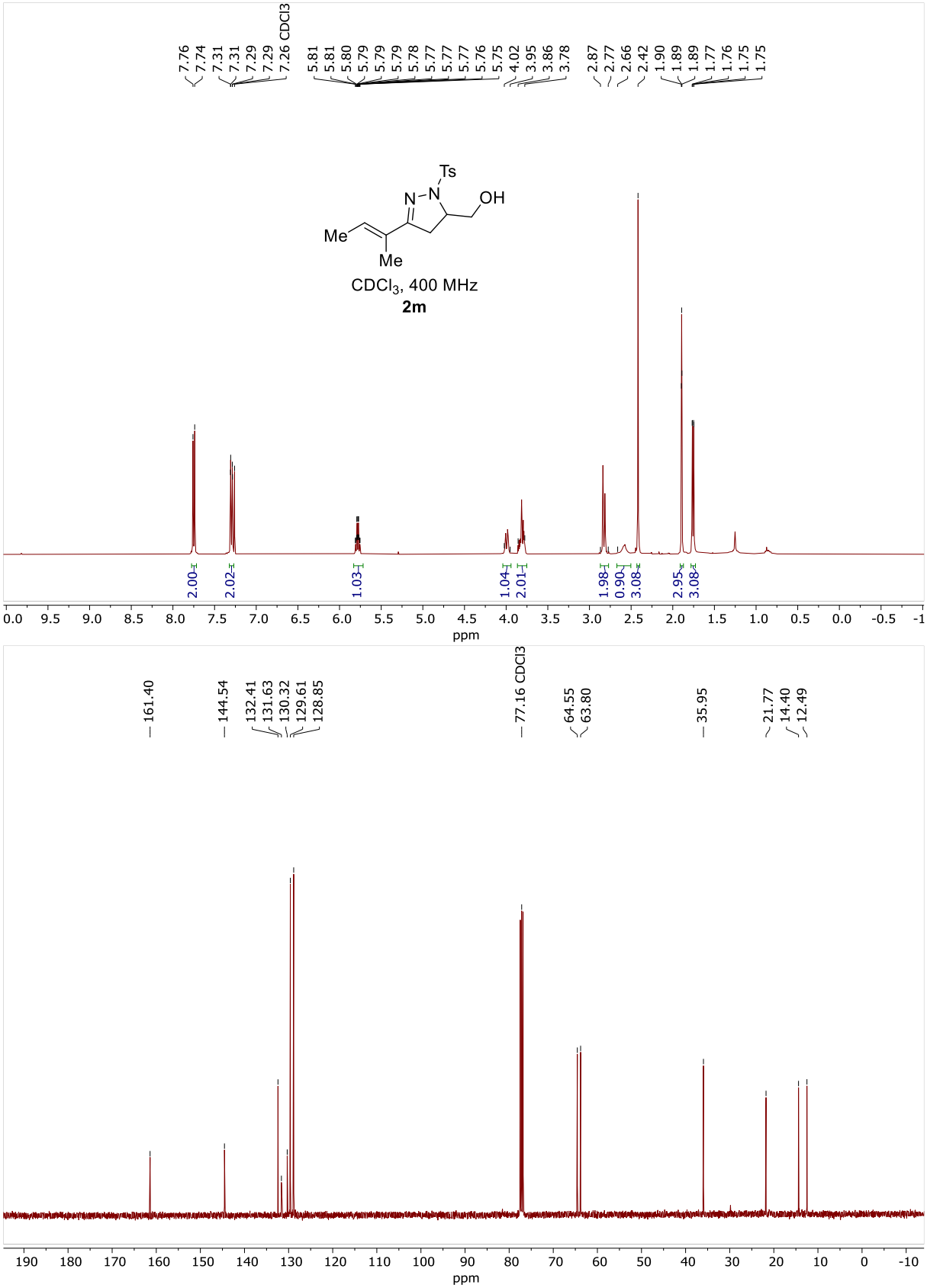
^{1}H NMR and ^{13}C NMR spectrum of compound **2k**



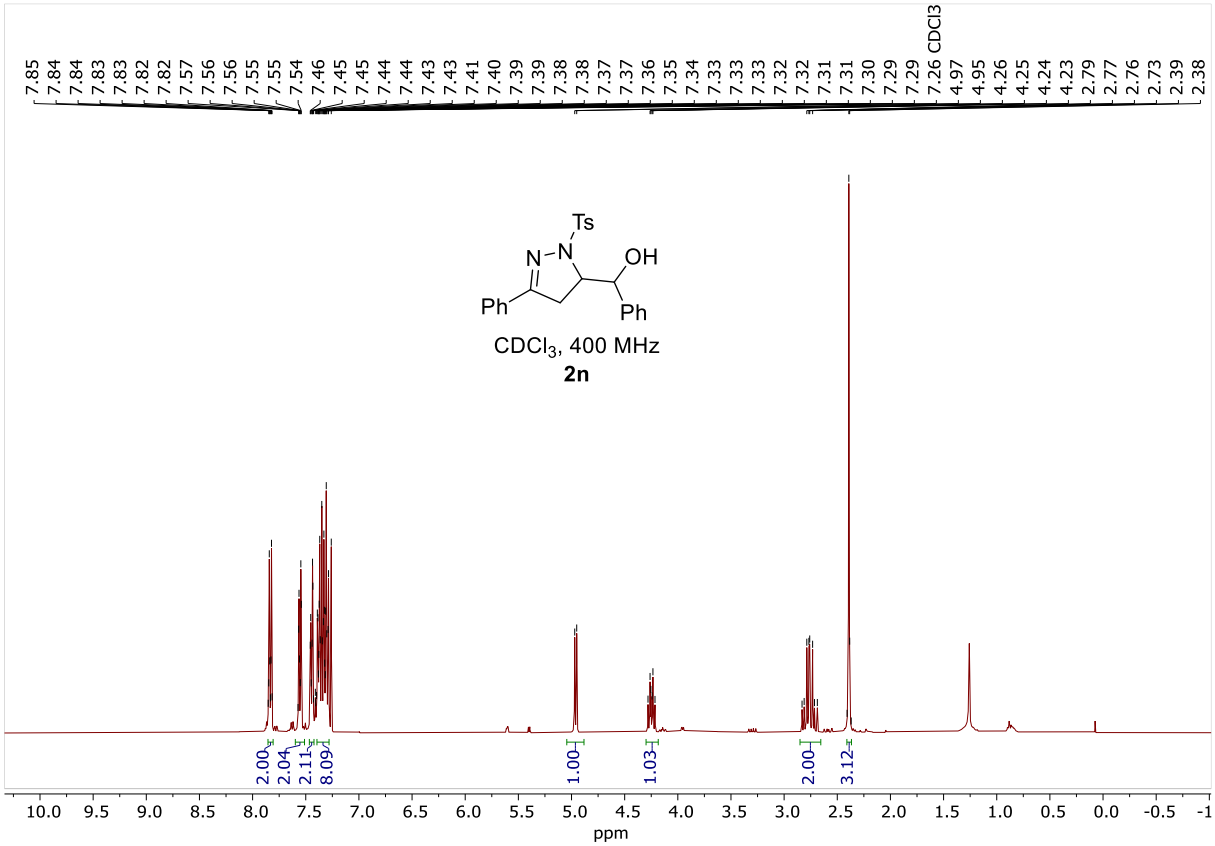
^{1}H NMR and ^{13}C NMR spectrum of compound **2l**

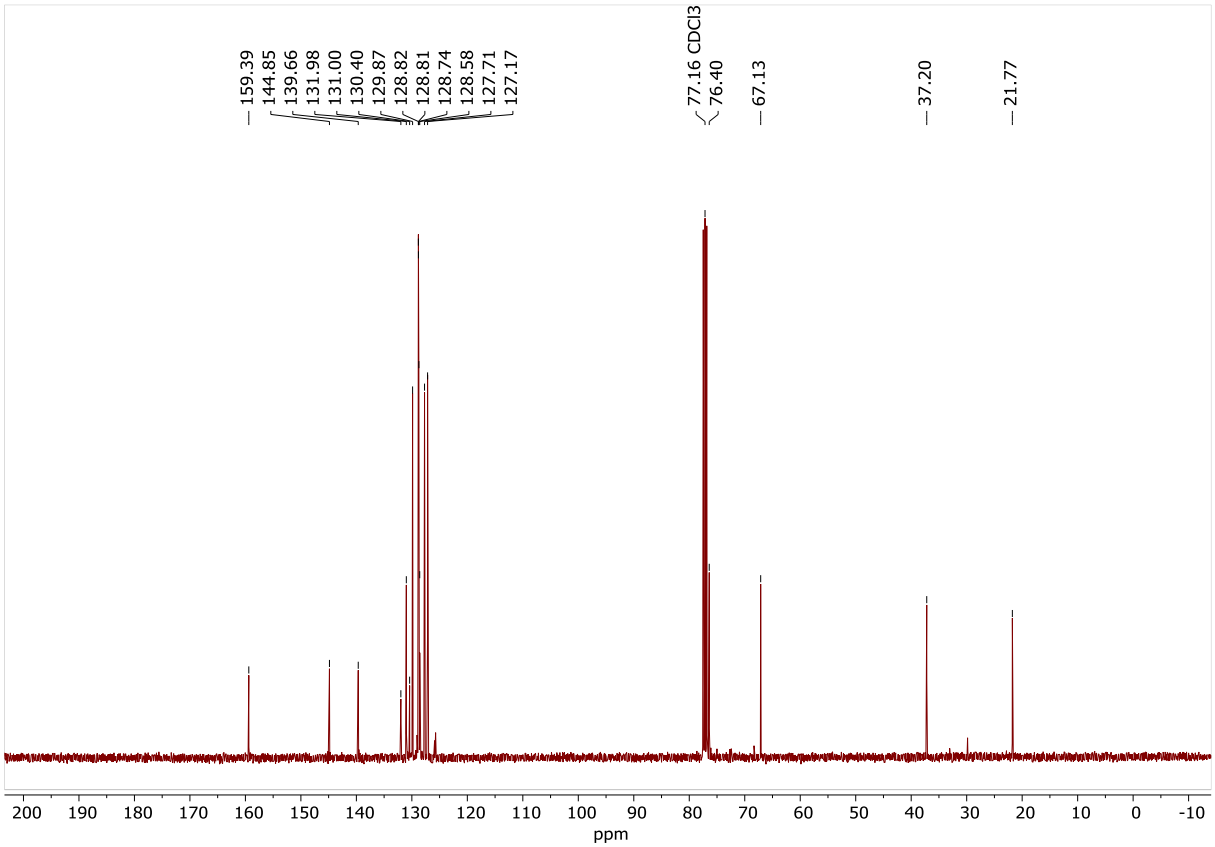


^{1}H NMR and ^{13}C NMR spectrum of compound **2m**

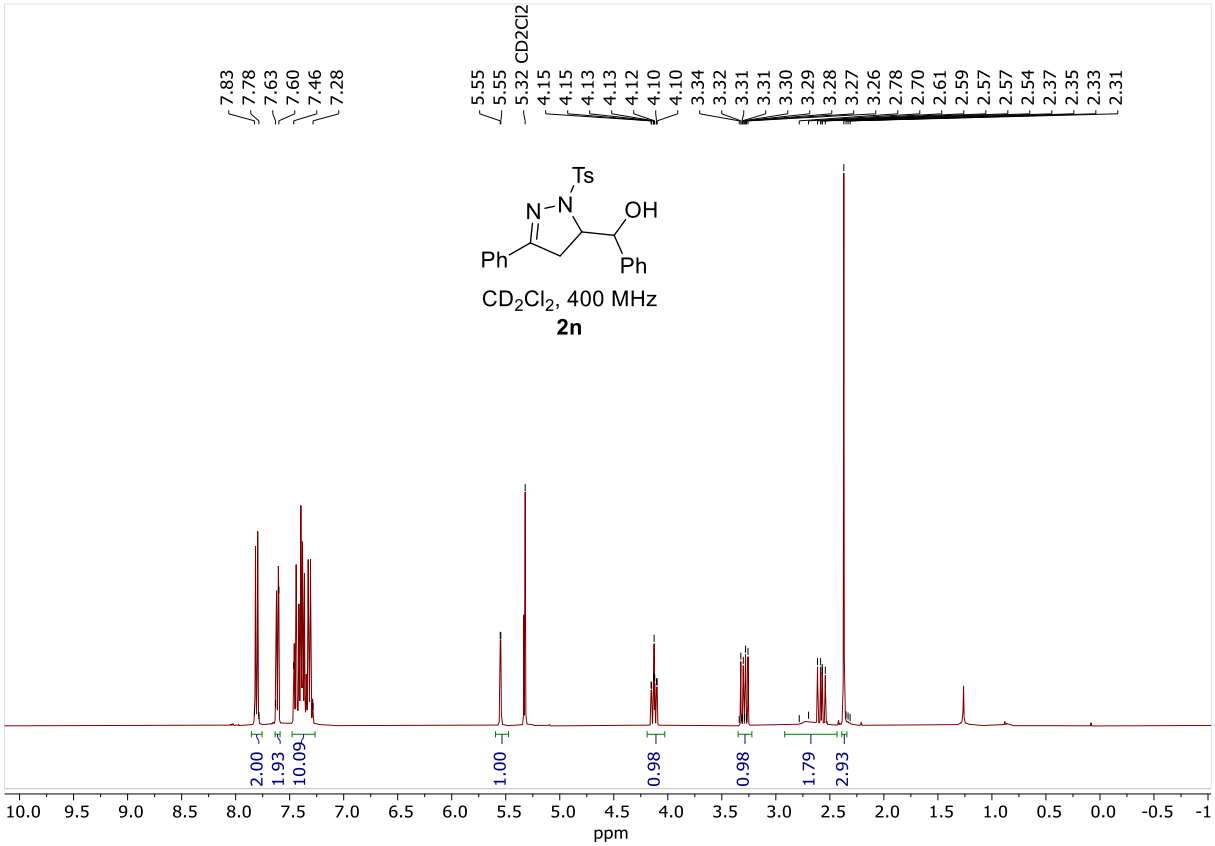


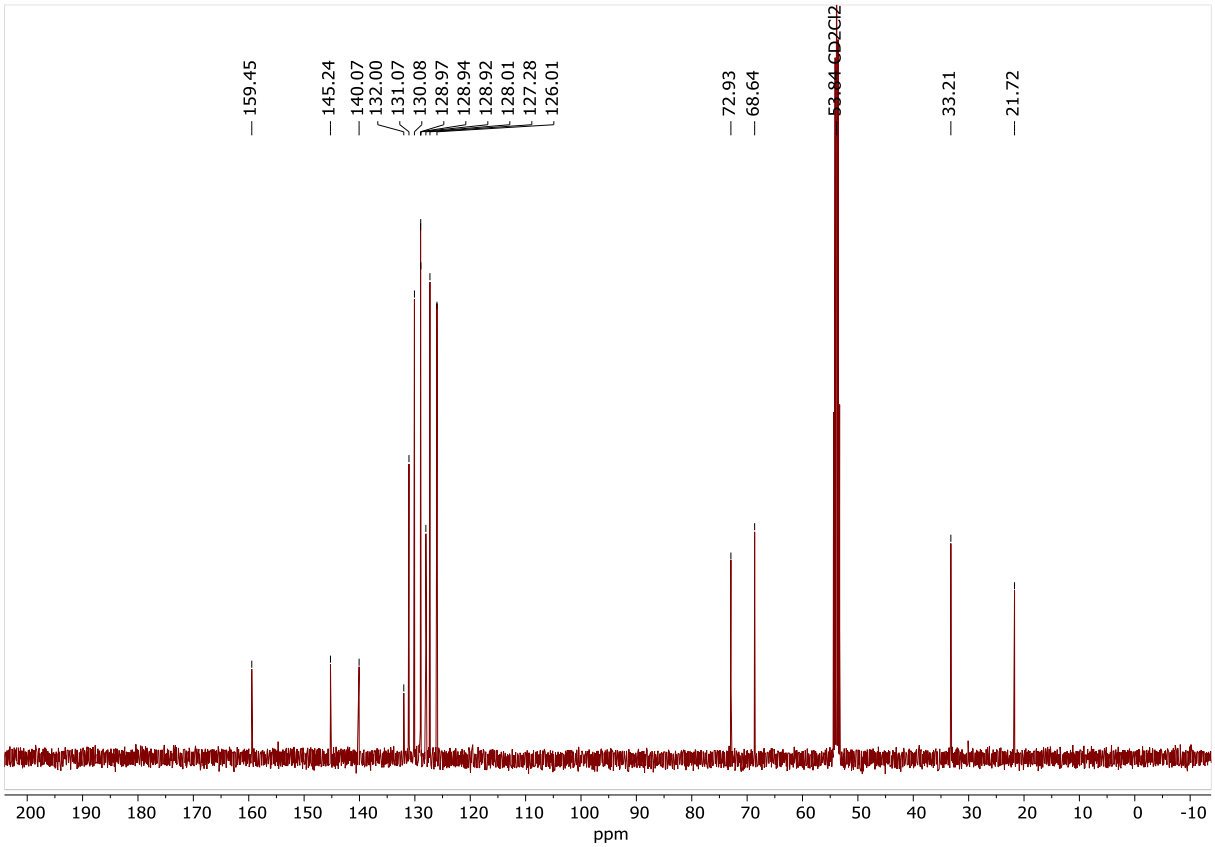
^{1}H NMR and ^{13}C NMR spectrum of compound **2n** (minor diastereomer)



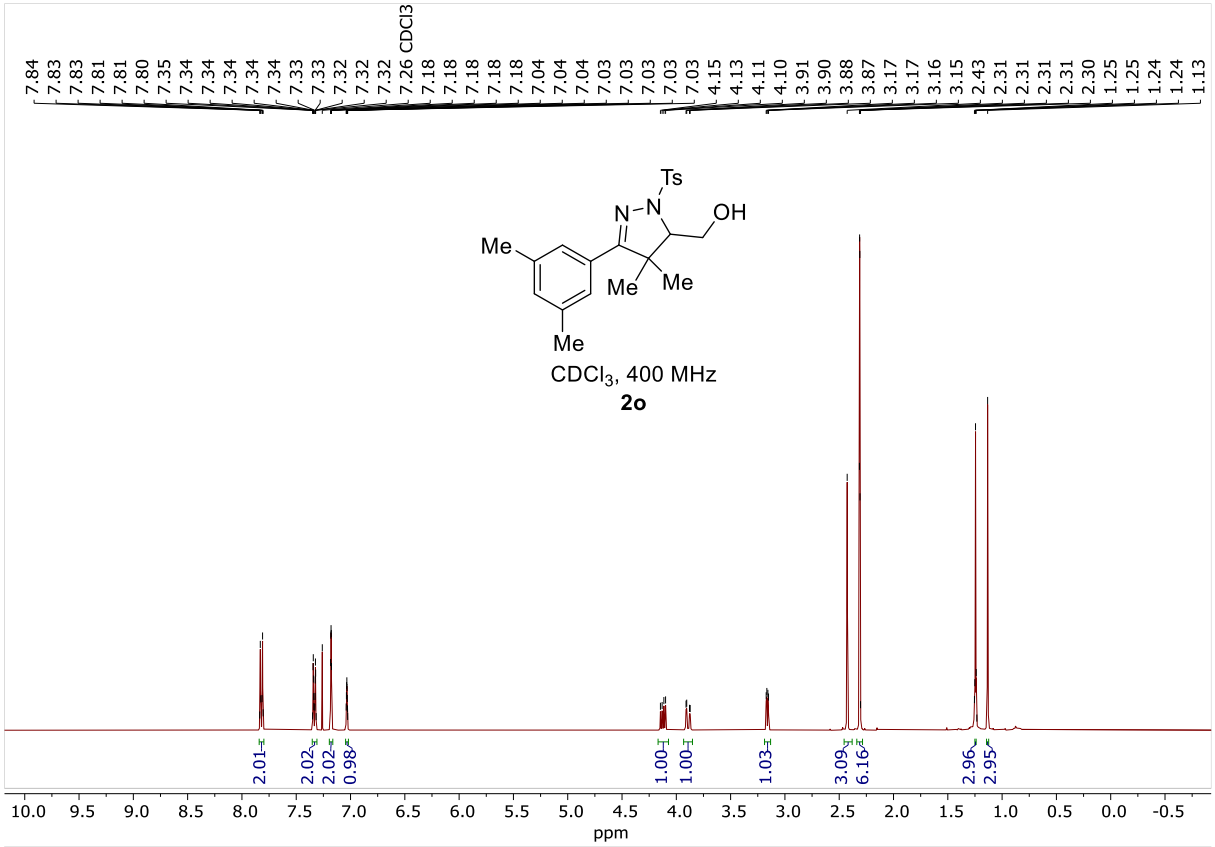


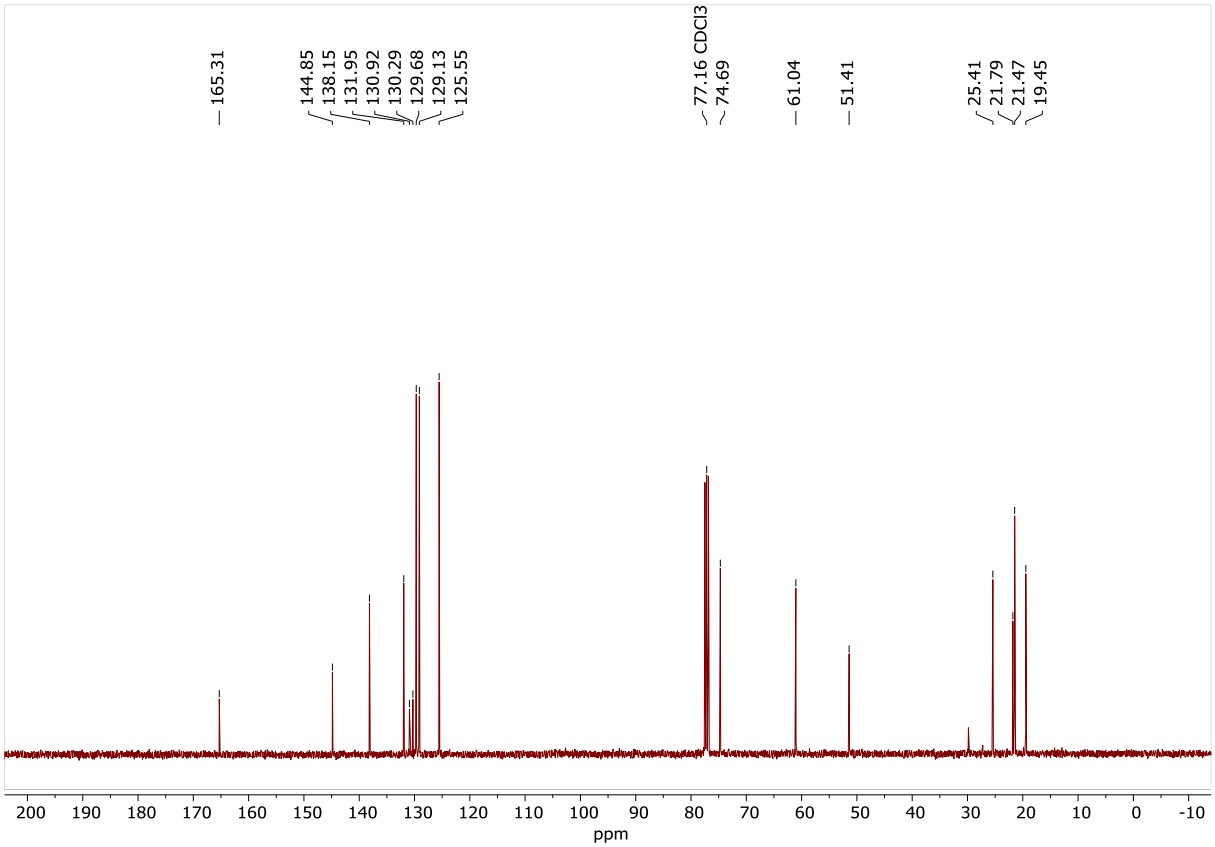
^{1}H NMR and ^{13}C NMR spectrum of compound **2n** (major diastereomer)



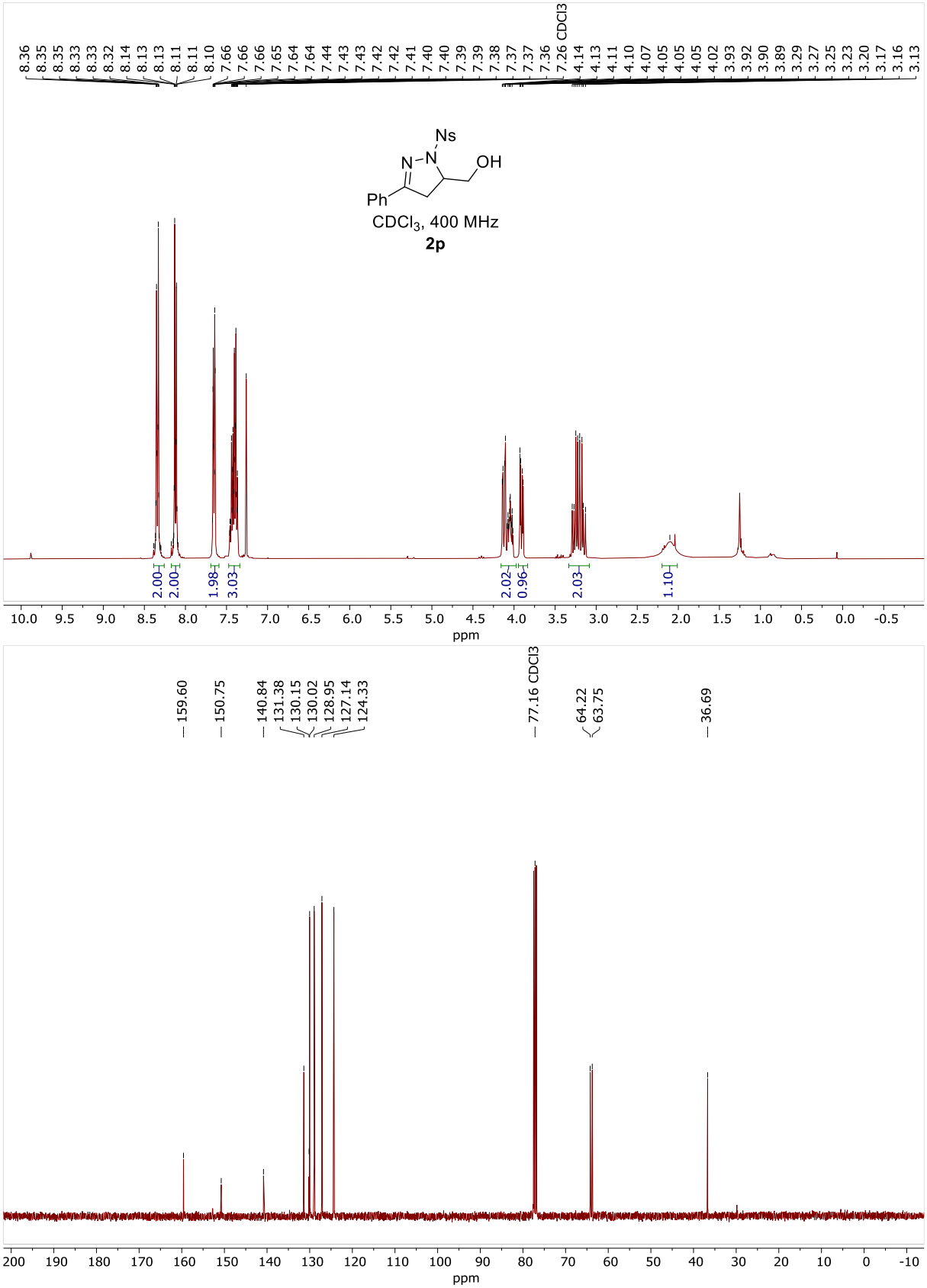


^{1}H NMR and ^{13}C NMR spectrum of compound **2o**

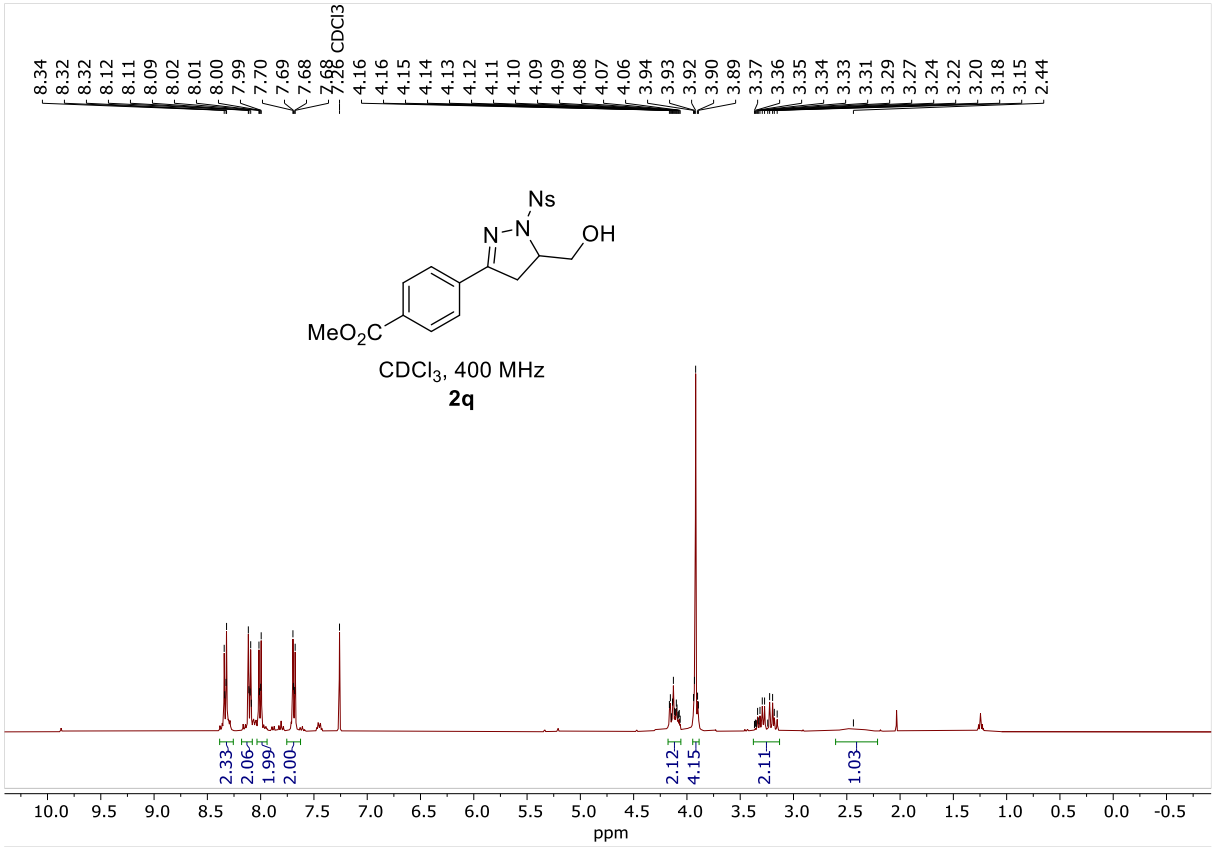


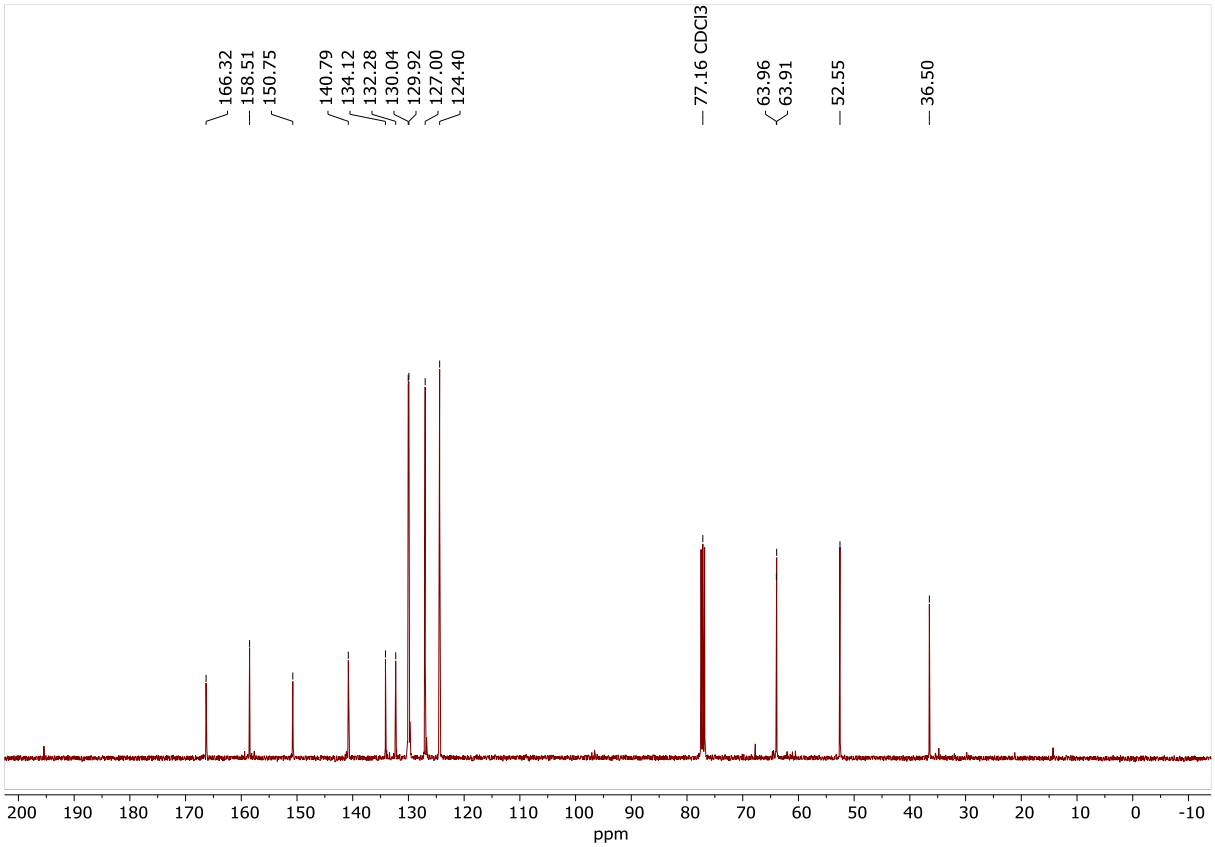


^{1}H NMR and ^{13}C NMR spectrum of compound **2p**

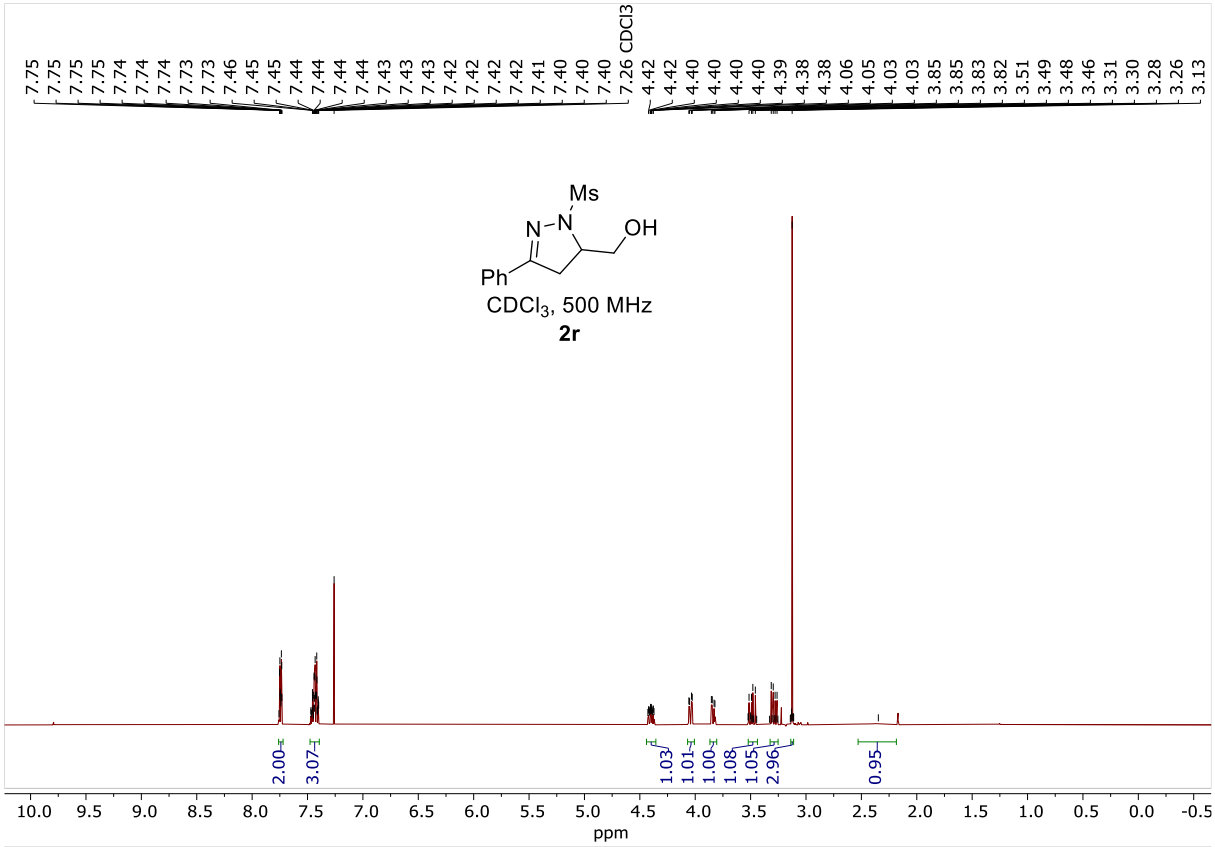


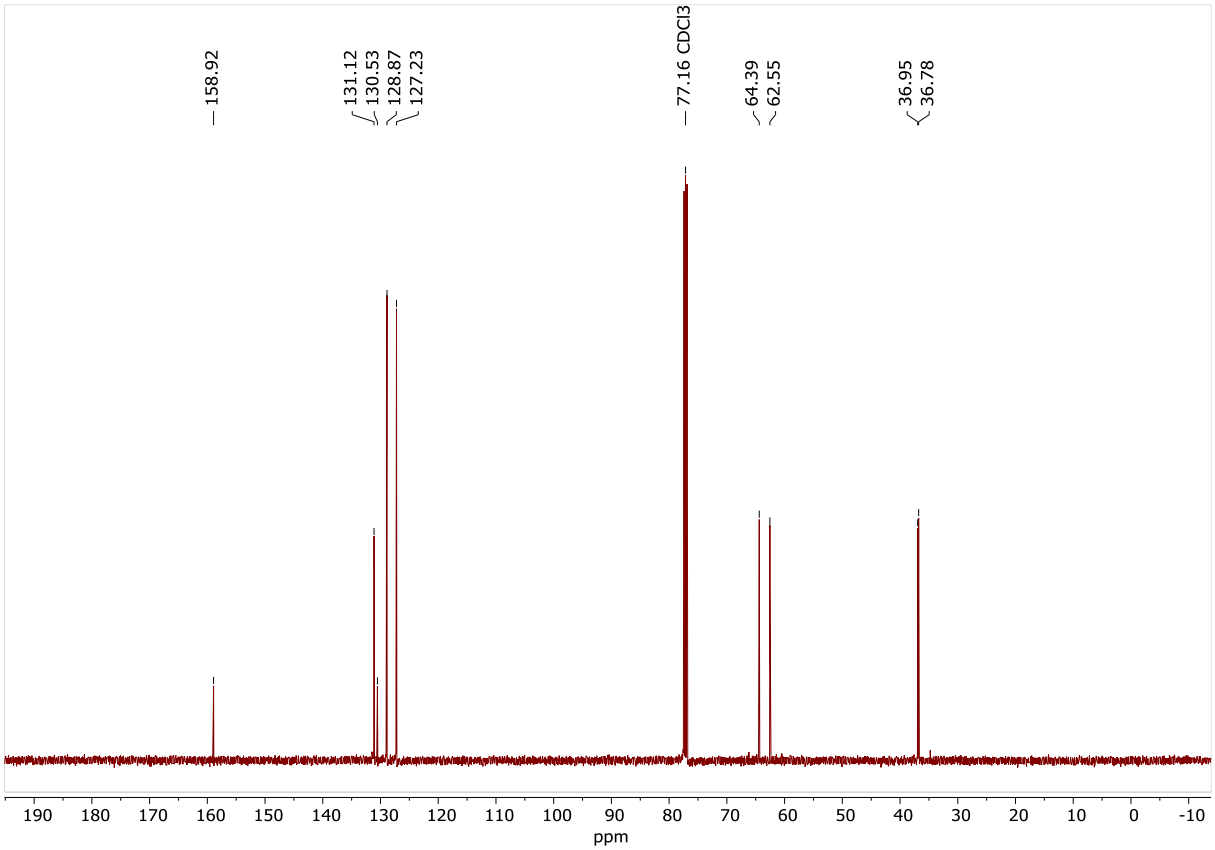
^{1}H NMR and ^{13}C NMR spectrum of compound **2q**



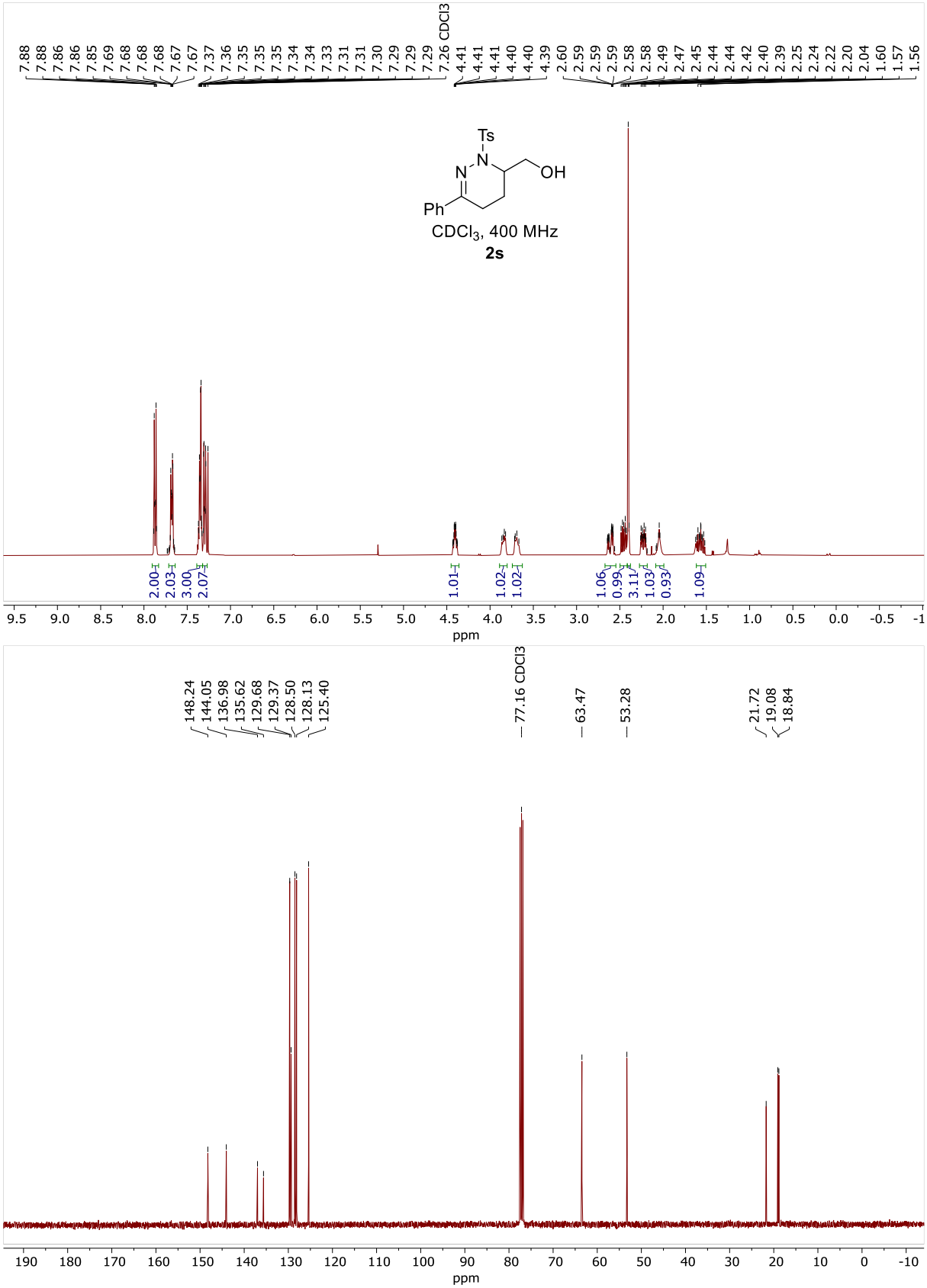


^{1}H NMR and ^{13}C NMR spectrum of compound **2r**

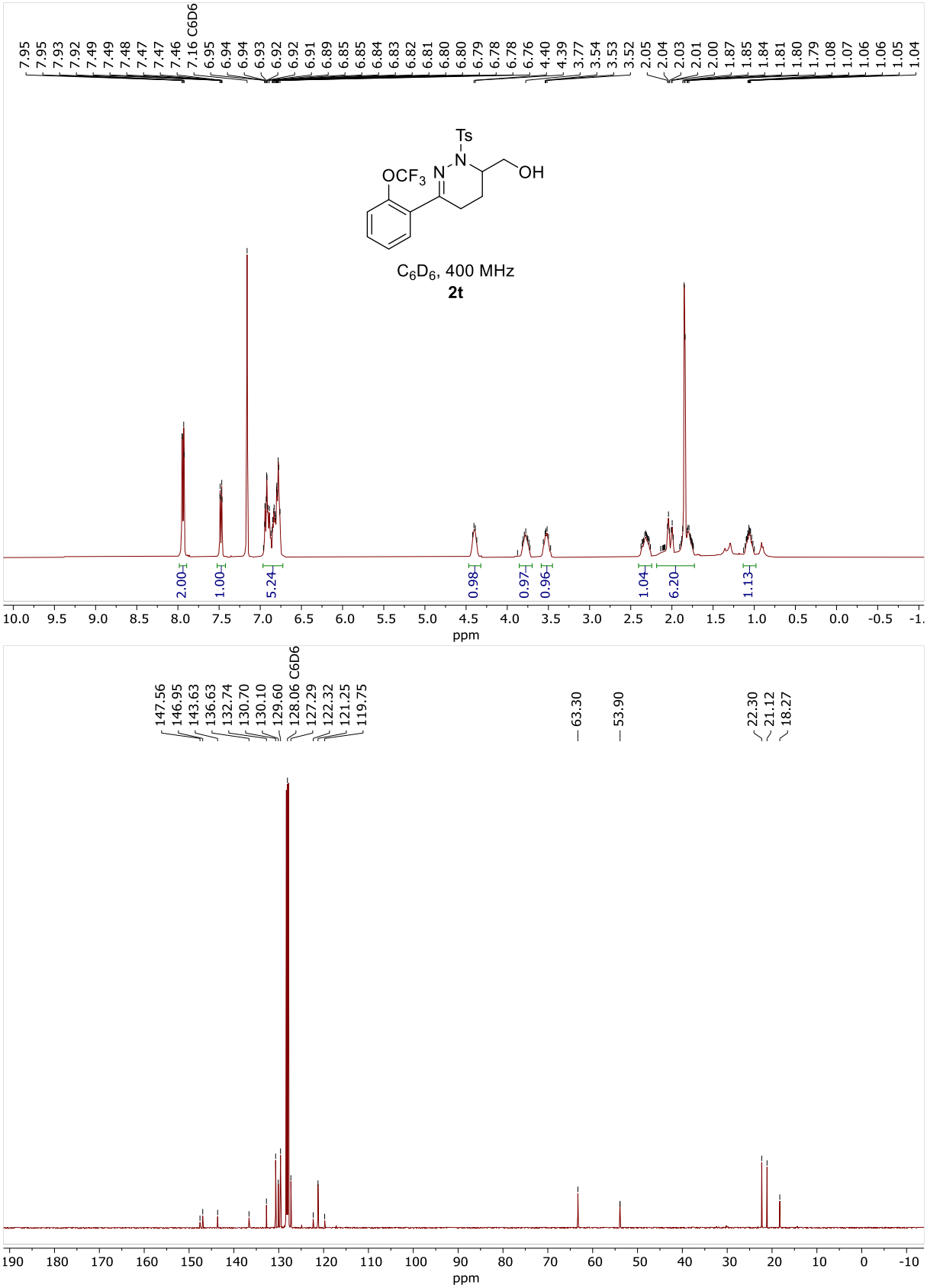




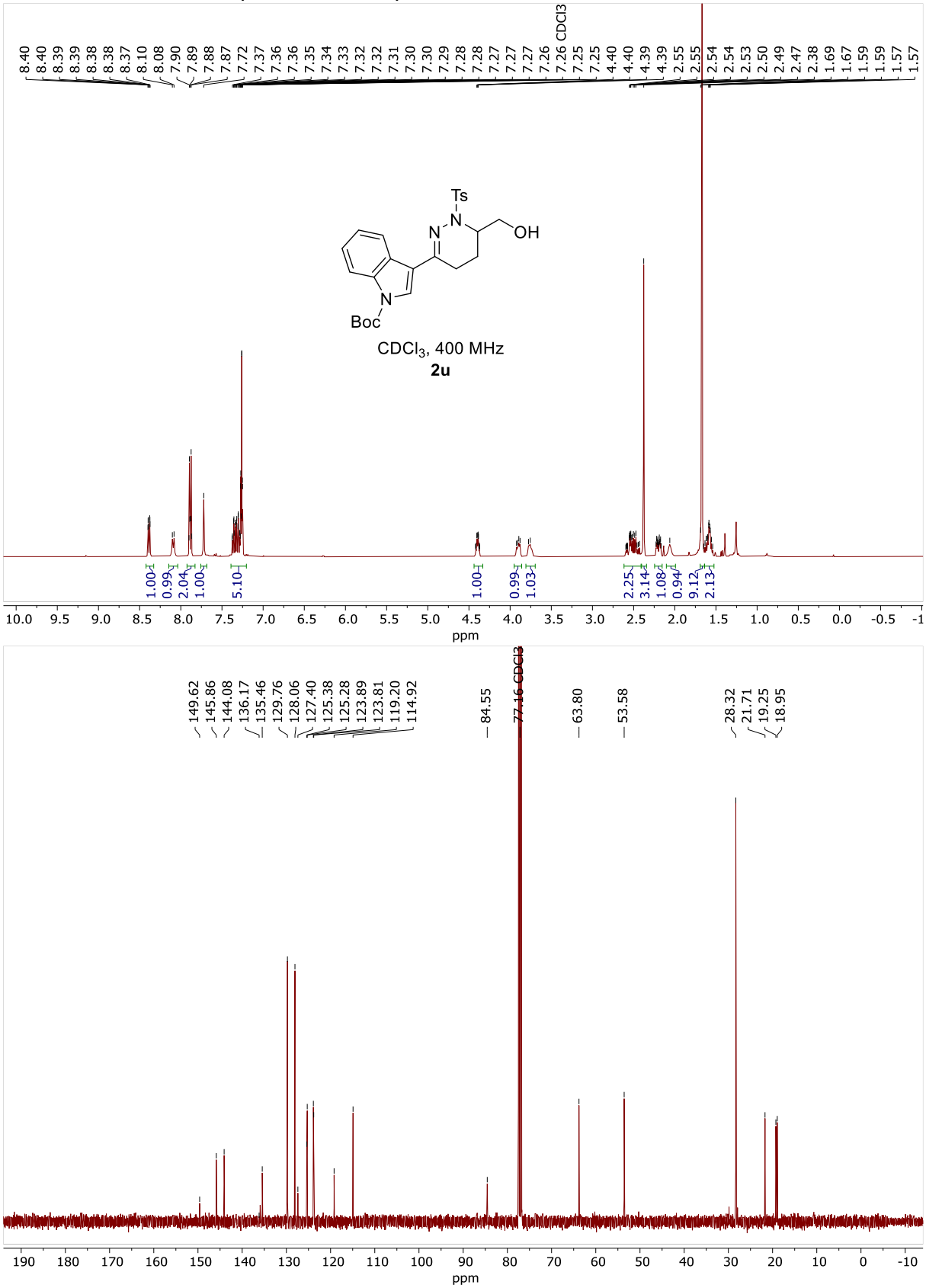
^{1}H NMR and ^{13}C NMR spectrum of compound **2s**



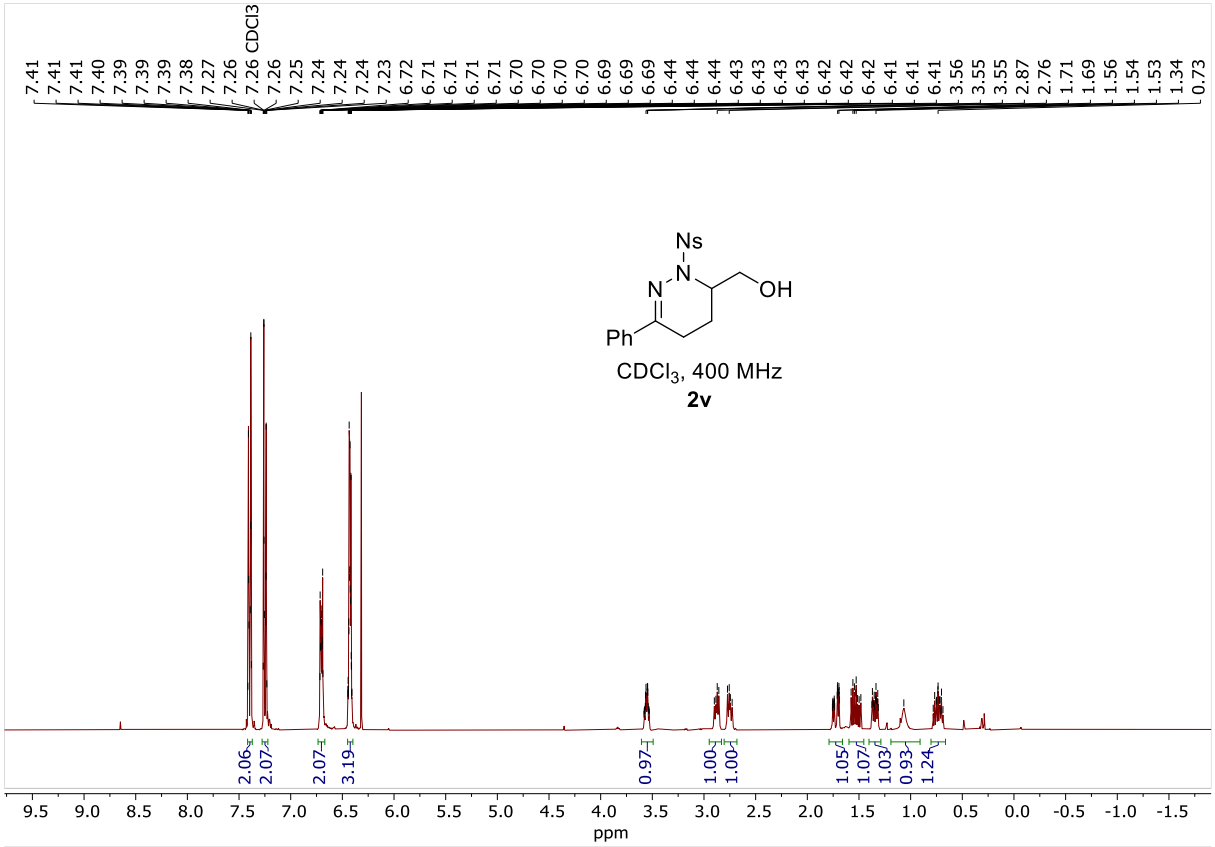
^{1}H NMR and ^{13}C NMR spectrum of compound **2t**

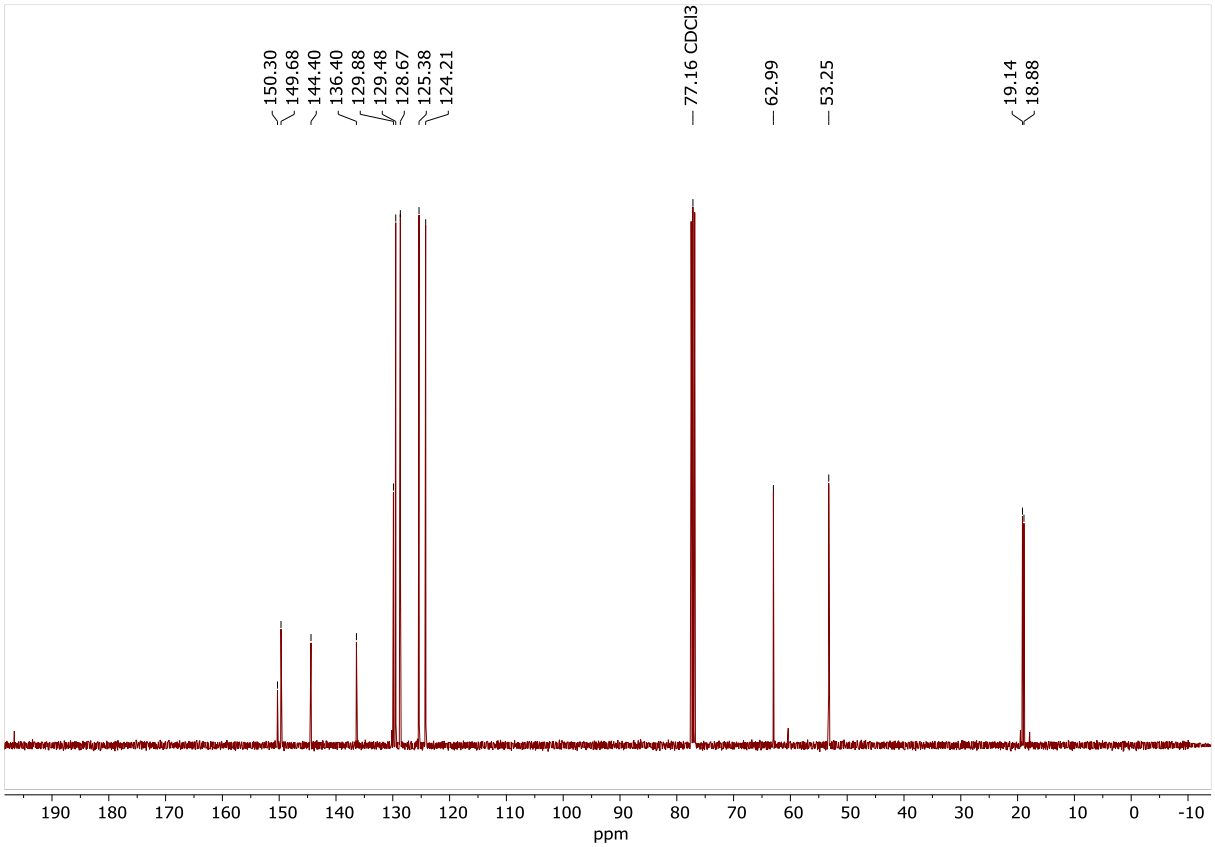


^{1}H NMR and ^{13}C NMR spectrum of compound **2u**

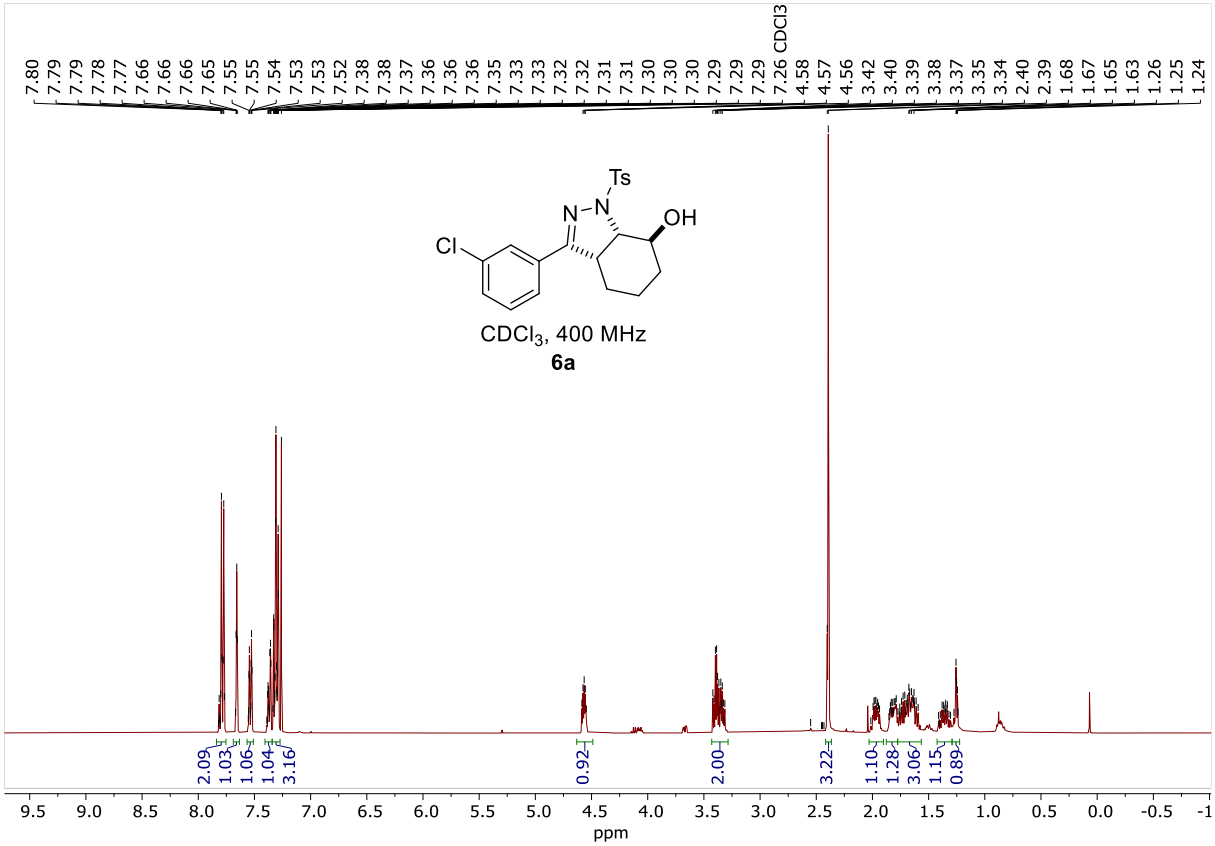


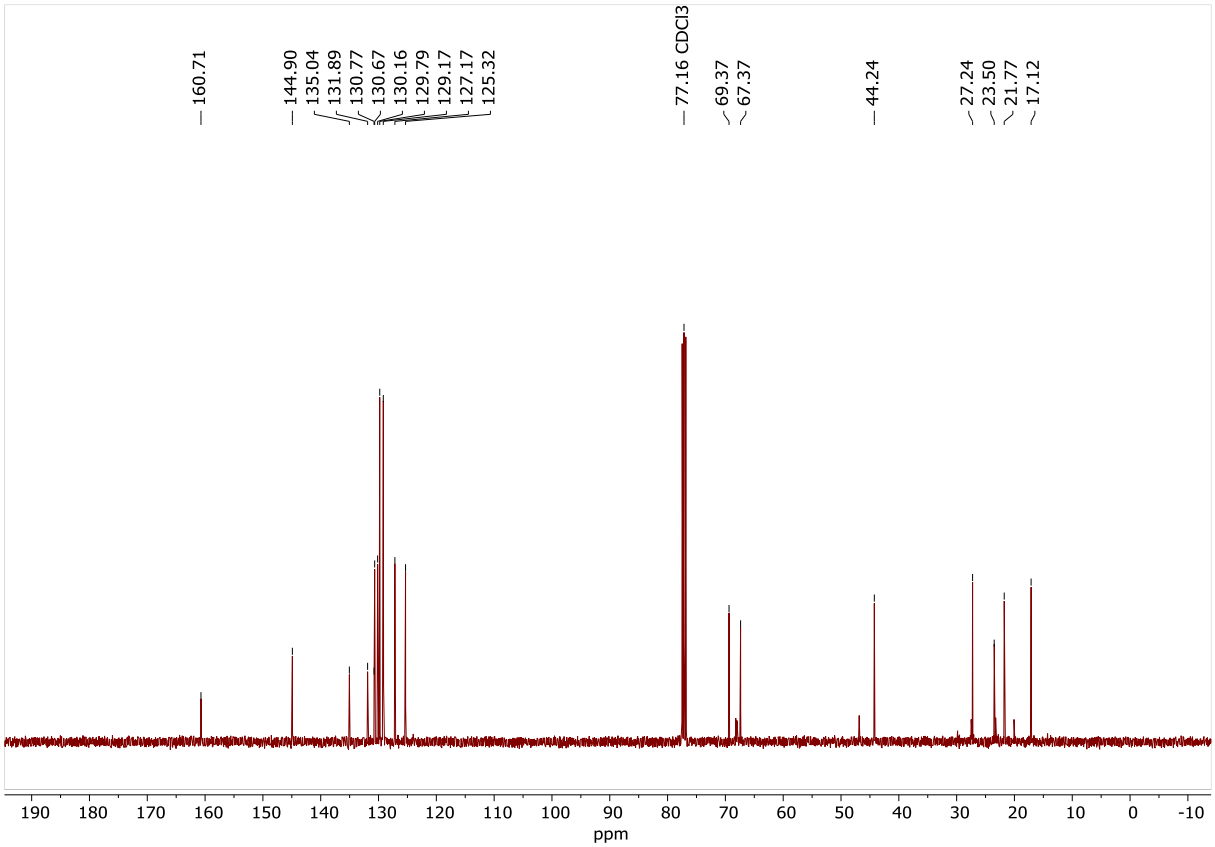
^{1}H NMR and ^{13}C NMR spectrum of compound **2v**



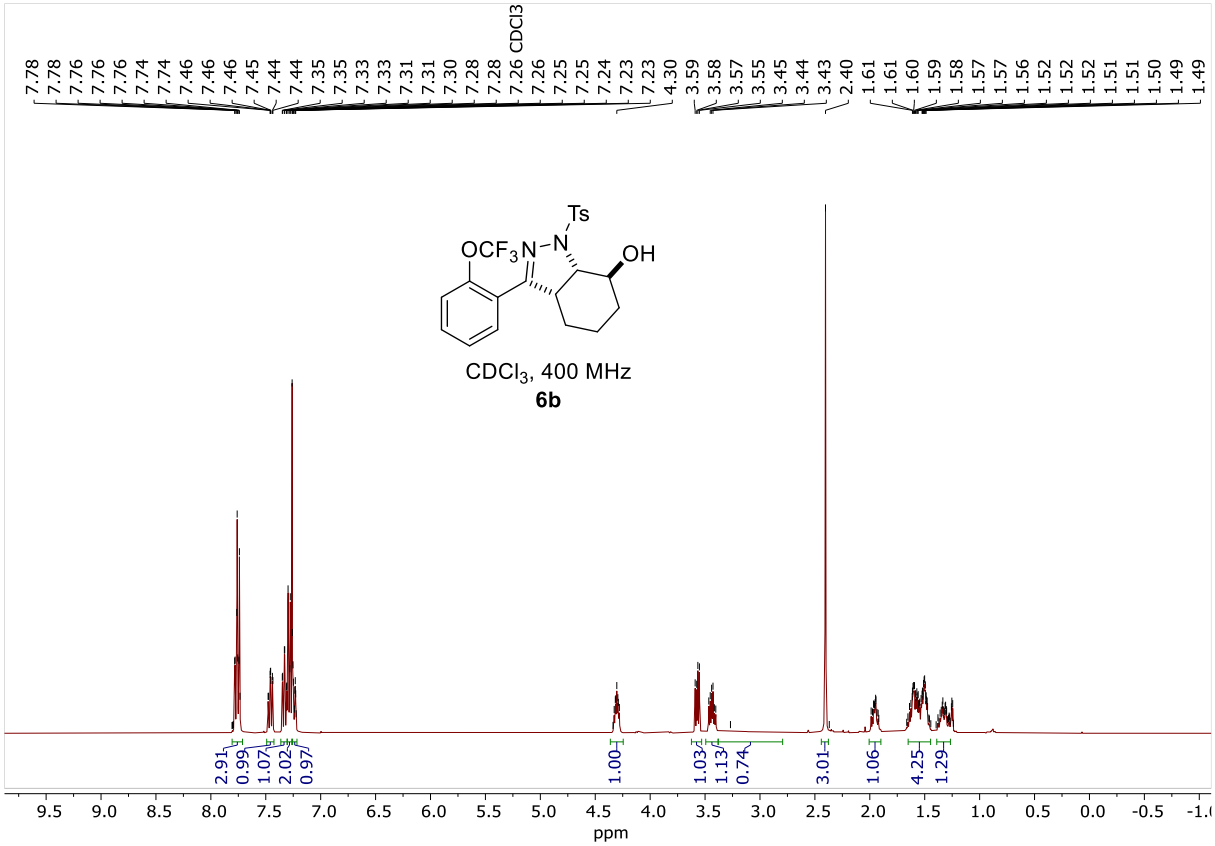


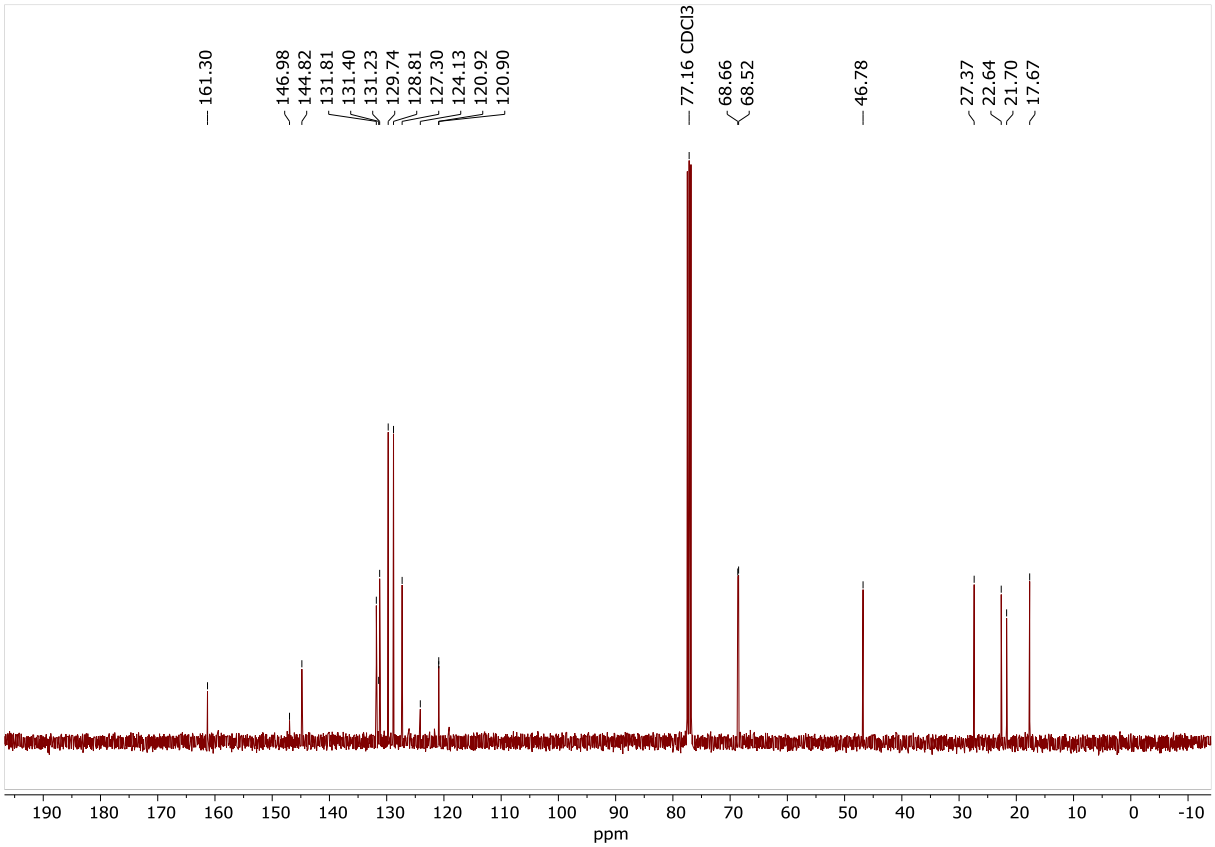
^{1}H NMR and ^{13}C NMR spectrum of compound **6a**



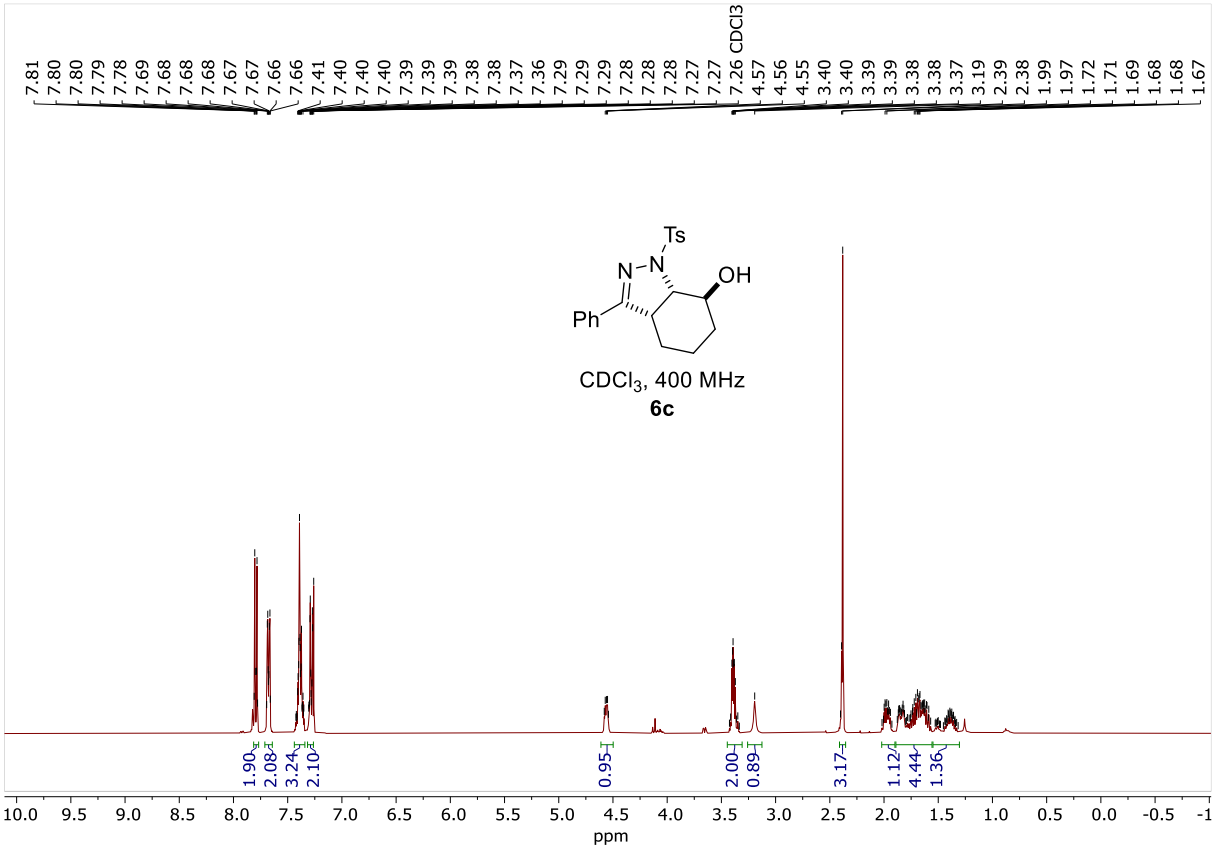


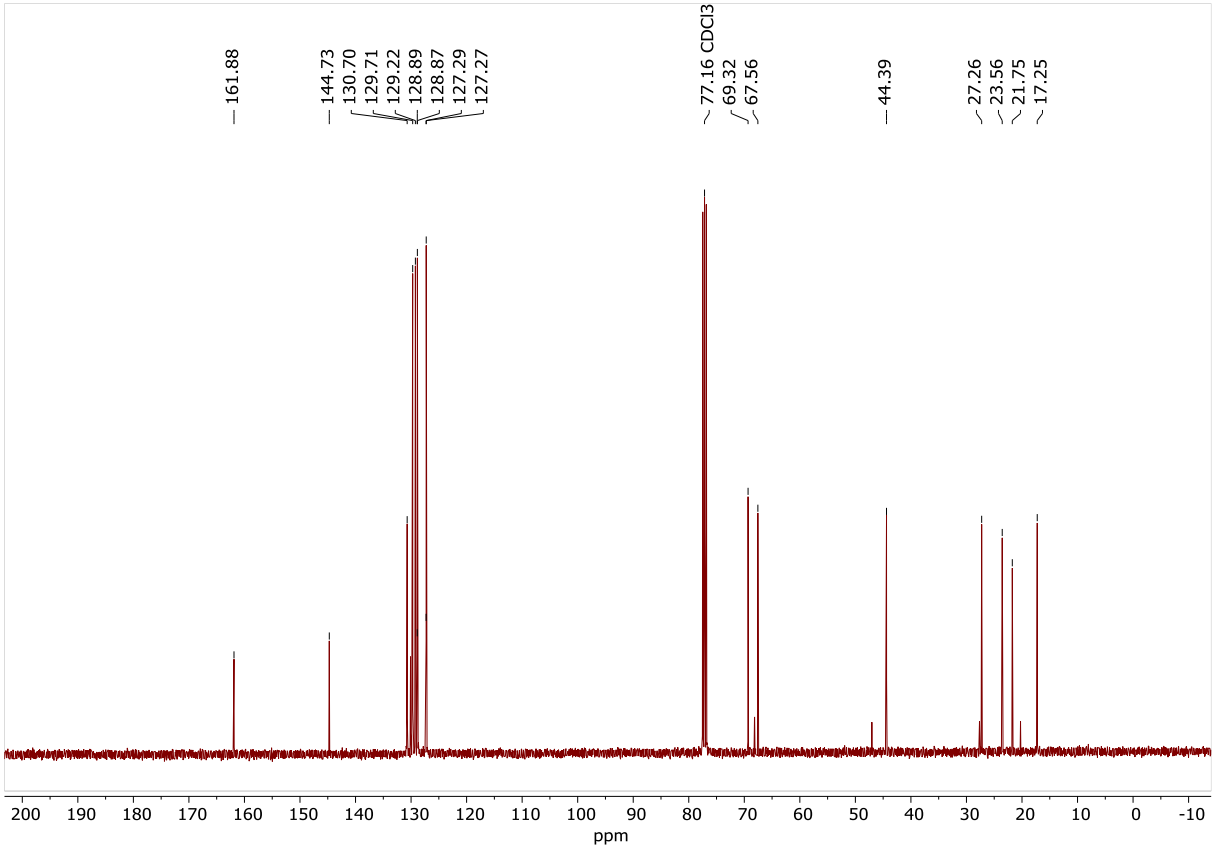
^{1}H NMR and ^{13}C NMR spectrum of compound **6b**



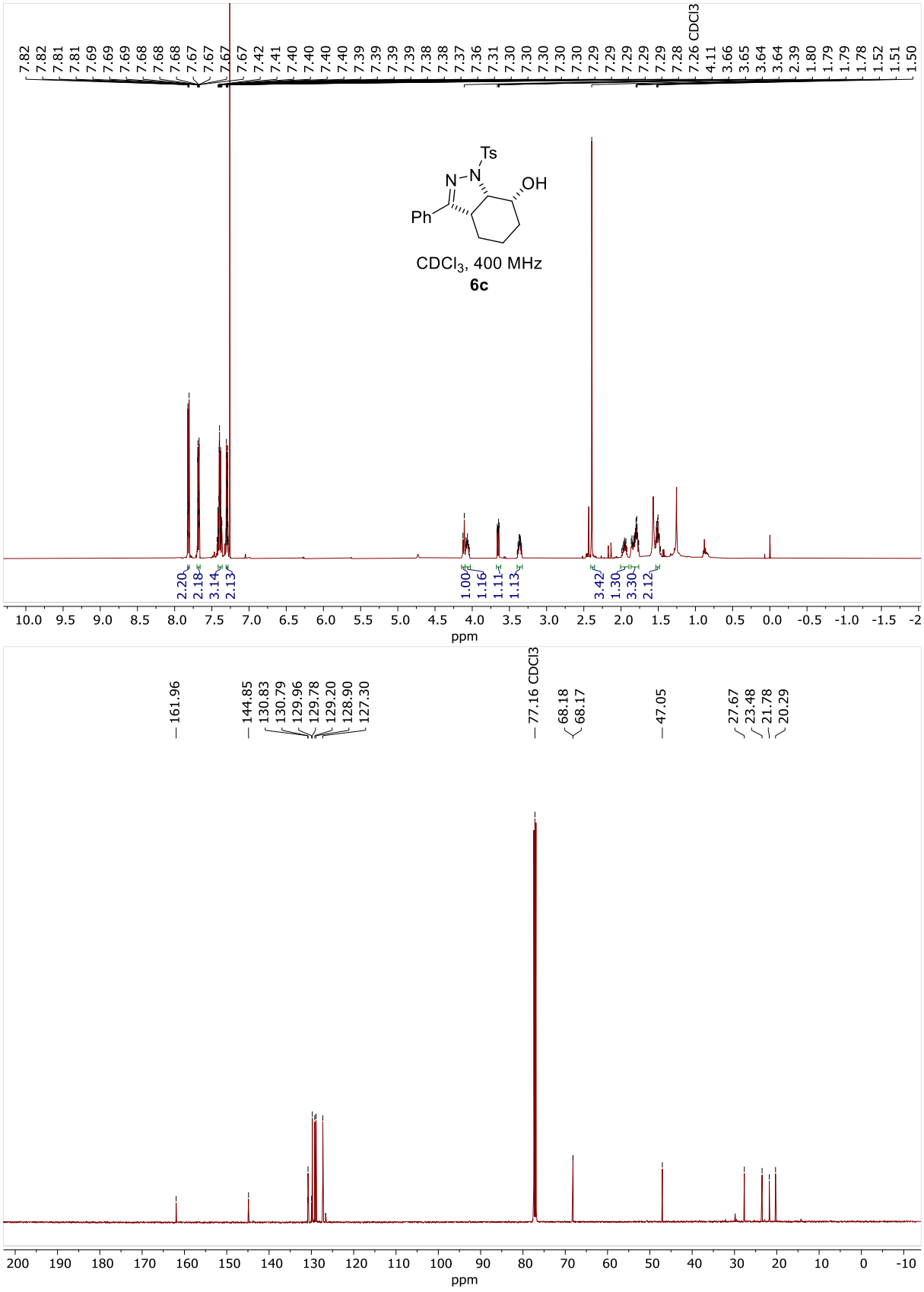


^{1}H NMR and ^{13}C NMR spectrum of compound **6c**

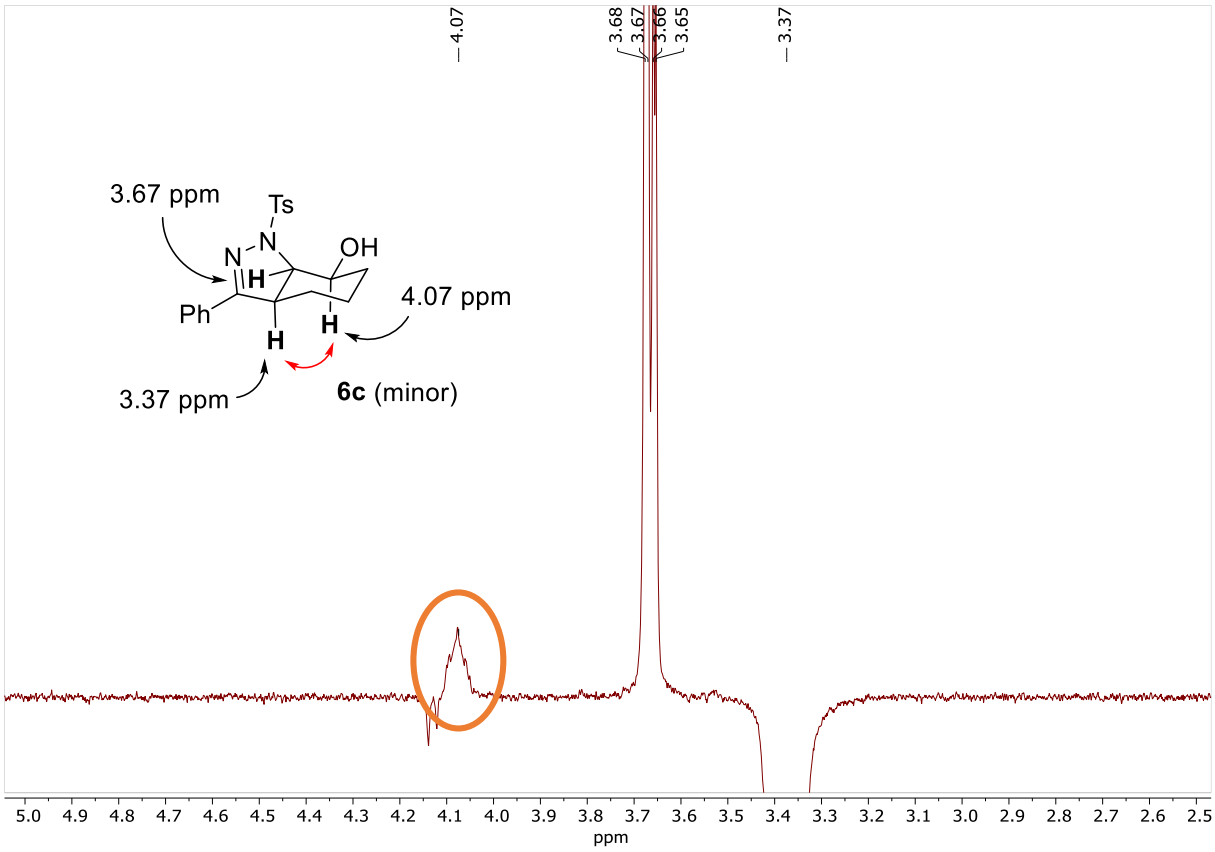




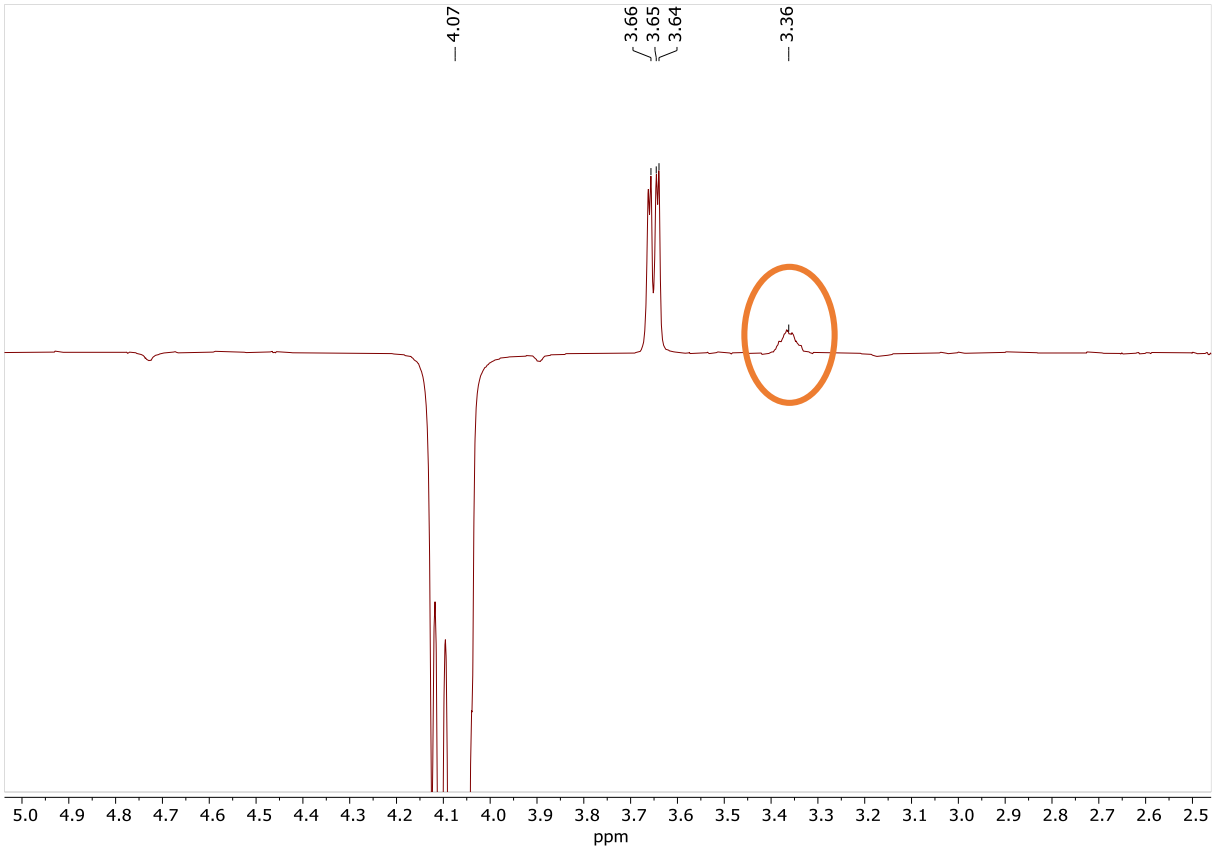
^{1}H NMR, ^{13}C NMR, 1D NOE spectra of compound **6c** (minor diastereomer)



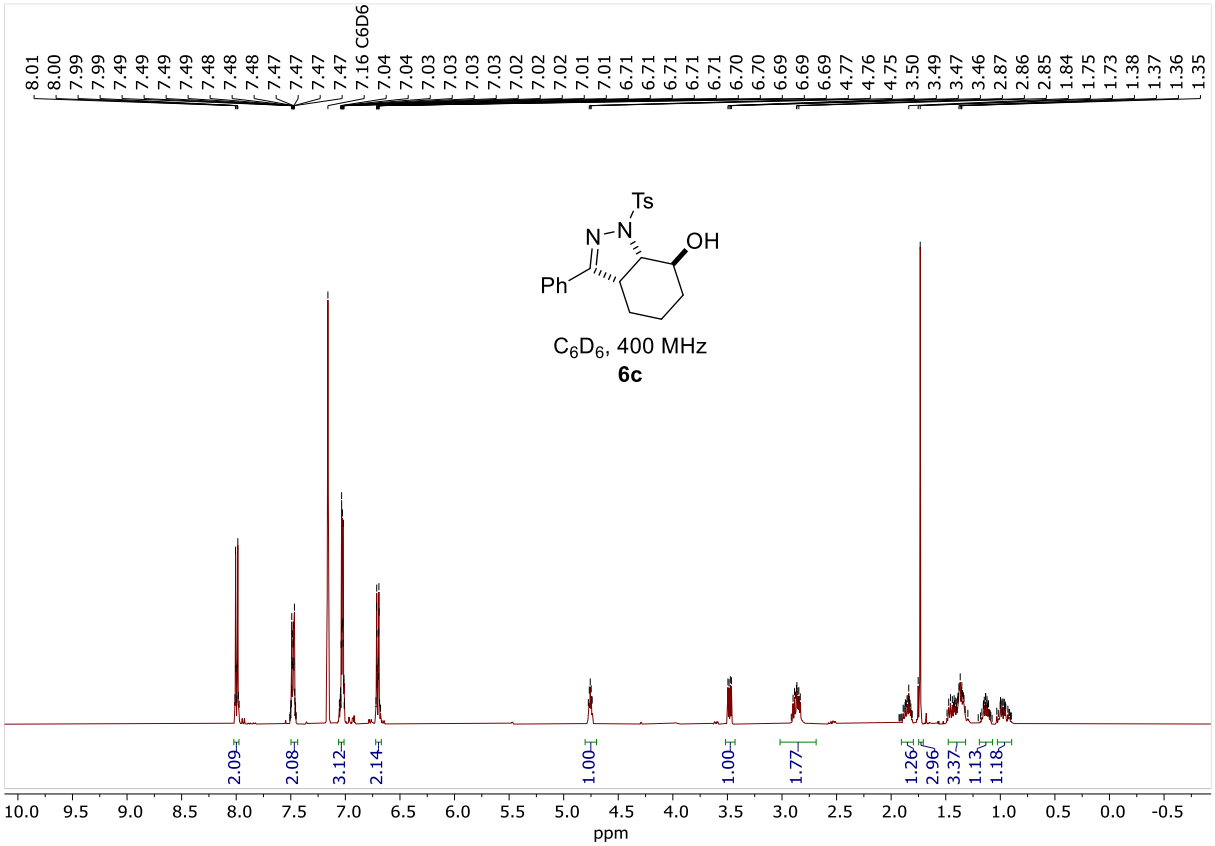
1D NOE NMR (500 MHz, $CDCl_3$) of **6c** (minor diasteromer) irradiated at 3.37 ppm.

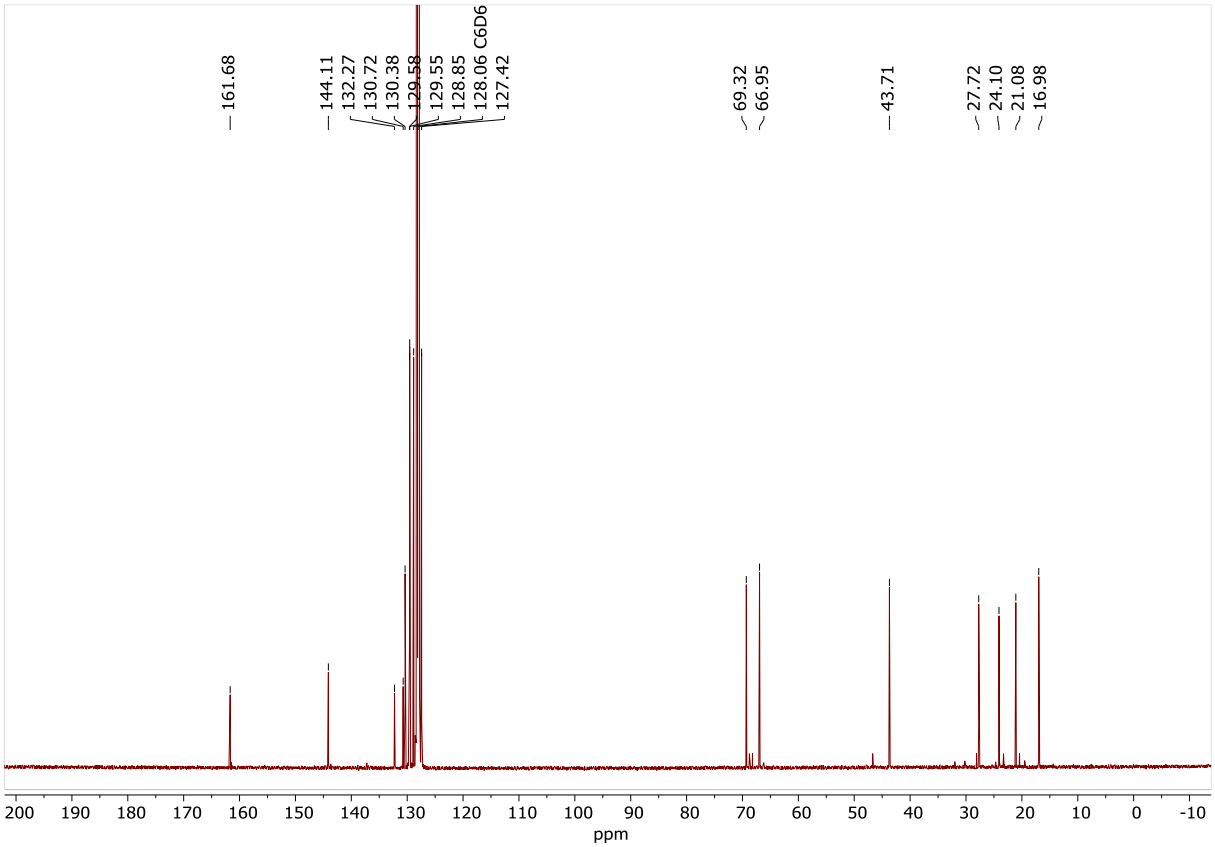


1D NOE NMR (500 MHz, $CDCl_3$) of **6c** (minor diasteromer) irradiated at 4.07 ppm.

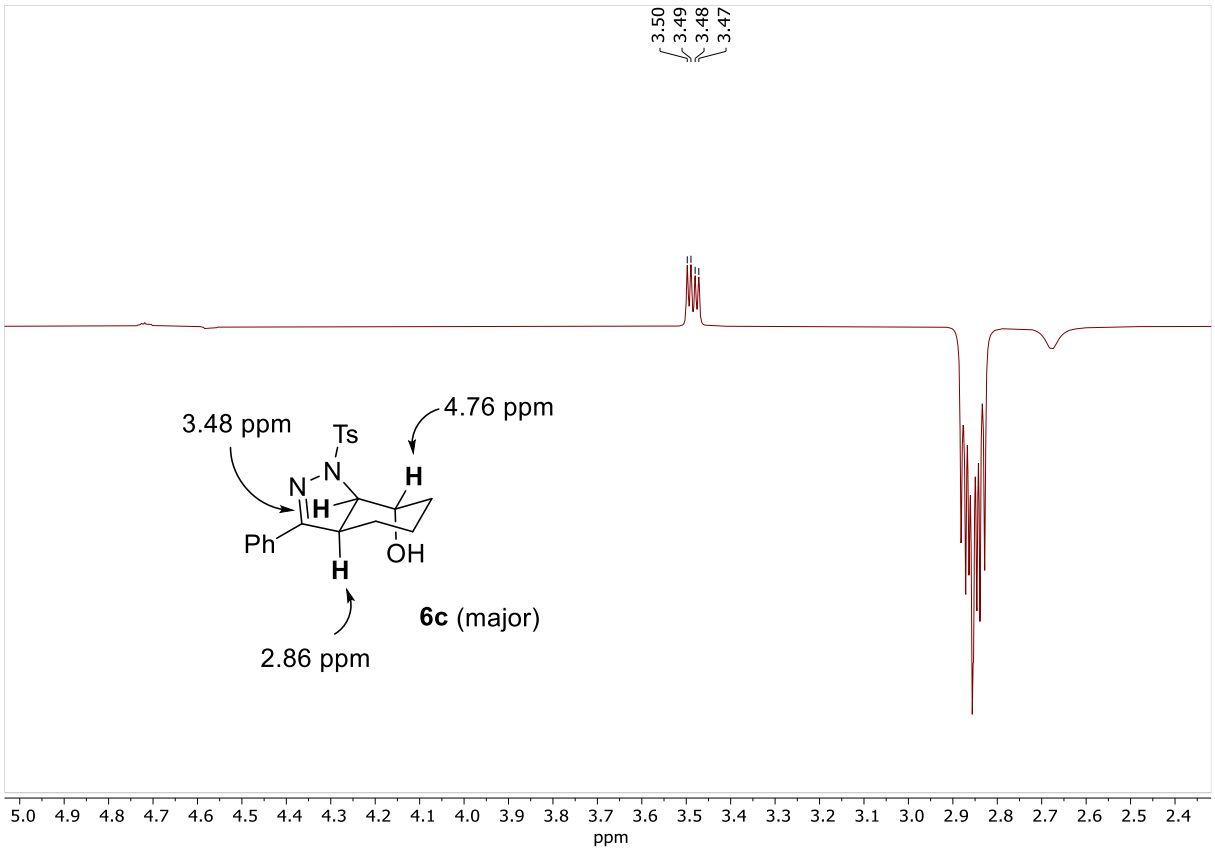


^{1}H NMR, ^{13}C NMR, 1D NOE spectra of compound **6c** (major diastereomer)

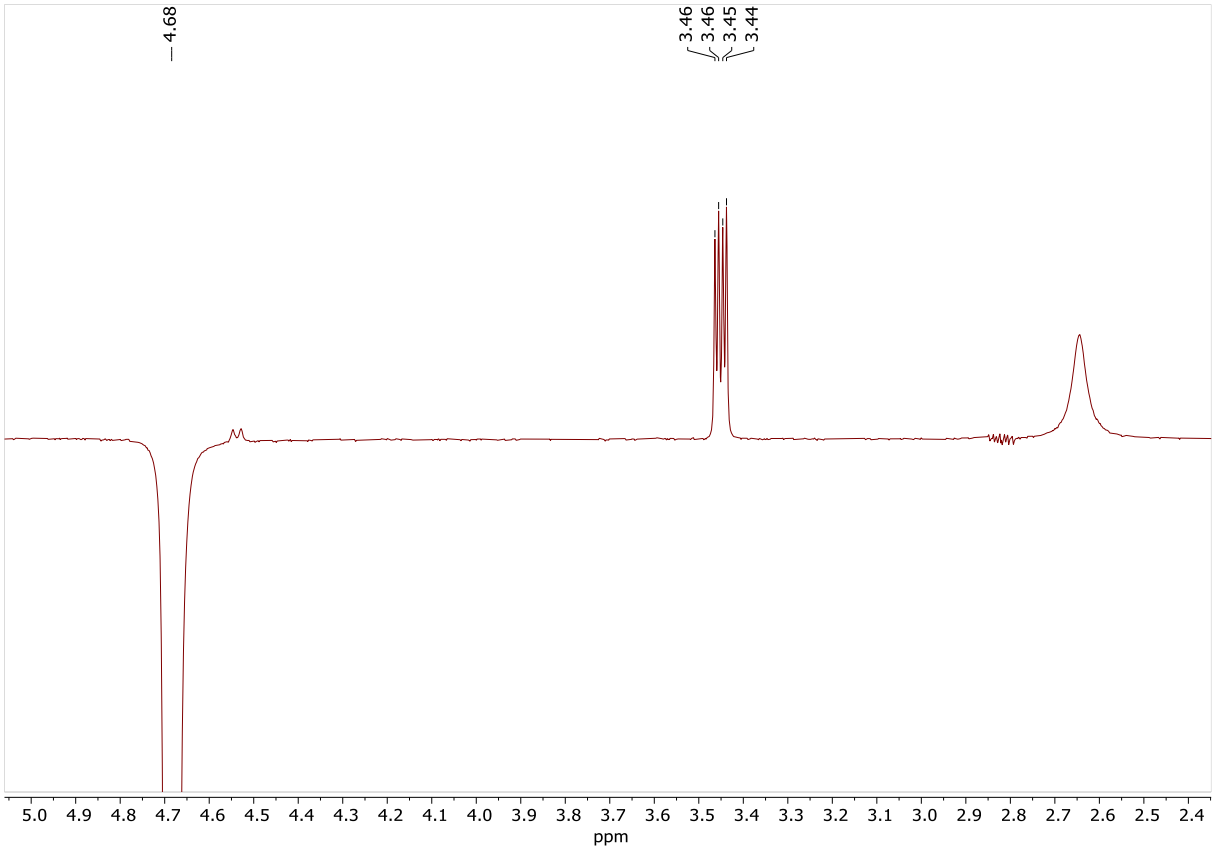




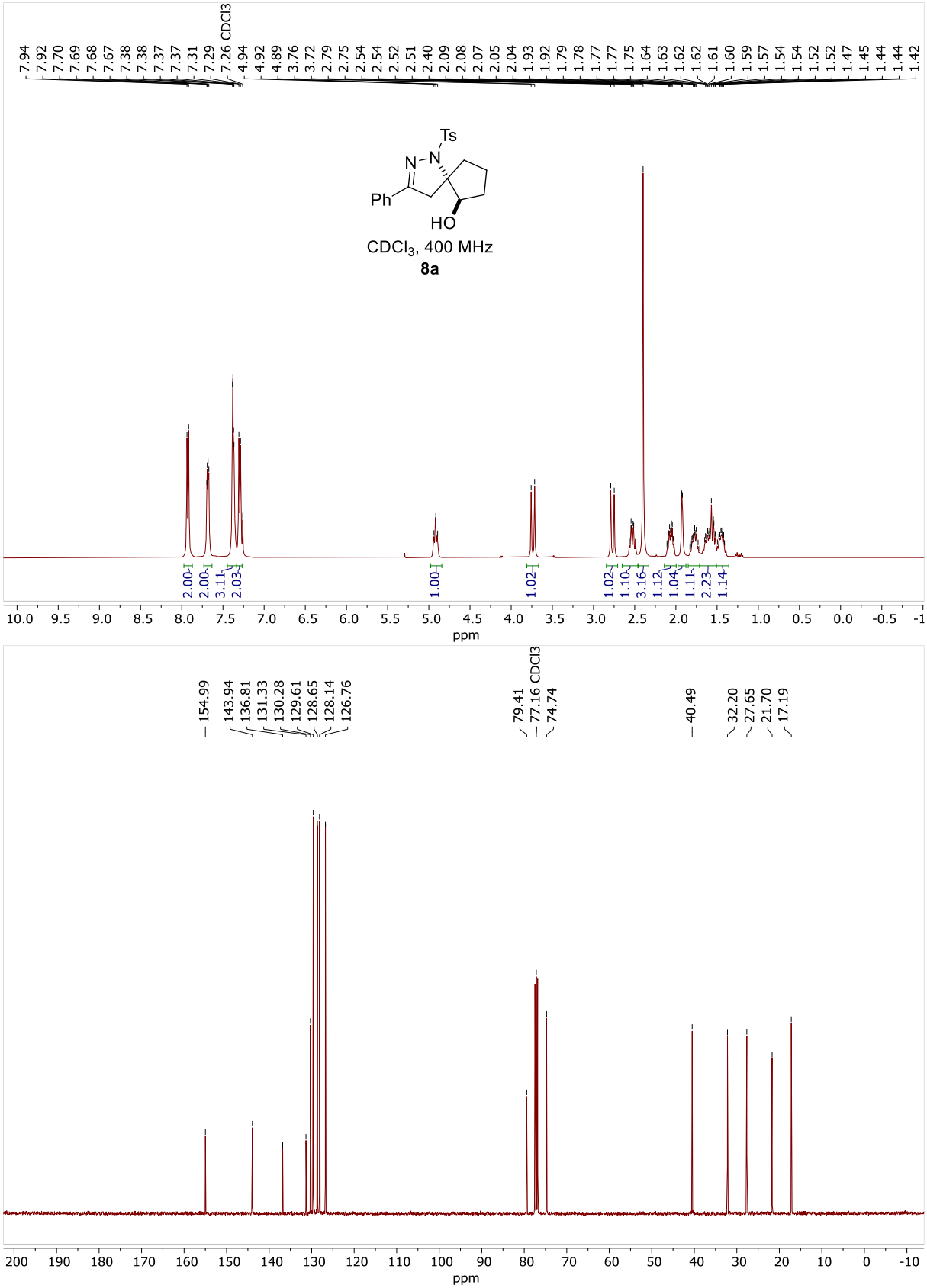
1D NOE NMR (500 MHz, C_6D_6) of **6c** (major diasteromer) irradiated at 2.86 ppm.



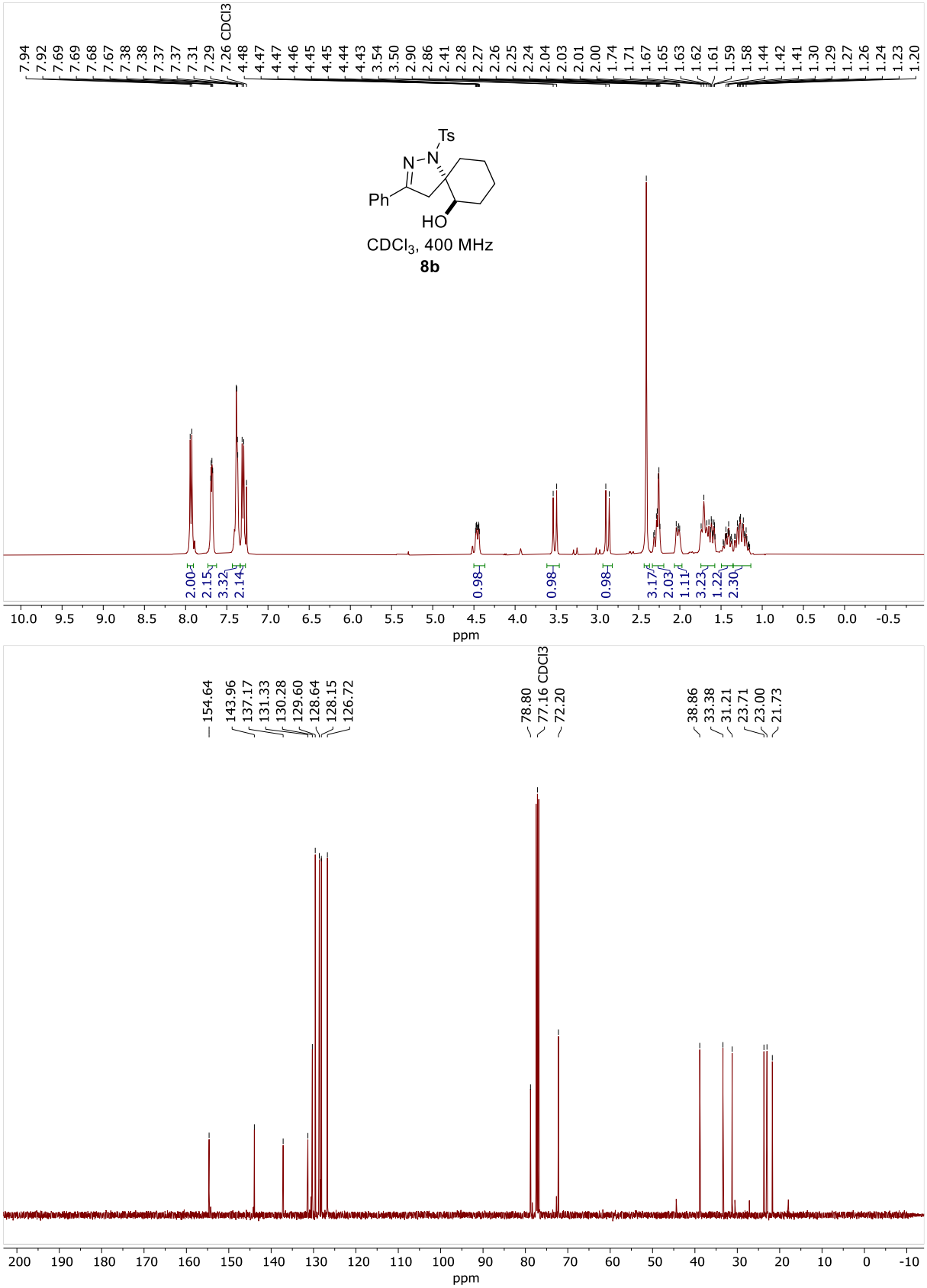
1D NOE NMR (500 MHz, C_6D_6) of **6c** (major diasteromer) irradiated at 4.76 ppm.



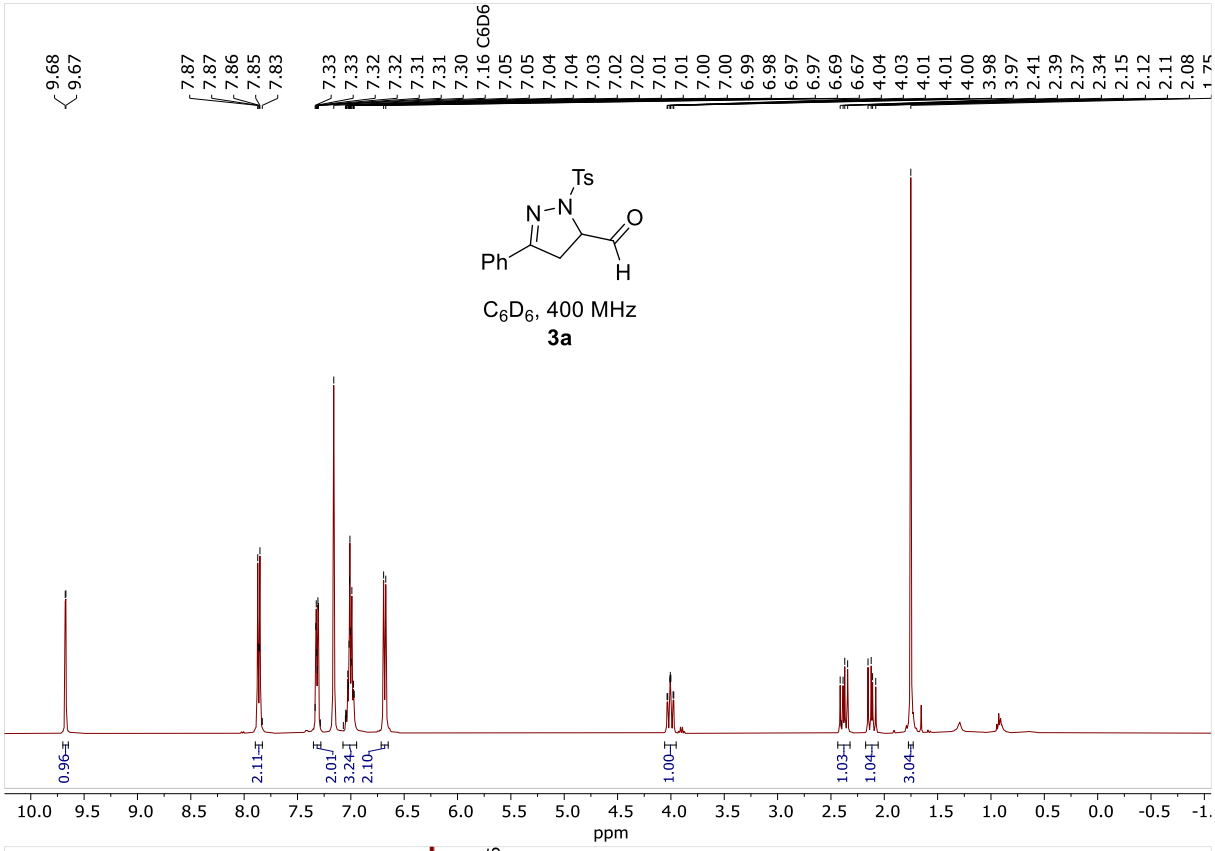
^{1}H NMR and ^{13}C NMR spectrum of compound **8a**

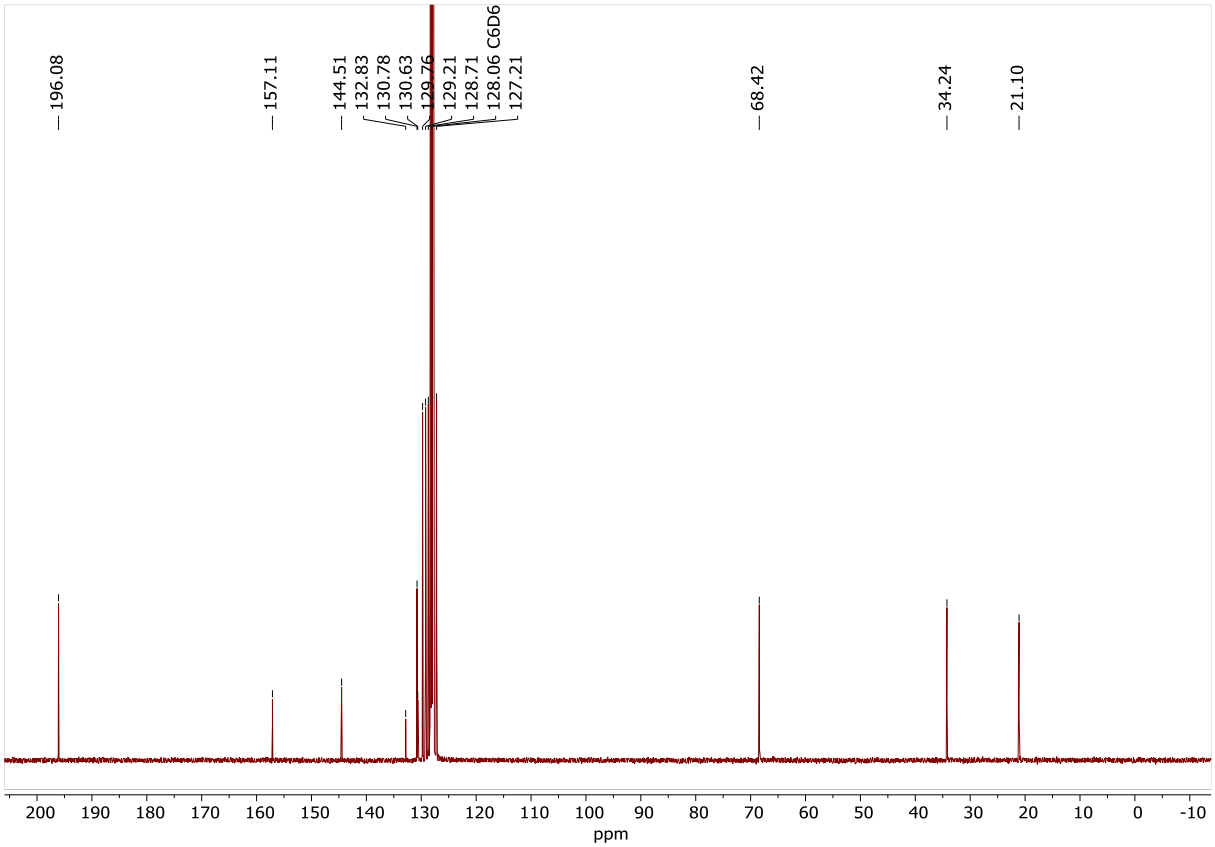


^{1}H NMR and ^{13}C NMR spectrum of compound **8b**

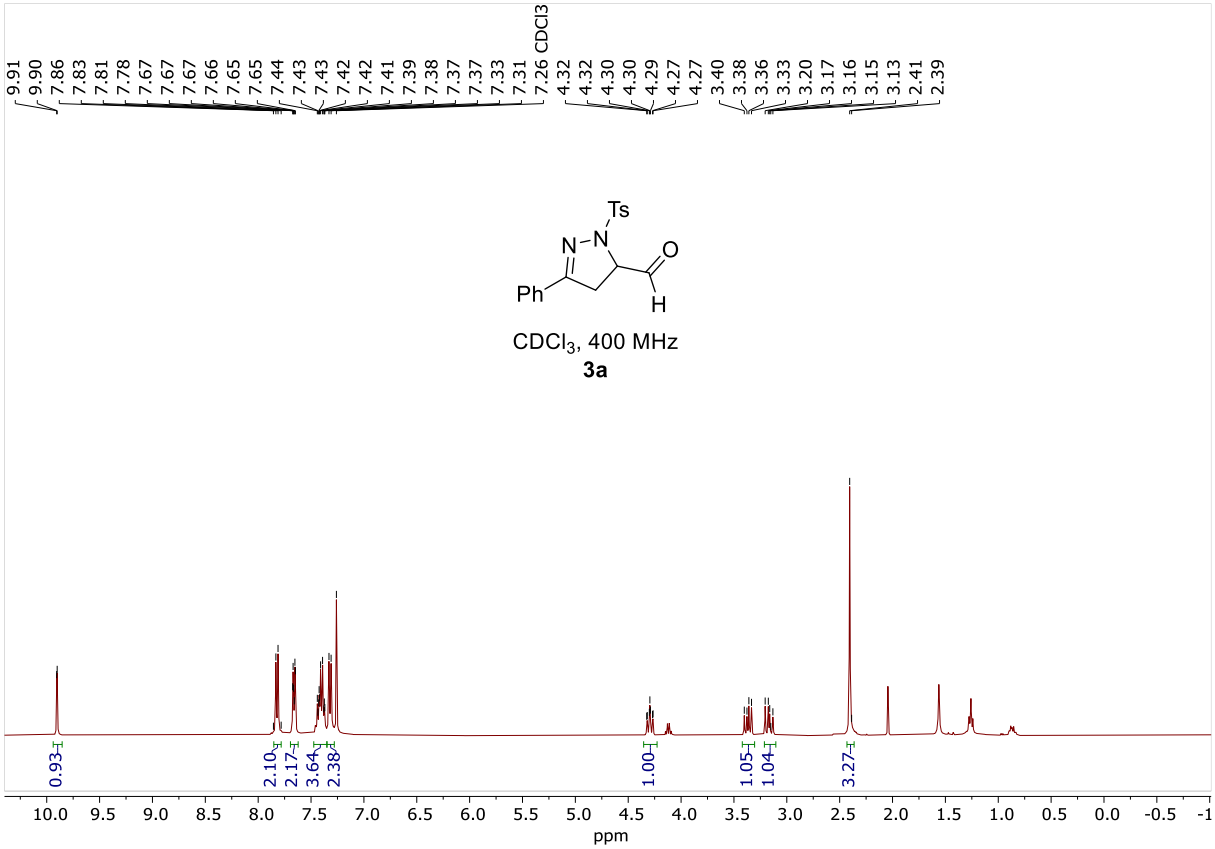


^{1}H NMR and ^{13}C NMR spectra of compound **3a**

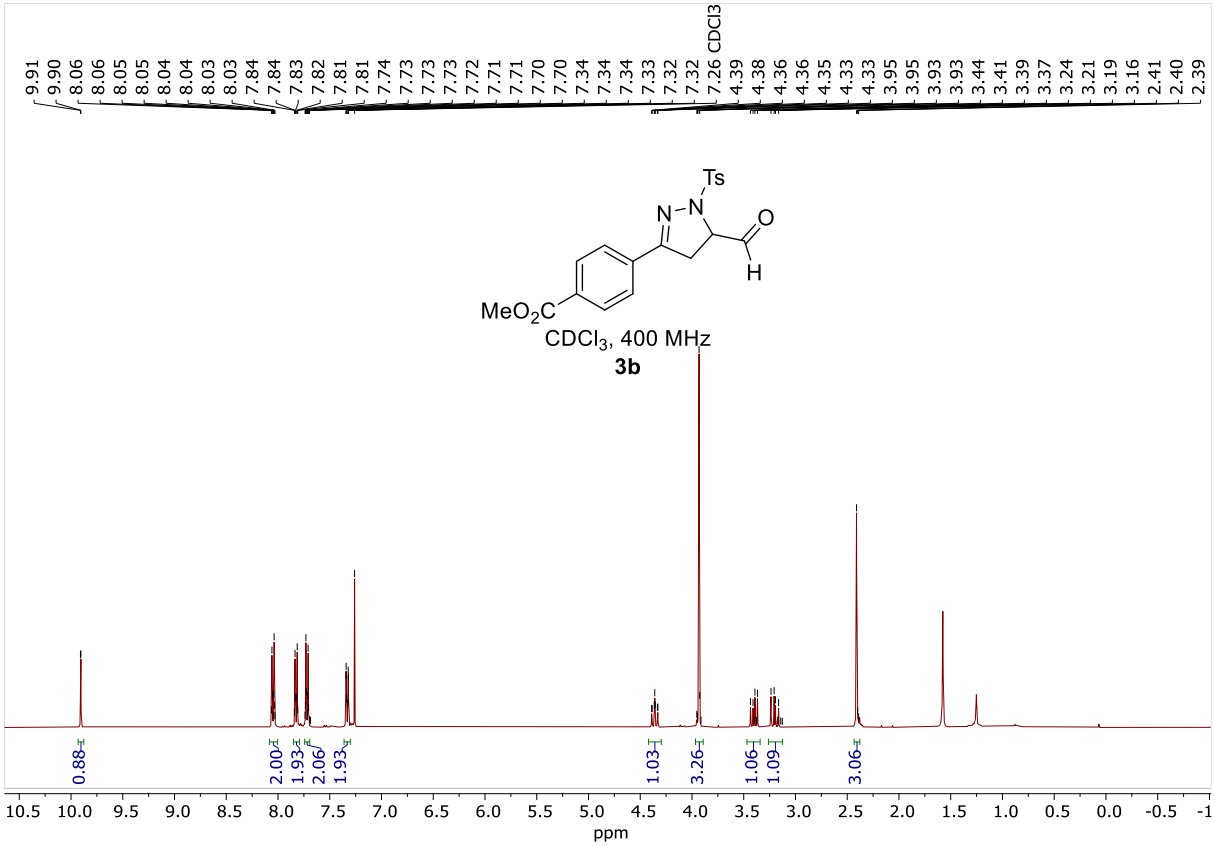


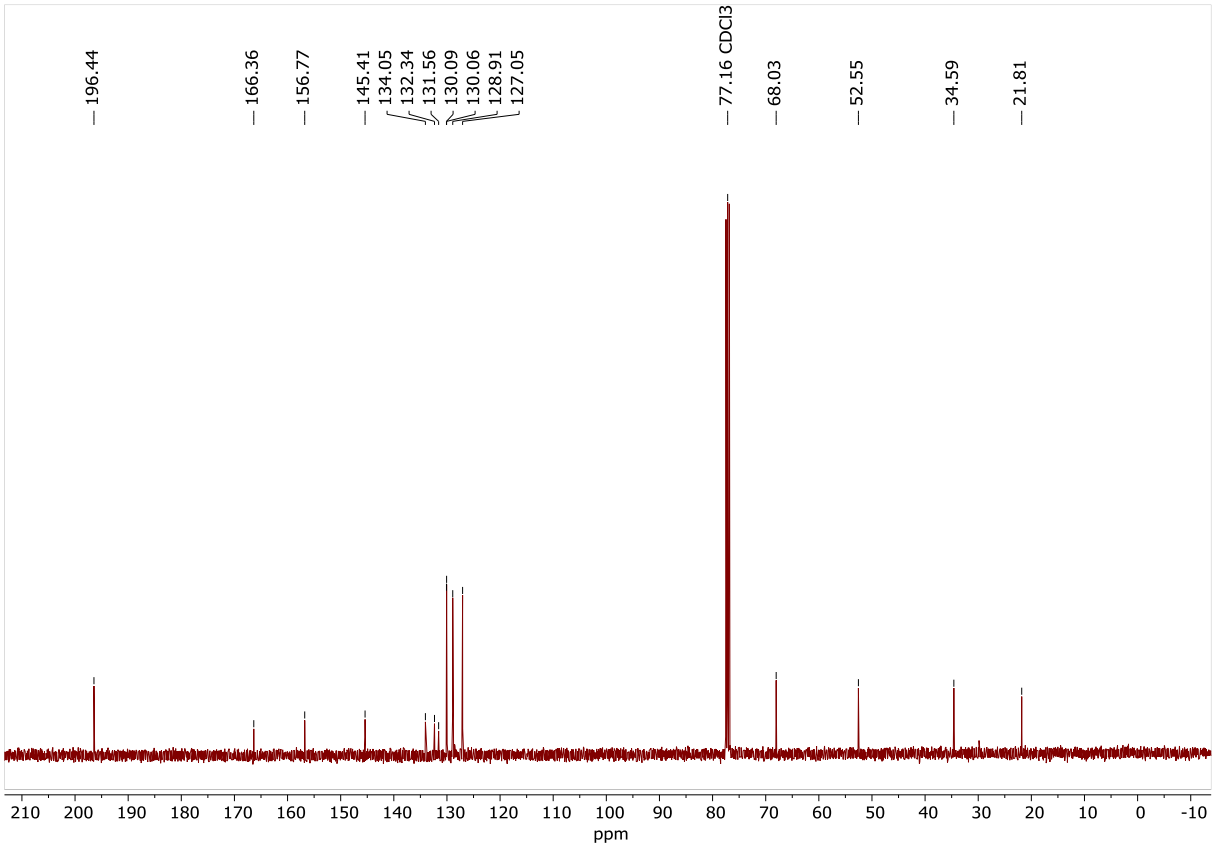


^{1}H NMR and ^{13}C NMR spectrum of compound **3a** in $CDCl_3$

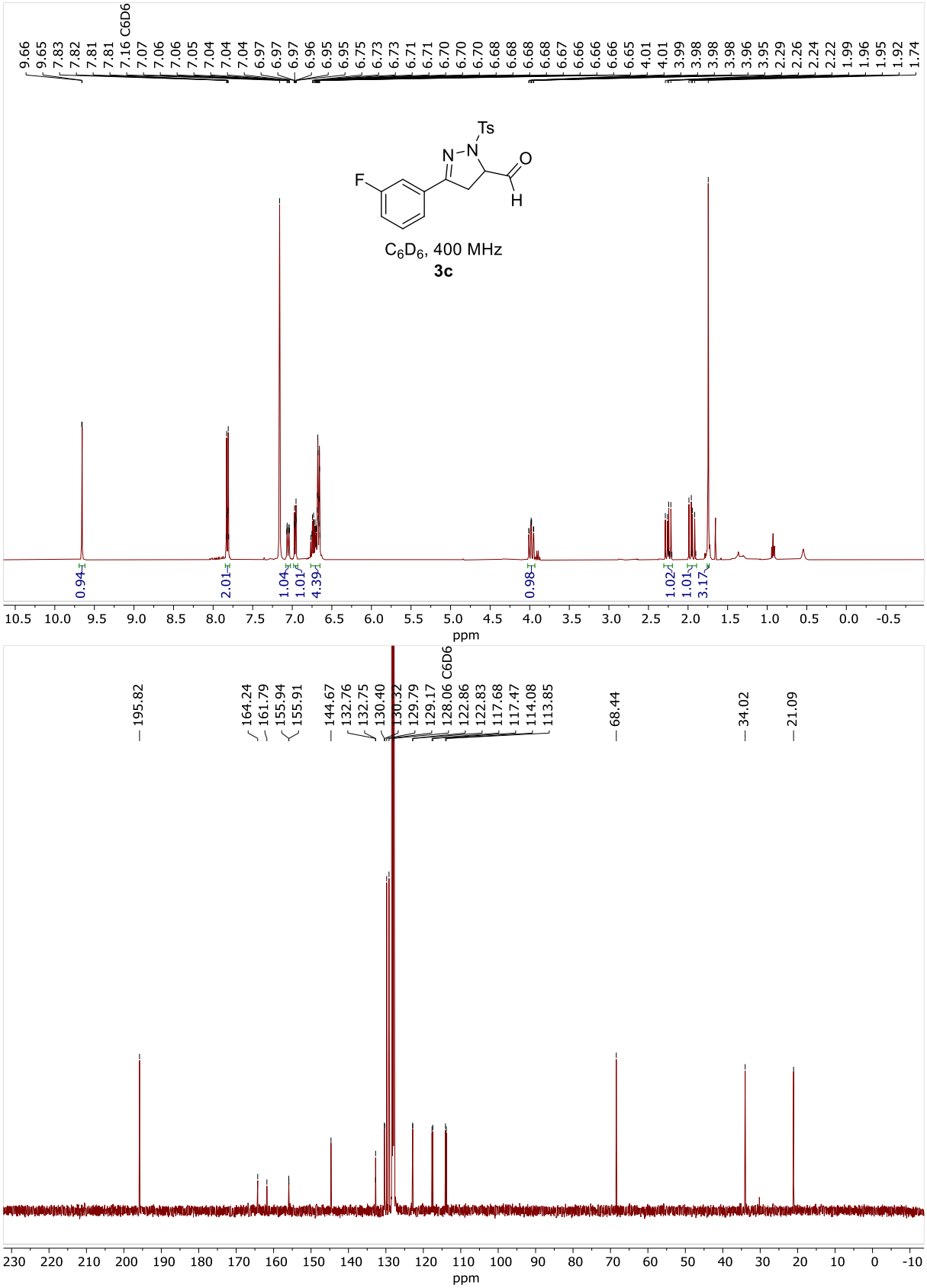


^{1}H NMR and ^{13}C NMR spectrum of compound **3b**

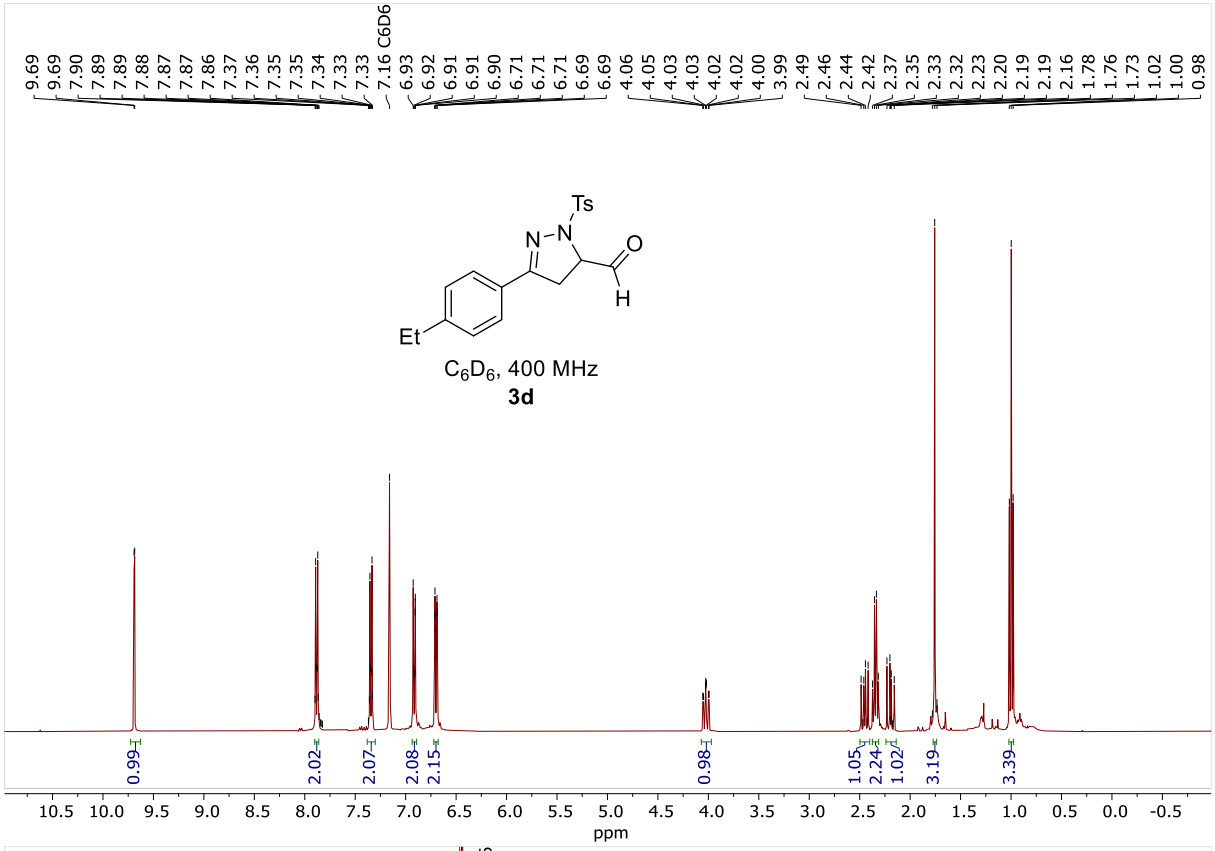


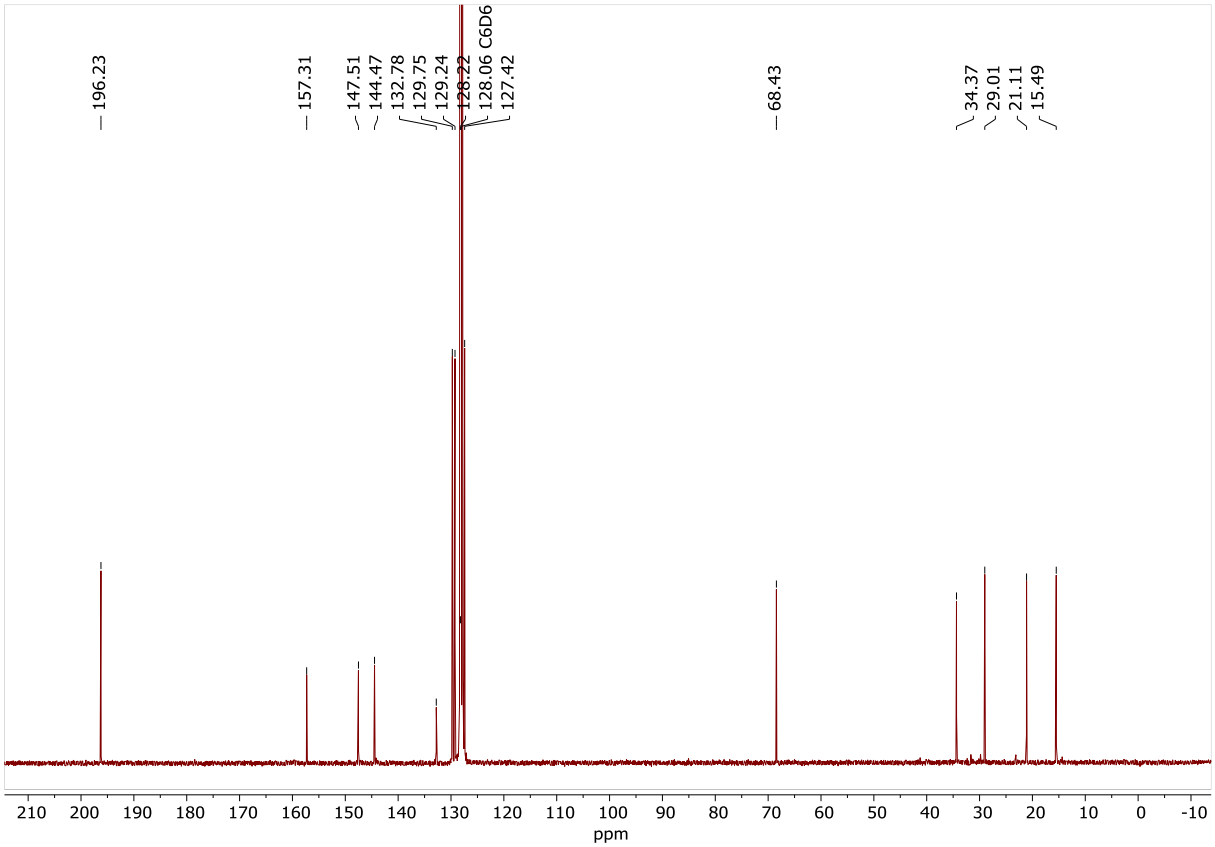


^{1}H NMR and ^{13}C NMR spectrum of compound **3c**

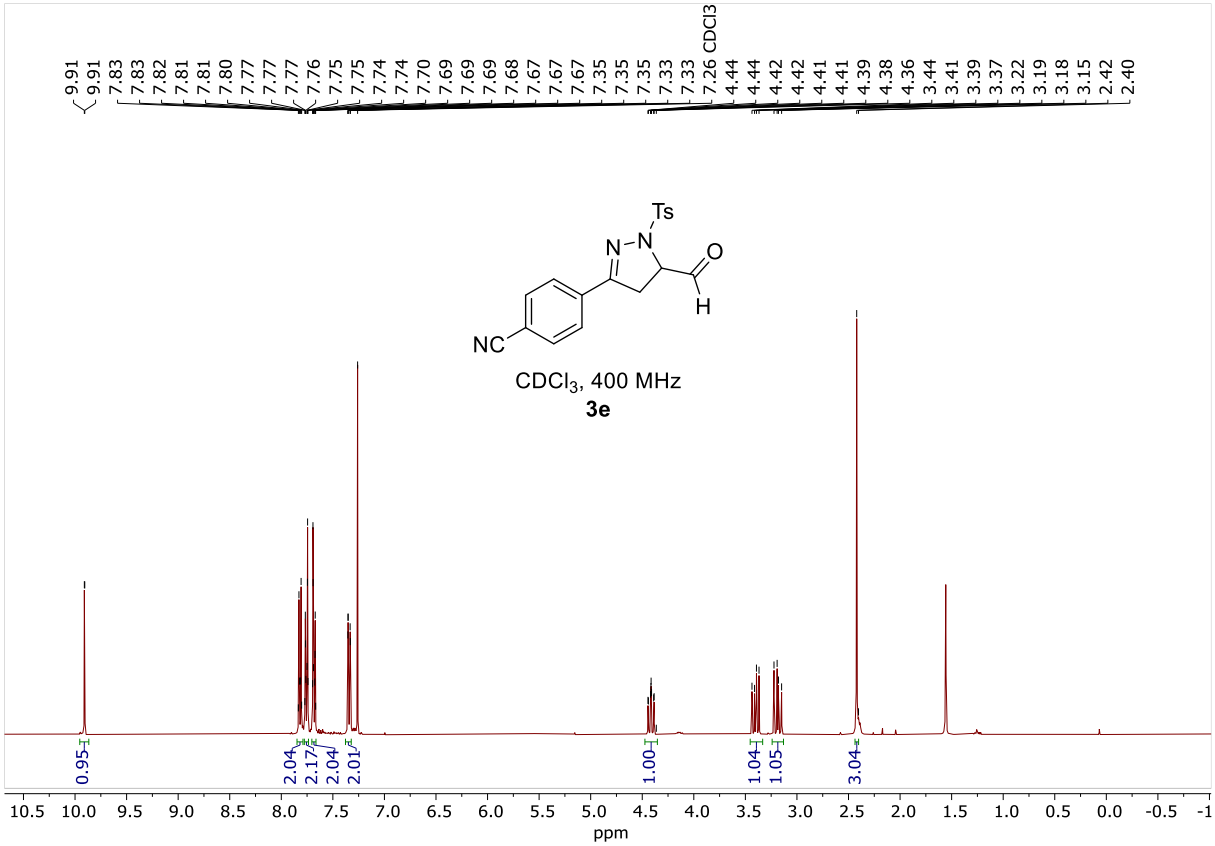


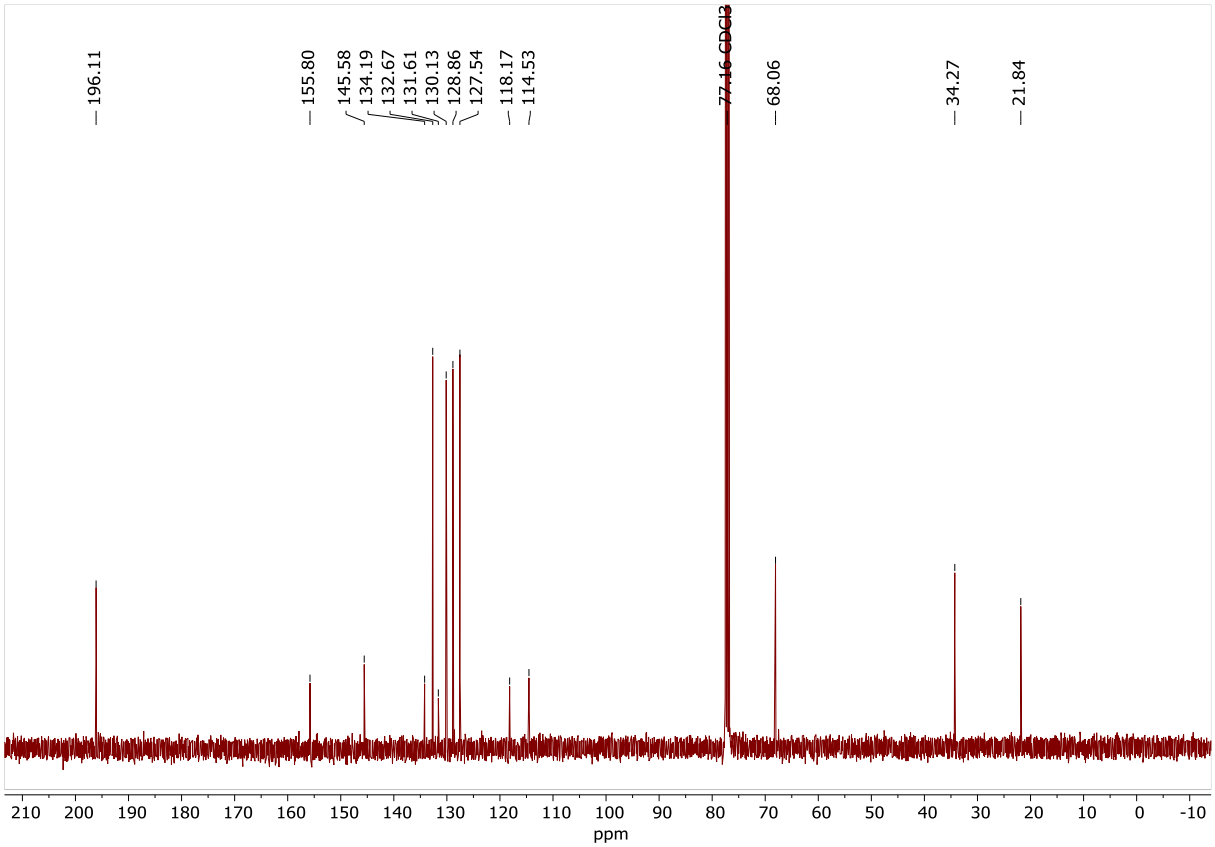
^{1}H NMR and ^{13}C NMR spectrum of compound **3d**



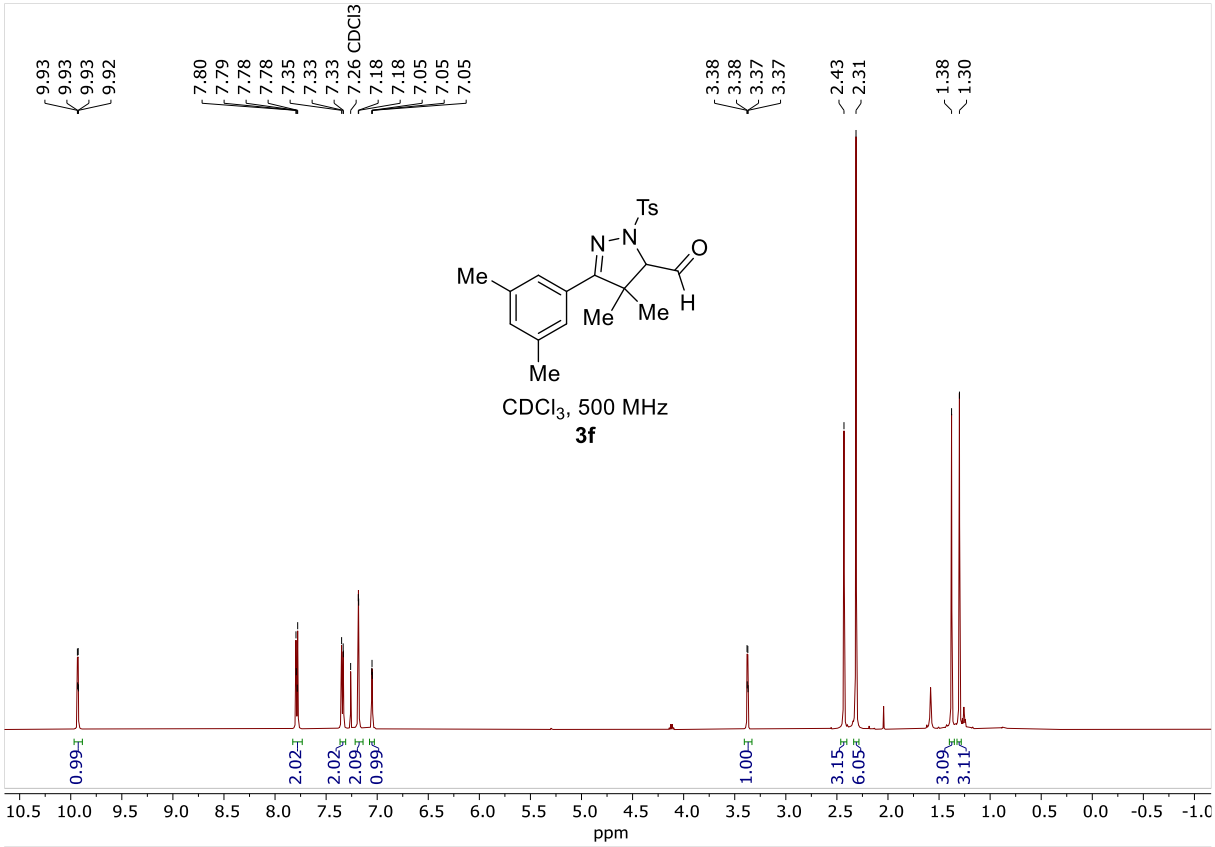


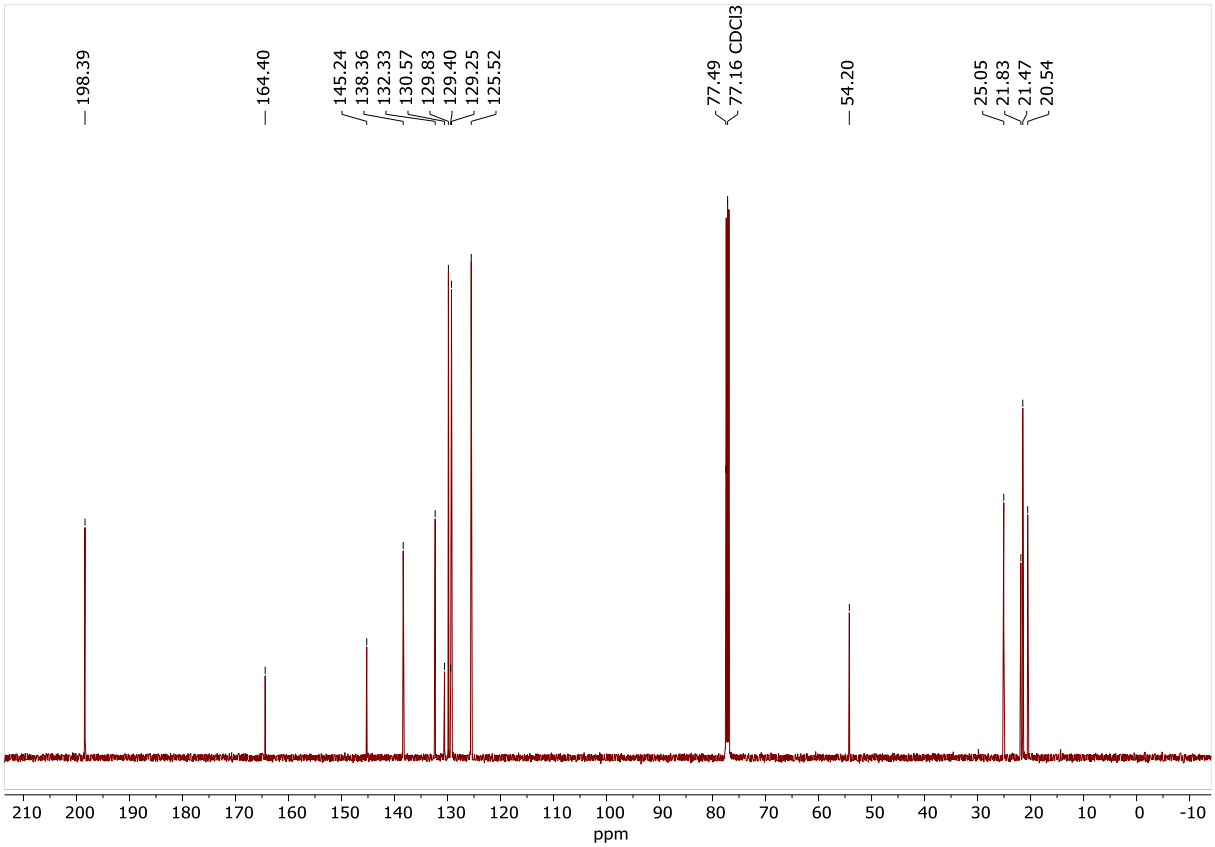
^{1}H NMR and ^{13}C NMR spectrum of compound **3e**



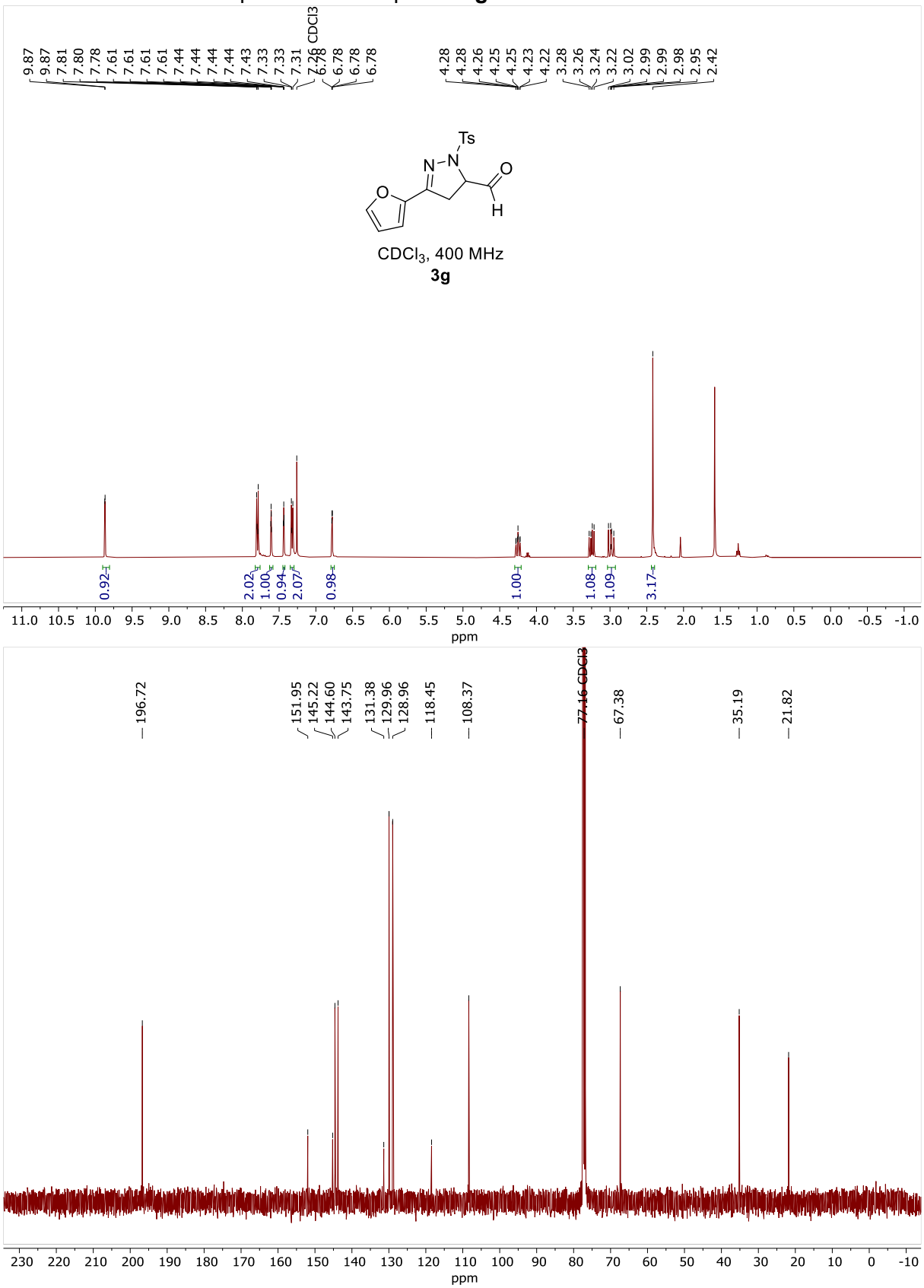


^{1}H NMR and ^{13}C NMR spectrum of compound **3f**

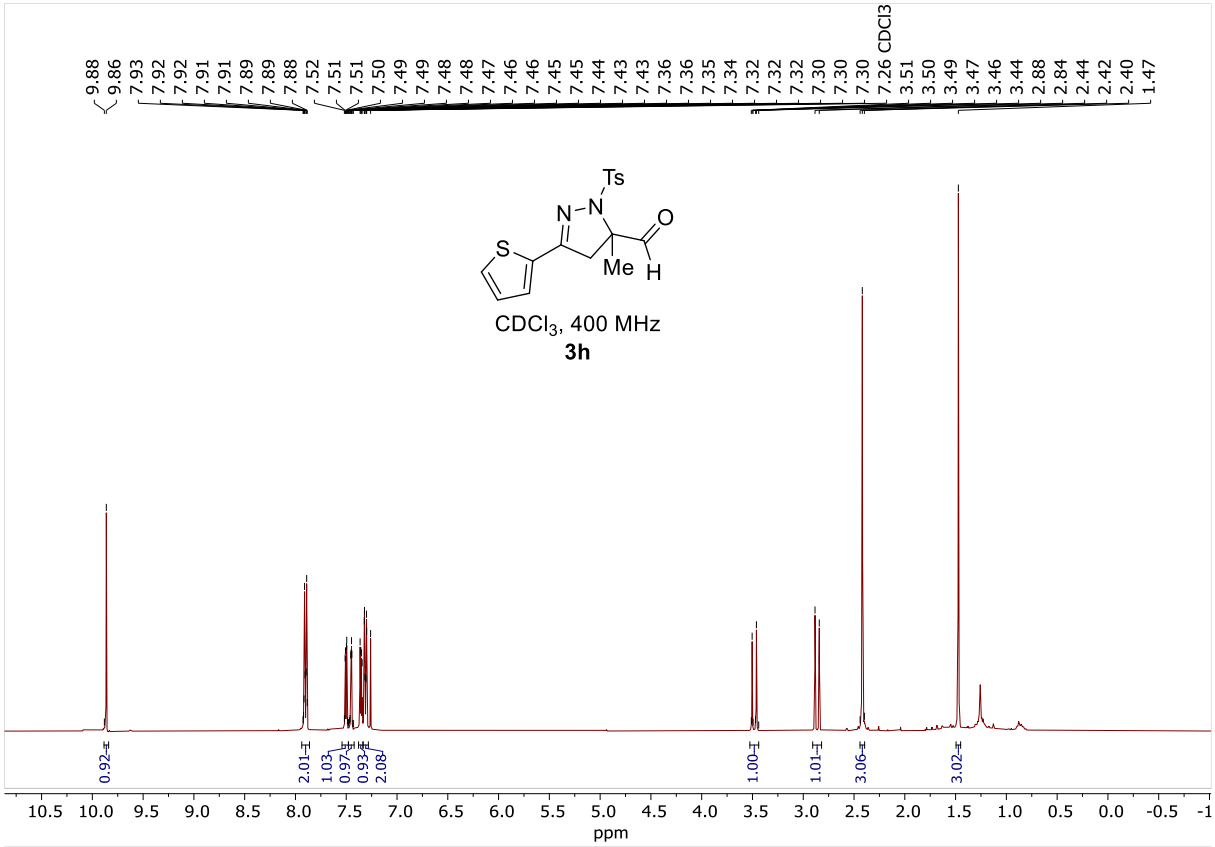


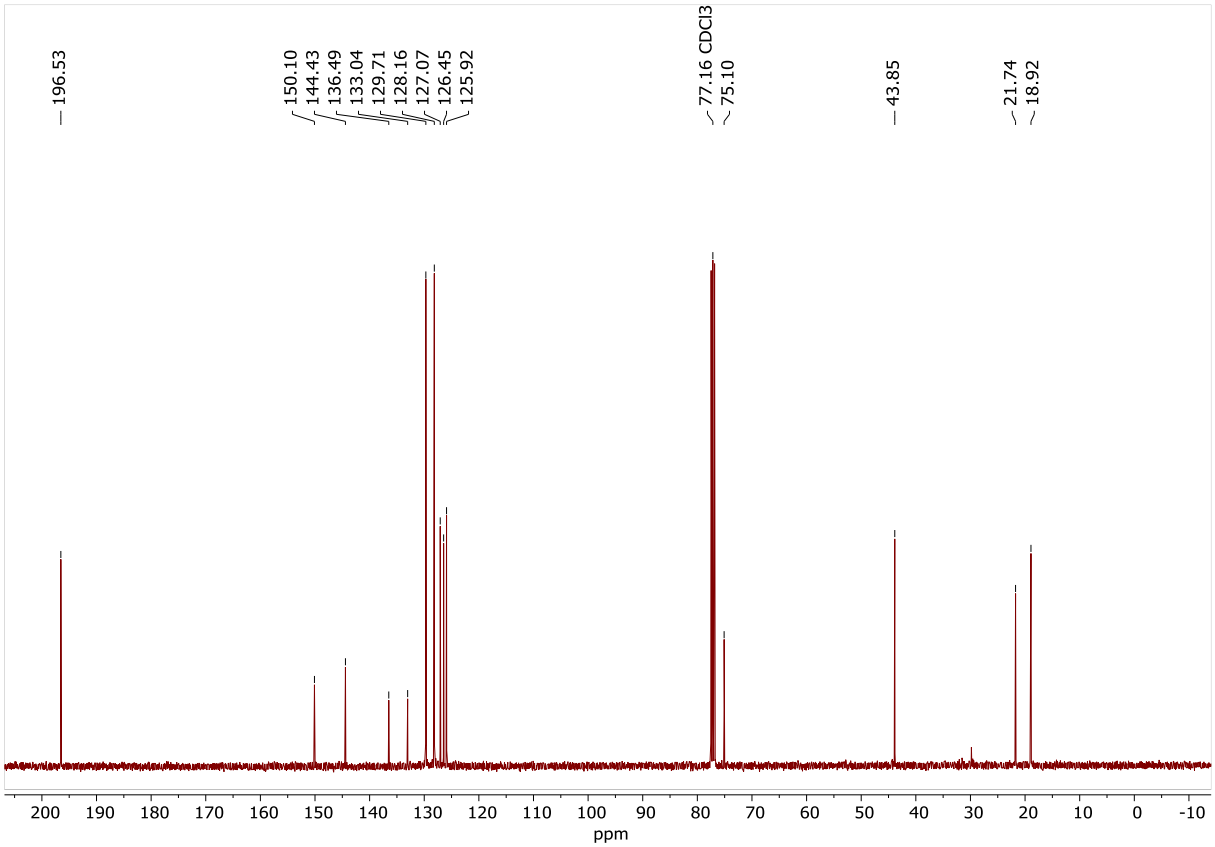


^{1}H NMR and ^{13}C NMR spectrum of compound **3g**

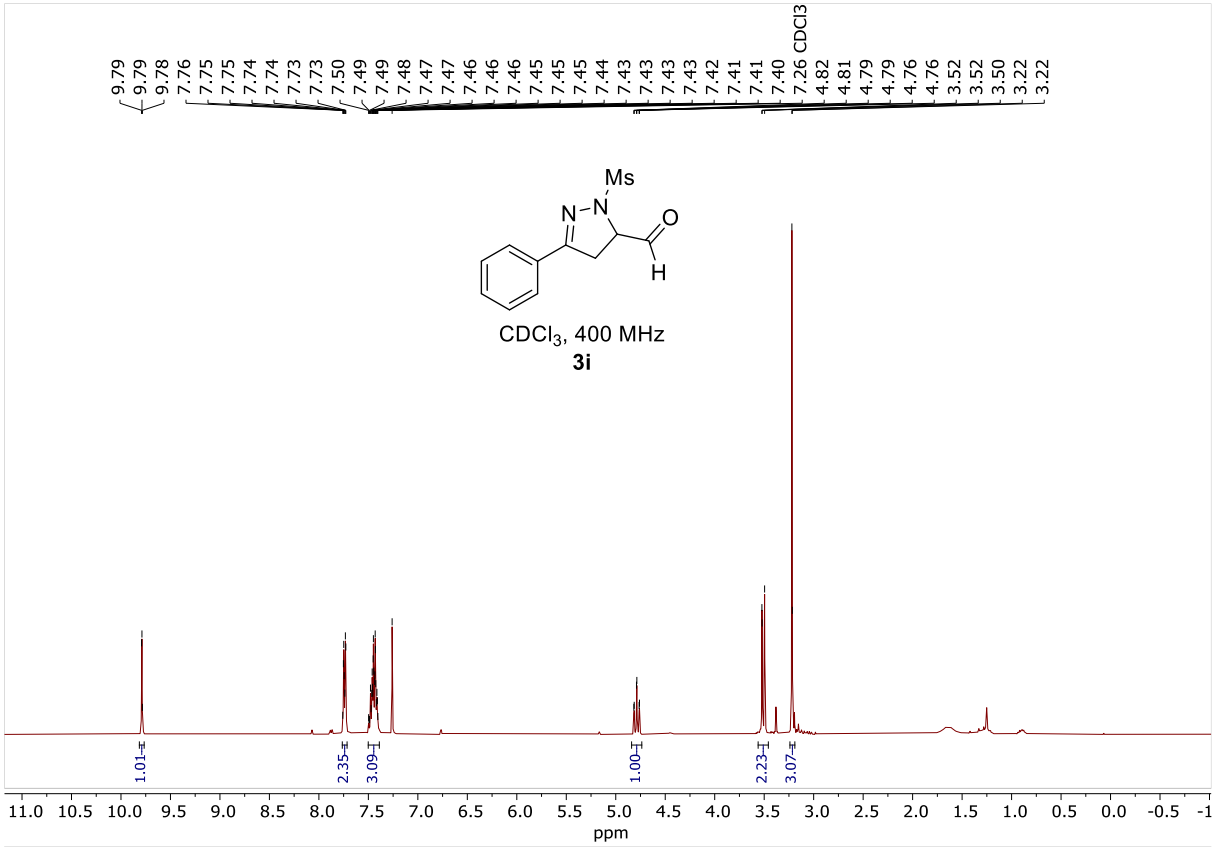


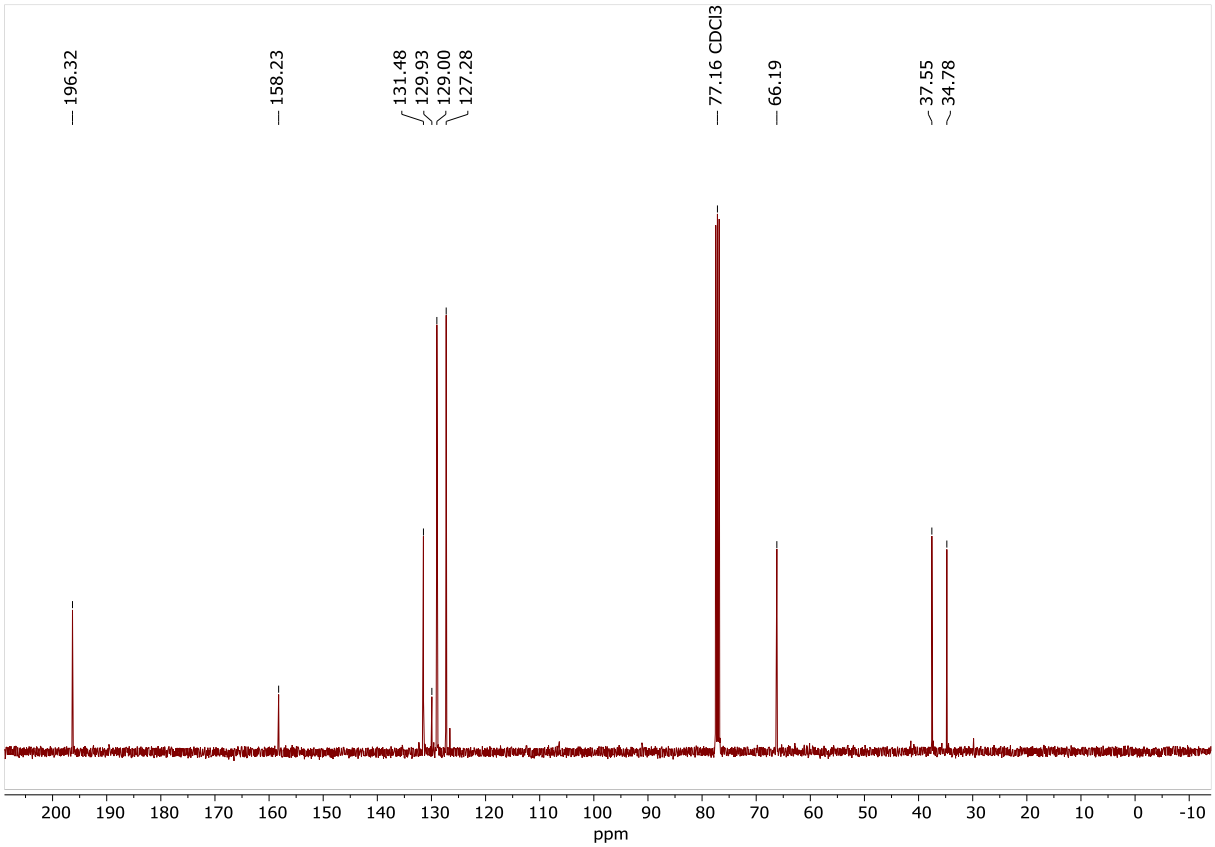
^{1}H NMR and ^{13}C NMR spectrum of compound **3h**



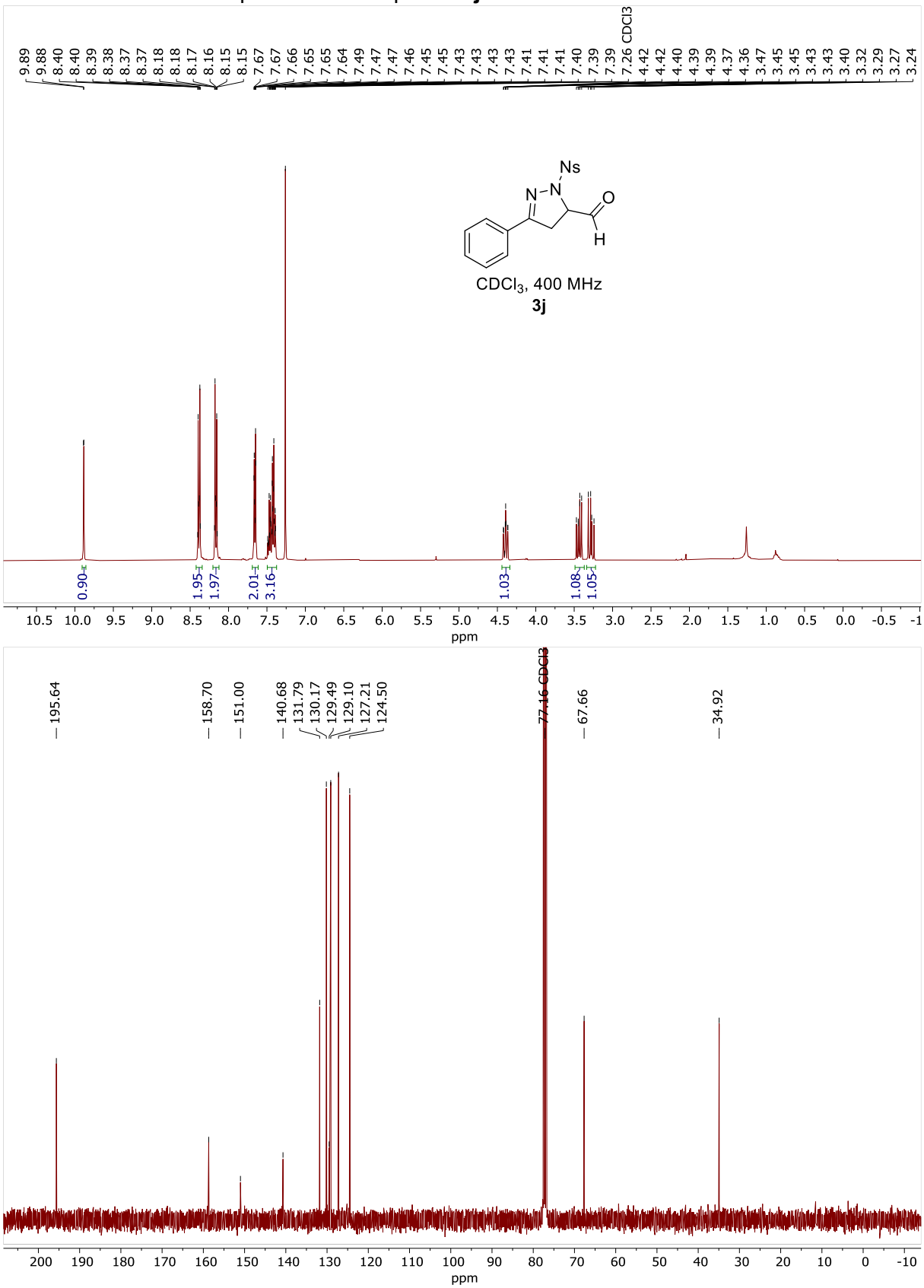


^{1}H NMR and ^{13}C NMR spectrum of compound **3i**

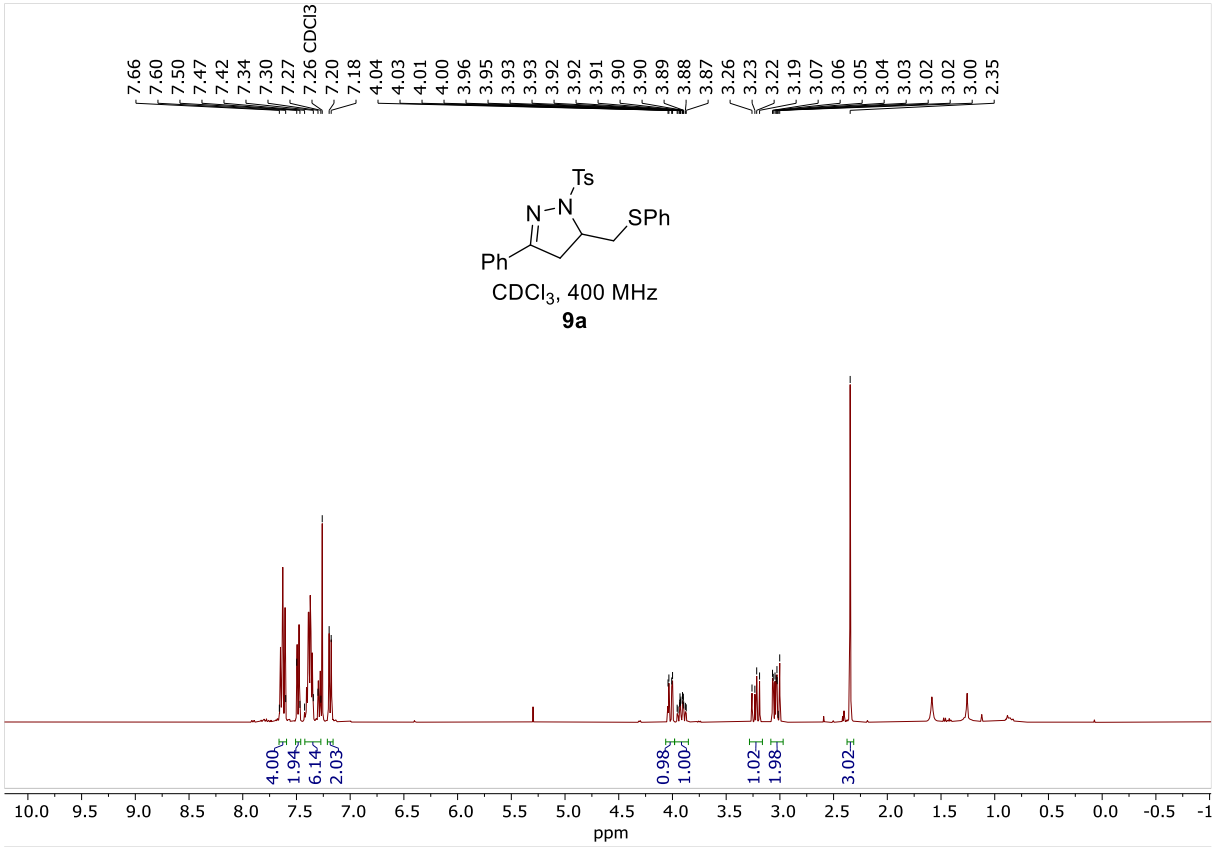


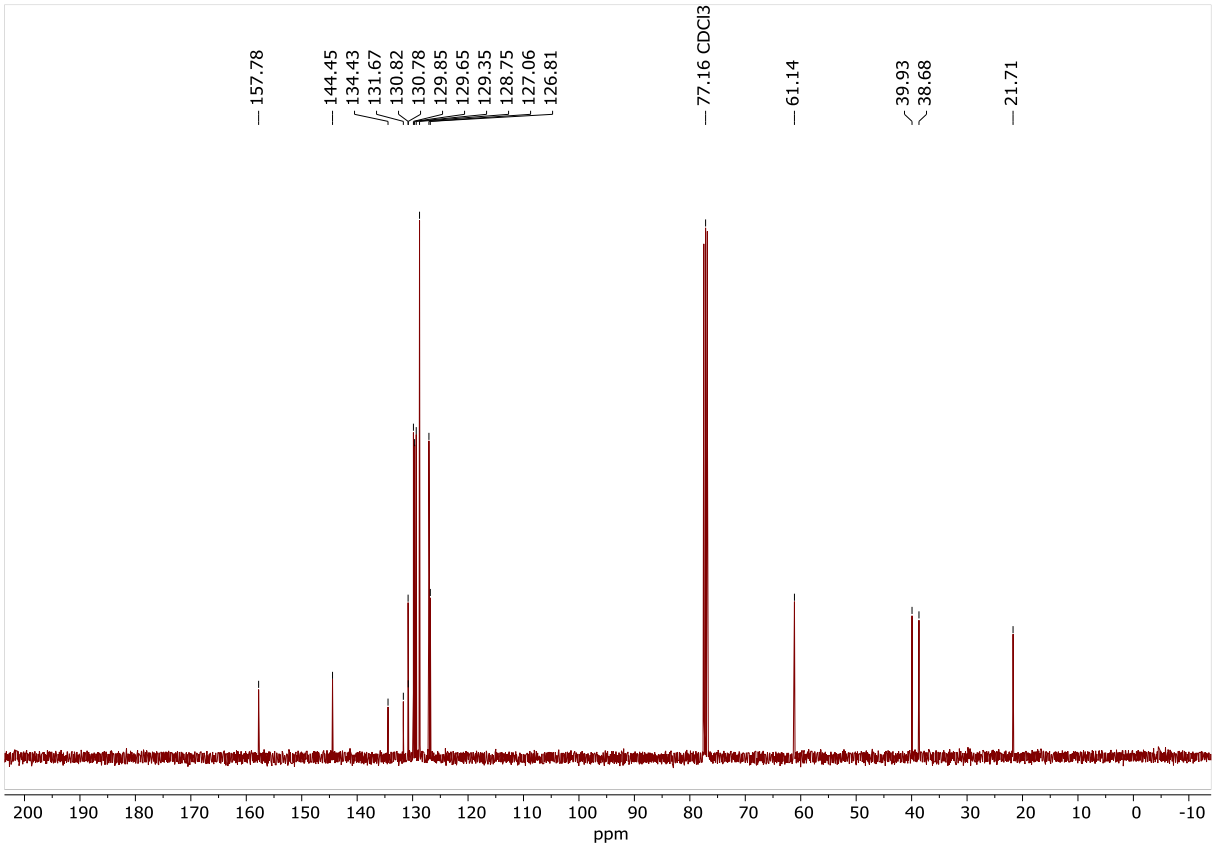


^{1}H NMR and ^{13}C NMR spectrum of compound **3j**

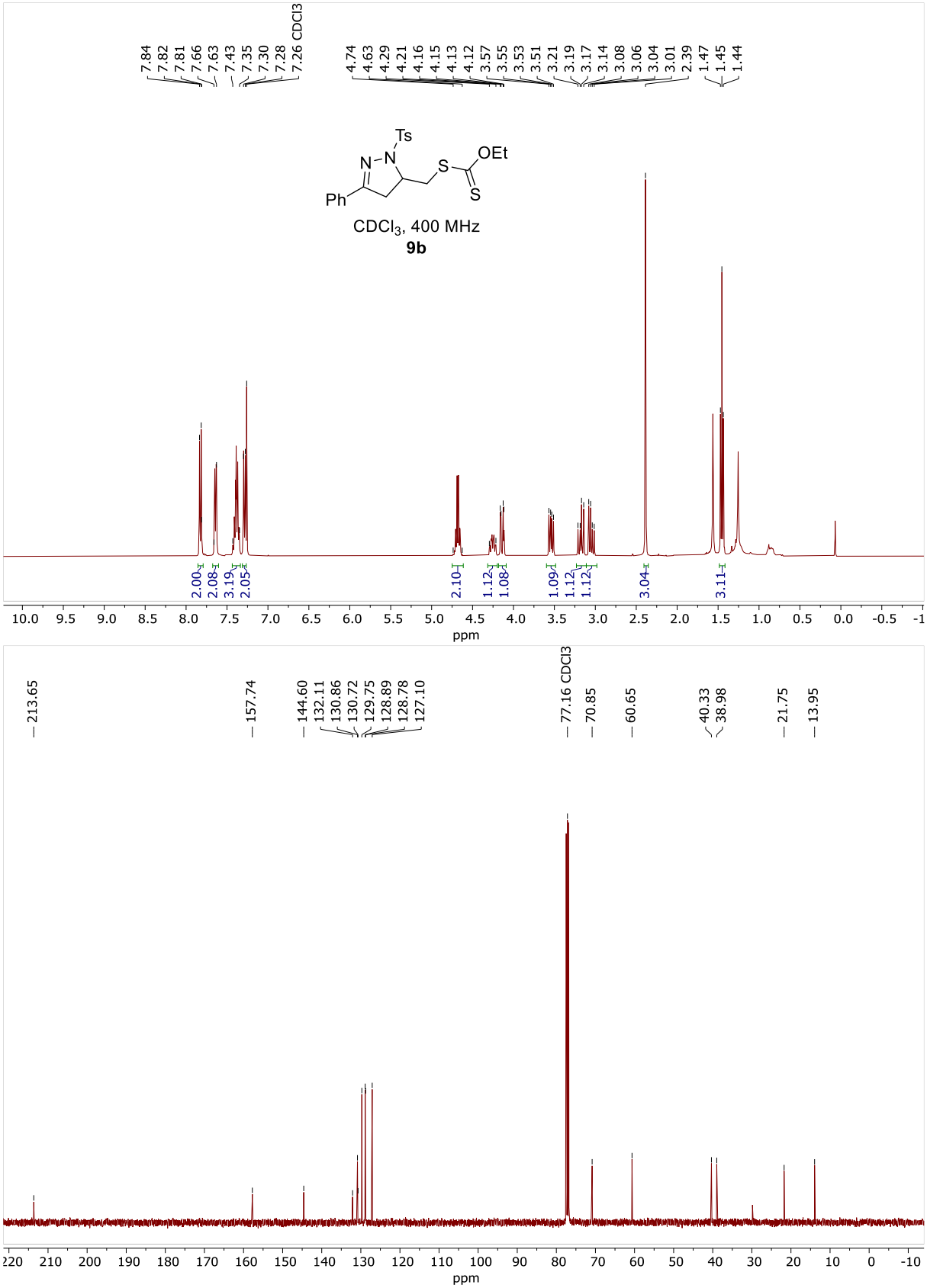


^{1}H NMR and ^{13}C NMR spectrum of compound **9a**

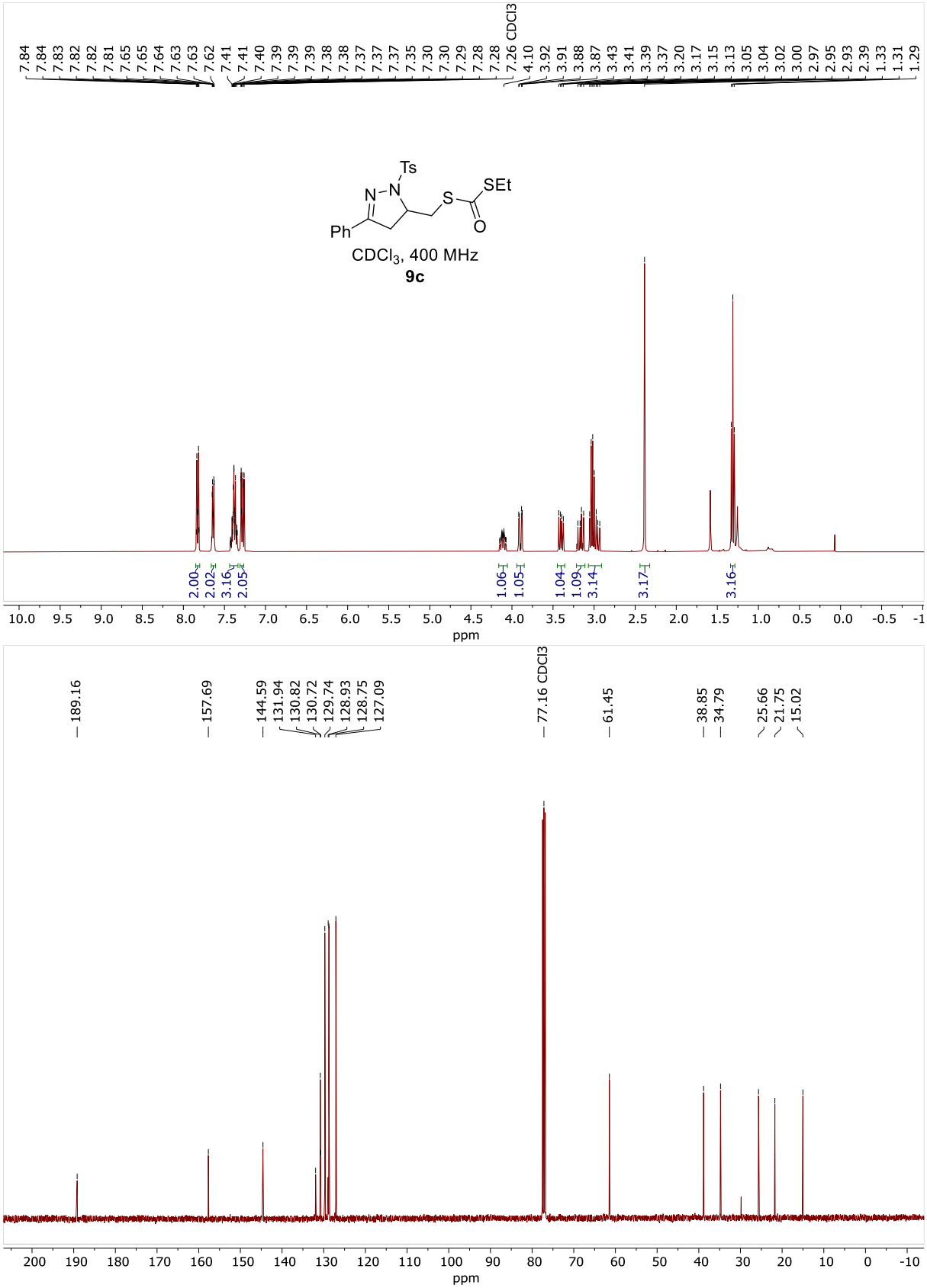




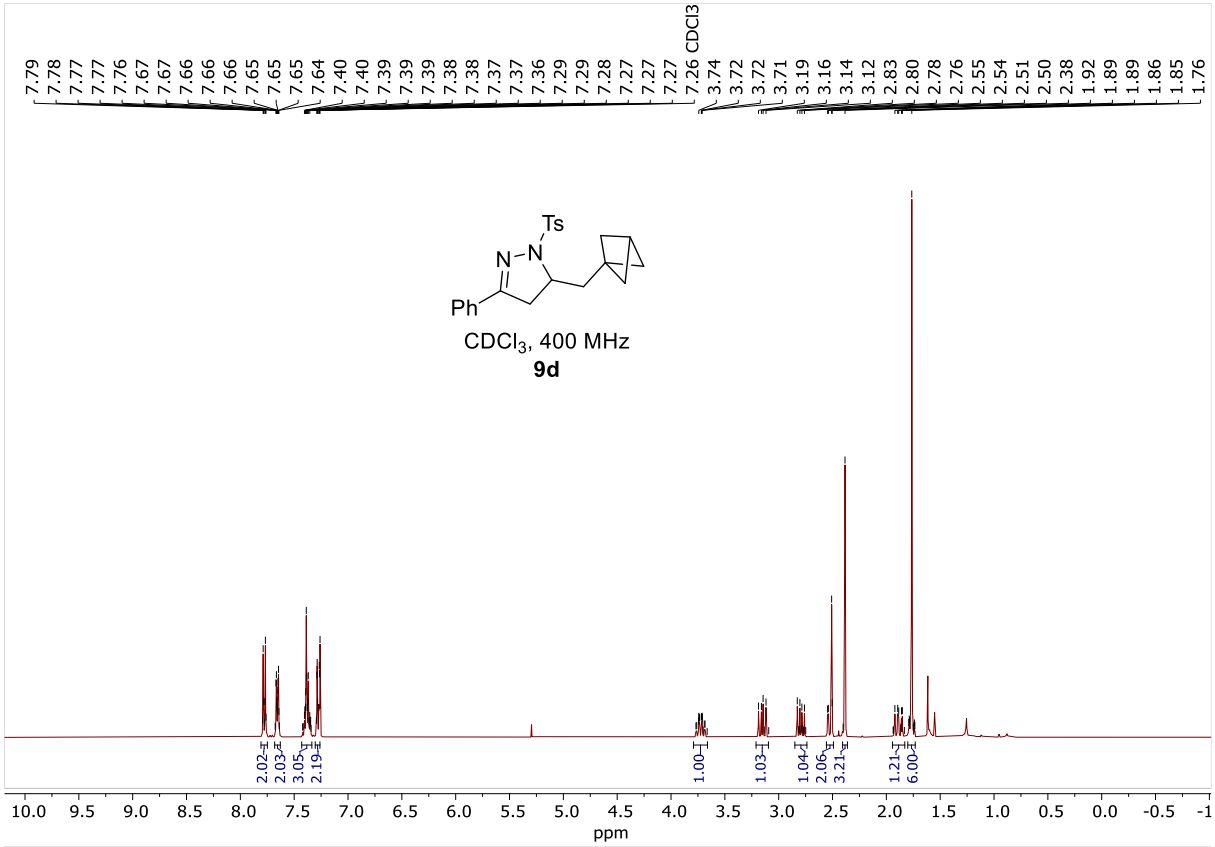
^{1}H NMR and ^{13}C NMR spectrum of compound **9b**

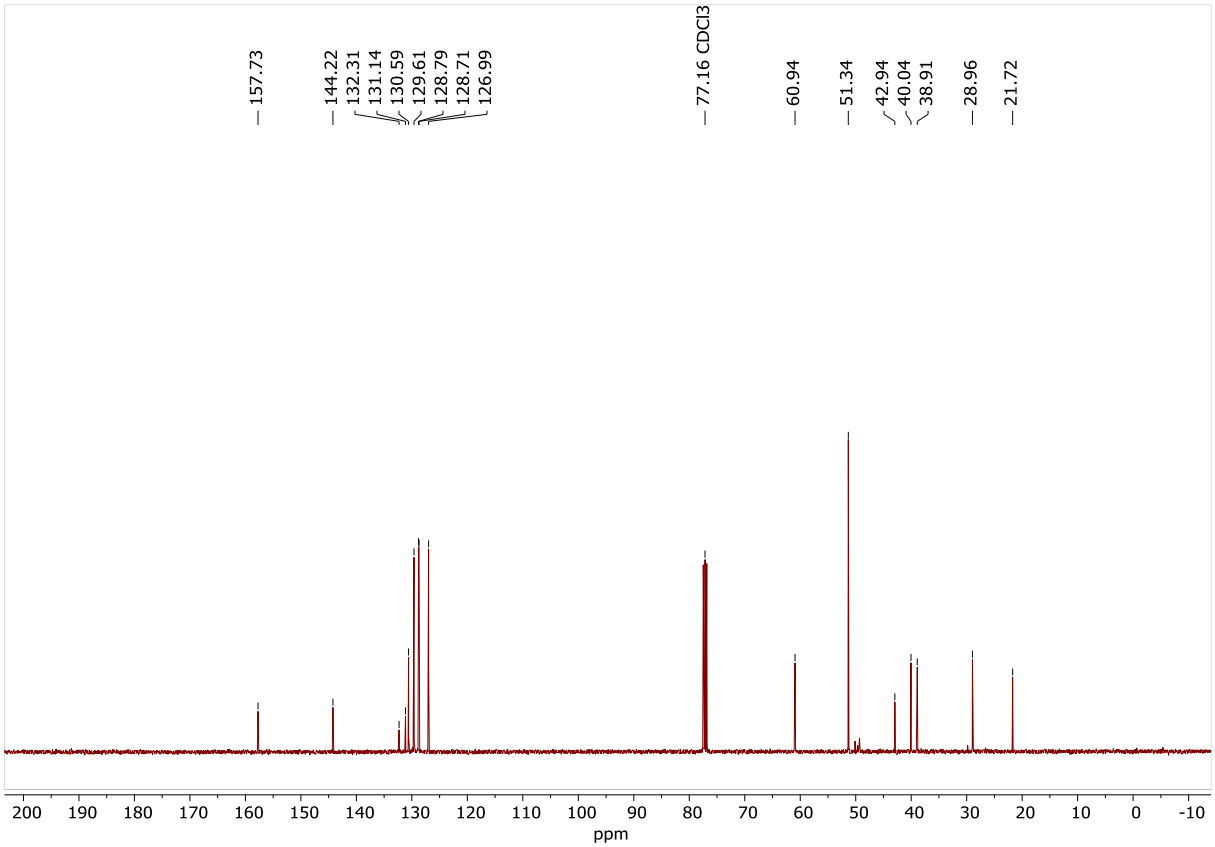


^{1}H NMR and ^{13}C NMR spectrum of compound **9c**

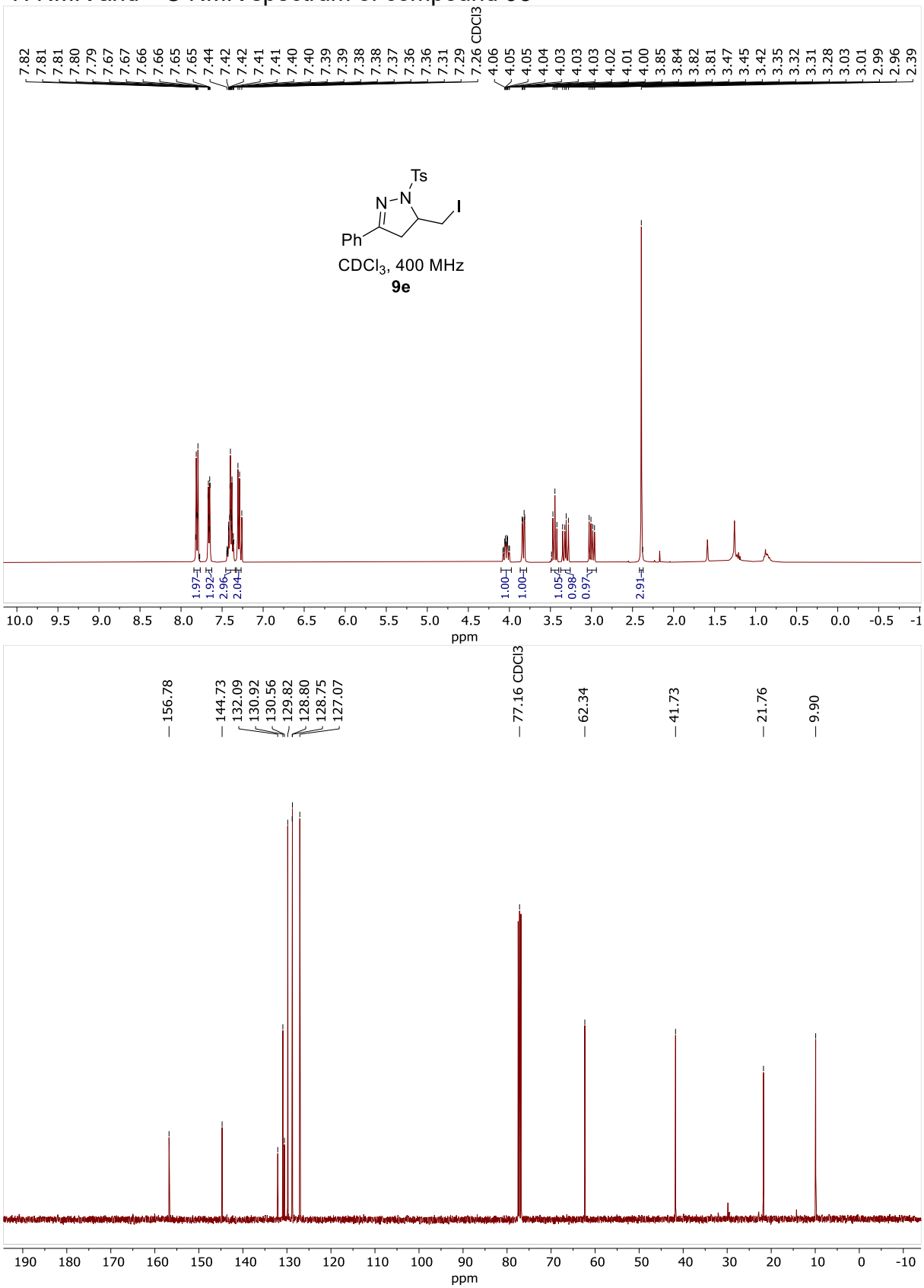


^{1}H NMR and ^{13}C NMR spectrum of compound **9d**

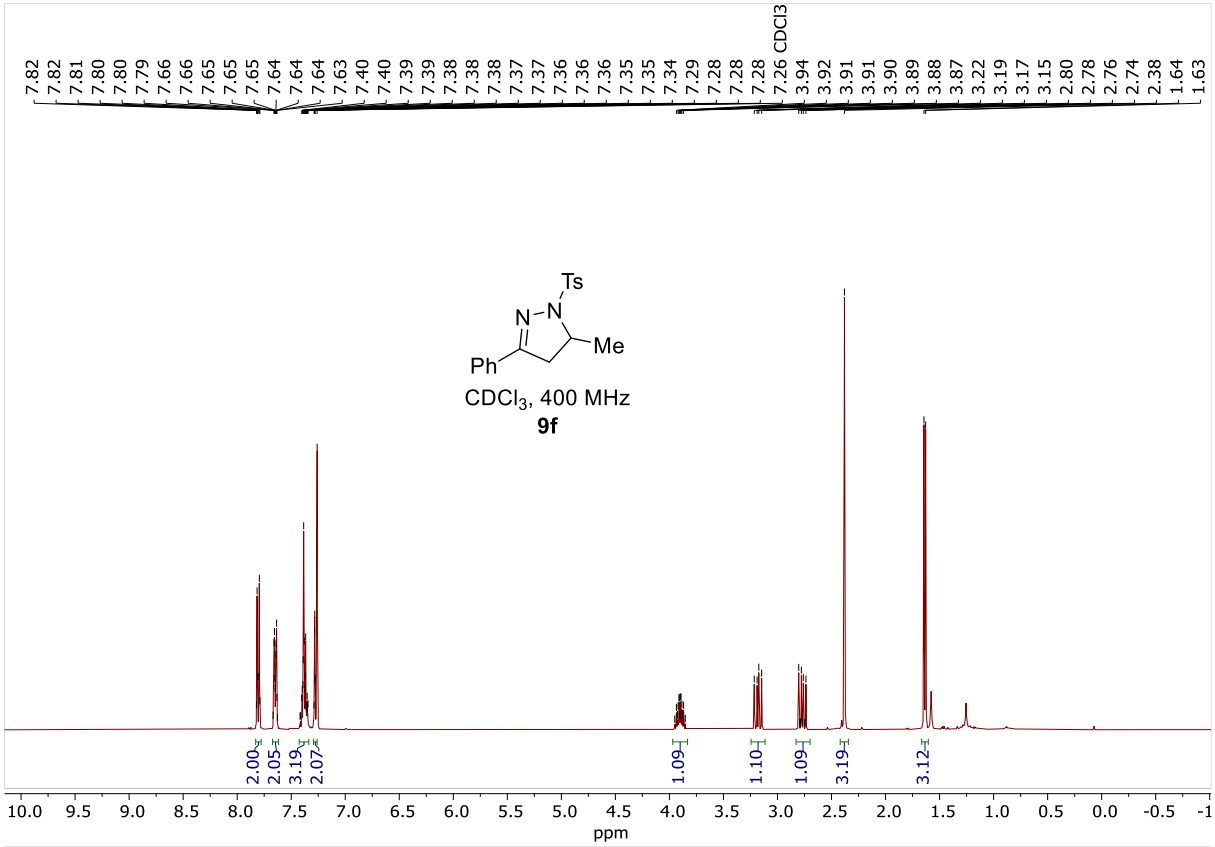


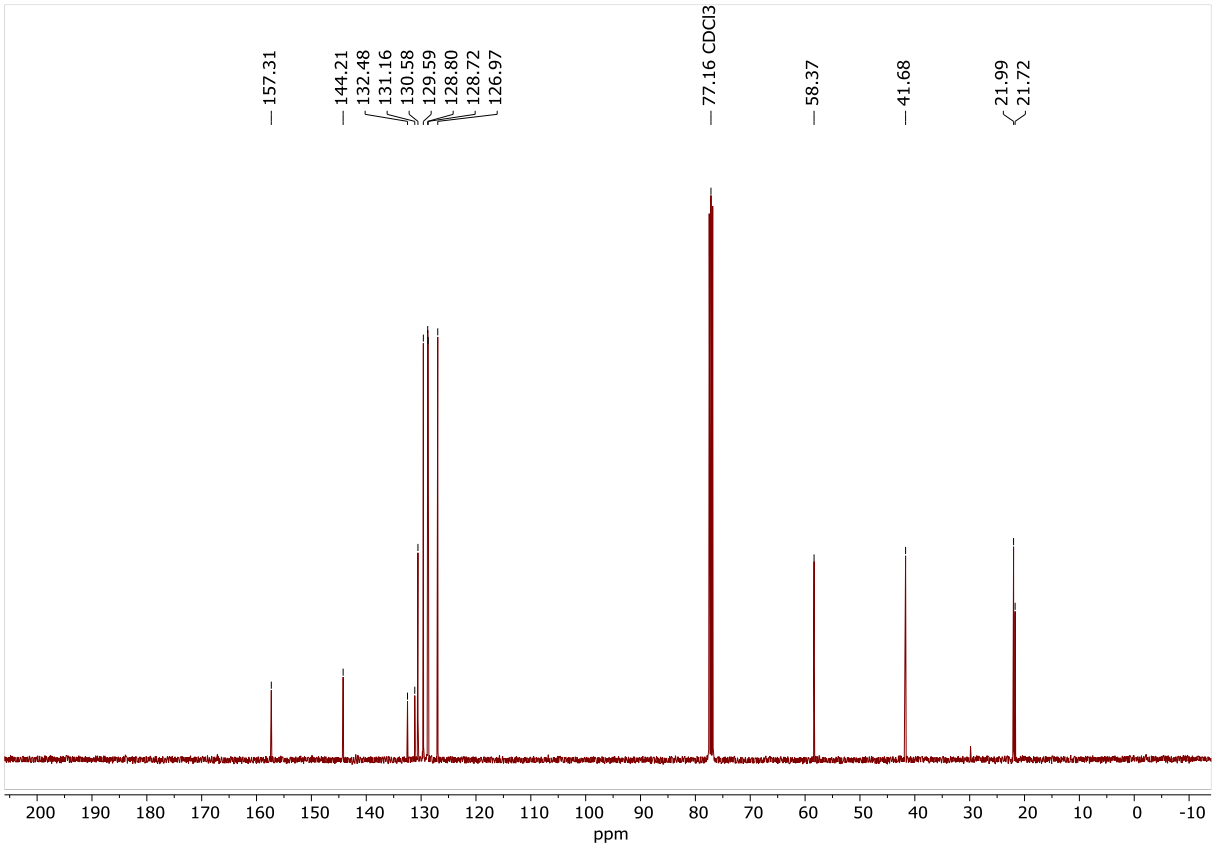


^{1}H NMR and ^{13}C NMR spectrum of compound **9e**

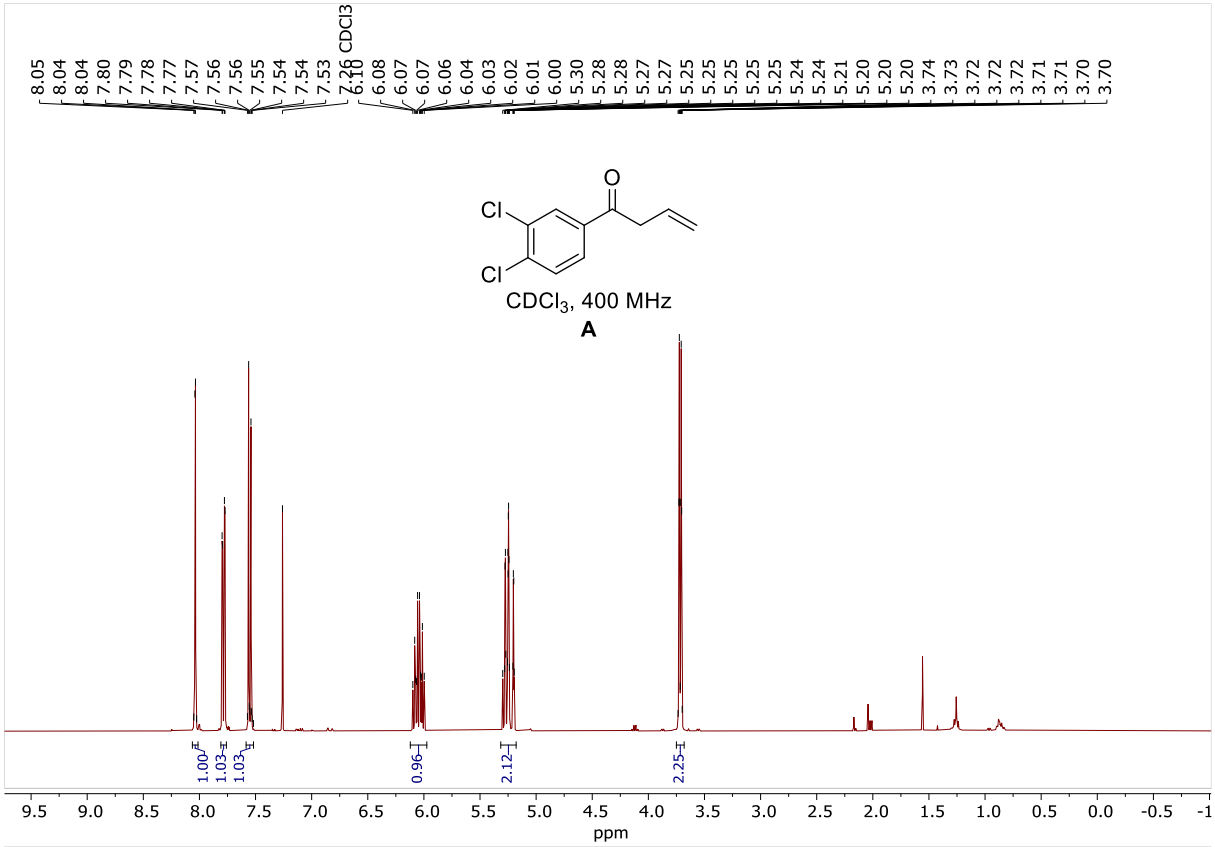


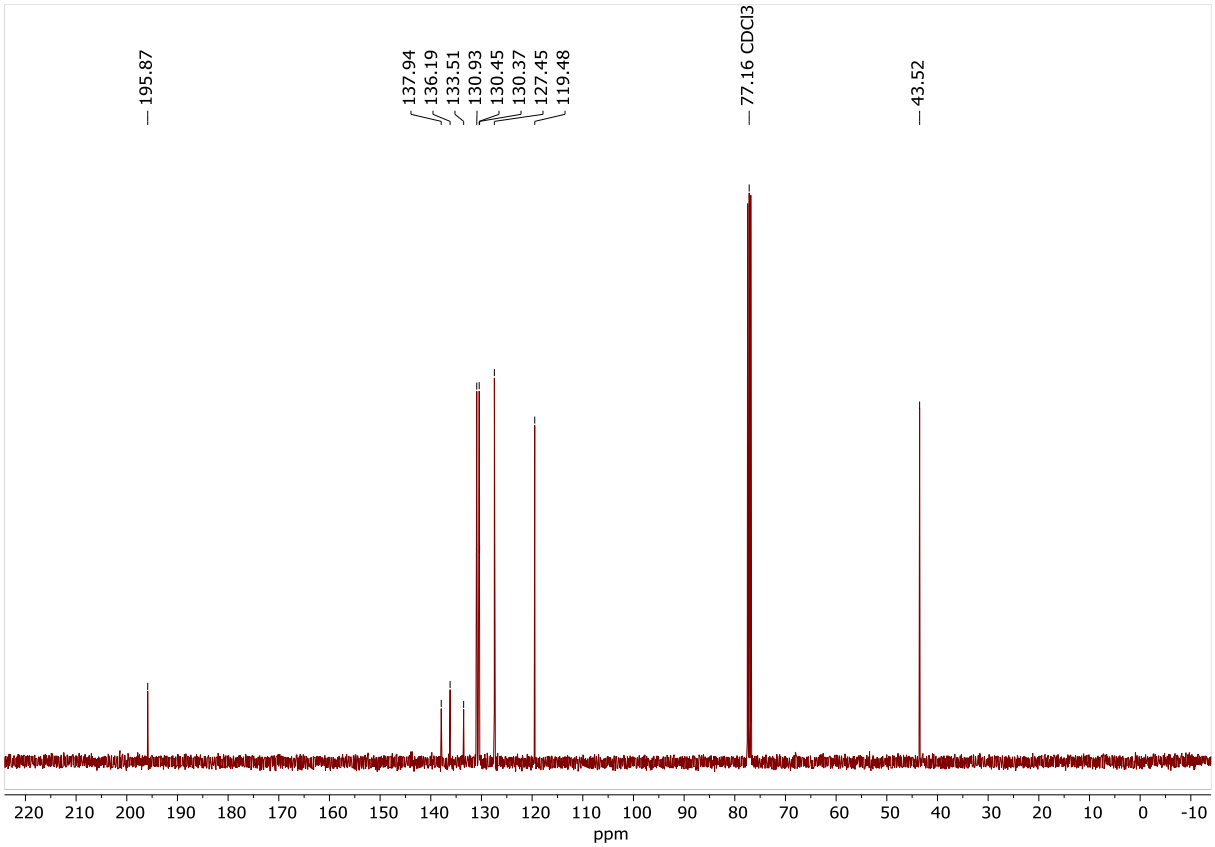
^{1}H NMR and ^{13}C NMR spectrum of compound **9f**



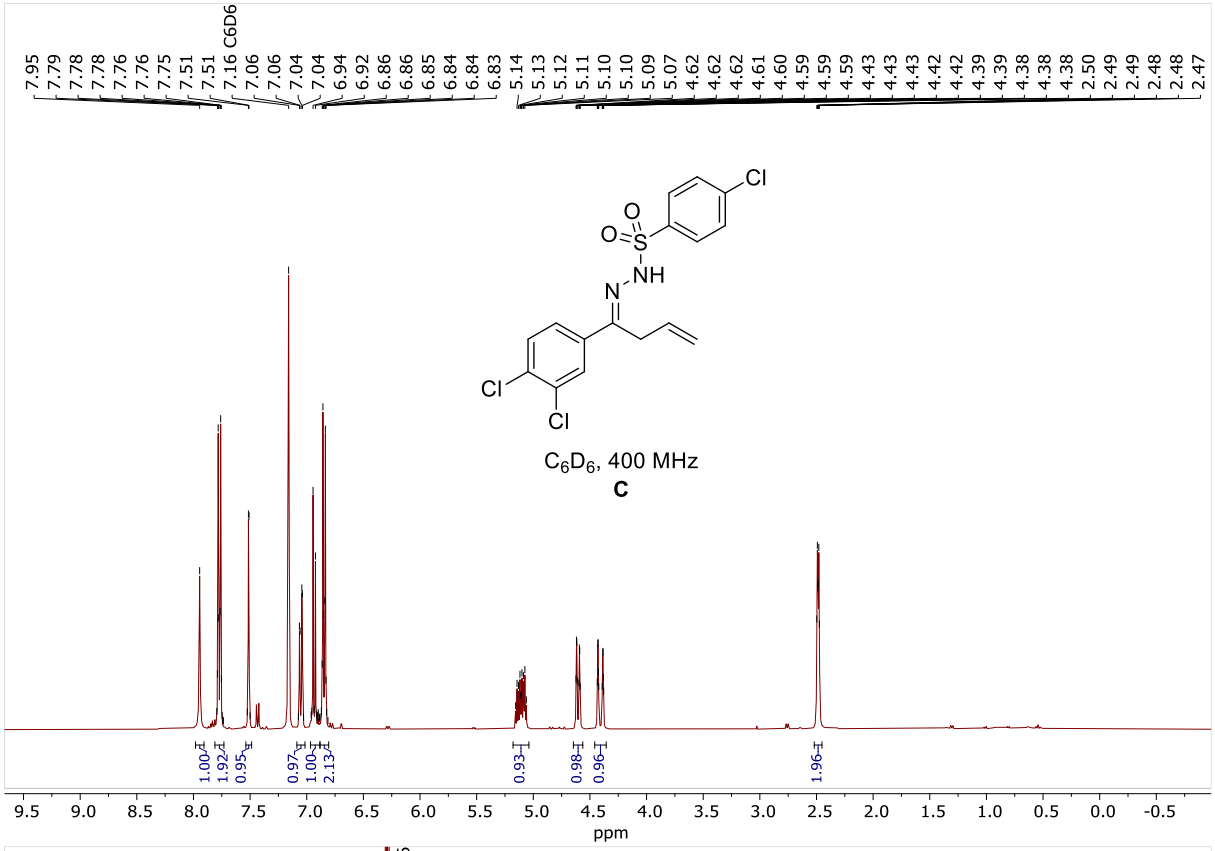


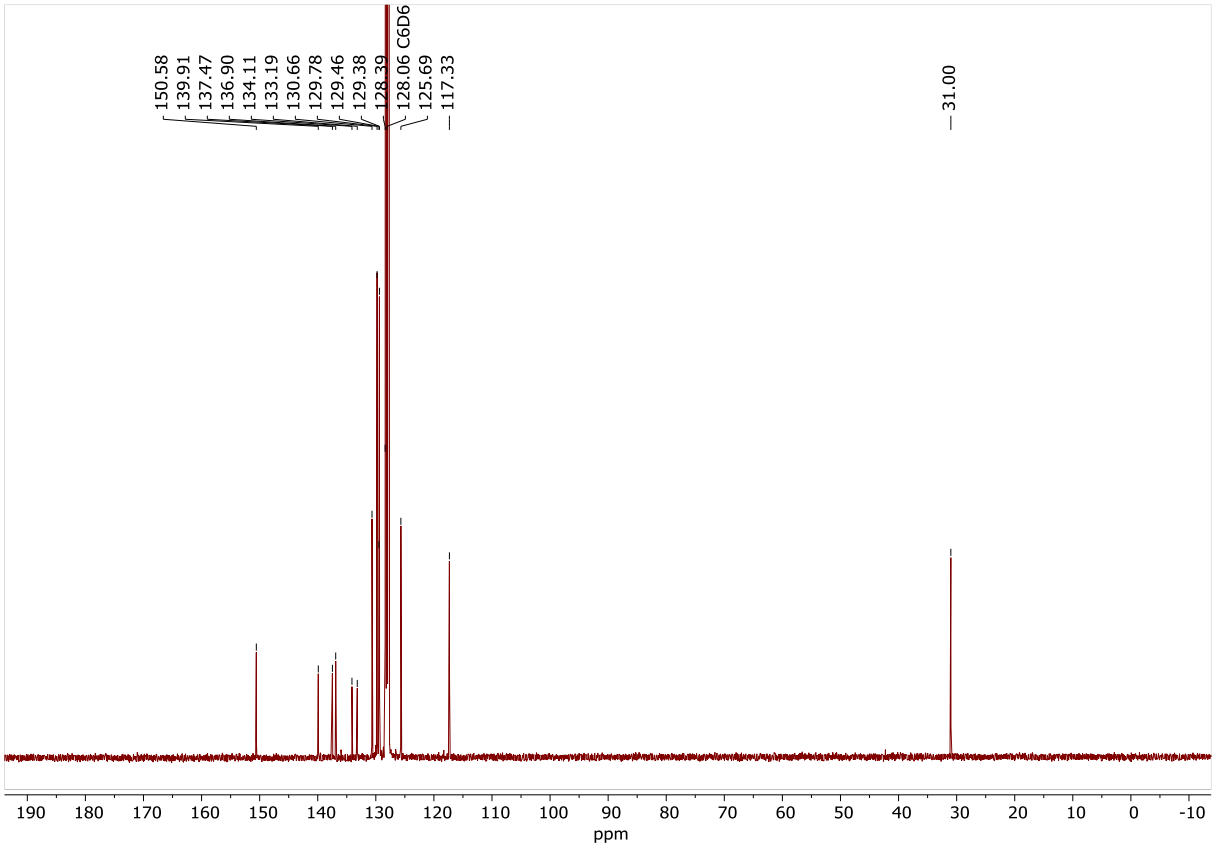
^{1}H NMR and ^{13}C NMR spectrum of compound **A**



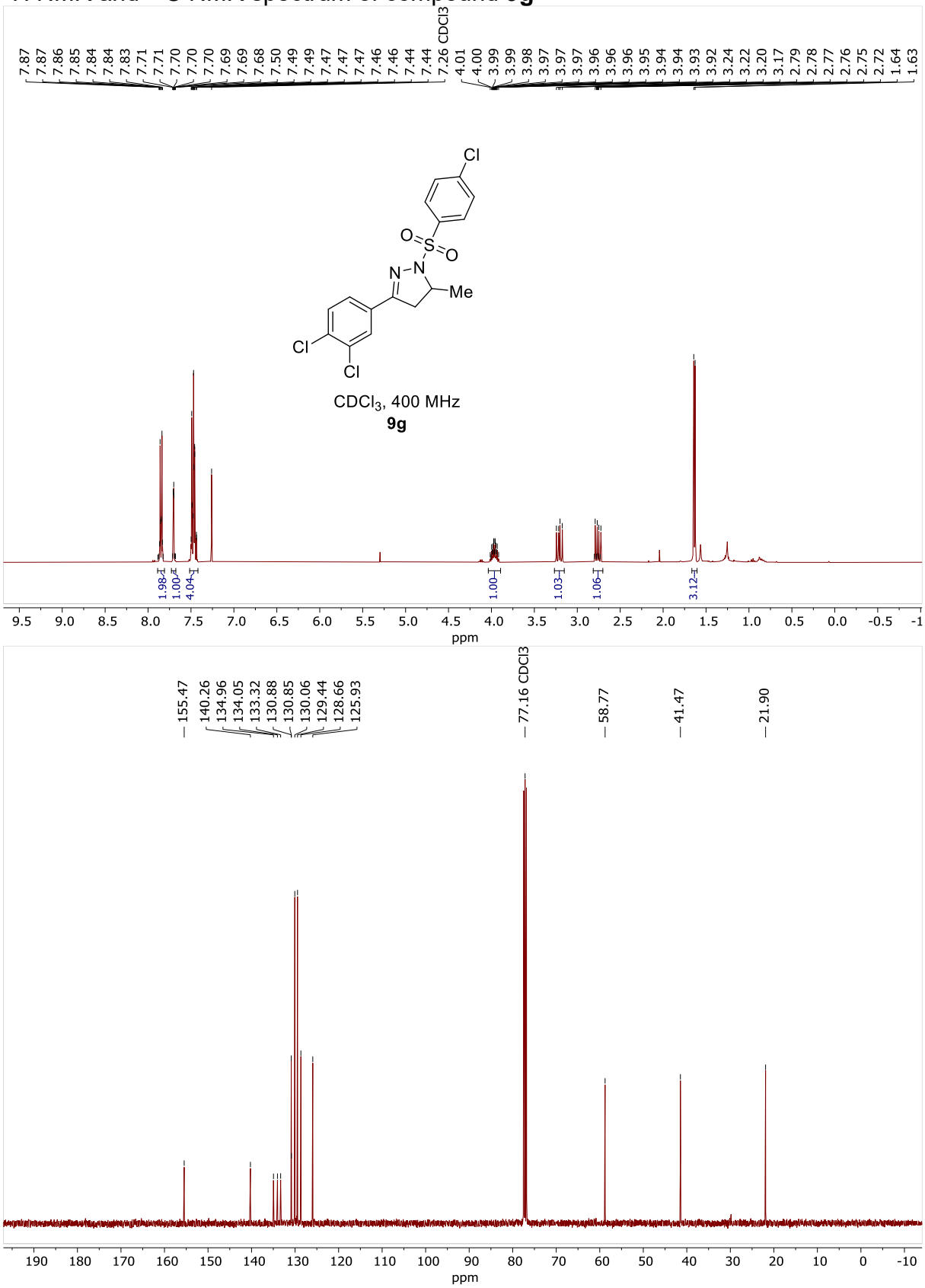


^{1}H NMR and ^{13}C NMR spectrum of compound **C**

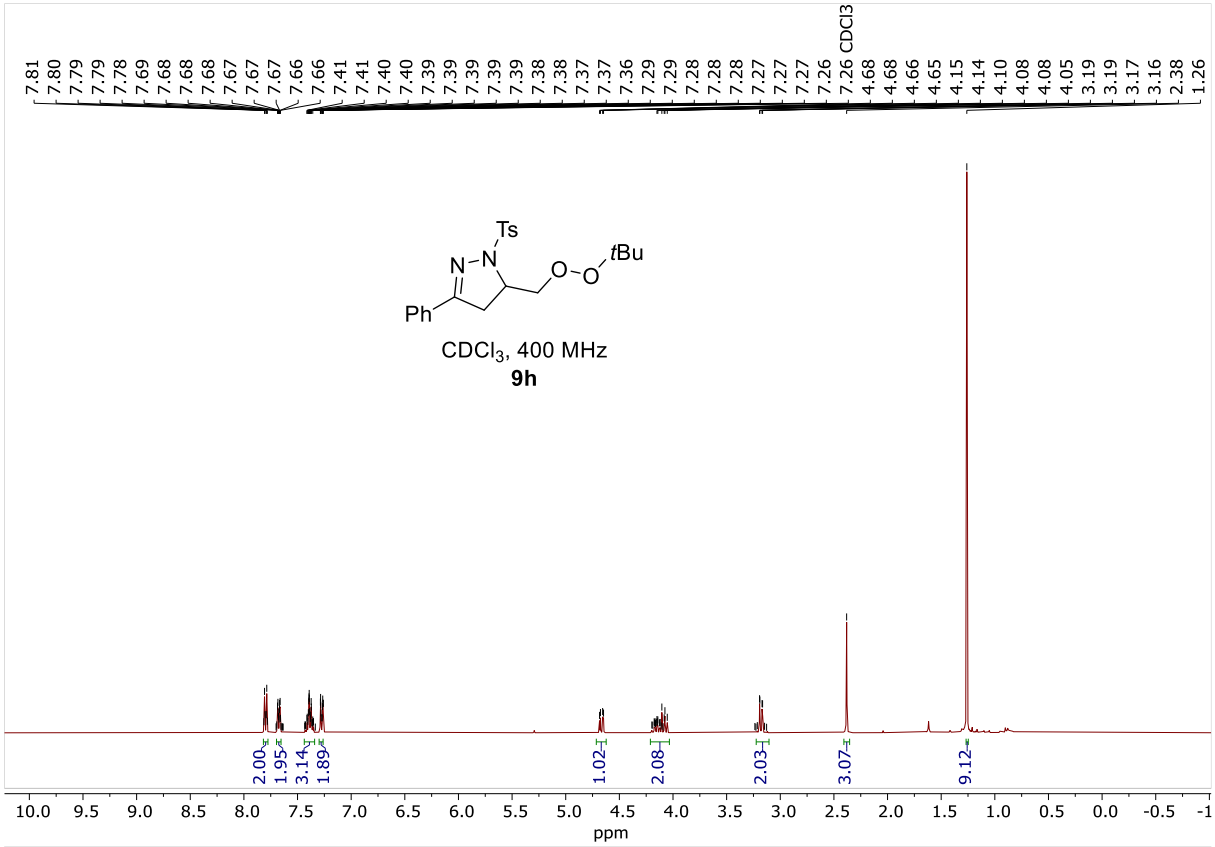


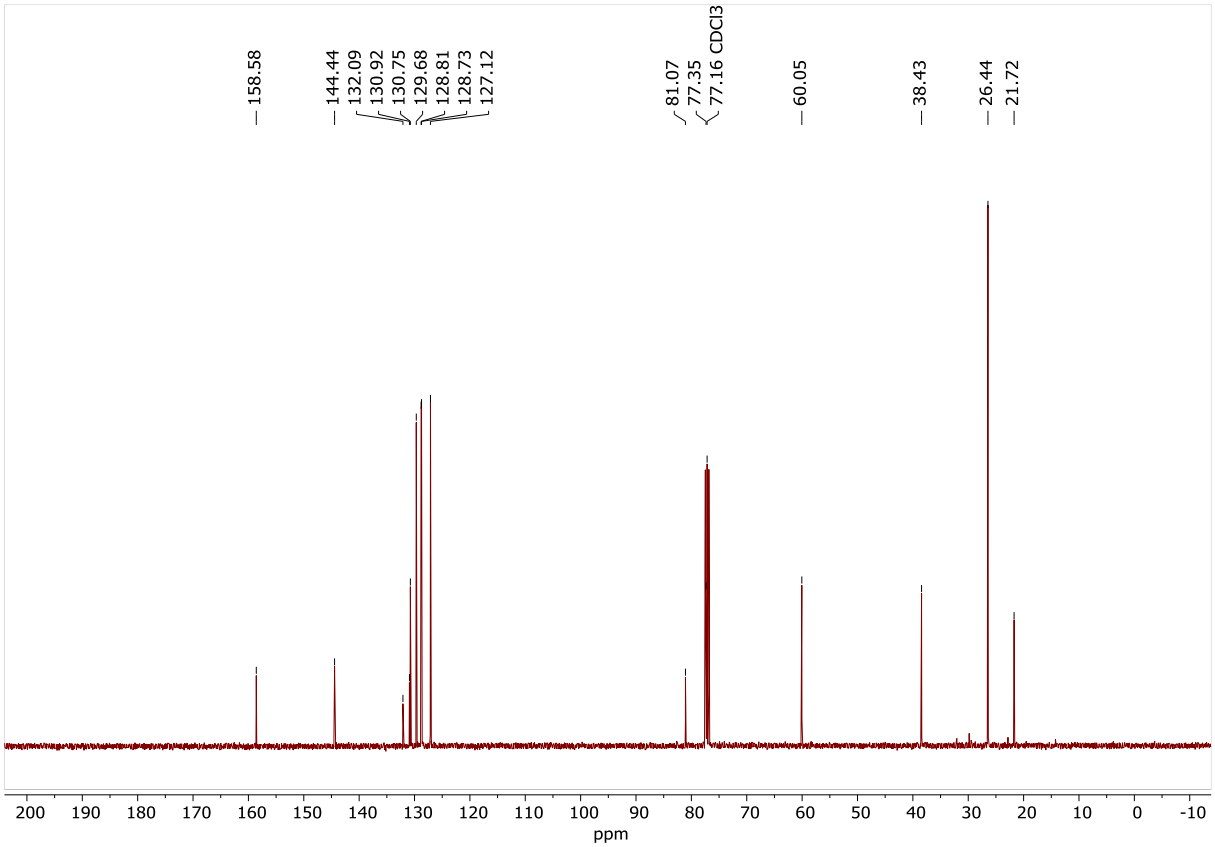


^{1}H NMR and ^{13}C NMR spectrum of compound **9g**

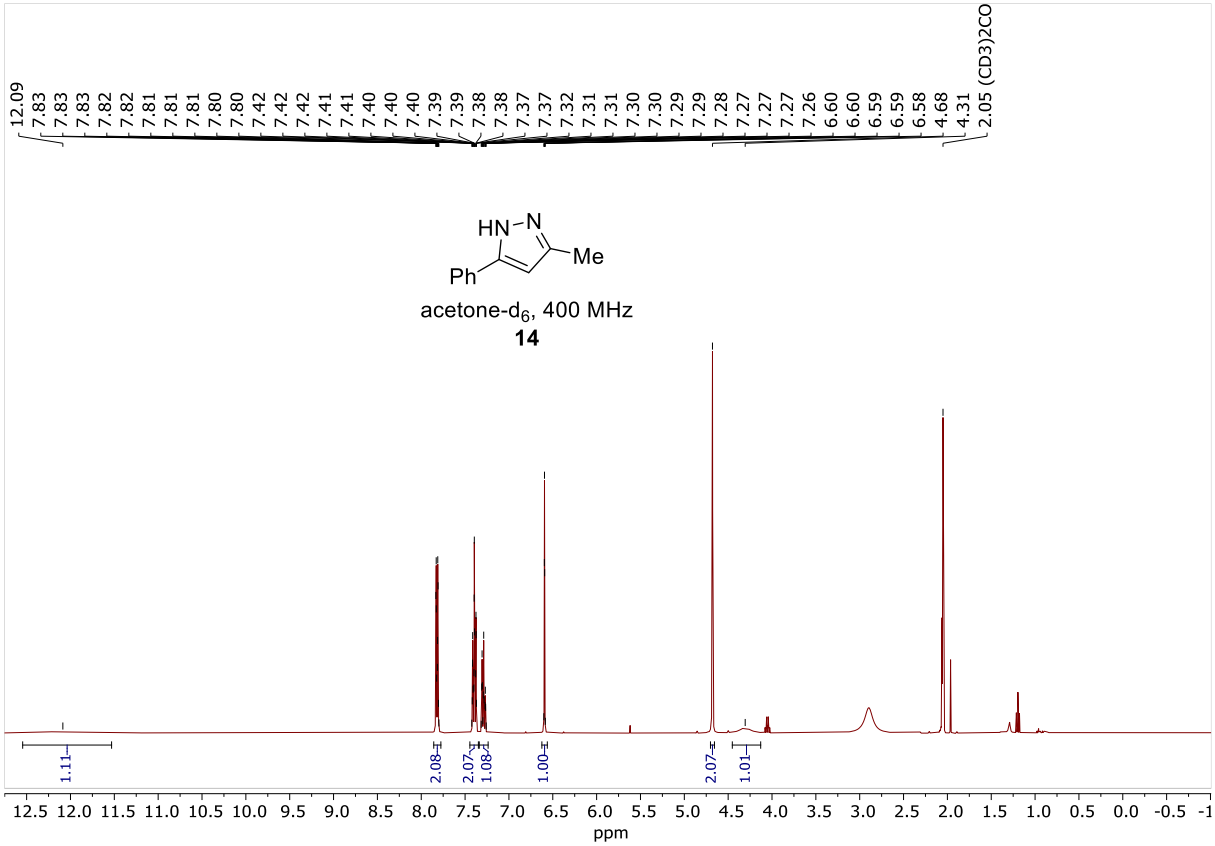


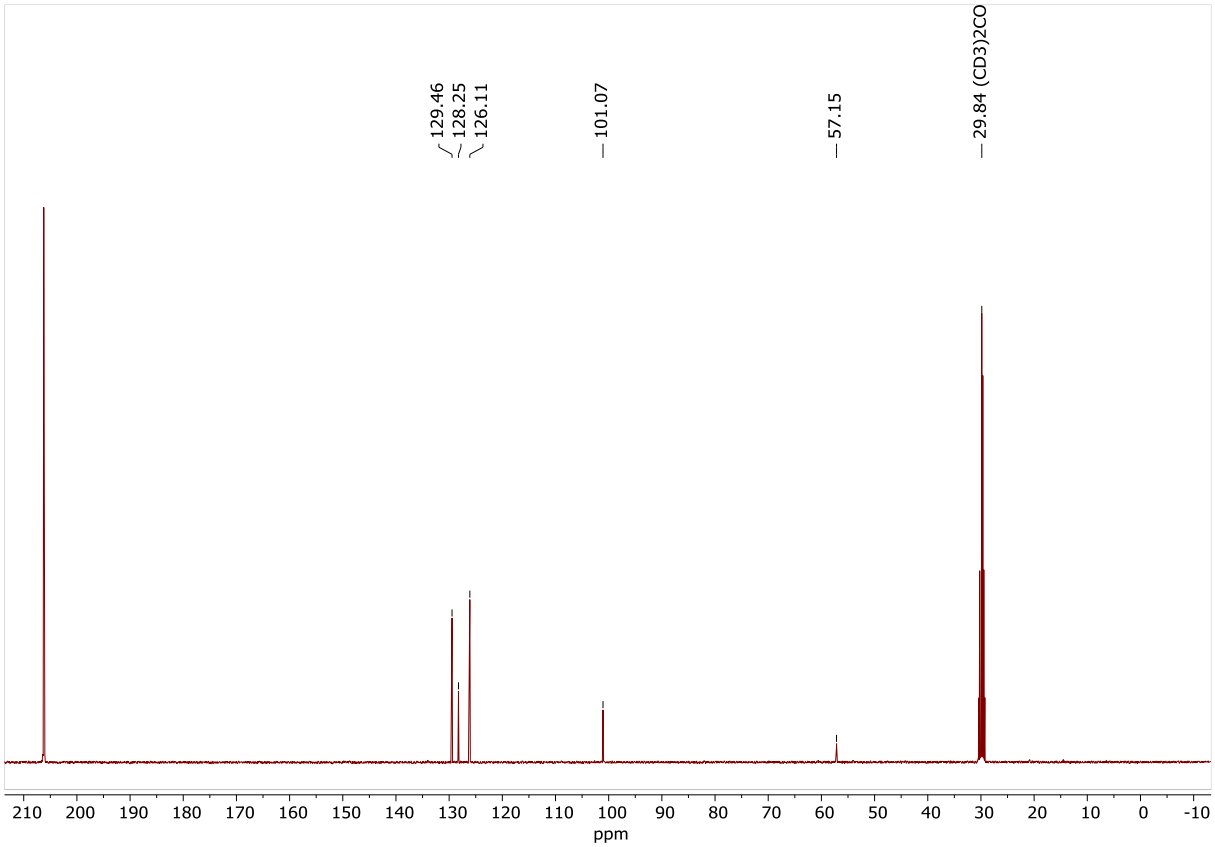
^{1}H NMR and ^{13}C NMR spectrum of compound **9h**

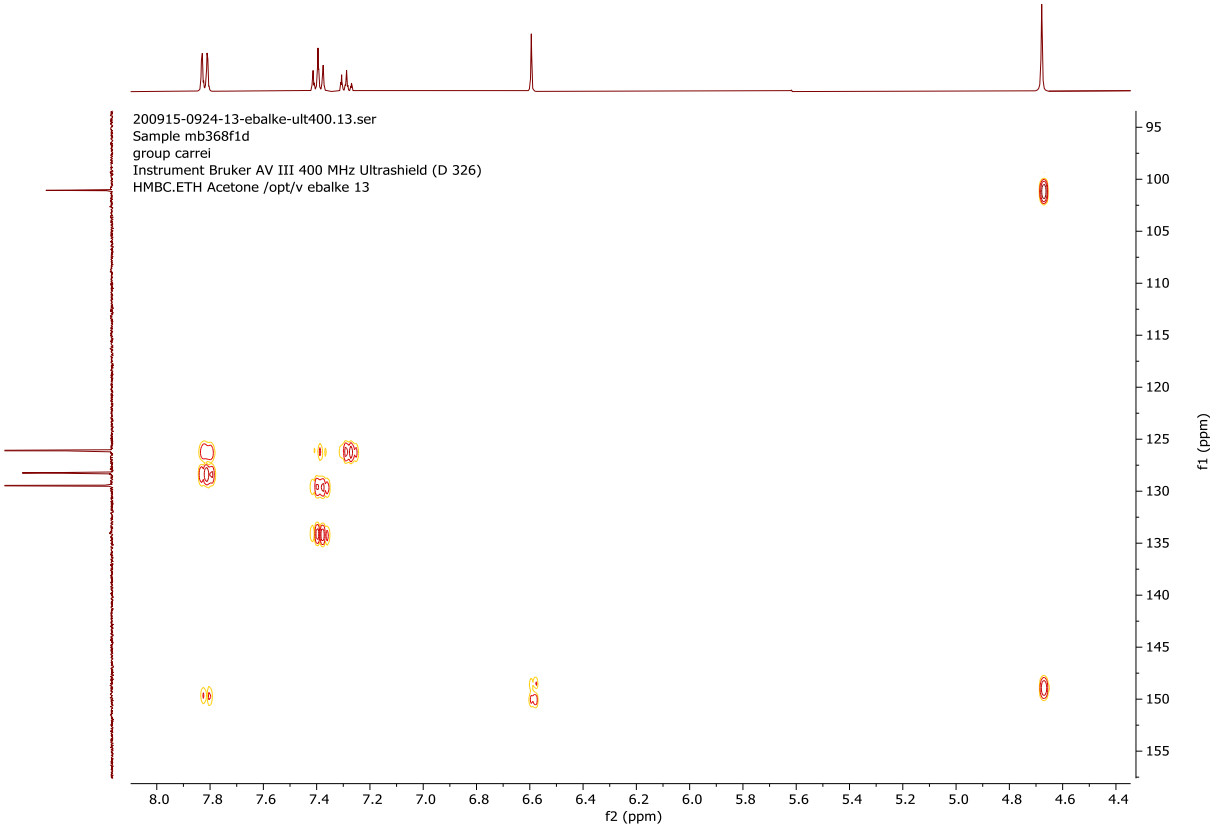




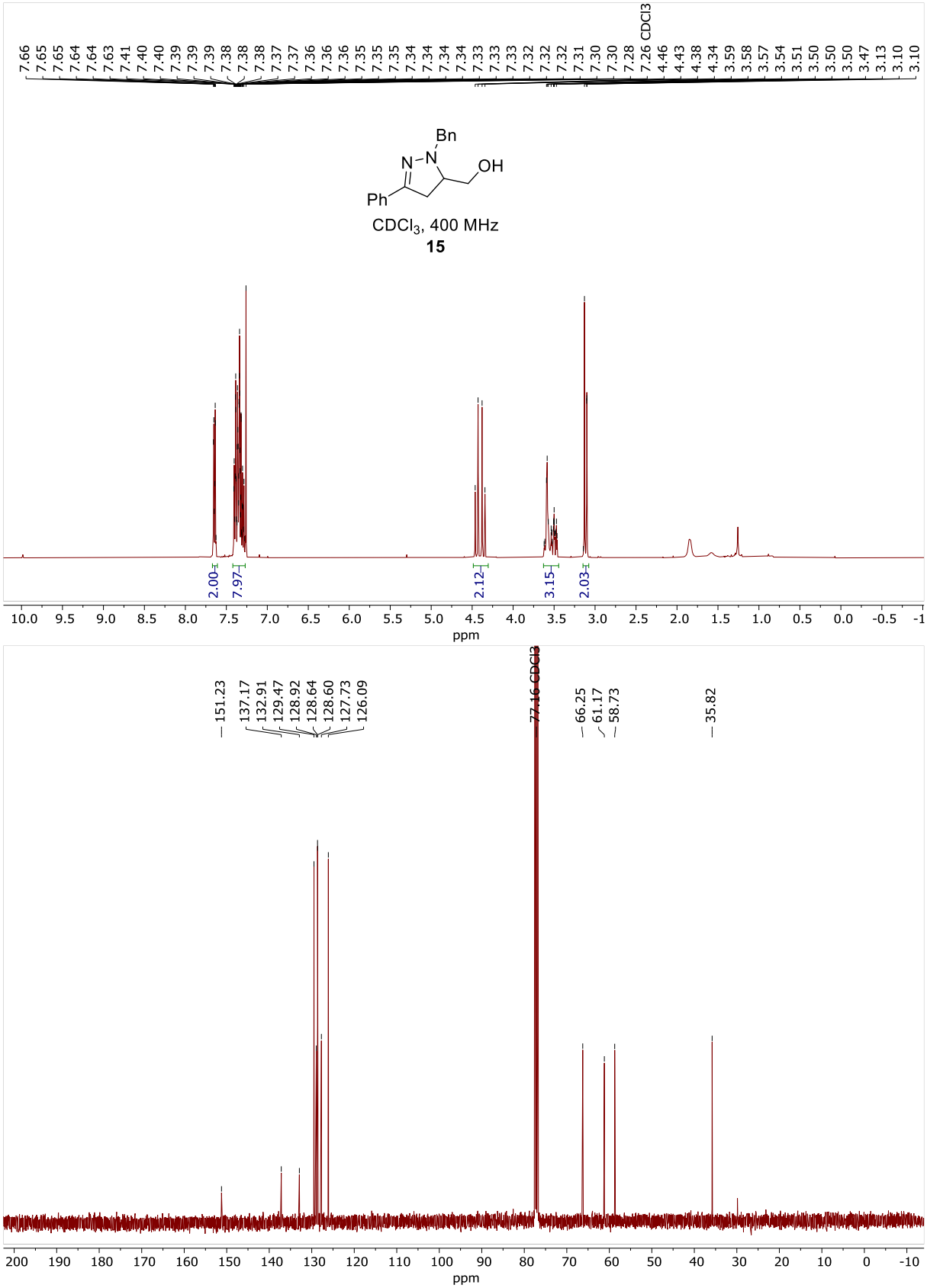
^{1}H NMR, ^{13}C NMR and HMBC spectrum of compound **14**



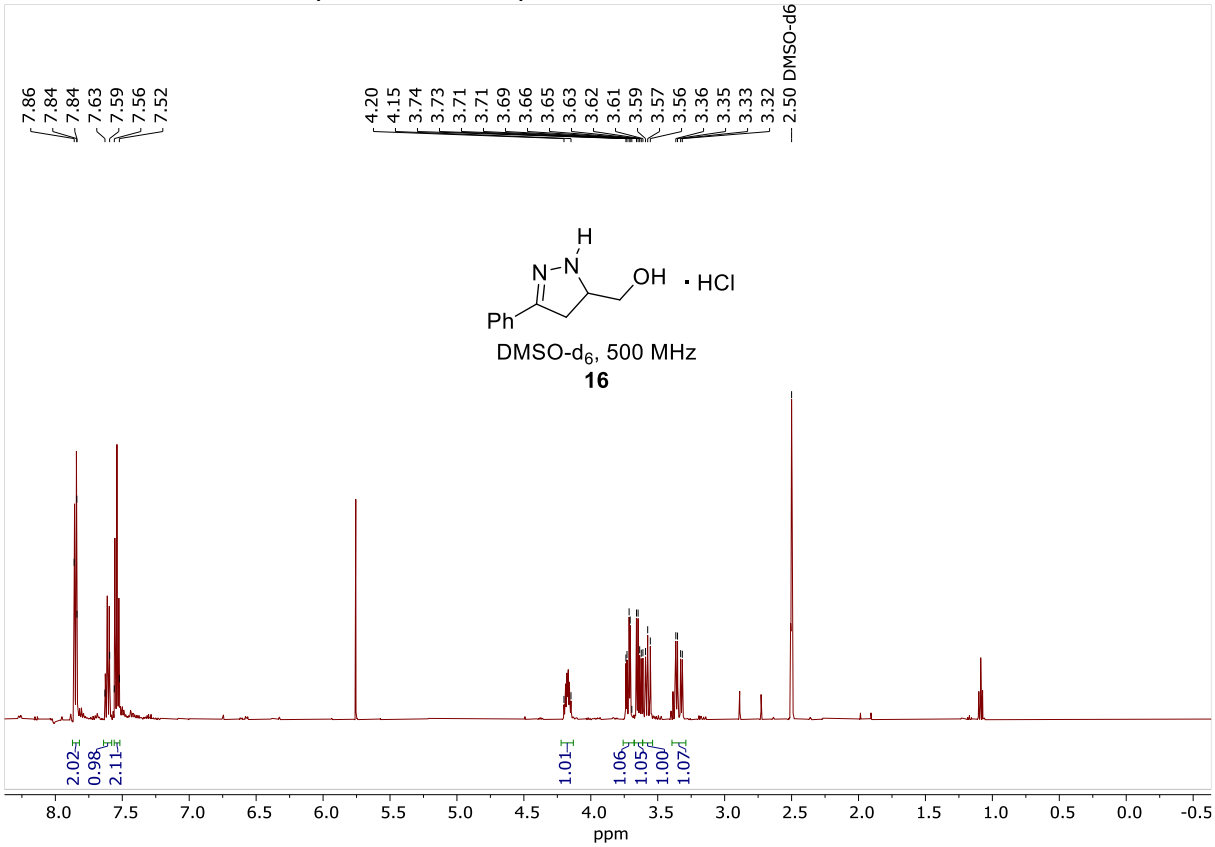


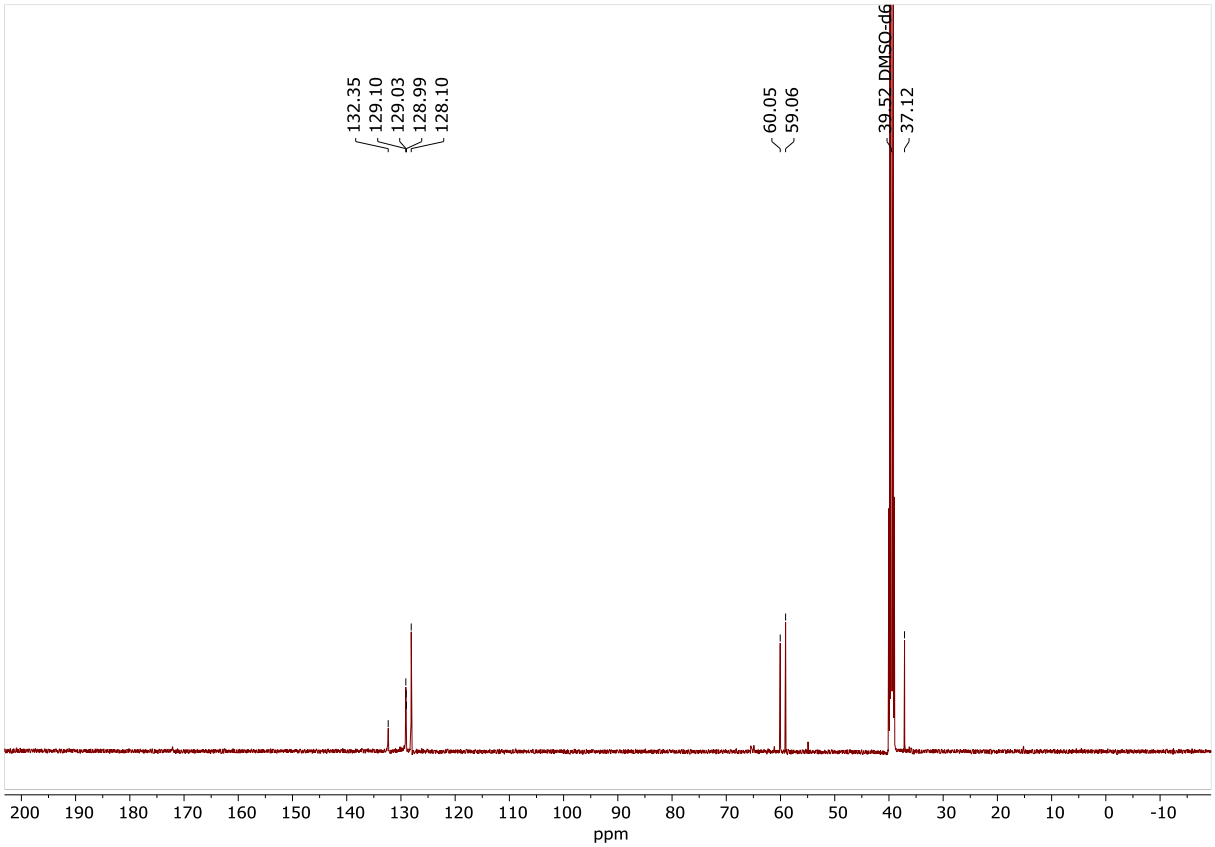

200915-0924-13-ebalke-ult400.13.ser
Sample mb368f1d
group carrei
Instrument Bruker AV III 400 MHz Ultrashield (D 326)
HMBC.ETH Acetone /opt/v ebalke 13
f1 (ppm)
f2 (ppm)

^{1}H NMR and ^{13}C NMR spectrum of compound **15**



^{1}H NMR and ^{13}C NMR spectrum of compound **16**





^{1}H NMR and ^{13}C NMR spectrum of compound **17**