Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

For

Regio- and Chemoselective Synthesis of Nitrogen-Containing Heterocycles via the Oxidative Cascade Cyclization of Unactivated 1,n-Enynes

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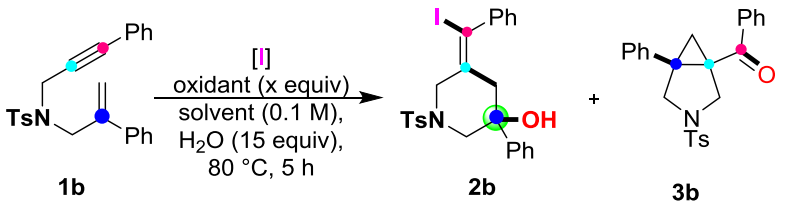
Table of Contents

1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Varian Unity Plus or Varian Mercury plus spectrometer. The chemical shift (δ) values are reported in parts per million (ppm), and the coupling constants (J) are given in Hz. The spectra were recorded using $CDCl_3$ as a solvent. ^{1}H NMR chemical shifts are referenced to tetramethylsilane (TMS) (0 ppm). ^{13}CNMR was referenced to $CDCl_3$ (77.0 ppm). The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, doublet of triplets; td, triplet of doublet; m, multiplet. Mass spectra and high-resolution mass spectra (HRMS) was measured using the LTQ Orbitrap XL (Thermo Fischer Scientific) Liquid chromatography–mass spectrometry at National Sun Yat-sen University. Melting points were determined on an EZ-Melt (Automated melting point apparatus). All the synthesized products showed ^{1}HNMR spectra in agreement with the assigned structures. Reaction progress and product mixtures were routinely monitored by TLC using Merck TLC aluminum sheets (silica gel 60 F254). Column chromatography was carried out with 230-400 mesh silica gel 60(Merck) using a mixture of hexane/ethyl acetate as the eluent. All compounds IUPAC names are not given in exact names because of some compounds have mixture of isomers.

2. Evaluation of the reaction parameters[a]

Table -S1 Optimization of reaction conditions for (*Z*)-5-(iodo(phenyl)methylene)-3-phenyl-1-tosylpiperidin-3-ol



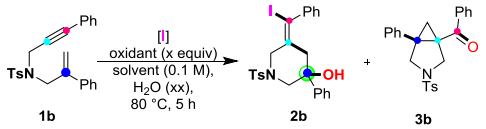
entry	I source (x equiv)	oxidant (y equiv)	solvent	yield[b] (%)	
				2b	**3b**
1	TBAI (1)	TBHP (3)	CH_3CN	46	<5
2	KI (1)	TBHP (3)	CH_3CN	35	<5
3	NaI (1)	TBHP (3)	CH_3CN	40	<5
4	PIDA (1)	TBHP (3)	CH_3CN	-	-
5	I_2 (0.5)	CHP (3)	CH_3CN	-	<5
6	I_2 (0.5)	DTBP (3)	CH_3CN	-	<5
7	I_2 (0.5)	TBPB (3)	CH_3CN	10	20
8[c]	I_2 (0.5)	H_2O_2 (3)	CH_3CN	<10	-
9[d]	I_2 (0.5)	$K_2S_2O_8$ (3)	CH_3CN	20	20
10	I_2 (0.5)	TBHP (3)	1,4-dioxane	30	20
11	I_2 (0.5)	TBHP (3)	$PhCF_3$	10	<5
12	I_2 (0.5)	TBHP (3)	DMSO	-	-
13	I_2 (0.5)	TBHP (3)	DMF	-	-
14	I_2 (0.5)	TBHP (3)	DCE	25	<5
15	I_2 (0.5)	TBHP (3)	CH_3NO_2	30	<5
16	I_2 (0.5)	TBHP (3)	PhCl	20	<10
17	I_2 (0.5)	TBHP (3)	EtOH	-	42
18	I_2 (0.5)	TBHP (3)	Ethylene glycol	-	-
19	I_2 (0.5)	TBHP (3)	n-Butanol	-	-
20[e]	I_2 (0.5)	TBHP (3)	CH_3CN+H_2O	61	<5
21[f]	I_2 (0.5)	TBHP (3)	CH_3CN+H_2O	58	<5
22[g]	I_2 (0.5)	TBHP (3)	CH_3CN+H_2O	60	<5
23[h]	I_2 (0.5)	TBHP (3)	CH_3CN+H_2O	48	<5

24	I_2 (0.5)	TBHP (3)	H_2O	-	10

[a] Reaction conditions: **1b** (0.1 mmol), iodine source (0.5 equiv), 70% aq. TBHP (3 equiv), H_2O (15 equiv), solvent (0.1 M) and stirring for 5 h at 90 ℃. [b] Isolated yields. [c] H_2O_2; 30% wt in H_2O. [d] $K_2S_2O_8$, potassium persulfate. [d]H_2O (15 equiv). [e]H_2O (100 equiv) was used. [f]H_2O (0.25 mL). [g]H_2O (0.5 mL). [h]H_2O (1 mL) was used. [h]H_2O (0.1 M). (with specific quantity of H_2O (15 equiv) improved the reaction yield after that increasing the water quantity either similar results or decreasing the reaction yield")

Subsequent reactions with other Iodine sources such as TBAI, KI, NaI, and PIDA (Table S1, entries 1-4) also failed to improve the reaction yield of **2b**. Later, reactions with other oxidants such as CHP, TBPB, DTBP, 36% H_2O_2 and $K_2S_2O_8$ (Table S1, entries 5-9) also failed to improve the reaction yield of **2b**. The effect of solvents was tested using 1,4-dioxane, $PhCF_3$, DMSO, DMF, DCE, CH_3NO_2, PhCl, EtOH, Ethylene glycol, n-Butanol (Table S1, entries 10-19). Although no solvents resulted in improved yields, MeOH solvent exclusively generated product **3b** in high yield compared to EtOH. Next, we carried out various protic solvent studies. However, all protic solvents is not afforded the desired product except EtOH and H_2O with low yields. The most likely reason for switch of the cyclization is becase of protic solvent. We tried the reaction with combinations of solvents, such as water and acetonitrile, which interestingly improved the yield of **2b**. This improvement could be due to the better solubility of starting material in the miscible solvent system. We checked the reaction with differenct qunatities of water combination with ACN or only H_2O as slovent (Table S1, entries 20-24). At this stage the additional 15 equivalents H_2O role in these radical reaction is not clear. But we speculate the excess of water can form a hydrogen bond with radical intermediates or products in the reaction, it could help improving the reaction yield.[1]

Table-S2. Comparsion of reaction yields with aq. TBHP and TBHP in decane in presence of H_2O



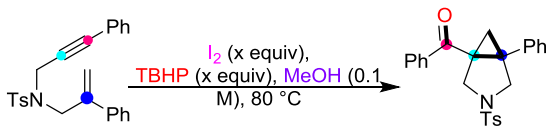
1b 2b 3b

entry	I source (x equiv)	oxidant (y equiv)	solvent	H_2O (Z equiv)	yield[b] (%) (**2b**)	yield[b] (%) (**3b**)
1[c]	I_2 (0.5)	TBHP (3)	ACN	5	61	<5%
2[d]	I_2 (0.5)	TBHP (3)	ACN	5	53	<5%
3[c]	I_2 (0.5)	TBHP (3)	ACN	15	64	<5%
4[d]	I_2 (0.5)	TBHP (3)	ACN	15	54	<5%
5[c]	I_2 (0.5)	TBHP (3)	ACN	25	63	<5%
6[d]	I_2 (0.5)	TBHP (3)	ACN	25	56	<5%
7[c]	I_2 (0.5)	TBHP (3)	ACN	35	63	<5%
8[d]	I_2 (0.5)	TBHP (3)	ACN	35	52	<5%

[a] Reaction condition: **1b** (0.1 mmol), iodine source (0.5 equiv), solvent (0.1 M) and stirred for 5 h at 90 °C. [b] Isolated yields. [c] 70% aq. TBHP (3 equiv).[d]TBHP (5-6 M in decane was used) (3 equiv).

The yield of the reaction was cross checked by using 70% aq.TBHP and TBHP in decane with increasing the qunatity of the water as shown in Table S2. From our additional experiments results suggests aq. TBHP with 15 equivalents H_2O is better reaction yield than aq. TBHP alone and TBHP in decane. At this stage the additional 15 equivalents H_2O role in these radical reaction is not clear. But we speculate the excess of water can form a hydrogen bond with radical intermediates in the reaction and it could help improving the reaction yield.[1]

Table-S3. Evaluation of the reaction parameters for the synthesis of 3-azabicyclo[3.1.0] hexane[a]



1b **3b**

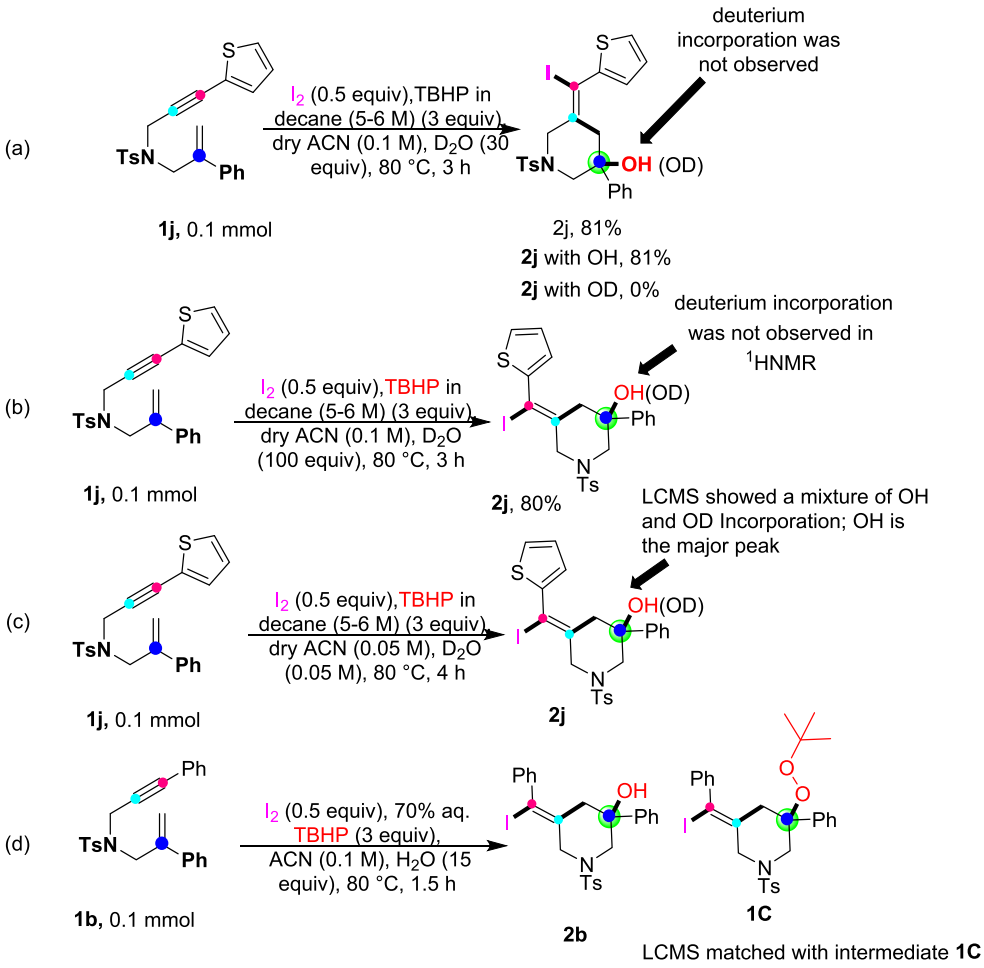
entry	I source (x equiv)	oxidant (y equiv)	solvent	yield[b] (%) **3b**
1[c]	I_2 (0.5)	TBHP (3)	MeOH	35
2	I_2 (0.25)	TBHP (3)	MeOH	15
3	I_2 (0.5)	TBHP (3)	PEG-400	-
4	I_2 (0.5)	TBHP (3)	HFIP	trace
5	I_2 (0.5)	TBHP (4)	MeOH	44
6	I_2 (0.5)	TBHP (5)	MeOH	46
7	I_2 (0.5)	TBHP (2)	MeOH:H_2O (1:1)	10

[a] Reaction condition: **1b** (0.1 mmol), iodine source (0.5 equiv), 70% aq. TBHP (3 equiv), solvent (0.1 M) and stirred for 5-24 h at 80 °C. [b] Isolated yields. [c] TBHP (5-6 M in decane was used) (3 equiv).

To improve the yield of 3-azabicyclo[3.1.0] hexane we tried to improve the reaction yield by modifying reaction conditions such as, changing various protic solvent, altering the quantity of iodine but the reaction yield was not improved. And also, we performed the reaction by increasing the equivalents of aq.TBHP in the reaction but unfortunately the reaction yield was not improved. We follows the original condition because we got better yields compared to these results.

3. Control Experiments:

3.1 Procedure for the use of D_2O in experiment (2j)



Procedure for the 30 equivlance of D_2O in experiment (2j)

To a overnight dried seal tube were added I_2 (50 mol %), 1,6-enyne **1a** (0.1 mmol), and ACN (0.1 M), D_2O (30 equiv).Then TBHP (5-6 M) (3 equiv.) was added into the solution. The mixture was stirred at 80 ^oC in closed atmosphere for indicated time until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was distill off the solvent and purified by column chromatography (Hexane/ethyl acetate) to afford **2j** with only OH insertion product in ^{1}HNMR.

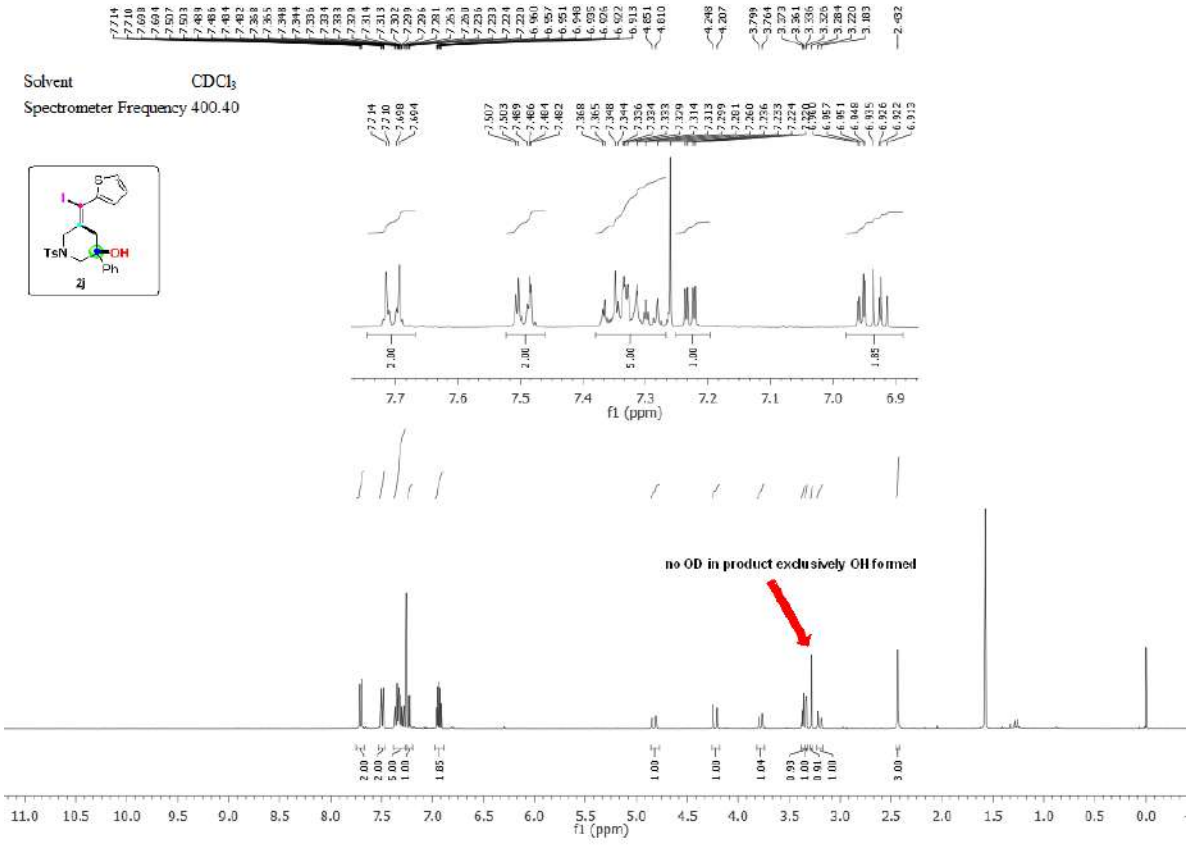


Figure S1. NMR spectra of the D_2O-mediated product

Procedure for the 100 equivlance of D_2O in experiment (2j)

To a overnight dried seal tube were added I_2 (50 mol%), 1,6-enyne **1a** (0.1 mmol) , and ACN (0.1 M), D_2O (100 equiv). Then TBHP (5-6 M) (3 equiv.) was added into the solution. The mixture was stirred at 80 ^oC in closed atmosphere for indicated time until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was distill off the solvent and purified by column chromatography (Hexane/ethyl acetate) to afford **2j** with only OH insertion product in ^{1}HNMR.

Procedure for the 0.05 M D_2O in experiment (2j)

To a overnight dried seal tube were added I_2 (50 mol %), 1,6-enyne **1a** (0.1 mmol) , and ACN (0.1 M), D_2O (100 equiv). Then TBHP (5-6 M) (3 equiv) was added into the solution. The mixture was stirred at 80 ^oC in closed atmosphere for indicated time until complete consumption of starting material as monitored by TLC. The crude reaction mixture checked LCMS. The LCMS shows OH and OD inserted product mass in the mass. And also the

dehydration product is the major peak in the spectrum becasue the acidic nature in the LCMS condition. These reaction supports our plausible reaction mechanism. The LCMS spectrum as shown below.

LC (Waters 2695 Separations Module)

• Flow Rate: 0.2 ml/min.

•Column: ZORBAX Eclipse Plus C18 Narrow Bore RR 2.1x100mm 3.5µm

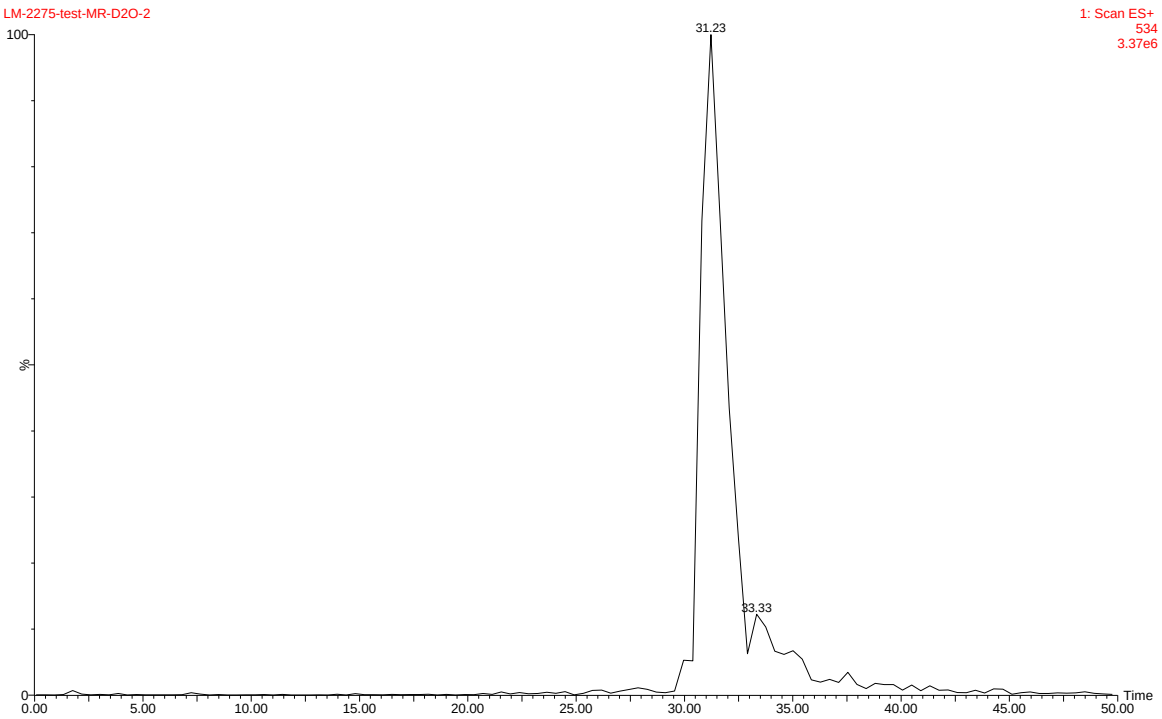
• Mobile Phase:

Time (min.)	0.02% Formic Acid in H_2O (%)	0.02% Formic Acid in MeOH (%)
0	75	25
5	75	25
30	0	100
60	0	100

MS (Waters micromassZQ)

•ESI-MS (Cone 20V, 35V, 50V)

RT: 0.00 - 50.00



Cone 20V

Figure S2. LCMS spectra of the D_2O (0.05M+0.05 M ACN)-mediated reaction with **1j**

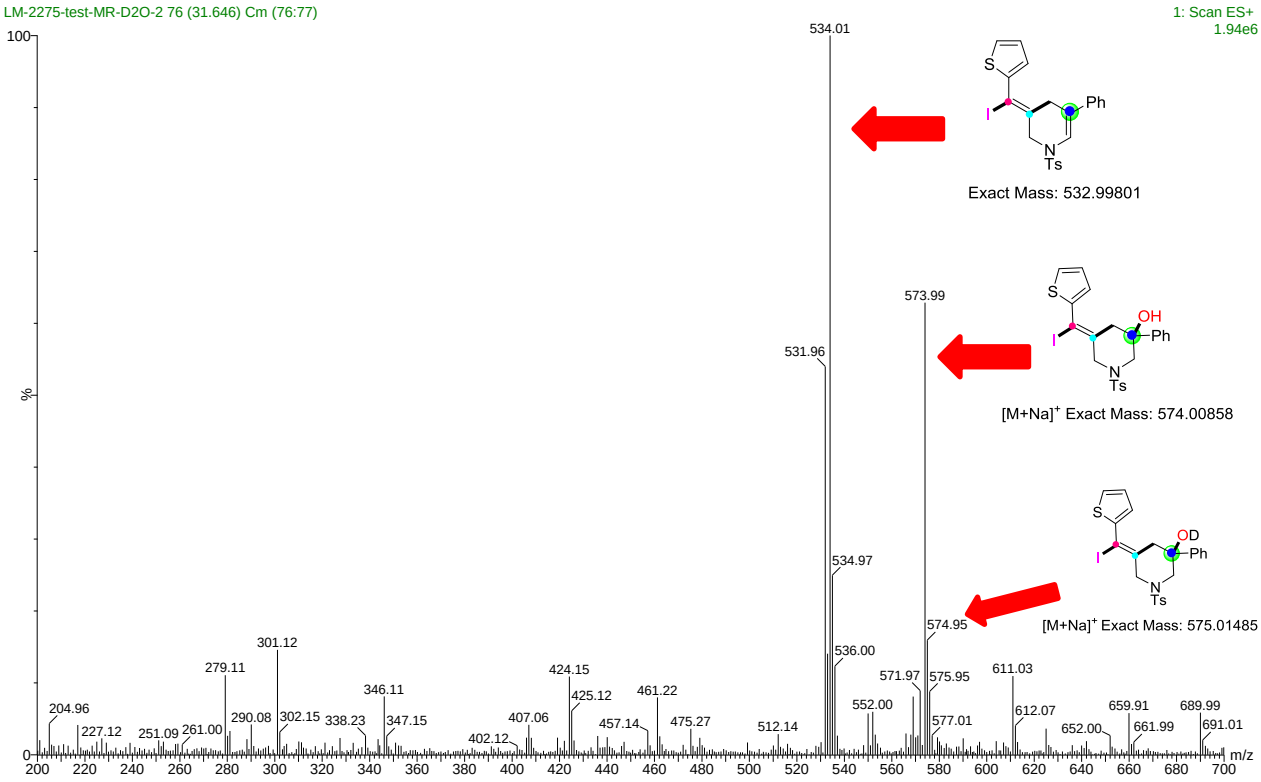
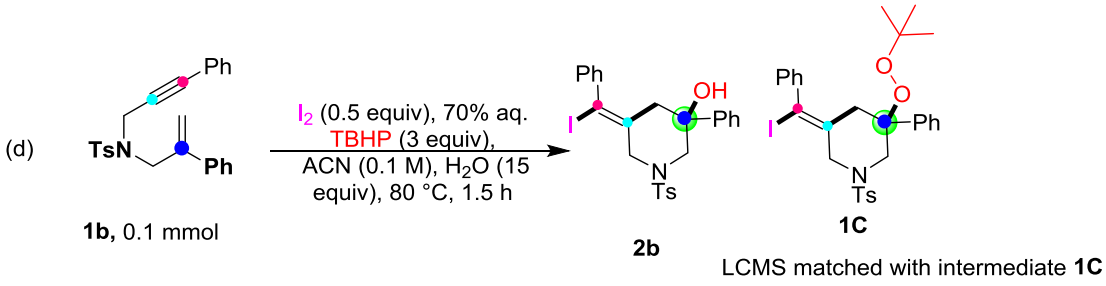


Figure S3. LCMS spectra of the D_2O (0.05M+0.05 M ACN)-mediated reaction with **1j**

3.2 Experiment to find the intermediate 1C



To a overnight dried seal tube were added I_2 (50 mol %), 1,6-enyne **1a** (0.1 mmol) , and ACN (0.1 M), H_2O (15 equiv). Then 70% aq. TBHP (3 equiv) was added into the solution. The mixture was stirred at 80 ^oC in closed atmosphere for indicated time to find the reactive intermidate. But unfortunately we did not obser any intermdiate in the TCL. Thus we checked the crude mixture with LCMS. The LCMS shows intermediate **1C**. It supports our pluasible reaction is going via 1C as the reactive intermediate. The LCMS shows as below.

LC (***Waters* 2695 Separations Module**)

♦ Flow Rate: 0.2 ml/min.

♦Column: **ZORBAX Eclipse Plus C18** Narrow Bore RR 2.1x100mm 3.5µm

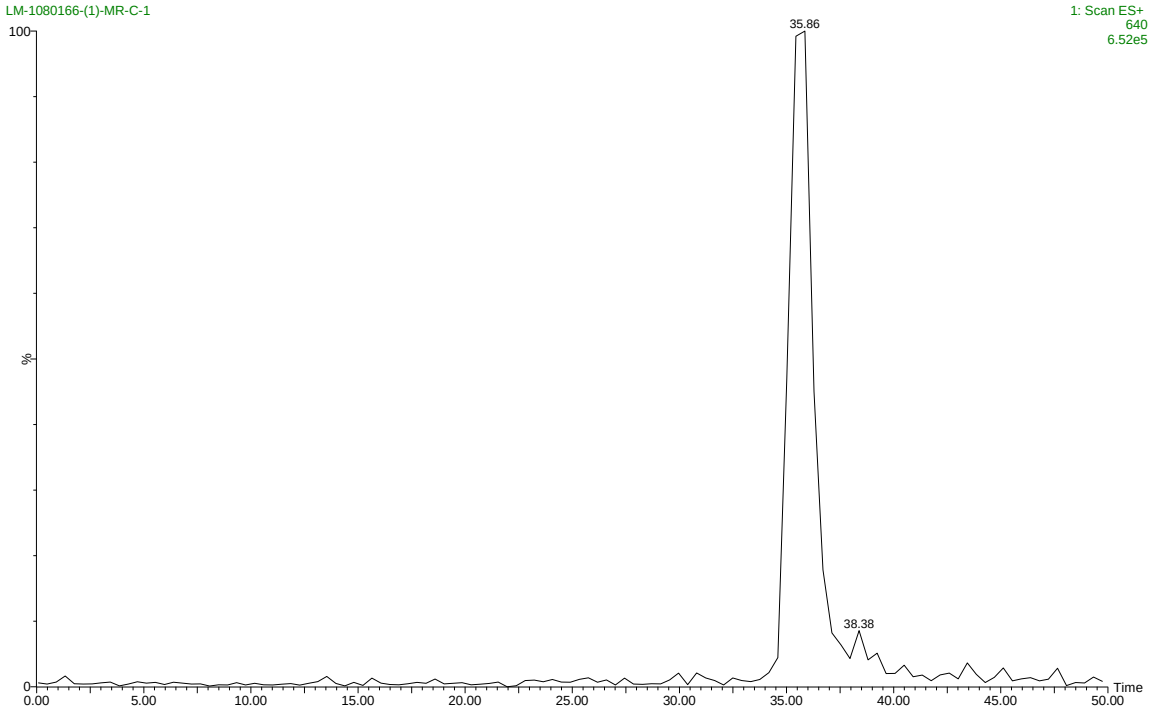
♦ Mobile Phase:

Time (min.)	0.02% Formic Acid in H_2O (%)	0.02% Formic Acid in MeOH (%)
0	75	25
5	75	25
30	0	100
60	0	100

MS (***Waters* micromass*ZQ***)

♦ESI-MS (Cone 20V, 35V, 50V)

RT: 0.00 - 50.00



Cone 20V

Figure S4. LCMS spectra for the reaction with **1b** at short interval of time

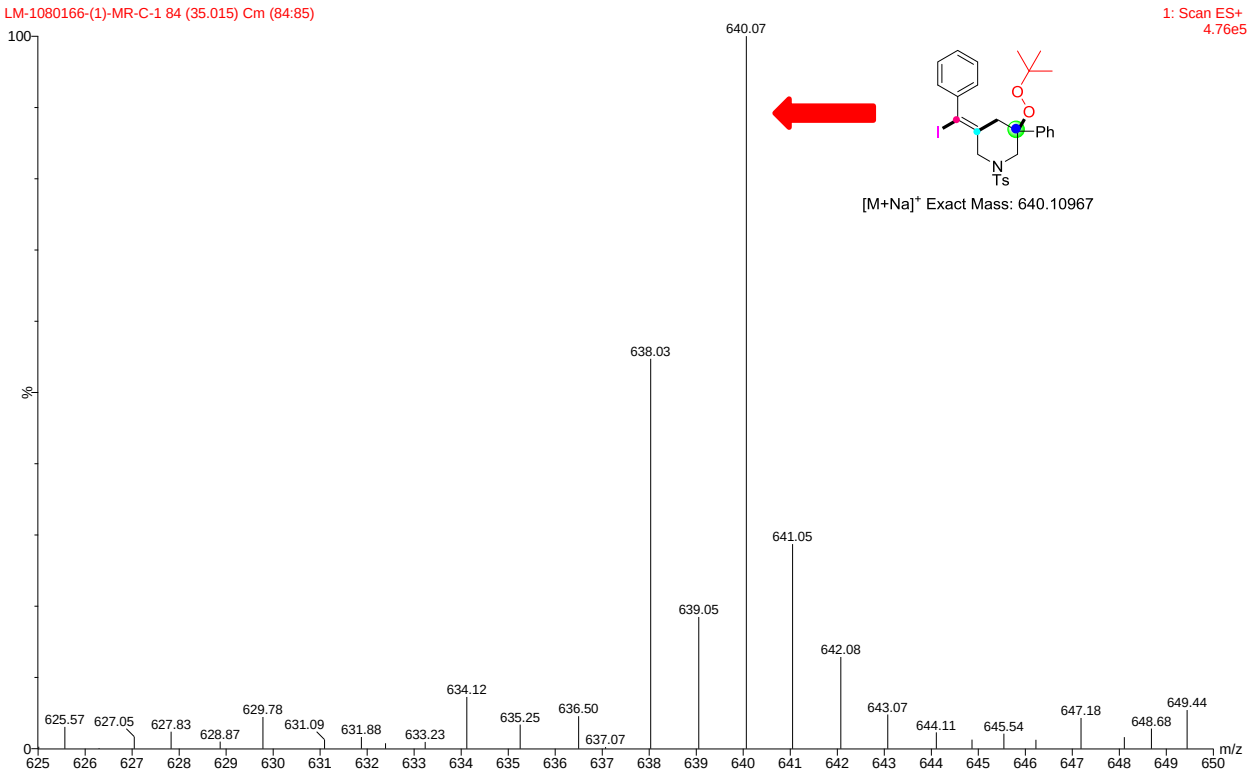
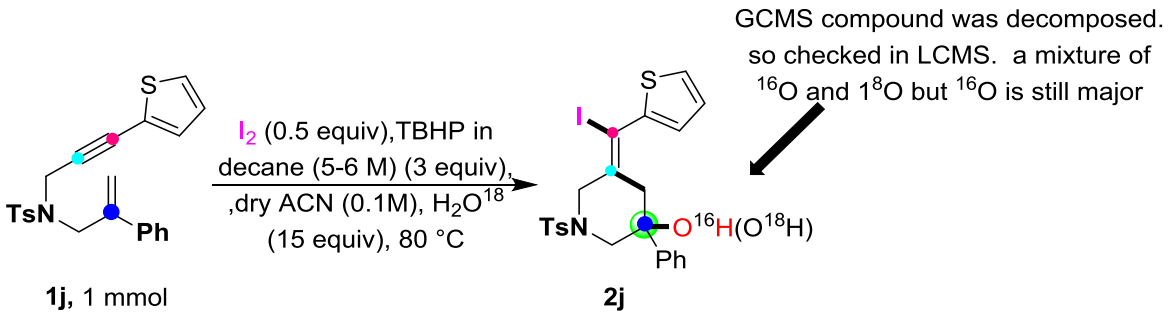


Figure S5. LCMS spectra for the reaction with **1b** at short interval of time

3.3 Procedure with 15 equiv of $H_2{}^{18}O$ Experiment (2j)[2]



To a overnight dried seal tube were added I_2 (50 mol%), 1,6-enyne 1a (0.1 mmol) , and ACN/$H_2{}^{18}O$ (15 equiv) (0.1 M), TBHP in decane (5-6 M) (3 equiv) was added into the solution. The mixture was stirred at 80 ^oC in closed atmosphere for indicated time until complete consumption of starting material as monitored by TLC. After the reaction was finished, the crude reaction mixture was checked GCMS but unfortunately the compound was decomposed without showing any desired product mass. So then same reaction mixture we checked with LCMS. In LCMS we observed major ^{16}O peak and minor ^{18}O peak. Based on our mechanistic studies and previous literature we hypothesized the hydroxy source is from aq.TBHP. And below show LCMS spectram of the reaction mixture.

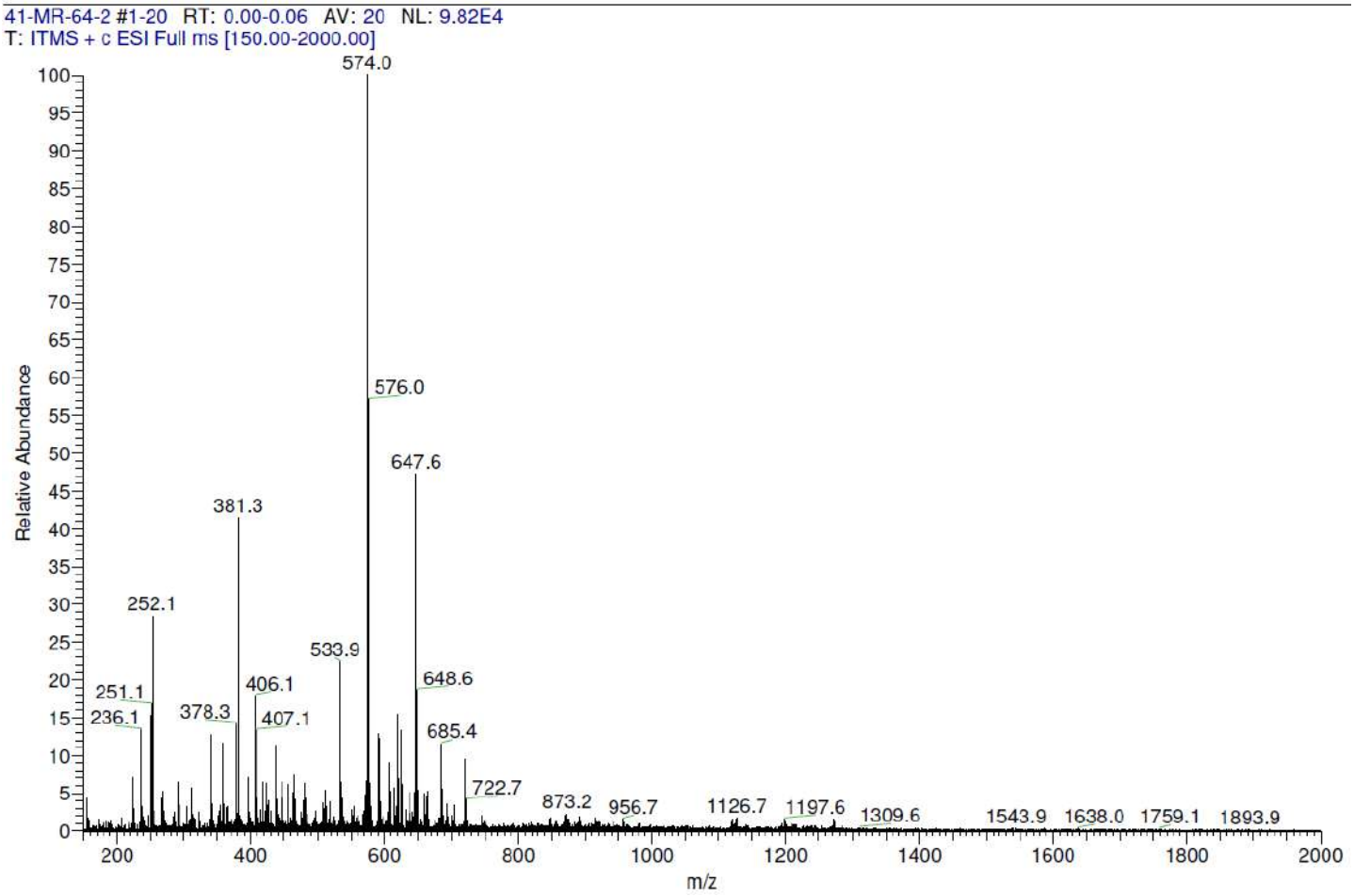


Figure S6. LCMS spectra for the $H_2{}^{18}O$ Experiment (**2j**)

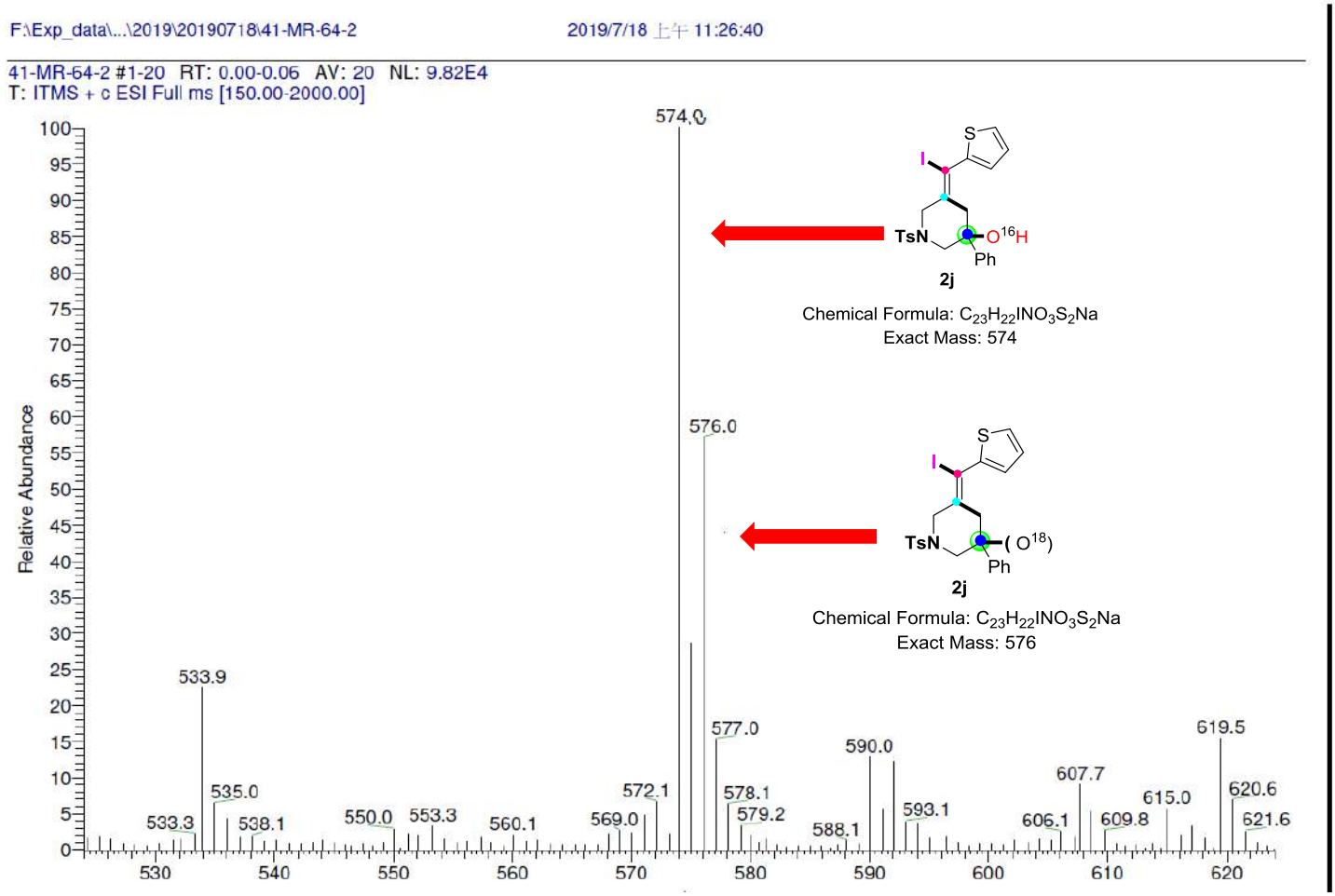


Figure S6. LCMS spectra for the $H_2{}^{18}O$ Experiment (**2j**)

F:\Exp_data\...\2019\20190718\41-MR-64-2 2019/7/18 上午 11:26:40

41-MR-64-2#1-20 RT: 0.00-0.06 AV: 20

I: IIMS + c ESI Full ms [150.00-2000.00]

m/z	Intensity	Relative
224.1	6872.2	7.00
236.1	13128.5	13.37
250.1	14938.0	15.21
251.1	16428.9	16.73
252.1	27925.8	28.44
253.2	6240.0	6.36
290.1	6332.4	6.45
311.3	5536.3	5.64
340.4	8044.4	8.19
341.4	12459.2	12.69
358.4	11481.9	11.69
378.3	13974.3	14.23
379.0	5703.9	5.81
381.3	40707.5	41.46
382.3	10100.7	10.29
395.3	6950.6	7.08
406.1	17566.2	17.89
407.1	13073.1	13.31
418.0	6263.6	6.38
424.2	6212.8	6.33
437.2	11037.6	11.24
446.1	6269.9	6.39
455.4	6089.3	6.20
464.1	7204.8	7.34
480.2	6139.4	6.25
511.5	5295.2	5.39
533.9	21954.5	22.36
535.0	6300.8	6.42
572.1	6505.4	6.63
574.0	98183.2	100.00
575.1	28090.1	28.61
576.0	56044.6	57.08
577.0	14994.2	15.27
578.1	6165.0	6.28
590.0	12627.8	12.86
591.1	5548.4	5.65
592.0	11946.8	12.17
607.7	8795.9	8.96
608.6	5189.4	5.29
615.0	5591.9	5.70
619.5	15093.3	15.37
620.6	6786.9	6.91
624.6	13073.1	13.32
625.7	5990.6	6.10
647.6	46302.7	47.16
648.6	18307.6	18.65
649.6	5337.7	5.44
685.4	11315.8	11.53
686.5	5363.5	5.46
721.6	9294.3	9.47

F:\Exp_data\...\20190723\23-MR-64-2-H 2019/7/23 上午 10:50:26

23-MR-64-2-H#1-20 RT: 0.01-0.28 AV: 20
T: FTMS + p ESI Full ms [150.00-2000.00]
m/z= 575.7881-576.1887

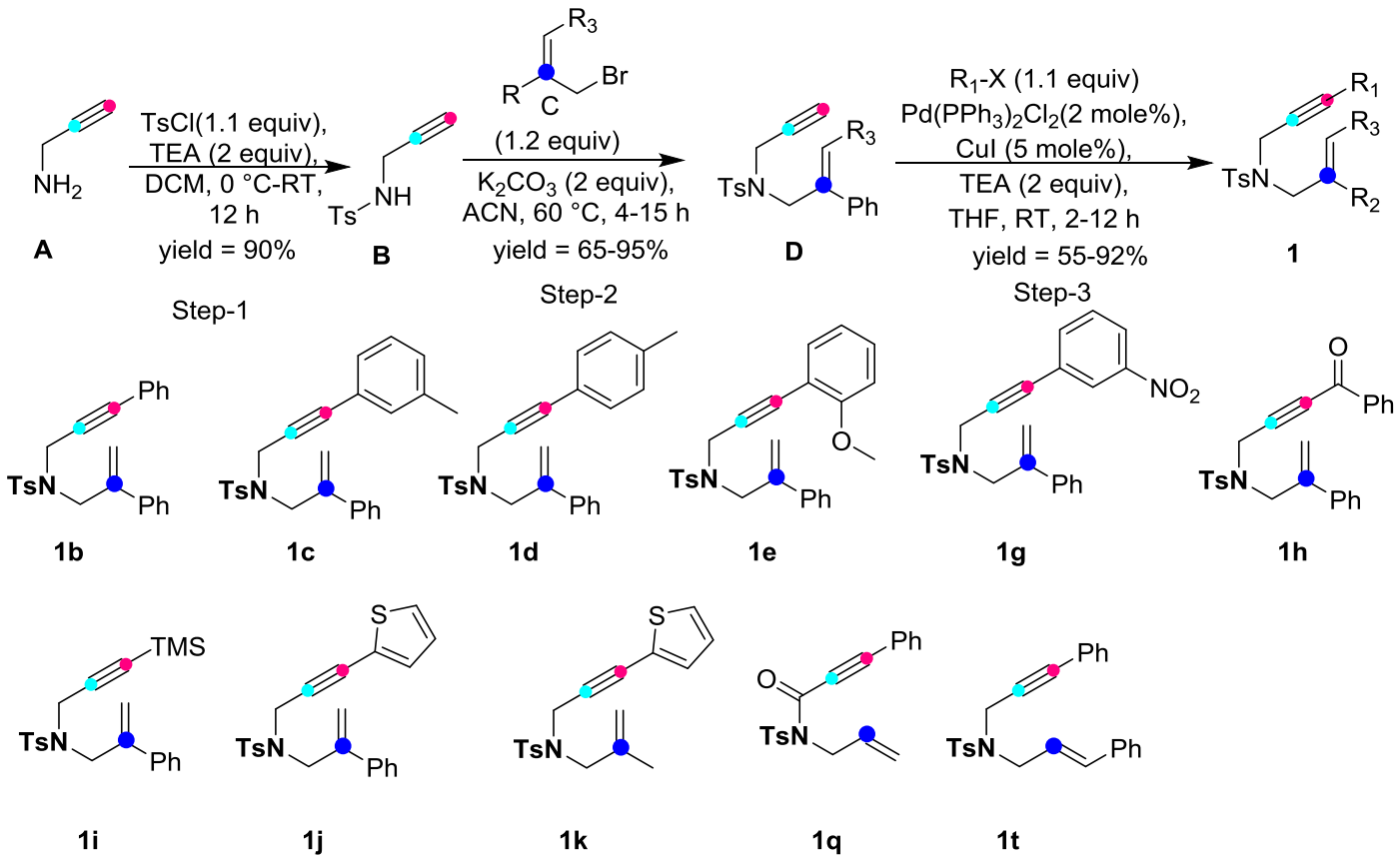
Isotope	Min	Max
N-14	0	1
O-16	0	2
C-12	0	23
H-1	0	23
Na-23	0	1
S-32	0	2
O-18	0	1
I-127	0	1

Charge 1
Mass tolerance 1000.00 ppm
Nitrogen rule not used
RDB equiv -1.00-100.00
max results 1

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
576.0019	521498.8	100.00	576.0020	-0.20	$C_{23}H_{22}O_2{}^{18}ONINaS_2$

4. Experimental procedures

4.1 Preparation of Starting Materials[3]



General procedure for synthesis of 1,n-enynes (A)

General procedure for Step-1:

To a solution of prop-2-yn-1-amine (1 equiv) in DCM at 0 °C, TEA (2 equiv) and TsCl (1.1 equiv) were added. The resulting mixture was continued at room temperature for 16 h. The solvent was removed under reduced pressure and the resulting solid was dissolved in ethyl acetate, washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was carried out without further purification (**B**).

General procedure for Step-2:

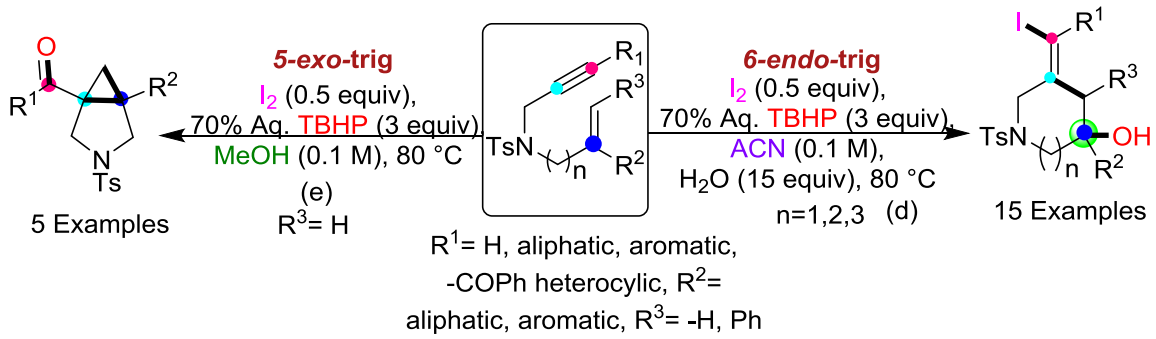
To a solution of A (1 equiv) in ACN at 0 °C, K_2CO_3 (2 equiv) and allylbromide **C** (40.0 mmol) were added. The resulting mixture was heated under at 60 °C for 4-15 h. The reaction mixture cooled to RT and the solvent was removed under reduced pressure and the resulting solid was dissolved in ethyl acetate, washed with water and

brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by chromatography to give compound (**D**).

General procedure for Step-3:

To a dried schlenk flask was added compound (**D**), iodoarene (1.1 equiv) followed by $Pd(PPh_3)_2Cl_2$ (2 mol %), CuI (5 mol %), in freshly distilled Et_3N under argon. The resulting mixture was stirred at RT for 2-12 h. After the completion of reaction by TLC, the reaction mixture was cooled to RT, diluted with water and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered and concentrated to give crude material. The crude material was purified by column chromatography using hexane-ethyl acetate as the eluent (**1**).

5.2. General procedure for the Synthesis of N-heterocyclic compounds (2, 3&4)



Scheme 1. Synthesis of Piperidine & Pyrrolidine

General procedure (B) for the Synthesis of 5-(iodomethylene)-1-tosylpiperidin-3-ol derivatives (2a-2n)

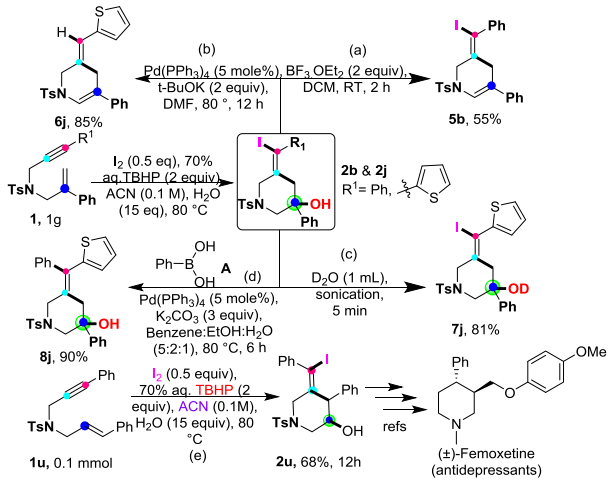
To a overnight dried seal tube were added I_2 (50 mol %), 1,6-enyne **1a** (0.1 mmol), and ACN (0.1 M), H_2O (15 equiv), then aq.TBHP (3 equiv) was added into the solution. The mixture was stirred at 80 ^oC closed atmosphere for indicated time until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and washed with $Na_2S_2O_3$ and saturated NaCl. The aqueous phase was extracted twice with ethyl acetate and washed with saturated NaCl. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, then purified by column chromatography (Hexane/ethyl acetate) to afford **2**.

General procedure (C) for the Synthesis of 3-tosyl-3-azabicyclo[3.1.0]hexane derivatives (3a, 3b, 3c, 3f, 3j, 3g, 3z)

To a overnight dried seal tube were added I_2 (50 mol %), 1,6-enyne **1** (0.1 mmol), and MeOH (0.1 M), then aq.TBHP (3 equiv) was added into the solution. The mixture was stirred at 80 ^oC closed atmosphere for indicated time until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and washed with $Na_2S_2O_3$ and

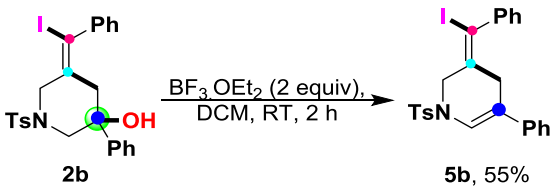
saturated NaCl. The aqueous phase was extracted twice with ethyl acetate and washed with saturated NaCl. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, then purified by column chromatography (Hexane/ethyl acetate) to afford **3**.

Table-S4. Gram-scale reactions and further transformation of cyclization product.



To demonstrate the synthetic application of the protocol, reaction scale-up experiments were performed (Table 4). The desired piperidine cores 2b, and 2j were formed in 65-85% yields without affecting quantity of the reaction. The synthetic value of this method was further demonstrated by investigating follow-up chemistry using 2b and 2j as substrates (Table S4). Selective elimination of the OH group was achieved by treating 2b with $BF_3.OEt_2$ in DCM to give the corresponding elimination product 5b in 55% yield (Table S4, b). When we treated 2j under palladium catalysis for 12h at 100 °C, we observed simultaneous dehydration as well as deiodination product 6j (Table S4, b). By sonication of 2j in 1 mL D2O, we observed deuterated compound 7j (Table S4, c). By using the traditional Suzuki reaction, we succeeded in incorporating phenyl group 8j (Table S4, d). Furthermore, our synthetic method was applied to synthesize key intermediate 2u, a precursor of the anti-depressant (±) femoxetine in 68% yield (Table S4, e).

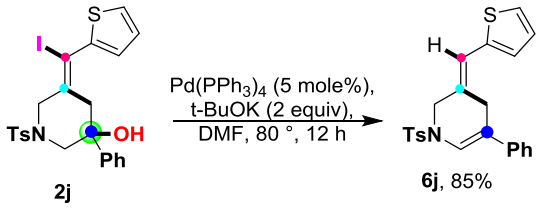
Procedure(D)for the synthesis of (Z)-3-(iodo(phenyl)methylene)-5-phenyl-1-tosyl-1,2,3,4-tetrahydropyridine (5b)



To a overnight dried round bottom flash were added $BF_3.OEt_2$ (2 equiv), **2a** (1 equiv), DCM (1 ml). The mixture was stirred at room temperature for indicated time until complete consumption of starting material as monitored by TLC. After the reaction was finished, diluted with DCM, and saturated NaCl. The aqueous phase was extracted

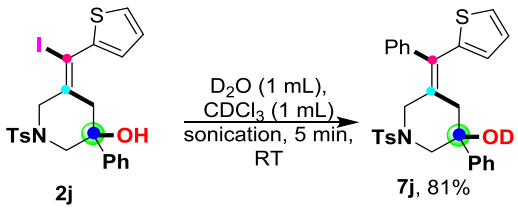
twice with DCM and washed with saturated NaCl. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, then purified by column chromatography (Hexane/ethyl acetate) to afford **5b** 55% yield.

Procedure (E)for the synthesis of (*E*)-5-phenyl-3-(thiophen-2-ylmethylene)-1-tosyl-1,2,3,4-tetrahydropyridine (6j)



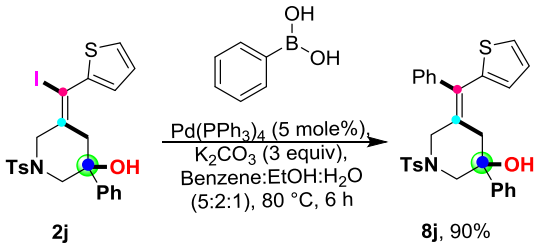
To a dried round bottom flask was added compound (**2j**), $Pd(PPh_3)_4$ (5 mole %), CuI (5 mole %), in DMF under argon. The resulting mixture was stirred at 100 °C for 12 h. After the completion of reaction by TLC, the reaction mixture was cooled to RT, diluted with water and extracted with ethyl acetate. The combined organic layer was dried washed with cold water to remove the excess DMF in reaction. The organic layer dried over anhydrous Na_2SO_4, filtered and concentrated to give crude material. The crude material was purified by column chromatography using hexane-ethyl acetate as the eluent to afford **6j** in 85% yield

Procedure (F)for the synthesis of (*E*)-3-phenyl-5-(phenyl(thiophen-2-yl)methylene)-1-tosylpiperidin-3-ol-d (7j)



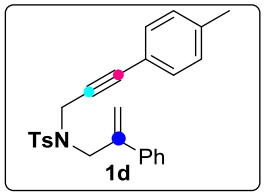
To a dried round bottom flask was added compound (**2j**), in $CDCl_3$ (1 mL), D_2O (1 mL) under argon. The resulting mixture was sonicated at room temperature for 5 min. Further without any isolation, the reaction mixture check the proton NMR and we observed disappearance of the hydroxy group proton and insertion of OD in the product **7j** in 81% yield.

Procedure (G)for the synthesis of (*E*)-3-phenyl-5-(phenyl(thiophen-2-yl)methylene)-1-tosylpiperidin-3-ol (8j)



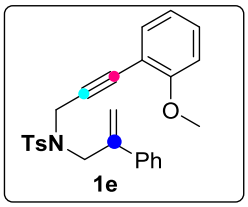
To a dried round bottom flask was added compound (**2j**), phenyl boronic acid (1.2 equiv), $Pd(PPh_3)_4$ (5 mole%), K_2CO_3 (3 equiv), in Benzene:EtOH:H_2O (5:2:1) under argon. The resulting mixture was stirred at 80 °C for 6 h. After the completion of reaction by TLC, the reaction mixture was cooled to RT, diluted with water and extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, then purified by column chromatography (Hexane/ethyl acetate) to afford **8j** in 90% yield.

4-methyl-N-(2-phenylallyl)-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (1d): : The title compound was



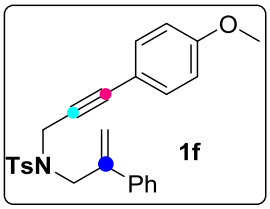
prepared according to the general procedure A to obtain as a white solid (150 mg, yield = 85%); Mp. 124.9-125.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.58-7.55 (m, 2H), 7.36-7.26 (m, 3H), 7.24 (d, *J* = 8 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.92-6.90 (m, 2H), 5.59 (d, *J* = 0.8 Hz, 1H), 5.37 (d, *J* = 0.8 Hz, 1H), 4.31 (s, 2H), 4.18 (s, 2H), 2.32 (s, 3H), 2.31 (S, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.42, 141.21, 138.42, 137.57, 135.45, 131.26, 129.41, 128.74, 128.36, 128.05, 127.86, 126.32, 118.98, 117.16, 86.14, 80.53, 50.15, 36.38, 21.33; HRMS (ESI): Calc'd for [$C_{26}H_{26}INNaO_3S$] $[M+Na]^+$ 582.05703, found 582.05708.

N-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-methyl-N-(2-phenylallyl)benzenesulfonamide (1e): The title



compound was prepared according to the general procedure A to obtain as a white solid (125 mg, yield = 70%); Mp. 124.2-125.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.60-7.57 (m, 2H), 7.37-7.27 (m, 3H), 7.24 (ddd, *J* = 8.0, 6.8, 2 Hz, 1H), 7.19 (dt, *J* = 2.5, 1.3 Hz, 2H), 6.91-6.87 (m, 1H), 6.82 (dd, *J* = 11.4, 4.4 Hz, 2H), 5.61 (d, *J* = 0.9 Hz, 1H), 5.47 (d, *J* = 1.1 Hz, 1H), 4.35 (s, 2H), 4.25 (s, 2H), 3.79 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.91, 143.36, 141.19, 137.74, 135.41, 133.23, 129.72, 129.31, 128.39, 128.05, 127.93, 126.38, 120.03, 117.32, 111.41, 110.31, 85.34, 82.70, 55.46, 50.01, 36.77, 21.33; HRMS (ESI): Calc'd for [$C_{26}H_{25}NNaO_3S$] $[M+Na]^+$ 454.14474, found 454.14450.

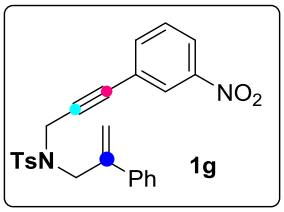
N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methyl-N-(2-phenylallyl)benzenesulfonamide(1f): The title compound was prepared according to the general procedure A to obtain as a yellow solid (200 mg, yield = 65%);



Mp. 103.1-104.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.58-7.56 (m, 2H), 7.37-7.30 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.98-6.96 (m, 2H), 6.77-6.74 (m, 2H), 5.49 (dd, *J* = 90, 0.4 Hz, 2H), 4.31 (s, 2H), 4.18 (s, 2H), 3.79 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.56, 143.43, 141.33, 137.67, 135.58, 132.88, 129.45, 128.43,

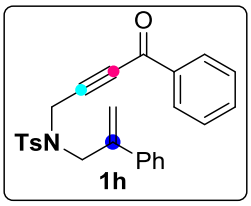
128.12, 127.96, 126.39, 117.17, 114.24, 113.66, 85.93, 79.89, 55.27, 50.18, 36.48, 21.44; HRMS (ESI): Calc'd for $[C_{26}H_{26}INNaO_4S]$ $[M+Na]^+$ 598.05194, found 598.05220.

4-methyl-N-(3-(3-nitrophenyl)prop-2-yn-1-yl)-N-(2-phenylallyl)benzenesulfonamide(1g): The title compound was prepared according to the general procedure A to obtain as a yellow solid (180 mg, yield = 85%);



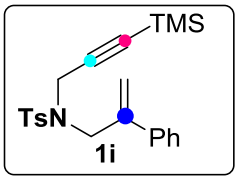
Mp. 94.3-95.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (ddd, *J* = 8.0, 3.6, 1.2 Hz, 1H), 7.81-7.79 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H),), 7.39-7.28 (m, 7H), 5.62 (d, *J* = 1.6 Hz, 1H), 5.36 (d, *J* = 0.8 Hz, 1H), 4.33 (s, 2H), 4.21 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.72, 143.90, 141.09, 137.28, 137.01, 135.32, 129.48, 129.16, 128.37, 128.15, 127.87, 126.24, 126.01, 123.70, 123.02, 117.27, 84.28, 83.42, 50.38, 36.09, 21.28; HRMS (ESI): Calc'd for $[C_{25}H_{22}N_2NaO_4S]$ $[M+Na]^+$ 469.11925, found 469.11902.

4-methyl-N-(4-oxo-4-phenylbut-2-yn-1-yl)-N-(2-phenylallyl)benzenesulfonamide (1h): The title compound



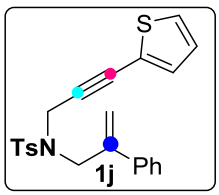
was prepared according to the general procedure A to obtain as a brown solid (71 mg, yield = 65%); Mp. 103.4-103.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (m, 4H), 7.64-7.59 (m, 1H), 7.55-7.52 (m, 2H), 7.45-7.40 (m, 2H), 7.38-7.29 (m, 3H), 7.20 (dd, *J* = 8.5, 0.6 Hz, 2H), 5.62 (s, 1H), 5.36 (s, 1H), 4.36 (s, 2H), 4.25 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.67, 144.25, 140.98, 137.14, 135.95, 134.83, 134.27, 129.78, 129.32, 128.54, 128.53, 128.37, 127.83, 126.35, 117.83, 86.65, 83.77, 58.79, 50.74, 35.86, 21.34; LCMS (ESI): Calc'd for $[C_{26}H_{23}O_3NNaS]$ $[M+Na]^+$ 452.1291, found 452.1284.

4-methyl-N-(2-phenylallyl)-N-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide (1i): The title



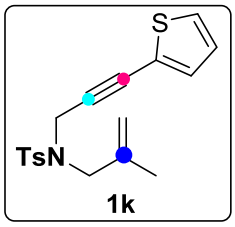
compound was prepared according to the general procedure A to obtain as a white solid (xx mg, yield = xx%); Mp. 109.4-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.56-7.54 (m, 2H), 7.37-7.29 (m, 5H), 5.45 (dd, *J* = 22.8, 1.2 Hz, 1H), 4.26 (s, 2H), 3.99 (s, 2H), 2.43 (s, 3H), 0.02 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.43, 141.13, 137.65, 135.52, 129.49, 128.42, 128.13, 127.92, 126.39, 117.25, 97.47, 91.39, 49.90, 36.48, 21.54, 0.44; HRMS (ESI): Calc'd for $[C_{22}H_{27}NNaO_2SSi]$ $[M+Na]^+$ 420.14240, found 420.14216.

4-methyl-N-(2-phenylallyl)-N-(3-(thiophen-2-yl)prop-2-yn-1-yl)benzenesulfonamide(1j): The title

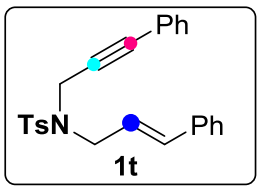


compound was prepared according to the general procedure A to obtain as a yellow solid (xx mg, yield = xx%); Mp. 121.1-121.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.8, 2.0 Hz, 2H), 7.63-7.51 (m, 2H), 7.38-7.28 (m, 5H), 7.19 (dd, *J* = 4.4, 2.0 Hz, 1H), 6.91-6.89 (m, 2H), 5.48 (dd, *J* = 95.9, 0.4 Hz, 2H), 4.29 (s, 2H), 4.20 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.66, 141.23, 137.55, 135.28, 132.09, 129.58, 128.45, 128.16, 127.84, 127.18, 126.71, 126.38, 122.05, 117.29, 85.39, 79.26, 50.30, 36.56, 21.53; HRMS (ESI): Calc'd for $[C_{23}H_{21}NNaO_2S_2]$ $[M+Na]^+$ 430.09059, found 430.09047.

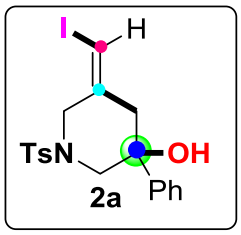
4-methyl-N-(2-methylallyl)-N-(3-(thiophen-2-yl)prop-2-yn-1-yl)benzenesulfonamide (1k): The title compound was prepared according to the general procedure A to obtain as a yellow solid (15mg, yield = 62%); Mp. 67.2-68.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 3H), 7.19 (t, *J* = 3.2 Hz, 2H), 6.90 (s, 1H), 6.89 (s, 1H) 5.00 (s, 2H), 4.26 (s, 2H), 3.76 (s, 2H), 2.36 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.48, 139.11, 135.68, 132.05, 129.50, 127.62, 127.11, 126.66, 122.02, 115.55, 85.48, 78.83, 52.67, 36.45, 21.47, 19.67; HRMS (ESI): Calc'd for $[C_{18}H_{19}NNaO_2S_2]$ $[M+Na]^+$ 368.07494, found 368.07501.



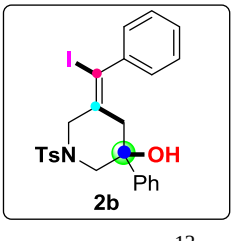
N-cinnamyl-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1t): The title compound was prepared according to the general procedure A to obtain as a white solid (155 mg, yield = 71%); Mp. 155.8-156.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.35-7.21 (m, 10H), 7.07 (dt, *J* = 6.0, 1.2 Hz 2H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.14 (dt, *J* = 14.0, 6.8 Hz, 1H), 4.33 (s, 2H), 4.05 (dd, *J* = 6.8, 1.1 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.47, 136.05, 135.86, 134.75, 131.41, 129.47, 128.53, 128.33, 128.05, 127.96, 127.76, 126.47, 123.02, 122.10, 85.73, 81.67, 48.83, 36.79, 21.35; HRMS (ESI): Calc'd for $[C_{25}H_{23}NNaO_2S]$ $[M+Na]^+$ 424.13417, found 424.13390.



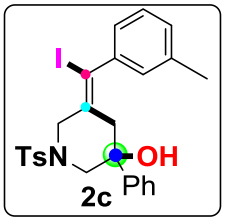
(*Z*)-5-(iodomethylene)-3-phenyl-1-tosylpiperidin-3-ol (2a): The title compound was prepared according to the general procedure B to obtain as a yellow solid (28 mg, yield = 58%); Mp. 111.6-118.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.27 (m, 5H), 6.28 (s, 1H), 4.75 (d, *J* = 12.9 Hz, 1H), 3.70 (d, *J* = 12.0 Hz, 1H), 3.03 – 2.84 (m, 2H), 2.67 (dt, *J* = 19.3, 13.1 Hz, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.17, 142.14, 139.52, 133.06, 129.94, 128.51, 127.88, 127.79, 124.80, 79.53, 71.29, 56.93, 53.02, 47.20, 21.58.



(*Z*)-5-(iodo(phenyl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (2b): The title compound was prepared according to the general procedure B to obtain as a yellow solid (35 mg, yield = 63%); Mp. 145.5-142.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.50-7.47 (m, 2H), 7.35-7.26 (m, 7H), 7.25-7.22 (m, 1H), 7.15-7.13 (m, 2H), 4.78 (d, *J* = 16.8 Hz, 1H), 4.21 (d, *J* = 16.4 Hz, 1H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.38-3.33 (m, 3H), 3.08 (d, *J* = 15.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.62, 147.27, 144.49, 144.00, 135.41, 129.97, 128.43, 128.20, 127.61, 127.48, 127.41, 127.21, 124.58, 109.96, 102.89, 95.27, 72.57, 62.15, 61.49, 58.80, 47.30, 21.54; HRMS (ESI): Calc'd for $[C_{25}H_{24}INNaO_3S]$ $[M+Na]^+$ 568.04138, found 568.04132.

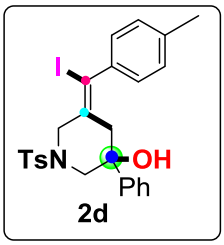


(*Z*)-5-(iodo(m-tolyl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (2c): The title compound was prepared according to the general procedure B to obtain as a yellow solid (39 mg, yield = 70%); Mp. 120.8-122.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 -7.70 (m, 2H), 7.51-7.46 (m, 2H), 7.34 (ddd, *J* = 7.3, 4.4, 1.0 Hz, 4H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.11-7.01 (m, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.77 (d, *J* = 16.4 Hz, 1H), 4.22 (d, *J* = 16.5 Hz, 1H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.36 (dd, *J* = 14.5, 5.0 Hz, 2H), 3.31 (s, 1H), 3.08 (d, J = 15.1 Hz, 1H), 2.44 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (101 MHz,

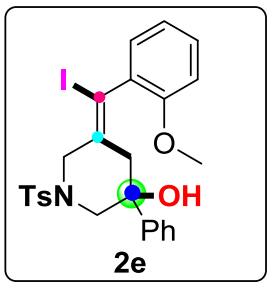


$CDCl_3$) δ 147.63, 147.26, 144.52, 143.96, 137.84, 135.47, 129.96, 128.41, 128.38, 128.11, 128.08, 127.98, 127.59, 127.22, 124.63, 124.49, 95.13, 72.69, 62.10, 61.47, 47.29, 21.55, 21.40; HRMS (ESI): Calc'd for $[C_{26}H_{26}INNaO_3S]$ $[M+Na]^+$ 582.05703, found 582.05719.

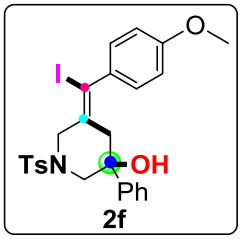
(*Z*)-5-(iodo(p-tolyl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (2d): The title compound was prepared according to the general procedure B to obtain as a yellow solid (36 mg, yield = 65%); Mp. 69.6-71.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.50-7.47 (m, 2H), 7.32 (dd, *J* = 4.8, 3.2 Hz, 3H), 7.28 (s, 1H), 7.11 – 7.07 (m, 3H), 7.04 (dd, *J* = 7.3, 5.4 Hz, 2H), 4.78 (d, *J* = 16.4 Hz, 1H), 4.21 (d, *J* = 16.4 Hz, 1H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.36 (d, *J* = 2.8 Hz, 1H), 3.33 (s, 2H), 3.07 (d, *J* = 15.1 Hz, 1H), 2.43 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.18, 144.75, 144.52, 143.96, 137.18, 129.95, 128.83, 128.42, 128.39, 127.57, 127.40, 127.21, 124.59, 94.97, 72.57, 62.14, 61.49, 47.39, 21.53, 21.20; HRMS (ESI): Calc'd for $[C_{26}H_{26}INNaO_3S]$ $[M+Na]^+$ 582.05703, found 582.05719.



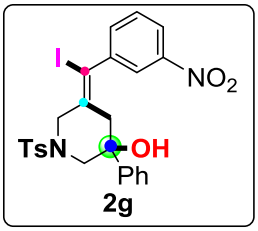
(*Z*)-5-(iodo(2-methoxyphenyl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (2e): The title compound was prepared according to the general procedure B to obtain as a yellow solid (41 mg, yield = 69%); Mp. 175.2-175.8 °C; ^{1}H NMR (400 MHz, CDCl3) δ 7.73-7.70 (m, 2H), 7.52-7.50 (m, 2H), 7.32 (ddd, *J* = 4.5, 1.8, 1.2 Hz, 4H), 7.27- 7.22 (m, 2H), 6.96-6.94 (m, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.78 (d, *J* = 17.6 Hz, 1H), 4.19 (dd, *J* = 17.6, 2.4 Hz, 1H), 4.04 (s, 1H), 3.98 (d, *J* = 13.6 Hz, 1H), 3.80 (s, 3H), 3.57 (d, *J* = 15.6 Hz, 1H), 3.27 (d, *J* = 13.6 Hz, 1H), 2.61 (d, *J* = 16.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 154.07, 146.87, 143.51, 139.95, 137.20, 136.58, 129.89, 129.76, 129.43, 128.99, 128.95, 128.329, 127.320, 127.16, 126.99, 124.47, 121.20, 111.06, 100.78, 75.92, 61.12, 59.68, 55.69, 45.70, 21.51; HRMS (ESI): Calc'd for $[C_{26}H_{26}IN\ NaO_4S]$ $[M+Na]^+$ 598.05194, found 598.05197.



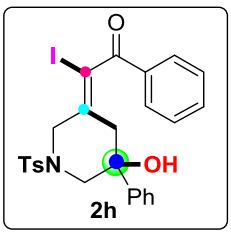
(*Z*)-5-(iodo(4-methoxyphenyl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (2f): The title compound was prepared according to the general procedure B to obtain as a white solid (45 mg, yield = 75%); Mp. 141.5-14.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, *J* = 5.3 Hz, 2H), 7.49 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.29 – 7.13 (m, 3H), 7.12 – 7.08 (m, 2H), 6.83 – 6.78 (m, 2H), 4.78 (d, *J* = 16.4 Hz, 1H), 4.19 (d, *J* = 16.4 Hz, 1H), 3.81 (s, 1H), 3.77 (s, 3H), 3.34 (dd, *J* = 15.2, 12.9 Hz, 3H), 3.07 (d, *J* = 15.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.67, 146.94, 144.51, 143.96, 139.96, 135.36, 129.95, 129.69, 128.96, 128.78, 128.40, 128.18, 127.56, 127.20, 124.58, 123.26, 113.75, 113.36, 94.83, 94.80, 72.36, 62.20, 61.49, 55.16, 47.43, 21.53; HRMS (ESI): Calc'd for $[C_{26}H_{26}INNaO_4S]$ $[M+Na]^+$ 598.05194, found 598.05220.



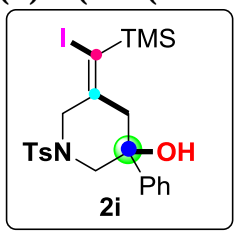
(*Z*)-5-(iodo(3-nitrophenyl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (2g): The title compound was prepared according to the general procedure B to obtain as a yellow solid (30 mg, yield = 48%); Mp. 215.5-216.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (ddd, *J* = 8.1, 2.3, 1.2 Hz, 1H), 7.76 (dd, *J* = 8.8, 2.1 Hz, 3H), 7.49-7.40 (m, 5H), 7.35 (ddd, *J* = 7.0, 3.9, 2.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.43 (dd, *J* = 18.9, 1.1 Hz, 1H), 4.17 (s, 1H), 4.00 (d, *J* = 10.9 Hz, 1H), 3.87 (t, *J* = 8.0 Hz, 2H), 3.55 (d, *J* = 14.9 Hz, 1H), 3.18 (d, *J* = 1.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.35, 142.39, 137.09, 135.58, 129.67, 129.16, 128.69, 128.12, 127.96, 126.24, 125.36, 123.74, 123.16, 84.88, 83.18, 75.83, 54.05, 39.48, 21.41, 20.21; HRMS (ESI): Calc'd for $[C_{25}H_{23}IN_2NaO_5S]$ $[M+Na]^+$ 613.02646, found 613.02627.



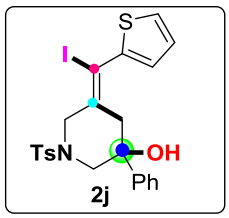
(*Z*)-2-(5-hydroxy-5-phenyl-1-tosylpiperidin-3-ylidene)-2-iodo-1-phenylethan-1-one (2h): The title compound was prepared according to the general procedure B to obtain as a yellow solid (33 mg, yield = 55%); Mp. 102.1-102.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.92 (m, 2H), 7.77-7.75 (m, 2H), 7.60-7.56 (m, 1H), 7.47-7.43 (m, 2H), 7.38-7.36 (m, 4H), 7.31-7.27 (m, 3H), 4.83 (d, *J* = 13.6 Hz, 1H), 3.70 (d, *J* = 12.4 Hz, 1H), 3.37 (d, *J* = 13.7 Hz, 1H), 2.91 (d, *J* = 12.4 Hz, 1H), 2.83 (s, 1H), 2.66 (q, *J* = 14.8 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.04, 144.24, 142.37, 138.42, 134.31, 133.39, 132.86, 130.24, 129.97, 128.82, 128.46, 127.92, 127.83, 124.80, 95.14, 71.70, 56.80, 55.00, 42.81, 21.61; LCMS (ESI): Calc'd for $[C_{26}H_{24}O_4NINaS]$ $[M+Na]^+$ 596.03629, found 596.03627.



(*Z*)-5-(iodo(trimethylsilyl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (2i): The title compound was prepared according to the general procedure B to obtain as a yellow solid (23 mg, yield = 42%); Mp. 85.6-86.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.3, 3.5 Hz, 2H), 7.47 (dd, *J* = 5.5, 3.5 Hz, 2H), 7.38 (ddd, *J* = 14.2, 8.0, 4.8 Hz, 3H), 7.27 (d, *J* = 8.1 Hz, 3H), 4.41 (s, 1H), 4.16 (d, *J* = 18.9 Hz, 1H), 3.91 (t, *J* = 8.1 Hz, 1H), 3.84 – 3.73 (m, 3H), 3.54 (d, *J* = 15.0 Hz, 1H), 3.31 (s, 1H), 2.40 (d, *J* = 3.0 Hz, 3H), -0.03 (s, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.80, 142.32, 135.49, 129.61, 129.45, 128.58, 128.17, 127.98, 127.91, 127.88, 127.39, 125.87, 125.45, 98.00, 91.28, 80.21, 75.32, 53.90, 53.24, 39.74, 39.57, 29.68, 26.26, 21.53, 20.00, 3.91, -0.43; HRMS (ESI): Calc'd for $[C_{22}H_{28}INNaO_3SSi]$ $[M+Na]^+$ 564.04961, found 564.04935.

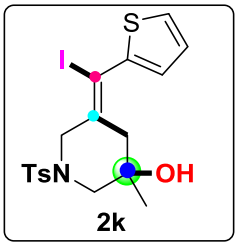


(*Z*)-5-(iodo(thiophen-2-yl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (2j); The title compound was prepared according to the general procedure B to obtain as a yellow solid (46 mg, yield = 83%); Mp. 166.0-166.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.4, 1.6 Hz, 2H), 7.50-7.48 (m, 2H), 7.36-7.27 (m, 5H), 7.22 (dd, *J* = 4.8, 1.2 Hz, 1H), 6.93 (ddd, *J* = 10, 4.8, 1.2 Hz, 2H), 4.83 (d, *J* = 16.4 Hz, 1H), 4.22 (d, *J* = 16.4 Hz, 1H), 3.78 (d, *J* = 14.0 Hz, 1H), 3.36 (d, *J* = 4.8 Hz, 1H), 3.33 (d, *J* = 4.0 Hz, 1H), 3.28 (s, 1H), 3.20 (d, *J* = 14.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.52, 144.30, 144.04, 140.60, 135.34, 130.00, 128.48, 127.66, 127.21, 126.93, 126.44, 125.54, 124.61,



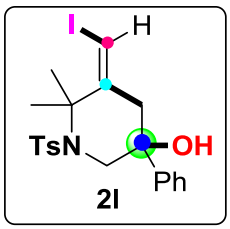
97.41, 72.58, 61.87 (d, *J* = 3.1 Hz), 48.38, 21.55; HRMS (ESI): Calc'd for [$C_{23}H_{22}INNaO_3S_2$] $[M+Na]^+$ 573.4574, found 573.99807.

(*Z*)-5-(iodo(thiophen-2-yl)methylene)-3-methyl-1-tosylpiperidin-3-ol (2k): The title compound was prepared



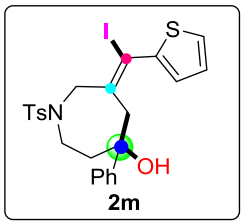
according to the general procedure B to obtain as a yellow solid (35 mg, yield = 79%); Mp. 111.6-118.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.35 (dd, *J* = 8.8, 0.8 Hz, 2H), 7.28 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.00-6.97 (m, 2H), 4.69 (d, *J* = 16.8 Hz, 1H), 4.13 (d, *J* = 16.0 Hz, 1H), 3.53 (dd, *J* = 14.0, 1.2 Hz, 1H), 3.16-3.10 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.93, 144.00, 139.86, 135.27, 130.00, 127.12, 126.60, 126.56, 125.43, 97.57, 71.53, 62.09, 60.03, 47.93, 26.05, 21.56; HRMS (ESI): Calc'd for [$C_{18}H_{20}INNaO_3S_2$] $[M+Na]^+$ 511.98215, found 511.98201.

(*Z*)-5-(iodomethylene)-6,6-dimethyl-3-phenyl-1-tosylpiperidin-3-ol (2l): The title compound was prepared



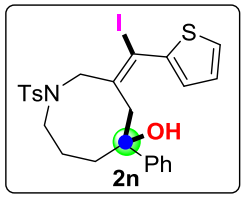
according to the general procedure B to obtain as a yellow solid (xx mg, yield = 75%); Mp. 120.7-121.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.78 (m, 2H), 7.50-7.47 (m, 2H), 7.36-7.32 (m, 2H), 7.31-7.25 (m, 3H), 6.14 (d, *J* = 0.8 Hz, 1H), 3.85 (d, *J* = 15.2 Hz, 1H), 3.55 (d, *J* = 14.8 Hz, 1H), 2.95 (d, *J* = 14.4 Hz, 1H), 2.77 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.72 (s, 1H), 2.41 (s, 3H), 1.82 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.57, 144.61, 143.28, 139.62, 129.62, 128.47, 127.58, 127.31, 124.64, 74.35, 69.55, 66.78, 56.85, 50.84, 24.55, 23.70, 21.48; HRMS (ESI): Calc'd for [$C_{21}H_{25}INO_3S$] $[M+Na]^+$ 498.05943, found 498.05931.

(*Z*)-6-(iodo(thiophen-2-yl)methylene)-4-phenyl-1-tosylazepan-4-ol (2m): The title compound was prepared



according to the general procedure B to obtain as a yellow solid (42 mg, yield = 72%); Mp. 115.2-115.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.40 (dt, *J* = 3.6, 1.6 Hz, 2H), 7.37-7.33 (m, 2H), 7.29 (ddd, *J* = 6.9, 3.7, 1.4 Hz, 1H), 7.21-7.19 (m, 3H), 6.93-6.90 (m, 2H), 4.24 (d, *J* = 4.0 Hz, 2H), 3.63 (q, *J* = 10.4 Hz, 2H), 3.34-3.27 (m, 1H), 2.99-2.89 (m, 1H), 2.65 (s, 1H), 2.45-2.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.56, 141.85, 135.13, 132.31, 129.52, 128.54, 127.62, 127.60, 127.30, 126.76, 125.07, 121.93, 85.88, 80.85, 78.79, 73.97, 43.39, 38.95, 38.23, 24.06, 21.50; HRMS (ESI): Calc'd for [$C_{24}H_{24}INNaO_3S_2$] $[M+Na]^+$ 588.01345, found 588.01323.

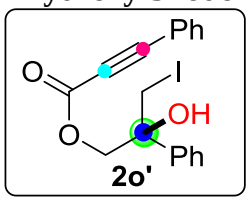
(*Z*)-3-(iodo(thiophen-2-yl)methylene)-5-phenyl-1-tosylazocan-5-ol (2n): The title compound was prepared



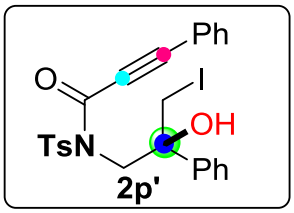
according to the general procedure B to obtain as a yellow solid (35 mg, yield = 67%); Mp. 88.0-88.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.29 (dd, *J* = 8.8, 4.0 Hz, 1H), 7.24 (d, *J* = 8 Hz, 3H), 7.18 (dd, *J* = 4.4, 1.6 Hz, 1H), 6.90-6.87 (m, 2H), 4.27 (d, *J* = 18.8 Hz, 1H), 4.07 (d, *J* = 18.8 Hz, 1H), 3.67 (s, 2H), 3.23-3.09 (m, 2H), 2.38 (s, 1H), 2.35 (s, 3H), 2.12-1.98 (m, 2H), 1.71-1.63 (m, 2H), 1.35-1.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.49, 142.84, 135.52, 132.19, 129.52, 128.44, 127.62, 127.40, 127.21, 126.72, 125.05, 121.94,

85.53, 78.76, 74.82, 46.12, 37.41, 36.76, 24.68, 22.27, 21.52; HRMS (ESI): Calc'd for [$C_{25}H_{26}INNaO_3S_2$] [M+Na]$^+$ 602.02910, found 602.02888.

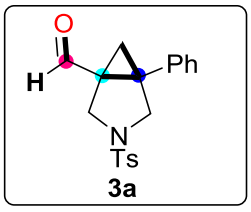
2-hydroxy-3-iodo-2-phenylpropyl 3-phenylpropiolate (2o'): The title compound was prepared according to the general procedure B to obtain as a yellow solid (21 mg, yield = 52%); Mp. 111.6-118.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.46 (dt, *J* = 8.4, 1.6 Hz, 3H), 7.45 (dt, *J* = 6.4, 1.6 Hz, 1H), 7.41-7.39 (m, 2H), 7.38-7.35 (m, 2H), 4.58 (s, 2H), 3.79 (d, *J* = 10.8 Hz, 1H), 3.68 (d, *J* = 10.8 Hz, 1H), 2.80 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.51, 140.46, 133.04, 130.87, 128.61, 128.57, 128.30, 125.35, 119.21, 87.77, 79.96, 74.02, 69.80, 16.72; LCSM (ESI): Calc'd for [$C_{18}H_{15}O_3INa$] [M+Na]$^+$ 428.9958, found 428.9955.



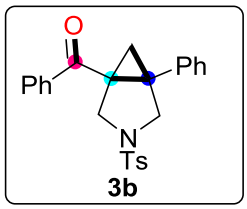
N-(2-hydroxy-3-iodo-2-phenylpropyl)-3-phenyl-N-tosylpropiolamide (2p'): The title compound was prepared according to the general procedure B to obtain as a yellow solid (32 mg, yield = 58%); Mp. 128.9-129.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.42- 7.30 (m, 7H), 7.27 (d, *J* = 8 Hz 2H), 4.79 (t, *J* = 6.6 Hz, 1H), 4.48 (q, *J* = 12 Hz, 2H), 3.44 (dd, *J* = 13.2, 8.0 Hz, 1H), 3.28-3.23 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.72, 143.73, 139.77, 136.24, 133.06, 130.92, 129.80, 128.75, 128.59, 128.22, 127.05, 125.37, 119.15, 87.91, 79.87, 74.69, 70.02, 49.99, 21.51; LCSM (ESI): Calc'd for [$C_{19}H_{18}O_4NINaS$] [M+Na]$^+$ 505.98934, found 505.98932.



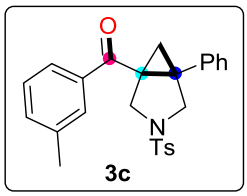
5-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexane-1-carbaldehyde (3a): The title compound was prepared according to the general procedure C to obtain as a colorless liquid (16 mg, yield = 45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.77-7.75 (m, 2H), 7.63-7.59 (m, 1H), 7.50-7.47 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.81 (s, 2H), 4.28 (d, *J* = 2.4 Hz, 2H), 2.44 (s, 3H), 2.11 (t, *J* = 2.8 Hz, 1H), 0.90-0.83 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.24, 143.81, 136.01, 134.74, 133.86, 129.62, 128.82, 128.01, 127.62, 74.38, 51.45, 37.31, 21.58, 0.02; LCSM (ESI): Calc'd for [$C_{19}H_{18}O_4NINaS$] [M+Na]$^+$ 505.98934, found 505.98932; LCSM (ESI): Calc'd for [$C_{19}H_{19}O_3NS$] [M+H]$^+$ 341.1080, found 341.3049.



phenyl-5-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methanone (3b): The title compound was prepared according to the general procedure C to obtain as a white solid (20 mg, yield = 48%); Mp. 162.2-175.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.43-7.36 (m, 3H), 7.30-7.27 (m, 3H), 7.25 (d, *J* = 6.6 Hz, 1H), 7.19-7.16 (m, 3H), 7.11-7.08 (m, 2H), 3.92-3.87 (m, 3H), 3.58 (d, *J* = 10.0 Hz, 1H), 2.49 (s, 3H), 2.25 (d, *J* = 5.6 Hz, 1H), 1.63 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.87, 143.98, 137.58, 134.80, 133.17, 131.91, 129.88, 128.47, 128.42, 128.20, 127.73, 127.70, 127.58, 55.15, 52.82, 43.43, 42.89, 21.61, 19.73; HRMS (ESI): Calc'd for [$C_{25}H_{23}NO_3NaS$] [M+Na]$^+$ 440.52300, found 440.52310.

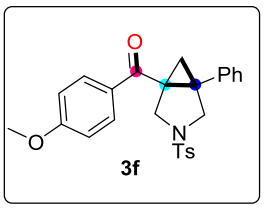


((1)-5-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)(m-tolyl)methanone (3c): The title compound was prepared according to the general procedure C to obtain as a colorless gumy (16 mg, yield = 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.39-7.36 (m, 2H), 7.2-7.15 (m, 4H), 7.14-7.12 (m, 1H), 7.10-7.08 (m, 3H), 7.06-7.05 (m, 1H), 3.90-3.85 (m, 3H), 3.58 (d, *J* = 10.0 Hz, 1H), 2.48 (s, 3H), 2.26 (s, 3H), 2.23 (s, 1H), 1.63 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.03, 143.94, 138.12, 137.61, 134.89, 133.19, 132.64, 129.87, 128.43, 128.38, 128.25, 127.95, 127.62, 127.59, 124.84, 55.08, 52.82, 43.24, 42.98, 21.59, 21.21, 19.65; HRMS (ESI): Calc'd for $[C_{26}H_{25}NNaO_3S]$ $[M+Na]^+$ 454.14474, found 454.14468.



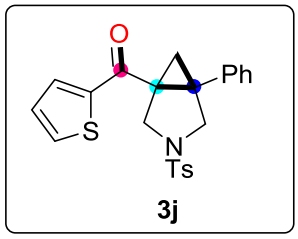
3c

(4-methoxyphenyl)((1)-5-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methanone (3f): The title compound was prepared according to the general procedure C to obtain as a colorless gumy (19 mg, yield = 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 2H), 7.44-7.42 (m, 3H), 7.39-7.36 (m, 2H), 7.20-7.14 (m, 3H), 7.10-7.08 (m, 2H), 6.78-6.74 (m, 2H), 3.88 (d, J = 10.0 Hz, 1H), 3.86 (s, 3H), 3.64 (d, *J* = 10.0 Hz, 1H), 2.49 (s, 3H), 2.14 (d, *J* = 5.6 Hz, 1H), 1.50 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.49, 162.90, 143.94, 135.21, 133.22, 130.58, 129.88, 128.41, 128.09, 127.60, 127.48, 113.53, 55.41, 55.01, 53.58, 42.50, 41.82, 21.61, 19.60; HRMS (ESI): Calc'd for $[C_{26}H_{25}NNaO_4S]$ $[M+Na]^+$ 470.13965, found 470.13947.



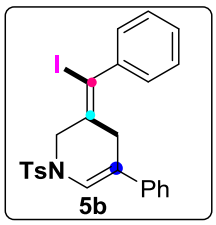
3f

((1)-5-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)(thiophen-2-yl)methanone (3j): The title compound was prepared according to the general procedure C to obtain as a white solid (18 mg, yield = 42%); Mp. 182.2-183.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.72 (m, 2H), 7.51 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.40-7.36 (m, 3H), 7.22-7.14 (m, 3H), 7.13-7.10 (m, 2H), 6.98 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.97 (q, *J* = 9.5 Hz, 2H), 3.88 (d, *J* = 9.6 Hz, 1H), 3.50 (d, *J* = 10.0 Hz, 1H), 2.48 (s, 3H), 2.20 (d, *J* = 5.2 Hz, 1H), 1.70 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.12, 144.03, 143.13, 134.99, 133.54, 133.06, 132.26, 129.90, 128.67, 128.45, 127.74, 127.65, 127.62, 55.42, 53.07, 42.42, 42.33, 21.60, 20.25; HRMS (ESI): Calc'd for $[C_{24}H_{21}NO_4NaS_2]$ $[M+Na]^+$ 451.09120, found 451.09121.



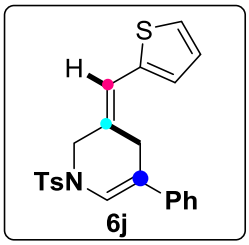
3j

(*Z*)-3-(iodo(phenyl)methylene)-5-phenyl-1-tosyl-1,2,3,4-tetrahydropyridine (5b): The title compound was prepared according to the general procedure D to obtain as a colorless liquid (28 mg, yield = 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.67 (m, 2H), 7.40-7.28 (m, 8H), 7.19 (dd, *J* = 8.6, 0.7 Hz, 2H), 7.07-6.99 (m, 2H), 6.23 (d, *J* = 2.1 Hz, 1H), 4.65 (s, 2H), 4.42 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.20, 144.52, 143.41, 140.14, 139.70, 136.19, 129.46, 129.30, 128.66, 128.33, 128.27, 128.12, 128.02, 127.61, 126.28, 95.91, 59.92, 49.34, 21.50; HRMS (ESI): Calc'd for $[C_{25}H_{22}INNaO_2S]$ $[M+Na]^+$ 550.03081, found 550.03099.



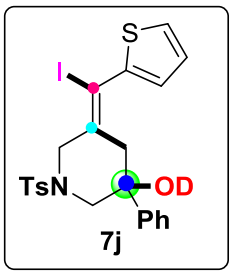
5b

(*E*)-5-phenyl-3-(thiophen-2-ylmethylene)-1-tosyl-1,2,3,4-tetrahydropyridine (6j): The title compound was



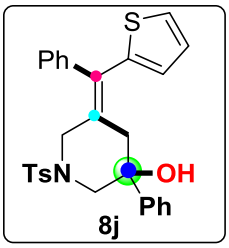
prepared according to the general procedure E to obtain as a yellow solid (32 mg, yield = 85%); Mp. 165.9-167.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.23-7.13 (m, 6H), 7.02 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.97 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.80-6.77 (m, 2H), 6.38 (dt, *J* = 4.4, 1.6 Hz, 1H), 6.12 (d, *J* = 4.4 Hz, 1H), 3.71 (d, *J* = 11.6 Hz, 1H), 3.46 (dd, *J* = 11.6, 1.2 Hz, 1H), 2.88-2.76 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.90, 142.48, 141.82, 134.30, 130.32, 129.62, 128.32, 128.12, 127.45, 127.38, 125.14, 123.51, 123.32, 120.02, 86.04, 81.87, 57.14, 40.84, 21.50; HRMS (ESI): Calc'd for $[C_{23}H_{21}NO_2NaS_2]$ $[M+Na]^+$ 430.54600, found 430.54610.

(Z)-5-(iodo(thiophen-2-yl)methylene)-3-phenyl-1-tosylpiperidin-3-ol (7j): The title compound was prepared



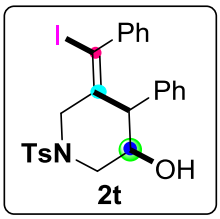
according to the general procedure F to obtain as a white solid (45 mg, yield = 81%); Mp. 183.2-184.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$+D_2O) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.50-7.48 (m, 2H), 7.36-7.27 (m, 5H), 7.22 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.96-6.91 (m, 2H), 4.82 (d, *J* = 16.8 Hz, 1H), 4.22 (d, *J* = 16.8 Hz, 1H), 3.78 (d, *J* = 14.0 Hz, 1H), 3.36-3.32 (m, 2H), 3.20 (d, *J* = 14.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$+D_2O) δ 148.53, 144.27, 144.05, 140.59, 135.34, 130.00, 128.48, 127.66, 127.21, 126.93, 126.44, 125.54, 124.62, 97.41, 72.52, 61.89, 61.80, 48.36, 21.54; HRMS (ESI): Calc'd for $[C_{23}H_{21}DINO_3NaS_2]$ $[M+Na]^+$ 575.46357, found 575.46358.

(*E*)-3-phenyl-5-(phenyl(thiophen-2-yl)methylene)-1-tosylpiperidin-3-ol (8j): The title compound was



prepared according to the general procedure G to obtain as a yellow solid (45 mg, yield = 90%); Mp. 227.5-228.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.56 (m, 4H), 7.38-7.34 (m, 2H), 7.31-7.22 (m, 8H), 6.99 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.68 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.56 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.64 (d, *J* = 15.6 Hz, 1H), 3.93 (d, *J* = 15.6 Hz, 1H), 3.86 (d, *J* = 13.6 Hz, 1H), 3.48 (d, *J* = 14.6 Hz, 1H), 3.35 (s, 1H), 3.28 (d, *J* = 13.2 Hz, 2H), 2.39 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.52, 144.83, 143.75, 141.36, 137.55, 135.04, 130.85, 129.85, 129.16, 128.49, 128.40, 127.49, 127.36, 127.21, 126.21, 125.70, 124.68, 71.99, 62.59, 54.89, 48.27, 21.50; HRMS (ESI): Calc'd for $[C_{29}H_{27}NNaO_3S_2]$ $[M+Na]^+$ 524.13246, found 524.13224.

(Z)-3-phenyl-5-(phenyl(thiophen-2-yl)methylene)-1-tosylpiperidin-3-ol (2t): The title compound was



prepared according to the general procedure B to obtain as a yellow solid (37 mg, yield = 68%); Mp. 155.8-156.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32-7.20 (m, 6H), 7.17 (dd, *J* = 6.7, 5.2 Hz, 2H), 7.01 (dd, *J* = 7.6, 2.4 Hz, 2H), 4.75 (t, *J* = 10 Hz, 1H), 4.34 (d, *J* = 16.4 Hz, 1H), 3.85 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.68 (dd, *J* = 16.4, 2.0 Hz, 1H), 2.90 (d, *J* = 6.3 Hz, 2H), 2.90-2.89 (m, 1H), 2.75 (dd, *J* = 12.4, 4.4 Hz, 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.35, 143.83, 142.82, 141.64, 132.07, 129.91, 128.33, 128.31, 128.08, 127.96, 127.79, 127.40, 125.86, 102.89, 94.48, 56.44, 49.35, 43.42, 21.57; HRMS (ESI): Calc'd for $[C_{25}H_{24}O_3NINaS]$ $[M+Na]^+$ 568.0414, found 568.0412.

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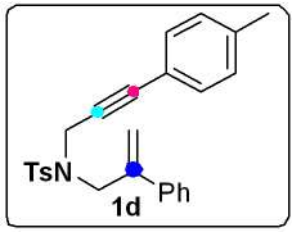
2. B. Liu, J. Cheng, Y. Li and J.-H. Li, *Chem. Commun*., 2019, **55**, 667-670.

3. (a) Y.-Q. Wang, Y.-T. He, L.-L. Zhang, X.-X. Wu, X.-Y. Liu and Y.-M. Liang, *Org. Lett*., 2015, **17**, 4280-4283; (b) X. Cao, X. Cheng and J. Xuan, *Org. Lett*., 2018, 20, 449-452; (c) S.-H. Kim-Lee, I. Alonso, P. Mauleon, R. G. Arrayas and J. C. Carretero, *ACS Catal*., 2018, 8, 8993-9005; (c) M. M. Hansmann, R. L. Melen, M. Rudolph, F. Rominger, H. Wadepohl, D. W. Stephan and A. S. K. Hashmi, *J. Am. Chem. Soc*., 2015, 137, 15469-15477.

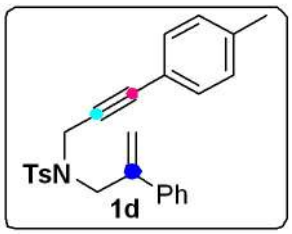
Solvent $CDCl_3$

Spectrometer Frequency 400.40



Solvent $CDCl_3$

Spectrometer Frequency 100.69



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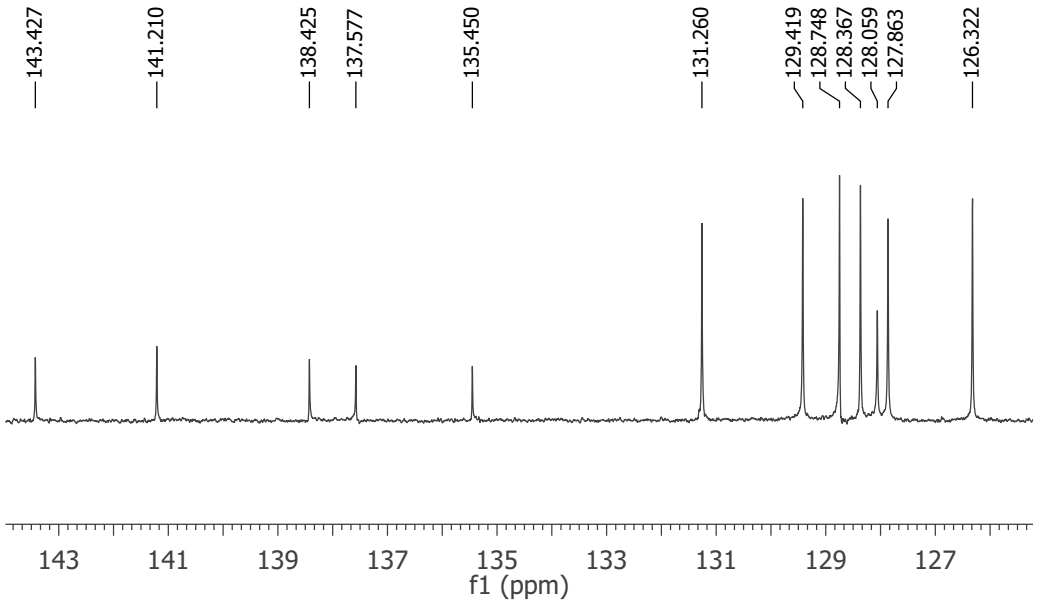

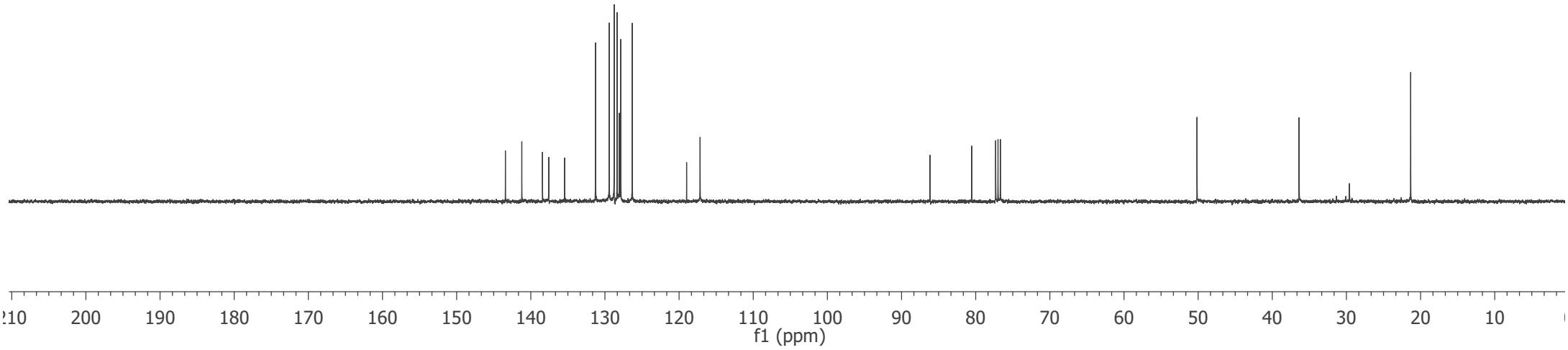

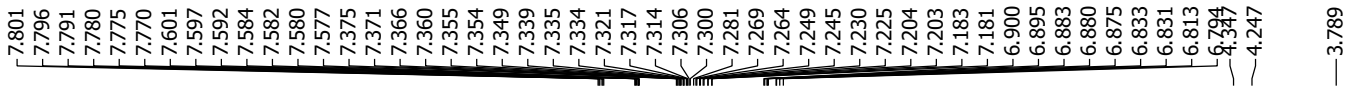

Solvent $CDCl_3$

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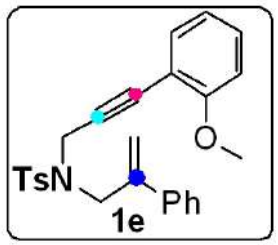
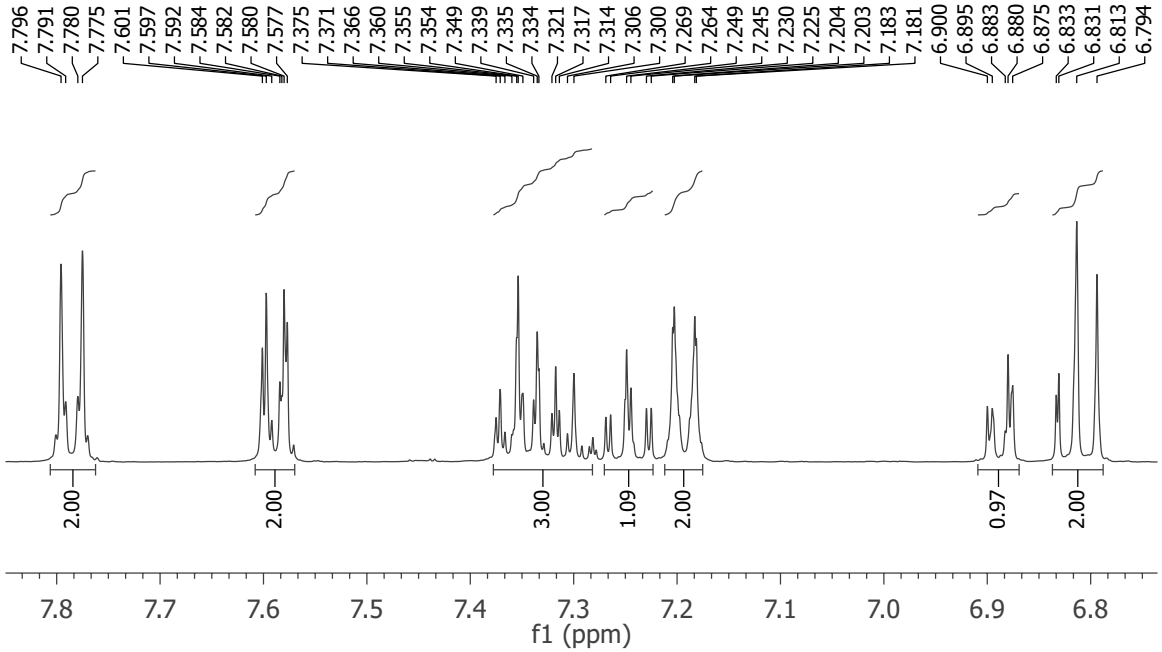
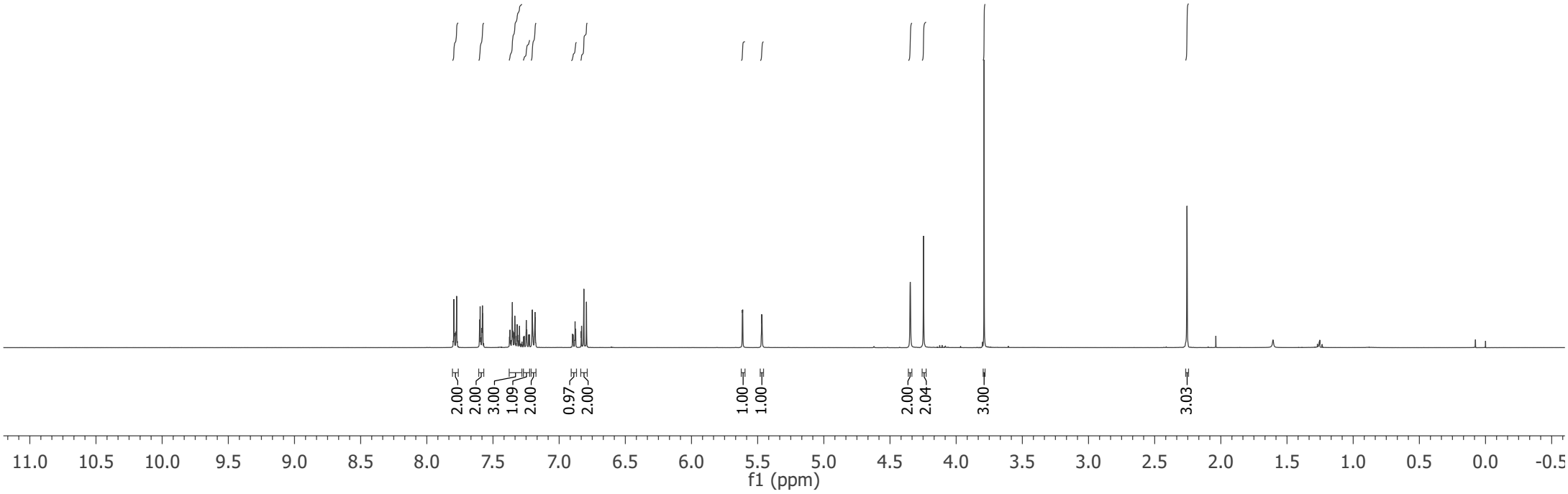
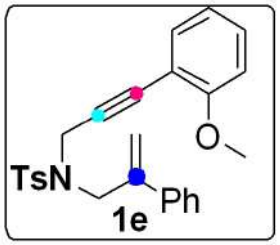






Solvent $CDCl_3$

Spectrometer Frequency 100.69



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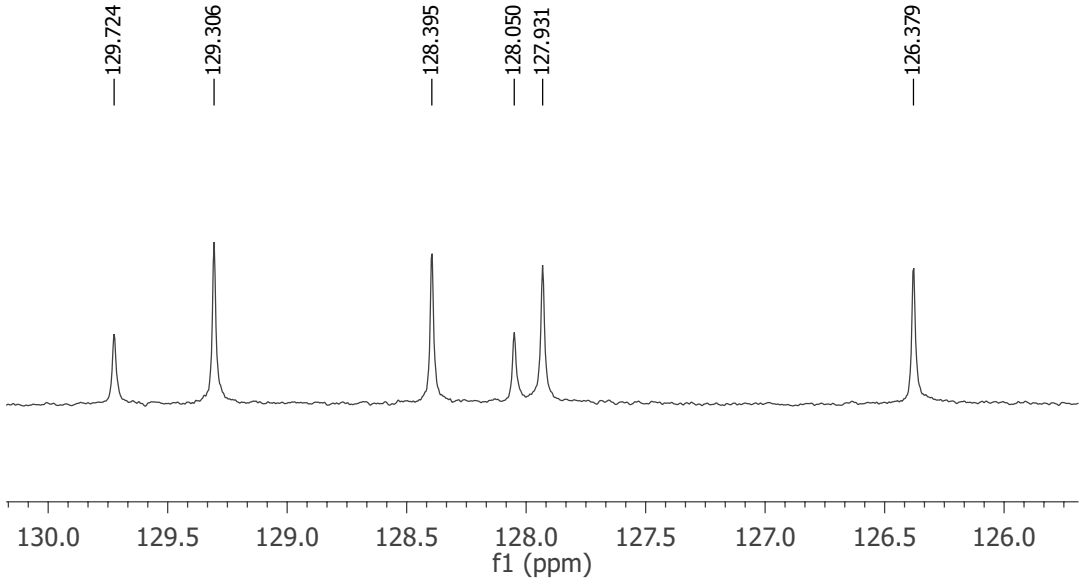
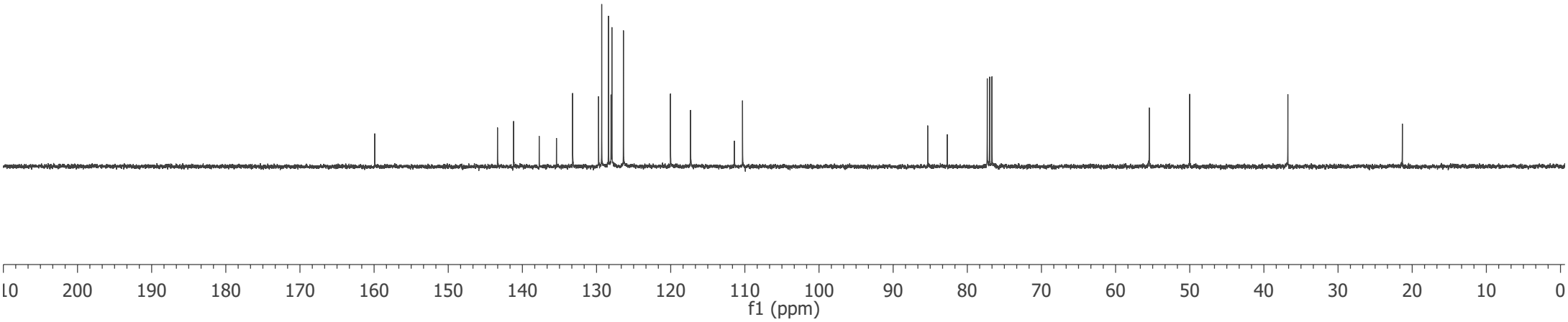
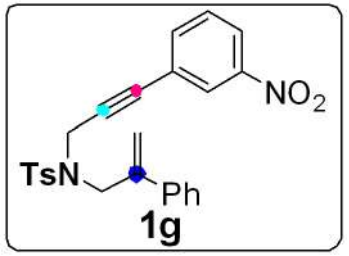
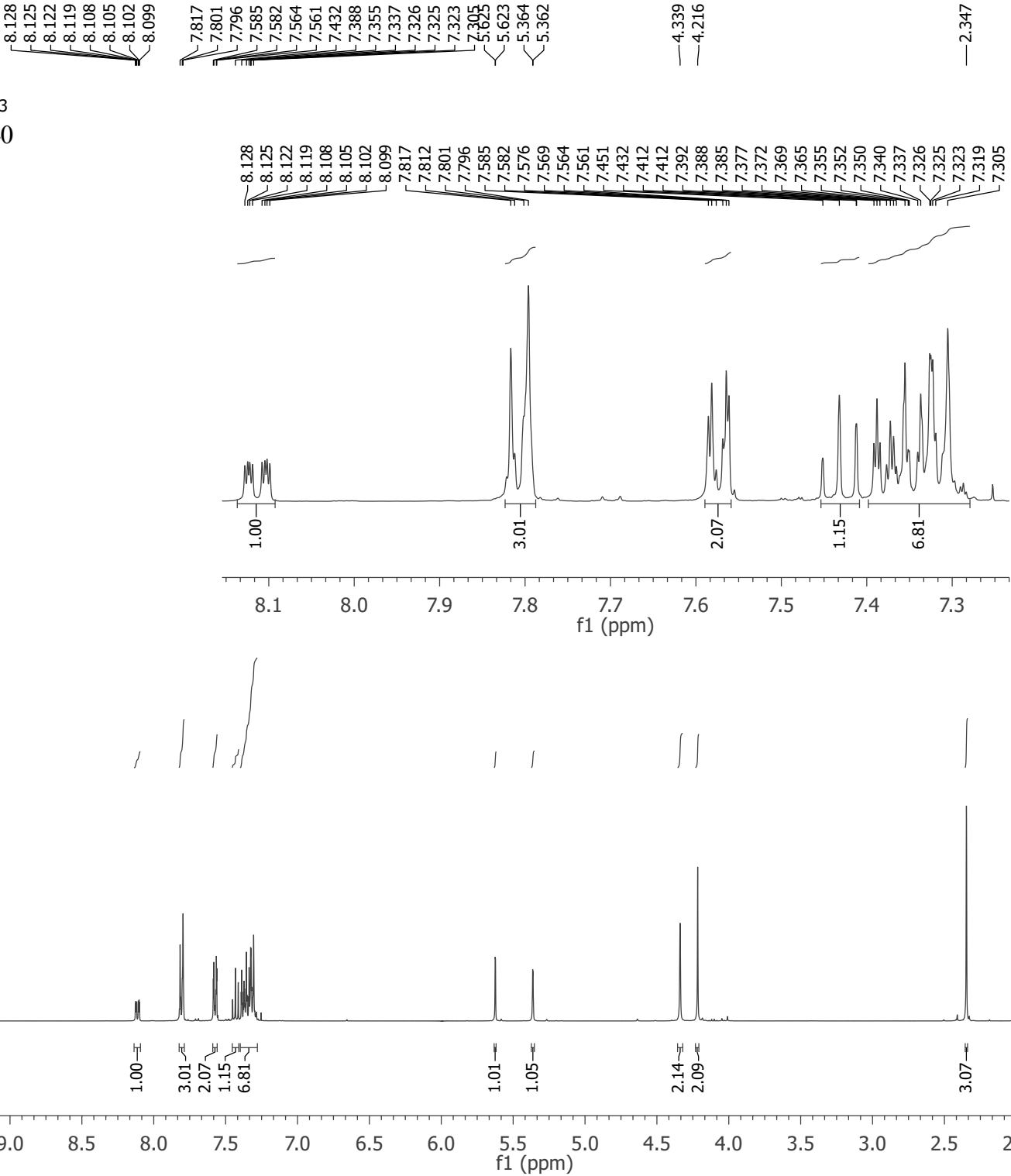




Solvent $CDCl_3$

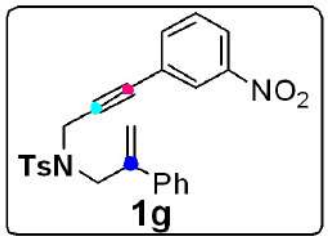
Spectrometer Frequency 400.40



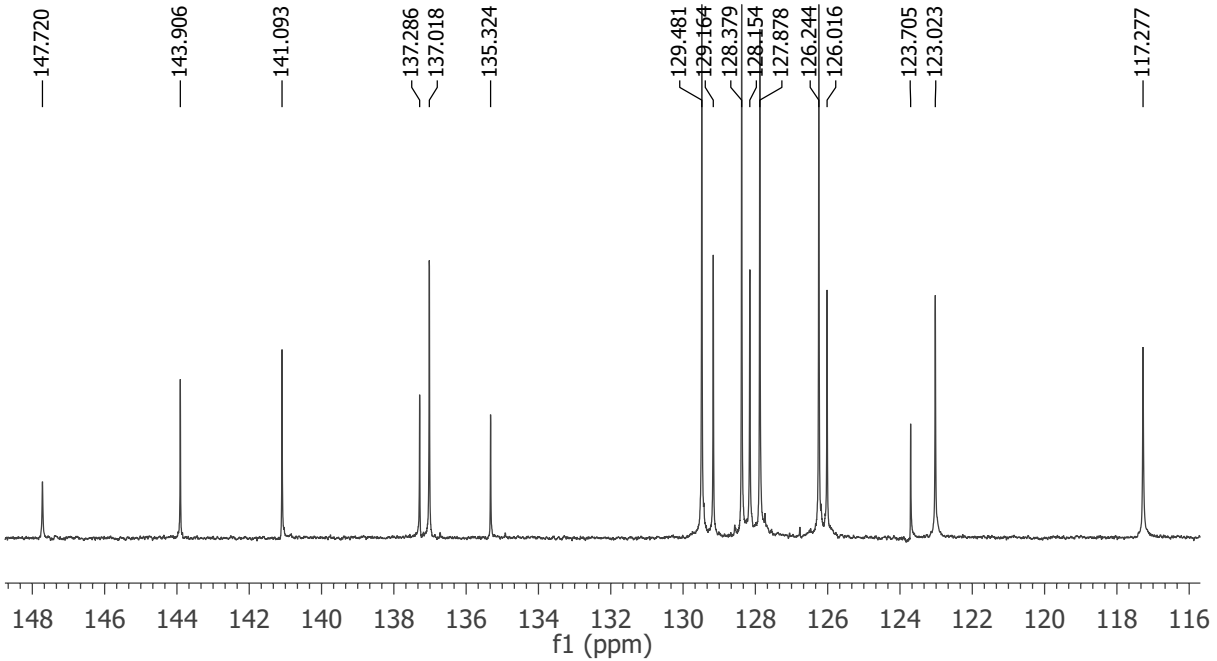


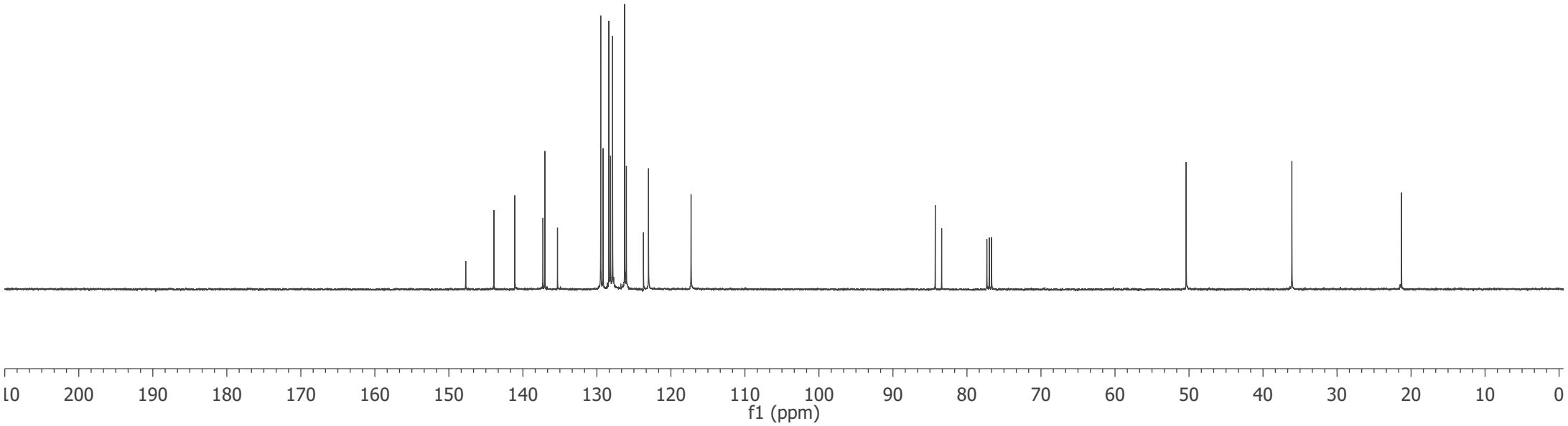
Solvent $CDCl_3$

Spectrometer Frequency 100.69



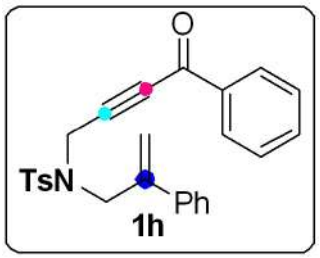
147.720 143.906 141.093 137.286 137.018 135.324 129.481 129.164 128.379 128.154 127.878 126.244 126.016 123.705 123.023 117.277 84.287 83.421 50.383 36.098 21.281

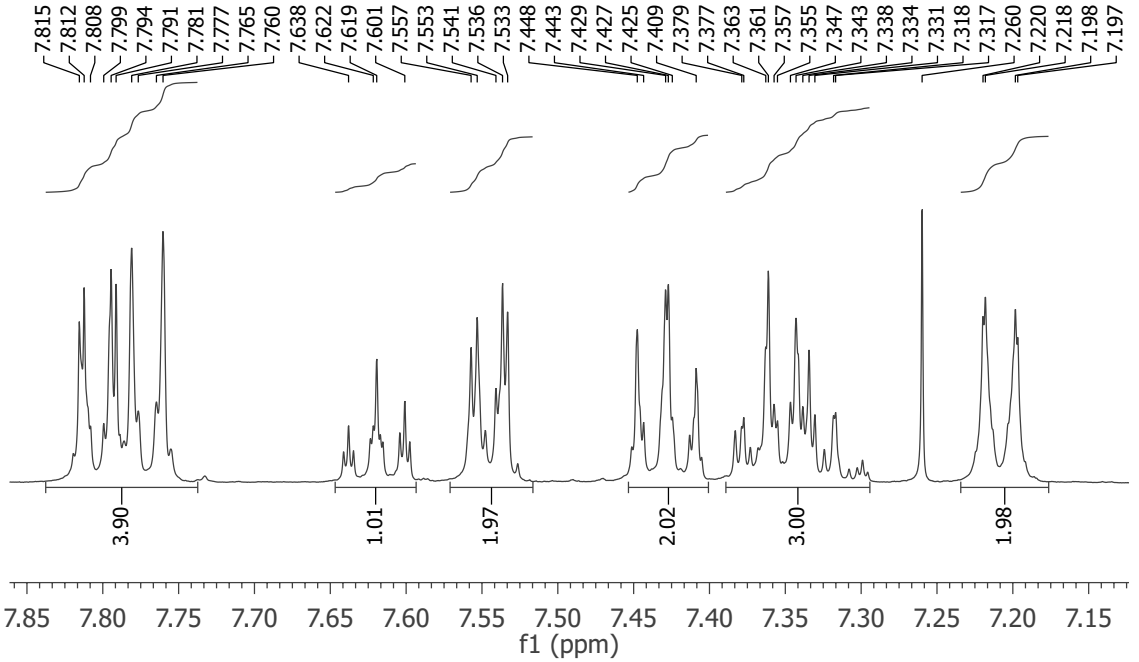


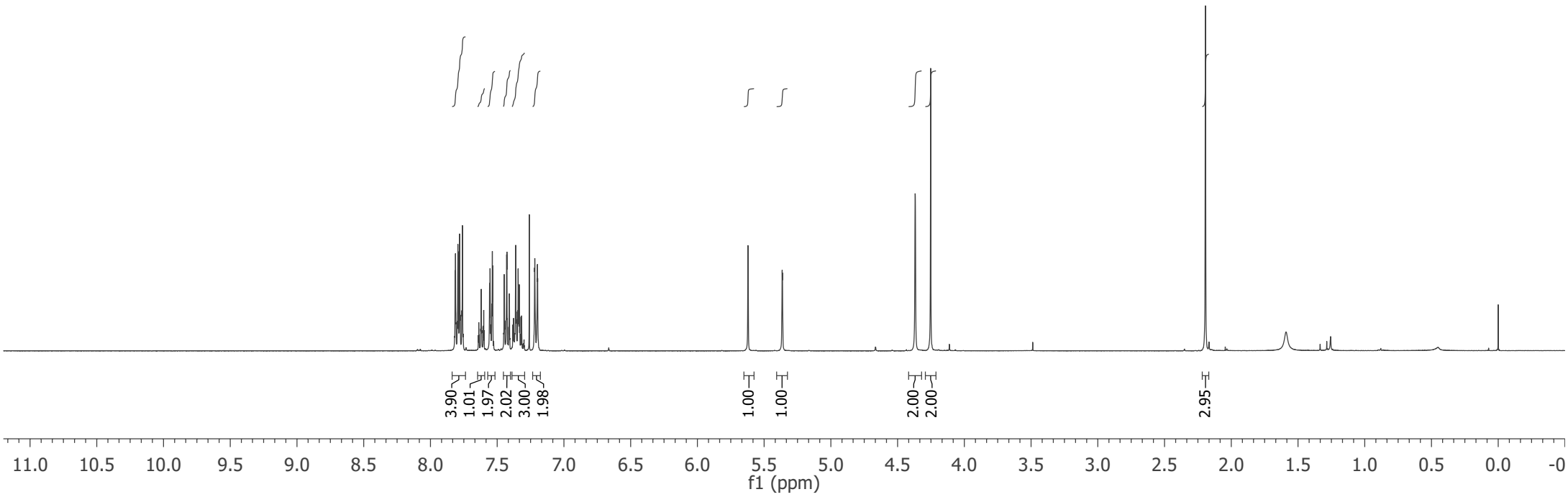


Solvent $CDCl_3$

Spectrometer Frequency 400.40







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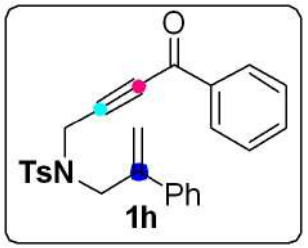
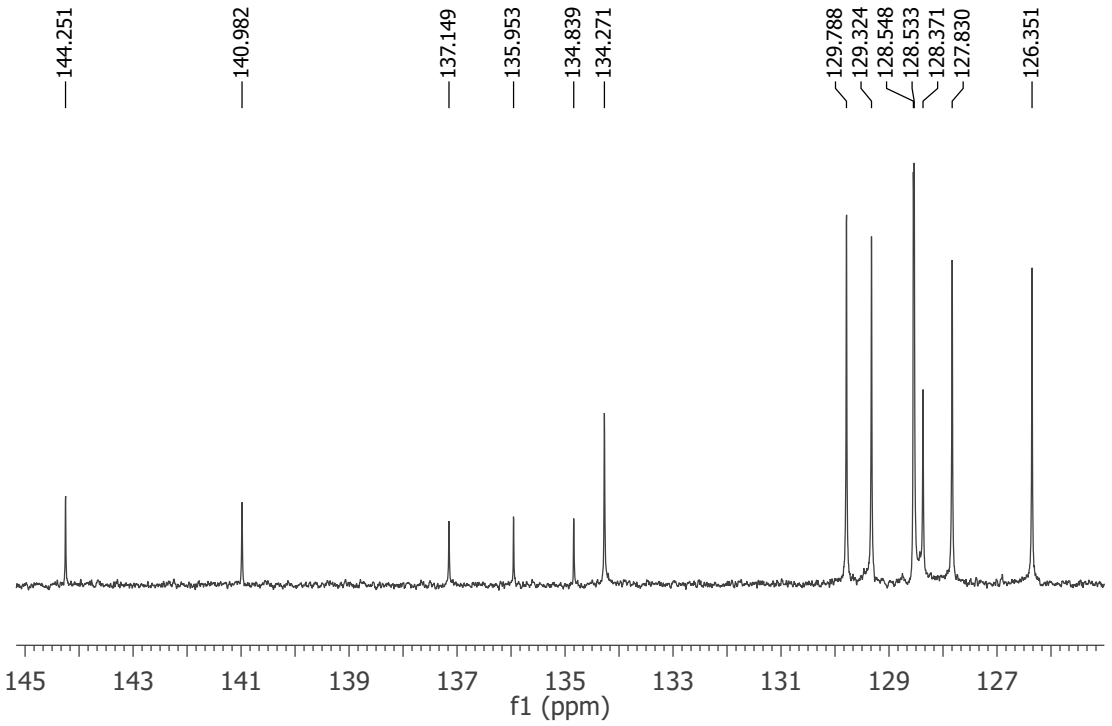
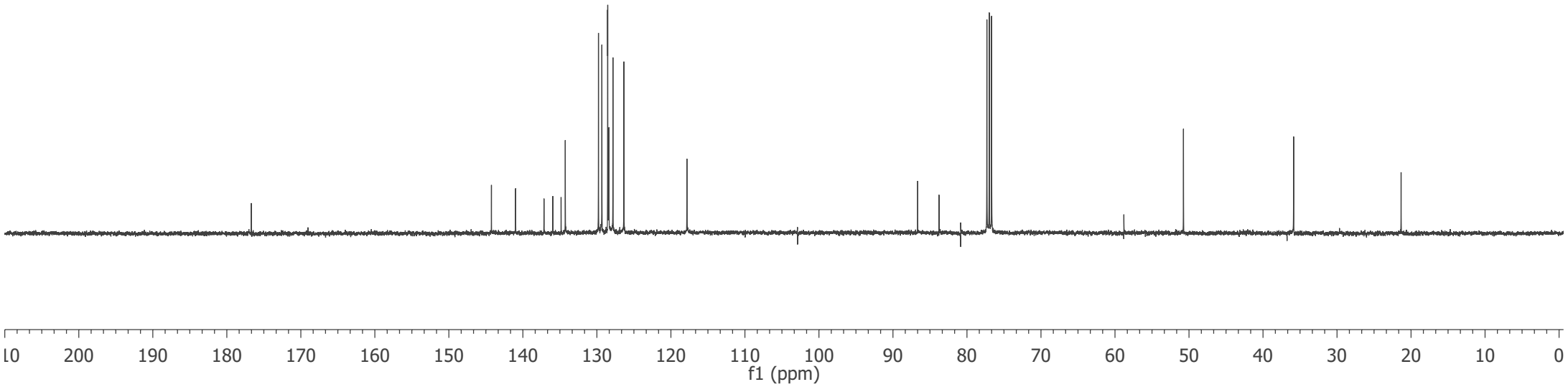
21.345

Solvent $CDCl_3$

Spectrometer Frequency 100.69

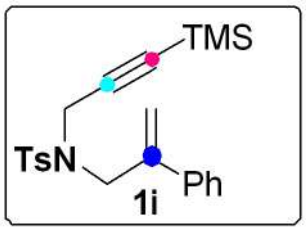






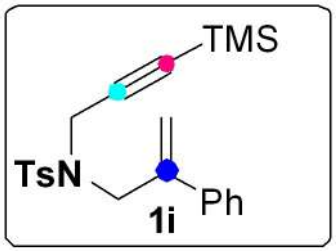
Solvent $CDCl_3$

Spectrometer Frequency 400.40



Solvent $CDCl_3$

Spectrometer Frequency 100.69



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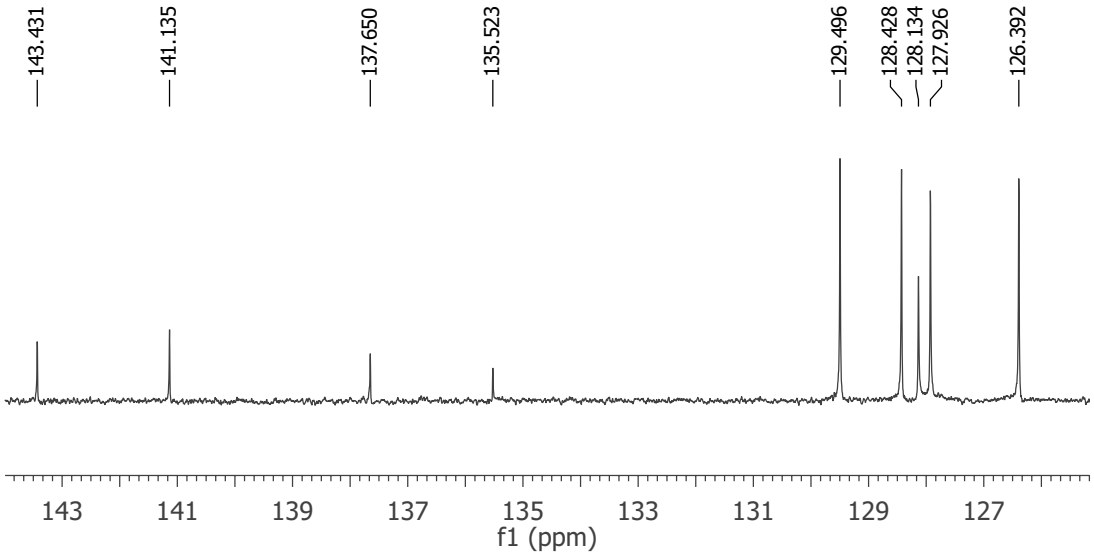
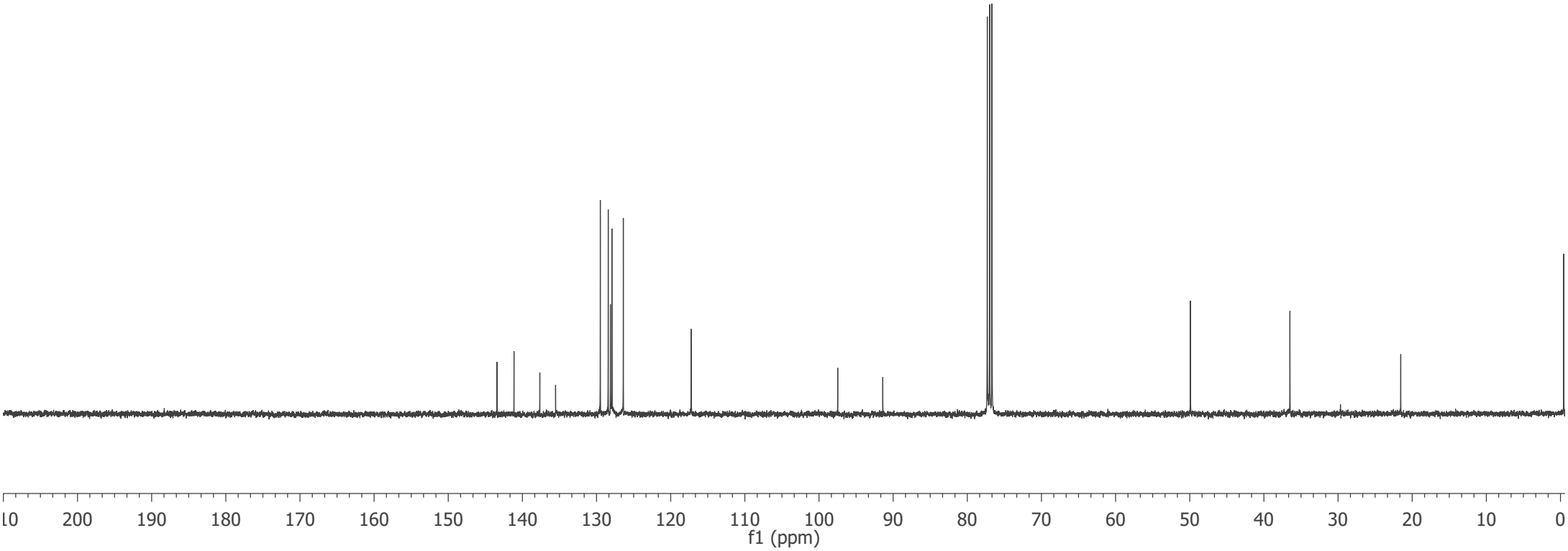
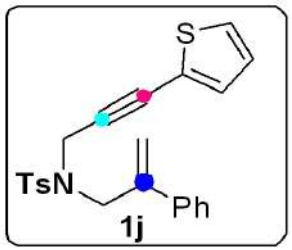
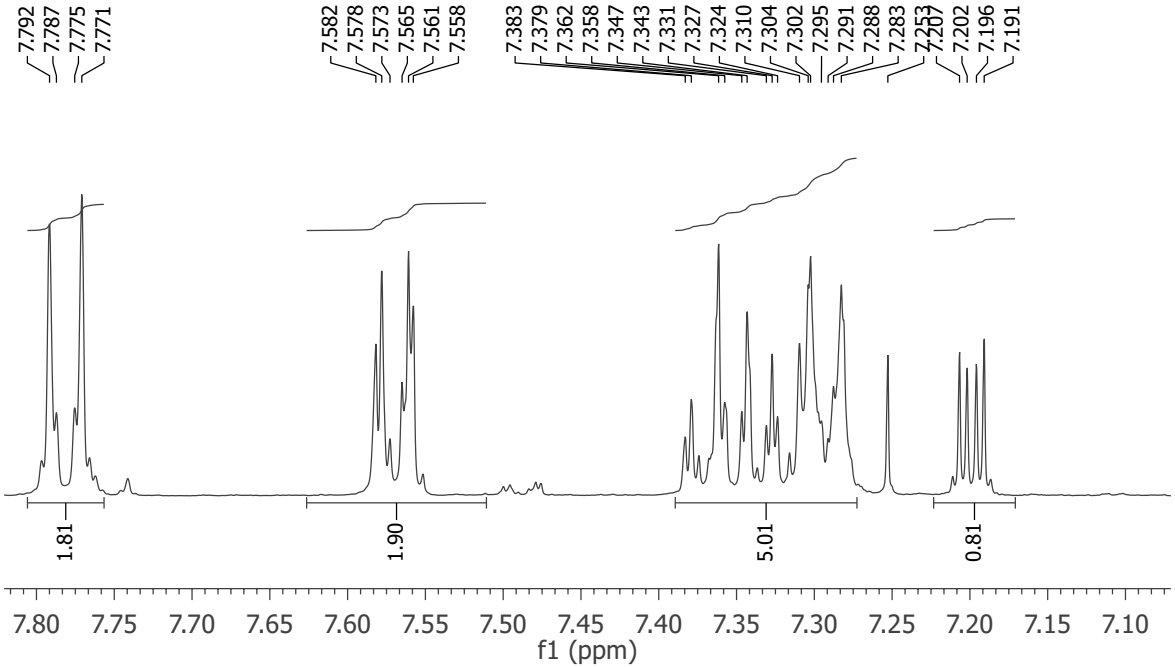


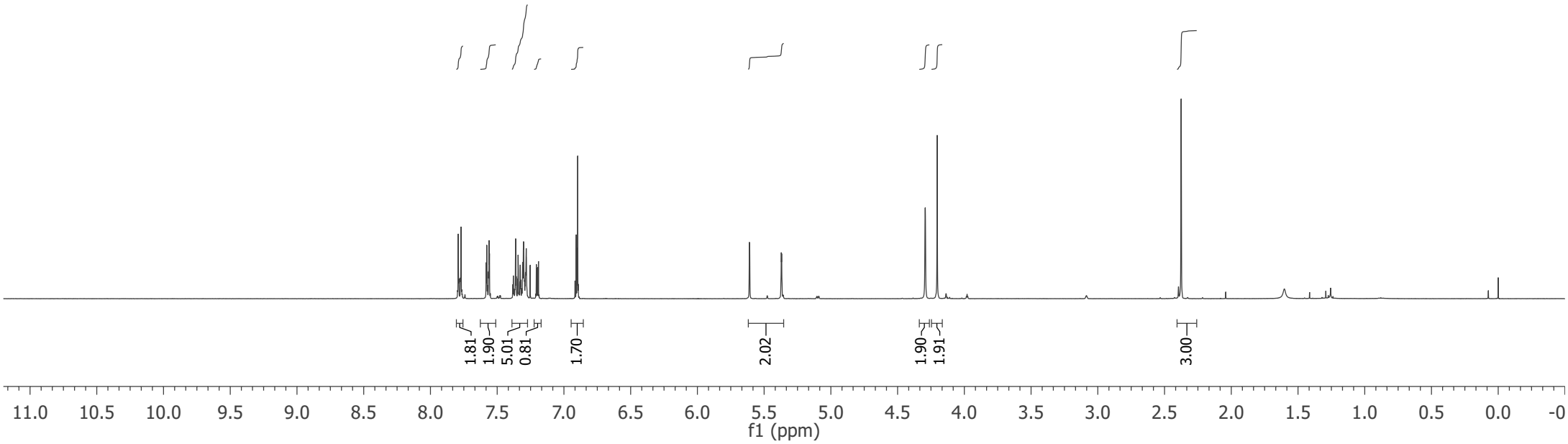


Solvent $CDCl_3$

Spectrometer Frequency 400.40

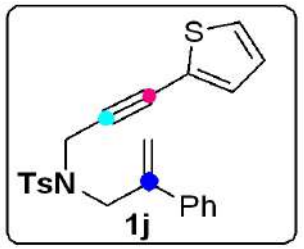






Solvent $CDCl_3$

Spectrometer Frequency 100.69



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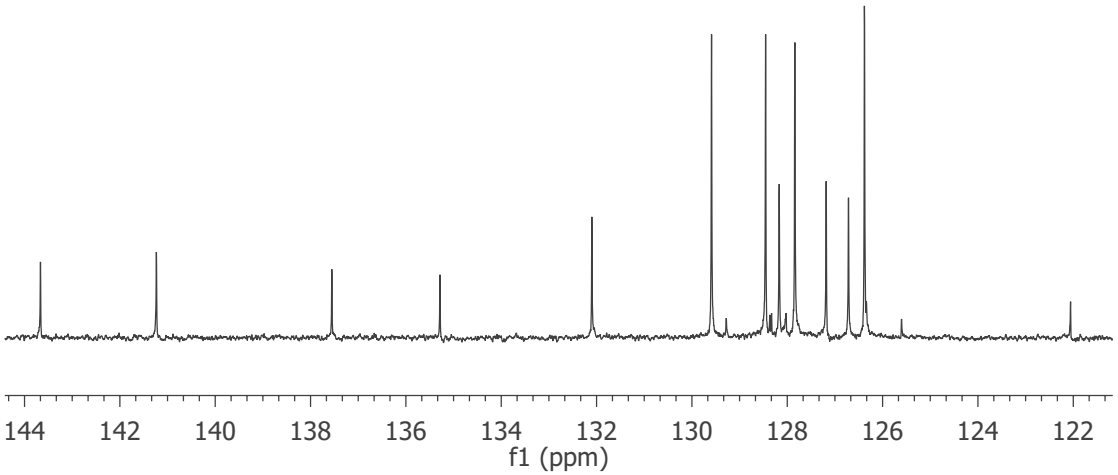
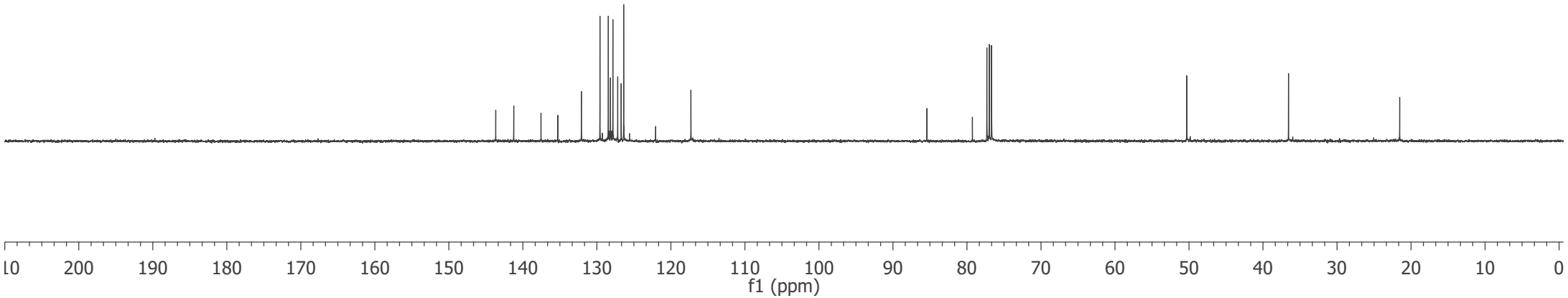
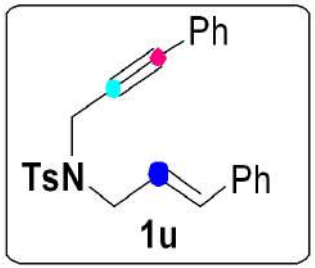




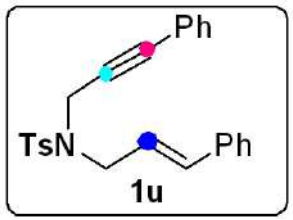
Solvent $CDCl_3$

Spectrometer Frequency 400.40



Solvent $CDCl_3$

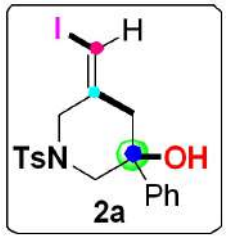
Spectrometer Frequency 100.69



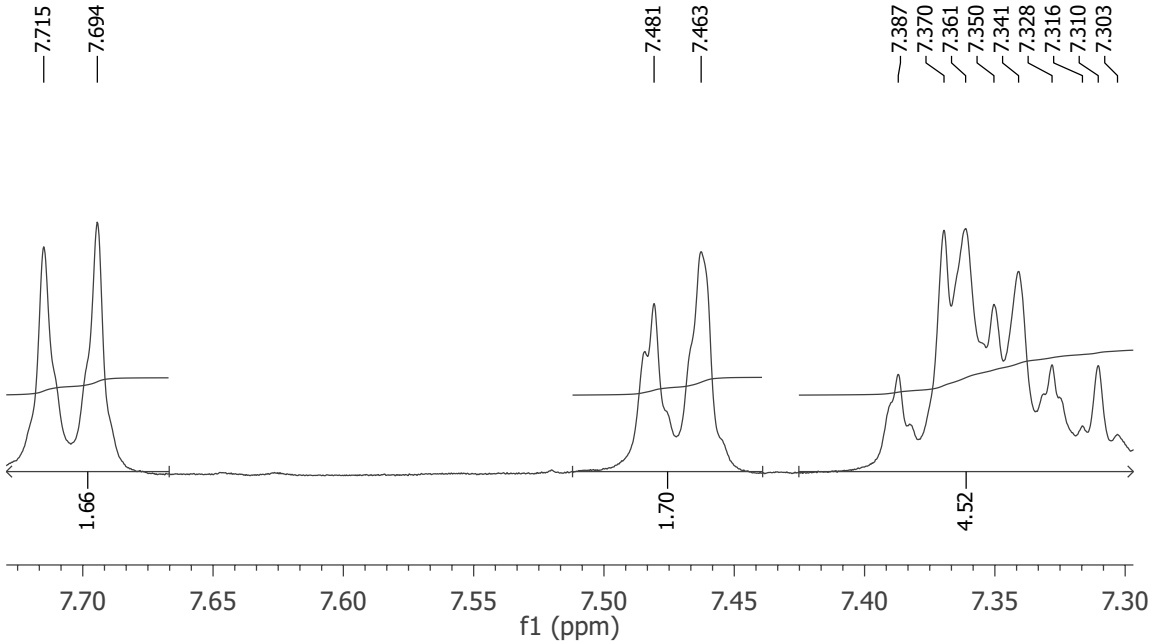
1u

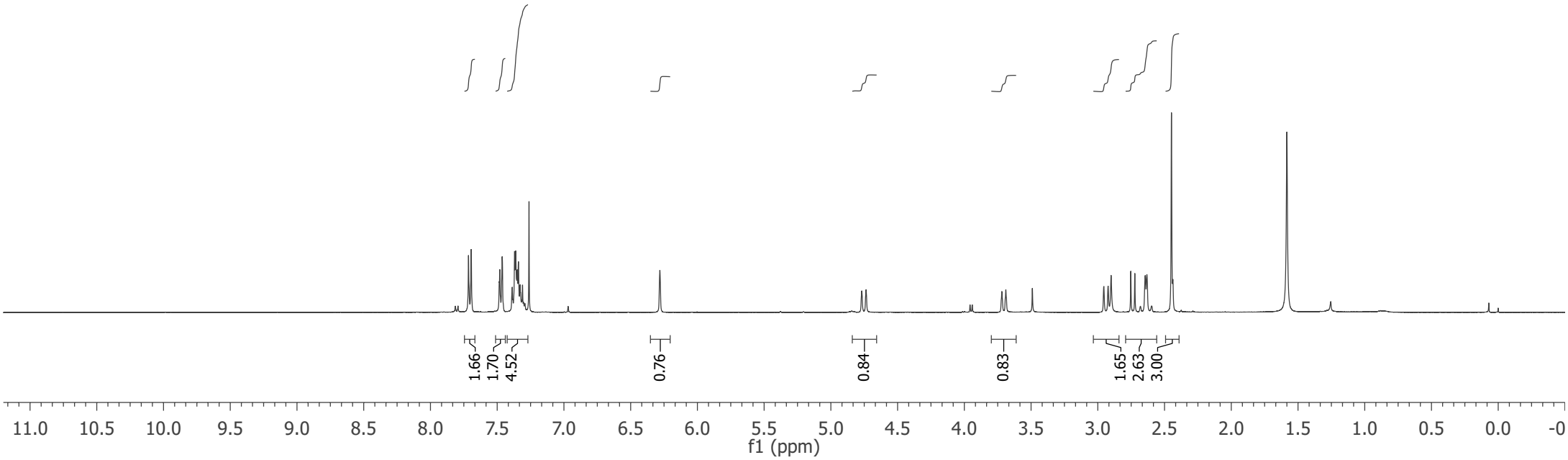
Solvent $CDCl_3$

Spectrometer Frequency 400.40



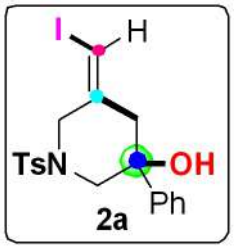
7.715 7.694 7.481 7.463 7.387 7.370 7.361 7.350 7.341 7.328 7.316 7.310 7.303 6.281 4.768 4.736 3.719 3.689 2.955 2.923 2.900 2.753 2.723 2.681 2.645 2.632 2.597 2.448





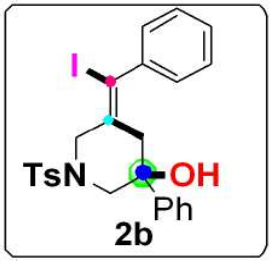
Solvent $CDCl_3$

Spectrometer Frequency 100.69



Solvent $CDCl_3$

Spectrometer Frequency 400.40



Solvent $CDCl_3$

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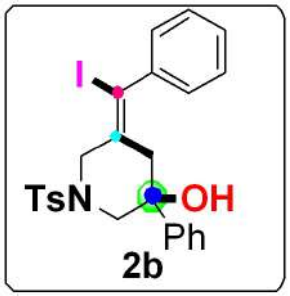

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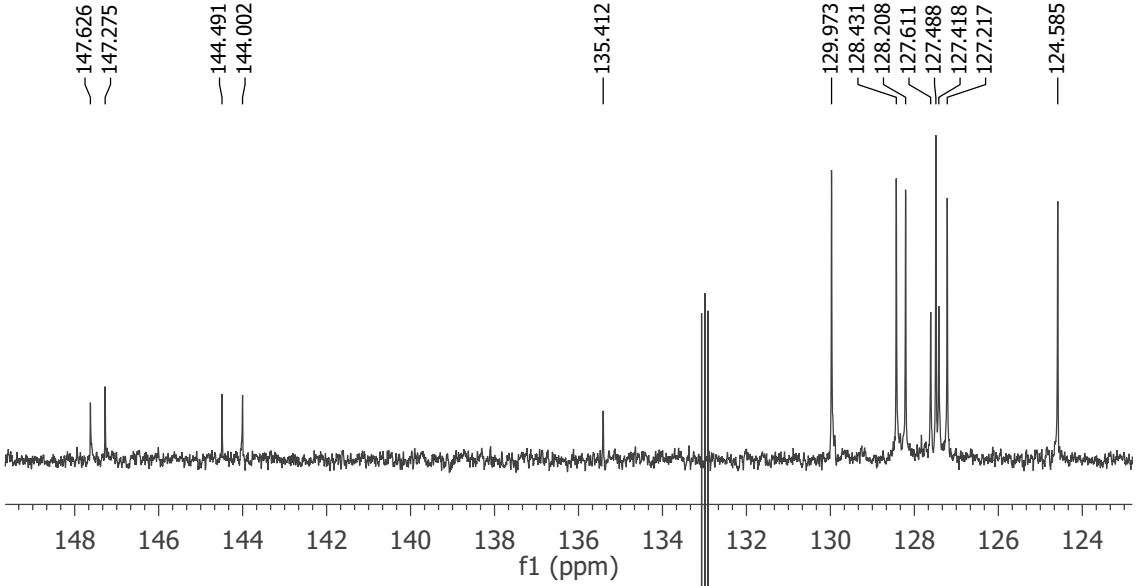
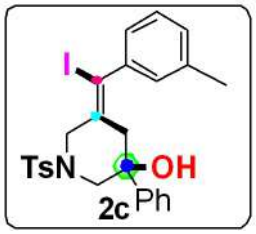
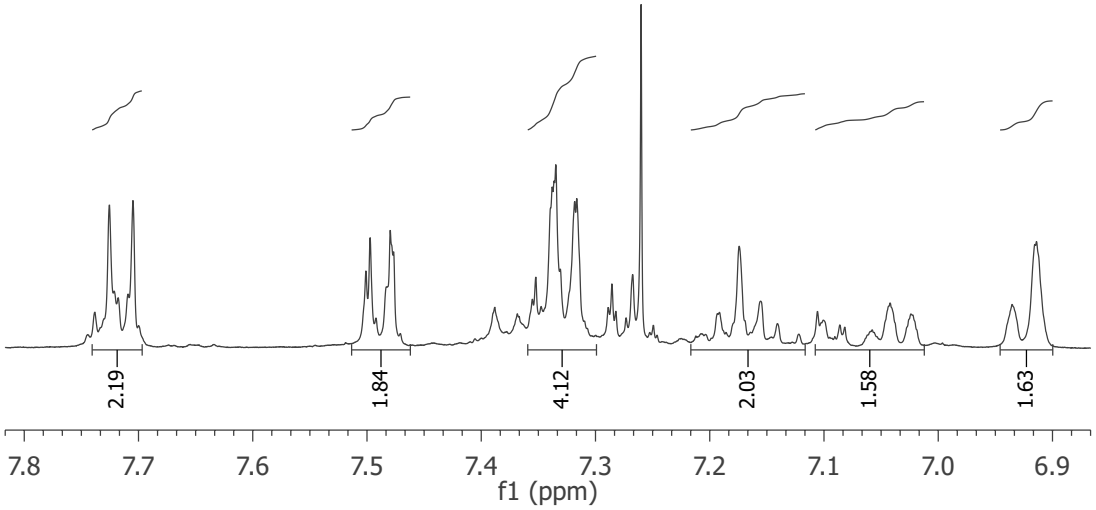
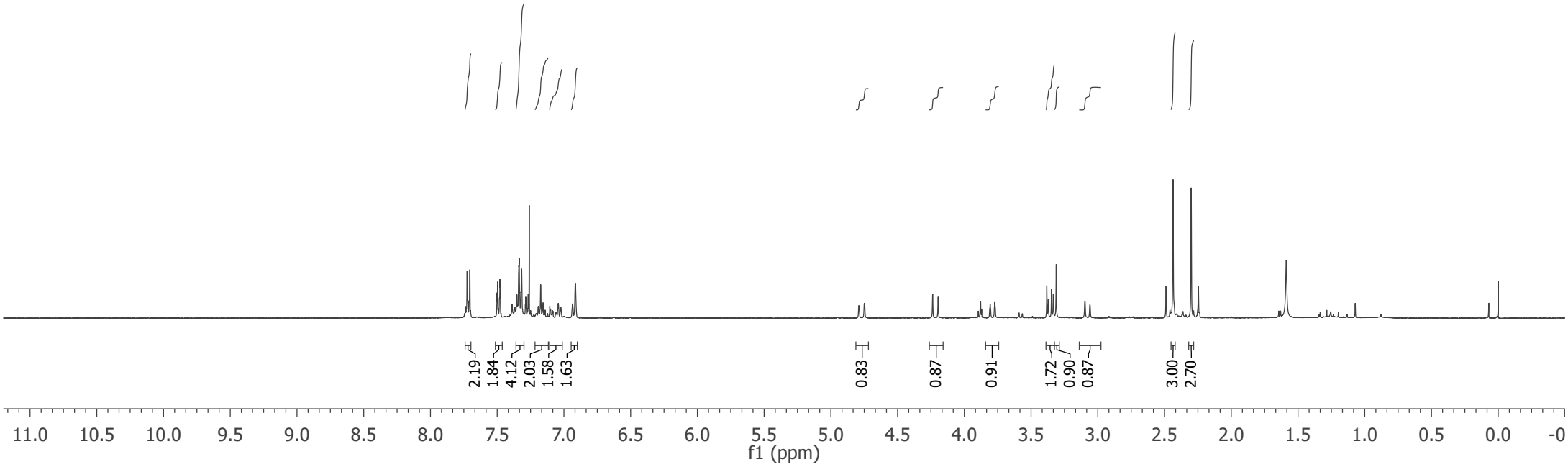


Solvent $CDCl_3$

Spectrometer Frequency 400.40

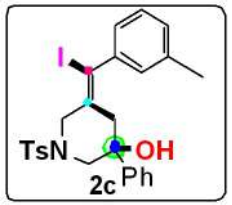






Solvent $CDCl_3$

Spectrometer Frequency 100.69



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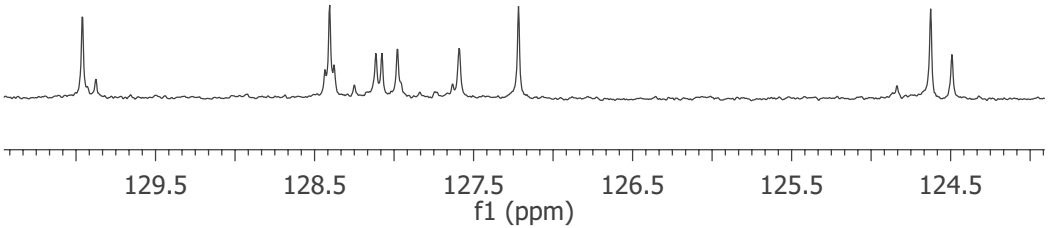
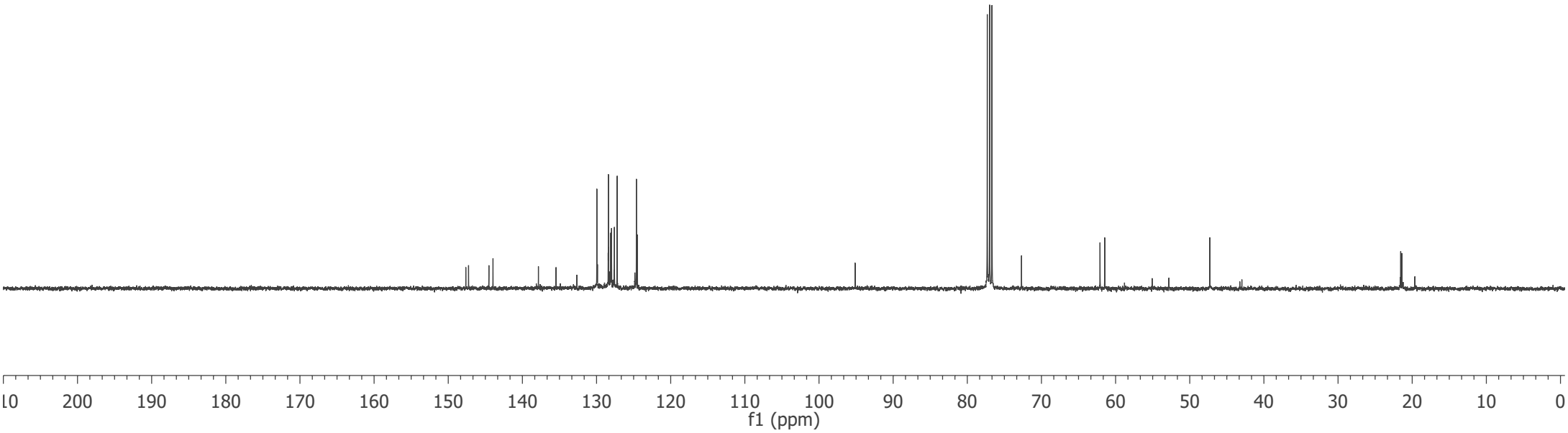
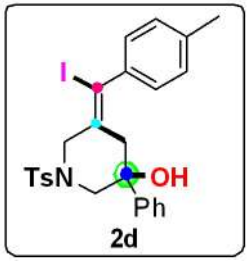
129.960, 128.405, 128.378, 128.114, 128.077, 127.979, 127.590, 127.217, 124.626, 124.492





Solvent $CDCl_3$

Spectrometer Frequency 400.40



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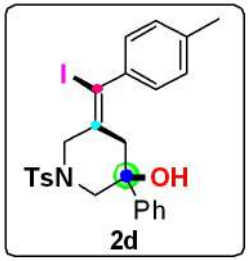
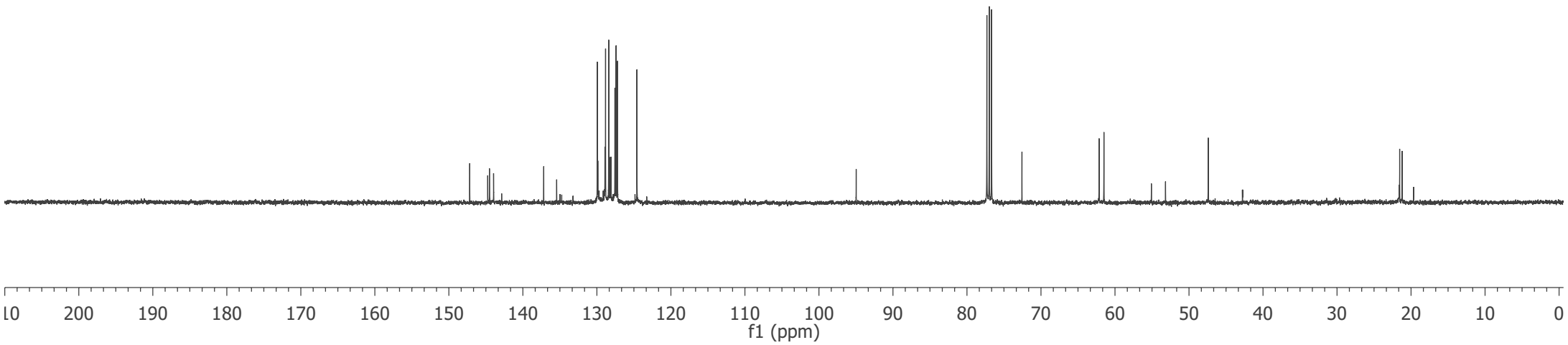
Solvent $CDCl_3$

Spectrometer Frequency 100.69

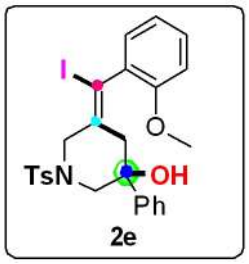


2d



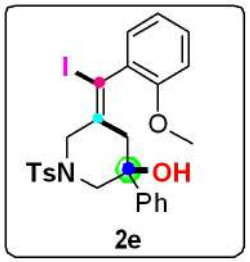
Solvent $CDCl_3$

Spectrometer Frequency 400.40



Solvent $CDCl_3$

Spectrometer Frequency 100.69



2e

154.077
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128.947
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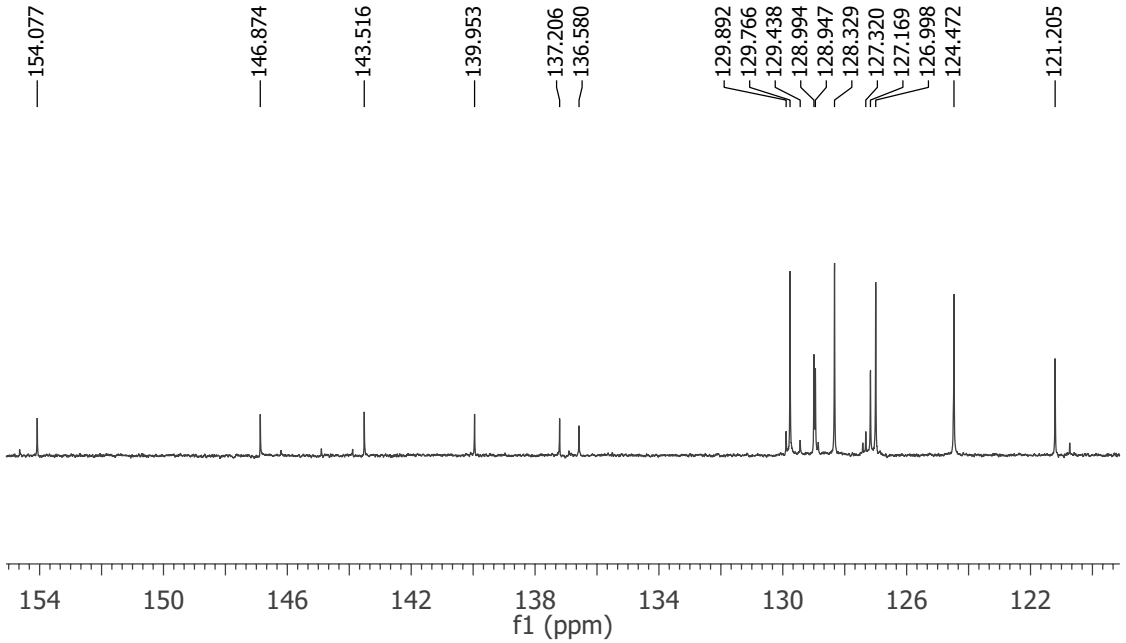
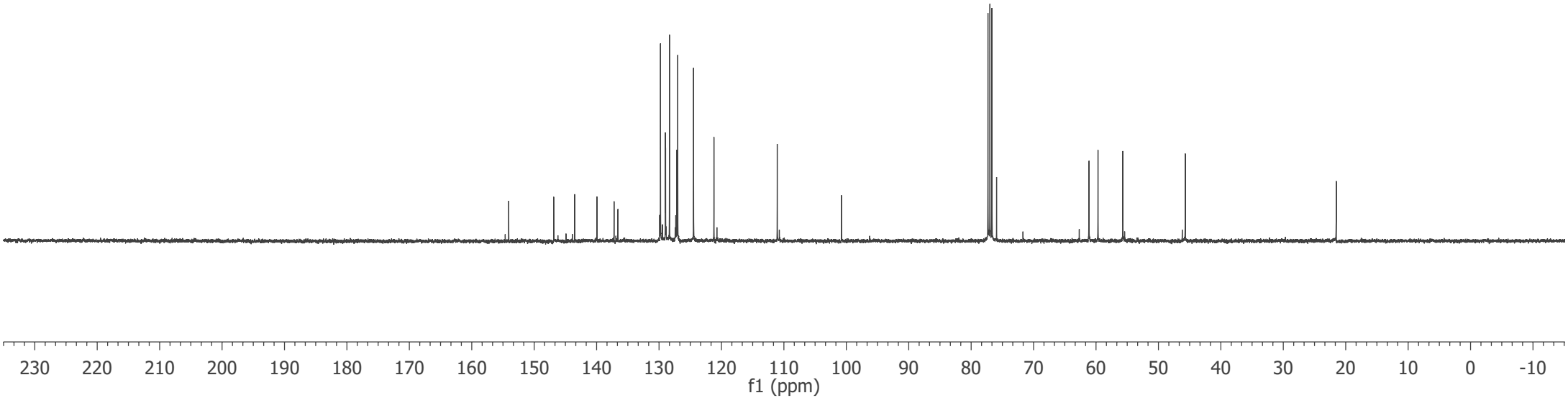
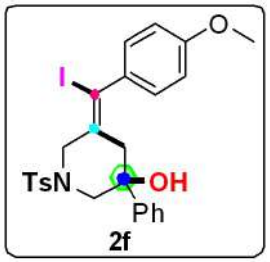
21.513





Solvent $CDCl_3$

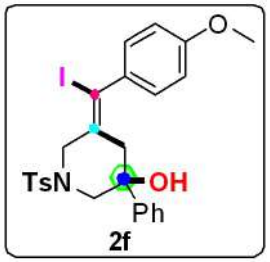
Spectrometer Frequency 400.40



2f

Solvent $CDCl_3$

Spectrometer Frequency 100.69



2f

158.667
146.937
144.512
143.958
139.962
135.364
129.948
128.962
128.783
128.404
127.565
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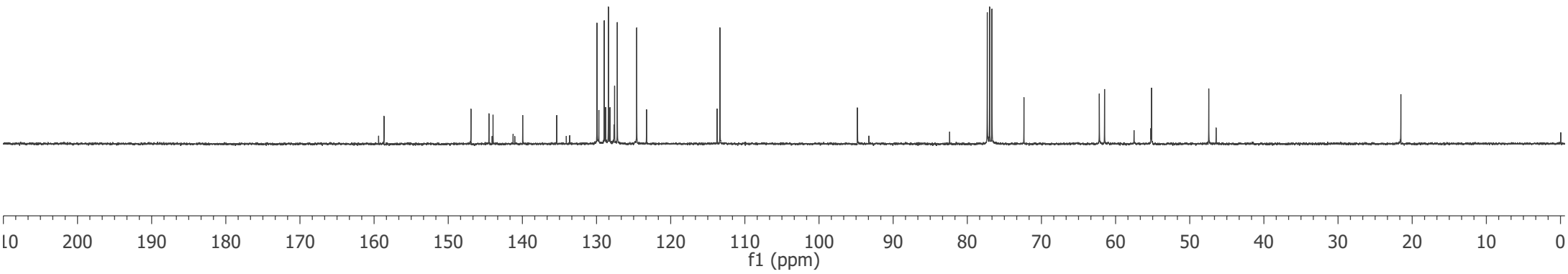
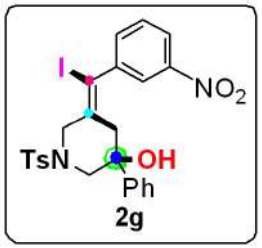
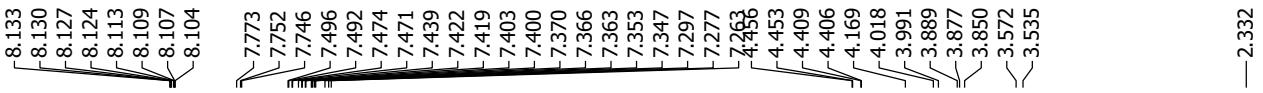
21.532

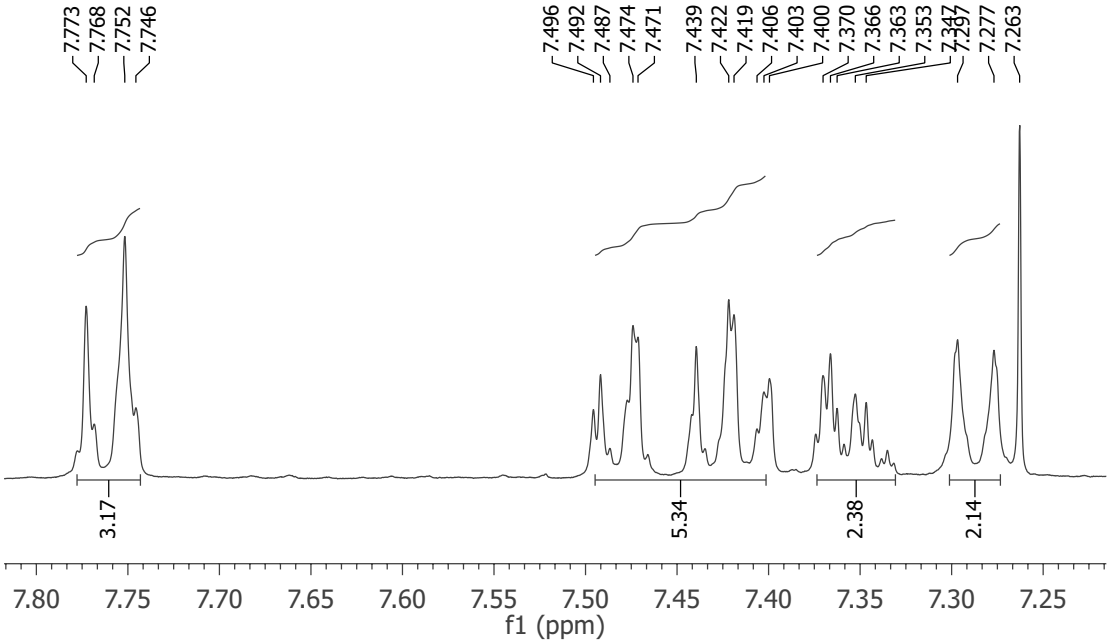


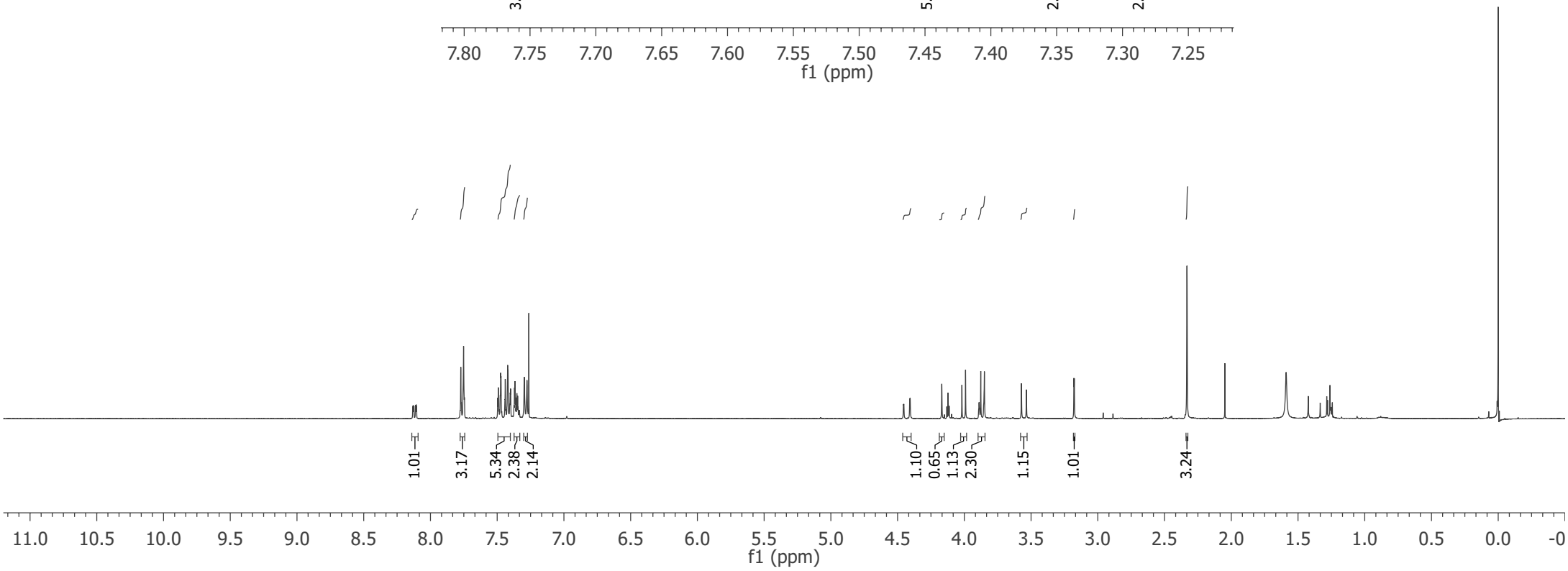
Solvent $CDCl_3$

Spectrometer Frequency 400.40





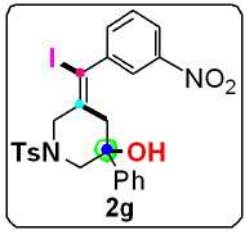


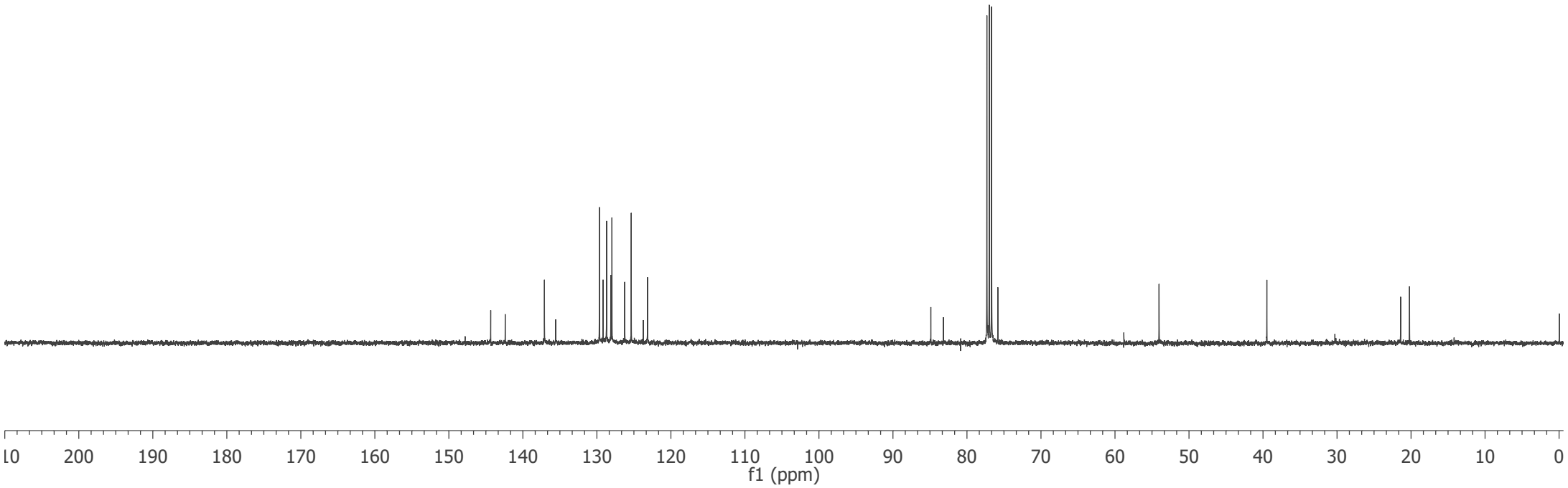


144.346
142.390
137.088
135.577
129.667
129.165
128.689
128.119
127.965
126.237
125.360
123.740
123.160
84.882
83.182
75.830
54.047
39.481
21.408
20.207

Solvent CDCl$_3$

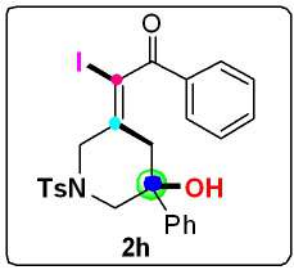
Spectrometer Frequency 100.69





Solvent $CDCl_3$

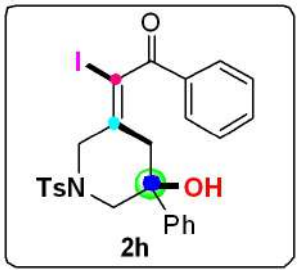
Spectrometer Frequency 400.40



192.041
144.240
142.371
138.428
134.313
133.392
132.868
130.241
129.970
128.825
128.469
127.927
127.835
124.808
95.149
71.704
56.801
55.005
42.817
21.614

Solvent $CDCl_3$

Spectrometer Frequency 100.69



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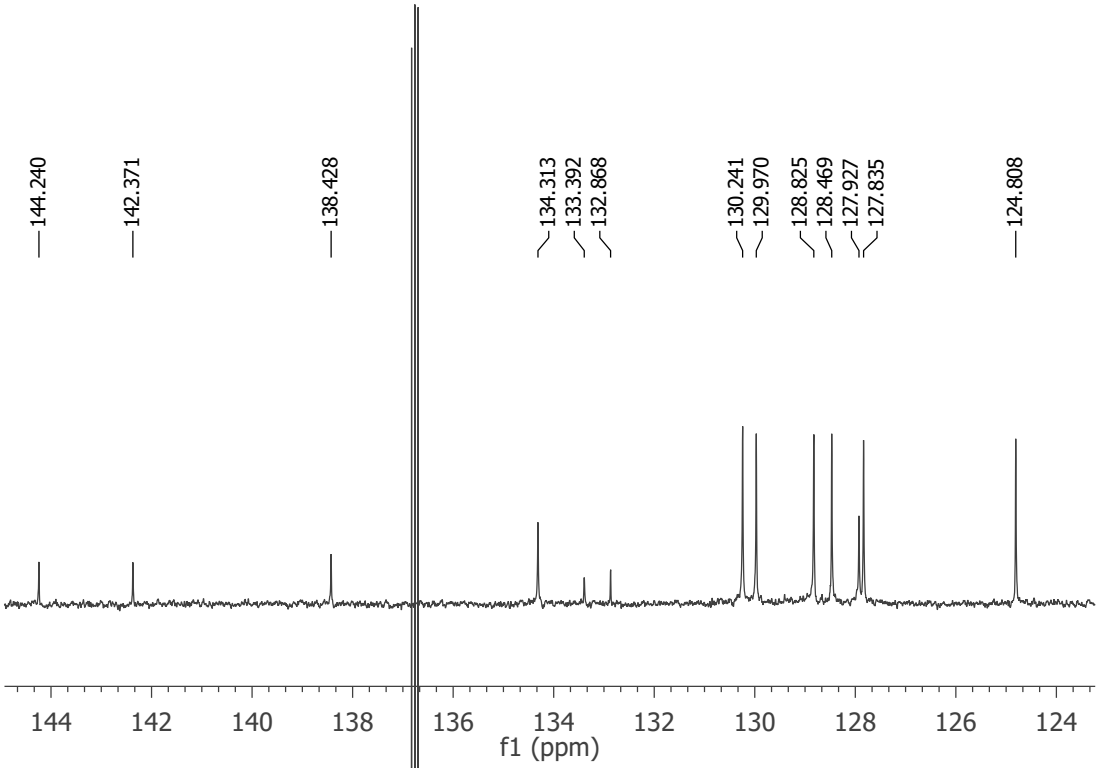
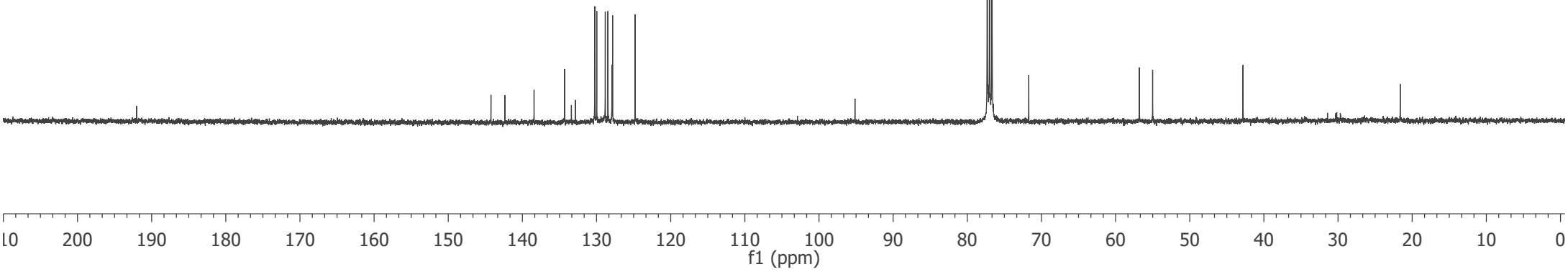
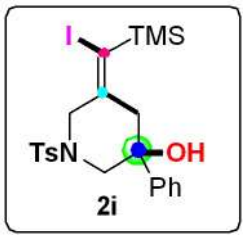




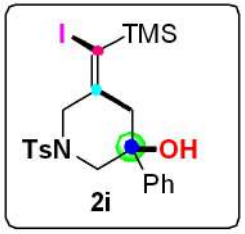
Solvent $CDCl_3$

Spectrometer Frequency 400.28

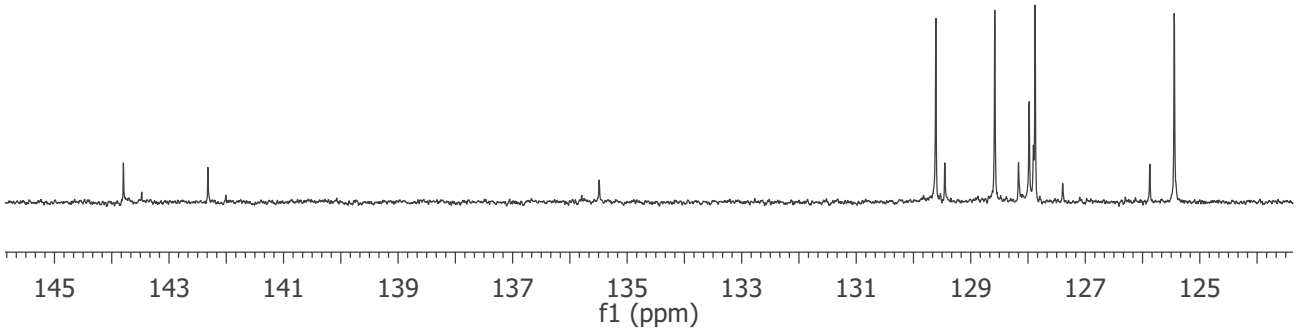


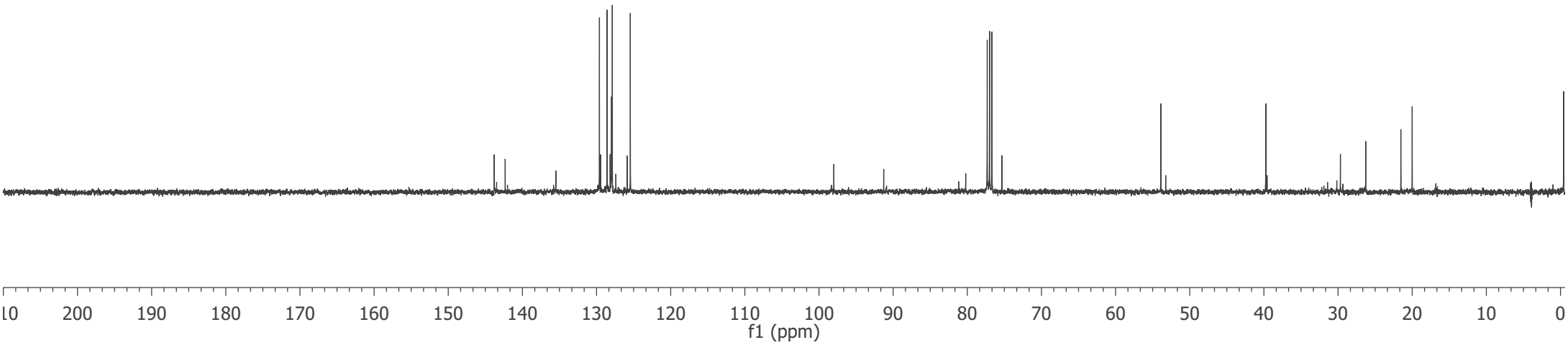
Solvent $CDCl_3$

Spectrometer Frequency 100.66



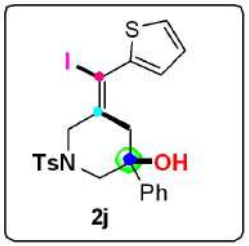
143.796
142.320
135.488
129.609
129.453
128.580
128.166
127.980
127.905
127.876
127.394
125.873
125.446
97.998
91.276
80.213
75.318
53.896
53.241
39.736
39.571
29.683
26.264
21.529
19.999
3.966
-0.425





Solvent $CDCl_3$

Spectrometer Frequency 400.40

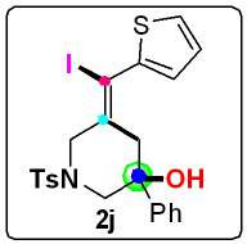


2j

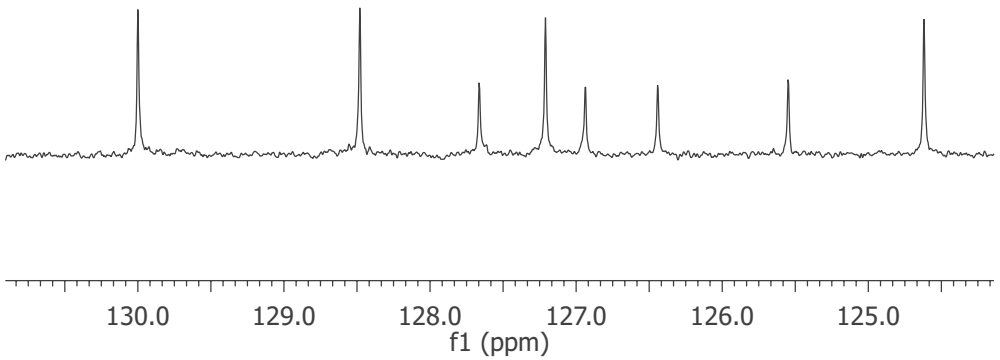
148.520 144.305 144.045 140.605 135.349 130.000 128.480 127.663 127.210 126.937 126.441 125.548 124.619 97.413 72.582 61.892 61.861 48.382 21.551

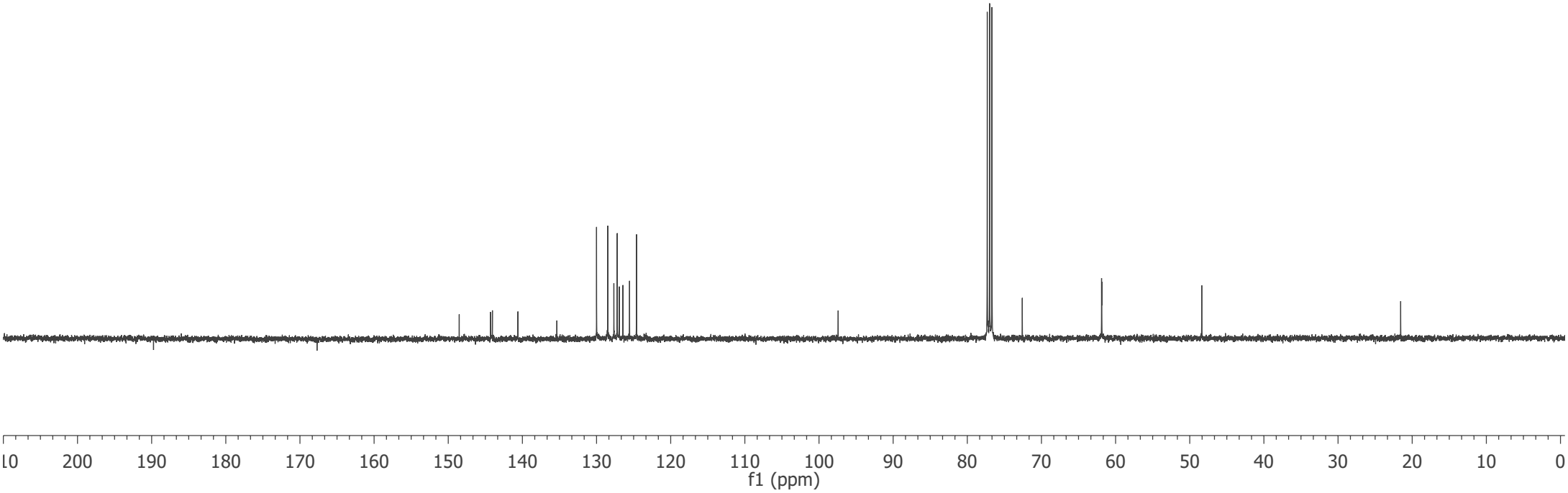
Solvent $CDCl_3$

Spectrometer Frequency 100.69



130.000 128.480 127.663 127.210 126.937 126.441 125.548 124.619





Solvent $CDCl_3$

Spectrometer Frequency 400.40

7.733 7.729 7.717 7.712 7.368 7.366 7.346 7.345 7.295 7.291 7.283 7.279 7.263 7.008 7.004 6.999 6.995 6.986 6.983 6.974 4.718 4.676 4.150 4.110 3.556 3.553 3.521 3.517 3.141 3.106 2.828 2.812 2.791 2.453 1.289

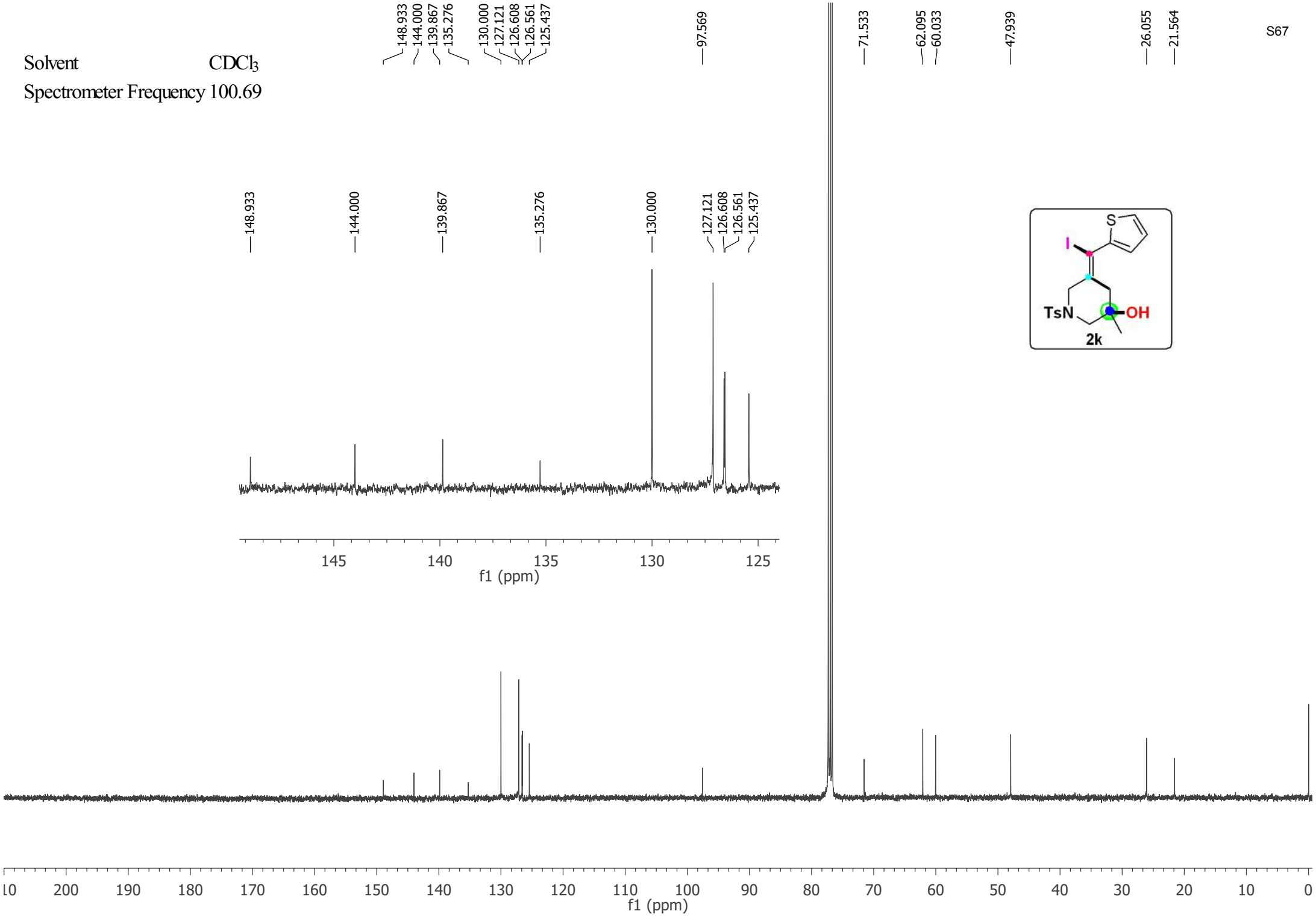
2.00 2.02 1.01 1.99 1.03 1.11 1.14 2.07 2.00 3.01 3.00

11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)

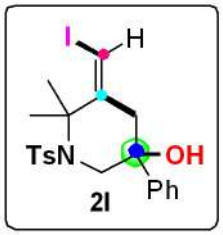
Solvent $CDCl_3$

Spectrometer Frequency 100.69



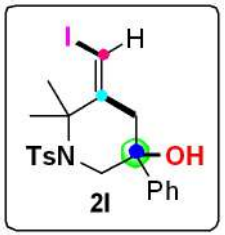
Solvent $CDCl_3$

Spectrometer Frequency 400.40

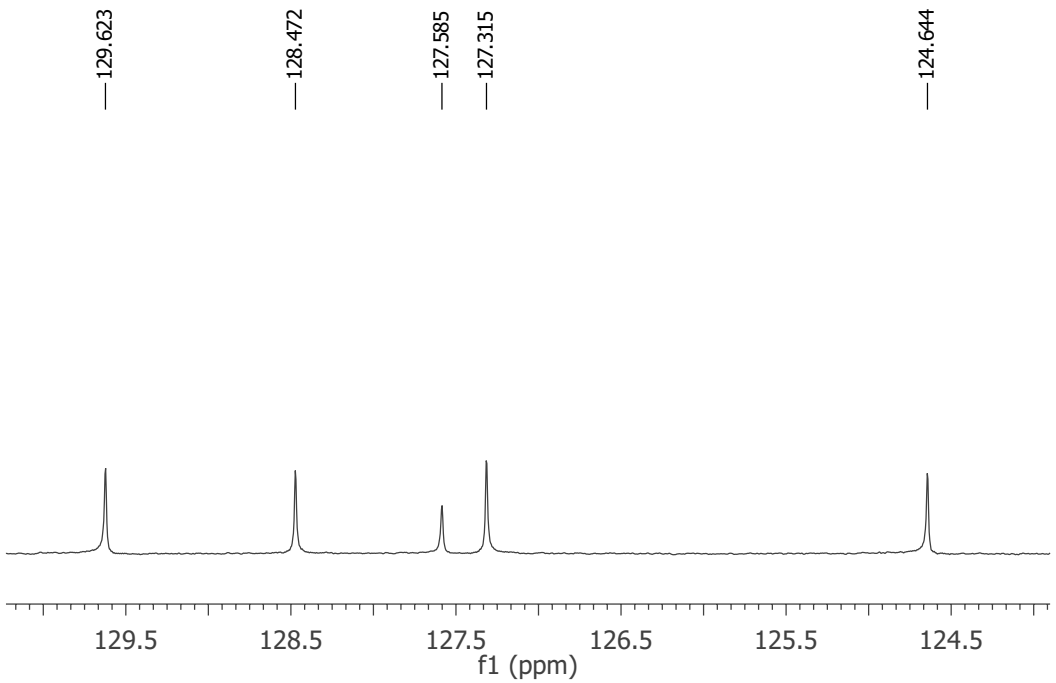


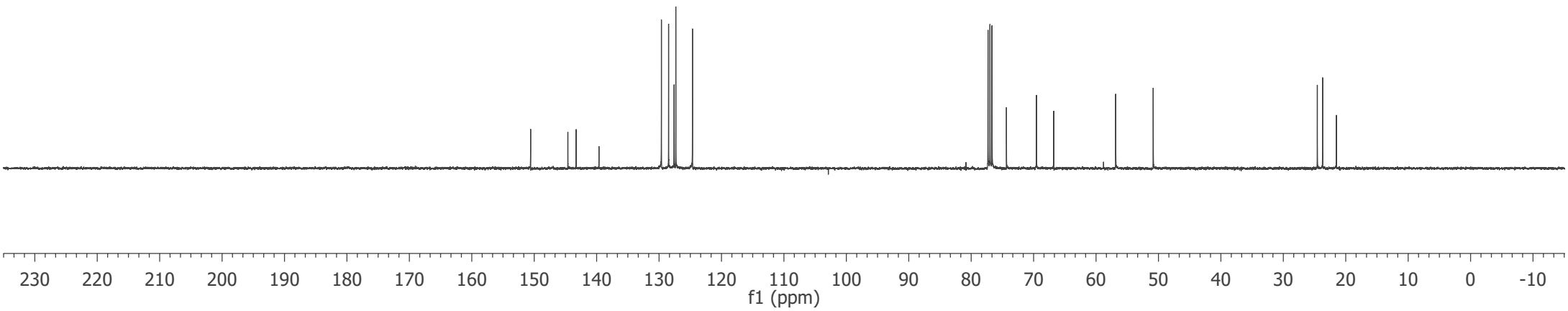
Solvent $CDCl_3$

Spectrometer Frequency 100.69



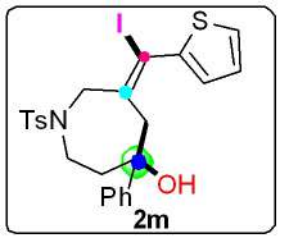
150.573, 144.610, 143.283, 139.626, 129.623, 128.472, 127.585, 127.315, 124.644, 74.354, 69.555, 66.788, 56.850, 50.841, 24.552, 23.705, 21.487





Solvent $CDCl_3$

Spectrometer Frequency 400.40

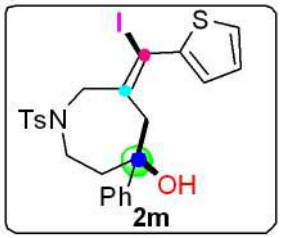


f1 (ppm)

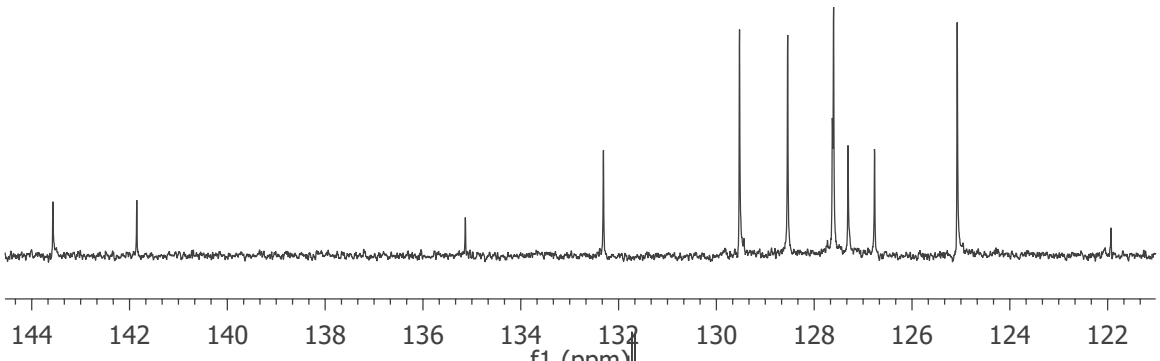
f1 (ppm)

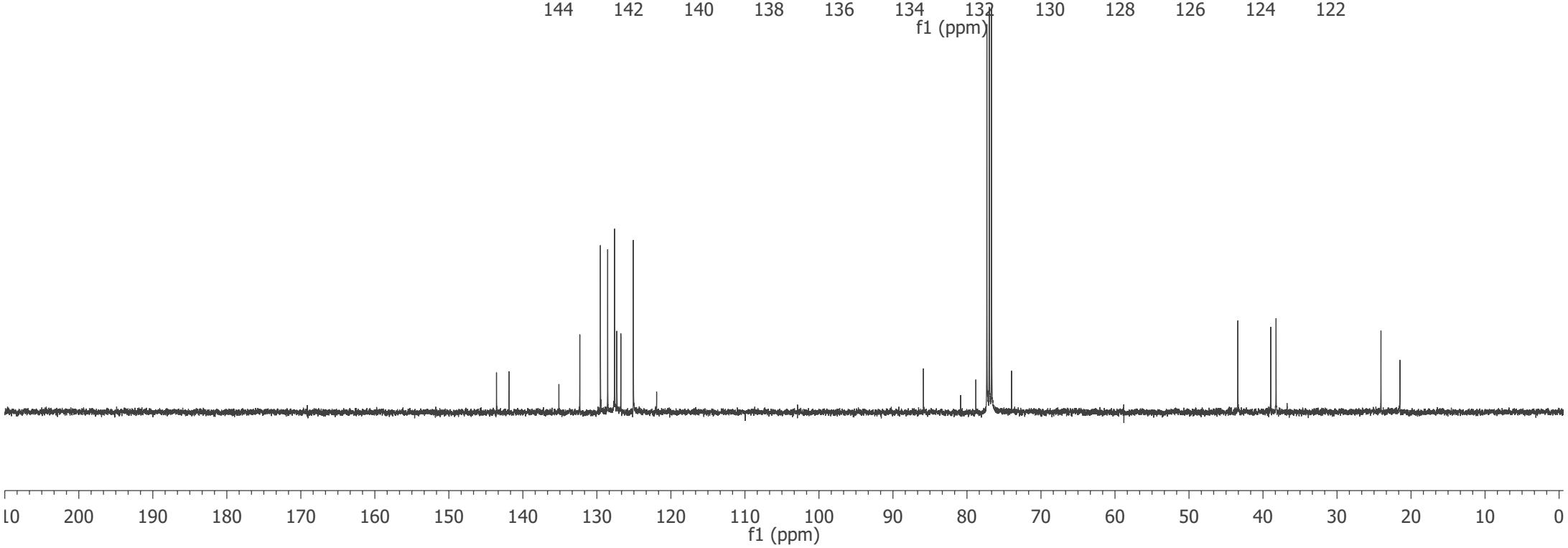
Solvent $CDCl_3$

Spectrometer Frequency 100.69



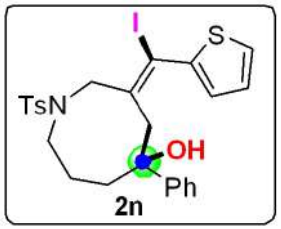
143.568 141.852 135.133 132.310 129.528 128.543 127.628 127.604 127.308 126.766 125.075 121.931 85.881 80.855 78.796 73.978 43.398 38.952 38.236 24.064 21.505





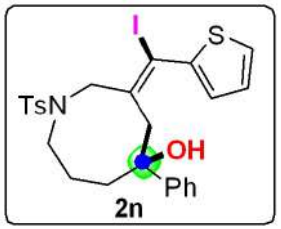
Solvent $CDCl_3$

Spectrometer Frequency 400.40



Solvent $CDCl_3$

Spectrometer Frequency 100.69



143.492
142.844
135.523
132.198
129.526
128.448
127.623
127.408
127.218
126.722
125.057
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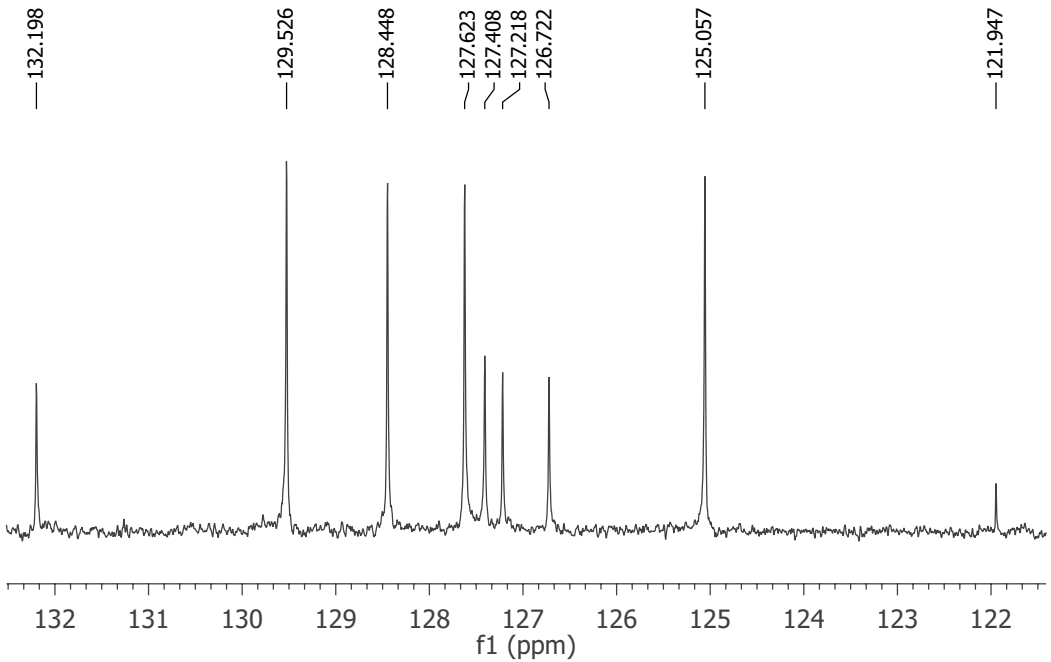
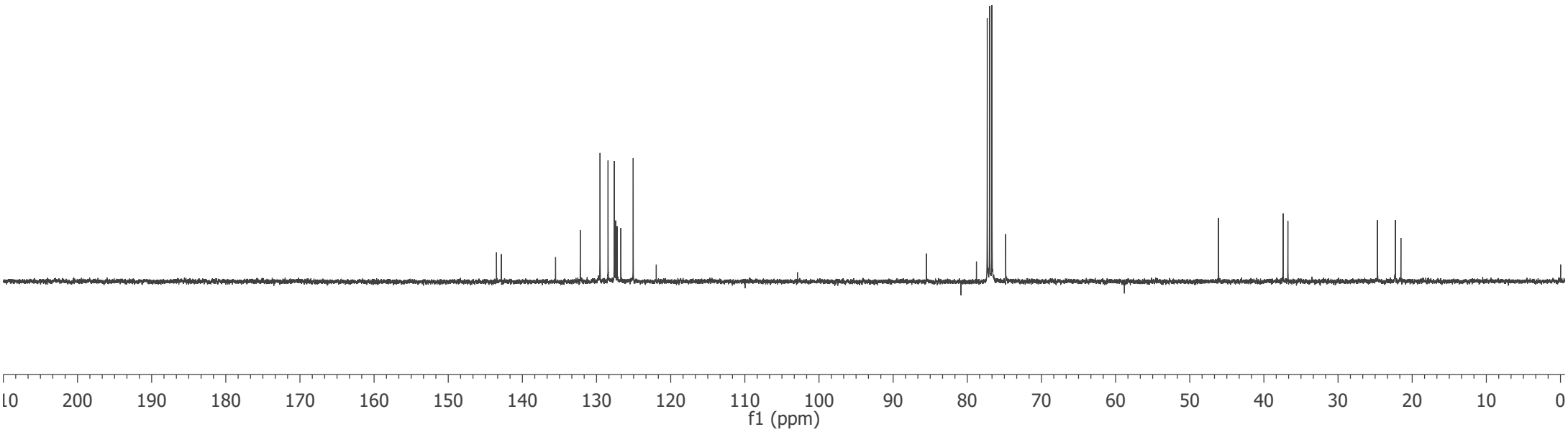
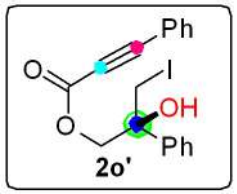
85.531
78.765
74.823
46.123
37.413
36.763
24.683
22.274
21.521





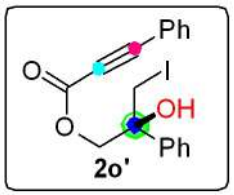
Solvent $CDCl_3$

Spectrometer Frequency 400.40

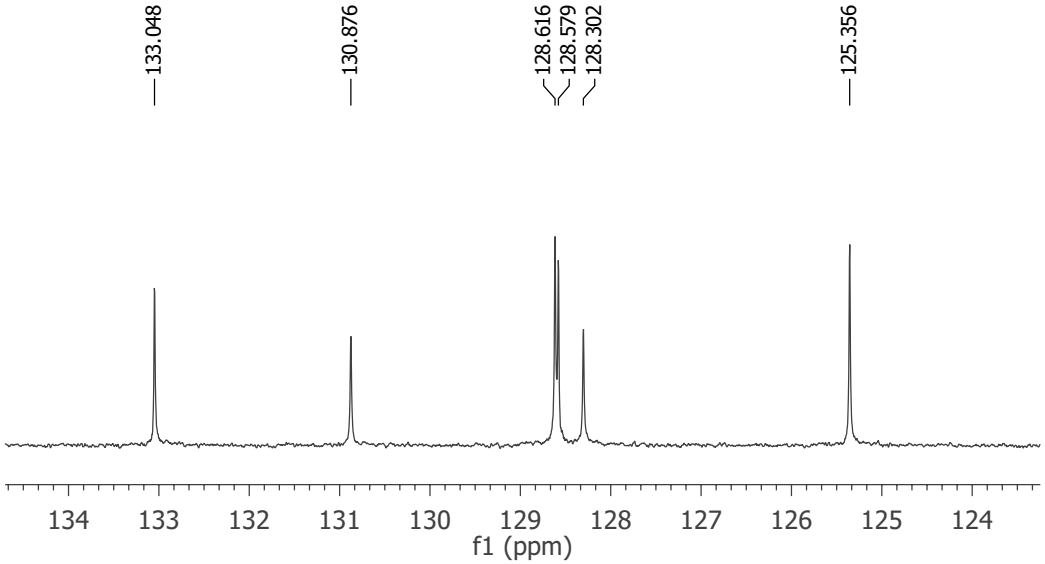


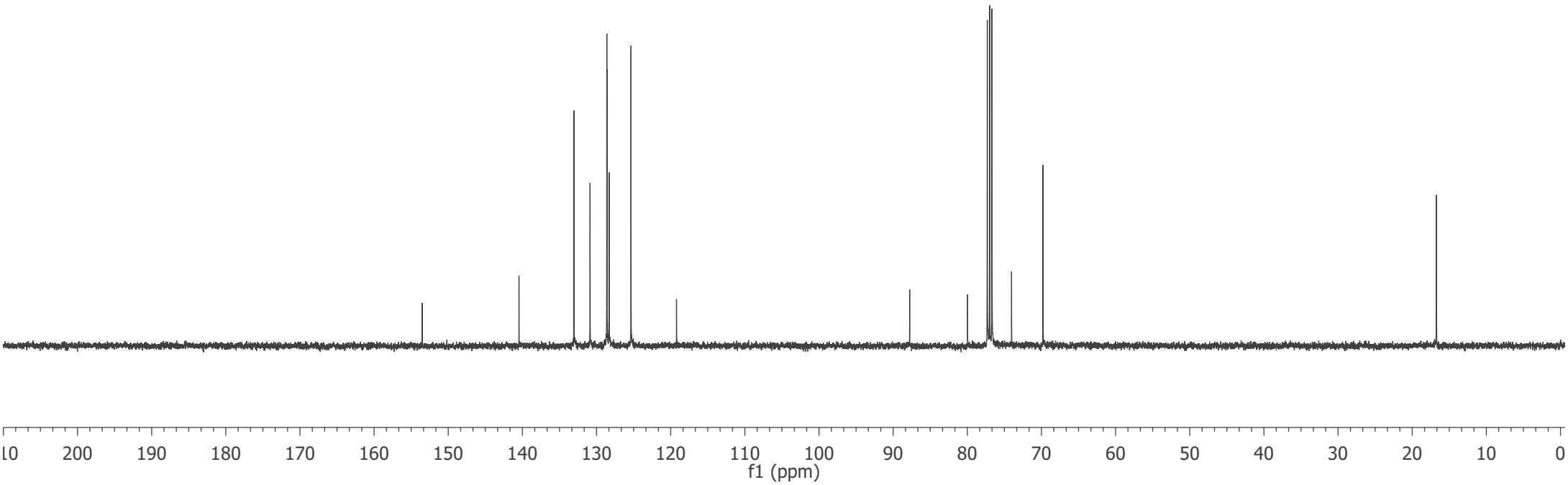
Solvent $CDCl_3$

Spectrometer Frequency 100.69



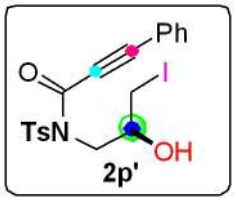
153.513, 140.462, 133.048, 130.876, 128.616, 128.579, 128.302, 125.356, 119.219, 87.774, 79.964, 74.029, 69.802, 16.722

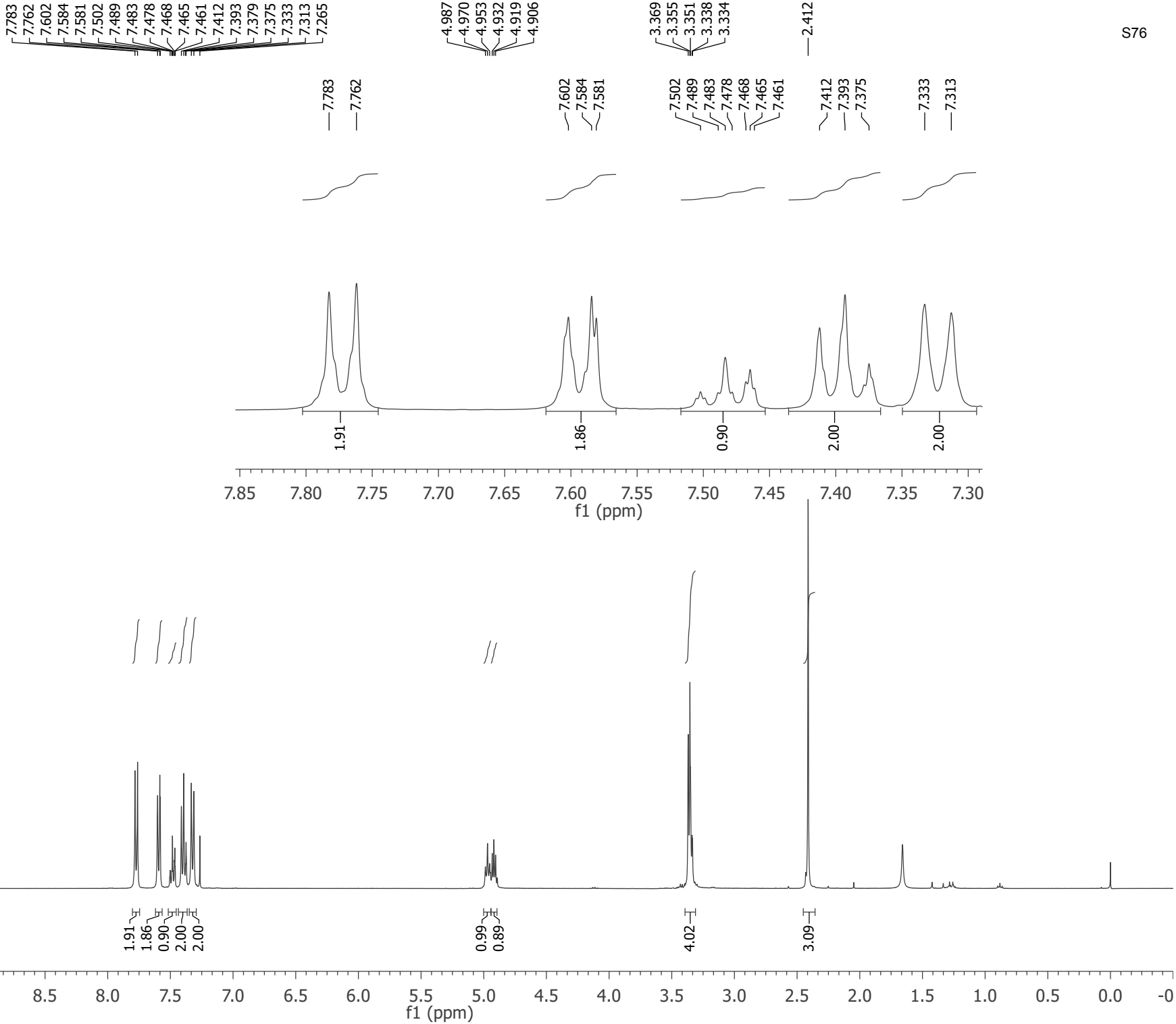




Solvent $CDCl_3$

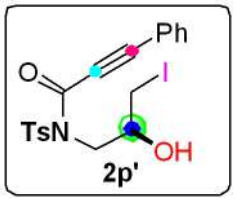
Spectrometer Frequency 400.40



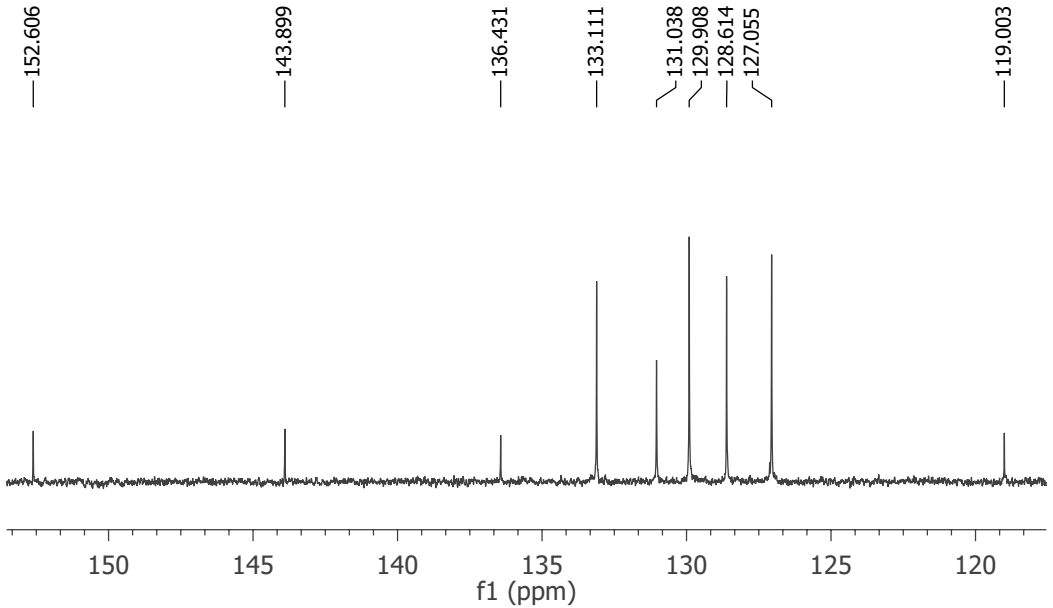


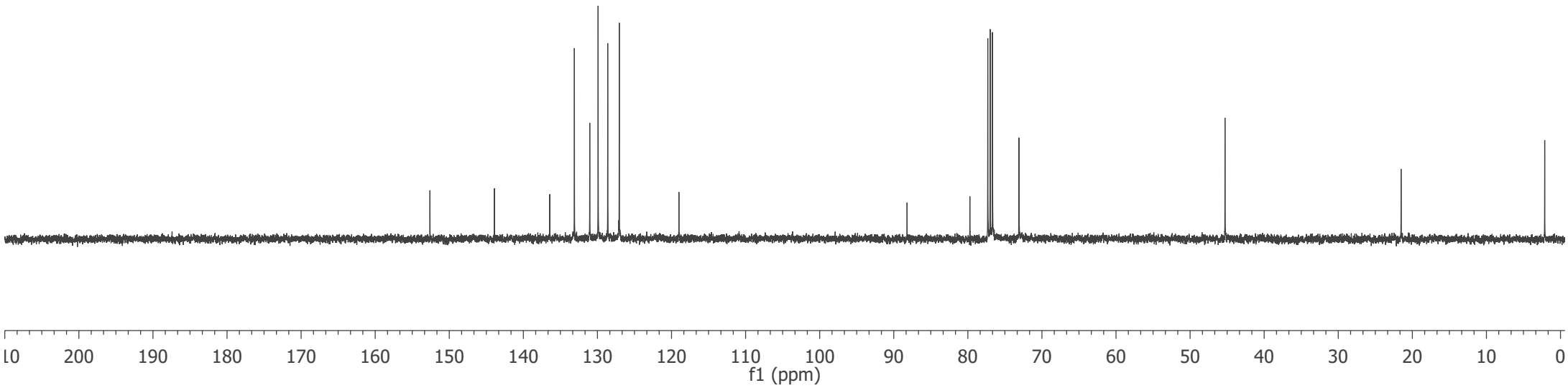
Solvent $CDCl_3$

Spectrometer Frequency 100.69



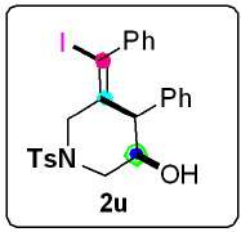
152.606 143.899 136.431 133.111 131.038 129.908 128.614 127.055 119.003 88.201 79.729 73.113 45.289 21.519 2.133





Solvent $CDCl_3$

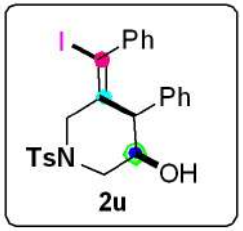
Spectrometer Frequency 400.40



2u

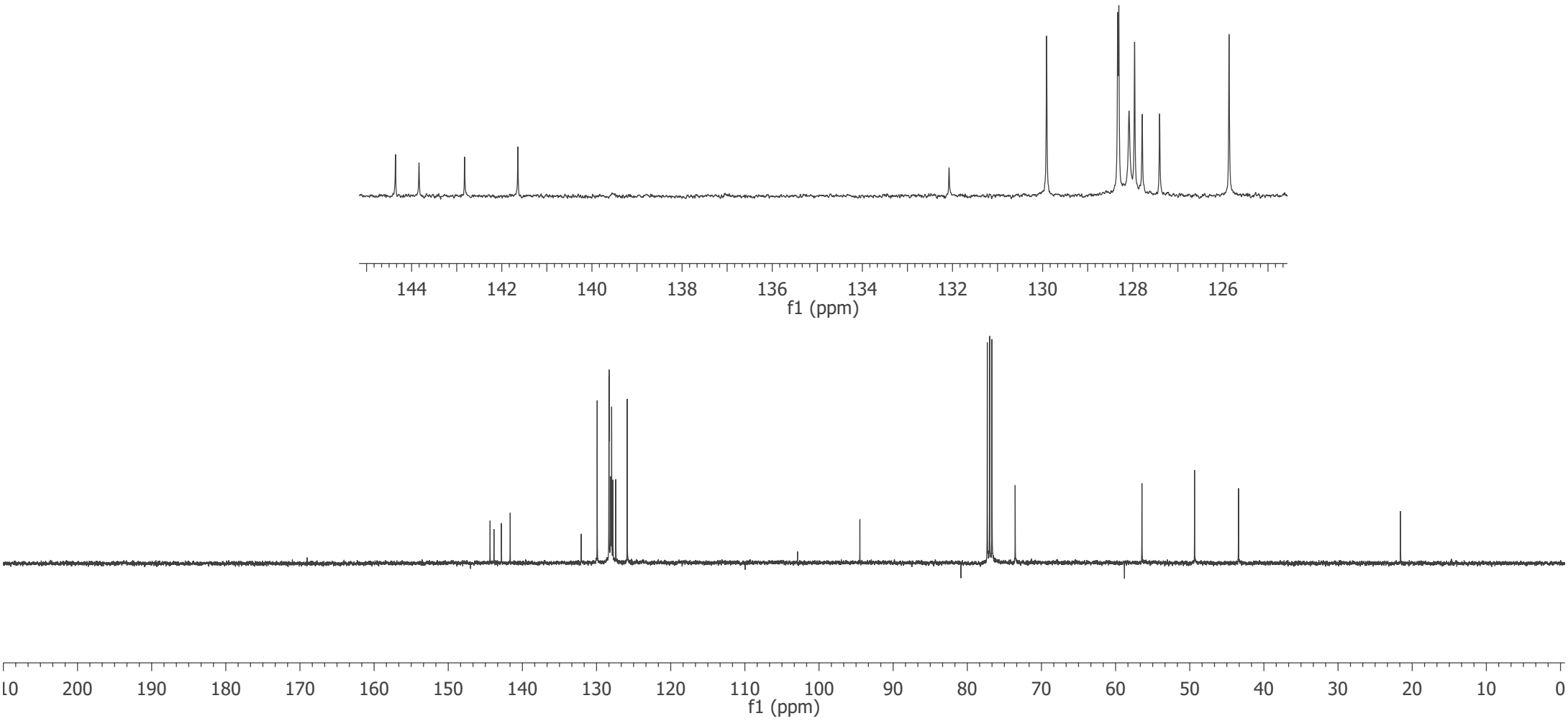
Solvent $CDCl_3$

Spectrometer Frequency 100.69



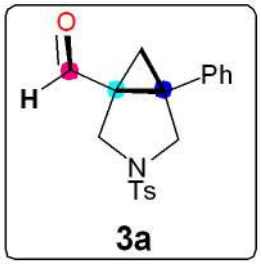
2u

144.358 143.837 142.825 141.643 132.076 129.912 128.335 128.310 128.084 127.960 127.792 127.405 125.864 102.898 94.488 56.448 49.356 43.429 21.572



Solvent $CDCl_3$

Spectrometer Frequency 400.40

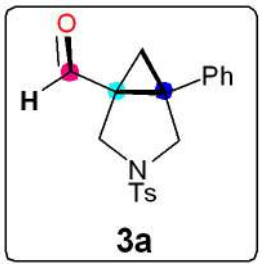


3a

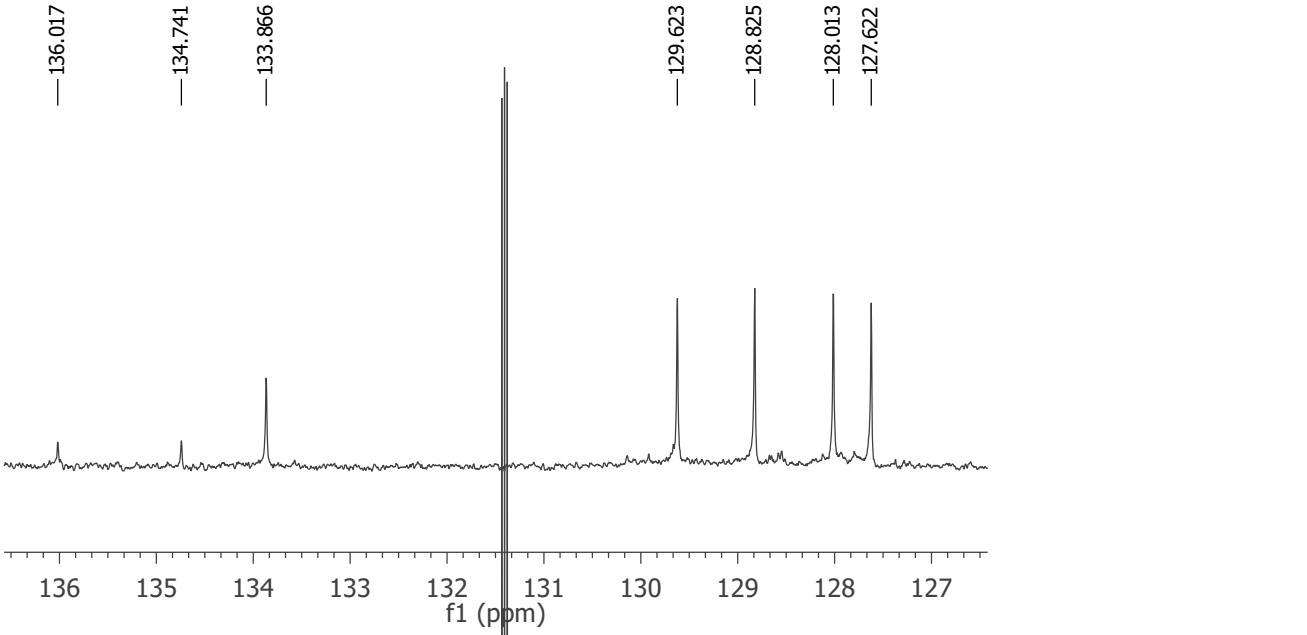
193.248
143.812
136.017
134.741
133.866
129.623
128.825
128.013
127.622
74.381
51.454
37.313
21.584
-0.021

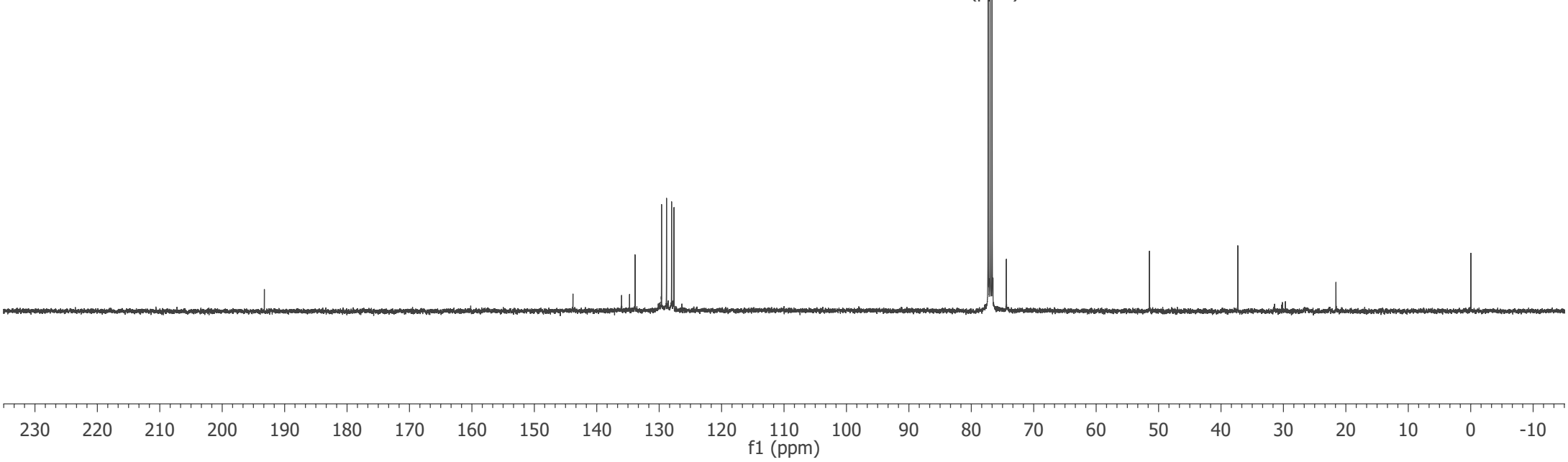
Solvent $CDCl_3$

Spectrometer Frequency 100.69



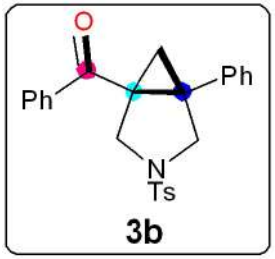
3a





Solvent $CDCl_3$

Spectrometer Frequency 400.40



3b

197.869

143.981
137.583
134.799
133.172
131.908
129.885
128.469
128.417
128.202
127.727
127.698
127.580

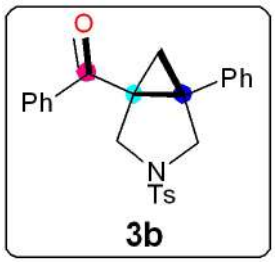
55.149
52.820

43.432
42.891

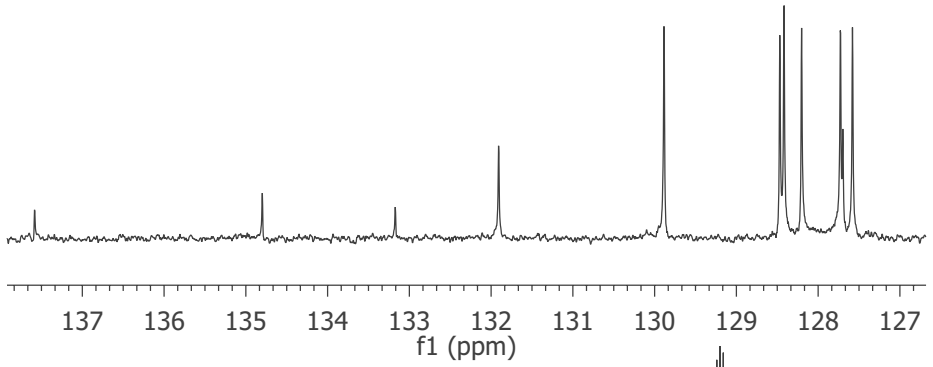
21.614
19.734

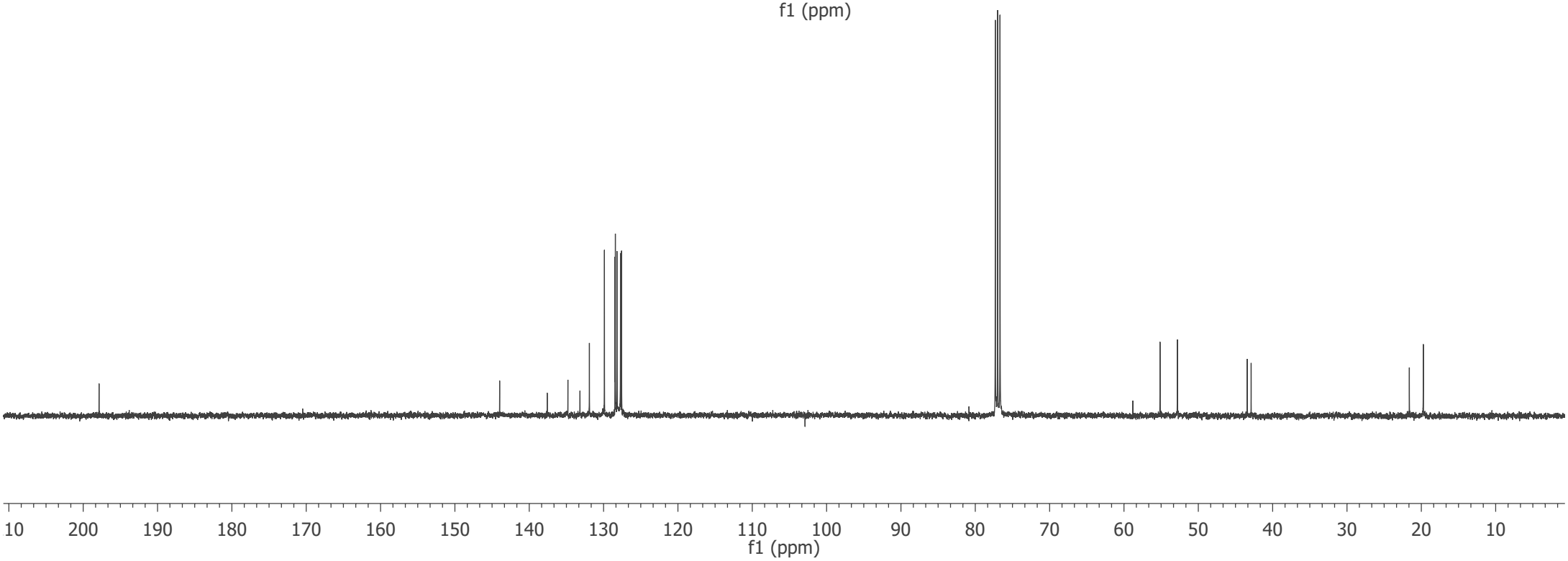
Solvent CDCl3

Spectrometer Frequency 100.69



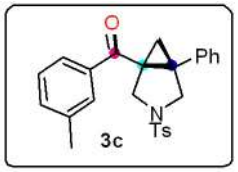
3b

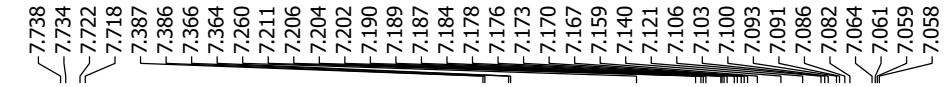


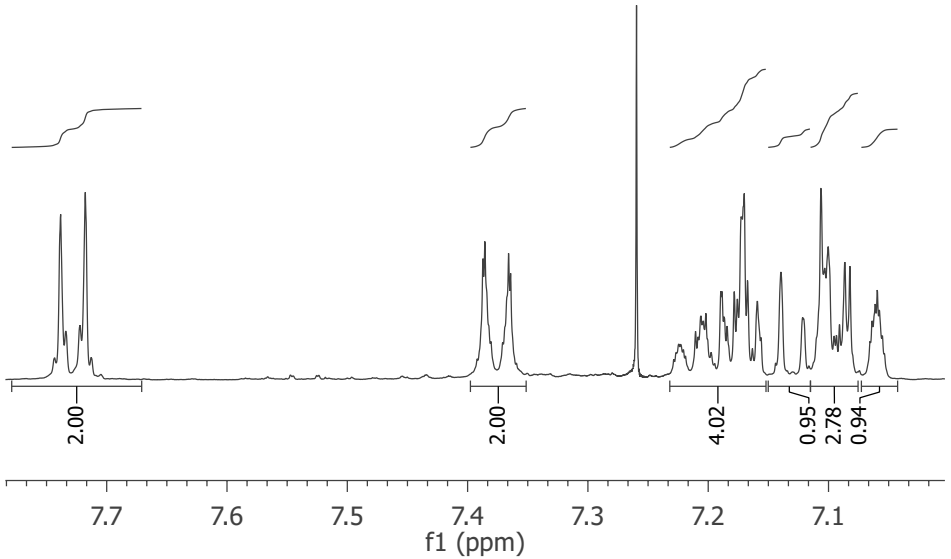


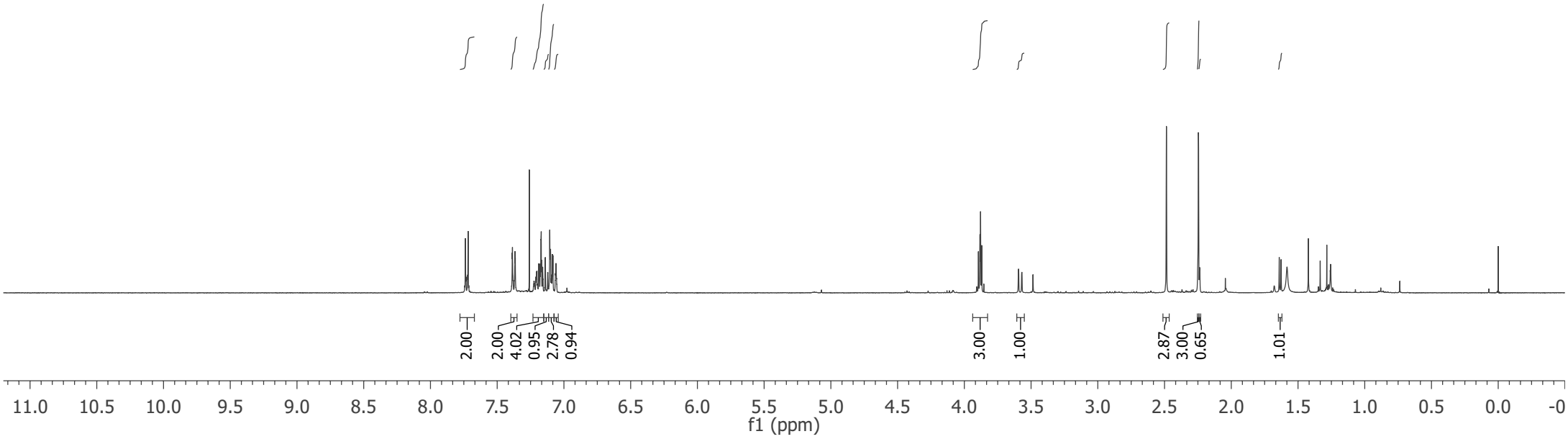
Solvent $CDCl_3$

Spectrometer Frequency 400.40





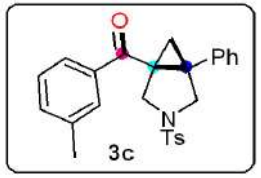


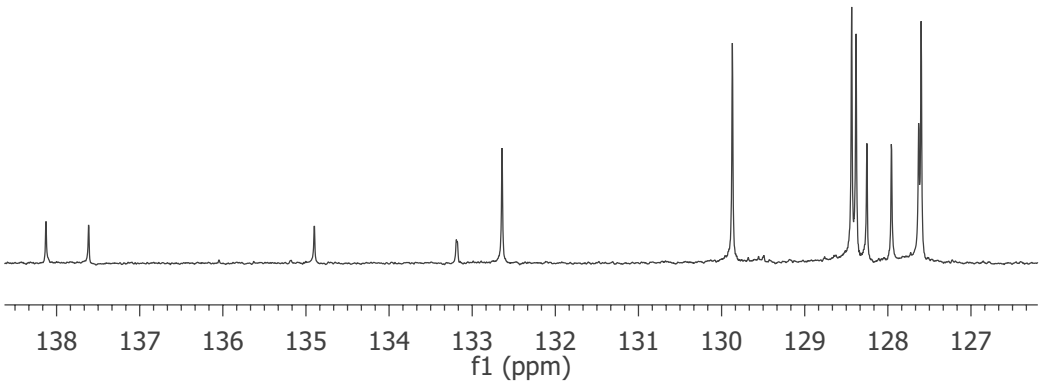


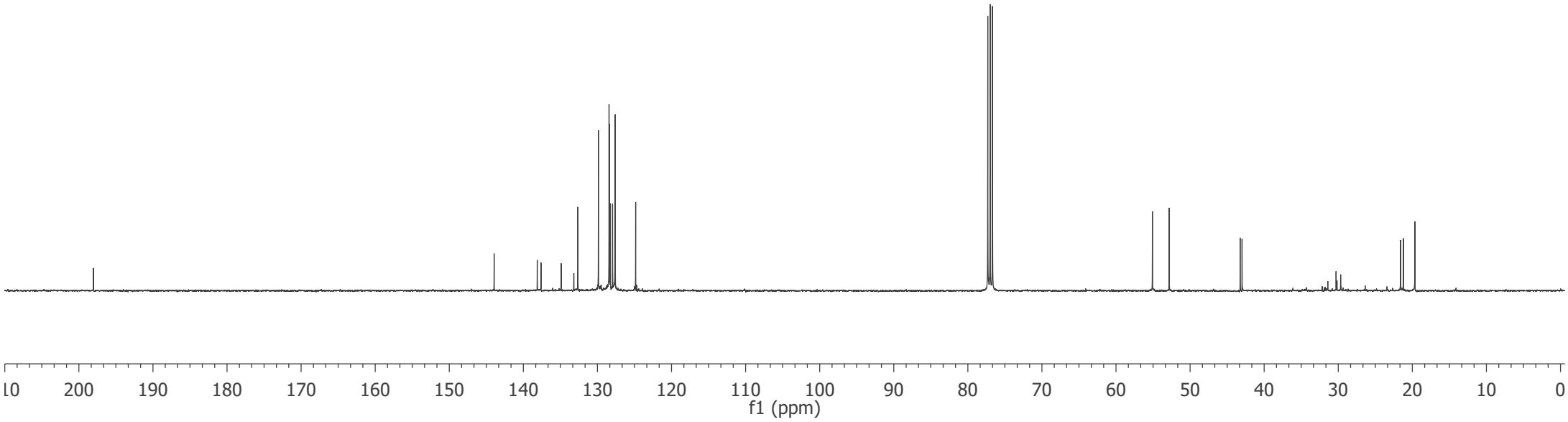
198.030
143.947
138.128
137.614
134.899
133.190
132.641
129.870
128.435
128.382
128.252
127.957
127.628
127.599
124.841
55.085
52.829
43.245
42.985
21.596
21.217
19.653

Solvent $CDCl_3$

Spectrometer Frequency 100.69

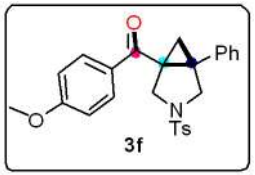




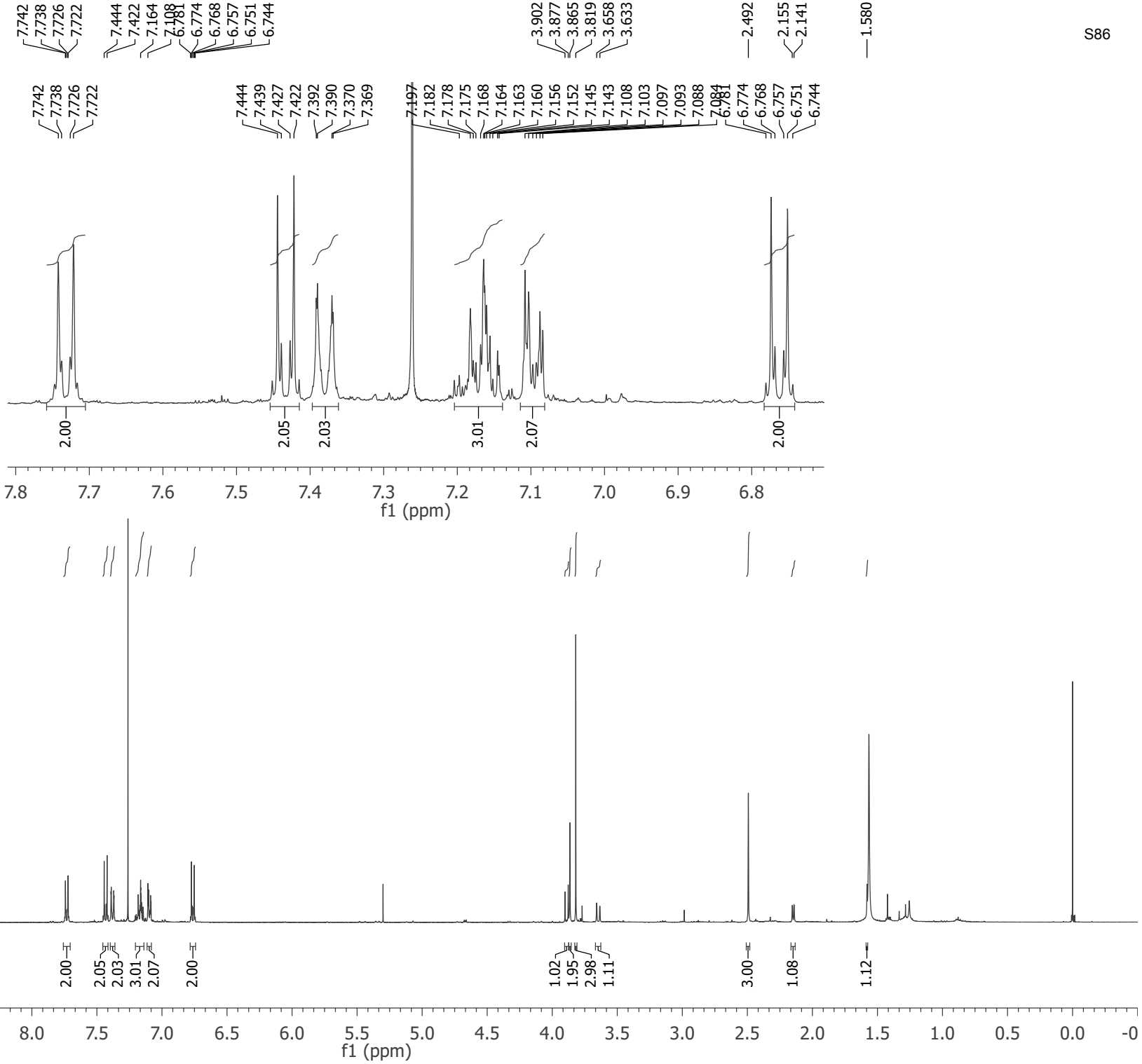


Solvent $CDCl_3$

Spectrometer Frequency 400.40



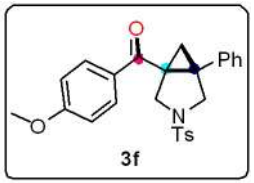
3f

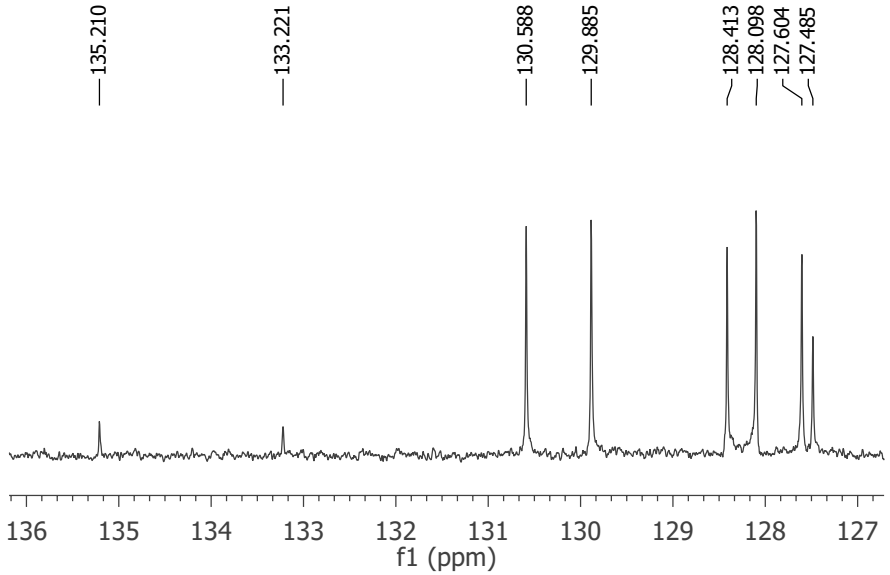


195.494 162.900 143.948 135.210 133.221 130.588 129.885 128.413 128.098 127.604 127.485 113.537 55.412 55.016 53.585 42.508 41.822 21.612 19.606

Solvent $CDCl_3$

Spectrometer Frequency 100.69

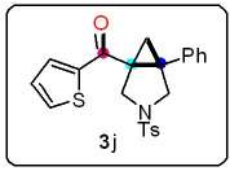




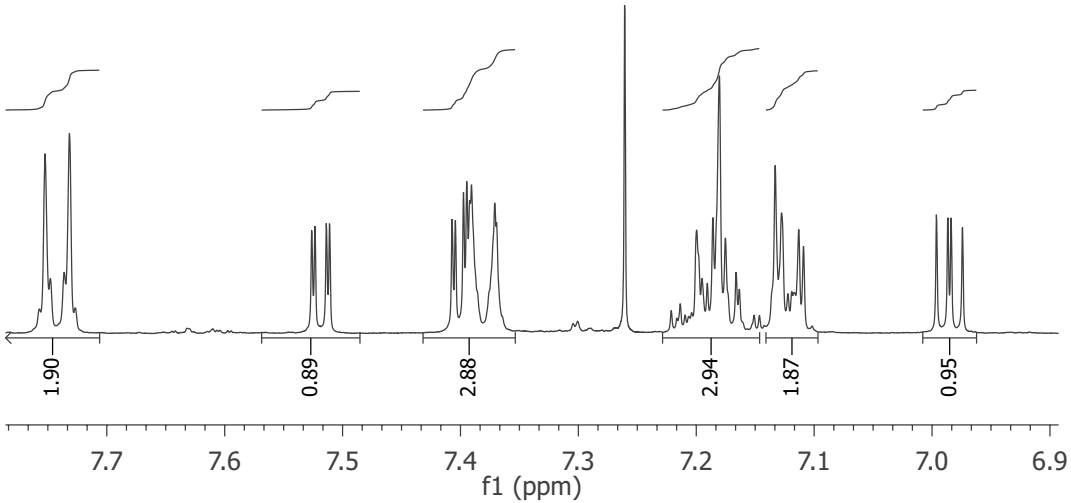
7.757 7.752 7.748 7.736 7.732 7.727 7.526 7.523 7.514 7.511 7.407 7.404 7.397 7.395 7.392 7.391 7.371 7.369 7.221 7.217 7.214 7.209 7.204 7.200 7.195 7.191 7.186 7.180 7.175 7.166 7.164 7.151 7.146 7.133 7.128 7.122 7.119 7.117 7.113 7.109 6.996 6.987 6.984 6.974 3.996 3.973 3.958 3.934 3.890 3.866 3.517 3.492 2.483 2.215 2.202 1.709 1.695

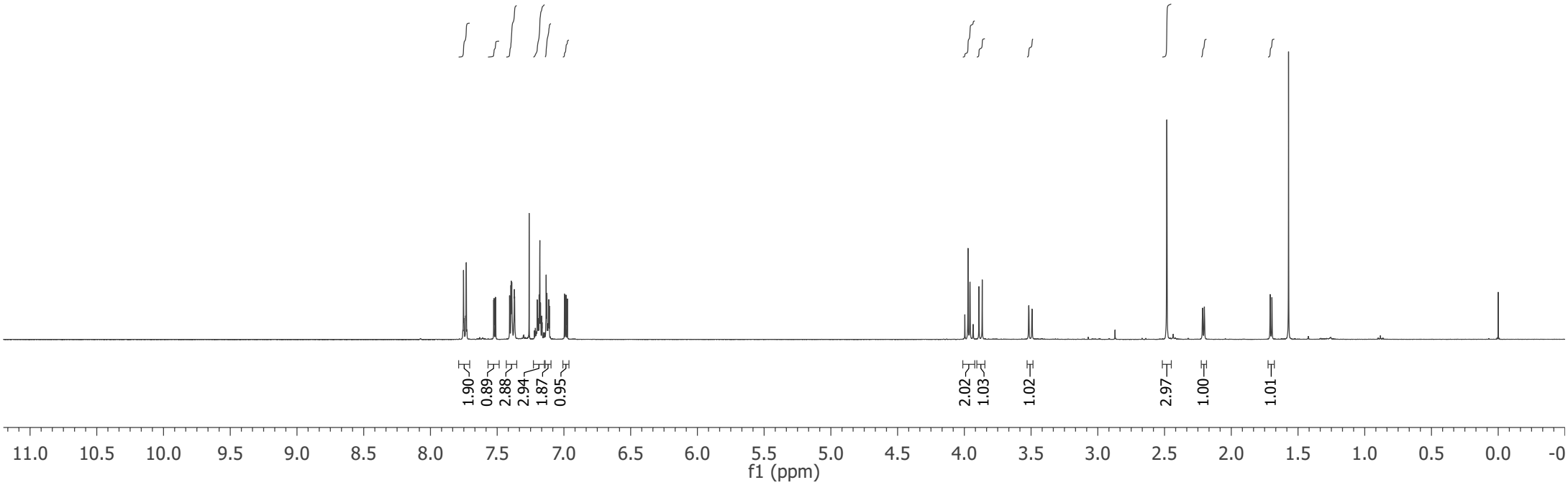
Solvent $CDCl_3$

Spectrometer Frequency 400.40



3j

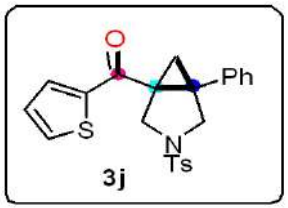


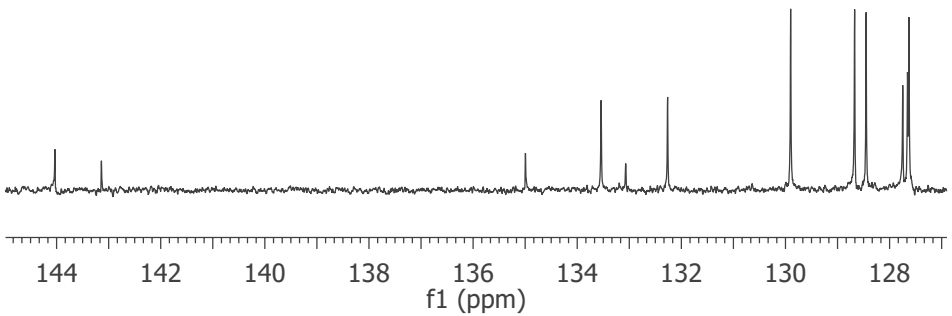


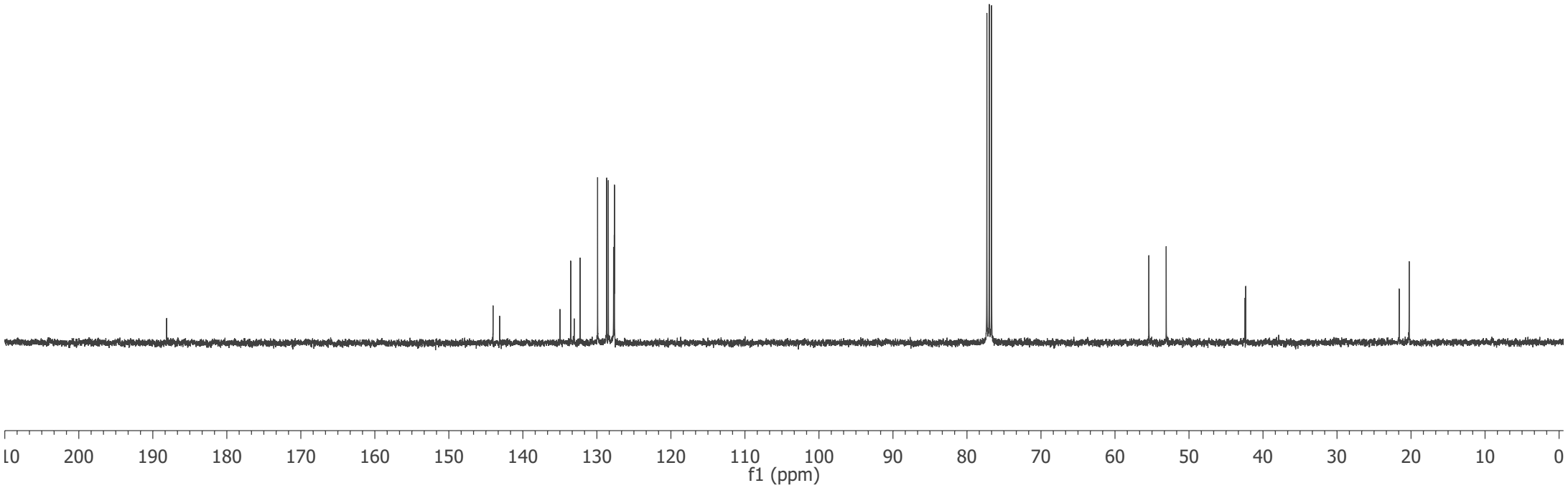
188.129
144.032
143.139
134.995
133.541
133.069
132.265
129.901
128.672
128.451
127.748
127.656
127.628
55.420
53.079
42.424
42.332
21.604
20.253

Solvent $CDCl_3$

Spectrometer Frequency 100.69







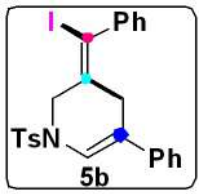
Solvent $CDCl_3$

Spectrometer Frequency 400.40

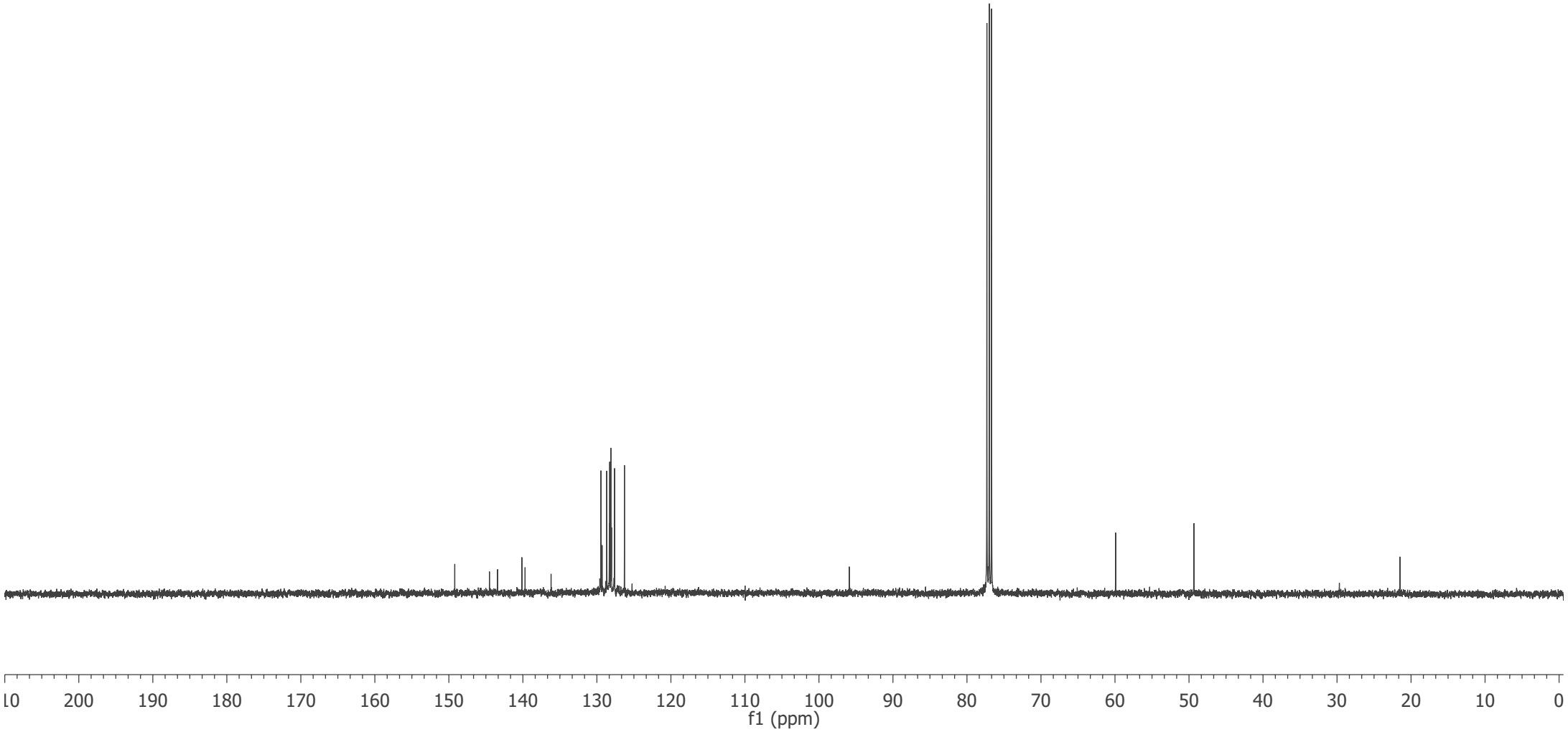
149.201
144.520
143.409
140.141
139.699
136.193
129.463
129.297
128.663
128.326
128.269
128.116
128.022
127.608
126.278
95.908
59.916
49.336
21.503

Solvent $CDCl_3$

Spectrometer Frequency 100.69



5b



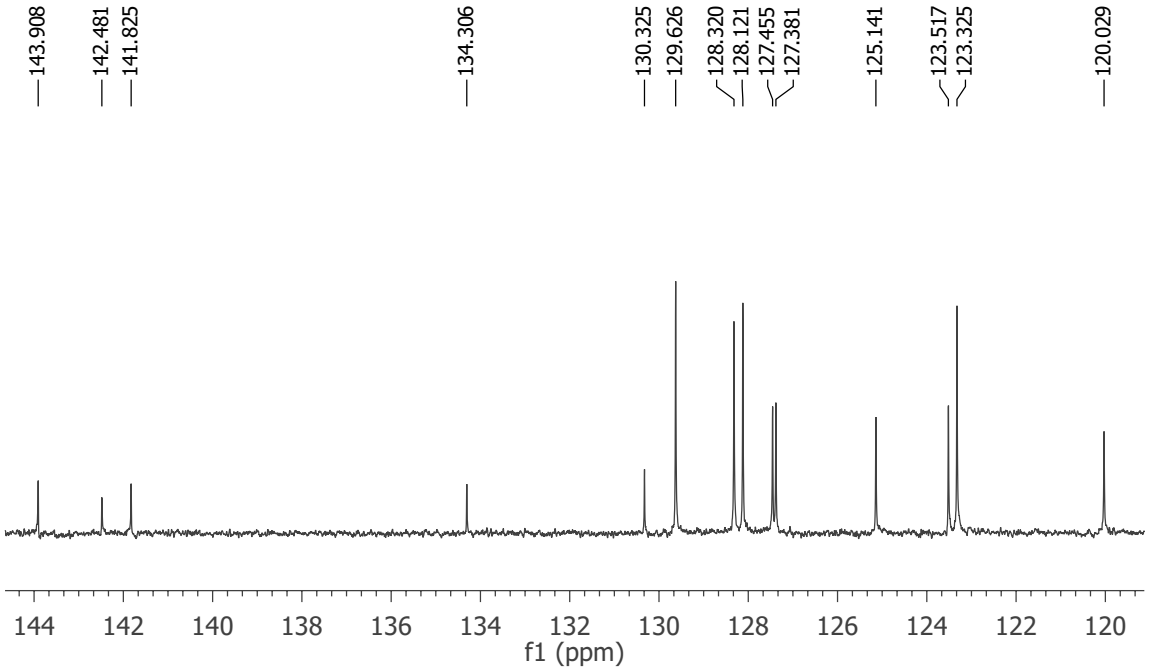
Solvent $CDCl_3$

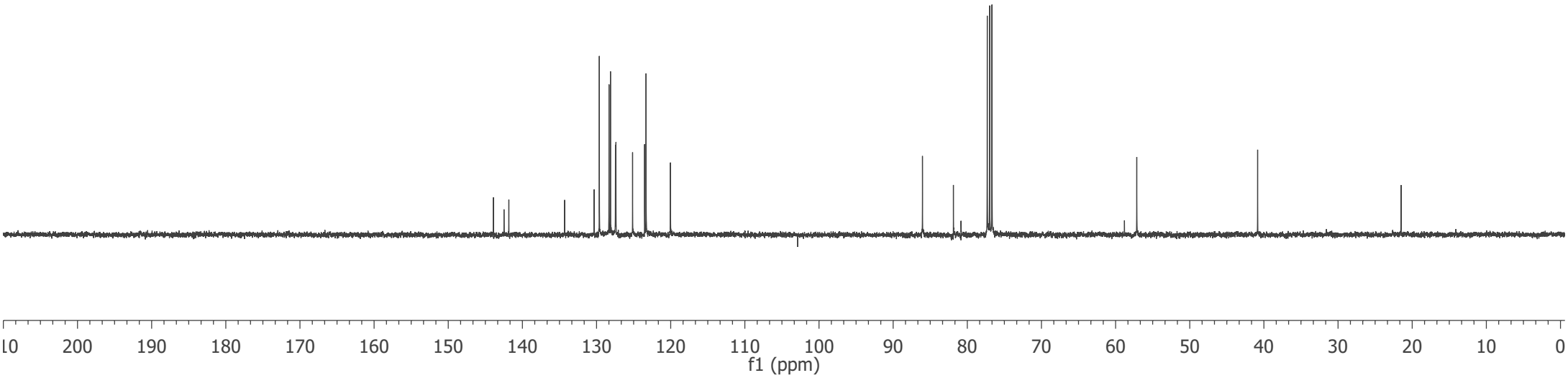
Spectrometer Frequency 400.40

Solvent $CDCl_3$

Spectrometer Frequency 100.69

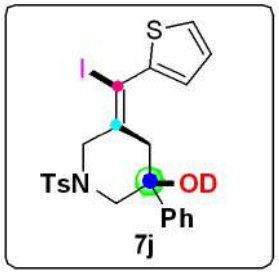
143.908 142.481 141.825 134.306 130.325 129.626 128.320 128.121 127.455 127.381 125.141 123.517 123.325 120.029 86.044 81.873 57.143 40.844 21.503





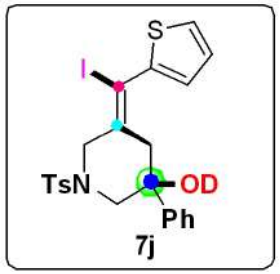
Solvent $CDCl_3+D_2O$

Spectrometer Frequency 400.40

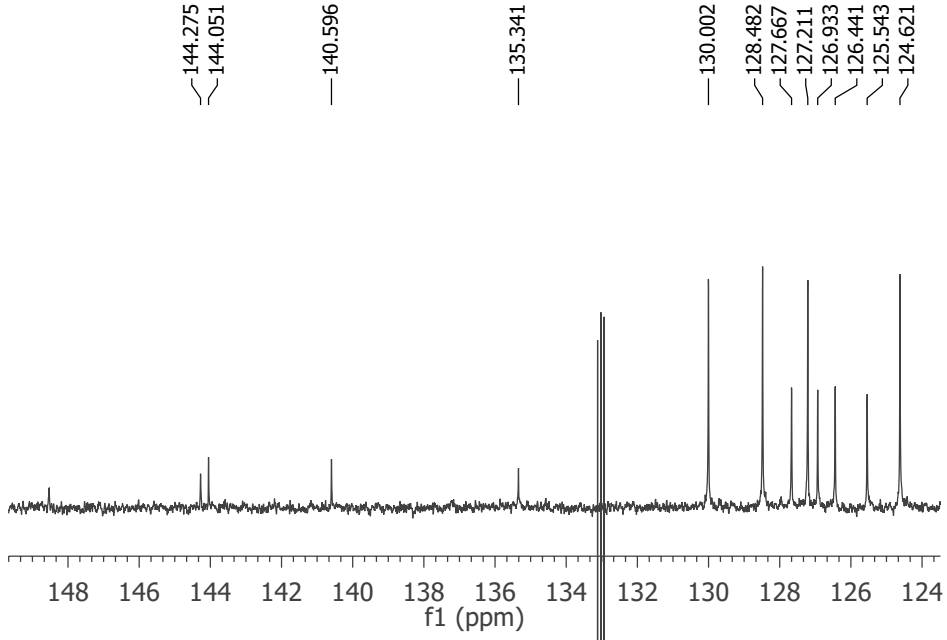


Solvent $CDCl_3+D_2O$

Spectrometer Frequency 100.69

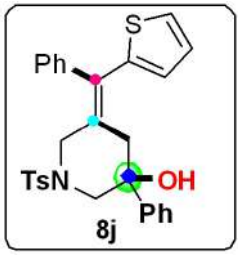


148.531
144.275
144.051
140.596
135.341
130.002
128.482
127.667
127.211
126.933
126.441
125.543
124.621
97.413
72.529
61.899
61.809
48.360
21.547



Solvent $CDCl_3$

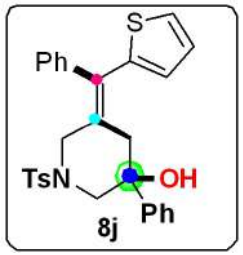
Spectrometer Frequency 400.40



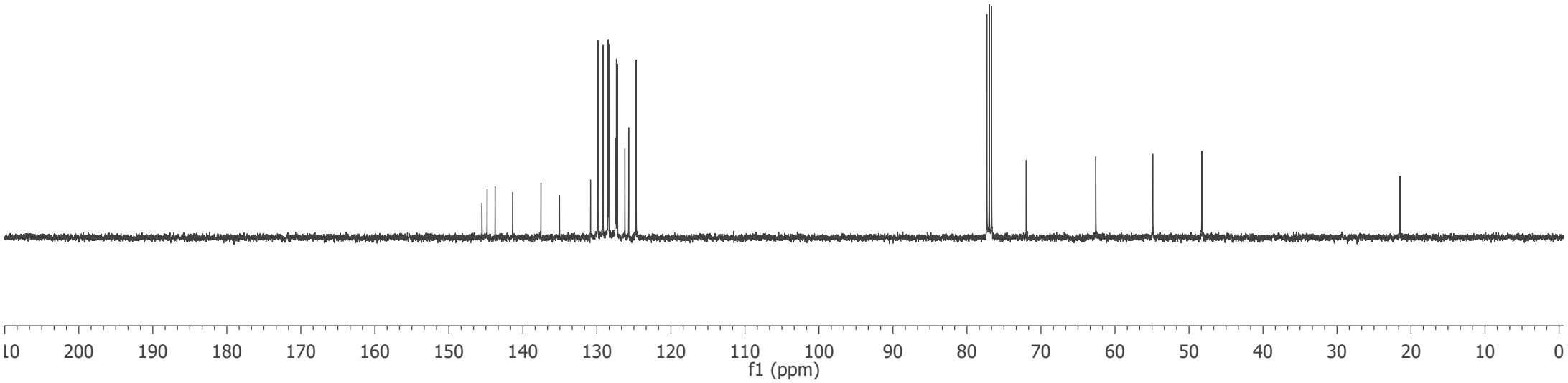
8j

Solvent $CDCl_3$

Spectrometer Frequency 100.69



145.526, 144.831, 143.756, 141.361, 137.555, 135.046, 130.856, 129.858, 129.169, 128.493, 128.403, 127.494, 127.368, 127.216, 126.213, 125.701, 124.688, 71.992, 62.593, 54.893, 48.274, 21.501



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mr05561

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mr05561

Bond precision: C-C = 0.0046 A Wavelength=0.71073

Cell: a=5.6140(5) b=12.5998(12) c=14.6937(15)
alpha=109.014(3) beta=93.175(3) gamma=102.642(3)
Temperature: 150 K

	Calculated	Reported
Volume	949.75(16)	949.75(16)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H20 I N O3 S	C19 H20 I N O3 S
Sum formula	C19 H20 I N O3 S	C19 H20 I N O3 S
Mr	469.32	469.32
Dx,g cm-3	1.641	1.641
Z	2	2
Mu (mm-1)	1.813	1.813
F000	468.0	468.0
F000’	467.47	
h,k,lmax	7,15,18	7,15,18
Nref	3892	3854
Tmin,Tmax	0.452,0.709	0.728,0.928
Tmin’	0.379	

Correction method= # Reported T Limits: Tmin=0.728 Tmax=0.928
AbsCorr = MULTI-SCAN

Data completeness= 0.990 Theta(max)= 26.415

R(reflections)= 0.0303(3441) wR2(reflections)= 0.0767(3854)

S = 1.012 Npar= 228

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT919_ALERT_3_B Reflection # Likely Affected by the Beamstop ... 1 Check

Alert level C

PLAT222_ALERT_3_C Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range 4.3 Ratio
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 27 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) . 1 Check
PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. 1 Check
PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S . 13.20 Check

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as mixed Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.003 Degree
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C7 Check
PLAT793_ALERT_4_G Model has Chirality at C11 (Centro SPGR) R Verify
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT898_ALERT_4_G Second Reported H-M Symbol in CIF Ignored ..... ! Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 9 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 7 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
7 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT222_mr05561
;
PROBLEM: Non-Solv.  Resd 1  H   Uiso(max)/Uiso(min) Range       4.3 Ratio
RESPONSE: ...
;
_vrf_PLAT911_mr05561
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600        27 Report
RESPONSE: ...
;
_vrf_PLAT918_mr05561
;
PROBLEM: Reflection(s) with I(obs) much Smaller I(calc) .         1 Check
RESPONSE: ...
;
_vrf_PLAT934_mr05561
;
PROBLEM: Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..         1 Check
```

```
RESPONSE: ...
;
_vrf_PLAT939_mr05561
;
PROBLEM: Large Value of Not (SHELXL) Weight Optimized S .      13.20 Check
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

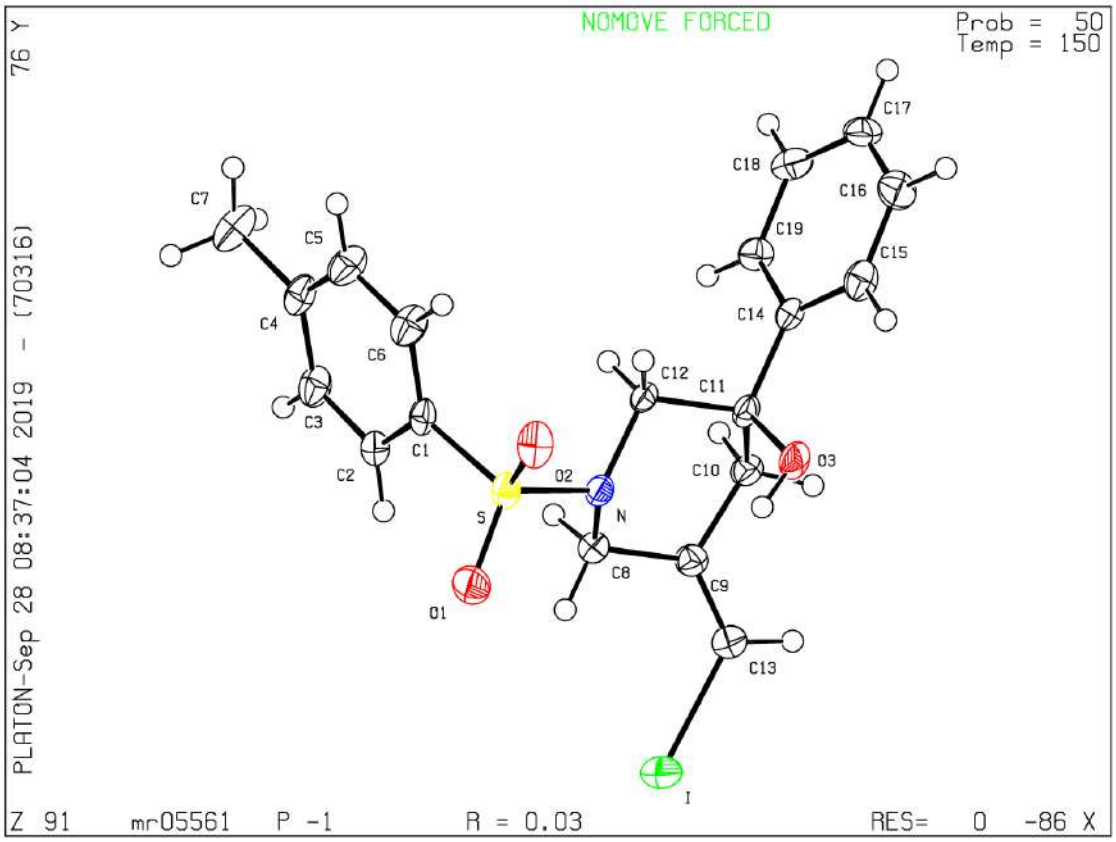
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock mr05561 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mr06

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: mr06

Bond precision: C-C = 0.0023 A Wavelength=0.71073

Cell: a=16.7081(9) b=9.0554(5) c=15.2793(8)
alpha=90 beta=117.039(2) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	2059.1(2)	2059.1(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C25 H23 N O3 S	C25 H23 N O3 S
Sum formula	C25 H23 N O3 S	C25 H23 N O3 S
Mr	417.50	417.50
Dx,g cm-3	1.347	1.347
Z	4	4
Mu (mm-1)	0.185	0.185
F000	880.0	880.0
F000’	880.87	
h,k,lmax	21,11,19	21,11,19
Nref	4563	4550
Tmin,Tmax	0.907,0.937	0.840,0.928
Tmin’	0.907	

Correction method= # Reported T Limits: Tmin=0.840 Tmax=0.928
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 27.141

R(reflections)= 0.0382(3817) wR2(reflections)= 0.1158(4550)

S = 1.004 Npar= 271

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT905_ALERT_3_C	Negative K value in the Analysis of Variance ...	-0.138 Report
PLAT910_ALERT_3_C	Missing # of FCF Reflection(s) Below Theta(Min).	7 Note
PLAT977_ALERT_2_C	Check Negative Difference Density on H7A	-0.32 eA-3

Alert level G

PLAT380_ALERT_4_G	Incorrectly? Oriented X(sp2)-Methyl Moiety	C7 Check
PLAT793_ALERT_4_G	Model has Chirality at C9 (Centro SPGR)	S Verify
PLAT793_ALERT_4_G	Model has Chirality at C11 (Centro SPGR)	R Verify
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT898_ALERT_4_G	Second Reported H-M Symbol in CIF Ignored	! Check
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	6 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	16 Info

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7 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT905_mr06
;
PROBLEM: Negative K value in the Analysis of Variance ...     -0.138 Report
RESPONSE: ...
;
_vrf_PLAT910_mr06
;
PROBLEM: Missing # of FCF Reflection(s) Below Theta(Min).          7 Note
RESPONSE: ...
;
_vrf_PLAT977_mr06
;
PROBLEM: Check Negative Difference Density on H7A              -0.32 eA-3
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock mr06 - ellipsoid plot