One-Pot Acid-Catalyzed Ring-Opening/Cyclization/Oxidation of Aziridines with *N*-Tosylhydrazones: Access to 1,2,4-Triazines

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1. General experimental methods

Solvent and reagents: All reactions were carried out under an argon atmosphere using oven-dried glassware unless using aqueous reagents. Unless otherwise stated, reagents were obtained from commercial sources and used without further purification. Anhydrous diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), toluene and tethrahydrofuran (THF) were obtained by the method of Grubbs and Pangborn.[1]

Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck 60 F254), visualised using ultraviolet light (254 nm) or an alkaline solution of potassium permanganate.

Flash column chromatography (FCC) was performed using high-purity grade silica gel Merck grade with 60-120 mesh particle size under air pressure. If necessary, the purification was performed using Florisil® with 100-200 mesh particle size for compounds sensitive to acidic media. All solvents used for chromatographic purification were distilled prior to use.

NMR characterisation: ^{1}H-NMR spectra were recorded on a DRX-600 spectrometer at 600 MHz and are reported as follows: chemical shift δ in ppm (multiplicity, coupling constants *J* in Hz, number of protons, assignment). The multiplicity and shape of the ^{1}H signals are designated by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, or combinations of thereof. All chemical shifts δ are reported to the nearest 0.01 (^{1}H) / 0.1(^{13}C) ppm, relative to the residual protic solvent as the internal reference ($CDCl_3$ = 7.26 (^{1}H) / 77.16 (^{13}C) ppm, $CO(CD_3)_2$ = 2.05 (^{1}H) / 29.84 (^{13}C) ppm, CD_3CN = 1.94 (^{1}H) / 1.32 (^{13}C) ppm, d^8-THF = 3.58, 1.73 (^{1}H) / 67.57, 25.37 (^{13}C) ppm). ^{19}F-NMR spectra were recorded on a Bruker DPX-400 spectrometer at 376 MHz with ^{1}H decoupling. All chemical shifts δ are reported to the nearest 0.1 ppm with $CFCl_3$ as the external standard ($CFCl_3$ = 0.0 ppm). ^{11}B-NMR spectra were recorded on a DRX-600 spectrometer 193 MHz with ^{1}H decoupling. All chemical shifts δ are reported to the nearest 0.1 ppm with $BF_3.OEt_2$ as the external standard ($BF_3{\cdot}OEt_2$ = 0.0 ppm). Spectra were assigned using ^{1}H-COSY, DEPT-135, HSQC and HMBC where appropriate to facilitate structural determination.

Infrared spectra were recorded neat as thin films on a Perkin-Elmer Spectrum One FTIR spectrometer. Absorbances were recored in the range 4000-650 cm^{-1}. The intensity and shape of the signals are designated by the following abbreviations: w = weak, m = medium, s = strong, br. = broad.

High resolution mass spectrometry (HRMS) was performed using a Waters Micromass LCT Premier™ spectrometer using time of flight mass detection and positive electrospray ionization method (+ESI). All reported values are within 5 ppm of the calculated value.

Melting points were recorded on a Stuart Scientific SMP3 melting point apparatus.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, R. J. *Organometallics* **1996**, *15*, 1518.

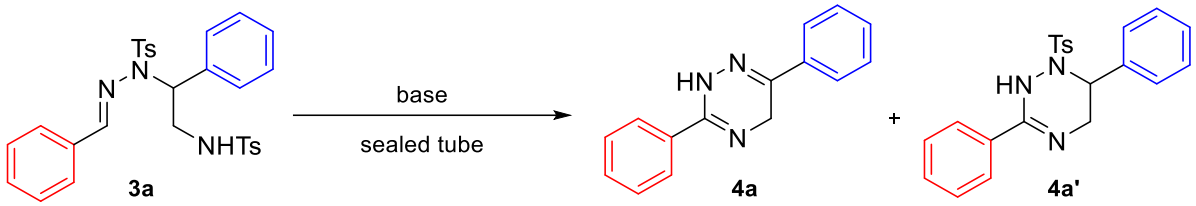
2. Optimisation of the “one-pot” procedure

The second and third steps were first optimized separately.

Second step

Table 1: Optimisation of the cyclization of aminohydrazone **3a**.

The optimisation process for the second step was attempted with the aminohydrazone **3a** (Table 1). All the reactions were performed in a sealed tube. No reaction occurred by heating the starting material at 110 °C in toluene for 2 h while only degradation was observed after 18 h (entries 1 and 2). The addition of cesium carbonate to the aminohydrazone in toluene at rt resulted in the recovery of the starting material (entry 3). Heating the mixture at 110 °C was necessary to observe conversion of the starting material. 1.1 equivalent of Cs_2CO_3 only afforded the compound **4a**' in 33% yield (entry 4). Increasing the amount of the base to 3 equivalents allowed the formation of the dihydrotriazine **4a** with 36% yield (entry 5). The cyclization step was found to be very dependant on the nature of the base, as potassium carbonate, triethylamine, guanidine, $CsHCO_3$ and *t*BuOK only led to recovery of the starting material or degradation (entries 7 to 11). DBU was found to be effective but never led to complete conversion, resulting in lower yield of **4a** compared to Cs_2CO_3 (entry 12). As the hydrolysis of the aminohydrazone was found to be the major by-product of the reaction into the corresponding aldehyde, addition of molecular sieves or $MgSO_4$ was attempted, but these resulted in a strong decrease in the conversion (entries 13 and 14). To finish, the solvent was changed to dichloroethane but only a mixture of several products was observed.



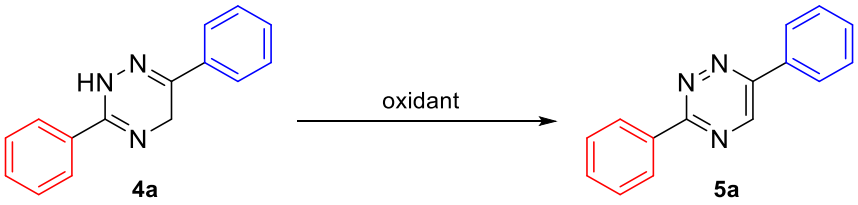
entry	base (equiv)	solvent	T (°C)	time (h)	conversion (%)	yield 4a (%)	yield 4a' (%)
1	/	toluene	110	2	0[a]	/	/
2	/	toluene	110	18	/[b]	/	/
3	Cs_2CO_3 (1.1)	toluene	25	18	0[a]	/	/
4	Cs_2CO_3 (1.1)	toluene	110	2	100	/	33
5	**Cs_2CO_3 (3)**	**toluene**	**110**	**2**	**100**	**36**	**/**
6	Cs_2CO_3 (3)	toluene	80	18	100	Mixture[c]	
7	K_2CO_3 (3)	toluene	110	2	0[a]	/	/
8	$CsHCO_3$ (3)	toluene	110	2	0[a]	/	/
9	Et_3N (3)	toluene	110	2	0[a]	/	/
10	Guanidine (3)	toluene	110	2	/[b]	/	/
11	*t*BuOK (3)	toluene	110	2	/[b]	/	/
12	DBU (3)	toluene	110	2	>90	30	/
13	Cs_2CO_3 (3)[e]	toluene	110	2	66	2	/
14	Cs_2CO_3 (3)[f]	toluene	110	2	0[a]	/	/
15	Cs_2CO_3 (3)	dichloroethane	110	2	100	/[d]	/[d]

[a] no reaction. [b] degradation of the starting material. [c] Mixture of **4a** and **4a'** and degradation observed. [d] mixture of several unknown products. [e] Addition of 3Å MS. [f] Addition of $MgSO_4$.

Third step

The optimisation process for the oxidation was attempted with dihydrotriazine **4a** (Table 2). Potassium permanganate ($KMnO_4$) was found to be an efficient oxidant for the reaction but was not chosen due to its strong oxidant behaviour limiting substrate scope (entry 1). DDQ (2,3-Dichloro-5,6-Dicyanobenzoquinone), while leading to the product, prevented the isolation of the triazines with high purity (entry 2). Fortunately, both activated MnO_2 and the mixture $K_3Fe(CN)_6/NaOH_{aq}$ allowed the formation of the triazine **5a** with excellent yields.

Table 2: Optimisation of oxidation step using dihydrotriazine **4a**.



4a **5a**

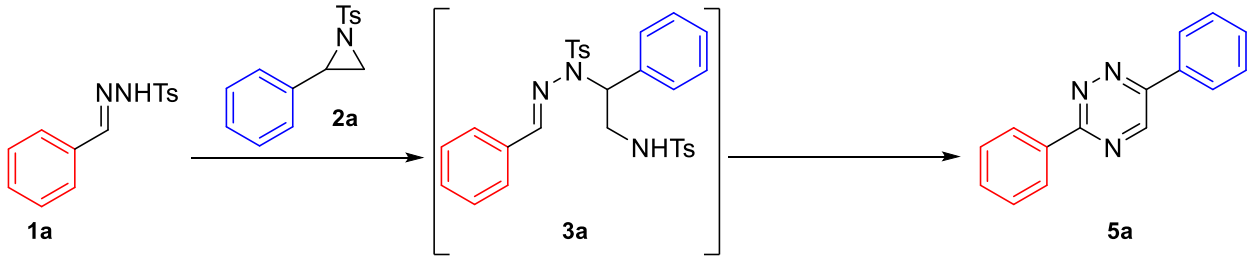
entry	oxidant (equiv)	solvent	T (°C)	time (h)	conversion (%)	yield 5a (%)
1	$KMnO_4$ (3)	acetone	rt	1	100	90
2	DDQ (1.5)	THF	rt	1.5	100	>100[b]
3	MnO2 (11)	CH_2Cl_2	rt reflux	6 3	0[a] 2	/
4	activated MnO_2 (5)	toluene	60	1	100	**88**
5	$K_3Fe(CN)_6$, $NaOH_{aq}$ (5)	toluene	rt	1	100	**90**

[a] no reaction. [b] the by-product resulting from the reduction of DDQ was found to co-elute with the triazine.

"One-pot" procedure

To finish, the merging of the three steps was attempted. The yield could be enhanced from 29 to 37% by merging the second and third steps using manganese dioxide as the oxidant (entries 1 and 2). In this case, 3.5 equivalents of Cs_2CO_3 was needed, as well as a strong excess of the oxidant. Moreover, the addition of the MnO_2 in 3 portions was necessary as adding it in one portion led only to uncomplete conversion to the dihydrotriazine intermediate. The use of sealed tube or reflux to perform the reaction was possible and resulted in similar yields (entries 2 and 3). The use of MnO_2 was found to be critical as the mixture $K_3Fe(CN)_6$, $NaOH_{aq}$ led to more by-products, inseparable from the desired triazine (entry 4). To finish, the one-pot procedure allowed the formation of the product with 41% overall yield (entry 5).

Table 3: Optimisation of one-pot procedure leading to the triazine **5a**.



entry	step 1	step 2	step 3	global yield 5a (%)
1	$BF_3.OEt_2$ (0.2 equiv), CH_2Cl_2, rt, 1 h 91%	Cs_2CO_3 (3 equiv), toluene, sealed tube, 2 h 36%	activated MnO_2 (5 equiv), toluene, 60 °C, 2 h 88%	29
2	$BF_3.OEt_2$ (0.2 equiv), CH_2Cl_2, rt, 1 h 91%	Cs_2CO_3 (3.5 equiv), MnO_2 (6+4+4 equiv), toluene, sealed tube, 3 h 41%		37
3	$BF_3.OEt_2$ (0.2 equiv), CH_2Cl_2, rt, 1 h 91%	Cs_2CO_3 (3.5 equiv), MnO_2 (6+4+4 equiv), toluene, reflux, 3 h 39%		35
4	$BF_3.OEt_2$ (0.2 equiv), CH_2Cl_2, rt, 1 h 91%	Cs_2CO_3 (3 equiv), toluene, reflux, 3h then $K_3Fe(CN)_6$ (3 equiv)/$NaOH_{aq}$ (5 equiv), rt, 18 h 35%[a]		32[a]
5	**$BF_3.OEt_2$ (0.2 equiv), CH_2Cl_2, rt, 1 h then Cs_2CO_3 (3.5 equiv), MnO_2 (6+4+4 equiv), toluene, reflux, 3 h**			**41**

[a] Product isolated with an impurity, impossible to separate by usual purification.

3. Synthetic procedure and characterisation data

3.1. Preparation of hydrazones **1a-1o**

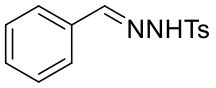
General procedure A[2]

The aldehyde (1.0 equiv) was added dropwise/portionwise to a suspension of tosylhydrazide (1.0 equiv) in MeOH (1 M). A midly exothermic reaction ensued and the hydrazide dissolved. The reaction mixture then was stirred at room temperature until complete conversion was observed by TLC.

A1 : If the hydrazone precipitated, the mixture was cooled to 0 °C and the solid was filtered, washed with a small quantity of cold MeOH and dried *in vacuo* to give the title compound **1**.

A2 : If not, the solvent was removed *in vacuo* and the crude solid was dissolved in dichloromethane or diethylether and was precipitated with petroleum ether (PE). The solid was filtered, washed with petroleum ether and dried *in vacuo* to give the title compound **1**.

N'-benzylidene-4-methylbenzenesulfonohydrazide (1a)

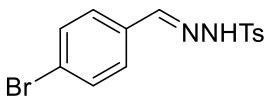


Prepared according to procedure **A1**, the title compound was isolated as a white solid (90%) with spectral data in agreement with literature values.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.21 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 1H), 7.57 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.37-7.32 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 147.9, 144.3, 135.3, 133.2, 130.4, 129.7, 128.6, 127.9, 127.4, 21.6.

N'-(4-bromobenzylidene)-4-methylbenzenesulfonohydrazide (1b)

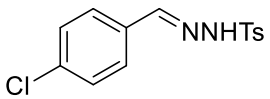


Prepared according to procedure **A1**, the title compound was isolated as a white solid (81%) with spectral data in agreement with literature values.[3]

^{1}H NMR (600 MHz, $CO(CD_3)_2$): δ/ppm 10.23 (s, 1H), 7.97 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.58-7.55 (m, 4H), 7.40 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CO(CD_3)_2$): δ/ppm 145.7, 143.8, 136.6, 133.4, 131.8, 129.5, 128.6, 127.7, 123.6, 20.5.

N'-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (1c)



Prepared according to procedure **A1**, the title compound was isolated as a white solid (91%) with spectral data in agreement with literature values.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.17 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.72 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 4H), 2.41 (s, 3H).

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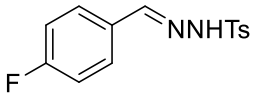
[2] Aggarwal, V. K.; Fulton, J. R.; Sheldon, C. G.; De Vicente, J. *J. Am. Chem. Soc.* **2003**, *125*, 6034.
[3] Liu, P.; Xu, Q-Q.; Dong, C.; Lei, X.; Lin, G-Q. *Synlett*, **2012**, *23*, 2087.

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 146.4, 144.4, 136.4, 135.1, 131.7, 129.8, 129.0, 128.5, 127.9, 21.6.

N'-(4-fluorobenzylidene)-4-methylbenzenesulfonohydrazide (1d)

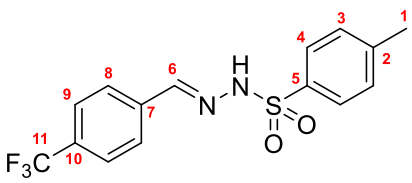


Prepared according to procedure **A2**, the title compound was isolated as a white solid (86%) with spectral data in agreement with literature values.[4]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.23 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 1H), 7.55-7.54 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 164.0 (d, *J* = 240 Hz), 146.7, 144.4, 135.2, 129.7, 129.4 (d, *J* = 3 Hz), 129.2 (d, *J* = 9 Hz), 127.9, 115.8 (d, *J* = 22 Hz), 21.6.

N'-(4-trifluoromethylbenzylidene)-4-methylbenzenesulfonohydrazide (1e)



Prepared according to procedure **A2**, the title compound was isolated as a white solid (79%).

R*f*: 0.14 (4/1 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.48 (s, 1H, NH), 7.89 (d, *J* = 8.4 Hz, 2H, H^4), 7.80 (s, 1H, H^6), 7.67 (d, *J* = 7.8 Hz, 2H, H^8), 7.59 (d, *J* = 7.8 Hz, 2H, H^9), 7.33 (d, *J* = 8.4 Hz, 2H, H^3), 2.41 (s, 3H, H^1).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -62.9.

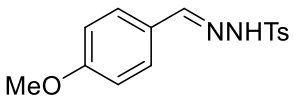
^{13}C NMR (150 MHz, $CDCl_3$) : δ/ppm 145.6 (C^6), 144.6 (C^2), 136.5 (C^7), 135.0 (C^5), 131.9 (q, $^2J_{CF}$ = 33 Hz, C^{10}), 129.8 (C^3), 127.9 (C^4), 127.4 (C^8), 125.6 (q, $^3J_{CF}$ = 4 Hz, C^9), 123.8 (q, $^1J_{CF}$ = 270 Hz, C^{11}), 21.6 (C^1).

M.p.: 148-150 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3204 (m), 1619 (w), 1599 (w), 1496 (w), 1448 (w), 1413 (w), 1362 (m), 1326 (s), 1312 (s-sh), 1298 (m-sh), 1226 (w), 1188 (w), 1161 (s), 1121 (s), 1106 (m), 1066 (s), 1019 (m), 954 (m), 941 (s), 835 (s), 814 (m), 761 (w), 703 (m), 673 (s), 662 (s).

HRMS (ESI+): m/z calcd for $C_{15}H_{14}F_3N_2O_2S$: 343.0728, found 343.0727 $[M+H]^+$.

N'-(4-methoxybenzylidene)-4-methylbenzenesulfonohydrazide (1f)



Prepared according to procedure **A2**, the title compound was isolated as a white solid (87%) with spectral data in agreement with literature values.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.12 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.73 (s, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.39 (s, 3H).

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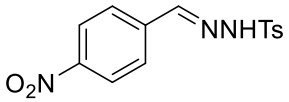
[4] Aggarwal, V. K.; Alonso, E.; Bae, I.; Hynd, G.; Lydon, K. M.; Palmer, M. J.; Patel, M.; Porcelloni, M.; Richardson, J.; Stenson, R. A.; Studley, J. R.; Vasse, J-L.; Winn, C. L. *J. Am. Chem. Soc*. **2003**, *125*, 10926.

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 161.4, 148.3, 144.2, 135.3, 129.7, 129.0, 127.9, 125.9, 114.1, 55.4, 21.6.

N'-(4-nitrobenzylidene)-4-methylbenzenesulfonohydrazide (1g)

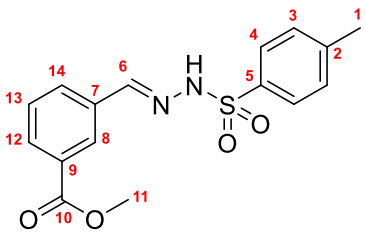


Prepared according to procedure **A1,** the title compound was isolated as a pale yellow solid (90%) with spectral data in agreement with literature values.[4]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.42 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 148.6, 144.8, 144.0, 139.0, 134.9, 129.9, 127.9, 127.8, 124.0, 21.6.

Methyl 3-((2-tosylhydrazono)methyl)benzoate (1h)



Prepared according to procedure **A1**, the title compound was isolated as a white solid (90%).

R*f*: 0.26 (6/4 hexane/EtOAc).

^{1}H NMR (600 MHz, $CO(CD_3)_2$): δ/ppm 10.33 (s, 1H, NH), 8.21 (s, 1H, H^{8}), 8.08 (s, 1H, H^{6}), 8.00 (d, *J* = 7.2 Hz, 1H, H^{12}), 7.88 (d, *J* = 7.2 Hz, 1H, H^{14}), 7.85 (d, *J* = 8.4 Hz, 2H, H^{4}), 7.54 (t, *J* = 7.2 Hz, 1H, H^{13}), 7.40 (d, *J* = 8.4 Hz, 2H, H^{3}), 3.90 (s, 3H, H^{11}), 2.39 (s, 3H, H^{1}).

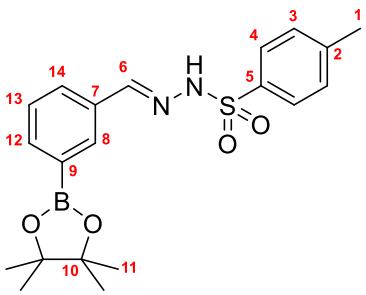
^{13}C NMR (150 MHz, $CO(CD_3)_2$): δ/ppm 165.8 (C^{10}), 145.9 (C^{6}), 143.9 (C^{2}), 136.6 (C^{5}), 134.7 (C^{7}), 130.9 (C^{14}), 130.8 (C^{9}), 130.5 (C^{12}), 129.5 (C^{3}), 129.0 (C^{13}), 127.7 (C^{8}), 127.6 (C^{4}), 51.6 (C^{11}), 20.5 (C^{1}).

M.p.: 160-162 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3240 (w), 3166 (w), 2957 (w), 1710 (s), 1694 (s), 1597 (w), 1435 (m), 1415 (w), 1362 (m), 1324 (m), 1304 (s), 1286 (s), 1217 (s), 1187 (w), 1160 (s), 1119 (m), 1091 (m), 1058 (m), 1020 (w), 987 (w), 963 (w), 946 (s), 868 (s), 809 (m), 752 (s), 704 (m), 684 (w), 682 (s), 672 (s).

HRMS (ESI+): m/z calcd for $C_{16}H_{16}N_2O_4S_2$: 332.0831, found 332.0833 $[M]^+$, 355.0725 $[M+Na]^+$.

4-methyl-N'-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)benzenesulfonohydrazide (1i)



Prepared according to procedure **A2**, the title compound was isolated as a white solid (88%).

R*f*: 0.39 (5/5 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.96 (s, 1H, NH), 7.88-7.87 (m, 3H, H^{4} and H^{8}), 7.80 (dt, *J* = 7.3, 1.2 Hz, 1H, H^{12}/H^{14}), 7.79 (dt, *J* = 7.8, 1.5 Hz, 1H, H^{12}/H^{14}), 7.77 (s, 1H,

H^6), 7.37 (t, J = 7.6 Hz, 1H, H^{13}), 7.31 (d, J = 8.4 Hz, 2H, H^3), 2.40 (s, 3H, H^1), 1.34 (s, 12H, H^{11}).

^{11}B NMR (193 MHz, $CDCl_3$): δ/ppm 30.0.

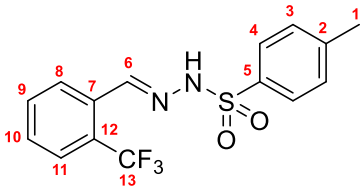
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 147.9 (C^6), 144.2 (C^2), 136.8 (C^{12}), 135.3 (C^5), 134.6 (C^8), 132.5 (C^7), 129.7 (C^3), 129.2 (C^{14}), 128.1 (C^{13}), 127.9 (C^4), 84.1 (C^{10}), 24.9 (C^{11}), 21.6 (C^1). The quaternary carbon C^9 was not observed.

M.p.: 180-182 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3194 (w-br), 2979 (w), 2929 (w), 2875 (w), 1599 (w), 1411 (m), 1356 (s), 1323 (s), 1276 (m), 1215 (m), 1184 (w), 1162 (s), 1141 (s), 1093 (m), 1052 (m), 956 (m), 879 (m), 852 (m), 812 (m), 800 (m), 703 (s), 667 (s).

HRMS (ESI+): m/z calcd for $C_{20}H_{25}BN_2O_4S$: 400.1628, found 400.1634 $[M]^{+,}$ 423.1526 $[M+Na]^+$.

N'-(2-trifluoromethylbenzylidene)-4-methylbenzenesulfonohydrazide (1j)



Prepared according to procedure **A2**, the title compound was isolated as a white solid (47%).

R*f*: 0.44 (8/2 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.37 (s, 1H, NH), 8.08-8.06 (m, 2H, H^6 and H^8), 7.89 (d, J = 8.4 Hz, 2H, H^4), 7.62 (d, J = 7.8 Hz, 1H, H^{11}), 7.53 (t, J = 7.8 Hz, 1H, H^9), 7.45 (t, J = 7.8 Hz, 1H, H^{10}), 7.33 (d, J = 8.4 Hz, 2H, H^3), 2.41 (s, 3H, H^1).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -57.8.

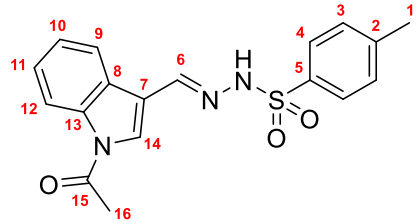
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.5 (C^2), 142.7 (q, $^4J_{CF}$ = 1.9 Hz, C^6), 135.2 (C^5), 132.0 (C^9), 131.2 (C^7), 129.8 (C^{10}), 129.7 (C^3), 128.2 (q, $^2J_{CF}$ = 31 Hz, C^{12}), 127.9 (C^4), 127.4 (C^8), 125.7 (q, $^3J_{CF}$ = 6 Hz, C^{11}), 123.9 (q, $^1J_{CF}$ = 270 Hz, C^{13}), 21.6 (C^1).

M.p.: 130-134 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3195 (w), 3000-2870 (w), 1598 (w), 1573 (w), 1494 (w), 1449 (w), 1401 (w), 1377 (w), 1311 (s), 1282 (m), 1216 (w), 1187 (w), 1158 (s), 1108 (s), 1052 (m), 1029 (m), 956 (m), 947 (m), 936 (w-sh), 835 (m), 809 (s), 760 (s), 745 (w), 704 (m), 678 (s), 658 (s).

HRMS (ESI+): m/z calcd for $C_{15}H_{13}F_3N_2O_2S$: 342.0650, found 342.0653 $[M]^+$, 365.0545 $[M+Na]^+$.

N'-((1-acetyl-1H-indol-3-yl)methylene)-4-methylbenzenesulfonohydrazide (1k)



Prepared according to procedure **A1**, the title compound was isolated as a white solid (88%).

R*f*: 0.07 (6/4 hexane/EtOAc).

^{1}H NMR (600 MHz, $CO(CD_3)_2$): δ/ppm 10.07 (s, 1H, NH), 8.39-8.38 (m, 1H, H^9), 8.27-8.26 (m, 1H, H^{12}), 8.18 (s, 1H, H^6), 8.05 (s, 1H, H^{14}), 7.90 (d, *J* = 8.4 Hz, 2H, H^4), 7.41-7.36 (m, 4H, H^3, H^{10} and H^{11}), 2.66 (s, 3H, H^{16}), 2.36 (s, 3H, H^1).

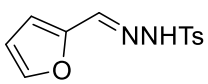
^{13}C NMR (150 MHz, $CO(CD_3)_2$): δ/ppm 168.9 (C^{15}), 143.8 (C^2), 142.4 (C^6), 136.5 (C^5), 136.4 (C^{13}), 129.9 (C^{14}), 129.5 (C^3), 127.8 (C^4), 126.9 (C^8), 125.7 (C^{10}), 124.1 (C^{11}), 122.5 (C^{12}), 117.0 (C^7), 116.1 (C^9), 23.0 (C^{16}), 20.5 (C^1).

M.p.: 184-186 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3185 (m), 1706 (s), 1621 (m), 1605 (w), 1596 (w), 1557 (w), 1495 (w), 1480 (w), 1449 (m), 1384 (m), 1360 (m), 1342 (m), 1330 (m), 1311 (m), 1304 (m-sh), 1253 (w), 1223 (m), 1166 (s), 1128 (m), 1096 (w), 1045 (w), 1020 (m), 947 (w), 924 (m), 819 (m), 800 (w), 787 (w), 764 (w), 750(m), 724 (w), 705 (w), 683 (m).

HRMS (ESI+): m/z calcd for $C_{18}H_{17}N_3O_3S$: 355.0991, found 355.0982 $[M]^+$, 378.0874 $[M+Na]^+$.

N'-(furan-2-ylmethylene)-4-methylbenzenesulfonohydrazide (1l)

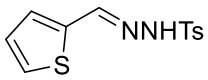


Prepared according to procedure **A2**, the title compound was isolated as a pale brown solid (80%) with spectral data in agreement with literature values.[4,5]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.19 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.72 (s, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 3.6 Hz, 1H), 6.43 (dd, *J* = 3.6, 1.8 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 148.6, 144.7, 144.4, 138.4, 135.2, 129.7, 127.9, 113.5, 111.8, 21.6.

N'-(thiophen-2-ylmethylene)-4-methylbenzenesulfonohydrazide (1m)

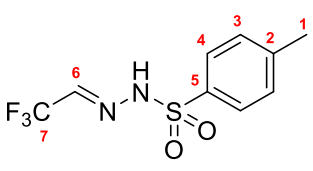


Prepared according to procedure **A2**, the title compound was isolated as a white solid (88%) with spectral data in agreement with literature values.[3]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.01 (s, 1H), 7.98 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 4.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 (dd, *J* = 3.6, 0.6 Hz, 1H), 7.00 (dd, *J* = 4.8, 3.6 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.3, 143.4, 137.9, 135.1, 130.3, 129.7, 128.8, 128.0, 127.4, 21.6.

4-methyl-N'-(2,2,2-trifluoroethylidene)benzenesulfonohydrazide (1n)



A solution of tosylhydrazide (1.86 g, 10 mmol, 1 equiv) in MeOH (6 mL, 1.67 M) was heated to 60 °C until the hydrazide was completely dissolved. Then, the 2,2,2-trifluoro-1-methoxyethanol (1.43 mL, 13 mmol, 1.3 equiv) was dropped slowly to the mixture. After heating at 60 °C for 18 h, the reaction was cooled to room

[5] Kabalka, G. W.; Maddox, J. T.; Bogas, E.; Kelley, S. W. *J. Org. Chem.* **1997**, *62*, 3688.

temperature and concentrated *in vacuo*. The residue was recrystallized with diethyl ether/hexane to afford 2.86 g of the desired product as a white solid with a quantitative yield.[3]

R*f*: 0.25 (8/2 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.60 (s, 1H, NH), 7.82 (d, *J* = 8.4 Hz, 2H, H^4), 7.36 (d, *J* = 8.4 Hz, 2H, H^3), 7.14 (q, *J* = 3.6 Hz, 1H, H^6), 2.45 (s, 3H, H^1).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -67.8.

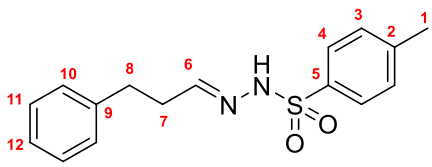
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 145.4 (C^2), 134.1 (C^5), 132.6 (q, $^{2}J_{CF}$ = 40 Hz, C^6), 130.0 (C^3), 128.0 (C^4), 119.3 (q, $^{1}J_{CF}$ = 272 Hz, C^7), 21.7 (C^1).

M.p.: 118-120 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3212 (w), 1635 (w), 1598 (w), 1366 (s), 1328 (m), 1288 (m), 1167 (s), 1121 (m), 1070 (s), 951 (m), 903 (w), 849 (m), 815 (m), 701 (m), 661 (s).

HRMS (ESI+): m/z calcd for $C_9H_{10}F_3N_2O_2S$: 267.0415, found 267.0420 $[M+H]^+$.

4-methyl-N'-(3-phenylpropylidene)benzenesulfonohydrazide (1o)



Prepared according to procedure **A2**, the title compound was isolated as a pale white solid (87%).

R*f*: 0.09 (8/2 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.80 (d, *J* = 8.4 Hz, 2H, H^4), 7.50 (s, 1H, NH), 7.32 (d, *J* = 8.4 Hz, 2H, H^3), 7.25 (t, *J* = 7.2 Hz, 2H, H^{11}), 7.22-7.17 (m, 1H, H^{12}), 7.11 (d, *J* = 7.2 Hz, 2H, H^{10}), 2.79 (t, *J* = 7.2 Hz, 2H, H^8), 2.58-2.46 (m, 2H, H^7), 2.45 (s, 3H, H^1).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 151.6 (C^6), 144.1 (C^2), 140.4 (C^9), 135.3 (C^5), 129.6 (C^3), 128.5 (C^{11}), 128.3 (C^{10}), 127.9 (C^4), 126.2 (C^{12}), 33.7 (C^8), 32.2 (C^7), 21.6 (C^1).

M.p.: 113-115 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3211 (w), 1597 (w), 1498 (w), 1435 (w), 1354 (m), 1319 (m), 1161 (s), 1092 (w), 1037 (m), 895 (m), 816 (m), 672 (s).

HRMS (ESI+): m/z calcd for $C_{16}H_{19}N_2O_2S$: 303.1167, found 303.1169 $[M+H]^+$.

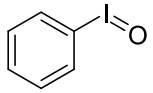
3.2. Preparation of tosylaziridines **2a-2k** and their precursors

General procedure B for the synthesis of alkene precursors

Following a typical Wittig reaction procedure, the alkyl phosphonium bromide (1.1 equiv) was suspended in THF (0.2 M) and the reaction mixture was cooled to 0 °C. *n*BuLi (1.1 equiv, 2.5 M in hexane) was added dropwise and the mixture was sitrred for 15 min. Then, a solution of the aldehyde (1 equiv) in THF (1 mL/mmol) was added dropwise. After 1 h, the reaction mixture was warmed to rt and stirred for 2 h. Sat. NH_4Cl was then added, the two phases separated and the aqueous phase was extracted with diethyl ether (x3). The

organic phase was dried over $MgSO_4$, filtered and solvent was removed *in vacuo*. The crude was purified by silica gel chromatography (95/5 hexane/EtOAc) to yield the desired alkene precursor.

Preparation of iodosylbenzene PhIO[6]

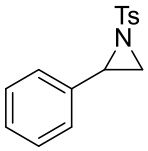


To iodosobenzene diacetate (7.73 g, 24 mmol) placed in a 250 mL conical flask was added 35 mL of a 3 N sodium hydroxide solution over a period of 10 min. The resulting yellow heterogeneous mixture was then stirred for 90 min at rt. The reaction medium was diluted with 40 mL of water and vigorously stirred for an additional hour. The yellow solid was collected on a Büchner funnel, washed with water (2 x 100 mL) and chloroform (100 mL) before being dried under vacuum for 6 h. Iodosylbenzene was obtained as a yellow powder (4.75 g, 21.6 mmol, 90%).

General procedure C for the synthesis of tosylaziridine[7,8]

In an oven-dried round bottom flask under Argon were introduced $Cu(MeCN)_4PF_6$ (0.1 equiv), $TsNH_2$ (1.4 equiv), activated 3Å MS (1 g/mmol of alkene), MeCN (0.4 M) and the corresponding alkene (1 equiv). PhIO (1.4 equiv) was introduced in one portion at 0 °C. The suspension was allowed to warm to rt and stirred overnight. The suspension was then filtered through a pad of celite and washed with MeCN (10 mL/mmol of alkene) then EtOAc (10 mL/mmol of alkene). The solvent was removed *in vacuo* and the residue was purified by column chromatography (hexane/EtOAc), yielding the desired aziridine **2**.

2-phenyl-1-tosylaziridine (2a)

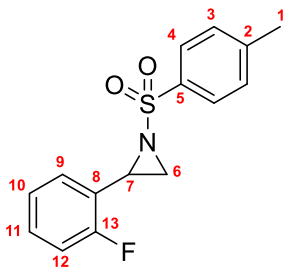


Following procedure **C**, the title compound was isolated as a white solid (57%) with spectral data in agreement with literature values.[9]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.88 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.32-7.28 (m, 3H), 7.23-7.22 (m, 2H), 3.78 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.00 (d, *J* = 7.2, 1H), 2.44 (s, 3H), 2.40 (d, J = 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.6, 135.1, 135.0, 129.7, 128.6, 128.3, 127.9, 126.6, 41.0, 35.9, 21.6.

2-(2-fluorophenyl)-1-tosylaziridine (2b)



Following procedure **C,** the title compound was isolated as a white solid (77%).

R*f*: 0.17 (8/2 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.88 (d, *J* = 8.4 Hz, 2H, H^4), 7.35 (d, *J* = 8.4 Hz, 2H, H^3), 7.25-2.22 (m, 1H, H^{11}), 7.13 (td, *J* = 7.6, 1.6 Hz, 1H, H^9), 7.05 (t, *J* = 7.6 Hz, 1H, H^{10}), 7.03-6.99 (m, 1H, H^{12}), 3.98 (dd, *J* = 7.2, 4.8 Hz, 1H, H^7), 3.02 (d, *J* = 7.2 Hz, 1H, H^6), 2.44 (s, 3H, H^1), 2.41 (d, *J* = 4.8 Hz, 1H, H^6).

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[6] Muller, P.; Ghanem, A. *Org. Lett*. **2004**, *6*, 4347.
[7] Dauban, P.; Sanière, L.; Tarrade, A.; Dodd, R. H. *J. Am. Chem. Soc*. **2001,** *123*, 7707.
[8] Craig II, R. A.; O'Connor, N. R.; Goldberg, A. F. G.; Stoltz, B. M. *Chem. Eur. J.* **2014**, *20*, 4806.
[9] Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc*. **1994**, *116*, 2742.

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -119.4.

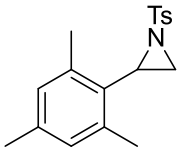
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 161.4 (d, $^2J_{CF}$ = 248 Hz, C^{13}), 144.8 (C^2), 134.7 (C^5), 129.8 (C^3), 129.7 (d, $^2J_{CF}$ = 13 Hz, C^{11}), 128.1 (C^4), 127.5 (d, $^3J_{CF}$ = 4 Hz, C^9), 124.3 (d, $^3J_{CF}$ = 4 Hz, C^{10}), 122.5 (d, $^2J_{CF}$ = 13 Hz, C^8), 115.3 (d, $^2J_{CF}$ = 21 Hz, C^{12}), 35.6 (d, $^3J_{CF}$ = 6 Hz, C^7), 35.1 (C^6), 21.7 (C^1).

M.p.: 48-50 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3054 (w), 2022 (w), 1589 (m), 1498 (s), 1462 (m), 1386 (m), 1319 (s), 1245 (s), 1209 (m), 1180 (m), 1160 (m), 1113 (s), 1093 (s), 1036 (w), 1020 (w), 984 (w), 910 (s), 831 (s), 809 (s), 761 (s), 736 (s), 696 (s), 658 (s).

HRMS (ESI+): m/z calcd for $C_{15}H_{14}FNO_2S$: 291.0729, found 291.0725 $[M]^+$, 314.0617 $[M+Na]^+$.

2-mesityl-1-tosylaziridine (2c)

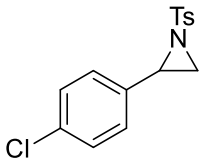


Following procedure **C,** the title compound was isolated as a white solid (44%) with spectral data in agreement with literature values.[10]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.88 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 2H), 3.86 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.94 (d, *J* = 7.2 Hz, 1H), 2.46 (s, 3H), 2.30 (s, 6H), 2.23 (s, 3H), 2.17 (d, *J* = 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.6, 137.5, 137.4, 135.1, 129.7, 128.3, 128.2, 39.4, 35.5, 21.6, 20.8, 20.1.

2-(4-chlorophenyl)-1-tosylaziridine (2d)

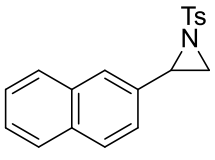


Following procedure **C,** the title compound was isolated as a white solid (50%) with spectral data in agreement with literature values.[9]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.86 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.74 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.98 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.35 (d, *J* = 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.8, 134.8, 134.2, 133.6, 129.8, 128.8, 127.9, 127.8, 40.3, 36.0, 21.7.

2-(naphthalen-2-yl)-1-tosylaziridine (2e)



Following procedure **C,** the title compound was isolated as a white solid (52%) with spectral data in agreement with literature values.[10]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.92 (d, *J* = 8.2 Hz, 2H), 7.82-7.76 (m, 3H), 7.74 (s, 1H), 7.50-7.45 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.28 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.94 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.08 (d, *J* = 7.2 Hz, 1H), 2.51 (d, *J* = 4.8 Hz, 1H), 2.43 (s, 3H).

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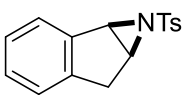
[10] (a) Vyas, R.; Gao, G-Y.; Harden, J. D.; Zhang, X. P. *Org. Lett.* **2004**, *6*, 1907. (b) Gao, G-Y.; Harden, J. D.; Zhang, X. P. *Org. Lett.* **2005**, *7*, 3191.

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.7, 135.0, 133.2, 133.0, 132.5, 129.8, 128.5, 128.0, 127.8, 127.7, 126.5, 126.3, 126.2, 123.7, 41.3, 36.0, 21.6.

(+/-)-(1*aR*,6*aS*)-1-tosyl-1,1a,6,6a-tetrahydroindeno[1,2-b]azirine (2f)

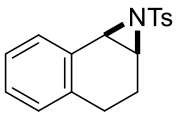


Following procedure **C,** the title compound was isolated as a beige solid (50%) as a single diastereoisomer (*cis*) with spectral data in agreement with literature values.[11]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.83 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.24 (td, *J* = 7.4, 1.2 Hz, 1H), 7.19-7.16 (m, 2H), 4.30 (d, *J* = 5.2 Hz, 1H), 3.91-3.90 (m, 1H), 2.15-2.14 (m, 1H), 2.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.4, 143.5, 138.2, 135.5, 129.7, 128.7, 127.7, 126.7, 125.6, 125.0, 50.1, 44.9, 34.6, 21.6.

(+/-)-(1*aS*,7*bR*)-1-tosyl-1a,2,3,7b-tetrahydro-1H-naphtho[1,2-b]azirine (2g)

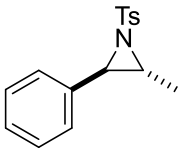


Following procedure **C,** the title compound was isolated as a beige solid (42%) as a single diastereoisomer (*cis*) with spectral data in agreement with literature values.[10]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.82 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 3H), 7.22 (td, *J* = 8.4, 1.2 Hz, 1H), 7.16 (t, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.4, 1H), 3.82 (d, *J* = 7.0, 1H), 3.56 (d, *J* = 7.0 Hz, 1H), 2.79-2.73 (m, 1H), 2.54 (dd, *J* = 15.5, 5.4 Hz, 1H), 2.42 (s, 3H), 2.28-2.24 (m, 1H), 1.71-1.65 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.3, 136.6, 136.5, 130.0, 129.7, 129.4, 128.6, 128.5, 127.6, 126.3, 42.1, 41.7, 24.7, 21.7, 21.0.

(+/-)-(2*R*,3*R*)-2-methyl-3-phenyl-1-tosylaziridine (2h)

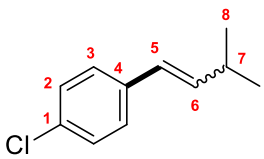


Following procedure **C,** the title compound was isolated as a pale yellow oil (61%) as a single diastereoisomer (*trans*) with spectral data in agreement with literature values.[10]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.84 (d, *J* = 8.4 Hz, 2H), 7.27-7.25 (m, 5H), 7.16-7.14 (m, 2H), 3.80 (d, *J* = 4.4 Hz, 1H), 2.94-2.90 (m, 1H), 2.40 (s, 3H), 1.85 (d, *J* = 6.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 143.9, 137.9, 135.6, 129.5, 128.5, 128.0, 127.2, 126.3, 49.2, 49.1, 21.6, 14.1.

(*Z/E*)-1-chloro-4-(3-methylbut-1-en-1-yl)benzene (6a)



Following procedure **B,** the title compound was isolated as a colorless oil (89%) as a mixture of alkenes (*Z/E* 67/33).

R*f*: 0.75 (8/2 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm (*alkene Z)* 7.30 (d, *J* = 8.4 Hz,

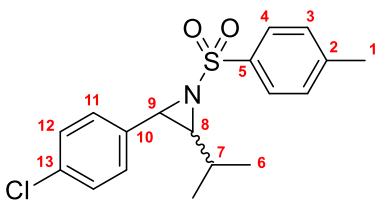
[11] Saikia, I.; Kashyap, B.; Phukan, P. *Chem. Commun*. **2011**, *47*, 2967.

2H, H^2/H^3), 7.19 (d, *J* = 8.4 Hz, 2H, H^2/H^3), 6.25 (d, *J* = 11.6 Hz, 1H, H^5), 5.50 (dd, *J* = 11.6, 10.4 Hz, 1H, H^6), 2.89-2.81 (m, 1H, H^7), 1.06 (d, *J* = 6.6 Hz, 6H, H^8). (*alkene E*) 7.27-7.25 (m, 4H, H^2 and H^3), 6.30 (d, *J* = 16.0 Hz, 1H, H^5), 6.18 (dd, *J* = 16.0, 6.6 Hz, 1H, H^6), 2.51-2.43 (m, 1H, H^7), 1.11 (d, *J* = 6.6 Hz, 6H, H^8).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm (*alkene Z*) 141.1 (C^6), 136.3 (C^4), 132.1 (C^1), 129.9 (C^2/C^3), 128.3 (C^2/C^3), 125.2 (C^5), 27.1 (C^7), 23.1 (C^8). (*alkene E*) 138.7 (C^6), 136.5 (C^4), 132.1 (C^1), 128.6(C^2/C^3), 127.2(C^2/C^3), 125.7 (C^5), 31.5 (C^7), 22.3 (C^8).

HRMS (ESI+): m/z calcd for $C_{11}H_{13}Cl$: 180.0706, found 180.0700 $[M]^+$.

(+/-)-2-(4-chlorophenyl)-3-isopropyl-1-tosylaziridine (2i)



Following procedure **C,** the title compound was isolated as a clear yellow oil (40%) as a mixture of diastereoisomers (*cis/trans* 40/60).

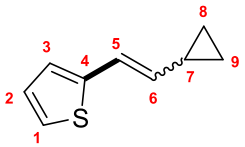
R*f*: 0.49 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm (*aziridine cis*) 7.78 (d, *J* = 8.4 Hz, 2H, H^4), 7.27 (d, *J* = 8.4 Hz, 2H, H^3), 7.23 (d, *J* = 8.4 Hz, 2H, H^{11}/H^{12}), 7.10 (*J* = 8.4 Hz, 2H, H^{11}/H^{12}), 3.72 (d, *J* = 4.5 Hz, 1H, H^9), 2.73-2.70 (m, 1H, H^8), 2.40 (s, 3H, H^1), 2.30-2.25 (m, 1H, H^7), 1.21 (d, *J* = 6.6 Hz, 3H, H^6), 1.10 (d, *J* = 6.6 Hz, 3H, H^6). (*aziridine trans*) 7.89 (d, *J* = 8.4 Hz, 2H, H^4), 7.34 (d, *J* = 8.4 Hz, 2H, H^3), 7.27 (d, *J* = 8.4 Hz, 2H, H^{11}/H^{12}), 7.21 (d, *J* = 8.4 Hz, 2H, H^{11}/H^{12}), 3.95 (d, *J* = 7.2 Hz, 1H, H^9), 2.73-2.70 (m, 1H, H^8), 2.45 (s, 3H, H^1), 1.13-1.11 (m, 1H, H^7), 0.82 (d, *J* = 6.6 Hz, 3H, H^6), 0.71 (d, *J* = 6.6 Hz, 3H, H^6).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm (*aziridine cis*) 129.5 (C^3), 128.6 (C^{11}/C^{12}), 128.3 (C^{11}/C^{12}), 127.4 (C^4), 59.1 (C^8), 47.7 (C^9), 28.9 (C^7), 21.6 (C^1), 21.2 (C^6), 20.9 ($C^{6'}$). (*aziridine trans*) 129.7 (C^3), 128.7 (C^{11}/C^{12}), 128.4 (C^{11}/C^{12}), 128.1 (C^4), 52.8 (C^8), 45.4 (C^9), 25.8 (C^7), 21.7 (C^1), 20.5 (C^6) 18.5 ($C^{6'}$).

HRMS (ESI+): m/z calcd for $C_{18}H_{21}NO_2SCl$: 350.0982, found 350.0982 $[M+H]^+$.

(*Z/E*)-2-(2-cyclopropylvinyl)thiophene (6b)



Following procedure **B,** the title compound was isolated as a yellow oil (91%) as a mixture of alkenes (*Z/E* 68/32).

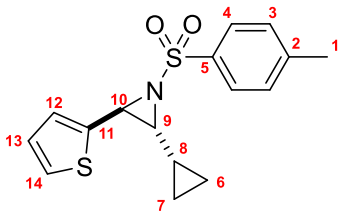
R*f*: 0.63 (8/2 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm (*alkene Z)* 7.23 (d, *J* = 3.4 Hz, 1H, H^1), 7.04 (d, *J* = 3.4 Hz, 1H, H^3), 7.01 (dd, *J* = 5.0, 3.4 Hz, 1H, H^2), 6.48 (d, *J* = 11.4 Hz, 1H, H^5), 5.04 (dd, *J* = 11.4, 9.6 Hz, 1H, H^6), 2.06-1.95 (m, 1H, H^7), 0.96-0.90 (m, 2H, H^8/H^9), 0.53-0.47 (m, 2H, H^8/H^9). (*alkene E*). 7.05 (d, *J* = 3.4 Hz, 1H, H^1), 6.92 (dd, *J* = 5.0, 3.4 Hz, 1H, H^2), 6.83 (d, *J* = 3.4 Hz, 1H, H^3), 6.59 (d, *J* = 15.6 Hz, 1H, H^5), 5.60 (dd, *J* = 15.6, 8.8 Hz, 1H, H^6), 1.55-1.45 (m, 1H, H^7), 0.85-0.77 (m, 2H, H^8/H^9), 0.53-0.47 (m, 2H, H^8/H^9).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm (*alkene Z*) 140.9 (C^4), 134.8 (C^6), 126.8 (C^2/C^3), 126.7 (C^2/C^3), 124.2 (C^1), 120.7 (C^5), 11.7 (C^7) 8.1 (C^8 and C^9). (*alkene E*) 143.1 (C^4), 134.8 (C^6), 127.2 (C^2), 123.6 (C^3), 122.6 (C^1), 120.8 (C^5), 14.3 (C^7), 7.2 (C^8 and C^9).

HRMS (ESI+): m/z calcd for $C_9H_{11}S$: 151.0581, found 151.0575 $[M+H]^+$.

(+/-)-(2*R*,3*S*)-2-cyclopropyl-3-(thiophen-2-yl)-1-tosylaziridine (2j)



Following procedure **C**, the title compound was isolated as a yellow oil (27%) as a single diastereoisomer (*trans*).

R*f*: 0.29 (8/2 hexane/EtOAc).

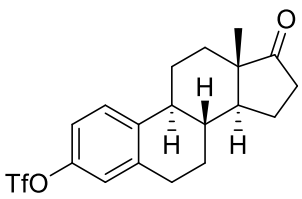
^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.85 (d, *J* = 8.4 Hz, 2H, H^4), 7.34 (d, *J* = 8.4 Hz, 2H, H^3), 7.19 (dd, *J* = 5.0, 1.2 Hz, 1H, H^{14}), 6.98 (d, *J* = 3.4 Hz, 1H, H^{12}), 6.93 (dd, *J* = 5.0, 3.4 Hz, 1H, H^{13}), 4.05 (d, *J* = 7.0 Hz, 1H, H^{10}), 2.70 (t, *J* = 7.0 Hz, 1H, H^9), 2.45 (s, 3H, H^1), 0.74-7.72 (m, 1H, H^8), 0.54-0.47 (m, 2H, H^6/H^7), 0.43-0.37 (m, 1H, H^6/H^7), 0.32-0.27 (m, 1H, H^6/H^7).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.6 (C^2), 136.3 (C^5), 135.0, 129.7 (C^3), 127.9 (C^4), 126.9 (C^{12}/C^{13}), 126.8 (C^{12}/C^{13}), 125.3 (C^{14}), 50.5 (C^9), 42.9 (C^{10}), 21.7 (C^1), 7.6 (C^8), 4.0 (C^6/C^7), 3.9 (C^6/C^7).

FTIR (ATR, neat): ν_{max}/cm^{-1} 3116-2959 (w), 1598 (w), 1494 (w), 1431 (w), 1404 (w), 1380 (w), 1322 (s), 1244 (w), 1156 (s), 1090 (s), 1018 (m), 966 (m), 879 (m), 845 (m), 814 (m), 703 (s), 669 (s).

HRMS (ESI+): m/z calcd for $C_{16}H_{18}NO_2S_2$: 320.0779, found 320.0774 $[M+H]^+$.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta [a]phenanthren-3-yl trifluoromethanesulfonate (7)



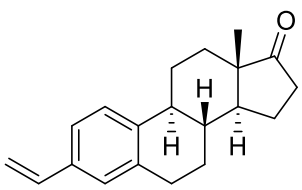
An oven-dried 50 mL round bottom flask under Argon was charged with estrone (0.8 g, 2.93 mmol, 1 equiv) and CH_2Cl_2 (14.7 mL, 0.2 M). The mixture was cooled to 0 °C and Et_3N (0.82 mL, 5.86 mmol, 2 equiv) and Tf_2O (0.54 mL, 3.22 mmol, 1.1 equiv) were added dropwise. The reaction mixture was allowed to warm to rt and stirred for 4 h. The brown resulting mixture was quenched with sat. $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2 (3x). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash column chromatography (8/2 hexane/EtOAc) to afford 0.91 g of a white solid (77%) with spectral date in agreement with literature values.[12]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.34 (d, *J* = 8.7 Hz, 1H), 7.04 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.0-6.99 (m, 1H), 2.96-2.91 (m, 2H), 2.52 (dd, *J* = 18.6, 8.7 Hz, 1H), 2.42-2.37 (m, 1H), 2.32-2.26 (m, 1H), 2.20-2.12 (m, 1H), 2.09-2.01 (m, 2H), 2.00-1.96 (m, 1H), 1.68-1.43 (m, 6H), 0.92 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 220.4, 147.6, 140.3, 139.3, 127.2, 121.2, 118.3, 50.4, 47.8, 44.1, 37.7, 35.8, 31.5, 29.4, 26.1, 25.7, 21.5, 13.8.

[12] (a) Horwitz, J. P.; Iyer, V. K.; Vardhan, H. B.; Corombos, J.; Brooks, S. C. *J. Med. Chem.* **1986**, *29*, 692. (b) Furuya, T.; Strom, A. E.; Ritter, T. *J. Am. Chem. Soc*. **2009**, *131*, 1662.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (8)

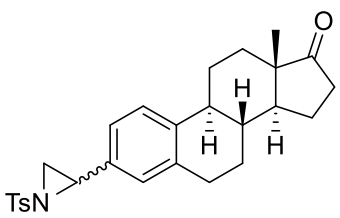


A microwave tube under argon was charged with triflate estrone **7** (485 mg, 1.21 mmol, 1 equiv), potassium vinyl trifluoroborate (333 mg, 2.41 mmol, 2 equiv), $PdCl_2$ (12.2 mg, 0.12 mmol, 0.1 equiv), PPh_3 (95 mg, 0.36 mmol, 0.3 equiv) and Cs_2CO_3 (1.18 g, 3.62 mmol, 3 equiv). THF (2.2 mL) and H_2O (0.3 mL) were added to the mixture. The tube was sealed and the reaction mixture was stirred at 85 °C for 20 h. After cooling to rt, the crude was diluted with CH_2Cl_2 and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2 (3x). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified with column chromatography (9/1 to 8/2 hexane/EtOAc) to afford 288 mg of a white solid (85%) with spectral data in agreement with literature values.[13]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.27-7.25 (m, 1H), 7.22-7.21 (m, 1H), 7.15 (s, 1H), 6.67 (dd, *J* = 18.0, 11.4 Hz, 1H), 5.71 (d, *J* = 18.0 Hz, 1H), 5.19 (d, *J* = 11.4 Hz, 1H), 2.95-2.89 (m, 2H), 2.51 (dd, *J* = 19.1, 8.6 Hz, 1H), 2.45-2.40 (m, 1H), 2.33-2.27 (m, 1H), 2.19-2.11 (m, 1H), 2.09-1.99 (m, 2H), 1.98-1.94 (m, 1H), 1.68-1.41 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 220.9, 139.5, 136.6, 135.2, 126.9, 125.5, 123.6, 113.2, 50.5, 48.0, 44.4, 38.1, 35.8, 31.6, 29.4, 26.5, 25.7, 21.6, 13.8.

(+/-)-(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(1-tosylaziridin-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2k)



Following procedure **C**, the title compound was isolated as a colorless oil (37%, mixture of diastereoisomers) with spectral data in agreement with literature values.[14]

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.86 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.95 (s, 1H), 3.73 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.95 (d, *J* = 7.2 Hz, 1H), 2.86 (dd, *J* = 8.8, 4.0 Hz, 1H), 2.50 (dd, *J* = 19.1, 8.8 Hz, 1H), 2.4 (s, 3H), 2.37 (d, *J* = 4.5 Hz, 1H), 2.29-2.23 (m, 1H), 2.18-1.91 (m, 5H), 1.67-1.35 (m, 6H), 0.89 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm *(carbons for the minor diastereoisomer are indicated in parentheses)* 220.7, 144.6, 140.0, 136.9, 135.0, 132.5, 129.7, 128.0, 127.2 (127.1), 125.6, 124.0 (123.9), 50.4, 47.9, 44.3, 40.9 (40.8), 38.0, 35.8 (35.7), 31.5, 29.3, 26.3, 25.7, 21.6, 21.5, 13.8.

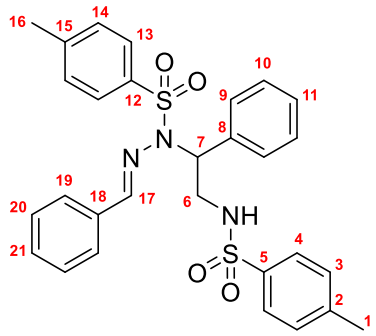
[13] (a) Yasu, Y. Koike, T.; Akita, M. *Org. Lett.* **2013**, *15*, 2136. (b) Guo, R.; Yang, H.; Tang, P. *Chem. Commun*. **2015**, *51*, 8829.
[14] Huang, C-Y.; Doyle, A. G. *J. Am. Chem. Soc*. **2012**, *134*, 9541.

3.3. Synthesis of amino-hydrazones **3a-3y**

General procedure D for the synthesis of aminohydrazones

Hydrazone **1** (0.2 mmol, 1 equiv) and aziridine **2** (0.24 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (1.0 mL, 0.2 M) in an oven-dried test tube under Argon. $BF_3{\cdot}OEt_2$ (0.04 mmol, 0.2 equiv) was introduced dropwise and the pale yellow/orange reaction mixture was stirred at rt for 1-2 h. The progression of the reaction was monitored by TLC (5/4/1 hexane/CH_2Cl_2/EtOAc). Sat. $NaHCO_3$ was then added, the two phases separated and the aqueous phase was extracted with CH_2Cl_2 (x3). The organic phase was dried with $MgSO_4$, filtered and solvent was removed *in vacuo*. The crude was purified by silica gel chromatography (5/4/0.5 to 5/4/1 hexane/CH_2Cl_2/EtOAc) except where noted and dried *in vacuo* to yield the desired product **3**.

***N*-(2-(2-benzylidene-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3a)**



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (99.8 mg, 0.182 mmol, 91%). With $BF_3{\cdot}THF$ as the Lewis acid, the product was obtained with 81% yield (88.2 mg, 0.161 mmol).

R*f*: 0.46 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.55 (s, 1H, H^{17}), 7.65 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.53 (d, J = 8.4 Hz, 2H, H^{19}), 7.47-7.43 (m, 1H, H^{21}), 7.41-7.38 (m, 4H, H^4/H^{13} and H^{20}), 7.24 – 7.17 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.10 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.36 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.66 (dd, J = 7.8, 4.8 Hz, 1H, NH), 3.50-3.46 (m, 1H, H^6), 3.41-3.36 (m, 1H, $H^{6'}$), 2.36 (s, 3H, H^1/H^{16}), 2.34 (s, 3H, H^1/H^{16}).

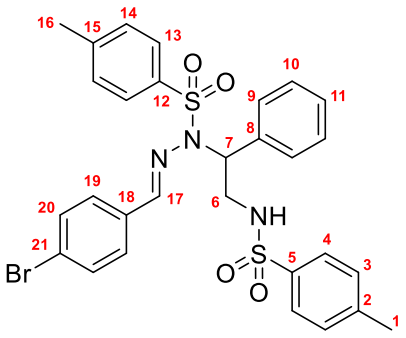
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 156.0 (C^{17}), 144.5 (C^2/C^{15}), 143.5 (C^2/C^{15}), 137.1 (C^8), 136.7 (C^5/C^{12}), 134.5 (C^5/C^{12}), 133.8 (C^{18}), 131.1 (C^{21}), 129.7 (C^3/C^{14}), 129.5 (C^3/C^{14}), 128.8 (C^{20}), 128.5 (C^{10}), 128.3 (C^{11}), 128.0 (C^4/C^{13}), 127.8 (C^{19}), 127.7 (C^9), 127.0 (C^4/C^{13}), 64.1 (C^7), 45.7 (C^6), 21.5 (C^1/C^{16}), 21.4 (C^1/C^{16}).

M.p.: 68-70 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3291(w-br), 3060-2878 (w), 1598 (w), 1573 (w), 1494 (w), 1449 (w), 1403 (w), 1381 (w), 1331 (m), 1223 (w), 1156 (s), 1088 (m), 1019 (w), 973 (w), 900 (w), 863 (m), 813 (m), 757 (m), 736 (m), 697 (m), 660 (s).

HRMS (ESI+): m/z calcd for $C_{29}H_{29}N_3O_4S_2$: 547.1592, found 547.1605 $[M]^+$, 570.1497 $[M+Na]^+$.

_N_-(2-(2-(4-bromobenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3b)



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (118.6 mg, 0.189 mmol, 95%).

R*f*: 0.39 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.45 (s, 1H, H^{17}), 7.66 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.52 (d, J = 8.4 Hz, 2H, H^{19}), 7.40 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.37 (d, J = 8.4 Hz, 2H, H^{20}), 7.24-7.16 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.11 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.40 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.60-58 (m, 1H, NH), 3.55-3.51 (m, 1H, H^6), 3.44-3.40 (m, 1H, $H^{6'}$), 2.37 (s, 3H, H^1/H^{16}), 2.35 (s, 3H, H^1/H^{16}).

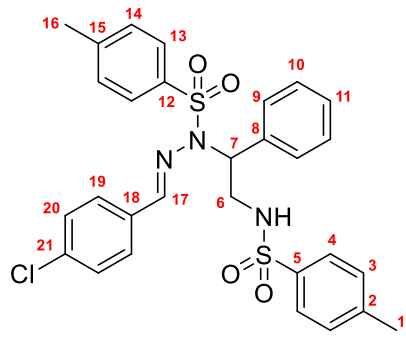
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 153.0 (C^{17}), 144.6 (C^2/C^{15}), 143.5 (C^2/C^{15}), 139.8 (C^8/C^5/C^{12}), 136.7 (C^8/C^5/C^{12}), 134.5 (C^5/C^{12}), 132.9 (C^{18}), 132.1 (C^{19}), 129.7 (C^3/C^{14}), 129.5 (C^3/C^{14}), 128.9 (C^{20}), 128.6 (C^{10}), 128.4 (C^{11}), 128.0 (C^4/C^{13}), 127.8 (C^9), 127.1 (C^4/C^{13}), 125.3 (C^{21}), 64.0 (C^7), 45.6 (C^6), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

M.p.: 80-82 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3287 (w-br), 3070-2878 (w), 1597 (w), 1488 (w), 1454 (w), 1401 (w), 1330 (m), 1302 (m), 1156 (s), 1088 (s), 1070 (m), 1033 (w), 1009 (m), 975 (m), 916 (w), 863 (m), 812 (s), 768 (w), 738 (w), 699 (s), 659 (s).

HRMS (ESI+): m/z calcd for $C_{29}H_{28}BrN_3O_4S_2$: 625.0705, found 625.0717 $[M]^+$, 648.0609 $[M+Na]^+$.

_N_-(2-(2-(4-chlorobenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3c)



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (109 mg, 0.187 mmol, 94%).

R*f*: 0.32 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.47 (s, 1H, H^{17}), 7.65 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.44 (d, J = 8.4 Hz, 2H, H^{19}), 7.40 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.36 (d, J = 8.4 Hz, 2H, H^{20}), 7.24-7.18 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.11 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.39 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.60-4.58 (m, 1H, NH), 3.55-3.50 (m, 1H, H^6), 3.44-3.40 (m, 1H, $H^{6'}$), 2.37 (s, 3H, H^1/H^{16}), 2.35 (s, 3H, H^1/H^{16}).

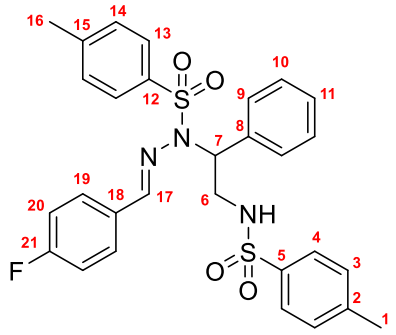
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 153.3 (C^{17}), 144.6 (C^2/C^{15}), 143.5 (C^2/C^{15}), 139.6 (C^5/C^{12}/C^{21}), 136.8 (C^5/C^{12}/C^{21}), 136.7 (C^8), 134.5 (C^5/C^{12}), 132.4 (C^{18}), 129.7 (C^3/C^{14}), 129.5 (C^3/C^{14}), 129.1 (C^{20}), 128.8 (C^{19}), 128.6 (C^{10}), 128.3 (C^{11}), 128.0 (C^4/C^{13}), 127.8 (C^9), 127.7 (C^9), 127.1 (C^4/C^{13}), 64.0 (C^7), 45.6 (C^6), 21.5 (C^1/C^{16}), 21.4 (C^1/C^{16}).

M.p.: 74-76 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3281 (w-br), 2960 (w), 2925 (w), 2854 (w), 1596 (w), 1492 (w), 1454 (w), 1404 (w), 1330 (m), 1305 (m), 1220 (w), 1186 (w), 1157 (s), 1119 (w), 1087 (s), 1013 (w), 977 (w), 916 (w), 864 (m), 812 (m), 769 (w), 740 (w), 701 (m), 659 (s).

HRMS (ESI+): m/z calcd for $C_{29}H_{28}ClN_3O_4S_2$: 581.1210, found 581.1218 $[M]^+$, 604.1110 $[M+Na]^+$.

<u>*N*-(2-(2-(4-fluorobenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3d)</u>



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (103.8 mg, 0.183 mmol, 92%).

R*f*: 0.37 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.52 (s, 1H, H^{17}), 7.66 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.53 (dd, J = 9.0, 5.4 Hz, 2H, H^{19}), 7.39 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.24-7.16 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.12 – 7.06 (m, 4H, H^3/H^{14} and H^{20}), 5.34 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.66 (dd, J = 7.2, 4.8 Hz, 1H, NH), 3.52-3.47 (m, 1H, H^6), 3.41-3.37 (m, 1H, $H^{6'}$), 2.37 (s, 3H, H^1/H^{16}), 2.34 (s, 3H, H^1/H^{16}).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -108.0.

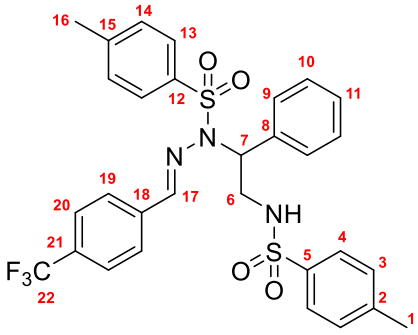
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 164.4 (d, $^1J_{CF}$ = 252 Hz, C^{21}), 155.3 (C^{17}), 144.5 (C^2/C^{15}), 143.5 (C^2/C^{15}), 136.9 ($C^8/C^5/C^{12}$), 136.7 ($C^8/C^5/C^{12}$), 134.5 (C^5/C^{12}), 130.1 (d, $^4J_{CF}$ = 3 Hz, C^{18}), 129.8 (d, $^3J_{CF}$ = 9 Hz, C^{19}), 129.7 (C^3/C^{14}), 129.5 (C^3/C^{14}), 128.5 (C^{10}), 128.3 (C^{11}), 128.0 (C^4/C^{13}), 127.8 (C^{19}), 127.9 (C^9), 127.1 (C^4/C^{13}), 116.1 (d, $^2J_{CF}$ = 22 Hz, C^{20}), 64.0 (C^7), 45.6 (C^6), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

M.p.: 70-72 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3293 (w-br), 3100-2880 (w), 1600 (m), 1510 (m), 1495 (w), 1455 (w), 1414 (w), 1331 (m), 1305 (w), 1231 (m), 1186 (w), 1155 (s), 1088 (m), 1018 (w), 977 (m), 872 (m), 836 (m), 812 (m), 768 (w), 734 (w), 699 (m), 660 (s).

HRMS (ESI+): m/z calcd for $C_{29}H_{28}FN_3O_4S_2$: 565.1505, found 565.1513 $[M]^+$, 588.1405 $[M+Na]^+$.

<u>4-methyl-*N*-(2-phenyl-2-(1-tosyl-2-(4-(trifluoromethyl)benzylidene)hydrazinyl)ethyl)benzenesulfonamide (3e)</u>



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (113.3 mg, 0.184 mmol, 92%).

R*f*: 0.46 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.47 (s, 1H, H^{17}), 7.68 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.62 (d, J = 8.4 Hz, 2H, H^{20}), 7.58 (d, J = 8.4 Hz, 2H, H^{19}), 7.44 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.26-7.19 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.14

(d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.50 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.60-4.58 (m, 1H, NH), 3.64-3.59 (m, 1H, H^6), 3.50-3.46 (m, 1H, $H^{6'}$), 2.36 (s, 3H, H^1/H^{16}), 2.35 (s, 3H, H^1/H^{16}).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -69.9.

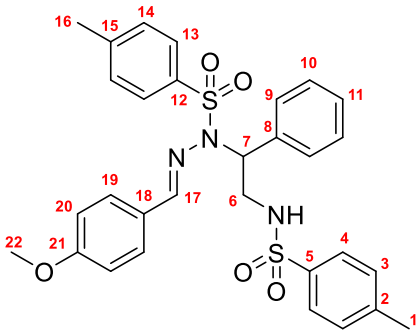
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 149.3 (C^{17}), 144.9 (C^2/C^{15}), 143.6 (C^2/C^{15}), 137.5 (C^{18}), 136.8 (C^8), 136.7 (C^5/C^{12}), 134.4 (C^5/C^{12}), 132.0 (q, $^2J_{CF}$ = 33 Hz, C^{21}), 129.7 (C^3/C^{14}), 129.6 (C^3/C^{14}), 128.7 (C^{10}), 128.5 (C^{11}), 128.0 (C^4/C^{13}), 127.7 (C^9), 127.5 (C^{19}), 127.1 (C^4/C^{13}), 125.7 (q, $^3J_{CF}$ = 4 Hz, C^{20}), 123.8 (q, $^1J_{CF}$ = 272 Hz, C^{22}), 64.1 (C^7), 45.7 (C^6), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

M.p.: 68-70 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3293 (w-br), 3070-2879 (w), 1598 (w), 1495 (w), 1455 (w), 1414 (w), 1381 (w), 1322 (s), 1226 (w), 1158 (s), 1122 (m), 1106 (m), 1089 (m), 1065 (s), 1017 (w), 976 (w), 917 (w), 868 (m), 838 (m), 813 (m), 766 (m), 731 (w), 699 (m), 659 (s).

HRMS (ESI+): m/z calcd for $C_{30}H_{28}F_3N_3O_4S_2$: 615.1473, found 615.1483 $[M]^+$, 638.1375 $[M+Na]^+$.

***N*-(2-(2-(4-methoxybenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3f)**



Prepared according to the general procedure **D**, the title compound was isolated as a yellow foam (112 mg, 0.194 mmol, 97%).

R*f*: 0.30 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.56 (s, 1H, H^{17}), 7.63 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.53 (d, J = 8.4 Hz, 2H, H^{19}), 7.37 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.21-7.13 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.09 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 6.93 (d, J = 8.4 Hz, 2H, H^{20}), 5.23 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.67-4.65 (m, 1H, NH), 3.88 (s, 3H, H^{22}), 3.42-3.37 (m, 1H, H^6), 3.33-3.29 (m, 1H, $H^{6'}$), 2.37 (s, 3H, H^1/H^{16}), 2.34 (s, 3H, H^1/H^{16}).

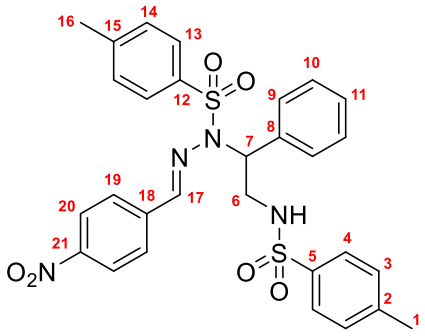
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 162.4 (C^{21}), 160.3 (C^{17}), 144.2 (C^2/C^{15}), 143.4 (C^2/C^{15}), 137.1 (C^8), 136.7 (C^5/C^{12}), 134.5 (C^5/C^{12}), 129.9 (C^{19}), 129.7 (C^3/C^{14}), 129.3 (C^3/C^{14}), 128.4 (C^{10}), 128.1 (C^{11}), 128.0 (C^9), 127.9 (C^4/C^{13}), 127.0 (C^4/C^{13}), 126.2 (C^{18}), 114.3 (C^{20}), 64.0 (C^7), 55.5 (C^{22}), 45.7 (C^6), 21.5 (C^1/C^{16}), 21.4 (C^1/C^{16}).

M-.p.: 76-78 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3290 (w-br), 3061-2841 (w), 1598 (m), 1568 (w), 1513 (m), 1495 (w), 1455 (w), 1422 (w), 1331 (m), 1306 (m), 1252 (m), 1157 (s), 1088 (m), 1028 (m), 871 (m), 832 (m), 812 (m), 768 (w), 734 (w), 699 (m), 660 (s).

HRMS (ESI+): m/z calcd for $C_{30}H_{31}N_3O_5S_2$: 577.1705, found 577.1708 $[M]^+$, 600.1600 $[M+Na]^+$.

4-methyl-*N*-(2-(2-(4-nitrobenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)benzenesulfonamide (3g)



Prepared according to the general procedure **D**, the title compound was isolated as a yellow foam (105.5 mg, 0.180 mmol, 90%).

R*f*: 0.44 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.42 (s, 1H, H^{17}), 8.20 (d, J = 8.4 Hz, 2H, H^{20}), 7.70 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.60 (d, J = 8.4 Hz, 2H, H^{19}), 7.48 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.29-7.22 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.17 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.58 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.63-4.59 (m, 1H, NH), 3.72-3.67 (m, 1H, H^6), 3.54-3.50 (m, 1H, $H^{6'}$), 2.38 (s, 3H, H^1/H^{16}), 2.36 (s, 3H, H^1/H^{16}).

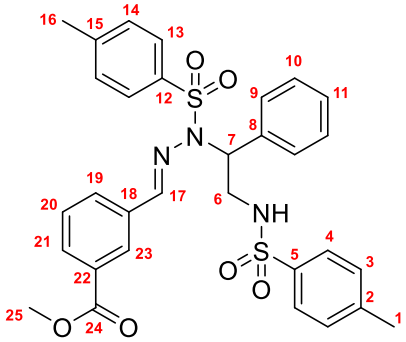
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 148.4 (C^{21}), 145.4 (C^{17}), 145.1 (C^2/C^{15}), 143.7 (C^2/C^{15}), 140.2 (C^{18}), 136.7 (C^8/C^5/C^{12}), 136.6 (C^8/C^5/C^{12}), 134.3 (C^5/C^{12}), 129.8 (C^3/C^{14}), 129.7 (C^3/C^{14}), 128.8 (C^{10}), 128.6 (C^{11}), 128.0 (C^4/C^{13}), 127.7 (C^{19}), 127.6 (C^9), 127.1 (C^4/C^{13}), 124.0 (C^{20}), 64.2 (C^7), 45.6 (C^6), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

M.p.: 82-86 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3293 (w-br), 3100-2900 (w), 1597(w), 1580 (w-sh), 1519 (m), 1495 (w), 1455 (w), 1412 (w), 1341 (s), 1226 (w), 1186 (w), 1159 (s), 1088 (m), 976 (m), 917 (w), 875 (w), 851 (m-sh), 838 (m), 813 (m), 768(w), 750 (w), 736 (w), 700 (m), 659 (s).

HRMS (ESI+): m/z calcd for $C_{29}H_{28}N_4O_6S_2$: 592.1450, found 592.1481 $[M]^+$, 615.1373 $[M+Na]^+$.

methyl 3-((2-(2-((4-methylphenyl)sulfonamido)-1-phenylethyl)-2-tosylhydrazono)methyl)benzoate (3h)



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (112.6 mg, 0.186 mmol, 93%).

R*f*: 0.25 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.49 (s, 1H, H^{17}), 8.14 (s, 1H, H^{23}), 8.08 (d, J = 8.4 Hz, 1H, H^{21}), 7.71 (d, J = 8.4 Hz, 2H, H^{19}), 7.68 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.48-7.42 (m, 3H, H^4/H^{13} and H^{20}), 7.26-7.20 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.14 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.45 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.68-4.62 (m, 1H, NH), 3.96 (s, 3H, H^{25}), 3.61-3.57 (m, 1H, H^6), 3.48-3.44 (m, 1H, $H^{6'}$), 2.35 (s, 6H, H^1 and H^{16}).

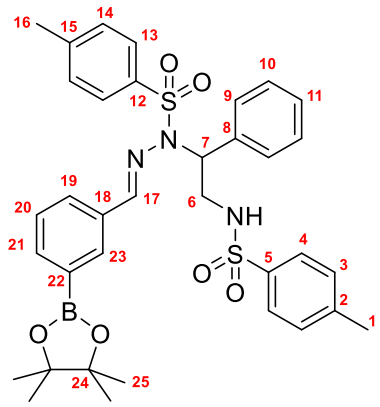
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 166.3 (C^{24}), 151.7 (C^{17}), 144.7 (C^2/C^{15}), 143.5 (C^2/C^{15}), 136.9 (C^5/C^{12}), 136.8 (C^8), 134.5 (C^5/C^{12}), 134.5 (C^{18}), 131.5 (C^{21}), 131.0 (C^{19}), 130.9 (C^{22}), 129.7 (C^3/C^{14}), 129.6 (C^3/C^{14}), 129.1 (C^{23}), 128.9 (C^{20}), 128.6 (C^{10}), 128.4 (C^{11}), 128.0 (C^4/C^{13}), 127.8 (C^9), 127.1 (C^4/C^{13}), 64.0 (C^7), 52.4 (C^{25}), 45.6 (C^6), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

M.p.: 70-72 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3293 (w-br), 3067-2872 (w), 1721 (m), 1598 (w), 1495 (w), 1444 (w), 1434 (w), 1332 (m), 1289 (m), 1212 (m), 1186 (m), 1157 (s), 1087 (w), 1019 (w), 973 (m), 906 (w), 813 (m), 753 (m), 739 (m), 700 (m), 685 (m), 660 (s).

HRMS (ESI+): m/z calcd for $C_{31}H_{31}N_3O_6S_2$: 605.1654, found 605.1668 $[M]^+$, 628.1560 $[M+Na]^+$.

4-methyl-*N*-(2-phenyl-2-(2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)-1-tosylhydrazinyl)ethyl)benzenesulfonamide (3i)



Prepared according to the general procedure **D**, the title compound was isolated as a crude white foam due to its instability on silica (128 mg, 0.190 mmol, 95%).

R*f*: 0.33 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.52 (s, 1H, H^{17}), 7.90 (s, 1H, H^{23}), 7.88 (d, J = 8.4 Hz, 1H, H^{21}), 7.65-7.67 (m, 3H, H^4/H^{13} and H^{19}), 7.43 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.38 (t, J = 8.4 Hz, 1H, H^{20}), 7.24-7.18 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.12 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.38 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.72-4.66 (m, 1H, NH), 3.53-3.48 (m, 1H, H^6), 3.43-3.39 (m, 1H, $H^{6'}$), 2.35 (s, 3H, H^1/H^{16}), 2.34 (s, 3H, H^1/H^{16}), 1.38 (s, 12H, H^{25}).

^{11}B NMR (193 MHz, $CDCl_3$): δ/ppm 30.1.

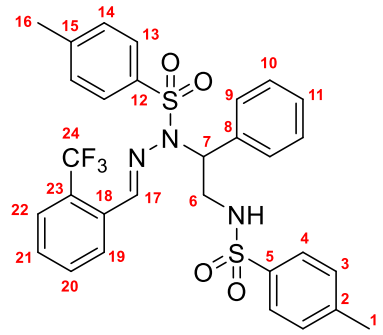
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 155.7 (C^{17}), 144.4 (C^2/C^{15}), 143.4 (C^2/C^{15}), 137.4 (C^{21}), 137.1 (C^8), 136.7 (C^5/C^{12}), 135.6 (C^{23}), 134.6 (C^5/C^{12}), 133.2 (C^{18}), 129.7 (C^3/C^{14} and C^{22}), 129.5 (C^3/C^{14}), 129.0 (C^{19}), 128.5 (C^{10}), 128.3 (C^{11} or C^{20}), 128.2 (C^{20} or C^{11}), 128.0 (C^4/C^{13}), 127.8 (C^9), 127.1 (C^4/C^{13}), 84.2 (C^{24}), 64.0 (C^7), 45.6 (C^6), 24.9 (C^{25}), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

M.p.: 80-82 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3290 (w-br), 2978 (w), 2929 (w), 2875 (w), 1598 (w), 1494 (w), 1455 (w), 1426 (w), 1357 (m), 1330 (m), 1277 (w), 1215 (w), 1186 (w), 1158 (s), 1142 (s), 1089 (m), 1019 (w), 965 (m), 905 (w), 854 (m), 812 (m), 768 (w), 738 (w), 701 (s), 660 (s).

HRMS (ESI+): m/z calcd for $C_{35}H_{40}BN_3O_6S_2$: 673.2452, found 673.2465 $[M]^+$, 696.2357 $[M+Na]^+$.

4-methyl-*N*-(2-phenyl-2-(1-tosyl-2-(2-(trifluoromethyl)benzylidene)hydrazinyl)ethyl)benzenesulfonamide (3j)



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (86 mg, 0.141 mmol, 70%). With $BF_3{\cdot}THF$ as the Lewis acid, the product was obtained with 89% yield (110 mg, 0.178 mmol).

R*f*: 0.37 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.59 (s, 1H, H^{17}), 7.80 (d, J = 8.4 Hz, 1H, H^{19}), 7.69 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.65 (d, J = 8.4 Hz, 1H, H^{22}), 7.54 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.51 (t, J = 8.4 Hz, 1H, H^{20}), 7.47 (t, J = 8.4 Hz, 1H, H^{21}), 7.28-7.23 (m, 7H, H^9, H^{10}, H^{11}), 7.20 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 7.18 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.63 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.65-4.53 (m, 1H, NH), 3.70-3.66 (m, 1H, H^6), 3.58-3.53 (m, 1H, $H^{6'}$), 2.36 (s, 3H, H^1/H^{16}), 2.33 (s, 3H, H^1/H^{16}).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -57.9.

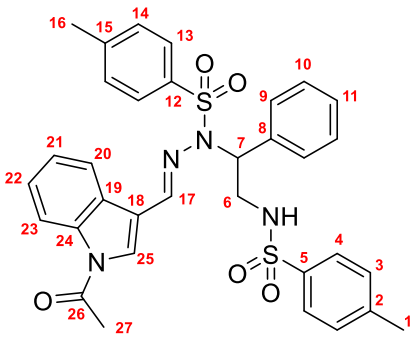
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.9 (C^2/C^{15}), 143.5 (C^2/C^{15}), 143.3 (q, $^4J_{CF}$ = 2.2 Hz, C^{17}), 137.0 (C^8), 136.7 (C^5/C^{12}), 134.5 (C^5/C^{12}), 132.4 (C^{18}), 131.9 (C^{20}), 129.7 (C^3/C^{14}), 129.7 (C^3/C^{14}), 129.6 (C^{21}), 128.8 (C^{10}), 128.5 (C^{11}), 128.4 (q, $^2J_{CF}$ = 31 Hz, C^{23}), 128.2 (C^4/C^{13}), 127.5 (C^9), 127.1 (C^4/C^{13}), 126.4 (C^{19}), 125.9 (q, $^3J_{CF}$ = 6 Hz, C^{22}), 123.9 (q, $^1J_{CF}$ = 272 Hz, C^{24}), 63.8 (C^7), 45.4 (C^6), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

M.p.: 60-62 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3307 (w-br), 3064-2870 (w), 1597 (w), 1571 (w), 1495 (w), 1453 (w), 1404 (w), 1333 (m), 1313 (s), 1281 (m), 1238 (w), 1220 (w), 1158 (s), 1118 (s), 1089 (s), 1058 (m), 1034 (m), 979 (m), 914 (w), 863 (w), 813 (m), 768 (m), 731 (w), 700 (m), 659 (s).

HRMS (ESI+): m/z calcd for $C_{30}H_{28}F_3N_3O_4S_2$: 615.1473, found 615.1481 $[M]^+$, 638.1373 $[M+Na]^+$.

***N*-(2-(2-((1-acetyl-1H-indol-3-yl)methylene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3k)**



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (116 mg, 0.186 mmol, 93%).

R*f*: 0.26 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, CD_3CN): δ/ppm 8.68 (s, 1H, H^{17}), 8.43 (d, J = 8.4 Hz, 1H, H^{20}), 8.08 (s, 1H, H^{25}), 7.92 (d, J = 8.4 Hz, 1H, H^{23}), 7.59 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.49 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.44 (t, J = 7.8 Hz, 1H, H^{21}), 7.32 (t, J = 7.8 Hz, 1H, H^{22}), 7.29-7.20 (m, 7H, H^9, H^{10}, H^{11}, H^3/H^{14}), 7.16 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 5.65 (t, J = 6.2 Hz, 1H, NH), 5.37 (t, J = 7.4 Hz, 1H, H^7), 3.38-3.34 (m, 1H, H^6), 3.30-3.26 (m, 1H, $H^{6'}$), 2.64 (s, 3H, H^{27}), 2.33 (s, 3H, H^1/H^{16}), 2.32 (s, 3H, H^1/H^{16}).

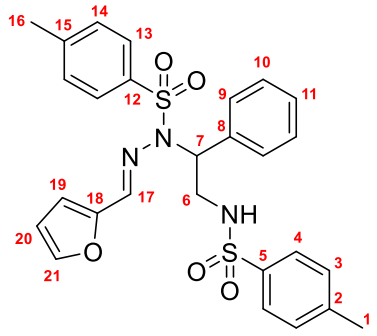
^{13}C NMR (150 MHz, CD_3CN): δ/ppm 170.5 (C^{26}), 156.9 (C^{17}), 145.6 (C^{2}/C^{15}), 145.5 (C^{2}/C^{15}), 138.1 (C^{8}), 138.0 (C^{5}/C^{12}), 137.6 (C^{24}), 136.0 (C^{5}/C^{12}), 133.9 (C^{25}), 130.6 (C^{3}/C^{14}), 130.4 (C^{3}/C^{14}), 129.4 (C^{9}), 129.3 (C^{10}), 129.1 (C^{11}), 129.0 (C^{4}/C^{13}), 127.7 (C^{4}/C^{13}), 127.4 (C^{18}), 127.1 (C^{21}), 125.5 (C^{22}), 123.2 (C^{23}), 117.7 (C^{19}), 117.3 (C^{20}), 64.4 (C^{7}), 45.9 (C^{6}), 24.3 (C^{27}), 21.6 (C^{1}/C^{16}), 21.5 (C^{1}/C^{16}).

M.p.: 168-172 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3315 (w-br), 3130-2920 (w), 1721 (m), 1615 (w), 1599 (w), 1548 (w), 1495 (w), 1480 (w), 1449 (m), 1418 (w), 1378 (m), 1360 (m), 1345 (m), 1319 (m), 1288 (w), 1257 (w), 1214 (m), 1161 (s), 1133 (m), 1088 (m), 1072 (m), 1055 (m), 1030 (w), 1018 (m), 939 (m), 915 (w), 866 (m), 837 (w), 814 (m), 759 (m), 702 (m), 660 (s).

HRMS (ESI+): m/z calcd for $C_{33}H_{32}N_4O_5S_2$: 628.1814, found 628.1823 $[M]^+$, 651.1715 $[M+Na]^+$.

***N*-(2-(2-(furan-2-ylmethylene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3l)**



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (90.2 mg, 0.168 mmol, 84%).

R*f*: 0.30 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.45 (s, 1H, H^{17}), 7.66 (d, J = 8.4 Hz, 2H, H^{4}/H^{13}), 7.54 (s, 1H, H^{21}), 7.45 (d, J = 8.4 Hz, 2H, H^{4}/H^{13}), 7.27-7.18 (m, 7H, H^{9}, H^{10}, H^{11}, H^{3}/H^{14}), 7.15 (d, J = 8.4 Hz, 2H, H^{3}/H^{14}), 6.74 (d, J = 3.4 Hz, 1H, H^{19}), 6.52 (dd, J = 3.4, 1.8 Hz, 1H, H^{20}), 5.33 (dd, J = 9.2, 5.0 Hz, 1H, H^{7}), 4.93 (dd, J = 7.2, 5.0 Hz, 2H, NH), 3.48-3.44 (m, 1H, H^{6}), 3.34-3.30 (m, 1H, $H^{6'}$), 2.39 (s, 3H, H^{1}/H^{16}), 2.36 (s, 3H, H^{1}/H^{16}).

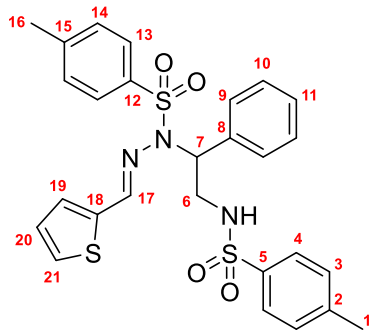
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 149.3 (C^{18}), 145.3 (C^{21}), 145.1 (C^{17}), 144.6 (C^{2}/C^{15}), 143.3 (C^{2}/C^{15}), 137.4 (C^{8}), 136.9 (C^{5}/C^{12}), 134.3 (C^{5}/C^{12}), 129.6 (C^{3}/C^{14}), 129.5 (C^{3}/C^{14}), 128.5 (C^{10}), 128.1 (C^{11}), 128.0 (C^{4}/C^{13}), 127.7 (C^{9}), 127.0 (C^{4}/C^{13}), 115.3 (C^{19}), 112.1 (C^{20}), 64.4 (C^{7}), 45.9 (C^{6}), 21.6 (C^{1}/C^{16}), 21.5 (C^{1}/C^{16}).

M.p.: 100-102 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3280 (w-br), 3120-2920 (w), 1614 (w), 1598 (m), 1494 (w), 1455 (w), 1401 (w), 1331 (m), 1305 (m), 1239 (w), 1186 (w), 1158 (s), 1089 (s), 1017 (m), 977 (w), 931 (m), 884 (w), 812 (m), 758 (m), 700 (m), 660 (s).

HRMS (ESI+): m/z calcd for $C_{27}H_{27}N_3O_5S_2$: 537.1392, found 537.1405 $[M]^+$, 560.1398 $[M+Na]^+$.

4-methyl-*N*-(2-phenyl-2-(2-(thiophen-2-ylmethylene)-1-tosylhydrazinyl)ethyl)benzenesulfonamide (3m)



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (87.5 mg, 0.158 mmol, 79%).

R*f*: 0.35 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.68 (s, 1H, H^{17}), 7.59 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.37 (d, J = 4.8 Hz, 1H, H^{21}), 7.35 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.28 (d, J = 3.0, 1H, H^{19}), 7.17 – 7.11 (m, 7H, H^9, H^{10}, H^{11} and H^3/H^{14}), 7.06-7.04 (m, 3H, H^3/H^{14} and C^{20}), 5.19 (dd, J = 9.6, 5.4 Hz, 1H, H^7), 4.56-4.54 (m, 1H, NH), 3.37-3.32 (m, 1H, H^6), 3.26-3.22 (m, 1H, $H^{6'}$), 2.32 (s, 3H, H^1/H^{16}), 2.29 (s, 3H, H^1/H^{16}).

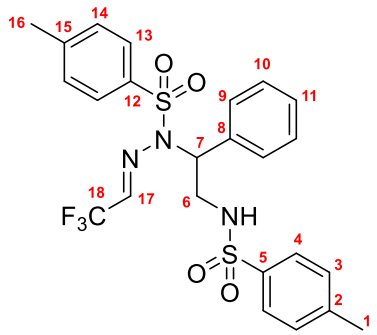
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 152.2 (C^{17}), 144.5 (C^2/C^{15}), 143.4 (C^2/C^{15}), 138.8 (C^{18}), 137.0 (C^8), 136.8 (C^5/C^{12}), 134.3 (C^5/C^{12}), 132.0 (C^{19}), 129.7 (C^3/C^{14}), 129.6 (C^{21}), 129.5 (C^3/C^{14}), 128.5 (C^{10}), 128.2 (C^{11}), 128.0 (C^4/C^{13}/C^9), 127.9 (C^{20}), 127.8 (C^4/C^{13}/C^9), 127.0 (C^4/C^{13}), 64.2 (C^7), 45.7 (C^6), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

M.p.:136-138 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3289 (w-br), 3114-2869 (w), 1588 (m), 1494 (w), 1456 (w), 1426 (w), 1401 (w), 1343 (m), 1327 (m), 1291 (w), 1245 (w), 1216 (w), 1187 (w), 1159 (s), 1121 (w), 1086 (m), 1045 (w), 1019 (w), 998 (w), 956 (w), 916 (w), 889 (m), 861 (w), 817 (m), 771 (m), 733 (m), 699 (m), 662 (s).

HRMS (ESI+): m/z calcd for $C_{27}H_{27}N_3O_4S_3$: 553.1164, found 553.1169 $[M]^+$, 576.1061 $[M+Na]^+$.

4-methyl-*N*-(2-phenyl-2-(1-tosyl-2-(2,2,2-trifluoroethylidene)hydrazinyl)ethyl)benzenesulfonamide (3n)



Prepared according to the general procedure **D**, the title compound was isolated as a colorless oil (59 mg, 0.109 mmol, 55%).

R*f*: 0.52 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.71 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.61 (d, J = 3.3 Hz, 1H, H^{17}), 7.52 (d, J = 8.4 Hz, 2H, H^4/H^{13}), 7.33-7.26 (m, 5H, H^3/H^{14}, H^{10}, H^{11}), 7.24 (d, J = 8.4 Hz, 2H, H^3/H^{14}), 7.20 (d, J = 7.8, 2H, H^9), 5.61 (dd, J = 9.4, 5.4 Hz, 1H, H^7), 4.58 (t, J = 6.4 Hz, 1H, NH), 3.61-3.56 (m, 1H, H^6), 3.43-3.39 (m, 1H, $H^{6'}$), 2.43 (s, 3H, H^1/H^{16}), 2.41 (s, 3H, H^1/H^{16}).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -67.5.

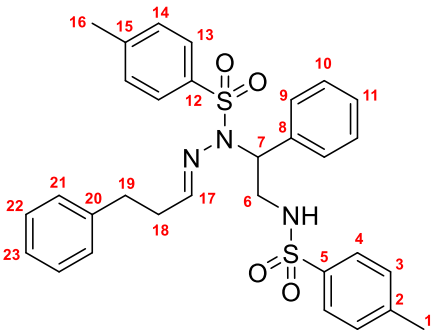
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 145.9 (C^2/C^{15}), 143.8 (C^2/C^{15}), 136.7 (C^5/C^{12}), 136.5 (C^8), 133.1 (C^5/C^{12}), 130.0 (C^3/C^{14}), 129.9 (d, $^2J_{CF}$ = 39 Hz, C^{17}), 129.8 (C^3/C^{14}), 128.9 (C^{10}),

128.8 (C^{11}), 128.1 (C^4/C^{13}), 127.4 (C^9), 127.0 (C^4/C^{13}), 119.8 (q, $^1J_{CF}$ = 272 Hz, C^{18}), 65.0 (C^7), 45.6 (C^6), 21.6 (C^1/C^{16}), 21.5 (C^1/C^{16}).

FTIR (ATR, neat): ν_{max}/cm^{-1} 3295 (br-w), 3075-2876 (w), 1626 (w), 1496 (w), 1455 (w), 1347 (m), 1288 (m), 1160 (s), 1120 (s), 1089 (s), 982 (m), 879 (m), 813 (m), 770 (w), 737 (m), 701 (m), 659 (s)..

HRMS (ESI+): m/z calcd for $C_{24}H_{26}N_3O_4S_3F_3$: 540.1239, found 540.1234 $[M+H]^+$.

4-methyl-*N*-(2-phenyl-2-(2-(3-phenylpropylidene)-1-tosylhydrazinyl)ethyl)benzenesulfonamide (3o)



Prepared according to the general procedure **D**, the title compound was isolated as a white solid (57 mg, 0.099 mmol, 50%) in the presence of an impurity (purity: 80%).

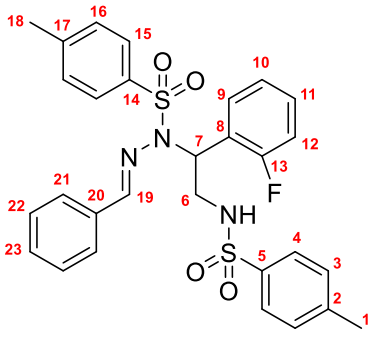
R*f*: 0.54 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.62 (d, *J* = 8.2 Hz, 2H, H^4/H^{13}), 7.44-7.42 (m, 2H, H^4/H^{13}), 7.36 (d, *J* = 8.2 Hz, 2H, H^9/H^{21}), 7.29-7.26 (m, 3H, H^3/H^{14}, H^{11}/H^{23}), 7.25-7.23 (m, 3H, H^{10}/H^{22}, H^{11}/H^{23}), 7.20-7.17 (m, 2H, H^{10}/H^{22}), 7.16 (d, *J* = 8.8 Hz, 2H, H^3/H^{14}), 6.97 (d, *J* = 7.2 Hz, 2H, H^9/H^{21}), 4.59 (d, *J* = 10.4 Hz, 1H, H^7), 4.23-4.19 (m, 1H, H^6), 4.14 (s, 1H, NH), 3.72 (dt, *J* = 9.4, 4.7 Hz, 1H, $H^{6'}$), 2.46-2.42 (m, 1H, H^{18}), 2.39 (s, 3H, H^1/H^{16}), 2.33-2.27 (m, 4H, H^1/H^{16}, $H^{18'}$), 2.19-2.13 (m, 1H, H^{19}), 1.30-1.26 (m, 1H, $H^{19'}$).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 156.8 (C^{17}), 144.0 (C^2/C^{15}), 143.6 (C^2/C^{15}), 140.8 (C^{20}), 136.4 (C^8/C^5/C^{12}), 135.9 (C^8/C^5/C^{12}), 135.1 (C^8/C^5/C^{12}), 129.7 (C^3/C^{14}), 129.3 (C^3/C^{14}), 128.9 (C^{10}/C^{22}), 128.5 (C^{10}/C^{22}), 128.3 (C^9/C^{21}), 128.2 (C^4/C^{13}), 127.9 (C^9/C^{21}), 127.3 (C^{11}/C^{23}), 127.0 (C^4/C^{13}), 125.9 (C^{11}/C^{23}), 68.9 (C^7), 44.1 (C^6), 31.5 (C^{18}), 28.9 (C^{19}), 21.5 (C^1 and C^{16}).

HRMS (ESI+): m/z calcd for $C_{31}H_{34}N_3O_4S_2$: 576.1991, found 596.1990 $[M+H]^+$.

***N*-(2-(2-benzylidene-1-tosylhydrazinyl)-2-(2-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (3p)**



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (91.6 mg, 0.162 mmol, 81%). With BF_3·THF as the Lewis acid, the product was obtained with 84% yield (95.3 mg, 0.169 mmol).

R*f*: 0.38 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.65 (s, 1H, H^{19}), 7.67 (d, *J* = 8.4 Hz, 2H, H^4/H^{15}), 7.59 (d, *J* = 8.4 Hz, 2H, H^{21}), 7.50-7.46 (m, 3H, H^4/H^{15} and H^{23}), 7.42 (t, *J* = 8.4 Hz, 2H, H^{22}), 7.34 – 7.29 (m, 1H, H^9), 7.21-7.17 (m, 3H, H^3/H^{16} and H^{11}), 7.13 (d, *J* = 8.4 Hz, 2H, H^3/H^{16}), 6.95-6.90 (m, 2H, H^{10} and H^{12}), 5.71 (dd, *J* = 9.6, 5.4 Hz, 1H, H^7), 4.90 (dd, *J* = 7.8, 4.8 Hz, 1H, NH), 3.52-3.48 (m, 1H, H^6), 3.42-3.38 (m, 1H, $H^{6'}$), 2.36 (s, 3H, H^1/H^{18}), 2.35 (s, 3H, H^1/H^{18}).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -116.2.

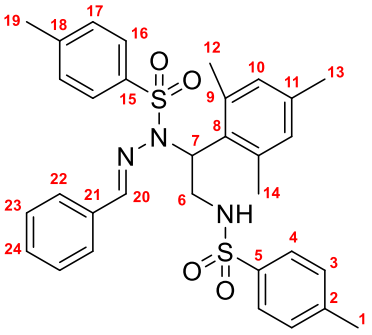
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 159.9 (d, $^{1}J_{CF}$ = 248 Hz, C^{13}), 157.6 (C^{19}), 144.6 (C^{2}/C^{17}), 143.4 (C^{2}/C^{17}), 136.7 (C^{5}/C^{14}), 134.5 (C^{5}/C^{14}), 133.7 (C^{20}), 131.3 (C^{23}), 129.8 (d, $^{3}J_{CF}$ = 6 Hz, C^{11}), 129.7 (C^{3}/C^{16}), 129.5 (C^{3}/C^{16}), 129.2 (d, $^{3}J_{CF}$ = 2 Hz, C^{9}), 128.9 (C^{22}), 128.0 (C^{21}), 127.9 (C^{4}/C^{15}), 127.0 (C^{4}/C^{15}), 124.3 (d, $^{2}J_{CF}$ = 13 Hz, C^{8}), 124.1 (d, $^{4}J_{CF}$ = 2 Hz, C^{10}), 115.3 (d, $^{2}J_{CF}$ = 22 Hz, C^{12}), 57.3 (d, $^{3}J_{CF}$ = 3 Hz, C^{7}), 45.2 (C^{6}), 21.5 (C^{1}/C^{18}), 21.4 (C^{1}/C^{18}).

M.p.: 110-114 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3307 (w-br), 331-2919 (w), 1598 (w), 1492 (w), 1332 (m), 1225 (w), 1159 (s), 1089 (m), 813 (m), 758 (m), 660 (s).

HRMS (ESI+): m/z calcd for $C_{29}H_{29}N_3O_4S_2F$: 566.1583, found 566.1584 $[M+H]^+$.

<u>*N*-(2-(2-benzylidene-1-tosylhydrazinyl)-2-mesitylethyl)-4-methylbenzenesulfonamide (3q)</u>



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (92 mg, 0.156 mmol, 78%). With BF_3·THF as the Lewis acid, the product was obtained with 73% yield (86 mg, 0.146 mmol).

R*f*: 0.52 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.73 (s, 1H, H^{20}), 7.65 (d, *J* = 8.2 Hz, 2H, H^{4}/H^{16}), 7.60 (d, *J* = 8.2 Hz, 2H, H^{4}/H^{16}), 7.56 (d, *J* = 8.2 Hz, 2H, H^{22}), 7.50 (t, *J* = 7.4 Hz, 1H, H^{24}), 7.44 (t, *J* = 7.4 Hz, 2H, H^{23}), 7.36 (d, *J* = 8.4 Hz, 2H, H^{3}/H^{17}), 7.23 (d, *J* = 8.2 Hz, 2H, H^{3}/H^{17}), 6.79 (br. s, 2H, H^{10}), 5.55 (dd, *J* = 10.0, 3.8 Hz, 1H, C^{7}), 4.83 (d, *J* = 7.6 Hz, 1H, NH), 3.54-3.48 (m, 1H, H^{6}), 3.14-3.08 (m, 1H, $H^{6'}$), 2.47 (s, 3H, H^{1}/H^{19}), 2.39 (s, 3H, H^{1}/H^{19}), 2.34-2.15 (m, 9H, H^{12}/H^{13}/H^{14}).

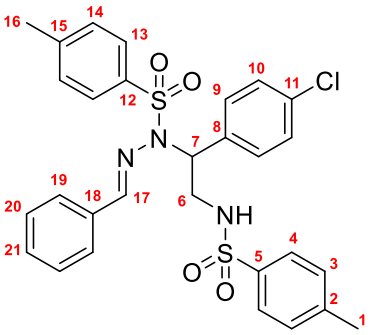
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 159.6 (C^{20}), 145.2 (C^{2}/C^{18}), 143.4 (C^{2}/C^{18}), 137.2 (C^{8}/C^{5}/C^{15}), 137.1 (C^{8}/C^{5}/C^{15}), 133.6 (C^{21}), 133.3 (C^{5}/C^{15}), 132.5 (C^{9}), 131.5 (C^{24}), 129.9 (C^{3}/C^{17}), 129.6 (C^{3}/C^{17}), 129.1 (C^{23}), 128.3 (C^{4}/C^{16}), 127.9 (C^{22}), 127.0 (C^{4}/C^{16}), 64.1 (C^{7}), 44.1 (C^{6}), 21.7 (C^{1}/C^{19}), 21.5 (C^{1}/C^{19}), 20.7 (C^{12} and C^{13} and C^{14}). C^{10} was not observed.

M.p.: 78-80 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3313 (w-br), 3066-2871 (w), 1598 (w), 1449 (w), 1332(m), 1160 (s), 1089 (m), 857 (m), 813 (m), 721 (m), 659 (s).

HRMS (ESI+): m/z calcd for $C_{32}H_{36}N_3O_4S_2$: 590.2147, found 590.2147 $[M+H]^+$.

N-(2-(2-benzylidene-1-tosylhydrazinyl)-2-(4-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (3r)



Prepared according to the general procedure **D**, the title compound was isolated as a white solid (114 mg, 0.196 mmol, 98%).

R*f*: 0.31 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.60 (s, 1H, H^{17}), 7.63 (d, *J* = 8.4 Hz, 2H, H^4/H^{13}), 7.55 (d, *J* = 8.4 Hz, 2H, H^{19}), 7.47 (t, *J* = 8.4 Hz, 1H, H^{21}), 7.43-7.38 (m, 4H, H^4/H^{13} and H^{20}), 7.20 (d, *J* = 8.4 Hz, 2H, H^3/H^{14}), 7.15-7.10 (m, 6H, H^3/H^{14}, H^9, H^{10}), 5.30 (dd, *J* = 9.4, 5.4 Hz, 1H, H^7), 4.66 (dd, *J* = 7.4, 4.8 Hz, 1H, NH), 3.46-3.41 (m, 1H, H^6), 3.36-3.31 (m, 1H, $H^{6'}$), 2.36 (m, 6H, H^1 and H^{16}).

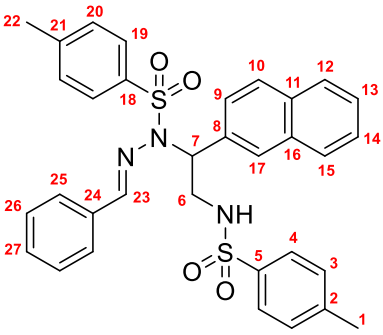
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 157.7 (C^{17}), 144.7 (C^2/C^{15}), 143.5 (C^2/C^{15}), 136.6 (C^5/C^{12}), 135.4 (C^8), 134.5 (C^5/C^{12}), 134.2 (C^{11}), 133.6 (C^{18}), 131.4 (C^{21}), 129.7 (C^3/C^{14}), 129.5 (C^3/C^{14}), 129.3 (C^9), 128.9 (C^{20}), 128.6 (C^{10}), 127.9 (C^4/C^{13}/C^{19}), 127.8 (C^4/C^{13}/C^{19}), 127.0 (C^4/C^{13}), 63.5 (C^7), 45.8 (C^6), 21.5 (C^1/C^{16}), 21.4 (C^1/C^{16}).

M.p.: 164-166 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3315 (w-br), 3065-2902 (w), 1598 (w), 1493 (w), 1450 (w), 1415 (w), 1335 (m), 1154 (s), 1089 (m), 1016 (w), 899 (w), 814 (m),, 661 (s).

HRMS (ESI+): m/z calcd for $C_{29}H_{29}N_3O_4S_2Cl$: 582.1288, found 582.1290 $[M+H]^+$.

N-(2-(2-benzylidene-1-tosylhydrazinyl)-2-(naphthalen-2-yl)ethyl)-4-methylbenzenesulfonamide (3s)



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (112.3 mg, 0.188 mmol, 94%).

R*f*: 0.39 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.65 (s, 1H, H^{23}), 7.77-7.74 (m, 1H, H^{12}/H^{15}), 7.65-7.60 (m, 7H, H^4/H^{19}, H^{10}, H^{12}/H^{15}, H^{13}, H^{14}, H^{17}), 7.48-7.43 (m, 5H, H^3/H^{20}, H^4/H^{19}, H^{27}), 7.37 (d, *J* = 8.4 Hz, 2H, H^{25}), 7.33 (dd, *J* = 8.4, 1.4 Hz, 1H, H^9), 7.16 (d, *J* = 8.4 Hz, 2H, H^3/H^{20}), 6.92 (d, *J* = 8.4 Hz, 2H, H^{26}), 5.50 (dd, *J* = 9.0, 5.6 Hz, 1H, H^7), 4.91-4.83 (m, 1H, NH), 3.61-3.56 (m, 1H, H^6), 3.52-3.47 (m, 1H, $H^{6'}$), 2.34 (s, 3H, H^1/H^{22}), 2.18 (s, 3H, H^1/H^{22}).

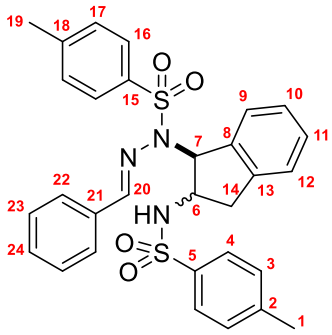
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 157.7 (C^{23}), 144.4 (C^2/C^{21}), 144.3 (C^2/C^{21}), 136.7 (C^5/C^{18}), 134.6 (C^5/C^{18}), 133.9 (C^8), 133.8 (C^{24}), 133.0 (C^{13}/C^{14}), 132.9 (C^{13}/C^{14}), 131.3 (C^{27}), 129.7 (C^3/C^{20}), 129.3 (C^{26}), 128.9 (C^3/C^{20}), 128.2 (C^{11}/C^{16}), 128.0 (C^{11}/C^{16}), 127.9 (C^{25}), 127.8 (C^4/C^{13}), 127.6 (C^{10}/C^{17}), 127.5 (C^{10}/C^{17}), 127.0 (C^4/C^{13}), 126.3 (C^{12}/C^{15}), 126.2 (C^{12}/C^{15}), 125.3 (C^9), 64.2 (C^7), 45.8 (C^6), 21.5 (C^1/C^{22}), 21.4 (C^1/C^{22}).

M.p.: 194-196 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3290 (br-w), 2920 (w), 1598 (w), 1448 (w), 1331 (m), 1223 (w), 1158 (s), 1089 (m), 1019 (w), 976 (w), 859 (w), 813 (m), 736 (m), 659 (s).

HRMS (ESI+): m/z calcd for $C_{33}H_{32}N_3O_4S_2$: 598.1834, found 598.1833 $[M+H]^+$.

(+/-)-*N*-(1-(2-benzylidene-1-tosylhydrazinyl)-2,3-dihydro-1H-inden-2-yl)-4-methylbenzenesulfonamide (3t)



Prepared according to the general procedure **D**, the title compound was isolated as a mixture of diastereoismers (combined yield : 96% - dr : 50:50). The diastereoisomers could be separated: the *trans* product was isolated as a white foam (56 mg, 0.100 mmol, 50%) while the *cis* product was formed in 46% yield (51.2 mg, 0.091 mmol, white foam).

Trans diasteroisomer:

R*f*: 0.36 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.81 (d, *J* = 8.2 Hz, 2H, H^4/H^{16}), 7.75 (d, *J* = 8.2 Hz, 2H, H^4/H^{16}), 7.72 (s, 1H, H^{20}), 7.37-7.32 (m, 3H, H^3/H^{17}, H^{24}), 7.29-7.24 (m, 5H, H^{11}, H^{22}, H^{23}), 7.18 (d, *J* = 8.2 Hz, 2H, H^3/H^{17}), 7.14-7.10 (m, 1H, H^{12}), 6.94-6.92 (m, 1H, H^{10}), 6.28 (d, *J* = 7.6 Hz, 1H, H^9), 5.64 (d, *J* = 9.0 Hz, 1H, H^7), 5.25 (br. s, 1H, NH), 3.98 (d, *J* = 7.6 Hz, 1H, H^6), 3.35 (dd, *J* = 15.7, 7.6 Hz, 1H, H^{14}), 2.84 (dd, *J* = 15.7, 8.9 Hz, 1H, H^{14}), 2.45 (s, 3H, H^1/H^{19}), 2.25 (s, 3H, H^1/H^{19}).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 154.2, (C^{20}), 144.8 (C^2/C^{18}), 143.4 (C^2/C^{18}), 138.8 (C^{13}), 136.4 (C^5/C^{15}), 136.1 (C^8), 133.7 (C^5/C^{15} and C^{21}), 130.7 (C^{24}), 130.1 (C^3/C^{17}), 129.6 (C^3/C^{17}), 128.5 (C^{23}), 128.3 (C^{11}), 127.9 (C^{22}), 127.6 (C^4/C^{16}), 127.5 (C^4/C^{16}), 126.8 (C^{10}), 125.2 (C^{12}), 124.5 (C^9), 69.4 (C^7), 57.6 (C^6), 37.6 (C^{14}), 21.7 (C^1/C^{19}), 21.4 (C^1/C^{19}).

M.p.: 146-150 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3231 (br-w), 2997-2919 (w), 1601 (w), 1572 (w), 1449 (w), 1337 (w), 1302 (w), 1218 (w), 1150 (s), 1089 (m), 109 (w), 995 (w), 924 (w), 811 (w), 751 (m), 658 (s).

HRMS (ESI+): m/z calcd for $C_{30}H_{30}N_3O_4S_2$: 560.1687, found 560.1683 $[M+H]^+$.

Cis diasteroisomer:

R*f*: 0.46 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.25 (s, 1H, H^{20}), 7.78 (d, *J* = 8.2 Hz, 2H, H^4/H^{16}), 7.73 (d, *J* = 8.2 Hz, 2H, H^4/H^{16}), 7.40-7.28 (m, 9H, H^3, H^{17}, H^{22}, H^{23}, H^{24}), 7.18 (t, *J* = 7.4 Hz, 1H, H^{11}), 7.07 (d, *J* = 7.4 Hz, 1H, H^{12}), 7.04 (t, *J* = 7.4 Hz, 1H, H^{10}), 6.83 (d, *J* = 7.6 Hz, 1H, H^9), 5.67 (d, *J* = 7.8 Hz, 1H, H^7), 5.44 (d, *J* = 9.0 Hz, 1H, NH), 4.33-4.23 (m, 1H, H^6), 2.98-2.94 (m, 1H, H^{14}), 2.92-2.89 (m, 1H, $H^{14'}$), 2.44 (s, 3H, H^1/H^{19}), 2.40 (s, 3H, H^1/H^{19}).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 156.8 (C^{20}), 144.8 (C^2/C^{18}), 143.4 (C^2/C^{18}), 140.9 (C^8/C^{13}), 137.9 (C^8/C^{13}), 137.8 (C^5/C^{15}), 135.6 (C^5/C^{15}), 133.5 (C^{21}), 131.1 (C^{24}), 130.0 (C^3/C^{17}), 129.7 (C^3/C^{17}), 129.0 (C^{11}), 128.8 (C^{23}), 128.0 (C^4/C^{16}), 127.7 (C^{22}), 127.2 (C^4/C^{16}),

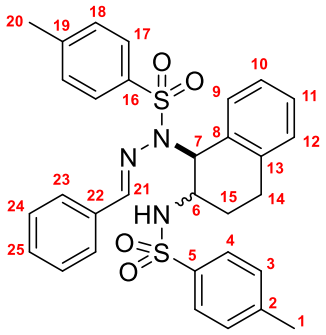
127.1 (C^{10}), 125.6 (C^{9}), 124.6 (C^{12}), 65.5 (C^{7}), 54.9 (C^{6}), 39.1 (C^{14}), 21.7 (C^{1}/C^{19}), 21.5 (C^{1}/C^{19}).

M.p.: 152-154 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3265 (w), 3070-2850 (w-br), 1599 (w), 1572 (w), 1494 (w), 1448 (w), 1399 (w), 1342 (s), 1324 (m), 1259 (w), 1220 (w), 1163 (s), 1121 (m), 1092 (s), 1014 (w), 990 (m), 948 (w), 918 (m), 849 (m), 814 (m), 756 (s), 717 (m), 705 (m), 690 (m), 659 (s).

HRMS (ESI+): m/z calcd for $C_{30}H_{29}N_3O_4S_2$: 559.1599, found 559.1612 $[M]^+$, 582.1504 $[M+Na]^+$.

(+/-)-*N*-(1-(2-benzylidene-1-tosylhydrazinyl)-1,2,3,4-tetrahydronaphthalen-2-yl)-4-methylbenzenesulfonamide (3u)



Prepared according to the general procedure **D**, the title compound was isolated as a mixture of diastereoismers (combined yield : 99% - dr : 50:50). The diastereoisomers could be separated: the *trans* product was isolated as a white foam (57.4 mg, 0.100 mmol, 50%) while the *cis* product was formed in 49% yield (56.1 mg, 0.098 mmol, white foam).

Trans diasteroisomer:

R*f*: 0.41 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 7.92 (d, *J* = 8.0 Hz, 2H, H^4/H^{17}), 7.62 (d, *J* = 8.0 Hz, 2H, H^4/H^{17}), 7.39 (d, *J* = 8.0 Hz, 2H, H^3/H^{18}), 7.28-7.21 (m, 3H, H^{24}, H^{25}), 7.07 (d, *J* = 7.2 Hz, 3H, H^{12}, H^{23}), 7.03 (t, *J* = 7.2 Hz, 1H, H^{11}), 6.93 (d, *J* = 8.0 Hz, 2H, H^3/H^{18}), 6.85 (s, 1H, H^{21}), 6.75 (t, *J* = 7.2 Hz, 1H, H^{10}), 6.14 (d, *J* = 7.8 Hz, 1H, H^9), 5.64 (d, *J* = 10.4 Hz, 1H, H^7), 5.43 (d, *J* = 5.0 Hz, 1H, NH), 3.68-3.62 (m, 1H, H^6), 2.98-2.85 (m, 2H, H^{14}), 2.69 (d, *J* = 10.7 Hz, 1H, H^{15}), 2.47 (s, 3H, H^1/H^{20}), 1.98-1.93 (m, 1H, $H^{15'}$), 1.89 (s, 3H, H^1/H^{20}).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 144.8 (C^2/C^{19}), 143.9 (C^{21}), 143.4 (C^2/C^{19}), 136.5 (C^{13}), 135.9 (C^5/C^{16}), 135.0 (C^5/C^{16}), 134.1 (C^{22}), 130.4 (C^8), 129.9 (C^3/C^{18}), 129.6 (C^{25}), 129.4 (C^3/C^{18}), 129.1 (C^{12}), 128.4 (C^4/C^{17}), 128.3 (C^{24}), 127.6 (C^9), 127.5 (C^4/C^{17}), 127.4 (C^{11}), 126.7 (C^{23}), 126.4 (C^{10}), 62.5 (C^7), 51.9 (C^6), 31.1 (C^{15}), 28.3 (C^{14}), 21.7 (C^1/C^{20}), 21.1 (C^1/C^{20}).

M.p.: 172-176 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3247 (w-br), 2925 (w), 2871 (w), 2850 (w), 1598 (w), 1490 (w), 1450 (w), 1437 (w), 1424 (w), 1395 (w), 1348 (m), 1336 (m), 1313 (m), 1295 (m), 1250 (w), 1230 (w), 1214 (w), 1151 (s), 1114 (m), 1088 (m), 1068 (m), 1017 (w), 986 (m), 956 (m), 941 (m), 929 (m), 915 (m), 868 (m), 850 (w), 833 (w), 809 (m), 757 (m), 748 (s), 704 (m), 690 (m), 658 (s).

HRMS (ESI+): m/z calcd for $C_{31}H_{31}N_3O_4S_2$: 573.1756, found 573.1762 $[M]^+$, 596.1654 $[M+Na]^+$.

Cis diasteroisomer:

R*f*: 0.50 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.46 (s, 1H, H^1), 7.73 (d, *J* = 7.8 Hz, 2H, H^4/H^{17}), 7.67 (d, *J* = 7.8 Hz, 2H, H^4/H^{17}), 7.43-7.30 (m, 6H, H^3/H^{18}, H^{23}, H^{24}), 7.30-7.22 (m, 3H, H^3/H^{18}, H^{25}), 7.13 (t, *J* = 7.4 Hz, 1H, H^{11}), 7.07 (d, *J* = 7.4 Hz, 1H, H^{12}), 6.89 (t, *J* = 7.2 Hz, 1H, H^{10}), 6.35 (d, *J* = 7.6 Hz, 1H, H^9), 6.08 (d, *J* = 4.5 Hz, 1H, NH), 5.40 (d, *J* = 3.0 Hz, 1H, H^7), 3.88-3.82 (m, 1H, H^6), 3.02-2.93 (m, 1H, H^{14}), 2.77-2.70 (m, 1H, $H^{14'}$), 2.48 (s, 3H, H^1/H^{20}), 2.45 (s, 3H, H^1/H^{20}), 2.26-2.22 (m, 1H, H^{15}), 1.98-1.90 (m, 1H, $H^{15'}$).

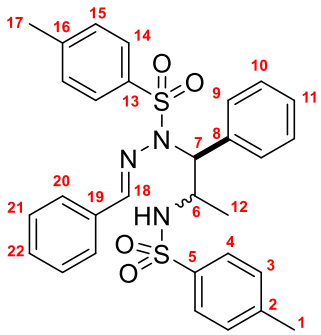
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 154.9 (C^{21}), 144.9 (C^2/C^{19}), 143.1 (C^2/C^{19}), 137.7 (C^{13}), 137.4 (C^5/C^{16}), 135.4 (C^5/C^{16}), 133.7 (C^{22}), 131.9 (C^{25}), 131.0 (C^8), 130.1 (C^3/C^{18}), 129.5 (C^3/C^{18}), 128.8 (C^{24}), 128.7 (C^{12}), 128.4 (C^9), 127.9 (C^4/C^{17}), 127.6 (C^{23}), 127.5 (C^{11}), 127.2 (C^4/C^{17}), 125.7 (C^{10}), 61.2 (C^7), 53.6 (C^6), 26.8 (C^{15}), 25.9 (C^{14}), 21.7 (C^1/C^{20}), 21.6 (C^1/C^{20}).

M.p.: 178-180 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3338 (br-w), 2960-2854 (w), 1598 (w), 1493 (w), 1429 (w), 1337 (m), 1158 (s), 1088 (m), 1009 (m), 895 (w), 814 (m), 753 (m), 667 (s).

HRMS (ESI+): m/z calcd for $C_{31}H_{31}N_3O_4S_2$: 573.1756, found 573.1766 $[M]^+$, 596.1658 $[M+Na]^+$.

(+/-)-*N*-(1-(2-benzylidene-1-tosylhydrazinyl)-1-phenylpropan-2-yl)-4-methylbenzenesulfonamide (3v)



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (107 mg, 0.190 mmol, 95% - mixture of diastereoisomers in a 50:50 ratio).

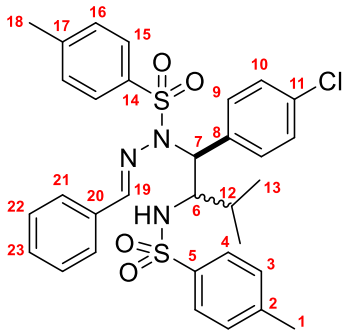
R*f*: 0.28 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm (*protons for the first diastereoisomer)* 8.51 (s, 1H, H^{18}), 7.60-7.58 (m, 2H, H^{20}), 7.48-7.37 (m, 5H, H^{arom}), 7.25-6.90 (m, 12H, H^{arom}), 5.07 (dd, J = 9.6, 1.8 Hz, 1H, H^7), 4.56 (d, *J* = 7.6 Hz, 1H, NH), 4.05-4.00 (m, 1H, H^6), 2.39 (s, 3H, H^1/H^{17}), 2.34 (s, 3H, H^1/H^{17}), 1.36 (d, *J* = 6.4 Hz, 3H, H^{12}). (*protons for the second diastereoisomer when different from the first diastereoisomer)* 8.33 (s, 1H, H^{18}), 8.18 (d, *J* = 8.4 Hz, 2H, H^{arom}), 7.48-7.37 (m, 5H, H^{arom}), 7.25-6.90 (m, 12H, H^{arom}),5.31 (d, *J* = 7.6 Hz, 1H, NH), 5.07 (dd, *J* = 9.6, 1.8 Hz, 1H, H^7), 3.97-3.91 (m, 1H, H^6), 2.26 (s, 3H, H^1/H^{17}), 2.14 (s, 3H, H^1/H^{17}), 1.09 (d, *J* = 6.4 Hz, 3H, H^{12}).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm (*carbon for the second diastereoisomer in parentheses)* 154.1 (153.0) (C^{18}), 144.2 (144.1) (C^2/C^{16}), 142.9 (142.8) (C^2/C^{16}), 137.5 (137.3) (C^5/C^{12}), 136.1 (135.5) (C^8), 134.5 (134.4) (C^5/C^{12}), 134.3 (134.1) (C^{19}), 130.8 (130.7), 129.4 (129.4) (C^3/C^{15}), 129.2 (129.2) (C^3/C^{15}), 129.0, 128.9, 128.7, 128.3, 128.2, 128.1, 128.1, 127.8 (127.8), 127.7 (127.6) (C^{20}), 127.0, 68.9 (68.5) (C^7), 53.0 (52.2) (C^6), 21.5 (21.5) (C^1/C^{17}), 21.4 (21.4) (C^1/C^{17}), 20.1 (19.9) (C^{12}).

HRMS (ESI+): m/z calcd for $C_{30}H_{32}N_3O_4S_2$: 562.1829, found 562.1834 $[M+H]^+$.

(+/-)-*N*-(1-(2-benzylidene-1-tosylhydrazinyl)-1-(4-chlorophenyl)-3-methylbutan-2-yl)-4-methylbenzenesulfonamide (3w)



Prepared according to the general procedure **D**, the title compound was isolated as a mixture of diastereoismers (combined yield : 97% - dr : 78:22). The diastereoisomers could be separated, as two white foams (94 mg, 0.151 mg, 76% and 26 mg, 0.042 mmol, 21%).

Major diasteroisomer:

R*f*: 0.49 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.50 (s, 1H, H^{19}), 7.60-7.57 (m, 2H, H^{22}), 7.50-7.47 (m, 5H, H^4/H^{15}, H^{21}, H^{23}), 7.20 (d, *J* = 8.4 Hz, 2H, H^4/H^{15}), 7.06 (d, *J* = 8.1 Hz, 2H, H^3/H^{16}), 7.01 (d, *J* = 8.4 Hz, 2H, H^9), 6.98 (d, *J* = 8.1 Hz, 2H, H^3/H^{16}), 6.92 (d, *J* = 8.4 Hz, 2H, H^{10}), 5.32 (t, *J* = 8.6 Hz, 2H, H^7 and NH), 3.89-3.82 (m, 1H, H^6), 2.33 (s, 3H, H^1/H^{18}), 2.31 (s, 3H, H^1/H^{18}), 1.69-1.62 (m, 1H, H^{12}), 1.01 (d, *J* = 6.8 Hz, 3H, H^{13}), 0.87 (d, *J* = 6.8 Hz, 3H, H^{13}).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 155.2 (C^{19}), 144.4 (C^2/C^{17}), 142.4 (C^2/C^{17}), 139.3 (C^5/C^{14}), 134.8 (C^5/C^{14}), 134.7 (C^8), 134.1 (C^{20}), 133.8 (C^{11}), 131.0 (C^{23}), 130.2 (C^9), 129.3 (C^3/C^{16}), 129.2 (C^3/C^{16}), 129.0 (C^{10}), 128.0 (C^{22}/C^4/C^{15}), 127.7 (C^{22}/C^4/C^{15}), 127.6 (C^{22}/C^4/C^{15}), 126.4 (C^{21}), 64.6 (C^7), 63.3 (C^6), 30.4 (C^{12}), 21.4 (C^1/C^{18}), 21.3 (C^1/C^{18}), 20.4 (C^{13}), 17.4 (C^{13}).

M.p.: 109-111 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3316 (br-w), 2977-2881 (w), 1598 (w), 1574 (w), 1492 (w), 1448 (w), 1386 (m), 1288 (w), 1155 (s), 1090 (m), 1032 (w), 1005 (w), 915 (w), 886 (w), 812 (w), 718 (m), 691 (w), 658 (s).

HRMS (ESI+): m/z calcd for $C_{32}H_{35}N_3O_4S_2$: 624.1758, found 624.1765 $[M+H]^+$.

Minor diasteroisomer:

R*f*: 0.39 (5/4/1 hexane/CH_2Cl_2/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.61 (s, 1H, H^{19}), 7.68-7.65 (m, 2H, H^{22}), 7.49-7.46 (m, 3H, H^{21}, H^{23}), 7.14 (d, *J* = 8.2 Hz, 2H, H^4/H^{15}), 7.10 (d, *J* = 8.4 Hz, 2H, H^9), 7.01 (dd, *J* = 8.0, 4.5 Hz, 4H, H^3/H^{16}, H^4/H^{15}), 6.89 (d, *J* = 8.2 Hz, 2H, H^3/H^{16}), 6.76 (d, *J* = 8.4 Hz, 2H, H^{10}), 5.05 (d, *J* = 10.8 Hz, 1H, H^7), 4.29 (d, *J* = 10.8 Hz, 1H, NH), 4.21 (td, *J* = 10.8, 2.2 Hz, 1H, H^6), 2.38 (s, 3H, H^1/H^{18}), 2.31-2.27 (m, 1H, H^{12}), 2.26 (s, 3H, H^1/H^{18}), 1.06 (d, *J* = 6.8 Hz, 3H, H^{13}), 1.03 (d, *J* = 6.8 Hz, 3H, H^{13}).

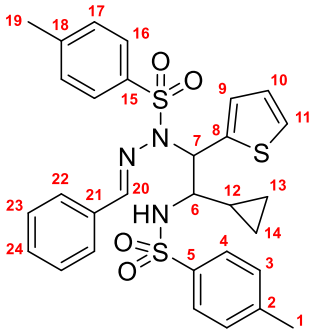
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 154.6 (C^{19}), 144.2 (C^2/C^{17}), 142.5 (C^2/C^{17}), 138.6, 135.2 (C^8), 134.3, 134.1 (C^{20}), 134.0 (C^{11}), 131.0 (C^{23}), 130.6 (C^9), 129.2 (C^3/C^{16}), 129.1 (C^3/C^{16}), 129.0 (C^{22}/C^4/C^{15}), 127.9 (C^{10}), 127.7 (C^{22}/C^4/C^{15}), 127.6 (C^{22}/C^4/C^{15}), 126.1 (C^{21}), 64.9 (C^7), 62.0 (C^6), 27.9 (C^{12}), 21.5 (C^1/C^{18}), 21.4 (C^1/C^{18}), 20.5 (C^{13}), 14.8 (C^{13}).

M.p.: 102-104 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3277 (br-w), 2964-2866 (w), 1599 (w), 1570 (w), 1492 (w), 1448 (w), 1319 (m), 1155 (s), 1090 (m), 1043 (w), 912 (w), 843 (w), 808 (m), 719 (m), 658 (s).

HRMS (ESI+): m/z calcd for $C_{32}H_{35}N_3O_4S_2$: 624.1758, found 624.1757 $[M+H]^+$.

(+/-)-*N*-(2-(2-benzylidene-1-tosylhydrazinyl)-1-cyclopropyl-2-(thiophen-2-yl)ethyl)-4-methylbenzenesulfonamide (3x)

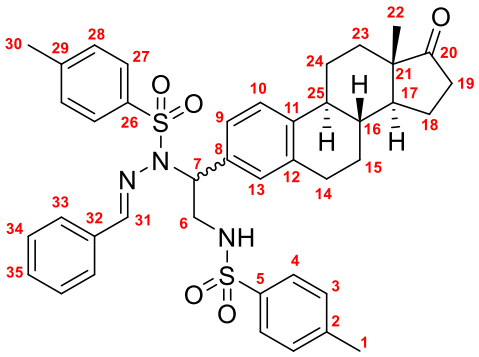


Prepared according to the general procedure **D**, the title compound couldn't be isolated due to its high instability. Its formation could only be confirmed by a mass experiment on the crude of the reaction.

R*f*: 0.27 (5/4/1 hexane/CH_2Cl_2/EtOAc).

MS (ESI+): m/z 594.15 $[M+H]^+$.

(+/-)-(2-(2-(benzylidene)-1-tosylhydrazinyl)-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)ethyl)-4-methylbenzenesulfonamide (3y)



Prepared according to the general procedure **D**, the title compound was isolated as a white foam (121.6 mg, 0.168 mmol, 84%) as a mixture of two diastereoisomeres.

R*f*: 0.36 (5/5 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.57 (d, J = 8.4 Hz, 1H, H^{31}), 7.64 (d, J = 8.0 Hz, 2H, H^4/H^{27}), 7.55 (d, J = 7.0 Hz, 2H, H^{33}), 7.47-7.37 (m, 5H, H^4/H^{27}, H^{34}, H^{35}), 7.19 (d, J = 7.6 Hz, 2H, H^3/H^{28}), 7.13-7.07 (m, 3H, H^3/H^{28} and H^{13}), 7.01-6.96 (m, 1H, H^{10}), 6.89 (d, J = 13.0 Hz, 1H, H^9), 5.30 (dd, J = 9.0, 5.6 Hz, 1H, H^7), 4.75 (t, J = 5.6 Hz, 1H, NH), 3.47-3.35 (m, 2H, H^6), 2.79-2.68 (m, 2H, H^{14}), 2.50 (dd, J = 19.0, 9.0 Hz, 1H, aliphatic H of estrone moiety), 2.35 (s, 6H, H^1 and H^{30}), 2.26-1.91 (m, 5H, aliphatic H of estrone moiety), 1.67-1.33 (m, 7H, aliphatic H of estrone moiety), 0.91 (s, 3H, H^{22}).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm (*carbons when the second diastereoisomer is observed are indicated in parentheses – non attributed signal belongs to the aliphatic carbons of the estrone moiety)* 220.7 (C^{20}), 156.9 (156.8) (C^{31}), 144.2 (C^2/C^{29}), 143.4 (C^2/C^{29}), 139.8 (C^8), 136.7, 136.5, 134.9 (134.8), 134.2 (134.1), 133.9, 131.1, 129.7 (C^3/C^{28}), 129.4 (129.3), 128.8, 128.7 (128.6) (C^9), 128.0, 127.9 (C^{33}), 127.0 (C^4/C^{27}), 125.5 (125.4), 125.1 (125.0) (C^{10}), 63.8 (C^7), 50.4, 47.9, 45.6 (C^6), 44.3, 31.5, 29.3 (29.2) (C^{14}), 26.4, 25.7, 21.6, 21.6 (C^1/C^{30}), 21.5 (C^1/C^{30}), 13.8 (C^{22}).

M.p.: 120-122 °C.

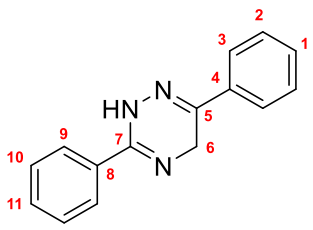
FTIR (ATR, neat): ν_{max}/cm^{-1} 3278 (w), 2917-2858 (w), 1735 (m), 1597 (w), 1335 (m), 1159 (s), 1087 (m), 861 (w), 813 (m), 660 (s).

HRMS (ESI+): m/z calcd for $C_{41}H_{46}N_3O_5S_2$: 724.2853, found 724.2879 $[M+H]^+$.

3.4. Synthesis of dihydrotriazine **4a**

During the optimization process of the cyclization step, the dihydrotriazine **4a** was isolated.

3,6-diphenyl-2,5-dihydro-1,2,4-triazine (4a)



In a microwave tube were added the aminohydrazone **3a** and Cs_2CO_3 (3 equiv), followed by dry toluene (0.1 M). The tube was sealed under Argon and heated at 110 °C for 2 h (observation of complete conversion by TLC). The yellow-orange suspension was cooled to room temperature, filtered through a small pad of celite and the solid washed with EtOAc. The solvent was removed *in vacuo* and the crude was suspended in a Et_2O/acetone mixture 1/1, filtered on a fritted funnel and washed with Et_2O. The solid was dried *in vacuo* to give the desired product **4a** as a white solid (36%). The spectral data were in agreement with literature values.[15]

R*f*: 0.18 (6/4 hexane/EtOAc).

^{1}H NMR (600 MHz, $CO(CD_3)_2$): δ/ppm 8.01 (d, *J* = 7.1 Hz, 2H, H^9), 7.85 (dd, *J* = 8.1, 1.4 Hz, 2H, H^3), 7.53-7.43 (m, 6H, H^1, H^2, H^{10}, H^{11}), 4.41 (s, 2H, H^6).

^{13}C NMR (150 MHz, $CO(CD_3)_2$): δ/ppm 141.7 (C^4/C^5/C^8), 135.0 (C^4/C^5/C^8), 133.0 (C^4/C^5/C^8), 130.4 (C^{11}), 129.2 (C^1), 128.5 (C^2/C^{10}), 128.4 (C^2/C^{10}), 126.5 (C^9), 126.0 (C^3), 43.8 (C^6). C^7 was not observed.

M.p.: 191-193 °C [lit. = 196 °C].[15]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3282 (w), 3056 (w), 3036 (w), 2998 (w), 2957 (w), 2921 (w), 2852 (w), 2819 (w), 1620 (m), 1599 (w), 1575 (w), 1492 (m), 1460 (s), 1443 (m), 1346 (m), 1326 (s), 1269 (m), 1227 (w), 1159 (m), 1135 (m), 1086 (m), 1023 (m), 1001 (w), 981 (m), 969 (m), 939 (m), 921 (w), 911 (m), 805 (w), 779 (s), 755 (s), 688 (s), 664 (w).

HRMS (ESI+): m/z calcd for $C_{15}H_{13}N_3$: 235.1109, found 235.1109 $[M]^+$, 236.1185 $[M+H]^+$.

3.5. Synthesis of triazines **5a-5y**

General procedure E for the synthesis of triazine from tosylhydrazone and aziridine

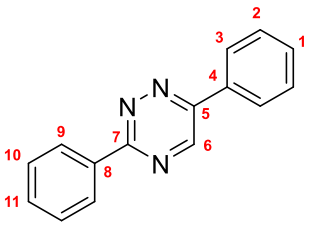
Hydrazone **1** (0.5 mmol, 1 equiv) and aziridine **2** (0.6 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (2.5 mL, 0.2 M) in an oven-dried tube under Argon. $BF_3{\cdot}OEt_2$ (0.1 mmol, 0.2 equiv) was introduced dropwise and the pale yellow/orange reaction mixture was stirred at rt for 1-2 h. The progression of reaction was monitored by TLC (hexane/CH_2Cl_2/EtOAc 5/4/1). The solvent was carefully evaporated via compressed air first and then *in vacuo*. Cs_2CO_3

[15] Atkinson, C. M.; Cossey, H. D. *J. Am. Chem. Soc*. **1962**, 1805.

(1.75 mmol, 3.5 equiv) and activated MnO_2 (3 mmol, 6 equiv) were added to the reaction mixture, followed by dry toluene (5 mL, 0.1 M). The tube was sealed under Argon and heated at 110 °C for 3 h in total. Two other portions of activated MnO_2 (2 mmol, 4 equiv) were added after 1 and 2 h. The progression of the reaction was monitored by TLC (7/3 hexane/EtOAc). The reaction mixture was cooled to rt, filtered through a plug of celite and washed with EtOAc. The filtrate was stirred with QuadraPure®-Benzylamine for 30 min, filtered and evaporated *in vacuo*. The crude was purified by silica gel chromatography (hexane/EtOAc or CH_2Cl_2/hexane) unless said otherwise and dried under vacuum to yield the desired product **5**.

N.B.: QuadraPure®-Benzylamine was used in order to scavenge the undesired aldehyde formed during the reaction (obtained from the hydrolysis of the aminohydrazone). The use of this resin allowed an easier purification of the triazine afterwards via column chromatography, the triazine and the aldehyde having the tendancy to co-elute.

3,6-diphenyl-1,2,4-triazine (5a)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (47.8 mg, 0.205 mmol, 41%). When the reaction was carried out under reflux of toluene with a condenser instead of a sealed tube, the product was isolated with 39% yield (45.5 mg, 0.195 mmol), with spectral data in agreement with literature values.[16]

R*f*: 0.54 (6/4 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.07 (s, 1H, H^6), 8.59 (dd, J = 6.6, 3.2 Hz, 2H, H^9), 8.17 (dd, J = 7.9, 1.4 Hz, 2H, H^3), 7.59-7.56 (m, 6H, H^1, H^2, H^{10}, H^{11}).

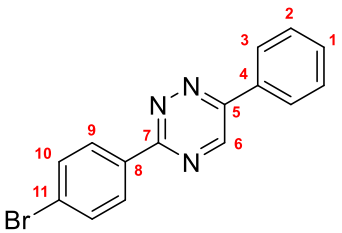
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 162.4 (C^7), 155.1 (C^5), 146.4 (C^6), 134.6 (C^4/C^8), 133.3 (C^4/C^8), 131.7 (C^{11}), 130.9 (C^1), 129.4 (C^2/C^{10}), 128.9 (C^2/C^{10}), 128.2 (C^9), 126.7 (C^3).

M.p.: 158-160 °C [lit. = 158-160 °C].[16]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3064 (w), 3035 (w), 2962 (w), 2925 (w), 2853 (w), 1600 (w), 1581 (w), 1507 (w), 1491 (w), 1453 (m), 1436 (m), 1403 (s), 1325 (m), 1262 (w), 1178 (w), 1163 (w), 1088 (m), 1026 (m), 1001 (m), 988 (m), 952 (w), 919 (m), 821 (w), 810 (m), 762 (s), 707 (m), 686 (s), 657 (m).

HRMS (ESI+): m/z calcd for $C_{15}H_{12}N_3$: 234.1031, found 234.1040 $[M+H]^+$.

3-(4-bromophenyl)-6-phenyl-1,2,4-triazine (5b)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (79.9 mg, 0.256 mmol, 51%).

R*f*: 0.55 (6/4 hexane/EtOAc).

[16] (a) Konno, S.; Osawa, N.; Yamanaka, H. *J. Agric. Food Chem.* **1995**, *43*, 838. (b) Saraswathi, T. V.; Srinivasan, V. R. *Tetrahedron* **1977**, *33*, 1043.

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.05 (s, 1H, H^6), 8.46 (d, *J* = 8.2 Hz, 2H, H^9), 8.16 (d, *J* = 6.4 Hz, 2H, H^3), 7.69 (d, *J* = 8.2 Hz, 2H, H^{10}), 7.62-7.55 (m, 3H, H^1, H^2).

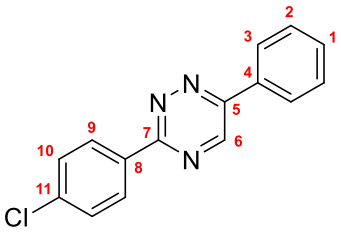
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 161.7 (C^7), 155.2 (C^5), 146.5 (C^6), 133.6 (C^4/C^8), 133.1 (C^4/C^8), 132.2 (C^{10}), 131.0 (C^1), 129.6 (C^9), 129.4 (C^2), 126.7 (C^3), 126.6 (C^{11}).

M.p.: 192-194 °C [lit. = 193-194 °C].[16a]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3048 (w), 2927 (w), 2854 (w), 1681 (w), 1588 (m), 1504 (w), 1490 (m), 1442 (m), 1407 (s), 1395 (s), 1328 (m), 1279 (m), 1180 (w), 1157 (m), 1106 (m), 1086 (s), 1071 (m), 1033 (m), 1028 (m), 1006 (s), 992 (m), 969 (m), 918 (m), 843 (s), 798 (s), 755 (s), 726 (w), 709 (w), 686 (s), 660 (m).

HRMS (ESI+): m/z calcd for $C_{15}H_{11}N_3Br$: 312.0136, found 312.0137 $[M+H]^+$.

3-(4-chloro phenyl)-6-phenyl-1,2,4-triazine (5c)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (75 mg, 0.280 mmol, 56%), with spectral data in agreement with literature values.[17]

R*f*: 0.50 (6/4 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.06 (s, 1H, H^6), 8.54 (d, *J* = 8.6 Hz, 2H, H^9), 8.16 (dd, *J* = 7.6, 1.7 Hz, 2H, H^3), 7.63-7.57 (m, 3H, H^1, H^2), 7.53 (d, *J* = 8.6 Hz, 2H, H^{10}).

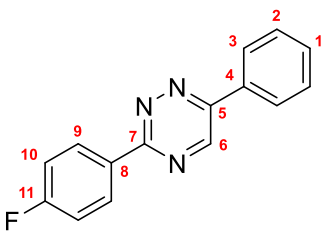
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 161.6 (C^7), 155.2 (C^5), 146.5 (C^6), 138.0 (C^{11}), 133.1 (C^4 and C^8), 131.0 (C^1), 129.4 (C^9), 129.3 (C^2/C^{10}), 129.2 (C^2/C^{10}), 126.7 (C^3).

M.p.: 186-188 °C [lit. = 187-188 °C].[17]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3062 (w-br), 2854 (w), 1687 (w), 1667 (w), 1593 (m), 1490 (m), 1444 (m), 1408 (s), 1397 (s), 1332 (m), 1287 (m), 1186 (w), 1173 (w), 1100 (m), 1087 (s), 1035 (m), 1010 (s), 992 (m), 955 (w), 923 (w), 851 (w), 842 (m), 798 (s), 757 (s), 738 (m), 688 (s), 663 (m).

HRMS (ESI+): m/z calcd for $C_{15}H_{11}N_3Cl$: 268.0642, found 268.0640 $[M+H]^+$, 270.0613 $[M+H+2]^+$.

3-(4-fluorophenyl)-6-phenyl-1,2,4-triazine (5d)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (44 mg, 0.175 mmol, 35%).

R*f*: 0.50 (6/4 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.05 (s, 1H, H^6), 8.60 (dd, *J* = 8.8, 5.5 Hz, 2H, H^9), 8.16 (dd, *J* = 7.8, 1.6 Hz, 2H, H^3), 7.61-7.54 (m, 3H, H^1, H^2), 7.24 (t, J = 8.8 Hz, 2H, H^{10}).

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[17] O'Rourke, M.; Lang, Jr., S. A.; Cohen, E. *J. Med. Chem.* **1977**, *20*, 723.

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -108.4.

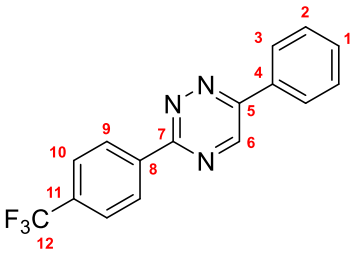
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 165.2 (d, $^{1}J_{CF}$ = 252 Hz, C^{11}), 161.6 (C^{7}), 155.0 (C^{5}), 146.5 (C^{6}), 133.2 (C^{4}), 130.9 (C^{1}), 130.8 (d, $^{4}J_{CF}$ = 3 HZ, C^{8}), 130.4 ($^{3}J_{CF}$ = 9 Hz, C^{9}), 129.4 (C^{2}), 126.7 (C^{3}), 116.1 (d, $^{2}J_{CF}$ = 22 Hz, C^{10}).

M.p.: 180-182 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3057 (w), 2956 (w), 2920 (w), 2853 (w), 1599 (m), 1559 (w), 1511 (m), 1500 (w), 1442 (m), 1403 (s), 1346 (w), 1323 (m), 1298 (m), 1227 (m), 1154 (m), 1098 (m), 1086 (m), 1041 (m), 1027 (m), 1013 (m), 993 (m), 950 (w), 924 (w), 846 (s), 826 (m), 806 (s), 762 (s), 700 (m), 682 (m), 655 (w).

HRMS (ESI+): m/z calcd for $C_{15}H_1N_3F$: 252.0937, found 252.0936 $[M+H]^+$.

6-phenyl-3-(4-(trifluoromethyl)phenyl)-1,2,4-triazine (5e)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (77.6 mg, 0.258 mmol, 52%), with spectral data in agreement with literature values.[18]

R*f*: 0.72 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.10 (s, 1H, H^{6}), 8.72 (d, *J* = 8.2 Hz, 2H, H^{9}), 8.19-8.17 (m, 2H, H^{3}), 7.82 (d, *J* = 8.2 Hz, 2H, H^{10}), 7.62-7.57 (m, 3H, H^{1}, H^{2}).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -62.9.

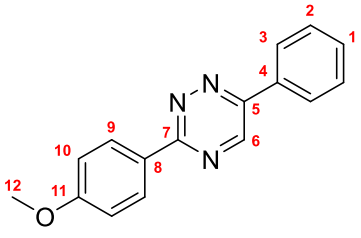
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 161.4 (C^{7}), 155.8 (C^{5}), 146.7 (C^{6}), 138.1 (C^{8}), 133.3 (q, $^{2}J_{CF}$ = 31.8 Hz, C^{11}), 133.0 (C^{4}), 131.4 (C^{1}), 129.6 (C^{2}), 128.6 (C^{9}), 127.0 (C^{3}), 126.0 (q, $^{3}J_{CF}$ = 4 Hz, C^{10}), 124.1 (q, $^{1}J_{CF}$ = 271 Hz, C^{12}).

M.p.: 194-196 °C [lit. = 194-197 °C].[18]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3619 (w), 3019 (w), 2927 (w), 2221 (w), 2178 (w), 1942 (w), 1691 (w), 1599 (w), 1518 (w), 1444 (w), 1415 (m), 1316 bm), 1169 (m), 1153 (m), 1107 (s), 1083 (s), 1066 (m), 1014 (m), 990 (m), 926 (w), 857 (s), 808 (s), 761 (m), 690 (s), 659 (m).

HRMS (ESI+): m/z calcd for $C_{16}H_{11}N_3F_3$: 302.0905, found 302.0898 $[M+H]^+$.

3-(4-methoxyphenyl)-6-phenyl-1,2,4-triazine (5f)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (31 mg, 0.118 mg, 24%), with spectral data in agreement with literature values.[16b]

R*f*: 0.54 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.99 (s, 1H, H^{6}), 8.54 (d, *J* = 8.9 Hz, 2H, H^{9}), 8.14 (d, *J* = 8.2 Hz, 2H, H^{3}), 7.58-7.54

[18] Ernd, M.; Heuschmann, M.; Zipse, H. *Helvetica Chimica Acta* **2005**, *88*, 1491.

(m, 3H, H^1, H^2), 7.05 (d, J = 8.9 Hz, 2H, H^{10}), 3.90 (s, 3H, H^{12}).

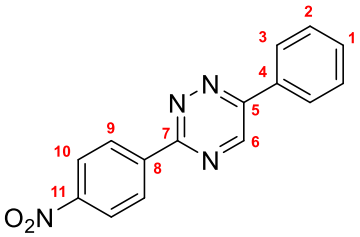
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 162.7 (C^7/C^{11}), 162.3 (C^7/C^{11}), 154.5 (C^5), 146.5 (C^6), 133.6 (C^4), 130.8 (C^1), 130.0 (C^9), 129.4 (C^2), 127.3 (C^8), 126.6 (C^3), 114.4 (C^{10}), 55.6 (C^{12}).

M.p.: 166-168 °C [lit. = 168 °C].[16b]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3734 (w), 3052 (w), 2988 (w), 2941 (w), 2841 (w), 2343 (w), 2082 (w), 1906 (w), 1721 (w), 1604 (m), 1581 (m), 1513 (w), 1443 (w), 1422 (m), 1402 (m), 1330 (m), 1298 (m), 1256 (m), 1184 (m), 1165 (m), 1111 (m), 1089 (w), 1036 (s), 921 (w), 839 (m), 800 (s), 759 (s), 694 (s), 681 (m).

HRMS (ESI+): m/z calcd for $C_{16}H_{14}N_3O$: 264.1131, found 264.1120 $[M+H]^+$.

3-(4-nitrophenyl)-6-phenyl-1,2,4-triazine (5g)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (47 mg, 0.169 mmol, 34%), with spectral data in agreement with literature values.[18]

R*f*: 0.41 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.14 (s, 1H, H^6), 8.79 (d, J = 8.9 Hz, 2H, H^{10}), 8.41 (d, J = 8.9 Hz, 2H, H^9), 8.20-8.18 (m, 2H, H^3) 7.62-7.60 (m, 3H, H^1, H^2).

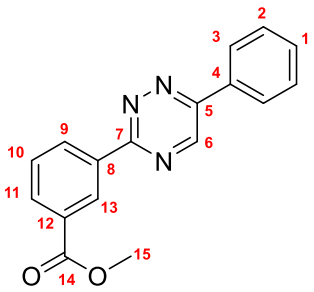
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 160.8 (C^7), 156.0 (C^5), 150.0 (C^{11}), 146.7 (C^6), 140.6 (C^8), 132.9 (C^4), 131.6 (C^1), 129.7 (C^2), 129.2 (C^{10}), 127.1 (C^3), 124.2 (C^9).

M.p.: 256-258 °C [lit. > 220 °C].[18]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3677 (w), 3083 (w), 2851 (w), 2214 (w), 2120 (w), 1941 (w), 1910 (w), 1698 (w), 1597 (w), 1555 (w), 1523 (s), 1444 (w), 1412 (m), 1397 (m), 1339 (m), 1314 (m), 1161 (w), 1110 (m), 1084 (m), 1031 (m), 1012 (m), 990 (w), 950 (w), 927 (w), 868 (m), 853 (m), 808 (s), 762 (s), 745 (m), 685 (s), 660 (m).

HRMS (ESI+): m/z calcd for $C_{15}H_{11}N_4O_4$: 279.0882, found 279.0885 $[M+H]^+$.

methyl 3-(6-phenyl-1,2,4-triazin-3-yl)benzoate (5h)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (86.7 mg, 0.298 mmol, 60%). The scale up was performed on a 5 mmol scale (see S50), leading to the desired product in 55% yield (806 mg, 2.77 mmol).

R*f*: 0.55 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.22 (t, J = 1.2 Hz, 1H, H^{13}), 9.06 (s, 1H, H^6), 8.76 (dt, J = 7.8, 1.2 Hz, 1H, H^9), 8.22 (dt, J = 7.8, 1.2 Hz, 1H, H^{11}), 8.16-8.13 (m, 2H, H^3), 7.62 (t, J = 7.8 Hz, 1H, H^{10}), 7.58-7.54 (m, 3H, H^1, H^2), 3.96 (s, 3H, H^{15}).

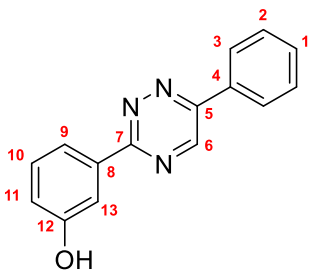
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 166.7 (C^{14}), 161.7 (C^{7}), 155.5 (C^{5}), 146.6 (C^{6}), 135.2 (C^{12}), 133.2 (C^{4}), 132.6 (C^{11}), 132.4 (C^{9}), 131.2 (C^{1}), 131.1 (C^{8}), 129.5 (C^{2}), 129.4 (C^{10}), 129.2 (C^{13}), 126.8 (C^{3}), 52.4 (C^{15}).

M.p.: 163-165 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3747 (w), 2952 (w), 1726 (s), 1602 (w), 1439 (m), 1404 (s), 1329 (w), 1291 (m), 1267 (m), 1251 (s), 1226 (m), 1190 (w), 1157 (w), 1116 (w), 1087 (m), 1041 (w), 1004 (w), 963 (w), 929 (w), 860 (w), 809 (m), 771 (s), 748 (s), 734 (m), 686 (s).

HRMS (ESI+): m/z calcd for $C_{17}H_{14}N_3O_2$: 292.1086, found 292.1089 $[M+H]^+$.

3-(6-phenyl-1,2,4-triazin-3-yl)phenol (5i)



Prepared according to the general procedure **E**, the Bpin triazine was formed and observed in the crude NMR (74% NMR yield). The Bpin triazine was then directly oxidized:[19] the crude mixture was dissolved in 5 mL THF and cooled to 0 °C. 2.5 mL of a 1 N NaOH solution and 0.28 mL 30% H_2O_2 were added and the mixture was stirred for 1 h before being diluted with CH_2Cl_2 and quenched with 3.5 mL 1 N HCl. The aqueous layer was washed with CH_2Cl_2 (3x). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude was purified by silica chromatography (19/1 CH_2Cl_2/EtOAc). The title compound was isolated as a yellow solid (68 mg, 0.273 mmol, 55%).

R*f*: 0.31 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, THF-d^{8}): δ/ppm 9.22 (s, 1H, H^{6}), 8.64 (br. s, 1H, OH), 8.27 (d, J = 6.9 Hz, 2H, H^{3}), 8.06 (d, J = 7.8 Hz, 1H, H^{9}), 8.03 (s, 1H, H^{13}), 7.58-7.51 (m, 3H, H^{1}, H^{2}), 7.34 (t, J = 7.8 Hz, 1H, H^{10}), 6.95 (dd, J = 7.8, 1.7, 1H, H^{11}).

^{13}C NMR (150 MHz, THF-d^{8}): δ/ppm 163.2 (C^{7}), 159.5 (C^{12}), 156.2 (C^{5}), 147.6 (C^{6}), 137.6 (C^{8}), 135.1 (C^{4}), 131.6 (C^{1}), 130.8 (C^{10}), 130.2 (C^{2}), 127.7 (C^{3}), 120.1 (C^{11}), 119.6 (C^{9}) 115.6 (C^{13}).

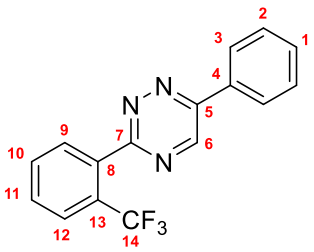
M.p.: 232-234 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3354 (w), 3262 (w), 3164 (bw), 3050 (w), 2852 (w), 2364 (bw), 2106 (bw), 1601 (m), 1500 (w), 1454 (m), 1413 (m), 1317 (m), 1257 (w), 1219 (m), 1179 (m), 1154 (m), 1087 (m), 1044 (m), 995 (m), 942 (w), 892 (m), 793 (m), 756 (m), 682 (s).

HRMS (ESI+): m/z calcd for $C_{15}H_{12}N_3O$: 250.0980, found 250.0979 $[M+H]^+$.

[19] Yamashita, Y.; Tellis, J. C.; Molander, G. A. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 12026.

6-phenyl-3-(2-(trifluoromethyl)phenyl)-1,2,4-triazine (5j)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (24 mg, 0.080 mmol, 16%) using 5 equiv of Cs_2CO_3 and 16 equiv of MnO_2.

R*f*: 0.44 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.13 (s, 1H, H^6), 8.23-8.18 (m, 2H, H^3), 7.91 (d, J = 7.8 Hz, 1H, H^9), 7.89 (d, J = 7.8 Hz, 1H, H^{12}), 7.74 (t, J = 7.8 Hz, 1H, H^{10}), 7.68 (t, J = 7.8 Hz, 1H, H^{11}), 7.63-7.58 (m, 3H, H^1, H^2).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -57.0.

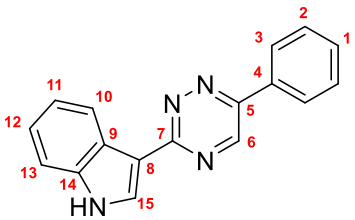
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 164.4 (C^7), 155.4 (C^5), 146.1 (C^6), 135.2 (q, $^3J_{CF}$ = 2 Hz, C^8), 132.9 (C^4), 132.1 (C^9), 132.0 (C^{10}), 131.4 (C^1), 130.3 (C^{11}), 129.6 (C^2), 129.4 (q, $^2J_{CF}$ = 32 Hz, C^{13}), 127.3 (q, $^3J_{CF}$ = 2 Hz, C^{12}), 127.1 (C^3), 124.0 (q, $^1J_{CF}$ = 274 Hz, C^{14}).

M.p.: 106-108 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3058 (w), 2922 (m), 2853 (w), 2191 (w), 2074 (w), 1737 (q), 1600 (w), 1492 (w), 1441 (w), 1401 (m), 1353 (w), 1309 (s), 1271 (m), 1160 (s), 1144 (s), 1109 (s), 1093 (s), 1051 (m), 1033 (s), 1000 (m), 939 (m), 822 (m), 767 (s), 693 (s), 655 (m).

HRMS (ESI+): m/z calcd for $C_{16}H_{11}N_3F_3$: 302.0900, found 302.0887 $[M+H]^+$.

1-(3-(6-phenyl-1,2,4-triazin-3-yl)-1H-indol-1-yl)ethan-1-one (5k)



Prepared according to the general procedure **E**, the title compound was isolated by column chromatography on Florisil® (9/1 hexane/EtOAc) as a yellow solid (35 mg, 0.129 mmol, 26%).

R*f*: 0.44 (7/3 hexane/EtOAc).

^{1}H NMR – protonated form (600 MHz, $CDCl_3$): δ/ppm 8.94 (s, 1H, NH), 8.77 (s, 1H, H^6), 8.59 (br. s, 1H, NH), 8.49-8.44 (m, 1H, H^{10}), 7.87-7.86 (m, 2H, H^3), 7.62 (d, J = 2.7 Hz, 1H, H^{15}), 7.48-7.43 (m, 3H, H^1, H^2), 7.43-7.41 (m, 1H, H^{13}), 7.33-7.28 (m, 2H, H^{11}, H^{12}).

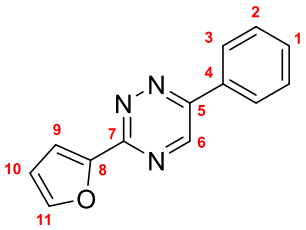
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 160.4 (C^6), 157.7 (C^5), 137.0 (C^7), 134.8 (C^4), 130.8 (C^1), 130.1 (C^{15}), 128.9 (C^2), 128.4 (C^3), 125.3 (C^9), 123.9 (C^{11}/C^{12}), 122.7 (C^{10}), 121.9 (C^{11}/C^{12}), 113.7 (C^8), 111.5 (C^{13}). The quaternary carbon C^{14} was not observed.

M.p.: 139-140 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3160 (m), 3115 (w), 3049 (w), 2924 (m), 2850 (w), 2576 (w), 1907 (w), 1615 (s), 1578 (m), 1552 (m), 1494 (m), 1438 (m), 1377 (m), 1340 (w), 1312 (m), 1281 (m), 1247 (s), 1186 (w), 1157 (m), 1125 (s), 1088 (m), 999 (m), 955 (m), 868 (m), 832 (w), 801 (m), 750 (s), 688 (s), 654 (m).

HRMS (ESI+): m/z calcd for $C_{17}H_{13}N_4$: 273.1140, found 273.1137 $[M+H]^+$.

3-(furan-2-yl)-6-phenyl-1,2,4-triazine (5l)



Prepared according to the general procedure **E**, the title compound was isolated as a brown solid (41 mg, 0.184 mmol, 37%), with spectral data in agreement with literature values.[16b]

R*f*: 0.39 (6/4 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.00 (s, 1H, H^6), 8.13 (dd, *J* = 7.8, 1.6 Hz, 2H, H^3), 7.74 (d, *J* = 0.8 Hz, 1H, H^9), 7.59-7.54 (m, 4H, H^1, H^2, H^{11}), 6.66 (dd, *J* = 3.4, 1.7 Hz, 1H, H^{10}).

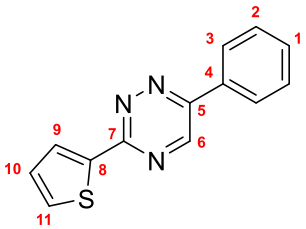
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 156.3 (C^7), 154.5 (C^5), 149.6 (C^8), 146.3 (C^6), 146.2 (C^9), 133.2 (C^4), 130.9 (C^1), 129.4 (C^2), 126.6 (C^3), 115.1 (C^{11}), 112.7 (C^{10}).

M.p.: 162-164 °C [lit. = 165 °C].[16b]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3138 (w), 3122 (w), 3107 (w), 3043 (w), 2920 (w), 2851 (w), 1600 (w), 1585 (m), 1552 (m), 1484 (m), 1441 (m), 1413 (s), 1376 (m), 1314 (m), 1261 (w), 1218 (m), 1187 (w), 1167 (m), 1090 (m), 1077 (m), 1040 (m), 1016 (s), 1006 (s), 948 (w), 926 (w), 910 (m), 882 (m), 845 (w), 809 (m), 757 (s), 698 (s), 670 (w).

HRMS (ESI+): m/z calcd for $C_{13}H_{10}N_3O$: 224.0824, found 224.0826 $[M+H]^+$.

6-phenyl-3-(thiophen-2-yl)-1,2,4-triazine (5m)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (79 mg, 0.330 mmol, 66%), with spectral data in agreement with literature values.[20]

R*f*: 0.49 (6/4 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.96 (s, 1H, H^6), 8.19 (dd, *J* = 3.6, 1.0 Hz, 1H, H^9), 8.13 (dd, *J* = 7.8, 1.6 Hz, 2H, H^3), 7.61-7.55 (m, 4H, H^1, H^2, H^{11}), 7.23 (dd, *J* = 4.8, 3.8 Hz, 1H, H^{10}).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 159.9 (C^7), 154.5 (C^5), 146.4 (C^6), 139.5 (C^8), 133.2 (C^4), 131.3 (C^{11}), 130.8 (C^1), 130.2 (C^9), 129.4 (C^2), 128.7 (C^{10}), 126.5 (C^3).

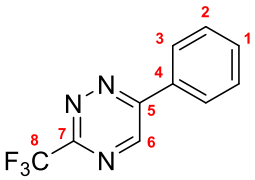
M.p.: 157-159 °C [lit. = 158-159 °C].[20]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3087 (w), 3052 (w), 3035 (w), 2923 (w),2852 (w), 1597 (w), 1579 (w), 1531 (m), 1488 (w), 1437 (s), 1394 (s), 1366 (m), 1317 (w), 1295 (w), 1254 (w), 1217 (w), 1186 (w), 1157 (w), 1081 (m), 1062 (s), 1046 (m), 1016 (m), 970 (m), 920 (w), 854 (s), 806 (s), 760 (s), 723 (m), 713 (s), 687 (s).

HRMS (ESI+): m/z calcd for $C_{13}H_{10}N_3S$: 240.0595, found 240.0591 $[M+H]^+$.

[20] Kozhevnikov, V. N.; Ustinova, M. M.; Slepukhin, P. A.; Santoro, A.; Bruce, D. W.; Kozhevnikov, D. N. *Tetrahedron Lett.* **2008**, *49*, 4096.

6-phenyl-3-(trifluoromethyl)-1,2,4-triazine (5n)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (56 mg, 0.249 mmol, 50%).

R*f*: 0.70 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.15 (s, 1H, H^6), 8.17 (d, J = 6.6 Hz, 2H, H^3), 7.65-7.60 (m, 3H, H^1, H^2).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -69.4.

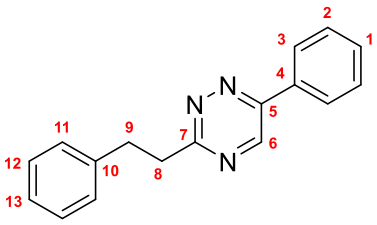
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 158.9 (C^5), 155.9 (q, $^2J_{CF}$ = 37 Hz, C^7), 147.1 (C^6), 132.4 (C^1), 131.9 (C^4), 129.8 (C^2), 127.6 (C^3), 119.9 (q, $^1J_{CF}$ = 275 Hz, C^8).

M.p.: 121-123 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3063 (w), 2924 (w), 2855 (w), 2538 (w), 2171 (w), 2095 (w), 1927 (w), 1834 (w), 1702 (w), 1600 (w), 1557 (w), 1507 (w), 1449 (w), 1355 (m), 1343 (m), 1323 (m), 1294 (m), 1263 (m), 1196 (m), 1148 (s), 1130 (s), 1079 (m), 1034 (m), 1005 (m), 959 (m), 935 (m), 852 (w), 821 (m), 763 (s), 745 (m), 689 (s).

HRMS (ESI+): m/z calcd for $C_{10}H_7N_3F_3$: 226.0587, found 226.0578 $[M+H]^+$.

3-phenethyl-6-phenyl-1,2,4-triazine (5o)



Prepared according to the general procedure **E**, the title compound was isolated as yellow solid (10 mg, 0.038 mmol, 8%).

R*f*: 0.6 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.95 (s, 1H, H^6), 8.10-8.07 (m, 2H, H^3), 7.59-7.54 (m, 3H, H^1, H^2), 7.32-7.27 (m, 4H, H^{11}, H^{12}), 7.22-7.19 (m, 1H, H^{13}), 3.51 (t, J = 8.1 Hz, 2H, H^8), 3.27 (t, J = 8.1 Hz, 2H, H^9).

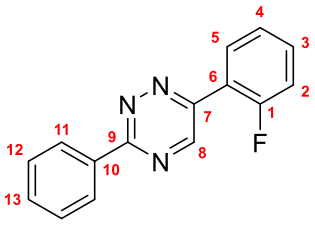
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 167.9 (C^7), 155.4 (C^5), 146.7 (C^6), 140.8 (C^{10}), 133.4 (C^4), 131.0 (C^1), 129.5 (C^2), 128.7 (C^{12}), 128.6 (C^{11}), 126.9 (C^3), 126.4 (C^{13}), 38.7 (C^8), 34.4 (C^9).

M.p.: 85-87 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3057 (w), 3028 (w), 2920 (m), 2851 (m), 2086 (bw), 1897 (w), 1738 (w), 1601 (w), 1494 (w), 1444 (w), 1411 (m), 1314 (w), 1246 (w), 1156 (w), 1078 (w), 1048 (m), 1006 (m), 920 (w), 869 (w), 799 (w), 761 (m), 728 (s), 691 (s).

HRMS (ESI+): m/z calcd for $C_{17}H_{16}N_3$: 262.1344, found 262.1343 $[M+H]^+$.

6-(2-fluorophenyl)-3-phenyl-1,2,4-triazine (5p)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (65 mg, 0.259 mmol, 52%).

R*f*: 0.74 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.14 (d, *J* = 2.4 Hz, 1H, H^{8}), 8.61-8.57 (m, 2H, H^{11}), 8.28 (td, *J* = 7.8, 1.7 Hz, 1H, H^{5}), 7.57-7.54 (m, 3H, H^{12}, H^{13}), 7.53-7.49 (m, 1H, H^{3}), 7.37 (td, *J* = 7.8, 1.0 Hz, 1H, H^{4}), 7.24 (ddd, *J* = 7.8, 3.0, 1.0 Hz, 1H, H^{2}).

^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm -115.6.

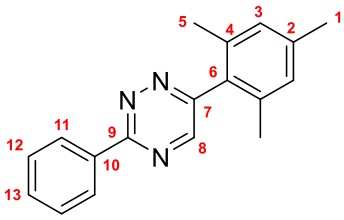
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 162.2 (C^{9}), 160.8 (d, $^{1}J_{CF}$ = 251 Hz, C^{1}), 152.7 (d, $^{3}J_{CF}$ = 3 Hz, C^{7}), 149.4 (d, $^{4}J_{CF}$ = 13 Hz, C^{8}), 134.6 (C^{10}), 132.7 (d, $^{3}J_{CF}$ = 9 Hz, C^{3}), 131.9 (C^{13}), 130.5 (d, $^{3}J_{CF}$ = 3 Hz, C^{5}), 129.0 (C^{12}), 128.4 (C^{11}), 125.4 (d, $^{4}J_{CF}$ = 3 Hz, C^{4}), 121.6 (d, $^{2}J_{CF}$ = 12 Hz, C^{6}), 116.6 (d, $^{2}J_{CF}$ = 22 Hz, C^{2}).

M.p.: 109-111 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3068 (w), 2922 (w), 2851 (w), 2103 (bw), 1910 (w), 1820 (w), 1663 (w), 1610 (w), 1579 (w), 1490 (m), 1456 (m), 1442 (w), 1398 (s), 1329 (w), 1293 (w), 1253 (m), 1232 (w), 1202 (m), 1116 (w), 1085 (m), 1026 (m), 996 (w), 930 (m), 870 (w), 831 (m), 763 (s), 752 (s), 690 (s).

HRMS (ESI+): m/z calcd for $C_{15}H_{11}N_3F$: 252.0937, found 252.0935 $[M+H]^+$.

6-mesityl-3-phenyl-1,2,4-triazine (5q)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (26 mg, 0.094 mmol, 19%).

R*f*: 0.80 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.64-8.60 (m, 2H, H^{11}), 8.59 (s, 1H, H^{8}), 7.60-7.55 (m, 3H, H^{12}, H^{13}), 7.03 (s, 2H, H^{3}), 2.38 (s, 3H, H^{1}), 2.12 (s, 6H, H^{5}).

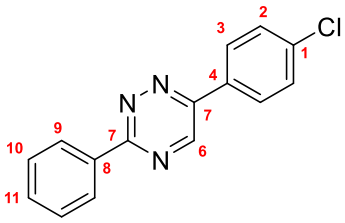
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 162.1 (C^{9}), 158.8 (C^{7}), 150.2 (C^{8}), 139.6 (C^{2}), 136.7 (C^{6}), 134.9 (C^{10}), 131.8 (C^{13}). 131.1 (C^{4}), 129.1 (C^{12}), 129.0 (C^{3}), 128.4 (C^{11}), 21.3 (C^{1}), 20.5 (C^{5}).

M.p.: 67-69 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3096 (w), 2921 (w), 2854 (w), 2250 (w), 1728 (w), 1683 (w), 1611 (w), 1553 (w), 1493 (w), 1434 (m), 1398 (s), 1312 (w), 1234 (w), 1174 (m), 1083 (m), 1026 (m), 985 (m), 928 (w), 857 (m), 801 (w), 752 (s), 742 (m), 686 (s), 667 (m).

HRMS (ESI+): m/z calcd for $C_{18}H_{18}N_3$: 276.1495, found 276.1487 $[M+H]^+$.

6-(4-chlorophenyl)-3-phenyl-1,2,4-triazine (5r)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (44 mg, 0.164 mmol, 33%), with spectral data in agreement with literature values.[16]

R*f*: 0.85 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.03 (s, 1H, H^6), 8.59-8.57 (m, 2H, H^9), 8.11 (d, *J* = 8.6 Hz, 2H, H^3), 7.58-7.53 (m, 5H, H^2, H^{10}, H^{11}).

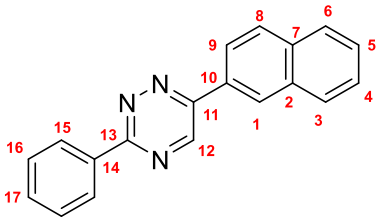
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 162.7 (C^7), 154.2 (C^5), 146.3 (C^6), 137.5 (C^1), 134.6 (C^8), 131.9 (C^4) 131.9 (C^{11}), 129.8 (C^2), 129.1 (C^{10}), 128.4 (C^9), 128.0 (C^3).

M.p.: 198-200 °C [lit. = 197-198 °C].[16]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3090 (w), 3058 (w), 2083 (bw), 2016 (w), 1918 (w), 1684 (w), 1593 (w), 1488 (w), 1449 (w), 1412 (m), 1395 (m), 1327 (m), 1234 (w), 1182 (w), 1088 (m), 1036 (m), 1013 (m), 992 (m), 952 (w), 931 (w), 841 (s), 814 (m), 748 (s), 717 (w), 691 (s), 669 (m).

HRMS (ESI+): m/z calcd for $C_{15}H_{11}N_3Cl$: 268.0642, found 268.0635 $[M+H]^+$.

6-(naphthalen-2-yl)-3-phenyl-1,2,4-triazine (5s)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (45 mg, 0.159 mmol, 32%).

R*f*: 0.68 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.20 (s, 1H, H^{12}), 8.63-8.61 (m, 3H, H^1, H^{15}), 8.31 (dd, *J* = 8.6, 1.8 Hz, 1H, H^9). 8.05 (d, *J* = 8.6 Hz, 1H, H^8), 8.01-7.98 (m, 1H, H^3), 7.94-7.91 (m, 1H, H^6), 7.60-7.56 (m, 5H, H^4, H^5, H^{16}, H^{17}).

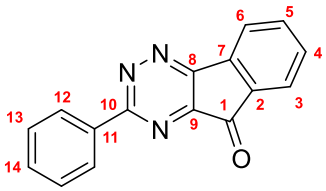
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 162.5 (C^{13}), 155.2 (C^{11}), 146.8 (C^{12}), 134.8 (C^{10}), 134.6 (C^{14}), 133.5 (C^7), 131.8 (C^{17}), 130.7 (C^2), 129.5 (C^8), 129.1 (C^3) 129.1 (C^{16}), 128.3 (C^{15}), 128.0 (C^4/C^5), 127.8 (C^6), 127.1 (C^4/C^5), 126.9 (C^1), 123.5 (C^9).

M.p.: 176-178 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3053 (w), 3018 (w), 2926 (w), 2853 (w), 2103 (w), 1917 (w), 1818 (w), 1770 (w), 1683 (w), 1628 (w), 1600 (w), 1492 (w), 1470 (w), 1405 (m), 1358 (w), 1296 (w), 1250 (w), 1195 (w), 1131 (w), 1088 (m), 1036 (m), 998 (w), 927 (w), 911 (m), 859 (m), 812 (s), 741 (s), 690 (s).

HRMS (ESI+): m/z calcd for $C_{19}H_{14}N_3$: 284.1188, found 284.1188 $[M+H]^+$.

3-phenyl-5H-indeno[2,1-e][1,2,4]triazin-5-one (5t)



Prepared according to the general procedure **E**, the title compound was isolated as a red solid (11 mg, 0.045 mmol, 9%).

R*f*: 0.36 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.62 (d, J = 6.8 Hz, 2H, H^{12}), 8.20 (d, J = 7.5 Hz, 1H, H^{6}), 7.95 (d, J = 7.5 Hz, 1H, H^{3}), 7.83 (td, J = 7.5, 0.9 Hz, 1H, H^{5}), 7.66 (td, J = 7.5, 0.9 Hz, 1H, H^{4}), 7.60-7.54 (m, 3H, H^{13}, H^{14}).

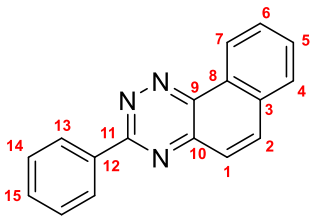
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 190.3 (C^{1}), 164.9 (C^{10}), 158.2 (C^{8}), 153.0 (C^{9}), 139.6 (C^{7}), 137.6 (C^{5}), 134.4 (C^{11}), 134.0 (C^{2}), 133.0 (C^{4}), 132.4 (C^{14}), 129.1 (C^{13}), 128.7 (C^{12}), 125.7 (C^{3}), 123.0 (C^{6}).

M.p.: 220-222 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3056 (w), 2923 (w), 2853 (w), 2093 (bw), 1734 (s), 1591 (m), 1455 (m), 1386 (s), 1359 (s), 1306 (m), 1257 (m), 1235 (w), 1187 (m), 1159 (m), 1114 (m), 1093 (m), 1050 (w), 1026 (m), 955 (m), 836 (m), 803 (m), 764 (s), 711 (s), 692 (s).

HRMS (ESI+): m/z calcd for $C_{16}H_{10}N_3O$: 260.0824, found 260.0828 $[M+H]^+$.

6-(naphthalen-2-yl)-3-phenyl-1,2,4-triazine (5u)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (31 mg, 0.120 mmol, 26%).

R*f*: 0.71 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.52 (d, J = 8.0 Hz, 1H, H^{7}), 8.80-7.76 (m, 2H, H^{13}), 8.20 (d, J = 9.1 Hz, 1H, H^{2}), 7.95 (d, J = 7.8 Hz, 1H, H^{4}), 7.90-7.87 (m, 1H, H^{6}), 7.86 (d, J = 9.1 Hz, 1H, H^{1}), 7.84-7.80 (m, 1H, H^{5}), 7.63-7.58 (m, 3H, H^{14}, H^{15}).

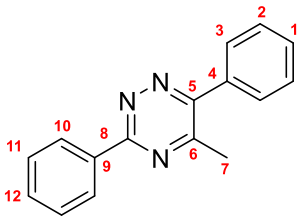
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 161.4 (C^{11}), 144.9 (C^{9}), 143.2 (C^{10}), 138.3 (C^{2}), 135.8 (C^{12}), 132.8 (C^{3}), 132.8 (C^{8}), 131.5 (C^{15}), 130.3 (C^{5}), 129.5 (C^{6}), 129.1 (C^{14}), 128.7 (C^{13}), 128.7 (C^{4}), 125.9 (C^{1}), 124.1 (C^{7}).

M.p.: 143-145 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3048 (w), 3015 (w), 2924 (w), 2343 (bw), 2104 (bw), 1720 (w), 1600 (w), 1562 (w), 1519 (m), 1468 (w), 1435 (m), 1383 (s), 1345 (m), 1311(w), 1276 (m), 1224 (w), 1160 (w), 1048 (m), 1023 (m), 962 (w), 928 (w); 882 (w), 848 (m), 815 (m), 783 (m), 760 (m), 738 (s), 689 (s).

HRMS (ESI+): m/z calcd for $C_{17}H_{12}N_3$ 258.1031, found 258.1029 $[M+H]^+$.

5-methyl-3,6-diphenyl-1,2,4-triazine (5v)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (50 mg, 0.202 mmol, 40%), with spectral data in agreement with literature values.[21]

R*f*: 0.66 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.60 (dd, *J* = 6.7, 3.0 Hz, 2H, H^{10}), 7.72 (dd, *J* = 8.0, 1.5 Hz, 2H, H^3), 7.58-7.50 (m, 6H, H^1, H^2, H^{11}, H^{12}), 2.70 (s, 3H, H^7).

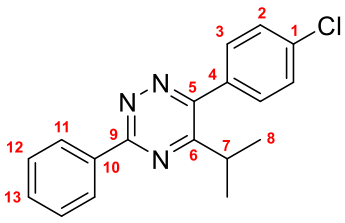
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 161.6 (C^8), 157.7 (C^5), 157.5 (C^6), 135.3 (C^9), 135.0 (C^4), 131.5 (C^{12}), 129.7 (C^1), 129.2 (C^3), 128.9 (C^{11}), 128.8 (C^2), 128.3 (C^{10}), 23.3 (C^7).

M.p.: 127-129 °C [lit. = 123-125 °C].[21]

FTIR (ATR, neat): ν_{max}/cm^{-1} 3059 (w), 2969 (w), 2406 (w), 2359 (w), 2119 (bw), 1601 (w), 1578 (w), 1508 (w), 1453 (w), 1421 (w), 1392 (m), 1377(m), 1256 (w), 1215 (w), 1177 (w), 1116 (w), 1077 (w), 1025 (w), 996 (w), 934 (w), 817 (w), 770 (m), 749 (w), 704 (m), 690 (s), 654 (s).

HRMS (ESI+): m/z calcd for $C_{16}H_{13}N_3$: 248.1182, found 248.1171 $[M+H]^+$.

6-(4-chlorophenyl)-5-isopropyl-3-phenyl-1,2,4-triazine (5w)



Prepared according to the general procedure **E**, the title compound was isolated as yellow solid (25 mg, 0.081 mmol, 16%).

R*f*: 0.80 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.64-8.61 (m, 2H, H^{11}), 7.60 (d, *J* = 8.5 Hz, 2H, H^3), 7.57-7.55 (m, 3H, H^{12}, H^{13}), 7.53 (d, *J* = 8.5 Hz, 2H, H^2), 3.36-3.30 (m, 1H, H^7), 1.34 (d, *J* = 6.7 Hz, 6H, H^8).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 165.1 (C^6), 162.1 (C^9), 156.2 (C^5), 135.9 (C^1), 135.1 (C^{10}), 133.9 (C^4), 131.7 (C^{13}), 130.6 (C^3), 129.2 (C^2), 128.9 (C^{12}), 128.4 (C^{11}), 31.4 (C^7), 21.9 (C^8).

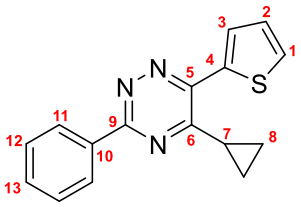
M.p.: 125-127 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3064 (w), 3040 (w), 2973 (w), 2931 (w), 2873 (w), 2104 (w), 1595 (w), 1520 (w), 1503 (m), 1447 (w), 1400 (s), 1356 (m), 1250 (w), 1174 (w), 1126 (w), 1087 (m), 1071 (m), 1025 (w), 1006 (m), 914 (w), 852 (m), 824 (m), 775 (m), 722 (w), 697 (s), 666 (m).

HRMS (ESI+): m/z calcd for $C_{18}H_{17}N_3Cl$: 310.1111, found 310.1115 $[M+H]^+$.

[21] Ohba, S. ; Konno, S.; Yamanaka, H. *Chem. Pharm. Bull*. **1991**, *39*, 486.

5-cyclopropyl-3-phenyl-6-(thiophen-2-yl)-1,2,4-triazine (5x)



Prepared according to the general procedure **E**, the title compound was isolated as a yellow solid (7 mg, 0.025 mmol, 5%).

R*f*: 0.64 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 8.54-8.49 (m, 2H, H^{11}), 7.79 (d, J = 3.6 Hz, 1H, H^{3}), 7.58 (d, J = 5.0 Hz, 1H, H^{1}), 7.54-7.50 (m, 3H, H^{12}, H^{13}), 7.22 (dd, J = 5.0, 3.6 Hz, 1H, H^{2}), 2.59-2.55 (m, 1H, H^{7}), 1.58-1.50 (m, 2H, H^{8}), 1.32-1.26 (m, 2H, H^{8}).

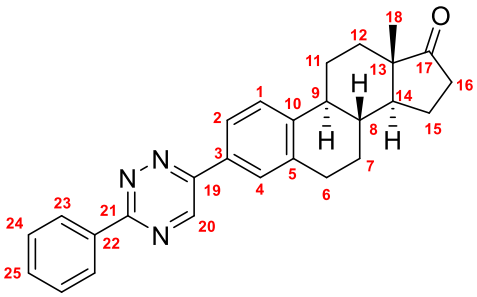
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 138.4 (C^{4}), 135.1 (C^{10}), 131.5 (C^{13}), 129.5 (C^{1}), 129.2 (C^{3}), 128.9 (C^{12}), 128.2 (C^{11}), 128.0 (C^{2}), 14.9 (C^{7}), 12.5 (C^{8}). The quaternary carbons C^{5}, C^{6} and C^{9} weren't observed.

M.p.: 76-78 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3084 (w), 3071 (w), 3005 (w), 2924 (w), 2856 (w), 2144 (bw), 1821 (w), 1732 (w), 1599 (w), 1532 (w), 1496 (s), 1433 (s), 1382 (s), 1352 (m), 1334 (w), 1295 (w), 1262 (w), 1212 (w), 1172 (w), 1126 (m), 1075 (m), 1029 (m), 967 (m), 932 (w), 907 (m), 858 (w), 811 (w), 768 (m), 737 (m), 720 (s), 693 (s).

HRMS (ESI+): m/z calcd for $C_{16}H_{14}N_3S$: 280.0908, found 280.0915 $[M+H]^+$.

(8R,9S,13S,14S)-13-methyl-3-(3-phenyl-1,2,4-triazin-6-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5y)



Prepared according to the general procedure **E**, the title compound was isolated as a pale yellow solid (54 mg, 0.132 mmol, 26%).

R*f*: 0.39 (7/3 hexane/EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm 9.01 (s, 1H, H^{20}), 8.58-8.56 (m, 2H, H^{23}), 7.92 (s, 1H, H^{4}), 7.89 (d, J = 8.2 Hz, 1H, H^{2}), 7.56-7.53 (m, 3H, H^{24}, H^{25}), 7.47 (d, J = 8.0, 1H, H^{1}), 3.06-3.00 (m, 2H, H^{6}), 2.52 (dd, J = 18.9, 8.6 Hz, 1H, H^{16}), 2.49-2.45 (m, 1H, H^{11}), 2.36 (td, J = 11.3, 4.1, 1H, H^{9}), 2.19-2.13 (m, 1H, H^{16}), 2.11-2.06 (m, 2H, H^{7}, H^{15}), 2.00 (td, J = 12.7, 3.1 Hz, 1H, H^{12}), 1.69-1.58 (m, 3H, H^{8}, H^{11}, H^{15}), 1.57-1.48 (m, 3H, H^{7}, H^{12}, H^{14}), 0.93 (s, 3H, H^{18}).

^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 220.7 (C^{17}), 162.3 (C^{21}), 155.0 (C^{19}), 146.4 (C^{20}), 143.2 (C^{10}), 137.9 (C^{5}), 134.8 (C^{22}), 131.7 (C^{25}), 130.8 (C^{3}), 129.0 (C^{24}), 128.2 (C^{23}), 127.3 (C^{4}), 126.5 (C^{1}), 124.0 (C^{2}), 50.6 (C^{14}), 48.0 (C^{13}), 44.6 (C^{9}), 38.1 (C^{8}), 35.9 (C^{16}), 31.7 (C^{12}), 29.6 (C^{6}), 26.4 (C^{7}), 25.7 (C^{11}), 21.7 (C^{15}), 14.0 (C^{18}).

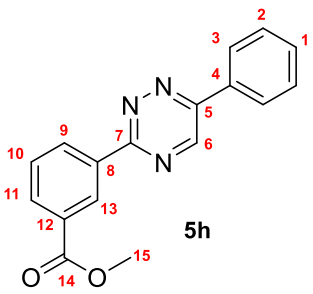
M.p.: 222-224 °C.

FTIR (ATR, neat): ν_{max}/cm^{-1} 3619 (w), 3469 (w), 3258 (w), 2929 (w), 2215 (w), 2018 (w), 1733 (m), 1407 (s), 1258 (w), 1091 (w), 1007 (w), 902 (w), 818 (w), 755 (m), 689 (s).

HRMS (ESI+): m/z calcd for $C_{27}H_{28}N_3O$: 410.2232, found 410.2223 $[M+H]^+$.

Scale-up reaction of general procedure E for the synthesis of triazine from tosylhydrazone and aziridine

General procedure **E** was scaled-up on a 5 mmol scale starting from tosylhydrazone **1h** and aziridine **2a** to form the triazine **5h**. The reaction was carried out under reflux of toluene instead of a sealed tube.

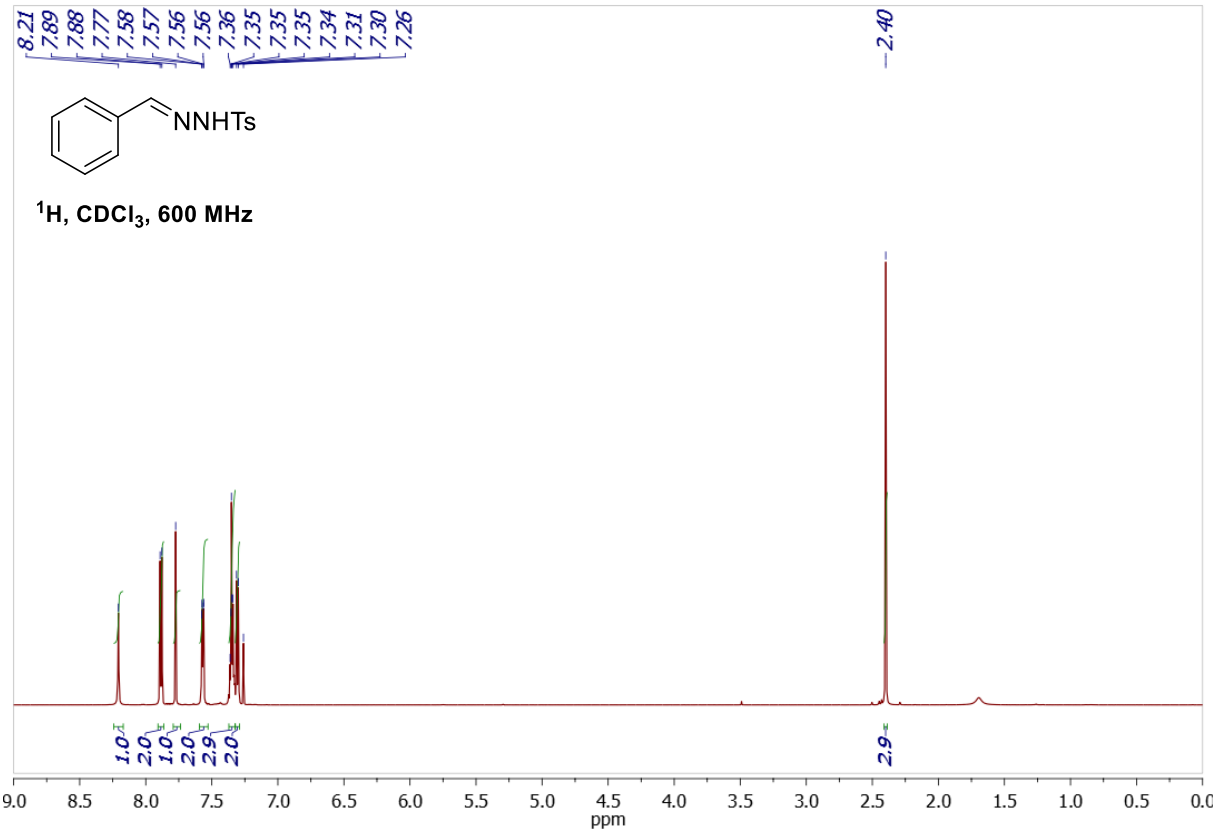


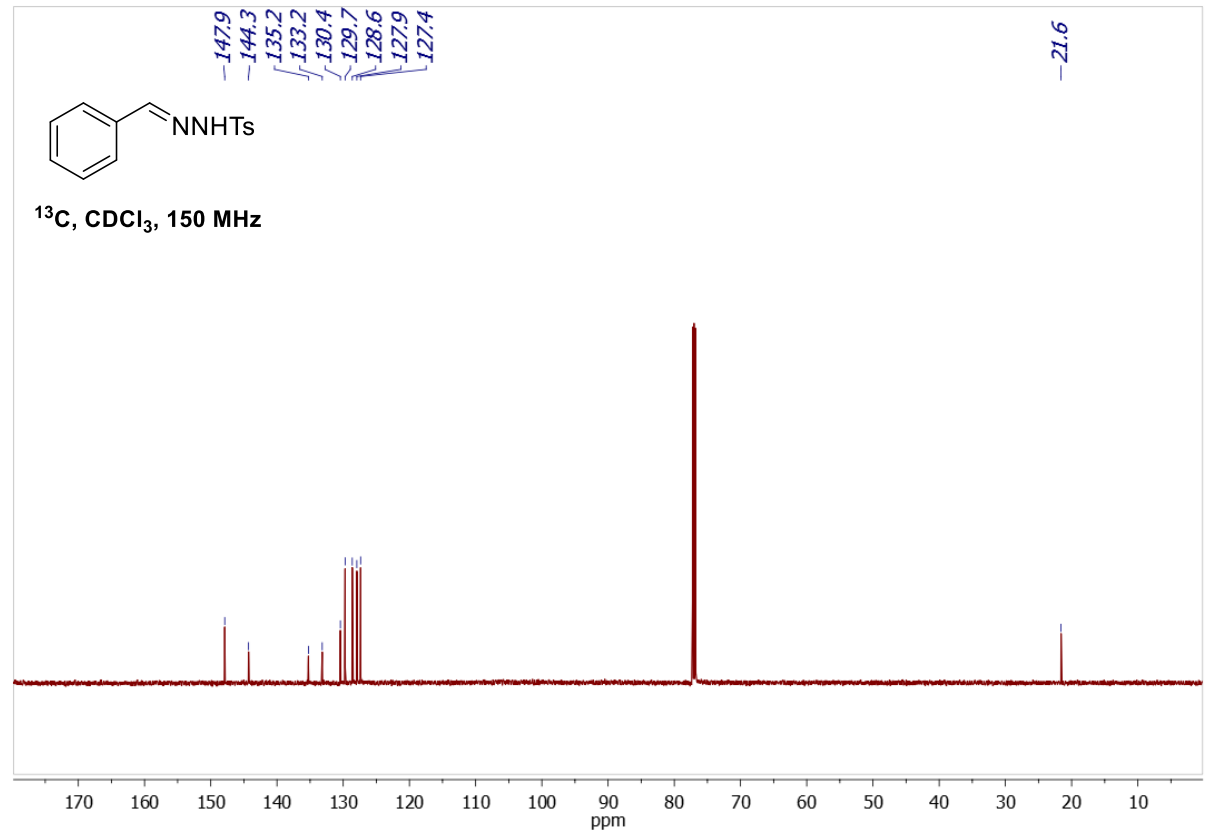
5h

Hydrazone **1h** (1.66 g, 5 mmol, 1 equiv) and aziridine **2a** (1.64 g, 6 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (25 mL, 0.2 M) in an oven-dried flask under Argon. $BF_3{\cdot}OEt_2$ (0.127 mL, 1 mmol, 0.2 equiv) was introduced dropwise and the pale yellow/orange reaction mixture was stirred at rt for 1-2 h. The progression of the reaction was monitored by TLC (hexane/CH_2Cl_2/EtOAc 5/4/1). The solvent was evaporated *in vacuo*. Cs_2CO_3 (5.70 g, 17.5 mmol, 3.5 equiv) and activated MnO_2 (2.61 g, 30 mmol, 6 equiv) were added to the reaction mixture under Argon, followed by dry toluene (50 mL, 0.1 M). The reaction mixture was heated at reflux of toluene (110 °C) for 3 h in total. Two other portions of activated MnO_2 (1.74 g, 20 mmol, 4 equiv) were added after 1 and 2 h. The progression of the reaction was monitored by TLC (7/3 hexane/EtOAc). The reaction mixture was cooled to rt, filtered through a plug of celite and washed with EtOAc. The filtrate was stirred with QuadraPure®-Benzylamine for 2h, filtered and evaporated *in vacuo*. The crude was purified by silica gel chromatography (19/1 to 9/1 hexane/EtOAc) and dried under vacuum to yield the desired product **5h** (806 mg, 2.77 mmol, 55%).

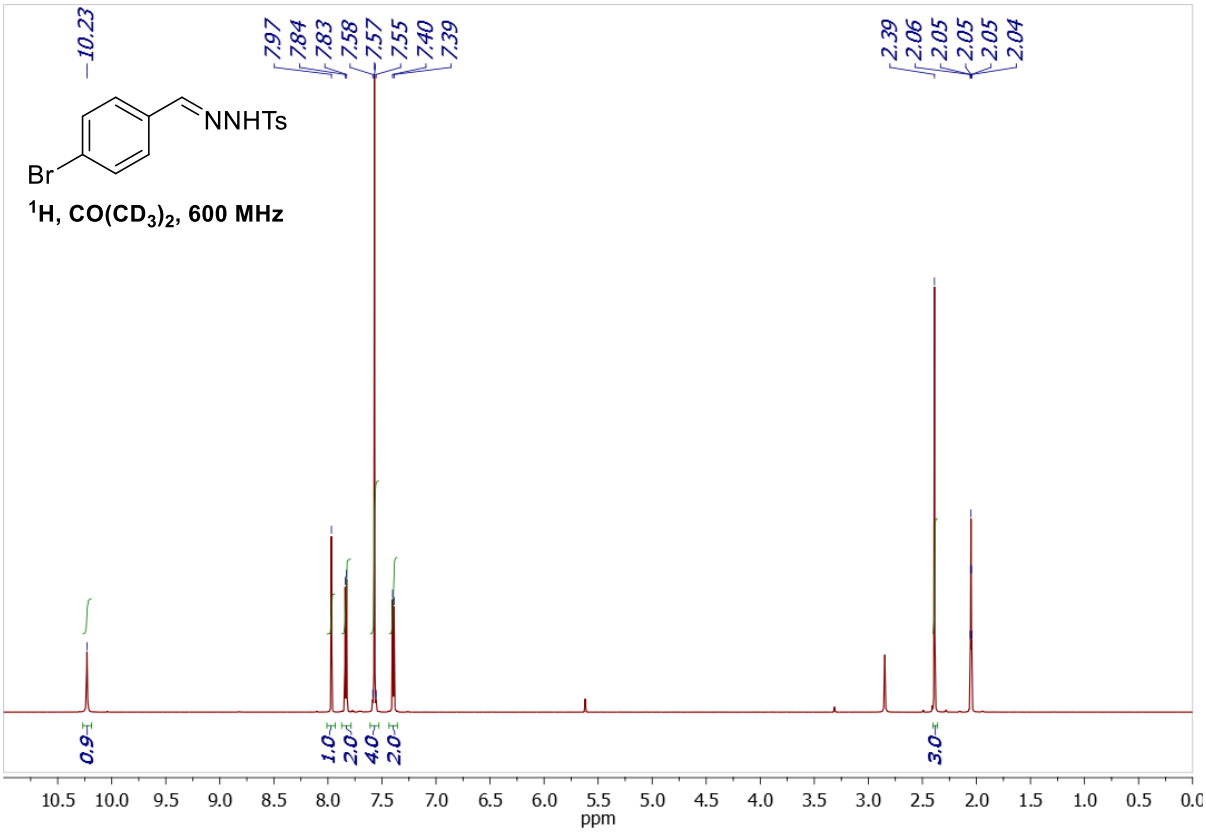
4. NMR spectra

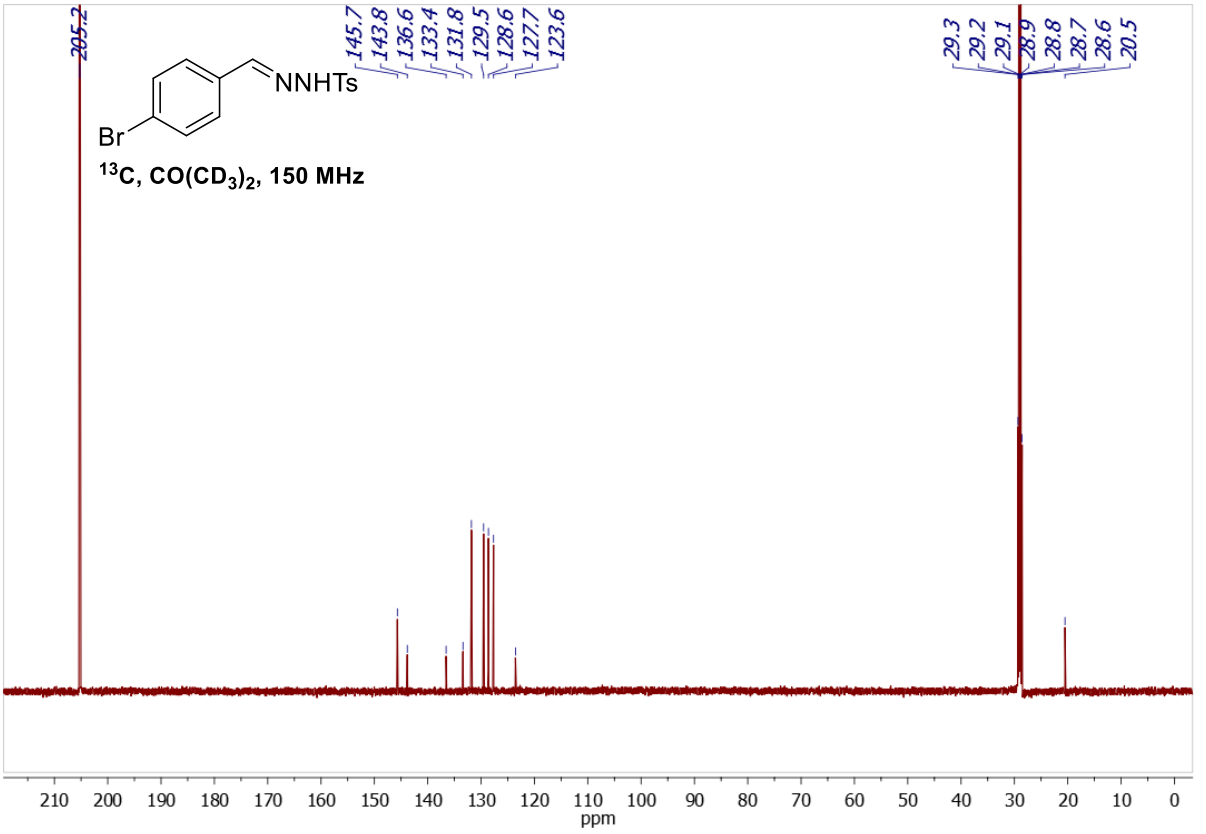
***N*'-benzylidene-4-methylbenzenesulfonohydrazide (1a)**



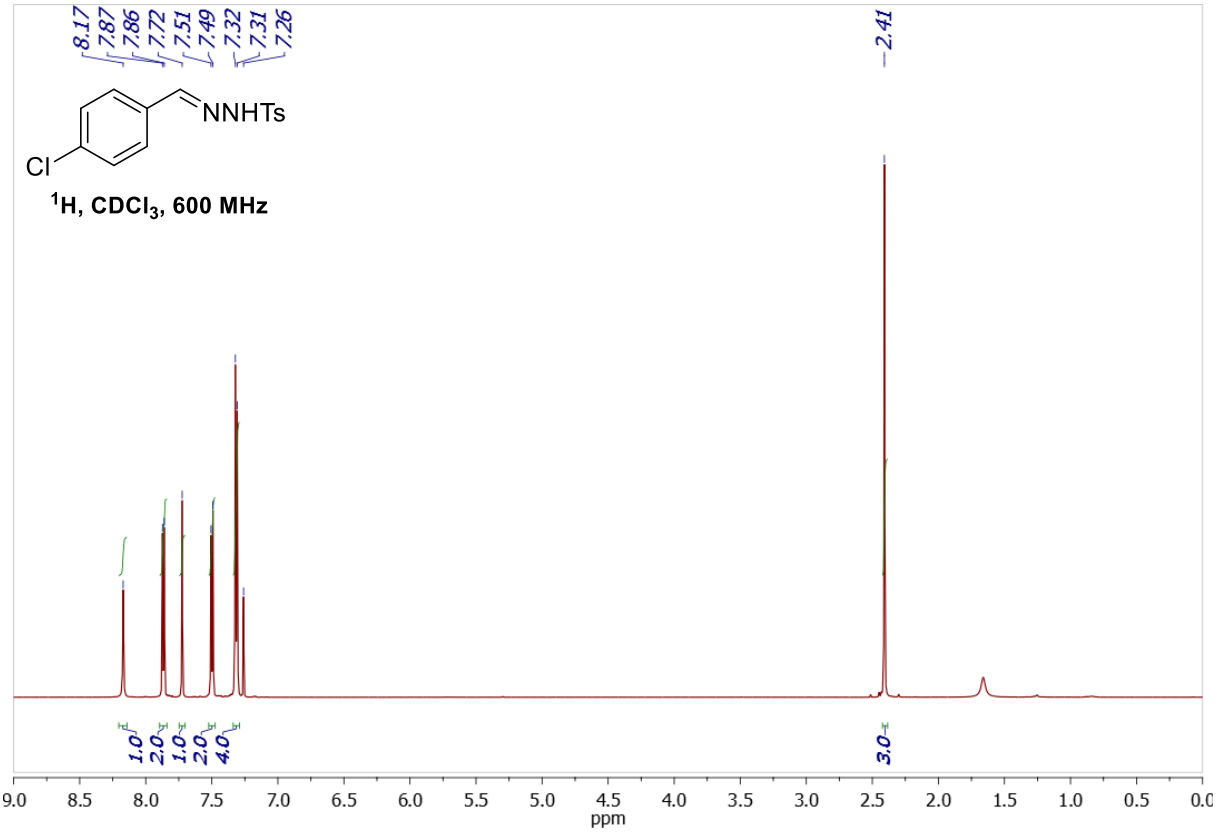


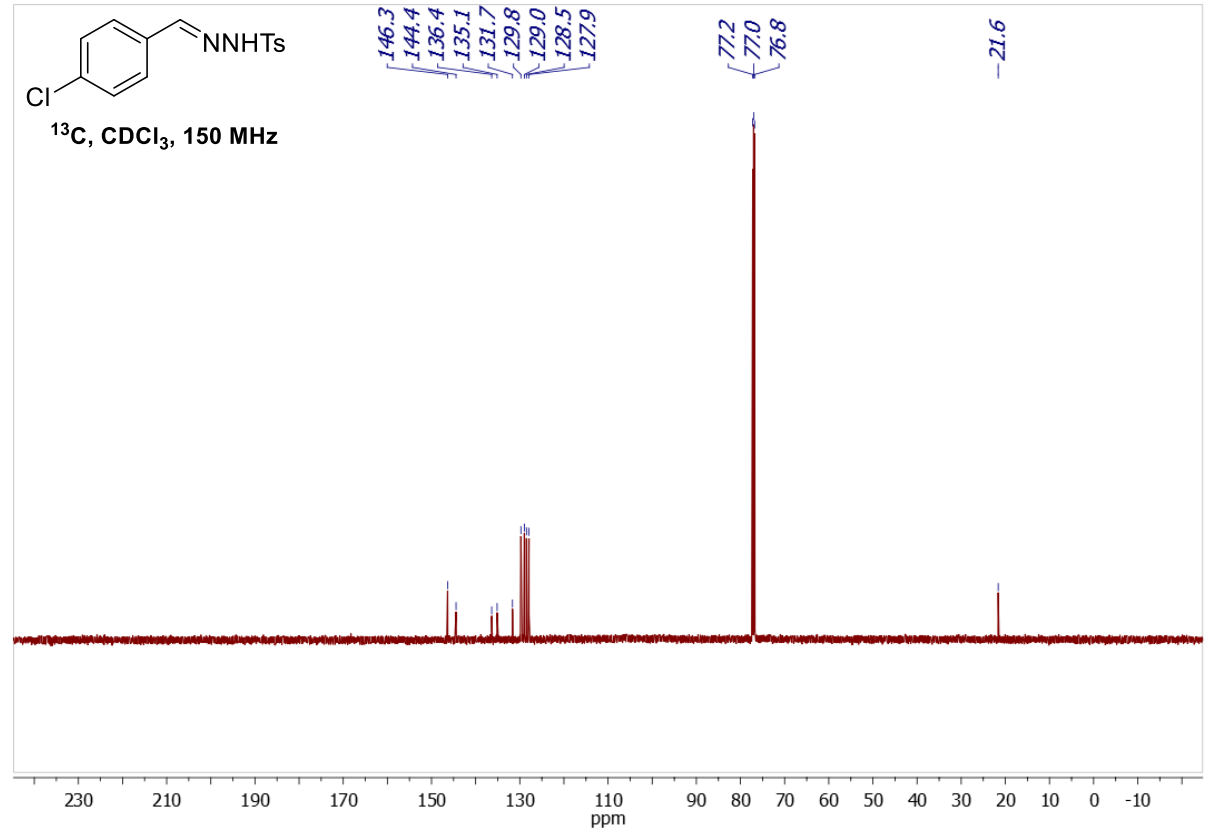
N'-(4-bromobenzylidene)-4-methylbenzenesulfonohydrazide (1b)



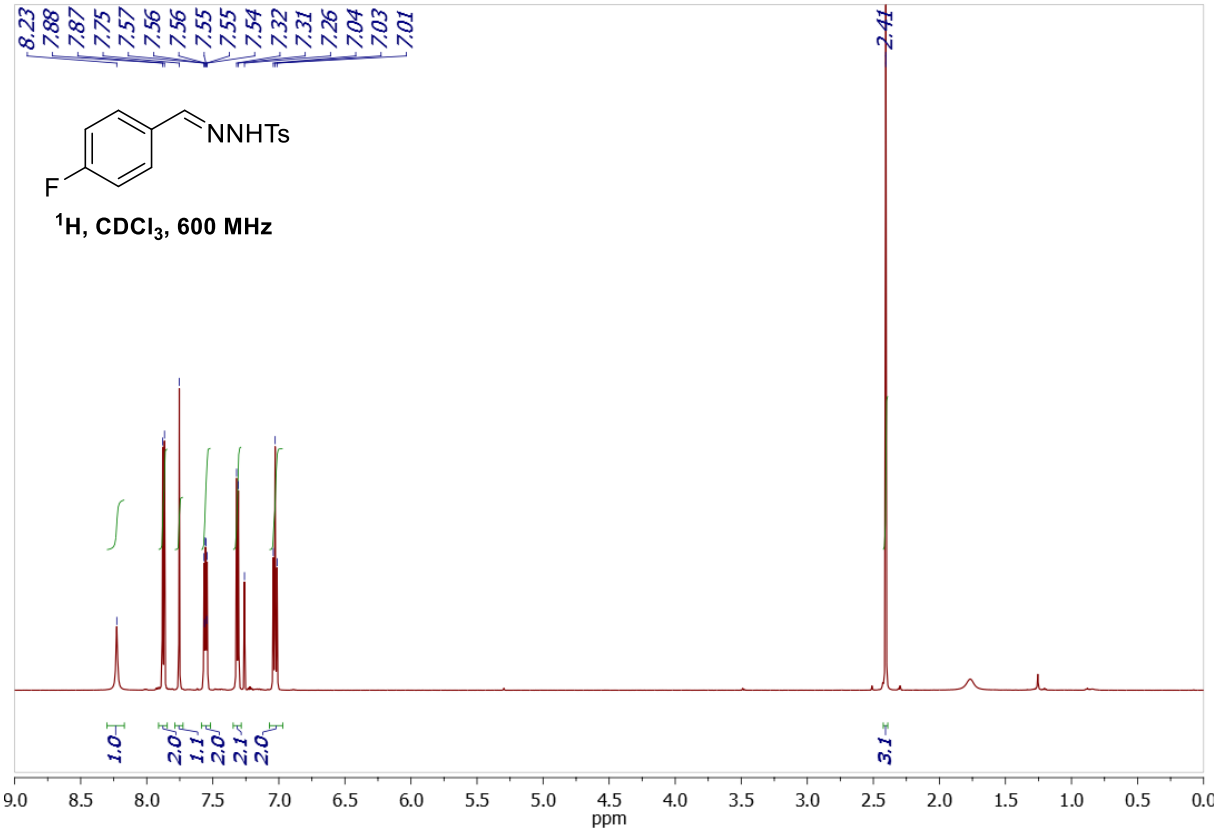


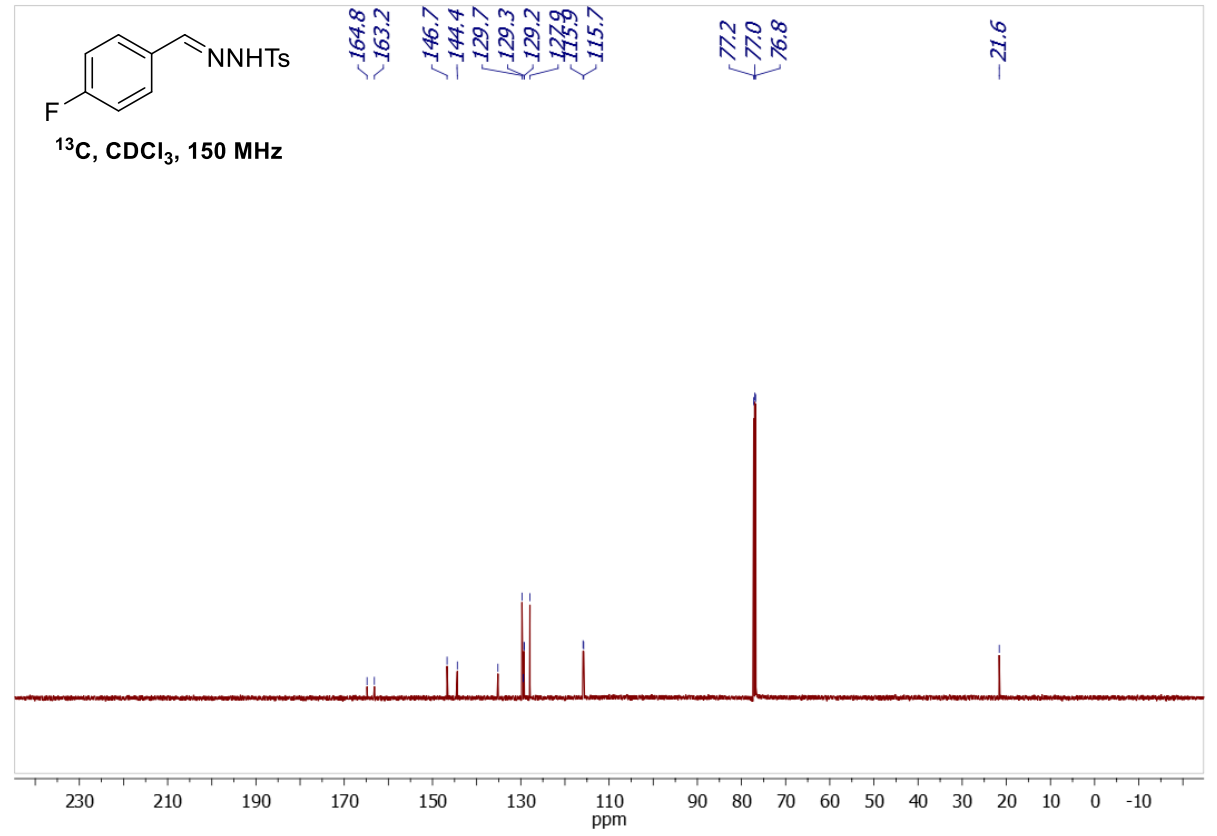
N'-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (1c)



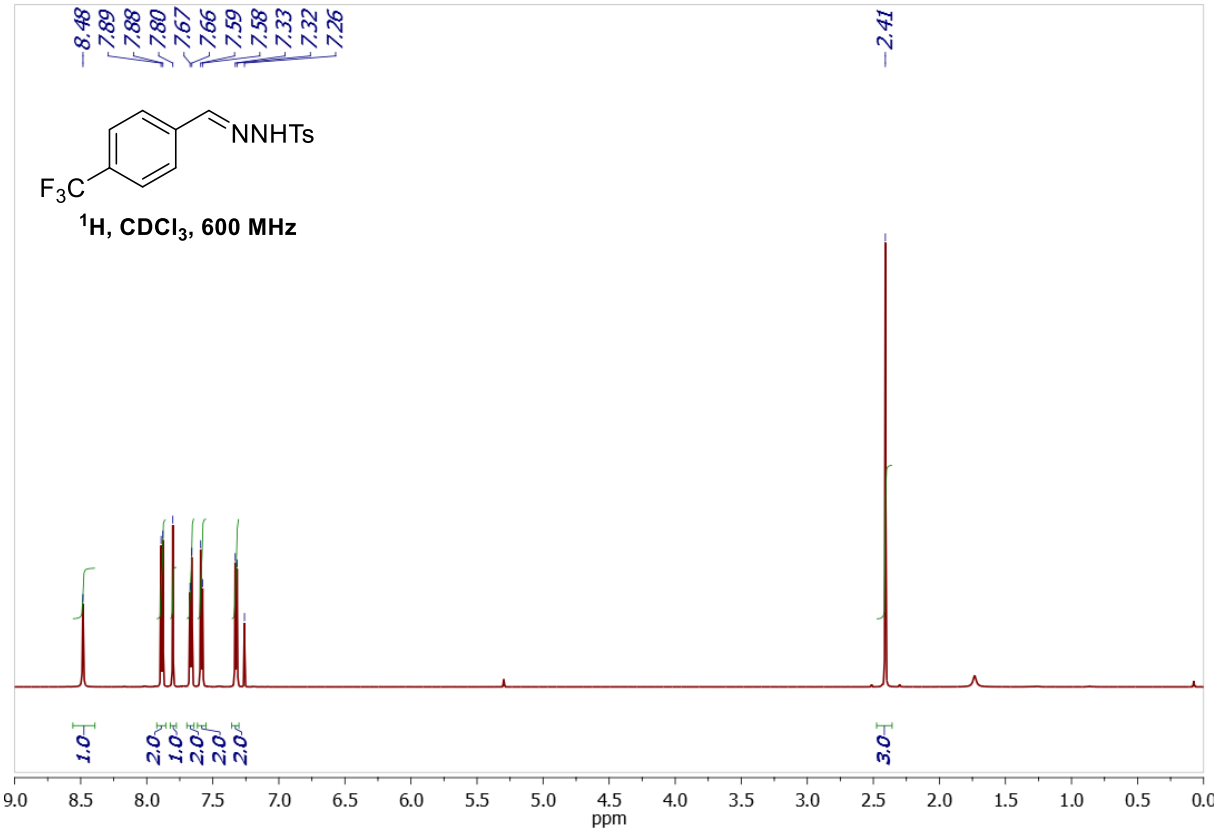


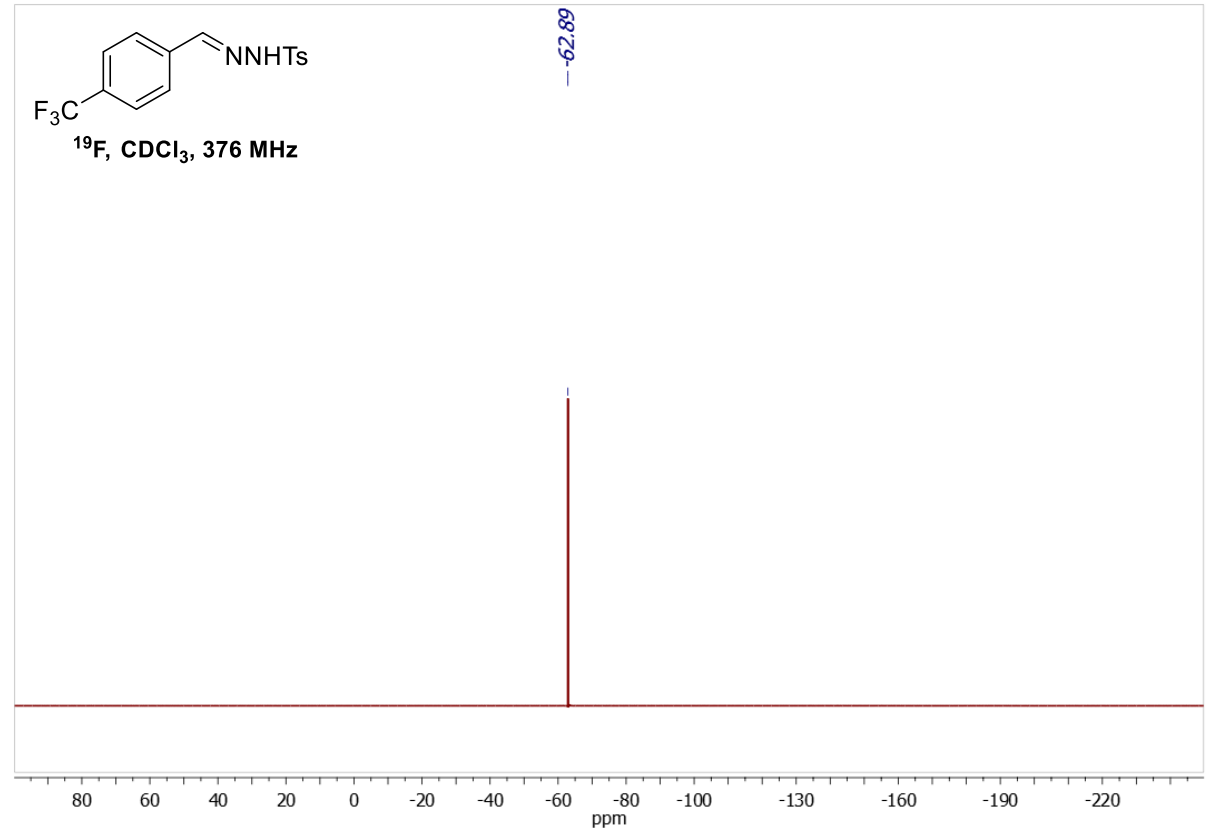
N'-(4-fluorobenzylidene)-4-methylbenzenesulfonohydrazide (1d)

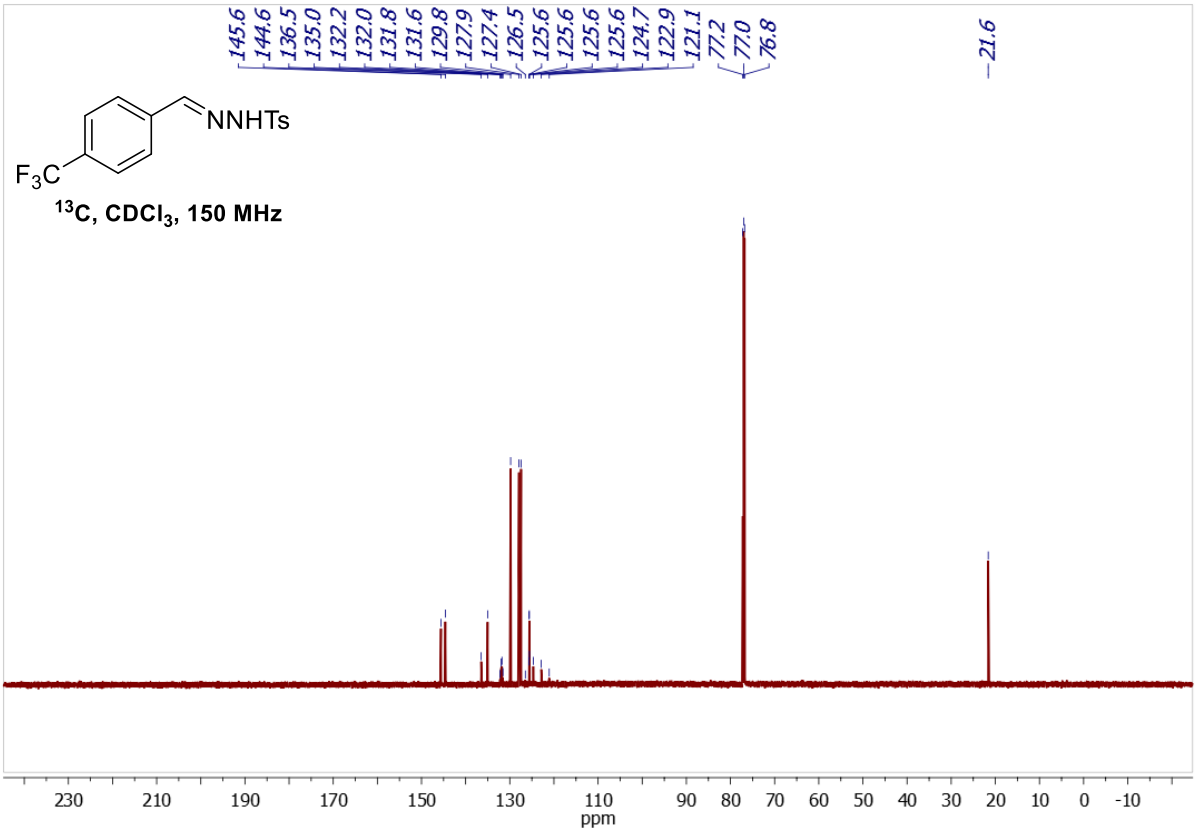




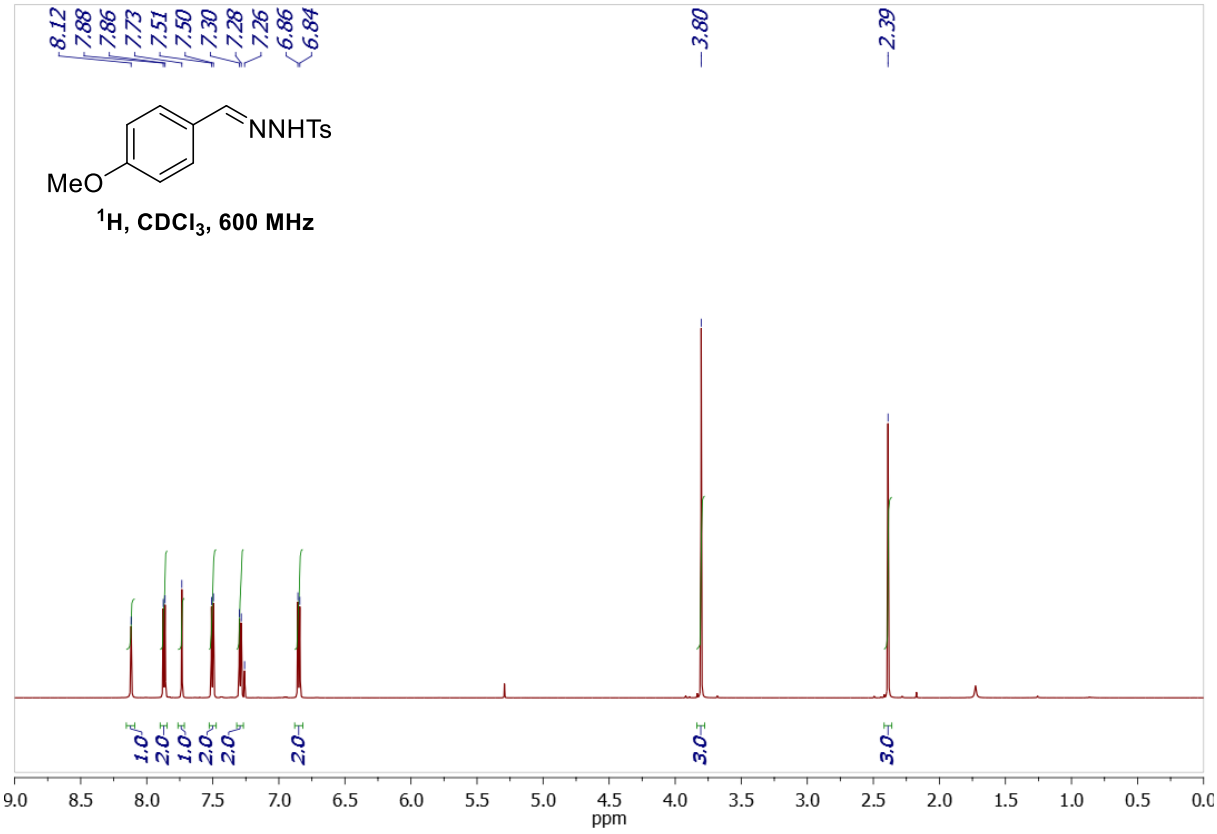
N'-(4-trifluoromethylbenzylidene)-4-methylbenzenesulfonohydrazide (1e)

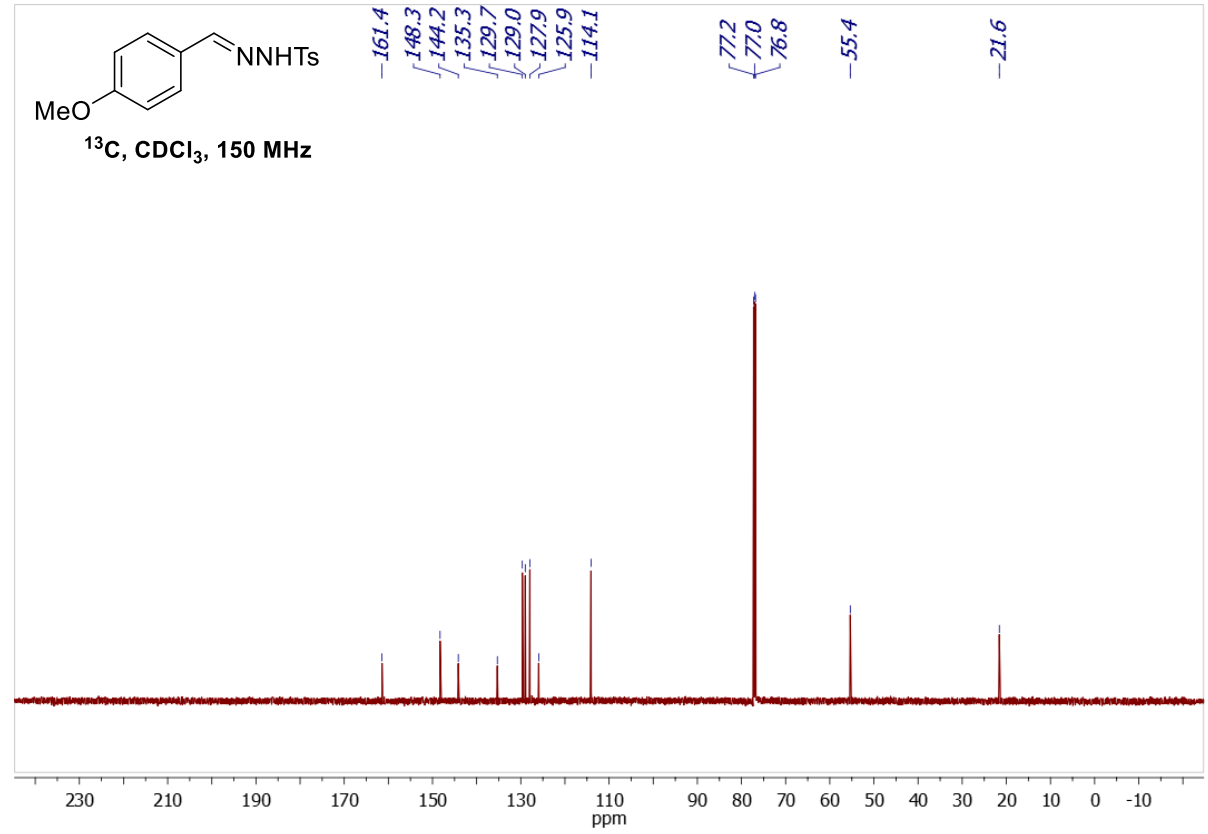




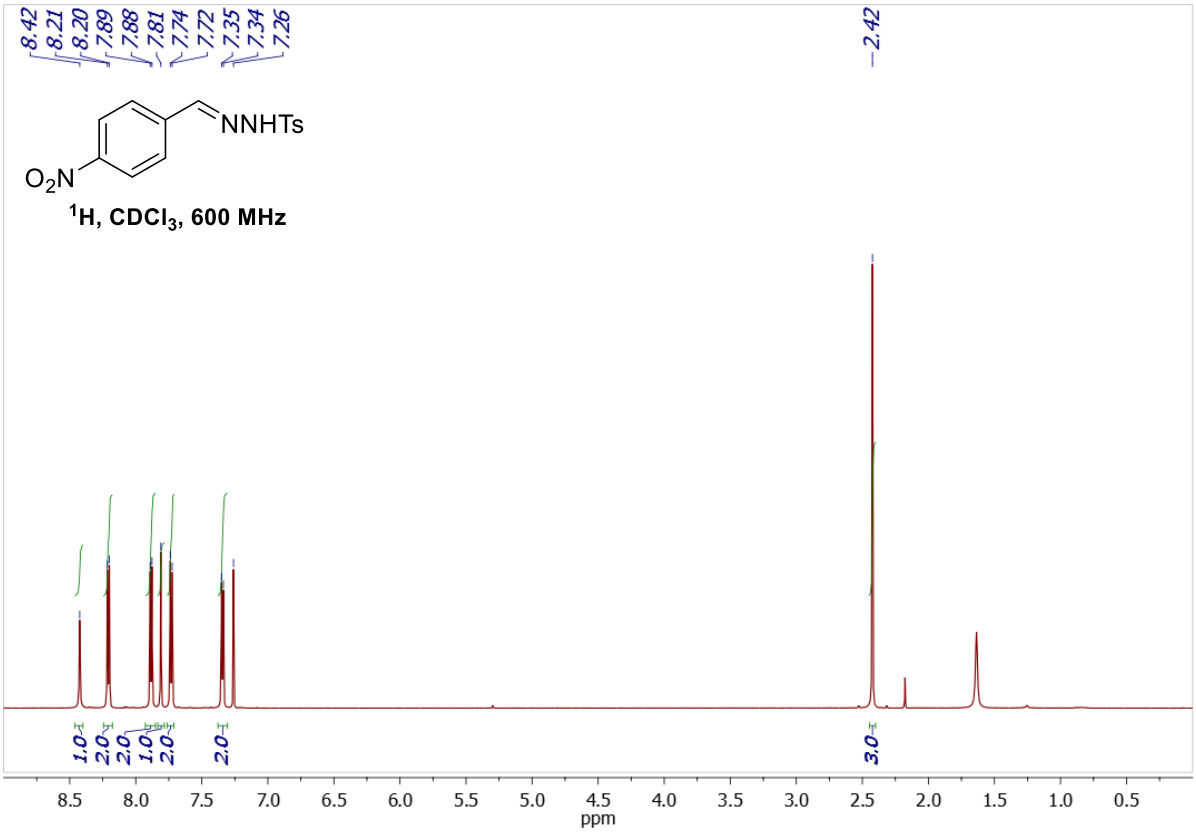

145.6
144.6
136.5
135.0
132.2
132.0
131.8
131.6
129.8
127.9
127.4
126.5
125.6
125.6
125.6
125.6
124.7
122.9
121.1
77.2
77.0
76.8
21.6
NNHTs
F3C
13C, CDCl3, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

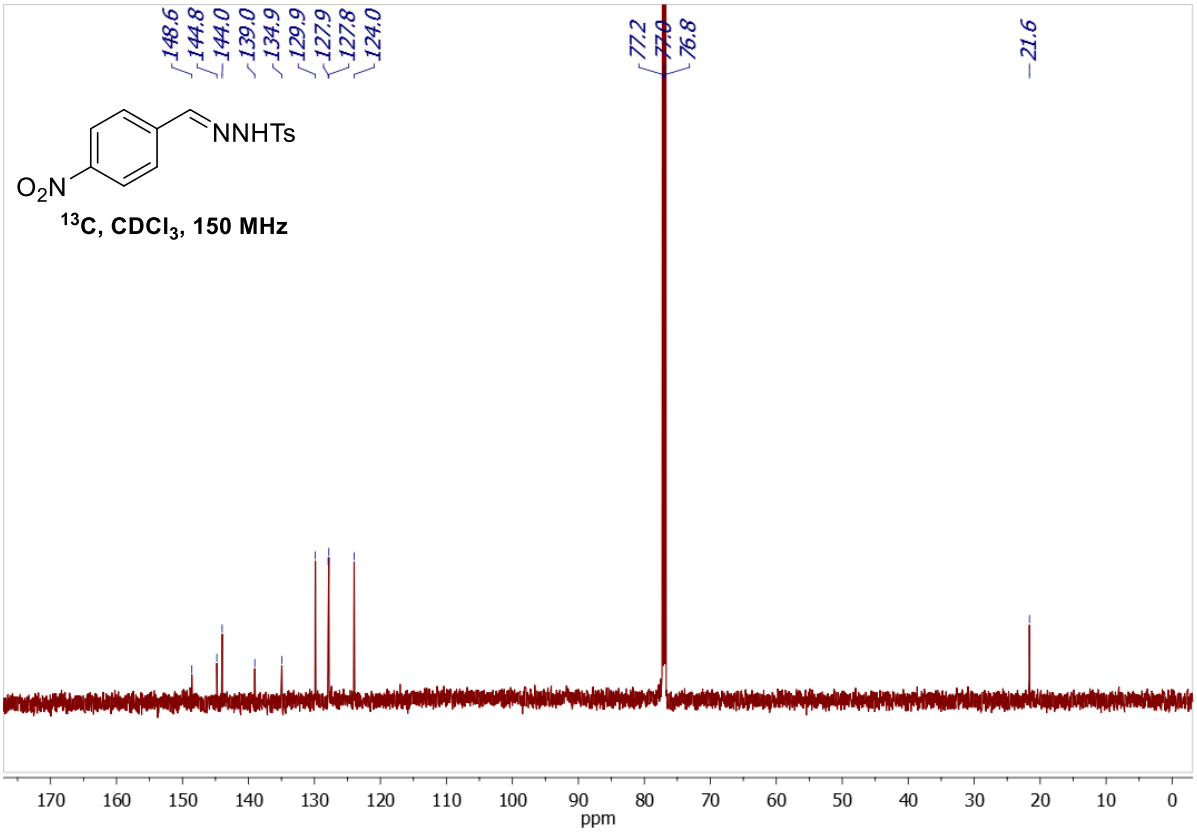
N'-(4-methoxybenzylidene)-4-methylbenzenesulfonohydrazide (1f)



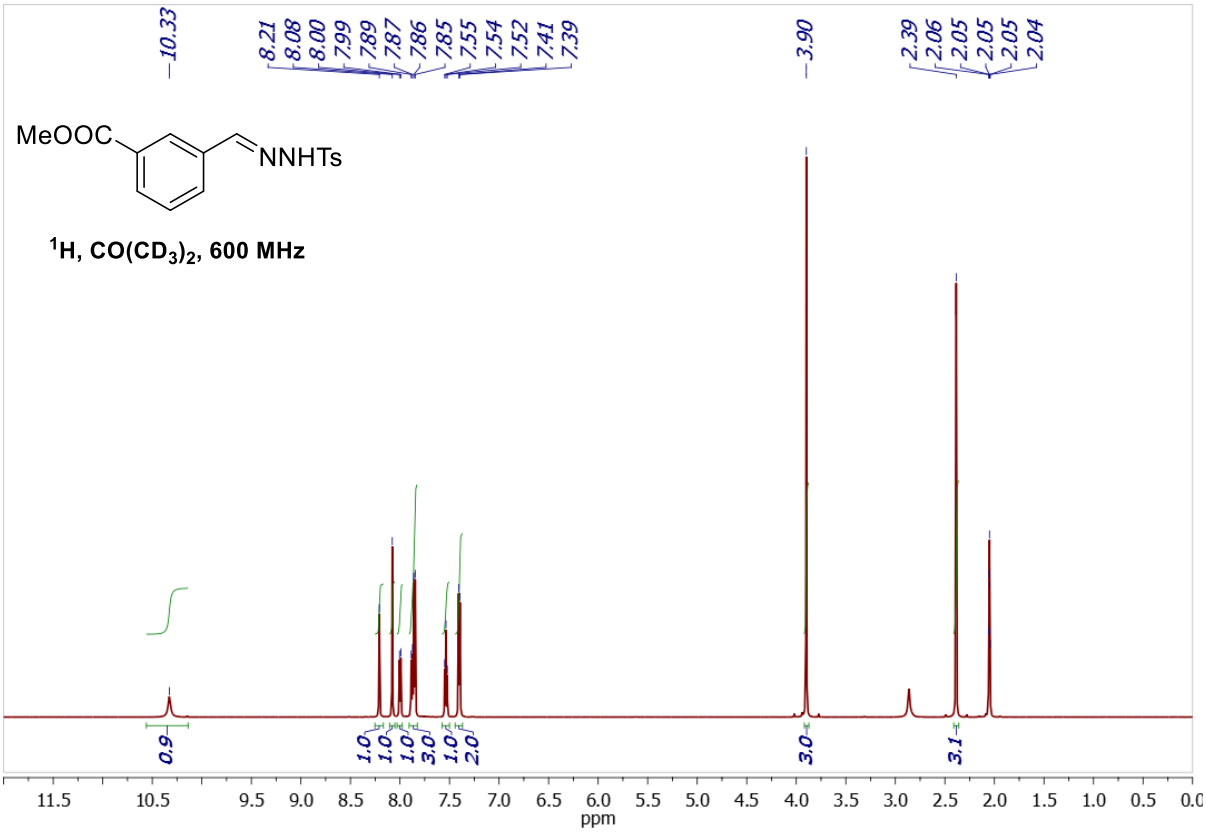


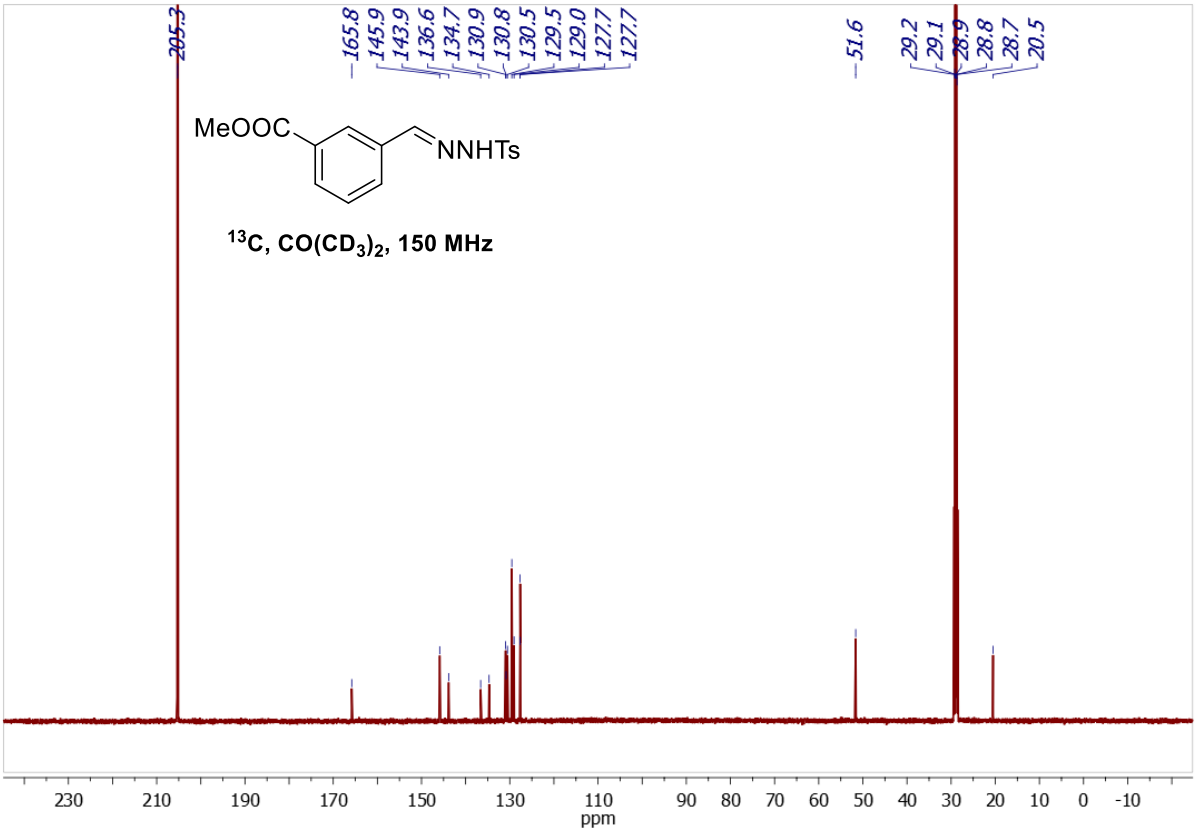
***N'*-(4-nitrobenzylidene)-4-methylbenzenesulfonohydrazide (1g)**



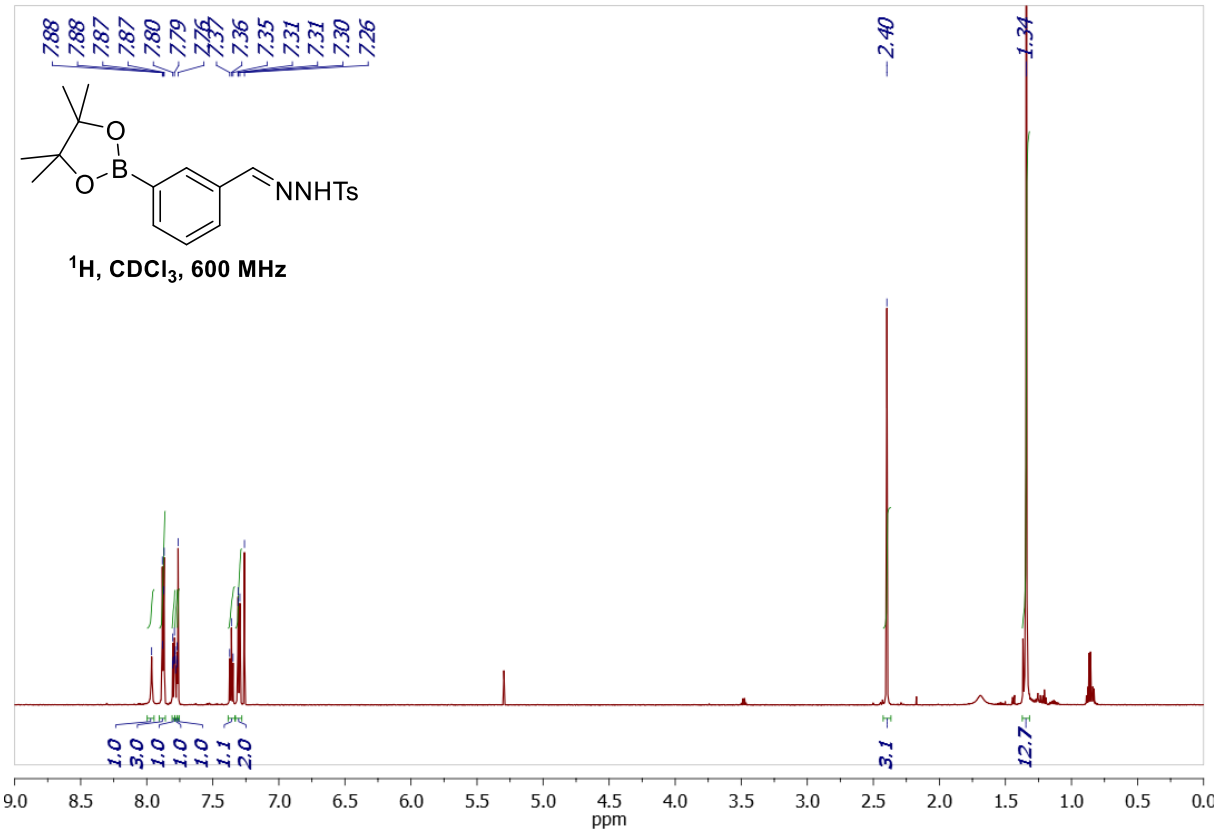


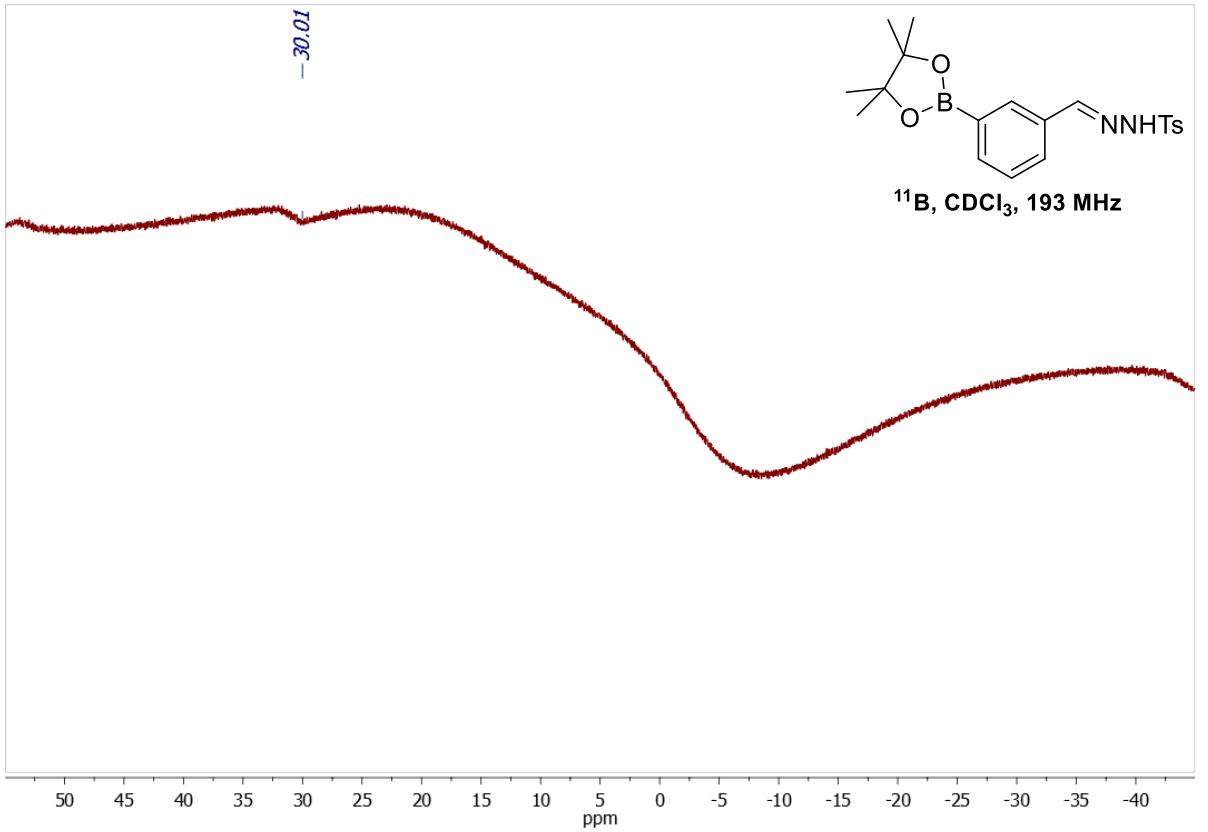
methyl 3-((2-tosylhydrazono)methyl)benzoate (1h)

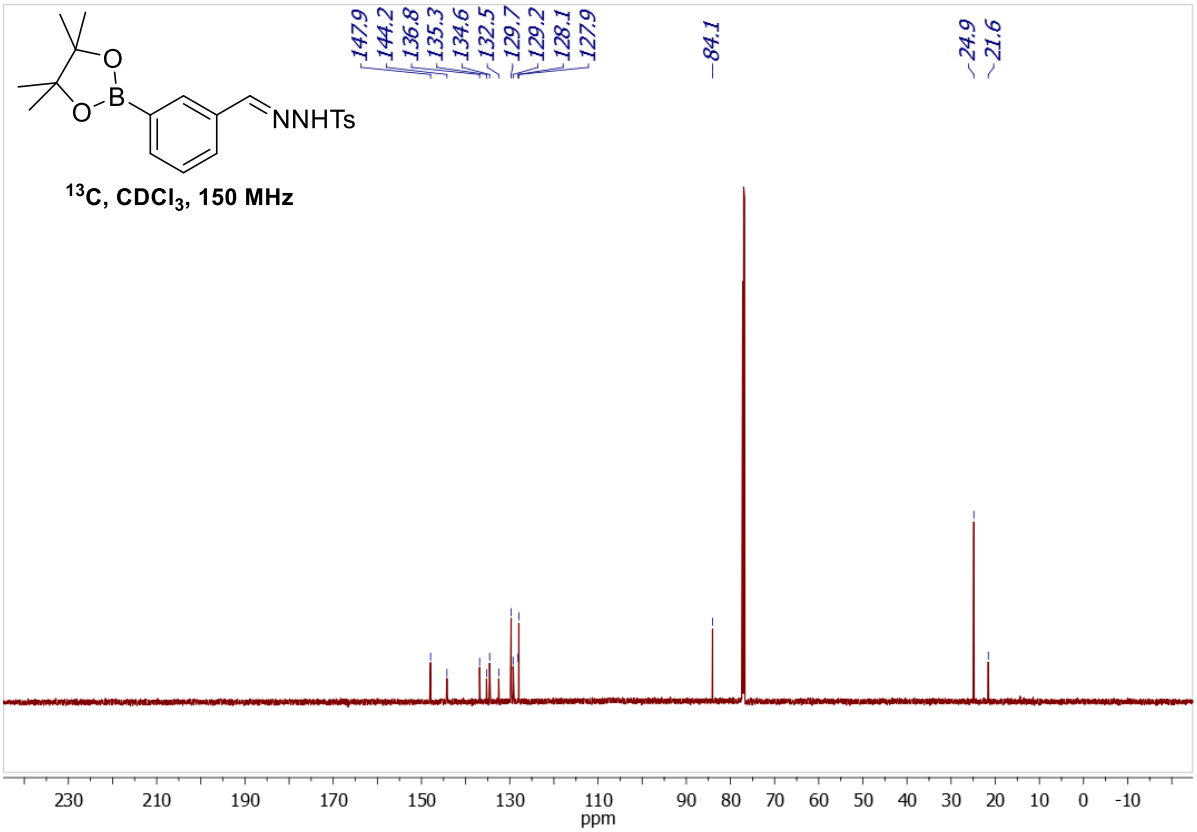




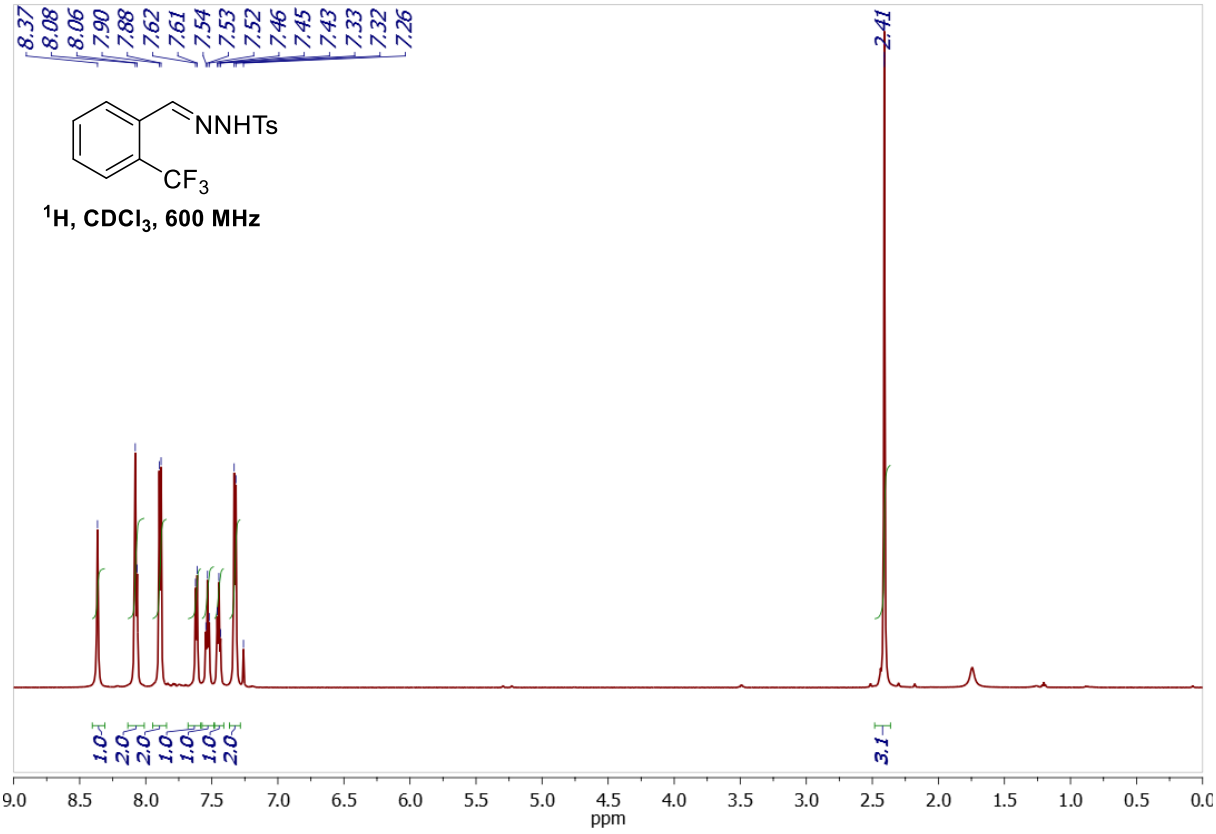
4-methyl-*N*'-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)benzenesulfonohydrazide (1i)

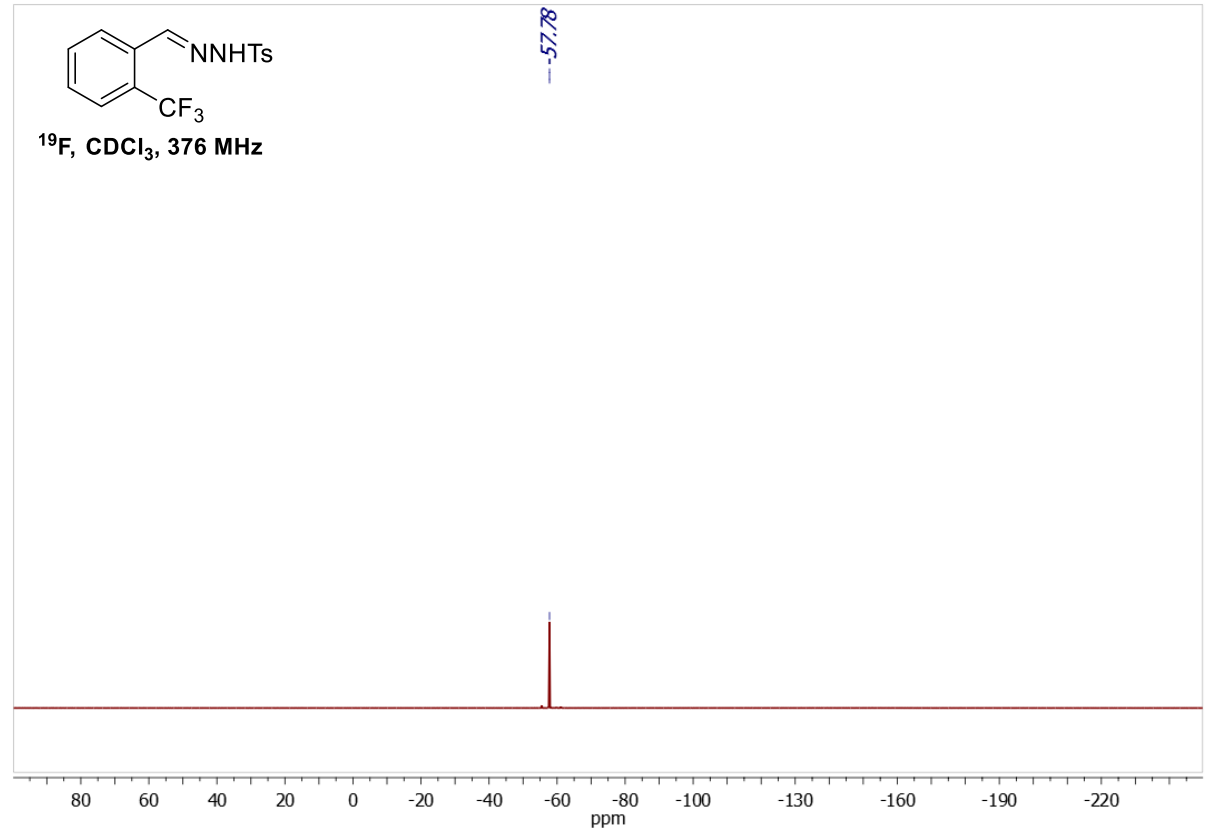


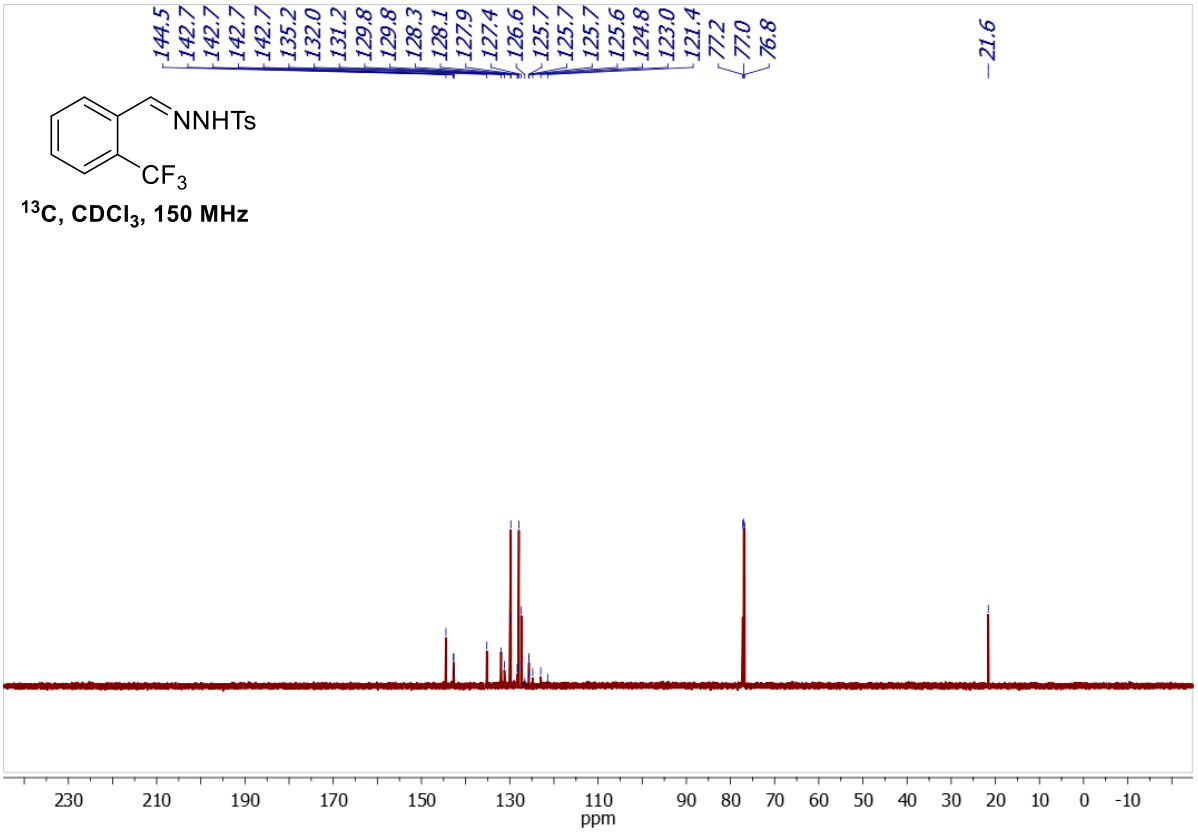



147.9
144.2
136.8
135.3
134.6
132.5
129.7
129.2
128.1
127.9
84.1
24.9
21.6
NNHTs
13C, CDCl3, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

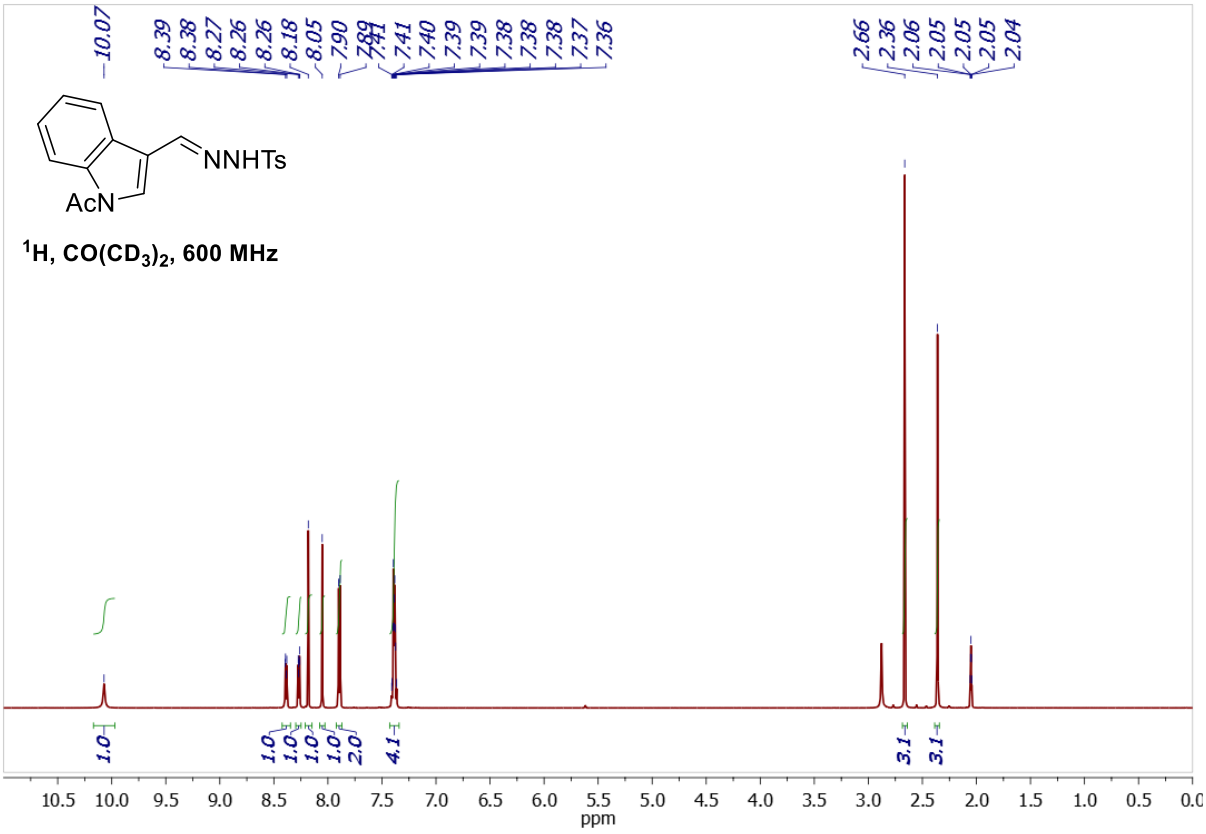
N'-(2-trifluoromethylbenzylidene)-4-methylbenzenesulfonohydrazide (1j)

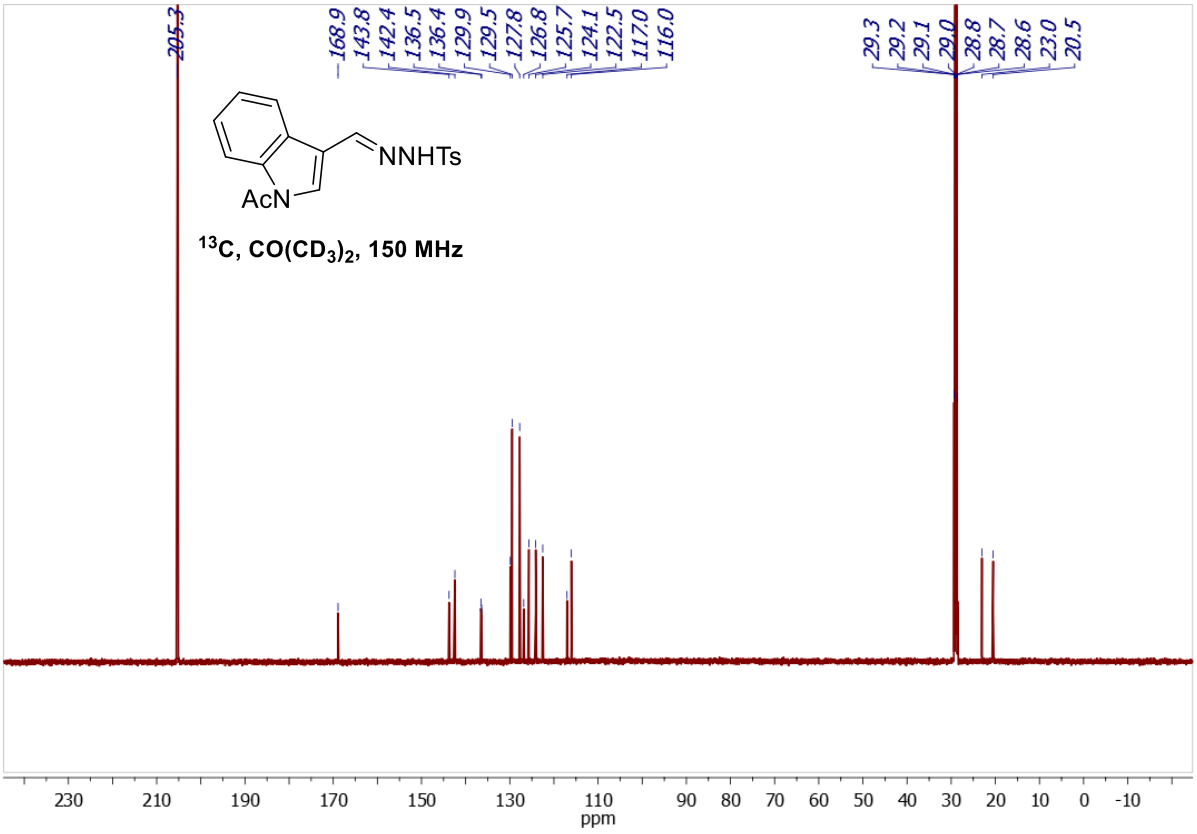




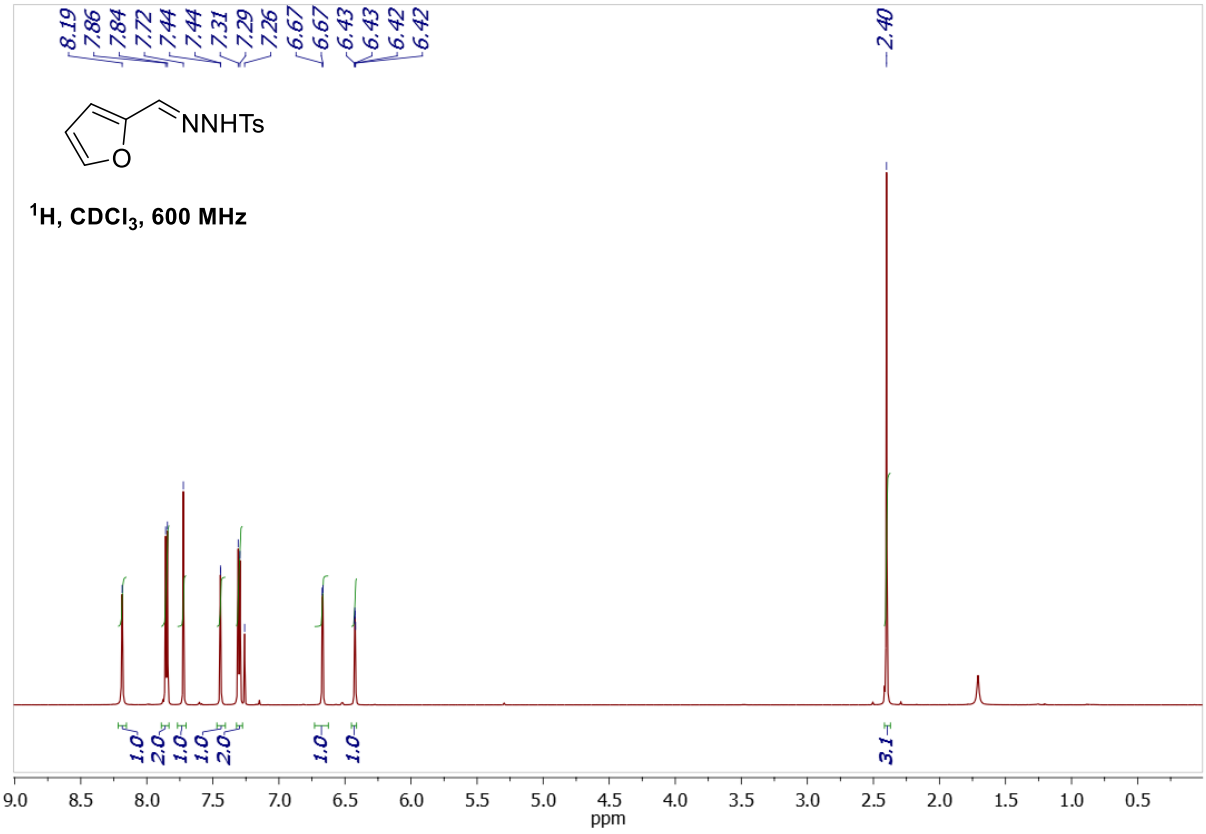

144.5
142.7
142.7
142.7
142.7
135.2
132.0
131.2
129.8
129.8
128.3
128.1
127.9
127.4
126.6
125.7
125.7
125.7
125.6
124.8
123.0
121.4
77.2
77.0
76.8
21.6
NNHTs
CF3
13C, CDCl3, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

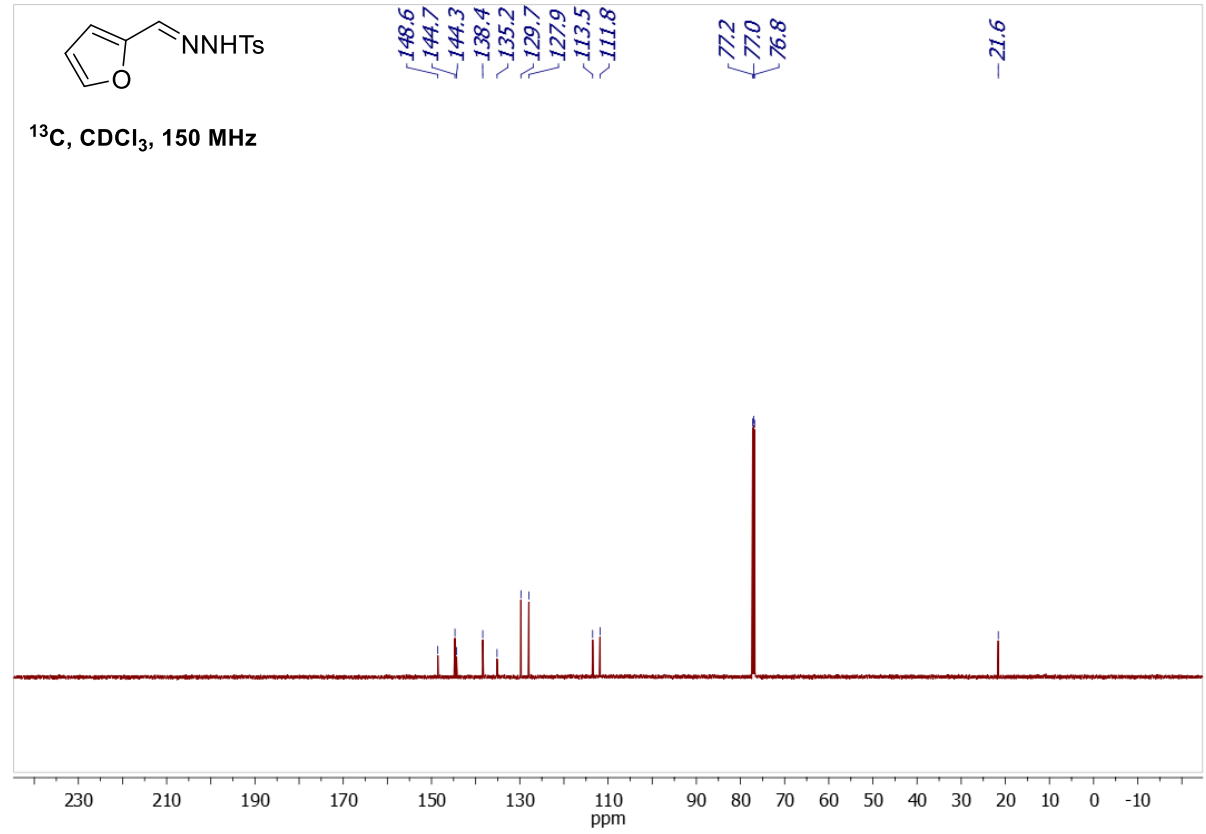
N'-((1-acetyl-1H-indol-3-yl)methylene)-4-methylbenzenesulfonohydrazide (1k)



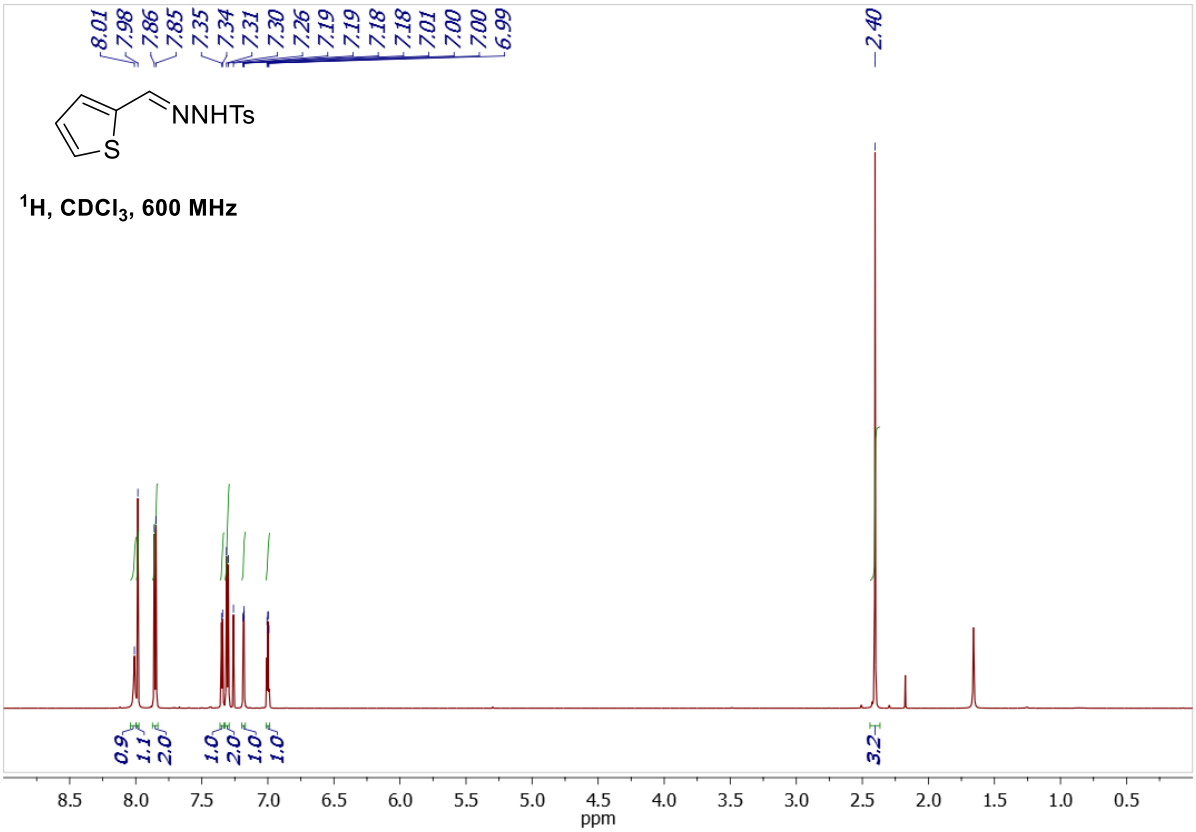


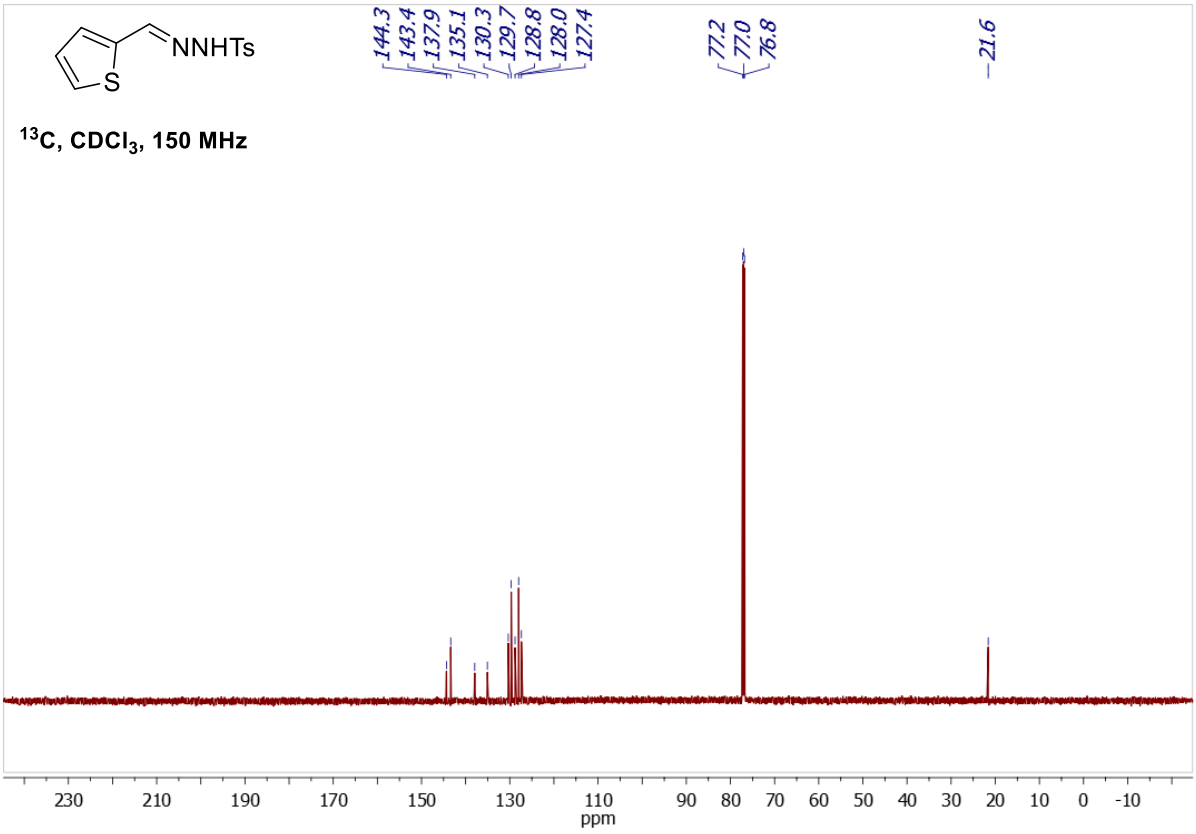
***N*'-(furan-2-ylmethylene)-4-methylbenzenesulfonohydrazide (1l)**



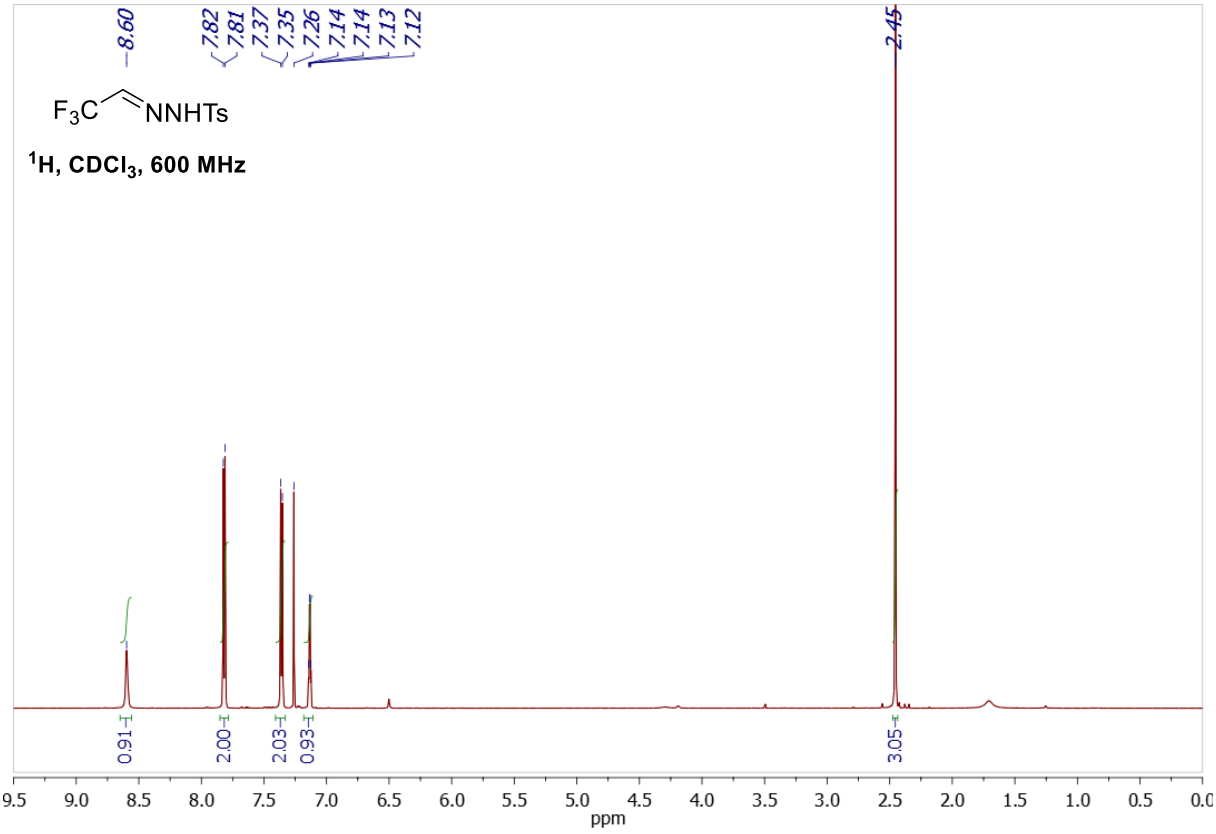


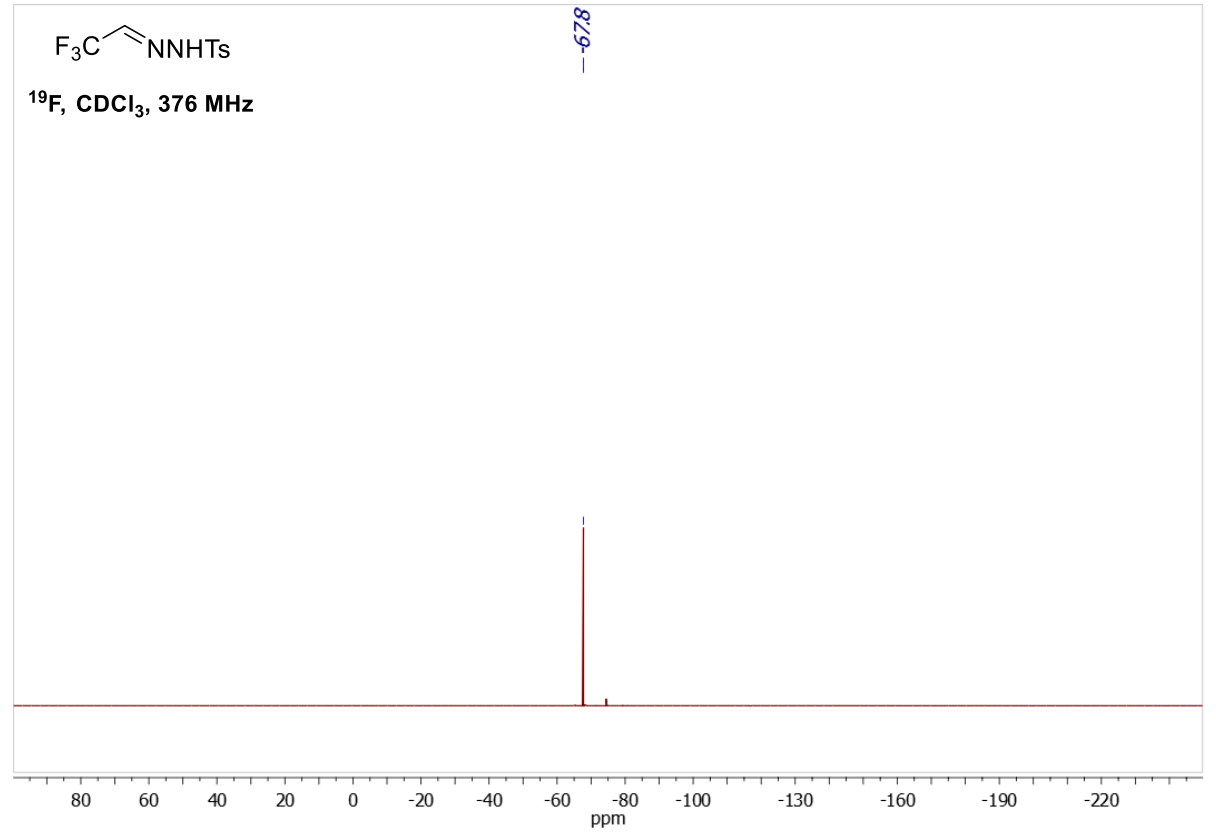
N'-(thiophen-2-ylmethylene)-4-methylbenzenesulfonohydrazide (1m)

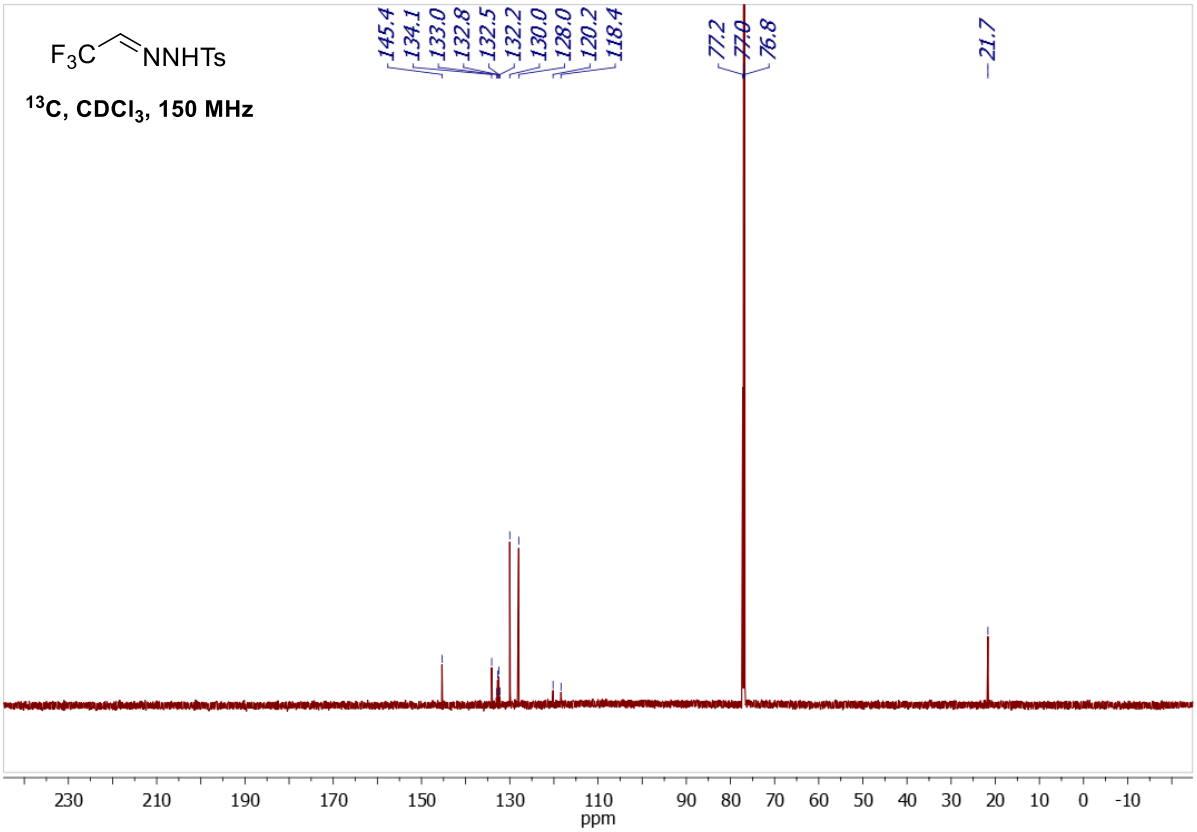




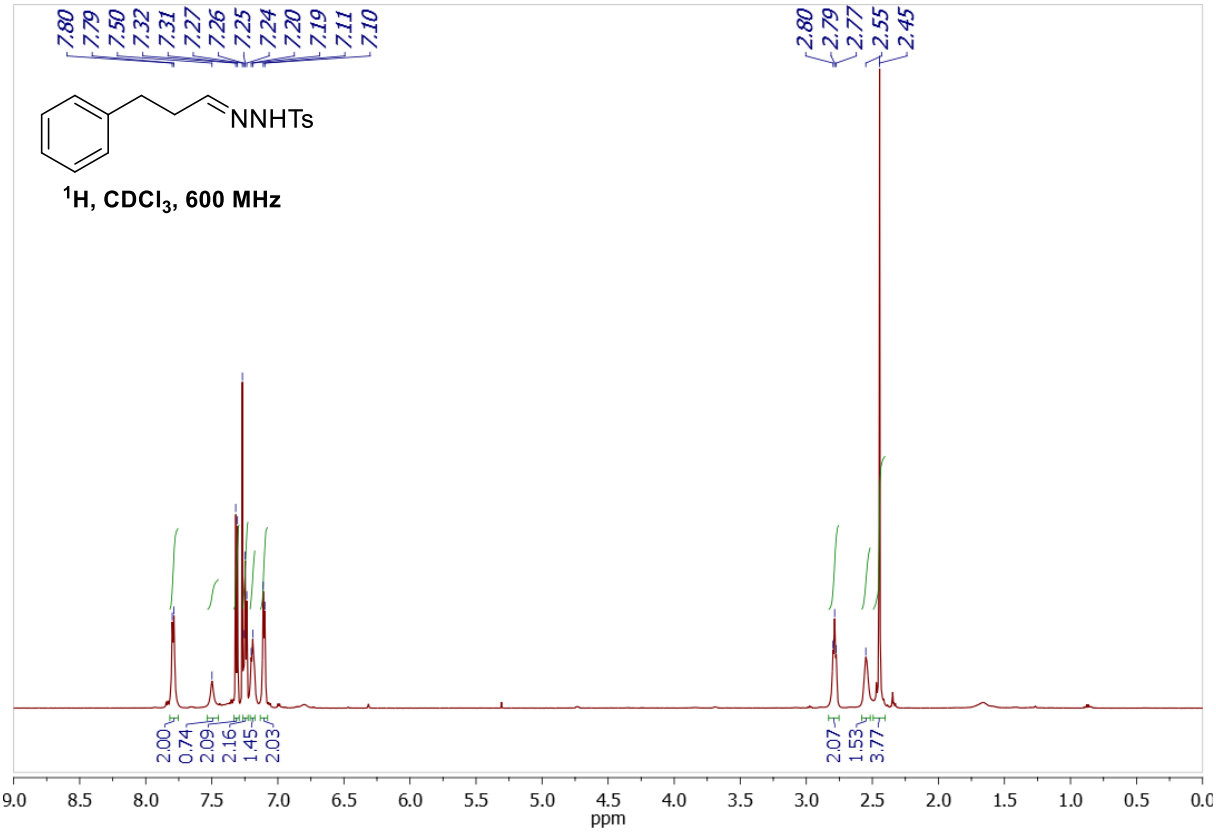
4-methyl-*N*'-(2,2,2-trifluoroethylidene)benzenesulfonohydrazide (1n)

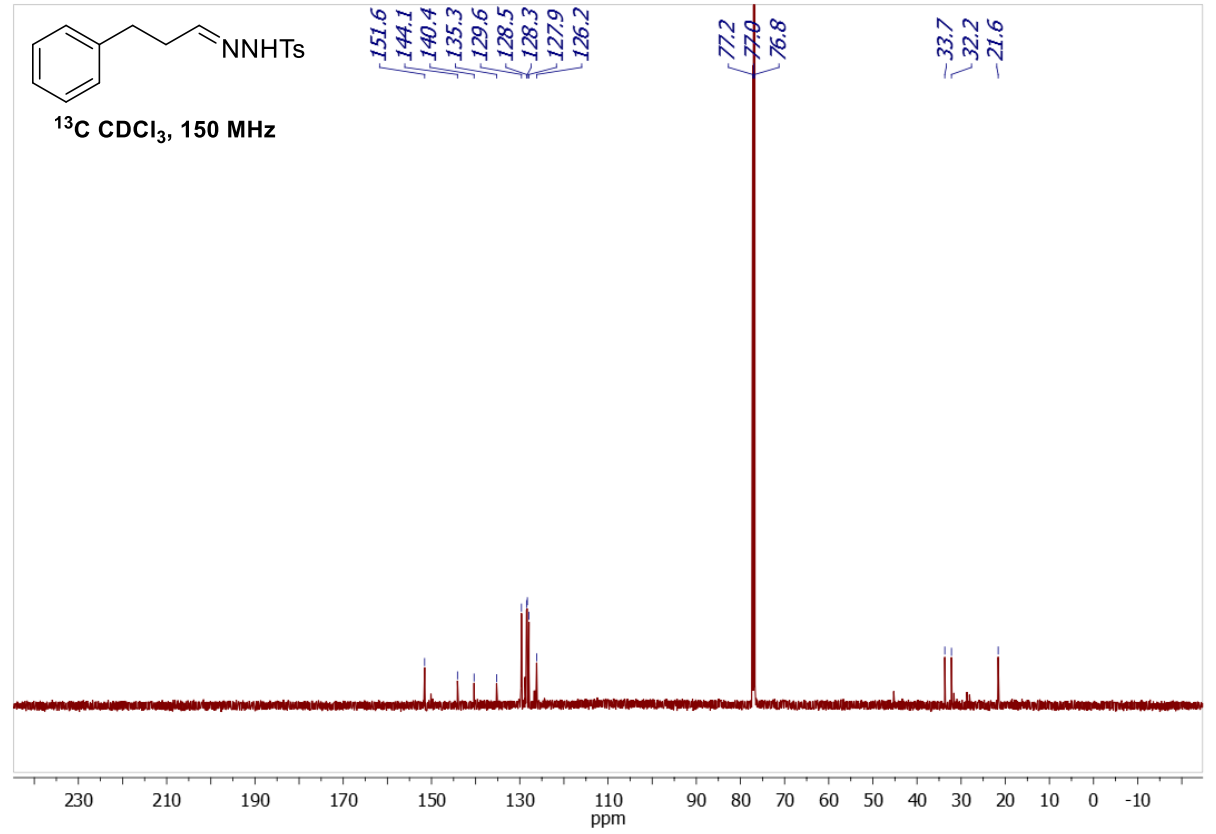




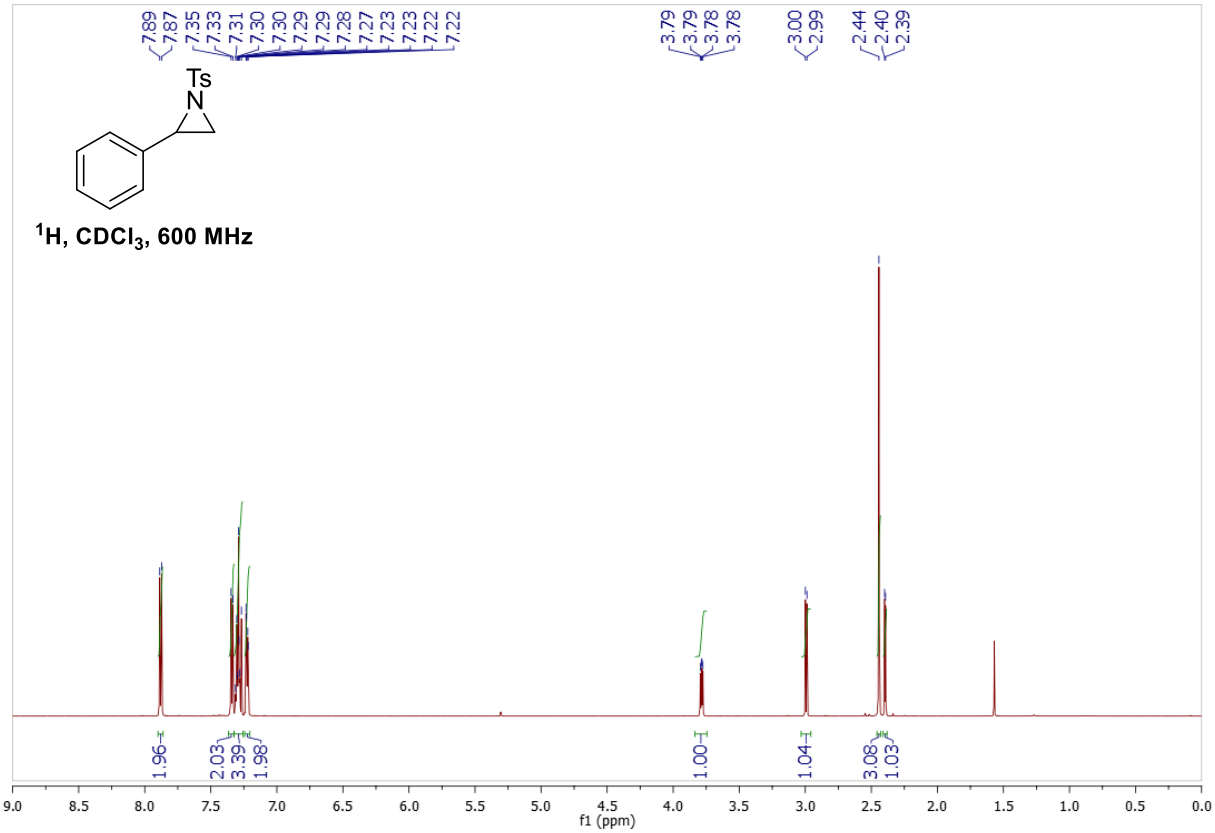

F3C
NNHTs
13C, CDCl3, 150 MHz
145.4
134.1
133.0
132.8
132.5
132.2
130.0
128.0
120.2
118.4
77.2
77.0
76.8
21.7
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

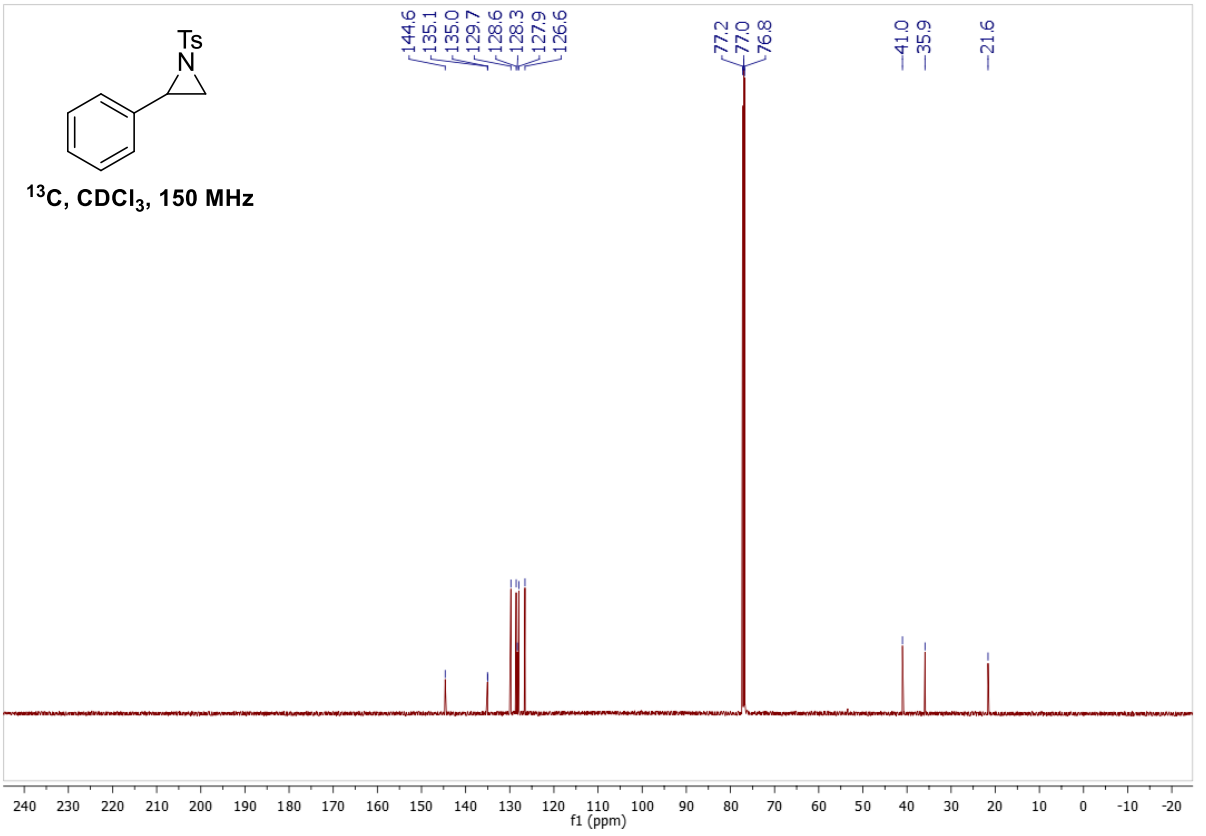
4-methyl-*N*'-(3-phenylpropylidene)benzenesulfonohydrazide (1o)



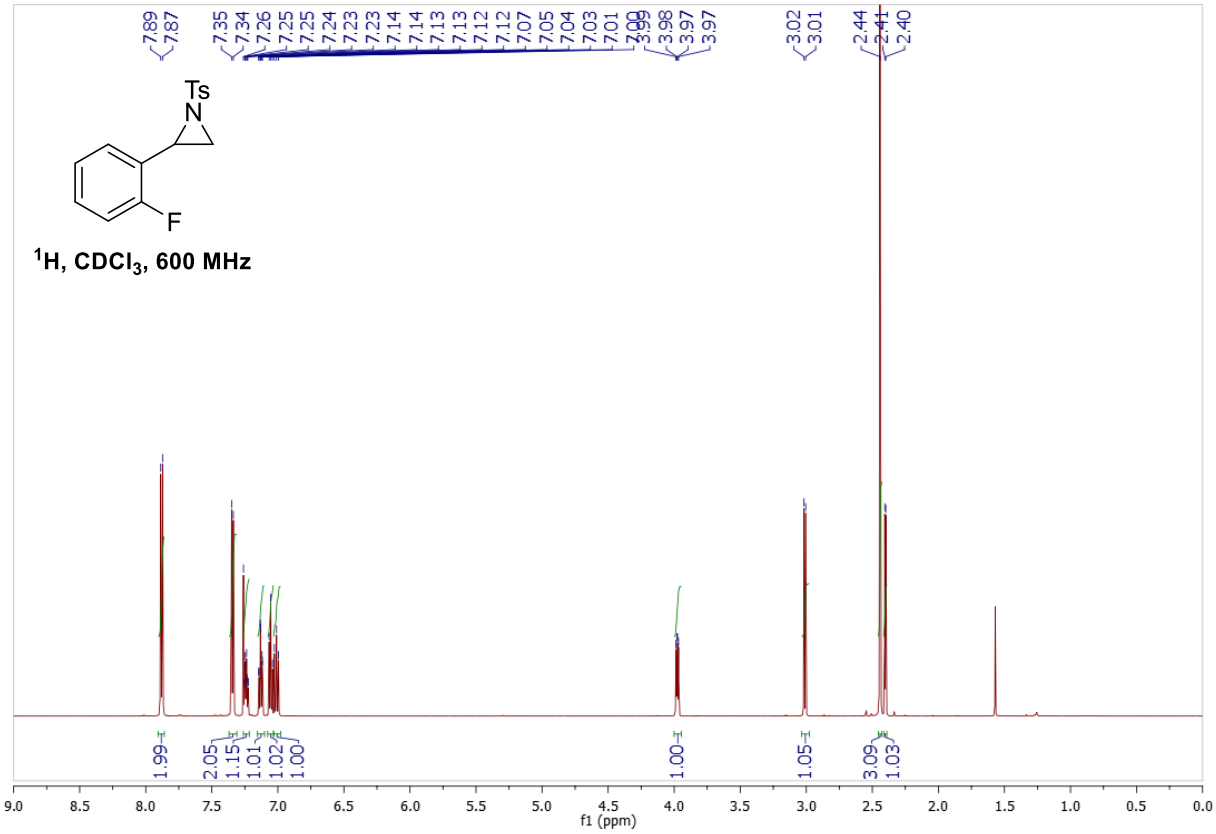


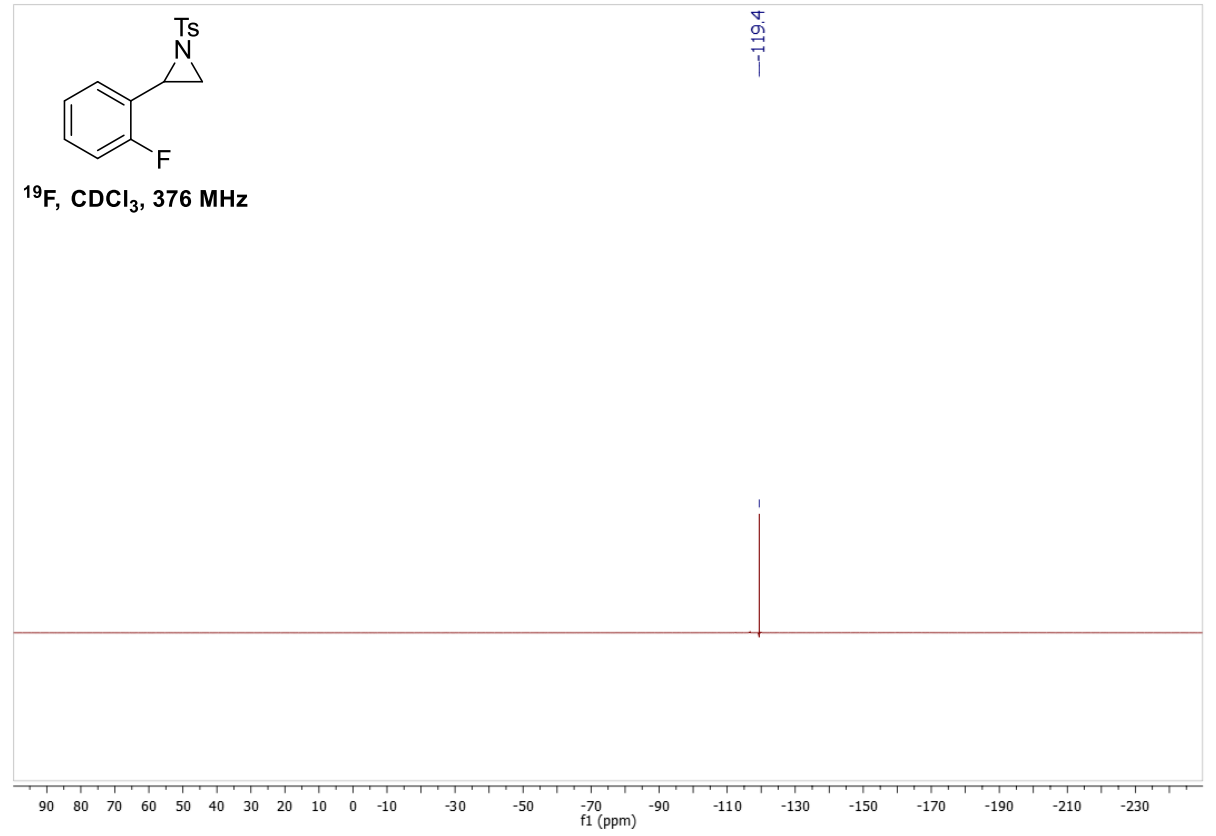
2-phenyl-1-tosylaziridine (2a)

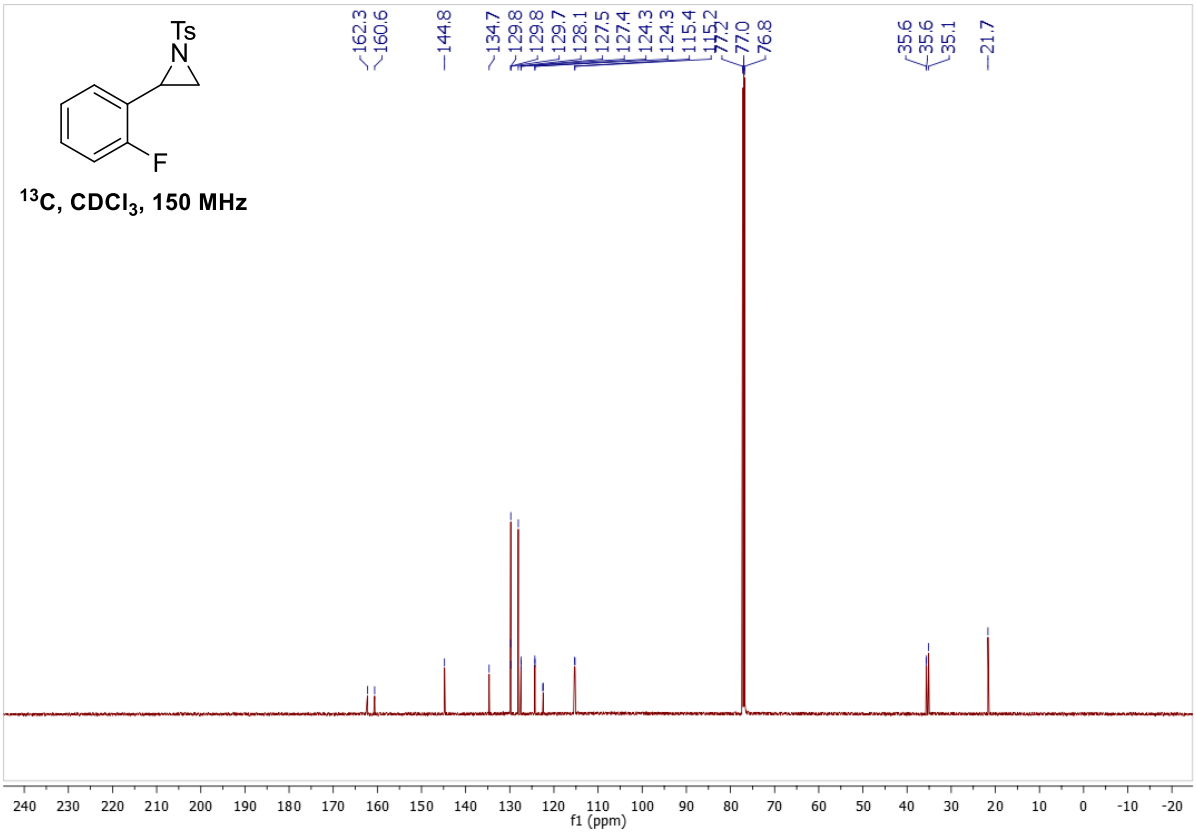




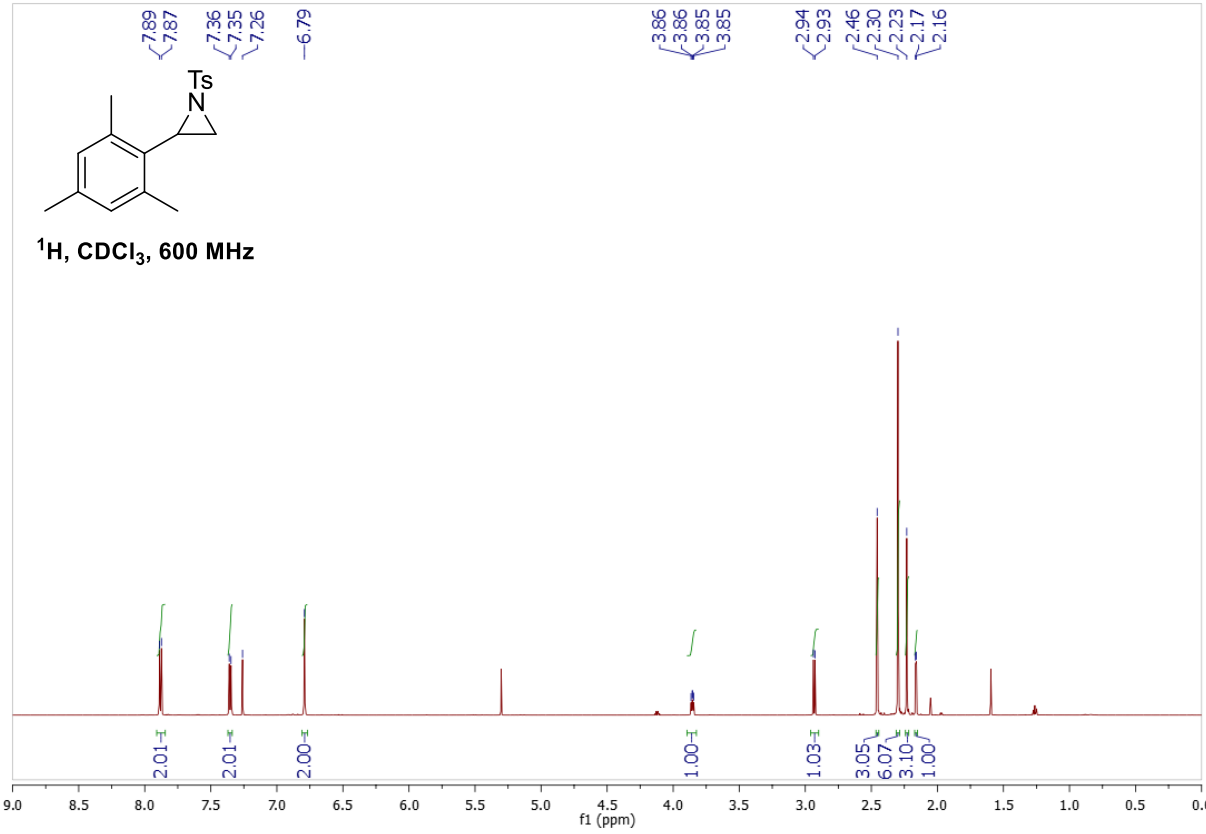
2-(2-fluorophenyl)-1-tosylaziridine (2b)

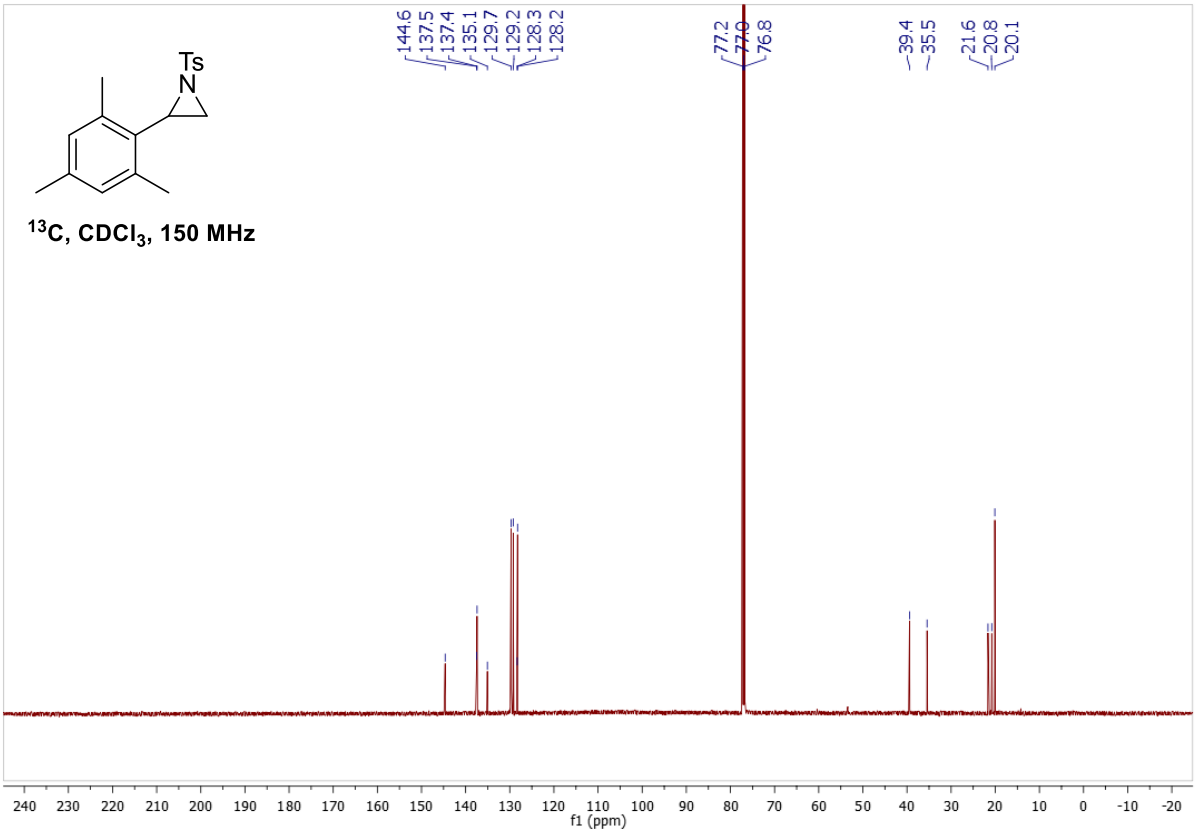




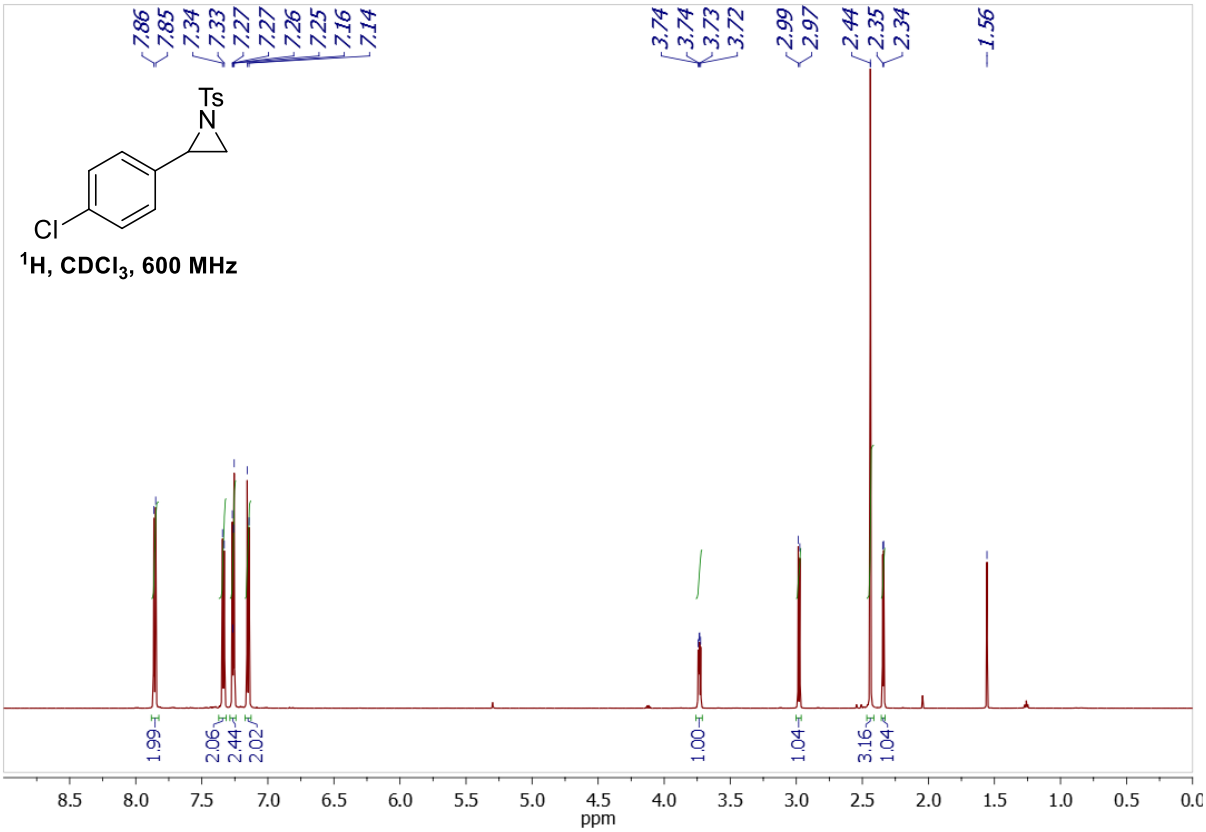

Ts
N
F
^{13}C, CDCl$_3$, 150 MHz
162.3
160.6
144.8
134.7
129.8
129.8
129.7
128.1
127.5
127.4
124.3
124.3
115.4
115.2
77.2
77.0
76.8
35.6
35.6
35.1
21.7
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

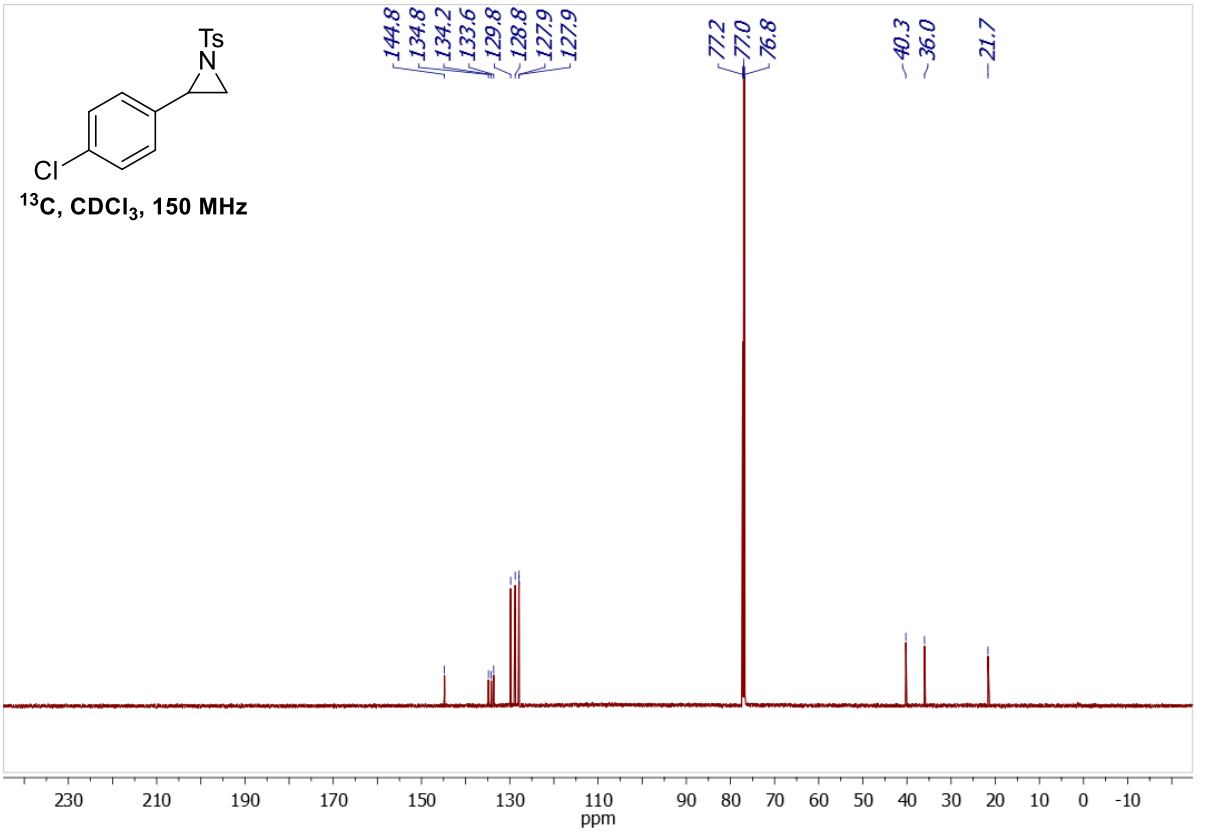
2-mesityl-1-tosylaziridine (2c)



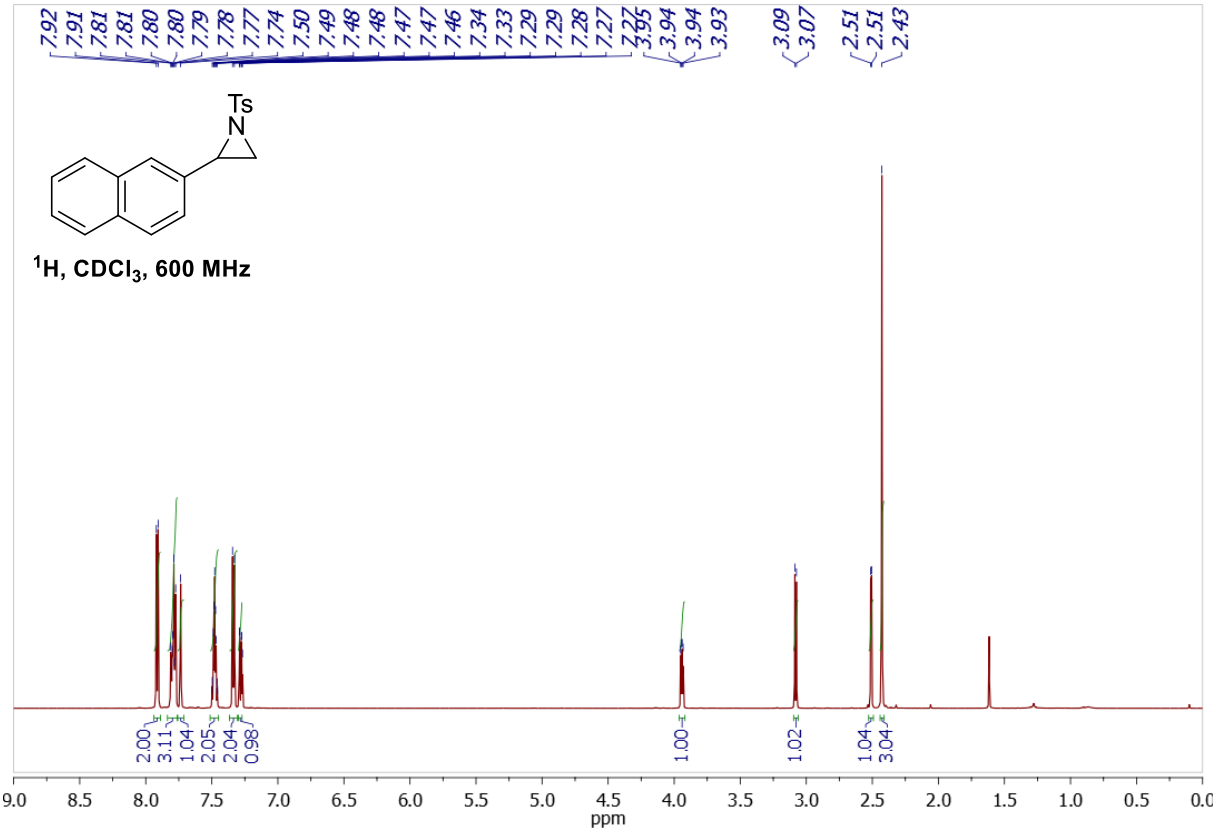


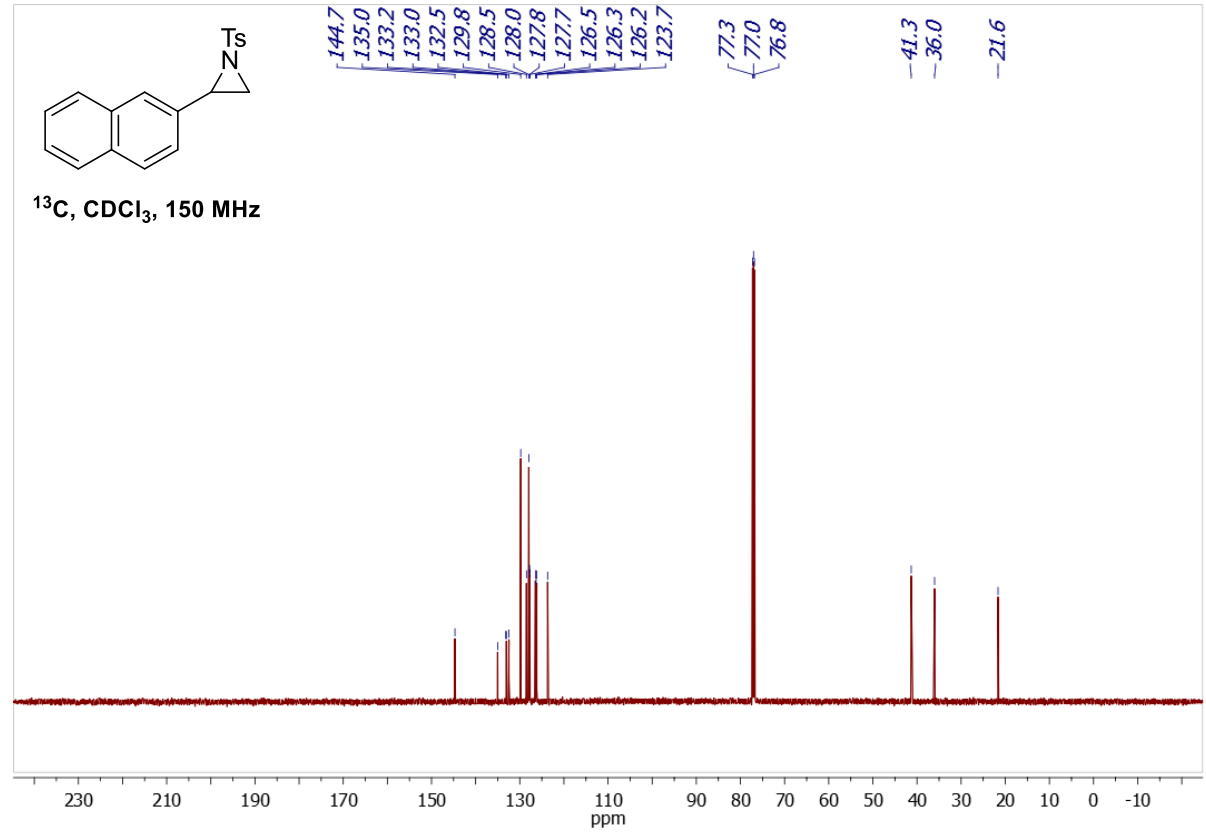
2-(4-chlorophenyl)-1-tosylaziridine (2d)



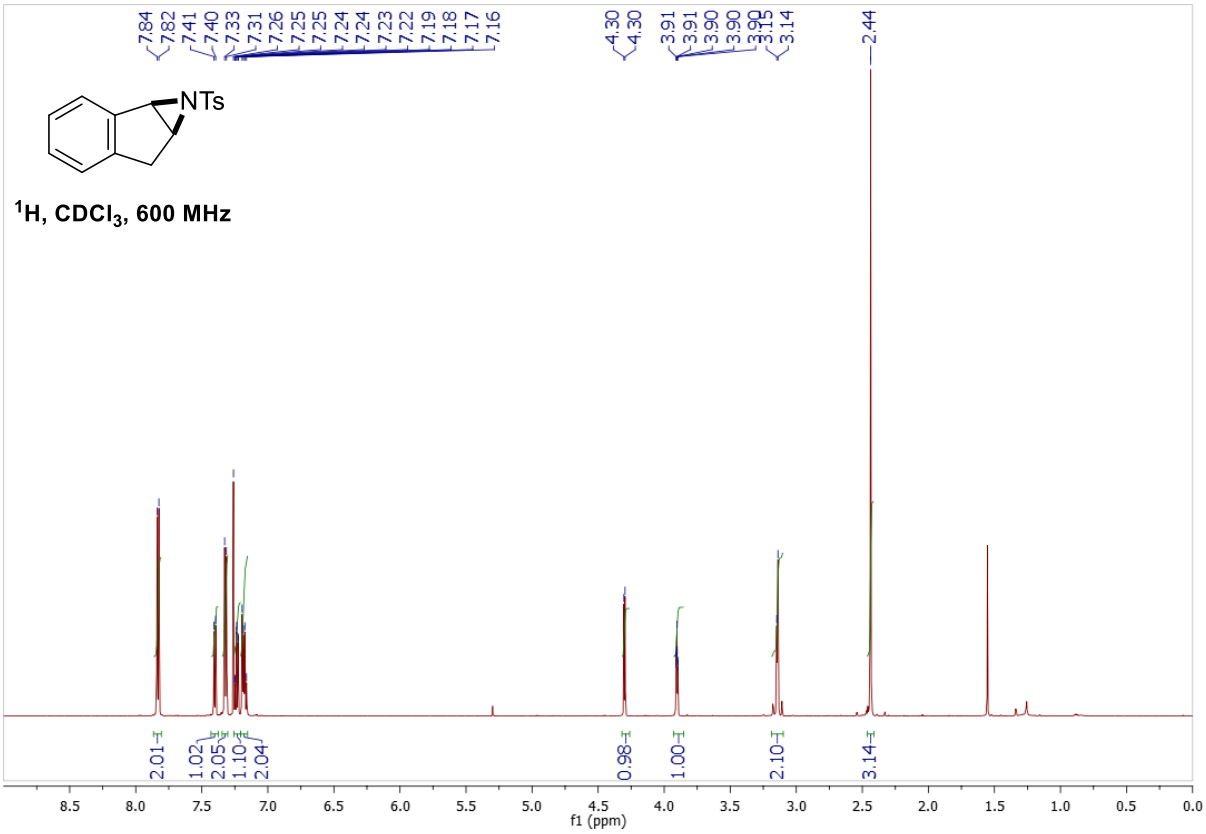


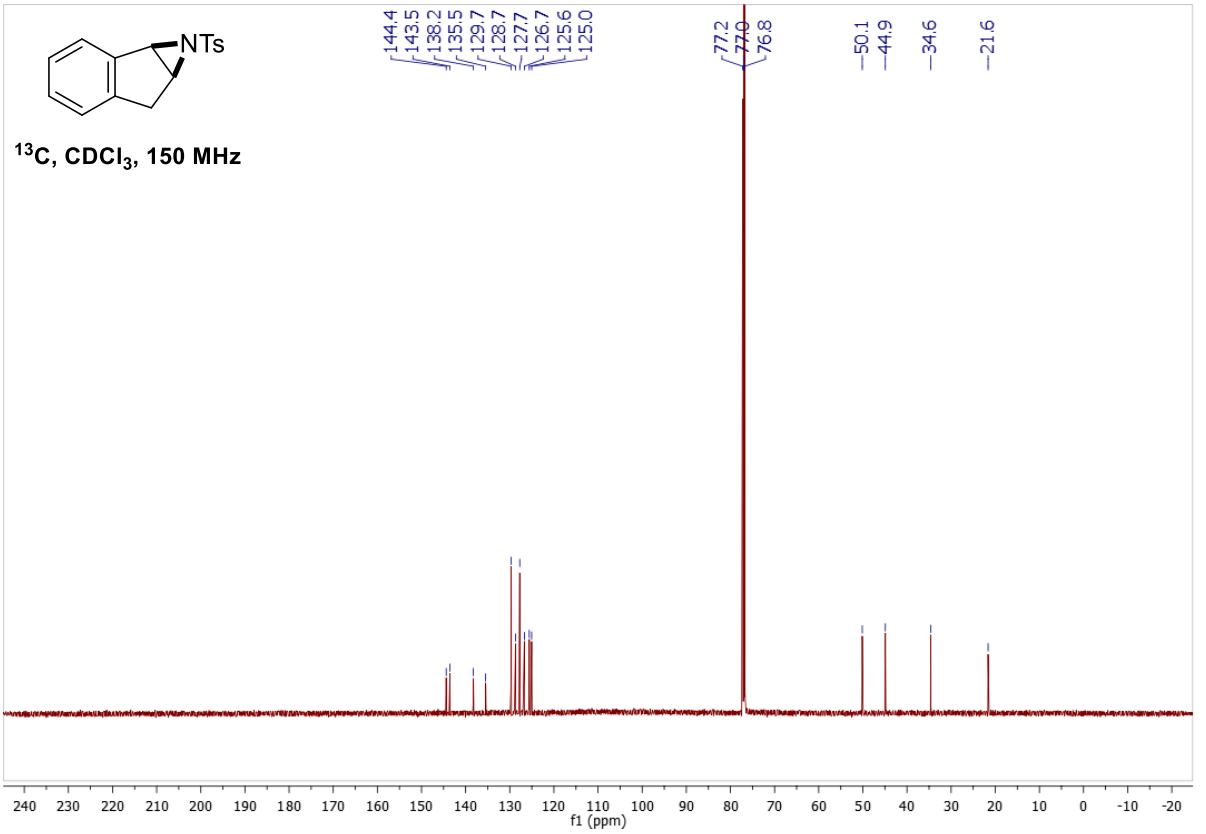
2-(naphthalen-2-yl)-1-tosylaziridine (2e)



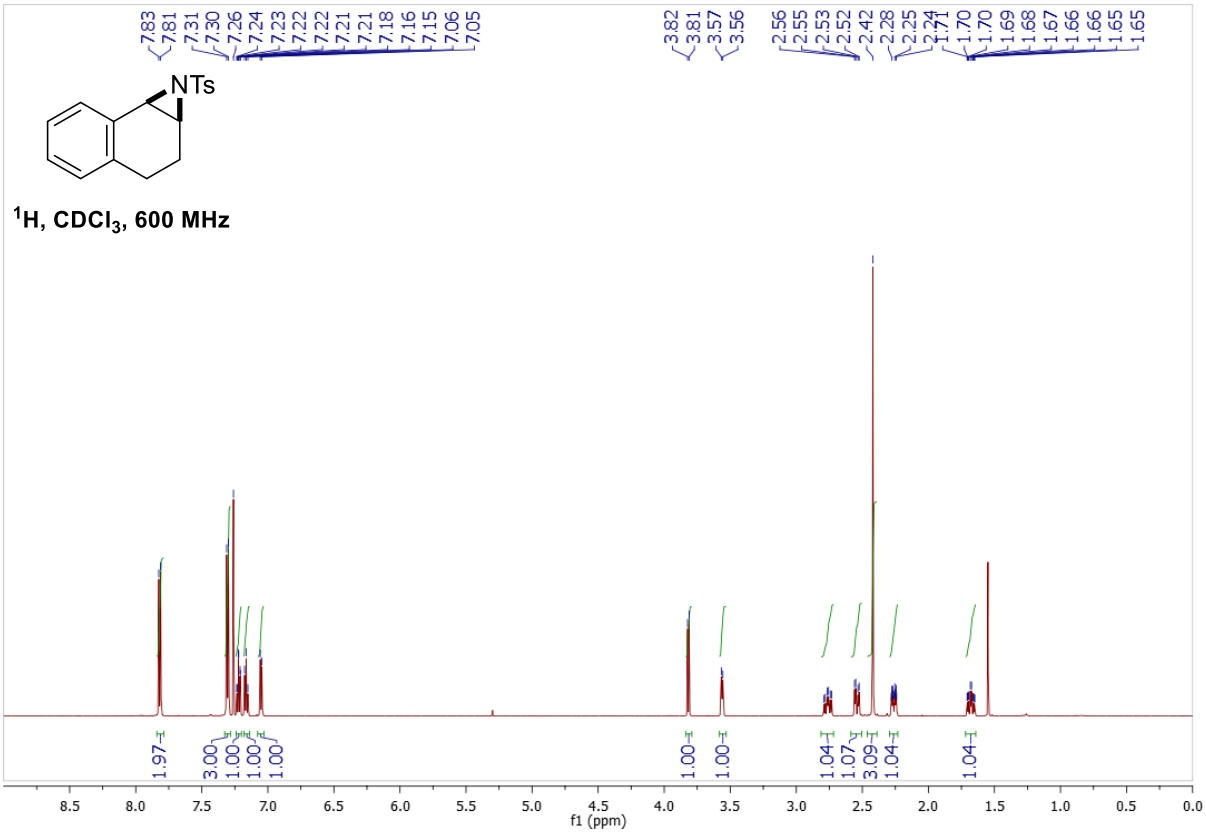


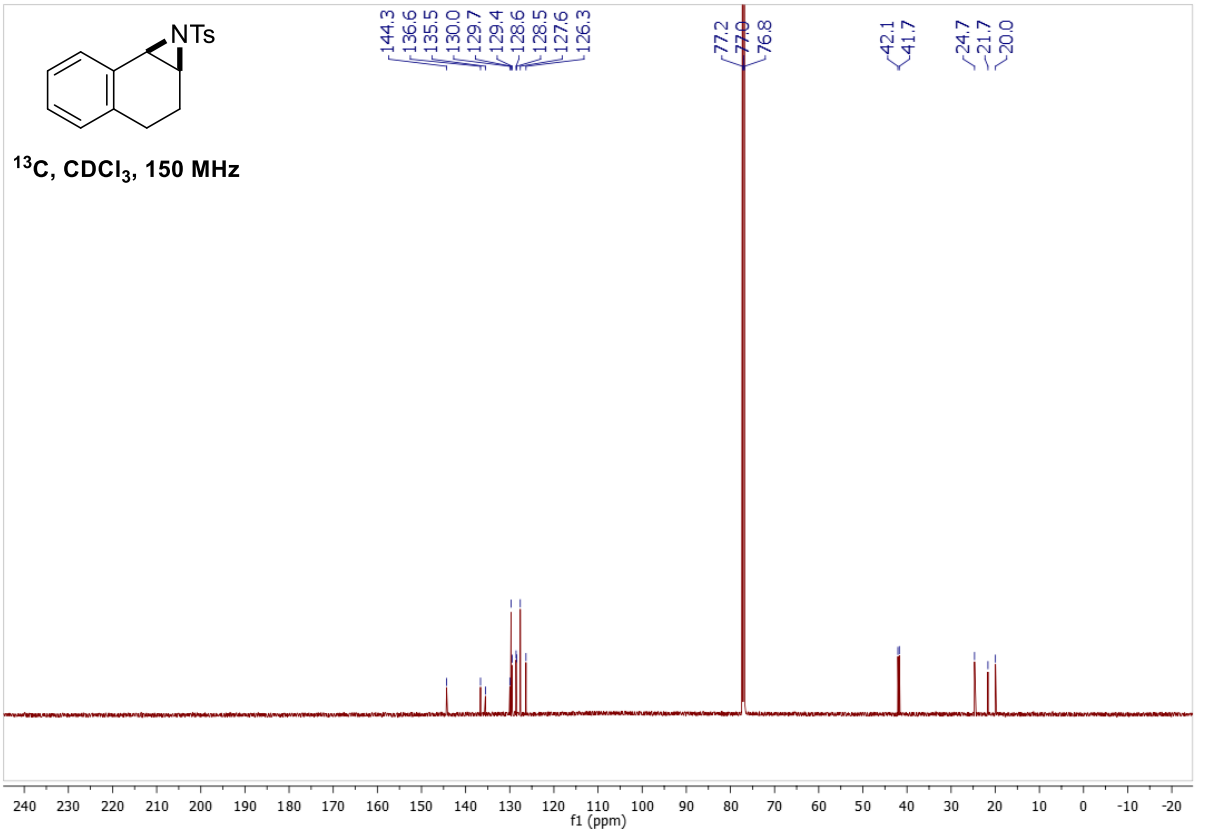
(+/-)-(1*aR*,6*aS*)-1-tosyl-1,1a,6,6a-tetrahydroindeno[1,2-b]azirine (2f)



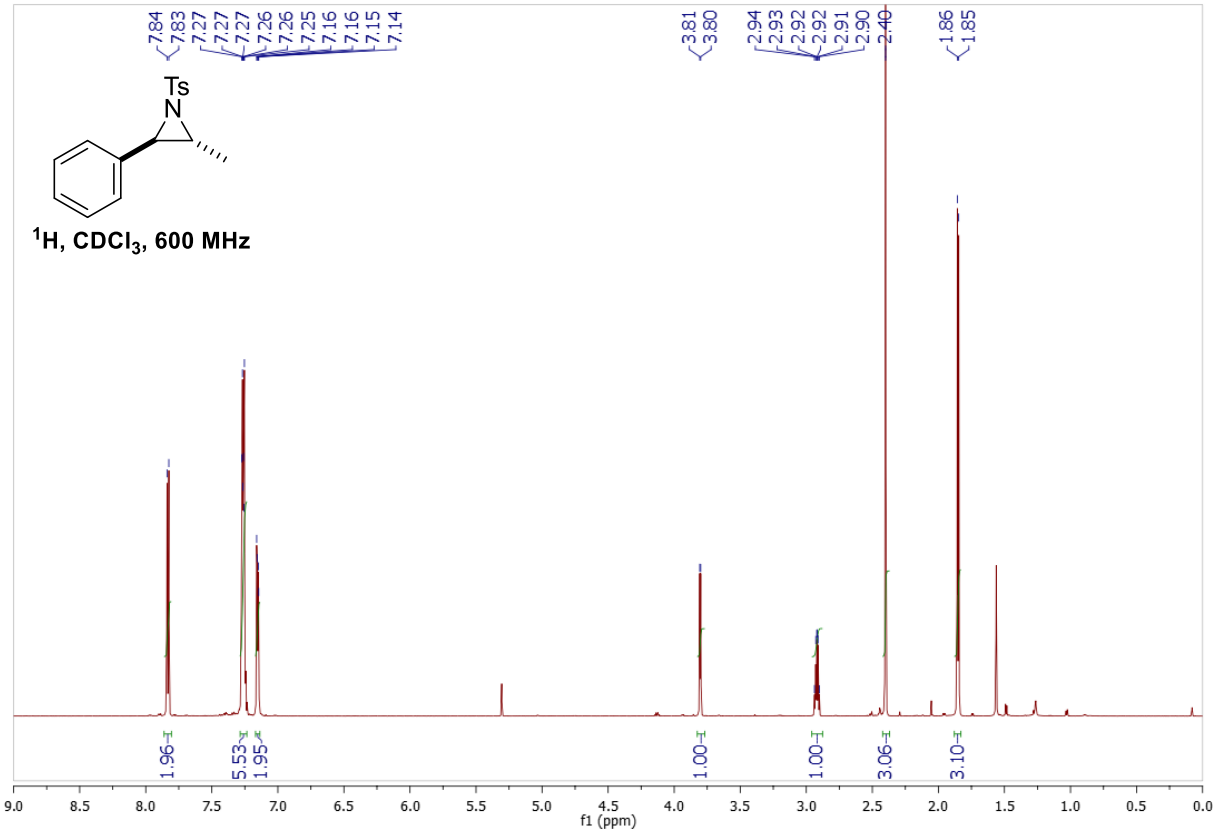


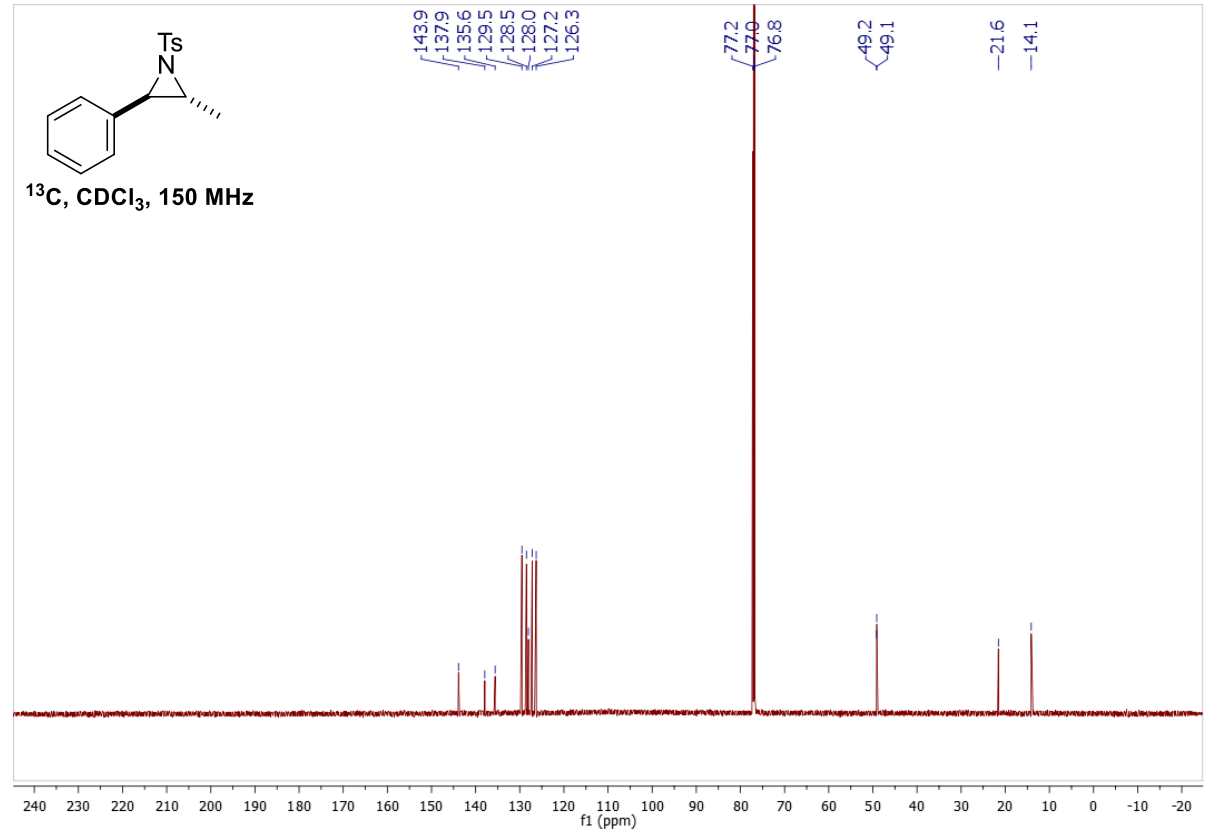
(+/-)-(1*aS*,7*bR*)-1-tosyl-1a,2,3,7b-tetrahydro-1H-naphtho[1,2-b]azirine (2g)



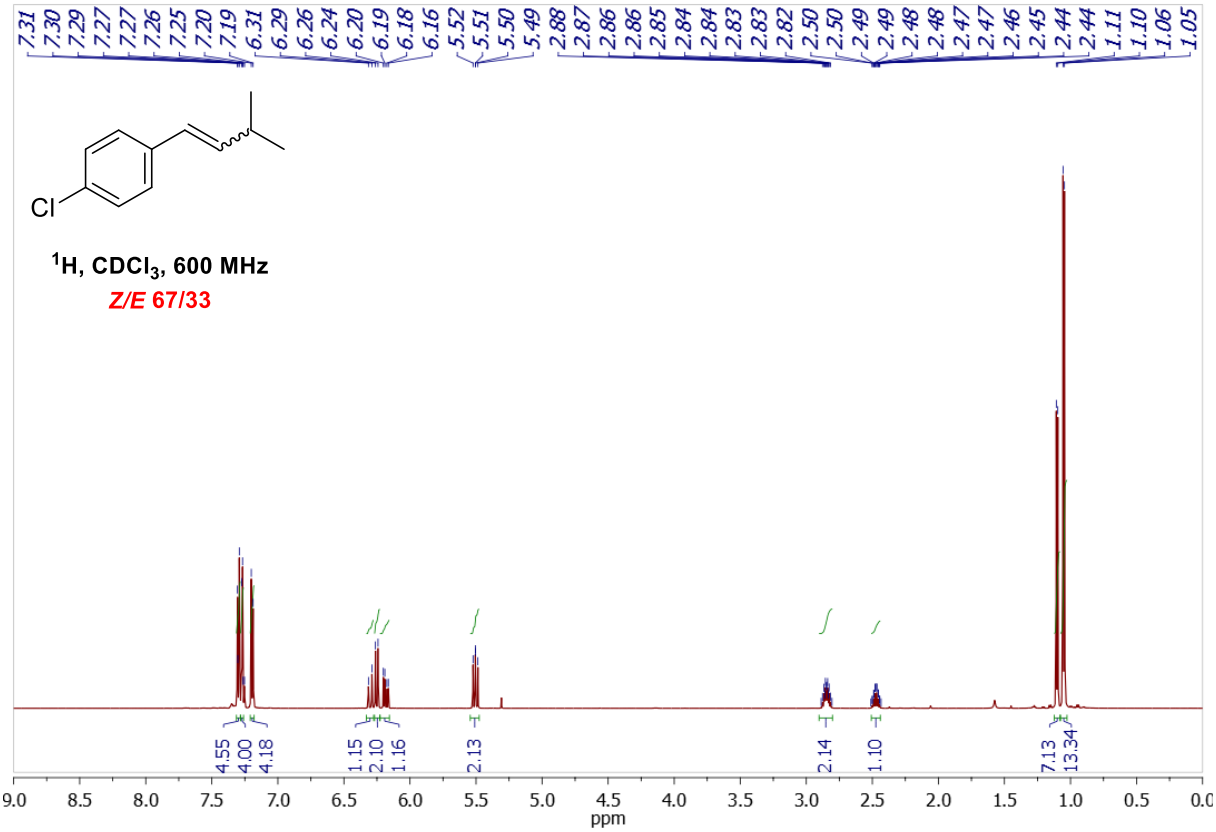


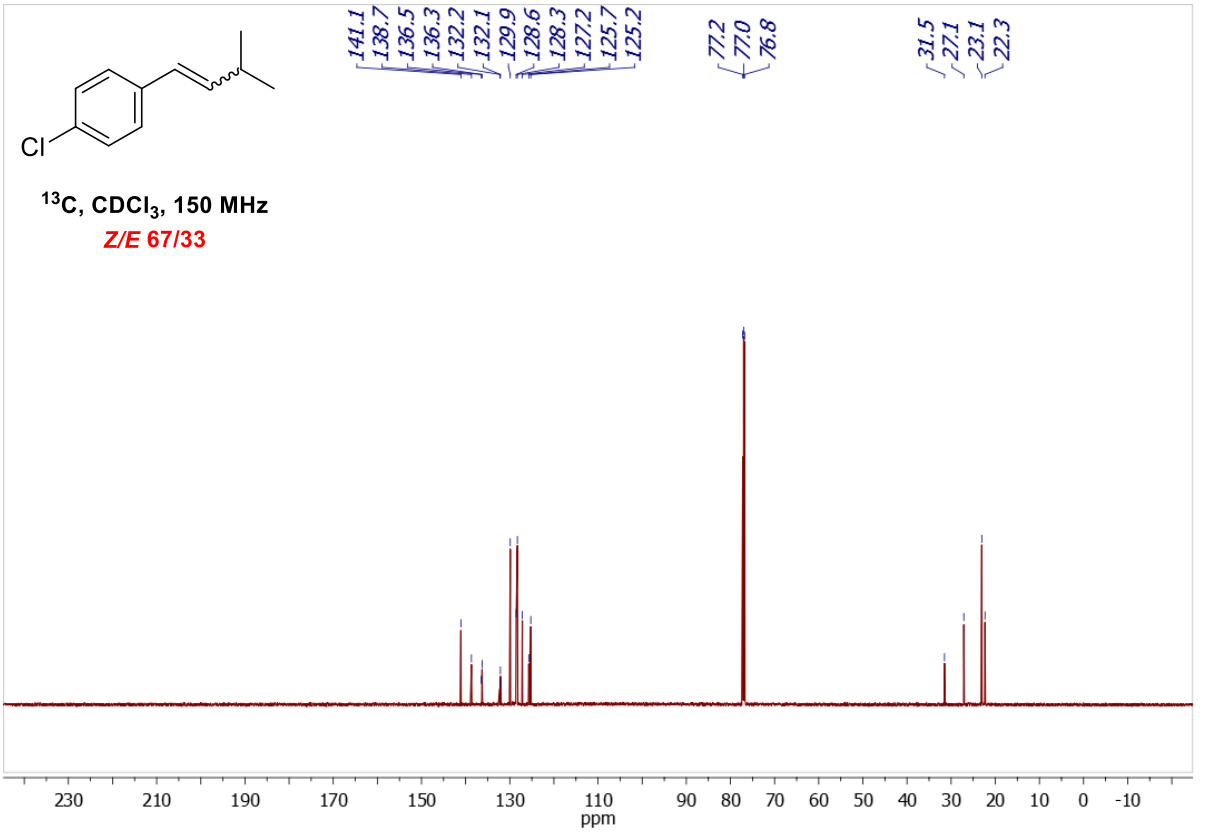
(+/-)-(2*R*,3*R*)-2-methyl-3-phenyl-1-tosylaziridine (2h)



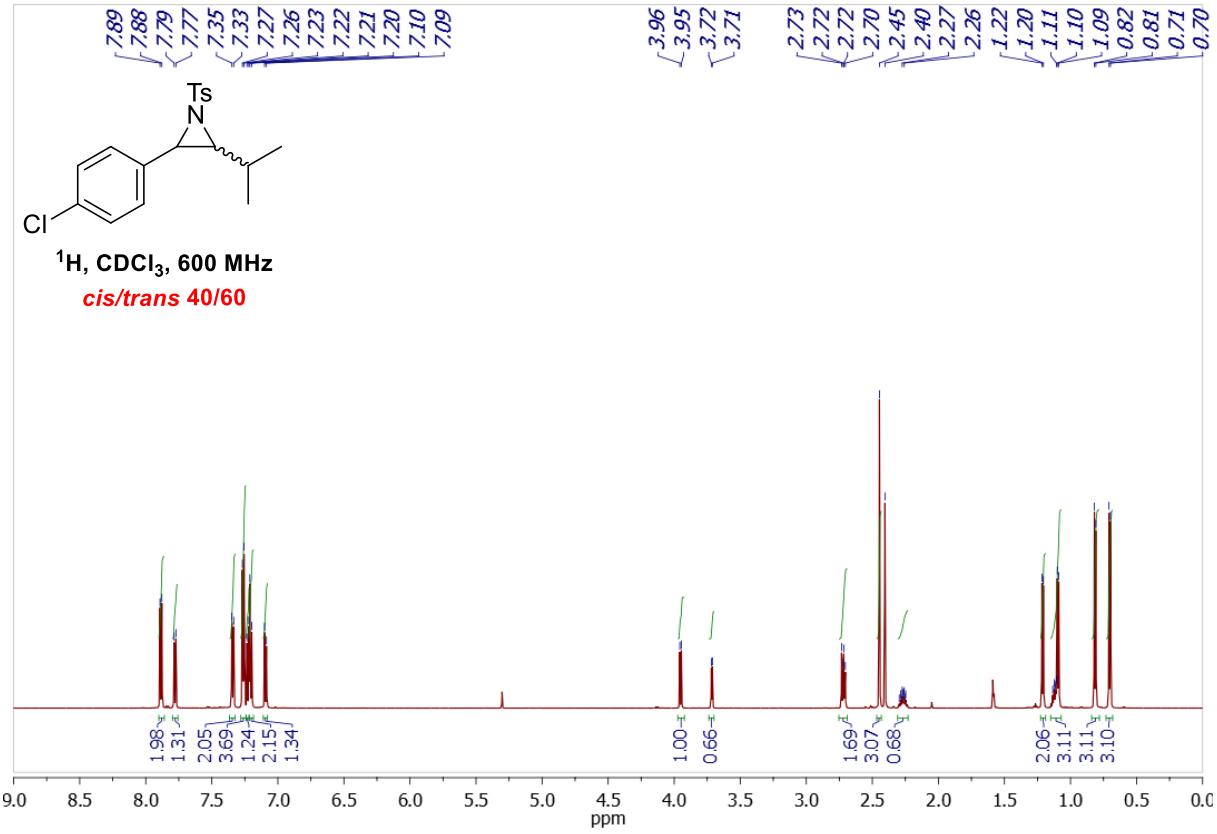


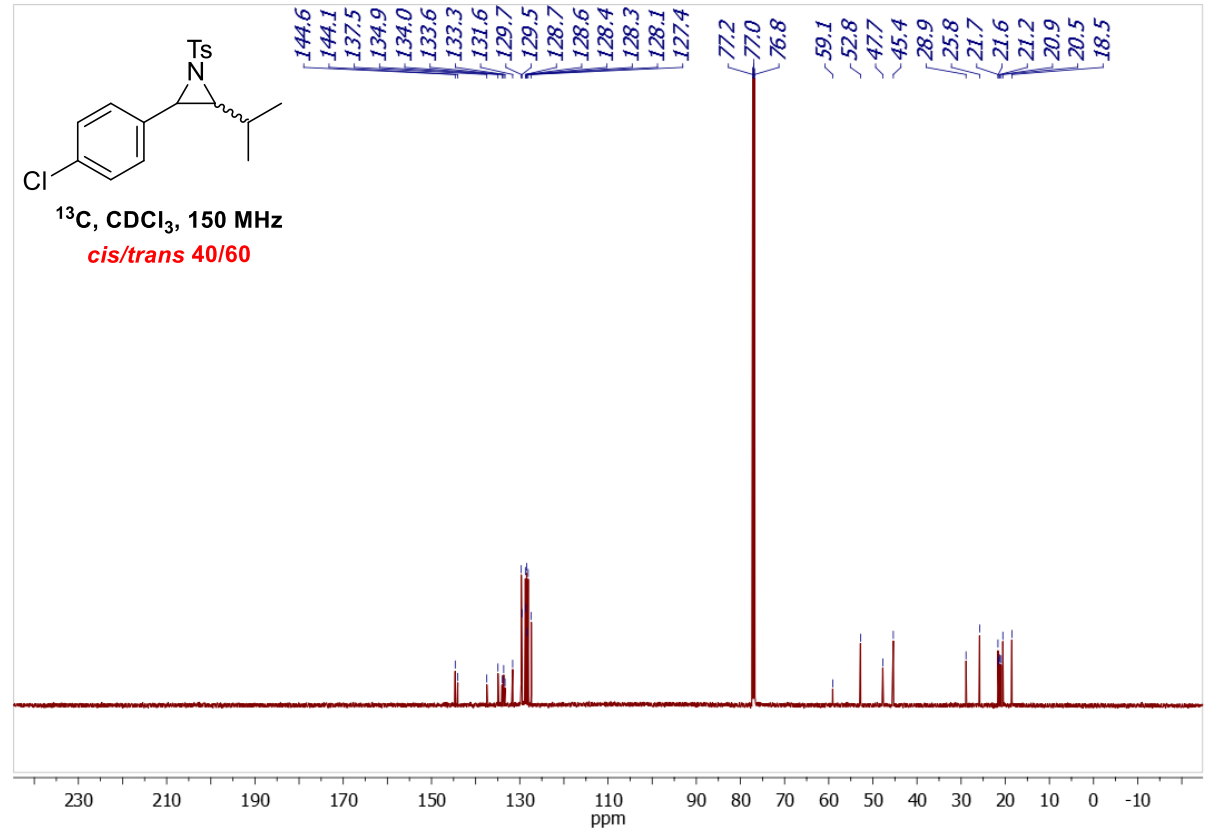
(*Z/E*)-1-chloro-4-(3-methylbut-1-en-1-yl)benzene (6a)



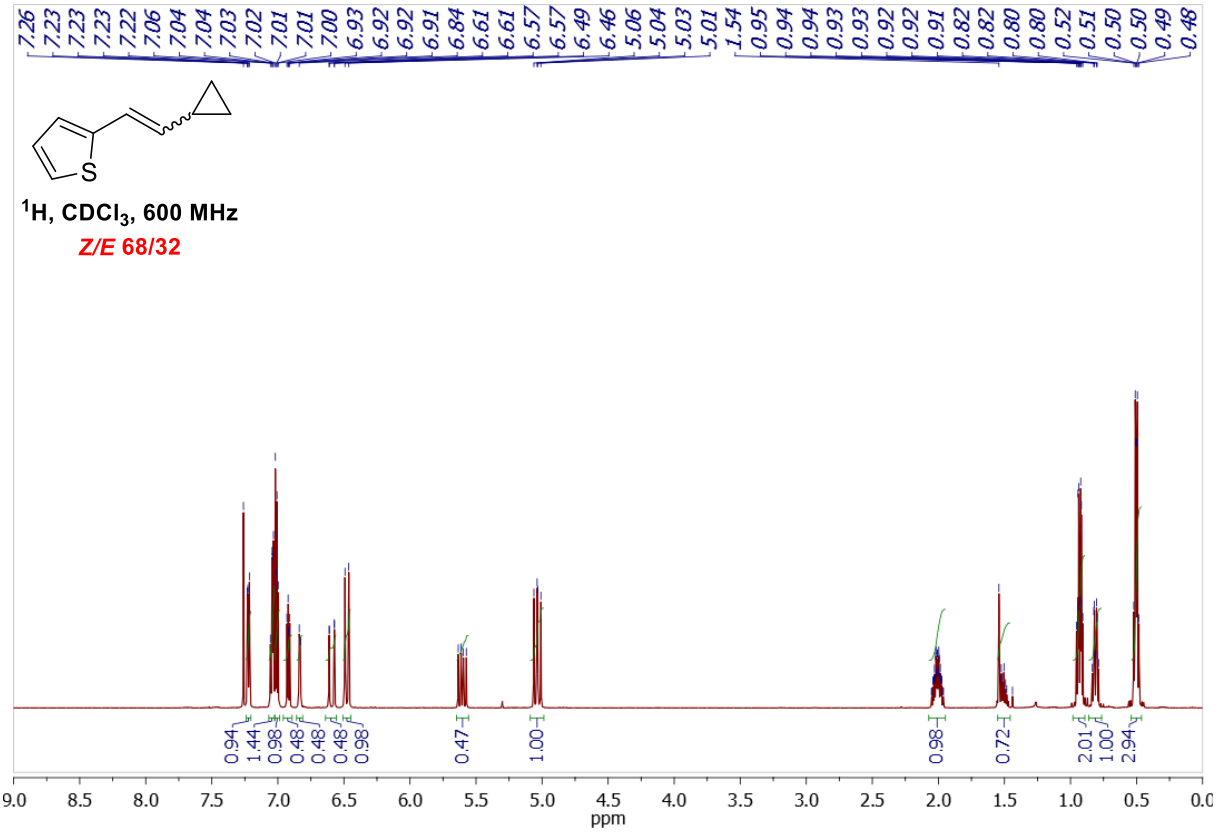


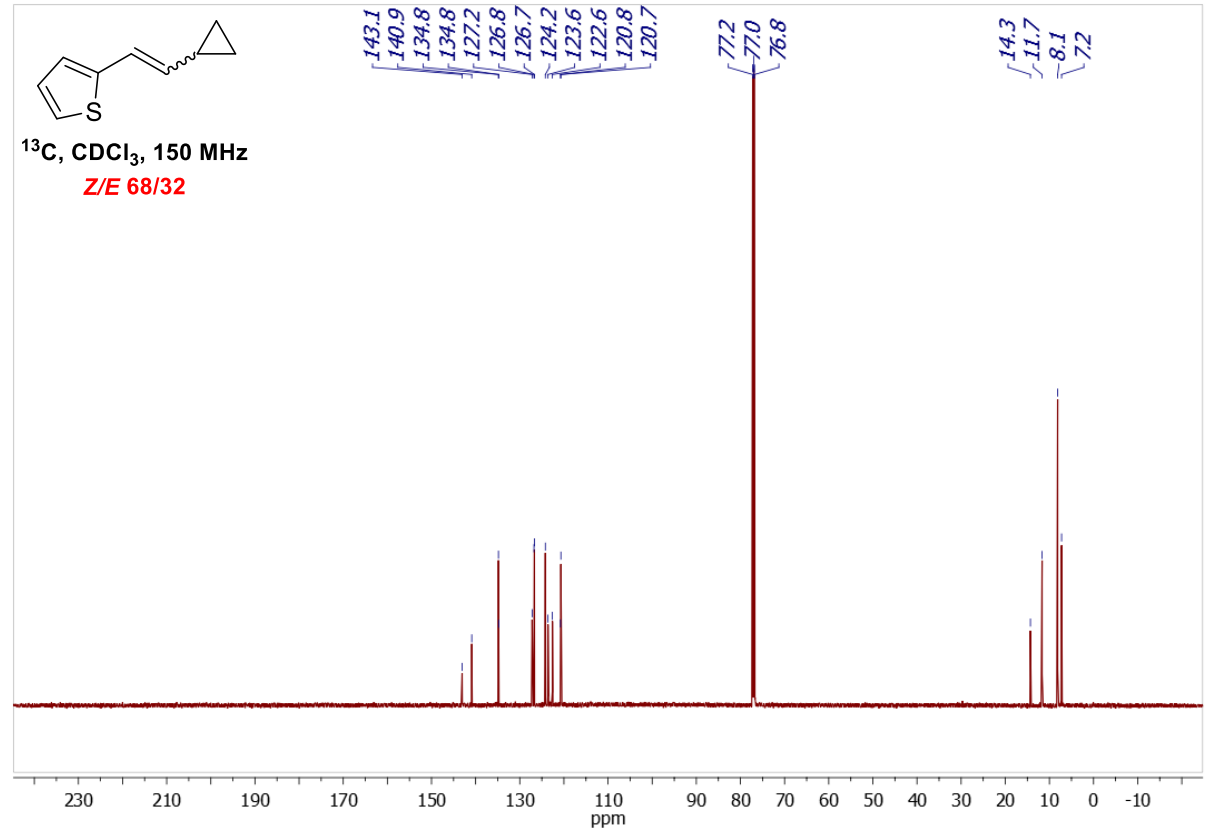
(+/-)-2-(4-chlorophenyl)-3-isopropyl-1-tosylaziridine (2i)



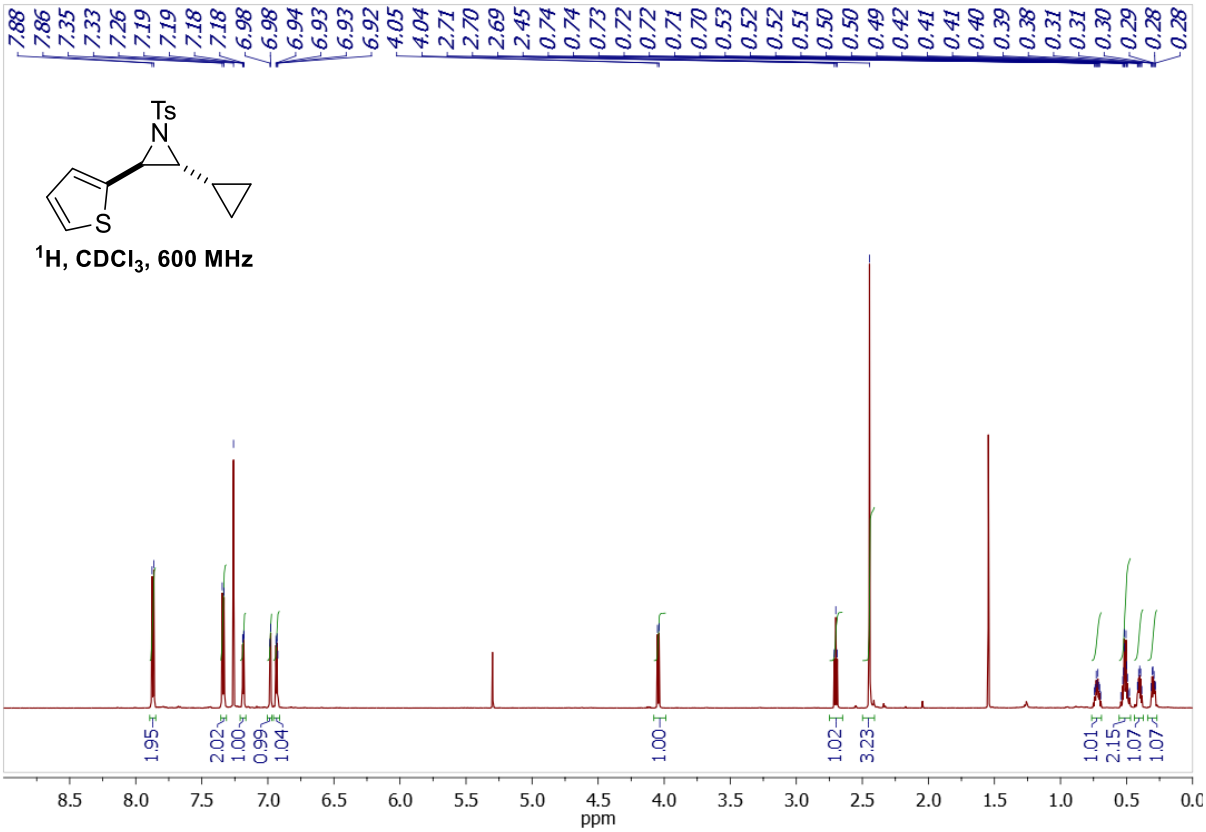


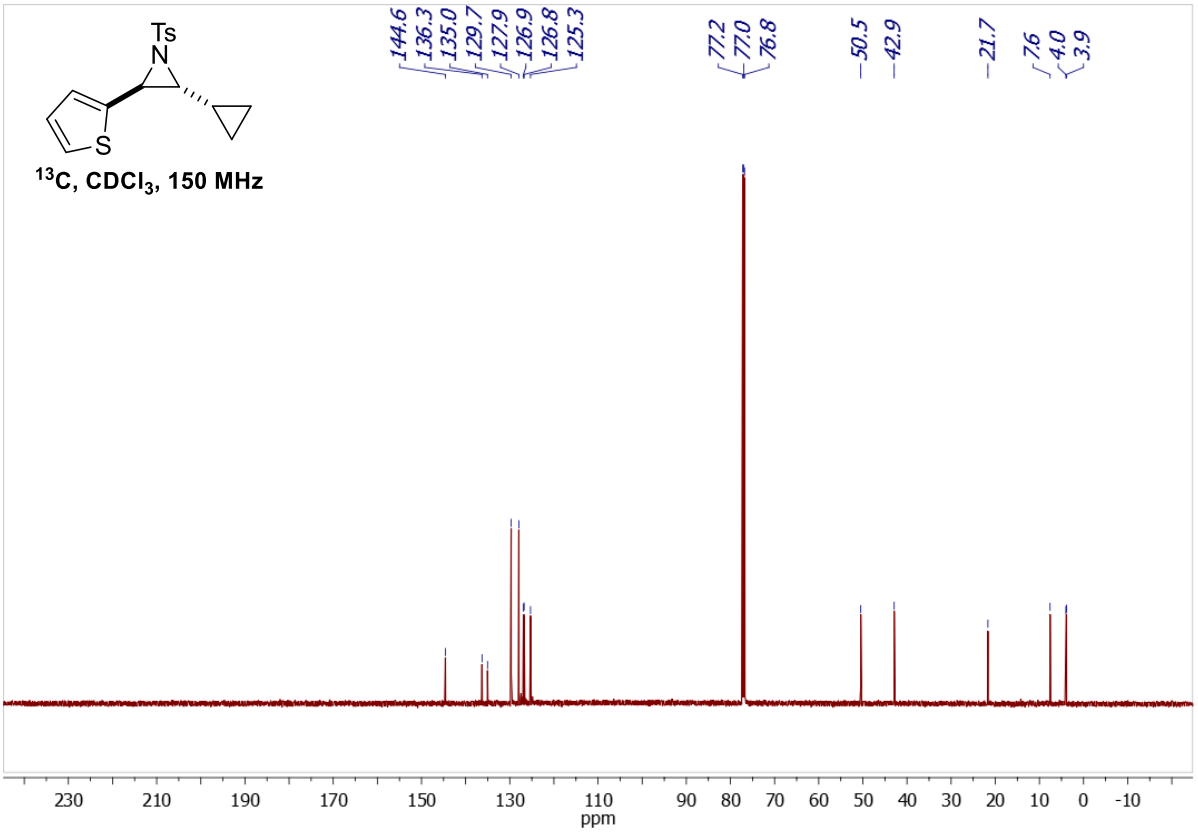
(*Z/E*)-2-(2-cyclopropylvinyl)thiophene (6b)



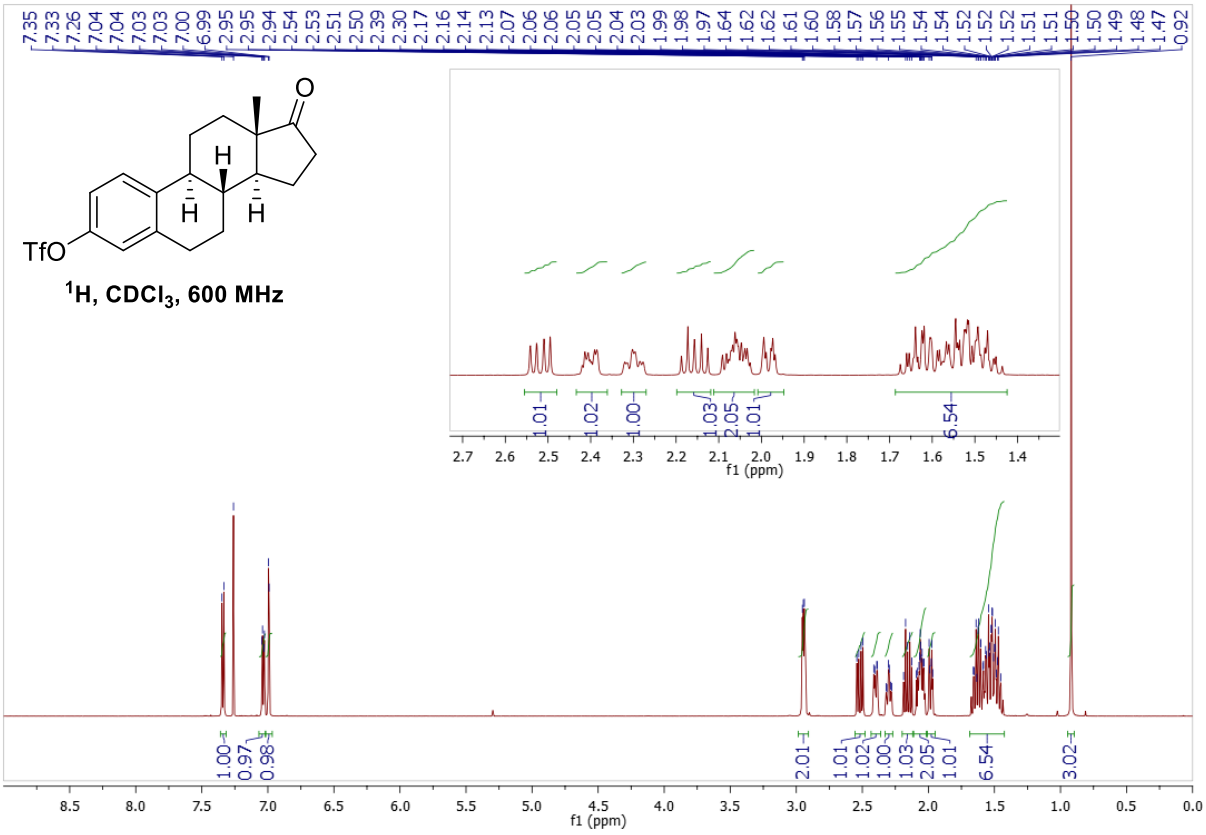


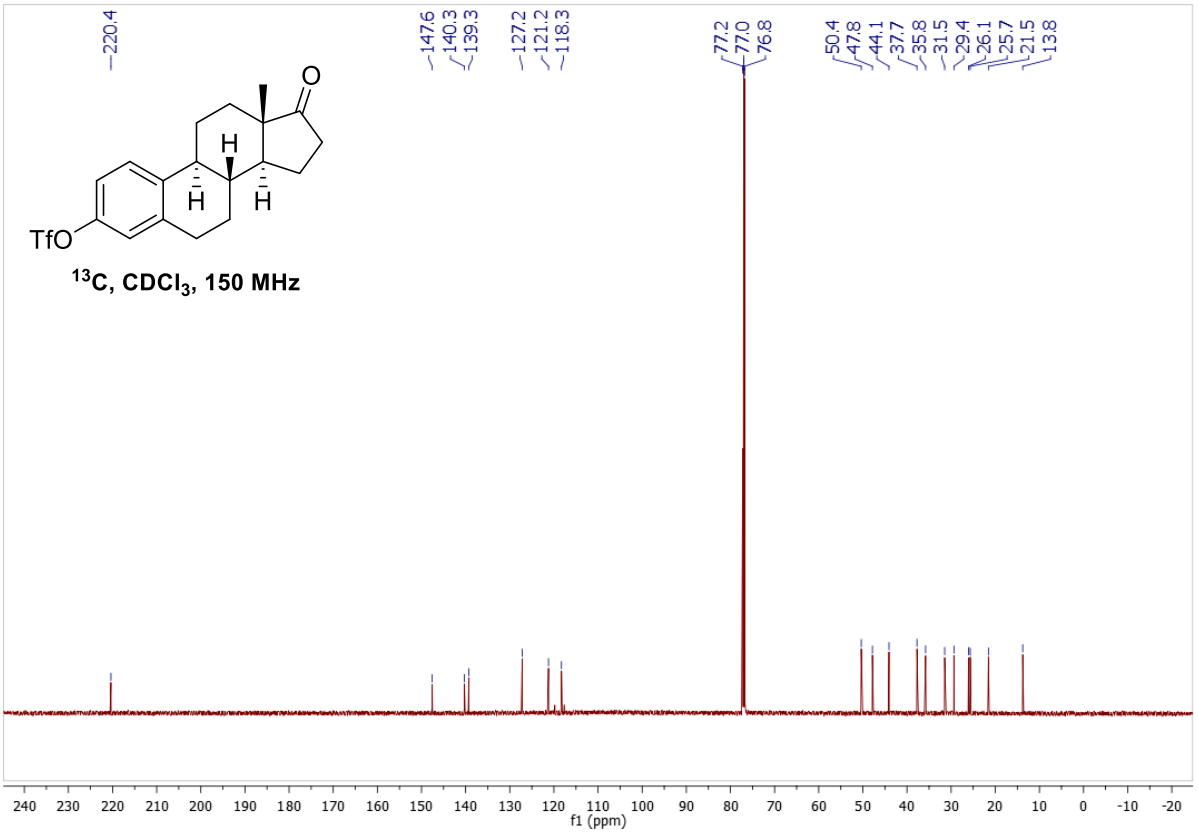
(+/-)-(2*R*,3*S*)-2-cyclopropyl-3-(thiophen-2-yl)-1-tosylaziridine (2j)



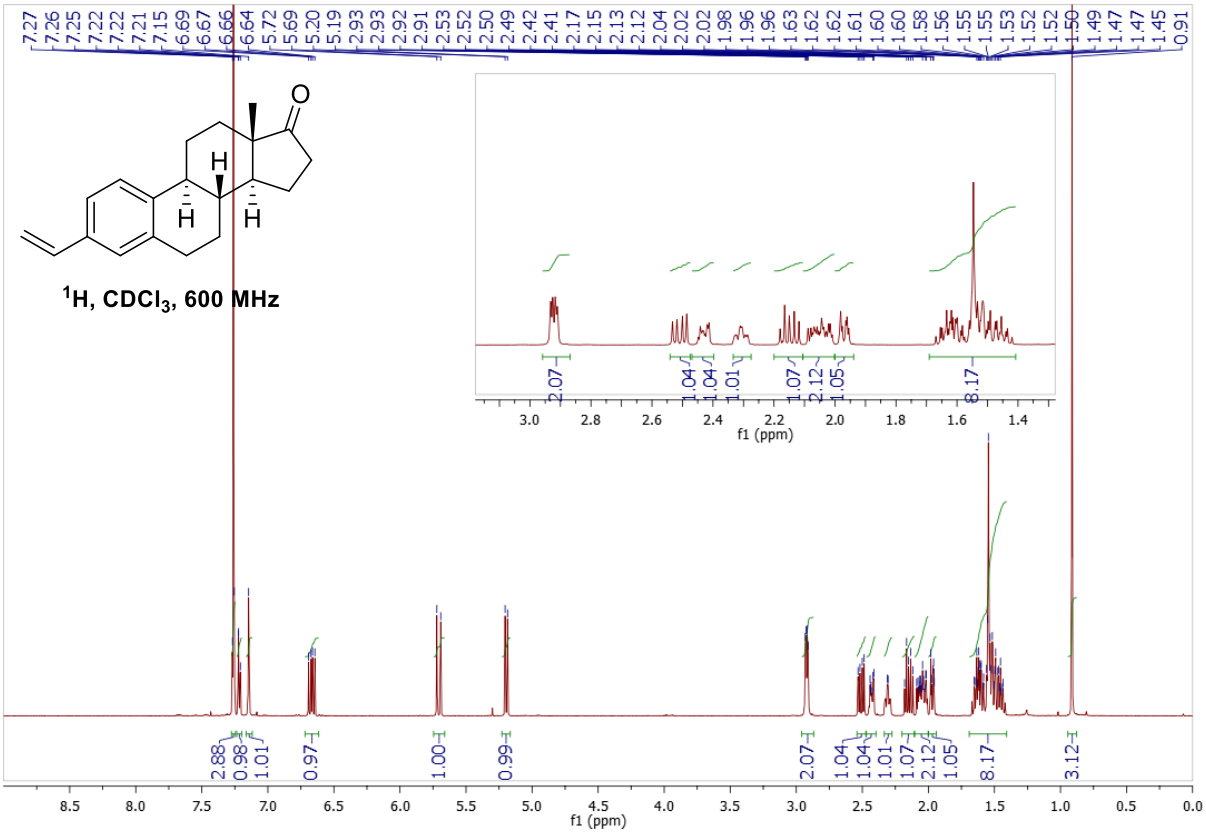


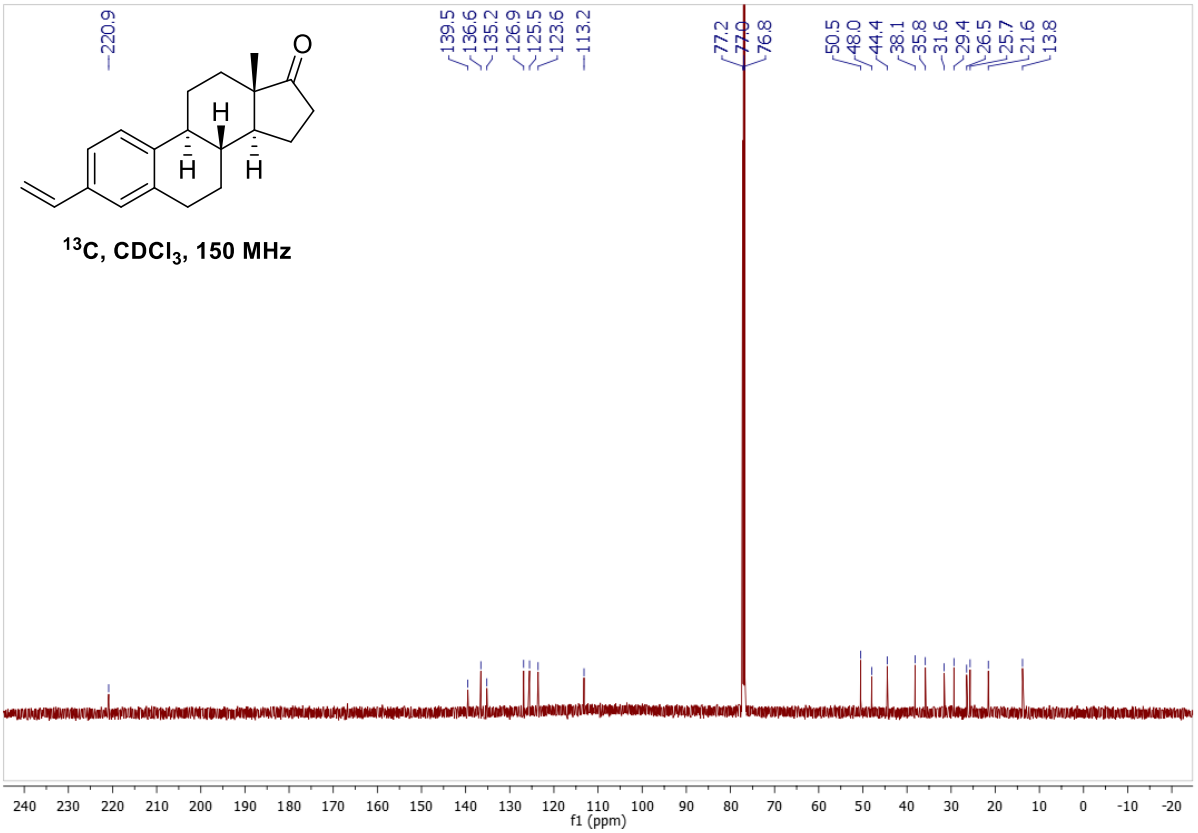
(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate (7)



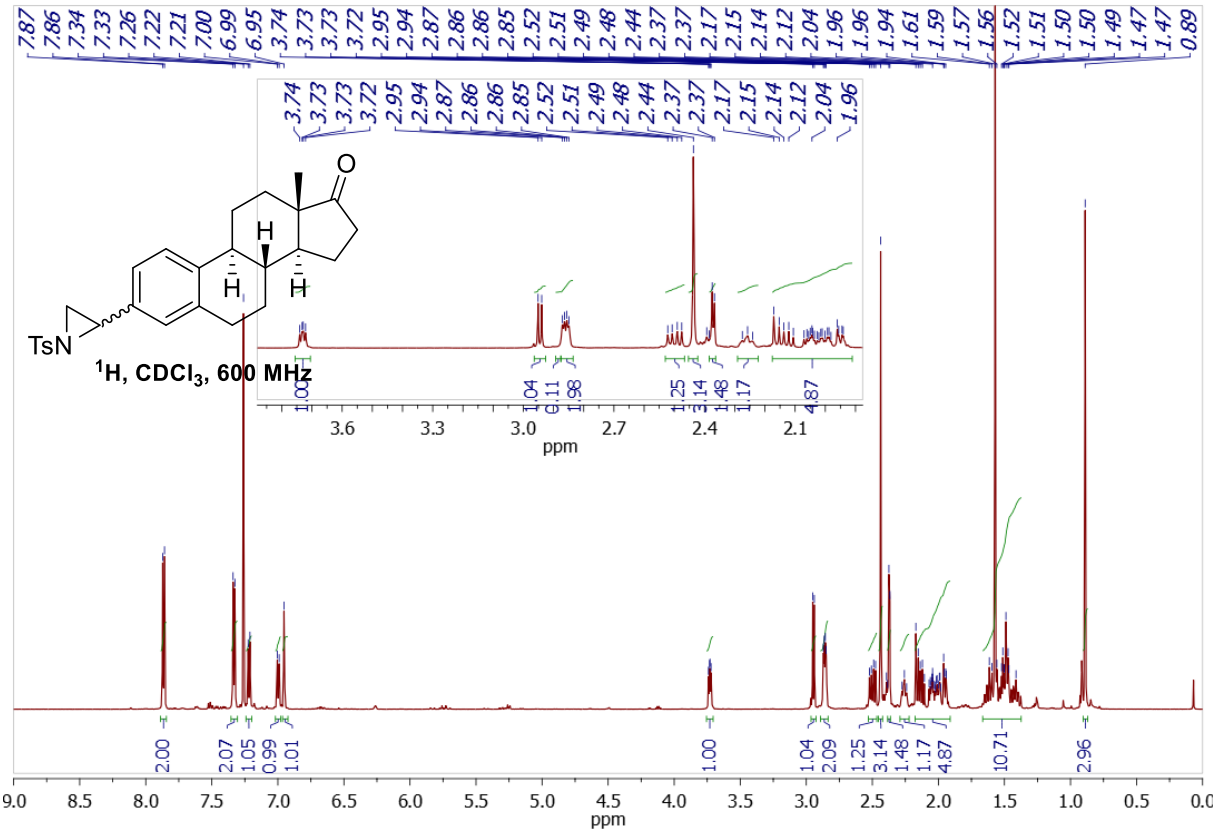


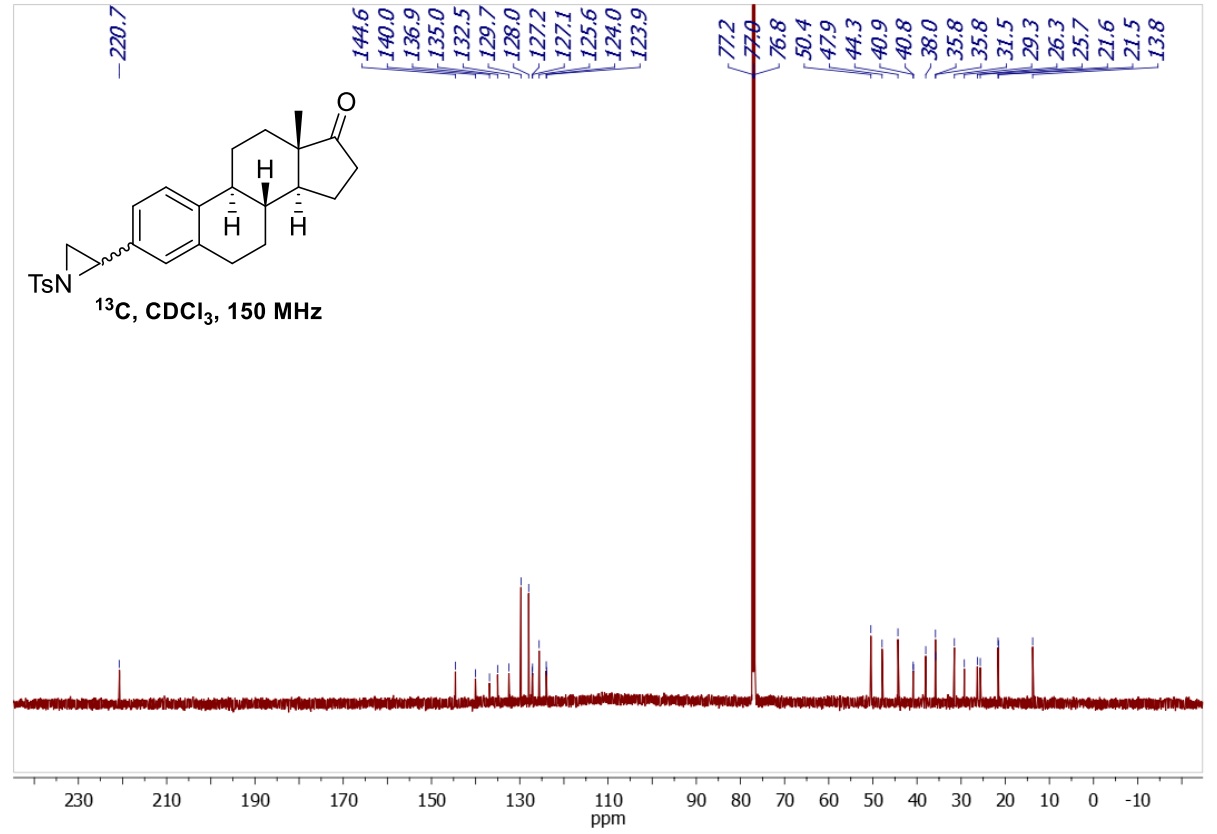
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (8)



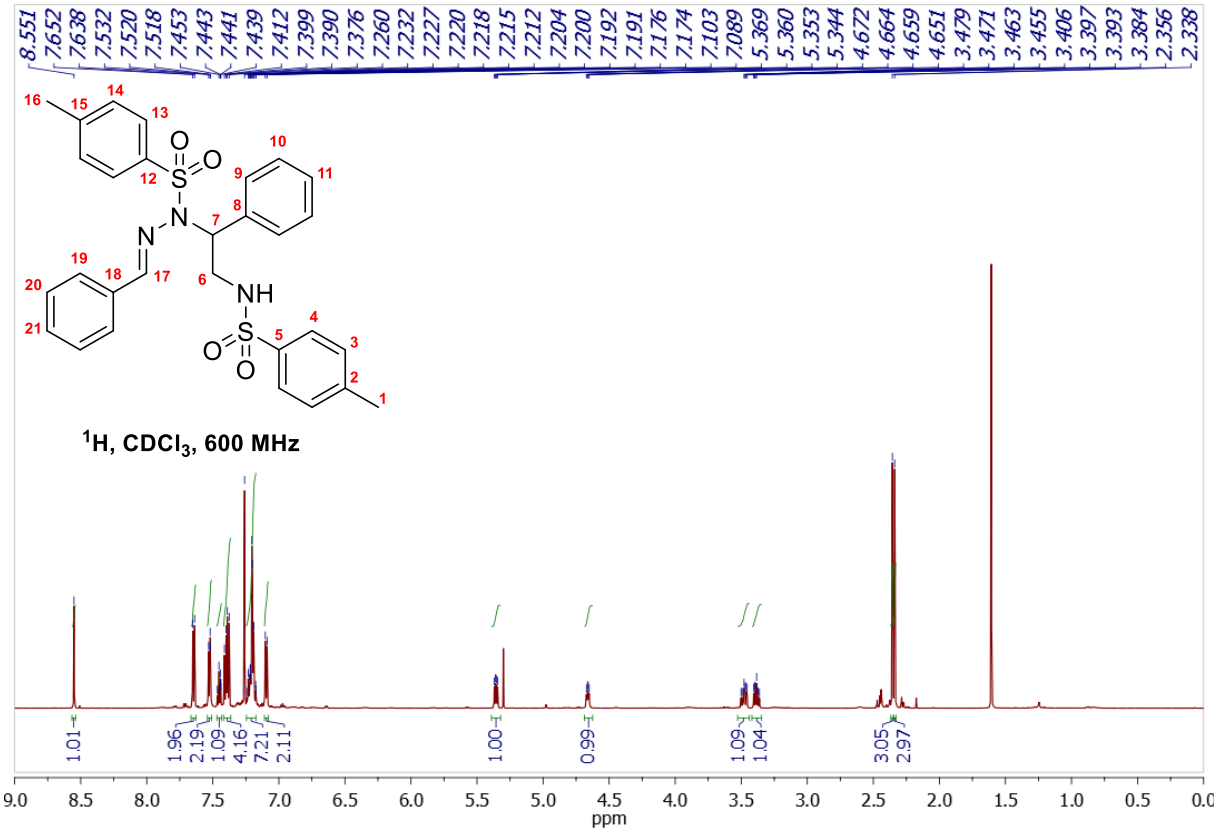


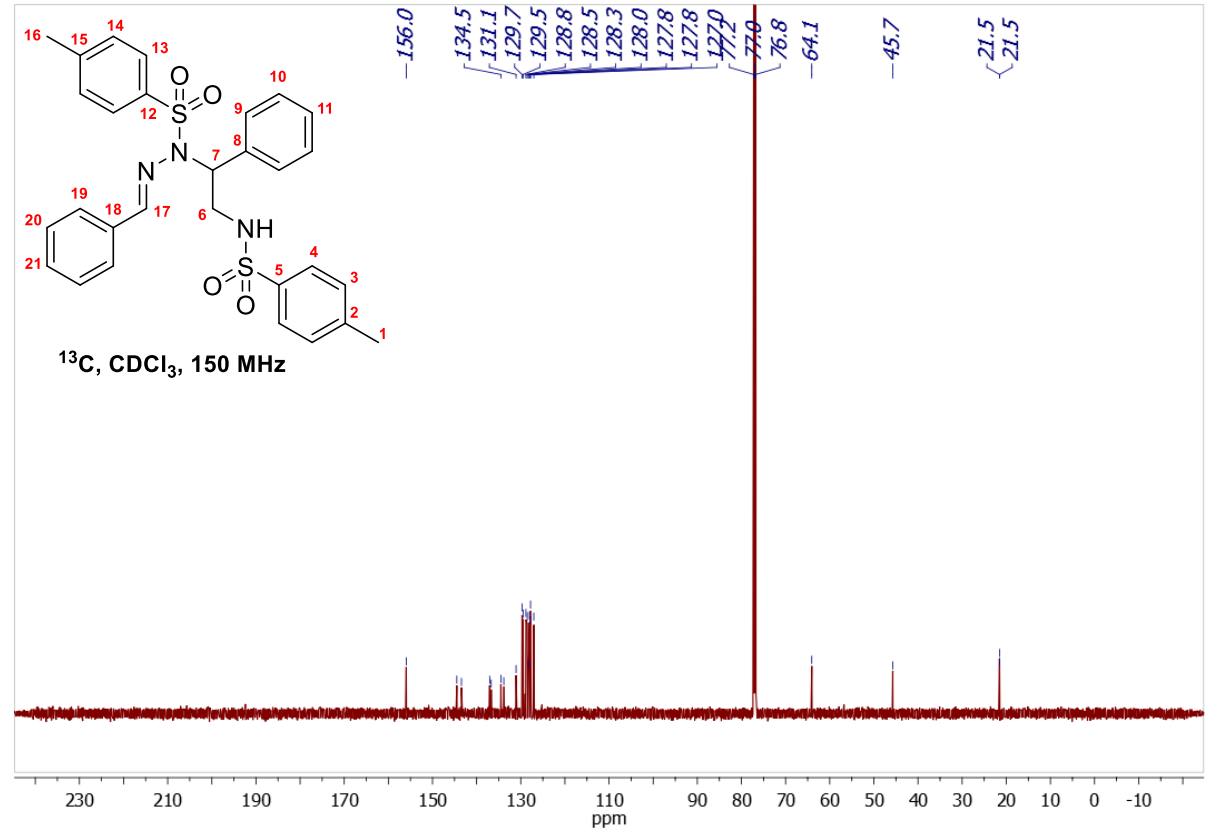
(+/-)-(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(1-tosylaziridin-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2k)



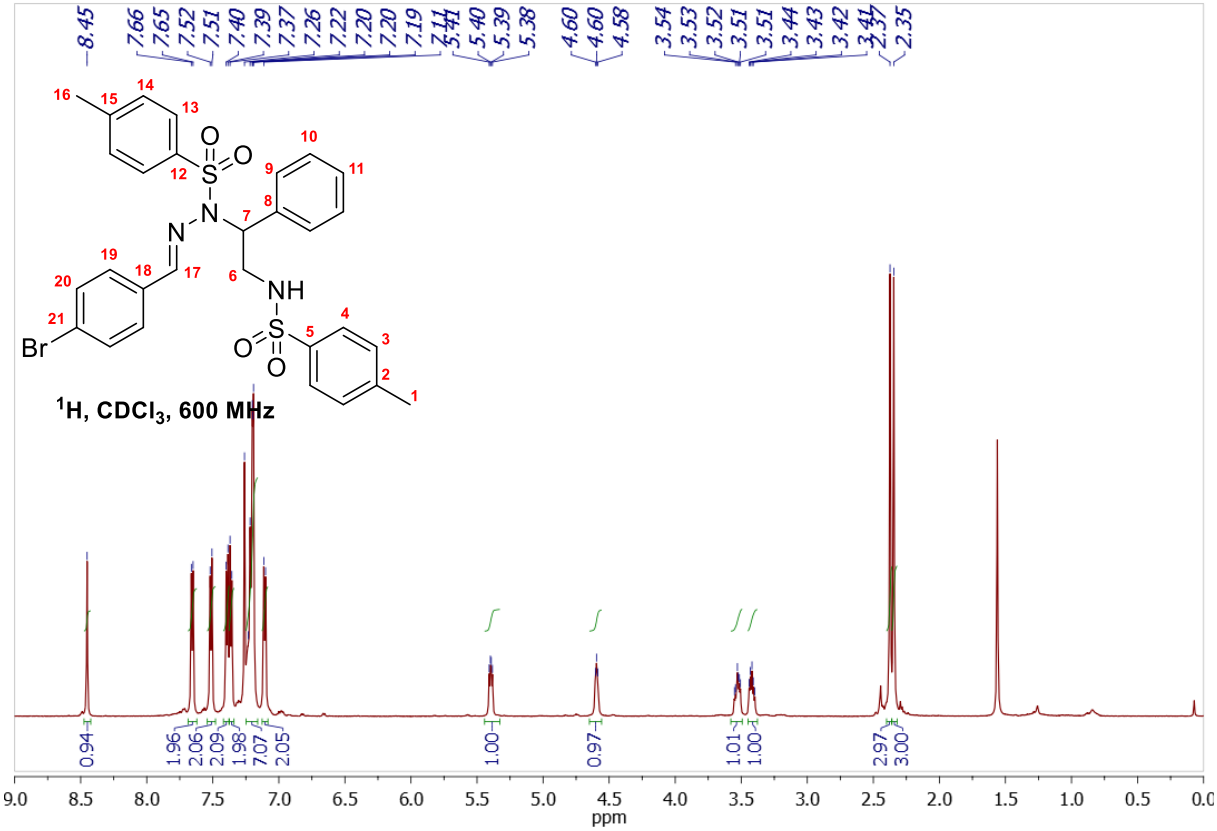


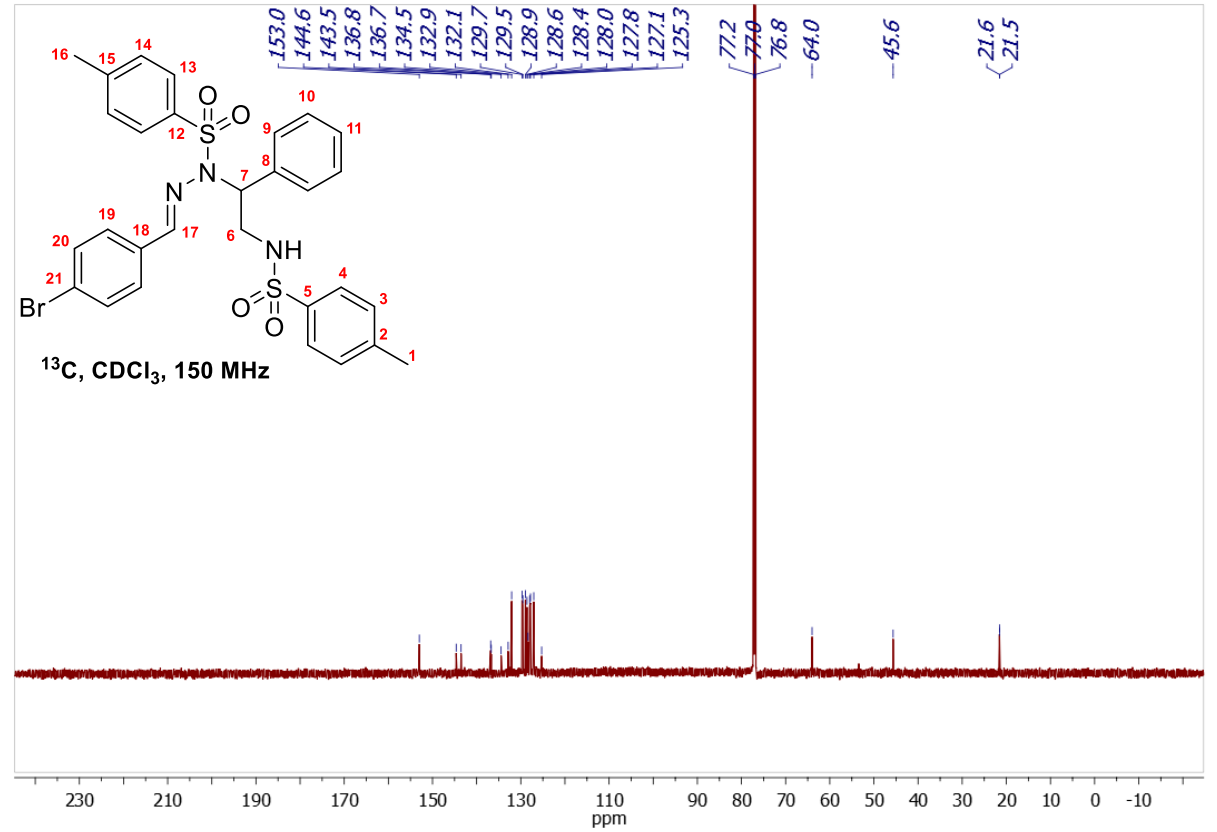
N-(2-(2-benzylidene-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3a)



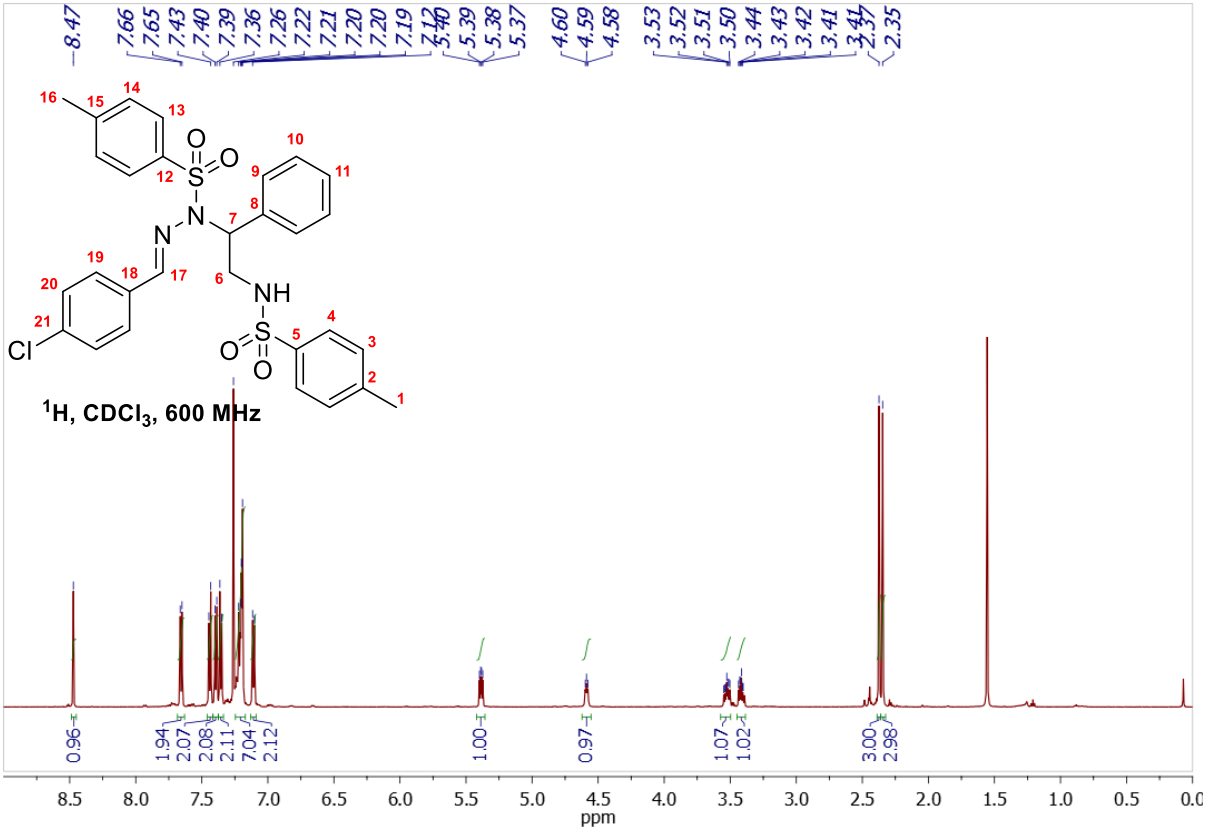


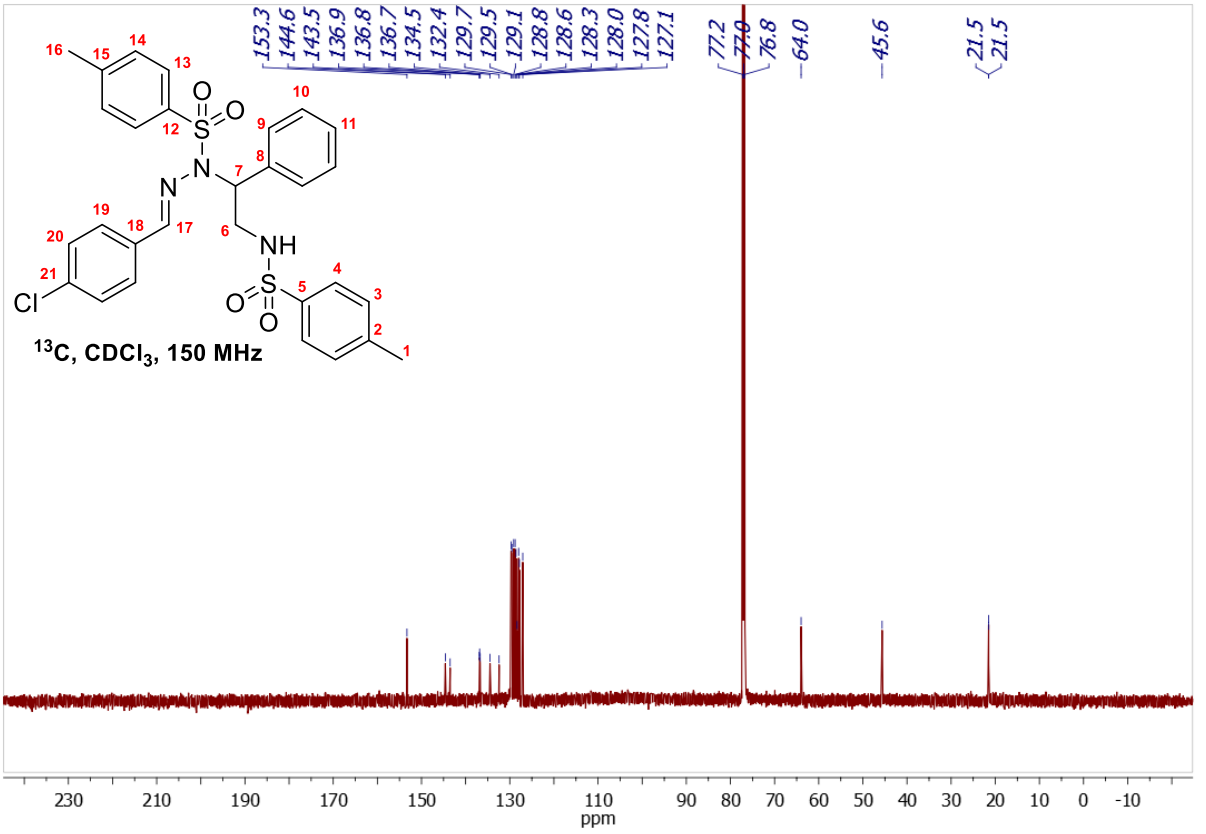
_N_-(2-(2-(4-bromobenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3b)



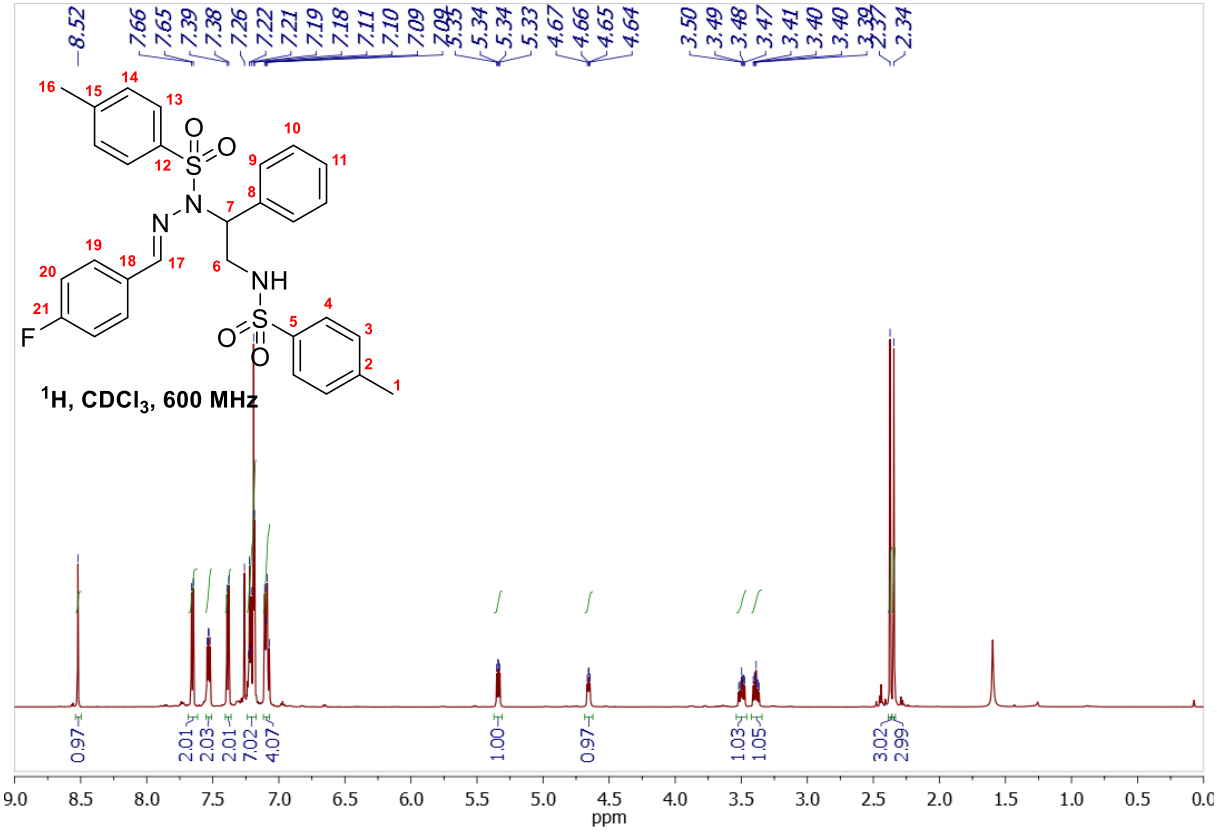


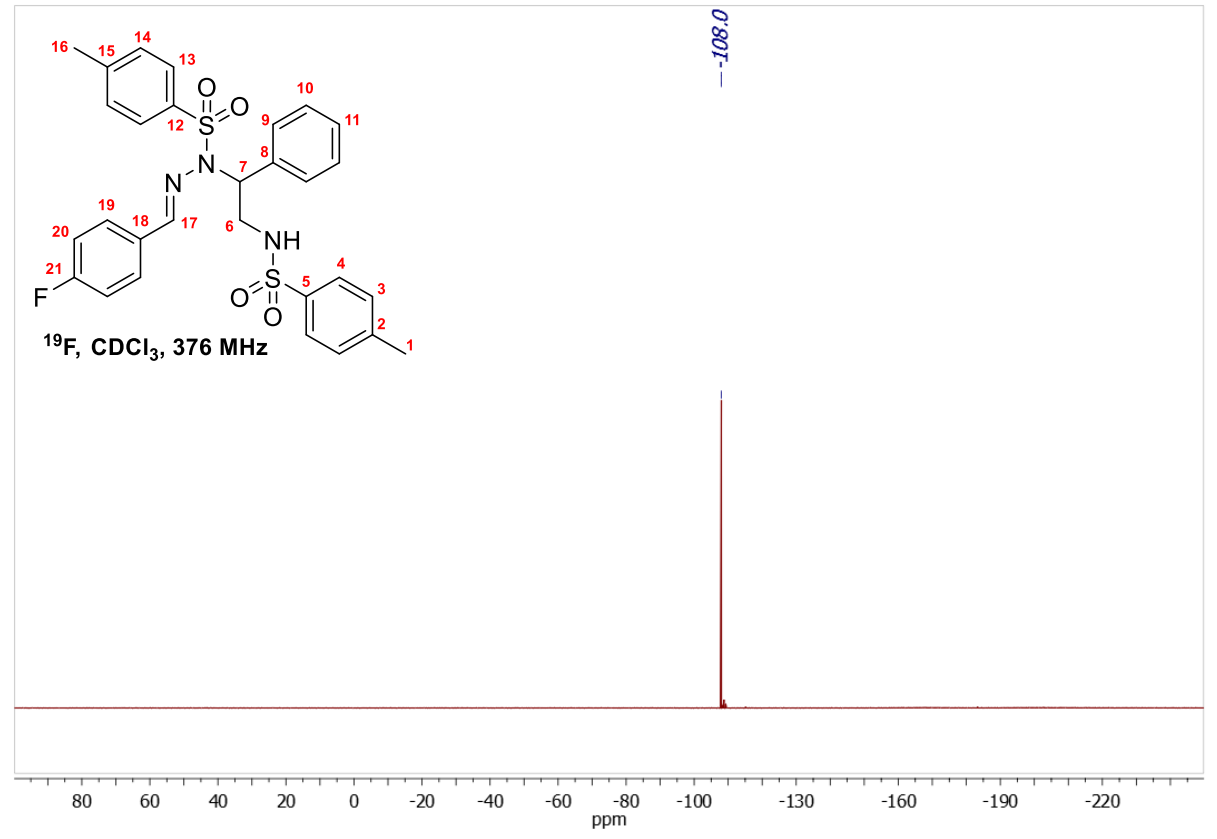
_N_-(2-(2-(4-chlorobenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3c)

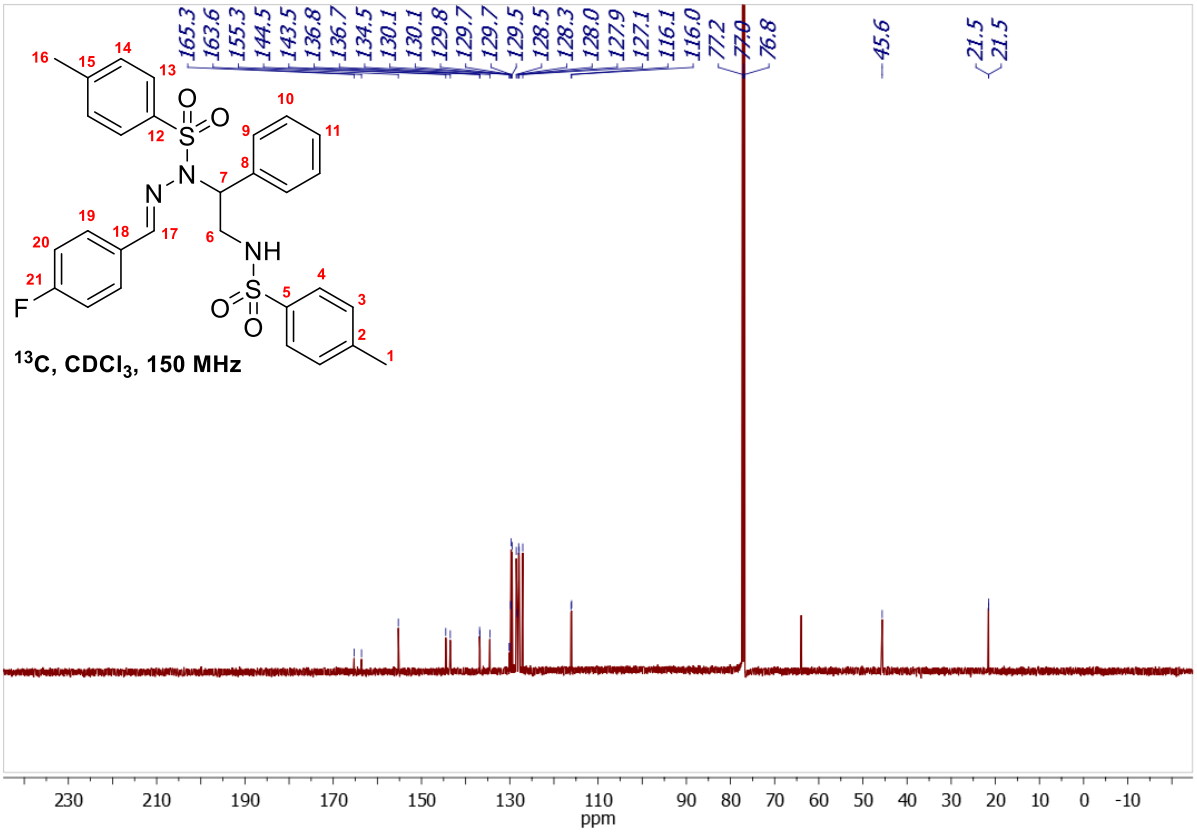




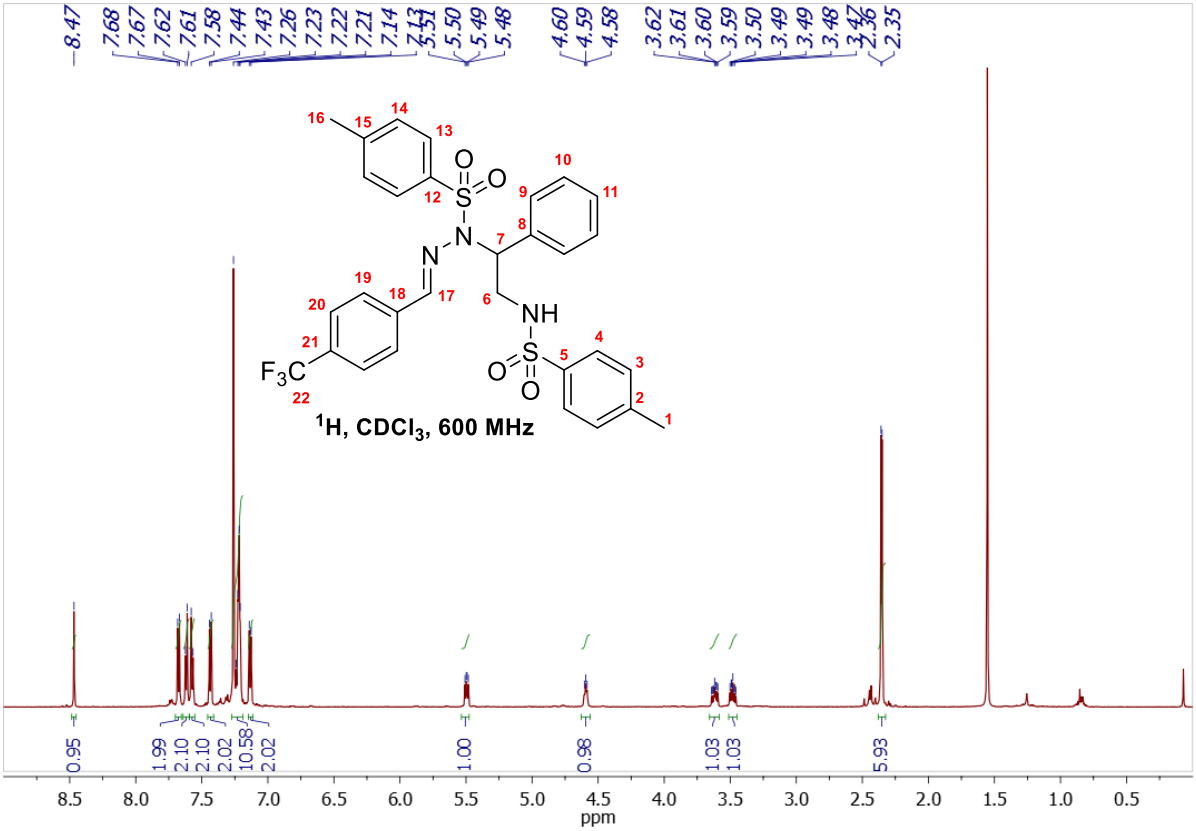
_N_-(2-(2-(4-fluorobenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3d)

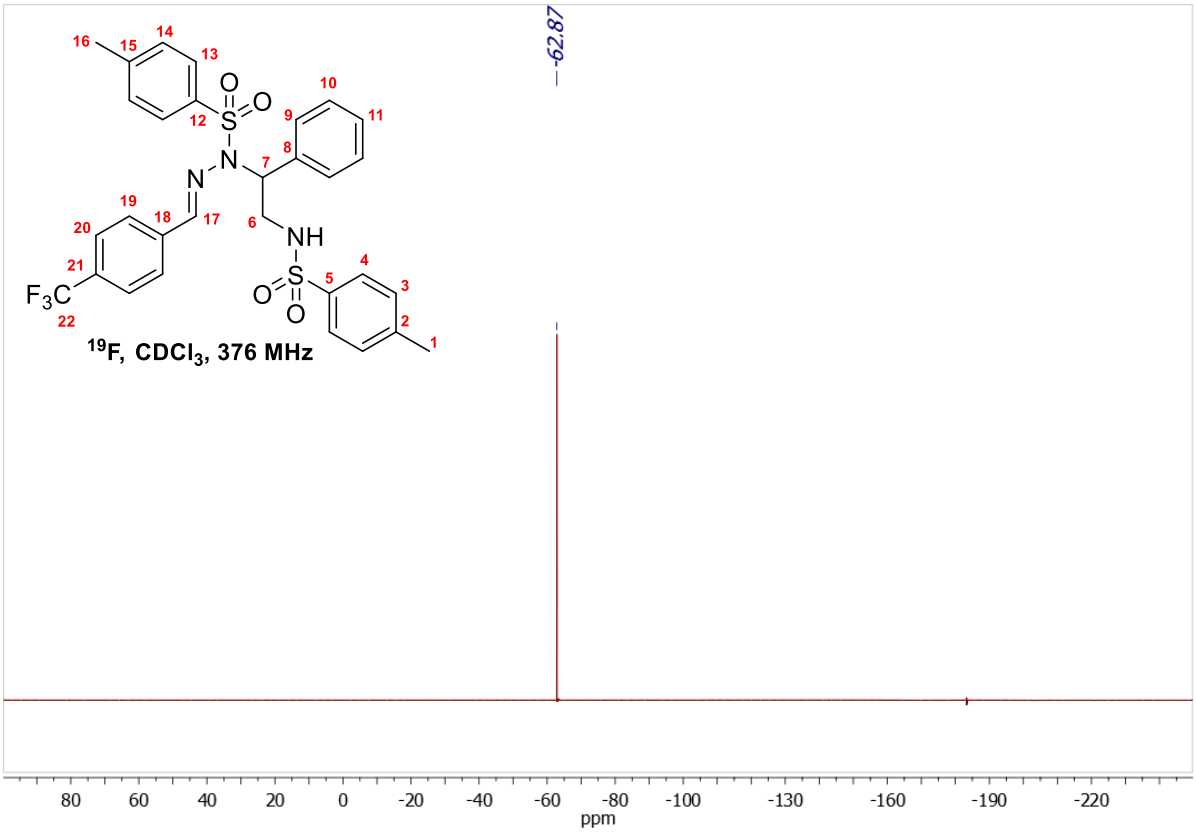


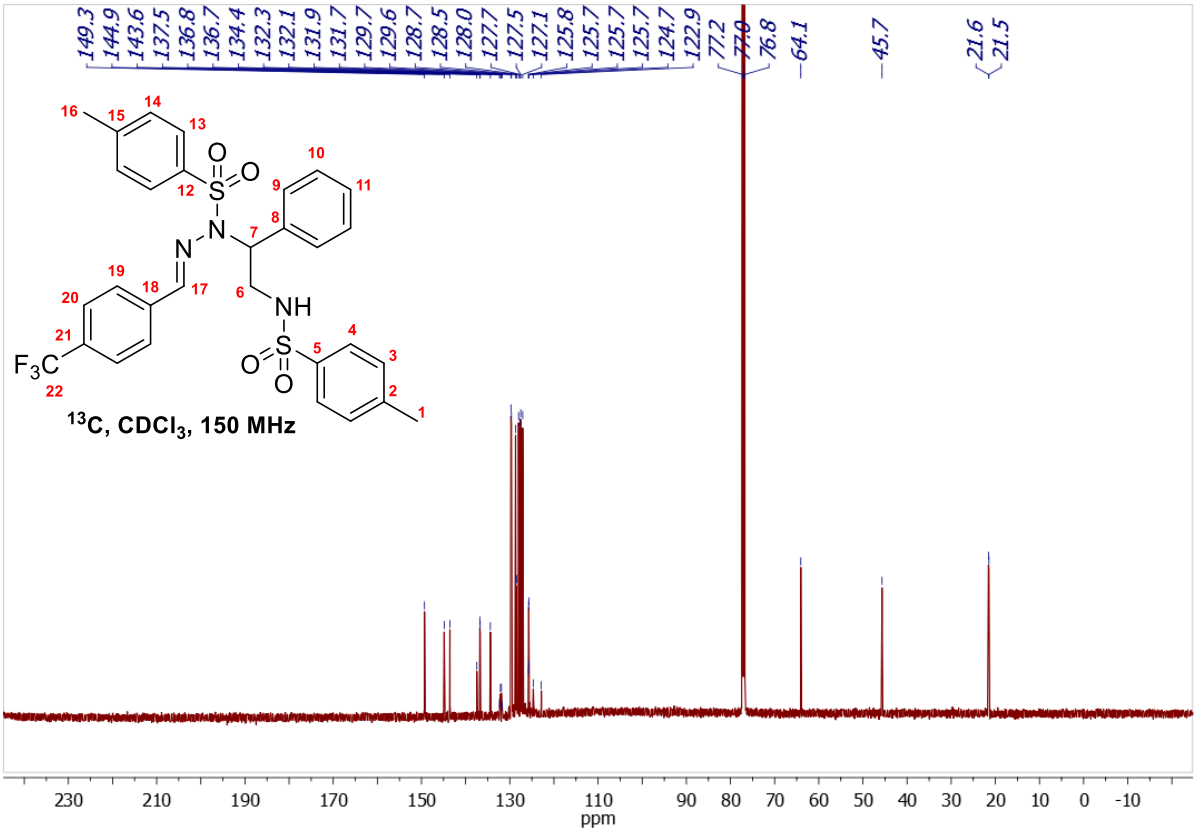



165.3
163.6
155.3
144.5
143.5
136.8
136.7
134.5
130.1
130.1
129.8
129.7
129.7
129.5
128.5
128.3
128.0
127.9
127.1
116.1
116.0
77.2
77.0
76.8
45.6
21.5
21.5
^{13}C, CDCl$_3$, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

4-methyl-*N*-(2-phenyl-2-(1-tosyl-2-(4-(trifluoromethyl)benzylidene)hydrazinyl)ethyl)benzenesulfonamide (3e)






149.3
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143.6
137.5
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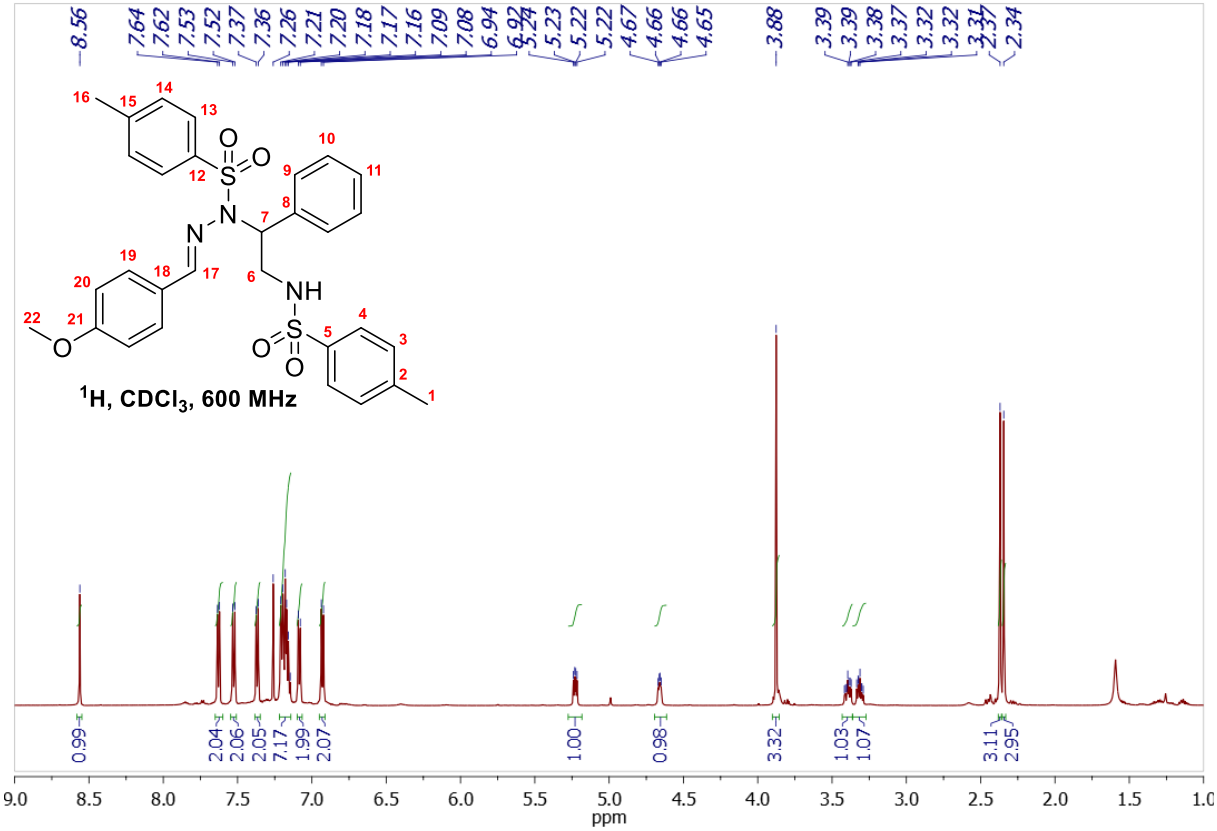
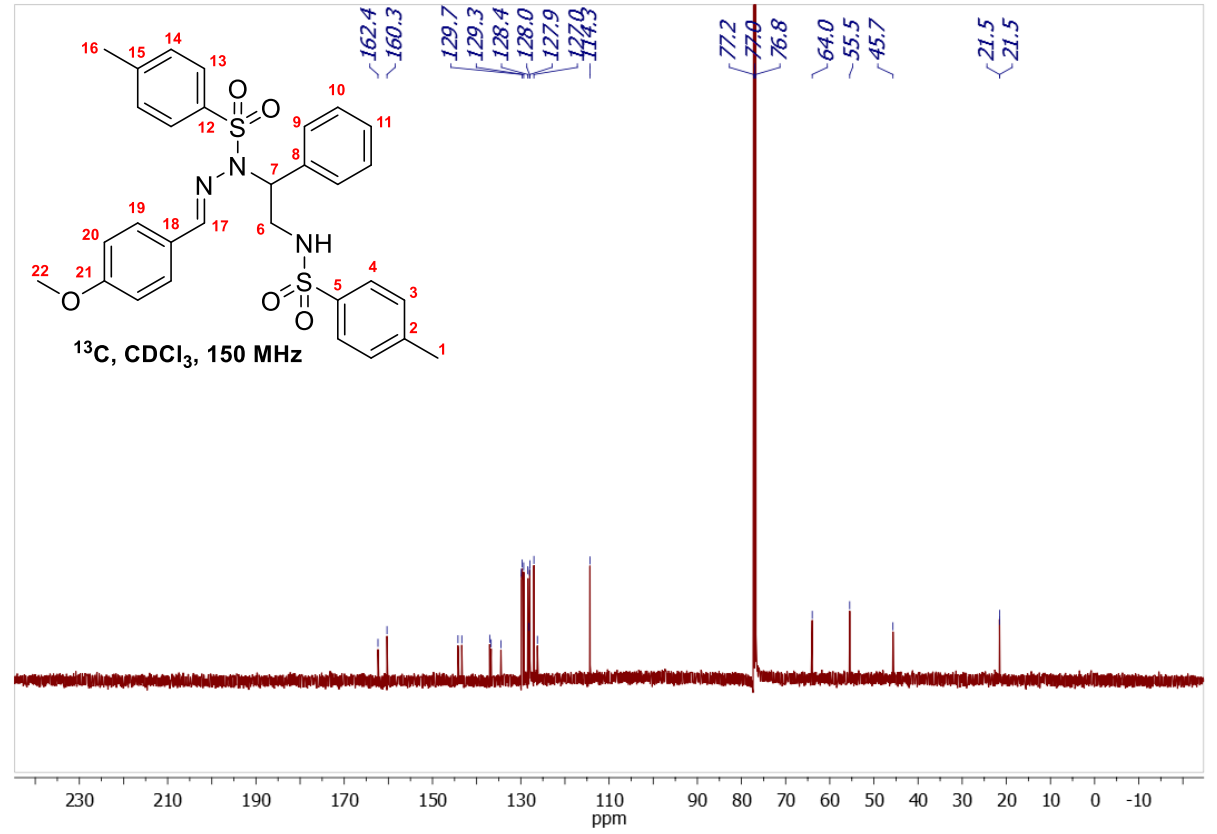
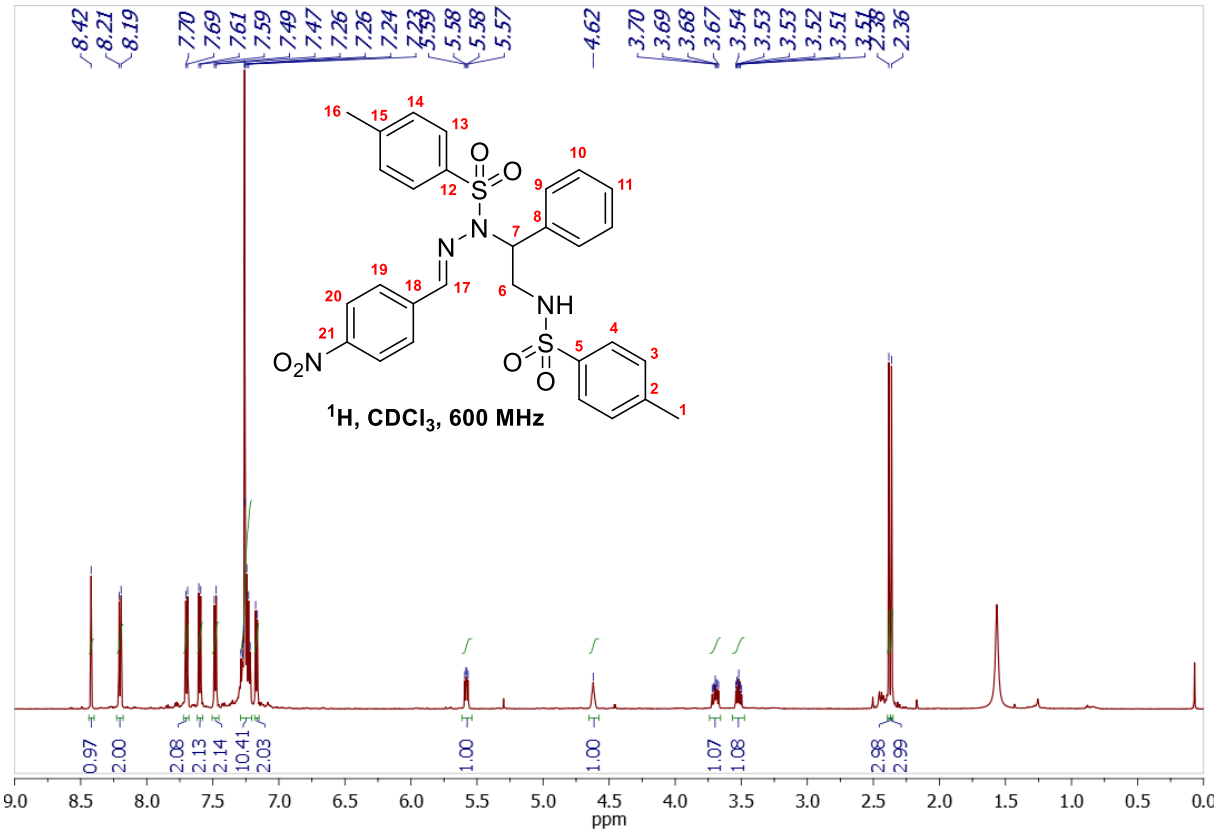
134.4
132.3
132.1
131.9
131.7
129.7
129.6
128.7
128.5
128.0
127.7
127.5
127.1
125.8
125.7
125.7
125.7
124.7
122.9
77.2
77.0
76.8
64.1
45.7
21.6
21.5
^{13}C, CDCl$_3$, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

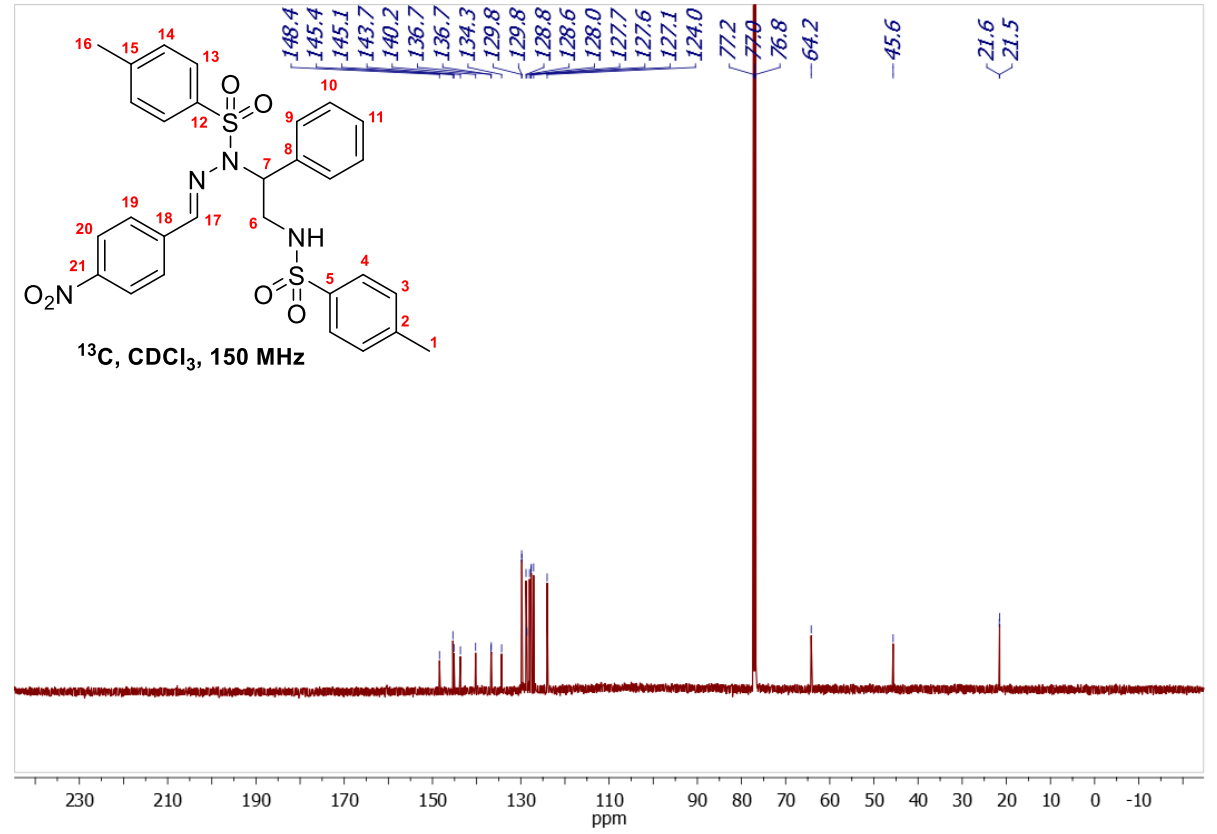
_N_-(2-(2-(4-methoxybenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3f)



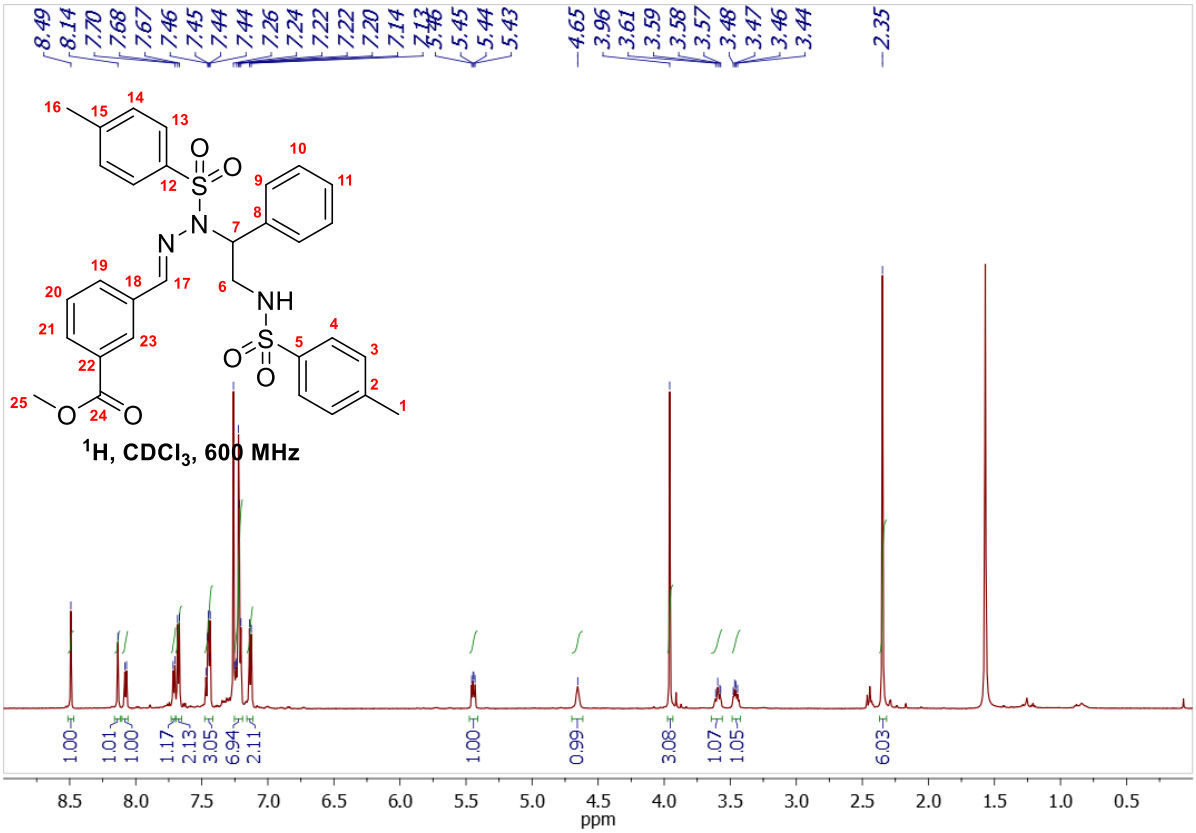


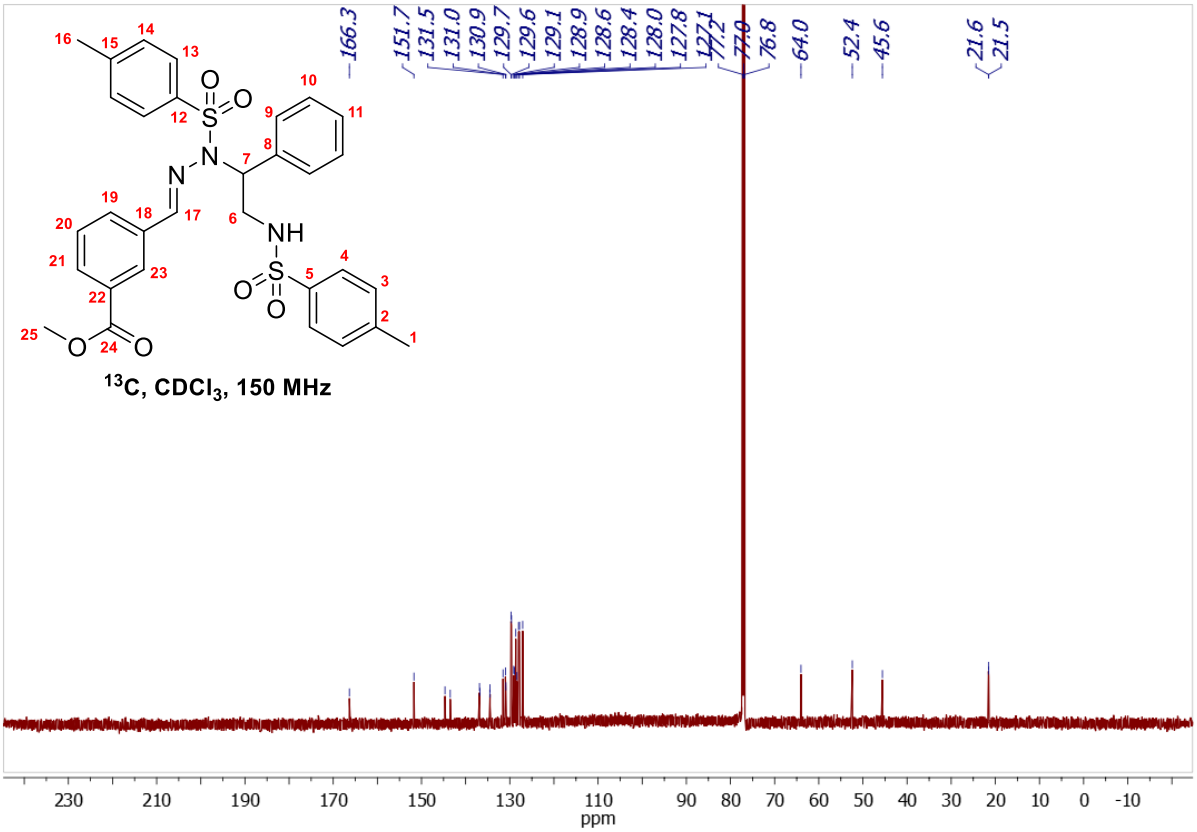
4-methyl-*N*-(2-(2-(4-nitrobenzylidene)-1-tosylhydrazinyl)-2-phenylethyl)benzenesulfonamide (3g)



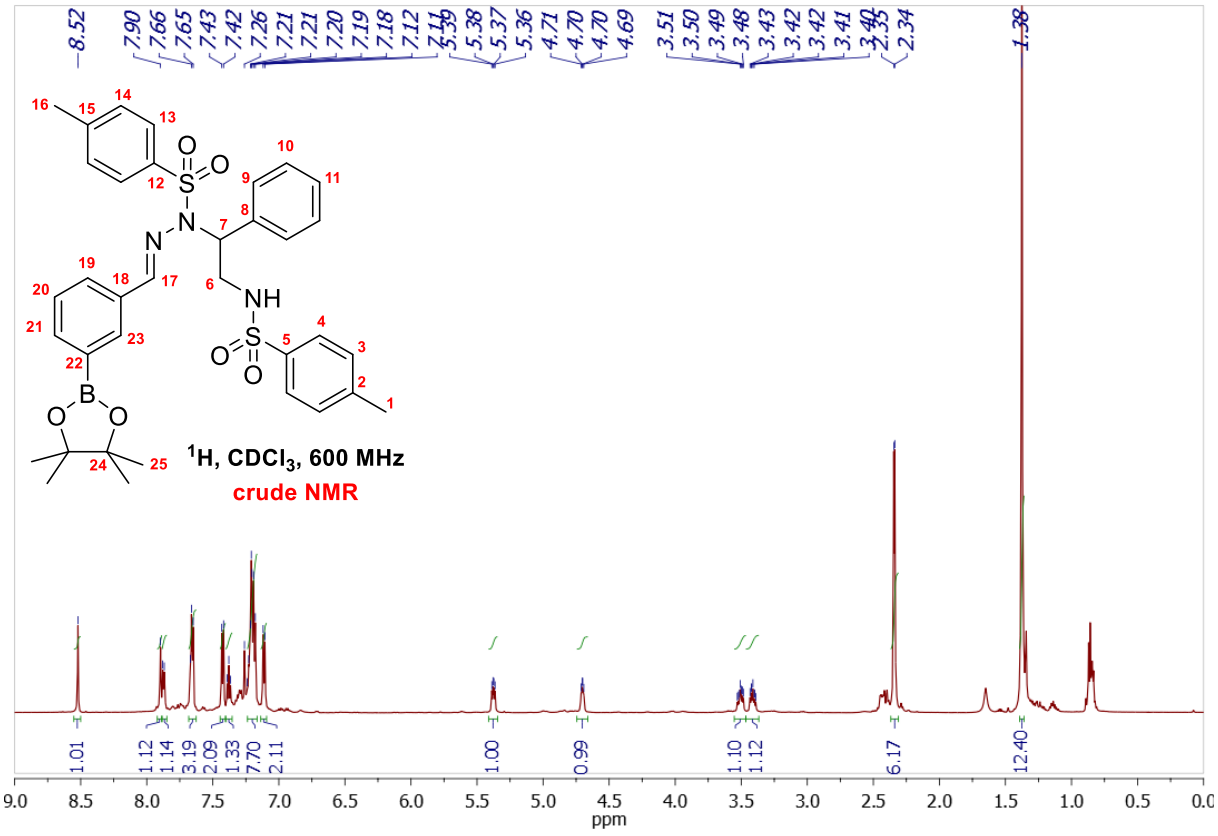


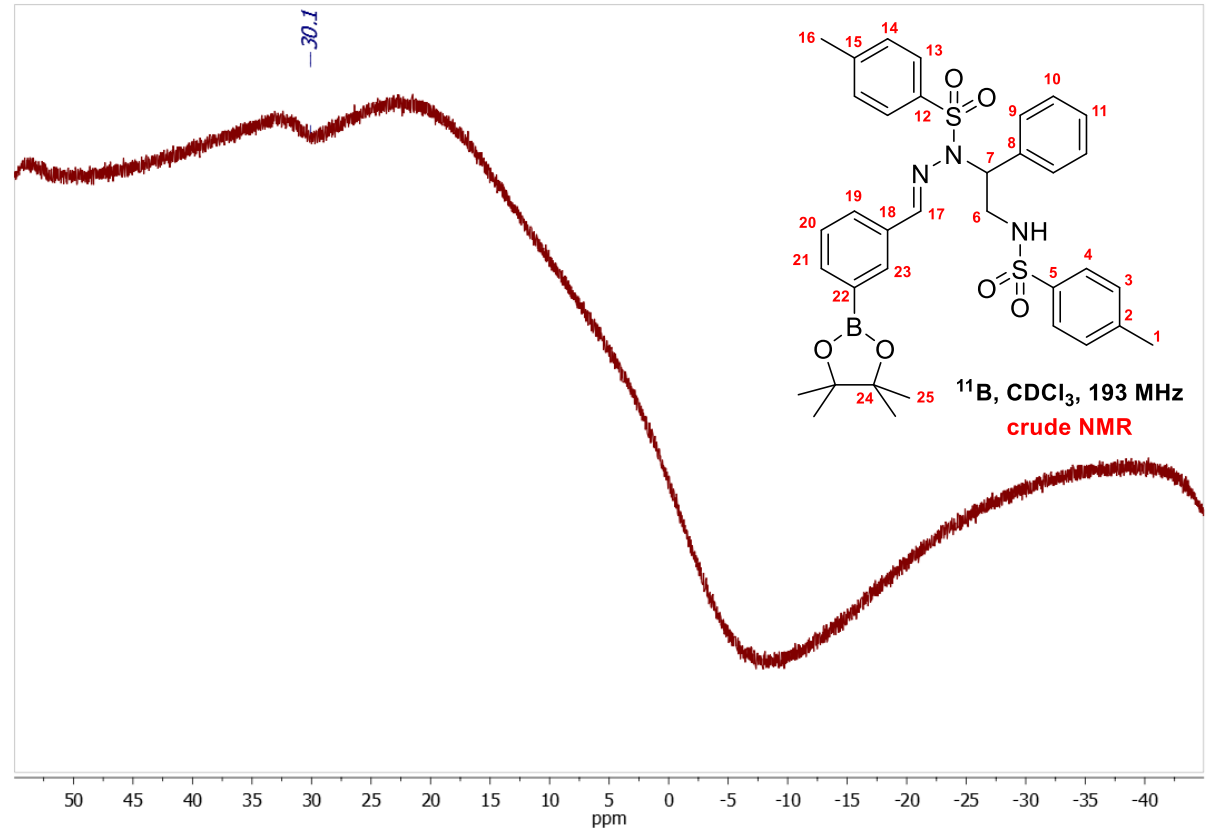
methyl 3-((2-(2-((4-methylphenyl)sulfonamido)-1-phenylethyl)-2-tosylhydrazono)methyl)benzoate (3h)

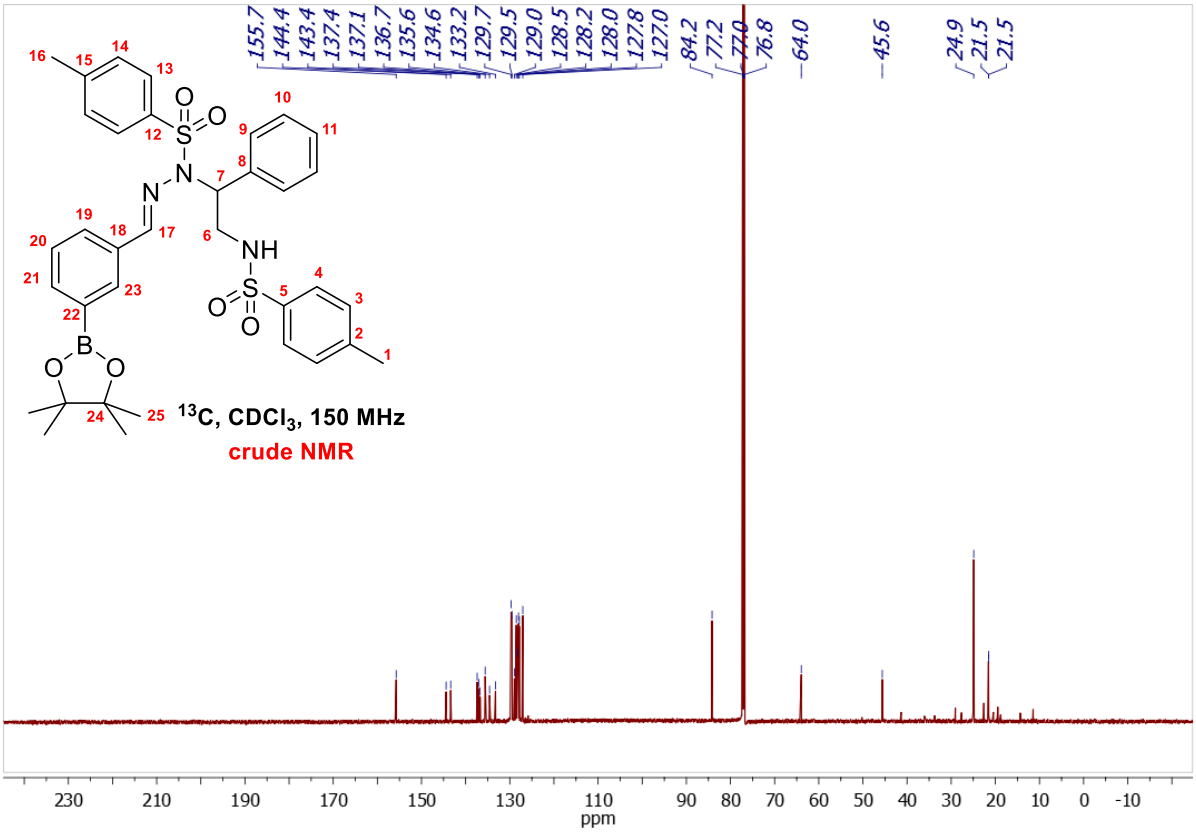




4-methyl-*N*-(2-phenyl-2-(2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)-1-tosylhydrazinyl)ethyl)benzenesulfonamide (3i)



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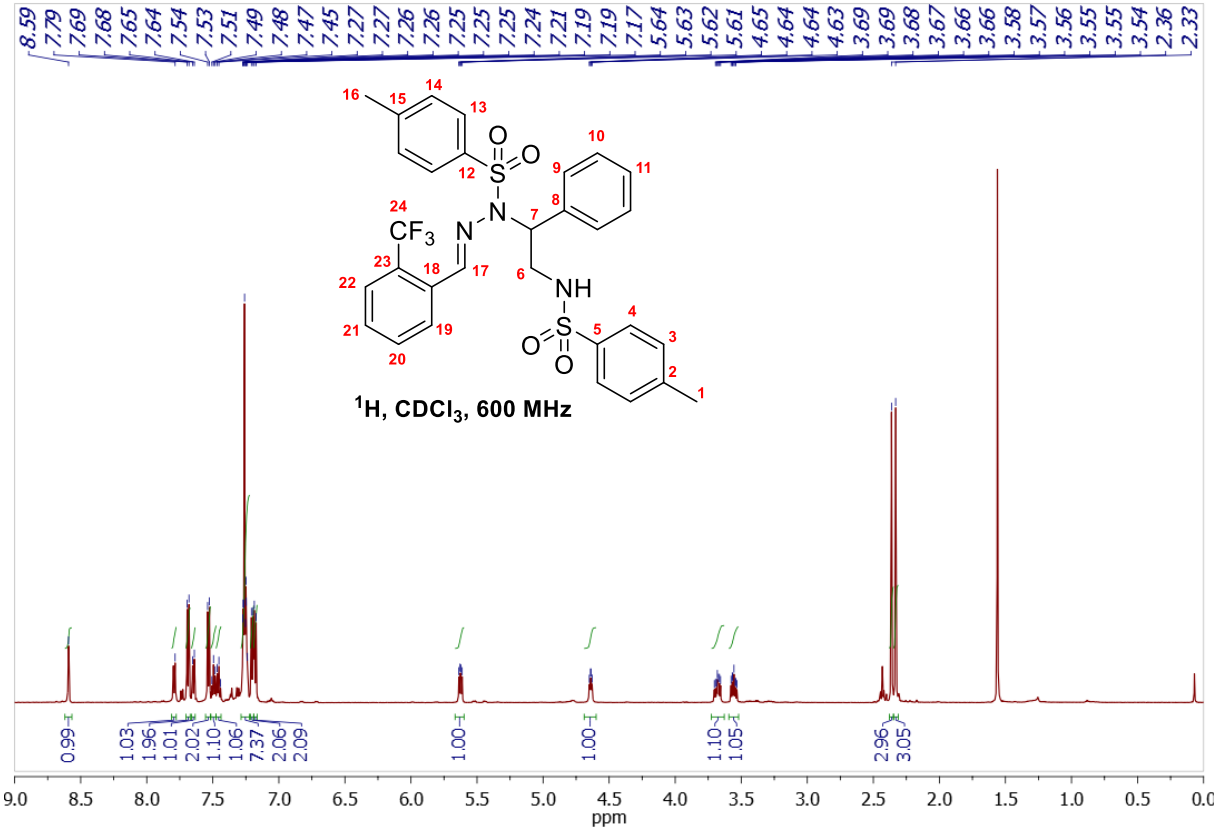
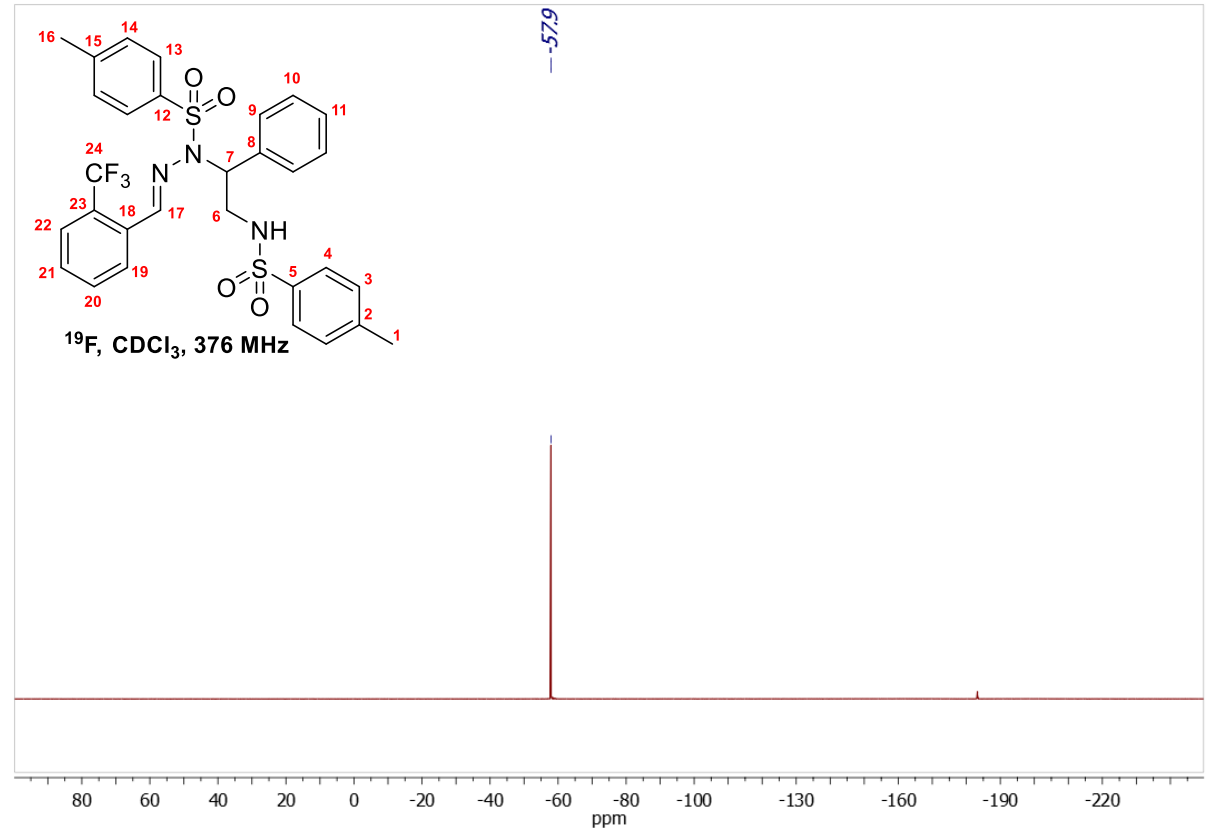
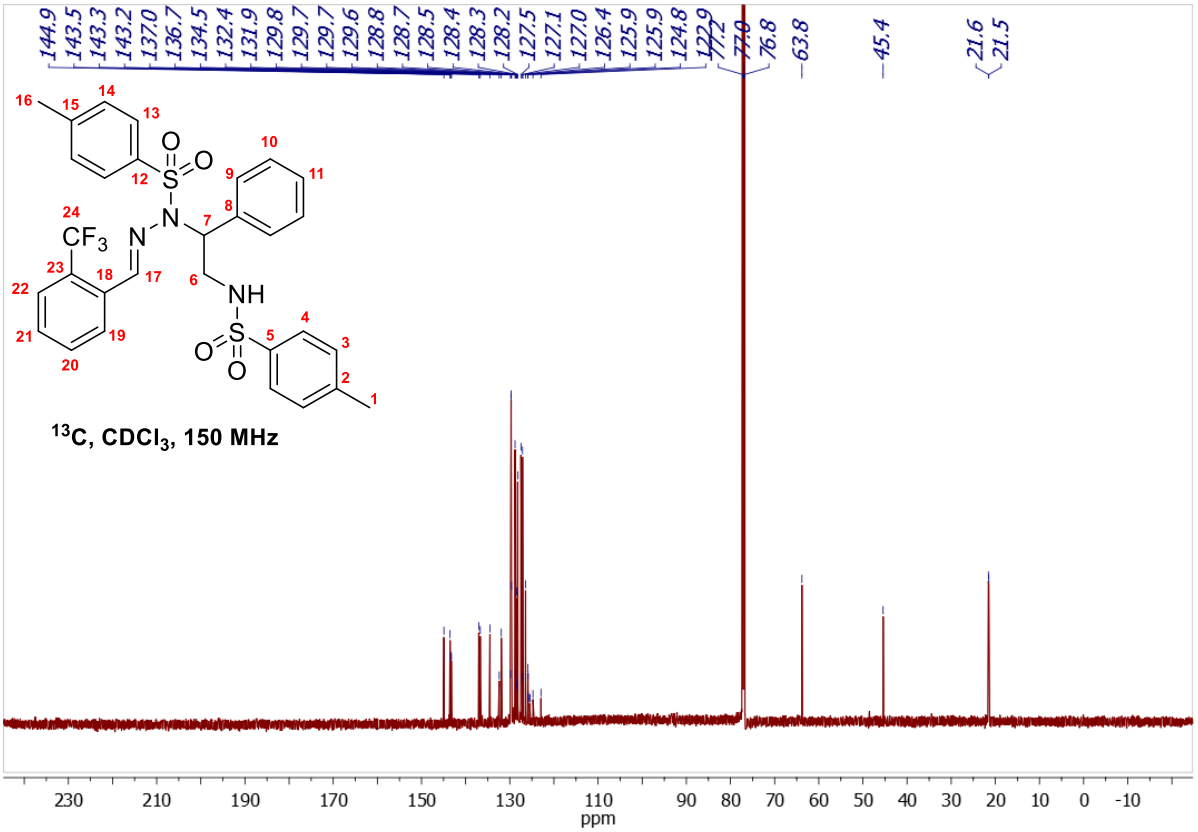
143.4
137.4
137.1
136.7
135.6
134.6
133.2
129.7
129.5
129.0
128.5
128.2
128.0
127.8
127.0
84.2
77.2
77.0
76.8
64.0
45.6
24.9
21.5
21.5
^{13}C, CDCl$_3$, 150 MHz
crude NMR
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

4-methyl-*N*-(2-phenyl-2-(1-tosyl-2-(2-(trifluoromethyl)benzylidene)hydrazinyl)ethyl)benzenesulfonamide (3j)






144.9
143.5
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143.2
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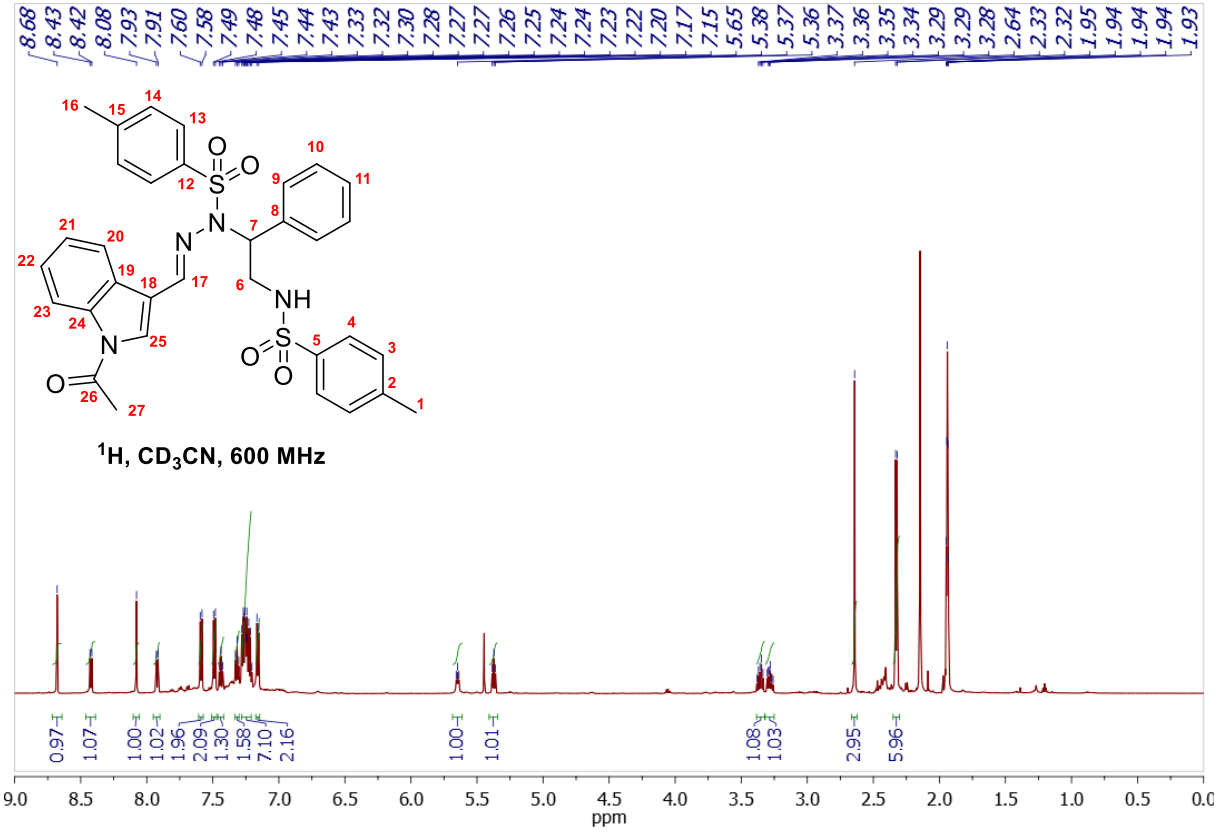
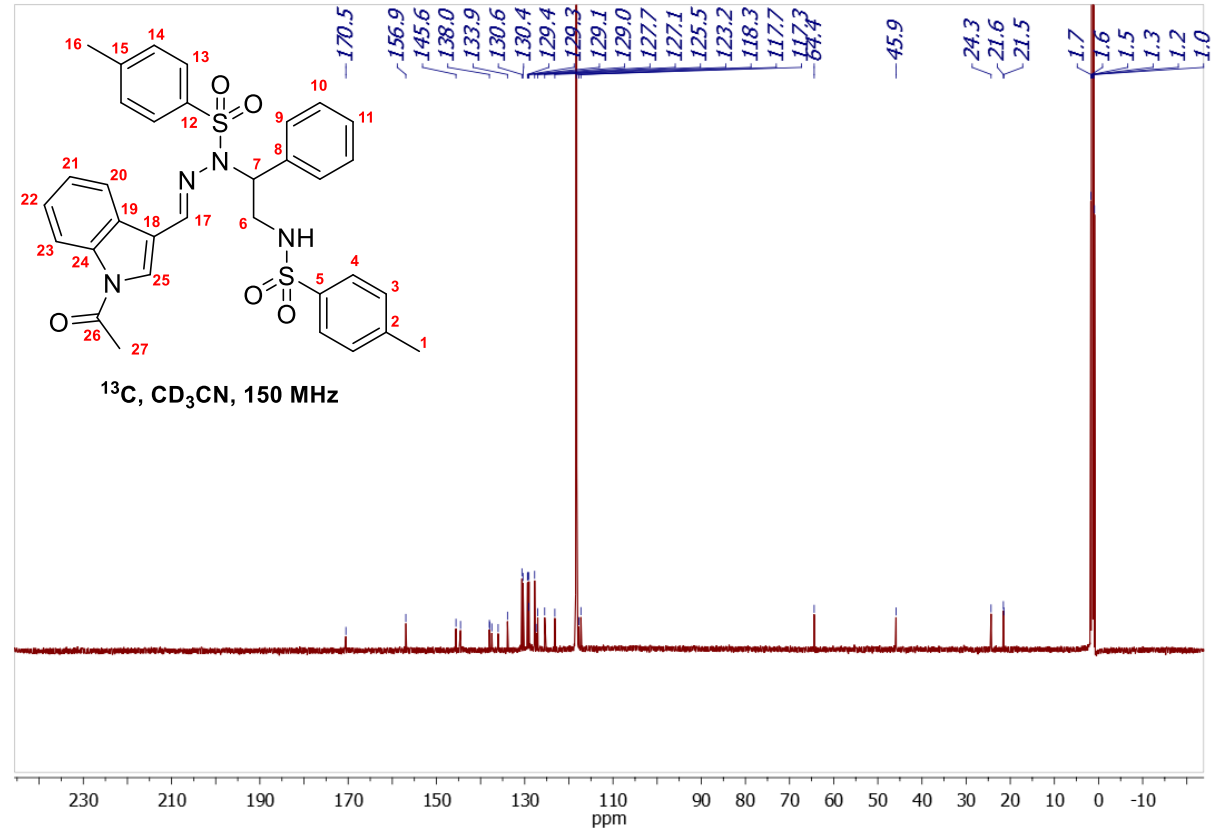
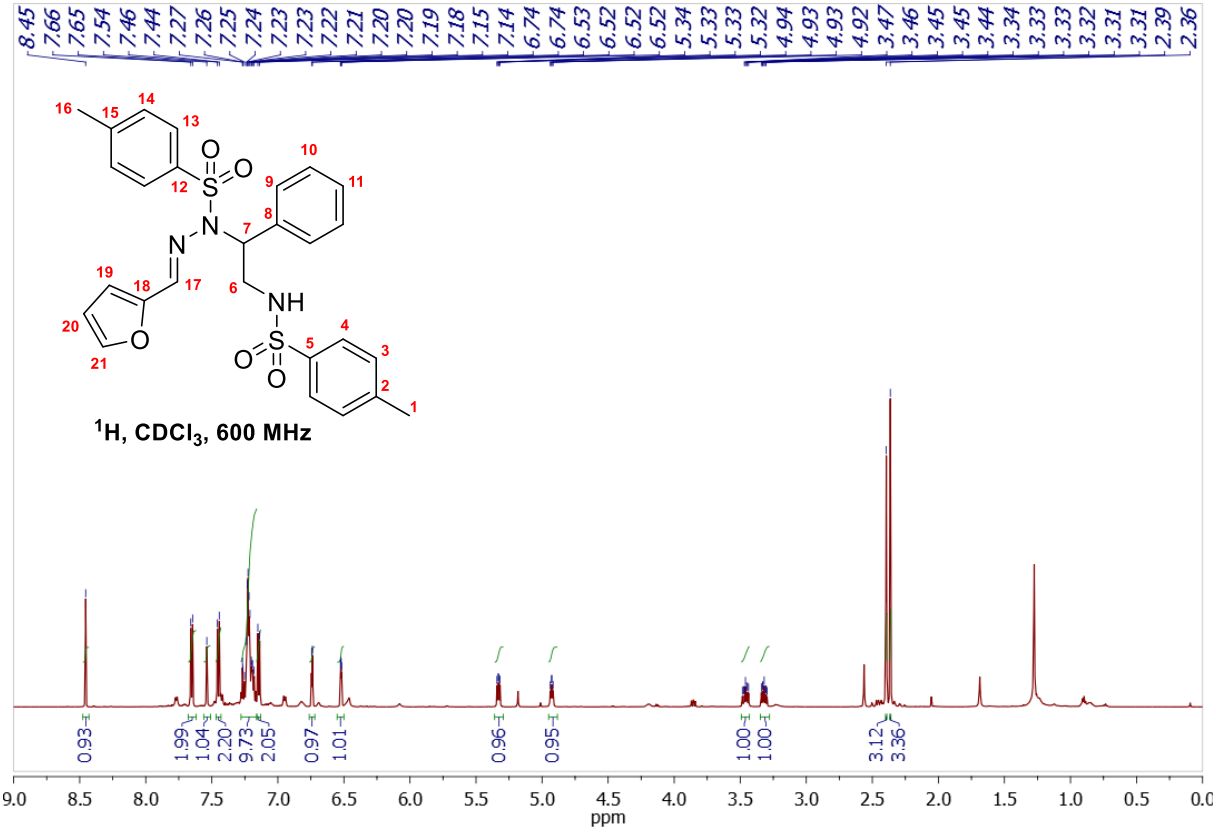
134.5
132.4
131.9
129.8
129.7
129.7
129.6
128.8
128.7
128.5
128.4
128.3
128.2
127.5
127.1
127.0
126.4
125.9
125.9
124.8
122.9
77.2
77.0
76.8
63.8
45.4
21.6
21.5
^{13}C, CDCl$_3$, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

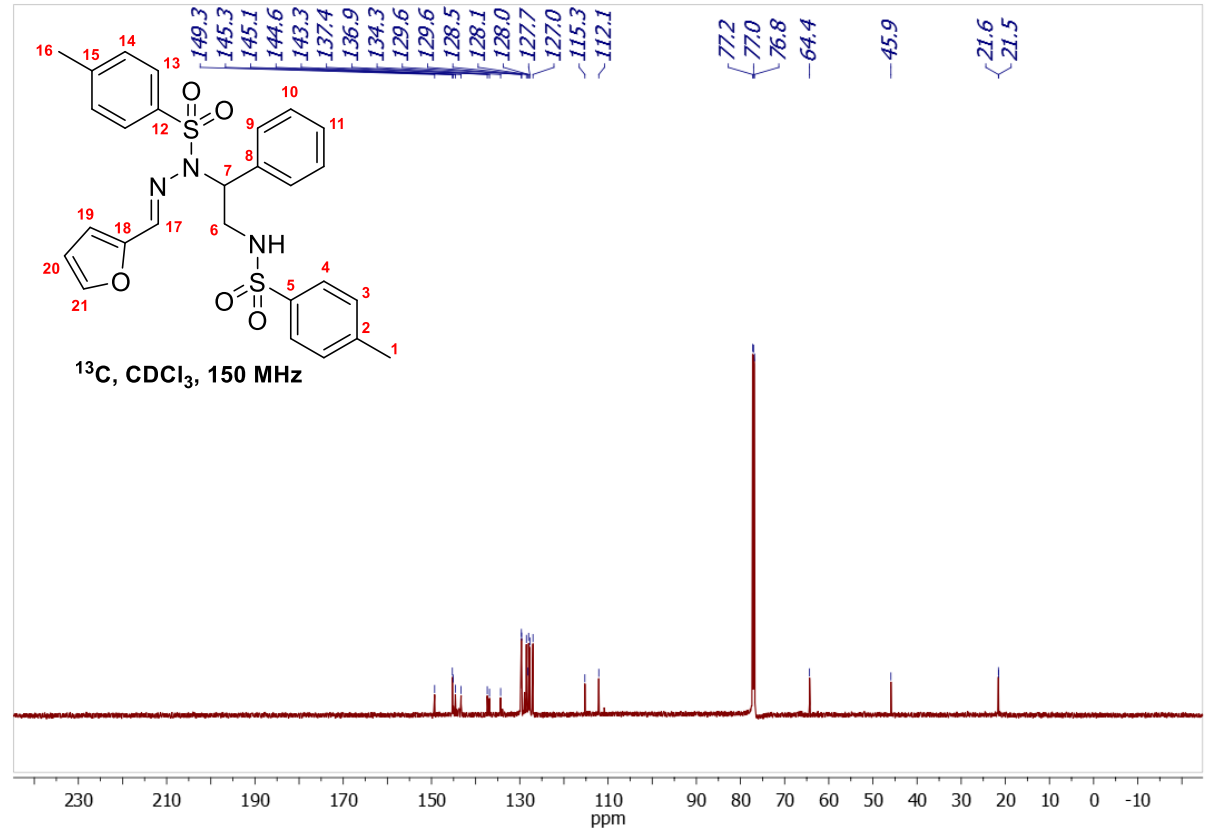
***N*-(2-(2-((1-acetyl-1H-indol-3-yl)methylene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3k)**



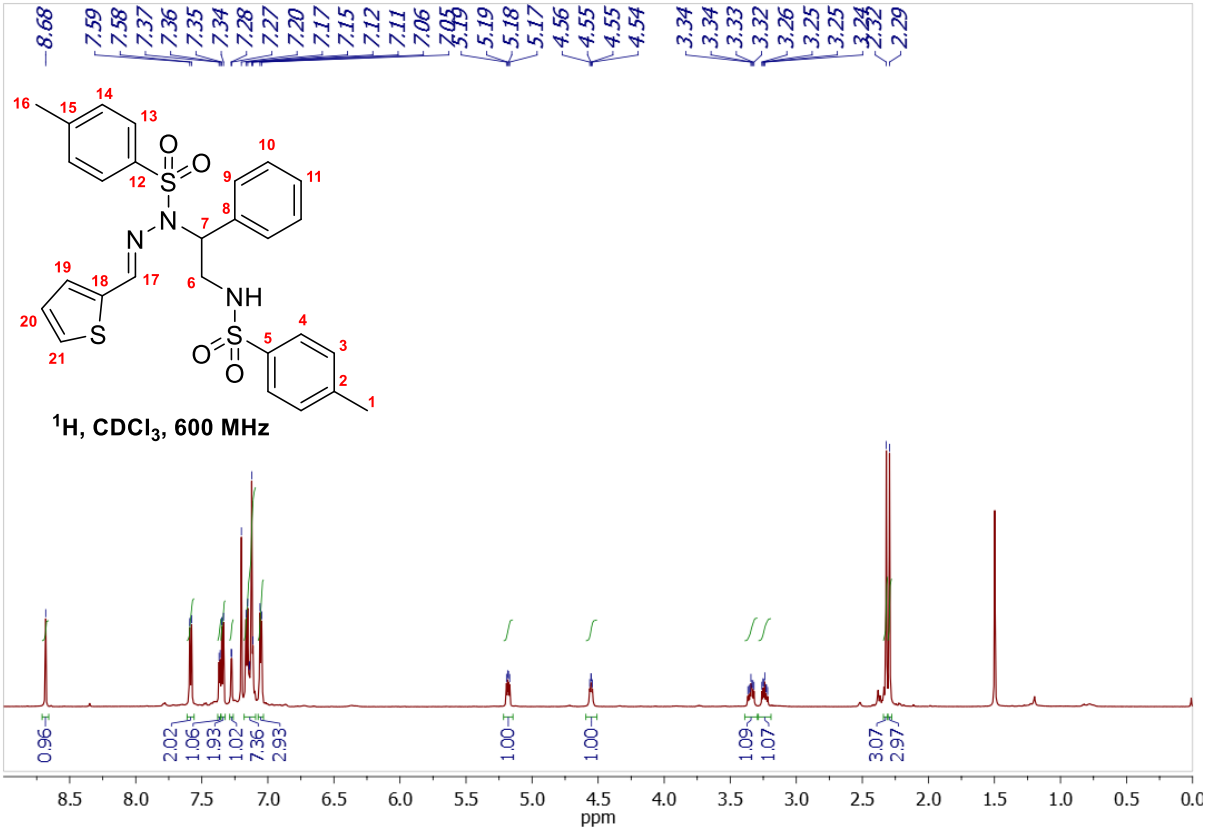


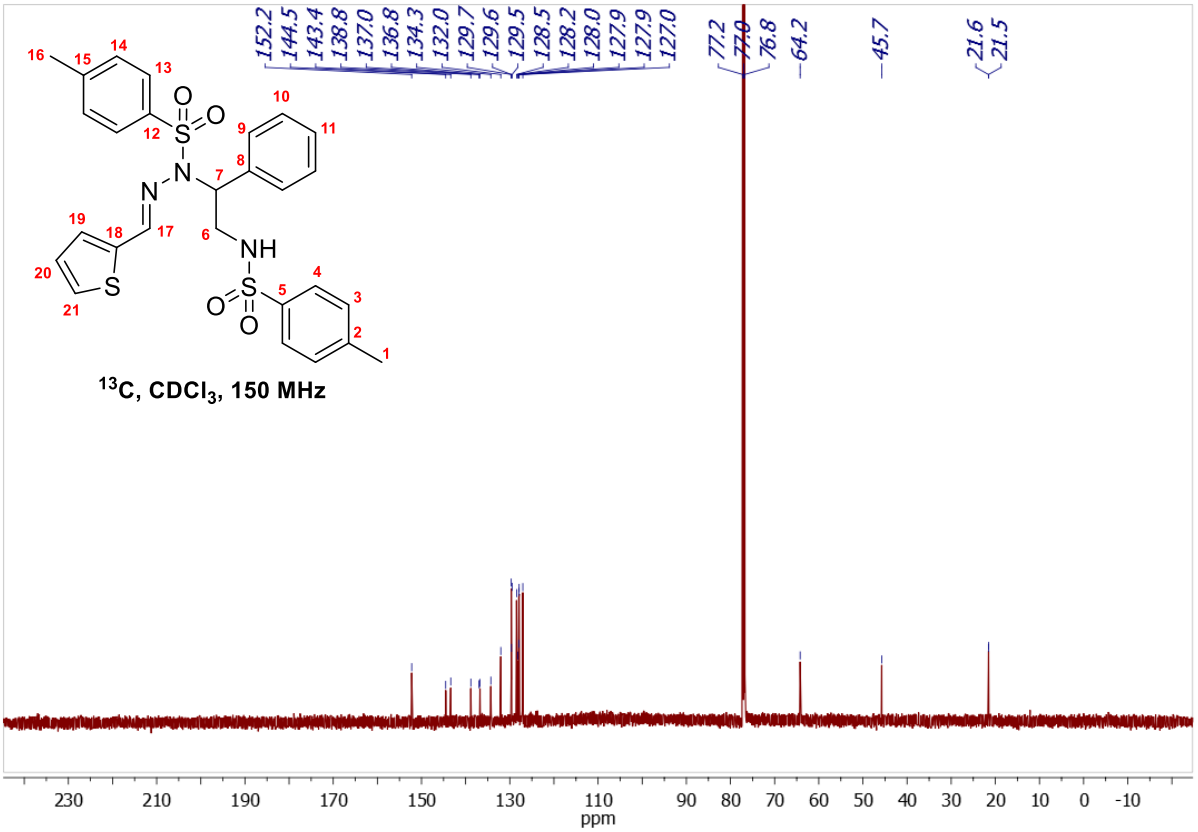
_N_-(2-(2-(furan-2-ylmethylene)-1-tosylhydrazinyl)-2-phenylethyl)-4-methylbenzenesulfonamide (3l)



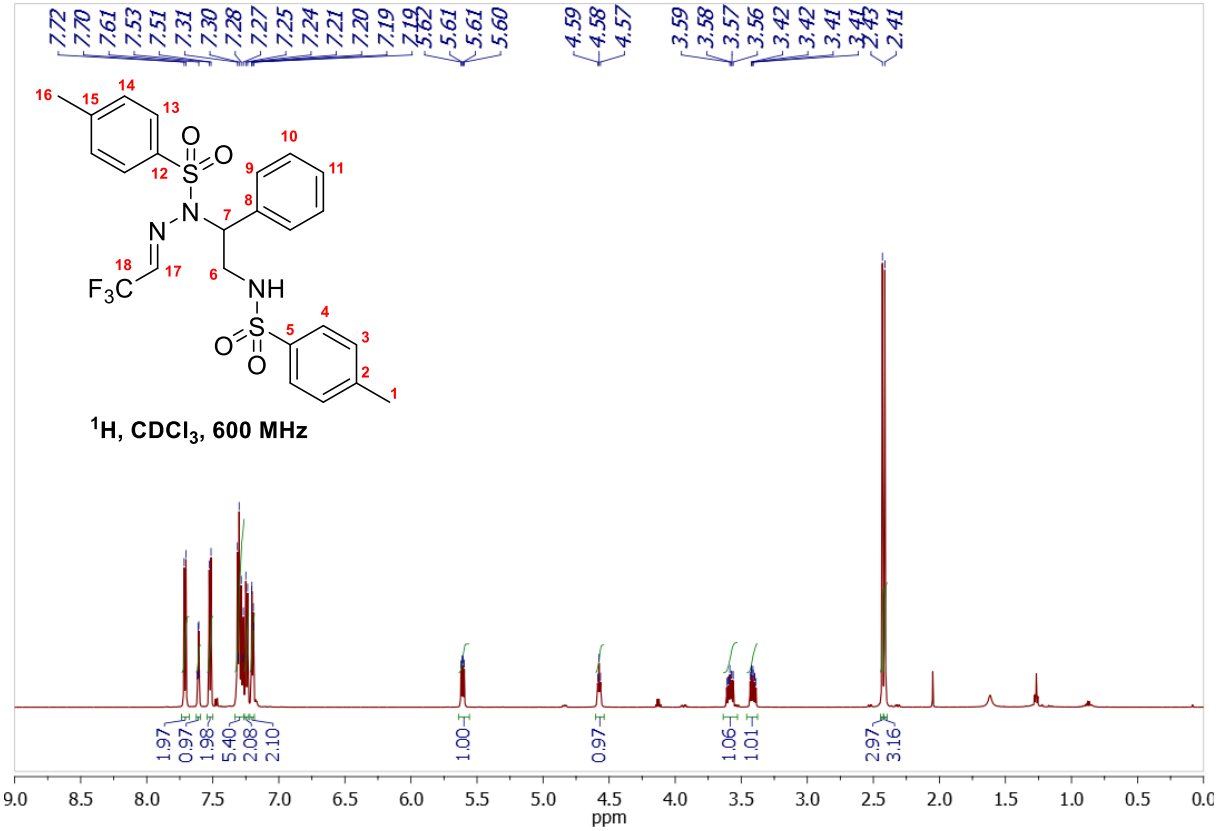


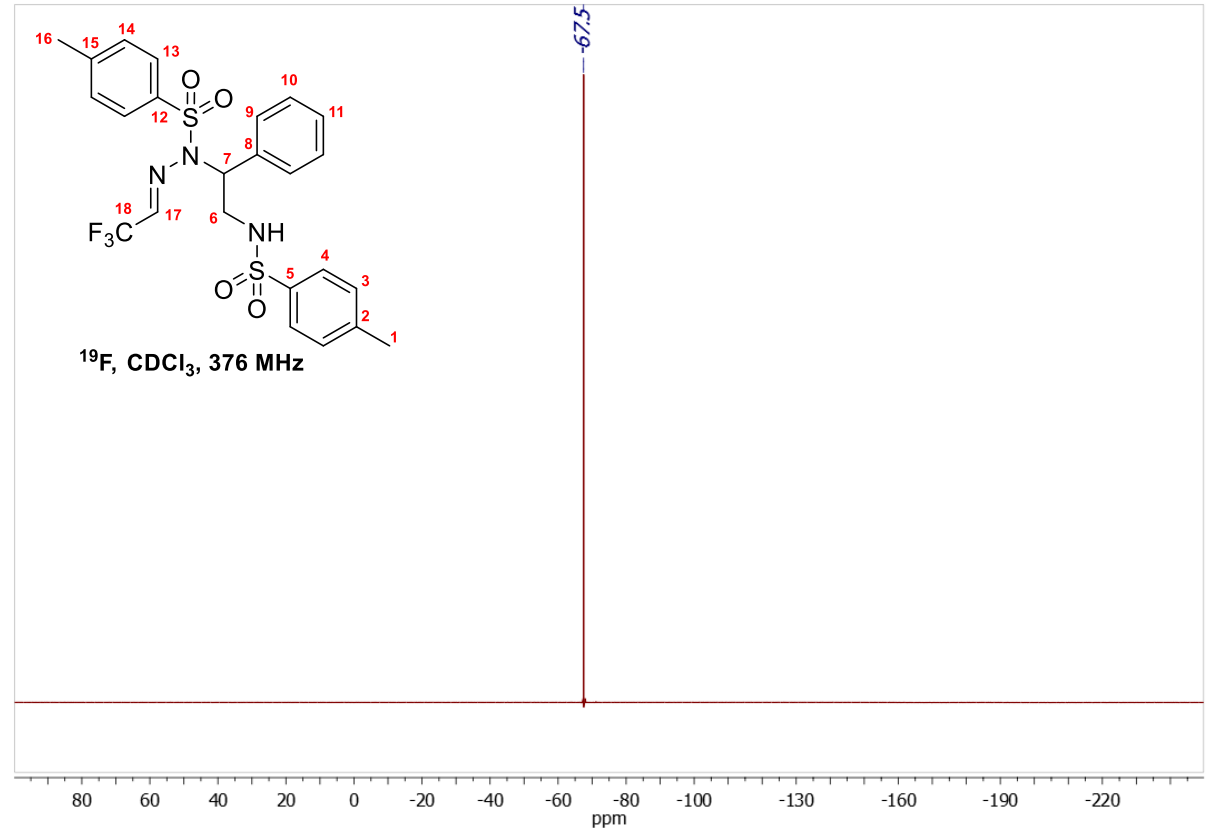
4-methyl-*N*-(2-phenyl-2-(2-(thiophen-2-ylmethylene)-1-tosylhydrazinyl)ethyl)benzenesulfonamide (3m)

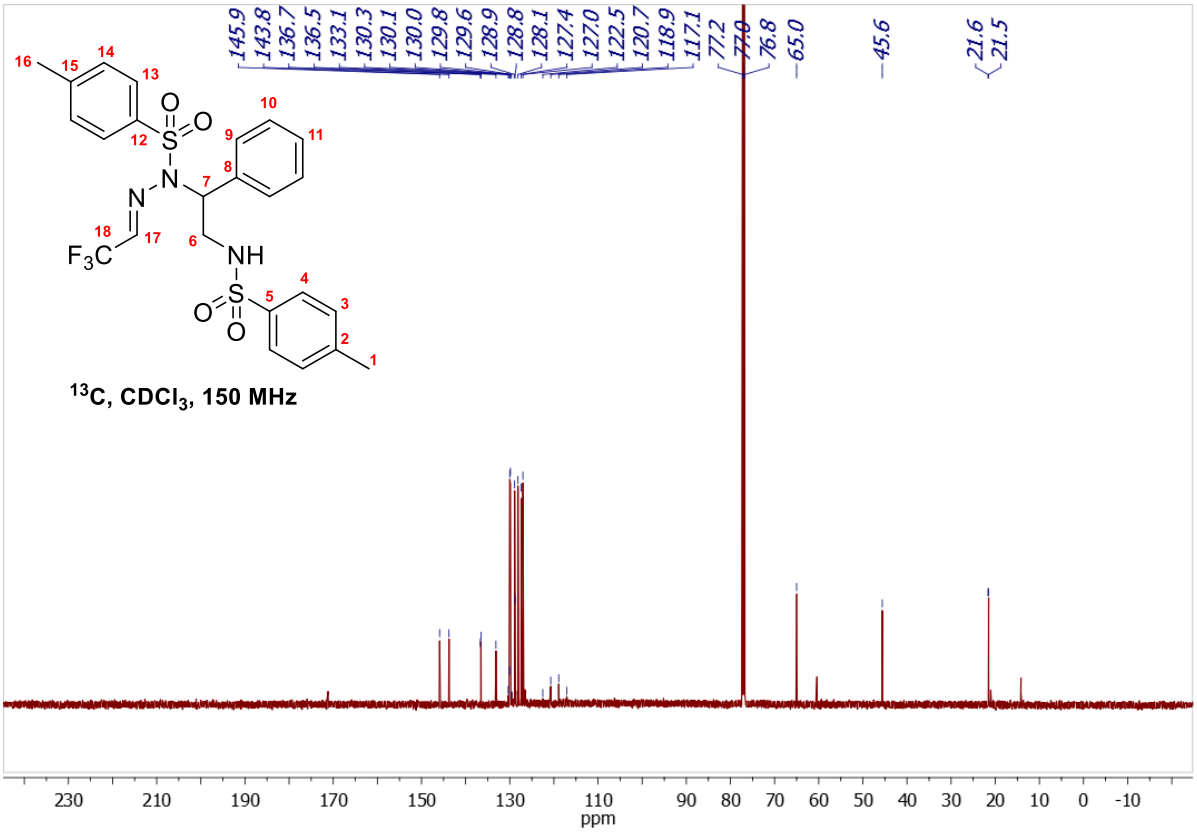




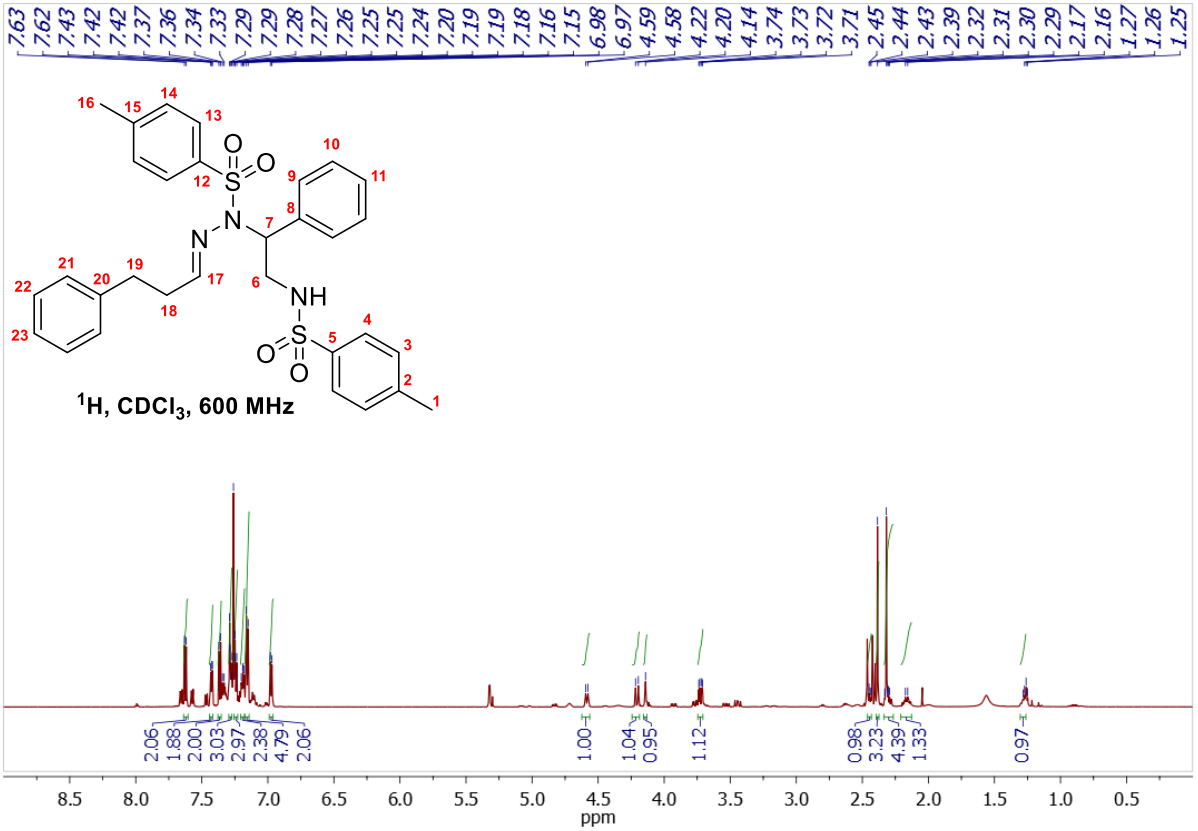
4-methyl-*N*-(2-phenyl-2-(1-tosyl-2-(2,2,2-trifluoroethylidene)hydrazinyl)ethyl)benzenesulfonamide (3n)

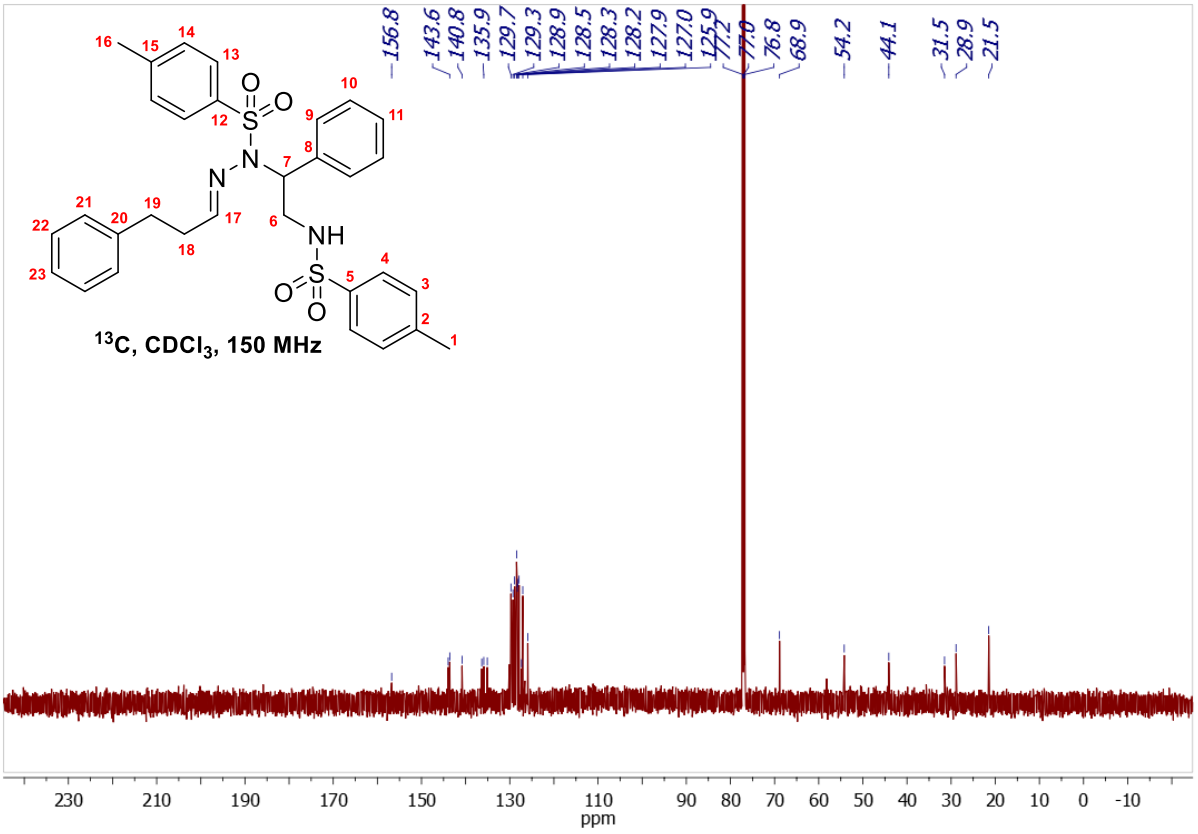




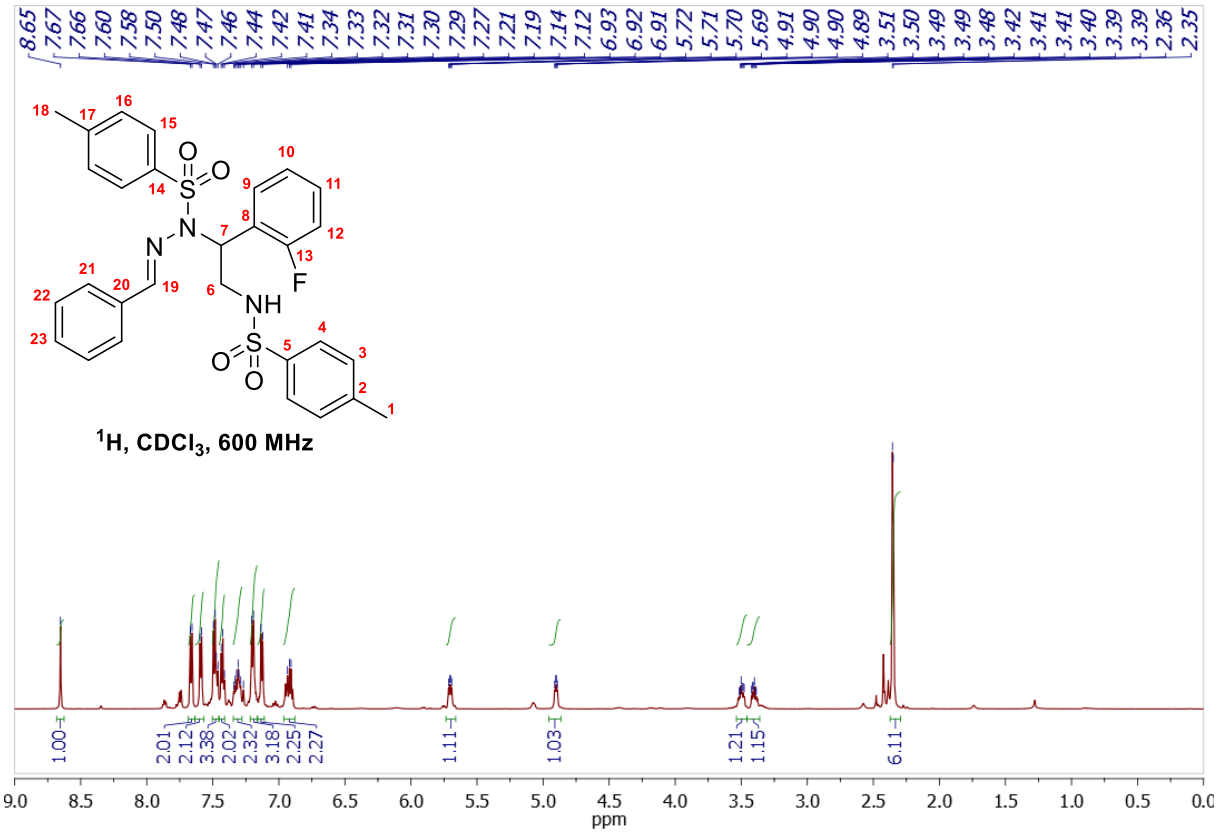

145.9
143.8
136.7
136.5
133.1
130.3
130.1
130.0
129.8
129.6
128.9
128.8
128.1
127.4
127.0
122.5
120.7
118.9
117.1
77.2
77.0
76.8
65.0
45.6
21.6
21.5
^{13}C, CDCl$_3$, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

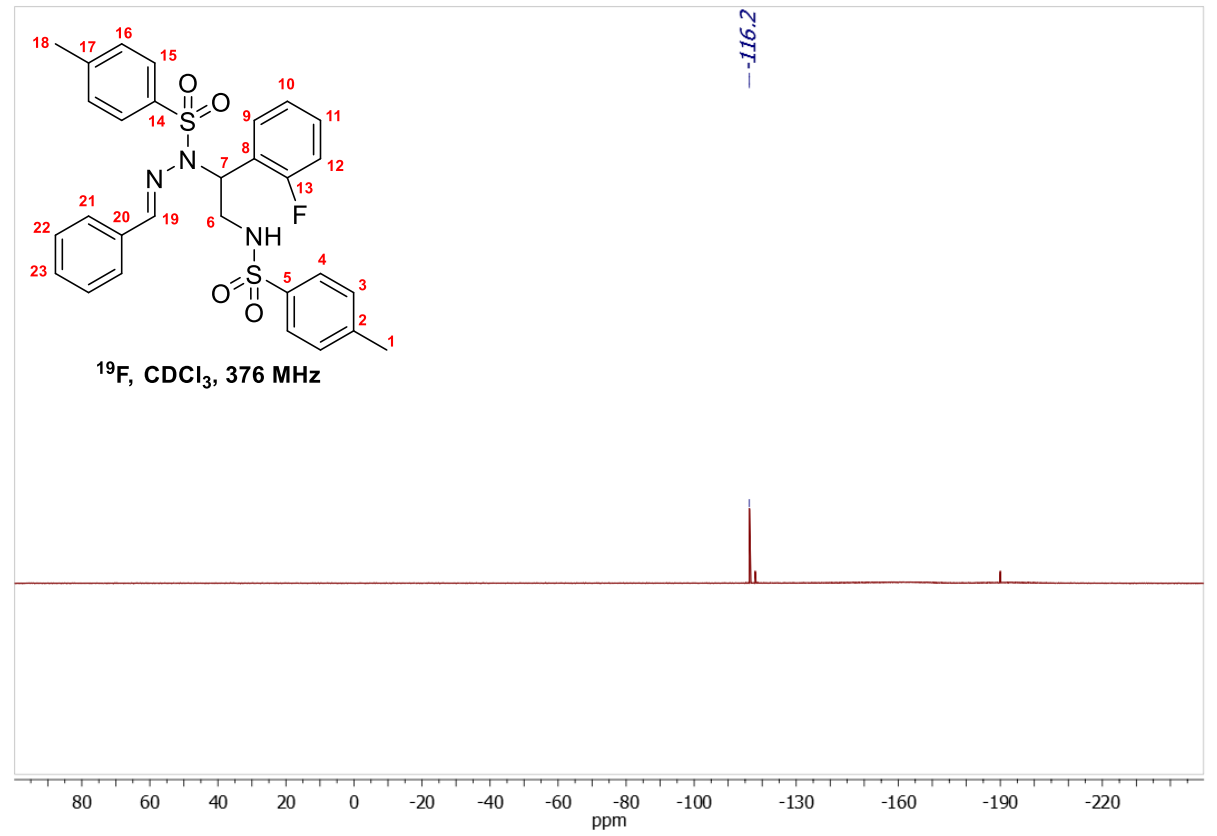
4-methyl-*N*-(2-phenyl-2-(2-(3-phenylpropylidene)-1-tosylhydrazinyl)ethyl)benzenesulfonamide (3o)

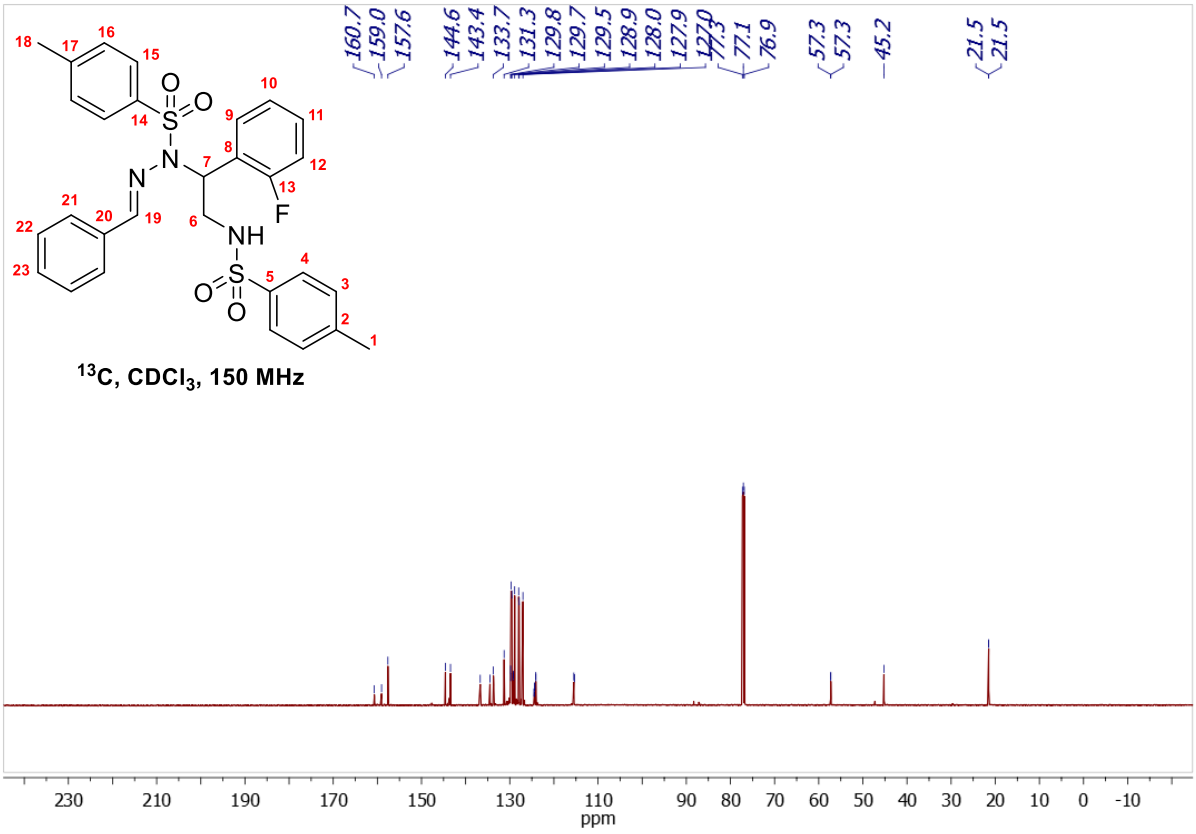




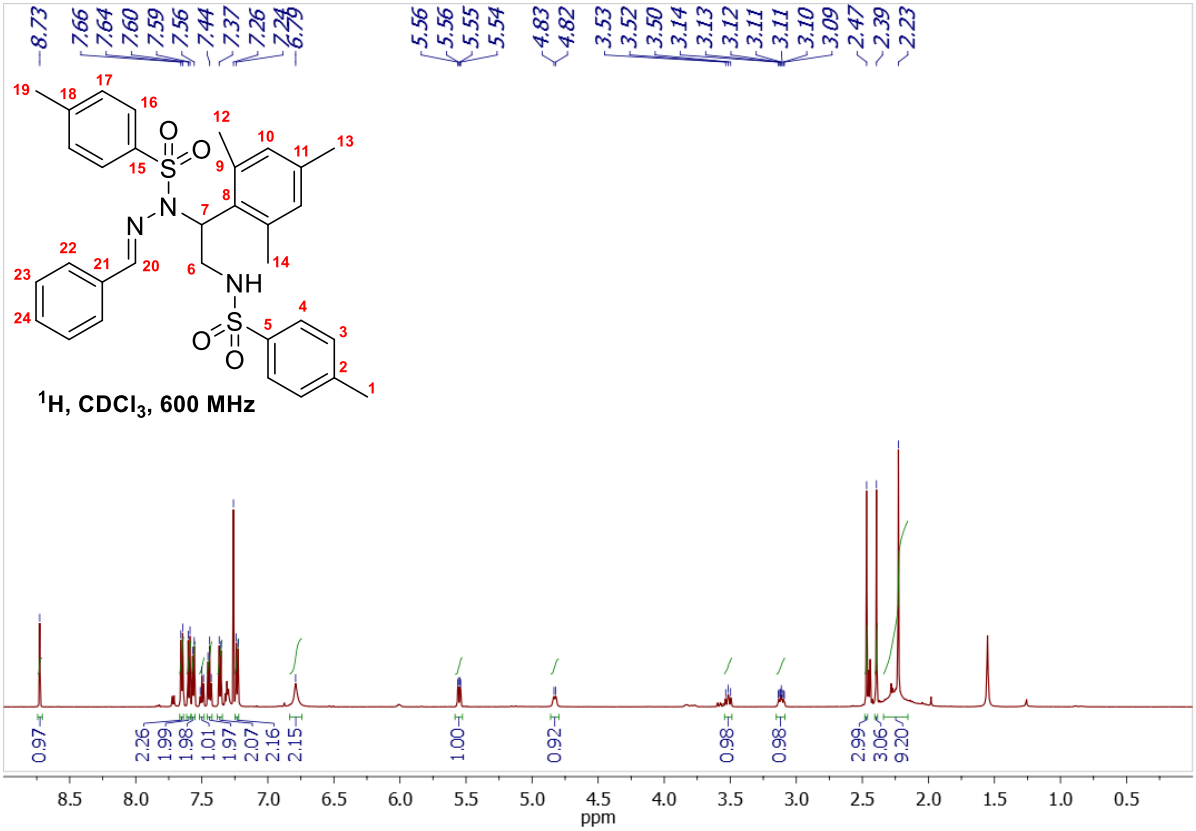
_N_-(2-(2-benzylidene-1-tosylhydrazinyl)-2-(2-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (3p)

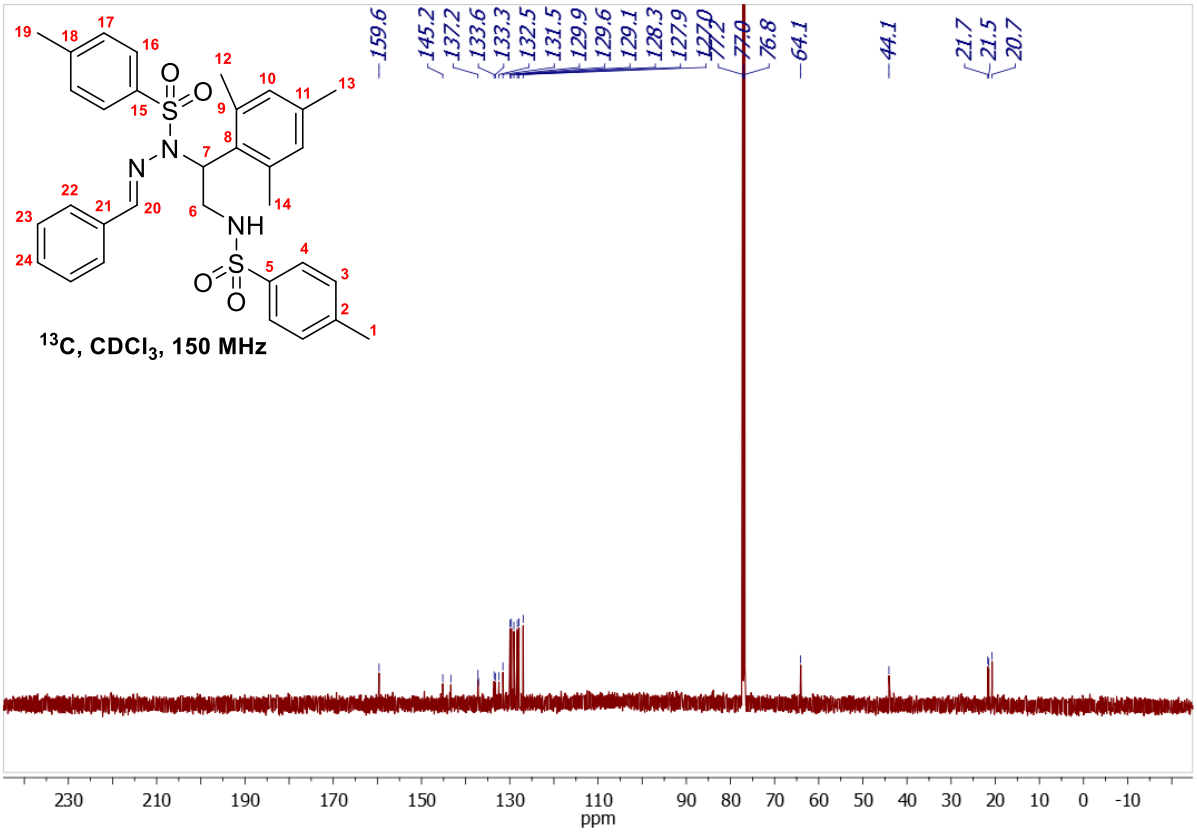




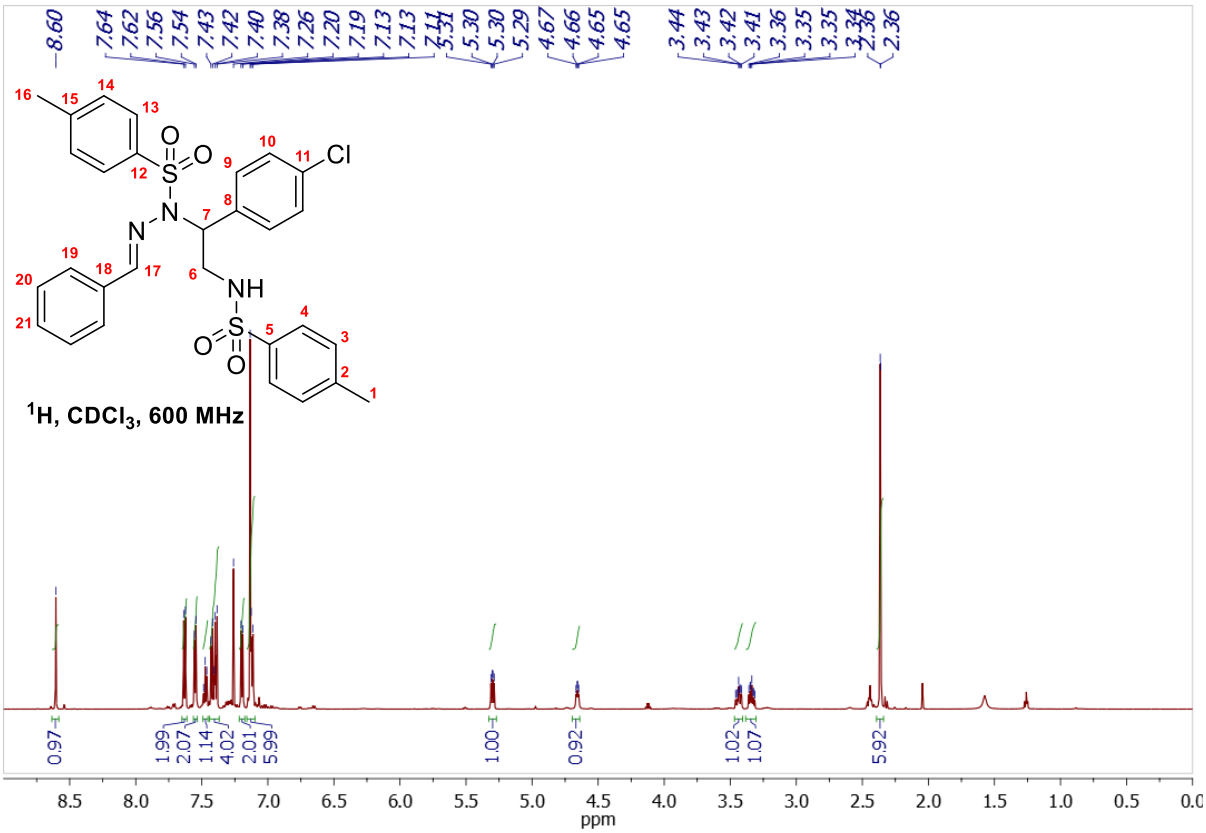

160.7
159.0
157.6
144.6
143.4
133.7
131.3
129.8
129.7
129.5
128.9
128.0
127.9
127.0
77.3
77.1
76.9
57.3
57.3
45.2
21.5
21.5
^{13}C, $CDCl_3$, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

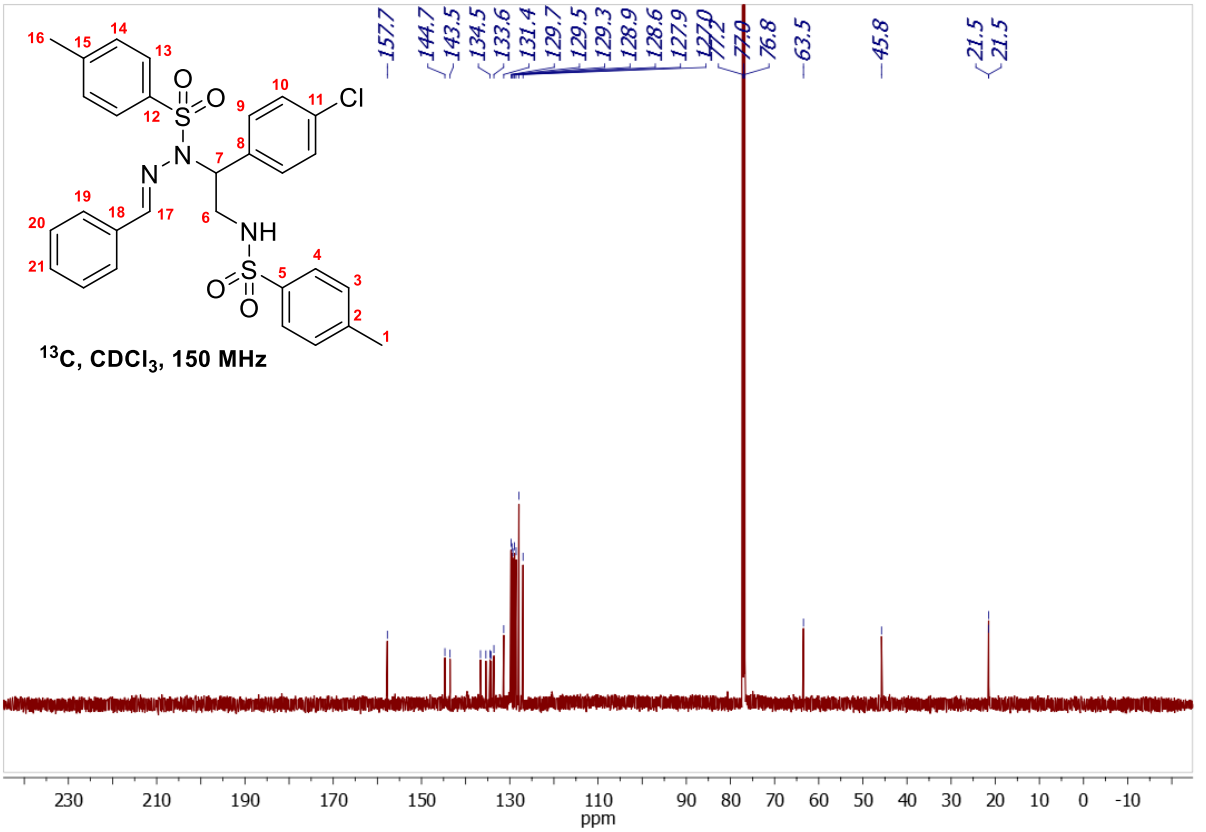
_N_-(2-(2-benzylidene-1-tosylhydrazinyl)-2-mesitylethyl)-4-methylbenzenesulfonamide (3q)



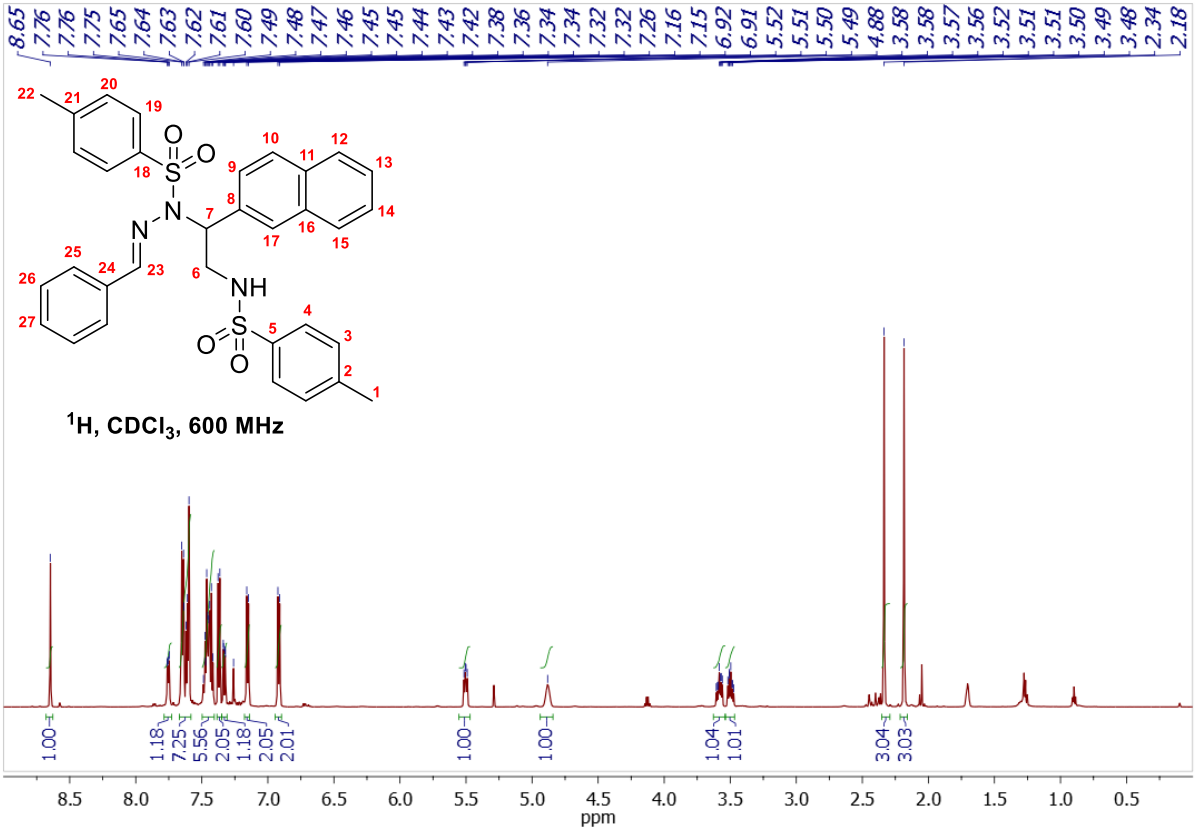


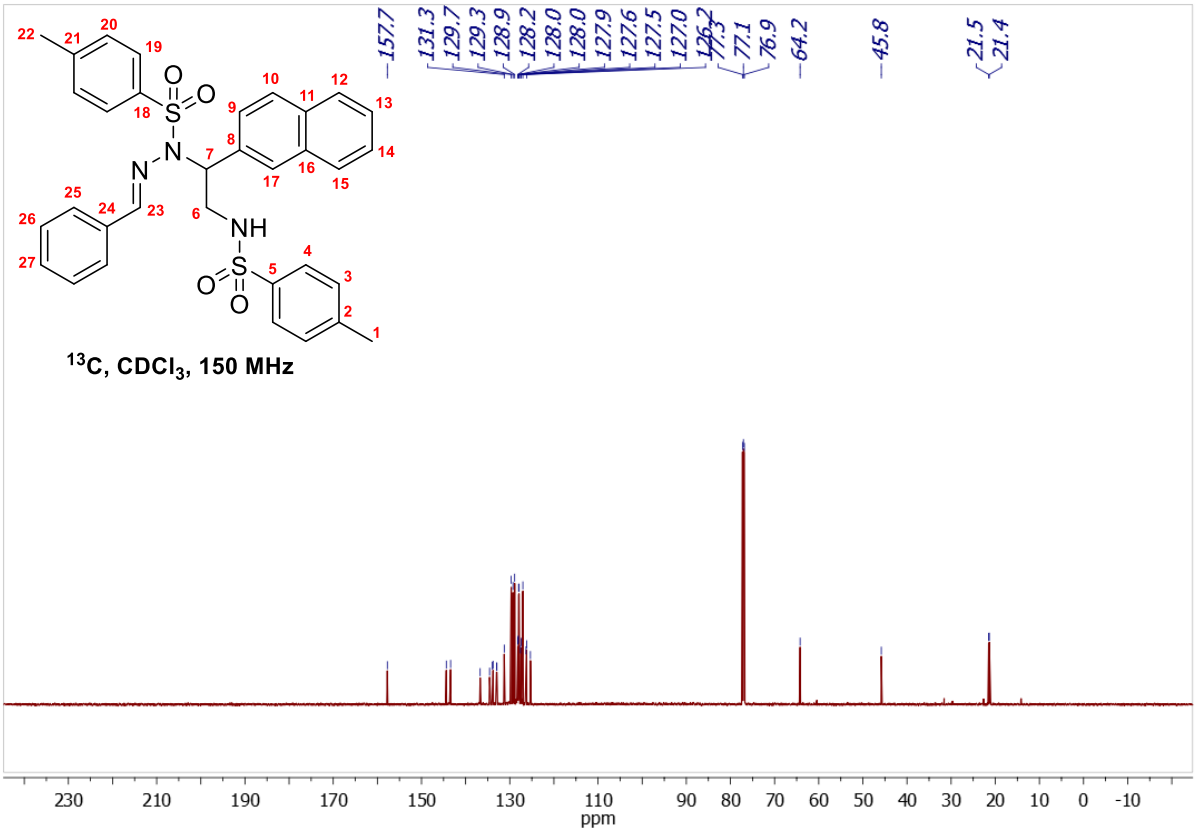
_N_-(2-(2-benzylidene-1-tosylhydrazinyl)-2-(4-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (3r)



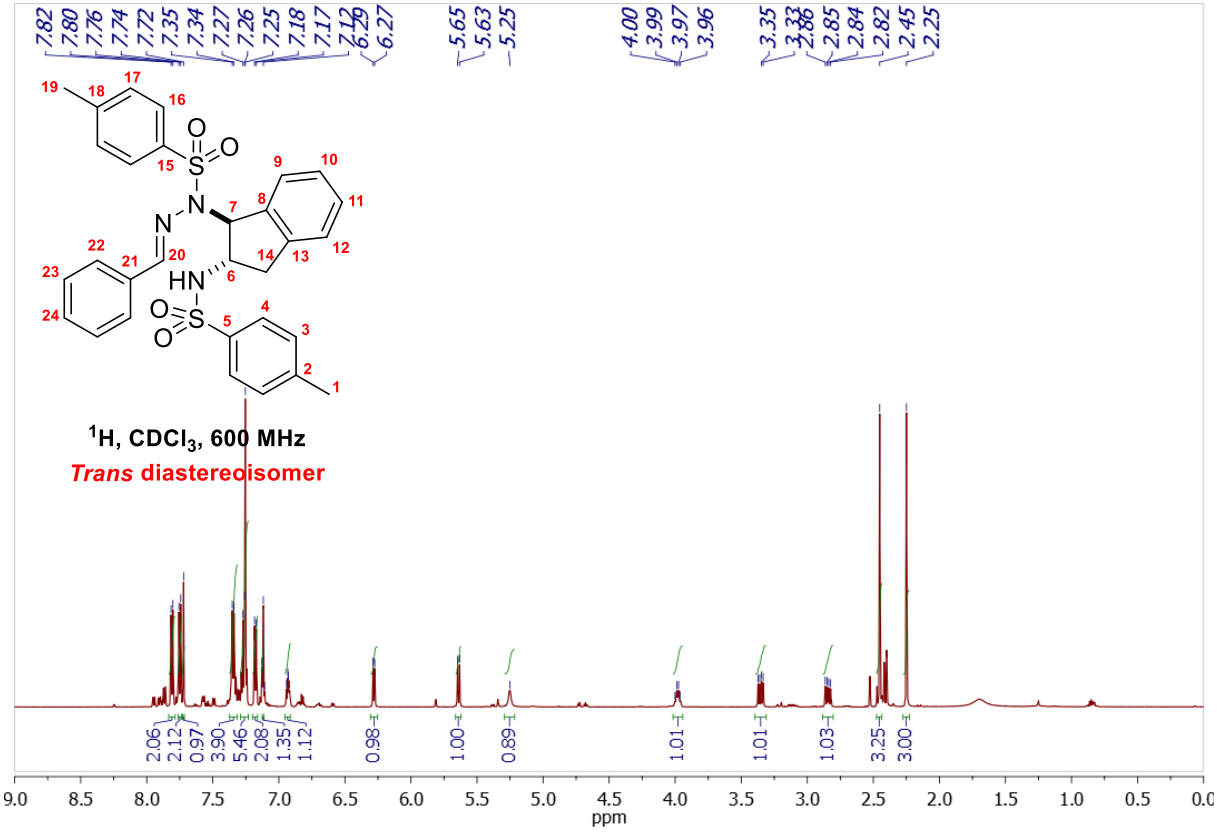


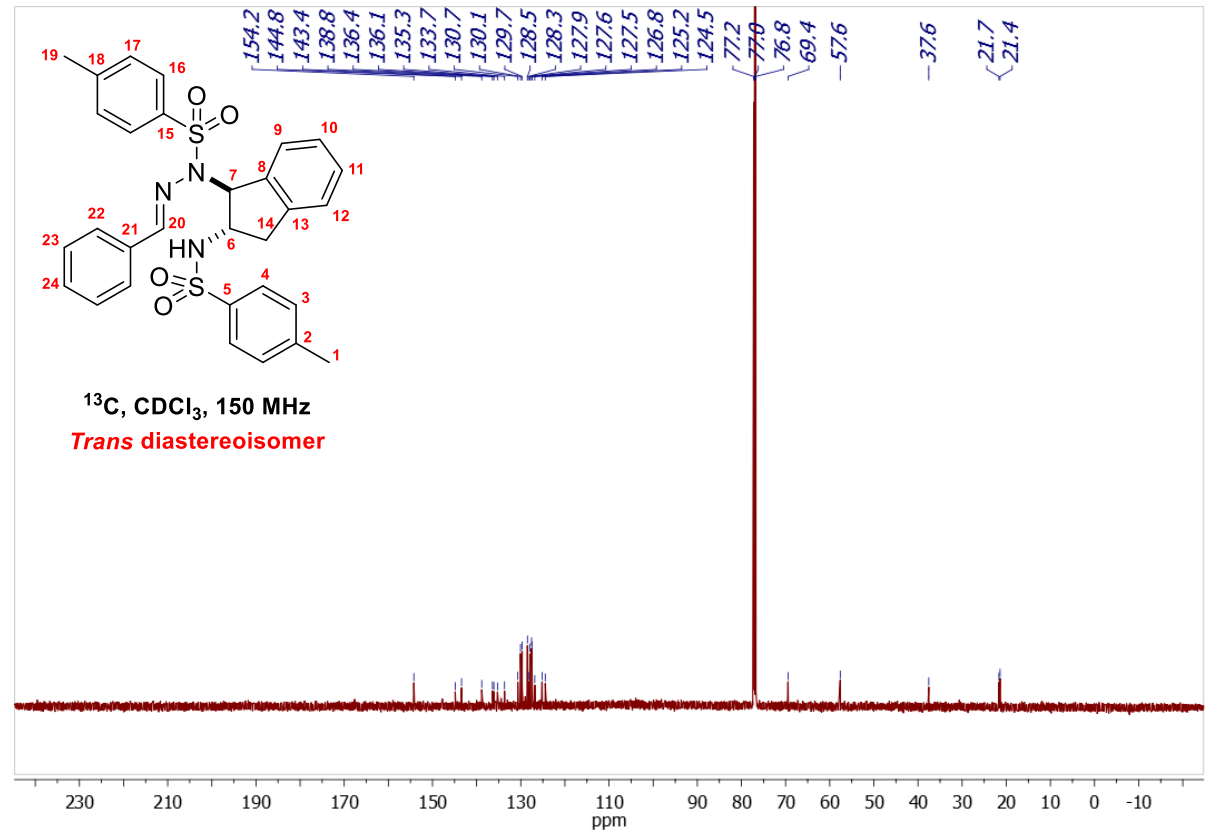
_N_-(2-(2-benzylidene-1-tosylhydrazinyl)-2-(naphthalen-2-yl)ethyl)-4-methylbenzenesulfonamide (3s)

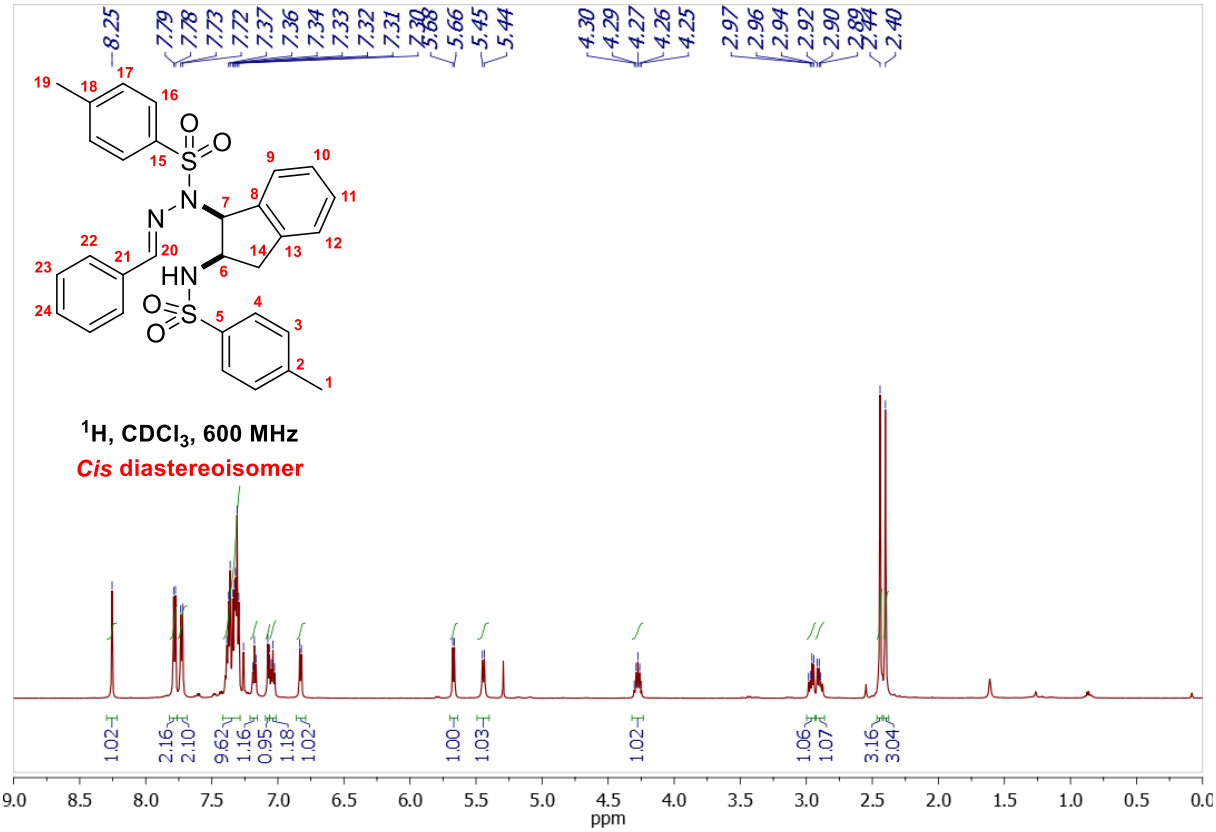




(+/-)-*N*-(1-(2-benzylidene-1-tosylhydrazinyl)-2,3-dihydro-1H-inden-2-yl)-4-methylbenzenesulfonamide (3t)

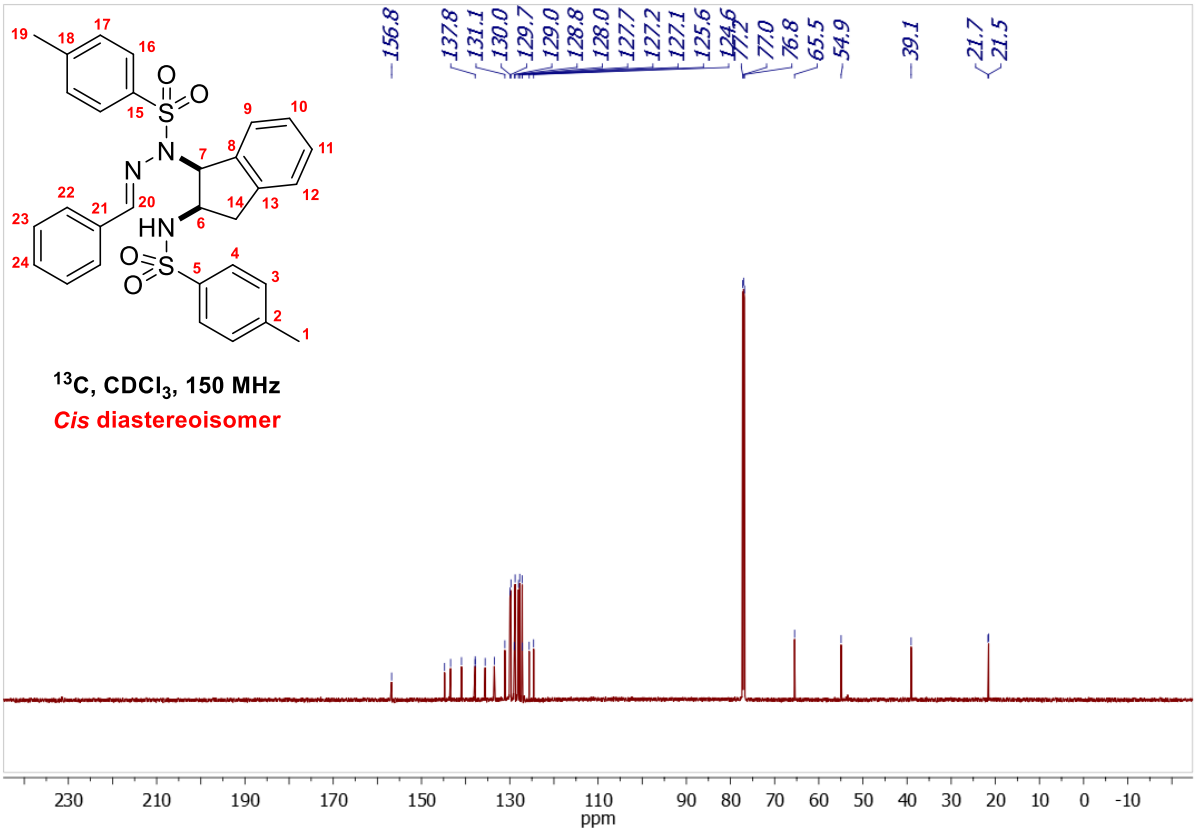






^{1}H, $CDCl_3$, 600 MHz

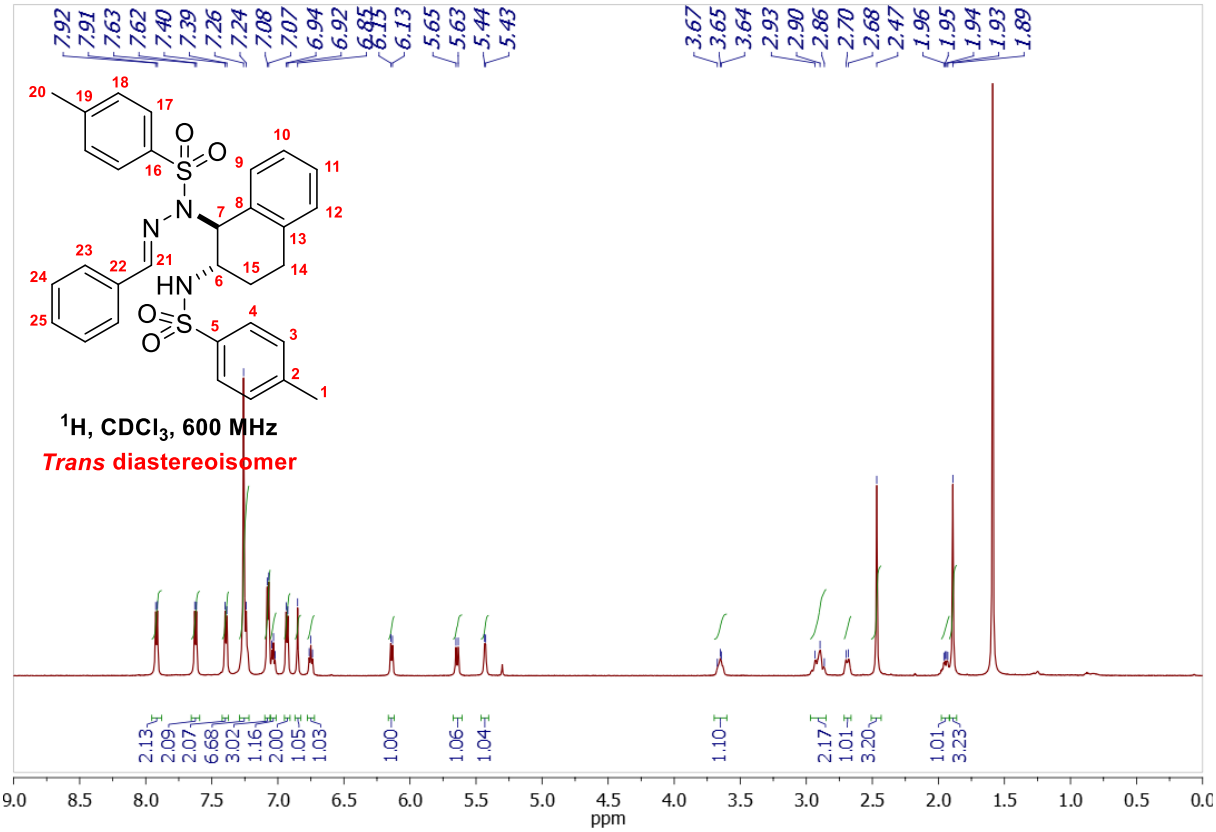
Cis diastereoisomer

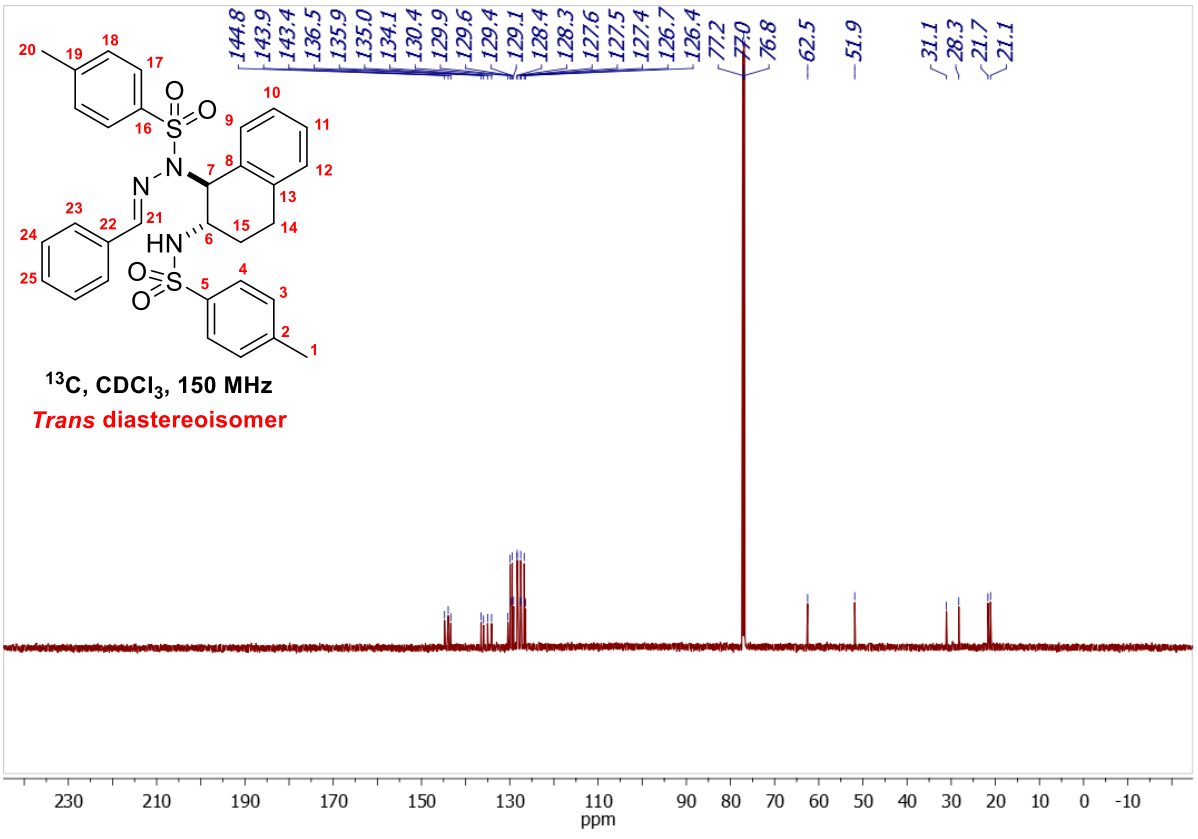


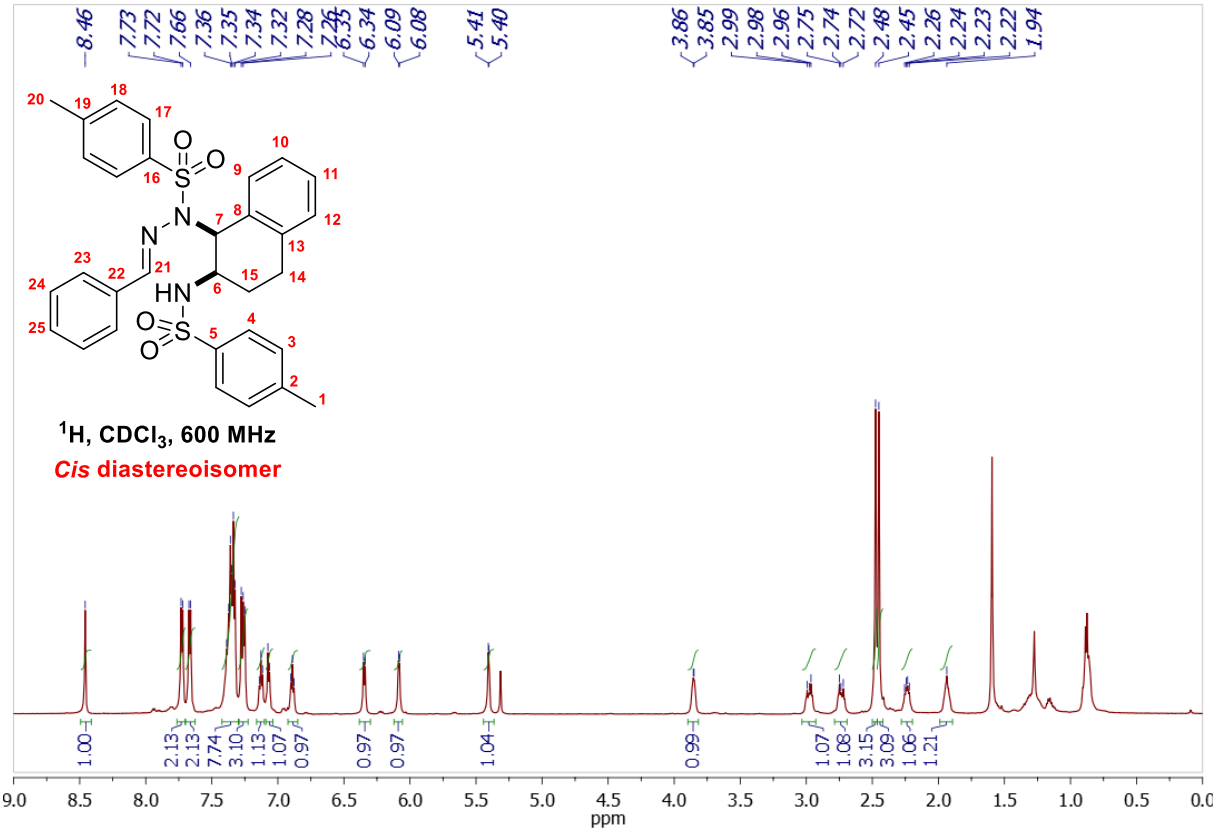
^{13}C, $CDCl_3$, 150 MHz

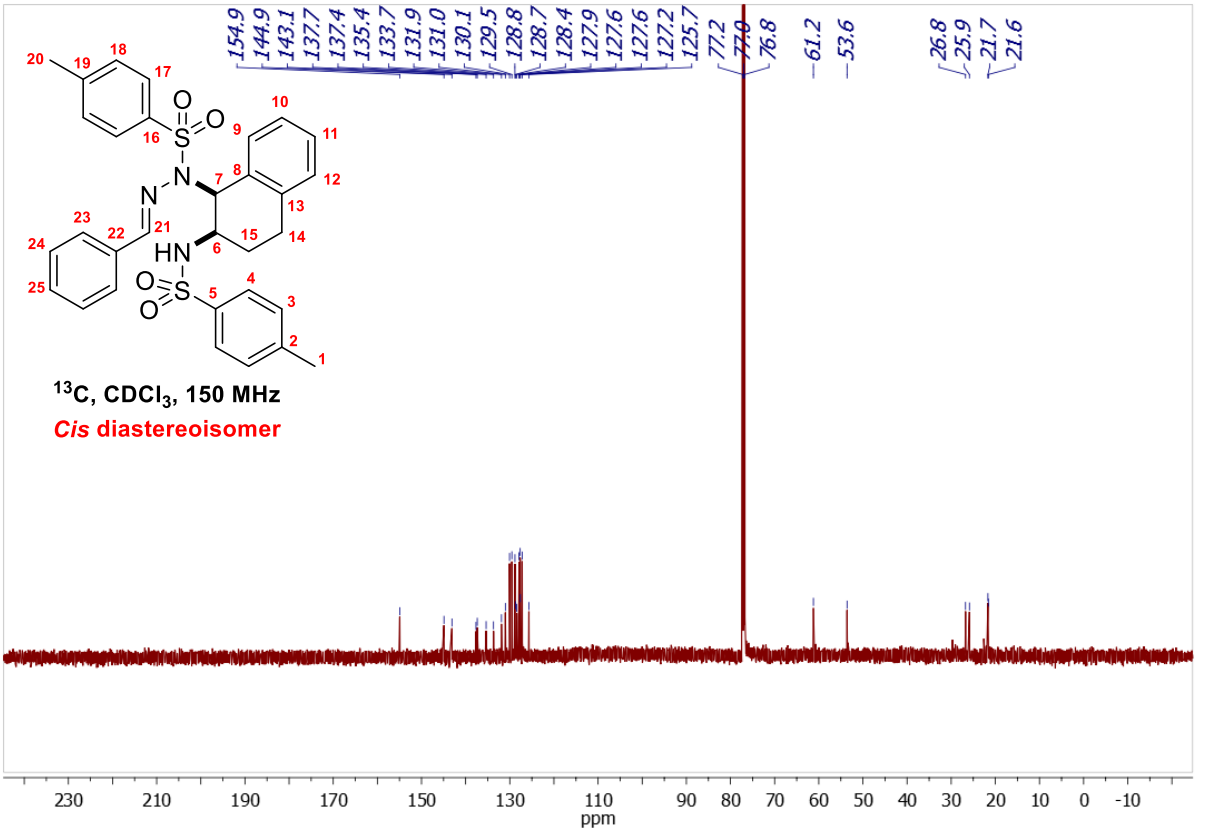
Cis diastereoisomer

(+/-)-*N*-(1-(2-benzylidene-1-tosylhydrazinyl)-1,2,3,4-tetrahydronaphthalen-2-yl)-4-methylbenzenesulfonamide (3u)

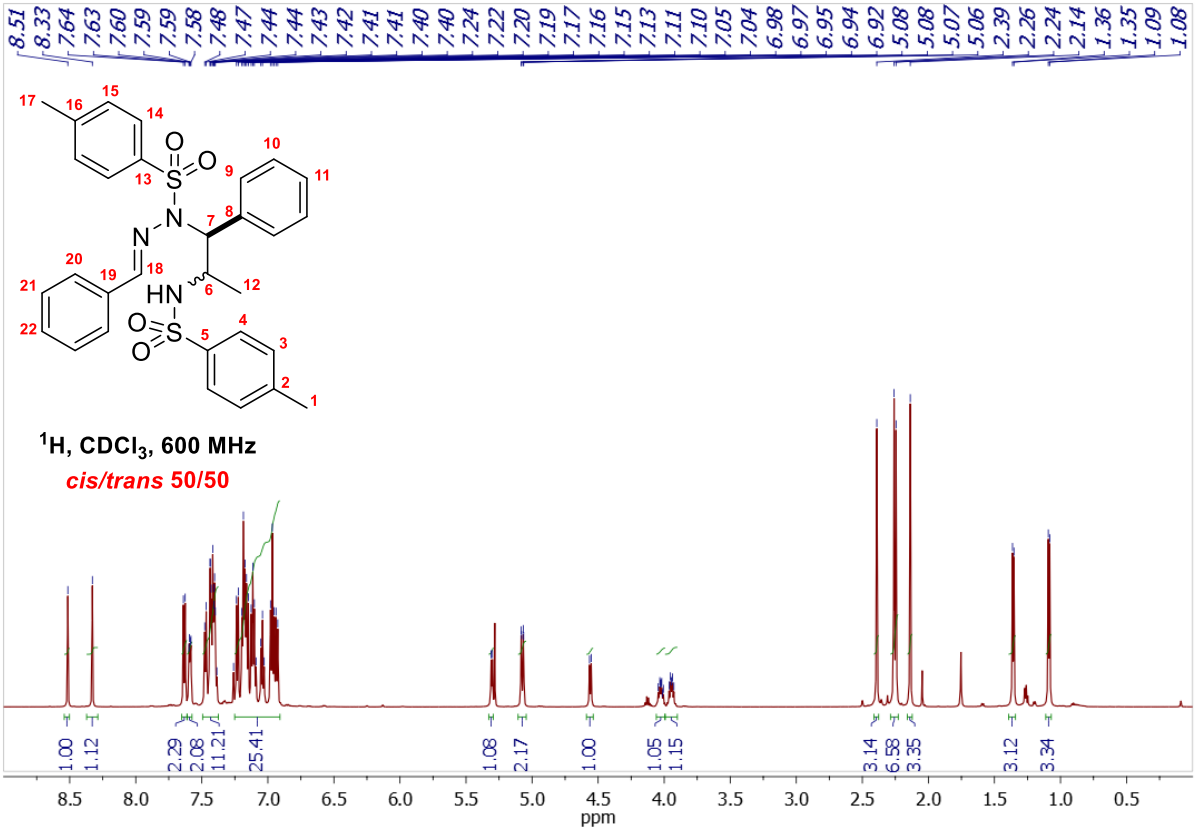


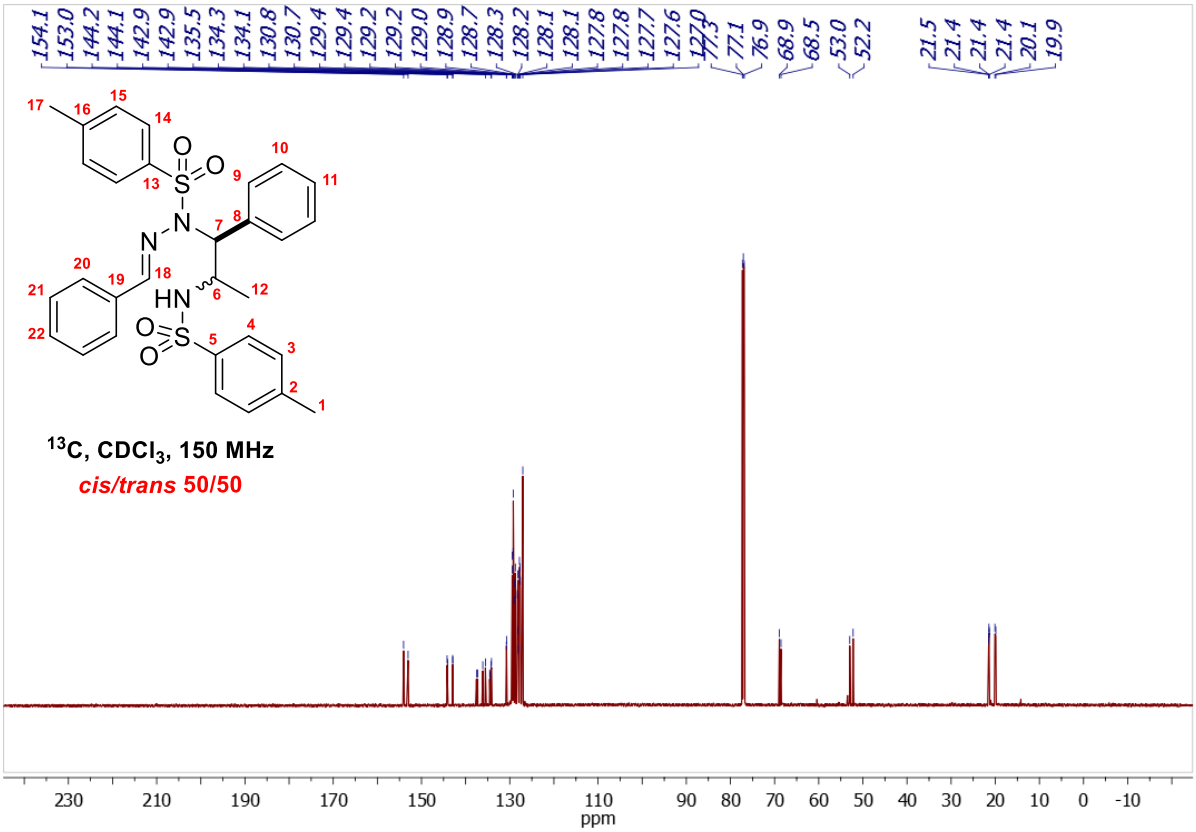



8.46
7.73
7.72
7.66
7.36
7.35
7.34
7.32
7.28
6.35
6.34
6.09
6.08
5.41
5.40
3.86
3.85
2.99
2.98
2.96
2.75
2.74
2.72
2.48
2.45
2.26
2.24
2.23
2.22
1.94
1H, CDCl3, 600 MHz
Cis diastereoisomer
1.00
2.13
2.13
7.74
3.10
1.13
1.07
0.97
0.97
0.97
1.04
0.99
1.07
1.08
3.15
3.09
1.06
1.21
ppm

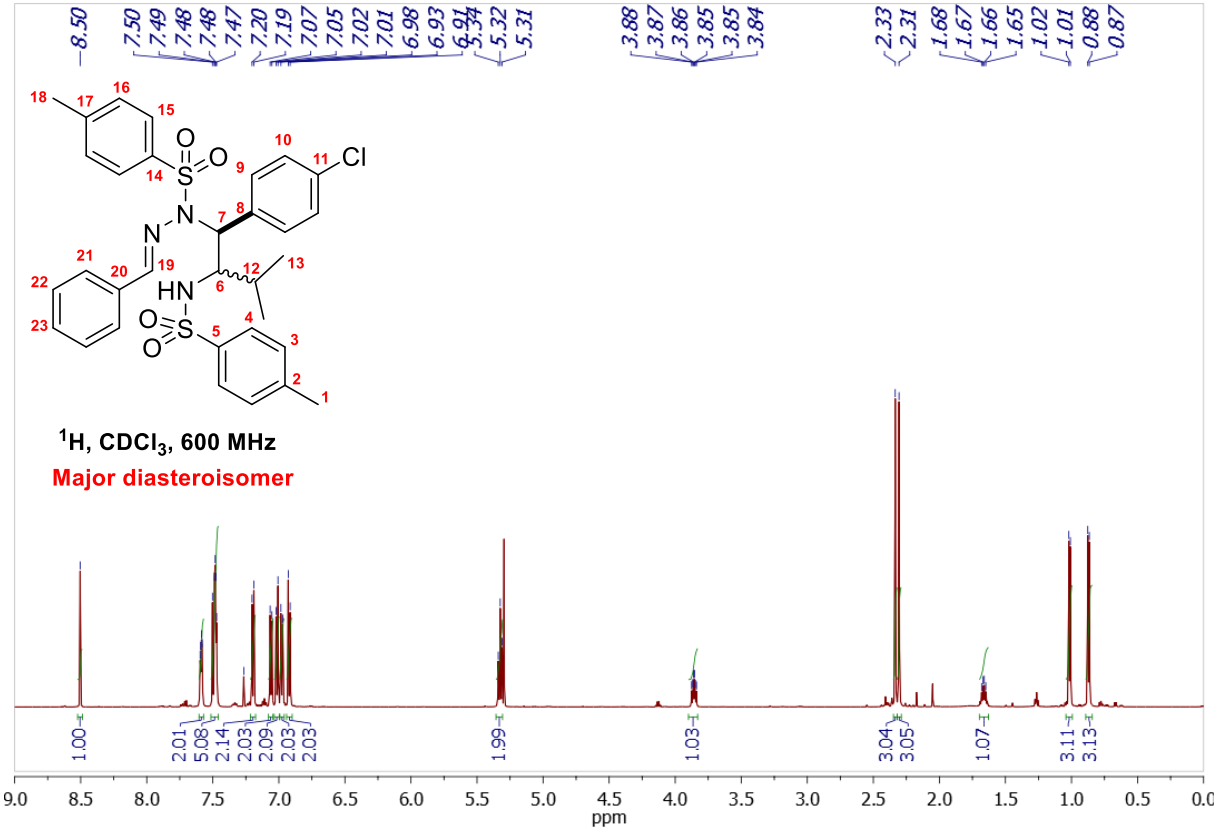

154.9
144.9
143.1
137.7
137.4
135.4
133.7
131.9
131.0
130.1
129.5
128.8
128.7
128.4
127.9
127.6
127.6
127.2
125.7
77.2
77.0
76.8
61.2
53.6
26.8
25.9
21.7
21.6
13C, CDCl3, 150 MHz
Cis diastereoisomer
ppm

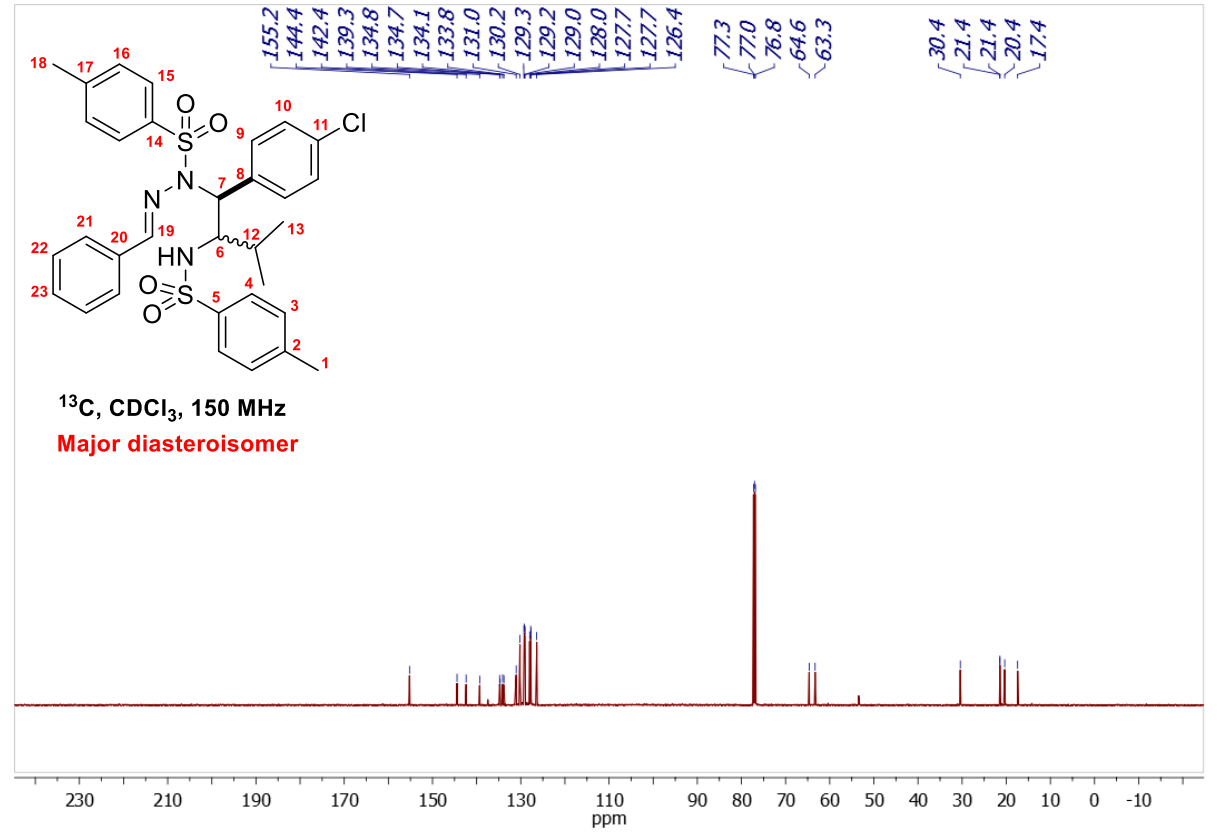
(+/-)-*N*-(1-(2-benzylidene-1-tosylhydrazinyl)-1-phenylpropan-2-yl)-4-methylbenzenesulfonamide (3v)

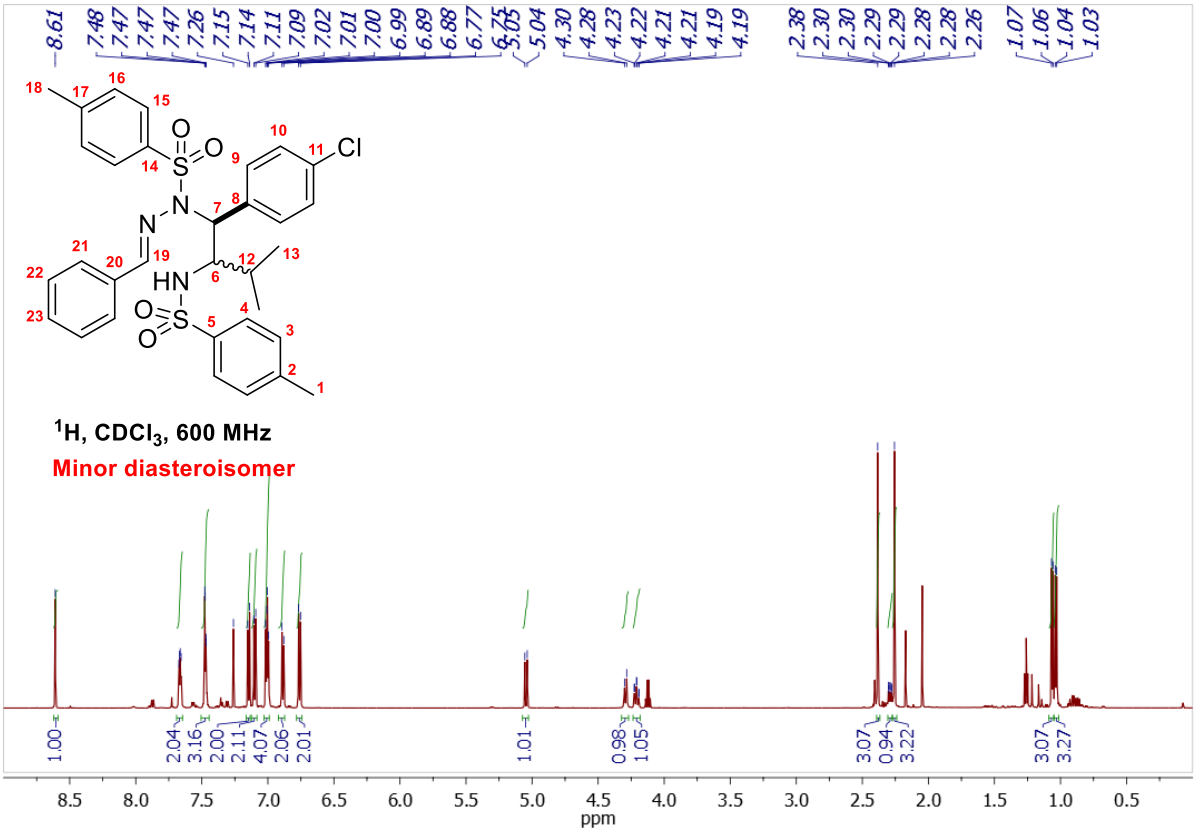


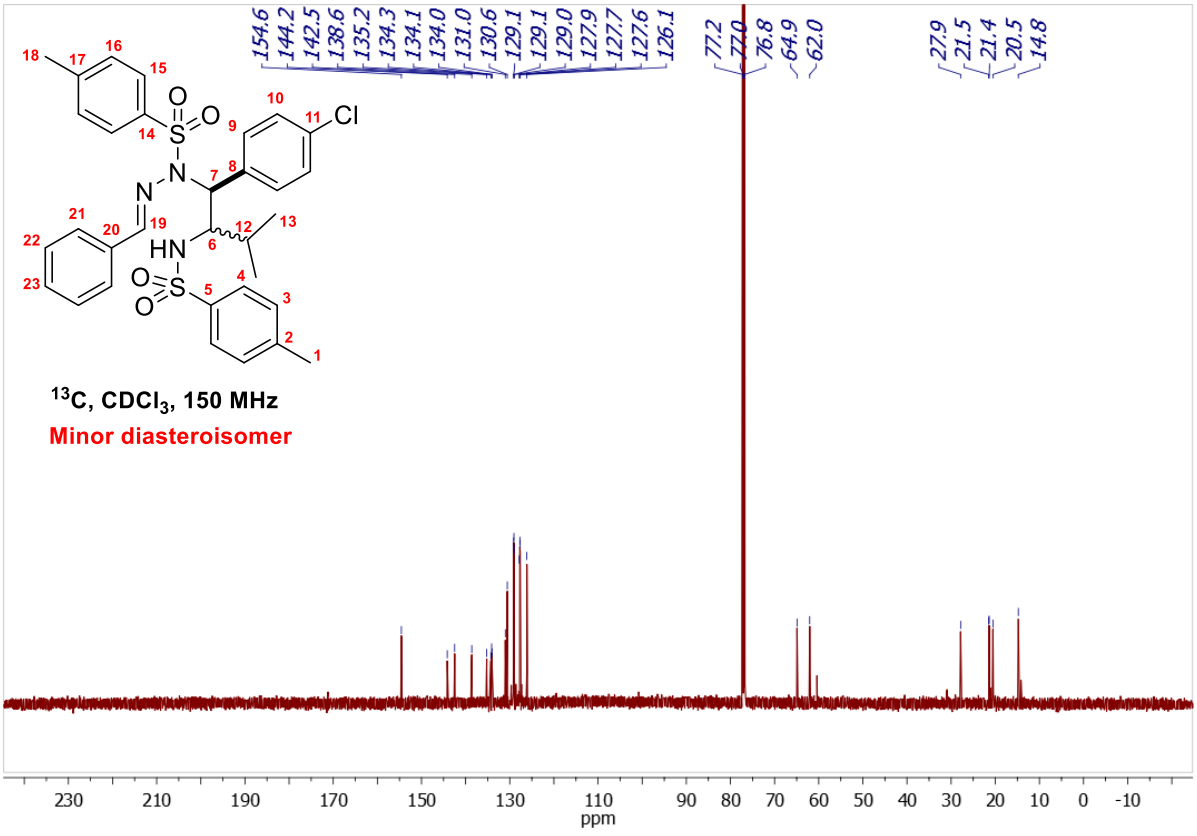


(+/-)-*N*-(1-(2-benzylidene-1-tosylhydrazinyl)-1-(4-chlorophenyl)-3-methylbutan-2-yl)-4-methylbenzenesulfonamide (3w)

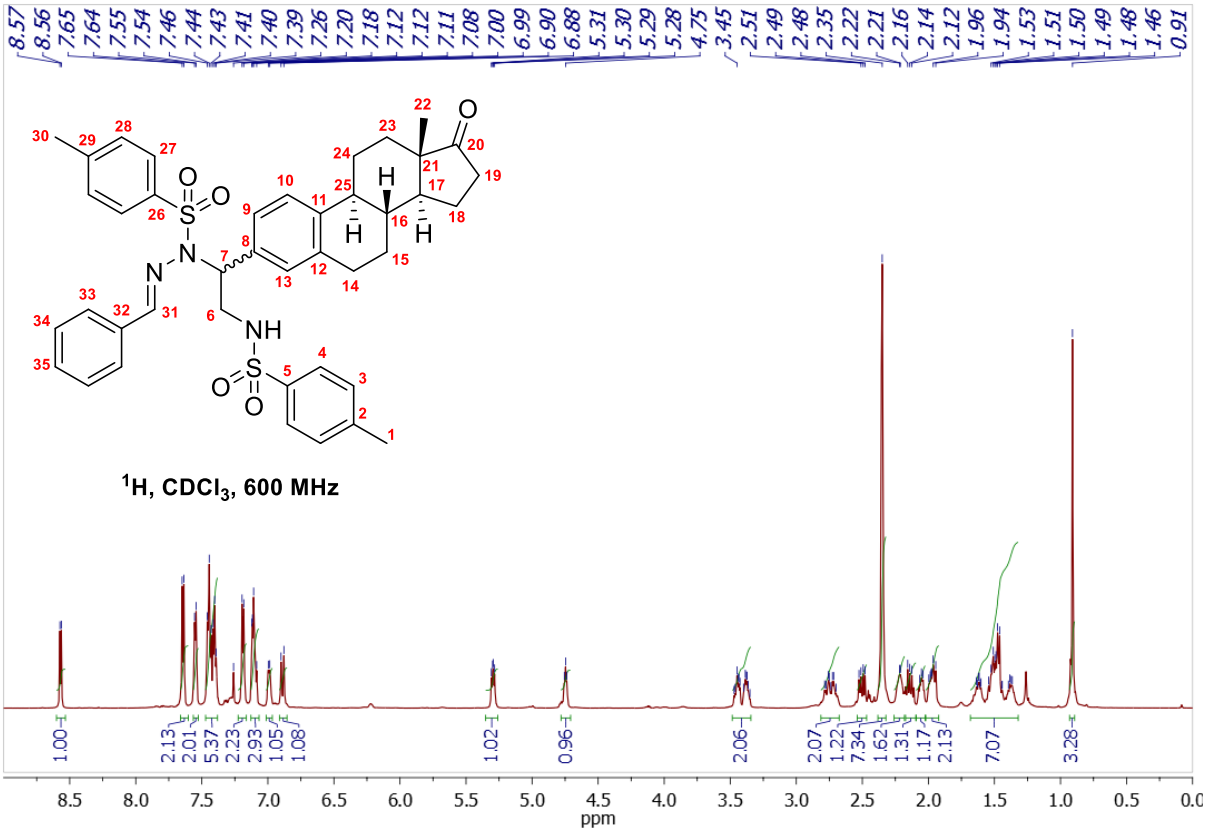


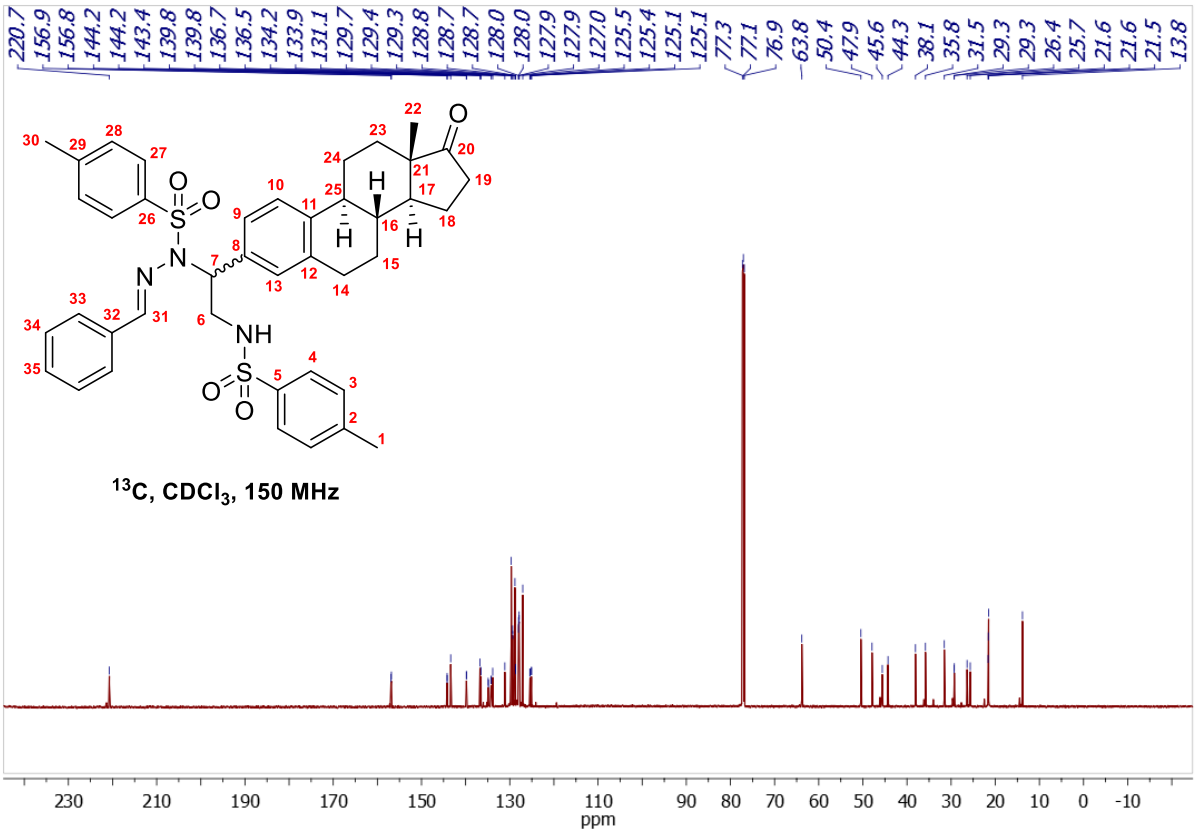



8.61
7.48
7.47
7.47
7.47
7.26
7.15
7.14
7.11
7.09
7.02
7.01
7.00
6.99
6.89
6.88
6.77
6.75
6.05
5.04
4.30
4.28
4.23
4.22
4.21
4.21
4.19
4.19
2.38
2.30
2.30
2.29
2.29
2.28
2.28
2.26
1.07
1.06
1.04
1.03
Cl
HN
^{1}H, CDCl$_3$, 600 MHz
Minor diasteroisomer
1.00
2.04
3.16
2.00
2.11
4.07
2.06
2.01
1.01
0.98
1.05
3.07
0.94
3.22
3.07
3.27
ppm

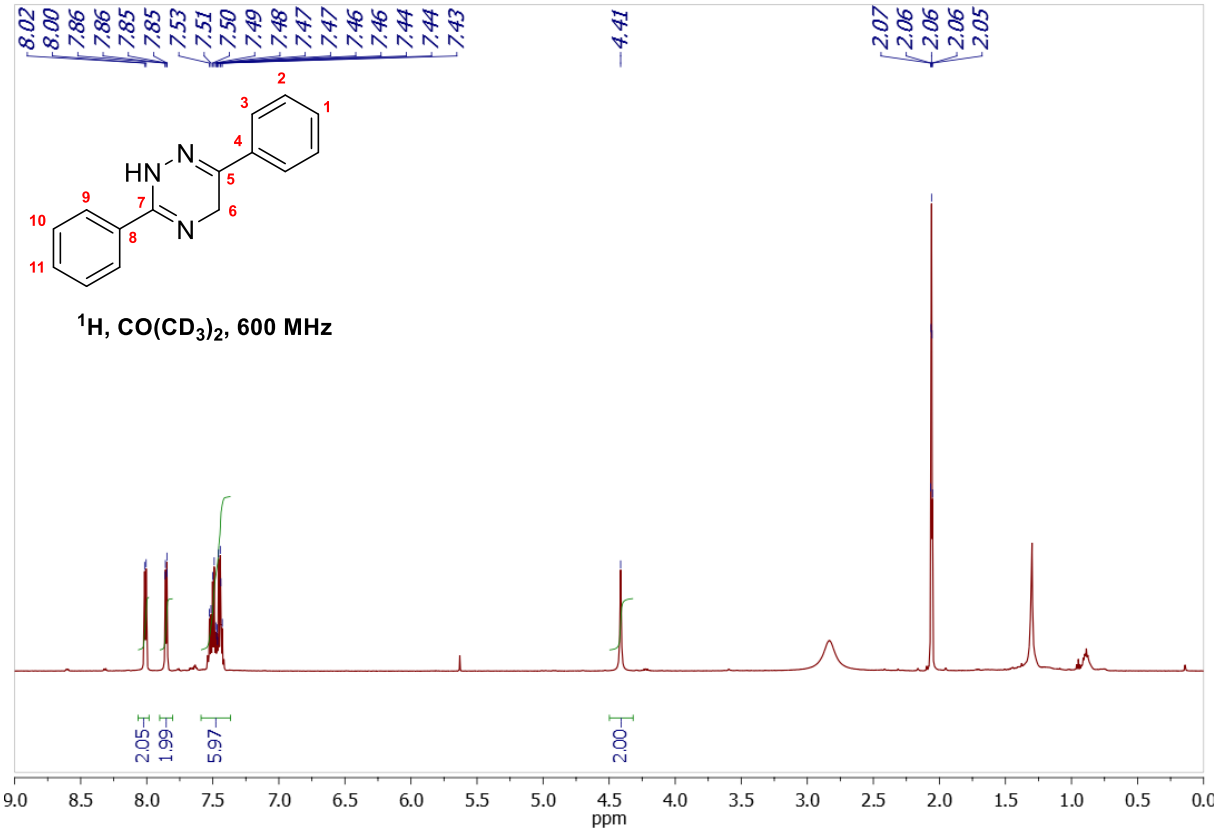

154.6
144.2
142.5
138.6
135.2
134.3
134.1
134.0
131.0
130.6
129.1
129.1
129.0
127.9
127.7
127.6
126.1
77.2
77.0
76.8
64.9
62.0
27.9
21.5
21.4
20.5
14.8
Cl
HN
^{13}C, CDCl$_3$, 150 MHz
Minor diasteroisomer
ppm

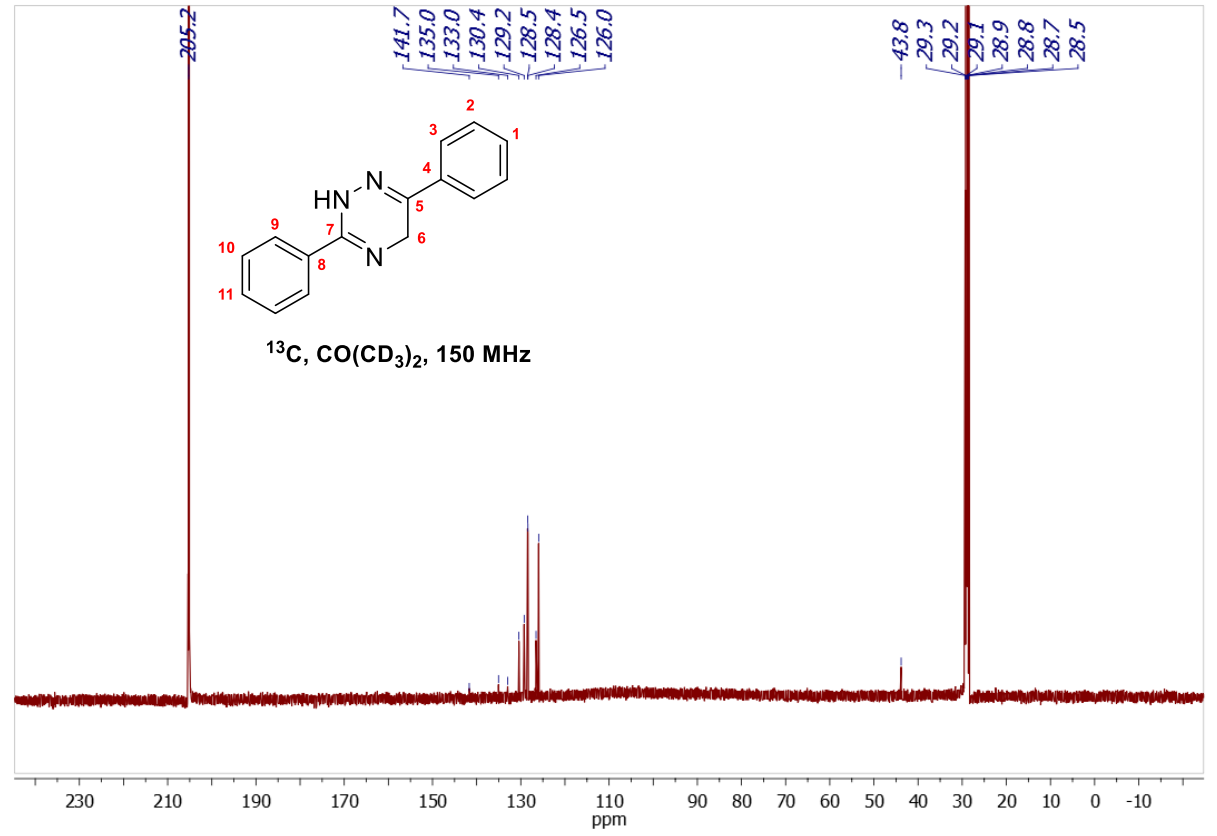
(+/-)-(2-(2-(benzylidene)-1-tosylhydrazinyl)-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)ethyl)-4-methylbenzenesulfonamide (3y)



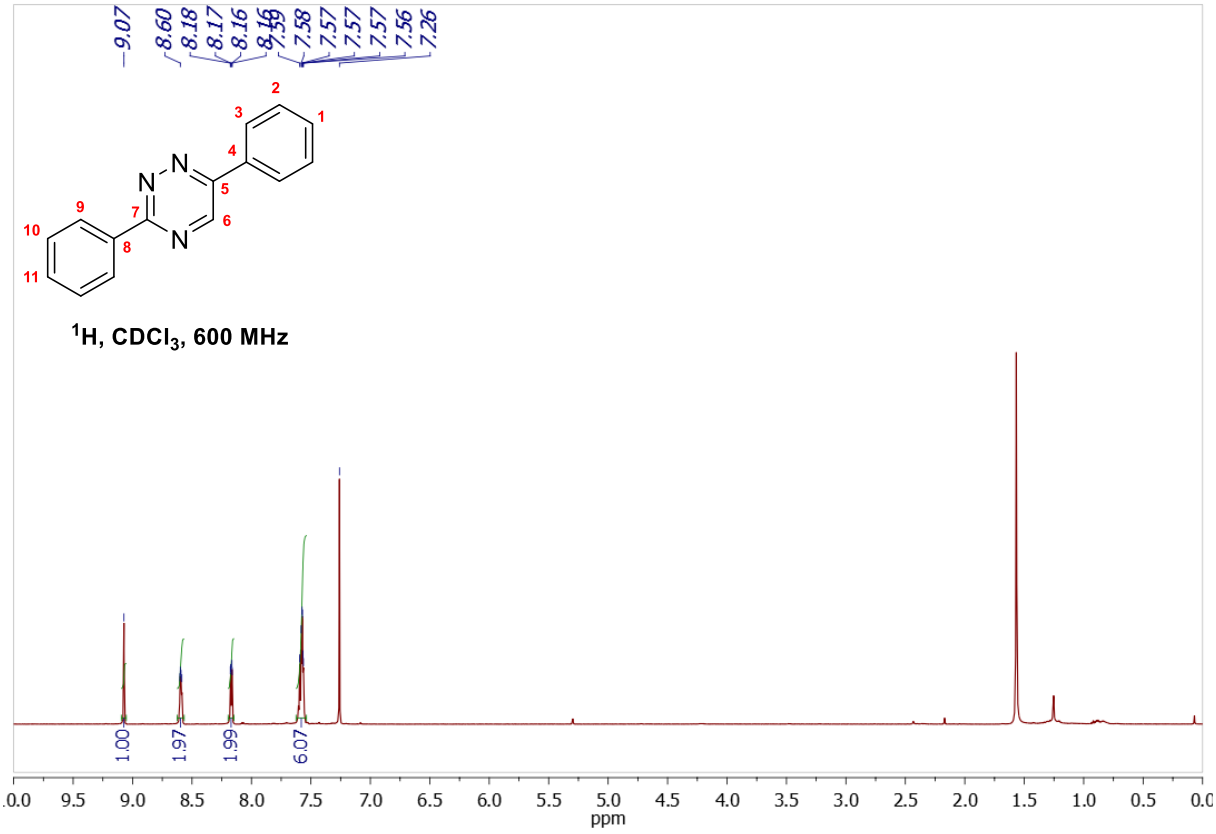


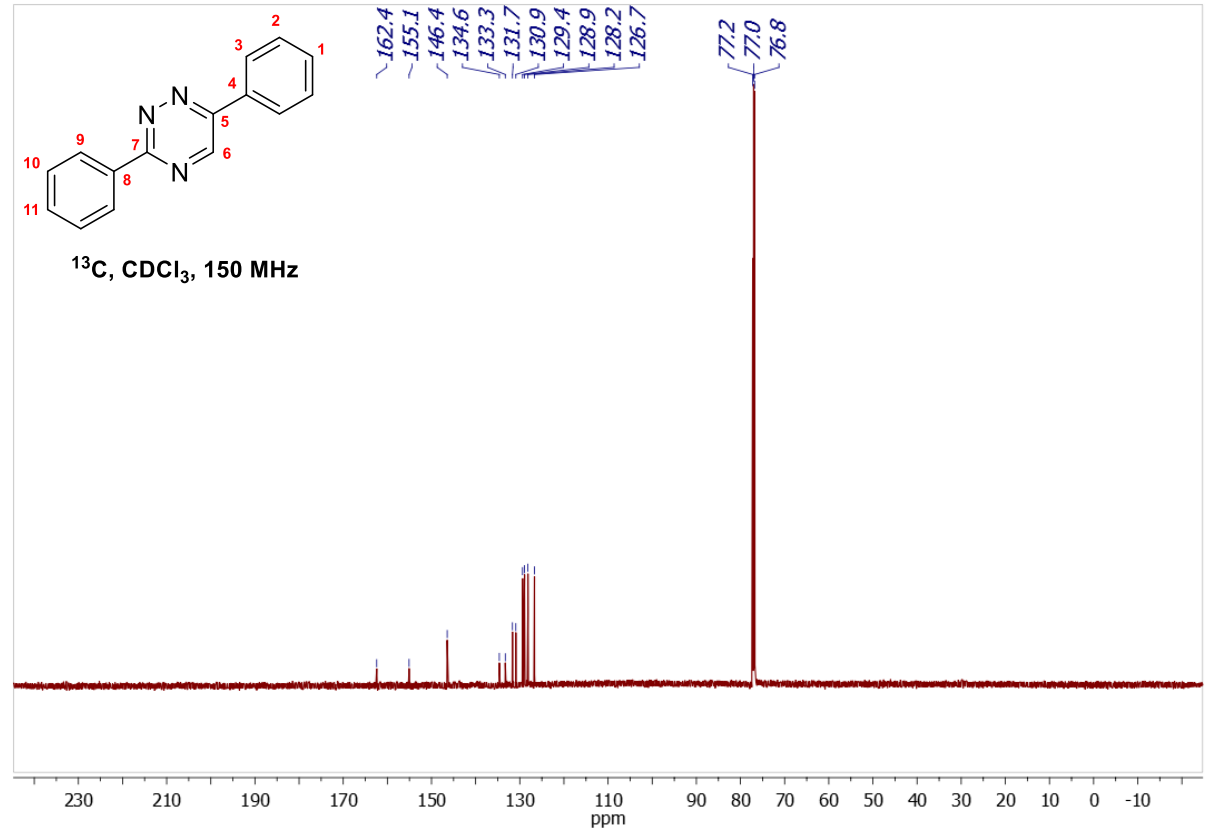
3,6-diphenyl-2,5-dihydro-1,2,4-triazine (4a)



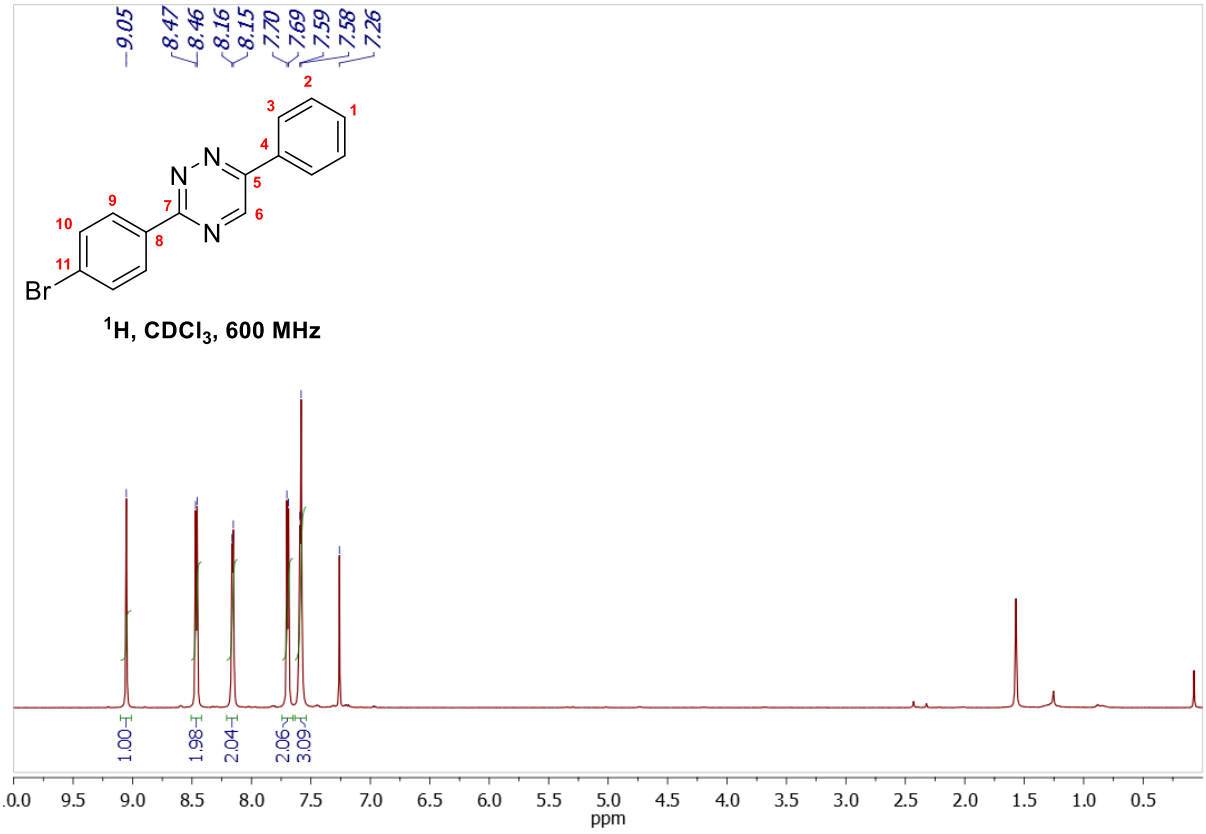


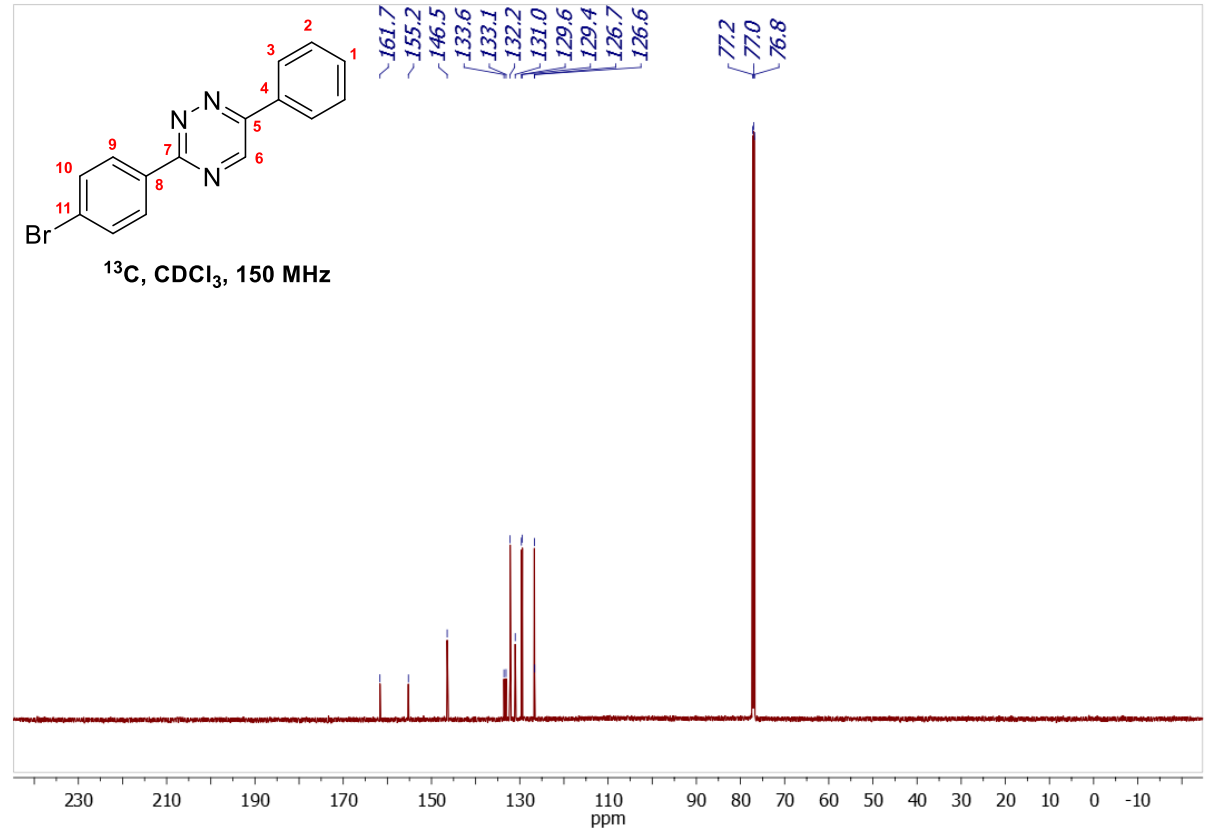
3,6-diphenyl-1,2,4-triazine (5a)



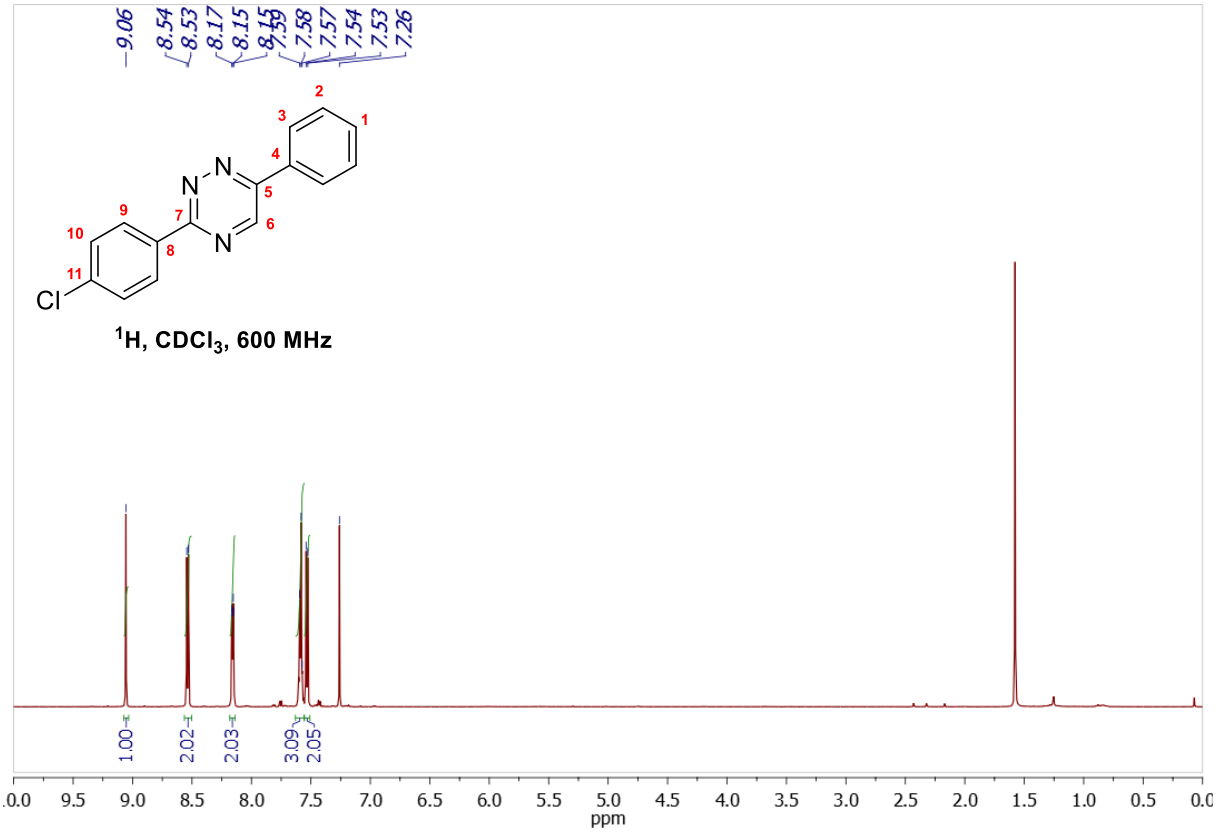


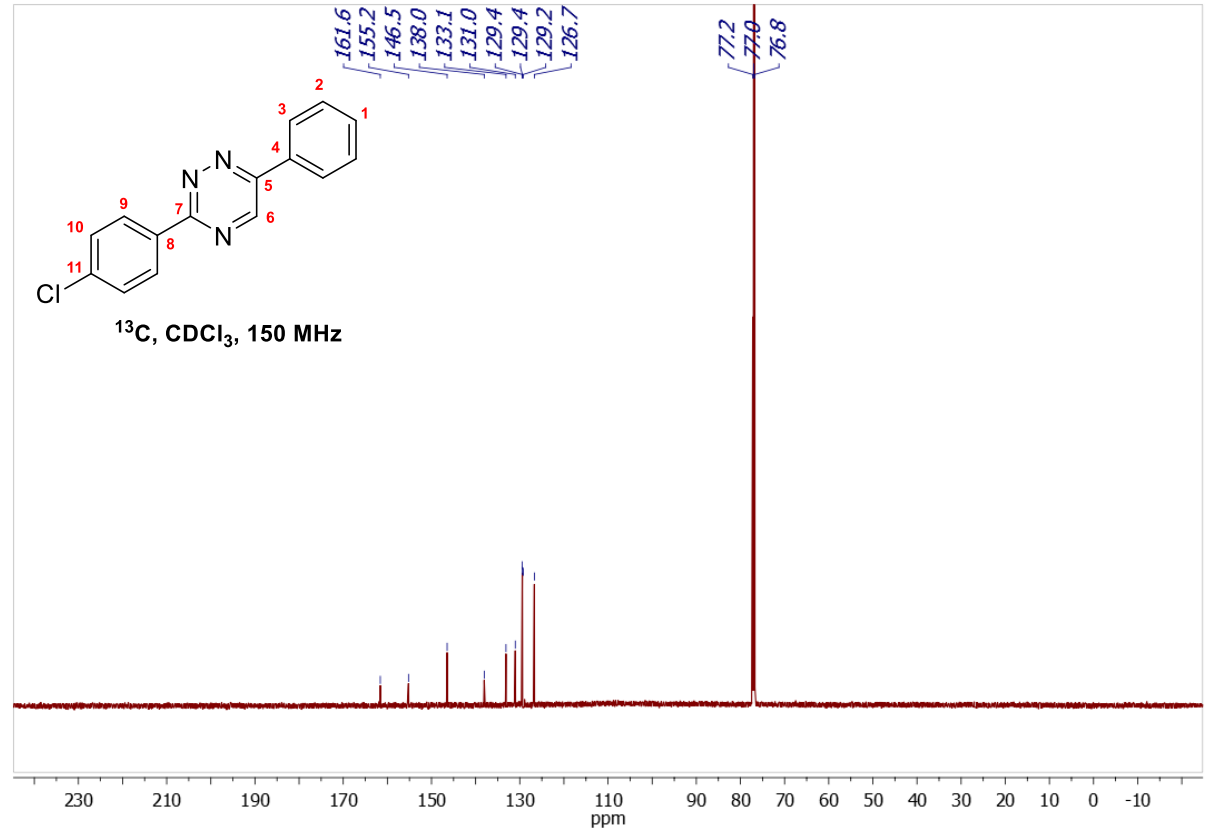
3-(4-bromophenyl)-6-phenyl-1,2,4-triazine (5b)



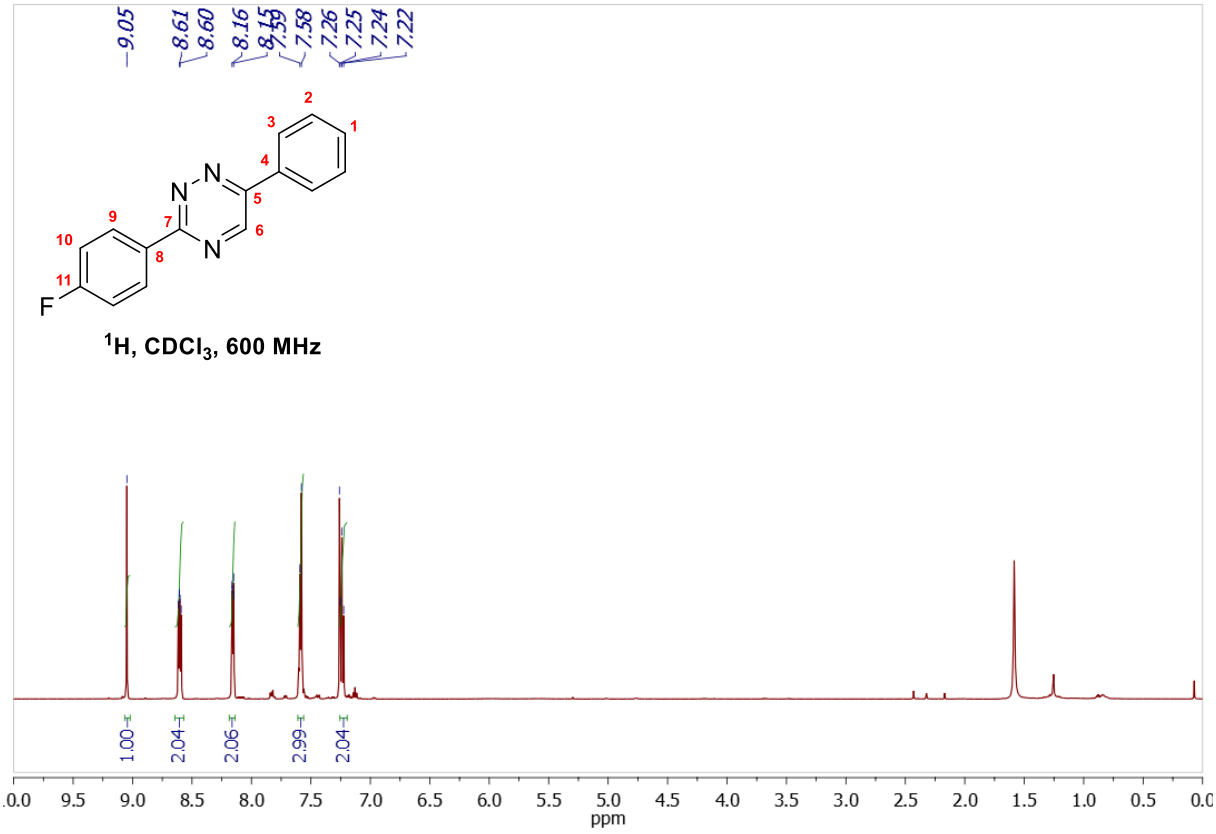


3-(4-chlorophenyl)-6-phenyl-1,2,4-triazine (5c)

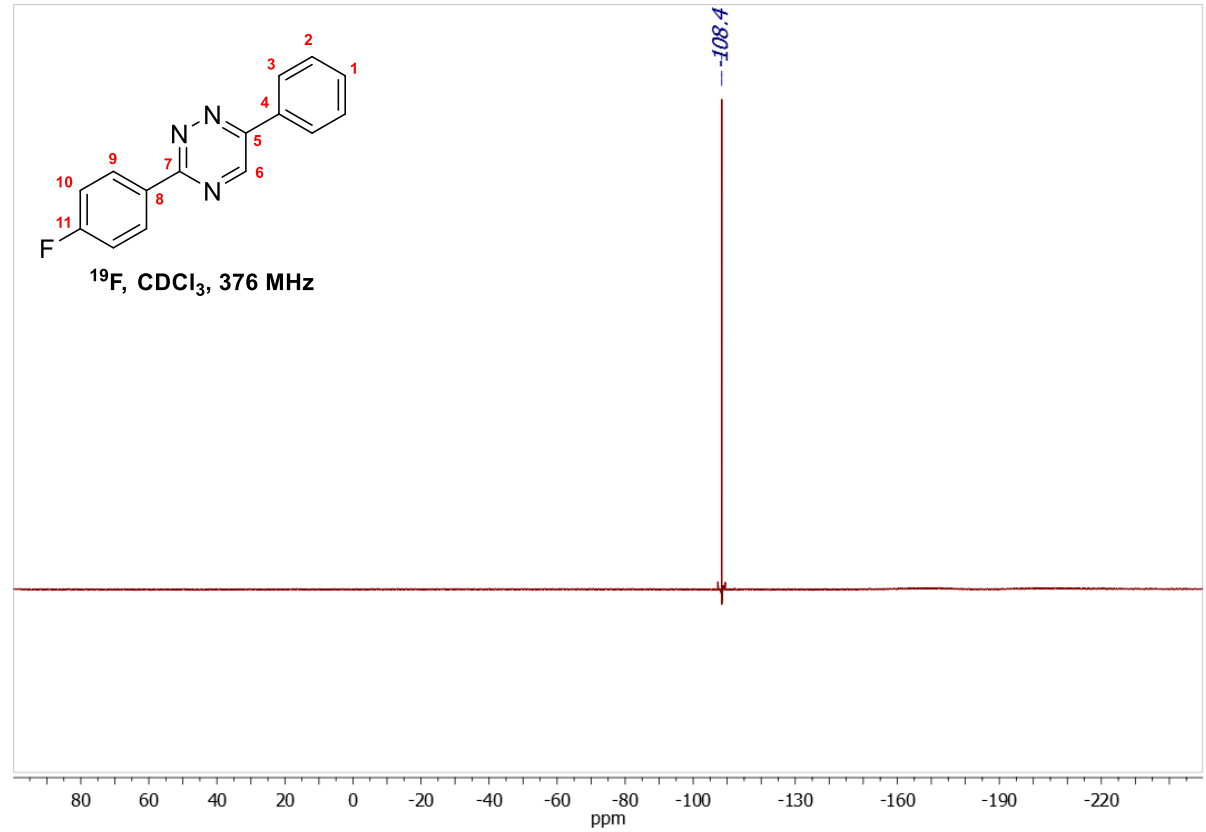




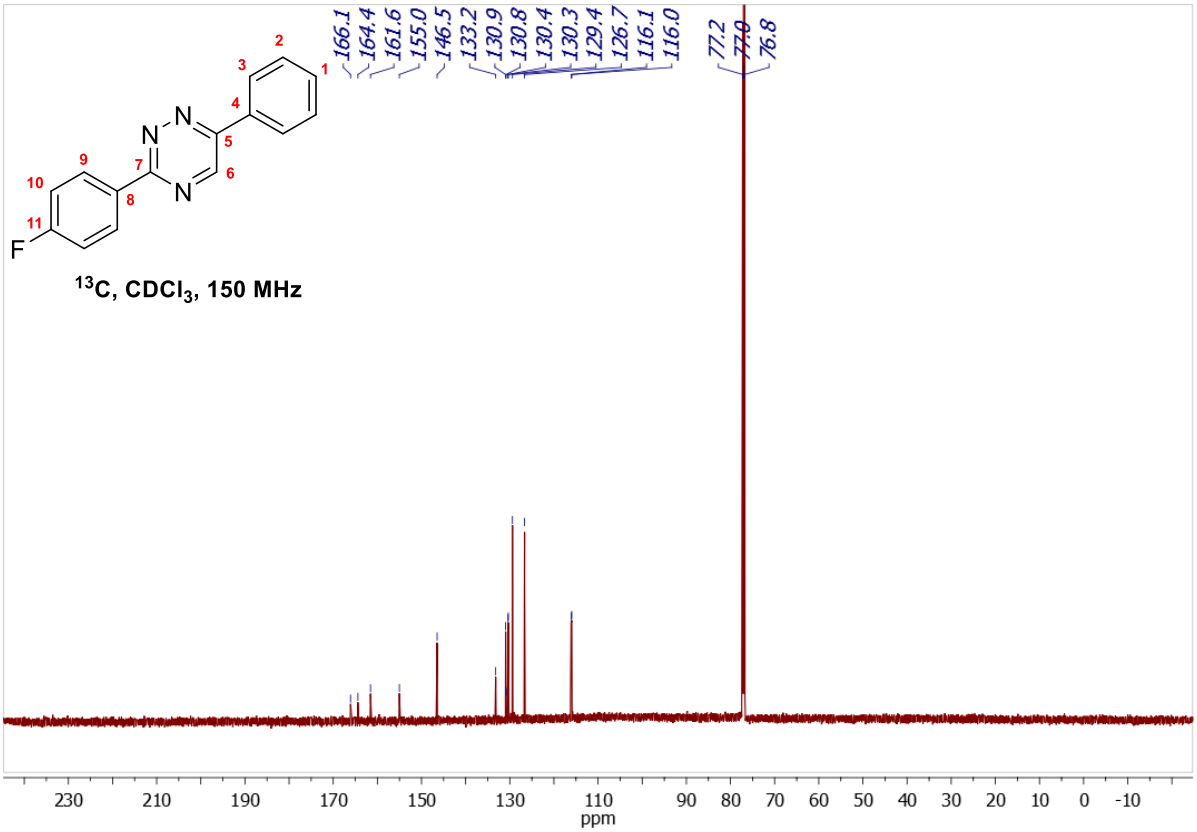
3-(4-fluorophenyl)-6-phenyl-1,2,4-triazine (5d)



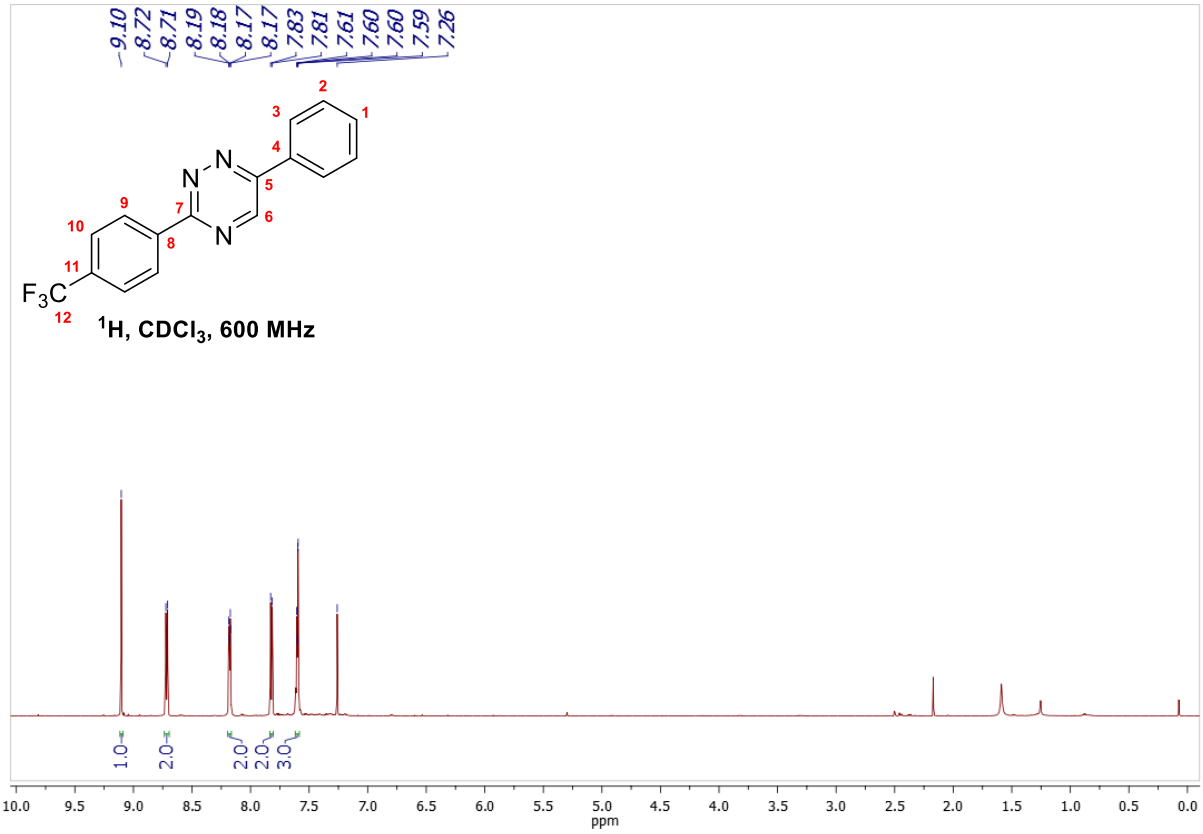
^{1}H, $CDCl_3$, 600 MHz



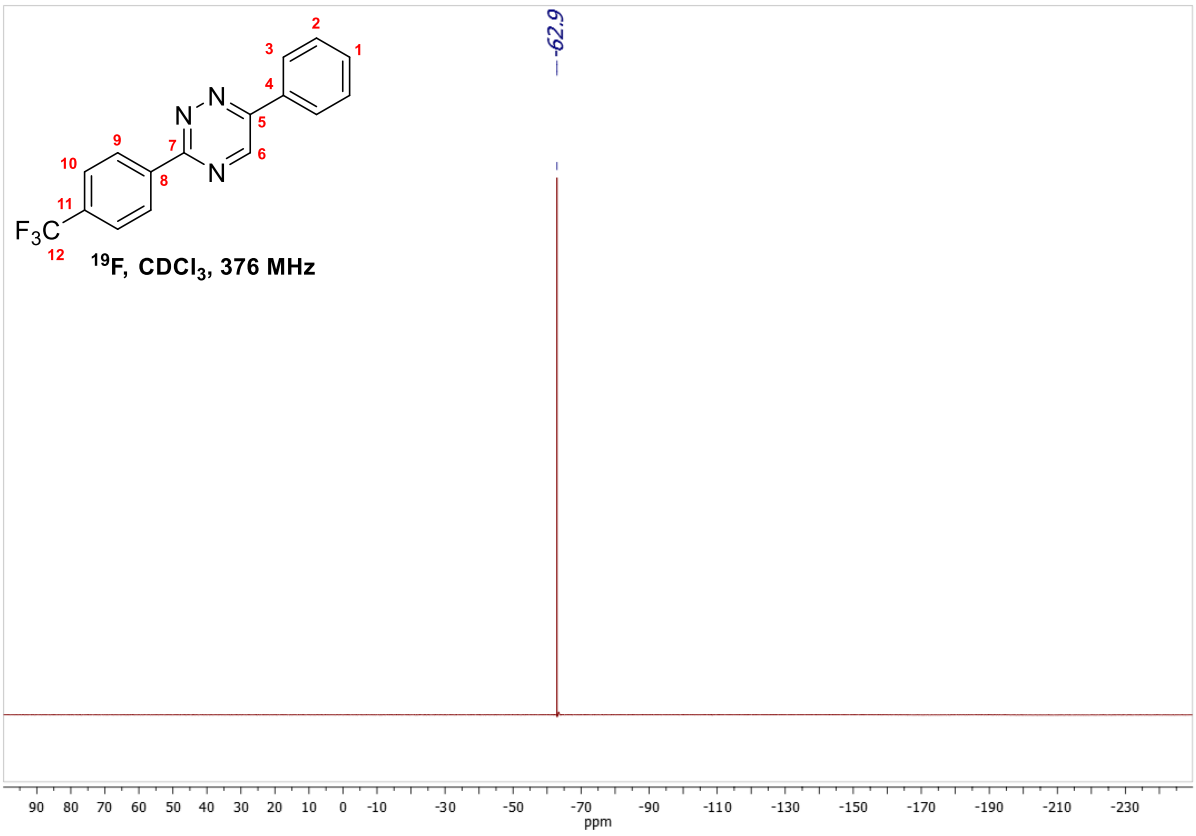
^{19}F, $CDCl_3$, 376 MHz


166.1
164.4
161.6
155.0
146.5
133.2
130.9
130.8
130.4
130.3
129.4
126.7
116.1
116.0
77.2
77.0
76.8
1
2
3
4
5
6
7
8
9
10
11
N
N
F
13C, CDCl3, 150 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

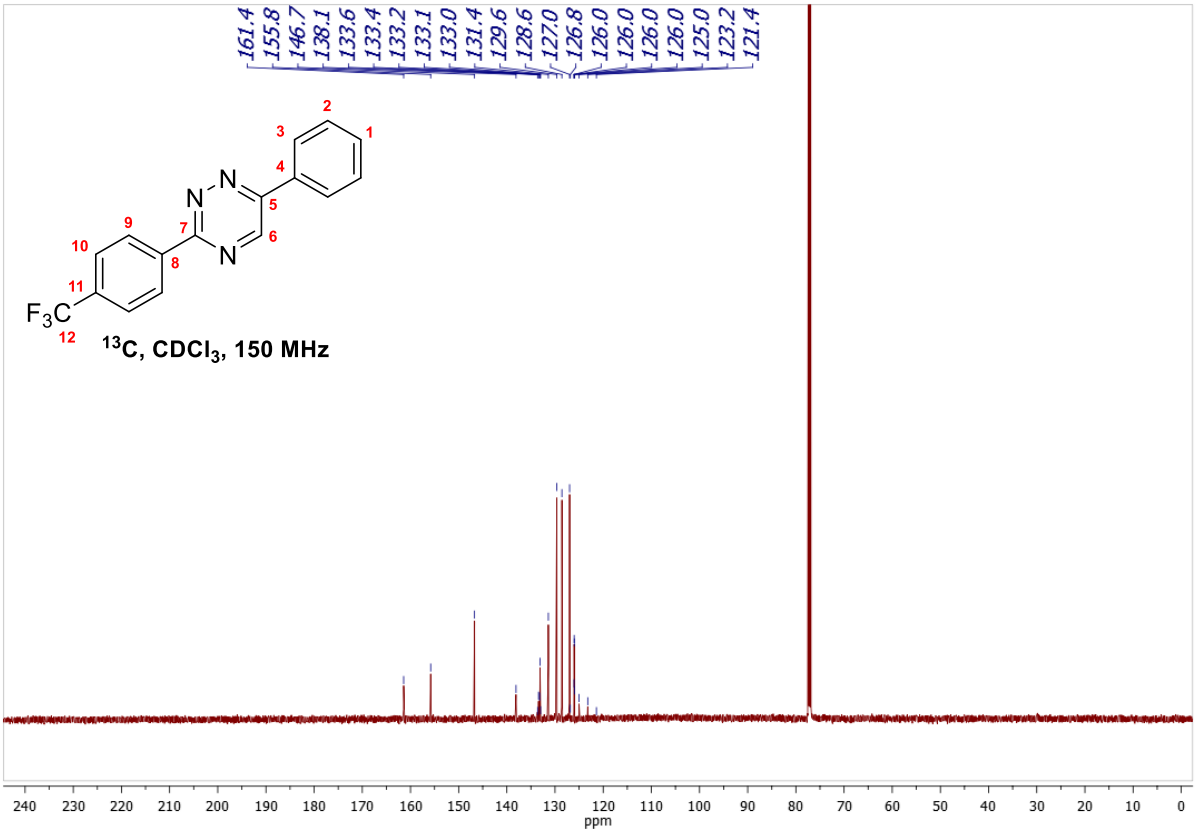
6-phenyl-3-(4-(trifluoromethyl)phenyl)-1,2,4-triazine (5e)



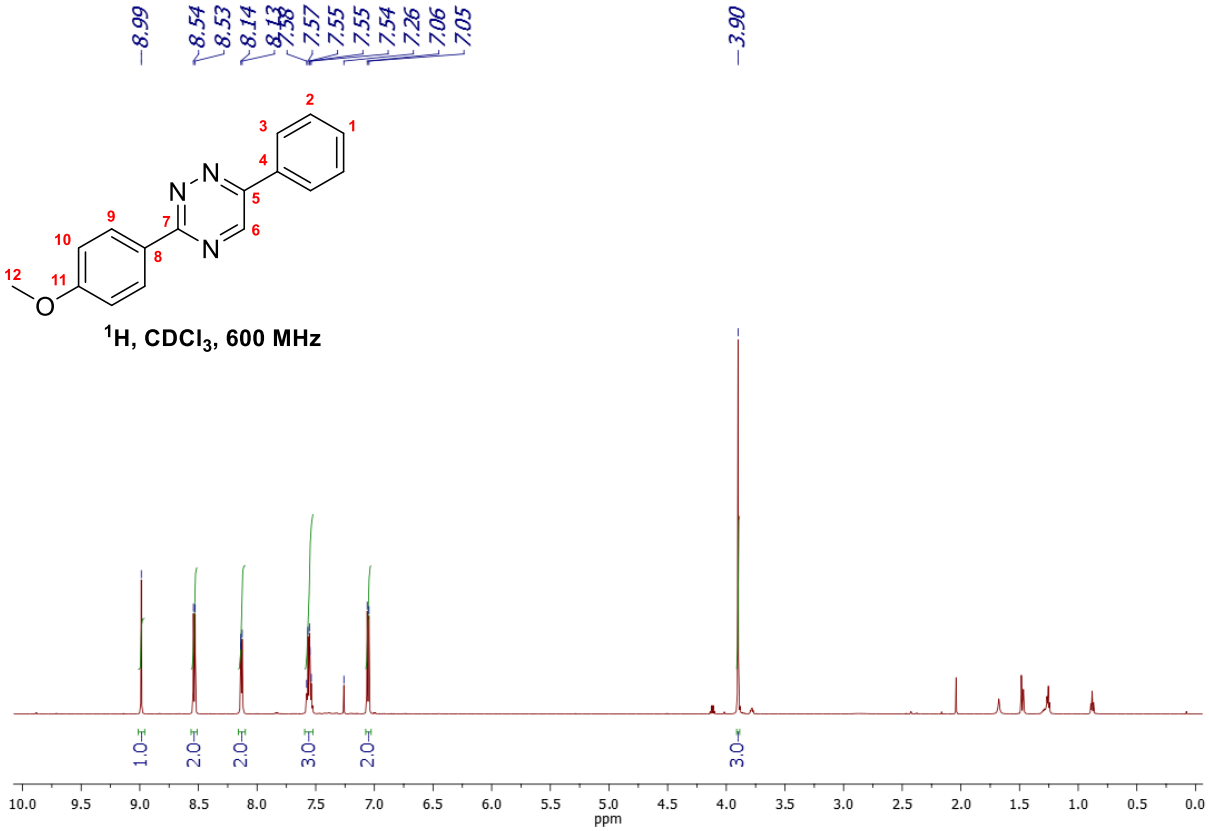
^{1}H, $CDCl_3$, 600 MHz



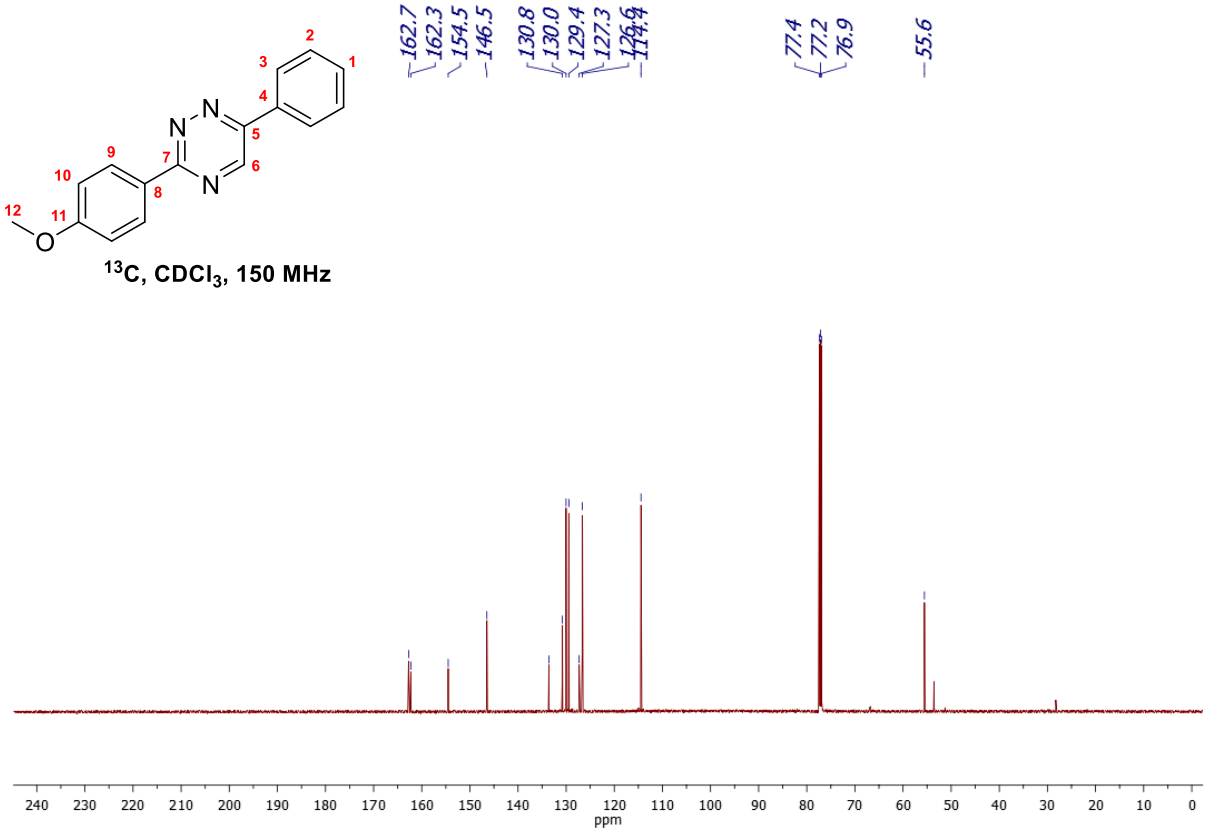
^{19}F, $CDCl_3$, 376 MHz


161.4
155.8
146.7
138.1
133.6
133.4
133.2
133.1
133.0
131.4
129.6
128.6
127.0
126.8
126.0
126.0
126.0
126.0
125.0
123.2
121.4
1
2
3
4
5
6
7
8
9
10
11
12
N
N
N
F3C
13C, CDCl3, 150 MHz
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3-(4-methoxyphenyl)-6-phenyl-1,2,4-triazine (5f)

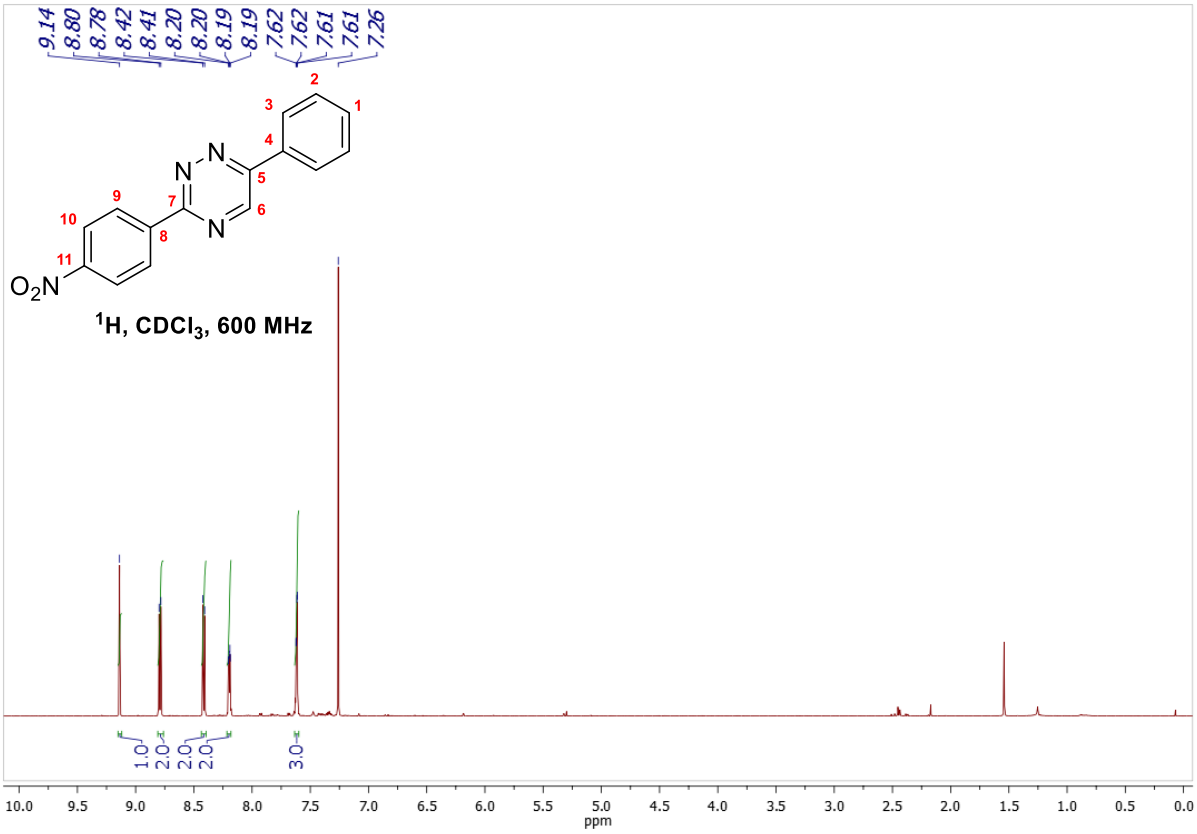


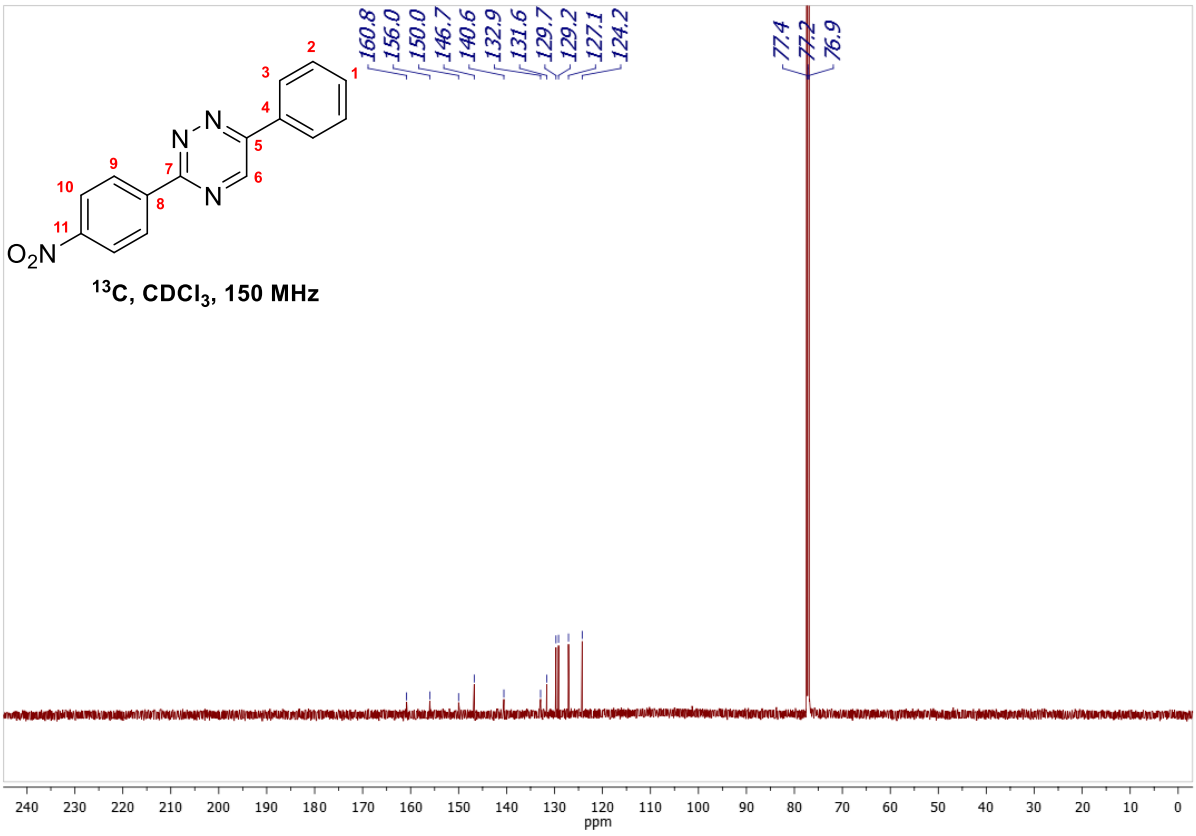
^{1}H, $CDCl_3$, 600 MHz



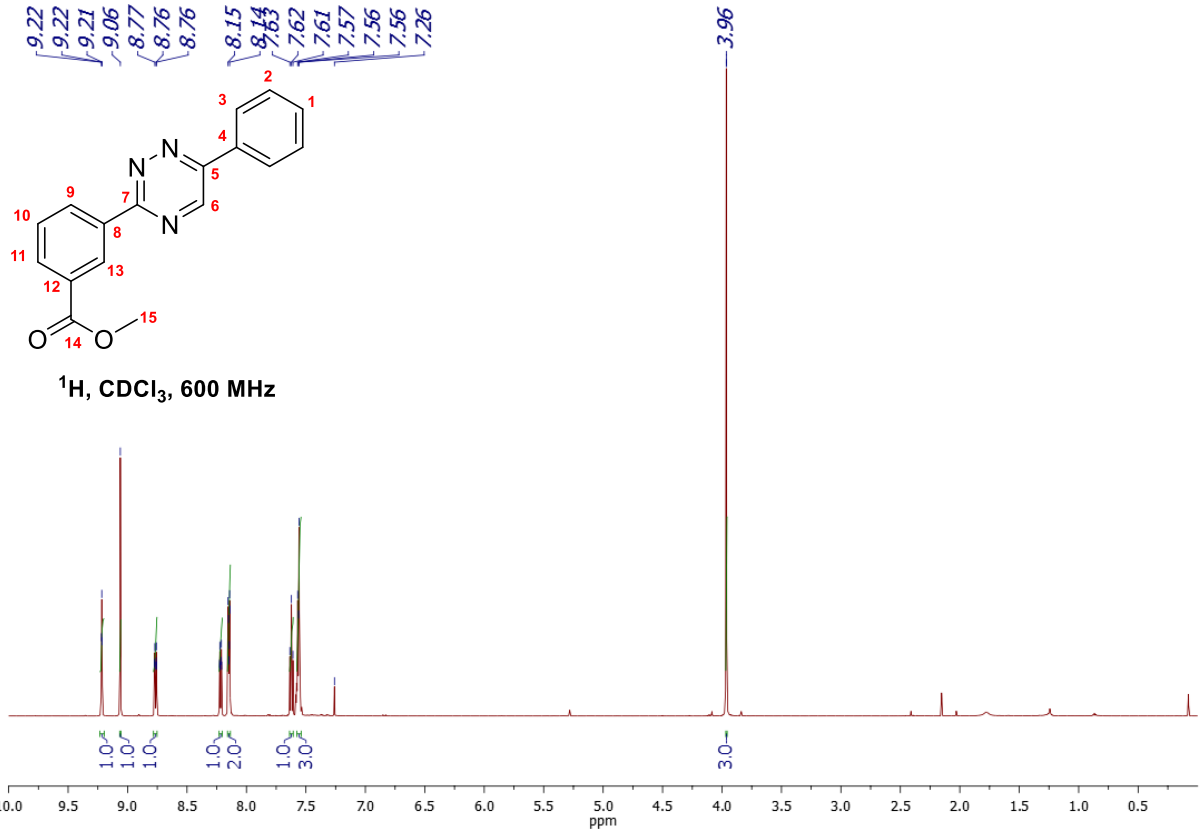
^{13}C, $CDCl_3$, 150 MHz

3-(4-nitrophenyl)-6-phenyl-1,2,4-triazine (5g)

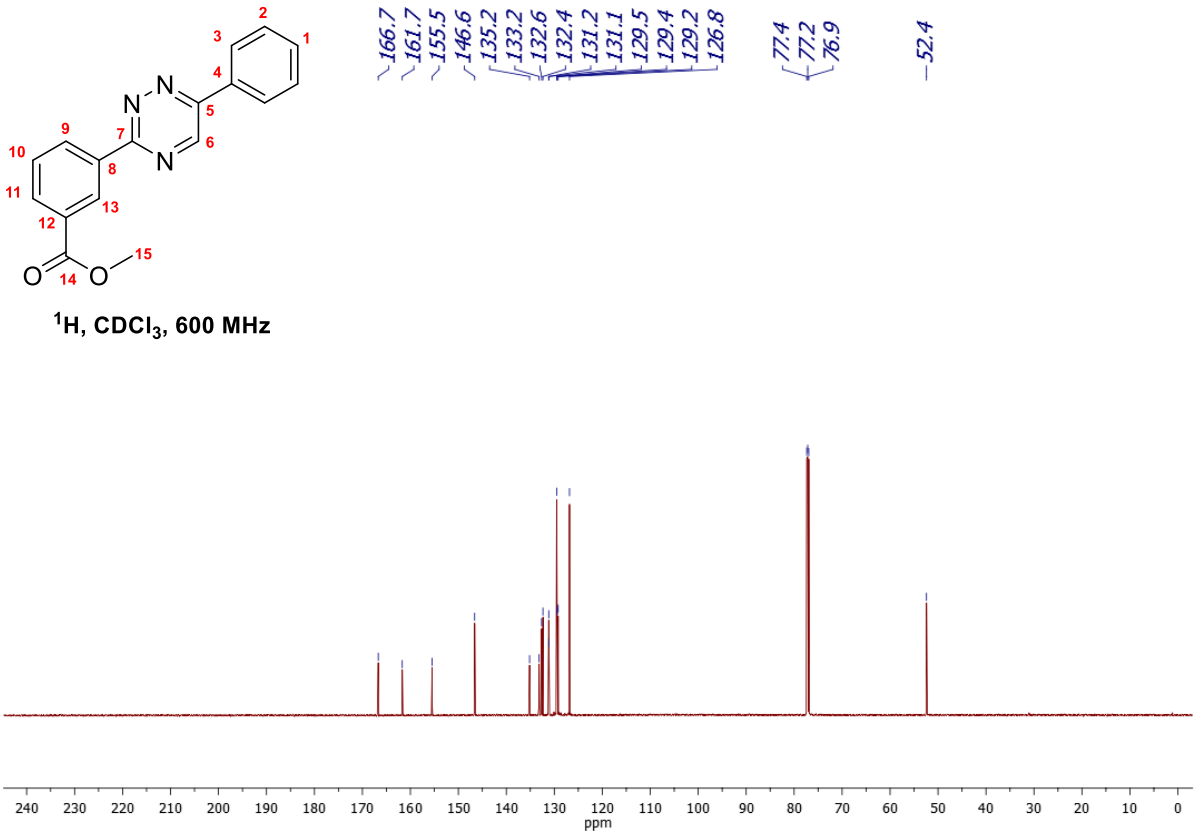




methyl 3-(6-phenyl-1,2,4-triazin-3-yl)benzoate (5h)

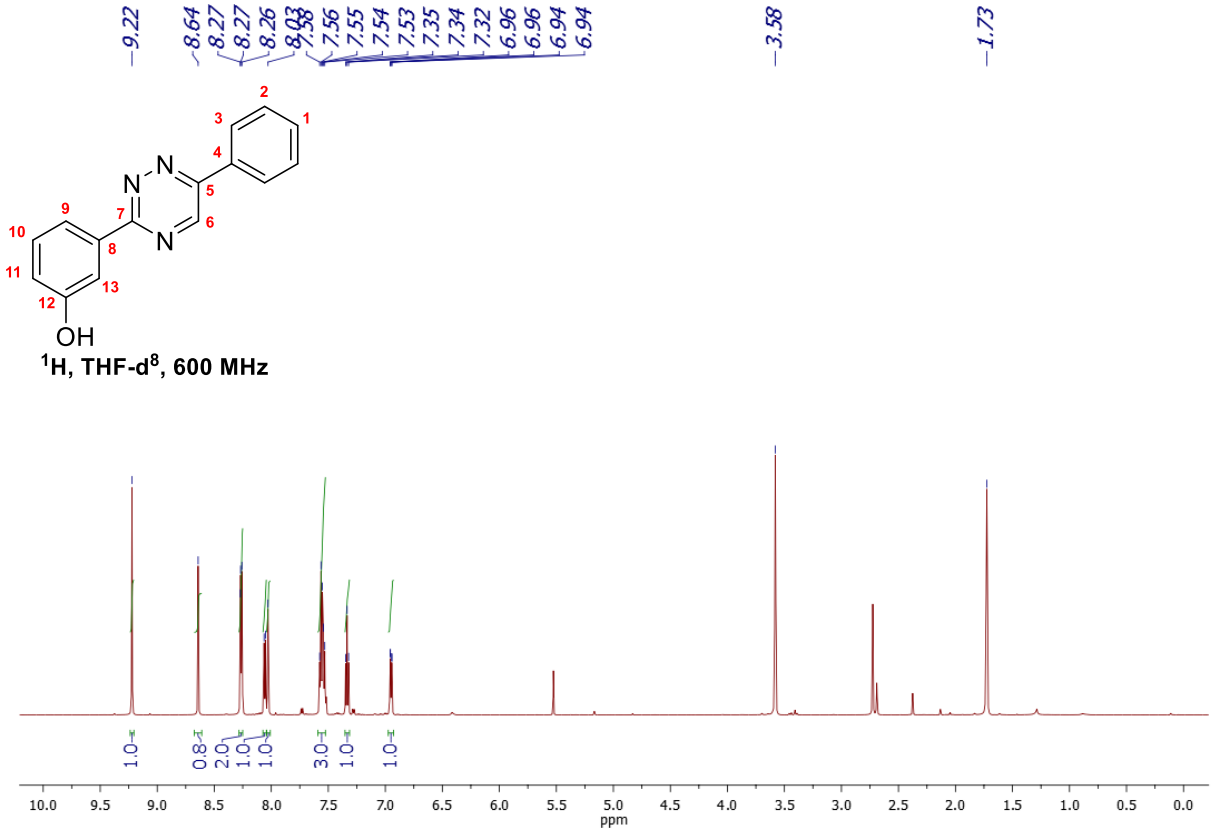


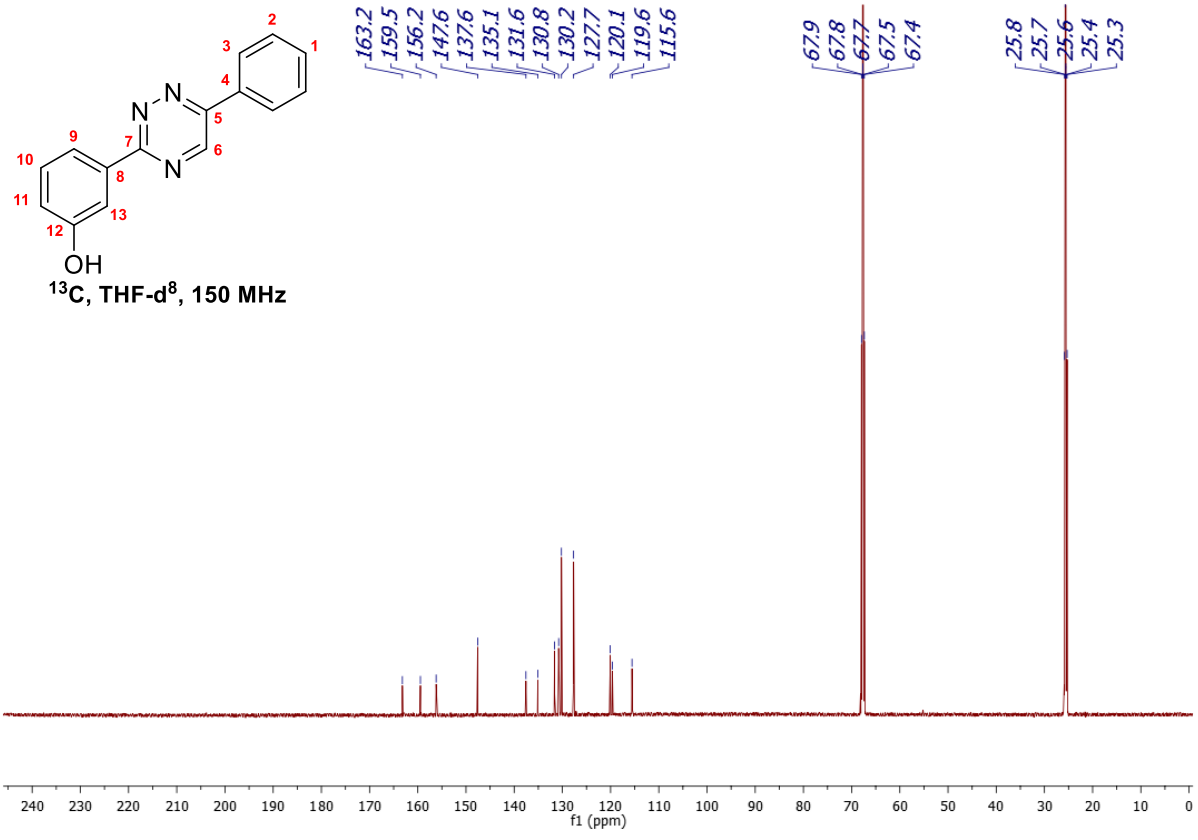
^{1}H, $CDCl_3$, 600 MHz



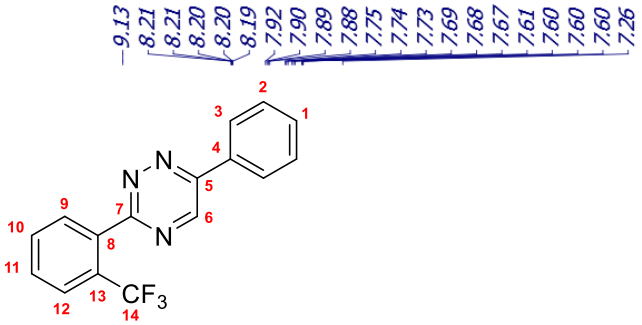
^{1}H, $CDCl_3$, 600 MHz

3-(6-phenyl-1,2,4-triazin-3-yl)phenol (5i)

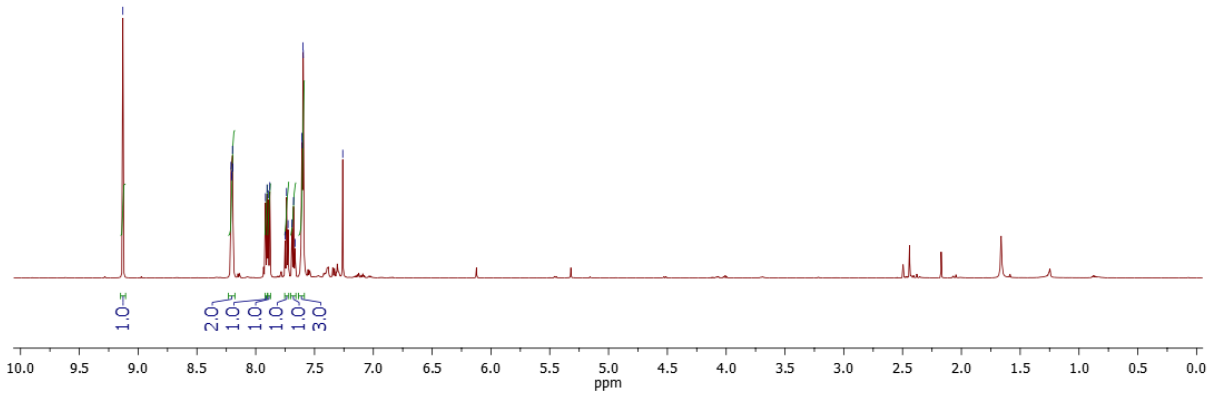


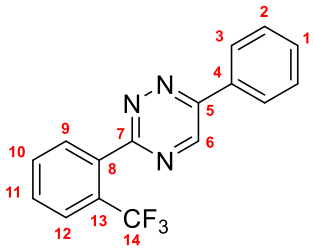


6-phenyl-3-(2-(trifluoromethyl)phenyl)-1,2,4-triazine (5j)

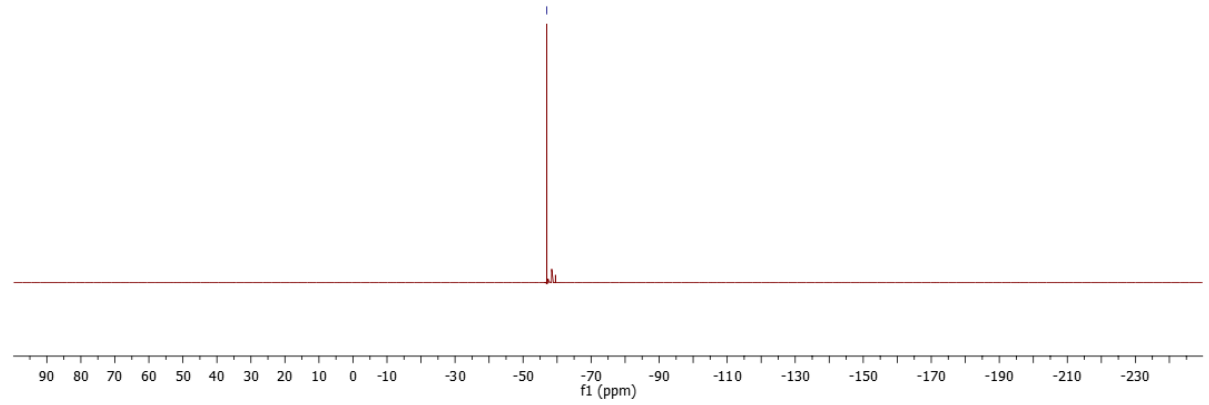


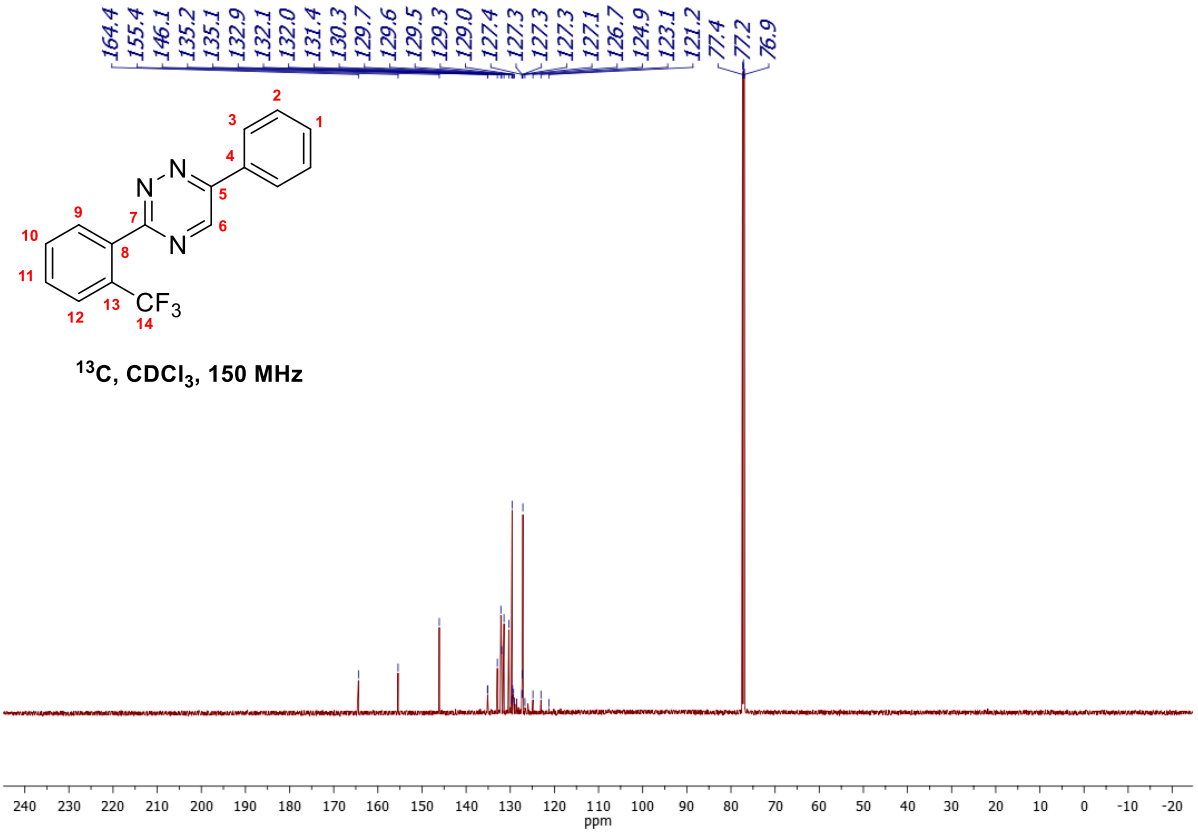
^{1}H, $CDCl_3$, 600 MHz





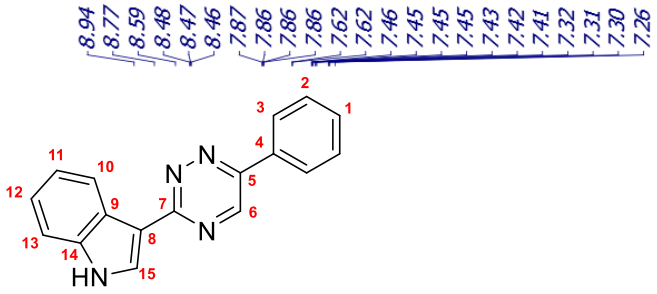
^{19}F, $CDCl_3$, 376 MHz



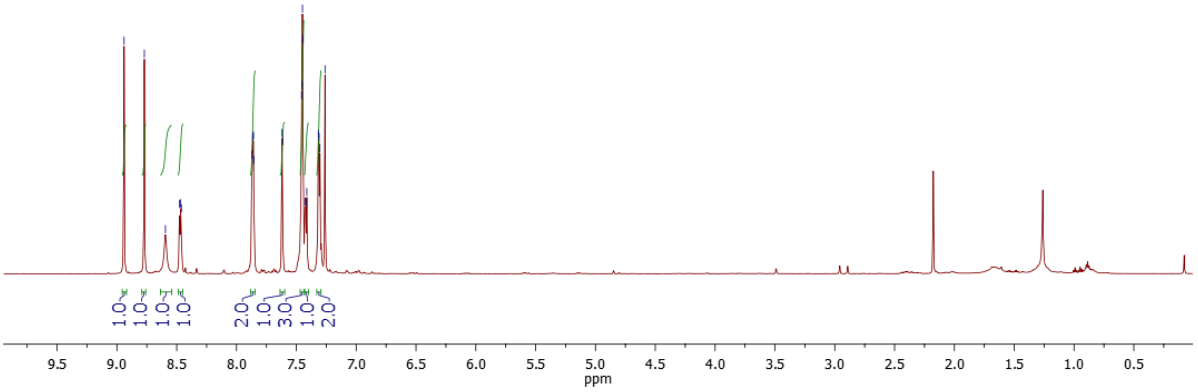


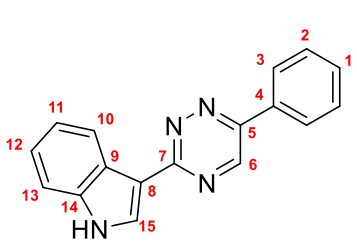
^{13}C, $CDCl_3$, 150 MHz

1-(3-(6-phenyl-1,2,4-triazin-3-yl)-1H-indol-1-yl)ethan-1-one (5k)



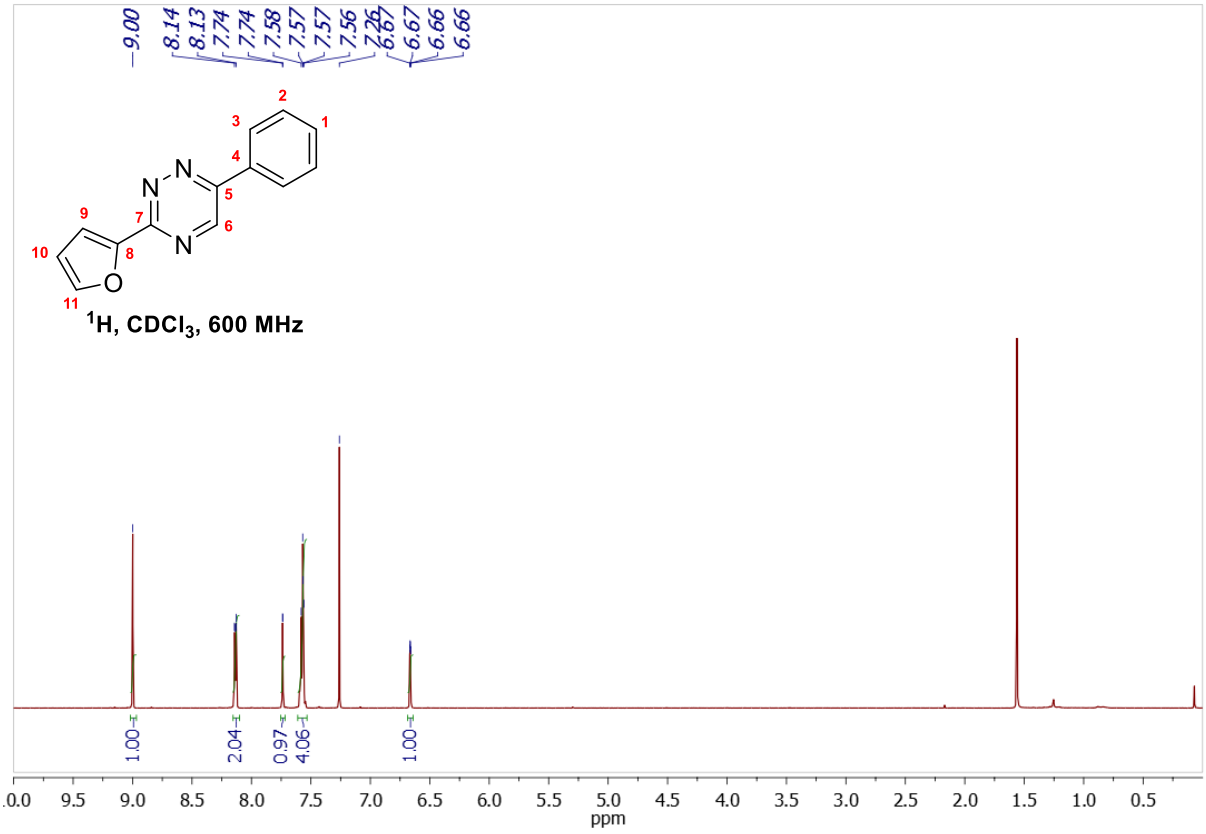
^{1}H, $CDCl_3$, 600 MHz



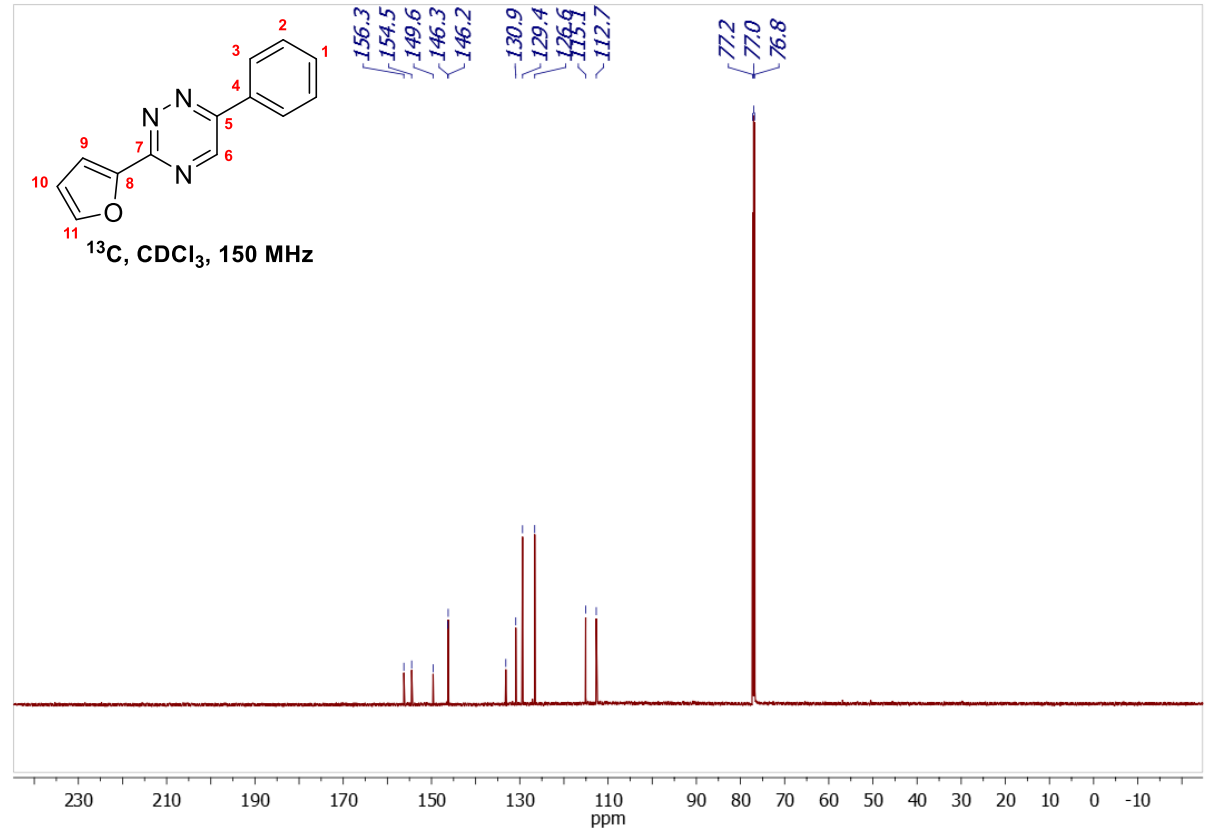


^{13}C, $CDCl_3$, 150 MHz

3-(furan-2-yl)-6-phenyl-1,2,4-triazine (5l)

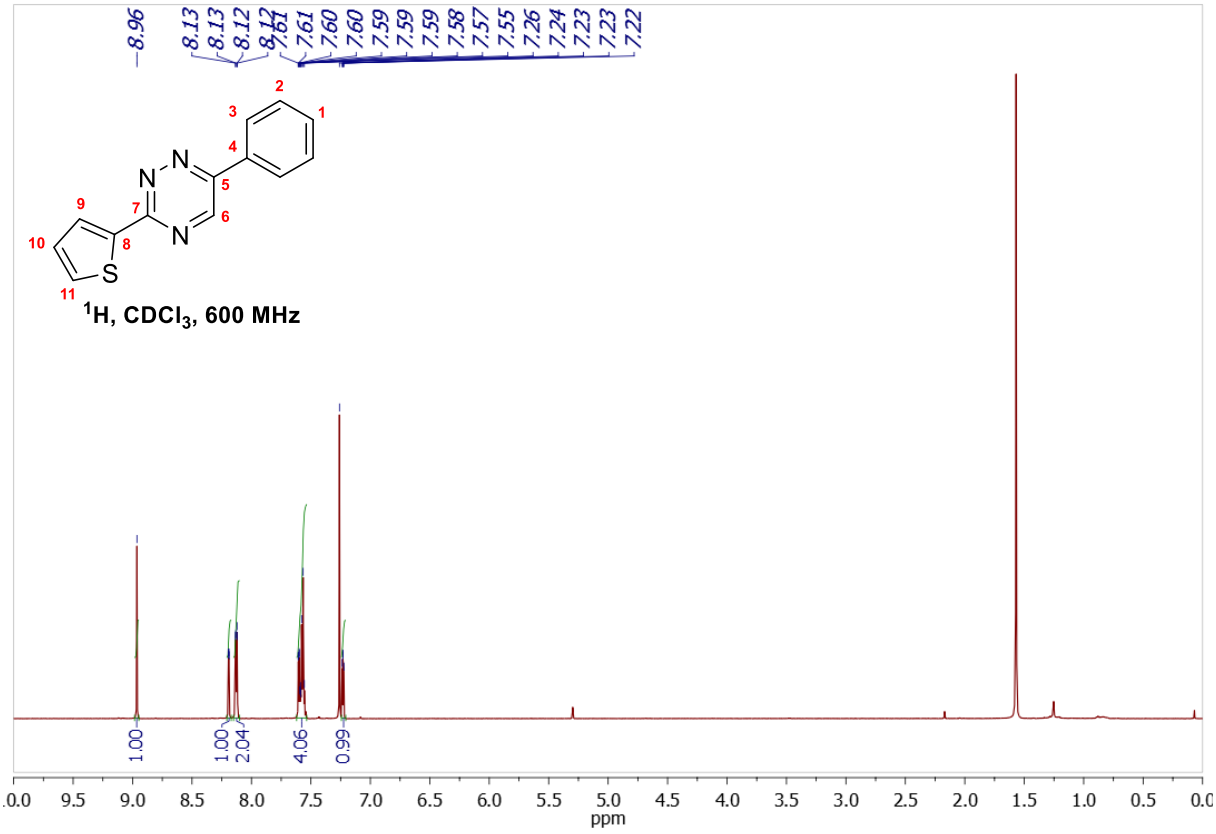


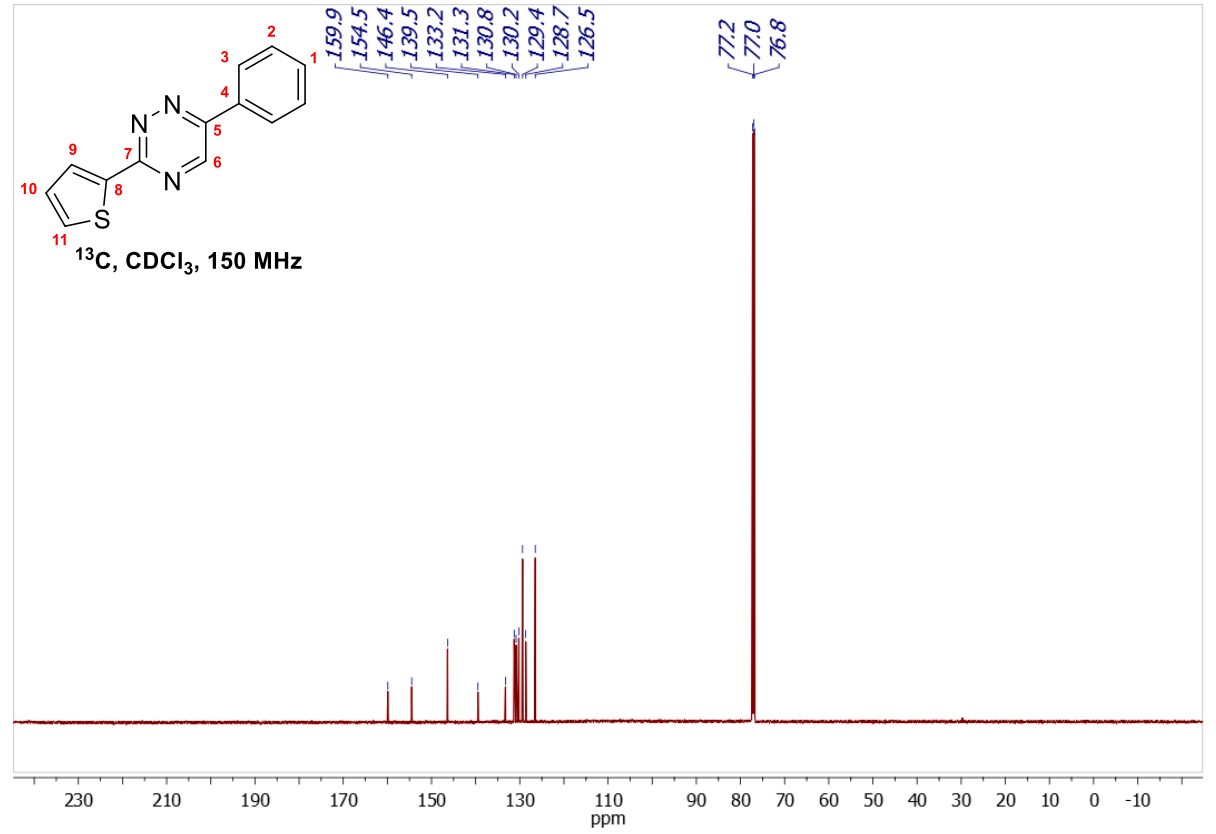
^{1}H, $CDCl_3$, 600 MHz



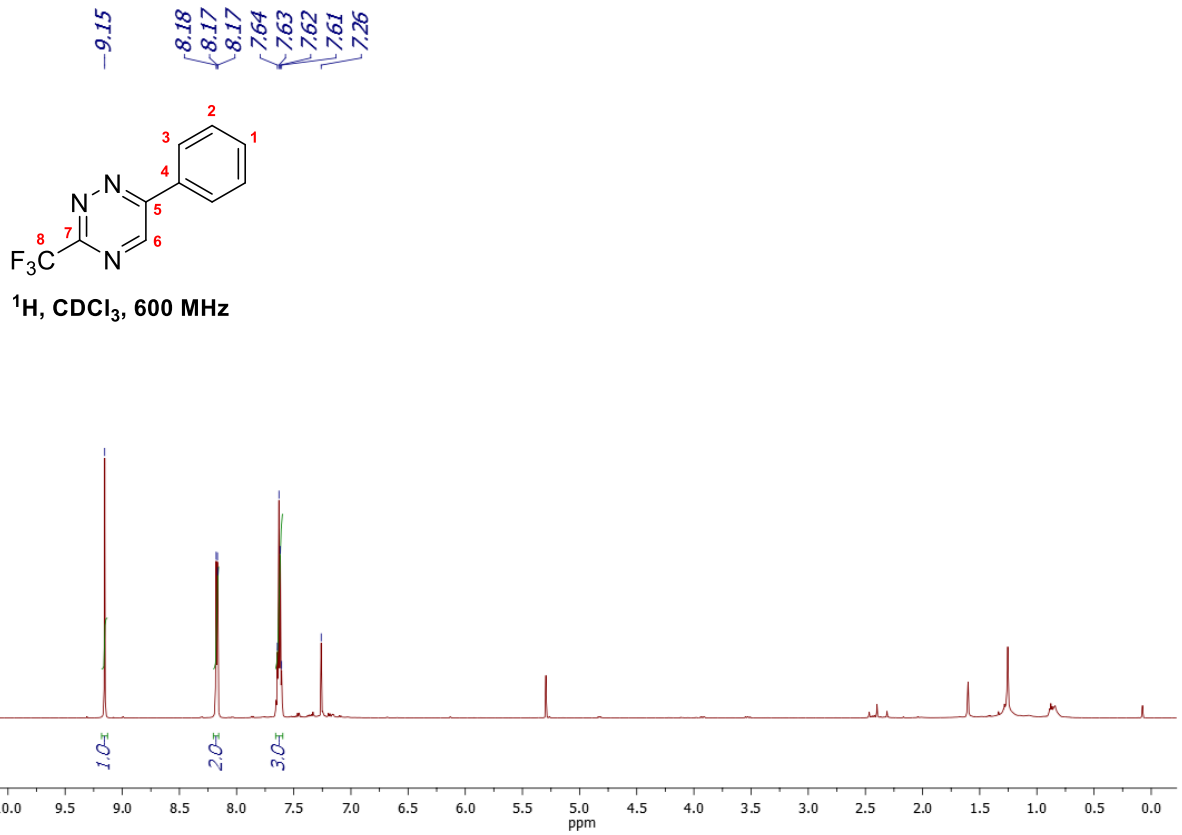
^{13}C, $CDCl_3$, 150 MHz

6-phenyl-3-(thiophen-2-yl)-1,2,4-triazine (5m)

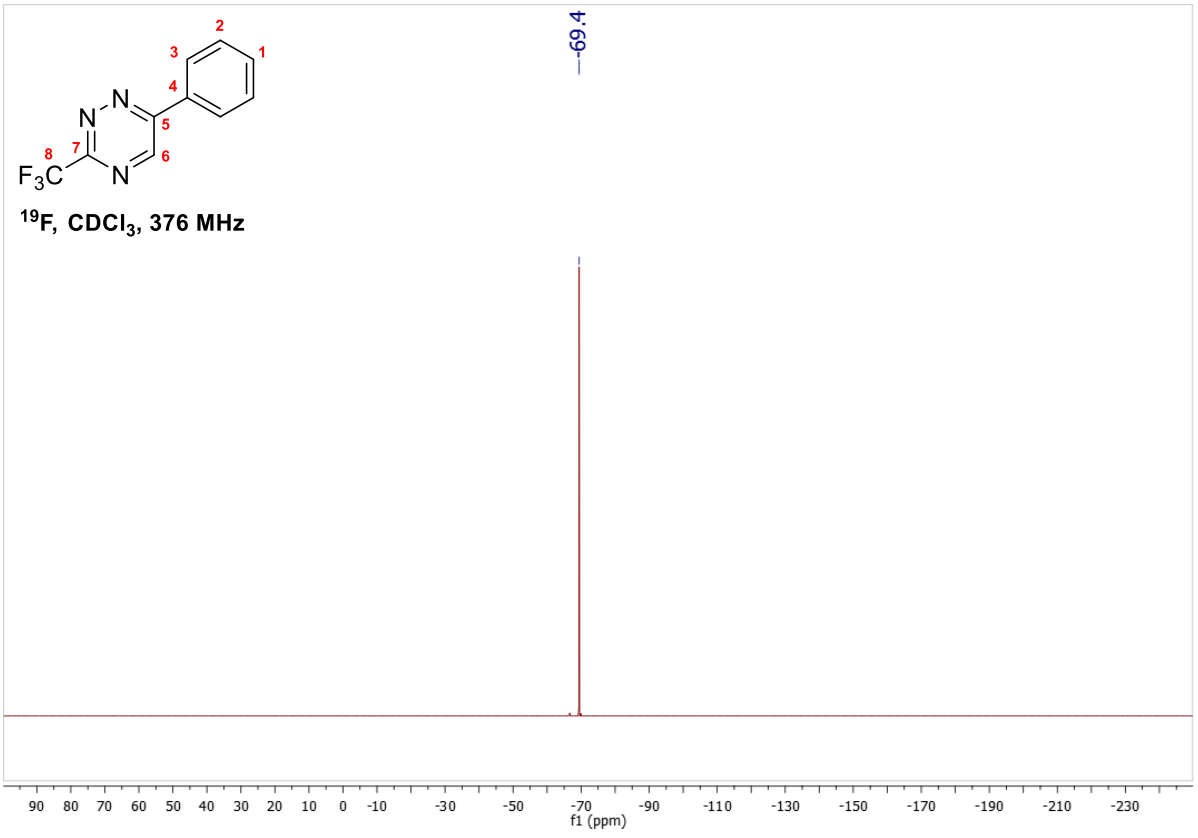




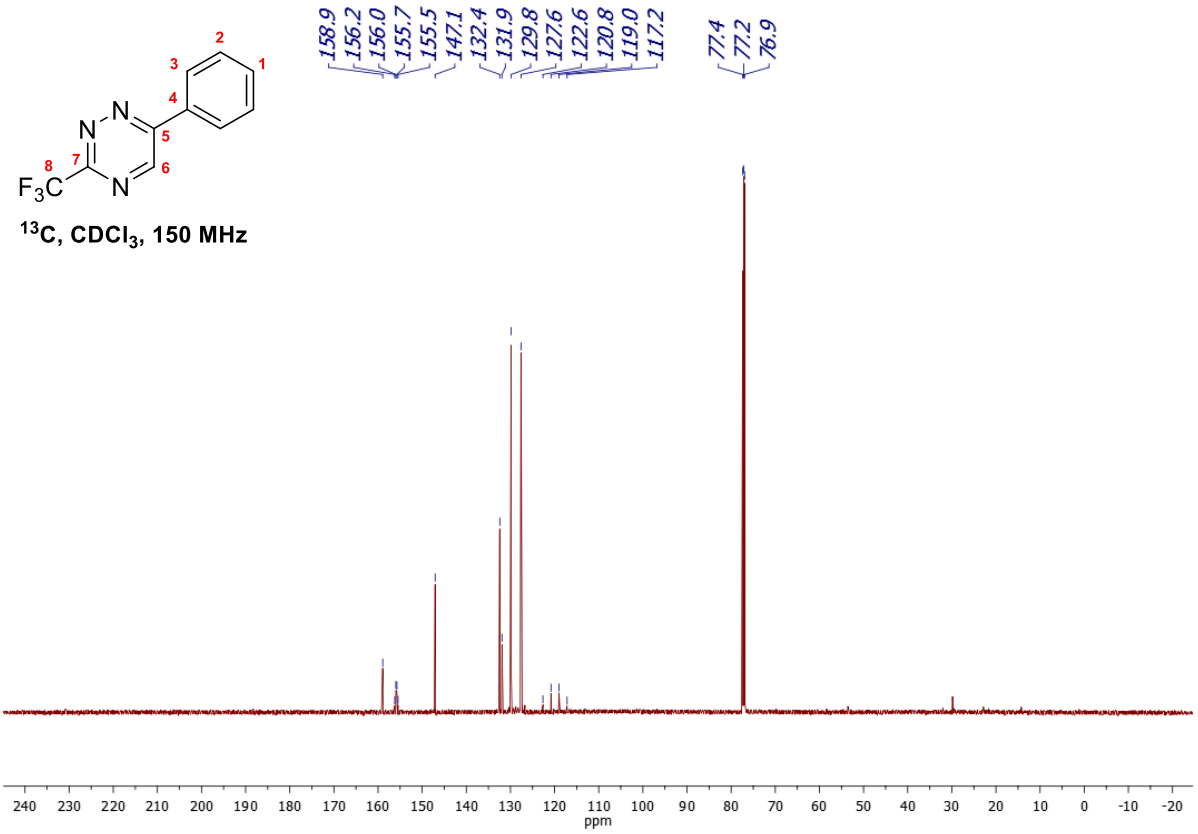
6-phenyl-3-(trifluoromethyl)-1,2,4-triazine (5n)



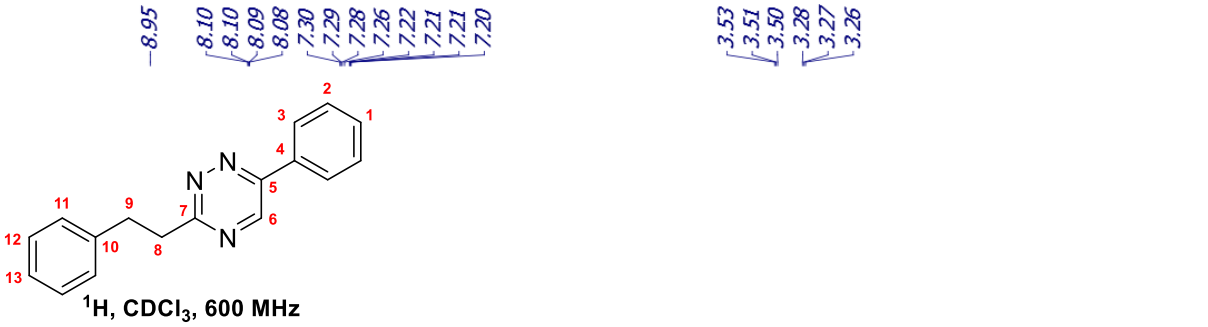
^{1}H, $CDCl_3$, 600 MHz

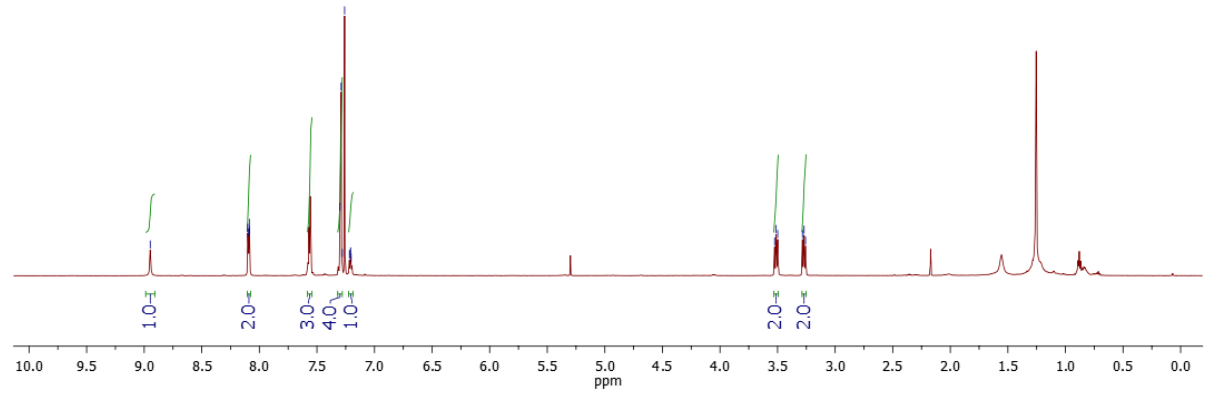


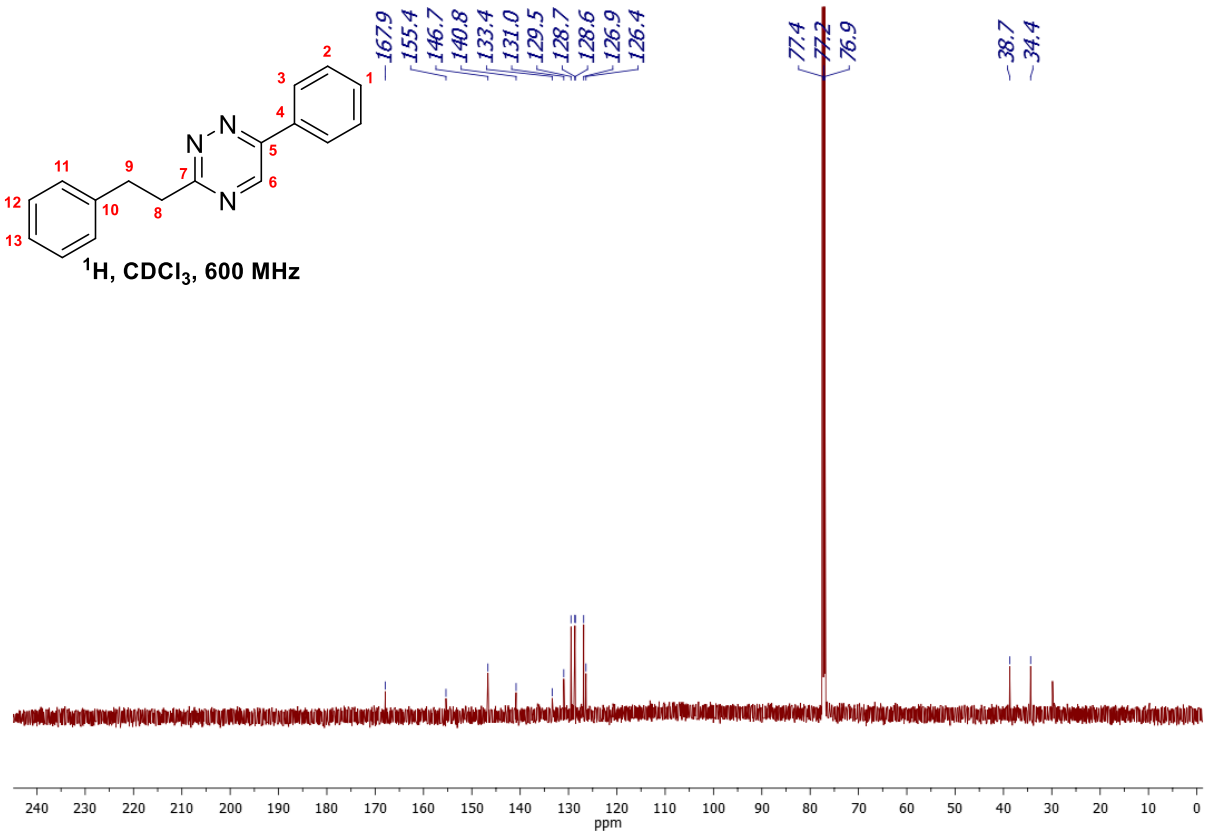
^{19}F, $CDCl_3$, 376 MHz


158.9
156.2
156.0
155.7
155.5
147.1
132.4
131.9
129.8
127.6
122.6
120.8
119.0
117.2
77.4
77.2
76.9
1
2
3
4
5
6
7
8
N
N
F3C
13C, CDCl3, 150 MHz
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm

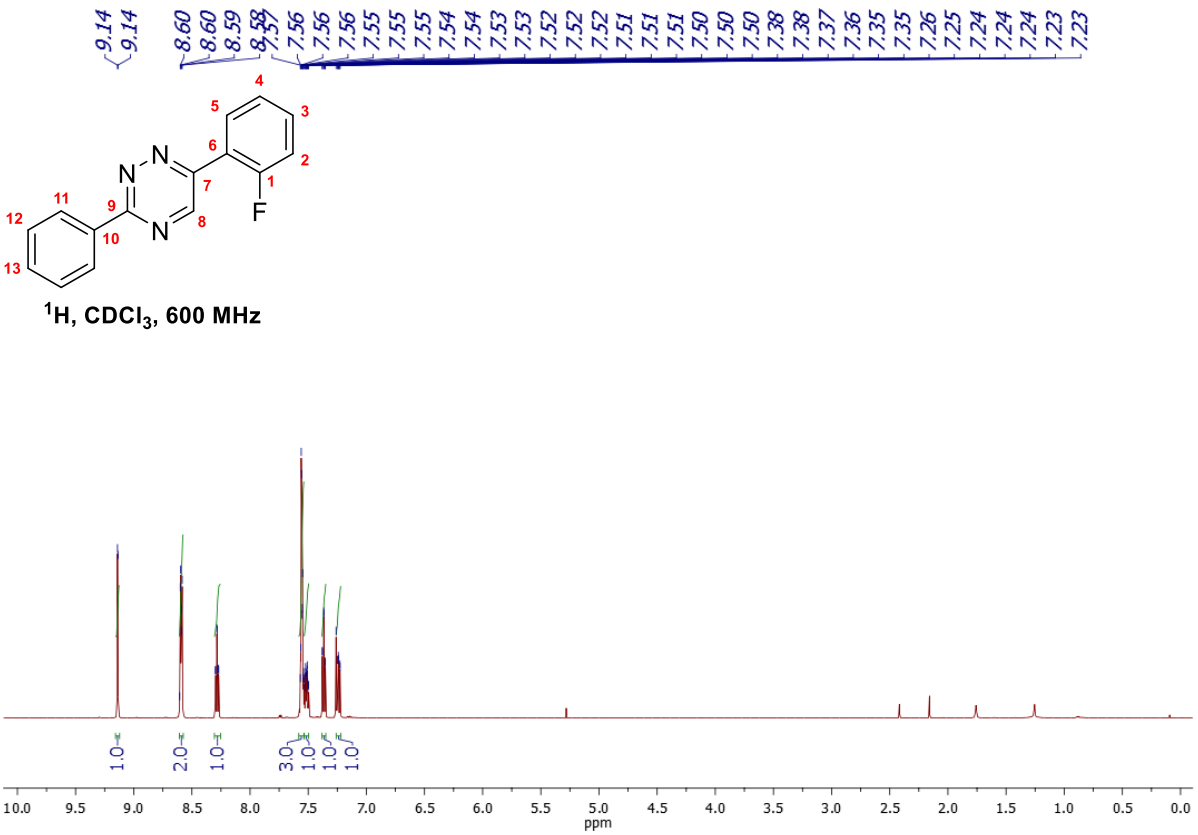
3-phenethyl-6-phenyl-1,2,4-triazine (5o)



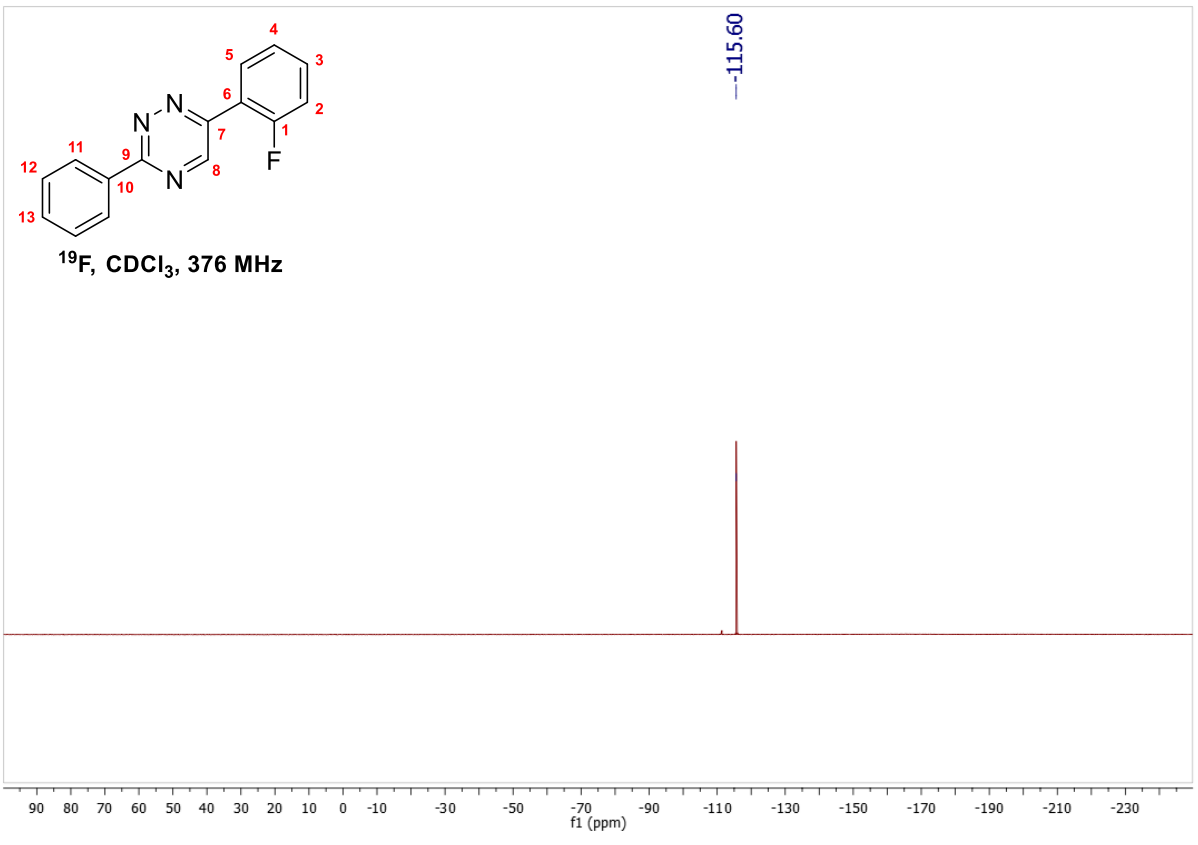




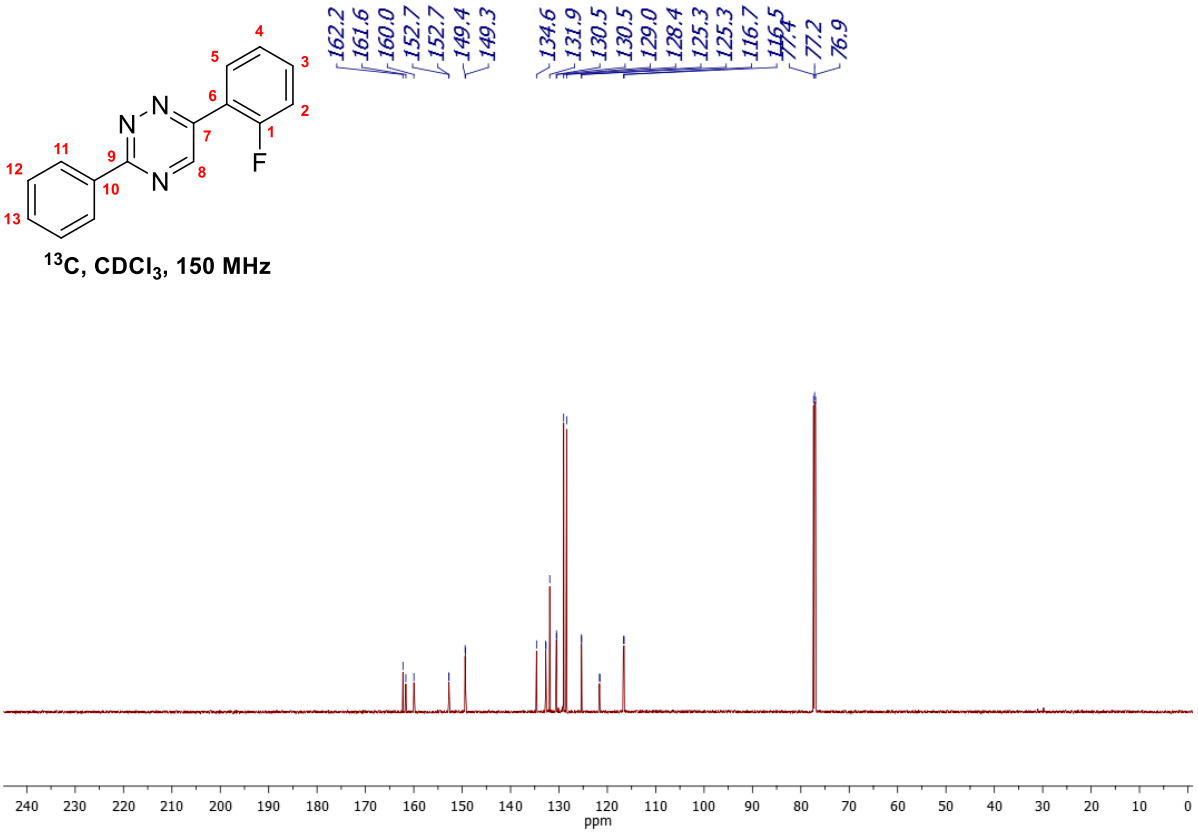
6-(2-fluorophenyl)-3-phenyl-1,2,4-triazine (5p)



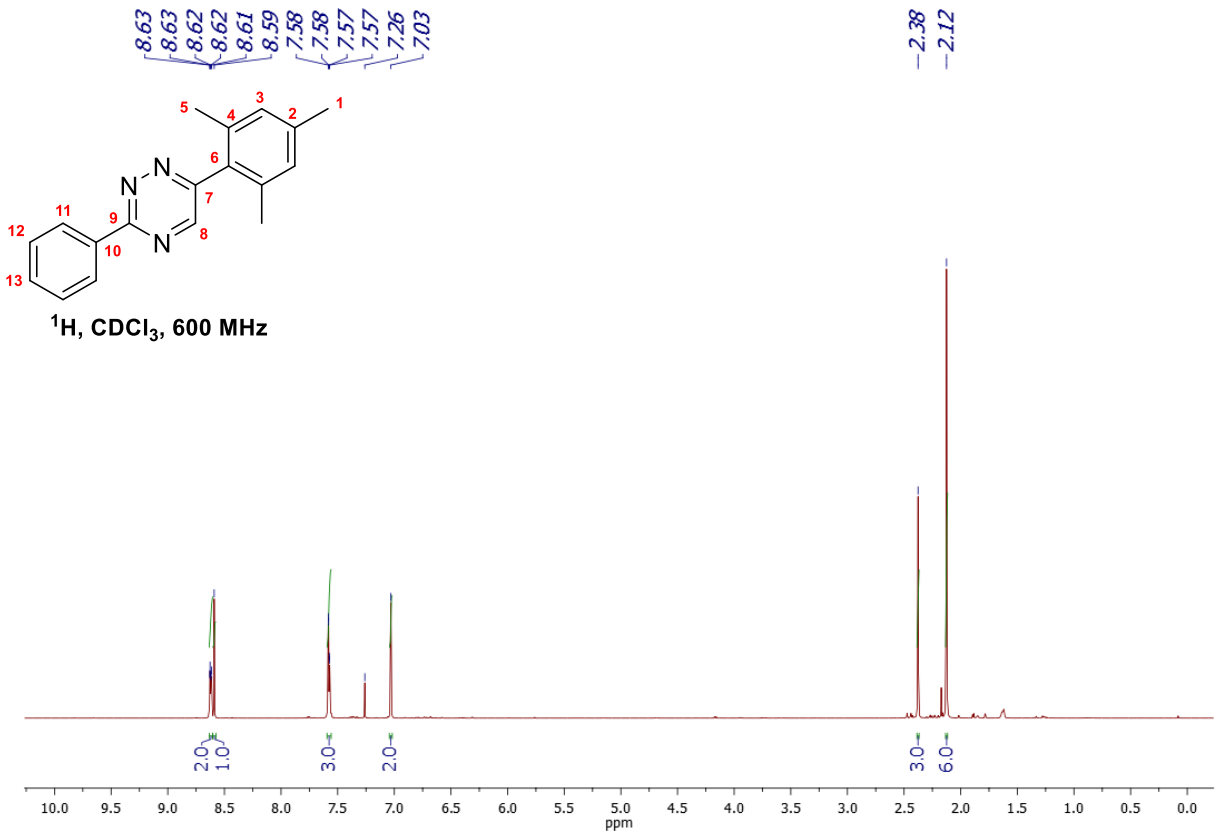
^{1}H, $CDCl_3$, 600 MHz



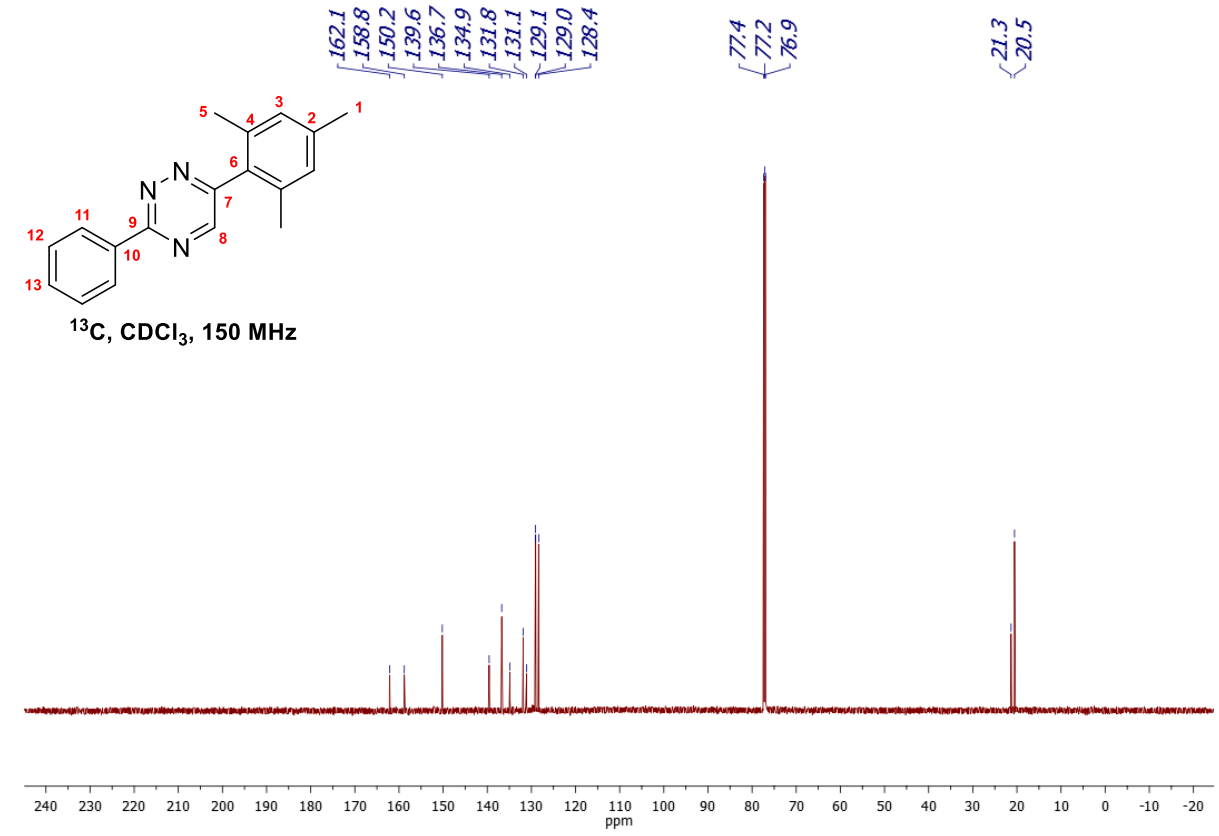
^{19}F, $CDCl_3$, 376 MHz


162.2
161.6
160.0
152.7
152.7
149.4
149.3
134.6
131.9
130.5
130.5
129.0
128.4
125.3
125.3
116.7
116.5
77.4
77.2
76.9
F
13C, CDCl3, 150 MHz
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

6-mesityl-3-phenyl-1,2,4-triazine (5q)

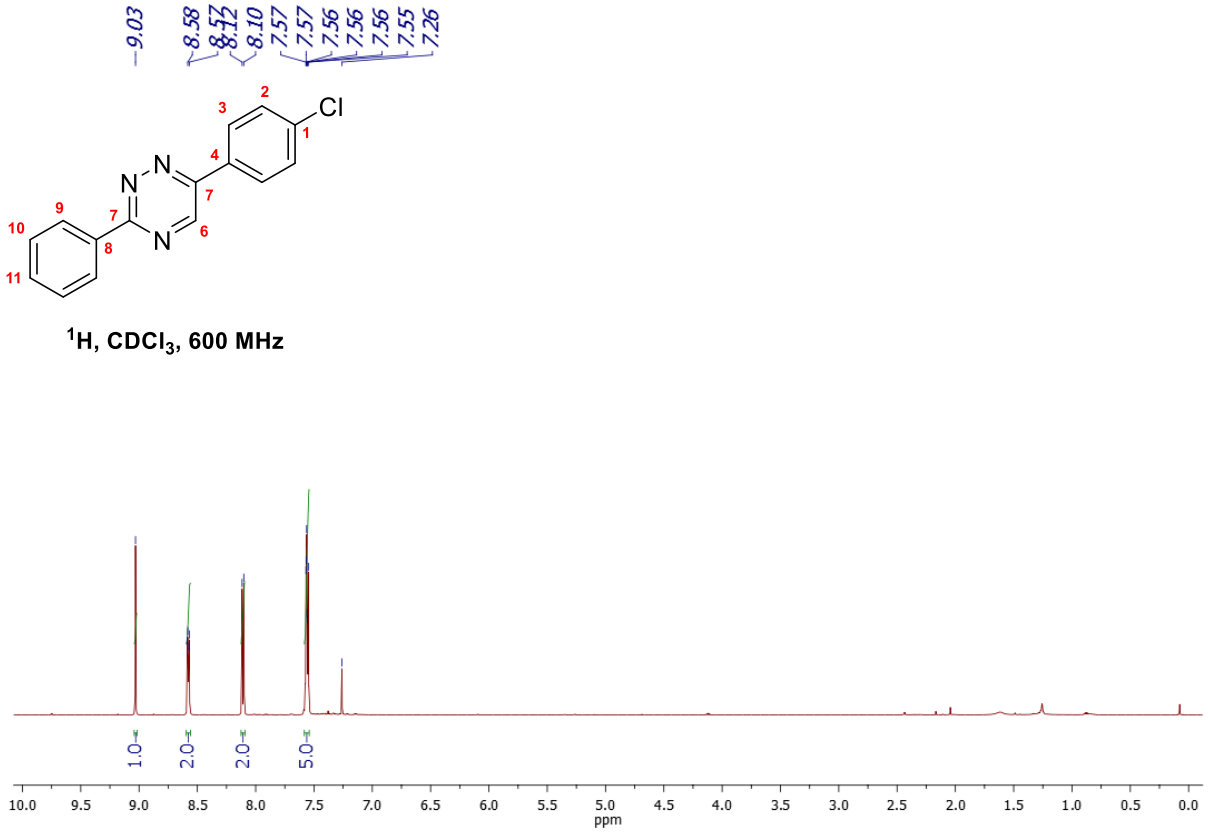


^{1}H, $CDCl_3$, 600 MHz

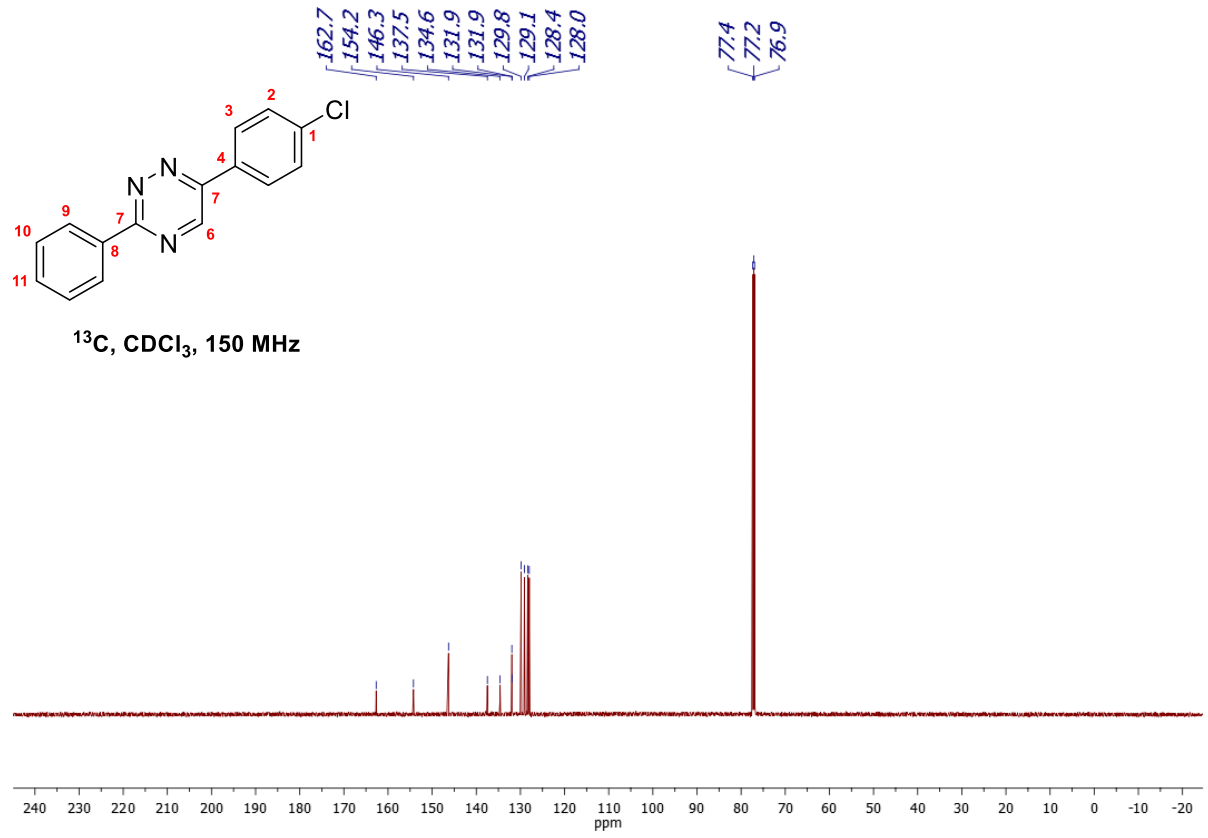


^{13}C, $CDCl_3$, 150 MHz

6-(4-chlorophenyl)-3-phenyl-1,2,4-triazine (5r)

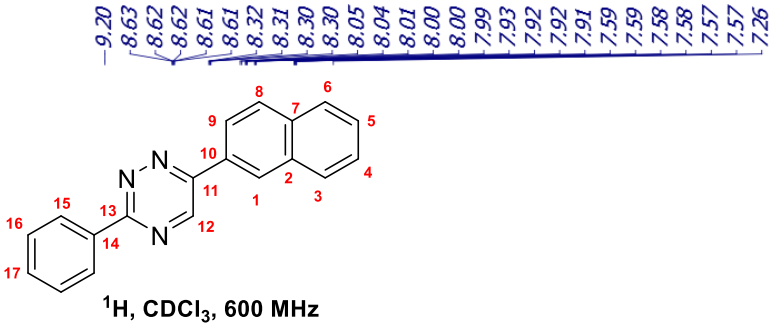


^{1}H, $CDCl_3$, 600 MHz

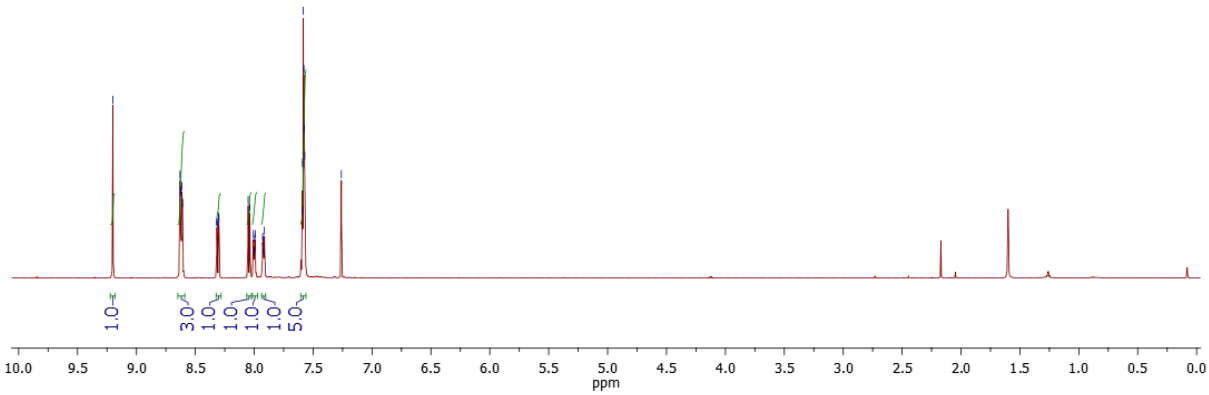


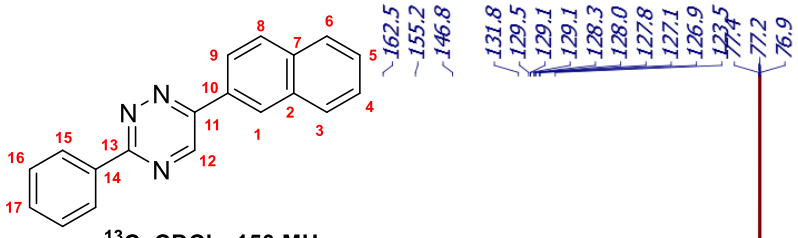
^{13}C, $CDCl_3$, 150 MHz

6-(naphthalen-2-yl)-3-phenyl-1,2,4-triazine (5s)

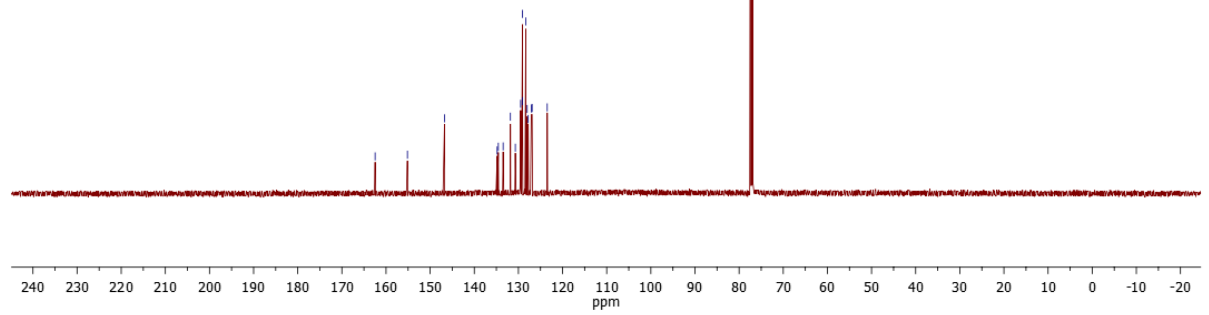


^{1}H, $CDCl_3$, 600 MHz

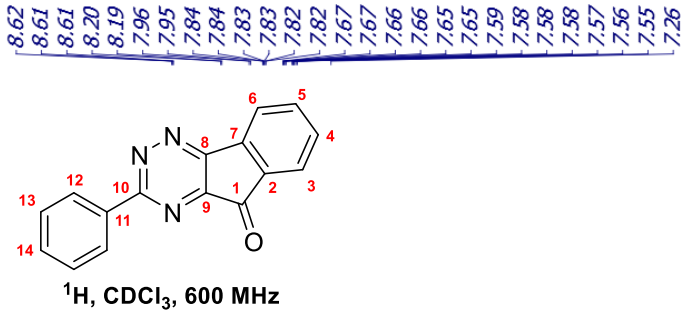




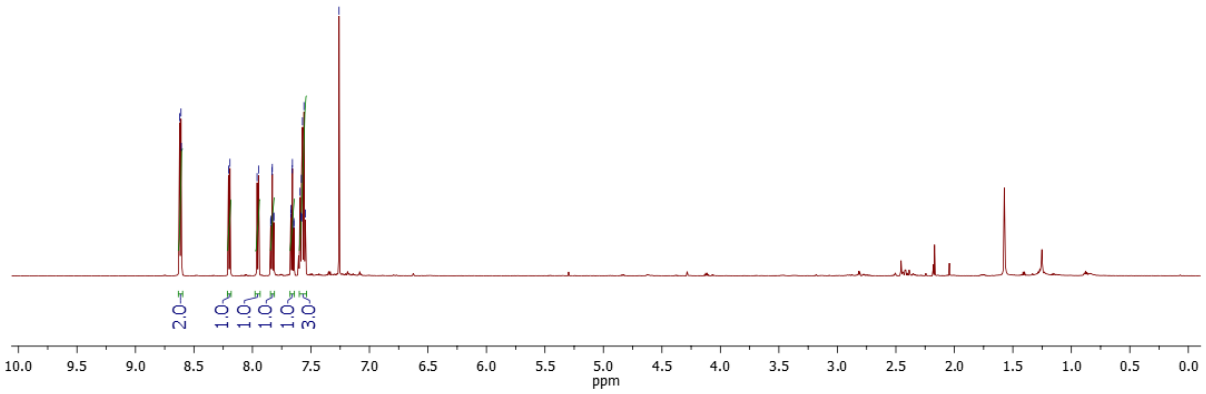
^{13}C, $CDCl_3$, 150 MHz

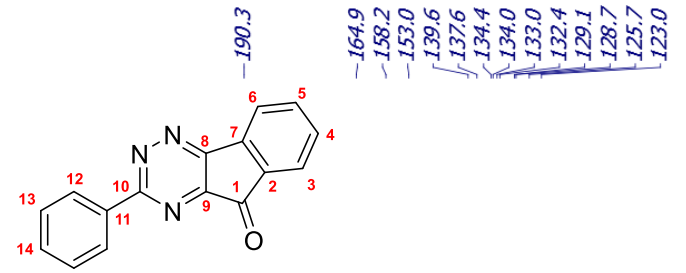


3-phenyl-5H-indeno[2,1-e][1,2,4]triazin-5-one (5t)

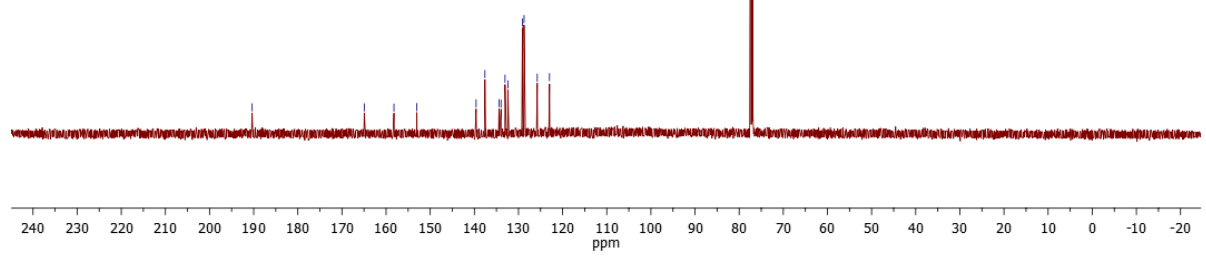


^{1}H, $CDCl_3$, 600 MHz

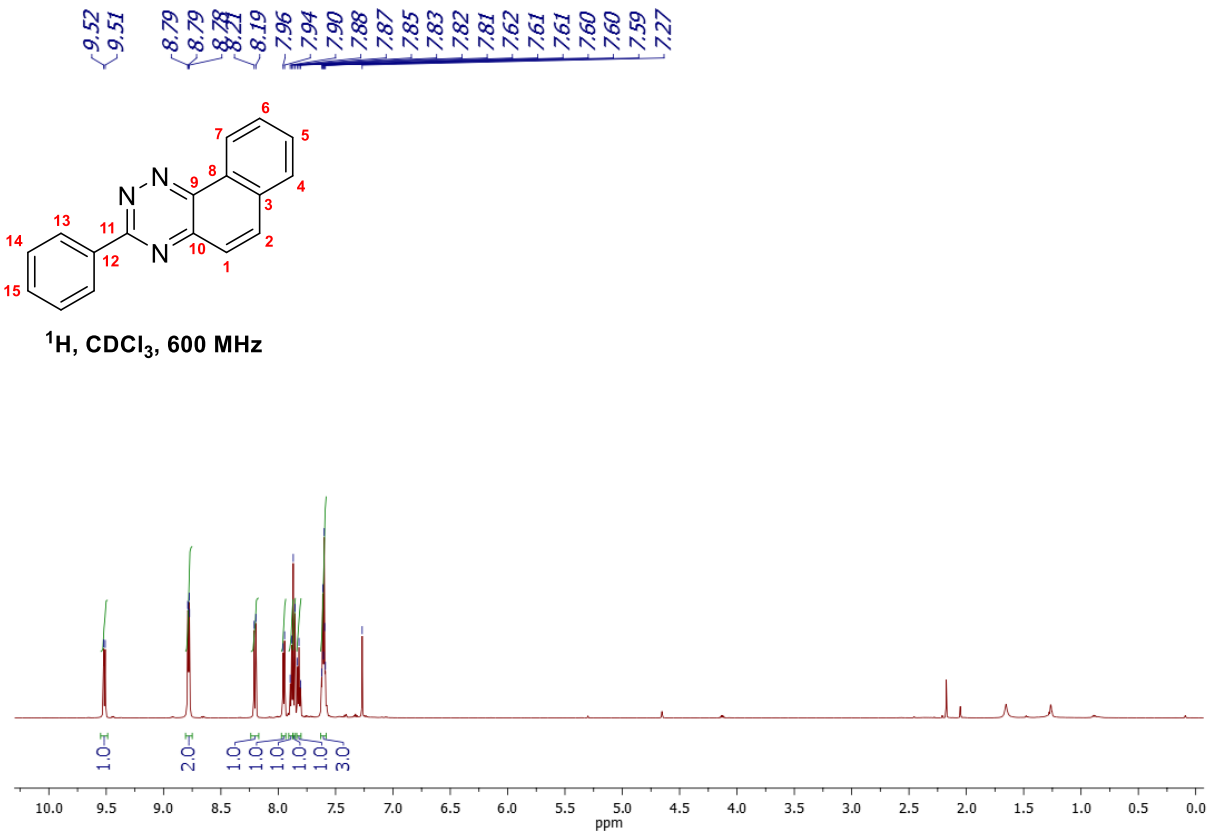




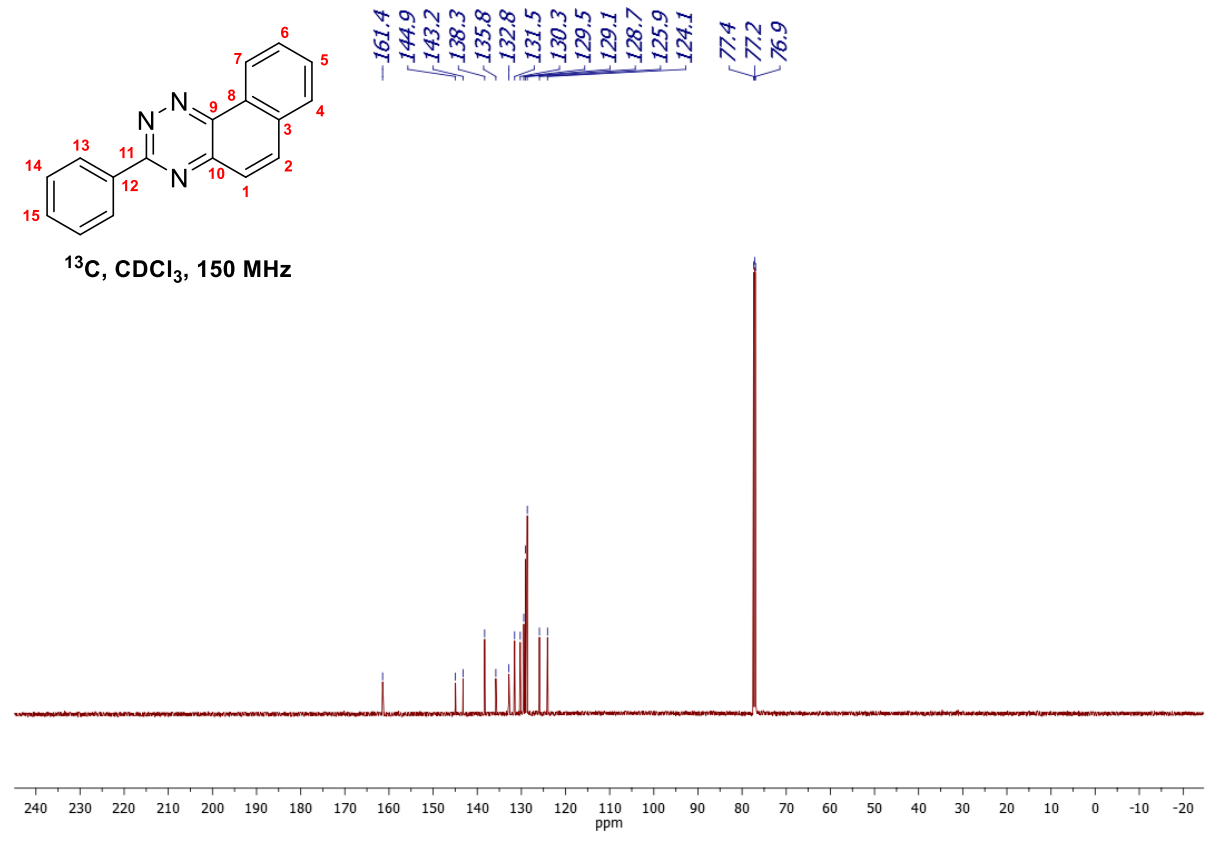
^{13}C, $CDCl_3$, 150 MHz



6-(naphthalen-2-yl)-3-phenyl-1,2,4-triazine (5u)

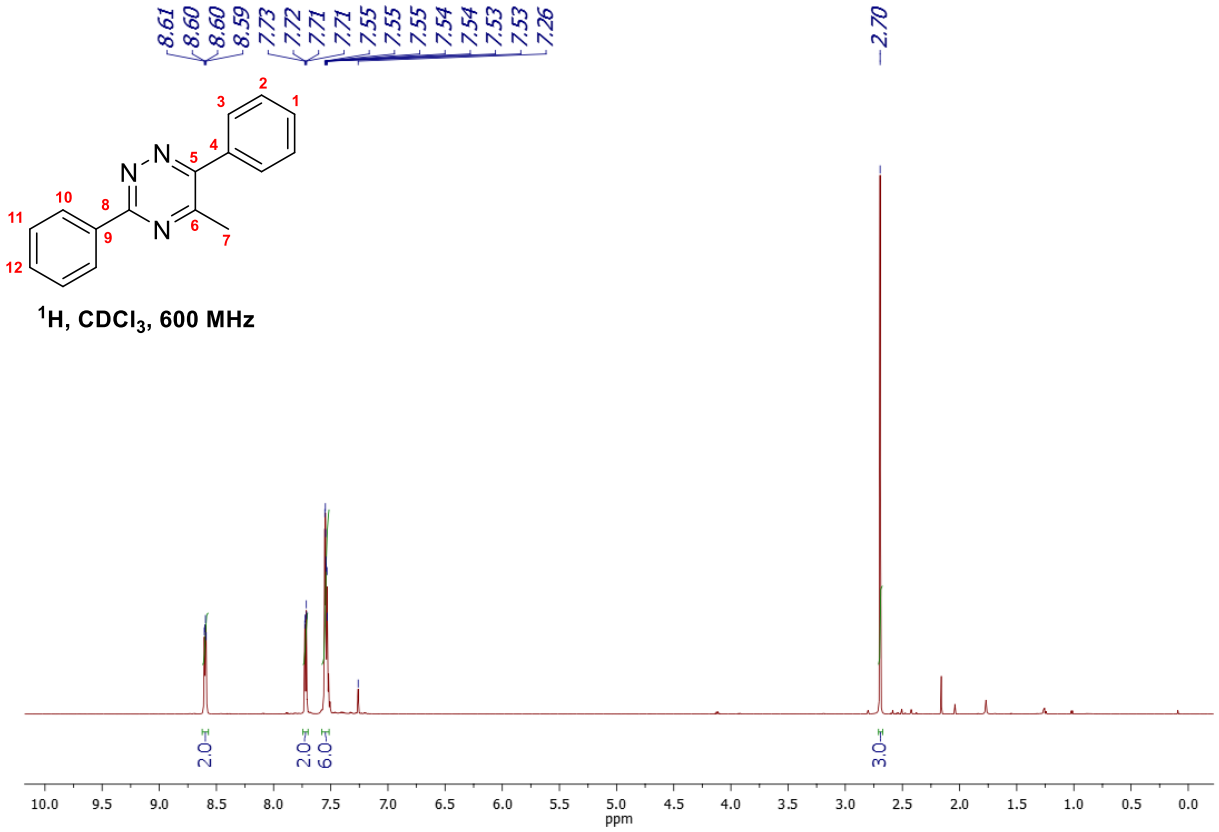


^{1}H, $CDCl_3$, 600 MHz

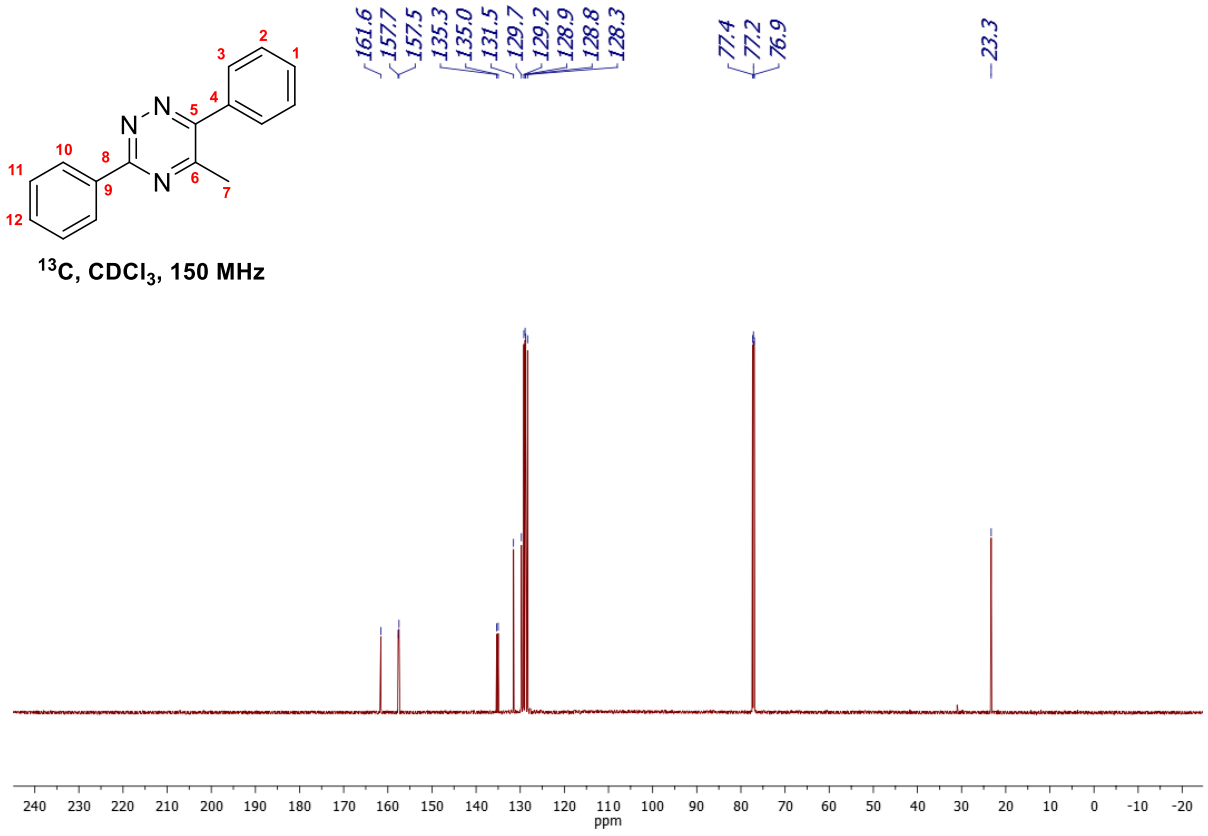


^{13}C, $CDCl_3$, 150 MHz

5-methyl-3,6-diphenyl-1,2,4-triazine (5v)

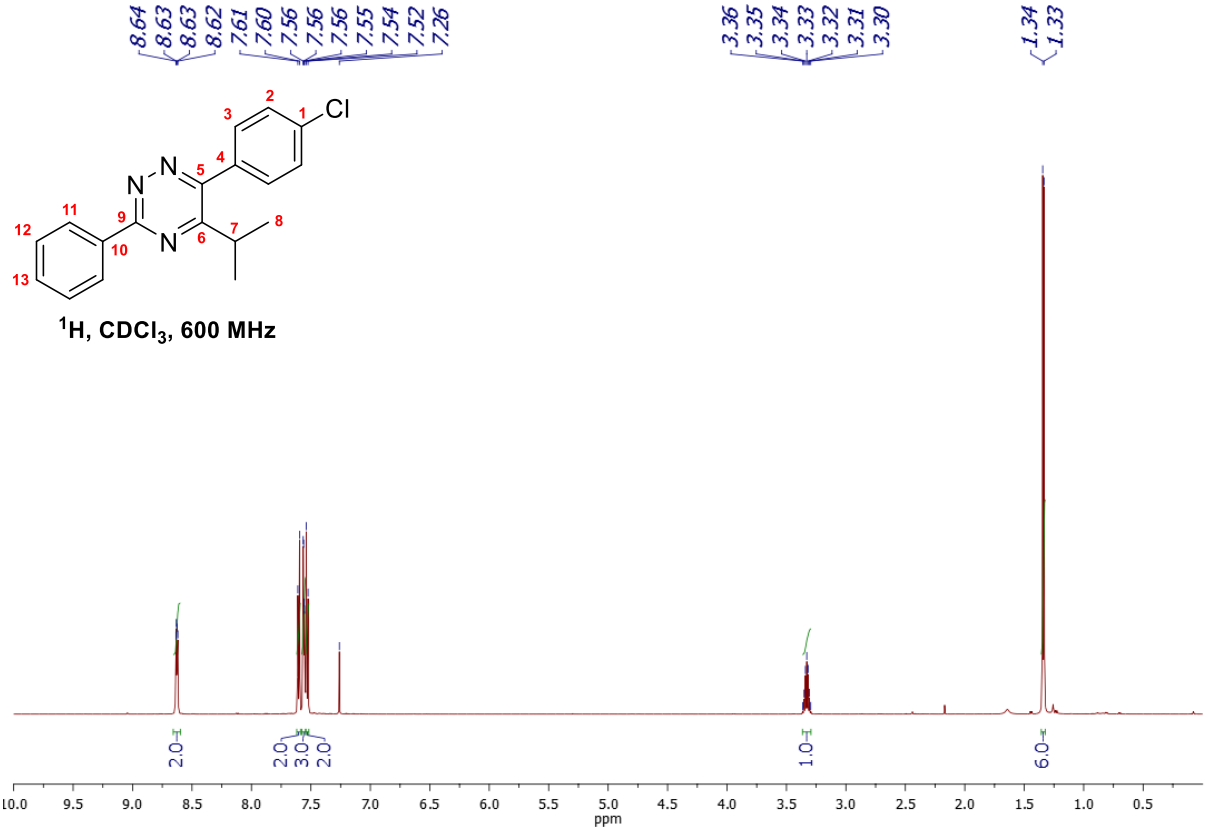


^{1}H, $CDCl_3$, 600 MHz

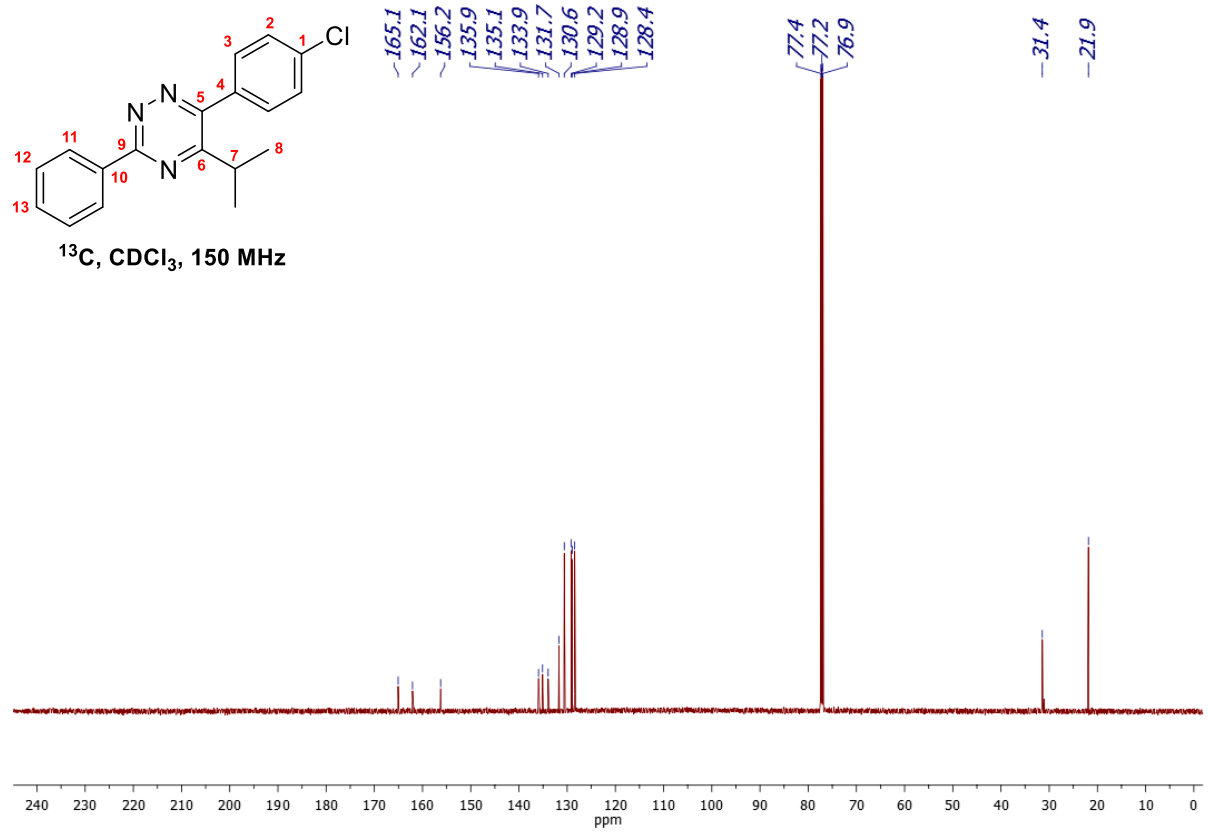


^{13}C, $CDCl_3$, 150 MHz

6-(4-chlorophenyl)-5-isopropyl-3-phenyl-1,2,4-triazine (5w)

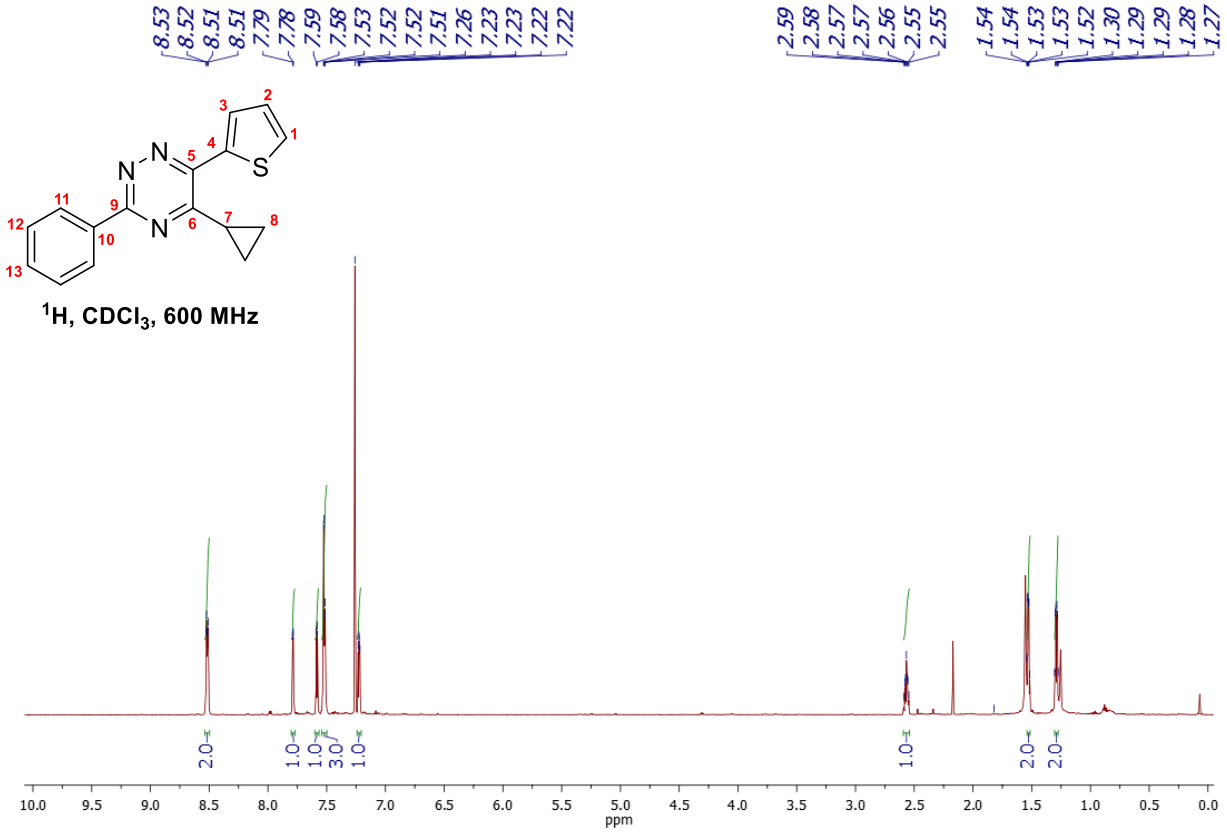


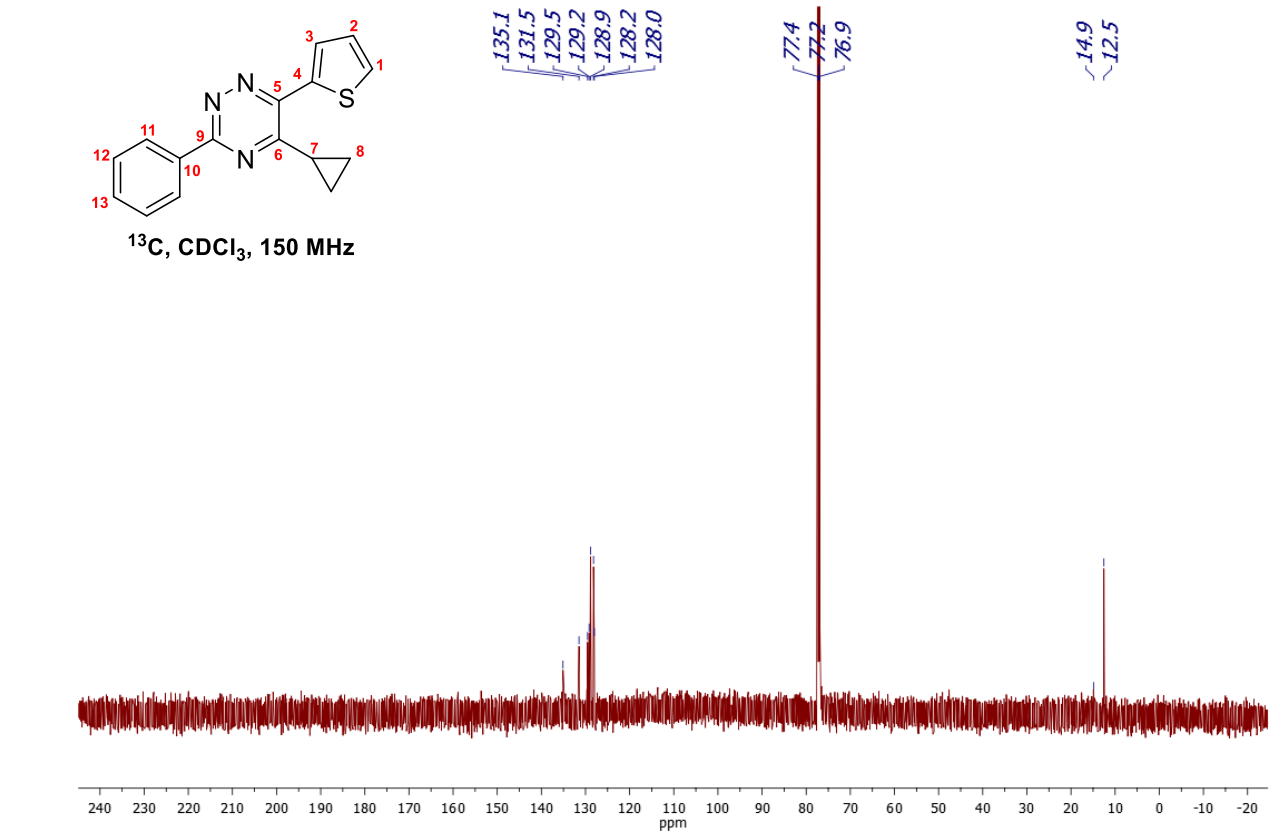
^{1}H, $CDCl_3$, 600 MHz



^{13}C, $CDCl_3$, 150 MHz

5-cyclopropyl-3-phenyl-6-(thiophen-2-yl)-1,2,4-triazine (5x)





(8R,9S,13S,14S)-13-methyl-3-(3-phenyl-1,2,4-triazin-6-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5y)