Cobalt-Catalyzed Cyclization of Unsaturated *N*-Acyl Sulfonamides: a Diverted Mukaiyama Hydration Reaction

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Supporting information

General Information

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

Chromatography

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

Analytical Data

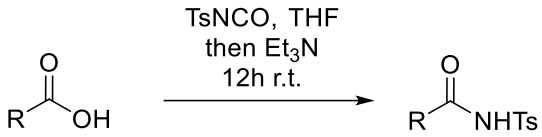
NMR: ^{1}H NMR spectra were recorded on a Bruker AVIII 600 MHz spectrometer with He or prodigy N_2 cryo-probes, Bruker AVIII HD 500 MHz and 400 spectrometers as well as Bruker Neo 500 MHz and 400 MHz spectrometers, and are reported in ppm with the solvent resonance as the reference unless noted otherwise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

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

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

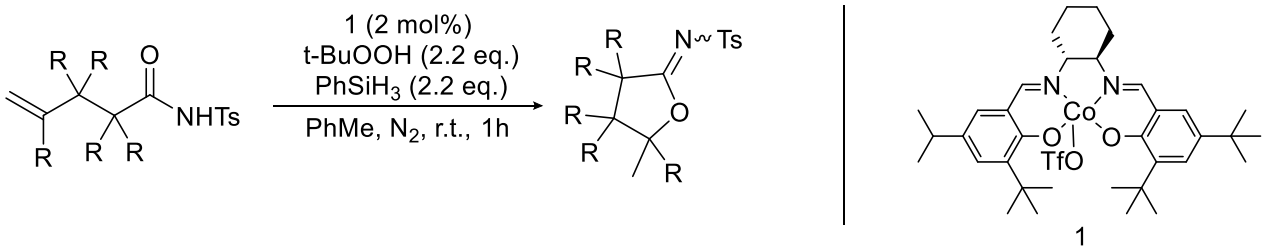
General Procedures

General Procedure 1: Preparation of unsaturated acyl sulfonamides



To a solution of carboxylic acid in dry THF (0.1M) under a nitrogen atmosphere, tosyl isocyanate (1.0 eq.) was added dropwise and the mixture stirred for 10 minutes. Then, Et_3N (1.0 eq.) was added dropwise (caution: gas evolution up addition) stirring was continued at r.t. for 12h.The reaction mixture was then diluted with EtOAc, washed with aq. HCl (3M, 20 mL) and brine (25 mL), dried using Na_2SO_4, filtered and the solvents removed in vacuo. Purification using silica gel chromatography with the appropriate eluent was employed were renecessary.

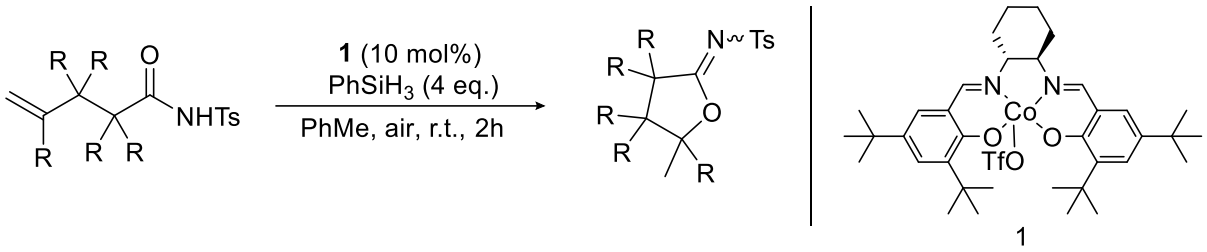
General Procedure 2: Cobalt catalyzed cycloisomerisation



1

Under nitrogen atmosphere, substrates **4a-4w** and **6a-6g** (0.3 mmol, 1.0 eq.) and catalyst **1** [d1](2 mol%), were dissolved in anhydrous toluene (3 mL, gentle heat was applied in case the substrate did not dissolve at r.t.). To the solution was then added sequentially *t*-BuOOH (5.5 M in decane, 0.6 mmol, 2.0 eq.) and $PhSiH_3$ (0.6 mmol, 2.0 eq.). The reaction mixture was then stirred at r.t. for 1-4h, transfered with EtOAc [d2]and the solvent removed in vacuo. Purification using silica gel chromatography with the appropriate eluent yielded the final products.

General Procedure 3: Cobalt catalyzed cycloisomerisation with air

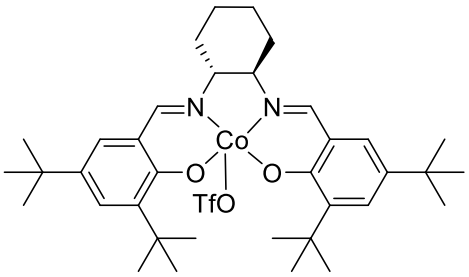


1

Selected substrates from **4a-4w** (0.3 mmol, 1.0 eq.) and catalyst **1** (10 mol%), were dissolved in toluene (3 mL, gentle heat was applied in case the substrate did not dissolve at r.t.). To the solution was then added $PhSiH_3$ (1.2 mmol, 4.0 eq.). The reaction mixture was then stirred open to ambient air at r.t. for 2h, diluted with EtOAc and the solvent removed in vacuo. Purification using silica gel chromatography with the appropriate eluent yielded the final products.

Catalyst synthesis

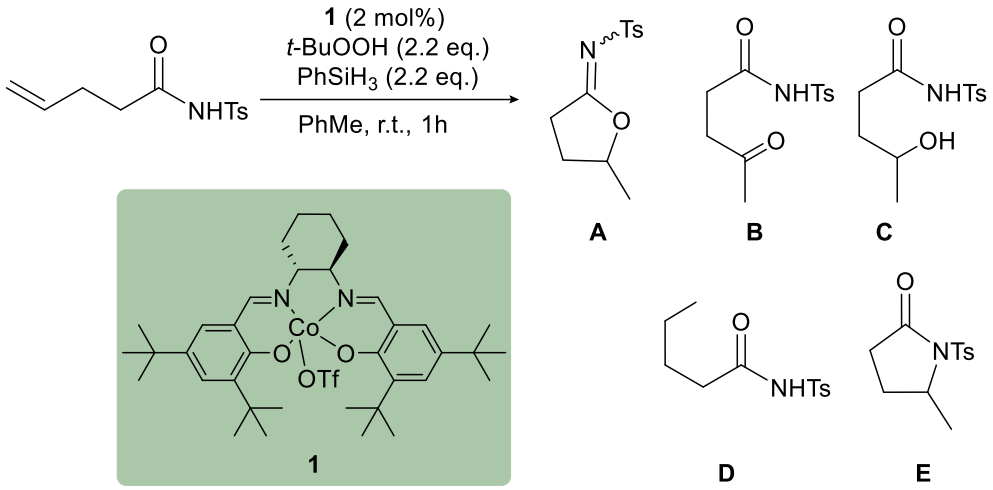
Co(III)-salen catalyst 1



1

Cobalt catalyst 1 was prepared according to literature.[1]

Optimization of the reaction with *t*-BuOOH



Solvent screen

Entry	Deviation from standard conditions	A (%)	B (%)	C (%)	D (%)	E (%)
1	none	85	0	0	0	0
2	*i*-PrOH instead of PhMe	41	0	0	40	0
3	THF instead of PhMe	21	0	19	0	0
4	$PhCF_3$ instead of PhMe	79	0	0	0	0
5	DCE instead of PhMe	50	0	0	0	0
6	CH_2Cl_2 instead of PhMe	62	0	0	13	0
7	2-MeTHF instead of PhMe	44	11	19	0	0
8	EtOH instead of PhMe	25	7	10	44	0
9	MeCN instead of PhMe	42		13		

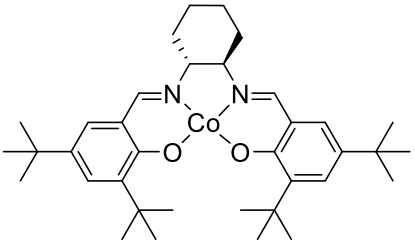
Oxidant screen

Entry	Deviation from standard conditions	A (%)	D (%)	E (%)

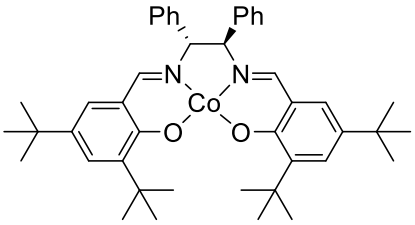
1	none	85	0	0
2	O_2 instead of *t*-BuOOH	62	0	0
4	Cumyl-OOH instead of *t*-BuOOH	60	0	0
5	MnO_2 instead of *t*-BuOOH	45	0	25
6	AgOTf instead of *t*-BuOOH	0	0	0
7	NMO instead of *t*-BuOOH	0	0	0
8	*t*-BuONO instead of *t*-BuOOH	0	0	0
9	0.2 eq. *t*-BuOOH	45	0	0
10	0.5 eq. *t*-BuOOH	59	0	0
11	1.0 eq. *t*-BuOOH	74	0	0
12	No oxidant, N_2	4	0	0
13	No oxidant, N_2, $_{48}$h	4	0	0
14	Air, 1 h	10		
15	Air, 24 h	54	0	0
16	Air, 4 eq. $PhSiH_3$, 10 mol% **1**	82	0	0

Catalyst screen

Entry	Deviation from standard conditions	A (%)	D (%)	E (%)
1	none	85	0	0
2	Co(II)-salen S1	18	0	39
3	Co(II)-salen S2	17	0	30
4	$Cr(III)Cl_3$	0	0	0
5	$Mn(dpm)_3$	0	0	0
6	$Fe(acac)_2$	0	0	0

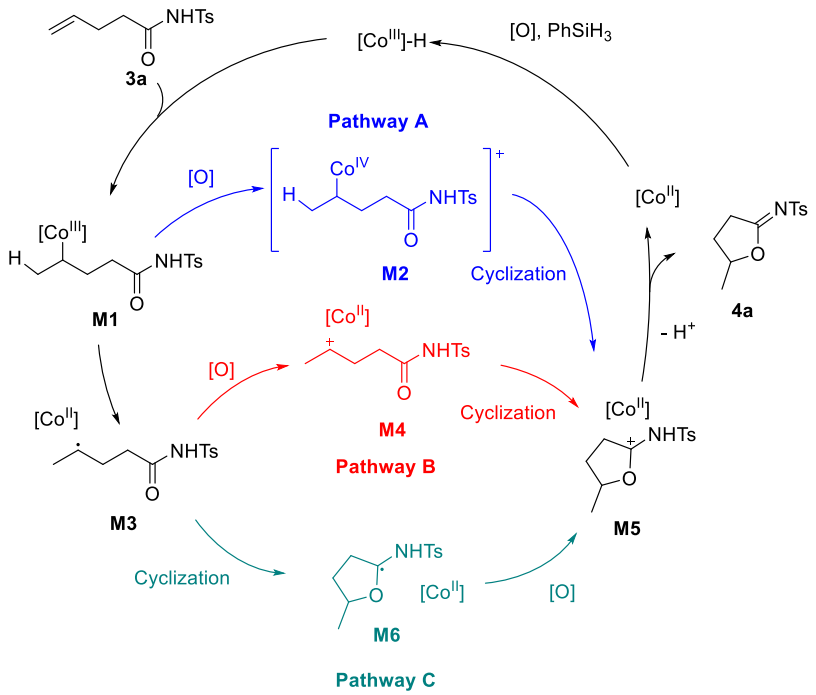


S1



S2

Mechanistic Discussion

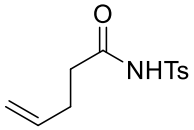


After initial formation of a Co(III) hydride species by the action of silane and oxidant, hydrocobaltation of olefin **3a** leads to secondary alkyl cobalt species **M1**. Shigehisa had previously proposed a pathway leading through high valent Co(IV) species, accessed either through external oxidation or by disproportionation of two Co(III) species, which we label as Pathway A in red. **M1** may be in equilibrium with Co(II) and a secondary alkyl radical **M3**, which may then alternatively proceed through one of two pathways to yield product **4a**. Pathway B involves initial oxidation of **M3** to cationic intermediate **M4** by either external oxidant (I our system, *tert*-BuOOH or O_2 in air) or a second Co (III) species. **M4** might then undergo trapping by the pendant N-acyl sulfonamide as nucleophile to give cation **M5** which following deprotonation leads to product **4a**. Both pathways A and B are adapted from proposals hypothesized by Shigehisa; however, it is important to note Shigehisa employs in all reactions reported a strong F+ oxidant, namely *N*-fluorocollidinium salts. As an alternative pathway, **M3** may undergo cyclization to yield stabilized radical **M6**, which subsequently could undergo oxidation, leading to intermediate **M5**.

Although data is lacking that would allow unambiguous determination of the mechanism of this transformation, Pathways A and B are in line with transformations reported for Co(II) with strong oxidant. In considering Pathway C, we note that cyclopropyl substituted substrate **3e** did not exhibit ring opening under the reaction conditions. However, radical oxidation in **M6** may be very fast such that competing cyclopropyl opening becomes negligible.

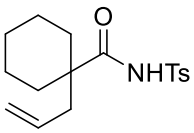
Starting material synthesis

N-Tosylpent-4-enamide (3a)



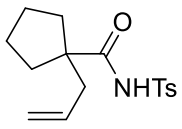
Acyl sulfonamide **3a** was prepared according to literature.[2]

1-Allyl-*N*-tosylcyclohexane-1-carboxamide (3b)



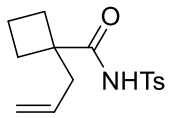
Acyl sulfonamide **3b** was prepared according to literature.[2]

1-Allyl-*N*-tosylcyclopentane-1-carboxamide (3c)



Acyl sulfonamide **3c** was prepared according to literature.[2]

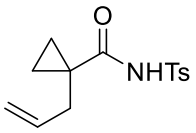
1-Allyl-*N*-tosylcyclobutane-1-carboxamide (3d)



Acyl sulfonamide **3d** was prepared via GP1 from the corresponding carboxylic acid[3] [d3](1.18 g, 8.41 mmol). The crude product was purified via column chromatography (0-40% EtOAc in hexanes, Rf (40% EtOAc in hexanes) = 0.5) to give **3d** (1.05 g, 3.57 mmol, 43%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.60 (s, 1H), 7.98 – 7.91 (m, 2H), 7.36 – 7.30 (m, 2H), 5.44 (ddt, J = 16.9, 10.2, 7.5 Hz, 1H), 4.90 (ddt, *J* = 10.2, 1.9, 0.9 Hz, 1H), 4.90 – 4.82 (m, 1H), 2.44 (s, 3H), 2.13 (dt, *J* = 7.5, 1.1 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.57 – 1.43 (m, 3H), 1.36 – 1.16 (m, 5H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 174.1, 145.0, 135.7, 132.0, 129.5, 128.5, 119.0, 48.0, 43.9, 33.4, 25.6, 22.6, 21.7. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} 3273, 2940, 1715, 1403, 1342, 1147, 1064, 906, 730, 545. **HRMS** (ESI) *m/z* calc. for $C_{15}H_{20}NO_3S$: 294.1158, found: 294.1157 $(M+H)^+$.

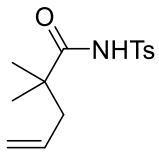
1-Allyl-*N*-tosylcyclopropane-1-carboxamide (3e)



Acyl sulfonamide **3e** was prepared via GP1 from the corresponding carboxylic acid[4] (1.18 g, 8.41 mmol). The crude product was purified via column chromatography (0-40% EtOAc in hexanes, Rf (40% EtOAc in hexanes) = 0.5) to give **3e** (1.05 g, 3.57 mmol, 43%) as a colourless oil.

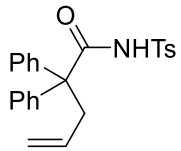
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.51 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 5.85 (ddt, *J* = 17.4, 10.3, 6.3 Hz, 1H), 5.35 – 5.21 (m, 2H), 2.43 (s, 3H), 2.32 (d, *J* = 6.4 Hz, 1H), 1.30 – 1.18 (m, 2H), 0.78 – 0.66 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 172.1, 144.9, 135.6, 135.4, 129.5, 128.5, 118.6, 37.5, 23.5, 21.7, 16.5. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} 3290, 1703, 1416, 1170, 1085, 660, 566, 547. **HRMS** (ESI) *m/z* calc. for $C_{14}H_{18}NO_3S$: 280.1002, found: 280.1000 $(M+H)^+$.

2,2-Dimethyl-*N*-tosylpent-4-enamide (3f)



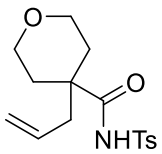
Acyl sulfonamide **3f** was prepared according to literature.[2]

2,2-Diphenyl-*N*-tosylpent-4-enamide (3g)



Acyl sulfonamide **3g** was prepared according to literature.[5]

4-Allyl-*N*-tosyltetrahydro-2H-pyran-4-carboxamide (3h)

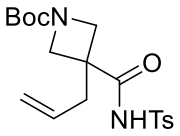


Acyl sulfonamide **3h** was prepared via GP1 from the corresponding carboxylic acid[4](1.00 g, 5.88 mmol). The crude product was purified via column chromatography (0-10% EtOAc in

CH_2Cl_2, Rf (5% EtOAc in CH_2Cl_2) = 0.3) to give **3h** (1.22 g, 3.77 mmol,64%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.38 (s, 1H), 7.97 – 7.91 (m, 2H), 7.38 – 7.32 (m, 2H), 5.46 (ddt, *J* = 16.8, 10.1, 7.4 Hz, 1H), 5.00 (ddt, *J* = 10.1, 1.7, 0.9 Hz, 1H), 4.94 (dq, *J* = 16.9, 1.3 Hz, 1H), 3.73 (dt, *J* = 12.1, 4.1 Hz, 2H), 3.45 – 3.37 (m, 2H), 2.46 (s, 3H), 2.22 (dt, *J* = 7.5, 1.1 Hz, 2H), 1.91 (dp, *J* = 14.2, 2.2 Hz, 2H), 1.55 (ddd, *J* = 14.2, 10.3, 4.1 Hz, 2H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 173.0, 145.5, 135.5, 131.1, 129.7, 128.7, 120.1, 64.6, 45.9, 43.8, 33.5, 21.9. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3271, 2950, 1711, 1416, 1343, 1168, 1123, 838, 659, 546. **HRMS** (ESI) *m/z* calc. for $C_{16}H_{21}NNaO_4S$: 346.1084, found: 346.1085 $(M+Na)^+$.

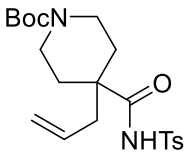
tert-Butyl 3-allyl-3-(tosylcarbamoyl)azetidine-1-carboxylate (3i)



Acyl sulfonamide **3i** was prepared via GP1 from the corresponding carboxylic acid[6] (442 mg, 1.83 mmol). The crude product was purified via column chromatography (0-5% MeOH in CH_2Cl_2, Rf (4% MeOH in CH_2Cl_2) = 0.3) to give **3i** (240 mg, 0.602 mmol, 33%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = δ 8.56 (s, 1H), 7.97 – 7.91 (m, 2H), 7.38 – 7.32 (m, 2H), 5.58 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.13 – 5.01 (m, 2H), 4.03 (d, *J* = 8.8 Hz, 2H), 3.76 – 3.69 (m, 2H), 2.54 (d, *J* = 7.1 Hz, 1H), 2.45 (s, 3H), 1.42 (s, 9H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 171.0, 156.4, 145.6, 135.2, 131.0, 129.8, 128.7, 128.5, 120.4, 80.6, 55.7, 43.5, 40.0, 28.4, 21.9. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2978, 1706, 1668, 1424, 1166, 856, 660, 566. **HRMS** (ESI) *m/z* calc. for $C_{19}H_{26}N_2NaO_5S$: 417.1455, found: 417.1456 $(M+Na)_{[d4]}^+$.

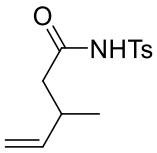
tert-Butyl 4-allyl-4-(tosylcarbamoyl)piperidine-1-carboxylate (3j)



Acyl sulfonamide **3j** was prepared via GP1 from the corresponding carboxylic acid[7] (433 mg, 2.20 mmol). The crude product was purified via column chromatography (0-5% MeOH in CH_2Cl_2, Rf (4% MeOH in CH_2Cl_2) = 0.3) to give **3j** (720 mg, 1.70 mmol, 85%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 8.81 (s, 1H), 7.95 – 7.89 (m, 2H), 7.38 – 7.31 (m, 2H), 5.44 (ddt, *J* = 16.9, 10.2, 7.4 Hz, 1H), 5.00 – 4.89 (m, 2H), 3.70 (s, 2H), 2.92 (s, 2H), 2.45 (s, 3H), 2.20 (d, *J* = 7.4 Hz, 2H), 1.93 (dddd, *J* = 13.9, 4.9, 3.0, 1.6 Hz, 2H), 1.42 (s, 9H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 173.1, 154.8, 145.4, 135.5, 131.2, 129.7, 128.6, 119.9, 79.9, 46.7, 43.3, 32.7, 28.5, 21.8. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3272, 2928, 1692, 1658, 1419, 1158, 855, 771, 730, 659, 546. **HRMS** (ESI) *m/z* calc. for $C_{21}H_{30}N_2NaO_5S$: 445.1768, found: 445.1768 $(M+Na)^+$.

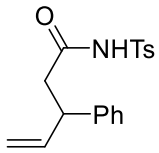
3-Methyl-*N*-tosylpent-4-enamide (3k)



Acyl sulfonamide **3k** was prepared via GP1 from the corresponding carboxylic acid (commercial) (571 mg, 8.00 mmol). The crude product was purified via column chromatography (0-40% EtOAc in hexanes, Rf (40% EtOAc in hexanes) = 0.6) to give **3k** (1.17 g, 4.40 mmol, 88%) as a colourless oil.

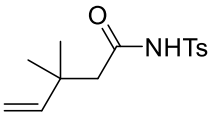
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.97 (s, 1H), 7.97 – 7.91 (m, 2H), 7.37 – 7.30 (m, 2H), 5.65 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1H), 4.94 – 4.85 (m, 2H), 2.66 – 2.54 (m, 1H), 2.44 (s, 3H), 2.28 (dd, *J* = 14.9, 7.3 Hz, 1H), 2.21 (dd, *J* = 14.9, 7.0 Hz, 1H), 0.96 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 169.9, 145.3, 141.7, 135.6, 129.7, 128.5, 114.4, 43.3, 34.4, 21.8, 19.7. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} 3242, 2966, 1694, 1436, 1164, 1086, 852, 660, 549. **HRMS** (ESI) *m/z* calc. for $C_{13}H_{17}NNaO_3S$: 290.0821, found: 290.0820 $(M+Na)^+$.[d5]

3-Phenyl-*N*-tosylpent-4-enamide (3l)



Acyl sulfonamide **3l** was prepared according to literature.[2]

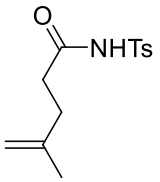
3,3-Dimethyl-*N*-tosylpent-4-enamide (3m)



Acyl sulfonamide **3m** was prepared via GP1 from the corresponding carboxylic acid [8](1.28 g, 10.0 mmol). The crude product was purified via column chromatography (0-40% EtOAc in hexanes, Rf (30% EtOAc in hexanes) = 0.5) to give **3m** (2.30 g, 8.17 mmol, 82%) as a colourless oil.

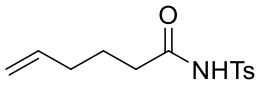
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.49 (s, 1H), 7.94– 7.91 (m, 2H), 7.35 – 7.29 (m, 2H), 5.81 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.06 – 4.91 (m, 2H), 2.44 (s, 3H), 2.21 (s, 2H), 1.03 (s, 5H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 168.9, 146.2, 145.2, 135.7, 129.6, 128.6, 113.1, 49.2, 36.7, 26.8, 21.8. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} 3251, 2966, 2932, 2871, 1719, 1597, 1425, 1334, 1164, 1082, 933, 812, 715, 658, 544. **HRMS** (ESI) *m/z* calc. for $C_{14}H_{19}NNaO_3S$: 304.0978, found: 304.0980 $(M+Na)^+$.

4-Methyl-*N*-tosylpent-4-enamide (3n)



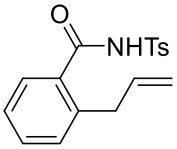
Acyl sulfonamide **3n** was prepared according to literature.[9]

_N_-Tosylhex-5-enamide (3o)



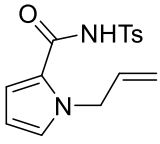
Acyl sulfonamide **3o** was prepared according to literature.[2]

2-Allyl-_N_-tosylbenzamide (3p)



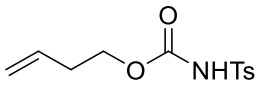
Acyl sulfonamide **3p** was prepared according to literature.[2]

1-Allyl-_N_-tosyl-1H-pyrrole-2-carboxamide (3q)



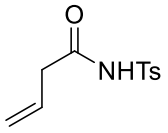
Acyl sulfonamide **3q** was prepared according to literature.[2]

But-3-en-1-yl tosylcarbamate (3r)



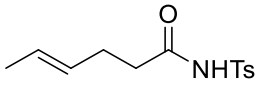
Acyl sulfonamide **3r** was prepared according to literature.[2]

***N*-tosylbut-3-enamide (3s)**



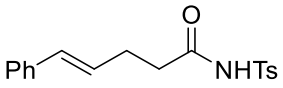
Acyl sulfonamide **3s** was prepared according to literature.[10]

(*E*)-5-Methyl-*N*-tosylpent-4-enamide (3t)



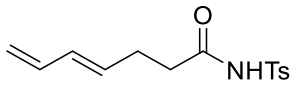
Acyl sulfonamide **3t** was prepared according to literature.[12]

(*E*)-5-Phenyl-*N*-tosylpent-4-enamide (3u)



Acyl sulfonamide **3u** was prepared according to literature.[11]

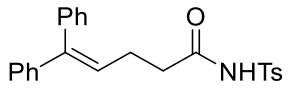
(*E*)-*N*-Tosylhepta-4,6-dienamide (3v)



Acyl sulfonamide **3v** was prepared via GP1 from the corresponding carboxylic acid[13] (1.10 g, 8.72 mmol). The crude product was purified via column chromatography (0-40% EtOAc in hexanes, Rf (30% EtOAc in hexanes) = 0.6) to give **3v** (1.71 g, 6.11 mmol, 70%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.00 (s, 1H), 7.97 – 7.90 (m, 2H), 7.37 – 7.30 (m, 2H), 6.21 (dtd, *J* = 16.9, 10.2, 0.7 Hz, 1H), 5.97 (dddt, *J* = 15.4, 10.4, 1.4, 0.7 Hz, 1H), 5.56 (dddt, *J* = 15.2, 6.9, 6.1, 0.7 Hz, 1H), 5.06 (ddt, *J* = 17.0, 1.7, 0.7 Hz, 1H), 4.98 (ddt, *J* = 10.1, 1.6, 0.7 Hz, 1H), 2.43 (d, *J* = 0.7 Hz, 3H), 2.41 – 2.29 (m, 4H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 170.5, 145.3, 136.7, 135.6, 132.6, 131.7, 129.8, 128.4, 116.2, 35.8, 27.2, 21.8. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3240, 2921, 1721, 1696, 1440, 1170, 1087, 855, 814, 662, 549. **HRMS** (ESI) *m/z* calc. for $C_{14}H_{18}NO_3S$: 280.1002, found: 280.1003 $(M+H)^+$.

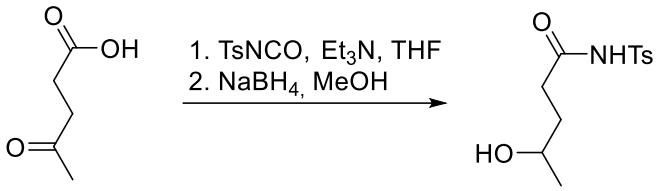
(*E*)-5-Phenyl-*N*-tosylpent-4-enamide (3w)



Acyl sulfonamide **3w** was prepared via GP1 from the corresponding carboxylic acid[14] (668 mg, 2.64 mmol). The crude product was purified via column chromatography (0-40% EtOAc in hexanes, Rf (25% EtOAc in hexanes) = 0.4) to give **3w** (963 mg, 2.37 mmol, 90%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.07 (s, 1H), 7.94 – 7.88 (m, 2H), 7.37 – 7.33 (m, 2H), 7.33 – 7.27 (m, 3H), 7.26 – 7.20 (m, 3H), 7.18 – 7.10 (m, 2H), 7.13 – 7.05 (m, 2H), 6.00 – 5.84 (m, 1H) 2.42 (d, *J* = 0.8 Hz, 3H), 2.40 – 2.32 (m, 4H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 169.8, 145.4, 144.0, 142.1, 139.5, 135.6, 129.8, 129.8, 128.6, 128.5, 128.3, 127.5, 127.4, 127.4, 126.1, 36.5, 24.7, 21.8. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3242, 2921, 1722, 1694, 1442, 1170, 1087, 813, 762, 701, 661, 550. **HRMS** (ESI) *m/z* calc. for $C_{24}H_{24}NO_3S$: 406.1471, found: 406.1474 $(M+H)^+$.

4-Hydroxy-*N*-tosylpentanamide (I)



To a solution of 4-oxo-pentanoic acid (547 mg, 4.71 mmol, 1.00 eq.) in dry THF (23.5 mL) under a nitrogen atmosphere, tosyl isocyanate (976 mg, 4.95 mmol, 1.05 eq.) was added dropwise and the mixture stirred for 10 minutes. Then, Et_3N (501 mg, 4.95 mmol, 1.05 eq.) was added dropwise (caution: gas evolution up addition) stirring was continued at r.t. for 12h.The reaction mixture was then diluted with EtOAc (50 mL), washed with aq. HCl (3M, 20 mL) and brine (25 mL), dried using Na_2SO_4, filtered and the solvents removed in vacuo. The crude product was used directly in the next step.

To a solution of the crude product in MeOH (23.5 mL) was added $NaBH_4$ (476 mg, 14.1 mmol, 3.00 eq.) and the mixture stirred at r.t. for 2h. Then the reaction was quenched by careful addition of sat. aq. NH_4Cl (5 mL). The organic solvent was removed in vacuo and the residue dissolved in EtOAc (20 mL), diluted with water and the organic phase isolated. The aqueous phase was extracted with EtOAc (3 x 15 mL), the combined organic extracts washed with brine and dried over Na_2SO_4, filtered and the solvent removed in vacuo. The crude product was purified via column chromatography (20-80% EtOAc in hexanes, Rf (60% EtOAc in hexanes) = 0.3) to give **I** (212 mg, 0.966 mmol, 21%) as a colourless oil.

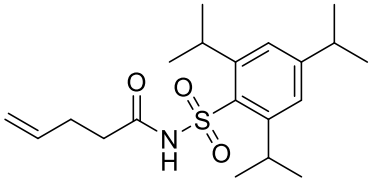
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.96 – 7.88 (m, 2H), 7.35 – 7.29 (m, 2H), 3.81 (dtd, *J* = 12.3, 6.2, 3.3 Hz, 1H), 2.42 (m, 3H), 2.46 – 2.35 (m, 2H), 1.79 (dddd, *J* = 14.4, 7.5, 6.9, 3.4 Hz, 1H), 1.68 – 1.57 (m, 1H), 1.18 (d, *J* = 6.2 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 171.9, 145.1, 135.8, 129.7, 128.5, 67.7, 33.3, 32.9, 23.7, 21.8. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} 3503, 3251, 2969, 1717, 1445, 1338, 1171, 1086, 852, 662, 549. **HRMS** (ESI) *m/z* calc. for $C_{12}H_{17}NNaO_4S$: 294.0770, found: 294.0770 $(M+Na)^+$.

4-Hydroxy-*N*-tosylpentanamide (I) was also prepared from acyl sulfonamide 3a via Mukaiyama hydration:

Under oxygen atmosphere, **3a** (50.6 mg, 0.200 mmol, 1.0 eq.) and $Co(acac)_2$[d6](2.6 mg, 0.010 mmol, 5 mol%), were dissolved in anhydrous THF (2 mL). To the solution was then added

$PhSiH_3$ (61.6 µL, 0.500 mmol, 2.5 eq.). The reaction mixture was then stirred at r.t. over night, and the solvent removed in vacuo. Purification using silica gel chromatography (20-80% EtOAc in hexanes, Rf (60% EtOAc in hexanes) = 0.3) gave **I** (25.0 mg, 0.0921 mmol, 46%) as a colourless oil.

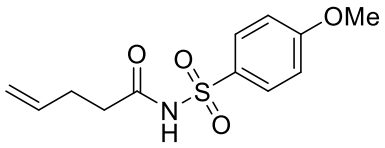
***N*-((2,4,6-Triisopropylphenyl)sulfonyl)pent-4-enamide (5a)**



Prepared according to modified literature procedure.[2] DMAP$_{[d7]}$ (672 mg, 5.50 mmol, 1.10 equiv) was added to a suspension of EDCI•HCl (1.05 g, 5.50 mmol, 1.10 equiv) in CH_2Cl_2 (20 mL). The mixture was stirred at rt until all the solids dissolved and then it was cooled to 0°C. 4-pentenoic acid (551 mg, 5.00 mmol, 1.00 equiv) was added, followed by triisopropylphenylsulfonamide (1.42 g, 5.50 mmol, 1.00 equiv) and the mixture was stirred at rt for 24 h. Et_2O (20 mL) was then added, the organic mixture washed with aq. HCl (2M, 30 mL) and the aqueous layer extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified via column chromatography (0-40% EtOAc in hexane, Rf (25% EtOAc in hexanes) = 0.3) to give **5a** (1.52 g, 4.16 mmol, 83% yield) as a colourless oil.

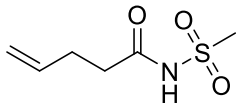
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 9.11 (s, 1H), 7.29 – 7.23 (m, 2H), 5.88 – 5.72 (m, 1H), 5.11 – 4.97 (m, 2H), 4.27 (hept, *J* = 6.8 Hz, 2H), 2.97 (p, *J* = 6.9 Hz, 1H), 2.46 – 2.33 (m, 4H), 1.37 (d, *J* = 6.8 Hz, 12H), 1.32 (d, *J* = 6.9 Hz, 6H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 170.6, 154.3, 151.4, 136.1, 131.3, 124.2, 116.3, 35.5, 34.4, 29.7, 28.2, 24.8, 23.6. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3233, 2960, 1724, 1599, 1429, 852, 659, 554. **HRMS** (ESI) *m/z* calc. for $C_{20}H_{32}NO_3S$: 366.2097, found: 366.2093 $(M+H)^+$.

***N*-((4-Methoxyphenyl)sulfonyl)pent-4-enamide (5b)**



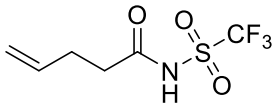
Acyl sulfonamide **5b** was prepared according to literature.[2]

***N*-(Methylsulfonyl)pent-4-enamide (5c)**



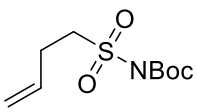
Acyl sulfonamide **5c** was prepared according to literature.[15]

***N*-((Trifluoromethyl)sulfonyl)pent-4-enamide (5d)**



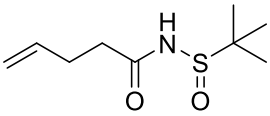
Acyl sulfonamide **5d** was prepared according to literature.[15]

***tert*-Butyl (but-3-en-1-ylsulfonyl)-l2-azanecarboxylate (5e)**



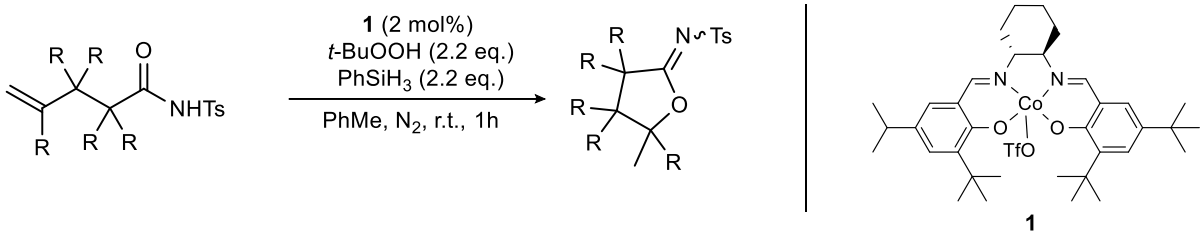
Acyl sulfonamide **5e** was prepared according to literature.[16]

***N*-(*tert*-Butylsulfinyl)pent-4-enamide (5f)**



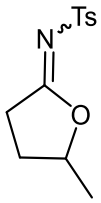
Acyl sulfinamide **5f** was prepared according to literature.[15]

Cobalt catalyzed cycloisomerization



1

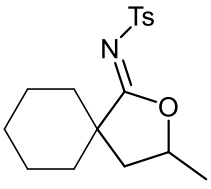
4-Methyl-N-(5-methyldihydrofuran-2(3H)-ylidene)benzenesulfonamide (4a)



Sulfonyl carboximidate **4a** was prepared via GP2, using acyl sulfonamide **3a** (76 mg, 0.30 mmol) and **1** (4.6 mg, 0.0060 mmol), and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, Rf (40% EtOAc in hexanes = 0.3) to give **4a** (64.5 mg, 0.25 mmol, 85%) as a pale yellow oil. The product was isolated as an inseparable mixture of interconverting E/Z isomers. **4a** was also prepared according to GP3 in 82% yield.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.85 – 7.79 (m, 2H), 7.24 (d, 2H), 4.76 (dp, *J* = 10.0, 6.1 Hz, 1H), 2.39 (s, 3H), 2.11 (dd, *J* = 12.7, 5.8 Hz, 1H), 1.60 (dd, *J* = 12.8, 10.0 Hz, 1H), 1.36 (d, *J* = 6.2 Hz, 3H), 1.23 (d, *J* = 2.6 Hz, 6H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 187.1, 180.3, 143.5, 138.5, 129.5, 127.6, 127.0, 85.5, 81.2, 32.8, 30.8, 30.4, 29.4, 21.7, 20.6. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2980, 2933, 1620, 1152, 1090, 812, 762, 580. **HRMS** (ESI) *m/z* calc. for $C_{12}H_{16}NO_3S$: 254.0845, found: 254.0846 $(M+H)^+$.

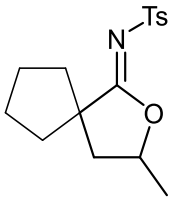
(*Z*)-4-Methyl-*N*-(3-methyl-2-oxaspiro[4.5]decan-1-ylidene)benzenesulfonamide (4b)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3b** (96.4 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.4) to give **4b** (69.3 mg, 0.216 mmol, 72%) as pale yellow crystals. **4b** was also prepared according to GP3 in 72% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.85 – 7.79 (m, 2H), 7.26 – 7.22 (m, 2H), 4.74 (dp, *J* = 9.6, 6.2 Hz, 1H), 2.40 – 2.35 (m, 3H), 2.35 (dd, *J* = 12.9, 6.2 Hz, 1H), 1.78 (td, *J* = 13.1, 3.8 Hz, 1H), 1.72 – 1.66 (m, 2H), 1.64 – 1.54 (m, 2H), 1.54 – 1.40 (m, 3H), 1.36 (d, *J* = 6.2 Hz, 3H), 1.35 – 1.08 (m, 3H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 179.9, 143.0, 138.8, 129.0, 127.4, 81.7, 49.6, 40.1, 34.9, 32.6, 25.0, 22.3, 21.6, 20.9. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2931, 1619, 1317, 1156, 1091, 804, 784, 689, 572. **HRMS** (ESI) *m/z* calc. for $C_{17}H_{23}NNaO_3S$: 344.1291, found: 344.1294 $(M+Na)^+$.

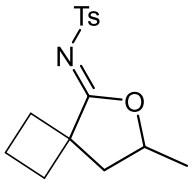
(*Z*)-4-Methyl-*N*-(3-methyl-2-oxaspiro[4.4]nonan-1-ylidene)benzenesulfonamide (4c)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3c** (92.0 mg, 0.300 mmol) and the reaction was stirred for 4h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.35) to give **4c** (76.0 mg, 0.247 mmol, 82%) as a pale-yellow oil. **4c** was also prepared according to GP3 in 87% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.85 – 7.76 (m, 2H), 7.25 – 7.20 (m, 2H), 4.71 (dp, *J* = 9.6, 6.1 Hz, 1H), 2.38 (s, 3H), 2.15 (dd, *J* = 12.7, 5.8 Hz, 2H), 1.86 – 1.72 (m, 3H), 1.75 – 1.65 (m, 1H), 1.66 – 1.51 (m, 4H), 1.35 (d, *J* = 6.3 Hz, 3H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 180.7, 143.0, 138.8, 129.0, 127.4, 81.9, 54.9, 44.3, 38.7, 37.8, 25.5, 25.3, 21.6, 20.4. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2955, 2870, 1617, 1316, 1302, 1155, 1087, 804, 786, 727, 581. **HRMS** (ESI) *m/z* calc. for $C_{16}H_{22}NO_3S$: 308.1315, found: 308.1316 $(M+H)^+$.

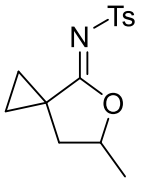
(*Z*)-4-Methyl-*N*-(7-methyl-6-oxaspiro[3.4]octan-5-ylidene)benzenesulfonamide (4d)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3d** (88.6 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.4) to give **4d** (69.1 mg, 0.236 mmol, 79%) as a pale-yellow oil. **4d** was also prepared according to GP3 in 70% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.90 – 7.83 (m, 2H), 7.26 (dt, *J* = 7.9, 0.7 Hz, 2H), 4.70 (dp, *J* = 8.5, 6.2 Hz, 1H), 2.62 – 2.51 (m, 1H), 2.47 – 2.35 (m, 5H), 2.10 – 1.88 (m, 2H), 1.83 (dd, *J* = 12.8, 8.5 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 13C NMR (126 MHz, CDCl3[d8]) δ 178.8, 143.2, 138.7, 129.1, 127.6, 81.6, 49.0, 43.0, 33.0, 30.5, 21.6, 20.5, 16.2. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2935, 1619, 1317, 1154, 1087, 803, 785, 653, 577. **HRMS** (ESI) *m/z* calc. for $C_{15}H_{20}NO_3S$: 294.1158, found: 294.1166 $(M+H)^+$.

4-Methyl-*N*-(6-methyl-5-oxaspiro[2.4]heptan-4-ylidene)benzenesulfonamide (4e)

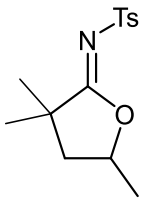


The title compound was prepared via general procedure 2, using acyl sulfonamide **3e** (83.8 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (30% EtOAc in hexanes) = 0.35) to give

4e (66.3 mg, 0.237 mmol, 79%) as a pale-yellow oil. **4e** was also prepared according to GP3 in 81% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.79 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 4.95 (ddt, *J* = 13.6, 7.3, 6.3 Hz, 1H), 2.38 (s, 3H), 2.25 (dd, *J* = 12.6, 7.3 Hz, 1H), 1.88 (dd, *J* = 12.6, 7.2 Hz, 1H), 1.37 (d, *J* = 6.3 Hz, 3H), 1.34 (dd, *J* = 6.8, 3.6 Hz, 1H), 1.27 (dd, *J* = 6.9, 3.6 Hz, 1H),1.05 – 0.99 (m, 2H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 178.5, 143.0, 138.7, 129.0, 127.4, 82.3, 36.9, 24.9, 21.6, 21.0, 18.1, 16.8. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2981, 1611, 1449, 1381, 1316, 1170, 1035, 833, 789, 663, 554. **HRMS** (ESI) *m/z* calc. for $C_{14}H_{18}NO_3S$: 280.1002, found: 280.1005 $(M+H)^+$.

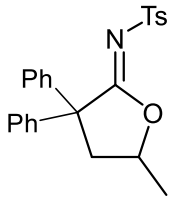
4-Methyl-*N*-(4,4,5-trimethyldihydrofuran-2(3H)-ylidene)benzenesulfonamide (4f)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3f** (84.0 mg, 0.300 mmol) and the reaction was stirred for 2h. The crude product was purified via column chromatography (0-60% EtOAc in hexane, R_f (30% EtOAc in hexanes) = 0.3) to give **4f** (54.5 mg, 0.195 mmol, 65%) as a pale-yellow oil. **4g** was also prepared according to GP3 in 57% yield.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 1H NMR (500 MHz, CDCl3) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.23 (m, 2H), 4.78 (dp, *J* = 10.0, 6.1 Hz, 1H), 2.40 (s, 3H), 2.12 (dd, *J* = 12.7, 5.8 Hz, 1H), 1.67 – 1.57 (m, 1H), 1.38 (d, *J* = 6.2 Hz, 3H), 1.25 (m, 6H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 180.0, 143.2, 138.7, 129.1, 127.6, 81.3, 45.1, 44.7, 25.9, 25.7, 21.7, 20.7. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2977, 2933, 1619, 1495, 1455, 1304, 1318, 1152, 805, 790, 665, 581. **HRMS** (ESI) *m/z* calc. for $C_{14}H_{20}NO_3S$: 282.1158, found: 282.1167 $(M+H)^+$.

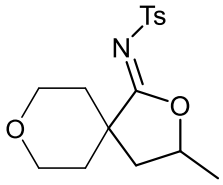
(*Z*)-4-Methyl-*N*-(5-methyl-3,3-diphenyldihydrofuran-2(3H)-ylidene)benzenesulfonamide (4g)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3g** (121 mg, 0.300 mmol) and the reaction was stirred for 4h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.4) to give **4g** (81.0 mg, 0.200 mmol, 67%) as a pale-yellow oil. **4g** was also prepared according to GP3 in 65% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.82 (d, *J* = 8.4 Hz, 2H), 7.30 (m, 5H), 7.27 – 7.22 (m, 5H), 7.19 (m, 2H), 4.76 – 4.62 (m, 1H), 2.97 (dd, *J* = 13.0, 4.6 Hz, 1H), 2.54 (dd, *J* = 13.0, 10.6 Hz, 1H), 2.41 (s, 2H), 1.48 (d, *J* = 6.1 Hz, 2H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 175.5, 143.2, 141.7, 140.1, 138.8, 129.1, 129.0, 128.2, 128.2, 128.0, 127.6, 127.4, 127.4, 80.9, 61.4, 45.7, 21.7, 19.9. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3060, 2980, 1625, 1598, 1446, 1319, 1156, 1987, 849, 782, 730, 541. **HRMS** (ESI) *m/z* calc. for $C_{24}H_{24}NO_3S$: 406.1471, found: 406.1478 $(M+H)^+$.

(*Z*)-4-Methyl-*N*-(3-methyl-2,8-dioxaspiro[4.5]decan-1-ylidene)benzenesulfonamide (4h)

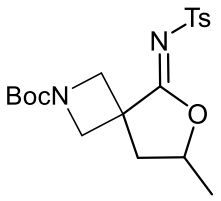


The title compound was prepared via general procedure 2, using acyl sulfonamide **3h** (97.2 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via

column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.3) to give **4h** (94.0 mg, 0.291 mmol, 97%) as a pale-yellow powder. **4h** was also prepared according to GP3 in 68% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.83 (d, *J* = 8.3 Hz, 2H), 7.26 (dd, *J* = 8.7, 0.7 Hz, 2H), 4.83 (dp, *J* = 9.8, 6.2 Hz, 1H), 3.93 (ddt, *J* = 19.0[d9], 12.0, 4.2 Hz, 2H), 3.50 (ddd, *J* = 12.0, 10.5, 2.8 Hz, 1H), 3.38 (ddd, *J* = 11.8, 10.7, 2.8 Hz, 1H), 2.45 (dd, *J* = 12.9, 6.0 Hz, 1H), 2.40 (s, 3H), 2.10 (ddd, *J* = 13.7, 10.7, 4.4 Hz, 1H), 1.86 (dddd, *J* = 13.6, 10.5, 4.3, 1.1 Hz, 1H), 1.63 (ddd, *J* = 13.0, 9.8, 1.1 Hz, 1H), 1.59 – 1.50 (m, 1H), 1.43 (m, 4H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 177.6, 143.3, 138.8, 129.2, 127.3, 81.4, 77.5, 77.2, 76.8, 64.1, 63.8, 46.8, 40.8, 34.5, 33.0, 21.6, 20.9. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2954, 1621, 1317, 1156, 1087, 817, 805, 787, 574. **HRMS** (ESI) *m/z* calc. for $C_{16}H_{21}NNaO_4S$: 346.1084, found: 346.1091 $(M+Na)^+$.

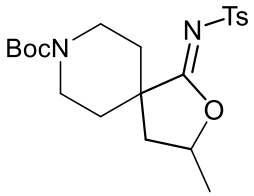
***tert*-Butyl (*Z*)-7-methyl-5-(tosylimino)-6-oxa-2-azaspiro[3.4]octane-2-carboxylate (4i)**



The title compound was prepared via general procedure 2, using acyl sulfonamide **3i** (118.8 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (60% EtOAc in hexanes) = 0.3) to give **4i** (74.7 mg, 0.188 mmol, 63%) as a pale-yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.87 – 7.83 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 4.79 (dt, *J* = 8.1, 6.2 Hz, 1H), 4.27 (d, *J* = 8.4 Hz, 1H), 4.15 (d, *J* = 8.2 Hz, 1H), 3.87 – 3.80 (m, 2H), 2.60 (dd, *J* = 13.3, 6.2 Hz, 1H), 2.41 (s, 3H), 2.05 (dd, *J* = 13.3, 8.0 Hz, 1H), 1.40 (m, 12H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 175.1, 155.8, 143.7, 138.2, 129.3, 127.6, 81.9, 80.4, 43.8, 41.3, 28.4, 21.7, 20.6. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2933, 1699, 1632, 1365, 1155, 1090, 813, 783, 728, 662, 579. **HRMS** (ESI) *m/z* calc. for $C_{19}H_{26}N_2NaO_5S$: 417.1455, found: 417.1456 $(M+Na)^+$.

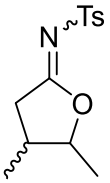
***tert*-Butyl (*Z*)-3-methyl-1-(tosylimino)-2-oxa-8-azaspiro[4.5]decane-8-carboxylate (4j)**



The title compound was prepared via general procedure 2, using acyl sulfonamide **3j** (127 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.28) to give **4j** (91.0 mg, 0.215 mmol, 72%) as a pale-yellow oil. **4j** was also prepared according to GP3 in 61% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.84 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 9.2 Hz, 2H), 4.84 (dt, *J* = 9.7, 6.1 Hz, 1H), 3.96 (bs, 1H), 2.98 (t, *J* = 12.3 Hz, 1H), 2.86 (t, *J* = 12.4 Hz, 1H), 2.42 (s, 3H), 2.37 (dd, *J* = 12.9, 6.0 Hz, 1H), 1.96 (ddd, *J* = 13.5, 11.0, 4.4 Hz, 1H), 1.75 (ddd, *J* = 14.4, 10.6, 4.3 Hz, 1H), 1.58 (dd, *J* = 11.9, 7.7 Hz, 1H), 1.46 (d, *J* = 6.3 Hz, 3H), 1.43 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 177.7, 154.5, 143.4, 138.7, 129.3, 127.4, 81.5, 80.1, 47.6, 40.4, 34.2, 32.5, 28.5, 21.7, 21.0. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2932, 1687, 1625, 1423, 1319, 1155, 818, 787, 574. **HRMS** (ESI) *m/z* calc. for $C_{21}H_{31}N_2O_5S$: 423.1948, found: 423.1945 $(M+H)^+$.

***N*-(4,5-Dimethyldihydrofuran-2(3H)-ylidene)-4-methylbenzenesulfonamide (4k)**



The title compound was prepared via general procedure 2, using acyl sulfonamide **3k** (80.2 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via

column chromatography (0-40% EtOAc in hexane, R_f (30% EtOAc in hexanes) = 0.30) to give two separable diastereomeric products **4k** (66.0 mg, 0.247 mmol, 82%, 1.2:1 dr) as pale-yellow oils. The products was isolated as an inseparable mixture of imine E/Z isomers.

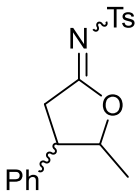
Major diastereomer:

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.82 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 4.39 (m, 0.3H), 4.21 (m, 0.7H), 3.61 (dd, J = 18.5, 7.9 Hz, 0.7H), 2.84 (m, 0.3H), 2.73 (dd, J = 18.7, 10.3 Hz, 0.7H), 2.44 (m, 0.3H), 2.40 (m, 3H), 2.26 – 2.09 (m, 1H), 1.41 (m, 3H), 1.17 – 1.08 (m, 3H).**^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 179.6, 143.5, 138.4, 129.5, 129.3, 127.6, 127.0, 90.8, 86.8, 40.6, 39.0, 38.7, 38.1, 21.6, 18.7, 16.2. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2974, 1626, 1303, 1156, 848, 775, 582. **HRMS** (ESI) *m/z* calc. for $C_{13}H_{18}NO_3S$: 268.1002, found: 268.1002 $(M+H)^+$.

Minor diastereomer:

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.81 (m, 2H), 7.27 (m, 2H), 4.91 (bs, 0.3H), 4.74 (m, 0.6H), 3.32 (m, 0.6H), 3.03 (m, 0.6H), 2.96 – 2.85 (m, 0.3H), 2.65 (m, 0.6H), 2.55 (m, 0.3H), 2.39 (s, 3H), 1.28 (m, 3H), 1.06 – 0.91 (m, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 179.9, 143.4, 138.5, 129.5, 129.2, 127.5, 127.0, 87.3, 83.2, 40.2, 38.3, 34.1, 33.3, 21.6, 15.1, 13.7. [d10]**FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2974, 1617, 1312, 1301, 1151, 1076, 760, 581. **HRMS** (ESI) *m/z* calc. for $C_{13}H_{18}NO_3S$: 268.1002, found: 268.1001 $(M+H)^+$.

N-(4,5-Dimethyldihydrofuran-2(3H)-ylidene)-4-phenylbenzenesulfonamide (4l)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3l** (98.8 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (25% EtOAc in hexanes) = 0.30) to give two separable diastereomeric products **4l** (65.0 mg, 0.207 mmol, 65%, 1.3:1 dr) as pale-yellow oils. The products were isolated as an inseparable mixture of imine E/Z isomers.

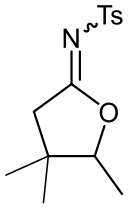
Major diastereomer: [d11]

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.95 – 7.85 (m, 2H), 7.30 (m, 5H), 7.07 – 6.84 (m, 2H), 5.16 (m, 0.4H[d12]), 5.00 (m, 0.6H), 3.79 (m, 0.6H), 3.63 (m, 1.6H), 3.21 (m, 0.3H), 2.97 (m, 0.3H), 2.42 (s, 3H), 1.01 (d, *J* = 7.0 Hz, 3H).**^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = δ 180.0, 143.6, 138.4, 136.8, 129.6, 129.3, 129.0, 127.9, 127.8, 127.1, 87.8, 83.5, 45.6, 45.1, 39.1, 36.7, 21.7, 16.4. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2928, 1627, 1302, 1154, 1091, 1068, 779, 699, 583. **HRMS** (ESI) *m/z* calc. for $C_{18}H_{20}NO_3S$: 330.1158, found: 330.1157 $(M+H)^+$.

Minor diastereomer:

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.85 (m, 2H), 7.36 – 7.28 (m, 5H), 7.25 – 7.17 (m, 2H), 4.82 (m, 0.3H), 4.64 (m, 0.6H), 3.90 (m, 0.6H), 3.36 – 2.99 (m, 1.4H), 2.42 (s, 3H), 1.45 (m, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 178.7, 143.6, 138.3, 137.1, 129.6, 129.4, 128.3, 127.7, 127.4, 127.1, 90.5, 86.4, 50.4, 49.5, 40.8, 38.8, 21.7, 18.9. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2979, 1628, 1315, 1287, 1155, 1068, 779, 700, 583. **HRMS** (ESI) *m/z* calc. for $C_{18}H_{19}NNaO_3S$: 352.0978, found: 352.0977 $(M+Na)^+$.

(*Z*)-4-Methyl-*N*-(4,4,5-trimethyldihydrofuran-2(3H)-ylidene)benzenesulfonamide (4m)

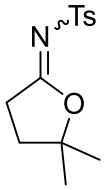


The title compound was prepared via general procedure 2, using acyl sulfonamide **3m** (84.0 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (30% EtOAc in hexanes) = 0.3) to give **4m** (37.0 mg, 0.131 mmol, 44%) as a pale-yellow oil. The product was isolated as an inseparable mixture of imine E/Z isomers.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.81 (m, 2H), 7.26 (m, 2H), 4.47 (m, 0.3H), 4.31 (m, 0.6H), 3.28 (d, *J* = 18.1 Hz, 0.6H), 2.91 (d, *J* = 18.1 Hz[d13], 0.6H), 2.61 (d, *J* = 16.6 Hz, 0.3H), 2.54 – 2.45 (m, 0.3H), 2.40 (s, 3H), 1.27 (m, 3H), 1.21 – 1.06 (m, 3H), 1.00 (s, 2H), 0.89 (t, *J* = 7.1 Hz, 1H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 188.5, 179.5, 143.5, 138.5, 129.5, 129.2,

127.6, 127.0, 91.8, 88.0, 47.3, 45.5, 40.3, 26.8, 24.8, 24.6, 21.6, 21.4, 21.1, 20.9, 13.9. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2966, 1619, 1430, 1345, 1165, 1086, 845, 660, 548. **HRMS** (ESI) *m/z* calc. for $C_{14}H_{22}NO_3S$: 284.1315, found: 284.1313 $(M+H)^+$.

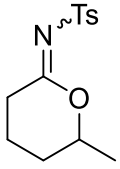
***N*-(5,5-Dimethyldihydrofuran-2(3H)-ylidene)-4-methylbenzenesulfonamide (4n)**



The title compound was prepared via general procedure 2, using acyl sulfonamide **3n** (80.2 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (30% EtOAc in hexanes) = 0.30) to give **4n** (43.7 mg, 0.164 mmol, 54%) as a pale-yellow oil. The product was isolated as an inseparable mixture of imine E/Z isomers.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.82 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 3.38 – 3.31 (m, 1.4H), 2.83 (m, 0.6H), 2.39 (s, 3H), 2.22 – 1.89 (m, 2H), 1.43 (s, 3H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 179.6, 143.4, 138.5, 129.4, 129.2, 127.7, 126.9, 89.6, 35.2, 34.3, 32.8, 30.9, 27.3, 21.6. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2977, 1620, 1310, 1302, 1154, 1091, 737, 577. **HRMS** (ESI) *m/z* calc. for $C_{13}H_{18}NO_3S$: 268.1002, found: 268.1006 $(M+H)^+$.

4-Methyl-*N*-(6-methyltetrahydro-2H-pyran-2-ylidene)benzenesulfonamide (4o)

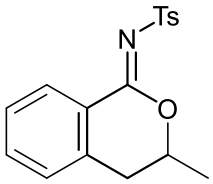


The title compound was prepared via general procedure 2, using acyl sulfonamide **3o** (80.2 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via

column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.4) to give **4o** (56.3 mg, 0.211 mmol, 70%) as a pale-yellow oil. The product was isolated as an inseparable mixture of imine E/Z isomers. **4o** was also prepared according to GP3 in 84% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.81 (d, *J* = 8.3 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 4.39 (ddp, *J* = 9.8, 6.3, 3.9, 3.3 Hz, 1H), 2.57 – 2.41 (m, 1H), 2.38 (s, 3H), 1.94 – 1.74 (m, 2H), 1.44 (m, 1H), 1.29 (d, *J* = 6.3 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 171.2, 143.1, 138.9, 129.1, 127.6, 79.4, 29.0, 28.7, 21.6, 20.9, 17.3. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2979, 1595, 1387, 1302, 1156, 788, 685, 542. **HRMS** (ESI) *m/z* calc. for $C_{13}H_{18}NO_3S$: 268.1002, found: 268.1002 $(M+H)^+$.

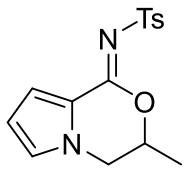
(*Z*)-4-Methyl-*N*-(3-methylisochroman-1-ylidene)benzenesulfonamide (4p)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3p** (94.6 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (30% EtOAc in hexanes) = 0.32) to give **4p** (75.0 mg, 0.238 mmol, 79%) as a pale-yellow oil. **4p** was also identically prepared on 1 mmol in 93% yield. **4p** was also prepared according to GP3 in 71% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.13 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.50 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 – 7.25 (m, 3H), 7.20 – 7.14 (m, 1H), 4.60 (dqd, *J* = 9.7, 6.3, 4.8 Hz, 1H), 2.99 – 2.83 (m, 2H), 2.42 (s, 3H), 1.45 (d, *J* = 6.3 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 163.2, 143.1, 139.3, 137.8, 134.3, 130.2, 129.1, 127.9, 127.8, 127.8, 125.0, 77.2, 34.3, 21.7, 20.2. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3065, 2981, 1611, 1589, 1562, 1315, 1300, 1158, 1132, 773, 552. **HRMS** (ESI) *m/z* calc. for $C_{17}H_{18}NO_3S$: 316.1002, found: 316.1007 $(M+H)^+$.

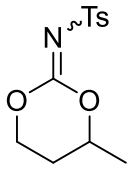
(Z)-4-methyl-N-(3-methyl-3,4-dihydro-1H-pyrrolo[2,1-c][1,4]oxazin-1-ylidene)benzenesulfonamide (4q)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3q** (91.3 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-60% EtOAc in hexane, R_f (50% EtOAc in hexanes) = 0.30) to give **4q** (79.4 mg, 0.261 mmol, 87%) as pale-yellow crystals.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.93 – 7.88 (m, 2H), 7.26 (m, 2H), 7.14 (dd, *J* = 4.1, 1.5 Hz, 1H), 6.86 (dd, *J* = 2.5, 1.5 Hz, 1H), 6.28 (dd, *J* = 4.1, 2.5 Hz, 1H), 4.71 (dqd, *J* = 9.8, 6.4, 3.3 Hz, 1H), 4.12 (dd, *J* = 13.2, 3.3 Hz, 1H), 3.90 (dd, *J* = 13.2, 9.9 Hz, 1H), 2.41 (s, 3H), 1.45 (d, *J* = 6.5 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 156.7, 142.9, 139.7, 129.1, 127.7, 126.7, 119.2, 118.5, 111.9, 75.7, 48.5, 21.7, 17.6. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3123, 1565, 1479, 1311, 1112, 1085, 807, 789, 579. **HRMS** (ESI) *m/z* calc. for $C_{15}H_{17}N_2O_3S$: 305.0954, found: 305.0952 $(M+H)^+$.

4-Methyl-*N*-(4-methyl-1,3-dioxan-2-ylidene)benzenesulfonamide (4r)

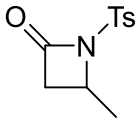


The title compound was prepared via general procedure 2, using acyl sulfonamide **3r** (80.8 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via

column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.4) to give **4r** (42.0 mg, 0.156 mmol, 2%) as a pale-yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.90 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.87 – 4.68 (m, 1H), 4.46 – 4.37 (m, 1H), 4.33 – 4.27 (m, 1H), 2.41 (s, 3H), 2.36 – 2.14 (m, 1H), 1.87 (ddd, *J* = 14.4, 2.8, 0.5 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H).**^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 148.6, 145.0, 136.0, 129.4, 129.1, 77.4, 77.2, 76.9, 64.4, 51.1, 28.8, 21.7, 21.1. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2961, 1750, 1445, 1160, 1089, 844, 662, 547. **HRMS** (ESI) *m/z* calc. for $C_{12}H_{16}NO_4S$: 270.0795, found: 270.0797 $(M+H)^+$.

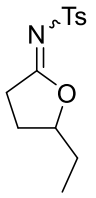
4-Methyl-1-tosylazetidin-2-one (4s)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3s** (71.1 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.32) to give **4s** (21.4 mg, 0.0894 mmol, 30%) as off-white crystals.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.88 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 4.17 (td, *J* = 6.1, 3.3 Hz, 1H), 3.12 (dd, *J* = 15.9, 6.0 Hz, 1H), 2.62 (dd, *J* = 15.9, 3.3 Hz, 1H), 2.45 (s, 3H), 1.52 (d, *J* = 6.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 163.7, 145.3, 136.4, 130.2, 127.5, 51.4, 44.2, 21.8, 20.0. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2978, 1785, 1359, 1167, 1135, 1090, 673. **HRMS** (ESI) *m/z* calc. for $C_{11}H_{14}NO_3S$: 240.0689, found: 240.0690 $(M+H)^+$.

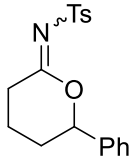
(*Z*)-*N*-(5-Ethyldihydrofuran-2(3H)-ylidene)-4-methylbenzenesulfonamide (4t)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3t** (80.2 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.3) to give **4t** (25.4 mg, 0.0935 mmol, 31%) as a pale-yellow oil and **4o** (20.4 mg, 0.0748 mmol, 25%). The products were isolated as an inseparable mixture of imine E/Z isomers.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.86 – 7.78 (m, 2H), 7.32 – 7.24 (m, 2H), 4.73 (m, 0.3H), 4.54 (m, 0.6H), 3.44 (m, 0.6H), 3.13 (m, 0.6H), 2.78 (m, 0.7H), 2.41 (brs, 3H), 1.91 (m, 0.3H), 1.78 – 1.61 (m, 3H), 0.97 (m, 3H).**^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 13C NMR (126 MHz, CDCl3) δ 180.4, 143.5, 138.5, 129.8, 129.5, 129.3, 127.7, 127.1, 126.6, 90.4, 86.2, 32.6, 30.6, 28.3, 28.1, 27.1, 21.7, 21.7, 9.7, 9.4. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2970, 2939, 1622, 1314, 1302, 1154, 818, 757, 691, 582. **HRMS** (ESI) *m/z* calc. $C_{13}H_{18}NO_3S$: 268.1002, found: 268.1000 $(M+H)^+$.

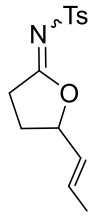
(*Z*)-4-Methyl-*N*-(6-phenyltetrahydro-2H-pyran-2-ylidene)benzenesulfonamide (4u)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3u** (98.8 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.3) to give **4u** (72.0 mg, 0.219 mmol, 73%) as a pale-yellow oil.

^{1}H-NMR (600 MHz, $CDCl_3$): δ / ppm = 7.75 (m, 2H), 7.41 – 7.32 (m, 3H), 7.24 (brs, 2H), 7.13 (brs, 2H), 5.32 (dd, *J* = 10.6, 3.5 Hz, 1H), 2.65 (m, 2H), 2.37 (s, 3H), 2.21 – 2.13 (m, 1H), 1.91 (m, 3H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ / ppm = 170.5, 143.1, 138.8, 138.3, 129.2, 128.8, 128.8, 127.8, 126.0, 83.7, 30.1, 28.9, 21.7, 17.7. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3034, 2924, 1599, 1314, 1302, 1155, 699, 565. **HRMS** (ESI) *m/z* calc. for $C_{18}H_{23}N_2O_3S$: 347.1424, found: 347.1420 $(M+NH_4)^+$.

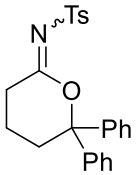
4-Methyl-*N*-((*Z*)-5-((*E*)-prop-1-en-1-yl)dihydrofuran-2(3H)-ylidene)benzenesulfonamide (4v)



The title compound was prepared via general procedure 2, using acyl sulfonamide **4v** (98.8 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.4) to give **4v** (36.7 mg, 0.131 mmol, 44%) as a pale-yellow oil. The product was isolated as an inseparable mixture of imine E/Z isomers. The product was contaminated with a small amount (<5%) of inseparable reduction product which has been accounted for in the yield calculation.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.86 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.27 (m, 2H), 5.86 (m, 1H), 5.50 (m, 1H), 5.26 – 4.89 (m, 1H), 3.44 (m, 0.6H), 3.26 – 3.04 (m, 0.6H), 2.80 (m, 0.6H), 2.43 (s, 4.2H), 2.14 – 1.85 (m, 1H), 1.76 – 1.74 (m, 3H).**^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 180.2, 143.5, 138.5, 132.4, 132.1, 129.5, 127.7, 127.5, 127.2, 127.0, 88.9, 84.9, 37.1, 32.5, 30.6, 29.4, 28.4, 21.7, 17.8, 13.8. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2923, 1625, 1343, 1155, 1094, 820, 769, 584. **HRMS** (ESI) *m/z* calc. for $C_{14}H_{18}NO_3S$: 280.1002, found: 280.1003 $(M+H)^+$.

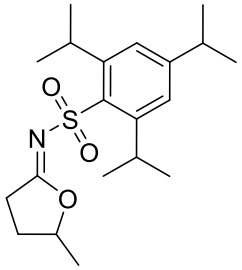
(*Z*)-*N*-(6,6-Diphenyltetrahydro-2H-pyran-2-ylidene)-4-methylbenzenesulfonamide (4w)



The title compound was prepared via general procedure 2, using acyl sulfonamide **3w** (121 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.3) to give **4w** (86.2 mg, 0.212 mmol, 71%) as a pale-yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.90 – 7.83 (m, 2H), 7.36 – 7.29 (m, 10H), 7.25 – 7.17 (m, 2H), 2.57 (t, *J* = 6.8 Hz, 2H), 2.46 (d, *J* = 9.8 Hz, 2H), 2.42 (s, 3H), 1.88 (qd, *J* = 7.2, 6.3 Hz, 2H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 170.4, 143.2, 142.4, 139.0, 129.3, 128.8, 128.1, 127.6, 125.9, 90.9, 33.0, 28.0, 21.7, 15.7. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3063, 2952, 1596, 1357, 1302, 1324, 1154, 1048, 853, 753, 582. **HRMS** (ESI) *m/z* calc. for $C_{24}H_{24}NO_3S$: 406.1471, found: 406.1470 $(M+H)^+$.

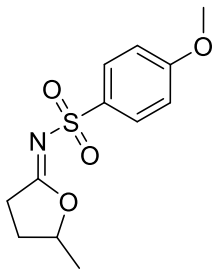
(*Z*)-2,4,6-Triisopropyl-*N*-(5-methyldihydrofuran-2(3H)-ylidene)benzenesulfonamide (6a)



The title compound was prepared via general procedure 2, using acyl sulfonamide **5a** (109 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-60% EtOAc in hexane, R_f (20% EtOAc in hexanes) = 0.3) to give **6a** (95.2 mg, 0.260 mmol, 87%) as a pale-yellow oil. The product was isolated as an inseparable mixture of imine E/Z isomers.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.12 (m, 2H), 4.76 (m, 1H), 4.25 (m, 2H), 3.34 (m, 0.5H), 3.06 (dt, *J* = 18.8, 9.3 Hz, 0.5H), 2.88 (bp, *J* = 6.9 Hz, 1H), 2.83 – 2.70 (m, 1H), 2.42 (m, 0.5H), 2.29 (m, 0.5H), 1.96 – 1.81 (m, 0.5H), 1.79 – 1.64 (m, 0.5H), 1.43 (d, *J* = 6.2 Hz, 1.5H), 1.24 (d, *J* = 19.8 Hz, 20H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm =179.6, 173.4, 152.6, 152.4, 149.8, 135.3, 134.4, 123.5, 123.4, 84.9, 80.8, 34.3, 32.6, 30.5, 30.4, 29.7, 29.5, 29.4, 24.8, 24.8, 23.7, 20.6, 20.4. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2957, 1628, 1460, 1384, 1150, 1038, 843, 765, 580. **HRMS** (ESI) *m/z* calc. for $C_{20}H_{32}NO_3S$: 366.2097, found: 366.2104 $(M+H)^+$.

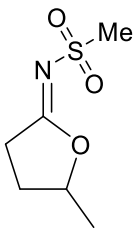
(*Z*)-4-methoxy-N-(5-methyldihydrofuran-2(3H)-ylidene)benzenesulfonamide (6b)



The title compound was prepared via general procedure 2, using acyl sulfonamide **7b** (80.8 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-60% EtOAc in hexane, R_f (30% EtOAc in hexanes) = 0.4) to give **6b** (70.7 mg, 0.263 mmol, 88%) as a pale-yellow oil. The product was isolated as an inseparable mixture of imine E/Z isomers.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 7.85 (m, J = 8.9 Hz, 2H[d14]), 6.95 – 6.92 [d15](m, 2H), 4.90 (m, 0.3H), 4.72 (m, 0.6H), 3.83 (s, 3H), 3.41 (m, 0.6H), 3.14 – 3.05 (m, 0.6H), 2.77 (m, 0.6H), 2.35 (m, 1H), 1.87 – 1.74 (m, 1H), 1.40 (m, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 180.1, 174.4, 163.0, 133.1, 129.7, 129.0, 114.0, 113.8, 85.5, 81.1, 55.7, 32.7, 30.7, 30.3, 29.3, 20.5. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2936, 1619, 1594, 1497, 1295, 1147, 1089, 1022, 806, 575. **HRMS** (ESI) *m/z* calc. for $C_{12}H_{16}NO_4S$: 270.0795, found: 270.0799 $(M+H)^+$.

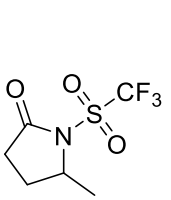
(*Z*)-*N*-(5-Methyldihydrofuran-2(3H)-ylidene)methanesulfonamide (6c)

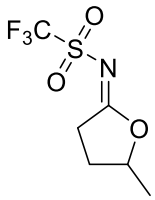


The title compound was prepared via general procedure 2, using acyl sulfonamide **5c** (53.8 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-40% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.3) to give **6c** (47.0 mg, 0.265 mmol, 88%) as a pale-yellow oil. The product was isolated as an inseparable mixture of imine E/Z isomers.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 4.98 – 4.96 (m, 0.3H), 4.77 – 4.74 (m, 0.6H), 3.31 (m, 0.6H), 3.12 – 3.04 (m, 0.6H), 3.01 (bs, 3H), 2.79 (m, 0.6H), 2.48 – 2.33 (m, 1H), 1.85 (m, 1H), 1.45 (m, 3H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 13C NMR (126 MHz, CDCl3) δ 180.5, 174.5, 85.7, 81.3, 42.5, 42.1, 32.5, 30.6, 30.2, 29.4, 20.5. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2981, 1620, 1295, 1141, 832, 811, 783, 551. **HRMS** (ESI) *m/z* calc. for $C_6H_{12}NO_3S$: 178.0532, found 178.0537 $(M+H)^+$.

(*Z*)-1,1,1-Trifluoro-*N*-(5-methyldihydrofuran-2(3H)-ylidene)methanesulfonamide (8d) and 5-Methyl-1-((trifluoromethyl)sulfonyl)pyrrolidin-2-one ([d16]6e)





The title compounds were prepared via general procedure 2, using acyl sulfonamide **5d** (69.4 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude products were purified via column chromatography (0-60% EtOAc in hexane, R_f (40% EtOAc in hexanes) = 0.3 and 0.5 respectively) to give[d17] **6d** (25.0 mg, 0.108 mmol, 36%) and **6e** (17.1 mg, 0.0735 mmol, 25%) as pale-yellow oils.

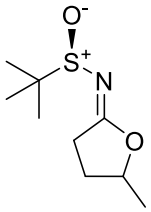
(*Z)-1,1,1-Trifluoro-N-(5-methyldihydrofuran-2(3H)-ylidene)methanesulfonamide (6d):*

^{1}H-NMR [d18](400 MHz, $CDCl_3$): δ / ppm = 5.03 (dp, *J* = 7.8, 6.4 Hz, 1H), 3.21 (m, 1H), 3.09 (dt, *J* = 18.9[d19], 9.4 Hz, 1H), 2.50 (dddd, *J* = 13.0, 9.4, 6.6, 4.2 Hz, 1H), 1.97 (dtd, *J* = 13.0, 9.4, 8.2 Hz, 1H), 1.55 (d, *J* = 6.3 Hz, 3H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 166.6 (weak due to F coupling), 119.0 (q, 320 Hz), 85.6, 32.7, 29.7, 20.4. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2940, 1611, 1350, 1188, 1130, 835, 786, 619. **HRMS** (ESI) *m/z* calc. for $C_6H_9F_3NO_3S$: 232.0250, found: 232.0247 $(M+H)^+$.

5-methyl-1-((trifluoromethyl)sulfonyl)pyrrolidin-2-one ([d20]6e)

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 1H NMR (500 MHz, CDCl3) δ 4.49 (m, 1H), 2.75 (m, 1H), 2.59 (m, 1H), 2.40 (m, 1H), 1.87 (m, 1H), 1.50 (m, 3H).**^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 172.6, 119.1 (q, *J* = 323 Hz), 77.4, 77.2, 76.9, 58.1, 30.5, 26.9, 21.5. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2993, 1770, 1403, 1134, 1068, 958, 714, 593. **HRMS** (ESI) *m/z* calc. for $C_6H_8F_3NNaO_3S$: 254.0069, found: 254.0074 $(M+Na)^+$.

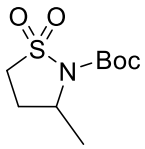
(*E*)-2-methyl-*N*-(5-methyldihydrofuran-2(3H)-ylidene)propane-2-sulfinamide (6f)



The title compound was prepared via general procedure 2, using acyl sulfonamide **5f** (70.5 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-5% MeOH in CH_2Cl_2, R_f (2% MeOH in CH_2Cl_2) = 0.3) to give **6f** (35.0 mg, 0.148 mmol, 50%) as a pale-yellow oil. The product was isolated as an inseparable mixture of E/Z isomers of the imine and as a 2:1 mixture of diastereomers with respect to sulphur.[d21]

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 4.85 – 4.70 (m, 0.3H), 4.68 – 4.55 (m, 0.6H), 3.28 (ddd, *J* = 17.7, 8.5, 4.0 Hz, 0.3H), 3.00 (dd, *J* = 9.7, 6.3 Hz, 0.6H), 2.85 – 2.67 (m, 1H), 2.33 (m, 1H), 1.79 (m, 1H), 1.41 (dd, *J* = 9.7, 6.2 Hz, 3H), 1.18 (s, 9H).**^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 180.0, 179.6, 174.6, 174.6, 82.8, 82.7, 79.4, 79.4, 56.1, 56.0, 55.5, 55.4, 31.8, 31.0, 30.7, 30.2, 29.6, 28.8, 21.9, 21.9, 20.7, 20.6. **FT-IR** (neat): $\tilde{\nu}$ / cm^{1} = 2977, 1633, 1184, 1076, 1050, 745, 549. **HRMS** (ESI) *m/z* calc. for $C_9H_{17}NNaO_2S$: 226.0872, found: 226.0872 $(M+Na)^+$.

***tert*-Butyl 3-methylisothiazolidine-2-carboxylate 1,1-dioxide (6g)**



The title compound was prepared via general procedure 2, using acyl sulfonamide **5g** (70.5 mg, 0.300 mmol) and the reaction was stirred for 1h. The crude product was purified via column chromatography (0-5% MeOH in CH_2Cl_2, R_f (2% MeOH in CH_2Cl_2) = 0.3) to give **6g** (35.0mg, 0.148 mmol,50%) as a pale-yellow oil.

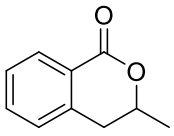
^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = δ 4.28 – 4.17 (m, 1H), 3.44 – 3.30 (m, 1H), 3.33 – 3.18 (m, 1H), 2.53 (ddt, *J* = 13.6, 10.1, 7.1 Hz, 1H), 1.99 (dddd, *J* = 13.5, 6.8, 5.4, 3.9 Hz, 1H), 1.52 (d, *J* = 0.8 Hz, 9H), 1.39 (d, *J* = 6.3 Hz, 3H).**^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 149.8, 84.1, 77.4, 77.2, 76.9, 53.1, 47.7, 28.2, 28.1, 25.7, 20.0. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2980, 1716, 1303, 1133, 1068, 837, 529. **HRMS** (ESI) *m/z* calc. for $C_9H_{17}NNaO_4S$: 258.077, found: 258.0774 $(M+Na)^+$.

Unsuccessful substrates

Two benzamide substrates (N-acyl pentafluorobenzamide and N-acyl benzamide) were explored as potential substrates. However, neither of those substrates was conducive to this transformation under our conditions.

Derivatizations *[d22]*

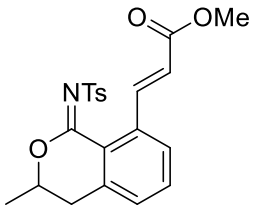
3-Methylisochroman-1-one (7a)



To a solution of sulfonyl carboximidate **4p** (65.0 mg, 0.206 mmol, 1.00 eq.) in DMF–H2O (95:5, 0.4 mL) was added DBU[d23] 9.43 [d24]mg, 61.8 µmol, 0.300 eq.) and the mixture stirred at rt for 12h. The reaction mixture was then diluted with EtOAc (20 mL) and washed with water (3x 10 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4, filtered and the solvent removed in vacuo. The crude product was purified via column chromatography (0-40% EtOAc in

hexane, Rf (40% EtOAc in hexanes = 0.3) to give **9a** (29.3 mg, 0.170 mmol, 82%) as a white solid. The spectra obtained were in accordance with the literature.[17]

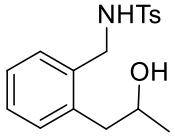
Methyl (*E*)-3-((*E*)-3-methyl-1-(tosylimino)isochroman-8-yl)acrylate (7b)



A 5 mL microwave vial equipped with a stirrer bar was charged with sulfonyl carboximidate **4p** (50.0 mg, 0.159 mmol, 1.00 eq), $[Cp^*RhCl_2]_2$ (2.45mg, 3.96 ymol, 2.5 mol%), $AgSbF_6$ (5.45 mg, 15.8 ymol, 10 mol%), and $Cu(OAc)_2$ (14.4, mg, 79.3 50 mol%) under air, followed by addition of dioxane (1 mL) and methyl acrylate (40.9 mg, 0.476 mmol, 3.00 eq.). Then, the vial tube was sealed with [d25]and the reaction mixture was stirred at 120 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing with ethyl acetate (20 mL). Subsequently, the filtrate was concentrated in vacuo. The crude product was purified via column chromatography (0-40% EtOAc in hexane, Rf (40% EtOAc in hexanes = 0.4) to give **9b** (50.5 mg, 0.126 mmol, 80%) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ / ppm = 8.32 (dt, *J* = 15.9, 0.6 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.51 – 7.44 (m, 1H), 7.40 (ddd, *J* = 7.8, 1.4, 0.7 Hz, 1H), 7.28 – 7.20 (m, 3H), 6.10 (d, *J* = 15.8 Hz, 1H), 4.62 (dp, *J* = 8.1, 6.3 Hz, 1H), 3.69 (s, 3H), 2.99 – 2.90 (m, 2H), 2.39 (s, 3H), 1.56 (d, *J* = 6.3 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ / ppm = 166.6, 161.3, 144.8, 142.8, 139.6, 139.5, 138.1, 133.3, 129.1, 129.0, 128.9, 128.4, 128.2, 127.3, 127.2, 123.9, 120.2, 76.4, 51.7, 35.4, 21.6, 20.1. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 2983, 2949, 1715, 1589, 1563, 1247, 1156, 1088, 989, 824, 689, 553. **HRMS** (ESI) *m/z* calc. for $C_{21}H_{22}NO_5S$: 400.1213, found: 400.1213 $(M+H)^+$.

N-(2-(2-hydroxypropyl)benzyl)-4-methylbenzenesulfonamide (7c)



To a solution of sulfonyl carboximidate **4p** (44.0 mg, 0.140 mmol, 1.00 eq.) in MeOH (3 mL) was added $NaBH_4$ 42.4 [d26]mg, 1.26 mmol, 9 eq.) portion wise over 3h (every hour 3 eq. were added) and the reaction stirred until loss of starting material (TLC). The solvent was removed in vacuo, the residue dissolved in EtOAc (20 mL) and water (10 mL). The aqueous phase was extracted with EtOAc (2x 20 mL) and the combined organic phases washed with brine (10 mL). The organic phase was dried over Na_2SO_4, filtered and the solvent removed in vacuo. The crude product was purified via column chromatography (0-80% EtOAc in hexane, Rf (60% EtOAc in hexanes = 0.35) to give **9c** (34.3 mg, 0.107 mmol, 77%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ / ppm = 7.80 – 7.74 (m, 2H), 7.32 – 7.25 (m, 2H), 7.23 (dd, *J* = 6.2, 1.4 Hz, 1H), 7.16 – 7.06 (m, 3H), 6.40 (t, *J* = 5.6 Hz, 1H), 4.07 – 3.94 (m, 3H), 2.61 (dd, *J* = 14.0, 3.3 Hz, 1H), 2.48 – 2.39 (m, 4H), 2.33 (dt, *J* = 3.5, 1.0 Hz, 1H), 1.25 (d, *J* = 6.1 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ / ppm = 143.4, 138.2, 136.8, 134.7, 130.8, 130.4, 129.7, 129.5, 128.5, 127.7, 127.5, 127.2, 126.9, 126.5, 69.7, 45.4, 40.9, 24.1, 21.7. **FT-IR** (neat): $\tilde{\nu}$ / cm^{-1} = 3491, 3275, 2927, 1155, 1092, 814, 660, 551. **HRMS** (ESI) *m/z* calc. for $C_{17}H_{22}NO_3S$: 320.1315, found: 320.1315 $(M+H)^+$.

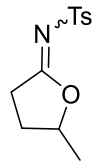
NMR experiments

NMR spectra of compound **4a** were obtained in the range of -60 °C to 100°C. At 40 °C coalescence of the two sets of signals was observed. Equation (1), derived from the Eyring equation provides a good estimate for the activation energy of isomerization.[18,19] From a coalescnec temperature of 40°C and a Δv of 20.5 Hz we arrived at a value of 16.0 kcal mol^{-1} for the ΔG‡ for the E/Z isomerization of the parent compound **4a**.

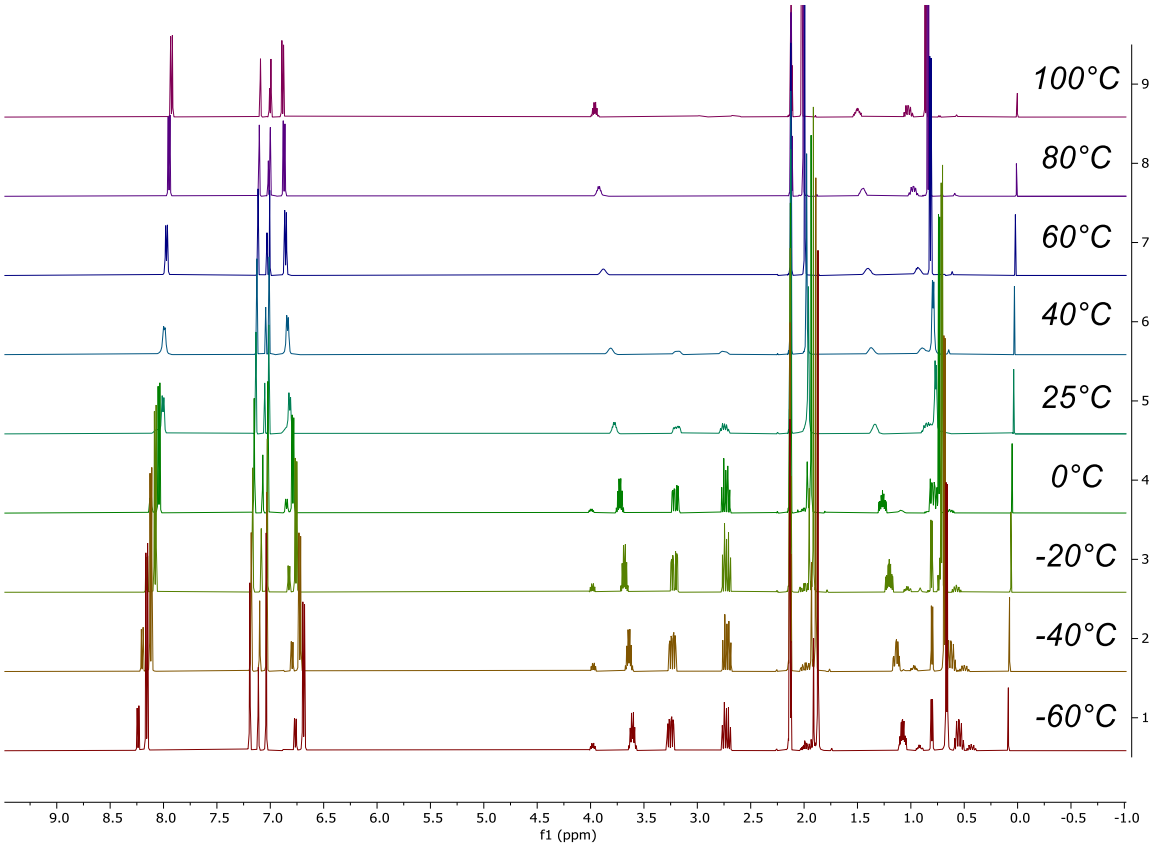
$$\Delta G^{\ddagger} = \mathrm{R}T_C[22.96 + \ln\left(\frac{T_C}{\Delta \mathrm{v}}\right)] \quad (1)$$

ΔG‡ = 66.8 kJ mol $^{-1}$

ΔG‡ = 16.0 kcal mol $^{-1}$



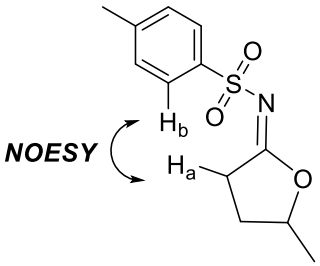
4a



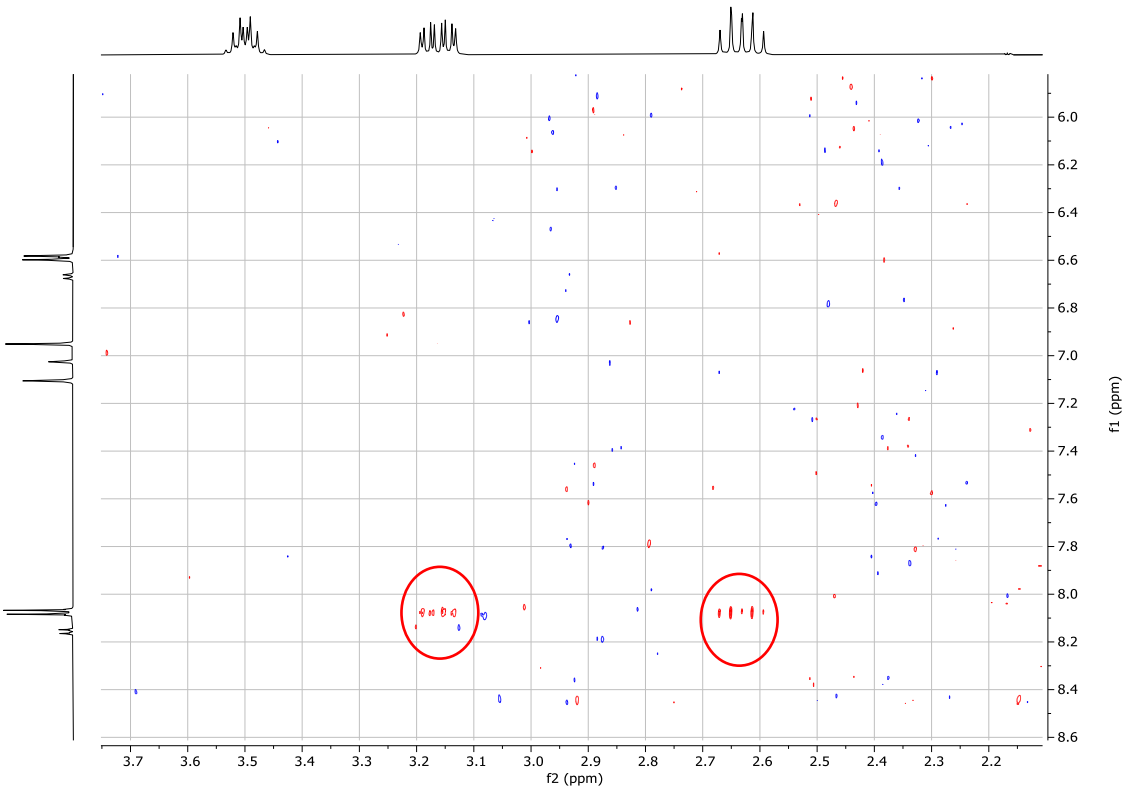
^{1}H NMR (400 MHz, toluene-d$_8$) at indicated tempertures

In order to determine the major isomer in solution at 25°C in toluene a low temperature NOESY was measured. A correlation between H_a and H_b allowed us to identify E as the major isomer.

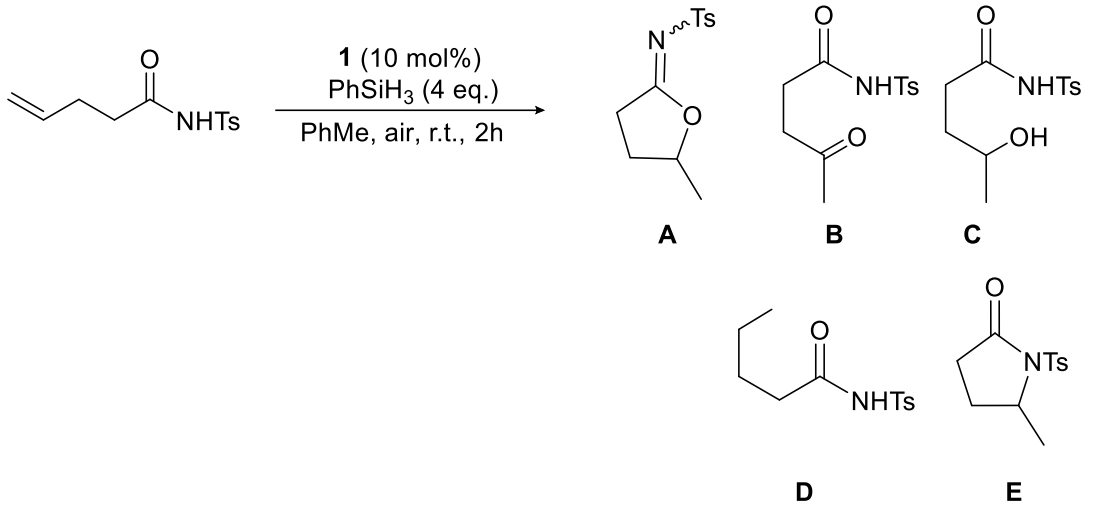
^{1}H-^{13}C HSQC



4a

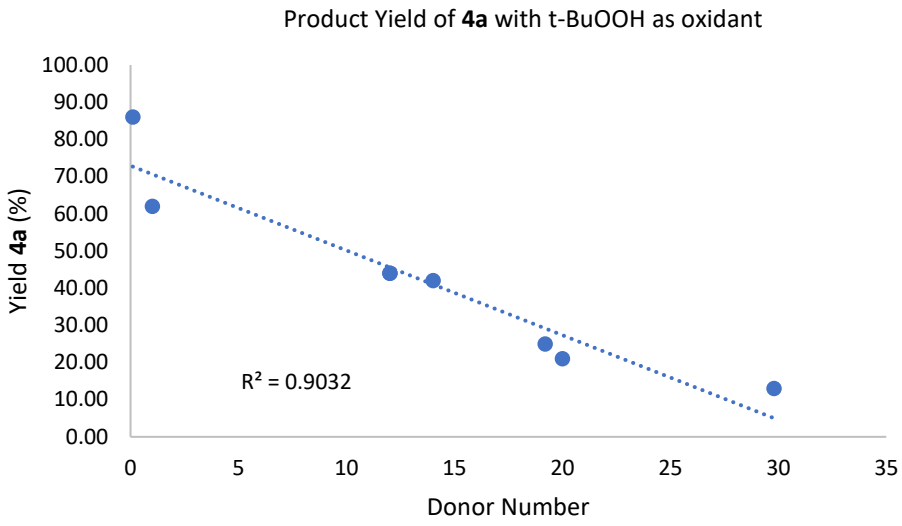


Investigations of the reaction with *air*

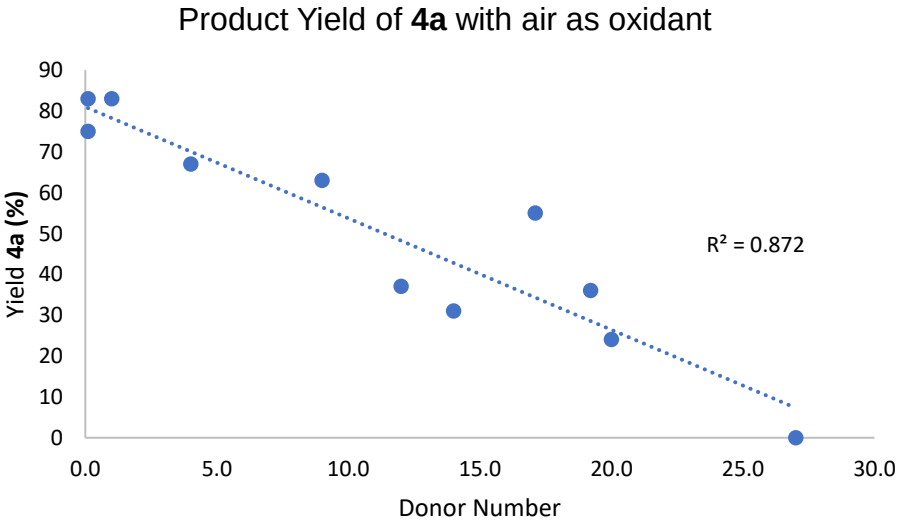


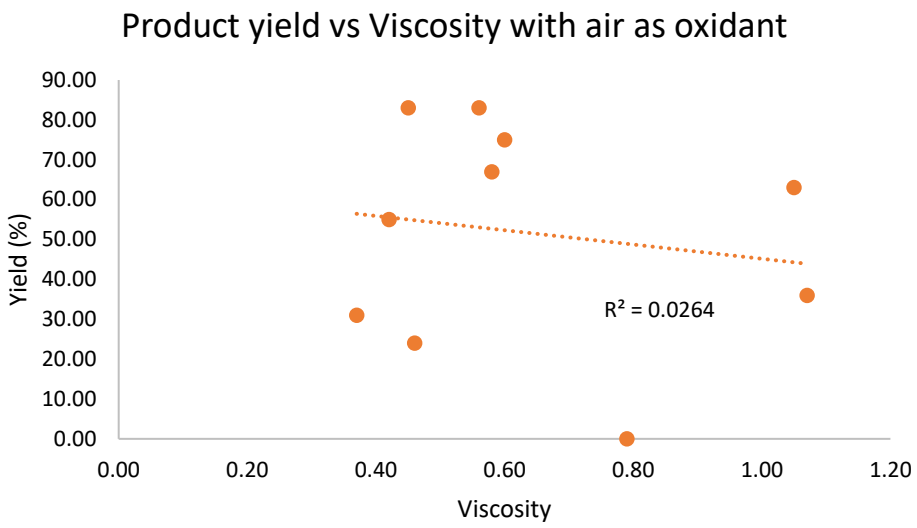
Solvent screening

Entry	Deviation from standard conditions	A (%)	B (%)	C (%)	D (%)	E (%)
1	none	83	0	0	0	0
2	THF instead of PhMe	24	34	29	0	0
3	CH_2Cl_2 instead of PhMe	83	0	0	0	0
4	2-MeTHF instead of PhMe	37	23	29	0	0
5	EtOH instead of PhMe	36	21	30	0	0
6	MeCN instead of PhMe	31	22	18	0	0
7	$CHCl_3$ instead of PhMe	67	0	0	0	0
8	DMF instead of PhMe	0	56	22		
9	PhH instead of PhMe	75	0	0	0	0
10	EtOAc instead of PhMe	55	25	5	0	0
11	PhOMe instead of PhMe	63	13	10	0	0



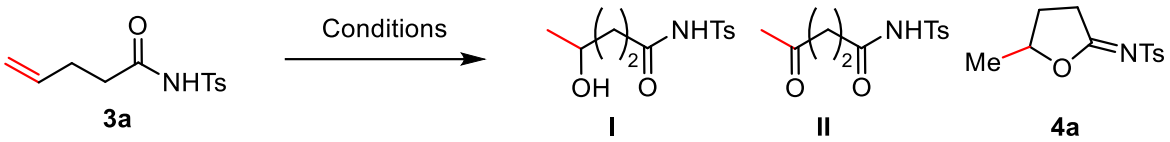
For the reaction with *t*-BuOOH protic solvents were excluded from the correlation plot since they led to product D.





No correlation between viscosity[20] and product yield could be determined.

Control experiments with Mukaiyama hydration conditions

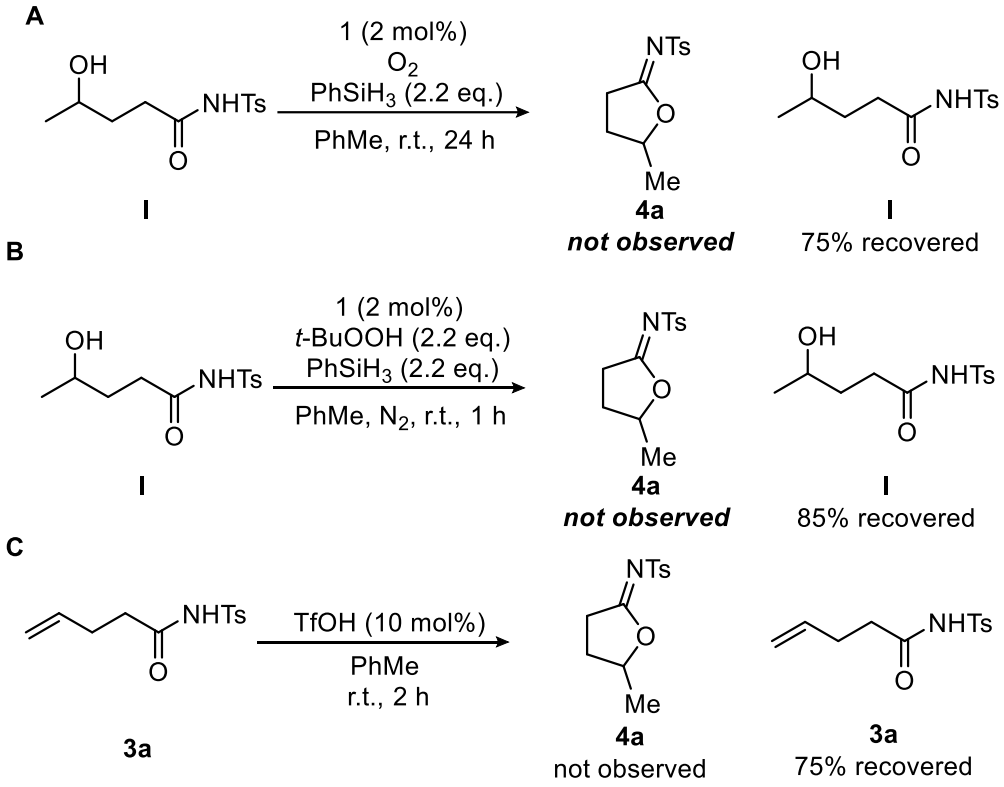


3a **I** **II** **4a**

Entry	Conditions	**I** (%)	**II** (%)	**4a** (%)
1	$Co(acac)_2$ (5 mol%), $PhSiH_3$ (2.5 eq.), O_2 (1 atm), THF (0.1 M),12 h	46	4	0
2	$Co(acac)_2$ (5 mol%), $PhSiH_3$ (2.5 eq.), O_2 (1 atm), PhMe (0.1 M),12 h	31	26	0
3	**1** (2 mol%), $PhSiH_3$ (2.5 eq.), *t*-BuOOH (2.2 eq.), THF (0.1 M), 2 h	15	0	21
4	**1** (2 mol%), $PhSiH_3$ (2.5 eq.), O_2 (1 atm), THF (0.1 M), 2 h	25	32	36

To a solution of **3a** (51.0 mg, 0.200 mmol, 1.0 eq.) and catalyst (5 mol%) under O_2 atmosphere (doubled toy balloon, atmosphere exchanges 3 times) was added respective solvent (2 mL) and $PhSiH_3$ (0.500 mmol, 2.5 eq.) and the reaction stirred at r.t. overnight. The solvent was then removed in vacuo Purification using silica gel chromatography (0-40% EtOAc in hexane, Rf (40% EtOAc in hexanes = 0.3) gave product **4a**.

Control experiments with Mukaiyama hydration conditions



A:

To a solution of **I** (54.3 mg, 0.200 mmol, 1.0 eq.) and catalyst (5 mol%) under O_2 atmosphere (doubled toy balloon, atmosphere exchanges 3 times) was added respective solvent (2 mL) and $PhSiH_3$ (0.500 mmol, 2.5 eq.) and the reaction stirred at r.t. overnight. The solvent was then removed in vacuo Purification using silica gel chromatography (0-100% EtOAc in hexane, Rf (60% EtOAc in hexanes = 0.3) gave starting material **I** (40.5 mg, 0.149 mmol, 75%).

B:

I (54.3 mg, 0.200 mmol, 1.0 eq.) was subjected to GP2. Purification using silica gel chromatography (0-100% EtOAc in hexane, Rf (60% EtOAc in hexanes = 0.3) gave starting material **I** (46.2 mg, 0.170 mmol, 85%).

C:

To a solution of **3a** (50.4 mg, 0.200 mmol, 1.0 eq.) in toluene (2 mL) was added TfOH (0.500 mmol, 2.5 eq.) and the reaction stirred at r.t. for 2h. The reaction mixture was then diluted with

EtOAc (30 mL), washed with saturated aq. $NaHCO_3$ (20 mL) and brine (25 mL), dried using Na_2SO_4, filtered and the solvents removed in vacuo. The solvent was then removed in vacuo. Purification using silica gel chromatography (0-40% EtOAc in hexane, Rf (40% EtOAc in hexanes = 0.3) gave starting material **3a** (38.1 mg, 0.150 mmol, 75%).

(1) White, D. E.; Tadross, P. M.; Lu, Z.; Jacobsen, E. N. A Broadly Applicable and Practical Oligomeric (Salen)Co Catalyst for Enantioselective Epoxide Ring-Opening Reactions. *Tetrahedron* **2014**, *70* (27), 4165–4180..
(2) Nicolai, S.; Piemontesi, C.; Waser, J. A Palladium-Catalyzed Aminoalkynylation Strategy towards Bicyclic Heterocycles: Synthesis of (±)-Trachelanthamidine. *Angew. Chem. Int. Ed.* **2011**, *50* (20), 4680–4683.
(3) Gao, R.; Canney, D. J. A Modified Prins Reaction for the Facile Synthesis of Structurally Diverse Substituted 5-(2-Hydroxyethyl)-3,3-Dihydrofurane-2(3H)-Ones. *Tetrahedron Lett.* **2009**, *50* (43), 5914–5916.
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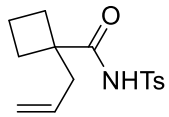
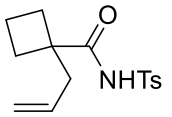


3d

i

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



3d

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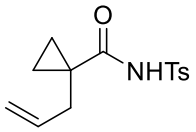

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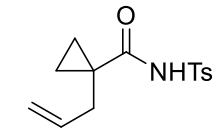

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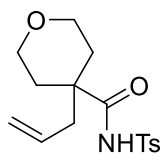

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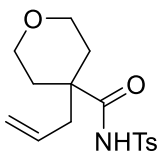

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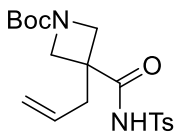

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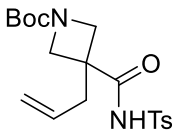

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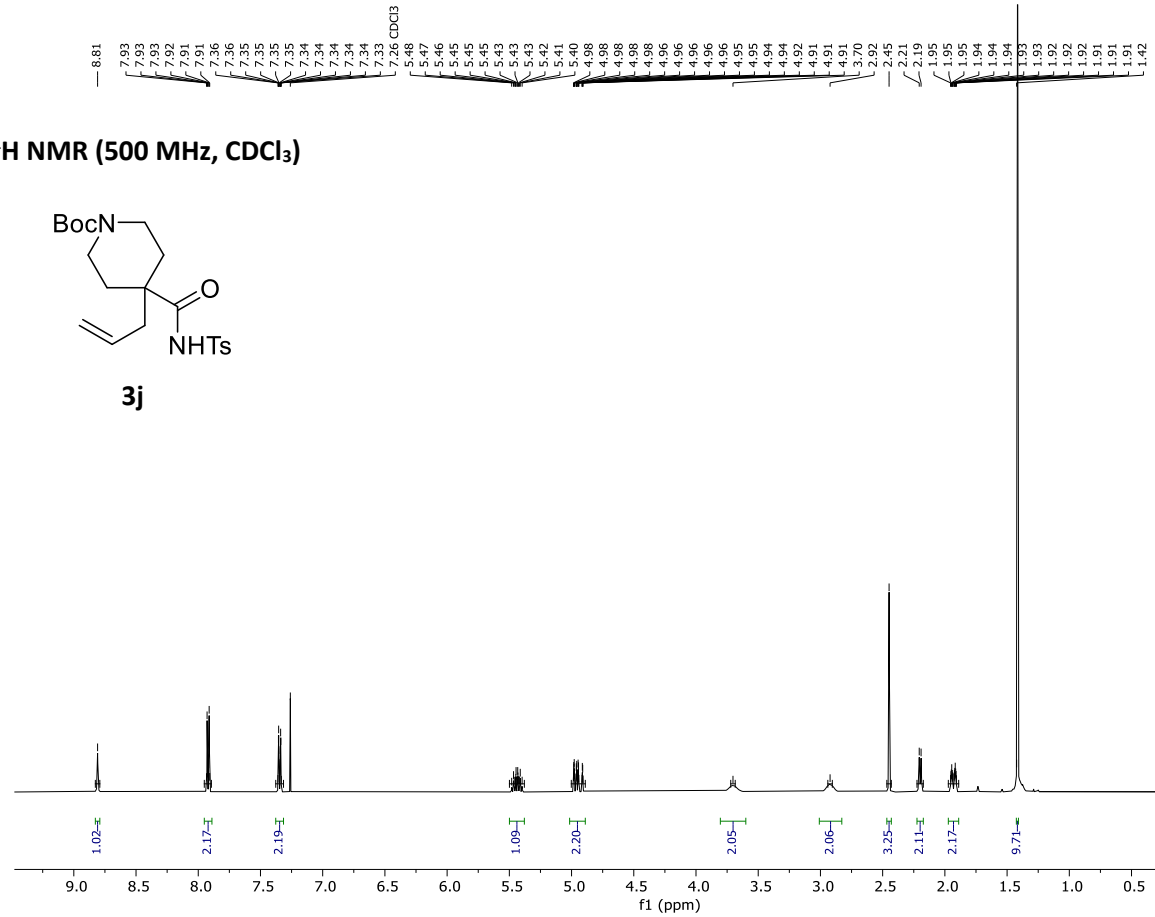

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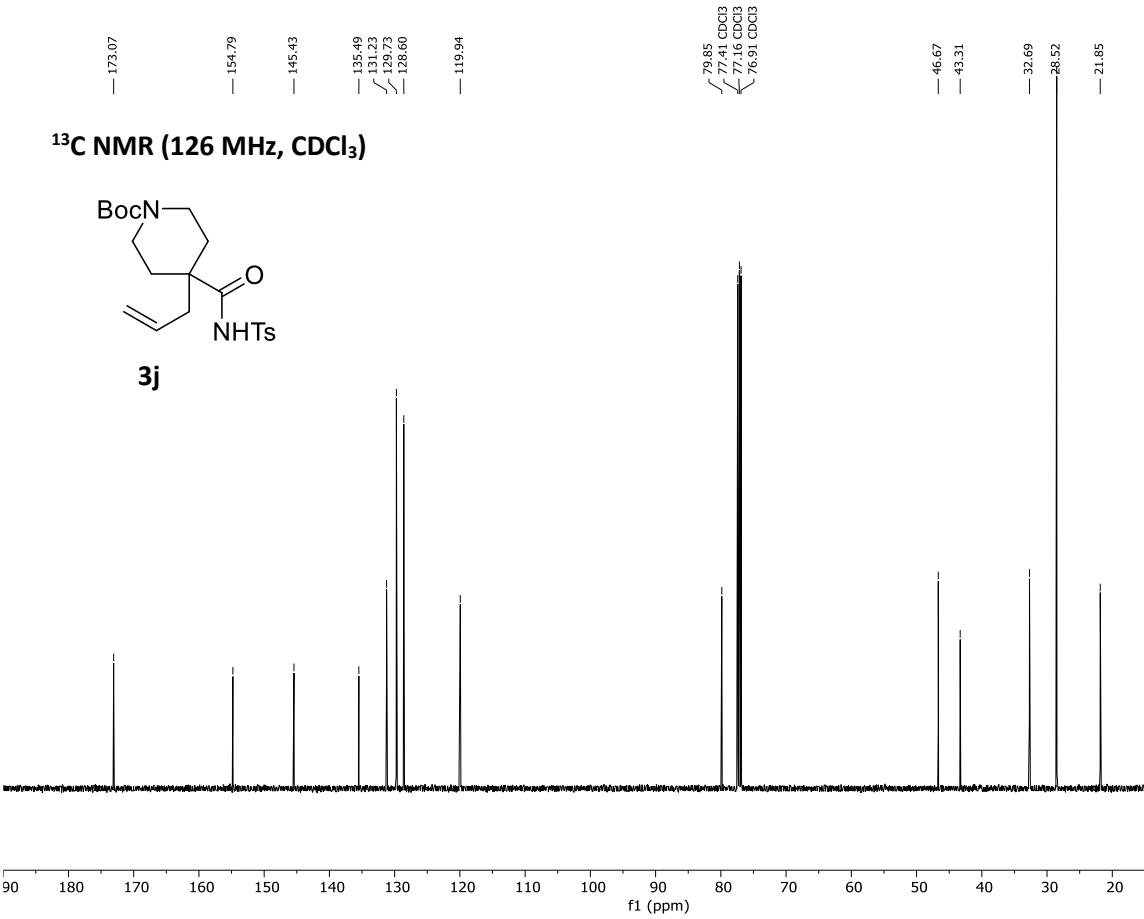

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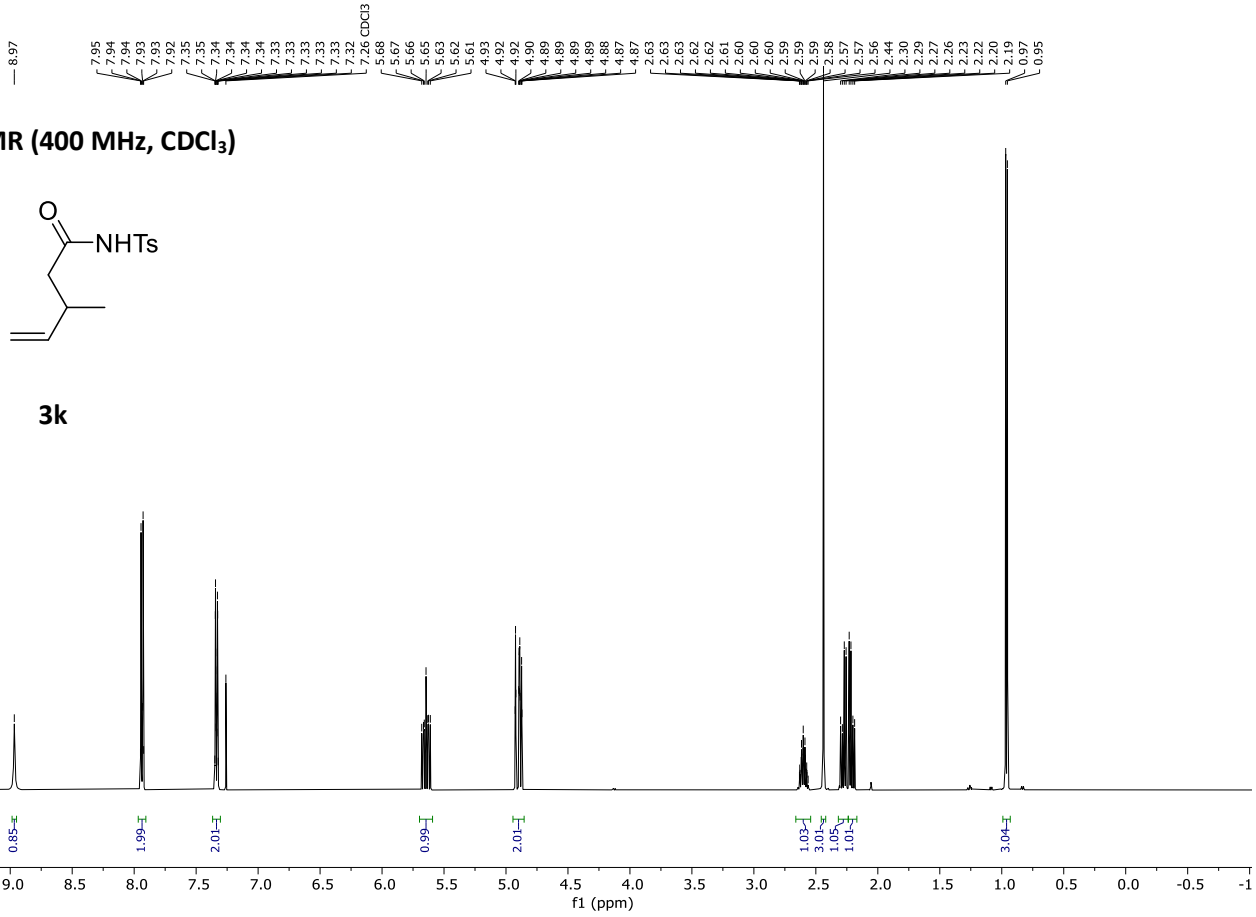

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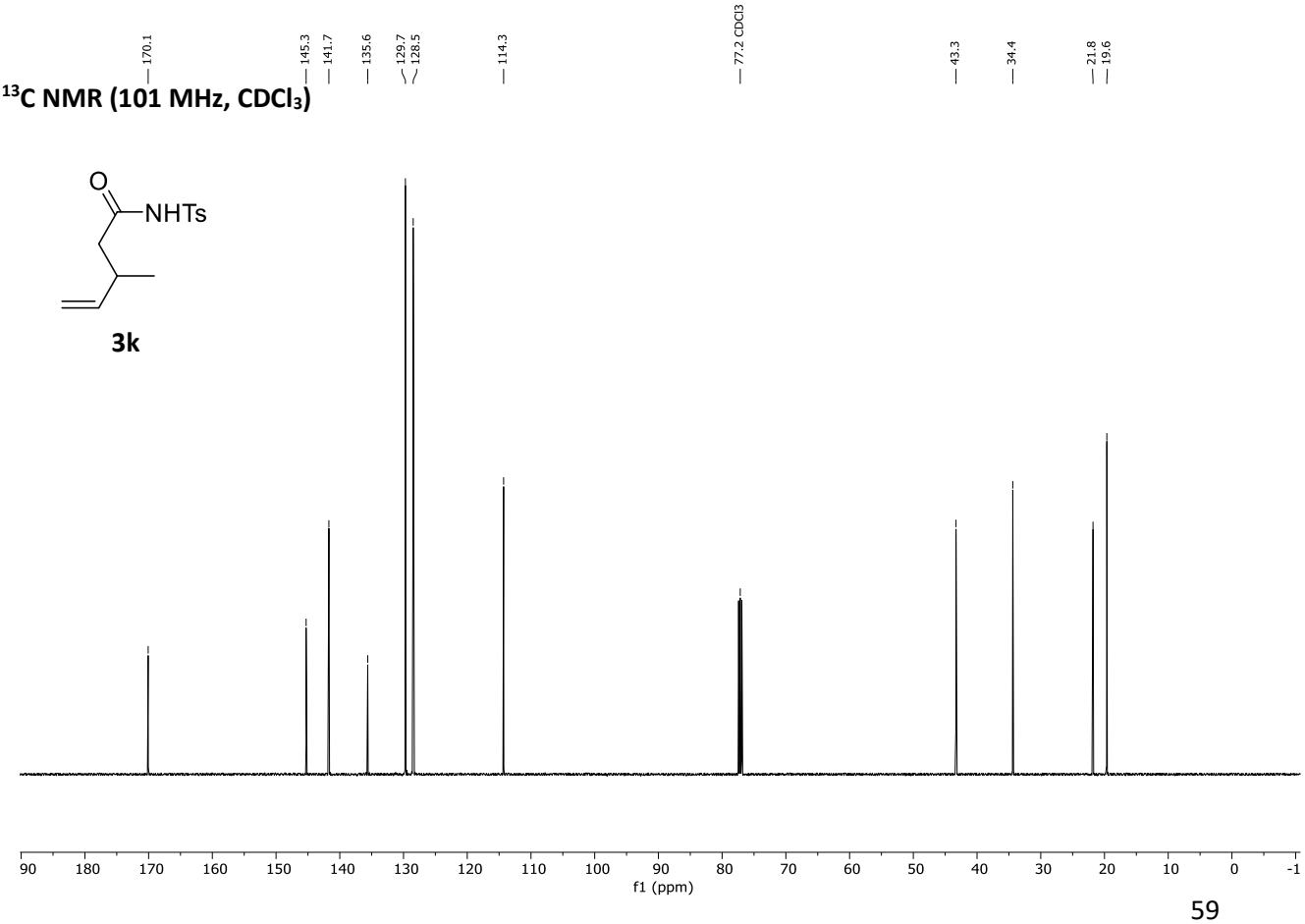

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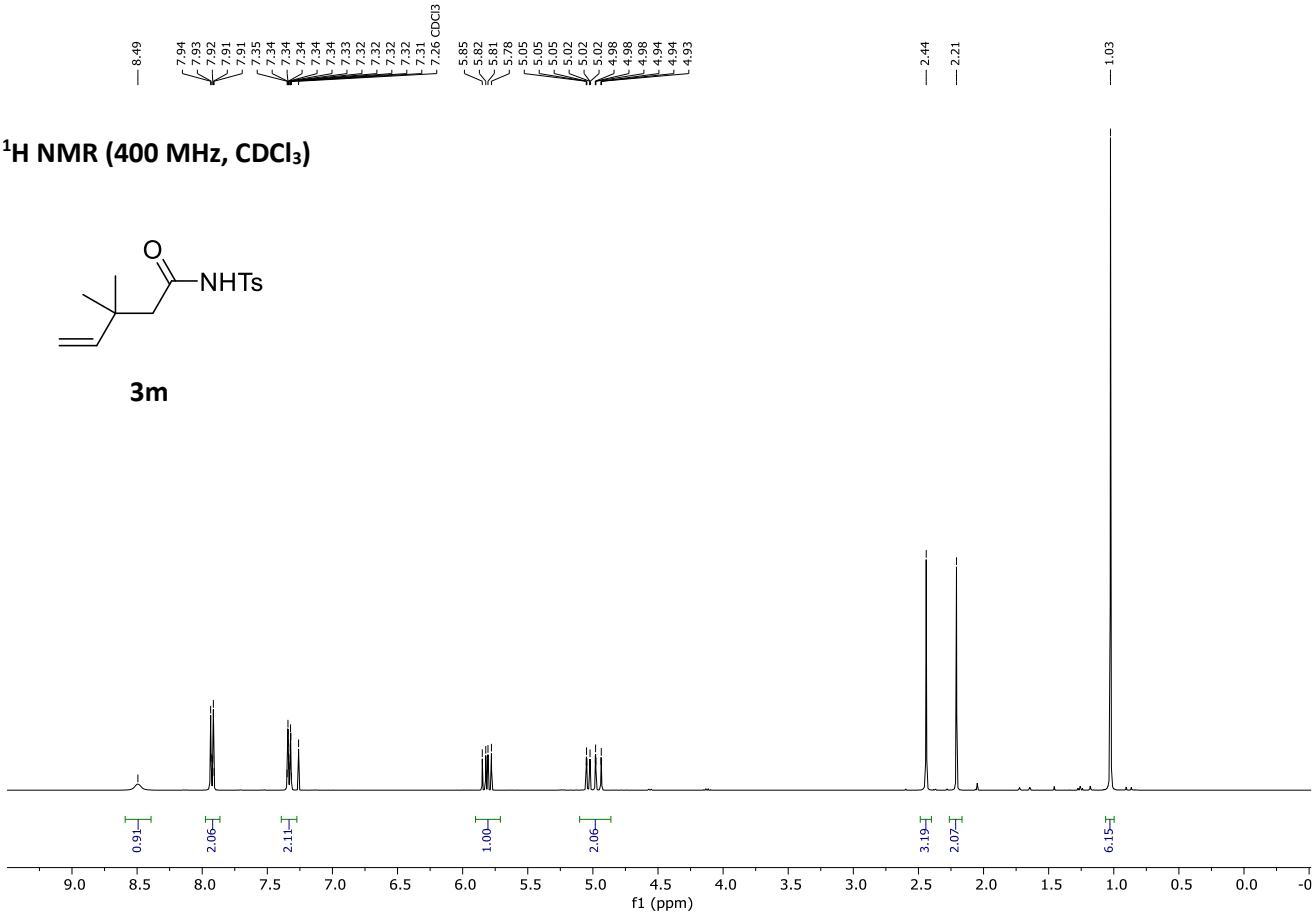

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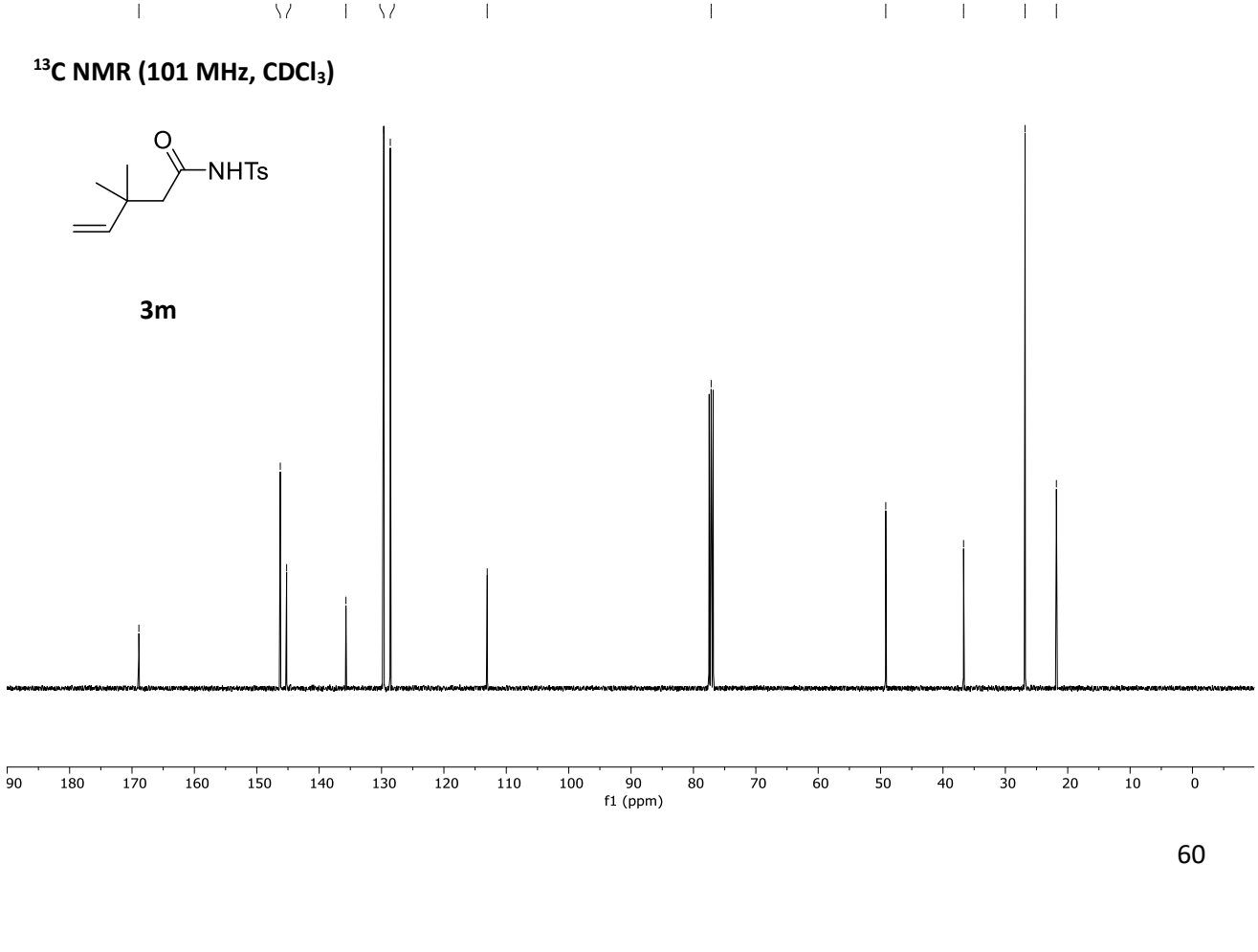
3m



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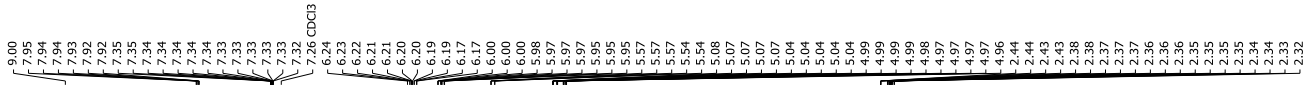
3m



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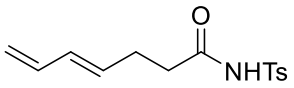

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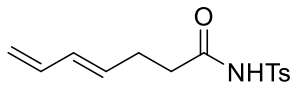

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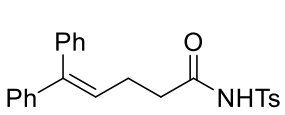

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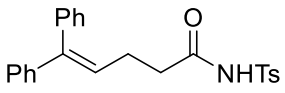

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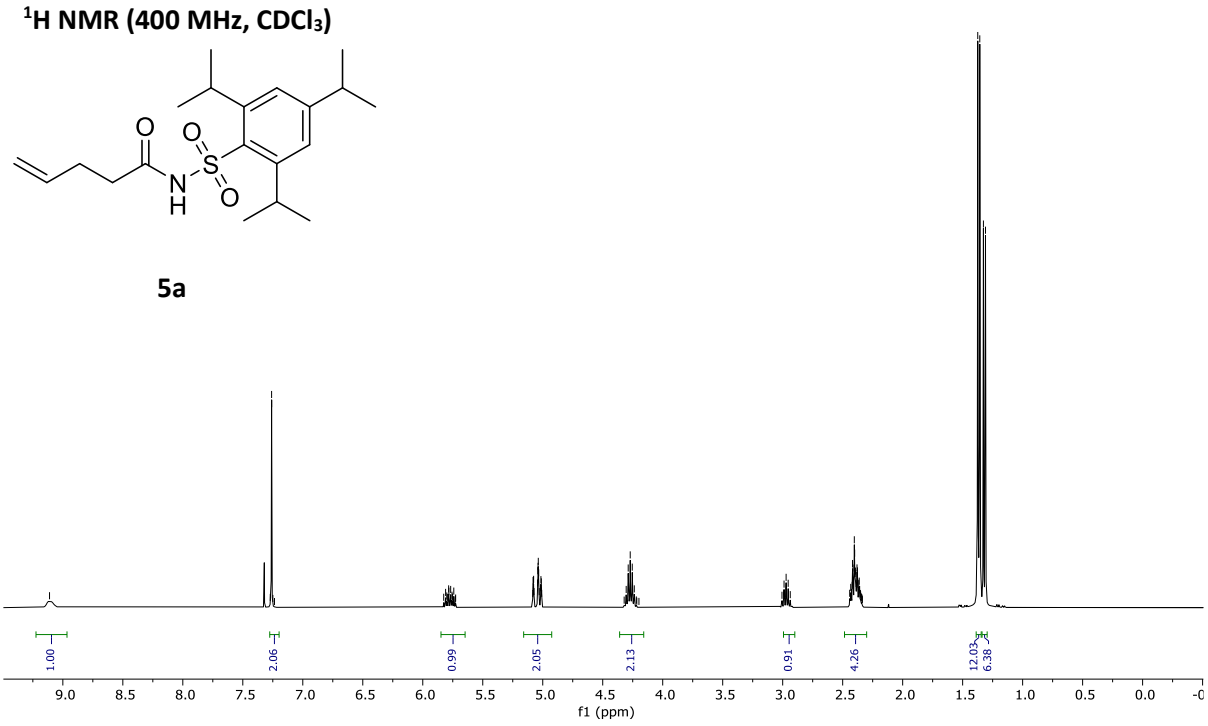

5a

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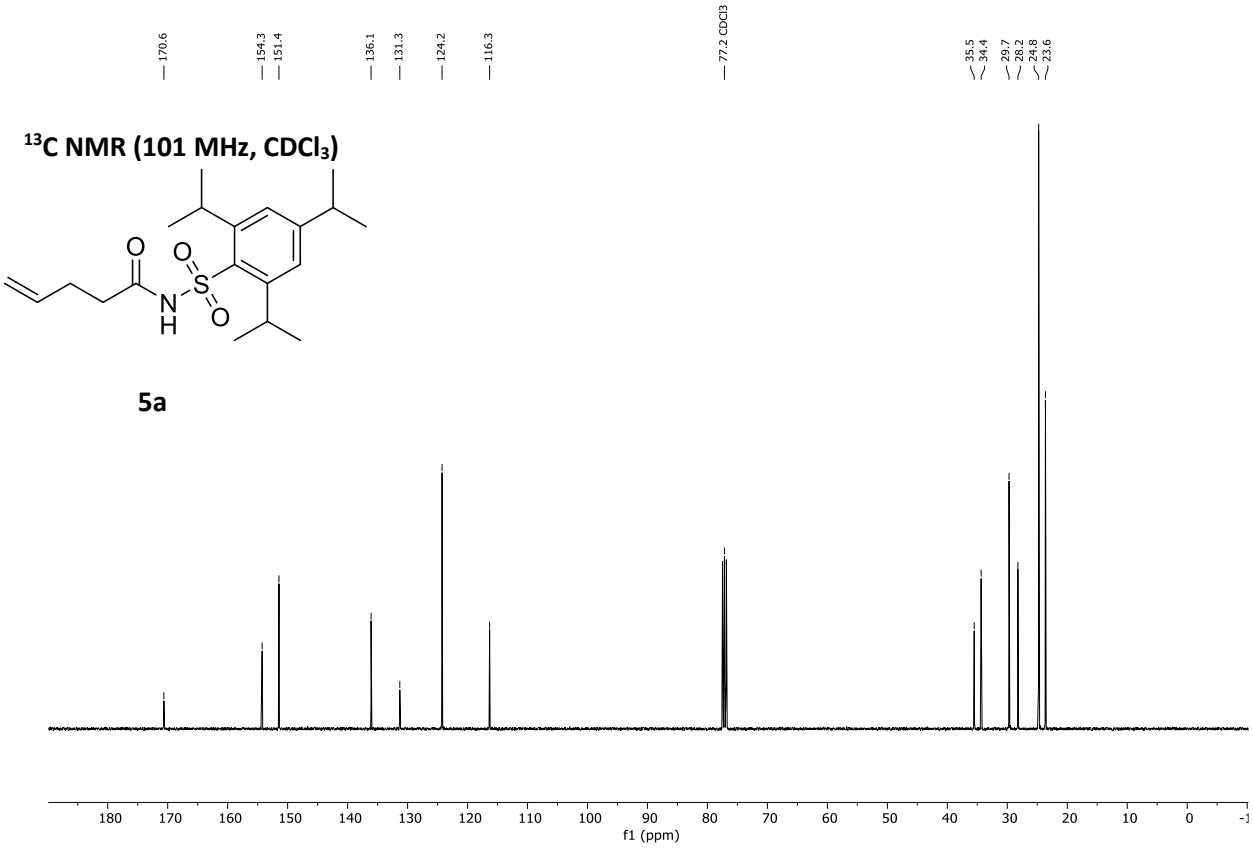

5a

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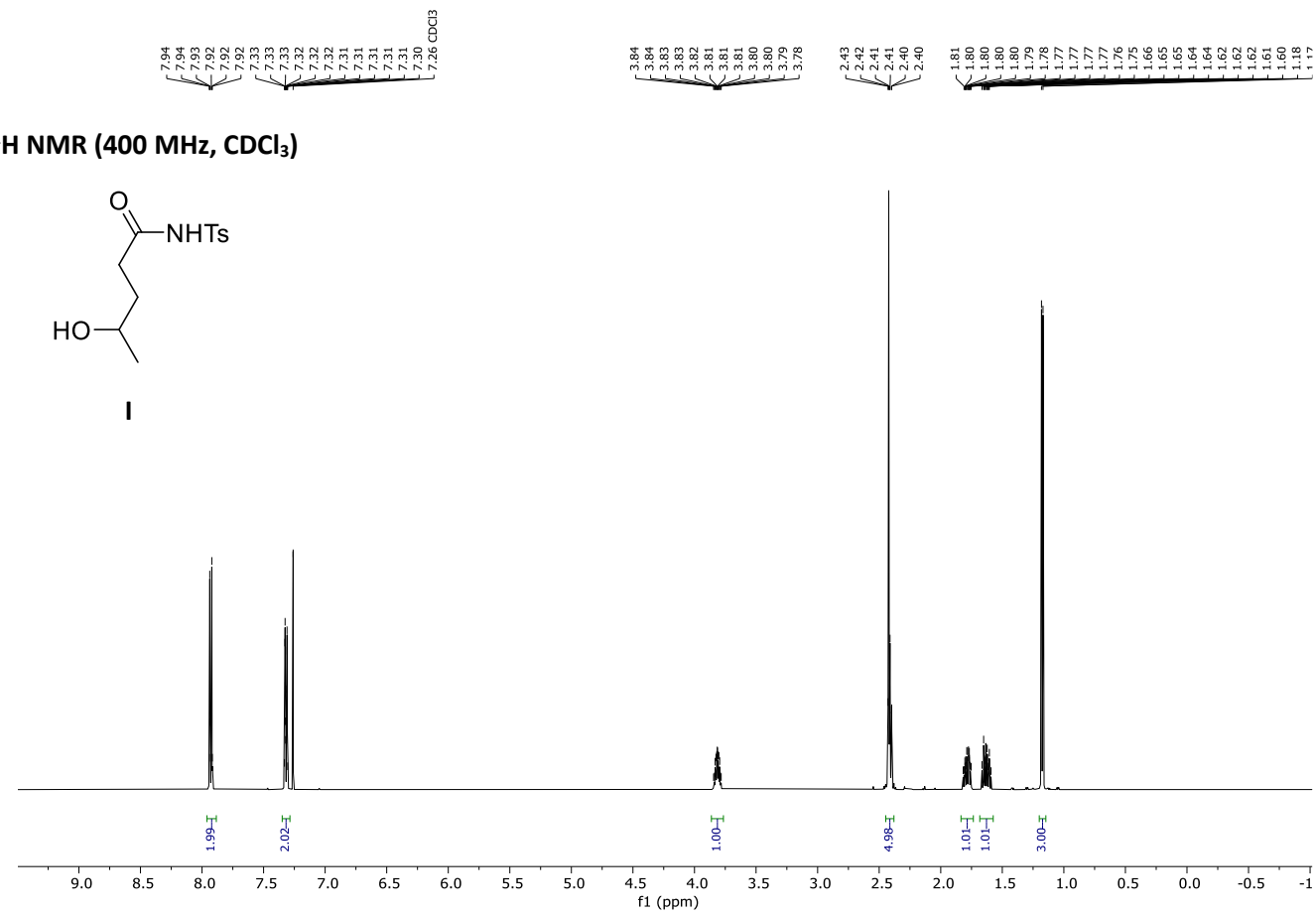

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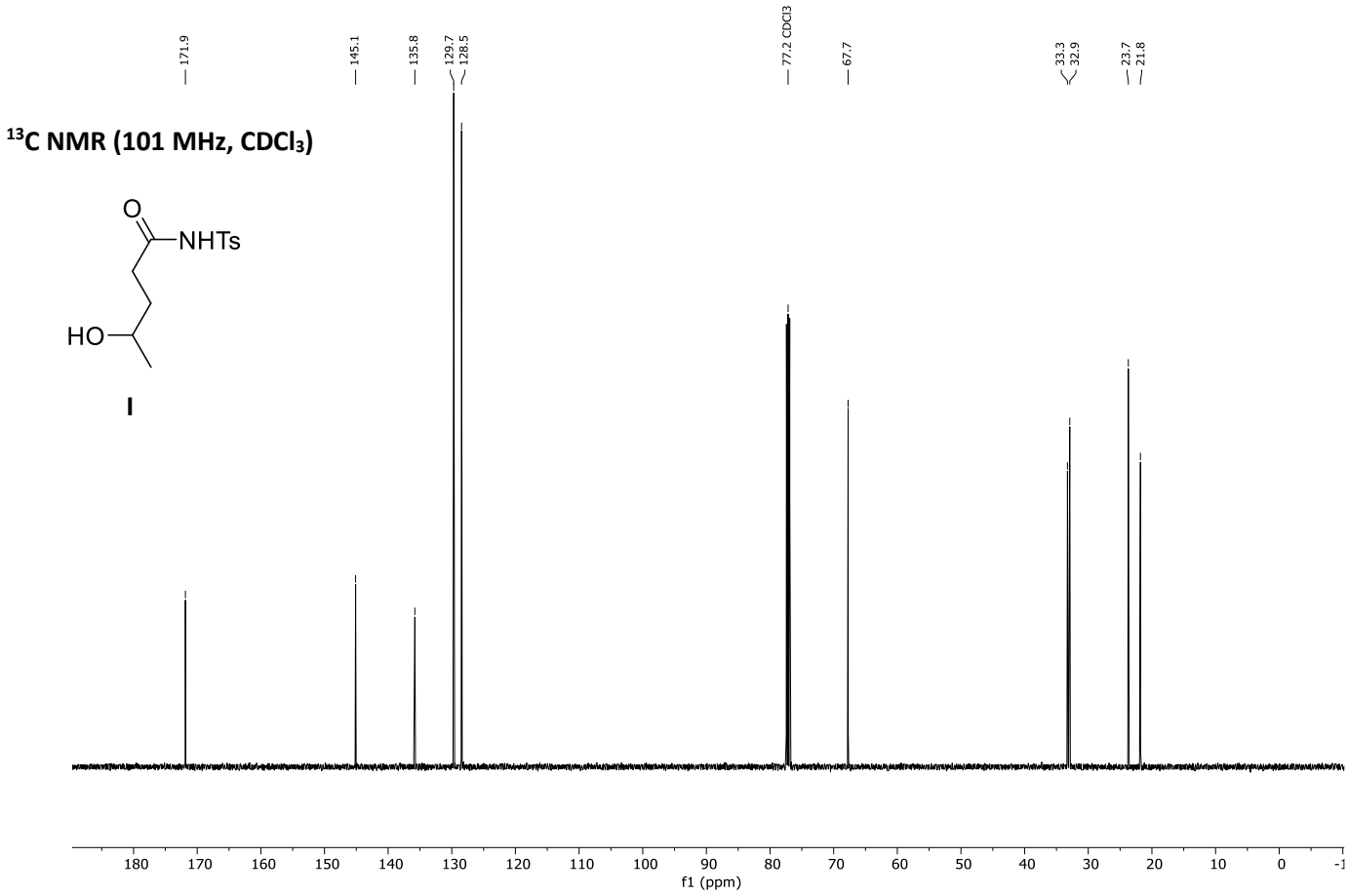

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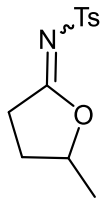
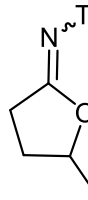


4a

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



4a

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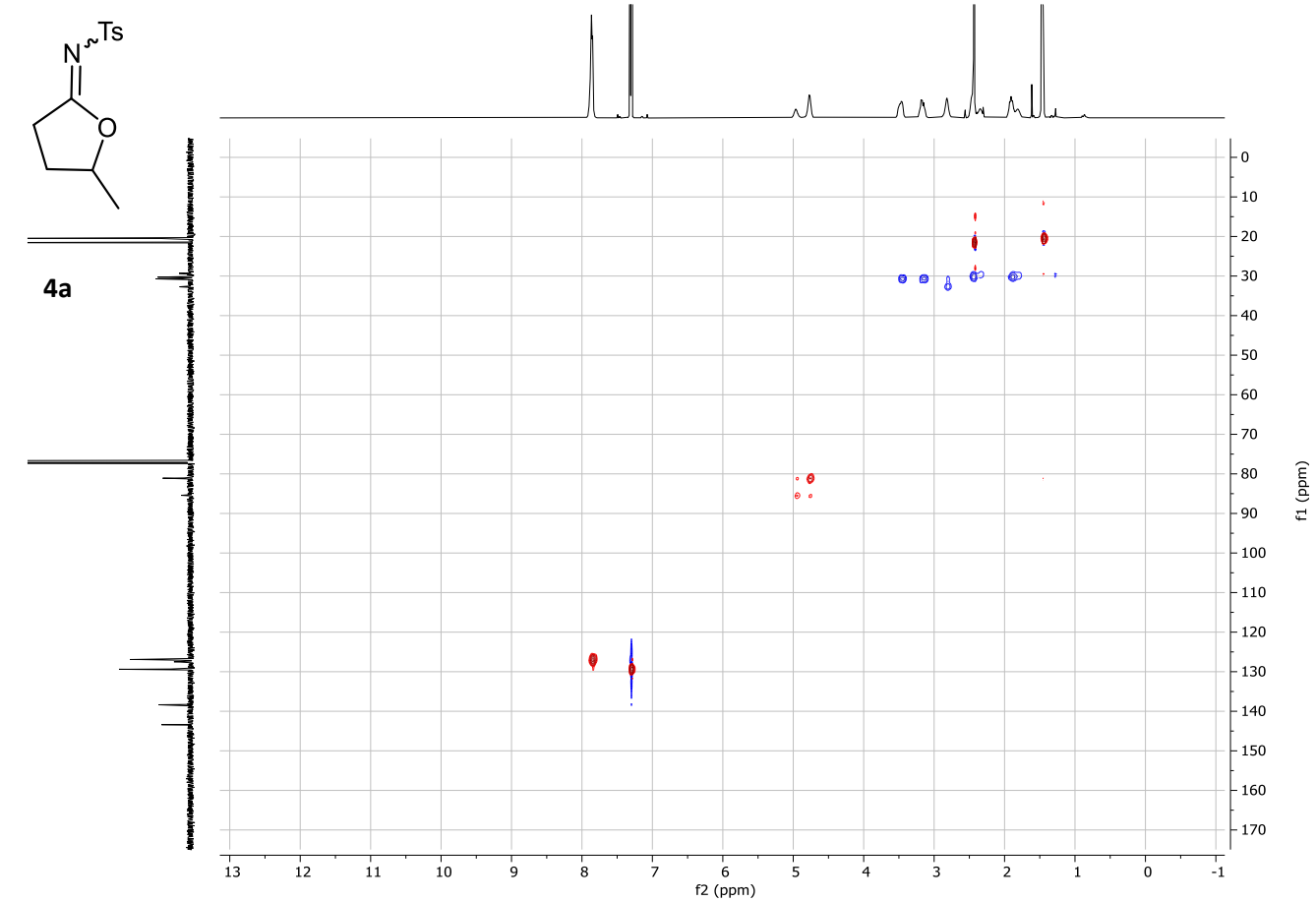
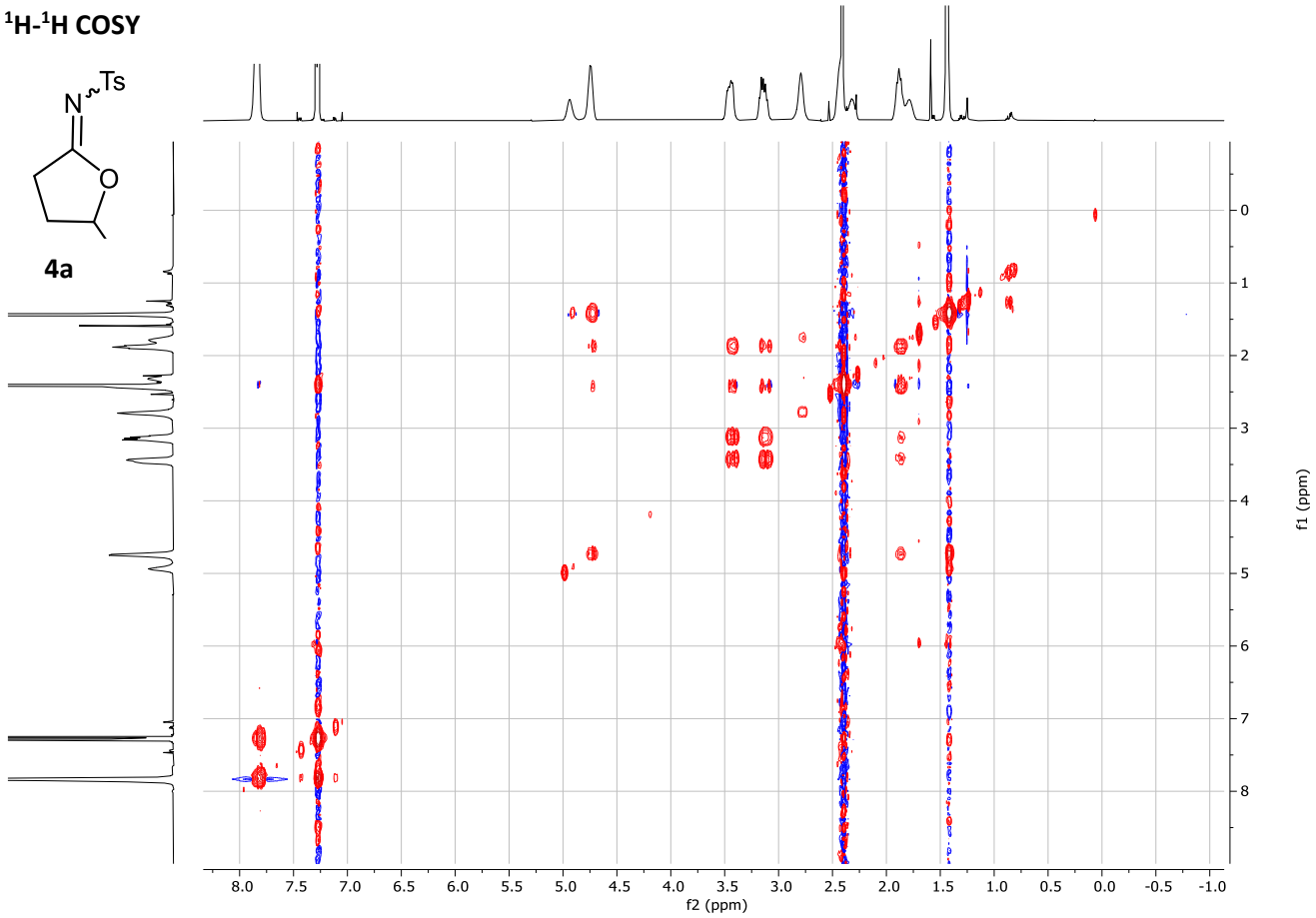


^{1}H-^{1}H COSY



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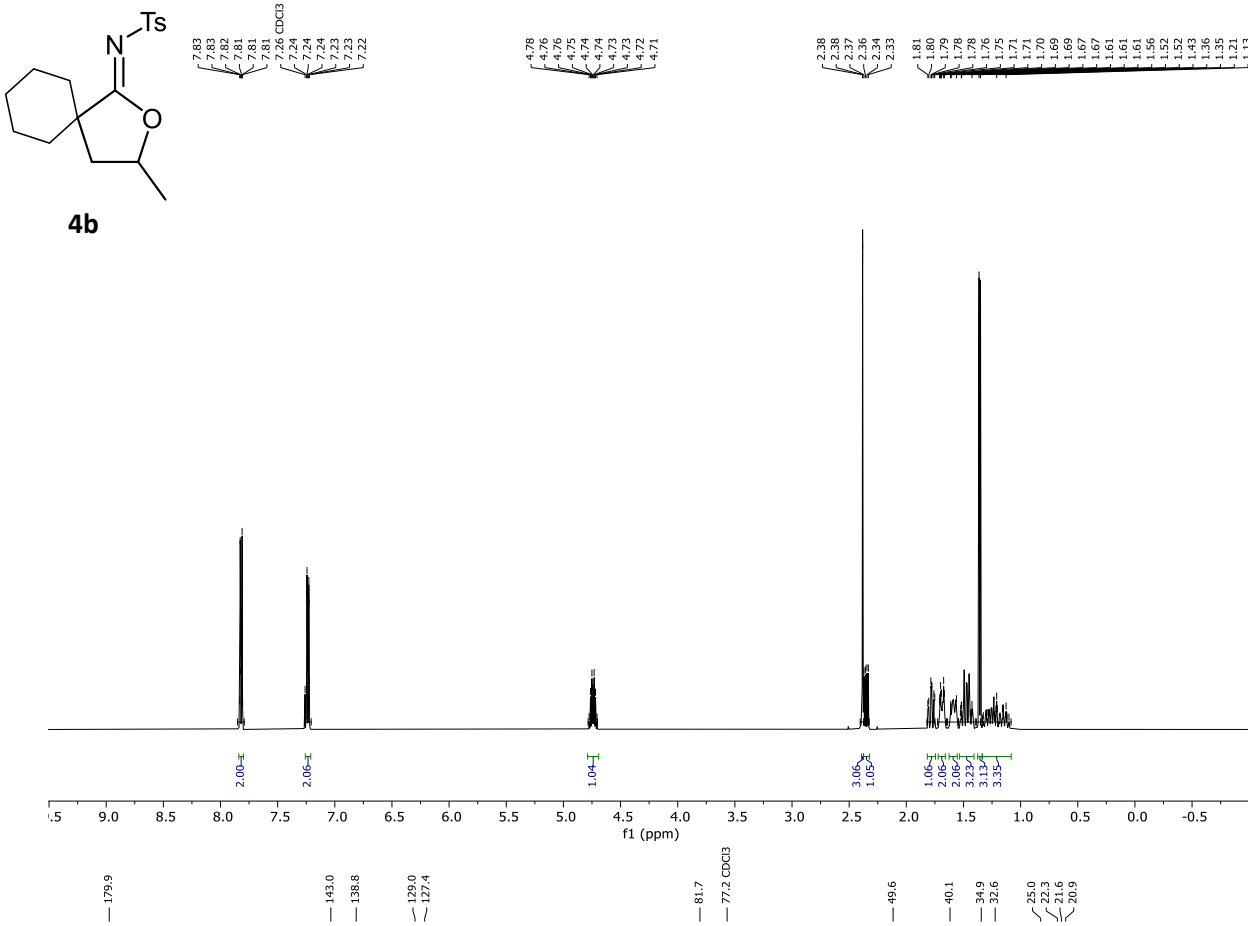

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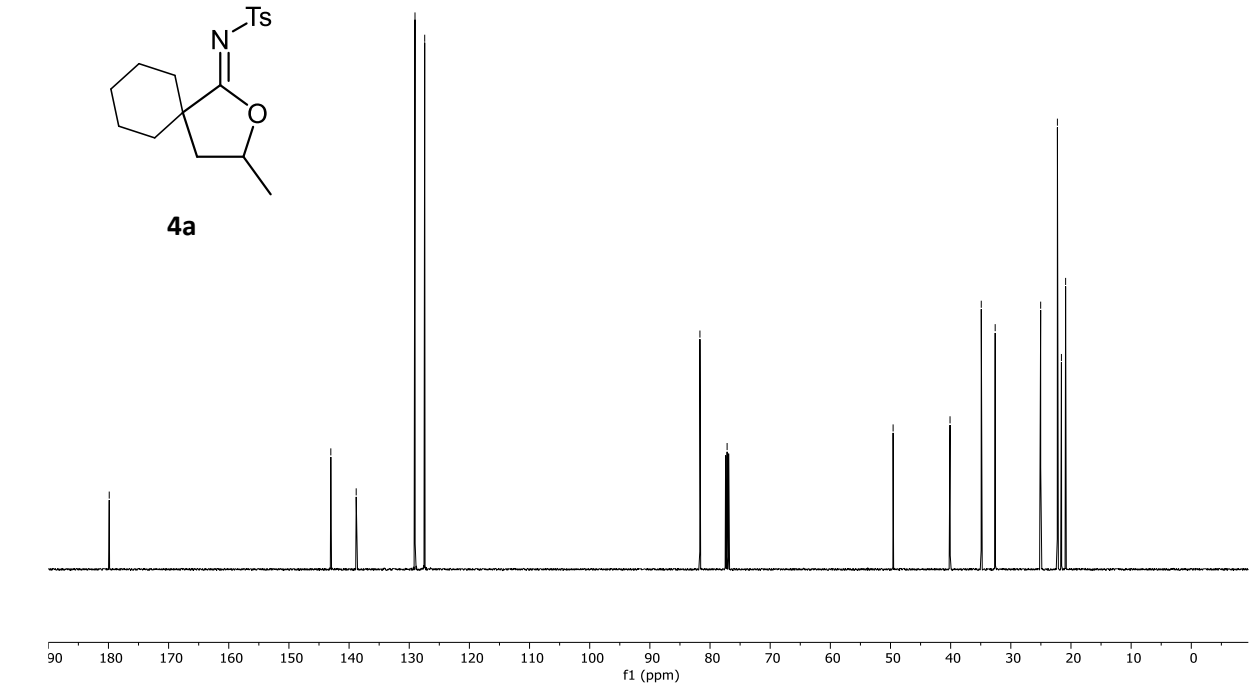

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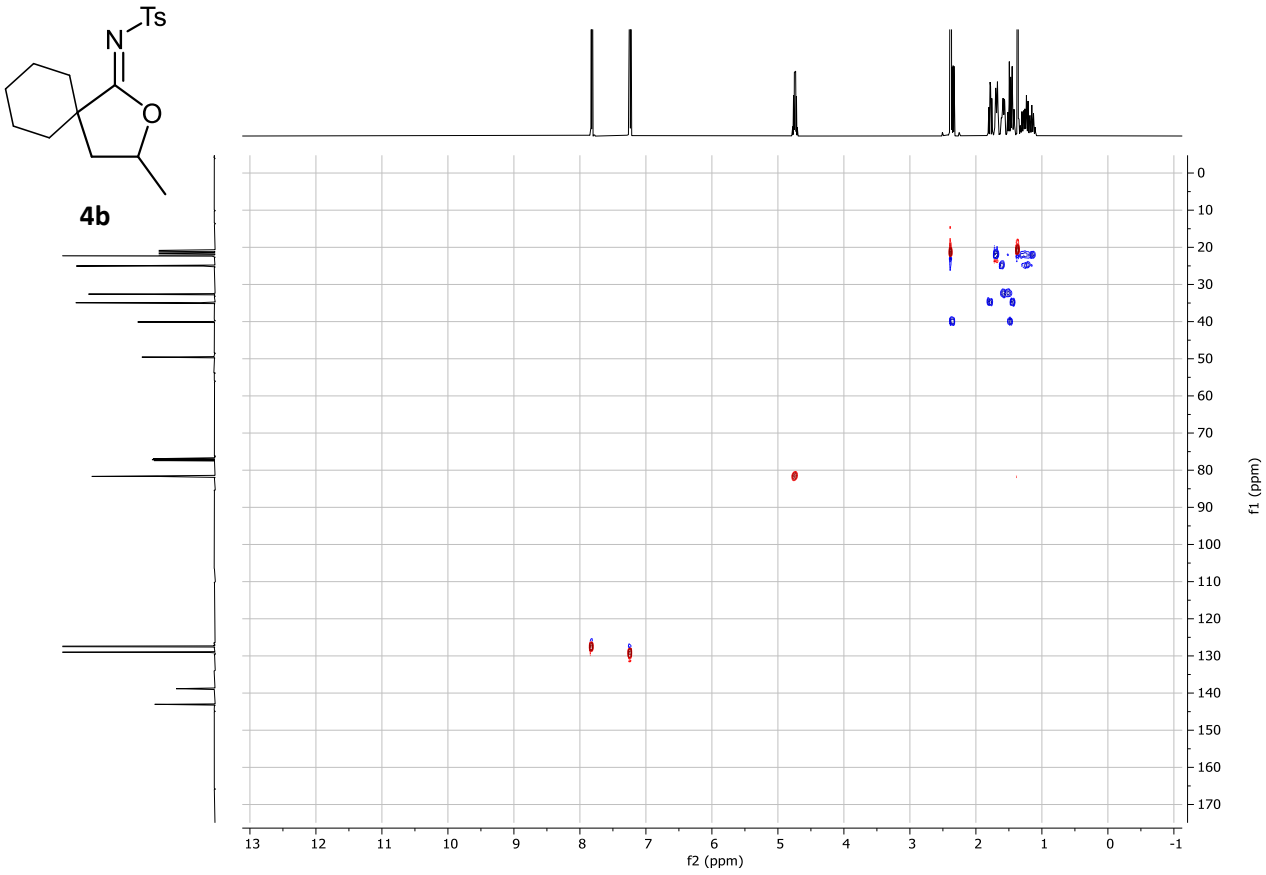

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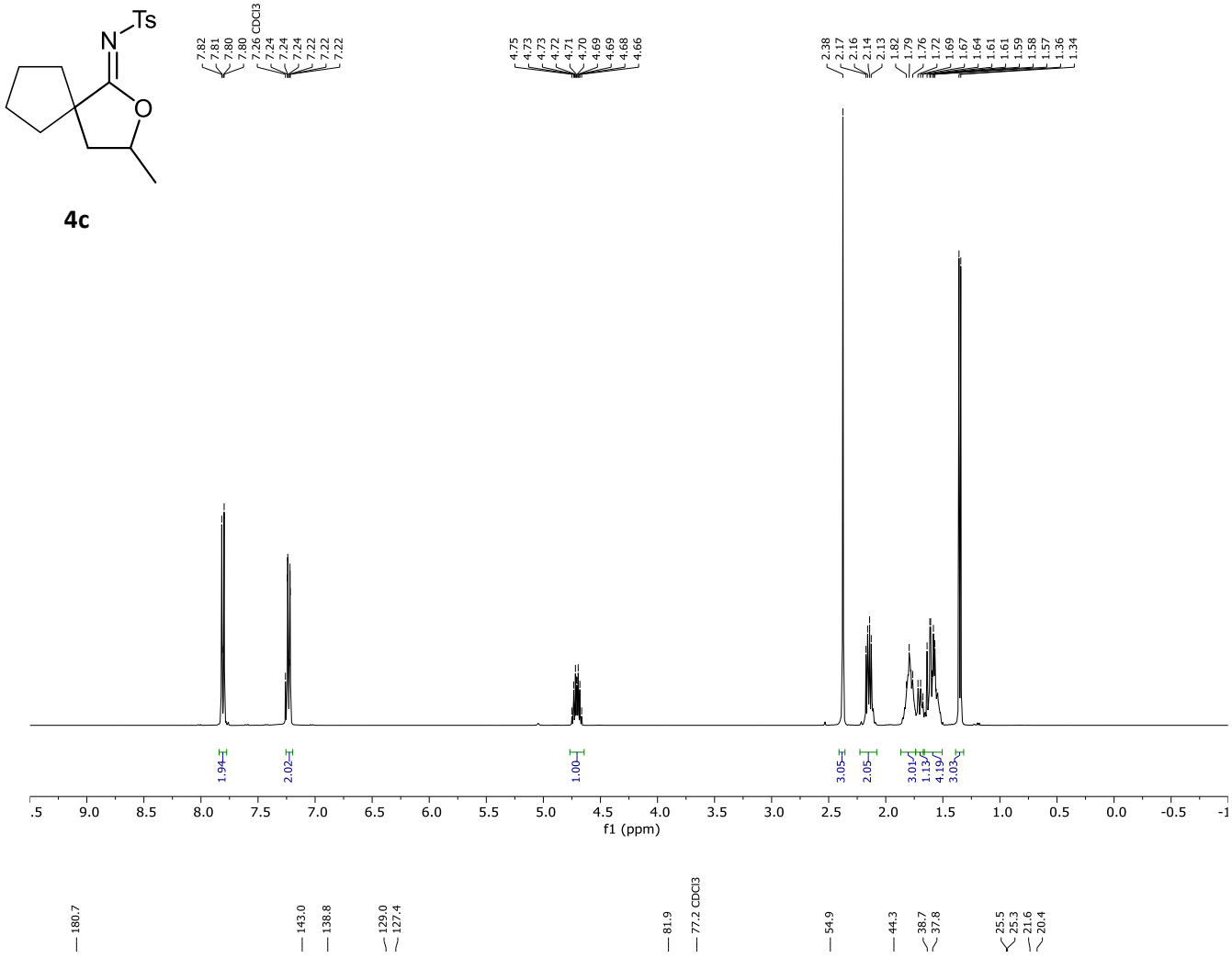

4c

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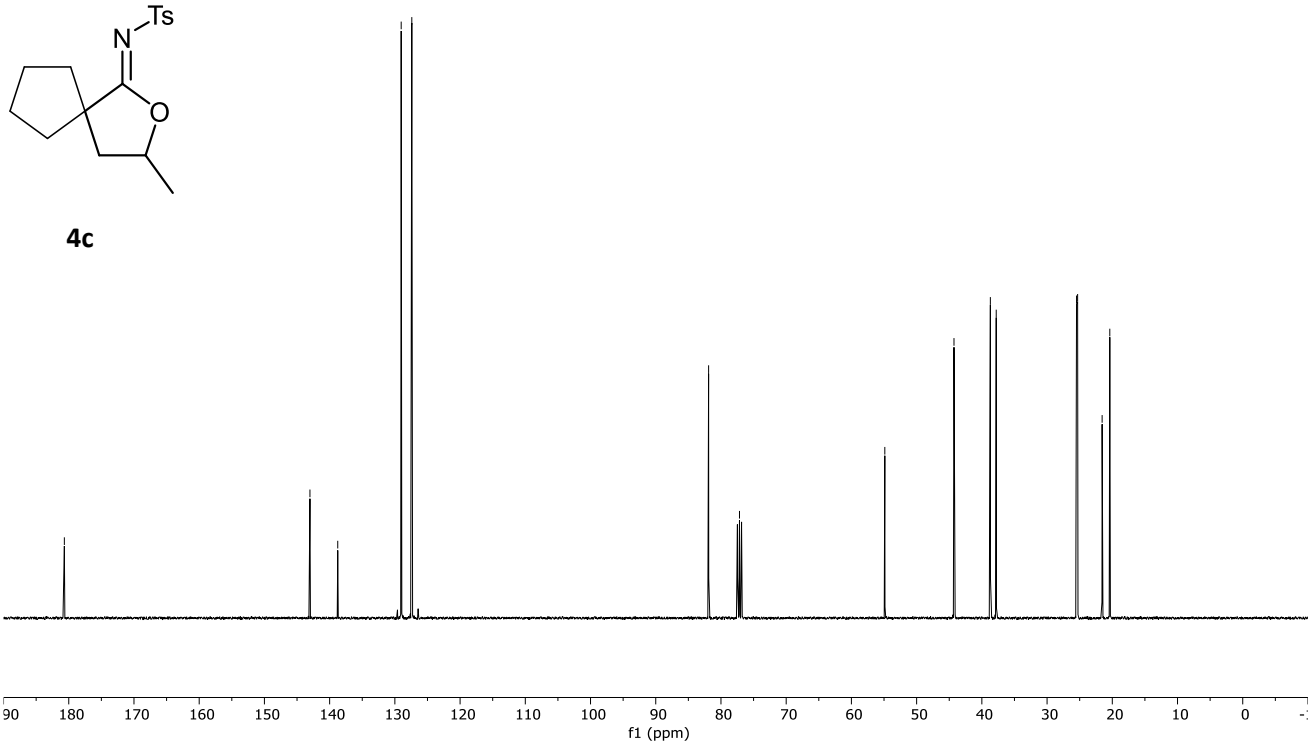

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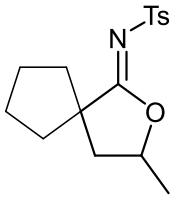

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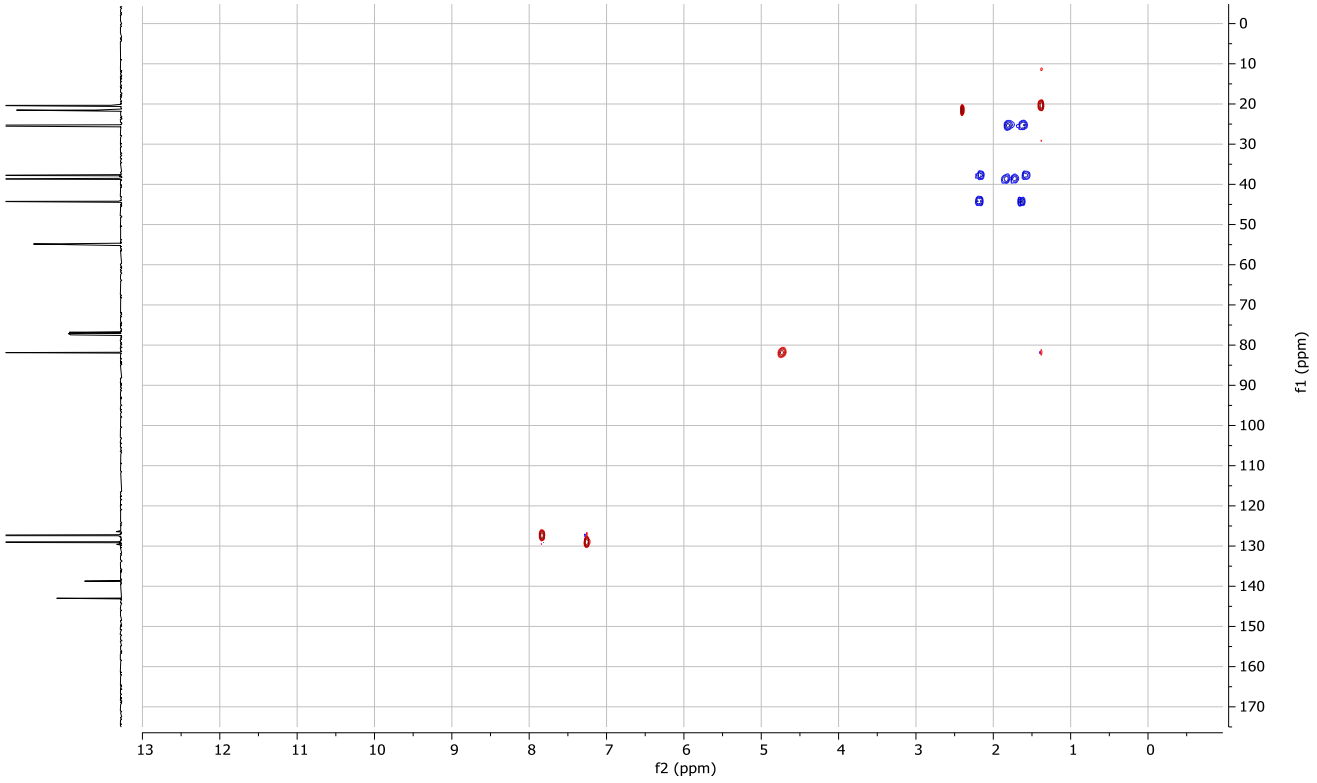

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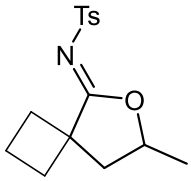

4d

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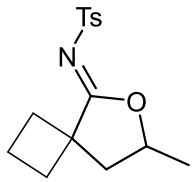

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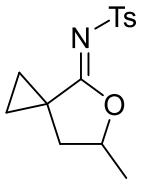

4e

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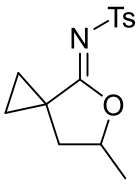

4e

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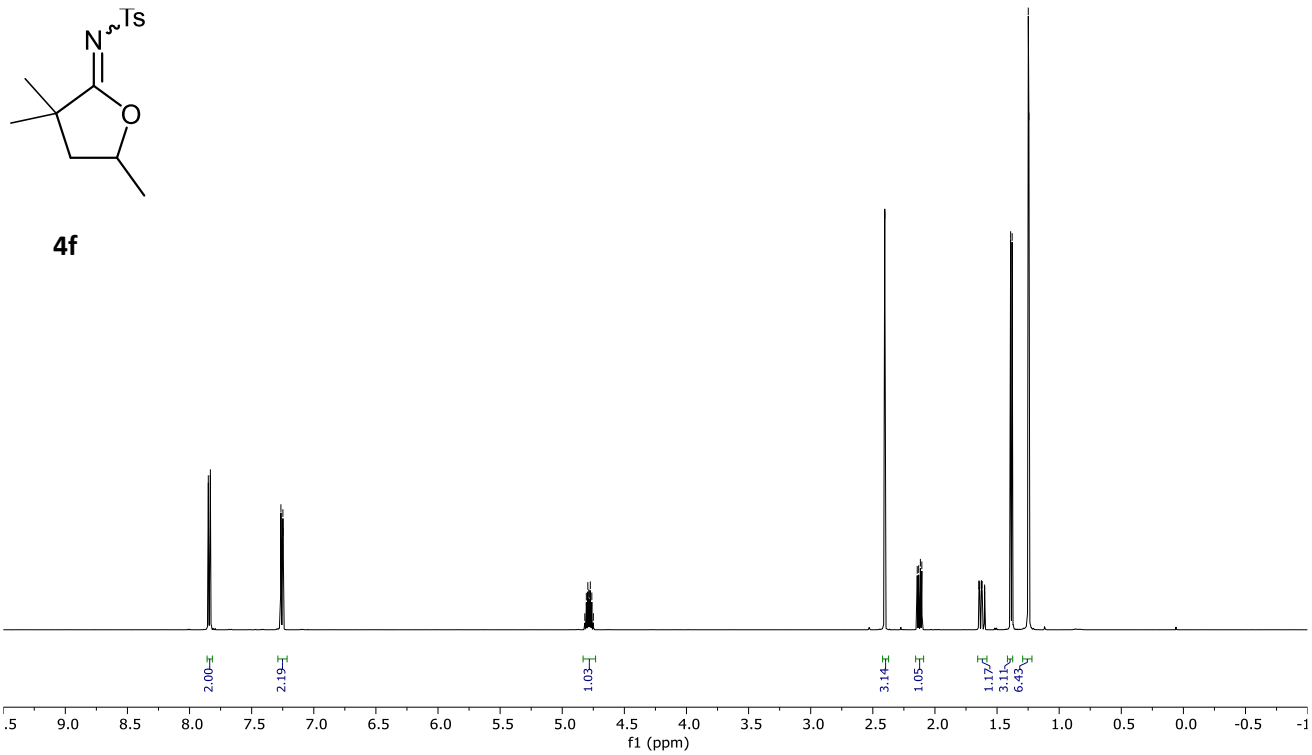

4f

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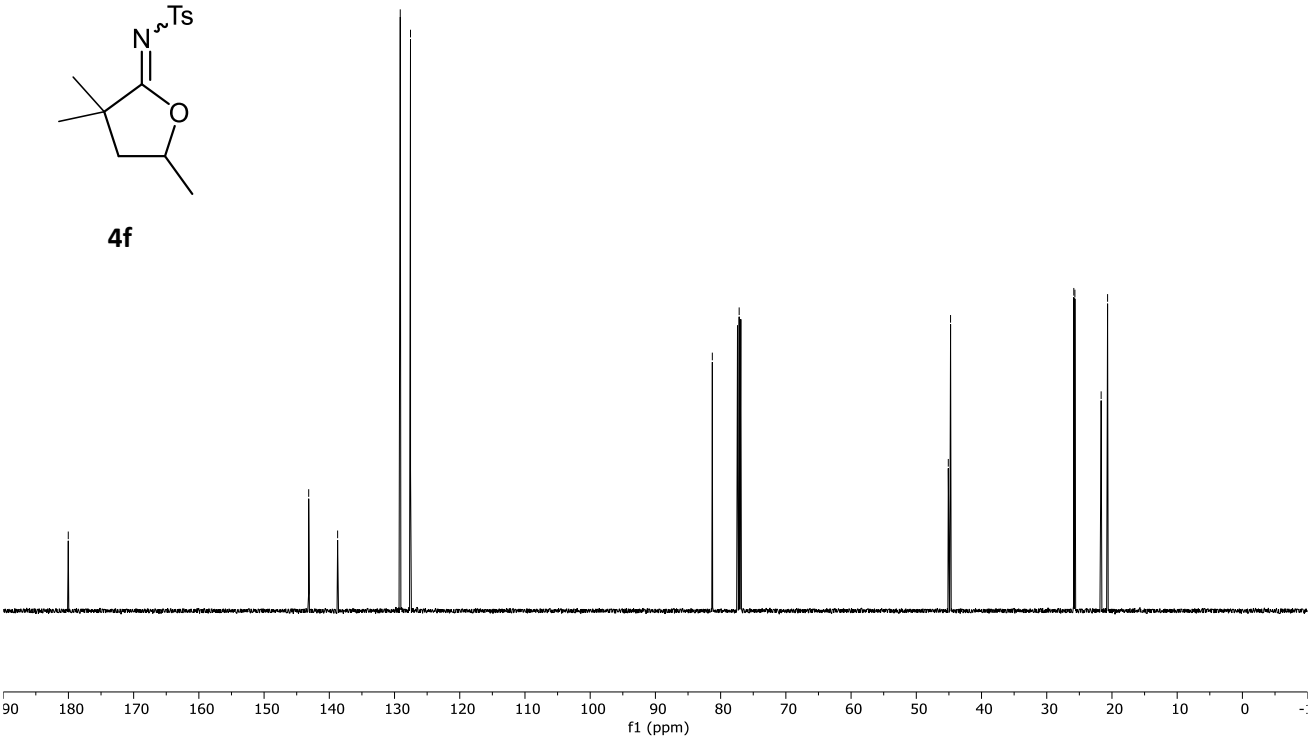

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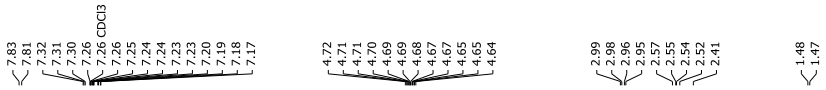

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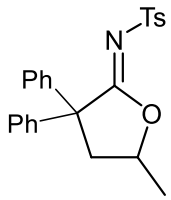

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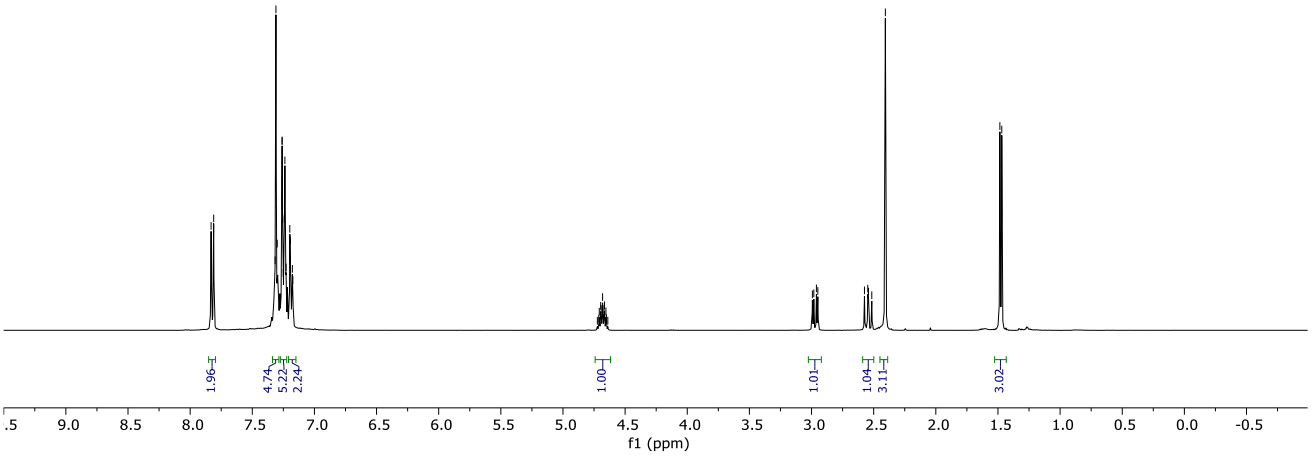

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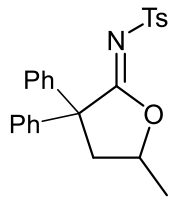

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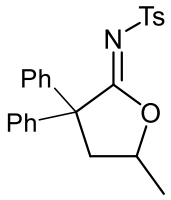
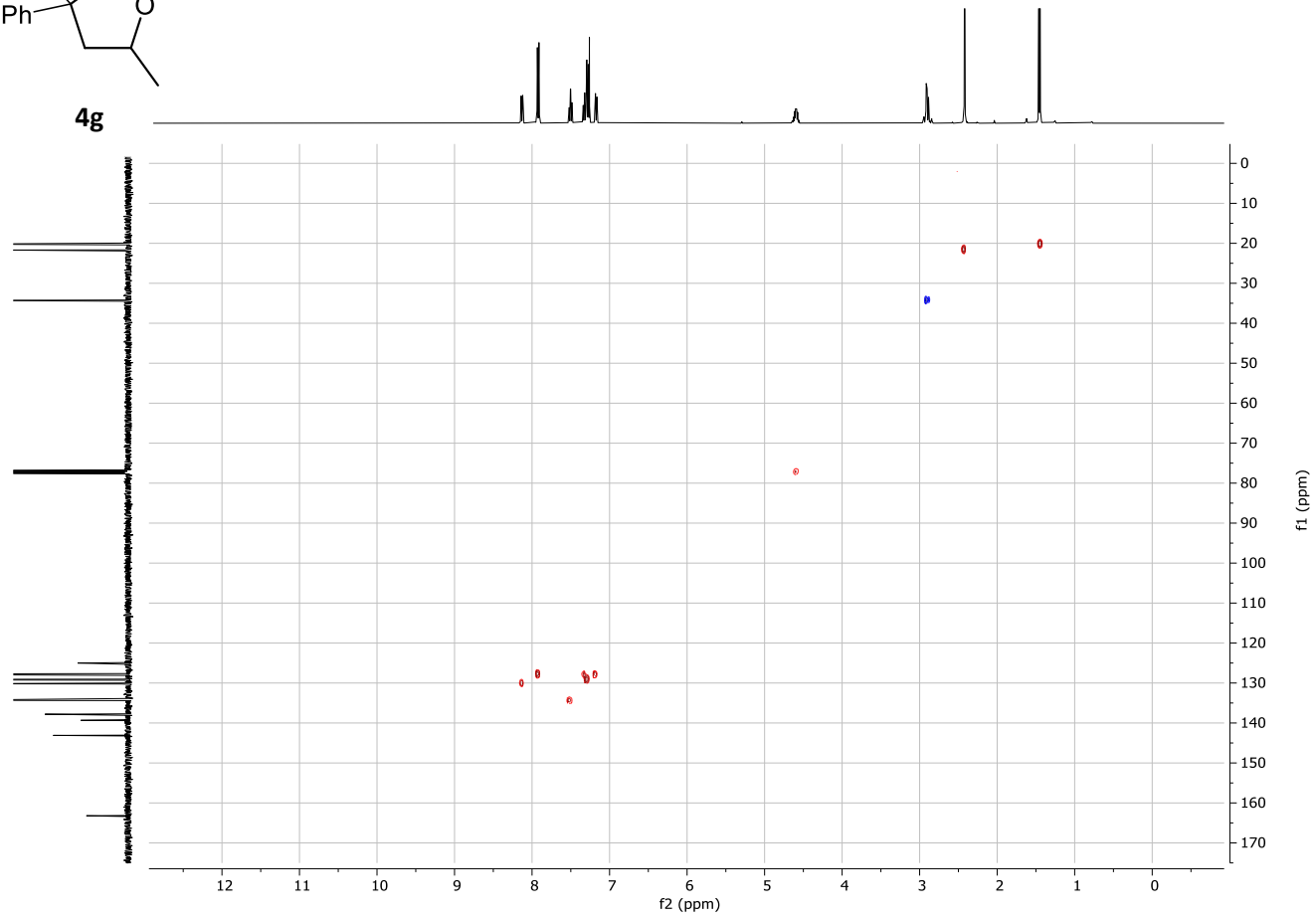
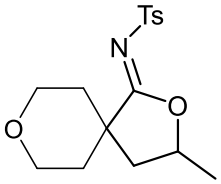


4g

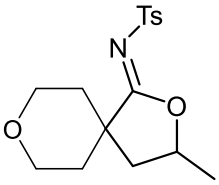


^{1}H NMR (400 MHz, $CDCl_3$)



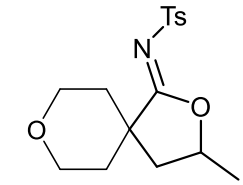
4h

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



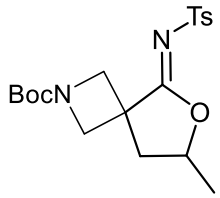
4h

^{1}H-^{13}C HSQC



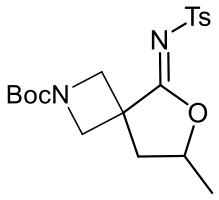
4g

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



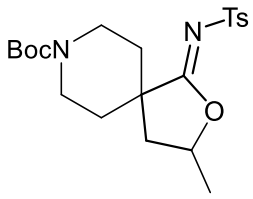
4i

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



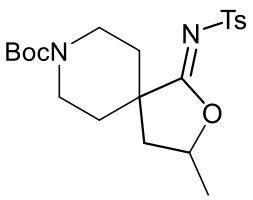
4i

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



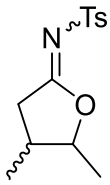
4j

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



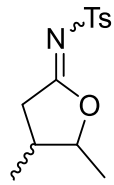
4j

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



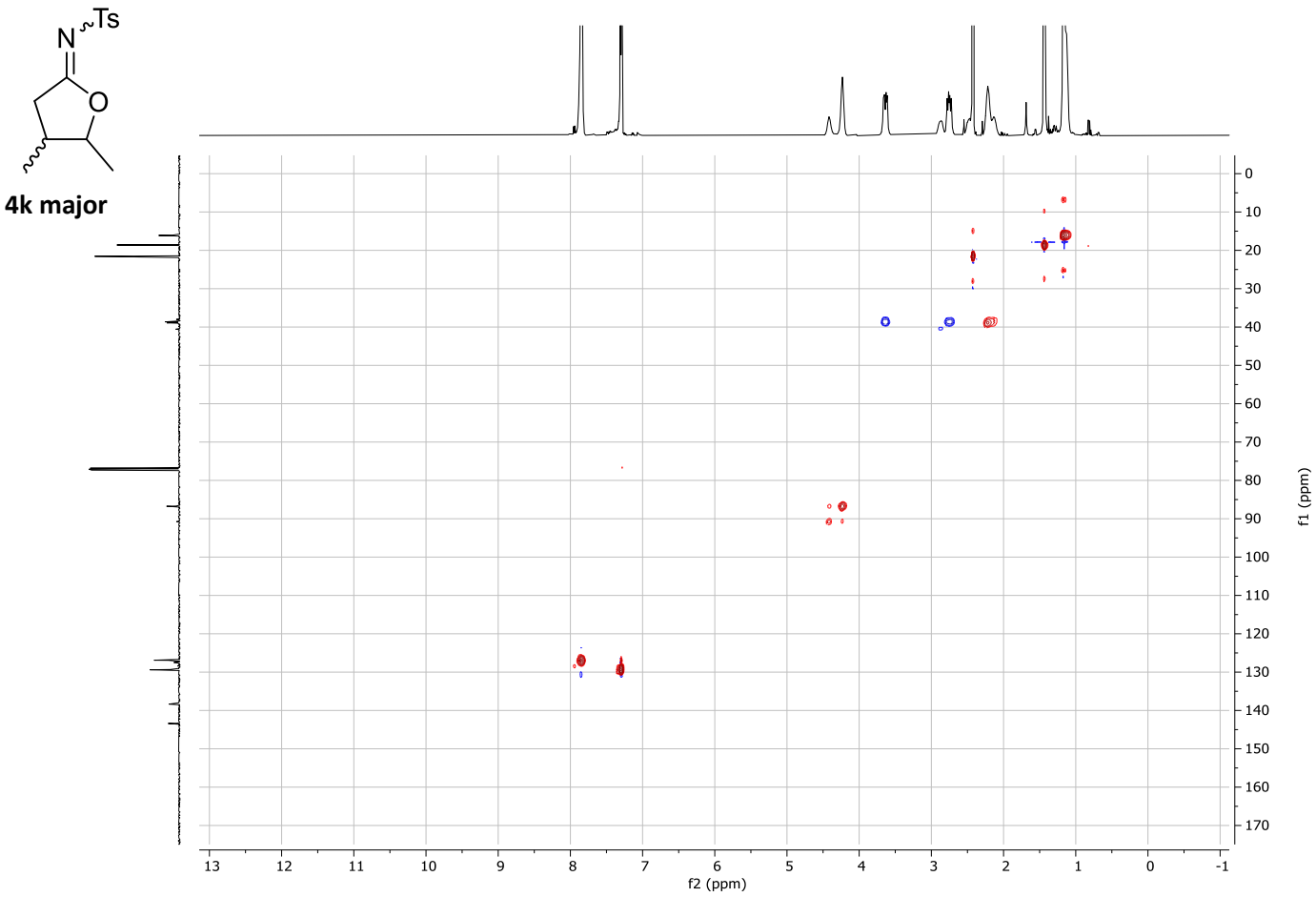
4k major

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

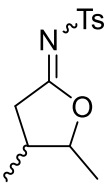


4k major

^{1}H-^{13}C HSQC

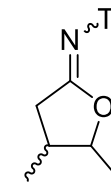


^{1}H NMR (500 MHz, $CDCl_3$)



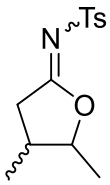
4k minor

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

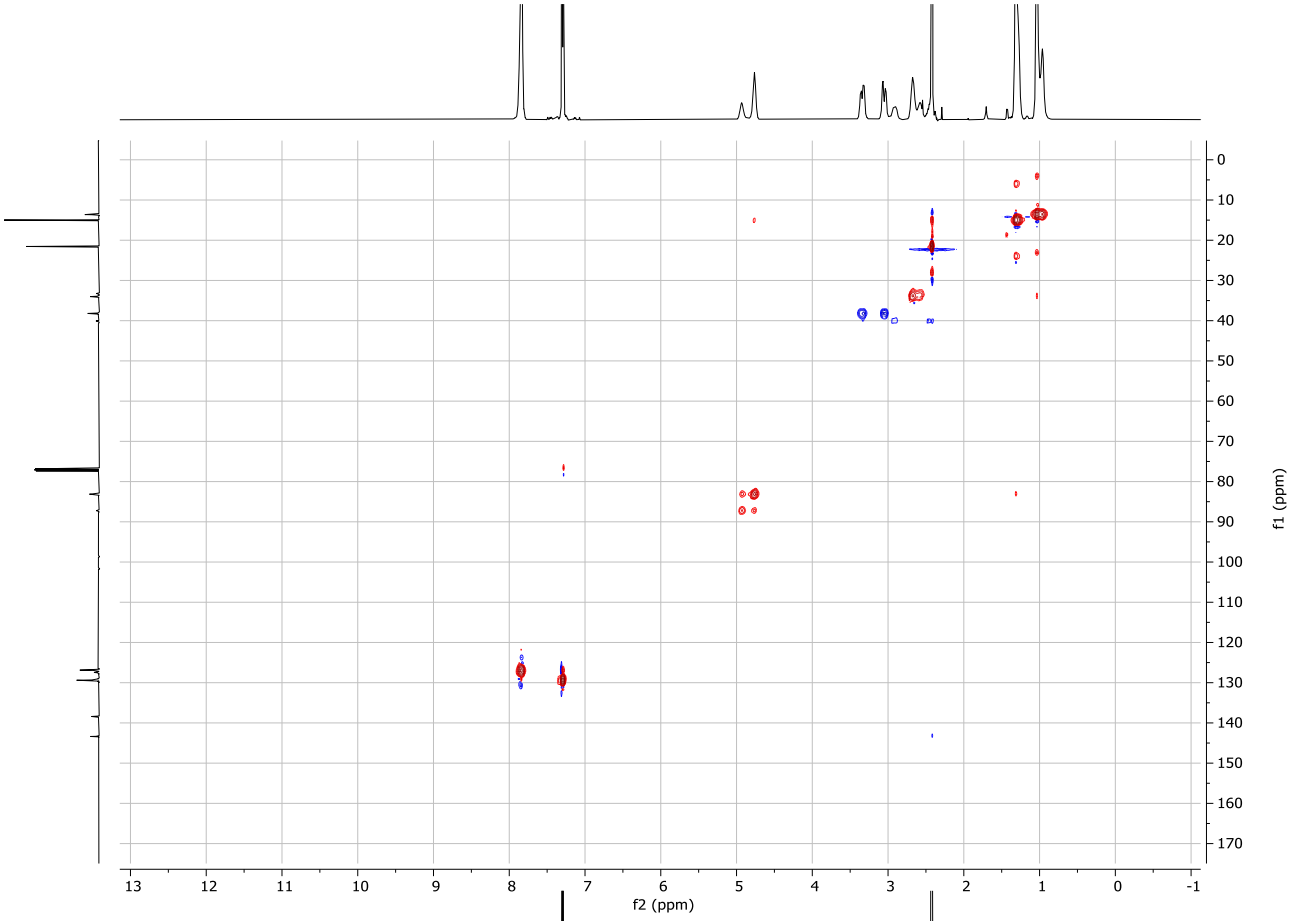


4k minor

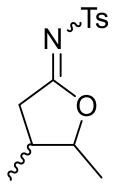
^{1}H-^{13}C HSQC



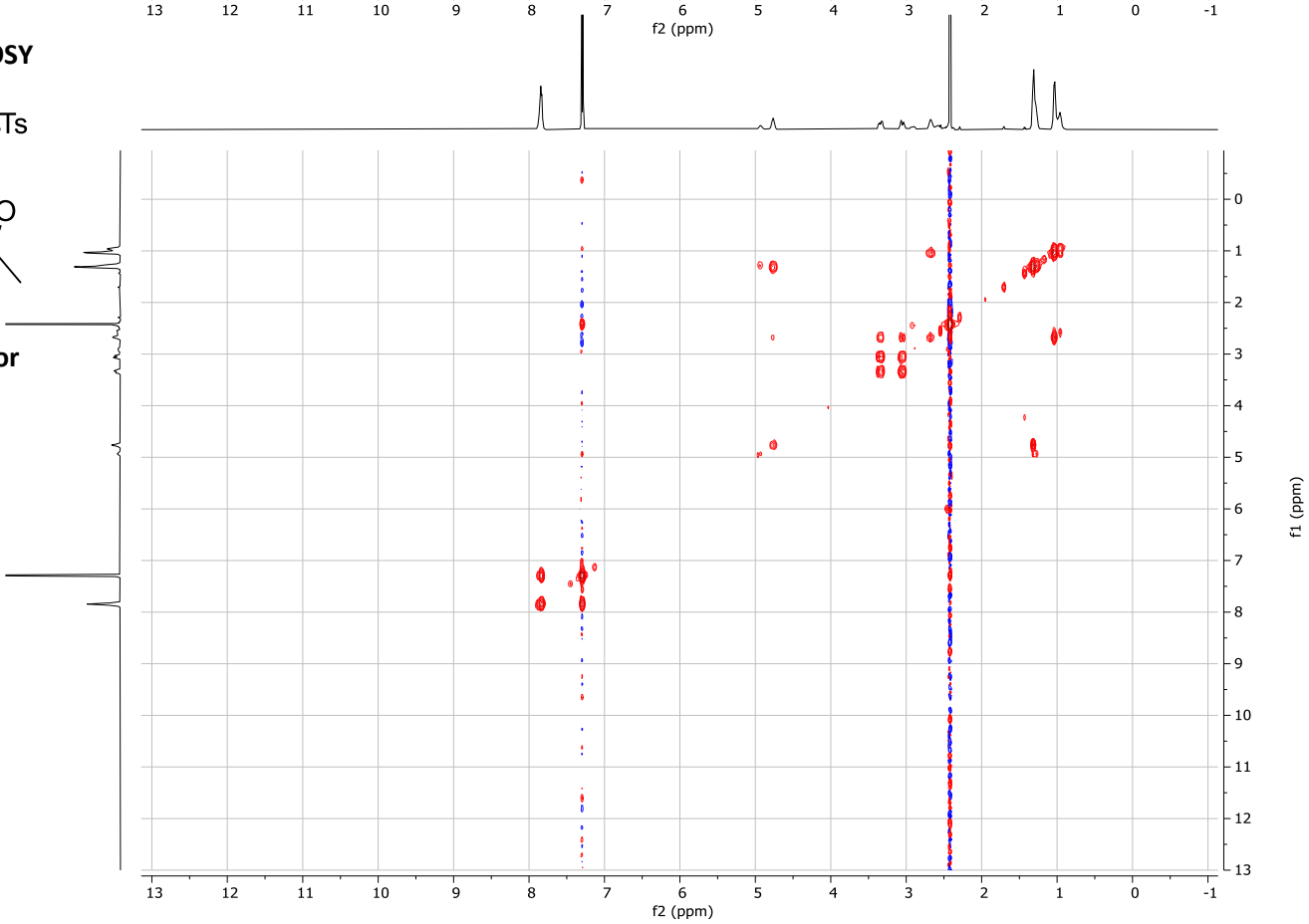
4k minor



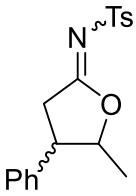
^{1}H-^{1}H COSY



4k minor

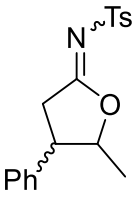


^{1}H NMR (500 MHz, $CDCl_3$)



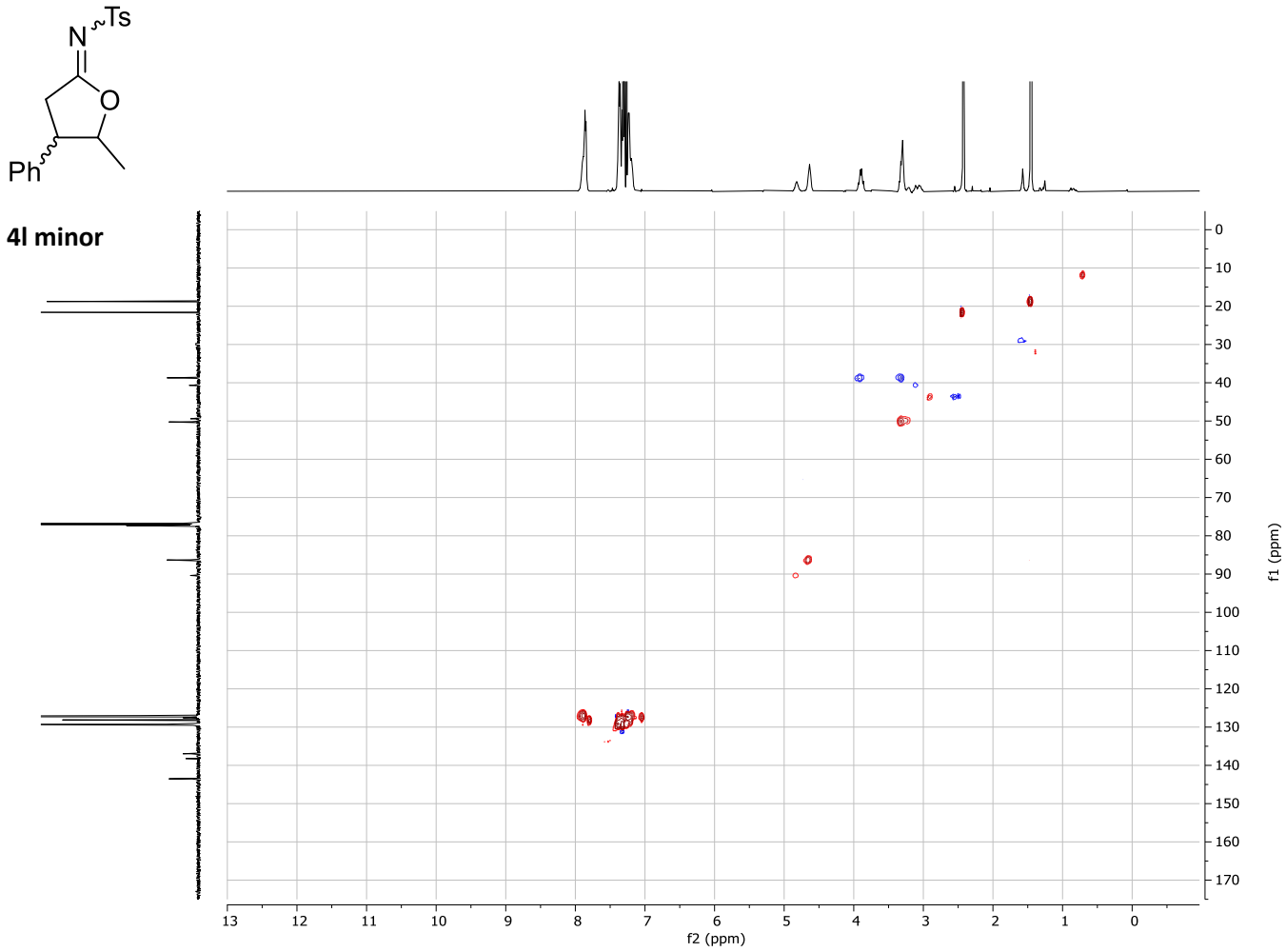
4l minor

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

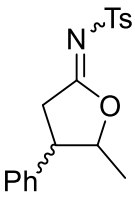


4l minor

^{1}H-^{13}C HSQC

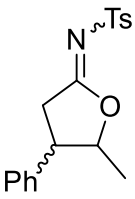


^{1}H NMR (500 MHz, $CDCl_3$)



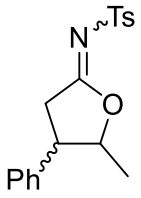
4l major

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

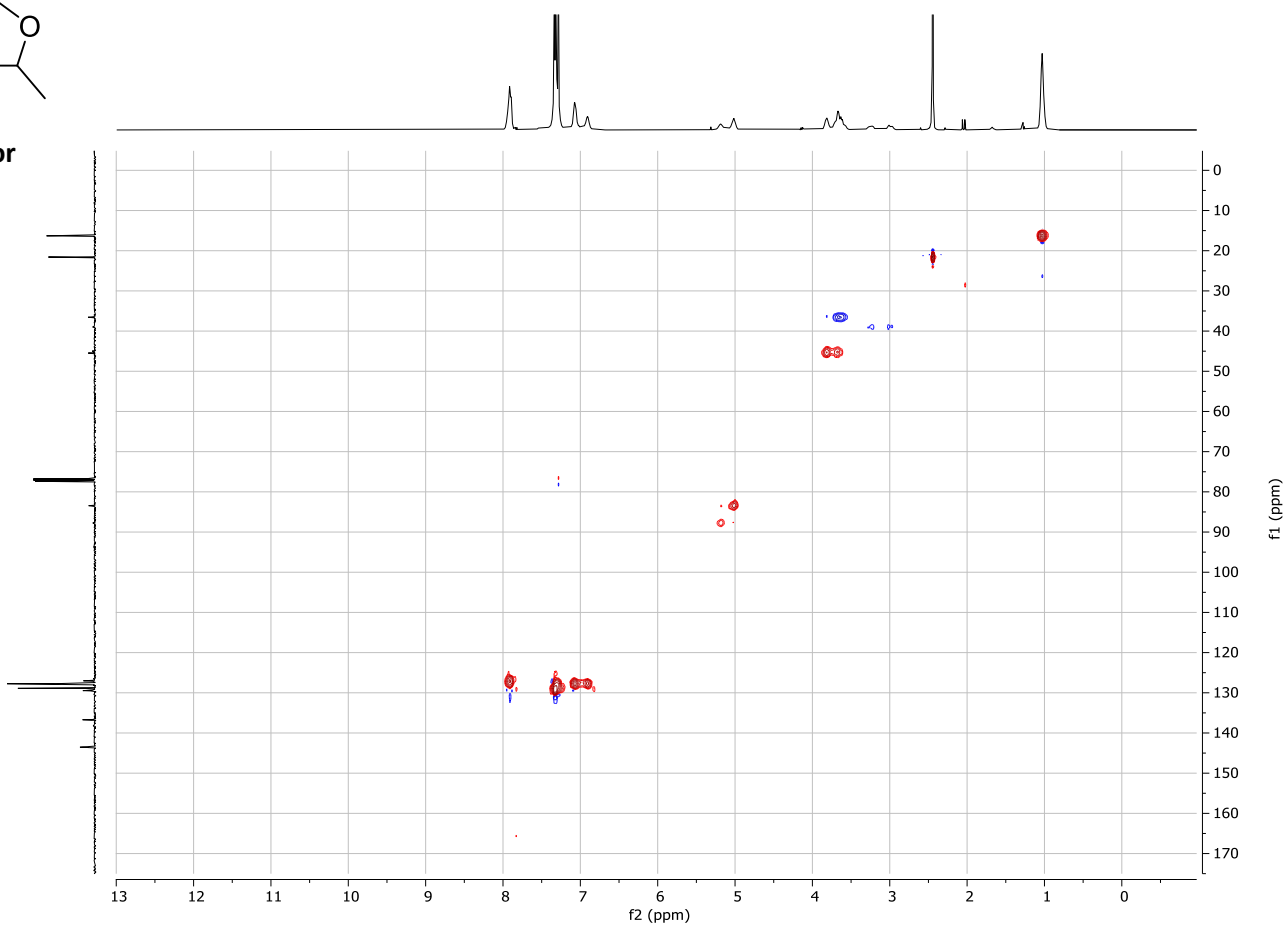


4k major

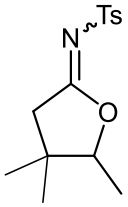
^{1}H-^{13}C HSQC



4l major

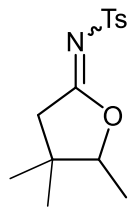


^{1}H NMR (400 MHz, $CDCl_3$)



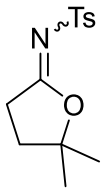
4m

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



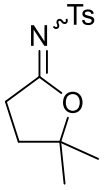
4m

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



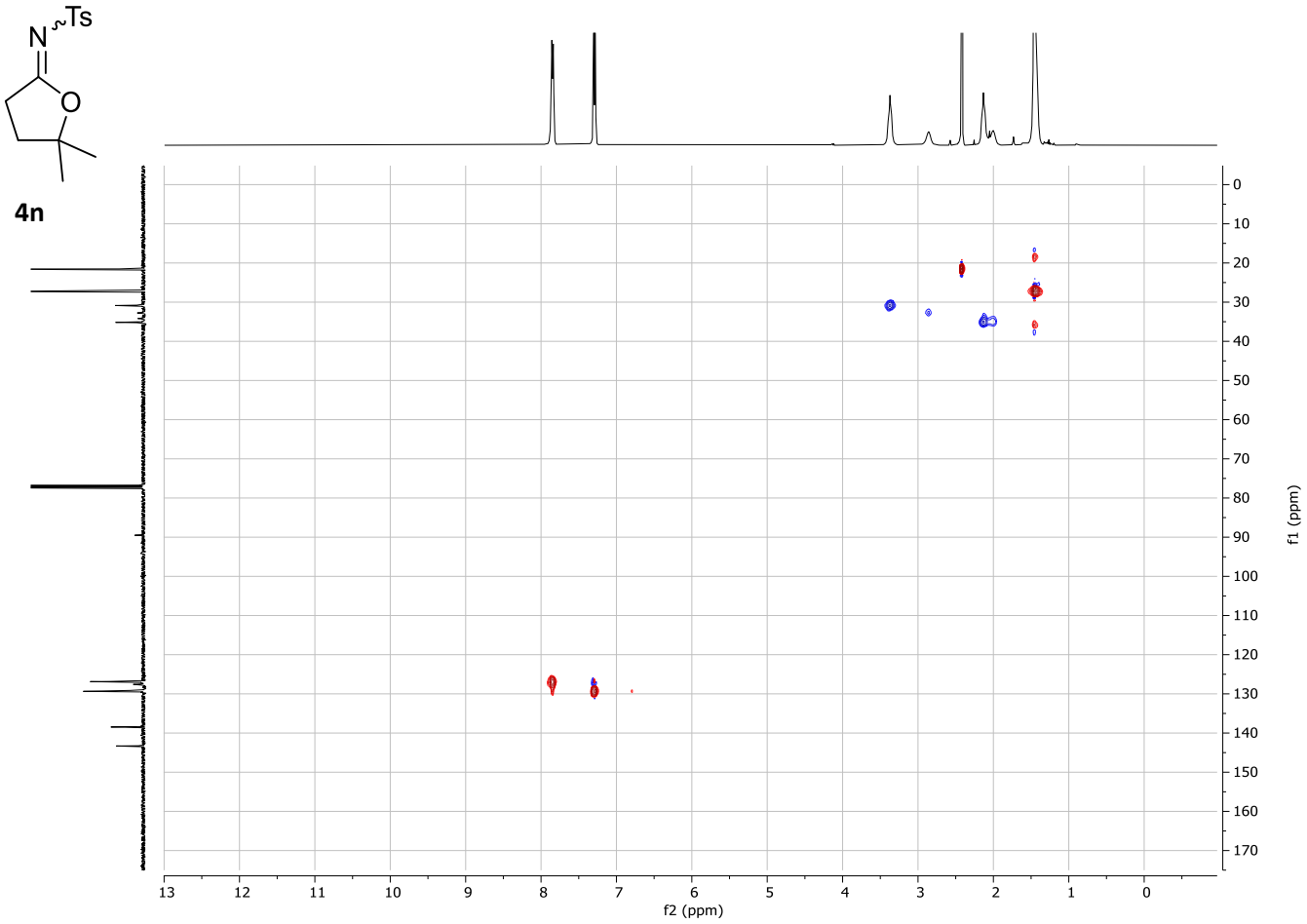
4n

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

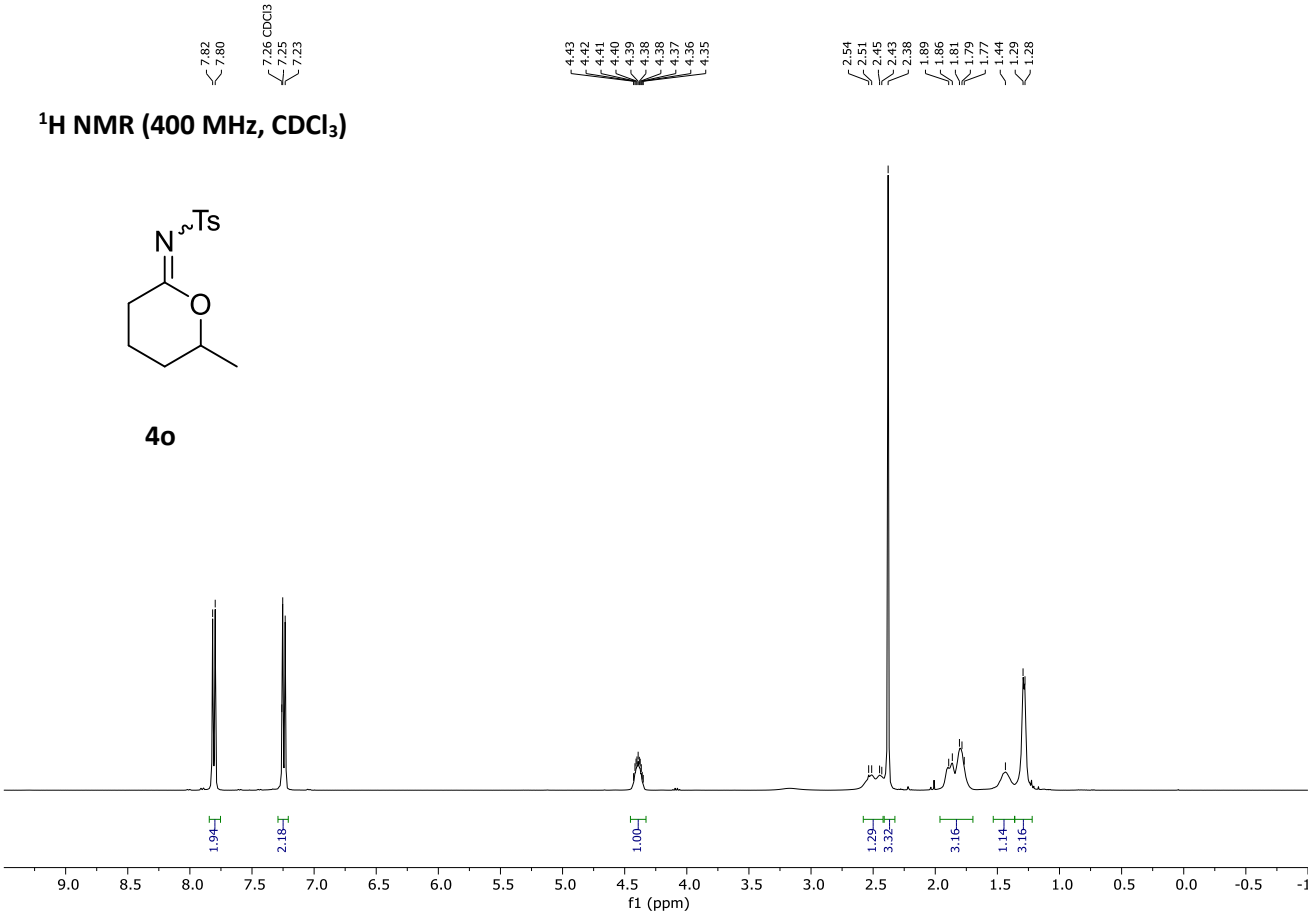


4n

^{1}H-^{13}C HSQC

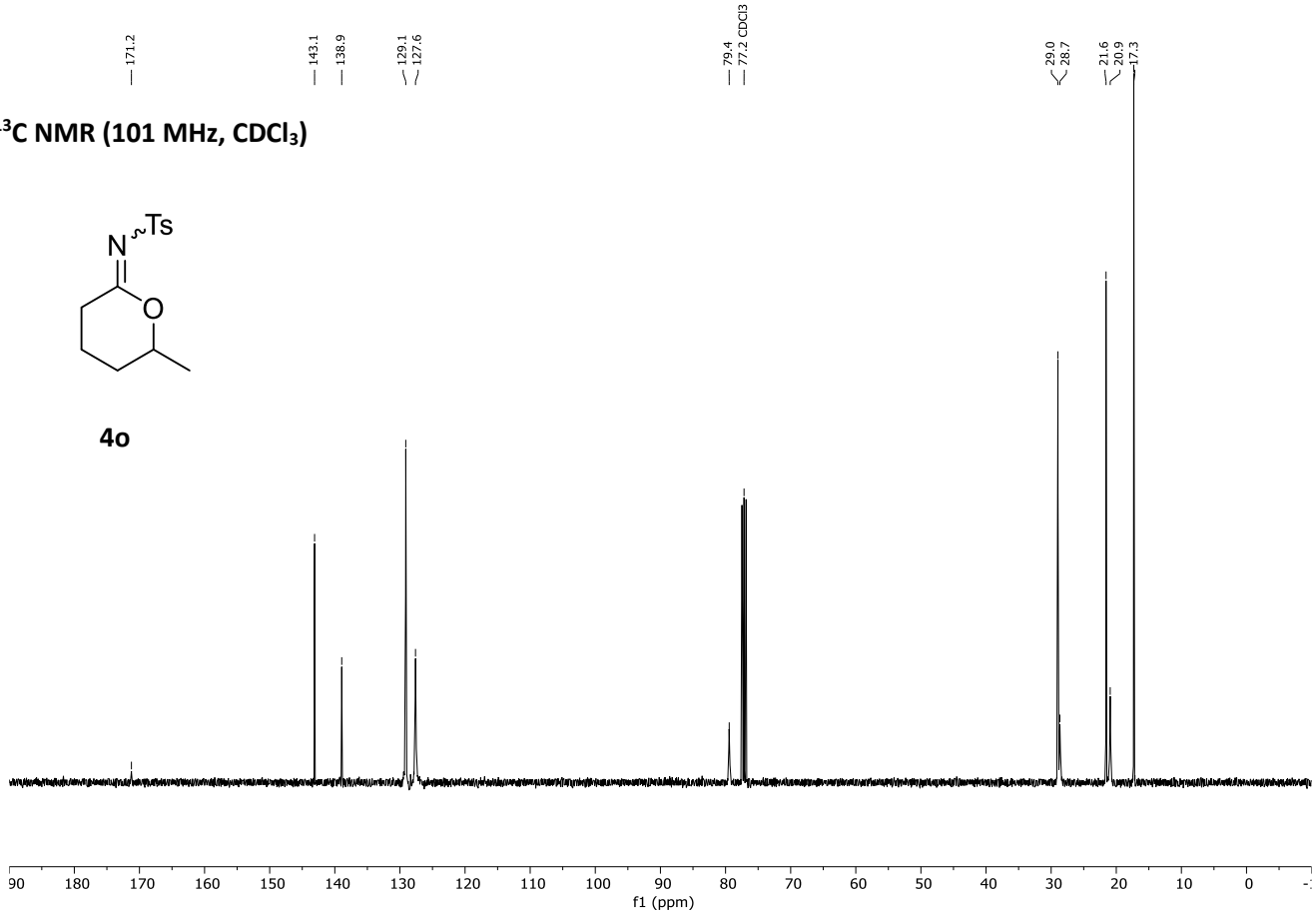


^{1}H NMR (400 MHz, $CDCl_3$)



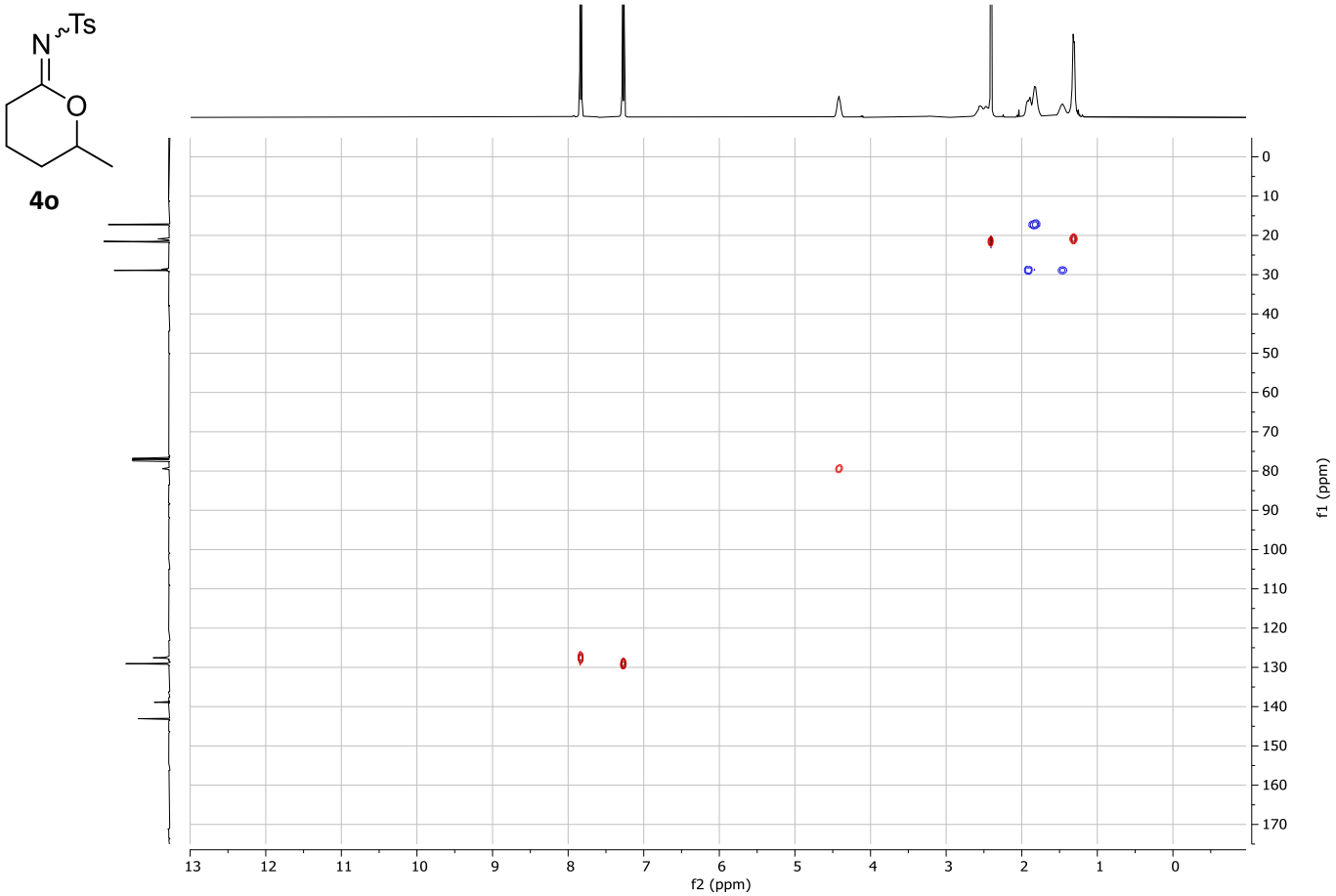
4o

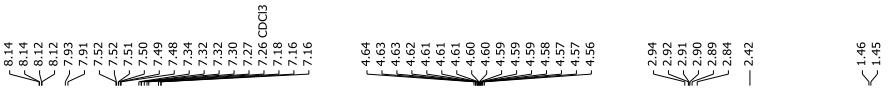
^{13}C NMR (101 MHz, $CDCl_3$)



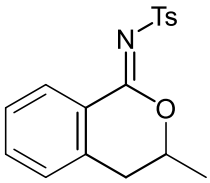
4o

^{1}H-^{13}C HSQC

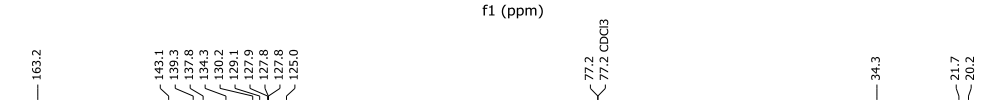




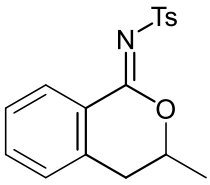
^{1}H NMR (400 MHz, $CDCl_3$)



4p

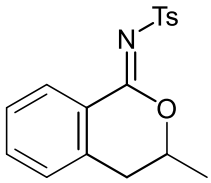


^{13}C NMR (101 MHz, $CDCl_3$)

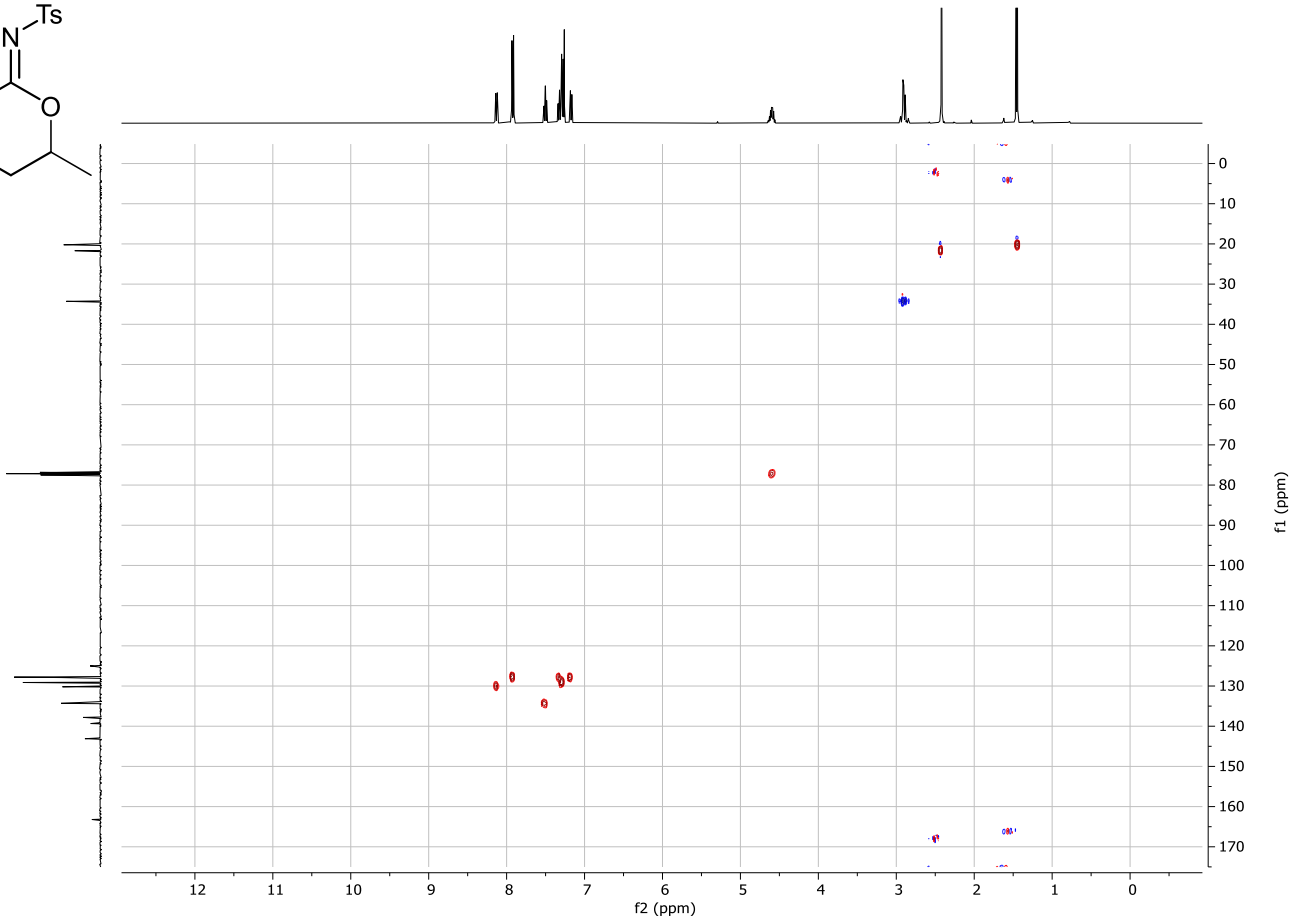


4p

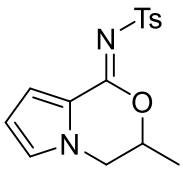
^{1}H-^{13}C HSQC



4o

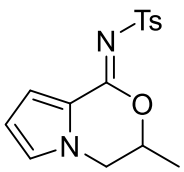


^{1}H NMR (400 MHz, $CDCl_3$)



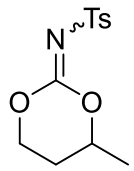
4q

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



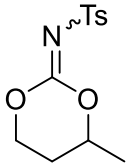
4q

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



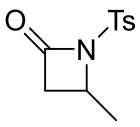
4r

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

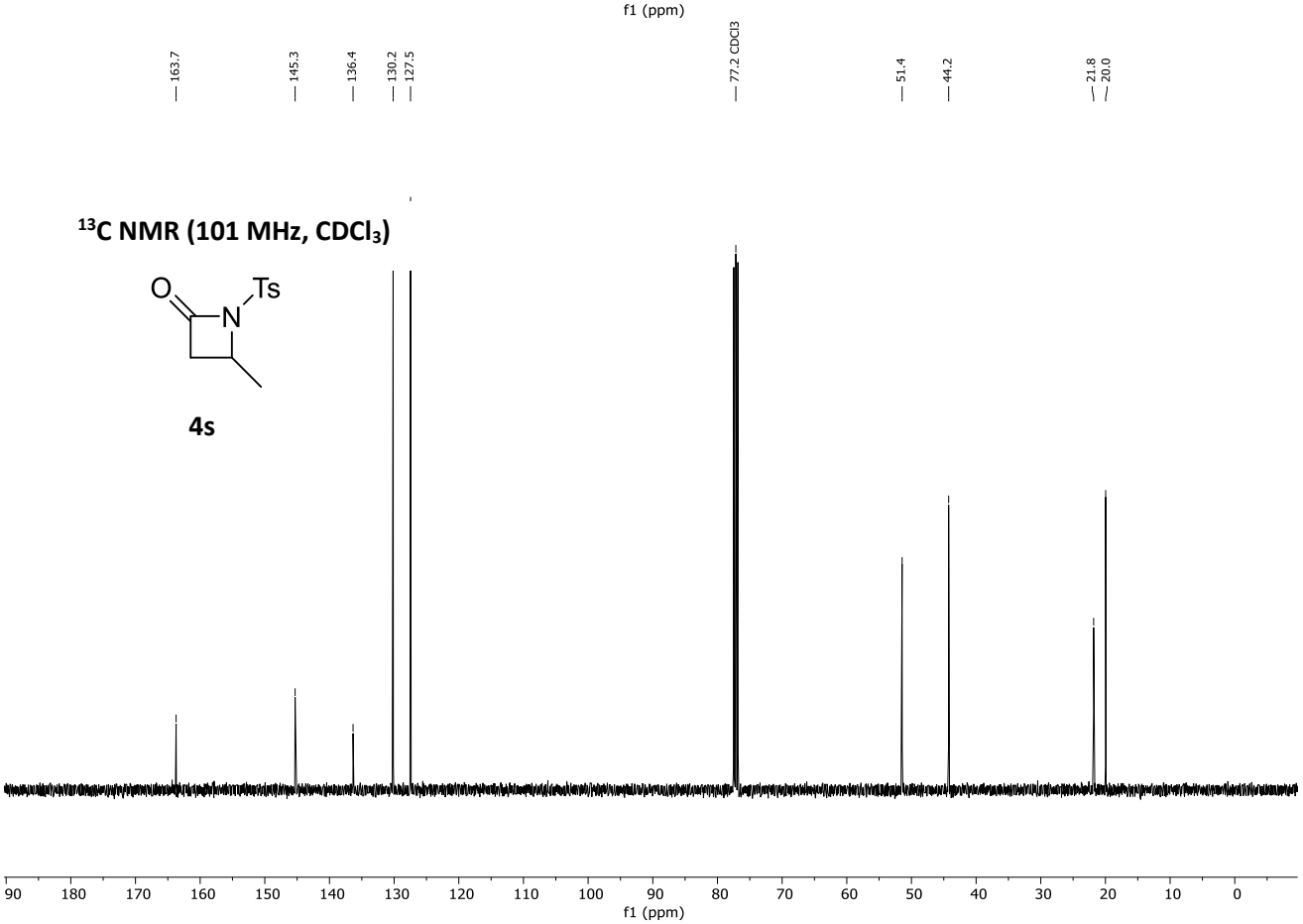


4r

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



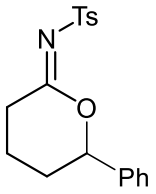
4s



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

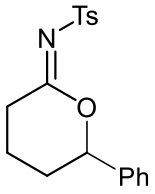
4s

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



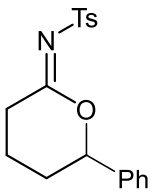
4u

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

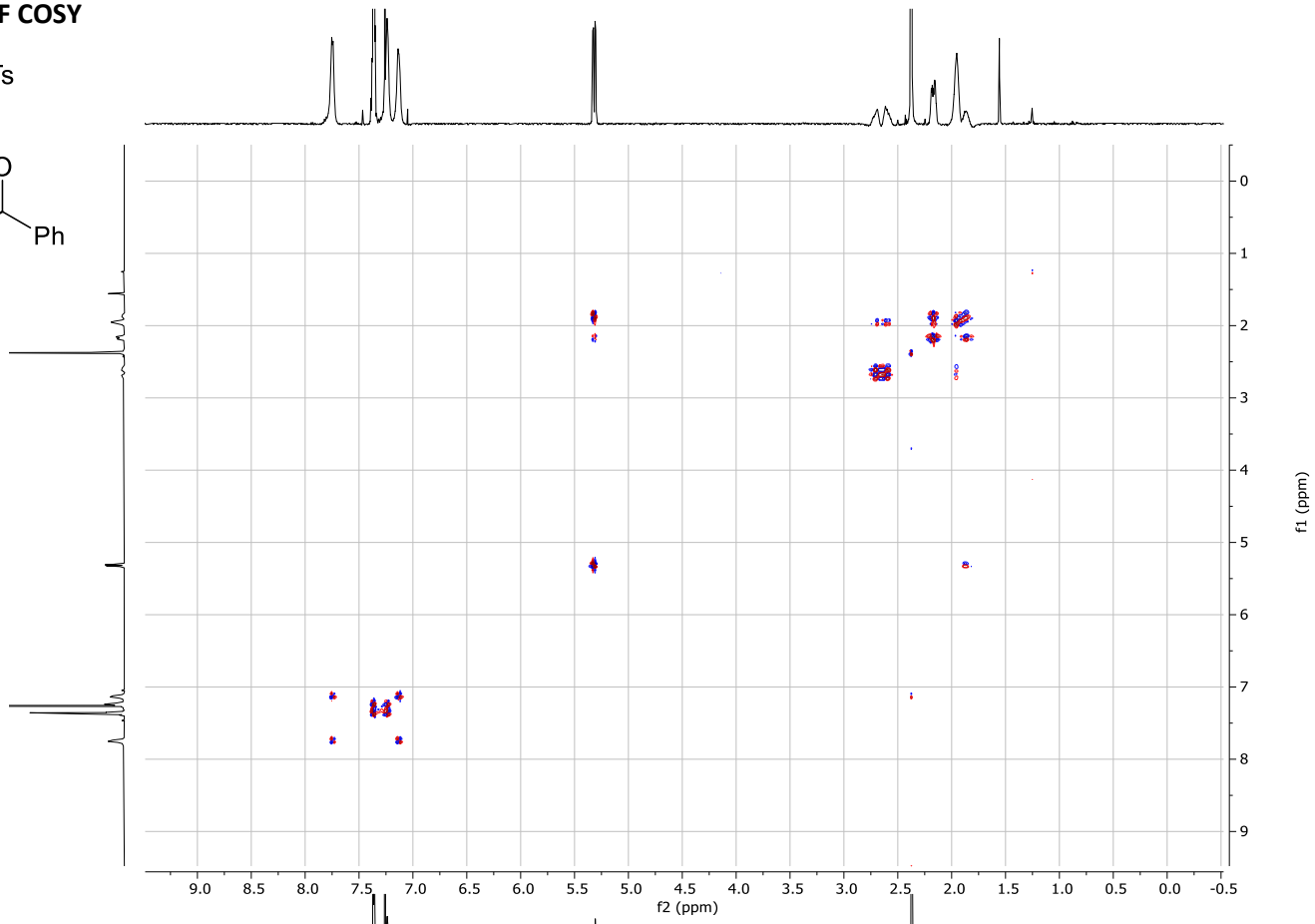


4u

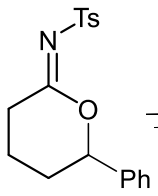
^{1}H-^{1}H DQF COSY



4u

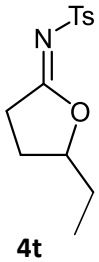


^{1}H-^{13}C HSQC



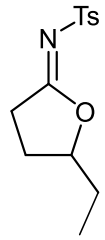
4u

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



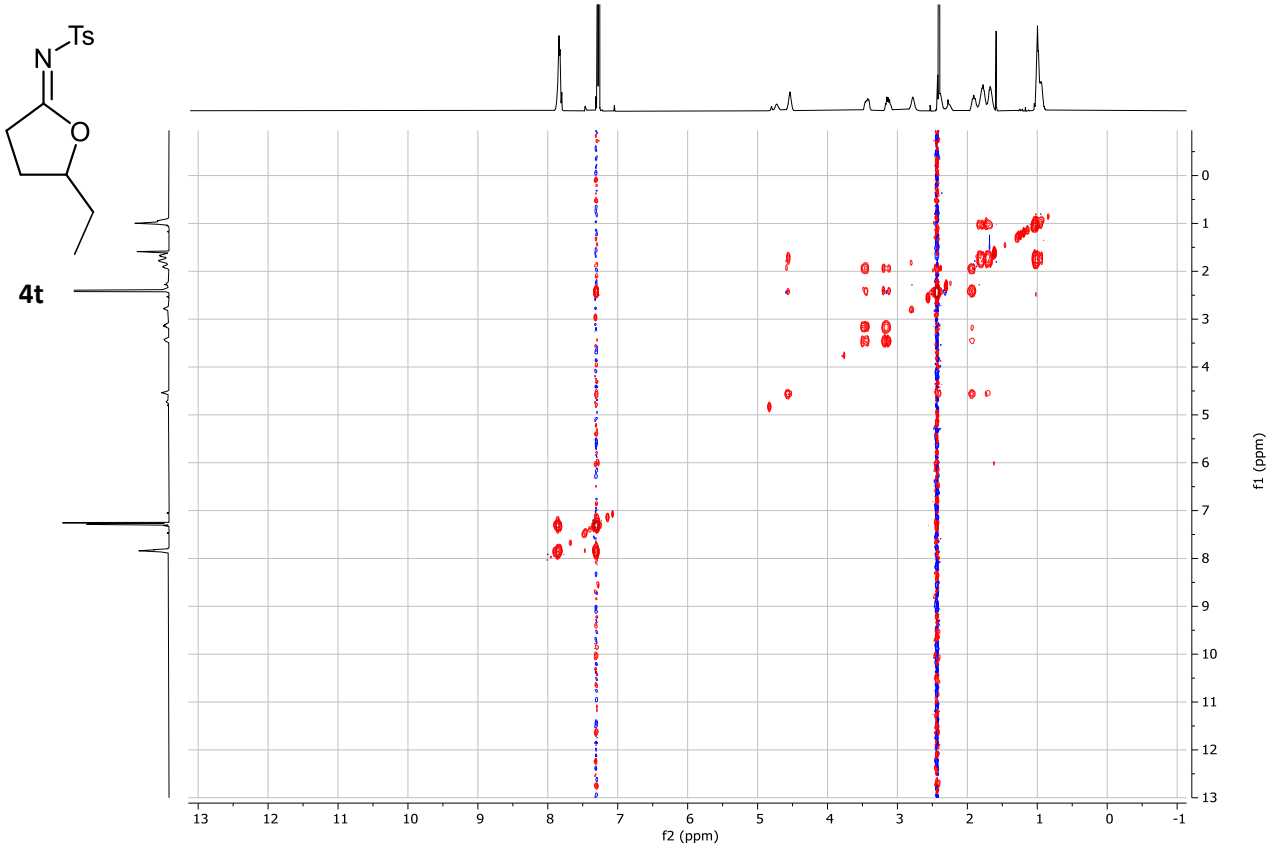
4t

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

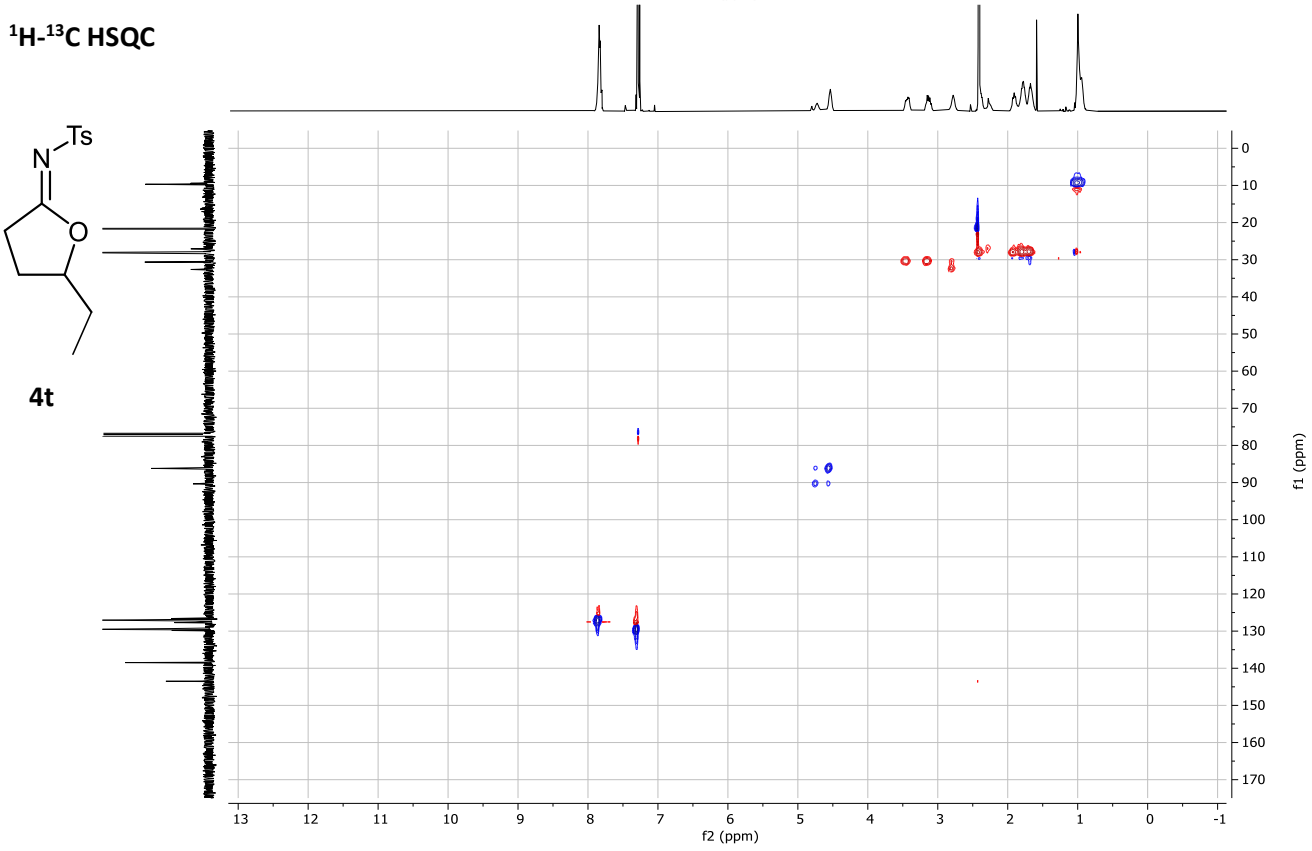


4t

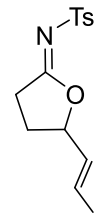
^{1}H-^{1}H COSY



^{1}H-^{13}C HSQC

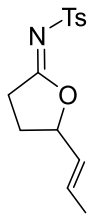


^{1}H NMR (500 MHz, $CDCl_3$)



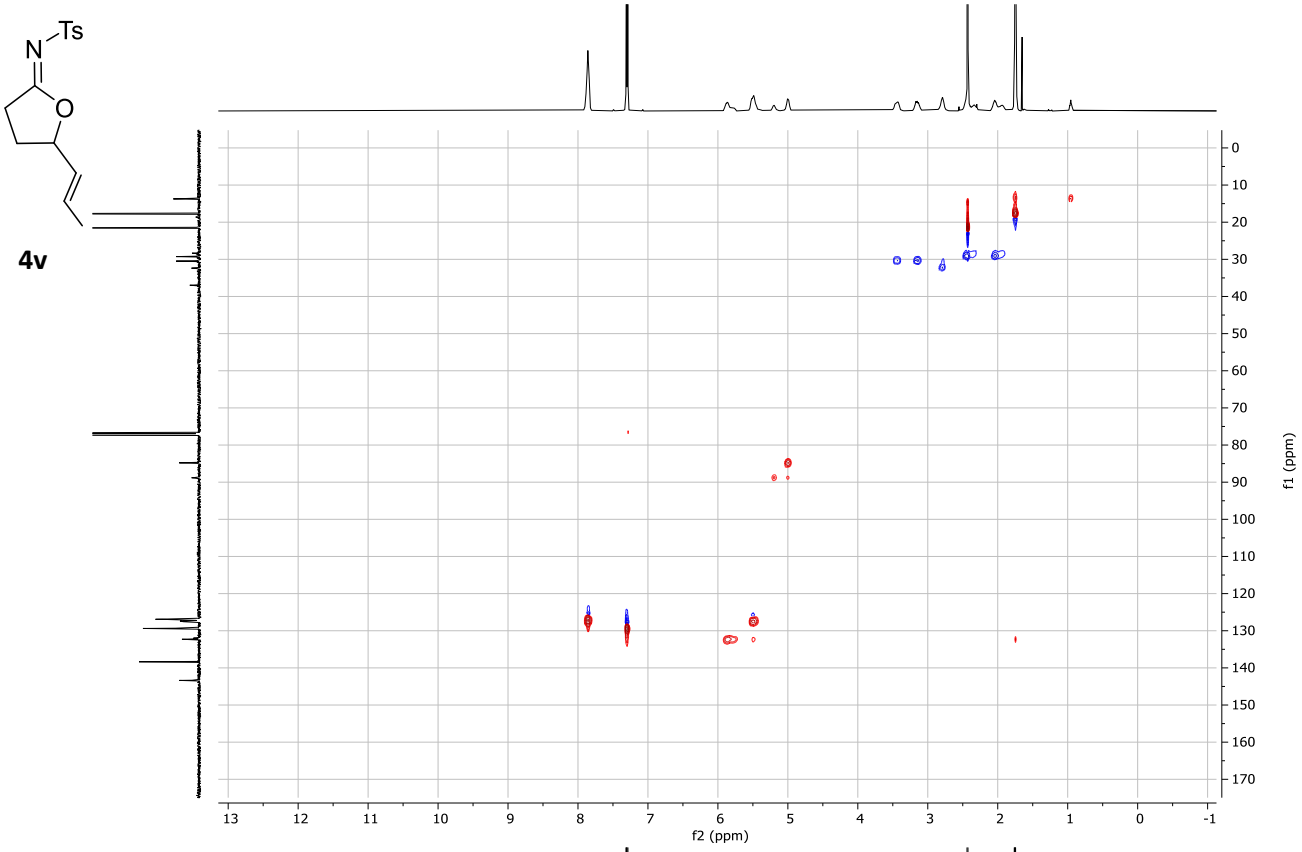
4v

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



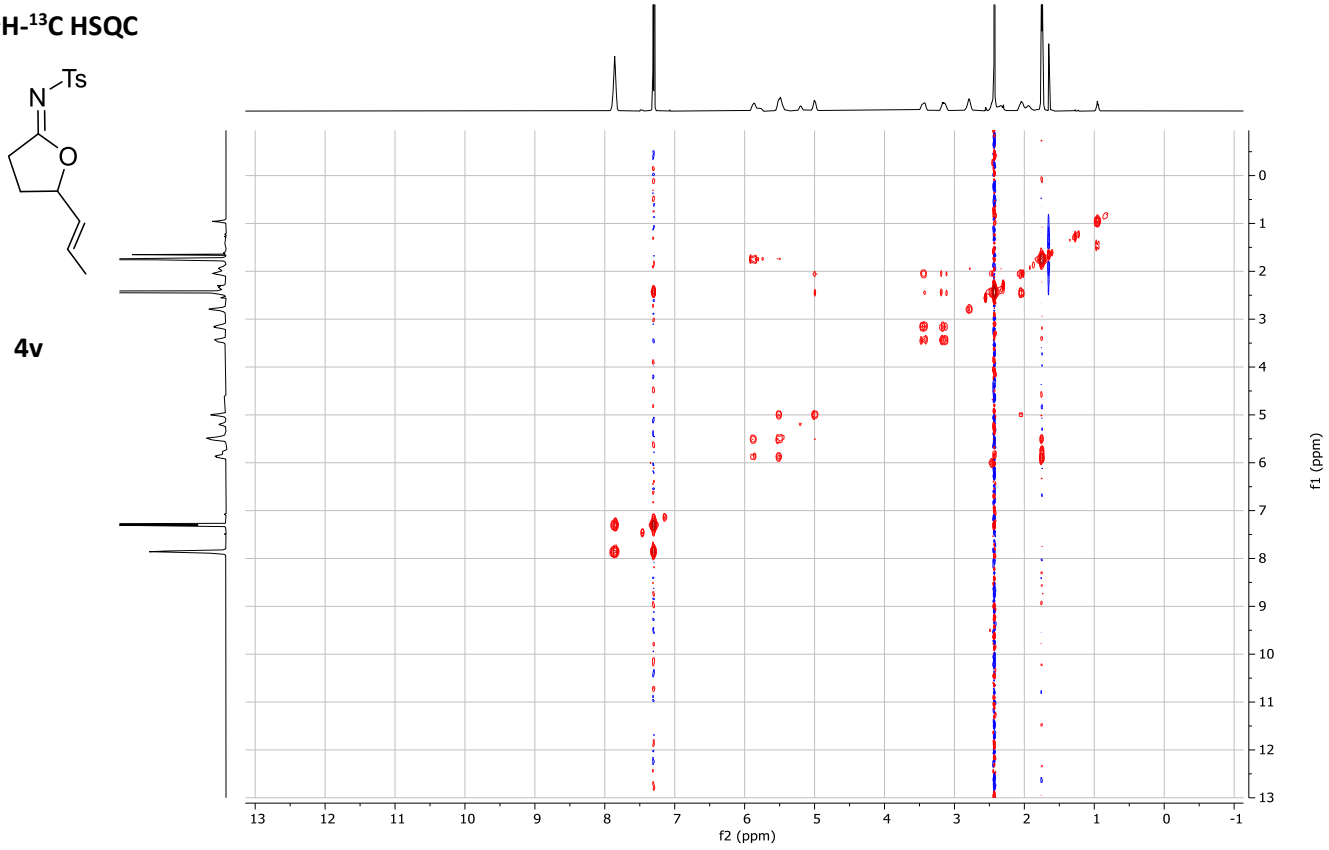
4v

^{1}H-^{1}H COSY



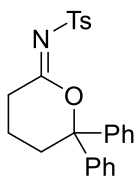
4v

^{1}H-^{13}C HSQC



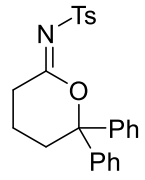
4v

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



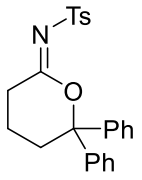
4w

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

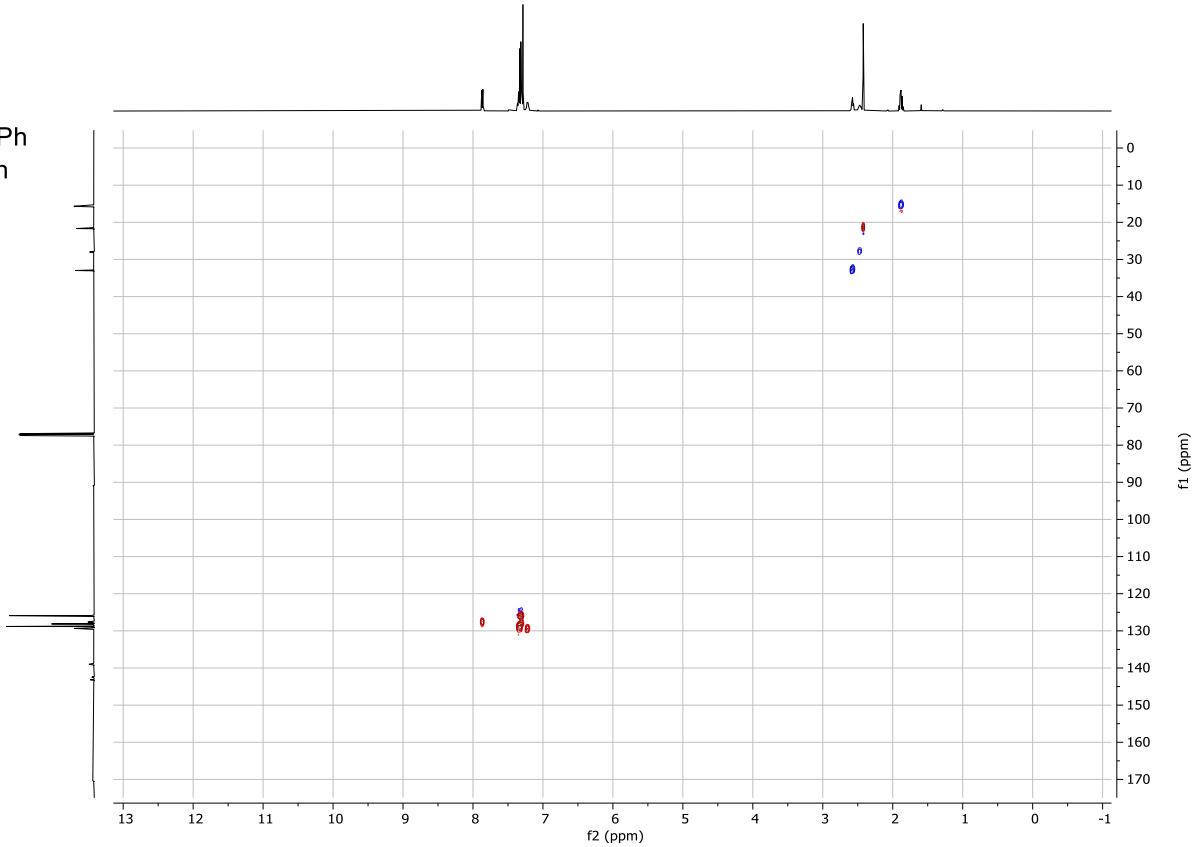


4w

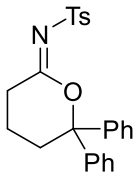
^{1}H-^{13}C HSQC



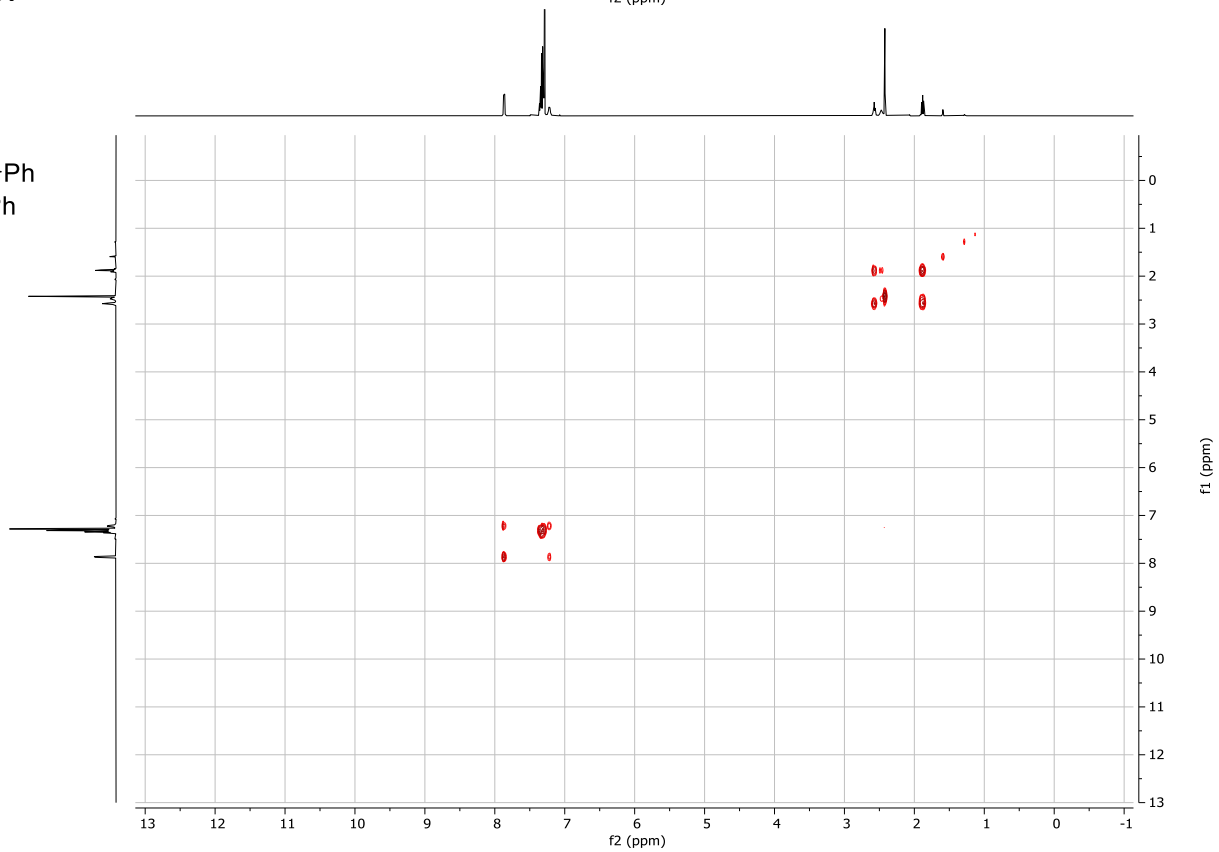
4w



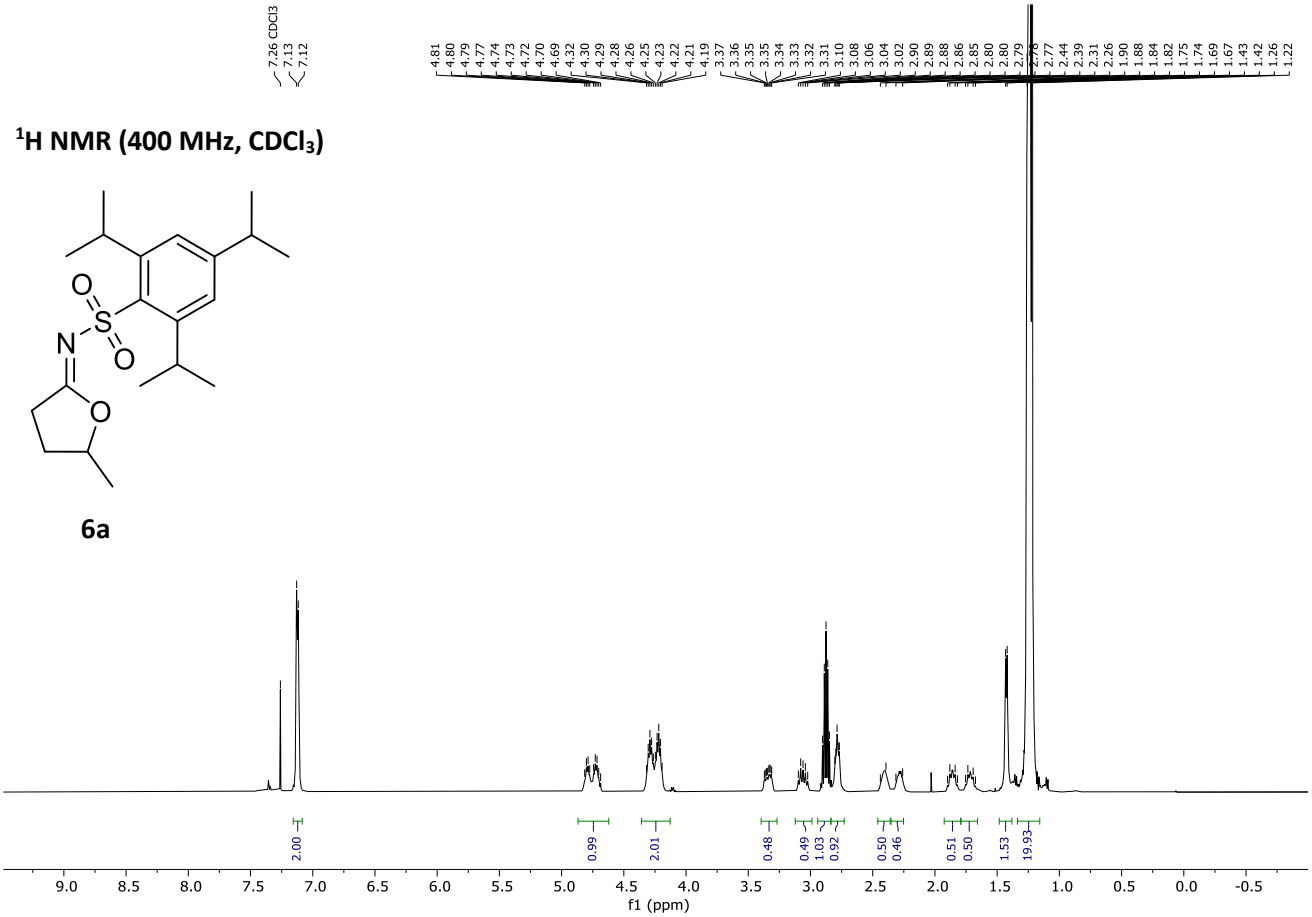
^{1}H-^{1}H COSY



4w

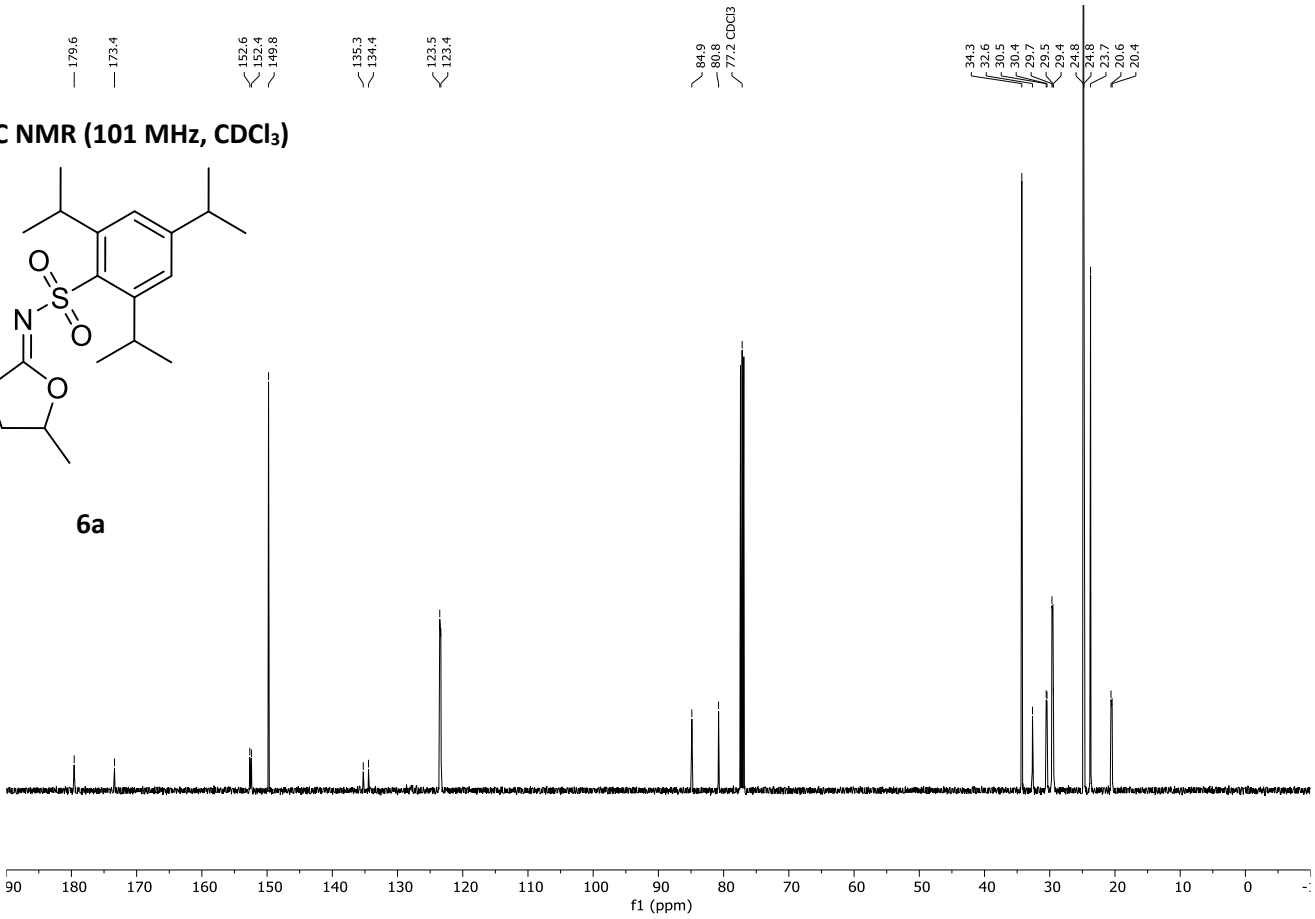


^{1}H NMR (400 MHz, $CDCl_3$)



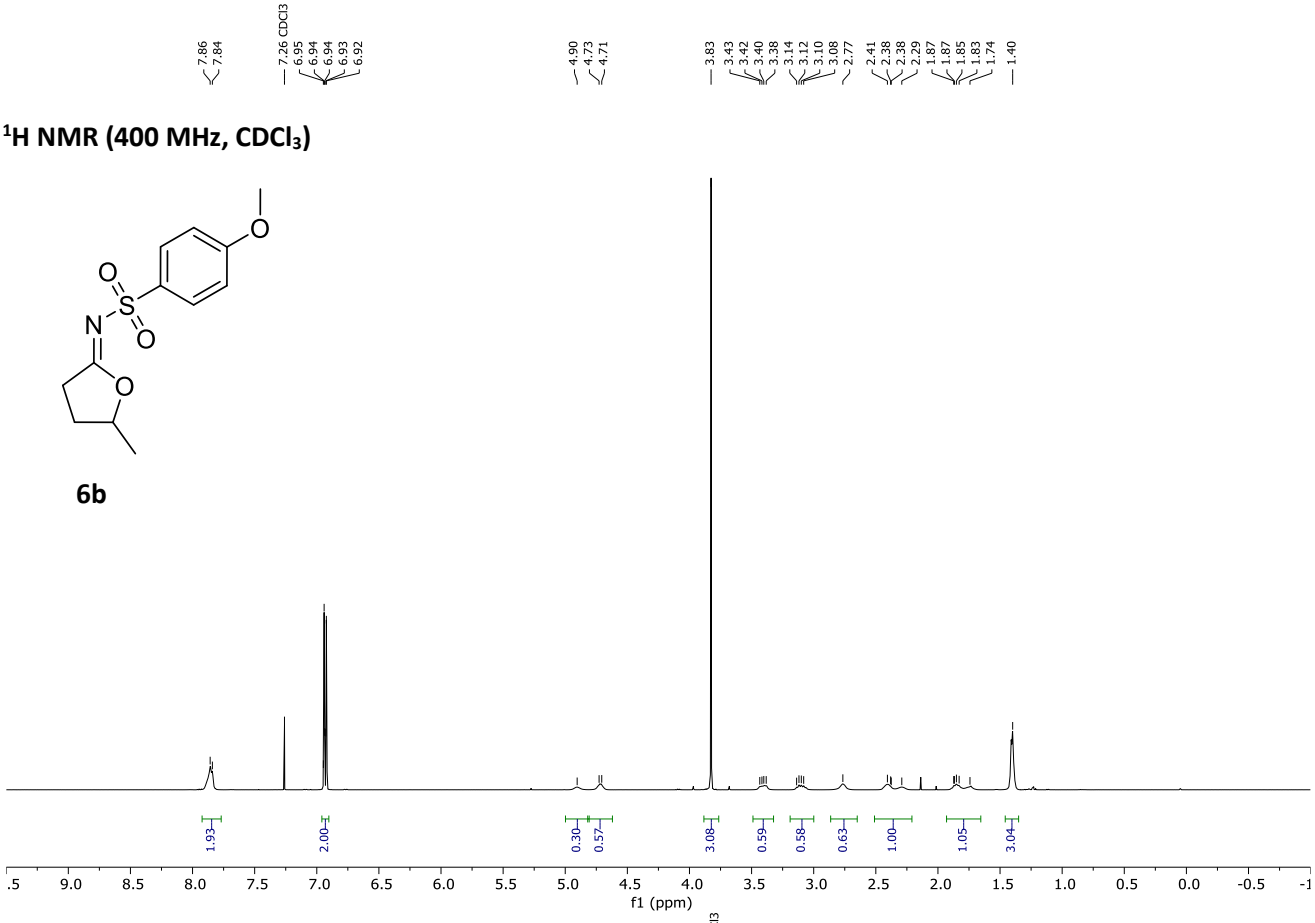
6a

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



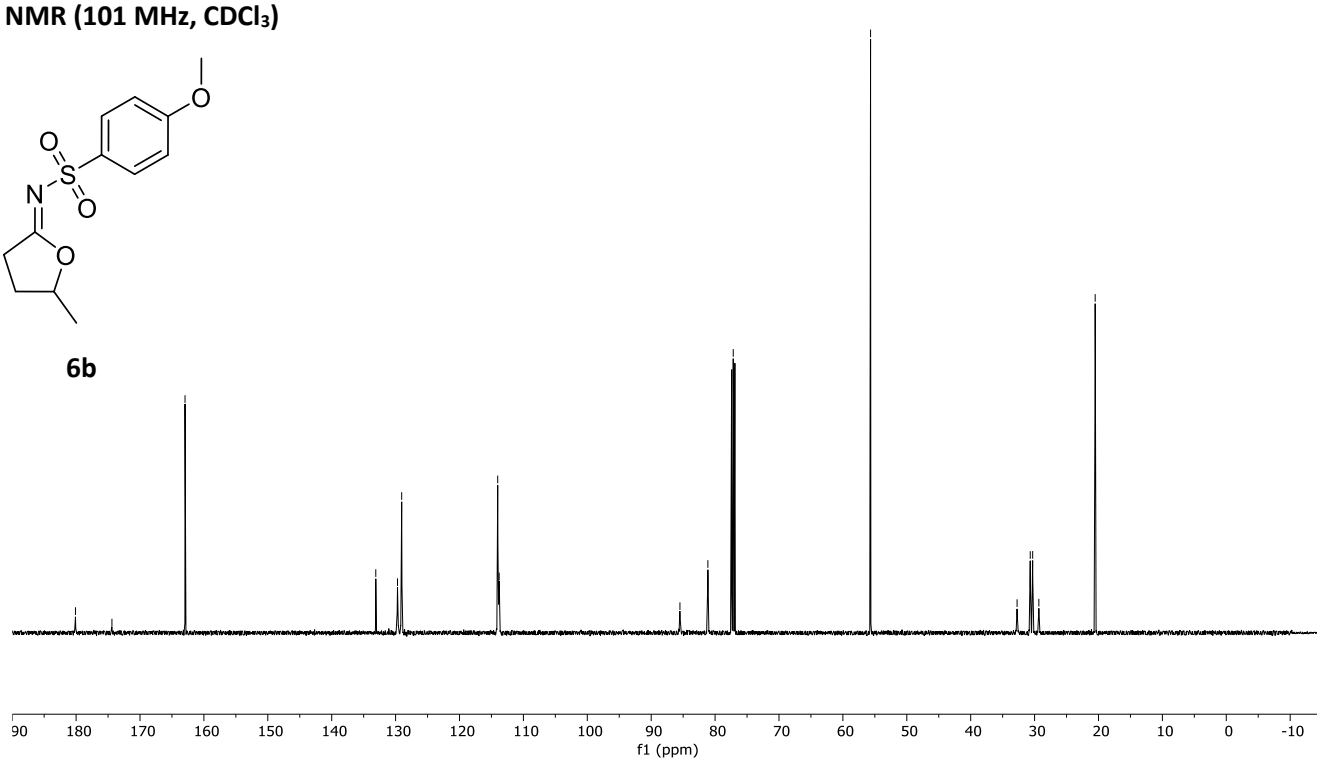
6a

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



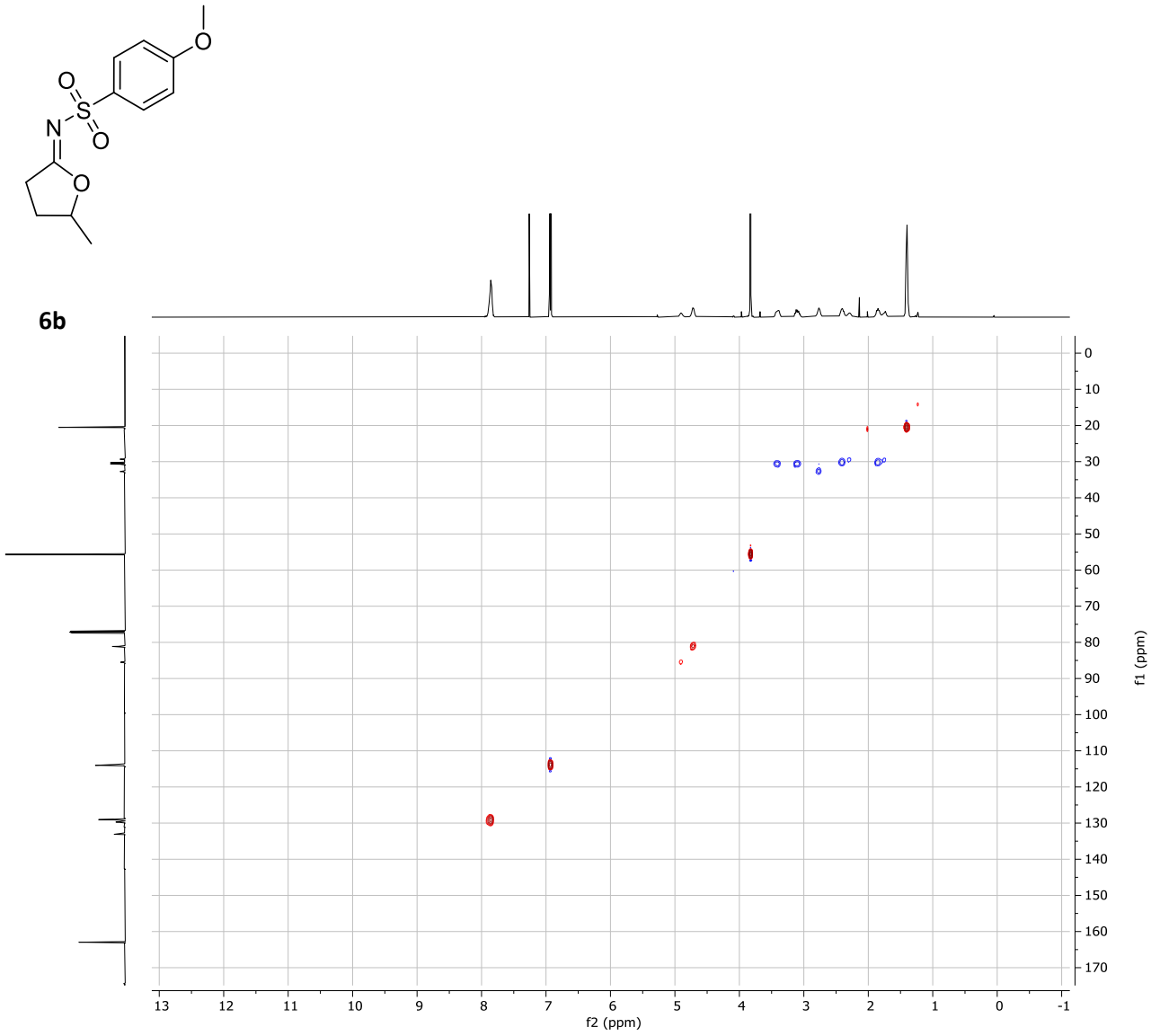
6b

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

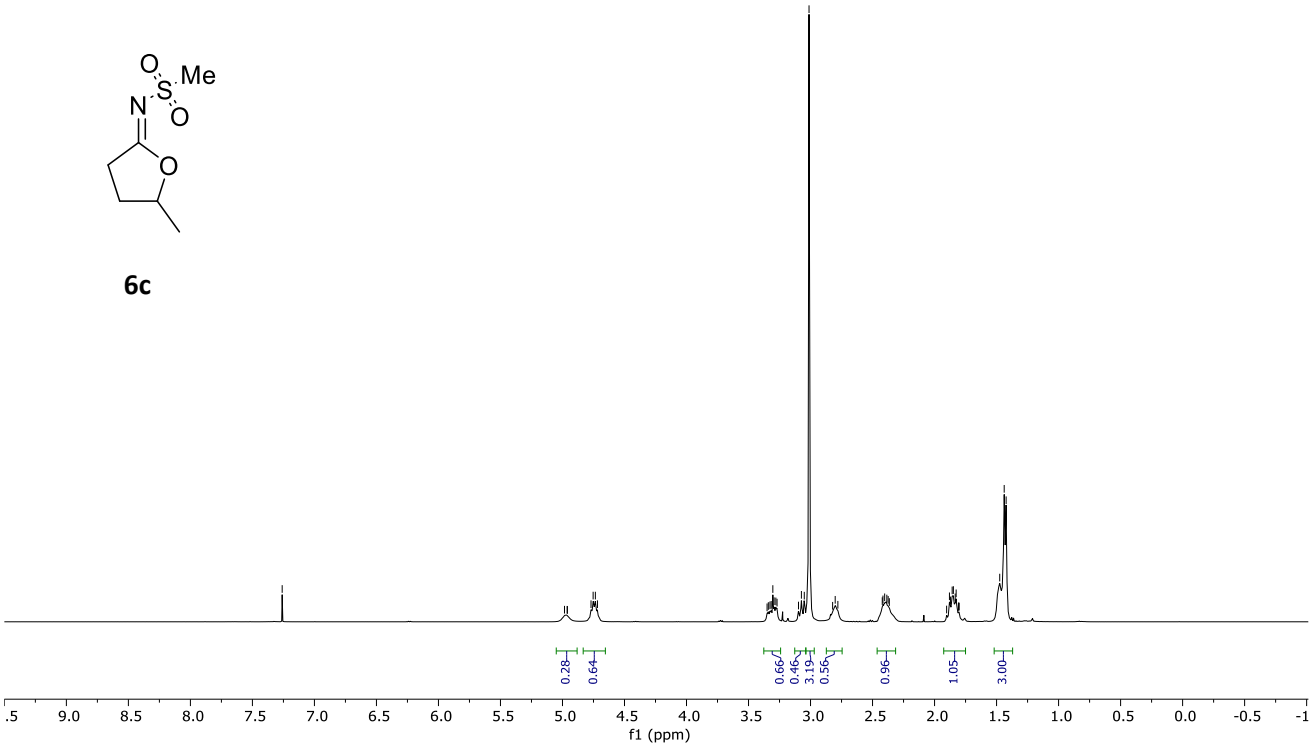


6b

^{1}H-^{13}C HSQC

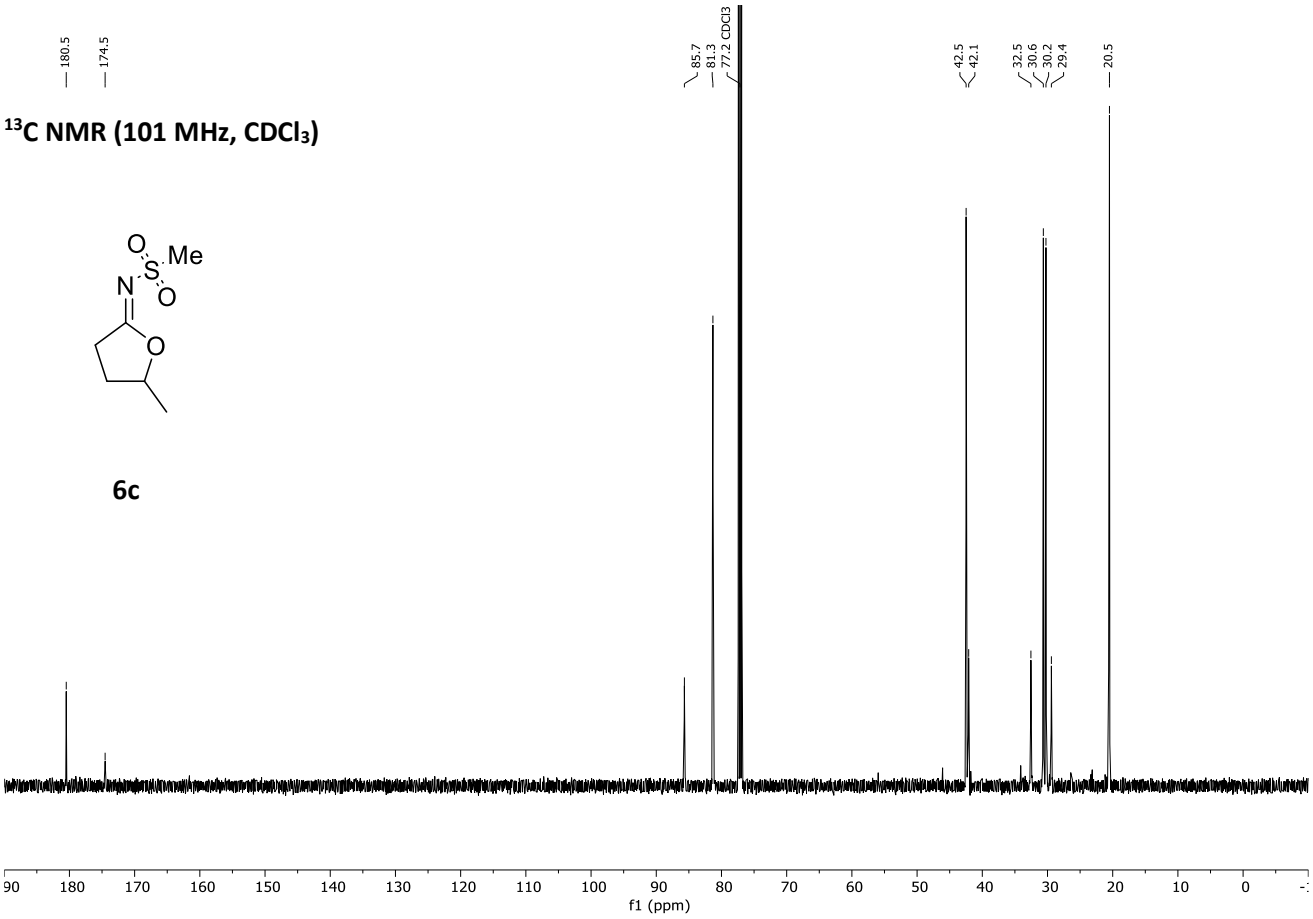


^{1}H NMR (400 MHz, $CDCl_3$)



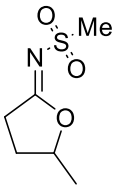
6c

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

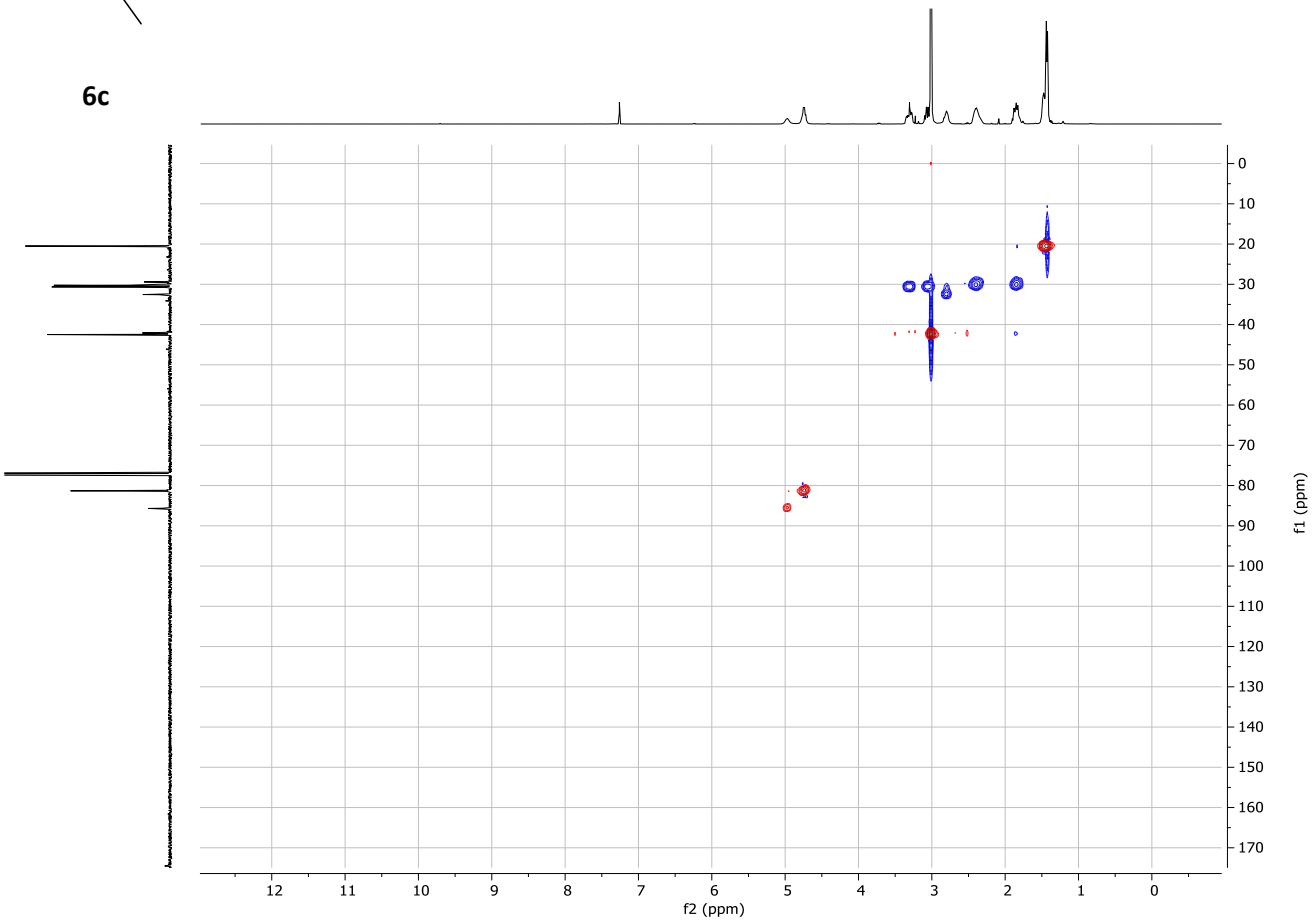


6c

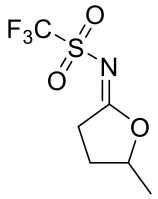
^{1}H-^{13}C HSQC



6c

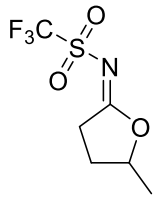


^{1}H NMR (400 MHz, $CDCl_3$)



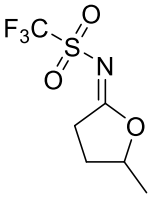
6d

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

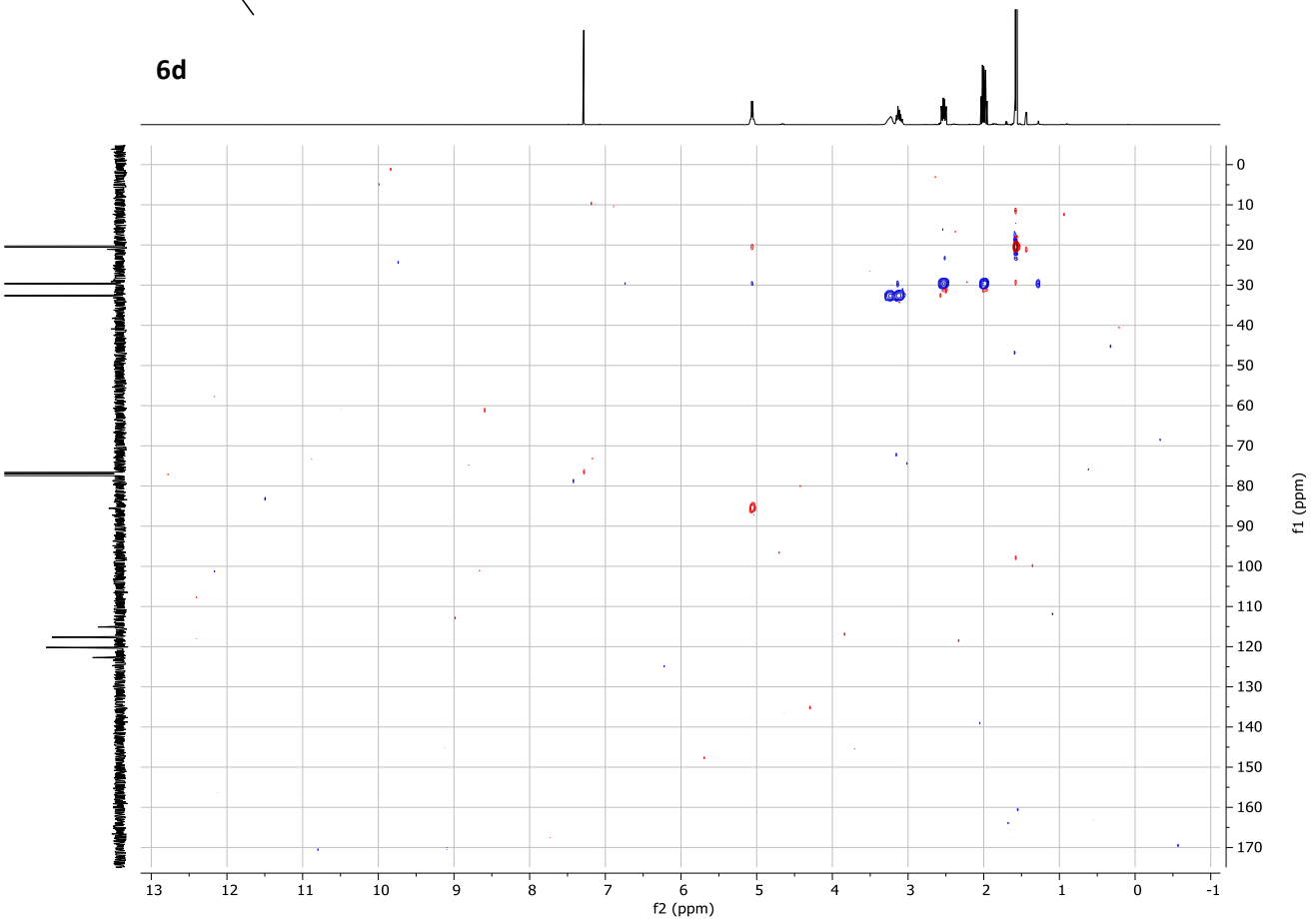


6d

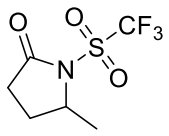
^{1}H-^{13}C HSQC



6d

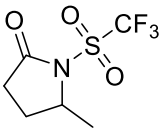


^{1}H NMR (500 MHz, $CDCl_3$)



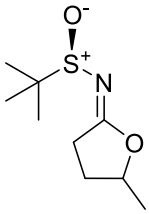
6e

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



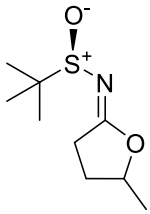
6e

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



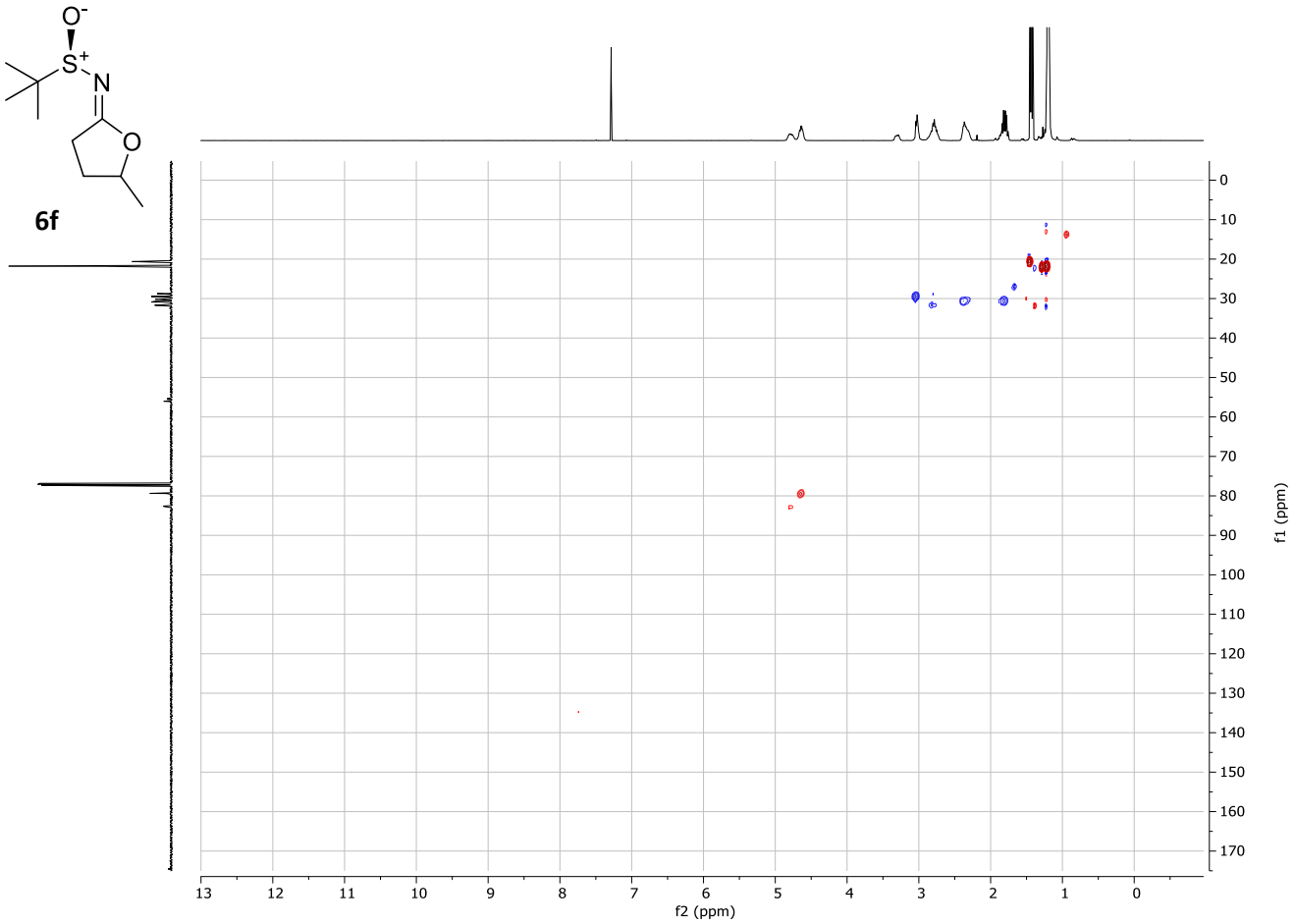
6f

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

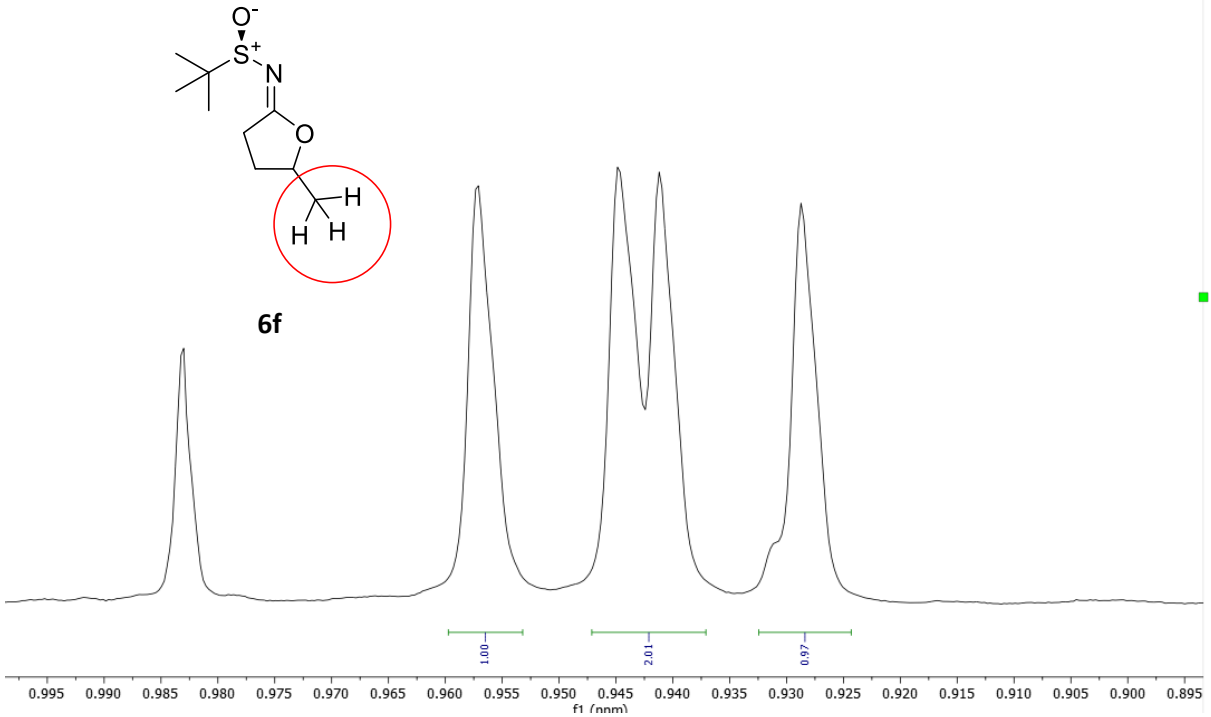


6f

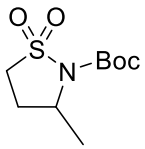
^{1}H-^{13}C HSQC



^{1}H NMR (500 MHz, $CDCl_3$, 100 °C)



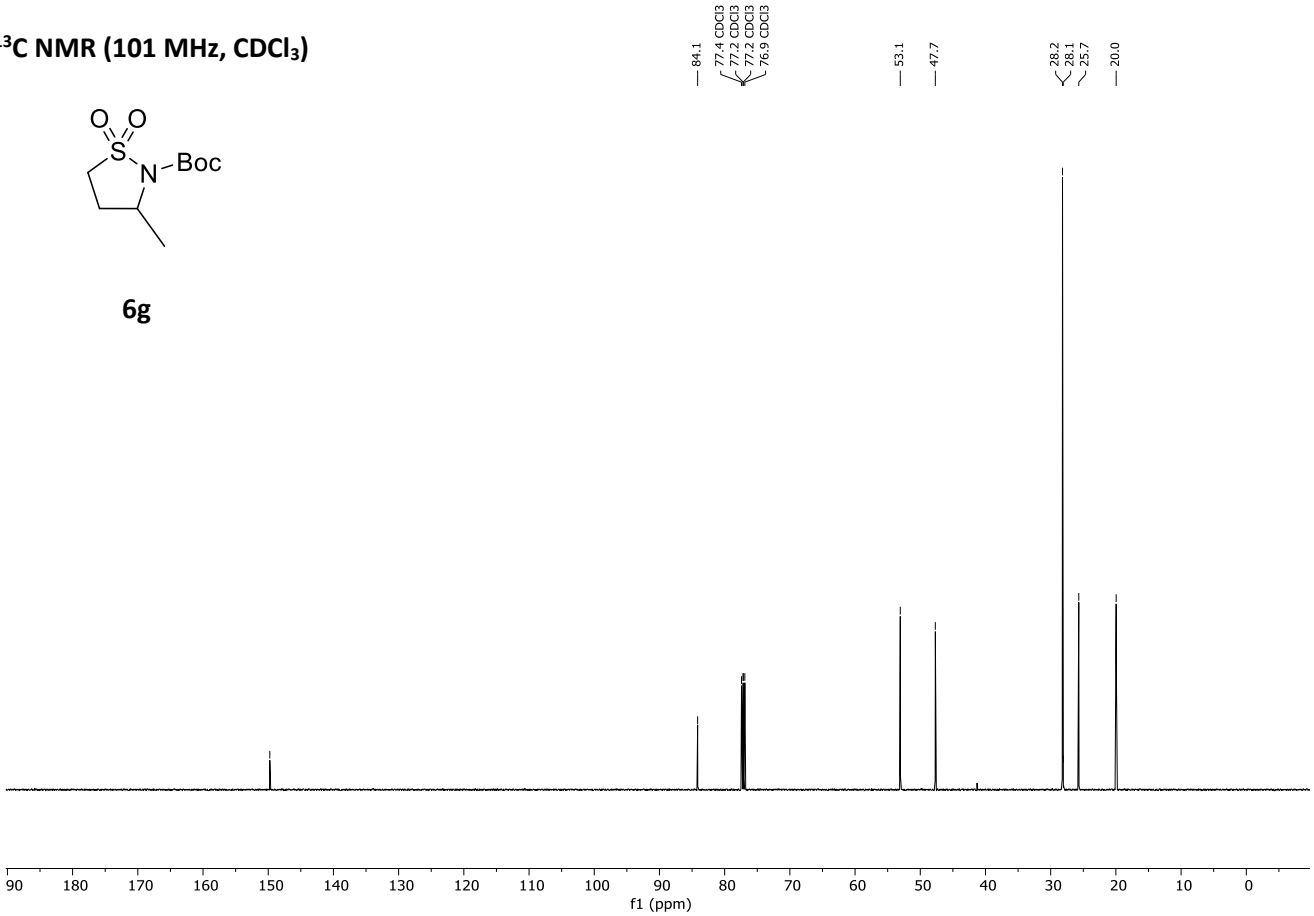
^{1}H NMR (400 MHz, $CDCl_3$)

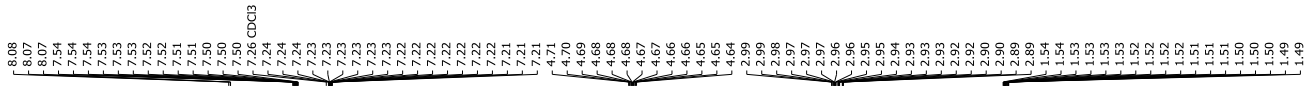


6g

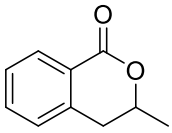
^{13}C NMR (101 MHz, $CDCl_3$)

6g

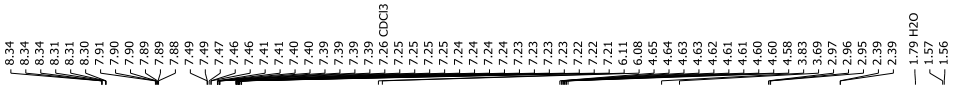




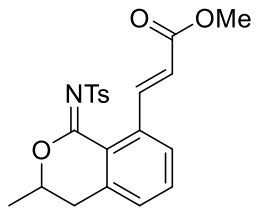
^{1}H NMR (400 MHz, $CDCl_3$)



7a



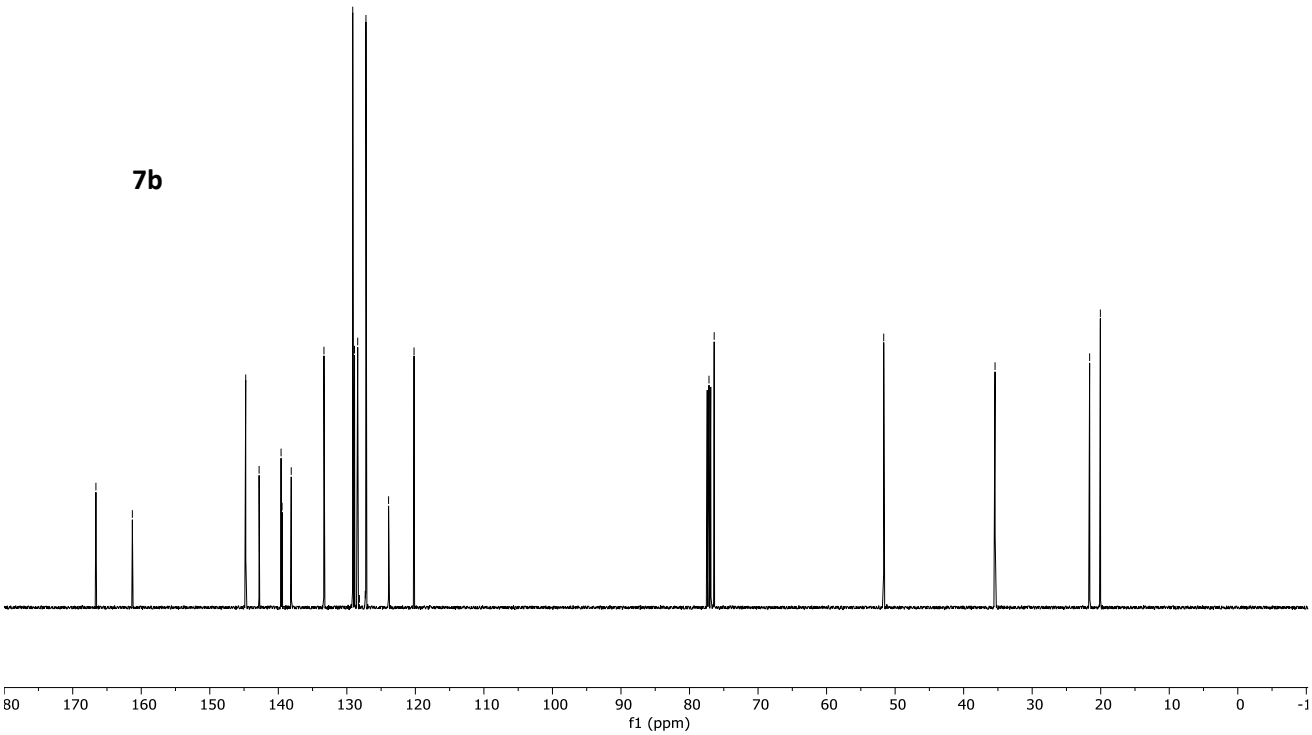
^{1}H NMR (400 MHz, $CDCl_3$)

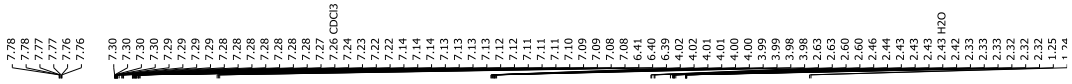


7b

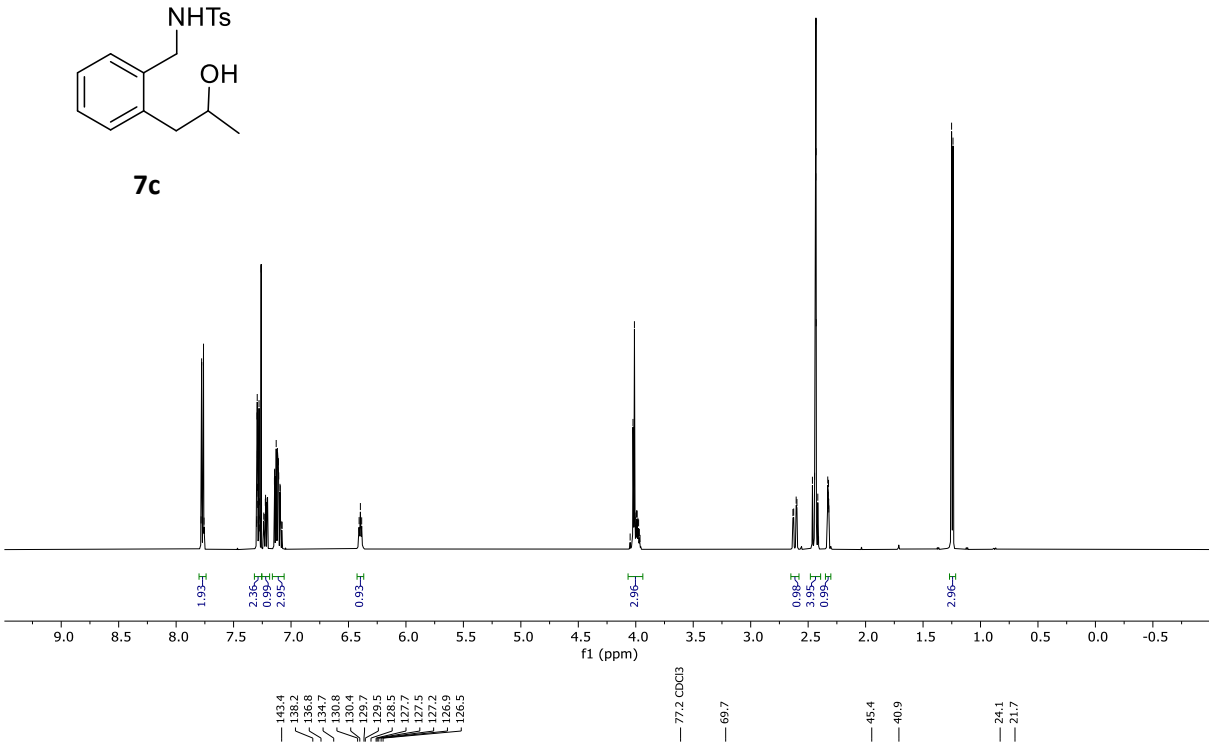
^{13}C NMR (101 MHz, $CDCl_3$)

7b

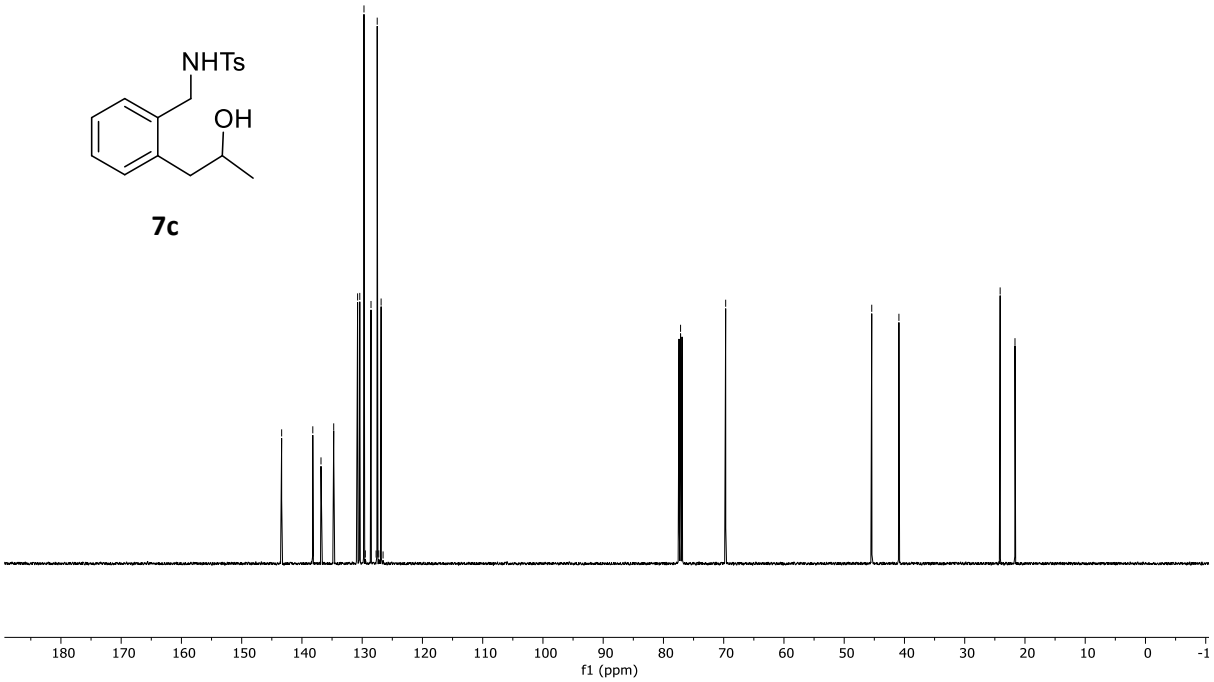




^{1}H NMR (500 MHz, $CDCl_3$)



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



Crystal Data for 4b

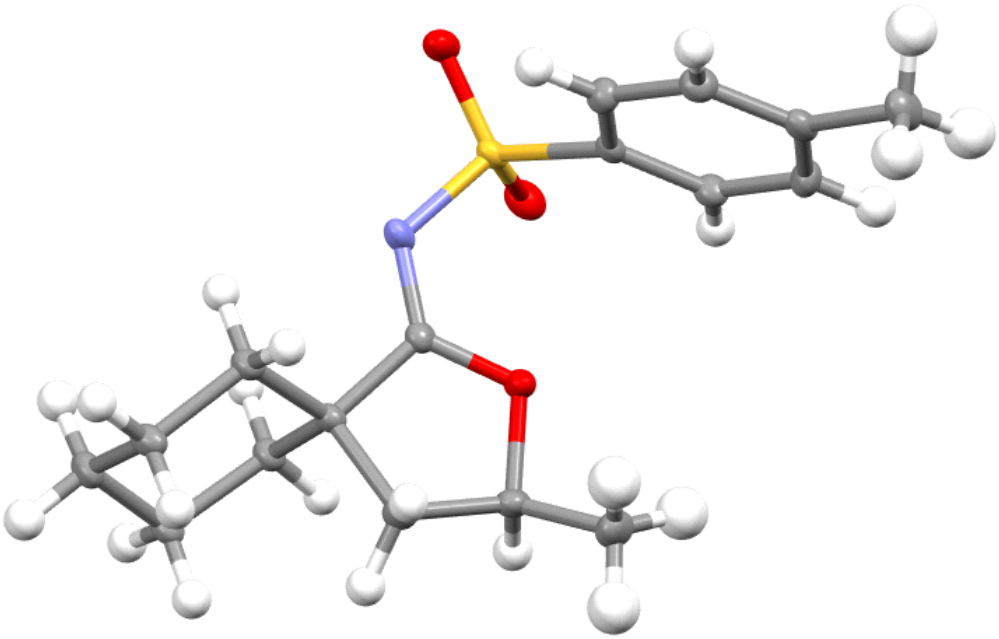


Figure S1. ORTEP diagram of **4b**. Atomic displacement parameters at 100 K are drawn at 50% probability level.

CCDC number: 2149820

Table S1 Crystal data and structure refinement for **4b.**

Identification code	ca030122_1_1
Empirical formula	$C_{17}H_{23}NO_3S$
Formula weight	321.42
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.07010(10)
b/Å	14.9683(2)
c/Å	11.03150(10)
α/°	90
β/°	95.9140(10)
γ/°	90

Volume/Å^3	1653.95(3)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	1.838
F(000)	688.0
Crystal size/mm^3	0.241 × 0.126 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.996 to 159.826
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -13 ≤ l ≤ 14
Reflections collected	21006
Independent reflections	3540 [R_{int} = 0.0388, R_{sigma} = 0.0233]
Data/restraints/parameters	3540/130/230
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0880
Final R indexes [all data]	R_1 = 0.0362, wR_2 = 0.0898
Largest diff. peak/hole / e Å^{-3}	0.29/-0.43

Crystal Data for 4h

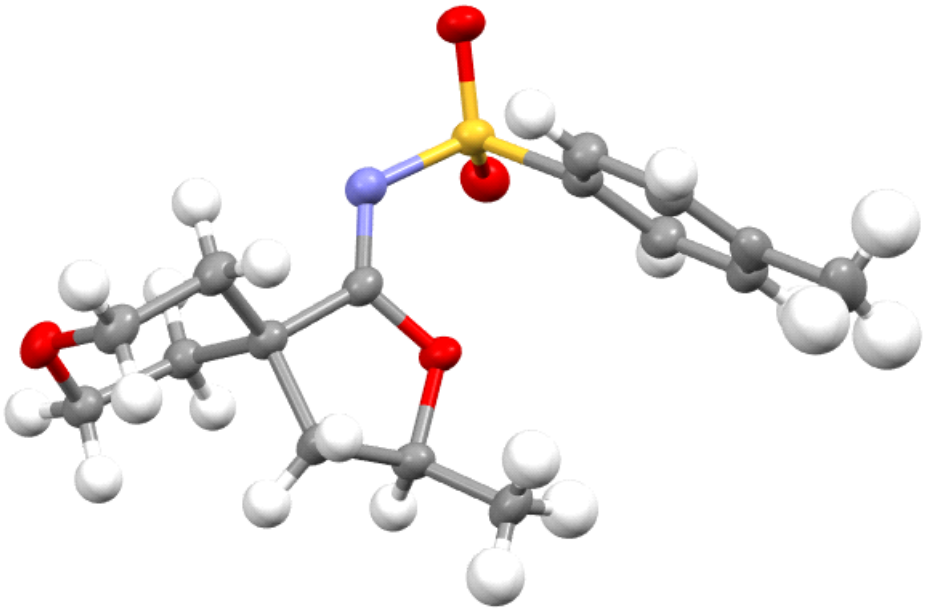


Figure S2. ORTEP diagram of **4b**. Atomic displacement parameters at 100 K are drawn at 50% probability level.

CCDC number: 2149821

Table S2 Crystal data and structure refinement for **4h.**

Identification code	ca010122_1_1
Empirical formula	$C_{16}H_{21}NO_4S$
Formula weight	323.40
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.8292(2)
b/Å	14.9090(2)

c/Å	12.9967(2)
α/°	90
β/°	109.811(2)
γ/°	90
Volume/Å^3	1609.56(5)
Z	4
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	1.941
F(000)	688.0
Crystal size/mm^3	0.236 × 0.139 × 0.055
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.354 to 159.86
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 19, -16 ≤ l ≤ 16
Reflections collected	31338
Independent reflections	3487 [R_{int} = 0.0787, R_{sigma} = 0.0317]
Data/restraints/parameters	3487/52/230
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.1195
Largest diff. peak/hole / e Å^{-3}	0.41/-0.48

Crystal Data for 4q

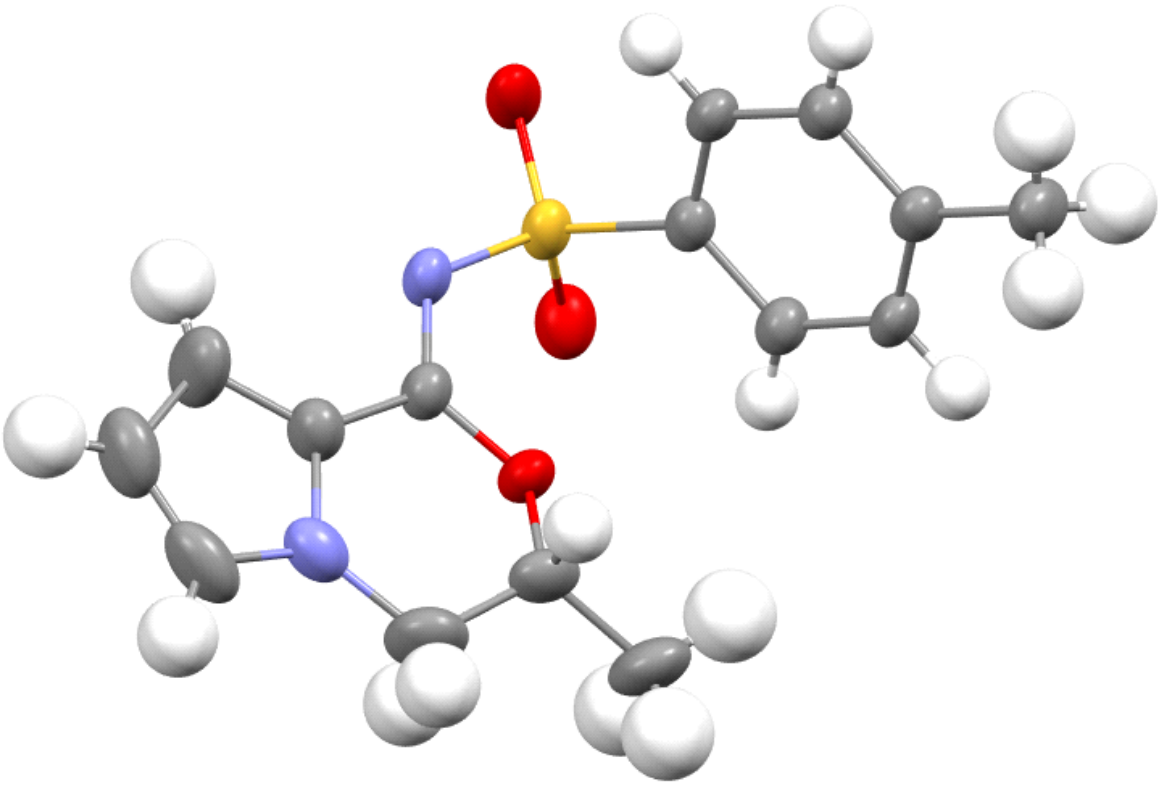


Figure S3. ORTEP diagram of **4q**. Atomic displacement parameters at 100 K are drawn at 50% probability level.

CCDC number: 2149822

Table S3 Crystal data and structure refinement for **4q.**

Identification code	ca020122_2_1
Empirical formula	$C_{15}H_{16}N_2O_3S$
Formula weight	304.36
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.0727(2)
b/Å	9.6509(2)
c/Å	9.8203(2)

α/°	90
β/°	104.349(2)
γ/°	90
Volume/Å^3	741.22(3)
Z	2
ρ_{calc}g/cm^3	1.364
μ/mm^{-1}	2.047
F(000)	320.0
Crystal size/mm^3	0.202 × 0.09 × 0.058
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.296 to 159.506
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12
Reflections collected	22389
Independent reflections	3150 [R_{int} = 0.0515, R_{sigma} = 0.0251]
Data/restraints/parameters	3150/70/212
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1057
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.1083
Largest diff. peak/hole / e Å^{-3}	0.16/-0.55
Flack parameter	0.044(13)

Crystal Data for 4s

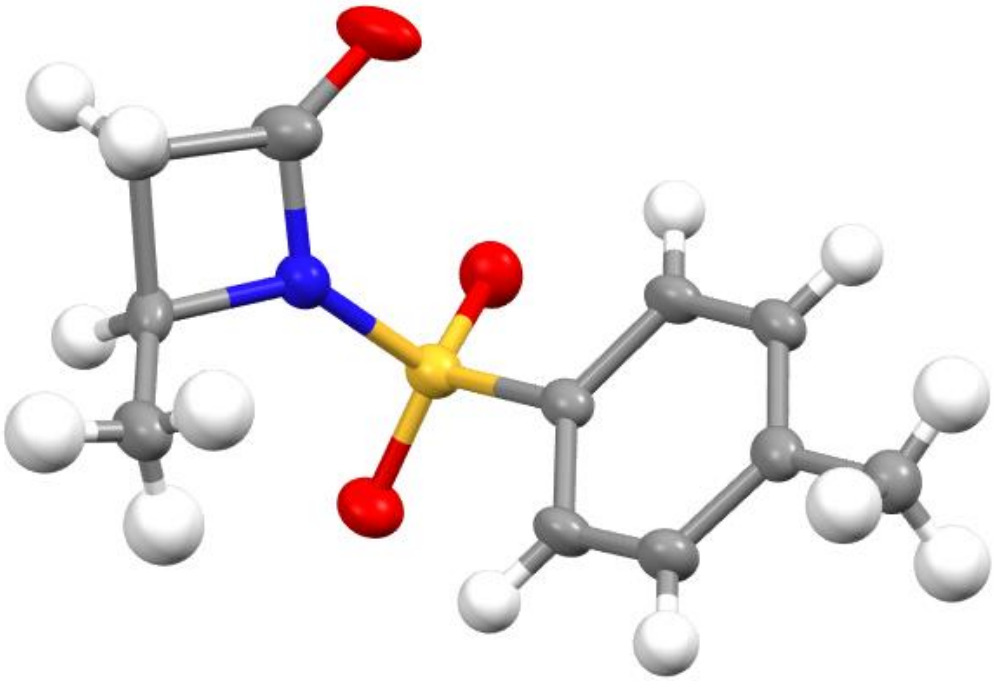


Figure S4. ORTEP diagram of **4s**. Atomic displacement parameters at 100 K are drawn at 50% probability level.

CCDC number: 2149823

Table S4 Crystal data and structure refinement for **4s.**

Identification code	ca121021_1_1
Empirical formula	$C_{11}H_{13}NO_3S$
Formula weight	239.28
Temperature/K	100.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	7.5584(2)

b/Å	11.0650(3)
c/Å	14.3491(4)
α/°	83.402(2)
β/°	81.007(2)
γ/°	75.074(2)
Volume/$Å^3$	1141.82(6)
Z	4
$\rho_{calc}g/cm^3$	1.392
μ/mm^{-1}	2.471
F(000)	504.0
Crystal size/mm^3	0.17 × 0.136 × 0.099
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.256 to 160.452
Index ranges	-8 ≤ h ≤ 9, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	24269
Independent reflections	4756 [R_{int} = 0.0394, R_{sigma} = 0.0272]
Data/restraints/parameters	4756/148/368
Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0590, wR_2 = 0.1346
Final R indexes [all data]	R_1 = 0.0636, wR_2 = 0.1368
Largest diff. peak/hole / e $Å^{-3}$	0.51/-0.66

Crystal Data for 4w

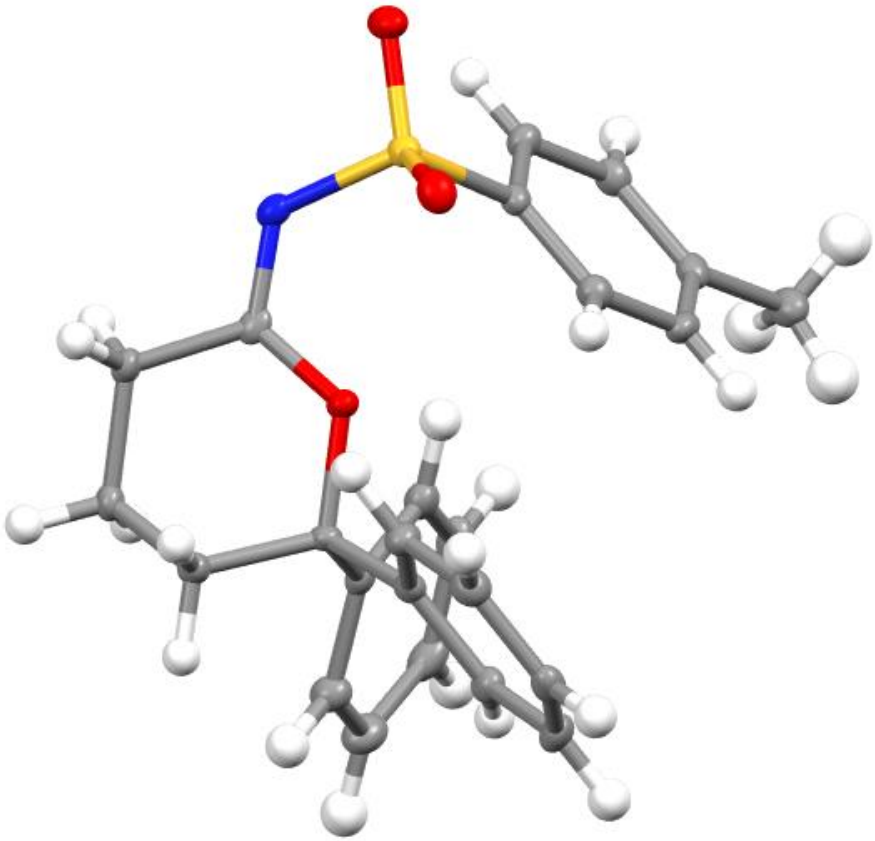


Figure S5. ORTEP diagram of **4w**. Atomic displacement parameters at 100 K are drawn at 50% probability level.

CCDC number: 2149819

Table S5 Crystal data and structure refinement for **4w.**

Identification code	ca270122_1_1
Empirical formula	$C_{24}H_{23}NO_3S$
Formula weight	405.49
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.35950(10)

b/Å	7.46330(10)
c/Å	11.66000(10)
α/°	90
β/°	97.8050(10)
γ/°	90
Volume/$Å^3$	979.369(18)
Z	2
$\rho_{calc}g/cm^3$	1.375
μ/mm^{-1}	1.680
F(000)	428.0
Crystal size/mm^3	0.277 × 0.155 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.652 to 159.556
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	20181
Independent reflections	4156 [R_{int} = 0.0473, R_{sigma} = 0.0332]
Data/restraints/parameters	4156/1/263
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0318, wR_2 = 0.0748
Final R indexes [all data]	R_1 = 0.0340, wR_2 = 0.0778
Largest diff. peak/hole / e $Å^{-3}$	0.29/-0.38
Flack parameter	-0.002(9)