Supporting Information

Photocatalytic S-alkylation of sulfinamides: access to sulfoximines

Ivan Sliusarevskyi[1], Haripriyo Mondal[2] and Rene M. Koenigs*[1,2]

[1]Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany.

[2]University of Bayreuth, Organic Chemistry II, Universitätsstraße 30, 95447 Bayreuth, Germany.

E-mail: rene.koenigs@uni-bayreuth.de

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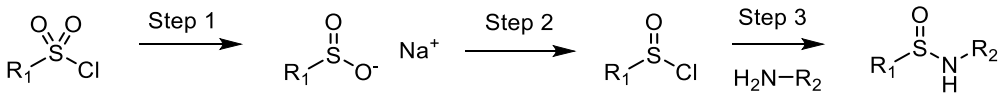
1. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem, BLD Pharm and Carl Roth. Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Varian AV600 in $CDCl_3$ and DMSO-d_6. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV. LEDs used in this manuscript were purchased from Kessil : KSPR160L PR160L Rating: 19VDC, 40W.

2. General Procedures

General procedure for the preparation of sulfinamides (GP-1) [1, 2]

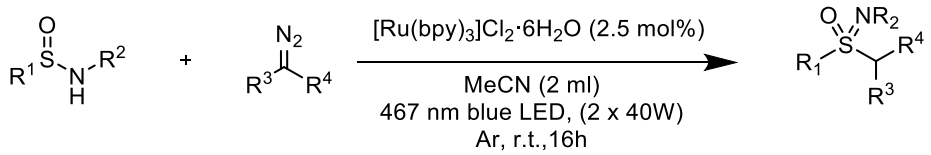


Step 1: To a solution of $NaHCO_3$ (2.0 mmol, 2.0 equiv.) and Na_2SO_3 (1.0 mmol, 2.0 equiv.) in distilled water (40 mL), the corresponding sulfonyl chloride (1.0 mmol, 1.0 equiv.) was added. The reaction mixture was heated to 90 °C and stirred for 5 h. After completion, the aqueous phase was azeotropically dried by co-evaporation with toluene under reduced pressure. The resulting residue was washed with hot methanol, and the solution was concentrated under high vacuum.

Step 2: The crude material was suspended in toluene (40 mL), cooled to 0 °C, and treated with oxalyl chloride (0.95 mmol, 0.95 equiv.). The mixture was then warmed to 20 °C and stirred for 1 h.

Step 3: The resulting solution was added dropwise to a mixture of the corresponding amine (1.05 mmol, 1.05 equiv.) and triethylamine (2.0 mmol, 2.0 equiv.) dissolved in toluene (20 mL) at 0 °C. After stirring for 2 h, the reaction mixture was transferred to a separating funnel, diluted with ethyl acetate (150 mL), and washed with brine (2 × 200 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel column chromatography afforded the desired product.

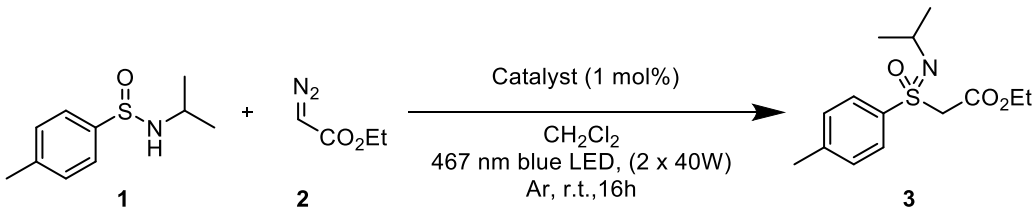
General procedure for the Photocatalytic S-Alkylation of Sulfinamides (GP-2)



To a reaction tube equipped with a magnetic stir bar, sulfinamide (0.2 mmol, 1.0 equiv.) and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (2.5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of diazo compound (1.2 mmol, 6.0 equiv.) dissolved in 2 mL anhydrous Acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate mixtures as eluent, affording the desired products.

3. Reaction Optimization

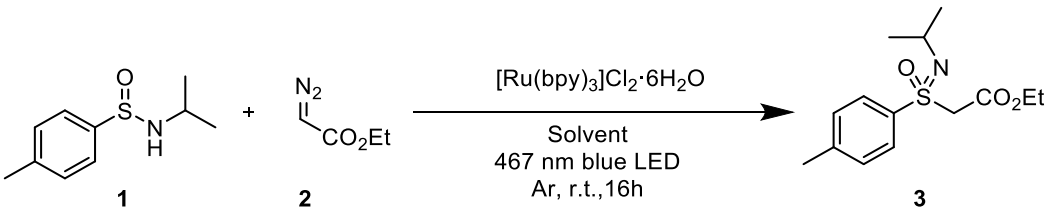
Table S1: Optimization of catalyst



Entry*	Catalyst	**3** (%)†
1	*4-CzIPN*	*trace*
2	Fluorescein	*trace*
3	Eosin Y	*trace*
4	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$	47
5	-	*trace*

*Reactions were carried out (**1**/**2** = 0.2/1.0 mmol) in 2.0 mL CH_2Cl_2 under blue light (2 x 40 W, 467 nm) with an external cooling fan. †Yields of **3** were determined by ^1H NMR spectroscopic analyses of the reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Table S2. Investigation of solvents, light intensity and catalyst loading.

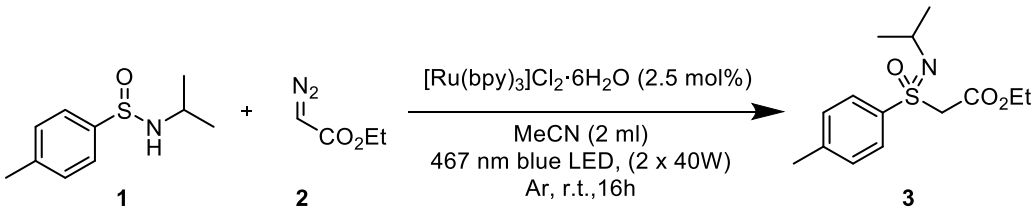


Entry*	Solvent	Light Intensity	Catalyst loading	**3** (%)†
1	$CHCl_3$	40W*2	1 mol%	36
2	DCE	40W*2	1 mol%	50
3	MeCN	40W*2	1 mol%	60
4	Toluen	40W*2	1 mol%	43
5	Acetone	40W*2	1 mol%	55
6	THF	40W*2	1 mol%	22
7	MeCN	20W*2	1 mol%	21
8	MeCN	30W*2	1 mol%	33
9	MeCN	40W*2	2.5 mol%	78
10	MeCN	40W*2	5 mol %	73

11	MeCN	40W*2	10 mol %	74

*Reactions were carried out (**1**/**2** = 0.2/1.0 mmol) in 2.0 mL solvent under blue light (467 nm) with an external cooling fan. †Yields of **3** were determined by ^{1}H NMR spectroscopic analyses of the reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Table S3. Investigation of equivalents and time

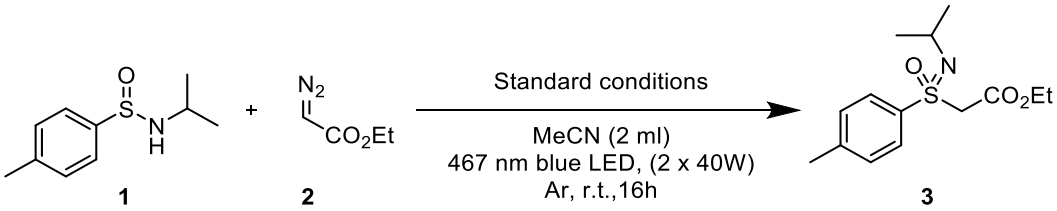


1 **2** **3**

Entry*	**1** : **2** (equiv.)	time	**3** (%)†
1	2:1	16 h	18
2	1:1	16 h	30
3	1:2	16 h	47
4	1:3	16 h	64
5	1:4	16 h	71
6	1:5	16 h	78
7	1:6	16 h	96
8	1:6	0.5 h	12
9	1:6	1 h	20
10	1:6	2 h	28
11	1:6	4 h	44

*Reactions were carried out in 2.0 mL MeCN solvent under blue light (2 x 40 W, 467 nm) with an external cooling fan. †Yields of **3** were determined by ^{1}H NMR spectroscopic analyses of the reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Table S4. Investigation of further changes.

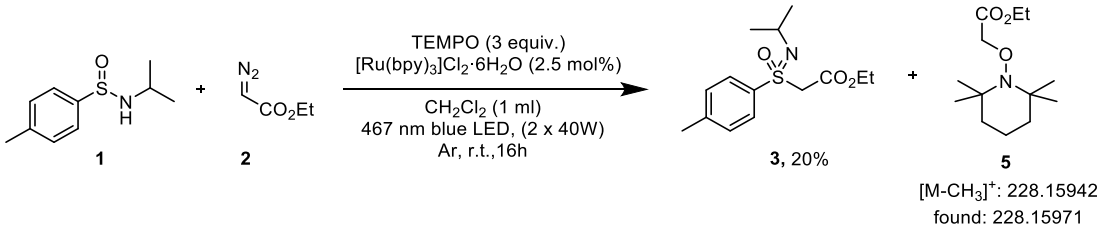


Entry*	changes	**3** (%)†
1	HFIP (1 equiv.)	61
2	NEt_3 (1 equiv.)	21
3	H_2O (2 equiv.)	27
4	under air	24
5	no Catalyst	trace
6	370 nm light	21
7	No light, 60°C	trace

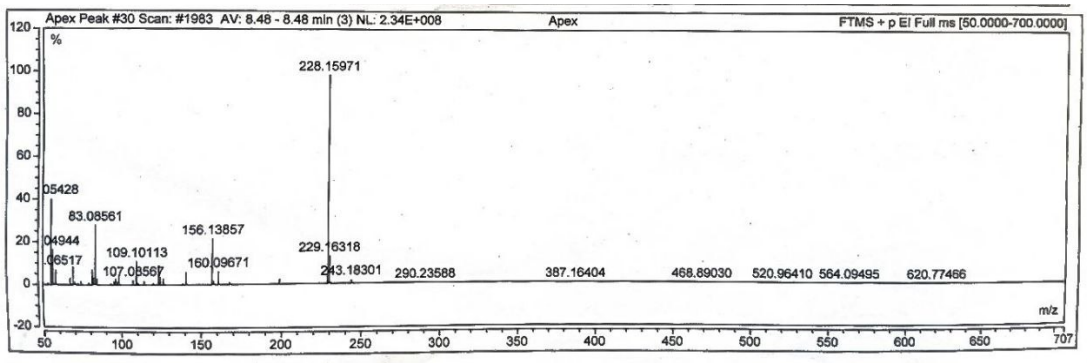
*Reactions were carried out (**1**/**2** = 0.2/1.2 mmol) in 2.0 mL MeCN under blue light (2 x 40 W, 467 nm) with an external cooling fan. †Yields of **3** were determined by ^{1}H NMR spectroscopic analyses of the reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

4. Control experiments

4a. Radical Trapping Experiment

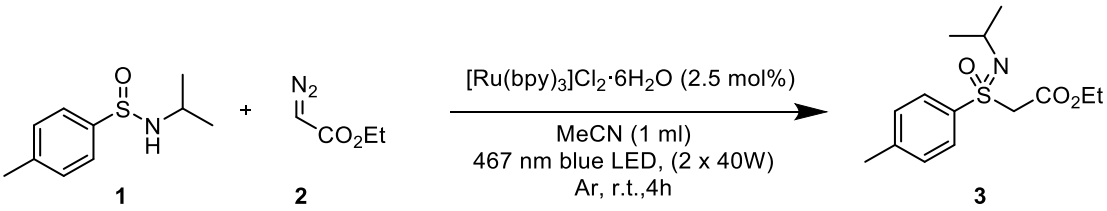


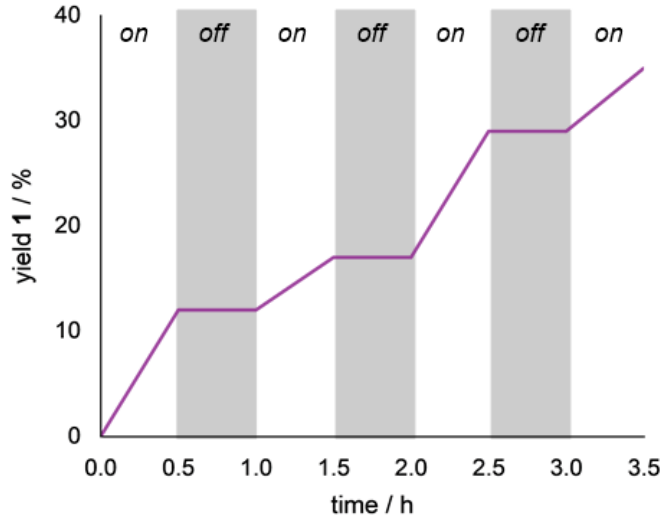
To a reaction tube equipped with a magnetic stir bar, sulfinamide (0.2 mmol, 1.0 equiv.), TEMPO (0.6 mmol, 3 equiv.) and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (2.5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of diazo compound (1.2 mmol, 6.0 equiv.) dissolved in 2 mL anhydrous Acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate mixtures as eluent, affording the desired products. The ^{1}H-NMR of the crude reaction mixture confirmed 20% of desired product **3** formation. In addition, the TEMPO adduct **5** was detected in HRMS. **HRMS** (ESI): *m/z*: $[M–CH_3]^+$ Calcd. for $C_{12}H_{22}NO_3^+$: 228.15942; Found: 228.15971.



4b. On-off Experiments

Several model reactions according to General Procedure GP2 were set up in parallel and irradiated with 2 x 40 W (467 nm) purple LEDs at a distance of ~1.5 cm (with cooling by the fan) and/or in the absence of light. Every 30 minutes, one reaction was analyzed by ^{1}H NMR to determine the yield of the corresponding product using 1,3,5-trimethoxybenzene as an internal standard.





4c. Fluoroscence quenching experiment

Fluorescence quenching experiments were performed on a Simazu RF-6000 Spectro Fluorophotometer. $Ru(bpy)_3Cl_2.6H_2O$ (0.01 mM) solutions were excited at 451 nm and emission intensity at 614 nm were collected. All the measurements were carried out mixing a solution of 0.01 mM solution of photocatalyst in dry degassed acetonitrile and appropriate amount of quencher dissolved in 0.01 mM solution of photocatalyst in a screw top 1.0 cm quartz cuvette. Samples were degassed and the emission spectra of the samples were collected. I_0 is the intensity without quencher, and I is the intensity with quencher. Plots were drawn according to the Stern-Volmer equation and K_q were calculated. Stern-Volmer equation: $I_0/I = 1+K_q[Q]$

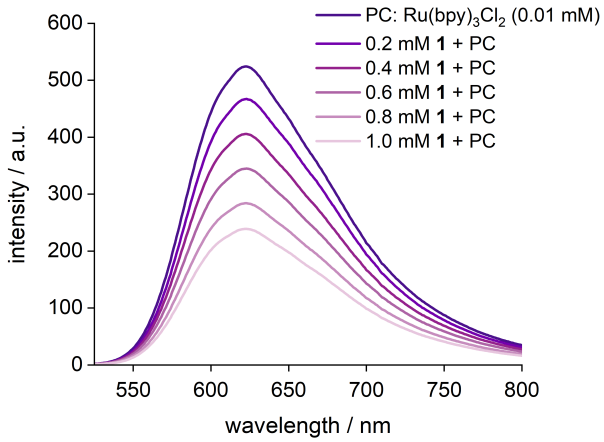


Figure S1. The luminescence spectra of $Ru(bpy)_3Cl_2.6H_2O$ with different concentration of **1** excited at 451 nm.

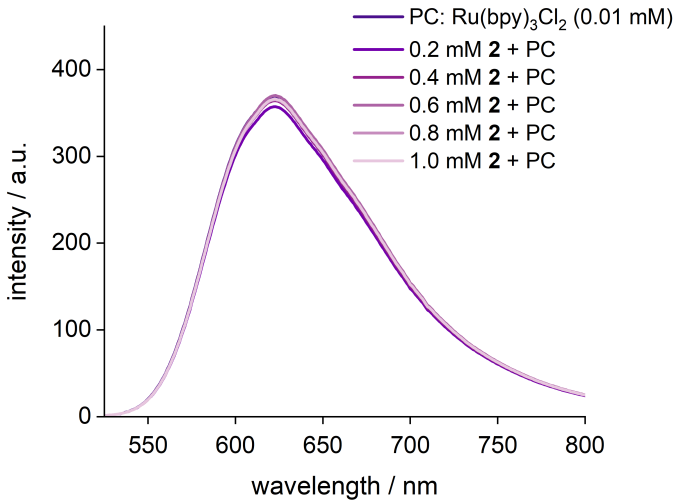


Figure S2. The luminescence spectra of $Ru(bpy)_3Cl_2.6H_2O$ with different concentration of **2** excited at 451 nm.

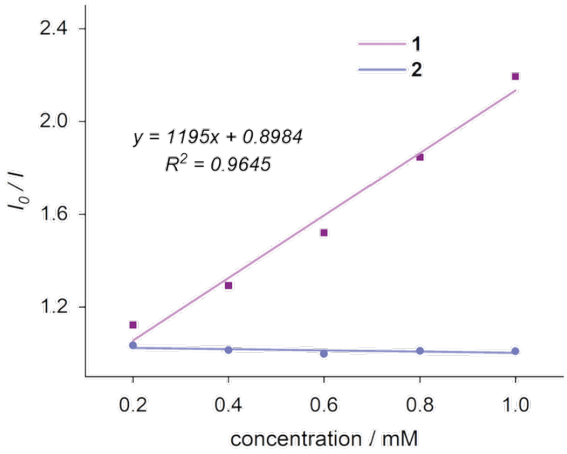
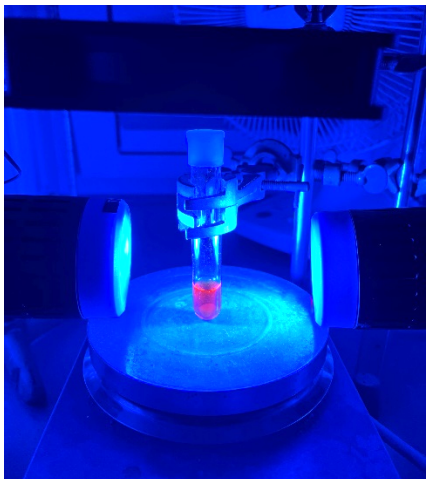


Figure S3. Stern-Volmer plot of $Ru(bpy)_3Cl_2.6H_2O$ at different quenchers

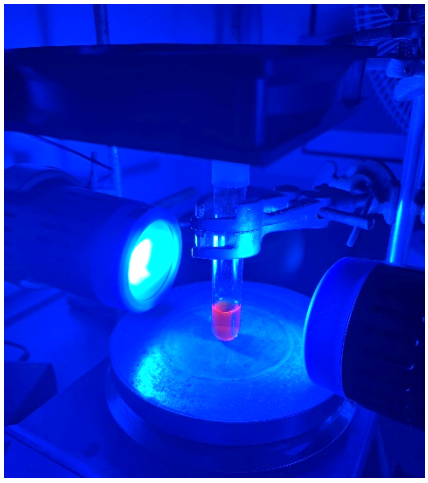
The reported excited-state lifetime for $Ru(bpy)_3Cl_2.6H_2O$ (1100 ns) was used for *Kq* calculations.[3] Calculated value of K_q for **1** was 1.09 x 10^9 $M^{-1}s^{-1}$.

4d. Image of photoinduced reaction set-up

Front view:



Side view:



4e. UV-Vis spectra

UV-Vis absorption spectra were recorded on a Shimadzu UV-1900i UV-Vis Spectrophotometer at room temperature using quartz cuvettes (1.0 cm path length). All samples were prepared in acetonitrile (CH_3CN) at a concentration of 10^{-2} M. The absorption spectra of **1**, **2**, and $Ru(bpy)_3Cl_2.6H_2O$ were measured independently under identical conditions. $Ru(bpy)_3Cl_2.6H_2O$ exhibited a maximum absorbance (λ_{max}) at 451 nm.

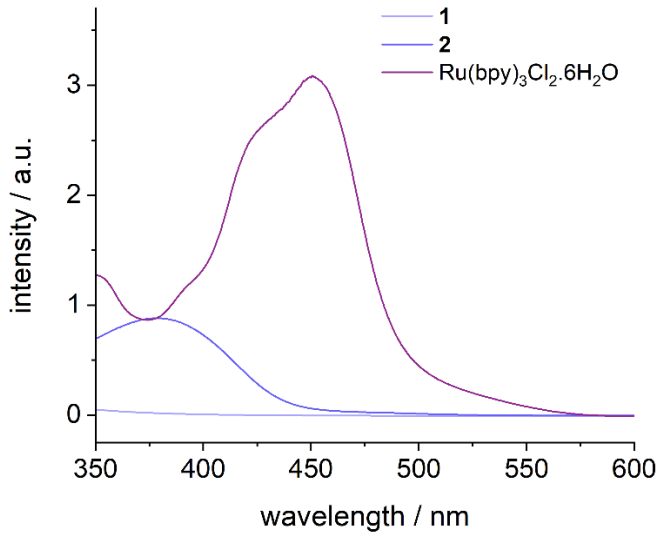


Figure S4. UV-Vis absorption spectra of **1**, **2**, and $Ru(bpy)_3Cl_2.6H_2O$ recorded in CH_3CN (10^{-2} M) at room temperature.

5. Incompatible substrates

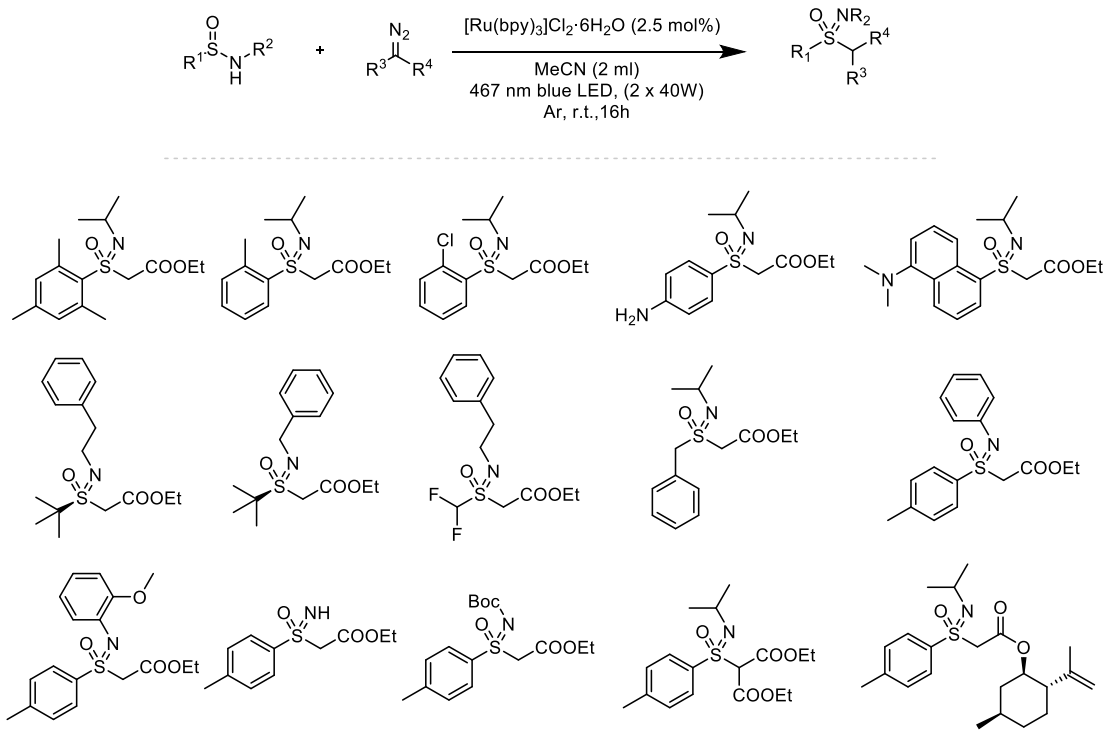
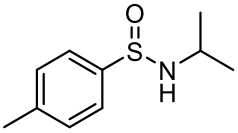


Figure S5: Incompatible substrates

To a reaction tube equipped with a magnetic stir bar, sulfinamide (0.2 mmol, 1.0 equiv.) and $[Ru(bpy)_3]Cl_2·6H_2O$ (2.5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of diazo compound (1.2 mmol, 6.0 equiv.) dissolved in 2 mL anhydrous Acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was analyzed by ^1H spectroscopy.

6. Physical Data

_N_-isopropyl-4-methylbenzenesulfinamide (1)



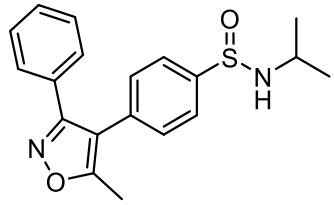
The title compound **1** was obtained either according to general procedure **GP-1** or via the hydrolysis protocol. **Hydrolysis protocol:** a stirred solution of ethyl 2-(N-isopropyl-4-methylphenylsulfonimidoyl)acetate (57 mg, 0.20 mmol, 1.0 equiv) and 4-acetamidobenzenesulfonyl azide (58 mg, 0.24 mmol, 1.2 equiv) in acetonitrile (2 mL) was cooled to 0 °C. Cesium carbonate (72 mg, 0.22 mmol, 1.1 equiv) was then added, and the reaction mixture was stirred for 16 h. Upon completion, the mixture was diluted with ethyl acetate (10 mL), and washed with brine (2 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel column chromatography (n-hexane:ethyl acetate, 1:2) afforded the desired product (GP-1: 159 mg, 81%; Hydrolysis procedure: 31 mg, 79%).

^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 7.58 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 3.82 (d, *J* = 6.4 Hz, 1H), 3.63 – 3.55 (m, *J* = 6.4 Hz, 1H), 2.40 (s, 3H), 1.28 (d, *J* = 6.4 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 142.2, 141.1, 129.4, 125.7, 46.0, 24.8, 24.4, 21.3 ppm.

HRMS (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_{16}NOS^+$: 198.09471; Found: 198.09481.

_N_-isopropyl-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfinamide (1m)



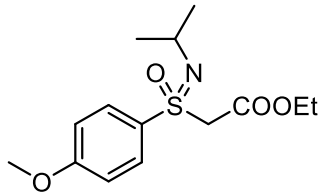
The title compound **1m** was synthesized according to the general procedure **(GP-1)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 1:2) as a yellow solid (65%, 44 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.34 – 7.28 (m, 4H), 3.89 (d, *J* = 6.3 Hz, 1H), 3.65 (h, *J* = 6.4 Hz, 1H), 2.48 (s, 3H), 1.31 (d, *J* = 6.4 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 167.0, 161.1, 144.7, 133.2, 130.0, 129.5, 128.7, 128.5, 128.4, 126.2, 114.8, 46.3, 24.8, 24.4, 11.7 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{20}N_2O_2SNa^+$: 363.11377; Found: 363.11277.

ethyl 2-(*N*-isopropyl-4-methoxyphenylsulfonimidoyl)acetate (3a)



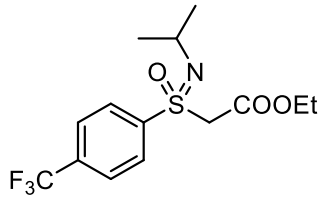
The title compound **3a** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 1:1) as a yellow oil (85%, 51 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.84 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 4.11 (s, 2H), 4.12 – 4.05 (m, 2H), 3.86 (s, 3H), 3.50 (h, *J* = 6.3 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.19 – 1.14 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.4, 163.2, 131.4, 130.0, 114.1, 61.8, 60.8, 55.6, 46.6, 26.7, 26.5, 13.9 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{21}NO_4SNa^+$: 322.10835; Found: 322.10804.

ethyl 2-(*N*-isopropyl-4-(trifluoromethyl)phenylsulfonimidoyl)acetate (3b)



The title compound **3b** was synthesized according to the general procedure **(GP-3)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 2:1) as a yellow oil (58%, 39 mg).

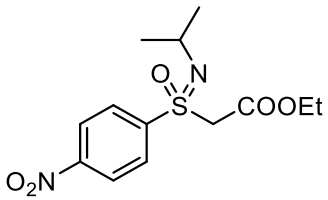
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.09 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 4.17 (s, 2H), 4.14 – 4.06 (m, 2H), 3.55 – 3.48 (m, 1H), 1.23 (d, *J* = 6.2 Hz, 3H), 1.20 – 1.15 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.7, 142.8, 134.8 (q, *J* = 32.9 Hz), 129.9, 126.0 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 273.4 Hz), 62.1, 60.6, 46.9, 26.6, 26.4, 13.8 ppm.

^{19}F NMR (564 MHz, Chloroform-*d*): δ = -63.11 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{18}NO_3F_3SNa^+$: 360.08517; Found: 360.08484.

ethyl 2-(*N*-isopropyl-4-nitrophenylsulfonimidoyl)acetate (3c)



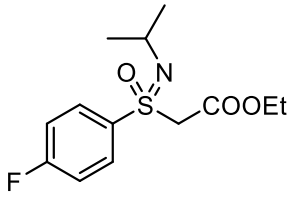
The title compound **3c** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 1:1) as a yellow oil (16%, 10 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.38 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 4.19 (s, 2H), 4.16 – 4.09 (m, 2H), 3.57 – 3.49 (m, 1H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.22 – 1.17 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.5, 150.5, 145.1, 130.7, 124.0, 62.2, 60.6, 47.0, 26.5, 26.3, 13.9 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{18}N_2O_5SNa^+$: 337.08286; Found: 337.08329.

ethyl 2-(4-fluoro-*N*-isopropylphenylsulfonimidoyl)acetate (3d)



The title compound **3d** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 2:1) as a yellow oil (92%, 53 mg).

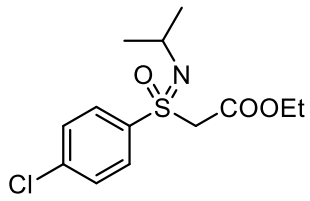
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.97 – 7.92 (m, 2H), 7.24 – 7.17 (m, 2H), 4.13 (s, 2H), 4.13 – 4.06 (m, 2H), 3.56 – 3.47 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.20 – 1.15 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 165.6 (d, *J* = 255.0 Hz), 162.9, 134.7, 132.1 (d, *J* = 9.6 Hz), 116.1 (d, *J* = 22.5 Hz), 62.0, 60.6, 46.7, 26.6, 26.4, 13.8 ppm.

^{19}F NMR (564 MHz, Chloroform-*d*): δ = -105.04 (ddd, *J* = 13.4, 8.5, 5.1 Hz) ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{18}NO_3FSNa^+$: 310.08836; Found: 310.08804.

ethyl 2-(4-chloro-N-isopropylphenylsulfonimidoyl)acetate (3e)



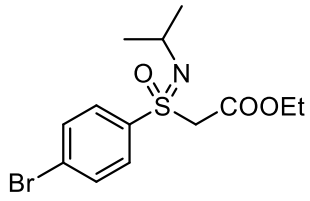
The title compound **3e** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column (*n*-hexane : ethyl acetate 2:1) as a yellow oil (74%, 45 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.87 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 4.13 (s, 2H), 4.13 – 4.06 (m, 2H), 3.55 – 3.45 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.19 – 1.16 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.8, 139.8, 137.4, 130.8, 129.2, 62.0, 60.7, 46.7, 26.6, 26.4, 13.8 ppm.

HRMS (ESI): *m/z*: $[M–CH_3]^+$ Calcd. for $C_{12}H_{15}NO_3ClS^+$: 288.04612; Found: 288.04577.

ethyl 2-(4-bromo-*N*-isopropylphenylsulfonimidoyl)acetate (3f)



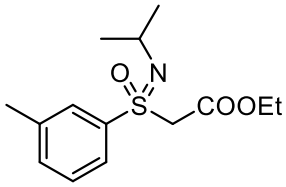
The title compound **3f** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 2:1) as a yellow oil (89%, 62 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.82 – 7.78 (m, 2H), 7.69 – 7.65 (m, 2H), 4.13 (s, 2H), 4.12 – 4.08 (m, 2H), 3.54 – 3.45 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.20 – 1.16 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.8, 138.0, 132.2, 130.9, 128.4, 62.0, 60.6, 46.8, 26.6, 26.4, 13.9 ppm.

HRMS (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{19}NO_3BrS^+$: 348.02635; Found: 348.02515.

ethyl 2-(*N*-isopropyl-3-methylphenylsulfonimidoyl)acetate (3g)



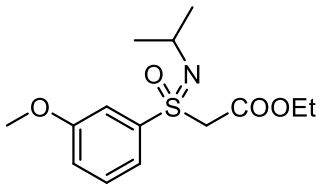
The title compound **3g** was synthesized according to the general procedure **(GP-3)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 2:1) as a yellow oil (51%, 29 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.76 – 7.71 (m, 2H), 7.43 – 7.39 (m, 2H), 4.13 (s, 2H), 4.12 – 4.05 (m, 2H), 3.57 – 3.49 (m, 1H), 2.43 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.0, 139.1, 138.7, 133.9, 129.5, 128.8, 126.3, 61.8, 60.6, 46.7, 26.6, 26.5, 21.3, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{21}NO_3SNa^+$: 306.11344; Found: 306.11244.

ethyl 2-(*N*-isopropyl-3-methoxyphenylsulfonimidoyl)acetate (3h)



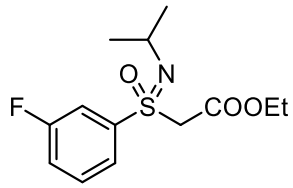
The title compound **3h** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 1:1) as a yellow oil (83%, 50 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.52 – 7.50 (m, 1H), 7.46 – 7.41 (m, 2H), 7.14 – 7.12 (m, 1H), 4.13 (s, 2H), 4.13 – 4.04 (m, 2H), 3.86 (s, 3H), 3.56 – 3.46 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.20 – 1.15 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.9, 159.9, 140.2, 129.9, 121.3, 119.5, 113.8, 61.9, 60.8, 55.6, 46.7, 26.7, 26.4, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{21}NO_4SNa^+$: 322.10835; Found: 322.10701.

ethyl 2-(3-fluoro-N-isopropylphenylsulfonimidoyl)acetate (3i)



The title compound **3i** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 2:1) as a yellow oil (38%, 22 mg).

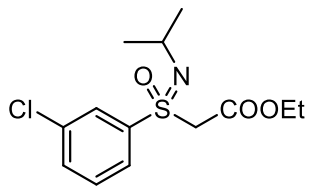
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.75 – 7.73 (m, 1H), 7.67 – 7.65 (m, 1H), 7.51 – 7.55 (m, 1H), 7.33 – 7.31 (m, 1H), 4.15 (s, 2H), 4.14 – 4.07 (m, 2H), 3.56 – 3.48 (m, 1H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.20 – 1.16 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.7, 162.4 (d, *J* = 251.3 Hz), 141.3 (d, *J* = 6.4 Hz), 130.6 (d, *J* = 7.6 Hz), 124.9 (d, *J* = 3.4 Hz), 120.3 (d, *J* = 21.3 Hz), 116.7 (d, *J* = 24.2 Hz), 62.0, 60.7, 46.8, 26.6, 26.4, 13.8 ppm.

^{19}F NMR (564 MHz, Chloroform-*d*): δ = -109.95 (td, *J* = 8.2, 5.3 Hz) ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{18}NO_3SFNa^+$: 310.08836; Found: 310.08752.

ethyl 2-(3-chloro-*N*-isopropylphenylsulfonimidoyl)acetate (3j)



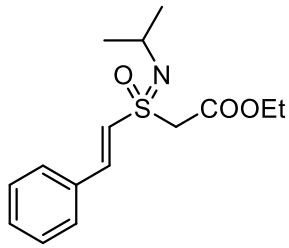
The title compound **3j** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 2:1) as a yellow oil (69%, 41 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.94 (t, *J* = 1.9 Hz, 1H), 7.83 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.59 – 7.58 (m, 1H), 7.50 – 7.47 (m, 1H), 4.14 (s, 2H), 4.14 – 4.06 (m, 2H), 3.56 – 3.48 (m, 1H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.21 – 1.15 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.7, 140.8, 135.2, 133.2, 130.1, 129.4, 127.3, 62.1, 60.7, 46.8, 26.6, 26.4, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{19}NO_3ClS^+$: 304.07687; Found: 304.07623.

ethyl (*E*)-2-(*N*-isopropyl-2-phenylvinylsulfonimidoyl)acetate (3k)



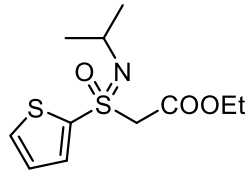
The title compound **3k** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 2:1) as a yellow oil. (47%, 28 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.56 (d, *J* = 15.5 Hz, 1H), 7.53 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.01 (d, *J* = 15.4 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.18 – 4.07 (m, 2H), 3.68 – 3.60 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 6.0 Hz, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.5, 159.0, 144.4, 132.6, 130.9, 129.0, 128.5, 125.6, 62.0, 59.5, 46.5, 41.9, 26.7, 26.5, 22.3, 14.0 ppm.

HRMS (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{22}NO_3S^+$: 296.13149; Found: 296.13078.

ethyl 2-(*N*-isopropylthiophene-2-sulfonimidoyl)acetate (3l)



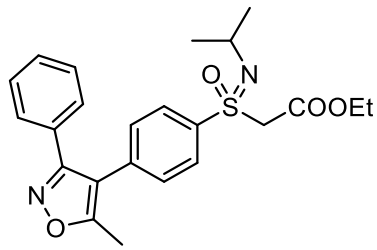
The title compound **3l** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 2:1) as a yellow oil (43%, 24 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.70 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.61 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.17 – 7.12 (m, 1H), 4.26 – 4.19 (m, 2H), 4.19 – 4.10 (m, 2H), 3.60 – 3.51 (m, 1H), 1.25 – 1.20 (m, 6H), 1.17 (d, *J* = 6.3 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.7, 140.4, 134.7, 134.3, 127.8, 62.6, 62.1, 47.0, 26.7, 26.2, 13.9 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{11}H_{17}NO_3S_2Na^+$: 398.05421; Found: 298.05351.

ethyl 2-(*N*-isopropyl-4-(5-methyl-3-phenylisoxazol-4-yl)phenylsulfonimidoyl) acetate (3m)



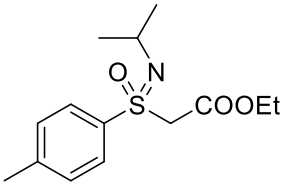
The title compound **3m** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 1:1) as a yellow oil (42%, 36 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.35 – 7.31 (m, 4H), 4.18 (s, 2H), 4.12 – 4.08 (m, 2H), 3.64 – 3.57 (m, 1H), 2.49 (s, 3H), 1.25 (d, *J* = 6.3 Hz, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.0, 161.1, 138.1, 135.7, 130.1, 129.6, 129.6, 128.6, 128.4, 114.5, 61.9, 60.3, 46.8, 26.6, 26.5, 13.9, 11.7 ppm.

HRMS (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{23}H_{27}N_2O_4S^+$: 427.16860; Found: 427.16816.

ethyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)acetate (3n)



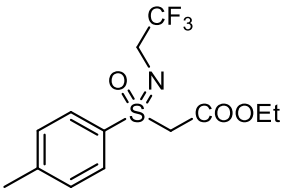
The title compound **3n** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow oil (92%, 52 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.13 (s, 2H), 4.12 – 4.05 (m, 2H), 3.55 – 3.45 (m, 1H), 2.43 (s, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.19 – 1.15 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.1, 144.0, 135.7, 129.6, 129.3, 61.9, 60.7, 46.6, 26.7, 26.4, 21.5, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{21}NO_3SNa^+$: 306.11344; Found: 306.11287.

ethyl 2-(4-methyl-*N*-(2,2,2-trifluoroethyl)phenylsulfonimidoyl)acetate (3o)



The title compound **3o** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow oil (49%, 30 mg).

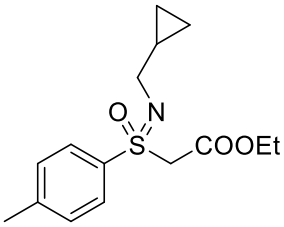
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 4.18 (s, 2H), 4.18 – 4.09 (m, 2H), 3.59 – 3.66 (m, 1H), 3.47 – 3.53 (m, 1H), 2.46 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.4, 145.0, 133.9, 130.0, 129.3, 125.18 (q, *J* = 278.0 Hz), 62.3, 61.2, 45.18 (q, *J* = 34.0 Hz), 44.8, 21.6, 13.8 ppm.

^{19}F NMR (564 MHz, Chloroform-*d*): δ = -72.57 (t, *J* = 9.2 Hz) ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{16}NO_3F_3SNa^+$: 346.06952; Found: 346.06899.

ethyl 2-(*N*-(cyclopropylmethyl)-4-methylphenylsulfonimidoyl)acetate (3p)



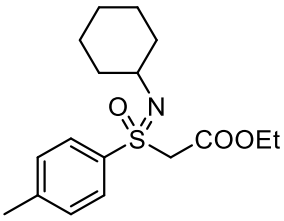
The title compound **3p** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow oil (91%, 51 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.17 – 4.13 (m, 2H), 4.13 – 4.06 (m, 2H), 3.02 – 2.91 (m, 2H), 2.43 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 2H), 1.05 – 1.03 (m, 1H), 0.48 – 0.44 (m, 2H), 0.23 – 0.12 (m, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.0, 144.1, 135.3, 129.7, 129.3, 61.9, 60.8, 48.7, 21.5, 13.8, 13.3, 3.8, 3.7 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{21}NO_3SNa^+$: 318.11344; Found: 318.11315.

ethyl 2-(*N*-cyclohexyl-4-methylphenylsulfonimidoyl)acetate (3q)



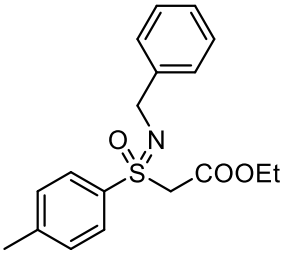
The title compound **3q** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow oil (89%, 55 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.13 – 4.10 (m, 2H), 4.10 – 4.05 (m, 2H), 3.18 – 3.09 (m, 1H), 2.43 (s, 3H), 1.89 – 1.78 (m, 2H), 1.74 – 1.65 (m, 2H), 1.55 – 1.48 (m, 1H), 1.48 – 1.34 (m, 2H), 1.28 – 1.18 (m, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.1, 143.9, 136.0, 129.6, 129.3, 61.8, 60.9, 54.2, 37.0, 36.7, 25.6, 25.2, 25.1, 21.5, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{25}NO_3SNa^+$: 346.14474; Found: 346.14452.

ethyl 2-(*N*-benzyl-4-methylphenylsulfonimidoyl)acetate (3r)



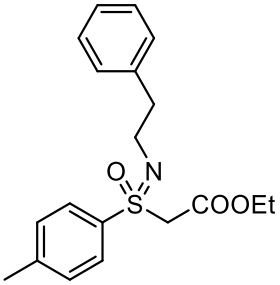
The title compound **3r** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow solid (51%, 34 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.85 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.37 – 4.22 (m, 2H), 4.18 (s, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.9, 144.3, 141.0, 134.9, 129.8, 129.3, 128.2, 127.3, 126.5, 62.0, 60.9, 47.0, 21.6, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+K]^+$ Calcd. for $C_{18}H_{21}NO_3SK^+$: 370.08737; Found: 370.08739.

ethyl 2-(4-methyl-*N*-phenethylphenylsulfonimidoyl)acetate (3s)



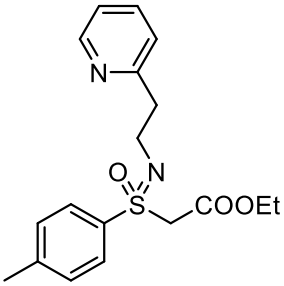
The title compound **3s** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow oil (91%, 63 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.21 (d, *J* = 6.6 Hz, 2H), 7.22 – 7.19 (m, 1H), 4.12 – 3.99 (m, 4H), 3.37 – 3.22 (m, 2H), 2.94 – 2.88 (m, 2H), 2.43 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.9, 144.1, 140.3, 134.9, 129.7, 129.3, 129.0, 128.2, 126.0, 61.9, 60.5, 45.6, 39.3, 21.5, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{23}NO_3SNa^+$: 368.12909; Found: 368.12959.

ethyl 2-(4-methyl-*N*-(2-(pyridin-2-yl)ethyl)phenylsulfonimidoyl)acetate (3t)



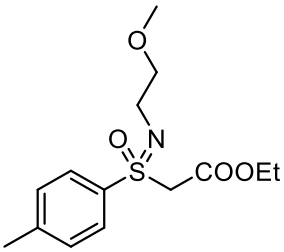
The title compound **3t** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 1:4) as a yellow oil (23%, 16 mg).

^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 8.51 (d, *J* = 4.5 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.57 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 1H), 7.12 – 7.10 (m, 1H), 4.13 – 3.99 (m, 4H), 3.54 – 3.41 (m, 2H), 3.08 (td, *J* = 7.1, 1.6 Hz, 2H), 2.42 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.9, 160.3, 149.1, 144.2, 136.0, 129.7, 129.3, 123.8, 121.1, 64.6, 61.9, 60.5, 43.8, 41.3, 21.5, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{18}H_{22}N_2O_3SNa^+$: 369.12433; Found: 369.12482.

ethyl 2-(*N*-(2-methoxyethyl)-4-methylphenylsulfonimidoyl)acetate (3u)



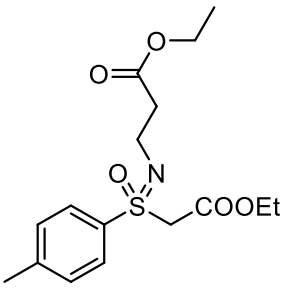
The title compound **3u** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 1:1) as a yellow oil (81%, 46 mg).

^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 7.82 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.20 – 4.13 (m, 2H), 4.13 – 4.07 (m, 2H), 3.54 – 3.51 (m, 2H), 3.36 (s, 3H), 3.33 – 3.20 (m, 2H), 2.43 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.0, 144.2, 134.9, 129.7, 129.3, 74.0, 61.9, 60.7, 58.8, 43.4, 21.5, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{21}NO_4SNa^+$: 322.10835; Found: 322.10809.

Ethyl 3-(((2-ethoxy-2-oxoethyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)amino)propanoate (3v)



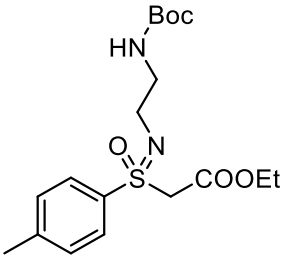
The title compound **3v** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 1:1) as a yellow oil (80%, 53 mg).

^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 4.17 – 4.05 (m, 6H), 3.43 – 3.31 (m, 2H), 2.60 – 2.57 (m, 2H), 2.43 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.3, 162.9, 144.3, 134.9, 129.7, 129.3, 61.9, 60.4, 60.2, 39.6, 37.6, 21.5, 14.2, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{16}H_{23}NO_5SNa^+$: 364.11891; Found: 364.11777.

Ethyl 2-(*N*-(2-((tert-butoxycarbonyl)amino)ethyl)-4-methylphenylsulfonimidoyl) acetate (3w)



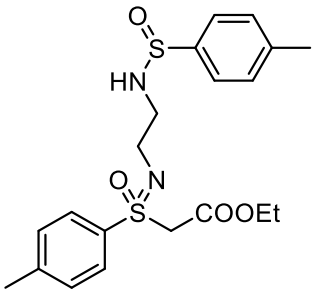
The title compound **3w** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow oil (73%, 54 mg).

^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 7.79 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 5.16 (s, 1H), 4.16 – 4.07 (m, 4H), 3.28 (t, *J* = 5.7 Hz, 2H), 3.17 (t, *J* = 5.6 Hz, 2H), 2.44 (s, 3H), 1.43 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.8, 156.0, 144.5, 134.6, 129.8, 129.2, 62.0, 60.6, 43.8, 42.4, 28.4, 21.5, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{18}H_{28}N_2O_5SNa^+$: 407.16111; Found: 407.16055.

ethyl 2-(4-methyl-N-(2-((p-tolylsulfinyl)amino)ethyl)phenylsulfonimidoyl)acetate (3x)



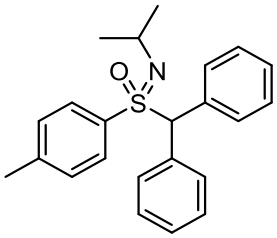
The title compound **3x** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 1:4) as a yellow oil (27%, 23 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 8.1, 5.2 Hz, 4H), 7.30 – 7.26 (m, 3H), 5.00 (t, *J* = 5.9 Hz, 2H), 4.23 – 4.10 (m, 2H), 4.10 – 4.02 (m, 2H), 3.31 – 3.16 (m, 3H), 2.99 – 2.82 (m, 1H), 2.44 (d, *J* = 3.4 Hz, 6H), 2.40 (s, 3H), 2.39 (s, 3H), 1.16 – 1.12 (m, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 144.5, 140.9, 129.87, 129.83, 129.49, 129.46, 129.3, 129.2, 126.1, 126.1, 62.1, 62.0, 60.3, 60.1, 44.8, 44.5, 42.9, 42.4, 21.6, 21.3, 13.8 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{20}H_{26}N_2O_4S_2Na^+$: 445.12262; Found: 445.12232.

benzhydryl(isopropylimino)(phenyl)-λ^6-sulfanone (3y)



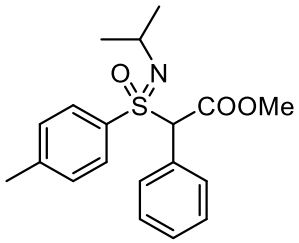
The title compound **3y** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 4:1) as a yellow oil (67%, 49 mg).

^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 7.49 (d, *J* = 7.1 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 7.24 – 7.17 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.1 Hz, 2H), 5.78 (s, 1H), 3.80 – 3.68 (m, 1H), 2.31 (s, 3H), 1.26 – 1.22 (m, 3H), 1.09 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 141.8, 141.0, 140.5, 140.4, 129.9, 129.1, 128.6, 128.1, 128.0, 127.2, 126.9, 126.1, 62.3, 48.8, 29.6, 23.3, 21.2 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{23}H_{25}NOSNa^+$: 386.15491; Found: 386.15393.

methyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)-2-phenylacetate (3z)



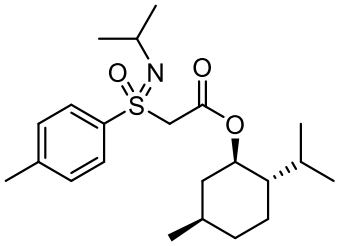
The title compound **3z** (1 : 1 mixture of two diastereoisomers) was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow oil (88%, 61 mg).

^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 7.44 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.27 – 7.22 (m, 4H), 7.22 – 7.15 (m, 6H), 7.15 – 7.11 (m, 2H), 5.25 (s, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 3.67 – 3.61 (m, 1H), 3.58 – 3.52 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 1.22 – 1.17 (m, 9H), 1.16 (d, *J* = 6.3 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 143.8, 143.7, 130.9, 130.4, 130.3, 129.0, 129.0, 128.9, 128.7, 128.0, 128.0, 75.5, 74.4, 52.8, 52.6, 46.9, 46.6, 26.7, 26.6, 26.6, 26.4, 21.5, 21.5 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{23}NO_3SNa^+$: 368.12909; Found: 368.12789.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)acetate (3aa)



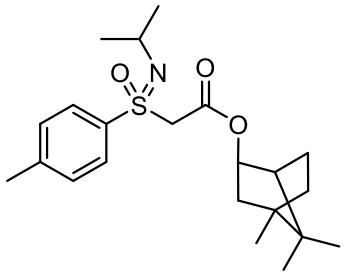
The title compound **3aa** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 4:1) as a yellow oil (1 : 1 mixture of two diastereoisomers) (57%, 45 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.80 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.66 – 4.53 (m, 1H), 4.16 – 4.03 (m, 2H), 3.52 – 3.38 (m, 1H), 2.43 (s, 3H), 1.87 – 1.85 (m, 1H), 1.77 – 1.79 (m, 1H), 1.65 – 1.62 (m, 2H), 1.41 – 1.39 (m, 1H), 1.34 – 1.23 (m, 3H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.02 – 0.94 (m, 1H), 0.87 (dd, *J* = 6.6, 2.3 Hz, 3H), 0.83 (dd, *J* = 7.1, 1.9 Hz, 3H), 0.67 (dd, *J* = 7.0, 1.9 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.6, 143.9, 129.6, 129.4, 76.2, 60.96, 60.91, 46.6, 46.56, 46.53, 34.04, 34.01, 31.3, 31.2, 29.6, 26.78, 26.76, 26.4, 25.69, 25.67, 23.08, 23.06, 21.9, 21.5, 20.7, 16.0 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{22}H_{35}NO_3SNa^+$: 416.22299; Found: 416.22134.

(2*R*)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)acetate (3ab)



The title compound **3ab** was synthesized according to the general procedure **(GP-2)** and was obtained after silica column chromatography (n-hexane : ethyl acetate 4:1) as a yellow oil (1 : 1 mixture of two diastereoisomers) (36%, 28 mg).

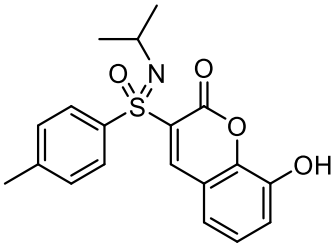
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.82 (d, *J* = 7.0 Hz, 2H), 7.33 (d, *J* = 6.8 Hz, 2H), 4.82 – 4.78 (m, 1H), 4.19 – 4.13 (m, 2H), 3.52 – 3.42 (m, 1H), 2.43 (s, 3H), 2.27 – 2.24 (m, 1H), 1.78 – 1.65 (m, 4H), 1.22 (dd, *J* = 6.3, 1.0 Hz, 3H), 1.16 (dd, *J* = 6.3,

2.3 Hz, 3H), 0.89 – 0.86 (m, 2H), 0.84 (dd, *J* = 4.9, 2.2 Hz, 6H), 0.75 (d, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.4, 163.3, 143.9, 135.99, 135.91, 129.77, 129.75, 129.2, 82.0, 60.98, 60.94, 48.7, 47.85, 47.82, 46.6, 44.6, 36.2, 36.1, 27.8, 27.7, 26.88, 26.86, 26.81, 26.49, 26.47, 21.5, 19.66, 19.62, 18.8, 18.7, 13.38, 13.31 ppm.

HRMS (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{22}H_{34}NO_3S^+$: 392.22539; Found: 392.22443.

8-hydroxy-3-(*N*-isopropyl-4-methylphenylsulfonimidoyl)-2H-chromen-2-one (4a)[4]



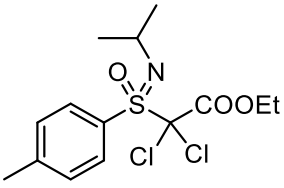
The title compound **4a** was synthesized according to the following procedure: **3a** (57 mg, 0.2 mmol, 1.0 equiv.), 2,3-dihydroxybenzaldehyde (28 mg, 0.2 mmol, 1.0 equiv.) and piperidine (9 mg, 0.1 mmol, 0.5 equiv.) was stirred in ethanol (5 mL) at 80°C for 6 h. After the reaction was completed, the solvent was evaporated under reduced pressure, and the crude product was obtained after silica column chromatography (n-hexane : ethyl acetate 1:4) as a yellow solid (84%, 60 mg).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.39 (s, 1H), 8.96 (s, 1H), 7.96 – 7.82 (m, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.17 (m, 2H), 3.40 – 3.35 (m, 1H), 2.36 (s, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6): δ = 155.0, 150.6, 144.9, 143.9, 143.8, 135.9, 129.7, 129.6, 126.9, 125.5, 121.3, 121.0, 119.1, 46.5, 27.4, 26.6, 21.4 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{19}NO_4SNa^+$: 380.09270; Found: 380.09298.

ethyl 2,2-dichloro-2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)acetate (4b)[5]



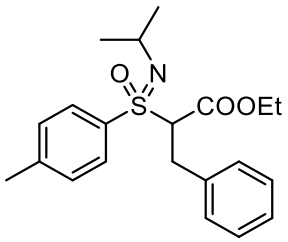
The title compound **4b** was synthesized according to the following procedure: **3a (**57 mg, 0.2 mmol, 1.0 equiv) and triethylamine (60 mg, 0.6, 3.0 equiv) in 2 mL of DCM was stirred for 20 min. N-chlorosuccinimide (80 mg, 0.6 mmol, 3.0 equiv) was added in to the reaction. The reaction was stirred at room temperature for 16 h. Then mixture was diluted with H_2O (10 mL) and then extracted with EtOAc (3×10 mL). The organic layers were combined and washed with brine then dried with Na_2SO_4. The crude product was concentrated in vacuo and was obtained after silica column chromatography (n-hexane : ethyl acetate 4:1) as a yellow oil (64%, 45 mg).

^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 7.89 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.27 (m, 2H), 4.31 – 4.18 (m, 2H), 2.43 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 162.9, 144.9, 131.6, 130.7, 129.0, 64.7, 47.3, 26.6, 25.6, 21.6, 13.6 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{19}NO_3SCl_2Na^+$: 374.03549; Found: 374.03563.

ethyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)-3-phenylpropanoate (4c)[6]



The title compound **4c** (1:1 mixture of two diastereoisomers) was synthesized according to the following procedure: To a stirred solution of the **3a** (57 mg, 0.2 mmol, 1.0 equiv), benzyl bromide (34 mg , 0.2 mmol, 1.0 equiv) and 18-crown-6 (21 mg 0.08 mmol, 0.4 equiv) in acetone (2 mL) was added K_2CO_3 (138 mg, 1.0 mmol, 5.0 equiv). The mixture was refluxed for 24 h. At the end, the reaction mixture was filtered and the acetone layer was concentrated. The residue obtained was extracted with chloroform, washed well with water, dried over anhydrous Na_2SO_4, filtered, and concentrated. The product was obtained after silica column chromatography (n-hexane : ethyl acetate 2:1) as a yellow oil (27%, 20 mg).

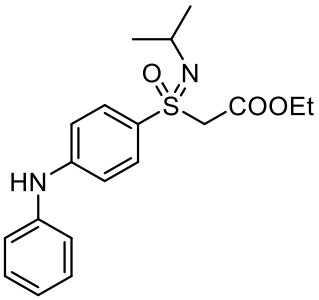
^{1}**H NMR** (600 MHz, Chloroform-*d*): δ = 7.80 (t, *J* = 8.7 Hz, 4H), 7.37 – 7.32 (m, 4H), 7.23 – 7.21 (m, 4H), 7.20 – 7.15 (m, 2H), 7.12 – 7.09 (m, 2H), 7.08 – 7.03 (m, 2H), 4.33 (dd, *J* = 12.3, 3.3 Hz, 1H), 4.28 (dd, *J* = 12.2, 3.2 Hz, 1H), 4.08 (q, *J* = 7.1 Hz,

2H), 3.99 – 3.91 (m, 2H), 3.60 – 3.50 (m, 2H), 3.39 (dd, *J* = 13.5, 3.3 Hz, 1H), 3.21 (dd, *J* = 13.6, 3.3 Hz, 1H), 3.05 (dd, *J* = 13.6, 12.3 Hz, 1H), 2.94 (t, *J* = 12.9 Hz, 1H), 2.45 (s, 6H), 1.26 (d, *J* = 6.4 Hz, 3H), 1.22 (dd, *J* = 6.3, 2.7 Hz, 6H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 166.3, 144.0, 130.6, 130.2, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 126.95, 126.91, 71.8, 71.0, 61.7, 61.5, 46.6, 46.3, 34.2, 33.4, 26.89, 26.83, 26.6, 26.5, 21.5, 13.9, 13.7 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{21}H_{27}NO_3SNa^+$: 396.16039; Found: 396.16065.

ethyl 2-(*N*-isopropyl-4-(phenylamino)phenylsulfonimidoyl)acetate (4d) [7]



The title compound **4d** was synthesized according to the following procedure: **3a** (57 mg, 0.2 mmol, 1.0 equiv), Aniline (21 mg, 0.3 mmol, 1.5 equiv) and 1 mL of a solution containing 4CzIPN (0.8 mg, 0.001 mmol, 0.005 equiv) and NiBr2•glyme (3.2 mg, 0.01 mmol, 0.05 equiv) dissolved in DMA. The reaction mixture was then degassed and refilled with nitrogen two times via a syringe needle before tert-butylamine (27.3 µL, 0.26 mmol, 1.3 equiv) was added via syringe. After degassing one more time and refilling with Argon, the reaction mixture was irradiated using a single blue LED (467 nm) for 16 h. After completion of the reaction, the reaction mixture was transferred to a separating funnel with ethyl acetate (10 mL) and was washed with 10 mL brine 5 times. The organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was obtained after silica column chromatography (n-hexane : ethyl acetate 1:1) as a yellow oil (89%, 64 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.74 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.18 – 7.17 (m, 2H), 7.08 – 7.11 (m, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.16 (s, 1H), 4.17 – 4.05 (m, 4H), 3.56 – 3.48 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.21 – 1.18 (m, 6H) ppm.

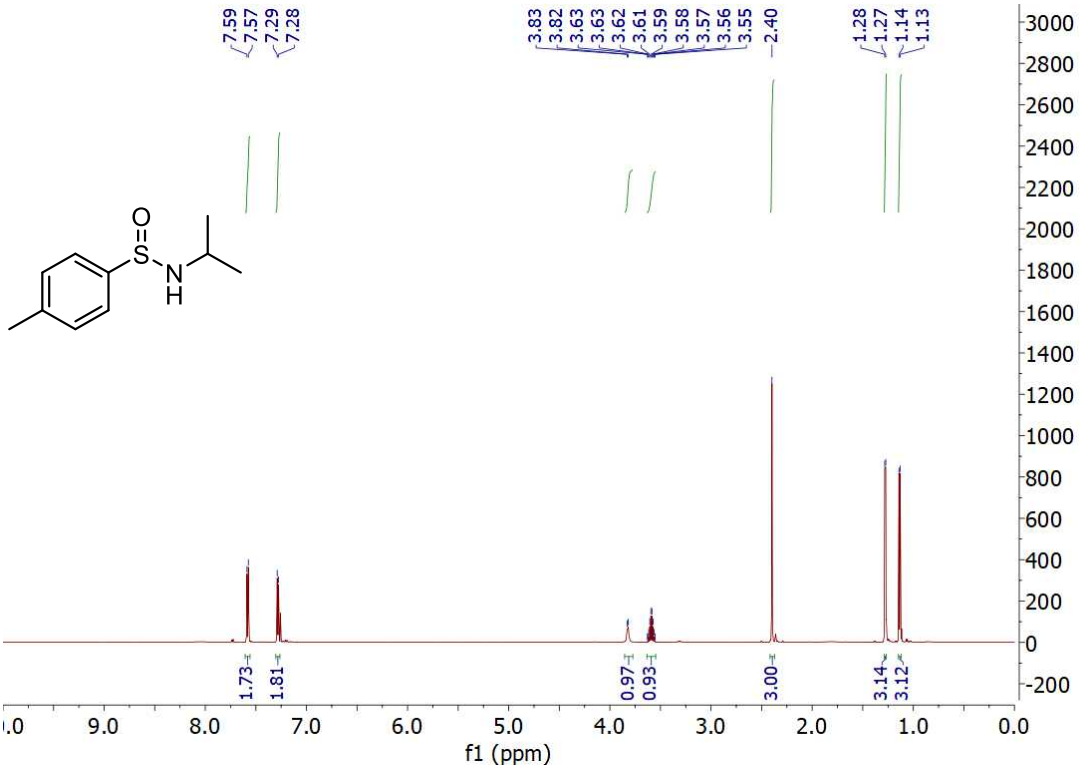
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.3, 148.5, 140.2, 131.3, 129.5, 127.6, 123.7, 121.0, 114.5, 61.8, 60.8, 46.5, 26.7, 26.5, 13.9 ppm.

HRMS (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{24}N_2O_3SNa^+$: 383.13998; Found: 383.13980.

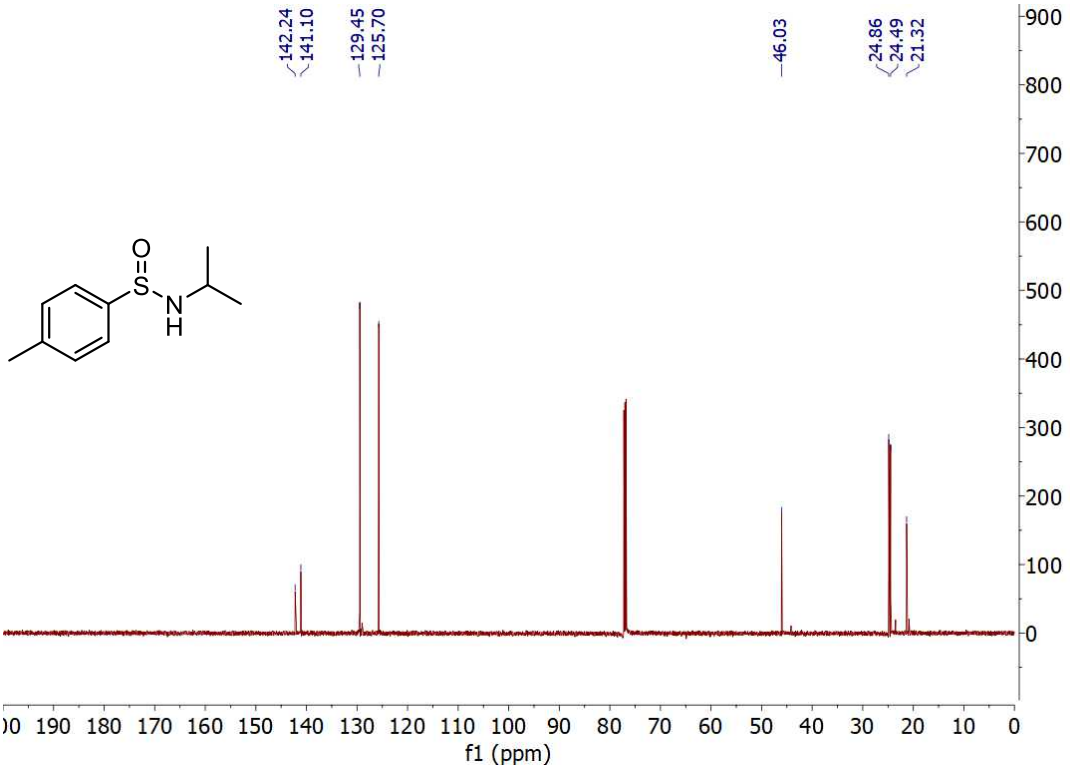
7. NMR data

N-isopropyl-4-methylbenzenesulfinamide (1)

^{1}H NMR (600 MHz, Chloroform-*d*)

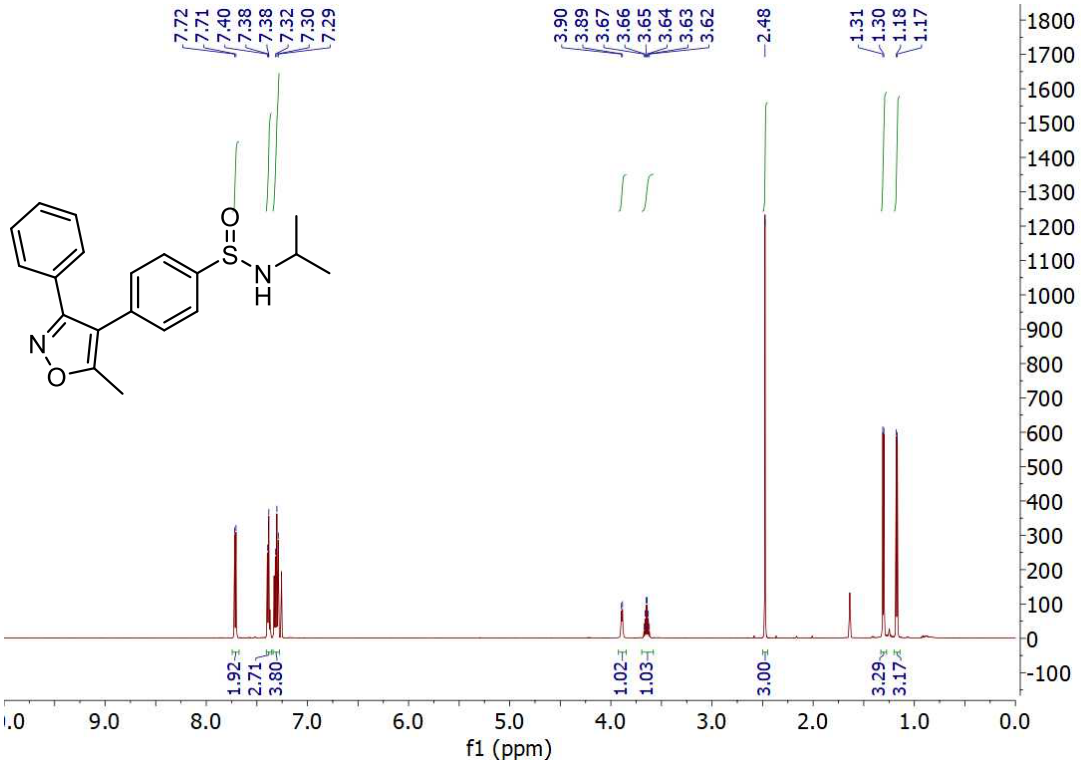


^{13}C NMR (151 MHz, Chloroform-*d)*

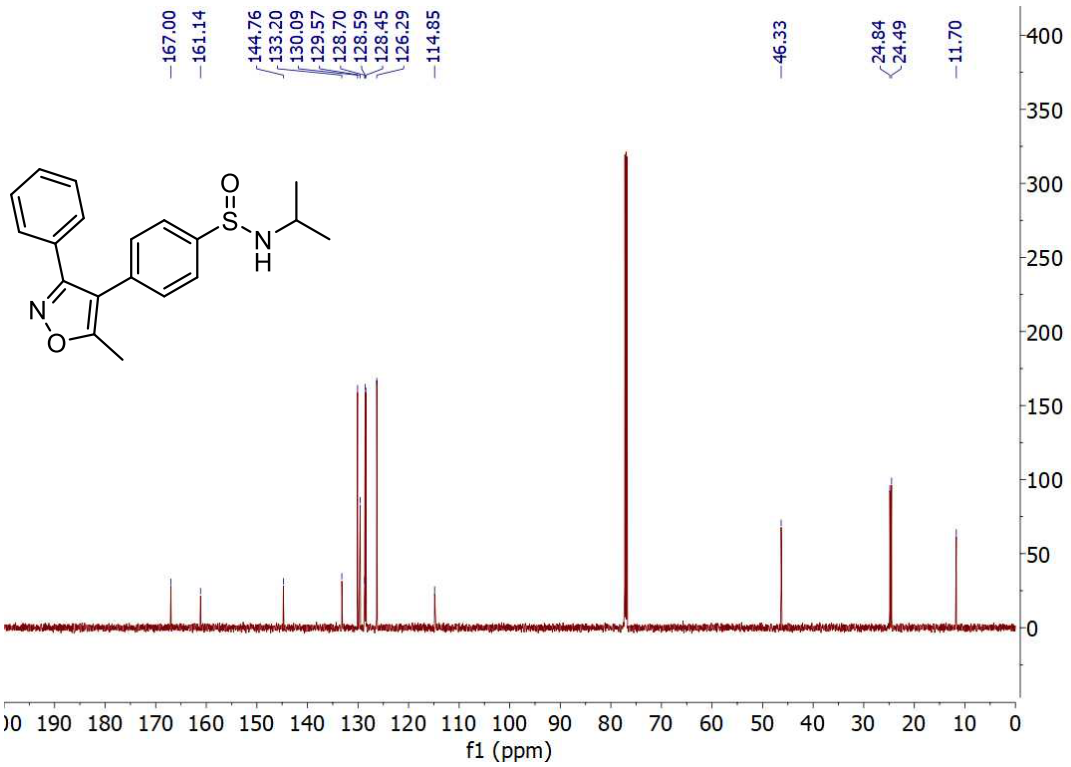


***N*-isopropyl-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfinamide (1m)**

^{1}H NMR (600 MHz, Chloroform-*d*)

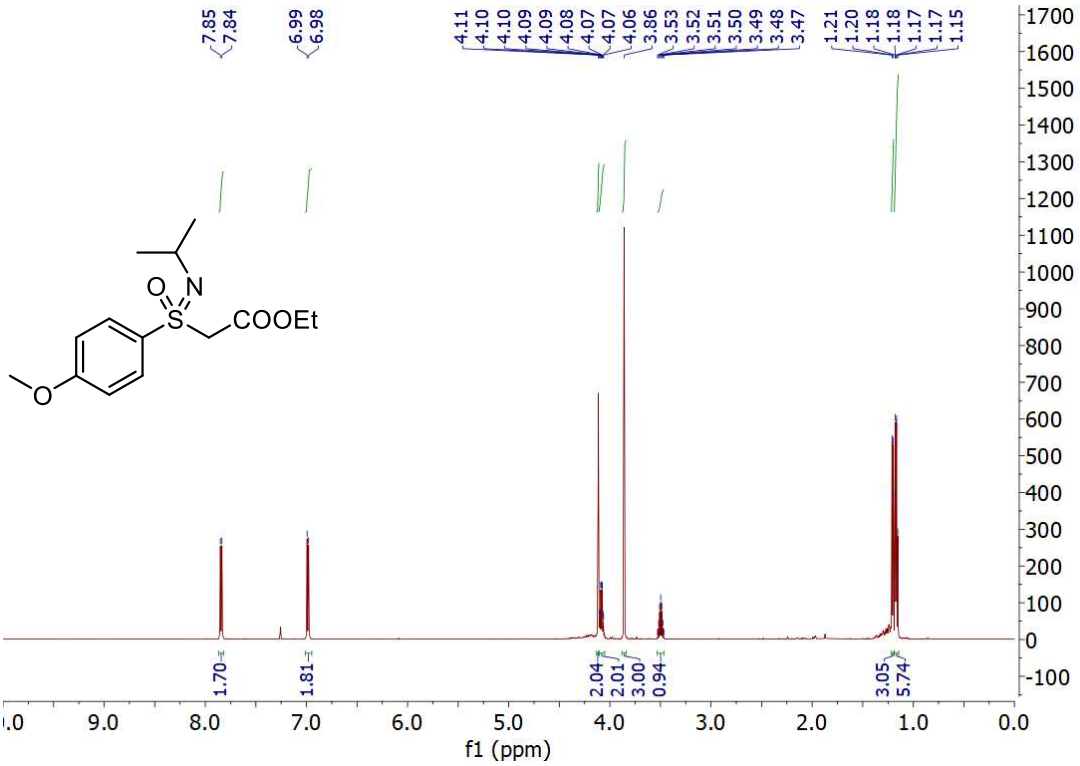


^{13}C NMR (151 MHz, Chloroform-*d*)

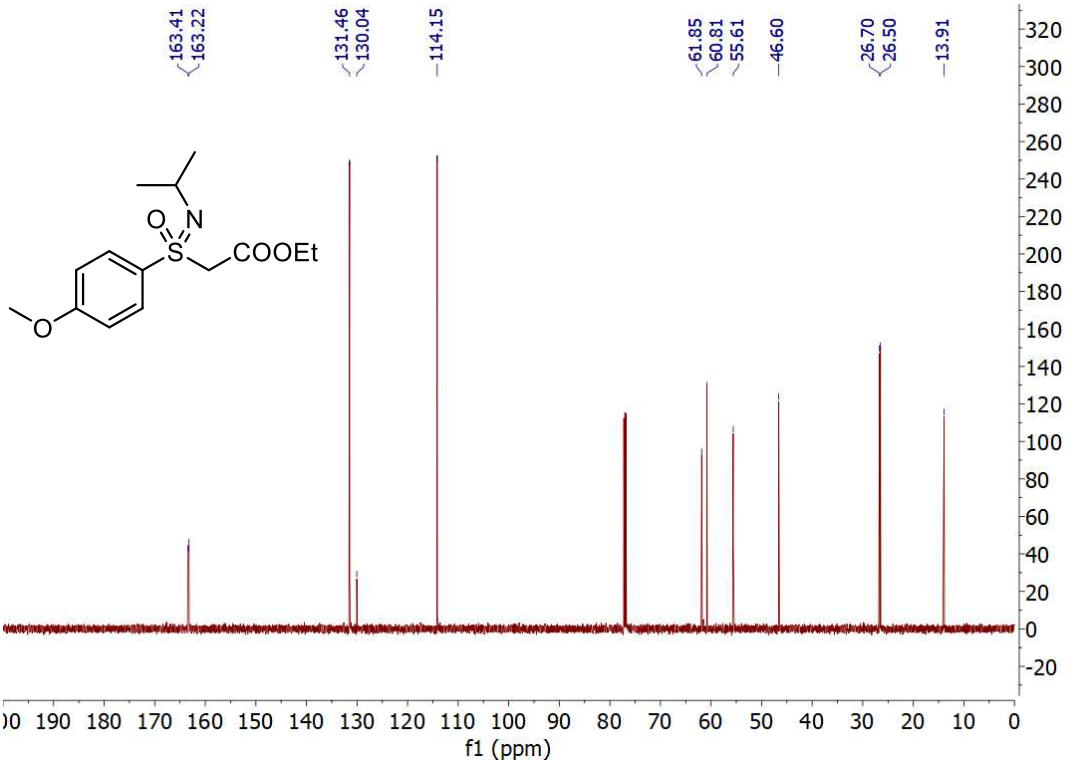


ethyl 2-(*N*-isopropyl-4-methoxyphenylsulfonimidoyl)acetate (3a)

[1]**H NMR** (600 MHz, Chloroform-*d*)

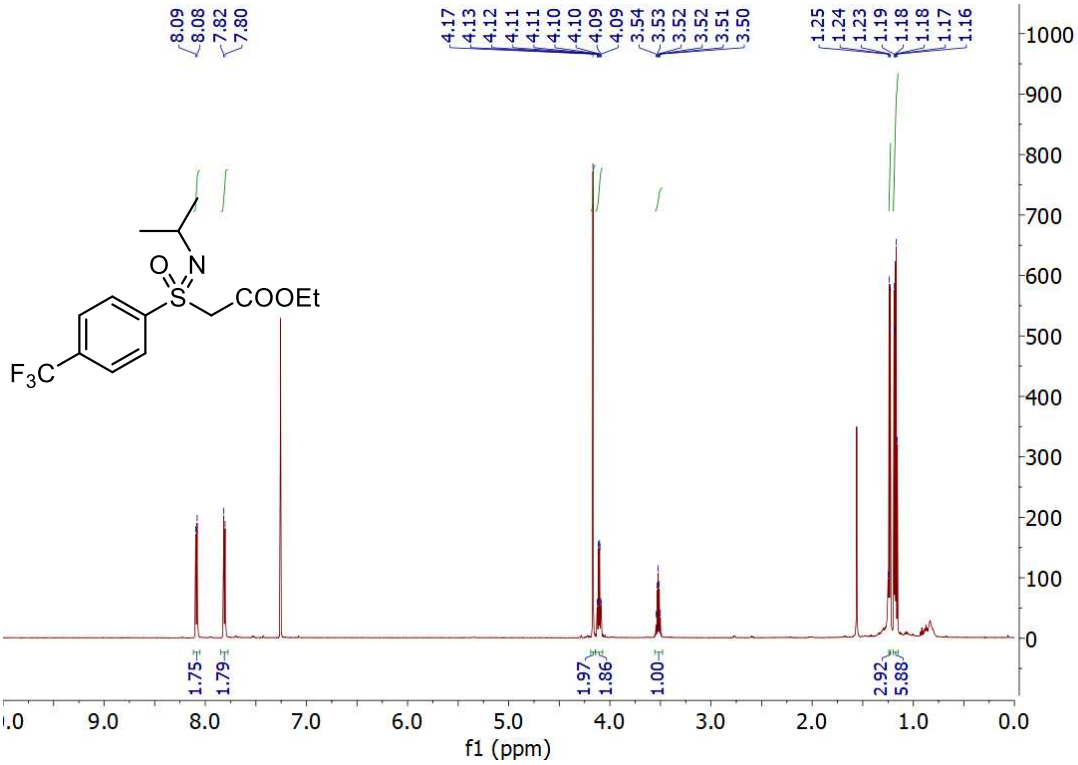


[13]**C NMR** (151 MHz, Chloroform-*d*)

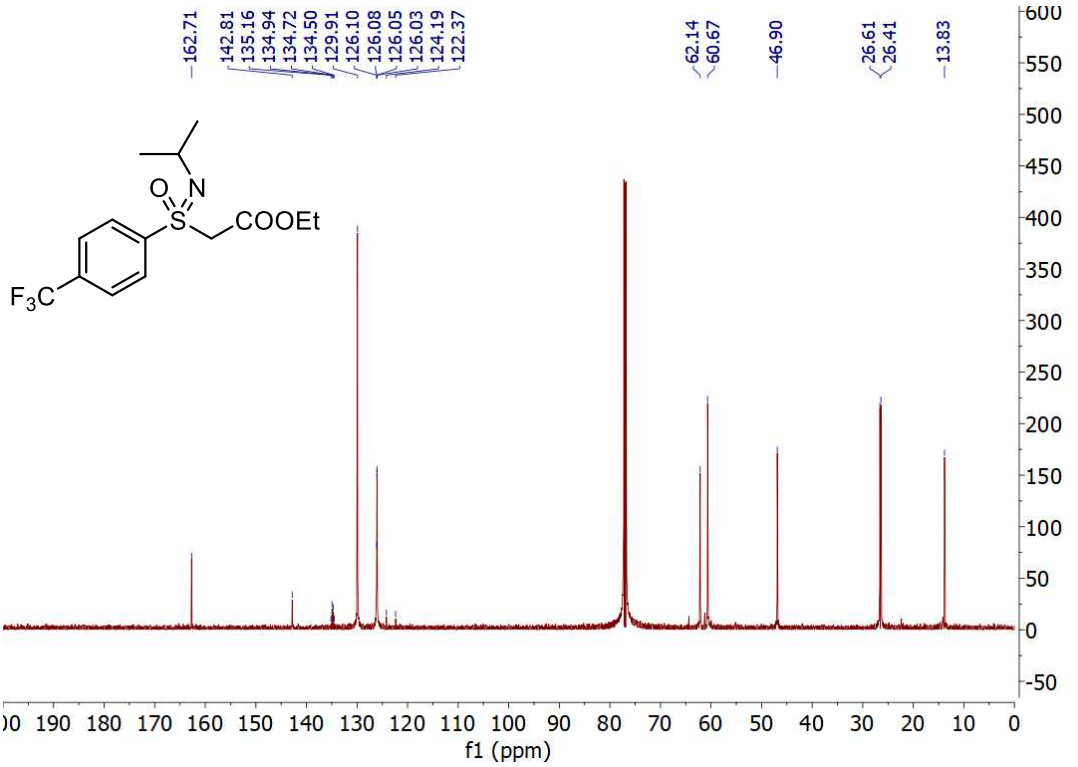


ethyl 2-(*N*-isopropyl-4-(trifluoromethyl)phenylsulfonimidoyl)acetate (3b)

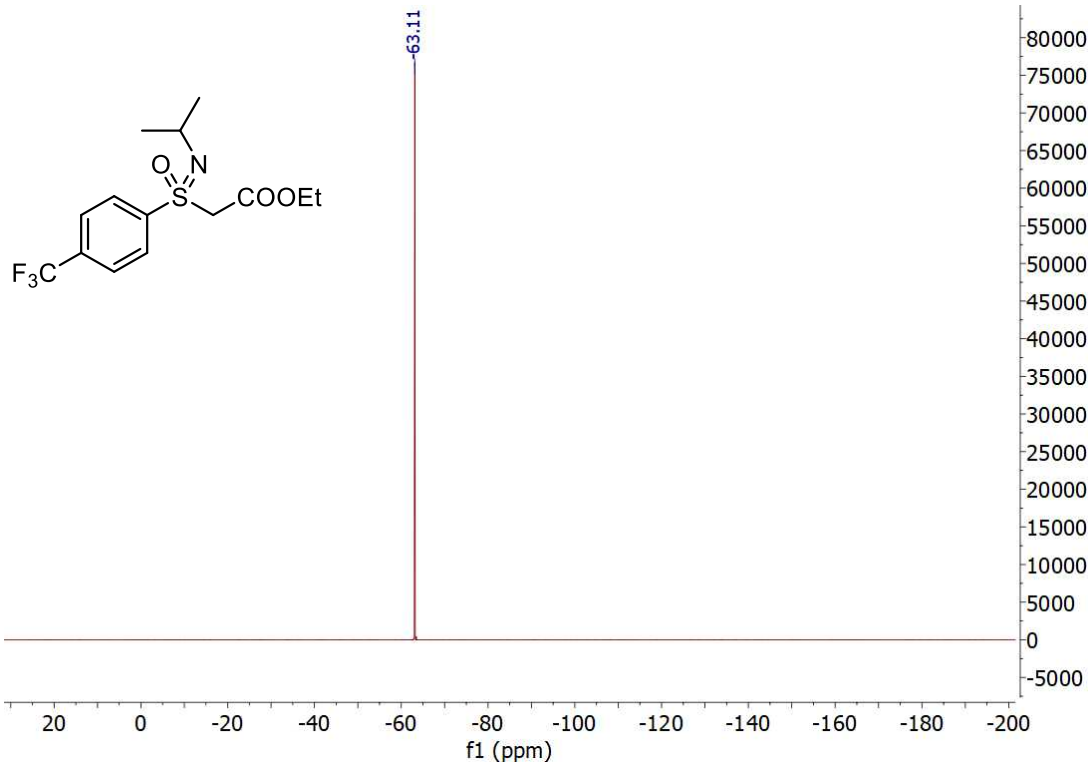
[1]**H NMR** (600 MHz, Chloroform-*d*)



[13]**C NMR** (151 MHz, Chloroform-*d*)

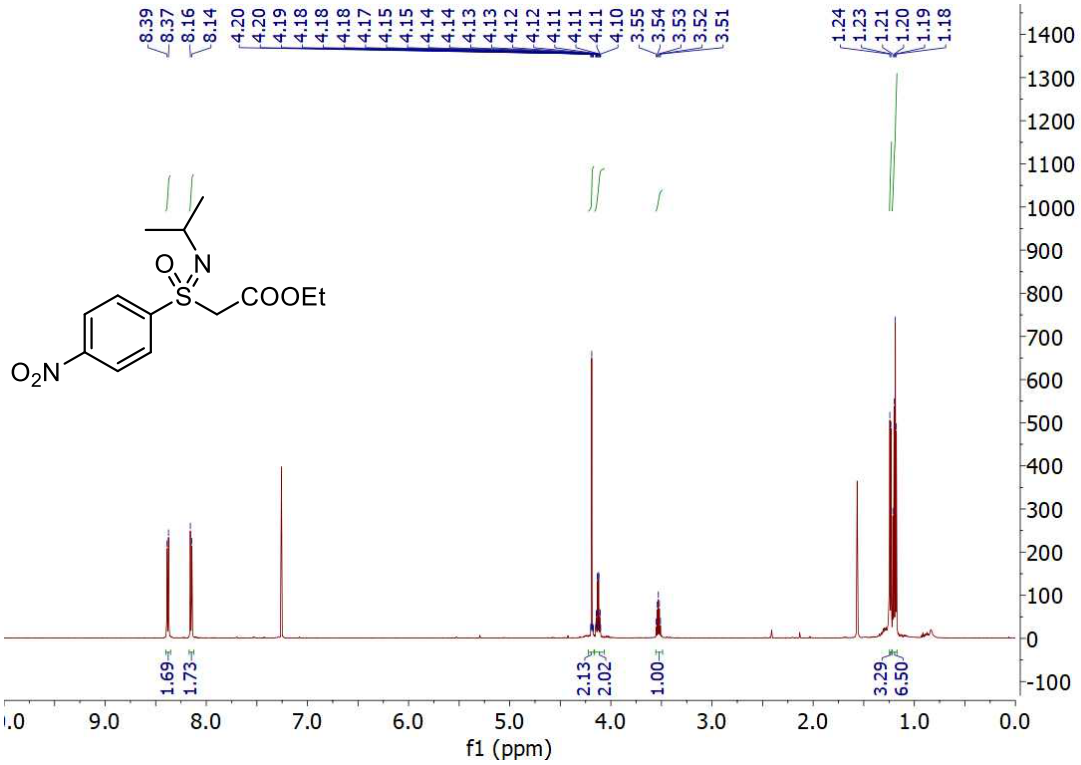


^{19}F NMR (564 MHz, Chloroform-*d*)

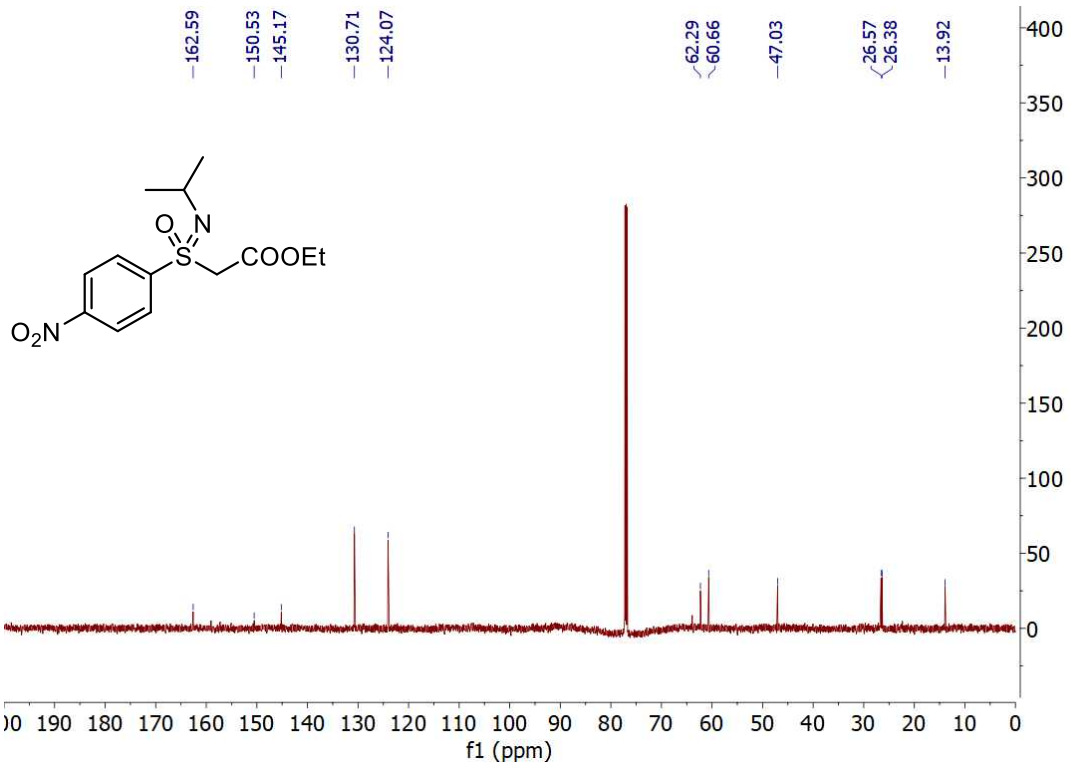


ethyl 2-(*N*-isopropyl-4-nitrophenylsulfonimidoyl)acetate (3c)

^{1}H NMR (600 MHz, Chloroform-*d*)

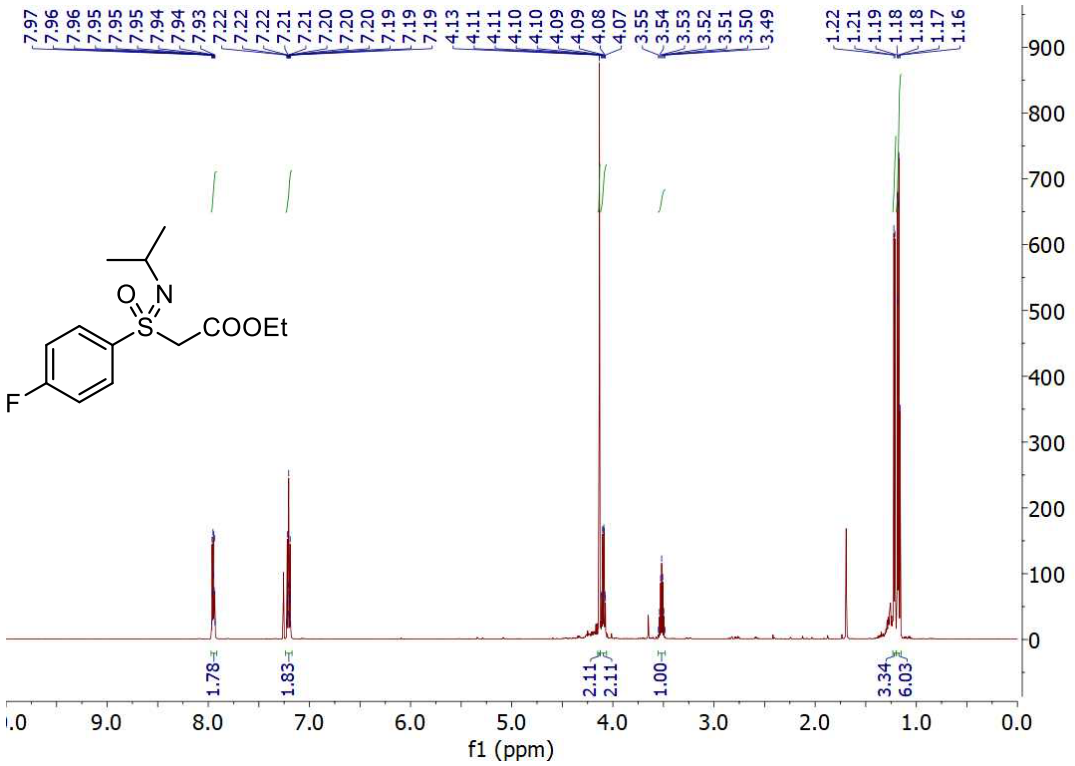


^{13}C NMR (151 MHz, Chloroform-*d*)

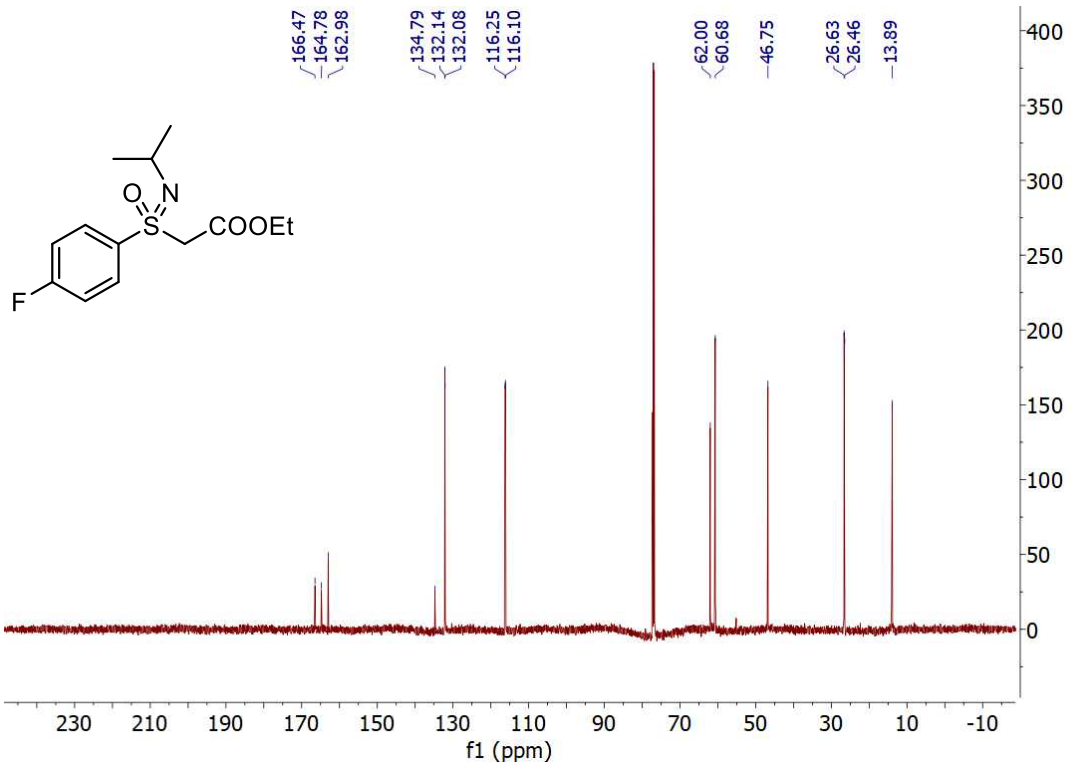


ethyl 2-(4-fluoro-*N*-isopropylphenylsulfonimidoyl)acetate (3d)

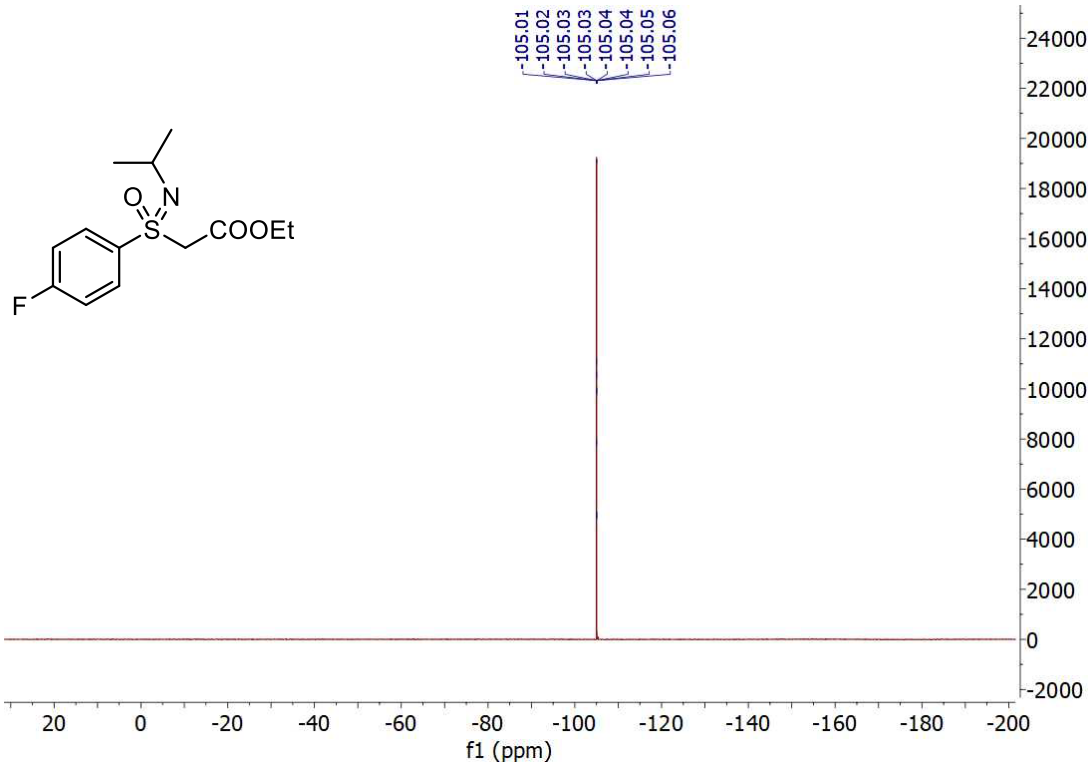
^{1}**H NMR** (600 MHz, Chloroform-*d*)



^{13}**C NMR** (151 MHz, Chloroform-*d*)

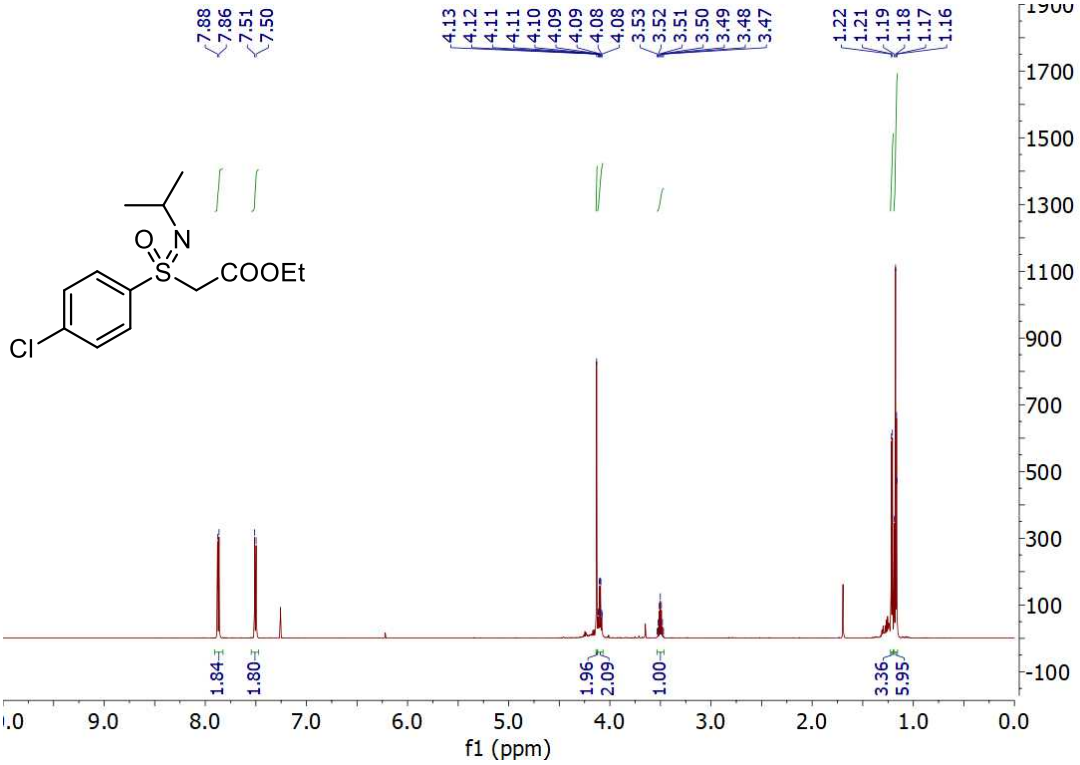


^{19}F NMR (564 MHz, Chloroform-*d*)

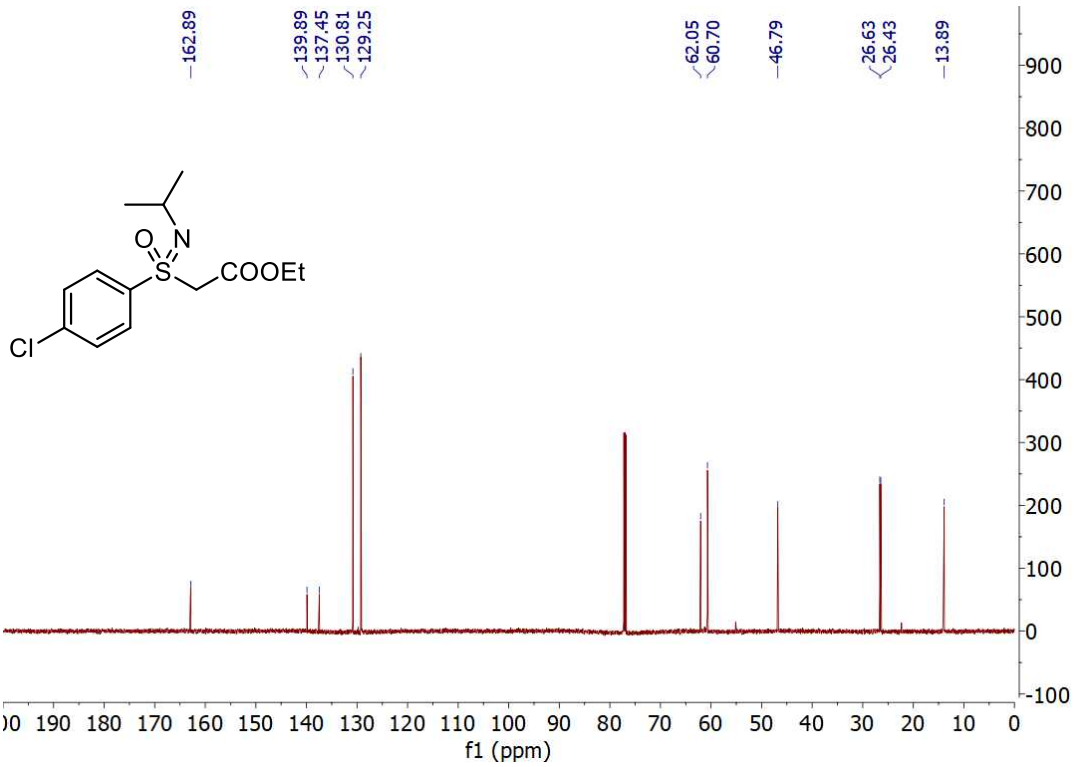


ethyl 2-(4-chloro-*N*-isopropylphenylsulfonimidoyl)acetate (3e)

[1]**H NMR** (600 MHz, Chloroform-*d*)

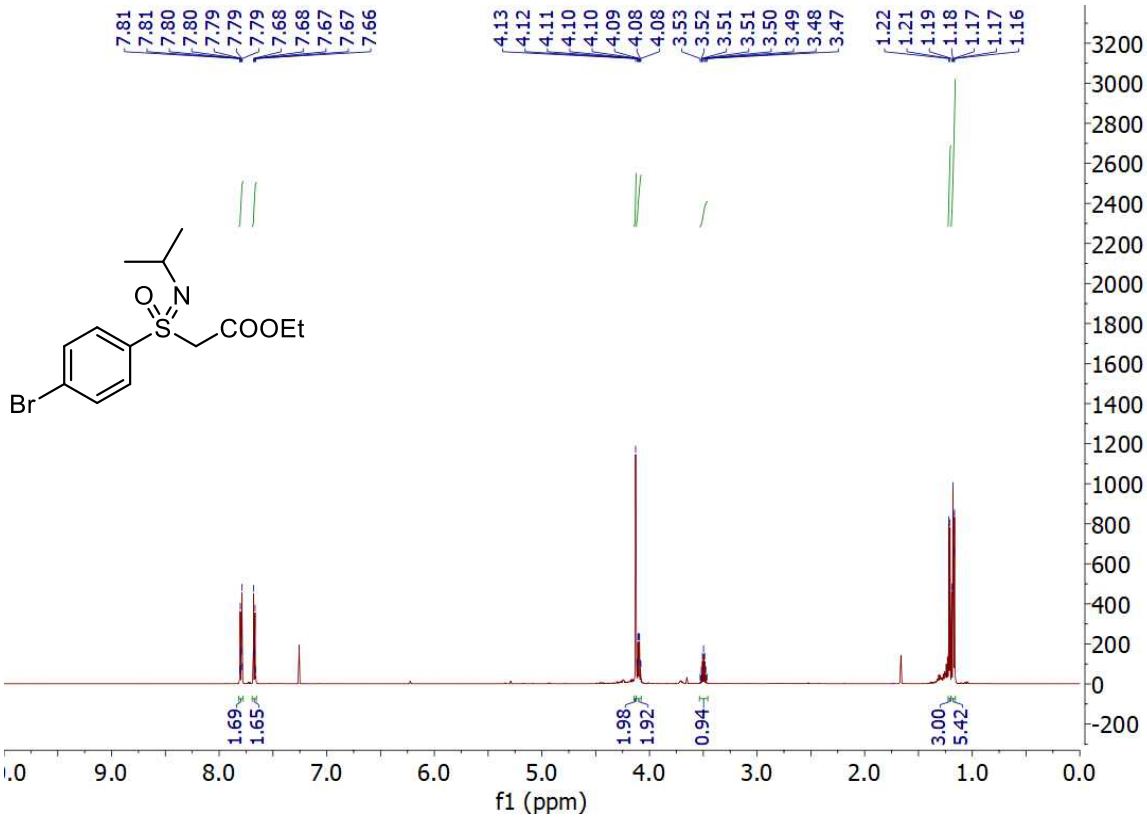


[13]**C NMR** (151 MHz, Chloroform-*d*)

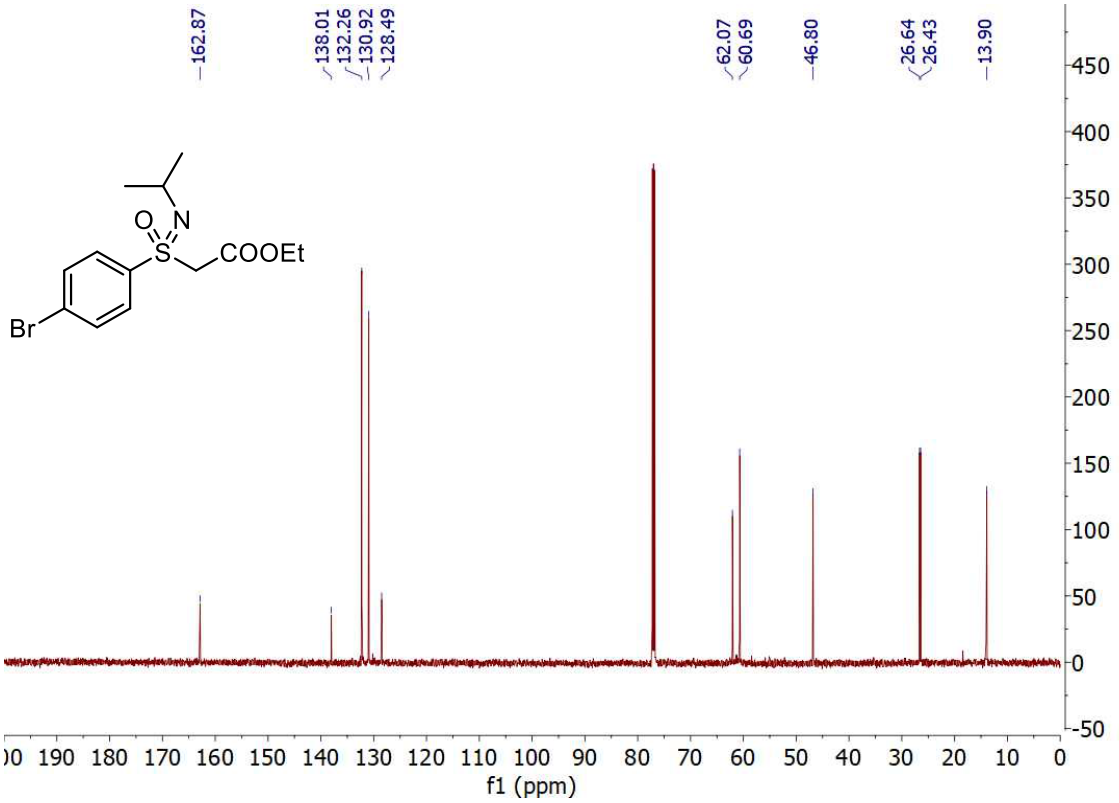


ethyl 2-(4-bromo-*N*-isopropylphenylsulfonimidoyl)acetate (3f)

[1]**H NMR** (600 MHz, Chloroform-*d*)

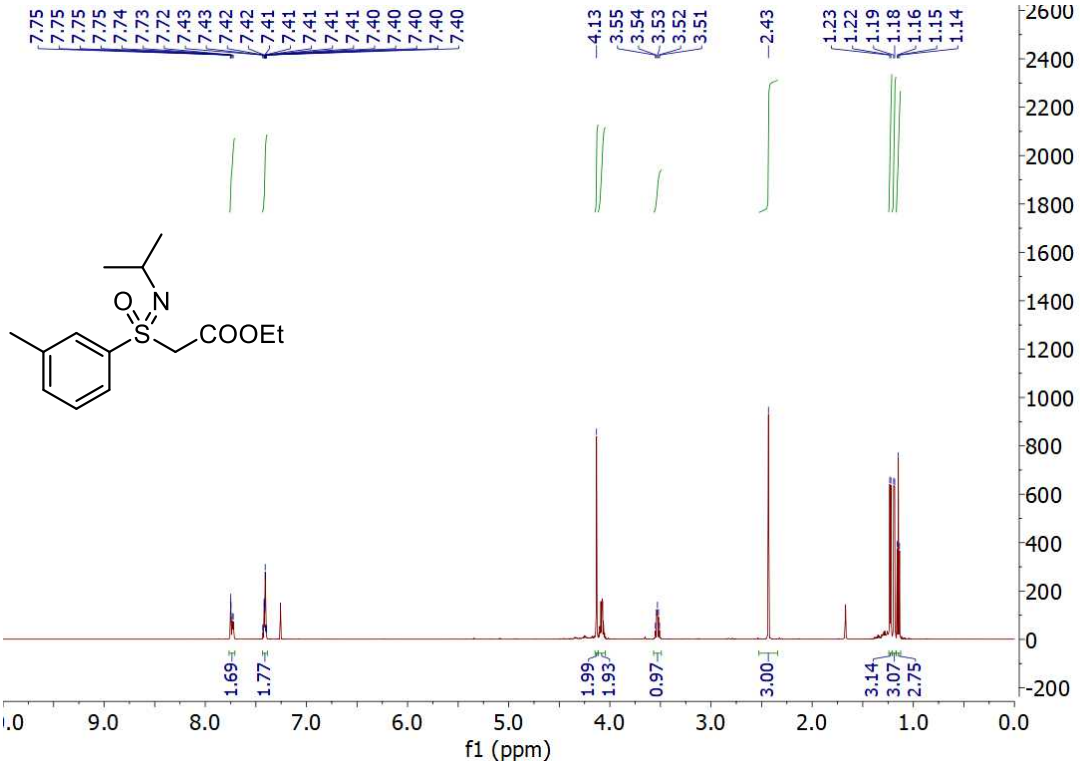


[13]**C NMR** (151 MHz, Chloroform-*d*)

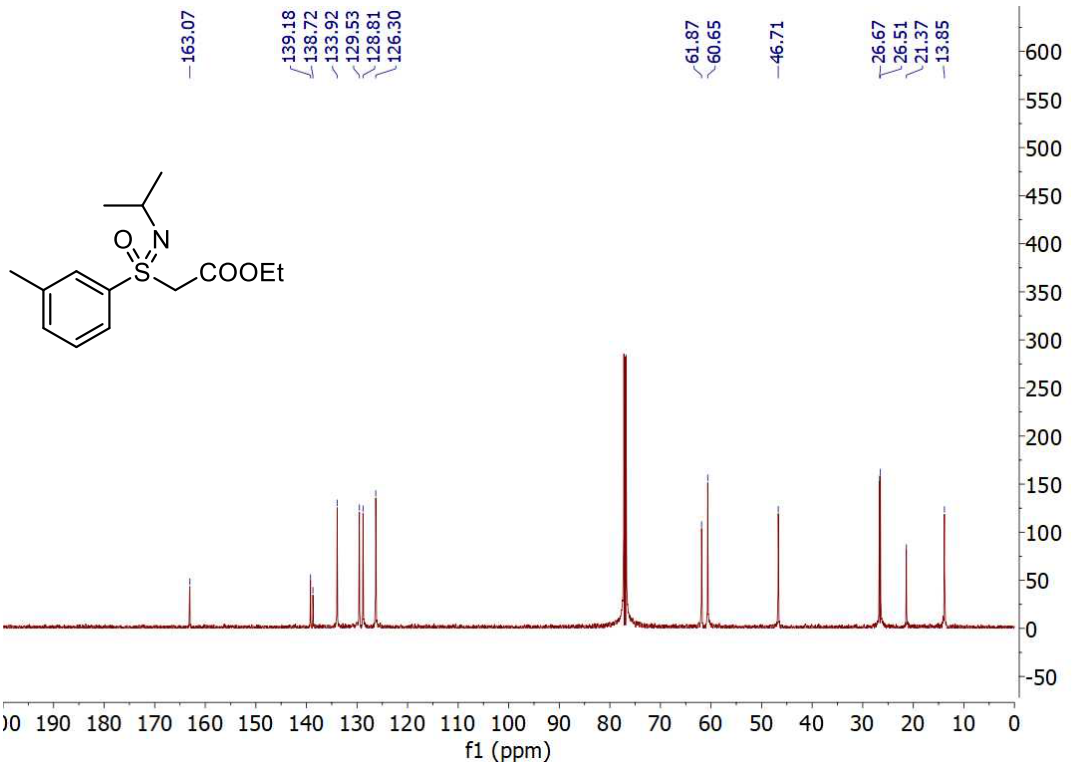


ethyl 2-(*N*-isopropyl-3-methylphenylsulfonimidoyl)acetate (3g)

[1]**H NMR** (600 MHz, Chloroform-*d*)

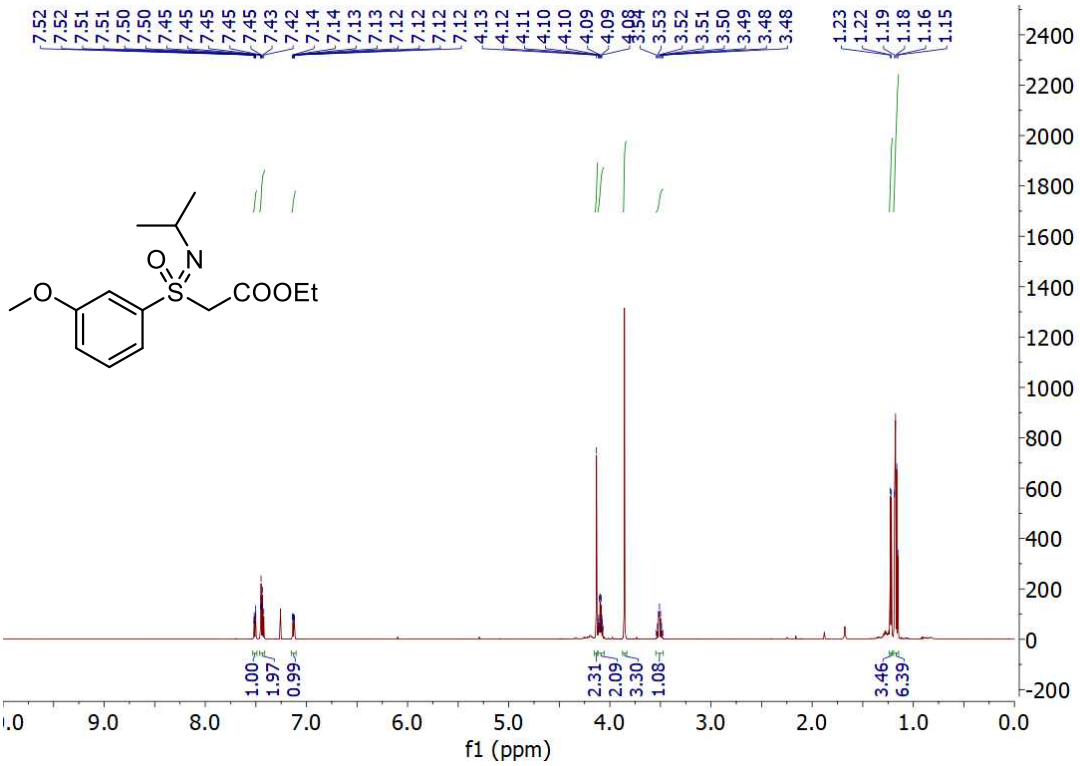


[13]**C NMR** (151 MHz, Chloroform-*d*)

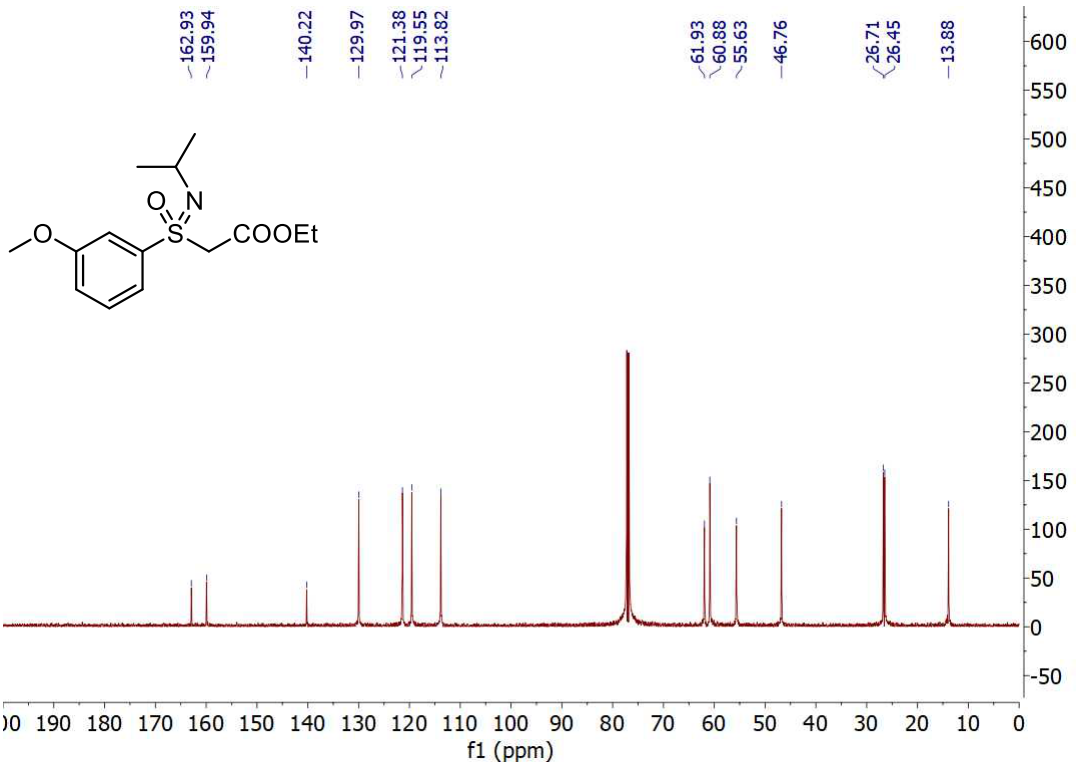


ethyl 2-(*N*-isopropyl-3-methoxyphenylsulfonimidoyl)acetate (3h)

^{1}**H NMR** (600 MHz, Chloroform-*d*)

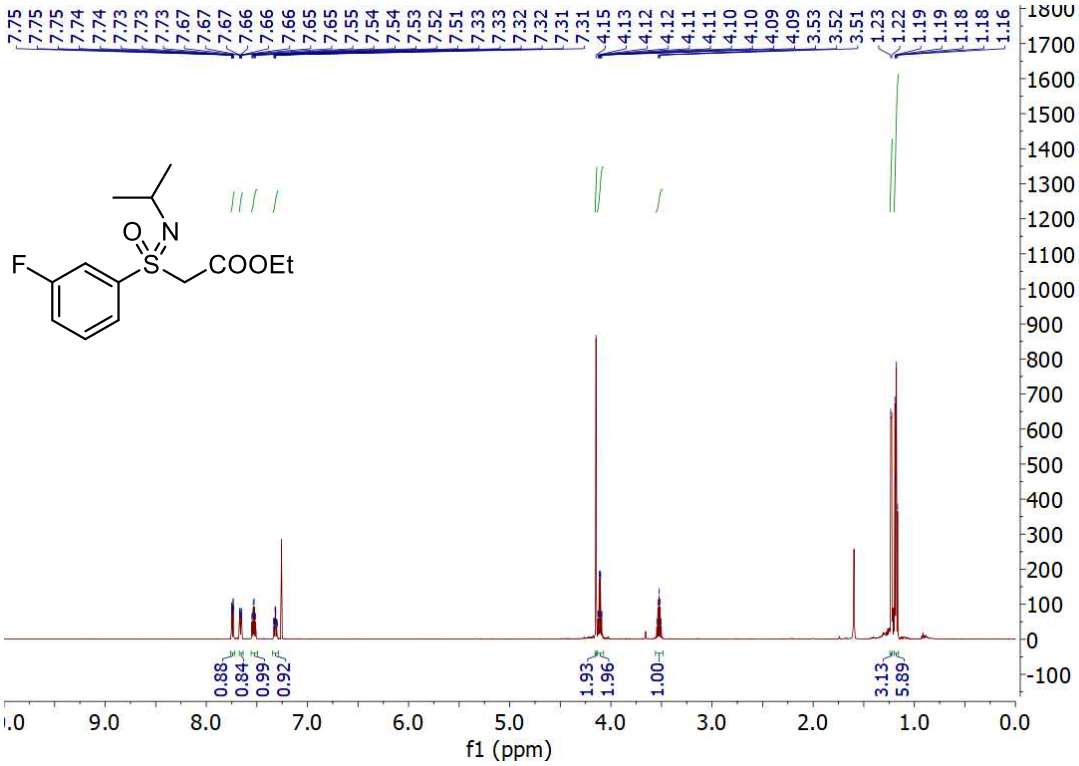


^{13}**C NMR** (151 MHz, Chloroform-*d*)

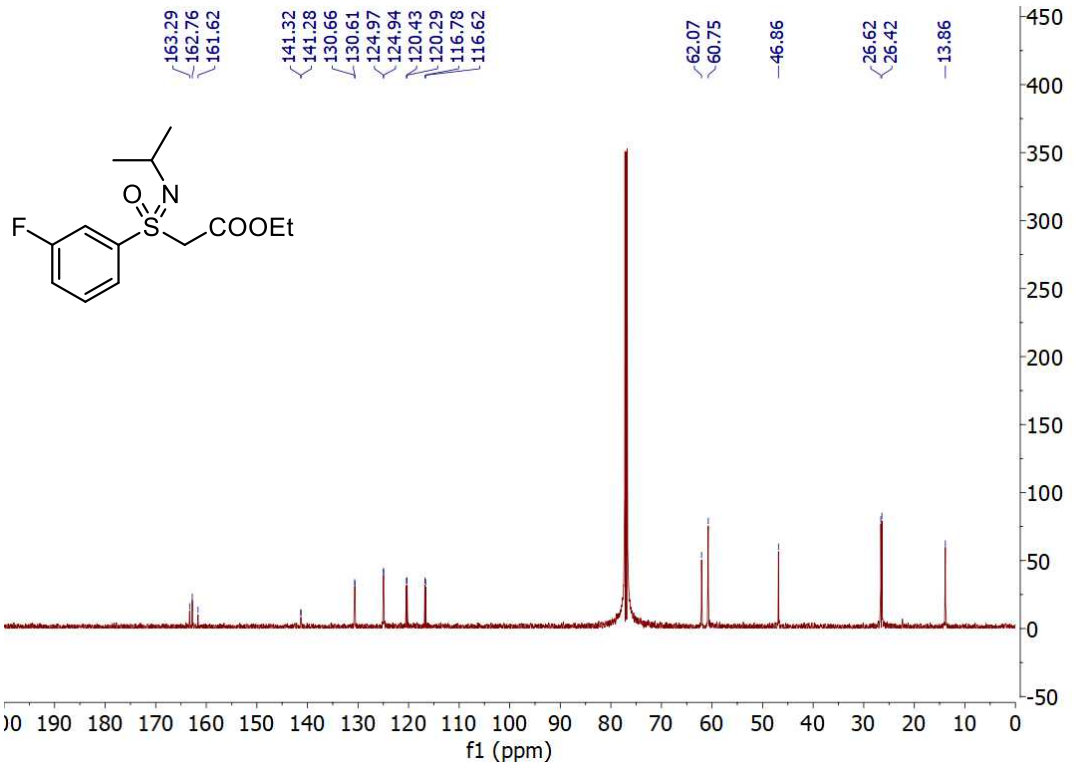


ethyl 2-(3-fluoro-*N*-isopropylphenylsulfonimidoyl)acetate (3i)

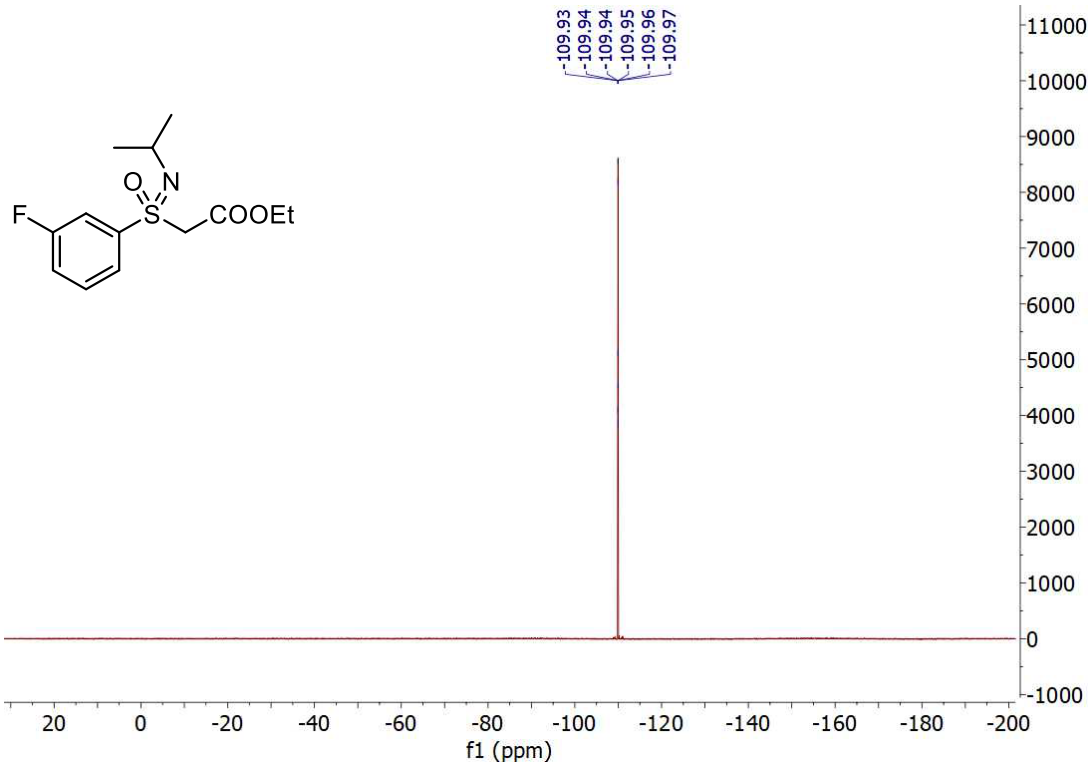
^{1}H NMR (600 MHz, Chloroform-*d*)



^{13}C NMR (151 MHz, Chloroform-*d*)

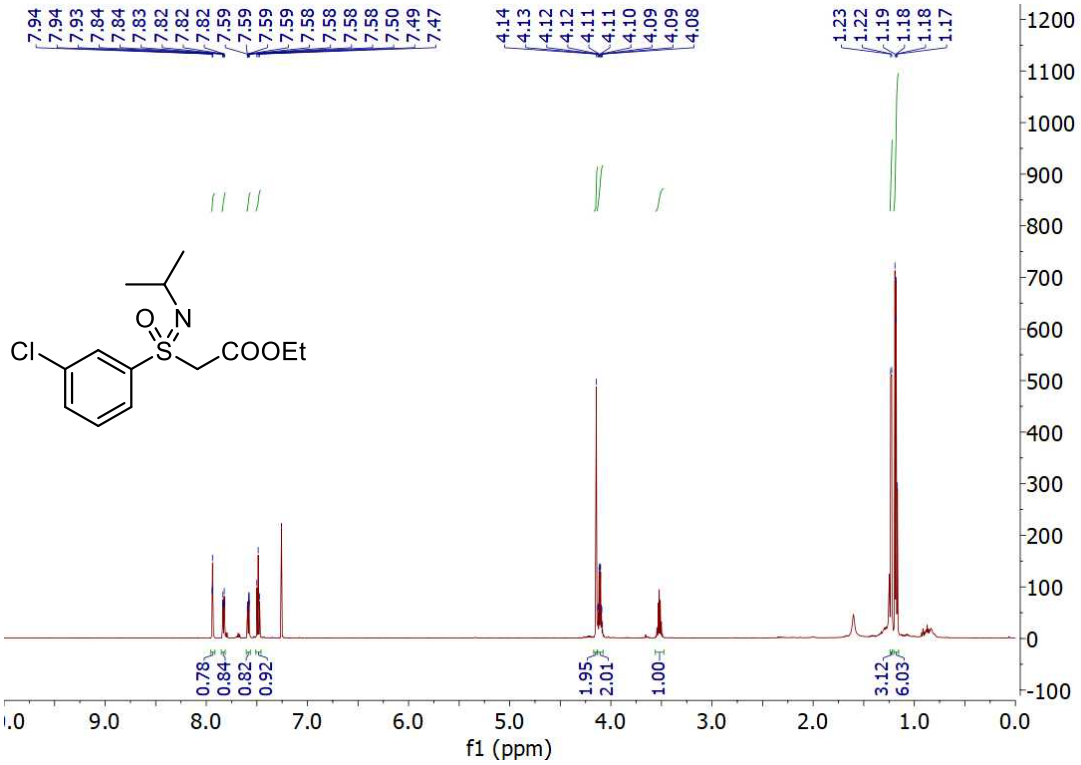


^{19}F NMR (564 MHz, Chloroform-*d*)

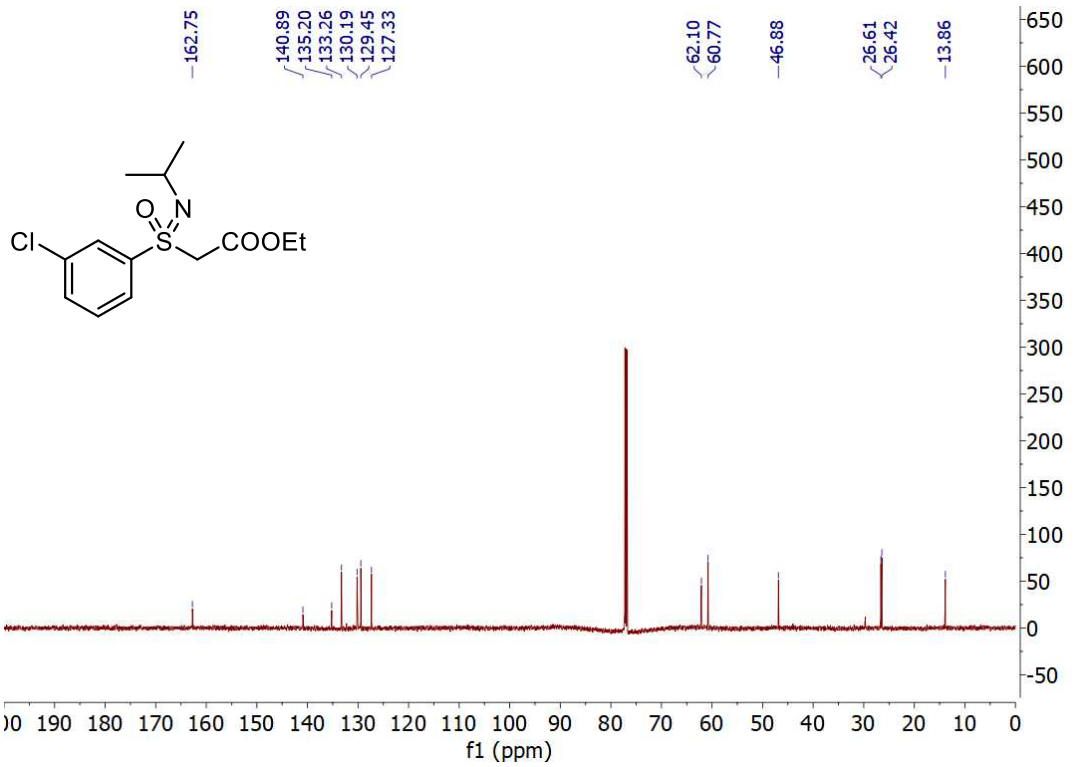


ethyl 2-(3-chloro-*N*-isopropylphenylsulfonimidoyl)acetate (3j)

[1]**H NMR** (600 MHz, Chloroform-*d*)

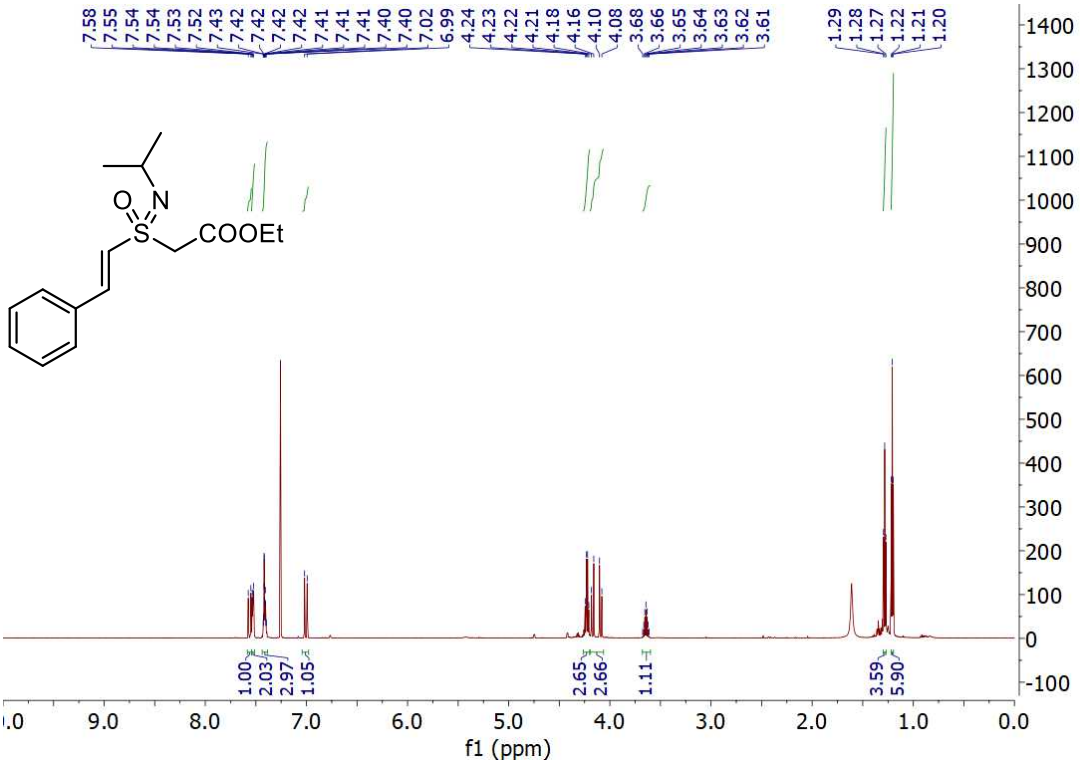


[13]**C NMR** (151 MHz, Chloroform-*d*)

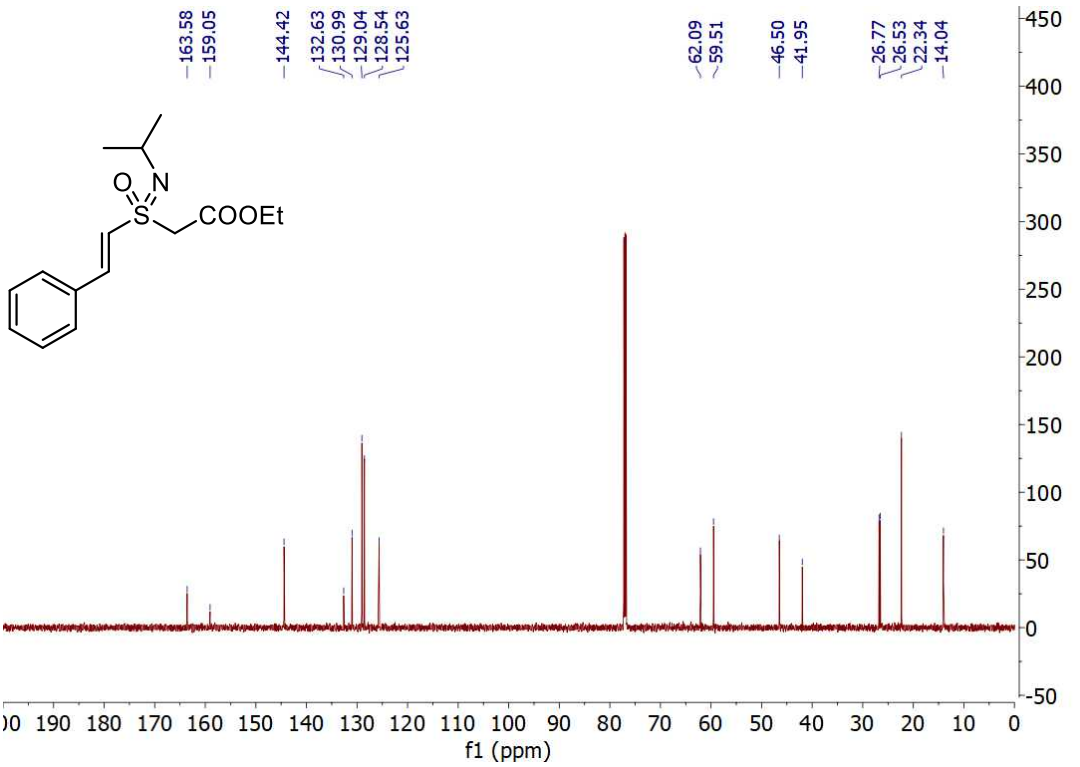


ethyl (*E*)-2-(*N*-isopropyl-2-phenylvinylsulfonimidoyl)acetate (3k)

^{1}**H NMR** (600 MHz, Chloroform-*d*)

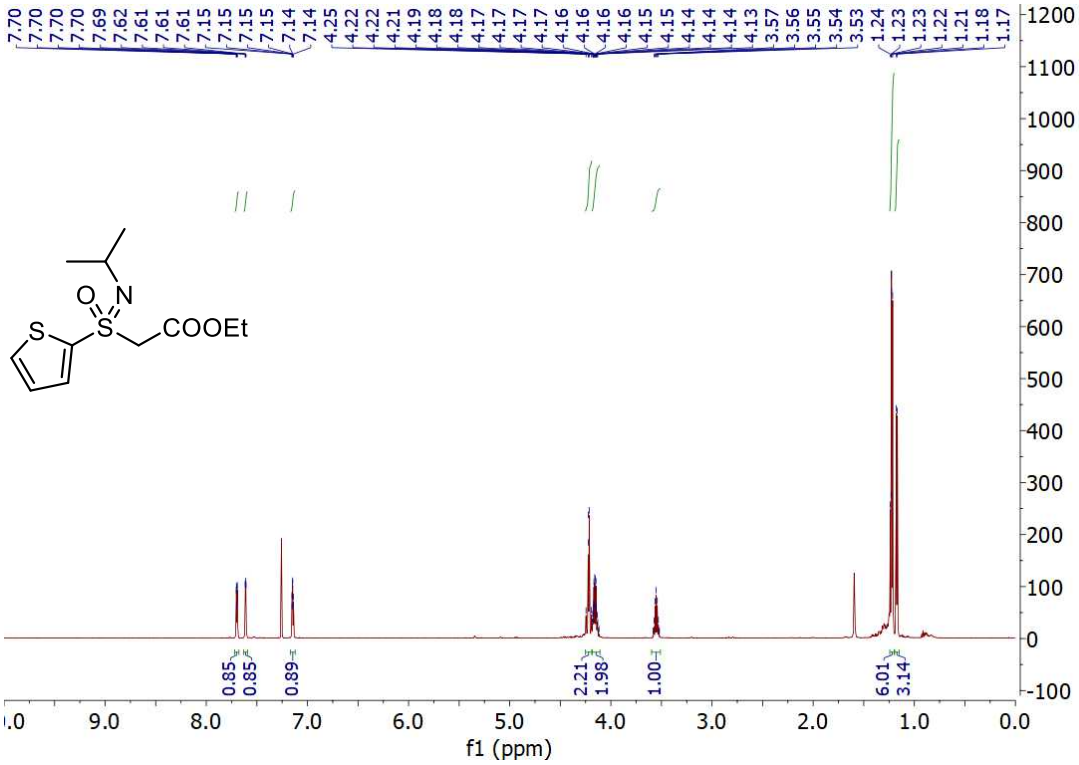


^{13}**C NMR** (151 MHz, Chloroform-*d*)

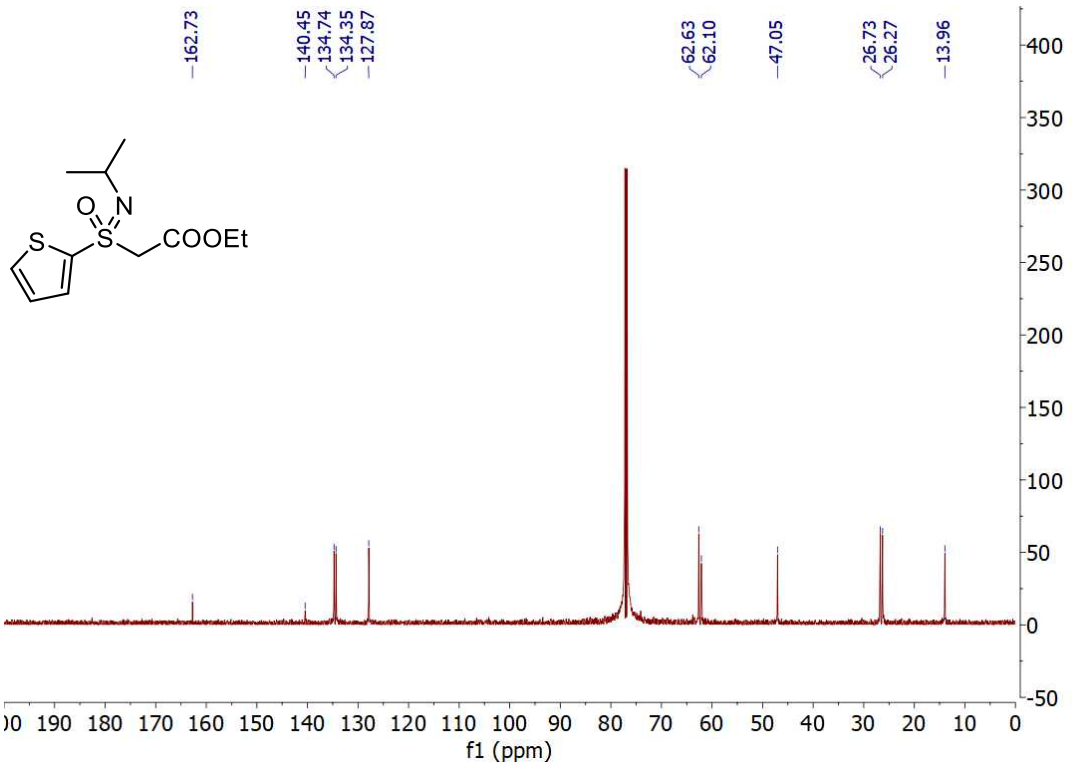


ethyl 2-(*N*-isopropylthiophene-2-sulfonimidoyl)acetate (3l)

^{1}**H NMR** (600 MHz, Chloroform-*d*)

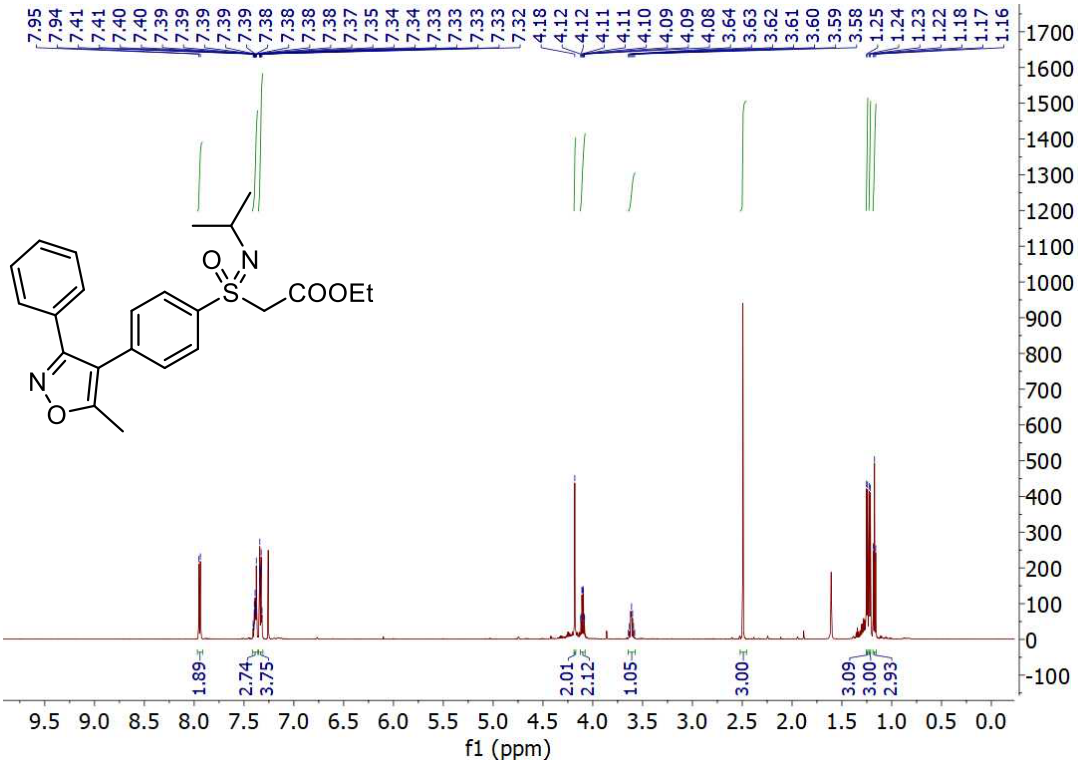


^{13}**C NMR** (151 MHz, Chloroform-*d*)

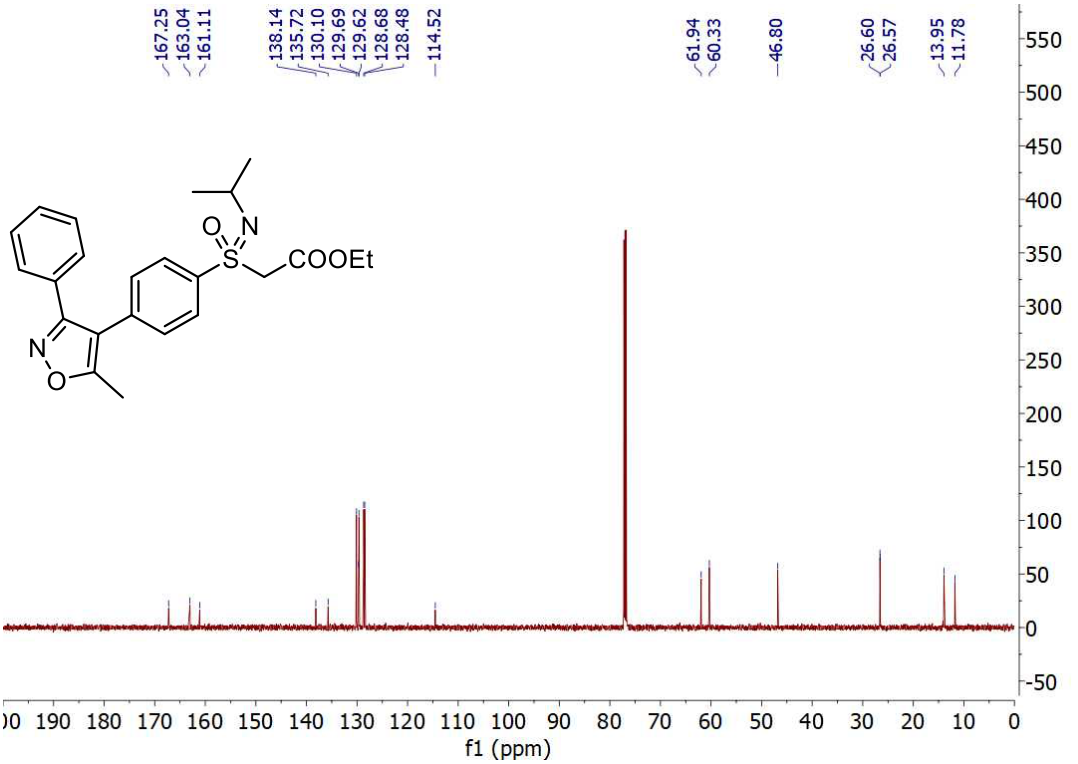


ethyl 2-(*N*-isopropyl-4-(5-methyl-3-phenylisoxazol-4-yl)phenylsulfonimidoyl)acetate (3m)

[1]**H NMR** (600 MHz, Chloroform-*d*)

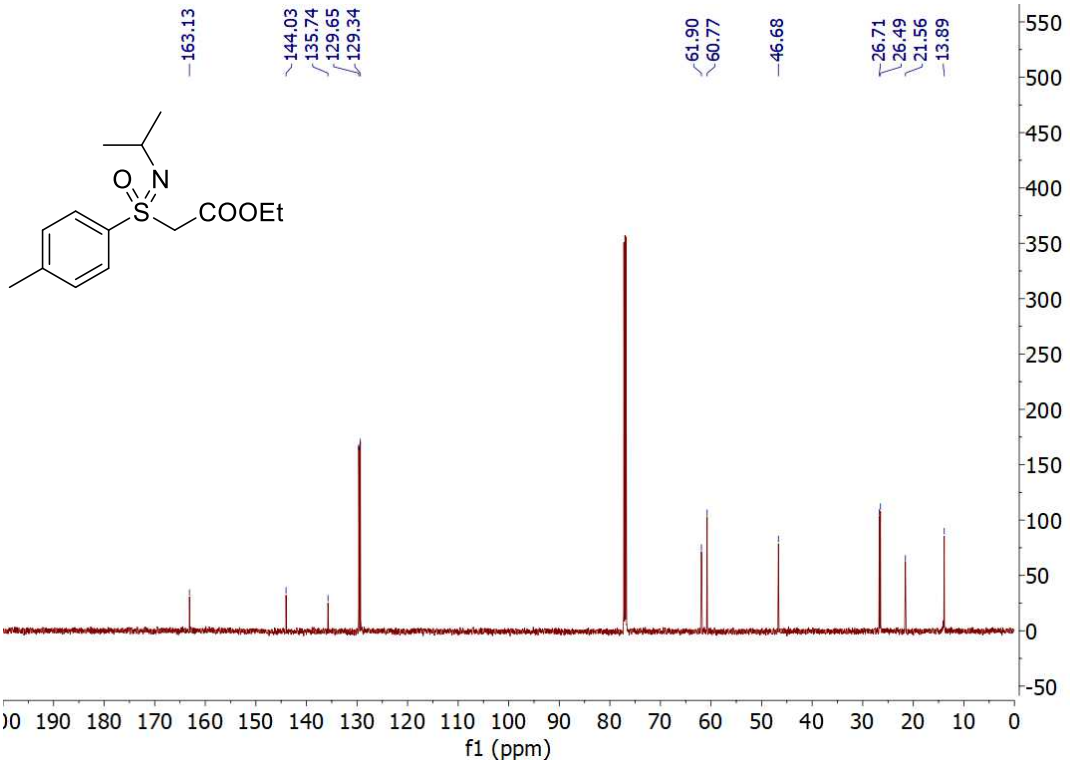


[13]**C NMR** (151 MHz, Chloroform-*d*)

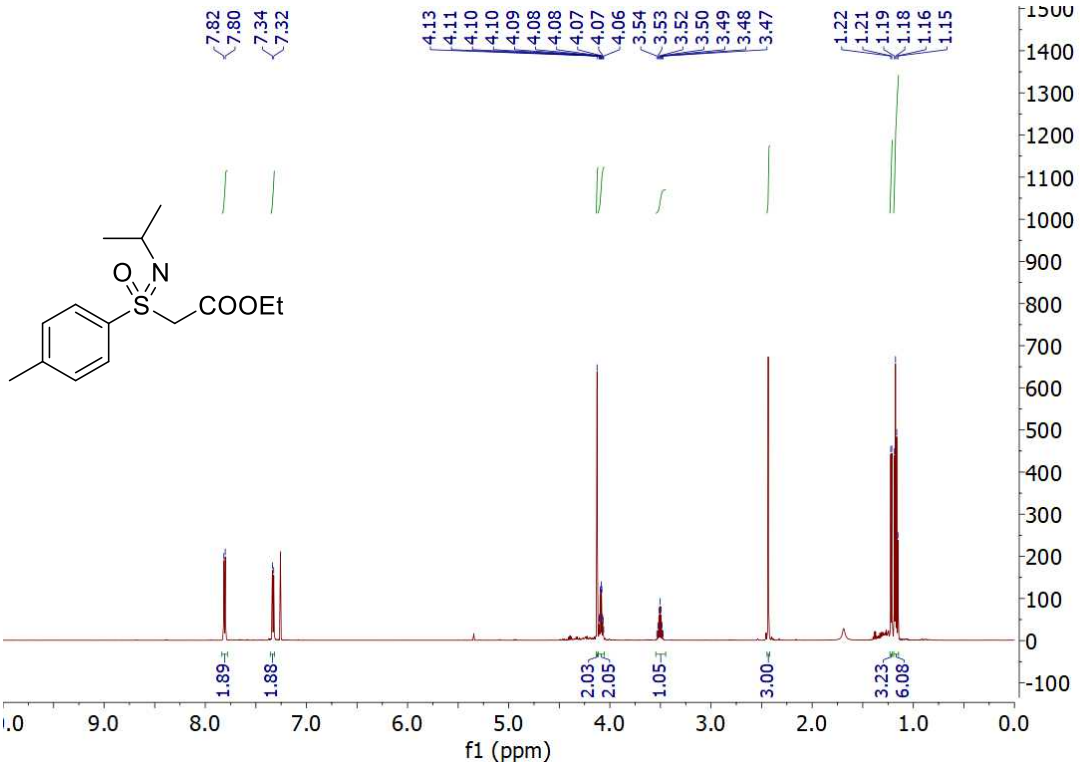


ethyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)acetate (3n)

[1]**H NMR** (600 MHz, Chloroform-*d*):

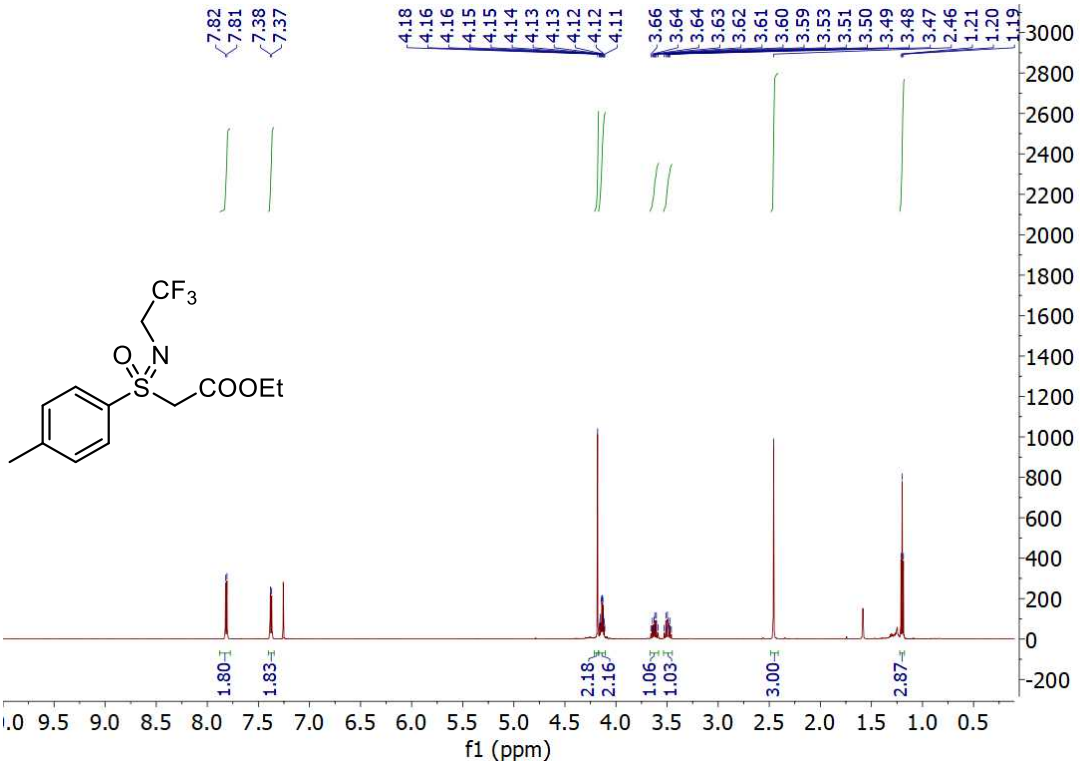


[13]**C NMR** (151 MHz, Chloroform-*d)*

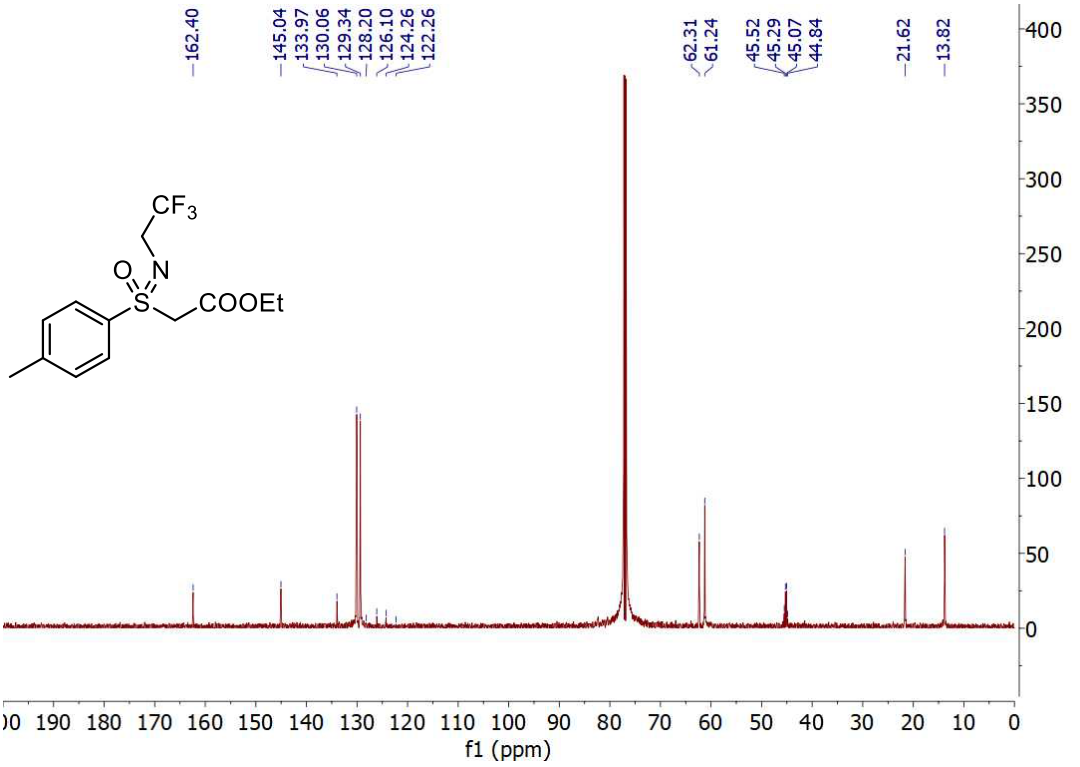


ethyl 2-(4-methyl-*N*-(2,2,2-trifluoroethyl)phenylsulfonimidoyl)acetate (3o)

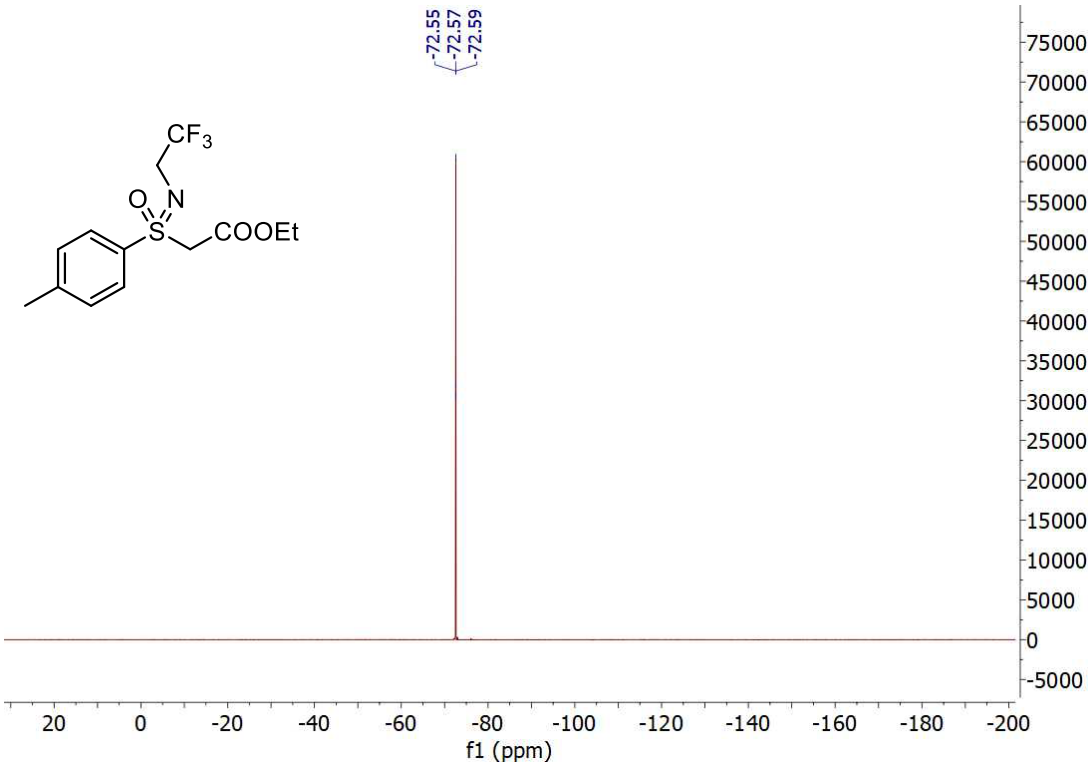
[1]**H NMR** (600 MHz, Chloroform-*d*)



[13]**C NMR** (151 MHz, Chloroform-*d*)

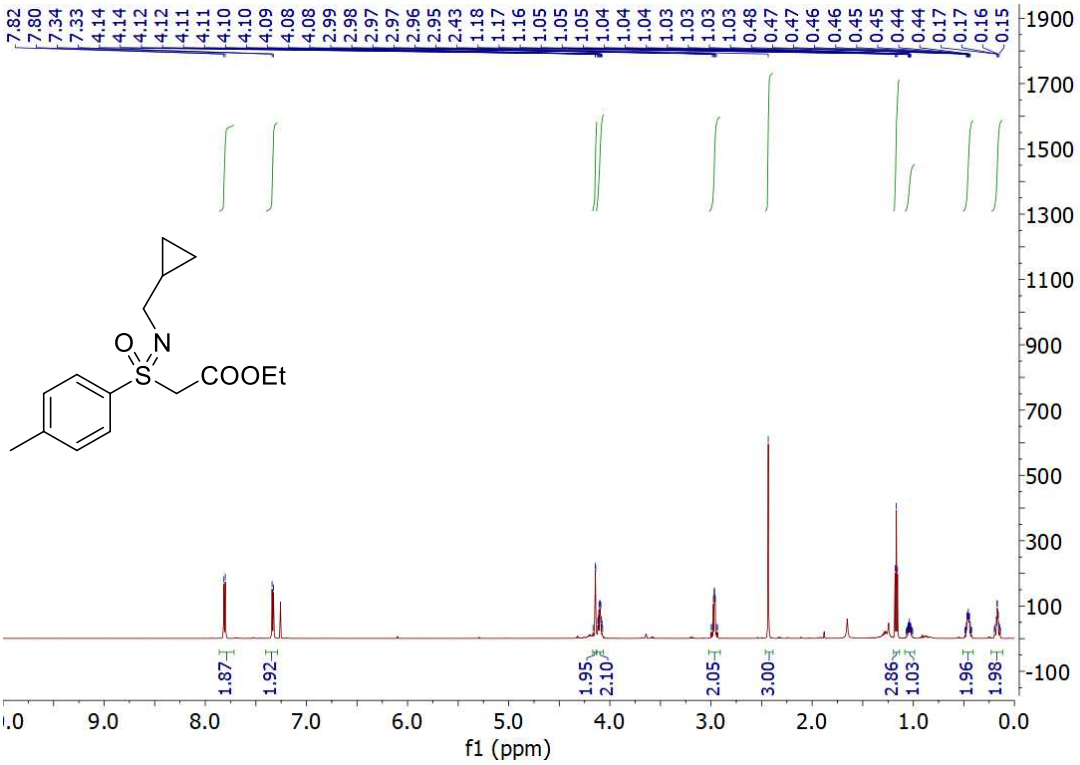


^{19}F NMR (564 MHz, Chloroform-*d*)

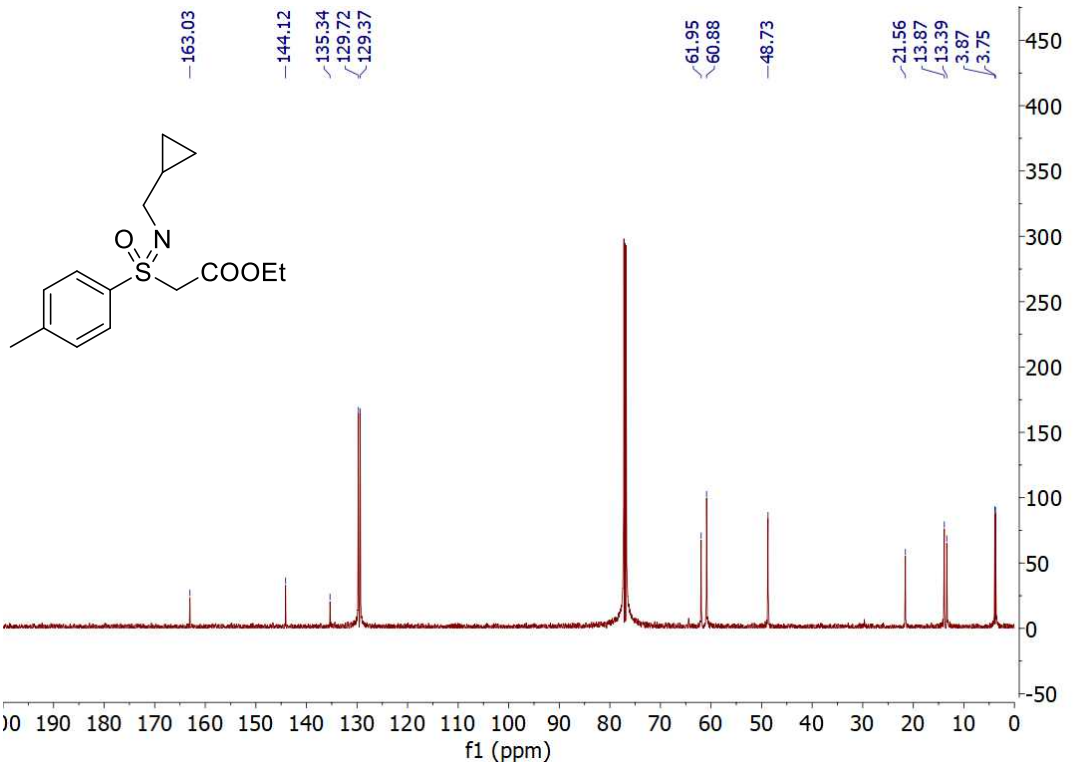


ethyl 2-(*N*-(cyclopropylmethyl)-4-methylphenylsulfonimidoyl)acetate (3p)

[1]**H NMR** (600 MHz, Chloroform-*d*)

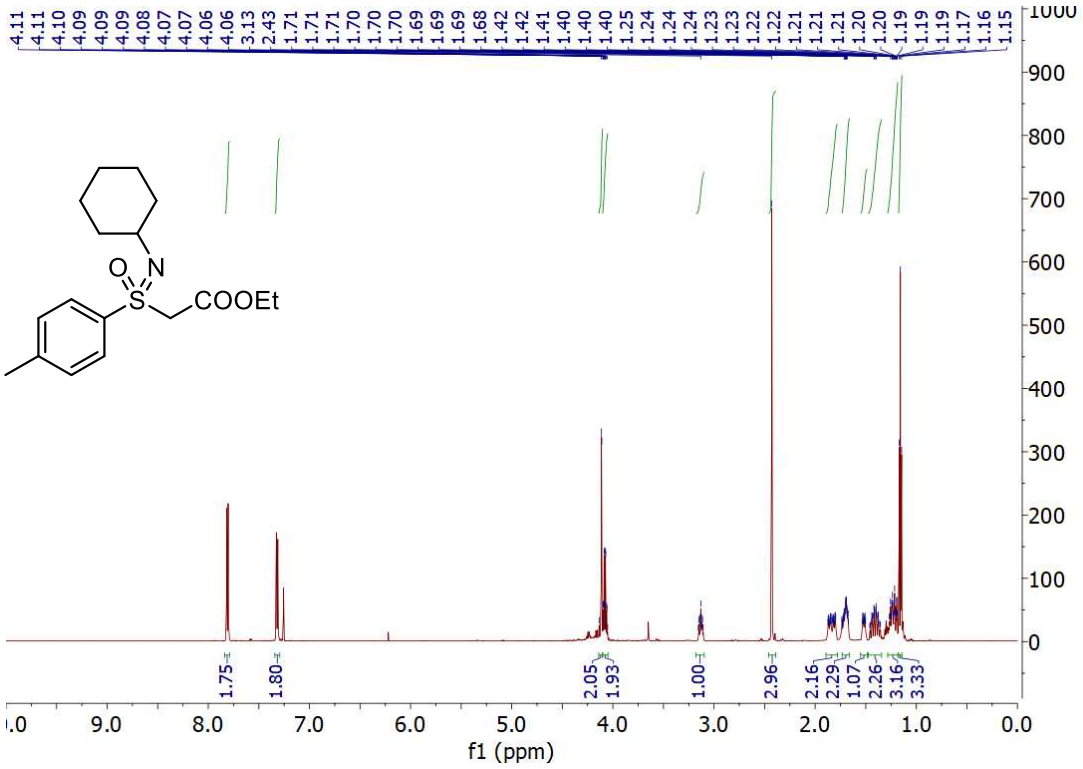


[13]**C NMR** (151 MHz, Chloroform-*d*)

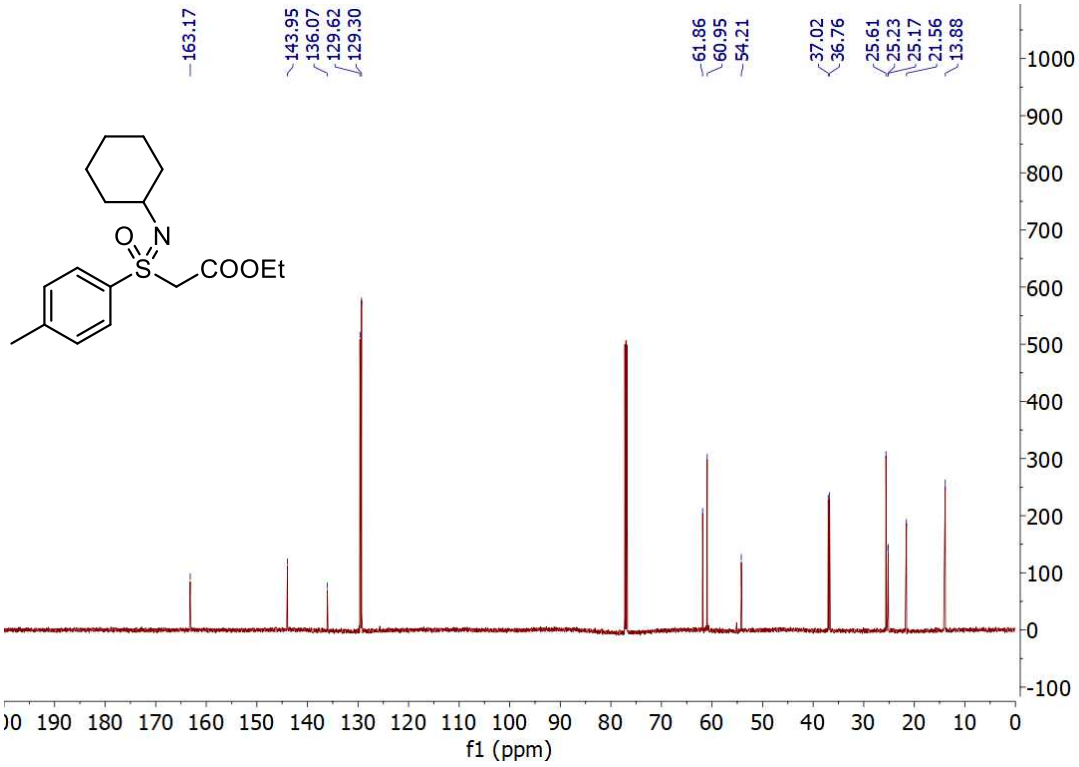


ethyl 2-(*N*-cyclohexyl-4-methylphenylsulfonimidoyl)acetate (3q)

[1]**H NMR** (600 MHz, Chloroform-*d*)

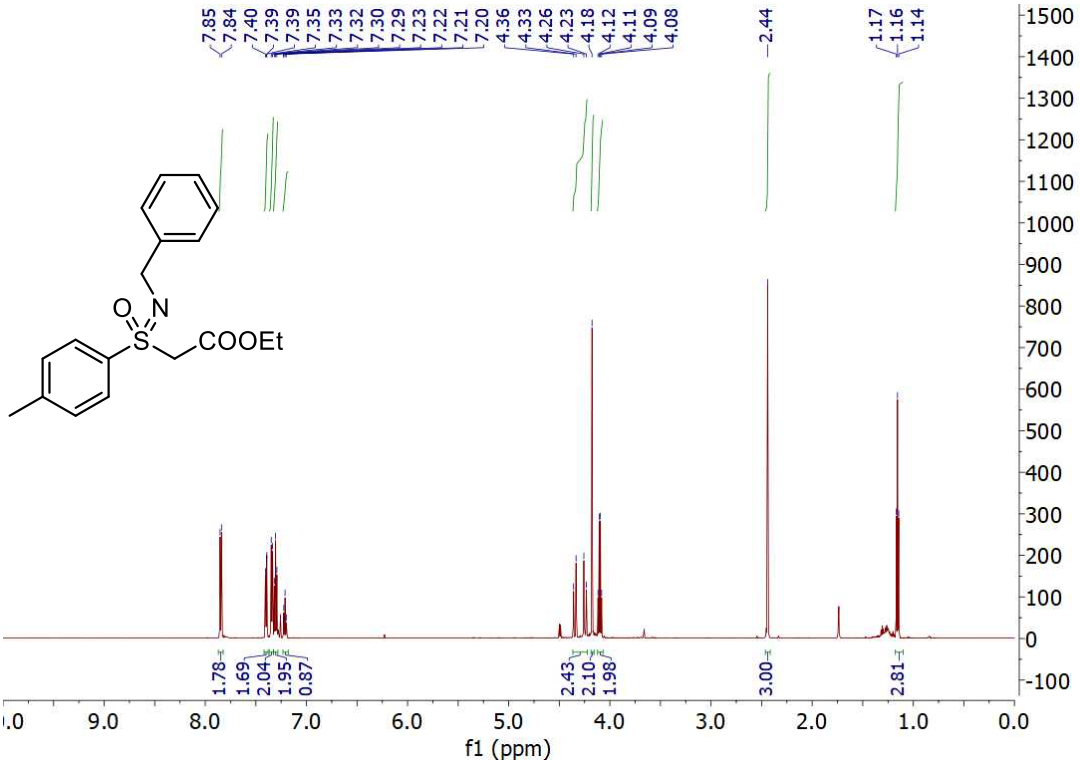


[13]**C NMR** (151 MHz, Chloroform-*d*)

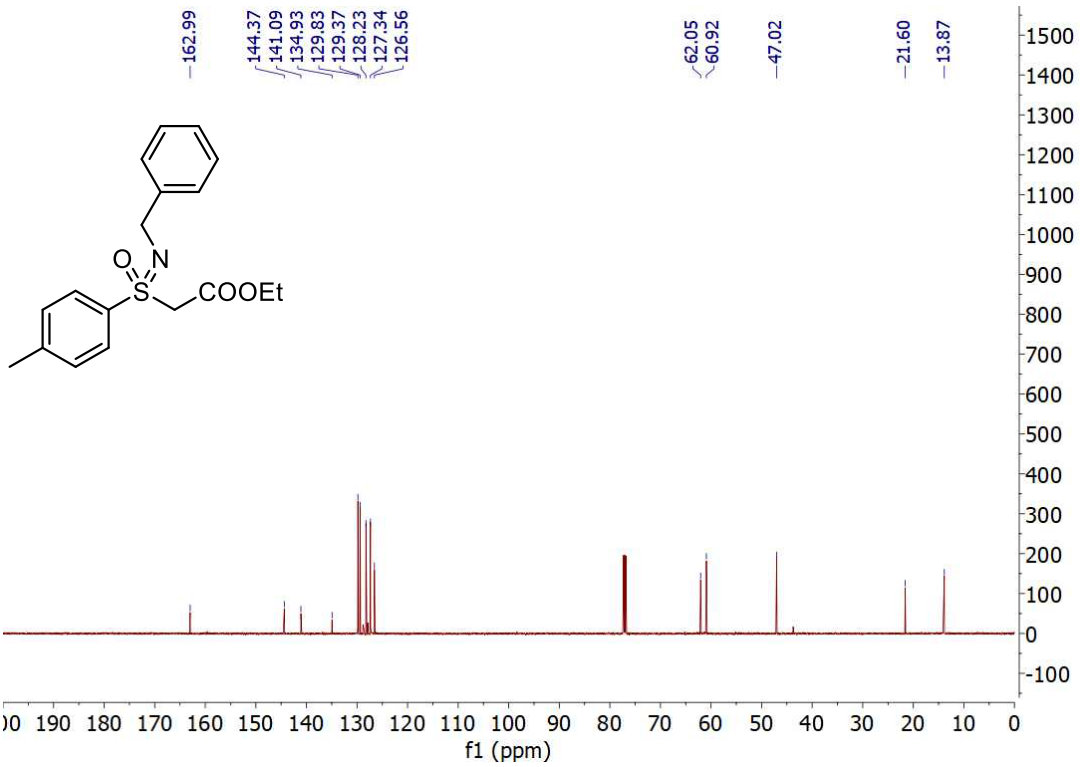


ethyl 2-(*N*-benzyl-4-methylphenylsulfonimidoyl)acetate (3r)

[1]**H NMR** (600 MHz, Chloroform-*d*)

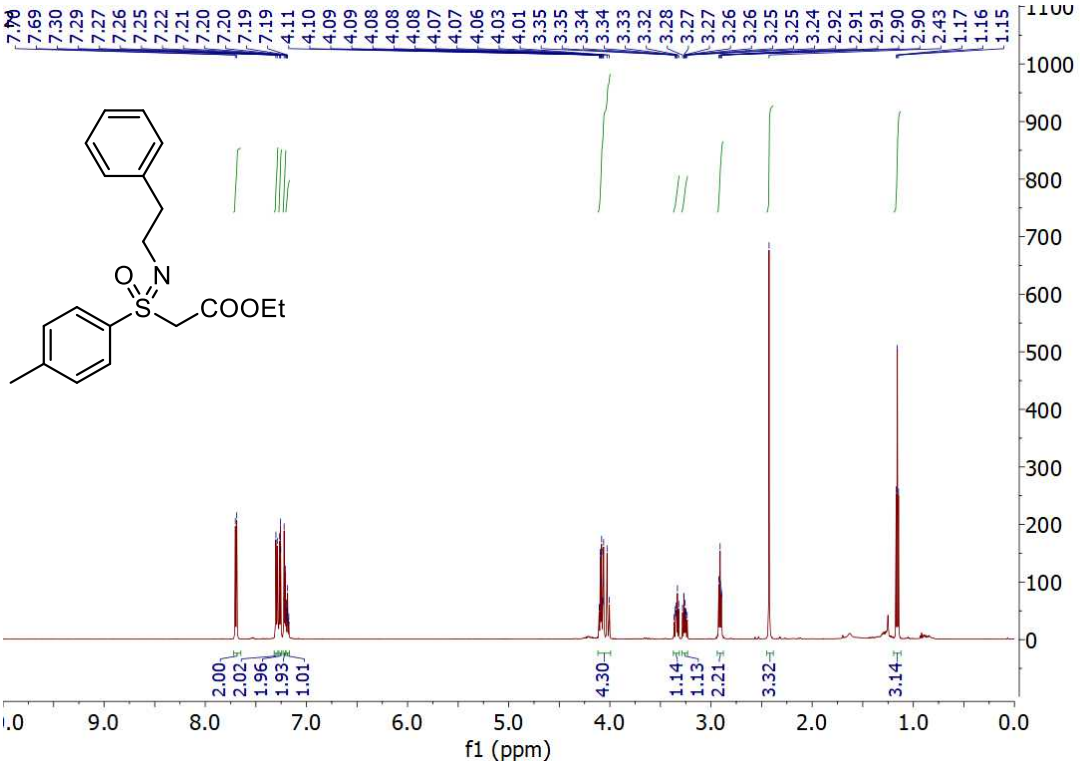


[13]**C NMR** (151 MHz, Chloroform-*d*)

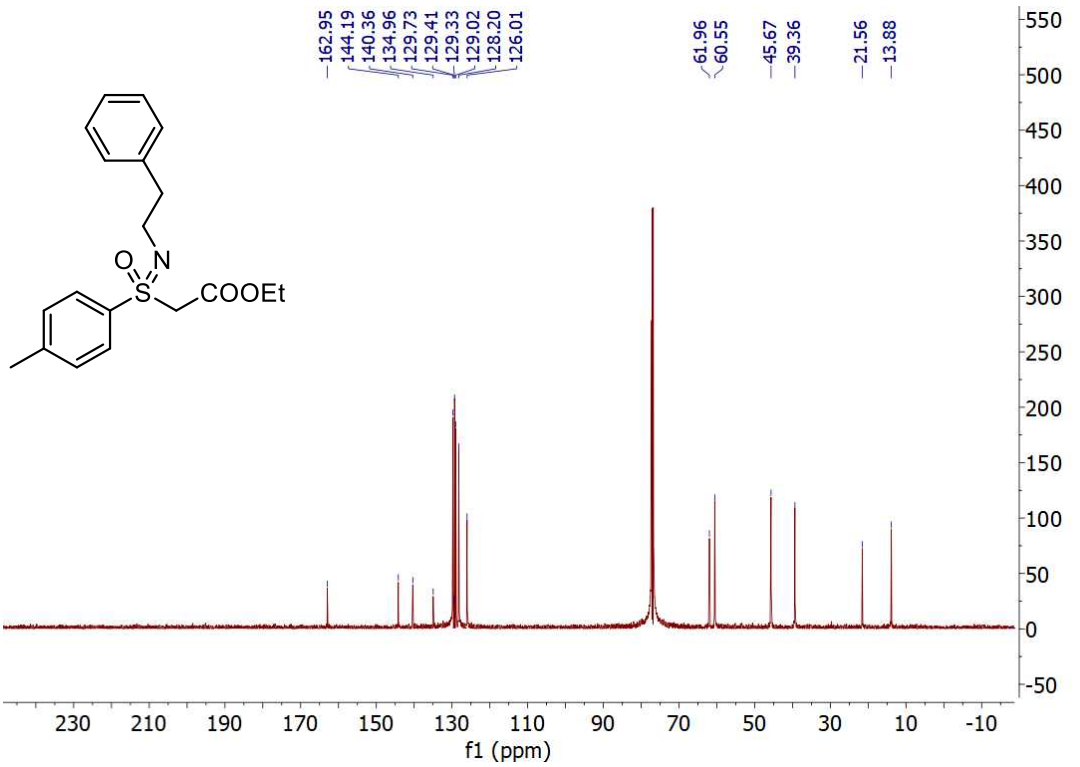


ethyl 2-(4-methyl-*N*-phenethylphenylsulfonimidoyl)acetate (3s)

[1]**H NMR** (600 MHz, Chloroform-*d*)

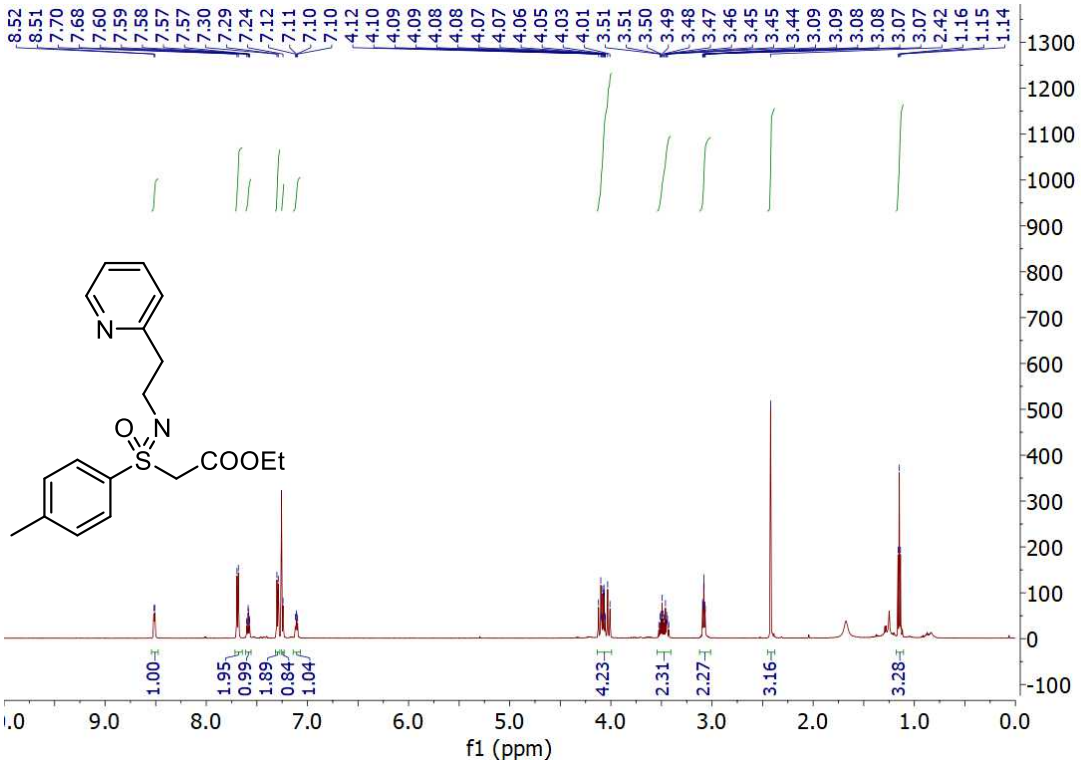


[13]**C NMR** (151 MHz, Chloroform-*d*)

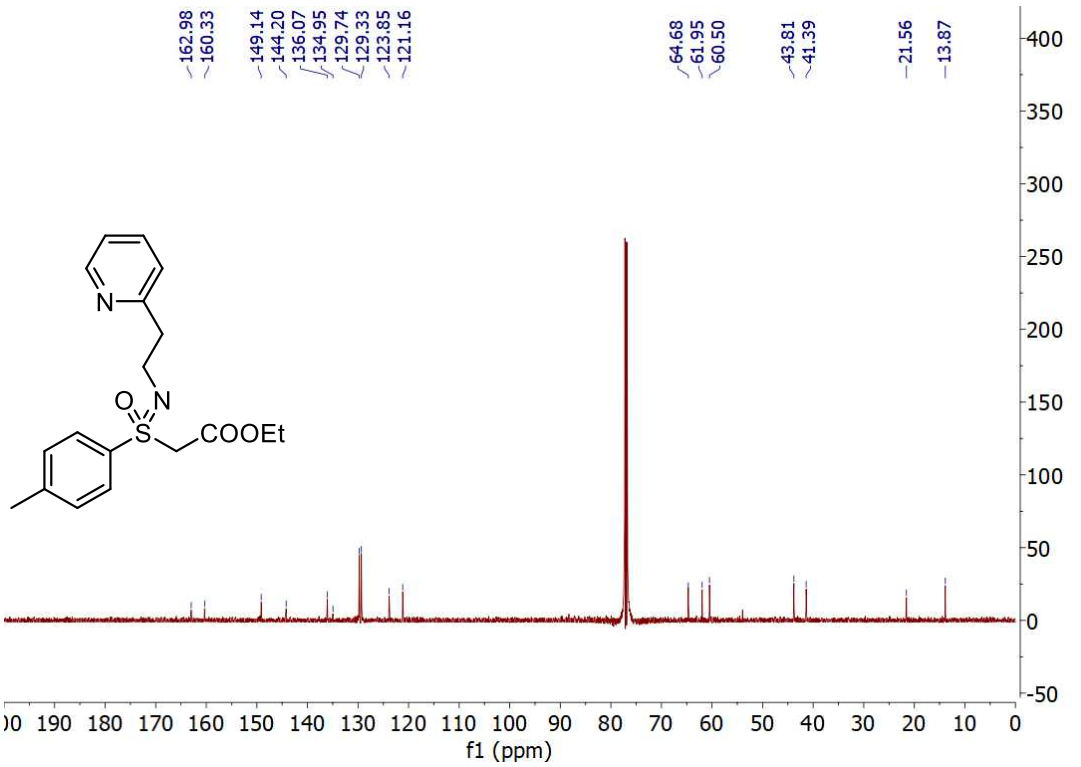


ethyl 2-(4-methyl-*N*-(2-(pyridin-2-yl)ethyl)phenylsulfonimidoyl)acetate (3t)

^{1}H NMR (600 MHz, Chloroform-*d*)

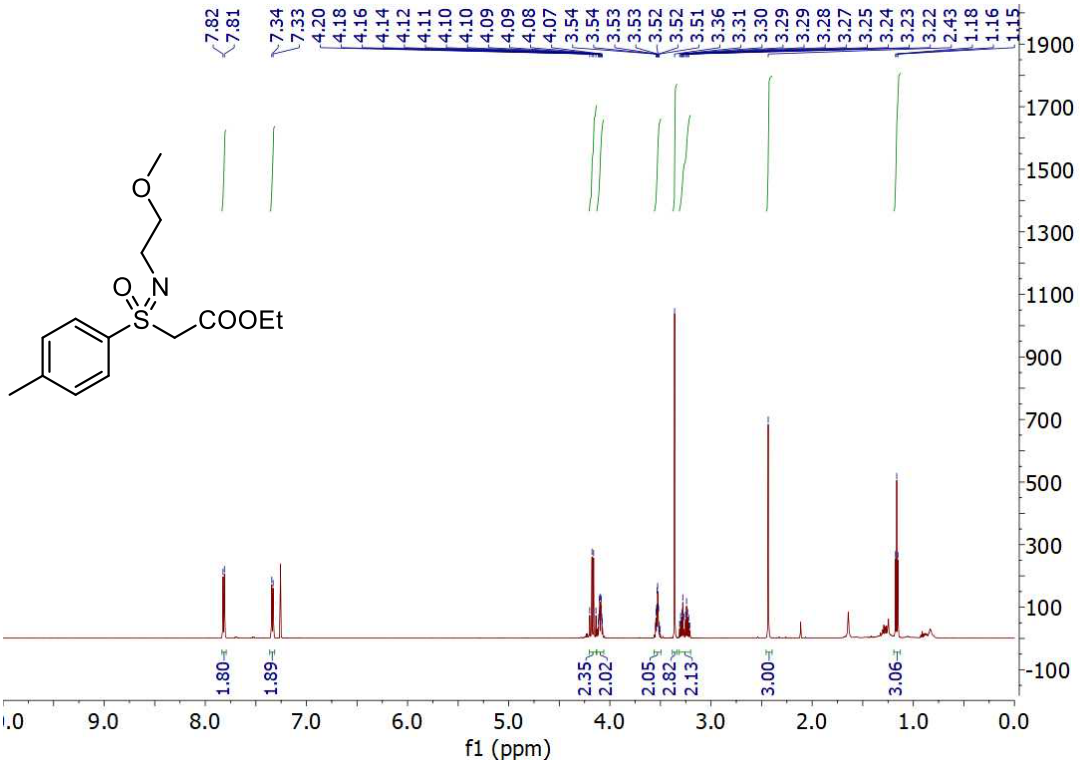


^{13}C NMR (151 MHz, Chloroform-*d*)

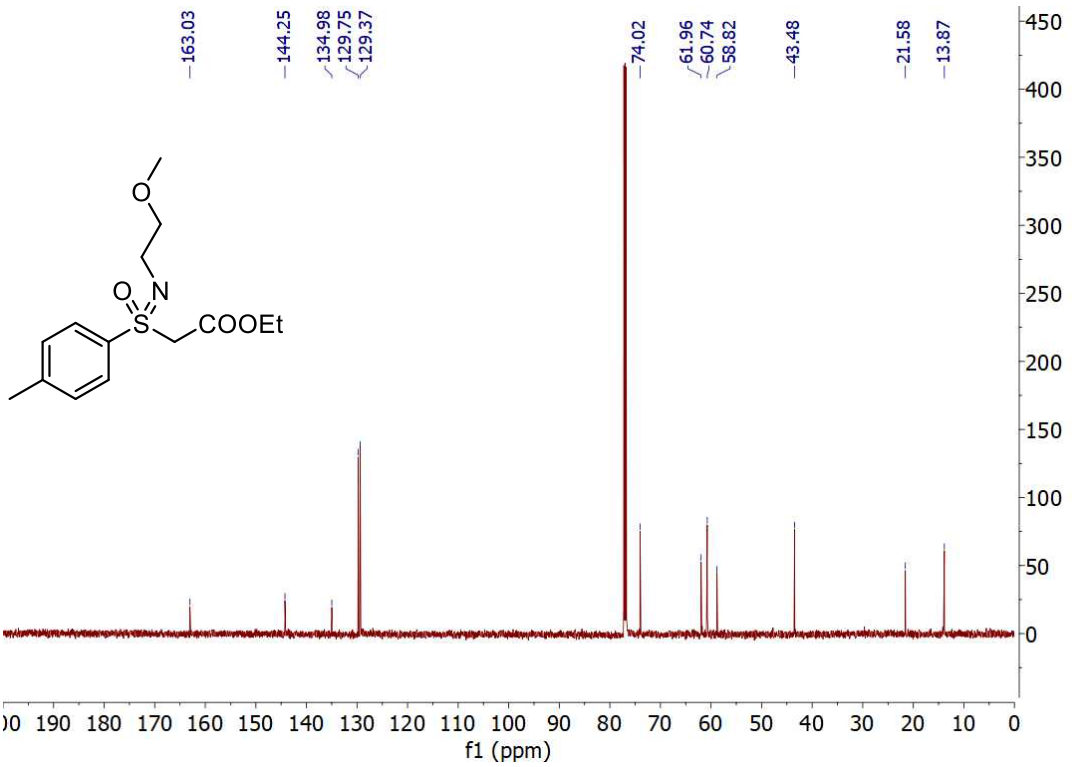


ethyl 2-(*N*-(2-methoxyethyl)-4-methylphenylsulfonimidoyl)acetate (3u)

[1]**H NMR** (600 MHz, Chloroform-*d*)

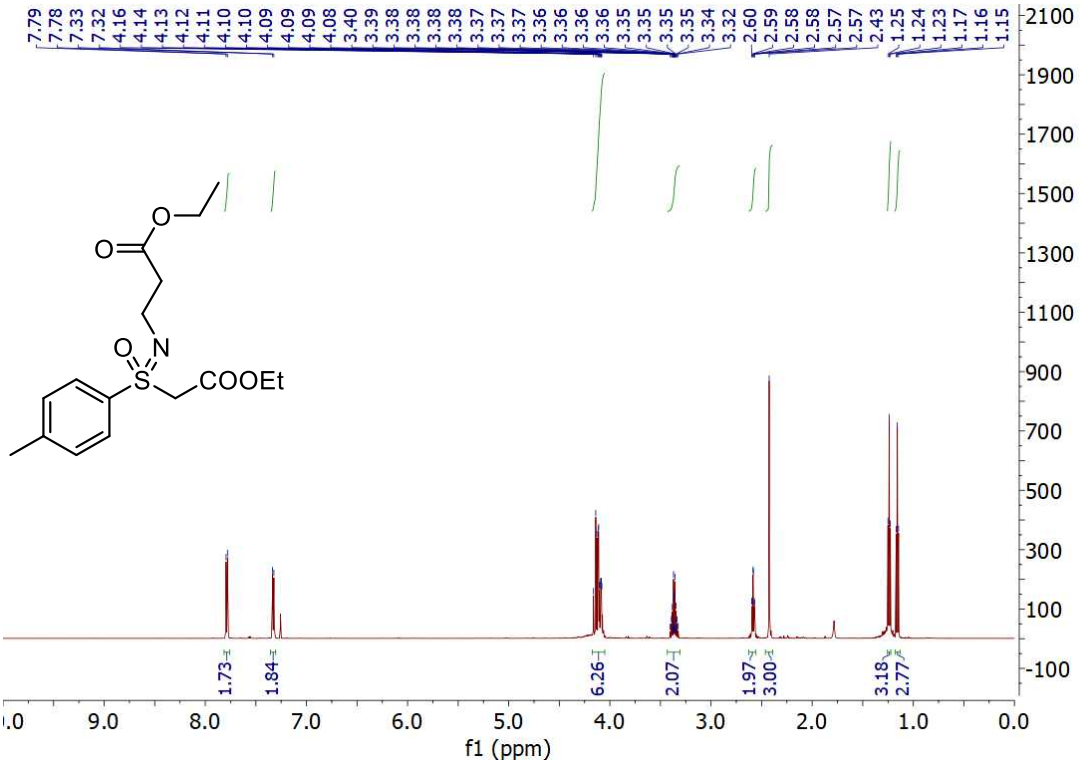


[13]**C NMR** (151 MHz, Chloroform-*d*)

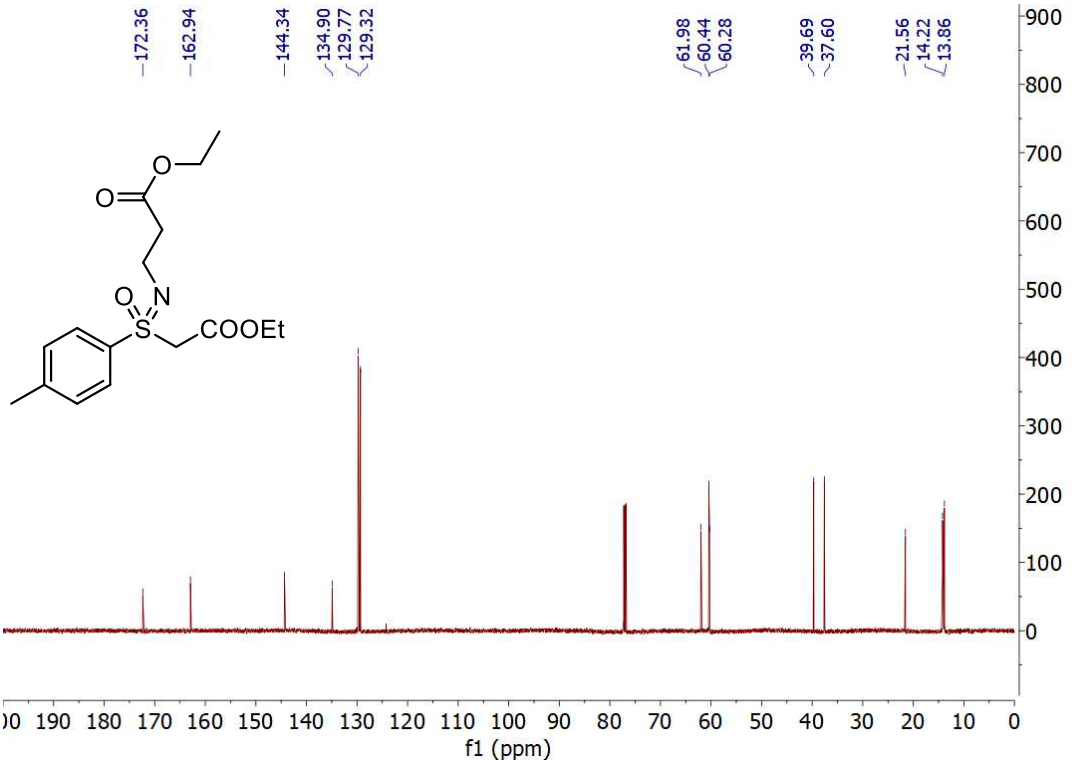


ethyl 3-(((2-ethoxy-2-oxoethyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)amino)propanoate (3v)

^{1}**H NMR** (600 MHz, Chloroform-*d*)

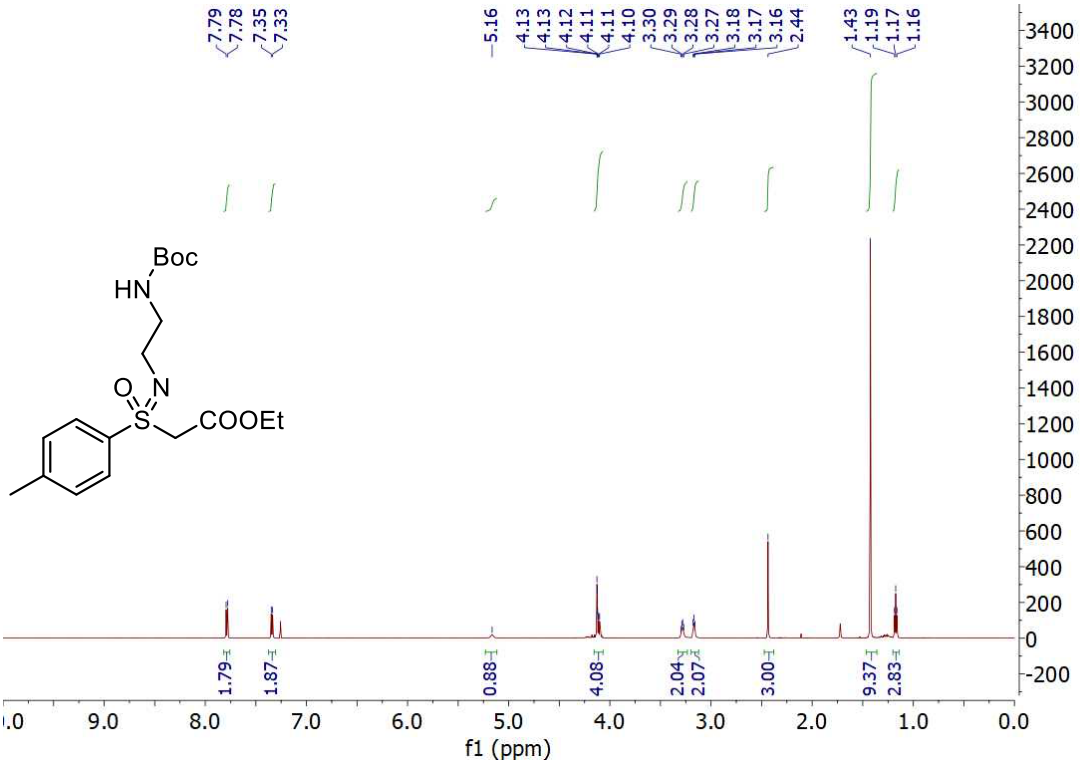


^{13}**C NMR** (151 MHz, Chloroform-*d*)

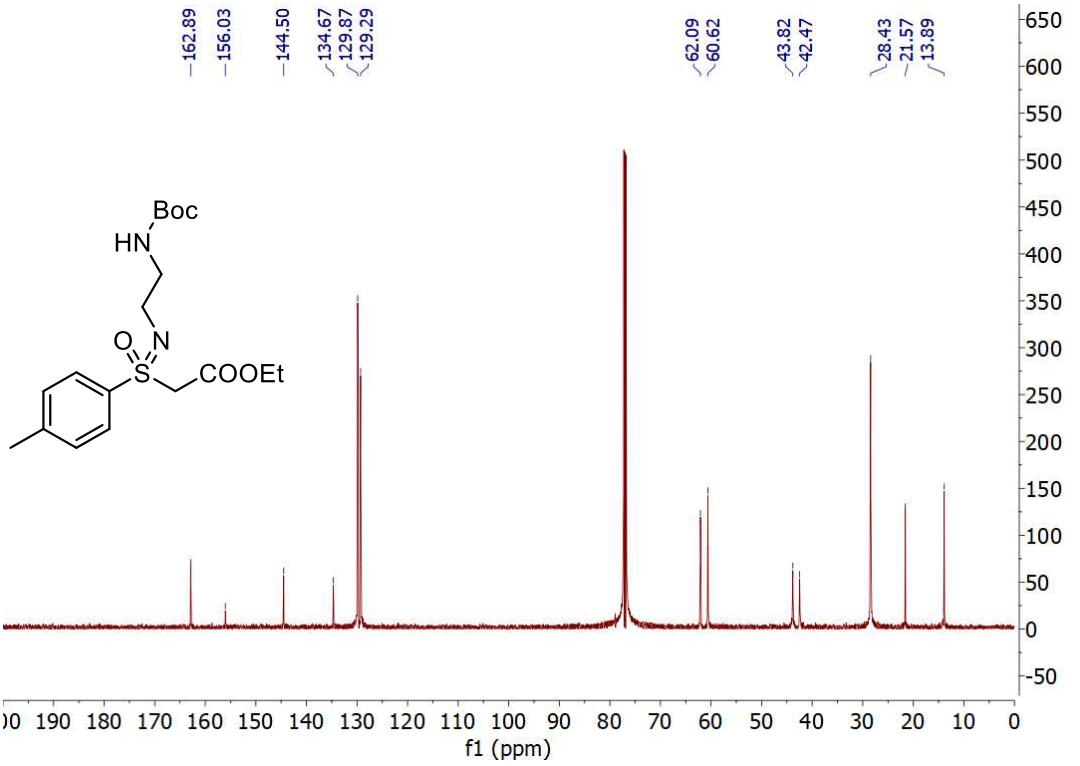


Ethyl 2-(*N*-(2-((tert-butoxycarbonyl)amino)ethyl)-4-methylphenylsulfonimidoyl)acetate (3w)

^{1}**H NMR** (600 MHz, Chloroform-*d*)

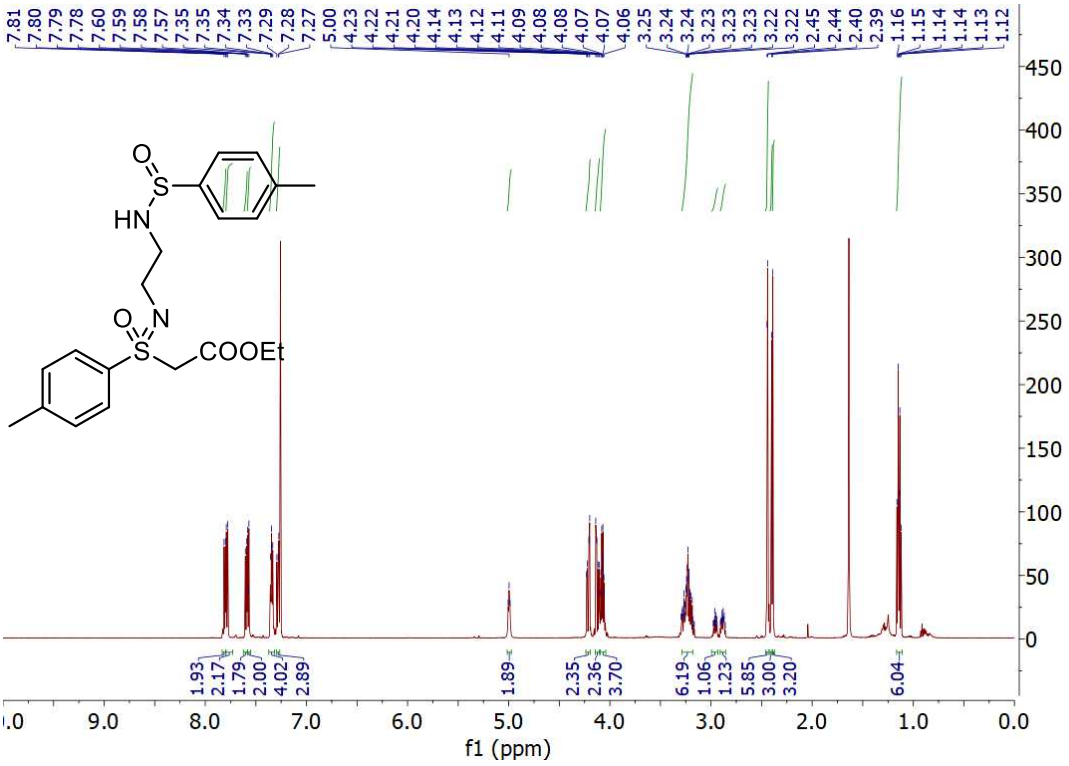


^{13}**C NMR** (151 MHz, Chloroform-*d*)

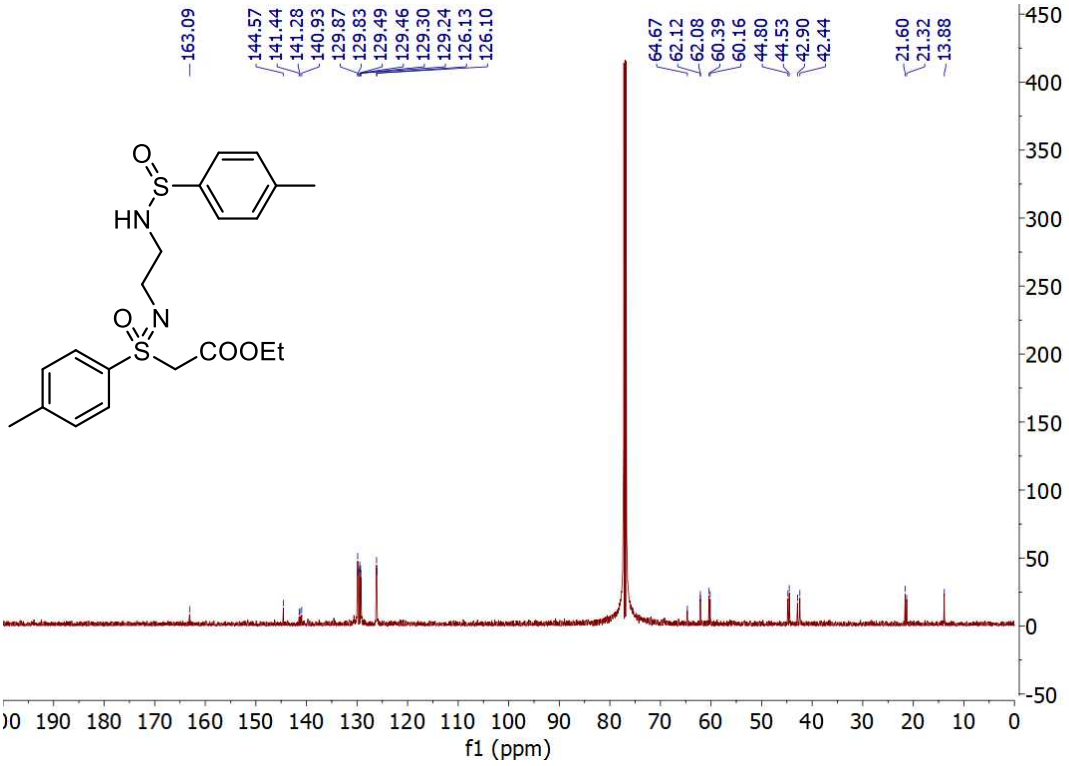


ethyl 2-(4-methyl-*N*-(2-((*p*-tolylsulfinyl)amino)ethyl)phenylsulfonimidoyl)acetate (3x)

[1]**H NMR** (600 MHz, Chloroform-*d*)

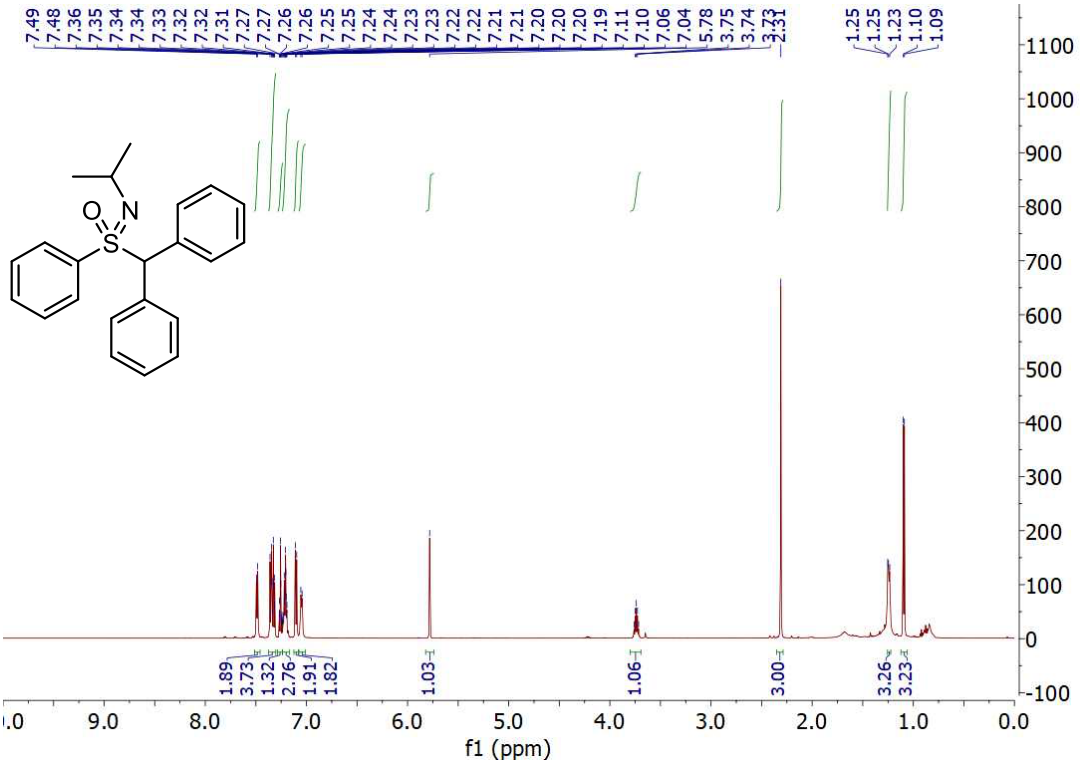


[13]**C NMR** (151 MHz, Chloroform-*d*)

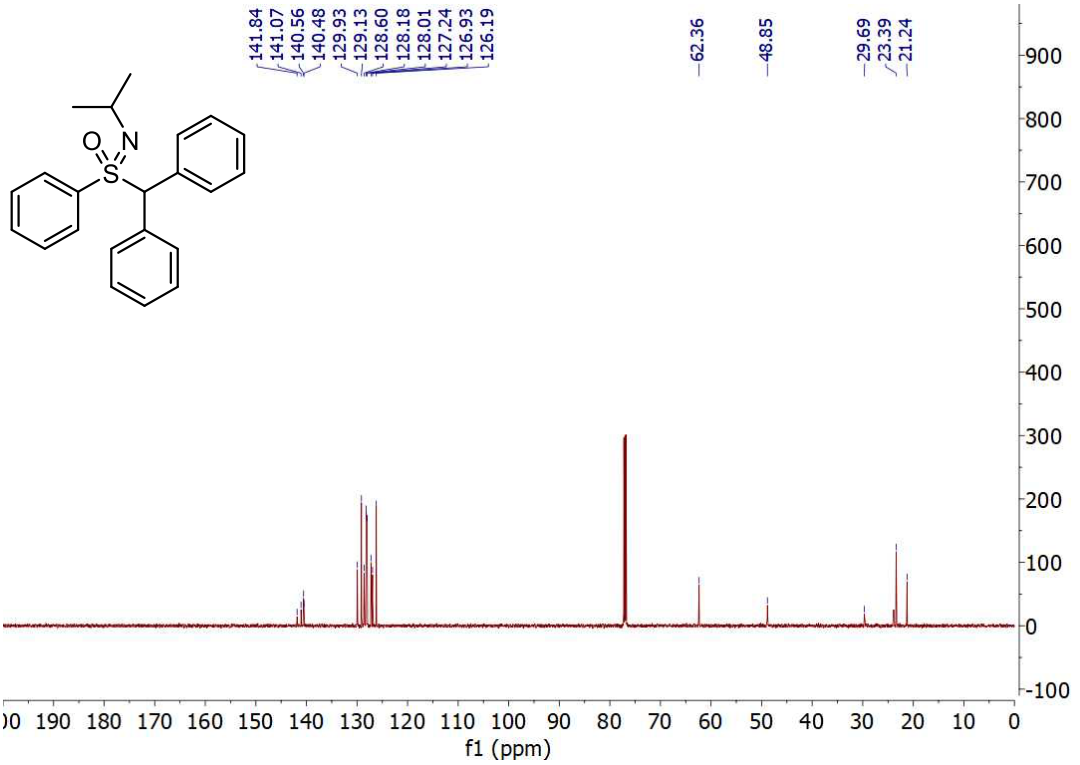


benzhydryl(isopropylimino)(phenyl)-λ⁶-sulfanone (3y)

^{1}H NMR (600 MHz, Chloroform-*d*)

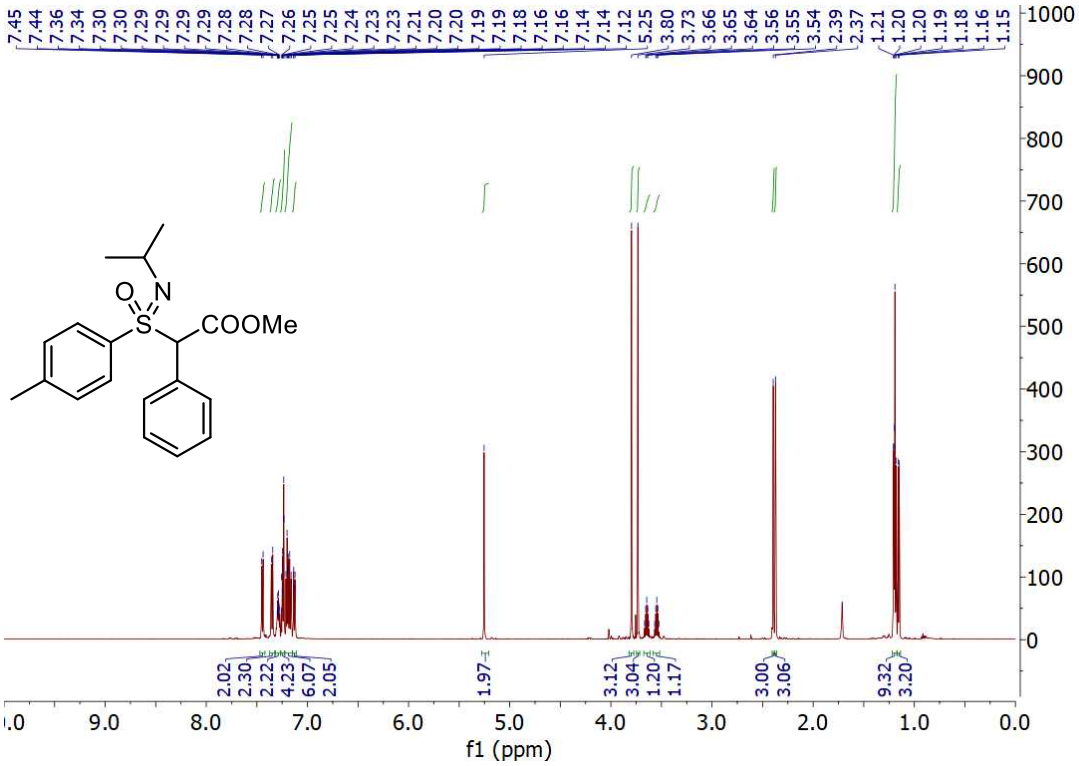


^{13}C NMR (151 MHz, Chloroform-*d*)

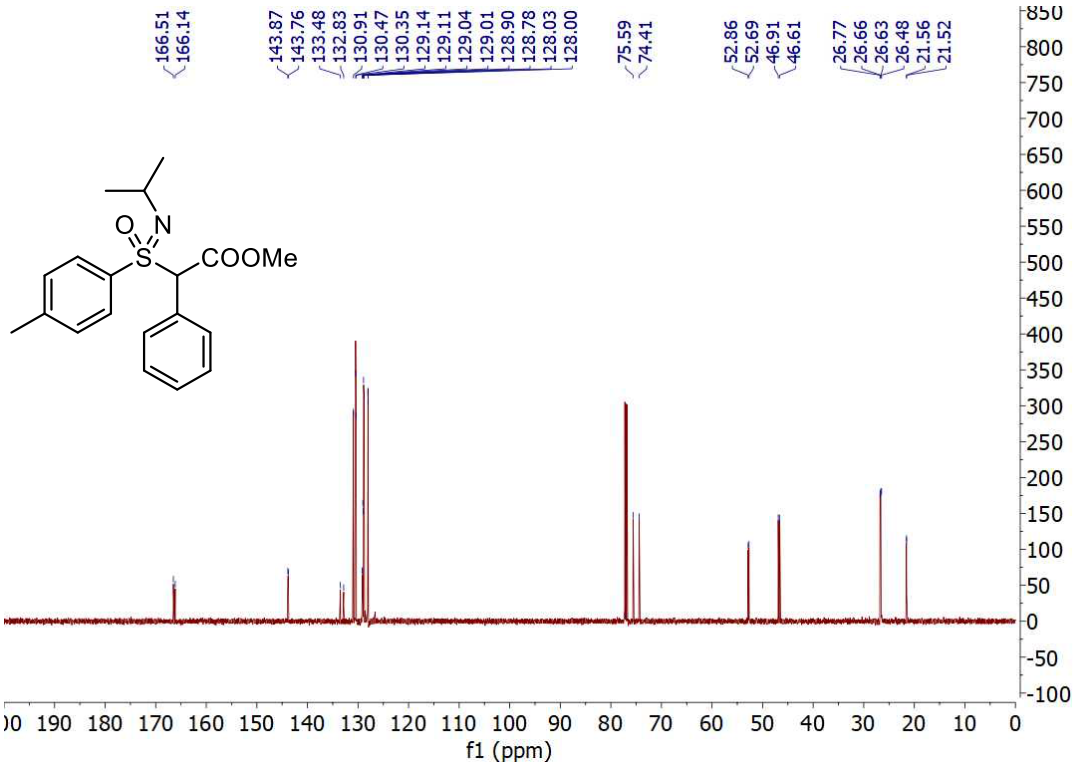


methyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)-2-phenylacetate (3z)

^{1}H NMR (600 MHz, Chloroform-*d*)

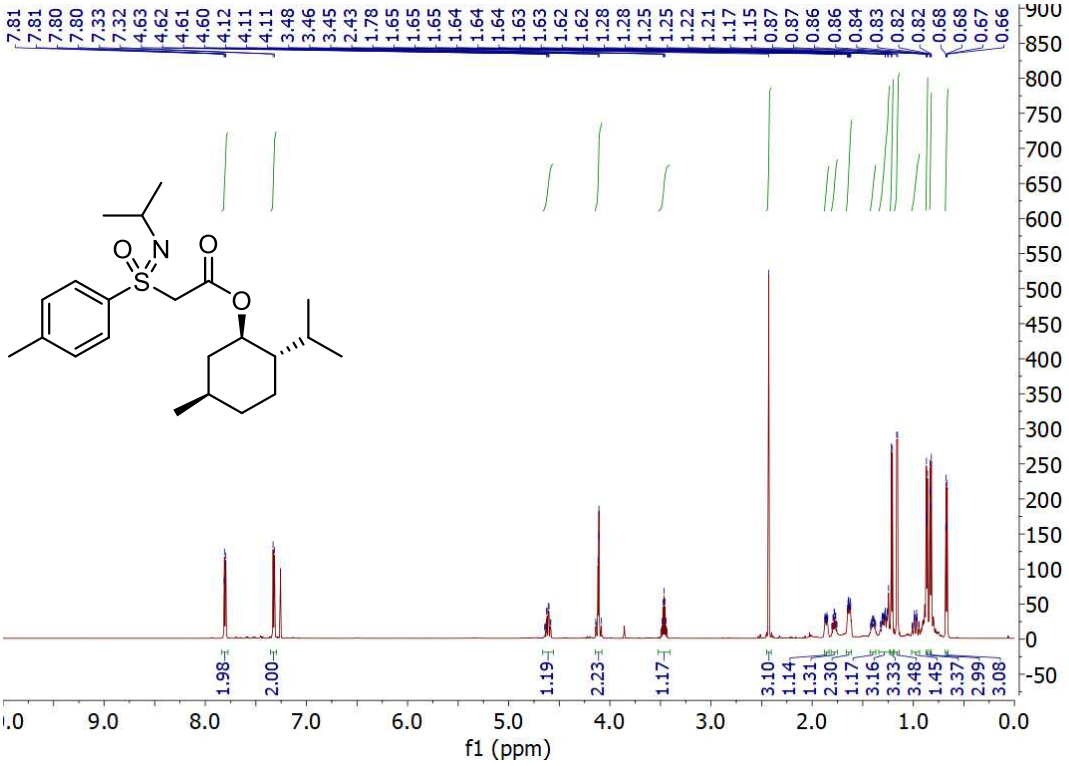


^{13}C NMR (151 MHz, Chloroform-*d*)

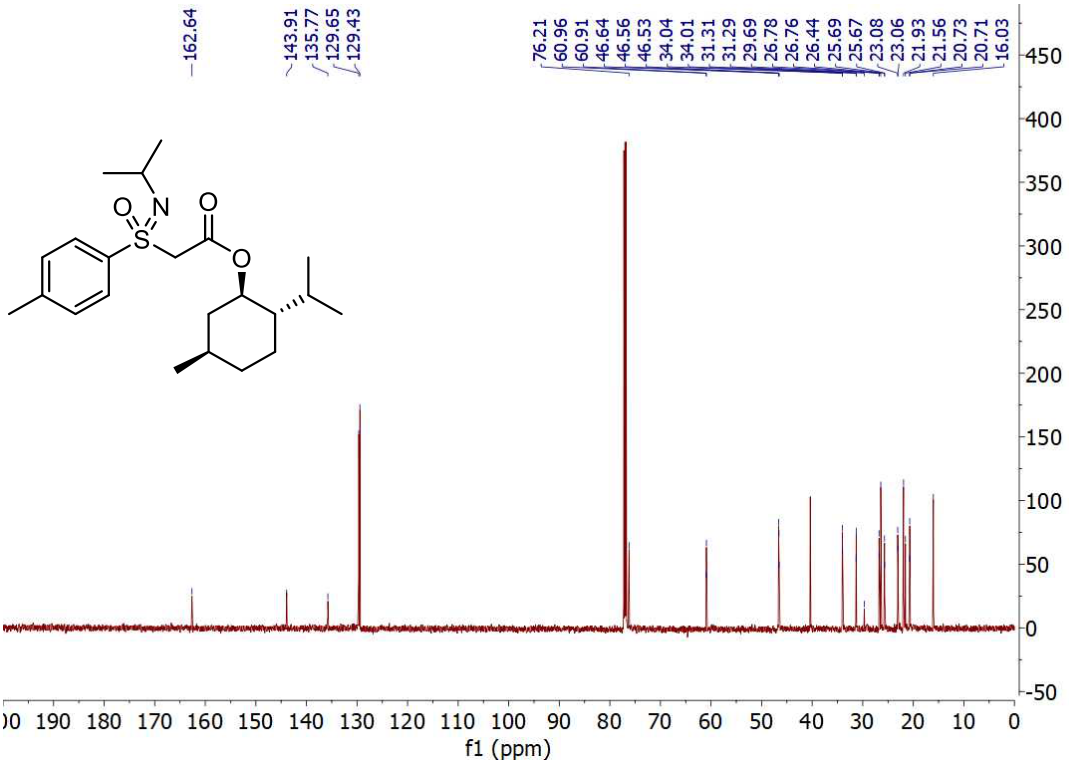


(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)acetate (3aa)

^{1}**H NMR** (600 MHz, Chloroform-*d*)

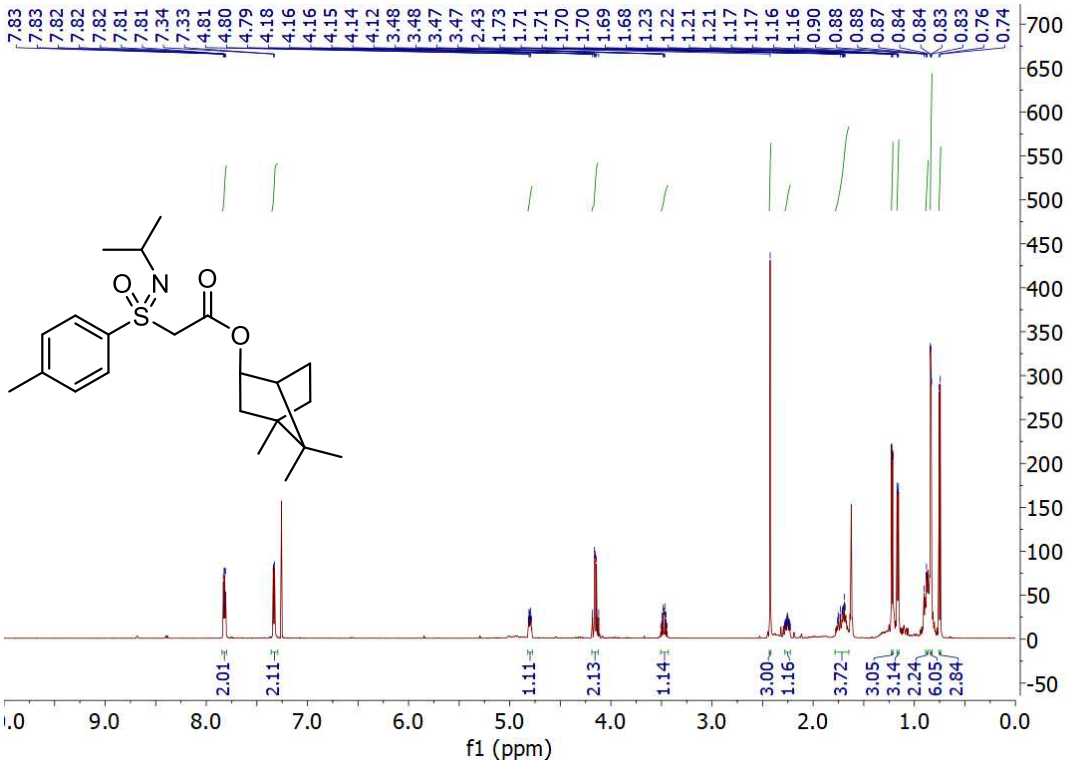


^{13}**C NMR** (151 MHz, Chloroform-*d*)

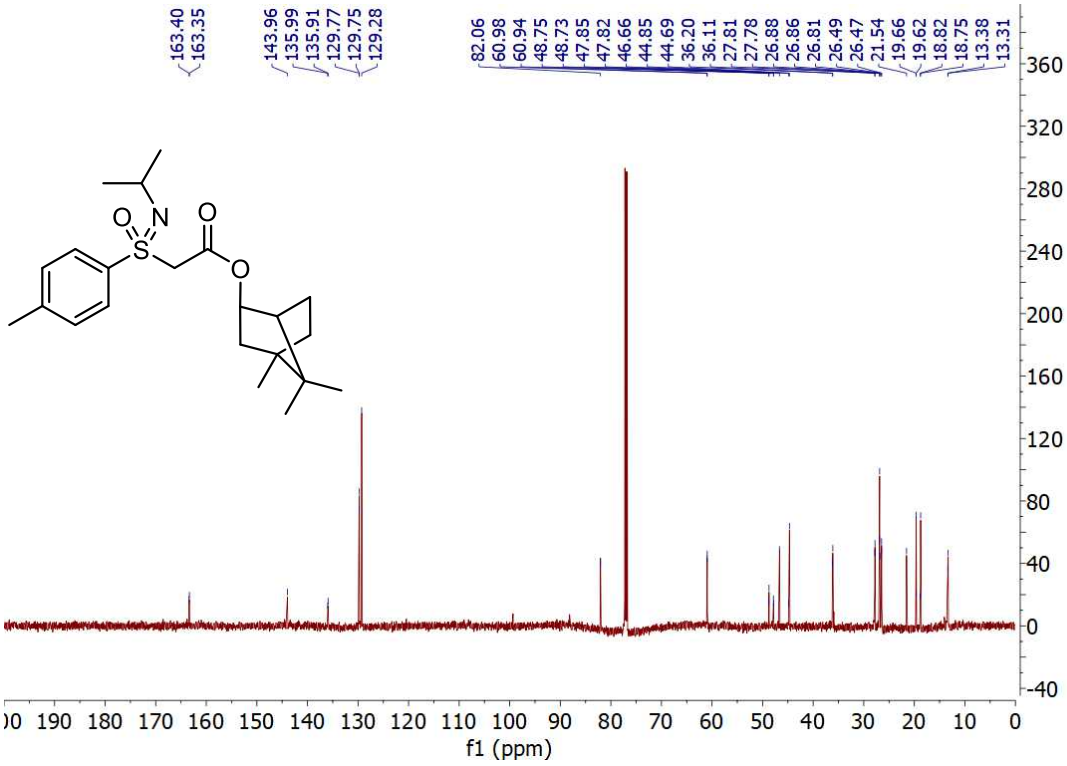


(2*R*)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(N-isopropyl-4-methylphenylsulfonimidoyl)acetate (3ab)

^{1}**H NMR** (600 MHz, Chloroform-*d*)

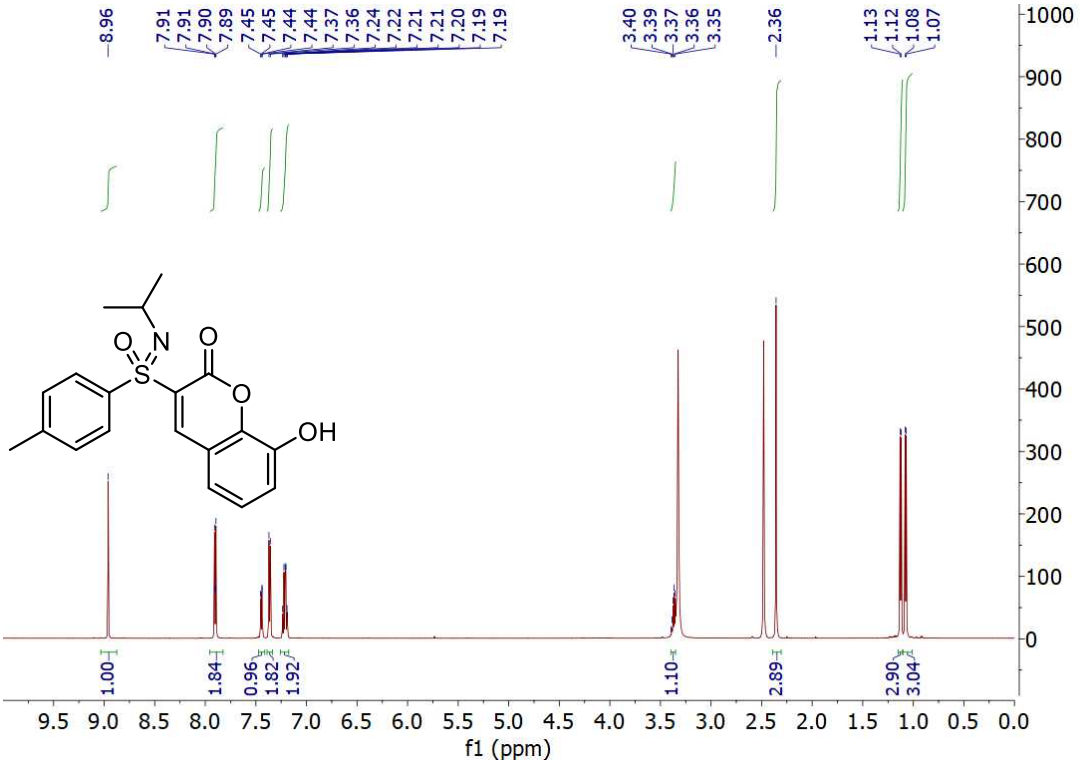


^{13}**C NMR** (151 MHz, Chloroform-*d*)

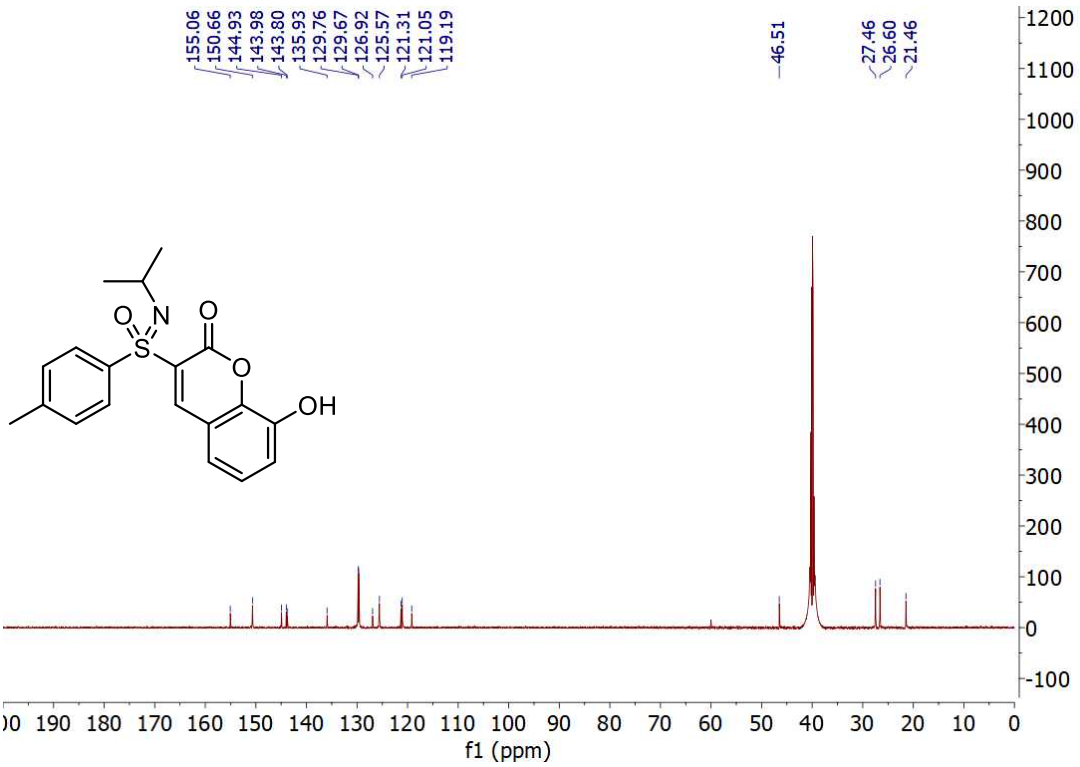


8-hydroxy-3-(*N*-isopropyl-4-methylphenylsulfonimidoyl)-2H-chromen-2-one (4a)

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

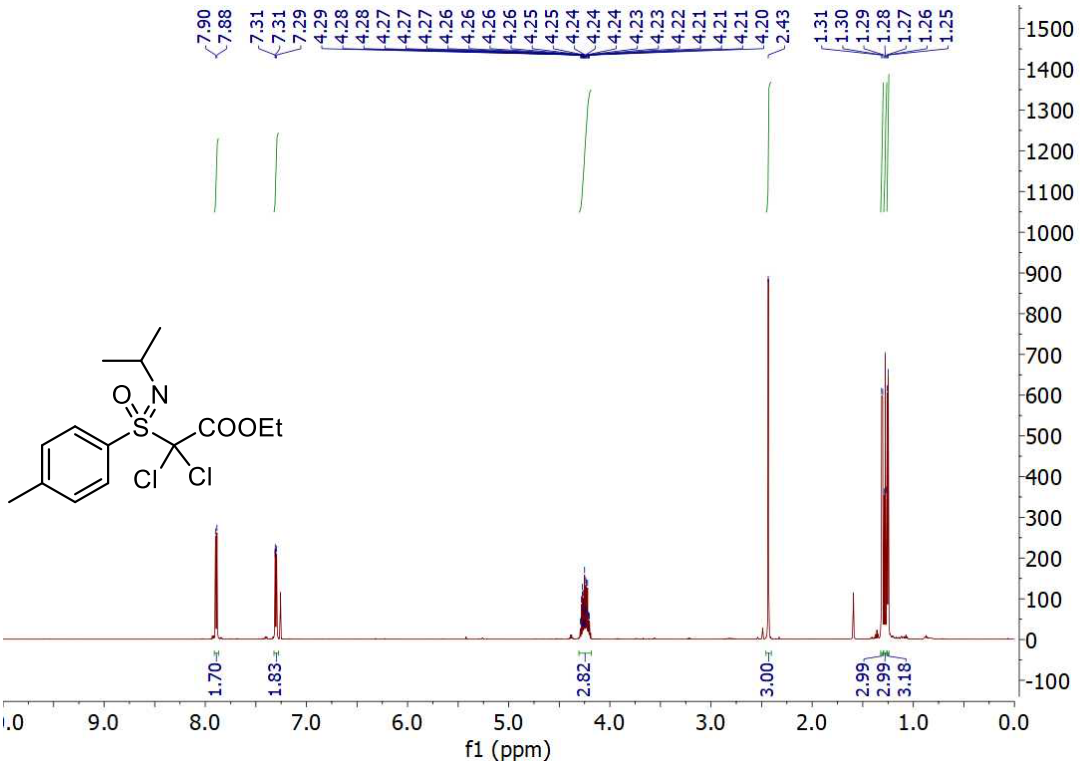


^{13}C NMR (151 MHz, DMSO-d_6)

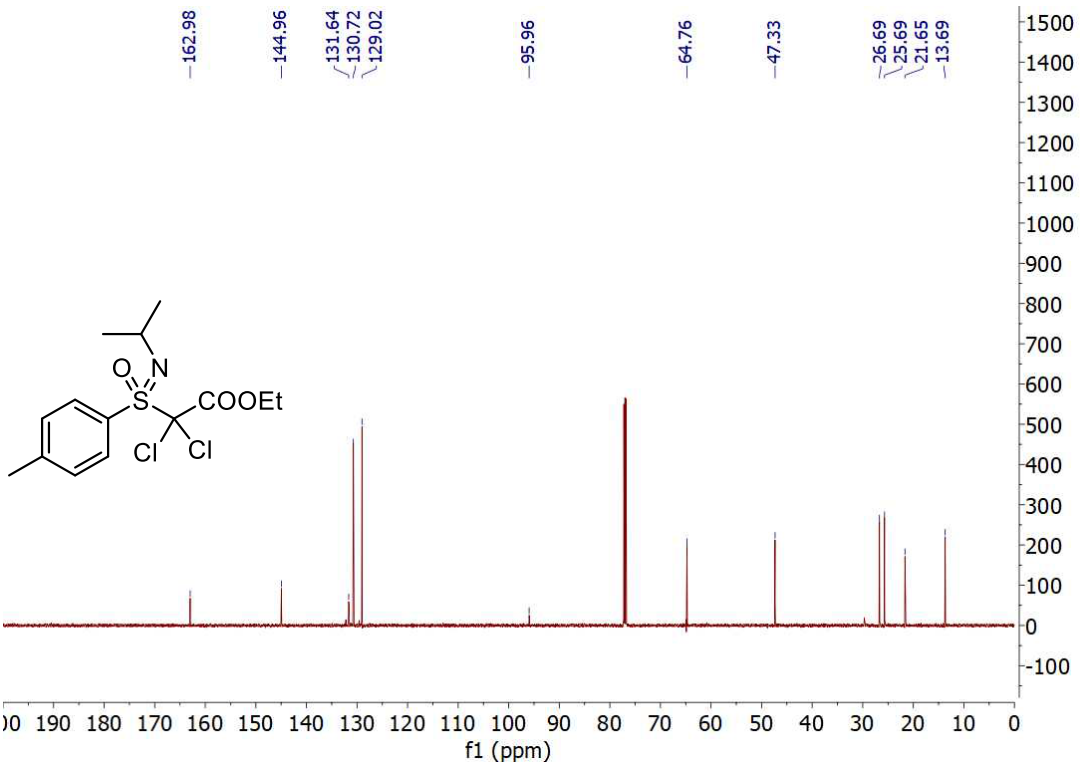


ethyl 2,2-dichloro-2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)acetate (4b)

[1]**H NMR** (600 MHz, Chloroform-*d*)

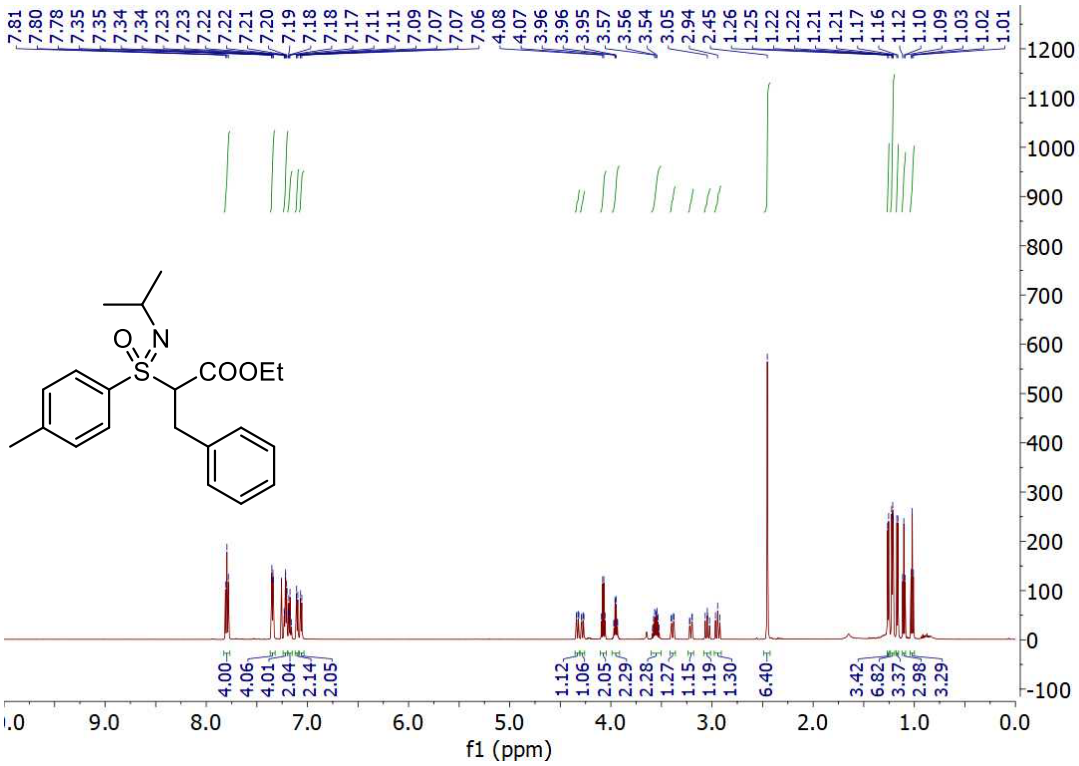


[13]**C NMR** (151 MHz, Chloroform-*d*)

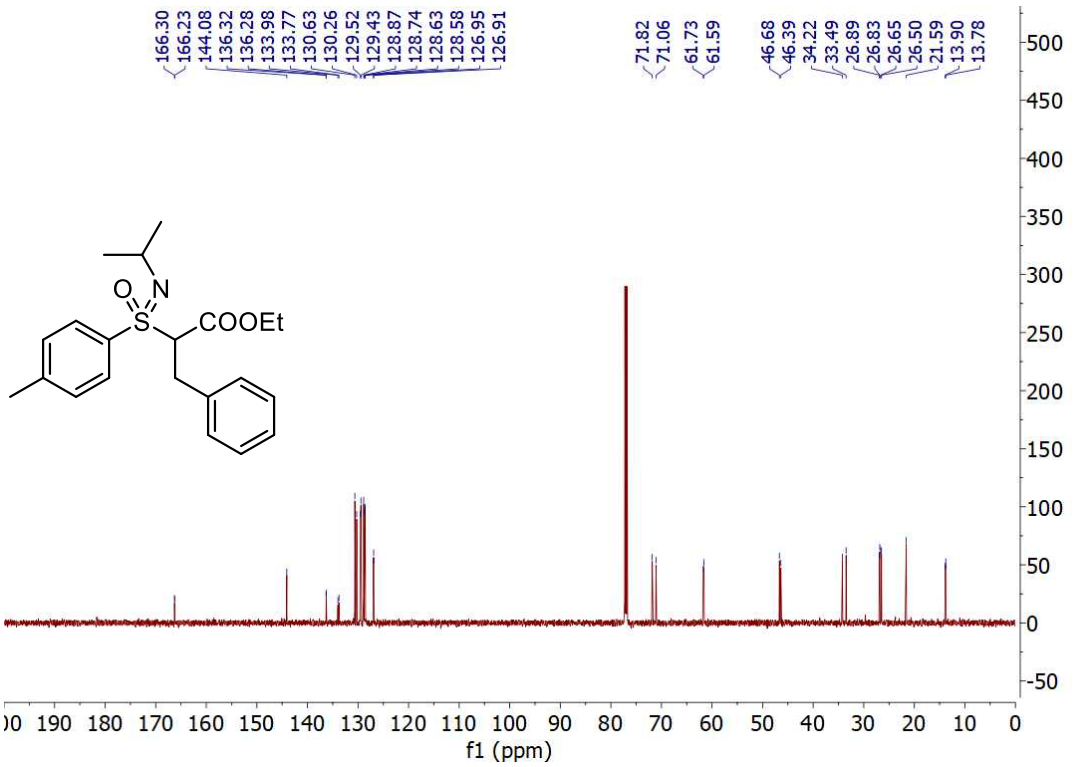


ethyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)-3-phenylpropanoate (4c)

^{1}H NMR (600 MHz, Chloroform-*d*)

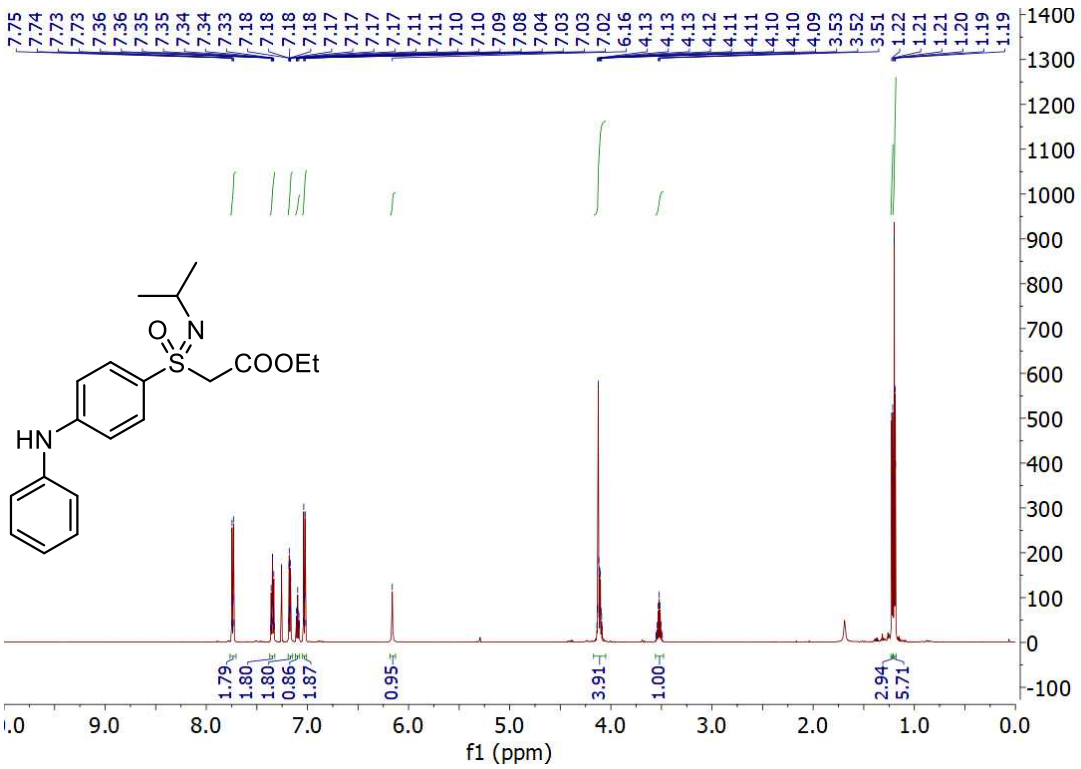


^{13}C NMR (151 MHz, Chloroform-*d*)

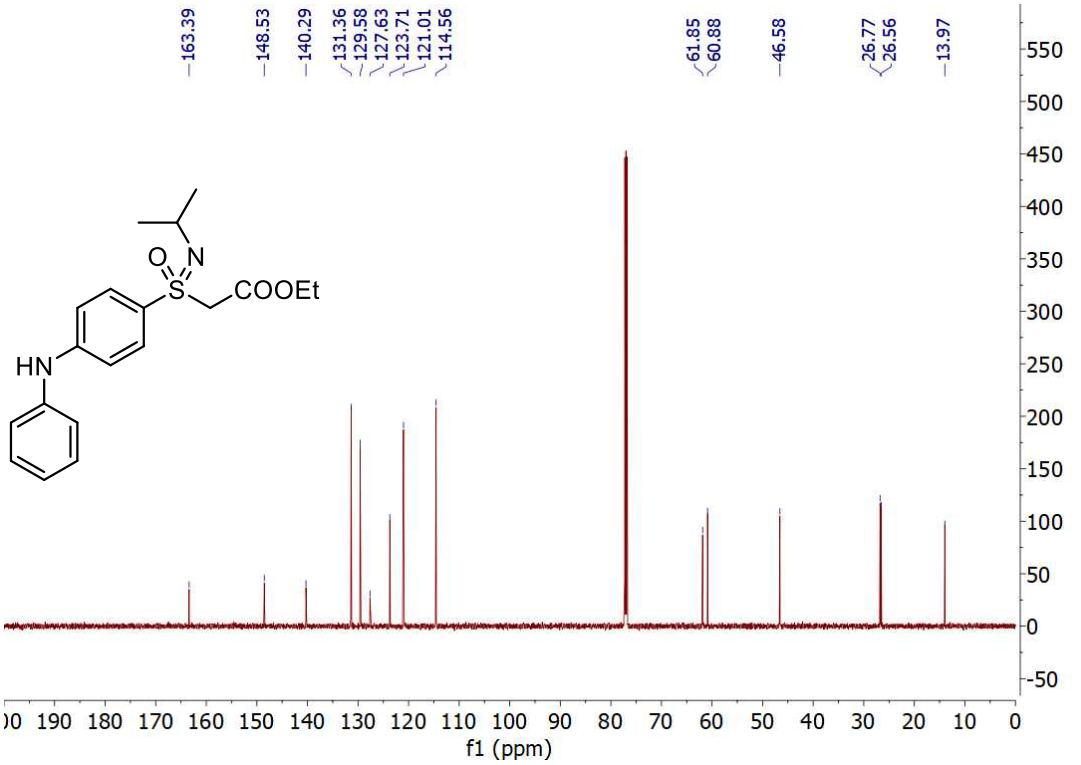


ethyl 2-(*N*-isopropyl-4-(phenylamino)phenylsulfonimidoyl)acetate (4d)

^{1}H NMR (600 MHz, Chloroform-*d*)



^{13}C NMR (151 MHz, Chloroform-*d*)



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