Supporting Information

E→*Z contra*-Thermodynamic Isomerization of Alkenes with SEGPHOS

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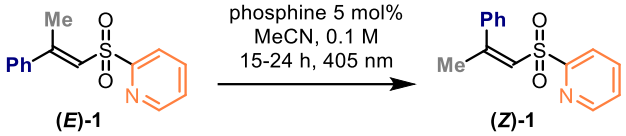
I. General information

Unless otherwise stated, all glassware was flame-dried before use and all reactions were performed under an atmosphere of argon. Solvents were distilled from appropriate drying agents prior to use. Acetonitrile 99.9% extra-dry AcroSeal was used for reactions. All reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminium plates coated with silica gel F254 with 0.2 mm thickness. Chromatograms were visualised by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed on an Isolera 4 medium pressure chromatography system (Biotage) using silica gel 60 (0.040-0.060 mm). Infrared spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers (ν_{max}) are reported in cm^{-1}. Mass spectra were obtained using a JEOL AccuTof 4G spectrometer, using electronic impact ionization (EI), or an Orbitrap Exploris 120, Thermo Scientific spectrometer, using electrospray ionization, or a Waters LCT Premier spectrometer, using electrospray ionization. All ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AV-400, AV-300 spectrometer at 300K. Chemical shifts are given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 ppm (^{1}H-NMR) and δ = 77.16 (^{13}C-NMR). Coupling constants are quoted in Hz (*J*). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q) as they appeared in the spectrum. If the appearance of a signal differs from the expected splitting pattern, the observed pattern is designated as apparent (app). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m) or broad (br). Irradiations were performed using Evoluchem LED lamps at the mentioned wavelengths from Hepatochem. Absorption Spectra were recorded on UV Visible Agilent Cary 60 spectrophotometer. Emission spectra were recorded on a Fluorolog 3, Horiba.

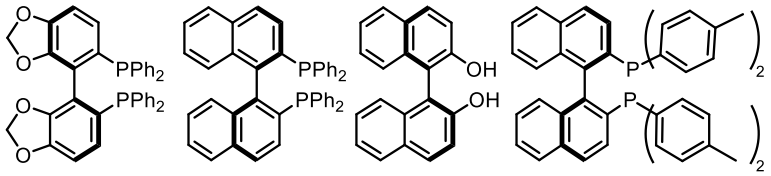
II. Optimisation tables

Phosphine Screening

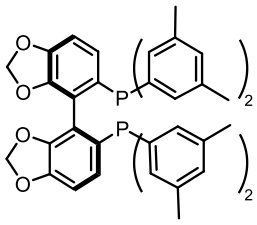


(*E*)-1 (*Z*)-1

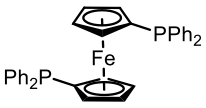
Entry	Phosphine	Time	*Z:E*
1	(*S*)-SEGPHOS	15h	95:5
2	(*R*)-BINAP	15h	87:13
3	(*S*)-BINOL	15h	44:56
4	(*R*)-Tol-BINAP	15h	7:93
5	(*S*)-DM-SEGPHOS	15h	31:69
6	PPh_3	15h	8:92
7	dppf	15h	3:97
8	dppbz	15h	30:70
9	$(CH_3OC_6H_4)_3P$	24h	9:91



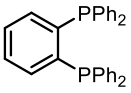
(*S*)-SEGPHOS (*R*)-BINAP (*S*)-BINOL (*R*)-TolBINAP



(*S*)-DM-SEGPHOS

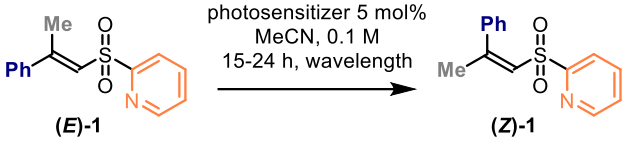


dppf



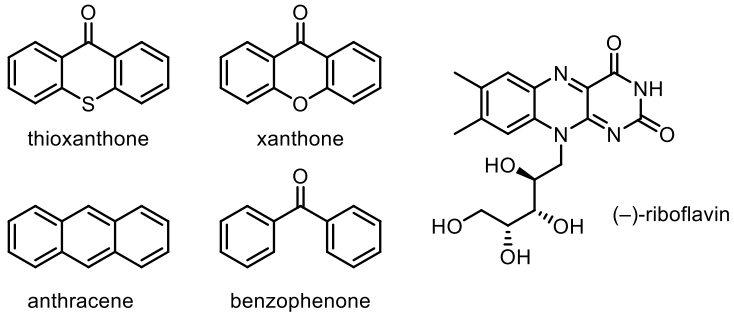
dppbz

Other Photosensitizer Screening

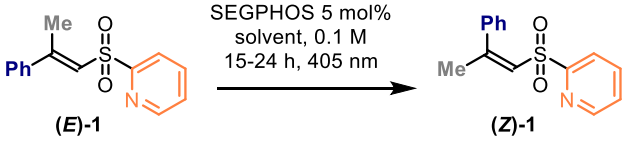


(*E*)-1 (*Z*)-1

Entry	Photosensitizers	Wavelength	Time	*Z:E*
1	thioxanthone	405 nm	15h	91:9
2	xanthone	365 nm	15h	96:4
3	xanthone	405 nm	15h	4:96
4	(–)-riboflavin	405 nm	15h	13:87
5	(–)-riboflavin	425 nm	15h	49:51
6	(–)-riboflavin	425 nm	22h	51:49
7	(–)-riboflavin	450 nm	23h	21:79
8	anthracene	365 nm	15h	74:26
9	benzophenone	365 nm	15h	92:8



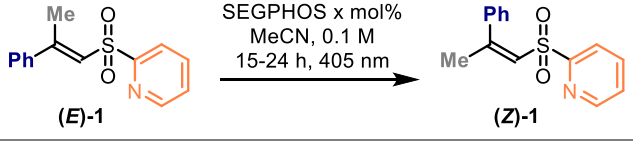
Solvent Screening



(*E*)-1 (*Z*)-1

Entry	Solvent	Time	*Z:E*
1	MeCN	15-24h	95:5
2	MeOH	22h	27:73
3	DMF	24h	12:88
4	EtOAc	23h	46:54
5	DCM	22h	95:5
6	THF	24h	94:6

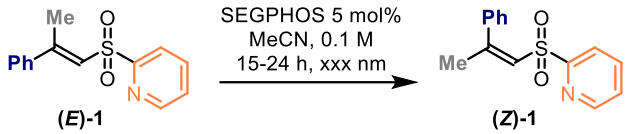
Catalytic loading



(*E*)-1 (*Z*)-1

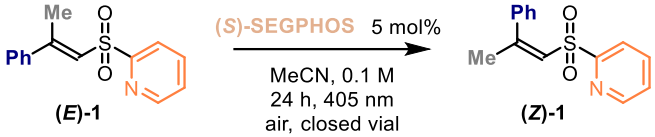
Entry	Catalytic loading	Time	*Z:E*
1	2 mol%	15h	13:87
2	5 mol%	15-24h	95:5
3	10 mol%	15h	95:5

Wavelength



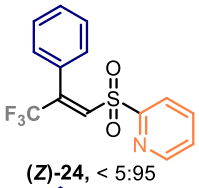
Entry	Wavelength	Time	*Z:E*
1	365 nm	15h	>95:5
2	405 nm	15-24h	95:5
3	425 nm	15h	8:92

Control experiments

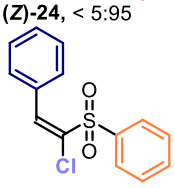


Entry	Catalyst	Activation	Time	Z:E
1	(S)-SEGPHOS	-	15h	2:98
2	-	405 nm	24h	6:94
3	(S)-SEGPHOS	55 °C	24h	0:100
4	-	55 °C	24h	0:100

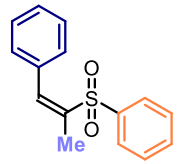
III. Limitations-Unsuccessful substrates



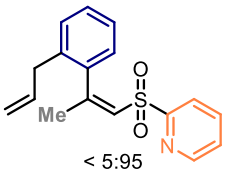
(*Z*)-24, < 5:95



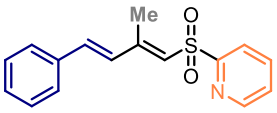
(*Z*)-25, < 5:95



(*Z*)-26, 25:75, 92%



< 5:95
traces of [2+2]

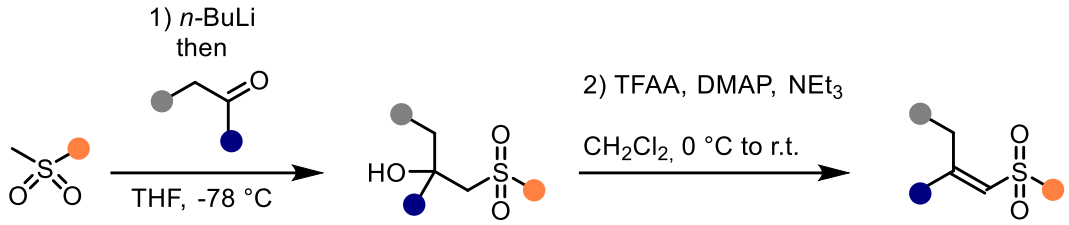


no selectivity observed/messy

IV. Starting material synthesis

A. General route to access vinyl sulfones

The compounds were obtained following a procedure described by Carretero and coworkers.[1]



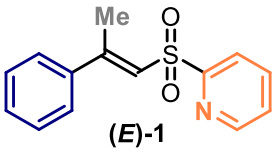
General procedure A:

To a solution of methyl sulfone (1.0 equiv.) in THF (0.2 M), cooled to -78 °C, was added a 2.5 M solution of *n*-BuLi in hexane (1.1 equiv.). The mixture was stirred at -78 °C for 30 min. The ketone/aldehyde (1.1 equiv.) was then added, and mixture was stirred at -78 °C for 90 min. The reaction was stopped by addition of aqueous saturated NH_4Cl. The organic layer was diluted with EtOAc, separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with water and brine before being dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude mixture was used without further purification.

The crude mixture of the resulting alcohol (theoretical 1.0 equiv.) and DMAP (0.10 equiv.) were dissolved in CH_2Cl_2 (0.2 M) under argon. The mixture was cooled to 0 °C before Et_3N (2.0 equiv.) and TFAA (1.2 mL) were successively added. The reaction mixture was allowed to reach room temperature and stirred between 16h and 3 days. The reaction was stopped with aqueous saturated $NaHCO_3$ and the aqueous layer was extracted twice with CH_2Cl_2 The combined organic layers were washed with water and brine before being dried ($MgSO_4$), filtered and concentrated under reduced pressure. The product was purified by column chromatography (SiO_2, PE/EtOAc or pentane/EtOAc, typical gradient: from 90/10 to 20/80 over 20 CV).

[1] T. Llamas, R. G. Arrayás and J. C. Carretero, *Angew. Chem. Int. Ed.* 2007, **46**, 3329–3332.

(*E*)-1: (*E*)-2-((2-phenylprop-1-en-1-yl)sulfonyl)pyridine

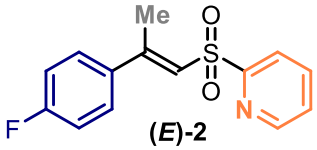


(*E*)-1

$C_{14}H_{13}NO_2S$
MW: 259 g.mol^{-1}
Yield: 63%
Colourless solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine[2] (1.70 g, 10.8 mmol), *n*-BuLi (4.8 mL, 2.5 M, 12 mmol), and acetophenone (1.4 mL, 12 mmol) for the first step, then DMAP (132 mg, 1.08 mmol), Et_3N (3.0 mL, 21.6 mmol) and TFAA (1.8 mL, 13.0 mmol) for the second step. The product was obtained as a colourless solid (1.77 g, 63%) over two steps.
Spectral properties were in accordance with those reported in the literature.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (ddd, *J* = 4.7, 1.5, 0.8 Hz, 1H), 8.16 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.96 (td, *J* = 7.8, 1.7 Hz, 1H), 7.53 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.35 (m, 3H), 6.76 (dd, *J* = 2.3, 1.1 Hz, 1H), 2.59 (d, *J* = 1.2 Hz, 3H). *See spectra*

(*E*)-2: (*E*)-2-((2-(4-fluorophenyl)prop-1-en-1-yl)sulfonyl)pyridine

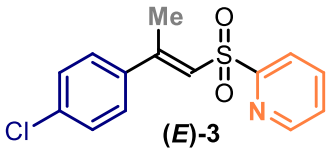


(*E*)-2

$C_{14}H_{12}FNO_2S$
MW: 277 g.mol^{-1}
Yield: 55%
Colourless solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.2 mL, 2.5 M, 5.5 mmol), and 4-fluoroacetophenone (668 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless solid (758 mg, 55%) over two steps.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 – 8.70 (m, 1H), 8.19 – 8.13 (m, 1H), 7.97 (td, *J* = 7.8, 1.7 Hz, 1H), 7.53 (ddd, *J* = 7.7, 4.7, 1.1 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.12 – 7.00 (m, 2H), 6.76 – 6.70 (m, 1H), 2.57 (d, *J* = 1.2 Hz, 3H). *See spectra*
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.82 (d, *J* = 250.8 Hz), 159.44, 154.80, 150.43, 138.24, 136.16 (d, *J* = 3.4 Hz), 128.48 (d, *J* = 8.5 Hz, 2C), 127.21, 124.89, 121.80, 115.83 (d, *J* = 21.8 Hz, 2C), 17.78.
^{19}F NMR (282 MHz, $CDCl_3$) δ -110.49.
HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{14}H_{13}FNO_2S^+$) requires 278.0646, found 278.0647.
IR (thin film) ν 3052, 1599, 1508, 1304, 1159, 1106, 810, 770, 590 cm^{-1}.

(*E*)-3: (*E*)-2-((2-(4-chlorophenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*E*)-3

$C_{14}H_{12}ClNO_2S$
MW: 293 g.mol^{-1}
Yield: 46%
Beige solid

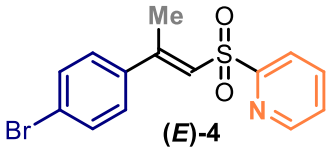
The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), and 4'-chloroacetophenone (648 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a beige solid (674 mg, 46%) over two steps.

[2] Prepared according to: P. Mauleón and J. C. Carretero, *Chem. Commun.*, 2005, 4961.

Spectral properties were in accordance with those reported in the literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.19 – 8.12 (m, 1H), 7.97 (td, *J* = 7.8, 1.7 Hz, 1H), 7.54 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.42 – 7.32 (m, 4H), 6.75 (app.dd, *J* = 2.3, 1.1 Hz, 1H), 2.57 (d, *J* = 1.2 Hz, 3H). *See spectra*

(*E*)-4: (*E*)-2-((2-(4-bromophenyl)prop-1-en-1-yl)sulfonyl)pyridine



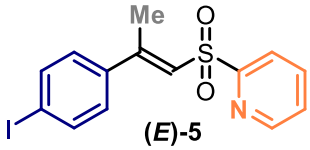
(*E*)-4

$C_{14}H_{12}BrNO_2S$
MW: 338 g.mol^{-1}
Yield: 52%
Orange solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), and 4'-bromoacetophenone (995 mg, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as an orange solid (881 mg, 52%) over two steps.
Spectral properties were in accordance with those reported in the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.15 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.97 (td, *J* = 7.8, 1.7 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.34 – 7.27 (m, 2H), 6.75 (app.dd, *J* = 2.3, 1.1 Hz, 1H), 2.55 (d, *J* = 1.2 Hz, 3H). *See spectra*

(*E*)-5: (*E*)-2-((2-(4-iodophenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*E*)-5

$C_{14}H_{12}INO_2S$
MW: 385 g.mol^{-1}
Yield: 31%
Beige solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), and 4'-iodoacetophenone (995 mg, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a beige solid (598 mg, 31%) over two steps.

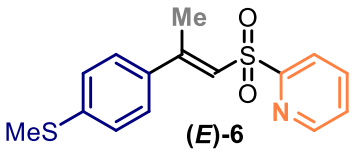
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (ddd, *J* = 4.7, 1.5, 0.8 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.97 (td, *J* = 7.8, 1.7 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.54 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 7.21 – 7.12 (m, 2H), 6.80 – 6.70 (m, 1H), 2.55 (d, *J* = 1.2 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 154.9, 150.5, 139.7, 138.3, 138.0 (2C), 128.2 (2C), 127.3, 125.4, 121.9, 96.4, 17.6.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{14}H_{13}INO_2S^+$) requires 385.9706, found 385.9710.

IR (thin film) ν 3051, 1600, 1577, 1426, 1308, 1161, 1003, 812, 775, 642, 574 cm^{-1}.

(*E*)-6: (*E*)-2-((2-(4-(methylthio)phenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*E*)-6

$C_{15}H_{15}NO_2S_2$
MW: 305 g.mol^{-1}
Yield: 57%
Light yellow solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), and 4'-(methylthio)acetophenone (831 mg, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL,

6.0 mmol) for the second step. The product was obtained as a light yellow solid (873 mg, 57%) over two steps.

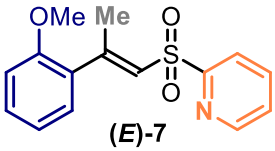
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.16 (dt, *J* = 7.9, 0.9 Hz, 1H), 8.00 (td, *J* = 7.8, 1.7 Hz, 1H), 7.55 (ddd, *J* = 7.7, 4.7, 1.1 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.23 – 7.18 (m, 2H), 6.80 (q, *J* = 1.2 Hz, 1H), 2.56 (d, *J* = 1.2 Hz, 3H), 2.47 (s, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 154.7, 150.1, 141.6, 138.0, 135.5, 126.9, 126.5 (2C), 125.4 (2C), 123.6, 121.4, 17.0, 14.8.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{15}H_{16}NO_2S_2^+$) requires 306.0617, found 306.0617.

IR (thin film) ν 1587, 1426, 1308, 1160, 1080, 991, 816, 773, 666, 579 cm^{-1}.

(*E*)-7: (*E*)-2-((2-(2-methoxyphenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*E*)-7

$C_{15}H_{15}NO_3S$
MW: 289 $g.mol^{-1}$
Yield: 46%
Colourless oil

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), and 2'-methoxyacetophenone (683 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless oil (670 mg, 46%) over two steps.

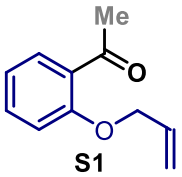
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 – 8.73 (m, 1H), 8.16 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.96 (td, *J* = 7.7, 1.6 Hz, 1H), 7.53 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 7.35 – 7.27 (m, 1H), 7.14 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.96 – 6.85 (m, 2H), 6.64 – 6.59 (m, 1H), 3.79 (s, 3H), 2.52 – 2.49 (m, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 156.7, 156.5, 150.4, 138.1, 130.7, 130.6, 128.9, 127.0, 126.8, 121.9, 120.7, 111.4, 55.6, 19.3.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{15}H_{16}NO_3S^+$) requires 290.0845, found 290.0842.

IR (thin film) ν 2944, 1577, 1488, 1427, 1307, 1248, 1160, 1108, 1023, 827, 754, 583 cm^{-1}.

S1: 1-(2-(allyloxy)phenyl)ethan-1-one



S1

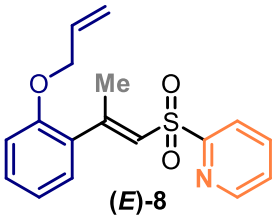
$C_{11}H_{12}O_2$
MW: 176 $g.mol^{-1}$
Yield: 72%
Colourless oil

1-(2-hydroxyphenyl)ethenone (1.20 mL, 10.0 mmol, 1.0 equiv.) and potassium carbonate (1.38 g, 10.0 mmol, 1.0 equiv.) were suspended in dry acetonitrile (40 mL, 0.25 M) under argon. Allyl bromide (865 µL, 10.0 mmol, 1.0 equiv.) was added and the mixture was stirred at 60 °C for 16 h. Allyl bromide (865 µL, 10.0 mmol, 1.0 equiv.) was added and the mixture was stirred at 60 °C for 36 additional hours. After cooling down to room temperature, the mixture was diluted with water and extracted thrice with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography (SiO_2, PE/Et_2O, from 100/0 to 90/10) to obtain the desired compound as a colourless oil (1.26 g, 72%). Spectral properties were in accordance with those reported in the literature.[3]

[3] W.-H. Cheung, S.-L. Zheng, W.-Y. Yu, G.-C. Zhou and C.-M. Che, *Org. Lett.*, 2003, **5**, 2535–2538.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.03 – 6.92 (m, 2H), 6.09 (dtd, *J* = 15.9, 10.6, 5.3 Hz, 1H), 5.44 (dd, *J* = 17.3, 0.9 Hz, 1H), 5.32 (dd, *J* = 10.5, 0.8 Hz, 1H), 4.64 (d, *J* = 5.3 Hz, 2H), 2.64 (s, 3H). *See spectra*

(*E*)-8: (*E*)-2-((2-(2-(allyloxy)phenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*E*)-8

$C_{17}H_{17}NO_3S$
MW: 315 g.mol^{-1}
Yield: 51%
Colourless oil

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (990 mg, 6.3 mmol), *n*-BuLi (2.8 mL, 2.5 M, 6.93 mmol), and **S1** (1.22 g, 6.93 mmol mmol) for the first step, then DMAP (77.0 mg, 0.63 mmol), Et_3N (1.8 mL, 12.6 mmol) and TFAA (1.05 mL, 7.6 mmol) for the second step. The product was obtained as a colourless oil (1.02 g, 51%) over two steps.

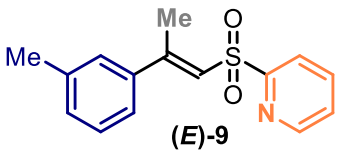
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 – 8.73 (m, 1H), 8.15 (m, 1H), 7.96 (td, *J* = 7.8, 1.7 Hz, 1H), 7.52 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.15 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.93 (td, *J* = 7.5, 0.7 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.61 (q, *J* = 1.2 Hz, 1H), 5.94 (ddt, *J* = 17.2, 10.3, 5.0 Hz, 1H), 5.31 (ddd, *J* = 17.3, 3.1, 1.5 Hz, 1H), 5.24 – 5.17 (m, 1H), 4.50 (dt, *J* = 4.9, 1.5 Hz, 2H), 2.53 (d, *J* = 1.2 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 156.7, 155.3, 150.4, 138.1, 132.7, 131.0, 130.4, 128.8, 127.0, 126.8, 121.8, 120.9, 117.3, 112.7, 69.1, 19.4.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{17}H_{17}NO_3S^+$) requires 315.0924, found 315.0913.

IR (thin film) ν 3055, 1597, 1577, 1447, 1426, 1247, 1161, 1109, 991, 754, 581 cm^{-1}.

(*E*)-9: (*E*)-2-((2-(*m*-tolyl)prop-1-en-1-yl)sulfonyl)pyridine



(*E*)-9

$C_{15}H_{15}NO_2S$
MW: 273 g.mol^{-1}
Yield: 65%
Colourless solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), and 3'-methylacetophenone (680 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless solid (886 mg, 65%) over two steps.

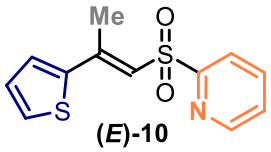
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (br.d, *J* = 4.6 Hz, 1H), 8.16 (br.d, *J* = 7.9 Hz, 1H), 7.96 (td, *J* = 7.8, 1.7 Hz, 1H), 7.52 (ddd, *J* = 7.6, 4.7, 0.9 Hz, 1H), 7.26 – 7.18 (m, 4H), 6.74 (q, *J* = 1.1 Hz, 1H), 2.57 (d, *J* = 1.0 Hz, 3H), 2.36 (s, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 156.4, 150.5, 140.2, 138.6, 138.2, 130.9, 128.7, 127.2, 127.1, 124.8, 123.7, 121.9, 21.5, 17.8.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{15}H_{16}NO_2S^+$) requires 274.0896, found 274.0898.

IR (thin film) ν 3052, 1577, 1426, 1305, 1108, 1080, 991, 887, 770, 629, 568 cm^{-1}.

(*E*)-10: (*E*)-2-((2-(thiophen-2-yl)prop-1-en-1-yl)sulfonyl)pyridine



(*E*)-10

$C_{12}H_{11}NO_2S_2$
MW: 265 g.mol^{-1}
Yield: 48%
Brown solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), and 2-acetylthiophene (594 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a brown solid (659 mg, 48%) over two steps.

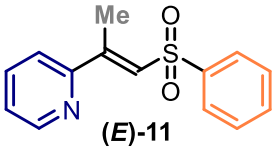
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.14 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.96 (td, *J* = 7.8, 1.7 Hz, 1H), 7.52 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.40 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.36 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.8 Hz, 1H), 6.84 (q, *J* = 1.1 Hz, 1H), 2.62 (d, *J* = 1.1 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 150.5, 148.4, 143.3, 138.2, 129.0, 128.3, 128.2, 127.1, 121.9, 121.8, 17.4.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{12}H_{11}NO_2S_2^+$) requires 265.0226, found 265.0231.

IR (thin film) ν 1578, 1425, 1307, 1161, 1108, 1080, 991, 815, 773, 710, 541 cm^{-1}.

(*E*)-11: (*E*)-2-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine



(*E*)-11

$C_{14}H_{13}NO_2S$
MW: 259 g.mol^{-1}
Yield: 59%
Colourless solid

The compound was prepared using general procedure A from methylphenylsulfone (781 mg, 5.0 mmol), *n*-BuLi (2.2 mL, 2.5 M, 5.5 mmol), and 2-acetylpyridine (661 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless solid (769 mg, 59%) over two steps.

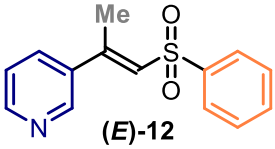
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.02 – 7.97 (m, 2H), 7.72 (td, *J* = 7.8, 1.8 Hz, 1H), 7.66 – 7.50 (m, 4H), 7.31 – 7.27 (m, 2H), 2.61 (d, *J* = 1.3 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 150.3, 149.5, 142.0, 137.1, 133.4, 129.7, 129.3 (2C), 127.5 (2C), 124.4, 121.2, 15.1.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{14}H_{14}NO_2S^+$) requires 260.0740, found 260.0754.

IR (thin film) ν 3056, 1580, 1446, 1302, 1141, 992, 812, 750, 696, 641 cm^{-1}.

(*E*)-12: (*E*)-3-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine



(*E*)-12

$C_{14}H_{13}NO_2S$
MW: 259 g.mol^{-1}
Yield: 64%
Colourless solid

The compound was prepared using general procedure A from methylphenylsulfone (781 mg, 5.0 mmol), *n*-BuLi (2.2 mL, 2.5 M, 5.5 mmol), and 3-acetylpyridine (605 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless solid (825 mg, 64%) over two steps.

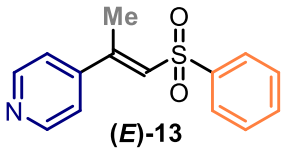
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 – 8.57 (m, 2H), 8.05 – 7.94 (m, 2H), 7.72 – 7.54 (m, 4H), 7.31 (ddd, *J* = 8.0, 4.8, 0.7 Hz, 1H), 6.65 – 6.60 (m, 1H), 2.57 (d, *J* = 1.3 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9, 150.1, 147.4, 141.7, 135.8, 133.7, 133.6, 129.4 (2C), 129.0, 127.4 (2C), 123.5, 17.1.

HRMS (ESI^+): exact mass calculated for $[M+H]^+$ ($C_{14}H_{14}NO_2S^+$) requires 260.0740, found 260.0747.

IR (thin film) ν 3042, 1604, 1446, 1300, 1142, 1083, 1021, 812, 751, 686, 614 cm^{-1}.

(*E*)-13: (*E*)-4-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine



(*E*)-13

$C_{14}H_{13}NO_2S$
MW: 259 $g.mol^{-1}$
Yield: 9%
Brown oil

The compound was prepared using general procedure A from methylphenylsulfone (781 mg, 5.0 mmol), *n*-BuLi (2.2 mL, 2.5 M, 5.5 mmol), and 4-acetylpyridine (608 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a brown oil (122 mg, 9%) over two steps.

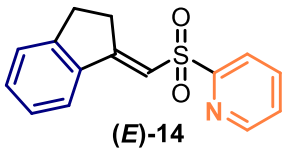
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 – 8.60 (m, 2H), 8.01 – 7.95 (m, 2H), 7.70 – 7.63 (m, 1H), 7.62 – 7.55 (m, 2H), 7.28 – 7.24 (m, 2H, below residual $CHCl_3$ peak), 6.67 (q, *J* = 1.3 Hz, 1H), 2.55 (d, *J* = 1.3 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 150.3 (2C), 147.9, 141.5, 133.8, 130.3, 129.5 (2C), 127.5 (2C), 120.8 (2C), 16.7.

HRMS (ESI^+): exact mass calculated for $[M+H]^+$ ($C_{14}H_{14}NO_2S^+$) requires 260.0740, found 260.0743.

IR (thin film) ν 3042, 1592, 1542, 1446, 1409, 1301, 1142, 1083, 995, 794, 752, 687, 621 cm^{-1}.

(*E*)-14: (*E*)-2-(((2,3-dihydro-1H-inden-1-ylidene)methyl)sulfonyl)pyridine



(*E*)-14

$C_{15}H_{13}NO_2S$
MW: 271 $g.mol^{-1}$
Yield: 69%
Beige solid

The compound was prepared using modified general procedure A. For the first step, 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), dimethylchloro aluminium (5.0 mL, 1 M, 1.0 equiv.) and indanone (727 mg, 5.5 mmol) were used. Dimethylchloro aluminium was added at -78 °C prior the addition of indanone. For the second step DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) were used. The product was obtained as a beige solid (936 mg, 69%) over two steps.

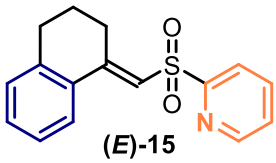
Spectral properties were in accordance with those reported in the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 – 8.70 (m, 1H), 8.18 – 8.12 (m, 1H), 7.94 (td, *J* = 7.8, 1.7 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.50 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.29 – 7.22 (m, 1H), 6.85 (app.t, *J* = 2.5 Hz, 1H), 3.41 (ddd, *J* = 8.8, 4.6, 2.5 Hz, 2H), 3.15 – 3.05 (m, 2H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 159.7, 150.4, 149.8, 138.5, 138.1, 132.1, 127.1, 127.0, 125.8, 122.4, 121.6, 114.8, 30.6, 29.9.

HRMS (ESI^+): exact mass calculated for $[M+H]^+$ ($C_{15}H_{14}NO_2S^+$) requires 272.0729, found 272.0740.

(*E*)-15: (*E*)-2-(((3,4-dihydronaphthalen-1(2*H*)-ylidene)methyl)sulfonyl)pyridine



(*E*)-15

$C_{16}H_{15}NO_2S$
MW: 285 g.mol^{-1}
Yield: 56%
Off-white solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.2 mL, 2.5 M, 5.5 mmol), and 1-tetralone (665 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as an off-white solid (801 mg, 56%) over two steps.

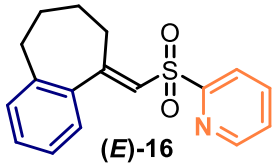
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.18 – 8.12 (m, 1H), 7.95 (td, *J* = 7.8, 1.7 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.51 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.30 (dd, *J* = 11.1, 3.7 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.18 – 7.12 (m, 1H), 6.90 (s, 1H), 3.19 – 3.11 (m, 2H), 2.81 (t, *J* = 6.2 Hz, 2H), 1.91 – 1.79 (m, 2H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 155.4, 150.4, 140.5, 138.2, 132.4, 130.8, 129.6, 127.0, 126.6, 125.4, 121.8, 120.6, 29.8, 27.5, 22.5.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{16}H_{17}NO_2S^+$) requires 286.0896, found 286.0890.

IR (thin film) ν 2936, 1576, 1426, 1306, 1158, 1106, 1080, 907, 750 cm^{-1}.

(*E*)-16: (*E*)-2-(((6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ylidene)methyl)sulfonyl)pyridine



(*E*)-16

$C_{17}H_{17}NO_2S$
MW: 299 g.mol^{-1}
Yield: 34%
Colourless solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (385 mg, 2.5 mmol), *n*-BuLi (1.1 mL, 2.5 M, 2.7 mmol), and 1-benzosuberone (367 µL, 2.5 mmol) for the first step, then DMAP (29.9 mg, 0.25 mmol), Et_3N (683 µL, 4.90 mmol) and TFAA (409 µL, 2.94 mmol) for the second step. The product was obtained as a colourless solid (251 mg, 34%) over two steps.

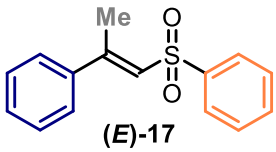
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.72 (m, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.97 (td, *J* = 7.8, 1.7 Hz, 1H), 7.54 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.20 – 7.09 (m, 3H), 6.51 (s, 1H), 3.00 (d, *J* = 5.5 Hz, 2H), 2.77 – 2.70 (m, 2H), 1.81 – 1.72 (m, 4H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 159.7, 150.4, 141.3, 139.8, 138.2, 129.4, 129.3, 127.5, 127.2, 126.6, 125.4, 121.8, 34.3, 30.6, 27.3, 26.8.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{17}H_{18}NO_2S^+$) requires 300.1053, found 300.1044.

IR (thin film) ν 2931, 1603, 1577, 1450, 1426, 1311, 1161, 1110, 1082, 991, 757, 582 cm^{-1}.

(*E*)-17: (*E*)-((2-phenylprop-1-en-1-yl)sulfonyl)benzene



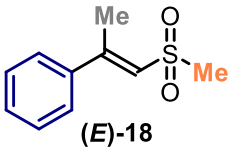
(*E*)-17

$C_{15}H_{14}O_2S$
MW: 258 g.mol^{-1}
Yield: 50%
Colourless solid

The compound was prepared using general procedure A from methylphenylsulfone (781 mg, 5.0 mmol), *n*-BuLi (2.2 mL, 2.5 M, 5.5 mmol), and acetophenone (660 µL, 5.5 mmol) for the first step,

then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless solid (640 mg, 50%) over two steps.
Spectral properties were in accordance with those reported in the literature.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.93 (m, 2H), 7.67 – 7.51 (m, 3H), 7.48 – 7.33 (m, 5H), 6.68 – 6.56 (m, 1H), 2.53 (d, *J* = 0.9 Hz, 3H). *See spectra*

(*E*)-18: (*E*)-(1-(methylsulfonyl)prop-1-en-2-yl)benzene

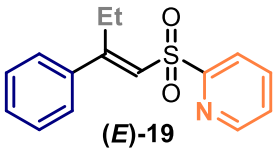


(*E*)-18

$C_{10}H_{12}O_2S$
MW: 196 g.mol^{-1}
Yield: 75%
Colourless oil

The compound was prepared using modified general procedure A from dimethylsulfone (471 mg, 5.0 mmol, 2.0 equiv.), *n*-BuLi (1.0 mL, 2.5 M, 2.5 mmol, 1.0 equiv.), and acetophenone (660 µL, 2.75 mmol, 1.1 equiv.) for the first step, then DMAP (24.4 mg, 0.20 mmol), Et_3N (558 µL, 4.0 mmol) and TFAA (334 µL, 2.4 mmol) for the second step. The product was obtained as a colourless oil (734 mg, 75%) over two steps.
Spectral properties were in accordance with those reported in the literature.[4]
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 5H), 6.55 (d, *J* = 1.1 Hz, 1H), 3.06 (s, 3H), 2.58 (d, *J* = 1.2 Hz, 3H). *See spectra*

(*E*)-19: (*E*)-2-((2-phenylbut-1-en-1-yl)sulfonyl)pyridine

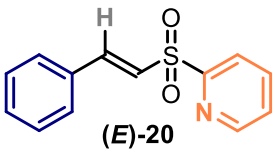


(*E*)-19

$C_{15}H_{15}NO_2S$
MW: 273 g.mol^{-1}
Yield: 15%
Colourless solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.2 mL, 2.5 M, 5.5 mmol), and propiophenone (738 mg, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless solid (203 mg, 15%) over two steps.
Spectral properties were in accordance with those reported in the literature.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.16 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.96 (td, *J* = 7.8, 1.7 Hz, 1H), 7.52 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.44 – 7.34 (m, 5H), 6.64 (s, 1H), 3.12 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). *See spectra*

(*E*)-20: (*E*)-2-(styrylsulfonyl)pyridine



(*E*)-20

$C_{13}H_{11}NO_2S$
MW: 245 g.mol^{-1}
Yield: 49%
Colourless solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.2 mL, 2.5 M, 5.5 mmol), and benzaldehyde (561 µL, 5.5 mmol) for the first step,

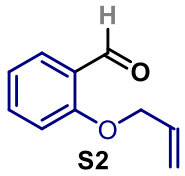
[4] H.-M. Guo, B.-Q. He and X. Wu, *Org. Lett.*, 2022, **24**, 3199–3204.

then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless solid (605 mg, 49%) over two steps.
Spectral properties were in accordance with those reported in the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.15 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.96 (td, *J* = 7.8, 1.7 Hz, 1H), 7.78 (d, *J* = 15.5 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.47 – 7.35 (m, 3H), 7.12 (d, *J* = 15.5 Hz, 1H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 150.5, 145.2, 138.3, 132.4, 131.5, 129.2 (2C), 128.8 (2C), 127.2, 124.7, 122.0.

S2: 2-(allyloxy)benzaldehyde



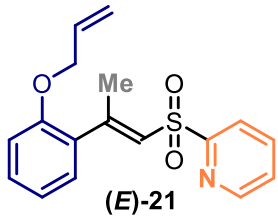
S2

$C_{10}H_{10}O_2$
MW: 162 g.mol^{-1}
Yield: 94%
Colourless oil

Salicylaldehyde (2.16 mL, 20.0 mmol, 1.0 equiv.) and potassium carbonate (2.76 g, 20.0 mmol, 1.0 equiv.) were suspended in dry acetonitrile (80 mL, 0.25 M) under argon. Allyl bromide (1.73 mL, 20.0 mmol, 1.0 equiv.) was added and the mixture was stirred at 60 °C for 16 h. Allyl bromide (1.73 mL, 20.0 mmol, 1.0 equiv.) was added and the mixture was stirred at 60 °C for 36 additional hours. After cooling down to room temperature, the mixture was diluted with water and extracted thrice with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography (SiO_2, PE/Et_2O, from 100/0 to 90/10) to obtain the desired compound as a colourless oil (3.24 g, 94%).
Spectral properties were in accordance with those reported in the literature.[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.54 (d, *J* = 0.7 Hz, 1H), 7.85 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.53 (ddd, *J* = 8.5, 7.4, 1.9 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.08 (ddt, *J* = 17.2, 10.4, 5.1 Hz, 1H), 5.46 (ddd, *J* = 17.3, 3.1, 1.6 Hz, 1H), 5.34 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.67 (dt, *J* = 5.1, 1.5 Hz, 2H). *See spectra*

(*E*)-21: (*E*)-2-((2-(allyloxy)styryl)sulfonyl)pyridine



(*E*)-21

$C_{16}H_{15}NO_3S$
MW: 301 g.mol^{-1}
Yield: 62%
Colourless oil

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.4 mL, 2.34 M, 5.5 mmol), and mr-xxx (892 mg, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a colourless solid (933 mg, 62%) over two steps.

[5] J.-N. Desrosiers, W. S. Bechara and A. B. Charette, *Org. Lett.*, 2008, **10**, 2315–2318.
[6] K. M. McQuaid, J. Z. Long and D. Sames, *Org. Lett.*, 2009, **11**, 2972–2975.

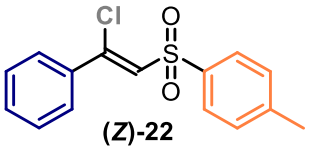
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.7, 1.4, 0.7 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 15.6 Hz, 1H), 7.87 (td, *J* = 7.8, 1.7 Hz, 1H), 7.43 (ddd, *J* = 7.7, 4.7, 1.1 Hz, 1H), 7.36 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.29 – 7.22 (m, 2H), 6.87 (td, *J* = 7.6, 0.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.94 (ddt, *J* = 17.2, 10.5, 5.2 Hz, 1H), 5.30 (ddd, *J* = 17.3, 3.0, 1.5 Hz, 1H), 5.19 (ddd, *J* = 10.6, 2.6, 1.2 Hz, 1H), 4.51 (dt, *J* = 5.2, 1.4 Hz, 2H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 157.6, 150.1, 140.6, 138.1, 132.6, 132.3, 130.6, 126.9, 125.1, 121.6, 121.1, 120.8, 117.9, 112.5, 69.0.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{16}H_{15}NO_3S^+$) requires 301.0767, found 301.0783.

IR (thin film) ν 3058, 1599, 1577, 1487, 1453, 1426, 1309, 1161, 1108, 991, 754, 571 cm^{-1}.

(*Z*)-22: (*Z*)-1-((2-chloro-2-phenylvinyl)sulfonyl)-4-methylbenzene



(*Z*)-22

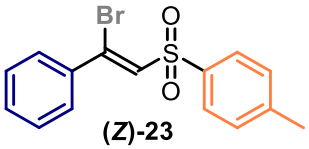
$C_{15}H_{13}NO_2SCl$
MW: 292 $g.mol^{-1}$
Yield: 72%
Colourless solid

(*Z*)-22 was obtained as a colourless solid (212 mg, 72%) using a reported procedure performed on 1.0 mmol scale.

Spectral properties were in accordance with those reported.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.49 – 7.32 (m, 5H), 7.13 (s, 1H), 2.46 (s, 3H). *See spectra*

(*Z*)-23: (*Z*)-1-((2-bromo-2-phenylvinyl)sulfonyl)-4-methylbenzene



(*Z*)-23

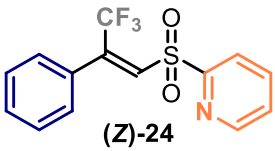
$C_{15}H_{13}NO_2SBr$
MW: 336 $g.mol^{-1}$
Yield: 67%
Colourless solid

(*Z*)-23 was obtained as a colourless solid (225 mg, 67%) using a reported procedure performed on 1.0 mmol scale.

Spectral properties were in accordance with those reported.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.46 – 7.34 (m, 5H), 7.31 (s, 1H), 2.46 (s, 3H). *See spectra*

(*Z*): (*Z*)-2-((3,3,3-trifluoro-2-phenylprop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-24

$C_{14}H_{10}F_3NO_2S$
MW: 313 $g.mol^{-1}$
Yield: 37%
Beige solid

The compound was prepared using general procedure A from 2-(methylsulfonyl)pyridine (786 mg, 5.0 mmol), *n*-BuLi (2.3 mL, 2.4 M, 5.5 mmol), and 2,2,2-trifluoroacetophenone (772 µL, 5.5 mmol) for the first step, then DMAP (61.1 mg, 0.50 mmol), Et_3N (1.4 mL, 10.0 mmol) and TFAA (834 µL, 6.0 mmol) for the second step. The product was obtained as a beige solid (584 mg, 37%) over two steps.

[7] B. Chen, X. Xia, X. Zeng and B. Xu, *Tetrahedron Lett.* 2018, **59**, 3950–3954.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.71 (td, *J* = 7.8, 1.7 Hz, 1H), 7.57 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.33 (m, 1H), 7.31 – 7.24 (m, 2H), 7.18 – 7.12 (m, 2H). *See spectra*

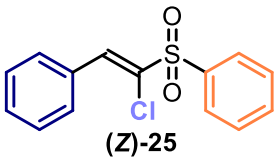
^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 150.4, 142.77 (q, *J* = 31.9 Hz), 138.0, 134.59 (q, *J* = 5.2 Hz), 130.1, 129.3 (2C), 128.2 (2C), 128.1, 127.6, 122.70, 121.66 (q, *J* = 276.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -67.80.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{14}H_{11}F_3NO_2S^+$) requires 314.0457, found 314.0456.

IR (thin film) ν 3058, 1579, 1428, 1325, 1251, 1136, 950, 772, 580 cm^{-1}.

(*Z*)-25: (*Z*)-(2-chloro-2-(phenylsulfonyl)vinyl)benzene



(*Z*)-25

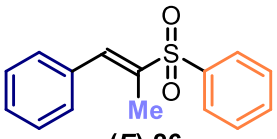
$C_{14}H_{11}ClO_2S$
MW: 278 $g.mol^{-1}$
Yield: 15%
Beige solid

Phenyl-*trans*-styrylsulfone (489 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (12 mL, 0.17 M) under argon. The mixture was cooled down to -78 °C and a solution of *n*-butyllithium (2.34 M in hexane, 0.86 mL, 2.0 mmol, 1.0 equiv.) was added dropwise. The mixture was stirred for 30 minutes at this temperature and *N*-chlorosuccinimide was added (267 mg, 2.0 mmol, 1.0 equiv.), the cooling bath was removed and the mixture was further stirred for 1 h. The reaction was stopped by addition of a saturated solution of NH_4Cl. The mixture was extracted thrice with EtOAc, the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography (SiO_2, PE/EtOAc, from 100/0 to 80/20) to obtain the desired compound as a beige solid (86 mg, 15%).

Spectral properties were in accordance with those reported in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.03 – 7.97 (m, 2H), 7.83 – 7.76 (m, 2H), 7.71 – 7.60 (m, 1H), 7.62 – 7.54 (m, 2H), 7.47 – 7.40 (m, 3H). *See spectra*

(*E*)-26: (*E*)-((1-phenylprop-1-en-2-yl)sulfonyl)benzene



(*E*)-26

$C_{15}H_{14}O_2S$
MW: 258 $g.mol^{-1}$
Yield: 81%
Colourless solid

(*E*)-26 was obtained as a colourless solid (417 mg, 81%) using a reported procedure performed on 2.0 mmol scale.

Spectral properties were in accordance with those reported.[9]

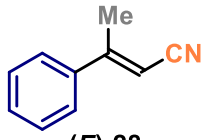
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.83 (q, *J* = 1.3 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.58 – 7.52 (m, 2H), 7.44 – 7.34 (m, 5H), 2.11 (d, *J* = 1.4 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 137.6, 137.3, 133.8, 133.4, 129.7 (2C), 129.5, 129.3 (2C), 128.8 (2C), 128.3 (2C), 13.3.

[8] J. N. Dominguez, C. Leon, J. Rodrigues, N. Gamboa De Dominguez, J. Gut and P. J. Rosenthal, *Eur. J. Med. Chem.* 2009, **44**, 1457–1462.

[9] M. Yamamoto, K. Suzuki, S. Tanaka and K. Yamada, *BCSJ* 1987, **60**, 1523–1524.

(*E*)-28: (*E*)-3-phenylbut-2-enenitrile



(*E*)-28

$C_{10}H_9N$
MW: 143 g.mol^{-1}
Yield: 88%
Colourless oil

(*E*)-28 was obtained as a colourless oil (1.43 g, 88%) using a reported procedure performed on 10.0 mmol scale.[10]

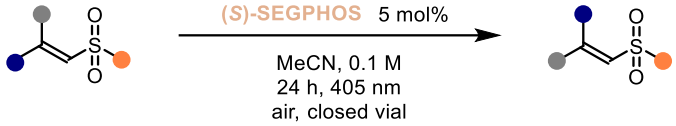
Spectral properties were in accordance with those reported.[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.35 (m, 5H), 5.62 (q, *J* = 1.0 Hz, 1H), 2.48 (d, *J* = 1.0 Hz, 3H). *See spectra*

[10] M. Skvorcova, L. T. Lukasevics and A. Jirgensons, *J. Org. Chem.* 2019, **84**, 3780–3792.
[11] T. Nishimura, Y. Nishiguchi, Y. Maeda and S. Uemura, *J. Org. Chem.* 2004, **69**, 5342–5347.

V. Isomerization of olefins

General procedure B:



Each reaction was run as a duplicate. An oven-dried HPLC vial (1.5 mL) equipped with a magnetic stir bar was charged with the substrate (0.10 mmol, 1.0 equiv.) and (*S*)-SEGPHOS (3.1 mg, 5.0 µmol, 5.0 mol%) under air. Dry CH_3CN (1.0 mL, 0.1 M) was then added to the vial and the reaction vessel was placed on a stirring plate, 5 cm away from the appropriate LED. The reaction was stirred for 24 hours under visible light irradiation (405 nm, 18 kW). The reaction mixture was then transferred to a round bottom flask using EtOAc and concentrated under reduced pressure. The *Z/E* isomer-ratio was determined by ^{1}H-NMR analysis. The reaction duplicates were then combined and purified by a single column chromatography (SiO_2, PE/EtOAc or pentane/EtOAc, typical gradient: from 85/15 to 40/60 over 10 CV). The combined isolated yield was calculated considering 0.20 mmol of starting *E*-isomer.

Reaction set-up pictures

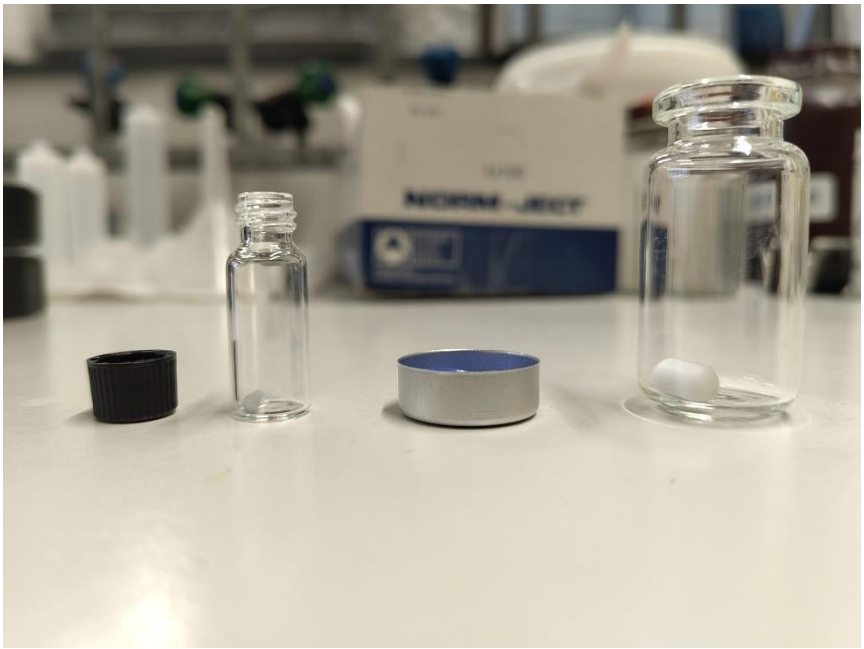


Figure 1: Reaction vessels. On the left: for 0.1 mmol scale. On the right: for 1 mmol scale

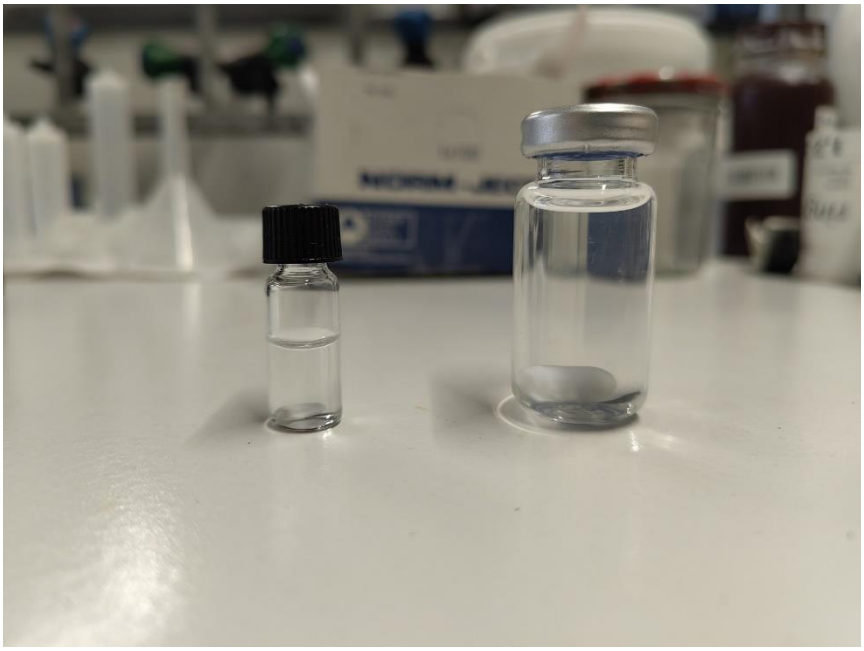


Figure 2: Reaction vessels ready for irradiation. On the left: for 0.1 mmol scale. On the right: for 1 mmol scale

Figure 3: Reaction set up before illumination. On the left: for 0.1 mmol scale. On the right: for 1 mmol scale

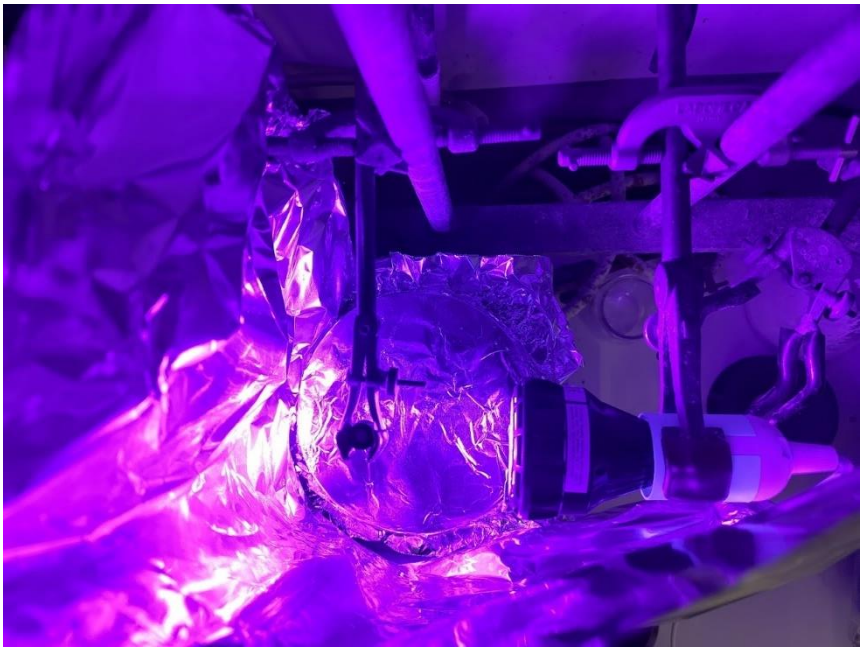
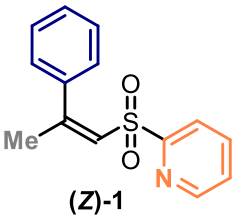


Figure 4: View from the top after the reaction was started

(*Z*)-1: (*Z*)-2-((2-phenylprop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-1

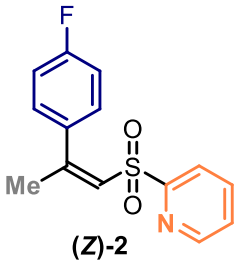
$C_{14}H_{13}NO_2S$
MW: 259 g.mol^{-1}
Yield: 86%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-1** (25.9 mg) from two experiments (d.r. 95:5, 95:5) and isolated in 86% yield (44.7 mg) after purification of the combined crude mixtures.

Scale-up (for pictures, *vide supra*): An oven-dried vial (12 mL) equipped with a magnetic stir bar was charged with the substrate (1.0 mmol, 1.0 equiv.) and (*S*)-SEGPHOS (30.5 mg, 50 µmol, 5.0 mol%) under air. Dry CH_3CN (10 mL, 0.1 M) was then added to the vial and the reaction vessel was placed on a stirring plate, 5 cm away from the 405 nm LED lamp. The reaction was stirred for 24 hours under visible light irradiation (405 nm, 18 kW). The reaction mixture was then transferred to a round bottom flask using EtOAc and concentrated under reduced pressure. The reaction was purified by column chromatography (SiO_2, PE/EtOAc or pentane/EtOAc, from 85/15 to 40/60 over 10 CV). **(*Z*)-1** was isolated in 83% yield as a colourless oil (214 mg, 83%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 7.62 (td, *J* = 7.7, 1.7 Hz, 1H), 7.49 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.36 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.24 – 7.13 (m, 3H), 7.09 – 7.01 (m, 2H), 6.74 (q, *J* = 1.4 Hz, 1H), 2.20 (d, *J* = 1.5 Hz, 3H). *See spectra*
^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 156.2, 150.0, 137.7, 137.5, 128.5, 128.0 (2C), 127.3 (2C), 127.0, 126.7, 122.5, 27.8.
HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{14}H_{13}NO_2S^+$) requires 259.0662, found 259.0679.
IR (thin film) ν 3054, 1577, 1427, 1303, 1161, 1148, 1107, 845, 763, 699, 607 cm^{-1}.

(*Z*)-2: (*Z*)-2-((2-(4-fluorophenyl)prop-1-en-1-yl)sulfonyl)pyridine

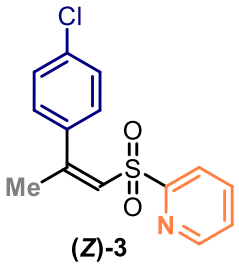


(*Z*)-2

$C_{14}H_{12}FNO_2S$
MW: 277 g.mol^{-1}
Yield: 85%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-2** (27.7 mg) from two experiments (d.r. 96:4, 95:5) and isolated in 85% yield (47.0 mg) after purification of the combined crude mixtures.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.71 (td, *J* = 7.7, 1.7 Hz, 1H), 7.60 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.40 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.93 – 6.83 (m, 2H), 6.72 (q, *J* = 1.4 Hz, 1H), 2.19 (d, *J* = 1.5 Hz, 3H). *See spectra*
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 248.6 Hz), 158.8, 155.0, 150.1, 137.7, 133.6 (d, *J* = 3.4 Hz), 129.4 (d, *J* = 8.5 Hz, 2C), 127.1, 126.9, 122.3, 115.0 (d, *J* = 21.7 Hz, 2C), 27.7.
^{19}F NMR (377 MHz, $CDCl_3$) δ -112.4.
HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{14}H_{13}FNO_2S^+$) requires 278.0646, found 278.0646.
IR (thin film) ν 3051, 1602, 1507, 1427, 1306, 1224, 1162, 1109, 991, 839, 775, 606, 540 cm^{-1}.

(*Z*)-3: (*Z*)-2-((2-(4-chlorophenyl)prop-1-en-1-yl)sulfonyl)pyridine

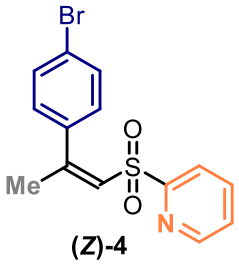


(*Z*)-3

$C_{14}H_{12}ClNO_2S$
MW: 293 g.mol^{-1}
Yield: 73%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-3** (29.4 mg) from two experiments (d.r. 92:8, 95:5) and isolated in 73% yield (42.7 mg) after purification of the combined crude mixtures.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.72 (td, *J* = 7.7, 1.7 Hz, 1H), 7.61 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.42 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.10 – 7.00 (m, 2H), 6.73 (q, *J* = 1.4 Hz, 1H), 2.19 (d, *J* = 1.5 Hz, 3H). *See spectra*
^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 154.8, 150.1, 137.7, 136.1, 134.7, 128.9 (2C), 128.2 (2C), 127.2, 126.9, 122.3, 27.6.
HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{14}H_{13}ClNO_2S^+$) requires 294.0350, found 294.0351.
IR (thin film) ν 3051, 1620, 1490, 1427, 1308, 1163, 1109, 11092, 829, 777, 608, 529 cm^{-1}.

(*Z*)-4: (*Z*)-2-((2-(4-bromophenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-4

$C_{14}H_{12}BrNO_2S$
MW: 337 g.mol^{-1}
Yield: 77%
Colourless solid

The compound was prepared using general procedure B from **(*E*)-3** (33.8 mg) from two experiments (d.r. 94:6, 95:5) and isolated in 77% yield (52.4 mg) after purification of the combined crude mixtures.

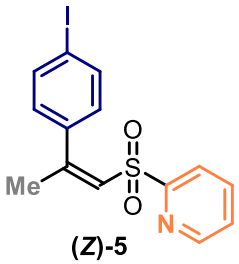
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 7.73 (td, *J* = 7.7, 1.7 Hz, 1H), 7.61 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.37 – 7.30 (m, 2H), 7.04 – 6.93 (m, 2H), 6.72 (q, *J* = 1.4 Hz, 1H), 2.18 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 154.7, 150.1, 137.7, 136.6, 131.2 (2C), 129.1 (2C), 127.2, 126.9, 122.9, 122.4, 27.5.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{14}H_{12}{}^{79}BrNO_2S^+$) requires 336.9767, found 336.9762; for $[M]^+$ ($C_{14}H_{12}{}^{81}BrNO_2S^+$) requires 338.9747, found 338.9743.

IR (thin film) ν 3051, 1578, 1484, 1426, 1303, 1304, 1147, 1107, 1008, 991, 775, 734, 606 cm^{-1}.

(*Z*)-5: (*Z*)-2-((2-(4-iodophenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-5

$C_{14}H_{12}INO_2S$
MW: 385 g.mol^{-1}
Yield: 92%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-5** (38.5 mg) from two experiments (d.r. 86:14, 90:10) and isolated in 92% yield (71.1 mg) after purification of the combined crude mixtures.

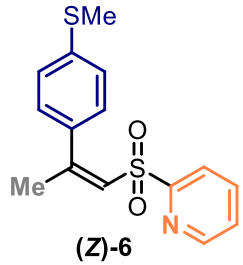
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 7.73 (td, *J* = 7.7, 1.7 Hz, 1H), 7.61 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.42 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 6.89 – 6.78 (m, 2H), 6.72 (q, *J* = 1.5 Hz, 1H), 2.18 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 154.8, 150.1, 137.7, 137.2, 137.1 (2C), 129.2 (2C), 127.2, 126.9, 122.4, 94.7, 27.5.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{14}H_{13}INO_2S^+$) requires 385.9706, found 385.9708.

IR (thin film) ν 3050, 1615, 1578, 1481, 1426, 1306, 1162, 1108, 1080, 1004, 820, 775, 732, 606 cm^{-1}.

(*Z*)-6: (*Z*)-2-((2-(4-(methylthio)phenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-6

$C_{15}H_{15}NO_2S_2$
MW: 305 g.mol^{-1}
Yield: 74%
Beige oil

The compound was prepared using general procedure B from **(*E*)-6** (30.5 mg) from two experiments (d.r. 88:12, 88:12) and isolated in 74% yield (45.1 mg) after purification of the combined crude mixtures.

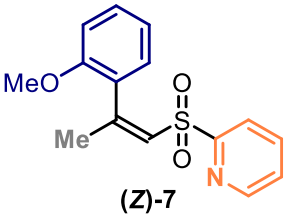
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.62 – 7.57 (m, 1H), 7.39 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1H), 7.08 – 7.00 (m, 4H), 6.70 (q, *J* = 1.4 Hz, 1H), 2.45 (s, 3H), 2.18 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 155.5, 150.0, 139.8, 137.6, 134.1, 128.0 (2C), 126.73, 126.65, 125.4 (2C), 122.4, 27.5, 15.5.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{15}H_{15}NO_2S_2^+$) requires 305.0539, found 305.0541.

IR (thin film) ν 2921, 1577, 1492, 1426, 1300, 1160, 1080, 818, 785, 525 cm^{-1}.

(*Z*)-7: (*Z*)-2-((2-(2-methoxyphenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-7

$C_{15}H_{15}NO_3S$
MW: 289 g.mol^{-1}
Yield: 79%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-7** (28.9 mg) from two experiments (d.r. 96:4, 96:4) and isolated in 79% yield (46.0 mg) after purification of the combined crude mixtures.

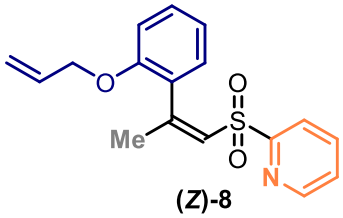
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 7.60 (td, *J* = 7.7, 1.7 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.18 (ddd, *J* = 8.3, 7.5, 1.8 Hz, 1H), 7.01 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.84 (td, *J* = 7.5, 0.9 Hz, 1H), 6.75 (q, *J* = 1.4 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 3.51 (s, 3H), 2.15 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 155.2, 155.1, 149.7, 137.2, 129.9, 129.4, 127.7, 126.32, 126.28, 122.2, 120.0, 110.1, 55.0, 26.1.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{15}H_{15}NO_3S^+$) requires 289.0767, found 289.0779.

IR (thin film) ν 2952, 1597, 1578, 1491, 1427, 1307, 1247, 1161, 1108, 1026, 846, 755, 554 cm^{-1}.

(*Z*)-8: (*Z*)-2-((2-(2-(allyloxy)phenyl)prop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-8

$C_{17}H_{17}NO_3S$
MW: 315 g.mol^{-1}
Yield: 62%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-8** (31.5 mg) from two experiments (d.r. 93:7, 97:3) and isolated in 62% yield (39.2 mg) after purification of the combined crude mixtures.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.5 Hz, 1H), 7.59 (td, *J* = 7.7, 1.6 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.18 (td, *J* = 8.4, 1.7 Hz, 1H), 7.04 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.86 (t, *J* = 7.4 Hz,

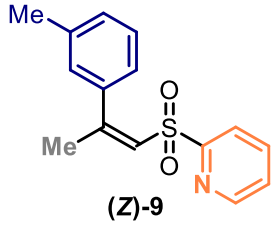
1H), 6.76 (q, *J* = 1.3 Hz, 1H), 6.58 (d, *J* = 8.3 Hz, 1H), 5.93 – 5.80 (m, 1H), 5.28 (dq, *J* = 17.3, 1.6, 1.6 Hz, 1H), 5.20 (dq, *J* = 10.6, 1.4, 1.4 Hz, 1H), 4.23 (d, *J* = 4.8 Hz, 2H), 2.17 (d, *J* = 1.3 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 155.4, 154.3, 149.8, 137.2, 132.8, 129.8, 129.7, 127.8, 126.6, 126.3, 122.2, 120.2, 117.2, 111.4, 68.5, 26.1.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{17}H_{18}NO_3S^+$) requires 316.1001, found 316.1004.

IR (thin film) ν 3054, 2919, 1621, 1596, 1578, 1488, 1426, 1305, 1242, 1159, 1106, 991, 846, 753, 553 cm^{-1}.

(*Z*)-9: (*Z*)-2-((2-(*m*-tolyl)prop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-9

$C_{15}H_{15}NO_2S$
MW: 273 $g.mol^{-1}$
Yield: 86%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-9** (27.3 mg) from two experiments (d.r. >95:5, 95:5) and isolated in 86% yield (46.0 mg) after purification of the combined crude mixtures.

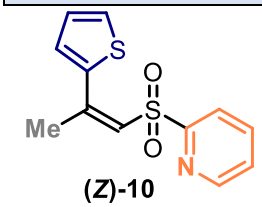
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.60 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.36 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.12 – 6.97 (m, 2H), 6.90 – 6.83 (m, 1H), 6.72 (m, 2H), 2.20 (s, 3H), 2.18 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 156.4, 149.9, 137.7, 137.5, 137.3, 129.3, 127.9, 127.7, 127.0, 126.5, 124.5, 122.5, 27.7, 21.4.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{15}H_{15}NO_2S^+$) requires 273.0818, found 273.0833.

IR (thin film) ν 3047, 1578, 1427, 1302, 1146, 1107, 991, 840, 774, 705, 625 cm^{-1}.

(*Z*)-10: (*Z*)-2-((2-(thiophen-2-yl)prop-1-en-1-yl)sulfonyl)pyridine



(*Z*)-10

$C_{12}H_{11}NO_2S_2$
MW: 265 $g.mol^{-1}$
Yield: 80%
Brown oil

The compound was prepared using general procedure B from **(*E*)-10** (26.5 mg) from two experiments (d.r. 66:34, 66:34) and isolated in 80% yield (42.2 mg) after purification of the combined crude mixtures.

The E-isomer could not be entirely separated during the purification.

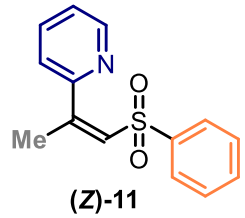
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.7, 1.5, 0.9 Hz, 1H), 7.82 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.76 (td, *J* = 7.6, 1.7 Hz, 1H), 7.53 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.40 (ddd, *J* = 7.4, 4.7, 1.4 Hz, 1H), 7.31 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.68 (q, *J* = 1.2 Hz, 1H), 2.28 (d, *J* = 1.4 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 150.1, 147.0, 137.8, 137.6, 131.1, 128.6, 127.2, 126.9, 125.9, 122.5, 28.1.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{14}H_{11}NO_2S_2^+$) requires 266.0304, found 266.0314.

IR (thin film) ν 3050, 1578, 1426, 1307, 1295, 1164, 1107, 1080, 991, 843, 774, 713, 623 cm^{-1}.

(*Z*)-11: (*Z*)-2-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine



(*Z*)-11

$C_{14}H_{13}NO_2S$
MW: 259 g.mol^{-1}
Yield: 89%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-11** (25.9 mg) from two experiments (d.r. 93:7, 94:6) and isolated in 89% yield (46.1 mg) after purification of the combined crude mixtures.

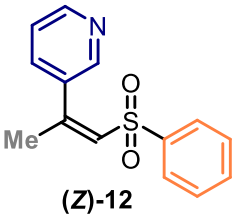
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 – 8.48 (m, 1H), 7.76 – 7.65 (m, 3H), 7.57 – 7.49 (m, 1H), 7.48 – 7.38 (m, 3H), 7.26 – 7.21 (m, 1H), 6.52 (q, *J* = 1.4 Hz, 1H), 2.22 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 152.8, 149.2, 141.3, 136.0, 133.2, 129.0 (3C), 127.7 (2C), 124.1, 123.3, 25.8.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{14}H_{13}NO_2S^+$) requires 259.0662, found 259.0661.

IR (thin film) ν 3057, 1584, 1446, 1302, 1141, 1083, 992, 842, 785, 719, 606 cm^{-1}.

(*Z*)-12: (*Z*)-3-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine



(*Z*)-12

$C_{14}H_{13}NO_2S$
MW: 259 g.mol^{-1}
Yield: 64%
Colourless solid

The compound was prepared using general procedure B from **(*E*)-12** (25.9 mg) from two experiments (d.r. 90:10, 89:11) and isolated in 86% yield (44.4 mg) after purification of the combined crude mixtures.

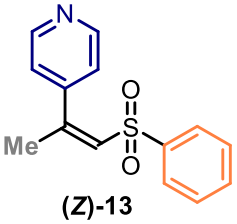
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.28 (d, *J* = 1.7 Hz, 1H), 7.61 – 7.49 (m, 4H), 7.44 – 7.37 (m, 2H), 7.28 – 7.23 (m, 1H), 6.62 (q, *J* = 1.3 Hz, 1H), 2.16 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 149.6, 147.4, 141.3, 135.3, 133.7, 133.4, 130.7, 129.1 (2C), 127.6 (2C), 122.9, 27.7.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{14}H_{13}NO_2S^+$) requires 259.0662, found 259.0666.

IR (thin film) ν 3034, 1617, 1585, 1446, 1302, 1140, 1084, 811, 713, 688, 611 cm^{-1}.

(*Z*)-13: (*Z*)-4-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine



(*Z*)-13

$C_{14}H_{13}NO_2S$
MW: 259 g.mol^{-1}
Yield: 98%
Brown oil

The compound was prepared using general procedure B from **(*E*)-13** (25.9 mg) from two experiments (d.r. 95:5, 95:5) and isolated in 98% yield (50.6 mg) after purification of the combined crude mixtures.

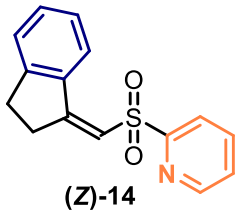
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.5 Hz, 2H), 7.60 – 7.50 (m, 3H), 7.43 – 7.36 (m, 2H), 7.04 – 6.98 (m, 2H), 6.56 (q, *J* = 1.5 Hz, 1H), 2.12 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 149.5 (2C), 146.0, 141.1, 133.4, 130.2, 129.1 (2C), 127.7 (2C), 122.0 (2C), 27.2.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{14}H_{13}NO_2S^+$) requires 259.0662, found 259.0678.

IR (thin film) ν 1592, 1446, 1409, 1305, 1148, 1086, 821, 758 cm^{-1}.

(*Z*)-14: (*Z*)-2-(((2,3-dihydro-1*H*-inden-1-ylidene)methyl)sulfonyl)pyridine



(*Z*)-14

$C_{15}H_{13}NO_2S$
MW: 271 $g.mol^{-1}$
Yield: 69%
Beige solid

The compound was prepared using general procedure B from **(*E*)-14** (27.1 mg) from two experiments (d.r. 46:54, 47:53) and isolated in 93% yield (50.7 mg) after purification of the combined crude mixtures.

The E-isomer could not be separated during the purification, the compound was characterized as a Z:E mixture (47:53).

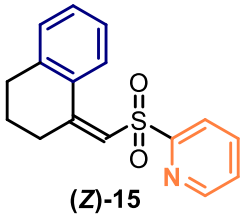
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 – 8.66 (m, 0.53H + 0.47H), 8.58 (d, *J* = 7.9 Hz, 0.47H), 8.18 (m, 0.47H), 8.13 (m, 0.53H), 7.93 (m, 0.47H + 0.53H), 7.55 – 7.44 (m, 1.06H + 0.47H), 7.42 – 7.20 (m, 1.41H + 1.59H), 6.84 (t, *J* = 2.5 Hz, 0.53H), 6.62 (m, 0.47H), 3.39 (m, 1.06H), 3.12 – 3.05 (m, 1.06H), 2.99 (m, 1.88H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 160.8, 159.8, 159.6, 151.7, 150.5, 150.2, 149.8, 138.6, 138.1 (1C + 1C), 135.3, 132.2, 131.8, 129.3, 127.2, 127.1, 127.0 (1C + 1C), 125.9, 125.3, 122.4, 121.8, 121.7, 117.1, 114.8, 36.0, 30.6, 29.9, 29.8.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{15}H_{14}NO_2S^+$) requires 272.0736, found 272.0740.

IR (thin film) ν 3048, 1611, 1596, 1577, 1426, 1307, 1161, 1108, 1080, 991, 847, 776, 752, 578 cm^{-1}.

(*Z*)-15: (*Z*)-2-(((3,4-dihydronaphthalen-1(2*H*)-ylidene)methyl)sulfonyl)pyridine



(*Z*)-15

$C_{16}H_{15}NO_2S$
MW: 285 $g.mol^{-1}$
Yield: 81%
Off-white oil

The compound was prepared using general procedure B from **(*E*)-15** (28.5 mg) from two experiments (d.r. 70:30, 72:28) and isolated in 81% yield (46.3 mg) after purification of the combined crude mixtures.

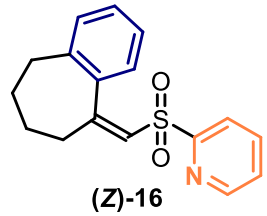
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 – 8.62 (m, 1H), 7.99 – 7.90 (m, 2H), 7.83 – 7.74 (m, 1H), 7.44 – 7.36 (m, 1H), 7.26 – 7.20 (m, 1H), 7.17 – 7.09 (m, 1H), 7.06 – 6.99 (m, 1H), 6.63 – 6.58 (m, 1H), 2.72 (t, *J* = 6.6 Hz, 2H), 2.57 (t, *J* = 6.7 Hz, 2H), 1.94 (p, *J* = 6.7 Hz, 2H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 154.8, 150.0, 139.6, 137.7, 131.7, 130.8, 130.6, 128.1, 126.8, 125.2, 122.3, 122.2, 35.1, 28.8, 22.5.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{16}H_{16}NO_2S^+$) requires 286.0896, found 286.0897.

IR (thin film) ν 3053, 2937, 1595, 1577, 1426, 1302, 1160, 1108, 1081, 991, 772, 604 cm^{-1}.

(*Z*)-16: (*Z*)-2-(((6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene)methyl)sulfonyl)pyridine



(*Z*)-16

$C_{17}H_{17}NO_2S$
MW: 299 g.mol^{-1}
Yield: 96%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-16** (29.9 mg) from two experiments (d.r. 54:46, 65:35) and isolated in 96% yield (57.5 mg) after purification of the combined crude mixtures.

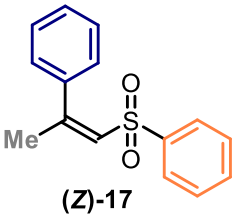
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.6, 1.6, 0.9 Hz, 1H), 7.50 (td, *J* = 7.8, 1.7 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.14 – 7.02 (m, 2H), 6.80 (br.s, 1H), 6.76 – 6.71 (m, 1H), 2.41 (br.s, 2H), 2.28 – 2.20 (m, 2H), 1.97 – 1.80 (m, 2H), 1.58 (br.s, 2H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 158.1, 149.7, 139.4, 137.4, 137.1, 129.0, 128.8, 128.5, 127.2, 126.5, 125.4, 122.2, 38.3, 35.0, 31.9, 27.0.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{17}H_{18}NO_2S^+$) requires 300.1053, found 300.1056.

IR (thin film) ν 3050, 2927, 2853 1614, 1577, 1448, 1427, 1305, 1149, 1108, 1081, 846, 761 cm^{-1}.

(*Z*)-17: (*Z*)-((2-phenylprop-1-en-1-yl)sulfonyl)benzene



(*Z*)-17

$C_{15}H_{14}O_2S$
MW: 258 g.mol^{-1}
Yield: 78%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-17** (25.8 mg) from two experiments (d.r. 94:6, 78:22) and isolated in 78% yield (40.3 mg) after purification of the combined crude mixtures.

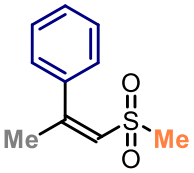
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.47 – 7.42 (m, 1H), 7.33 – 7.20 (m, 5H), 7.09 – 7.02 (m, 2H), 6.53 (q, *J* = 1.3 Hz, 1H), 2.12 (d, *J* = 1.3 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 141.6, 137.6, 132.9, 129.2, 128.7 (2C), 128.6, 128.1 (2C), 127.7 (2C), 127.4 (2C), 27.8.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{15}H_{14}O_2S^+$) requires 258.0710, found 258.0713.

IR (thin film) ν 3059, 1616, 1597, 1446, 1302, 1137, 1084, 842, 755, 687, 544 cm^{-1}.

(*Z*)-18: (*Z*)-(1-(methylsulfonyl)prop-1-en-2-yl)benzene



(*Z*)-18

$C_{10}H_{12}O_2S$
MW: 196 g.mol^{-1}
Yield: 95%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-18** (19.6 mg) from two experiments (d.r. 78:22, 78:22) and isolated in 95% yield (37.3 mg) after purification of the combined crude mixtures.

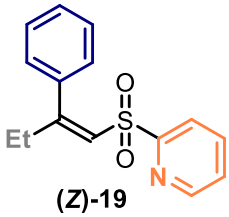
The E-isomer could not be entirely separated during the purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 5H), 6.44 (q, *J* = 1.4 Hz, 1H), 2.60 (s, 3H), 2.25 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 137.5, 129.2, 128.62, 128.55 (2C), 127.5 (2C), 43.3, 27.6.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{10}H_{13}O_2S^+$) requires 197.0631, found 197.0631.
IR (thin film) ν 3033, 2928, 1622, 1575, 1437, 1295, 1125, 961, 766, 700, 688, 526 cm^{-1}.

(*Z*)-19: (*Z*)-2-((2-phenylbut-1-en-1-yl)sulfonyl)pyridine



(*Z*)-19

$C_{15}H_{15}NO_2S$
MW: 273 g.mol^{-1}
Yield: 90%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-19** (27.3 mg) from two experiments (d.r. 80:20, 88:12) and isolated in 90% yield (49.1 mg) after purification of the combined crude mixtures.

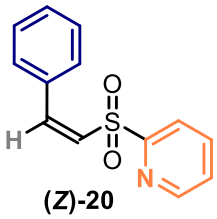
The E-isomer could not be separated during the purification, the compound was characterized as a Z:E mixture (87:13).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.69 (m, 0.13H), 8.69 – 8.60 (m, 0.87H), 8.15 (d, *J* = 7.9 Hz, 0.13H), 7.95 (td, *J* = 7.8, 1.6 Hz, 0.13H), 7.58 (td, *J* = 7.8, 1.6 Hz, 0.87H), 7.51 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 0.13H), 7.45 – 7.31 (m, 0.65H + 1.74H), 7.23 – 7.18 (m, 0.87H), 7.17 – 7.11 (m, 1.74H), 6.98 – 6.92 (m, 1.74H), 6.70 (s, 0.87H), 6.63 (s, 0.13H), 3.11 (q, *J* = 7.5 Hz, 0.26H), 2.45 (qd, *J* = 7.3, 1.3 Hz, 1.74H), 1.05 (t, *J* = 7.3 Hz, 2.61H), 0.98 (t, *J* = 7.5 Hz, 0.39H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 161.5, 159.7, 158.9, 150.4, 150.0, 138.9, 138.2, 137.4, 137.1, 129.9, 128.9 (2C), 128.3, 127.8 (2C), 127.6 (2C), 127.1, 127.0 (2C), 126.6, 126.1, 124.7, 122.5, 121.8, 34.0, 24.3, 13.4, 11.7.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{15}H_{15}NO_2S^+$) requires 273.0818, found 273.0817.
IR (thin film) ν 3053, 2972, 1617, 1596, 1577, 1426, 1304, 1147, 1107, 1080, 991, 764, 699, 604 cm^{-1}.

(*Z*)-20: (*Z*)-2-(styrylsulfonyl)pyridine



(*Z*)-20

$C_{13}H_{11}NO_2S$
MW: 245 g.mol^{-1}
Yield: 98%
Colourless solid

The compound was prepared using general procedure B from **(*E*)-20** (24.5 mg) from two experiments (d.r. 46:54, 48:52) and isolated in 98% yield (48.0 mg) after purification of the combined crude mixtures.

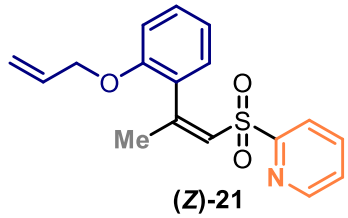
The E-isomer could not be separated during the purification, the compound was characterized as a Z:E mixture (45:55).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 0.55H), 8.67 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 0.45H), 8.13 (dt, *J* = 7.9, 1.0 Hz, 0.55H), 7.99 – 7.90 (m, 0.55H + 0.45H), 7.81 (td, *J* = 7.7, 1.7 Hz, 0.45H), 7.77 (d, *J* = 15.6 Hz, 0.55H), 7.57 – 7.48 (m, 1.65H + 0.90H), 7.46 – 7.35 (m, 1.65H + 0.45H), 7.33 – 7.26 (m, 1.35H), 7.24 (d, *J* = 12.1 Hz, 0.45H), 7.11 (d, *J* = 15.5 Hz, 0.55H), 6.77 (d, *J* = 12.1 Hz, 0.45H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 158.4, 150.5, 150.2, 145.2, 143.3, 138.3, 137.9, 132.5, 132.4, 131.5, 130.2 (2C), 129.9, 129.2 (2C), 128.9 (2C), 128.4, 128.1 (2C), 127.3, 127.2, 124.7, 122.3, 122.0.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{13}H_{11}NO_2S^+$) requires 245.0505, found 245.0524.
IR (thin film) ν 1592, 1446, 1409, 1305, 1148, 1086, 821, 720, 688, 613, 546 cm^{-1}.

(*Z*)-21: (*Z*)-2-((2-(allyloxy)styryl)sulfonyl)pyridine



(*Z*)-21

$C_{16}H_{15}NO_3S$
MW: 301 g.mol^{-1}
Yield: 73%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-21** (30.1 mg) from two experiments (d.r. 53:47, 54:46) and isolated in 73% yield (44.2 mg) after purification of the combined crude mixtures.

The E-isomer could not be separated during the purification, the compound was characterized as a Z:E mixture (56:44).

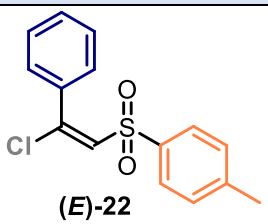
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 0.44H), 8.67 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 0.56H), 8.13 (dt, *J* = 7.9, 0.9 Hz, 0.44H), 8.00 (d, *J* = 15.6 Hz, 0.44H), 7.97 – 7.87 (m, 0.44H + 0.56H), 7.78 (app.td, *J* = 7.7, 1.7 Hz, 1.12H), 7.53 – 7.40 (m, 0.88H + 1.12H), 7.39 – 7.24 (m, 0.88H + 0.56H), 7.00 – 6.87 (m, 0.88H + 0.56H), 6.80 – 6.70 (m, 1.12H), 6.12 – 5.89 (m, 0.44H + 0.56H), 5.45 – 5.21 (m, 0.88H + 1.12H), 4.62 (dt, *J* = 5.2, 1.4 Hz, 0.88H), 4.45 (dt, *J* = 5.1, 1.5 Hz, 1.12H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 158.7, 158.1, 156.3, 150.5, 150.1, 141.1, 139.7, 138.2, 137.7, 132.9, 132.7, 132.6, 132.2, 131.6, 131.1, 128.1, 127.03, 126.96, 125.5, 122.3, 122.0, 121.8, 121.6, 121.1, 120.2, 118.4, 117.8, 112.7, 111.4, 69.4, 69.1.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{16}H_{16}NO_3S^+$) requires 302.0845, found 302.0847.

IR (thin film) ν 3057, 1599, 1577, 1485, 1452, 1426, 1308, 1249, 1162, 1108, 991, 754 cm^{-1}.

(*E*)-22: (*E*)-1-((2-chloro-2-phenylvinyl)sulfonyl)-4-methylbenzene



(*E*)-22

$C_{15}H_{13}NO_2SCl$
MW: 292 g.mol^{-1}
Yield: 87%
Colourless solid

The compound was prepared using general procedure B from **(*Z*)-22** (29.3 mg) from two experiments (d.r. 91:9, 88:12) and isolated in 87% yield (51.1 mg) after purification of the combined crude mixtures.

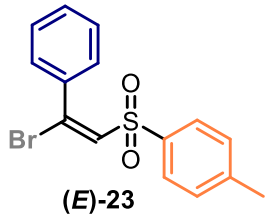
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.33 (m, 5H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.92 (s, 1H), 2.40 (s, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 144.7, 137.7, 134.5, 131.1, 130.8, 129.8 (2C), 129.0 (2C), 128.1 (2C), 127.9 (2C), 21.7.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{15}H_{13}NO_2S^{35}Cl^+$) requires 292.0320, found 292.0328; ($C_{15}H_{13}NO_2S^{37}Cl^+$) requires 294.0290, found 294.0300.

IR (thin film) ν 3046, 1593, 1445, 1320, 1291, 1148, 1085, 899, 717, 653, 562 cm^{-1}.

(*E*)-23: (*E*)-1-((2-bromo-2-phenylvinyl)sulfonyl)-4-methylbenzene



(*E*)-23

$C_{15}H_{13}NO_2SBr$
MW: 336 g.mol^{-1}
Yield: 81%
Colourless solid

The compound was prepared using general procedure B from **(*Z*)-23** (29.3 mg) from two experiments (d.r. 65:35, 63:37) and isolated in 81% yield (54.3 mg) after purification of the combined crude mixtures.

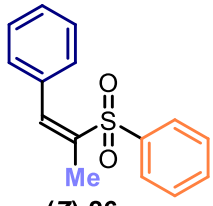
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.30 (m, 5H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.14 (s, 1H), 2.40 (s, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 138.4, 137.6, 136.2, 134.5, 130.5, 129.8 (2C), 128.7 (2C), 128.1 (2C), 128.0 (2C), 21.8.

HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{15}H_{14}{}^{79}BrNO_2S^+$) requires 336.9892, found 336.9895; ($C_{15}H_{14}{}^{81}BrNO_2S^+$) requires 338.9872, found 338.9872.

IR (thin film) ν 3047, 1592, 1488, 1444, 1323, 1291, 1149, 1084, 878, 773, 692, 648, 553 cm^{-1}.

(*Z*)-26: (*Z*)-((1-phenylprop-1-en-2-yl)sulfonyl)benzene



(*Z*)-26

$C_{15}H_{14}O_2S$
MW: 258 g.mol^{-1}
Yield: 92%
Colourless solid

The compound was prepared using general procedure B from **(*E*)-26** (25.8 mg) from two experiments (d.r. 22:78, 27:73) and isolated in 92% yield (47.3 mg) after purification of the combined crude mixtures.

The E-isomer could not be separated during the purification, the compound was characterized as a Z:E mixture (25:75).

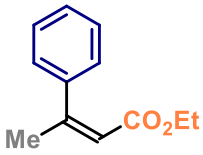
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 1.0 Hz, 1.50H), 7.83 (d, *J* = 0.9 Hz, 0.75H), 7.67 – 7.50 (m, 3.00H), 7.49 – 7.30 (m, 1.50H + 3.00H), 7.23 (d, *J* = 3.1 Hz, 1.00H), 7.06 (s, 0.25H), 2.24 – 2.20 (m, 0.75H), 2.11 (d, *J* = 1.0 Hz, 2.25H). *See spectra*

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 139.5, 139.2, 138.9, 137.6, 137.4, 134.2, 133.9, 133.4, 133.1, 129.7 (2C), 129.5, 129.3 (2C), 129.0 (2C), 128.8 (2C), 128.7 (2C), 128.3 (2C), 128.2, 127.8 (2C), 127.8 (2C), 20.8, 13.3.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{15}H_{14}O_2S^+$) requires 258.0709, found 258.0724.

IR (thin film) ν 3060, 1631, 1446, 1302, 1150, 1109, 1072, 966, 773, 738, 569 cm^{-1}.

(*Z*)-27: ethyl (*Z*)-3-phenylbut-2-enoate



(*Z*)-27

$C_{12}H_{14}O_2$
MW: 190 g.mol^{-1}
Yield: 84%
Colourless oil

The compound was prepared using general procedure B from **Ethyl trans-β-methylcinnamate** (18 μL) from two experiments (d.r. 86:14, 87:13) and isolated in 84% yield (31.9 mg) after purification of the combined crude mixtures.

Spectral properties were in accordance with those reported in the literature.[12]

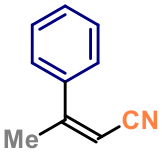
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 3H), 7.24 – 7.17 (m, 2H), 5.94 – 5.87 (m, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.18 (d, *J* = 1.3 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 155.5, 141.0, 128.0 (2C), 127.9, 127.0 (2C), 117.9, 59.9, 27.3, 14.1.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{12}H_{14}O_2^+$) requires 190.0988, found 190.0991.

IR (thin film) ν 2979, 1724, 1639, 1443, 1375, 1275, 1229, 1160, 1046, 768, 697 cm^{-1}.

(*Z*)-28: (*Z*)-3-phenylbut-2-enenitrile



(*Z*)-28

$C_{10}H_9N$
MW: 143 g.mol^{-1}
Yield: 76%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-28** (14.3 μL) from two experiments (d.r. 78:22, 64:36) and isolated in 76% yield (21.6 mg) after purification of the combined crude mixtures.

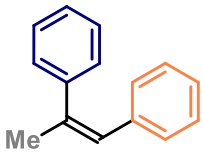
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.46 – 7.40 (m, 3H), 5.40 (q, *J* = 1.4 Hz, 1H), 2.29 (d, *J* = 1.5 Hz, 3H). *See spectra*

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 138.0, 130.0, 128.8 (2C), 127.2 (2C), 117.7, 95.6, 24.8.

HRMS (EI$^+$): exact mass calculated for $[M]^+$ ($C_{10}H_9N^+$) requires 143.0730, found 143.0743.

IR (thin film) ν 3057, 2215, 1612, 1439, 1358, 1214, 1027, 806, 766, 697 cm^{-1}.

(*Z*)-29: (*Z*)-prop-1-ene-1,2-diyldibenzene



(*Z*)-29

$C_{15}H_{14}$
MW: 194 g.mol^{-1}
Yield: 77%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-α-methylstilbene** (19.4 mg) from two experiments (d.r. 79:21, 78:22) and isolated in 77% yield (30.0 mg) after purification of the combined crude mixtures.

The E-isomer could not be separated during the purification, the compound was characterized as a Z:E mixture (78:22).

[12] B. Scheiper, M. Bonnekessel, H. Krause and A. Fürstner, *J. Org. Chem.* 2004, **69**, 3943–3949.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 0.44H), 7.40 – 7.32 (m, 1.32H), 7.30 – 7.13 (m, 0.44H + 3.90H), 7.11 – 7.01 (m, 2.34H), 6.96 – 6.89 (m, 1.56H), 6.82 (s, 0.22H), 6.45 (s, 0.78H), 2.27 (d, *J* = 1.2 Hz, 0.44H), 2.19 (d, *J* = 1.4 Hz, 2.34H). *See spectra*

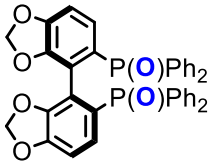
HRMS (EI^+): exact mass calculated for $[M]^+$ ($C_{15}H_{14}^+$) requires 194.1090, found 194.1101.

IR (thin film) ν 3023, 1599, 1494, 1441, 1026, 916, 757, 696 cm^{-1}.

VI. Mechanistic investigations

A. Synthesis of SEGPHOS-oxide derivatives

SEGPHOSO$_2$



SEGPHOSO$_2$

$C_{38}H_{28}O_6P_2$
MW: 642 g.mol^{-1}
Yield: >99%
Colourless solid

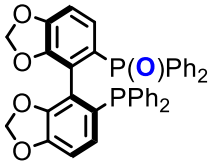
To a solution of SEGPHOS (122 mg, 0.20 mmol. 1.0 equiv.) in CH_2Cl_2 at 0 °C was added a solution of hydrogen peroxide in water (35%, 1.0 mL, excess). The reaction was stirred for 2 hours at this temperature. Water (6 mL) was added and the mixture was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography to afford quantitatively SEGPHOSO as a colourless solid.

Spectral properties were in accordance with those reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 4H), 7.61 – 7.52 (m, 4H), 7.46 – 7.28 (m, 8H), 7.27 – 7.19 (m, 4H), 6.73 (dd, *J* = 14.1, 8.1 Hz, 2H), 6.61 (dd, *J* = 8.1, 1.9 Hz, 2H), 5.66 (d, *J* = 1.1 Hz, 2H), 5.21 (d, *J* = 2.5 Hz, 2H). *See spectra*

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.96.

SEGPHOSO



SEGPHOSO

$C_{38}H_{28}O_5P_2$
MW: 626 g.mol^{-1}
Yield: 45%
Colourless solid

The compound was obtained according to a modification of Grushin's procedure.[14,15] Under argon, (*S*)-SEGPHOS (61.1 mg, 0.10 mmol) and PdI_2 (54.0 mg, 0.15 mmol, 1.5 equiv.) were stirred in CH_2Cl_2 (10 mL) for 1.5 h at room temperature. Unreacted PdI_2 was filtered off using a syringe filter.The filtrate was transferred to a new flask under argon and further stirred stirred with bis(p-methoxybenzylidene)acetone (25.8 mg, 0.11 mmol, 1.1 equiv.) and an aqueous NaOH solution (3.75 M, 4.9 mL) at room temperature for 16 h. The organic layer was separated and stirred with dppe (79.7 mg, 0.20 mmol, 2.0 equiv.) at room temperature for 3 h to remove Pd. The resulting solution was filtered on a silica gel pad and washed with CH_2Cl_2 (this filtrate was discarded). The pad was then eluted with a 2:1 CH_2Cl_2/EtOAc mixture and concentrated under reduced pressure. The product was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc, from 100/0 to 30/70). SEGPHOSO was obtained as a colourless solid (28.0 mg, 45%). The product of double oxidation (SEGPHOSOO) was detected after column.

Spectral properties were in accordance with those reported in the literature.

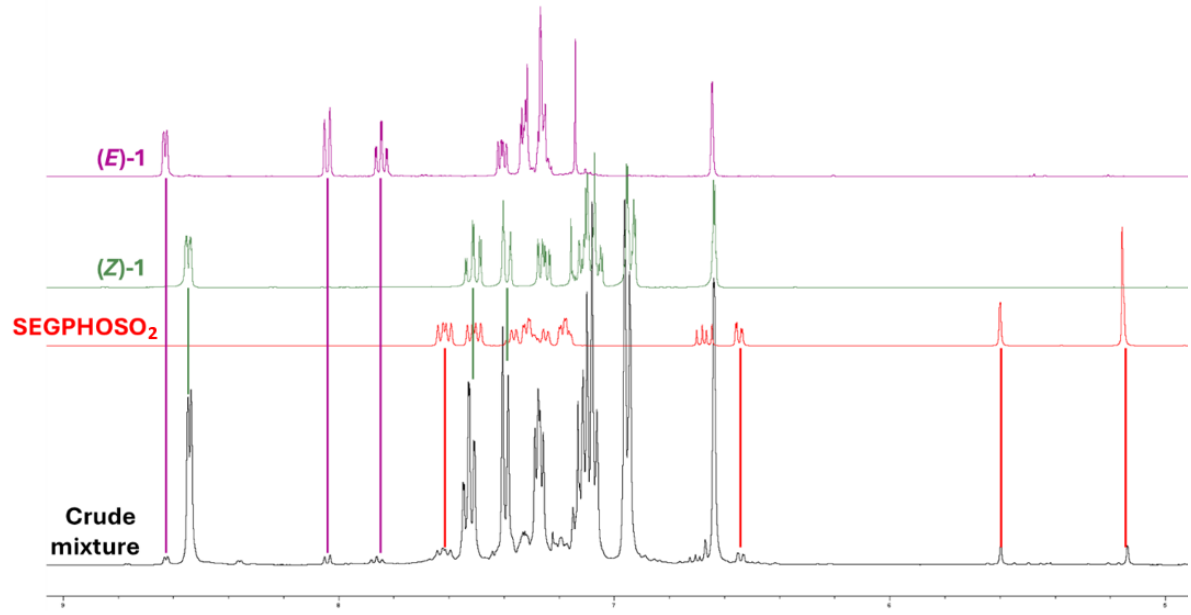
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.64 – 7.57 (m, 2H), 7.48 – 7.41 (m, 2H), 7.36 (ddd, *J* = 7.4, 5.2, 2.0 Hz, 4H), 7.29 – 7.19 (m, 10H), 6.98 (dd, *J* = 14.1, 8.1 Hz, 1H), 6.75 (dd, *J* = 8.1, 1.9 Hz,

[13] Z. Zuo, R. S. Kim and D. A. Watson, *J. Am. Chem. Soc.*, 2021, **143**, 1328–1333.
[14] V. V. Grushin, *Organometallics*, 2001, **20**, 3950–3961.
[15] J. Hu, H. Hirao, Y. Li and J. (Steve) Zhou, *Angew. Chem. Int. Ed.*, 2013, **52**, 8676–8680.

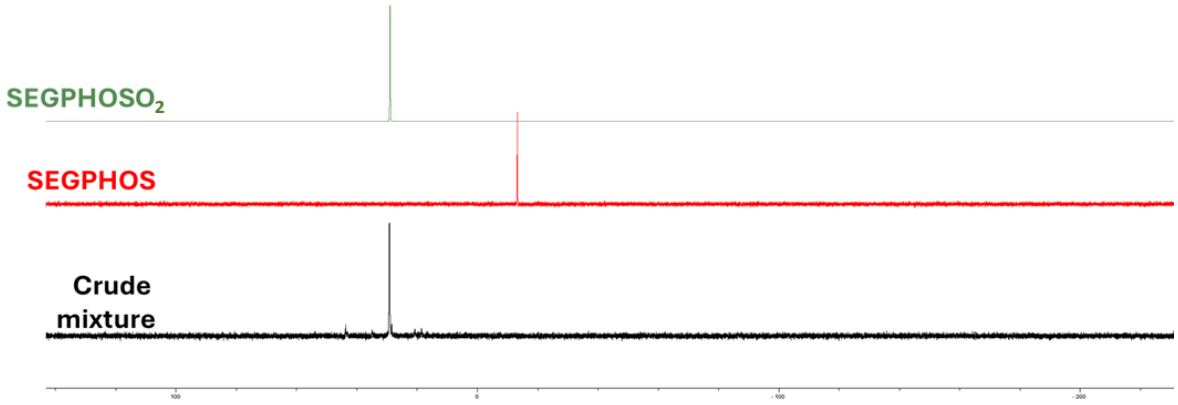
1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 8.0, 3.4 Hz, 1H), 5.71 (d, *J* = 1.6 Hz, 1H), 5.66 (d, *J* = 1.4 Hz, 1H), 5.23 (d, *J* = 1.6 Hz, 1H), 4.82 (d, *J* = 1.4 Hz, 1H).

B. NMR analysis of the reaction crude mixture

^{1}H-NMR analysis of the crude mixture:



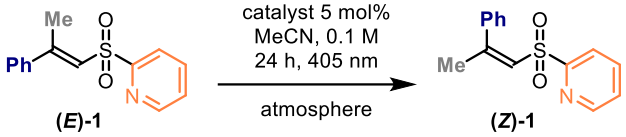
^{31}P-NMR analysis of the crude mixture:



The NMR analysis of the reaction crude mixture on large scale revealed the conversion of SEGPHOS into SEGPHOSO$_2$. Integration in ^{1}H NMR permitted to approximate the quantity of SEGPHOSO$_2$ in the crude mixture to 3 mol%.

C. Mechanistic experiments

Impact of SEGPHOS oxidation state and atmosphere

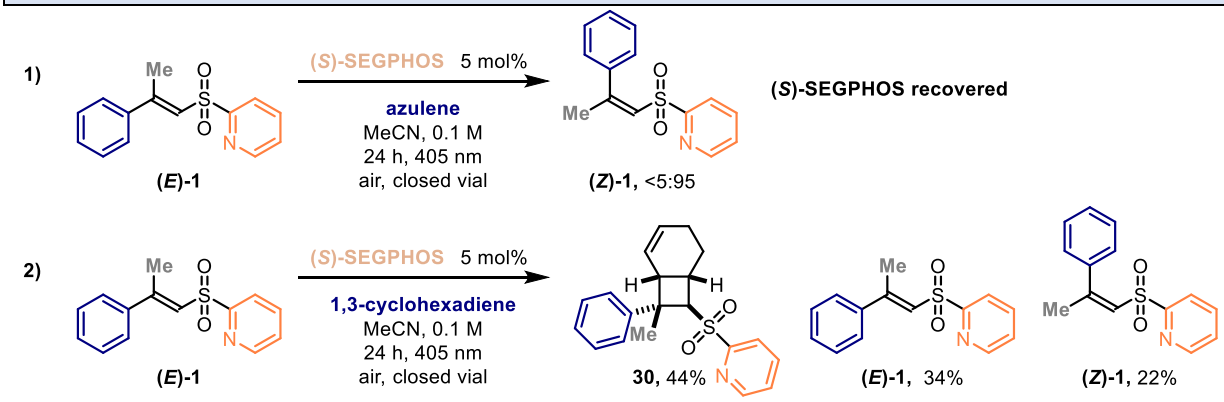


Entry	Catalyst	Atmosphere	*Z:E*
1	(*S*)-SEGPHOS	air	95:5
2	SEGPHOSO	air	86:14
3	$SEGPHOSO_2$	air	80:20
4	(*S*)-SEGPHOS	Open to air	52:48
5	(*S*)-SEGPHOS	glovebox	52:48
6	SEGPHOSO	glovebox	95:5
7	$SEGPHOSO_2$	glovebox	95:5

The reactions were carried out using general procedure B with the following alterations:

- (2), (6) SEGPHOSO (3.1 mg, 5.0 µmol, 5.0 mol%) was used instead of SEGPHOS.
- (3), (7) $SEGPHOSO_2$ (3.2 mg, 5.0 µmol, 5.0 mol%) was used instead of SEGPHOS.
- (4) Atmosphere exchange with ambient air was permitted through two needles.
- (5), (6), (7) The reaction was set up in a glovebox using degazed MeCN (3 freeze-pump-thaw cycles).

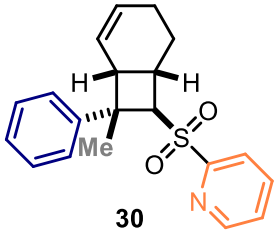
Trapping experiments



The reactions were carried out using general procedure B with the following alterations:

- (1) Azulene (12.8 mg, 0.10 mmol, 1.0 equiv.) was added to the reaction vessel prior the addition of MeCN.
- (2) 1,3-cyclohexadiene (9.5 µL, 0.10 mmol, 1.0 equiv.) was added to the reaction mixture after the addition of MeCN.

30: (±)-2-(((1*R*,6*S*,7*R*,8*S*)-8-methyl-8-phenylbicyclo[4.2.0]oct-2-en-7-yl)sulfonyl)pyridine



30

$C_{20}H_{21}NO_2S$
MW: 339 g.mol^{-1}
Yield: 44%
Colourless oil

The compound was prepared using general procedure B from **(*E*)-1** (25.9 mg) and additional 1,3-cyclohexadiene (9.5 µL, 0.10 mmol, 1.0 equiv.) and isolated in 44% yield (11.3 mg) after purification.

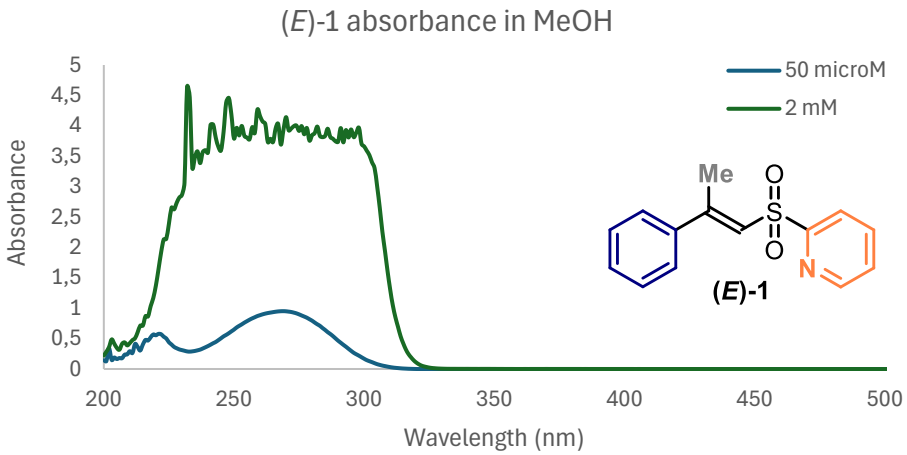
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.17 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.98 (td, *J* = 7.8, 1.7 Hz, 1H), 7.56 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.34 – 7.28 (m, 4H), 7.21 – 7.15 (m, 1H), 5.59 – 5.44 (m, 2H), 4.68 (d, *J* = 10.0 Hz, 1H), 3.48 – 3.37 (m, 1H), 2.91 – 2.80 (m, 1H), 1.96 (s, 3H), 1.83 – 1.72 (m, 2H), 1.36 – 1.24 (m, 1H), 1.07 – 0.96 (m, 1H). *See spectra*

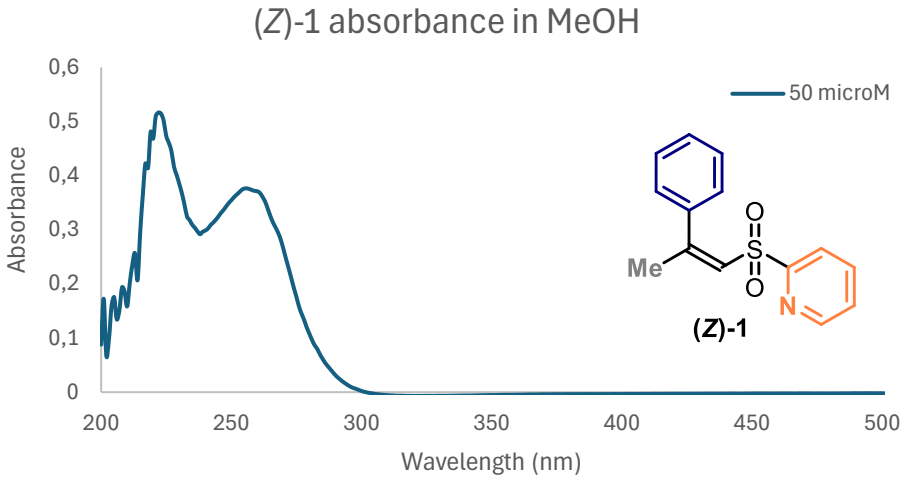
^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 150.4, 145.3, 138.3, 128.2 (2C), 127.7, 127.5, 127.0, 126.5 (2C), 126.1, 122.4, 58.3, 54.0, 41.6, 32.4, 26.7, 20.6, 20.5.

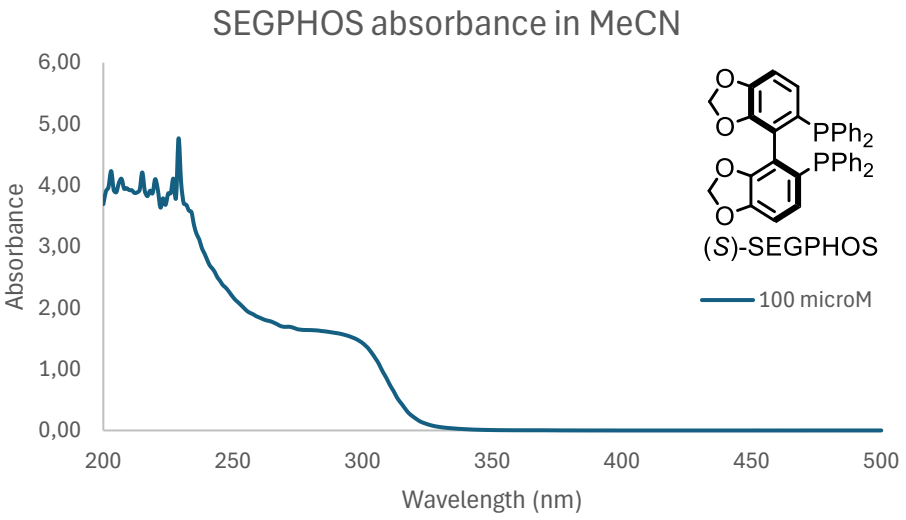
HRMS (ESI$^+$): exact mass calculated for $[M+H]^+$ ($C_{20}H_{21}NO_2S^+$) requires 340.1366, found 340.1360.

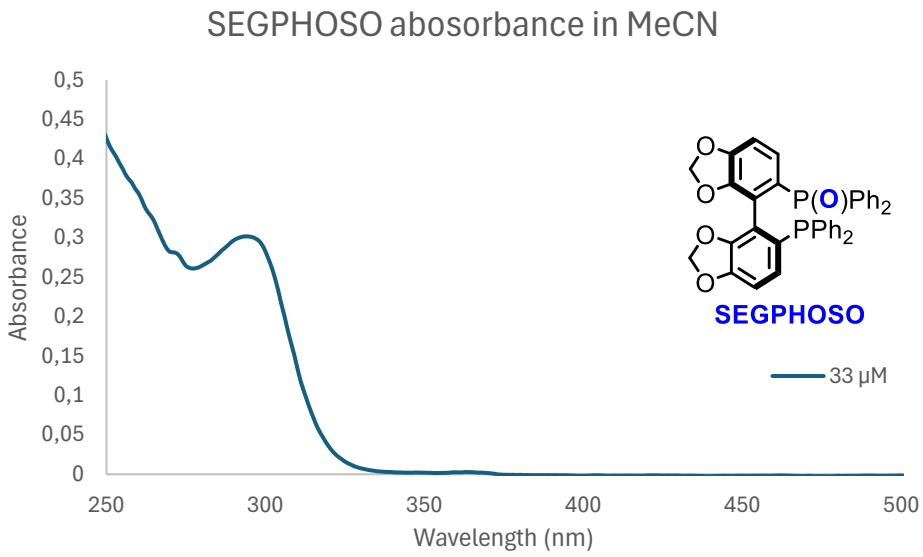
VII. Spectroscopic studies

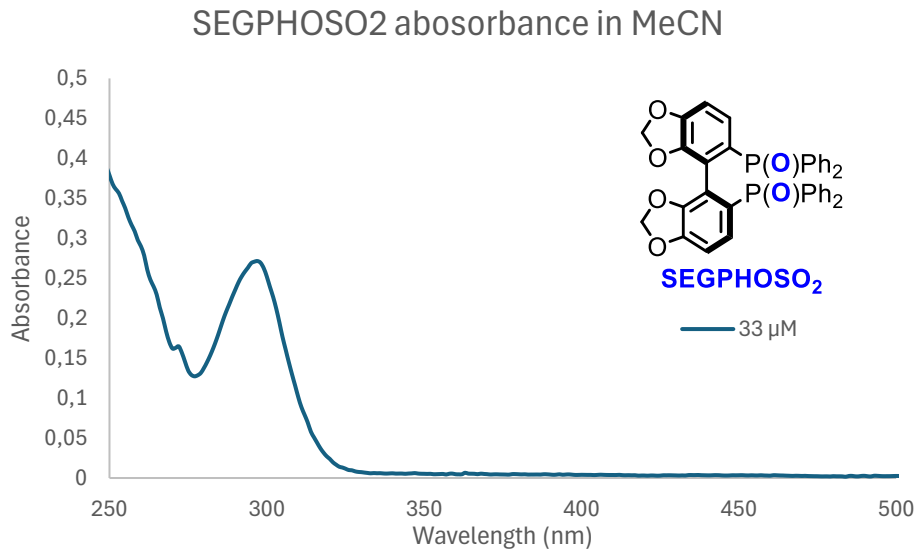
A. Absorption spectra



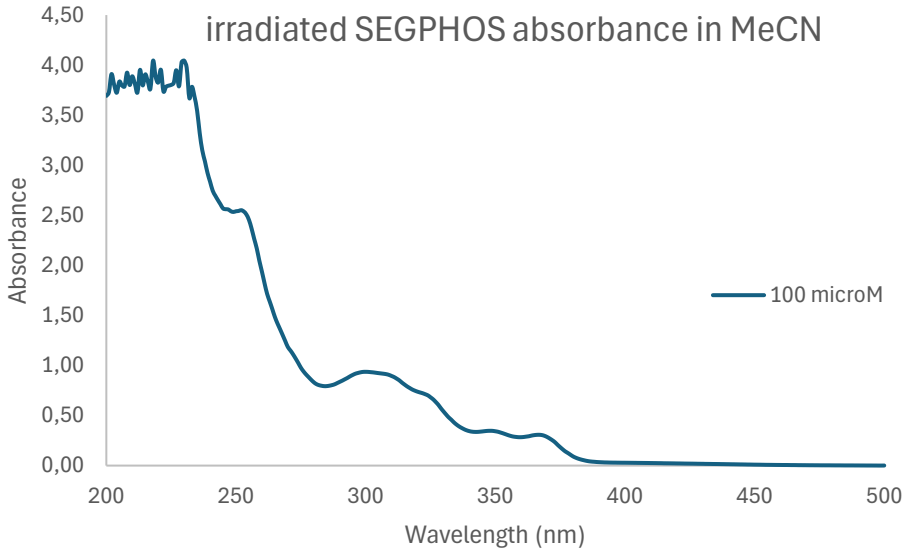


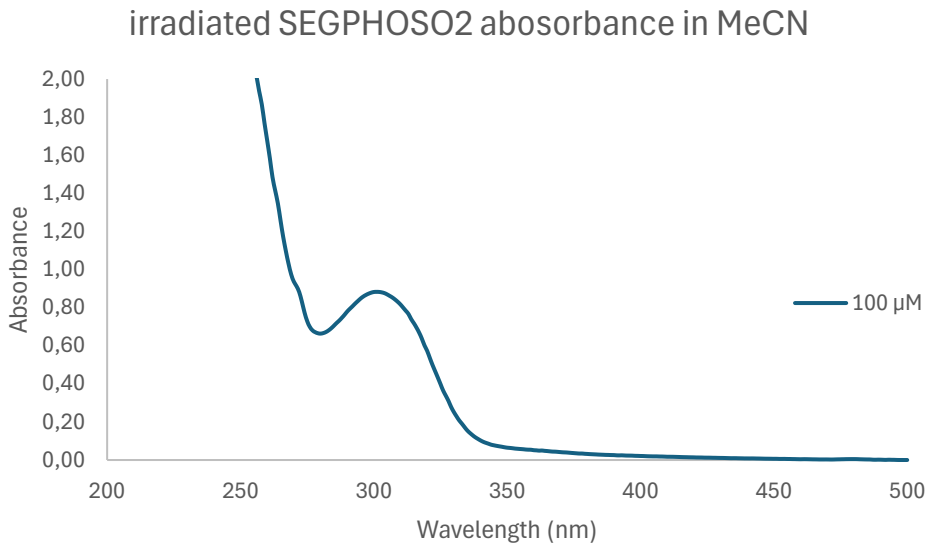



SEGPHOSO abosorbance in MeCN
Absorbance
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
250
300
350
400
450
500
Wavelength (nm)
P(O)Ph2
PPh2
SEGPHOSO
33 µM

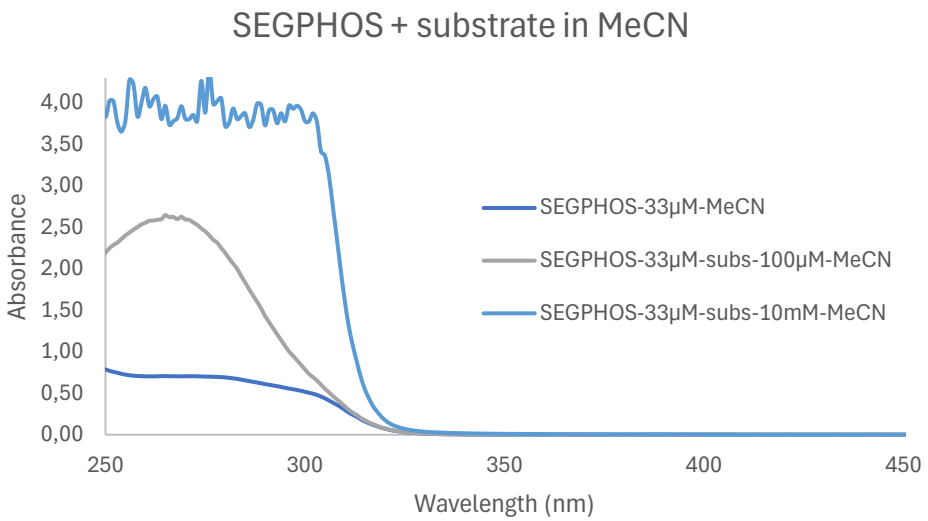

SEGPHOSO2 abosorbance in MeCN
Absorbance
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
250
300
350
400
450
500
Wavelength (nm)
P(O)Ph2
P(O)Ph2
SEGPHOSO2
33 µM

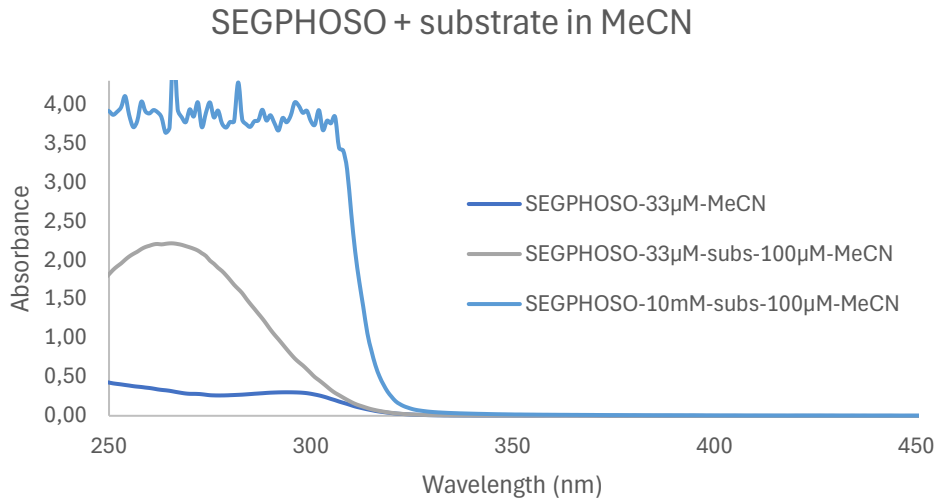
A stirred solution of SEGPHOS or SEGPHOSO2 were irradiated in the fluorimeter until the fluorescent signal reached the steady state.

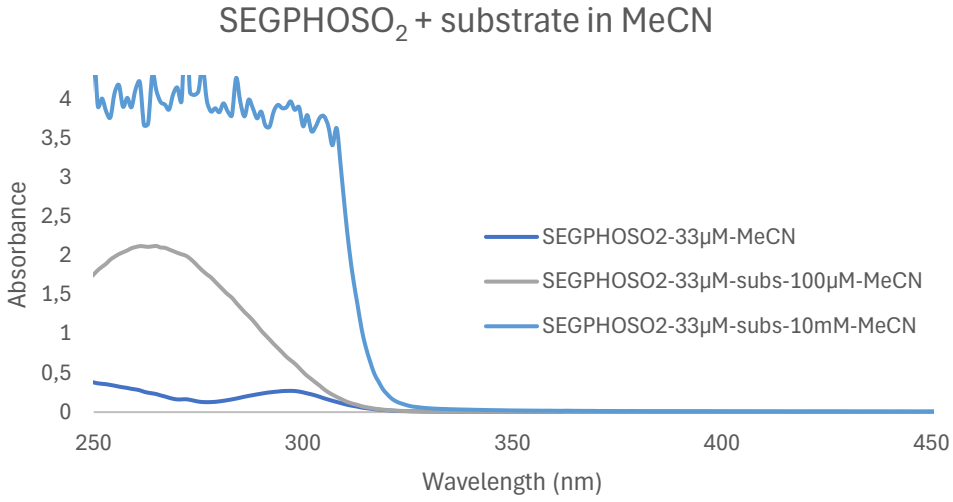




B. Investigation for a potential charge-transfer complex formation.

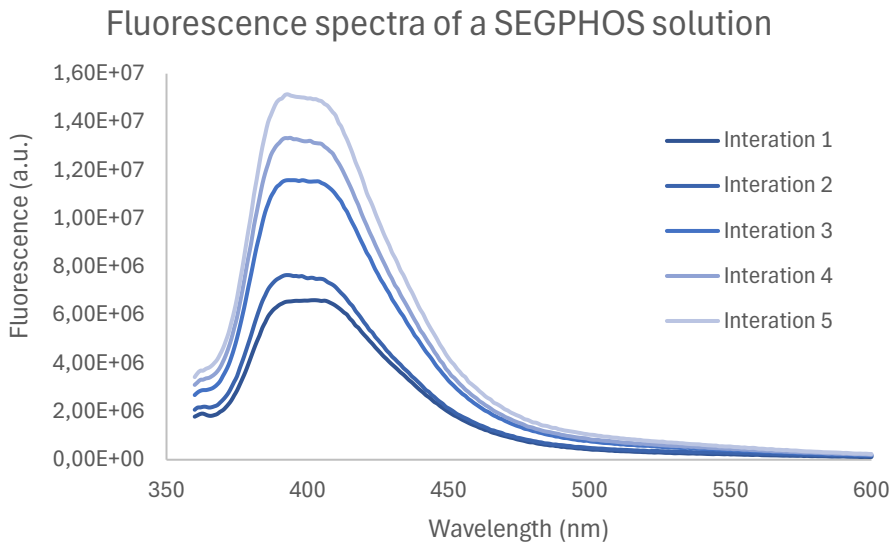






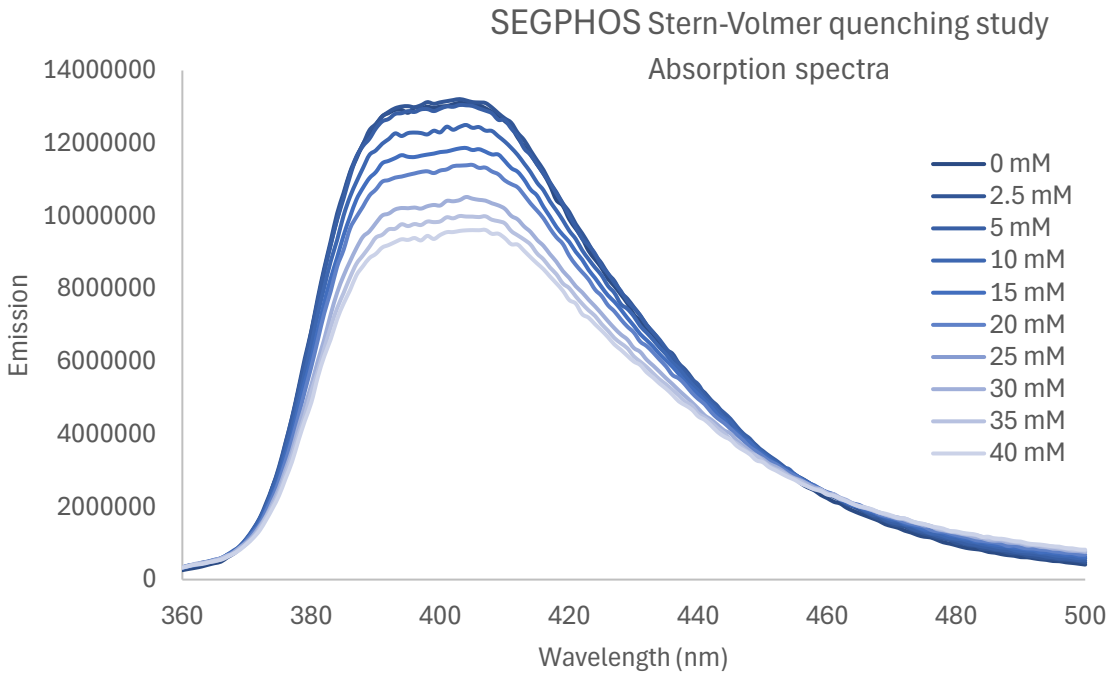
C. Fluorescence and Stern-Volmer quenching studies

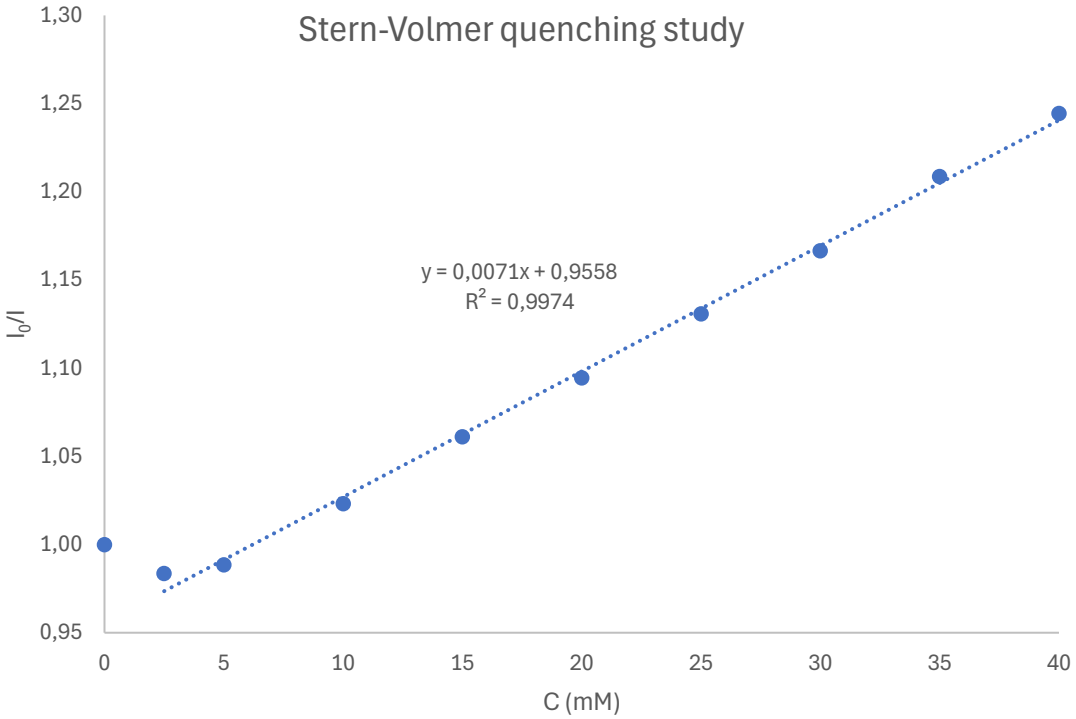
The fluorescence spectrum recording of a SEGPHOS solution showed irreproducibility with an enhancement of the signal over accumulations. The same behaviour was observed when the fluorescence signal of $SEGPHOSO_2$ was measured.



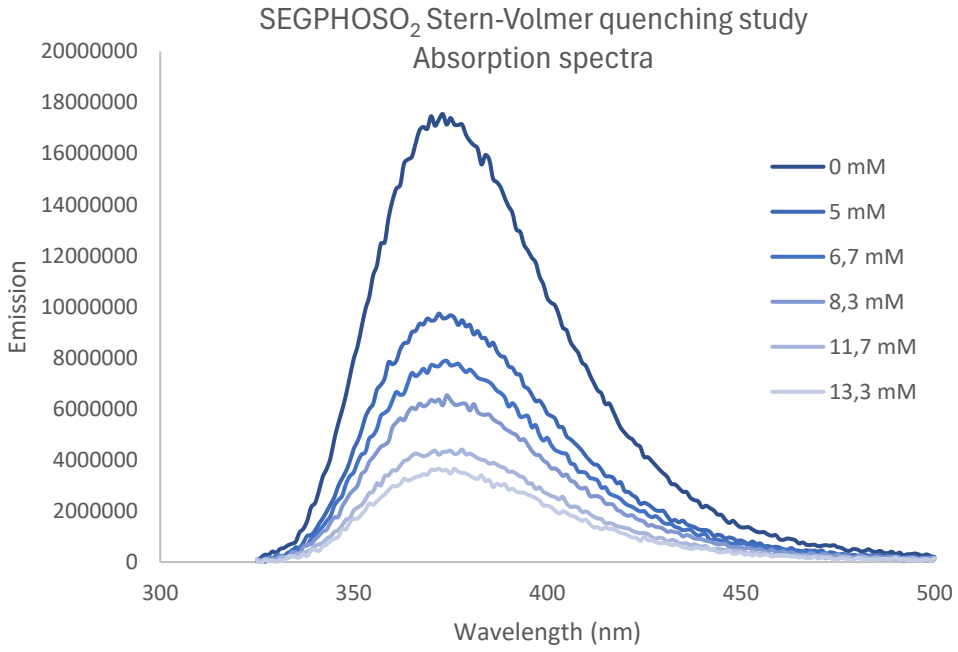
Once the steady state reached, the absorption spectrum measured and the solution was appropriately diluted to a concentration corresponding to initially 33 microM of SEGPHOS and 100 microM of $SEGPHOSO_2$.

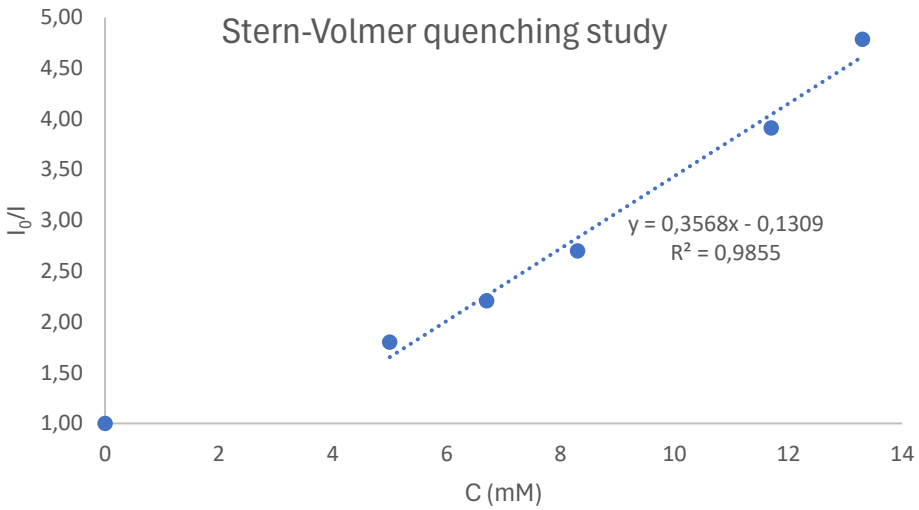
Increasing amounts of **(*E*)-1** (5-40 mM final, x times 10 µL of a 1 M solution in MeCN) were added to the solution (2 mL) to measure the fluorescence quenching effect.





Increasing amounts of **(*E*)-1** (5-13,3 mM final, x additions of a 1 M solution in MeCN) were added to the solution (3 mL) to measure the fluorescence quenching effect.

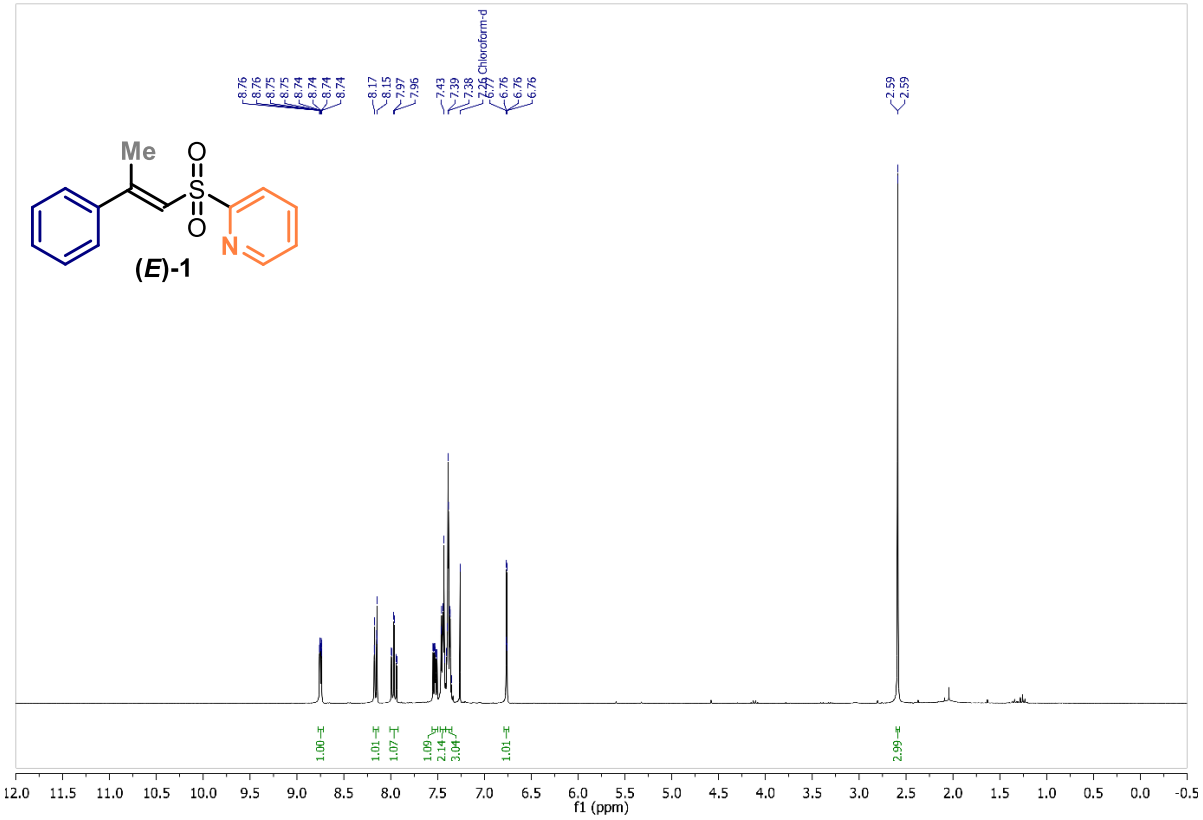



Stern-Volmer quenching study
5,00
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
I_0/I
0
2
4
6
8
10
12
14
C (mM)
y = 0,3568x - 0,1309
R² = 0,9855

VIII. NMR spectra

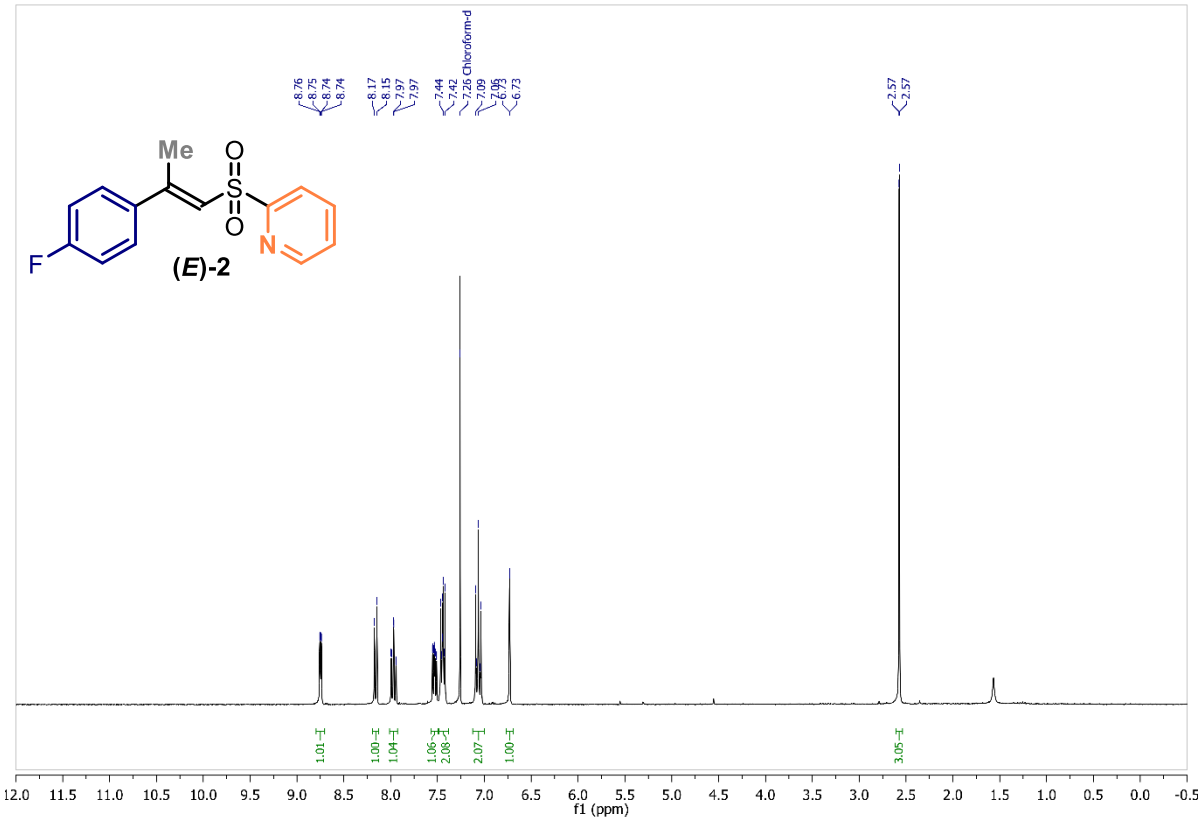
(*E*)-1: (*E*)-2-((2-phenylprop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

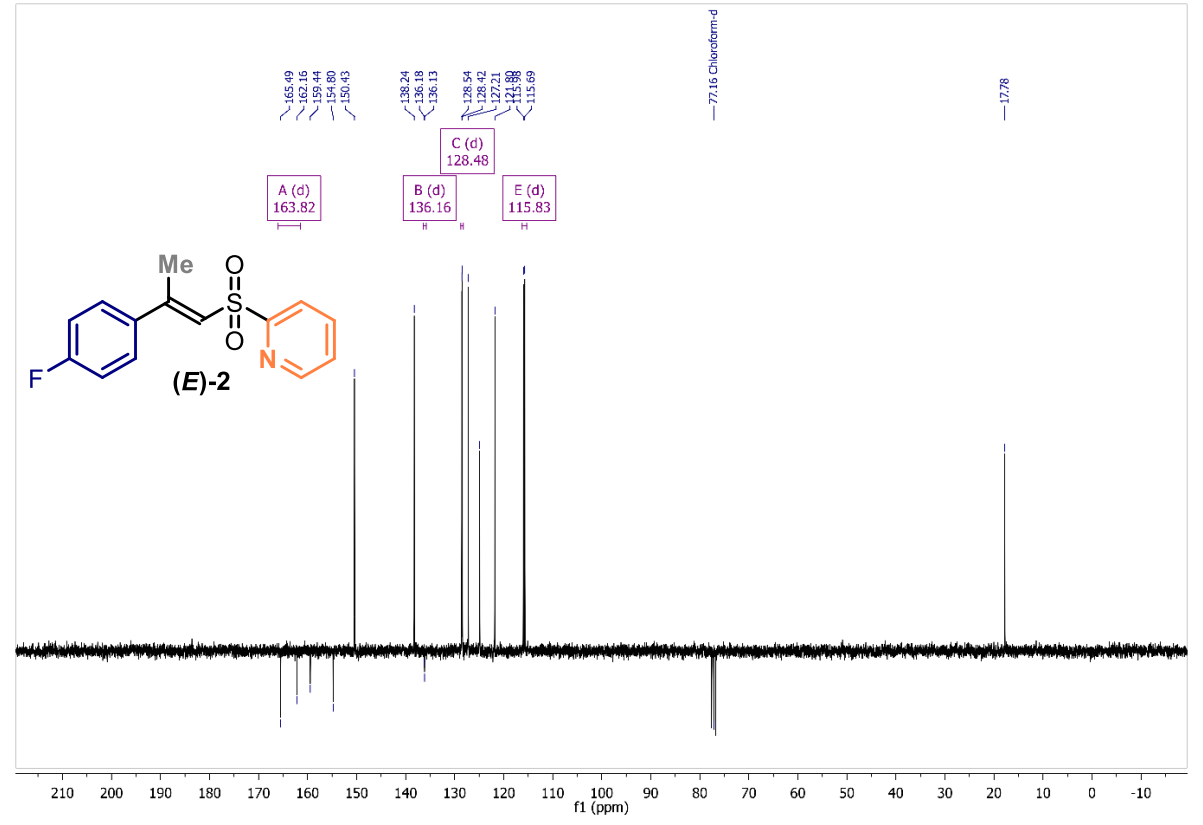


(*E*)-2: (*E*)-2-((2-(4-fluorophenyl)prop-1-en-1-yl)sulfonyl)pyridine

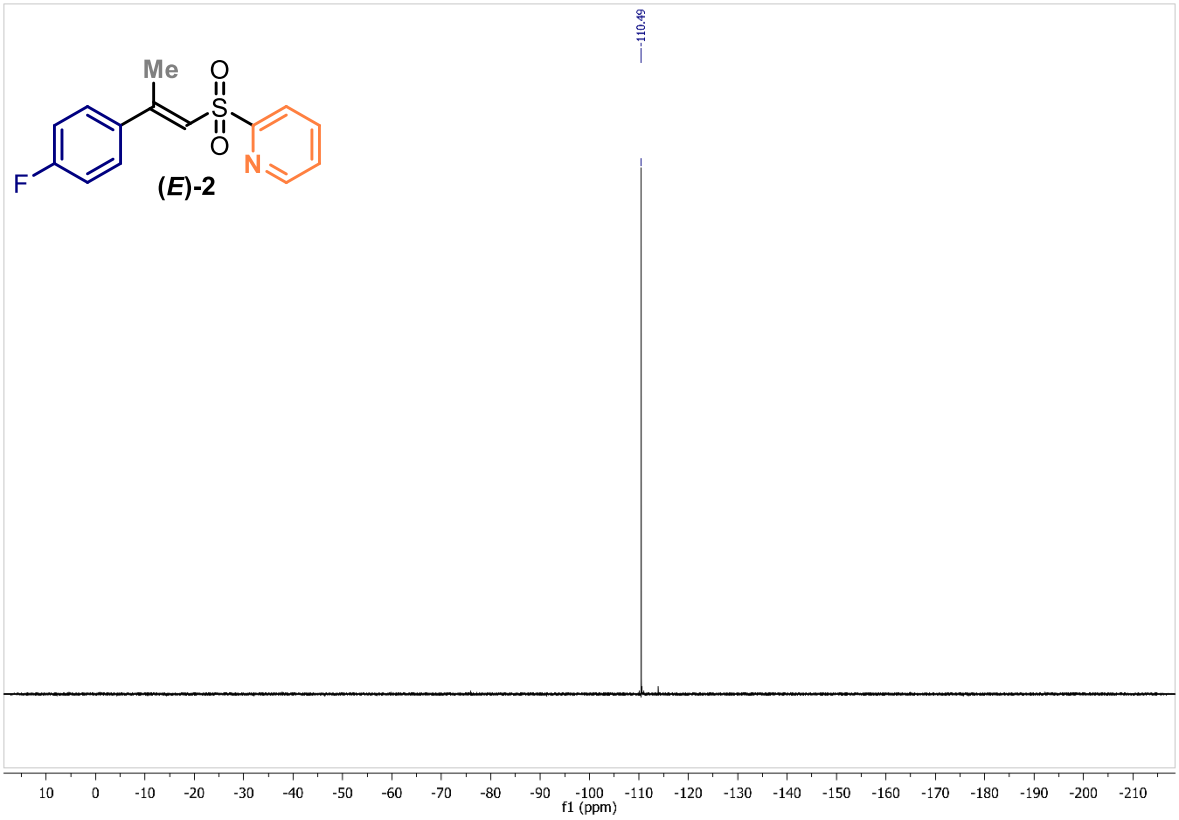
^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*



^{13}C NMR (75 MHz, $CDCl_3$)

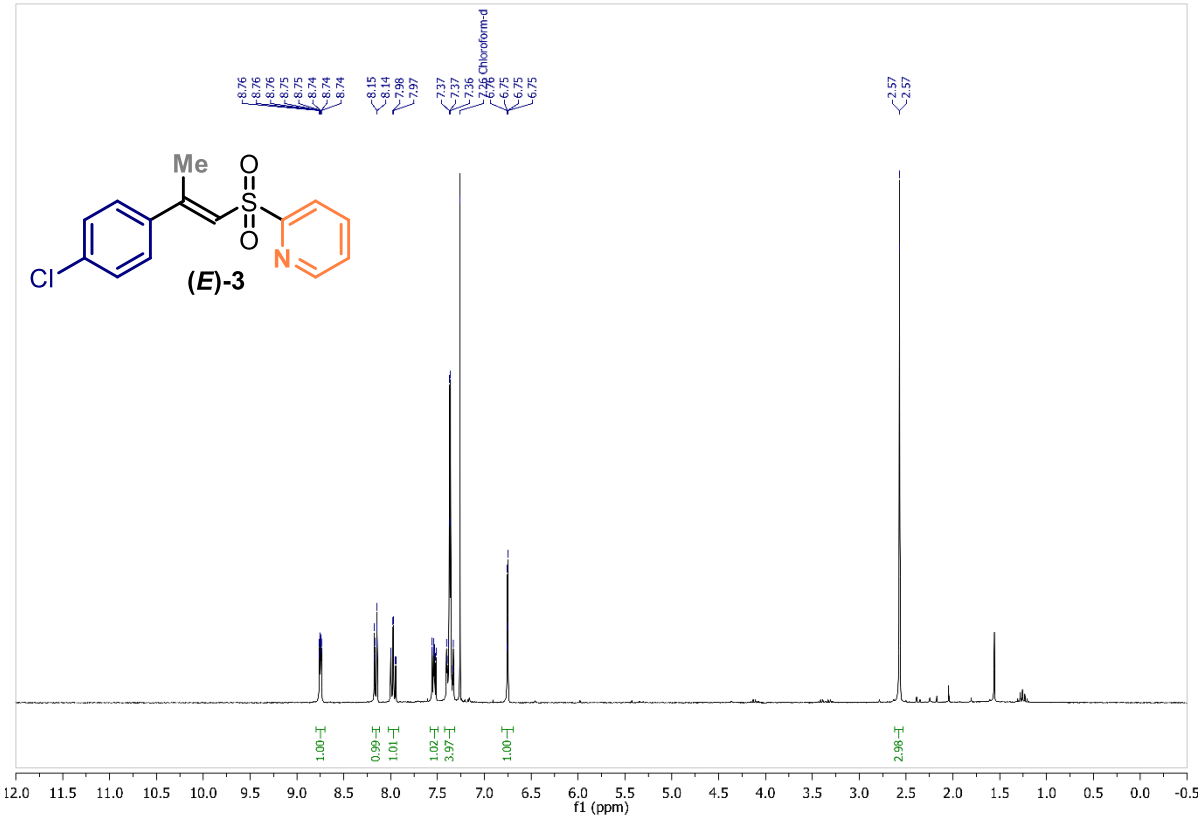


^{19}F NMR (282 MHz, $CDCl_3$)



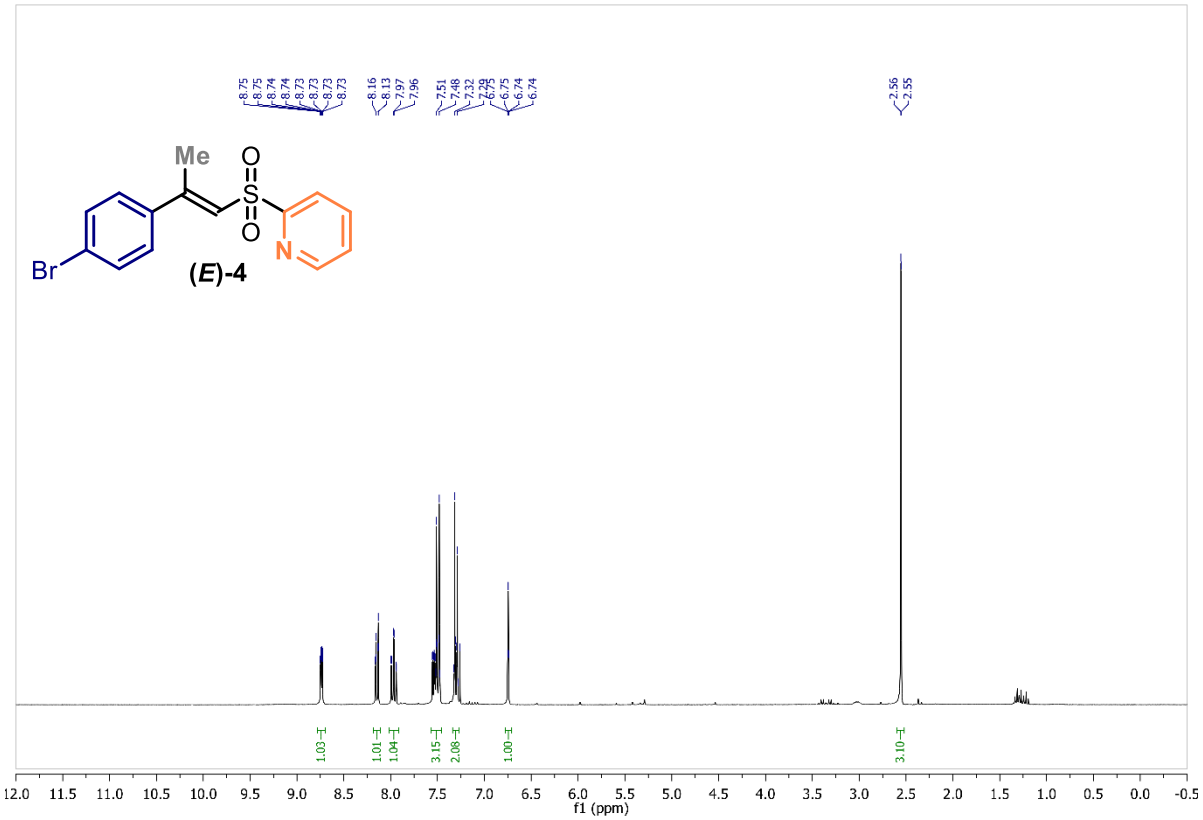
(*E*)-3: (*E*)-2-((2-(4-chlorophenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*



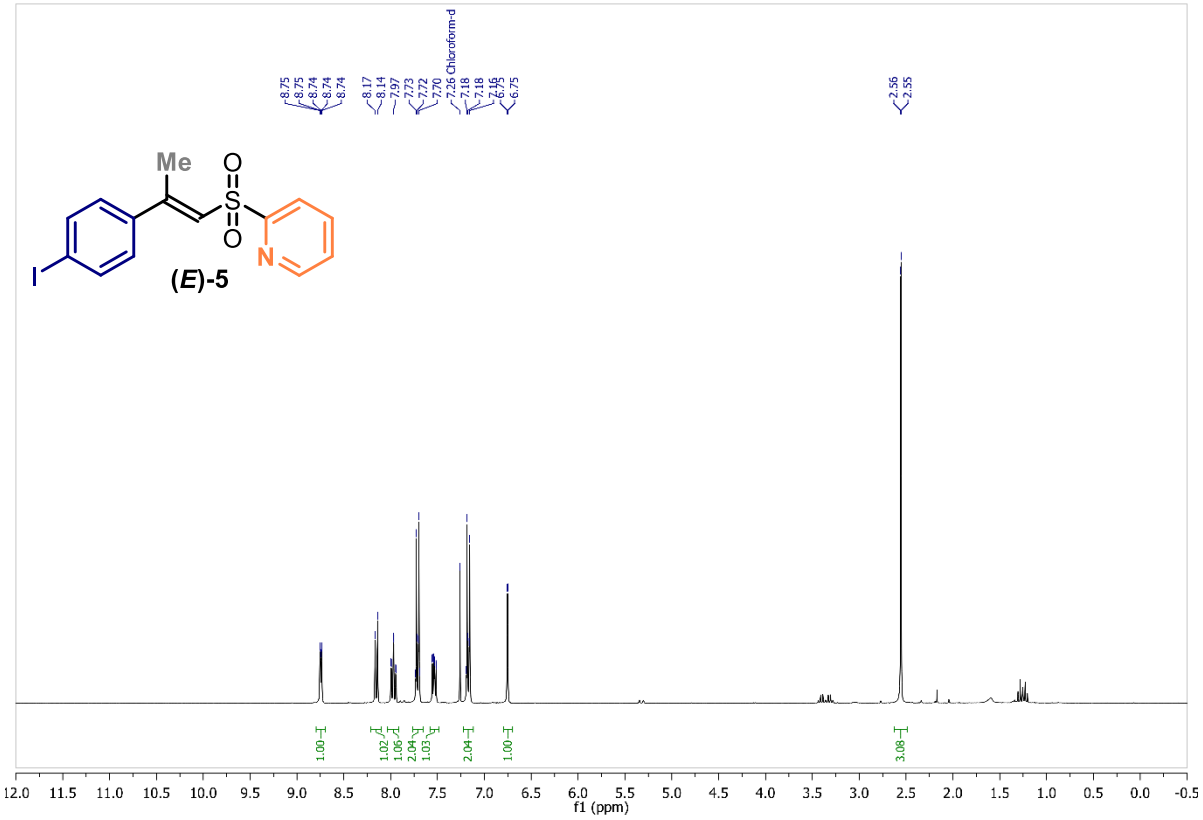
(*E*)-4: (*E*)-2-((2-(4-bromophenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

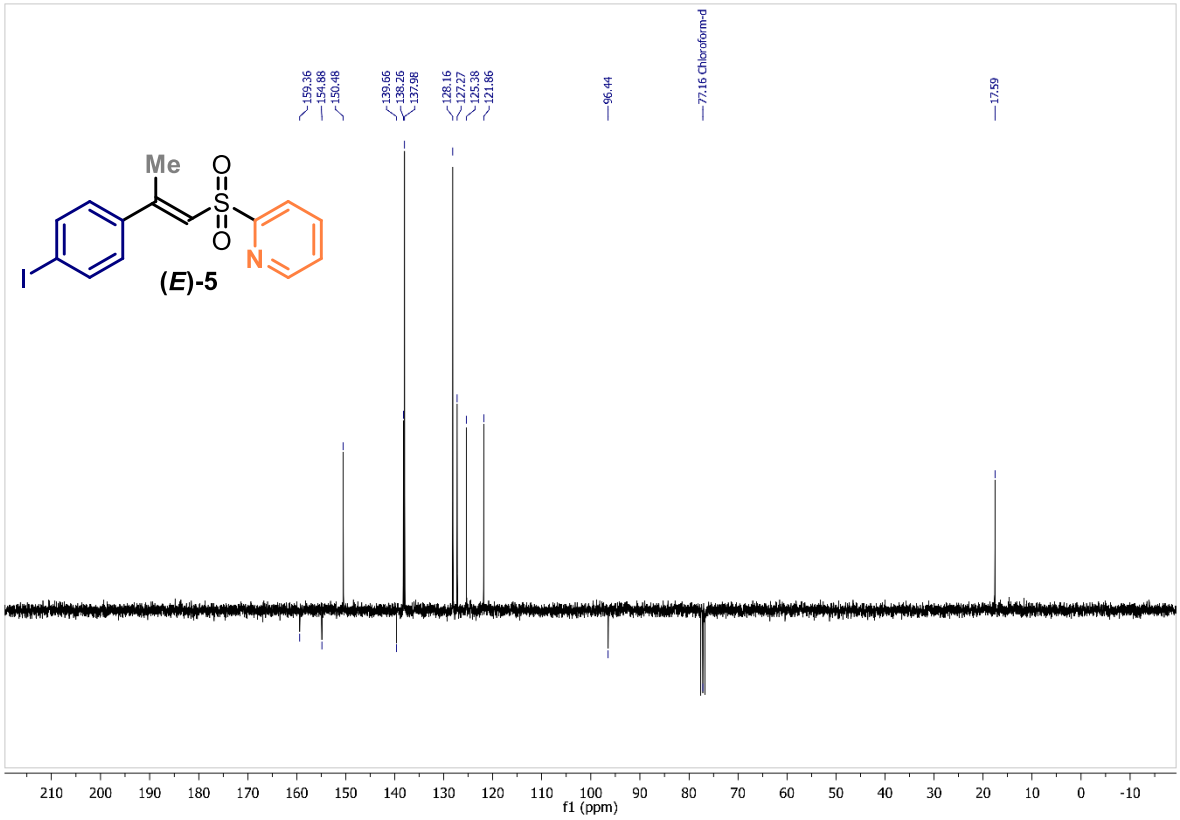


(*E*)-5: (*E*)-2-((2-(4-iodophenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

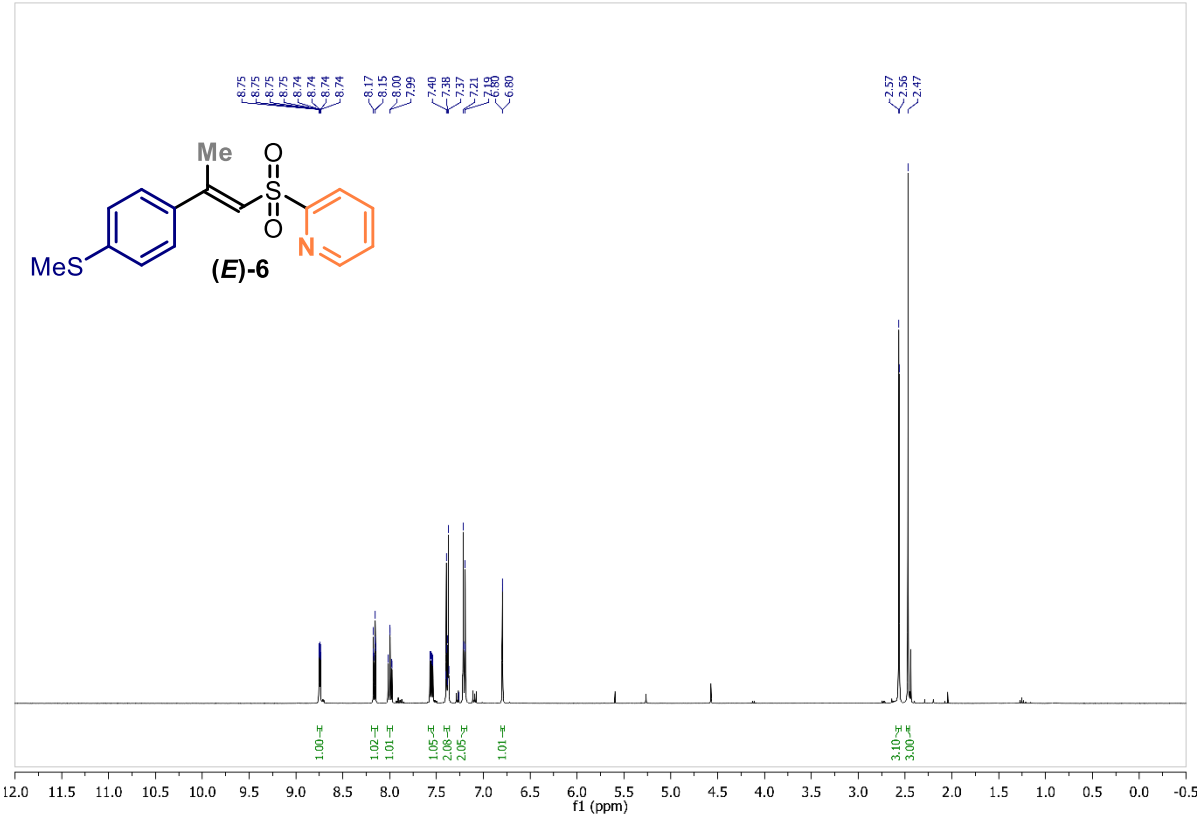


^{13}C NMR (75 MHz, $CDCl_3$)

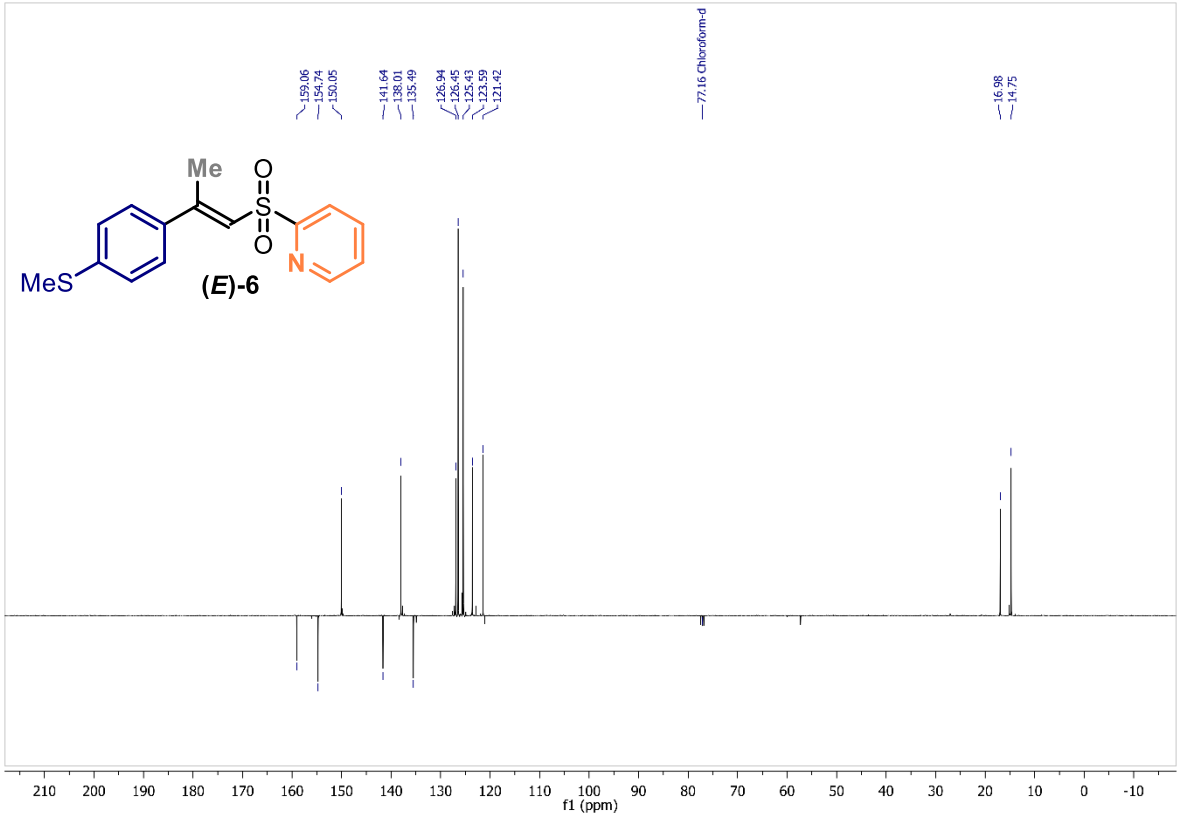


(*E*)-6: (*E*)-2-((2-(4-(methylthio)phenyl)prop-1-en-1-yl)sulfonyl)pyridine

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

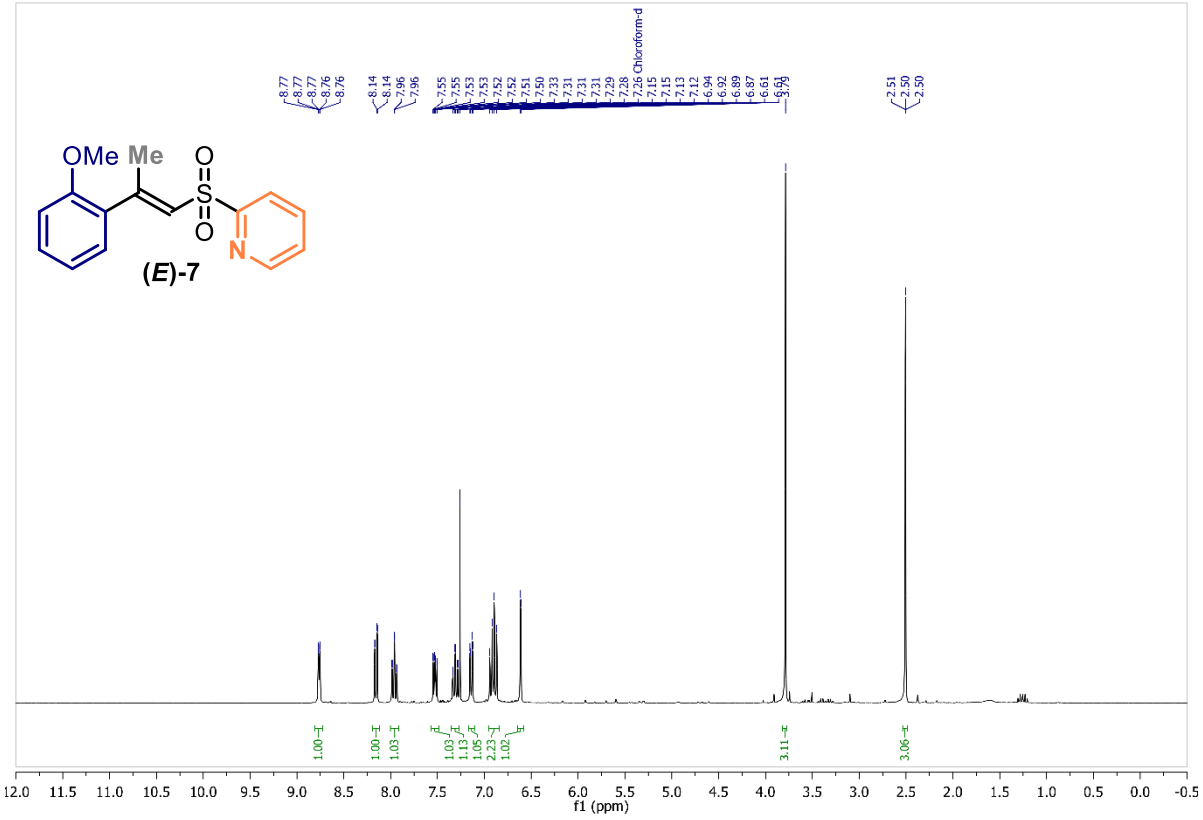


^{13}C NMR (101 MHz, $CDCl_3$)

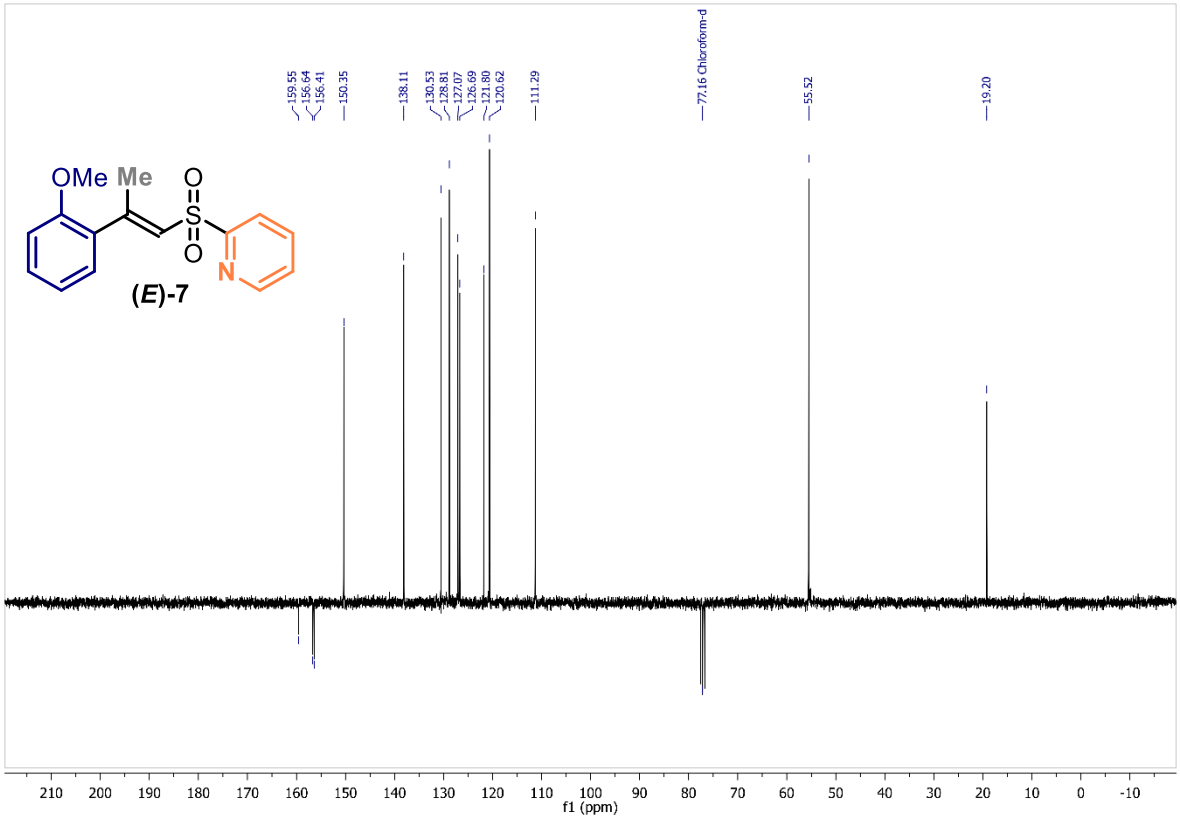


(*E*)-7: (*E*)-2-((2-(2-methoxyphenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

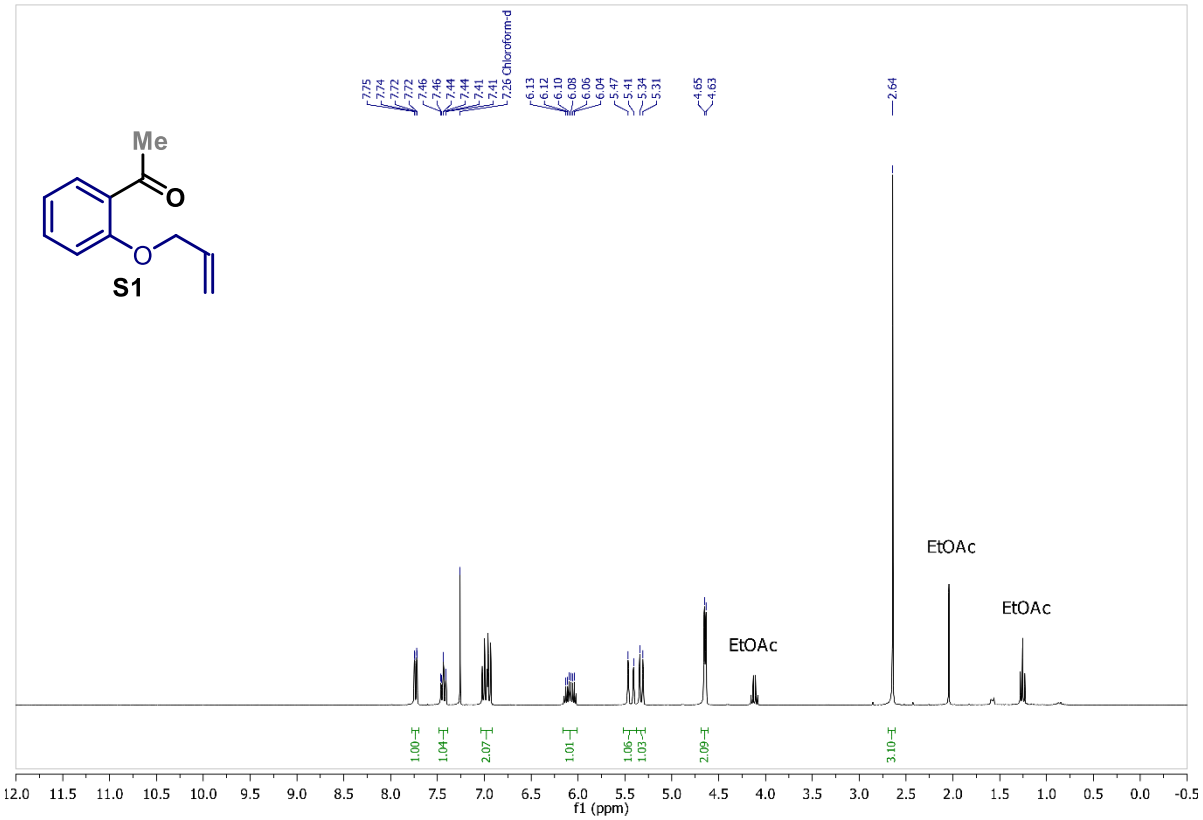


^{13}C NMR (101 MHz, $CDCl_3$)



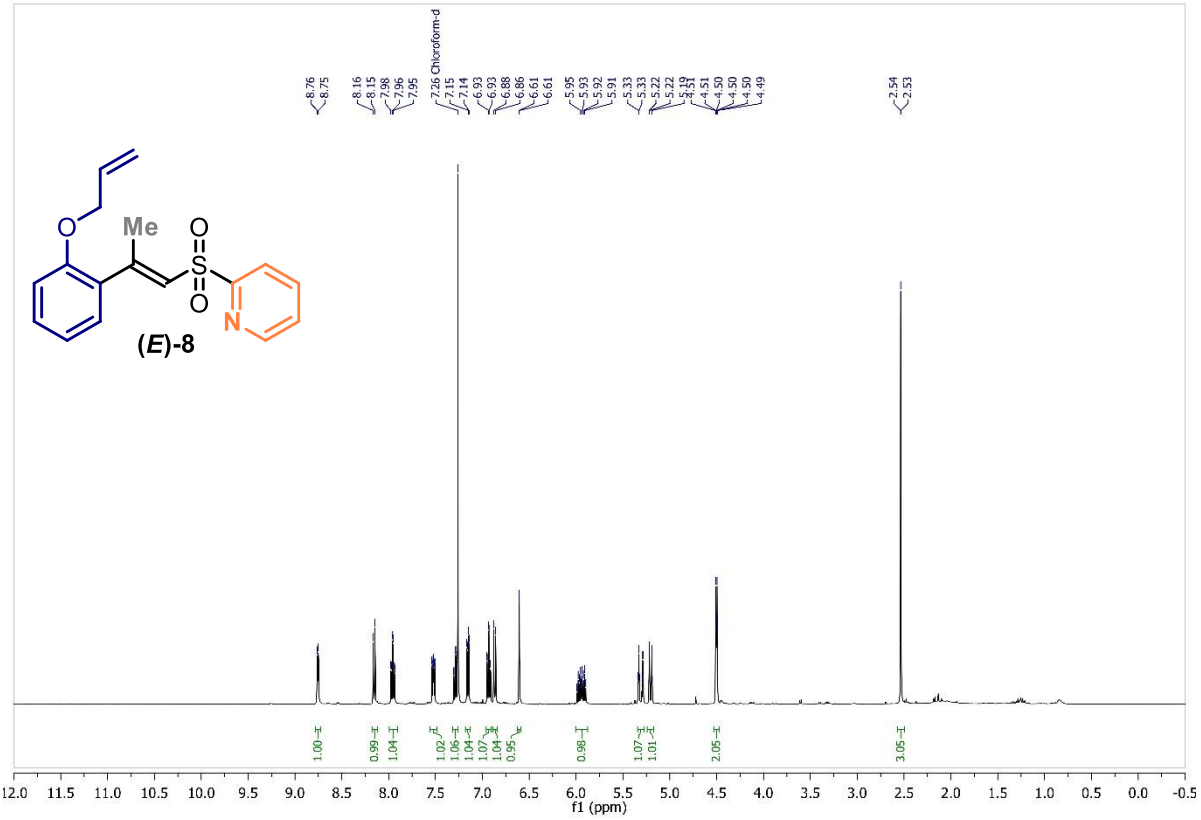
S1: 1-(2-(allyloxy)phenyl)ethan-1-one

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

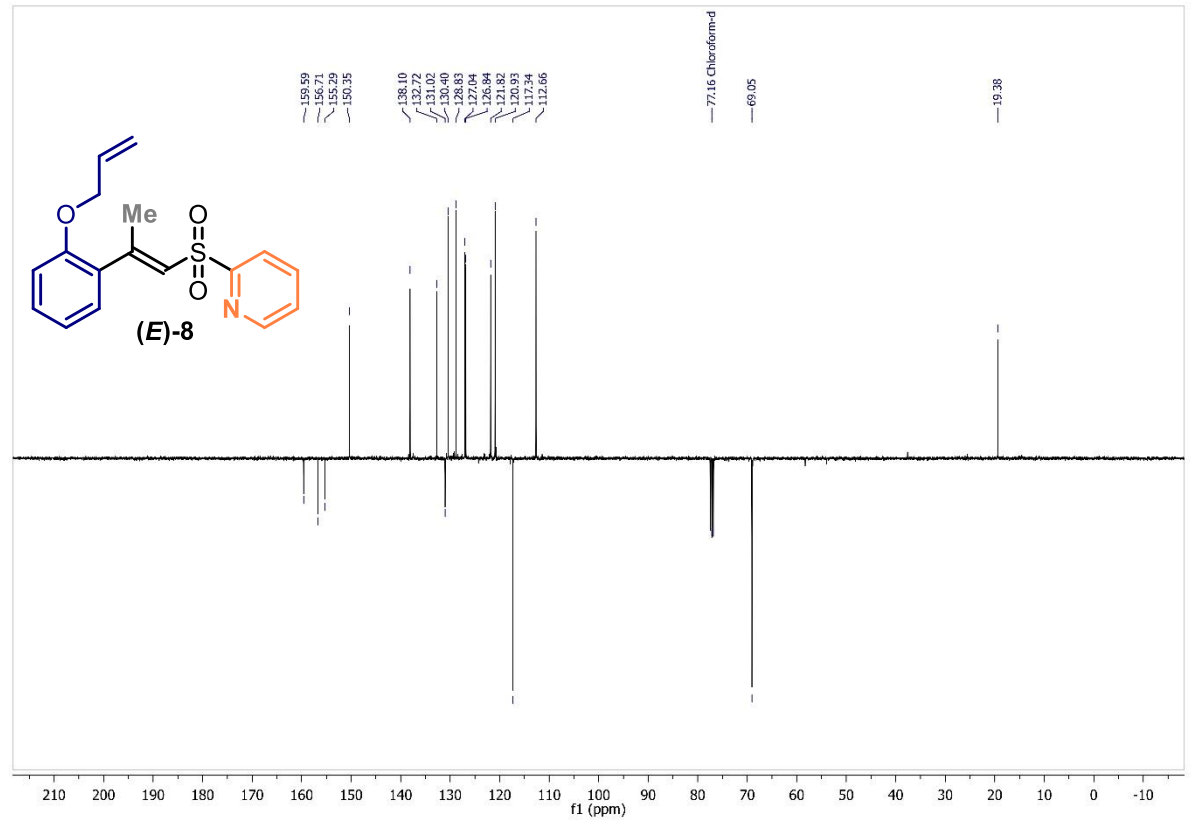


(*E*)-8: (*E*)-2-((2-(2-(allyloxy)phenyl)prop-1-en-1-yl)sulfonyl)pyridine

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

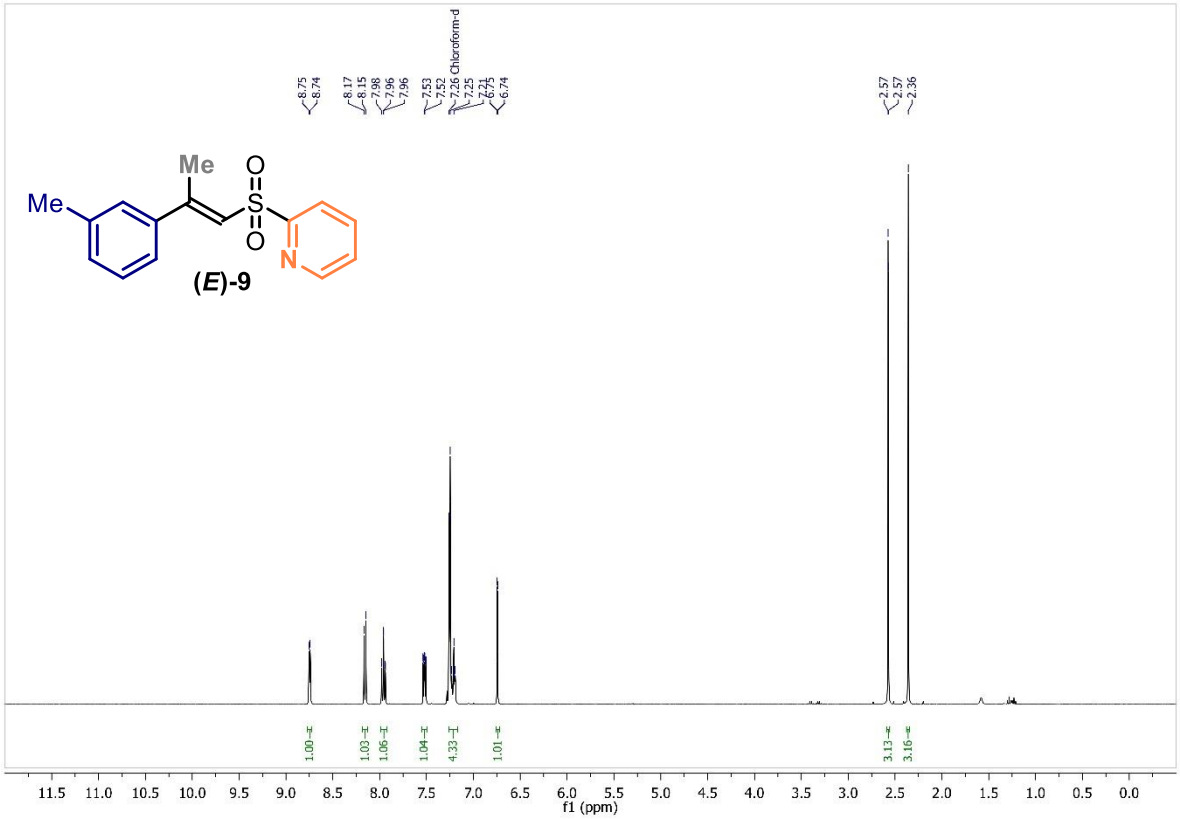


^{13}C NMR (101 MHz, $CDCl_3$)

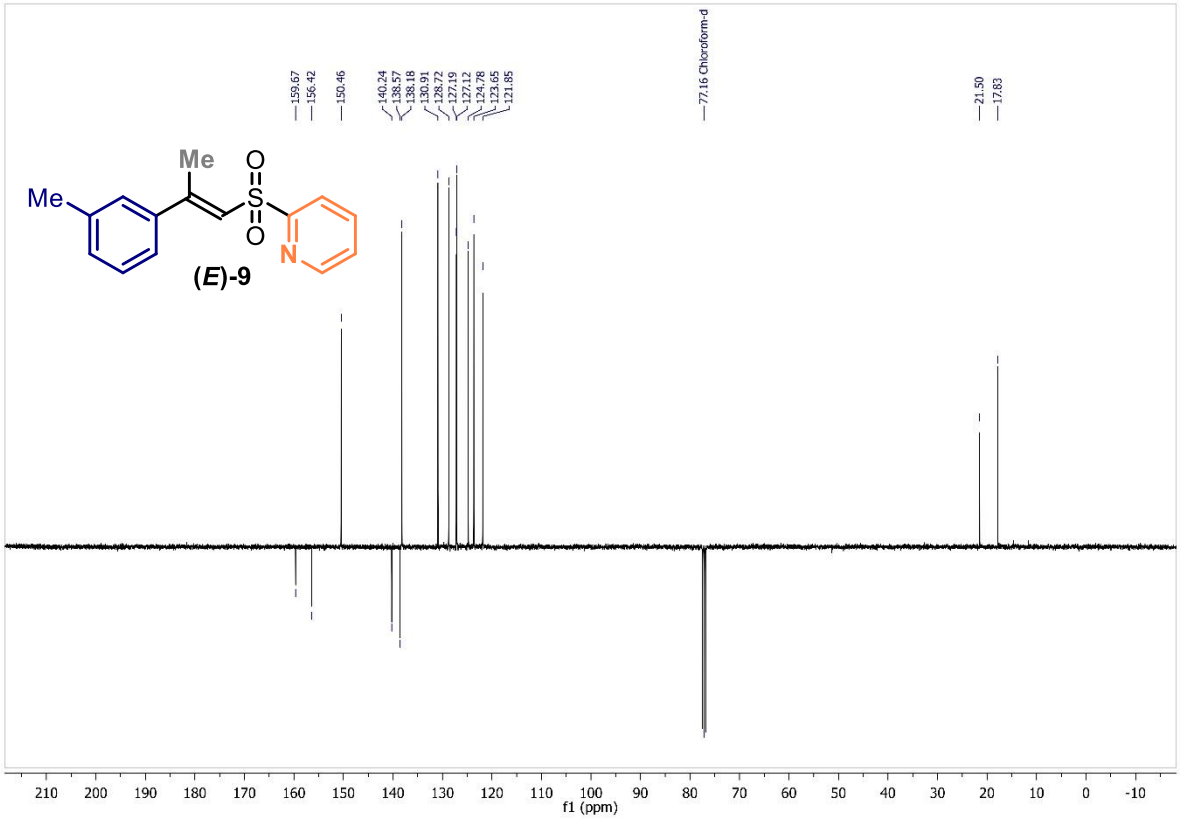


(*E*)-9: (E)-2-((2-(m-tolyl)prop-1-en-1-yl)sulfonyl)pyridine

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

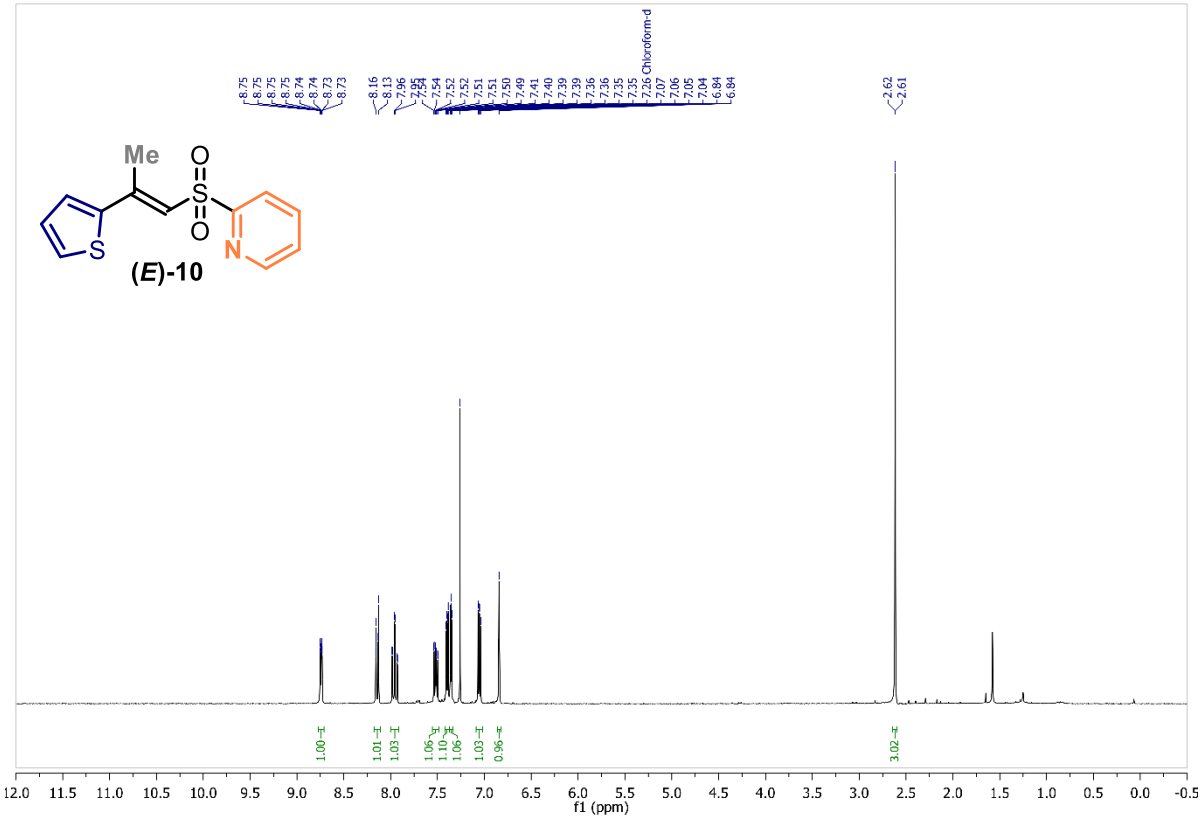


^{13}C NMR (101 MHz, $CDCl_3$)

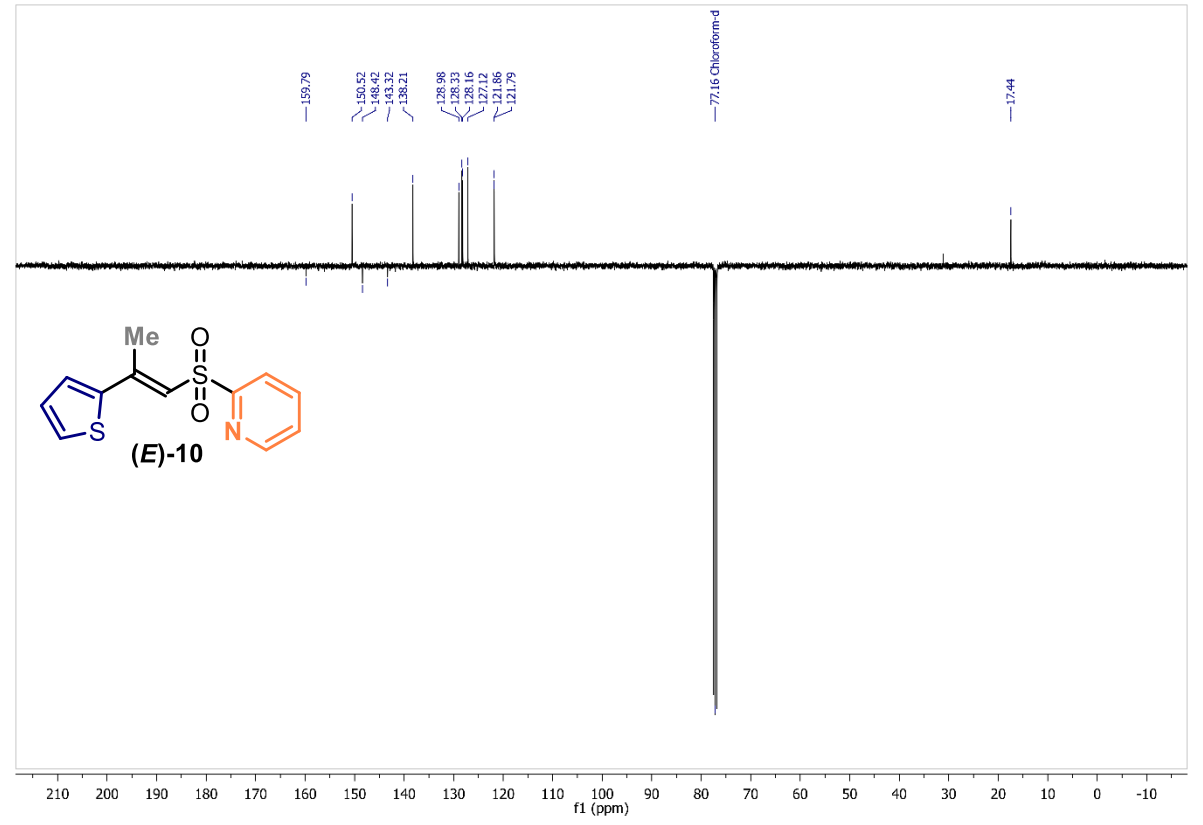


(*E*)-10: (*E*)-2-((2-(thiophen-2-yl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

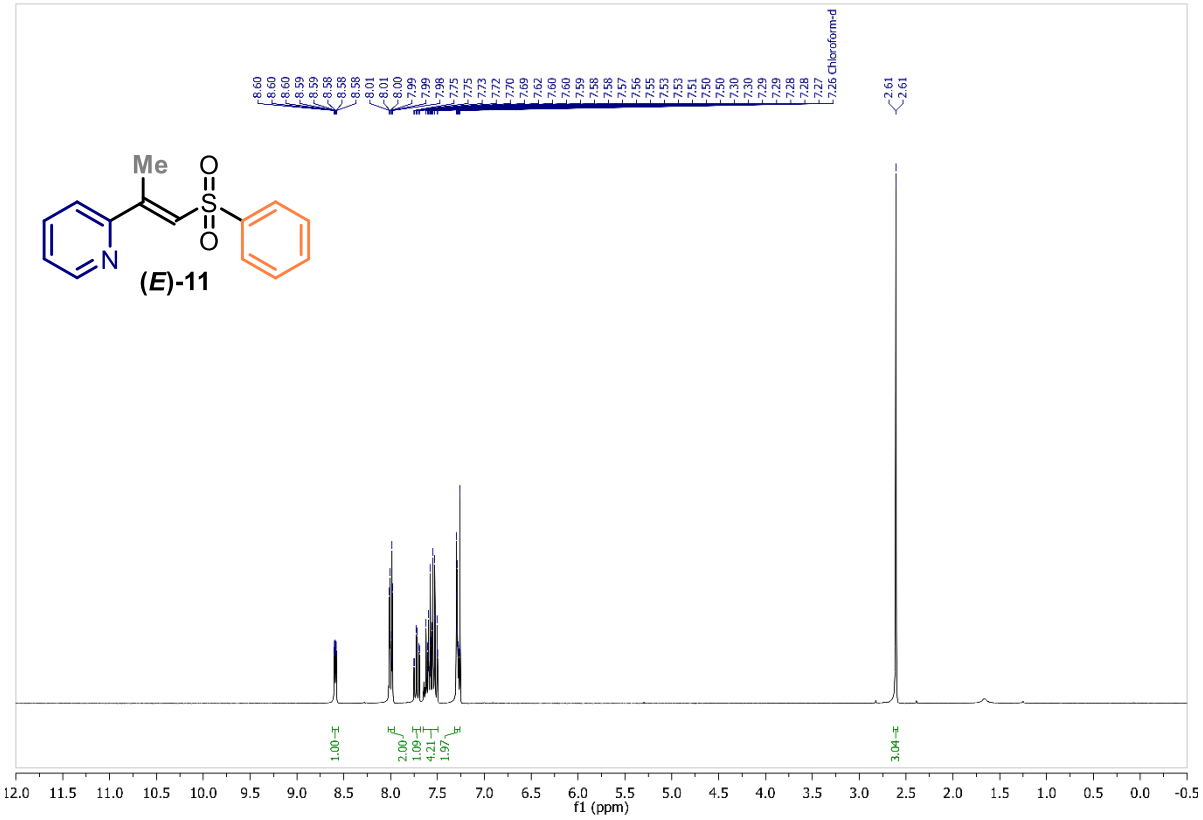


^{13}C NMR (101 MHz, $CDCl_3$)

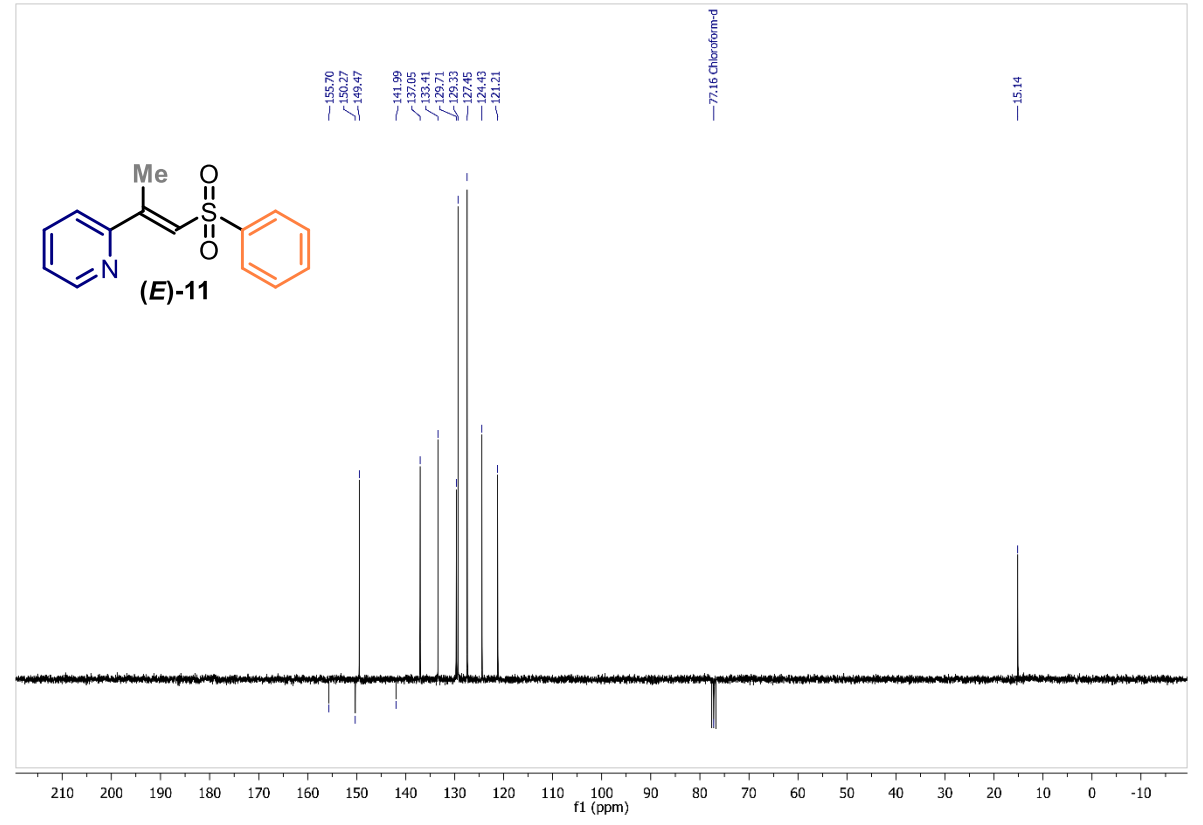


(*E*)-11: (*E*)-2-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

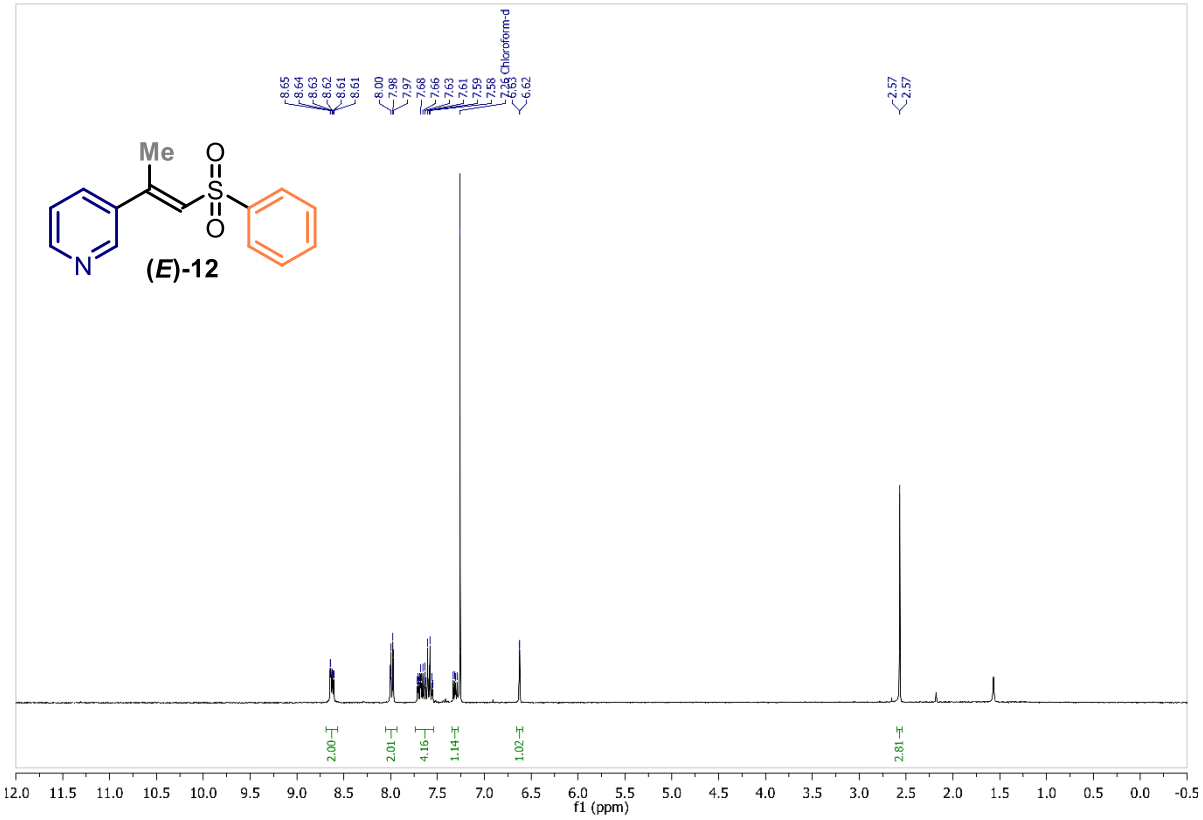


^{13}C NMR (75 MHz, $CDCl_3$)

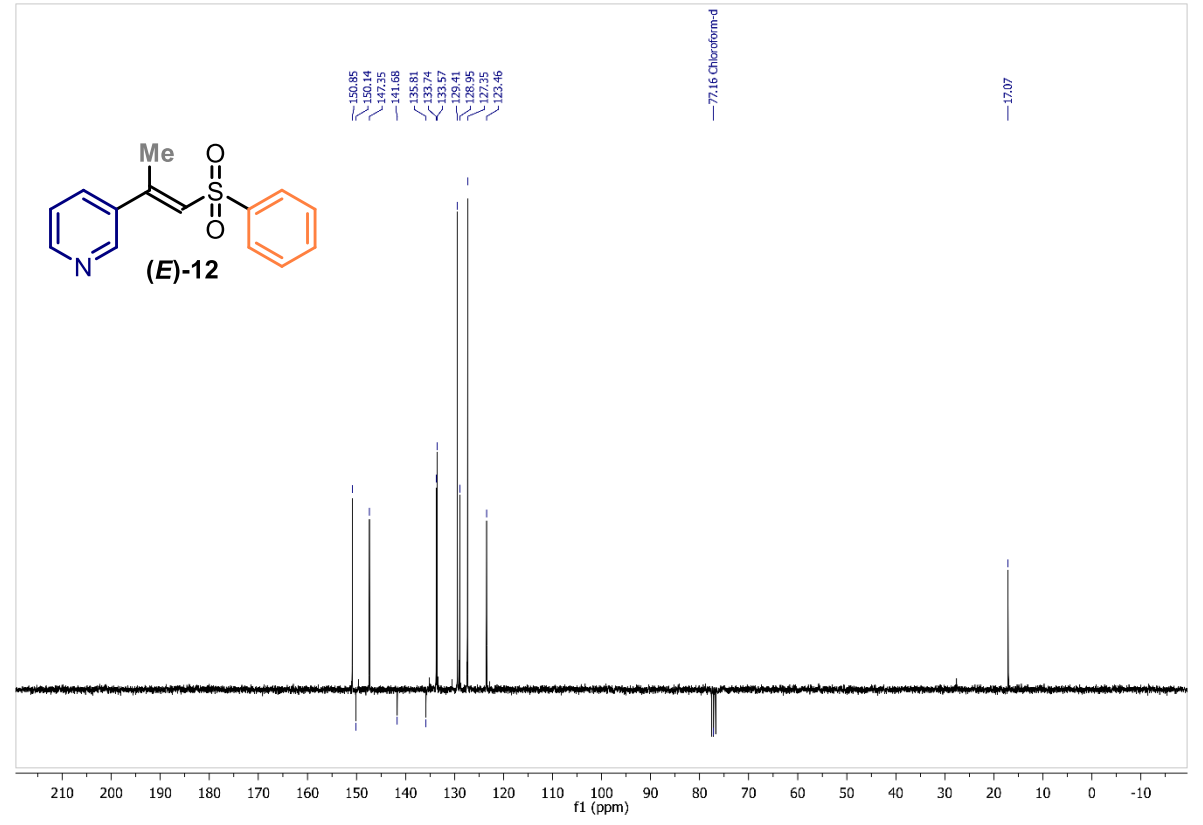


(*E*)-12: (*E*)-3-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

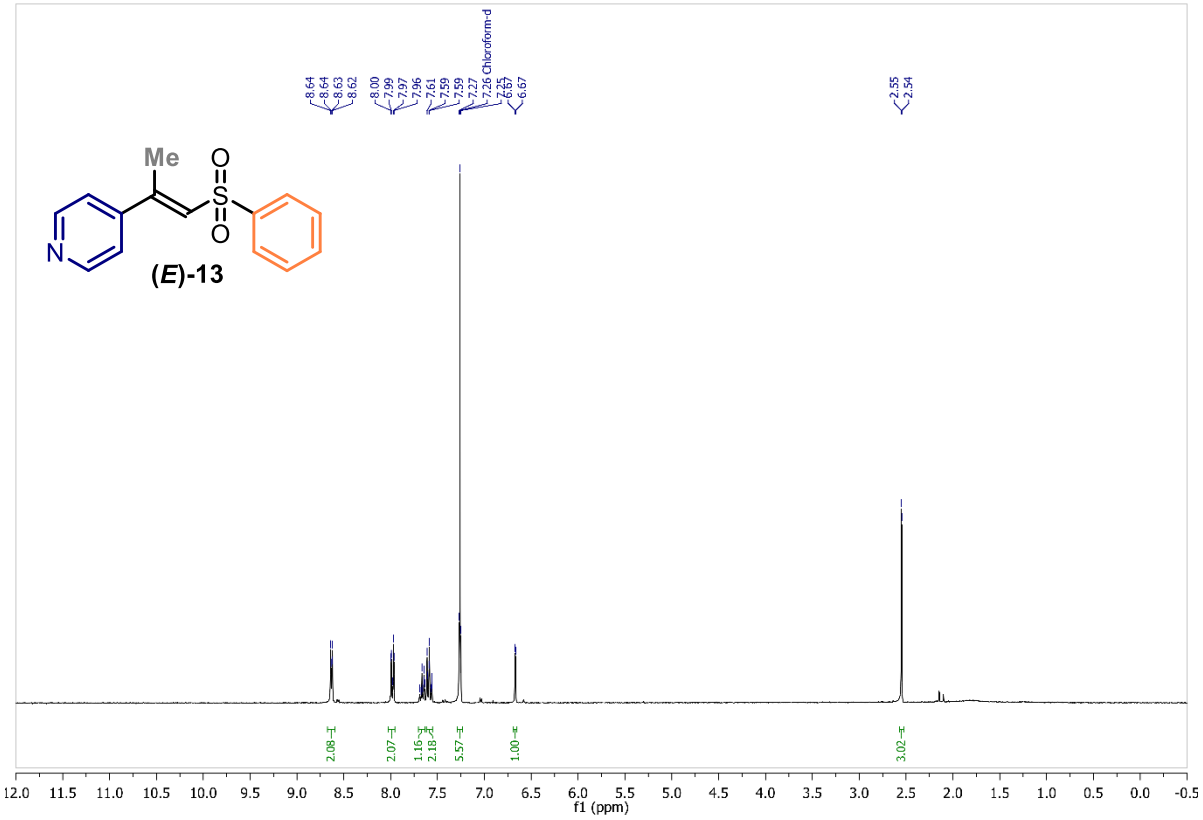


^{13}C NMR (75 MHz, $CDCl_3$)

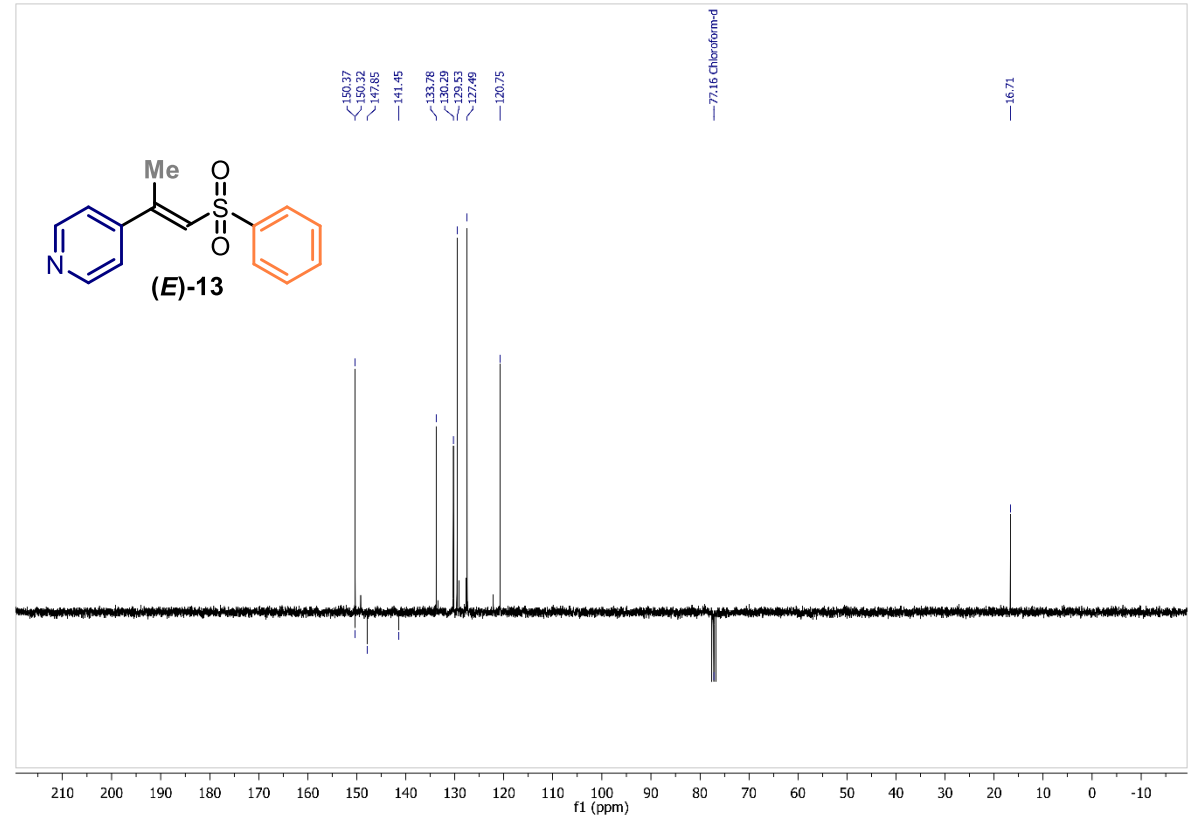


(*E*)-13: (*E*)-4-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

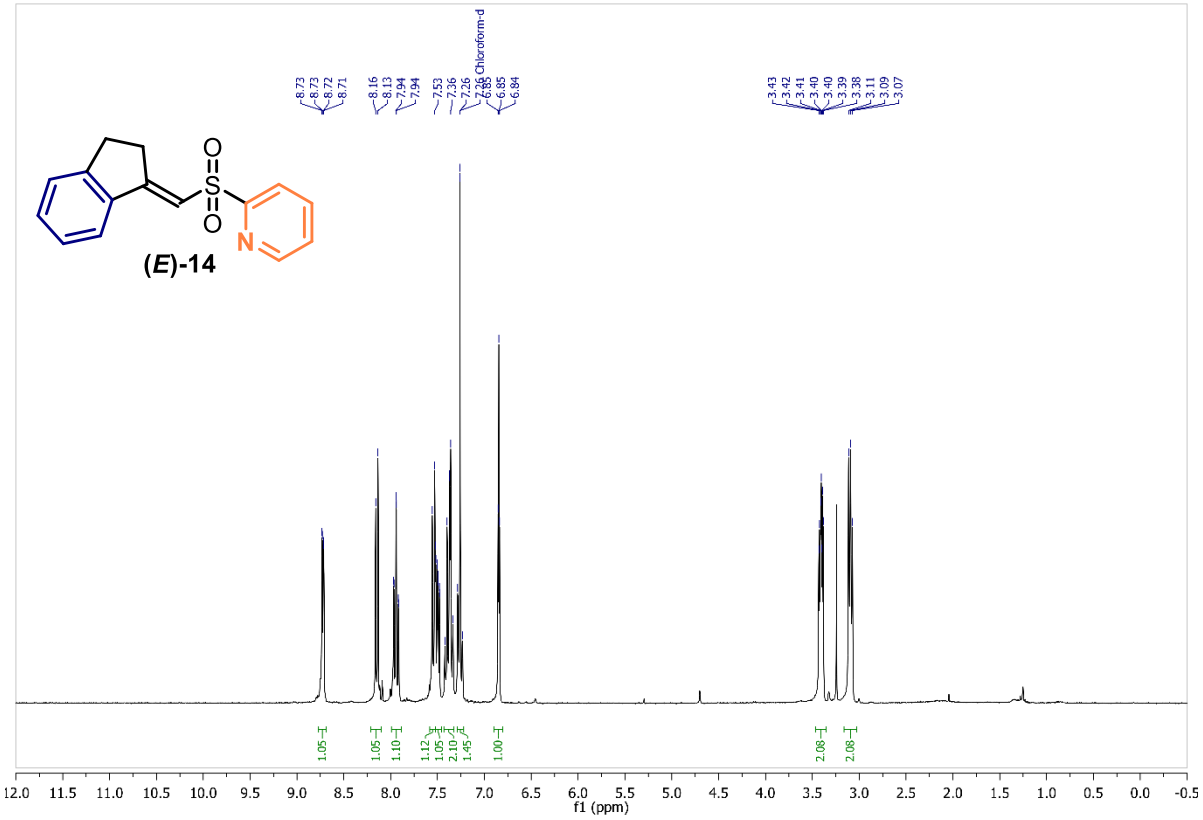


^{13}C NMR (75 MHz, $CDCl_3$)

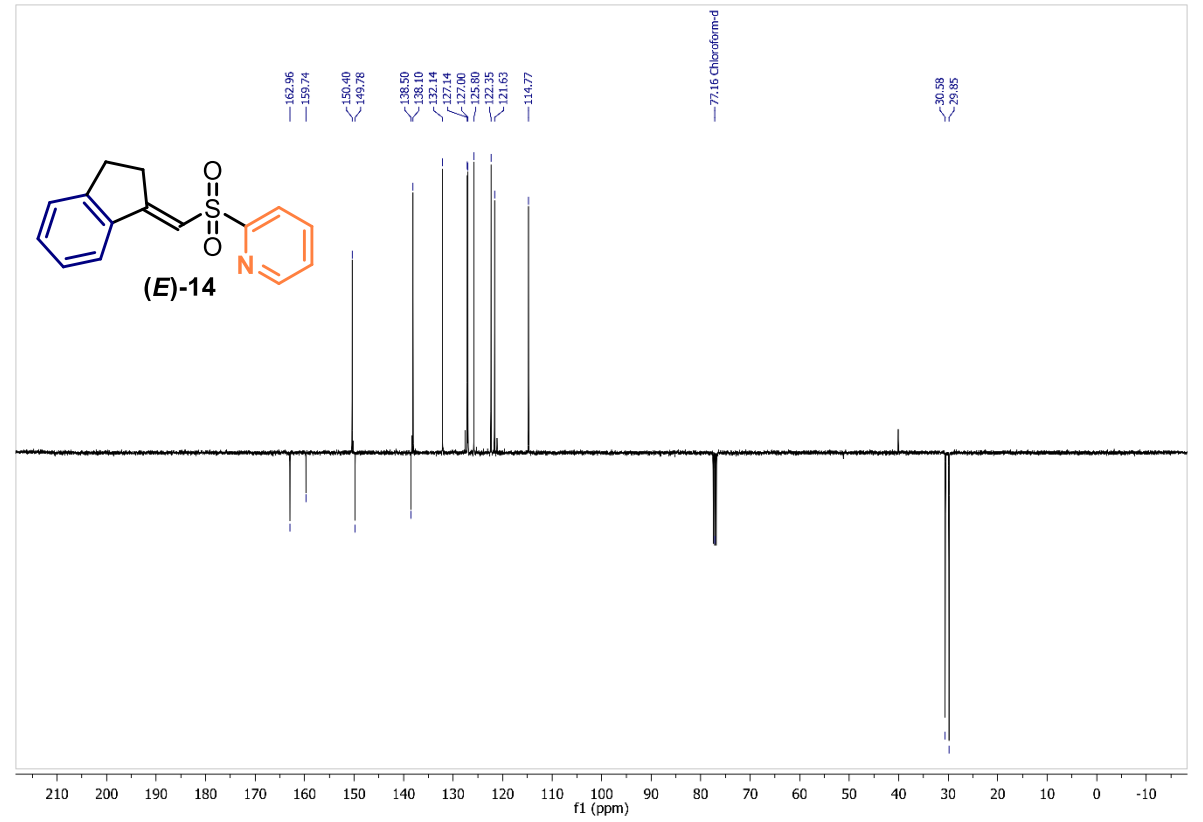


(*E*)-14: (*E*)-2-(((2,3-dihydro-1H-inden-1-ylidene)methyl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

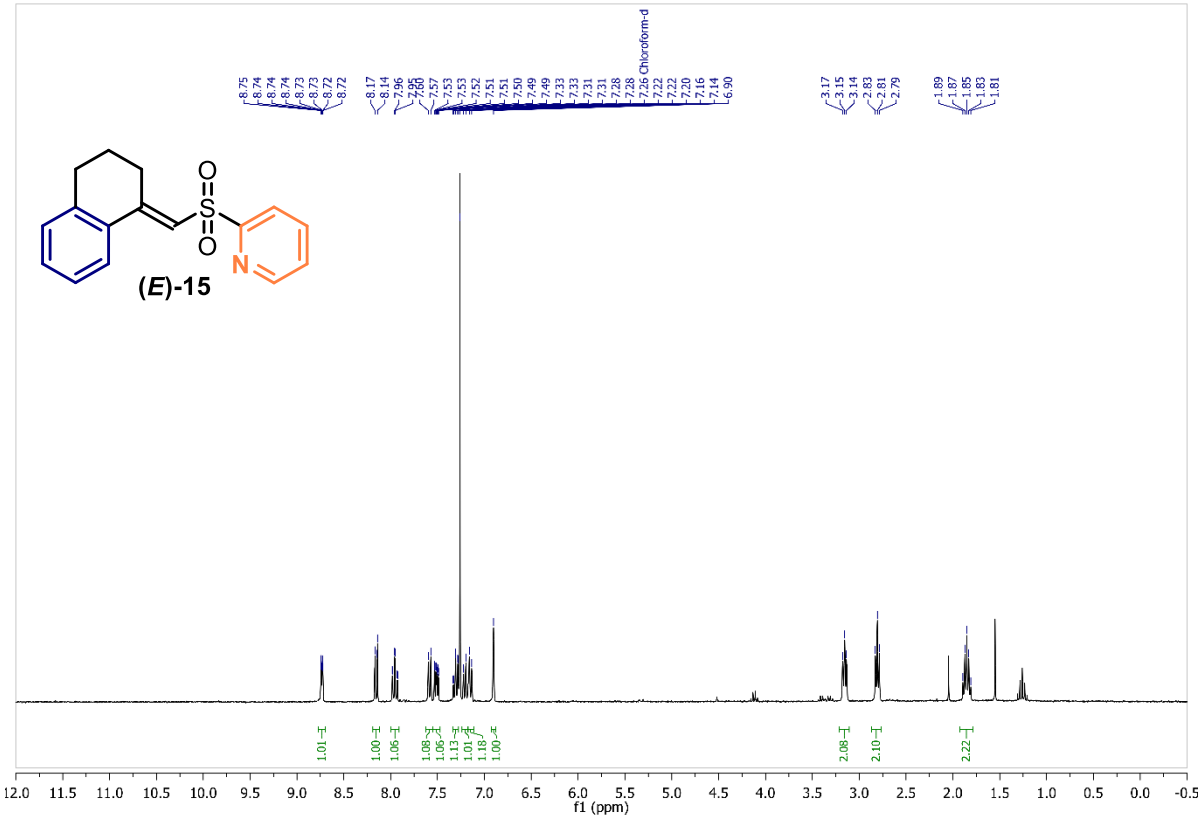


^{13}C NMR (101 MHz, $CDCl_3$)

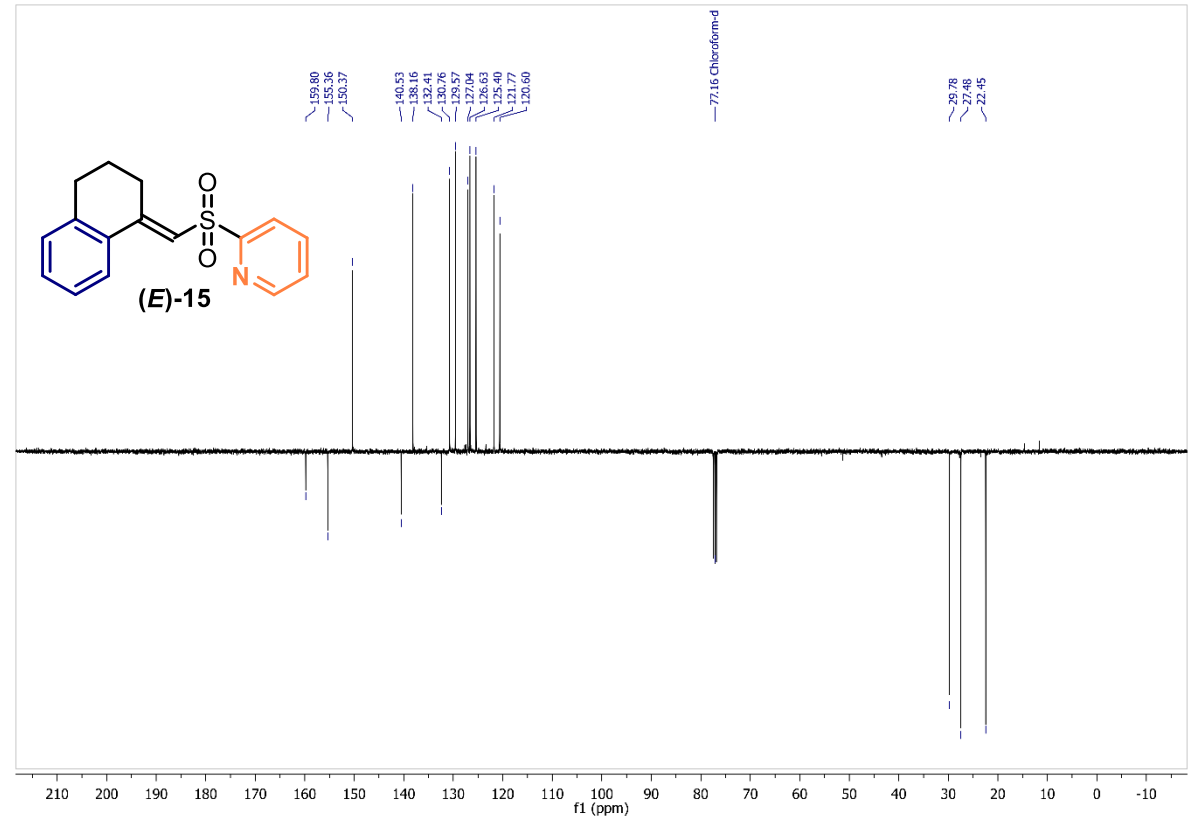


(*E*)-15: (*E*)-2-(((3,4-dihydronaphthalen-1(2H)-ylidene)methyl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

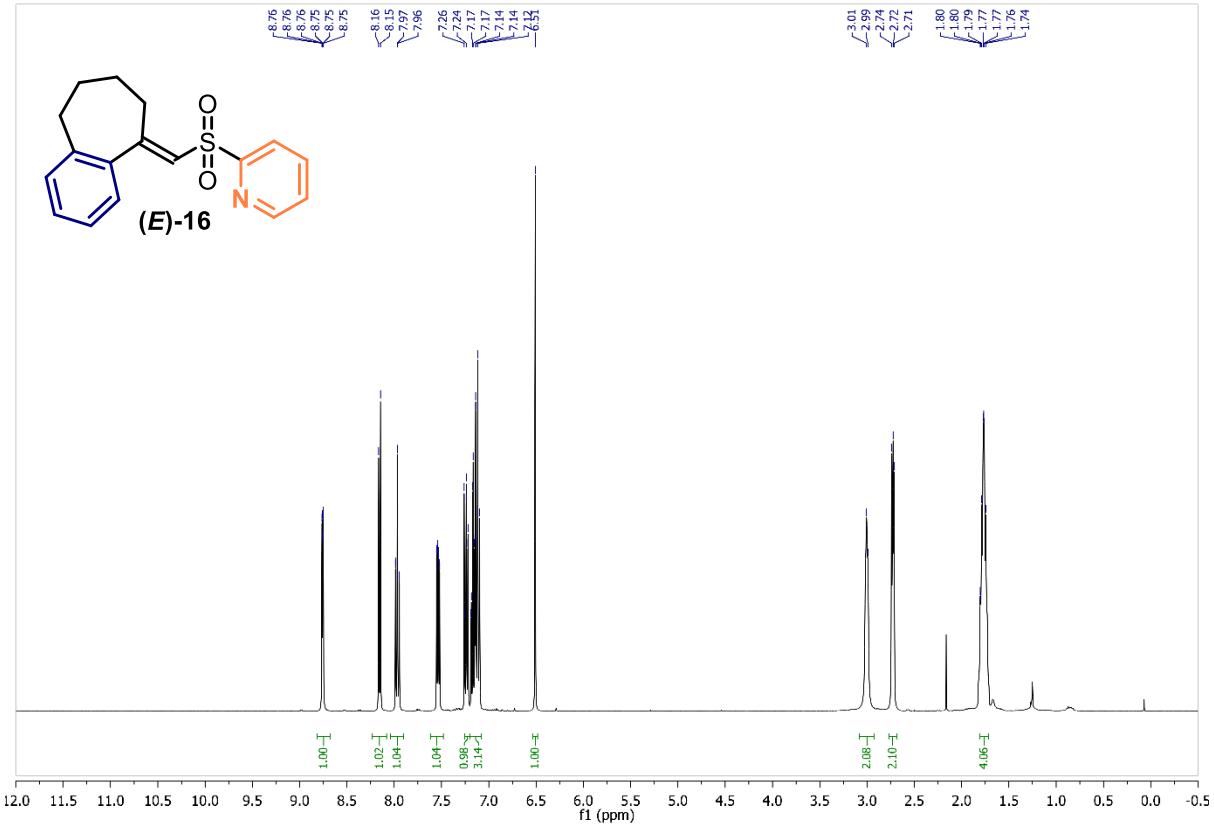


^{13}C NMR (101 MHz, $CDCl_3$)

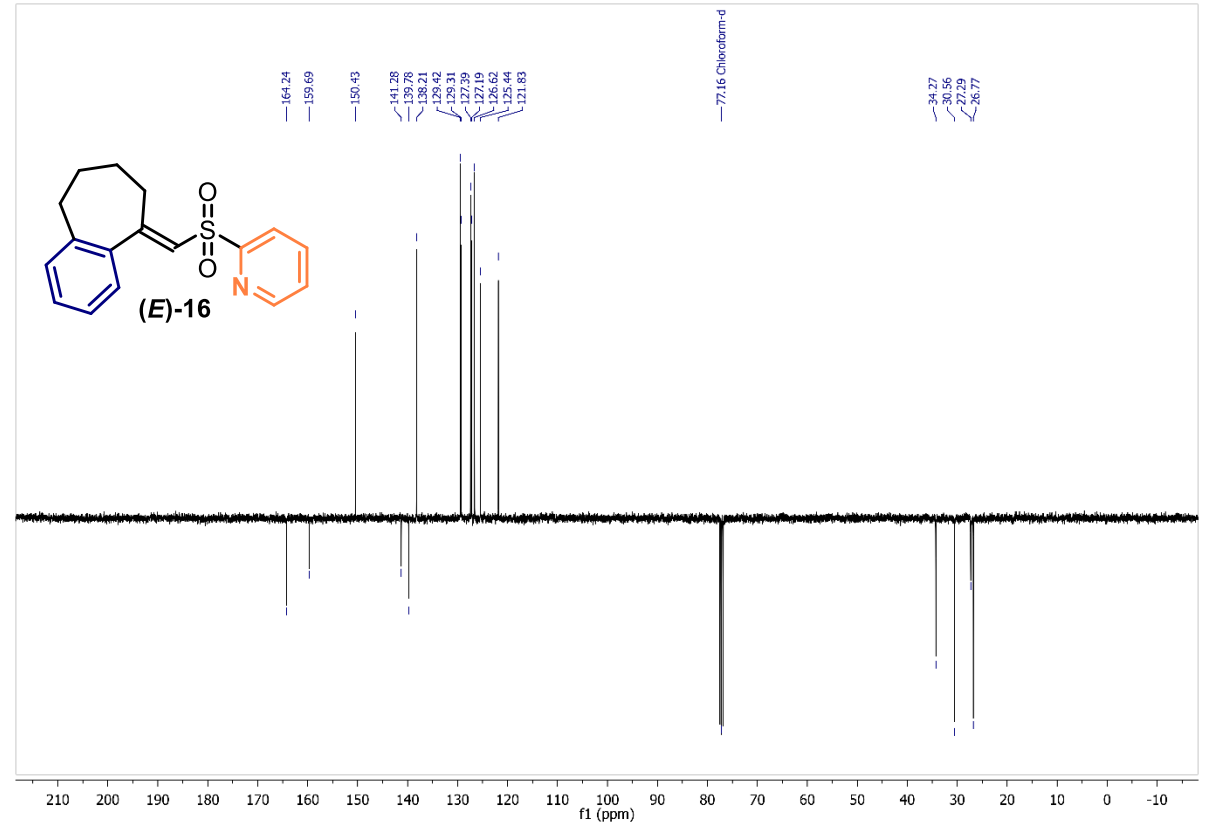


(*E*)-16: (*E*)-2-(((6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene)methyl)sulfonyl)pyridine

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

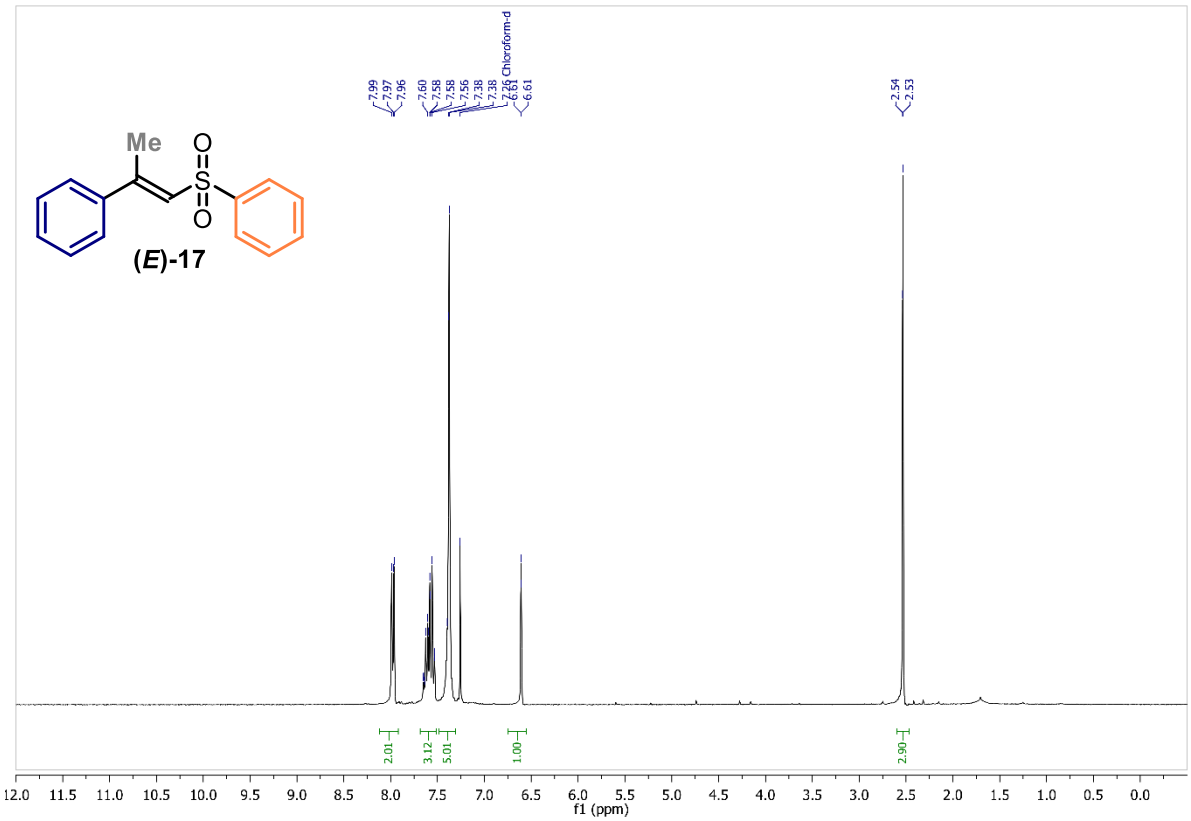


^{13}C NMR (101 MHz, $CDCl_3$)



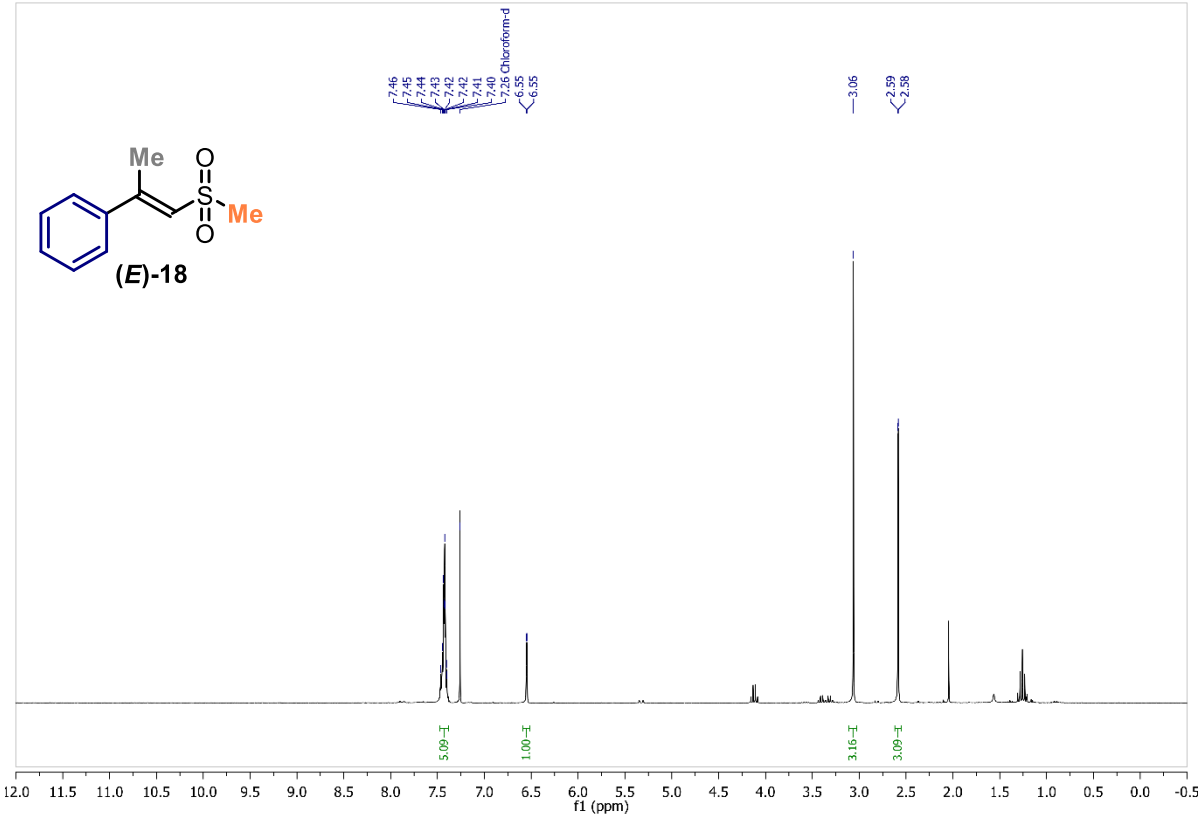
(*E*)-17: (*E*)-((2-phenylprop-1-en-1-yl)sulfonyl)benzene

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*



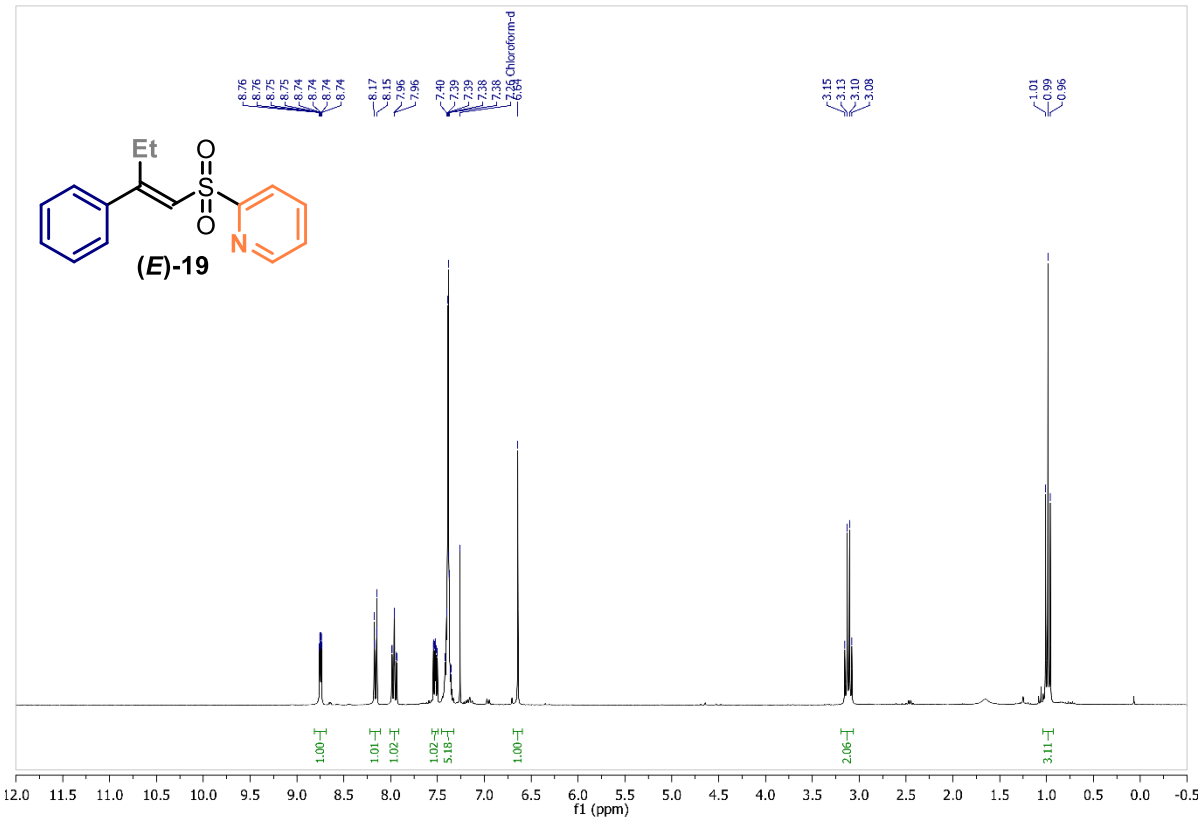
(*E*)-18: (*E*)-(1-(methylsulfonyl)prop-1-en-2-yl)benzene

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*



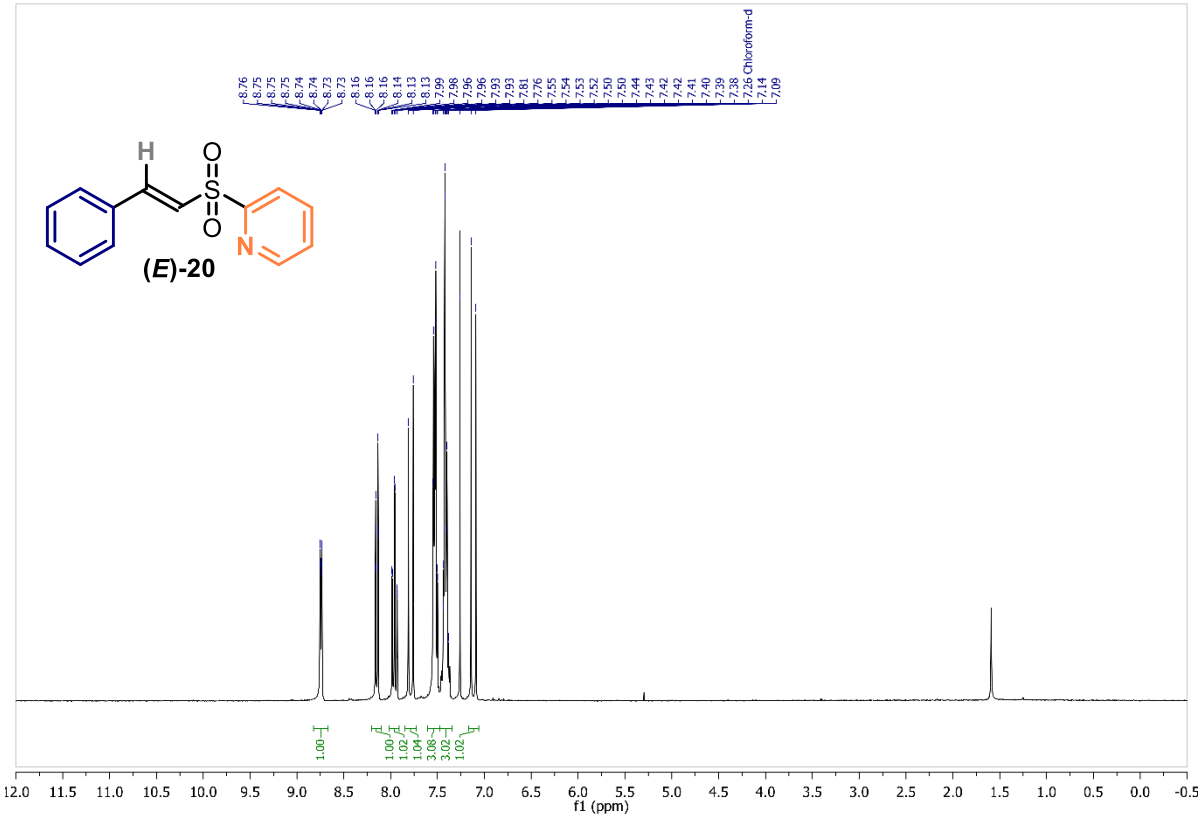
(*E*)-19: (*E*)-2-((2-phenylbut-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

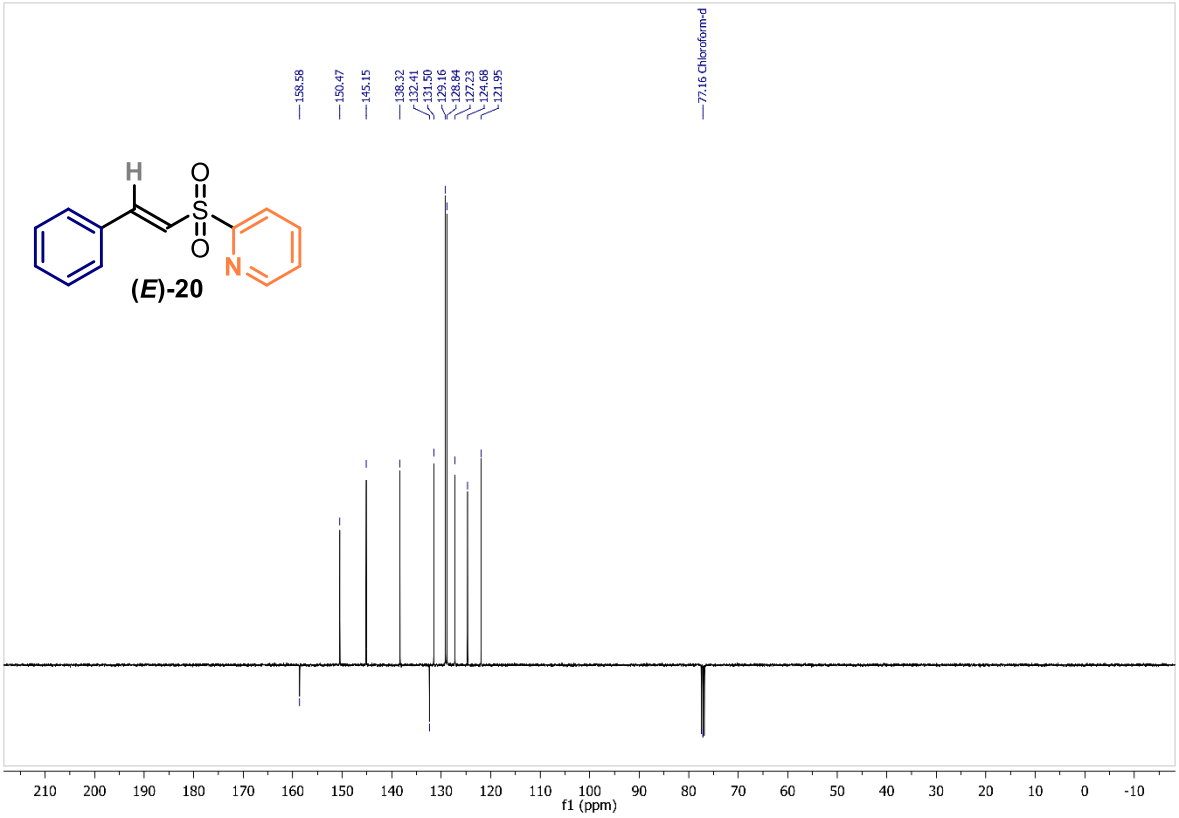


(*E*)-20: (*E*)-2-(styrylsulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

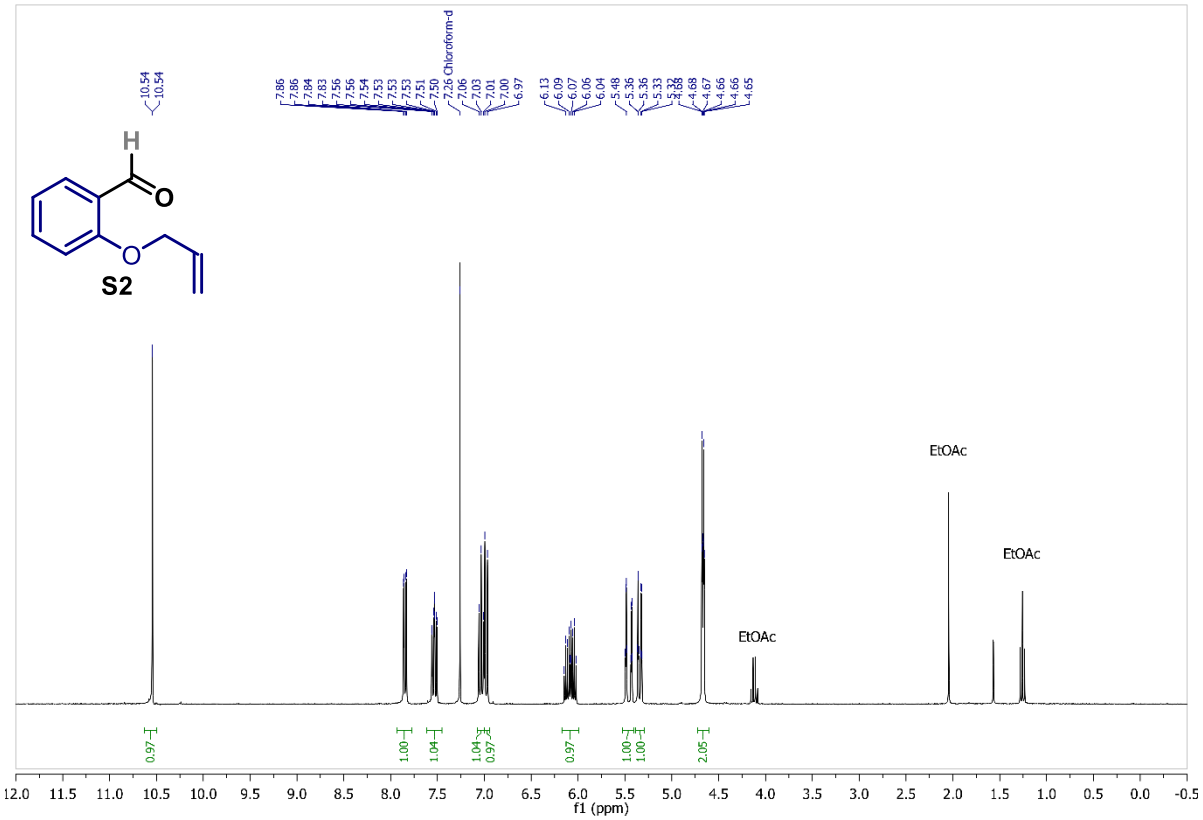


^{13}C NMR (101 MHz, $CDCl_3$)



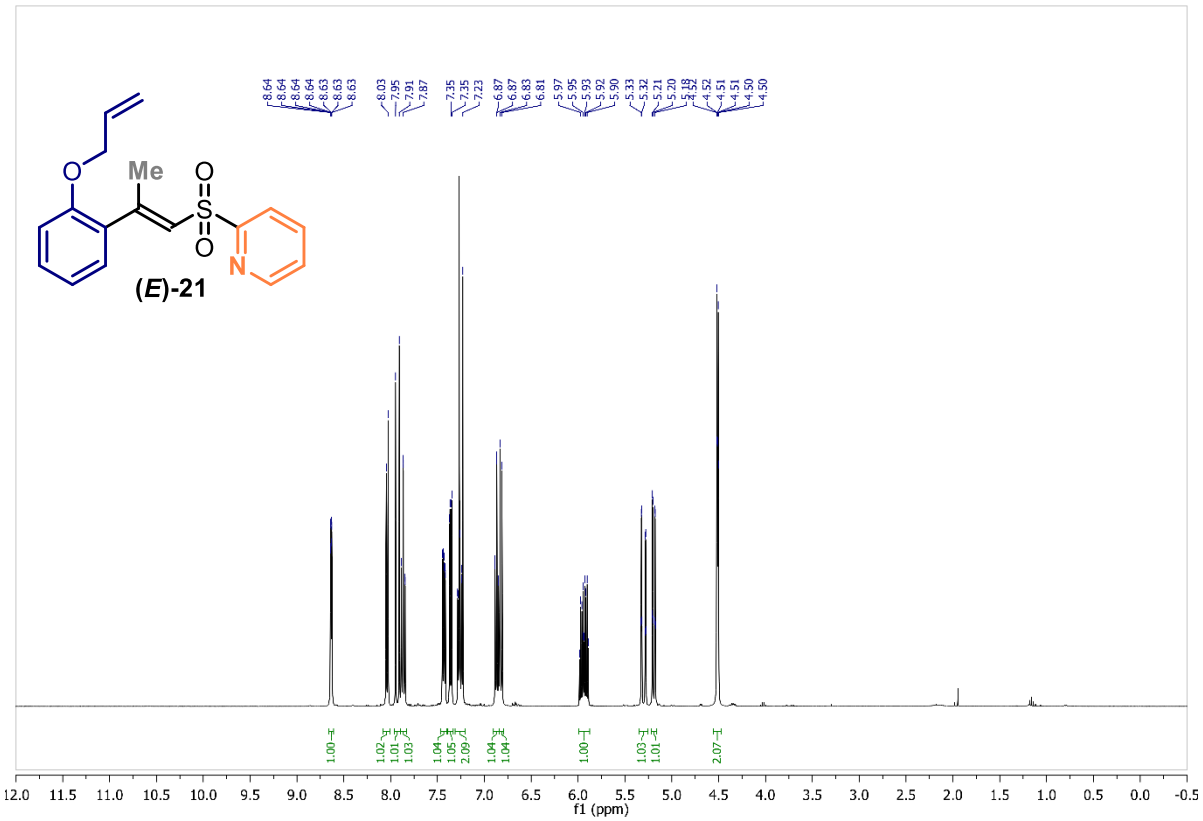
S2: 2-(allyloxy)benzaldehyde

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

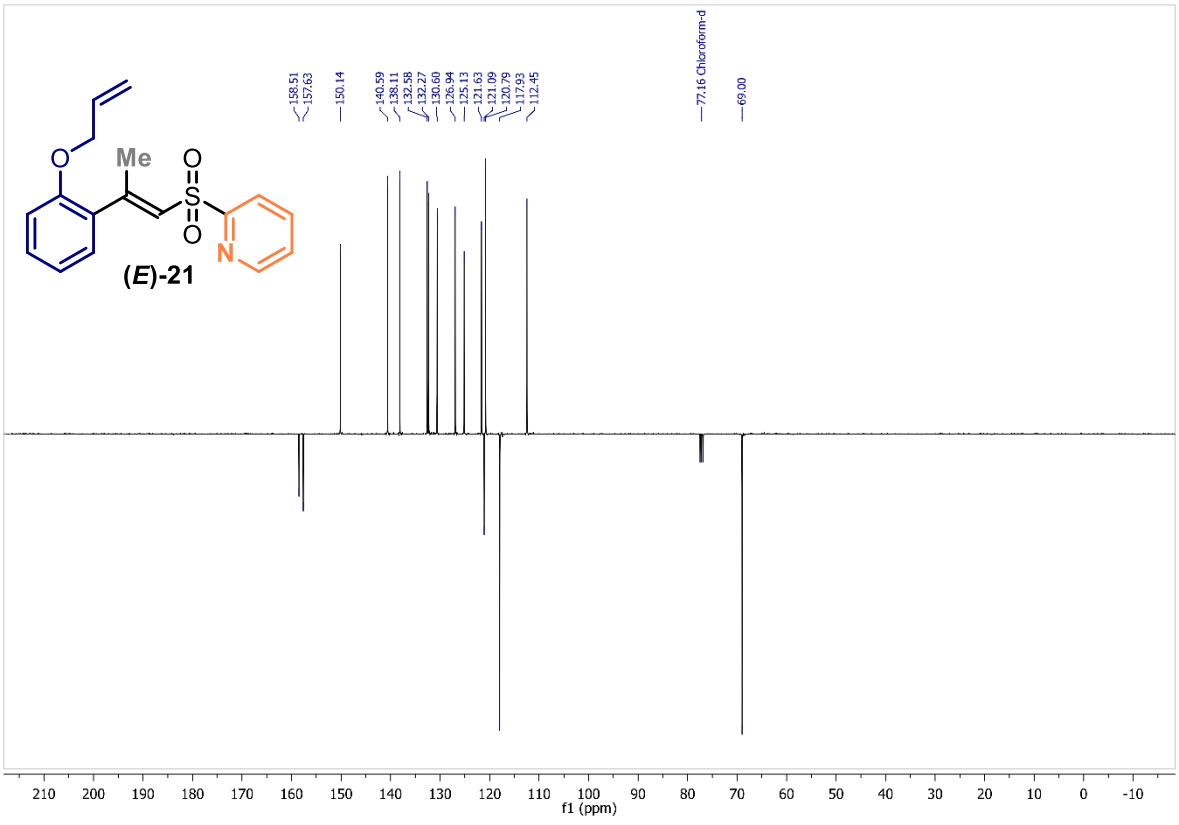


(*E*)-21: (*E*)-2-((2-(allyloxy)styryl)sulfonyl)pyridine

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

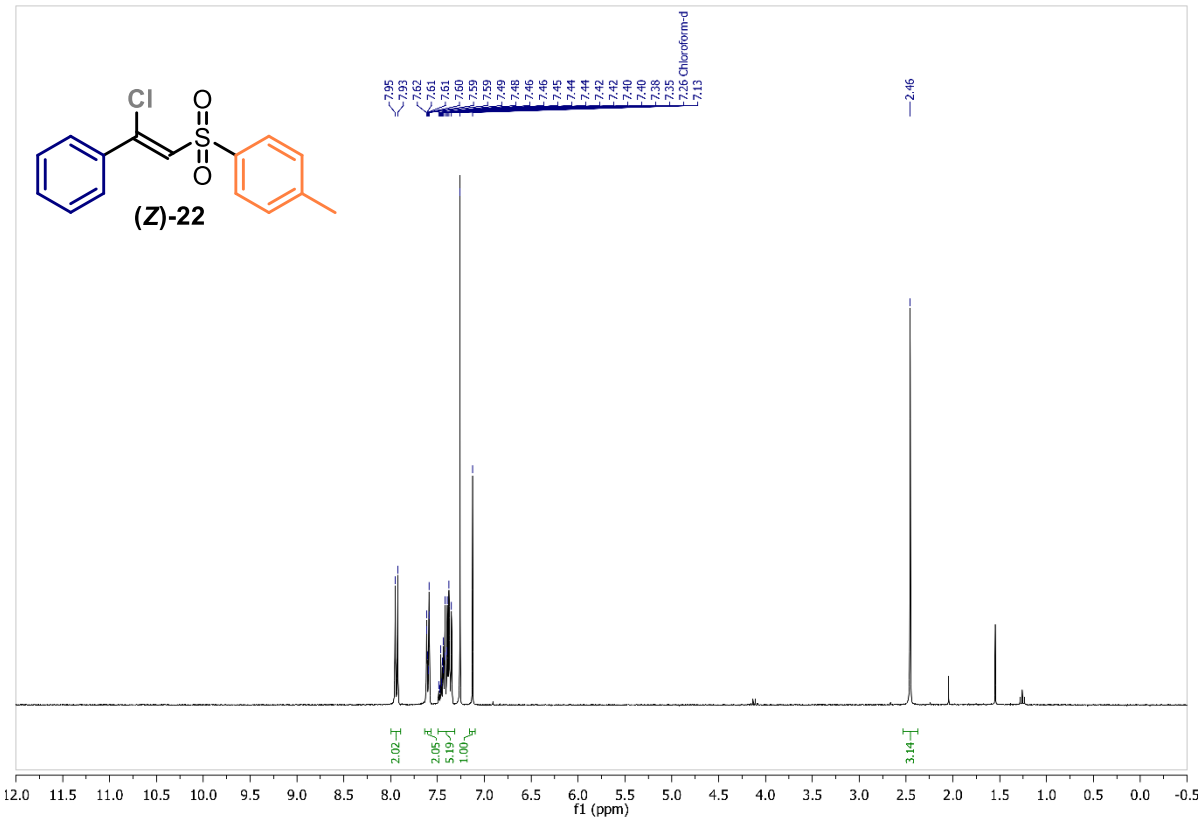


^{13}C NMR (101 MHz, $CDCl_3$)



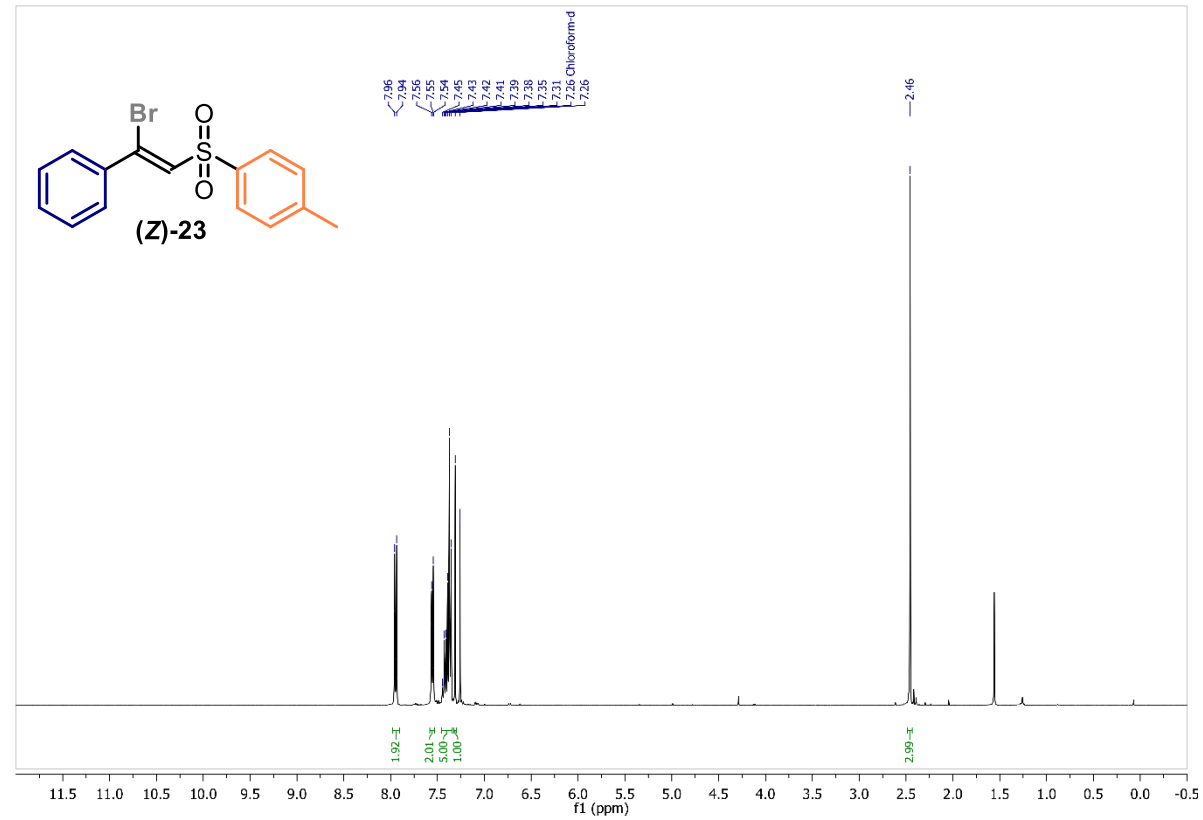
(*Z*)-22: (*Z*)-1-((2-chloro-2-phenylvinyl)sulfonyl)-4-methylbenzene

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*



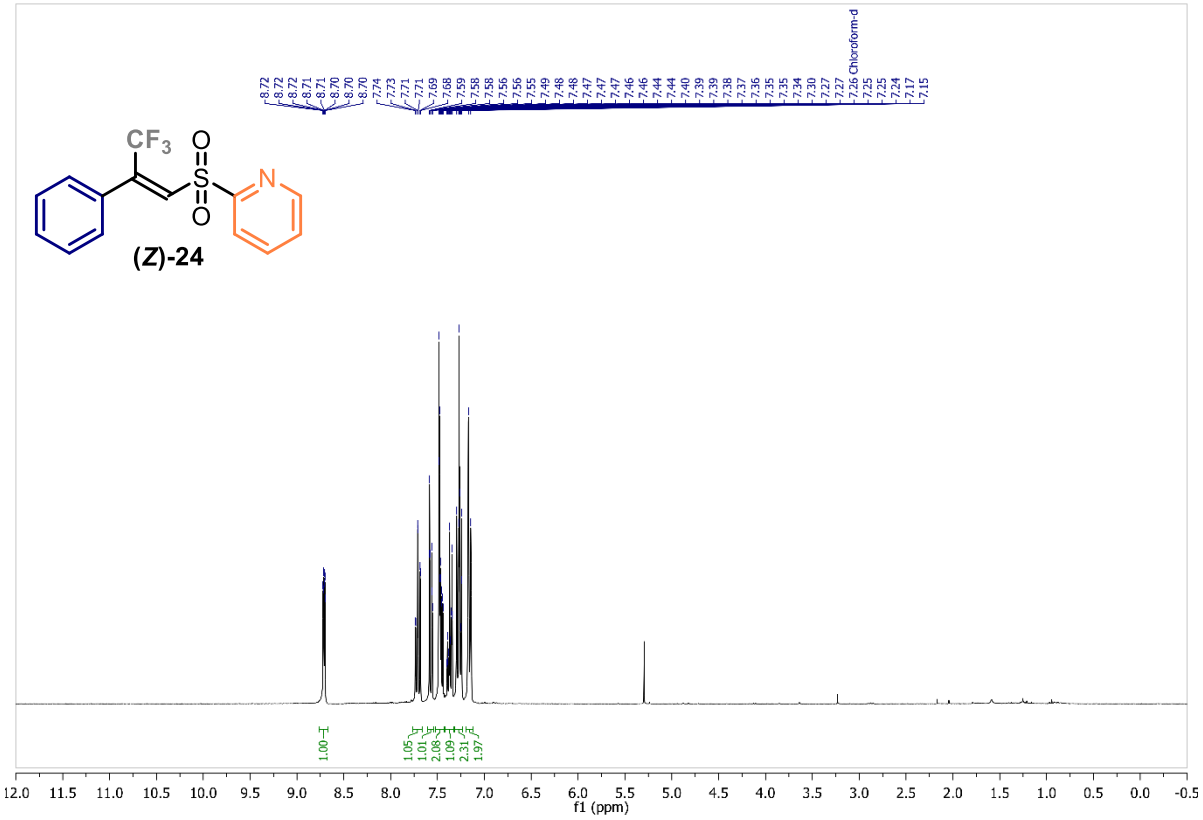
(*Z*)-23: (*Z*)-1-((2-bromo-2-phenylvinyl)sulfonyl)-4-methylbenzene

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

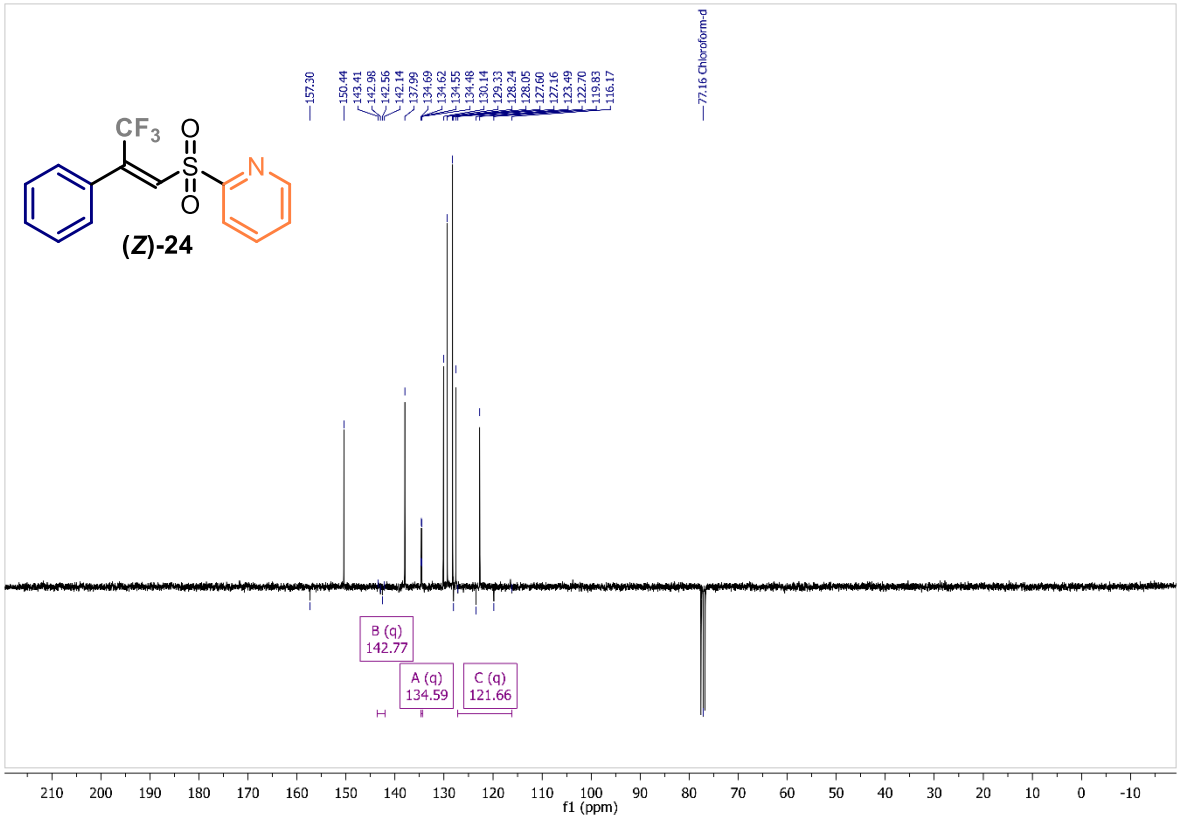


(*Z*)-24: (*Z*)-2-((3,3,3-trifluoro-2-phenylprop-1-en-1-yl)sulfonyl)pyridine

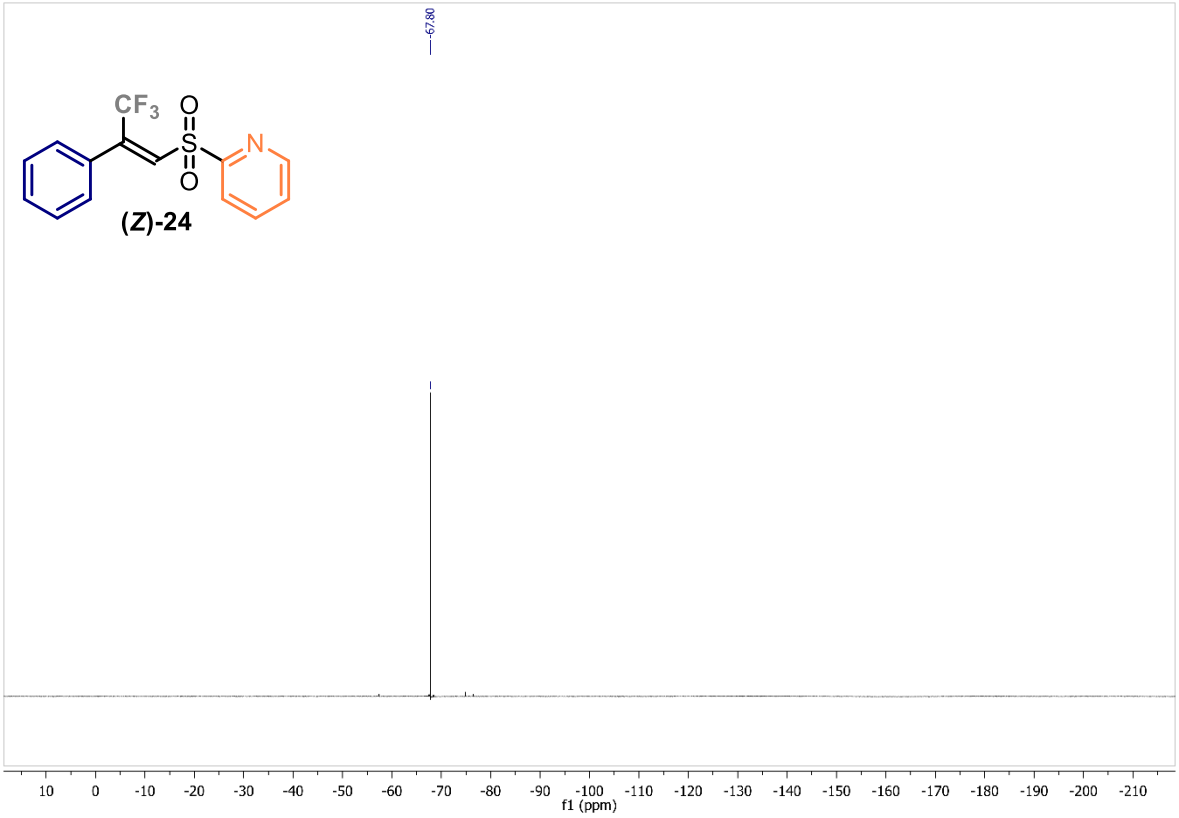
^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*



^{13}C NMR (75 MHz, $CDCl_3$)

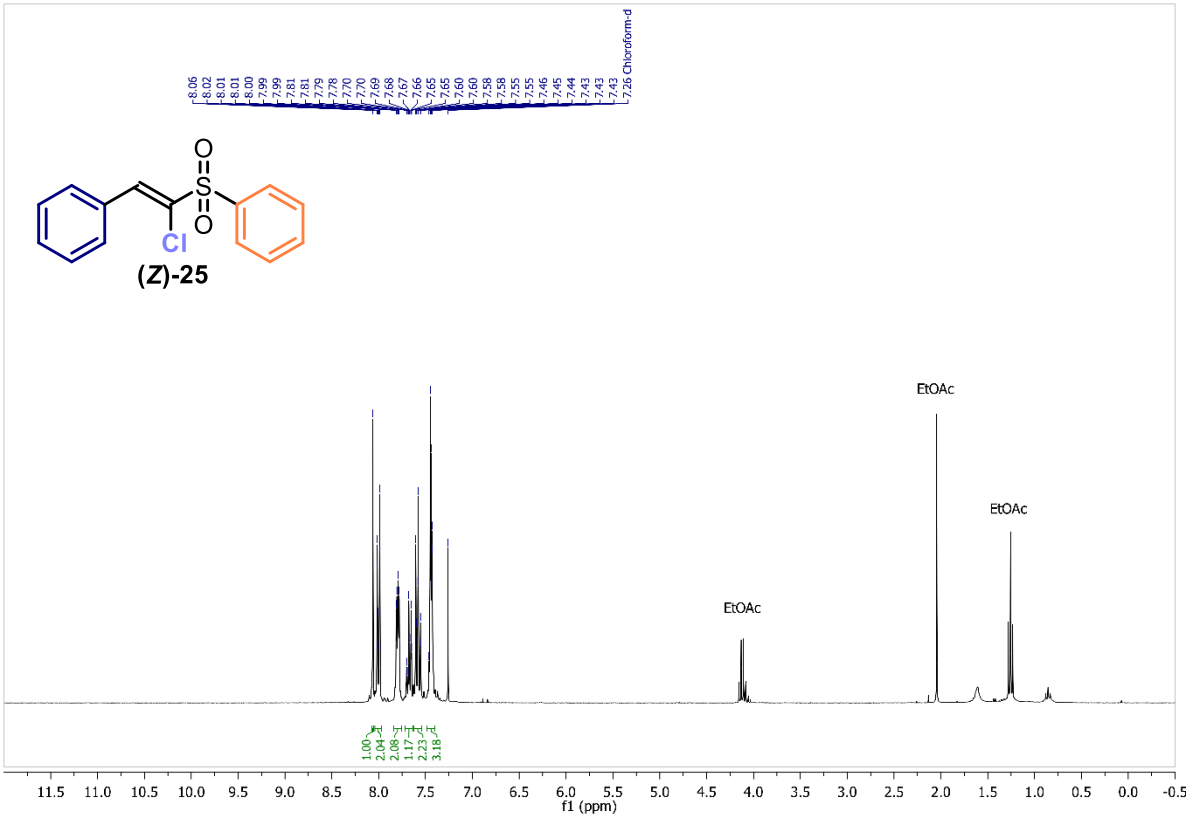


^{19}F NMR (282 MHz, $CDCl_3$)



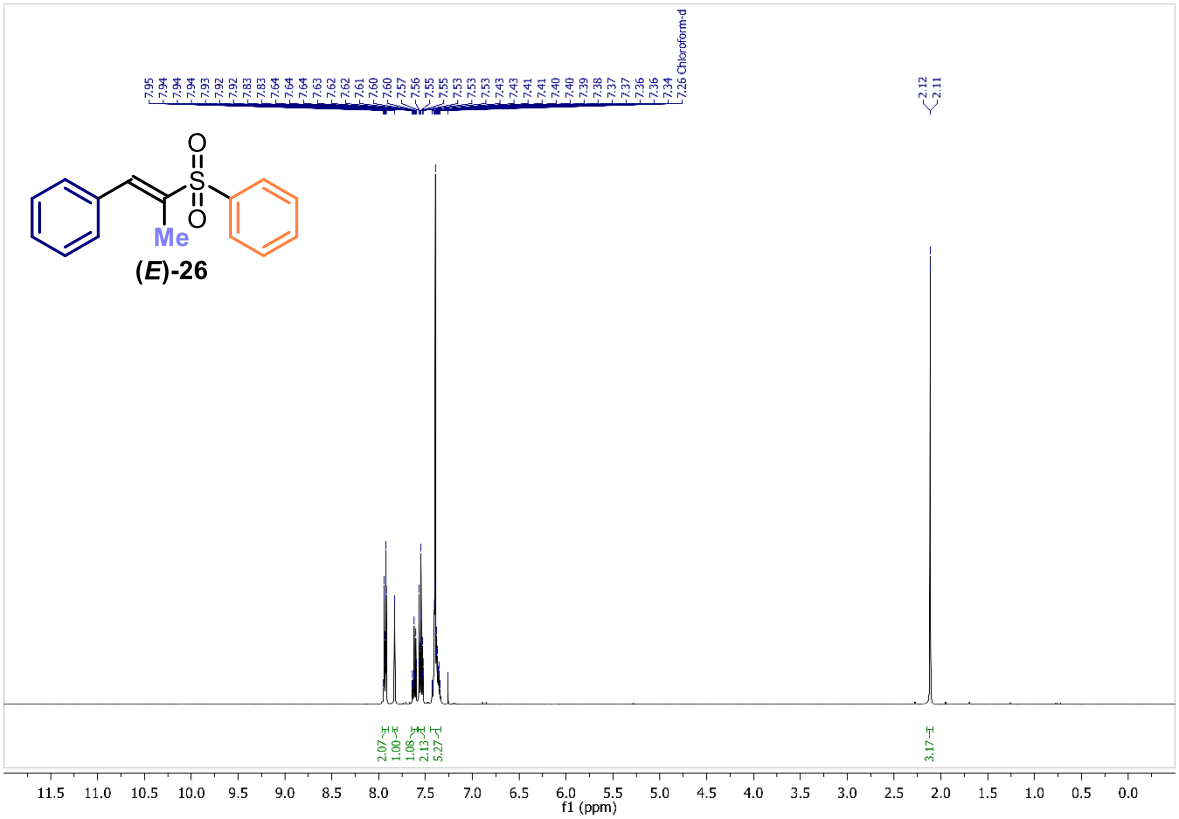
(*Z*)-25: (*Z*)-(2-chloro-2-(phenylsulfonyl)vinyl)benzene

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

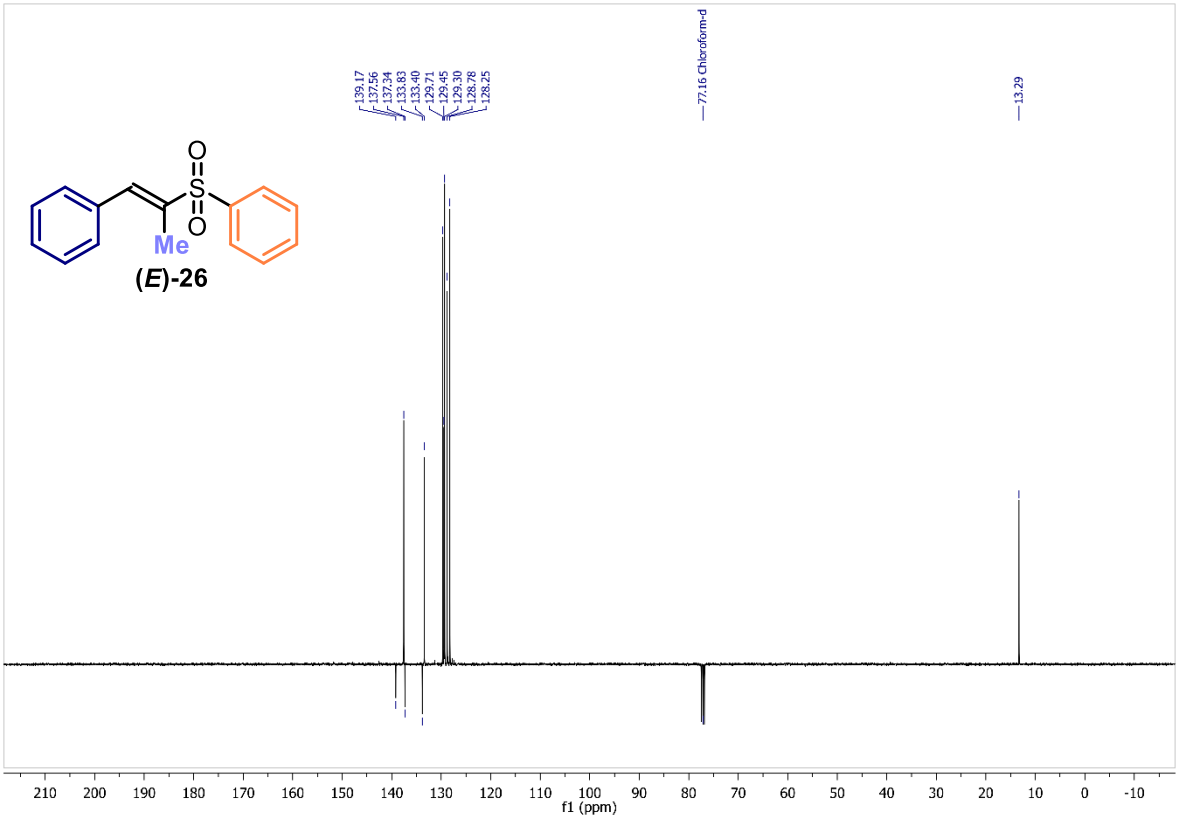


(*E*)-26: (*E*)-((1-phenylprop-1-en-2-yl)sulfonyl)benzene

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

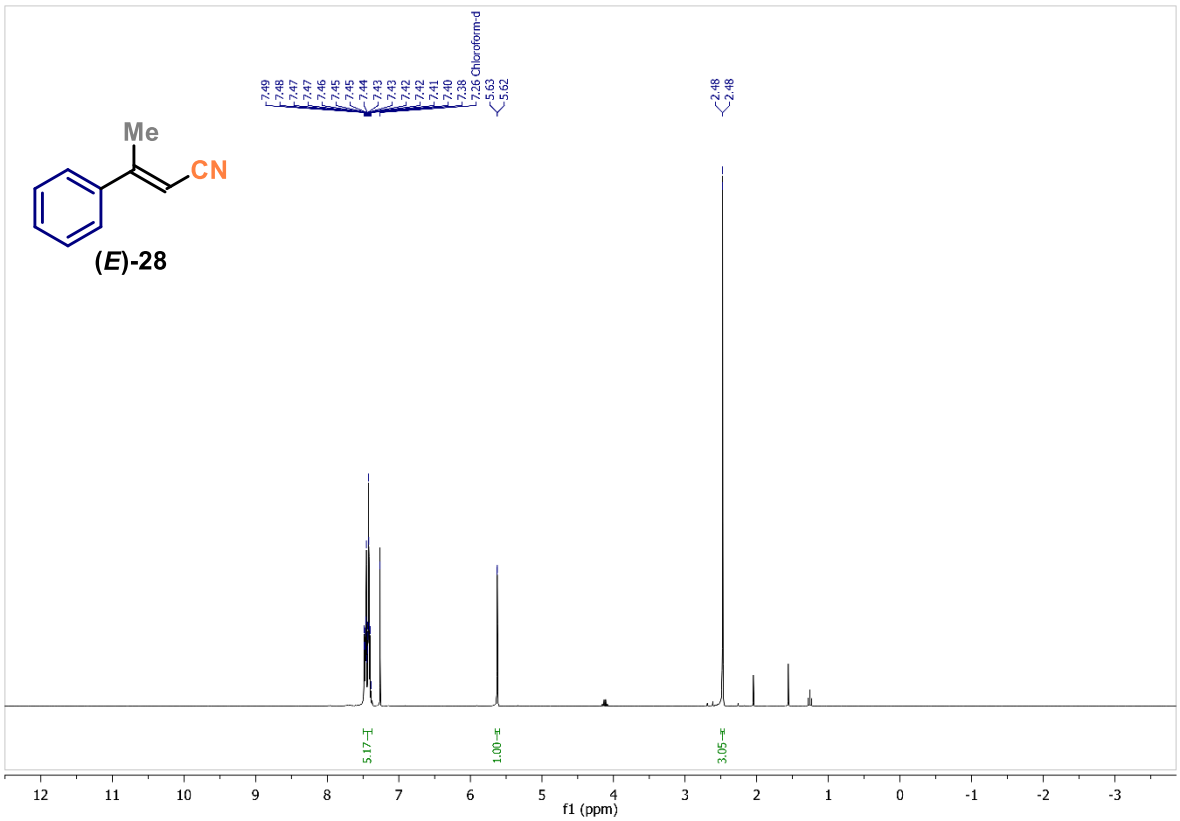


^{13}C NMR (101 MHz, $CDCl_3$)



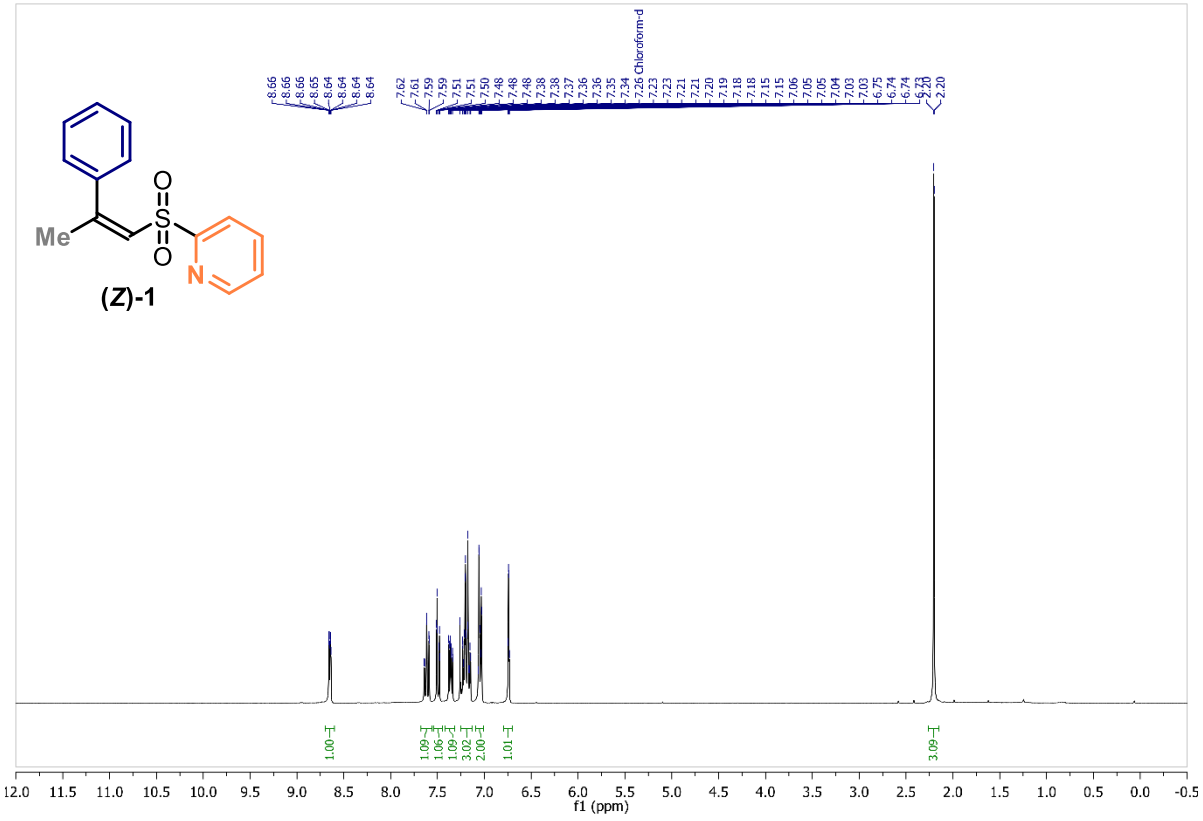
(*E*)-28: (*E*)-3-phenylbut-2-enenitrile

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

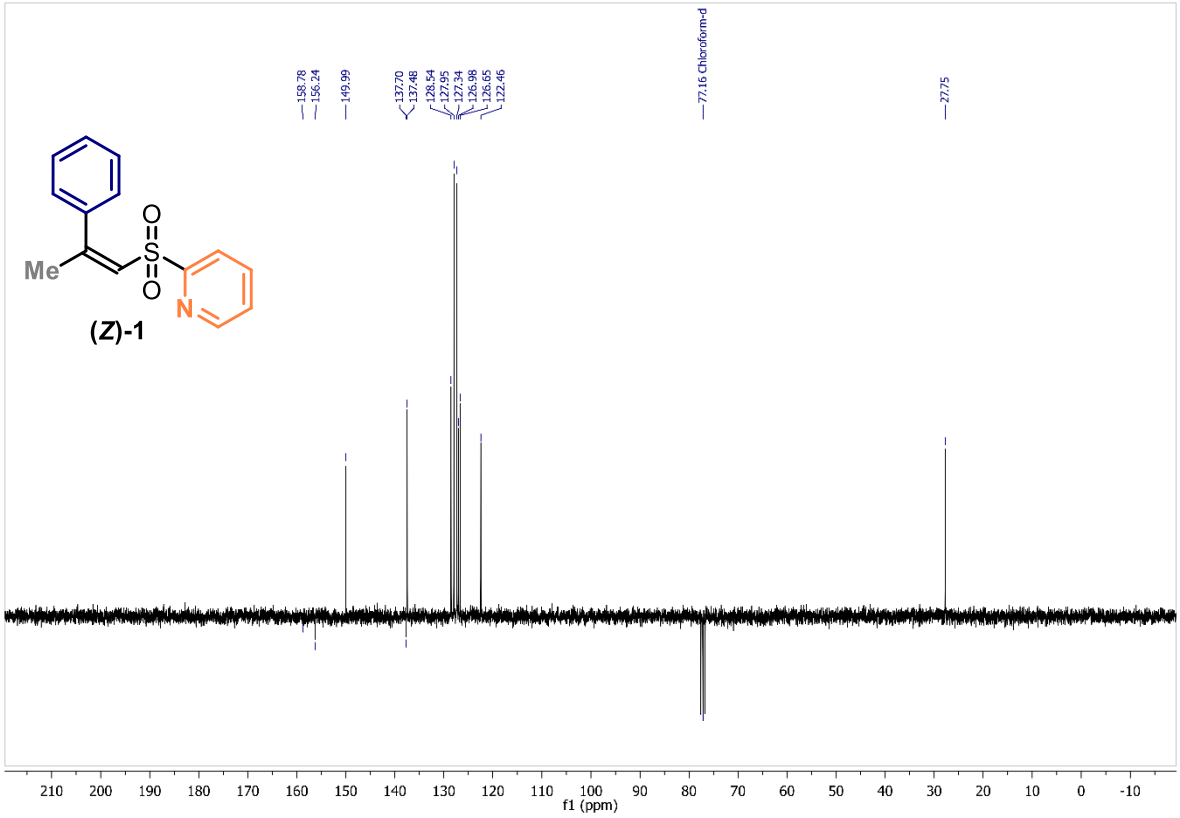


(*Z*)-1: (*Z*)-2-((2-phenylprop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

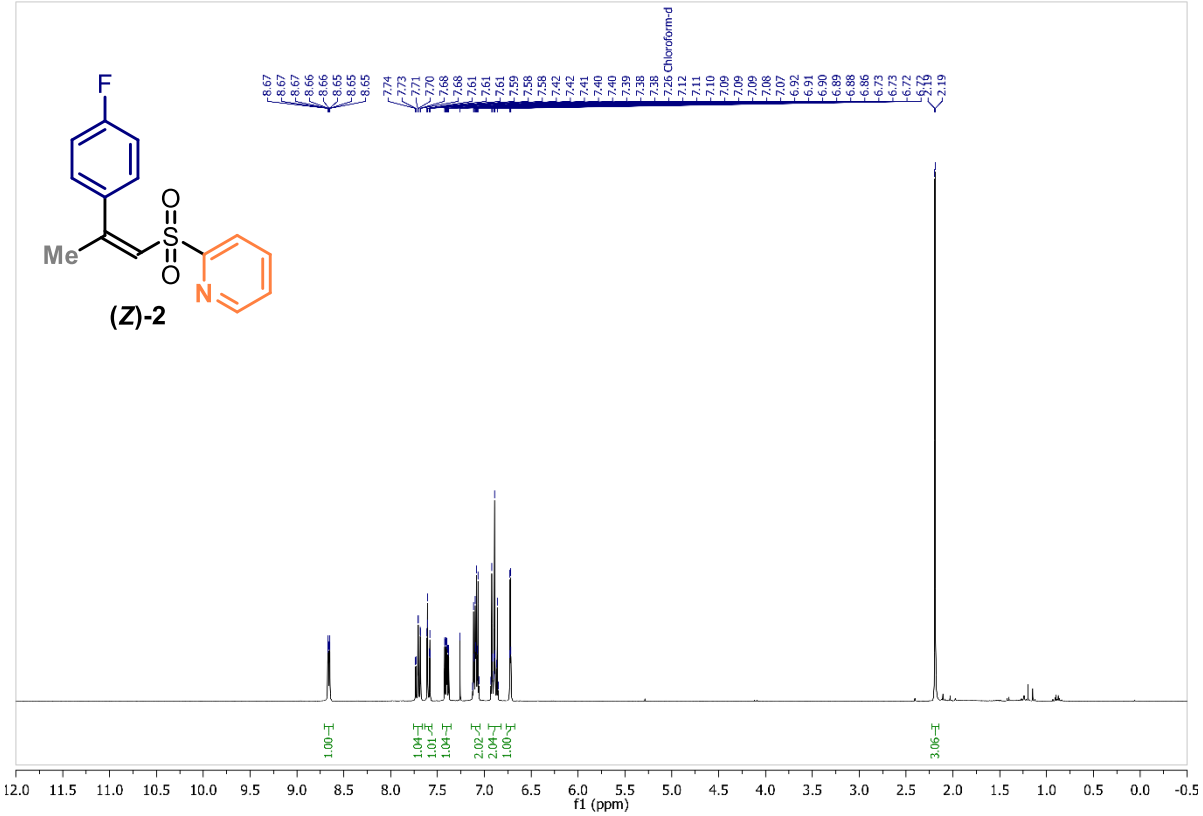


^{13}C NMR (75 MHz, $CDCl_3$)

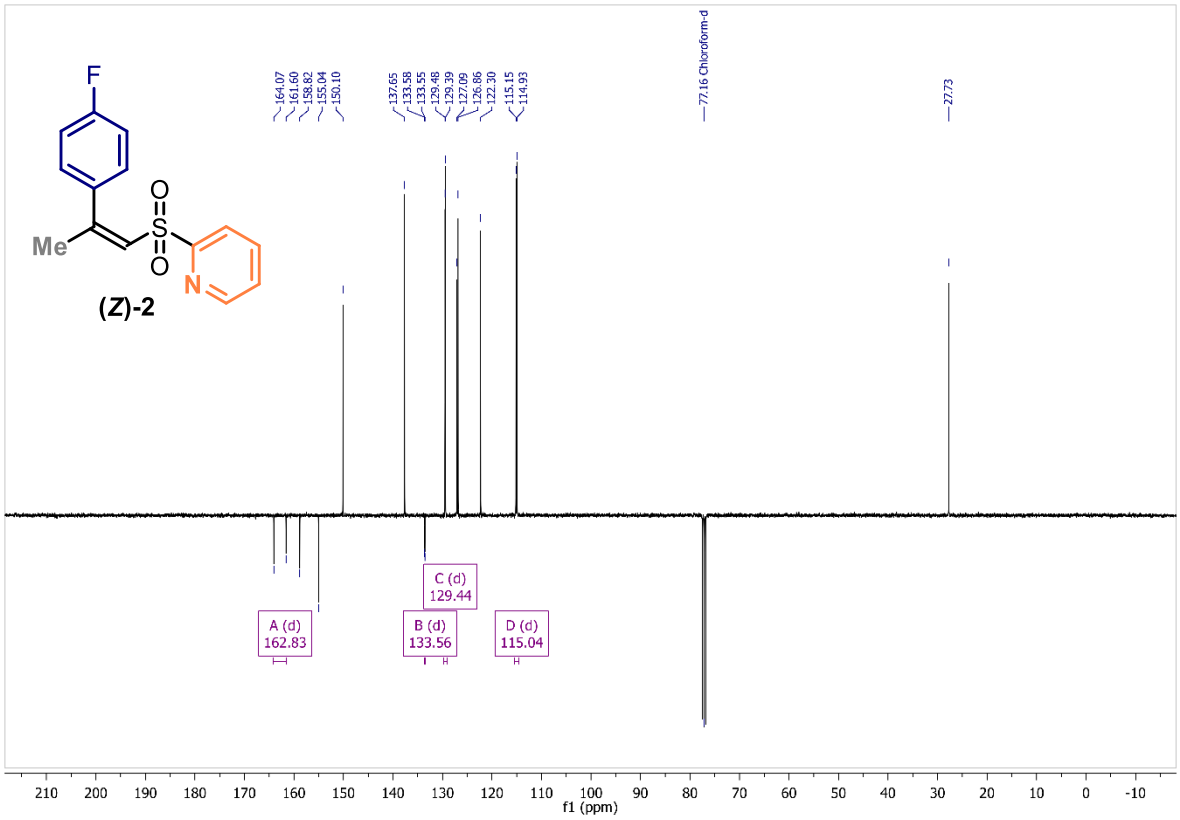


(Z)-2: (Z)-2-((2-(4-fluorophenyl)prop-1-en-1-yl)sulfonyl)pyridine

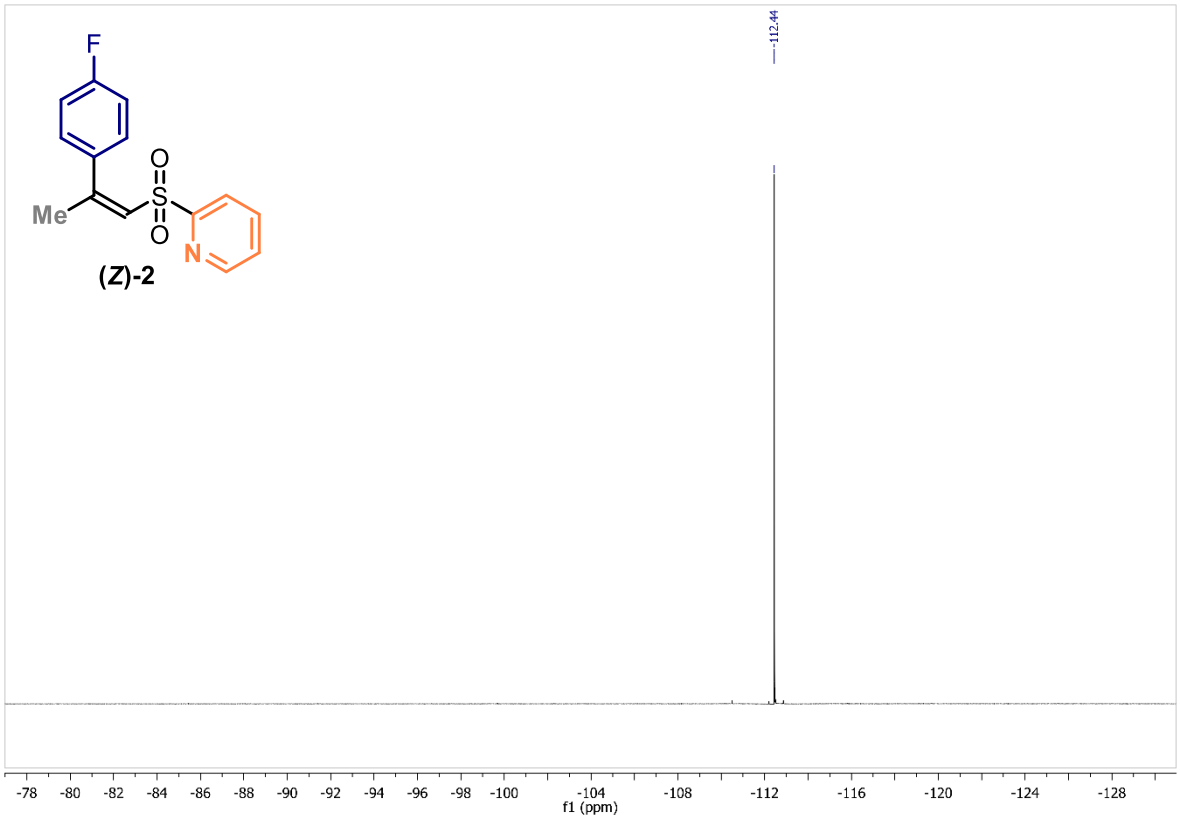
^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*



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

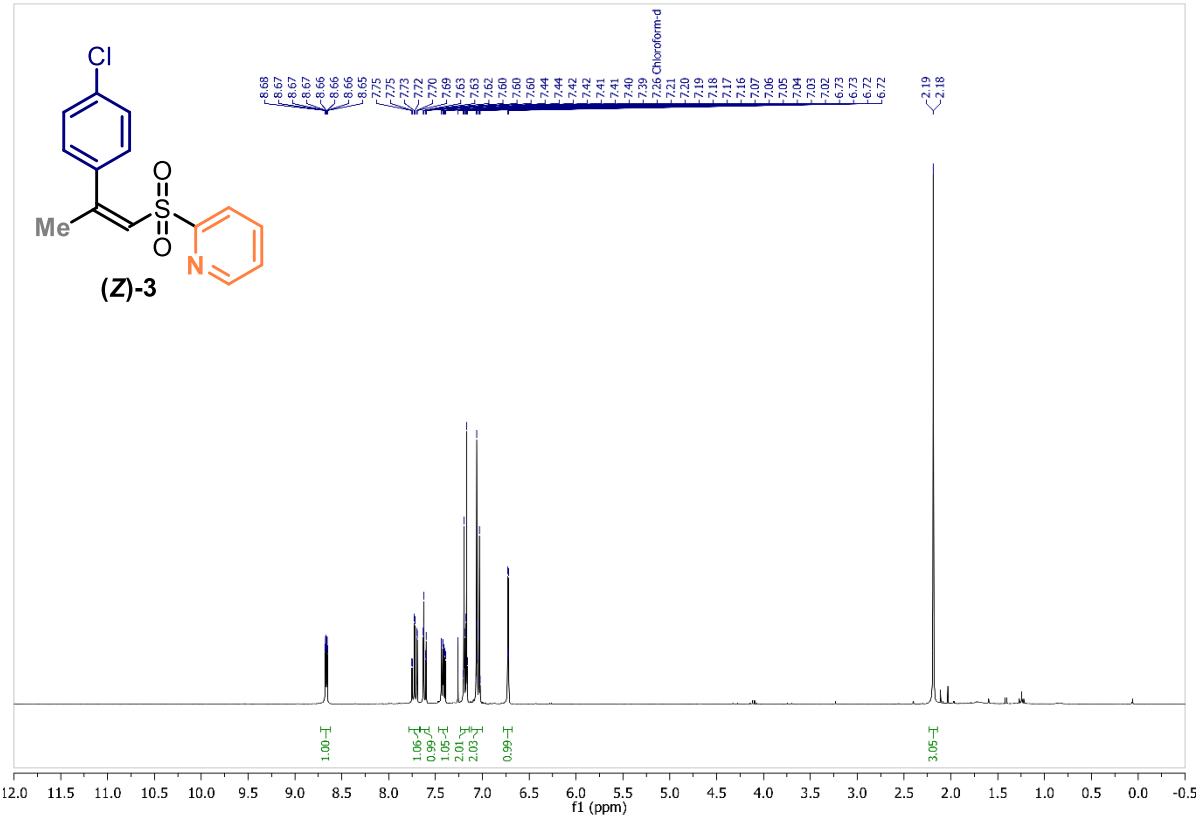


^{19}F NMR (377 MHz, $CDCl_3$)

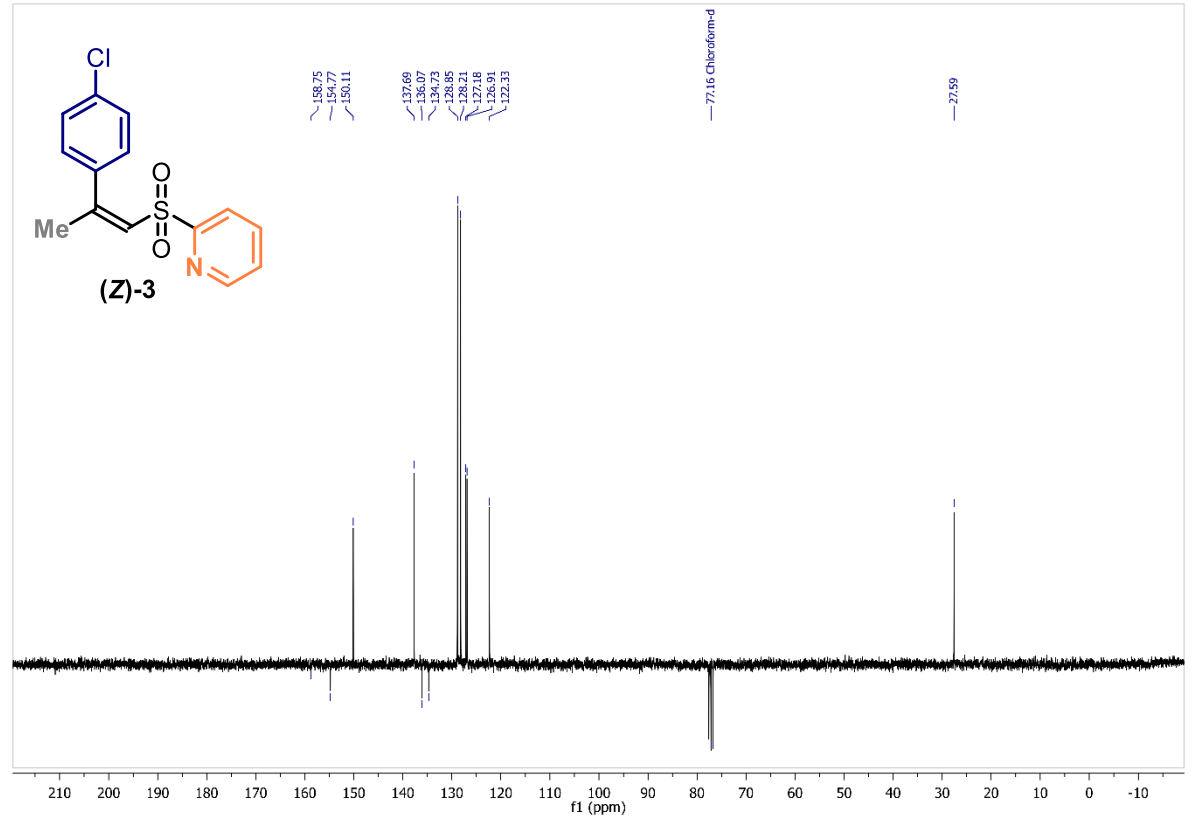


(*Z*)-3: (*Z*)-2-((2-(4-chlorophenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

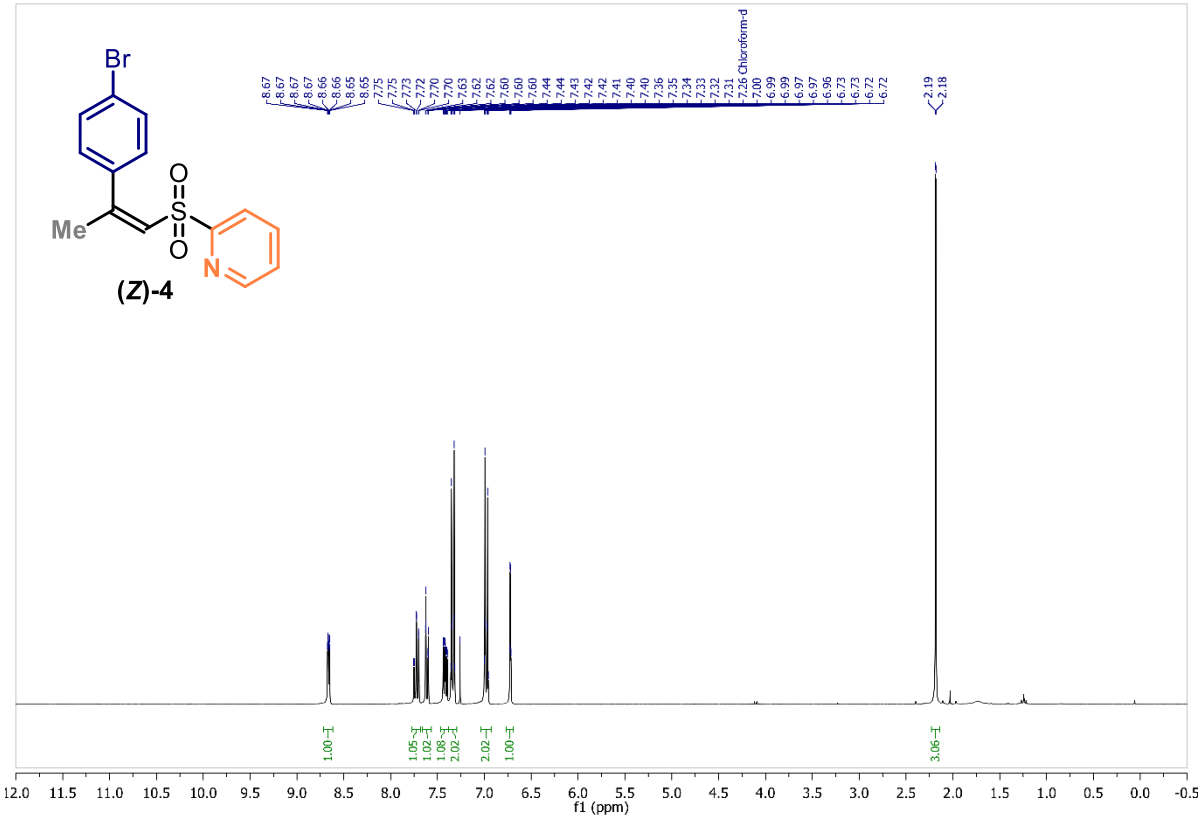


^{13}C NMR (75 MHz, $CDCl_3$)

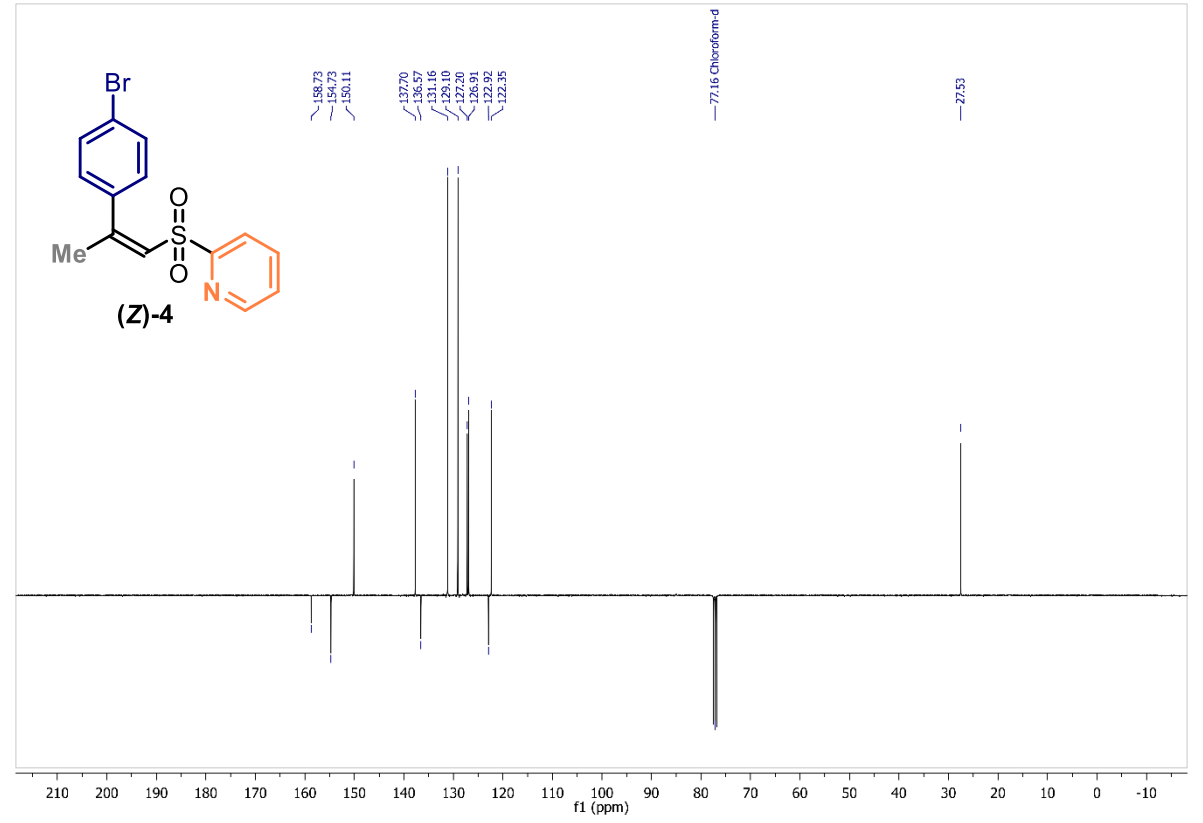


(*Z*)-4: (*Z*)-2-((2-(4-bromophenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

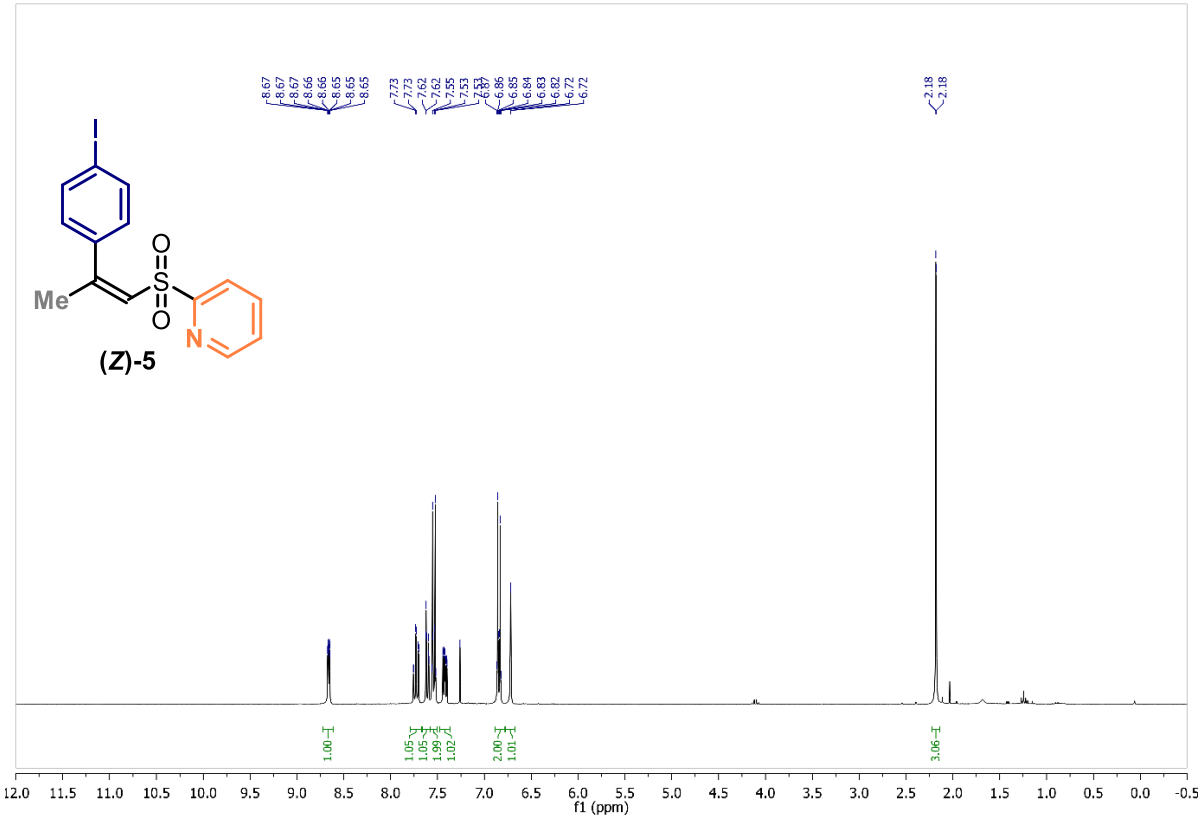


^{13}C NMR (101 MHz, $CDCl_3$)

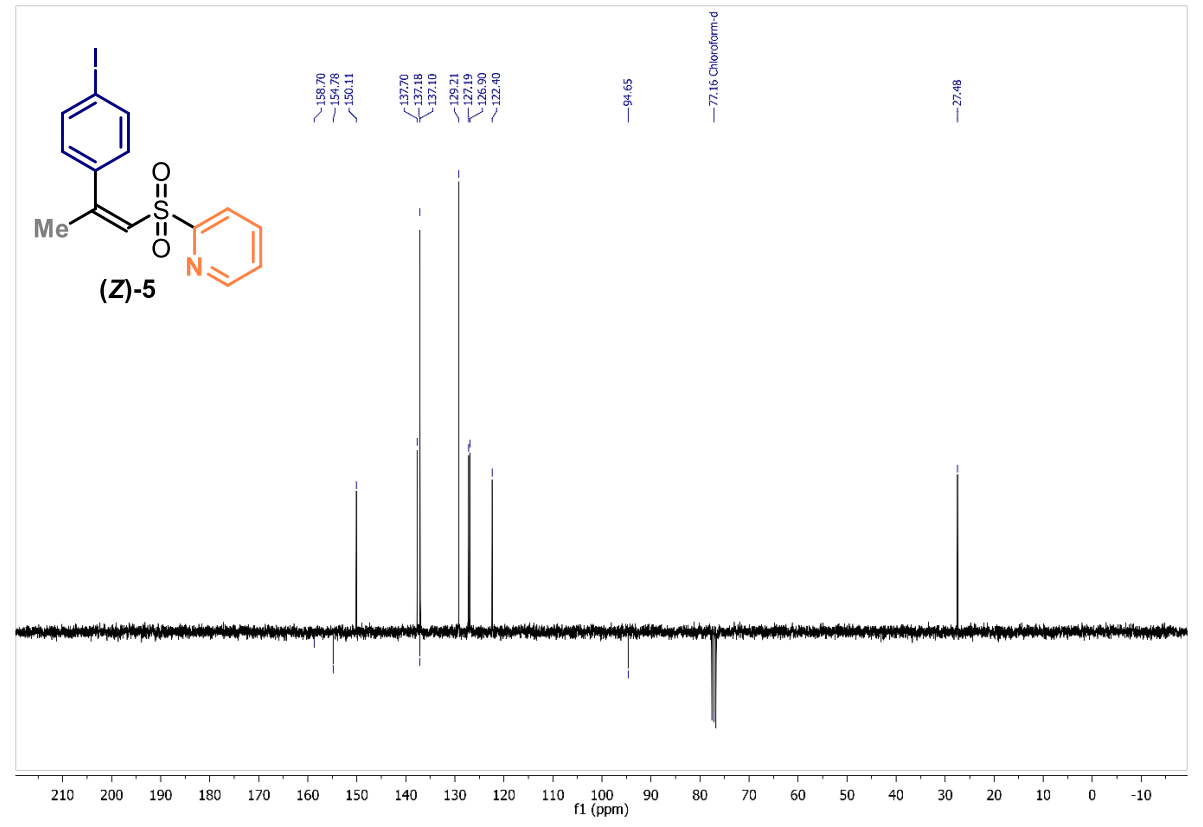


(*Z*)-5: (*Z*)-2-((2-(4-iodophenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

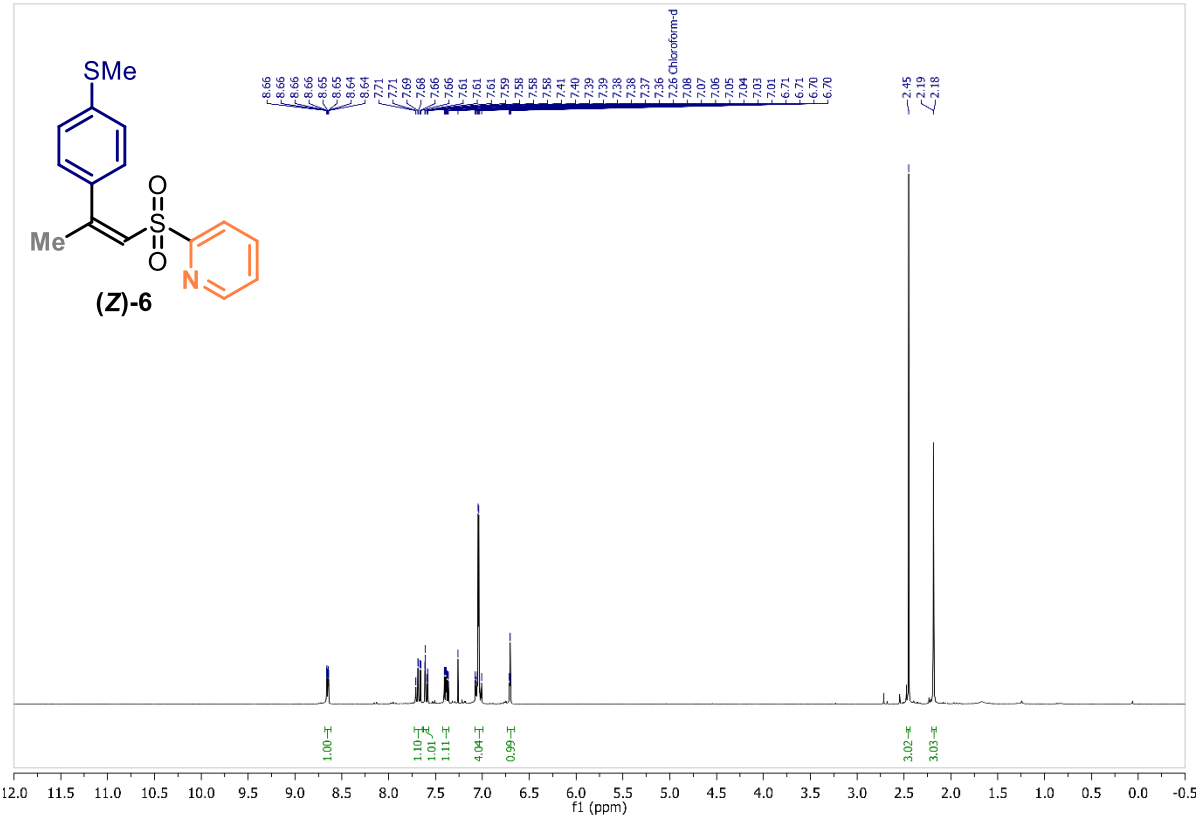


^{13}C NMR (75 MHz, $CDCl_3$)

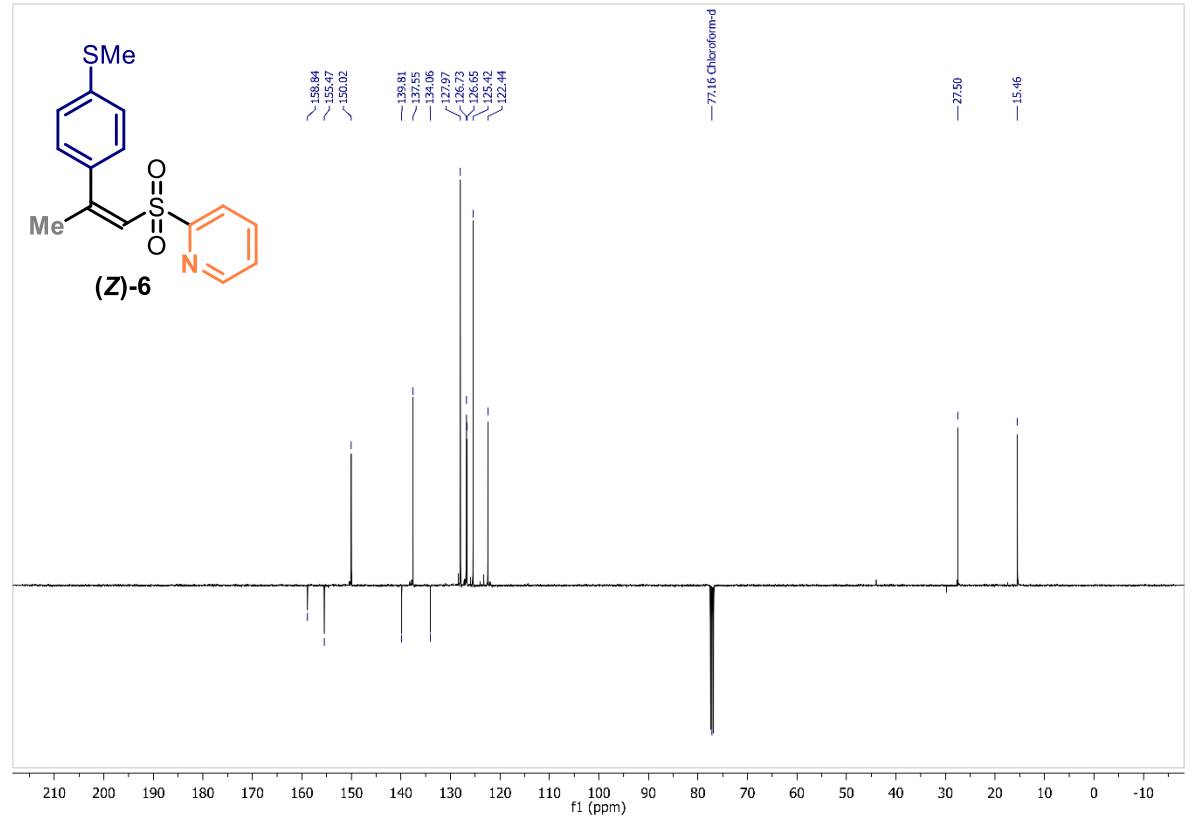


(*Z*)-6: (*Z*)-2-((2-(4-(methylthio)phenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

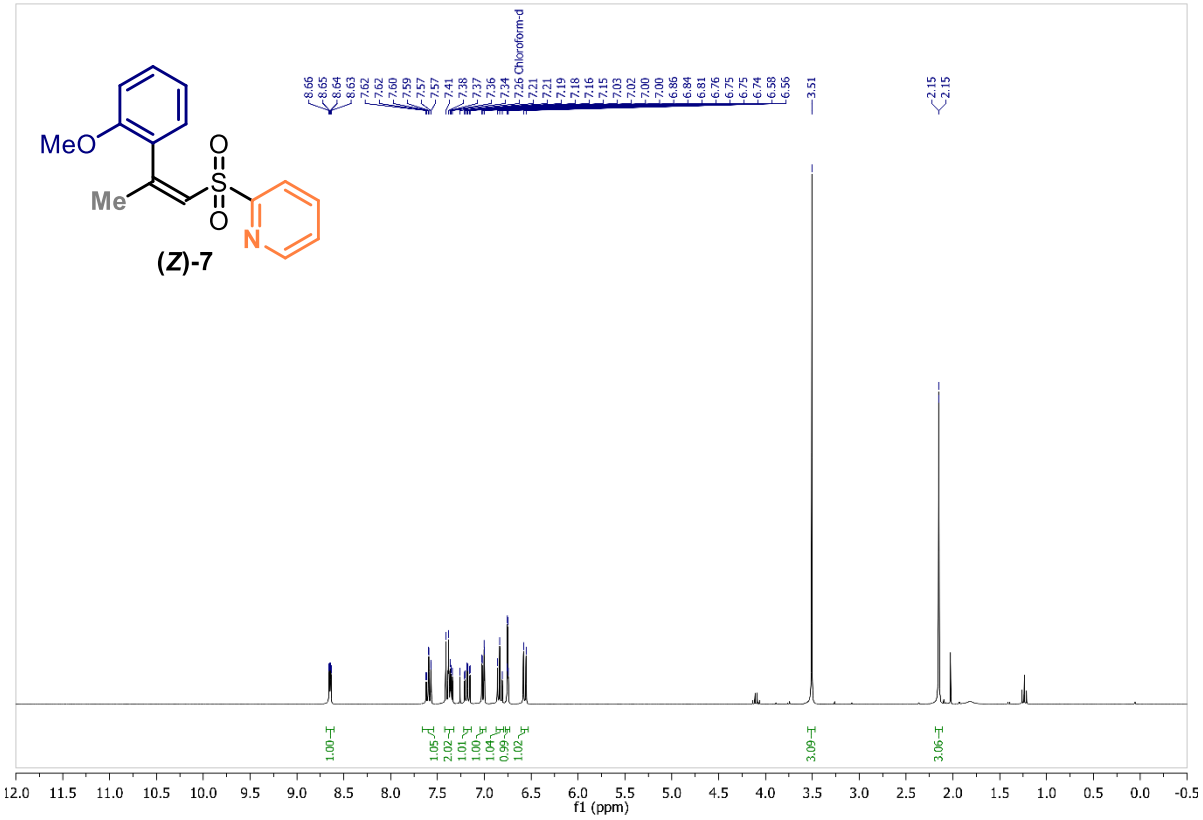


^{13}C NMR (101 MHz, $CDCl_3$)

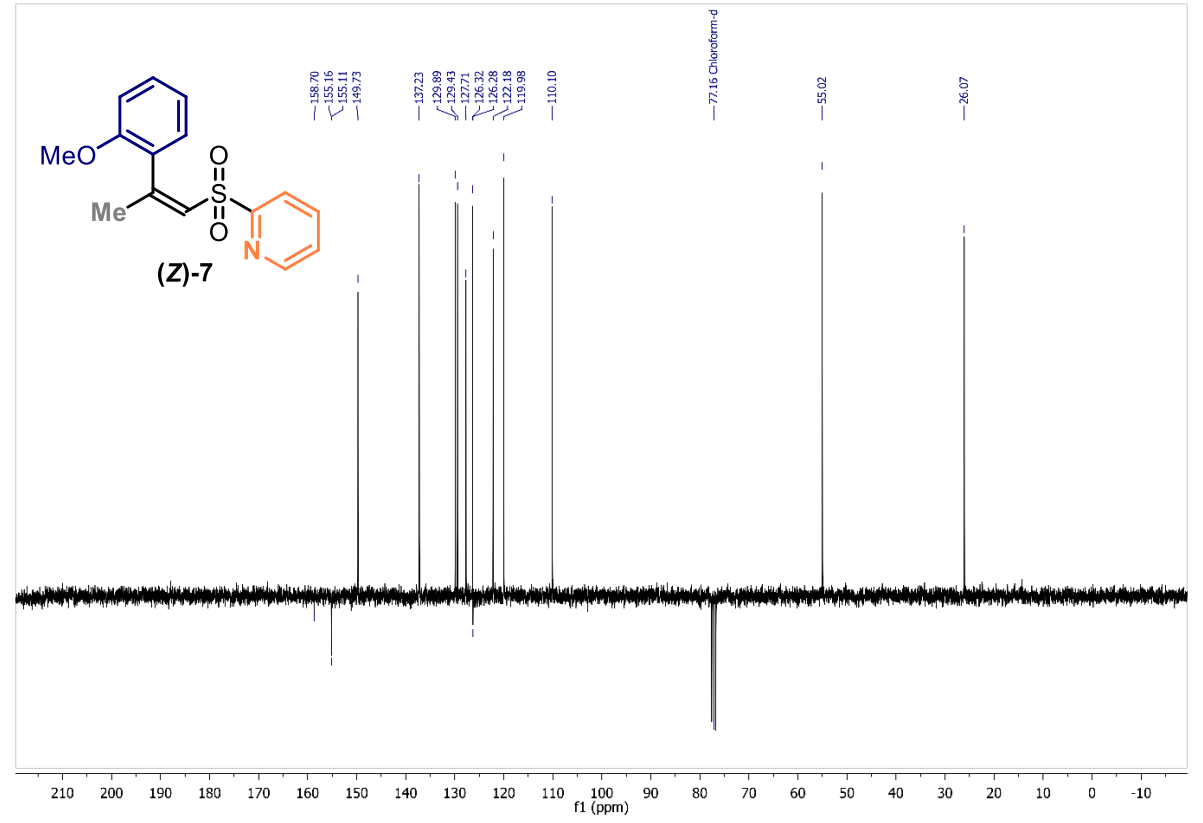


(*Z*)-7: (*Z*)-2-((2-(2-methoxyphenyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

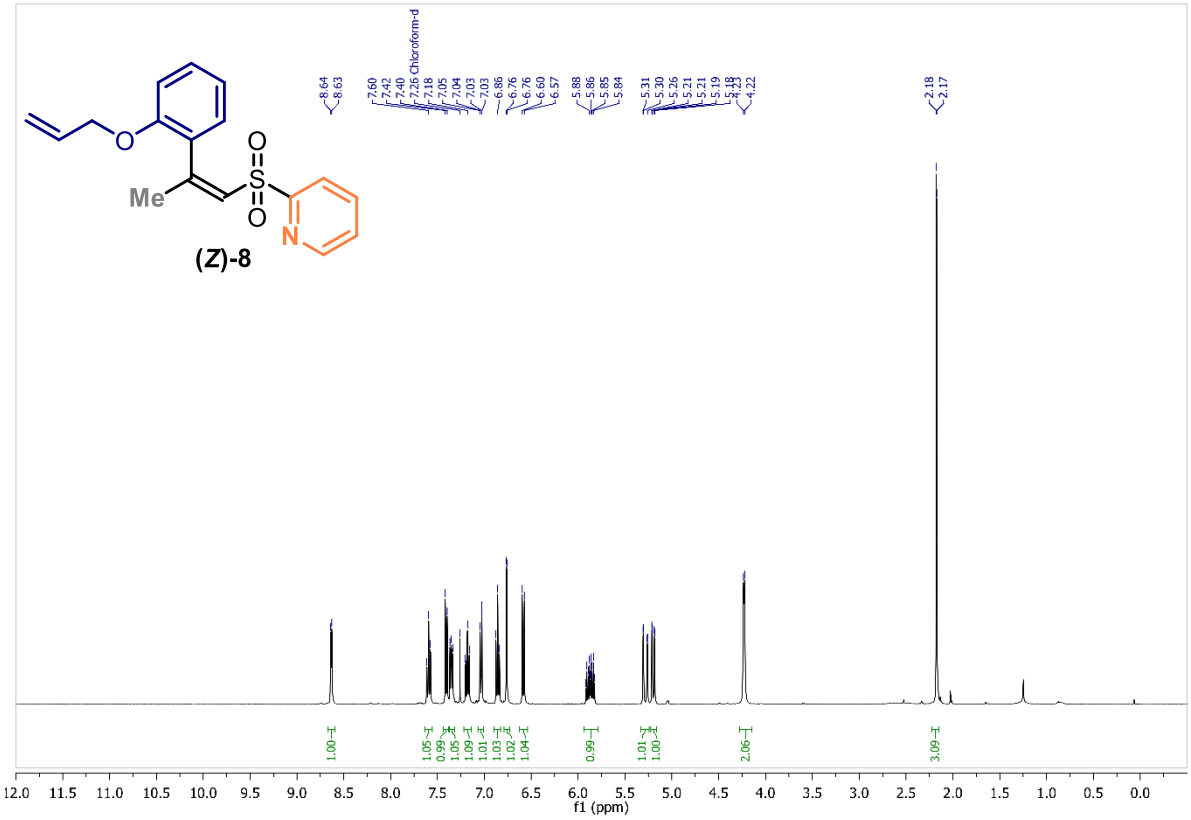


^{13}C NMR (75 MHz, $CDCl_3$)

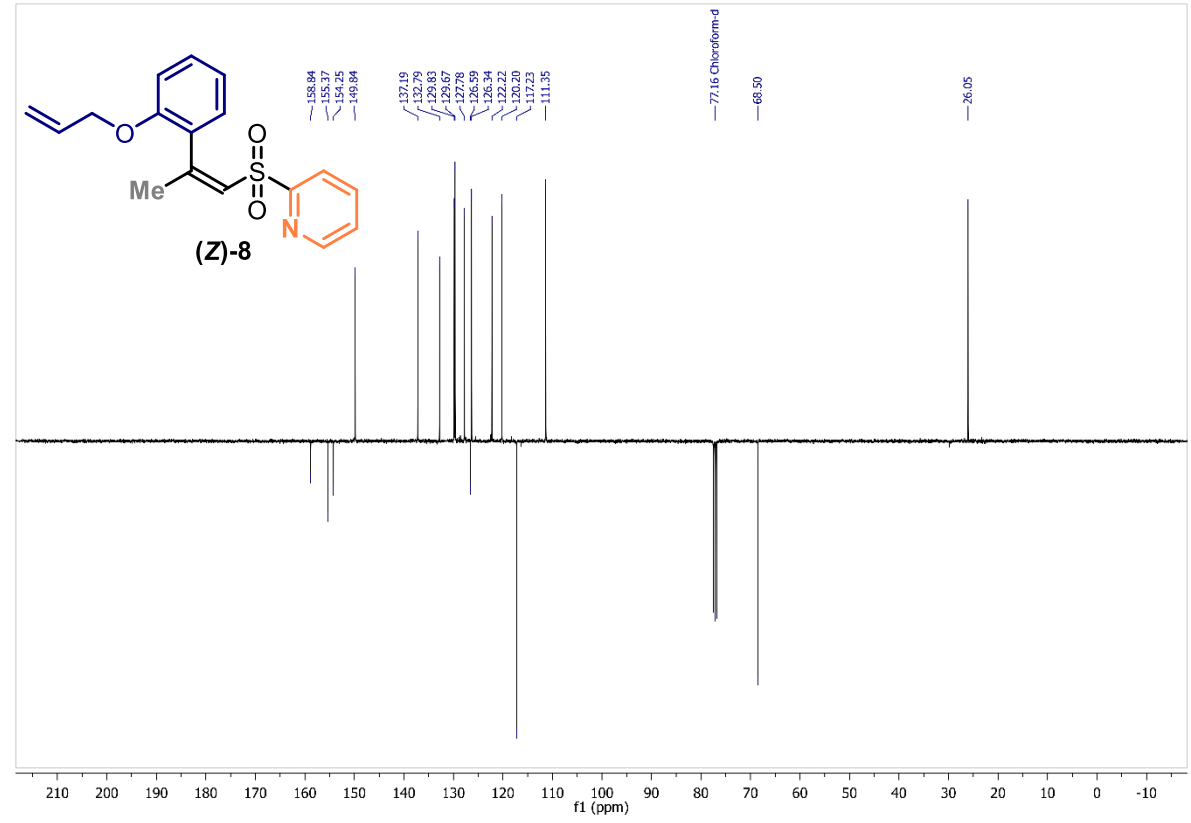


(*Z*)-8: (*Z*)-2-((2-(2-(allyloxy)phenyl)prop-1-en-1-yl)sulfonyl)pyridine

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

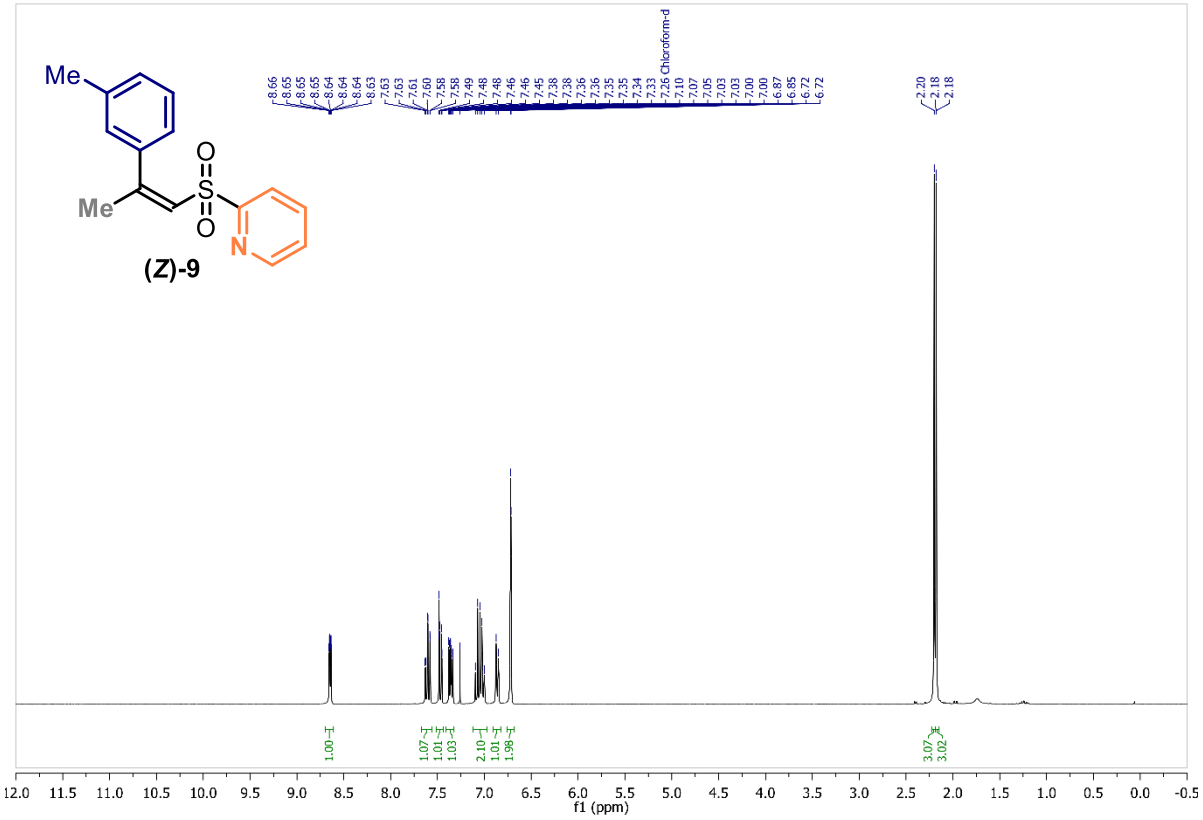


^{13}C NMR (101 MHz, $CDCl_3$)

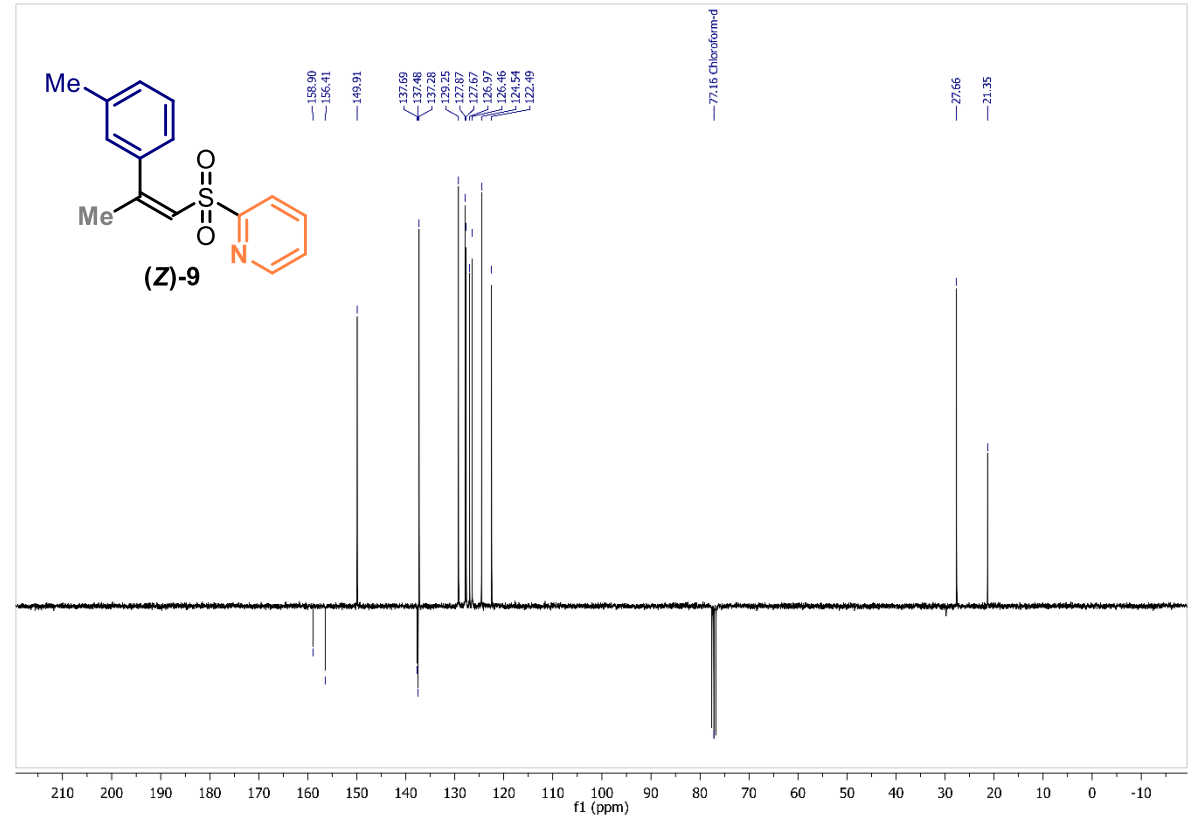


(*Z*)-9: (*Z*)-2-((2-(m-tolyl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

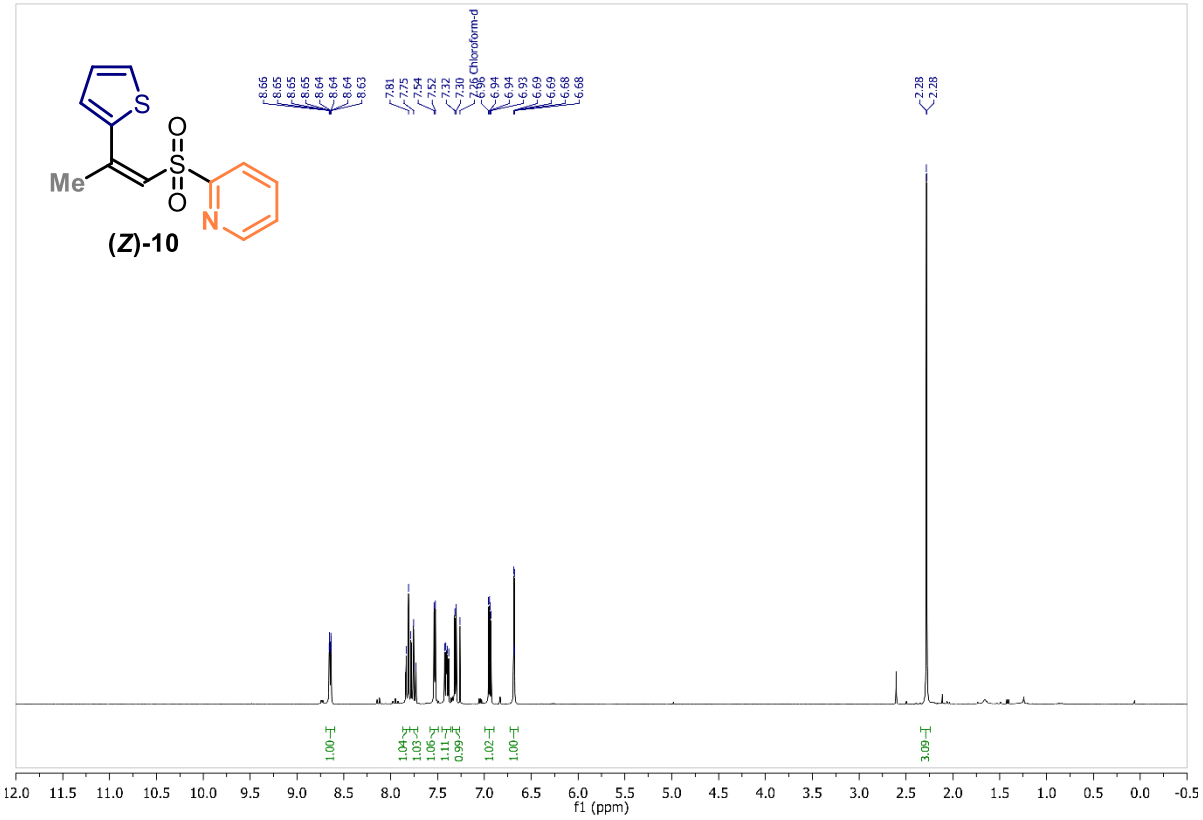


^{13}C NMR (75 MHz, $CDCl_3$)

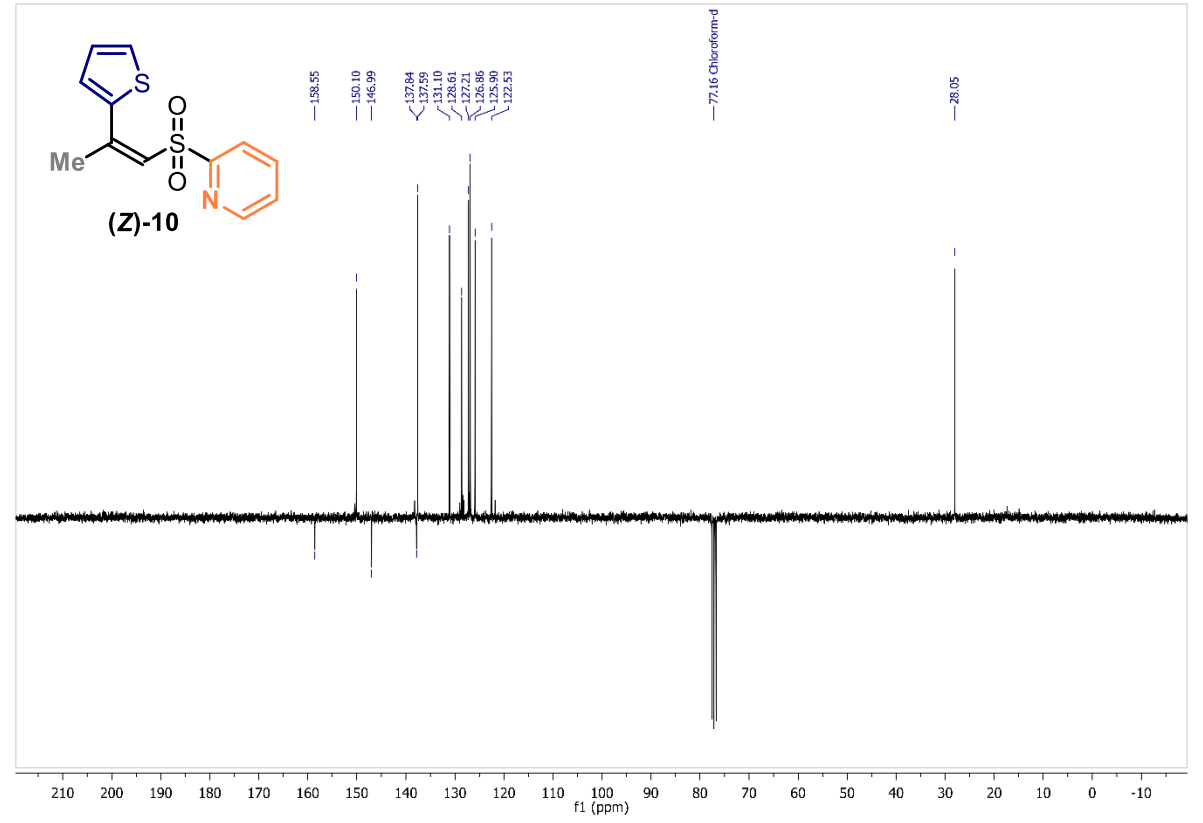


(*Z*)-10: (*Z*)-2-((2-(thiophen-2-yl)prop-1-en-1-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

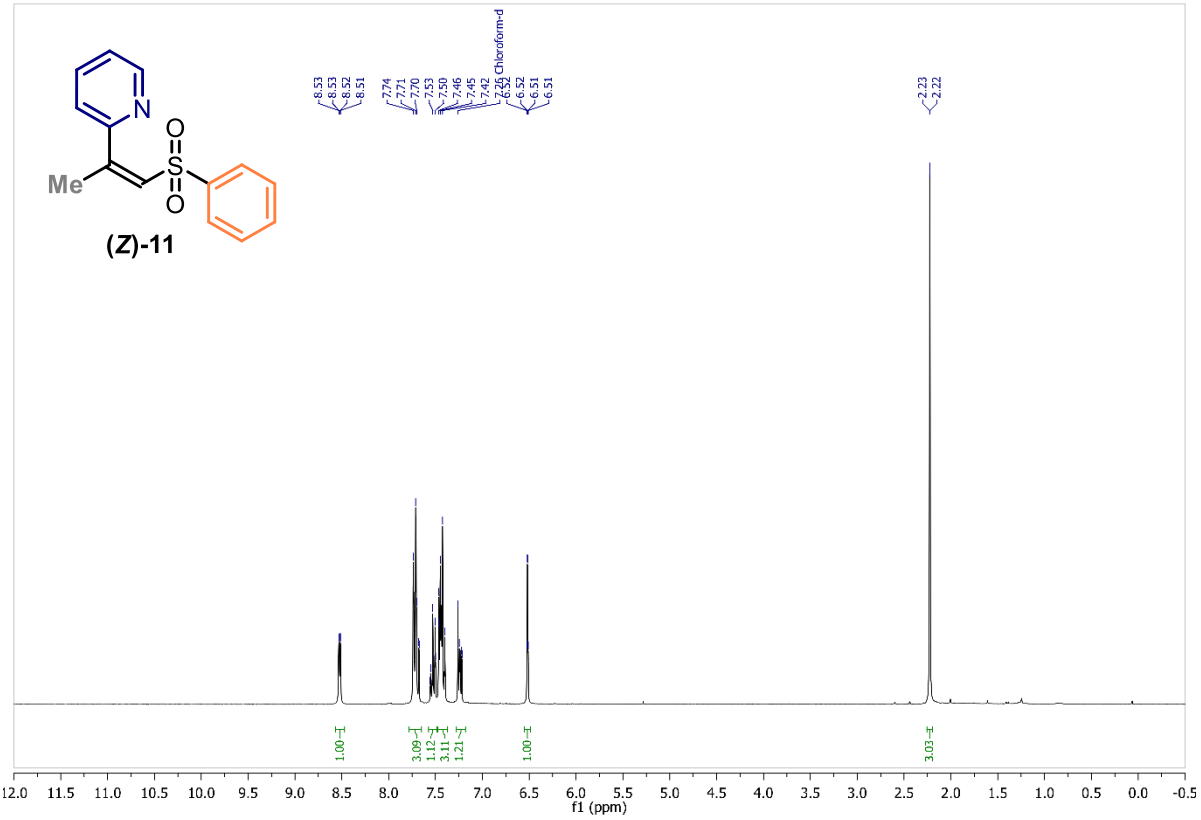


^{13}C NMR (75 MHz, $CDCl_3$)

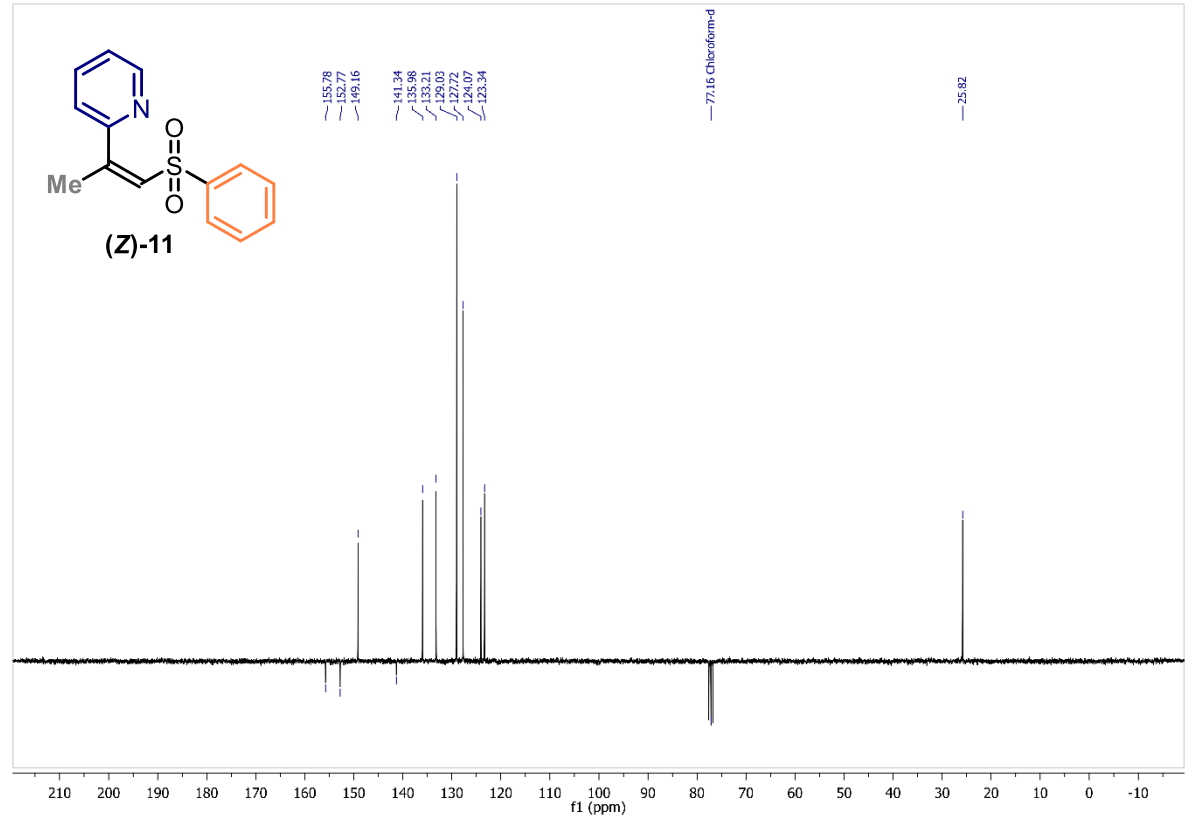


(*Z*)-11: (*Z*)-2-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

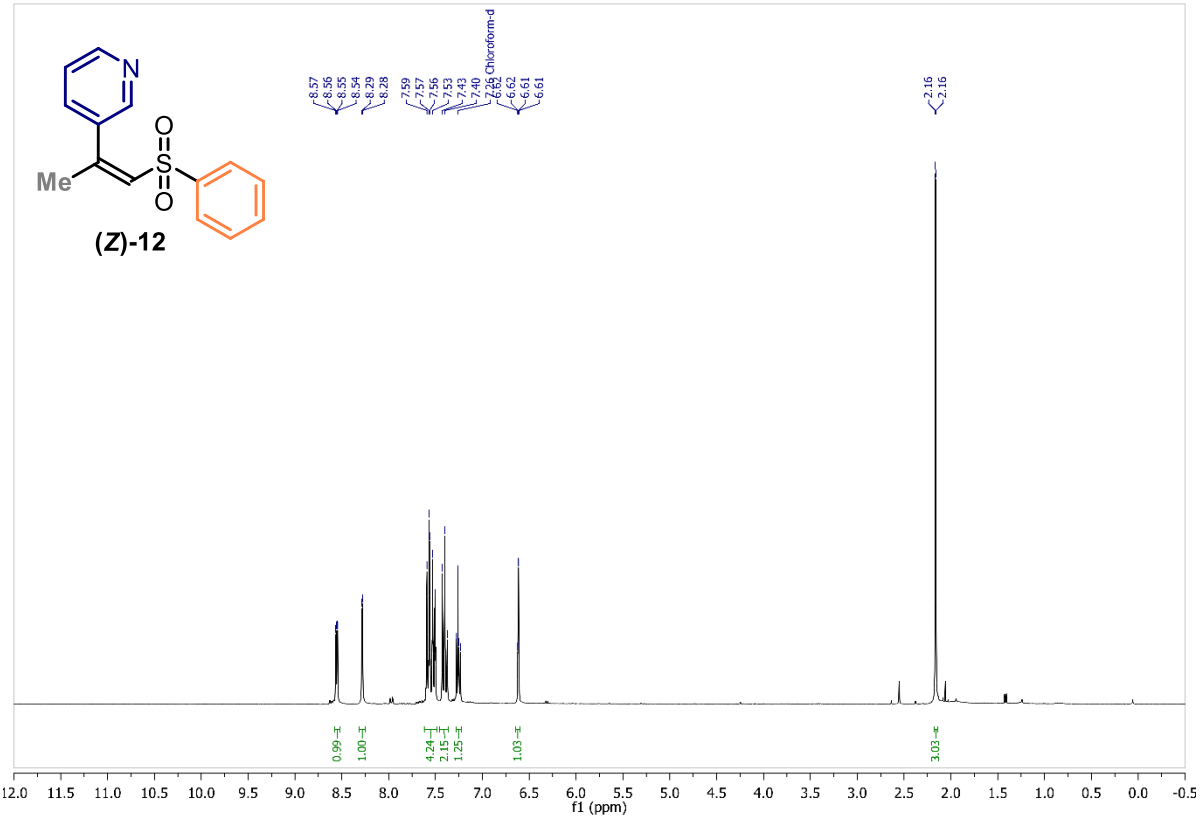


^{13}C NMR (75 MHz, $CDCl_3$)

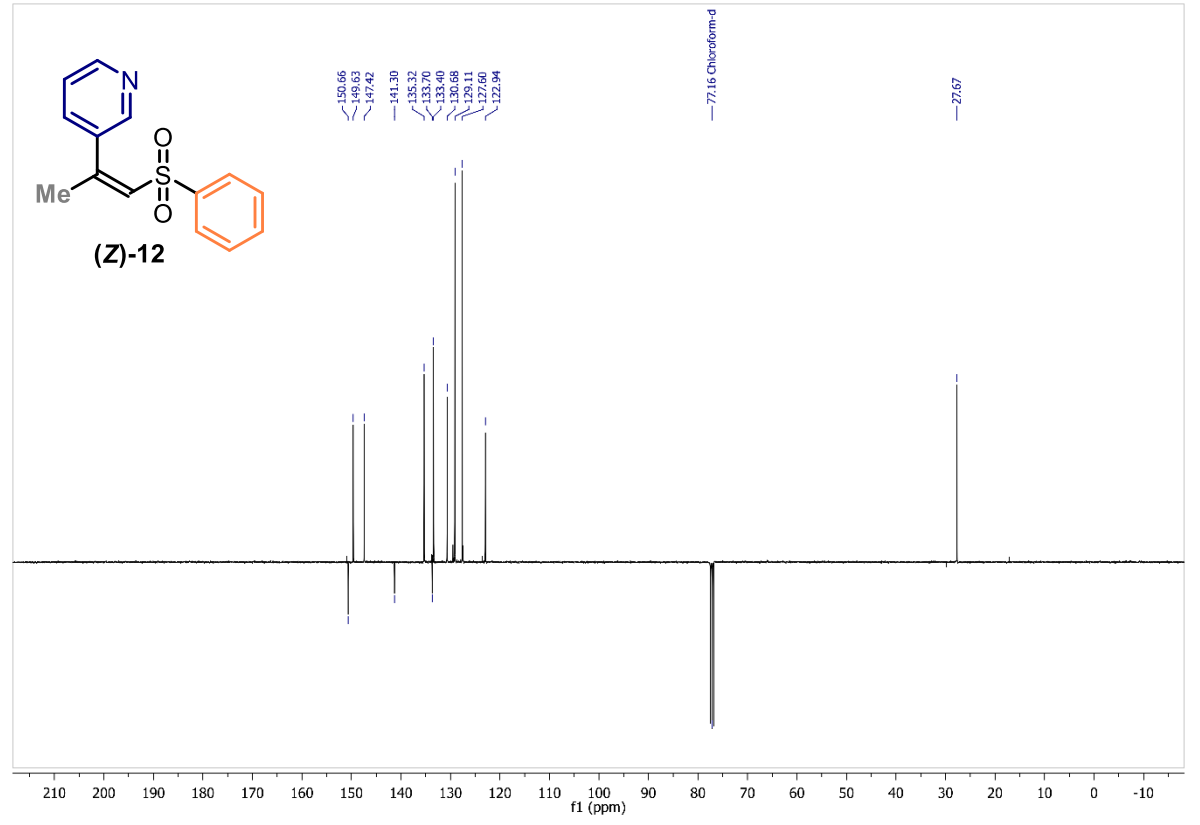


(*Z*)-12: (*Z*)-3-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

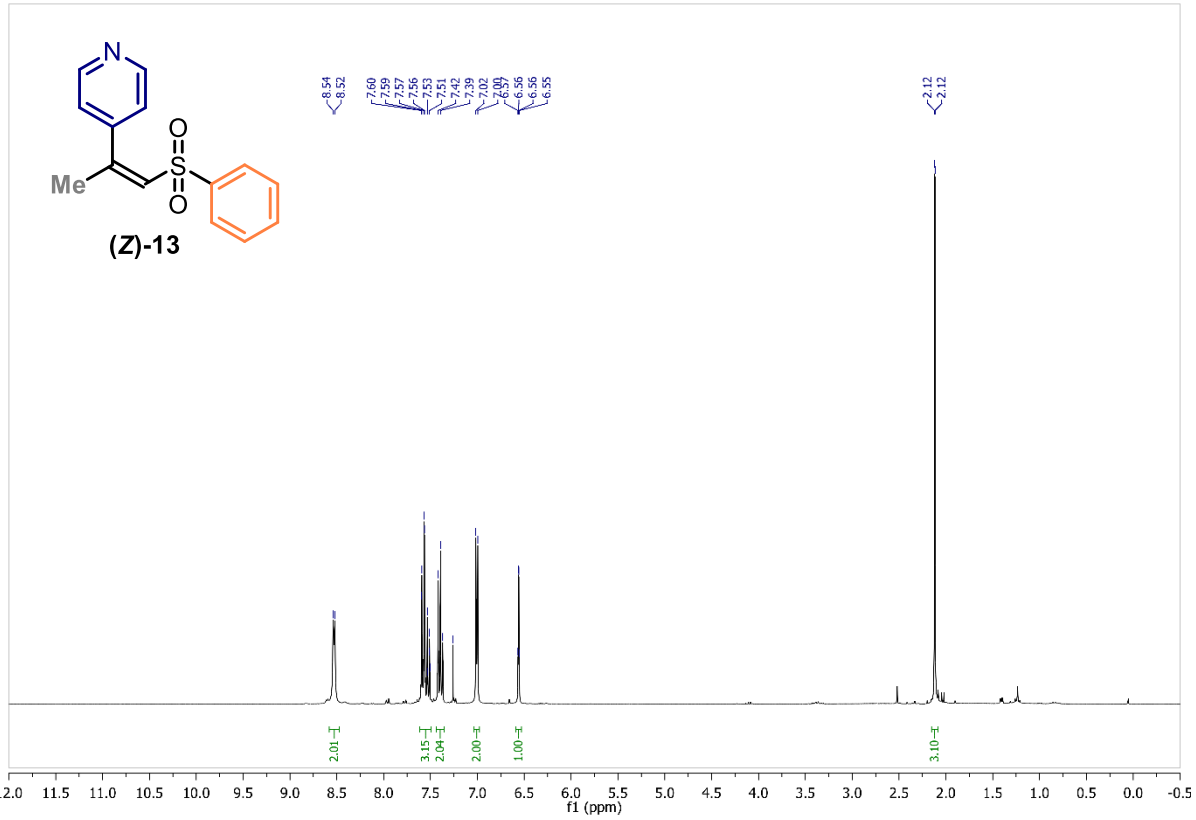


^{13}C NMR (101 MHz, $CDCl_3$)

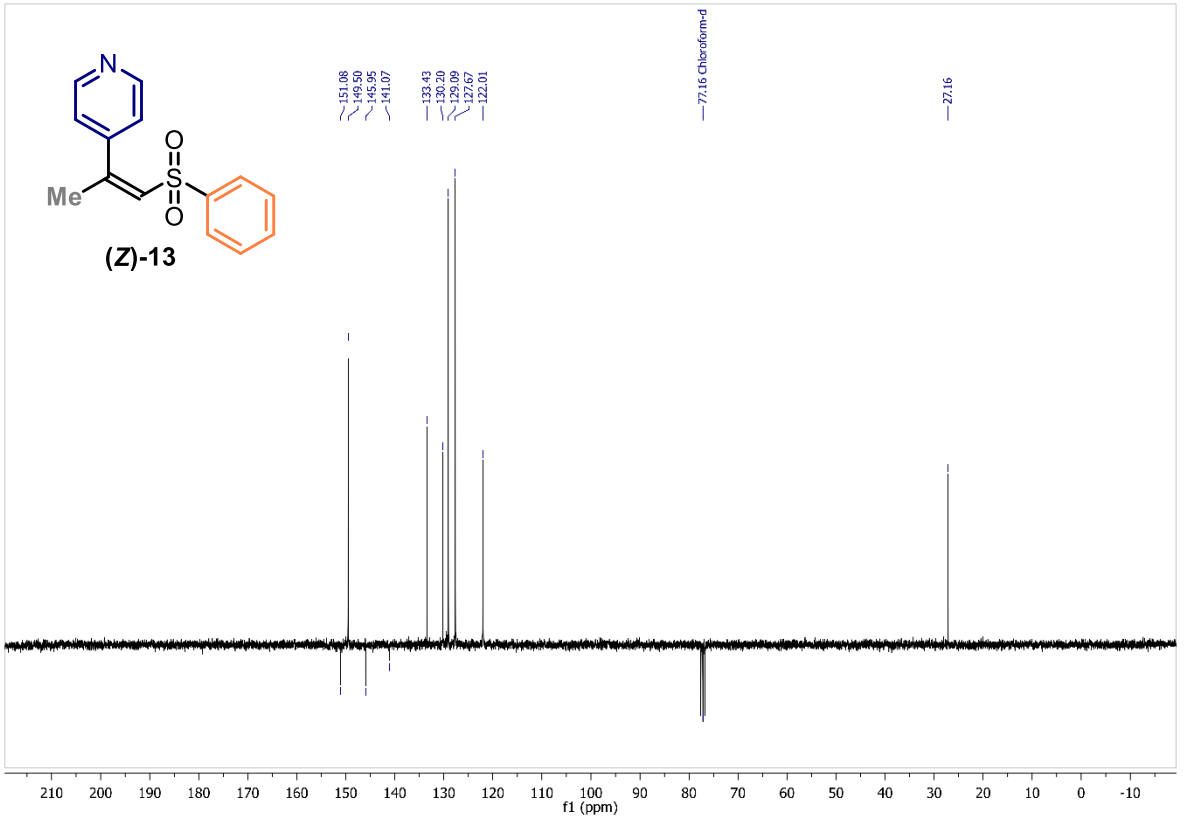


(*Z*)-13: (*Z*)-4-(1-(phenylsulfonyl)prop-1-en-2-yl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

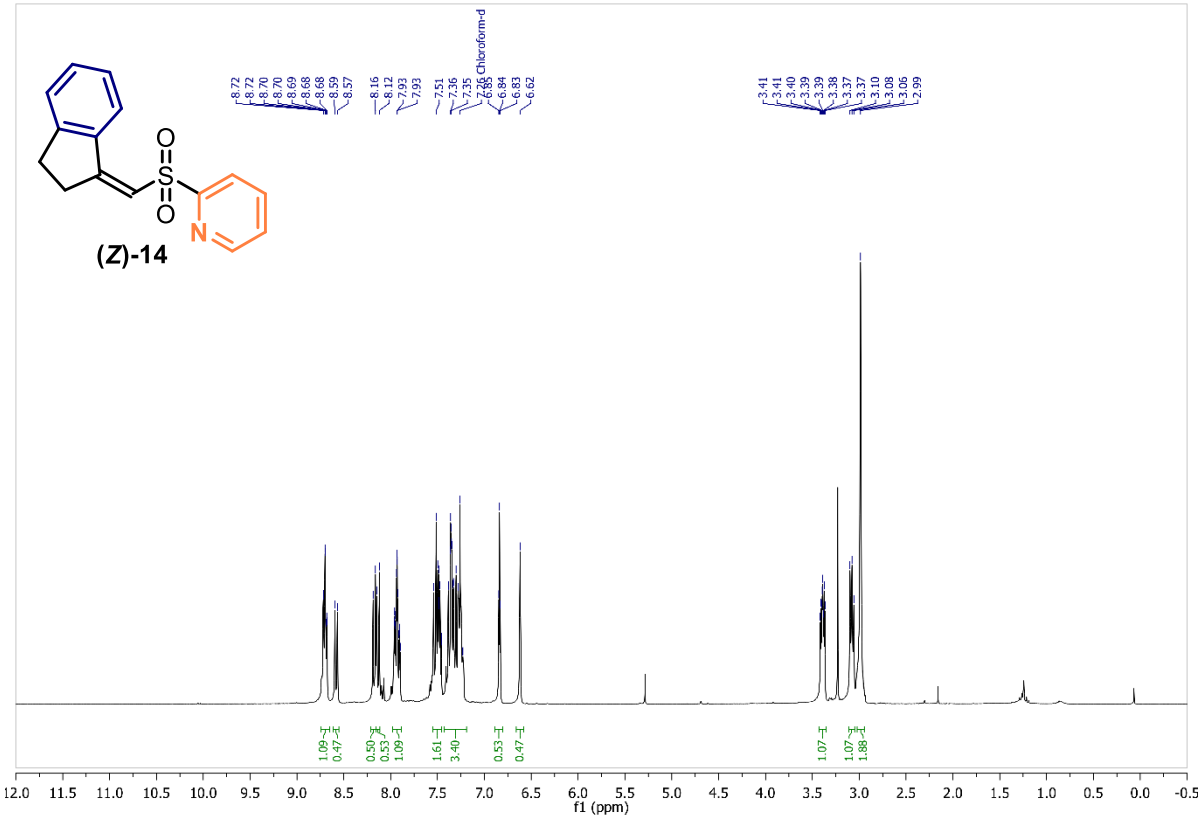


^{13}C NMR (75 MHz, $CDCl_3$)

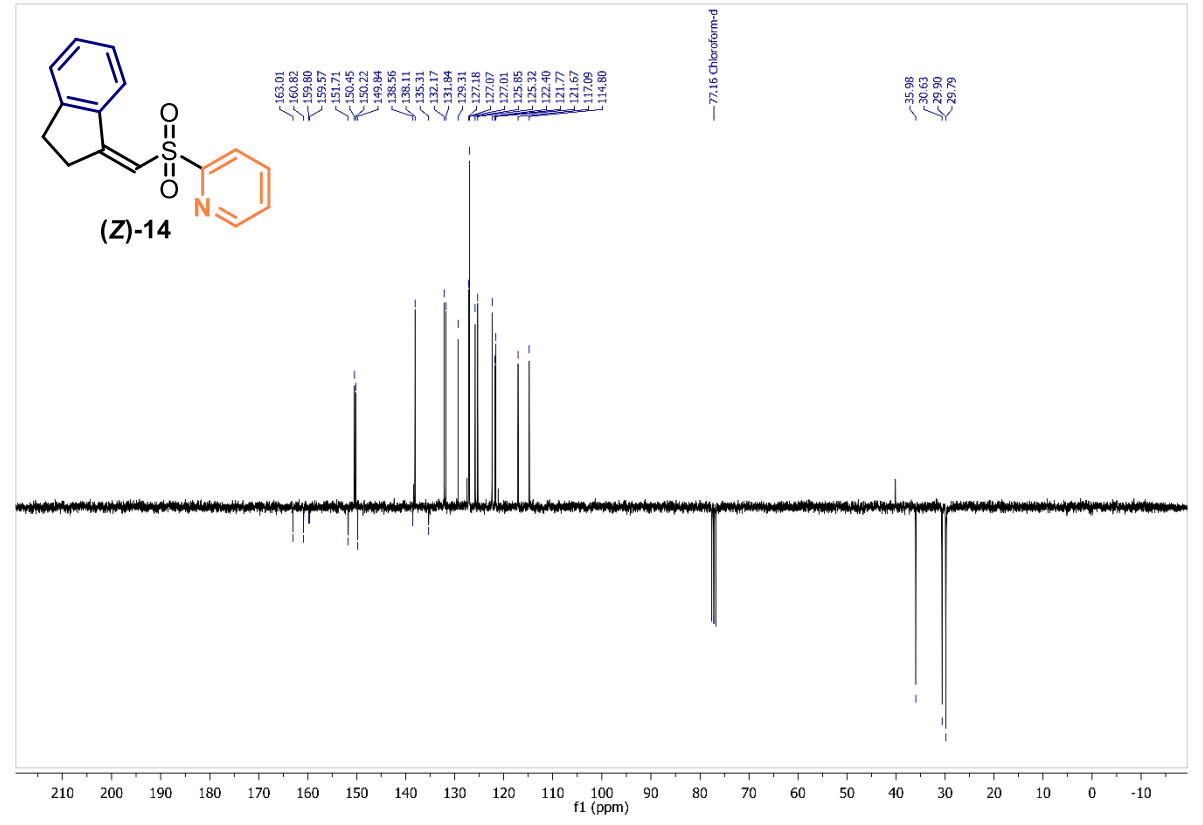


(*Z*)-14: (*Z*)-2-(((2,3-dihydro-1*H*-inden-1-ylidene)methyl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

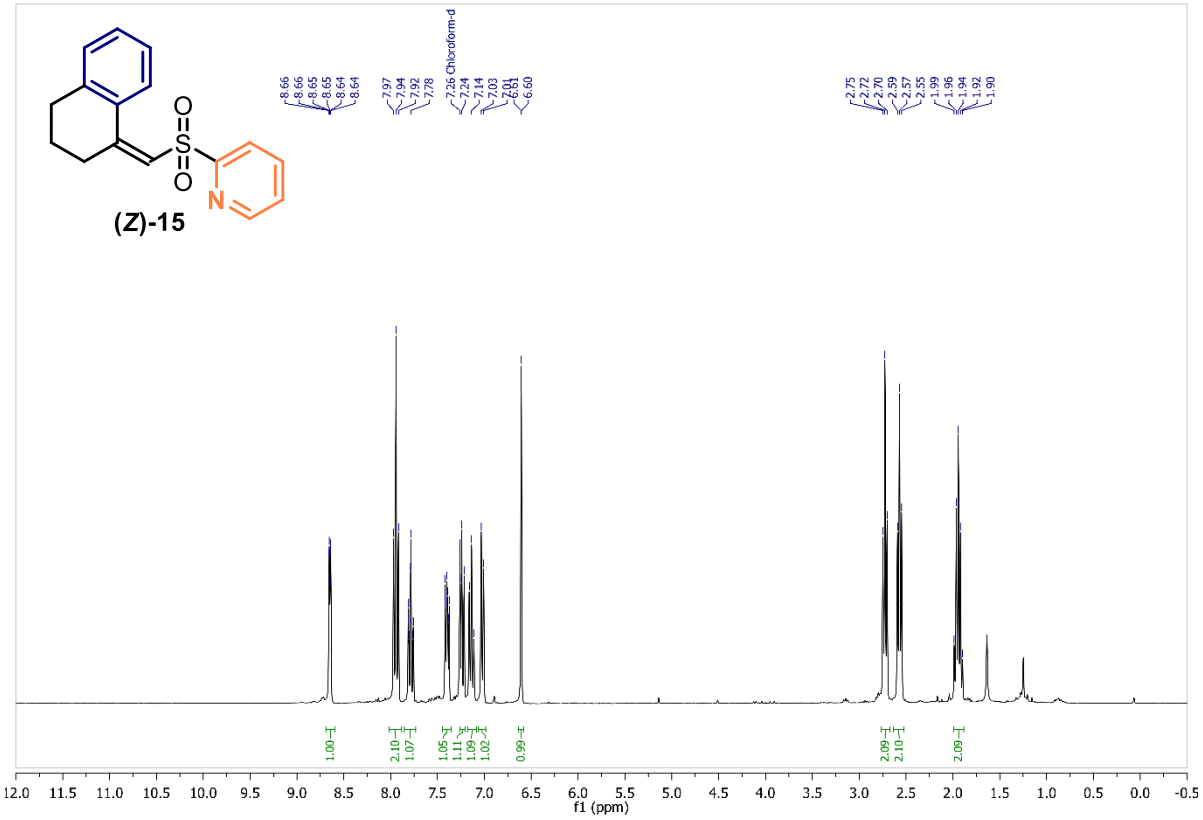


^{13}C NMR (75 MHz, $CDCl_3$)

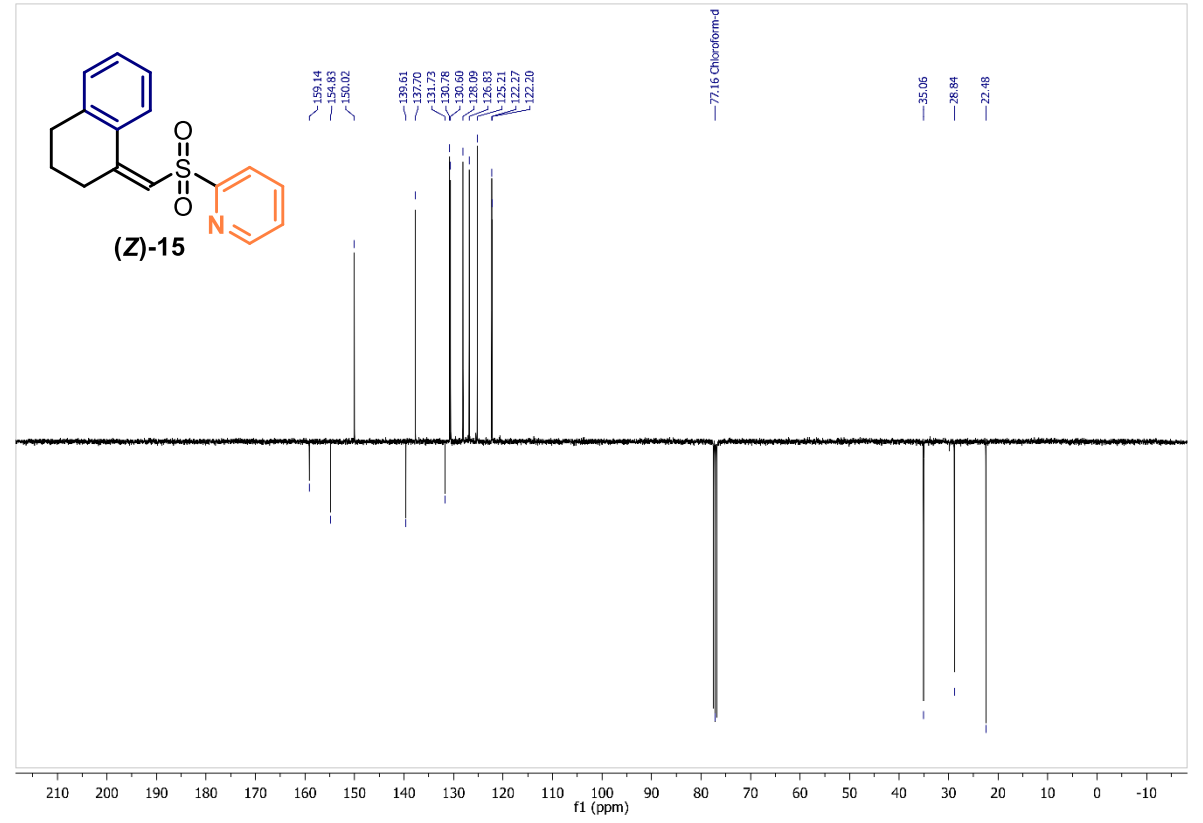


(*Z*)-15: (*Z*)-2-(((3,4-dihydronaphthalen-1(2*H*)-ylidene)methyl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

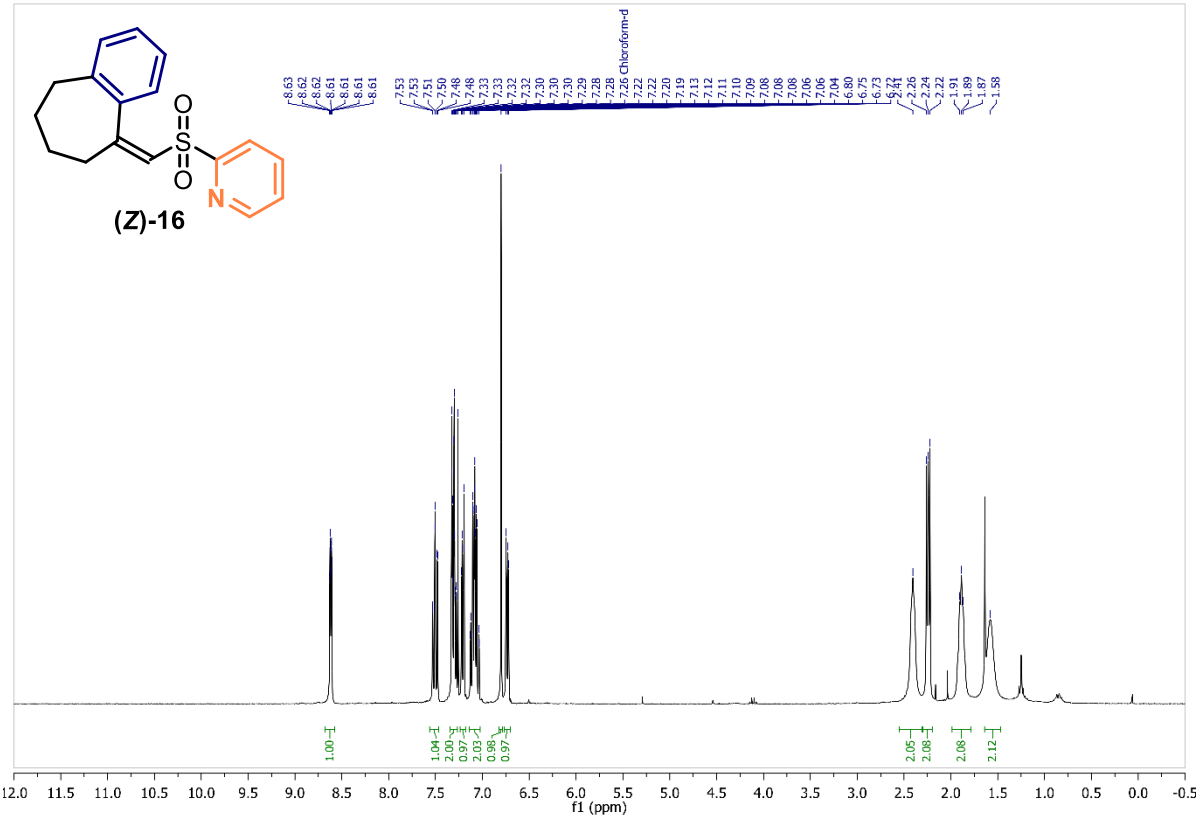


^{13}C NMR (101 MHz, $CDCl_3$)

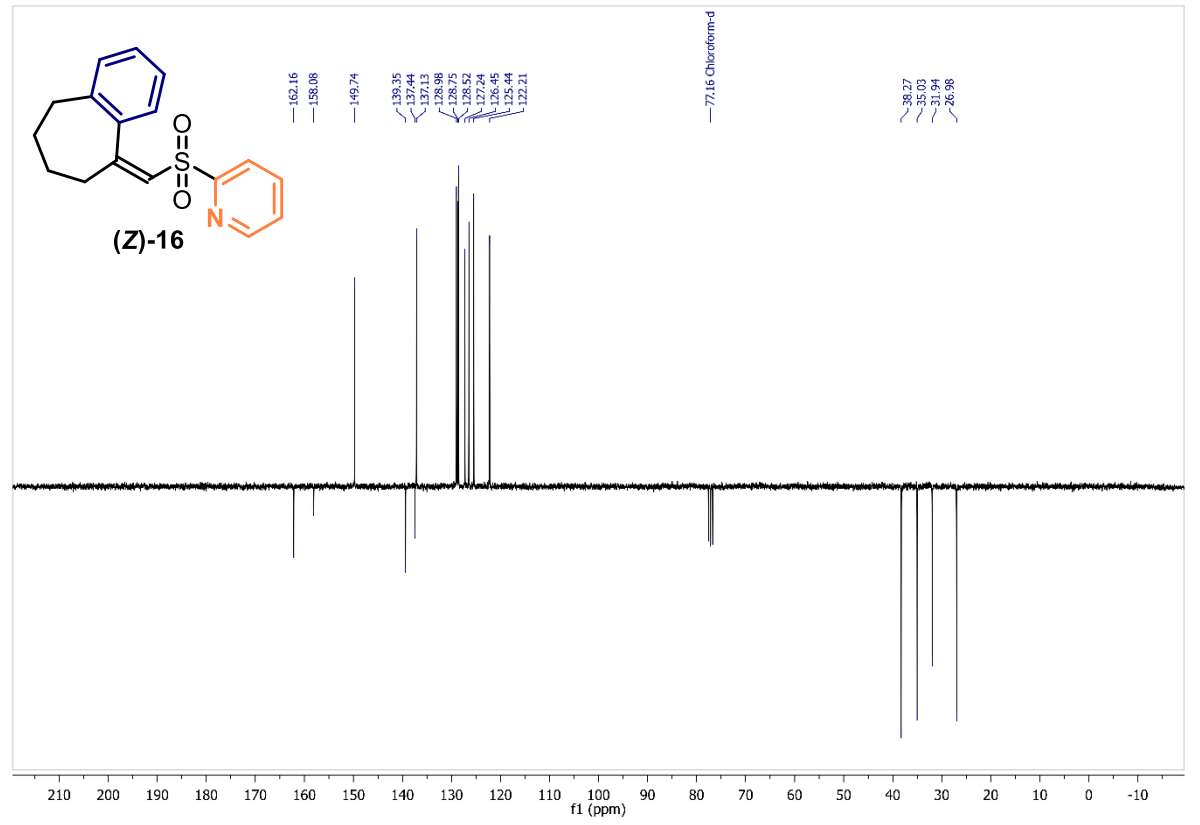


(*Z*)-16: (*Z*)-2-(((6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ylidene)methyl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

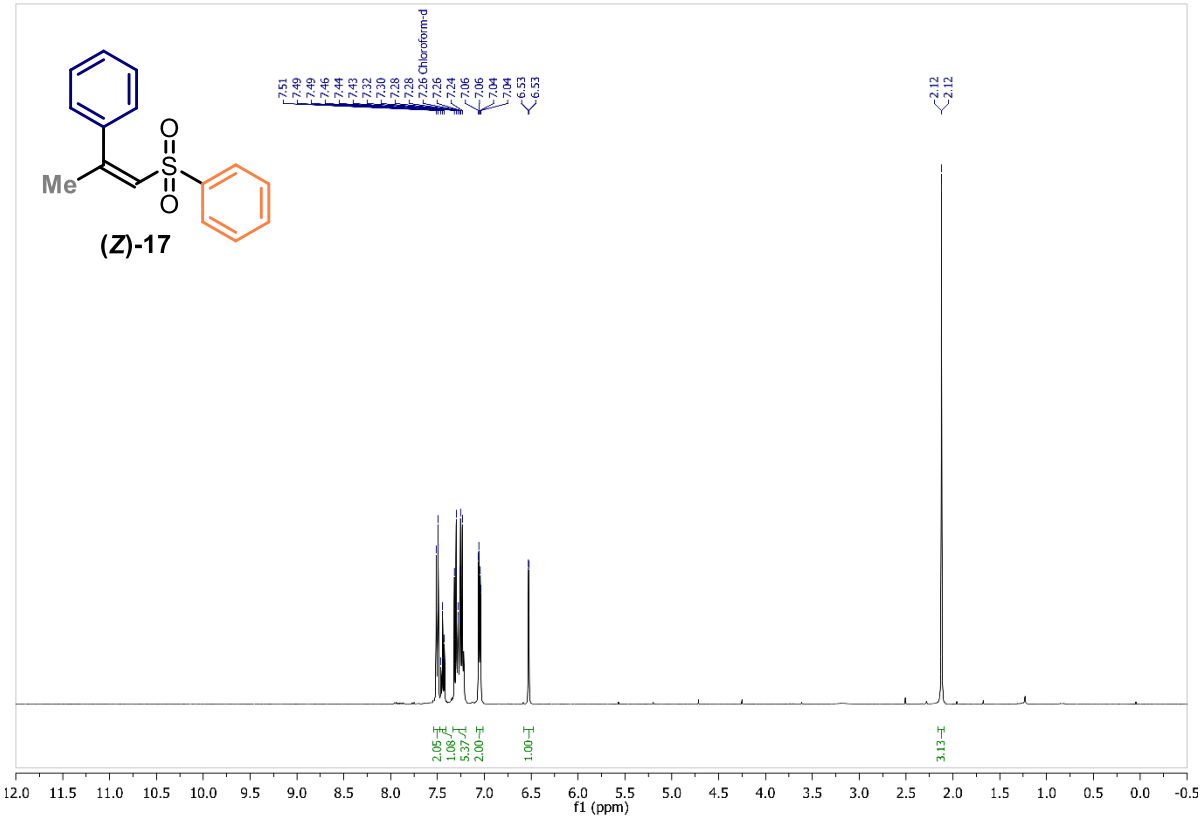


^{13}C NMR (75 MHz, $CDCl_3$)

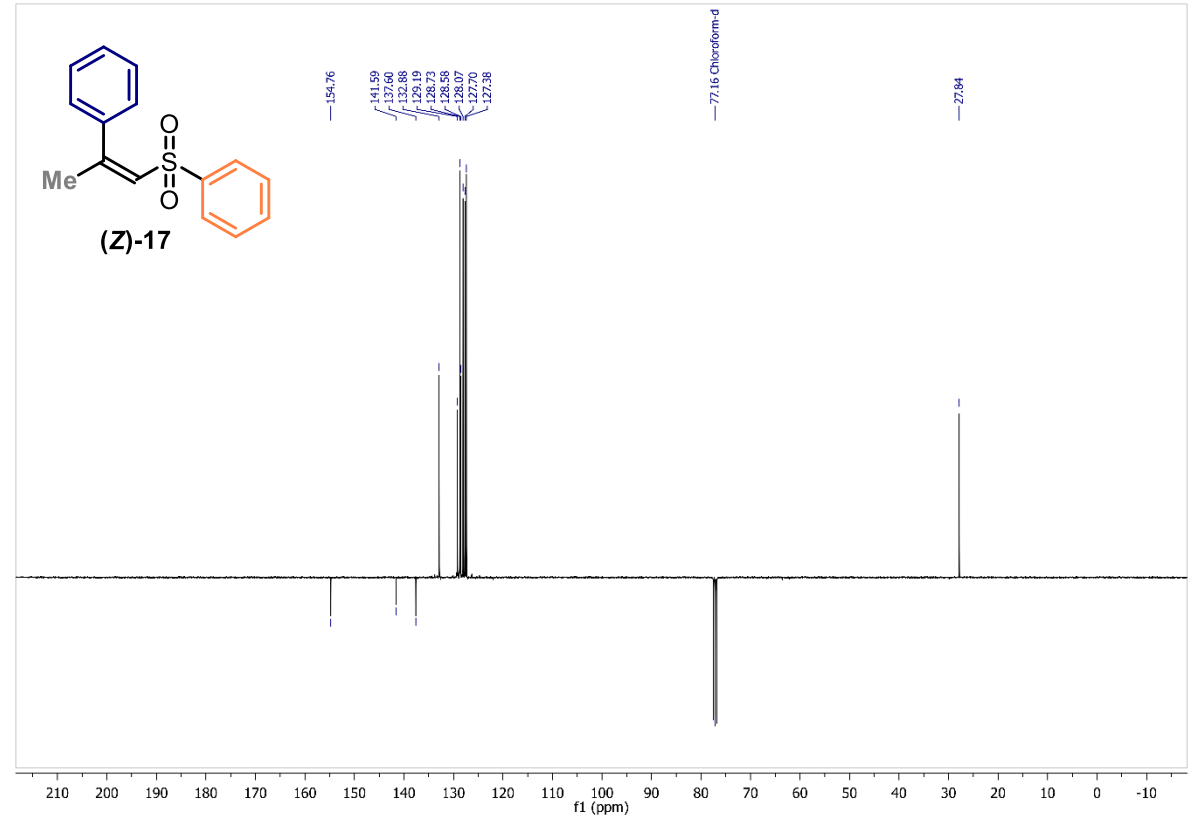


(*Z*)-17: (*Z*)-((2-phenylprop-1-en-1-yl)sulfonyl)benzene

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

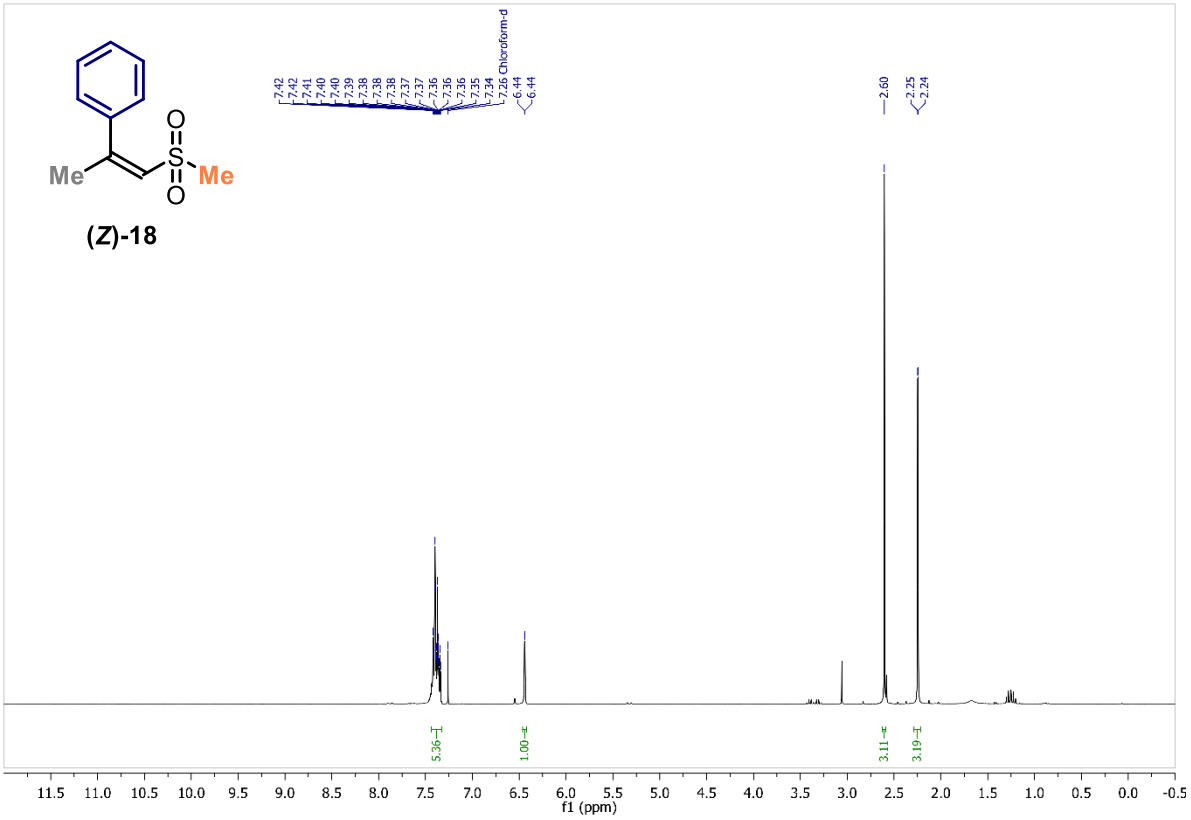


^{13}C NMR (101 MHz, $CDCl_3$)

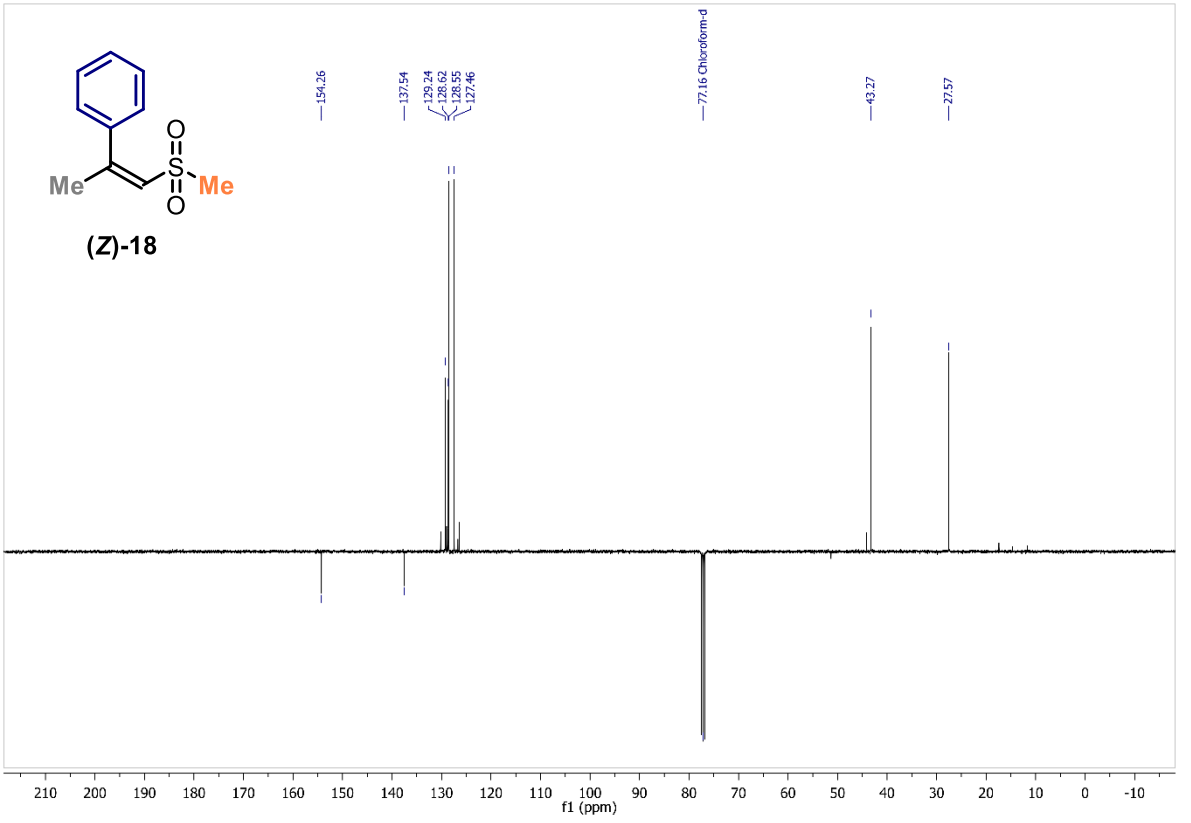


(*Z*)-18: (*Z*)-(1-(methylsulfonyl)prop-1-en-2-yl)benzene

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

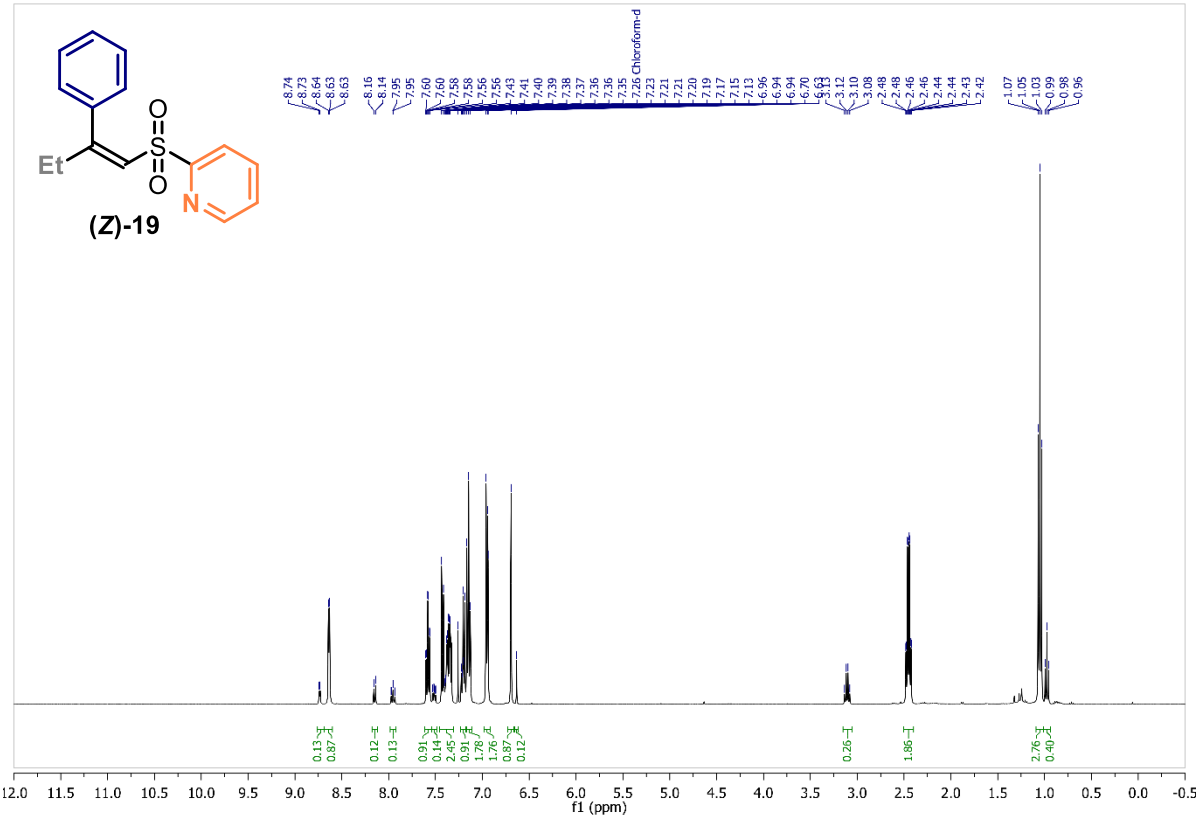


^{13}C NMR (101 MHz, $CDCl_3$)

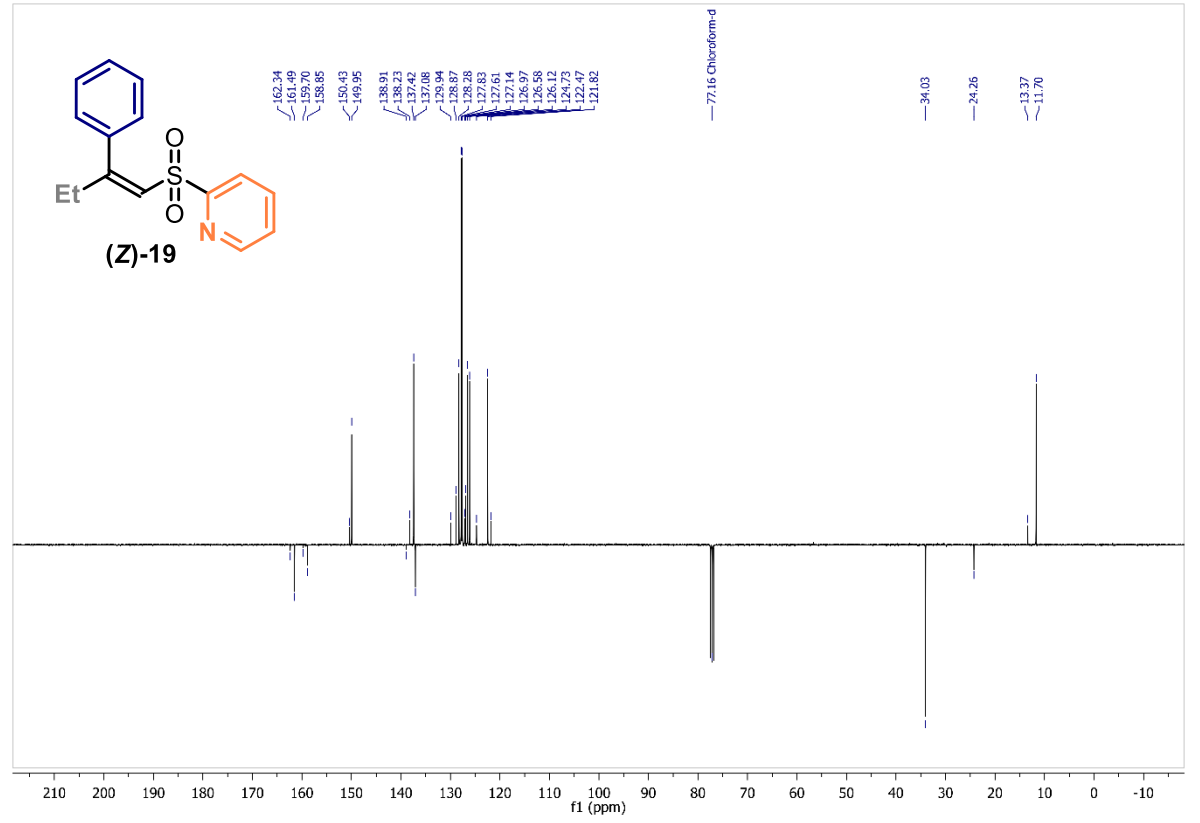


(*Z*)-19: (*Z*)-2-((2-phenylbut-1-en-1-yl)sulfonyl)pyridine

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

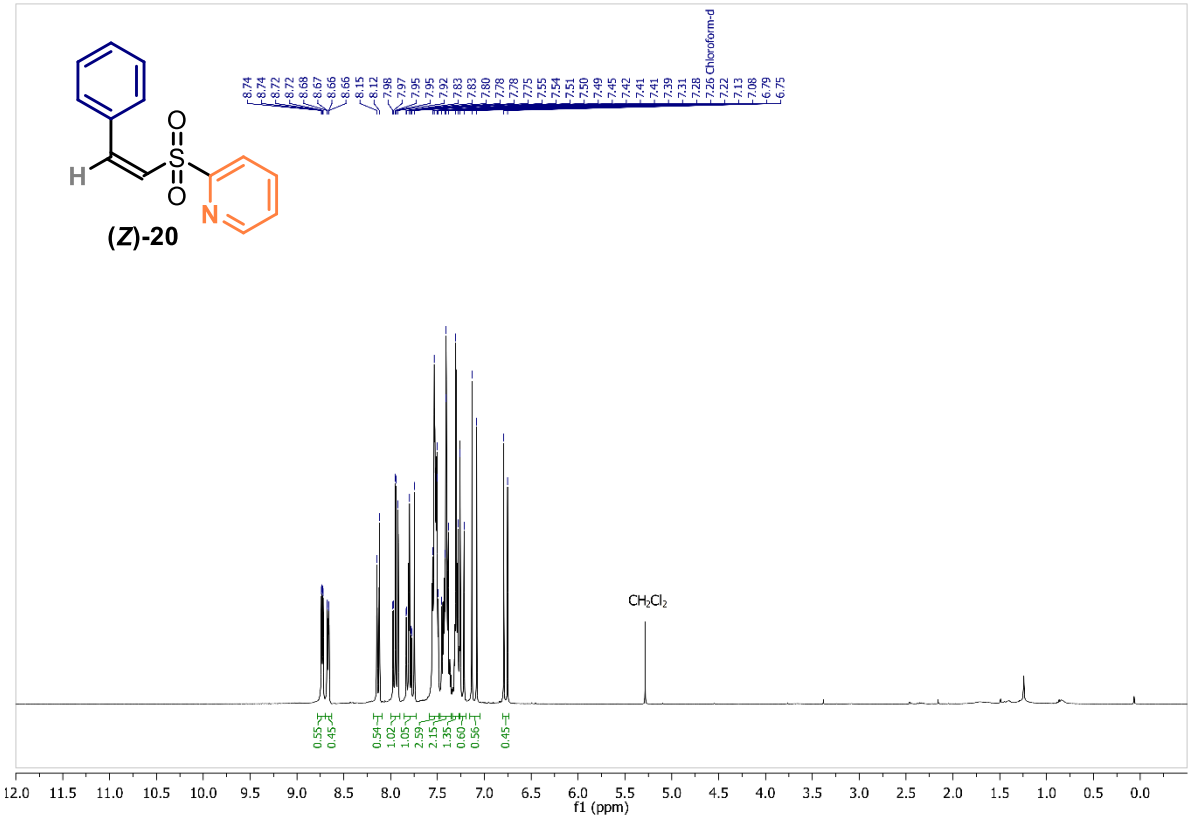


^{13}C NMR (101 MHz, $CDCl_3$)

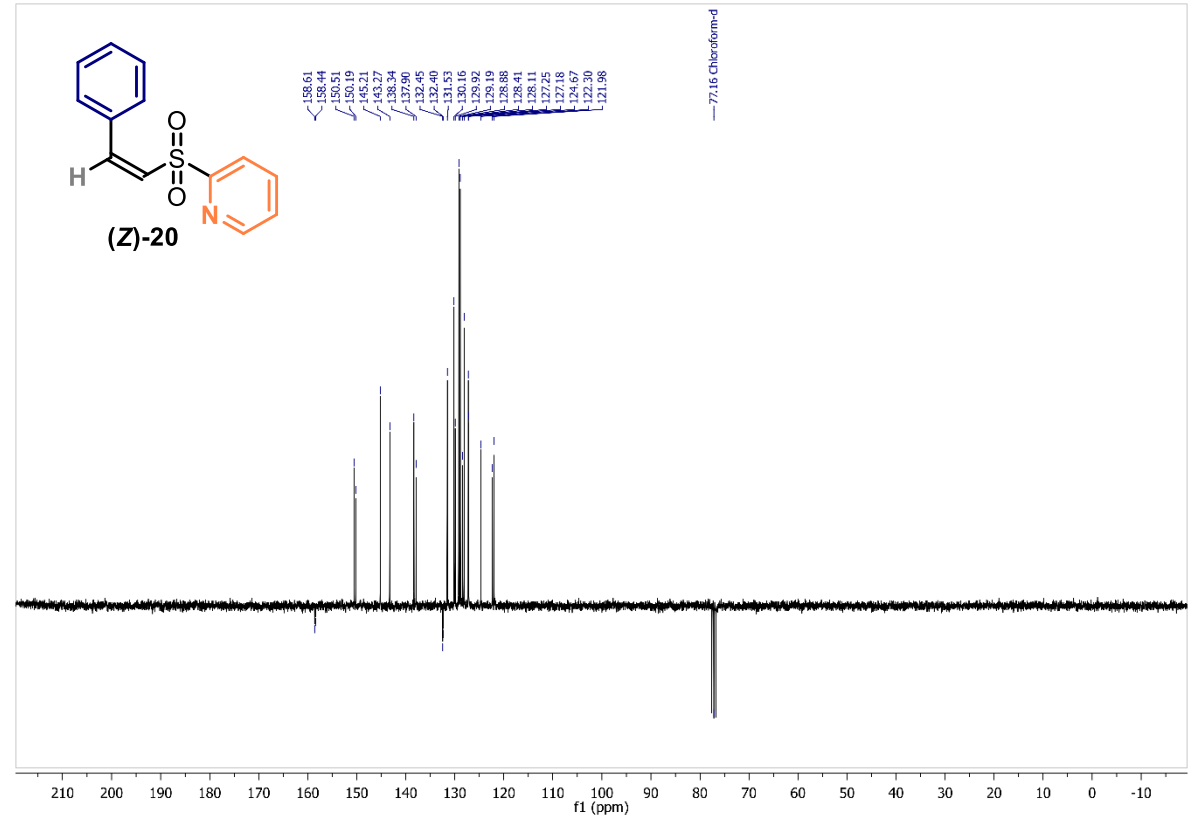


(*Z*)-20: (*Z*)-2-(styrylsulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

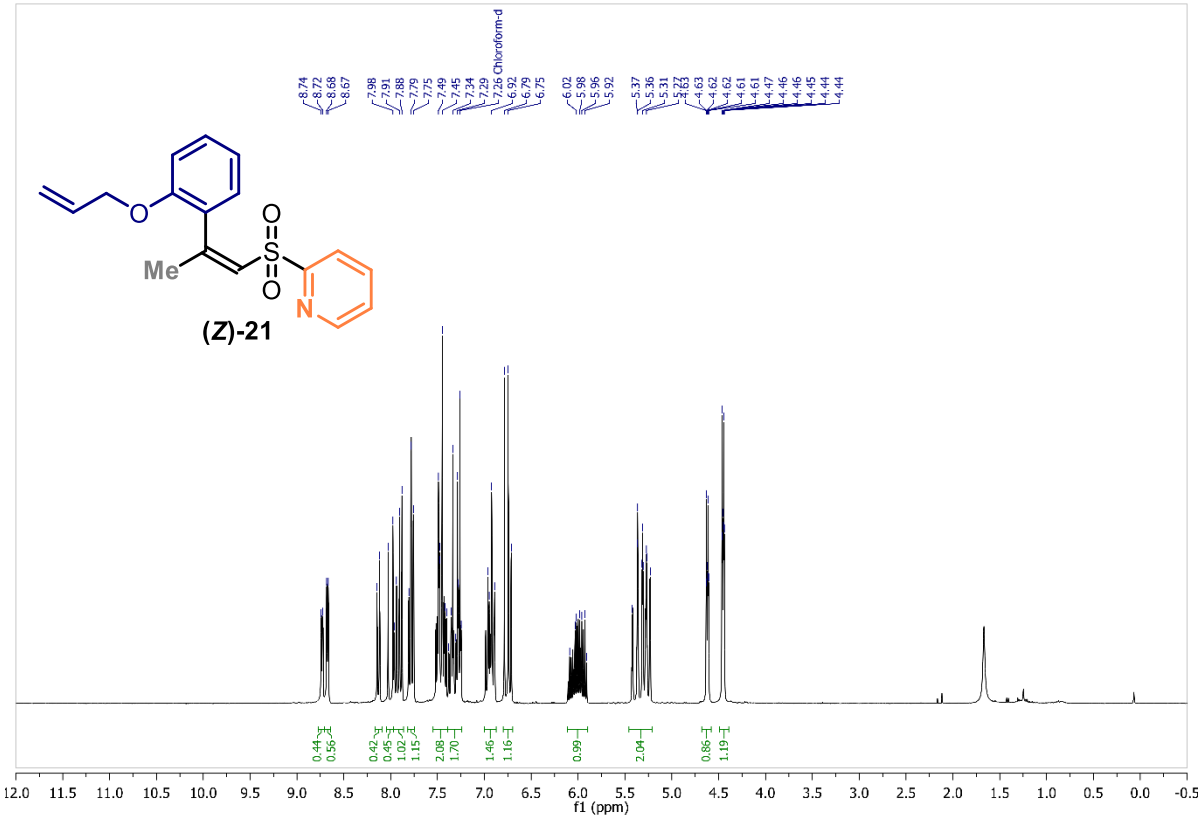


^{13}C NMR (75 MHz, $CDCl_3$)

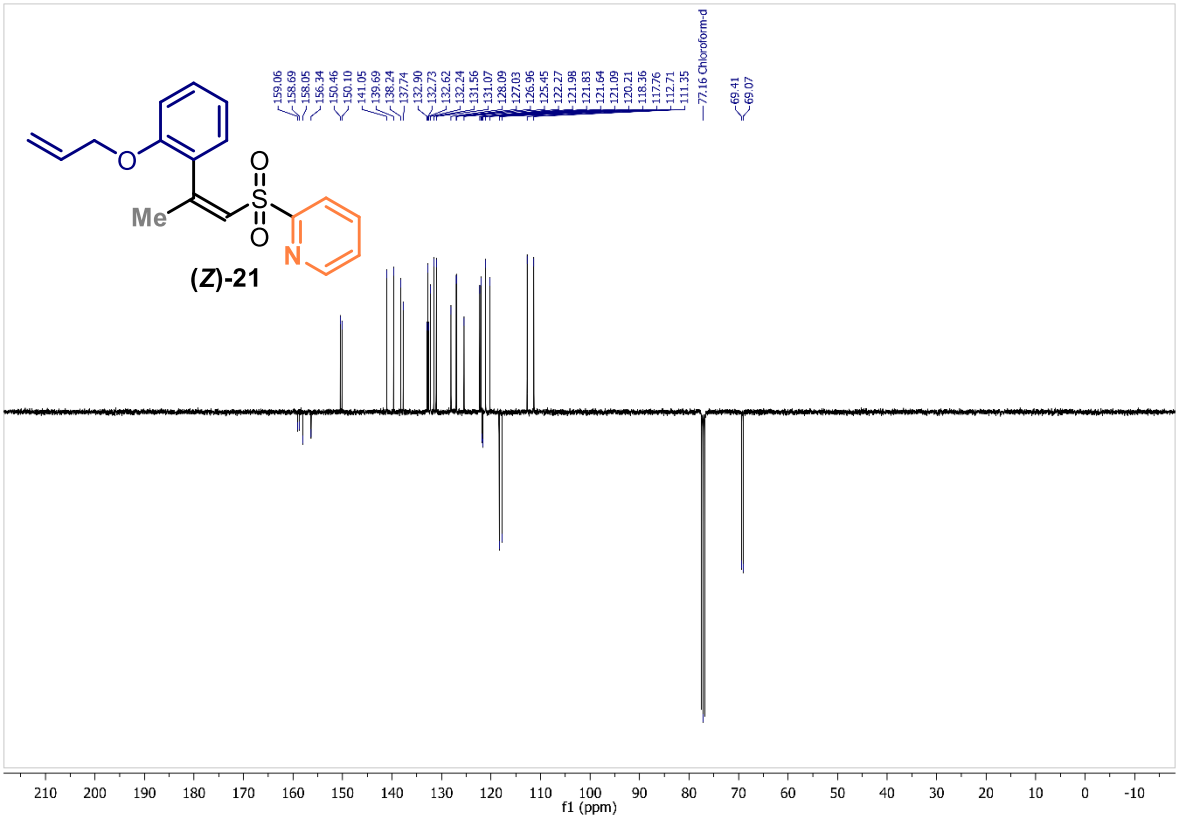


(*Z*)-21: (*Z*)-2-((2-(allyloxy)styryl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

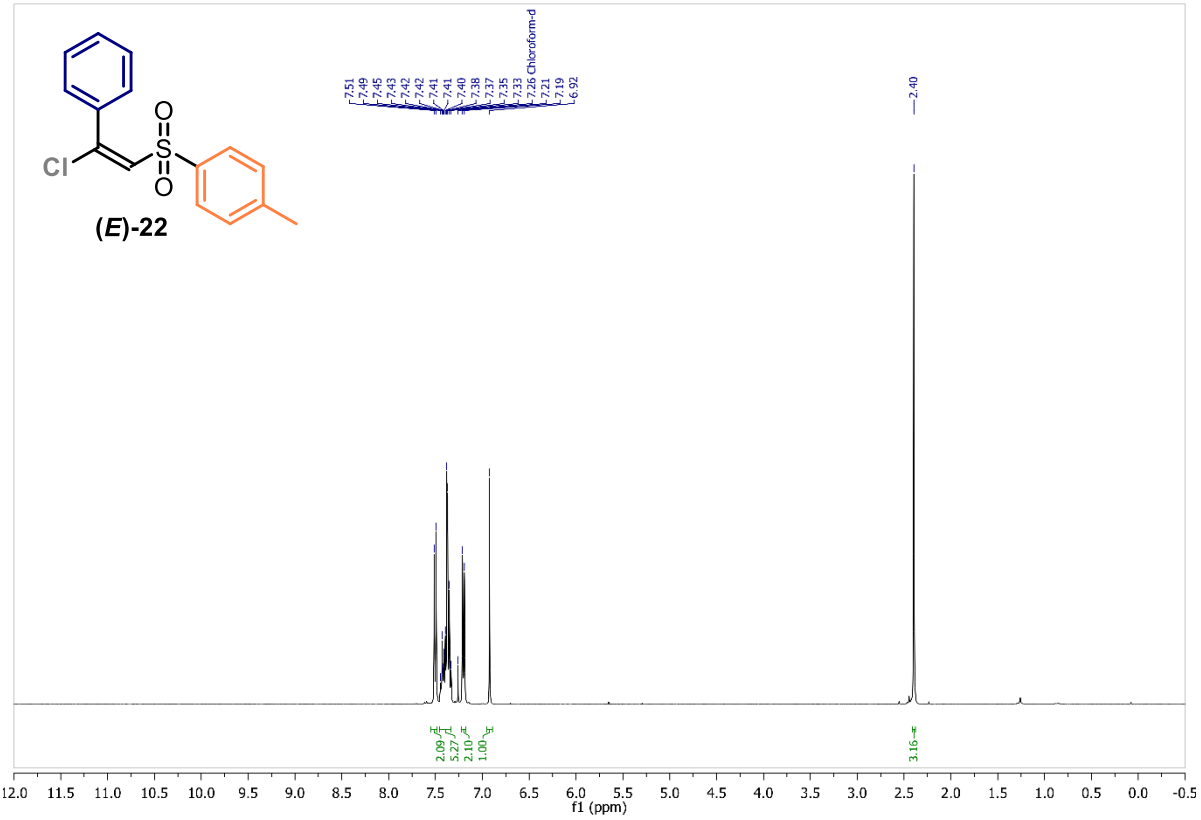


^{13}C NMR (101 MHz, $CDCl_3$)

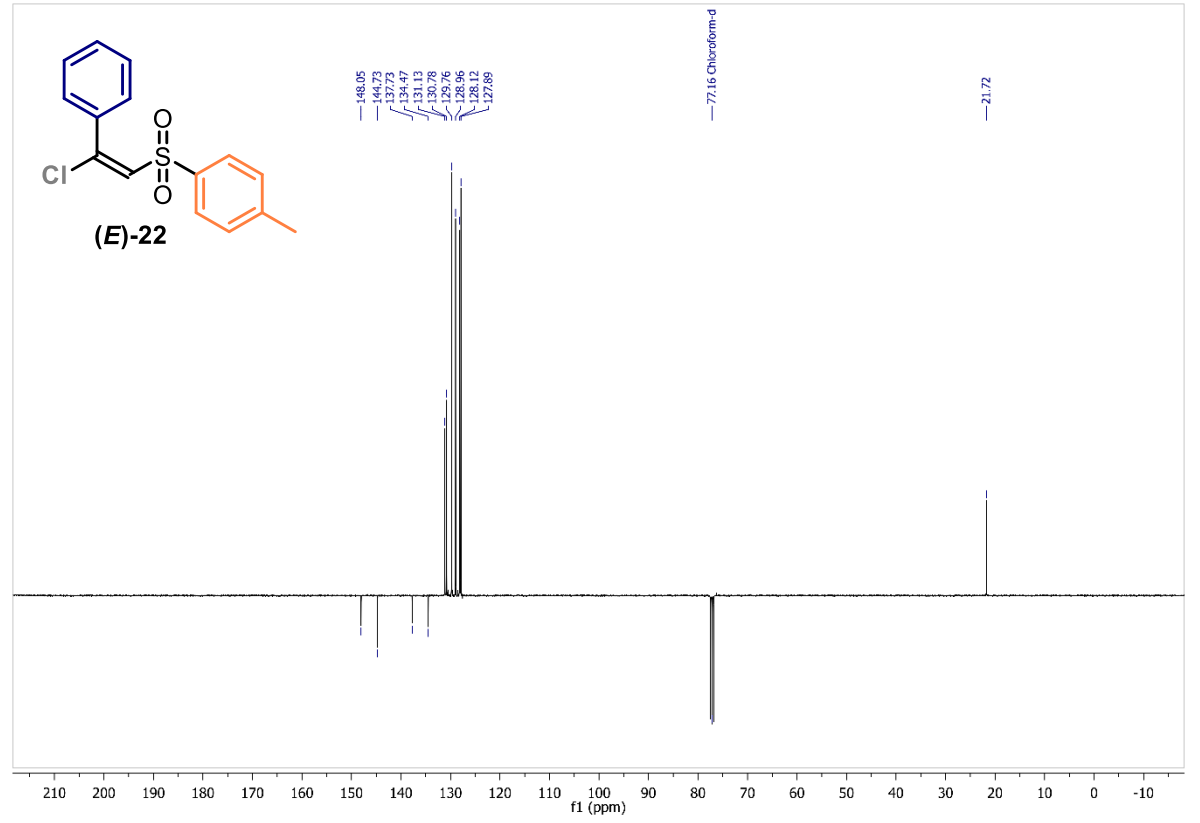


(*E*)-22: (*E*)-1-((2-chloro-2-phenylvinyl)sulfonyl)-4-methylbenzene

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

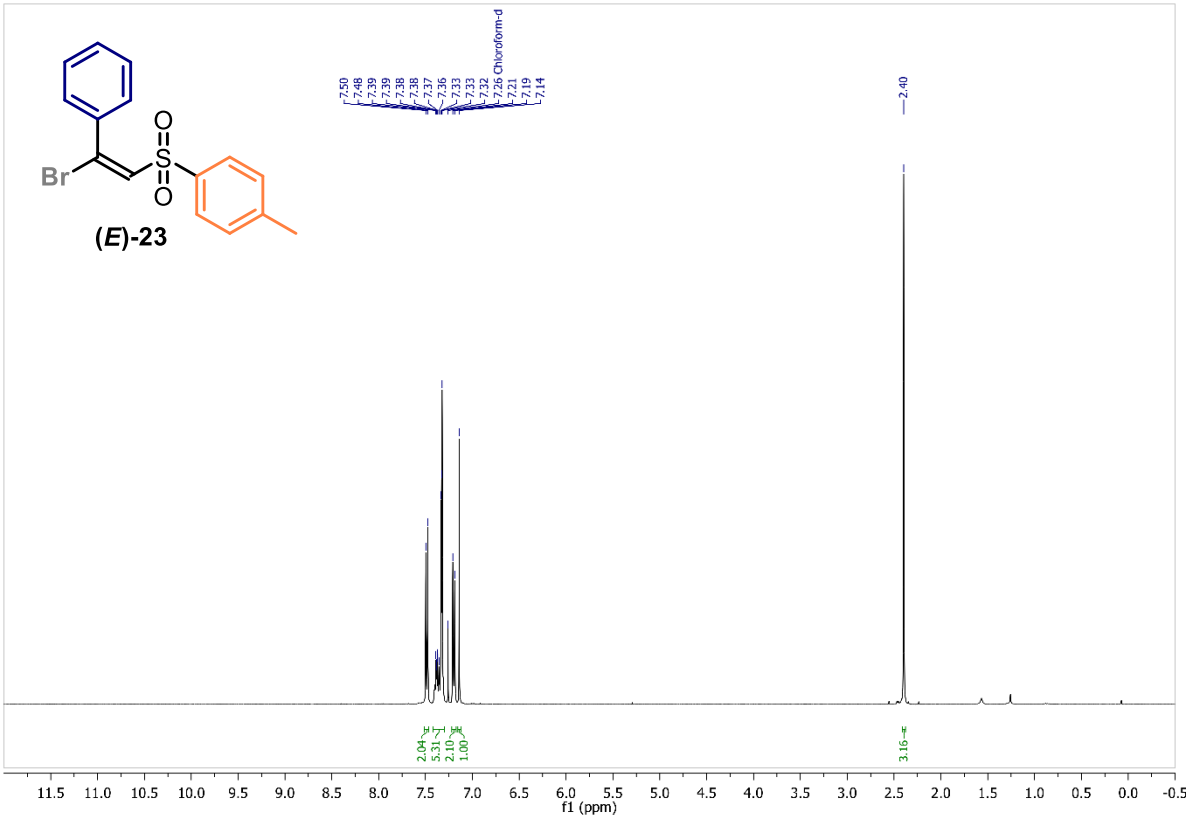


^{13}C NMR (101 MHz, $CDCl_3$)

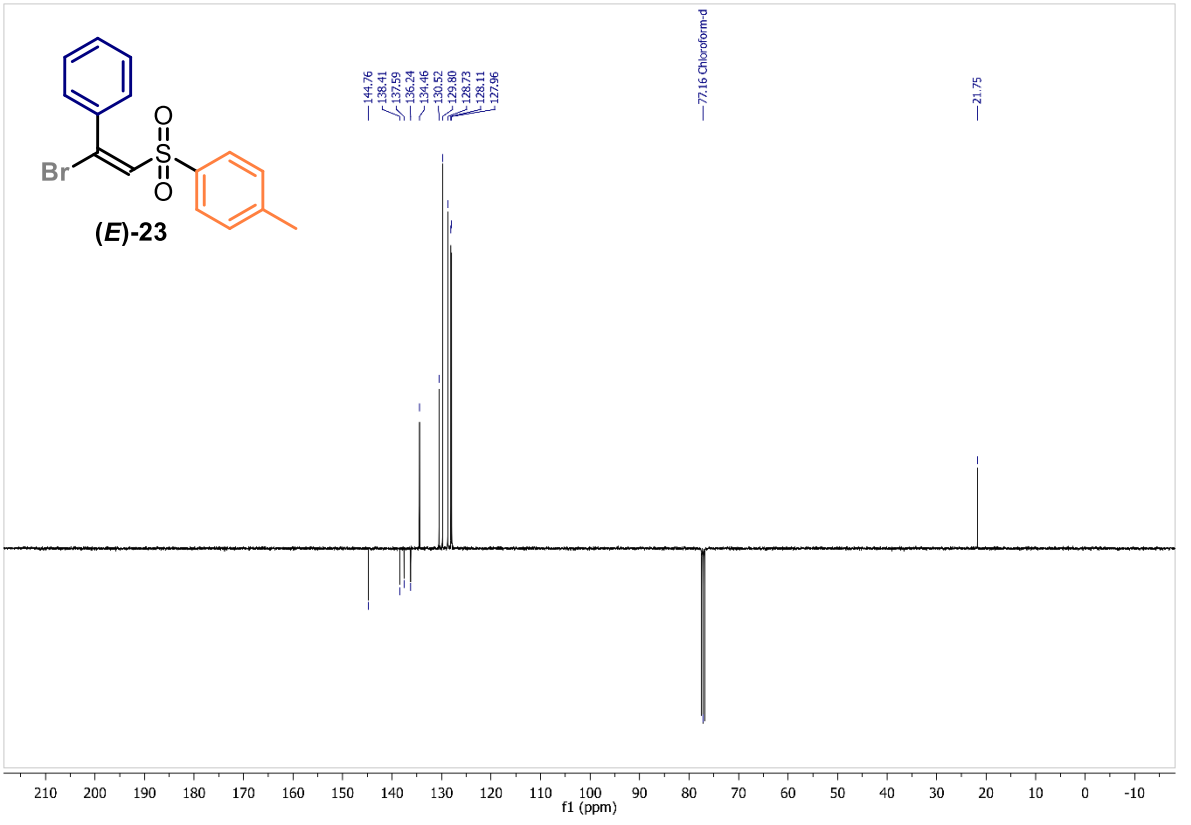


(*E*)-23: (*E*)-1-((2-bromo-2-phenylvinyl)sulfonyl)-4-methylbenzene

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

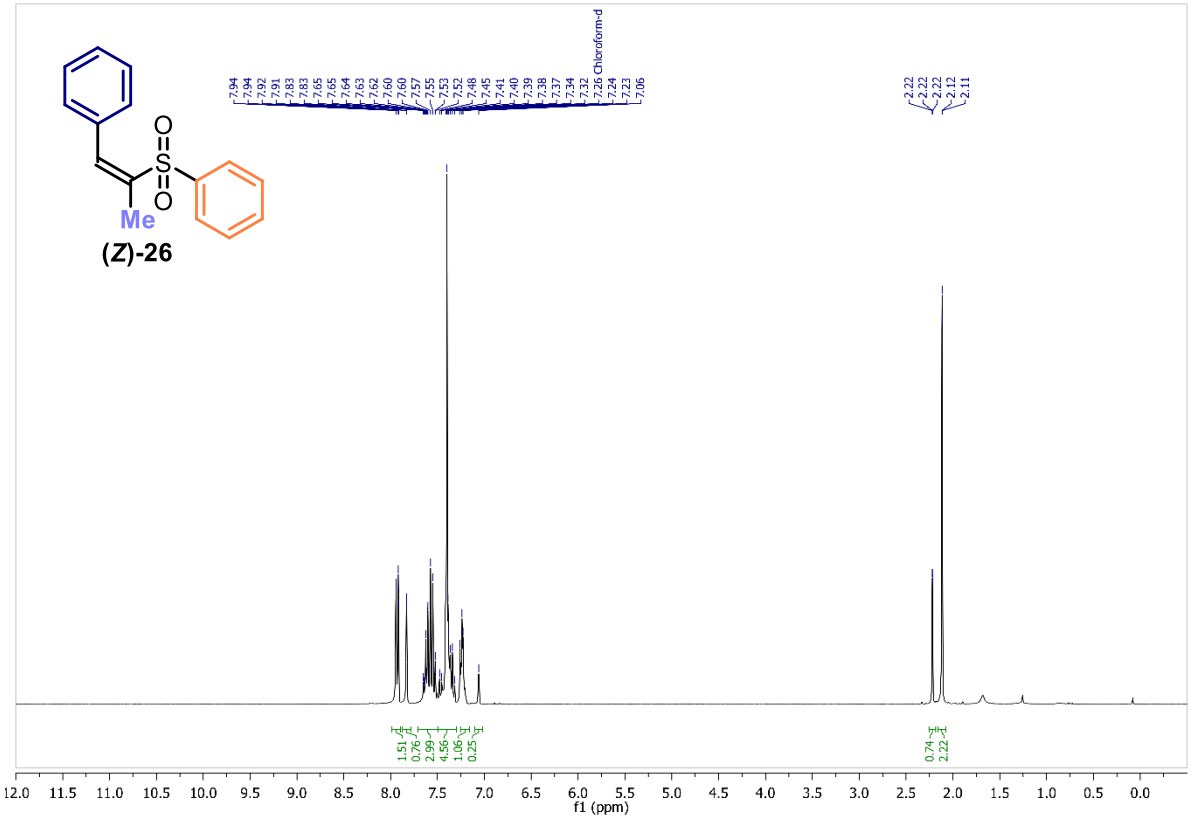


^{13}C NMR (101 MHz, $CDCl_3$)

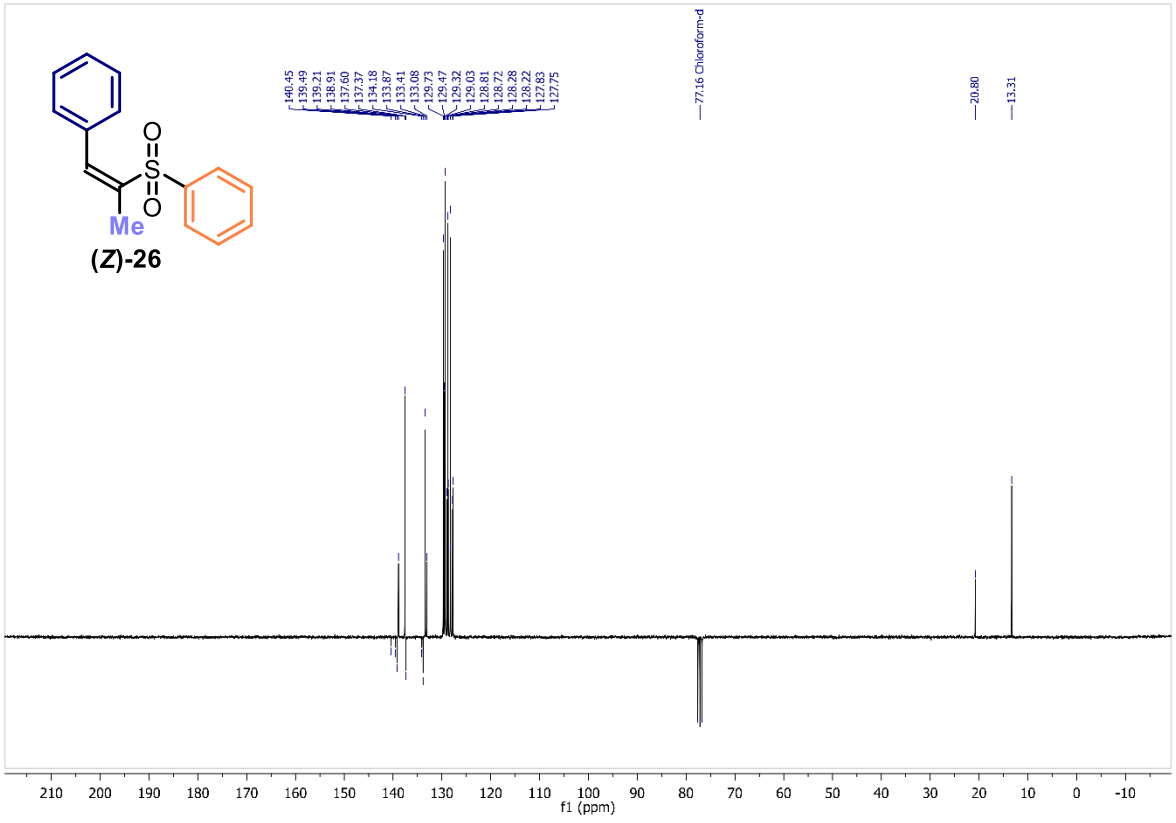


(*Z*)-26: (*Z*)-((1-phenylprop-1-en-2-yl)sulfonyl)benzene

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

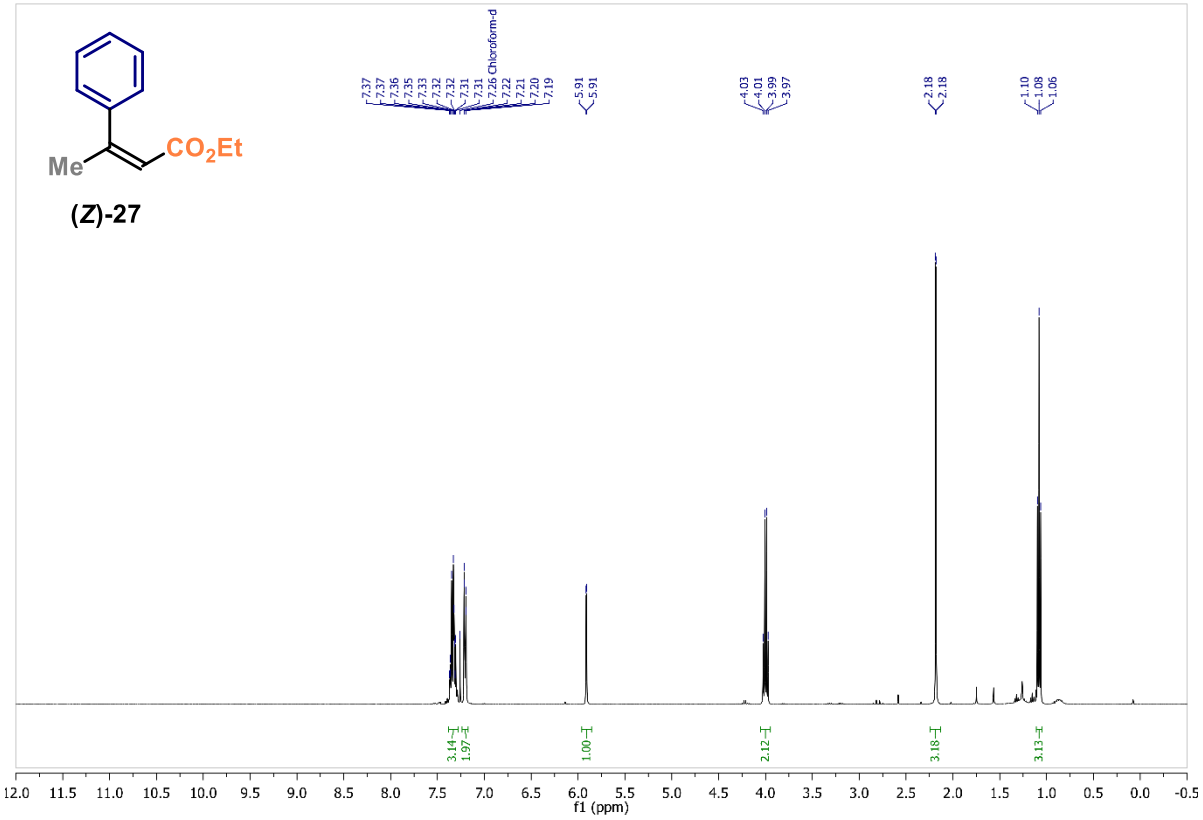


^{13}C NMR (75 MHz, $CDCl_3$)

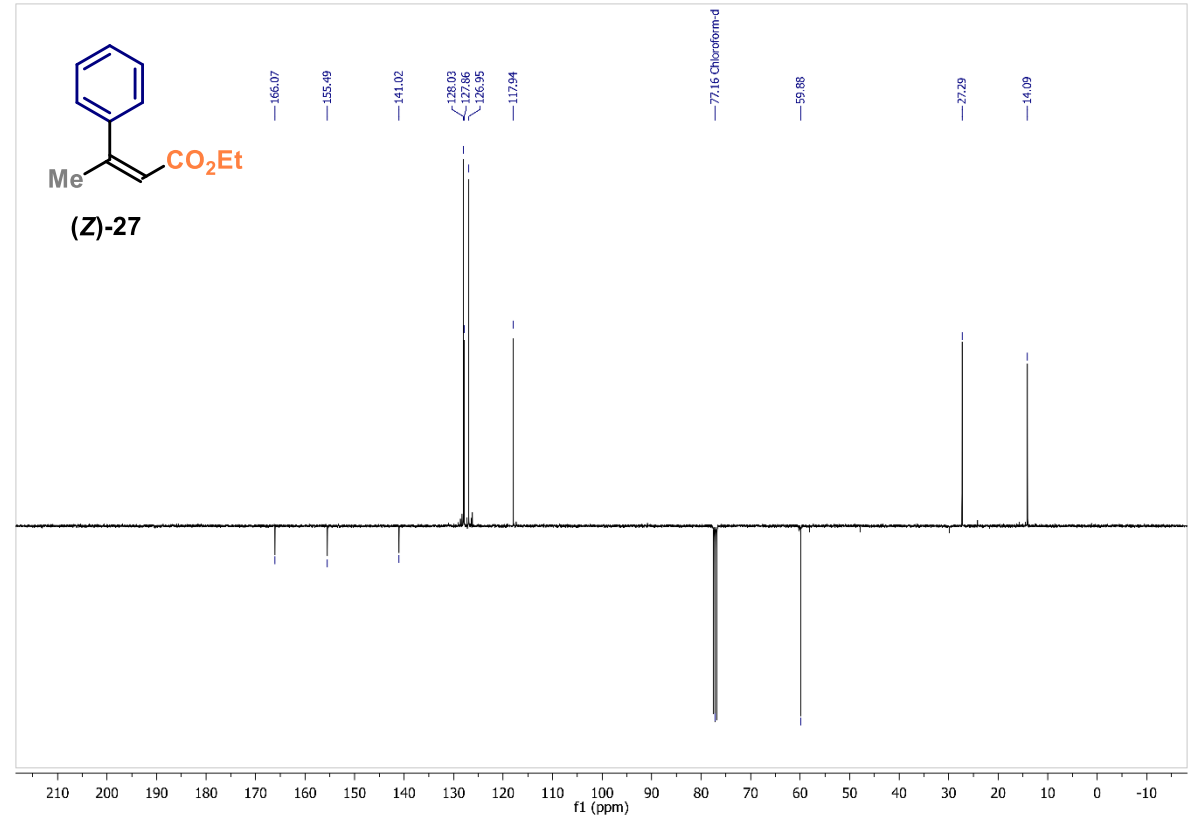


(*Z*)-27: ethyl (*Z*)-3-phenylbut-2-enoate

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

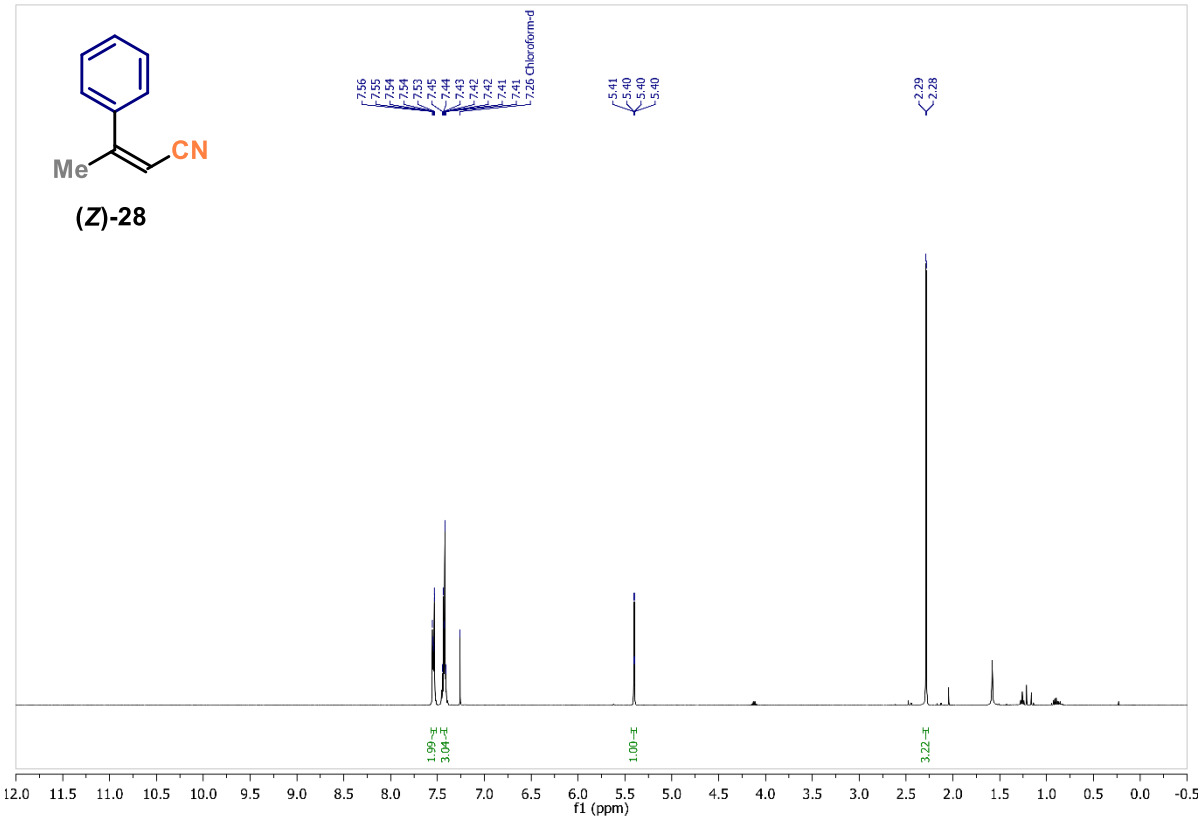


^{13}C NMR (101 MHz, $CDCl_3$)

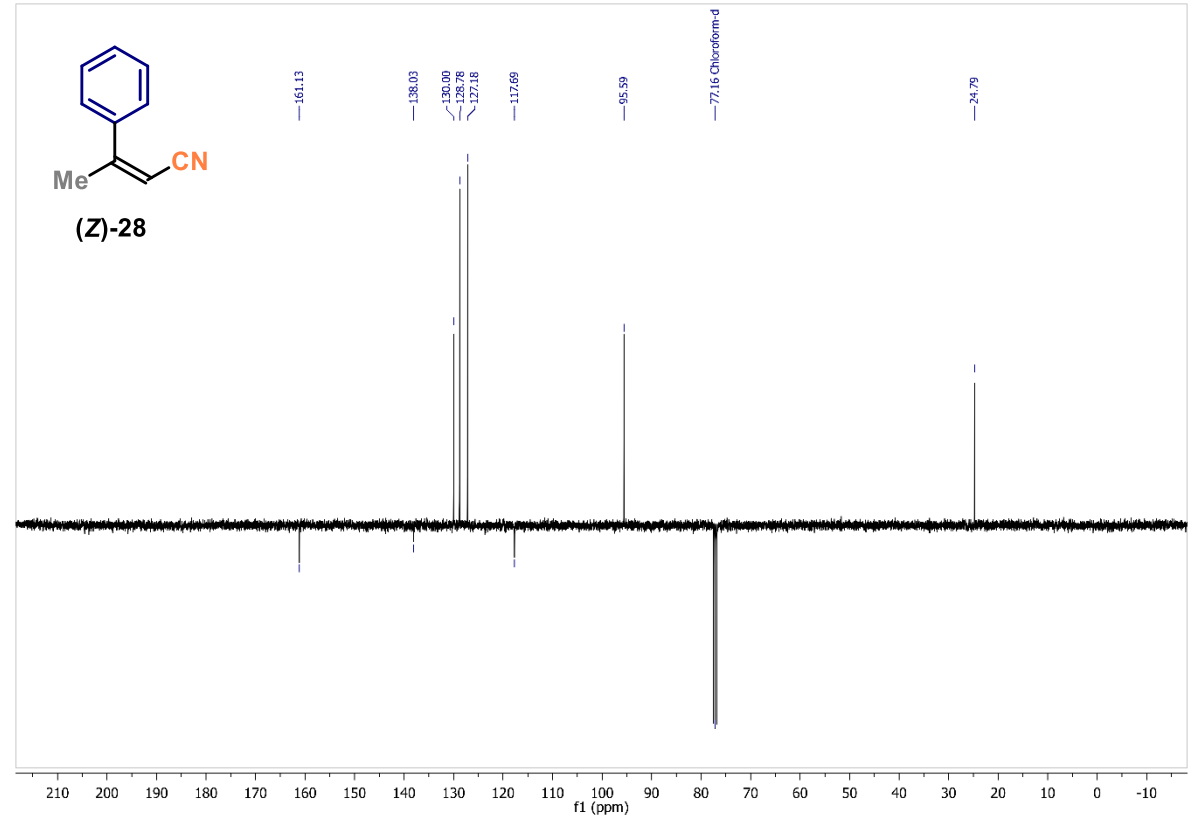


(*Z*)-28: (*Z*)-3-phenylbut-2-enenitrile

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

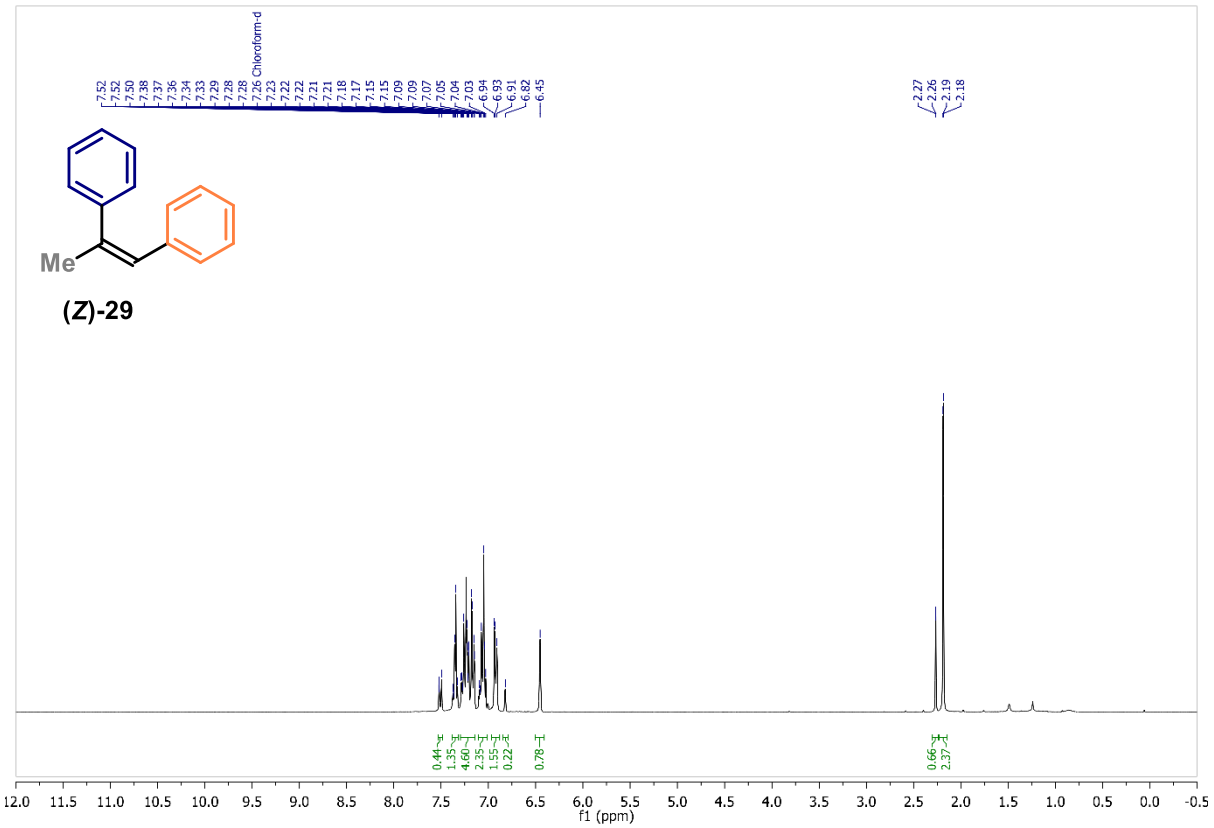


^{13}C NMR (101 MHz, $CDCl_3$)



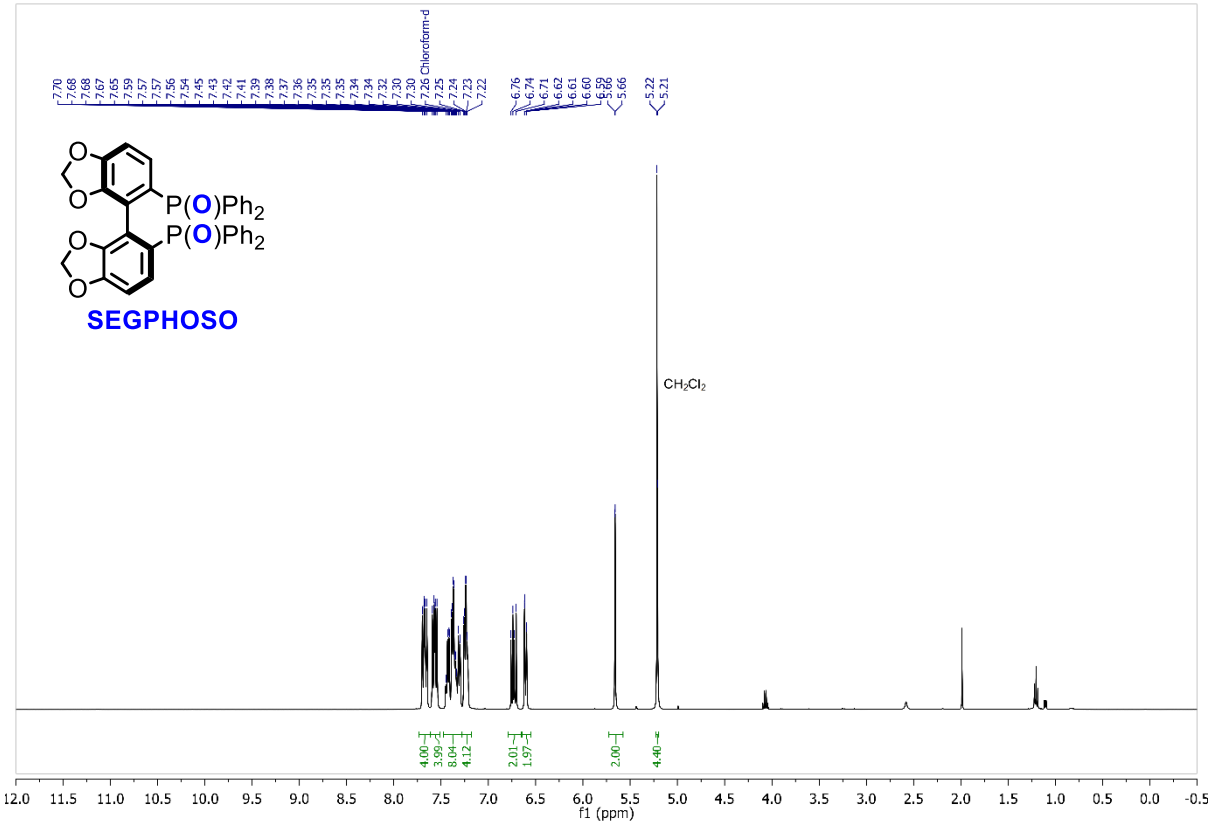
(*Z*)-29: (*Z*)-prop-1-ene-1,2-diyldibenzene

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*

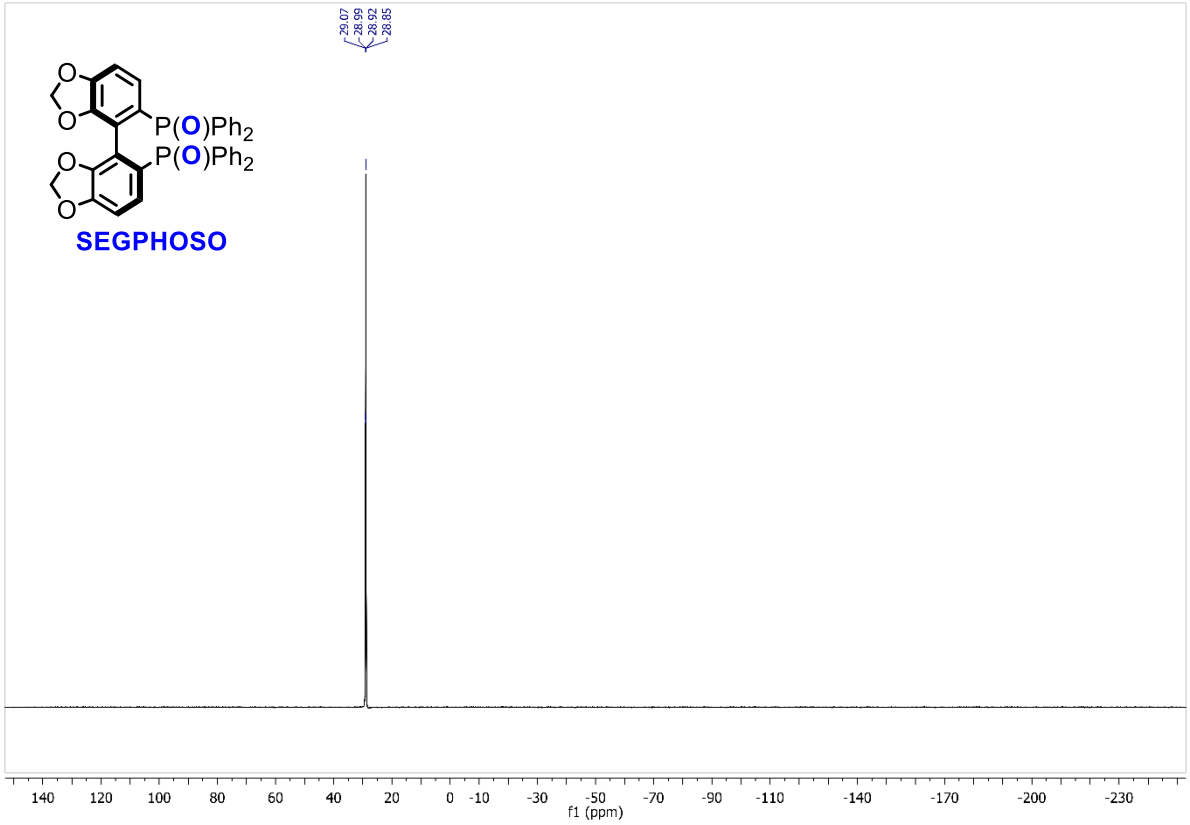


SEGPHOSO

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

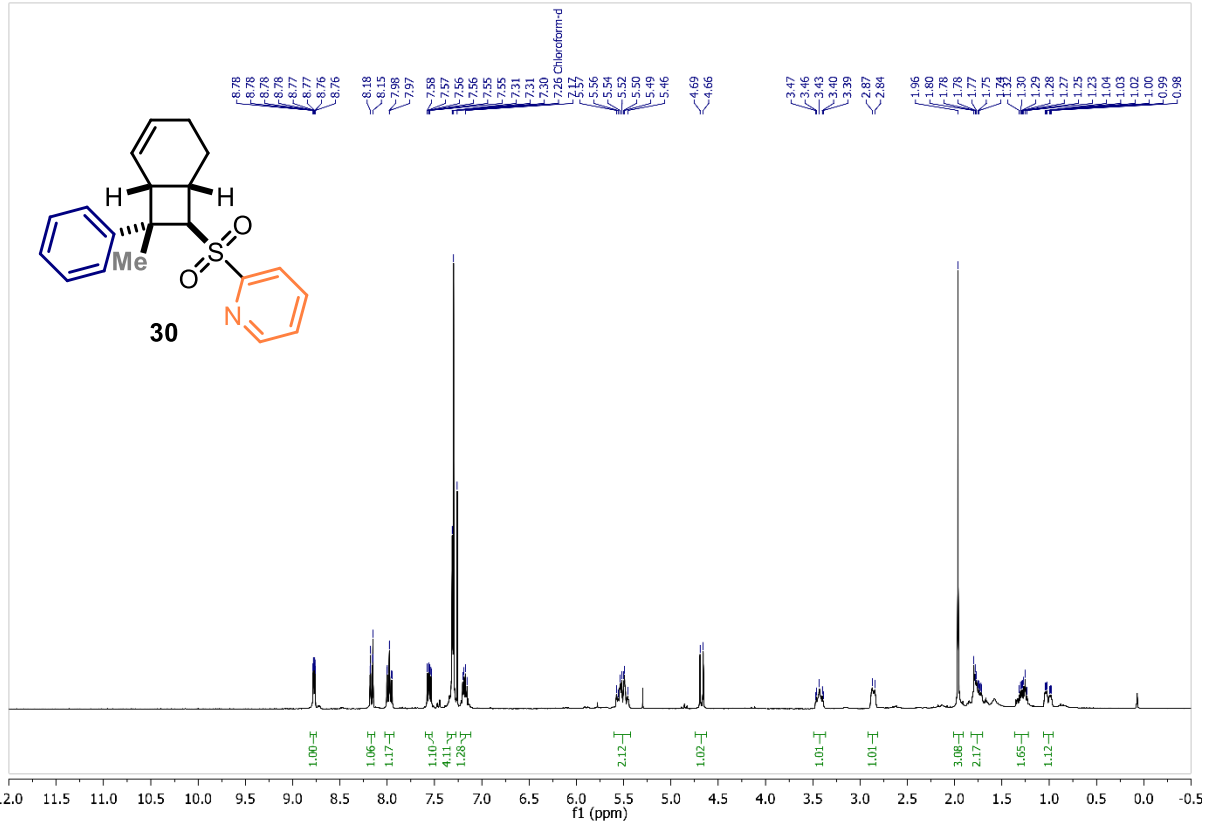


^{31}P NMR (162 MHz, $CDCl_3$)



30: (±)-2-(((1*R*,6*S*,7*R*,8S)-8-methyl-8-phenylbicyclo[4.2.0]oct-2-en-7-yl)sulfonyl)pyridine

^{1}H NMR (300 MHz, $CDCl_3$) *See procedure*



^{13}C NMR (75 MHz, $CDCl_3$)