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The Pd-catalysed asymmetric allylic alkylation reactions of sulfamidate imines

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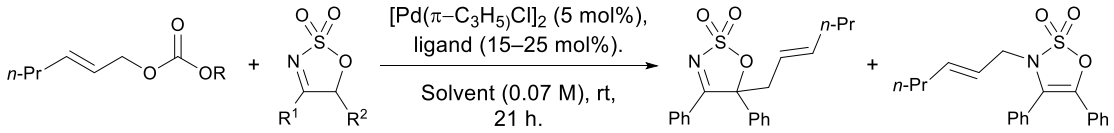
Supporting information

1. General

Reagents and solvents were acquired from commercial suppliers and were used either without further purification or purified by standard techniques. Anhydrous solvents were passed through activated alumina for dryness before being stored under N_2 over 4 Å molecular sieves. Anhydrous THF was obtained by distillation from a sodium/benzophenone ketyl still under nitrogen. Air- and moisture-sensitive reactions were performed in oven-dried glassware under an inert N_2 atmosphere. For thin-layer chromatography (TLC), silica gel plates were obtained from Merck & Co., visualised under UV light and/or by treatment with either potassium permanganate or cerium molybdate TLC stain solution, followed by heating. Purification was carried out using flash column chromatography (FCC) with silica gel 60 (0.04 – 0.06) mm obtained from Chem-Supply. Solvent used for NMR analysis was deuterated chloroform ($CDCl_3$) with 0.1% w/v tetramethylsilane (TMS), obtained from Sigma–Aldrich. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded with either a Bruker Avance III 400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) or a Bruker Avance Neo 500 spectrometer equipped with a BBO Prodigy N_2 cryoprobe (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR, and 470 MHz for ^{19}F NMR). Trifluorotoluene was used as an external reference for ^{19}F NMR analysis and was referenced to 0.00 ppm. Abbreviations used in the descriptions of NMR resonances include: singlet (s), doublet (d), triplet (t), quartet (q), heptet (h), multiplet (m), broad singlet (br s), doublet of doublet (dd), doublet of doublet of doublet (ddd). High-performance liquid chromatography (HPLC) was performed using a Shimadzu Nexera X2 UHPLC equipped with a PDA detector. Optical rotation values were measured using a Jasco P-2000 polarimeter with a 10 cm, 2 mL cell. Melting point analysis was carried out using a Buchi Melting Point M-560 instrument.

2. Table of reaction optimisation results[a]

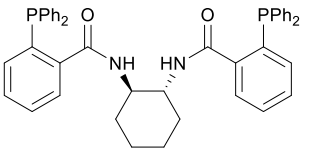


1a: R = *t*-Bu
***i*-1a:** R = *i*-Bu

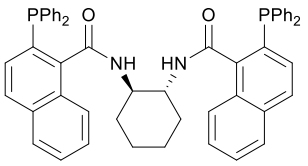
2a

3aa

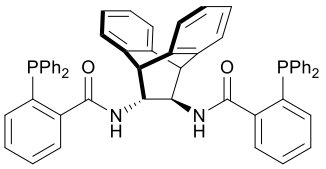
4aa



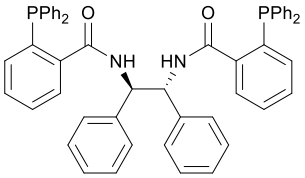
L1



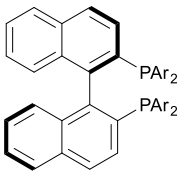
L2



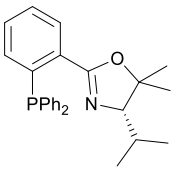
L3



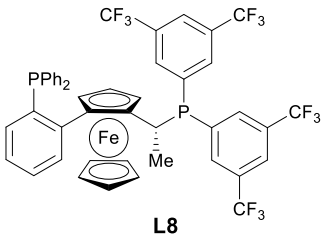
L4



L5: Ar = Ph
L6: Ar = *p*-Tol



L7



L8

Entry	Ligand	Solvent	Temperature	Additive (equiv.)	%Yield[b]		*er*[c]
					3aa	**4aa**	
1	PPh_3	MeCN	rt	_	49[d]	30[d]	_
2	PCy_3	MeCN	rt	_	NR		_
3	P(*o*-tol)$_3$	MeCN	rt	_	NR		_
4	P(*p*-tol)$_3$	MeCN	rt	_	43[d]	18[d]	_
5	$P(C_6F_5)_3$	MeCN	rt	_	NR		_
6	P(*p*-$C_6H_4Cl)_3$	MeCN	rt	_	15[d]	23[d]	_
7	P(2-furyl)$_3$	MeCN	rt	_	43[d]	31[d]	_
8	PPh_3	MeCN	0–5 °C	_	26	20	_
9	PPh_3	MeCN	40 °C	_	49	18	_
10	PPh_3	MeCN	reflux	_	28	4	_
11[e]	PPh_3	MeCN	rt	_	27	23	_
12[f]	PPh_3	MeCN	rt	_	56	18	_
13	_	MeCN	rt	_	NR		_
14	PPh_3	THF	rt	_	89	_	_
15	PPh_3	THF	rt	LiCl (1.0)	NR		_
16	PPh_3	THF	rt	$AgBF_4$ (0.13)	70	_	_
17	PPh_3	THF	rt	Bu_4NCl (1.0)	21	20	_
18	PPh_3	CH_2Cl_2	rt	_	70	_	_
19	PPh_3	PhMe	rt	_	trace	trace	_
20	PPh_3	MeOH	rt	_	16	17	_
21	PPh_3	DMF	rt	_	41	22	_
22	PPh_3	DMSO	rt	_	61	12	_
23[g]	L1	THF	rt	_	90	_	93:7
24	L1	THF	0–5 °C	_	26	_	93:7
25[h]	L1	THF	rt	_	84	_	92:8
26[i]	L1	THF	rt	_	83	3	92:8
27[f]	L1	THF	rt	_	64	7	92:8
28[j]	L1	THF	rt	_	86	_	93:7

29	L2	THF	rt	_	NR		_
30	L3	THF	rt	_	NR		_
31	L4	THF	rt	_	73	6	83:17
32	L5	THF	rt	_	97	_	91:9
33	L6	THF	rt	_	67	_	67:33
34	L7	THF	rt	_	NR		_
35	L8	THF	rt	_	61	21	55:45
36[k]	L1	CH_2Cl_2	rt	_	90	_	91:9
37	L2	CH_2Cl_2	rt	_	17	10	84:16
38	L3	CH_2Cl_2	rt	_	6	9	62:38
39	L4	CH_2Cl_2	rt	_	54	6	85:15
40[l]	L5	CH_2Cl_2	rt	_	7	_	35:65
41	L1	CH_2Cl_2	0–5 °C	_	77	_	93:7
42	L1	CH_2Cl_2	-20 °C	_	66	_	92:8
43	L1	CH_2Cl_2	0–5 °C	$AgBF_4$ (0.13)	45	4	90:10
44	L1	CH_2Cl_2	0–5 °C	Bu_4NCl (0.12)	78	_	93:7
45	L1	CH_2Cl_2	0–5 °C	_	77	_	93:7
46[m]	L1	CH_2Cl_2	rt	_	85	_	93:7
47[f]	L1	CH_2Cl_2	rt	_	86	_	91:9
48[i]	L1	CH_2Cl_2	rt	_	78	_	91:9
49[j]	L1	CH_2Cl_2	rt	_	84	_	92:8
50	L1	MeCN	0–5 °C	_	51	10	89:11
51	L1	DCE	0–5 °C	_	50	6	93:7
52	L1	2-Me-THF	0–5 °C	_	69	0	94:6
53	L1	DME	0–5 °C	_	66	0	92:8
54	L1	2-Me-THF	rt	_	41	0	92:8
55	L1	DME	rt	_	72	0	91:9
56	L1	Dioxane	rt	_	72	0	91:9

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.22 mmol, 1.1 equiv.), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (5 mol%), PR_3 (25 mol%) or **L** (15 mol%), solvent (0.07 M wrt **1a**), rt, 21 h.

[b]Yield determined by ^1H NMR integration against an internal standard (1,3,5-trimethoxybenzene, dimethyl sulfone or *trans*-stilbene oxide).

[c]Enantiomeric ratio determined by chiral HPLC.

[d]Isolated yield

[e]0.14 M wrt **1a**

[f]0.03M wrt **1a**

[g]Reaction reached completion after 3 h.

[h]$[Pd(\pi\text{-}C_3H_4Ph)Cp]$ (10 mol%) used.

[i]$[Pd(\pi\text{-}C_3H_5)Cl]_2$ (2.5 mol%), **L** (7.5 mol%).

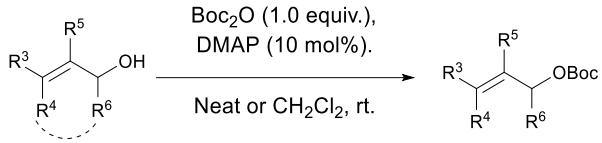
[j]***i*-1a**(1.0 equiv.) used instead of **1a**.

[k]Reaction reached completion after 1 h.

[l]Reversed enantioselectivity compared to Entry 32

[m]$Pd_2dba_3 \bullet CHCl_3$ (5 mol%).

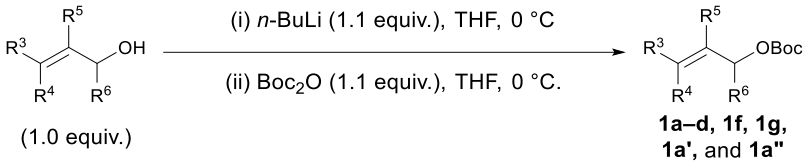
3. Synthesis of allyl carbonates



(1.2–3.5 equiv.) **1c, 1e,** and **1h**

General procedure A:

To a homogeneous mixture of Boc_2O (1.0 equiv.) and allyl alcohol (1.2–3.5 equiv.) (either neat or in CH_2Cl_2) at rt was added DMAP (5 mol%) in one portion. The resulting solution was stirred at rt overnight and monitored by TLC. Upon completion, indicated by TLC, the reaction mixture was concentrated *in vacuo*, followed by purification by FCC.

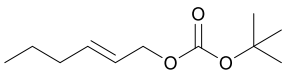


(1.0 equiv.) **1a–d, 1f, 1g, 1a',** and **1a"**

General procedure B:

To a solution of allyl alcohol (1.0 equiv.) in THF (0.1 M) at 0 °C was added *n*-BuLi (1.1 equiv.) dropwise. The resulting solution was stirred at the same temperature for 15 min, after which a solution of Boc_2O (1.1 equiv.) in THF was added dropwise. The reaction mixture was then stirred at 0 °C and monitored by TLC. Upon completion, the reaction was quenched with water, extracted with Et_2O, and the combined ethereal extracts were washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*, and then purified by FCC.

(*E*)-*tert*-Butyl hex-2-en-1-yl carbonate (1a).



1a

The titled compound was prepared following the General procedure B using *trans*-2-hexen-1-ol (1.1 mL, 9.324 mmol), *n*-BuLi (6.8 mL, 1.6 M solution in hexane, 10.880 mmol), and Boc_2O (2.102 g, 9.629 mmol) in THF (50 mL). Purification by FCC (4:96 EtOAc:hexane) yielded **1a** as a colourless oil (1.4758 g, 79%).

$\mathbf{R_f}$ = 0.31 (4:96 EtOAc:hexane).

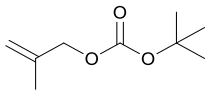
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89 – 5.73 (m, 1H), 5.66 – 5.53 (m, 1H), 4.50 (d, *J* = 6.6 Hz, 2H), 2.03 (q, *J* = 7.1 Hz, 2H), 1.49 (d, *J* = 0.7 Hz, 9H), 1.40 (app. h, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.4, 137.0, 123.5, 82.0, 67.8, 34.3, 27.8, 22.0, 13.7.

LRESI-MS (ESI +ve): *m/z* 223 $[M + Na]^+$ (10%).

The NMR spectroscopic data agreed with those reported.[1]

***tert*-Butyl (2-methylallyl) carbonate (1b).**



1b

The titled compound was prepared following the General procedure B using 2-methyl-2-propen-1-ol (0.12 mL, 1.426 mmol), *n*-BuLi (1.0 mL, 1.6 M solution in hexane, 1.600 mmol), and Boc_2O (331.8 mg, 1.520 mmol) in THF (6 mL). Purification by FCC (2:98 EtOAc:hexane) yielded **1b** as a colourless oil (178.2 mg, 73%).

R_f = 0.18 (2:98 EtOAc:hexane).

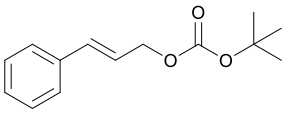
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.00 (s, 1H), 4.94 (s, 1H), 4.48 (dt, *J* = 1.4, 0.6 Hz, 2H), 1.83 – 1.71 (m, 3H), 1.49 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 139.8, 113.1, 82.1, 70.2, 27.8, 19.4.

LRESI-MS (ESI +ve): *m/z* 227 $[M + Na + MeOH]^+$ (100%).

The spectroscopic data agreed with those reported.[2]

***tert*-Butyl cinnamyl carbonate (1c).**



1c

The titled compound was prepared following the General procedure A using cinnamyl alcohol (0.916 g, 6.830 mmol), Boc_2O (1.0946 g, 5.015 mmol), and DMAP (48.1 mg, 0.394 mmol) in CH_2Cl_2 (5 mL). Purification by FCC (1:9 Et_2O:hexane) yielded **1c** as a colourless oil (1.1183 g, 95%).

R_f = 0.35 (1:9 Et_2O:hexane).

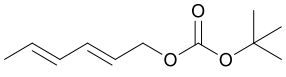
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.35 (m, 2H), 7.36 – 7.28 (m, 2H), 7.30 – 7.21 (m, 1H), 6.67 (dt, *J* = 16.0, 1.4 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.72 (dd, *J* = 6.4, 1.4 Hz, 2H), 1.50 (s, 9H).

^{13}C NMR (100MHz, $CDCl_3$): δ 153.4, 136.2, 134.4, 128.6, 128.1, 126.7, 122.9, 82.2, 67.5, 27.8.

LRESI-MS (ESI +ve): *m/z* 257 $[M + Na]^+$ (30%).

The NMR spectroscopic data agreed with those reported.[3]

***tert*-Butyl ((2*E*,4*E*)-hexa-2,4-dien-1-yl) carbonate (1d).**



1d

The titled compound was prepared following the General procedure B using *trans*,*trans*-2,4-hexadien-1-ol (0.37 mL, 3.284 mmol), *n*-BuLi (4.0 mL, 1.2 M solution in hexane, 4.720 mmol), and Boc_2O (960.5 mg, 4.401 mmol) in THF (3 mL). Purification by FCC (2.5:97.5 EtOAc:hexane) yielded **1d** as a colourless oil (321.5 mg, 49%).

R_f = 0.18 (2.5:97.5 EtOAc:hexane).

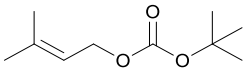
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.38 – 6.17 (m, 1H), 6.13 – 5.96 (m, 1H), 5.84 – 5.69 (m, 1H), 5.71 – 5.57 (m, 1H), 4.66 – 4.51 (m, 2H), 1.82 – 1.71 (m, 3H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.4, 135.2, 131.4, 130.4, 123.4, 82.0, 67.4, 27.8, 18.1.

LRESI-MS (ESI +ve): *m/z* 253 $[M + Na + MeOH]^+$ (30%).

The spectroscopic data agreed with those reported.[3]

***tert*-Butyl (3-methylbut-2-en-1-yl) carbonate (1e).**



1e

The titled compound was prepared following the General procedure A using prenol (1.0 mL, 9.843 mmol), Boc_2O (614.3 mg, 2.815 mmol), and DMAP (7.6 mg, 0.062 mmol). Purification by FCC (5:95 EtOAc:hexane) yielded **1e** as a colourless oil (351.1 mg, 67%).

R_f = 0.37 (5:95 EtOAc:hexane).

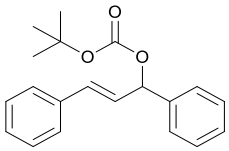
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.54 – 5.24 (m, 1H), 4.56 (dt, *J* = 7.2, 0.9 Hz, 2H), 1.77 – 1.73 (m, 3H), 1.72 – 1.68 (m, 3H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7, 139.4, 118.4, 81.8, 63.7, 27.8, 25.8, 18.0.

LRESI-MS (ESI +ve): *m/z* 209 $[M + Na]^+$ (10%).

The spectroscopic data agreed with those reported.[4]

(*E*)-*tert*-Butyl (1,3-diphenylallyl) carbonate (1f).



1f

The titled compound was prepared following the General procedure B using racemic *trans*-1,3-diphenyl-2-propen-1-ol (376.4 mg, 1.790 mmol), *n*-BuLi (1.6 mL, 1.2 M solution in hexane, 1.888 mmol), and Boc_2O (441.8 mg, 2.024 mmol) in THF (10 mL). Recrystallisation from warm pentane yielded **1f** as a white solid (275.9 mg, 50%).

R_f = 0.28 (4:96 EtOAc:hexane).

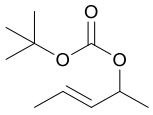
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 7.19 (m, 10H), 6.74 – 6.60 (m, 1H), 6.37 (dd, *J* = 15.8, 7.0 Hz, 1H), 6.26 – 6.17 (m, 1H), 1.48 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 139.1, 136.2, 132.6, 128.63, 128.56, 128.2, 128.1, 127.4, 126.9, 126.8, 82.4, 79.2, 27.8.

LRESI-MS (ESI +ve): *m/z* 333 $[M + Na]^+$ (100%).

The spectroscopic data agreed with those reported.[5]

(*E*)-*tert*-Butyl pent-3-en-2-yl carbonate (1g).



1g

The titled compound was prepared following the General procedure B using racemic 3-penten-2-ol (predominantly *trans*, 0.33 mL, 3.230 mmol), *n*-BuLi (3.4 mL, 1.2 M solution in hexane, 4.012 mmol), and Boc_2O (858.7 mg, 3.935 mmol) in THF (3 mL). Purification by FCC (2.5:97.5 EtOAc:hexane) yielded **1g** as a colourless oil (195.5 mg, 32%).

$\mathbf{R_f}$ = 0.25 (2.5:97.5 EtOAc:hexane).

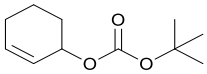
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (dqd, *J* = 15.4, 6.5, 1.0 Hz, 1H), 5.50 (ddq, *J* = 15.3, 7.1, 1.6 Hz, 1H), 5.22 – 4.97 (m, 1H), 1.69 (ddd, *J* = 6.5, 1.7, 0.7 Hz, 3H), 1.48 (s, 9H), 1.33 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 130.6, 128.5, 81.7, 74.3, 27.9, 20.4, 17.7.

LRESI-MS (ESI +ve): *m/z* 209 $[M + Na]^+$ (5%).

The spectroscopic data agreed with those reported.[6]

***tert*-Butyl cyclohex-2-en-1-yl carbonate (1h).**



1h

The titled compound was prepared following the General procedure A using 2-cyclohexen-1-ol (0.22 mL, 2.242 mmol), Boc_2O (413.4 mg, 1.894 mmol), and DMAP (31.9 mg, 0.261 mmol). Purification by FCC (1:3 CH_2Cl_2:hexane) yielded **1h** as a colourless oil (168.6 mg, 45%).

$\mathbf{R_f}$ = 0.25 (1:3 CH_2Cl_2:hexane).

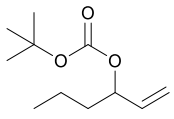
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.00 – 5.91 (m, 1H), 5.81 – 5.73 (m, 1H), 5.12 – 5.03 (m, 1H), 2.13 – 2.02 (m, 1H), 2.03 – 1.92 (m, 1H), 1.94 – 1.83 (m, 1H), 1.86 – 1.71 (m, 2H), 1.69 – 1.56 (m, 1H), 1.49 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 132.9, 125.4, 81.8, 70.8, 28.3, 27.9, 24.9, 18.8.

LRESI-MS (ESI +ve): *m/z* 221 $[M + Na]^+$ (10%).

The spectroscopic data agreed with those reported.[7]

***tert*-Butyl hex-1-en-3-yl carbonate (1a′).**



1a′

The titled compound was prepared following the General procedure B using racemic 1-hexen-3-ol (0.36 mL, 2.998 mmol), *n*-BuLi (2.8 mL, 1.2 M solution in hexane, 3.304 mmol), and Boc_2O (723.4 mg, 3.315 mmol) in THF (5 mL). Purification by FCC (4:96 EtOAc:hexane) yielded **1a´** as a colourless oil (491.4 mg, 82%).

R_f = 0.25 (4:96 EtOAc:hexane).

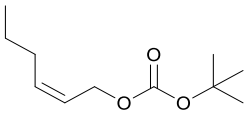
^{1}H NMR (400 MHz, $CDCl_3$): δ δ 5.87 – 5.73 (m, 1H), 5.34 – 5.15 (m, 2H), 5.12 – 4.95 (m, 1H), 1.77 – 1.63 (m, 1H), 1.63 – 1.53 (m, 1H), 1.48 (s, 9H), 1.44 – 1.30 (m, 2H), 0.93 (app. t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 136.5, 116.9, 81.9, 77.9, 36.4, 27.8, 18.4, 13.8.

LRESI-MS (ESI +ve): *m/z* 223 $[M + Na]^+$ (5%).

The spectroscopic data agreed with those reported.[8]

(*Z*)-*tert*-Butyl hex-2-en-1-yl carbonate (1a´´).



1a´´

The titled compound was prepared following the General procedure B using *cis*-2-hexen-1-ol (0.35 mL, 2.960 mmol), *n*-BuLi (2.8 mL, 1.2 M solution in hexane, 3.304 mmol), and Boc_2O (795.4 mg, 3.644 mmol) in THF (5 mL). Purification by FCC (4:96 EtOAc:hexane) yielded **1a´´** as a colourless oil (445.7 mg, 75%).

R_f = 0.24 (4:96 EtOAc:hexanes).

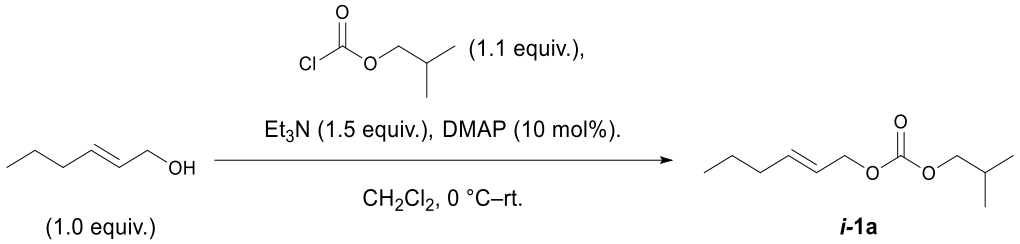
IR (neat): 859, 1089, 1158, 1251, 1273, 1368, 1738, 2874, 2933, 2963 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ δ 5.69 – 5.61 (m, 1H), 5.61 – 5.52 (m, 1H), 4.65 – 4.60 (m, 2H), 2.16 – 2.02 (m, 2H), 1.49 (s, 9H), 1.40 (app. h, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7, 135.5, 123.4, 82.3, 63.0, 29.7, 28.0, 22.7, 13.9.

HRESI-MS (ESI +ve): Found 201.1489, calc for $C_{11}H_{21}O_3$ 201.1491 $[M + H]^+$.

(*E*)-Hex-2-en-1-yl isobutyl carbonate (*i*-1a).



Procedure:

To a mixture of 2-hexenyl-1-ol (220.7 mg, 2.20 mmol), Et_3N (326.7 mg, 3.23 mmol), and DMAP (28.0 mg, 0.23 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added isobutyl chloroformate (326.4 mg, 2.39 mmol) dropwise. The resulting solution was allowed to warm to rt with stirring and monitored by TLC. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and 1M HCl (20 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 10 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrate *in vacuo*. Purification by flash column chromatography (3:1 hexane:CH_2Cl_2) furnished the desired product ***i*-1a** as a colourless oil (434.0 mg, 98%).

R_f = 0.26 (3:1 hexane:CH_2Cl_2).

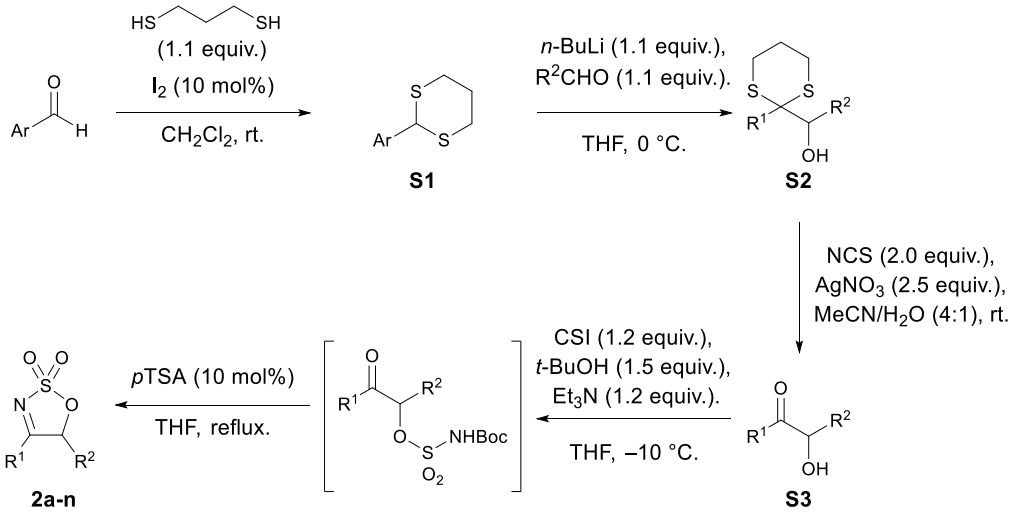
IR (neat): 791, 922, 940, 966, 1180, 1240, 1304, 1384, 1401, 1465, 1743, 2933, 2960 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.81 (dtt, *J* = 14.8, 6.7, 1.2 Hz, 1H), 5.60 (dtt, *J* = 15.4, 6.6, 1.5 Hz, 1H), 4.57 (dd, *J* = 6.6, 1.0 Hz, 2H), 3.92 (d, *J* = 6.7 Hz, 2H), 2.09 – 1.98 (m, 2H), 2.02 – 1.91 (m, 1H), 1.41 (app. h, *J* = 7.4 Hz, 2H), 0.95 (dd, *J* = 6.7, 2.1 Hz, 6H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 155.3, 137.3, 123.4, 74.0, 68.6, 34.3, 27.8, 22.0, 18.9, 13.64.

HRESI-MS (ESI +ve): Found 223.1301, calc for $C_{11}H_{20}O_3Na$ 223.1310 $[M + Na]^+$.

4. Preparation of cyclic sulfamidate imines



(Note: Various attempts to prepare the imines bearing an electron enriched aryl substituent at C5 (R^1 = Ph, R^2 = 4-methoxyphenyl, 2-thienyl, and 2-furyl) were unsuccessful. However, some of the precursors prepared were novel compounds, and hence their experimental data are reported for future reference)

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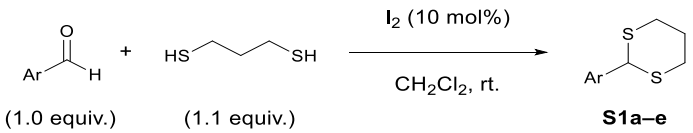
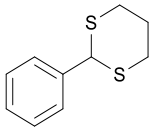
a. Synthesis of dithianes



General procedure C:[9]

To a stirred solution of aryl aldehyde (1.0 equiv.) and 1,3-propanedithiol (1.1 equiv.) in $CHCl_3$ (0.2 M) at rt was added I_2 (10 mol%) in one portion. The resulting solution was stirred at rt and monitored by TLC. Upon completion, the reaction was quenched with 0.1 M $Na_2S_2O_3$ (0.5 equiv.), extracted with $CHCl_3$, then the combined organic extracts were washed with 3 M NaOH (6 equiv.) and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*, and then purified by FCC.

2-Phenyl-1,3-dithiane (S1a).



S1a

The titled compound was prepared following the General procedure C using benzaldehyde (5.1 mL, 50.17 mmol), 1,3-propanedithiol (5.5 mL, 54.78 mmol), and I_2 (1.290 g, 5.08 mmol) in $CHCl_3$ (100 mL). The white solid residue obtained (9.313 g, 95%) after aqueous work-up was sufficiently pure to be used in the subsequent step without further purification.

R_f = 0.30 (1:9 EtOAc:hexane).

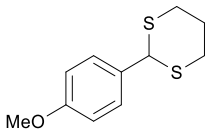
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 – 7.43 (m, 2H), 7.39 – 7.27 (m, 3H), 5.17 (s, 1H), 3.15 – 3.00 (m, 2H), 2.92 (dddd, *J* = 13.7, 4.4, 3.0, 1.0 Hz, 2H), 2.26 – 2.13 (m, 1H), 2.06 – 1.86 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.3, 129.0, 128.7, 128.0, 51.7, 32.3, 25.3.

LRESI-MS (ESI +ve): *m/z* 197 $[M + H]^+$ (30%).

The spectroscopic data agreed with those reported.[10]

2-(4-Methoxyphenyl)-1,3-dithiane (S1b).



S1b

The titled compound was prepared following the General procedure C using *p*-anisaldehyde (0.61 mL, 5.014 mmol), 1,3-propanedithiol (0.55 mL, 5.478 mmol), and I_2 (160.6 mg, 0.633 mmol) in $CHCl_3$ (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S1b** as a white solid (1.032 g, 91%).

R_f = 0.27 (1:9: EtOAc:hexane).

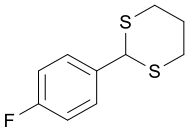
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.33 (m, 2H), 6.95 – 6.80 (m, 2H), 5.13 (s, 1H), 3.79 (s, 3H), 3.15 – 2.99 (m, 2H), 2.89 (ddd, *J* = 14.4, 4.4, 3.0 Hz, 2H), 2.21 – 2.09 (m, 1H), 2.03 – 1.82 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 131.5, 129.1, 114.3, 55.5, 50.9, 32.4, 25.3.

LRESI-MS (ESI +ve): *m/z* 227 $[M + H]^+$ (10%).

The spectroscopic data agreed with those reported.[10]

2-(4-Fluorophenyl)-1,3-dithiane (S1c).



S1c

The titled compound was prepared following the General procedure C using 4-fluorobenzaldehyde (626.4 mg, 5.047 mmol), 1,3-propanedithiol (0.55 mL, 5.478 mmol), and I_2 (184.0 mg, 0.725 mmol) in $CHCl_3$ (40 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **S1c** as a white solid (301.6 mg, 28%).

$\mathbf{R_f}$ = 0.45 (1:4 EtOAc:hexane).

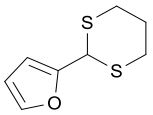
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.37 (m, 2H), 7.11 – 6.96 (m, 2H), 5.14 (s, 1H), 3.15 – 2.98 (m, 2H), 2.91 (dddd, *J* = 13.5, 4.4, 3.0, 1.2 Hz, 2H), 2.27 – 2.10 (m, 1H), 2.01 – 1.85 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7 (d, *J* = 247.5 Hz), 135.2 (d, *J* = 3.2 Hz), 129.7 (d, *J* = 8.3 Hz), 115.9 (d, *J* = 21.6 Hz), 50.7, 32.3, 25.2.

LRESI-MS (ESI +ve): *m/z* 215 $[M + H]^+$ (100%).

The spectroscopic data agreed with those reported.[11]

2-(1,3-Dithian-2-yl)furan (S1d).



S1d

The titled compound was prepared following the General procedure C using furfural (0.41 mL, 4.950 mmol), 1,3-propanedithiol (0.55 mL, 5.478 mmol), and I_2 (125.2 mg, 0.493 mmol) in $CHCl_3$ (20 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **S1d** as a brown oil (1.032 g, 91%).

$\mathbf{R_f}$ = 0.47 (1:4 EtOAc:hexane).

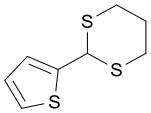
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.40 (dt, *J* = 3.3, 0.9 Hz, 1H), 6.35 (dd, *J* = 3.3, 1.9 Hz, 1H), 5.22 (s, 1H), 3.00 – 2.94 (m, 4H), 2.22 – 2.08 (m, 1H), 2.07 – 1.92 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0, 142.5, 110.8, 108.1, 42.3, 30.5, 25.5.

LRESI-MS (ESI +ve): *m/z* 227 $[M + H]^+$ (20%).

The spectroscopic data agreed with those reported.[11]

2-(2-Thienyl)-1,3-dithiane (S1e).



S1e

The titled compound was prepared following the General procedure C using 2-thiophenecarboxaldehyde (0.47 mL, 5.029 mmol), 1,3-propanedithiol (0.57 mL, 5.674 mmol), and I_2 (159.0 mg, 0.627 mmol) in $CHCl_3$ (25 mL). The yellow solid residue obtained (1.168 g, ~quant.) was sufficiently pure to be used in the following step without further purifications.

R_f = 0.40 (1:9 EtOAc:hexane).

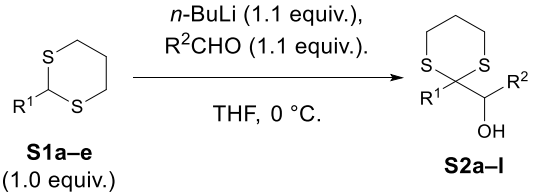
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.17 (dt, *J* = 3.6, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.41 (d, *J* = 0.8 Hz, 1H), 3.06 – 2.89 (m, 4H), 2.22 – 2.10 (m, 1H), 2.06 – 1.84 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 142.4, 126.8, 126.2, 125.7, 44.6, 31.0, 25.0.

LRESI-MS (ESI +ve): *m/z* 203 $[M + H]^+$ (40%).

The spectroscopic data agreed with those reported.[10]

b. Synthesis of dithiane alcohols

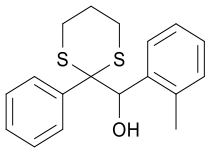


General procedure D:[12]

To a stirred solution of 2-substituted-1,3-dithiane (1.0 equiv.) in THF (0.2 M) at 0 °C was added *n*-BuLi (1.1 equiv.) dropwise. The resulting solution was stirred at 0 °C for 30 min, after which aryl aldehyde (1.1 equiv.) was added dropwise. The reaction mixture was then stirred 0 °C and monitored by TLC. Upon completion, the reaction was quenched with saturated NH_4Cl solution, extracted with CH_2Cl_2,

then the combined organic extracts were washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*, and then purified by FCC.

(2-Phenyl-1,3-dithian-2-yl)(*o*-tolyl)methanol (S2a).



S2a

The titled compound was prepared following the General procedure D using dithiane **S1a** (801.5 mg, 4.082 mmol), *n*-BuLi (3.8 mL, 1.2 M solution in hexane, 4.560 mmol), and *o*-tolualdehyde (0.52 mL, 4.497 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2a** as a sticky colourless oil (1.222 g, 94%).

$\mathbf{R_f}$ = 0.22 (1:9 EtOAc:hex).

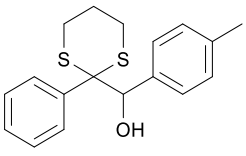
IR (neat): 646, 688, 724, 757, 881, 975, 1035, 1205, 1448, 1677, 2870, 2927, 2954, 3338 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.67 (m, 2H), 7.33 – 7.04 (m, 6H), 7.03 – 6.88 (m, 1H), 5.23 (d, *J* = 3.8 Hz, 1H), 2.87 (d, *J* = 3.8 Hz, 1H), 2.83 – 2.62 (m, 3H), 2.54 (ddd, *J* = 14.4, 10.7, 4.5 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 137.1, 135.9, 131.1, 129.7, 128.5, 128.2, 128.0, 127.5, 124.9, 76.6, 67.8, 27.5, 26.8, 24.8, 19.5.

HRESI-MS (ESI +ve): Found 339.0836, calc for $C_{18}H_{20}OS_2Na$ 339.0853 $[M + Na]^+$.

(2-Phenyl-1,3-dithian-2-yl)(*p*-tolyl)methanol (S2b).



S2b

The titled compound was prepared following the General procedure D using dithiane **S1a** (655.9 mg, 3.341 mmol), *n*-BuLi (3.2 mL, 1.2 M solution in hexane, 3.840 mmol), and *p*-tolualdehyde (0.46 mL,

3.901 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2b** as a sticky colourless oil (1.034 g, 98%).

R_f = 0.17 (1:9 EtOAc:hexane).

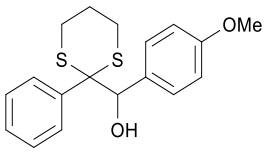
IR (neat): 583, 700, 721, 812, 876, 972, 1052, 1238, 1441, 2859, 2929, 2953, 3435 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 – 7.65 (m, 2H), 7.39 – 7.17 (m, 3H), 7.01 – 6.90 (m, 2H), 6.81 – 6.70 (m, 2H), 4.97 (d, *J* = 3.5 Hz, 1H), 2.83 (d, *J* = 3.8 Hz, 1H), 2.78 – 2.58 (m, 4H), 2.28 (s, 3H), 1.97 – 1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.8, 137.4, 134.2, 130.6, 129.1, 128.1, 128.0, 127.7, 127.5, 125.8, 80.9, 66.4, 27.2, 27.0, 24.8, 21.1.

HRESI-MS (ESI +ve): Found 339.0861, calc for $C_{18}H_{20}OS_2Na$ 339.0853 $[M + Na]^+$.

(4-Methoxyphenyl)(2-phenyl-1,3-dithian-2-yl)methanol (S2c).



S2c

The titled compound was prepared following the General procedure D using dithiane **S1a** (621.2 mg, 3.164 mmol), *n*-BuLi (3.0 mL, 1.2 M solution in hexane, 3.600 mmol), and *p*-anisaldehyde (0.42 mL, 3.452 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2c** as a sticky colourless oil (519.7 mg, 49%).

R_f = 0.09 (1:9 EtOAc:hexane).

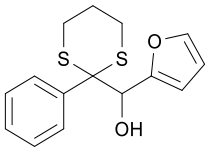
IR (neat): 700, 806, 972, 1032, 1171, 1247, 1442, 1510, 1599, 2859, 2931, 2956, 3405 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 – 7.59 (m, 2H), 7.42 – 7.09 (m, 3H), 6.85 – 6.72 (m, 2H), 6.71 – 6.54 (m, 2H), 4.94 (d, *J* = 3.6 Hz, 1H), 3.73 (s, 3H), 2.92 (d, *J* = 3.6 Hz, 1H), 2.80 – 2.51 (m, 4H), 1.99 – 1.81 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 137.6, 130.7, 129.6, 129.4, 128.2, 127.6, 112.5, 80.8, 66.7, 55.2, 27.4, 27.1, 24.9.

HRESI-MS (ESI +ve): Found 355.0791, calc for $C_{18}H_{20}O_2S_2Na$ 355.0802 $[M + Na]^+$.

Furan-2-yl(2-phenyl-1,3-dithian-2-yl)methanol (S2d).



S2d

The titled compound was prepared following the General procedure D using dithiane **S1a** (828.3 mg, 4.219 mmol), *n*-BuLi (3.0 mL, 1.6 M solution in hexane, 4.800 mmol), and furfural (0.38 mL, 4.497 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2d** as a sticky orange oil (925.4 mg, 75%).

$\mathbf{R_f}$ = 0.11 (1:9 EtOAc:hexane).

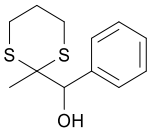
IR (neat): 699, 731, 811, 1009, 1053, 1147, 1265, 1442, 2906, 2954, 3440 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 – 7.73 (m, 2H), 7.40 – 7.23 (m, 3H), 7.23 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.25 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.05 (dt, *J* = 3.3, 0.8 Hz, 1H), 5.03 (d, *J* = 6.4 Hz, 1H), 2.85 – 2.54 (m, 5H), 2.01 – 1.82 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 142.0, 137.9, 130.3, 128.5, 127.9, 110.3, 109.4, 75.7, 65.5, 27.5, 27.4, 24.9.

HRESI-MS (ESI +ve): Found 315.0497, calc for $C_{15}H_{16}O_2S_2Na$ 315.0489 $[M + Na]^+$.

(2-Methyl-1,3-dithian-2-yl)(phenyl)methanol (S2e).



S2e

The titled compound was prepared following the General procedure D using 2-methyl-1,3-dithiane (0.54 mL, 4.509 mmol), *n*-BuLi (3.2 mL, 1.6 M solution in hexane, 5.120 mmol), and benzaldehyde (0.51 mL, 5.017 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2e** as a sticky light yellow oil (953.5 mg, 88%).

$\mathbf{R_f}$ = 0.15(1:9 EtOAc:hexane).

IR (neat): 464, 596, 703, 756, 1023, 1189, 1266, 1325, 1389, 1451, 1490, 2895, 2930, 3452 cm^{-1}.

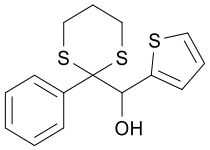
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.41 (m, 2H), 7.40 – 7.30 (m, 3H), 5.20 – 5.01 (m, 1H), 3.29 – 3.15 (m, 2H), 3.09 (ddd, *J* = 14.4, 11.8, 2.8 Hz, 1H), 2.82 – 2.60 (m, 2H), 2.17 (dtt, *J* = 16.0, 5.3, 2.8 Hz, 1H), 1.92 (dtt, *J* = 13.8, 11.6, 3.3 Hz, 1H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 128.5, 128.0, 127.3, 73.8, 54.0, 26.7, 26.0, 24.3, 22.4.

LRESI-MS (ESI +ve): *m/z* 263 $[M + Na]^+$ (60%).

The NMR spectroscopic data agreed with those reported.[13]

2-Phenyl-1,3-dithian-2-yl)(2-thienyl)methanol S2).



S2f

The titled compound was prepared following the General procedure D using dithiane **S1a** (900.4 mg, 4.586 mmol), *n*-BuLi (3.2 mL, 1.6 M solution in hexane, 5.120 mmol), and 2-thiophenecarboxaldehyde (0.51 mL, 5.010 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2f** as a sticky colourless oil (1.047 g, 72%).

R_f = 0.15 (1:9 EtOAc:hexane).

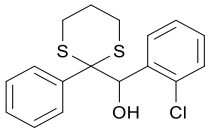
IR (neat): 435, 586, 700, 760, 1038, 1136, 1217, 1264, 1339, 1373, 1440, 1492, 2915, 3473 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 – 7.75 (m, 2H), 7.37 – 7.27 (m, 3H), 7.17 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.82 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.54 (ddd, *J* = 3.6, 1.2, 0.7 Hz, 1H), 5.35 – 5.15 (m, 1H), 3.08 (d, *J* = 3.8 Hz, 1H), 2.85 – 2.62 (m, 4H), 2.04 – 1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.8, 138.0, 130.5, 128.5, 128.0, 126.8, 125.9, 125.6, 78.0, 66.3, 27.6, 27.4, 24.9.

HRESI-MS (ESI +ve): Found 331.0259, calc for $C_{15}H_{16}OS_3Na$ 331.0261 $[M + Na]^+$.

(2-Chlorophenyl)(2-phenyl-1,3-dithian-2-yl)methanol (S2g).



S2g

The titled compound was prepared following the General procedure D using dithiane **S1a** (926.0 mg, 4.717 mmol), *n*-BuLi (4.4 mL, 1.2 M solution in hexane, 5.280 mmol), and 2-chlorobenzaldehyde (0.60 mL, 5.327 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2g** as a sticky colourless oil (1.076 g, 68%).

R_f = 0.18 (1:9 EtOAc:hexane).

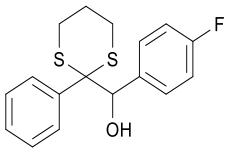
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.63 (m, 2H), 7.34 – 7.23 (m, 3H), 7.21 – 7.08 (m, 4H), 5.56 (d, *J* = 3.6 Hz, 1H), 2.99 (d, *J* = 3.6 Hz, 1H), 2.82 – 2.68 (m, 3H), 2.59 (ddd, *J* = 14.3, 10.9, 3.5 Hz, 1H), 2.03 – 1.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 135.4, 134.5, 130.7, 130.5, 129.2, 128.8, 128.2, 127.7, 125.7, 75.9, 66.9, 27.6, 26.9, 24.7.

LRESI-MS (ESI +ve): *m/z* 339 $[M + Na]^+$ (30%).

The NMR spectroscopic data agreed with those reported.[14]

(4-Fluorophenyl)(2-phenyl-1,3-dithian-2-yl)methanol (S2h).



S2h

The titled compound was prepared following the General procedure D using dithiane **S1a** (734.0 mg, 3.739 mmol), *n*-BuLi (3.6 mL, 1.2 M solution in hexane, 4.320 mmol), and 4-fluorobenzaldehyde (0.44 mL, 4.102 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2h** as a sticky colourless oil (979.5 mg, 82%).

R_f = 0.16 (1:9 EtOAc:hexane).

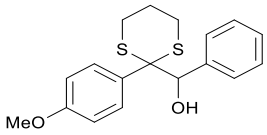
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.52 (m, 2H), 7.42 – 7.27 (m, 3H), 6.94 – 6.68 (m, 4H), 4.97 (d, *J* = 3.4 Hz, 1H), 3.01 (d, *J* = 3.4 Hz, 1H), 2.88 – 2.50 (m, 4H), 2.06 – 1.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, *J* = 246.8 Hz), 137.3, 132.9 (d, *J* = 2.7 Hz), 130.4, 129.8 (d, *J* = 8.2 Hz), 128.3, 127.7, 113.9 (d, *J* = 21.4 Hz), 80.4, 66.5, 27.3, 26.9, 24.7.

LRESI-MS (ESI +ve): *m/z* 343 $[M + Na]^+$ (70%).

The NMR spectroscopic data agreed with those reported.[15]

(2-(4-Methoxyphenyl)-1,3-dithian-2-yl)(phenyl)methanol (S2i).



S2i

The titled compound was prepared following the General procedure D using dithiane **S1b** (645.0 mg, 2.851 mmol), *n*-BuLi (2.6 mL, 1.2 M solution in hexane, 3.120 mmol), and benzaldehyde (0.32 mL, 3.148 mmol) in THF (20 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **S2i** as a sticky colourless oil (822.8 mg, 87%).

R_f = 0.25 (1:4 EtOAc:hexane).

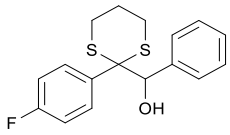
IR (neat): 558, 610, 700, 756, 1033, 1163, 1248, 1503, 1602, 2901, 3398 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 – 7.52 (m, 2H), 7.24 – 7.18 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.89 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.86 – 6.72 (m, 2H), 4.97 (d, *J* = 3.8 Hz, 1H), 3.83 (s, 3H), 2.91 (d, *J* = 3.8 Hz, 1H), 2.81 – 2.58 (m, 4H), 2.01 – 1.85 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 137.6, 132.1, 129.3, 128.5, 128.3, 127.2, 113.6, 81.3, 66.3, 55.5, 27.4, 27.2, 25.1.

HRESI-MS (ESI +ve): Found 355.0796, calc for $C_{18}H_{20}O_2S_2Na$ 355.0802 $[M + Na]^+$.

(2-(4-Fluorophenyl)-1,3-dithian-2-yl)(phenyl)methanol (S2j).



S2j

The titled compound was prepared following the General procedure D using dithiane **S1c** (1.161 g, 5.416 mmol), *n*-BuLi (5.0 mL, 1.2 M solution in hexane, 6.000 mmol), and benzaldehyde (0.62 mL,

6.100 mmol) in THF (20 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S2j** as a sticky colourless oil (925.4 mg, 75%).

R_f = 0.18 (1:9 EtOAc:hexane).

IR (neat): 543, 611, 661, 700, 758, 837, 1041, 1158, 1221, 1498, 1594, 2904, 3423 cm^{-1}.

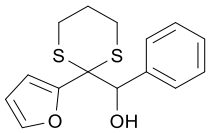
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.49 (m, 2H), 7.25 – 7.18 (m, 1H), 7.18 – 7.10 (m, 2H), 7.02 – 6.91 (m, 2H), 6.91 – 6.80 (m, 2H), 4.99 (d, *J* = 3.2 Hz, 1H), 2.90 (d, *J* = 3.5 Hz, 1H), 2.84 – 2.37 (m, 4H), 2.06 – 1.75 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.2 (d, *J* = 247.8 Hz), 137.1, 133.1 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 8.2 Hz), 128.2, 128.2, 127.1, 114.82 (d, *J* = 21.3 Hz), 81.0, 65.7, 27.2, 26.9, 24.7.

^{19}F NMR (470 MHz, $CDCl_3$): δ −52.55 (s).

HRESI-MS (ESI +ve): Found 343.0598, calc for $C_{17}H_{17}OS_2FNa$ 343.0603 $[M + Na]^+$.

(2-(Furan-2-yl)-1,3-dithian-2-yl)(phenyl)methanol (S2k).



S2k

The titled compound was prepared following the General procedure D using dithiane **S1d** (763.2 mg, 4.097 mmol), *n*-BuLi (2.8 mL, 1.6 M solution in hexane, 4.480 mmol), and benzaldehyde (0.50 mL, 4.919 mmol) in THF (20 mL) at –78 °C. Purification by FCC (1:9 EtOAc:hexane) furnished **S2k** as a sticky dark orange oil (491.6 mg, 41%).

R_f = 0.09 (1:9 EtOAc:hexane).

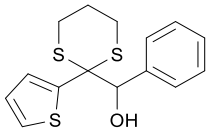
IR (neat): 595, 700, 740, 1008, 1048, 1150, 1198, 1241, 1277, 1396, 1448, 1493, 2905, 3496 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.32 – 7.13 (m, 3H), 7.00 (dt, *J* = 6.6, 1.7 Hz, 2H), 6.39 (dd, *J* = 3.3, 1.4 Hz, 2H), 5.07 (d, *J* = 4.2 Hz, 1H), 3.01 (d, *J* = 4.2 Hz, 1H), 2.88 – 2.67 (m, 4H), 2.06 – 1.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 142.9, 137.5, 128.4, 127.5, 127.4, 113.2, 110.9, 80.0, 60.0, 27.6, 27.2, 24.8.

HRESI-MS (ESI +ve): Found 315.0494, calc for $C_{15}H_{16}O_2S_2Na$ 315.0489 $[M + Na]^+$.

Phenyl(2-(2-thienyl)-1,3-dithian-2-yl)methanol (S2l).



S2l

The titled compound was prepared following the General procedure D using dithiane **S1e** (1.168 g, 5.771 mmol), *n*-BuLi (4.0 mL, 1.6 M solution in hexane, 6.400 mmol), and benzaldehyde (0.65 mL, 6.395 mmol) in THF (20 mL) at –78 °C. Purification by FCC (1:9 EtOAc:hexane) furnished **S2l** as a sticky orange oil (1.437 g, 81%).

$\mathbf{R_f}$ = 0.12 (1:9 EtOAc:hexane).

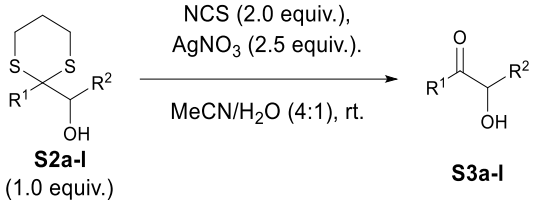
IR (neat): 607, 699, 1046, 1196, 1227, 1277, 1386, 1449, 1491, 2900, 3495 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.30 – 7.15 (m, 3H), 7.05 – 6.97 (m, 2H), 6.98 – 6.90 (m, 2H), 5.00 (d, *J* = 3.2 Hz, 1H), 3.04 – 2.69 (m, 5H), 2.11 – 1.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 137.2, 130.1, 128.3, 128.0, 127.6, 127.2, 127.1, 81.7, 62.3, 27.7, 27.4, 24.7.

HRESI-MS (ESI +ve): Found 331.0264, calc for $C_{15}H_{16}OS_3Na$ 331.0261 $[M + Na]^+$.

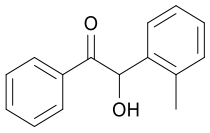
c. Synthesis of α-hydroxy ketones



General procedure E:[14]

To a stirred solution of dithiane alcohol (1.0 equiv.) in MeCN/H_2O (4:1, 0.05 M) at rt was added $AgNO_3$ (2.5 equiv.), followed by *N*-chlorosuccinimide NCS (2.0 equiv.). The resulting solution was stirred at rt and monitored by TLC. Upon completion, the reaction was quenched with saturated aq. $Na_2S_2O_3$, extracted with EtOAc, and the combined organic extracts were then washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*, and then purified by FCC.

2-Hydroxy-1-phenyl-2-(*o*-tolyl)ethan-1-one (S3a).



S3a

The titled compound was prepared following the General procedure E using dithiane alcohol **S2a** (690.0 mg, 2.180 mmol), $AgNO_3$ (764.3 mg, 4.499 mmol), and NCS (329.2 mg, 2.465 mmol) in MeCN/H_2O (4:1, 40 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S3a** as a white solid (201.2 mg, 42%).

$\mathbf{R_f}$ = 0.15 (1:9 EtOAc:hexane).

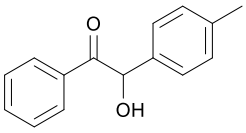
IR (neat): 647, 699, 717, 1047, 1204, 1273, 1382, 1450, 1491, 1599, 1678, 2928, 3426 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 – 7.78 (m, 2H), 7.60 – 7.46 (m, 1H), 7.46 – 7.34 (m, 2H), 7.25 – 7.15 (m, 2H), 7.13 – 7.08 (m, 1H), 7.05 – 6.98 (m, 1H), 6.05 (d, *J* = 5.3 Hz, 1H), 4.39 (d, *J* = 5.3 Hz, 1H), 2.54 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 200.4, 137.9, 137.0, 134.3, 134.1, 131.9, 129.4, 129.22, 129.16, 128.8, 127.2, 74.8, 19.8.

HRESI-MS (ESI +ve): Found 249.0884, calc for $C_{15}H_{14}O_2Na$ 249.0891 $[M + Na]^+$.

2-Hydroxy-1-phenyl-2-(*p*-tolyl)ethan-1-one (S3b).



S3b

The titled compound was prepared following the General procedure E using dithiane alcohol **S2b** (604.0 mg, 1.906 mmol), $AgNO_3$ (659.7 mg, 3.884 mmol), and NCS (279.9 mg, 2.096 mmol) in MeCN/H_2O (4:1, 40 mL). Purification by FCC (1.5:8.5 EtOAc:hexane) furnished **S3b** as a white solid (187.0 mg, 43%).

$\mathbf{R_f}$ = 0.24 (1.5:8.5 EtOAc:hexane).

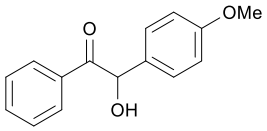
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 – 7.84 (m, 2H), 7.52 (ddt, *J* = 7.8, 7.0, 1.3 Hz, 1H), 7.48 – 7.36 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 5.92 (s, 1H), 4.49 (s, 1H), 2.29 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 199.3, 138.7, 136.3, 134.1, 133.8, 130.1, 129.4, 128.9, 127.9, 76.2, 21.4.

LRESI-MS (ESI +ve): *m/z* 249 $[M + Na]^+$ (20%), *m/z* 281 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[16]

2-Hydroxy-2-(4-methoxyphenyl)-1-phenylethan-1-one (S2c).



S3c

The titled compound was prepared following the General procedure E using dithiane alcohol **S2c** (519.7 mg, 1.563 mmol), $AgNO_3$ (669.8 mg, 3.943 mmol), and NCS (419.6 mg, 3.142 mmol) in MeCN/H_2O (4:1, 30 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **S3c** as a white solid (214.2 mg, 57%).

R_f = 0.21 (1:4 EtOAc:hexane).

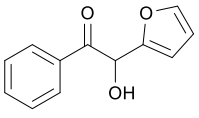
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 – 7.81 (m, 2H), 7.58 – 7.48 (m, 1H), 7.49 – 7.32 (m, 2H), 7.35 – 7.19 (m, 3H), 6.84 (d, *J* = 8.7 Hz, 1H), 5.91 (d, *J* = 6.0 Hz, 1H), 4.48 (d, *J* = 6.1 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 199.0, 159.7, 133.8, 133.6, 131.2, 129.14, 129.09, 128.7, 114.6, 75.7, 55.2.

LRESI-MS (ESI +ve): *m/z* 265 $[M + Na]^+$ (20%), *m/z* 297 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[17]

2-(Furan-2-yl)-2-hydroxy-1-phenylethan-1-one (S3d).



S3d

The titled compound was prepared following the General procedure E using dithiane alcohol **S2d** (76.4 mg, 0.261 mmol), $AgNO_3$ (147.9 mg, 0.8707 mmol), and NCS (85.0 mg, 0.637 mmol) in MeCN/H_2O (4:1, 5 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S3d** as a white solid (25.5 mg, 48%).

R_f = 0.11 (1:9 EtOAc:hexane).

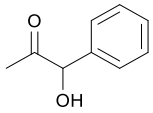
^{1}H NMR (500 MHz, $CDCl_3$ δ 7.97 – 7.92 (m, 2H), 7.60 – 7.56 (m, 1H), 7.47 – 7.42 (m, 2H), 7.34 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.36 – 6.29 (m, 2H), 6.02 (d, *J* = 6.4 Hz, 1H), 4.40 (d, *J* = 6.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 195.9, 151.6, 143.1, 134.2, 133.2, 129.0, 128.8, 110.9, 109.2, 69.3.

LRESI-MS (ESI +ve): *m/z* 225 $[M + Na]^+$ (20%), *m/z* 257 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[18]

1-Hydroxy-1-phenylpropan-2-one (S3e).



S3e

The titled compound was prepared following the General procedure E using dithiane alcohol **S3e** (747.0 mg, 3.108 mmol), $AgNO_3$ (1.358 g, 7.993 mmol), and NCS (872.9 mg, 6.537 mmol) in $MeCN/H_2O$ (4:1, 40 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **E79e** as a yellow oil (158.1 mg, 34%).

R_f = 0.24 (1:4 EtOAc:hexane).

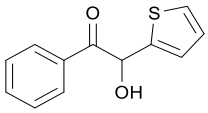
^{1}H NMR (500 MHz, $CDCl_3$ δ 7.43 – 7.29 (m, 5H), 5.10 (d, *J* = 4.2 Hz, 1H), 4.29 (d, *J* = 4.2 Hz, 1H), 2.09 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.0, 137.9, 129.0, 128.7, 127.3, 80.1, 25.2.

LRESI-MS (ESI -ve): *m/z* 149 $[M - H]^-$.

The NMR spectroscopic data agreed with those reported.[19]

2-Hydroxy-1-phenyl-2-(2-thienyl)ethan-1-one (S3f).



S3f

The titled compound was prepared following the General procedure E using dithiane alcohol **S2f** (390.1 mg, 1.265 mmol), $AgNO_3$ (553.1 mg, 3.256 mmol), and NCS (342.9 mg, 2.568 mmol) in $MeCN/H_2O$ (4:1, 25 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S3f** as an orange oil (151.4 mg, 65%).

R_f = 0.09 (1:9 EtOAc:hexane).

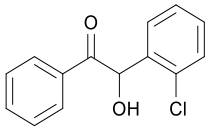
IR (neat): 644, 694, 719, 1055, 1222, 1263, 1383, 1449, 1490, 1595, 1679, 2922, 3404 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 – 7.92 (m, 2H), 7.56 (ddt, *J* = 7.8, 7.0, 1.3 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.25 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.91 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.23 (d, *J* = 6.6 Hz, 1H), 4.50 (d, *J* = 6.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$ δ 197.5, 142.1, 134.4, 133.5, 129.4, 129.0, 127.4, 126.8, 126.7, 70.9.

HRESI-MS (ESI +ve): Found 219.0477, calc for $C_{12}H_{11}O_2S$ 219.0480 $[M + H]^+$.

2-(2-Chlorophenyl)-2-hydroxy-1-phenylethan-1-one (S3g).



S3g

The titled compound was prepared following the General procedure E using dithiane alcohol **S2g** (742.6 mg, 2.204 mmol), $AgNO_3$ (952.0 mg, 5.604 mmol), and NCS (585.7 mg, 4.386 mmol) in MeCN/H_2O (4:1, 45 mL). Purification by FCC (1:9 EtOAc:hexane) furnished **S3g** as a white solid (351.0 mg, 65%).

R_f = 0.21 (1:9 EtOAc:hexane).

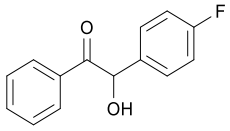
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 – 7.85 (m, 2H), 7.53 (ddt, *J* = 8.7, 7.0, 1.3 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.26 – 7.19 (m, 1H), 7.18 (td, *J* = 7.5, 1.4 Hz, 1H), 7.11 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.38 (d, *J* = 5.6 Hz, 1H), 4.56 (d, *J* = 5.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 198.7, 136.7, 134.1, 133.6, 133.1, 130.3, 130.0, 129.2, 128.9, 128.8, 127.7, 72.8.

LRESI-MS (ESI +ve): *m/z* 269 $[M + Na]^+$ (40%), *m/z* 301 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[20]

2-(4-Fluorophenyl)-2-hydroxy-1-phenylethan-1-one (S3h).



S3h

The titled compound was prepared following the General procedure E using dithiane alcohol **S2h** (601.6 mg, 1.877 mmol), $AgNO_3$ (802.8 mg, 4.726 mmol), and NCS (519.2 mg, 3.888 mmol) in MeCN/H_2O (4:1, 40 mL). Purification by FCC (1:9 EtOAc:hexane) furnished an inseparable mixture of **S3h** and **S3j** (6.7:1) as a white solid (253.2 mg, 59% combined yield).

R_f = 0.06 (1:9 EtOAc:hexane).

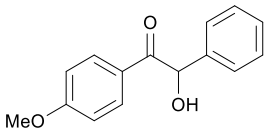
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 – 7.85 (m, 2H), 7.58 – 7.48 (m, 1H), 7.45 – 7.38 (m, 2H), 7.36 – 7.28 (m, 2H), 7.05 – 6.97 (m, 2H), 5.94 (d, J = 6.0 Hz, 1H), 4.53 (d, *J* = 6.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 199.0, δ 162.9 (d, *J* = 247.8 Hz), 161.9, 135.2 (d, *J* = 3.2 Hz), 134.3, 133.5, 129.8 (d, *J* = 8.4 Hz), 129.3, 129.0, 116.4 (d, *J* = 21.7 Hz), 75.6.

LRESI-MS (ESI +ve): *m/z* 253 $[M + Na]^+$ (20%), *m/z* 285 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[21]

2-Hydroxy-1-(4-methoxyphenyl)-2-phenylethan-1-one (S3i).



S3i

The titled compound was prepared following the General procedure E using dithiane alcohol **S2i** (592.4 mg, 1.782 mmol), $AgNO_3$ (832.2 mg, 4.899 mmol), and NCS (477.9 mg, 3.579 mmol) in MeCN/H_2O (4:1, 35 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **S3i** as a white solid (297.8 mg, 69%).

R_f = 0.17 (1:4 EtOAc:hexane).

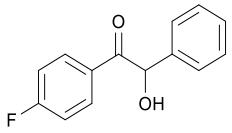
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 – 7.84 (m, 2H), 7.37 – 7.23 (m, 5H), 6.94 – 6.80 (m, 2H), 5.89 (d, *J* = 6.1 Hz, 1H), 4.63 (d, *J* = 6.1 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 197.6, 164.6, 140.1, 132.1, 129.6, 128.9, 128.2, 126.7, 114.4, 76.3, 56.0.

LRESI-MS (ESI +ve): *m/z* 265 $[M + Na]^+$ (20%), *m/z* 297 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[17]

1-(4-Fluorophenyl)-2-hydroxy-2-phenylethan-1-one (S3j).



S3j

The titled compound was prepared following the General procedure E using dithiane alcohol **S2j** (561.8 mg, 1.753 mmol), $AgNO_3$ (807.4 mg, 4.753 mmol), and NCS (481.5 mg, 3.606 mmol) in $MeCN/H_2O$ (4:1, 35 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **S3j** as a white solid (241.7 mg, 60%).

$\mathbf{R_f}$ = 0.20 (1:4 EtOAc:hexane).

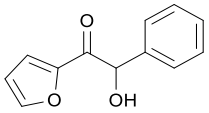
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 – 7.87 (m, 2H), 7.38 – 7.23 (m, 5H), 7.18 – 7.03 (m, 2H), 5.90 (d, *J* = 6.1 Hz, 1H), 4.50 (d, *J* = 6.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 197.3, 166.0 (d, *J* = 257.0 Hz), 138.8, 131.9 (d, *J* = 9.5 Hz), 129.8 (d, *J* = 3.1 Hz), 129.2, 128.7, 127.7, 116.0 (d, *J* = 22.1 Hz), 76.2.

LRESI-MS (ESI +ve): *m/z* 253 $[M + Na]^+$ (20%), *m/z* 285 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[22]

1-(Furan-2-yl)-2-hydroxy-2-phenylethan-1-one (S3k).



S3k

The titled compound was prepared following the General procedure E using dithiane alcohol **S2k** (387.0 mg, 1.324 mmol), $AgNO_3$ (576.8 mg, 3.396 mmol), and NCS (387.9 mg, 2.905 mmol) in $MeCN/H_2O$ (4:1, 25 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **S3k** as a dark orange solid (78.3 mg, 29%).

$\mathbf{R_f}$ = 0.14 (1:4 EtOAc:hexane).

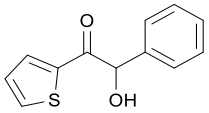
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (dd, J = 1.7, 0.8 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.20 (dd, *J* = 3.7, 0.8 Hz, 1H), 6.48 (dd, *J* = 3.7, 1.7 Hz, 1H), 5.75 (d, *J* = 5.9 Hz, 1H), 4.37 (d, *J* = 5.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 187.3, 149.9, 147.3, 138.6, 128.8, 128.6, 127.6, 119.9, 112.5, 76.0.

LRESI-MS (ESI +ve): *m/z* 225 $[M + Na]^+$ (20%), *m/z* 257 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[22]

2-Hydroxy-2-phenyl-1-(2-thienyl)ethan-1-one (S3l).



S3l

The titled compound was prepared following the General procedure E using dithiane alcohol **S2l** (201.6 mg, 0.654 mmol), $AgNO_3$ (288.8 mg, 1.700 mmol), and NCS (193.0 mg, 1.445 mmol) in $MeCN/H_2O$ (4:1, 10 mL). Purification by FCC (1:4 EtOAc:hexane) furnished **S3l** as an orange solid (88.5 mg, 62%).

R_f = 0.21 (1:4 EtOAc:hexane).

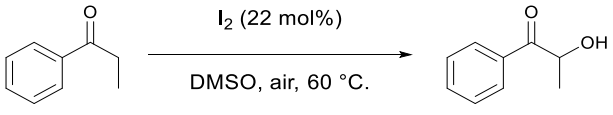
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 – 7.56 (m, 2H), 7.44 – 7.30 (m, 5H), 7.05 (dd, *J* = 4.8, 4.0 Hz, 1H), 5.74 (d, *J* = 5.8 Hz, 1H), 4.42 (d, *J* = 5.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 191.7, 139.8, 139.5, 135.2, 134.4, 129.4, 129.1, 128.5, 128.1. (^{13}C resonance corresponding to CHOH was not observed).

LRESI-MS (ESI +ve): *m/z* 241 $[M + Na]^+$ (30%), *m/z* 273 $[M + Na + MeOH]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[23]

2-Hydroxy-1-phenylpropan-1-one (S3m).



(1.0 equiv.) **S3m**

Procedure:[24]

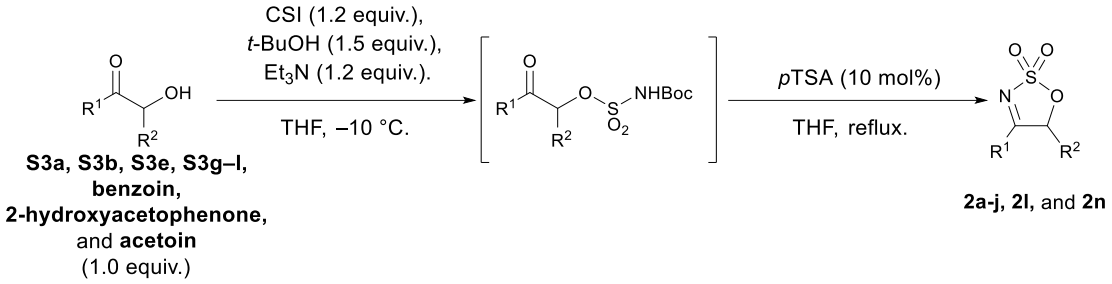
To a stirring solution of propiophenone (1 mL, 7.520 mmol) in DMSO (5 mL) at rt under air was added I_2 (427.2 mg, 1.683 mmol) in one portion. The resulting solution was stirred at 60 °C, monitored by TLC. Upon completion, the reaction mixture was allowed to cool to rt, diluted with EtOAc, washed with 0.1 M $Na_2S_2O_3$, and extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, concentrated *in vacuo*, and then purified by FCC. Purification by FCC (1:9 EtOAc:hexane) yielded **S3m** as a light orange oil (278.3 mg, 25%).

R_f = 0.09 (1:9 EtOAc:hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 – 7.89 (m, 2H), 7.70 – 7.58 (m, 1H), 7.58 – 7.47 (m, 2H), 5.31 – 5.04 (m, 1H), 3.78 (d, *J* = 6.2 Hz, 1H), 1.46 (d, *J* = 7.0 Hz, 3H).

The NMR spectroscopic data agreed with those reported.[16]

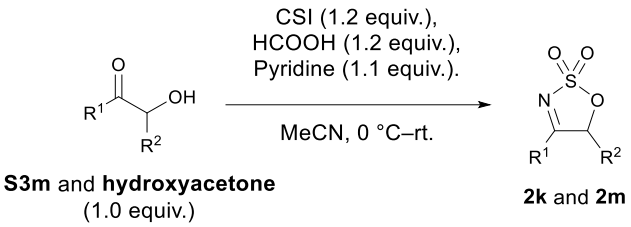
d. Synthesis of cyclic sulfamidate imines



General procedure F:

To a stirring solution of *t*-BuOH (1.5 equiv.) in THF at −10 °C was added chlorosulfonyl isocyanate (CSI) (1.2 equiv.) dropwise, followed by rapid stirring at the same temperature for 30 min. A solution of α-hydroxy ketone (1.0 equiv.) in THF was then added to the CSI/*t*-BuOH mixture, followed by the dropwise addition of Et_3N (1.2 equiv.). The resulting solution was then stirred at −10 °C and monitored by TLC. Upon completion, the reaction was quenched with water, extracted with EtOAc, then the combined organic extracts were washed with water and brine. The combined layer was dried over $MgSO_4$, filtered, and then concentrated *in vacuo*.

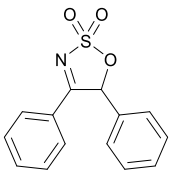
The residue was then dissolved in THF (0.1 M), followed by addition of *p*TSA (10 mol%). The reaction mixture was then heated at reflux overnight. Upon completion, as indicated by TLC, the reaction mixture was cooled down to rt then quenched with saturated $NaHCO_3$ solution, extracted with EtOAc, then the combined organic layers were washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*, and then purified by FCC.



General procedure G:[25]

Anhydrous formic acid (1.2 equiv.) was added dropwise to neat CSI (1.2 equiv.) at 0 °C with rapid stirring. Rapid gas evolution was observed, followed by solidification of the reaction mixture. The solid material was dissolved with MeCN (1.0 M) and the solution was stirred at rt until gas evolution ceased, then the solution was cooled to 0 °C. A solution of the α-hydroxyketone (1.0 equiv.) and pyridine (1.1 equiv.) in MeCN, was then added dropwise to the cooled (0 °C) CSI/HCOOH mixture with rapid stirring. The reaction mixture was stirred and allowed to warm to rt overnight. Upon completion, as indicated by TLC, the reaction mixture was filtered through a short pad of silica, and the filter cake was washed with EtOAc. The filtrate was then concentrated *in vacuo*, followed by purification by either FCC or recrystallisation.

4,5-Diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2a).



2a

The titled compound was prepared following the General procedure F using benzoin (569.6 mg, 2.684 mmol), CSI (0.28 mL, 3.191 mmol), *t*-BuOH (0.39 mL, 4.066 mmol), and Et_3N (0.44 mL, 3.189 mmol) in THF (25 mL), then *p*TSA•H_2O (116.1 mg, 0.611 mmol) in THF (50 mL). Recrystallisation of the crude reasidue from CH_2Cl_2/Et_2O furnished the desired product **2a** as a white solid (781.5 mg, 80%).

$\mathbf{R_f}$ = 0.13 (1:4 EtOAc:hexane).

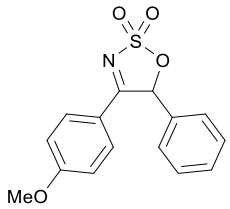
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 – 7.75 (m, 2H), 7.68 – 7.54 (m, 1H), 7.53 – 7.32 (m, 7H), 6.65 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 176.3, 135.1, 132.6, 130.8, 130.2, 129.7, 129.2, 128.5, 127.0, 89.7.

LRESI-MS (ESI -ve): *m/z* 272 $[M - H]^-$ (100%).

The NMR spectroscopic data agreed with those reported.[26]

4-(4-Methoxyphenyl)-5-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2b).



2b

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3i** (297.8 mg, 1.229 mmol), CSI (0.13 mL, 1.494 mmol), *t*-BuOH (0.18 mL, 1.882 mmol), and Et_3N (0.21 mL, 1.507 mmol) in THF (12 mL), then *p*TSA•H_2O (22.7 mg, 0.119 mmol) in THF (15 mL). Purification by FCC (1:3 EtOAc:hexane) yielded **2b** as a white solid (244.3 mg, 66%).

Mp: 133–135 °C

$\mathbf{R_f}$ = 0.15 (1:3 EtOAc:hexane).

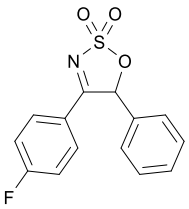
IR (neat): 488, 495, 615, 685, 753, 780, 806, 901, 951, 1018, 1038, 1190, 1261, 1363, 1457, 1514, 1556, 1590 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.77 (m, 2H), 7.53 – 7.32 (m, 5H), 6.91 – 6.82 (m, 2H), 6.60 (s, 1H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 165.2, 133.2, 132.8, 130.8, 129.8, 128.6, 119.4, 114.8, 89.5, 55.7.

HRESI-MS (ESI -ve): Found 302.0498, calc for $C_{15}H12NO_4S$ 302.0487 $[M - H]^-$.

4-(4-Fluorophenyl)-5-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2c).



2c

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3j** (241.7 mg, 1.050 mmol), CSI (0.11 mL, 1.264 mmol), *t*-BuOH (0.15 mL, 1.568 mmol), and Et_3N (0.18 mL, 1.291 mmol) in THF (11 mL), then *p*TSA•H_2O (17.4 mg, 0.091 mmol) in THF (10 mL). Purification by FCC (1:4 EtOAc:hexane) yielded **2c** as a semi solid (114.1 mg, 37%).

R_f = 0.16 (1:4 EtOAc:hexane).

IR (neat): 494, 597, 654, 684, 748, 781, 893, 954, 1033, 1191, 1242, 1367, 1458, 1512, 1571, 1601 cm^{-1}.

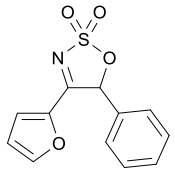
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.84 (m, 2H), 7.54 – 7.34 (m, 5H), 7.11 (dd, *J* = 8.9, 8.1 Hz, 2H), 6.61 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8, 166.7 (d, *J* = 260.5 Hz), 133.1 (d, *J* = 9.8 Hz), 132.5, 131.1, 129.9, 128.6, 123.48 (d, *J* = 3.2 Hz), 116.9 (d, *J* = 22.3 Hz), 89.6.

^{19}F NMR (470 MHz, $CDCl_3$) δ −37.01 (tt, *J* = 8.0, 5.1 Hz).

HRESI-MS (ESI –ve): Found 290.0277, calc for $C_{14}H_9NO_3SF$ 290.0287 $[M - H]^-$.

4-(Furan-2-yl)-5-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2d).



2d

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3k** (93.1 mg, 0.460 mmol), CSI (0.05 mL, 0.574 mmol), *t*-BuOH (0.07 mL, 0.732 mmol), and Et_3N (0.10 mL, 0.717 mmol) in THF (5 mL), then *p*TSA•H_2O (7.2 mg, 0.038 mmol) in THF (5 mL). Purification by FCC (1:3 EtOAc:hexane) yielded **2d** as a dark orange semi solid (53.0 mg, 44%).

R_f = 0.13 (1:3 EtOAc:hexane).

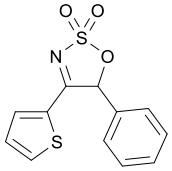
IR (neat): 508, 596, 662, 685, 750, 913, 981, 1035, 1195, 1230, 1376, 1459, 1540, 1598 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.52 – 7.41 (m, 5H), 7.27 (m, 1H), 6.60 (dd, *J* = 3.8, 1.7 Hz, 1H), 6.50 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 150.1, 144.1, 132.6, 131.0, 129.7, 128.5, 123.7, 114.1, 88.8.

HRESI-MS (ESI –ve): Found 262.0169, calc for $C_{12}H_8NO_4S$ 262.0174 $[M - H]^-$.

5-Phenyl-4-(2-thienyl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (2e).



2e

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3l** (517.0 mg, 2.369 mmol), CSI (0.25 mL, 2.872 mmol), *t*-BuOH (0.35 mL, 3.660 mmol), and Et_3N (0.40 mL, 2.870 mmol) in THF (23 mL), then *p*TSA•H_2O (46.3 mg, 0.243 mmol) in THF (25 mL). Purification by FCC (3:7 EtOAc:hexane) yielded **2e** as a white solid (196.4 mg, 30%).

Mp: 162–165 °C

R_f = 0.28 (3:7 EtOAc:hexane).

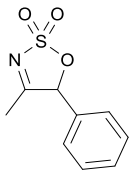
IR (neat): 497, 585, 659, 690, 729, 848, 888, 949, 986, 1067, 1183, 1359, 1415, 1574 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.59 – 7.38 (m, 6H), 7.08 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.49 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 137.5, 137.0, 133.0, 131.4, 131.2, 130.0, 129.4, 129.0, 89.5.

HRESI-MS (ESI –ve): Found 277.9942, calc for $C_{12}H_8NO_3S_2$ 277.9946 $[M - H]^-$.

4-Methyl-5-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2f).



2f

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3e** (303.8 mg, 2.023 mmol), CSI (0.21 mL, 2.413 mmol), *t*-BuOH (0.30 mL, 1.643 mmol), and Et_3N (0.35 mL, 2.511 mmol) in THF (10 mL), then *p*TSA•H_2O (39.1 mg, 0.206 mmol) in THF (20 mL). Purification by FCC (1:4 EtOAc:hexane) yielded **2f** as a yellow oil (246.5 mg, 54%).

R_f = 0.09 (1:4 EtOAc:hexane).

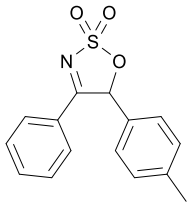
^{1}H NMR (500 MHz, $CDCl_3$ δ 7.52 – 7.45 (m, 3H), 7.38 – 7.32 (m, 2H), 6.00 (s, 1H), 2.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 182.4, 131.5, 131.3, 130.2, 127.8, 91.9, 17.9.

LRESI-MS (ESI –ve): *m/z* 210 $[M - H]^-$ (80%).

The NMR spectroscopic data agreed with those reported.[27]

4-Phenyl-5-(*p*-tolyl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (2g).



2g

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3b** (187.0 mg, 0.826 mmol), CSI (0.14 mL, 1.608 mmol), *t*-BuOH (0.15 mL, 1.568 mmol), and Et_3N (0.15 mL, 1.076 mmol) in THF (4 mL), then *p*TSA•H_2O (12.1 mg, 0.064 mmol) in THF (8 mL). Purification by FCC (1:3 EtOAc:hexane) yielded **2g** as a white solid (51.8 mg, 22%).

Mp: 144–147 °C

R_f = 0.28 (1:3 EtOAc:hexane).

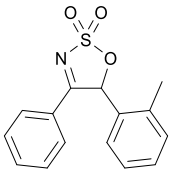
IR (neat): 468, 497, 565, 675, 769, 812, 899, 953, 1183, 1360, 1450, 1495, 1567, 1595 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.78 (m, 2H), 7.63 – 7.52 (m, 1H), 7.49 – 7.33 (m, 2H), 7.32 – 7.24 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.64 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 141.3, 135.1, 130.5, 130.3, 129.7, 129.2, 128.5, 127.3, 89.8, 21.3.

HRESI-MS (ESI –ve): Found 286.0536, calc for $C_{15}H_{12}NO_3S$ 286.0538 $[M - H]^-$.

4-Phenyl-5-(*o*-tolyl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (2h).



2h

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3a** (350.0 mg, 1.5468 mmol), CSI (0.19 mL, 2.183 mmol), *t*-BuOH (0.25 mL, 2.614 mmol), and Et_3N (0.26

mL, 1.865 mmol) in THF (5 mL), then *p*TSA•H_2O (27.5 mg, 0.145 mmol) in THF (16 mL). Purification by FCC (1:4 EtOAc:hexane) yielded **2h** as a white solid (244.1 mg, 48%).

Mp: 135–138 °C

R_f = 0.20 (1:4 EtOAc:hexane).

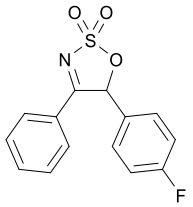
IR (neat): 449, 470, 502, 598, 675, 769, 810, 906, 937, 949, 1182, 1364, 1450, 1493, 1568, 1595 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.74 (m, 2H), 7.60 (ddt, *J* = 8.3, 7.3, 1.5 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.37 – 7.28 (m, 2H), 7.18 (td, *J* = 7.4, 1.8 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.87 (s, 1H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 137.2, 135.2, 131.7, 131.04, 131.01, 130.1, 129.4, 129.1, 127.5, 127.4, 87.0, 19.2.

HRESI-MS (ESI –ve): Found 286.0549, calc for $C_{15}H_{12}NO_3S$ 286.0538 $[M - H]^-$.

5-(4-Fluorophenyl)-4-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2i).



2i

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3h** (410.7 mg, 1.784 mmol), CSI (0.19 mL, 2.183 mmol), *t*-BuOH (0.26 mL, 2.719 mmol), and Et_3N (0.40 mL, 2.870 mmol) in THF (18 mL), then *p*TSA•H_2O (18.4 mg, 0.097 mmol) in THF (20 mL). Purification by FCC (1:4 EtOAc:hexane) yielded **2i** as a white solid (304.2 mg, 59%).

Mp: 175–177 °C

R_f = 0.19 (1:4 EtOAc:hexane).

IR (neat): 473, 507, 615, 677, 773, 811, 900, 964, 1190, 1362, 1450, 1510, 1567, 1594 cm^{-1}.

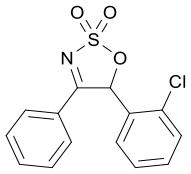
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 – 7.81 (m, 2H), 7.65 – 7.58 (m, 1H), 7.50 – 7.37 (m, 5H), 7.17 – 7.09 (m, 2H), 6.67 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 175.9, 163.9 (d, *J* = 252.0 Hz), 135.4, 130.7 (d, *J* = 9.0 Hz), 130.2, 129.4, 128.6 (d, *J* = 3.5 Hz), 126.9, 117.1 (d, *J* = 22.3 Hz), 88.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ −45.70 (tt, *J* = 8.3, 5.0 Hz).

HRESI-MS (ESI –ve): Found 290.0297, calc for $C_{14}H_9NO_3SF$ 290.0287 $[M - H]^-$.

5-(2-Chlorophenyl)-4-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2j).



2j

The titled compound was prepared following the General procedure F using α-hydroxyketone **S3g** (597.7 mg, 2.423 mmol), CSI (0.26 mL, 2.987 mmol), *t*-BuOH (0.35 mL, 3.660 mmol), and Et_3N (0.40 mL, 2.870 mmol) in THF (23 mL), then *p*TSA•H_2O (54.2 mg, 0.285 mmol) in THF (25 mL). Purification by FCC (1:4 EtOAc:hexane) yielded **2j** as an off-white solid (464.7 mg, 62%).

Mp: 139–140 °C

R_f = 0.22 (1:4 EtOAc:hexane).

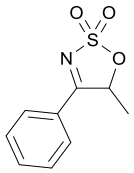
IR (neat): 472, 515, 591, 671, 770, 810, 910, 959, 1184, 1370, 1445, 1477, 1568, 1595 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.80 (m, 2H), 7.61 (ddt, *J* = 8.7, 7.1, 1.2 Hz, 1H), 7.52 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.38 (ddd, *J* = 8.1, 7.2, 1.8 Hz, 1H), 7.31 – 7.18 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 135.5, 134.1, 132.3, 130.6, 130.0, 129.9, 129.5, 128.5, 126.9, 85.6.

HRESI-MS (ESI –ve): Found 305.9994, calc for $C_{14}H_9NO_3S^{35}Cl$ 305.9992 $[M - H]^-$.

5-Methyl-4-phenyl-5H-1,2,3-oxathiazole 2,2-dioxide (2k).



2k

The titled compound was prepared following the General procedure G using α-hydroxyketone **S3m** (500.0 mg, 3.329 mmol), CSI (0.6 mL, 6.885 mmol), HCOOH (0.25 mL, 6.612 mmol), and pyridine (0.55

mL, 6.827 mmol) in MeCN (13mL). Purification by FCC (1:6 EtOAc:hexane) yielded **2k** as an orange solid (266.0 mg, 38%).

R_f = 0.03 (1:6 EtOAc:hexane).

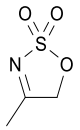
^{1}H NMR (500 MHz, $CDCl_3$ δ 8.02 – 7.85 (m, 2H), 7.80 – 7.65 (m, 1H), 7.66 – 7.53 (m, 2H), 5.95 (q, *J* = 7.0 Hz, 1H), 1.77 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.4, 135.5, 129.7, 129.6, 126.9, 83.9, 20.1.

LRESI-MS (ESI +ve): *m/z* 234 $[M + Na]^+$ (10%).

The NMR spectroscopic data agreed with those reported.[28]

4-Methyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2l).



2l

The titled compound was prepared following the General procedure G using 2-hydroxyacetone (0.5 mL, 7.303 mmol), CSI (2.0 mL, 22.978 mmol), HCOOH (0.85 mL, 22.480 mmol), and pyridine (0.85 mL, 10.5514 mmol) in MeCN (15 mL). Recrystallisation from CH_2Cl_2/hexane furnished the desired product **2l** as an off-white solid (405.0 mg, 41%).

R_f = 0.11 (1:1 EtOAc:hexane).

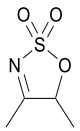
^{1}H NMR (400 MHz, $CDCl_3$): 5.06 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9, 76.9, 17.9.

LRESI-MS (ESI –ve): *m/z* 134 $[M - H]^-$ (70%).

The NMR spectroscopic data agreed with those reported.[29]

4,5-Dimethyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2m).



2m

The titled compound was prepared following the General procedure F using acetoin (0.5 mL, 5.749 mmol), CSI (0.60 mL, 6.893 mmol), *t*-BuOH (0.83 mL, 8.679 mmol), and Et_3N (0.96 mL, 6.888 mmol) in THF (30 mL), then *p*TSA•H_2O (92.7 mg, 0.487 mmol) in THF (60 mL). Purification by FCC (2:3 EtOAc:hexane) yielded **2m** as a yellow oil (286.2 mg, 33%).

R_f = 0.19 (2:3 EtOAc:hexane).

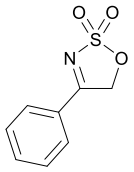
IR (neat): 511, 572, 659, 744, 803, 822, 899, 986, 1056, 1083, 1191, 1228, 1357, 1427, 1626 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.26 (q, *J* = 7.1 Hz, 1H), 2.37 (s, 3H), 1.66 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 184.3, 86.2, 17.8, 17.2.

HRESI-MS (ESI +ve): Found 150.0227, calc for $C_4H_8NO_3S$ 150.0225 $[M + H]^+$.

4-Phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (2n).



2n

The titled compound was prepared following the General procedure F using 2-hydoxyacetophenone (2.1620 g, 15.880 mmol), CSI (1.5 mL, 17.233 mmol), *t*-BuOH (2.2 mL, 23.003 mmol), and Et_3N (3.2 mL, 22.959 mmol) in THF (70 mL), then *p*TSA•H_2O (308.5 mg, 1.622 mmol) in THF (50 mL). Recrystallisation from CH_2Cl_2/hexane furnished the desired product **2n** as an off-white solid (2.1451 g, 68%).

R_f = 0.15 (1:4 EtOAc:hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.89 (m, 2H), 7.74 (ddt, *J* = 7.9, 7.1, 1.3 Hz, 1H), 7.66 – 7.54 (m, 2H), 5.59 (s, 2H).

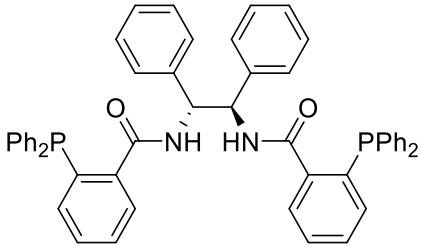
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 135.9, 129.7, 128.9, 127.2, 74.3.

LRESI-MS (ESI –ve): *m/z* 196 $[M - H]^-$ (100%).

The NMR spectroscopic data agreed with those reported.[26]

5. Synthesis of chiral ligand

***N*,*N*'-((1*R*,2*R*)-1,2-Diphenylethane-1,2-diyl)bis(2-(diphenylphosphaneyl)benzamide) (L4).**



L4

Procedure:[30]

To a stirring solution of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (51.1 mg, 0.241 mmol),), 2-(diphenylphosphino)benzoic acid (159.5 mg, 0.521 mmol), and DMAP (7.1 mg, 0.058 mmol) in anhydrous CH_2Cl_2 (5 mL) at rt was added DCC (150.1 mg, 0.727 mmol). The mixture was then stirred at rt for 3.5 h at rt, and the reaction was monitored by TLC. Upon completion, the reaction mixture was filtered through a thin pad of Celite, and the filter cake was washed with CH_2Cl_2. The filtrate was concentrated *in vacuo*, followed by purification by FCC (1:2 EtOAc:hexane) to give **L4** as a white solid (144.8 mg, 76%).

R_f = 0.53 (1:2 EtOAc:hexane)

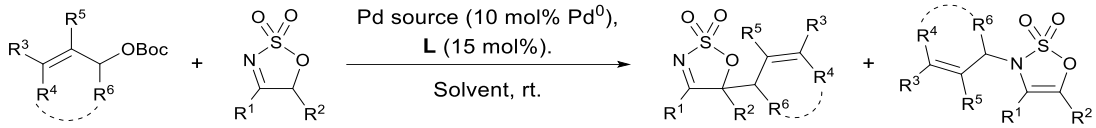
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (ddd, *J* = 5.9, 3.9, 1.8 Hz, 2H), 7.40 – 7.29 (m, 2H), 7.29 – 7.00 (m, 28H), 7.00 – 6.92 (m, 4H), 6.89 (ddd, *J* = 7.1, 3.9, 1.7 Hz, 2H), 5.42 (dd, *J* = 5.5, 2.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ δ 169.3, 140.4 (d, *J* = 24.3 Hz), 138.4, 137.7 (d, *J* = 12.1 Hz), 137.3 (d, *J* = 11.7 Hz), 136.9 (d, *J* = 22.5 Hz), 134.3, 133.9 (d, *J* = 20.2 Hz), 133.6 (d, *J* = 20.2 Hz), 130.3, 128.6, 128.5, 128.4, 128.4, 128.3, 127.91, 127.86, 127.7, 127.4, 59.5.

LRESI-MS (ESI +ve): *m/z* 789 $[M + H]^+$ (100%).

The NMR spectroscopic data agreed with those reported.[30]

6. Synthesis of 3- and 5-allyl cyclic sulfamidate imines



General procedure H:

To a reaction vial charged with $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (5 mol%) and (*R*,*R*)-DACH-Phenyl Trost ligand (15 mol%) was added anhydrous CH_2Cl_2 (0.01 M wrt the Pd(II) dimer), and the resulting solution was stirred for 30 min at rt. In a separate reaction vial, a solution of allyl *tert*-butyl carbonate (1.0 equiv.) and cyclic sulfamidate imine (1.1 equiv.) was prepared in anhydrous CH_2Cl_2 (0.2 M wrt the allyl carbonate). The solution of allyl carbonate and imine was then transferred to the catalyst solution via a cannula, rinsing with anhydrous CH_2Cl_2 (0.2 M wrt the allyl carbonate). The resulting reaction mixture was stirred at rt and monitored by TLC. Upon completion, the reaction was quenched with water, extracted with CH_2Cl_2, and the combined extracts were then washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo,* and then purified by FCC.

*(Note: Most racemate samples were prepared following this procedure using 25 mol% PPh_3 in place of the Trost ligand. The only exception to this was (rac)-**6ca**, which was prepared using a 50:50 mixture of (R,R)- and (S,S)-DACH Phenyl Trost ligand).*

General procedure I:

To a reaction vial charged with $Pd_2dba_3{\bullet}CHCl_3$ (5 mol%) and (*R*,*R*)-DACH-Phenyl Trost ligand (15 mol%) was added anhydrous CH_2Cl_2 (0.01 M wrt $Pd_2dba_3{\bullet}CHCl_3$), and the resulting solution was stirred for 30 min at rt. In a separate reaction vial, a solution of allyl *tert*-butyl carbonate (1.1 equiv.) and cyclic sulfamidate imine (1.0 equiv.) was prepared in anhydrous CH_2Cl_2 (0.2 M wrt the imine). The solution of allyl carbonate and imine was then transferred to the catalyst solution via a cannula, rinsing with anhydrous CH_2Cl_2 (0.2 M wrt the imine). The resulting reaction mixture was stirred at rt and monitored by TLC. Upon completion, the reaction was quenched with water, extracted with CH_2Cl_2, and the combined organic extracts were then washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo,* and then purified by FCC.

General procedure J:

To a reaction vial charged with $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (5 mol%) and (*S*)-BINAP ligand (15 mol%) was added anhydrous THF (0.01 M wrt the Pd(II) dimer), and the resulting solution was stirred for 30 min at rt. In a separate reaction vial, a solution of allyl *tert*-butyl carbonate (1.0 equiv.) and cyclic sulfamidate imine

(1.1 equiv.) was prepared in anhydrous THF (0.2 M wrt the allyl carbonate). The solution of allyl carbonate and imine was then transferred to the catalyst solution via a cannula, rinsing with anhydrous THF (0.2 M wrt the allyl carbonate). The resulting reaction mixture was stirred at rt and monitored by TLC. Upon completion, the reaction was quenched with water, extracted with EtOAc, and the combined extracts were then washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo,* and then purified by FCC.

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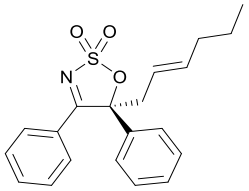
a. 5-Allyl cyclic sulfamidate imines

(*S,E*)-5-(Hex-2-en-1-yl)-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3aa).



3aa

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (43.5 mg, 0.217 mmol), imine **2a** (65.9 mg, 0.241 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.1 mg, 0.011 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (17.8 mg, 0.026 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded **3aa** as a low-melting point white solid (55.7 mg, 72%).

Mp: 75–78 °C

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ +51.9 (*c* 0.10, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 10% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 6.3 min, t_r (major) = 6.7 min.

R_f = 0.15 (1:9 EtOAc:hexane).

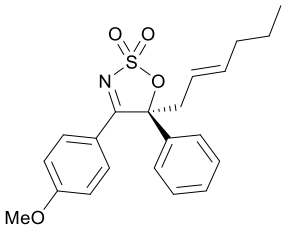
IR (neat): 534, 600, 654, 755, 813, 853, 957, 975, 1041, 1195, 1364, 1449, 1565, 1593, 2871, 2927, 2959 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 – 7.63 (m, 2H), 7.61 – 7.51 (m, 3H), 7.51 – 7.43 (m, 3H), 7.42 – 7.32 (m, 2H), 5.42 (dddt, *J* = 15.4, 8.4, 5.5, 1.5 Hz, 1H), 5.35 – 5.20 (m, 1H), 3.44 (ddq, *J* = 14.7, 5.6, 1.3 Hz, 1H), 3.15 (ddd, *J* = 14.7, 8.5, 0.8 Hz, 1H), 1.98 – 1.81 (m, 2H), 1.23 (h, *J* = 7.4 Hz, 2H), 0.78 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): 179.1, 138.5, 135.7, 134.5, 130.6, 130.5, 129.6, 129.6, 129.0, 127.6, 126.9, 119.7, 100.2, 39.0, 34.5, 22.1, 13.6.

HRESI-MS (ESI –ve): Found 354.1181, calc for $C_{20}H_{20}NO_3S$ 354.1164 $[M - H]^-$.

(*S,E*)-5-(Hex-2-en-1-yl)-4-(4-methoxyphenyl)-5-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ab).



3ab

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (41.5 mg, 0.207 mmol), imine **2b** (74.2 mg, 0.245 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.7 mg, 0.010 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (24.3 mg, 0.035 mmol). Purification by FCC (1.5:8.5 EtOAc:hexane) yielded **3ab** as a colourless oil (51.4 mg, 64%).

$[\alpha]_D^{25}$ +37.7 (*c* 0.50, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 15.2 min, t_r (major) = 18.5 min.

R_f = 0.16 (1.5:8.5 EtOAc:hexane).

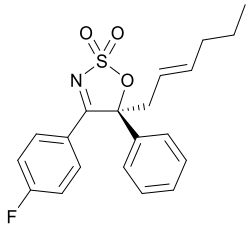
IR (neat): 558, 694, 756, 817, 842, 930, 972, 1032, 1169, 1195, 1265, 1360, 1451, 1512, 1549, 1581, 2871, 2928, 2958 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.64 (m, 2H), 7.58 – 7.50 (m, 2H), 7.50 – 7.42 (m, 3H), 6.92 – 6.74 (m, 2H), 5.43 (dddt, *J* = 15.2, 8.2, 5.4, 1.3 Hz, 1H), 5.30 (dt, *J* = 15.2, 6.7 Hz, 1H), 3.83 (s, 3H), 3.45 (ddq, *J* = 14.5, 5.6, 1.2 Hz, 1H), 3.14 (dd, *J* = 14.5, 8.2 Hz, 1H), 1.95 – 1.82 (m, 2H), 1.33 – 1.15 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 164.6, 138.2, 136.2, 133.1, 130.3, 129.5, 126.9, 120.0, 119.7, 114.5, 99.7, 55.6, 39.4, 34.5, 22.1, 13.6.

HRESI-MS (ESI +ve): Found 408.1238, calc for $C_{21}H_{23}NO_4SNa$ 408.1245 $[M + Na]^+$.

(*S,E*)-4-(4-Fluorophenyl)-5-(hex-2-en-1-yl)-5-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ac).



3ac

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (37.8 mg, 0.189 mmol), imine **2c** (61.9 mg, 0.213 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.7 mg, 0.010 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (20.6 mg, 0.030 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded **3ac** as a colourless oil (44.3 mg, 60%).

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ +47.5 (*c* 0.39, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 9.2 min, t_r (major) = 10.3 min.

R_f = 0.18 (1:9 EtOAc:hexane).

IR (neat): 556, 648, 694, 756, 819, 847, 930, 975, 1038, 1159, 1194, 1243, 1283, 1367, 1451, 1508, 1570, 1600, 2872, 2928, 2959 cm^{-1}.

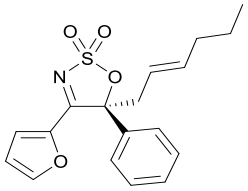
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.65 (m, 2H), 7.58 – 7.42 (m, 5H), 7.10 – 7.00 (m, 2H), 5.42 (dddt, *J* = 15.2, 8.2, 5.4, 1.3 Hz, 1H), 5.34 – 5.21 (m, 1H), 3.46 (ddq, J = 14.6, 5.4, 1.2 Hz, 1H), 3.19 – 3.05 (m, 1H), 1.95 – 1.84 (m, 2H), 1.28 – 1.17 (m, 2H), 0.79 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.7, 166.3 (d, *J* = 259.3 Hz), 138.5, 135.6, 133.4, 133.3 (d, *J* = 9.5 Hz), 130.7, 129.8, 129.7, 126.8, 123.89 (d, *J* = 3.3 Hz), 119.6, 116.5 (d, *J* = 22.2 Hz), 99.9, 39.1, 34.5, 22.1, 13.5.

^{19}F NMR (470 MHz, $CDCl_3$) δ −46.60 (tt, *J* = 8.1, 4.9 Hz).

HRESI-MS (ESI +ve): Found 374.1225, calc for $C_{20}H_{21}NO_3SF$ 374.1226 $[M + H]^+$.

(*S,E*)-4-(Furan-2-yl)-5-(hex-2-en-1-yl)-5-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ad).



3ad

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (33.0 mg, 0.165 mmol), imine **2d** (51.8 mg, 0.197 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.2 mg, 0.009 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (17.1 mg, 0.025 mmol). Purification by FCC (1:4 EtOAc:hexane) yielded **3ad** as light yellow solid (38.1 mg, 67%).

Mp: 87–90 °C

$[\alpha]_D^{25}$ +100.3 (*c* 0.11, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 190 nm, t_r (minor) = 12.8 min, t_r (major) = 13.9 min.

R_f = 0.17 (1:4 EtOAc:hexane).

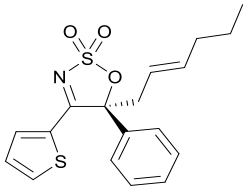
IR (neat): 559, 651, 694, 756, 779, 822, 856, 933, 970, 1049, 1161, 1192, 1356, 1466, 1540, 1583, 1597, 2870, 2927, 2957 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, J = 1.7, 0.7 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.46 – 7.32 (m, 4H), 6.60 (dd, *J* = 3.7, 1.7 Hz, 1H), 5.61 – 5.34 (m, 2H), 3.48 – 3.21 (m, 2H), 1.92 (tdd, *J* = 7.0, 4.5, 1.7 Hz, 2H), 1.36 – 1.14 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 149.3, 144.2, 138.1, 135.5, 129.9, 129.1, 126.8, 123.1, 120.4, 113.7, 99.2, 39.3, 34.5, 22.1, 13.5.

HRESI-MS (ESI +ve): Found 346.1128, calc for $C_{18}H_{20}NO_4S$ 346.1113 $[M + H]^+$.

(*S,E*)-5-(Hex-2-en-1-yl)-5-phenyl-4-(2-thienyl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ae).



3ae

The titled compound was prepared following the General procedure H using allyl carbonate **1** (32.9 mg, 0.164 mmol), imine **2e** (51.5 mg, 0.184 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.4 mg, 0.009 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (18.6 mg, 0.027 mmol). Purification by FCC (1:4 EtOAc:hexane) yielded **3ae** as a white solid (32.8 mg, 55%).

Mp: 91–93 °C

$[\alpha]_D^{25}$ +63.6 (*c* 0.10, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 13.5 min, t_r (major) = 16.1 min.

$\mathbf{R_f}$ = 0.20 (1:4 EtOAc:hexane).

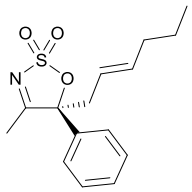
IR (neat): 559, 651, 694, 756, 779, 822, 856, 933, 970, 1049, 1161, 1192, 1356, 1466, 1540, 1583, 1597, 2870, 2927, 2957 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.63 – 7.51 (m, 2H), 7.51 – 7.37 (m, 4H), 7.06 (dd, *J* = 5.0, 4.0 Hz, 1H), 5.55 – 5.34 (m, 2H), 3.51 – 3.37 (m, 1H), 3.24 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.01 – 1.86 (m, 2H), 1.35 – 1.16 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 138.4, 136.6, 136.4, 135.7, 130.8, 130.5, 129.5, 129.0, 127.1, 119.9, 99.3, 39.7, 34.5, 22.1, 13.6.

HRESI-MS (ESI +ve): Found 384.0717, calc for $C_{18}H_{19}NO_3S_2Na$ 384.0704 $[M + Na]^+$.

(*S,E*)-5-(Hex-2-en-1-yl)-4-methyl-5-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3af).



3af

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (32.6 mg, 0.163 mmol), imine **2f** (39.2 mg, 0.186 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.0 mg, 0.008 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (19.3 mg, 0.028 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded **3af** as a light yellow oil (27.0 mg, 57%).

$[\alpha]_D^{25}$ +174.6 (*c* 0.19, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 190 nm, t_r (minor) = 10.7 min, t_r (major) = 12.1 min.

R_f = 0.09 (1:9 EtOAc:hexane).

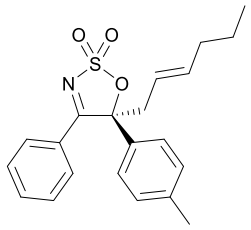
IR (neat): 543, 696, 754, 791, 823, 851, 920, 977, 1042, 1198, 1368, 1450, 1626, 1651, 2872, 2928, 2959 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.37 (m, 5H), 5.72 (dtt, *J* = 15.1, 6.7, 1.2 Hz, 1H), 5.43 (dddt, *J* = 15.1, 8.4, 5.6, 1.5 Hz, 1H), 3.14 (ddq, *J* = 14.8, 5.6, 1.3 Hz, 1H), 3.02 (ddd, *J* = 14.9, 8.3, 0.9 Hz, 1H), 2.15 (s, 3H), 2.06 – 1.96 (m, 2H), 1.44 – 1.32 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 138.2, 134.4, 129.9, 129.4, 126.0, 120.1, 100.5, 38.5, 34.5, 22.1, 16.3, 13.5.

HRESI-MS (ESI +ve): Found 316.0995, calc for $C_{15}H_{19}NO_3SNa$ 316.0983 $[M + Na]^+$.

(*S*,*E*)-5-(Hex-2-en-1-yl)-4-phenyl-5-(*p*-tolyl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ag).



3ag

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (42.8 mg, 0.214 mmol), imine **2h** (60.0 mg, 0.209 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.6 mg, 0.010 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (23.4 mg, 0.039 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded **3ag** as an beige solid (52.0 mg, 66%).

Mp: 109–111 °C

$[\alpha]_D^{25}$ +30.0 (*c* 0.10, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 8.0 min, t_r (major) = 8.4 min.

R_f = 0.20 (1:9 EtOAc:hexane).

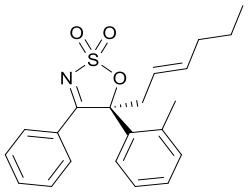
IR (neat): 535, 671, 771, 805, 854, 924, 960, 1043, 1194, 1283, 1361, 1448, 1565, 1595, 2872, 2924, 2956 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.59 (m, 2H), 7.62 – 7.50 (m, 1H), 7.51 – 7.32 (m, 4H), 7.32 – 7.20 (m, 2H), 5.41 (dddt, *J* = 15.4, 8.3, 5.4, 1.4 Hz, 1H), 5.23 (dt, *J* = 15.4, 6.7 Hz, 1H), 3.42 (ddq, *J* = 14.6, 5.6, 1.3 Hz, 1H), 3.11 (dd, *J* = 14.6, 8.5 Hz, 1H), 2.38 (s, 3H), 1.95 – 1.80 (m, 2H), 1.22 (h, *J* = 7.4 Hz, 2H), 0.78 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.2, 140.8, 138.3, 134.4, 132.8, 130.6, 130.3, 129.0, 127.7, 126.9, 126.8, 119.8, 100.3, 39.1, 34.5, 22.1, 21.3, 13.6.

HRESI-MS (ESI +ve): Found 392.1299, calc for $C_{21}H_{23}NO_3SNa$ 392.1296 $[M + Na]^+$.

(*S,E*)-5-(Hex-2-en-1-yl)-4-phenyl-5-(*o*-tolyl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ah).



3ah

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (42.2 mg, 0.211 mmol), imine **2h** (70.6 mg, 0.246 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.0 mg, 0.011 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (24.2 mg, 0.035 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded **3ah** as a colourless oil (48.1 mg, 62%).

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 7.3 min, t_r (major) = 7.7 min.

R_f = 0.20 (1:9 EtOAc:hexane).

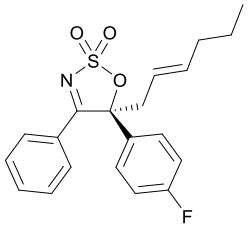
IR (neat): 536, 598, 654, 755, 808, 854, 928, 961, 1195, 1281, 1365, 1448, 1562, 1592, 2871, 2927, 2958 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dt, *J* = 7.7, 1.3 Hz, 2H), 7.58 (ddt, *J* = 8.7, 7.2, 1.2 Hz, 1H), 7.41 – 7.24 (m, 5H), 7.21 (ddd, *J* = 6.8, 1.9, 1.0 Hz, 1H), 5.54 (dddt, *J* = 15.0, 7.5, 6.1, 1.4 Hz, 1H), 5.37 (dtt, *J* = 15.0, 6.8, 1.2 Hz, 1H), 3.61 – 3.45 (m, 1H), 3.08 (ddt, *J* = 15.1, 7.6, 1.0 Hz, 1H), 2.32 (s, 3H), 2.02 – 1.86 (m, 2H), 1.34 – 1.17 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8, 139.0, 137.9, 134.8, 133.6, 133.2, 130.6, 130.5, 129.1, 128.1, 127.9, 126.5, 120.9, 99.2, 41.5, 34.6, 22.1, 20.8, 13.6.

HRESI-MS (ESI +ve): Found 392.1289, calc for $C_{21}H_{23}NO_3SNa$ 392.1296 $[M + Na]^+$.

(*S,E*)-5-(4-Fluorophenyl)-5-(hex-2-en-1-yl)-4-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ai).



3ai

The titled compound was prepare following the General procedure H using allyl carbonate **1a** (42.7 mg, 0.213 mmol), imine **2i** (68.6 mg, 0.236 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.1 mg, 0.011 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (24.0 mg, 0.035 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded an inseparable mixture of **3ai** and **3ac** (7.1:1 molar ratio) as a colourless oil (56.2 mg, 71%).

Mp: 82–86 °C

Chiral HPLC: Chiralpak® IG-3, 1.5% isopropanol/hexanes, 0.75 mL/min, 206 nm, t_r (major) = 38.5 min, t_r (minor) = 43.2 min.

R_f = 0.23 (1.5:8.5 EtOAc:hexane).

IR (neat): 553, 687, 759, 816, 857, 922, 972, 1038, 1180, 1284, 1356, 1452, 1513, 1562, 1593, 2871, 2924, 2958 cm^{-1}.

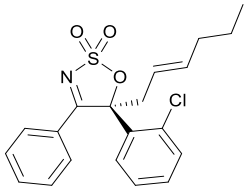
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.63 (m, 2H), 7.63 – 7.49 (m, 3H), 7.45 – 7.35 (m, 2H), 7.21 – 7.11 (m, 2H), 5.40 (dddt, *J* = 15.2, 8.1, 5.4, 1.3 Hz, 1H), 5.26 (dt, *J* = 15.2, 6.5 Hz, 1H), 3.49 – 3.37 (m, 1H), 3.13 (dd, *J* = 14.5, 8.3 Hz, 1H), 1.97 – 1.81 (m, 2H), 1.23 (app. h, *J* = 7.3 Hz, 2H), 0.78 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.8, 163.6 (d, *J* = 252.0 Hz), 138.7, 138.5, 134.6, 133.4, 131.8 (d, *J* = 3.6 Hz), 130.7, 130.6, 130.5, 129.7, 129.2, 129.1, 129.0, 127.4, 126.8, 119.5, 116.8 (d, *J* = 21.9 Hz), 99.4, 39.3, 34.5, 22.0, 13.5.

^{19}F NMR (470 MHz, $CDCl_3$) δ −38.42 (tt, *J* = 8.1, 5.2 Hz).

HRESI-MS (ESI +ve): Found 396.1053, calc for $C_{20}H_{20}NO_3SFNa$ 396.1046 $[M + Na]^+$.

(*S,E*)-5-(2-Chlorophenyl)-5-(hex-2-en-1-yl)-4-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3aj).



3aj

The titled compound was prepared following the General procedure I using allyl carbonate **1a** (43.2 mg, 0.217 mmol), imine **2j** (59.6 mg, 0.194 mmol), Pd_2dba_3•$CHCl_3$ (9.5 mg, 0.009 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (21.4 mg, 0.030 mmol). Purification by FCC (1:4 EtOAc:hexane) yielded **3aj** as a light yellow oil (48.5 mg, 64%).

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 14.6 min, t_r (major) = 12.7 min.

R_f = 0.19 (1:4 EtOAc:hexane).

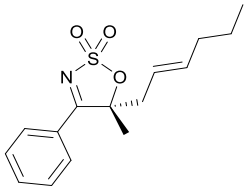
IR (neat): 554, 685, 753, 808, 856, 933, 975, 1033, 1195, 1279, 1366, 1448, 1563, 1593, 2871, 2928, 2958 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.80 (m, 1H), 7.78 – 7.70 (m, 2H), 7.59 (ddt, *J* = 8.7, 7.2, 1.2 Hz, 1H), 7.46 – 7.32 (m, 5H), 5.53 (dddt, *J* = 15.1, 7.5, 6.1, 1.3 Hz, 1H), 5.38 (dtt, *J* = 14.9, 6.8, 1.2 Hz, 1H), 3.66 – 3.42 (m, 1H), 3.09 (ddq, *J* = 14.9, 7.5, 0.9 Hz, 1H), 1.95 – 1.83 (m, 2H), 1.40 – 1.15 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.8, 138.2, 135.0, 134.8, 132.8, 132.5, 131.8, 130.2, 129.6, 129.6, 129.1, 127.9, 127.4, 120.5, 97.1, 41.4, 34.6, 22.0, 13.6

HRESI-MS (ESI +ve): Found 412.0752, calc for $C_{20}H_{20}NO_3S^{35}ClNa$ 412.0750 $[M + Na]^+$.

(*R,E*)-5-(Hex-2-en-1-yl)-5-methyl-4-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ak).



3ak

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (33.0 mg, 0.165 mmol), imine **2k** (41.3 mg, 0.196 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.3 mg, 0.009 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (18.2 mg, 0.026 mmol). Purification by FCC (1.5:8.5 EtOAc:hexane) yielded **3ak** as a light yellow oil (27.0 mg, 56%).

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 11.0 min, t_r (major) = 11.6 min.

R_f = 0.13 (1.5:8.5 EtOAc:hexane).

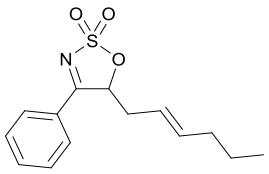
IR (neat): 654, 695, 778, 820, 861, 920, 974, 991, 1173, 1200, 1363, 1450, 1562, 1593, 2872, 2929, 2959 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 – 7.96 (m, 2H), 7.75 – 7.63 (m, 1H), 7.63 – 7.50 (m, 2H), 5.51 – 5.38 (m, 1H), 5.33 (dddt, *J* = 15.3, 7.9, 6.7, 1.2 Hz, 1H), 2.93 – 2.79 (m, 2H), 1.96 – 1.83 (m, 5H), 1.31 – 1.18 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 181.0, 138.3, 134.9, 130.4, 129.5, 127.5, 120.4, 98.5, 42.7, 34.6, 25.4, 22.3, 13.7.

HRESI-MS (ESI +ve): Found 316.0992, calc for $C_{15}H_{19}NO_3SNa$ 319.0983 $[M + Na]^+$.

(*E*)-5-(Hex-2-en-1-yl)-4-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3an).



3an

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (46.5 mg, 0.232 mmol), imine **2l** (51.1 mg, 0.259 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.3 mg, 0.012 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (26.6 mg, 0.039 mmol). Purification by FCC (1:5 EtOAc:hexane) yielded **3an** as an orange solid (38.4 mg, 59%).

Mp: 65–68 °C

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 21.6 min, t_r (major) = 19.0 min.

R_f = 0.14 (1:5 EtOAc:hexane).

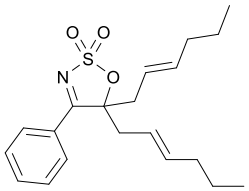
IR (neat): 459, 529, 641, 654, 686, 773, 804, 883, 945, 974, 1193, 1359, 1449, 1571, 1601, 2873, 2926, 2961 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 – 7.83 (m, 2H), 7.78 – 7.67 (m, 1H), 7.63 – 7.53 (m, 2H), 5.91 (dd, *J* = 6.8, 3.5 Hz, 1H), 5.50 – 5.30 (m, 2H), 2.90 – 2.75 (m, 1H), 2.70 – 2.57 (m, 1H), 2.00 – 1.88 (m, 2H), 1.31 (h, *J* = 7.4 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 178.5, 137.3, 135.2, 129.5, 129.5, 127.5, 120.6, 87.8, 36.8, 34.5, 22.1, 13.6.

HRESI-MS (ESI +ve): Found 302.0827, calc for $C_{14}H_{17}NO_3SNa$ 302.0821 $[M + Na]^+$.

5,5-Di((*E*)-hex-2-en-1-yl)-4-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3aan).



3aan

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (46.5 mg, 0.232 mmol), imine **2l** (51.1 mg, 0.259 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.3 mg, 0.012 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (26.6 mg, 0.039 mmol). Purification by FCC (1:5 EtOAc:hexane) **3aan** as a colourless oil (7.0 mg, 8%).

R_f = 0.35 (1:5 EtOAc:hexane).

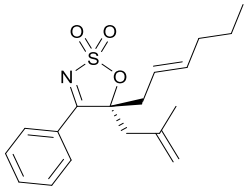
IR (neat): 447, 534, 624, 655, 694, 775, 820, 862, 949, 973, 1196, 1365, 1448, 1563, 1593, 2872, 2928, 2958 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 – 7.97 (m, 2H), 7.71 – 7.65 (m, 1H), 7.60 – 7.49 (m, 2H), 5.48 – 5.31 (m, 4H), 2.96 – 2.88 (m, 2H), 2.85 – 2.77 (m, 2H), 1.96 – 1.83 (m, 4H), 1.29 – 1.19 (m, 4H), 0.76 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 180.0, 137.9, 134.6, 130.2, 130.1, 129.3, 129.2, 127.8, 120.2, 101.8, 41.5, 34.4, 22.1, 13.5.

HRESI-MS (ESI +ve): Found 384.1611, calc for $C_{20}H_{27}NO_3SNa$ 384.1609 $[M + Na]^+$.

(*R,E*)-5-(Hex-2-en-1-yl)-5-(2-methylallyl)-4-phenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3abn).



3abn

The titled compound was prepared following the General procedure I using allyl carbonate **1b** (33.2 mg, 0.193 mmol), imine **3al** (59.8 mg, 0.214 mmol), Pd_2dba_3•$CHCl_3$ (11.1 mg, 0.010 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (20.7 mg, 0.030 mmol). Purification by FCC (1:9 EtOAc:hexane) **3abn** as a colourless oil (44.6 mg, 61%).

Chiral HPLC: Chiralpak® IG-3, 7.5% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 9.7 min, t_r (major) = 10.4 min.

R_f = 0.15 (1:4 EtOAc:hexane).

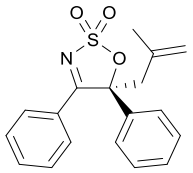
IR (neat): 688, 775, 818, 864, 951, 1180, 1196, 1364, 1448, 1562, 1593, 2927, 2958 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.96 (m, 2H), 7.75 – 7.62 (m, 1H), 7.64 – 7.45 (m, 2H), 5.43 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.37 – 5.26 (m, 1H), 4.96 (app. t, *J* = 1.5 Hz, 1H), 4.70 (app. s, 1H), 3.00 – 2.79 (m, 4H), 1.95 – 1.73 (m, 5H), 1.32 – 1.14 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.1, 138.2, 138.1, 134.7, 130.4, 129.3, 127.8, 120.1, 117.9, 101.1, 45.6, 41.3, 34.4, 24.1, 22.1, 13.4.

HRESI-MS (ESI +ve): Found 334.1477, calc for $C_{18}H_{24}NO_3S$ 334.1483 $[M + H]^+$.

(*S*)-5-(2-Methylallyl)-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ba).



3ba

The titled compound was prepared following the General procedure H using allyl carbonate **1b** (43.6 mg, 0.253 mmol), imine **2a** (79.4 mg, 0.291 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (5.2 mg, 0.014 mmol), and (*R*,*R*)-

DACH-Phenyl Trost ligand (29.1 mg, 0.042 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded **3ba** as a beige solid (48.2 mg, 58%).

Mp: 106–108 °C

$[\alpha]_D^{25}$ +62.5 (*c* 0.12, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 254 nm, t_r (minor) = 10.1 min, t_r (major) = 11.4 min.

R_f = 0.12 (1:9 EtOAc:hexane).

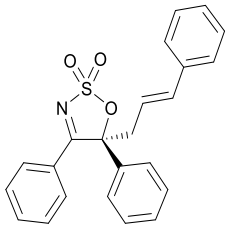
IR (neat): 653, 690, 771, 808, 861, 930, 956, 1186, 1198, 1369, 1448, 1563, 1591 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.66 (m, 2H), 7.61 – 7.54 (m, 3H), 7.51 – 7.44 (m, 3H), 7.42 – 7.35 (m, 2H), 4.93 (app. t, *J* = 1.5 Hz, 1H), 4.44 (app. s, 1H), 3.44 (d, *J* = 14.5 Hz, 1H), 3.29 (dd, *J* = 14.4, 1.0 Hz, 1H), 1.80 (dd, *J* = 1.5, 0.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 137.5, 136.0, 134.4, 130.7, 130.5, 129.6, 129.2, 127.9, 126.9, 118.3, 99.9, 42.9, 24.4.

HRESI-MS (ESI +ve): Found 350.0833, calc for $C_{18}H_{17}NO_3SNa$ 350.0827 $[M + Na]^+$.

(*S*)- 5-Cinnamyl-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ca).



3ca

The titled compound was prepared following the General procedure H using allyl carbonate **1c** (49.4 mg, 0.211 mmol), imine **2a** (67.1 mg, 0.246 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.1 mg, 0.011 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (23.0 mg, 0.033 mmol). Purification by FCC (1:1:8 EtOAc:acetone:hexane) yielded **3ca** as a white solid (44.4 mg, 54%).

Mp: 155–160 °C

$[\alpha]_D^{25}$ +153.3 (*c* 0.09, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 10% isopropanol/hexanes, 0.5 mL/min, 254 nm, t_r (minor) = 22.0 min, t_r (major) = 24.2 min.

R_f = 0.09 (1:1:8 EtOAc:acetone:hexane).

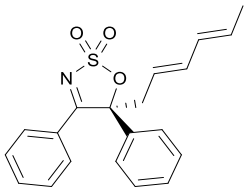
IR (neat): 652, 688, 769, 818, 865, 922, 966, 984, 1181, 1194, 1366, 1448, 1565, 1595 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.61 (m, 2H), 7.61 – 7.53 (m, 3H), 7.52 – 7.45 (m, 3H), 7.40 – 7.32 (m, 2H), 7.29 – 7.18 (m, 5H), 6.20 (ddd, *J* = 15.8, 8.7, 5.2 Hz, 1H), 6.15 – 6.05 (m, 1H), 3.66 (ddd, *J* = 14.7, 5.3, 1.5 Hz, 1H), 3.32 (dd, *J* = 14.5, 8.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 136.4, 136.3, 135.5, 134.5, 130.6, 130.5, 129.7, 129.1, 128.5, 127.9, 127.5, 126.9, 126.5, 119.7, 99.9, 39.3.

HRESI-MS (ESI –ve): Found 388.1003, calc for $C_{23}H_{18}NO_3S$ 388.1007 $[M - H]^-$.

(*S*)-5-((2*E*,4*E*)-Hexa-2,4-dien-1-yl)-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3da).



3da

The titled compound was prepared following the General procedure H using allyl carbonate **1d** (49.0 mg, 0.247 mmol), imine **2a** (76.2 mg, 0.279 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.6 mg, 0.013 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (26.0 mg, 0.038 mmol). Purification by FCC (1:4 Et_2O:hexane) yielded **3da** as a beige solid (26.0 mg, 30%).

Mp: 118–122 °C

$[\alpha]_D^{25}$ +101.1 (*c* 0.21, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 2% isopropanol/hexanes, 1.0 mL/min, 206 nm, t_r (minor) = 11.8 min, t_r (major) = 13.2 min.

R_f = 0.18 (1:4 Et_2O:hexane).

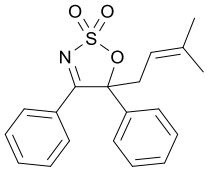
IR (neat): 654, 692, 772, 810, 853, 937, 963, 1182, 1196, 1361, 1448, 1564, 1595 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.61 (m, 2H), 7.59 – 7.51 (m, 3H), 7.51 – 7.44 (m, 3H), 7.41 – 7.31 (m, 2H), 6.11 – 5.91 (m, 1H), 5.87 – 5.67 (m, 1H), 5.65 – 5.37 (m, 2H), 3.50 (ddd, *J* = 15.2, 5.9, 1.3 Hz, 1H), 3.32 – 3.06 (m, 1H), 1.76 – 1.62 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 137.0, 135.6, 134.4, 130.6, 130.5, 130.4, 129.7, 129.0, 127.6, 126.9, 119.7, 99.9, 39.0, 18.0.

HRESI-MS (ESI +ve): Found 376.0998, calc for $C_{20}H_{19}NO_3SNa$ 376.0983 $[M + Na]^+$.

5-(3-Methylbut-2-en-1-yl)-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ea).



3ea

The titled compound was prepared following the General procedure H using allyl carbonate **1e** (44.3 mg, 0.238 mmol), imine **2a** (72.1 mg, 0.264 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.5 mg, 0.012 mmol), and Ph_3P ligand (18.8 mg, 0.072 mmol). Purification by FCC (1:5 EtOAc:hexane) yielded **3ea** as a white solid (12.9 mg, 16%).

Mp: 126–128 °C

R_f = 0.17 (1:5 EtOAc:hexane).

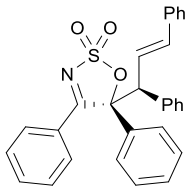
IR (neat): 654, 693, 772, 806, 862, 930, 965, 1177, 1197, 1362, 1448, 1564, 1594 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 – 7.64 (m, 2H), 7.61 – 7.52 (m, 3H), 7.53 – 7.44 (m, 3H), 7.42 – 7.33 (m, 2H), 5.10 (ddp, *J* = 7.7, 6.1, 1.4 Hz, 1H), 3.50 – 3.31 (m, 1H), 3.20 (dd, *J* = 14.9, 8.4 Hz, 1H), 1.65 (s, 3H), 1.26 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.4, 139.6, 136.1, 134.6, 130.72, 130.70, 129.8, 129.2, 127.8, 127.1, 114.0, 100.7, 34.6, 26.1, 18.0.

HRESI-MS (ESI –ve): Found 340.1016, calc for $C_{19}H_{18}NO_3S$ 340.1007 $[M – H]^-$.

(*S*)-5-((*S,E*)-1,3-diphenylallyl)-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3fa).



3fa

The titled compound was prepared following the General procedure J using allyl carbonate **1f** (61.2 mg, 0.197 mmol), imine **2a** (71.6 mg, 0.262 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.9 mg, 0.011 mmol), and (*S*)-BINAP ligand (21.4 mg, 0.034 mmol). Purification by FCC (1:6 EtOAc:hexane) followed by recrystallisation from THF/*n*-hexane (1:2) yielded the major diastereoisomer of **3fa** as a white solid (49.6 mg, 42%).

Mp: 176–178 °C

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ +278.1 (*c* 0.13, $CHCl_3$)

R_f = 0.15 (1:6 EtOAc:hexane).

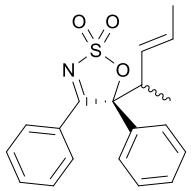
IR (neat): 662, 689, 764, 816, 933, 970, 1195, 1366, 1448, 1564, 1593 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 5H), 7.52 – 7.44 (m, 2H), 7.44 – 7.32 (m, 5H), 7.32 – 7.15 (m, 8H), 6.45 (dd, *J* = 15.7, 9.7 Hz, 1H), 5.92 (d, *J* = 15.7 Hz, 1H), 4.62 (d, *J* = 9.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.1, 137.7, 136.0, 134.1, 134.0, 133.7, 130.4, 129.9, 129.5, 129.1, 129.0, 128.9, 128.6, 128.6, 128.3, 128.1, 127.4, 126.7, 125.7, 102.5, 54.2.

HRESI-MS (ESI +ve): Found 488.1300, calc for $C_{29}H_{23}NO_3SNa$ 488.1296 $[M + Na]^+$.

(*E*)-5-(Pent-3-en-2-yl)-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ga).



3ga

The titled compound was prepared following the General procedure J using allyl carbonate **1g** (47.1 mg, 0.253 mmol), imine **2a** (79.2 mg, 0.290 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.8 mg, 0.013 mmol), and (*S*)-

BINAP ligand (37.1 mg, 0.060 mmol). Purification by FCC (1:4 EtOAc:hexane) yielded a mixture of two diastereoisomers of **3ga** (*dr* = 1.4:1) as a colourless oil (30.9 mg, 36%).

R_f = 0.34 (1:4 EtOAc:hexane).

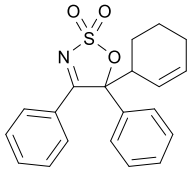
IR (neat): 655, 694, 773, 822, 937, 974, 1196, 1360, 1448, 1560, 1589 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) (1.4:1 mixture of two diastereoisomers, minor isomer labelled with an asterisk): δ 7.83 – 7.28 (m, 20H), 5.77 – 5.64* (m, 1H), 5.59* (ddq, *J* = 15.5, 7.7, 1.5 Hz, 1H), 5.49 (ddq, *J* = 15.3, 9.1, 1.6 Hz, 1H), 5.10 (dq, *J* = 15.3, 6.5 Hz, 1H), 3.60* (app. p, J = 7.0 Hz, 1H), 3.49 (dq, *J* = 9.1, 6.7 Hz, 1H), 1.67* (dd, *J* = 6.3, 1.5 Hz, 3H), 1.51 (dd, *J* = 6.5, 1.7 Hz, 3H), 1.32 (d, *J* = 6.6 Hz, 3H), 1.14* (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) (1.4:1 mixture of two diastereoisomers, distinguishable resonances of the minor isomer are labelled with an asterisk): δ 180.1, 179.7, 135.1, 134.4, 134.3, 133.9, 130.5, 130.3, 130.2, 130.2*, 129.9*, 129.9, 129.7, 129.6, 129.4, 129.3, 129.1, 129.0, 128.7, 128.6, 128.0, 128.0, 127.8, 127.8, 126.9, 103.6, 103.2, 42.0, 41.5*, 18.2*, 17.8, 16.7, 16.6*.

HRESI-MS (ESI +ve): Found 364.0995, calc for $C_{19}H_{19}NO_3SNa$ 364.0983 $[M + Na]^+$.

5-(Cyclohex-2-en-1-yl)-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (3ha).



3ha

The titled compound was prepared following the General procedure H using allyl carbonate **1h** (44.0 mg, 0.222 mmol), imine **2a** (68.5 mg, 0.251 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4. 6 mg, 0.013 mmol), and Ph_3P ligand (17.7 mg, 0.067 mmol). Purification by FCC (1:5 EtOAc:hexane) yielded a mixture of two diastereoisomers of **3ha** (*dr* = 1.7:1) as a colourless oil (47.1 mg, 60%).

R_f = 0.31 (1:5 EtOAc:hexane).

IR (neat): 669, 691, 756, 817, 941, 968, 1194, 1360, 1448, 1558, 1590, 2938 cm^{-1}.

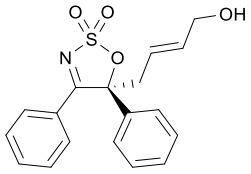
^{1}H NMR (500 MHz, $CDCl_3$) (1.7:1 mixture of two diastereoisomers, minor isomer labelled with an asterisk): δ 7.89 – 7.33 (m, 15H), 6.01–5.97* (app. m, *J* = 10.2, 3.9, 2.8 Hz, 0.6 H), 5.92–5.87 (app. m,

1H), 5.74 (dp, *J* = 10.3, 1.9 Hz, 1H), 5.37* (app. d, *J*=10.3 Hz, 0.6H), 3.68 (dtt, *J* = 10.8, 4.2, 2.2 Hz, 1H), 3.62* (ddp, *J* = 8.3, 5.6, 2.7 Hz, 0.6 H), 2.20 – 1.41 (m, 6.6 H).

^{13}C NMR (125 MHz, $CDCl_3$, 1.7:1 mixture of two diastereoisomers, distinguishable resonances of the minor isomer are labelled with an asterisk): δ 180.3*, 179.1, 134.4, 134.3, 134.2, 134.1, 133.9*, 131.5, 130.1, 130.0, 129.9, 129.7, 129.5*, 129.2, 129.1, 129.0, 128.3, 127.9, 127.7, 127.3, 123.8, 122.4*, 103.7, 102.9, 40.3, 40.1*, 24.7*, 24.6, 24.3*, 23.2, 21.7, 21.1*.

HRESI-MS (ESI –ve): Found 352.1021, calc for $C_{20}H_{18}NO_3S$ 352.1007 $[M - H]^-$.

(*S,E*)-5-(4-Hydroxybut-2-en-1-yl)-4,5-diphenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide (6aa).



6aa

The titled compound was prepared following the General procedure I using 2-vinyloxirane (20 µL, 0.248 mmol), imine **2a** (61.6 mg, 0.225 mmol), Pd_2dba_3•$CHCl_3$ (11.2 mg, 0.011 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (27.1 mg, 0.039 mmol). Purification by FCC (1:2 EtOAc:hexane) yielded **6aa** as a colourless oil (42.6 mg, 49%).

Chiral HPLC: Chiralpak® IG-3, 20% isopropanol/hexanes, 0.5 mL/min, 254 nm, t_r (minor) = 50.4 min, t_r (major) = 55.5 min.

R_f = 0.09 (1:2 EtOAc:hexane).

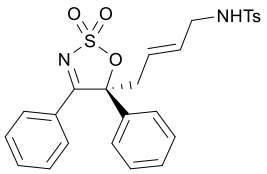
IR (neat): 692, 756, 812, 937, 964, 1193, 1361, 1448, 1563, 1593, 2926, 3359 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.33 (m, 10 H), 5.77 – 5.46 (m, 2H), 4.09 – 3.92 (m, 2H), 3.60 – 3.36 (m, 1H), 3.24 (dd, *J* = 14.3, 6.7 Hz, 1H), 1.97 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.8, 137.5, 135.4, 134.8, 130.7, 130.6, 129.7, 129.2, 127.2, 126.8, 121.4, 99.9, 62.8, 38.3.

HRESI-MS (ESI +ve): Found 366.0769, calc for $C_{18}H_{17}NO_4SNa$ 366.0776 $[M + Na]^+$.

(*S,E*)-*N*-(4-(2,2-Dioxido-4,5-diphenyl-5*H*-1,2,3-oxathiazol-5-yl)but-2-en-1-yl)-4-methylbenzenesulfonamide (6ba).



6ba

The titled compound was prepared following the General procedure H using 1-tosyl-2-vinylaziridine (44.7 mg, 0.200 mmol), imine **2a** (63.0 mg, 0.231 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.5 mg, 0.010 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (29.2 mg, 0.031 mmol). Purification by FCC (1:2 EtOAc:hexane) yielded **6ba** as a colourless oil (51.6 mg, 52%).

Chiral HPLC: Chiralpak® IB-3, 15% isopropanol/hexanes, 1.0 mL/min, 206 nm, t_r (minor) = 25.8 min, t_r (major) = 29.2 min.

R_f = 0.14 (1:2 EtOAc:hexane).

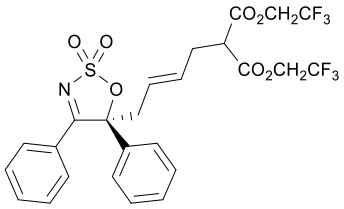
IR (neat): 692, 756, 810, 927, 961, 1155, 1195, 1364, 1448, 1563, 1593, 3294 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 2H), 7.70 – 7.62 (m, 2H), 7.57 (td, *J* = 7.4, 1.3 Hz, 1H), 7.54 – 7.43 (m, 5H), 7.41 – 7.32 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.45 – 5.33 (m, 2H), 4.83 (dd, *J* = 6.9, 5.3 Hz, 1H), 3.48 (ddd, *J* = 13.6, 6.9, 4.0 Hz, 1H), 3.44 – 3.32 (m, 2H), 3.25 – 3.08 (m, 1H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1, 143.8, 137.2, 135.6, 135.4, 133.5, 131.1, 131.0, 130.13, 130.11, 129.7, 127.5, 127.2, 127.1, 124.2, 100.1, 45.2, 38.5, 21.9.

HRESI-MS (ESI –ve): Found 495.1053, calc for $C_{25}H_{23}N_2O_5S_2$ 495.1048 $[M - H]^-$.

Bis(2,2,2-trifluoroethyl) (*S,E*)-2-(4-(2,2-dioxido-4,5-diphenyl-5*H*-1,2,3-oxathiazol-5-yl)but-2-en-1-yl)malonate (6ca).



6ca

The titled compound was prepared following the General procedure H using bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate (70.3 mg, 0.220 mmol), imine **2a** (69.6 mg, 0.255 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.9 mg, 0.011 mmol), and (*R*,*R*)-DACH-Phenyl Trost ligand (24.8 mg, 0.036 mmol). Purification by FCC (1:4 EtOAc:hexane) yielded **6ca** as a colourless oil (57.0 mg, 44%).

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ +41.4 (*c* 0.21, $CHCl_3$)

Chiral HPLC: Chiralpak® IB-3, 10% isopropanol/hexanes, 1.0 mL/min, 206 nm, t_r (minor) = 10.7 min, t_r (major) = 12.3 min.

R_f = 0.15 (1:4 EtOAc:hexane).

IR (neat): 693, 757, 811, 962, 1159, 1198, 1369, 1449, 1566, 1595, 1755 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 2H), 7.58 (ddt, *J* = 8.7, 7.2, 1.2 Hz, 1H), 7.55 – 7.46 (m, 5H), 7.46 – 7.32 (m, 2H), 5.51 (dddt, *J* = 15.2, 7.5, 6.1, 1.2 Hz, 1H), 5.45 – 5.17 (m, 1H), 4.62 – 4.37 (m, 4H), 3.56 (t, *J* = 7.3 Hz, 1H), 3.43 (ddd, *J* = 14.7, 6.3, 1.2 Hz, 1H), 3.23 – 3.10 (m, 1H), 2.72 – 2.53 (m, 2H).

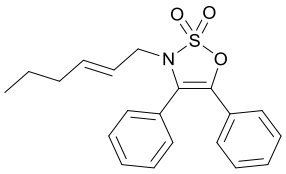
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 166.3 (d, *J* = 11.4 Hz), 135.4, 134.7, 132.5, 130.7, 130.6, 129.7, 129.2, 127.3, 126.8, 124.0, 122.6 (q, *J* = 277.3 Hz), 99.4, 61.1 (two overlapping quartets, *J* = 37.4 Hz), 50.4, 38.7, 31.2.

HRESI-MS (ESI +ve): Found 616.0841, calc for $C_{25}H_{21}NO_7SF_6Na$ 616.0861 $[M + Na]^+$.

b. 3-Allyl cyclic sulfamidate imines

Only a few *N*-allylated products were isolated in any significant amount, and their experimental data are listed below.

(*E*)-3-(Hex-2-en-1-yl)-4,5-diphenyl-3*H*-1,2,3-oxathiazole 2,2-dioxide (4aa).



4aa

The titled compound was prepared following the General procedure H using allyl carbonate **1a*** (46.8 mg, 0.234 mmol), imine **2a** (79.3 mg, 0.290 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.3 mg, 0.012 mmol), and Ph_3P (13.8 mg, 0.053 mmol). Purification by FCC (1:2 EtOAc:hexane) yielded **4aa** as a beige solid (25.8 mg, 31%).

Mp: 69–71 °C

R_f = 0.37 (1:2 EtOAc:hexane).

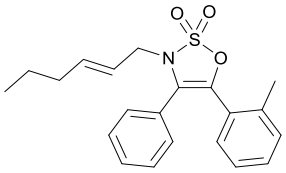
IR (neat): 693, 786, 976, 1007, 1127, 1196, 1375, 1448, 2926, 2955 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.36 (m, 5H), 7.25 – 7.17 (m, 5H), 5.59 – 5.34 (m, 2H), 3.85 (dd, *J* = 6.2, 1.0 Hz, 2H), 1.94 (tdd, *J* = 7.6, 6.3, 1.1 Hz, 2H), 1.39 – 1.26 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.6, 135.3, 130.1, 129.9, 129.2, 128.5, 128.4, 127.7, 127.5, 125.6, 122.6, 48.4, 34.2, 22.0, 13.6.

HRESI-MS (ESI +ve): Found 378.1133, calc for $C_{20}H_{21}NO_3SNa$ 378.1140 $[M + Na]^+$.

(*E*)-3-(Hex-2-en-1-yl)-4-phenyl-5-(o-tolyl)-3*H*-1,2,3-oxathiazole 2,2-dioxide (4ah).



4ah

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (19.8 mg, 0.099 mmol), imine **2h** (29.7 mg, 0.103 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (3.3 mg, 0.009 mmol), and Ph_3P (16.3 mg, 0.062 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded **4ah** as a colourless oil (19.0 mg, 52%).

R_f = 0.19 (1:9 EtOAc:hexane).

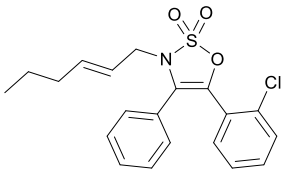
IR (neat): 696, 768, 970, 1010, 1126, 1194, 1381, 1447, 2928, 2958 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (dtt, *J* = 7.7, 3.8, 2.2 Hz, 4H), 7.23 – 7.15 (m, 4H), 7.11 (td, *J* = 7.5, 1.3 Hz, 1H), 5.58 (dtt, *J* = 14.6, 6.6, 1.4 Hz, 1H), 5.51 – 5.41 (m, 1H), 3.95 (dd, *J* = 6.6, 1.0 Hz, 2H), 2.24 (s, 4H), 2.01 – 1.92 (m, 2H), 1.40 – 1.28 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.5, 138.3, 130.8, 130.4, 129.4, 129.0, 128.6, 126.2, 122.5, 50.4, 34.5, 22.2, 19.9, 13.8.

HRESI-MS (ESI +ve): Found 392.1286, calc for $C_{21}H_{23}NO_3SNa$ 392.1296 $[M + Na]^+$.

(*E*)-5-(2-Chlorophenyl)-3-(hex-2-en-1-yl)-4-phenyl-3*H*-1,2,3-oxathiazole 2,2-dioxide (4aj).



4aj

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (21.5 mg, 0.107 mmol), imine **2j** (37.0 mg, 0.127 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (1.9 mg, 0.005 mmol), and Ph_3P (9.2 mg, 0.035 mmol). Purification by FCC (1:9 EtOAc:hexane) yielded **4aj** as a colourless solid (19.2 mg, 55%).

Mp: 57–59 °C

R_f = 0.16 (1:9 EtOAc:hexane).

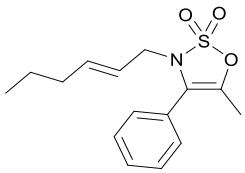
IR (neat): 698, 752, 971, 1012, 1074, 1195, 1370, 1434, 2930, 2955 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.37 – 7.25 (m, 4H), 7.27 – 7.14 (m, 4H), 5.57 (dtt, *J* = 15.4, 6.3, 1.2 Hz, 1H), 5.45 (dtt, *J* = 15.4, 6.7, 1.0 Hz, 1H), 3.96 (app. d, *J* = 6.4 Hz, 2H), 2.06 – 1.87 (m, 2H), 1.34 (app. h, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 135.0, 134.3, 132.3, 131.4, 130.2, 129.5, 128.8, 128.7, 128.5, 127.6, 126.9, 122.3, 50.0, 34.3, 22.0, 13.6.

HRESI-MS (ESI +ve): Found 390.0941, calc for $C_{20}H_{21}NO_3SCl$ 390.0931 $[M + H]^+$.

(*E*)-3-(Hex-2-en-1-yl)-5-methyl-4-phenyl-3*H*-1,2,3-oxathiazole 2,2-dioxide (4ak).



4ak

The titled compound was prepared following the General procedure H using allyl carbonate **1a** (44.0 mg, 0.220 mmol), imine **2k** (52.7 mg, 0.249 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.7 mg, 0.013 mmol), and Ph_3P (18.7 mg, 0.071 mmol). Purification by FCC (1:6 EtOAc:hexane) yielded **4ak** as a pale yellow oil (11.8 mg, 18%).

R_f = 0.35 (1:6 EtOAc:hexane).

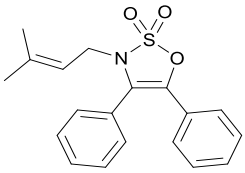
IR (neat): 615, 699, 754, 904, 970, 1185, 1370, 1447, 2872, 2928, 2957 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.27 (m, 5H), 5.55 – 5.32 (m, 2H), 3.79 (app. d, *J* = 6.5 Hz, 2H), 2.13 (s, 3H), 1.93 (tdd, *J* = 7.5, 6.3, 1.0 Hz, 2H), 1.35–1.28 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.7, 136.1, 129.1, 128.9, 128.5, 128.1, 125.5, 122.5, 50.1, 34.2, 22.0, 13.5, 12.2.

HRESI-MS (ESI +ve): Found 316.0976, calc for $C_{15}H_{19}NO_3SNa$ 316.0983 $[M + Na]^+$.

3-(3-Methylbut-2-en-1-yl)-4,5-diphenyl-3*H*-1,2,3-oxathiazole 2,2-dioxide (4ea).



4ea

The titled compound was prepared following the General procedure H using allyl carbonate **1e** (44.3 mg, 0.238 mmol), imine **2a** (72.1 mg, 0.264 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.5 mg, 0.012 mmol), and Ph_3P (18.8 mg, 0.072 mmol). Purification by FCC (1:5 EtOAc:hexane) yielded **4ea** as a white solid (12.8 mg, 16%).

Mp: 104–106 °C

R_f = 0.32 (1:5 EtOAc:hexane).

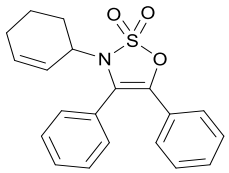
IR (neat): 612, 691, 766, 911, 964, 1188, 1354, 1445, 1657, 2935 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.37 (m, 5H), 7.25 – 7.15 (m, 5H), 5.30–5.23 (m, 1H), 3.93 – 3.87 (m, 2H), 1.65 (d, *J* = 1.2 Hz, 3H), 1.27 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 135.1, 130.0, 129.9, 129.2, 128.4, 128.3, 127.7, 127.5, 125.7, 125.5, 117.4, 44.4, 25.7, 17.3.

HRESI-MS (ESI +ve): Found 364.0986, calc for $C_{19}H_{19}NO_3SNa$ 364.0983 $[M + Na]^+$.

3-(Cyclohex-2-en-1-yl)-4,5-diphenyl-3H-1,2,3-oxathiazole 2,2-dioxide (4ha).



4ha

The titled compound was prepared following the General procedure H using allyl carbonate **1h** (44.0 mg, 0.222 mmol), imine **2a** (68.5 mg, 0.251 mmol), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (4.6 mg, 0.013 mmol), and Ph_3P (17.7 mg, 0.067 mmol). Purification by FCC (1:5 EtOAc:hexane) yielded **4ha** as a white solid (7.7 mg, 10%).

Mp: 149–152 °C

$\mathbf{R_f}$ = 0.33 (1:5 EtOAc:hexane).

IR (neat): 503, 613, 690, 764, 912, 978, 1192, 1352, 1445, 1662, 2941 cm^{-1}.

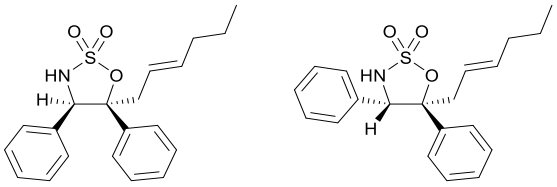
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 – 7.41 (m, 5H), 7.22 – 7.10 (m, 5H), 5.88 – 5.79 (m, 1H), 5.75 (app. d, *J* = 10.1 Hz, 1H), 4.18–4.11 (m, 1H), 2.07 – 1.84 (m, 3H), 1.79 (dtt, *J* = 13.3, 5.4, 3.4 Hz, 1H), 1.49 – 1.36 (m, 1H), 1.33 – 1.22 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 135.3, 132.4, 130.6, 130.4, 129.5, 128.6, 128.5, 128.2, 127.8, 125.5, 125.3, 125.3, 55.7, 27.6, 24.5, 21.7.

HRESI-MS (ESI +ve): Found 376.0989, calc for $C_{20}H_{19}NO_3SNa$ 376.0983 $[M + Na]^+$.

7. Post-synthetic modifications

(4*R*,5*S*)-5-((*E*)-Hex-2-en-1-yl)-4,5-diphenyl-1,2,3-oxathiazolidine 2,2-dioxide (7aa-majordiastereoisomer) and (4*S*,5*S*)-5-((*E*)-hex-2-en-1-yl)-4,5-diphenyl-1,2,3-oxathiazolidine 2,2-dioxide (7aa-minor diastereoisomer).



major diastereoisomer minor diastereoisomer

7aa

Procedure—$NaBH_4$ reduction:

To a stirring solution of imine **3aa** (70.1 mg, 0.193 mmol) in MeOH (8 mL) at 0 °C was added solid $NaBH_4$ (11.2 mg, 0.870 mmol) in one portion, and the resulting solution was then stirred at 0 °C for 1 h. By this time, TLC analysis suggested the complete consumption of the imine starting material. The reaction was then concentrated *in vacuo*, dissolved in EtOAc, and washed with water. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*, then used directly in the subsequent step without further purification due to the instability of the product on silica column (71:29 *dr*). Only a small amount of the major diastereoisomer was isolated by FCC for characterisation.

Procedure—K-selectride reduction:

To a stirring solution of imine **3aa** (48.5 mg, 0.152 mmol) in THF (1.5 mL) at −10 °C was added a solution of K-selectride (1.0 M in THF, 0.3 mL, 0.300 mmol) dropwise, and the resulting solution was then stirred at −10 °C for 1 h. By this time, TLC analysis suggested the complete consumption of the imine starting material. The reaction mixture was quenched with saturated NH_4Cl, extracted with EtOAc, and the combined organic layers were then washed with H_2O and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*, then used directly in the subsequent step without further purification due to the instability of the product on silica column (91:9 *dr*).

R_f = 0.09 (1:9 EtOAc:hexane).

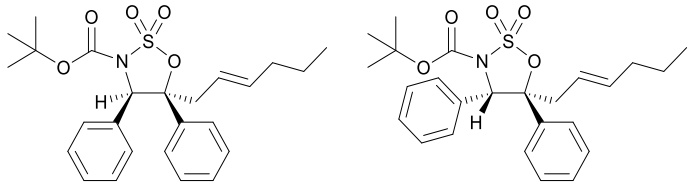
IR (neat): (major diastereoisomer): 505, 696, 758, 878, 970, 1029, 1179, 1335, 1448, 2871, 2928, 2957, 3255 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) (major diastereoisomer): δ 7.31 – 7.09 (m, 6H), 6.95 – 6.86 (m, 2H), 6.83 – 6.73 (m, 2H), 5.66 (dtt, *J* = 15.2, 6.7, 1.3 Hz, 1H), 5.44 (dddt, *J* = 15.2, 7.5, 6.0, 1.4 Hz, 1H), 5.23 (d, *J* = 8.2 Hz, 1H), 4.80 (d, *J* = 8.2 Hz, 1H), 3.10 – 2.88 (m, 2H), 2.09 – 1.90 (m, 2H), 1.40 – 1.27 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (major diastereoisomer): δ 137.0, 135.8, 132.0, 129.2, 128.5, 128.1, 127.8, 127.5, 126.7, 122.2, 99.3, 67.2, 41.5, 34.6, 22.3, 13.5.

HRESI-MS (ESI –ve): Found 356.1337, calc for $C_{20}H_{22}NO_3S$ 356.1320 $[M - H]^-$.

***tert*-Butyl (4*R*,5*S*)-5-((*E*)-hex-2-en-1-yl)-4,5-diphenyl-1,2,3-oxathiazolidine-3-carboxylate 2,2-dioxide (8aa-major diastereoisomer) and *tert*-butyl (4*S*,5*S*)-5-((*E*)-hex-2-en-1-yl)-4,5-diphenyl-1,2,3-oxathiazolidine-3-carboxylate 2,2-dioxide (8aa-minordiastereoisomer).**



major diastereoisomer minor diastereoisomer

8aa

Procedure:[31]

To a stirring solution of sulfamidate **7aa** (crude reaction isolate from the $NaBH_4$ reduction step, approx. 0.193 mmol OR crude reaction isolate from the K-selectride reduction step, approx. 0.136 mmol) in CH_2Cl_2 (1 mL) at rt was added a solution of Boc_2O (52.2 mg, 0.239 mmol OR 77.1 mg, 0.353 mmol) in CH_2Cl_2 (1 mL) via a cannula, rinsing with CH_2Cl_2 (1 mL), followed by DMAP (8.3 mg, 0.068 mmol OR 5.5 mg, 0.045 mmol). The resulting mixture was then stirred at rt overnight. Upon completion, as indicated by TLC analysis, the reaction mixture was concentrated *in vacuo*, and the residue was then purified by FCC (1:9 EtOAc:hex) to furnish an inseparable mixture of both diastereoisomers of *N*-Boc sulfamate **8aa** as a colourless oil (65.4 mg, 74% after two steps, 74:26 *dr* OR 33.1 mg, 53% over two steps, 94:6 *dr*).

R_f = 0.07 (1:9 EtOAc:hexane).

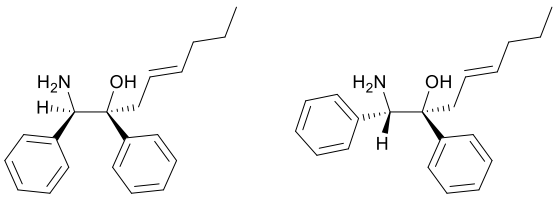
IR (neat): 528, 567, 697, 760, 970, 1188, 1318, 1367, 1450, 1723, 2872, 2929, 2960 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) (2.9:1 mixture of two diastereoisomers, minor isomer labelled with an asterisk): δ 7.56 – 7.32* (m, 9H), 7.29 – 7.26* (m, 1H), 7.20 – 7.13 (m, 2H), 7.13 – 6.94 (m, 8H), 5.70 – 5.47 (m, 1H), 5.34 (s, 1H), 5.18 (dtt, *J* = 15.5, 6.9, 1.4 Hz, 1H), 5.14 – 5.06* (m, 1H), 4.83* (dtt, *J* = 15.4, 6.9, 1.5 Hz, 1H), 3.71 – 3.47 (m, 1H), 3.01 (ddd, *J* = 14.7, 6.7, 1.2 Hz, 1H), 2.45* (ddd, *J* = 14.7, 6.7, 1.3 Hz, 1H), 2.11* (ddd, *J* = 14.6, 7.3, 1.1 Hz, 1H), 1.93–1.82 (m, 2H), 1.80 – 1.67* (m, 2H), 1.44 (s, 9H), 1.34* (s, 9H), 1.31 – 1.19 (m, 2H), 1.18 – 1.05* (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H), 0.68* (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) (2.9:1 mixture of two diastereoisomers, distinguishable minor isomer resonances labelled with an asterisk): δ 148.4, 148.2*, 138.7*, 137.4, 136.7*, 135.6, 135.5, 134.9*, 129.1*, 128.9*, 128.7*, 128.5*, 128.2, 128.1, 128.0, 127.8, 127.7, 125.6*, 125.5, 121.1, 120.9*, 94.3, 93.5*, 85.5, 85.4*, 71.2*, 70.8, 43.1, 42.2*, 34.5, 34.4*, 27.8, 27.7*, 22.2, 22.1*, 13.4 (overlapping resonances).

HRESI-MS (ESI +ve): Found 480.1830, calc for $C_{25}H_{31}NO_5SNa$ 480.1821 $[M + Na]^+$.

(1*R*,2*S*,*E*)-1-Amino-1,2-diphenyloct-4-en-2-ol (9aa-major diastereoisomer) and (1*S*,2*S*,*E*)-1-amino-1,2-diphenyloct-4-en-2-ol (9aa-minor diastereoisomer).



major diastereoisomer minor diastereoisomer

9aa

Procedure:[32]

To a stirring solution of $LiAlH_4$ (1.0 M in THF, 0.9 mL, 0.900 mmol) at 0 °C was added dropwise a solution of imine **3aa** (104.2 mg, 0.293 mmol) in THF (3.5 mL) via a cannula, which was rinsed with THF (3.5 mL). The reaction mixture was then heated to reflux and stirred at reflux for 1 h. The reaction mixture was then cooled down to rt, then HCl 1 M (1 mL) was added, and the mixture was again heated to reflux for 1 h. After having cooled to rt, the reaction mixture was then washed with CH_2Cl_2. The aqueous layer was separated, basified with aq. NaOH soltution, and then extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered, concentrated *in vacuo*, and then purified by FCC (1:2 EtOAc:hex) to furnish the major diastereoisomer **9aa** as a colourless oil (53.6 mg, 62%) and the minor diastereoisomer **9aa** as a colourless oil (16.5 mg, 19%)

R_f (major diastereoisomer) = 0.06 (1:2 EtOAc:hexane).

IR (neat): (major diastereoisomer) 698, 755, 968, 1179, 1379, 1447, 2870, 2927, 2956, 3322 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) (major diastereoisomer): δ 7.24 – 7.04 (m, 8H), 7.00 – 6.87 (m, 2H), 5.60 – 5.44 (m, 1H), 5.35 – 5.12 (m, 1H), 4.12 (s, 1H), 2.78 (app. dd, *J* = 14.1, 5.7 Hz, 1H), 2.63 (app. dd, *J* = 14.2, 8.4 Hz, 1H), 1.98 – 1.82 (m, 2H), 1.38 – 1.20 (m, 3H), 0.79 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (major diastereoisomer): δ 142.5, 141.7, 135.6, 128.4, 127.7, 127.5, 127.3, 127.1, 126.7, 125.2, 77.9, 64.4, 42.3, 34.9, 22.8, 13.7.

R_f (minor diastereoisomer) = 0.09 (1:2 EtOAc:hexane).

^{1}H NMR (500 MHz, $CDCl_3$) (minor diastereoisomer): δ 7.53 – 7.16 (m, 10H), 5.30 – 5.18 (m, 1H), 5.04 – 4.93 (m, 1H), 4.23 (br s, 1H), 2.56 – 2.41 (m, 1H), 2.08 – 1.98 (m, 1H), 1.84–1.70 (m, 2H), 1.25 – 1.10 (m, 2H), 0.70 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (minor diastereoisomer): δ 145.2, 141.2, 134.7, 128.8, 128.3, 128.2, 127.8, 126.8, 126.4, 124.8, 78.0, 64.4, 42.4, 34.8, 22.6, 13.6.

HRESI-MS (ESI +ve): Found 296.2019, calc for $C_{20}H_{26}NO$ 296.2014 $[M + H]^+$.

8. Crystallographic data

X-ray crystallography was analysed on a XtaLAB Mini II diffractometer. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using CGLS minimisation.

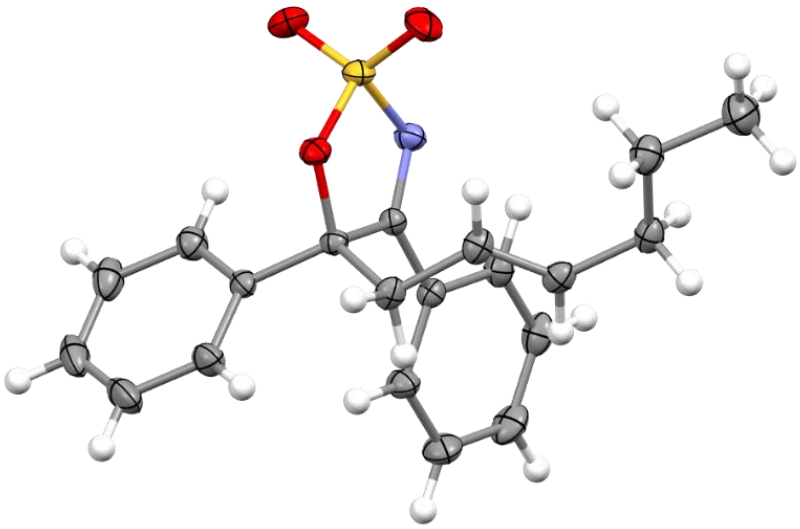


Figure S1. Crystal structure of (*rac*)-**3aa**

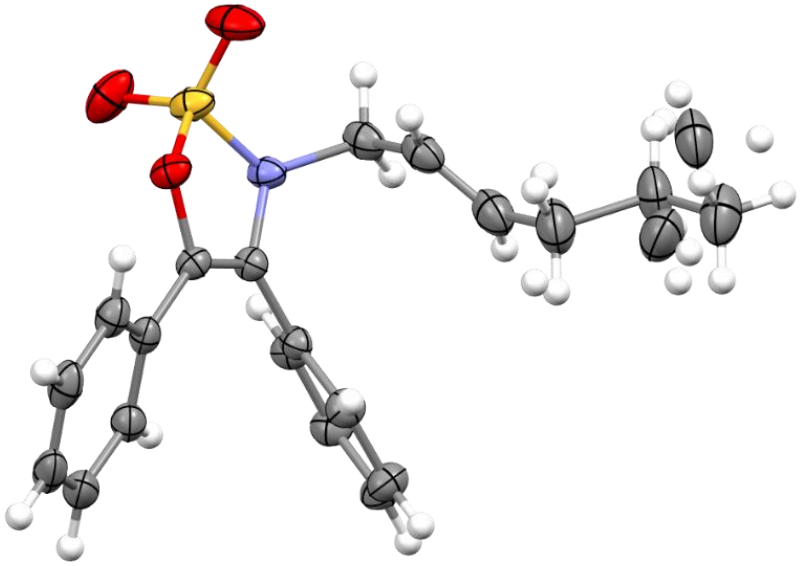


Figure S2. Crystal structure of **4aa**

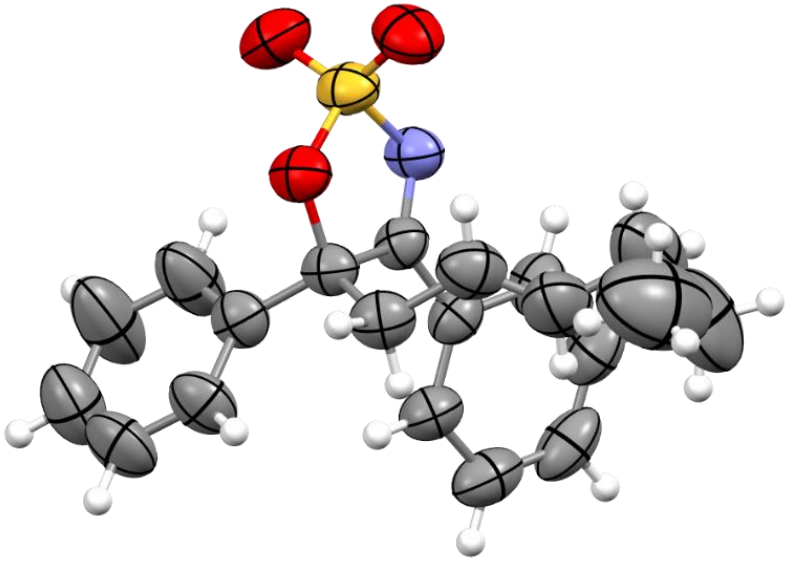


Figure S3. Crystal structure of **(*S*)-3aa**

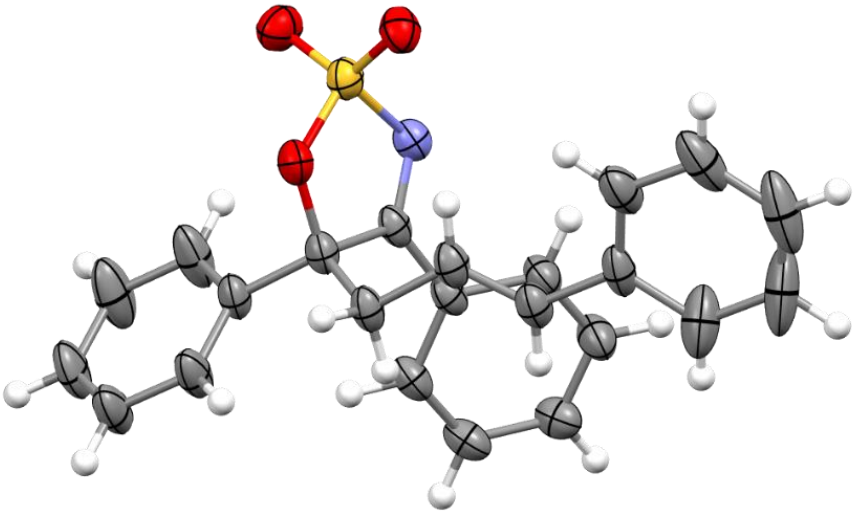


Figure S4. Crystal structure of **(*S*)-3ca**

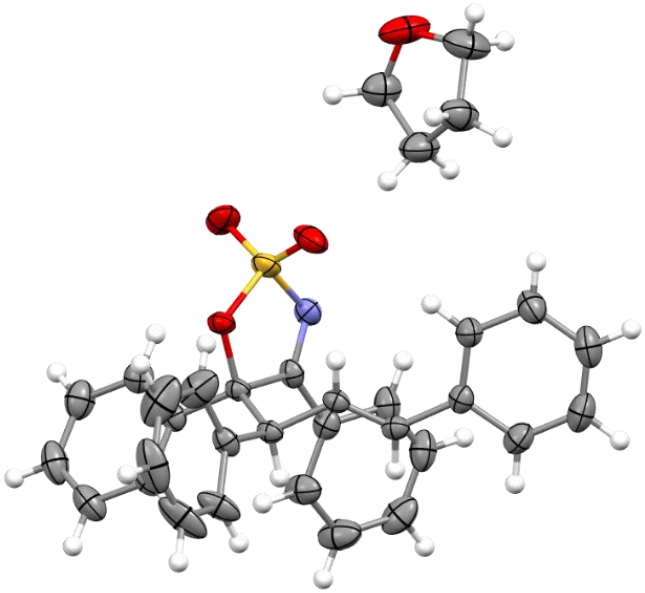


Figure S5. Crystal structure of **(*S,S*)-3fa**

Crystal data and structure refinement.					
Identification code	**(*rac*)-3aa**	**4aa**	**(*S*)-3aa**	**(*S*)-3ca**	**(*S,S*)-3fa**
Empirical formula	$C_{20}H_{21}NO_3S$	$C_{20}H_{21}NO_3S$	$C_{20}H_{21}NO_3S$	$C_{23}H_{19}NO_3S$	$C_{33}H_{31}NO_4S$
Formula weight	355.44	355.44	355.44	389.45	537.65
Temperature/K	150.00(10)	149.99(10)	293.0(10)	150.00(10)	149.99(10)
Crystal system	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	P-1	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_1$
a/Å	8.9169(3)	8.4602(2)	10.0914(4)	9.2466(2)	9.0008(2)
b/Å	10.0932(3)	10.8079(3)	10.2497(4)	10.2138(3)	15.0151(3)
c/Å	10.9734(4)	19.9865(5)	18.7657(7)	10.4986(3)	10.6877(2)
α/°	82.217(3)	90	90	90	90
β/°	83.123(3)	90	90	94.584(2)	107.229(2)
γ/°	67.004(3)	90	90	90	90
Volume/Å^3	898.33(5)	1827.51(8)	1941.01(13)	988.34(5)	1379.60(5)
Z	2	4	4	2	2
ρ_{calc}g/cm^3	1.314	1.292	1.216	1.309	1.294
μ/mm^{-1}	0.199	0.195	0.184	0.187	0.157
F(000)	376.0	752.0	752.0	408.0	568.0
Crystal size/mm^3	0.56 × 0.5 × 0.35	0.39 × 0.2 × 0.18	0.61 × 0.21 × 0.11	0.35 × 0.31 × 0.15	0.44 × 0.38 × 0.31
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.404 to 61.006	4.284 to 59.148	4.342 to 59.138	3.892 to 56.564	3.99 to 58.25
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15	-10 ≤ h ≤ 11, -14 ≤ k ≤ 15, -27 ≤ l ≤ 27	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -26 ≤ l ≤ 25	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13	-12 ≤ h ≤ 12, -20 ≤ k ≤ 20, -14 ≤ l ≤ 14
Reflections collected	23029	25213	32513	17523	44315
Independent reflections	5236 [R_{int} = 0.0230, R_{sigma} = 0.0156]	5129 [R_{int} = 0.0295, R_{sigma} = 0.0310]	5428 [R_{int} = 0.0369, R_{sigma} = 0.0371]	4872 [R_{int} = 0.0246, R_{sigma} = 0.0247]	7355 [R_{int} = 0.0284, R_{sigma} = 0.0241]
Data/restraints/parameters	5236/0/227	5129/16/248	5428/4/226	4872/1/253	7355/1/352
Goodness-of-fit on F^2	1.048	1.062	1.004	1.036	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0958	R_1 = 0.0365, wR_2 = 0.0856	R_1 = 0.0514, wR_2 = 0.1270	R_1 = 0.0380, wR_2 = 0.0971	R_1 = 0.0389, wR_2 = 0.0943
Final R indexes [all data]	R_1 = 0.0385, wR_2 = 0.0984	R_1 = 0.0481, wR_2 = 0.0906	R_1 = 0.1076, wR_2 = 0.1524	R_1 = 0.0443, wR_2 = 0.1009	R_1 = 0.0470, wR_2 = 0.0989
Largest diff. peak/hole / e Å^{-3}	0.43/-0.42	0.19/-0.28	0.19/-0.19	0.48/-0.23	0.23/-0.28
Flack parameter		0.20(8)	-0.02(3)	0.032(19)	0.007(18)
CCDC	2087721	2087722	2087723	2087724	2087725

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10. NMR spectra of novel compounds

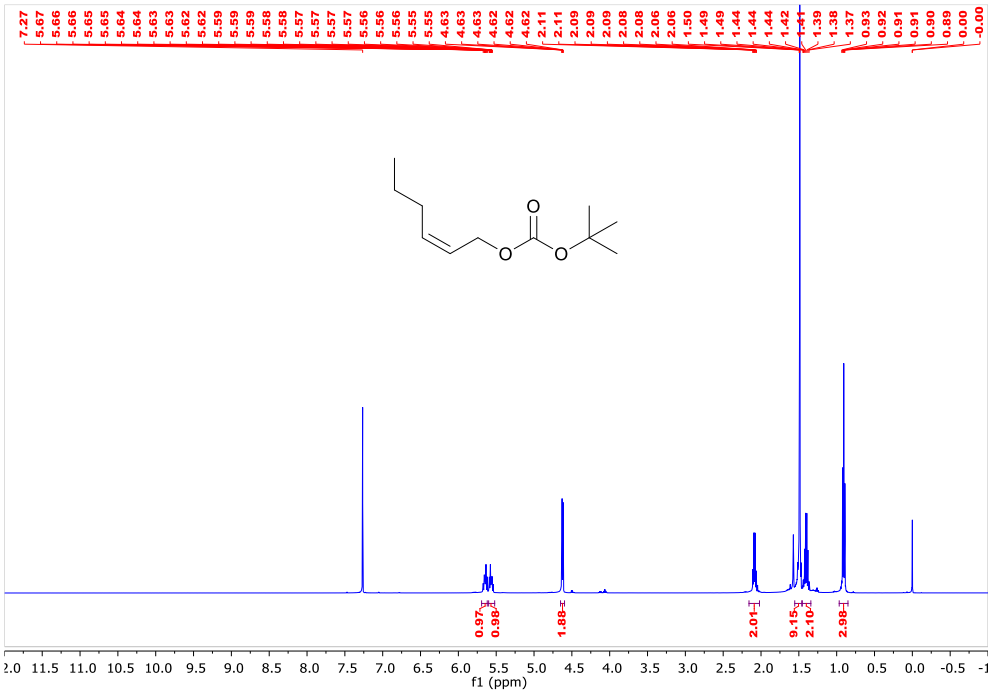


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **1a"**

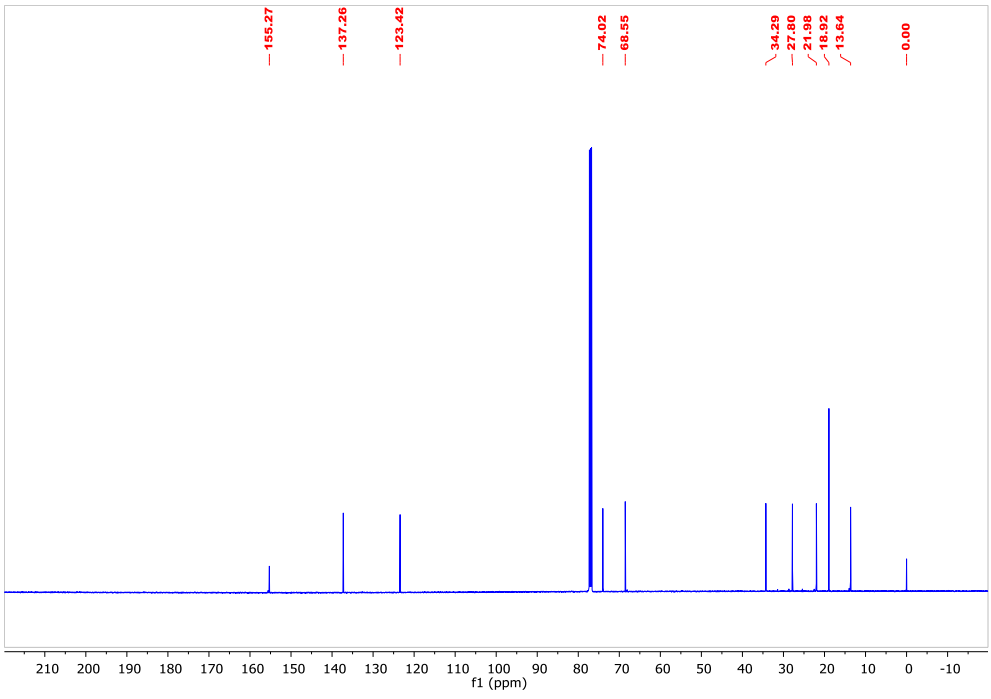


Figure S7. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **1a"**

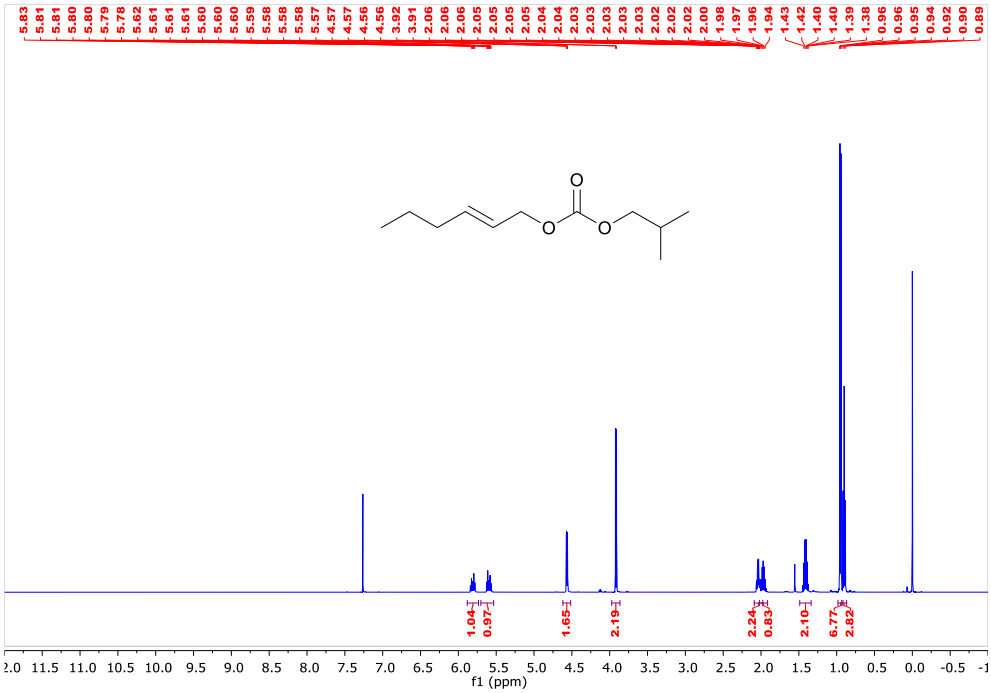


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of ***i*-1a**

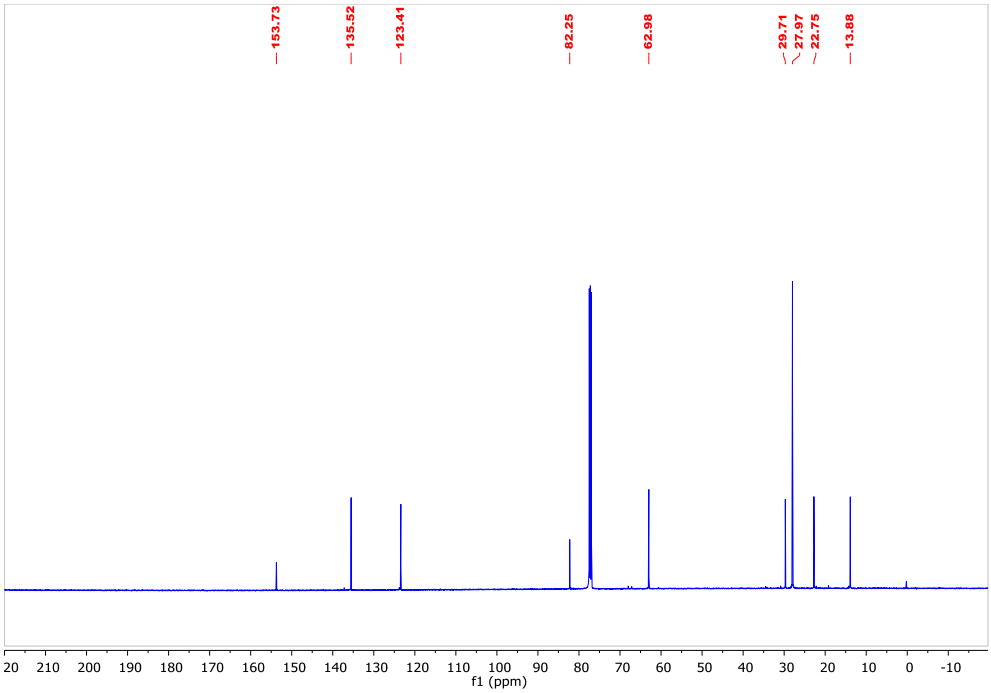


Figure S9. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of ***i*-1a**

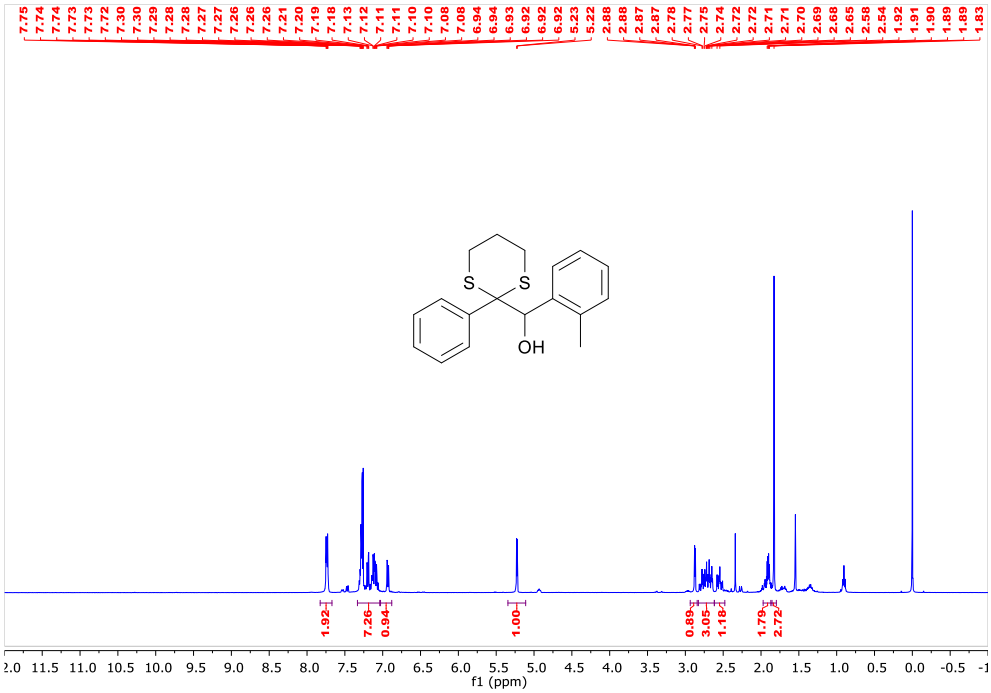


Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S2a**

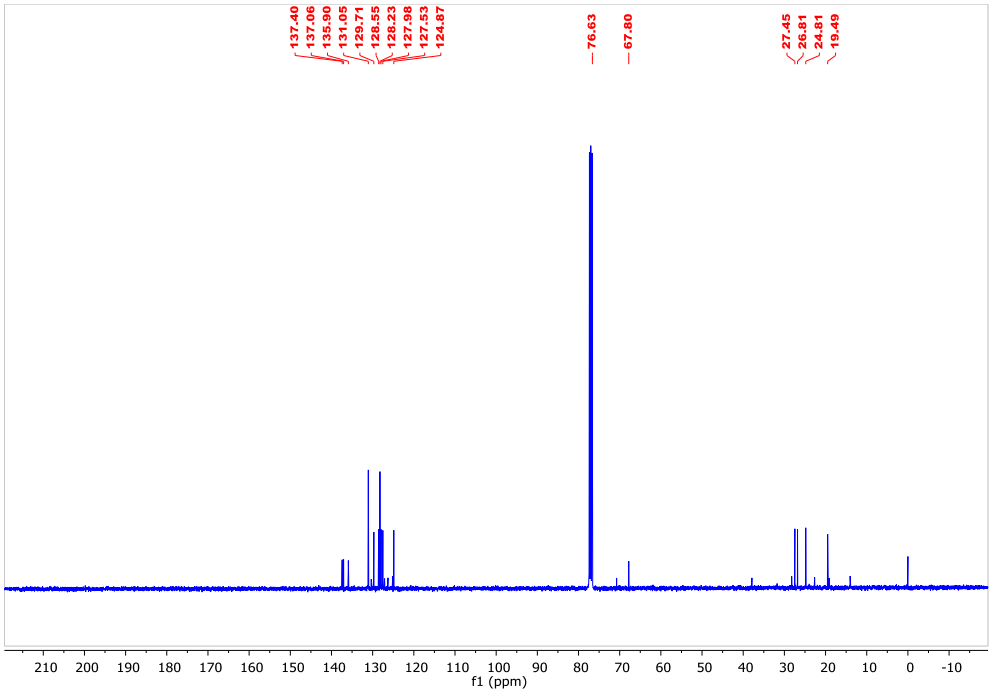


Figure S11. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S2a**

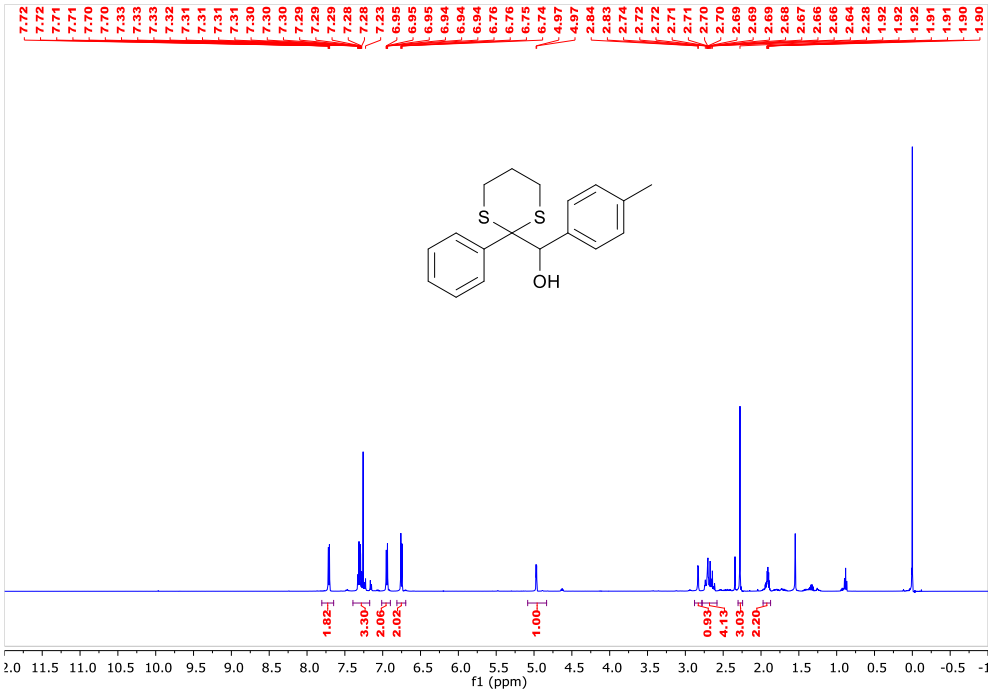


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S2b**

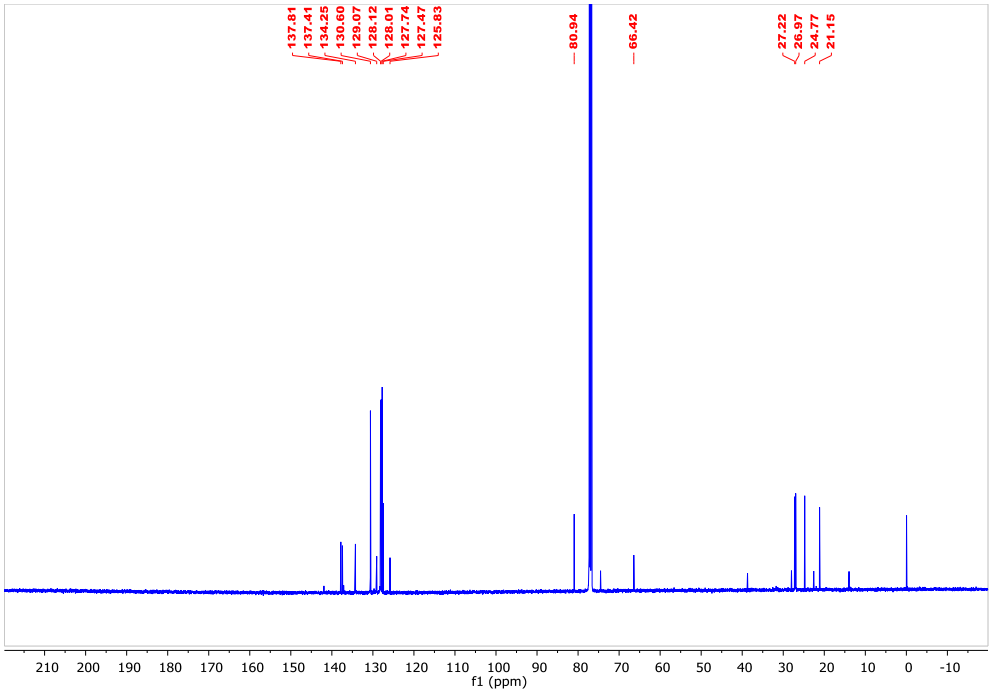


Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S2b**

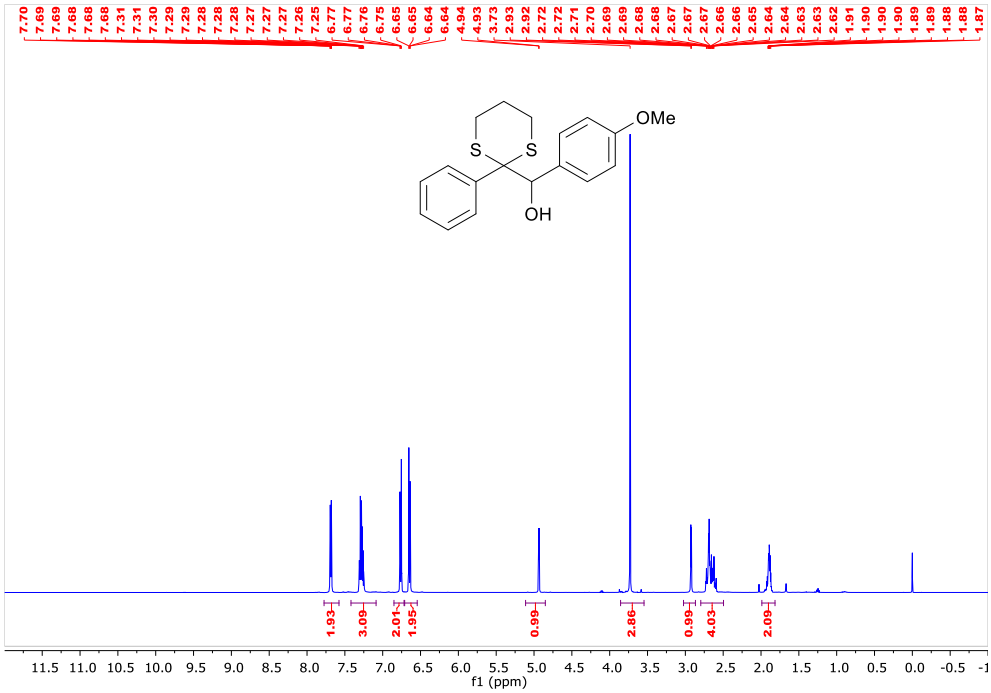


Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S2c**

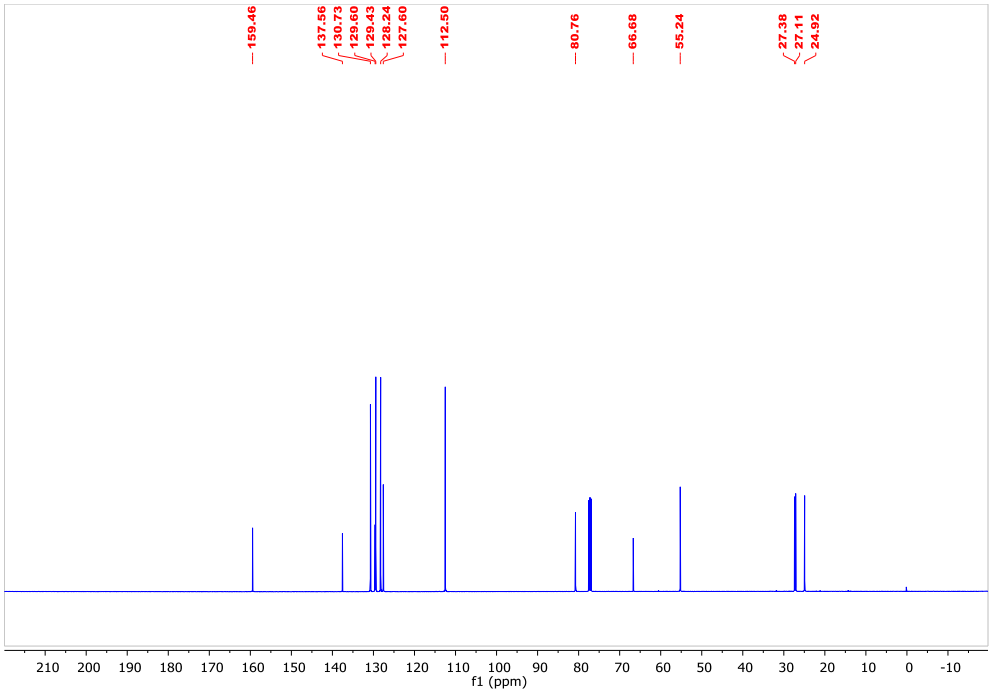


Figure S15. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S2c**

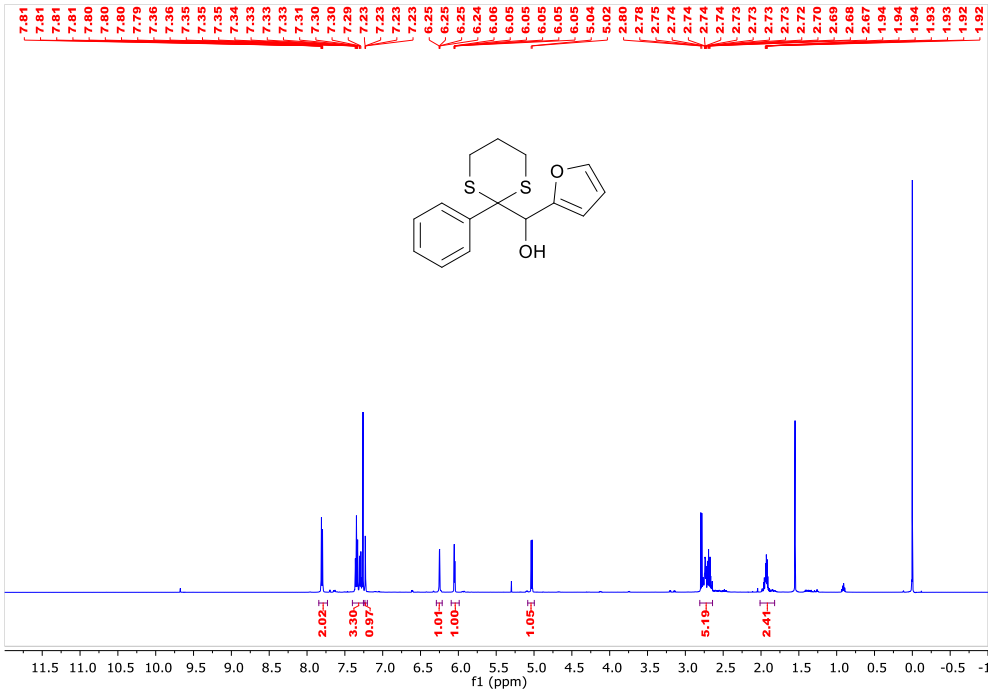


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S2d**

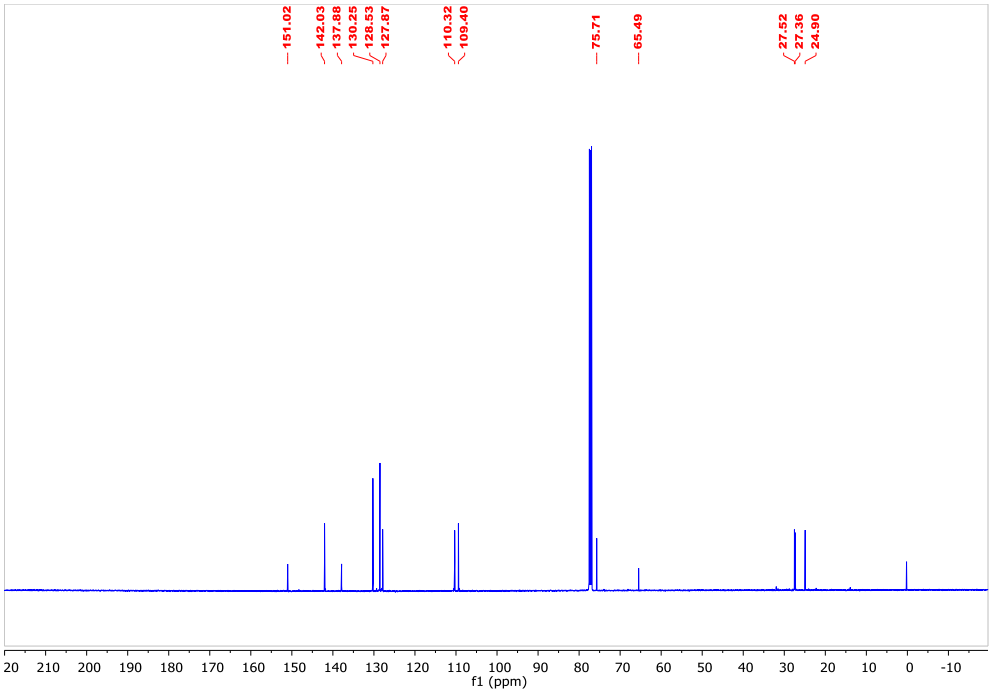


Figure S17. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S2d**

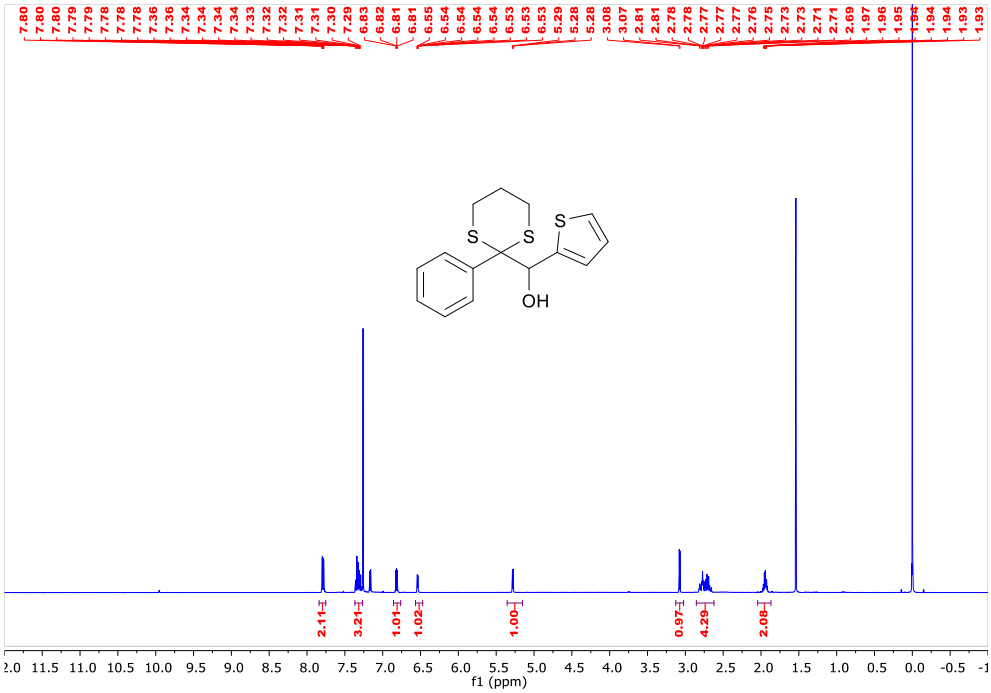


Figure S18. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S2f**

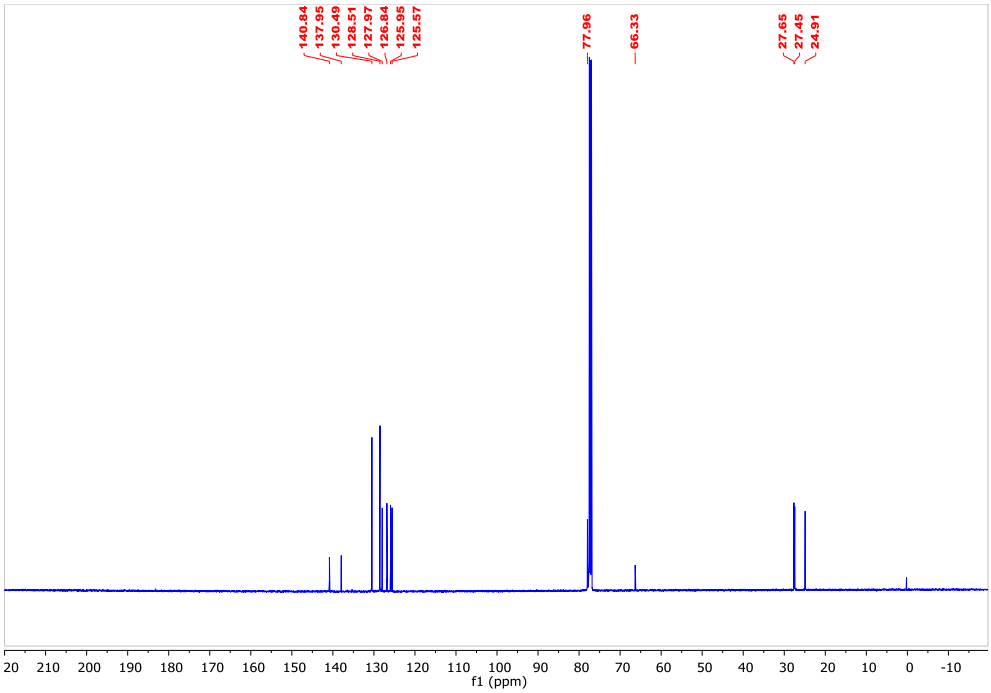


Figure S19. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S2f**

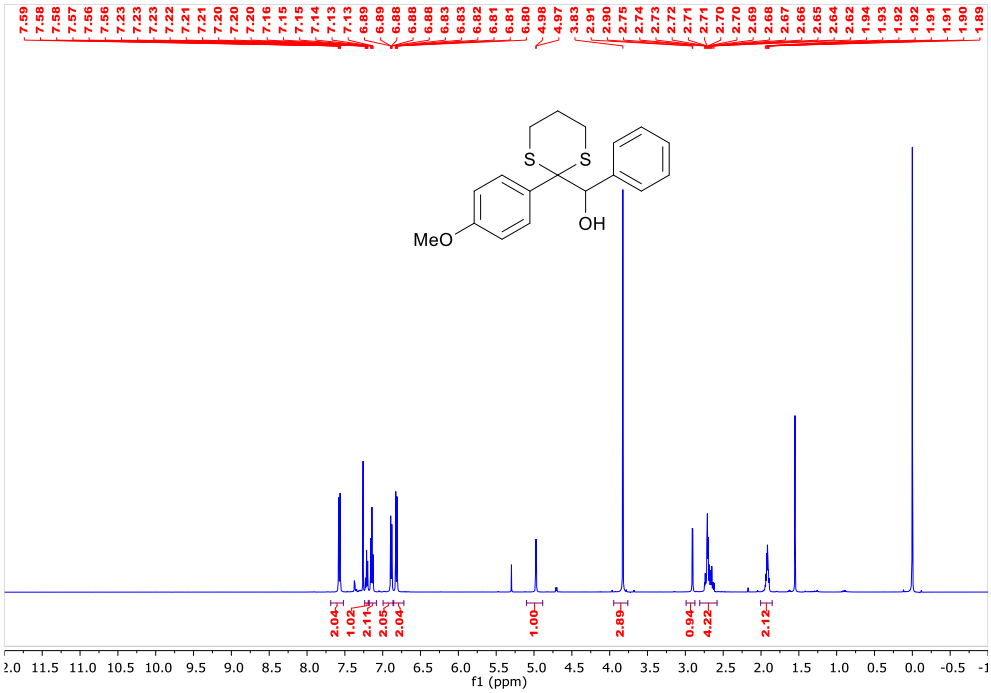


Figure S20. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S2i**

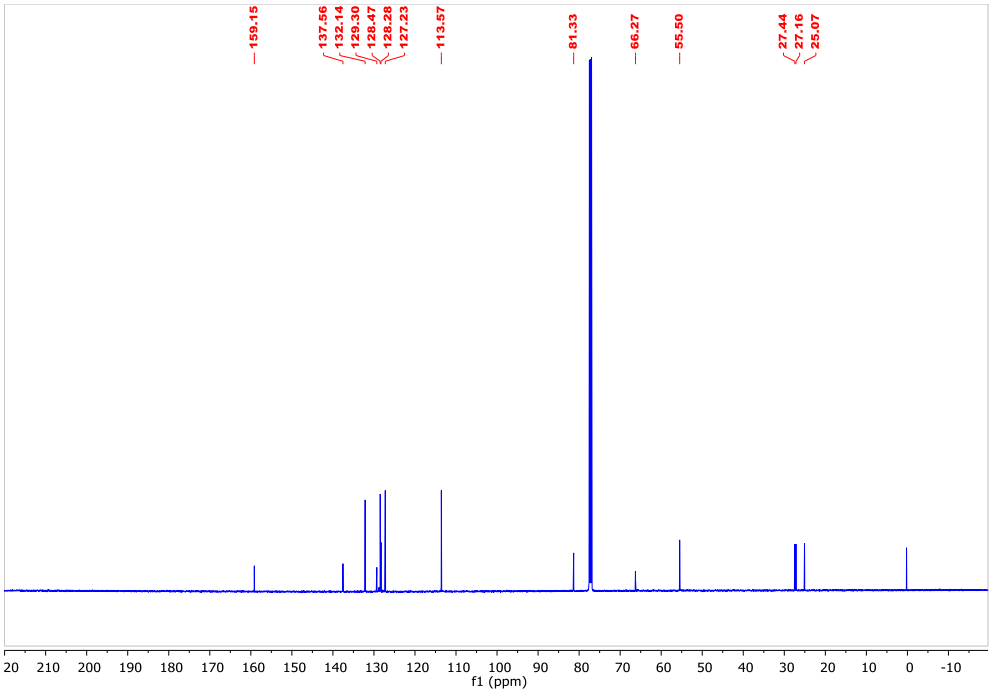


Figure S21. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S2i**

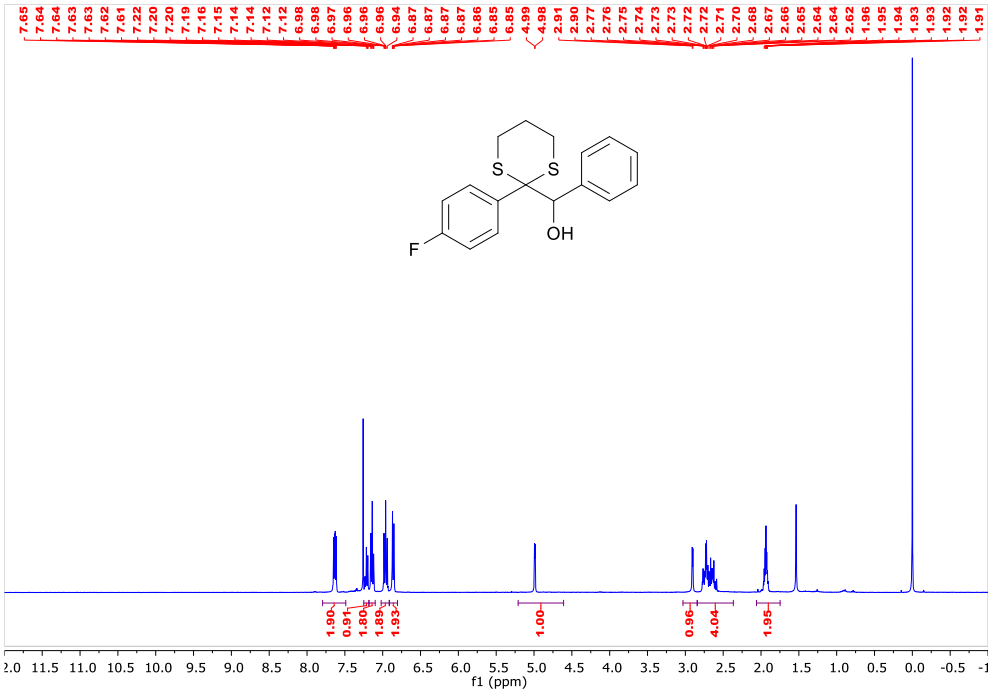


Figure S22. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S2j**

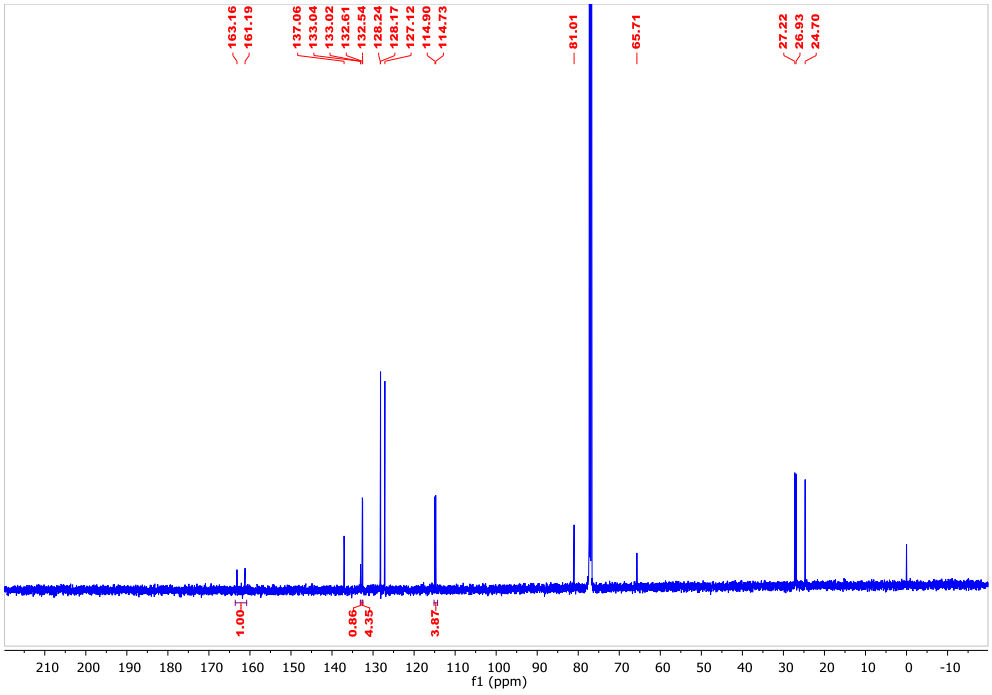


Figure S23. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S2j**

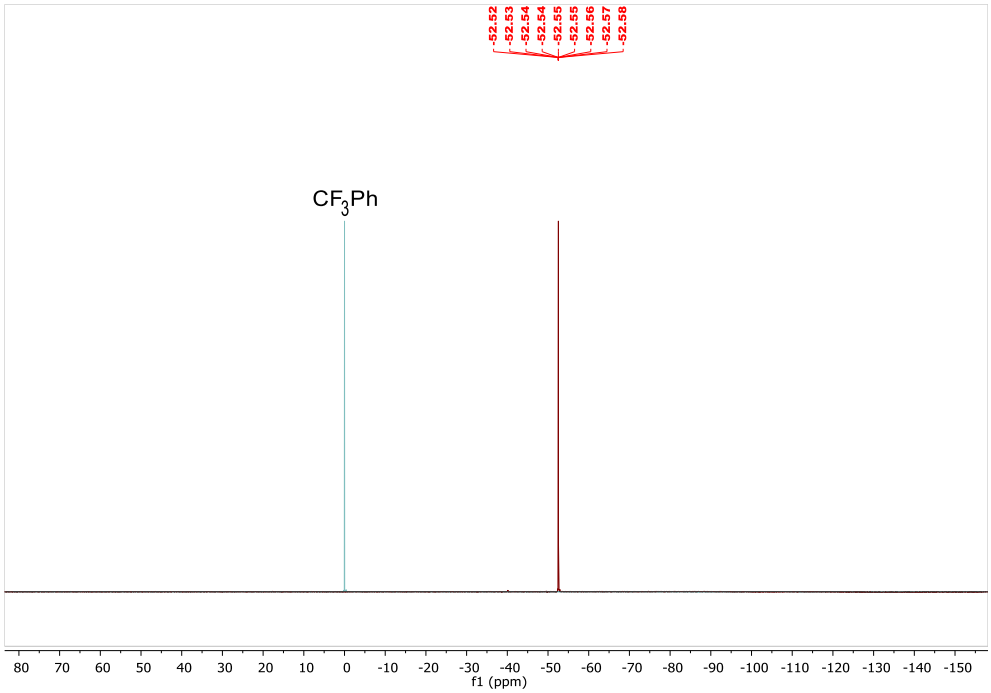


Figure S24. ^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of **S2j**

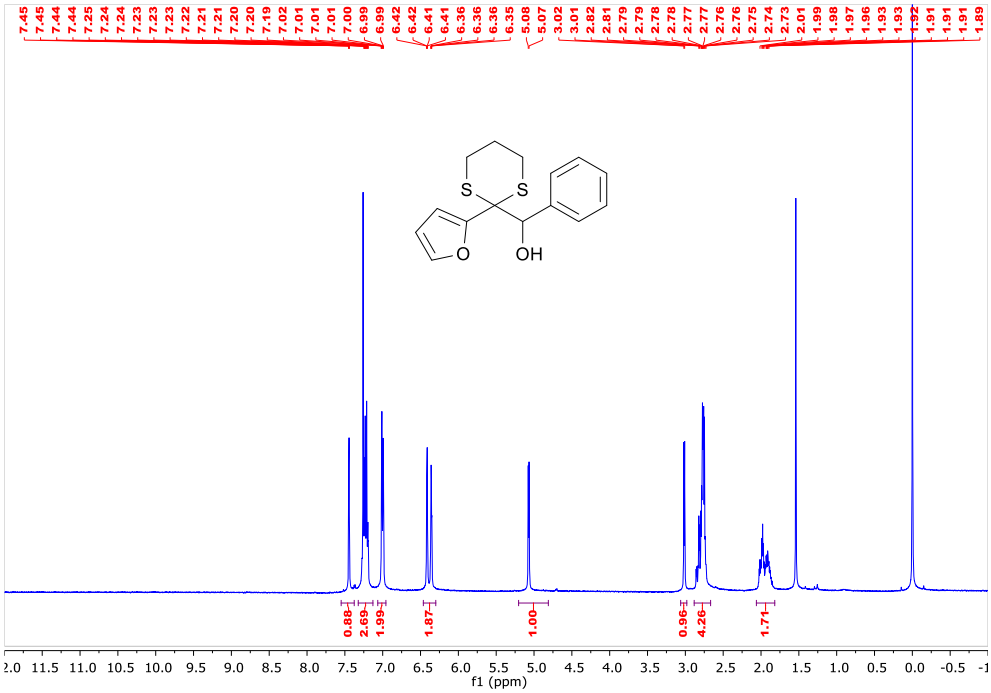


Figure S25. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S2k**

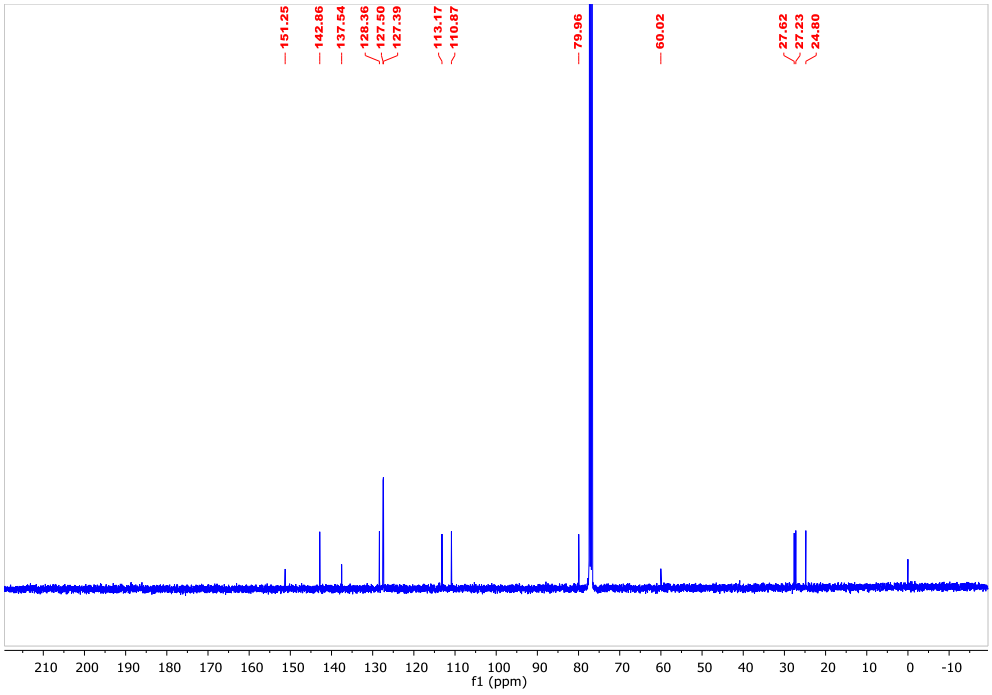


Figure S26. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S2k**

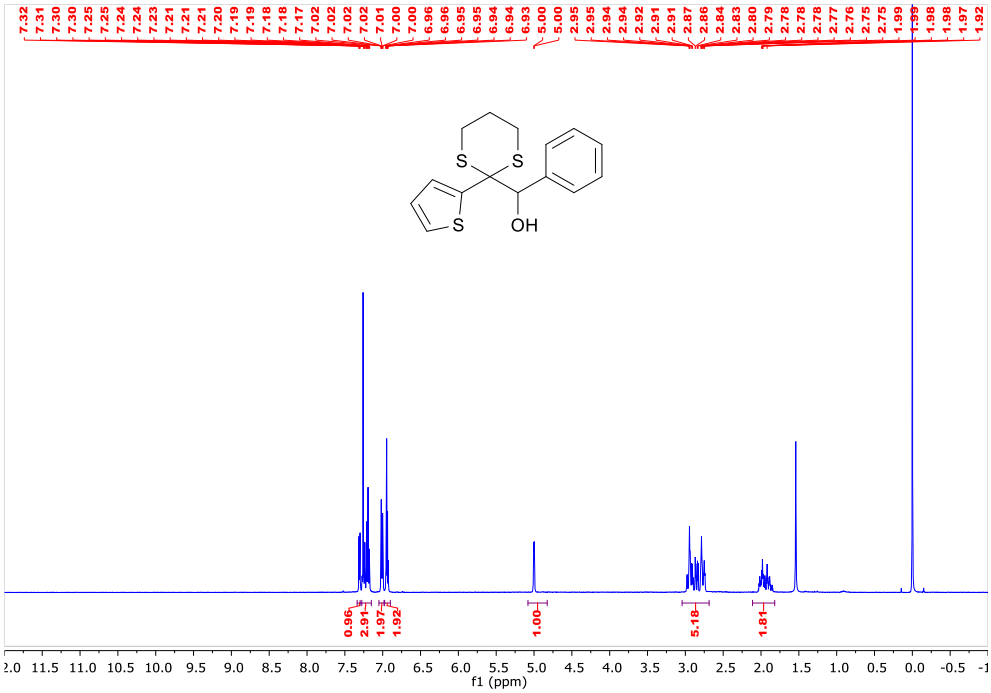


Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **S2l**

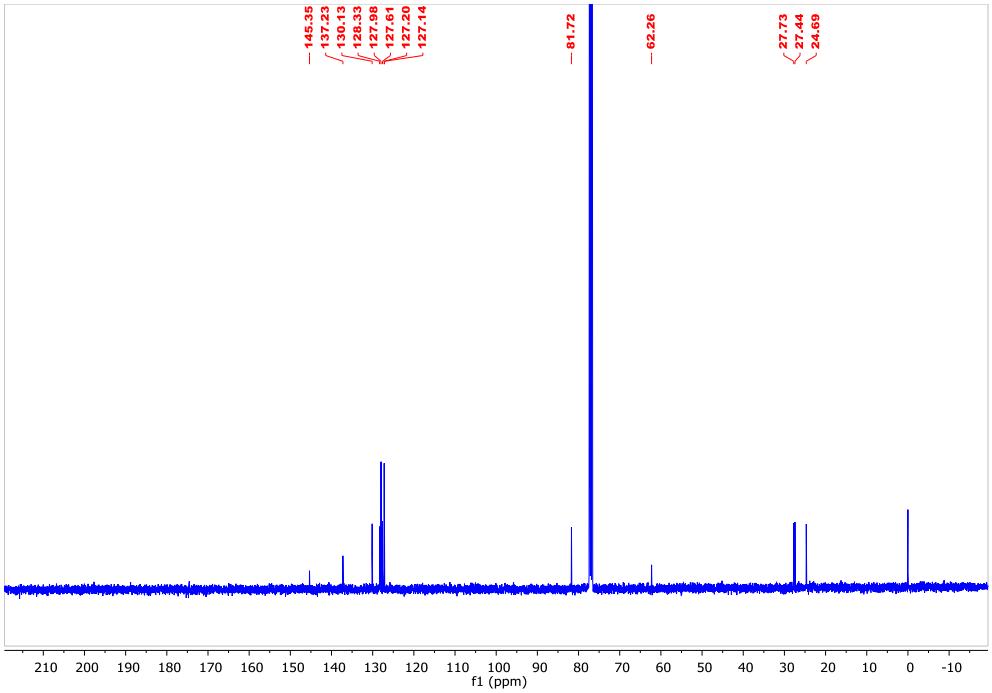


Figure S28. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **S2l**

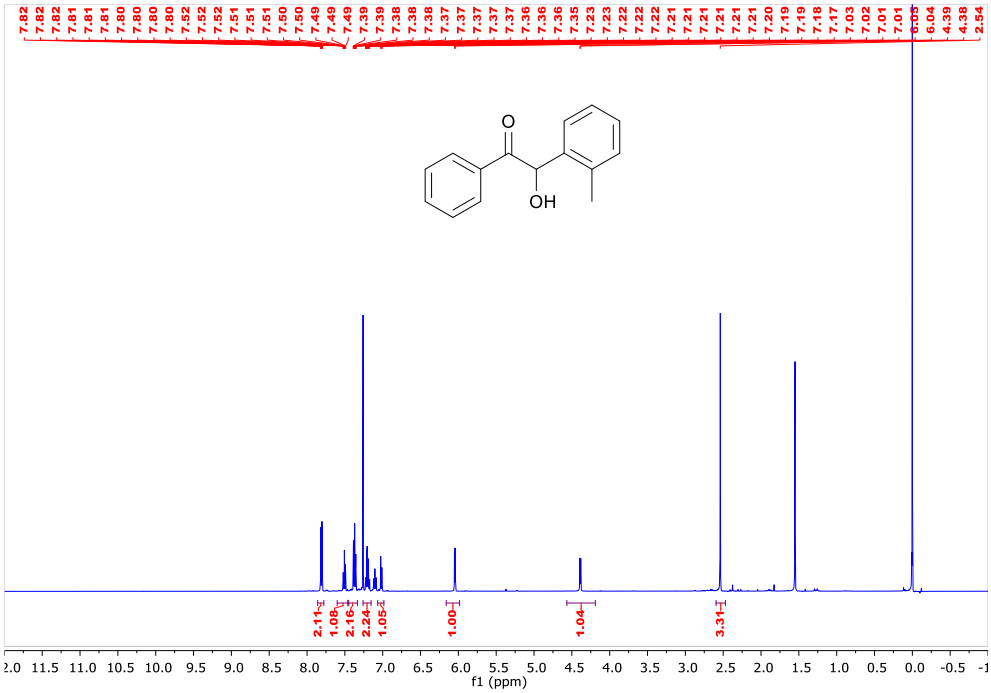


Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S3a**

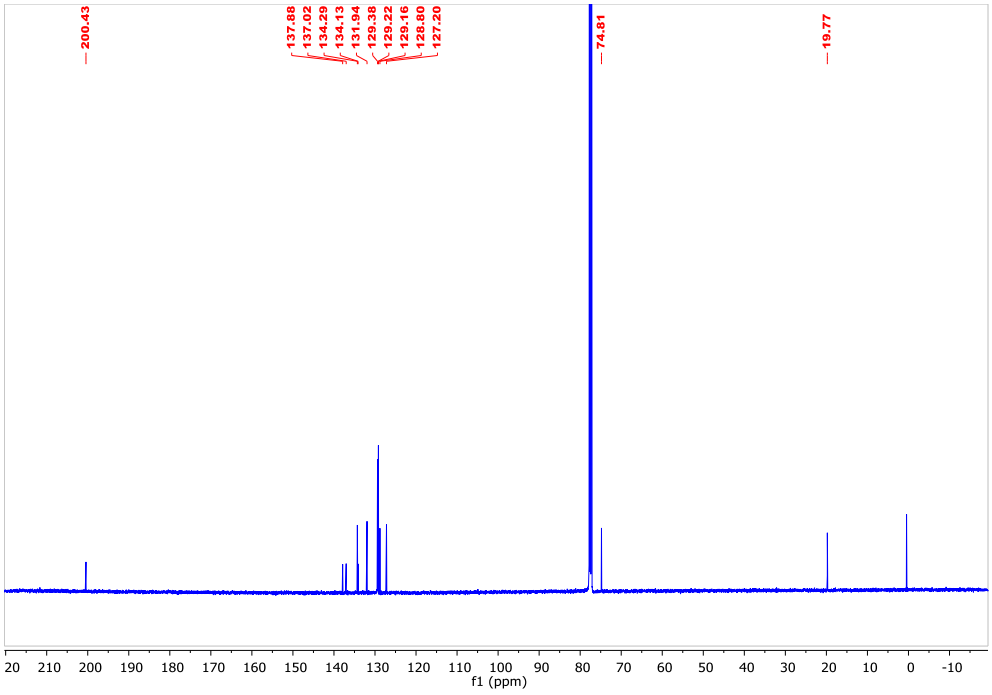


Figure S30. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S3a**

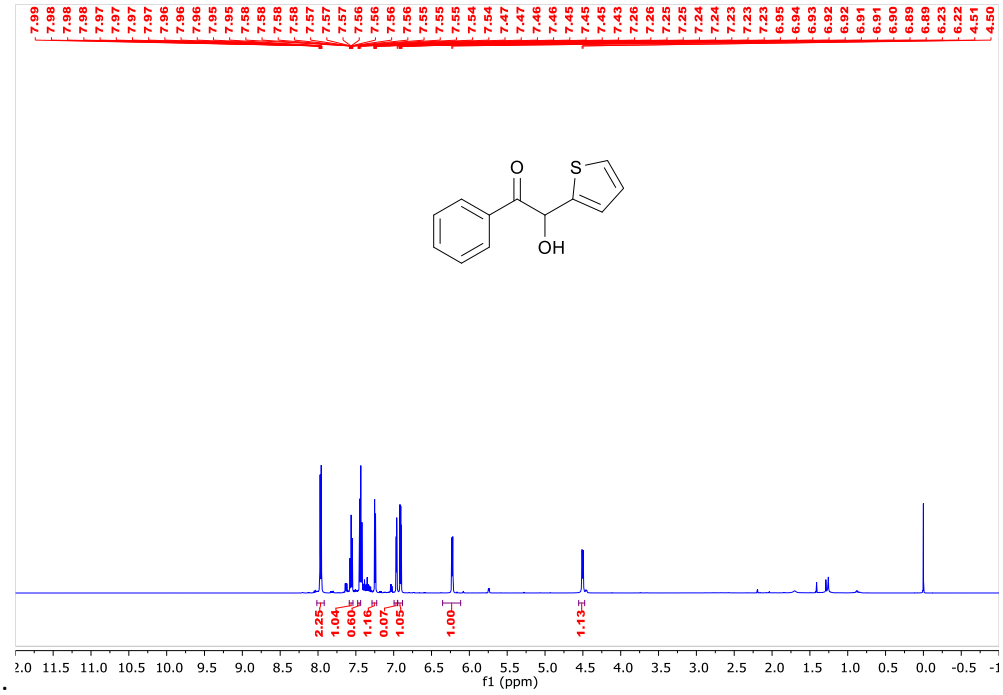


Figure S31. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **S3f**

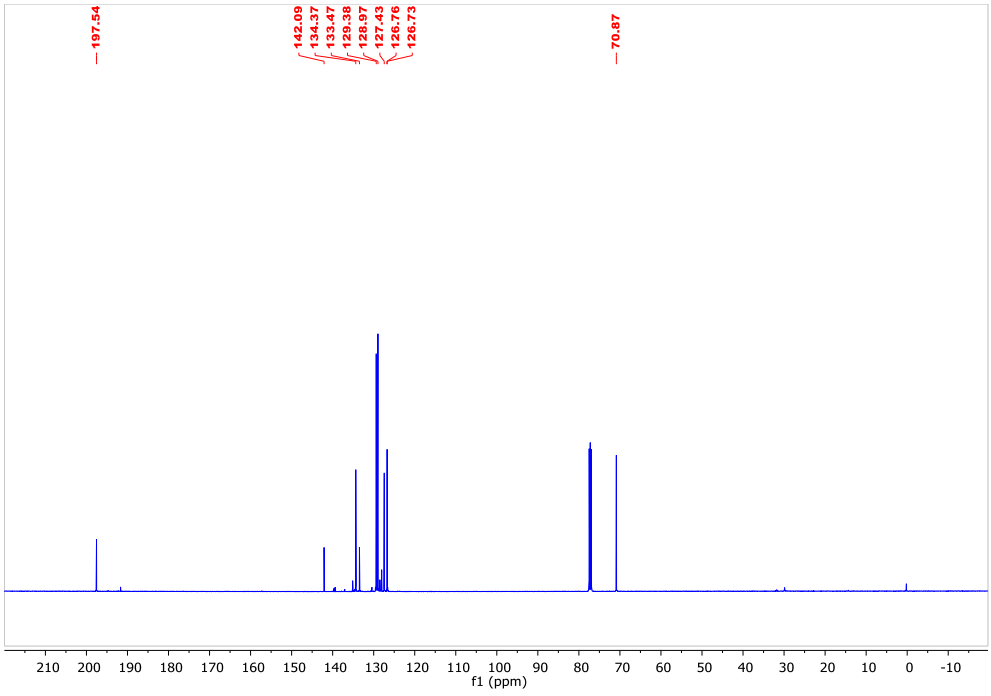


Figure S32. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **S3f**

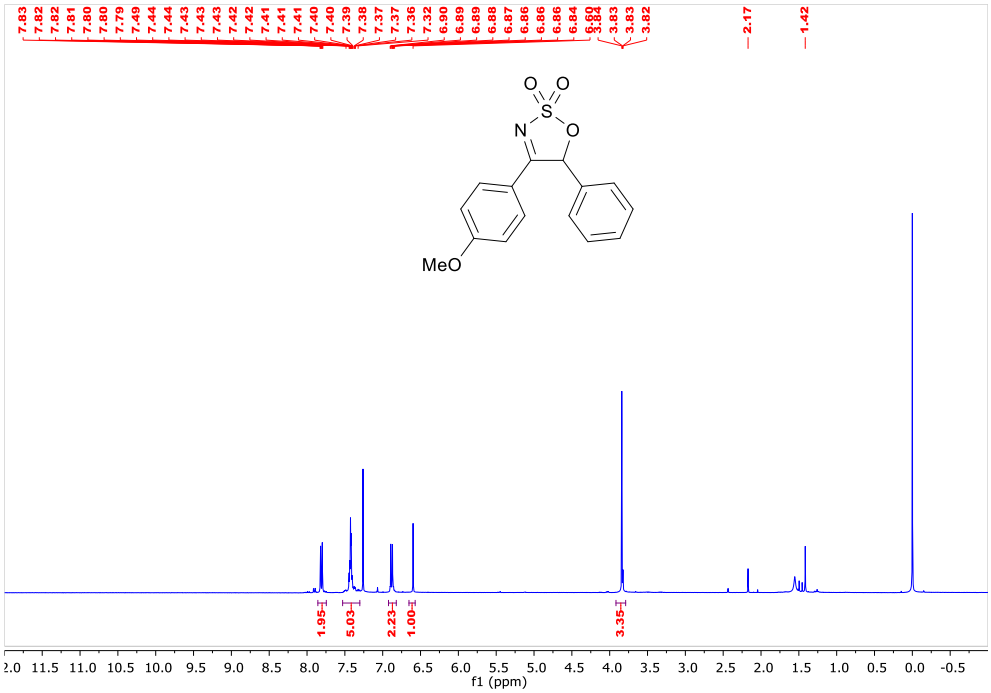


Figure S33. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2b**

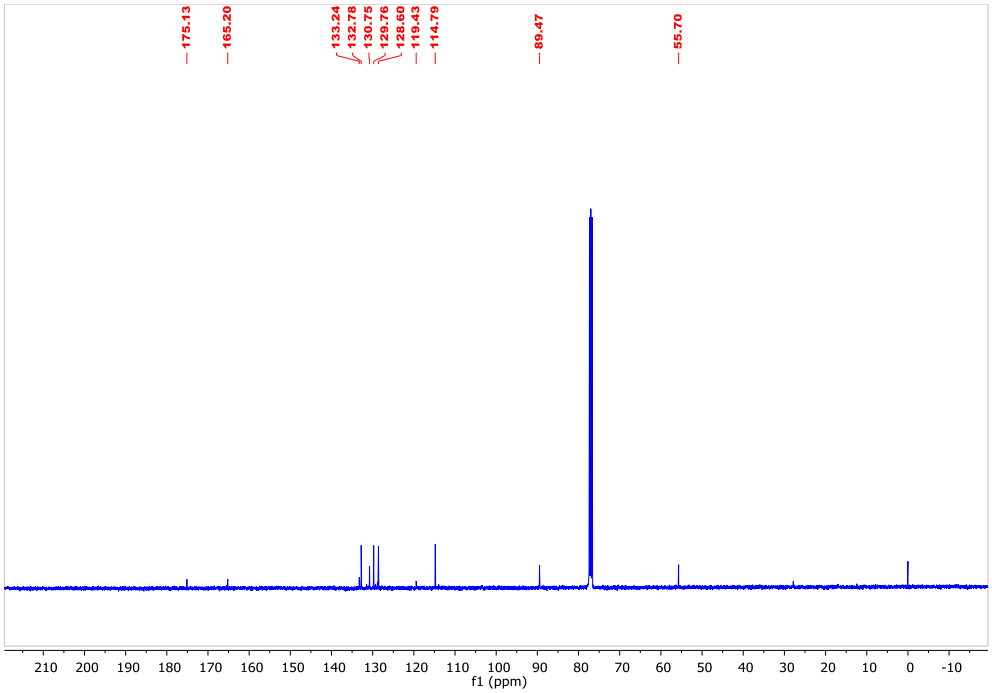


Figure S34. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2b**

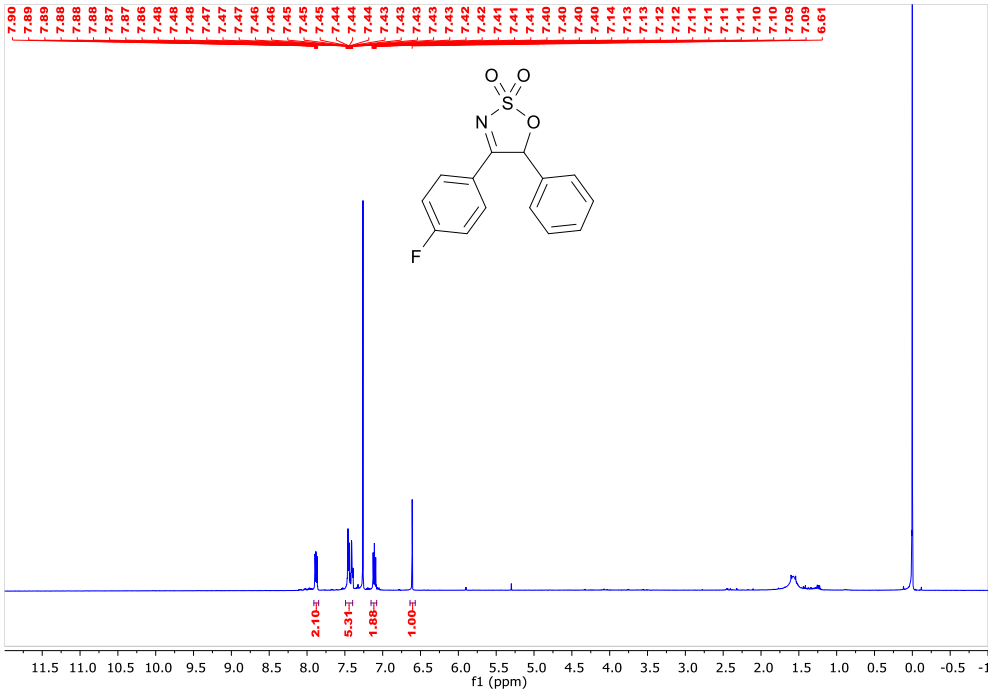


Figure S35. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2c**

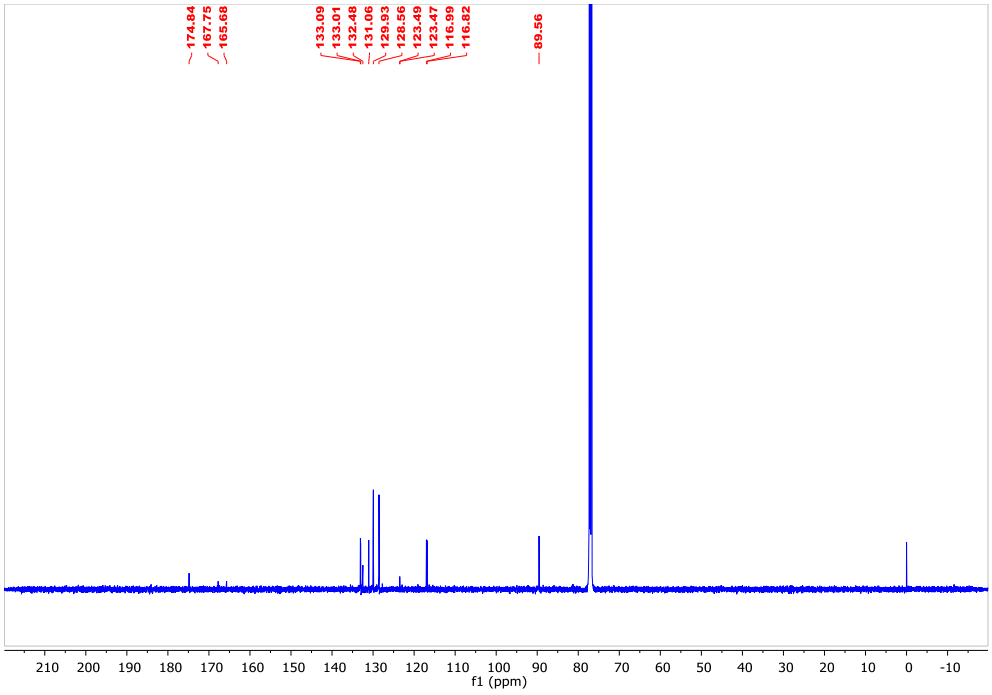


Figure S36. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **2c**

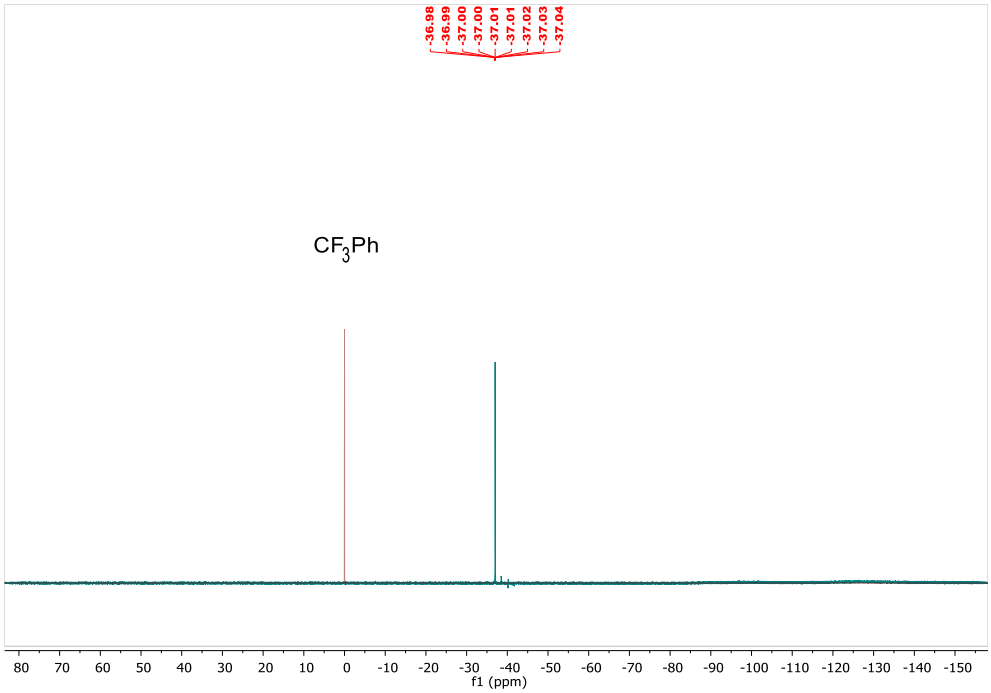


Figure S37. ^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of **2c**

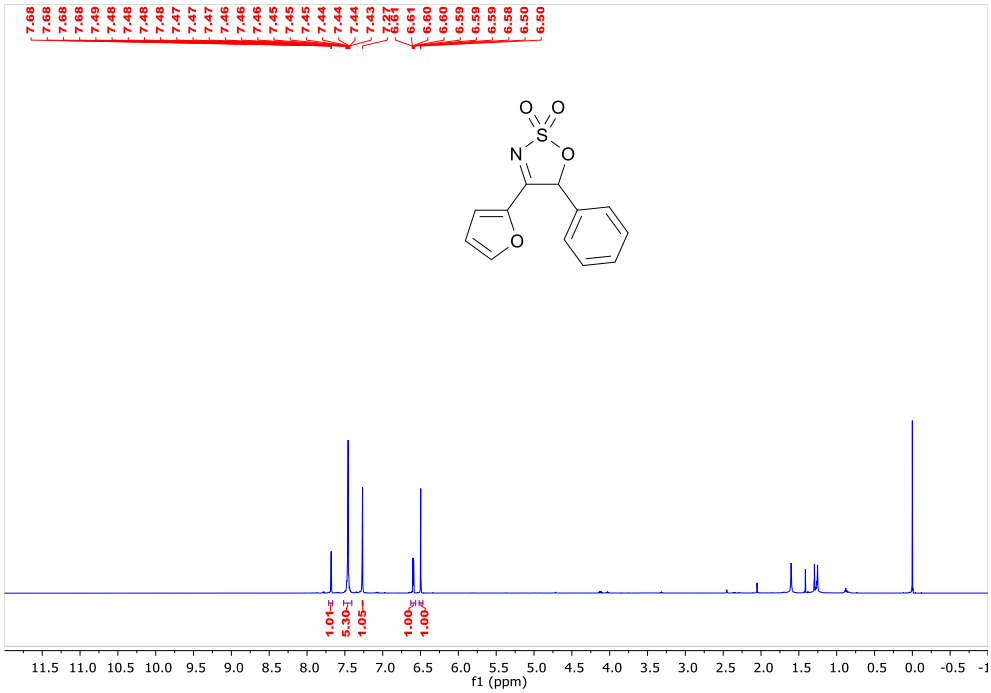


Figure S38. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **2d**

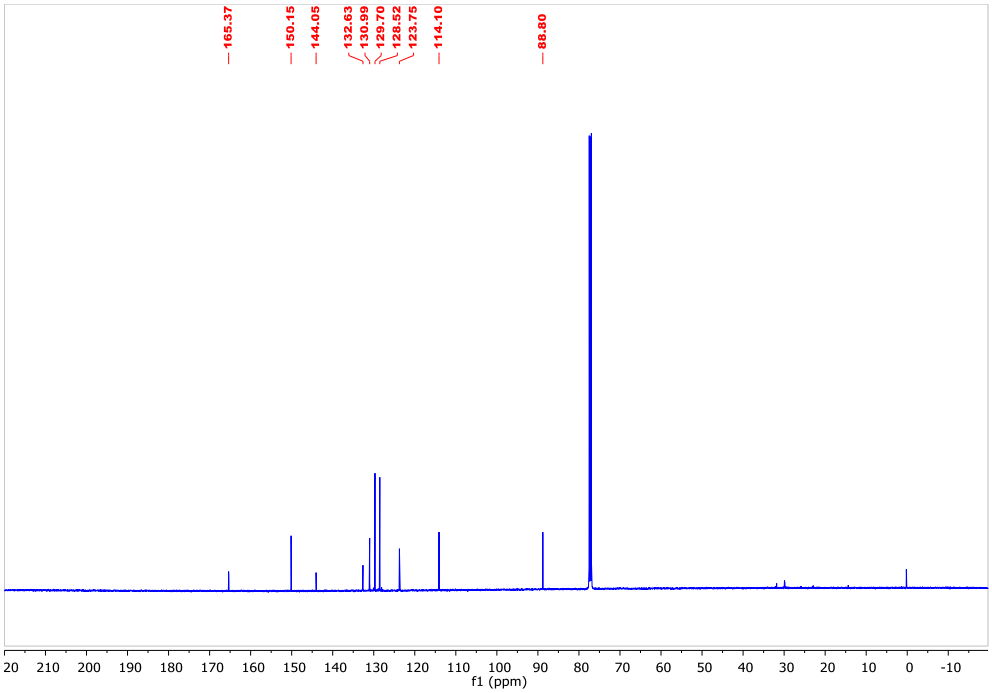


Figure S39. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **2d**

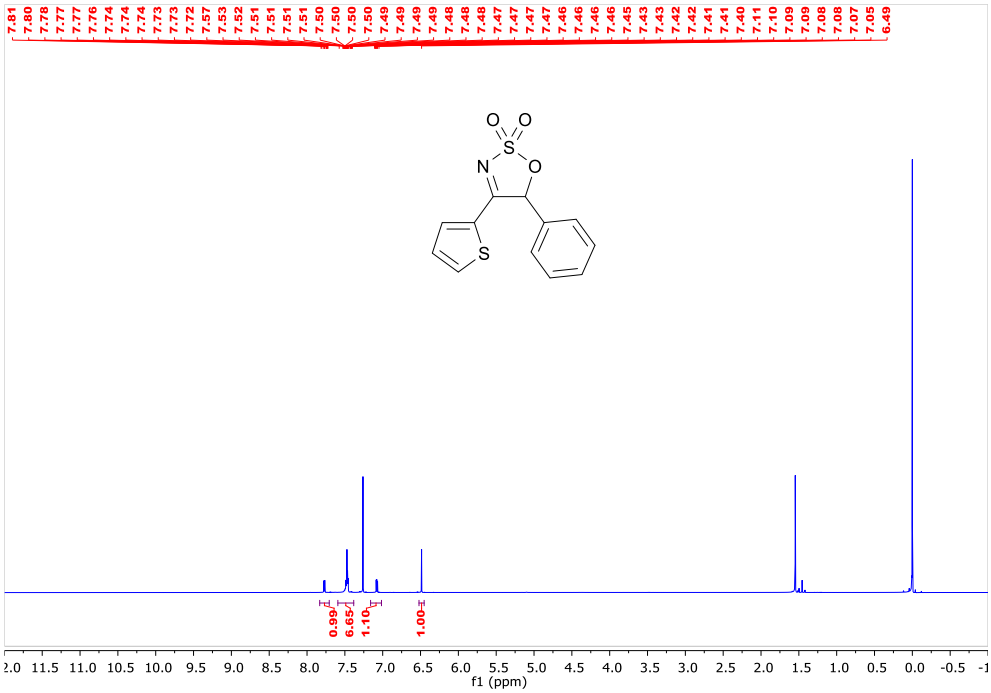


Figure S40. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **2e**

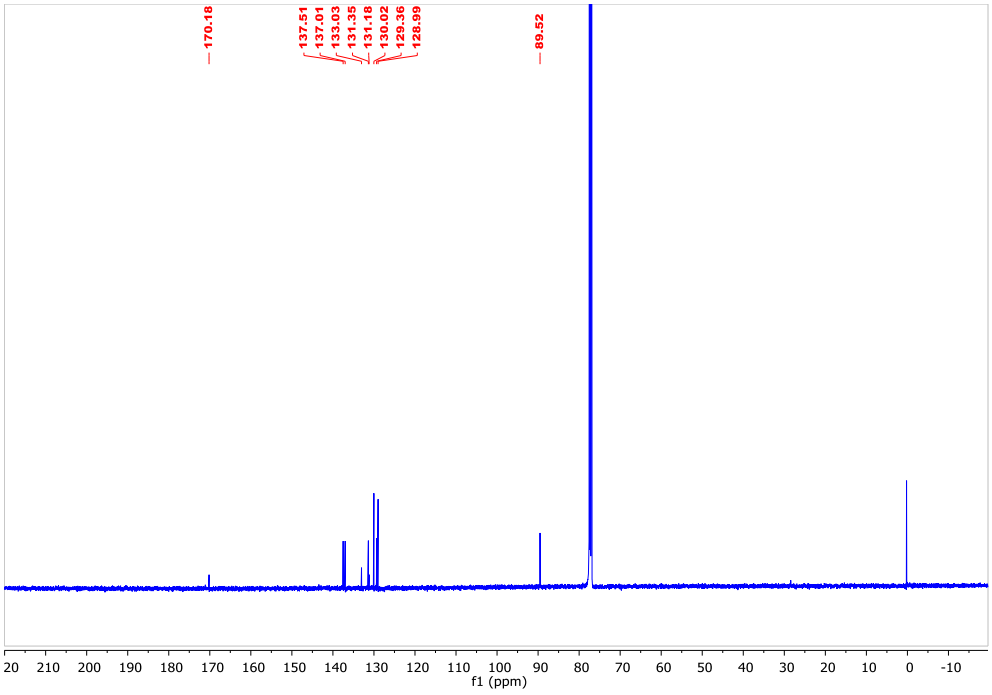


Figure S41. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **2e**

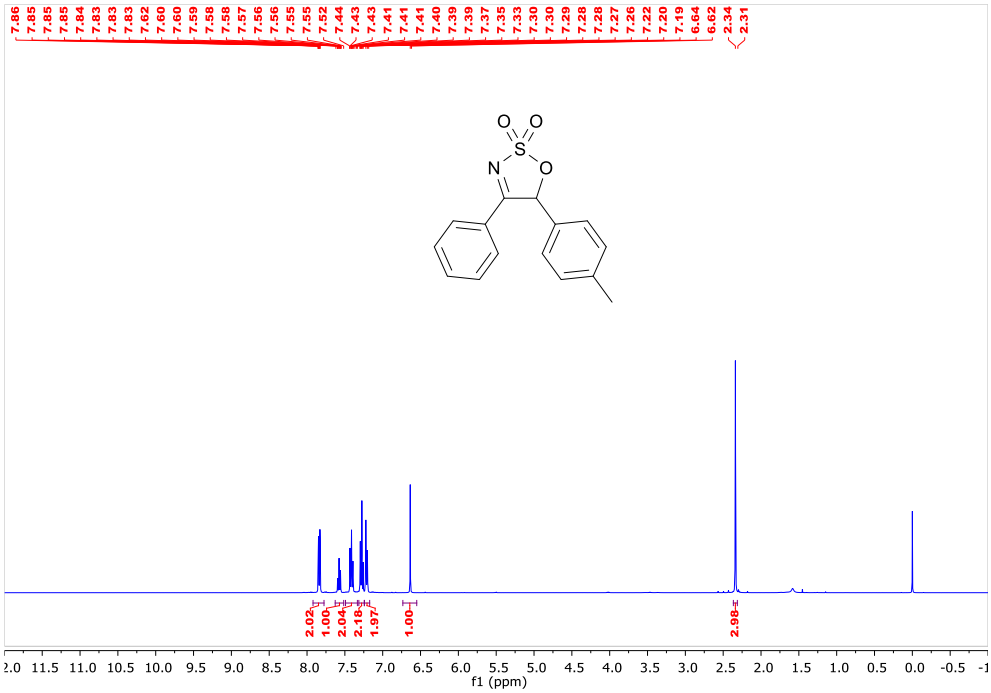


Figure S42. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2g**

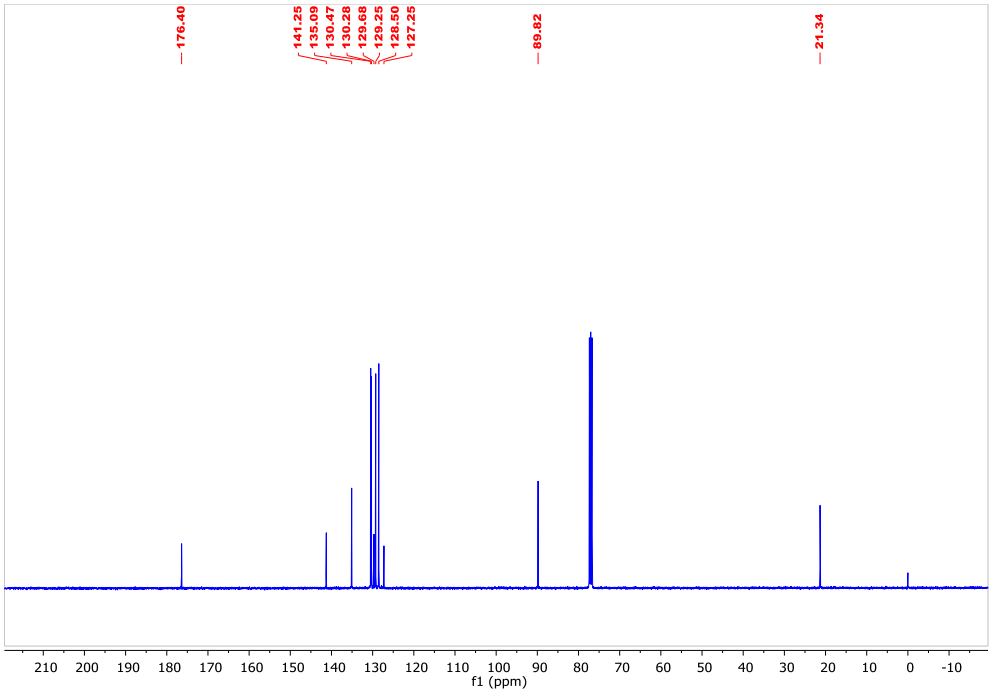


Figure S43. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2g**

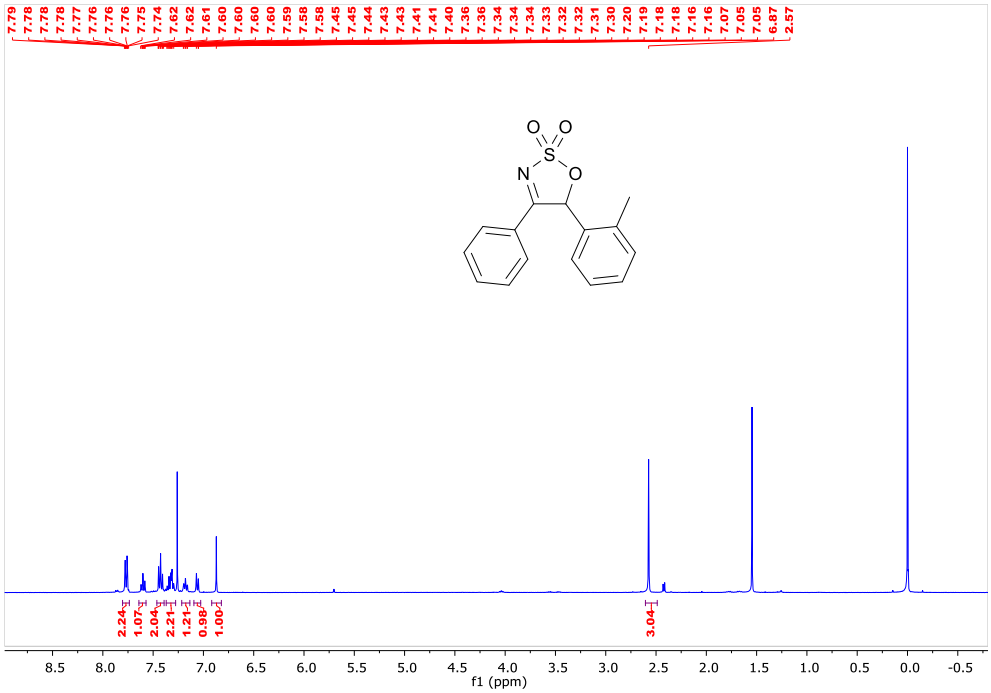


Figure S44. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2h**

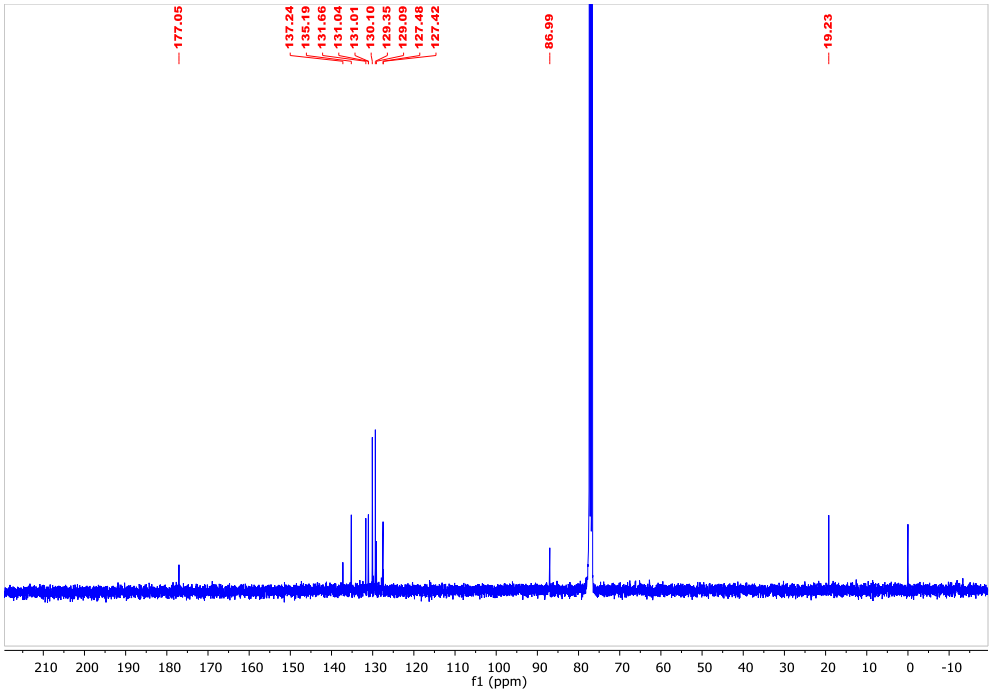


Figure S45. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2h**

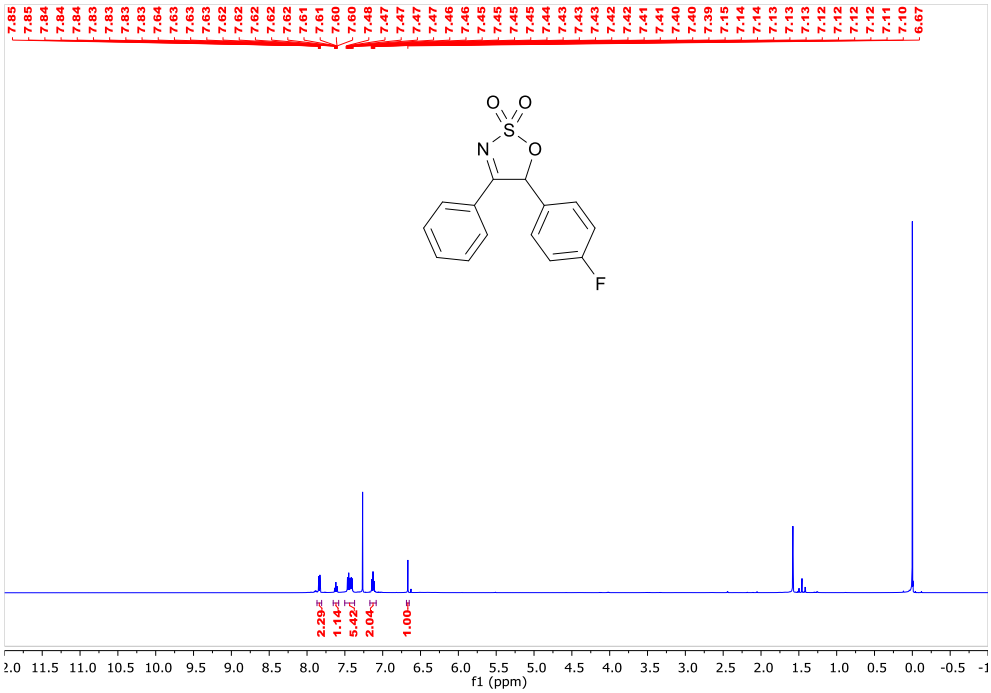


Figure S46. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2i**

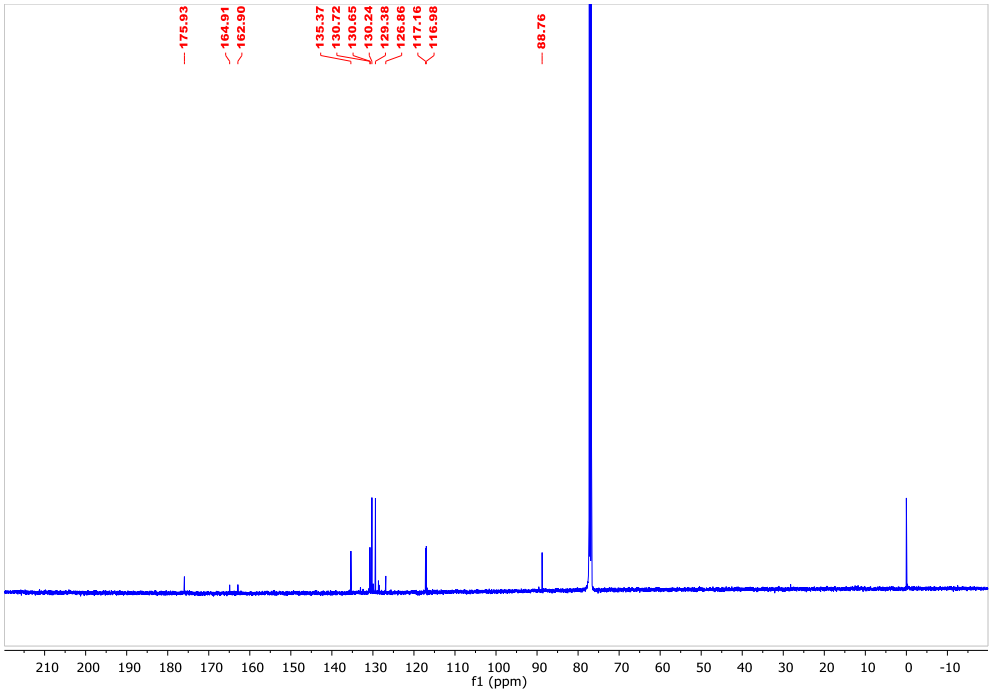


Figure S47. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2i**

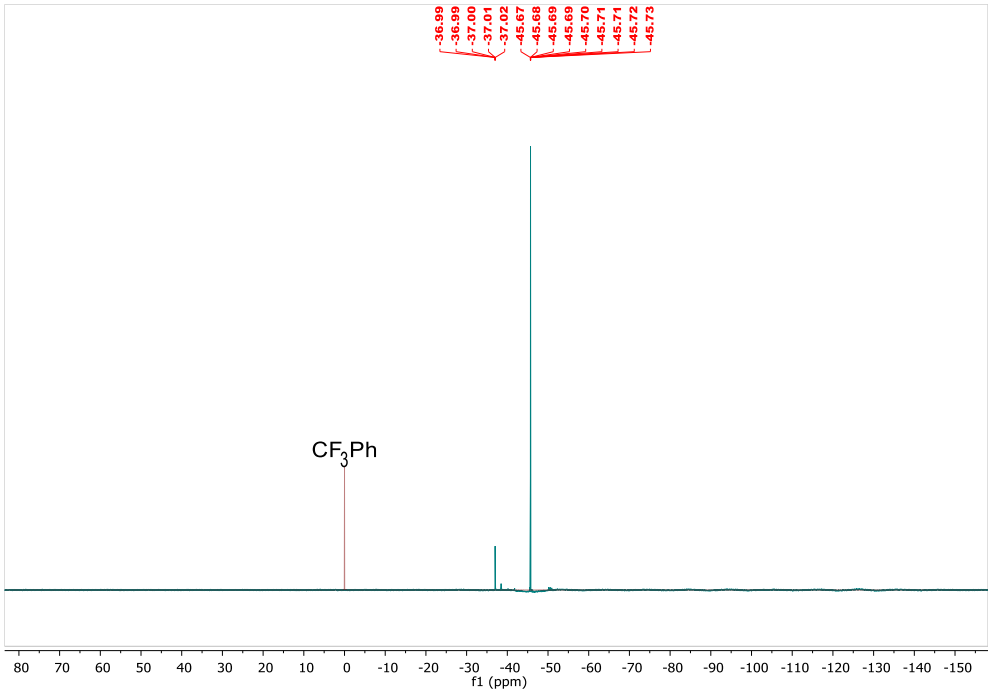


Figure S48. ^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of **2i**

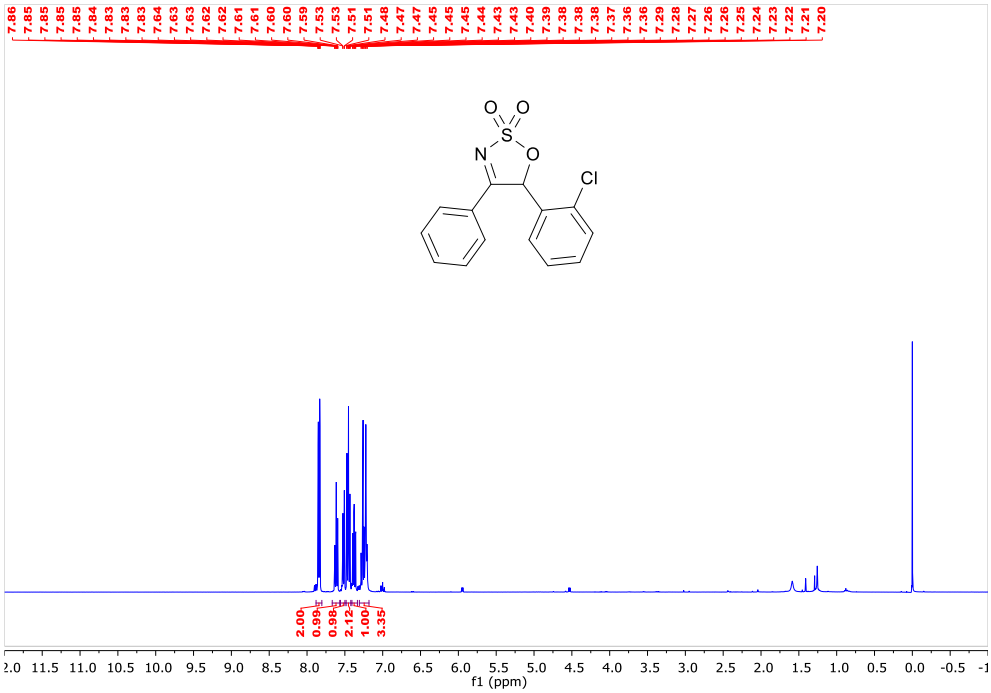


Figure S49. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2j**

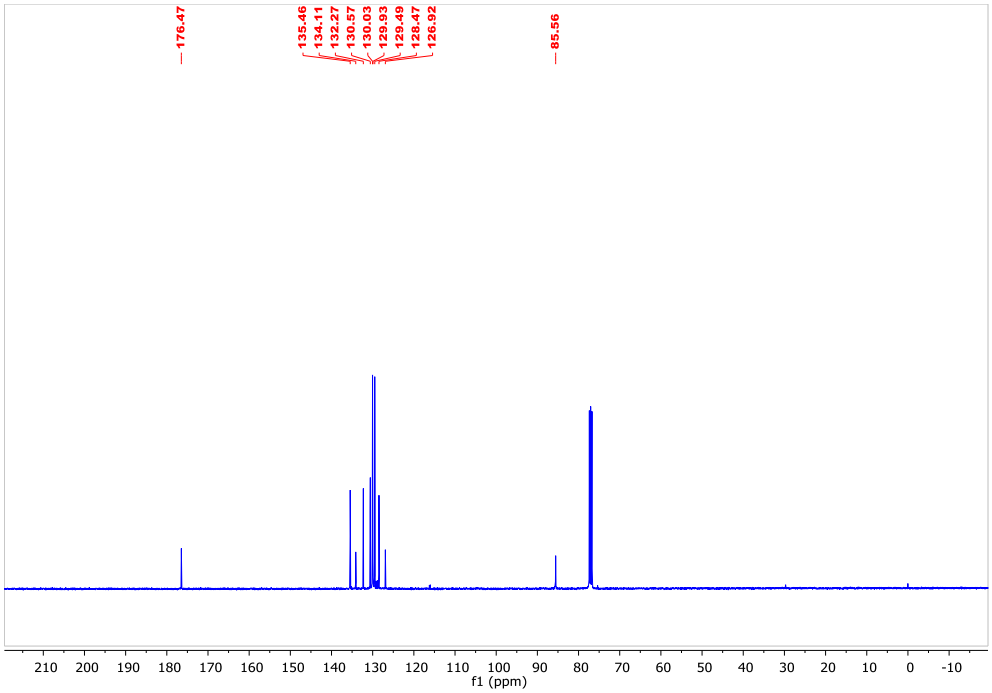


Figure S50. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **2j**

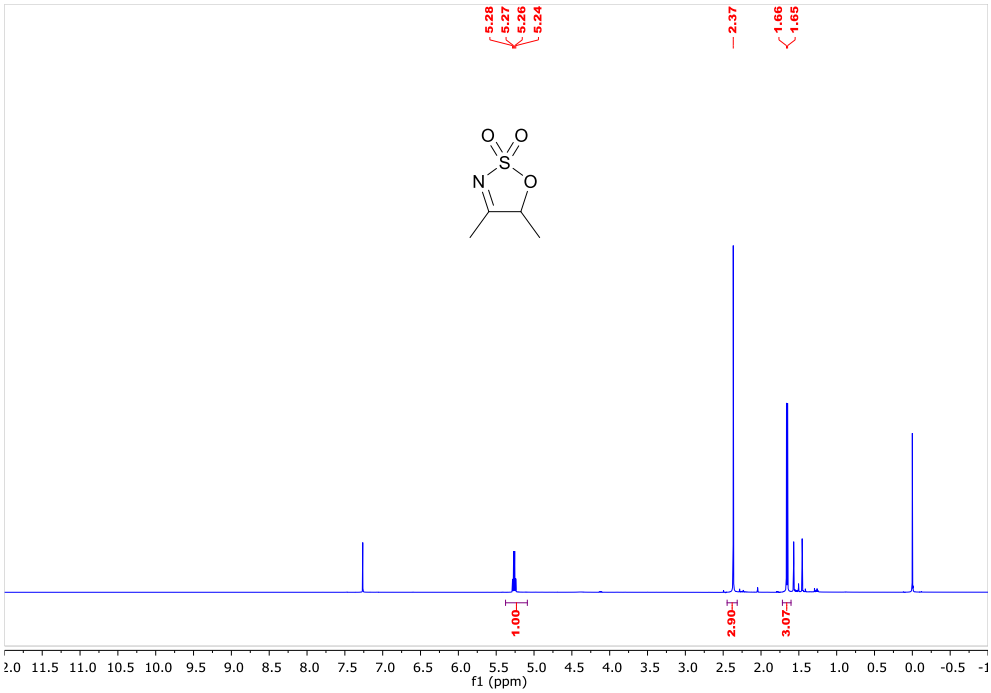


Figure S51. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **2n**

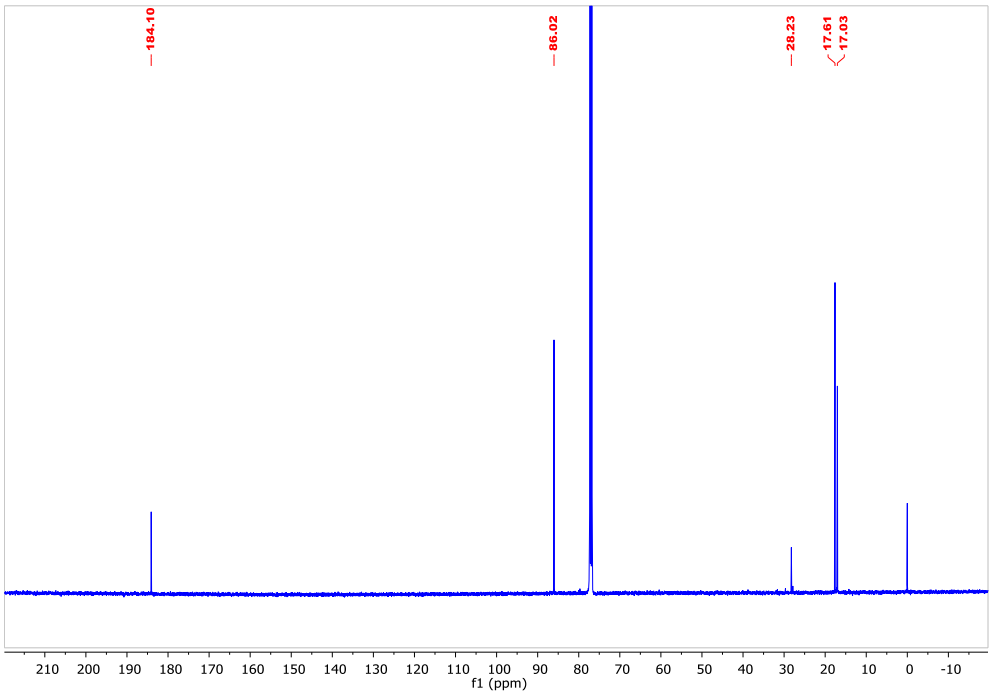


Figure S52. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **2n**

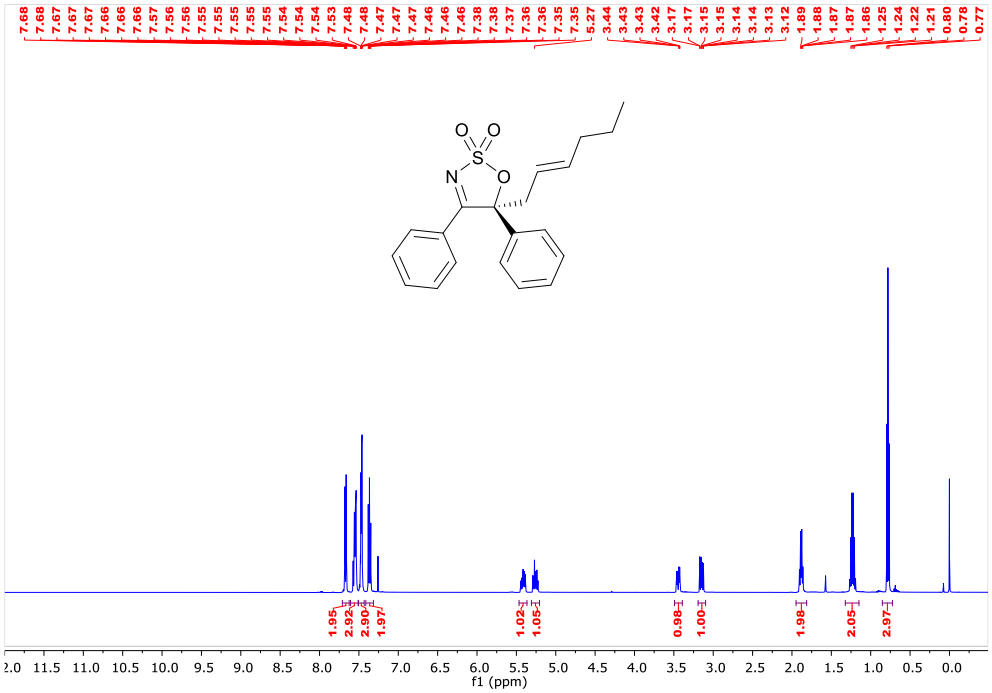


Figure S53. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **3aa**

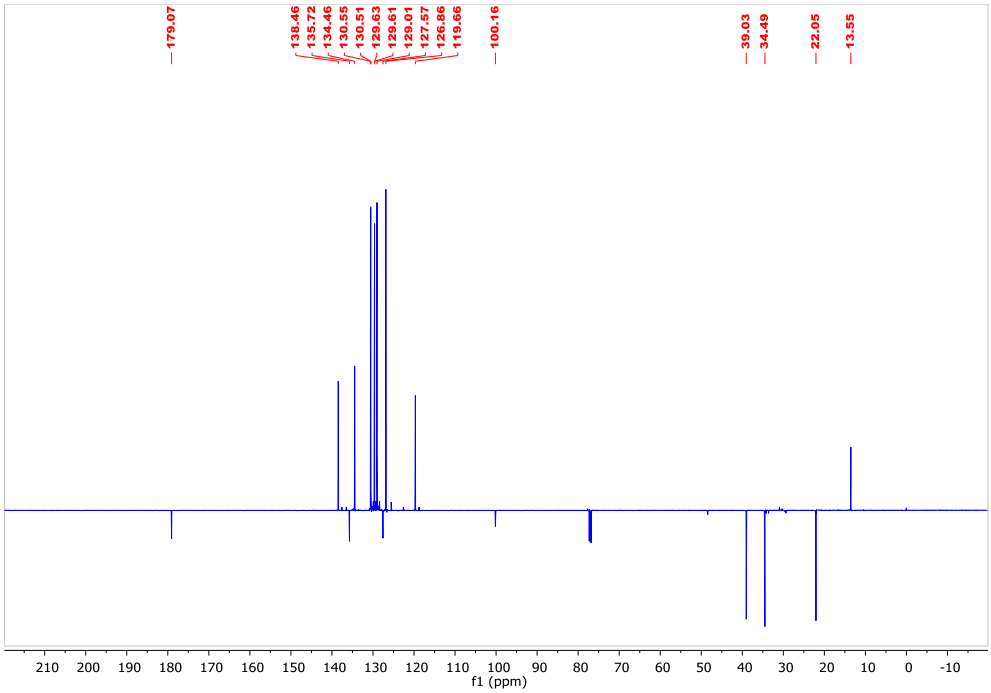


Figure S54. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **3aa**

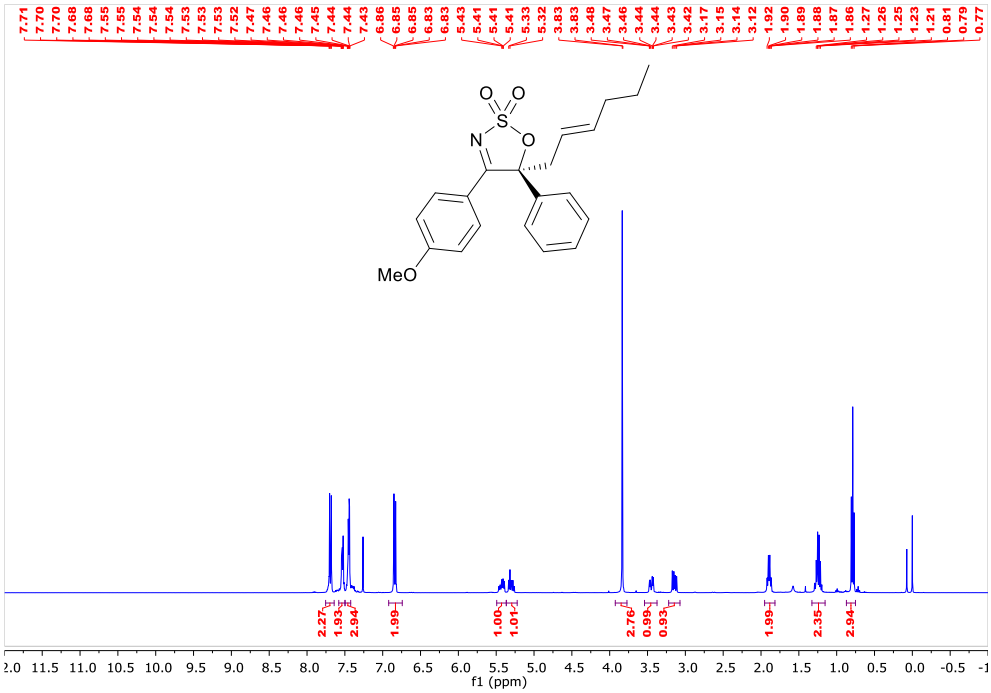


Figure S55. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ab**

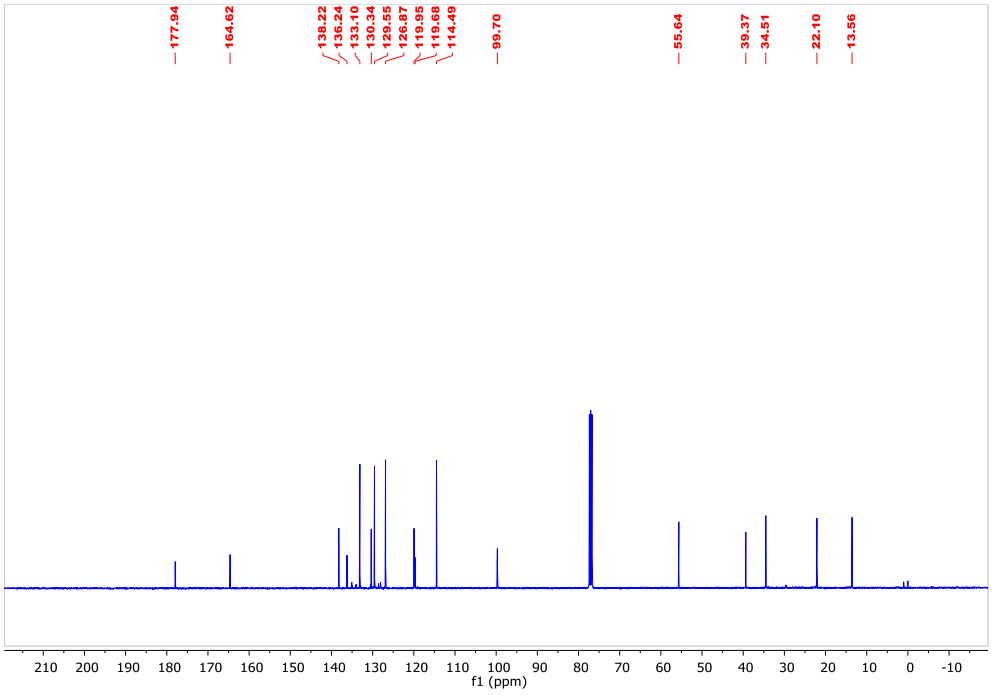


Figure S56. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ab**

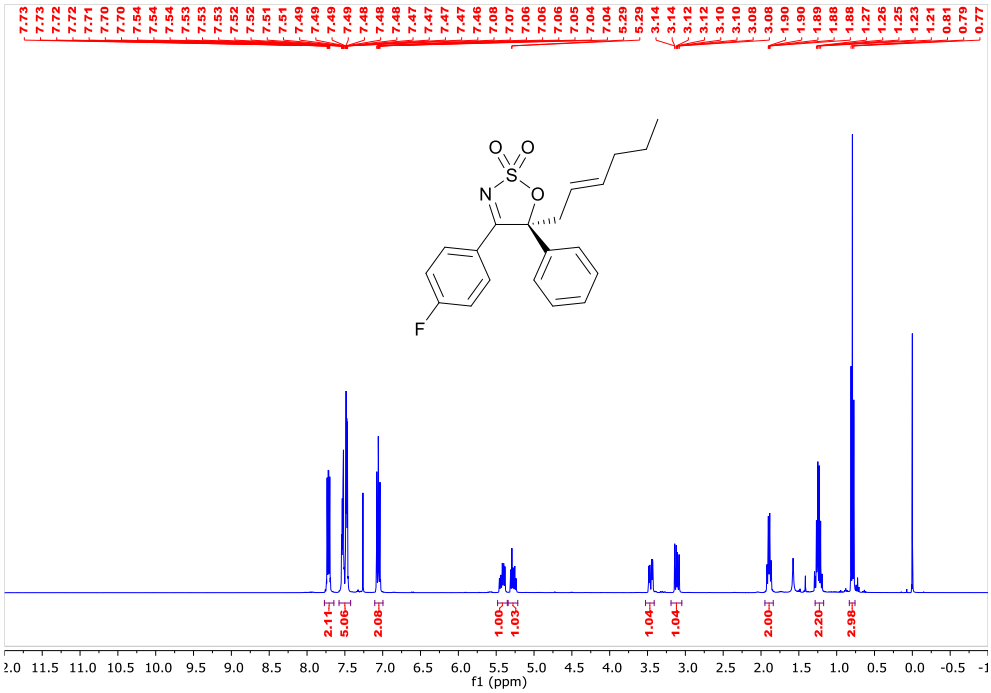


Figure S57. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ac**

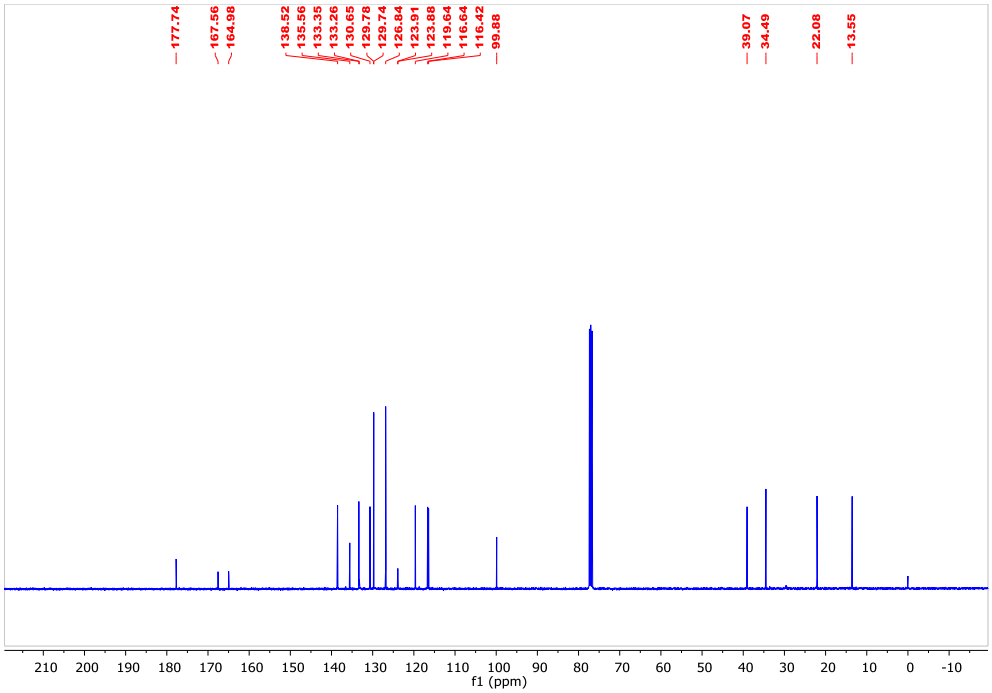


Figure S58. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ac**

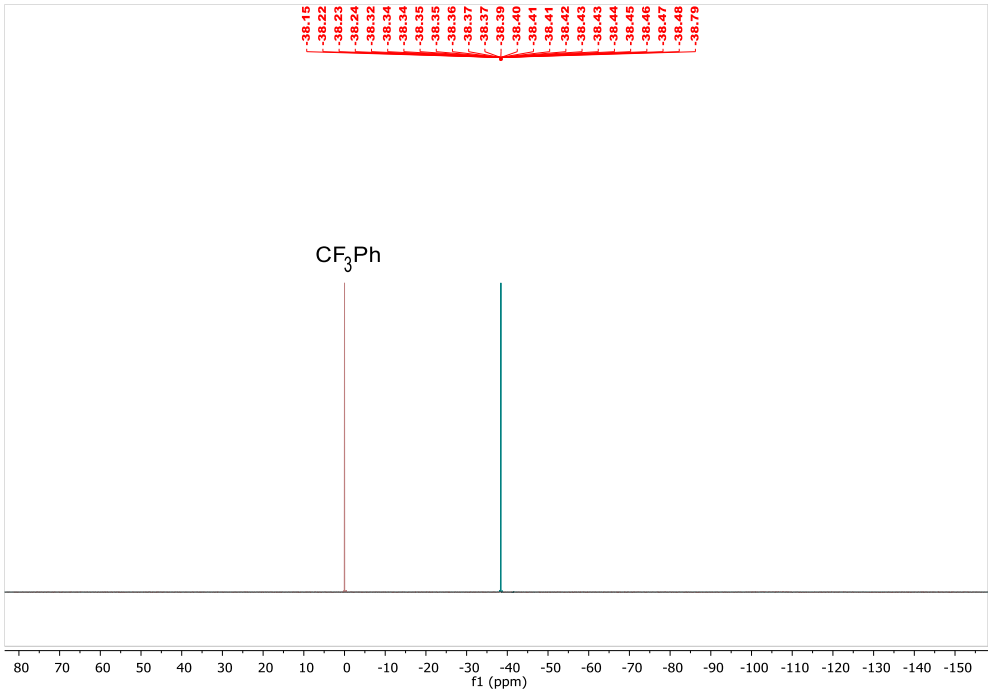


Figure S59. ^{19}C NMR spectrum ($CDCl_3$, 470 MHz) of **3ac**

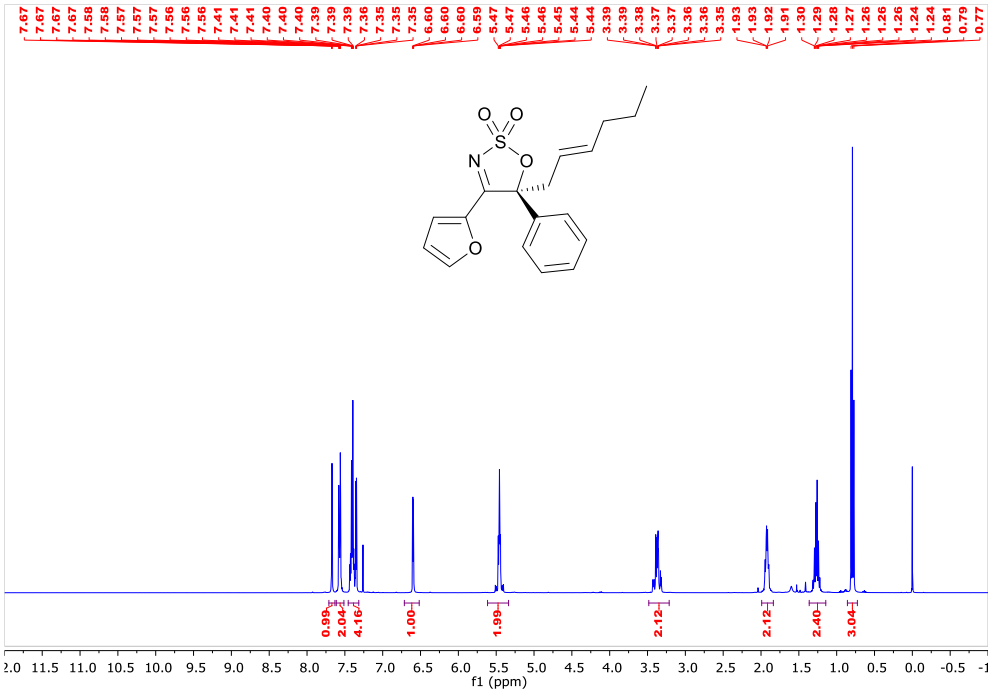


Figure S60. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ad**

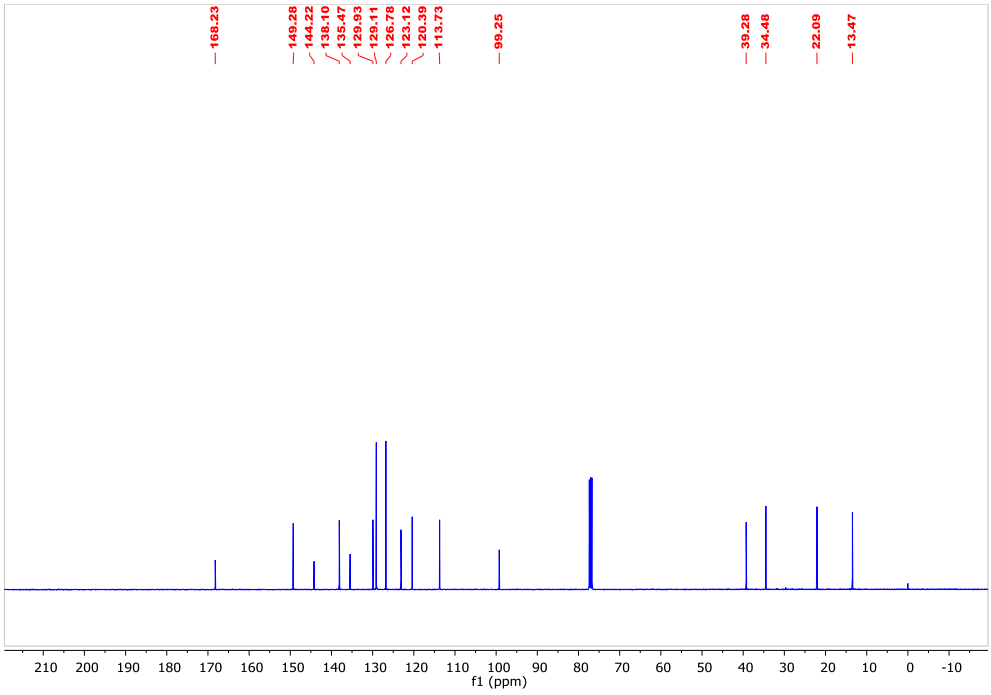


Figure S61. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ad**

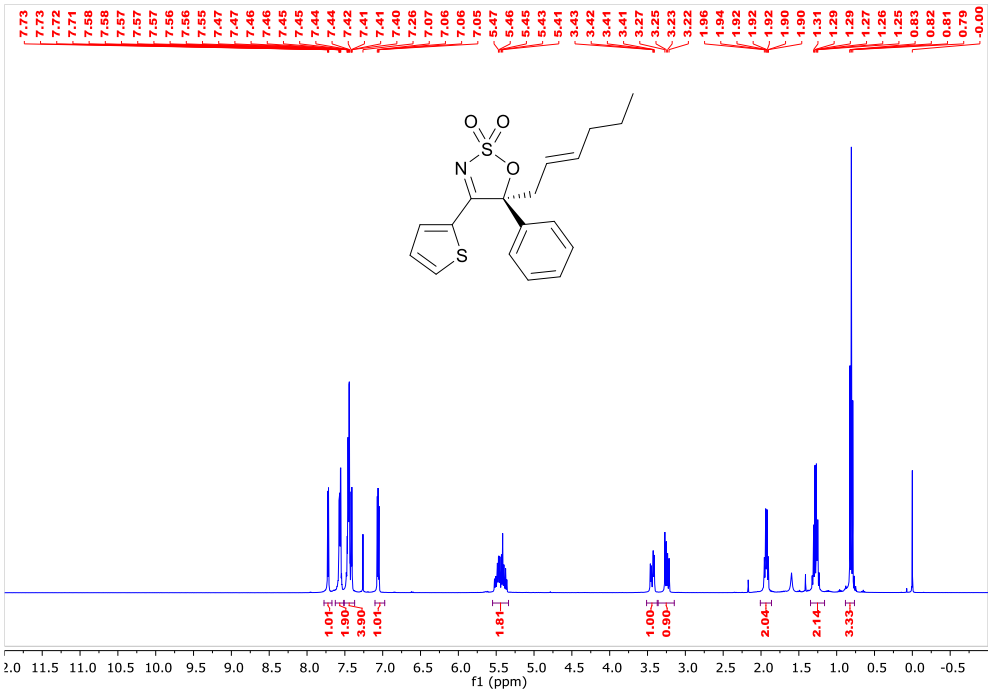


Figure S62. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ae**

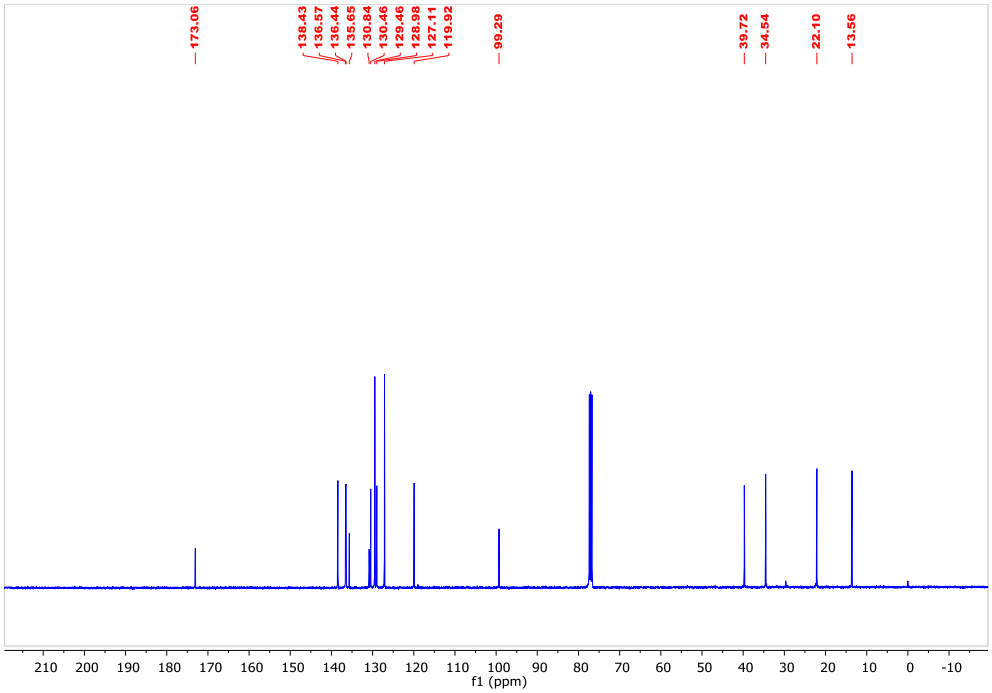


Figure S63. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ae**

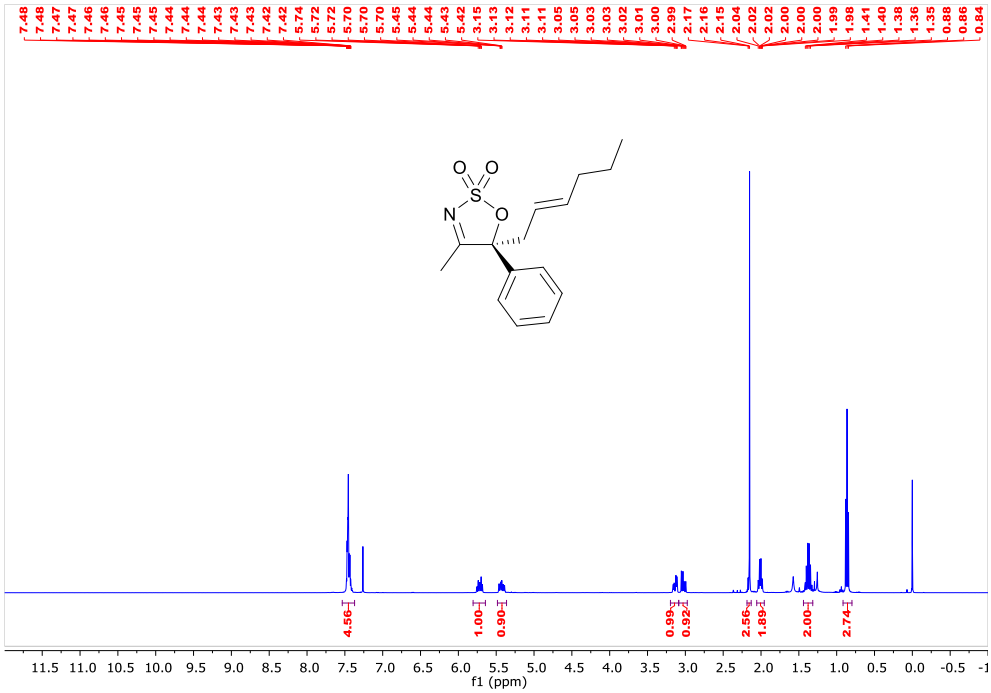


Figure S64. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3af**

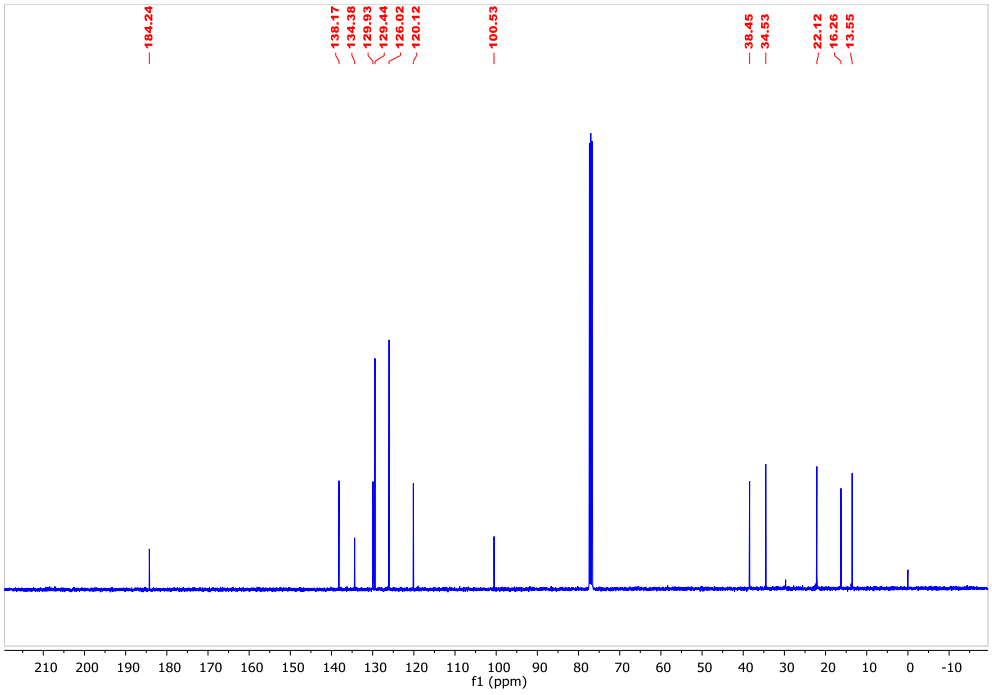


Figure S65. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3af**

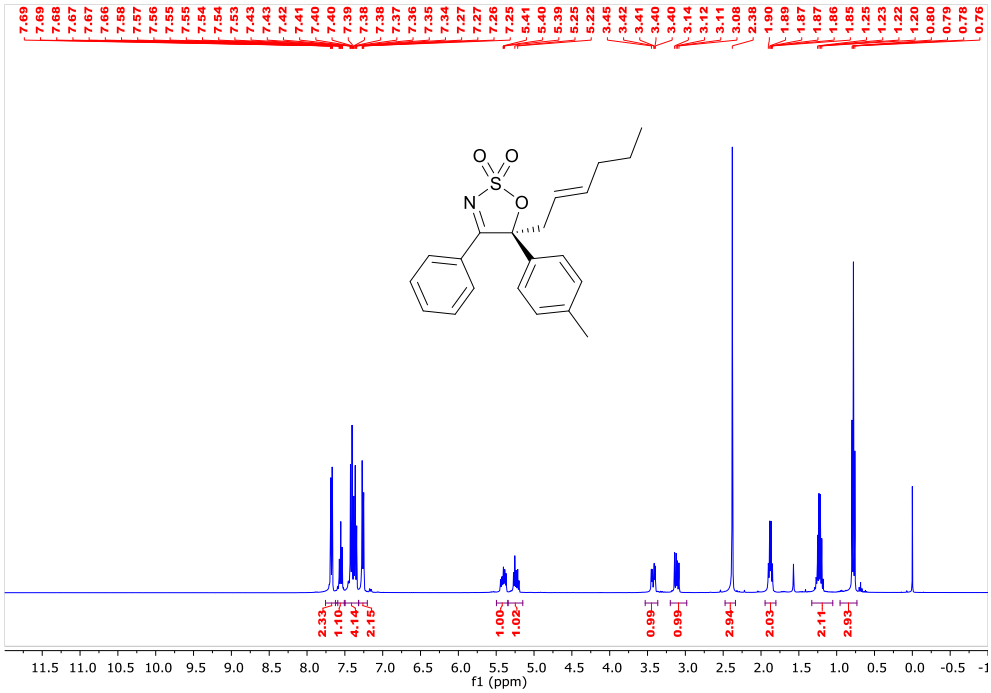


Figure S66. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ag**

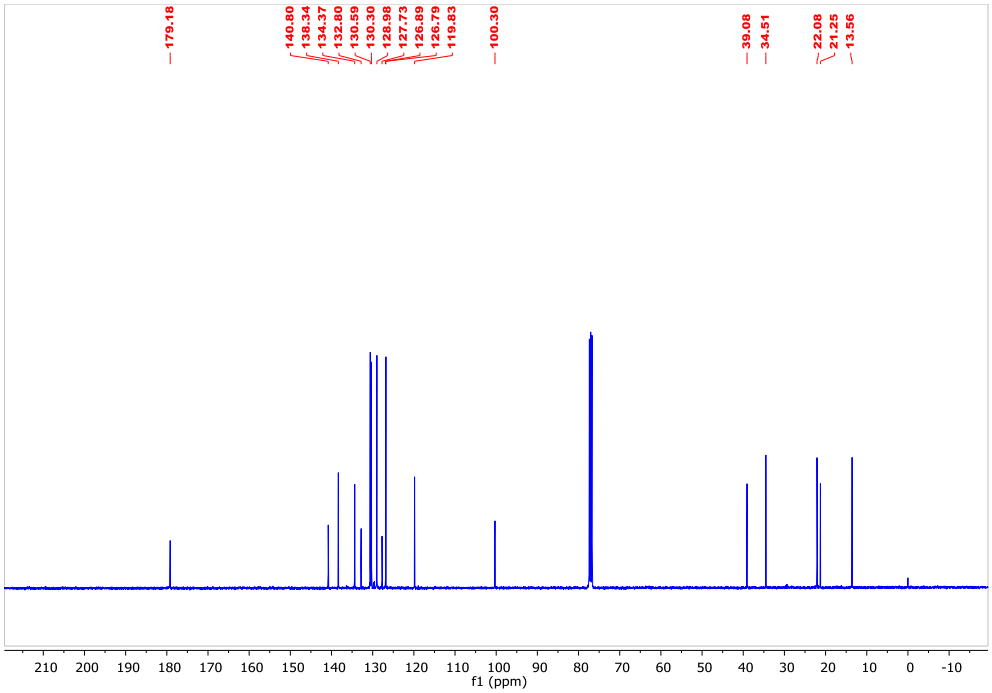


Figure S67. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ag**

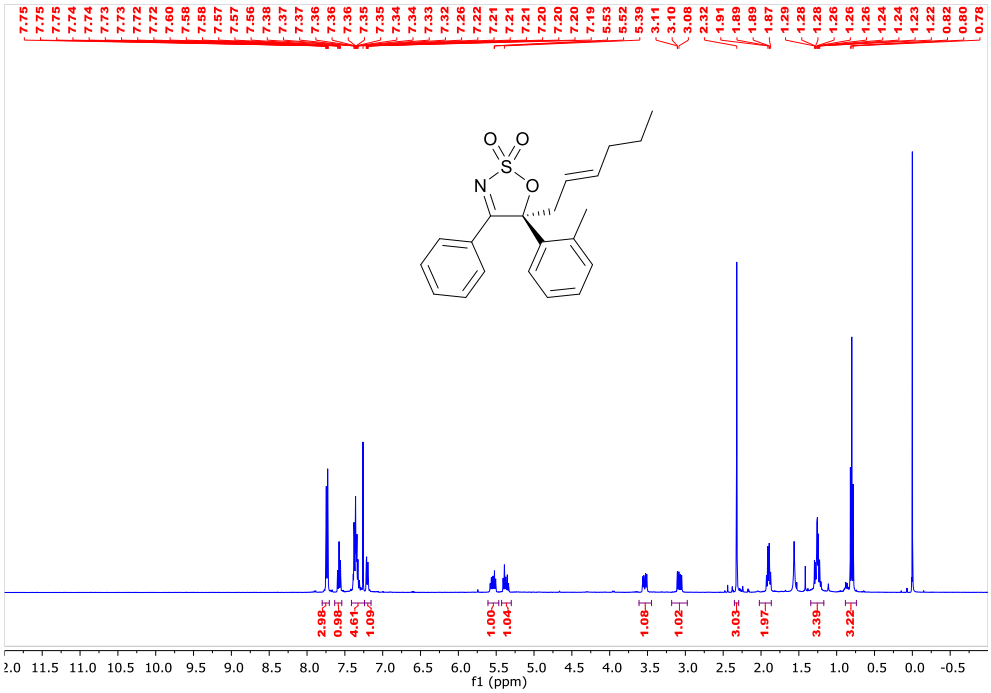


Figure S68. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ah**

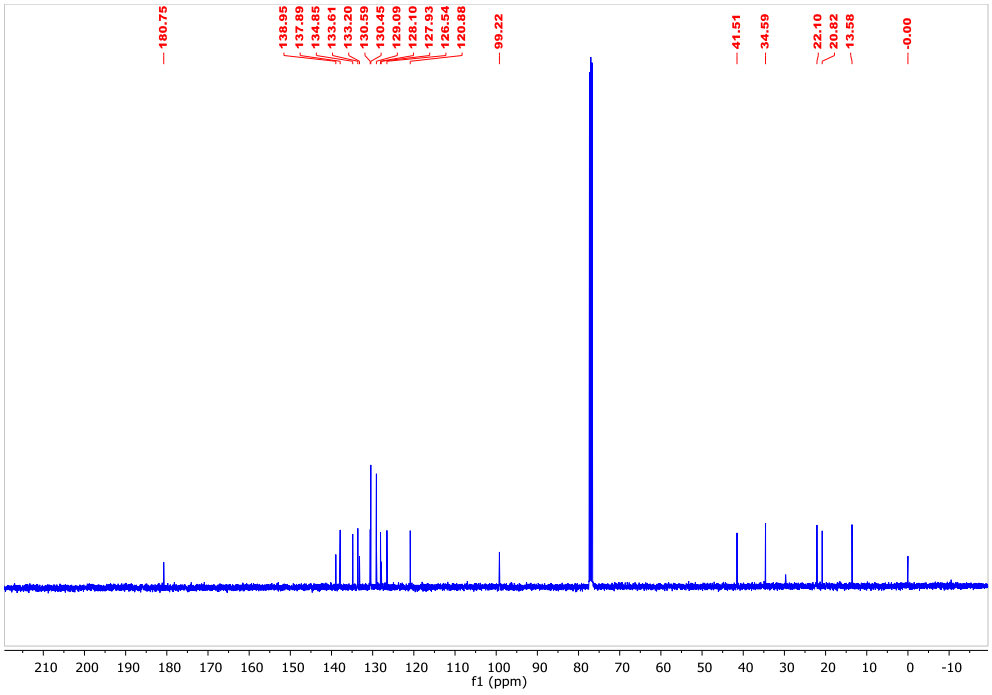


Figure S69. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ah**

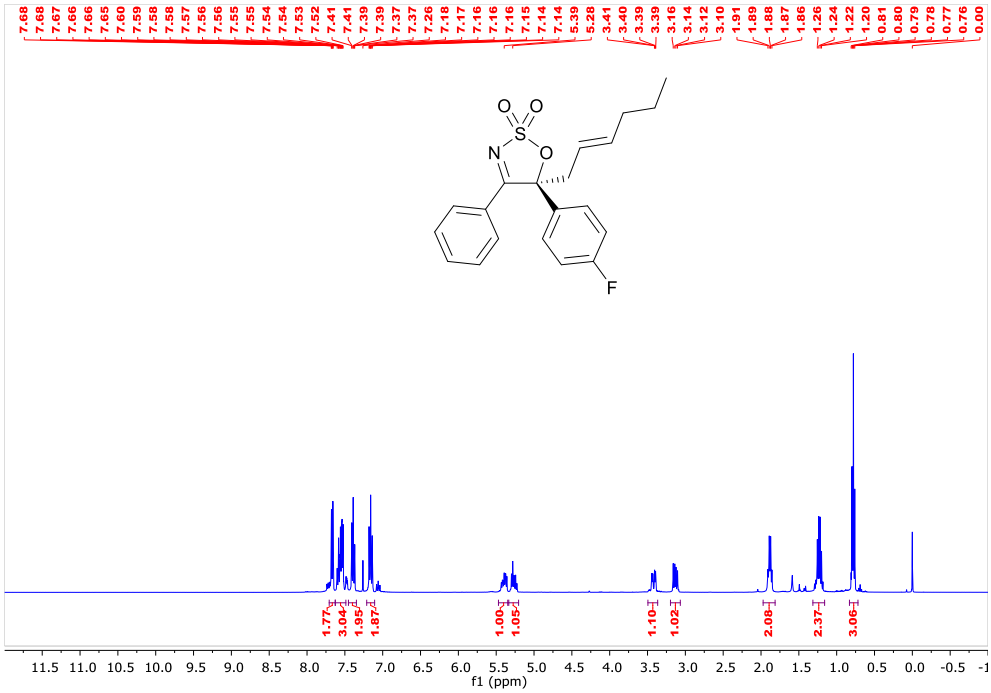


Figure S70. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ai**

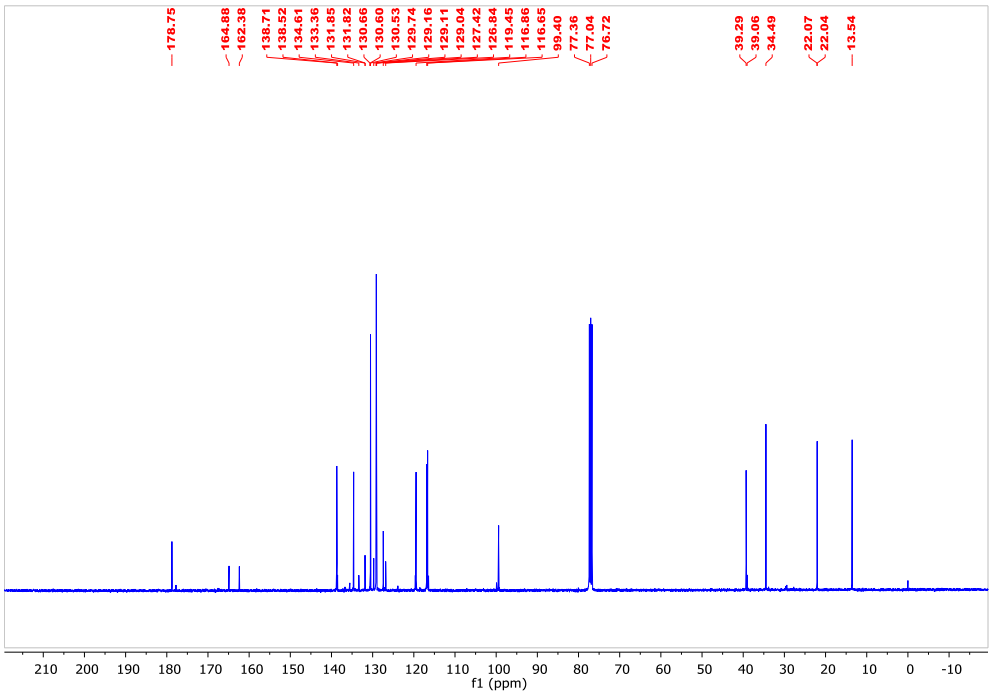


Figure S71. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ai**

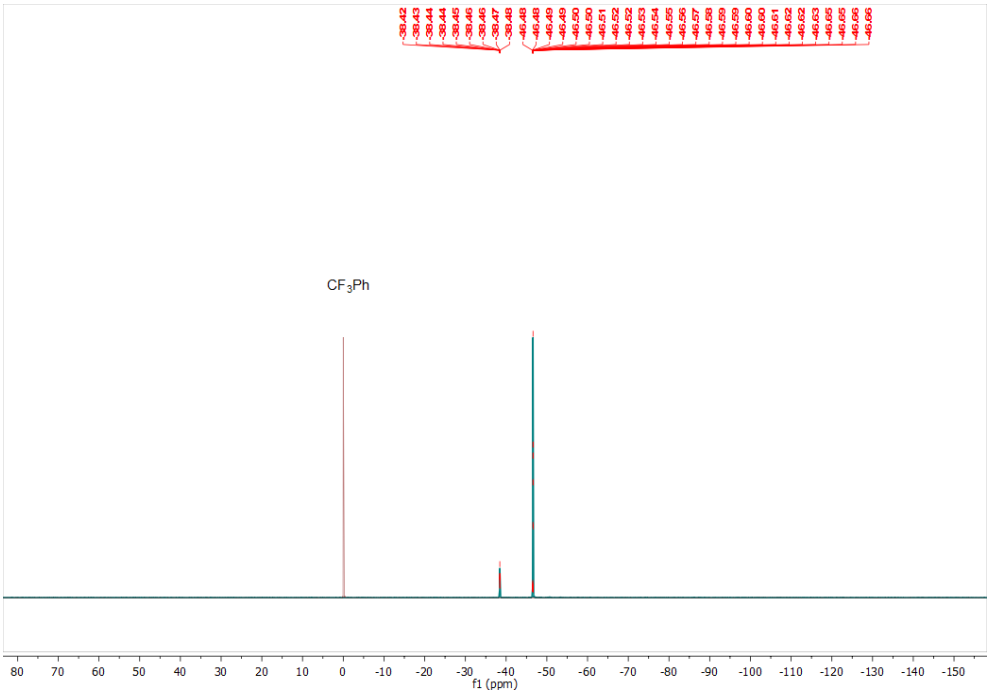


Figure S72. ^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of **3ai**

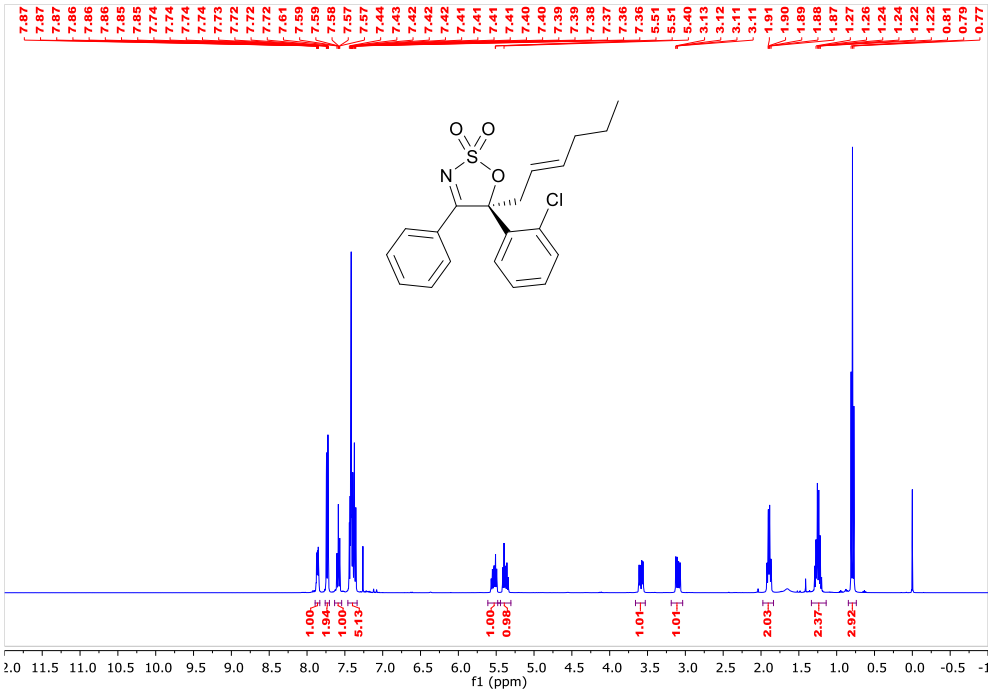


Figure S73. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3aj**

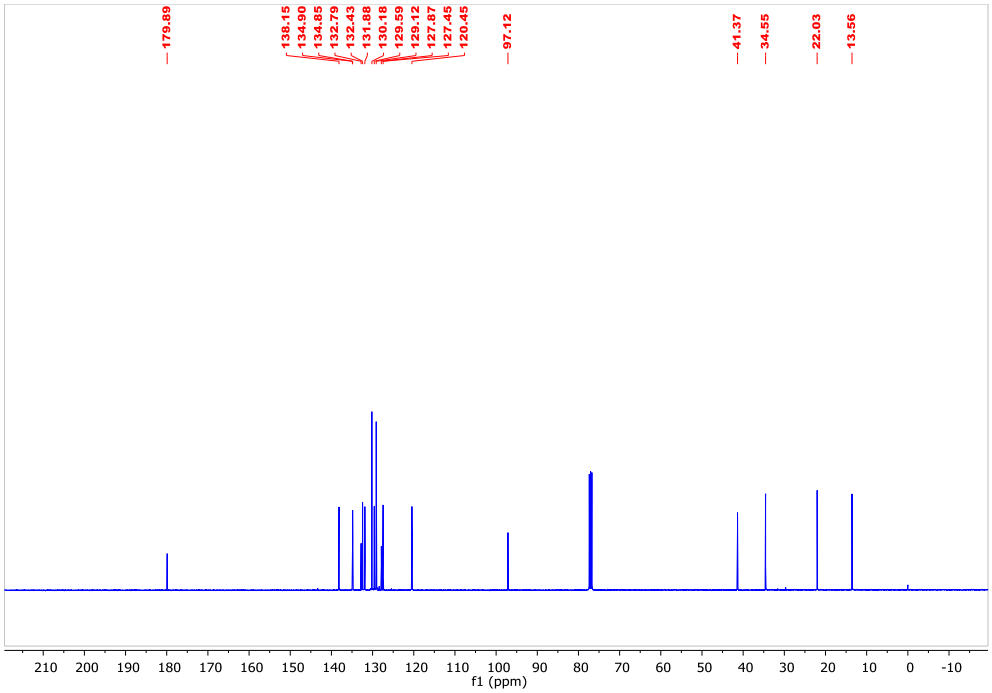


Figure S74. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3aj**

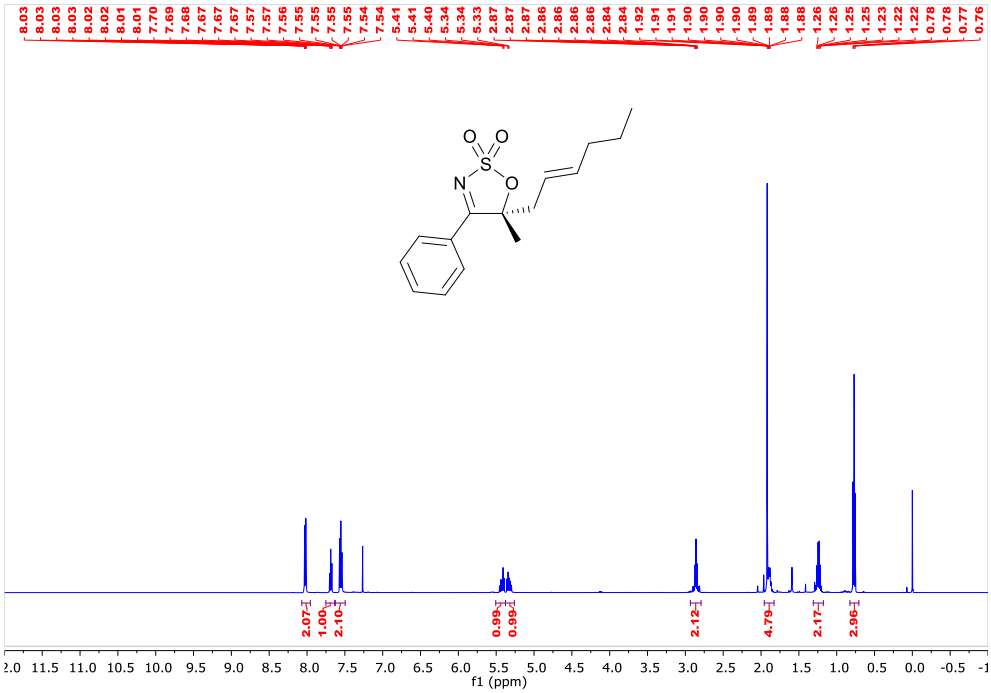


Figure S75. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **3ak**

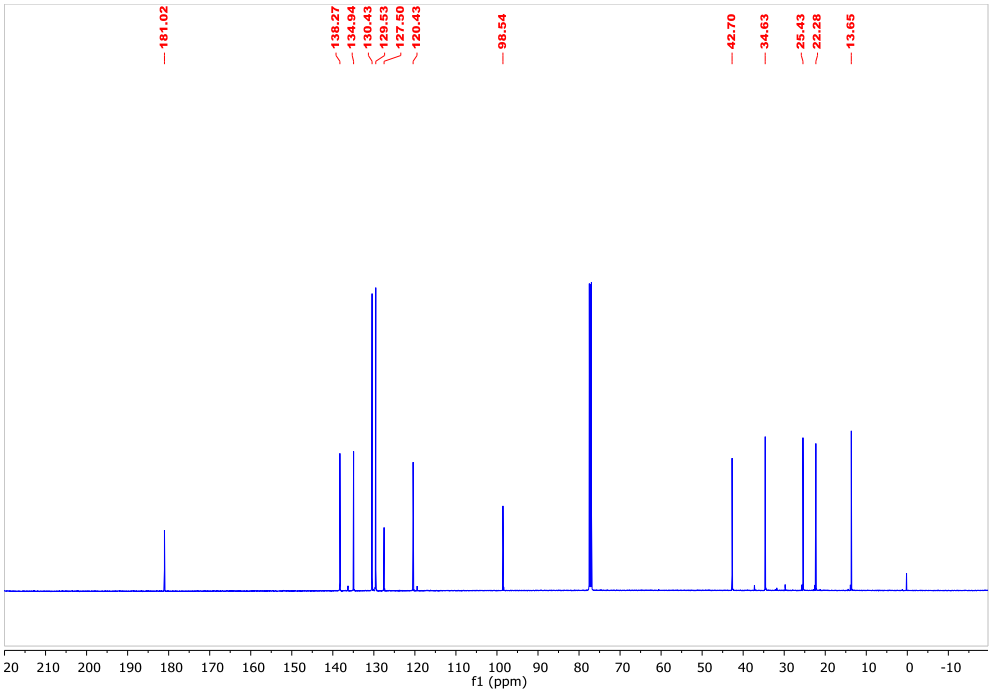


Figure S76. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **3ak**

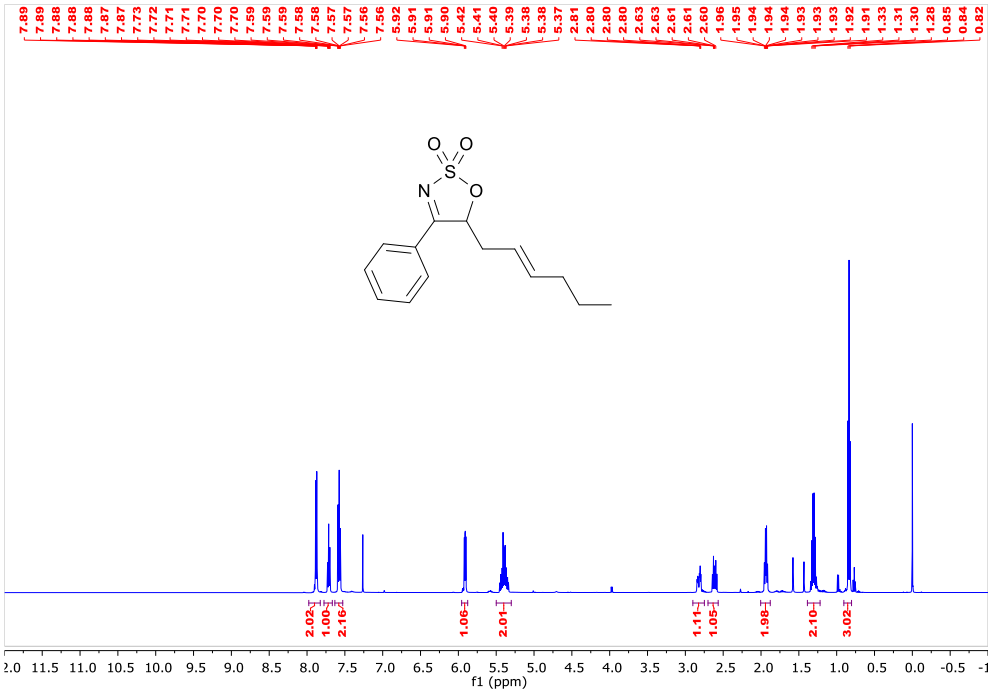


Figure S77. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **3an**

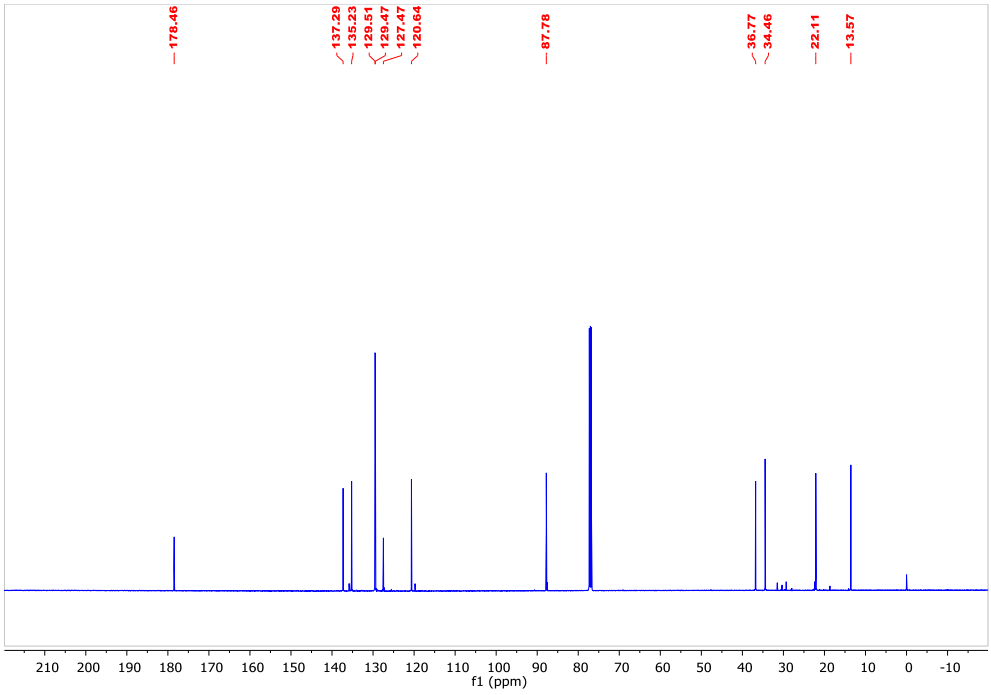


Figure S78. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **3an**

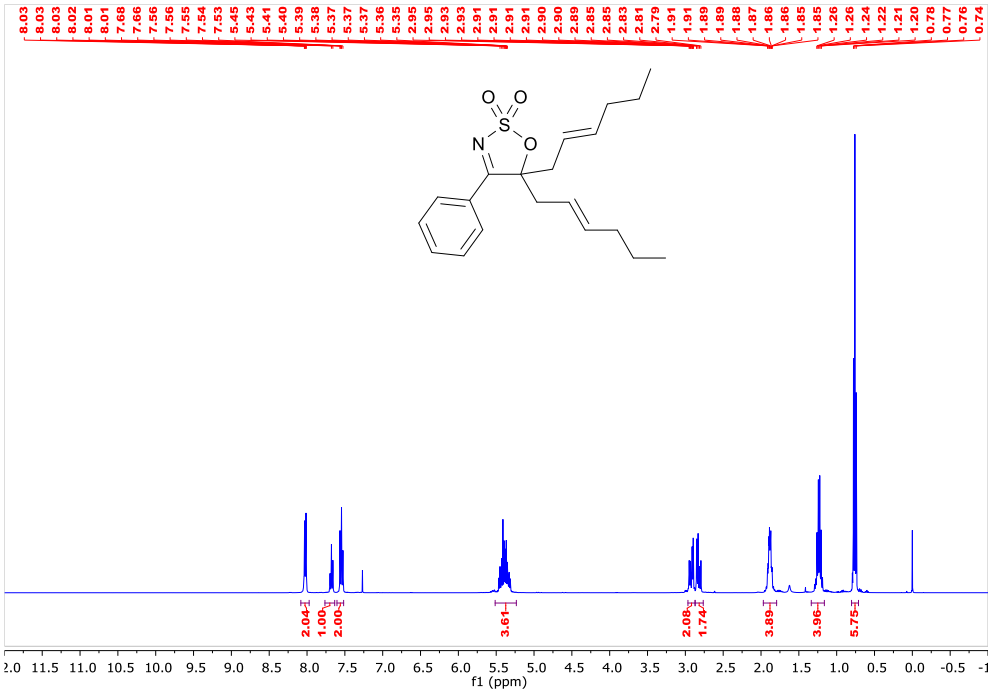


Figure S79. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **3aan**

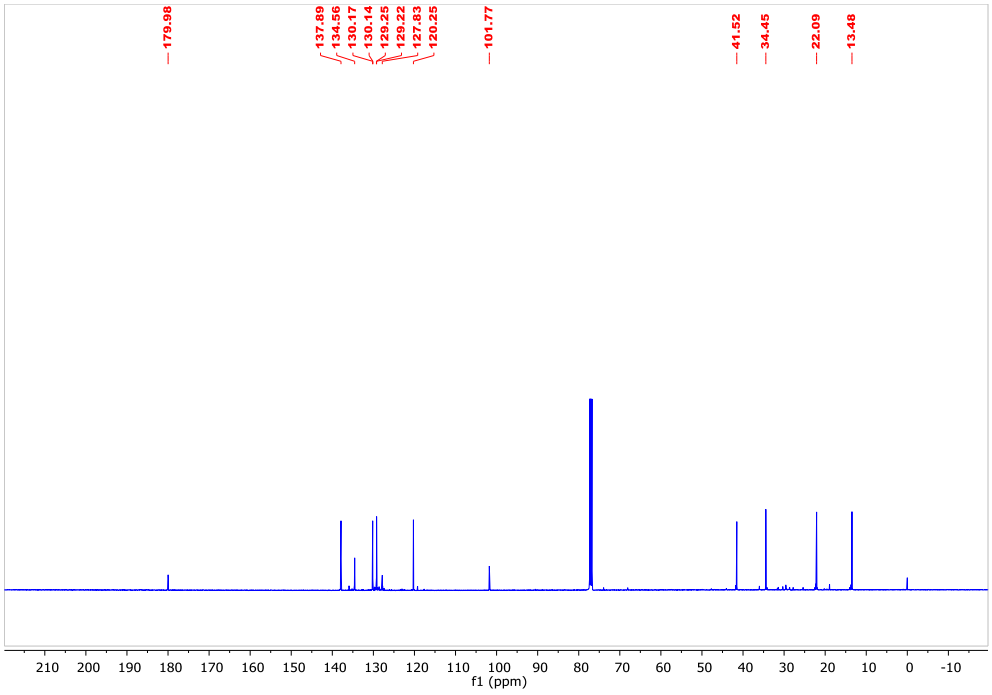


Figure S80. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **3aan**

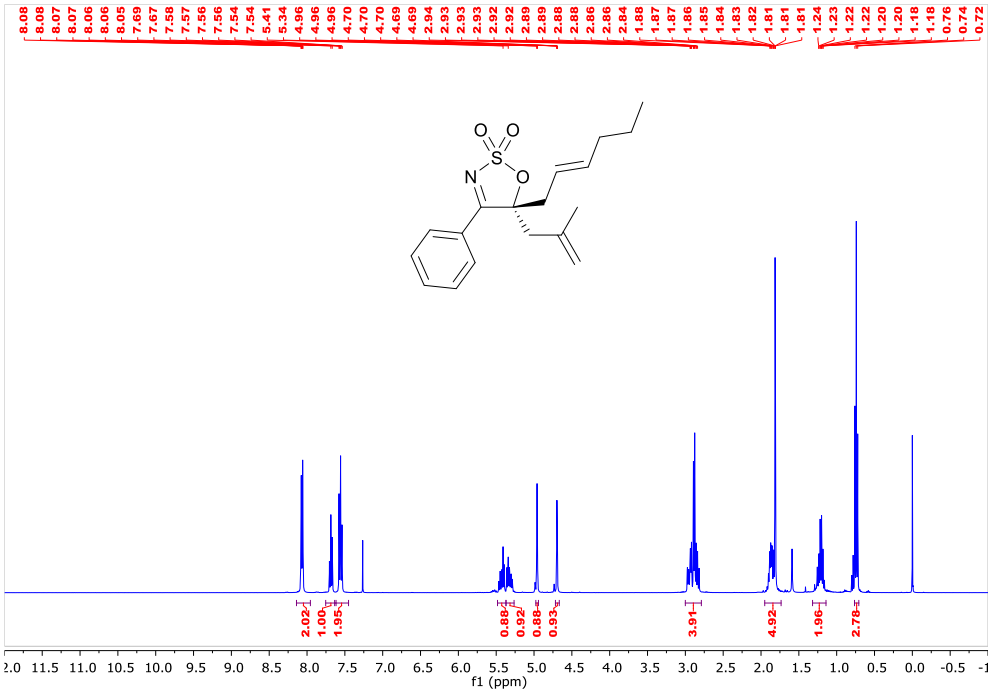


Figure S81. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3abn**

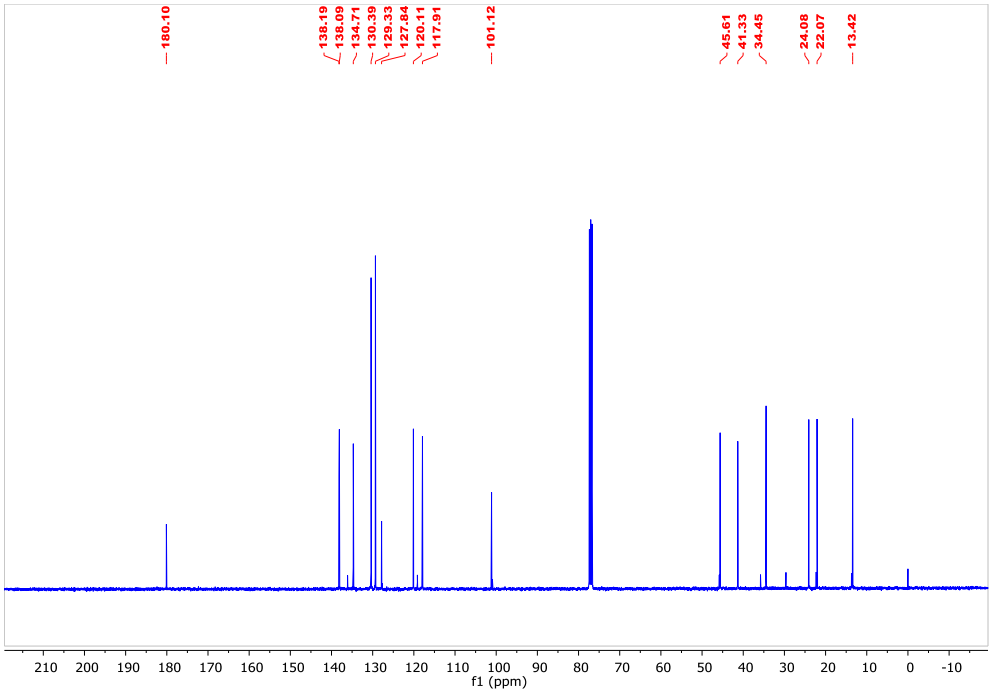


Figure S82. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3abn**

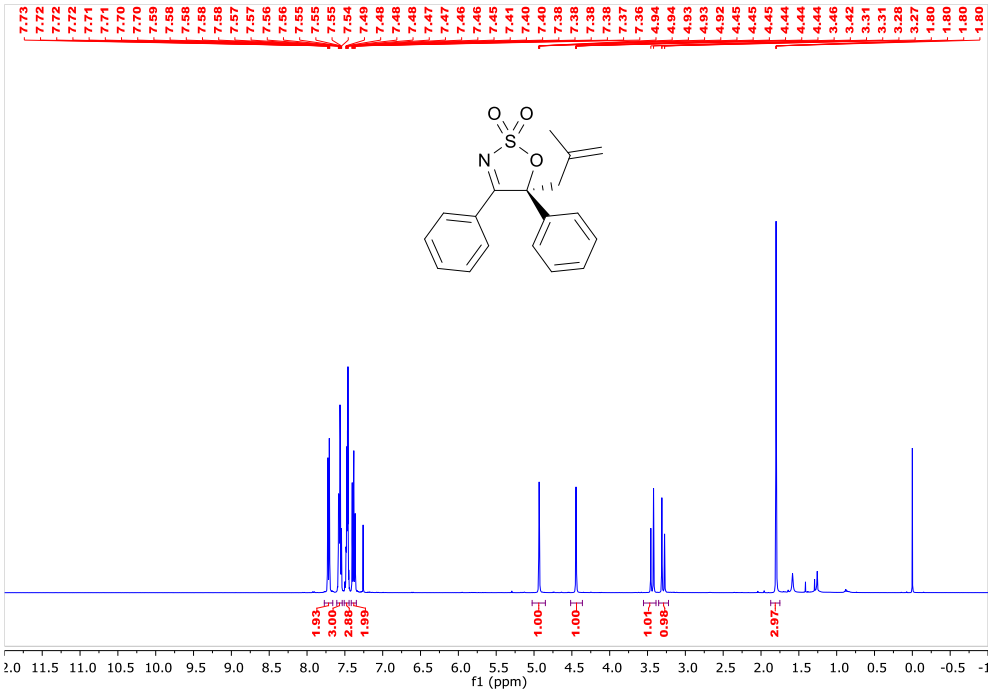


Figure S83. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ba**

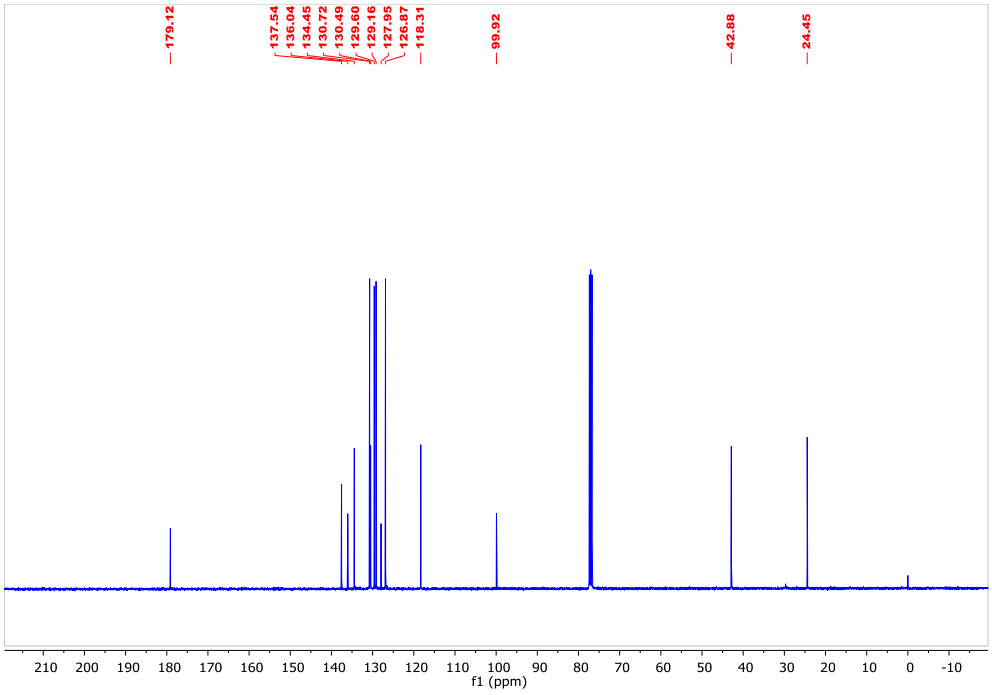


Figure S84. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ba**

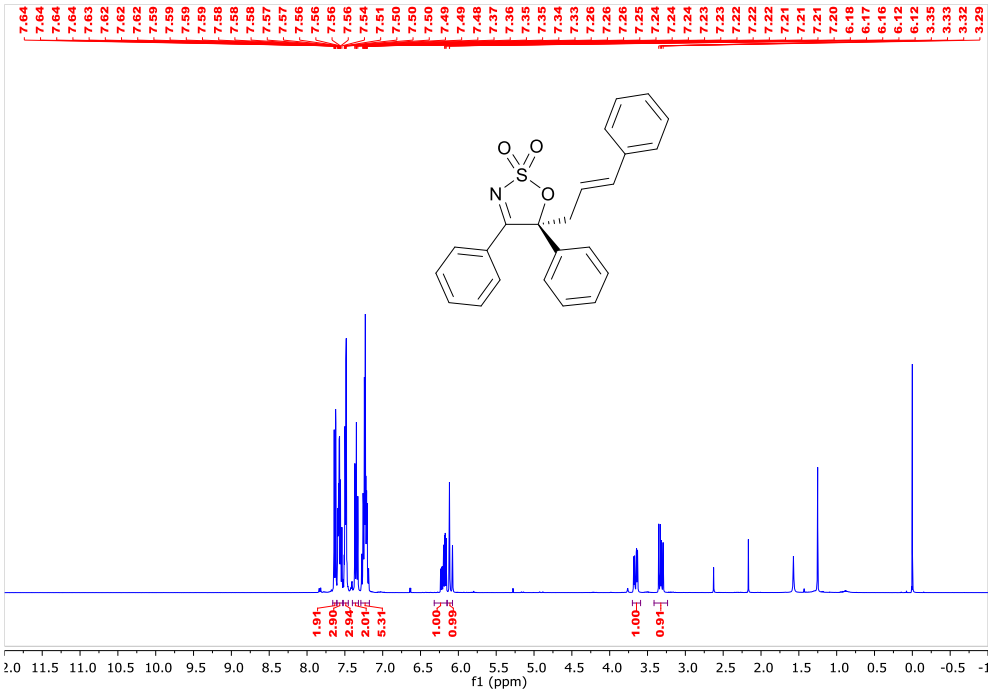


Figure S85. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ca**

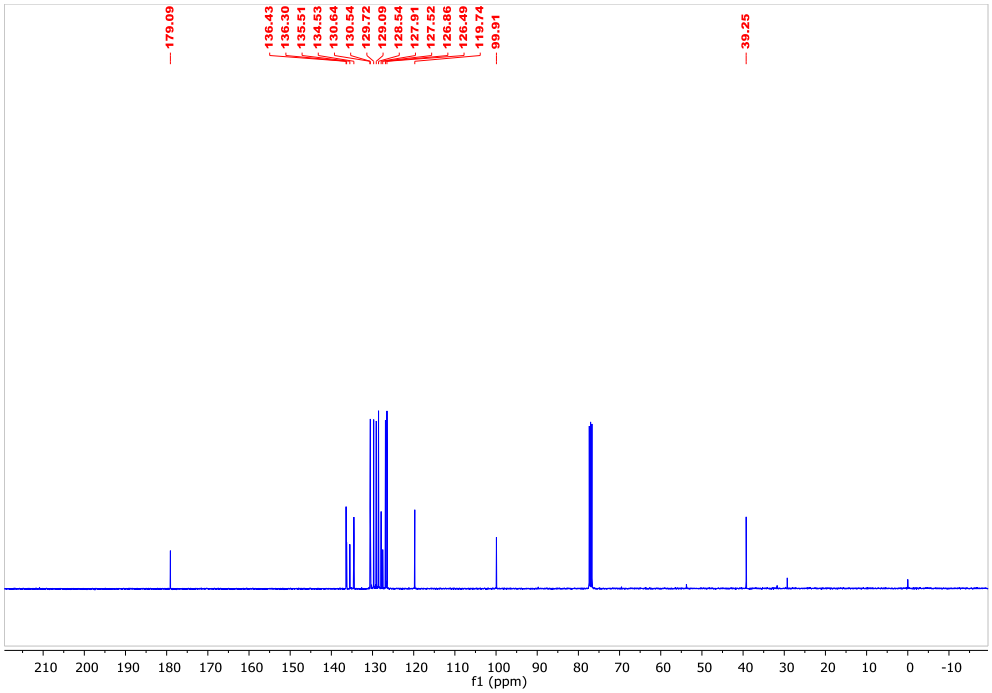


Figure S86. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ca**

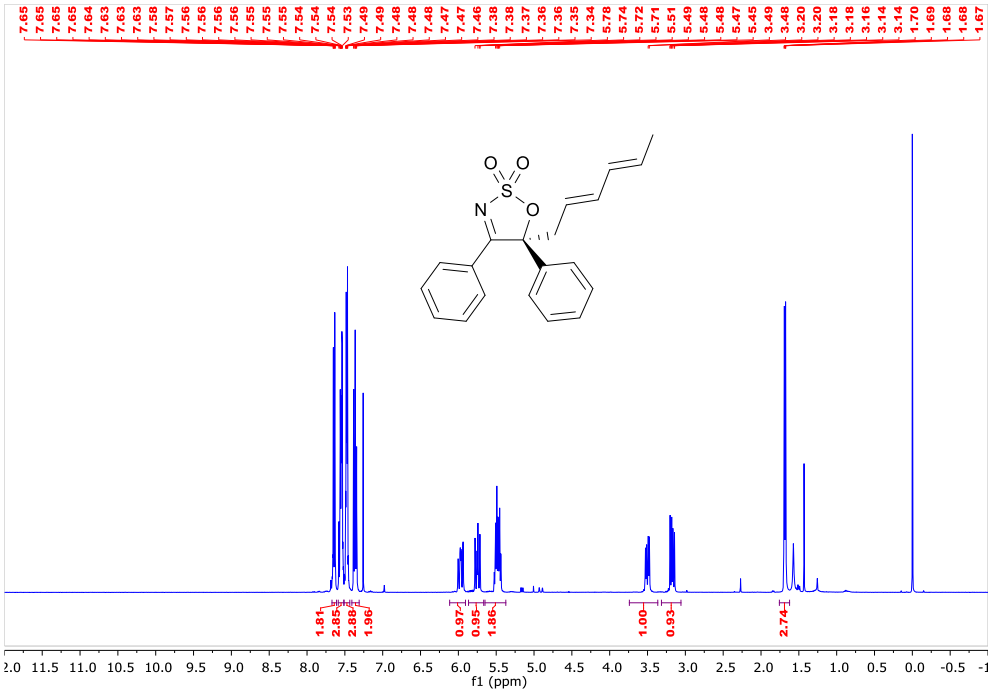


Figure S87. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3da**

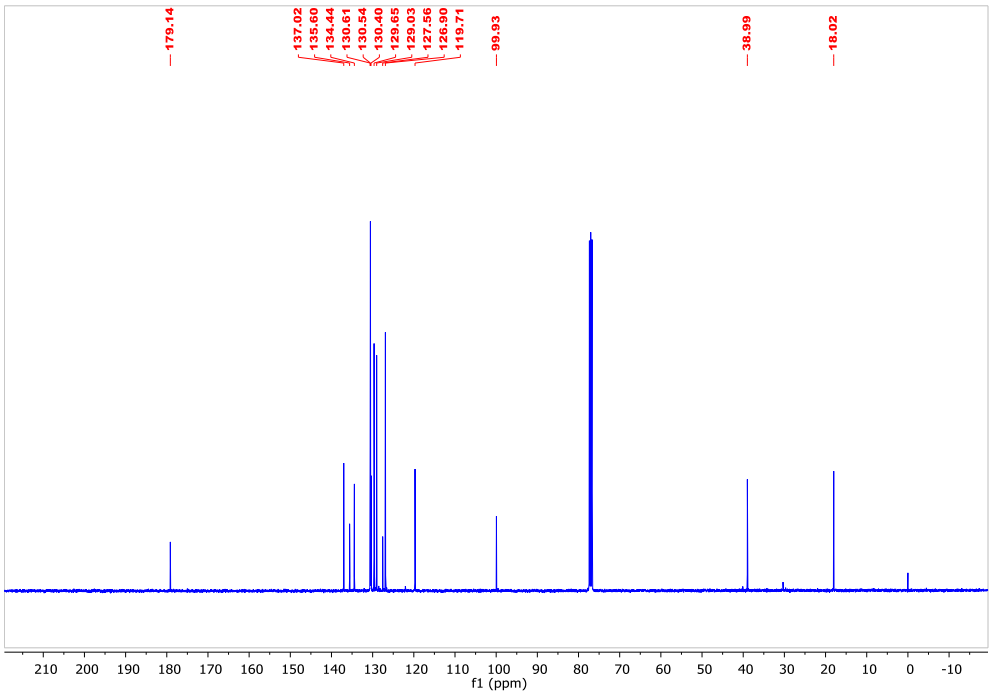


Figure S88. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3da**

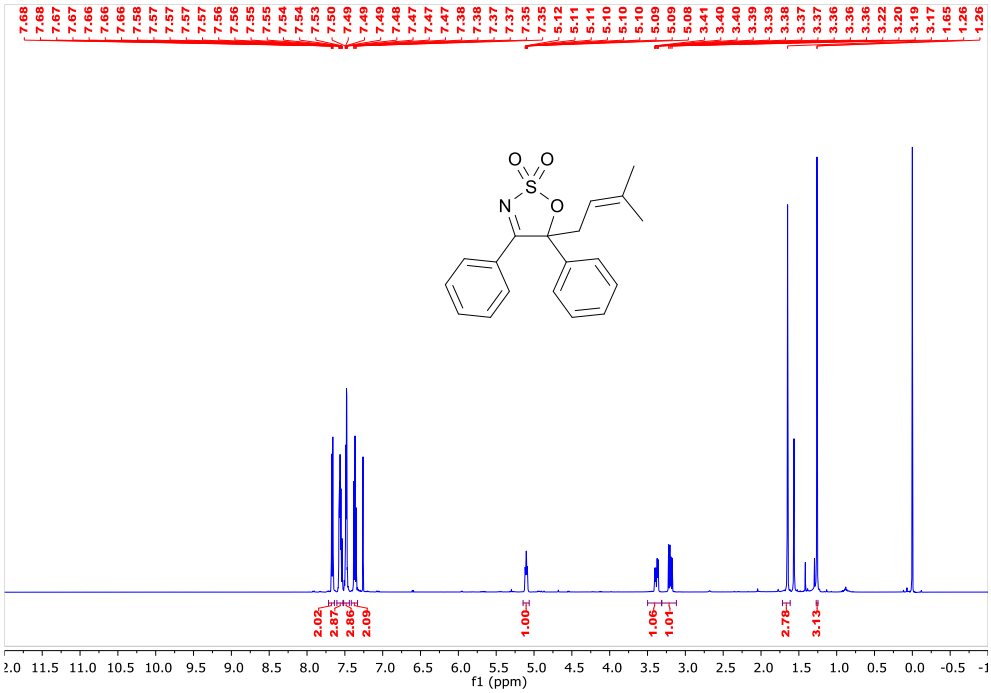


Figure S89. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **3ea**

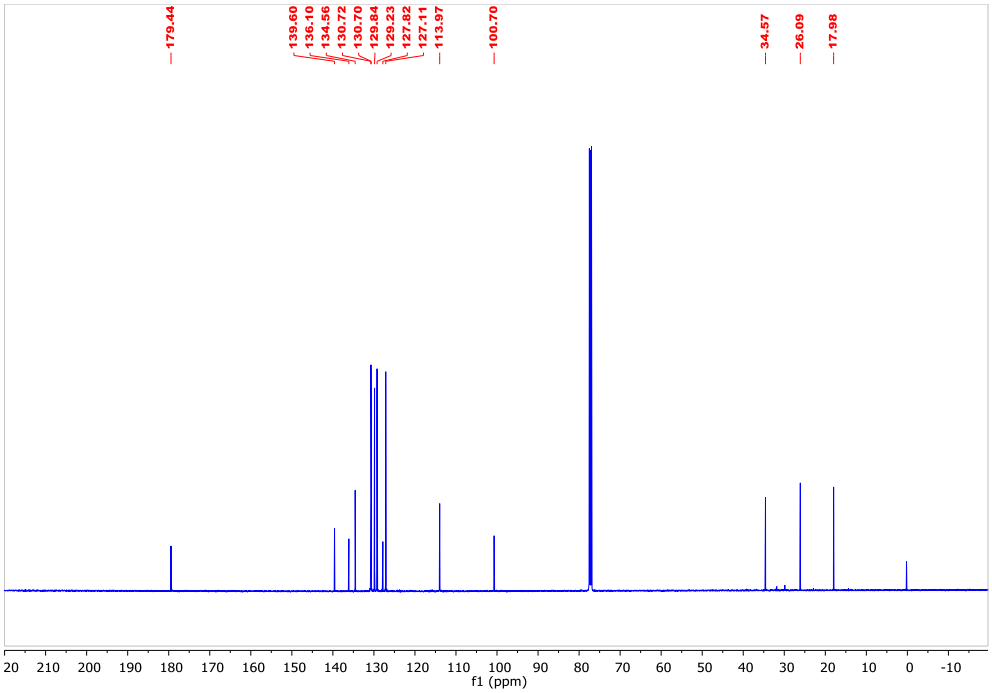


Figure S90. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **3ea**

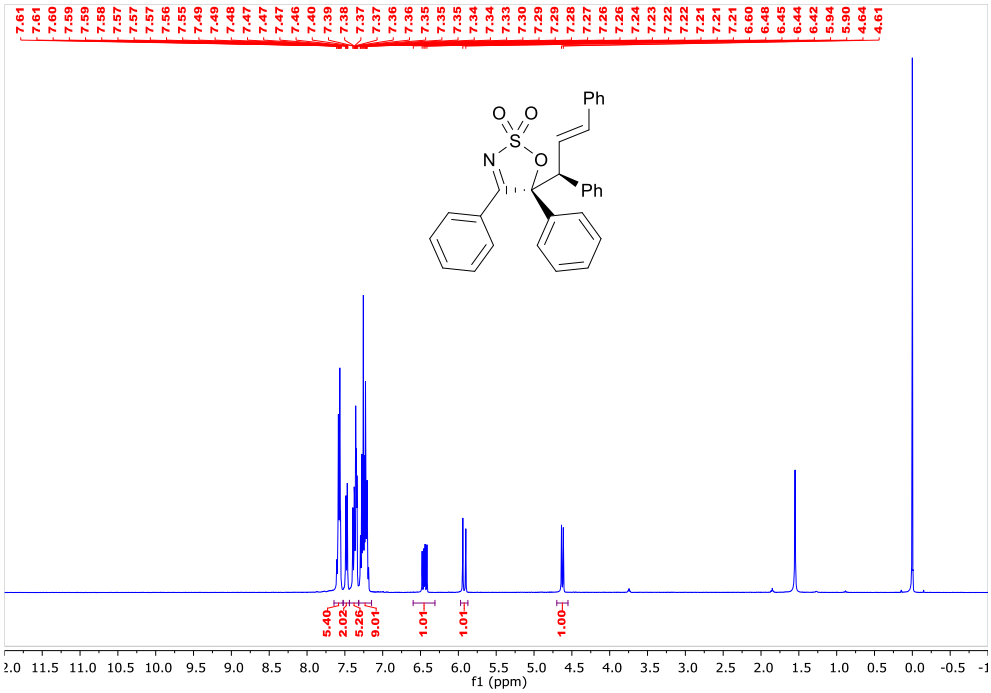


Figure S91. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3fa**

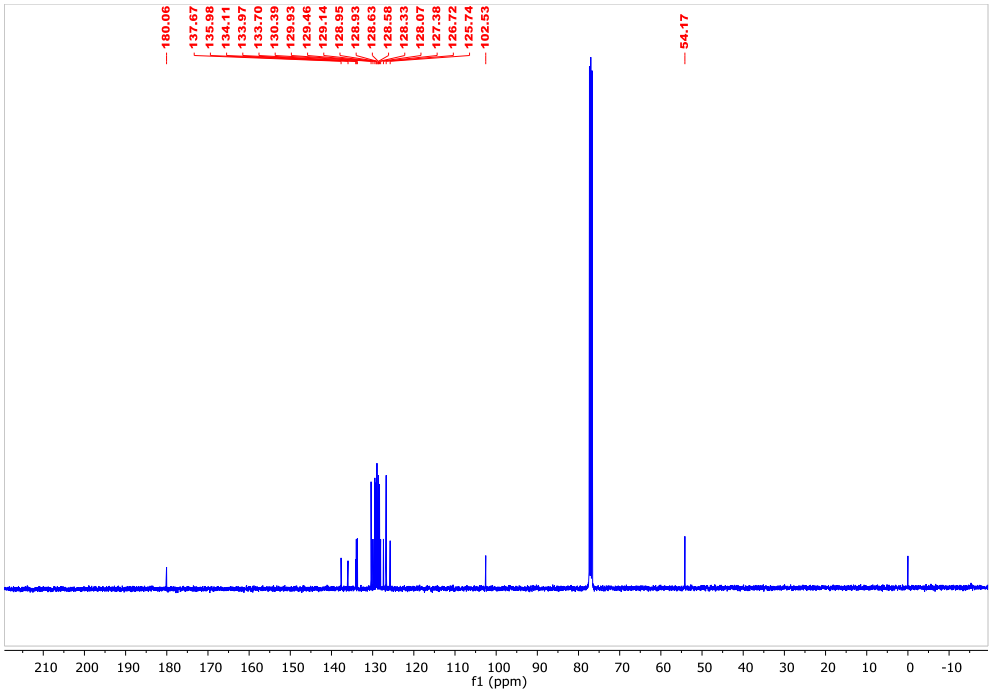


Figure S92. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3fa**

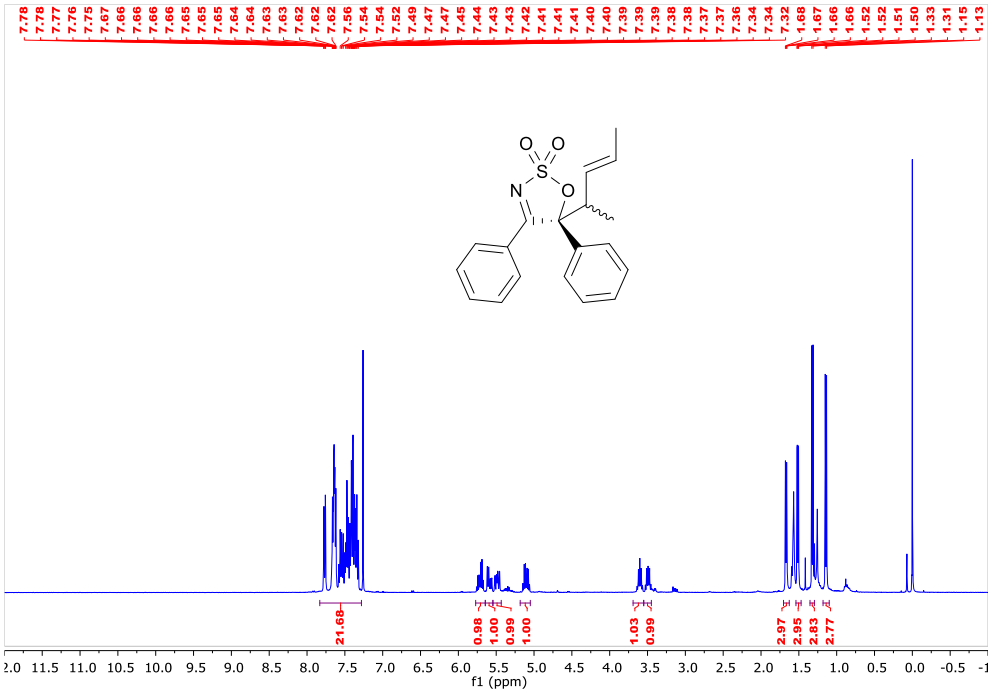


Figure S93. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3ga**

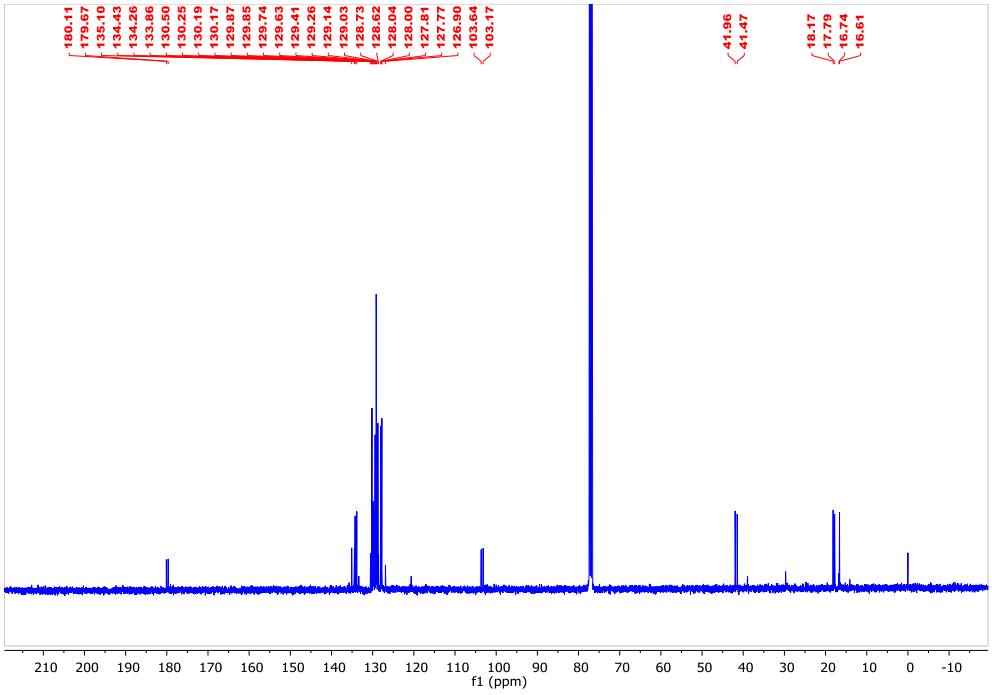


Figure S94. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **3ga**

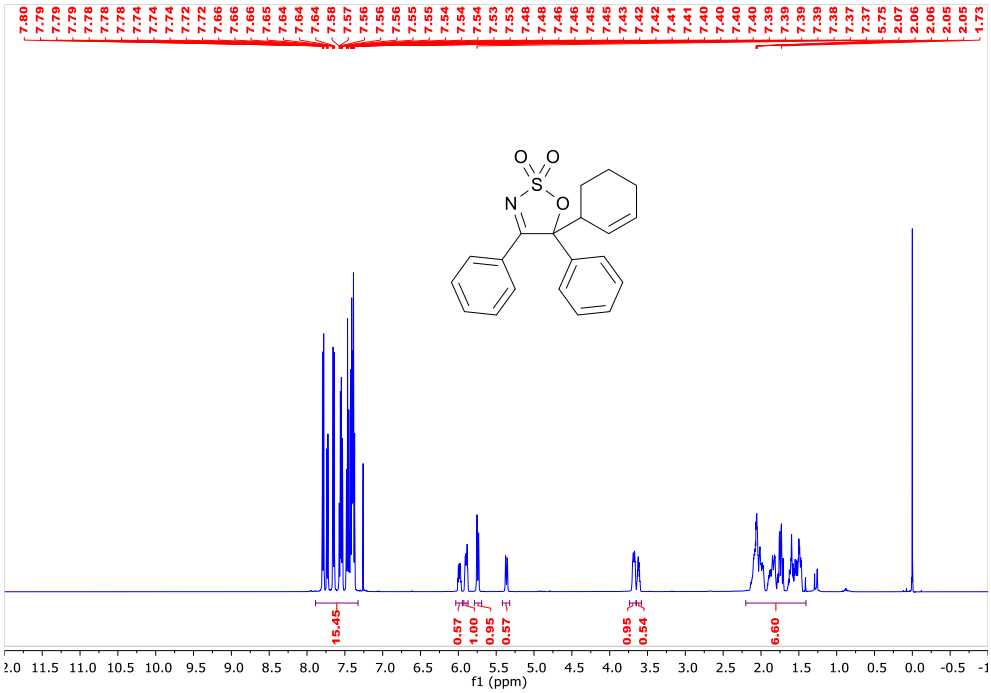


Figure S95. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **3ha**

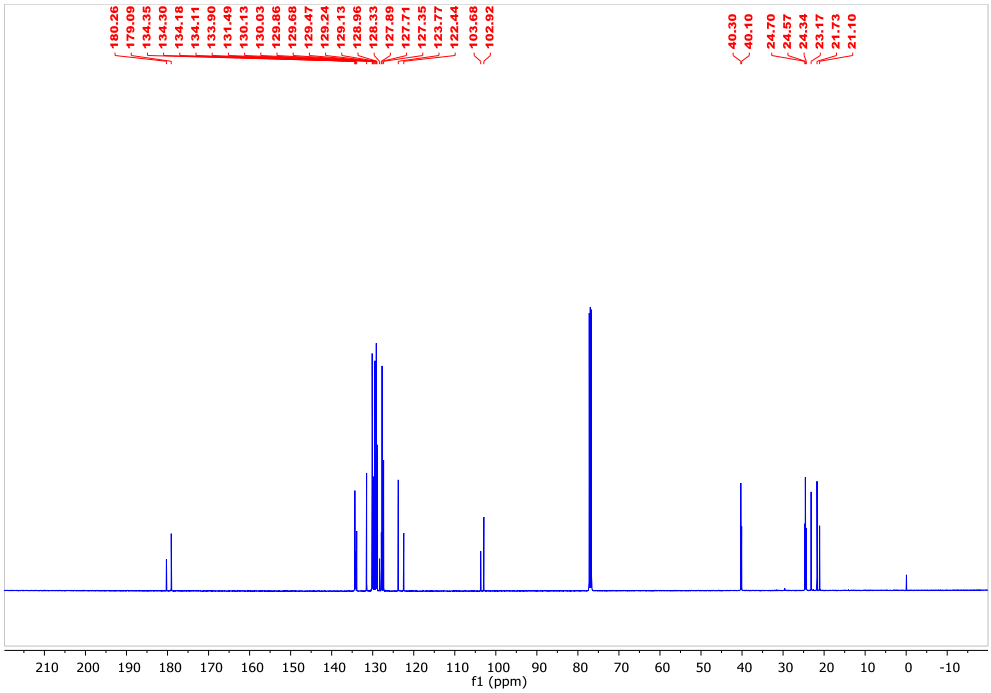


Figure S96. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **3ha**

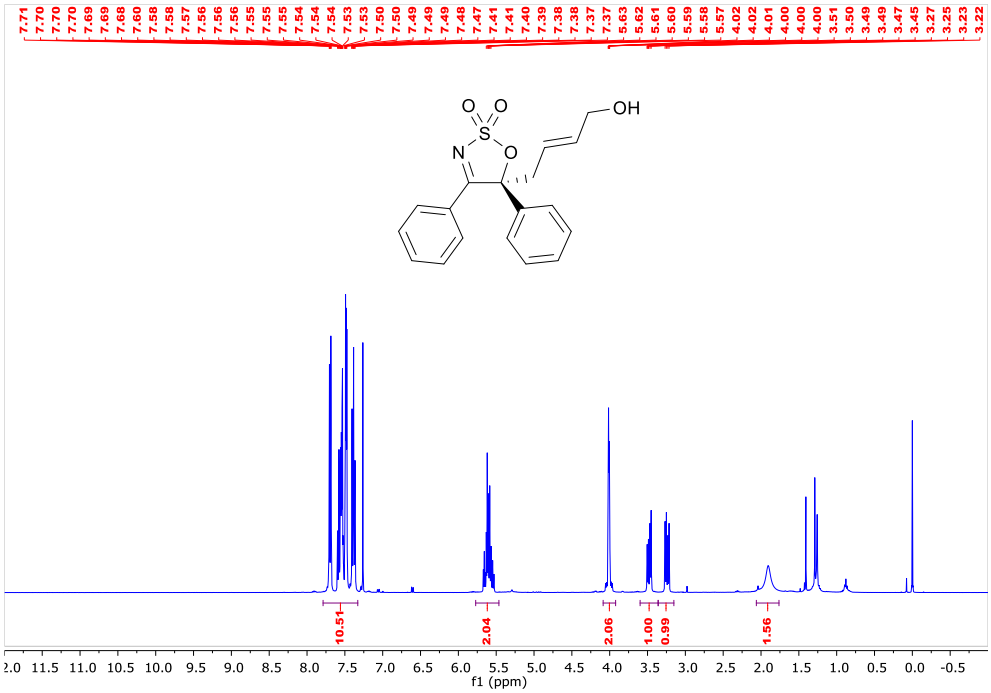


Figure S97. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6aa**

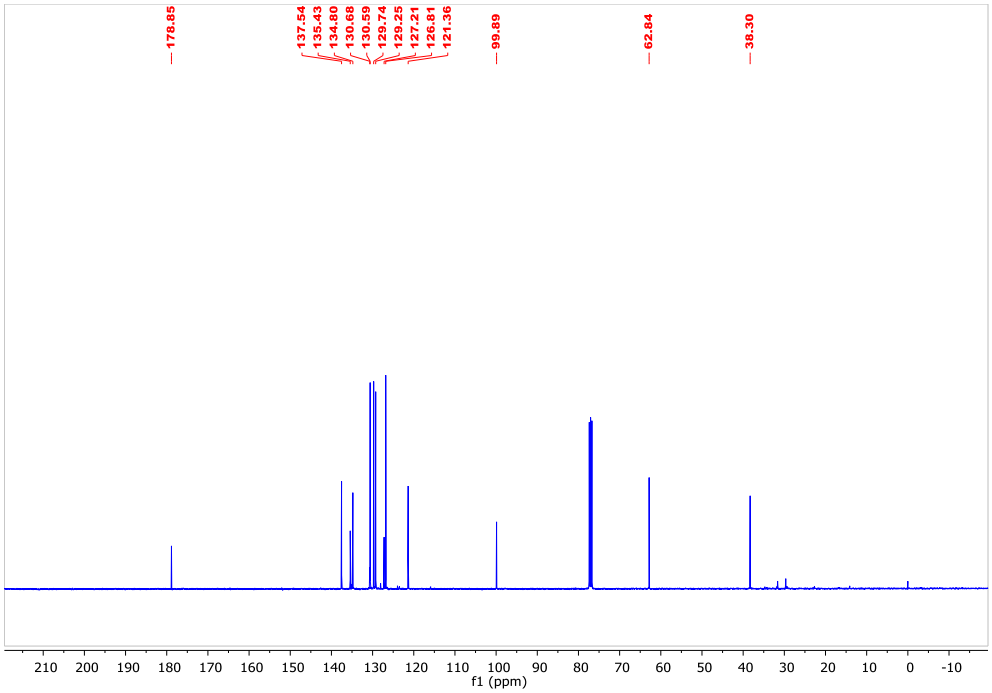


Figure S98. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6aa**

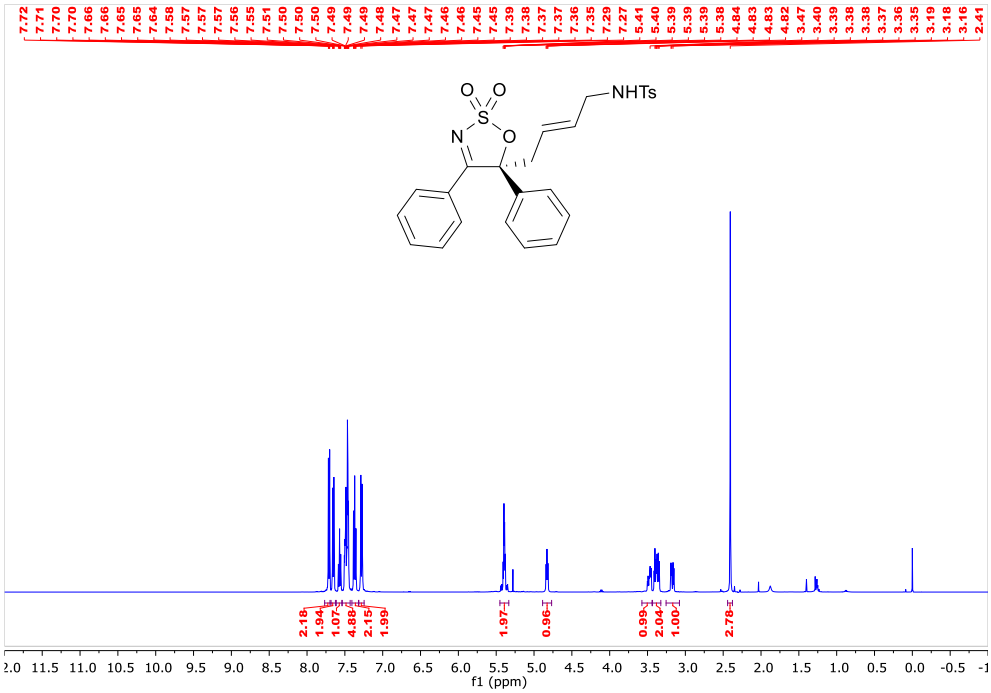


Figure S99. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **6ba**

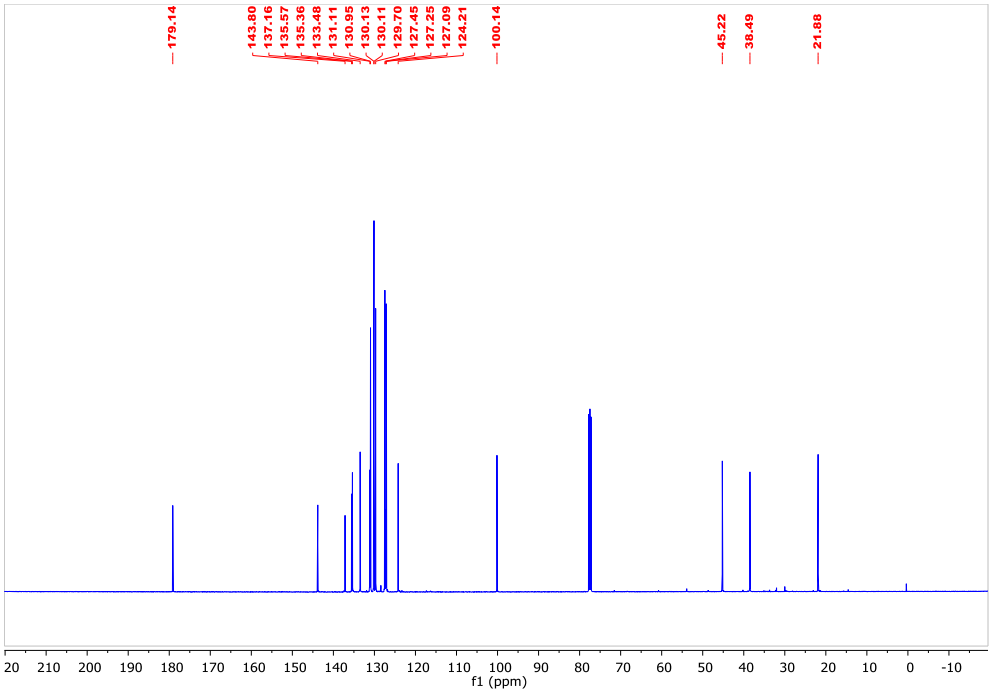


Figure S100. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **6ba**

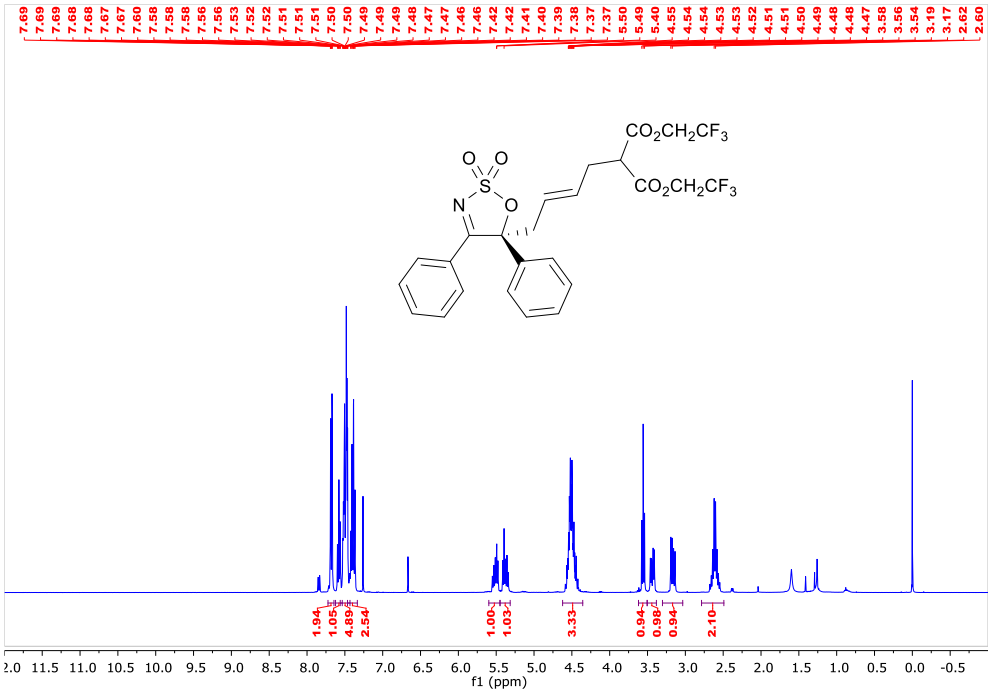


Figure S101. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6ca**

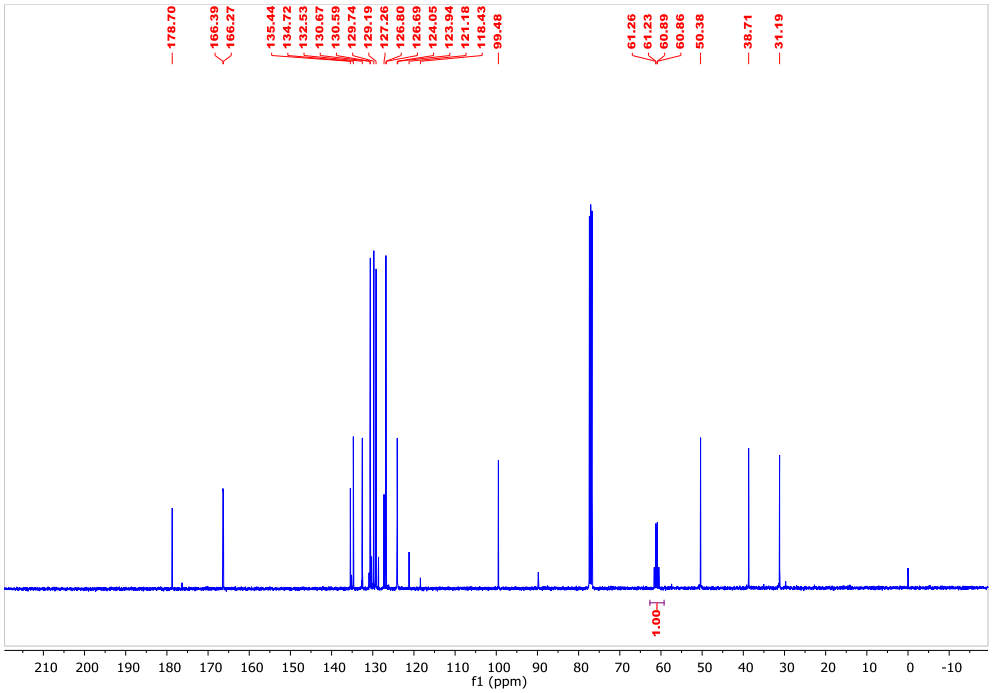


Figure S102. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6ca**

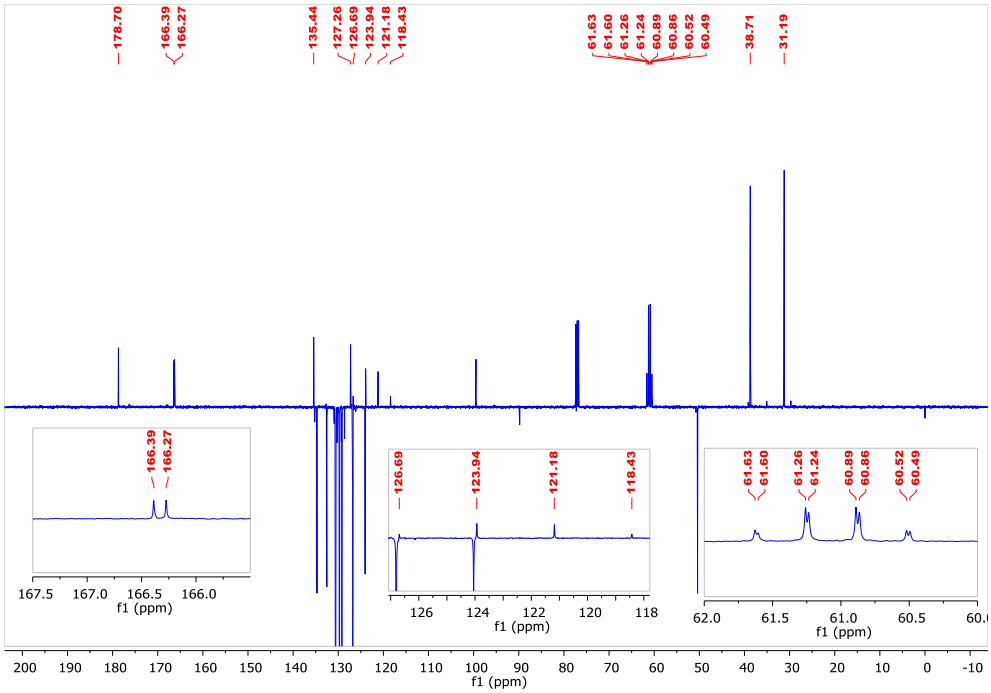


Figure S103. DEPTQ NMR spectrum ($CDCl_3$, 100 MHz) of **6ca**

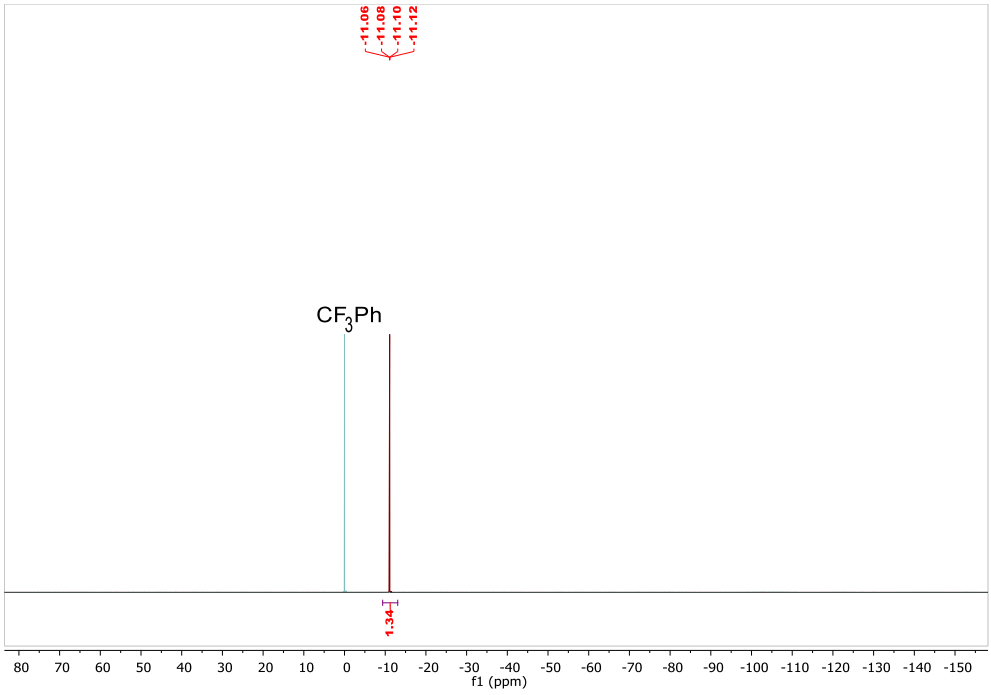


Figure S104. ^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of **6ca**

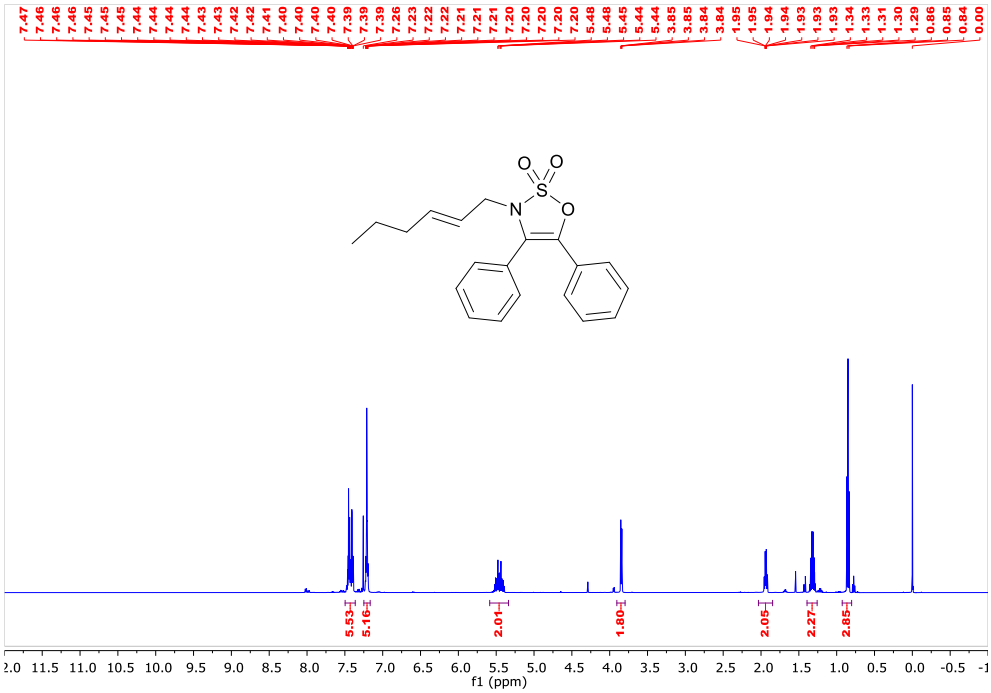


Figure S105. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4aa**

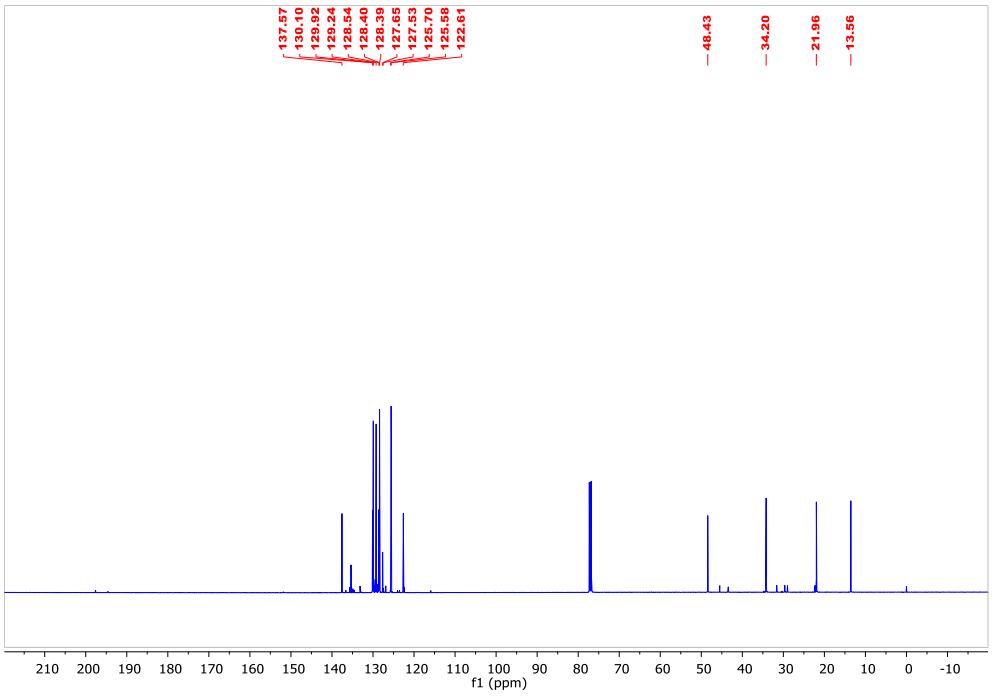


Figure S106. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4aa**

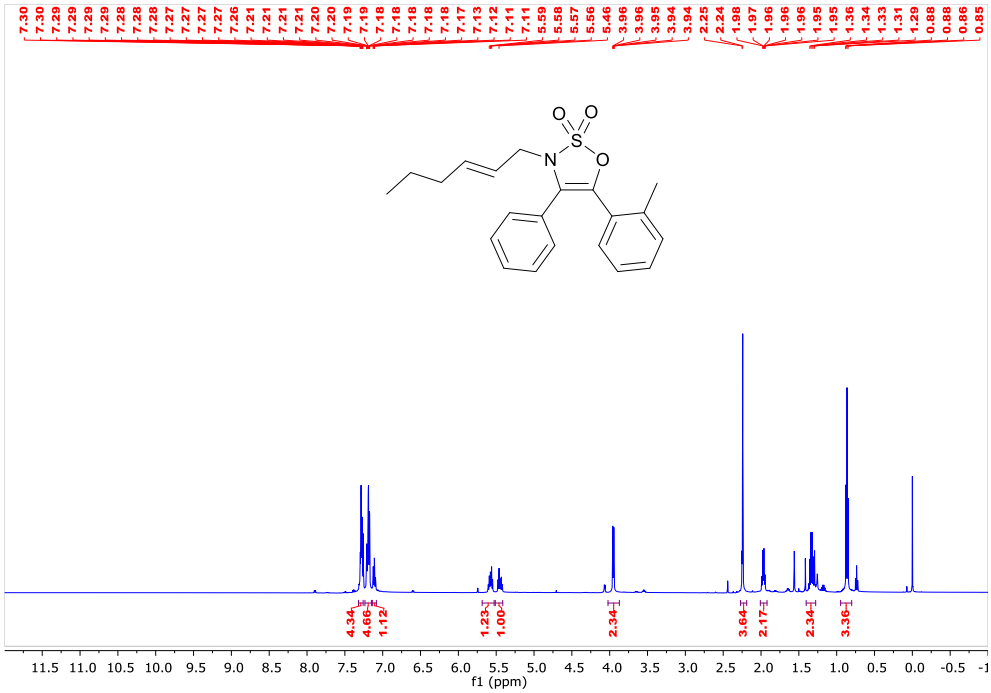


Figure S107. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4ah**

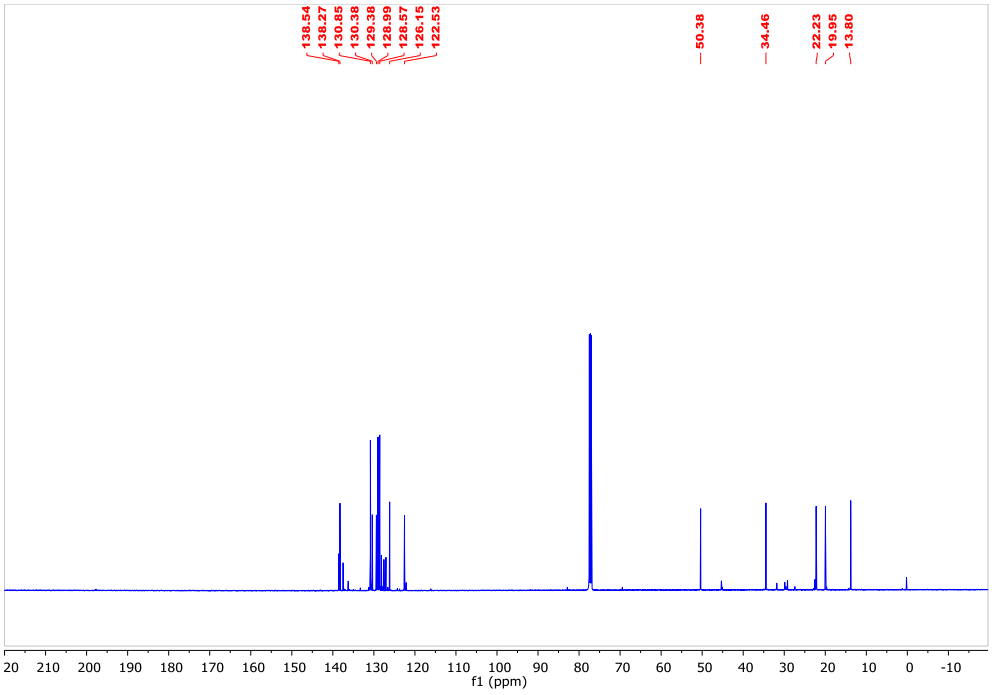


Figure S108. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4ah**

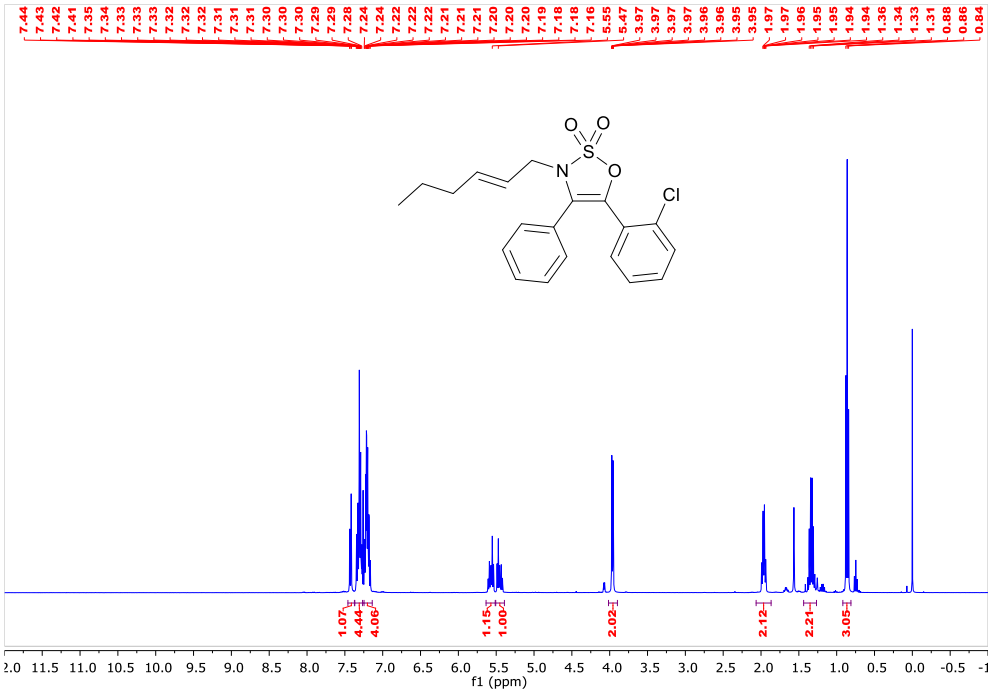


Figure S109. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4aj**

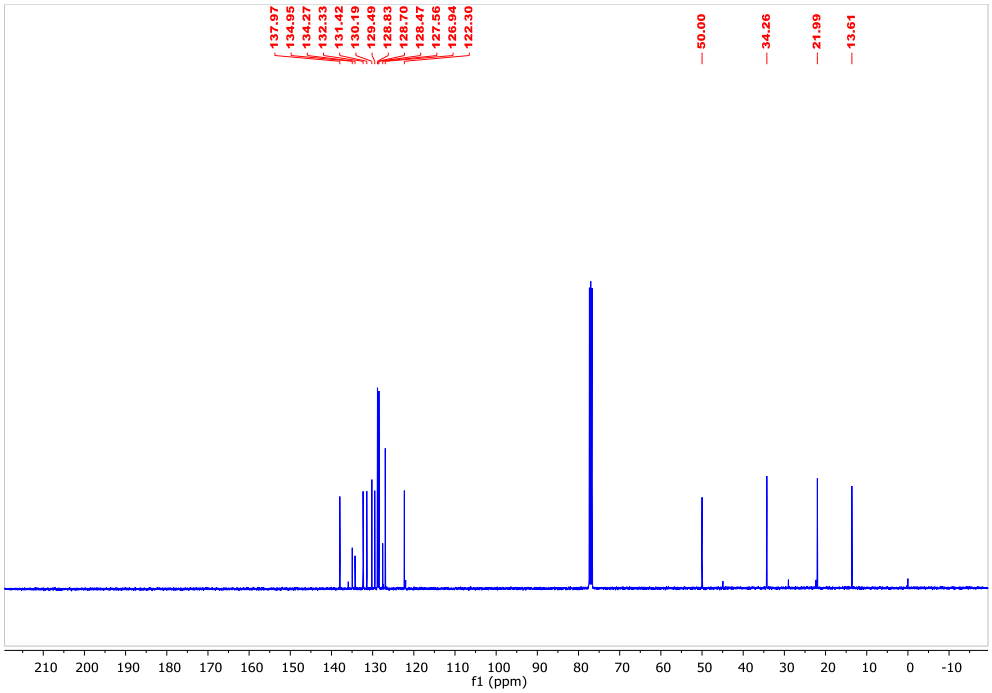


Figure S110. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4aj**

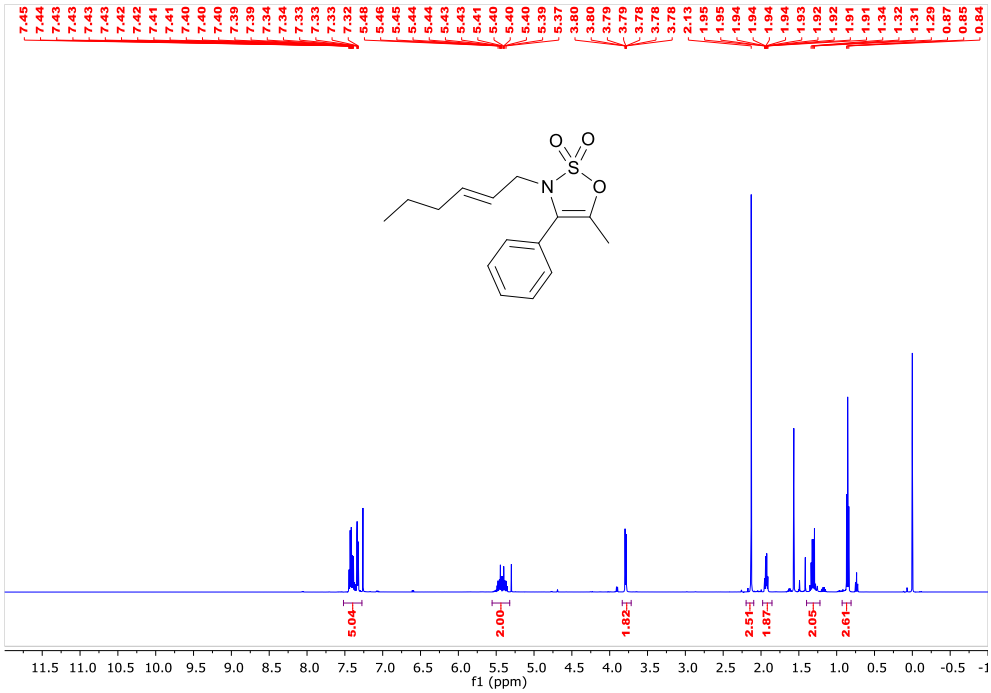


Figure S111. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4ak**

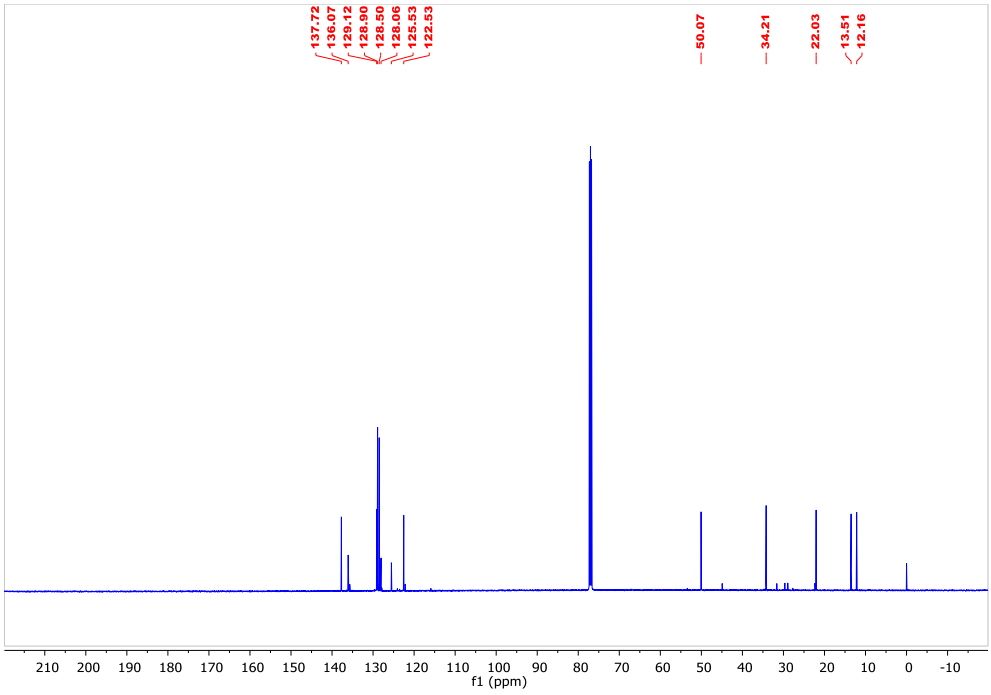


Figure S112. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4ak**

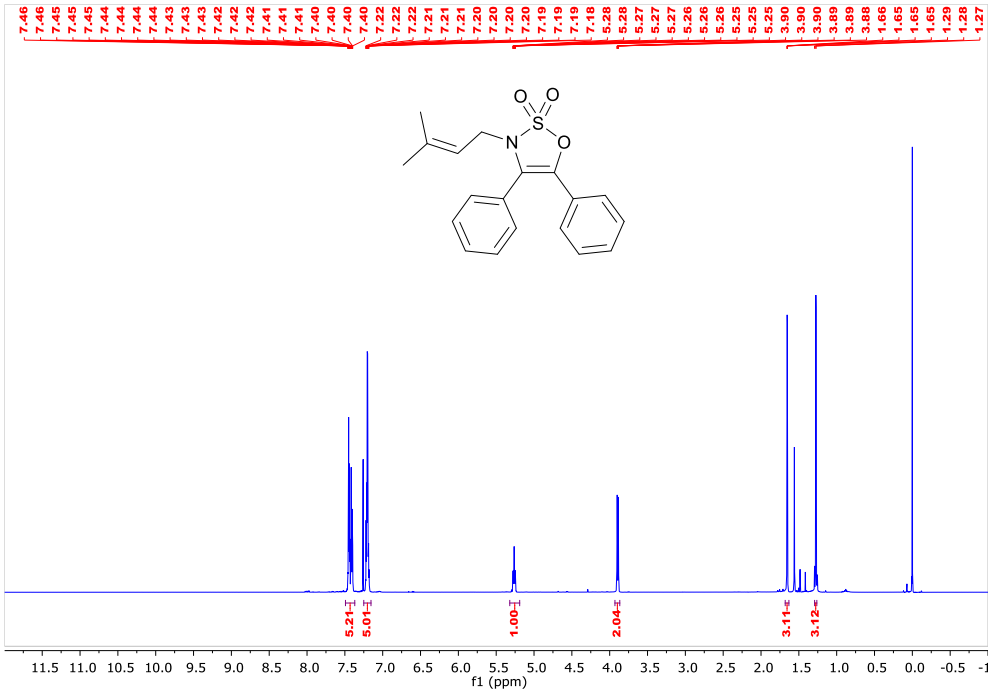


Figure S113. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4ea**

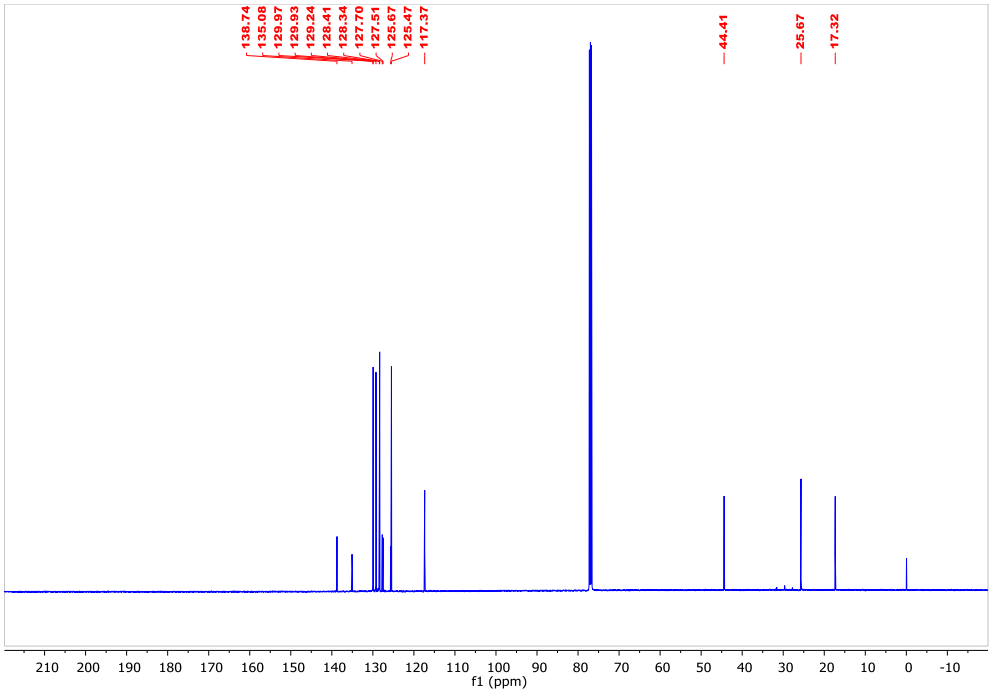


Figure S114. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4ea**

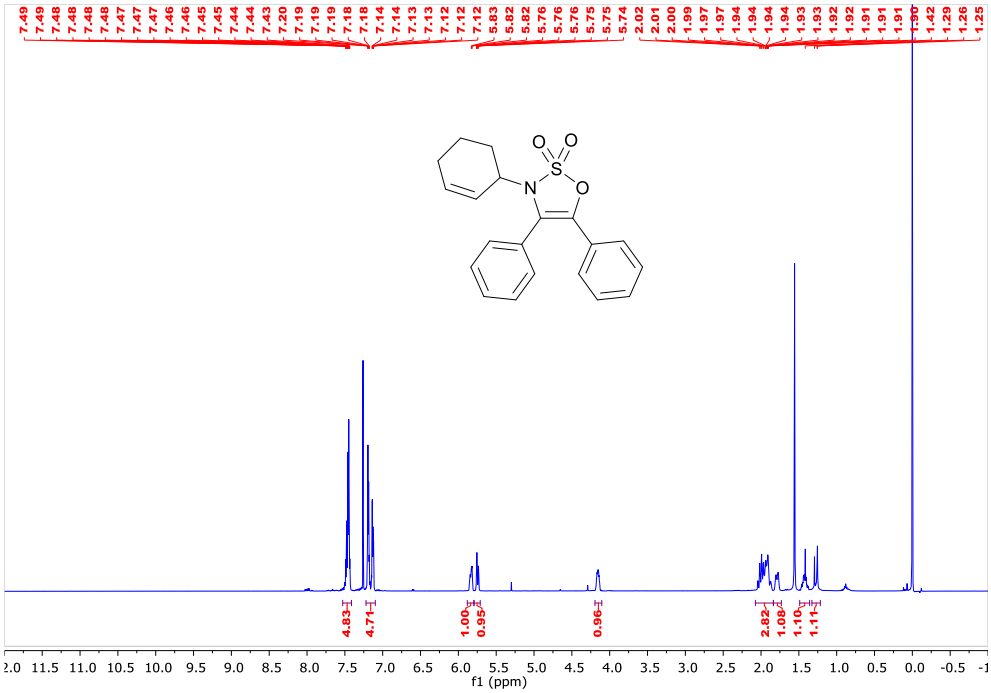


Figure S115. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4ha**

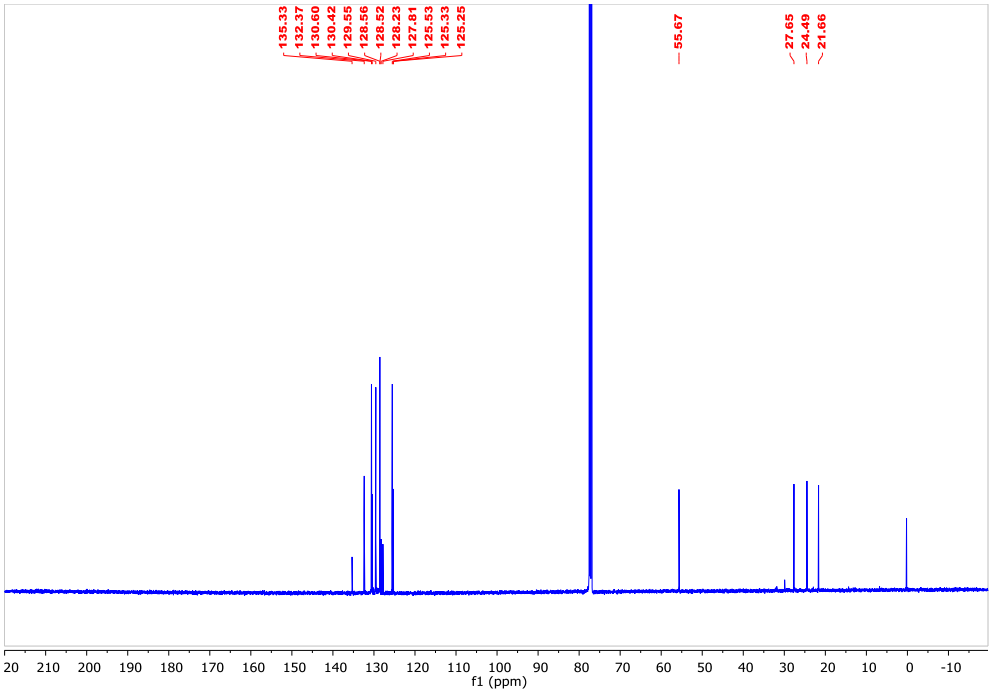


Figure S116. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4ha**

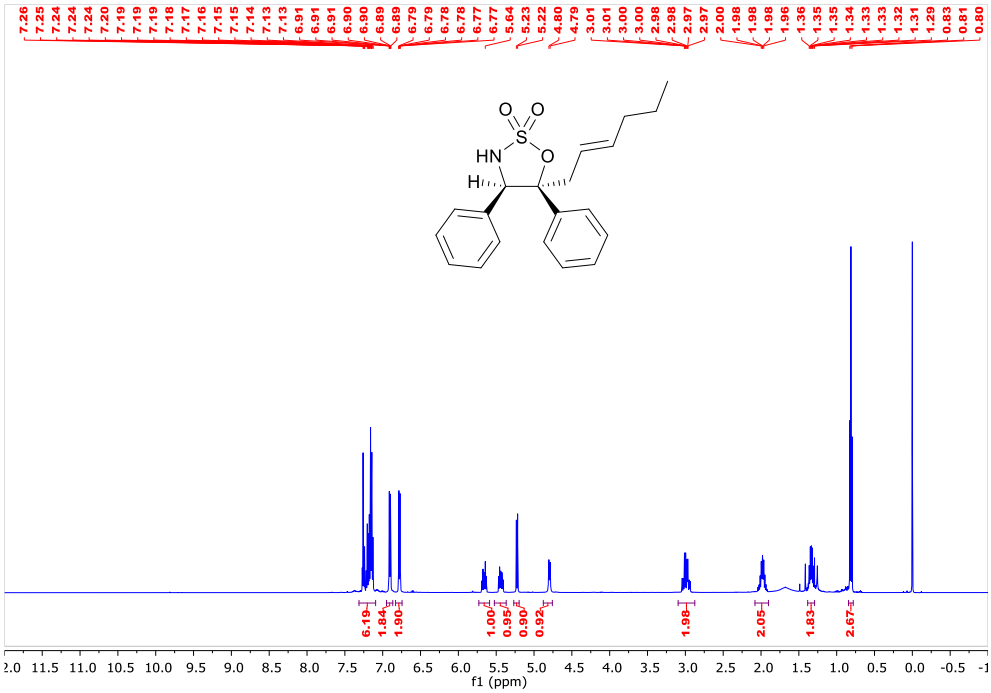


Figure S117. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **7aa-major diastereoisomer**

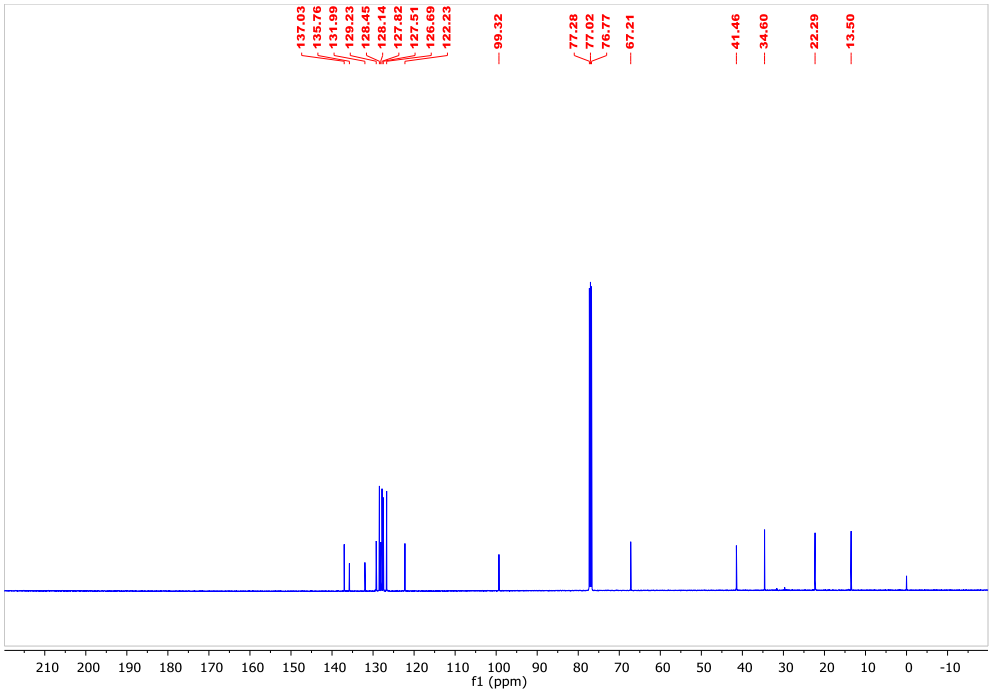


Figure S118. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **7aa-major diastereoisomer**

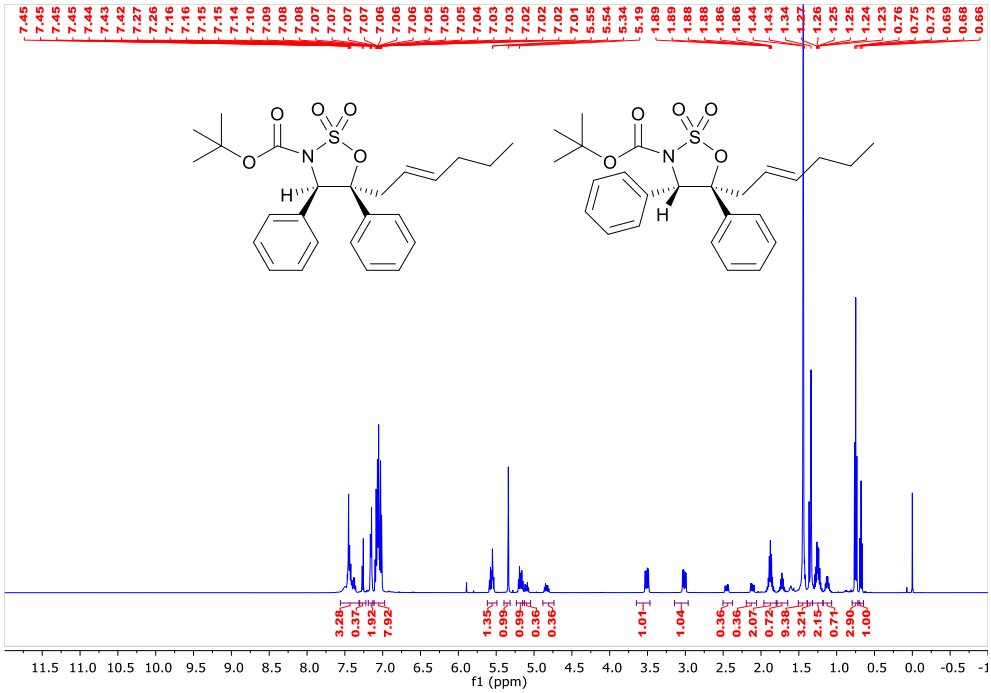


Figure S119. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **8aa-mixture of two diastereoisomers**

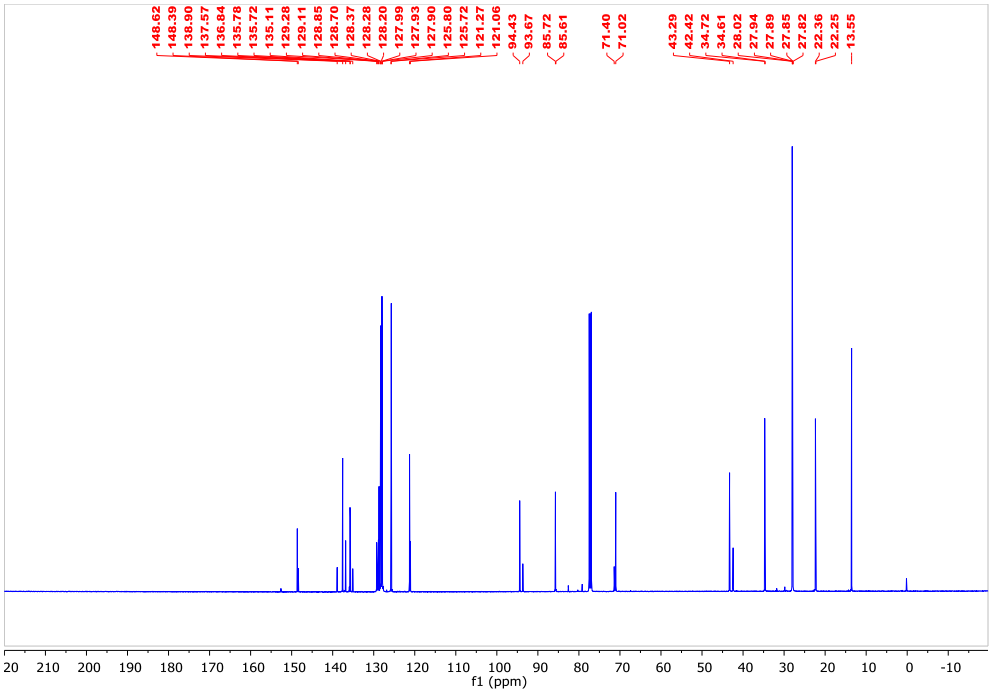


Figure S120. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **8aa-mixture of two diastereoisomers**

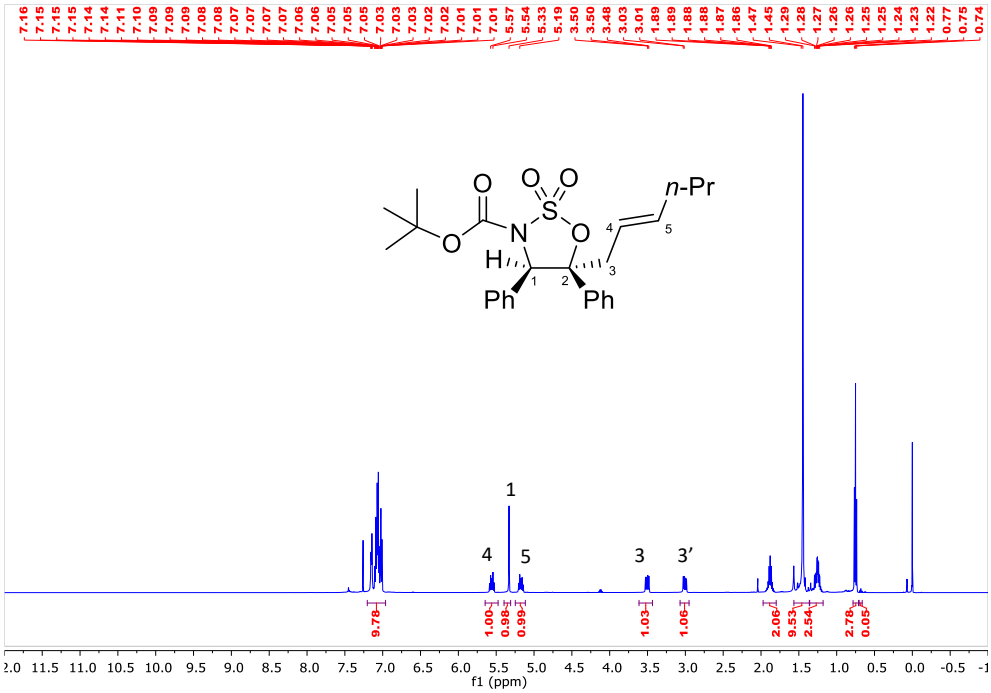


Figure S121. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **8aa-major diastereoisomer**

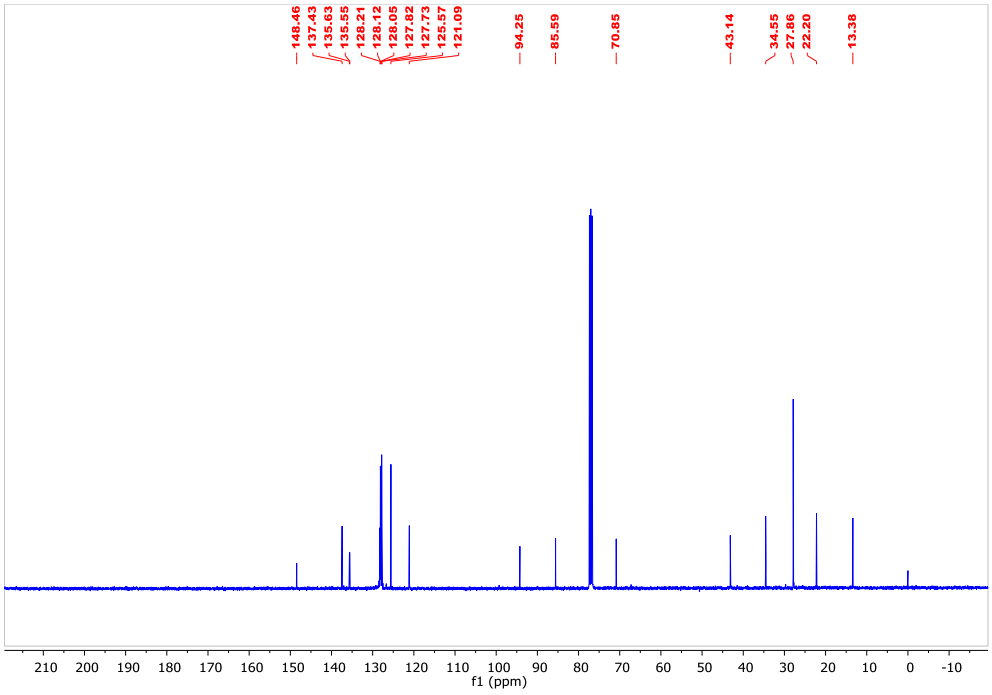


Figure S122. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **8aa-major diastereoisomer**

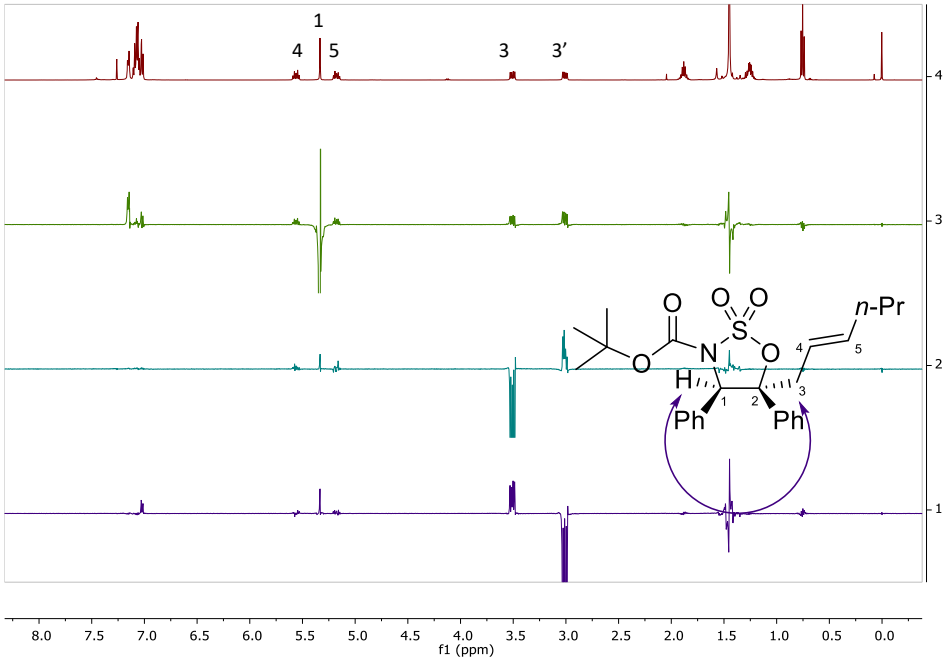


Figure S123. ^{1}H NMR and 1D NOE spectra ($CDCl_3$, 500 MHz) of **8aa-major diastereoisomer**

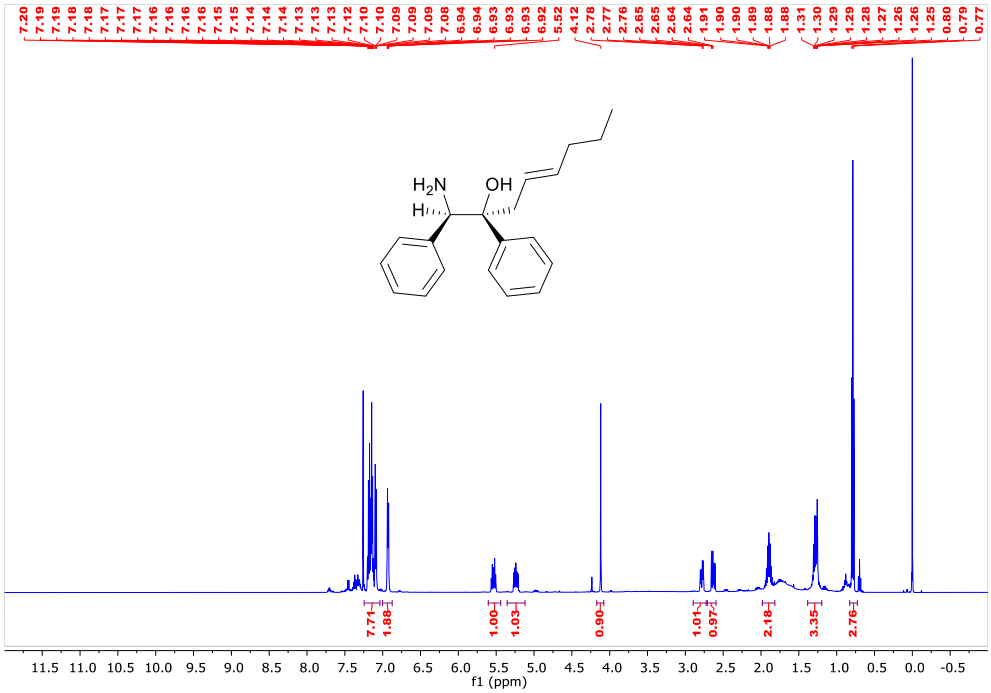


Figure S124. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **9aa-major diastereoisomer**

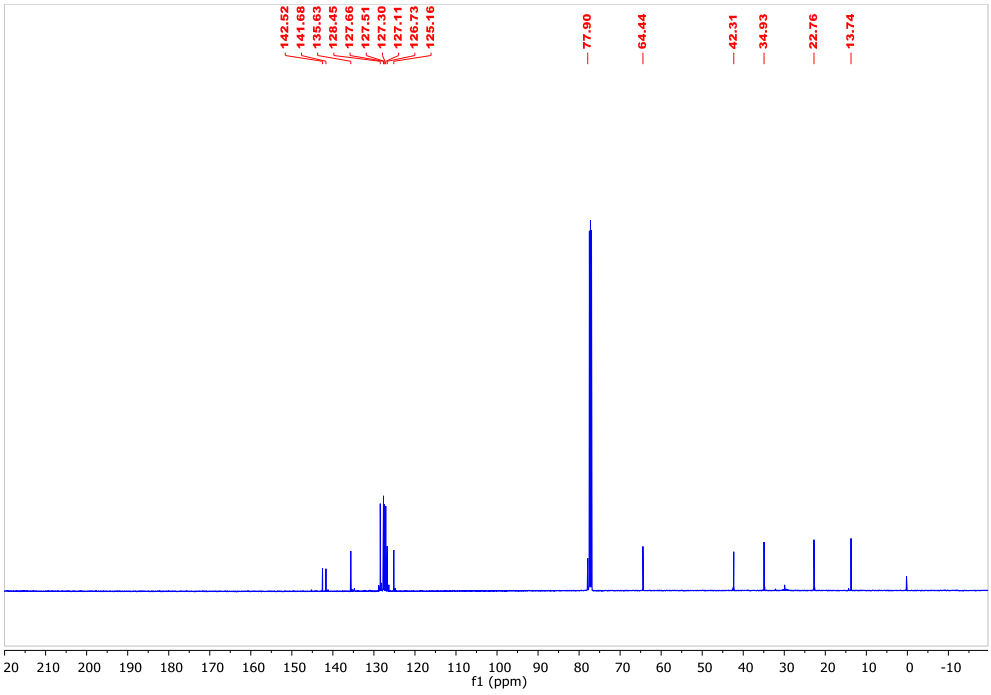


Figure S125. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **9aa-major diastereoisomer**

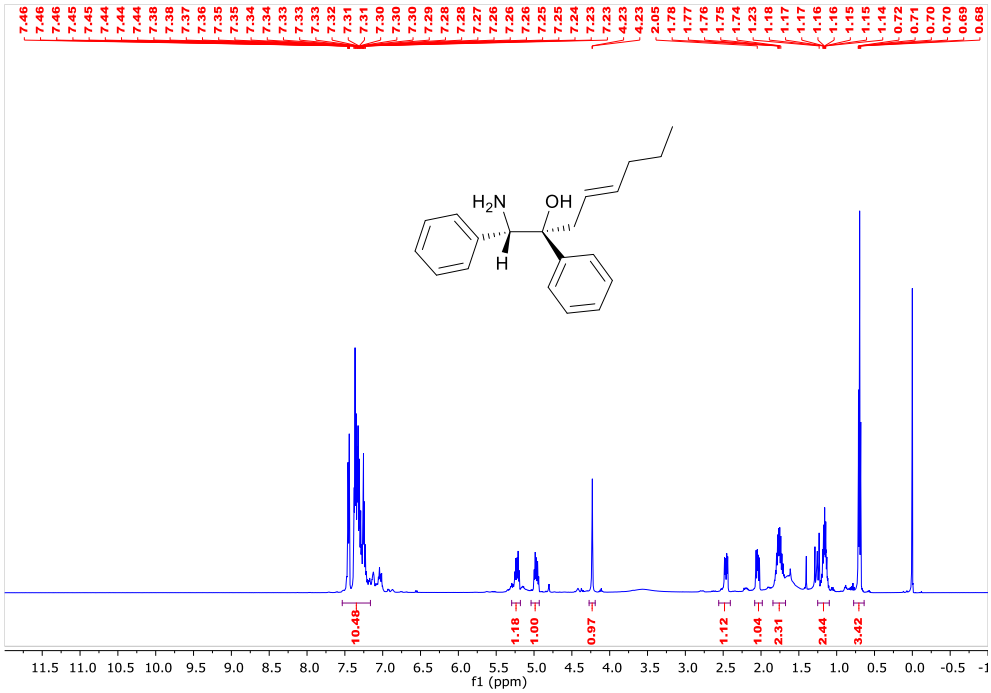


Figure S126. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **9aa-minor diastereoisomer**

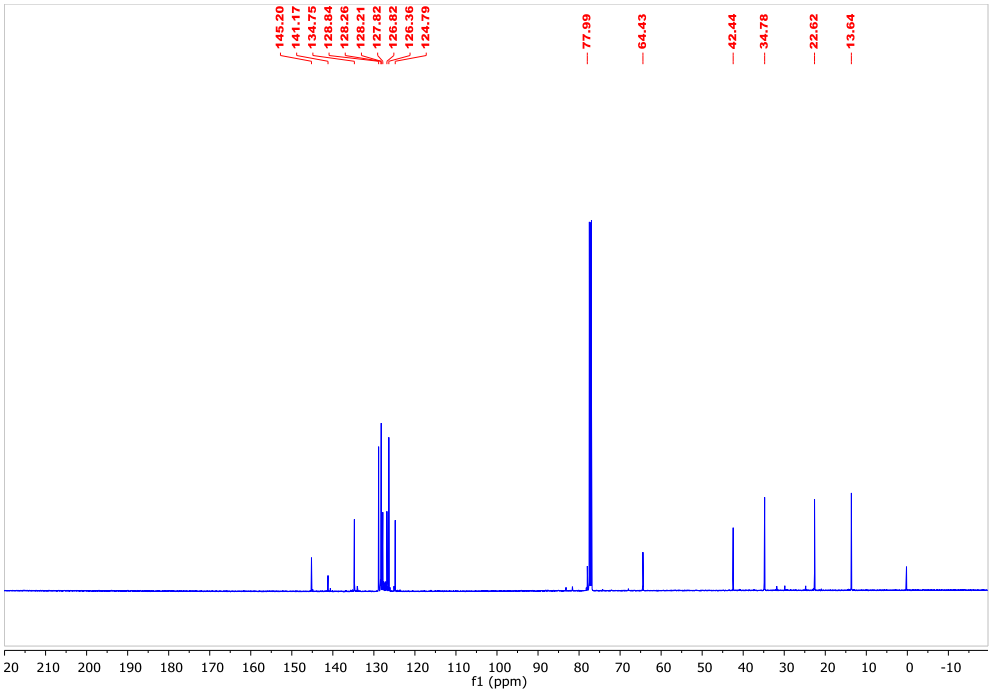
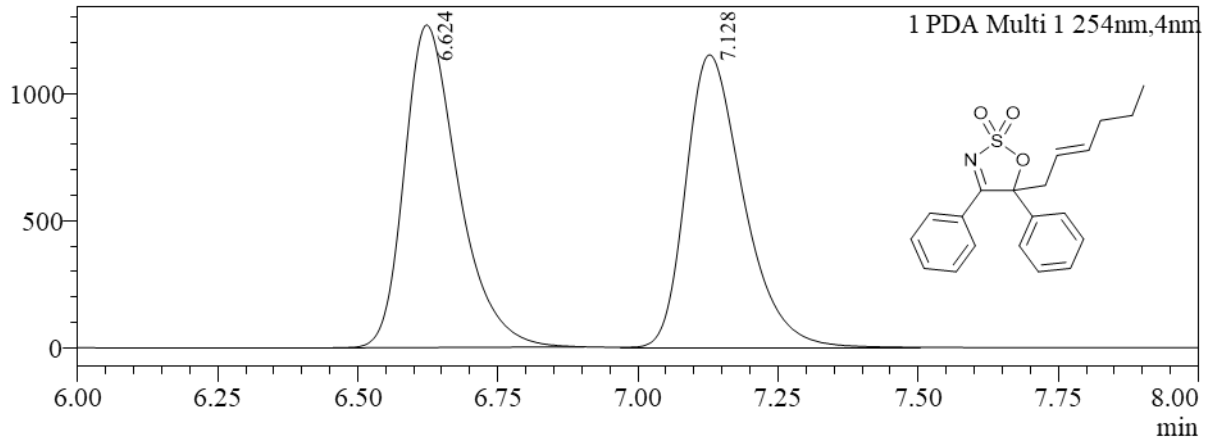


Figure S127. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **9aa-minor diastereoisomer**

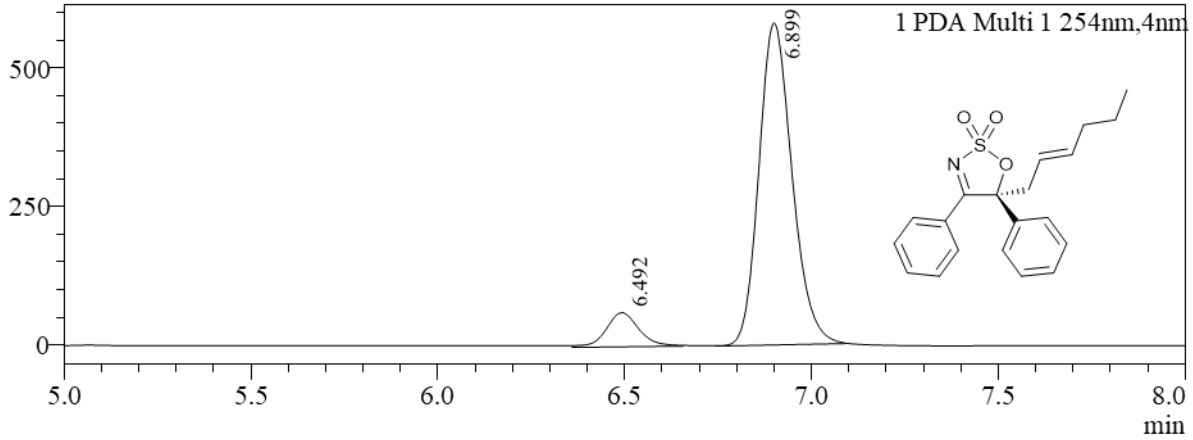
11. HPLC chromatograms

(*rac*)-3aa



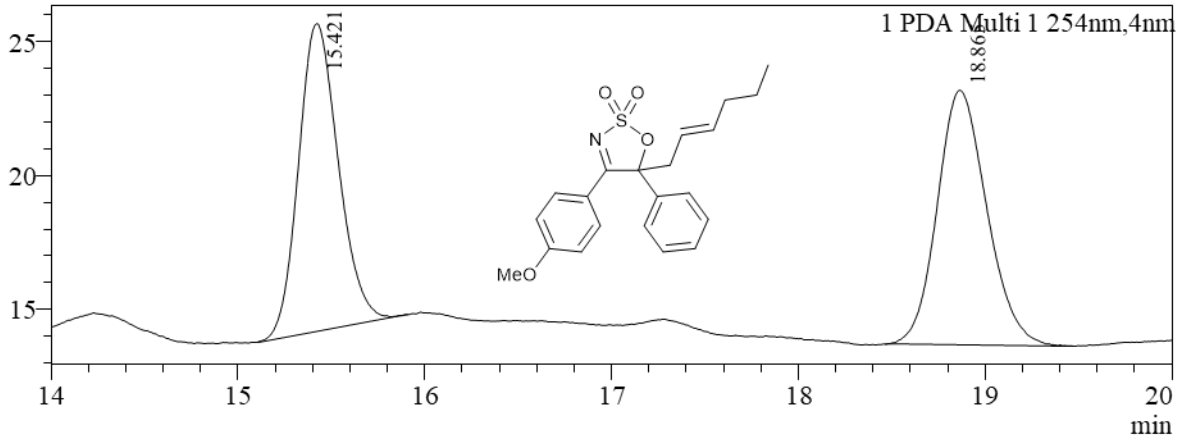
Peak#	Ret. Time	Area%	Name
1	6.624	50.799	
2	7.128	49.201	
Total		100.000	

(*S*)-3aa



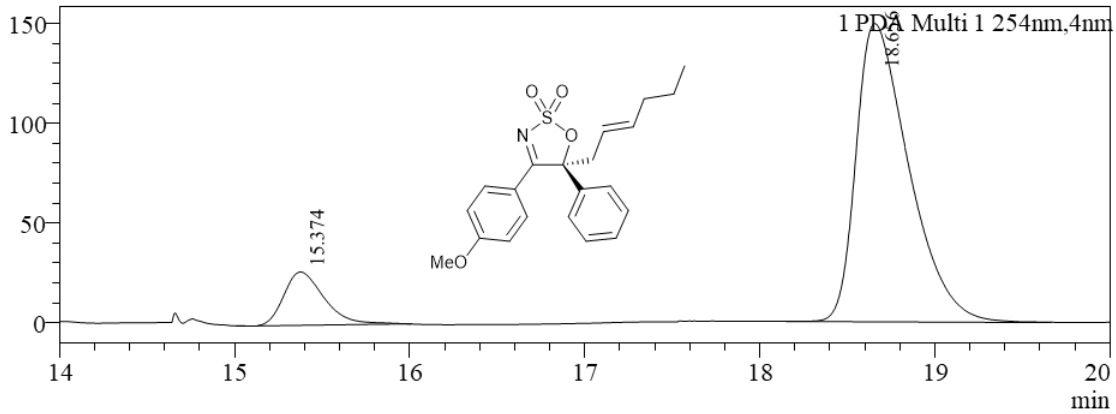
Peak#	Ret. Time	Area%	Name
1	6.492	8.732	
2	6.899	91.268	
Total		100.000	

(*rac*)-3ab



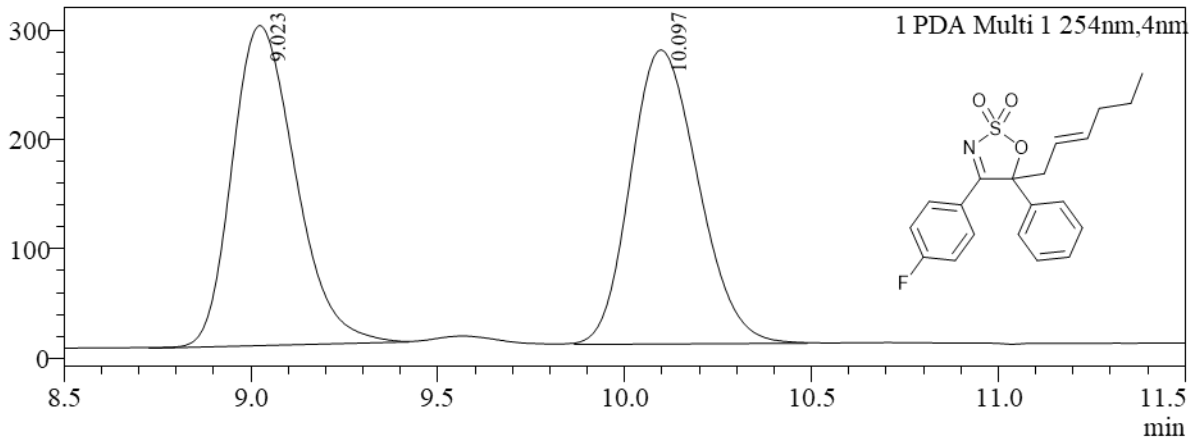
Peak#	Ret. Time	Area%	Name
1	15.421	49.454	
2	18.865	50.546	
Total		100.000	

(*S*)-3ab



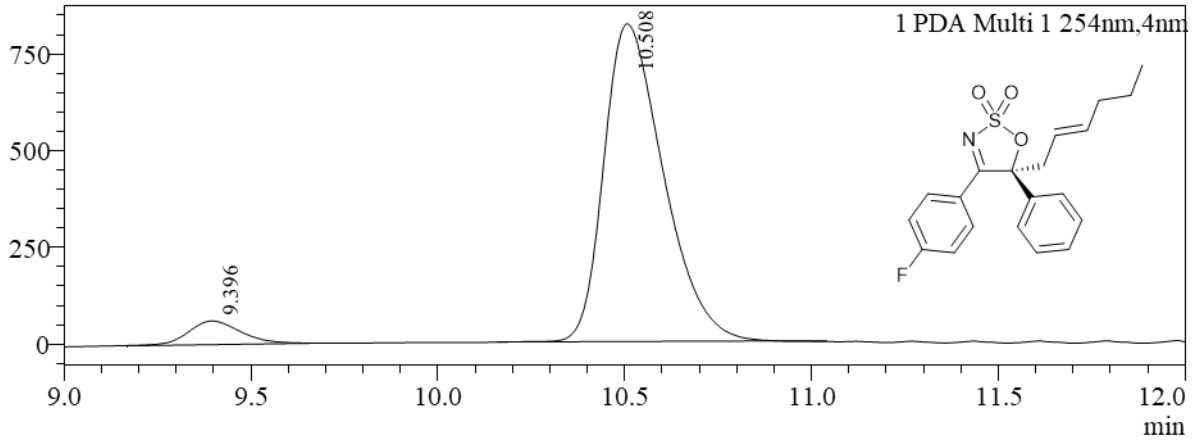
Peak#	Ret. Time	Area%	Name
1	15.374	12.036	
2	18.656	87.964	
Total		100.000	

(*rac*)3ac



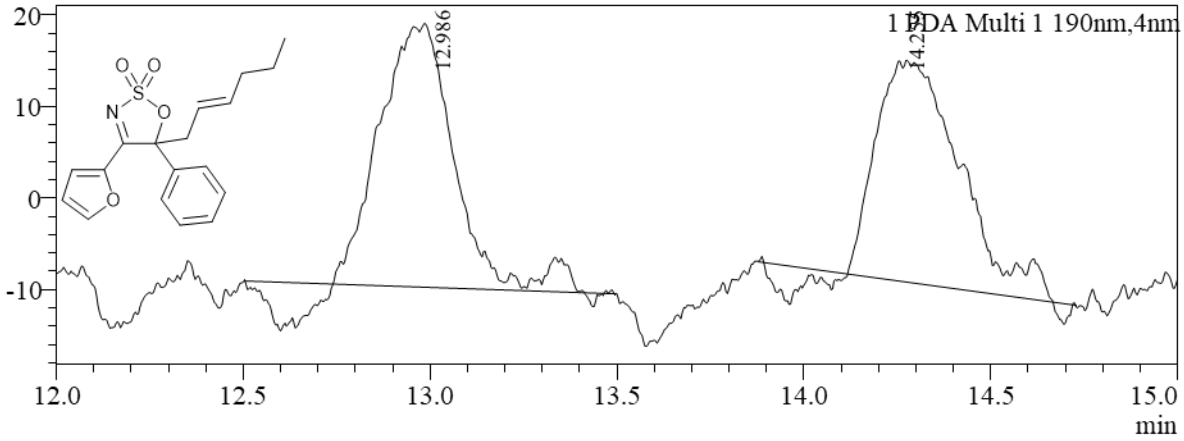
Peak#	Ret. Time	Area%	Name
1	9.023	50.406	
2	10.097	49.594	
Total		100.000	

***(S)*-3ac**



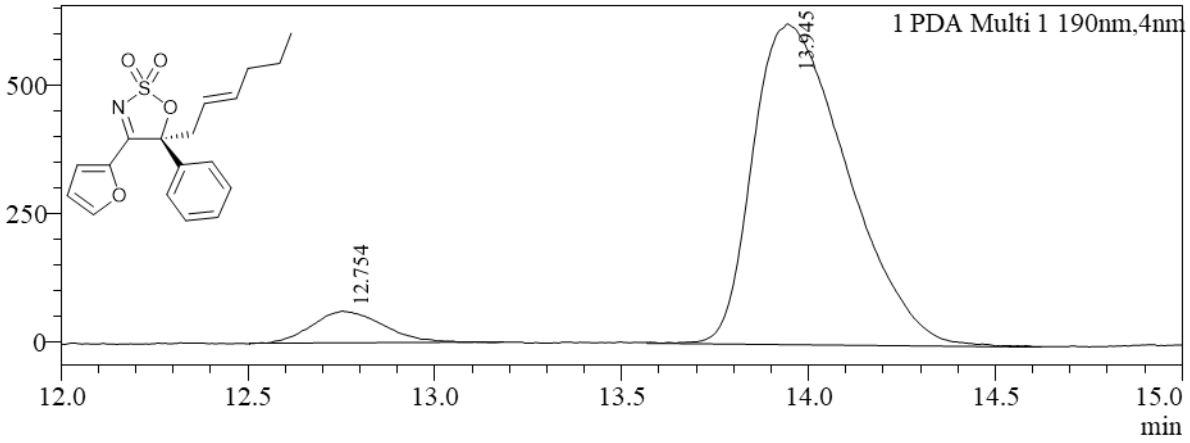
Peak#	Ret. Time	Area%	Name
1	9.396	6.045	
2	10.508	93.955	
Total		100.000	

(*rac*)-3ad



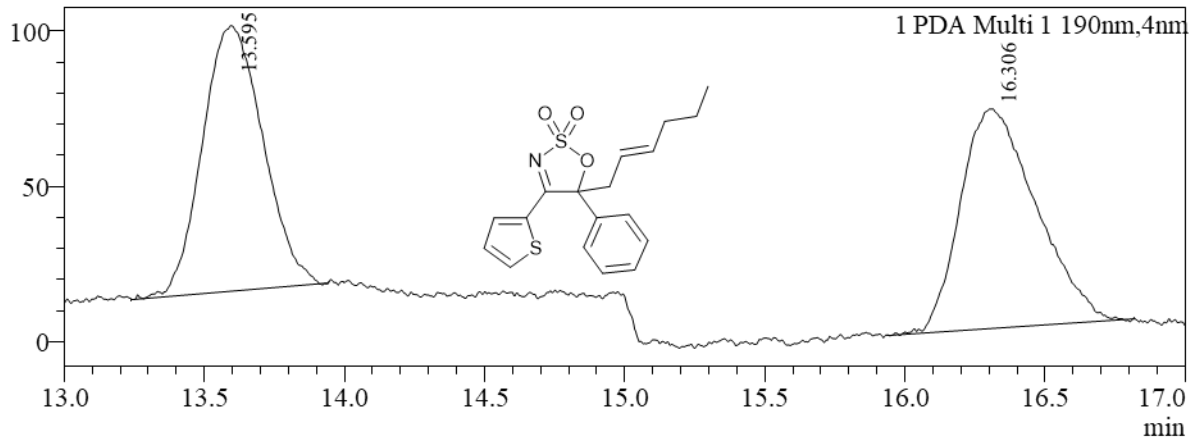
Peak#	Ret. Time	Area%	Name
1	12.986	50.678	
2	14.255	49.322	
Total		100.000	

(*S*)-3ad



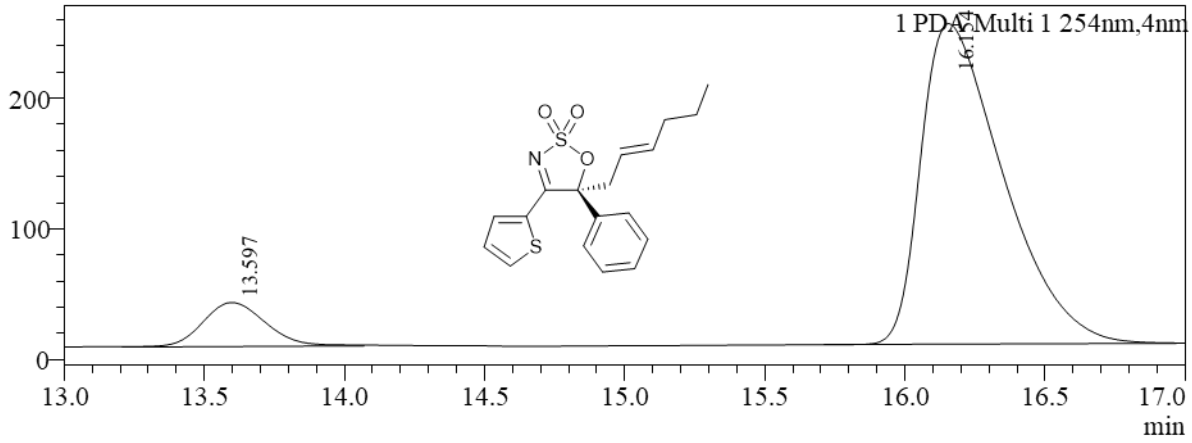
Peak#	Ret. Time	Area%	Name
1	12.754	6.887	
2	13.945	93.113	
Total		100.000	

(*rac*)-3ae



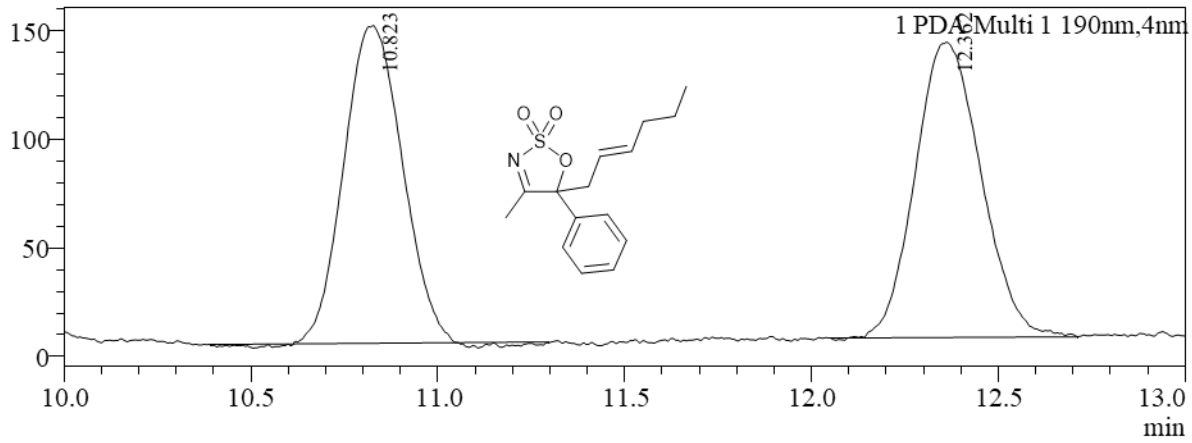
Peak#	Ret. Time	Area%	Name
1	13.595	49.271	
2	16.306	50.729	
Total		100.000	

(*S*)-3ae



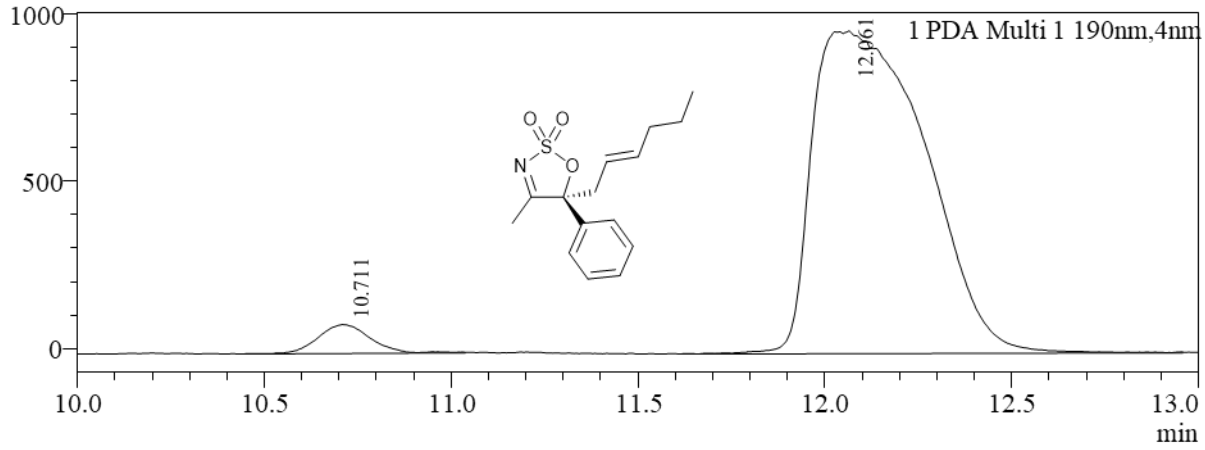
Peak#	Ret. Time	Area%	Name
1	13.597	9.173	
2	16.154	90.827	
Total		100.000	

(*rac*)-3af



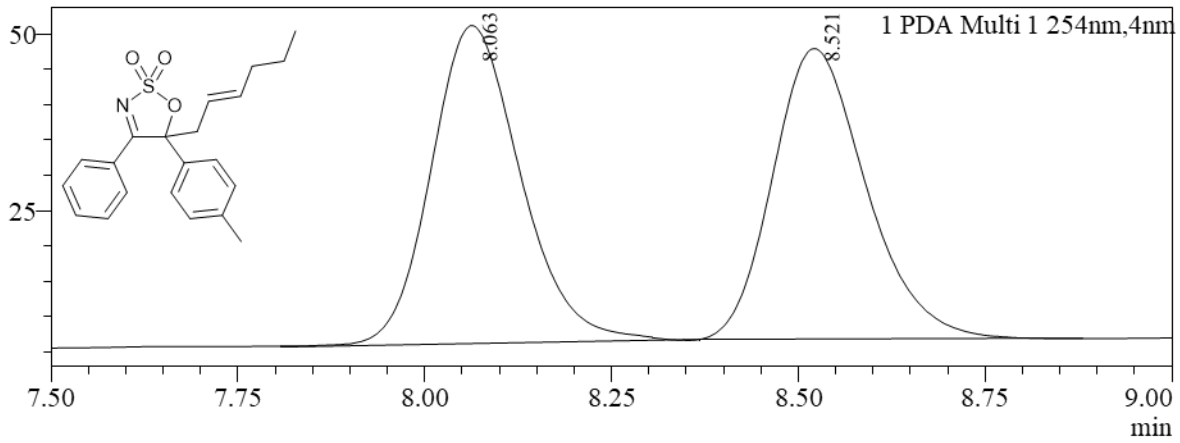
Peak#	Ret. Time	Area%	Name
1	10.823	48.713	
2	12.362	51.287	
Total		100.000	

(*S*)-3af



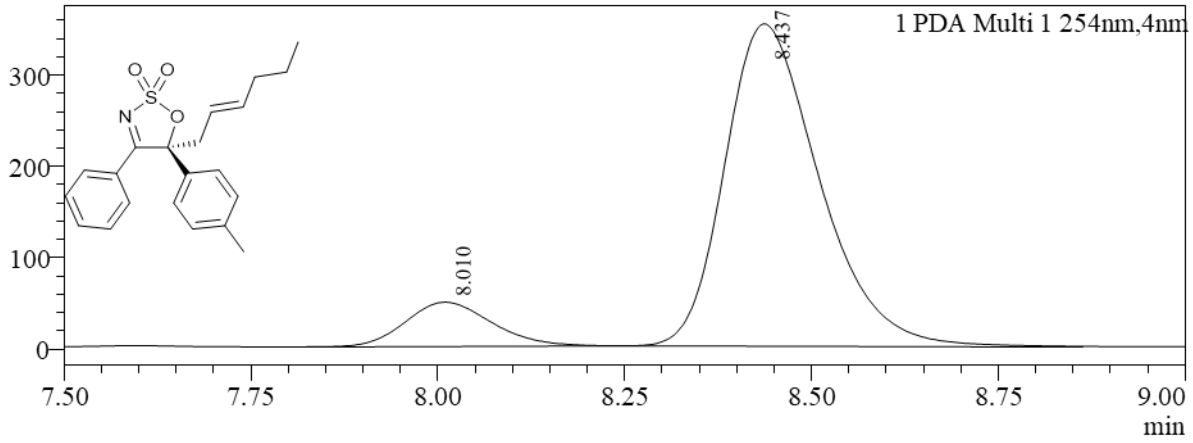
Peak#	Ret. Time	Area%	Name
1	10.711	3.888	
2	12.061	96.112	
Total		100.000	

(*rac*)-3ag



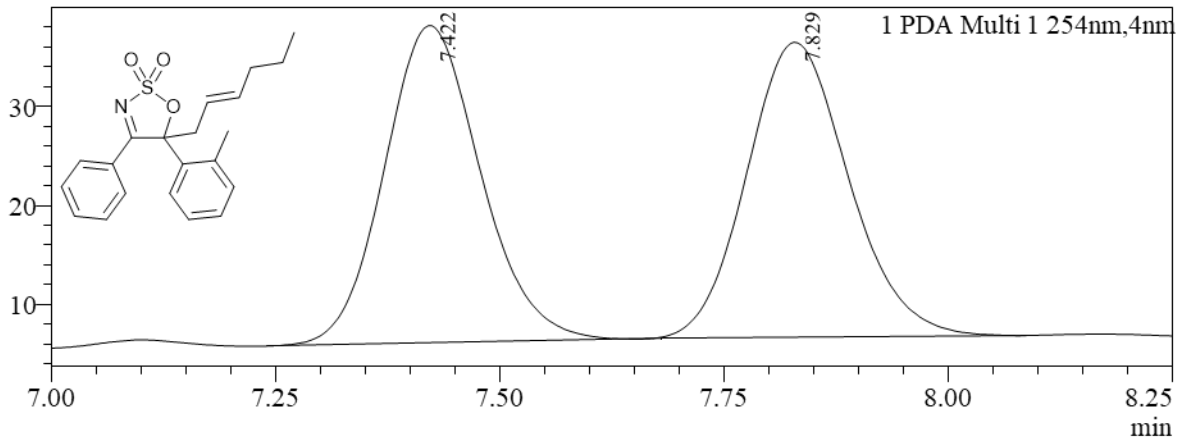
Peak#	Ret. Time	Area%	Name
1	8.063	50.943	
2	8.521	49.057	
Total		100.000	

(*S*)-3ag



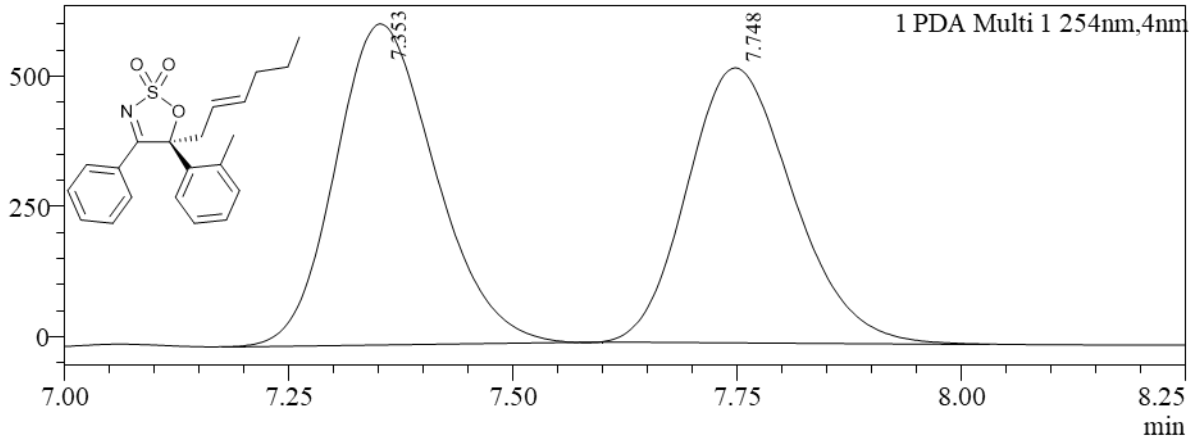
Peak#	Ret. Time	Area%	Name
1	8.010	11.185	
2	8.437	88.815	
Total		100.000	

(*rac*)-3ah



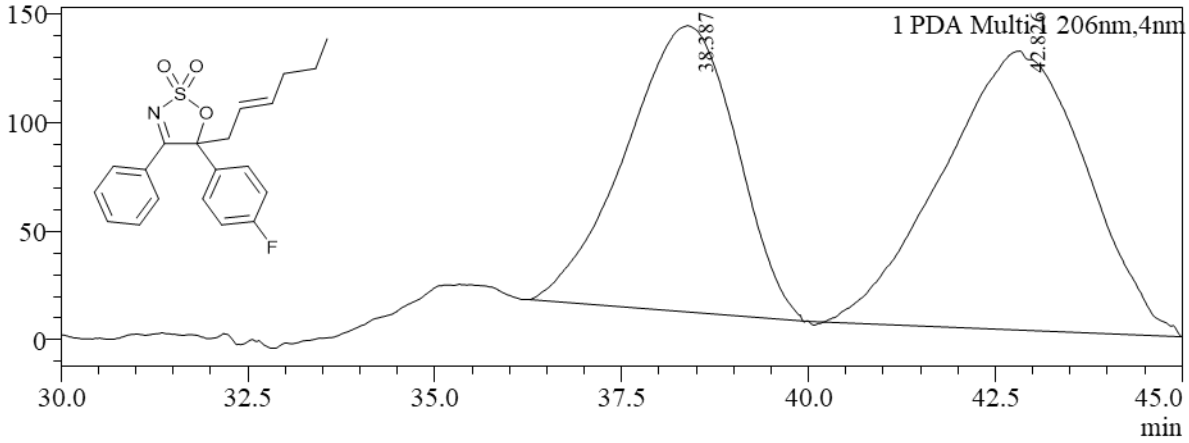
Peak#	Ret. Time	Area%	Name
1	7.422	50.339	
2	7.829	49.661	
Total		100.000	

(*S*)-3ah



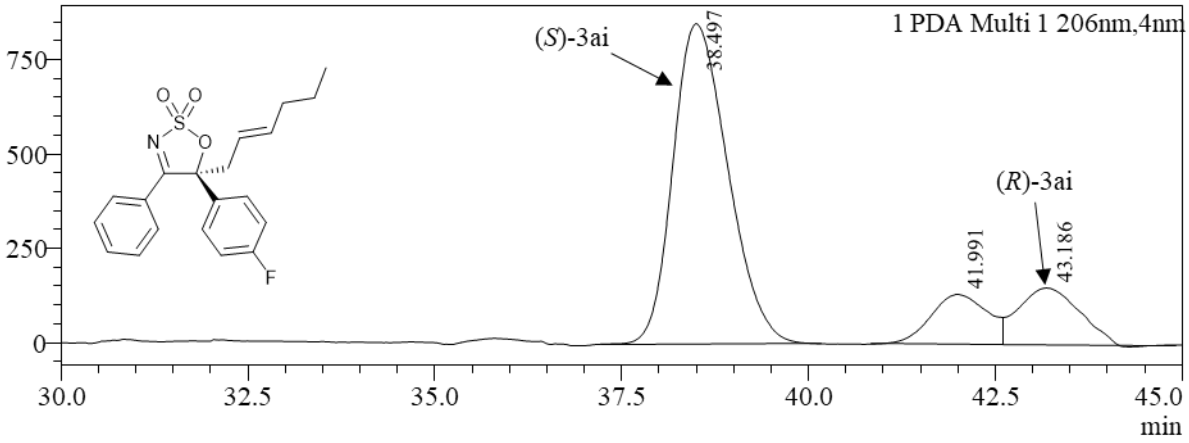
Peak#	Ret. Time	Area%	Name
1	7.353	52.341	
2	7.748	47.659	
Total		100.000	

(*rac*)-3ai



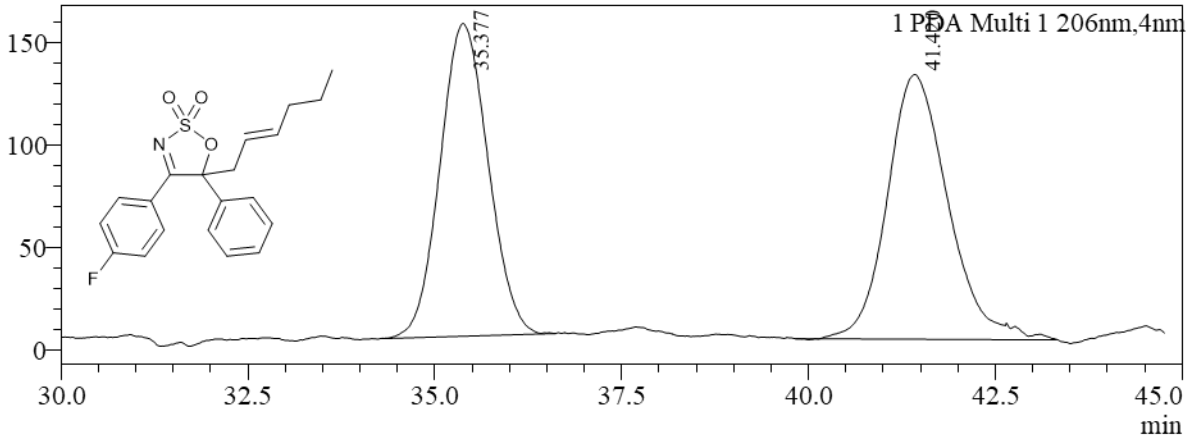
Peak#	Ret. Time	Area%	Name
1	38.387	44.141	
2	42.826	55.859	
Total		100.000	

(*S*)-3ai

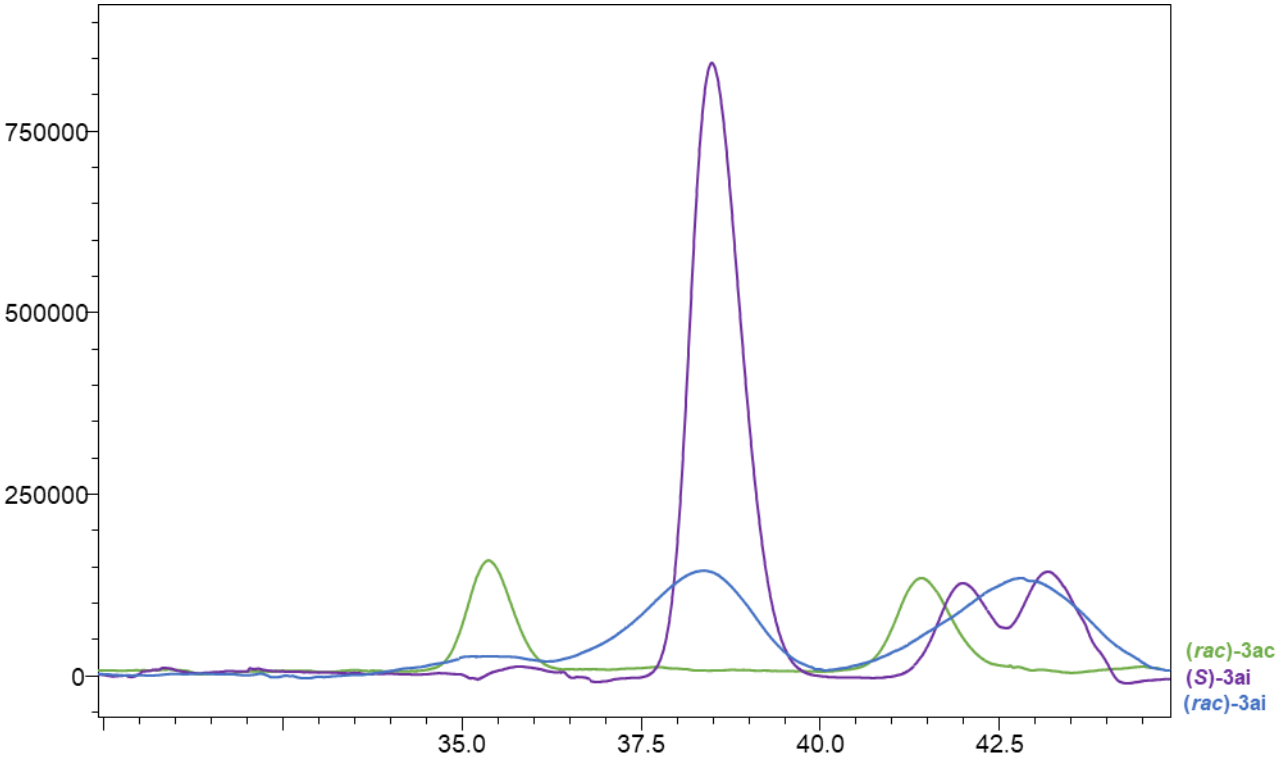


Peak#	Ret. Time	Area%	Name
1	36.922	73.448	
2	40.288	11.540	
3	41.461	15.012	
Total		100.000	

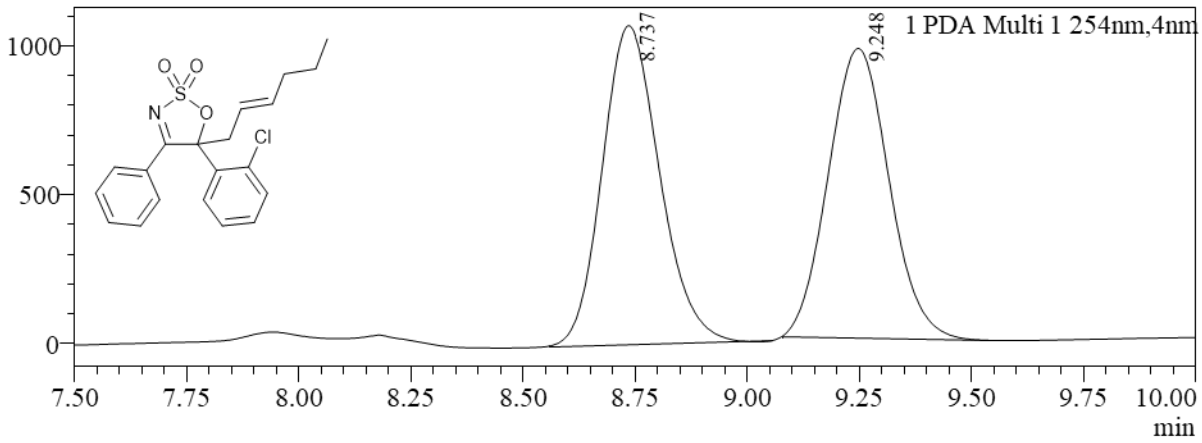
(*rac*)-3ac



Peak#	Ret. Time	Area%	Name
1	35.377	47.988	
2	41.420	52.012	
Total		100.000	

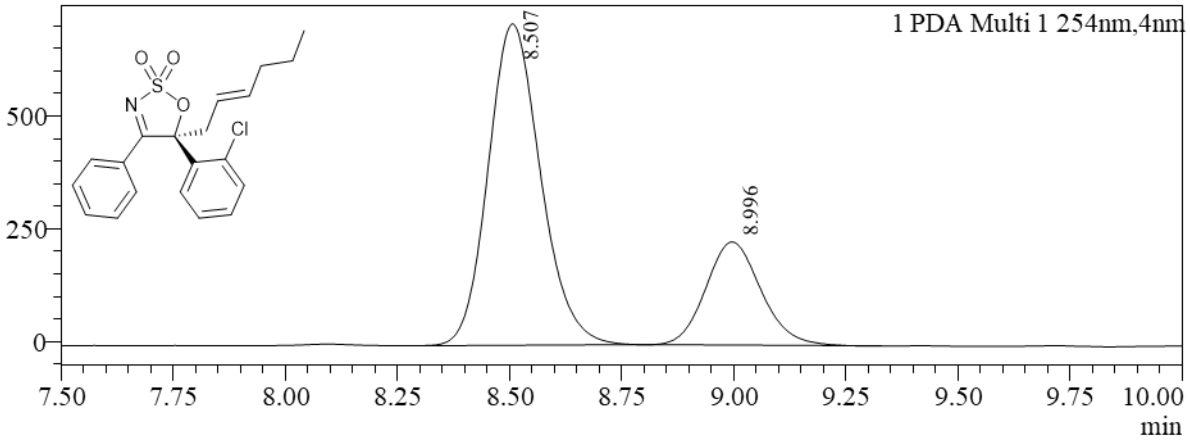


(*rac*)-3aj



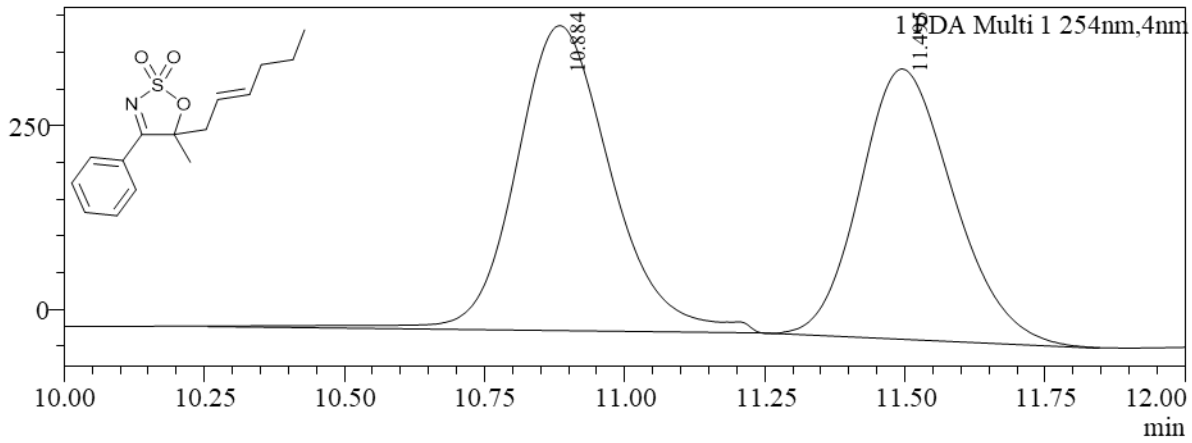
Peak#	Ret. Time	Area%	Name
1	8.737	50.852	
2	9.248	49.148	
Total		100.000	

(*S*)-3aj



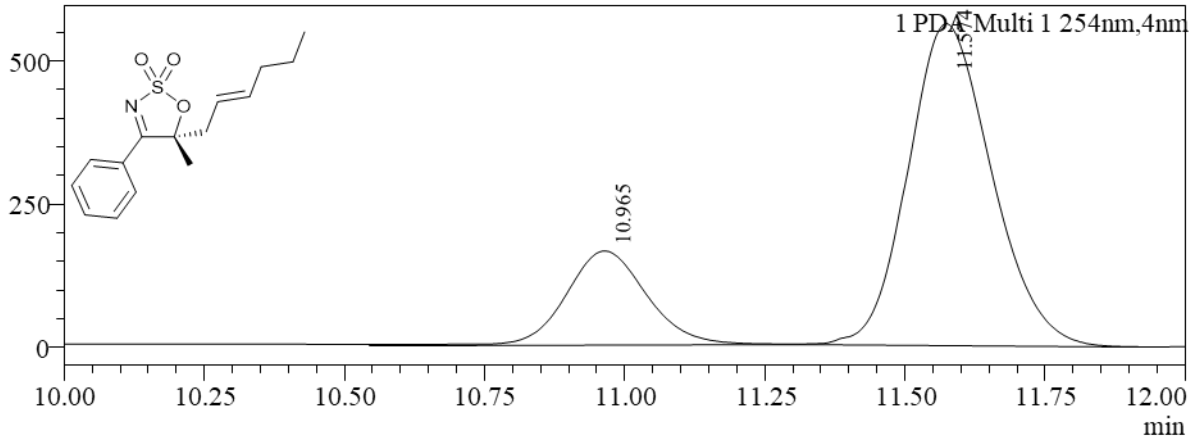
Peak#	Ret. Time	Area%	Name
1	8.507	74.661	
2	8.996	25.339	
Total		100.000	

(*rac*)-3ak



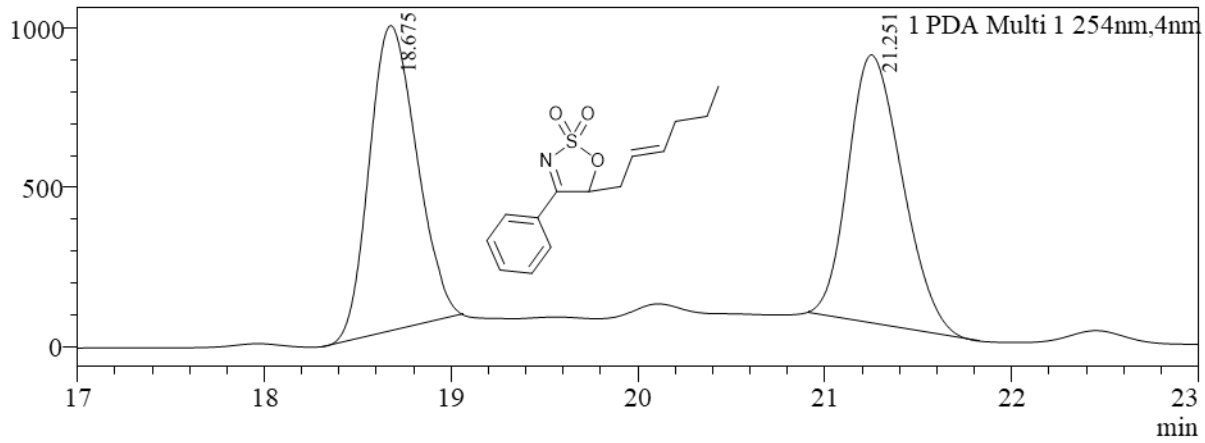
Peak#	Ret. Time	Area%	Name
1	10.884	53.480	
2	11.495	46.520	
Total		100.000	

(*S*)-3ak



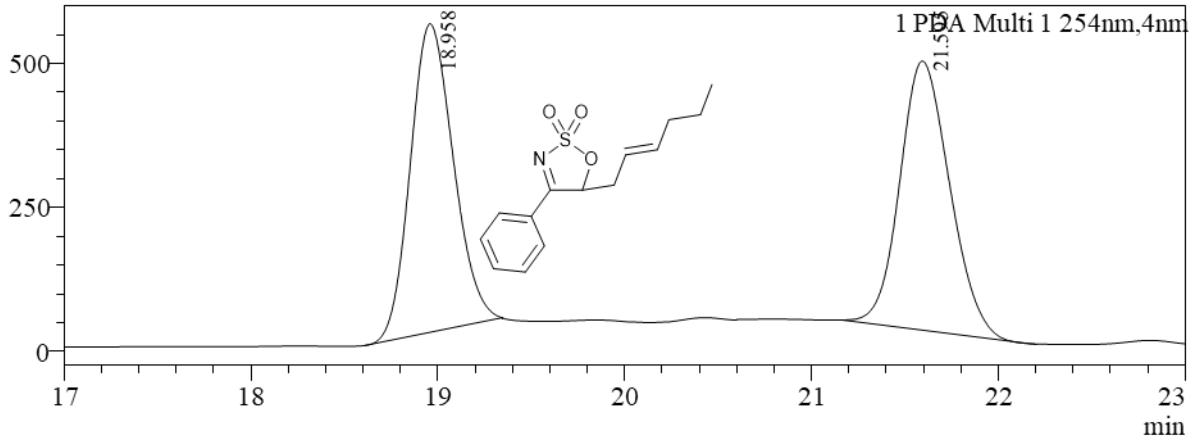
Peak#	Ret. Time	Area%	Name
1	10.965	21.695	
2	11.574	78.305	
Total		100.000	

(*rac*)-3an



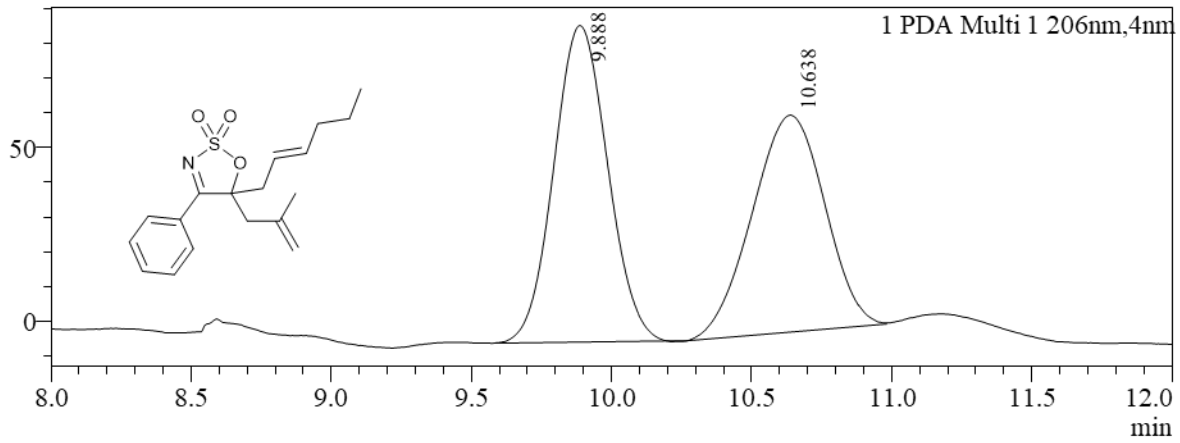
Peak#	Ret. Time	Area%	Name
1	18.675	49.942	
2	21.251	50.058	
Total		100.000	

(*rac*)-3an



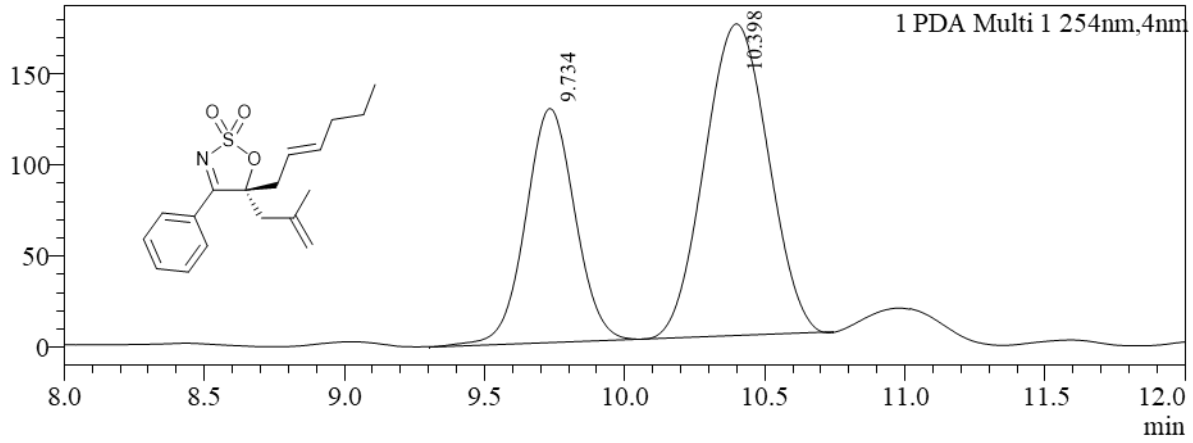
Peak#	Ret. Time	Area%	Name
1	18.958	49.572	
2	21.595	50.428	
Total		100.000	

(*rac*)-3abn



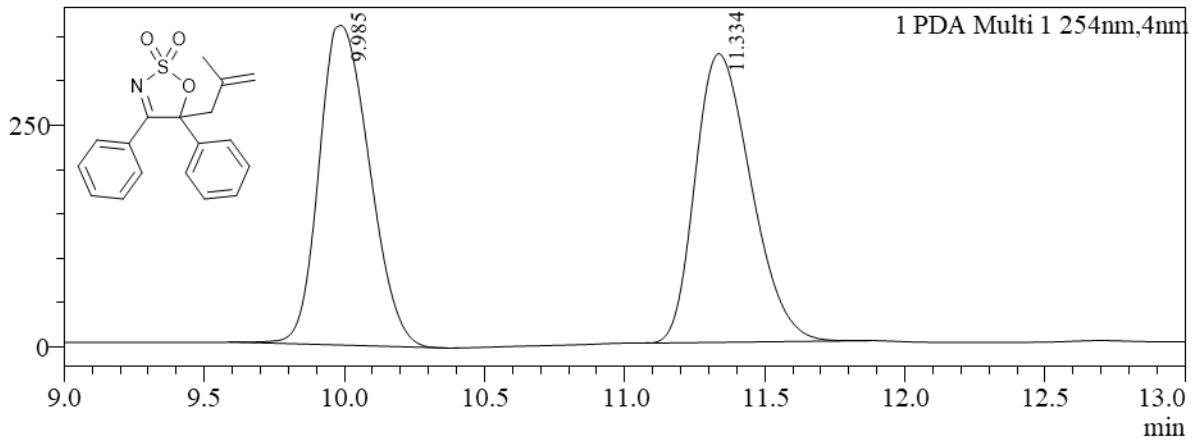
Peak#	Ret. Time	Area%	Name
1	9.888	52.066	
2	10.638	47.934	
Total		100.000	

(*S*)-3abn



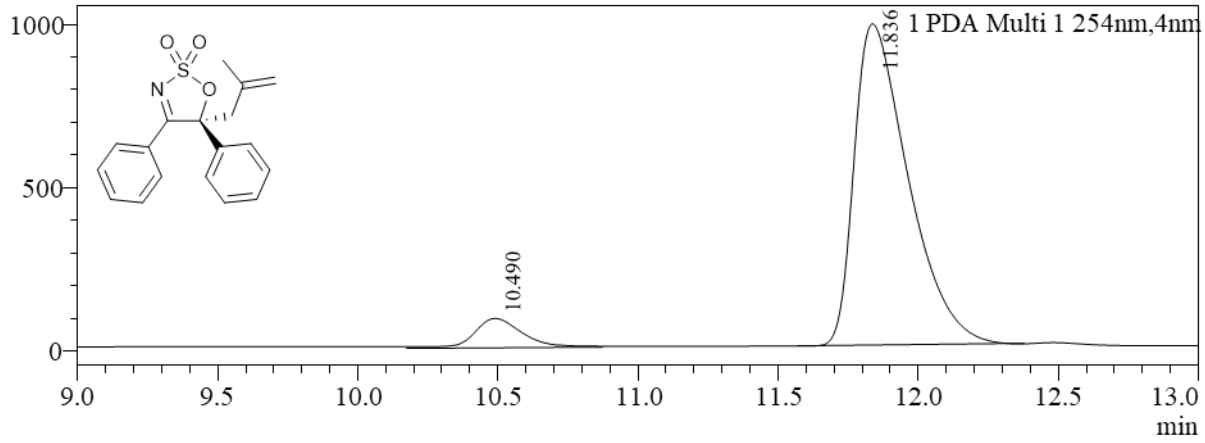
Peak#	Ret. Time	Area%	Name
1	9.734	36.651	
2	10.398	63.349	
Total		100.000	

(*rac*)-3ba



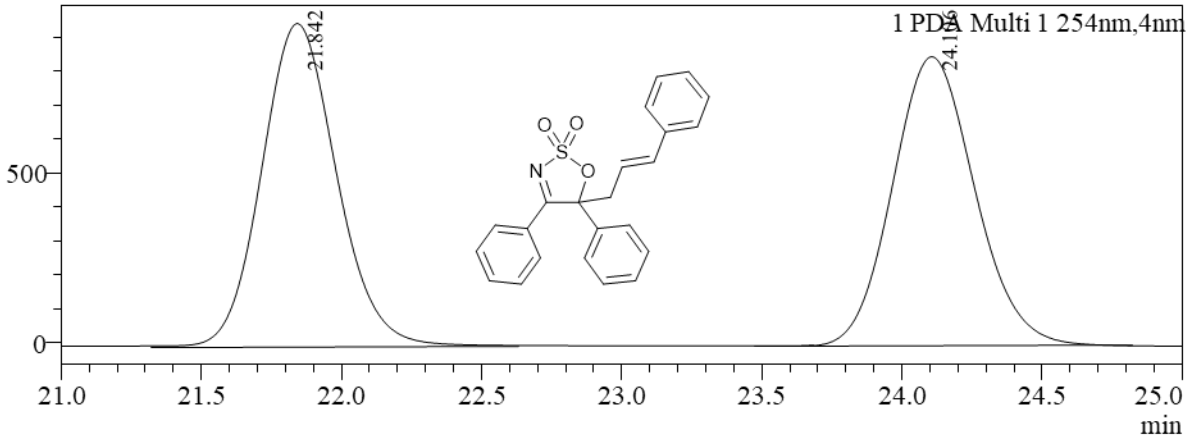
Peak#	Ret. Time	Area%	Name
1	9.985	49.885	
2	11.334	50.115	
Total		100.000	

(*S*)-3ba



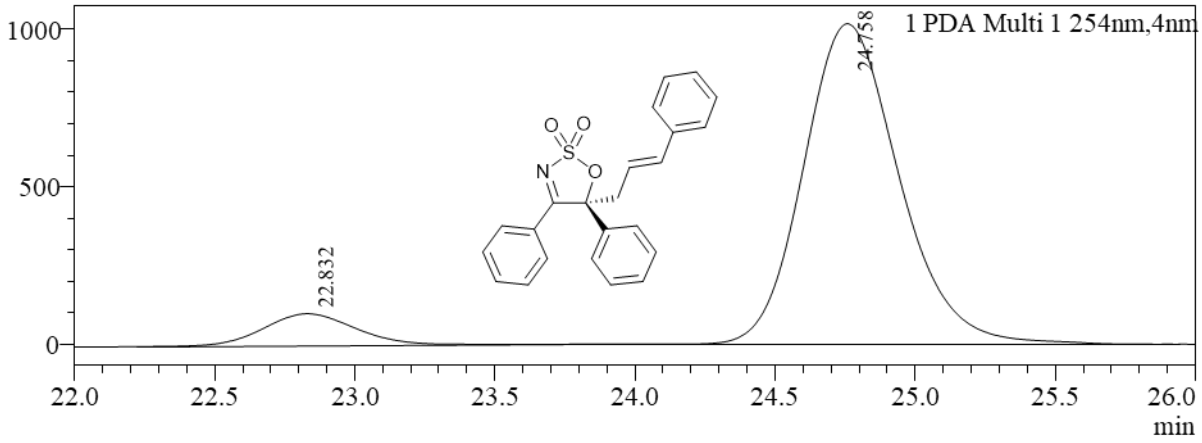
Peak#	Ret. Time	Area%	Name
1	10.490	6.688	
2	11.836	93.312	
Total		100.000	

(*rac*)-3ca



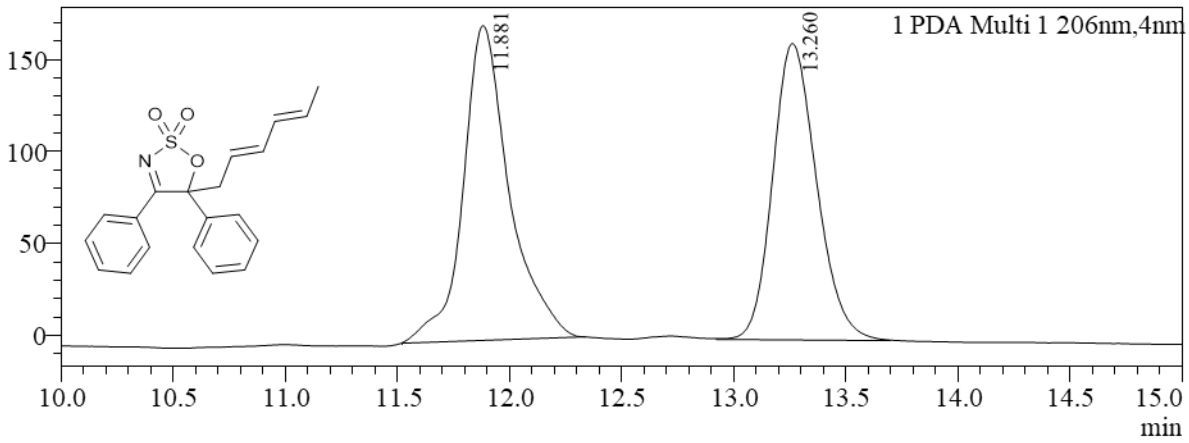
Peak#	Ret. Time	Area%	Name
1	21.842	50.076	
2	24.106	49.924	
Total		100.000	

(*S*)-3ca



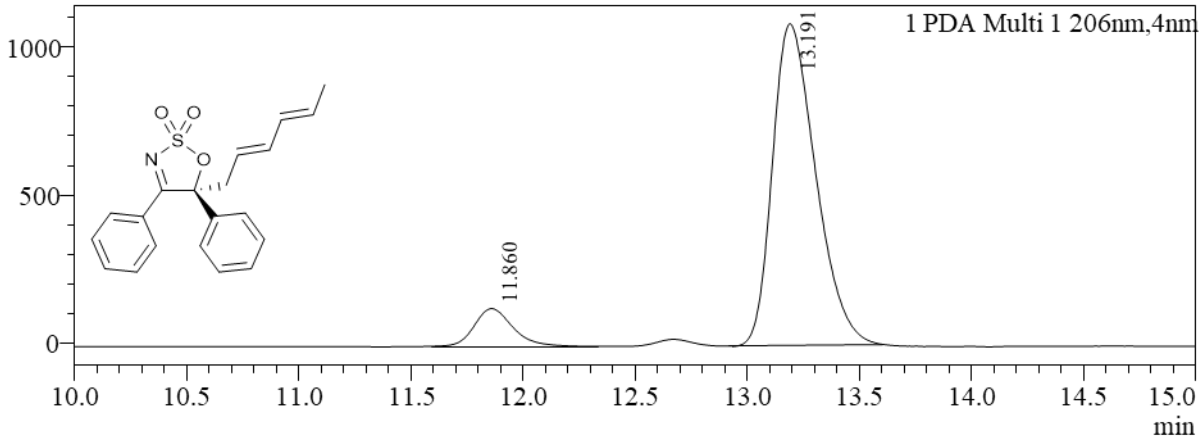
Peak#	Ret. Time	Area%	Name
1	22.832	8.813	
2	24.758	91.187	
Total		100.000	

(*rac*)-3da



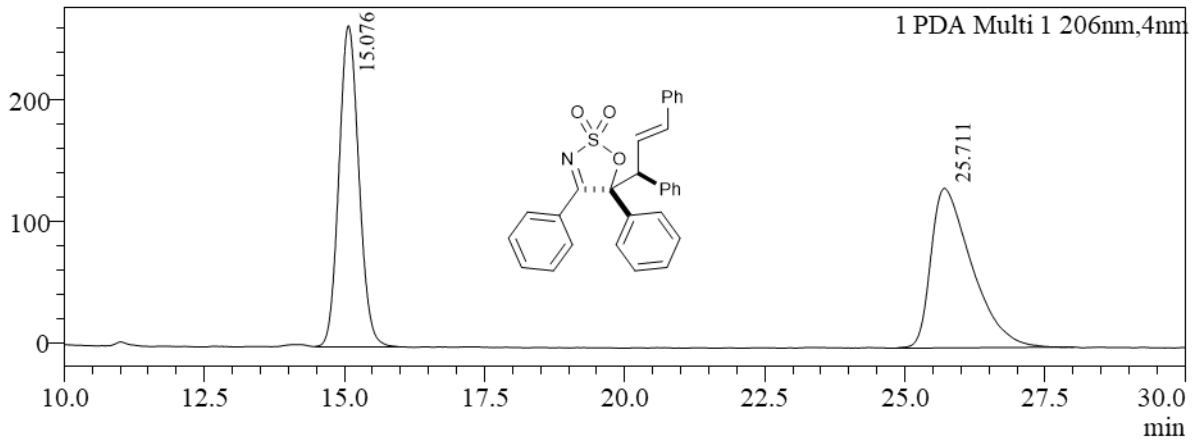
Peak#	Ret. Time	Area%	Name
1	11.881	52.758	
2	13.260	47.242	
Total		100.000	

(*S*)-3da



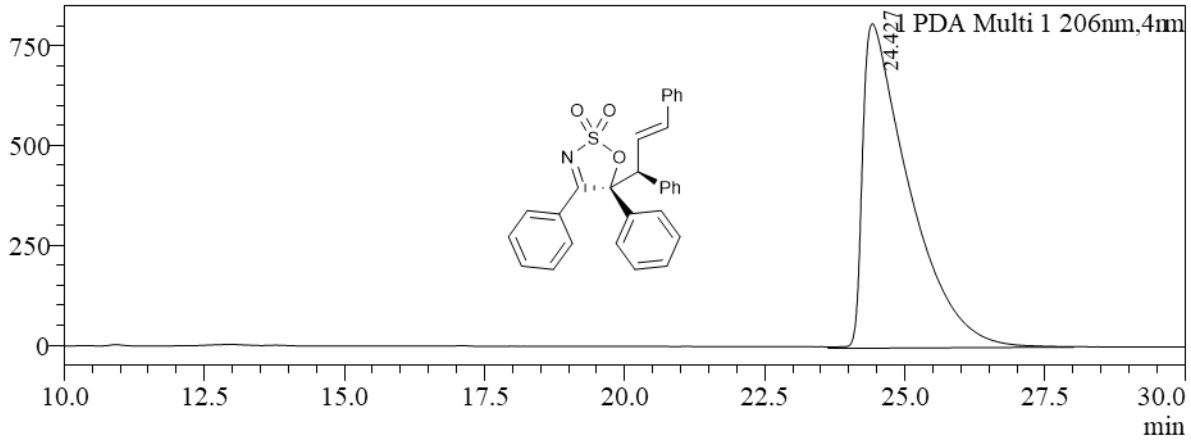
Peak#	Ret. Time	Area%	Name
1	11.860	9.527	
2	13.191	90.473	
Total		100.000	

(*rac*)-3fa



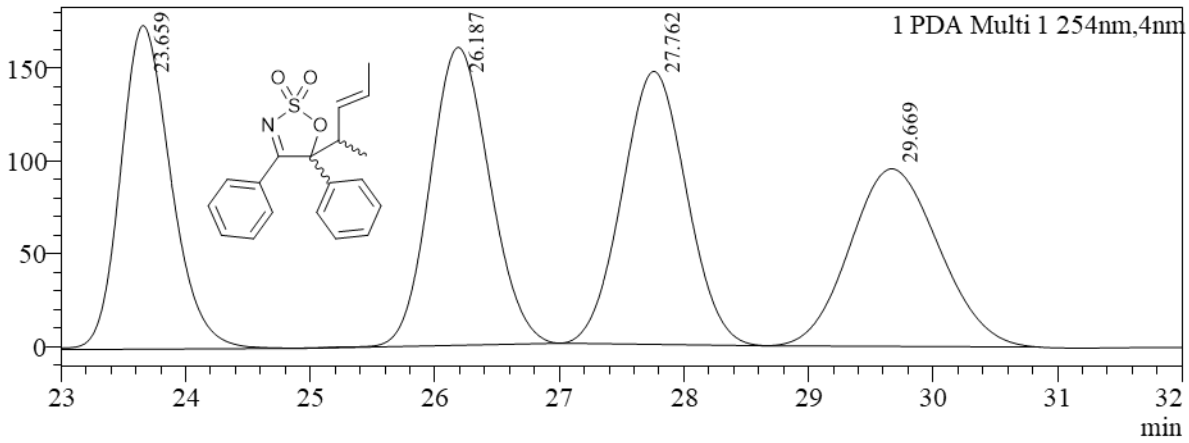
Peak#	Ret. Time	Area%	Name
1	15.076	49.904	
2	25.711	50.096	
Total		100.000	

(*S,S*)-3fa



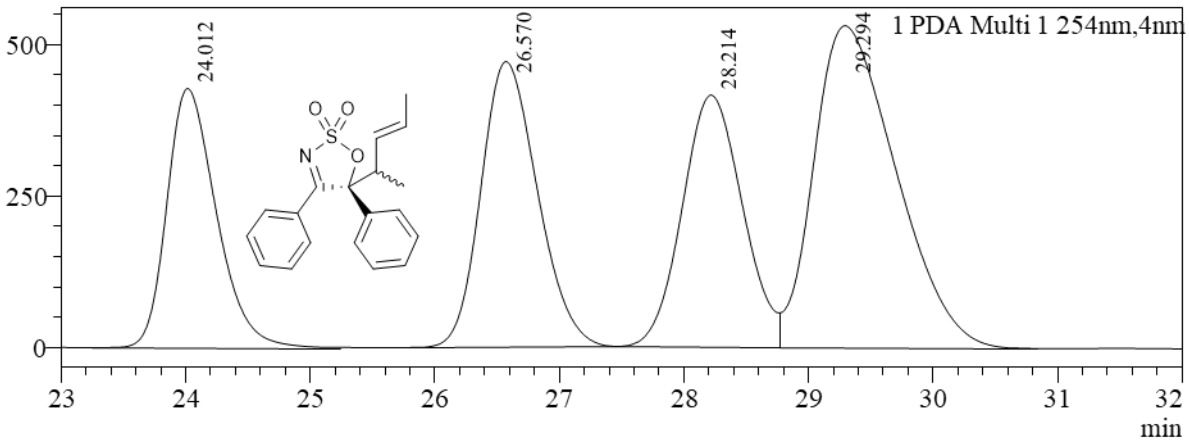
Peak#	Ret. Time	Area%	Name
1	24.427	100.000	
Total		100.000	

(*rac*)-3ga



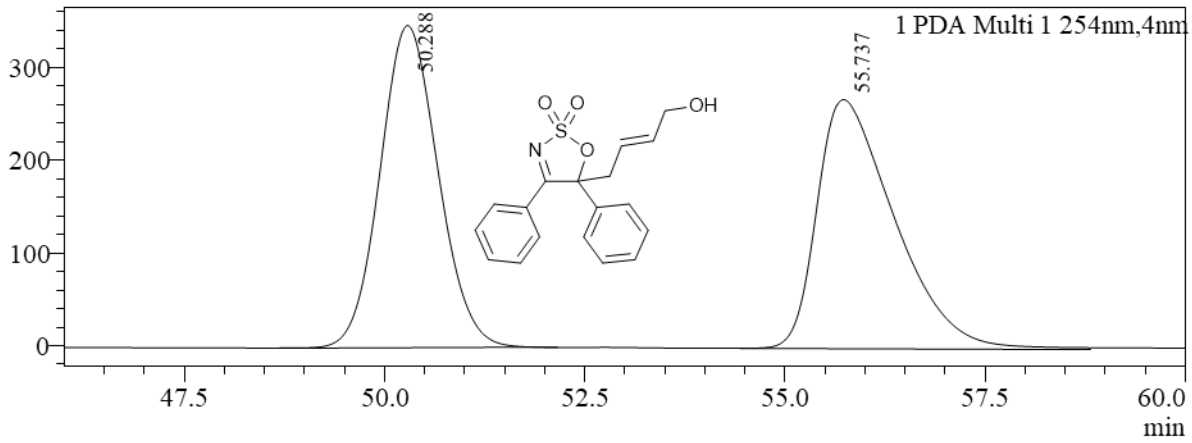
Peak#	Ret. Time	Area%	Name
1	23.659	24.071	
2	26.187	26.352	
3	27.762	26.083	
4	29.669	23.493	
Total		100.000	

“enantioenriched” 3ga



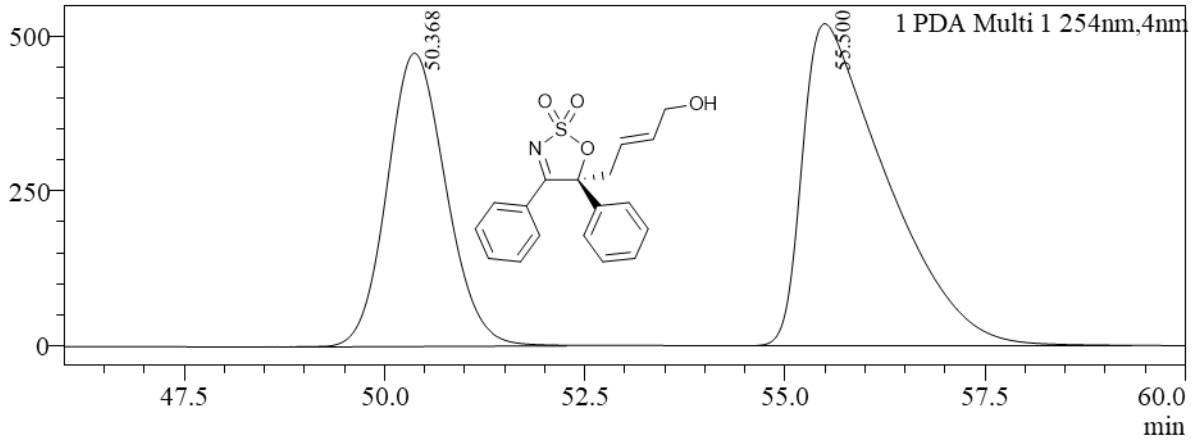
Peak#	Ret. Time	Area%	Name
1	24.012	18.086	
2	26.570	23.051	
3	28.214	21.527	
4	29.294	37.336	
Total		100.000	

(*rac*)-6aa



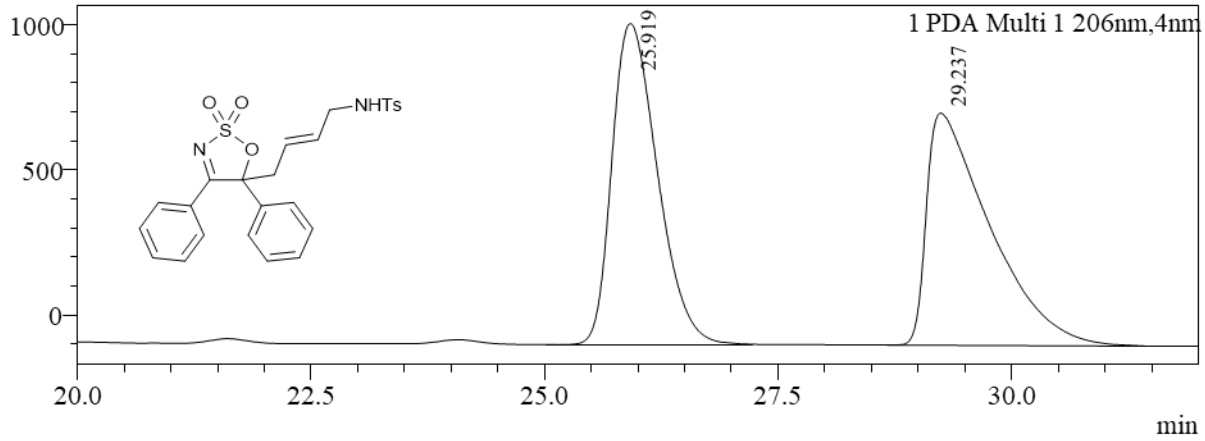
Peak#	Ret. Time	Area%	Name
1	50.288	49.956	
2	55.737	50.044	
Total		100.000	

(*S*)-6aa



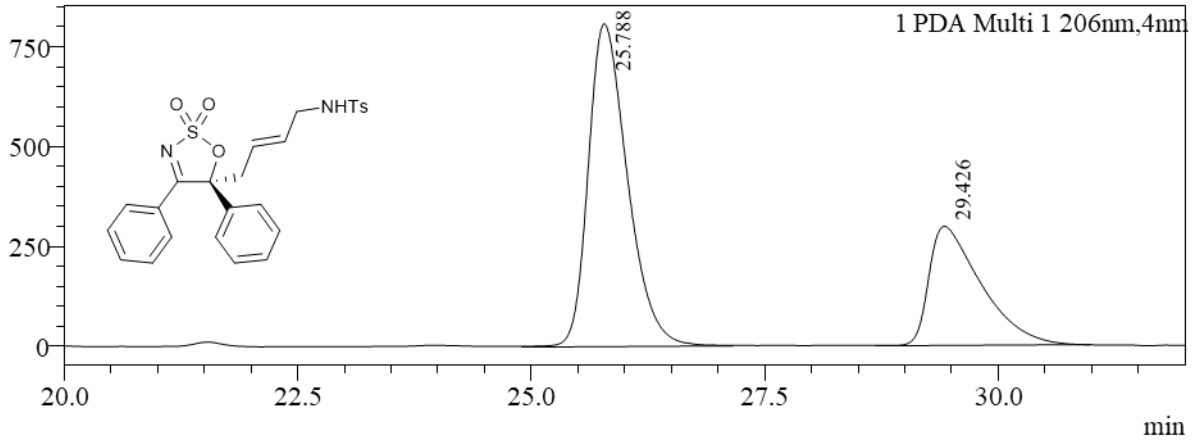
Peak#	Ret. Time	Area%	Name
1	50.368	38.914	
2	55.500	61.086	
Total		100.000	

(*rac*)-6ba



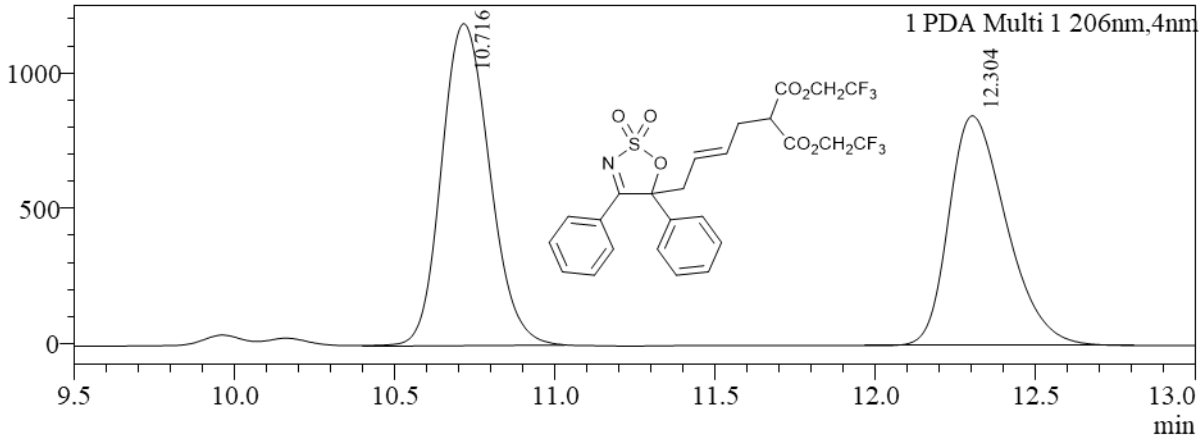
Peak#	Ret. Time	Area%	Name
1	25.919	49.318	
2	29.237	50.682	
Total		100.000	

(*S*)-6ba



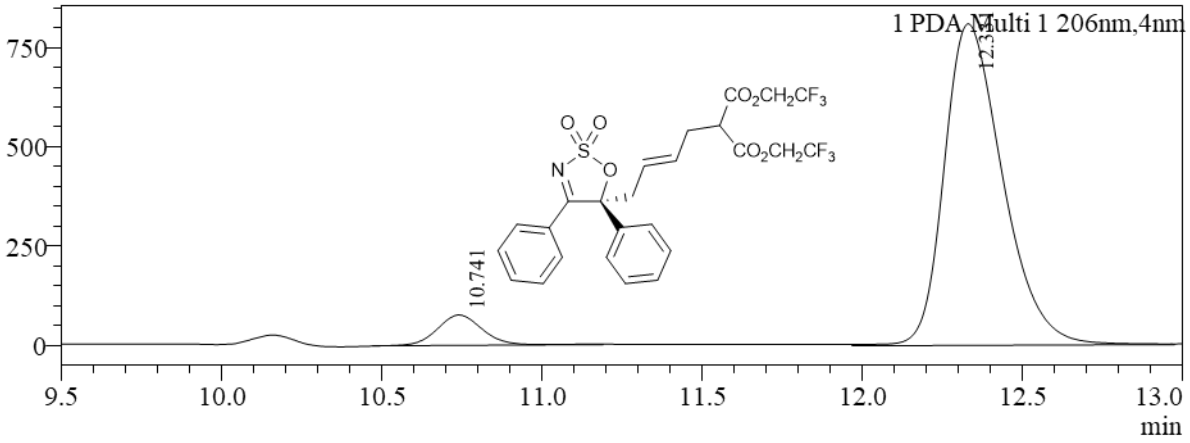
Peak#	Ret. Time	Area%	Name
1	25.788	66.904	
2	29.426	33.096	
Total		100.000	

(*rac*)-6ca



Peak#	Ret. Time	Area%	Name
1	10.716	53.781	
2	12.304	46.219	
Total		100.000	

(*S*)-6ca



Peak#	Ret. Time	Area%	Name
1	10.741	6.932	
2	12.331	93.068	
Total		100.000	