Supporting Information for

Organocatalytic Kinetic Resolution of Sulfoximines

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(A) General information

Optical rotation was measured with a Perkin-Elmer model 241 polarimeter (25 ^{o}C, λ = 589 nm). Specific rotations are reported as follows: $[\alpha]_D^{25}$ (*c*: g·100 mL^{-1}, in solvent).The unit is deg·cm^3·g^{-1}·dm^{-1}. All ee values were determined by high-performance liquid chromatography (HPLC) on systems of an Agilent 1100 or 1200 series with chiral stationary phases (Chiralpak AD-H, Chiralpak IA, Chiralpak IB, CHIRACEL OJ) from Chiral Technologies Inc. The enantiomers were identified and confirmed by comparing their HPLC retention times with those of authentic racemates. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on an Agilent 400 or 600 MHz spectrometer. The chemical shifts were given in ppm relative to the residual peak of the non-deuterated solvent was used as internal standard ($CDCl_3$ δ 7.26 ppm; DMSO-d_6 δ 2.54 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (in Hz), integration. $^{13}C\{^1H\}$ NMR data were collected at 100 or 150 MHz with complete proton decoupling ($CDCl_3$ δ 77.16 ppm; DMSO-d_6 δ 39.52 ppm). IR spectra were recorded on a Perkin Elmer 100 FT/IR spectrometer, and the wave numbers of the absorption peaks are given in cm^{-1}. Mass (MS) were acquired on a Finnigan SSQ 7000 spectrometer [electron ionization (EI), 70 eV] High resolution mass spectra (HRMS) analyses were recorded on a Thermo Scientific LTQ Orbitrap XL with positive ion mode. Reactions were monitored by thin layer chromatography (TLC) from Merck. Column chromatography was performed using silica gel 60 (63–200 μm) from Merck.

(B) Materials

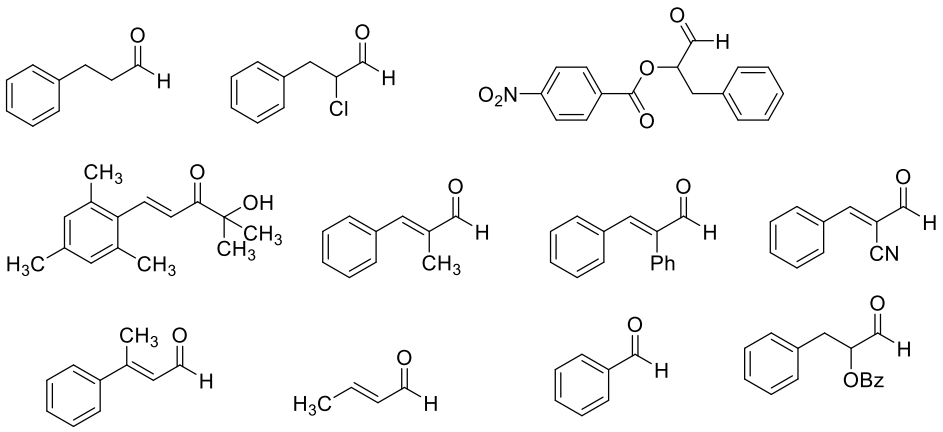
Unless otherwise noted, all commercially available chemicals were used directly as received. THF (assay: 99.8%) used for the kinetic resolution reactions was perchased from Acros. Cinnamaldehydes **2a**, **2b**, **2c**, **2f** and 1-bromo-2,4,6-triisopropylbenzene were obtained from Sigma-Aldrich. **2a** was distilled prior to use. **2b** and **2c** were used after recrystallization in pentane and ethyl acetate. Cinnamaldehydes **2d** and **2e** were synthesized by Wittig reactions using (triphenylphosphoranylidene)acetaldehyde and the corresponding aryl aldehydes.[1] 9-Bromophenanthrene, 4-bromopyrene and trimethyloxonium tetrafluoroborate were from TCI. Chiral amines were purchased from Alfa Aesar except for (*S*)-3,3-dimethylbutan-2-amine (from BASF). Sulfoximines were prepared according to the reported procedures.[2]

(C) Typical procedure for the asymmetric kinetic resolution reaction

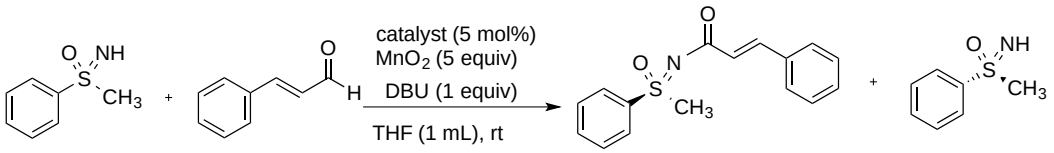
All reactions were performed under argon. To a stirred solution of triazolium salt (5 mol%), sulfoximine **1a** (31 mg, 0.20 mmol), 4 Å MS (30 mg), cinnamaldehyde **2b** (21 mg, 0.12 mmol) and MnO_2 (87 mg, 1.0 mmol) or quinone **7** (49 mg, 0.12 mmol) in THF (1 mL) was added DBU (30 μL, 0.2 mmol) at –60 °C. After stirring for 96 h (and detection by) TLC, the product was purified by column chromatography on silica gel to afford amide **3ab** (pentane/EtOAc = 3/1 to 1/1.5 as eluent) as a light yellow oil. The unreacted sulfoximine **1a** was recovered (pentane/EtOAc = 1/5 to EtOAc as eluent) as a colorless oil. The yields of **3ab** and recovered **1a** were calculated according to the amount of sulfoximine **1a**.

Hydrolysis of 3ab: Amide **3ab** (66 mg, 0.20 mmol, 80% ee) was dissolved in CH_2Cl_2 (2 mL) and aqueous HCl (12 N, 30 equiv.) was added. The reaction was stirred at 80 °C for 5 h. The mixture was diluted with water and washed with ether, the aqueous layer was basified with aqueous NaOH (2 N) and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give **1a** (26.5 mg, 80%ee).

(D) Optimization of the reaction conditions



Scheme 1: Unreactive compounds

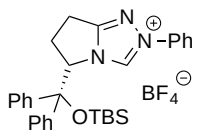


rac-**1a**
0.20 mmol

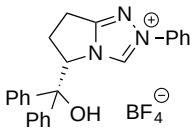
2a
0.15 mmol

3aa

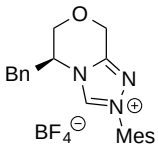
1a



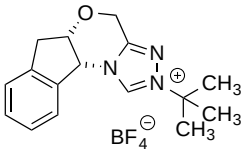
NR



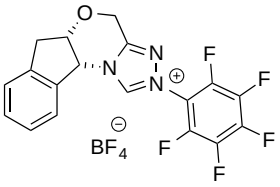
NR



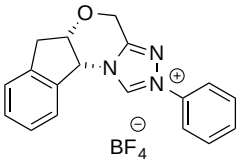
P: 50% yield, –11% ee
S: 50% yield, –11% ee



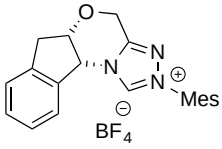
NR



NR

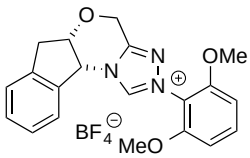


P: 8% yield, 40% ee
S: 90% yield, 3% ee



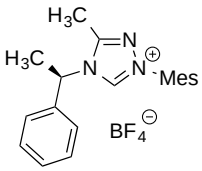
P: 35% yield, 42% ee
S: 60% yield, 20 % ee

0 °C, *s* = 3
P: 52% yield, 36% ee
S: 43% yield, 40% ee



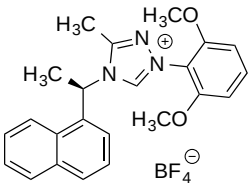
0 °C, *s* = 3
P: 64% yield, 27% ee
S: 29% yield, 62% ee

Mes = 2,4,6-trimethylphenyl,
P: product,
S: recovered sulfoximine.



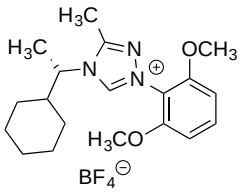
C1

Racemic



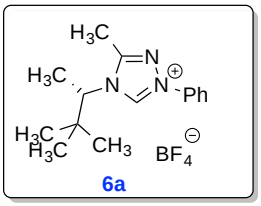
C2

0 °C, *s* = 3
P: 15% yield, –45% ee
S: 80% yield, –9% ee



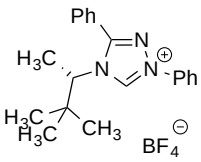
C3

0 °C, *s* = 4
P: 26% yield, 53% ee
S: 70% yield, 19% ee



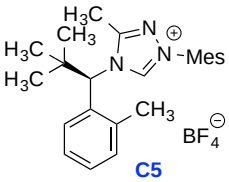
6a

0 °C, *s* = 6
P: 14% yield, 70% ee
S: 82% yield, 12% ee



C4

NR

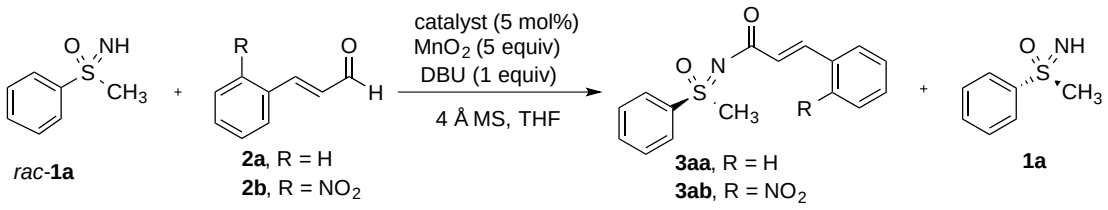


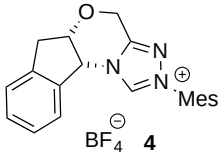
C5

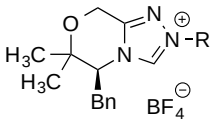
0 °C, *s* = 2
P: 20% yield, –20% ee
S: 75% yield, –5% ee

Scheme 2. Pre-screening of catalysts

Table 1. Optimization of the reaction conditions[a]





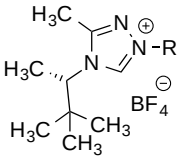


5a: R = 2,4,6-trimethylphenyl (Mes)

5b: R = 2,4,6-triisopropylphenyl

5c:R = 9-phenanthrenyl

5d: R = 4-pyrenyl



6a: R = Ph

6b: R = Mes

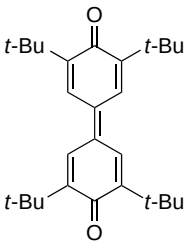
6c: R = 2,4,6-triisopropylphenyl

6d: R = 2,4,6-tricyclohexylphenyl

6e: R = 2,4,6-tricyclopentylphenyl

6f: R = 9-phenanthrenyl

6g: R = 4-pyrenyl

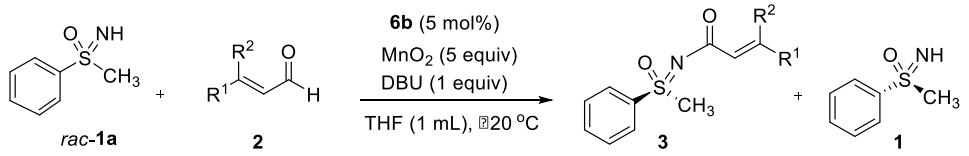


7

entry	catalyst	T (°C)	t (h)	yield of **3** (%)	ee of **3** (%)[b]	yield of **1a** (%)	ee of **1a** (%)[b]	*S*[c]
1[d]	**4**	−20	48	53 (**3aa**)	39	44	45	4
2[d]	**5a**	−20	48	58 (**3aa**)	−45	40	−62	5
3	**5a**	−20	24	42 (**3ab**)	−68	50	−50	9
4	**6a**	−20	48	30 (**3ab**)	72	65	32	8
5	**6b**	−20	48	45 (**3ab**)	70	52	57	10
6	**6c**	−20	48	54 (**3ab**)	67	42	81	12
7	**6d**	−20	48	57 (**3ab**)	63	40	84	11
8	**6e**	−20	48	50 (**3ab**)	70	45	70	12
9	**6f**	−20	48	54 (**3ab**)	67	41	80	12
10	**5b**	−20	48	51 (**3ab**)	−70	46	−70	12
11	**5c**	−20	72	51 (**3ab**)	-68	45	−70	11
12	**6c**	−45	72	38 (**3ab**)	78	58	50	13
13[e]	**6c**	−45	72	59 (**3ab**)	64	38	94	15
14[e,f]	**6c**	−60	96	53 (**3ab**)	81	43	91	30
15[e]	**6g**	−60	96	53 (**3ab**)	70	44	80	14
16[e]	**5b**	−60	96	56 (**3ab**)	−75	42	−95	25
17[e]	**5d**	−60	96	57 (**3ab**)	−67	40	−90	15

[a] Unless otherwise noted, all reactions were carried out with **cat**. (5 mol%), **1a** (31 mg, 0.20 mmol), **2b** (21 mg, 0.12 mmol), DBU (30 μL, 0.2 mmol), 4 Å MS (30 mg) and MnO_2 (87 mg, 1.0 mmol) in THF (1 mL). [b] Determined by CSP-HPLC analysis. [c] Selectivity factors (*s*), calculated according to the following equation: $s = \ln[(1-C)*(1-ee_{1a})]/\ln[(1-C)*(1+ee_{1a})]$, $C = (ee_{1a})/(ee_{1a}+ee_3)$. [d] **2a** (19 μL, 0.15 mmol) was used instead of **2b**. [e] 3,3',5,5'-Tetra-*tert*-butyl-[1,1'-bi- (cyclohexylidene)]-2,2',5,5'- tetraene-4,4'-dione **7** (49 mg, 0.6 equiv.) was used as the oxidant instead of MnO_2. [f] The absolute configuration of the major enantiomer **1a** was determined to be (*S*) by comparing the specific rotation with the reported value.

Table 2: The screening of substituted enals[a]

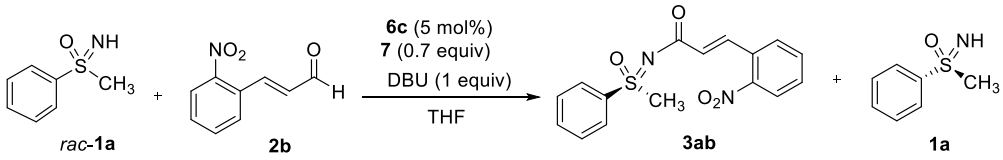


rac-**1a** + **2** → **3** + **1**

entry	R^1	R^2	yield of **3** (%)	ee of **3** (%)[b]	yield of **1a** (%)	ee of **1a** (%)[c]	*s*[d]
1	C_6H_5 (**2a**)	H	31 (**3aa**)	69	65	33	8
2	2-$NO_2C_6H_4$ (**2b**)	H	45 (**3ab**)	69	52	57	10
3	4-$NO_2C_6H_4$ (**2c**)	H	43 (**3ac**)	69	53	53	9
4	2-BrC_6H_4 (**2d**)	H	47 (**3ad**)	66	50	59	9
5	2-$CH_3OC(O)C_6H_4$ (**2e**)	H	37 (**3ae**)	74	45	42	10
6	C_6H_5 (**2f**)	C_6H_5	NR	--	0	0	--

[a] Unless otherwise noted, all reactions were carried out with **6b** (5 mol%), **1a** (31 mg, 0.20 mmol), **2** (0.12 mmol), DBU (30 μL, 0.20 mmol), 4 Å MS (30 mg) and MnO_2 (87 mg, 1.0 mmol) in THF (1 mL) at −20 °C for 48 h.

Table 3: The ratio of two starting materials[a]



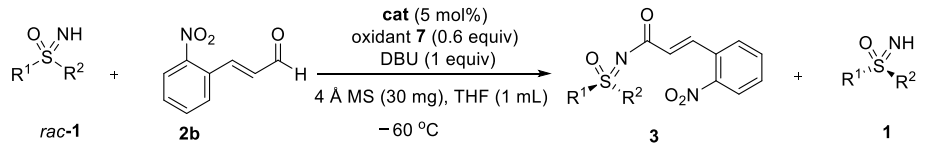
rac-**1a** + **2b** → **3ab** + **1a**

entry	**2b** (equiv)	T (°C)	product **3ab**		recovered **1a**	
			yield (%)	ee (%)	yield (%)	ee (%)
1	0.55	−45	50	81	48	80
2	0.6	−45	54	76	44	90
3	0.65	−45	55	74	42	93
4	0.67	−45	56	72	40	95
5	0.7	−45	58	69	39	97
6[b]	0.7	−45	64	−55	33	−99
7[b]	0.6	−45	57	−69	40	−92

[a] Unless otherwise noted, all reactions were carried out with **6c** (5 mol%), **1a** (0.20 mmol), **2b**, DBU (30 μL, 0.2 mmol), 4 Å MS (30 mg) and oxidant **7** (57 mg, 0.14 mmol) in THF (1 mL) for 72 h. [b] Using **5b** as the catalyst instead of **6c**.

(E) Substrate scope for kinetic resolutions of sulfoximines with enal 2b

Table 4: Substrate scope for kinetic resolutions of sulfoximines with enal **2b**[a]

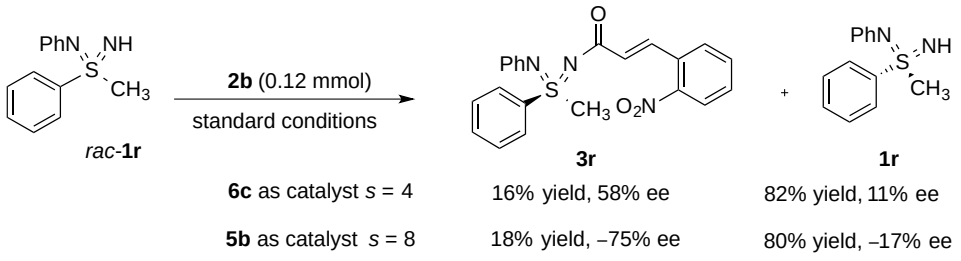


rac-**1** + **2b** → **3** + **1**

entry	R^1	R^2	t (h)	yield of **3** (%)	ee of **3** (%)[b]	yield of **1** (%)	ee of **1** (%)[b]	*s*
1	C_6H_5	CH_3	96	53 (**3ab**)	81	43 (**1a**)	91	30
2[c]	C_6H_5	CH_3	96	56 (**3ab**)	−75	42 (**1a**)	−95	25
3	2-BrC_6H_4	CH_3	96	54 (**3b**)	78	43 (**1b**)	92	26
4[c]	2-BrC_6H_4	CH_3	96	57 (**3b**)	−67	40 (**1b**)	−90	16
5	3-BrC_6H_4	CH_3	96	59 (**3c**)	67	38 (**1c**)	99	25
6[c]	3-BrC_6H_4	CH_3	96	56 (**3c**)	−74	42 (**1c**)	−93	22
7	4-BrC_6H_4	CH_3	96	56 (**3d**)	73	41 (**1d**)	96	24
8[c]	4-BrC_6H_4	CH_3	96	54 (**3d**)	−77	42 (**1d**)	−94	27
9	2-ClC_6H_4	CH_3	96	53 (**3e**)	80	45 (**1e**)	92	29

10[c]	2-ClC_6H_4	CH_3	96	56 (**3e**)	−69	40 (**1e**)	−85	14
11	4-ClC_6H_4	CH_3	96	53 (**3f**)	81	45 (**1f**)	94	33
12[c]	4-ClC_6H_4	CH_3	96	54 (**3f**)	−76	43 (**1f**)	−90	22
13	4-FC_6H_4	CH_3	108	54 (**3g**)	72	42 (**1g**)	85	16
14[c]	4-FC_6H_4	CH_3	108	53 (**3g**)	−75	42 (**1g**)	−88	20
15	4-$CH_3C_6H_4$	CH_3	96	52 (**3h**)	82	44 (**1h**)	94	35
16[c]	4-$CH_3C_6H_4$	CH_3	96	54 (**3h**)	−80	43 (**1h**)	−95	33
17	4-$CH_3OC_6H_4$	CH_3	96	52 (**3i**)	78	42 (**1i**)	89	24
18[c]	4-$CH_3OC_6H_4$	CH_3	96	57 (**3i**)	−73	41 (**1i**)	−97	26
19	4-$CH_3OC(O)C_6H_4$	CH_3	108	52 (**3j**)	78	42 (**1j**)	87	23
20[c]	4-$CH_3OC(O)C_6H_4$	CH_3	108	55 (**3j**)	−52	42 (**1j**)	−65	6
21[d]	4-$NO_2C_6H_4$	CH_3	108	41 (**3k**)	93	55 (**1k**)	65	54
22[c,d]	4-$NO_2C_6H_4$	CH_3	108	41 (**3k**)	−96	53 (**1k**)	−69	101
23	4-$CF_3C_6H_4$	CH_3	96	54 (**3l**)	76	44 (**1l**)	91	23
24[c]	4-$CF_3C_6H_4$	CH_3	96	52 (**3l**)	−80	47 (**1l**)	−87	25
25	4-$SF_5C_6H_4$	CH_3	96	53 (**3m**)	75	43 (**1m**)	88	20
26[c]	4-$SF_5C_6H_4$	CH_3	96	56 (**3m**)	−73	41 (**1m**)	−93	21
27	2-naphthyl	CH_3	96	54 (**3n**)	79	43 (**1n**)	96	33
28[c]	2-naphthyl	CH_3	96	54 (**3n**)	−80	44 (**1n**)	−95	33
29	2-pyridyl	CH_3	120	52 (**3o**)	43	44 (**1o**)	48	4
30[c]	2-pyridyl	CH_3	120	54 (**3o**)	−53	44 (**1o**)	−63	6
31	C_6H_5	cyclopropyl	96	54 (**3p**)	84	44 (**1p**)	99	60
32[c]	C_6H_5	cyclopropyl	96	54 (**3p**)	−79	44 (**1p**)	−93	29
33	C_6H_5	$C_6H_5CH_2$	96	53 (**3q**)	78	45 (**1q**)	90	25
34[c]	C_6H_5	$C_6H_5CH_2$	96	56 (**3q**)	−69	40 (**1q**)	−90	16
35	C_6H_5	CF_3	72	53 (**3s**)	20	30 (**1s**)	30	2
36[c]	C_6H_5	CF_3	72	50 (**3s**)	0	35 (**1s**)	0	0
37	*t*-Bu	CH_3	48	35 (**3t**)	27	60 (**1t**)	ND	--
38[c]	*t*-Bu	CH_3	48	36 (**3t**)	−37	58 (**1t**)	ND	--
39	2-$NHBocC_6H_4$	C_6H_5	96	20 (**3u**)	0	65 (**1u**)	0	--
40[c]	2-$NHBocC_6H_4$	C_6H_5	96	25 (**3u**)	−14	68 (**1u**)	ND	--
41	4-$CH_3C(O)C_6H_4$	C_6H_5	96	55 (**3v**)	44	42 (**1v**)	57	4
42[c]	4-$CH_3C(O)C_6H_4$	C_6H_5	96	52 (**3v**)	−52	46 (**1v**)	−58	6

[a] Unless otherwise noted, all reactions were carried out with **6c** (5 mol %), **1** (0.20 mmol), **2b** (21 mg, 0.12 mmol), DBU (30 μL, 0.2 mmol), 4 Å MS (30 mg) and oxidant **7** (49 mg, 0.12 mmol) in THF (1.0 mL) at −60 °C. [b] Determined by HPLC analysis. [c] Catalyst **5b** was used instead of **6c**. [d] 10 mol % of catalysts were used.



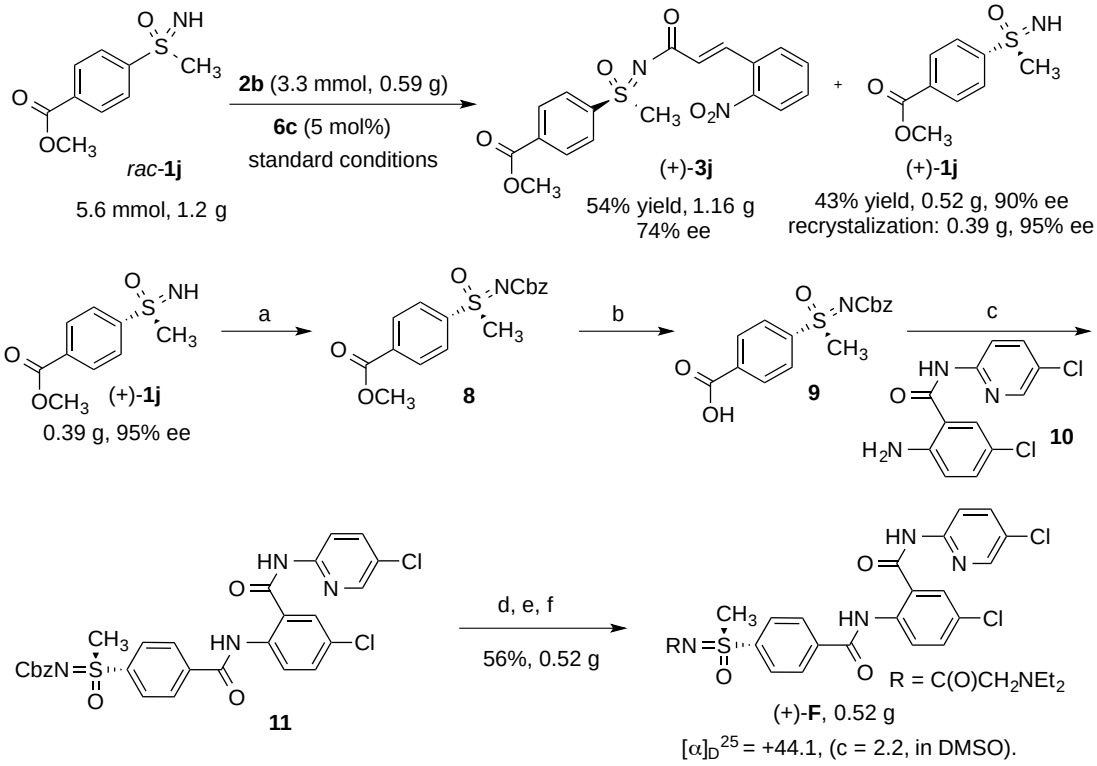
Scheme 3. Sulfondiimide as the substrate

(F) Scale-up experiment and its application

To a stirred solution of triazolium salt **6c** (0.12 g, 5 mol%), sulfoximine **1j** (1.20 g, 5.6 mmol), 4 Å MS (0.84 g), cinnamaldehyde (**2b**, 0.59 g, 3.3 mmol) and quinone **7** (1.34 g, 3.3 mmol) in THF (25 mL) was added DBU (0.84 mL, 5.6 mmol) at −60 °C. After stirring for 108 h (detection by TLC), the mixture was filtered through a plug of celite, and the filtrate was concentrated under reduced pressure. The product was purified by column chromatography (silica

gel) to afford amide **3j** (pentane/EtOAc = 4/1 to 1/1 as eluent) as a light yellow oil (1.20 g). Unreacted sulfoximine **1j** was recovered (pentane/EtOAc = 1/5 to EtOAc as eluent) as a white solid (0.52 g). The yields of **3j** and recovered **1j** were calculated according to the amount of sulfoximine **1j**.

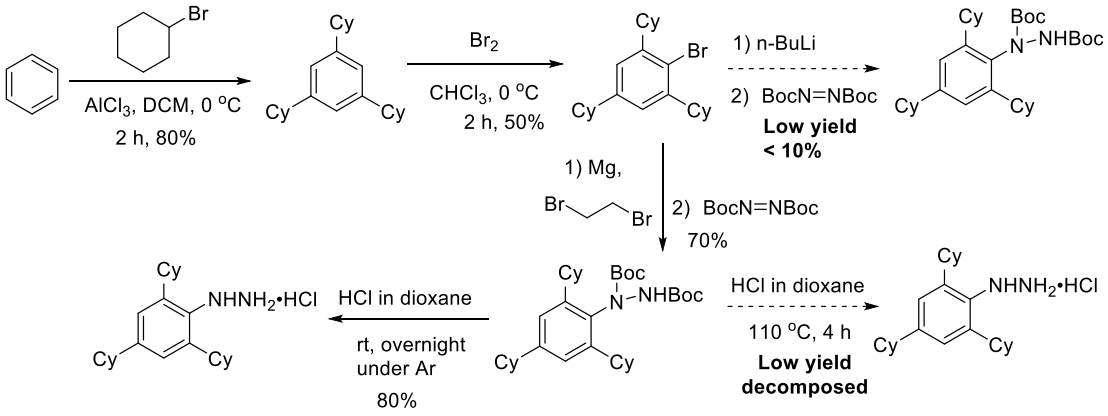
For details of the synthesis of **F**, see ref. 2b.



(a) ClC(O)OBn, py, CH_2Cl_2, 98%; (b) NaOH, THF/H_2O (v/v, 1/1), 96%; (c) oxalyl chloride, CH_2Cl_2; then **10**, 94%; (d) H_2SO_4; (e) $ClCH_2C(O)Cl$, TEA,THF; (f) $NH(Et)_2$, KI, DMF, 56% over 3 steps.

Scheme 4. Scale-up experiment and its application

(G) Typical procedure for preparations of the hydrazine hydrochlorides



Scheme 5. Typical procedure for peparations of the hydrazine hydrochlorides

(1) Synthesis of aryl magnesium bromides:

(2,4,6-Triisopropylphenyl)magnesium bromide, (2,4,6-tricyclopentylphenyl) magnesium bromide and (2,4,6-tricyclohexylphenyl)magnesium bromide were prepared according to the reported procedures.[3] 9-Phenanthrenylmagnesium bromide and 4-pyrenylmagnesium bromide were synthesized from the reactions of corresponding arylbromides and Mg.

(2) Synthesis of Boc-protected hydrazines:[4]

Azodicarboxylate (15 mmol) was dissolved in dry THF (10 mL) under an argon atmosphere and added to a stirred solution of the corresponding arylmagnesium bromide (20 mmol) in THF (40 mL) at –78 °C. The mixture was stirred at –78 °C for 4 h, and then, acetic acid (20 mmol) was added. After warming up to rt, H_2O (40 mL) was added to the reaction mixture and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated to give the product, which was purified by flash chromatography.

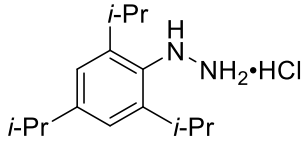
(3) Synthesis of hydrazine hydrochlorides:

The Boc-hydrazine (10 mmol) was dissolved in *i*-PrOH (12.5 mL) under an argon atmosphere, and HCl (4 M in dioxane, 12.5 mL, 50 mmol) was added to the solution. *The reaction mixture was stirrred at rt overnight.* (If the reaction

was stirred at 110 °C for 4 h, the yield of the hydrazine hydrochloride was low probably due to decomposition.) After full consumption of the starting material, the mixture was cooled to 0 °C and diluted with Et_2O (10 mL). The formed precipitate was collected by filtration, washed with Et_2O and dried under high-vacuum to give the corresponding arylhydrazine hydrochloride as a white to gray solid.

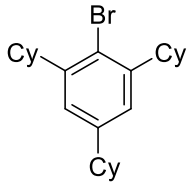
Due to their poor solubility and pronounced instability towards oxygen and light, some products were only characterized by HRMS.

(2,4,6-Triisopropylphenyl)hydrazine hydrochloride (12)



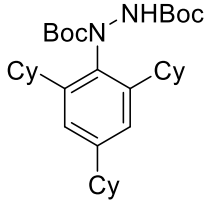
(**$C_{15}H_{27}ClN_2$**) 80% yield, white solid. **HRMS (ESI)** (*m*/*z*) [**$C_{15}H_{27}N_2$**]$^+$: Calcd. 235.2169, found 235.2167.

(2-Bromobenzene-1,3,5-triyl)tricyclohexane (13)



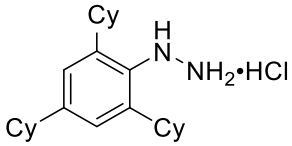
($C_{24}H_{35}Br$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2H), 3.06 (tt, *J* = 11.4, 2.9 Hz, 2H), 2.44 (s, 1H), 1.91 – 1.75 (m, 15H), 1.52 – 1.18 (m, 15H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 146.97, 146.46, 124.12, 123.49, 123.05, 115.17, 44.95, 44.64, 44.29, 34.73, 34.64, 33.71, 27.15, 27.06, 26.50, 26.42, 26.29.

Di-*tert*-butyl 1-(2,4,6-tricyclohexylphenyl)hydrazine-1,2-dicarboxylate (14)



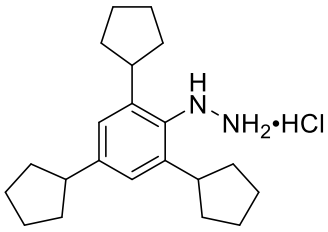
(**$C_{34}H_{54}N_2O_4$**) (1.9:1 mixture of carbamate rotamers): 70% yield; yellow solid; eluent: petane/ethyl acetate (1/20); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.94 (d, *J* = 13.4 Hz, 2H), 6.27 (s, 1H), 2.89 (s, 2H), 2.56 – 2.38 (m, 1H), 1.94 – 1.68 (m, 15H), 1.56 – 1.23 (m, 33H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 155.59, 155.48, 148.24, 148.06, 145.85, 145.24, 135.13, 134.93, 123.45, 123.13, 81.35, 44.89, 44.68, 39.18, 39.00, 34.87, 34.55, 28.35, 28.28, 28.23, 27.16, 27.08, 26.99, 26.74, 26.44, 26.40, 26.33 (1.9:1 mixture of carbamate rotamers). **MS (ESI)**: ([M+Na]$^+$) 557.396. **HRMS (ESI)** (*m*/*z*) [**$C_{34}H_{54}N_2O_4$+Na**]$^+$: Calcd. 577.3976, found 577.3972.

(2,4,6-Tricyclohexylphenyl)hydrazine hydrochloride (15)



(**$C_{24}H_{39}ClN_2$**) 80% yield, a white solid**. ^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 9.67 (s, 3H), 6.93 (s, 2H), 6.46 (s, 1H), 3.03 (t, *J* = 11.4 Hz, 2H), 2.42 (d, *J* = 8.5 Hz, 1H), 1.71 – 1.68 (m, 15H), 1.51 – 1.28 (m, 15H). **^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$)** δ 146.92, 144.99, 135.84, 122.48, 43.95, 37.31, 34.05, 33.98, 26.38, 26.30, 25.76, 25.56. **HRMS (ESI)** (*m*/*z*) [**$C_{24}H_{39}N_2$**]$^+$: Calcd. 355.3108, found 355.3104.

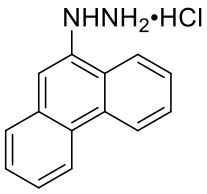
(2,4,6-Tricyclopentylphenyl)hydrazine hydrochloride (16)



(**$C_{21}H_{33}ClN_2$**) 70% yield, a grey solid.

HRMS (ESI) (*m*/*z*) [**$C_{21}H_{33}N_2$**]$^+$: Calcd. 313.2638, found 313.2644.

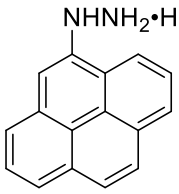
Phenanthren-9-ylhydrazine hydrochloride (17)



(**$C_{14}H_{13}ClN_2$**) 83% yield, a yellow solid.

HRMS (ESI) (*m*/*z*) [**$C_{14}H_{13}N_2$**]$^+$: Calcd. 209.1073, found 209.1073.

Pyren-4-ylhydrazine hydrochloride (18)

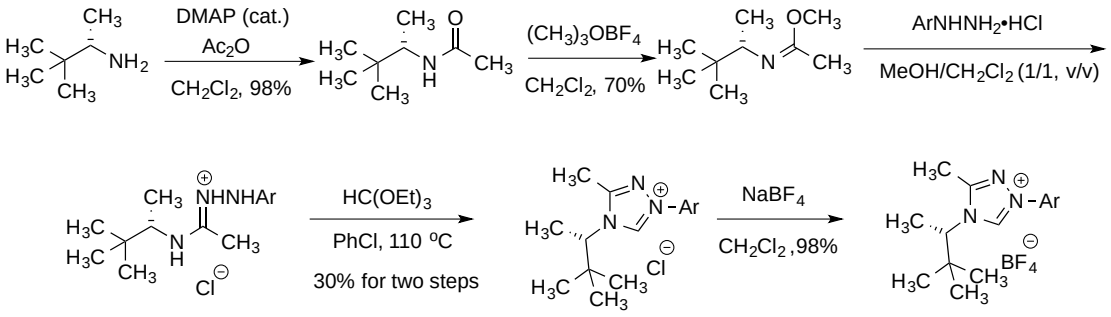


(**$C_{16}H_{13}ClN_2$**) 85% yield, a yellow solid.

HRMS (ESI) (*m*/*z*) [**$C_{16}H_{13}N_2$**]$^+$: Calcd. 233.1073, found 233.1073.

Note: *Di-tert-butyl 1-(2,4,6-tri-tert-butylphenyl)hydrazine-1,2-dicarboxylate could not be obtained probably due to the large steric hindrance. 9-Anthracenylhydrazine hydrochloride decomposed in the reaction mixture due to poor stability towards oxygen and light.*

(H) Typical procedure for preparations of the *N*-heterocyclic carbenes[5]



Scheme 6. Typical procedure for the NHC preparations

(1) Synthesis of amides:

To a solution of the chiral amine (20 mmol) and DMAP (1 mmol) in CH_2Cl_2 was added acetic anhydride (22 mmol). The resulting reaction mixture was stirred at rt for 4 h. Then, the reaction mixture was sequentially washed by 1 N HCl, 1 N NaOH and brine, dried over Na_2SO_4 and concentrated to give the crude product, which was directly used in next step without further purification.

(2) Synthesis of imidates:

To a solution of the chiral amide (8 mmol) in CH_2Cl_2 (20 mL) was added trimethyloxonium tetrafluoroborate (12 mmol, 1.5 equiv) under an argon atmosphere. The mixture was stirred at rt overnight. Sat. $NaHCO_3$ (20 mL) was then added to the reaction mixture, and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated to give the crude product, which was directly used in next step without further purification.

Note: *(a) Because the boiling point of methyl (S,Z)-N-(3,3-dimethylbutan-2-yl) acetimidate is low, do not remove the solvent (CH_2Cl_2) at more than 35 °C. (b) Some amine-derived acetimidates, for example, methyl (S,Z)-N-(3,3-dimethylbutan-2-yl)-acetimidate, are not stable and decompose during the process of flash column chromatography on silica.*

(3) Synthesis of the triazolium salts:

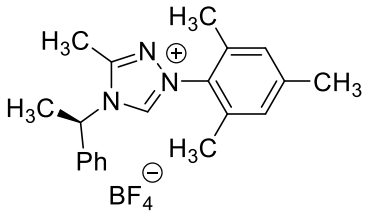
The acetimidate and the hydrazine hydrochloride (4 mmol) were dissolved in the mixed solvent of CH_2Cl_2 and MeOH (10 mL, v/v, 1/1) under the protection of argon. HCl (4 M in dioxane, 0.1 mL, 0.4 mmol) was added to the solution. The reaction mixture was stirrred at rt for 4 h. The mixture was evaporated to dryness to afford the crude product, which was directly used in the next step without further purification.

The crude arylacetimidohydrazide hydrochloride was dissolved in chlorobenzene (3 mL) and then, $HC(OEt)_3$ (5 mL) and HCl (4 M in dioxane, 1 mL, 4 mmol) were added. The reaction mixture was heated at 110 °C for 1-3 h untill it became a clear solution. The solvent was removed under reduced pressure and the product was purified via flash column chromatography on silica gel (CH_2Cl_2/MeOH = 15/1) to afford the triazolium salt as white solid.

(4) Counter ions exchange[6]

The triazolium salt was dissolved in CH_2Cl_2 and $NaBF_4$ (3 equiv.) was added. The reaction mixture was stirred at rt for 6 h. Then. it was filtered through a plug of celite, and the filtrate was concentrated under reduced pressure to give an off-white solid triazolium salt.

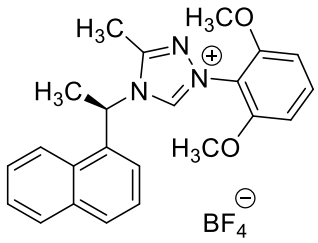
(*R*)-1-Mesityl-3-methyl-4-(1-phenylethyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (C1)



(**$C_{20}H_{24}BF_4N_3$**) a white solid, 47% yield, melting point: 136–137 °C. $[\alpha]_D^{25}$ = –55.9 (*c* = 1.35, in CH_2Cl_2). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.86 (s, 1H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.36 (dd, *J* = 10.4, 4.2 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 2H), 6.98 (d, *J* = 13.8 Hz, 2H), 5.80 (q, *J* = 6.9 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H), 2.05 (s, 6H), 2.03 (d, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)** δ 154.31, 142.69, 141.84, 137.60, 135.03, 131.06, 129.86, 129.72, 129.39, 126.42, 59.53, 21.31, 17.24, 11.25. **IR (ATR)**: ν = 2993, 2288, 1740, 1589, 1452, 1373, 1220, 1044, 883, 768, 703. **MS (EI)**: *m*/*z* = 104.4 (15), 105.3 (13), 109.3 (13), 119.3 (12), 124.3

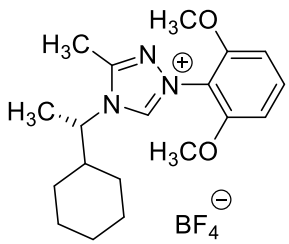
(11), 132.3 (15), 133.3 (22), 134.3 (42), 159.3 (100), 160.3 (25). 200.3 (19), 201.3 (86), 202.3 (13), 304.4 (22), 306.4 $[M]^+$ (1). **MS (ESI)**: ($[M]^+$) 306.197. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{20}H_{24}N_3}]^+$: Calcd. 306.1965, found 306.1965.

(*R*)-1-(2,6-Dimethoxyphenyl)-3-methyl-4-[1-(naphthalen-1-yl)ethyl]-4H-1,2,4-triazol-1-ium tetrafluoroborate (C2)



($\mathbf{C_{23}H_{24}BF_4N_3O_2}$) a white solid, 52% yield, melting point: 172–173 °C. $[\alpha]_D^{25}$ = –108.0 (*c* = 0.5, in CH_2Cl_2). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.93 (s, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.69 – 6.60 (m, 3H), 3.80 (s, 6H), 2.28 (s, 3H), 2.14 (d, *J* = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)** δ 155.46, 153.50, 144.85, 133.96, 133.53, 133.05, 130.09, 129.80, 129.40, 127.96, 126.73, 125.66, 123.73, 121.79, 112.49, 104.47, 56.61, 55.51, 21.07, 11.04. **IR (ATR)**: ν = 2953, 2099, 1933, 1739, 1591, 1463, 1377, 1256, 1040, 777. **MS (EI)**: *m*/*z* = 150.2 (20), 151.2 (16), 152.2 (47), 153.3 (100), 154.3 (98), 155.3 (16), 159.3 (59), 160.3 (14), 165.3 (14), 174.3 (29), 177.3 (28), 219.3 (61), 220.3 (10), 308.3 (14). **MS (ESI)**: ($[M]^+$) 374.188. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{23}H_{24}N_3O_2}]^+$: Calcd. 374.1863, found 374.1858.

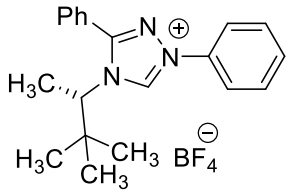
***(S)*-4-(1-Cyclohexylethyl)-1-(2,6-dimethoxyphenyl)-3-methyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (C3)**



($\mathbf{C_{19}H_{28}BF_4N_3O_2}$) a white solid, 45% yield, melting point: 171–172 °C. $[\alpha]_D^{25}$ = +23.3 (*c* = 0.63, in CH_2Cl_2). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.79 (s, 1H), 7.45 (t, *J* = 8.6 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 2H), 4.33 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.81 (s, 6H), 2.67 (s, 3H), 1.96 – 1.87 (m, 1H), 1.86 – 1.69 (m, 3H), 1.66 (d, *J* = 6.9 Hz, 4H), 1.27 (dddd, *J* = 16.0, 14.2, 12.7, 7.8 Hz, 3H), 1.19 – 1.02 (m, 2H), 0.95 (qd, *J* = 12.3, 3.5 Hz, 1H). **^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)** δ 155.29, 152.82, 144.96, 133.49, 112.51, 104.53, 61.25, 56.62, 42.99, 29.46, 29.03, 25.79, 25.50,

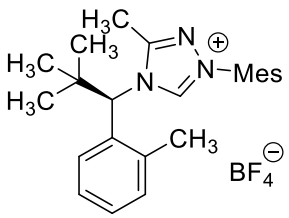
25.48, 18.03, 11.28. **IR (ATR)**: ν = 3462, 3100, 2932, 2284, 2092, 1923, 1740, 1588, 1465, 1261, 1058, 779. **MS (EI)**: *m*/*z* = 105.3 (34), 149.3 (13), 150.3 (10), 159.3 (22), 160.3 (14), 177.3 (14), 178.3 (11), 198.3 (13), 200.3 (22), 201.3 (14), 219.3 (20), 220.3 (30), 247.3 (57), 248.3 (10), 276.2 (31), 304.4 (86), 305.5 (30), 330.4 $[M]^+$ (5). **MS (ESI)**: ($[M]^+$) 330.217. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{19}H_{28}N_3O_2}]^+$: Calcd. 330.2176, found 330.2176.

(*S*)-4-(3,3-Dimethylbutan-2-yl)-1,3-diphenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (C4)



($\mathbf{C_{20}H_{24}BF_4N_3}$) a white solid; 10% yield, melting point: 85–86 °C. $[\alpha]_D^{25}$ = +1.2 (*c* = 0.43, in CH_2Cl_2), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.51 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 2H), 7.67 (dd, *J* = 8.2, 7.4 Hz, 3H), 7.65 – 7.60 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 4.49 (d, *J* = 7.2 Hz, 1H), 1.76 (d, *J* = 7.2 Hz, 3H), 0.79 (s, 9H). **^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)** δ 156.06, 139.20 (d, J = 9.4 Hz), 134.99, 132.48, 130.94, 130.28, 130.05, 129.78, 123.18, 120.90, 65.22, 35.98, 26.37, 15.26. **IR (ATR)**: ν = 3634, 3124, 2966, 2323, 2101, 1926, 1562, 1470, 1377, 1303, 1241, 1184, 1046, 762, 689. **MS (EI)**: *m*/*z* = 194.3 (22), 221.4 (100), 222.4 (16), 306.4 $[M]^+$ (1). **MS (ESI)**: ($[M]^+$) 306.196. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{20}H_{24}N_3}]^+$: Calcd. 306.1965, found 306.1965.

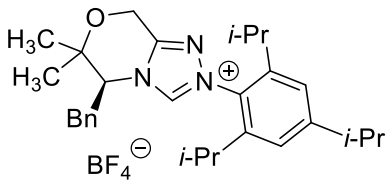
(*R*)-4-[2,2-Dimethyl-1-(o-tolyl)propyl]-1-mesityl-3-methyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (C5)[7]



($\mathbf{C_{24}H_{32}BF_4N_3}$) a white solid; 20% yield, melting point: 92–93 °C. $[\alpha]_D^{25}$ = –72 (*c* = 0.5, in CH_2Cl_2), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.42 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.31 – 7.24 (m, 2H), 7.01 (s, 2H), 5.74 (s, 1H), 2.63 (s, 3H), 2.55 (s, 3H), 2.33 (s, 3H), 2.03 (s, 6H), 1.22 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 154.69, 143.38, 142.05, 136.81, 134.57, 131.96, 131.79, 131.16, 129.83,

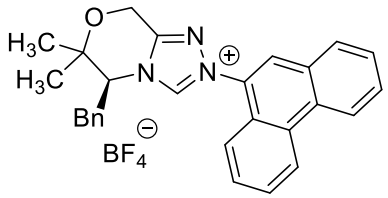
129.48, 128.39, 127.70, 67.85, 37.51, 27.43, 21.38, 20.58, 17.38, 11.68. **IR (ATR)**: ν = 3640, 3126, 2966, 2305, 2072, 1998, 1715, 1582, 1529, 1476, 1379, 1295, 1200, 1042, 854, 752, 675. **MS (EI)**: *m*/*z* =49.4 (12), 57.4 (14), 65.3 (11), 77.3 (16), 91.3 (37), 103.2 (12), 105.2 (19), 115.2 (24), 116.2 (12), 117.2 (39), 118.2 (13), 119.3 (80), 120.3 (12), 128.3 (13),129.3 (11), 130.3 (16), 131.3 (12), 132.3 (19), 145.3 (91), 146.3 (13), 159.2 (100), 160.3 (69), 180.3 (15), 200.2 (12), 201.3 (73), 202.3 (26). **MS (ESI)**: ($[M]^+$) 362.258. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{24}H_{32}N_3}]^+$: Calcd. 362.2591, found 362.2584.

(*S*)-5-Benzyl-6,6-dimethyl-2-(2,4,6-triisopropylphenyl)-5,6-dihydro-8H-[1, 2,4]triazolo[3,4-c][1,4]oxazin-2-ium tetrafluoroborate (5b)



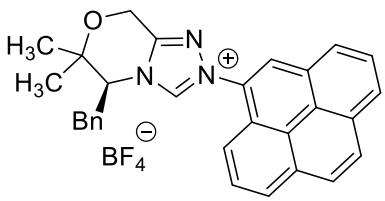
($\mathbf{C_{29}H_{40}BF_4N_3O}$) a white solid; 55% yield, melting point: 98–99 °C. $[\alpha]_D^{25}$ = −79.8 (*c* = 0.5, in CH_2Cl_2), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (s, 1H), 7.37 – 7.22 (m, 5H), 7.07 (s, 1H), 7.00 (d, *J* = 1.4 Hz, 1H), 5.38 (dd, *J* = 11.7, 4.4 Hz, 1H), 5.14 (dd, *J* = 71.4, 17.5 Hz, 2H), 3.53 (dd, *J* = 14.1, 4.3 Hz, 1H), 2.99 (dd, *J* = 14.0, 11.9 Hz, 1H), 2.90 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.11 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.67 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.60 (s, 3H), 1.46 (s, 3H), 1.21 (dd, *J* = 23.4, 6.8 Hz, 9H), 1.02 (dd, *J* = 10.8, 4.2 Hz, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 153.58, 148.50, 146.47, 144.47, 144.08, 134.46, 129.70, 129.64, 128.22, 128.14, 122.87, 121.98, 74.21, 63.29, 57.01, 36.89, 34.59, 28.74, 28.58, 25.16, 24.97, 24.76, 23.89, 23.84, 23.22, 23.03, 22.27. **IR (ATR)**: ν = 3927, 3877, 3837, 3723, 3645, 3279, 3143, 3067, 2966, 2872, 2662, 2491, 2331, 2226, 2182, 2101, 2060, 1998, 1972, 1935, 1812, 1696, 1653, 1574, 1526, 1497, 1456, 1390, 1285, 1231, 1055, 975, 879, 828, 801, 758, 703, 671. **MS (EI)**: *m*/*z* = 91.1 (100), 145.1 (11). **MS (ESI)**: ($[M]^+$) 446.317. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{29}H_{40}N_3O}]^+$: Calcd. 446.3166, found 446.3171.

(*S*)-5-Benzyl-6,6-dimethyl-2-(phenanthren-9-yl)-5,6-dihydro-8H-[1,2,4]triazolo[3,4-c][1,4]oxazin-2-ium tetrafluoroborate (5c)



(**$C_{28}H_{26}BF_4N_3O$**) a yellow solid; 43% yield, melting point: 132–133 °C. $[\alpha]_D^{25}$ = –177.5 (*c* = 0.83, in CH_2Cl_2), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.62 (d, *J* = 8.2 Hz, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.35 (s, 1H), 7.86 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.68 (dd, *J* = 10.9, 4.4 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.23 (dt, *J* = 19.3, 5.2 Hz, 4H), 7.13 (t, *J* = 7.2 Hz, 1H), 5.18 (dd, *J* = 68.5, 13.9 Hz, 2H), 5.07 – 5.03 (m, 1H), 3.46 (dd, *J* = 13.7, 4.7 Hz, 1H), 3.04 (dd, *J* = 13.6, 11.6 Hz, 1H), 1.55 (d, *J* = 12.4 Hz, 6H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 148.84, 143.18, 135.20, 131.13, 130.16, 129.81, 129.78, 129.57, 129.40, 129.14, 128.34, 128.29, 127.92, 127.86, 127.01, 125.48, 123.36, 122.66, 122.22, 73.99, 64.06, 56.88, 37.00, 24.85, 22.51. **IR (ATR)**: ν =3835, 3642, 3142, 3069, 2986, 2936, 2662, 2334, 2227, 2183, 2104, 2015, 1986, 1819, 1575, 1526, 1497, 1452, 1392, 1347, 1286, 1211, 1050, 921, 899, 856, 830, 800, 756, 711, 660. **MS (EI)**: *m*/*z* =48.2 (24), 49.2 (100) 91.1 (69), 98.1 (15), 127.0 (17), 131.1 (18), 146.1 (10), 165.1 (52), 193.1 (37), 203.0 (14), 204.1 (11), 218.1 (25), 321.2 (29), 418.2 (15), 419.2 (11), 420.2 $[M]^+$ (3). **MS (ESI)**: ($[M]^+$) 420.208. **HRMS (ESI)** (*m*/*z*) **$[C_{28}H_{26}N_3O]^+$**: Calcd. 420.2070, found 420.2072.

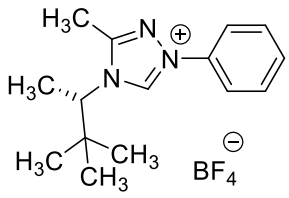
(*S*)-5-Benzyl-6,6-dimethyl-2-(pyren-4-yl)-5,6-dihydro-8H-[1,2,4]triazolo[3,4-c][1,4]oxazin-2-ium tetrafluoroborate (5d)



(**$C_{30}H_{26}BF_4N_3O$**) a yellow solid; 67% yield, melting point: 275–276 °C. $[\alpha]_D^{25}$ = –322.8 (*c* = 0.57, in CH_2Cl_2), **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.93 (s, 1H), 8.54 – 8.49 (m, 2H), 8.46 (dd, *J* = 16.4, 8.4 Hz, 2H), 8.39 (d, *J* = 9.0 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 8.23 (t, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.41 (dd, *J* = 7.8, 5.7 Hz, 4H), 7.32 (td, *J* = 5.7, 2.8 Hz, 1H), 5.33 (dd, *J* = 125.1, 17.2 Hz, 2H), 4.92 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.48 (dd, *J* = 13.8, 5.2 Hz, 1H), 3.23 (dd, *J* = 13.7, 9.7 Hz, 1H), 1.58 (s,

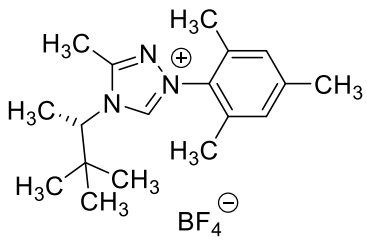
3H), 1.45 (s, 3H). **$^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6)** δ 149.12, 143.95, 136.11, 132.81, 130.52, 130.23, 130.00, 129.79, 129.15, 127.55, 127.54, 127.45, 127.18, 126.93, 126.85, 125.36, 124.88, 124.27, 123.77, 122.92, 120.45, 73.58, 63.99, 56.43, 36.06, 23.61, 23.20. **IR (ATR)**: ν = 3150, 3050, 2979, 2323, 2190, 2099, 2000, 1961, 1920, 1809, 1669, 1580, 1529, 1495, 1451, 1403, 1347, 1284, 1233, 1184, 1054, 845, 764, 715, 683, 662. **MS (EI)**: *m*/*z* = 47.3 (100), 48.23 (88), 49.3 (22), 83.2 (76), 85.1 (41). **MS (ESI)**: ([M]$^+$) 444.209. **HRMS (ESI)** (*m*/*z*) [$\mathbf{C_{30}H_{26}N_3O}$]$^+$: Calcd. 444.2070, found 444.2083.

(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (6a)



(**$C_{15}H_{22}BF_4N_3$**) a white solid; 50% yield, melting point: 104–105 °C. $[\alpha]_D^{25}$ = +22.1 (*c* = 0.72, in CH_2Cl_2), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.16 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.49 (dt, *J* = 25.7, 7.3 Hz, 3H), 4.36 (d, *J* = 6.9 Hz, 1H), 2.69 (s, 3H), 1.62 (d, *J* = 7.1 Hz, 3H), 0.97 (s, 9H). **$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$)** δ 154.59, 138.55, 134.81, 130.78, 130.21, 120.56, 64.69, 35.79, 26.21, 15.71, 11.52. **IR (ATR)**: ν = 3136, 2964, 2324, 2110, 1882, 1582, 1539, 1476, 1381, 1300, 1231, 1200, 1044, 916, 863, 826, 762, 684. **MS (EI)**: *m*/*z* = 132.3 (11), 159.3 (100), 160.3 (26), 186.3 (19), 187.4 (53), 243.4 (17), 244.4 [M]$^+$ (6). **MS (ESI)**: ([M]$^+$) 244.181. **HRMS (ESI)** (*m*/*z*) [$\mathbf{C_{15}H_{22}N_3}$]$^+$: Calcd. 244.1808, found 244.1808.

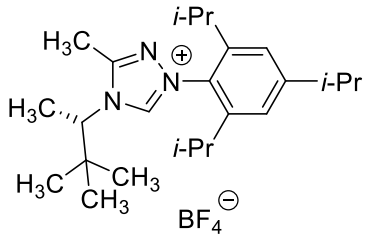
(*S*)-4-(3,3-Dimethylbutan-2-yl)-1-mesityl-3-methyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (6b)



(**$C_{18}H_{28}BF_4N_3$**) a white solid; 18% yield, melting point: 188–189 °C. $[\alpha]_D^{25}$ = +10.1 (*c* = 0.35, in CH_2Cl_2), **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.79 (s, 1H), 6.98 (s, 2H), 4.47 (d, *J* = 6.7 Hz, 1H), 2.72 (s, 3H), 2.32 (s, 3H), 2.02 (s, 6H), 1.67 (d, *J* = 7.0 Hz, 3H), 1.00 (s,

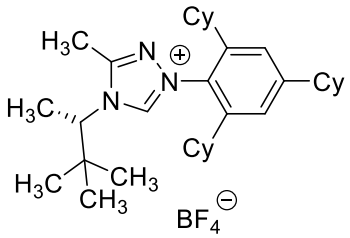
9H). **$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$)** δ 154.64, 143.10, 141.91, 134.61, 131.19, 129.79, 64.47, 35.89, 26.34, 21.31, 17.29, 15.86, 11.62. **IR (ATR)**: ν = 3120, 2965, 2294, 2111, 1993, 1928, 1694, 1579, 1531, 1460, 1390, 1288, 1220, 1196, 1025, 860, 766, 734, 680. **MS (EI)**: *m*/*z* = 49.2 (30), 51.2 (20), 52.2 (13), 53.2 (25), 55.2 (22), 56.3 (10), 63.2 (12), 65.2 (25), 67.2 (11), 69.2 (57), 77.2 (37), 78.2 (15), 79.2 (15), 84.2 (21), 89.1 (11), 91.1 (64), 103.1 (22), 104.1 (14), 105.1 (14), 115.1 (21), 116.1 (20), 117.1 (41), 118.1 (16), 119.1 (18), 130.1 (22), 131.1 (17), 132.1 (29), 133.1 (14), 134.1 (15), 144.1 (16), 145.0 (27), 146.1 (21), 159.0 (100), 160.1 (34), 200.1 (15), 201.1 (49), 202.1 (19), 229.2 (24), 286.2 $[M]^+$ (6). **MS (ESI)**: ($[M]^+$) 286.227. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{18}H_{28}N_3}]^+$: Calcd. 286.2278, found 286.2278.

(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(2,4,6-triisopropylphenyl)-4H-1, 2,4-triazol-1-ium tetrafluoroborate (6c)



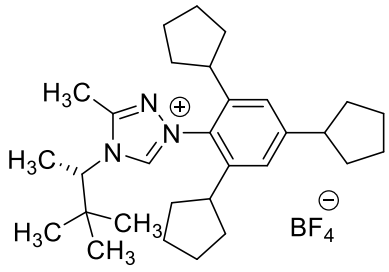
($\mathbf{C_{24}H_{40}BF_4N_3}$) a white solid; 25% yield, melting point: 207–208 °C. $[\alpha]_D^{25}$ = +7.6 (*c* = 0.71, in CH_2Cl_2), **^1H NMR (400 MHz, $CDCl_3$)** δ 9.72 (s, 1H), 7.08 (dd, *J* = 11.9, 1.8 Hz, 2H), 4.55 (q, *J* = 6.9 Hz, 1H), 3.00 – 2.86 (m, 1H), 2.72 (s, 3H), 2.22 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.06 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.68 (d, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.18 – 1.08 (m, 12H), 0.99 (s, 9H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 154.55, 153.25, 145.69, 144.88, 143.46, 128.55, 122.63, 122.17, 64.42, 35.88, 34.53, 29.10, 28.90, 26.25, 24.14, 24.08, 23.89, 23.72, 23.62, 15.93, 11.65. **IR (ATR)**: ν = 3110, 3077, 3038, 2964, 2876, 2330, 2138, 2109, 1976, 1579, 1529, 1464, 1388, 1367, 1310, 1281, 1249, 1219, 1191, 1026, 968, 875, 770, 734, 688. **MS (EI)**: *m*/*z* =49.2 (24), 53.2 (12), 55.2 (25), 56.3 (10), 57.2 (100), 69.2 (54), 84.2 (19), 85.2 (16), 91.1 (16), 115.1 (12.3), 117.1 (12), 128.0 (13), 144.1 (13), 146.1 (14), 172.0 (10), 184.0 (11), 186.1 (14), 187.1 (11), 188.1 (13), 200.1 (11), 202.1 (14), 212.1 (16), 213.1 (61), 214.12 (11), 228.1 (15), 229.1 (71), 230.12 (36), 284.2 (15), 285.2 (37), 286.2 (13), 313.3 (19), 370.3. $[M]^+$ (5). **MS (ESI)**: ($[M]^+$) 370.322. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{24}H_{40}N_3}]^+$: Calcd. 370.3217, found 370.3217.

(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(2,4,6-tricyclohexylphenyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (6d)



(**$C_{33}H_{52}BF_4N_3$**) a white solid; 23% yield, melting point: 247–248 °C. $[\alpha]_D^{25}$ = +9.8 (*c* = 0.9, in CH_2Cl_2), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.63 (s, 1H) , 7.07 (d, *J* = 14.4 Hz, 2H), 4.58 (d, *J* = 6.6 Hz, 1H), 2.77 (s, 3H), 2.52 (s, 1H), 1.94 – 1.56 (m, 21H), 1.50 – 1.13 (m, 14H), 1.04 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 154.43, 152.33, 144.66, 143.86, 143.30, 128.65, 123.86, 123.42, 64.54, 45.00, 40.13, 39.67, 36.04, 34.52, 34.38, 34.23, 27.03, 26.95, 26.88, 26.56, 26.53, 26.34, 26.16, 26.01, 25.87, 16.10, 11.81. **IR (ATR)**: ν = 3781, 3113, 3079, 2925, 2853, 2662, 2326, 2226, 2183, 2105, 1982, 1945, 1578, 1530, 1448, 1394, 1369, 1308, 1282, 1224, 1194, 1055, 890, 862, 765, 730, 687. **MS (EI)**: *m*/*z* =49.2 (19), 53.2 (14), 55.2 (100), 56.3 (64), 57.3 (16), 67.2 (26), 69.2 (59), 81.2 (12), 83.2 (44), 84.2 (20), 348.2 (12), 404.2 (11), 405.2 (37), 406.2 (12). **MS (ESI)**: ($[M]^+$) 490.415. **HRMS (ESI)** (m/z) [**$C_{33}H_{52}N_3$**]$^+$: Calcd. 490.4156, found 490.4154.

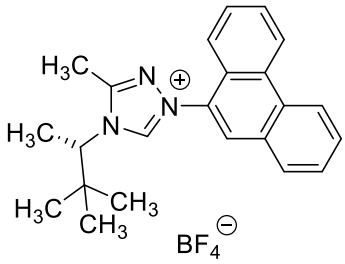
(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(2,4,6-tricyclopentylphenyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (6e)



(**$C_{30}H_{46}BF_4N_3$**) a white solid; 30% yield, melting point: 113–114 °C. $[\alpha]_D^{25}$ = +11.6 (*c* = 0.79, in CH_2Cl_2), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.64 (s, 1H), 7.12 (d, *J* = 16.2 Hz, 2H), 4.58 (d, *J* = 6.9 Hz, 1H), 3.09 – 2.94 (m, 1H), 2.77 (s, 3H), 2.46 – 2.32 (m, 1H), 2.21 – 2.02 (m, 3H), 1.93 – 1.41 (m, 25H), 1.02 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 154.58, 150.98, 143.88, 143.25, 142.48, 130.08, 123.83, 123.31, 64.46, 46.28, 40.79, 40.13, 35.92, 35.21, 34.91, 34.70, 26.27, 25.94, 25.83, 25.61, 25.43, 15.97, 11.80. **IR (ATR)**: ν = 3782, 3115, 3080, 2952, 2869, 2328, 2180, 2115, 1992, 1936, 1700, 1578, 1530, 1452, 1394, 1370, 1307, 1220, 1195, 1054, 872, 765, 731, 686. **MS (EI)**: *m*/*z* = 49.2 (30), 53.2 (14), 55.2 (27), 57.3 (15), 59.2 (12), 67.2 (31), 69.2 (100), 84.1 (20), 115.0 (10), 128.0 (13), 141.0 (10), 154.0 (11), 155.0 (10), 156.0 (11), 167.0 (12), 168.0 (15),

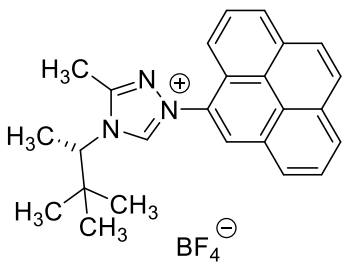
169.0 (10), 236.0 (13), 238.1 (10), 253.1 (11), 264.1 (10), 277.1 (11), 293.1 (27), 294.2 (15), 305.1 (19), 306.1 (30), 362.1 (12), 363.1 (54), 364.2 (16). **MS (ESI):** ($[M]^+$) 448.367. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{30}H_{46}N_3}]^+$: Calcd. 448.3686, found 448.3686.

(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(phenanthren-9-yl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (6f)



($\mathbf{C_{23}H_{26}BF_4N_3}$) a yelow solid; 34% yield, melting point: 166–167 °C. $[\alpha]_D^{25}$ = +33.2 (*c* = 0.53, in CH_2Cl_2), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 8.64 (d, *J* = 8.3 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.13 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.56 (m, 4H), 7.50 (t, *J* = 7.4 Hz, 1H), 4.38 (q, *J* = 6.8 Hz, 1H), 2.69 (s, 3H), 1.60 (d, *J* = 7.0 Hz, 3H), 0.96 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 154.73, 142.41, 131.27, 131.12, 130.37, 129.83, 129.44, 129.21, 128.18, 128.07, 127.80, 126.96, 126.77, 125.78, 123.31, 122.55, 64.74, 35.84, 26.30, 15.57, 11.66. **IR (ATR)**: ν = 3566, 3120, 3086, 2961, 2880, 2331, 2184, 2090, 2007, 1937, 1824, 1580, 1529, 1475, 1454, 1391, 1370, 1309, 1225, 1175, 1061, 919, 881, 854, 767, 747, 724, 692, 663. **MS (EI)**: *m*/*z* =49.3 (14), 57.3 (14), 69.2 (57), 81.6 (27), 82.3 (22), 84.2 (28), 95.6 (32). 168.0 (13), 164.0 (11), 165.1 (13), 176.1 (14), 190.0 (65), 192.1 (10), 193.1 (22), 204.0 (12), 218.1 (38), 259.1 (100), 260.2 (22), 304.2 (13), 344.3 $[M]^+$ (1). **MS (ESI)**: ($[M]^+$) 344.212. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{23}H_{26}N_3}]^+$: Calcd. 344.2121, found 344.2116.

(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(pyren-4-yl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (6g)

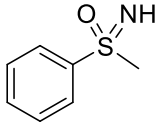


($\mathbf{C_{25}H_{26}BF_4N_3}$) a yellow solid; 37% yield, melting point: 240–241 °C. $[\alpha]_D^{25}$ = –15.0 (*c* = 0.38, in CH_2Cl_2), **^{1}H NMR (600 MHz, DMSO-d_6)** δ 11.00 (s, 1H), 8.58 (d, *J* = 8.2 Hz, 1H), 8.50 (t, *J* = 7.2 Hz, 2H), 8.47 – 8.43 (m, 2H), 8.40 (dd, *J* = 32.8, 9.0 Hz, 2H), 8.24 (t, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 9.2 Hz, 1H), 4.68 (q, *J* = 7.0 Hz, 1H), 2.83 (s, 3H), 1.67 (d, *J*

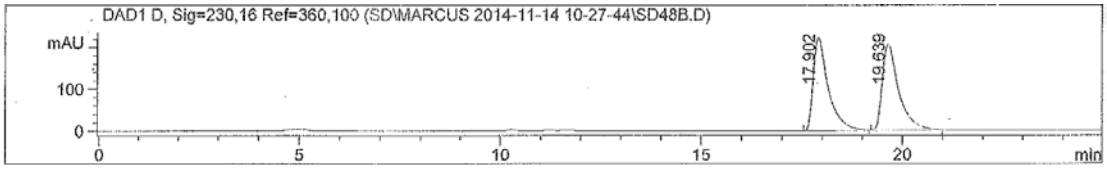
= 7.0 Hz, 3H), 1.09 (s, 9H). **$^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6)** δ 154.48, 144.16, 132.75, 130.56, 130.11, 130.02, 129.66, 127.87, 127.41, 127.09, 127.00, 126.72, 125.44, 124.91, 124.59, 123.90, 122.98, 120.83, 62.89, 35.39, 25.76, 15.81, 11.08. **IR (ATR)**: ν = 3126, 2965, 2187, 2108, 2043, 2002, 1956, 1826, 1584, 1534, 1465, 1393, 1308, 1227, 1190, 1056, 847, 776, 721, 683. **MS (EI)**: *m*/*z* =187.3 (10), 214.3 (46), 215.3 (71), 216.3 (13) 283.3 (100), 284.3 (20). **MS (ESI)**: ($[M]^+$) 368.214. **HRMS (ESI)** (*m*/*z*) $[\mathbf{C_{25}H_{26}N_3}]^+$: Calcd. 368.2121, found 368.2125.

(I) Spectral characterization data and HPLC conditions

NH-*S*-Methyl-*S*-phenyl-sulfoximine (1a)[8]

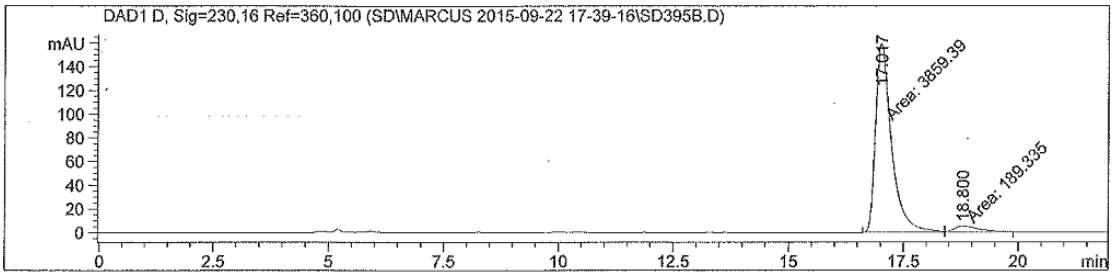


(**C_7H_9NOS**) a colorless oil. For cat **6c**: 43% yield, 91% ee. $[\alpha]_D^{25}$ = +17.0 (*c* = 0.76, in $CHCl_3$). For cat **5b**: 42% yield, –95% ee. $[\alpha]_D^{25}$ = –18.7 (*c* = 0.67, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 20/80, flow rate = 0.6 mL/min, λ = 230 nm, retention time: 17.9 min (*S*), 19.6 min (*R*). **^1H NMR (400 MHz, $CDCl_3$)** δ 7.97 – 7.91 (m, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.46 (m, 2H), 3.04 (s, 3H), 2.72 (s, 1H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 143.46, 132.99, 129.21, 127.61, 46.16. $[\alpha]_D^{25}$ = +30.8 (*c* = 0.95, in acetone; 91% ee), [$[\alpha]_D^{23}$ = –36.2 (*c* = 1.06 in acetone, enantiopure (*R*)-enantiomer)].[8]



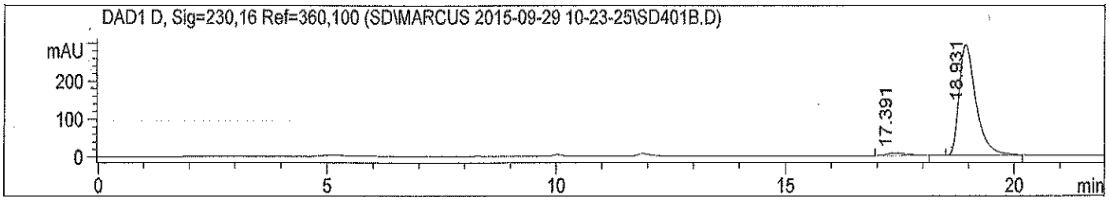
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.902	0.3851	223.40295	5843.19141	50.0554
2	19.639	0.4177	206.33871	5830.26123	49.9446



Signal 3: DAD1 D, Sig=230,16 Ref=360,100

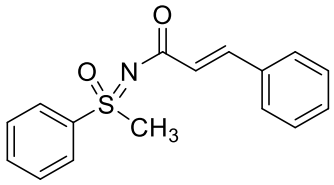
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.017	MF	0.4043	3859.38745	159.08342	95.3236
2	18.800	FM	0.6044	189.33450	5.22117	4.6764



DAD1 D, Sig=230,16 Ref=360,100

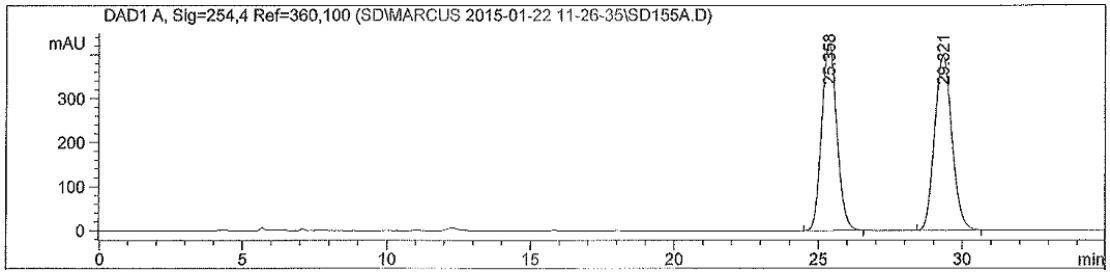
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.391	0.4424	7.01075	211.77266	2.7491
2	18.931	0.3867	292.61261	7491.47070	97.2509

N-[Methyl(oxo)(phenyl)- λ^6-sulfanylidene]cinnamamide (3aa)



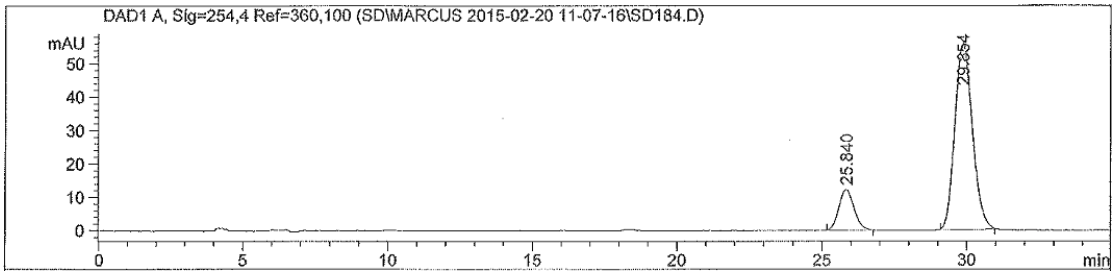
(**$C_{16}H_{15}NO_2S$**) a white solid; 31% yield, 69% ee, melting point: 136–137 °C. $[\alpha]_D^{25}$ = +21.7 (*c* = 0.70, in $CHCl_3$), HPLC ADH, 2-propanol /*n*-heptane = 25/75, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 25.3 min, 29.3 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 – 7.94 (m, 2H), 7.73 – 7.62 (m, 2H), 7.62 – 7.55 (m, 2H), 7.55 – 7.47 (m, 2H), 7.40 – 7.28 (m, 3H), 6.61 (d, *J* = 15.9 Hz, 1H), 3.40 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 174.50, 142.88, 139.05, 135.16, 133.88, 129.86, 129.77, 128.89, 128.15, 127.25, 124.96, 44.43. **IR (ATR)**: ν = 3529, 3022, 2926, 2301, 2168, 2058, 1903, 1637, 1597, 1487, 1446, 1406, 1313, 1195, 1094, 1052, 970, 885, 832, 746, 684. **MS (EI)**: 51.4 (12), 77.3 (34), 102.3 (18), 103.3 (19), 125.3 (29), 129.3 (15), 130.3 (27), 131.3 (18), 141.3 (12), 156.3 (99), 182.3 (100), 183.3 (10), 192.3 (12), 207.3 (30), 222.4 (48), 270.3 (53) 286.3 $[M]^+$ (9). **MS (ESI)**: ($[M+Na]^+$) 308.070. **HRMS (ESI)** (*m*/*z*) [**$C_{16}H_{15}NO_2S$+Na**]$^+$: Calcd. 308.0721,

found 308.0715.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

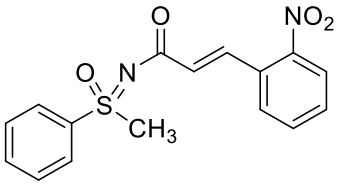
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.358	BB	0.5643	1.56157e4	427.39447	48.3662
2	29.321	BB	0.6567	1.66706e4	397.96985	51.6338



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

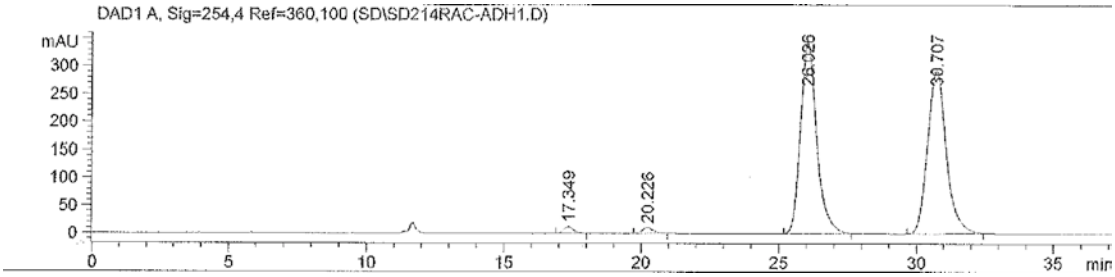
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.840	BB	0.4480	440.92123	12.13345	15.7488
2	29.854	BB	0.6354	2358.79541	56.00438	84.2512

_(E)-N_-[Methyl(oxo)(phenyl)-λ^6-sulfanylidene]- 3-(2-nitrophenyl) acrylamide (3ab)

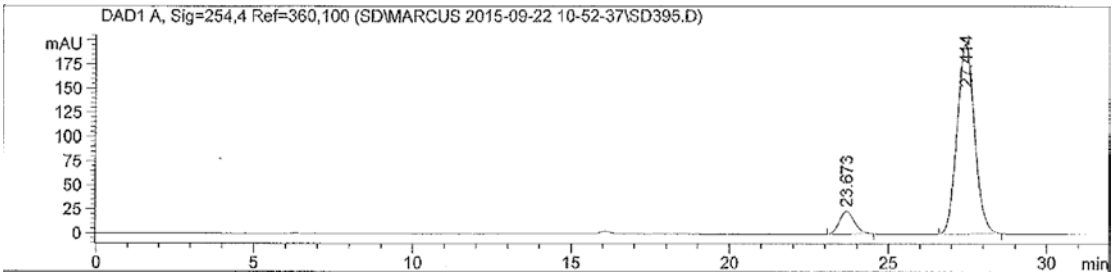


(**$C_{16}H_{14}N_2O_4S$**) a yellow oil. For cat **6c**: 53% yield, 81% ee. $[\alpha]_D^{25}$ = +31.8 (*c* = 1.7, in $CHCl_3$). For cat **5b**: 56% yield, –75% ee. $[\alpha]_D^{25}$ = –32.0 (c = 1.90, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 26.0 min, 30.7 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 15.7 Hz, 1H), 8.03 (ddt, *J* = 9.2, 8.2, 1.7 Hz, 3H), 7.71 – 7.65 (m, 2H), 7.65 – 7.59 (m, 3H), 7.54 – 7.42 (m, 1H), 6.51 (d, *J* = 15.7 Hz, 1H),

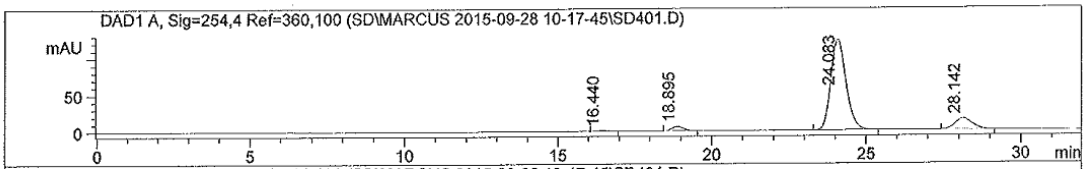
3.43 (s, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 173.57, 148.51, 138.79, 137.86, 134.02, 133.48, 131.25, 130.07, 129.90, 129.84, 129.22, 127.28, 124.90, 44.45. **IR (ATR)**: ν = 3066, 3024, 2928, 2332, 2106, 1909, 1732, 1640, 1605, 1521, 1444, 1405, 1283, 1204, 1096, 1046, 969, 890, 858, 786, 743, 686. **MS (EI)**: *m/z* = 51.3 (43), 63.3 (17), 65.3 (49), 77.3 (56), 93.2 (15), 94.2 (17), 125.1 (16), 130.2 (10), 156.1 (11), 182.1 (100), 284.1 (14), 331.1 $[M+1]^+$ (3). **MS (ESI)**: ($[M+H]^+$) 331.075. **HRMS (ESI)** (*m/z*) **$[C_{16}H_{14}N_2O_4S+H]^+$**: Calcd. 331.0747, found 331.0747.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
3	26.026	BB	0.6242	1.40463e4	342.70193	48.9204
4	30.707	BB	0.7356	1.40623e4	293.18570	48.9761



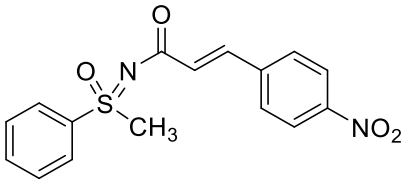
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.673	BB	0.5022	791.55939	23.66637	9.4617
2	27.414	BB	0.5943	7574.40527	196.22772	90.5383



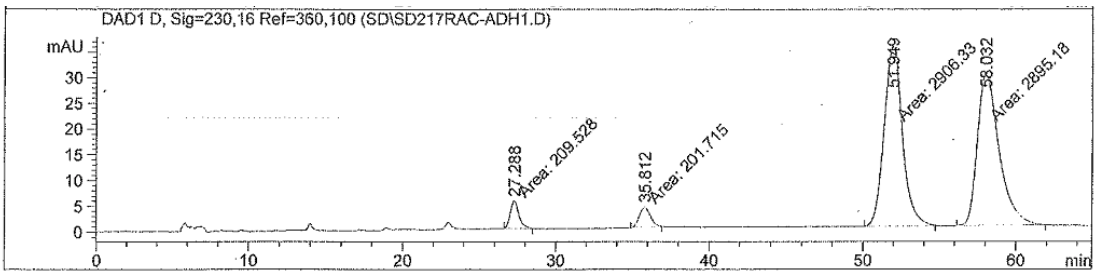
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	16.440	0.3707	0.99192	22.06370	0.4472
2	18.895	0.3655	5.96579	150.06769	3.0413
3	24.083	0.5683	122.68548	4183.56689	84.7861
4	28.142	0.5471	14.76563	578.56305	11.7254

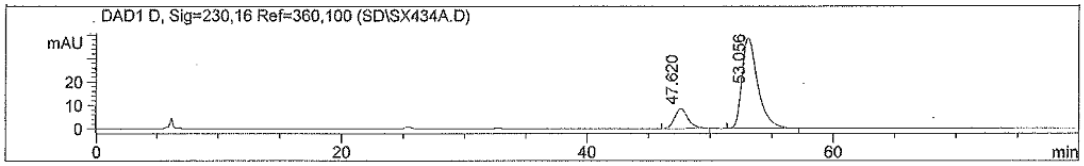
***(E)-N*-[Methyl(oxo)(phenyl)-λ^6-sulfanylidene]-3-(4-nitrophenyl)acrylamide (3ac)**



(**$C_{16}H_{14}N_2O_4S$**) a yellow oil, 43% yield, 69% ee. $[\alpha]_D^{25}$ = +19.5 (*c* = 1.21, in $CHCl_3$), HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 230 nm, retention time: 51.9 min, 58.0 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 – 8.17 (m, 2H), 8.03 (ddd, *J* = 7.1, 3.2, 1.9 Hz, 2H), 7.73 – 7.57 (m, 6H), 6.72 (d, *J* = 15.9 Hz, 1H), 3.44 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.46, 148.23, 141.50, 139.72, 138.64, 134.10, 129.86, 129.23, 128.62, 127.19, 124.19, 44.40 (d, *J* = 3.3 Hz). **IR (ATR)**: 3514, 3026, 2931, 2324, 2101, 1912, 1744, 1608, 1514, 1412, 1308, 1200, 1092, 976, 847, 741. **MS (EI)**: *m/z* = 94.4 (19), 125.3 (19), 156.3 (94), 175.3 (60), 176.3 (20), 182.3 (100), 315.2 (13) 331.3 $[M+1]^+$ (1). **MS (ESI)**: ($[M+Na]^+$) 353.056. **HRMS (ESI)** (*m/z*) [**$C_{16}H_{14}N_2O_4S$+Na**]$^+$: Calcd. 353.0570, found 353.0564.



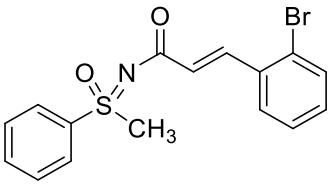
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.288	MM	0.6565	209.52809	5.31921	3.3725
2	35.812	MM	0.8413	201.71494	3.99614	3.2468
3	51.949	MM	1.3820	2906.33228	35.04949	46.7801
4	58.032	MM	1.6319	2895.17896	29.56872	46.6006



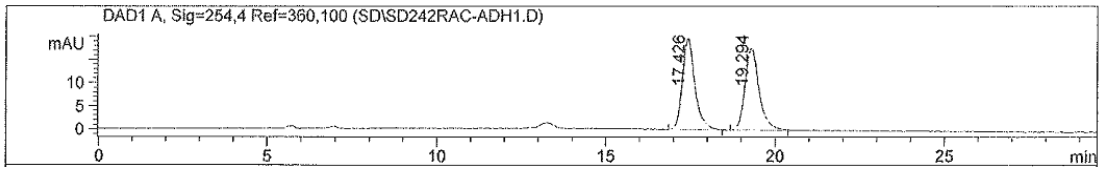
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	47.620	1.2434	8.41692	627.93951	15.4860
2	53.056	1.4801	38.59017	3426.93652	84.5140

(E)-3-(2-Bromophenyl)-*N*-[methyl(oxo)(phenyl)-λ^6-sulfanylidene]acrylamide (3ad)

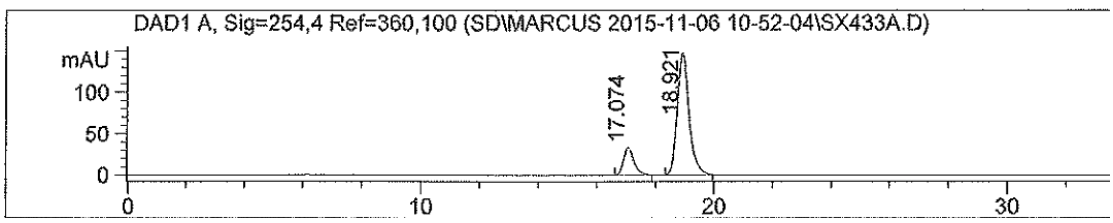


(**$C_{16}H_{14}BrNO_2S$**) a colorless oil, 47% yield, 66% ee. $[\alpha]_D^{25}$ = +7.8 (*c* = 0.94, in $CHCl_3$), HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 17.4 min, 19.3 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 – 8.03 (m, 3H), 7.71 – 7.65 (m, 1H), 7.65 – 7.56 (m, 4H), 7.33 – 7.27 (m, 1H), 7.19 (td, *J* = 7.8, 1.6 Hz, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 3.43 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 174.01, 141.22, 138.96, 135.16, 133.95, 133.42, 130.83, 129.80, 127.90, 127.74, 127.70 (d, *J* = 1.9 Hz), 127.27, 125.40, 44.42 (d, *J* = 2.7 Hz). **IR (ATR)**: ν 3365, 3024, 2929, 2329, 2099, 1911, 1717, 1610, 1445, 1199, 1077, 979, 859, 741. **MS (EI)**: *m*/*z* = 102.3 (11), 125.3 (18), 156.3 (100), 182.2 (49), 208.1 (27), 209.1 (11), 210.2 (27), 211.2 (10), 284.2 (38). **MS (ESI)**: ([M+Na]$^+$) 385.982, 387.980. **HRMS (ESI)** (*m*/*z*) [**$C_{16}H_{14}BrNO_2S$+Na**]$^+$: Calcd. 385.9821, 387.9800, found 385.9821, 387.9800.



DAD1 A, Sig=254,4 Ref=360,100

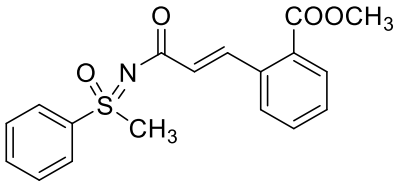
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.426	0.4302	19.55596	504.75256	50.0312
2	19.294	0.4787	17.55059	504.12329	49.9688



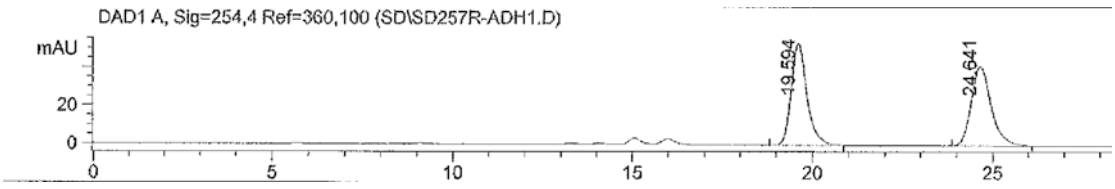
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.074	0.4151	33.19492	826.70404	16.7298
2	18.921	0.4226	146.97795	4114.79492	83.2702

Methyl-(*E*)-2-(3-{[methyl(oxo)(phenyl)-λ^6-sulfanylidene]amino}-3-oxoprop-1-en-1-yl)benzoate (3ae)

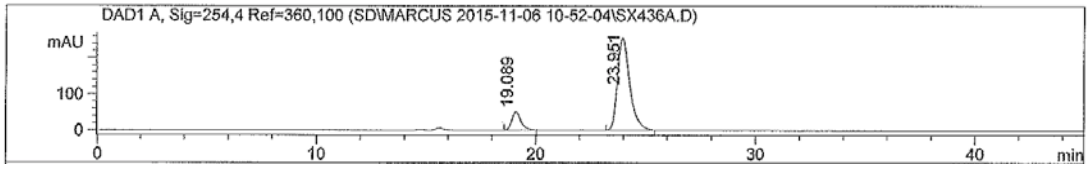


(**$C_{18}H_{17}NO_4S$**) a colorless oil, 37% yield, 74% ee. $[\alpha]_D^{25}$ = +15.4 (*c* = 0.55, in CH_2Cl_2), HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 19.6 min, 24.6 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, *J* = 15.7 Hz, 1H), 8.12 – 8.03 (m, 2H), 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.69 – 7.57 (m, 4H), 7.54 – 7.46 (m, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 3.91 (s, 3H), 3.44 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 141.74, 139.09, 136.81, 133.88, 132.29, 130.76, 130.08, 129.74, 129.05, 127.96, 127.76, 127.35, 52.42, 44.41. **IR (ATR)**: ν 3061, 3022, 2941, 2328, 2102, 1910, 1715, 1609, 1443, 1201, 1091, 972, 851, 741. **MS (EI)**: *m*/*z* = 161.3 (100), 173.2 (11), 182.3 (31), 284.3 (60) 343.1 $[M+1]^+$ (1). **MS (ESI)**: ($[M+Na]^+$) 366.076. **HRMS (ESI)** (*m*/*z*) [**$C_{18}H_{17}NO_4S$+Na**]$^+$: Calcd. 366.0770, found 366.0765.



DAD1 A, Sig=254,4 Ref=360,100

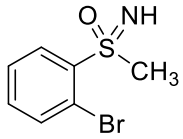
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	19.594	0.5073	53.23308	1620.34143	50.1746
2	24.641	0.6461	41.50748	1609.06738	49.8254



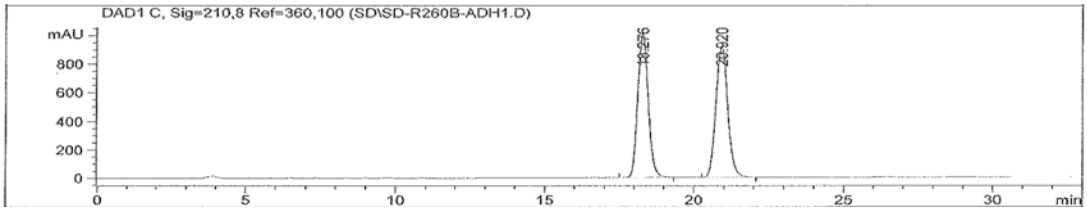
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	19.089	0.4463	51.60894	1505.14282	13.1608
2	23.951	0.5860	256.33926	9931.43652	86.8392

NH-S-(2-Bromophenyl)-*S*-methyl- sulfoximine (1b)[9]

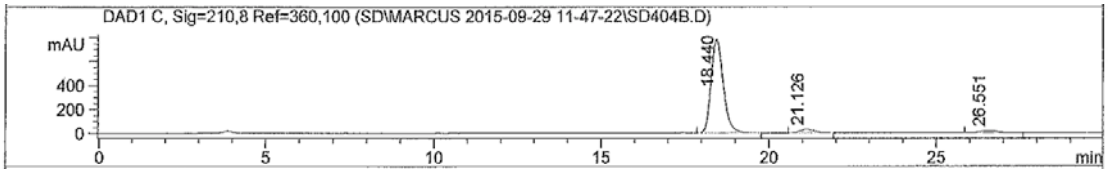


(**C_7H_8BrNOS**) a white solid. For cat **6c**: 43% yield, 92% ee. $[\alpha]_D^{25}$ = +39.0 (*c* = 0.78, in $CHCl_3$). For cat **5b**: 40% yield, –90% ee. $[\alpha]_D^{25}$ = –35.0 (*c* = 0.81, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 20/80, flow rate = 0.8 mL/min, λ = 210 nm, retention time: 18.3 min, 20.9 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.50 (td, *J* = 7.6, 1.2 Hz, 1H), 7.42 (td, *J* = 7.6, 1.8 Hz, 1H), 3.32 (s, 3H), 2.59 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 142.74, 135.75, 134.11, 131.05, 128.18, 120.83, 43.22.

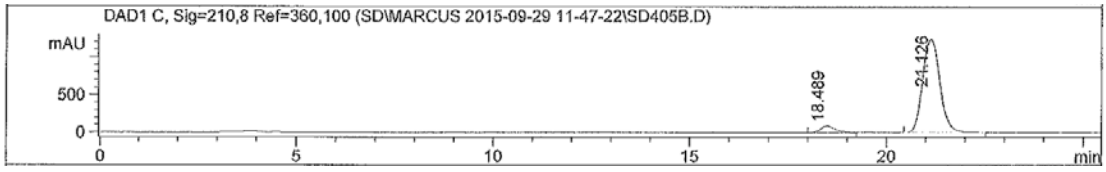


Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.276	BB	0.3860	2.48308e4	1005.71100	49.5909
2	20.920	BB	0.4318	2.52405e4	909.38849	50.4091

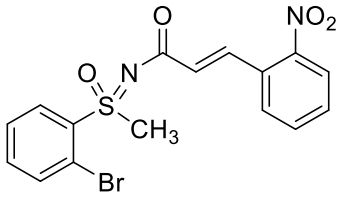


Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	18.440	0.4206	776.49915	19595.63477	93.3971
2	21.126	0.4447	27.82069	812.51660	3.8726
3	26.551	0.4980	13.98288	572.84473	2.7303

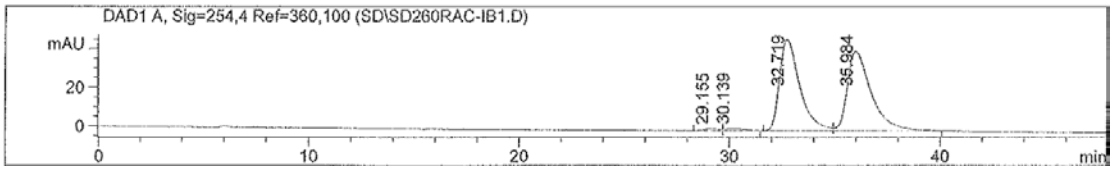


Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	18.489	0.3827	83.15352	2114.43970	5.3296
2	21.126	0.4788	1235.08569	37558.80078	94.6704

(*E*)-*N*-[(2-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3b)

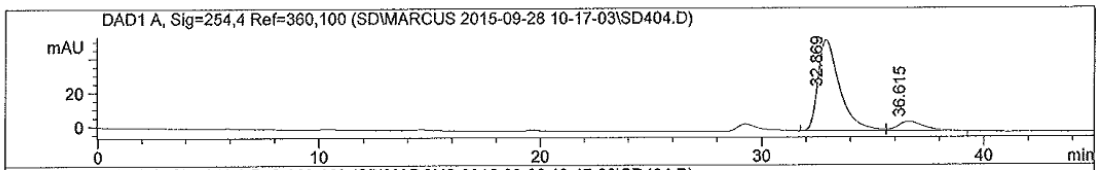


(**$C_{16}H_{13}BrN_2O_4S$**) a yellow oil. For cat **6c**: 54% yield, 78% ee. $[\alpha]_D^{25}$ = +9.5 (*c* = 2.21, in $CHCl_3$). For cat **5b**: 57% yield, –67% ee. $[\alpha]_D^{25}$ = –7.7 (*c* = 2.39, in $CHCl_3$). HPLC IB, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 32.7 min, 36.0 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.13 (d, *J* = 15.6 Hz, 1H), 7.99 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.78 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.71 – 7.56 (m, 3H), 7.50 (tdd, *J* = 6.9, 5.0, 1.6 Hz, 2H), 6.46 (d, *J* = 15.6 Hz, 1H), 3.55 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.01, 148.51, 138.36, 137.70, 135.92, 134.89, 133.45, 132.03, 131.27, 129.91, 129.50, 129.22, 128.60, 124.88, 119.56, 42.01. **IR (ATR)**: ν = 3864, 3559, 3298, 3078, 3023, 2927, 2860, 2679, 2315, 2234, 2141, 2029, 1934, 1719, 1607, 1519, 1435, 1335, 1288, 1201, 1099, 1027, 965, 858, 751. **MS (EI)**: *m*/*z* = 50.3 (13), 63.3 (32), 75.2 (26), 76.4 (29), 77.3 (15), 89.2 (37), 90.3 (11), 91.2 (22), 92.2 (10), 102.2 (23), 130.1 (19), 142.9 (11), 155.0 (20), 157.0 (18), 171.0 (20), 172.0 (33), 173.1 (20), 174.1 (18), 175.1 (26), 202.9 (14), 204.8 (15), 233.9 (32), 235.9 (35), 259.9 (100), 261.1 (15), 261.9 (95), 329.0 (13), 361.9 (39), 363.9 (43). **MS (ESI)**: ([M+Na]$^+$) 430.966, 432.964. **HRMS (ESI)** (*m*/*z*) [**$C_{16}H_{13}BrN_2O_4S$+Na**]$^+$: Calcd. 430.9672, 432.9651, found 430.9663, 432.9640.



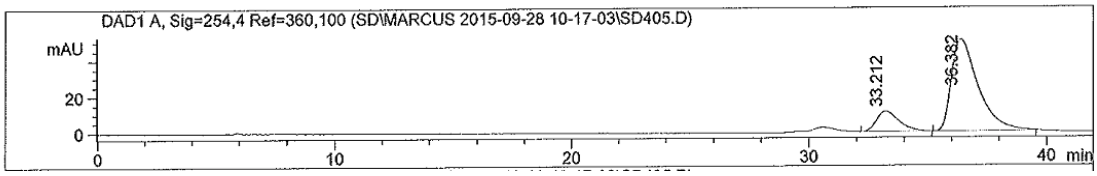
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	29.155	0.8294	1.17728	58.58292	0.8873
2	30.139	1.0338	1.19039	73.83624	1.1183
3	32.719	1.1118	47.65208	3178.81738	48.1448
4	35.984	1.3240	41.43357	3291.38013	49.8496



DAD1 A, Sig=254,4 Ref=360,100

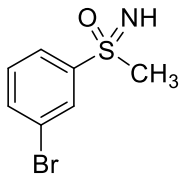
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	32.869	1.1364	53.69778	3661.26636	88.8679
2	36.615	1.3753	5.55790	458.63101	11.1321



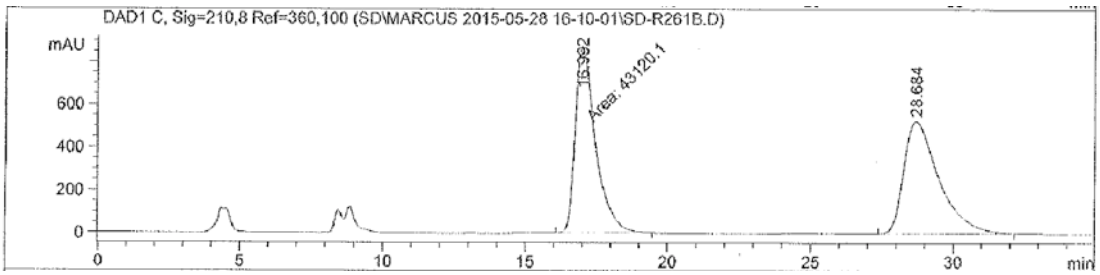
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	33.212	1.1028	11.39455	753.95416	16.0182
2	36.382	1.2962	50.82732	3952.89526	83.9818

NH-S-(3-Bromophenyl)-*S*-methyl- sulfoximine (1c)[10]

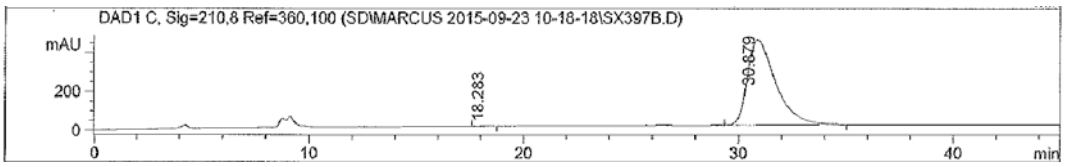


(**C_7H_8BrNOS**) a white solid. For cat **6c**: 38% yield, 99% ee. $[\alpha]_D^{25}$ = +15.4 (*c* = 0.85, in $CHCl_3$). For cat **5b**: 42% yield, –93% ee. $[\alpha]_D^{25}$ = –14.2 (*c* = 0.92, in $CHCl_3$). HPLC OJ, 2-propanol/*n*-heptane = 30/70, flow rate = 0.7 mL/min, λ = 210 nm, retention time: 17.0 min, 28.7 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (t, *J* = 1.8 Hz, 1H), 7.93 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1H), 7.73 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 3.10 (s, 3H), 2.47 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 145.66, 136.23, 130.90, 130.85, 126.37, 123.38, 46.21.

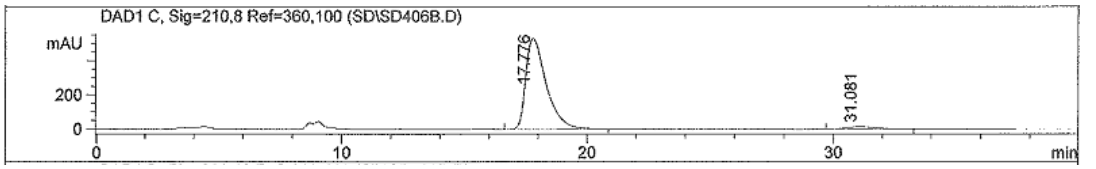


Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.992	MM	0.8221	4.31201e4	874.21368	48.8783
2	28.684	BB	1.2482	4.50993e4	524.99542	51.1217
Totals :				8.82194e4	1399.20911	

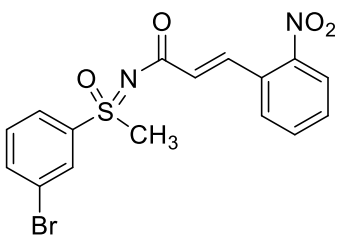


Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	18.283	0.6085	1.61085	58.80740	0.1487
2	30.879	1.5080	436.37665	39483.87109	99.8513
Total				39542.67849	100.0000



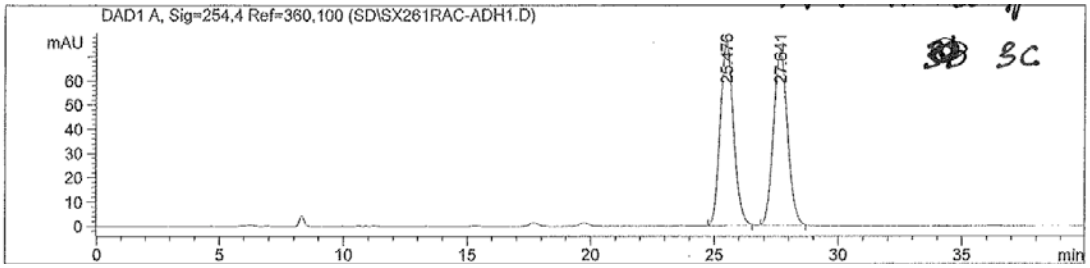
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.776	0.9686	529.84937	30791.46289	96.3553
2	31.081	1.3740	14.12767	1164.69836	3.6447
Total				31956.16125	100.0000

(*E*)-*N*-[(3-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3c)



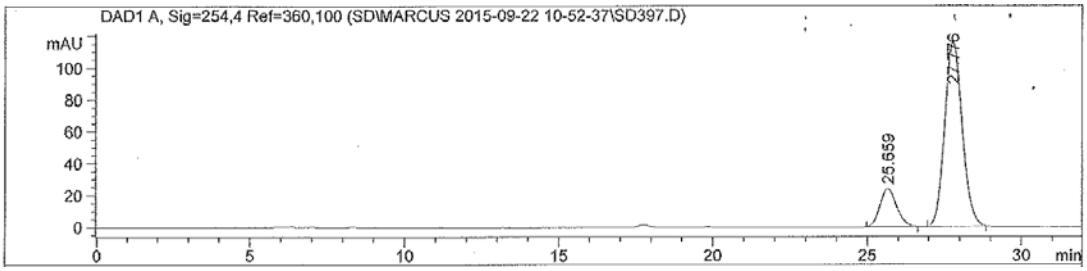
(**$C_{16}H_{13}BrN_2O_4S$**) a yellow solid, melting point: 94-95 °C. For cat **6c**: 59% yield, 67% ee. $[\alpha]_D^{25}$ = +29.1 (*c* = 2.36, in $CHCl_3$). For cat **5b**: 56% yield, –74% ee. $[\alpha]_D^{25}$ = –31.5 (*c* = 2.30, in $CHCl_3$). HPLC ADH, 2-propanol /*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 25.5 min, 27.6 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (dd, *J*

= 9.6, 7.8 Hz, 2H), 8.05 – 7.91 (m, 2H), 7.80 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.71 – 7.58 (m, 2H), 7.50 (ddd, *J* = 8.0, 5.9, 2.1 Hz, 2H), 6.50 (d, *J* = 15.6 Hz, 1H), 3.42 (s, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 173.47, 148.51, 140.72, 138.27, 137.11, 133.50, 131.32, 131.11, 130.24, 130.01, 129.68, 129.22, 125.88, 124.93, 123.79, 44.45. **IR (ATR)**: ν = 3065, 2927, 2335, 2097, 1893, 1732, 1609, 1521, 1290, 1202, 1089, 972, 863, 756. **MS (EI)**: *m*/*z* = 63.3 (11), 75.3 (13), 76.3 (22), 89.2 (12), 155.0 (20), 157.0 (14), 172.0 (14), 175.1 (13), 259.9 (100), 262.0 (84), 362.0 (27), 363.9 (38). **MS (ESI)**: ($[M+Na]^+$) 430.966, 432.964. **HRMS (ESI)** (*m*/*z*) **$[C_{16}H_{13}BrN_2O_4S+Na]^+$**: Calcd. 430.9672, 432.9651, found 430.9665, 432.9641.



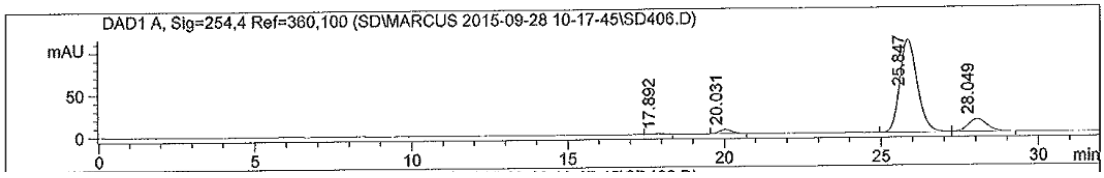
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.476	BB	0.5741	2830.29980	75.70992	49.9659
2	27.641	BB	0.6129	2834.16528	72.04626	50.0341



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

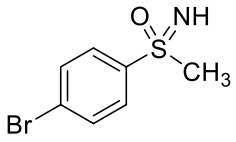
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.659	BB	0.5705	911.61450	24.03331	16.5486
2	27.776	BB	0.6196	4597.09082	115.69849	83.4514



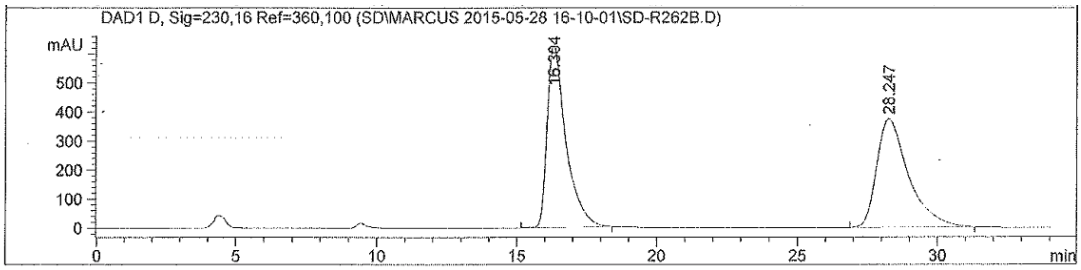
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.892	0.3802	0.78885	17.99625	0.3592
2	20.031	0.3896	4.96885	136.11705	2.7171
3	25.847	0.6426	109.77354	4232.21826	84.4822
4	28.049	0.6870	15.11985	623.26630	12.4414

NH-S-(4-Bromophenyl)-*S*-methyl-sulfoximine (1d)[11]

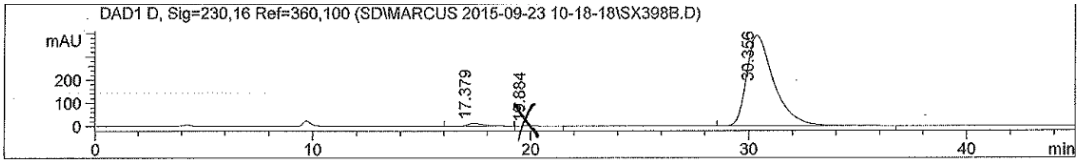


(**C_7H_8BrNOS**) a white solid; For cat **6c**: 41% yield, 96% ee. $[\alpha]_D^{25}$ = +17.8 (*c* = 0.93, in $CHCl_3$). For cat **5b**: 42% yield, –94% ee. $[\alpha]_D^{25}$ = –16.9 (*c* = 0.92, in $CHCl_3$). HPLC OJ, 2-propanol/*n*-heptane = 30/70, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 16.3 min (*R*), 28.2 min (*S*). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 – 7.80 (m, 2H), 7.76 – 7.61 (m, 2H), 3.09 (s, 3), 2.50 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 142.74, 132.66, 129.47, 128.42, 46.33. (*R*)-**1d**: $[\alpha]_D$ = –13.0 (*c* = 1.07, ≥99% ee, in MeOH)[11a].



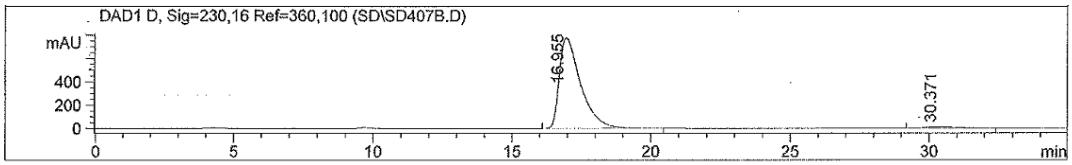
Signal 3: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.304	BB	0.6868	2.93625e4	631.12866	49.8041
2	28.247	BB	1.1786	2.95936e4	374.21097	50.1959



DAD1 D, Sig=230,16 Ref=360,100

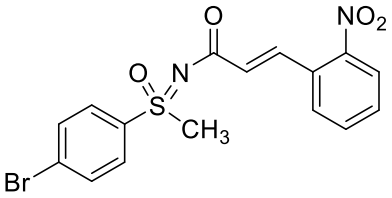
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.379	0.8429	13.18658	666.88403	1.9425
2	19.884	1.0149	0.90353	55.01755	0.1603
3	30.356	1.4354	390.24210	33609.72656	97.8973



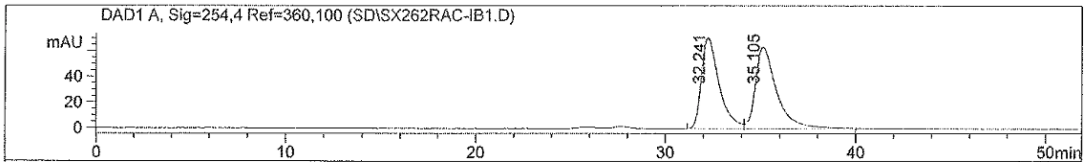
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	16.955	0.8959	776.62769	41745.04297	97.1253
2	30.371	1.3307	15.47513	1235.57214	2.8747

(*E*)-*N*-[(4-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3d)

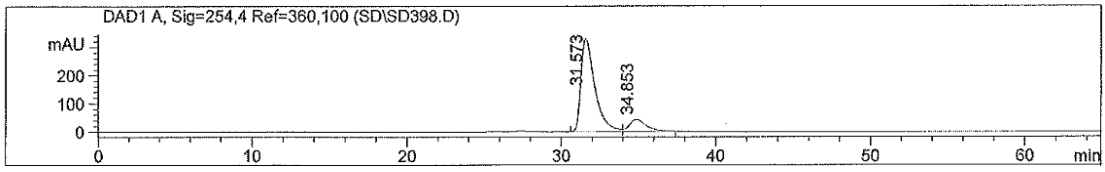


(**$C_{16}H_{13}BrN_2O_4S$**) a yellow oil. For cat **6c**: 56% yield, 73% ee. $[\alpha]_D^{25}$ = +28.8 (*c* = 2.12, in $CHCl_3$). For cat **5b**: 54% yield, –77% ee. $[\alpha]_D^{25}$ = –33.4 (*c* = 2.34, in $CHCl_3$). HPLC IB, 2-propanol /*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 32.2 min, 35.1 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 15.6 Hz, 1H), 8.00 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.79 – 7.74 (m, 2H), 7.68 – 7.59 (m, 2H), 7.54 – 7.47 (m, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 3.42 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.52, 148.50, 138.22, 137.87, 133.52, 133.17, 131.15, 130.00, 129.77, 129.45, 129.22, 128.88, 124.95, 44.43. **IR (ATR)**: ν = 3495, 3026, 2927, 2314, 2081, 1909, 1732, 1605, 1518, 1291, 1199, 1066, 969, 749. **MS (EI)**: *m*/*z* = 63.3 (13), 75.4 (13), 76.3 (13), 89.2 (12), 155.0 (13), 157.0 (11), 170.2 (13), 171.1 (22), 172.1 (20), 173.0 (18), 175.0 (25), 202.9 (13), 204.9 (14), 233.9 (37), 236.0(38), 259.9 (93), 261.9 (100), 361.9 (32), 363.9 (35). **MS (ESI)**: ($[M+Na]^+$) 430.966, 432.964. **HRMS (ESI)** (*m*/*z*) [**$C_{16}H_{13}BrN_2O_4S$+Na**]$^+$: Calcd. 430.9672, 432.9651, found 430.9665, 432.9643.



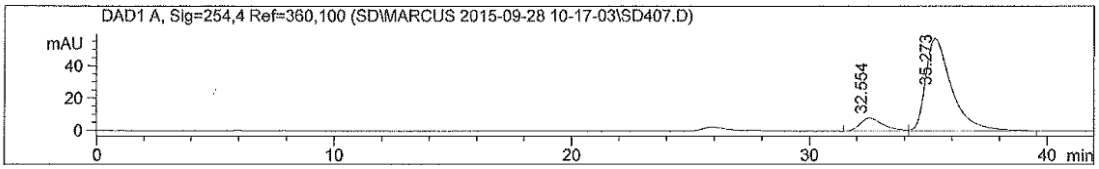
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	32.241	1.0772	70.37314	4548.46631	48.4893
2	35.105	1.2736	63.23286	4831.87598	51.5107



DAD1 A, Sig=254,4 Ref=360,100

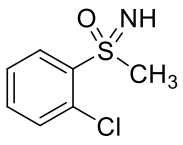
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	31.573	1.0499	330.94489	20846.69531	86.2757
2	34.853	1.2705	43.50177	3316.17896	13.7243



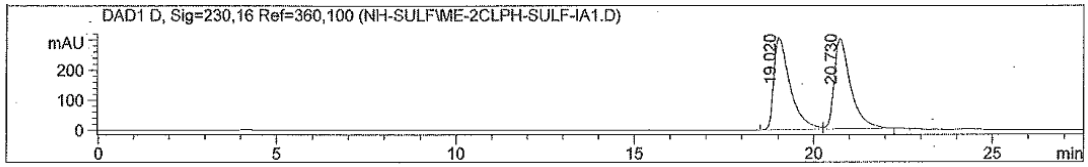
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	32.554	1.1246	8.13971	549.22559	11.2202
2	35.273	1.2670	57.16551	4345.74854	88.7798
Total				4894.97412	100.0000

NH-S-(2-Chlorophenyl)-*S*-methyl- sulfoximine (1e)[2c,11]

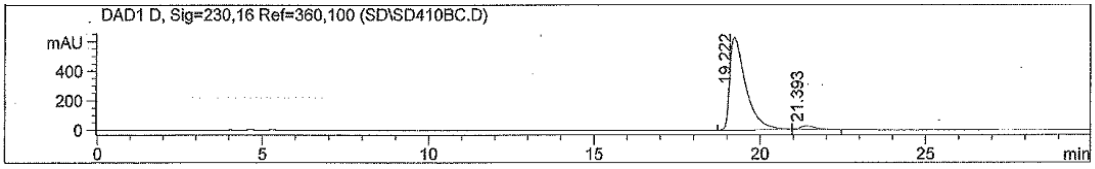


(**C_7H_8ClNOS**) a white solid; For cat **6c**: 45% yield, 92% ee. $[\alpha]_D^{25}$ = +31.2 (*c* = 0.80, in $CHCl_3$). For cat **5b**: 40% yield, –85% ee. $[\alpha]_D^{25}$ = –37.0 (*c* = 0.76, in $CHCl_3$). HPLC IA, 2-propanol/*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 19.0 min, 20.7 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 – 7.95 (m, 1H), 7.56 – 7.48 (m, 2H), 7.44 (ddd, *J* = 7.9, 6.2, 2.5 Hz, 1H), 3.30 (s, 3H), 2.73 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 141.06, 134.12, 132.46, 132.15, 130.75, 127.52, 43.59.



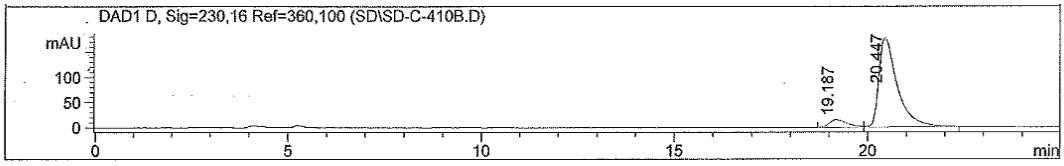
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	19.020	0.5276	305.93484	9685.17773	49.9610
2	20.730	0.5387	300.09048	9700.31543	50.0390



DAD1 D, Sig=230,16 Ref=360,100

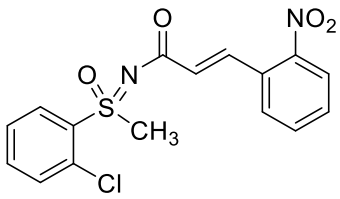
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	19.222	0.5598	628.35632	21106.05273	95.8817
2	21.393	0.5876	25.71187	906.54767	4.1183



DAD1 D, Sig=230,16 Ref=360,100

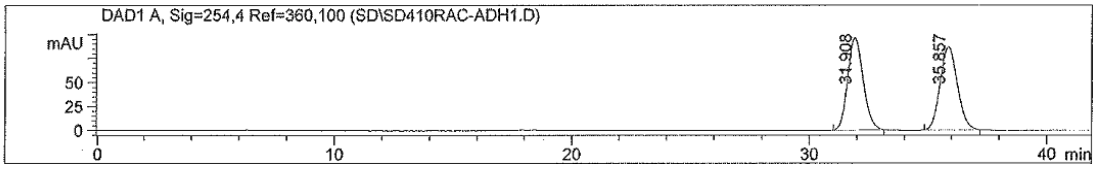
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	19.187	0.5288	15.06720	478.02396	7.4652
2	20.447	0.5570	177.31323	5925.31543	92.5348

(*E*)-*N*-[(2-Chlorophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3e)



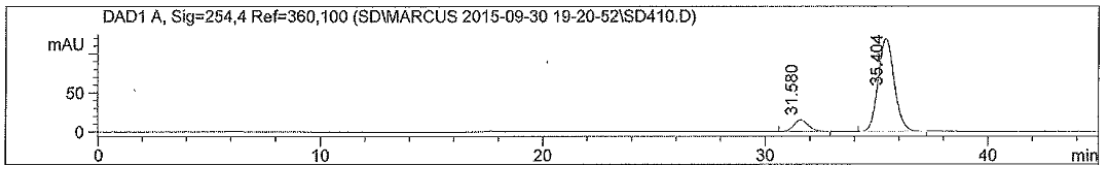
(**$C_{16}H_{13}ClN_2O_4S$**) a yellow oil. For cat **6c**: 53% yield, 80% ee. $[\alpha]_D^{25}$ = +15.1 (*c* = 2.15, in $CHCl_3$). For cat **5b**: 56% yield, –69% ee. $[\alpha]_D^{25}$ = –15.7 (*c* = 2.34, in $CHCl_3$). HPLC ADH, 2-propanol /*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 31.9 min, 35.8 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.32 – 8.27 (m, 1H), 8.11 (d, *J* = 15.6 Hz, 1H), 7.98 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.68 – 7.53 (m, 5H), 7.52 – 7.46 (m, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 3.54 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.99, 148.52, 138.20, 136.05, 134.95, 133.42, 132.33, 131.80, 131.44, 131.22, 129.90, 129.52, 129.20, 128.00, 124.87, 42.34. **IR (ATR)**: ν = 3071, 2930, 2256, 2103, 1740, 1611, 1521, 1446, 1291, 1203, 1047, 969, 887, 736. **MS (EI)**: *m*/*z* = 50.3 (29), 51.3 (50), 52.3 (13), 55.3 (13), 57.3 (30), 63.2 (100), 64.2 (19), 65.3 (43), 69.3 (13), 71.2 (19), 74.2 (12), 75.2 (71), 76.2 (40), 77.2 (42), 89.2 (57), 90.2 (23), 91.2 (25), 92.2 (23), 99.1 (79), 101.1 (34), 102.1 (49), 111.1 (56), 113.1 (14), 127.0 (40), 128.1 (90), 129.1 (21), 130.1 (59), 131.1 (15), 159.0 (32), 175.1 (21), 190.0 (20), 215.9 (77), 218.0 (21), 318.0 (42), 320.0 (18), 329.0 (15), 364.9 (11). **MS**

(ESI): ([M+Na]$^+$) 387.016, 389.013. **HRMS (ESI)** (*m*/*z*) [$\mathbf{C_{16}H_{13}ClN_2O_4S}$+**Na**]$^+$: Calcd. 387.0177, 389.0147, found 387.0163, 389.0133.



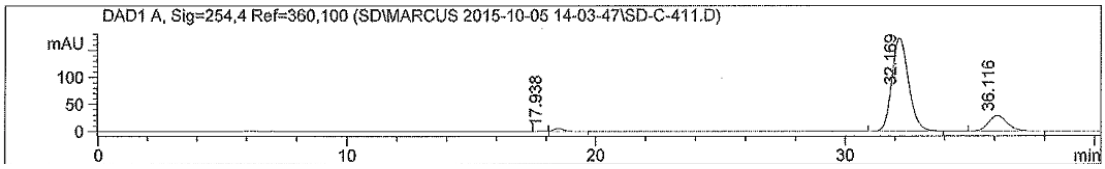
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	31.908	0.7102	96.31115	4410.16211	49.9726
2	35.857	0.7589	86.87320	4414.99316	50.0274



DAD1 A, Sig=254,4 Ref=360,100

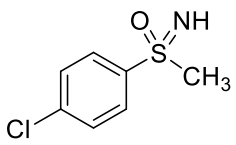
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	31.580	0.7607	14.84503	677.58728	10.1847
2	35.404	0.8405	118.48962	5975.39209	89.8153
Total				6652.97937	100.0000



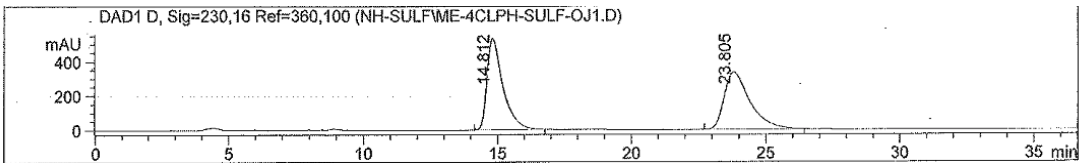
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.938	0.3135	1.02674	19.31595	0.2012
2	18.488	0.4407	5.37964	142.23415	1.4817
3	32.169	0.7737	171.94371	7981.87988	83.1476
4	36.116	0.8575	28.30407	1456.21997	15.1695

NH-S-(4-chlorophenyl)-*S*-methyl- sulfoximine (1f)[11]

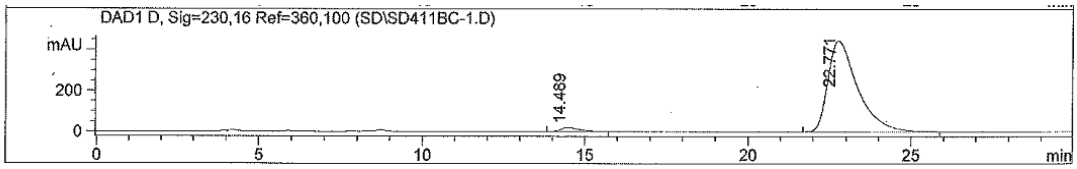


(**C_7H_8ClNOS**) a white solid; For cat **6c**: 45% yield, 94% ee. $[\alpha]_D^{25}$ = +17.3 (*c* = 0.92, in $CHCl_3$). For cat **5b**: 43% yield, –90% ee. $[\alpha]_D^{25}$ = –17.8 (*c* = 0.86, in $CHCl_3$). HPLC OJ, 2-propanol/*n*-heptane = 30/70, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 14.8 min, 23.8 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 – 7.92 (m, 2H), 7.53 – 7.49 (m, 2H), 3.09 (s, 3H), 2.54 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 142.21, 139.87, 129.64, 129.35, 46.36.



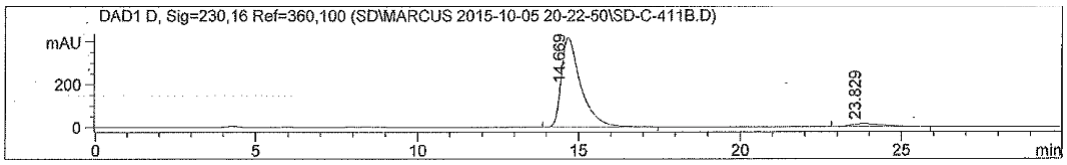
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.812	0.6106	534.49127	22110.35352	49.9065
2	23.805	0.9928	335.03723	22193.20898	50.0935



DAD1 D, Sig=230,16 Ref=360,100

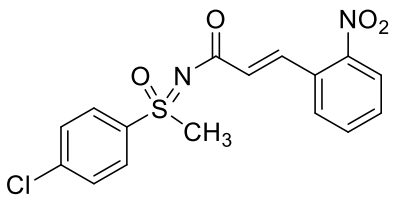
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.489	0.6598	20.59085	815.20551	2.8011
2	22.771	1.0599	444.80258	28287.40430	97.1989
Total				29102.60980	100.0000



DAD1 D, Sig=230,16 Ref=360,100

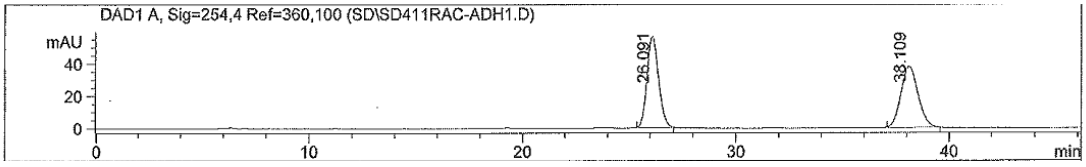
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.669	0.6941	414.01340	17243.10937	95.0658
2	23.829	1.0739	13.88979	894.96362	4.9342

_(E)-N_-[(4-Chlorophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl) acrylamide (3f)



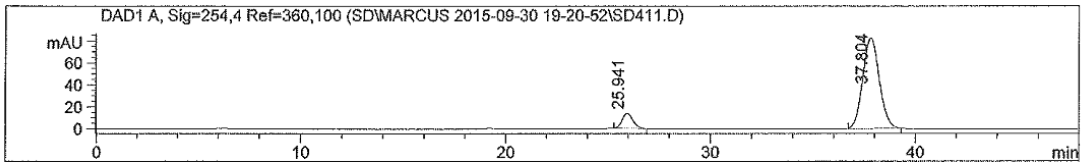
(**$C_{16}H_{13}ClN_2O_4S$**) a yellow solid, melting point: 109-110 °C. For cat **6c**: 52% yield, 80% ee. $[\alpha]_D^{25}$ = +36.7 (*c* = 2.21, in $CHCl_3$). For cat **5b**: 54% yield, –76% ee. $[\alpha]_D^{25}$ = –35.2 (*c* = 2.07, in $CHCl_3$). HPLC ADH, 2-propanol /*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 26.1 min, 38.1 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 15.6 Hz, 1H), 8.00 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.98 – 7.95 (m, 2H), 7.64 (ddd, *J* = 7.9, 7.4, 1.2 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.50 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 6.49 (d, *J* =

15.6 Hz, 1H), 3.42 (s, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 173.50, 148.49, 140.87, 138.18, 137.27, 133.51, 131.13, 130.17, 129.99, 129.78, 129.20, 128.83, 124.93, 44.46. **IR (ATR)**: ν = 3032, 2928, 2321, 2104, 1918, 1736, 1608, 1519, 1294, 1200, 1091, 1040, 970, 730. **MS (EI)**: *m/z* = 50.2 (27), 51.3 (44), 52.3 (10), 63.2 (99), 64.2 (20), 65.2 (38), 74.2 (12), 75.2 (68), 76.2 (48), 77.2 (39), 89.2 (54), 90.2 (20), 91.2 (16), 92.2 (21), 99.1 (58), 101.1 (32), 102,1 (44), 103.2 (11), 111.1 (59), 113.1 (18), 116.1 (13), 127.0 (100), 128.0 (70), 129.0 (46), 131.0 (59), 131.1 (14), 159.0 (47), 161.0 (12), 175.1 (39), 190.0 (41), 192.0 (16), 216.0 (94), 218.0 (32), 318.0 (47), 320.0 (18), 365.0 $(M+1)^+$ (8). **MS (ESI)**: ($[M+Na]^+$) 387.016, 389.013. **HRMS (ESI)** (*m/z*) **$[C_{16}H_{13}ClN_2O_4S+Na]^+$**: Calcd. 387.0177, 389.0147, found 387.0170, 389.0140.



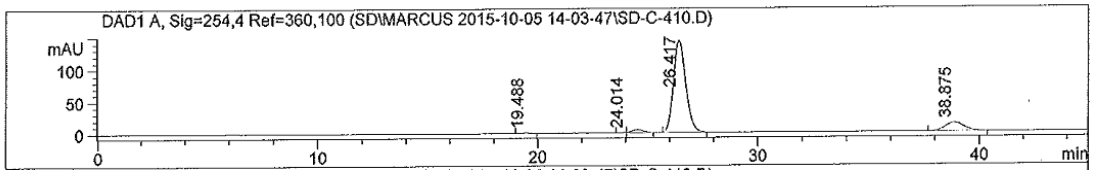
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	26.091	0.5777	56.43488	2126.99609	49.8756
2	38.109	0.8196	38.04002	2137.60425	50.1244
Total				4264.60034	100.0000



DAD1 A, Sig=254,4 Ref=360,100

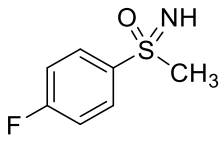
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	25.941	0.5216	13.73117	503.29477	9.8010
2	37.804	0.8498	82.40132	4631.86035	90.1990



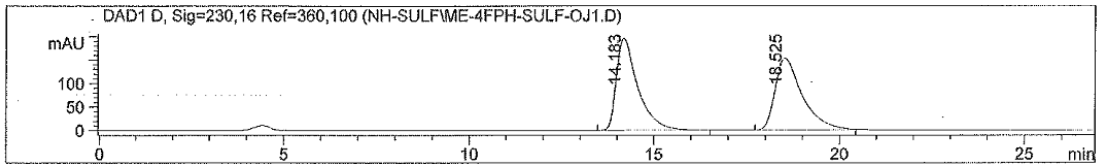
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	19.488	0.4164	0.82665	20.65311	0.3169
2	24.014	0.2299	0.91352	12.60220	0.1933
3	24.535	0.6034	4.72165	170.92854	2.6223
4	26.417	0.6487	142.85426	5559.80518	85.2961
5	38.875	0.9592	13.10597	754.25488	11.5714

NH-S-(4-Fulorophenyl)-*S*-methyl- sulfoximine (1g)[12]

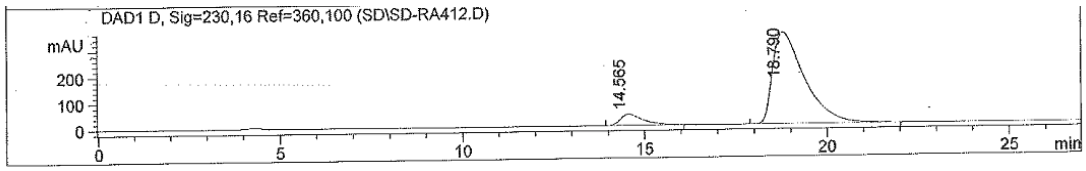


(**C_7H_8FNOS**) a white solid; For cat **6c**: 42% yield, 84% ee. $[\alpha]_D^{25}$ = +13.2 (*c* = 0.75, in $CHCl_3$). For cat **5b**: 42% yield, –88% ee. $[\alpha]_D^{25}$ = –14.1 (*c* = 0.74, in $CHCl_3$). HPLC OJ, 2-propanol/*n*-heptane = 30/70, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 14.2 min, 18.5 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 – 7.82 (m, 2H), 7.25 – 7.18 (m, 2H), 3.09 (s, 3H), 2.55 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.61 (d, *J* = 254.8 Hz), 139.65 (d, *J* = 3.0 Hz), 130.64 (d, *J* = 9.5 Hz), 116.55 (d, *J* = 22.4 Hz), 46.53. **^{19}F NMR (375 MHz, $CDCl_3$)** δ –105.21 (dq, *J* = 8.3, 5.1 Hz).



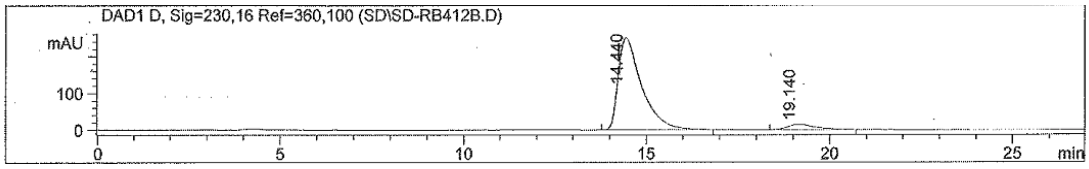
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.183	0.6709	196.21474	7899.00928	50.3988
2	18.525	0.7563	152.60385	7774.01172	49.6012



DAD1 D, Sig=230,16 Ref=360,100

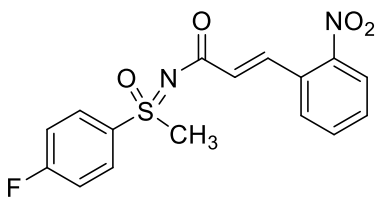
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.565	0.7023	43.40452	1828.87573	7.9083
2	18.790	1.0163	349.24695	21297.08203	92.0917



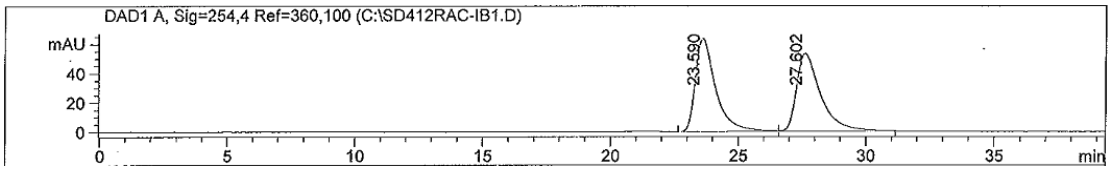
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.440	0.7396	251.27304	11150.43164	93.7740
2	19.140	0.8590	14.36328	740.31781	6.2260

(*E*)-*N*-[(4-Fluorophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3g)

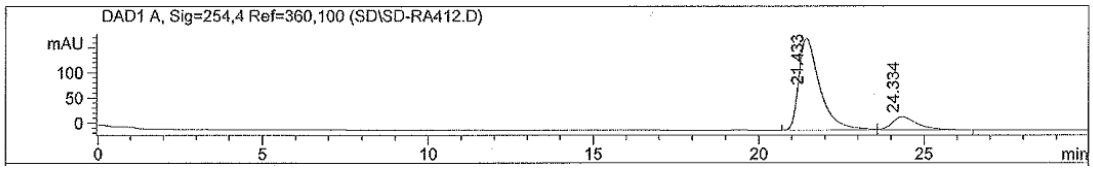


(**$C_{16}H_{13}FN_2O_4S$**) a yellow oil. For cat **6c**: 54% yield, 71% ee. $[\alpha]_D^{25}$ = +31.0 (*c* = 2.21, in $CHCl_3$). For cat **5b**: 53% yield, –75% ee. $[\alpha]_D^{25}$ = –31.6 (*c* = 1.97, in $CHCl_3$). HPLC IB, 2-propanol /*n*-heptane = 50/50, flow rate = 0.6 mL/min, λ= 254 nm, retention time: 23.6 min, 27.6 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 15.6 Hz, 1H), 8.08 – 8.01 (m, 2H), 7.99 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.49 (ddd, *J* = 8.5, 7.2, 1.7 Hz, 1H), 7.33 – 7.25 (m, 2H), 6.48 (d, *J* = 15.6 Hz, 1H), 3.42 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.53, 166.06 (d, *J* = 256.8 Hz), 148.50, 138.13, 134.66 (d, *J* = 3.1 Hz), 133.52, 131.19, 130.25 (d, *J* = 9.6 Hz), 129.98, 129.89, 129.22, 124.94, 117.24 (d, *J* = 22.9 Hz), 44.66. **^{19}F NMR (375 MHz, $CDCl_3$)** δ –103.07 – –103.16 (m). **IR (ATR)**: ν = 3072, 2929, 2251, 2113, 1912, 1726, 1599, 1521, 1404, 1286, 1207, 1097, 1047, 970, 905, 832, 726. **MS (EI)**: *m*/*z* = 63.3 (12), 75.2 (12), 83.2 (14), 89.1 (12), 95.1 (19), 102.1 (12), 111.1 (30), 112.1 (24), 130.1 (16), 143.0 (33), 158.1 (10), 174.0 (52), 175.0 (20), 200.1 (100). **MS (ESI)**: ([M+Na]$^+$) 371.046. **HRMS (ESI)** (*m*/*z*) [**$C_{16}H_{13}FN_2O_4S$+Na**]$^+$: Calcd. 371.0472, found 371.0473.



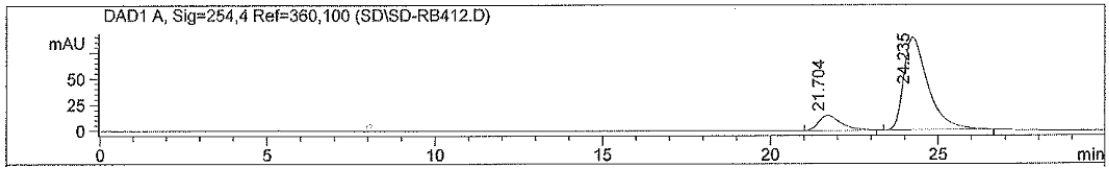
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	23.590	0.9217	63.89056	3533.40894	50.1486
2	27.602	1.0995	53.24116	3512.46680	49.8514



DAD1 A, Sig=254,4 Ref=360,100

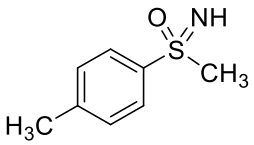
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	21.433	0.7370	183.05394	8095.00146	85.3401
2	24.334	0.8883	26.09118	1390.58069	14.6599



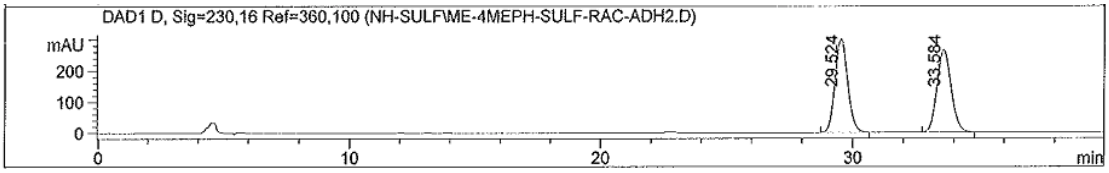
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	21.704	0.7632	14.43681	661.10846	12.8706
2	24.235	0.8401	88.78366	4475.47656	87.1294

***NH*-*S*-Methyl-*S*-(*p*-tolyl)-sulfoximine (1h)[11c]**

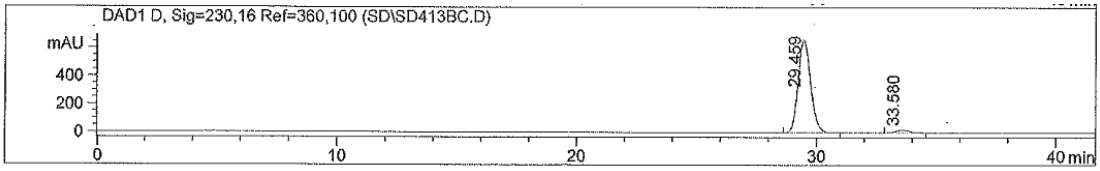


(**$C_8H_{11}NOS$**) a white solid; For cat **6c**: 44% yield, 94% ee. $[\alpha]_D^{25}$ = +19.0 (*c* = 0.72, in $CHCl_3$). For cat **5b**: 43% yield, –94% ee. $[\alpha]_D^{25}$ = –19.1 (*c* = 0.71, in $CHCl_3$). HPLC ADH, EtOH/*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 29.5 min (*S*), 33.6 min (*R*). Or HPLC ADH, 2-propanol/*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 14.6 min (*S*), 15.7 min (*R*). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 – 7.66 (m, 2H), 7.33 (dd, *J* = 8.5, 0.6 Hz, 2H), 3.07 (s, 3H), 2.52 (s, 1H), 2.43 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 144.02, 140.68, 129.97, 127.82, 46.42, 21.61. (*S*)-**1h**: $[\alpha]_{546}^{25}$ = +38.5 (*c* = 0.71, acetone)



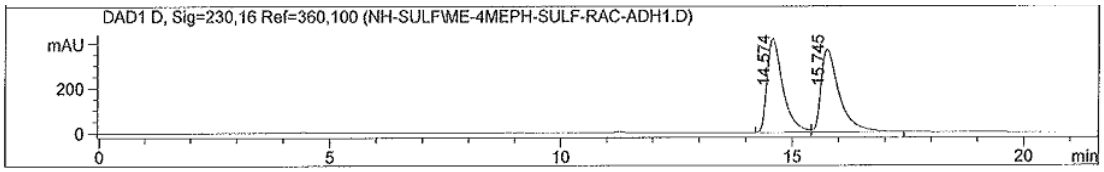
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	29.524	0.5424	299.30762	10476.98730	49.9813
2	33.584	0.6151	264.14975	10484.83594	50.0187



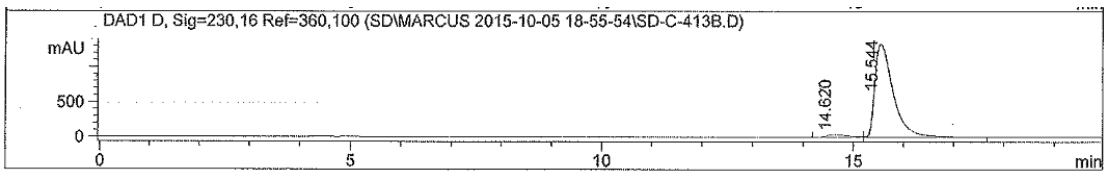
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	29.459	0.6066	662.92096	24127.38086	96.9792
2	33.580	0.6624	18.91046	751.53827	3.0208



DAD1 D, Sig=230,16 Ref=360,100

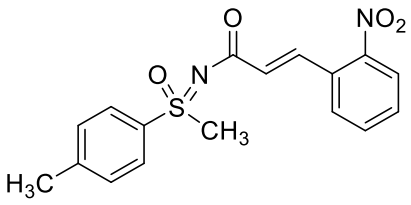
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.574	0.3507	418.01590	9842.77051	49.4298
2	15.745	0.4042	369.16998	10069.85645	50.5702



DAD1 D, Sig=230,16 Ref=360,100

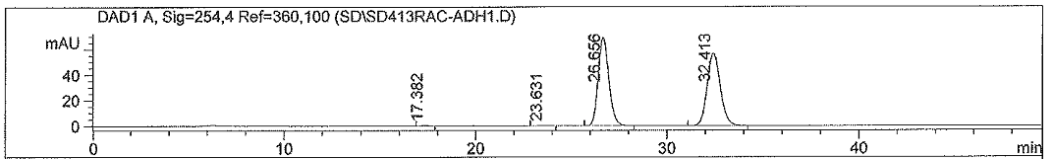
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.620	0.4588	36.92802	1016.56653	2.9233
2	15.544	0.4235	1328.62781	33757.58984	97.0767

(*E*)-*N*-[(Methyl)(*p*-tolyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3h)



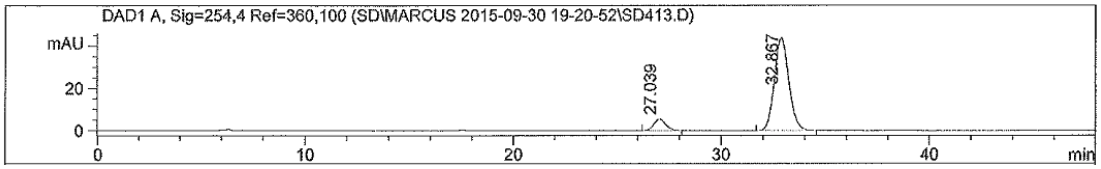
(**$C_{17}H_{16}N_2O_4S$**) a yellow oil. For cat **6c**: 52% yield, 82% ee. $[\alpha]_D^{25}$ = +35.8 (*c* = 2.22, in $CHCl_3$). For cat **5b**: 54% yield, –80% ee. $[\alpha]_D^{25}$ = –34.0 (*c* = 2.01, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 26.6 min, 32.4 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 15.6 Hz, 1H), 8.00 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.57 (m, 2H), 7.50 (dd, *J* = 11.1, 4.3 Hz, 1H),

7.41 (d, *J* = 8.1 Hz, 2H), 6.51 (d, *J* = 15.6 Hz, 1H), 3.42 (s, 3H), 2.46 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 173.58, 148.53, 145.16, 137.72, 135.70, 133.46, 131.31, 130.47, 130.20, 129.86, 129.22, 127.30, 124.90, 44.55, 21.75. **IR (ATR)**: ν = 3614, 3037, 2928, 2268, 2099, 1610, 1523, 1297, 1203, 1087, 972, 735. **MS (EI)**: *m*/*z* = 63.2 (12), 65.2 (15), 77.2 (17), 79.2 (18), 91.1 (33), 107.1 (100), 108.1 (22), 139.1 (11), 170.1 (17), 196.0 (15). **MS (ESI)**: ([M+Na]$^+$) 367.071. **HRMS (ESI)** (*m*/*z*) [**$C_{17}H_{16}N_2O_4S$+Na**]$^+$: Calcd. 367.0723, found 367.0726.



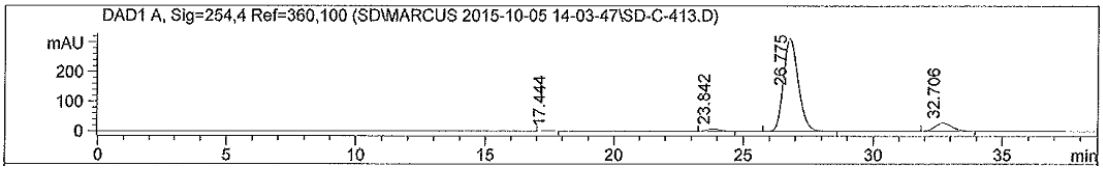
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.382	0.3743	0.53858	12.09626	0.2246
2	23.631	0.6309	0.47858	18.11552	0.3364
3	26.656	0.6455	69.06002	2674.49438	49.6687
4	32.413	0.7886	56.63833	2679.96362	49.7703



DAD1 A, Sig=254,4 Ref=360,100

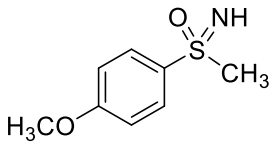
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	27.039	0.6557	5.39267	212.16930	9.1687
2	32.867	0.8004	43.76657	2101.89380	90.8313



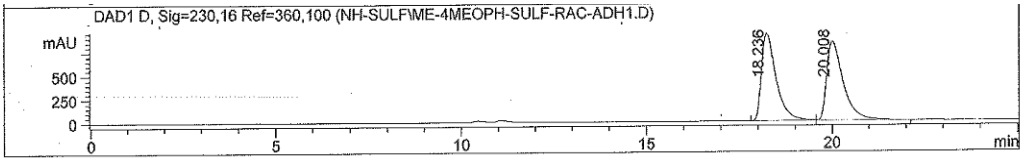
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.444	0.3863	1.22086	28.29897	0.2022
2	23.842	0.4513	8.20732	271.06189	1.9372
3	26.775	0.6597	312.20190	12357.78613	88.3190
4	32.706	0.6711	28.16105	1335.06458	9.5415

***NH*-*S*-(4-Methoxyphenyl)-*S*-methylsulfoximine (1i)[2a]**

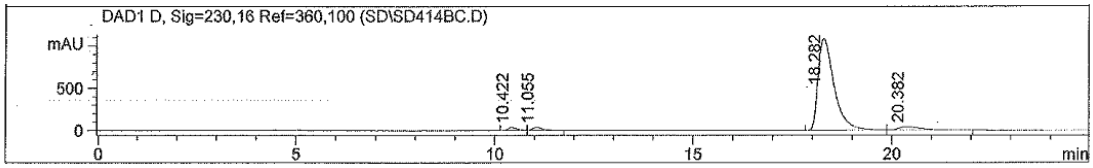


(**$C_8H_{11}NO_2S$**) a white solid; For cat **6c**: 42% yield, 89% ee. $[\alpha]_D^{25}$ = +12.9 (*c* = 0.78, in $CHCl_3$). For cat **5b**: 41% yield, –97% ee. $[\alpha]_D^{25}$ = –13.4 (*c* = 0.69, in $CHCl_3$). HPLC ADH, 2-propanol /*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 18.2 min, 20.0 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 – 7.77 (m, 2H), 7.11 – 6.83 (m, 2H), 3.86 (s, 3H), 3.07 (s, 3H), 2.47 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 163.40, 135.11, 129.95, 114.48, 55.79, 46.68.



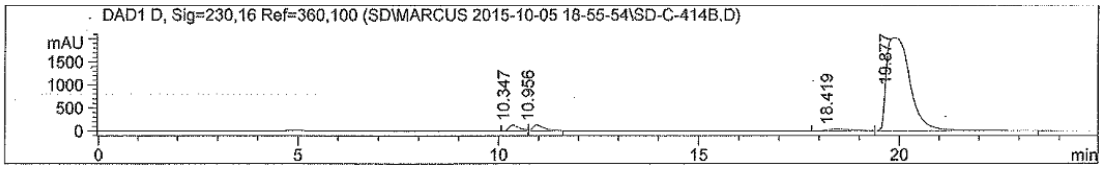
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	18.236	0.4592	925.03711	25485.97656	49.4809
2	20.008	0.5177	837.76349	26020.72852	50.5191



DAD1 D, Sig=230,16 Ref=360,100

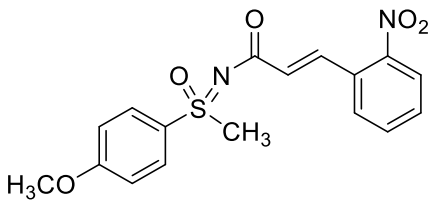
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	10.422	0.2815	35.27355	595.80536	1.7909
2	11.055	0.3213	34.77941	670.52325	2.0155
3	18.282	0.4655	1083.44788	30262.49414	90.9627
4	20.382	0.6874	42.19483	1740.31519	5.2310



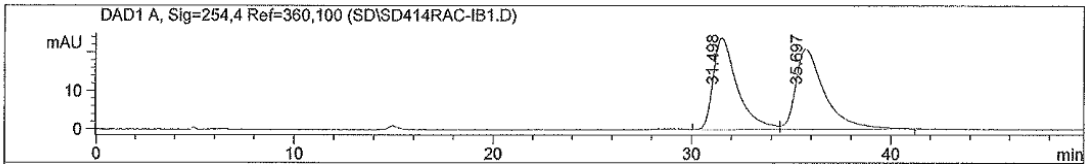
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	10.347	0.3052	124.42525	2278.82153	2.5575
2	10.956	0.3413	126.68128	2594.15234	2.9114
3	18.419	0.6251	43.10360	1616.58191	1.8143
4	19.877	0.6811	2021.55920	82614.78125	92.7169

(*E*)-*N*-[(4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3i)

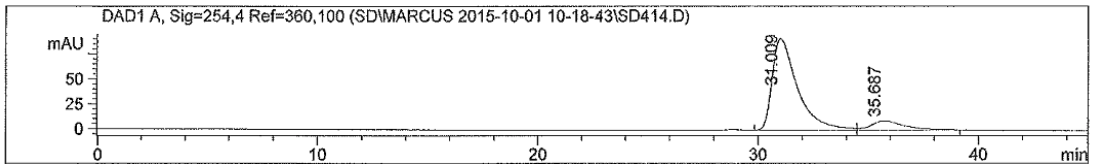


(**$C_{17}H_{16}N_2O_5S$**) a yellow oil. For cat **6c**: 52% yield, 78% ee. $[\alpha]_D^{25}$ = +35.2 (*c* = 2.10, in $CHCl_3$). For cat **5b**: 57% yield, –73% ee. $[\alpha]_D^{25}$ = –33.8 (*c* = 2.16, in $CHCl_3$). HPLC IB, 2-propanol/*n*-heptane = 50/50, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 31.5 min, 35.7 min. **^{1}H NMR (400 MHz, CDCl3)** δ 8.14 (d, J = 15.6 Hz, 1H), 8.00 (dd, J = 8.2, 1.1 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.70 – 7.58 (m, 2H), 7.54 – 7.44 (m, 1H), 7.12 – 7.02 (m, 2H), 6.52 (d, J = 15.6 Hz, 1H), 3.89 (s, 3H), 3.43 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.42, 163.94, 148.36, 137.49, 133.32, 131.18, 130.15, 129.69, 129.63, 129.34, 129.07, 124.75, 114.93, 55.77, 44.65. **IR (ATR)**: ν = 3021, 2933, 2594, 2254, 2091, 1902, 1596, 1513, 1278, 1198, 1094, 1029, 971, 823, 729. **MS (EI)**: *m*/*z* = 123.1 (100), 155.0 (38), 186.0 (12), 212.1 (27). **MS (ESI)**: ([M+Na]$^+$) 383.068. **HRMS (ESI)** (*m*/*z*) [**$C_{17}H_{16}N_2O_5S$+Na**]$^+$: Calcd. 383.0672, found 383.0675.



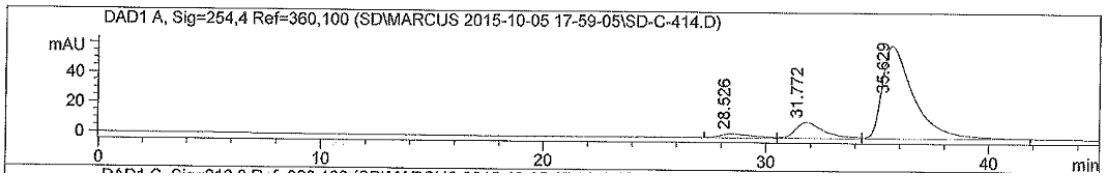
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	31.498	1.3953	23.72923	1986.53125	48.6948
2	35.697	1.6744	20.83304	2093.02124	51.3052



DAD1 A, Sig=254,4 Ref=360,100

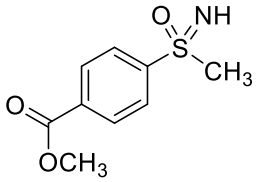
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	31.009	1.3237	91.70594	7283.70508	88.7724
2	35.687	1.6821	9.12748	921.21484	11.2276



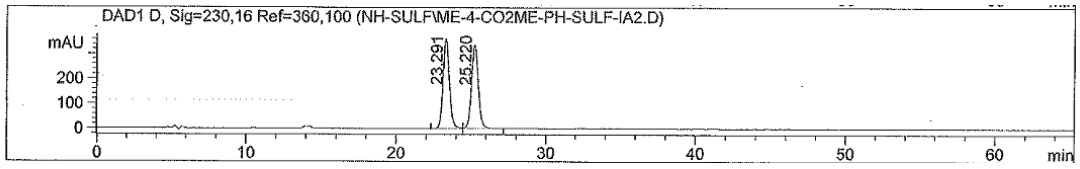
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	28.526	1.5699	2.75343	259.35294	3.5253
2	31.772	1.4737	10.70985	946.98456	12.8720
3	35.629	1.6541	61.97117	6150.57568	83.6027

NH-S-[4-(Methoxycarbonyl)phenyl]-*S*-methyl-sulfoximine (1j)[2b]

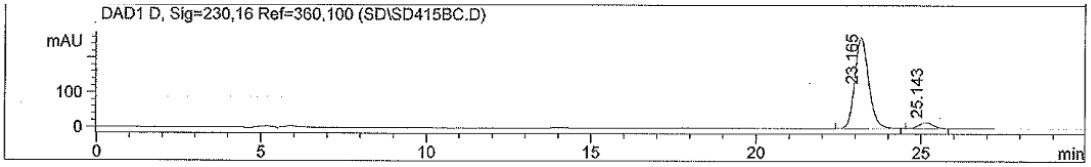


(**$C_9H_{11}NO_3S$**) a white solid, melting point: 127-128 °C. For cat **6c**: 42% yield, 87% ee. $[\alpha]_D^{25}$ = +19.2 (*c* = 0.88, in $CHCl_3$). For cat **5b**: 42% yield, –65% ee. $[\alpha]_D^{25}$ = –13.6 (*c* = 0.88, in $CHCl_3$). HPLC IA, EtOH/*n*-heptane = 40/60, flow rate = 0.6 mL/min, λ = 230 nm, retention time: 23.2 min, 25.2 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 3H), 3.10 (s, 3H), 2.68 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.67, 147.57, 134.31, 130.51, 127.83, 52.77, 46.05.



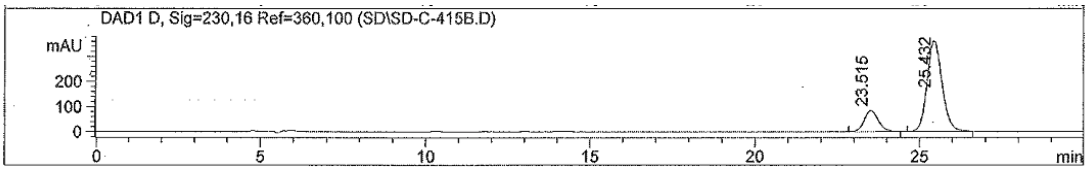
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	23.291	0.4948	359.96408	10686.73438	49.7732
2	25.220	0.5326	337.44434	10784.14551	50.2268



DAD1 D, Sig=230,16 Ref=360,100

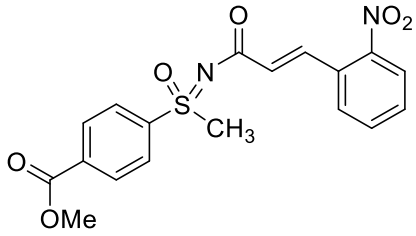
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	23.165	0.4906	261.74963	7705.28564	93.6179
2	25.143	0.5070	17.26686	525.28589	6.3821
Total				8230.57153	100.0000



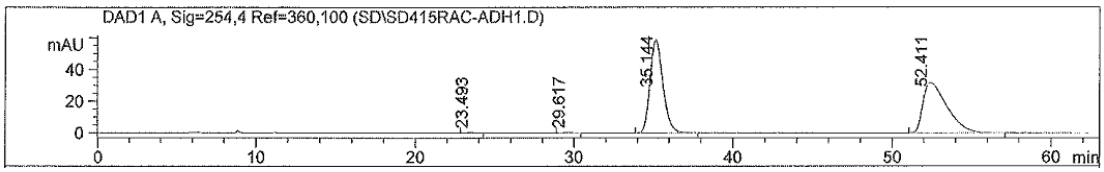
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	23.515	0.4542	84.50294	2492.75635	17.8356
2	25.432	0.4929	361.17230	11483.54199	82.1644

Methyl-(*E*)-4-{*S*-methyl-*N*-[3-(2-nitrophenyl)acryloyl]sulfonimidoyl}benz oate (3j)

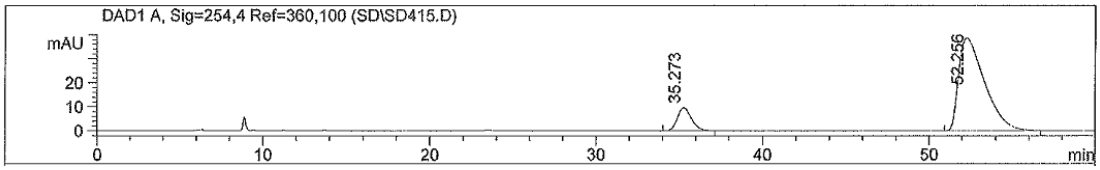


(**$C_{18}H_{16}N_2O_6S$**) a yellow oil. For cat **6c**: 52% yield, 78% ee. $[\alpha]_D^{25}$ = +69.5 (*c* = 1.91, in $CHCl_3$). For cat **5b**: 55% yield, –52% ee. $[\alpha]_D^{25}$ = –23.9 (*c* = 2.28, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 35.1 min, 52.4 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 – 8.24 (m, 2H), 8.18 – 8.08 (m, 3H), 8.00 (dd, J = 8.2, 1.0 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.50 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 6.49 (d, J = 15.6 Hz, 1H), 3.97 (s, 3H), 3.44 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.50, 165.43, 148.50, 142.85, 138.29, 135.14, 133.51, 131.12, 130.93, 130.01, 129.68, 129.21, 127.46, 124.94, 44.22. **IR (ATR)**: ν = 3036, 2929, 2257, 2093, 1928, 1724, 1612, 1521, 1288, 1204, 1082, 974, 835, 735, **MS (EI)**: *m*/*z* = 47.2 (42), 48.2 (22), 49.2 (12), 50.2 (14), 55.2 (14), 57.3 (25), 63.2 (16), 65.3 (17), 71.3 (16), 77.2 (13), 83.0 (100), 85.1 (55), 91.1 (12), 92.2 (15), 389.0 $(M+1)^+$ (1). **MS (ESI)**: ($[M+Na]^+$) 411.061. **HRMS (ESI)** (*m*/*z*) [**$C_{18}H_{16}N_2O_6S$+Na**]$^+$: Calcd. 411.0621, found 411.0621.



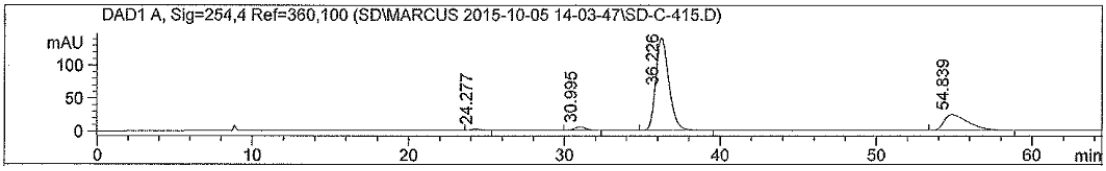
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	23.493	0.5561	0.48491	16.17918	0.2417
2	29.617	0.6847	0.33556	13.78568	0.2060
3	35.144	0.9441	58.72052	3326.20459	49.6987
4	52.411	1.7520	31.74010	3336.56885	49.8536



DAD1 A, Sig=254,4 Ref=360,100

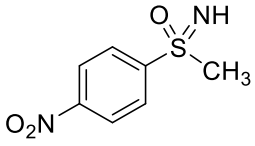
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	35.273	0.9691	9.59646	557.96973	11.7814
2	52.256	1.8034	38.61266	4178.05762	88.2186



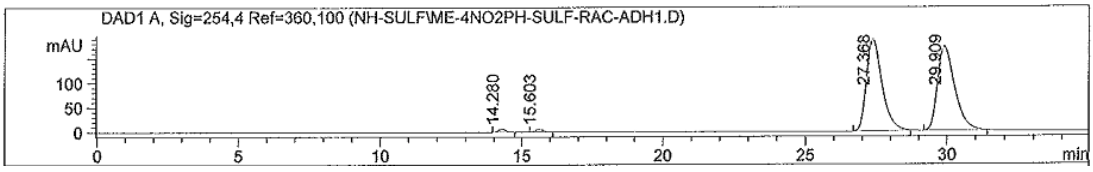
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	24.277	0.6066	2.16065	78.64447	0.7088
2	30.995	0.8051	5.13148	247.87189	2.2338
3	36.226	0.9761	140.16263	8208.52832	73.9760
4	54.839	1.7952	23.77806	2561.16089	23.0814

NH-S-Methyl-*S*-(4-nitrophenyl)-sulfoximine (1k)[2a]

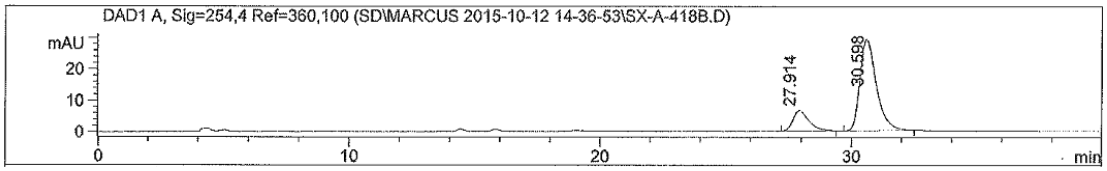


(**$C_7H_8N_2O_3S$**) a yellow solid; For cat **6c**: 55% yield, 65% ee. $[\alpha]_D^{25}$ = +15.2 (*c* = 0.52, in $CHCl_3$). For cat **5b**: 53% yield, –69% ee. $[\alpha]_D^{25}$ = –14.0 (*c* = 0.39, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 254 nm, retention time: 27.4 min (*R*), 29.9 min (*S*). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 – 8.29 (m, 2H), 8.29 – 8.02 (m, 2H), 3.14 (s, 3H), 2.70 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 150.61, 149.51, 129.25, 124.58, 46.05. (*S*)-**1k:** $[\alpha]_D^{25}$ = 18 (c = 1, MeOH).[2d]



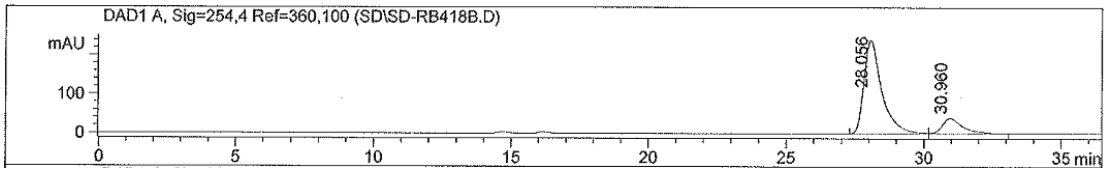
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.280	0.2732	6.75939	120.03467	0.8201
2	15.603	0.2860	6.24298	119.86845	0.8189
3	27.368	0.5797	187.83084	7207.75977	49.2437
4	29.909	0.6342	171.81041	7189.24072	49.1172



DAD1 A, Sig=254,4 Ref=360,100

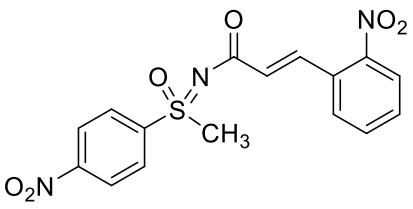
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	27.914	0.7274	6.51864	284.48700	17.7336
2	30.598	0.7561	29.09169	1319.73645	82.2664



DAD1 A, Sig=254,4 Ref=360,100

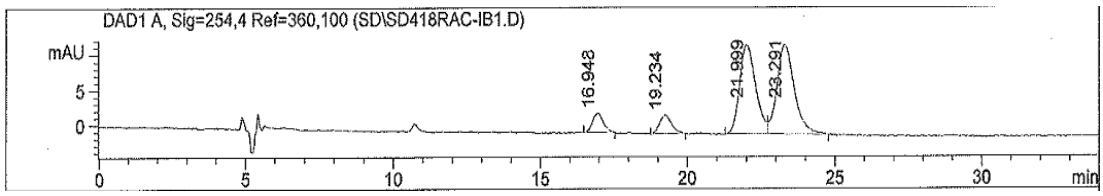
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	28.056	0.7544	240.27162	10876.21973	84.3006
2	30.960	0.8585	39.32306	2025.49048	15.6994

(*E*)-*N*-[Methyl(4-nitrophenyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3k)



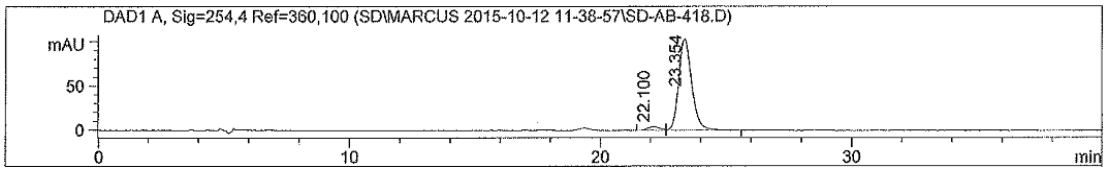
(**$C_{16}H_{13}N_3O_6S$**) a yellow oil. For cat **6c**: 41% yield, 93% ee. $[\alpha]_D^{25}$ = +3.27 (*c* = 1.99, in DMSO). For cat **5b**: 41% yield, –96% ee. $[\alpha]_D^{25}$ = –2.34 (*c* = 0.99, in DMSO). HPLC IB, EtOH/*n*-heptane = 50/50, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 22.0 min, 23.3 min. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.52 – 8.46 (m, 2H), 8.31 – 8.22 (m, 2H), 8.04 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.94 (d, *J* = 6.7 Hz, 1H), 7.81 (d, *J* = 15.7 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.68 – 7.61 (m, 1H), 6.64 (d, *J* = 15.7 Hz, 1H), 3.66 (s, 3H). **^{13}C{^{1}H}**

NMR (100 MHz, DMSO-d_6) δ 172.08, 150.45, 148.41, 144.43, 136.70, 133.80, 130.67, 129.42, 129.13, 129.02, 124.66, 42.54. **IR (ATR)**: ν = 3456, 3089, 2924, 2653, 2302, 2094, 1912, 1740, 1604, 1518, 1200, 976, 755. **MS (EI)**: *m*/*z* = 130.2 (16), 181.1 (89), 227.0 (100), 228.1 (13). **MS (ESI)**: ([M+Na]$^+$) 398.041. **HRMS (ESI)** (*m*/*z*) [$C_{16}H_{13}N_3O_6S$+Na]$^+$: Calcd. 398.0417, found 398.0416.



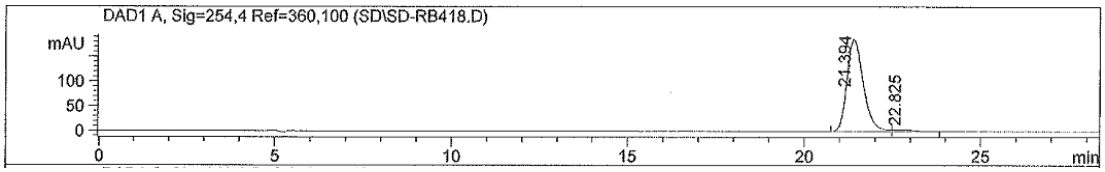
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	16.948	0.4310	2.77501	71.75449	6.2534
2	19.234	0.4602	2.65260	73.24674	6.3835
3	21.999	0.6287	12.71004	479.42862	41.7823
4	23.291	0.6788	12.84140	523.01398	45.5808



DAD1 A, Sig=254,4 Ref=360,100

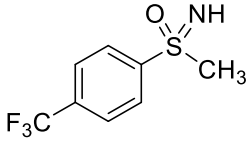
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	22.100	0.5635	4.24963	143.67755	3.7203
2	23.354	0.6013	103.05841	3718.32178	96.2797



DAD1 A, Sig=254,4 Ref=360,100

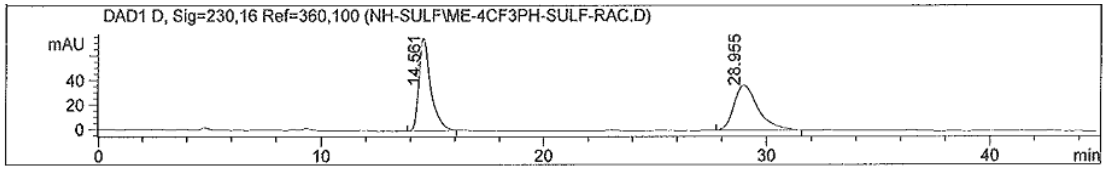
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	21.394	0.5395	185.69749	6010.58691	97.7735
2	22.825	0.6498	3.51052	136.87077	2.2265

NH-S-Methyl-*S*-[4-(trifluoromethyl)phenyl]-sulfoximine (1l)[13]

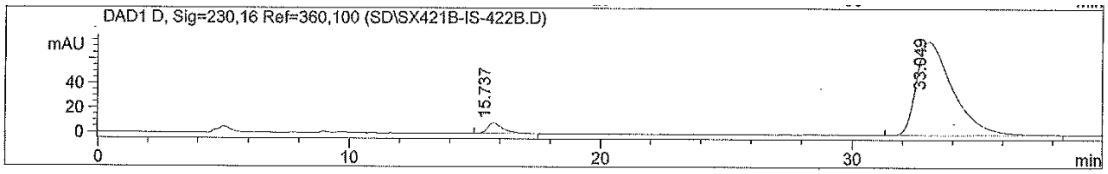


(**$C_8H_8F_3NOS$**) a white solid. For cat **6c**: 44% yield, 91% ee. $[\alpha]_D^{25}$ = +16.3 (*c* = 1.1, in $CHCl_3$). For cat **5b**: 47% yield, –87% ee. $[\alpha]_D^{25}$ = –15.3 (*c* = 0.8, in $CHCl_3$). HPLC OJ,

EtOH/*n*-heptane = 30/70, flow rate = 0.6 mL/min, λ = 230 nm, retention time: 14.6 min, 29.0 min. Or HPLC ADH, EtOH/*n*-heptane = 15/85, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 30.1 min, 33.0 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 3.12 (s, 3H), 2.58 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 147.32, 135.01 (q, *J* = 33.0 Hz), 128.47, 126.57 (q, *J* = 3.7 Hz), 123.35 (d, *J* = 273.0 Hz), 46.14. **^{19}F NMR (375 MHz, $CDCl_3$)** δ −63.15.

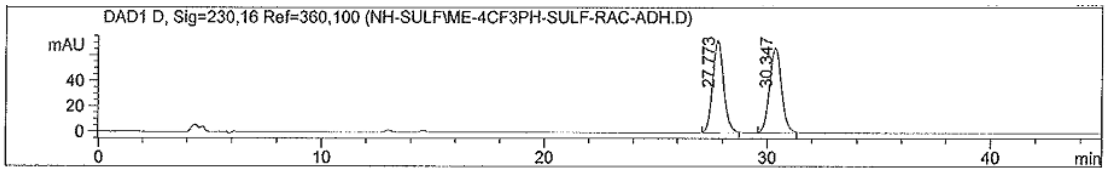


Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	14.561	0.6291	184.08417	6948.41797	49.6580
2	28.981	1.2700	92.43967	7044.13086	50.3420



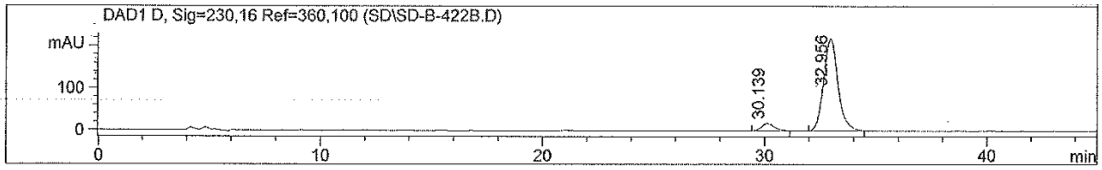
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	15.737	0.7060	8.77597	371.74878	4.6175
2	33.049	1.6874	75.84718	7679.03516	95.3825



DAD1 D, Sig=230,16 Ref=360,100

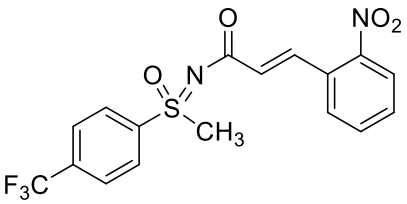
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	27.773	0.5227	72.18268	2454.39111	50.0429
2	30.347	0.5664	66.41125	2450.18677	49.9571



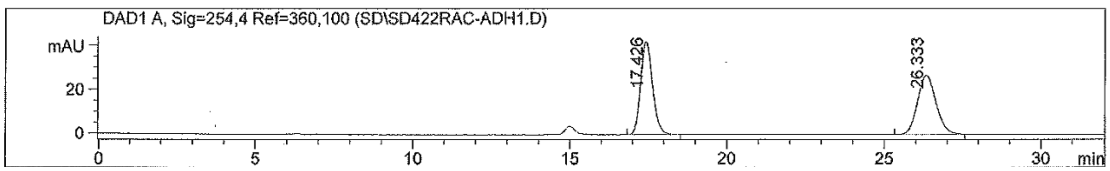
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	30.139	0.5521	17.49603	687.02271	6.5199
2	32.956	0.6876	219.46620	9850.32422	93.4801

(*E*)-*N*-{Methyl(oxo)[4-(trifluoromethyl)phenyl]-λ^6-sulfanylidene}-3-(2-nitrophenyl)acrylamide (3l)

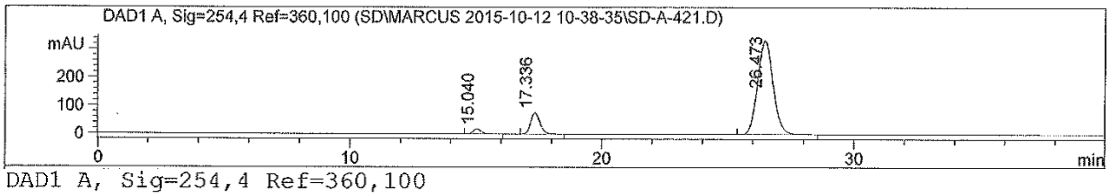


(**$C_{17}H_{13}F_3N_2O_4S$**) a yellow solid, melting point: 104-105 °C. For cat **6c**: 54% yield, 76% ee. $[\alpha]_D^{25}$ = +30.8 (*c* = 2.26, in $CHCl_3$). For cat **5b**: 52% yield, –80% ee. $[\alpha]_D^{25}$ = –31.2 (*c* = 2.04, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 17.4 min, 26.3 min. **^{1}H NMR (100 MHz, $CDCl_3$)** δ 8.19-8.15 (m, 3H), 8.02 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.61 (m, 2H), 7.52 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 3.44 (s, 3H). **^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$)** δ 173.56, 148.54, 142.65, 138.57, 136.28, 135.78 (q, *J* = 33.3 Hz), 131.12, 130.10, 129.55, 129.25, 128.07, 127.05 (dd, *J* = 7.2, 3.5 Hz),125.00, 123.17 (d, *J* = 273.3 Hz), 44.30. **^{19}F NMR (375 MHz, $CDCl_3$)** δ –63.27. **IR (ATR)**: ν = 3880, 3366, 3066, 2919, 2655, 2316, 2104, 1926, 1610, 1522, 1439, 1304, 1199, 983, 872, 756. **MS (EI)**: *m*/*z* = 50.3 (28), 51.3 (30), 62.2 (11), 63.2 (100), 64.2 (16), 65.3 (25), 74.2 (19), 75.2 (48), 76.2 (53), 77.2 (26), 89.1 (83), 90.2 (23), 91.1 (13), 92.2 (16), 95.2 (19), 101.1 (15), 102.1 (36), 125.1 (20), 126.1 (11), 130.1 (10), 133.1 (13), 145.1 (75), 165.0 (18), 192.0 (17), 193.0 (47), 208.0 (10), 250.0 (36). **MS (ESI)**: ([M+Na]$^+$) 421.043. **HRMS (ESI)** (*m*/*z*) [**$C_{17}H_{13}F_3N_2O_4S$+Na**]$^+$: Calcd. 421.0440, found 421.0433.



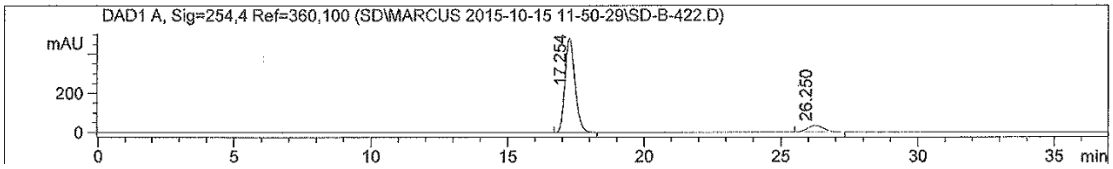
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.426	0.4382	42.34636	1113.45337	50.0798
2	26.333	0.6878	26.89562	1109.90430	49.9202



DAD1 A, Sig=254,4 Ref=360,100

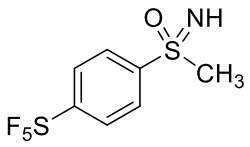
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	15.040	0.3537	17.41046	369.50061	2.2396
2	17.336	0.4319	75.03887	1944.60315	11.7864
3	26.473	0.7089	333.50058	14184.59766	85.9740



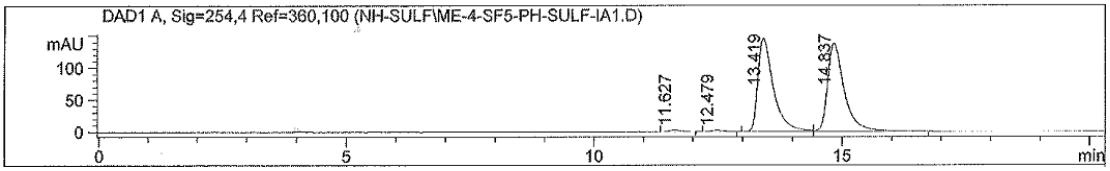
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.254	0.3951	481.12769	12333.77539	89.7934
2	26.250	0.6104	34.47836	1401.95117	10.2066

NH-S-Methyl-*S*-[4-(pentafluorosulfanyl)phenyl]-sulfoximine (1m)[14]

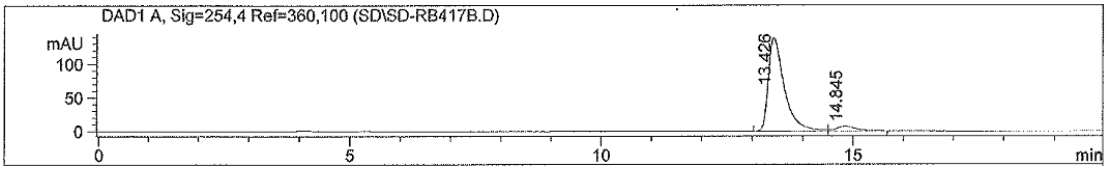


($C_7H_8F_5NOS_2$) a white solid; For cat **6c**: 43% yield, 88% ee. $[\alpha]_D^{25}$ = +12.9 (*c* = 0.93, in $CHCl_3$). For cat **5b**: 41% yield, −93% ee. $[\alpha]_D^{25}$ = −13.1 (*c* = 1.05, in $CHCl_3$). HPLC IA, 2-propanol /*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 254 nm, retention time: 13.4 min, 14.8 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.98 – 7.92 (m, 2H), 3.13 (s, 3H), 2.61 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 157.09 (t, *J* = 18.7 Hz), 146.96, 128.57, 127.59 – 126.68 (m), 46.08. **^{19}F NMR (375 MHz, $CDCl_3$)** δ 81.92 (tt, *J* = 155.3, 147.6 Hz, 1F), 62.62 (d, *J* = 150.5, 4F).



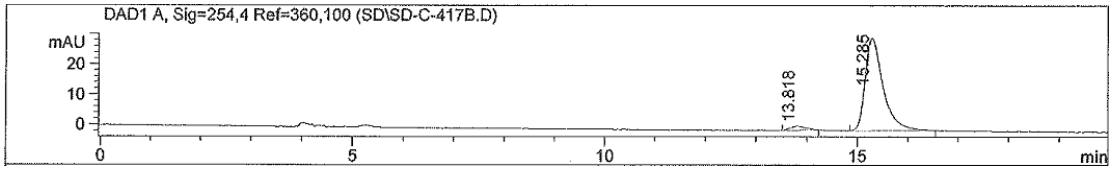
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	11.627	0.2154	2.77682	47.45623	0.7327
2	12.479	0.2316	2.51225	44.28370	0.6837
3	13.419	0.3612	145.77846	3159.22656	48.7770
4	14.837	0.3899	137.88666	3225.90894	49.8066



DAD1 A, Sig=254,4 Ref=360,100

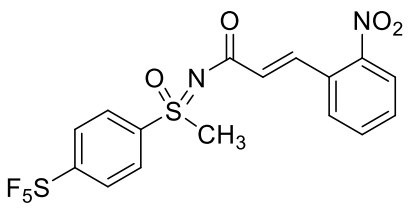
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	13.426	0.3659	138.79639	3047.37036	94.0190
2	14.845	0.4412	7.32243	193.85893	5.9810



DAD1 A, Sig=254,4 Ref=360,100

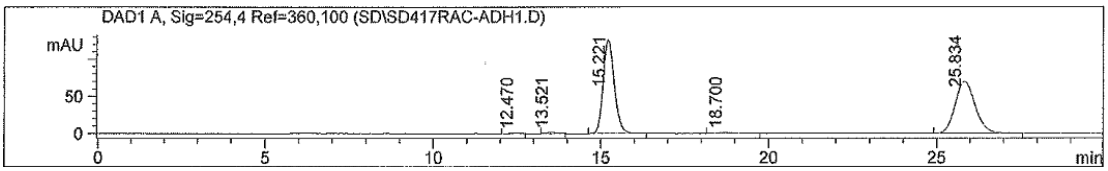
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	13.818	0.3554	1.34639	28.70843	3.6511
2	15.285	0.4130	30.57507	757.59357	96.3489

(*E*)-*N*-{Methyl(oxo)[4-(pentafluoro-λ^6-sulfanyl)phenyl]-λ^6-sulfanylidene}-3-(2-nitrophenyl)acrylamide (3m)



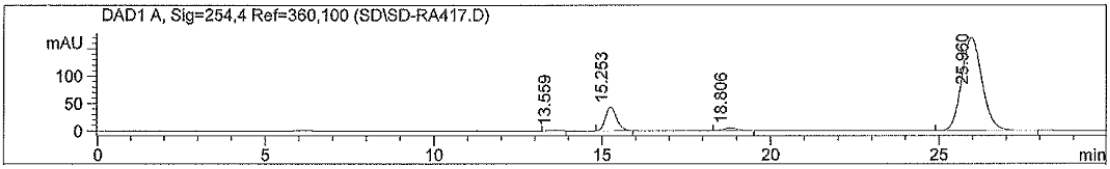
(**$C_{16}H_{13}F_5N_2O_4S_2$**) a yellow solid, melting point: 110-111 °C. For cat **6c**: 53% yield, 75% ee. $[\alpha]_D^{25}$ = +27.8 (*c* = 2.34, in $CHCl_3$). For cat **5b**: 56% yield, –73% ee. $[\alpha]_D^{25}$ = –27.0 (*c* = 2.50, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 15.2 min, 25.8 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 – 8.13 (m, 3H), 8.02 (dd, *J* = 7.1, 1.9 Hz, 3H), 7.70 – 7.60 (m, 2H), 7.52 (ddd, *J* = 8.6, 6.9, 2.0 Hz, 1H), 6.48 (d, *J* = 15.7 Hz, 1H), 3.44 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.35, 157.40 (t, *J* = 18.7 Hz), 148.32, 142.12, 138.51, 133.43, 130.85, 129.98, 129.21, 129.06, 128.02, 127.77 – 127.47 (m),124.82, 44.05. **^{19}F NMR (375 MHz, $CDCl_3$)** δ

82.58 – 79.99 (m, 1F), 62.51 (d, *J* = 150.5 Hz, 4F). **IR (ATR)**: ν = 3032, 2931, 2257, 1741, 1612, 1522, 1294, 1207, 1102, 976, 832, 736. **MS (EI)**: *m/z* = 50.2 (15), 51.2 (20), 63.1 (45), 64.2 (12), 65.2 (20), 75.1 (25), 76.1 (25), 77.1 (18), 83.2 (12), 89.1 (68), 90.1 (12), 92.1 (14), 95.1 (17), 102.0 (17), 130.1 (19), 308.0 (100), 410.0 (28). **MS (ESI)**: ([M+Na]$^+$) 479.012. **HRMS (ESI)** (*m/z*) [$\mathbf{C_{16}H_{13}F_5N_2O_4S_2}$+**Na**]$^+$: Calcd. 479.0129, found 479.0126.



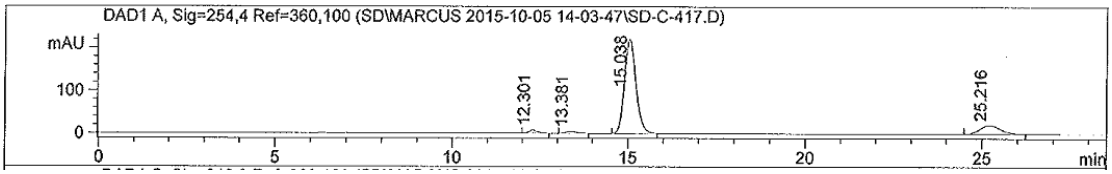
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	12.470	0.2976	0.71048	12.68594	0.2153
2	13.521	0.2406	1.48437	28.82849	0.4894
3	15.221	0.3847	126.09164	2910.43091	49.4033
4	18.700	0.5810	1.08672	37.88031	0.6430
5	25.834	0.6929	69.78643	2901.34082	49.2490



DAD1 A, Sig=254,4 Ref=360,100

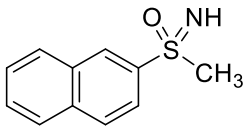
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	13.559	0.3460	1.43098	29.70414	0.3588
2	15.253	0.3529	43.37567	999.93292	12.0775
3	18.806	0.3907	5.00032	142.58319	1.7222
4	25.960	0.6988	169.51630	7107.10547	85.8416



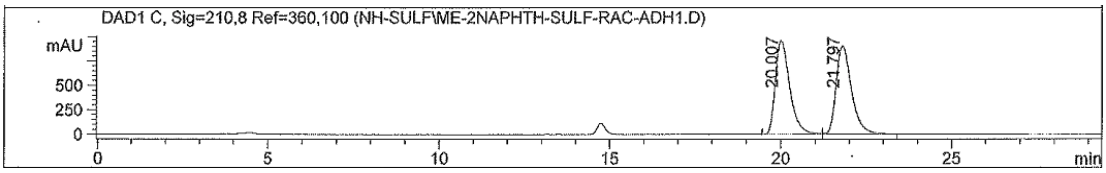
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	12.301	0.2638	7.62835	131.93282	2.2066
2	13.381	0.2972	4.62994	91.77205	1.5349
3	15.038	0.3464	220.45569	4957.48828	82.9167
4	25.216	0.5760	20.40696	797.68298	13.3417

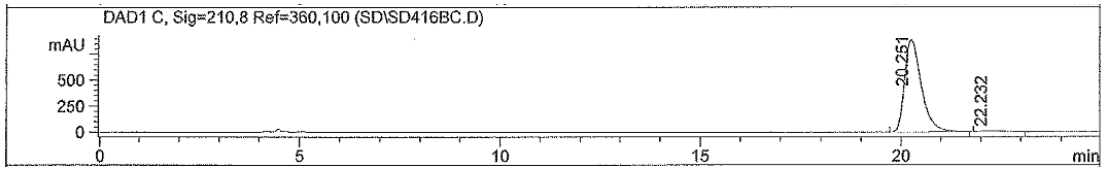
***NH-S*-Methyl-*S*-(2-naphthyl)-sulfoximine (1n)[2a,11]**



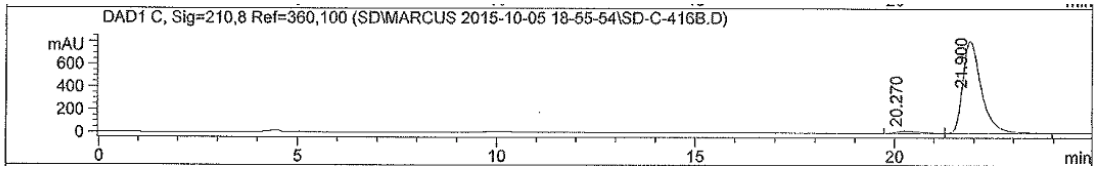
(**$C_{11}H_{11}NOS$**) a white solid, melting point: 144-145 °C. For cat **6c**: 43% yield, 96% ee. $[\alpha]_D^{25}$ = +20.8 (*c* = 0.88, in $CHCl_3$). For cat **5b**: 44% yield, –95% ee. $[\alpha]_D^{25}$ = –19.5 (*c* = 0.82, in $CHCl_3$). HPLC ADH, 2-propanol /*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 210 nm, retention time: 20.0 min, 21.8 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (d, *J* = 0.7 Hz, 1H), 8.01 – 7.95 (m, 3H), 7.95 – 7.89 (m, 1H), 7.69 – 7.58 (m, 2H), 3.16 (s, 3H), 2.65 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 140.48, 135.11, 132.41, 129.66, 129.42, 129.12, 129.06, 128.00, 127.70, 122.94, 46.28.



Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	20.007	0.4494	959.38928	28071.63672	49.7713
2	21.797	0.4777	903.71429	28329.64648	50.2287

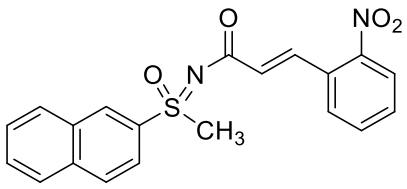


Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	20.251	0.4859	890.46887	25961.85938	98.8110
2	22.232	0.5637	9.23589	312.40036	1.1890

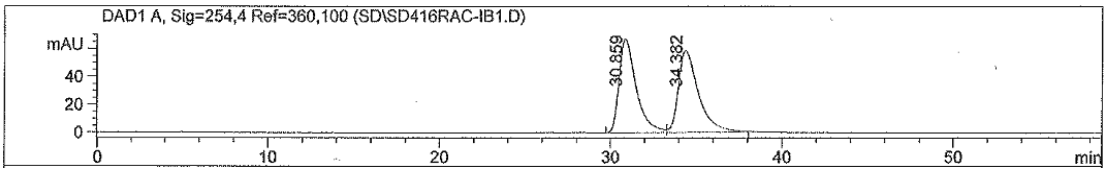


Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	20.270	0.5876	20.88005	736.09375	2.7345
2	21.900	0.5389	809.79309	26182.21289	97.2655

Methyl-(*E*)-4-{*S*-methyl-*N*-[3-(2-nitrophenyl)acryloyl]sulfonimidoyl}benz oate (3n)

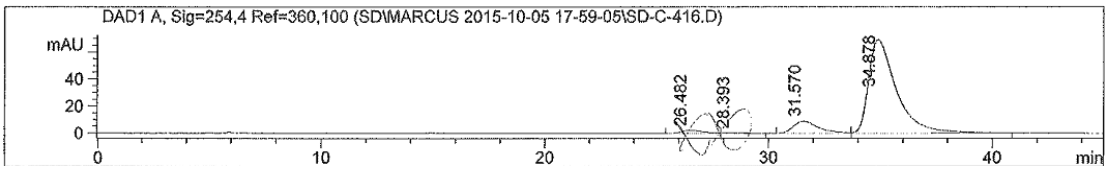


(**$C_{20}H_{16}N_2O_4S$**) a yellow oil. For cat **6c**: 54% yield, 79% ee. $[\alpha]_D^{25}$ = +34.3 (*c* = 1.87, in $CHCl_3$). For cat **5b**: 54% yield, –80% ee. $[\alpha]_D^{25}$ = –35.5 (*c* = 1.66, in $CHCl_3$). HPLC IB, 2-propanol/*n*-heptane = 50/50, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 30.9 min, 34.4 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (d, *J* = 1.8 Hz, 1H), 8.20 (d, *J* = 15.6 Hz, 1H), 8.05 (t, *J* = 7.3 Hz, 2H), 8.00 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.72 – 7.59 (m, 4H), 7.53 – 7.44 (m, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 3.50 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.64, 148.52, 137.89, 135.47, 133.47, 132.42, 131.23, 130.29, 130.10, 129.90, 129.64, 129.61, 129.44, 129.20, 128.12, 128.06, 124.91, 121.61, 44.45. **IR (ATR)**: ν = 3040, 2928, 2255, 2094, 1612, 1521, 1293, 1204, 1074, 974, 831, 740. **MS (EI)**: *m*/*z* = 47.2 (63), 48.2 (37), 49.1 (20), 50.1 (13), 83.0 (100), 85.0 (62), 87.0 (10). **MS (ESI)**: ([M+Na]$^+$) 403.072. **HRMS (ESI)** (*m*/*z*) [**$C_{20}H_{16}N_2O_4S$+Na**]$^+$: Calcd. 403.0723 , found 403.0724.



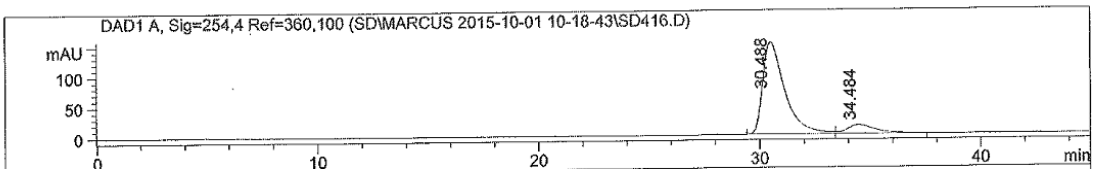
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	30.859	1.1656	66.97008	4683.51123	49.4349
2	34.382	1.3612	58.65851	4790.58398	50.5651



DAD1 A, Sig=254,4 Ref=360,100

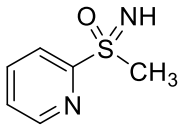
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	26.482	1.1587	2.12867	147.99055	2.1785
2	28.393	1.1458	0.42542	29.24714	0.4305
3	31.570	1.2530	9.00661	677.09027	9.9670
4	34.878	1.4275	69.34054	5938.99463	87.4240



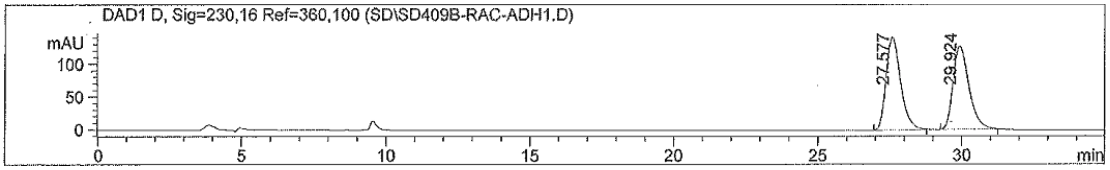
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	30.488	1.1404	151.31187	10353.42383	89.2644
2	34.484	1.4479	14.33308	1245.18506	10.7356

NH-S-Methyl-*S*-(2-pyridyl)-sulfoximine (10)[2a,11]

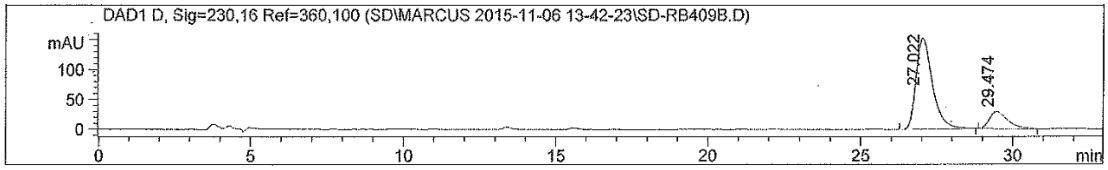


(**$C_6H_8N_2OS$**) a yellow solid. For cat **6c**: 44% yield, 65% ee. $[\alpha]_D^{25}$ = +9.3 (*c* = 0.69, in $CHCl_3$). For cat **5b**: 44% yield, –61% ee. $[\alpha]_D^{25}$ = –8.5 (*c* = 0.63, in $CHCl_3$). HPLC ADH, EtOH/*n*-heptane = 20/80, flow rate = 0.8 mL/min, λ = 230 nm, retention time: 27.6 min, 29.9 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (d, *J* = 4.3 Hz, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.93 (td, *J* = 7.8, 1.7 Hz, 1H), 7.49 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 3.24 (s, 3H), 2.70 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 160.59, 150.12, 138.34, 126.81, 121.16, 42.41.



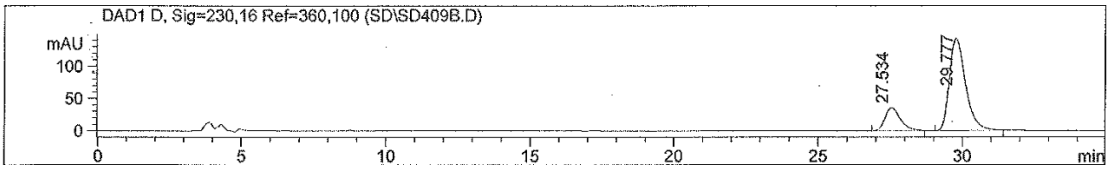
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	27.577	0.5369	141.07852	4969.00146	50.3565
2	29.924	0.5931	126.68403	4898.65430	49.6435



DAD1 D, Sig=230,16 Ref=360,100

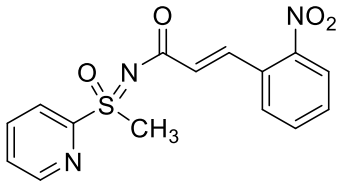
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	27.022	0.6296	152.91451	5776.82178	82.4245
2	29.474	0.7013	29.27465	1231.80444	17.5755



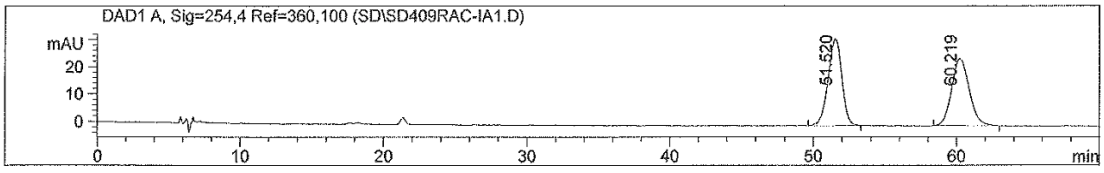
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	27.534	0.6152	35.64132	1315.69421	19.1090
2	29.777	0.6516	142.46613	5569.51709	80.8910

(*E*)-*N*-[(Methyl)(2-pyridyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (30)[2a,11]

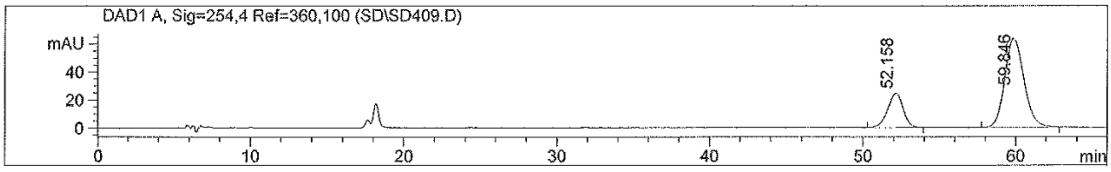


(**$C_{15}H_{13}N_3O_4S$**) a yellow oil. For cat **6c**: 52% yield, 43% ee. $[\alpha]_D^{25}$ = +12.0 (*c* = 1.67, in $CHCl_3$). For cat **5b**: 54% yield, –53% ee. $[\alpha]_D^{25}$ = –16.0 (*c* = 1.86, in $CHCl_3$). HPLC IA, EtOH/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 51.5 min, 60.2 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.33 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.07 (d, *J* = 15.7 Hz, 1H), 8.02 (td, *J* = 7.8, 1.7 Hz, 1H), 7.96 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.50 – 7.45 (m, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 3.51 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.32, 156.80, 150.10, 148.51, 138.43, 137.87, 133.39, 131.08, 129.89, 129.51, 129.12, 127.57, 124.84, 123.51, 39.87. **IR (ATR)**: ν = 3510, 3041, 2929, 2326, 1876, 1732, 1606, 1521, 1436, 1296, 1202, 974, 858, 753. **MS (EI)**: *m*/*z* = 51.4 (11), 78.3 (100), 88.2 (40), 96.2 (35), 130.2 (18), 183.1 (50), 285.0 (15). **MS (ESI)**: ([M+Na]$^+$) 354.051. **HRMS (ESI)** (*m*/*z*) [**$C_{15}H_{13}N_3O_4S$+Na**]$^+$: Calcd. 354.0519, found 354.0512.



DAD1 A, Sig=254,4 Ref=360,100

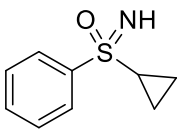
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	51.520	1.1108	31.85859	2123.39844	50.3210
2	60.219	1.4249	24.52022	2096.30640	49.6790



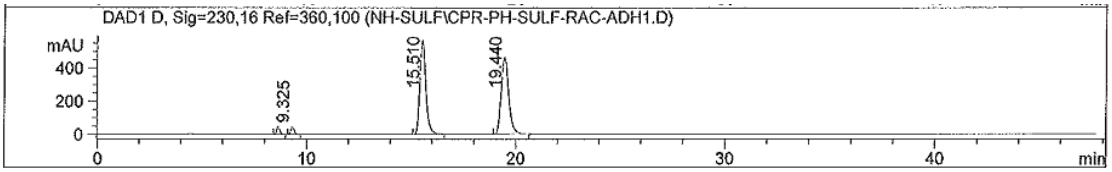
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	52.158	1.1749	24.36259	1717.41382	23.4880
2	59.846	1.4642	63.67914	5594.47314	76.5120

NH-S-Cyclopropyl-*S*-phenyl-sulfoximine (1p)[11b]

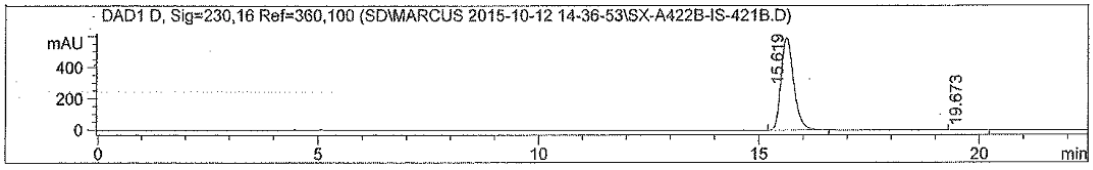


(**$C_9H_{11}NOS$**) a white solid; For cat **6c**: 44% yield, 99% ee. $[\alpha]_D^{25}$ = –11.8 (*c* = 0.76, in $CHCl_3$). For cat **5b**: 44% yield, –93% ee. $[\alpha]_D^{25}$ = +10.8 (*c* = 0.61, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 15.5 min, 19.4 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (ddd, *J* = 7.0, 3.2, 1.9 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.56 – 7.48 (m, 2H), 2.57 – 2.49 (m, 2H), 1.37 (ddt, *J* = 9.8, 7.0, 4.9 Hz, 1H), 1.22 – 1.14 (m, 1H), 1.08 – 0.98 (m, 1H), 0.94 – 0.85 (m, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 143.23, 132.85, 129.20, 127.93, 34.32, 6.09, 5.72.



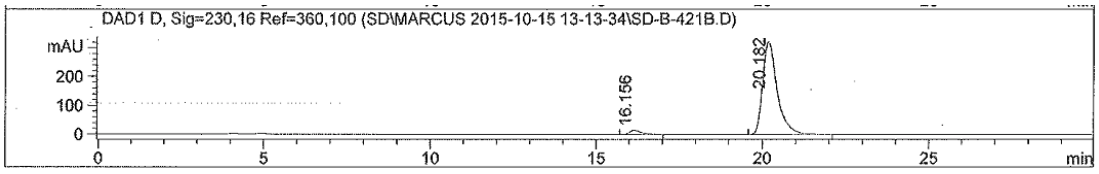
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	8.642	0.1646	46.81973	499.85938	2.0471
2	9.325	0.1743	43.95275	498.28677	2.0406
3	15.510	0.3157	564.58356	11697.48633	47.9050
4	19.440	0.3894	462.99667	11722.44531	48.0072



DAD1 D, Sig=230,16 Ref=360,100

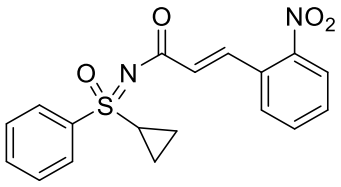
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	15.619	0.3069	593.01263	11837.69238	99.5042
2	19.673	0.3846	2.22950	58.97961	0.4958



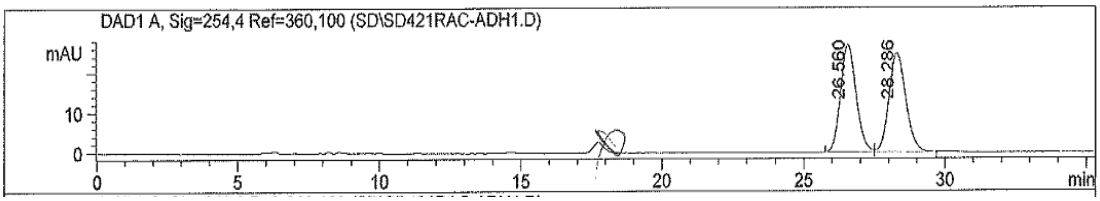
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	16.156	0.4159	14.78821	369.02640	3.6356
2	20.182	0.5048	322.96982	9781.45020	96.3644

(*E*)-*N*-[Cyclopropyl(oxo)(phenyl)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acryl amide (3p)

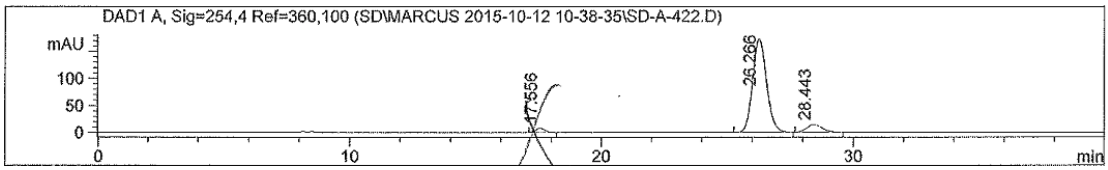


(**$C_{18}H_{16}N_2NaO_4S$**) a yellow solid, melting point: 105-106 °C. For cat **6c**: 54% yield, 84% ee. $[\alpha]_D^{25}$ = +11.4 (*c* = 2.00, in $CHCl_3$). For cat **5b**: 54% yield, –79% ee. $[\alpha]_D^{25}$ = –9.26 (*c* = 2.22, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 26.6 min, 28.3 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 15.6 Hz, 1H), 8.00 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.96 (dt, *J* = 3.4, 2.4 Hz, 2H), 7.70 – 7.55 (m, 5H), 7.53 – 7.45 (m, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 2.74 (tt, *J* = 7.9, 4.8 Hz, 1H), 1.68 (ddt, *J* = 10.3, 7.4, 5.1 Hz, 1H), 1.36 (ddt, *J* = 10.3, 7.3, 5.1 Hz, 1H), 1.26 (dtd, *J* = 12.9, 7.8, 5.4 Hz, 1H), 1.10 – 1.00 (m, 1H). **^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$)** δ 173.03, 148.50, 139.05, 137.54, 133.58, 133.45, 131.30, 130.25, 129.83, 129.71, 129.18, 127.36, 124.90, 33.46, 7.10, 5.52. **IR (ATR)**: ν = 3504, 3060, 2861, 2661, 2324, 2097, 1907, 1612, 1519, 1287, 1199, 1068, 884, 727. **MS (EI)**: *m*/*z* = 89.2 (26), 125.1 (100), 130.2 (20), 133.1 (27), 182.1 (10), 208.1 (29), 357.0 (M+1) $^+$ (9). **MS (ESI)**: ([M+Na$^+$]) 379.071. **HRMS (ESI)** (*m*/*z*) [**$C_{18}H_{16}N_2NaO_4S$+Na**]$^+$: Calcd. 379.0723, found 379.0721.



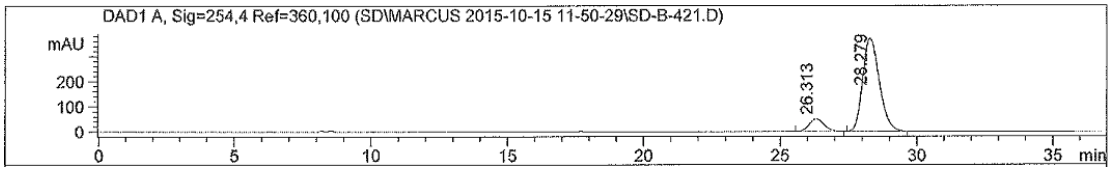
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	26.560	0.6397	26.87556	1031.61096	50.0261
2	28.286	0.6936	24.76398	1030.53491	49.9739



DAD1 A, Sig=254,4 Ref=360,100

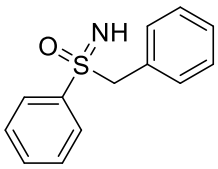
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.556	0.3588	7.92529	194.84795	2.6425
2	26.266	0.6371	172.59323	6597.81738	89.4786
3	28.443	0.6812	14.21398	580.96027	7.8789



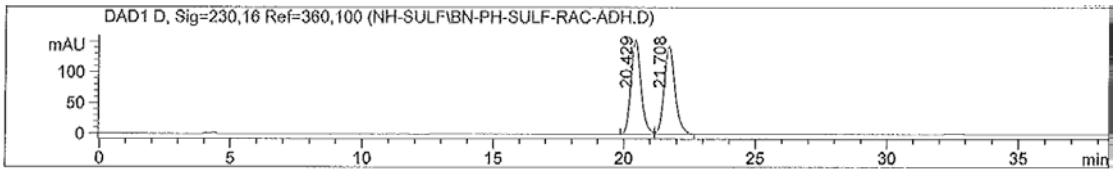
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	26.313	0.5870	50.03959	1900.20007	10.8178
2	28.279	0.6593	370.49664	15665.36719	89.1822

NH-S-Benzyl-*S*-phenyl-sulfoximine (1q)[15]

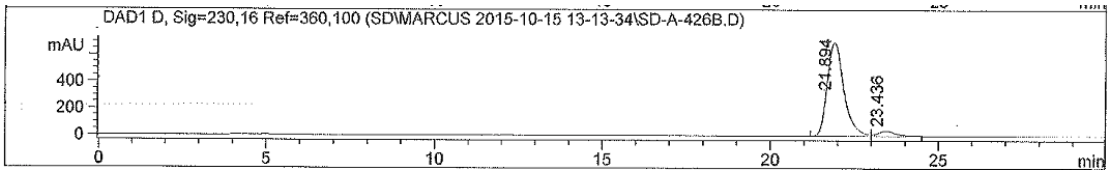


(**$C_{13}H_{13}NOS$**) a white solid; For cat **6c**: 45% yield, 90% ee. $[\alpha]_D^{25}$ = –22.4 (*c* = 0.97, in $CHCl_3$). For cat **5b**: 40% yield, –90% ee. $[\alpha]_D^{25}$ = +22.3 (*c* = 0.79, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 20.4 min, 21.7 min. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.77 (dd, *J* = 7.8, 0.6 Hz, 2H), 7.64 – 7.51 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 4.39 (d, *J* = 13.4 Hz, 1H), 4.31 (d, *J* = 13.4 Hz, 1H), 2.81 (s, 1H). **^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)** δ 140.41, 133.19, 131.11, 128.92, 128.84, 128.65, 128.56, 64.71.



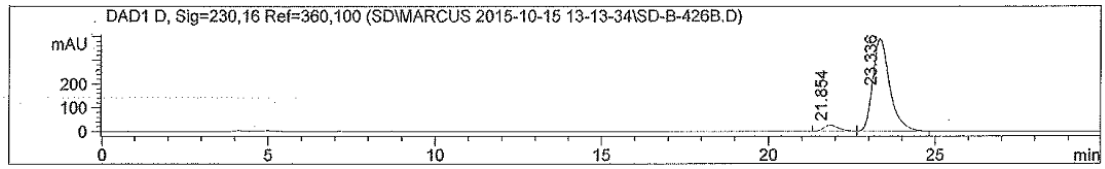
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	20.429	0.4057	152.40967	4045.67285	49.9402
2	21.708	0.4336	142.66501	4055.35596	50.0598
Total				8101.02881	100.0000



DAD1 D, Sig=230,16 Ref=360,100

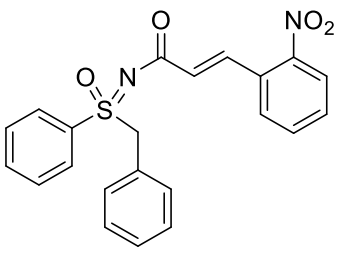
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	21.894	0.5272	699.91089	24067.11328	94.5746
2	23.436	0.5246	38.47472	1380.63464	5.4254



DAD1 A, Sig=254,4 Ref=360,100

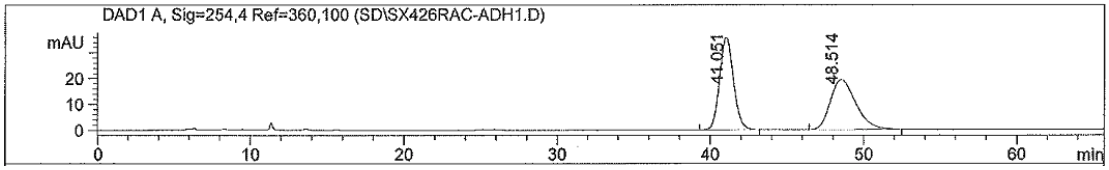
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	21.847	0.3610	3.63931	108.87419	5.0938
2	23.336	0.5233	59.26561	2028.50208	94.9062

(*E*)-*N*-[Benzyl(oxo)(phenyl)-λ^6-sulfanylidene]-3-(2-nitrophenyl) acrylamide (3q)



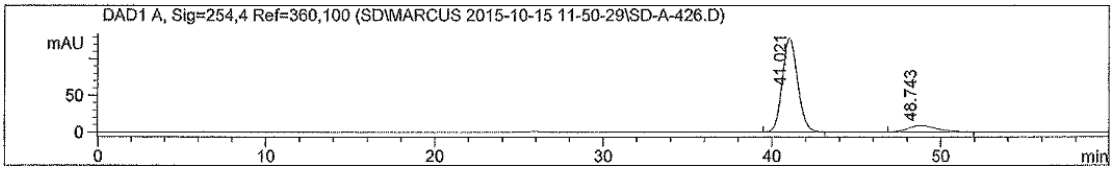
(**$C_{22}H_{18}N_2O_4S$**) a yellow solid, melting point: 116-117 °C. For cat **6c**: 53% yield, 78% ee. $[\alpha]_D^{25}$ = +77.3 (*c* = 2.23, in $CHCl_3$). For cat **5b**: 56% yield, –69% ee. $[\alpha]_D^{25}$ = –75.5 (*c* = 2.61, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 41.1 min, 48.5 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (dd, *J* = 15.6, 4.8 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.60 (dt, *J* = 16.5, 6.5 Hz, 5H), 7.49 – 7.36 (m, 3H), 7.30 – 7.13 (m, 3H), 6.97 (d, *J* = 6.7 Hz, 2H), 6.48 (dd, *J* = 15.6, 5.0 Hz, 1H), 4.77 (dt, *J* = 13.6, 11.3 Hz, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.92, 148.56, 137.81, 135.40, 134.03, 133.49, 131.42, 131.27, 130.32,

129.91, 129.36, 129.27, 129.20, 128.72, 128.68, 127.24, 124.94, 62.46. **IR (ATR)**: ν = 3534, 3312, 3064, 2927, 2666, 2331, 2106, 1994, 1900, 1734, 1640, 1605, 1521, 1446, 1404, 1340, 1288, 1210, 1092, 973, 892, 752, 692. **MS (EI)**: *m*/*z* = 65.4 (12), 91.3 (100), 130.3 (11). **MS (ESI)**: ([M+Na]$^+$) 429.086. **HRMS (ESI)** (*m*/*z*) [$\mathbf{C_{22}H_{18}N_2O_4S}$+**Na**]$^+$: Calcd. 429.0879, found 429.0879.



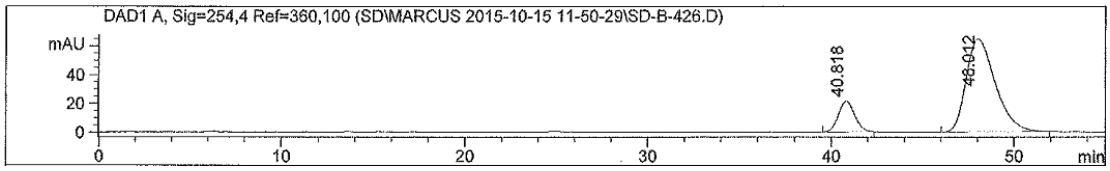
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	41.051	1.0493	35.70842	2248.10059	50.3263
2	48.514	1.9164	19.29782	2218.95190	49.6737



DAD1 A, Sig=254,4 Ref=360,100

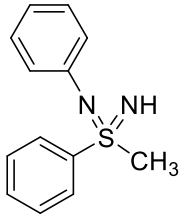
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	41.021	1.0474	128.02086	8044.97070	89.1635
2	48.743	1.9102	8.53108	977.74750	10.8365



DAD1 A, Sig=254,4 Ref=360,100

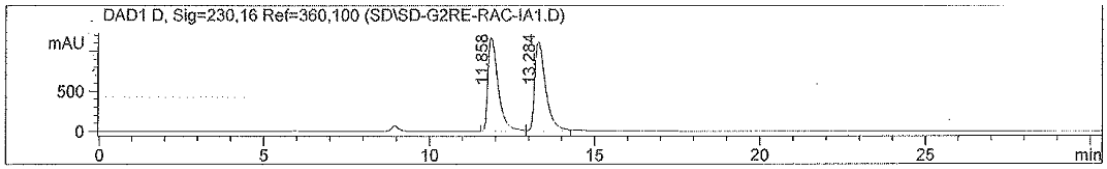
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	40.818	1.0252	21.35405	1313.47058	15.5311
2	48.012	1.8456	64.51118	7143.53809	84.4689

NH-N'-Phenyl-*S*-methyl-*S*-phenyl-sulfondiimide (1r)[16]



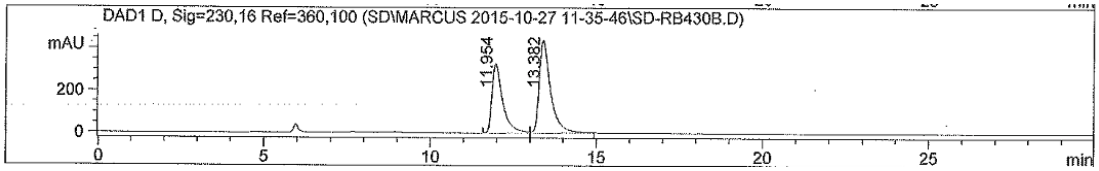
(**$C_{13}H_{14}N_2S$**) a grey solid. For cat **6c**: 82% yield, 11% ee. $[\alpha]_D^{25}$ = –11.3 (*c* = 0.79, in $CHCl_3$). For cat **5b**: 80% yield, –17% ee. $[\alpha]_D^{25}$ = +17.7 (*c* = 0.82, in $CHCl_3$). HPLC IA, 2-propanol/*n*-heptane = 30/70, flow rate = 0.6 mL/min, λ = 230 nm, retention time: 11.9 min (*S*), 13.3

min (*R*). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 – 8.13 (m, 2H), 7.62 – 7.50 (m, 3H), 7.20 – 7.12 (m, 2H), 7.11 – 7.06 (m, 2H), 6.92 – 6.81 (m, 1H), 3.24 (s, 3H), 2.25 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 146.00, 141.94, 132.72, 129.42, 129.04, 127.83, 123.11, 121.01, 48.33. (*R*)-**1r**: $[\alpha]_D^{25}$ = +110.5 (*c* = 1.0, 99% ee,$CHCl_3$)[16]



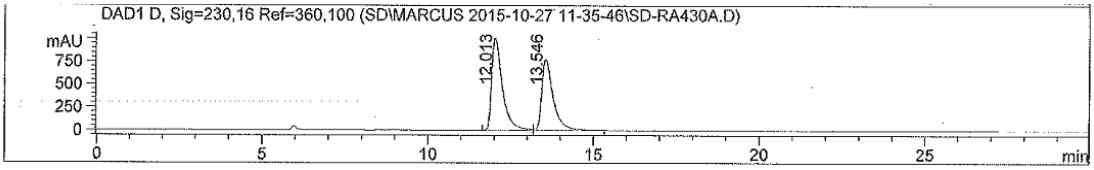
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	11.858	0.3610	1163.13611	25192.28125	49.2144
2	13.284	0.3894	1112.56506	25996.51367	50.7856



DAD1 D, Sig=230,16 Ref=360,100

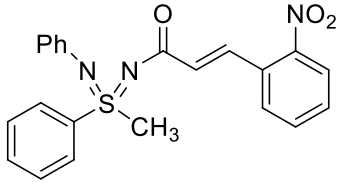
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	11.954	0.3288	328.16852	7391.08008	41.2334
2	13.382	0.3545	438.05786	10533.89844	58.7666



DAD1 A, Sig=254,4 Ref=360,100

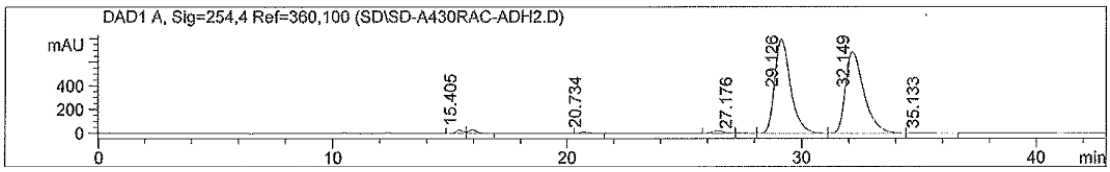
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	12.013	0.3285	936.23303	20907.77344	55.4630
2	13.546	0.3534	700.92310	16789.04688	44.5370

(*E*)-*N*-[Methyl(phenyl)(phenylimino)-λ^6-sulfanylidene]-3-(2-nitrophenyl) acrylamide (3r)



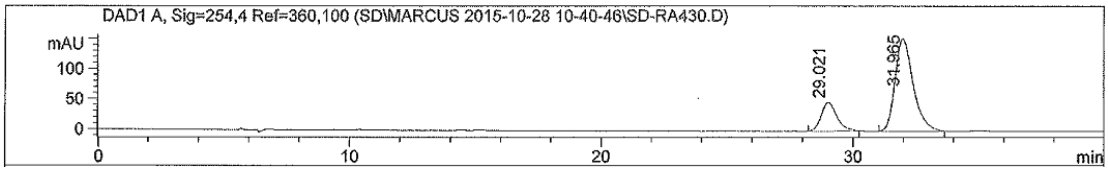
(**$C_{22}H_{19}N_3O_3S$**) a yellow oil. For cat **6c**: 16% yield, 58% ee. $[\alpha]_D^{25}$ = +6.4 (*c* = 0.44, in $CHCl_3$). For cat **5b**: 18% yield, –75% ee. $[\alpha]_D^{25}$ = –7.5 (*c* = 0.42, in $CHCl_3$). HPLC ADH, EtOH/*n*-heptane = 50/50, flow rate = 0.5

mL/min, λ = 254 nm, retention time: 29.1 min, 32.1 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21 (d, *J* = 15.7 Hz, 1H), 8.17 (dt, *J* = 3.5, 2.1 Hz, 2H), 8.02 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.72 – 7.58 (m, 5H), 7.53 – 7.46 (m, 1H), 7.13 (dt, *J* = 9.1, 1.9 Hz, 2H), 7.09 – 7.04 (m, 2H), 6.91 – 6.86 (m, 1H), 6.58 (d, *J* = 15.7 Hz, 1H), 3.72 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.94, 148.53, 144.34, 137.92, 137.08, 133.73, 133.46, 131.51, 130.92, 130.03, 129.75, 129.23, 129.10, 128.27, 124.96, 123.63, 122.01, 45.70. **IR (ATR)**: ν = 3473, 3063, 2928, 2857, 2245, 2112, 1922, 1717, 1639, 1595, 1520, 1484, 1445, 1404, 1256, 1193, 1065, 969, 905, 836, 731, 689. **MS (EI)**: *m*/*z* = 51.4 (32), 55.4 (12), 57.4 (19), 63.3 (13), 64.3 (19), 65.4 (23), 77.3 (36), 78.3 (13), 91.3 (31), 109.3 (15), 124.2 (100), 125.2 (16), 130.2 (29), 166.2 (20), 200.3 (16). **MS (ESI)**: ([M+Na]$^+$) 428.104. **HRMS (ESI)** (*m*/*z*) [$C_{22}H_{19}N_3O_3S$+**Na**]$^+$: Calcd. 428.1039, found 428.1039.



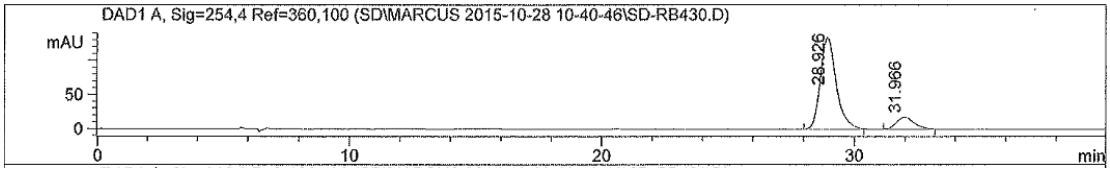
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	15.405	0.3372	31.34211	634.03296	0.8163
2	15.952	0.4050	31.88547	774.75769	0.9975
3	20.734	0.5063	13.14050	399.20367	0.5140
4	26.409	0.5720	21.06226	722.85175	0.9307
5	27.176	0.4054	1.71589	58.32091	0.0751
6	29.126	0.7801	793.92291	37161.28125	47.8452
7	32.149	0.9117	688.19604	37644.51562	48.4673
8	35.133	0.8676	5.28169	274.92816	0.3540



DAD1 A, Sig=254,4 Ref=360,100

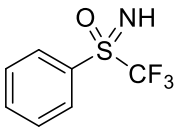
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	29.021	0.6056	47.53400	2035.47913	20.9100
2	31.965	0.7493	152.93034	7698.99902	79.0900



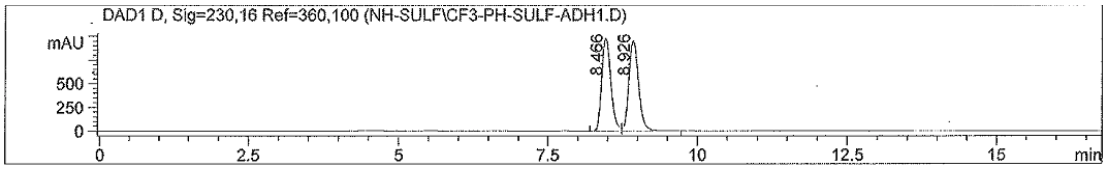
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	28.926	0.6509	134.07367	5847.94824	87.1650
2	31.966	0.5862	17.80624	861.10730	12.8350

NH-S-Phenyl-*S*-trifluoromethylsulfoximine (1s)[17]

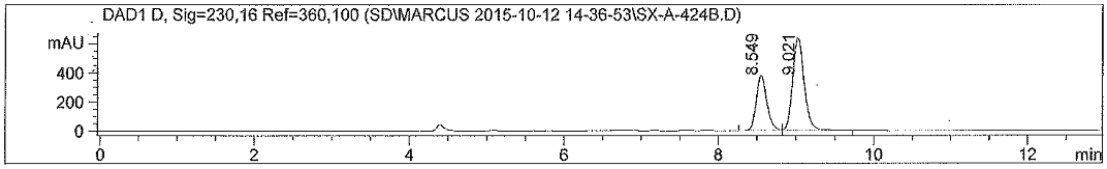


(**$C_7H_6F_3NOS$**) a white solid. For cat **6c**: 30% yield, 30% ee. $[\alpha]_D^{25}$ = +13.3 (*c* = 0.03, in $CHCl_3$). For cat **5b**: 35% yield, 0% ee. HPLC ADH, 2-propanol/*n*-heptane = 20/80, flow rate = 0.7 mL/min, λ = 230 nm, retention time: 8.5 min (*S*), 8.9 min (*R*). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 – 8.12 (m, 2H), 7.82 – 7.74 (m, 1H), 7.68 – 7.60 (m, 2H), 3.63 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 135.58, 131.67, 130.71, 129.60, 121.04 (q, *J* = 332.3 Hz, CF_3). **^{19}F NMR (375 MHz, $CDCl_3$)** δ -78.87. (*R*)-**1s**: $[\alpha]_D^{25}$ = +16.6 (*c* = 0.023, in CH_2Cl_2)[17b]



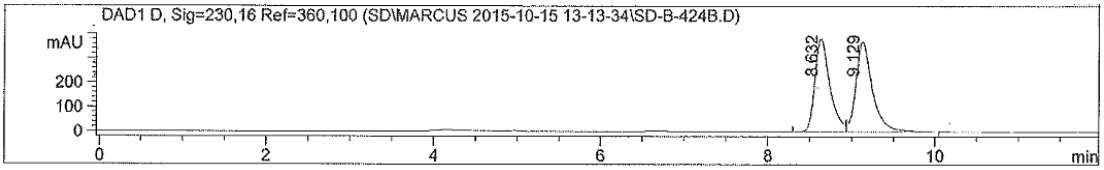
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	8.466	0.1773	984.13007	10466.56934	49.2063
2	8.926	0.1890	952.53247	10804.20996	50.7937



DAD1 D, Sig=230,16 Ref=360,100

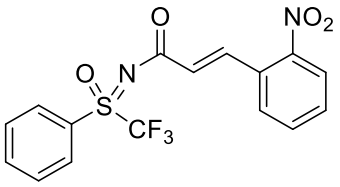
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	8.549	0.1449	380.40948	3616.21362	35.2720
2	9.021	0.1585	642.44836	6636.14160	64.7280



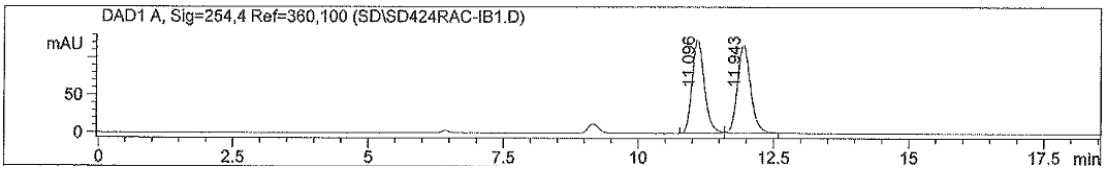
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	8.632	0.1855	381.66580	4758.68066	48.3523
2	9.129	0.2024	369.61230	5083.01074	51.6477

(*E*)-3-(2-*N*itrophenyl)-*N*-[oxo(phenyl)(trifluoromethyl)-λ^6-sulfanylidene] acrylamide (3s)

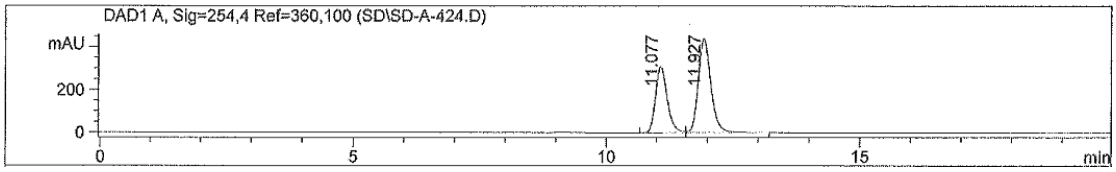


(**$C_{16}H_{11}F_3N_2O_4S$**) a yellow solid, melting point: 192-193 °C. For cat **6c**: 53% yield, 20% ee. $[\alpha]_D^{25}$ = +7.1 (*c* = 2.16, in $CHCl_3$). For cat **5b**: 50% yield, 0% ee. HPLC IB, 2-propanol /*n*-heptane = 50/50, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 11.1 min, 12.0 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 15.6 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 2H), 8.07 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.76 – 7.63 (m, 4H), 7.55 (ddd, *J* = 8.6, 6.9, 1.9 Hz, 1H), 6.54 (d, *J* = 15.6 Hz, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.12, 148.45, 140.51, 136.37, 133.71, 130.84, 130.45, 130.38, 130.32, 129.61, 129.36, 128.42, 125.14, 120.46 (q, *J* = 328.5 Hz). **^{19}F NMR (375 MHz, $CDCl_3$)** δ -74.22. **IR (ATR)**: ν = 3081, 2929, 2643, 2304, 2090, 1912, 1640, 1518, 1236, 1104, 842, 749, 687. **MS (EI)**: *m*/*z* = 51.3 (29), 63.2 (11), 65.2 (20), 69.2 (11), 76.2 (15), 77.2 (68), 89.1 (17), 92.1 (11), 97.1 (18), 102.1 (26), 125.0 (49), 130.1 (72), 151.0 (71), 176.0 (16), 194.0 (12), 221.1 (11), 236.0 (100), 338.0 (26). **MS (ESI)**: ([M+Na]$^+$) 407.027. **HRMS (ESI)** (*m*/*z*) [**$C_{16}H_{11}F_3N_2O_4S$+Na**]$^+$: Calcd. 407.0284, found 407.0279.



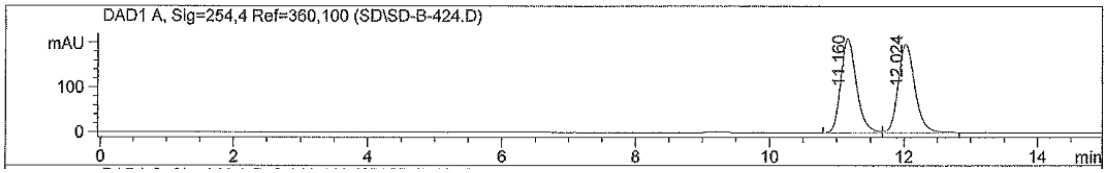
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	11.096	0.2430	124.29418	1971.23523	49.8238
2	11.943	0.2589	117.62961	1985.18054	50.1762



DAD1 A, Sig=254,4 Ref=360,100

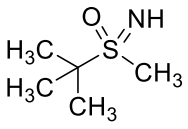
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	11.077	0.2683	309.05746	4975.41162	39.4660
2	11.927	0.2894	439.55841	7631.42432	60.5340



DAD1 A, Sig=254,4 Ref=360,100

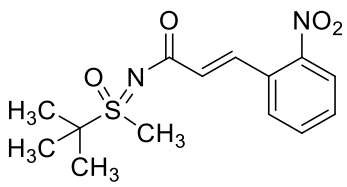
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	11.160	0.2701	209.70497	3398.22534	49.8416
2	12.024	0.2878	198.05962	3419.82642	50.1584

NH-*S*-*tert*-Butyl-*S*-methylsulfoximine (1t)[18]



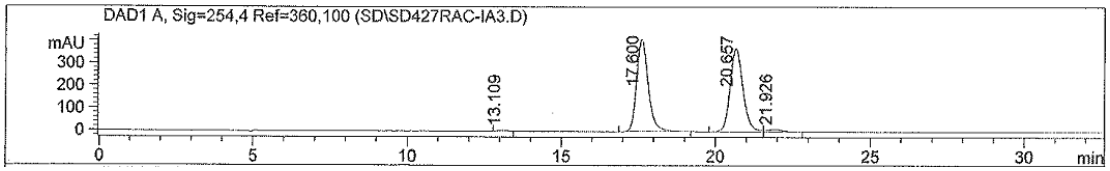
($C_5H_{13}NOS$) a white solid; For cat **6c**: 60% yield. For cat **5b**: 58% yield, $[\alpha]_D^{25}$ = –4.3 (*c* = 1.14, in $CHCl_3$). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 2.79 (s, 3H), 2.29 (s, 1H), 1.35 (s, 9H).

(*E*)-*N*-[*tert*-Butyl(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3t)



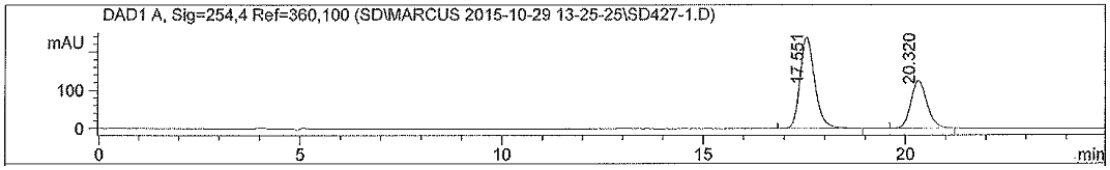
($C_{14}H_{18}N_2O_4S$) a yellow oil. For cat **6c**: 35% yield, 27% ee. $[\alpha]_D^{25}$ = –21.1 (*c* = 1.08, in $CHCl_3$). For cat **5b**: 36% yield, –37% ee. $[\alpha]_D^{25}$ = +28.4 (*c* = 0.58, in $CHCl_3$). HPLC IA, EtOH/*n*-heptane = 30/70, flow rate = 0.7 mL/min, λ = 254 nm, retention time: 17.6 min, 20.7 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 15.6 Hz, 1H), 8.01 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.67 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 (td, *J* = 7.6, 0.7 Hz, 1H), 7.53 – 7.45 (m, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 3.36 (s, 3H), 1.54 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 174.07, 148.45, 137.20, 133.49, 131.44, 130.88, 129.76, 129.20, 124.96, 60.61, 32.49, 23.14. **IR (ATR)**: ν = 3520, 2982, 2937, 2664, 2326, 2251, 2107, 1994, 1909, 1725, 1639, 1600,

1521, 1472, 1406, 1293, 1200, 1052, 962, 904, 840, 727. **MS (EI)**: *m*/*z* = 57.5 (17), 130.3 (10), 176.3 (100), 208.3 (40). **MS (ESI)**: ([M+Na]$^+$) 333.087. **HRMS (ESI)** (*m*/*z*) [$\mathbf{C_{14}H_{18}N_2O_4S}$+**Na**]$^+$: Calcd. 333.0879, found 333.0877.



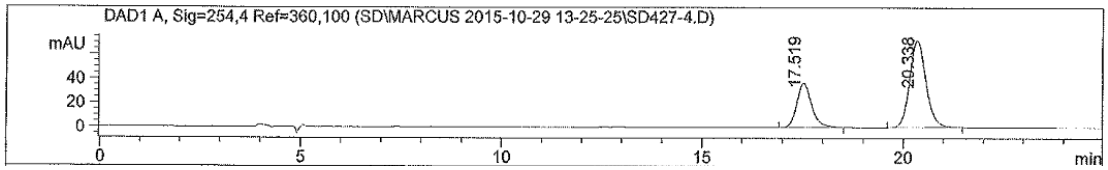
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	13.109	0.2781	5.31948	88.76286	0.4055
2	17.600	0.4384	410.26688	10790.51855	49.2969
3	20.657	0.4820	369.41321	10683.94238	48.8100
4	21.926	0.4953	10.95728	325.60956	1.4876



DAD1 A, Sig=254,4 Ref=360,100

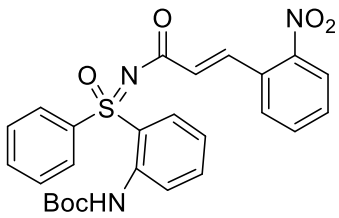
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.551	0.4243	239.32700	6092.45361	63.6446
2	20.320	0.4664	124.36111	3480.16382	36.3554



DAD1 A, Sig=254,4 Ref=360,100

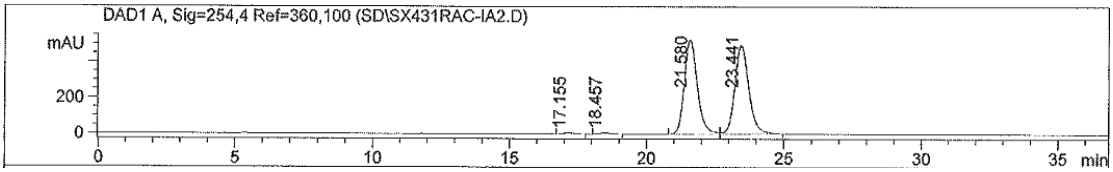
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.519	0.4284	36.72999	944.08710	31.4718
2	20.338	0.4758	72.01142	2055.70142	68.5282

tert-Butyl-(*E*)-(2-{*N*-[3-(2-nitrophenyl)acryloyl]phenylsulfonimidoyl}phenyl)carbamate (3u)



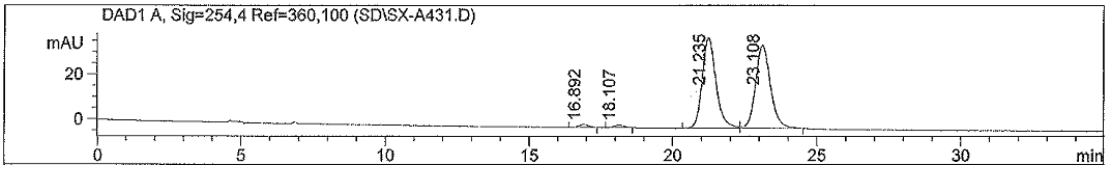
(**$C_{26}H_{25}N_3O_6S$**) a yellow oil. For cat **6c**: 20% yield, 0% ee. For cat **5b**: 25% yield, –10% ee. $[\alpha]_D^{25}$ = +7.0 (*c* = 0.43, in $CHCl_3$). HPLC IA, 2-propanol/*n*-heptane = 25/75, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 21.6 min, 23.4 min. **^{1}H NMR (400 MHz, $CDCl_3$)**

δ 9.39 (s, 1H), 8.27 (d, *J* = 15.7 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.96 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.63 – 7.59 (m, 1H), 7.58 – 7.49 (m, 4H), 7.19 – 7.15 (m, 1H), 6.57 (d, *J* = 15.7 Hz, 1H), 1.45 (s, 9H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 172.71, 152.21, 148.46, 139.15, 138.56, 138.47, 135.05, 133.87, 133.53, 131.13, 130.12, 129.77, 129.66, 129.26, 129.23, 127.50, 125.04, 124.88, 123.11, 122.04, 81.29, 28.31. **IR (ATR)**: ν = 3356, 3075, 2978, 2930, 2665, 2327, 2256, 2107, 1913, 1730, 1646, 1587, 1520, 1436, 1343, 1236, 1157, 1085, 1033, 970, 905, 844, 729. **MS (EI)**: *m*/*z* = 47.4 (27), 48.4 (19), 83.2 (100), 85.2 (67), 87.3 (15), 97.3 (11), 109.3 (14), 118.1 (10), 120.1 (10), 149.3 (16), 153.3 (11), 154.3 (43), 155.3 (10), 173.3 (13), 202.3 (81), 203.3 (15). **MS (ESI)**: ($[M+Na]^+$) 530.134. **HRMS (ESI)** (*m*/*z*) **$[C_{26}H_{25}N_3O_6S+Na]^+$**: Calcd. 530.1356, found 530.1344.



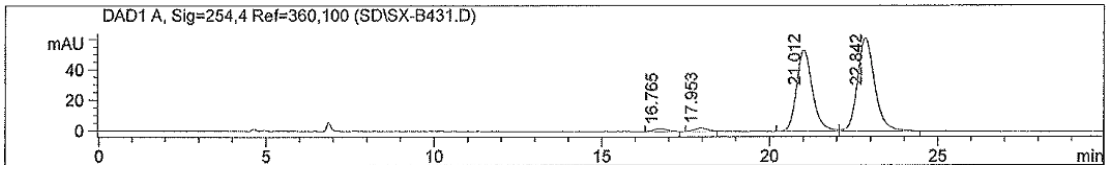
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	17.155	0.3417	6.80606	167.86649	0.4809
2	18.457	0.3183	6.23681	160.54379	0.4599
3	21.580	0.5067	524.95502	17218.27734	49.3222
4	23.441	0.5384	491.23978	17363.13477	49.7371



DAD1 A, Sig=254,4 Ref=360,100

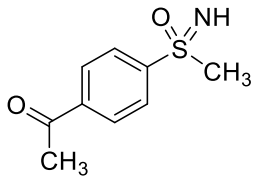
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	16.892	0.3851	1.19617	27.63950	1.0194
2	18.107	0.3713	1.11675	24.87896	0.9176
3	21.235	0.5566	40.07304	1338.30957	49.3576
4	23.108	0.5966	36.89022	1320.62744	48.7055



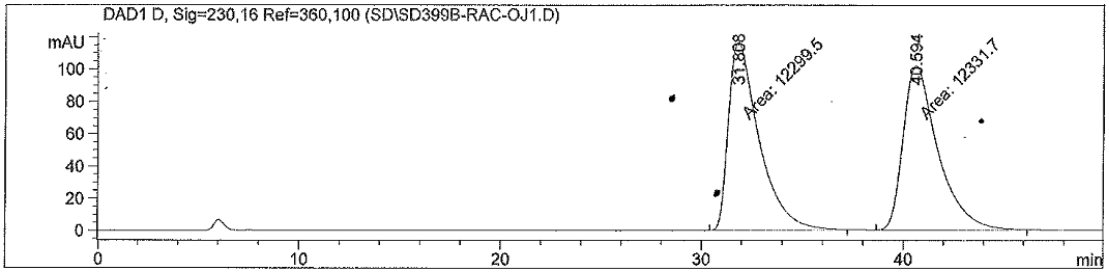
DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	16.765	0.4311	1.87910	48.59937	1.2046
2	17.953	0.4347	2.15237	56.13601	1.3914
3	21.012	0.5464	53.41651	1751.32361	43.4096
4	22.842	0.5932	61.20741	2178.35913	53.9944

***NH*-*S*-[4-Acetylphenyl]-*S*-methyl-sulfoximine (1v)[11]**

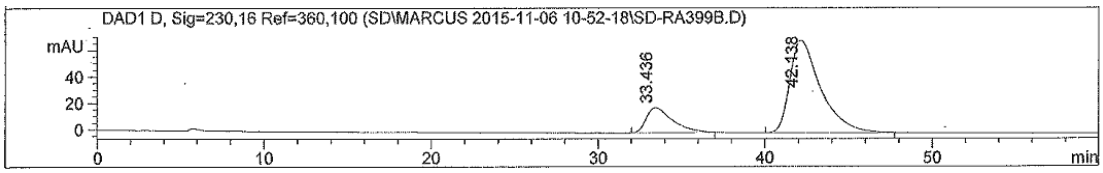


(**$C_9H_{11}NO_2S$**) a white solid, melting point: 98–98.6 °C. For cat **6c**: 42% yield, 57% ee. $[\alpha]_D^{25}$ = +12.7 (*c* = 0.80, in $CHCl_3$). For cat **5b**: 46% yield, –58% ee. $[\alpha]_D^{25}$ = –12.8 (*c* = 0.89, in $CHCl_3$). HPLC OJ, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 31.8 min, 40.6 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 – 7.98 (m, 4H), 3.06 (s, 3H), 2.81 (s, 1H), 2.59 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 196.82, 147.36, 140.29, 129.00, 127.99, 45.93, 26.93. **IR (ATR)**: ν = 3172, 3000, 2295, 2098, 1682, 1389, 1218, 1106, 964, 834, 731. **MS (EI):** *m*/*z* = 92.1 (22), 106.2 (46), 119.2 (32), 121.2 (12), 134.3 (84), 152.2 (15), 167.2 (18), 182.2 (100), 183.2 (17), 197.2 (14), 198.2 (M+1)$^+$ (78). **MS (ESI)**: ([M+H]$^+$) 198.058. **HRMS (ESI)** (*m*/*z*) [**$C_9H_{11}NO_2S$**+H]$^+$: Calcd. 198.0583, found 198.0579.



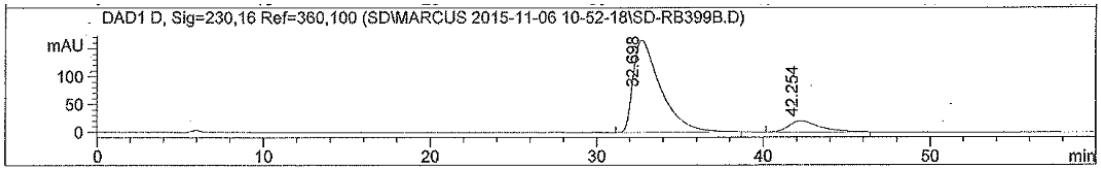
Signal 3: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.808	MM	1.7603	1.22995e4	116.45171	49.9347
2	40.594	MM	2.0188	1.23317e4	101.80810	50.0653



DAD1 D, Sig=230,16 Ref=360,100

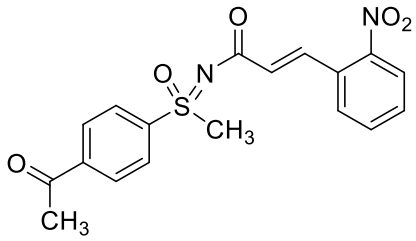
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	33.436	1.8211	19.03669	2080.01831	18.7620
2	42.138	2.1406	70.12296	9006.33398	81.2380



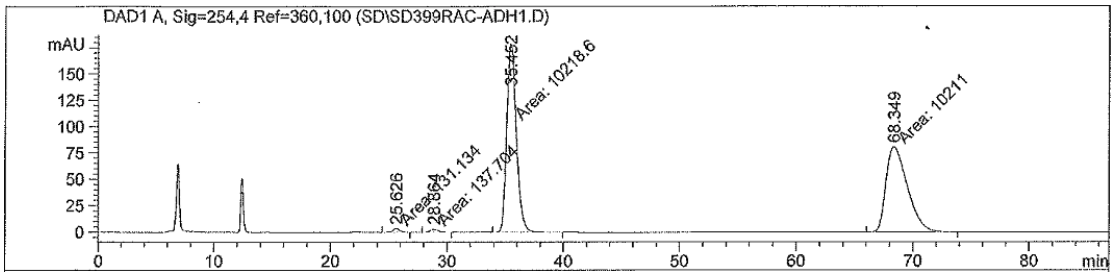
DAD1 D, Sig=230,16 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	32.698	1.9023	165.18648	18854.05078	88.1083
2	42.254	2.0923	20.27018	2544.66797	11.8917

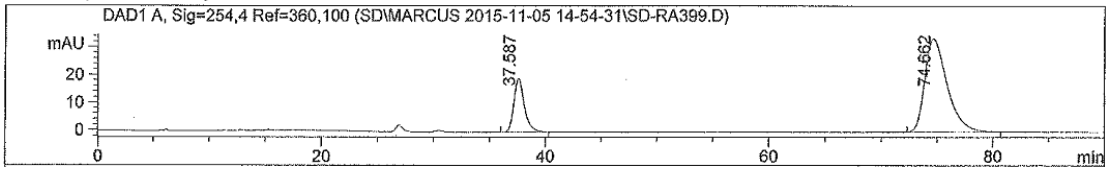
(*E*)-*N*-[(4-Acetylphenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl) acrylamide (3v)



(**$C_{18}H_{16}N_2O_5S$**) a yellow oil. For cat **6c**: 55% yield, 44% ee. $[\alpha]_D^{25}$ = +19.3 (*c* = 2.2, in $CHCl_3$). For cat **5b**: 52% yield, –52% ee. $[\alpha]_D^{25}$ = –21.7 (*c* = 2.2, in $CHCl_3$). HPLC ADH, 2-propanol/*n*-heptane = 50/50, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 35.5 min, 68.4 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 – 8.09 (m, 5H), 7.99 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.50 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 3.43 (s, 3H), 2.66 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 196.66, 173.48, 148.48, 142.74, 141.09, 138.29, 133.52, 131.07, 130.03, 129.61, 129.51, 129.19, 127.75, 124.92, 44.16, 27.06. **IR (ATR):** ν = 3615, 3018, 2930, 2674, 2329, 2104, 1919, 1691, 1605, 1521, 1436, 1399, 1269, 1208, 1101, 1054, 967, 892, 832, 783, 733. **MS (EI):** *m*/*z* = 51.2 (14), 55.2 (40), 56.2 (21), 57.3 (72), 64.2 (18), 67.2 (11), 69.2 (27), 70.2 (17), 71.3 (39), 77.2 (20), 81.2 (14), 83.1 (32), 85.2 (31), 91.1 (100), 95.1 (13), 97.1 (22), 201.1 (21). **MS (ESI)**: ([M+Na$^+$]) 395.066. **HRMS (ESI)** (*m*/*z*) [**$C_{18}H_{16}N_2O_5S$+Na**]$^+$: Calcd. 395.0672, found 395.0672.

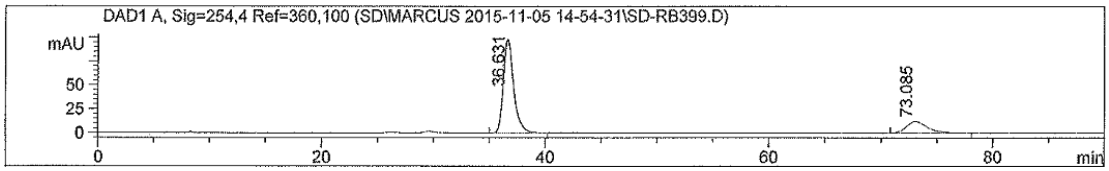


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
3	35.452	MM	0.9529	1.02186e4	178.72801	49.3690
4	68.349	MM	2.1213	1.02110e4	80.22574	49.3321



DAD1 A, Sig=254,4 Ref=360,100

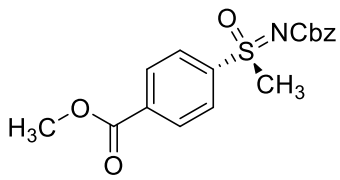
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	37.587	1.0792	19.20394	1243.43628	20.9297
2	74.662	2.3387	33.47750	4697.58984	79.0703



DAD1 A, Sig=254,4 Ref=360,100

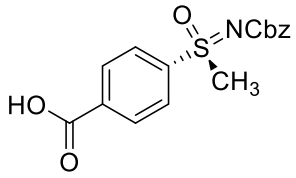
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	36.631	1.0550	98.14758	6212.47754	80.2029
2	73.085	2.1608	11.82785	1533.47461	19.7971

Methyl 4-{*N*-[(benzyloxy)carbonyl]-*S*-methylsulfonimidoyl}benzoate (8)



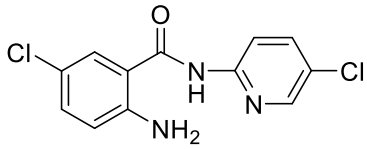
(**$C_{17}H_{17}NO_5S$**), a white solid, 98% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.31 – 8.06 (m, 2H), 8.06 – 7.80 (m, 2H), 7.32 – 7.17 (m, 5H), 5.09 (d, *J* = 12.3 Hz, 1H), 5.01 (d, *J* = 12.3 Hz, 1H), 3.97 (s, 3H), 3.30 (s, 3H). **^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)** δ 165.35, 158.38, 142.41, 136.01, 135.15, 130.84, 128.47, 128.35, 128.16, 127.64, 68.07, 52.91, 44.37.

4-{*N*-[(Benzyloxy)carbonyl]-*S*-methylsulfonimidoyl}benzoic acid (9)



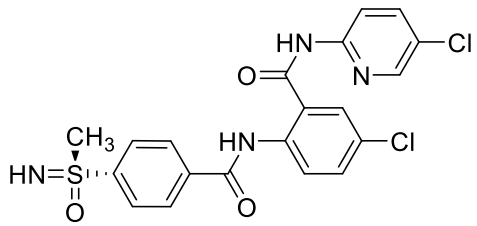
(**$C_{16}H_{15}NO_5S$**), a white solid, 96% yield. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.21 – 8.13 (m, 2H), 8.11 – 8.03 (m, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.18 (m, 2H), 4.97 (d, *J* = 12.6 Hz, 1H), 4.92 (d, *J* = 12.6 Hz, 1H), 3.52 (s, 3H).

2-Amino-5-chloro-*N*-(5-chloropyridin-2-yl)benzamide (10)



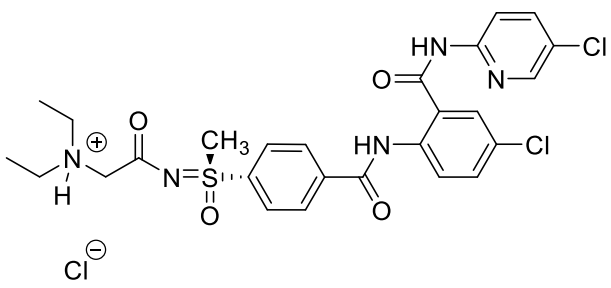
(**$C_{12}H_9Cl_2N_3OS$**), a yellow solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.77 (s, 1H), 8.40 (dd, *J* = 2.7, 0.6 Hz, 1H), 8.10 (dd, *J* = 8.9, 0.6 Hz, 1H), 7.91 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.77 (d, *J* = 2.5 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.55 (s, 2H). **^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6)** δ 167.19, 150.85, 149.04, 146.31, 137.65, 132.46, 128.62, 125.47, 118.17, 117.96, 116.06, 114.72.

5-Chloro-*N*-(5-chloropyridin-2-yl)-2-[4-(*S*-methylsulfonimidoyl)benzamido]benzamide (11)



(**$C_{20}H_{16}Cl_2N_4O_3S$**), a yellow solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.26 (s, 1H), 11.19 (s, 1H), 8.44 (d, *J* = 2.6 Hz, 1H), 8.14 (d, *J* = 4.0 Hz, 1H), 8.11 (d, *J* = 4.2 Hz, 1H), 8.07 (s, 4H), 7.95 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.92 (d, *J* = 2.5 Hz, 1H), 7.68 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.40 (s, 1H), 3.11 (s, 3H).

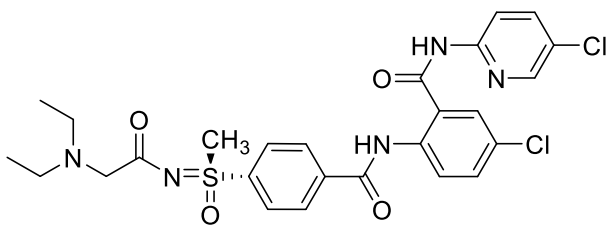
(*S*)-2-({[4-({4-Chloro-2-[(5-chloropyridin-2-yl)carbamoyl]phenyl}carbamoyl)phenyl](methyl)(oxo)-λ6-sulfanylidene}amino)-*N,N*-diethyl-2-oxoethan-1-aminium chloride (F')



(**$C_{26}H_{28}Cl_3N_5O_4S$**) a yellow solid, melting point: 178–179 °C. $[\alpha]^{D}_{25}$ = +38.3, (*c* = 0.6, in DMSO). **^{1}H NMR (600 MHz, DMSO-d_6)** δ

11.31 (s, 1H), 11.27 (s, 1H), 9.20 (s, 1H), 8.51 – 8.43 (m, 1H), 8.26 – 8.22 (m, 2H), 8.21 – 8.18 (m, 2H), 8.13 (dd, *J* = 8.8, 6.8 Hz, 2H), 8.00 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.96 (d, *J* = 2.5 Hz, 1H), 7.73 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.14 (s, 2H), 3.70 (s, 3H), 3.16 (d, *J* = 7.1 Hz, 4H), 1.20 (t, *J* = 6.4 Hz, 6H). **^{13}C{^{1}H} NMR (150 MHz, DMSO-d$_6$)** δ 172.91, 166.16, 163.82, 150.49, 146.49, 140.45, 139.30, 137.85, 135.99, 131.76, 129.28, 128.55, 128.28, 127.80, 127.12, 125.99, 124.73, 116.26, 55.65, 48.43, 42.90, 8.88. **HRMS (ESI)** (*m*/*z*) [**$C_{26}H_{27}ClN_5O_4S$+H**]$^+$: Calcd. 576.1234, found 576.1237.

(*S*)-5-Chloro-*N*-(5-chloropyridin-2-yl)-2-{4-[*N*-(diethylglycyl)-S-methylsulfonimidoyl]benzamido}benzamide (F)



(**$C_{26}H_{27}Cl_2N_5O_4S$**) yellow solid, 56% yield for three steps. $[\alpha]^{D}_{25}$ = +44.1, (*c* = 2.2, in DMSO). **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 11.34 (s, 2H), 8.51 – 8.44 (m, 1H), 8.18 (dd, *J* = 8.5, 4.9 Hz, 4H), 8.12 (d, *J* = 8.6 Hz, 2H), 7.97 (dd, *J* = 9.5, 2.5 Hz, 2H), 7.70 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.53 (s, 3H), 3.30 (s, 2H), 2.61 (q, *J* = 7.1 Hz, 4H), 0.98 (t, *J* = 7.2 Hz, 6H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d$_6$)** δ 178.93, 166.06, 164.09, 150.68, 146.40, 141.65, 139.12, 138.27, 137.80, 131.63, 129.19, 128.44, 127.89, 127.50, 127.00, 125.80, 124.64, 116.22, 57.73, 46.90, 43.00, 12.20. **HRMS (ESI)** (*m*/*z*) [**$C_{26}H_{27}Cl_2N_5O_4S$+H**]$^+$: Calcd. 576.1234, found 576.1237.

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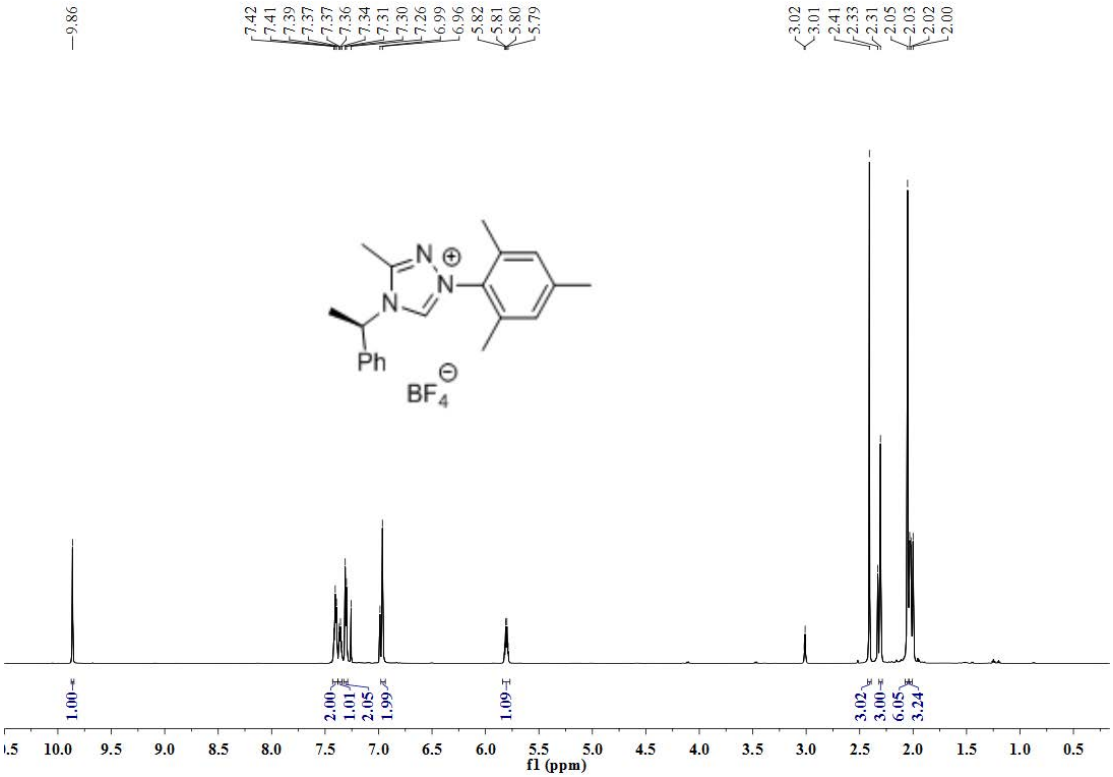
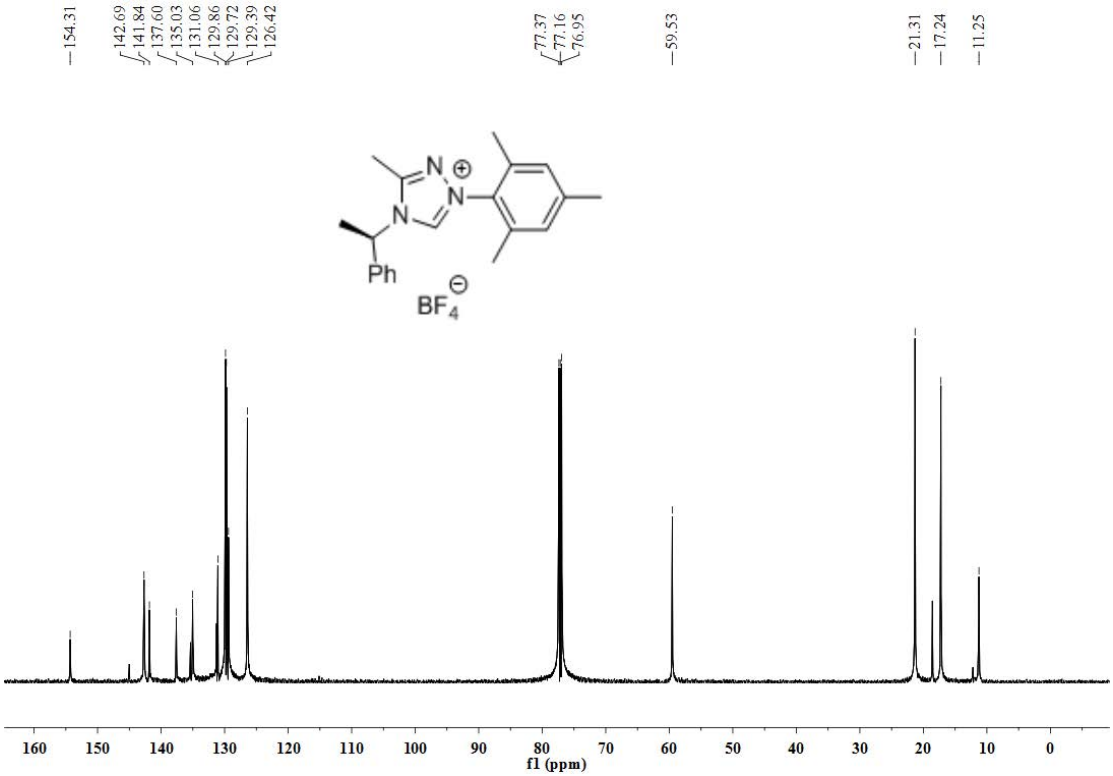
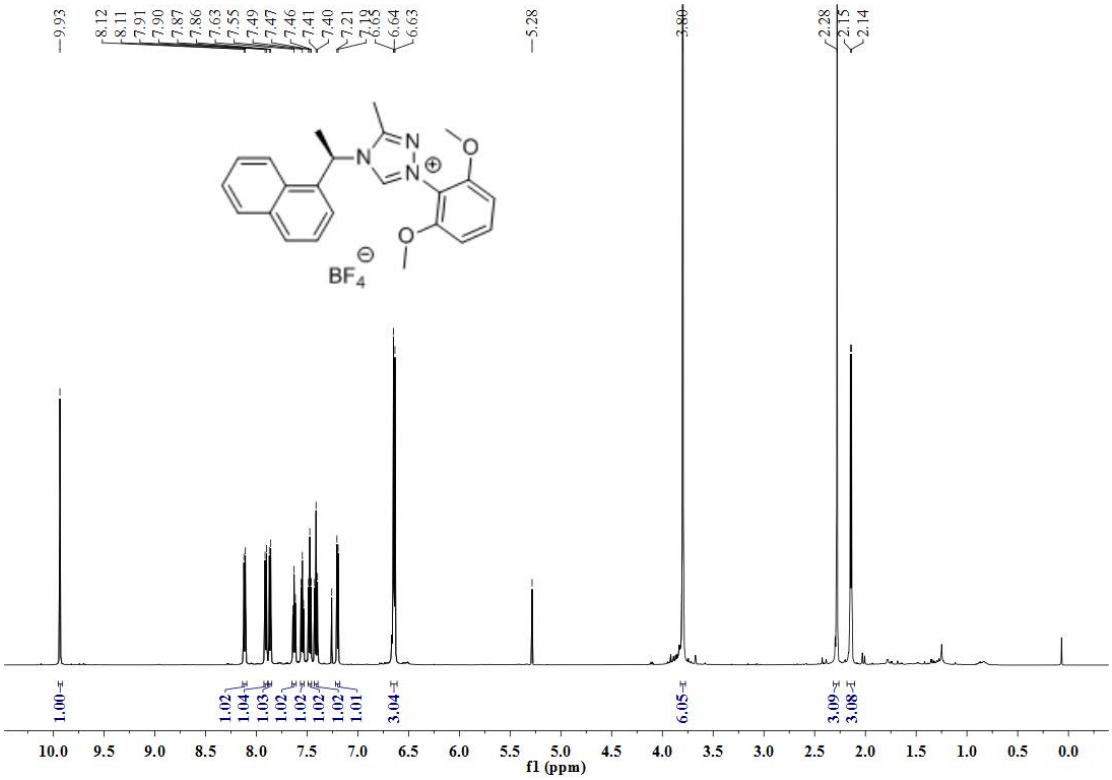
(K) Copies of NMR spectra for the catalysts and products

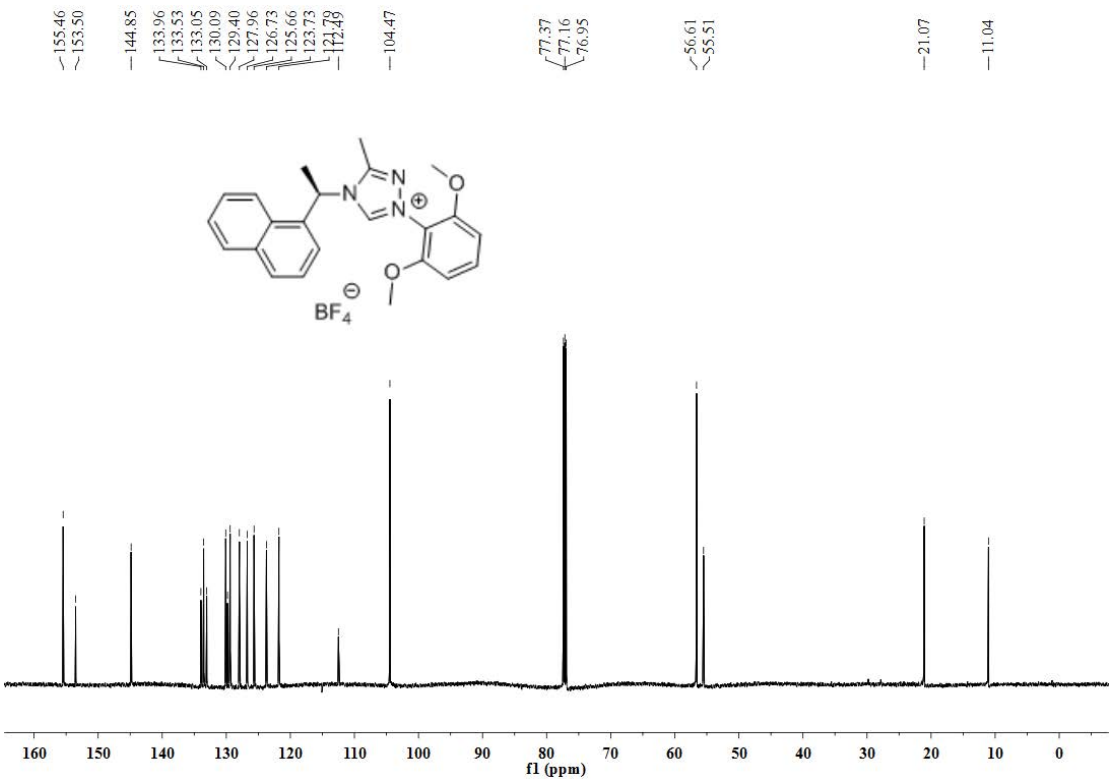
(*R*)-1-Mesityl-3-methyl-4-(1-phenylethyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (C1)



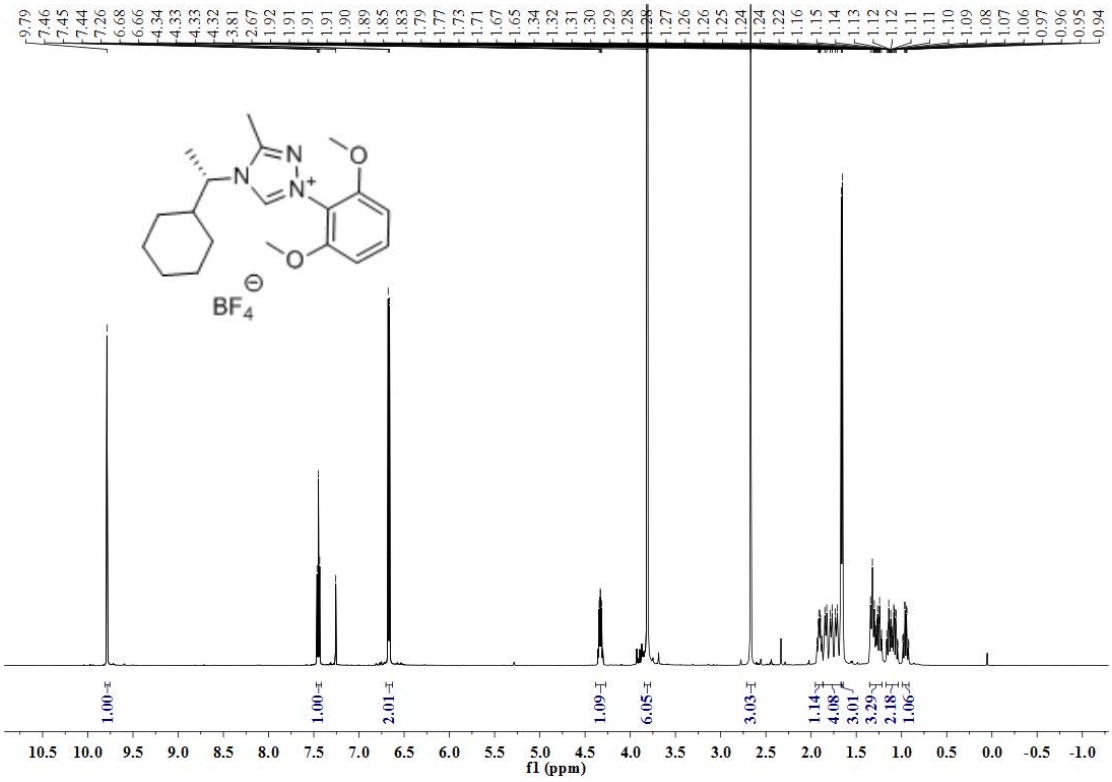


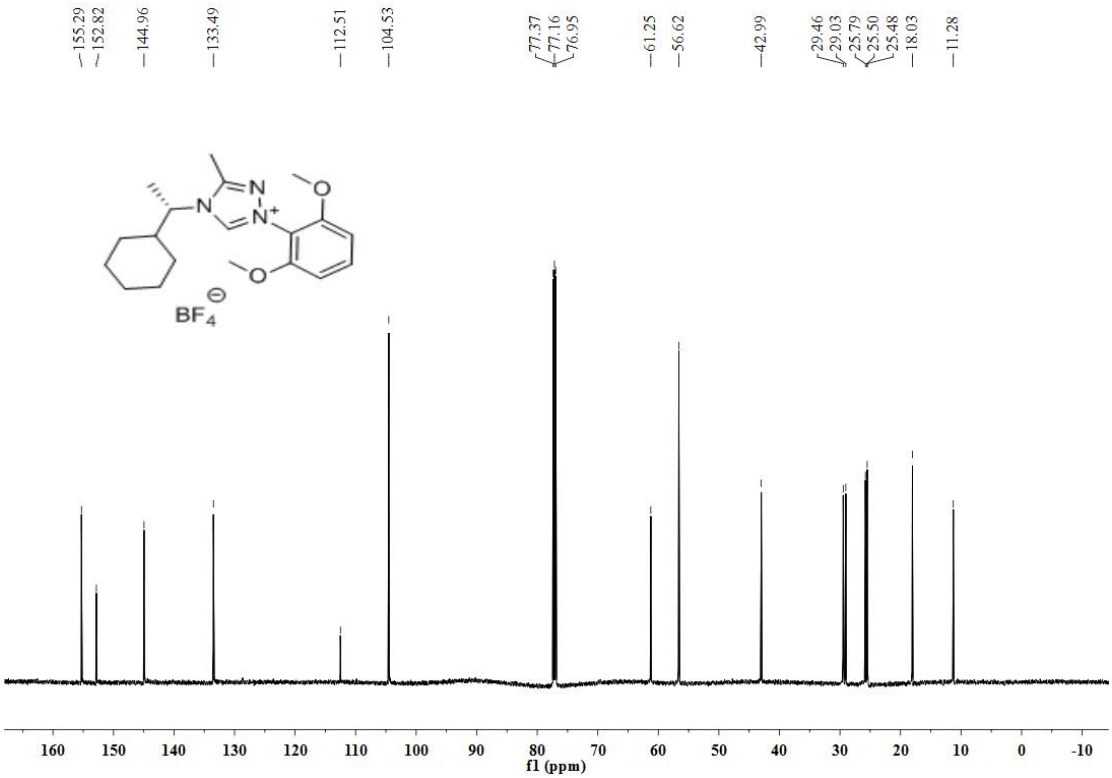
(*R*)-1-(2,6-Dimethoxyphenyl)-3-methyl-4-[1-(naphthalen-1-yl)ethyl]-4H-1,2,4-triazol-1-ium tetrafluoroborate (C2)



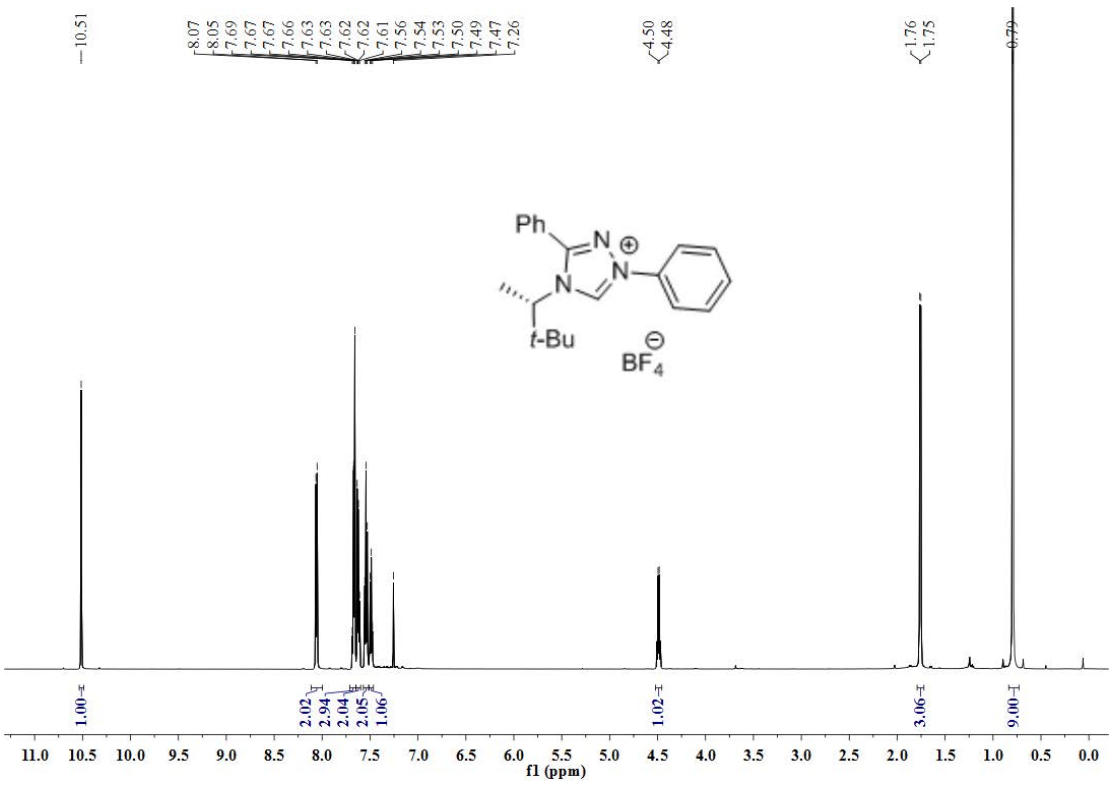


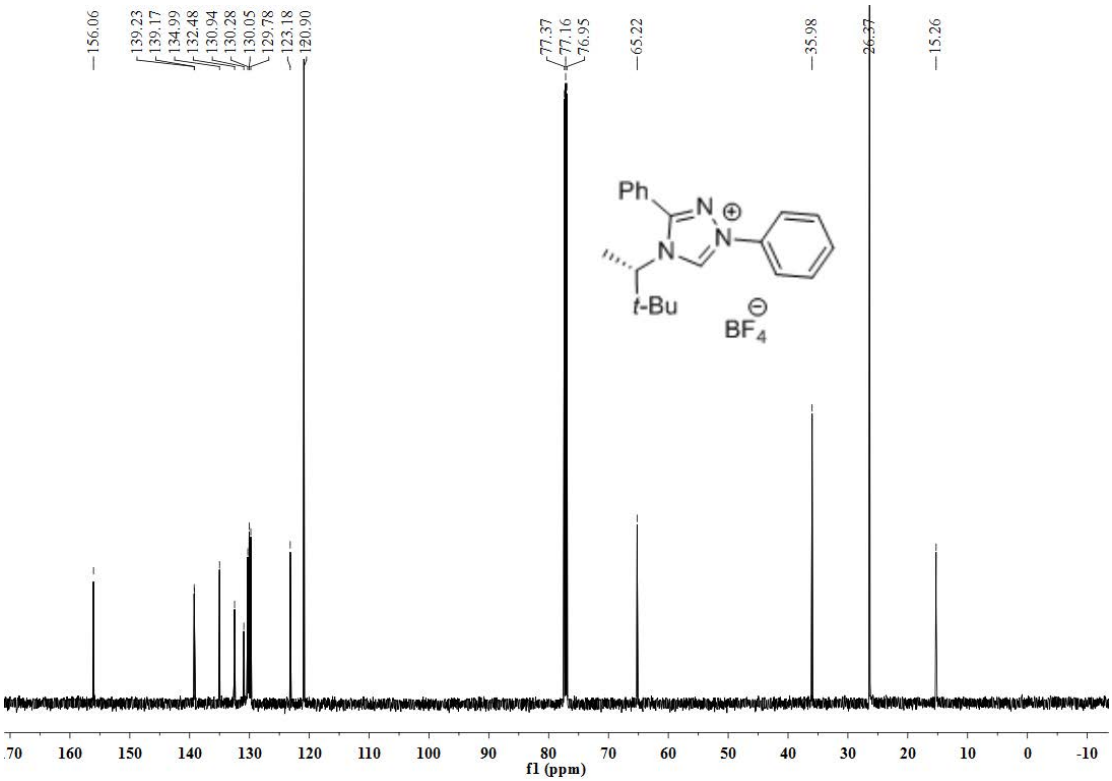
(S)-4-(1-cyclohexylethyl)-1-(2,6-dimethoxyphenyl)-3-methyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (C3)



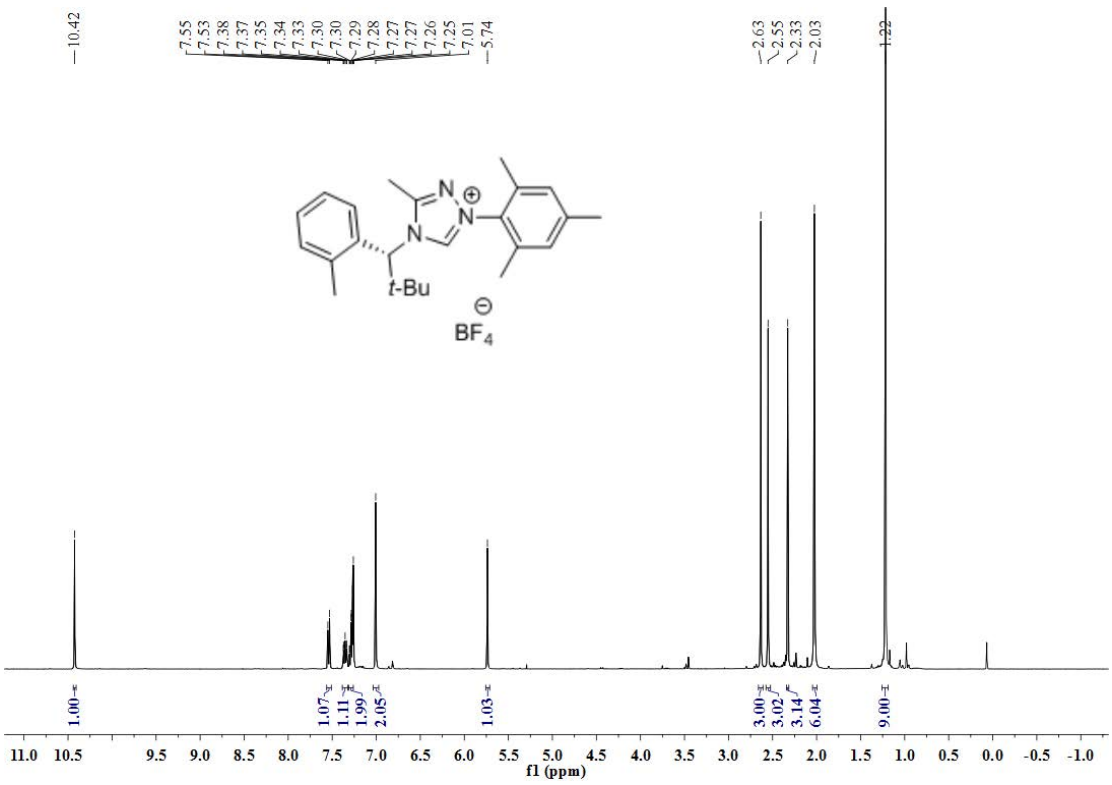


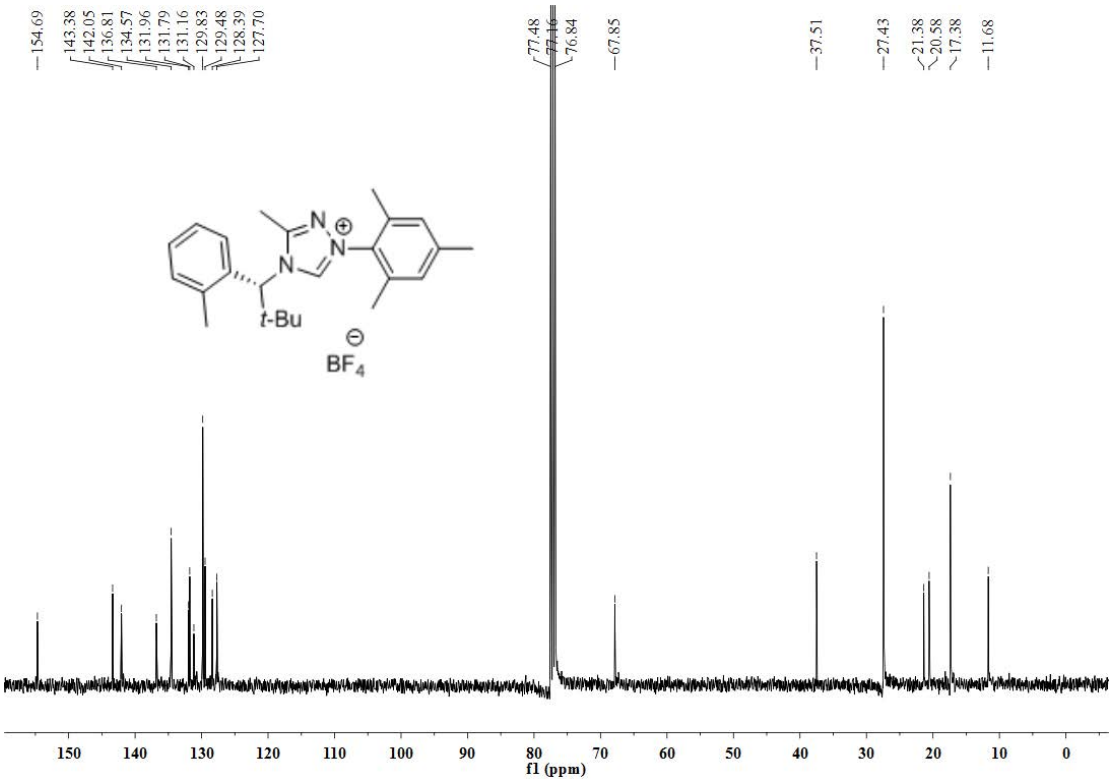
(*S*)-4-(3,3-Dimethylbutan-2-yl)-1,3-diphenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (C_4)



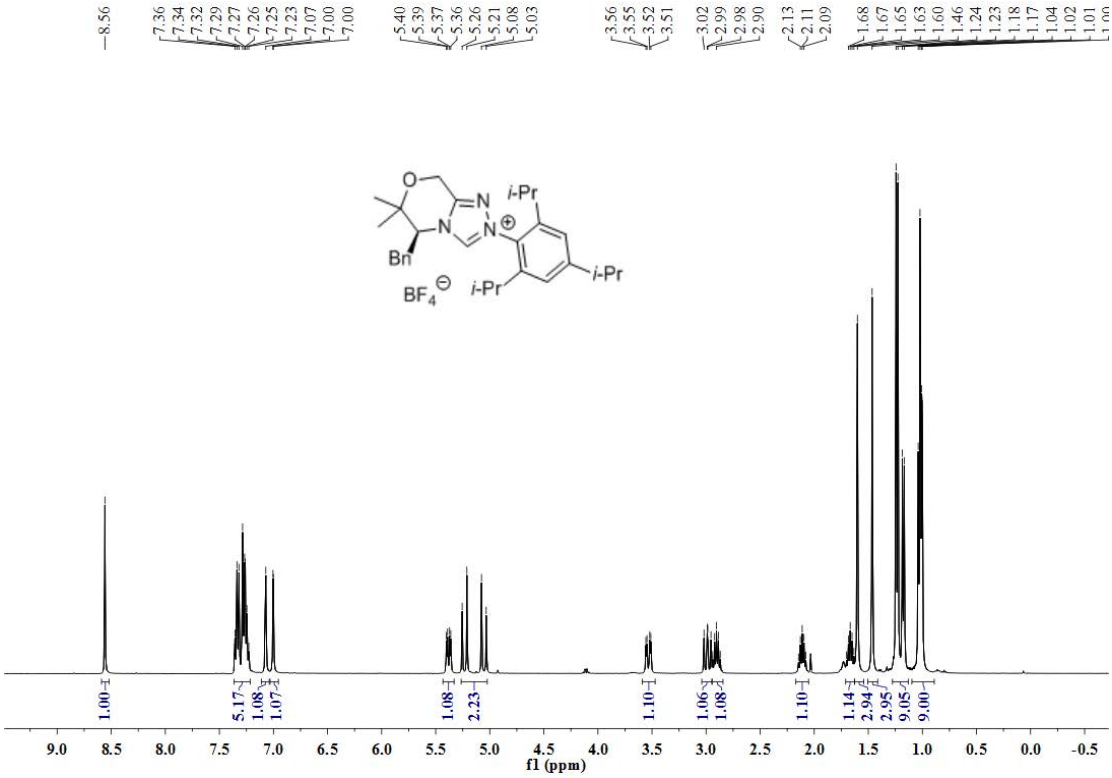


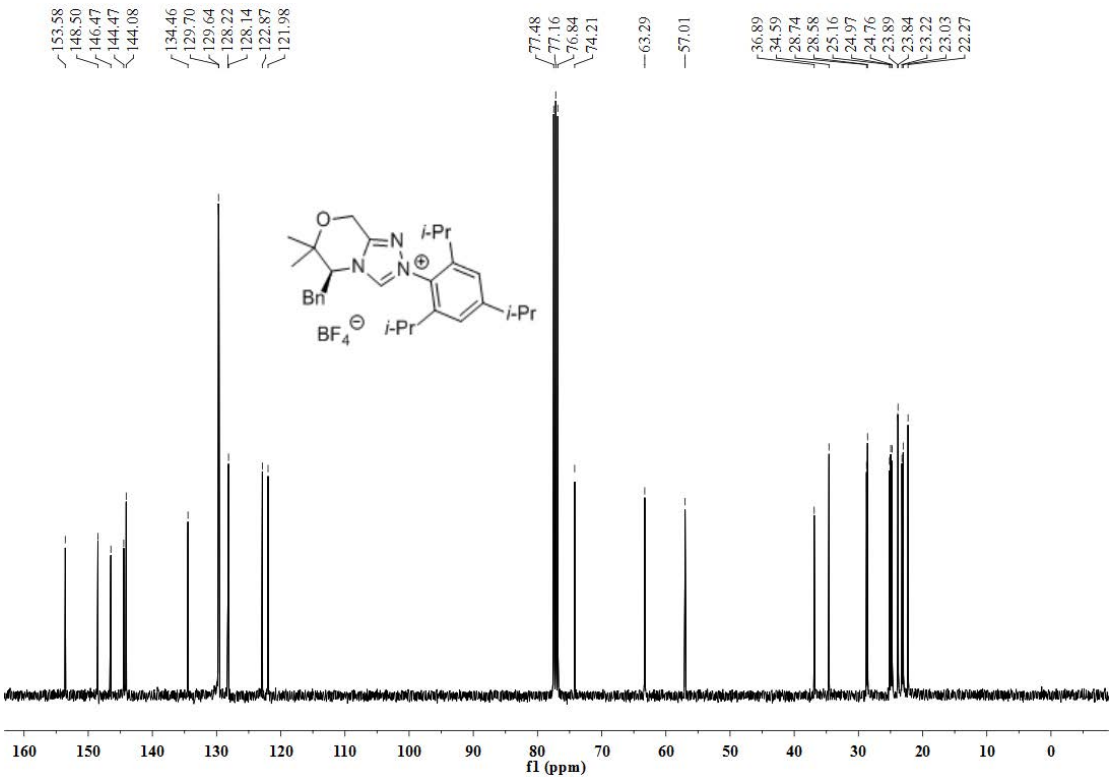
(*R*)-4-[2,2-Dimethyl-1-(*o*-tolyl)propyl]-1-mesityl-3-methyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (C5)



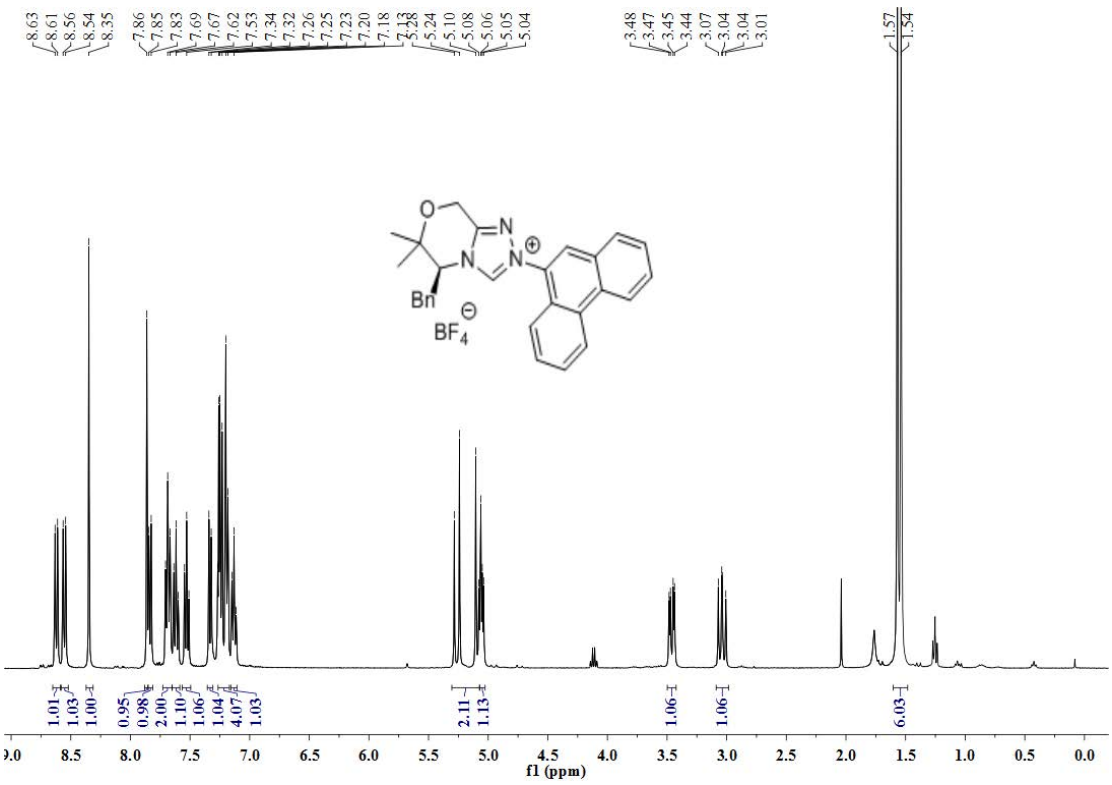


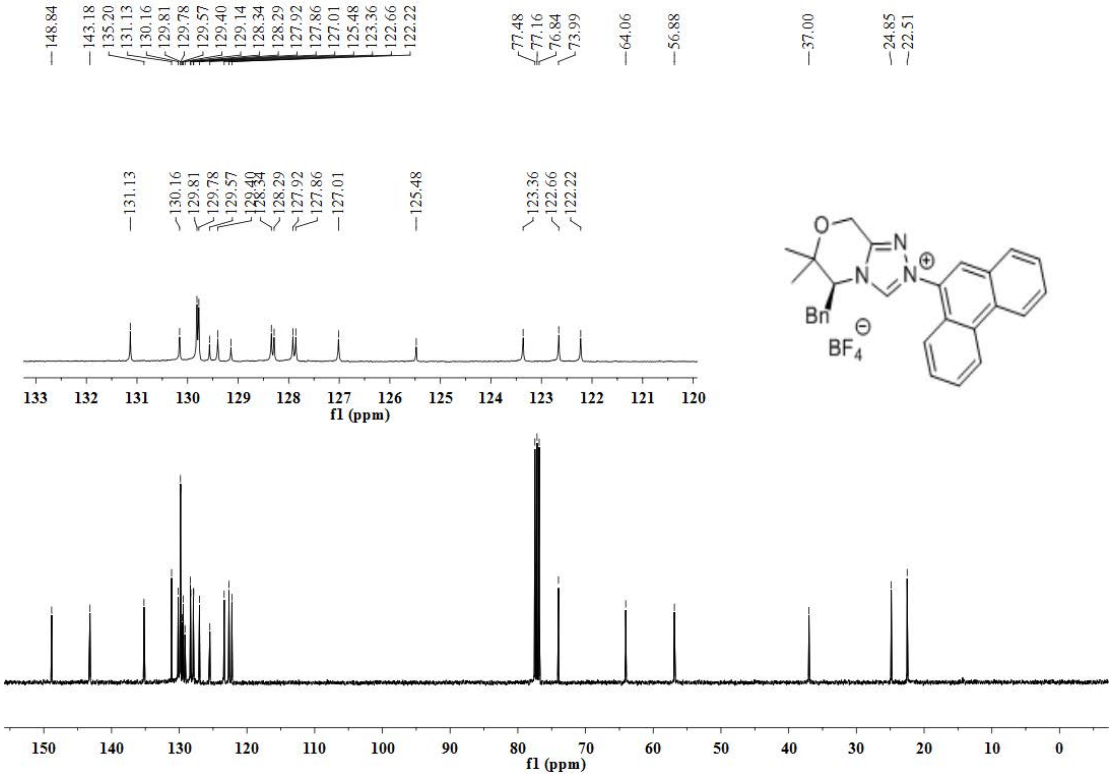
(*S*)-5-Benzyl-6,6-dimethyl-2-(2,4,6-triisopropylphenyl)-5,6-dihydro-8H-[1,2,4]triazolo[3,4-c][1,4]oxazin-2-ium tetrafluoroborate (5b)



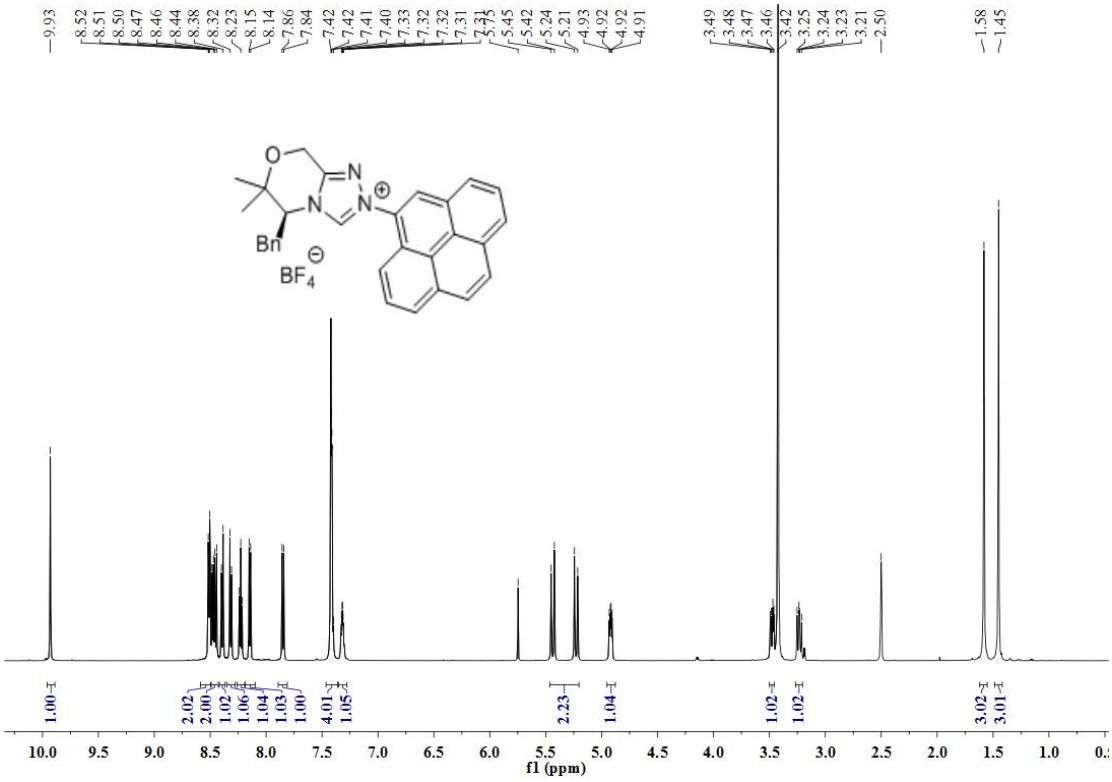


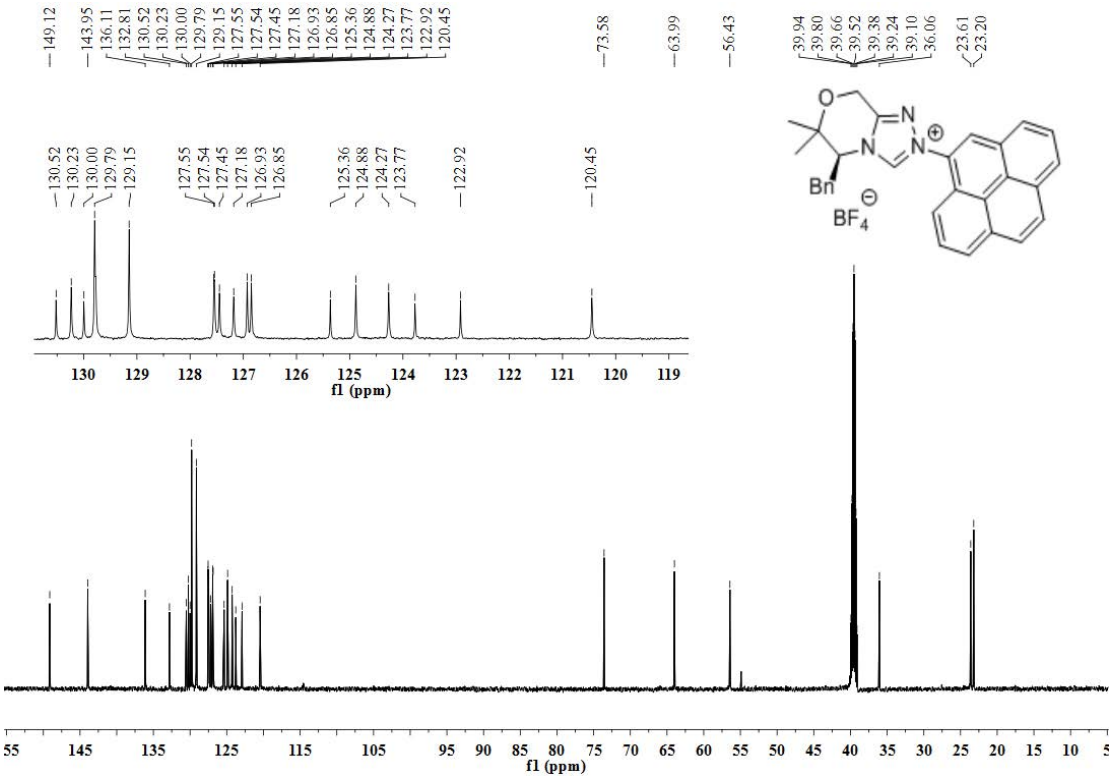
(*S*)-5-Benzyl-6,6-dimethyl-2-(phenanthren-9-yl)-5,6-dihydro-8H-[1,2,4]triazolo[3,4-c][1,4]oxazin-2-ium tetrafluoroborate (5c)



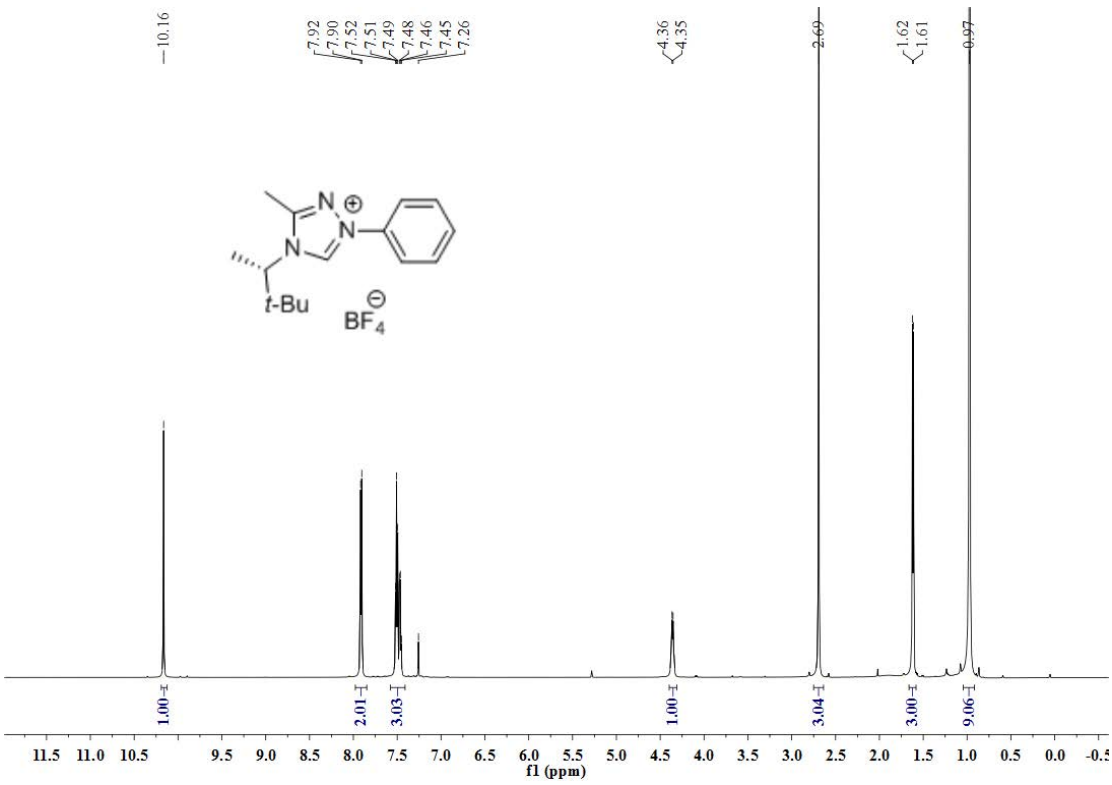


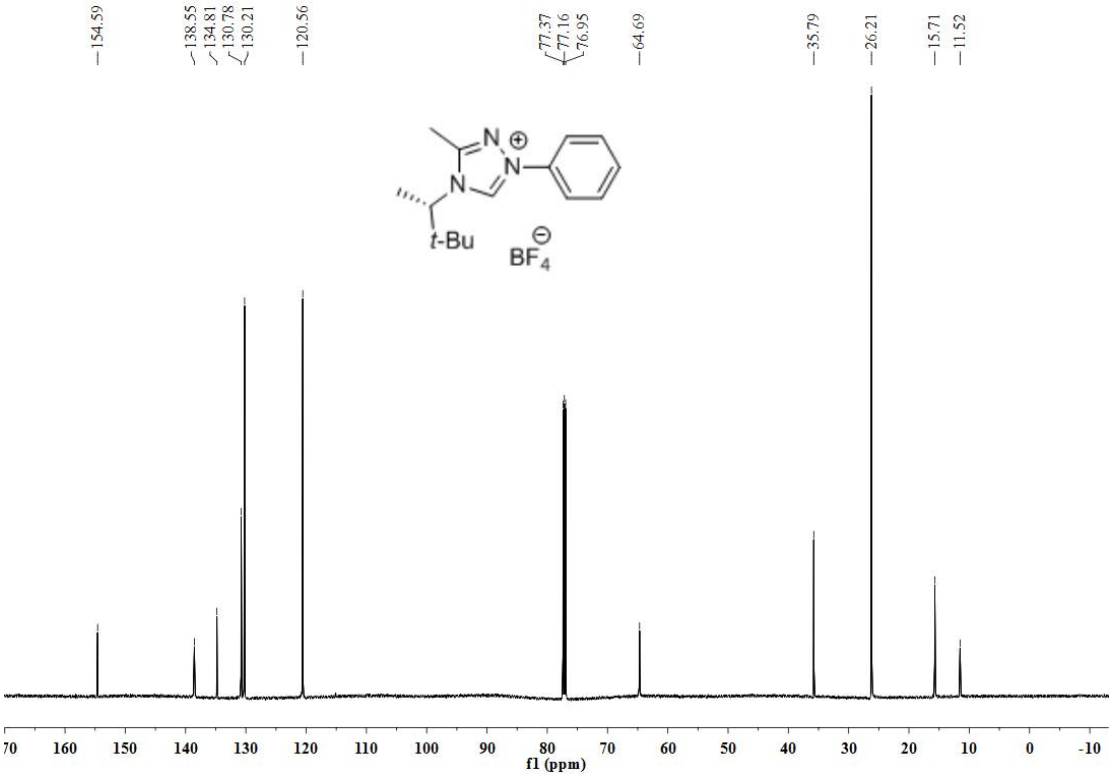
(*S*)-5-Benzyl-6,6-dimethyl-2-(pyren-4-yl)-5,6-dihydro-8H-[1,2,4]triazolo[3,4-c][1,4]oxazin-2-ium tetrafluoroborate (5d)



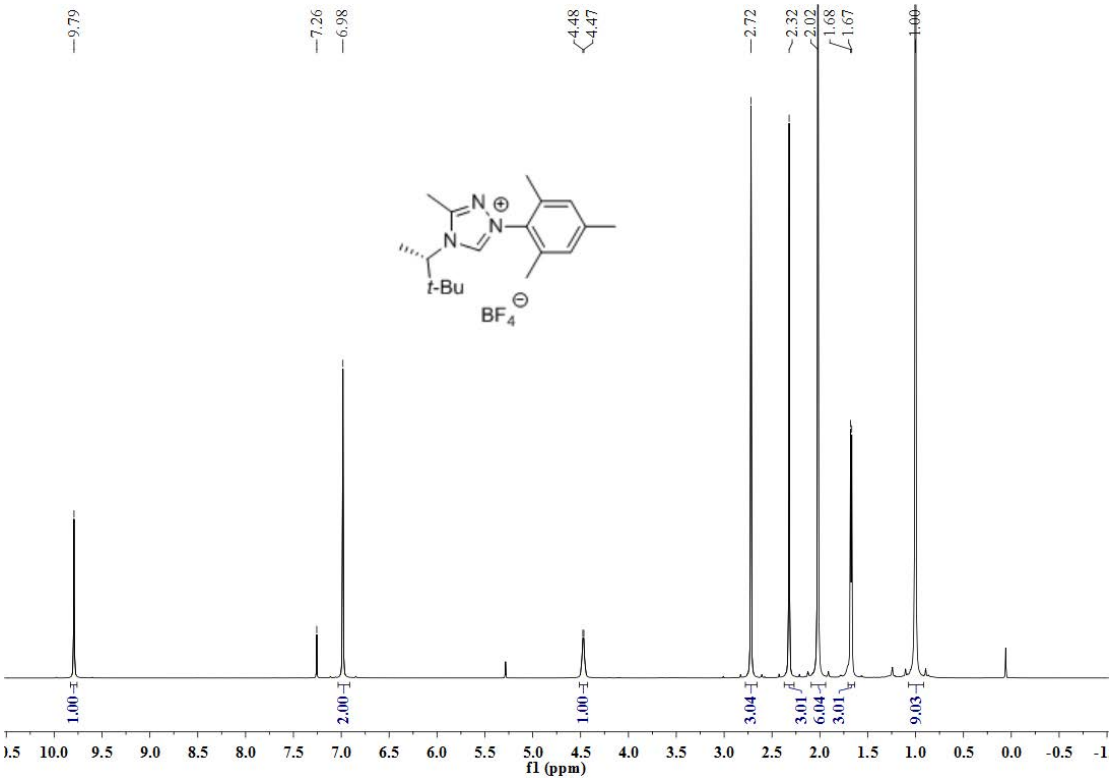


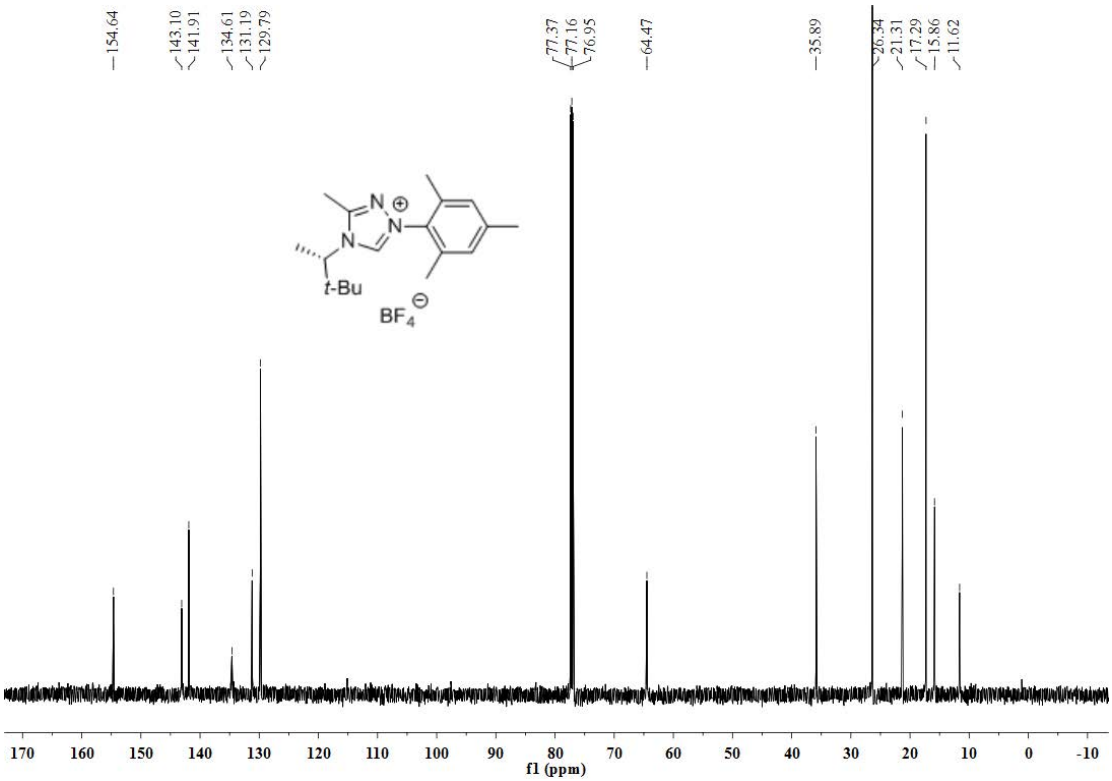
(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (6a)



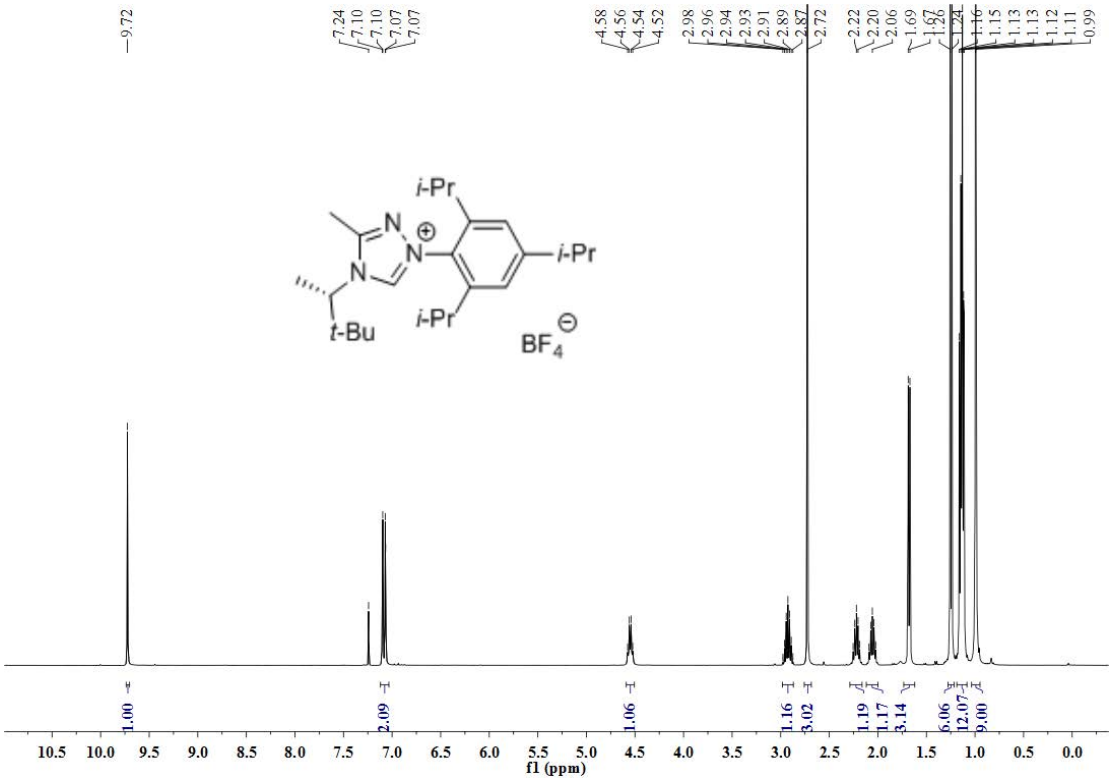


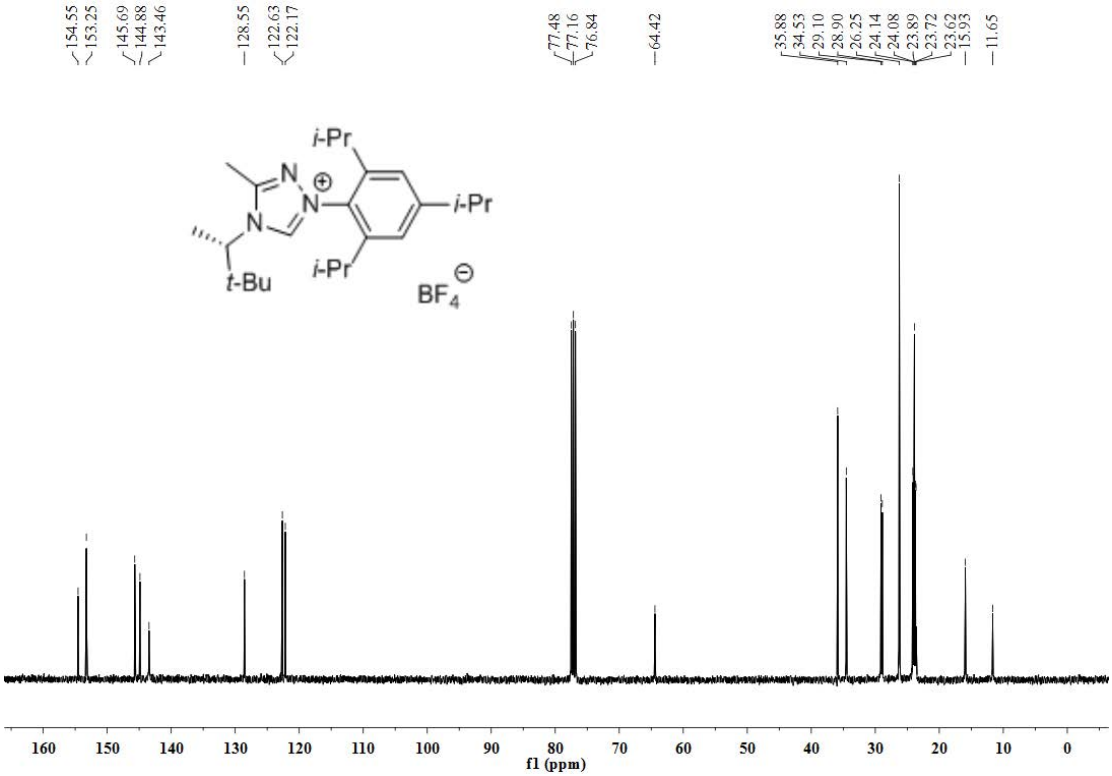
(*S*)-4-(3,3-Dimethylbutan-2-yl)-1-mesityl-3-methyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (6b)



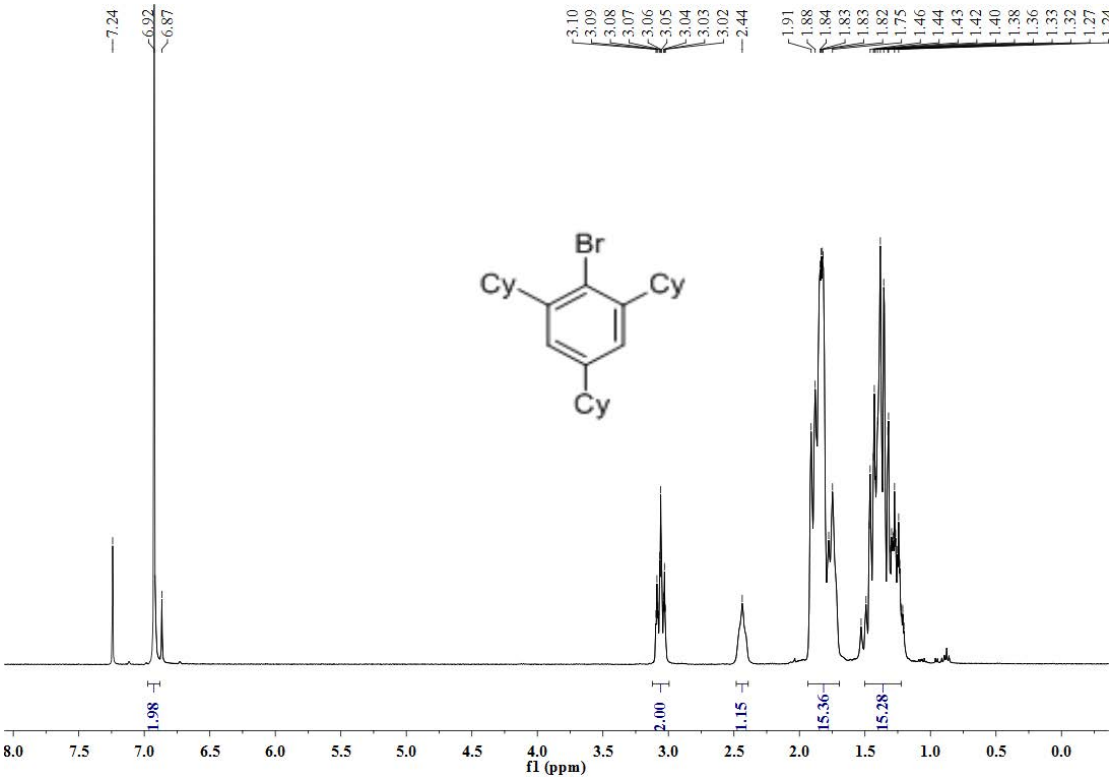


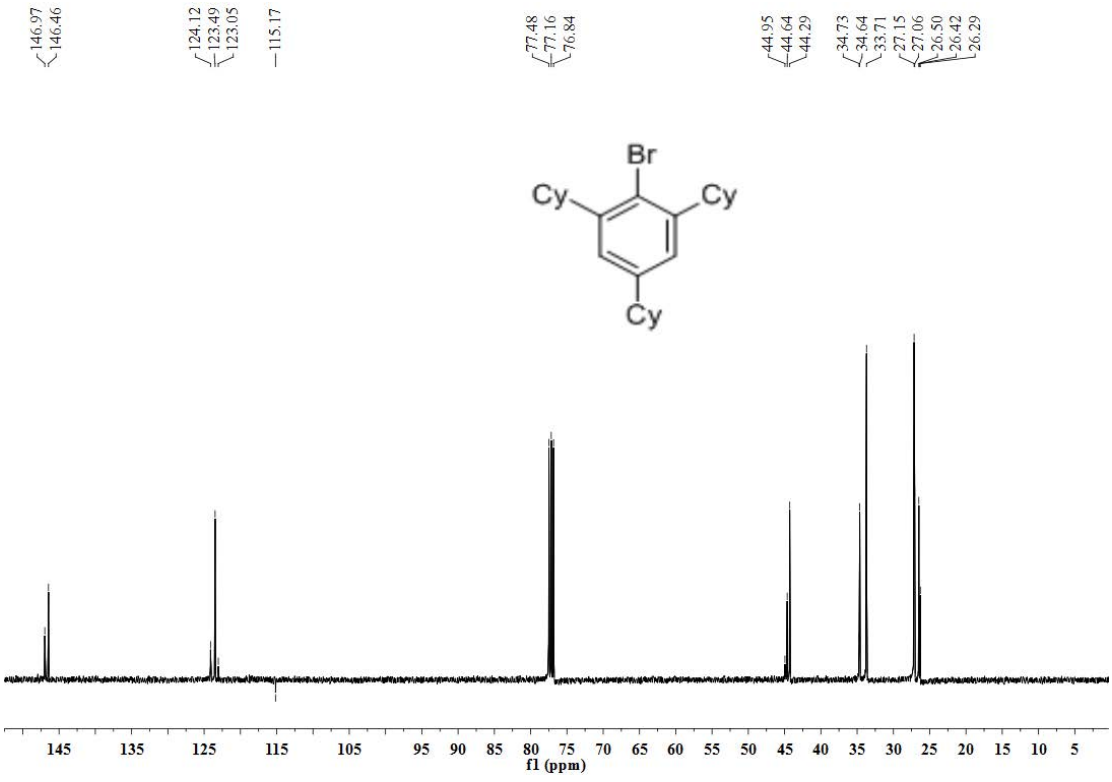
(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(2,4,6-triisopropylphenyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (6c)



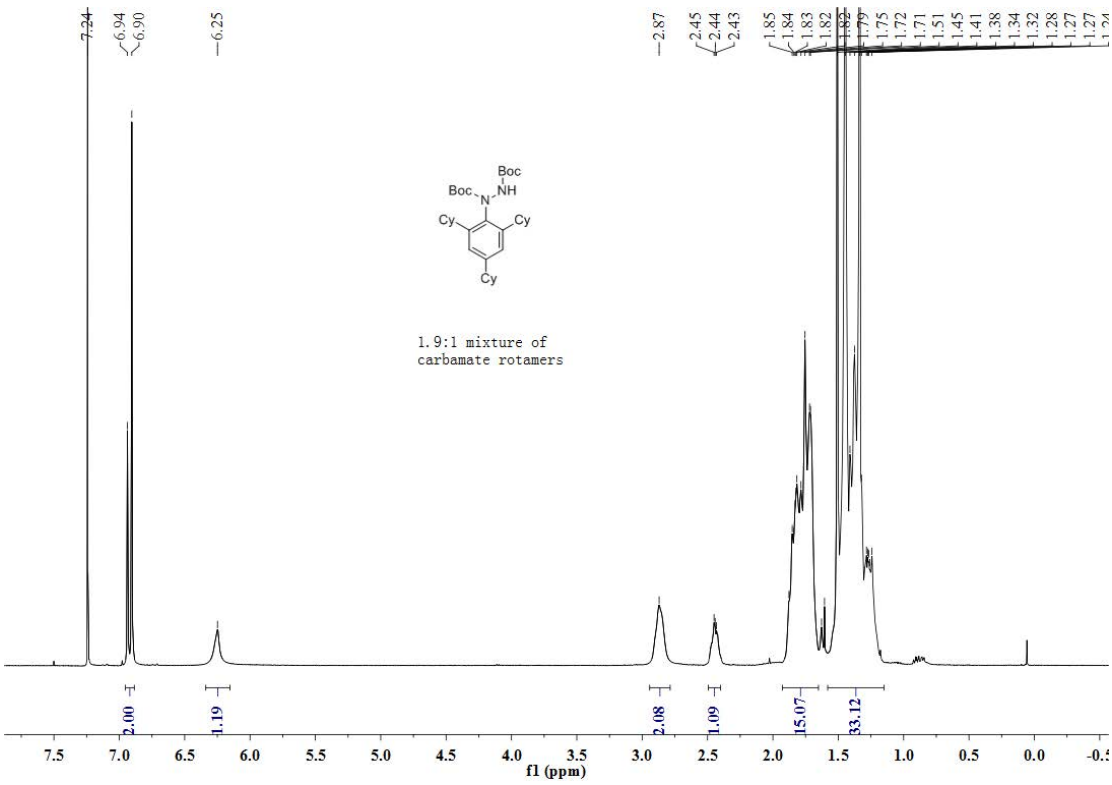


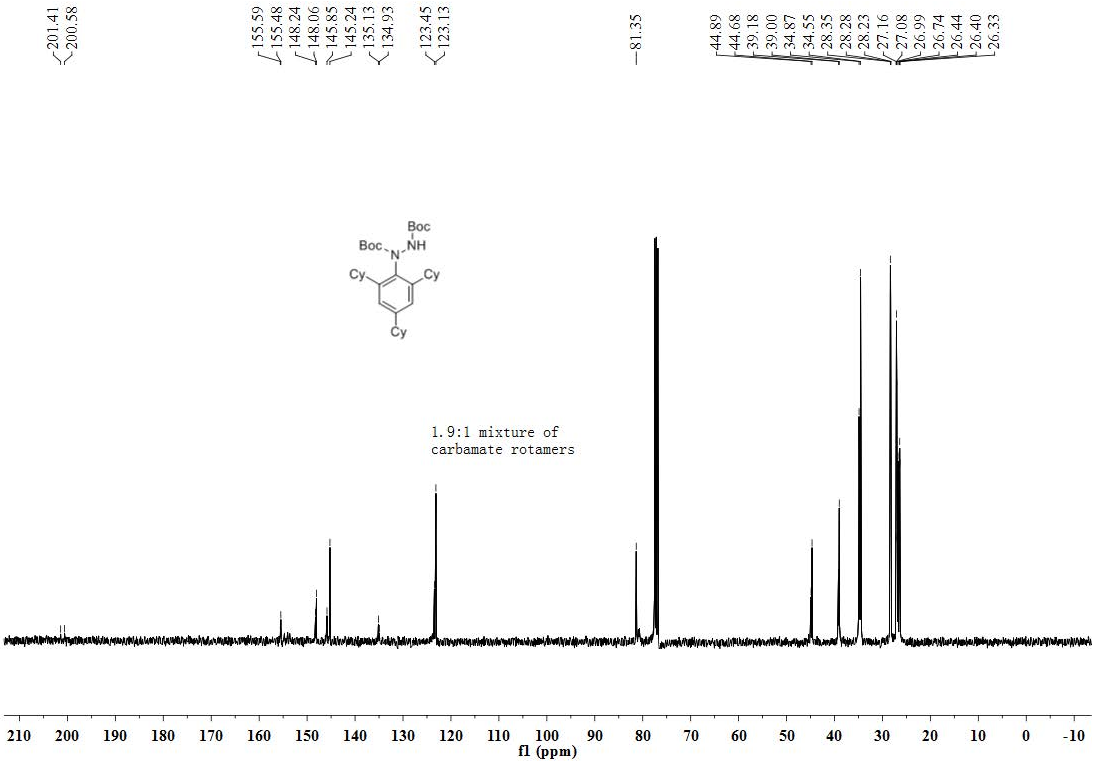
(2-Bromobenzene-1,3,5-triyl)tricyclohexane (13)



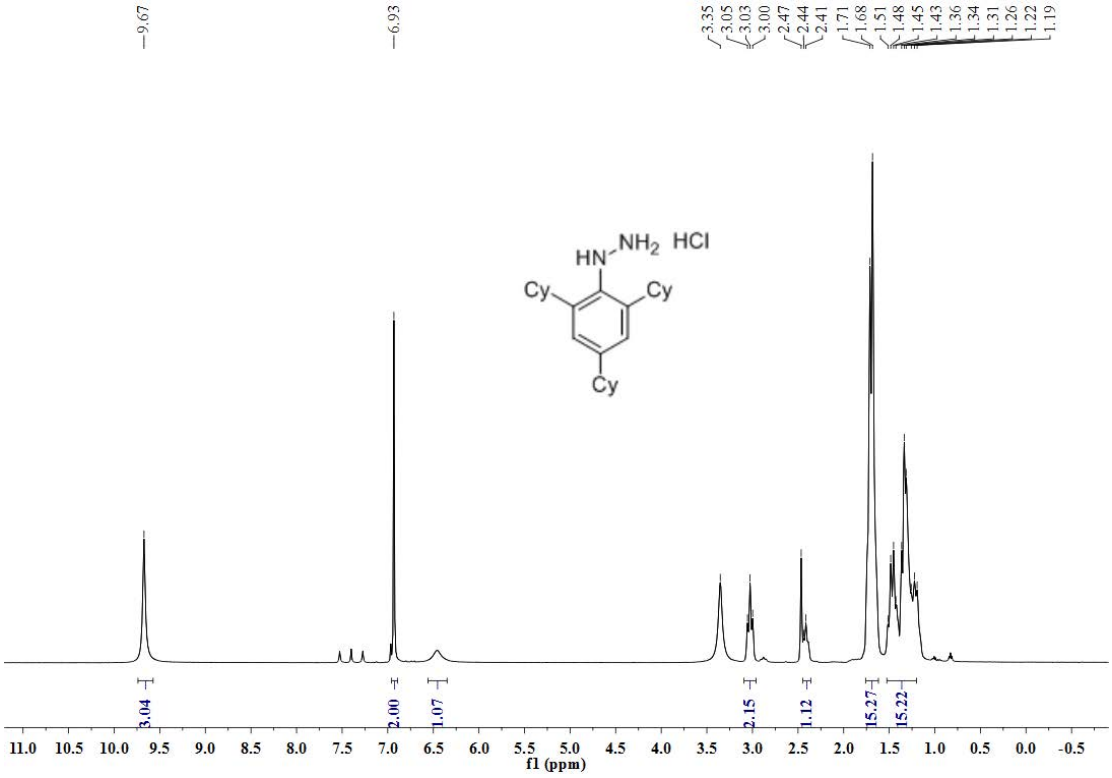


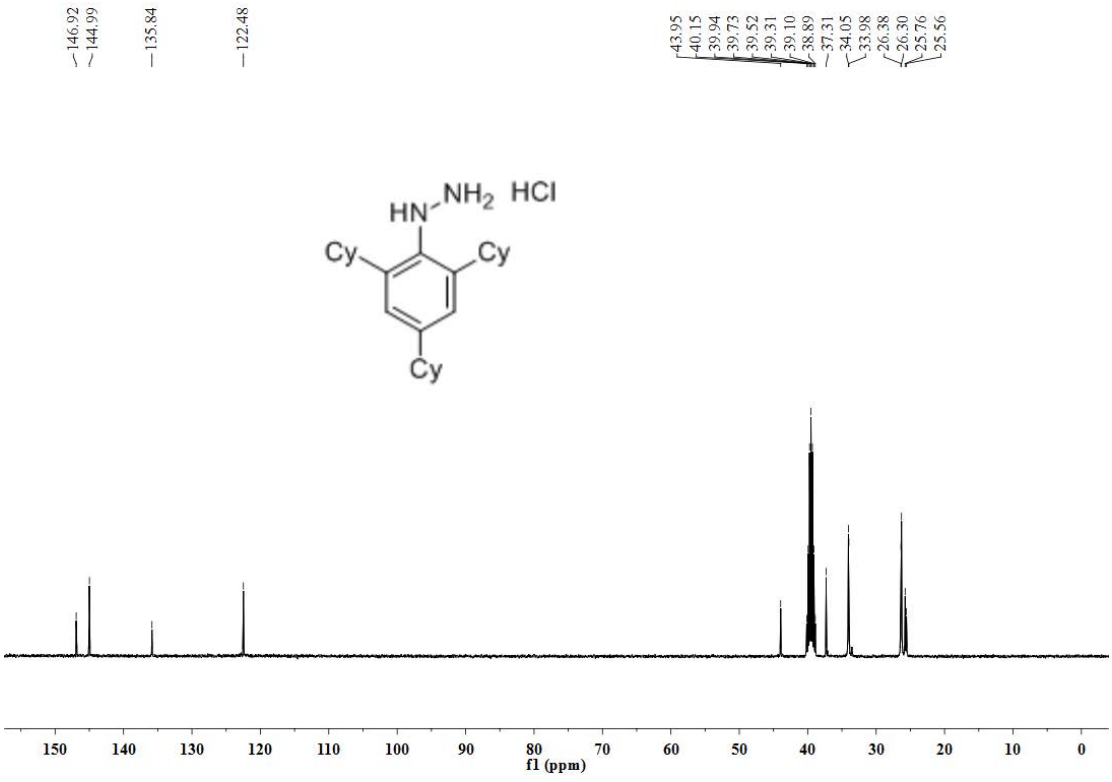
Di-*tert*-butyl 1-(2,4,6-tricyclohexylphenyl)hydrazine-1,2-dicarboxylate (14)



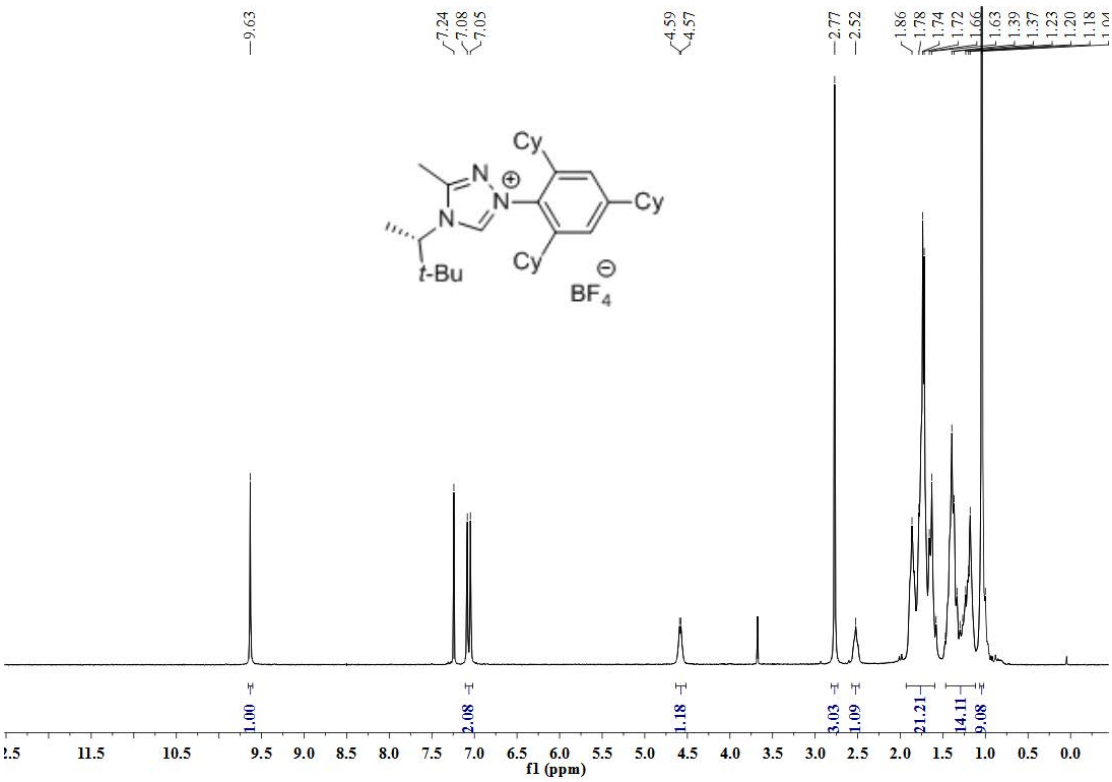


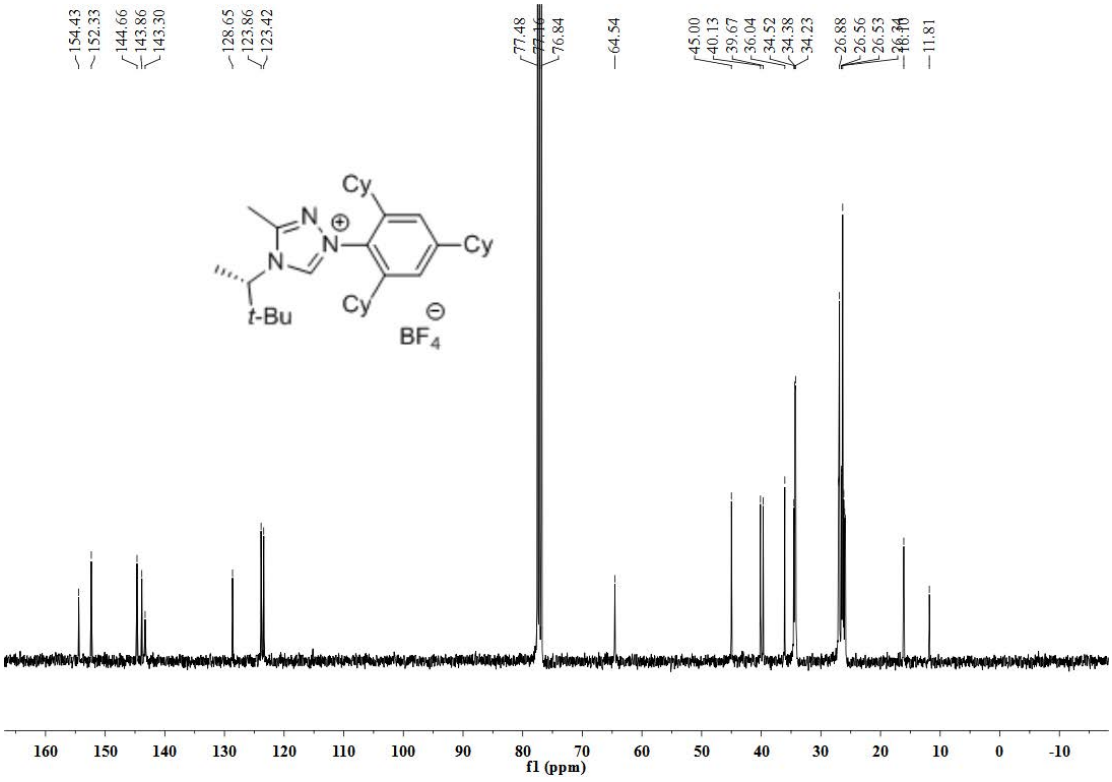
(2,4,6-Tricyclohexylphenyl)hydrazine hydrochloride (15)



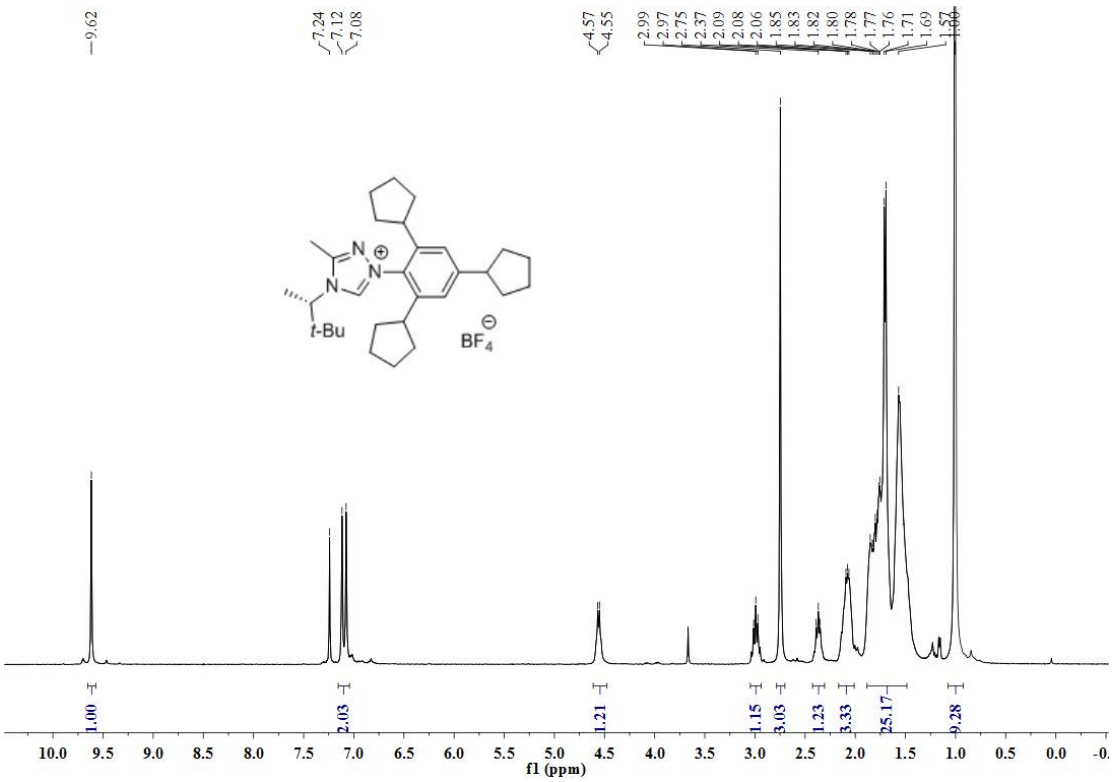


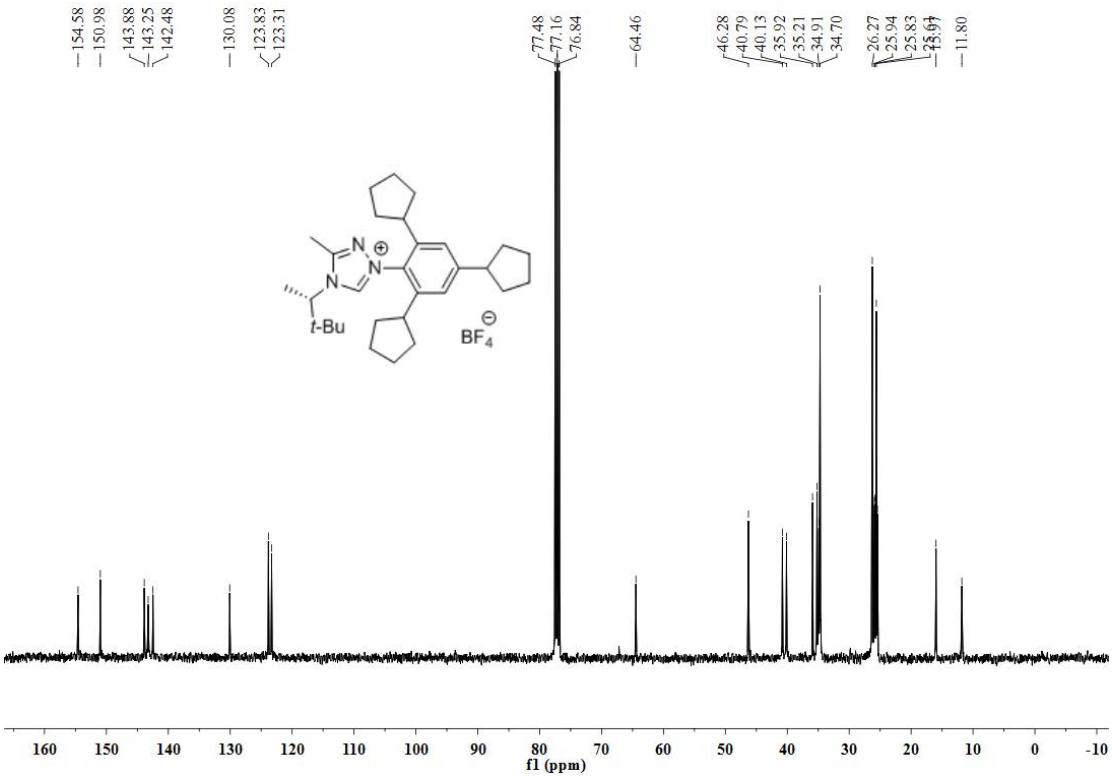
(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(2,4,6-tricyclohexylphenyl)-4H-1, 2,4-triazol-1-ium tetrafluoroborate (6d)



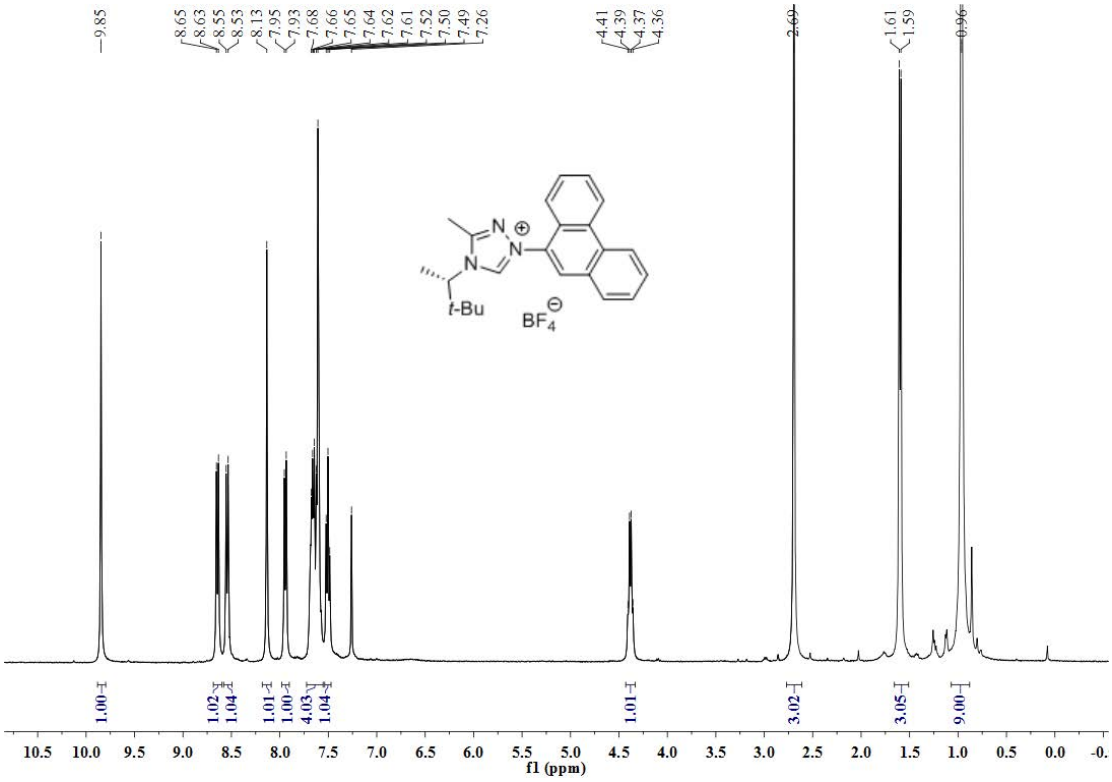


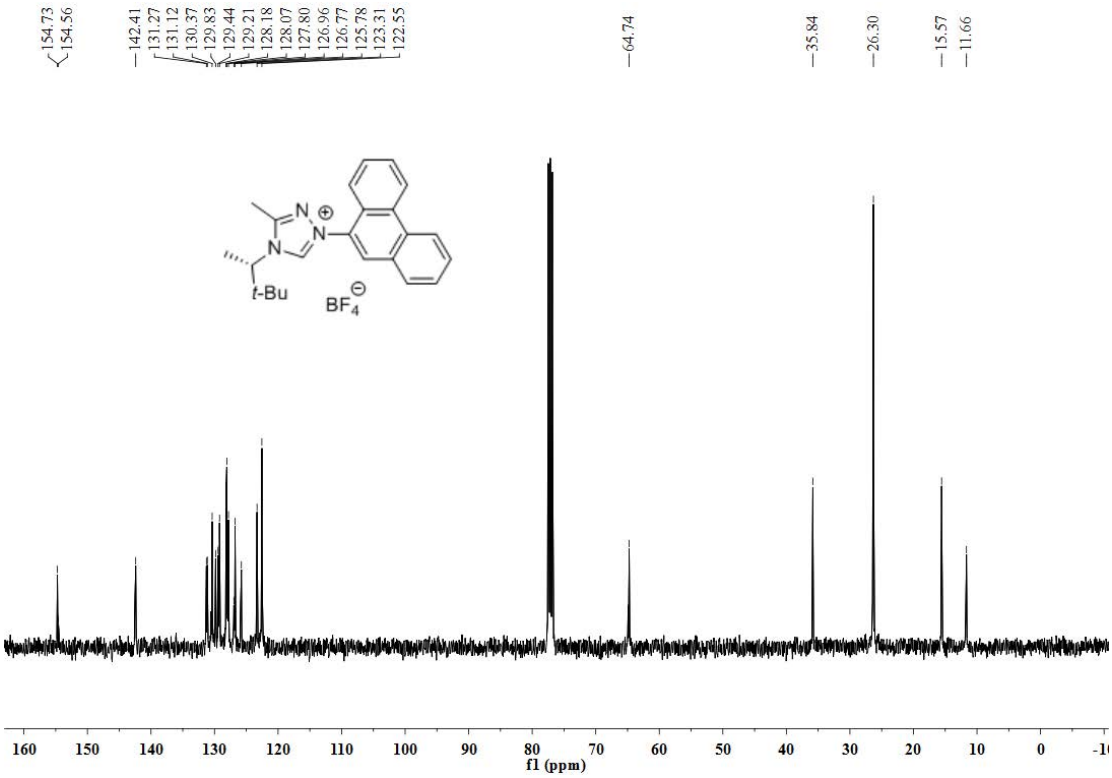
(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(2,4,6-tricyclopentylphenyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (6e)



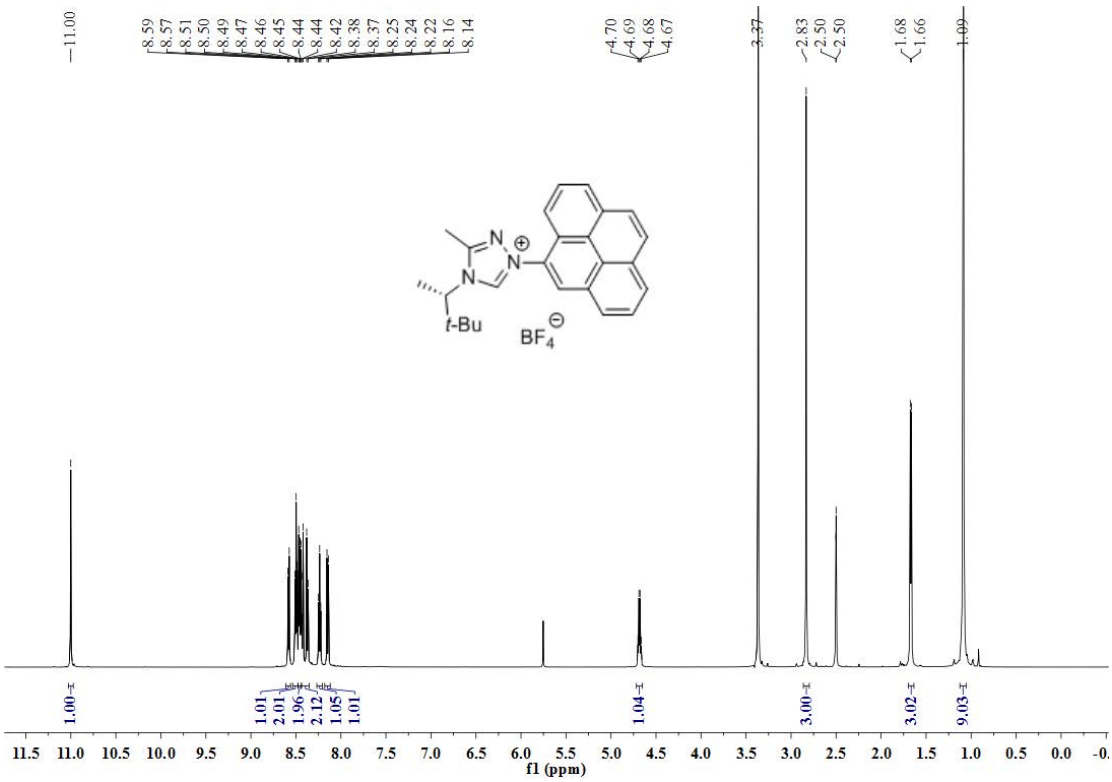


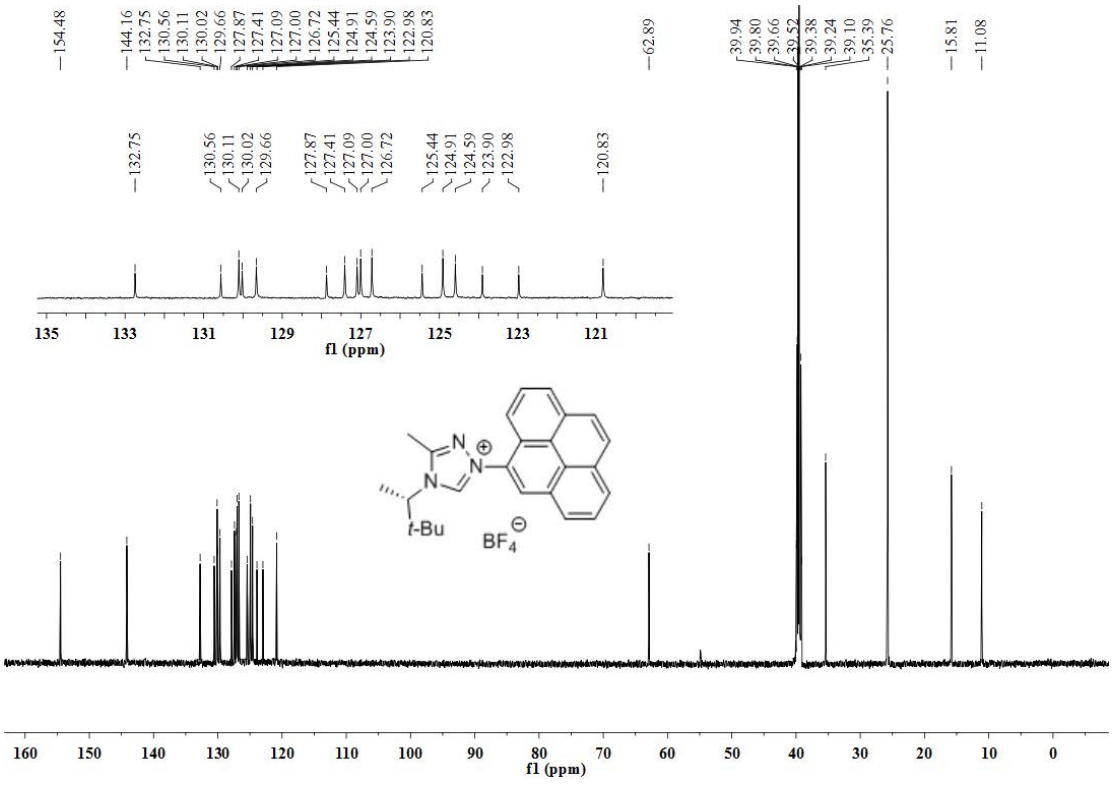
(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(phenanthren-9-yl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (6f)



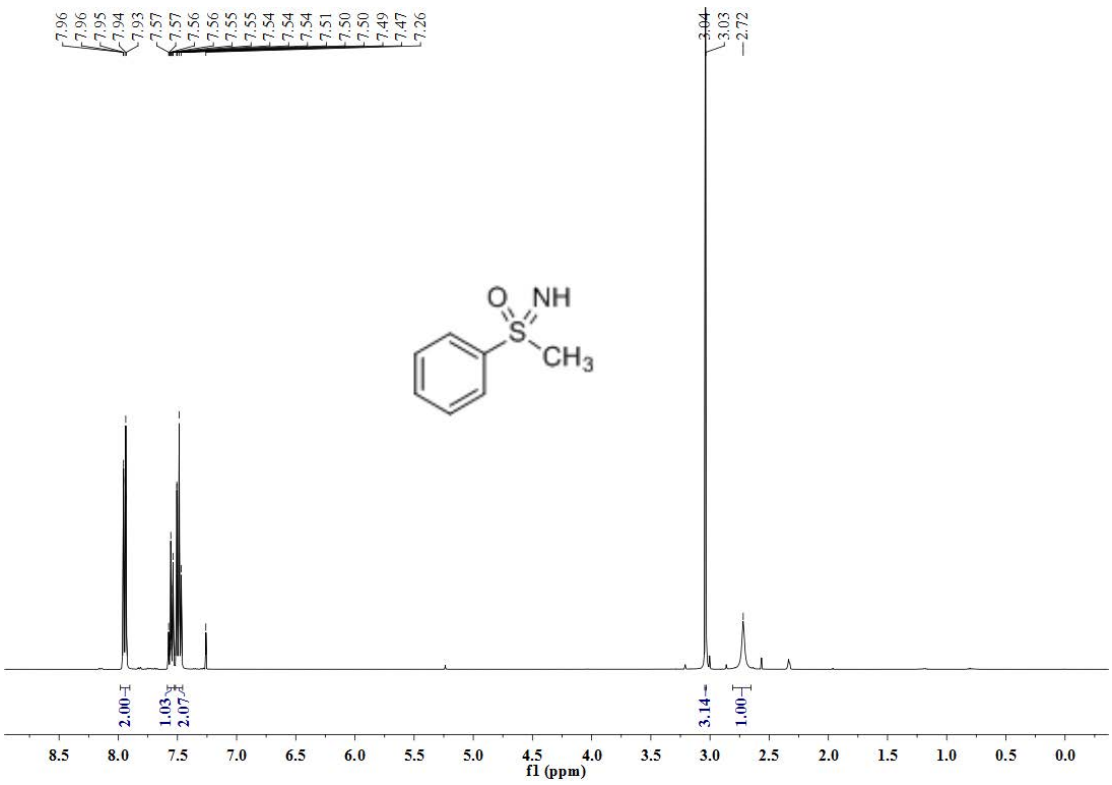


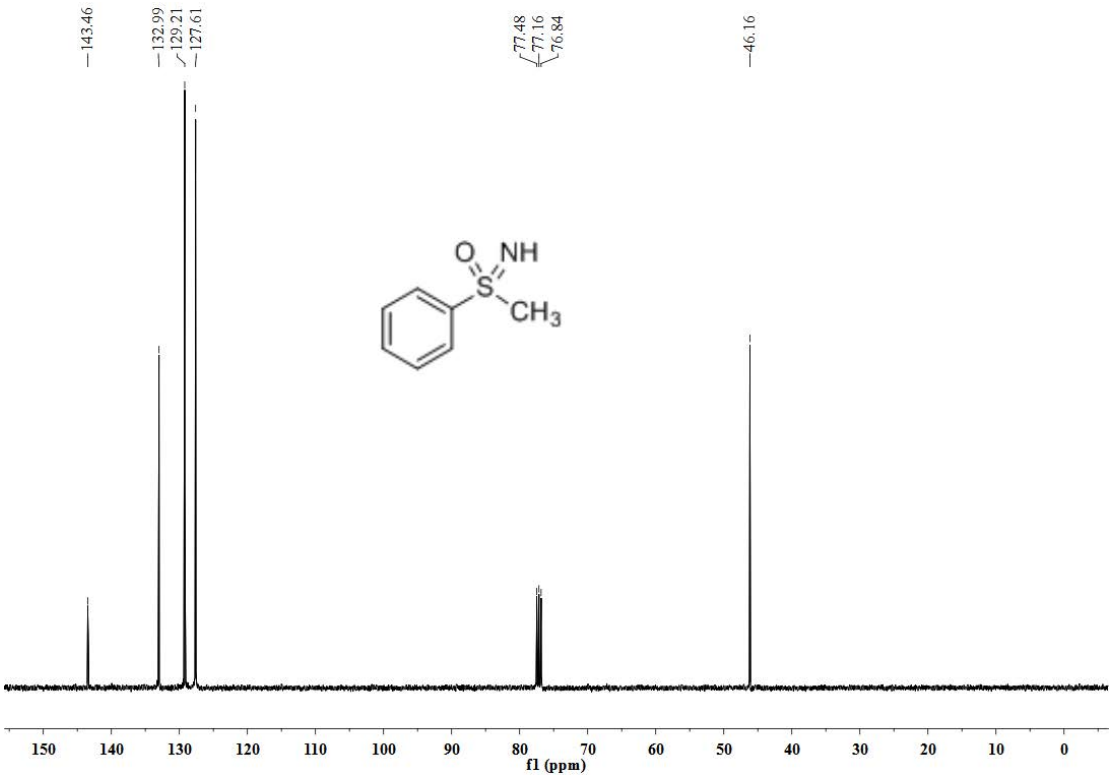
(*S*)-4-(3,3-Dimethylbutan-2-yl)-3-methyl-1-(pyren-4-yl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (6g)



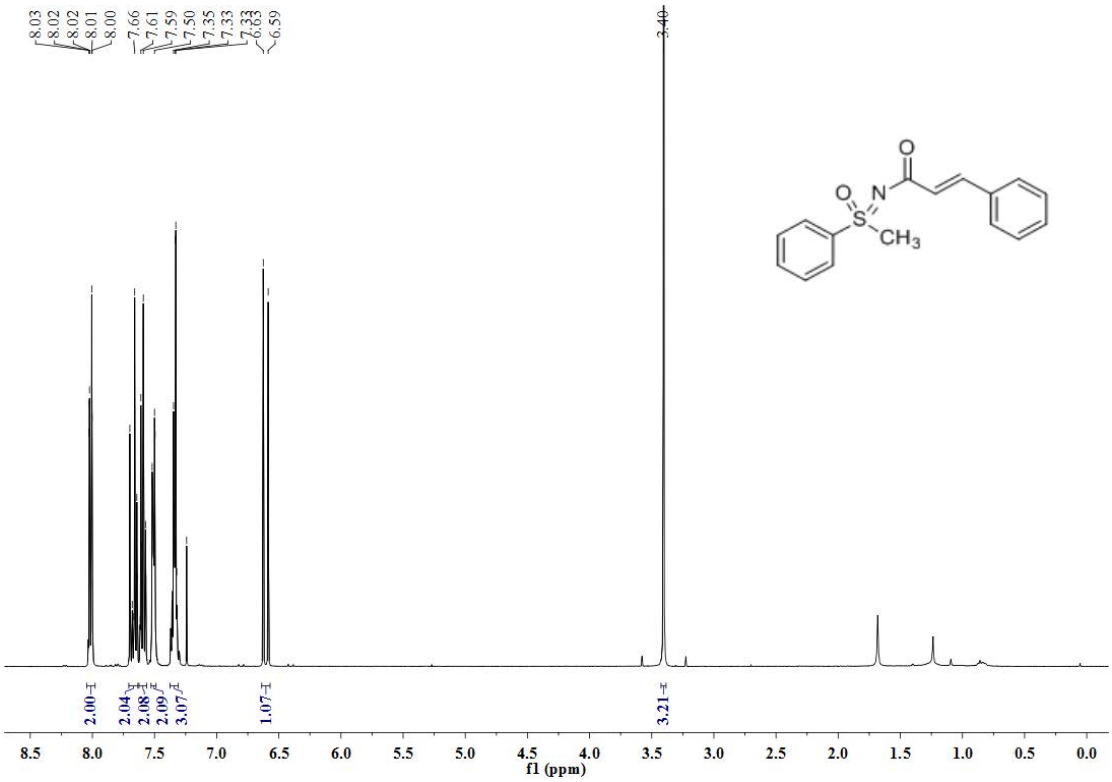


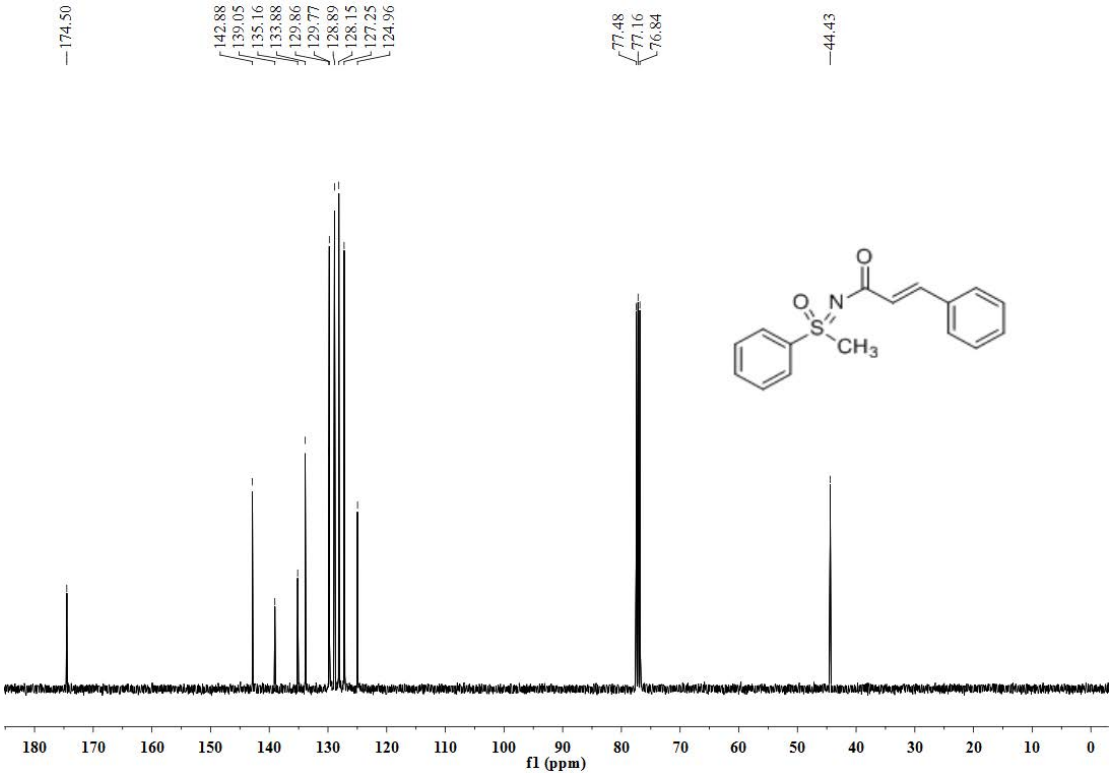
NH-*S*-Methyl-*S*-phenyl-sulfoximine (1a)



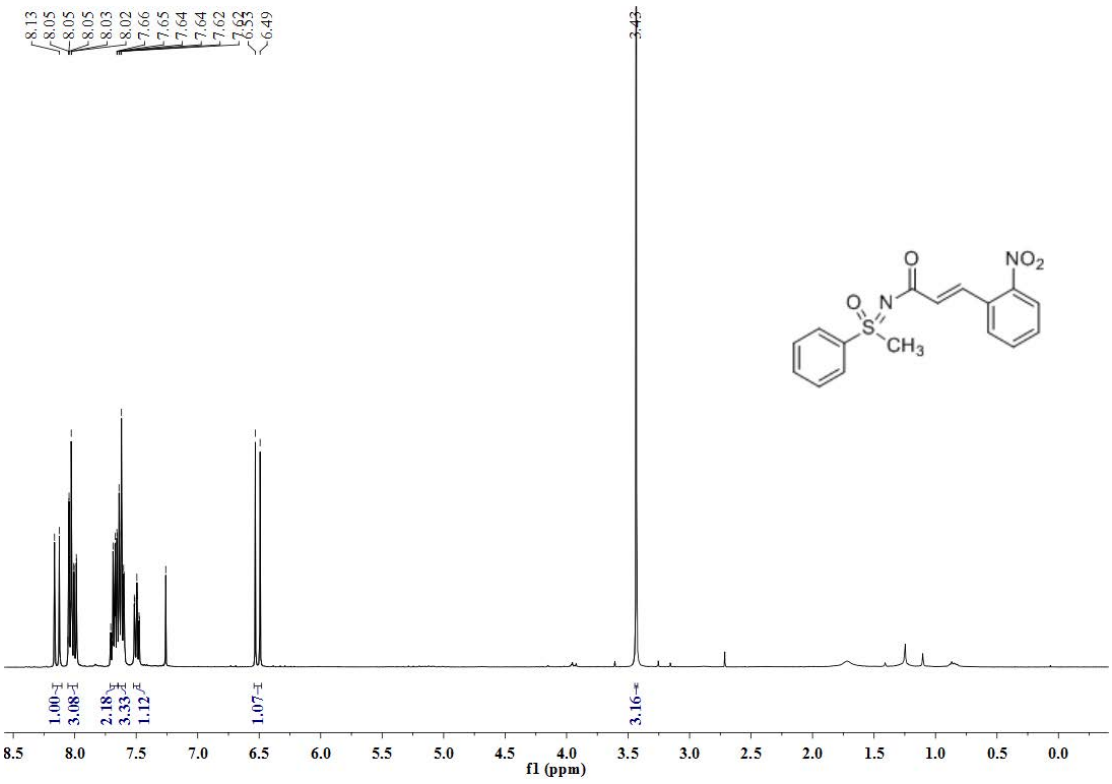


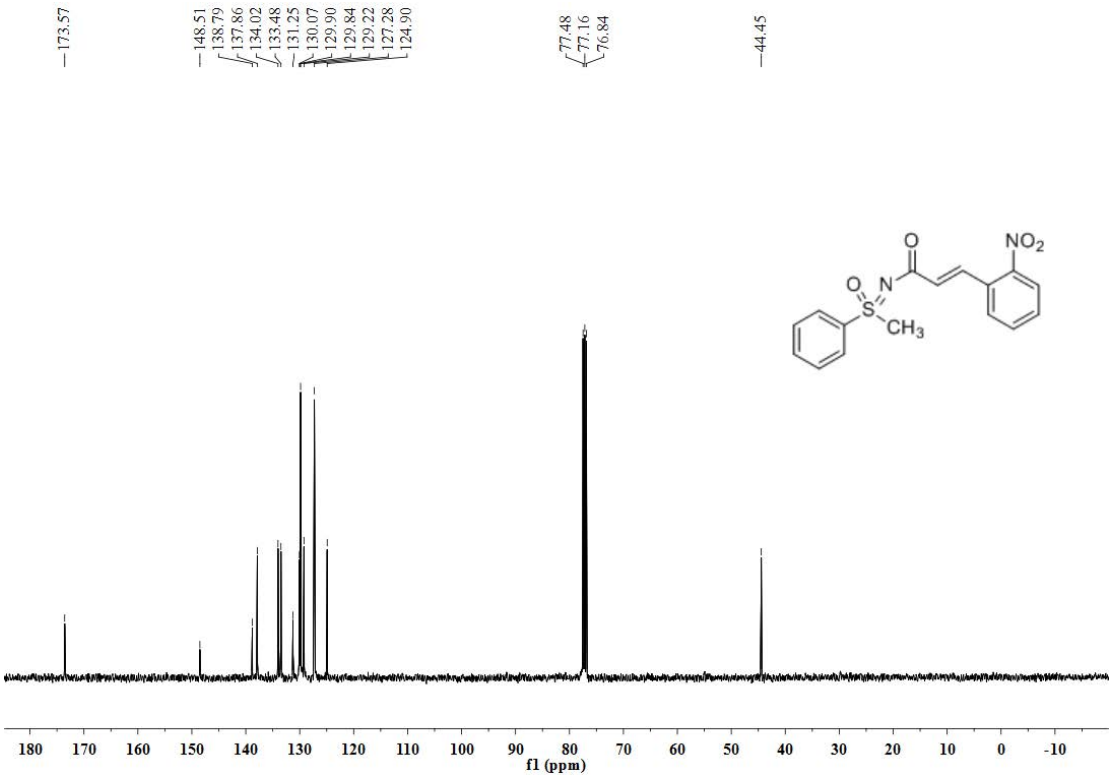
N-[Methyl(oxo)(phenyl)- λ^6-sulfanylidene]cinnamamide (3aa)



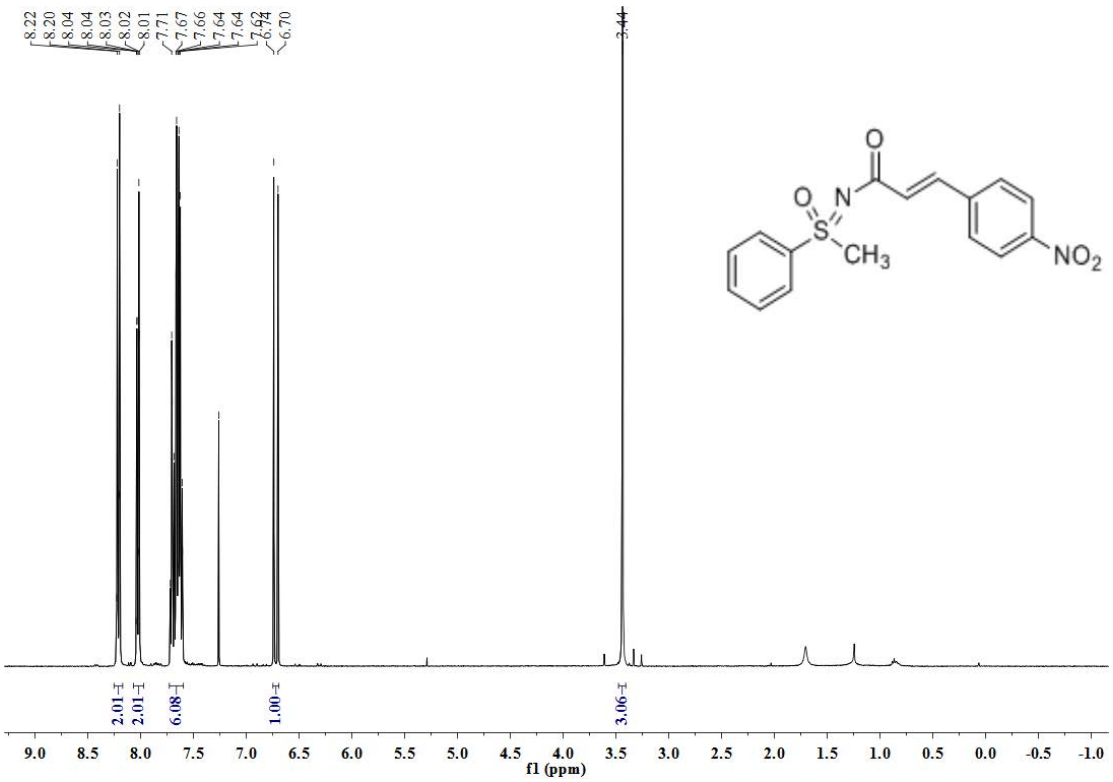


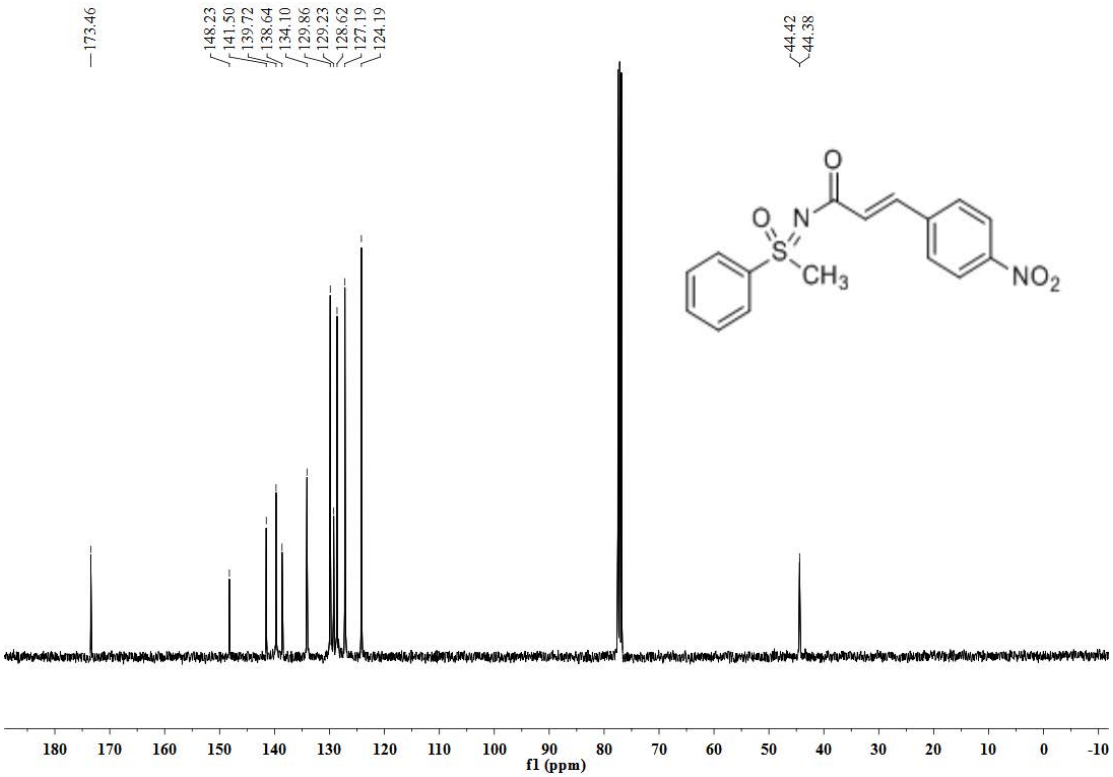
(E)-N-[Methyl(oxo)(phenyl)-λ^6-sulfanylidene]- 3-(2-nitrophenyl) acrylamide (3ab)



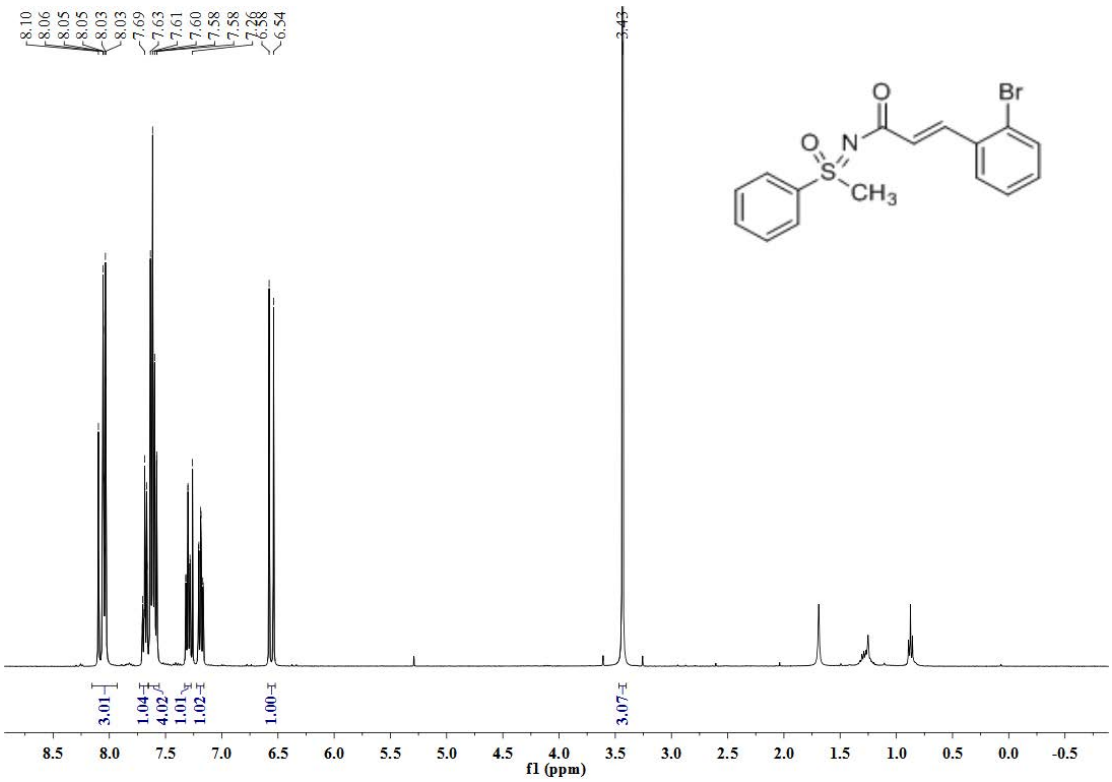


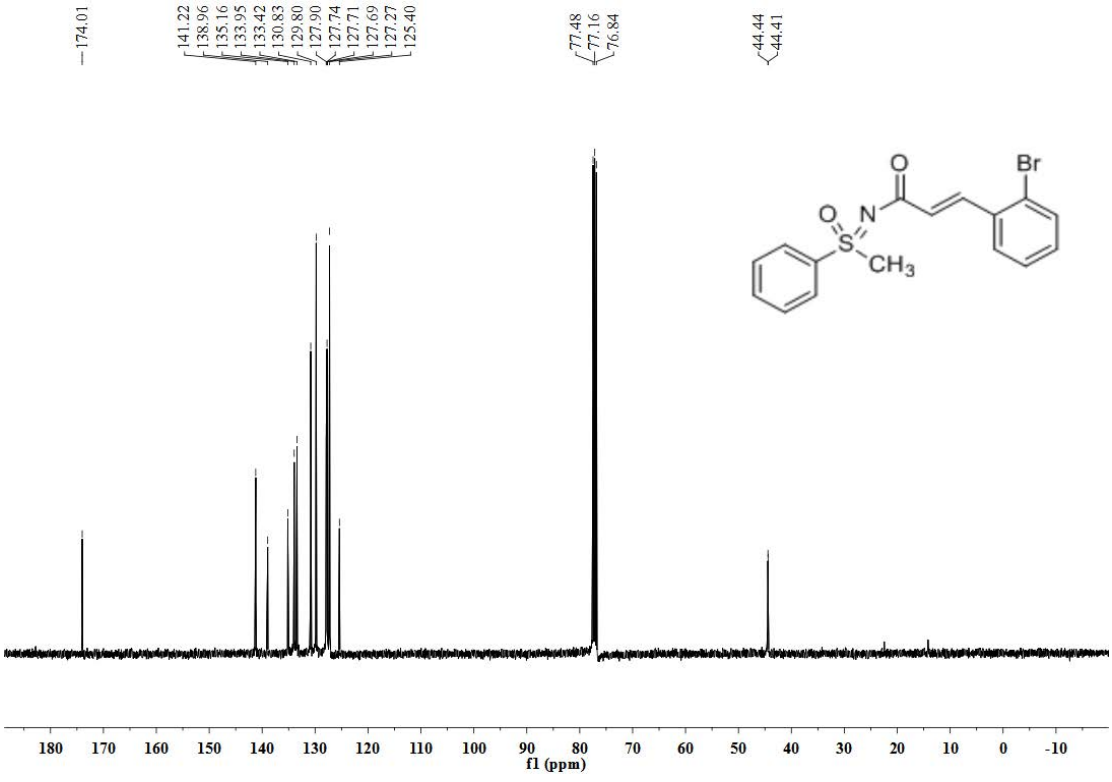
(*E*)-*N*-[Methyl(oxo)(phenyl)- λ^6-sulfanylidene]-3-(4-nitrophenyl)acrylamide (3ac)



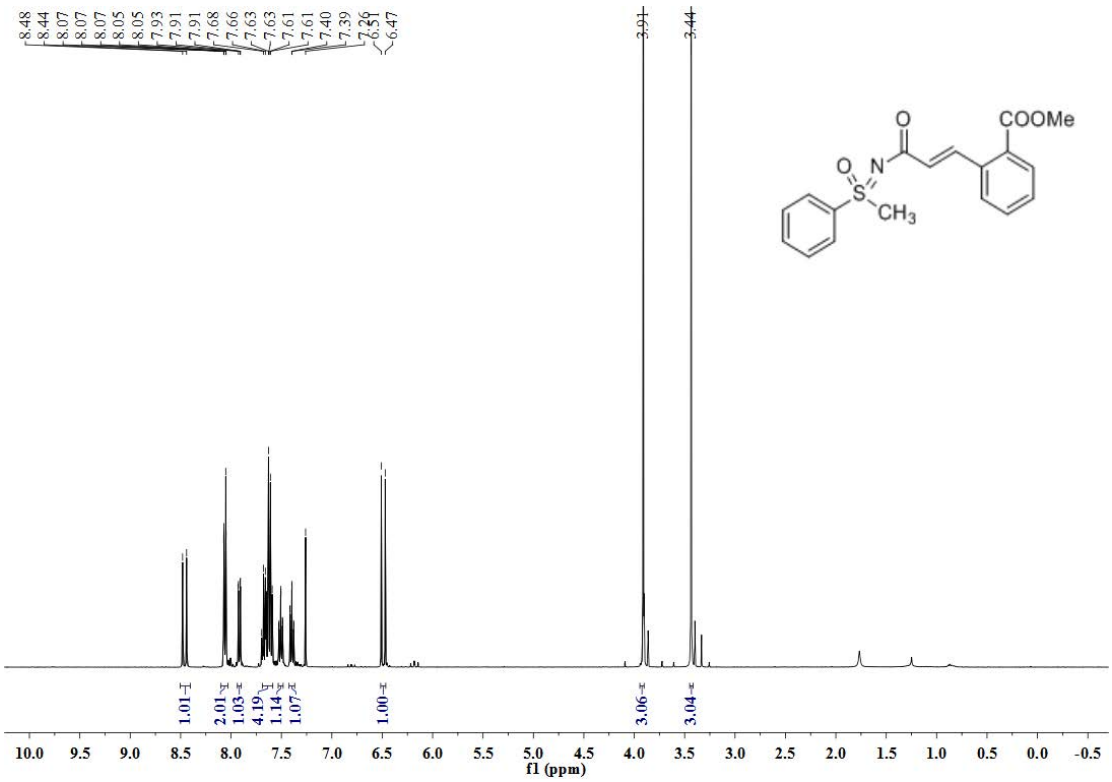


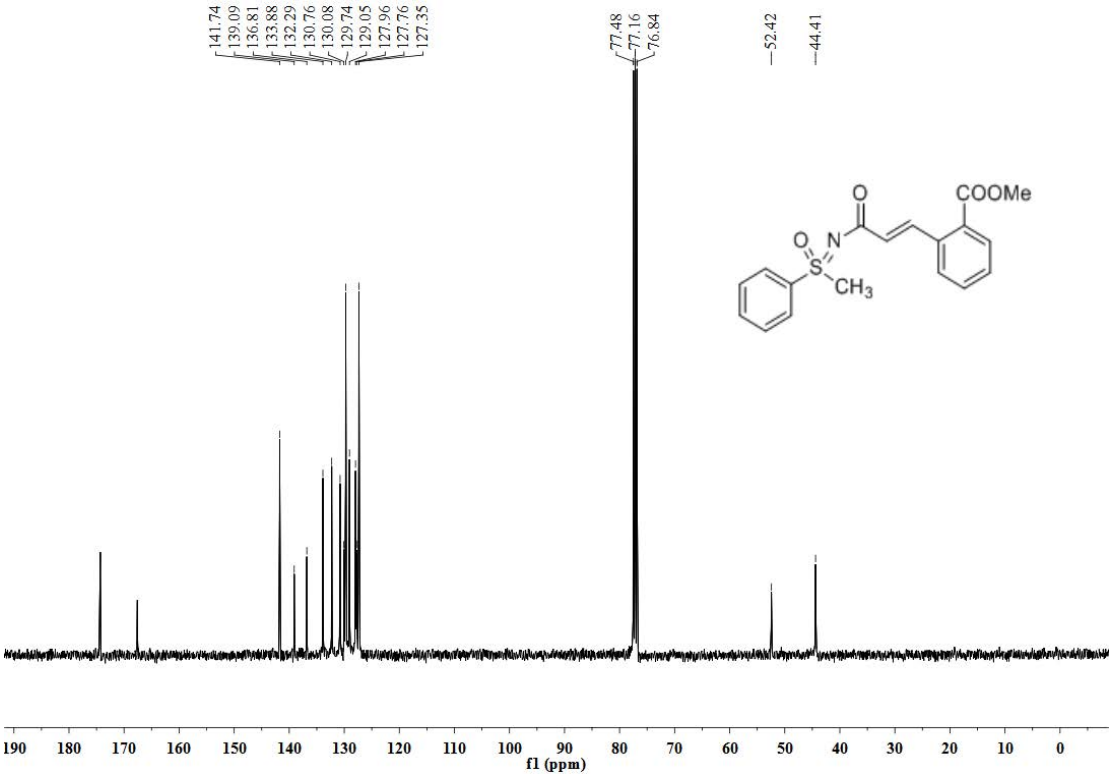
(*E*)-3-(2-Bromophenyl)-*N*-[methyl(oxo)(phenyl)-λ^6-sulfanylidene]acrylamide (3ad)



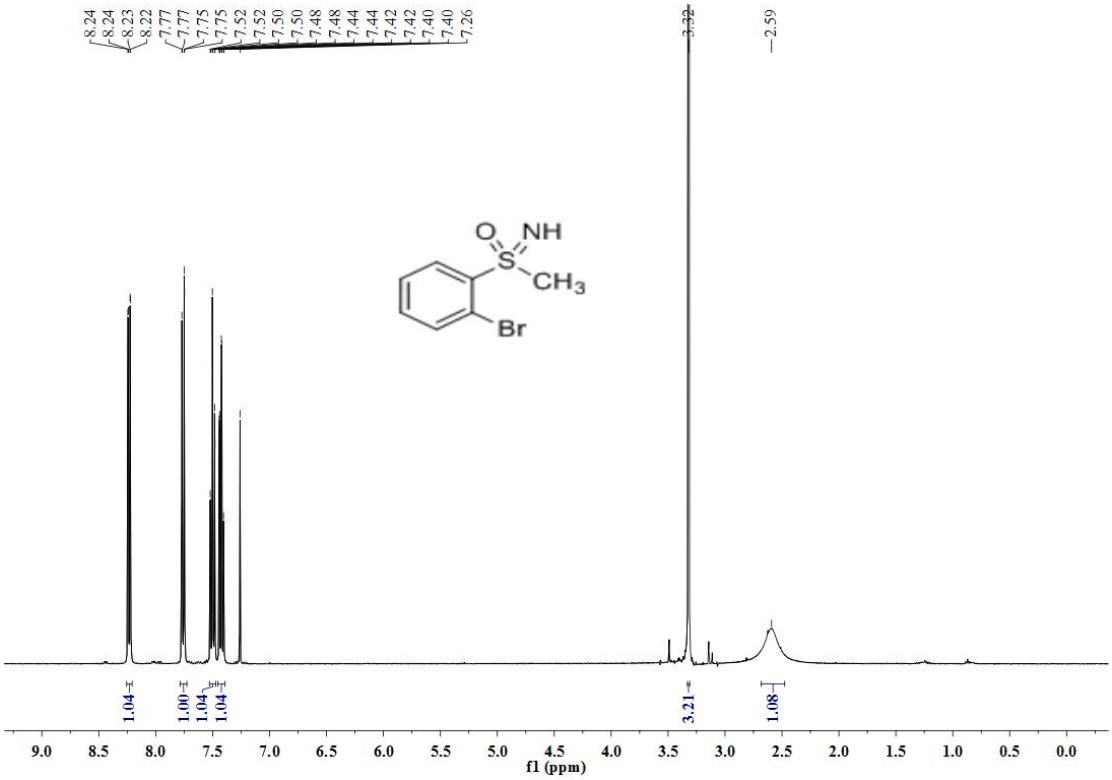


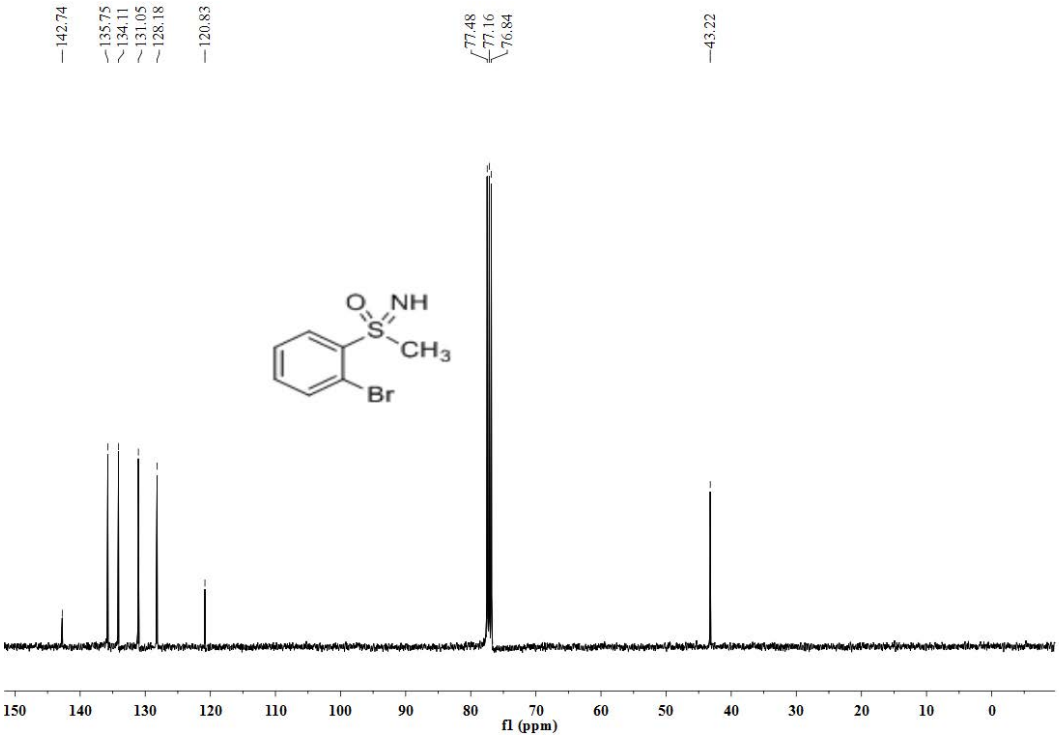
Methyl-(*E*)-2-(3-{[methyl(oxo)(phenyl)-λ^6-sulfanylidene]amino}-3-oxoprop-1-en-1-yl)benzoate (3ae)



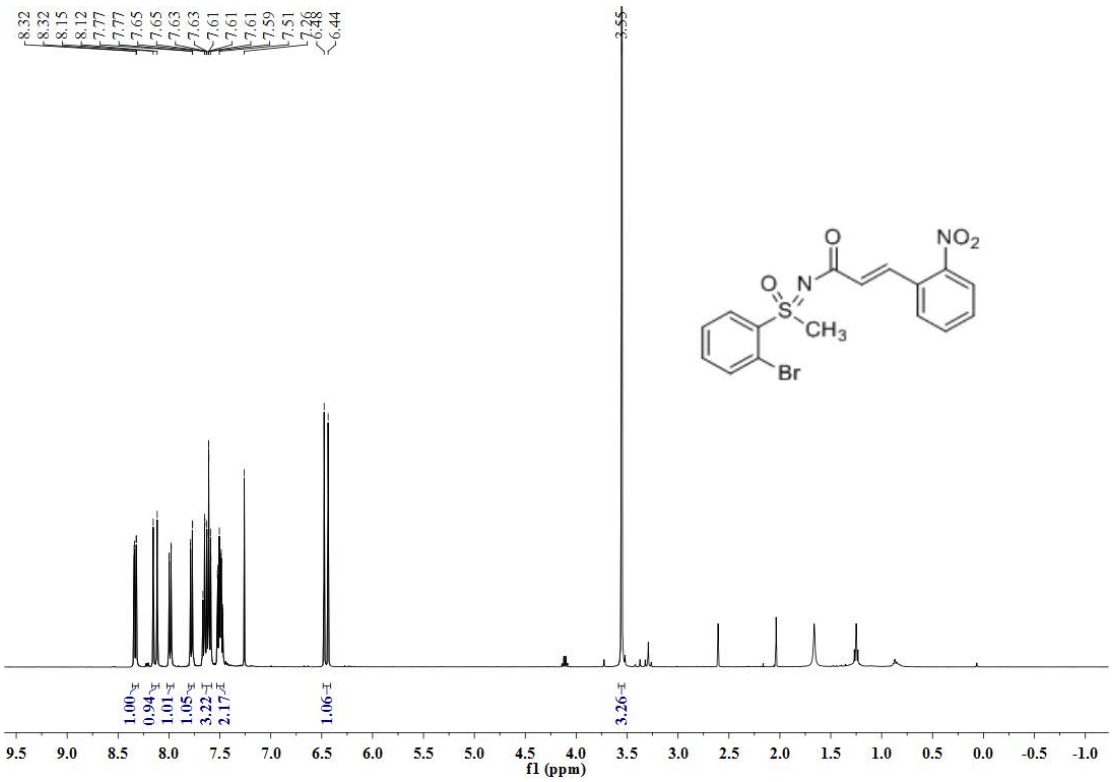


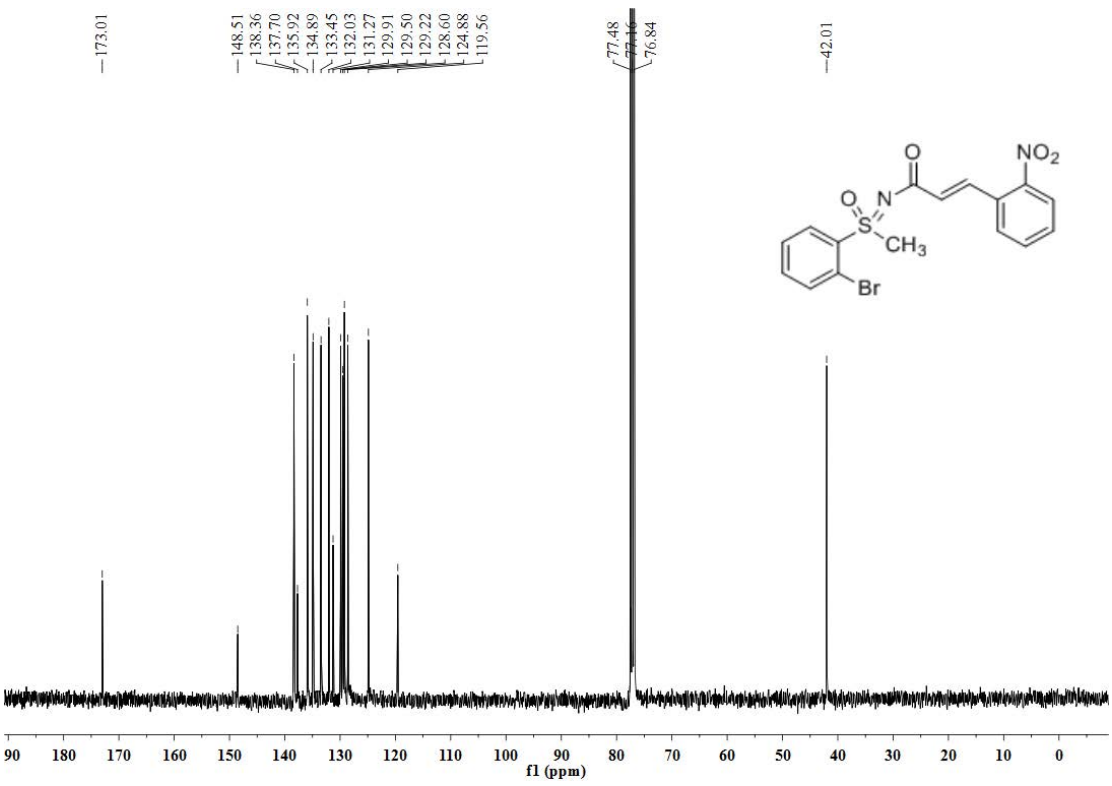
NH-*S*-(2-Bromophenyl)-*S*-methyl-sulfoximine (1b)



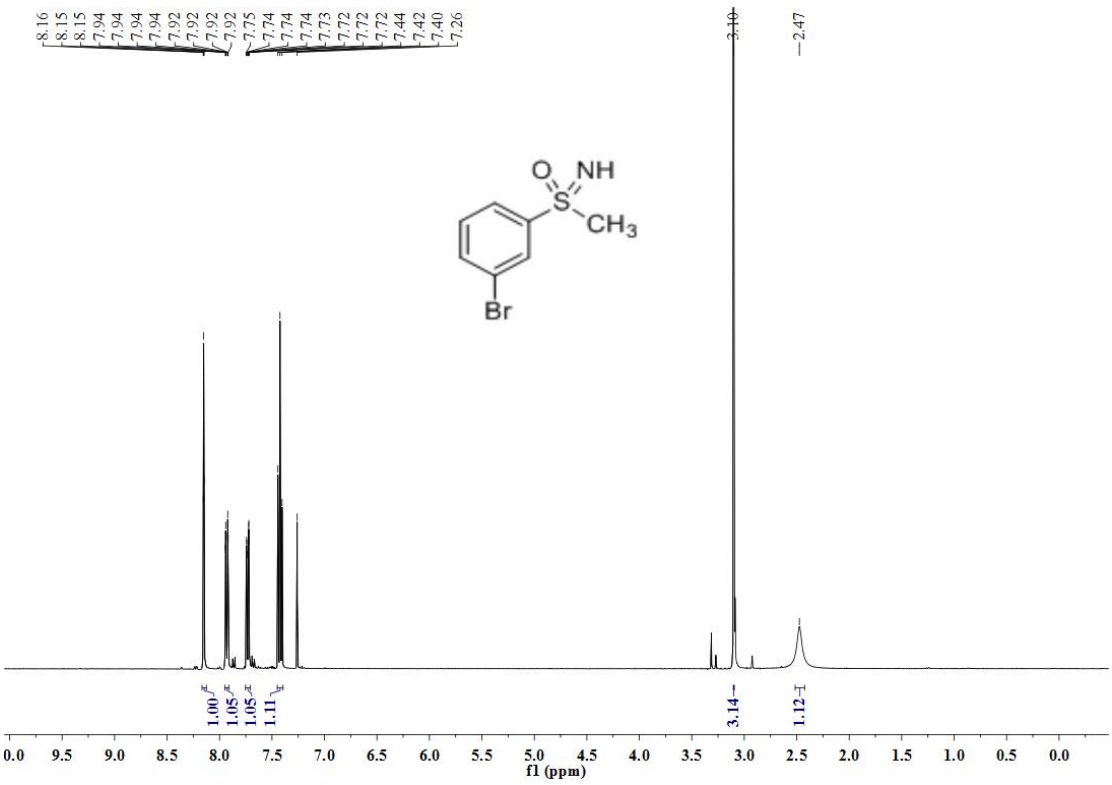


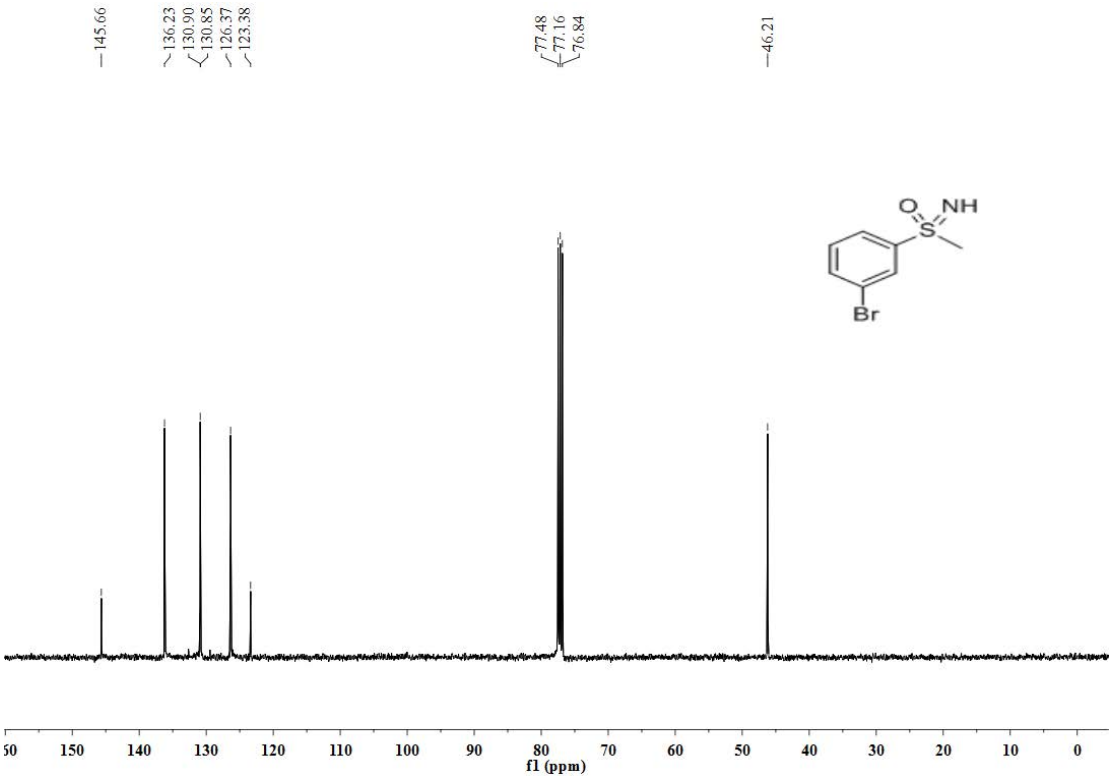
(*E*)-*N*-[(2-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3b)



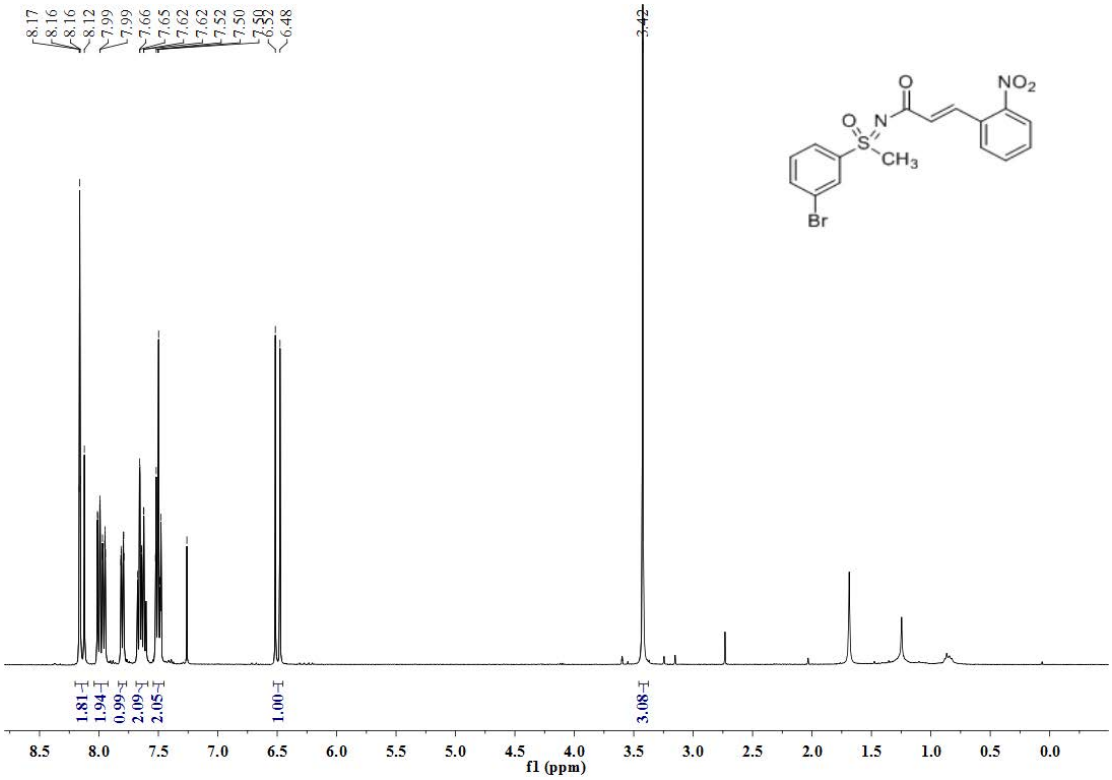


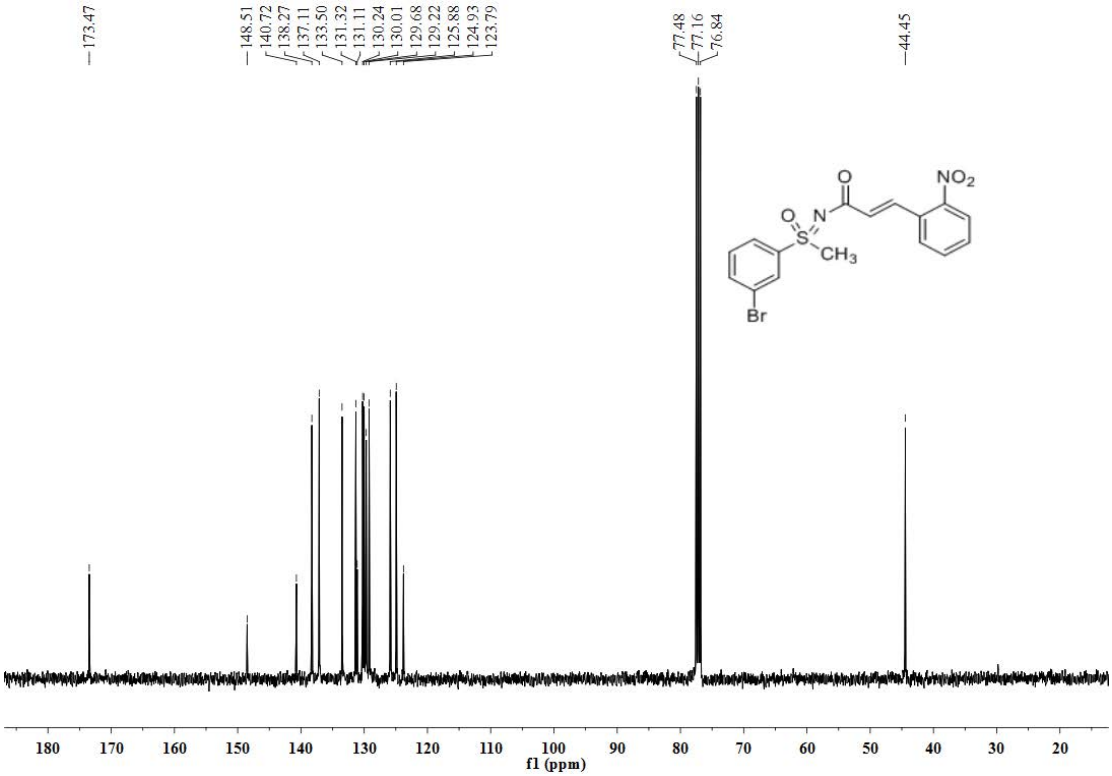
NH-S-(3-Bromophenyl)-*S*-methyl- sulfoximine (1c)



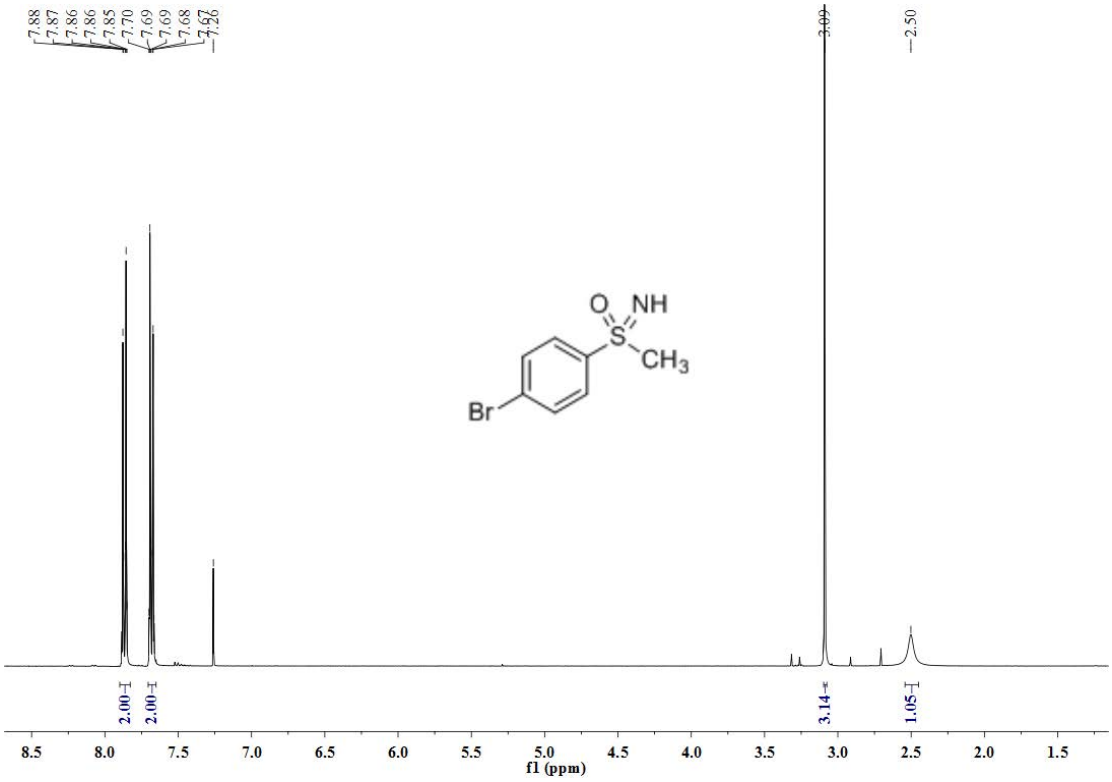


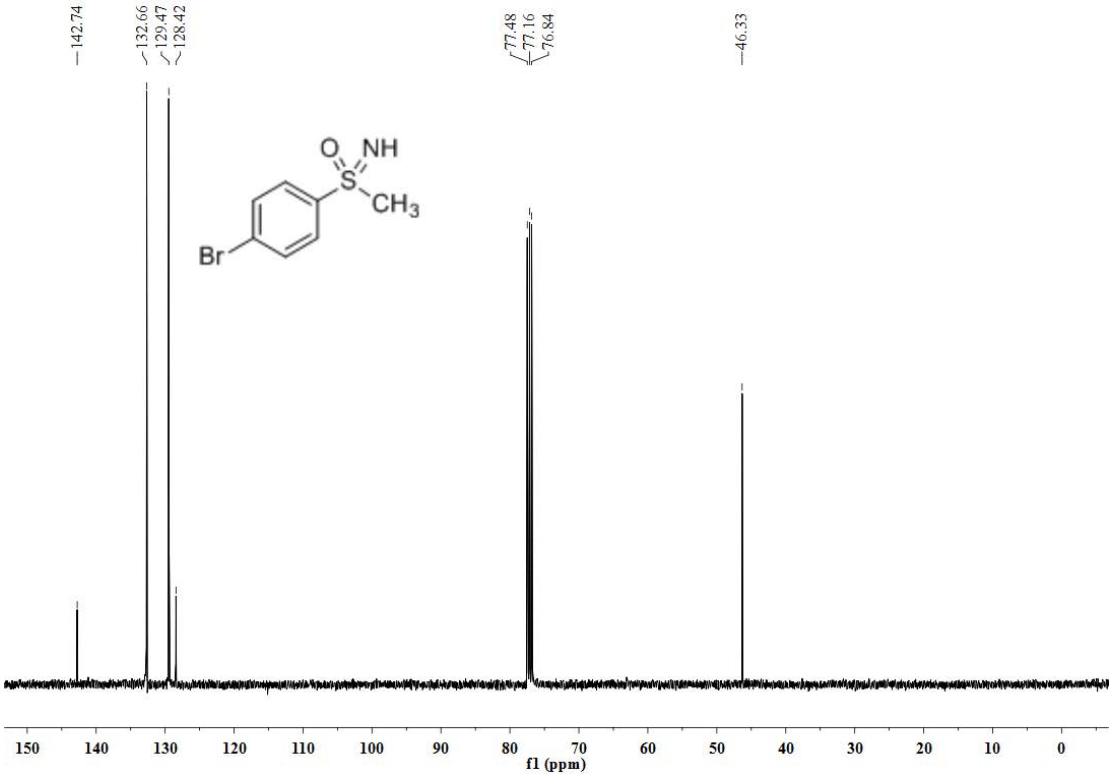
(*E*)-*N*-[(3-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3c)



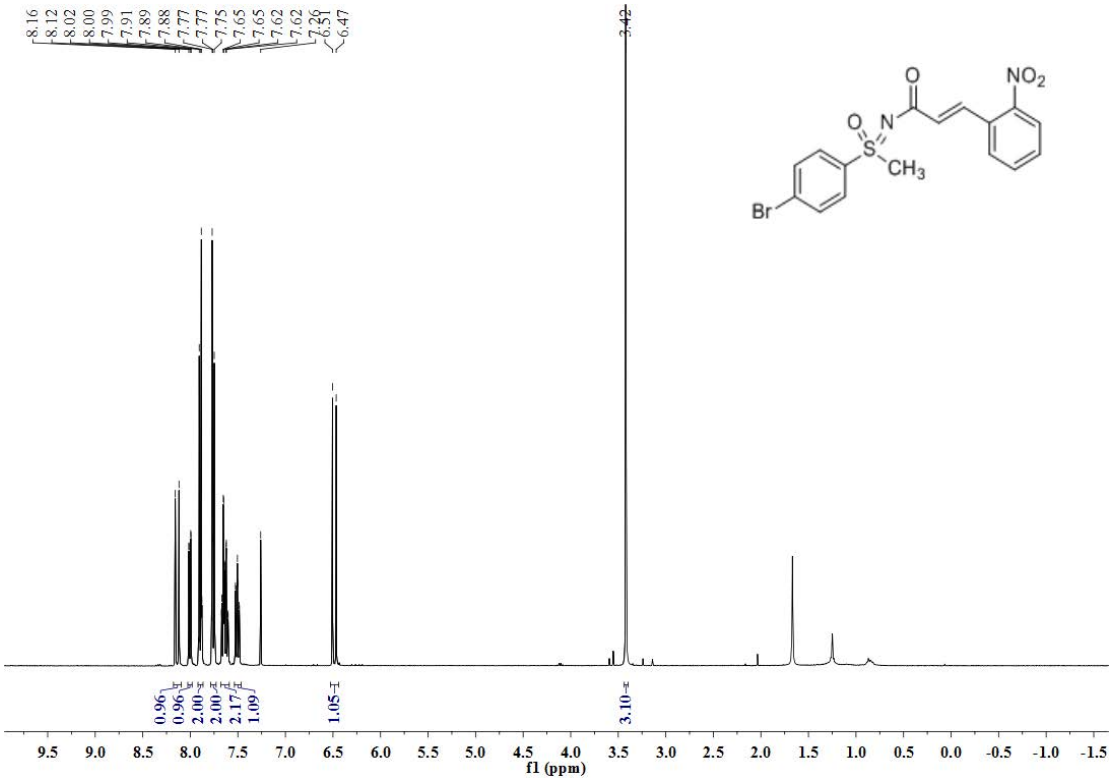


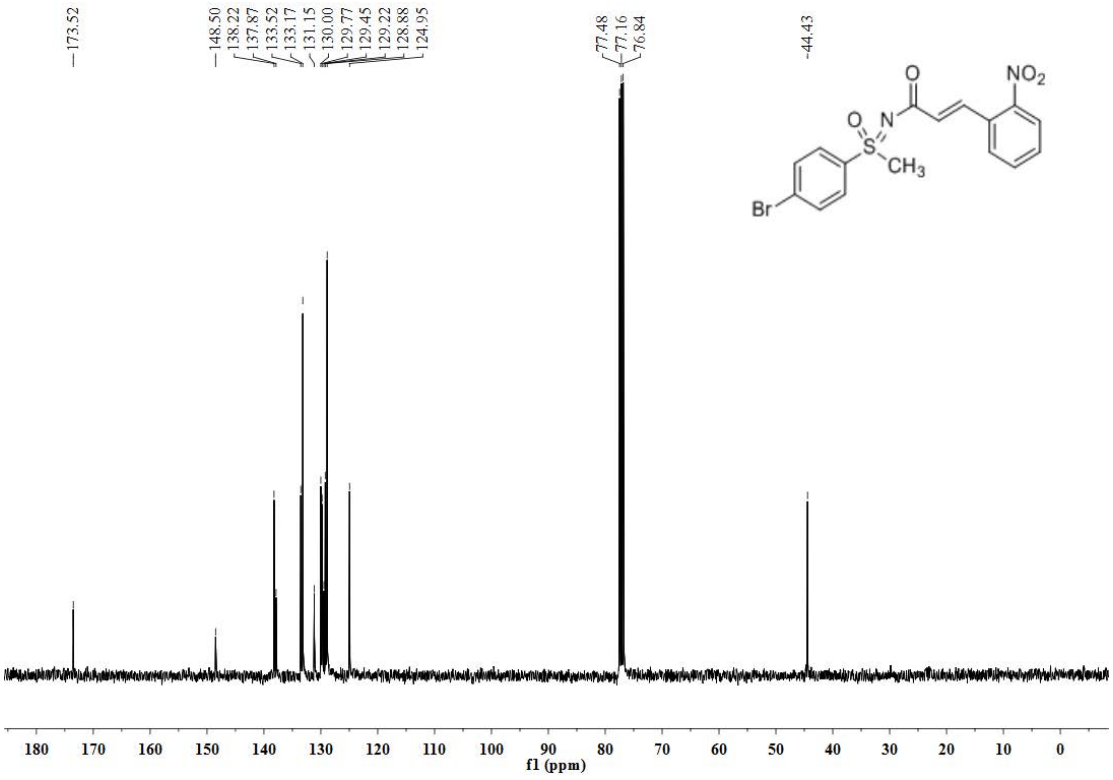
NH-*S*-(4-Bromophenyl)-*S*-methyl-sulfoximine (1d)



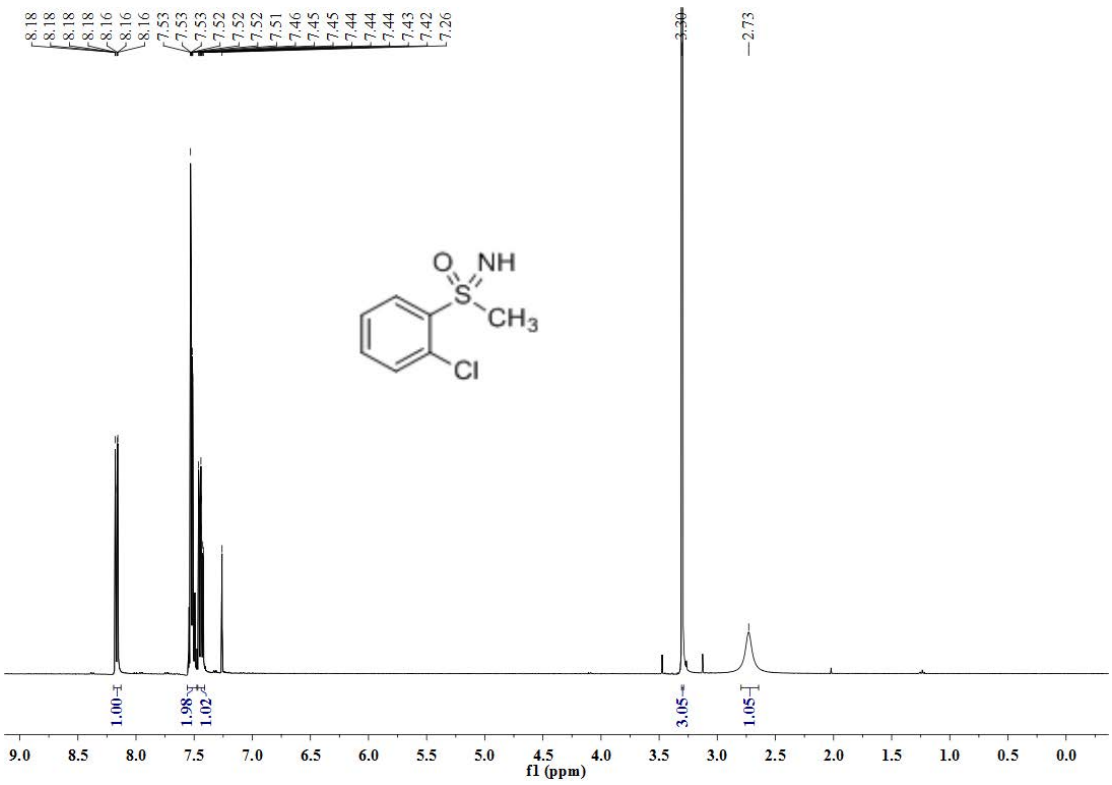


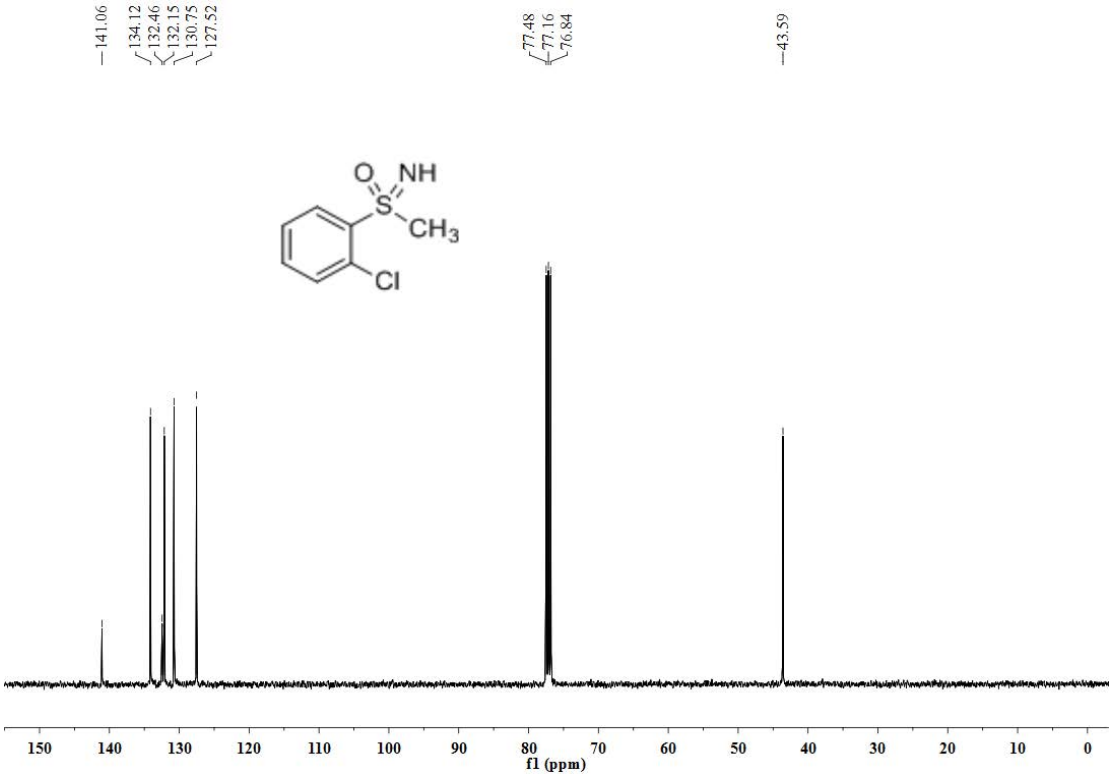
(*E*)-*N*-[(4-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3d)



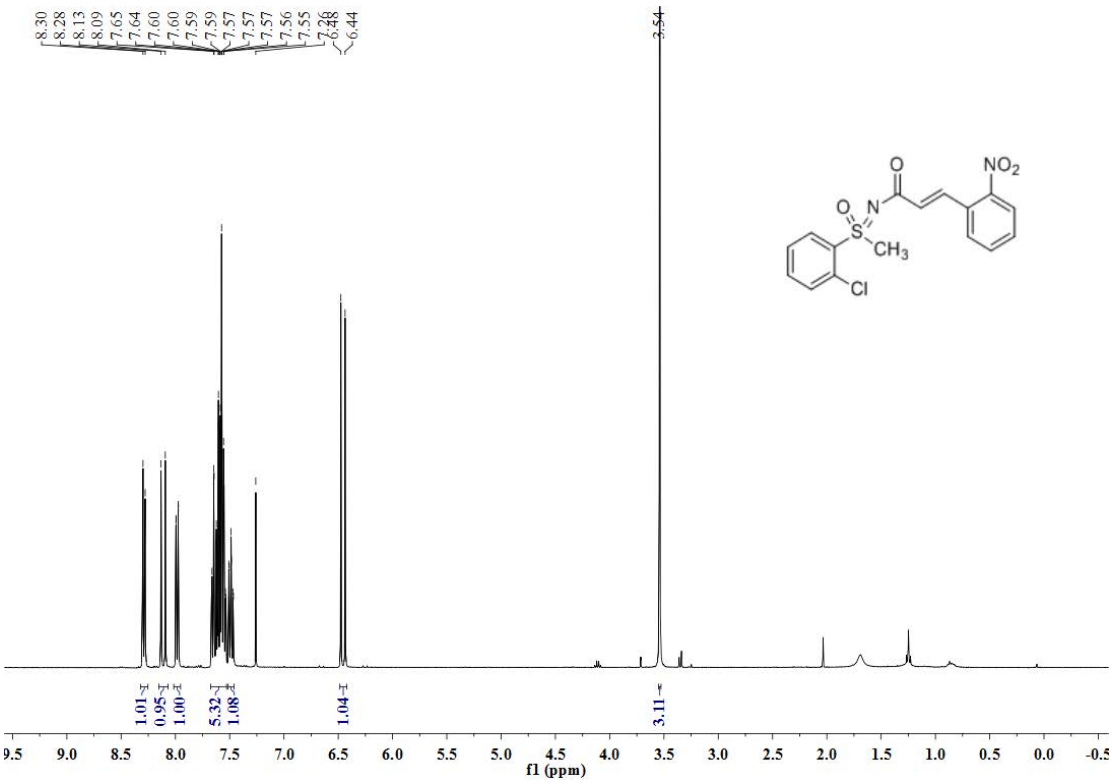


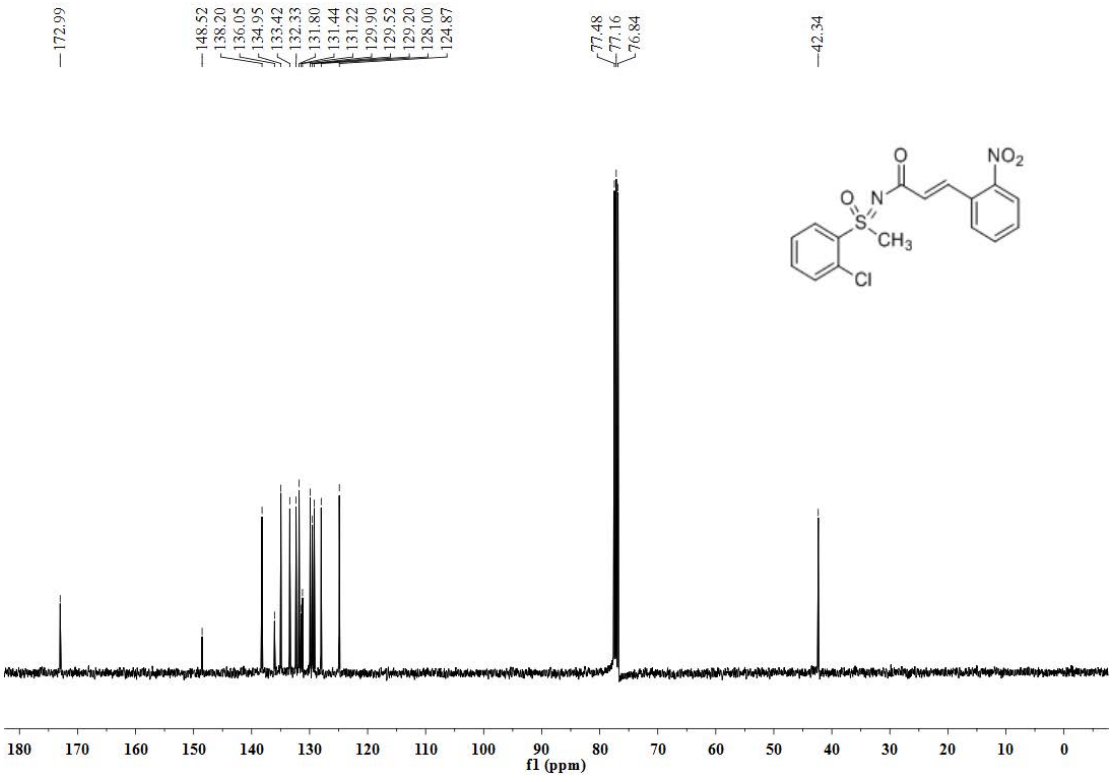
NH-S-(2-Chlorophenyl)-*S*-methyl- sulfoximine (1e)



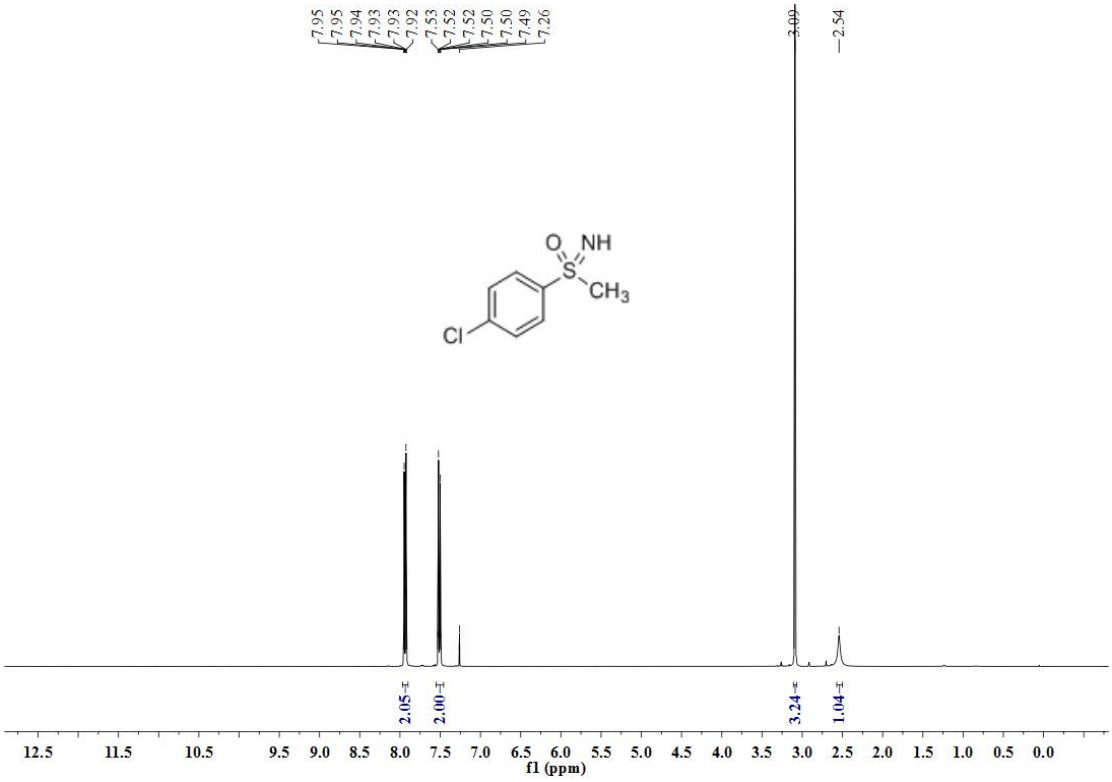


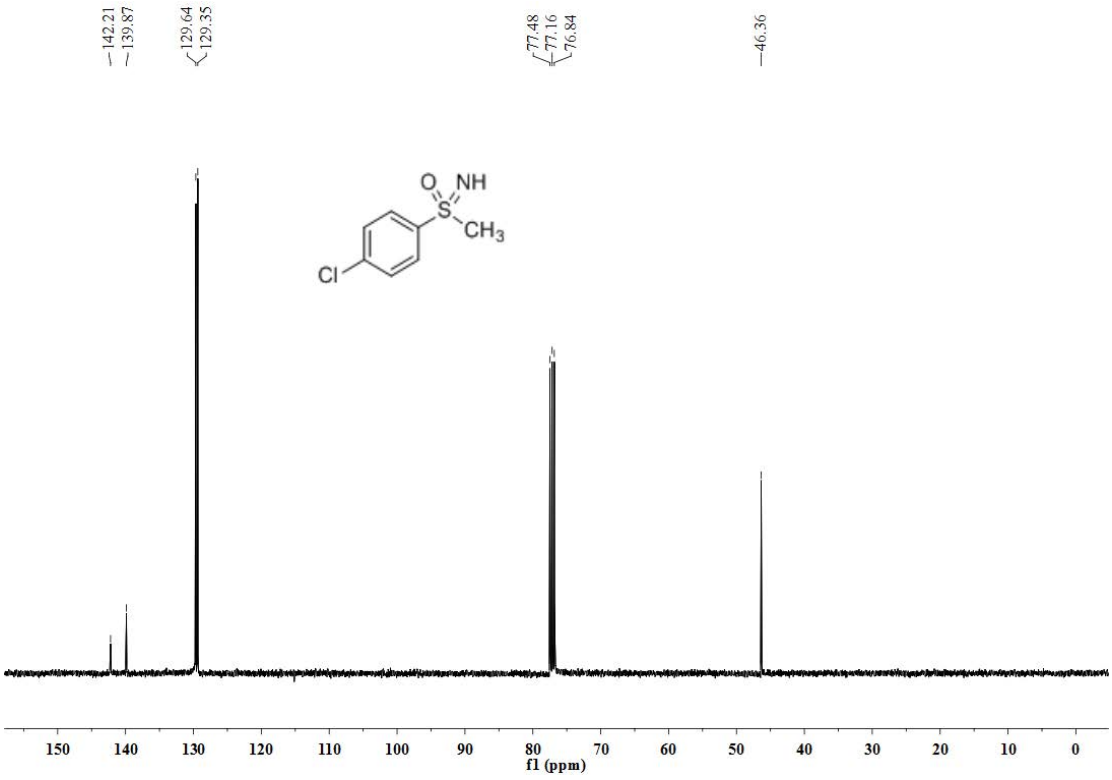
(*E*)-*N*-[(2-Chlorophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3e)



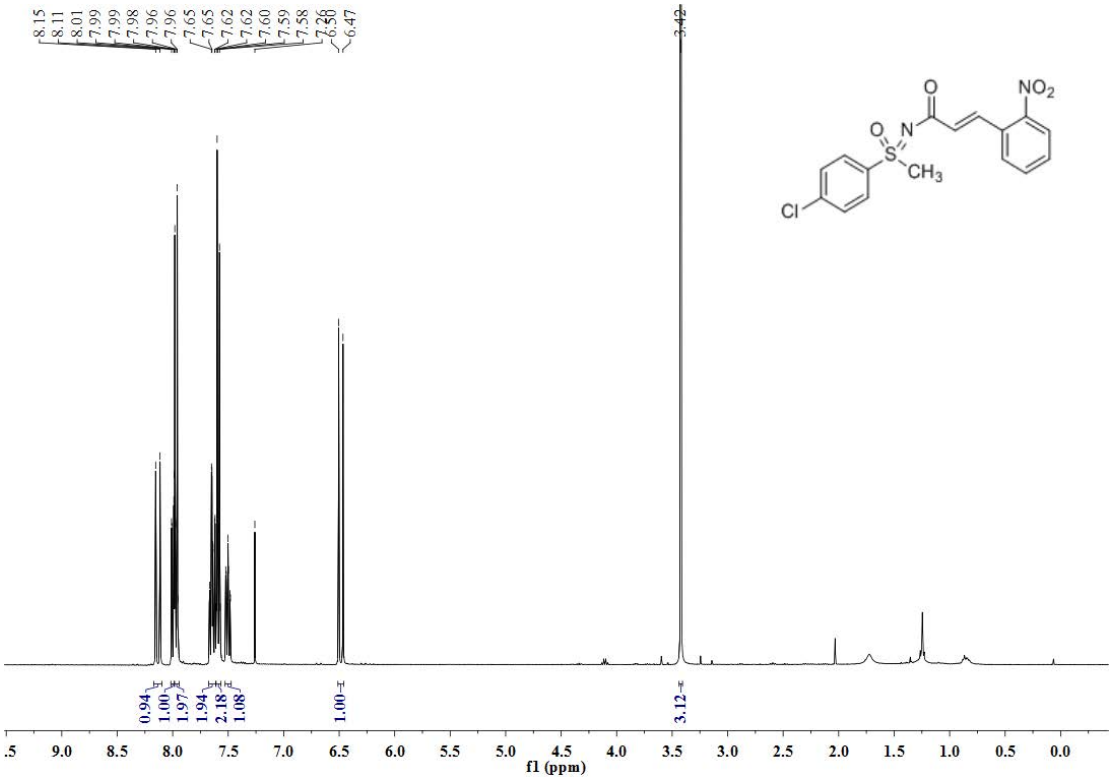


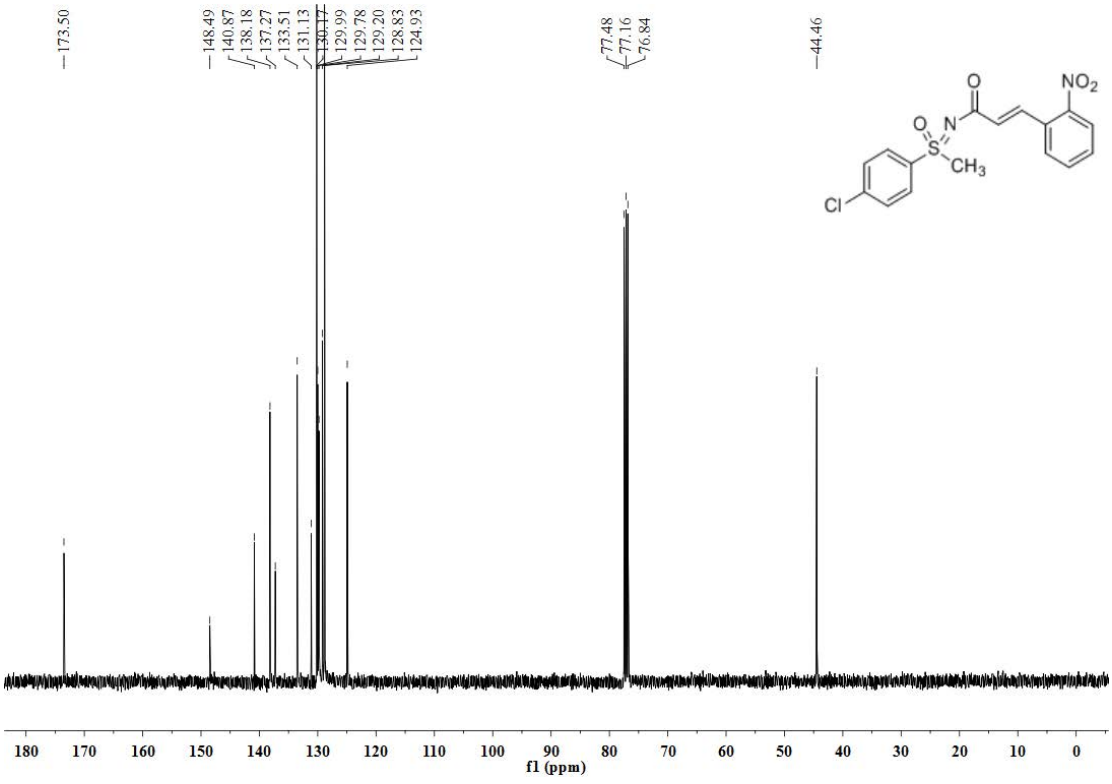
NH-*S*-(4-Chlorophenyl)-*S*-methyl- sulfoximine (1f)



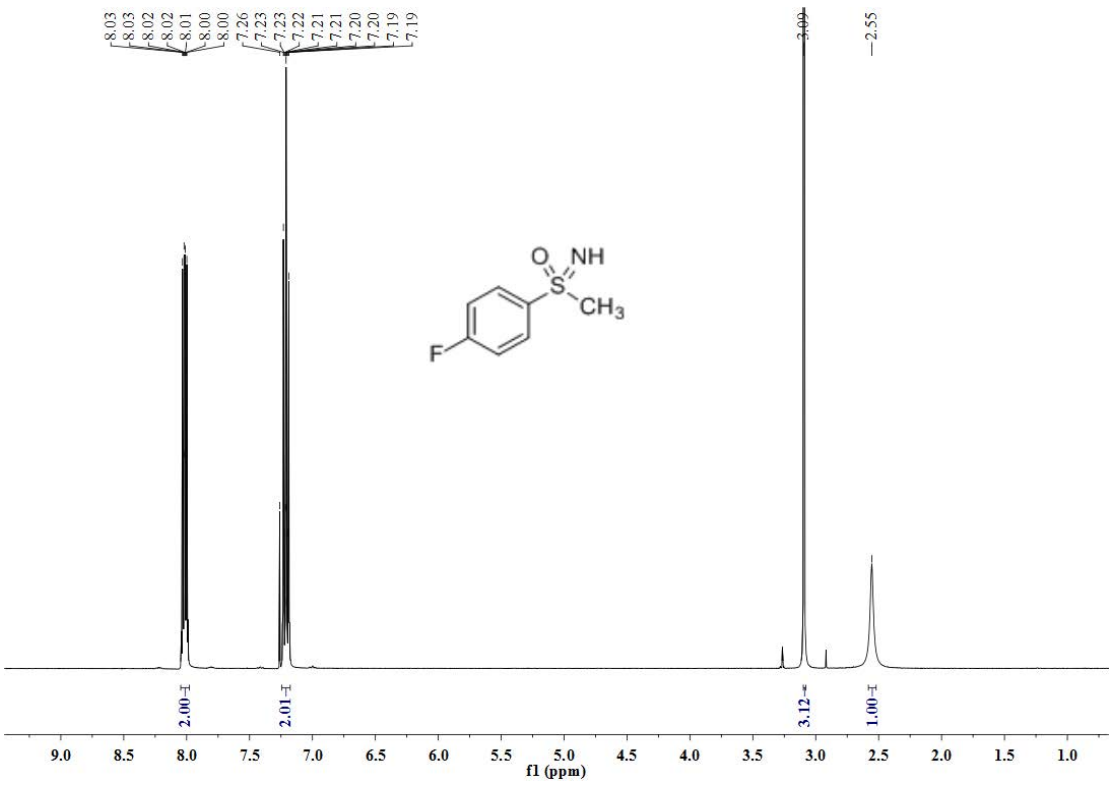


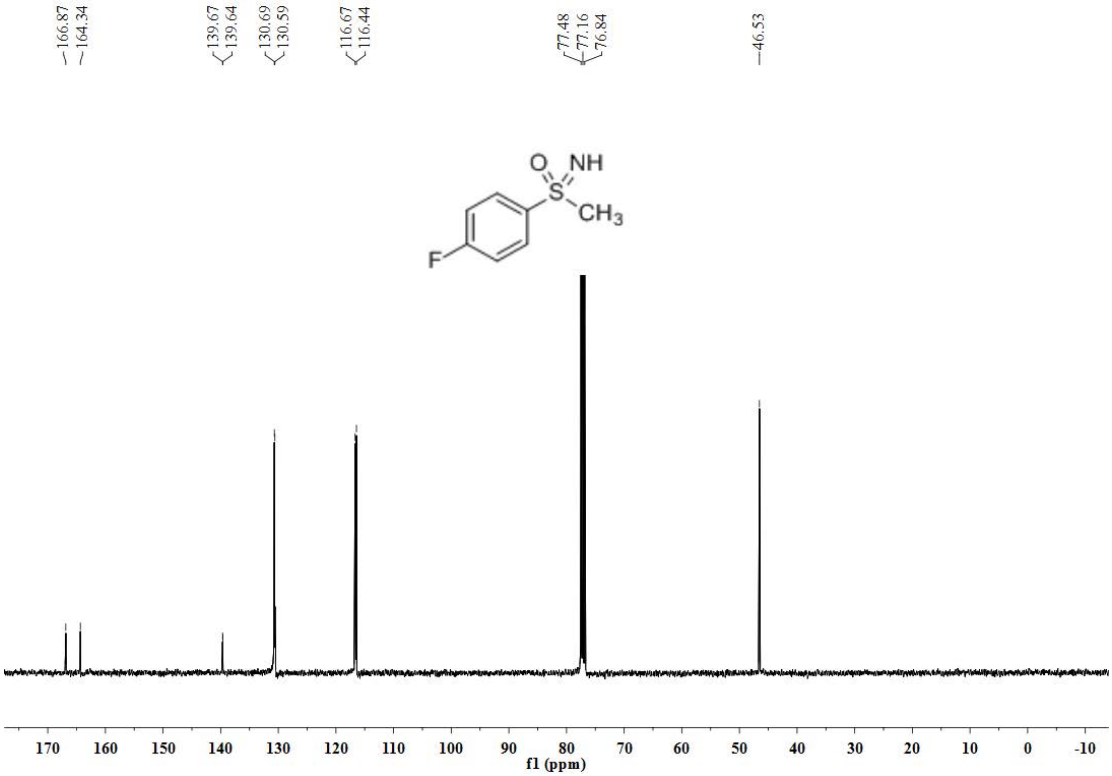
(*E*)-*N*-[(4-Chlorophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl) acrylamide (3f)

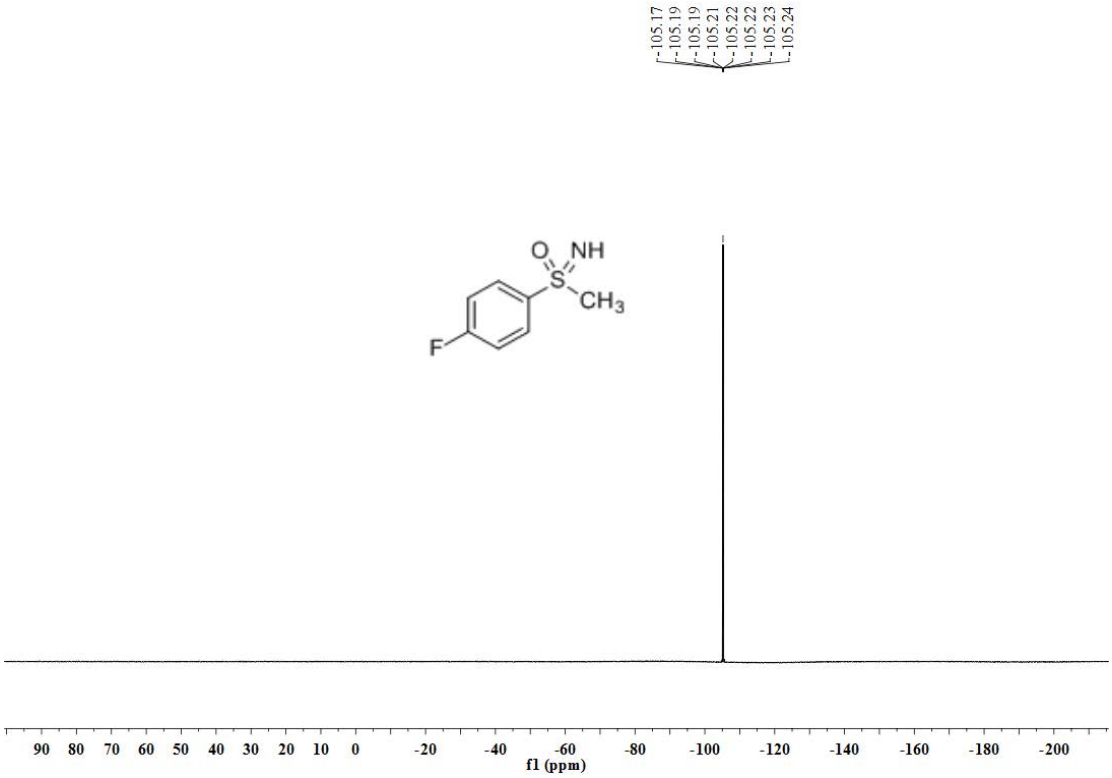




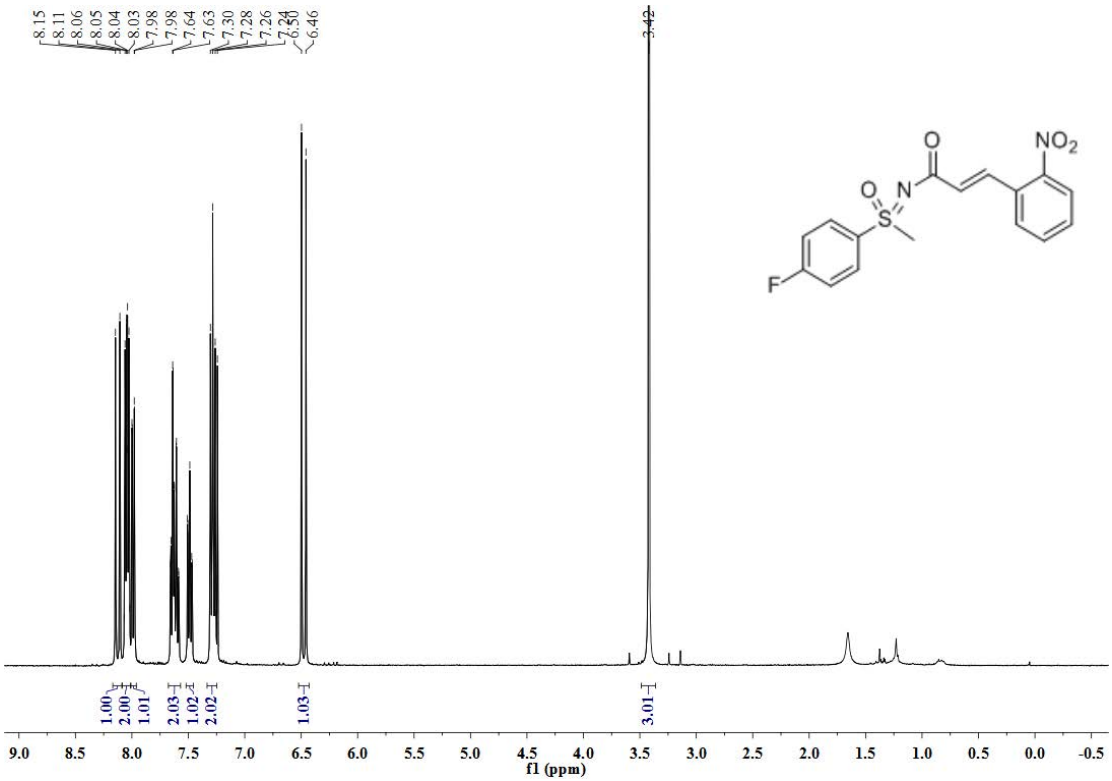
NH-*S*-(4-Fluorophenyl)-*S*-methyl- sulfoximine (1g)

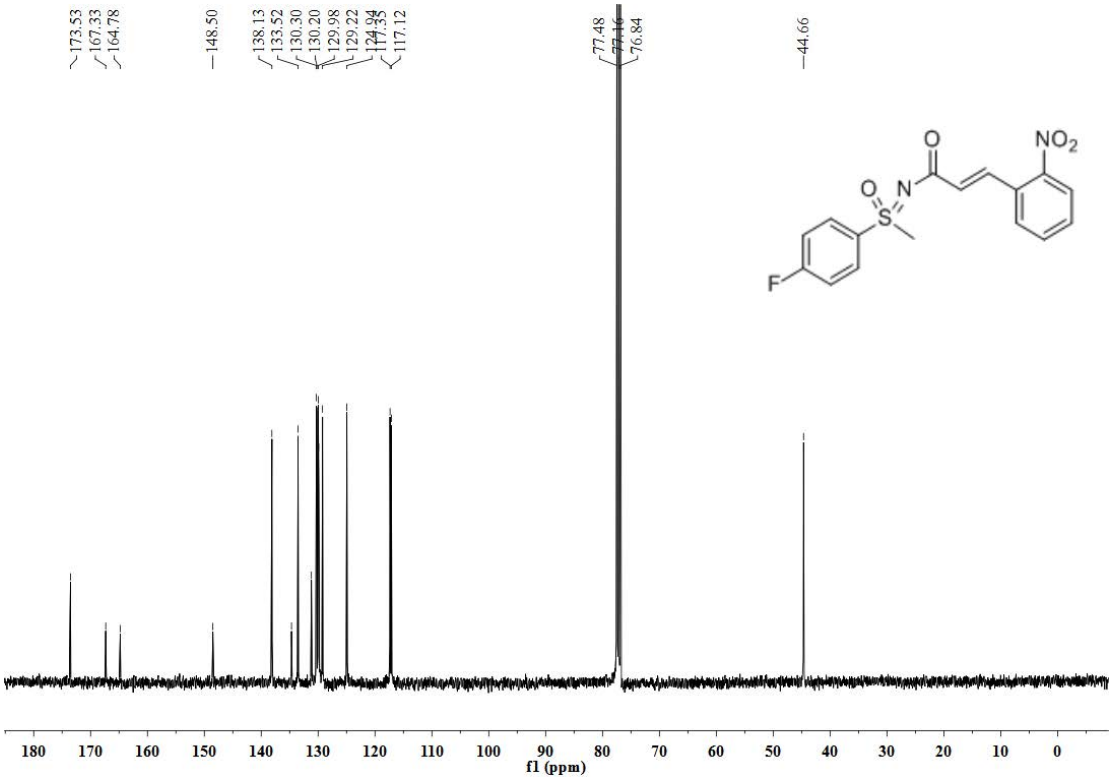






(*E*)-*N*-[(4-Fluorophenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3g)

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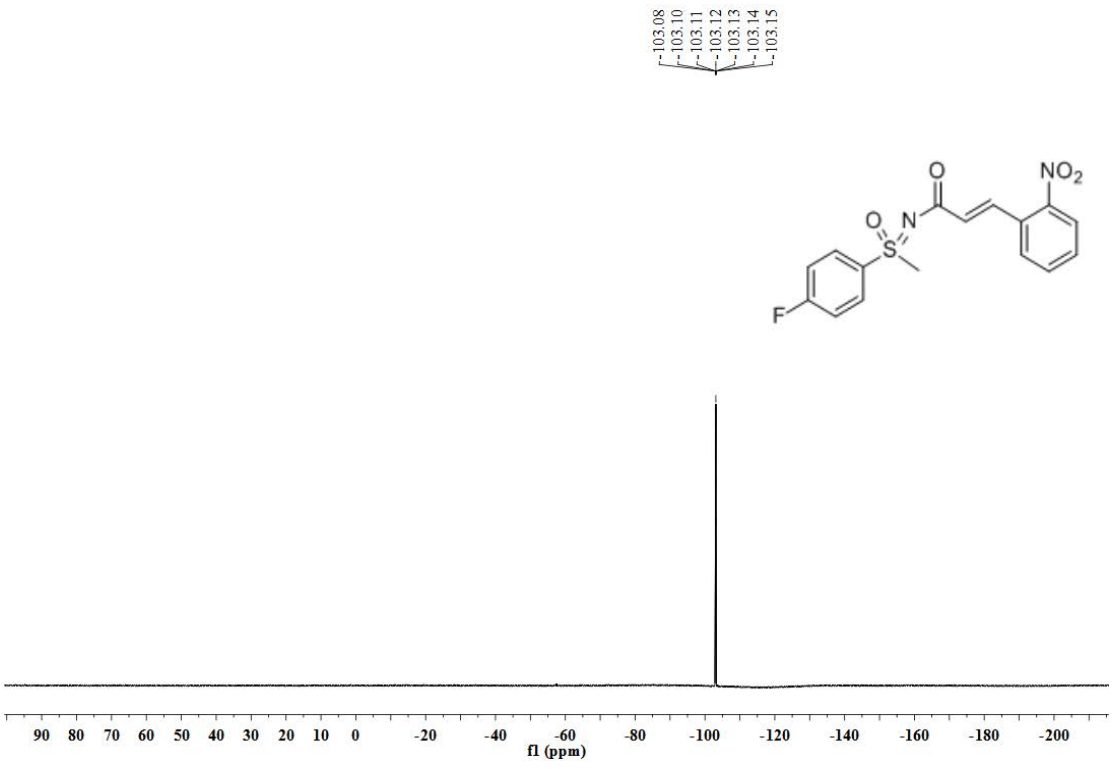
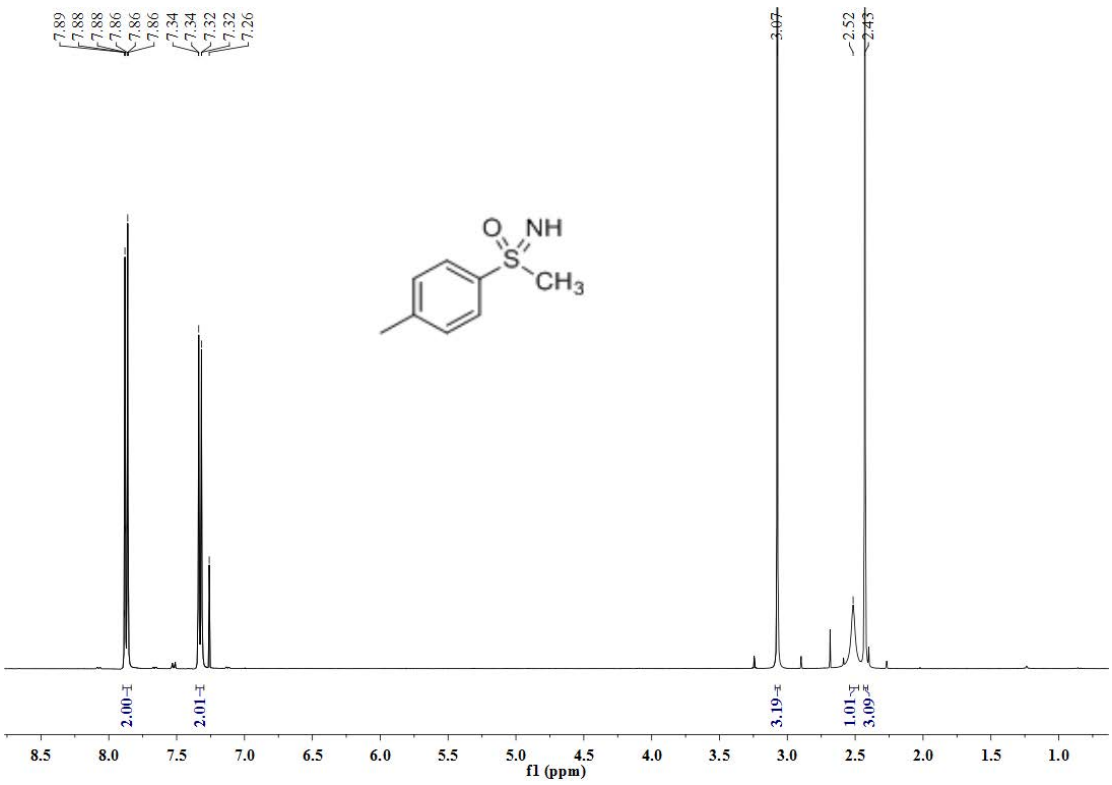
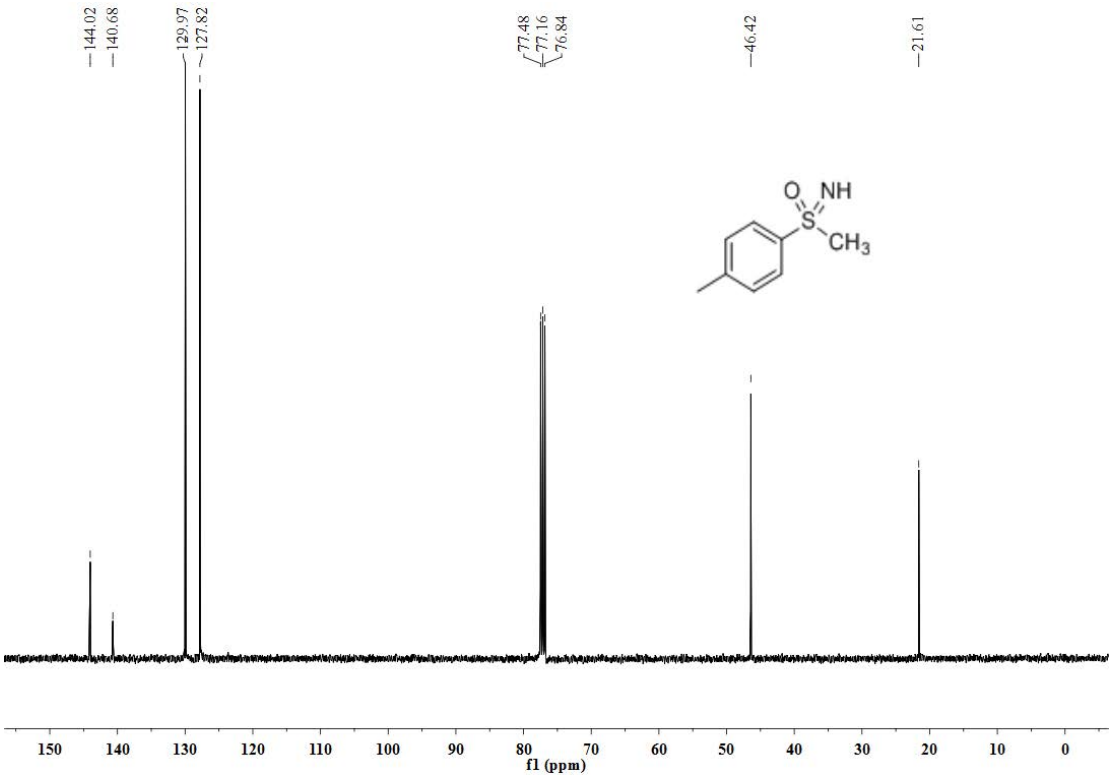
133.52
130.30
130.20
129.98
129.22
124.94
117.35
117.12
77.48
77.16
76.84
44.66
O
NO2
O
N
S
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

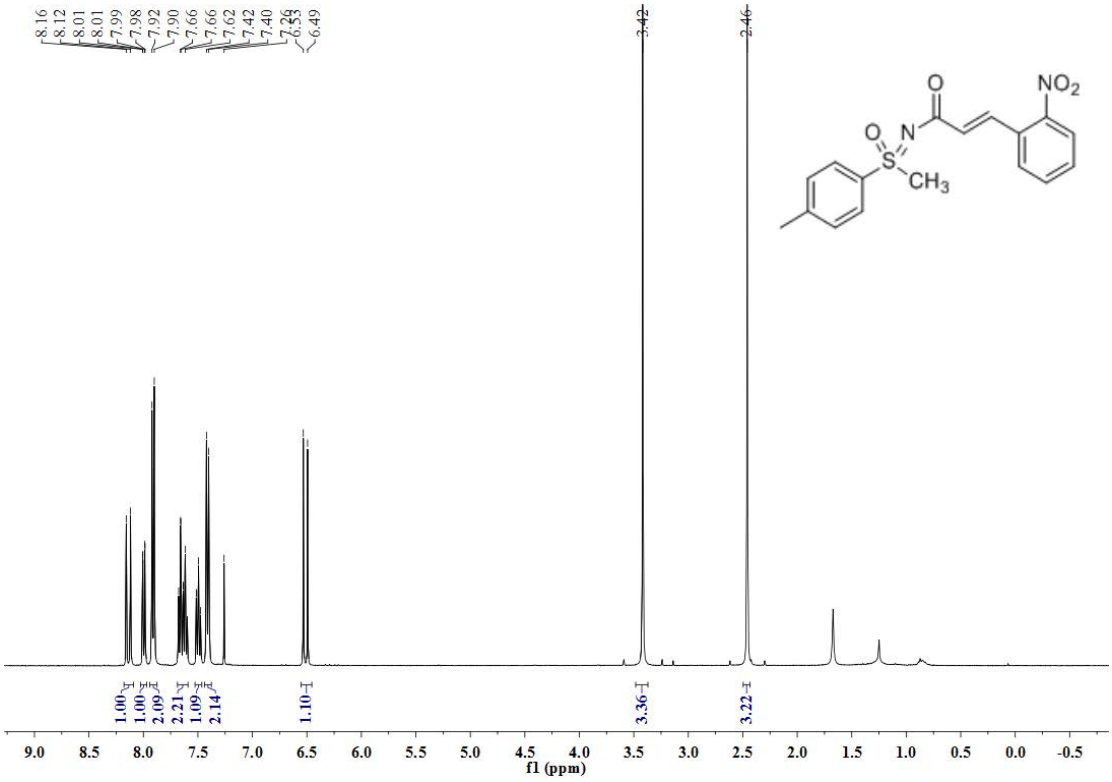

103.08
103.10
103.11
103.12
103.13
103.14
103.15
O
NO2
O
N
S
F
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

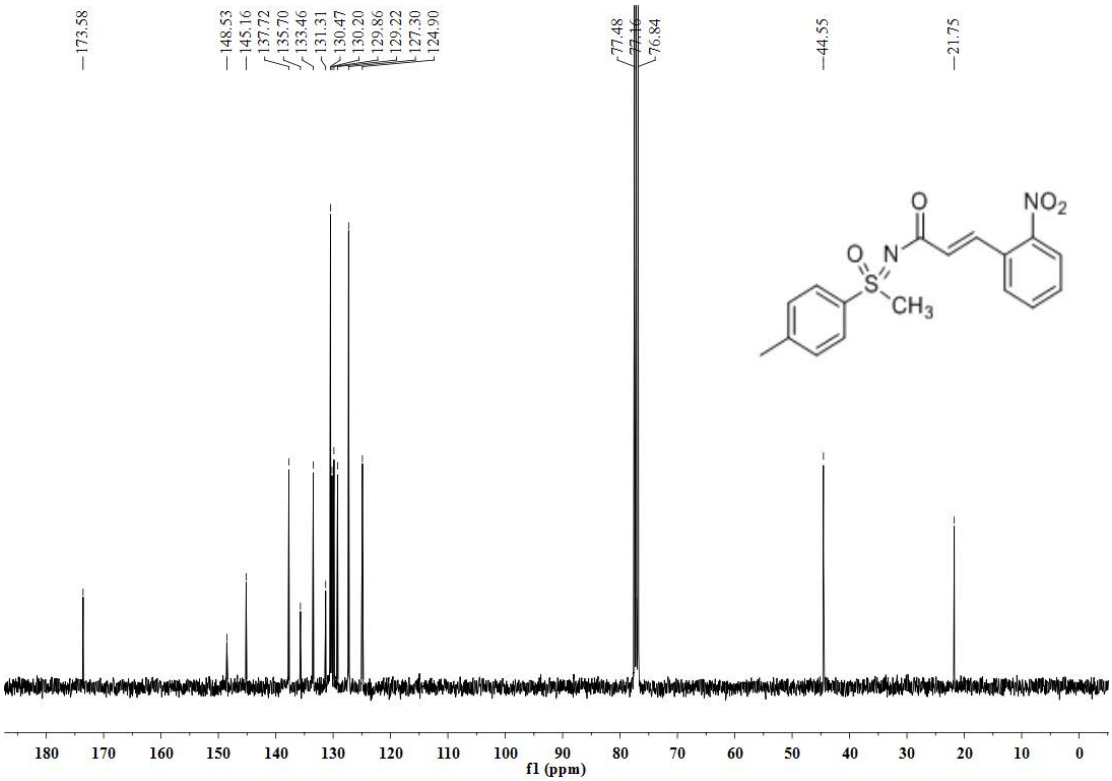
NH-*S*-Methyl-*S*-(*p*-tolyl)-sulfoximine (1h)



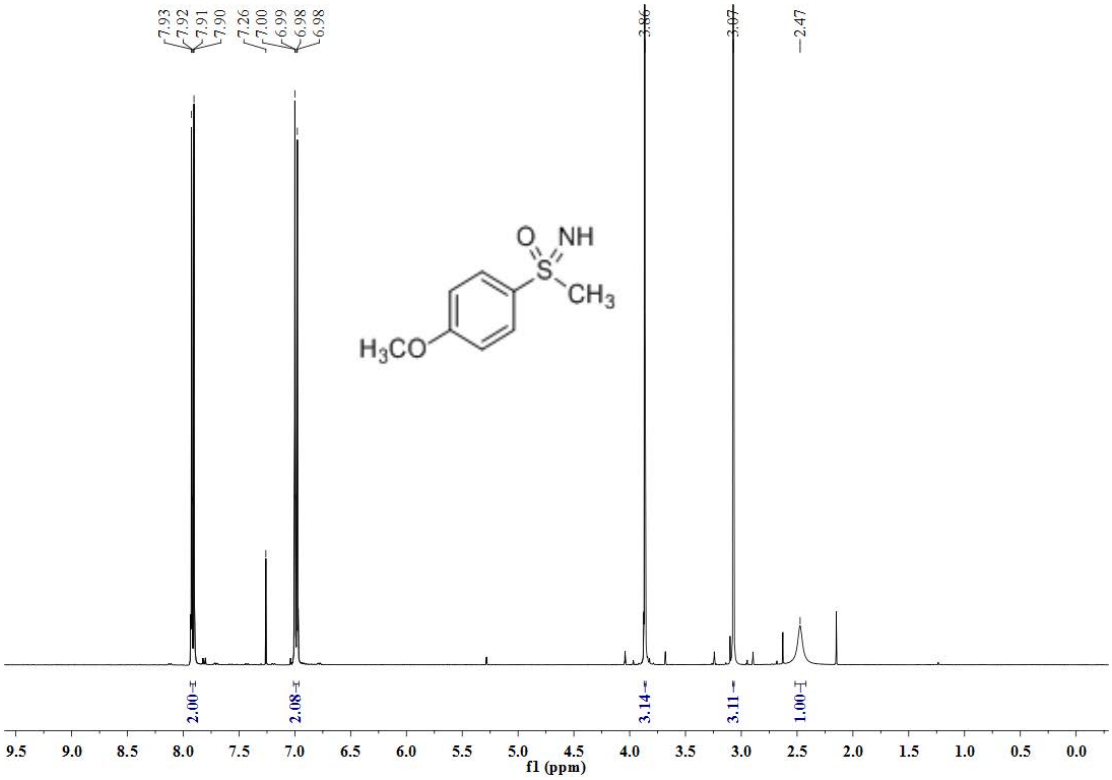


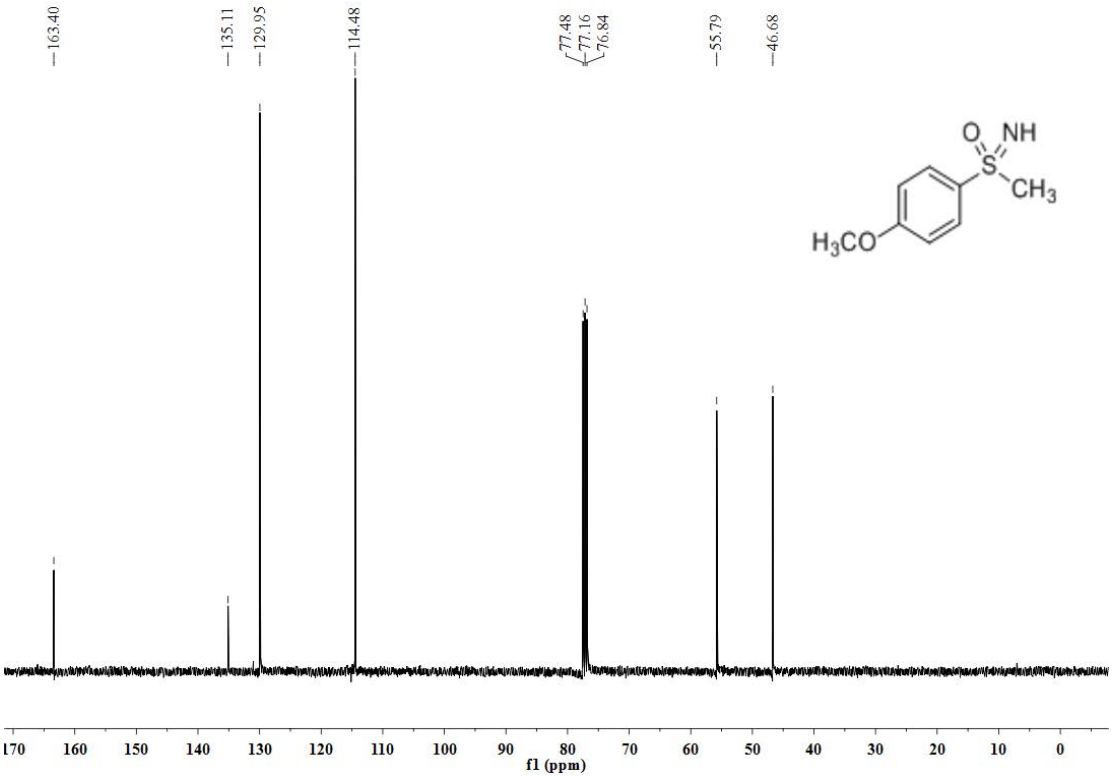
(*E*)-*N*-[(Methyl)(*p*-tolyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3h)



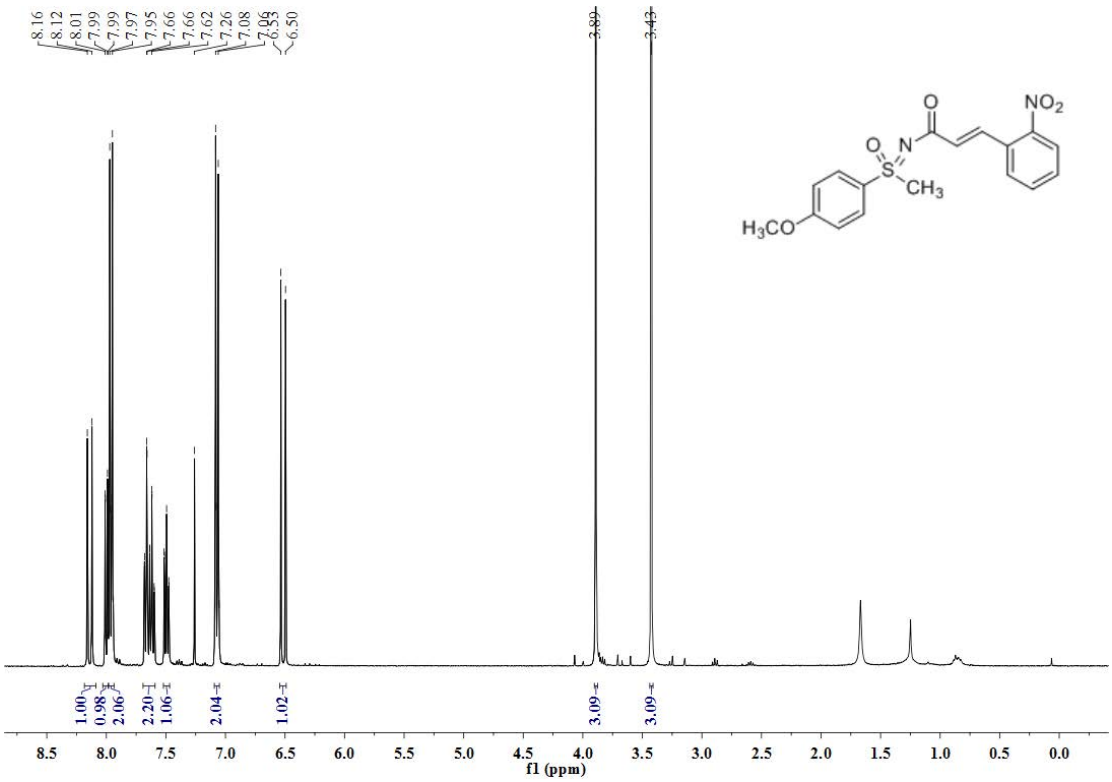


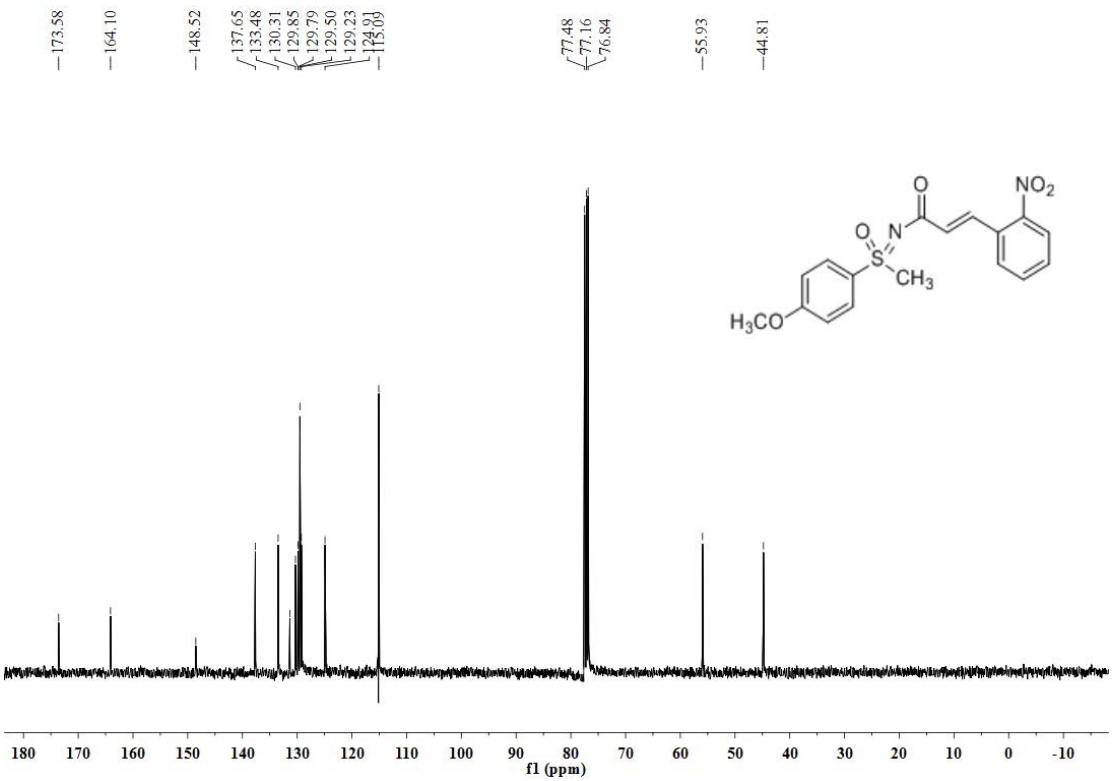
NH-*S*-(4-Methoxyphenyl)-*S*-methylsulfoximine (1i)



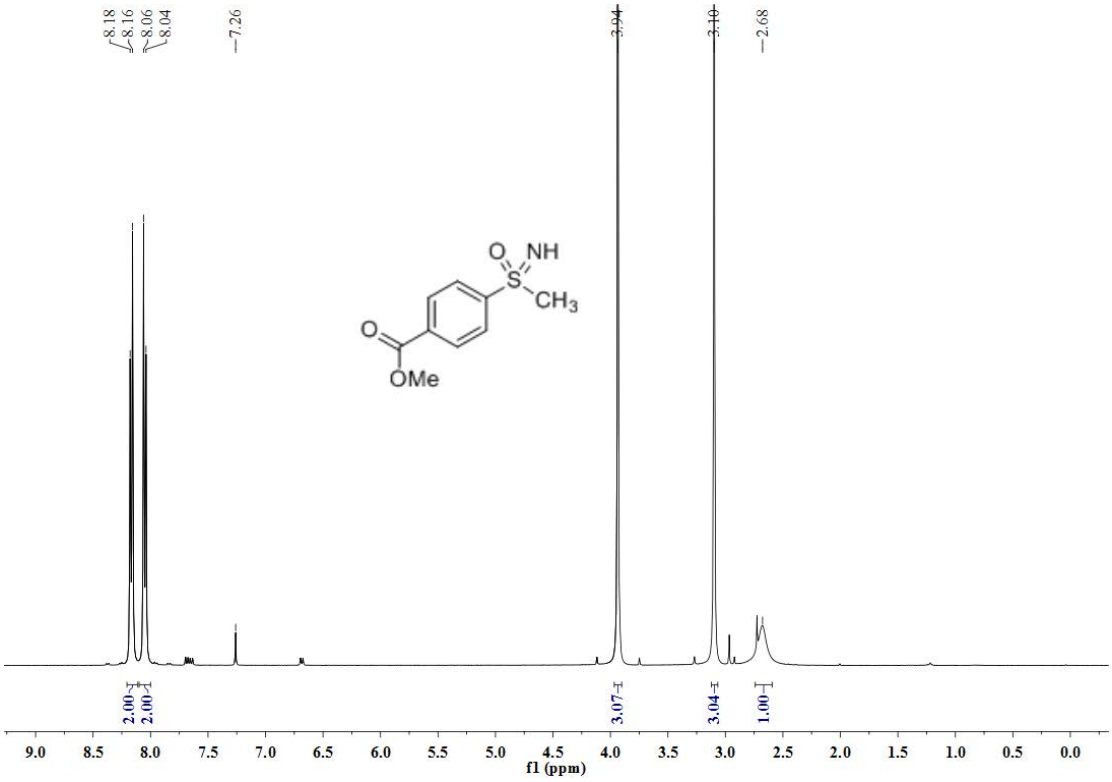


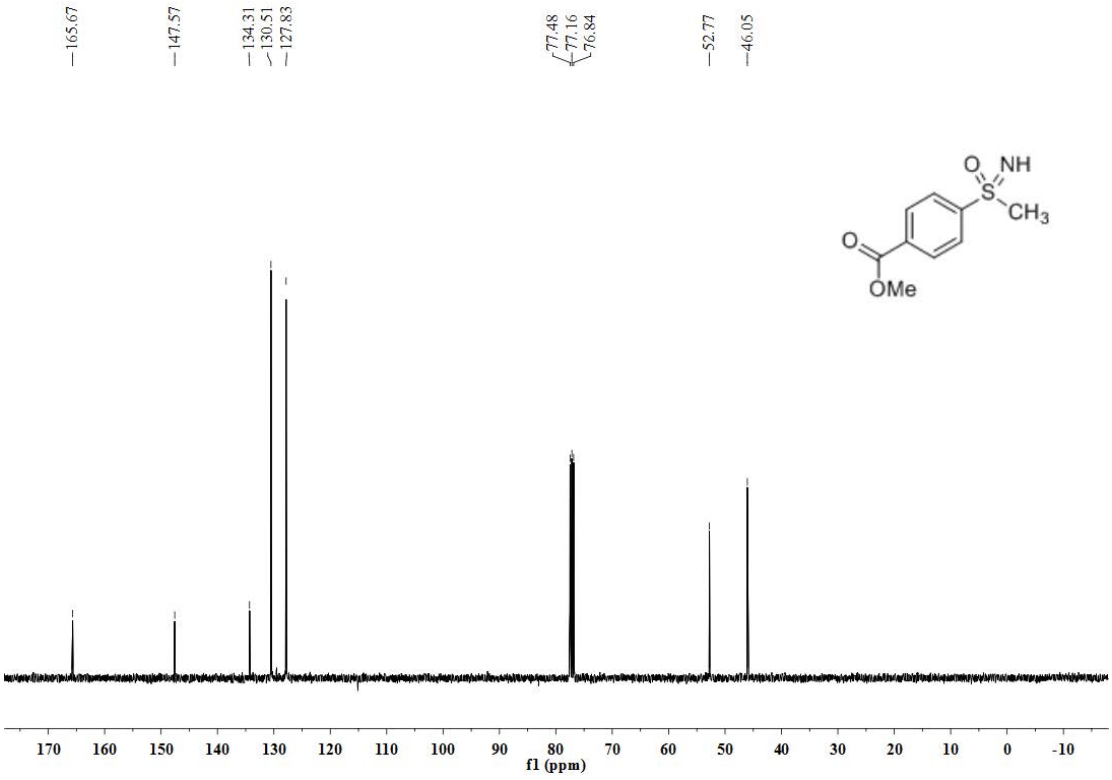
(*E*)-*N*-[(4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3i)



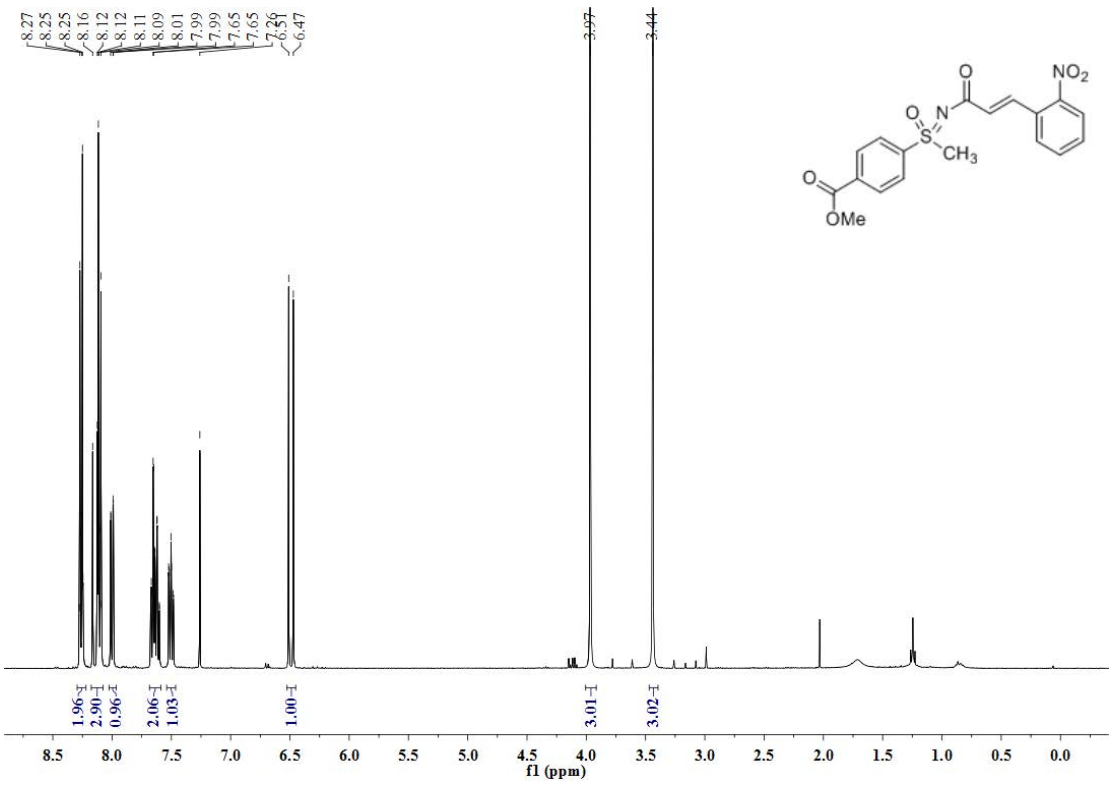


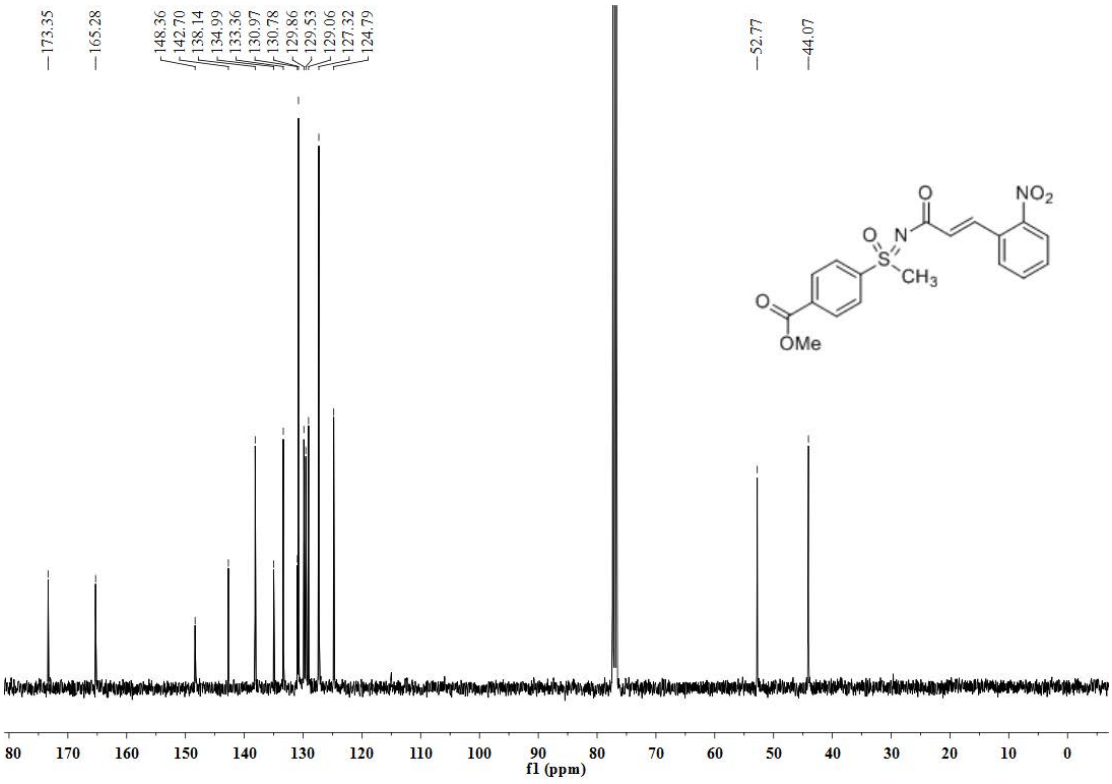
NH-*S*-(4-(Methoxycarbonyl)phenyl)-*S*-methy -sulfoximine (1j)



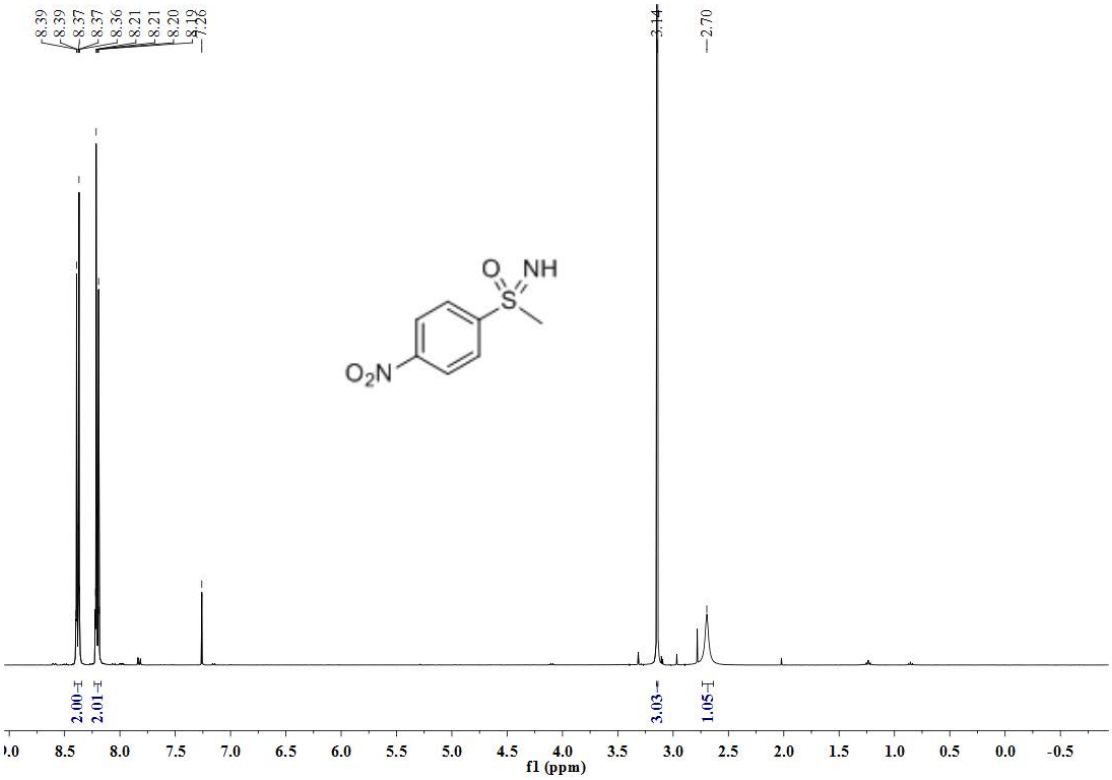


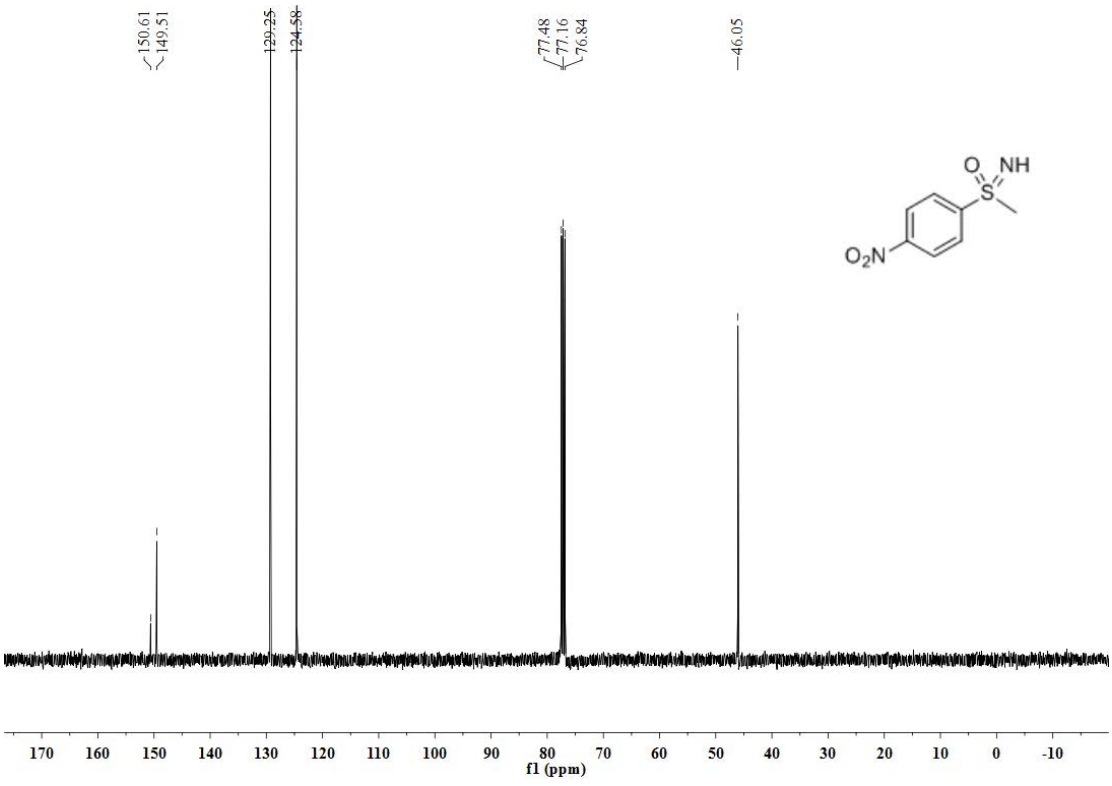
Methyl-(*E*)-4-{*S*-methyl-*N*-[3-(2-nitrophenyl)acryloyl]sulfonimidoyl}benzoate (3j)



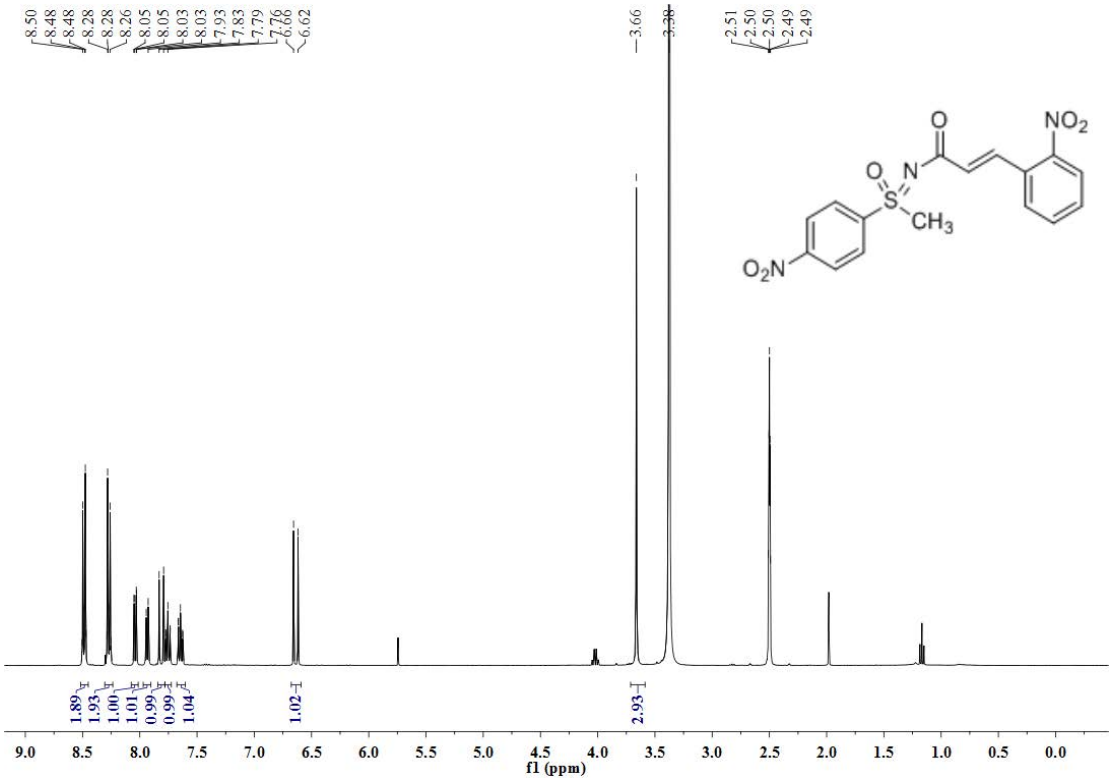


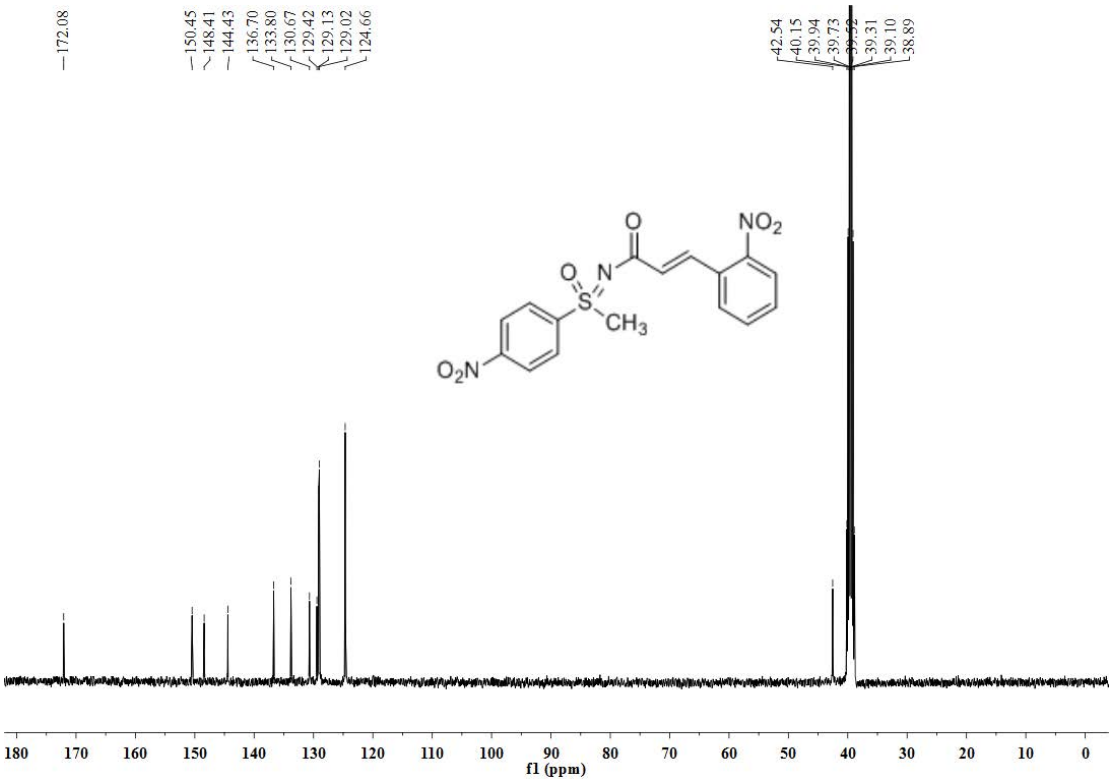
NH-*S*-Methyl-*S*-(4-nitrophenyl)-sulfoximine (1k)



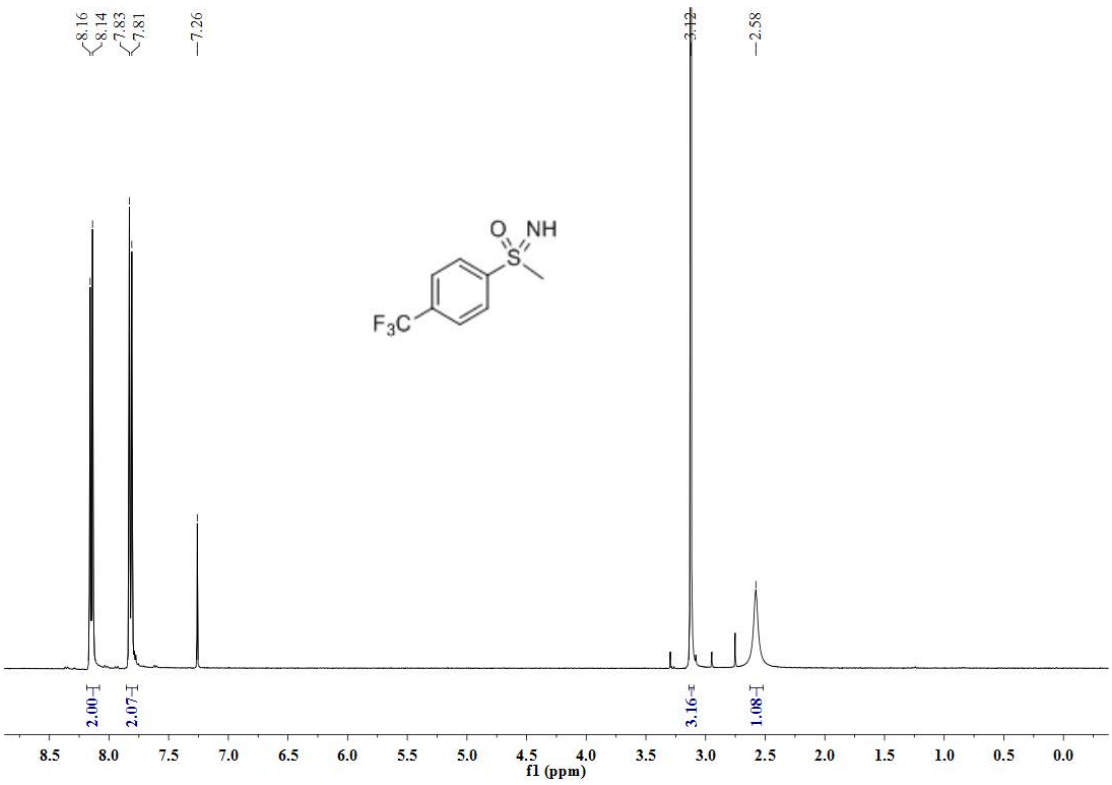


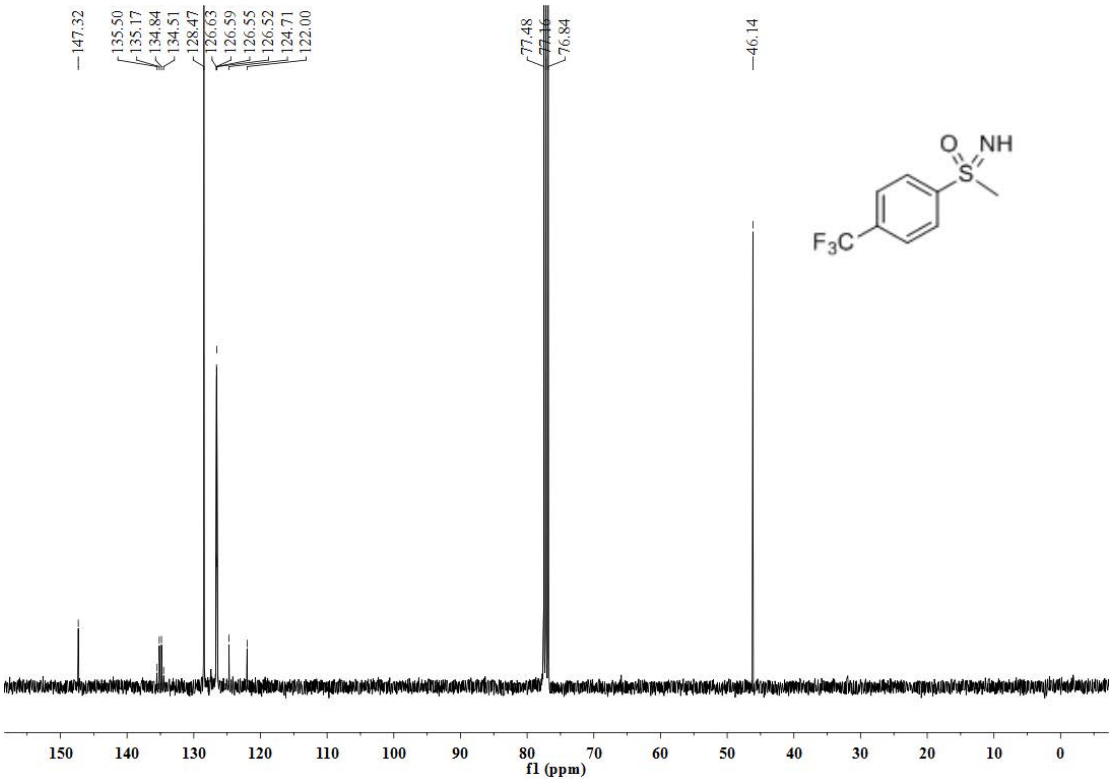
(*E*)-*N*-[Methyl(4-nitrophenyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3k)

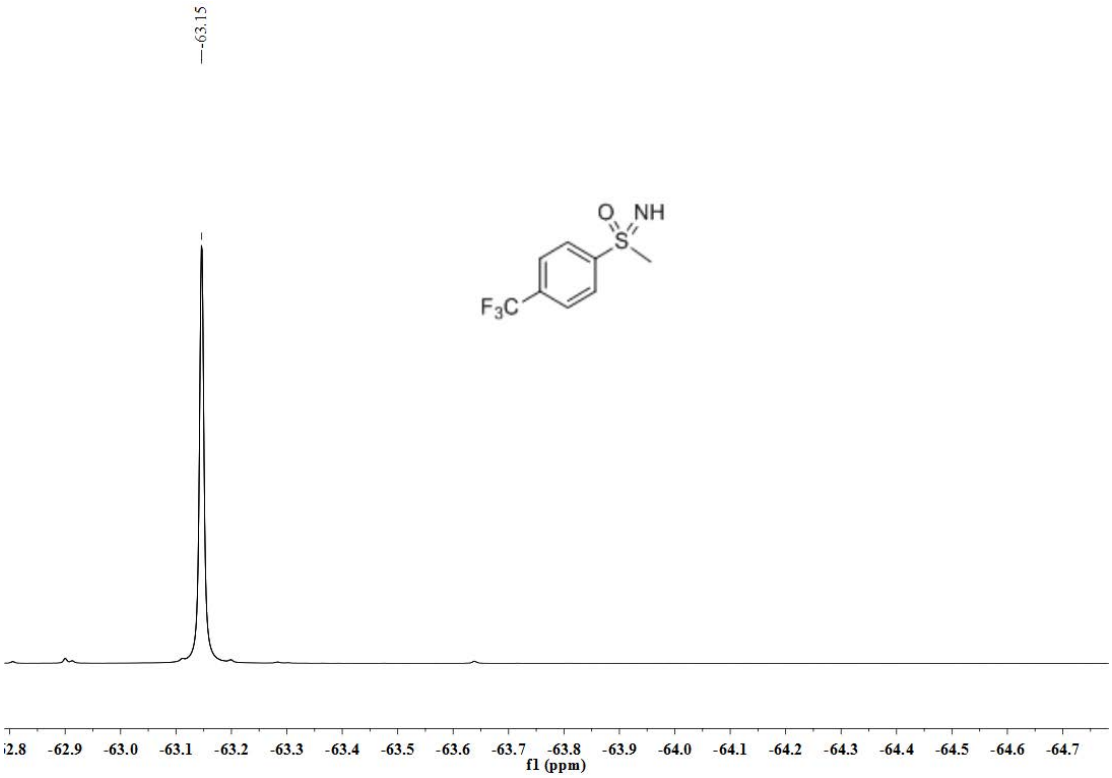




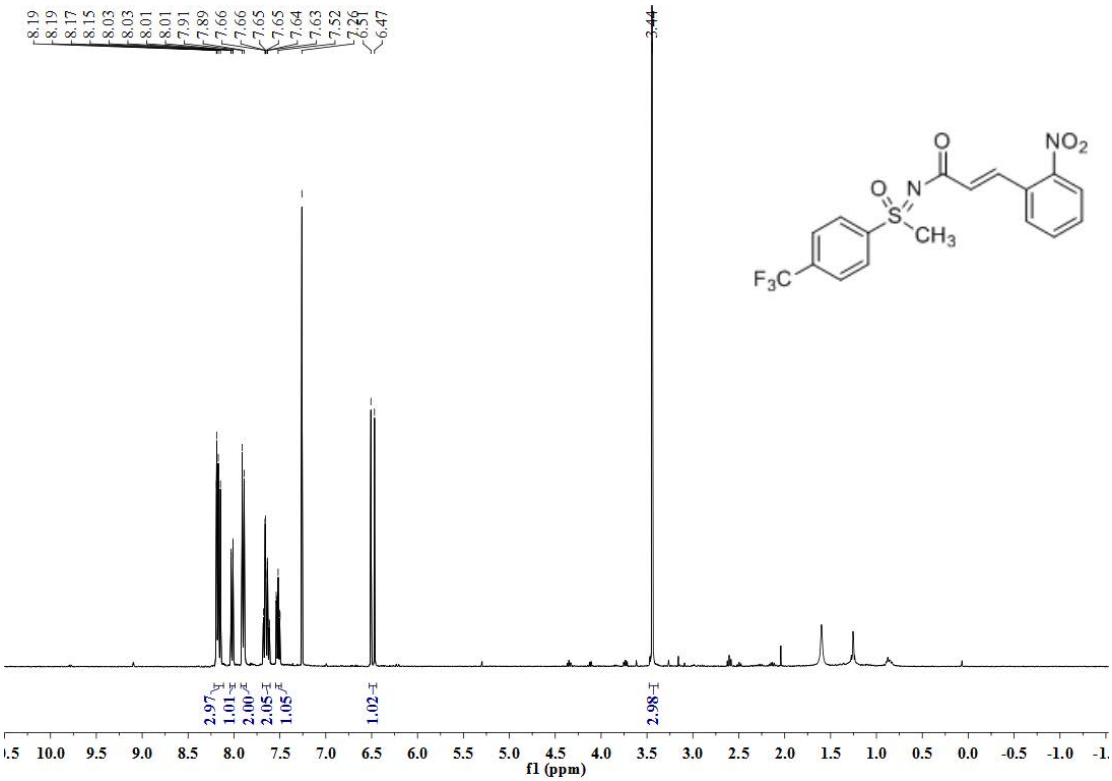
NH-*S*-Methyl-*S*-[4-(trifluoromethyl)phenyl]-sulfoximine (1l)

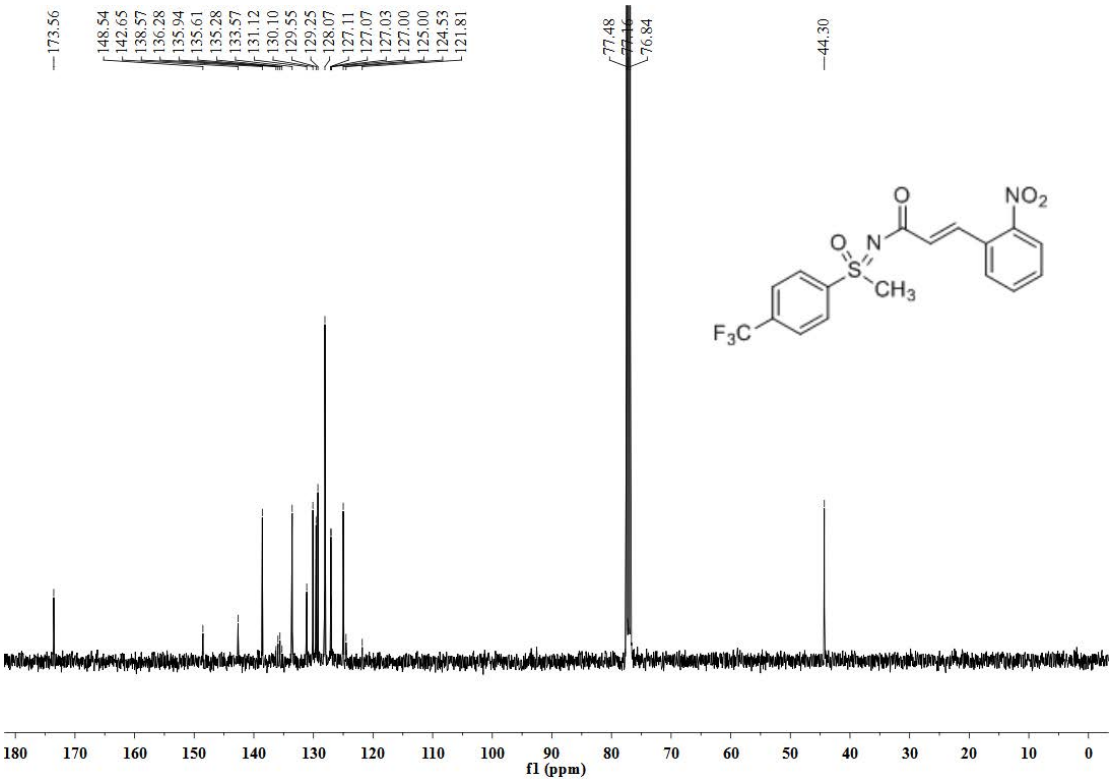






(*E*)-*N*-{Methyl(oxo)[4-(trifluoromethyl)phenyl]-λ^6-sulfanylidene}-3-(2-nitrophenyl)acrylamide (3l)

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138.57
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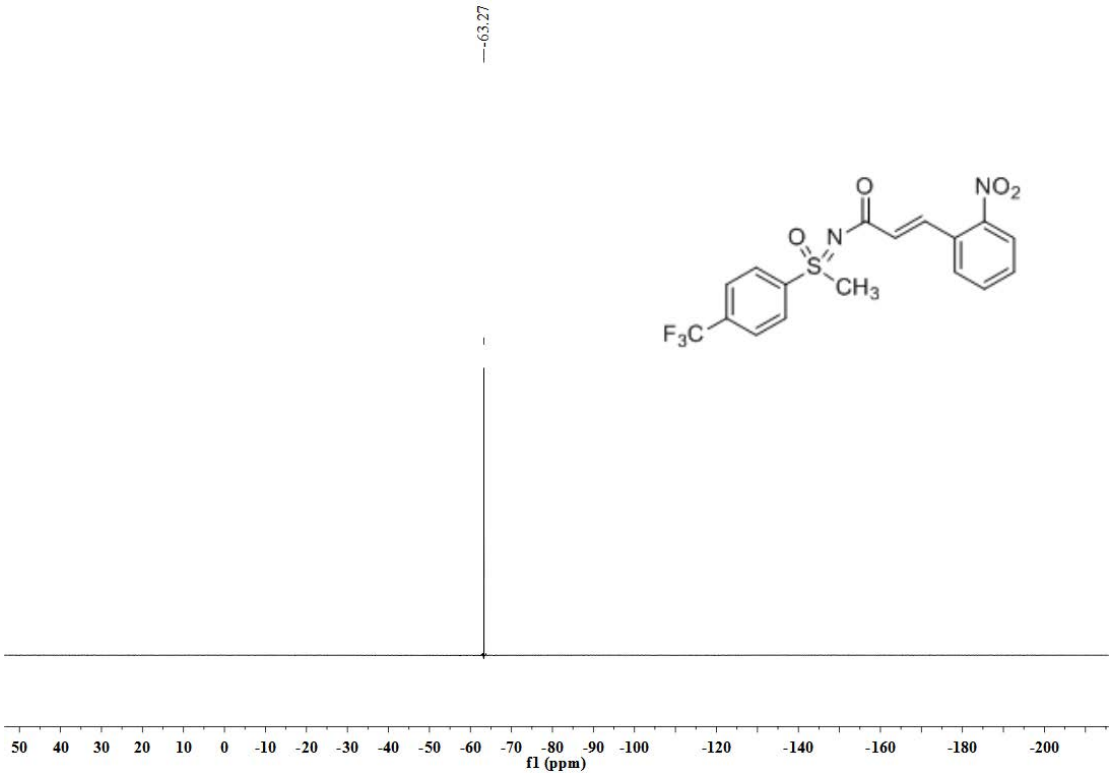
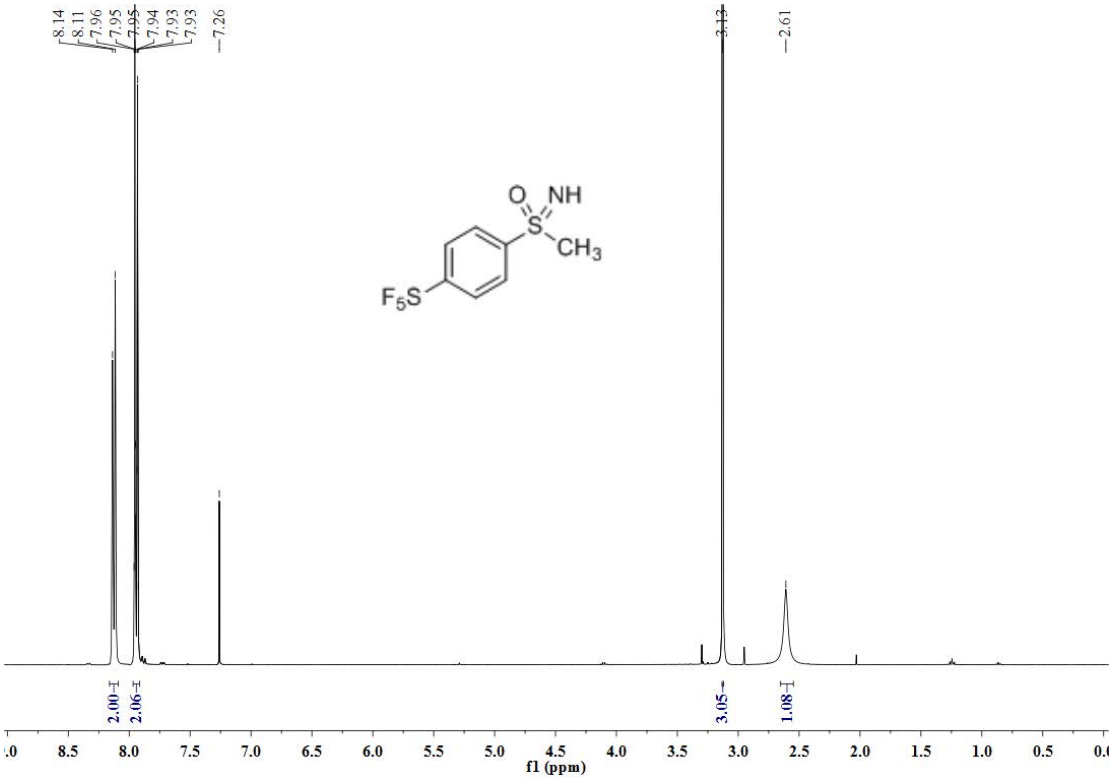
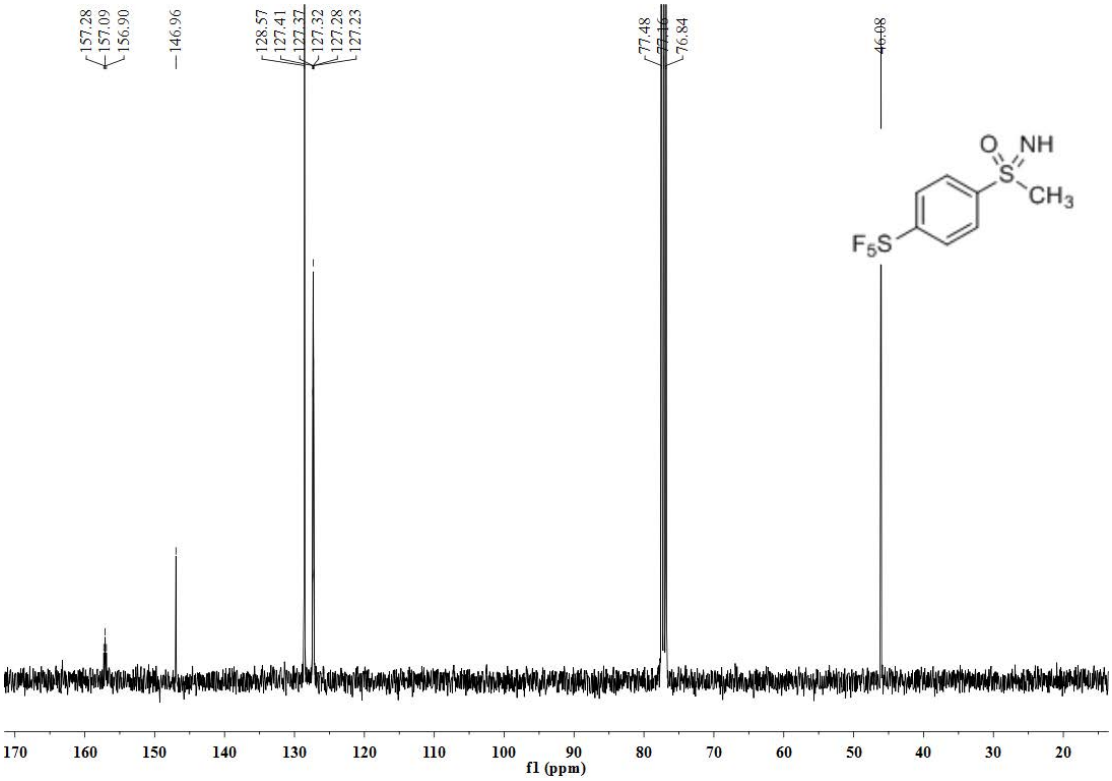
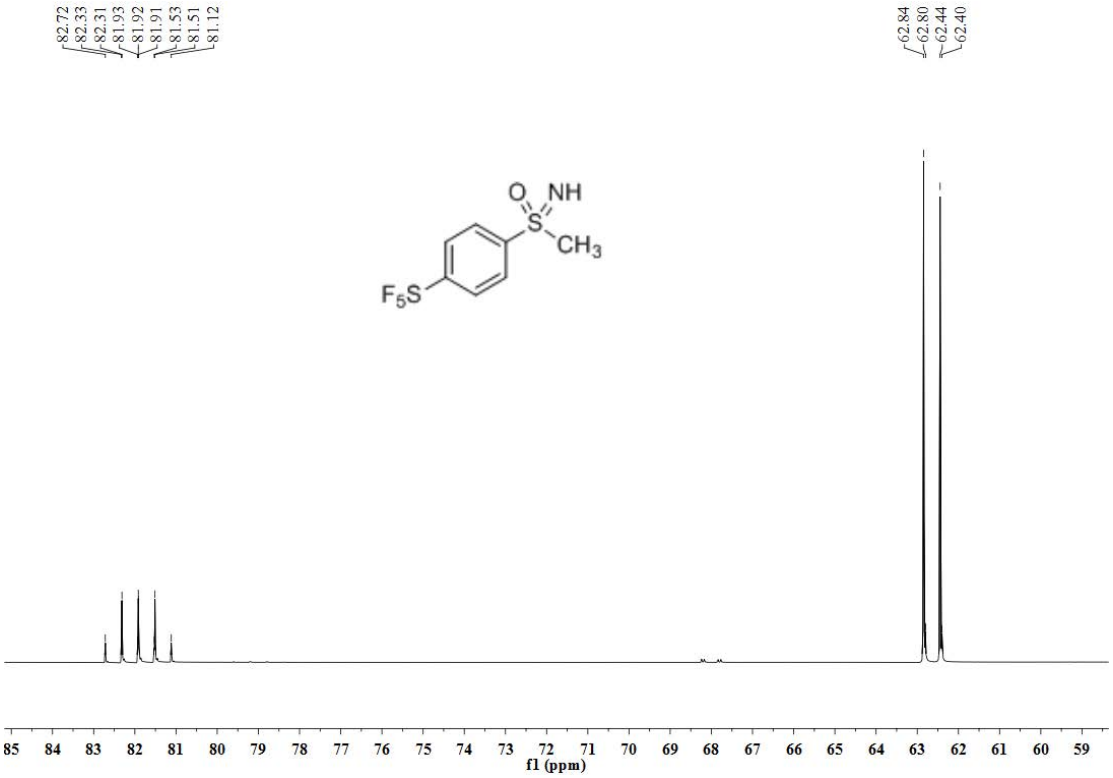
135.94
135.61
135.28
133.57
131.12
130.10
129.55
129.25
128.07
127.11
127.07
127.03
127.00
125.00
124.53
121.81
77.48
77.16
76.84
44.30
O
NO2
O
N
S
CH3
F3C
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.27
O
NO2
O
N
S
CH3
F3C
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

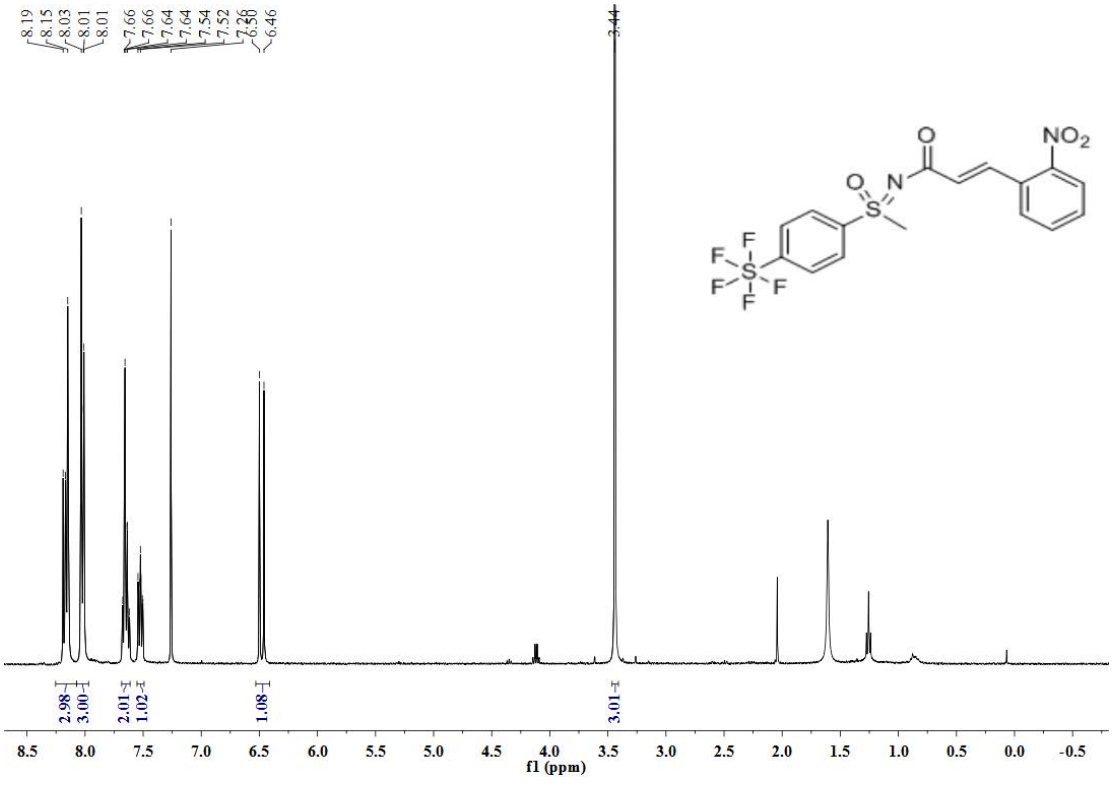
NH-*S*-Methyl-*S*-[4-(pentafluorosulfanyl)phenyl]-sulfoximine (1m)

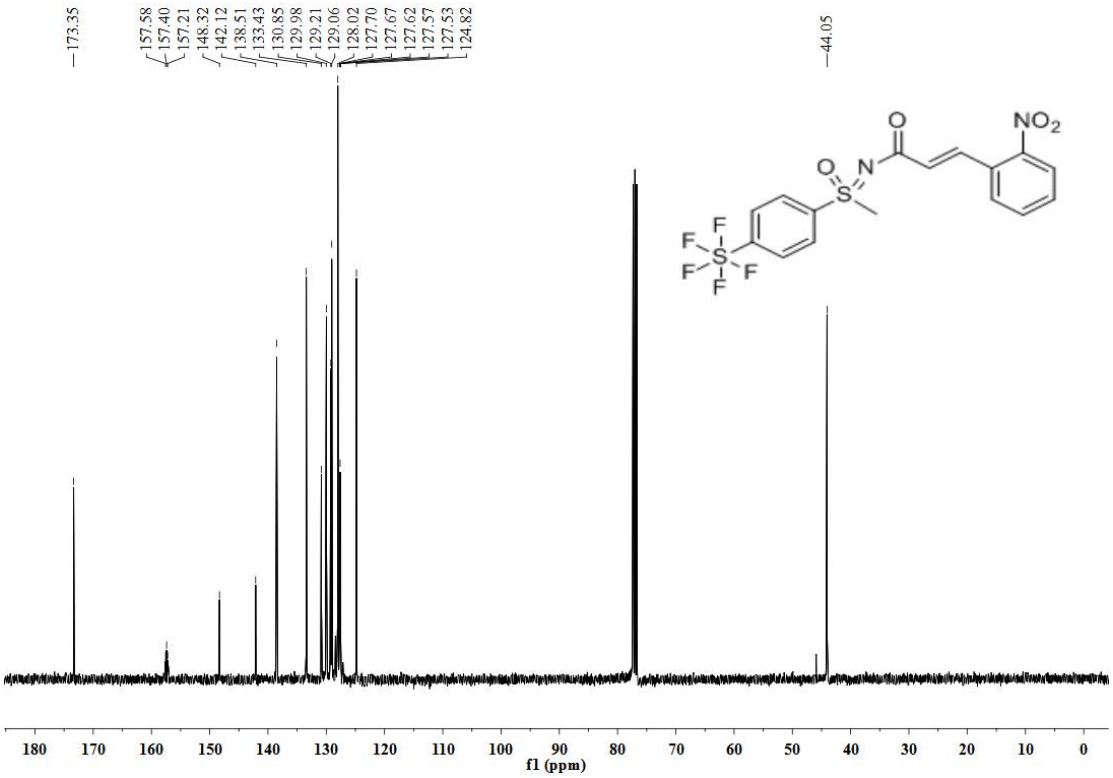






(*E*)-*N*-{Methyl(oxo)[4-(pentafluoro-λ^6-sulfanyl)phenyl]-λ^6-sulfanylidene}-3-(2-nitrophenyl)acrylamide (3m)

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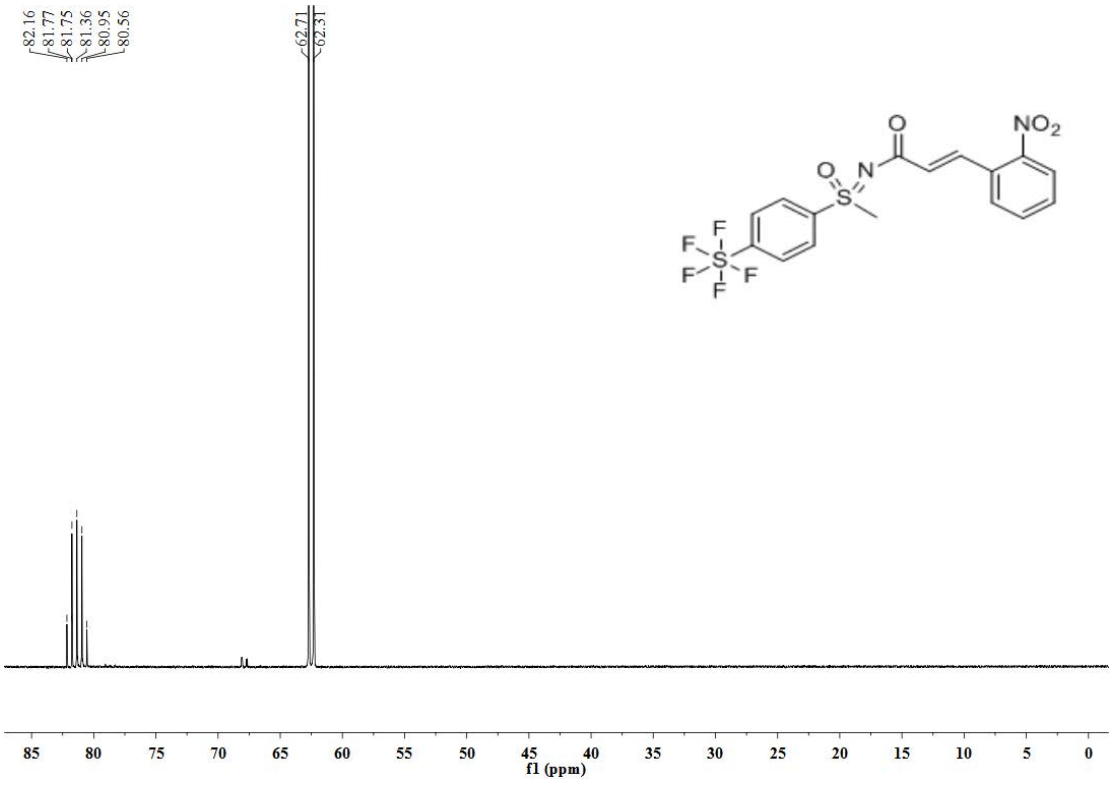
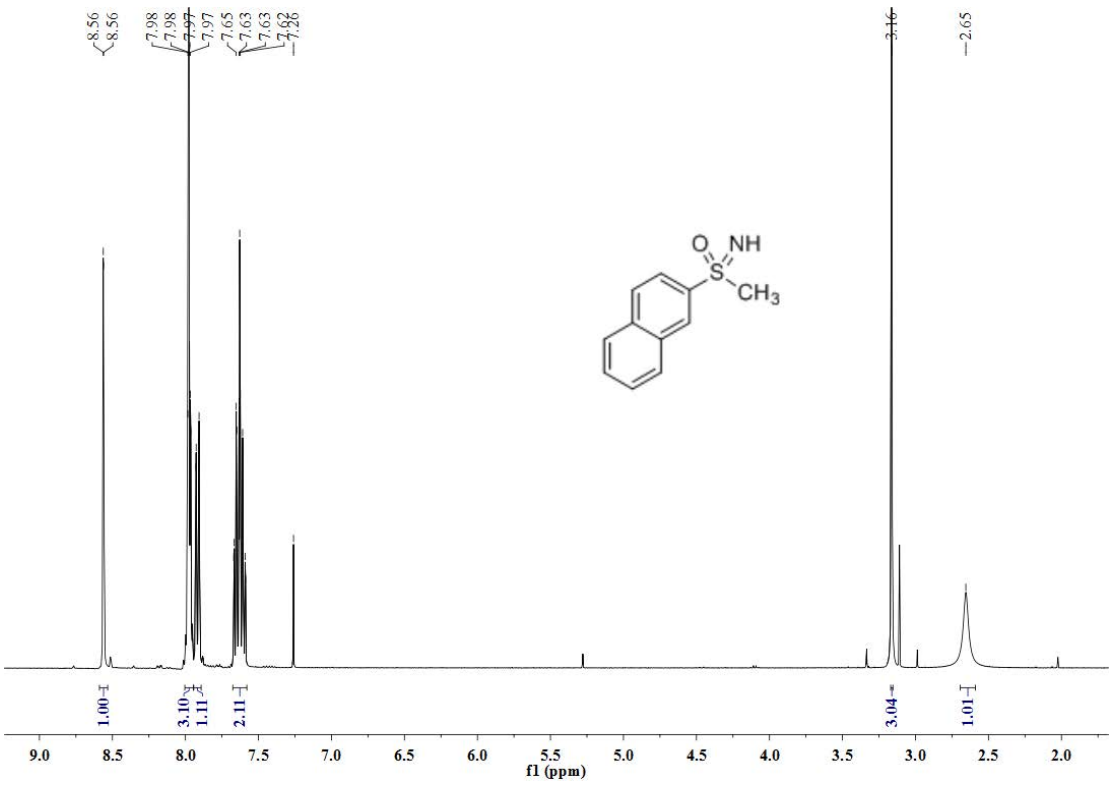
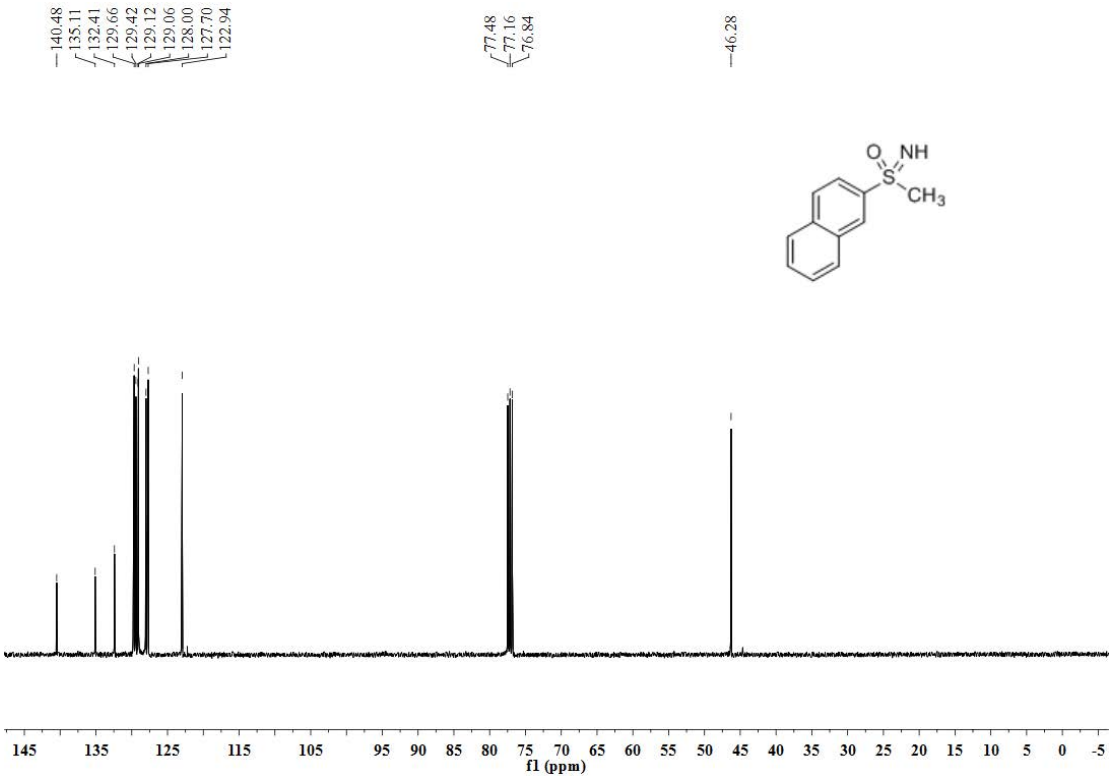
157.40
157.21
148.32
142.12
138.51
133.43
130.85
129.98
129.21
129.06
128.02
127.70
127.67
127.62
127.57
127.53
124.82
44.05
NO2
O
N
S
F
F
F
F
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

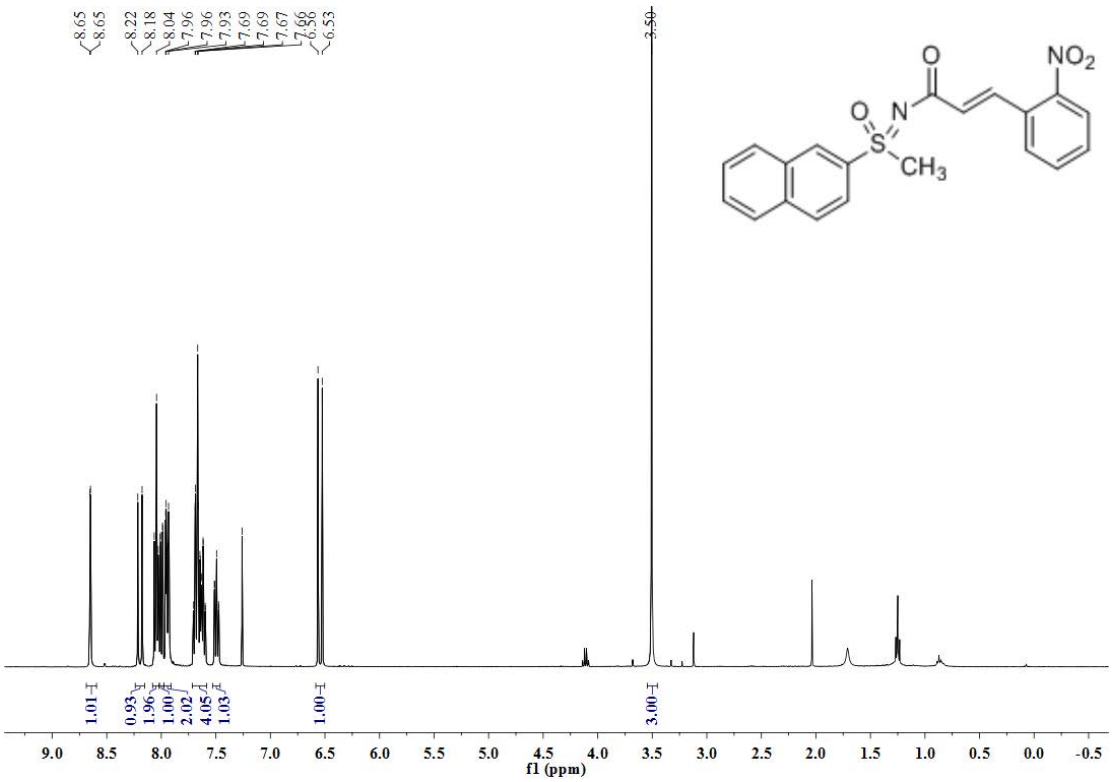

82.16
81.77
81.75
81.36
80.95
80.56
62.71
62.31
NO2
O
N
S
F
F
F
F
F
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

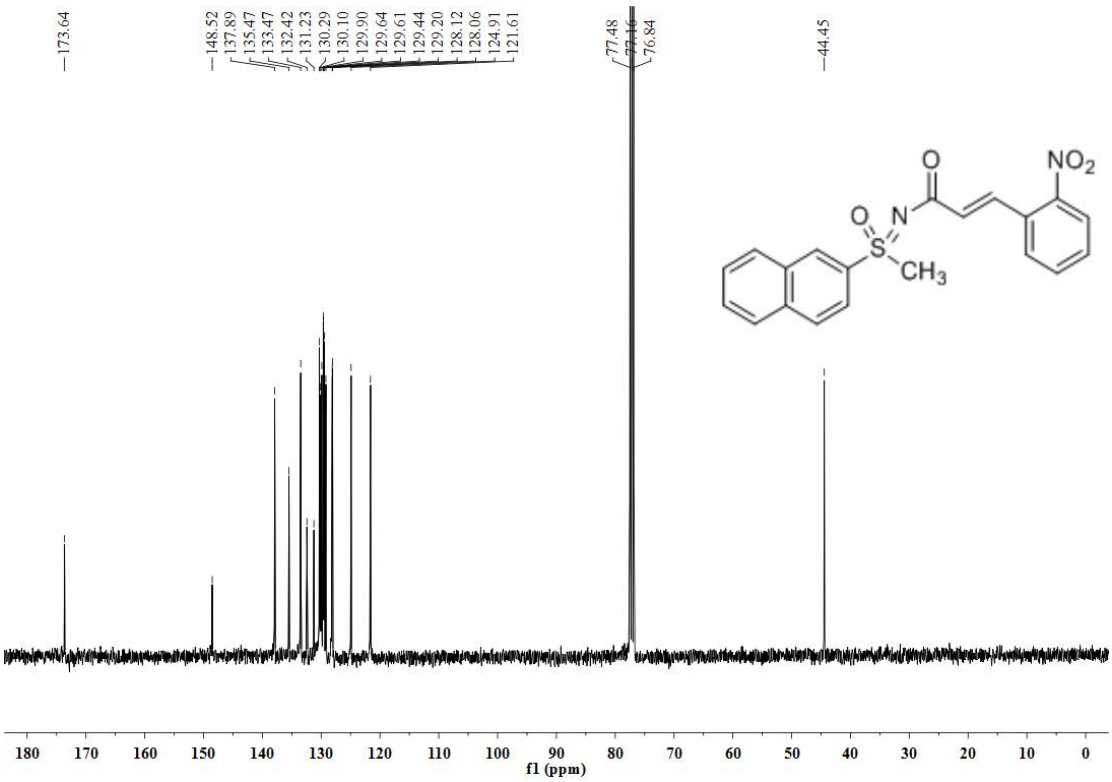
NH-*S*-Methyl-*S*-(2-naphthyl)-sulfoximine (1n)



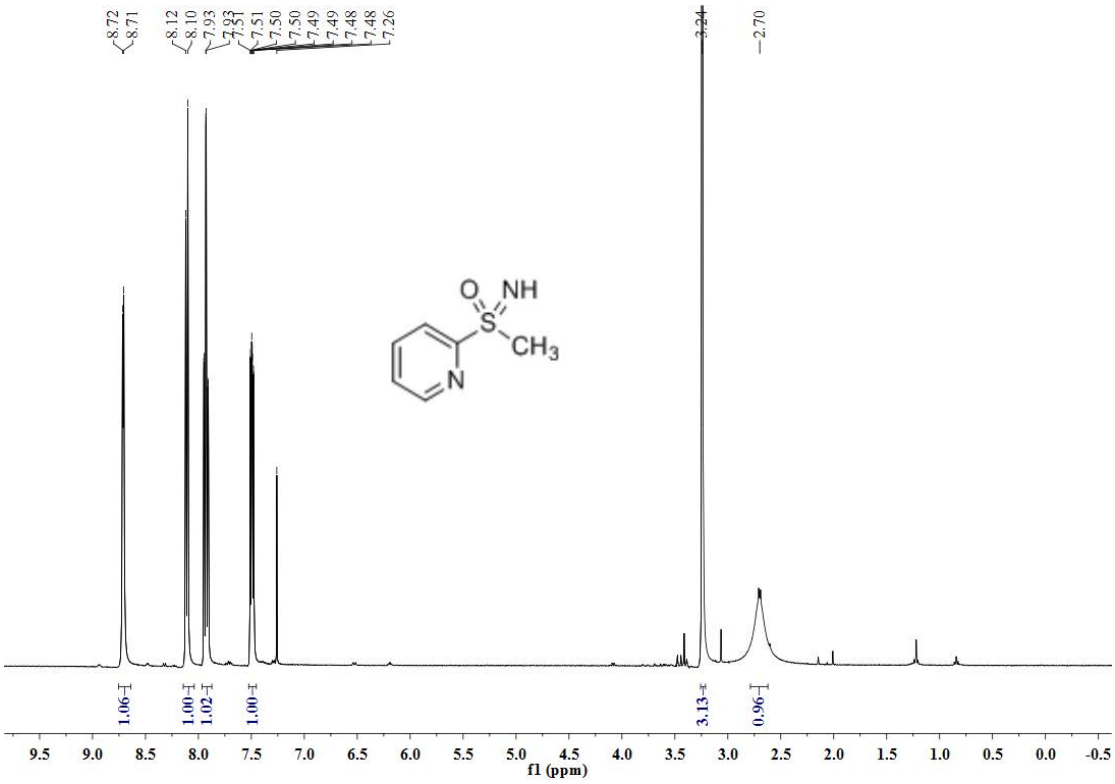


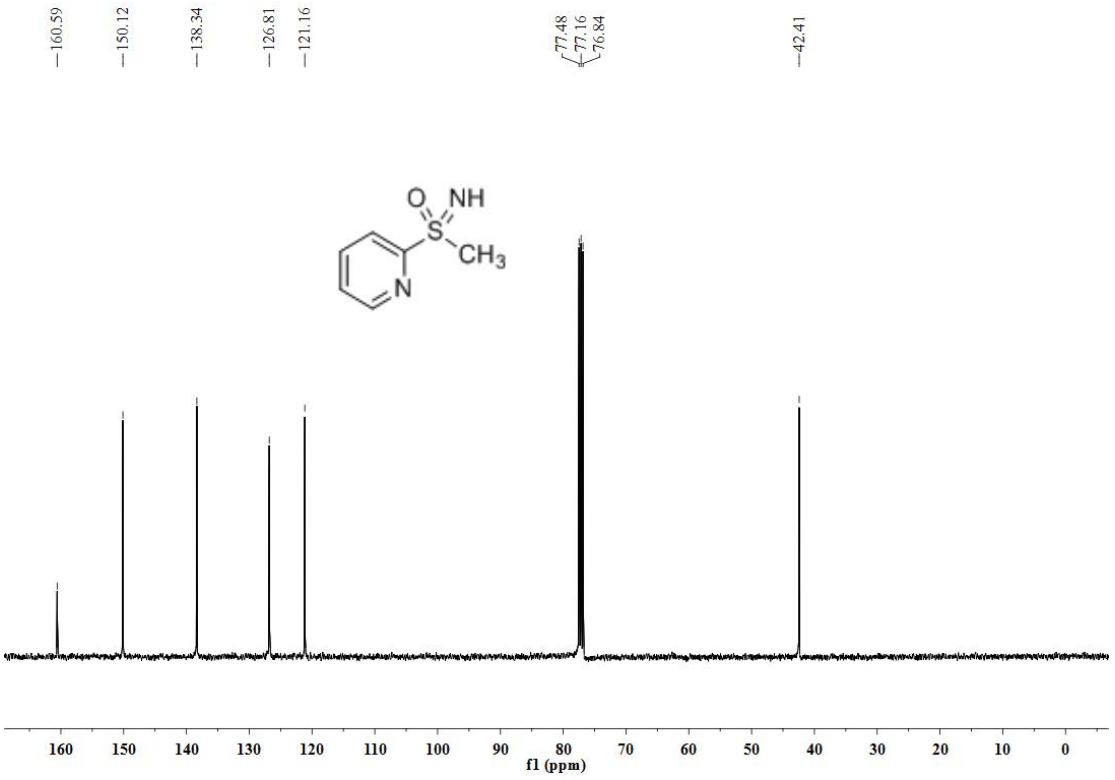
Methyl-(*E*)-4-{*S*-methyl-*N*-[3-(2-nitrophenyl)acryloyl]sulfonimidoyl}benzoate (3n)



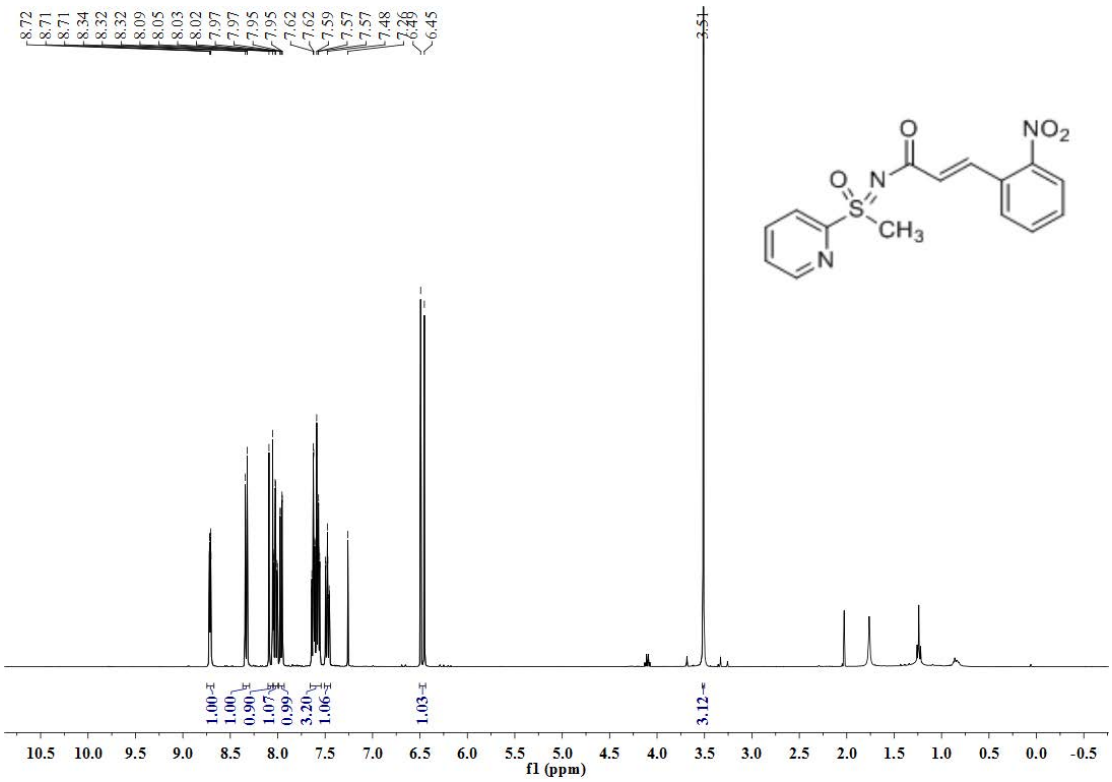


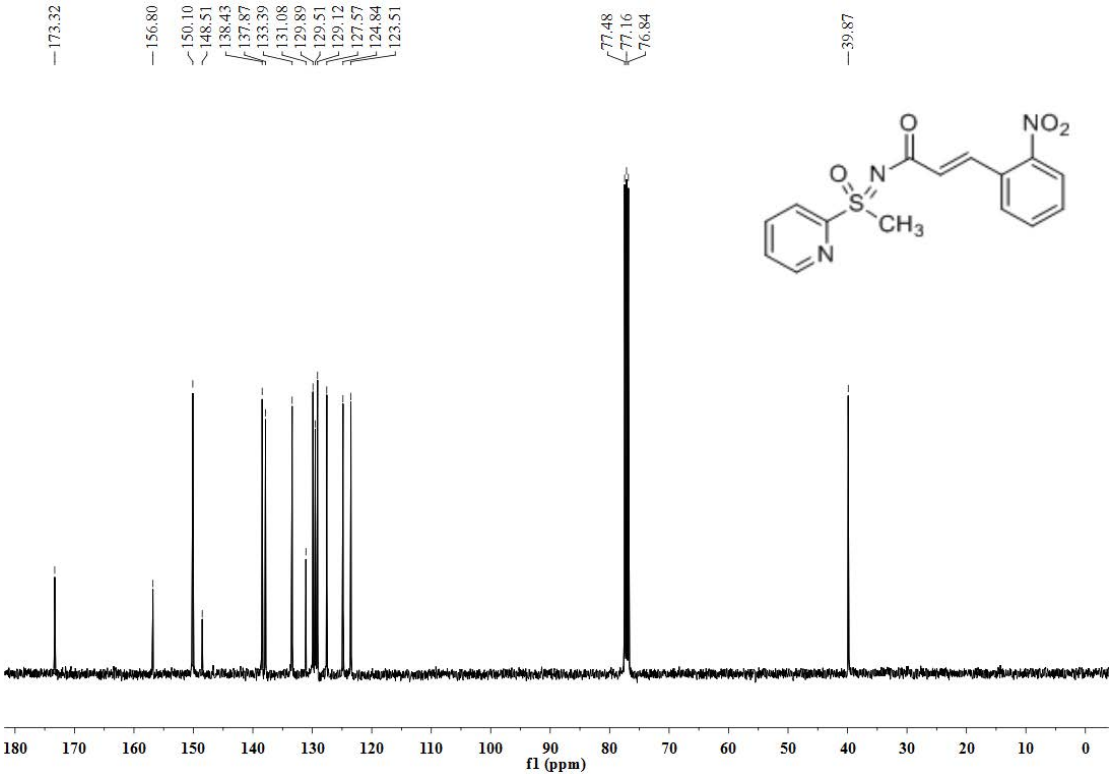
NH-*S*-Methyl-*S*-(2-pyridyl)-sulfoximine (10)



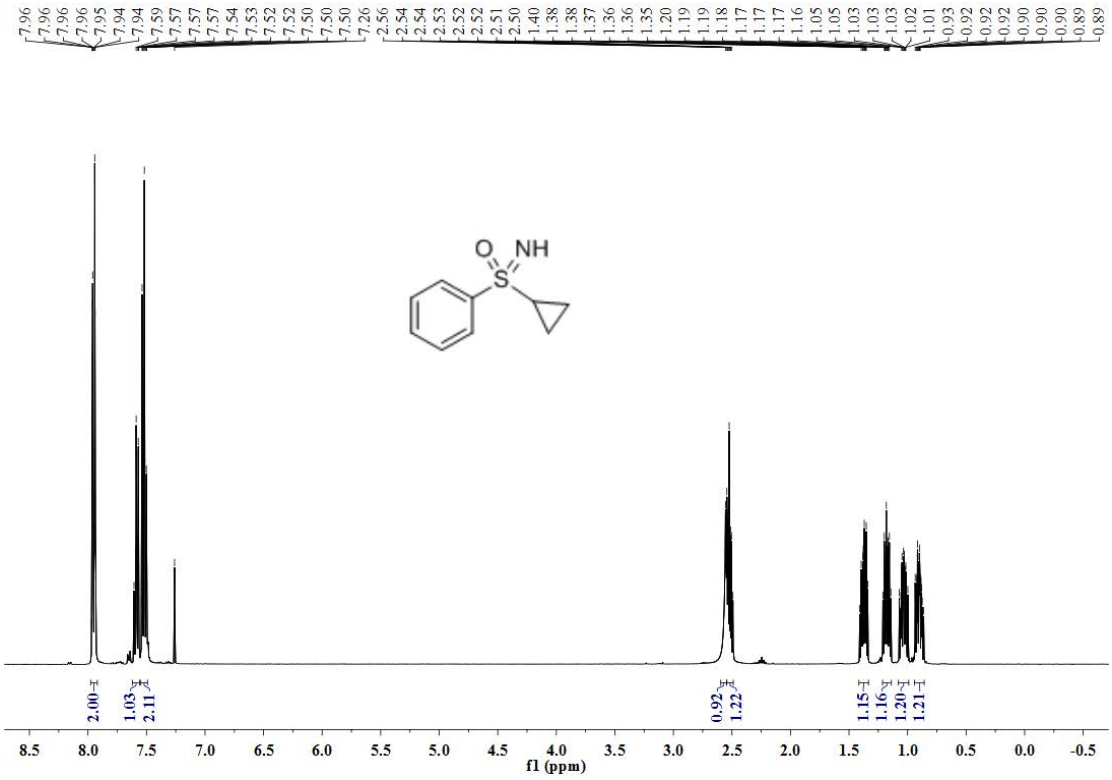


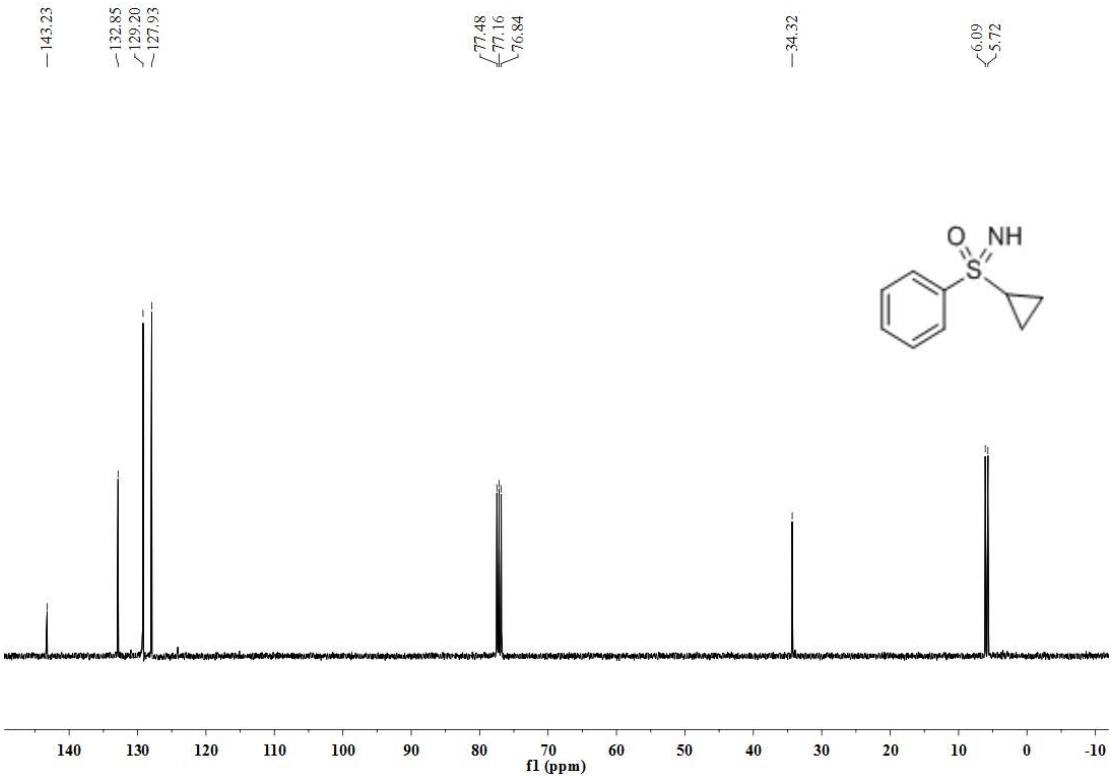
(*E*)-*N*-[(Methyl)(2-pyridyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (30)



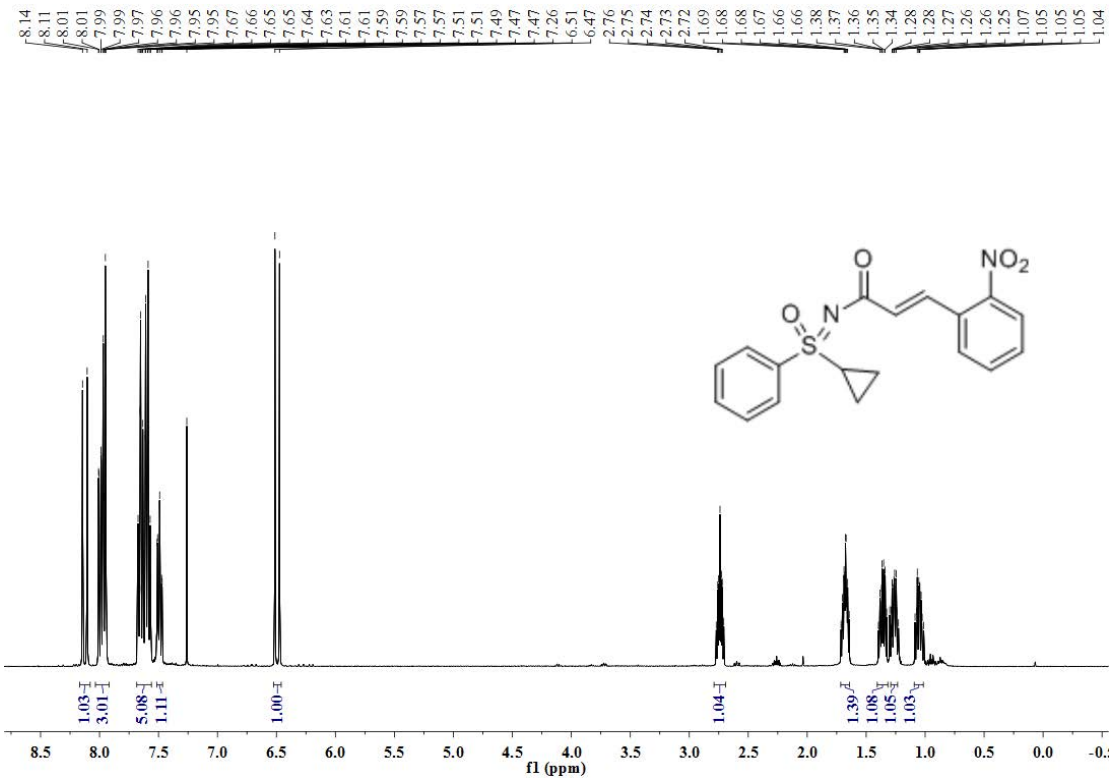


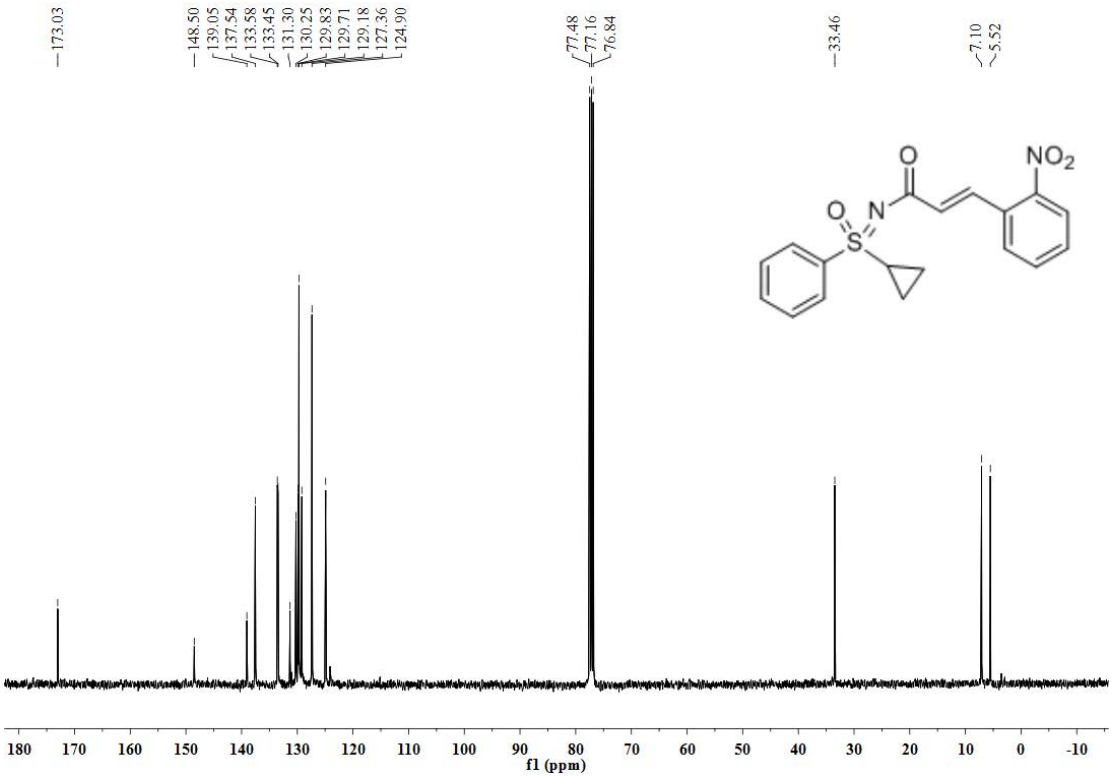
NH-*S*-Cyclopropyl-*S*-phenyl-sulfoximine (1p)



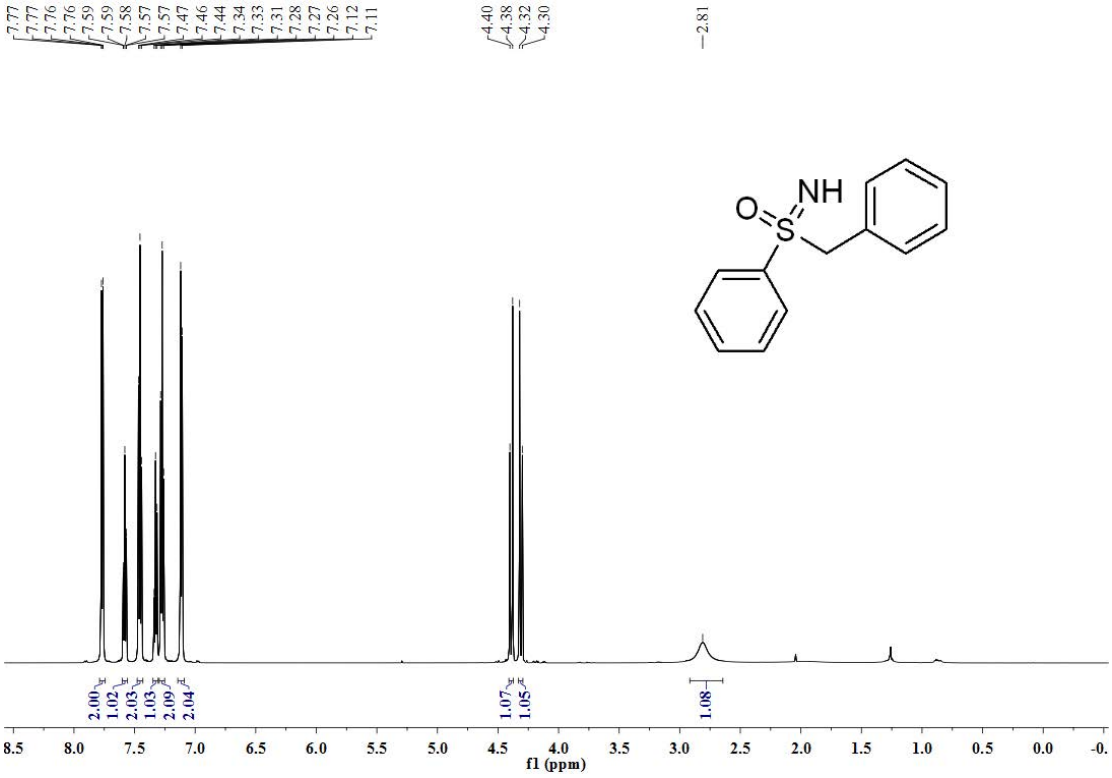


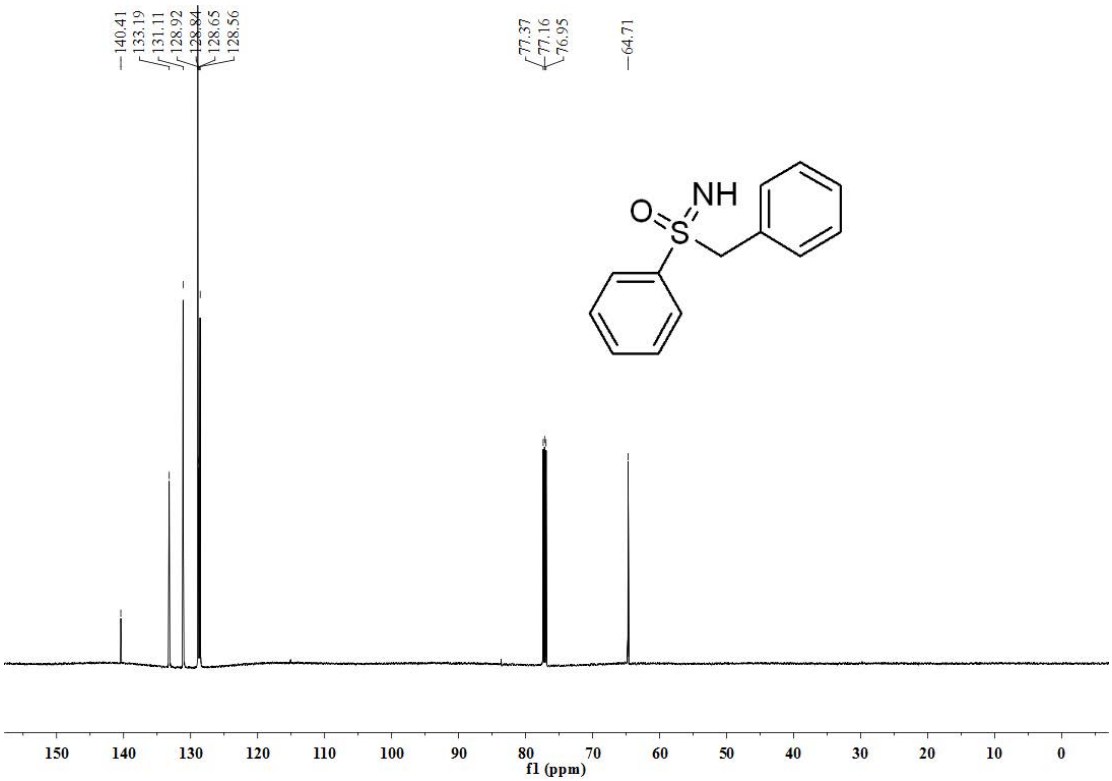
(*E*)-*N*-[Cyclopropyl(oxo)(phenyl)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3p)



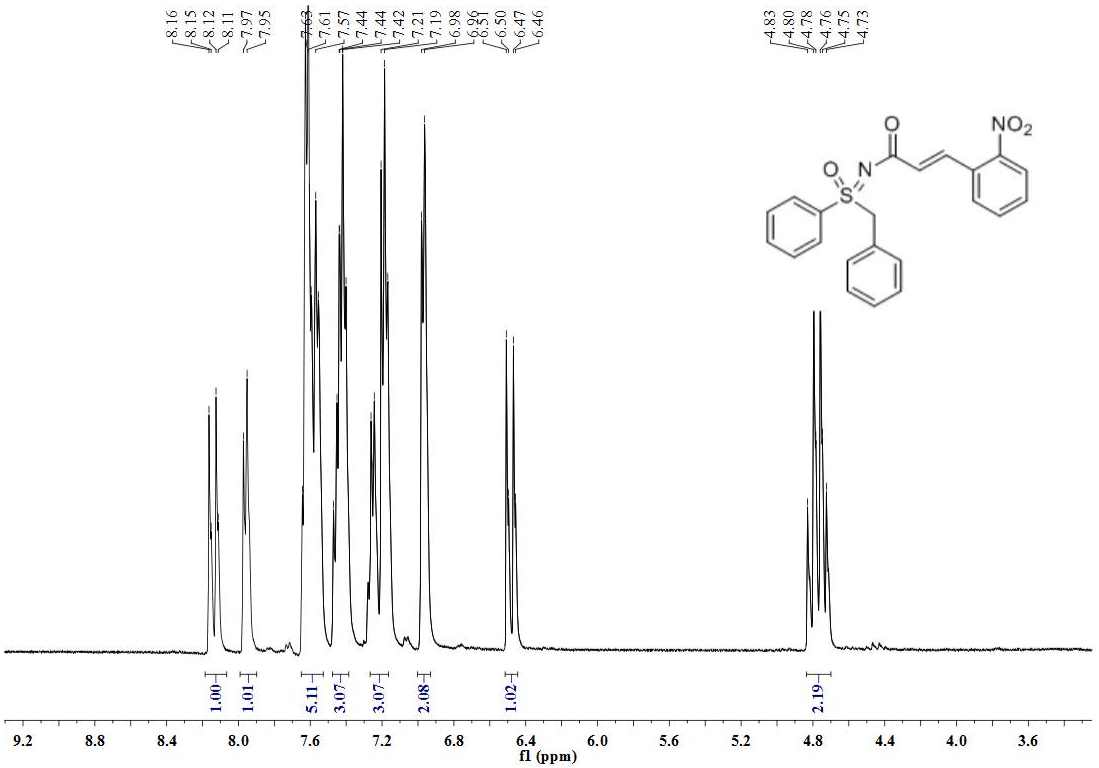


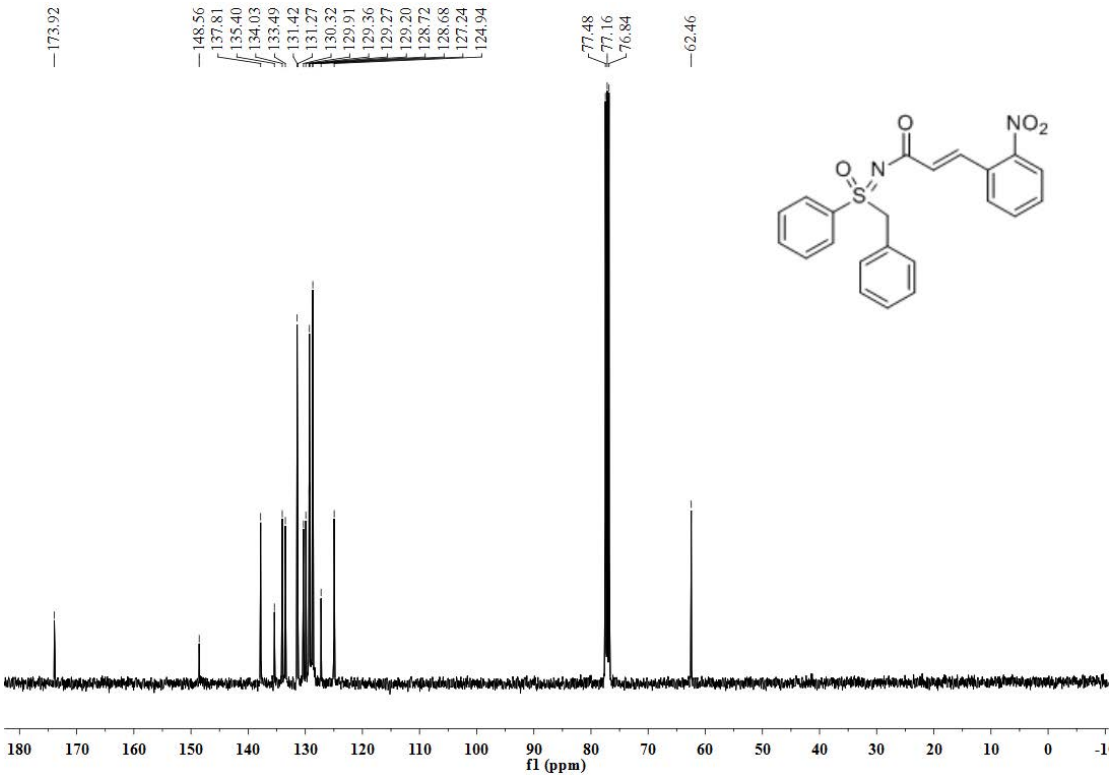
NH-*S*-Benzyl-*S*-phenyl-sulfoximine (1q)



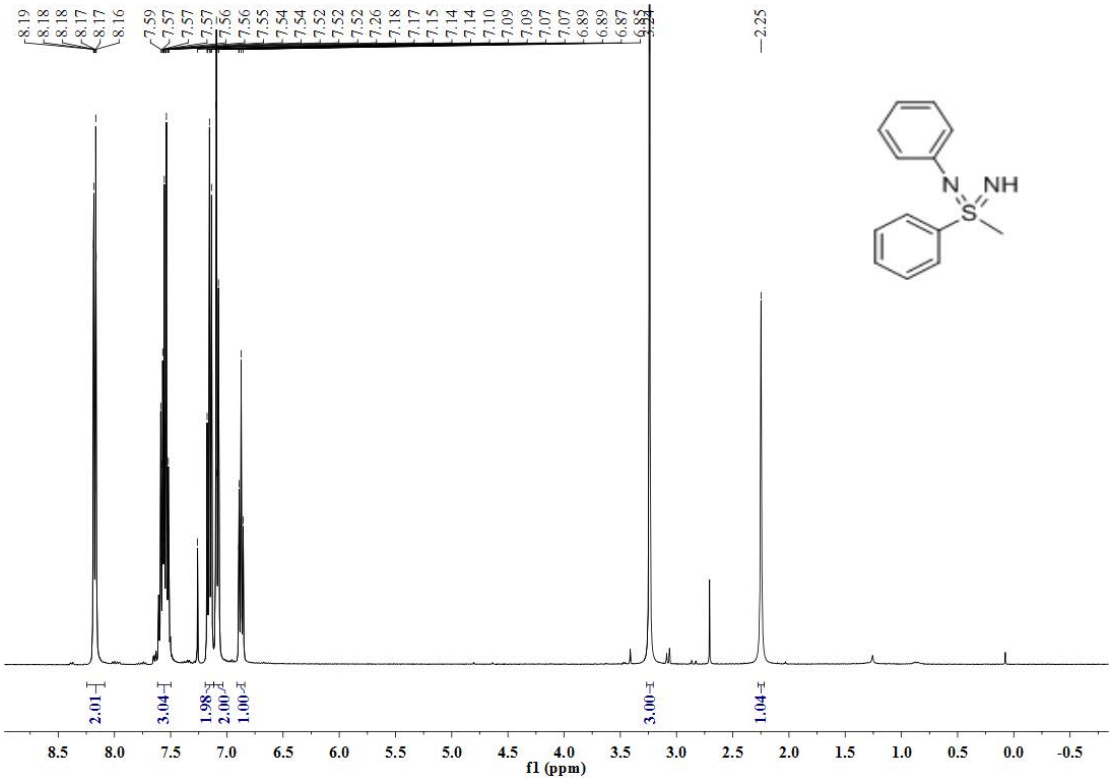


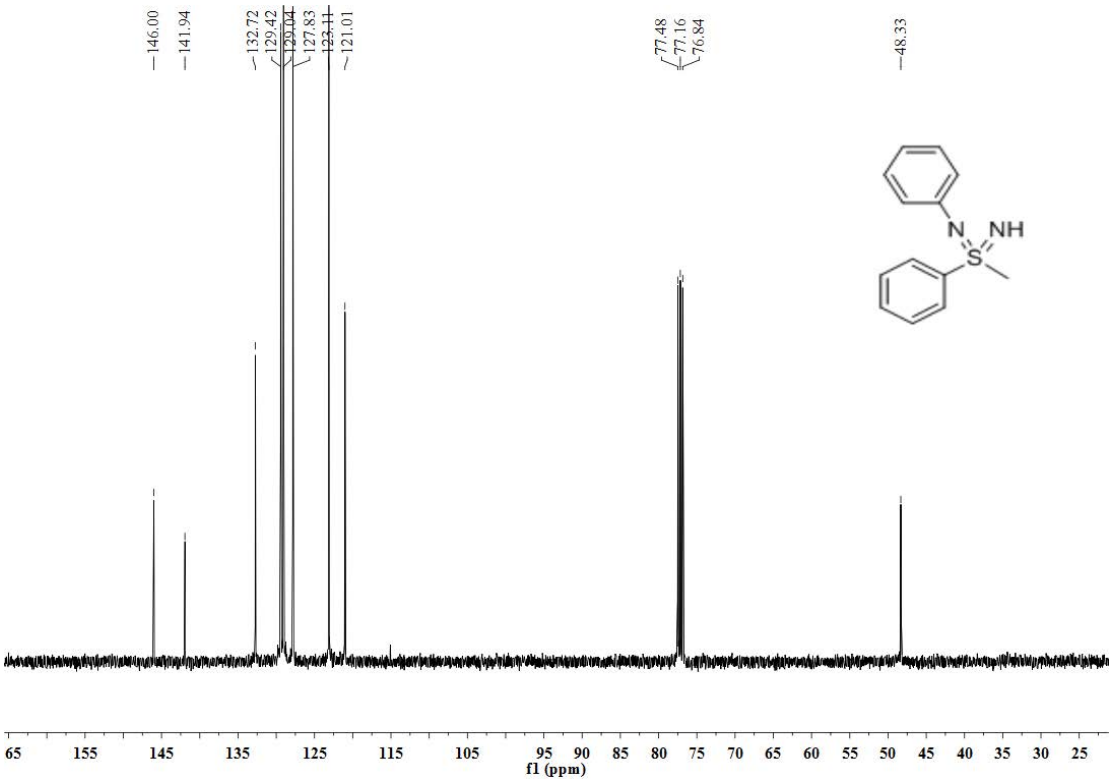
(*E*)-*N*-[Benzyl(oxo)(phenyl)-λ^6-sulfanylidene]-3-(2-nitrophenyl) acrylamide (3q)



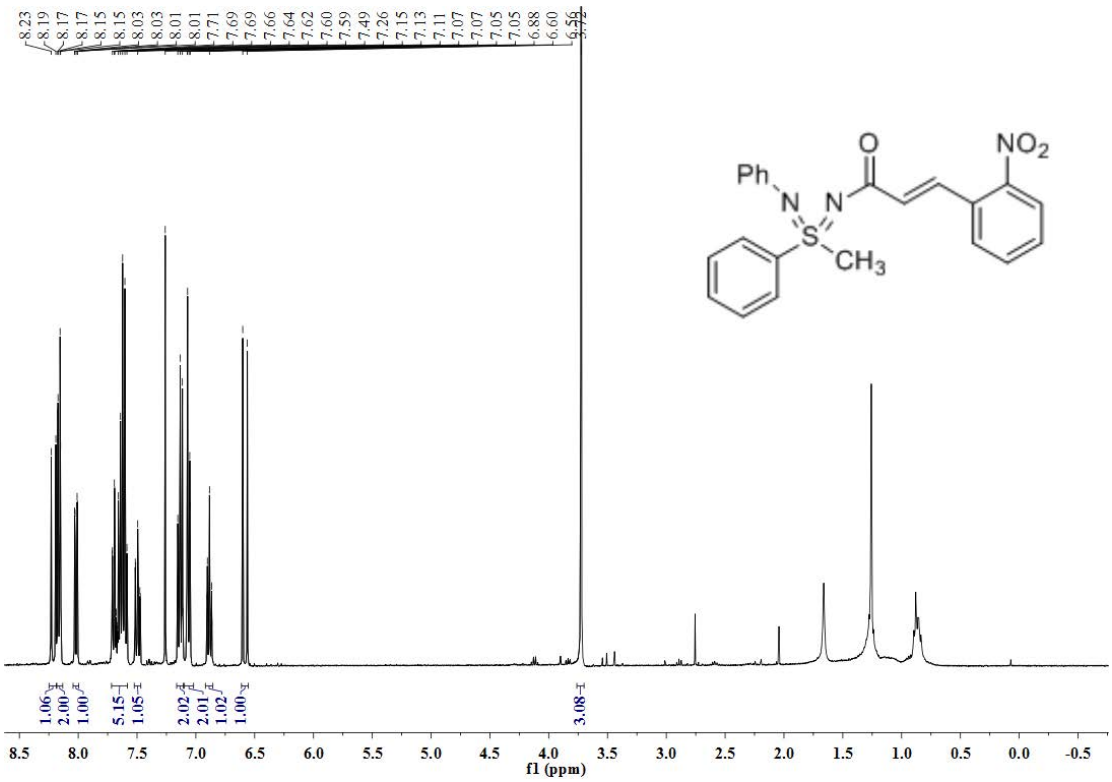


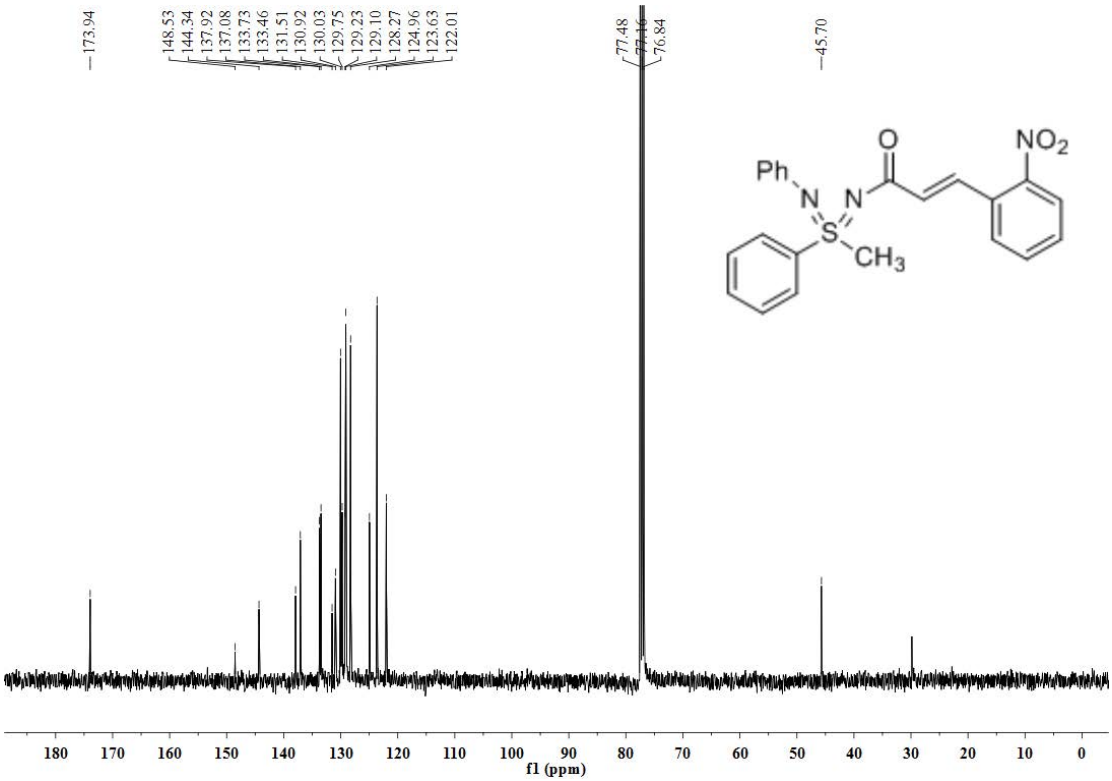
NH-N'-Phenyl-*S*-methyl-*S*-phenyl-sulfondiimide (1r)



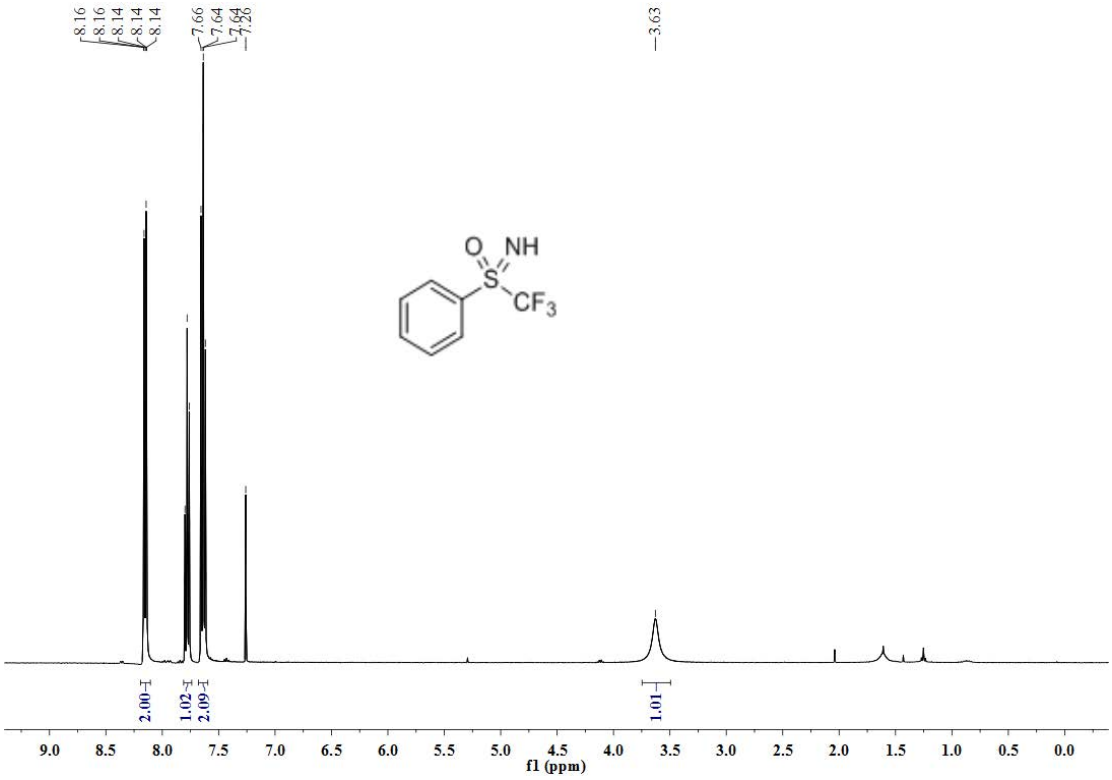


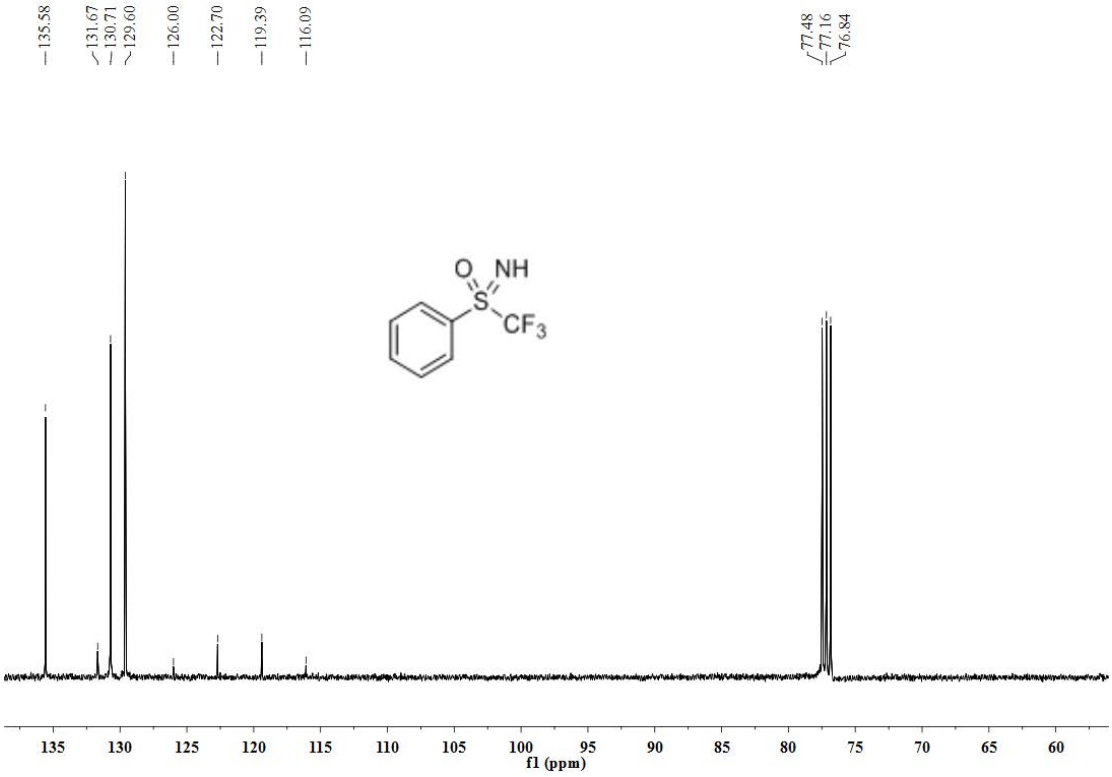
(*E*)-*N*-[Methyl(phenyl)(phenylimino)-λ^6-sulfanylidene]-3-(2-nitrophenyl) acrylamide (3r)

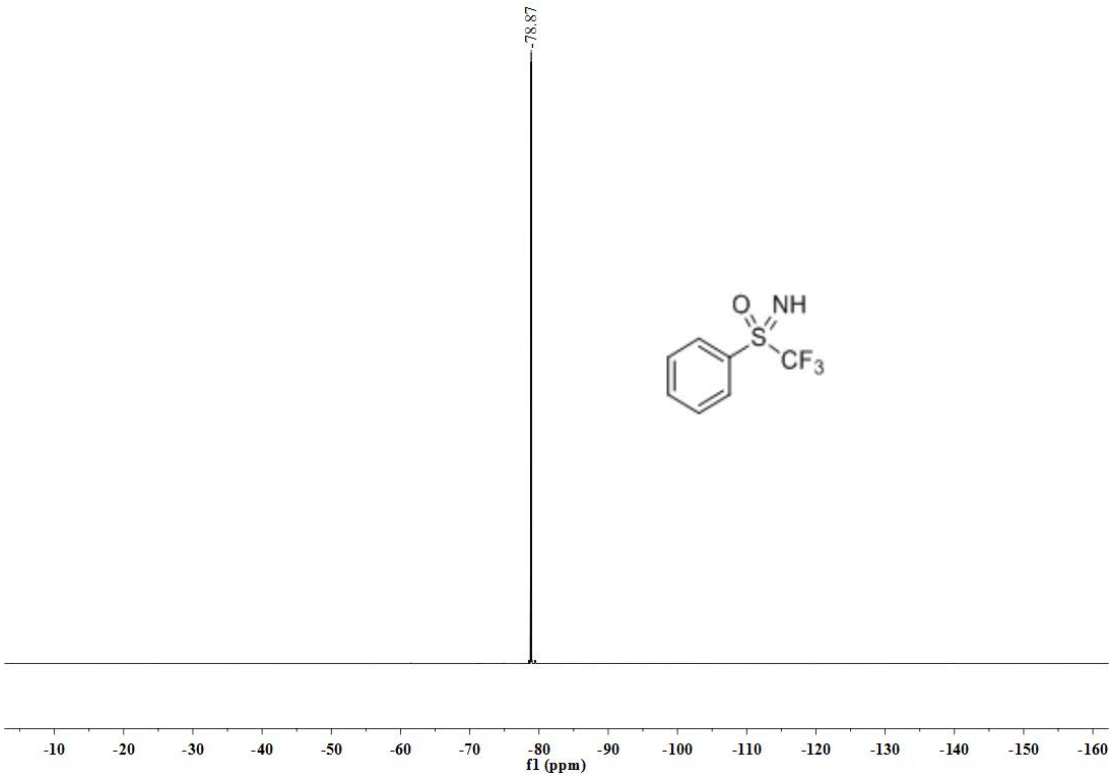




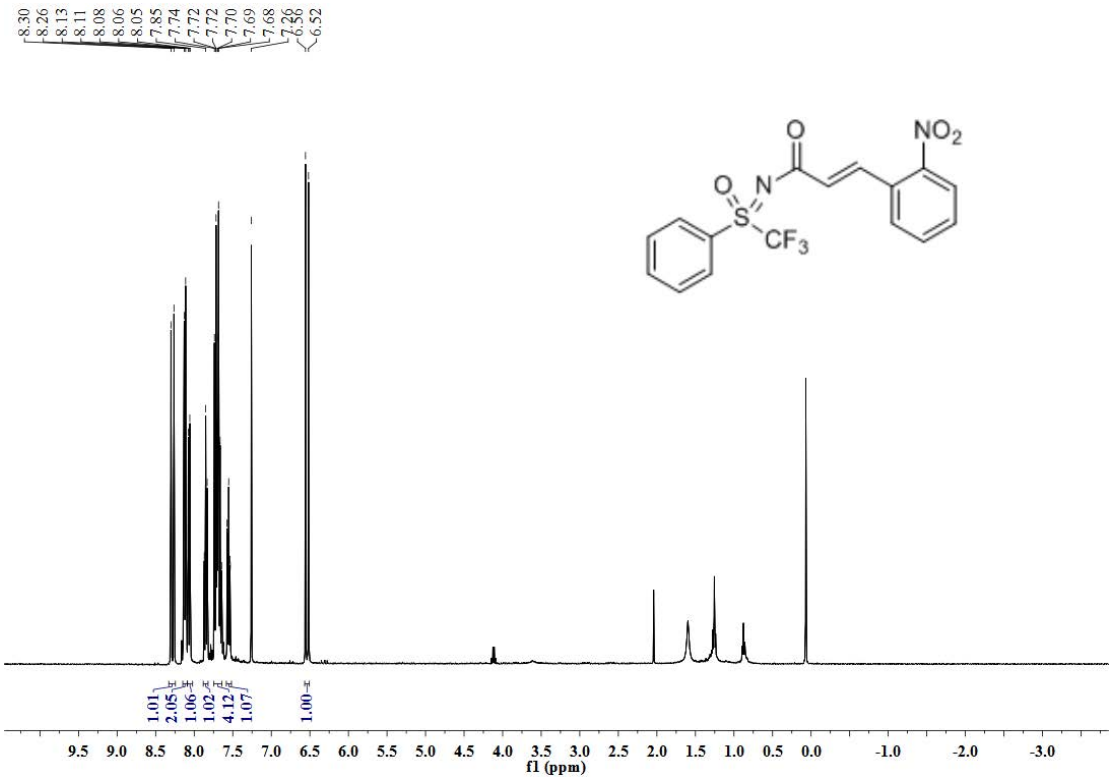
NH-*S*-Phenyl-*S*-trifluoromethyl-sulfoximine (1s)

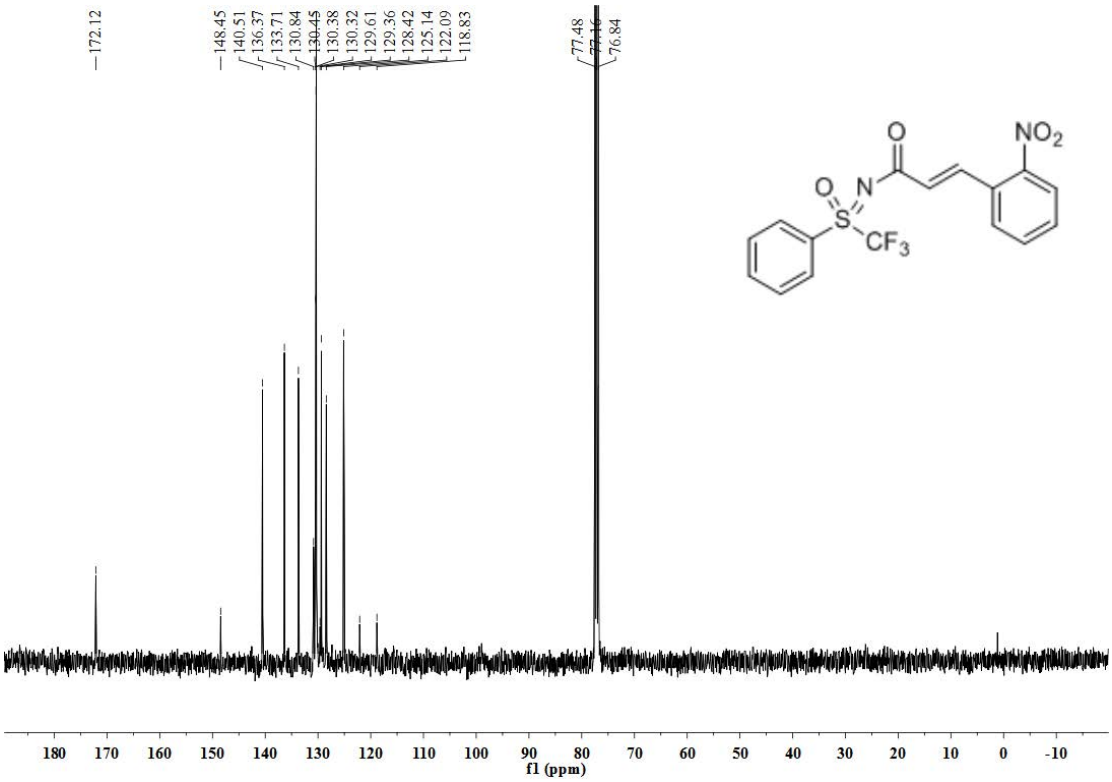


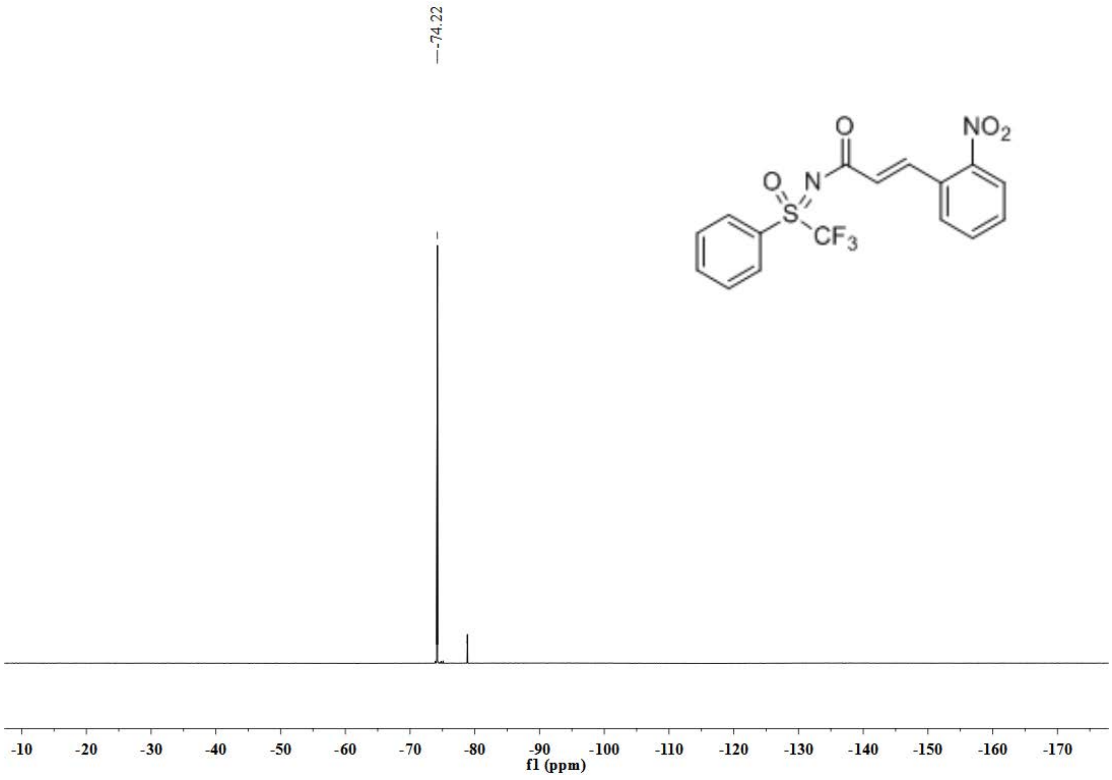




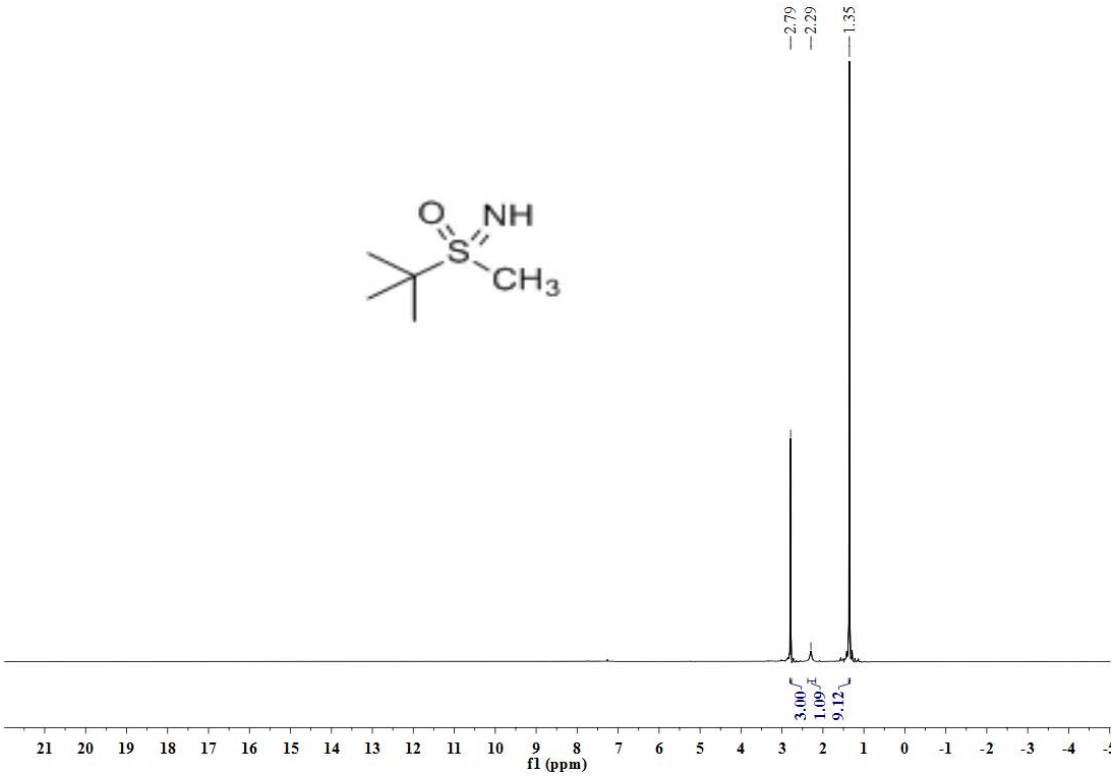
(*E*)-3-(2-*N*itrophenyl)-*N*-[oxo(phenyl)(trifluoromethyl)-λ^6-sulfanylidene] acrylamide (3s)



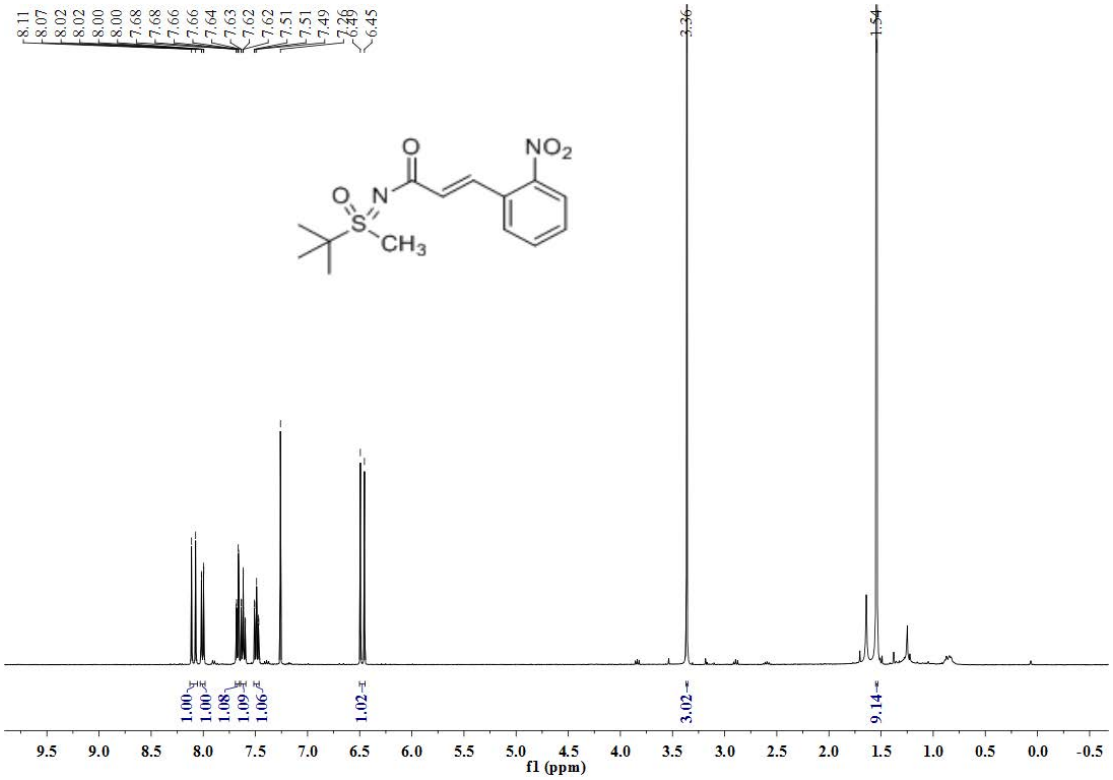

172.12
148.45
140.51
136.37
133.71
130.84
130.45
130.38
130.32
129.61
129.36
128.42
125.14
122.09
118.83
77.48
77.16
76.84
O
NO2
O
N
S
CF3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

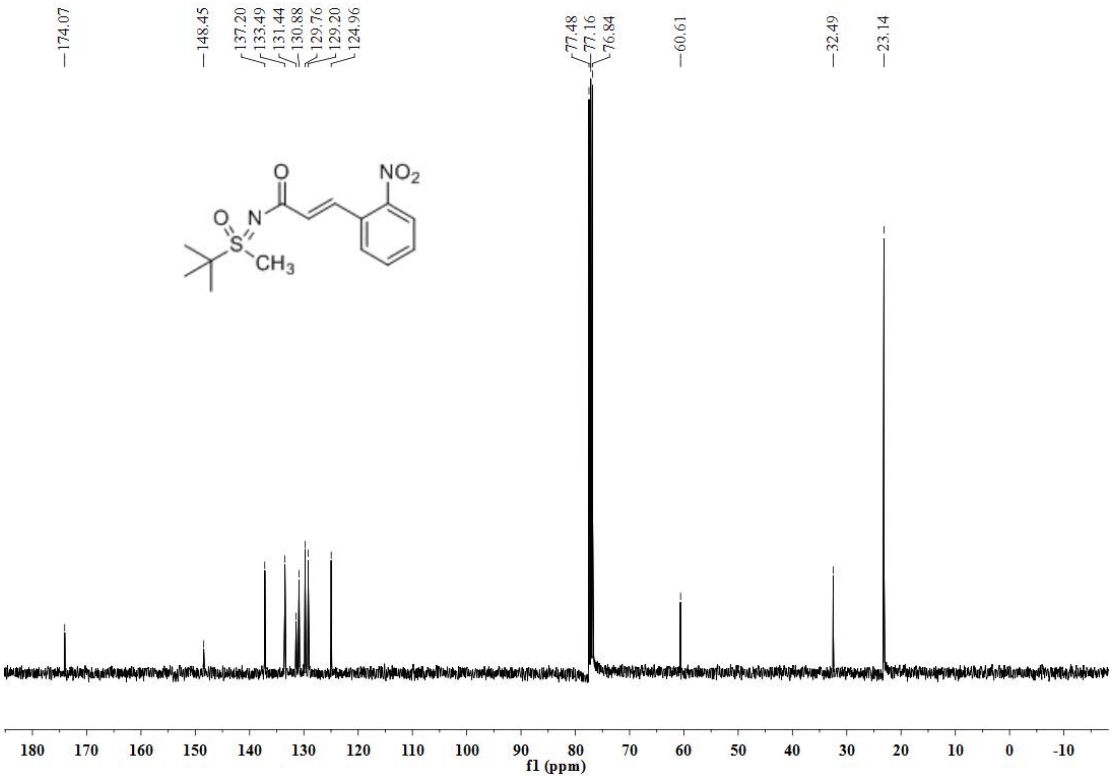

-74.22
O
NO2
O
N
S
CF3
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

NH-S-tert-Butyl-methyl-*S*- sulfoximine (1t)

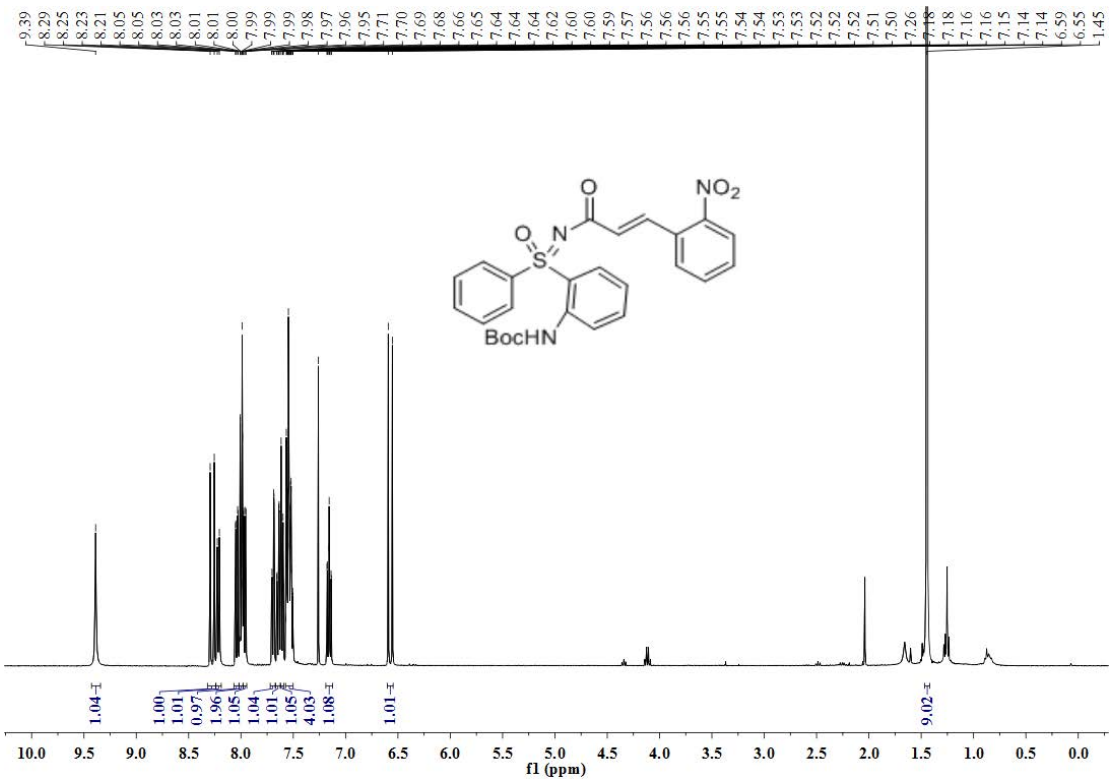


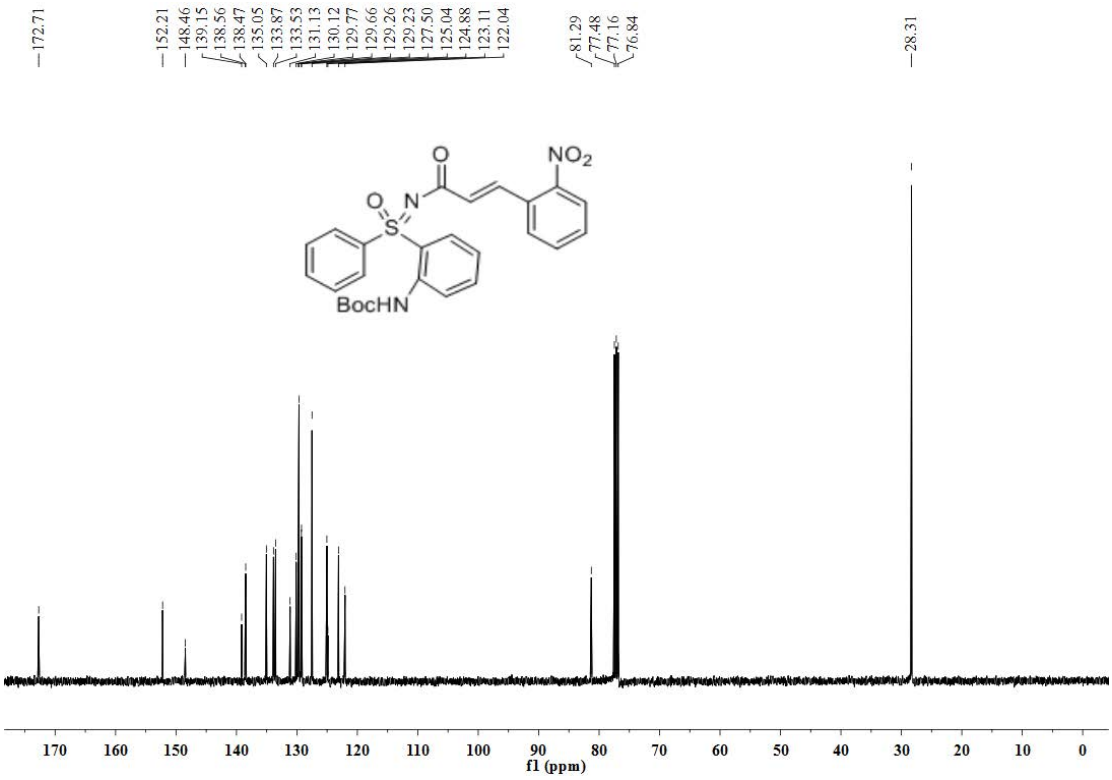
(*E*)-*N*-[*tert*-Butyl(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl)acrylamide (3t)



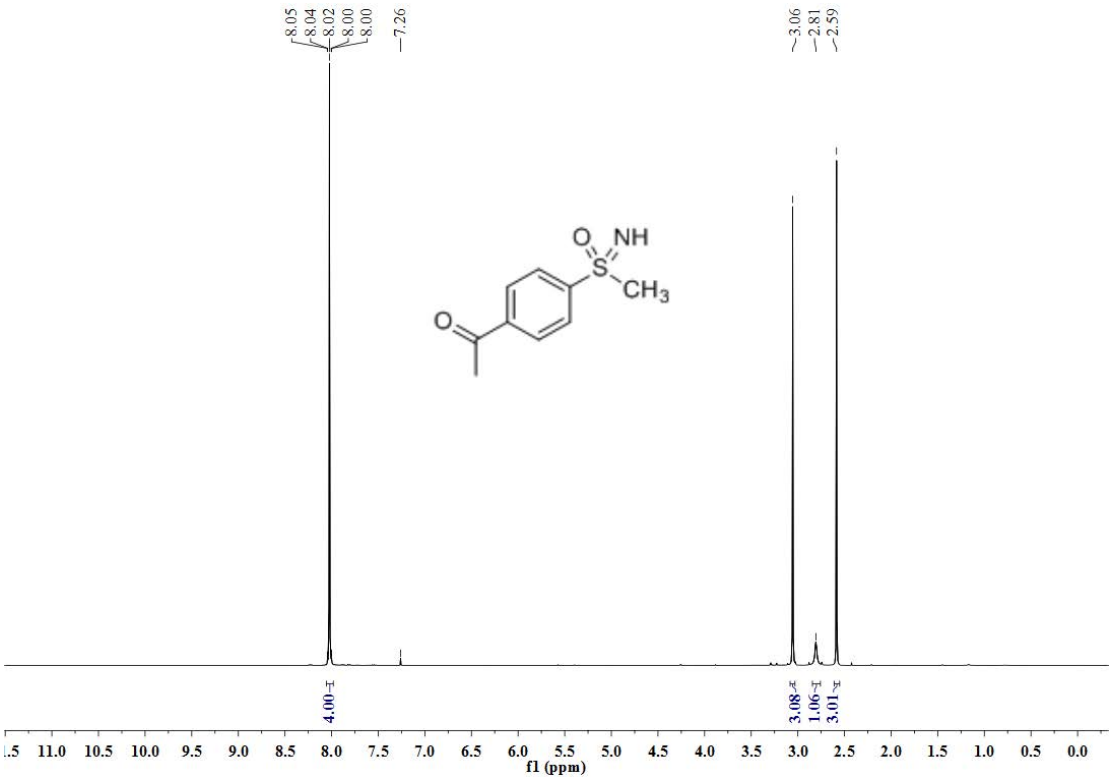


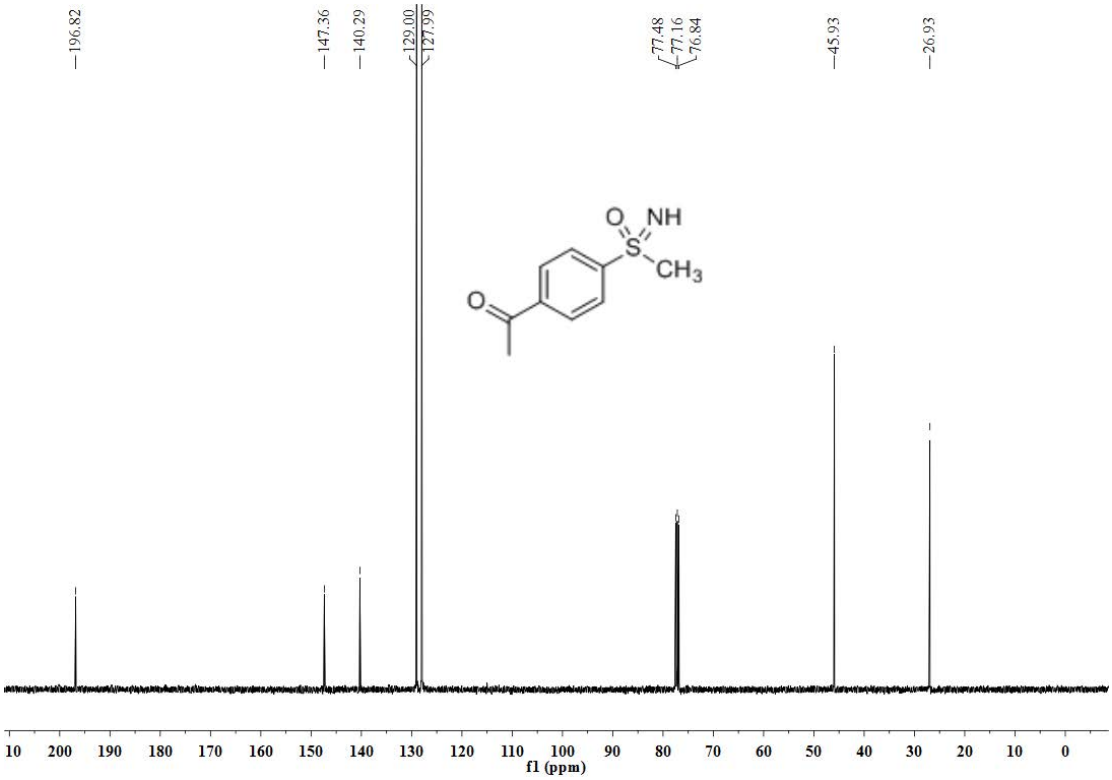
tert-Butyl-(_E_)-(2-{_N_-[3-(2-nitrophenyl)acryloyl]phenylsulfonimidoyl}phenyl)carbamate (3u)



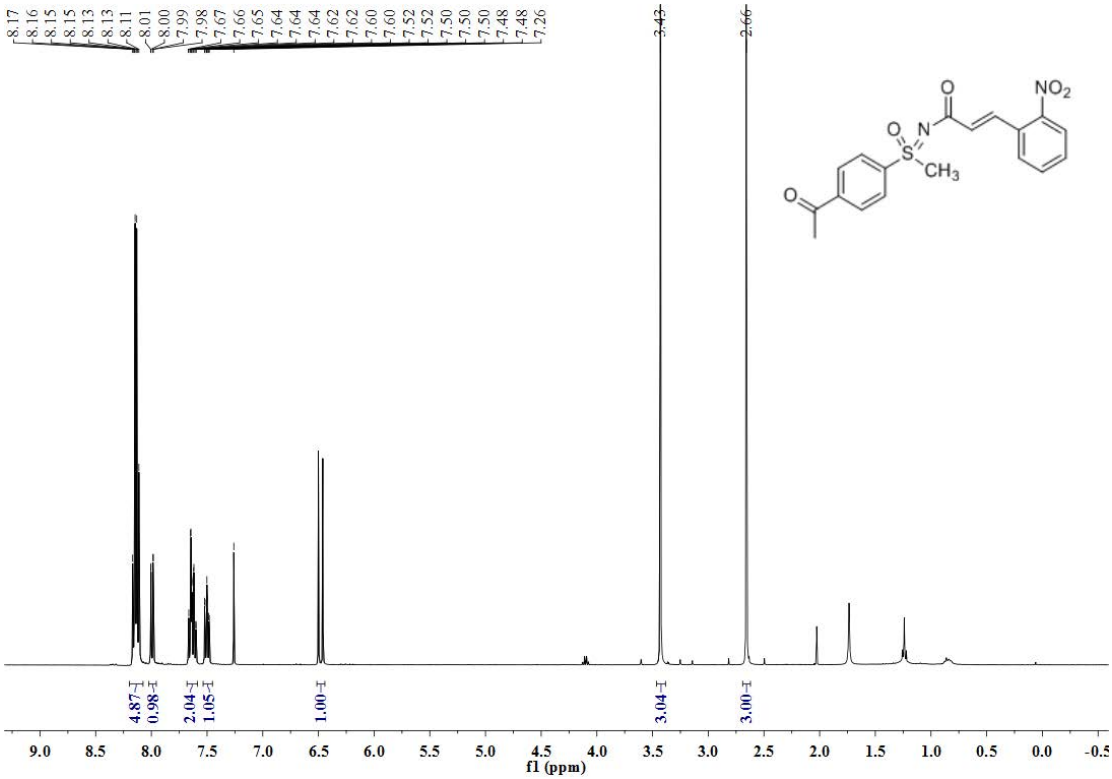


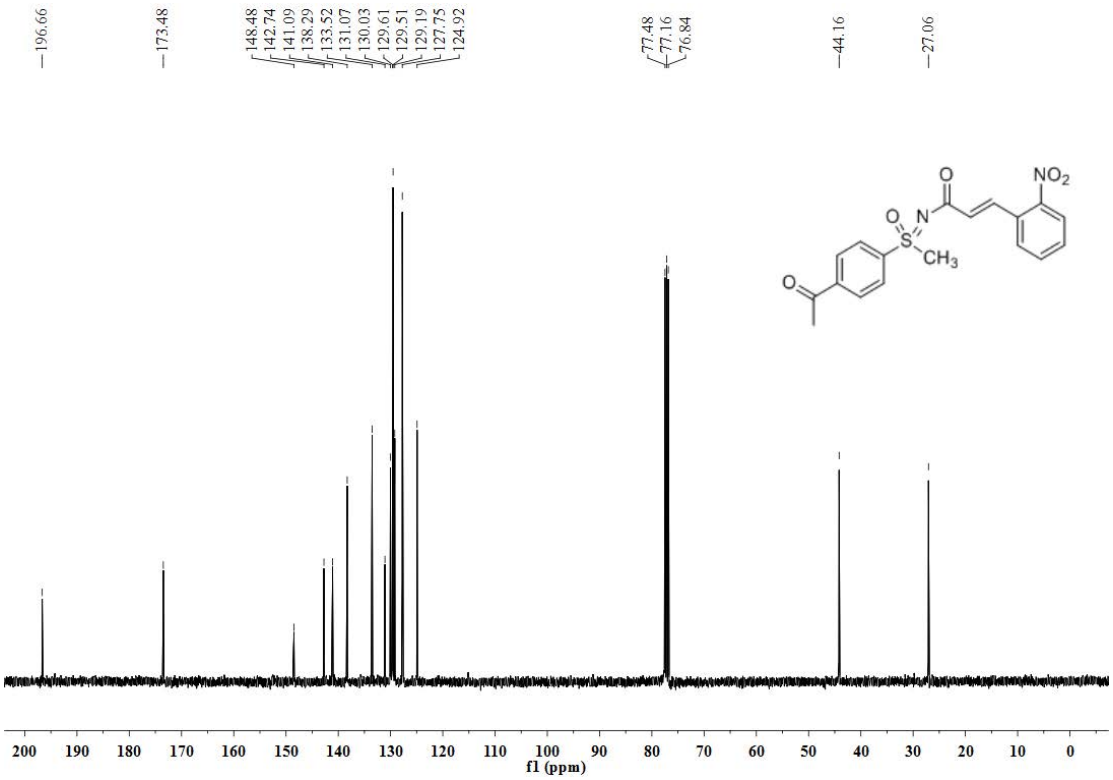
NH-*S*-[4-Acetylphenyl]-*S*-methyl-sulfoximine (1v)



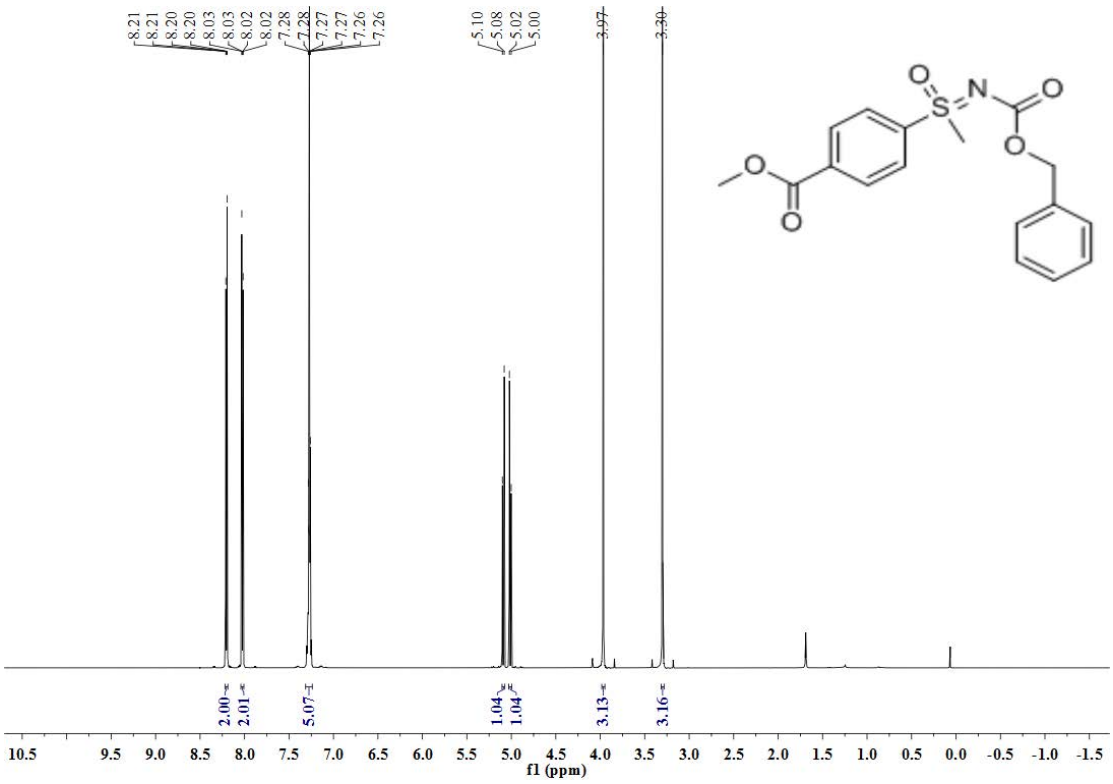


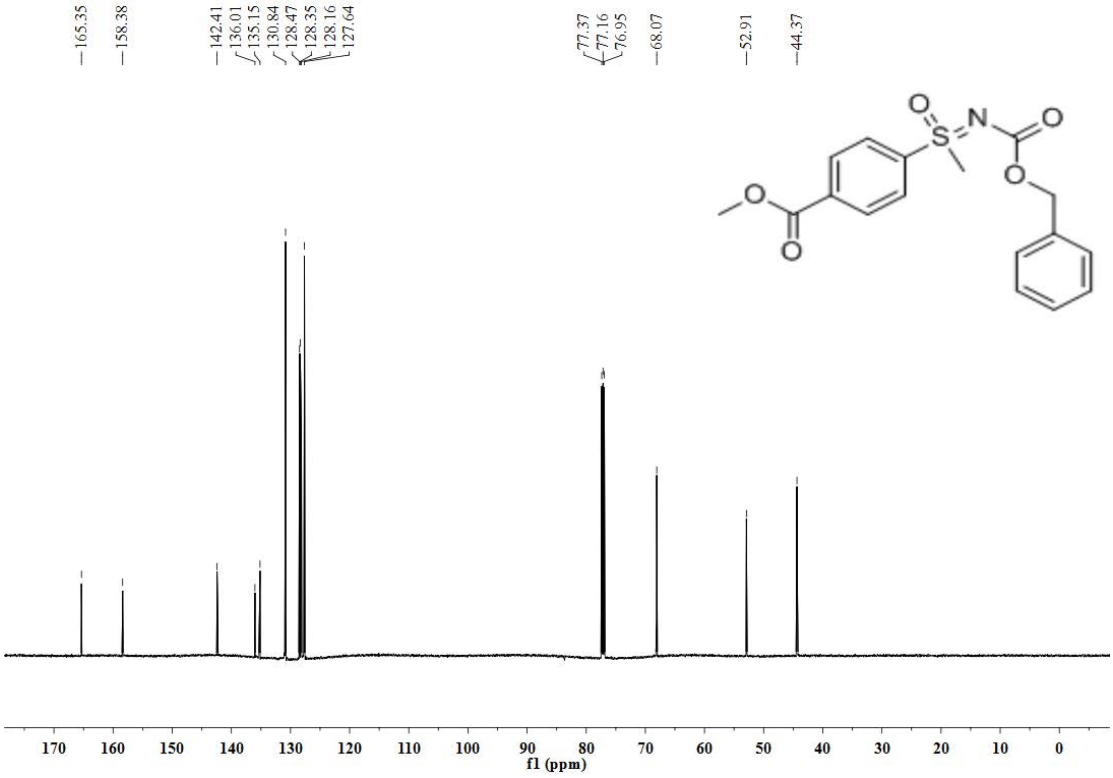
(*E*)-*N*-[(4-Acetylphenyl)(methyl)(oxo)-λ^6-sulfanylidene]-3-(2-nitrophenyl) acrylamide (3v)



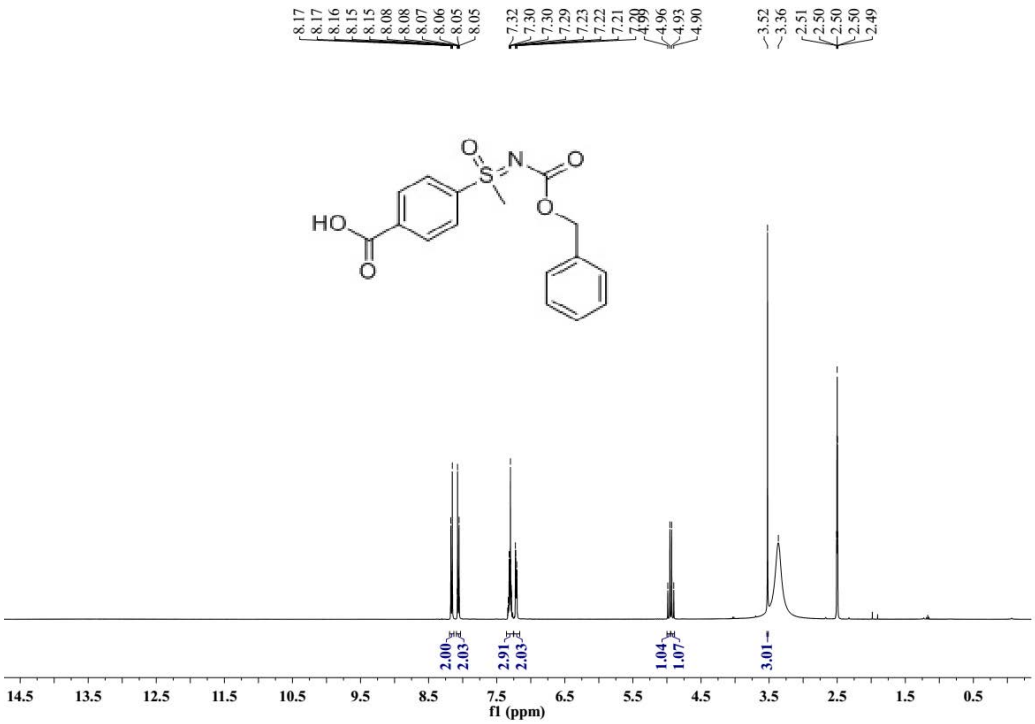


Methyl 4-{*N*-[(benzyloxy)carbonyl]-*S*-methylsulfonimidoyl}benzoate (8)

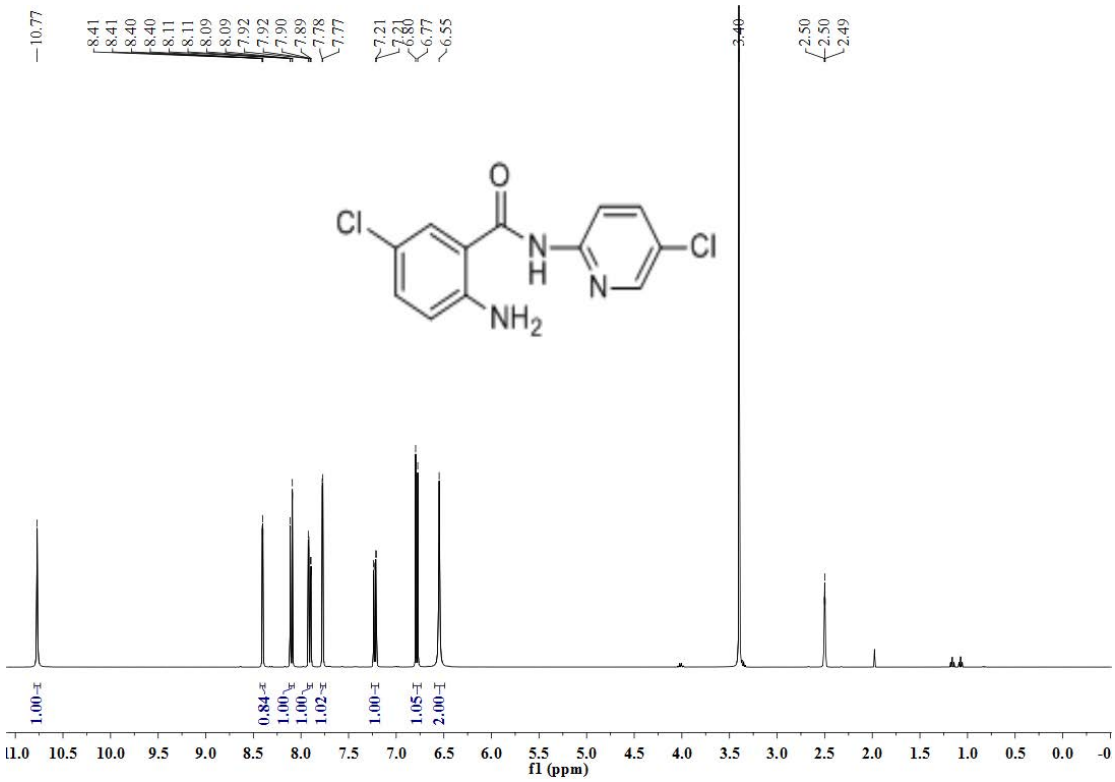


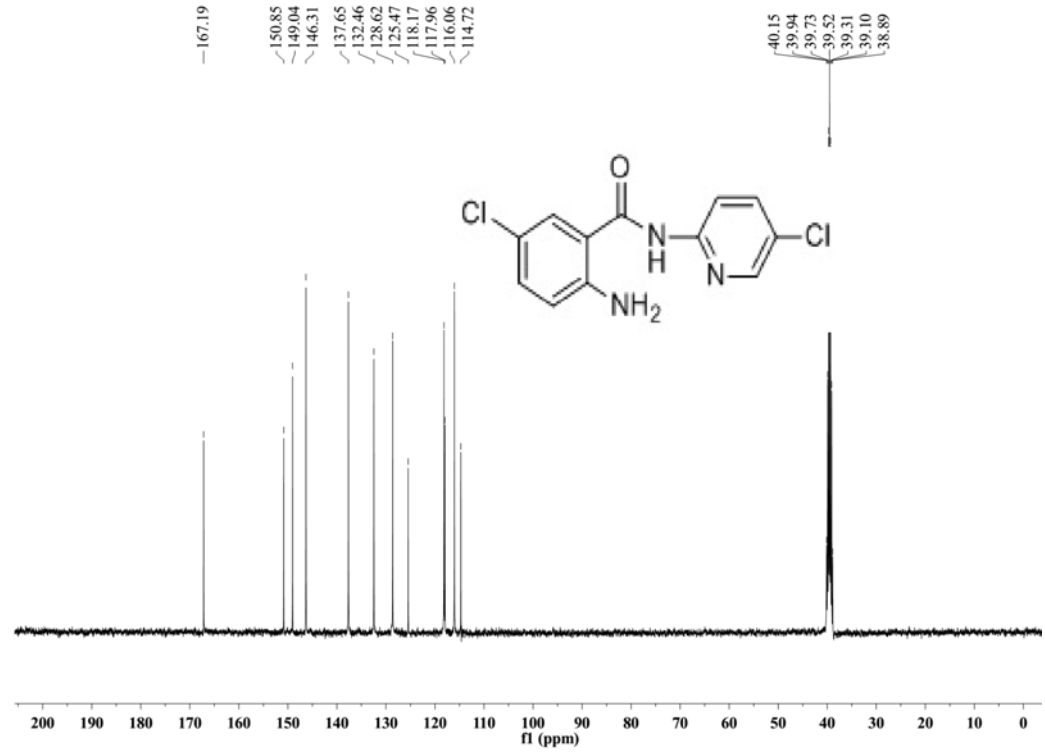


4-{*N*-[(Benzyloxy)carbonyl]-*S*-methylsulfonimidoyl}benzoic acid (9)

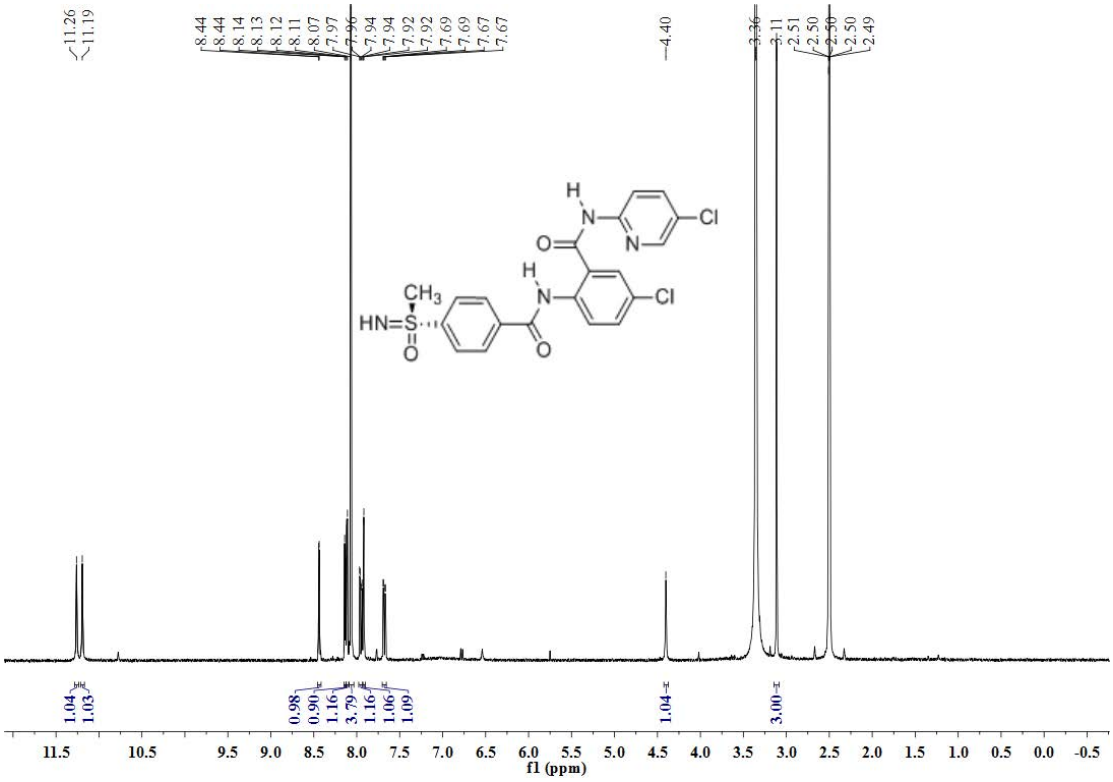


2-Amino-5-chloro-*N*-(5-chloropyridin-2-yl)benzamide (10)

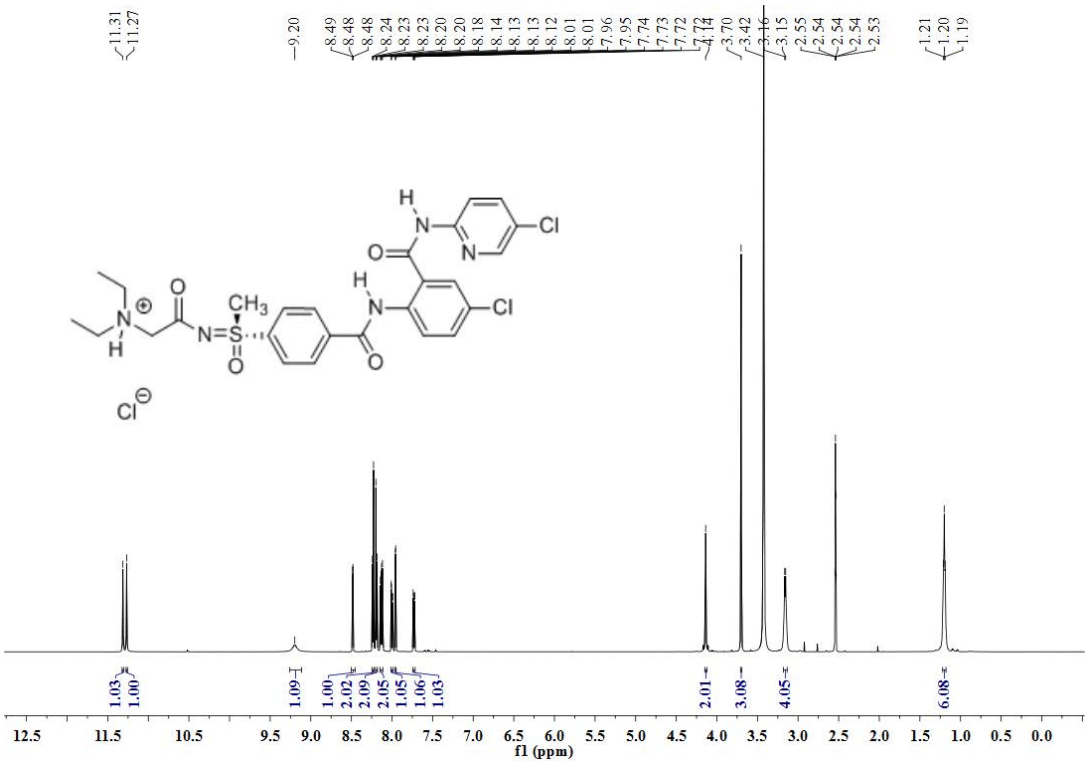


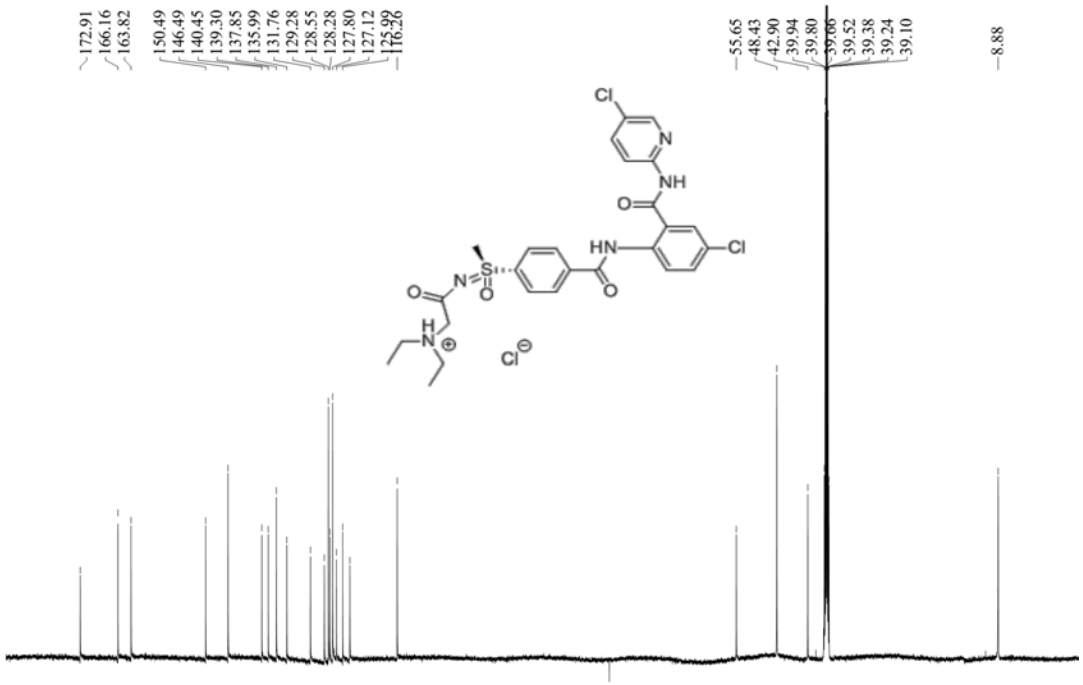


5-Chloro-*N*-(5-chloropyridin-2-yl)-2-[4-(*S*-methylsulfonimidoyl)benzamido]benzamide (11)



(*S*)-2-({[4-({4-Chloro-2-[(5-chloropyridin-2-yl)carbamoyl]phenyl}carbamoyl)phenyl](methyl)(oxo)-λ6-sulfanylidene}amino)-*N*,*N*-diethyl-2-oxoethan-1-aminium chloride (F')





(*S*)-5-Chloro-*N*-(5-chloropyridin-2-yl)-2-{4-[*N*-(diethylglycyl)-S-methylsulfonimidoyl]benzamido}benzamide (F)