Stereoselective Synthesis of Isoxazolidine Ring via Manganese (III)-Catalysed Aminoperoxidation of Unactivated Alkene Using Molecular Oxygen in the Air under Ambient Conditions

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Supplementary Information

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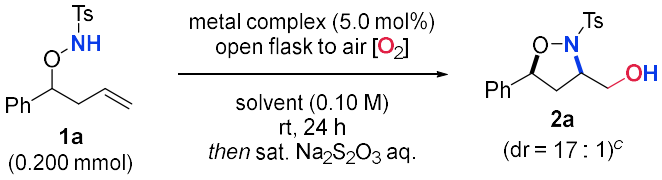
I. General information

IR spectra were obtained using a JASCO FT/IR 460-plus spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained on Agilent Technologies 400-MR DD2, 400-MR spectrometers. The chemical shifts are expressed in ppm downfield from internal solvent peaks $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR) and coupling constants (*J* values) are given in Hertz. The coupling patterns are expressed by s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), t (triplet), dt (double of triplets), ddt (doublet of doublet of triplets), td (triplet of doublets), quint (quintet), m (multiplet) and br (broad signal). MS spectra were measured with JEOL JMS-AX505HA, JEOL JMS-700V MStation and JEOL JMS-T100LP spectrometers. Melting points (M.p.) were obtained on Stanford Research Systems MPA100 melting point apparatus. X-ray analysis was performed on a Rigaku R-AXIS RAPID diffractometer. Commercial reagents and solvents were used without further purification unless otherwise indicated. Flash column chromatography was carried out with Kanto Chemical silica gel (Kanto Chemical Co., Inc., silica gel 60N, spherical neutral, particle size 63–210 mm). TLC was performed on 0.25 mm Merck silica gel 60 F254 plates.

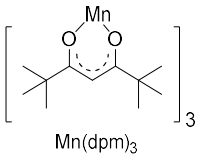
II. Detailed experimental results

Evaluation of metal complex effect for aminoperoxidation (Table S1-4).

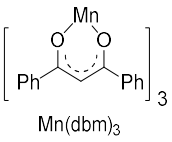
Table S1. Detailed experimental results for Table 1.[a]



entry	metal complex	solvent	yield[b]
1	$Mn(acac)_2$	MeCN	24
2	$Mn(acac)_2$	CH_2Cl_2	21
3	$Mn(dbm)_3$	MeCN	12
4	$Mn(dbm)_3$	CH_2Cl_2	15
5	$Mn(dpm)_3$	MeCN	24
6	$Mn(dpm)_3$	CH_2Cl_2	19
7	$Mn(OAc)_3$	MeCN	9
8	$Mn(OAc)_3$	CH_2Cl_2	0



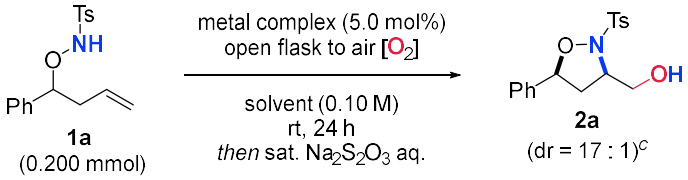
$Mn(dpm)_3$



$Mn(dbm)_3$

[a] Reaction conditions: **1a** (0.200 mmol), O_2 (open flask to air). [b] The yield was determined by ^{1}H-NMR analysis of the crude reaction mixture of products by using 1,2-dichloroethane as an internal standard. [c] The ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture of products.

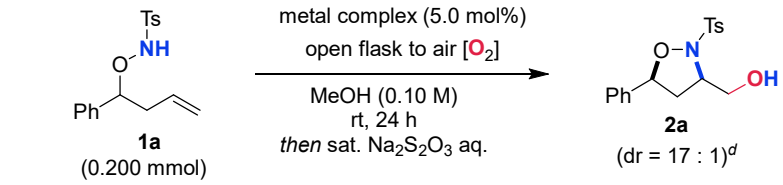
Table S2. Detailed experimental results for Table 1. [a]

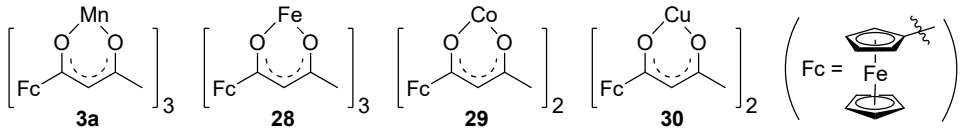


entry	metal complex	solvent	yield[b]
1	$Fe(acac)_3$	MeOH	0
2	$Fe(acac)_3$	MeCN	0
3	$Fe(acac)_3$	CH_2Cl_2	0
4	$Co(acac)_3$	MeOH	0
5	$Co(acac)_3$	MeCN	0
6	$Co(acac)_3$	CH_2Cl_2	0
7	$Co(acac)_2$	MeOH	0
8	$Co(acac)_2$	MeCN	0
9	$Co(acac)_2$	CH_2Cl_2	0
10	$Cu(acac)_2$	MeOH	0
11	$Cu(acac)_2$	MeCN	10
12	$Cu(acac)_2$	CH_2Cl_2	8

[a] Reaction conditions: **1a** (0.200 mmol), O_2 (open flask to air). [b] The yield was determined by ^{1}H-NMR analysis of the crude reaction mixture using 1,2-dichloroethane as an internal standard. [c] The ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture.

Table S3. Detailed experimental results for Table 1. [a, e]

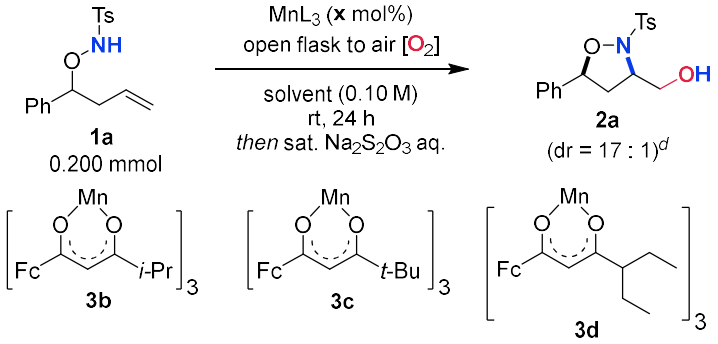




entry	metal complex	yield[b]
1	**3a**	60[c]
2	**28**	0
3	**29**	50[c]
4	**30**	18

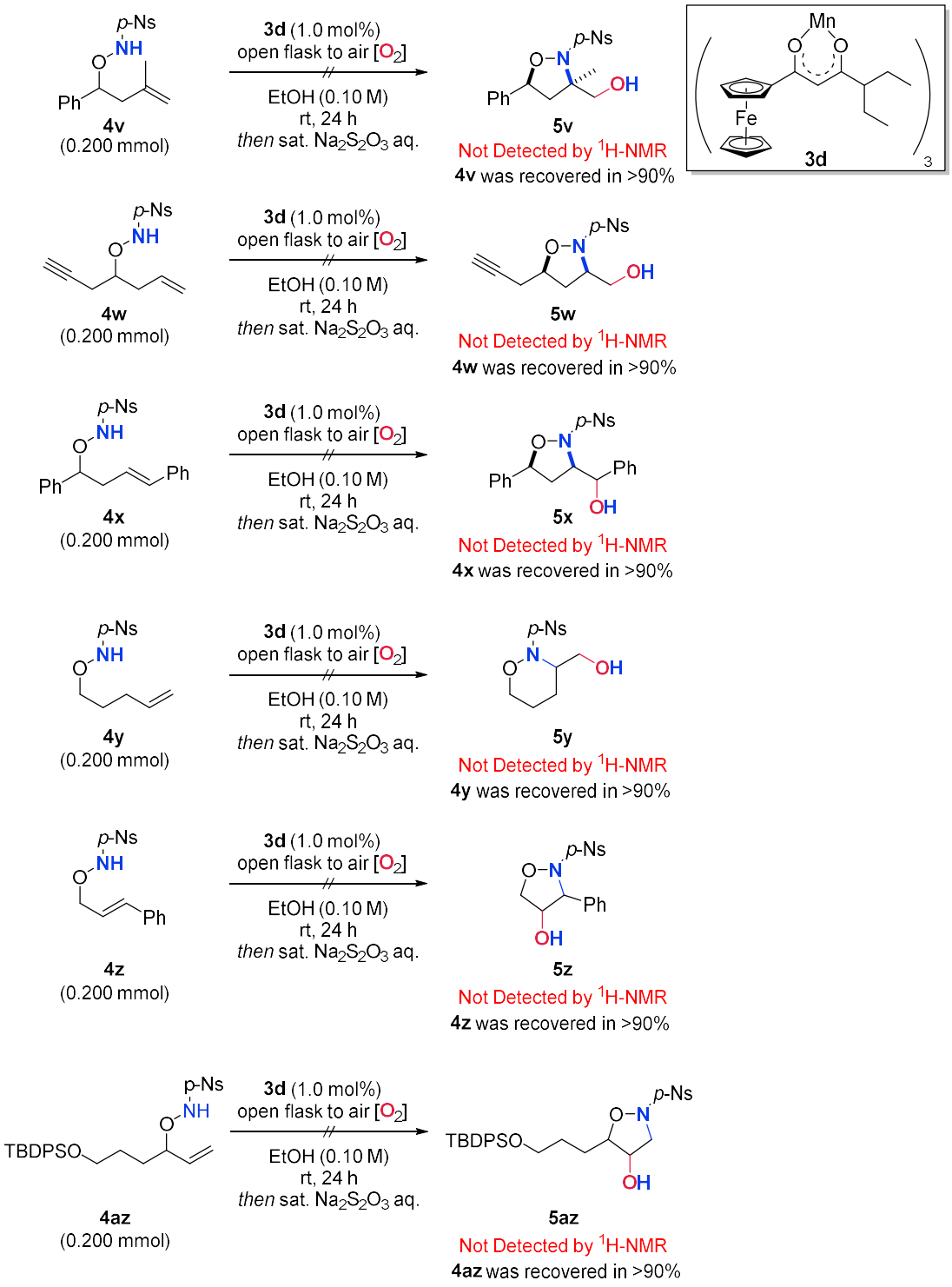
[a] Reaction conditions: **1a** (0.200 mmol), O_2 (open flask to air). [b] The yield was determined by ^{1}H-NMR analysis of the crude reaction mixture using 1,2-dichloroethane as an internal standard. [c] Isolated yield. [d] The ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture. [e] Metal complexes **28**–**30** were prepared by a known procedure. [1]

Table S4. Detailed experimental results for Table 2.[a]

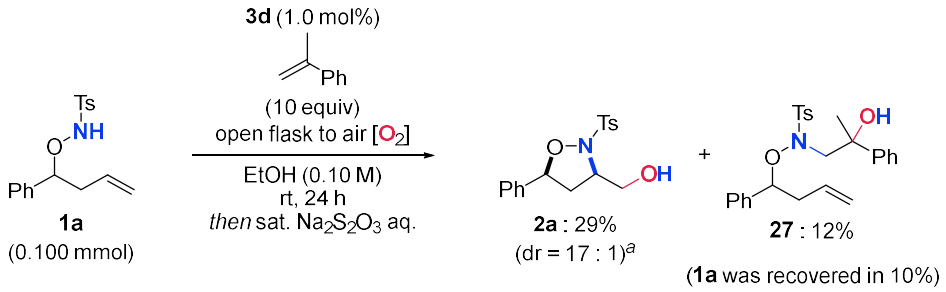


entry	MnL_3	x (mol%)	solvent	yield (%)[b]
1	**3b**	5.0	MeOH	77
2	**3b**	1.0	MeOH	23
3	**3b**	1.0	EtOH	71
4	**3b**	1.0	*i*-PrOH	30
5	**3b**	1.0	*t*-BuOH	0[c]
6	**3b**	1.0	CF_3CH_2OH	9[c]
7	**3b**	1.0	$(CF_3)_2CHOH$	0[c]
8	**3c**	1.0	MeOH	33
9	**3c**	1.0	EtOH	52
10	**3c**	1.0	*i*-PrOH	26
11	**3c**	1.0	*t*-BuOH	< 1[c]
12	**3d**	1.0	MeOH	34[c]
13	**3d**	1.0	EtOH	75
14	**3d**	1.0	*i*-PrOH	0[c]
15	**3d**	1.0	*t*-BuOH	0[c]

[a] Reaction conditions: **1a** (0.200 mmol), O_2 (open flask to air). [b] Isolated yield [c] The yield was determined by ^{1}H-NMR analysis of the crude reaction mixture using 1,2-dichloroethane as an internal standard. [d] The ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture.



Scheme S1. Unapplicable substrates



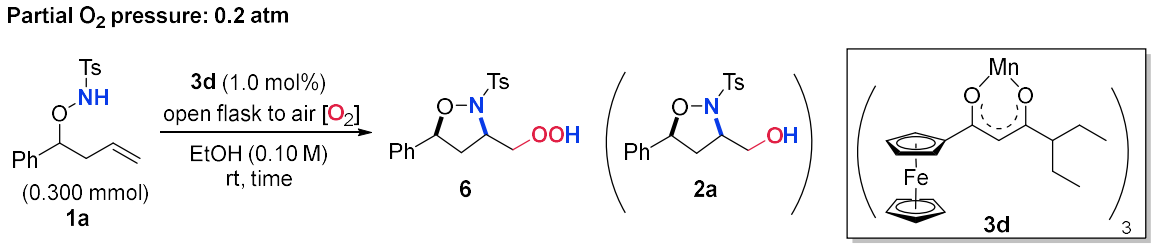
[a] The ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture of products.

Scheme S2. Mn(III)-catalysed aminoperoxidation of **1a** in the presence of α-methylstyrene

In order to confirm the reactivity of nitrogen on **1a**, we carried out the present Mn(III)-catalysed reaction in the presence of α-methylstyrene under atmospheric conditions. As a result, **2a** and *N*-directed coupling product **27** were obtained in 29% and 12% yield, respectively (Scheme S2).

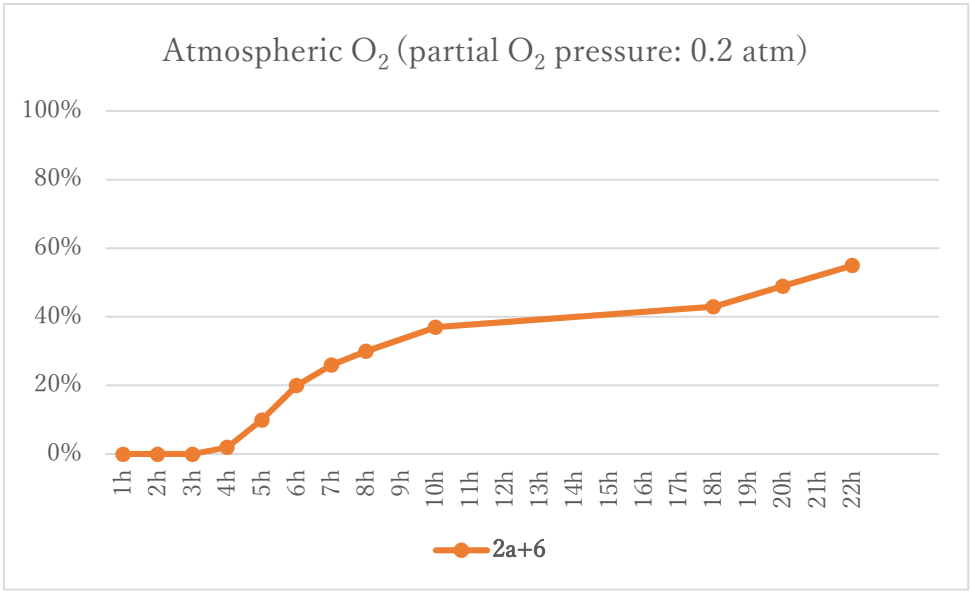
Preliminary studies on the reaction mechanism

1-A) The kinetic profile under atmospheric conditions. (Partial O_2 pressure: 0.2 atm)



Scheme S3. Mn(III)-catalysed aminoperoxidation of **1a** using O_2 in air.

To a stirred solution of sulphonamide **1a** (95.2 mg, 0.300 mmol) in EtOH (3.00 mL) at room temperature was added Mn(III)-complex **3d** (3.1 mg, 3.0 μmol) under air (open flask, partial O_2 pressure: 0.2 atm). At 1, 2, 3, 4, 5, 6, 7, 8, 10, 18, 20, and 22 h, respectively, 30.0 μL of sample was collected from the reaction mixture by syringe. The sample (30.0 μL) was diluted with 2-propanol to total volume of 1.0 mL. 10.0 μL of the diluted solution was injected into the HPLC column (COSMOSIL Packed Column 5SL-II, ϕ0.46 cm × 25 cm, hexane/*i*-PrOH = 99 : 1, detection at 254 nm, flow rate 1.0 mL/min, t_R = 14.6 min for **6** , 54.0 min for **2a**). Based on the calibration curve (Figures S5 and 6), the yield was estimated from the peak area (Figure S1).

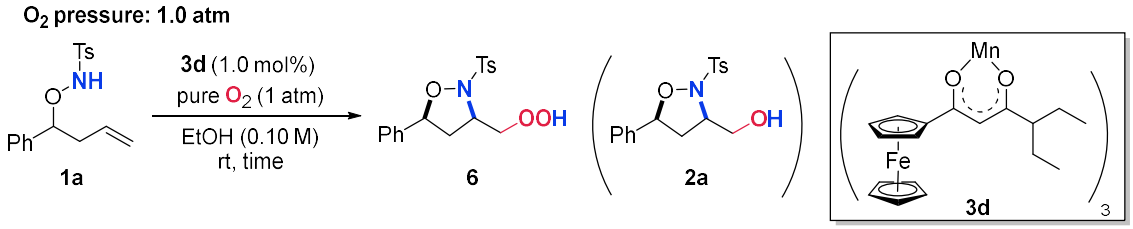


	1 h	2 h	3 h	4 h	5 h	6 h	7 h	8 h	10 h	18 h	20 h	22 h
2a+6	0%	0%	0%	2%	10%	20%	26%	30%	37%	43%	49%	55%

Figure S1[a]**.** The kinetic profile of Mn(III)-catalysed oxygenative aminoperoxidation under air.

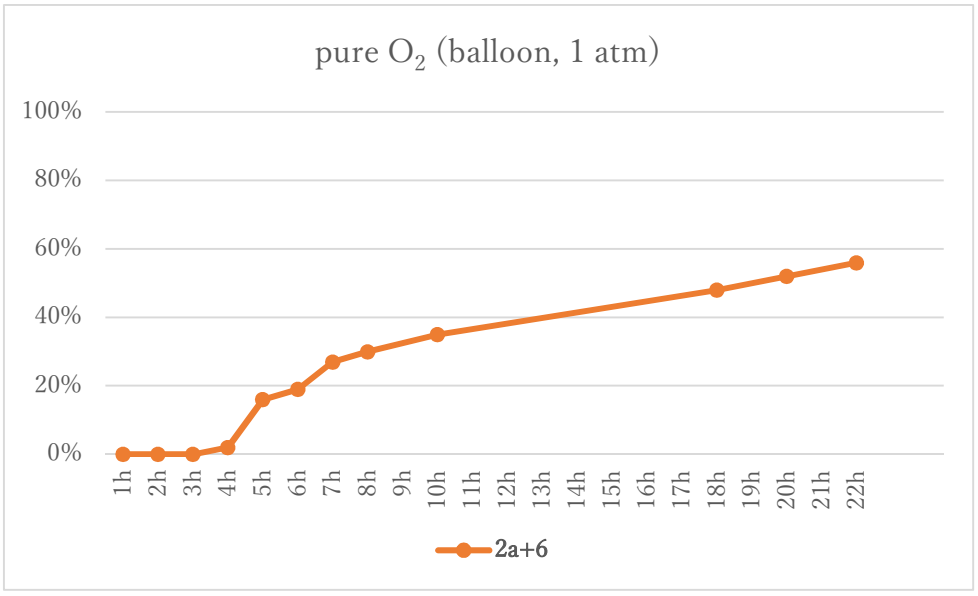
[a] Peroxide **6** was partially converted to **2a** in HPLC column (normal phase). The yield was estimated by HPLC analysis.

1-B) The kinetic profile under pure O_2 atmosphere. (O_2 pressure: 1 atm)



Scheme S4. Mn(III)-catalysed aminoperoxidation of **1a** using pure O_2 (balloon, 1 atm)

To a stirred solution of sulphonamide **1a** (95.2 mg, 0.300 mmol) in EtOH (3.00 mL) at room temperature was added Mn(III)-complex **3d** (3.1 mg, 3.0 μmol) under pure O_2 (balloon, O_2 pressure: 1 atm). At 1, 2, 3, 4, 5, 6, 7, 8, 10, 18, 20, and 22 h, respectively, 30.0 μL of sample was collected from the reaction mixture by syringe. The sample (30.0 μL) was diluted with 2-propanol to total volume of 1.0 mL. 10.0 μL of the diluted solution was injected into the HPLC column (COSMOSIL Packed Column 5SL-II, ϕ0.46 cm × 25 cm, hexane/*i*-PrOH = 99 : 1, detection at 254 nm, flow rate 1.0 mL/min, t_R = 14.6 min for **6** , 54.0 min for **2a**). Based on the calibration curve (Figures S5 and 6), the yield was estimated from the peak area (Figure S2).



	1 h	2 h	3 h	4 h	5 h	6 h	7 h	8 h	10 h	18 h	20 h	22 h
2a+6	0%	0%	0%	2%	10%	19%	27%	30%	35%	48%	52%	56%

Figure S2[a]**.** The kinetic profile of Mn(III)-catalysed oxygenative aminoperoxidation under pure oxygen atmosphere (1 atm).

[a] Peroxide **6** was partially converted to **2a** in HPLC column (normal phase). The yield was estimated by HPLC analysis.

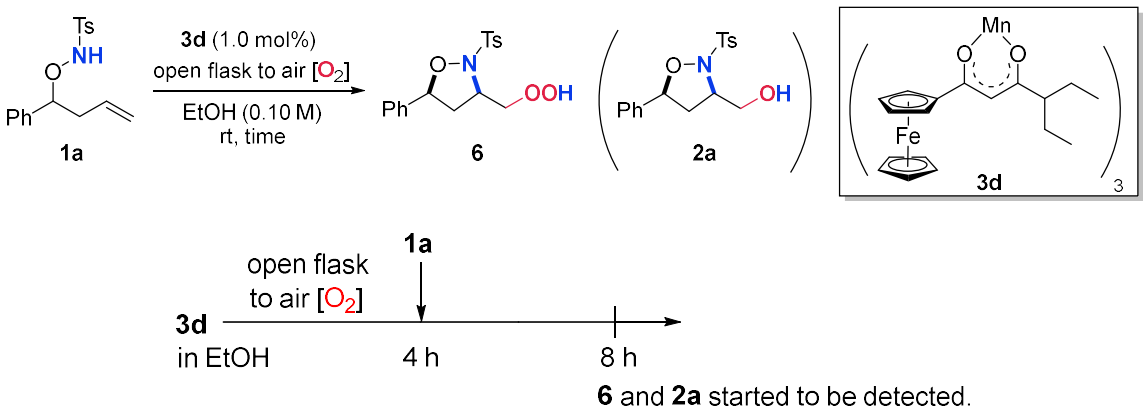
Based on the results of the both kinetic experiments **1-A** and **1-B**, the following two conclusions can be drawn.

1. An incubation time of about 4 h is required to start the reaction under both atmospheric pressure (partial O_2 pressure: 0.2 atm) and oxygen atmosphere (O_2 pressure: 1 atm) conditions.
2. The kinetic profiles of **1-A** and **1-B** are similar under both atmospheric pressure (partial O_2 pressure: 0.2 atm) and oxygen atmosphere (O_2 pressure: 1 atm) conditions, and there is little difference in the reaction rate between different oxygen pressures in this range.

2) Studies on the incubation time

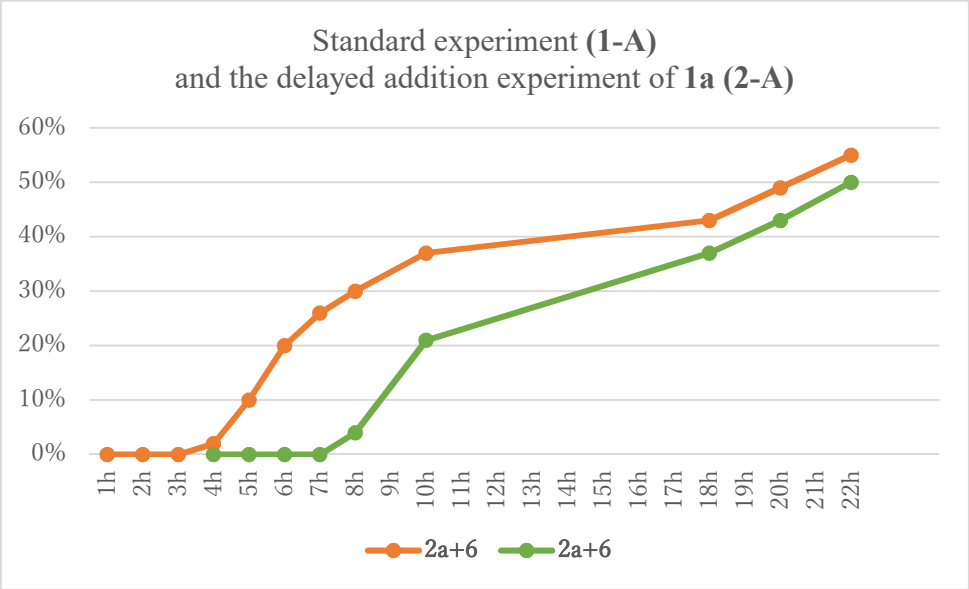
2-A) The delayed addition experiment of 1a

The following control experiments were performed to consider the active Mn(III)-complex generated during the incubation time in this reaction (Scheme S5 and S6).



Scheme S5. The delayed addition experiment of **1a**

A solution of Mn(III)-complex **3d** (3.1 mg, 3.0 μmol) in EtOH (2.70 mL) was stirred under air (open flask). After 4 h, a solution of sulphonamide **1a** (95.2 mg, 0.300 mmol) in EtOH (0.300 mL) was added and stirred under air (open flask). After 1, 2, 3, 4, 6, 14, 16 and 18 h, respectively, 30.0 μL of sample was collected from the reaction mixture by syringe. The sample (30.0 μL) was diluted with 2-propanol to total volume of 1.0 mL. 10.0 μL of the diluted solution was injected into the HPLC column (COSMOSIL Packed Column 5SL-II, ϕ0.46 cm × 25 cm, hexane/*i*-PrOH = 99 : 1, detection at 254 nm, flow rate 1.0 mL/min, t_R = 14.6 min for **6** , 54.0 min for **2a**). As a result, the expected product **6** and **2a** started to be detected in 8 h (Figure S3).



	1 h	2 h	3 h	4 h	5 h	6 h	7 h	8 h	10 h	18 h	20 h	22 h
Standard	0%	0%	0%	2%	10%	20%	26%	30%	37%	43%	49%	55%
Delayed addition	—	—	—	0%	0%	0%	0%	4%	21%	37%	43%	50%

Figure S3[a)]**.** Comparison of the kinetic profiles of the standard experiment (**1-A**) and the delayed addition experiment of **1a** (**2-A**).

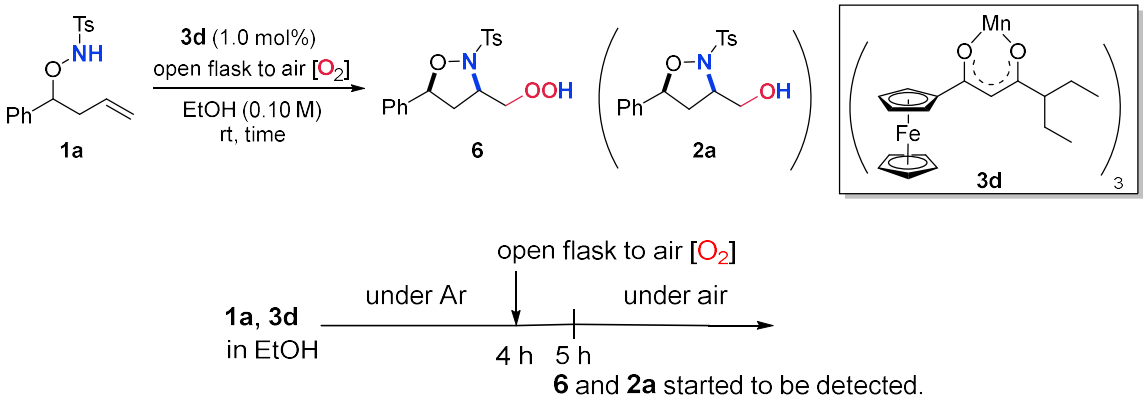
[a)] Peroxide **6** was partially converted to **2a** in HPLC column (normal phase). The yield was estimated by HPLC analysis.

Comparison of the standard experiment (**1-A**) and the delayed addition experiment of **1a** (**2-A**) showed the following result.

- ✓ When a stirred solution of Mn(III)-complex **3d** in EtOH was exposed to oxygen in air for 4 h, and then sulphonamide **1a** was added, another 4 h of incubation time was required before the aminoperoxydation reaction started.

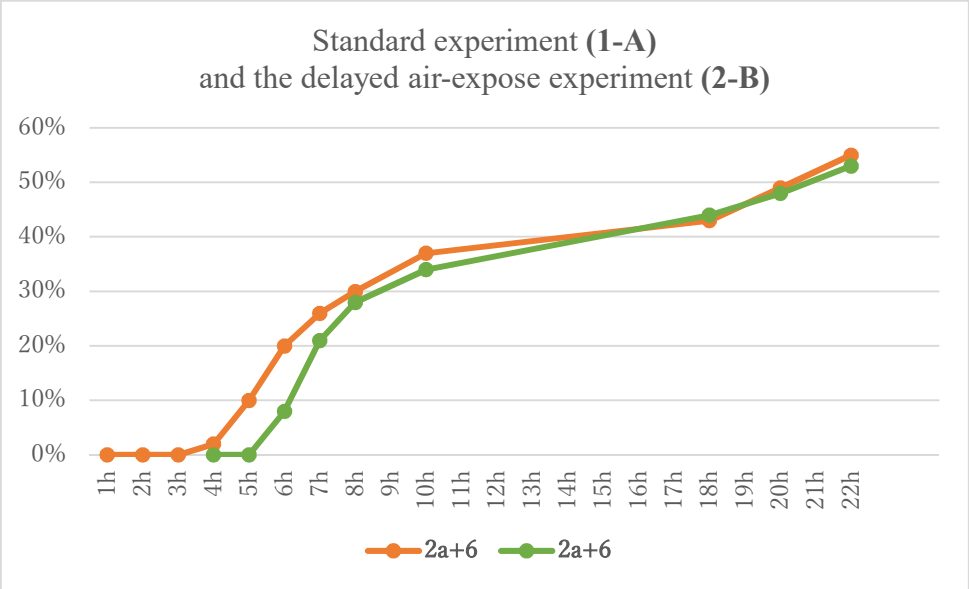
This result suggests that the formation of the true active species of catalyst requires the presence Mn(III)-complex **3d**, oxygen, and substrate **1a**, as well as an incubation time of 4 h.

2-B) Delayed air-expose experiment



Scheme S6. Mn(III)-catalysed aminoperoxidation of **1a**

A solution of sulphonamide **1a** (95.2 mg, 0.300 mmol) and Mn(III)-complex **3d** (3.1 mg, 3.0 μmol) in EtOH (3.0 mL) was stirred under Ar atomosphere. After 4 h, the reaction mixture was opened to air. After 1, 2, 3, 4, 6, 14, 16 and 18 h, respectively, 30.0 μL of sample was collected from the reaction mixture by syringe. The sample (30.0 μL) was diluted with 2-propanol to total volume of 1.0 mL. 10.0 μl of the diluted solution was injected into the HPLC column (COSMOSIL Packed Column 5SL-II (ϕ 0.46 cm × 25 cm), hexane/*i*-PrOH = 99 : 1, detection at 254 nm, flow rate 1.0 mL/min, t_R = 6.8 min (**1a**), 14.6 min (**6**) , 54.0 min (**2a**)). As a result, the expected product **6** and **2a** started to be detected in 5 h (Figure S4).



	1 h	2 h	3 h	4 h	5 h	6 h	7 h	8 h	10 h	18 h	20 h	22 h
Standard	0%	0%	0%	2%	10%	20%	26%	30%	37%	43%	49%	55%
Delayed air-expose	–	–	–	0%	0%	8%	21%	28%	34%	44%	48%	53%

Figure S4[a)]**.** Comparison of the kinetic profiles of the standard experiment (**1-A**) and the delayed air-expose experiment (**2-B**).

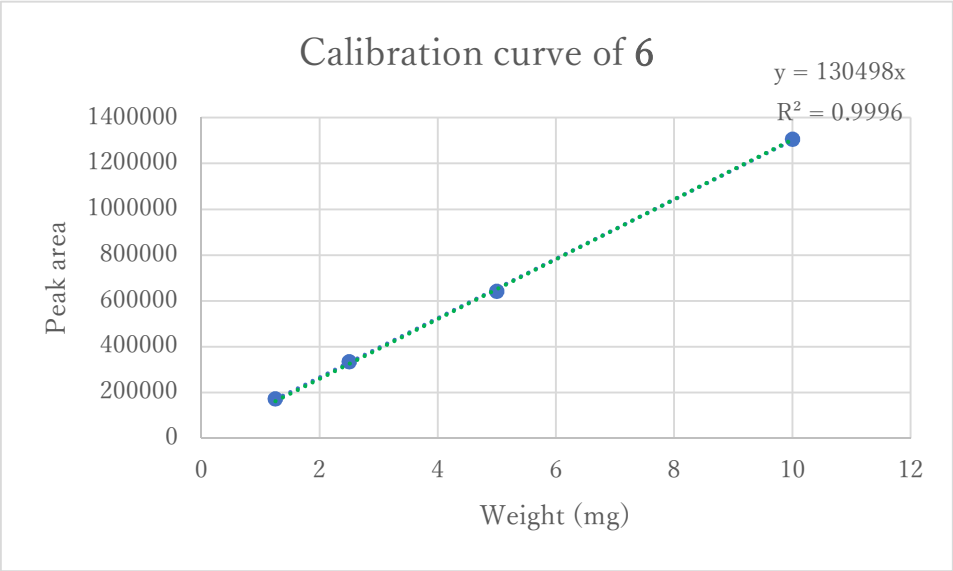
[a)] Peroxide **6** was partially converted to **2a** in HPLC column (normal phase). The yield was estimated by HPLC analysis.

Comparison of the standard experiment (**1-A**) and the delayed air-expose experiment (**2-B**) showed the following result.

✓ When a solution of sulphonamide **1a** and Mn(III)-complex **3d** in EtOH was stirred in the absence of oxygen (under Ar atmosphere), and then exposed to oxygen (under air atmosphere), the progress of the aminoperoxydation reaction was detected within 2 h instead of the usual 4 h.

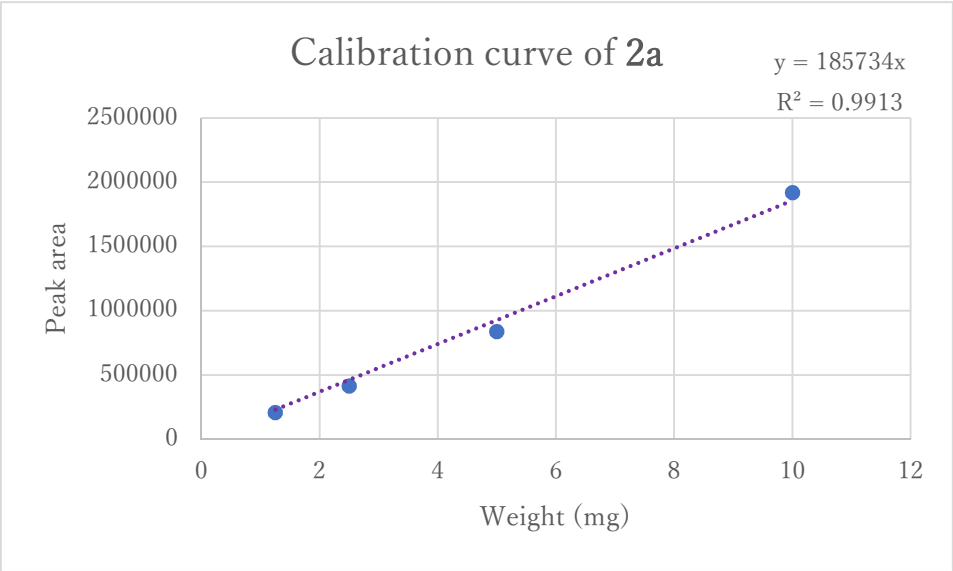
It is noteworthy that the delayed air-expose experiment (**2-B**) does not require an additional 4 hours of incubation time. We assume that the reaction in this experimental condition proceeds through the following reaction mechanism.

1. Stirring a solution of sulphonamide **1a** and Mn(III)-complex **3d** in EtOH under Ar atmosphere caused a ligand exchange reaction between the ligand of **3d** and **1a** to give a new intermediate [**1a**– H^+]•MnL_2 with high coordination ability to oxygen molecules.
2. The intermediate [**1a**– H^+]•MnL_2 coordinated molecular oxygen in air to give [**1a**– H^+]•O_2•MnL_2 complex, which allowed the aminoperoxydation reaction to proceed.



6	1.25 mg	2.50 mg	5.00 mg	10.0 mg
peak area	173243	335711	642363	1306410

Figure S5 Calibration curve of **6**



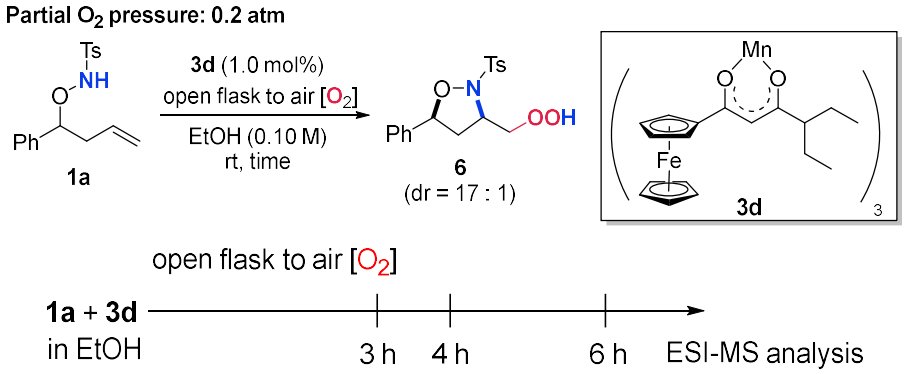
2a	1.25 mg	2.50 mg	5.00 mg	10.0 mg
peak area	208804	413315	837904	1918401

Figure S6 Calibration curve of **2a**

3) Preliminary studies on intermediates by ESI-MS

The search for intermediates derived from Mn(III)-complex **3d** in the reaction mixtures was performed by ESI-MS.

3-A) Detection of intermediates under atmospheric conditions. (Partial O_2 pressure: 0.2 atm)



Scheme S7. Mn(III)-catalysed aminoperoxidation of **1a** using O_2 in air.

To a stirred solution of sulphonamide **1a** (69.7 mg, 0.200 mmol) in EtOH (2.00 mL) at room temperature was added Mn(III)-complex **3d** (2.1 mg, 2.0 μmol) under air (open flask). At 3, 4 and 6 h, respectively, 10.0 μL of sample was collected from the reaction mixture by syringe. The sample (10.0 μL) was diluted with methanol to total volume of 1.0 mL. 10.0 μL of the diluted solution was injected into an ESI-Mass spectrometer (JEOL JMS-T100LP).

The following results were obtained by ESI-MS analysis.

[Results at 3 and 4 h]

- ✓ The molecular ion peak 340.09 derived from stating material **1a** was observed (Figures S7 and S8).

[Results at 6 h]

- ✓ The molecular ion peaks 340.0868 and 372.0756 derived from stating material **1a** and expected product **6** were observed, respectively (Figure S9).
- ✓ The molecular ion peaks 1022.2555 and 1054.2622, which were good agreement with being derived from [**1a**− H^+]•MnL_2 and [**1a**− H^+]•O_2•MnL_2, respectively, were observed along with other molecular ion peaks (Figure S9, enlarged view).

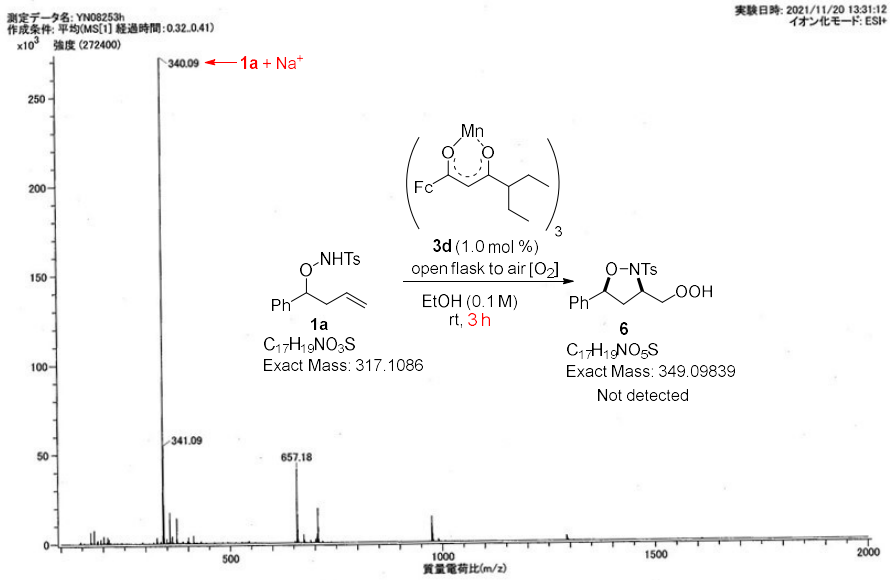


Figure S7 ESI-MS analysis of the reaction mixture at 3 h.

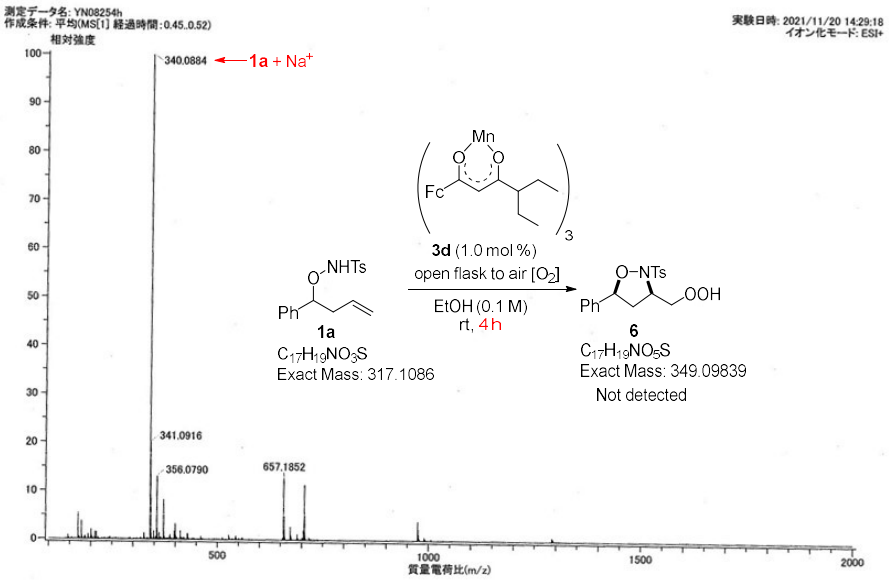


Figure S8 ESI-MS analysis of the reaction mixture at 4 h under air.

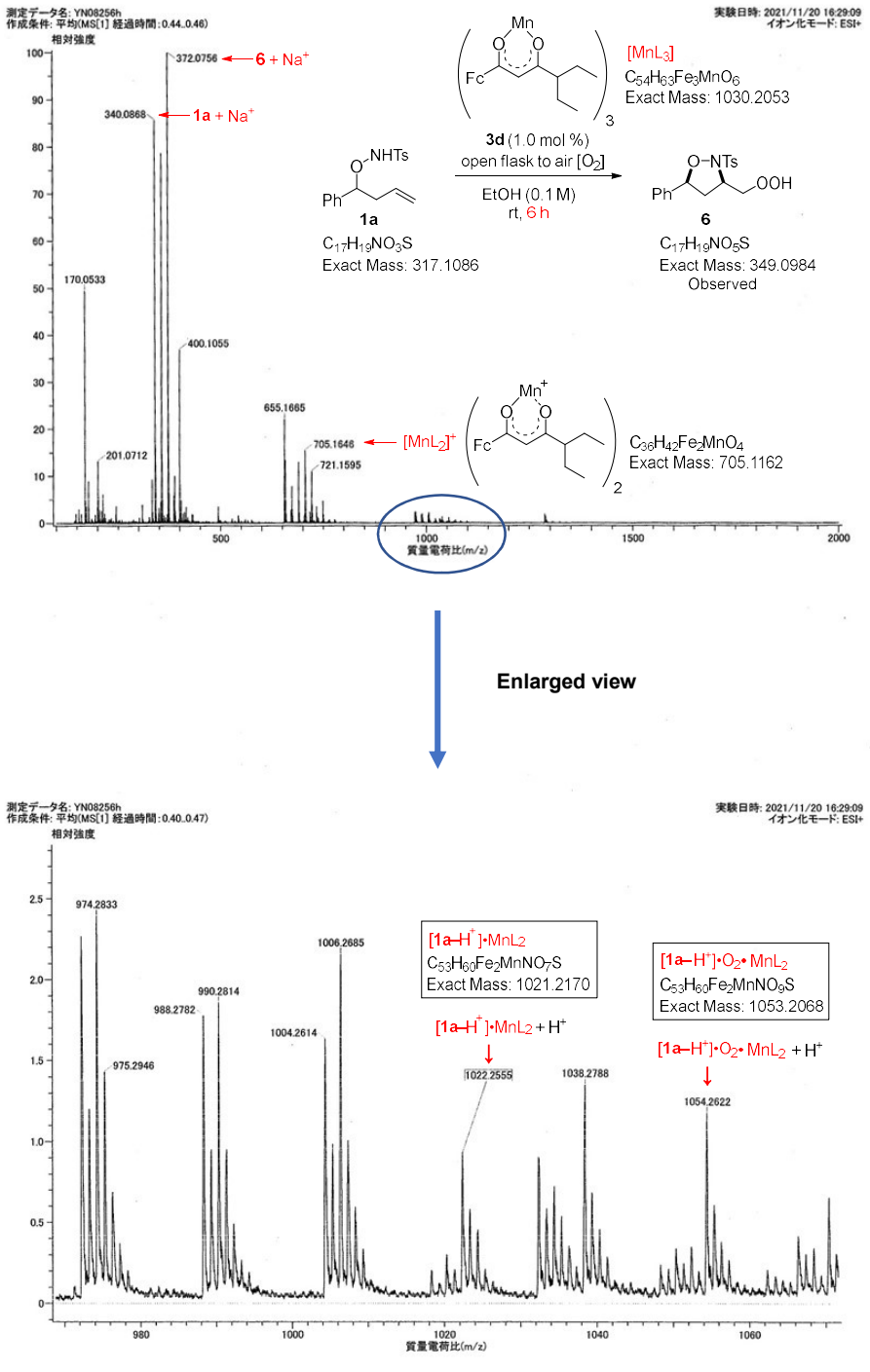
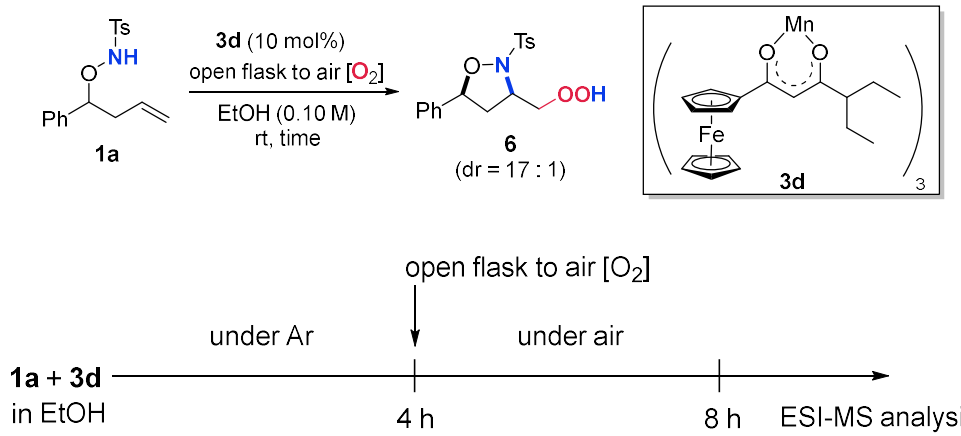


Figure S9 ESI-MS analysis of the reaction mixture at 6 h under air.

3-B) Delayed air-expose experiment



Scheme S8 Mn(III)-catalysed aminoperoxidation of **1a**

A solution of sulphonamide **1a** (95.2 mg, 0.300 mmol) and Mn(III)-complex **3d** (30.9 mg, 30.0 μmol) in EtOH (3.0 mL) was stirred under Ar atomosphere. After 4 h, the reaction mixture was opened to air. At 4, 8 h, respectively, 10.0 μL of sample was collected from the reaction mixture by syringe. The sample (10.0 μL) was diluted with methanol to total volume of 1.0 mL. 10.0 μL of the diluted solution was injected into an ESI-Mass spectrometer (JEOL JMS-T100LP).

The following results were obtained by ESI-MS analysis.

[Results at 4 h]

- ✓ The molecular ion peak 340.0924 derived from stating material **1a** was observed (Figure S10).
- ✓ The molecular ion peak 705.0992 and 1022.2107, which were good agreement with being derived from $[MnL_2]^+$ and $[\mathbf{1a}-H^+]\bullet MnL_2$, respectively, were observed (Figure S10, enlarged view).

[Results at 8 h]

- ✓ The molecular ion peaks 340.0941 and 372.0843 derived from stating material **1a** and expected product **6** were observed, respectively (Figure S11).
- ✓ The molecular ion peaks 1022.1988 and 1054.1997, which were good agreement with being derived from $[\mathbf{1a}-H^+]\bullet MnL_2$ and $[\mathbf{1a}-H^+]\bullet O_2\bullet MnL_2$, respectively, were observed (Figure S11, enlarged view).

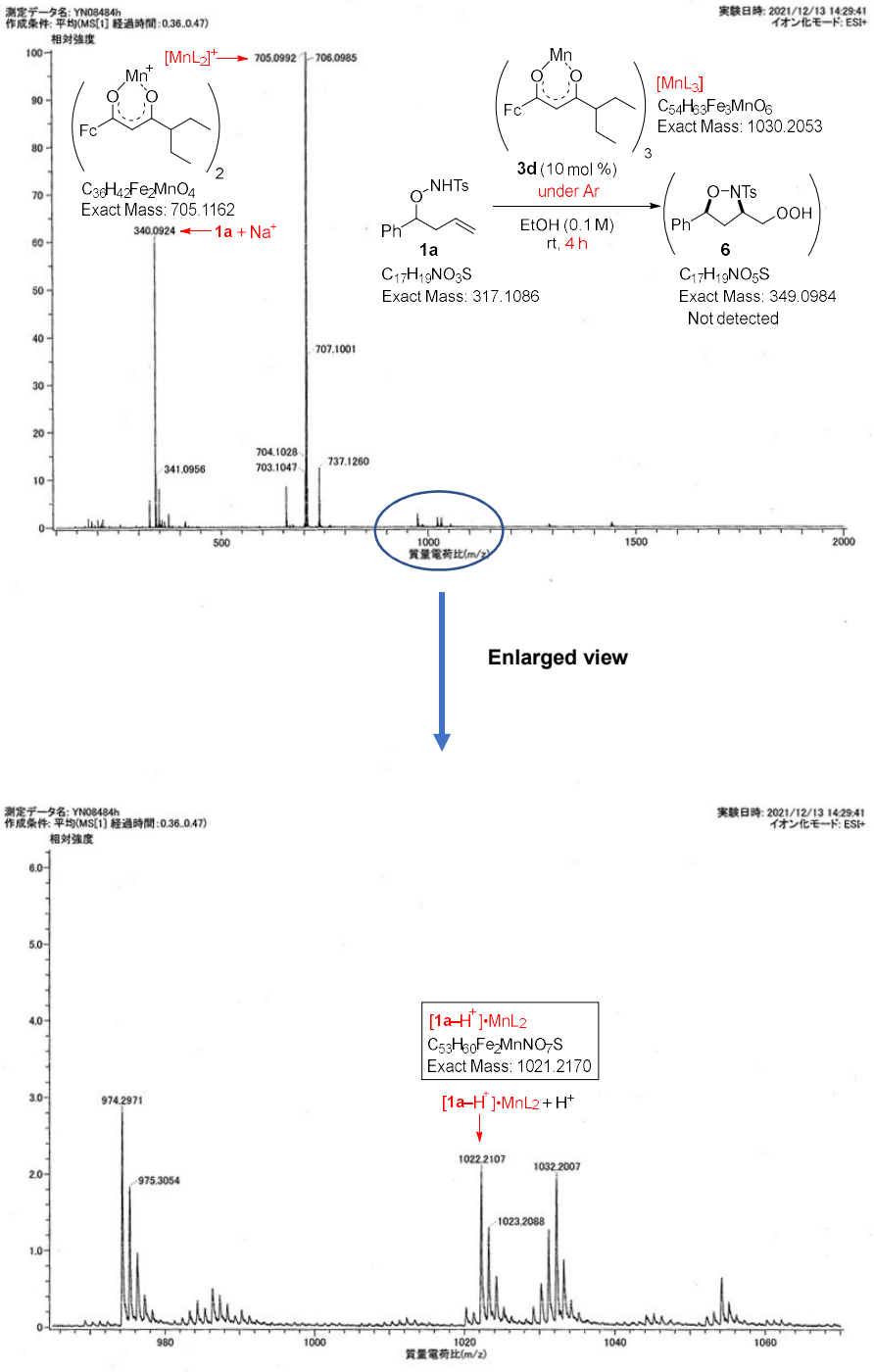


Figure S10 ESI-MS analysis of the reaction mixture at 4 h under Ar.

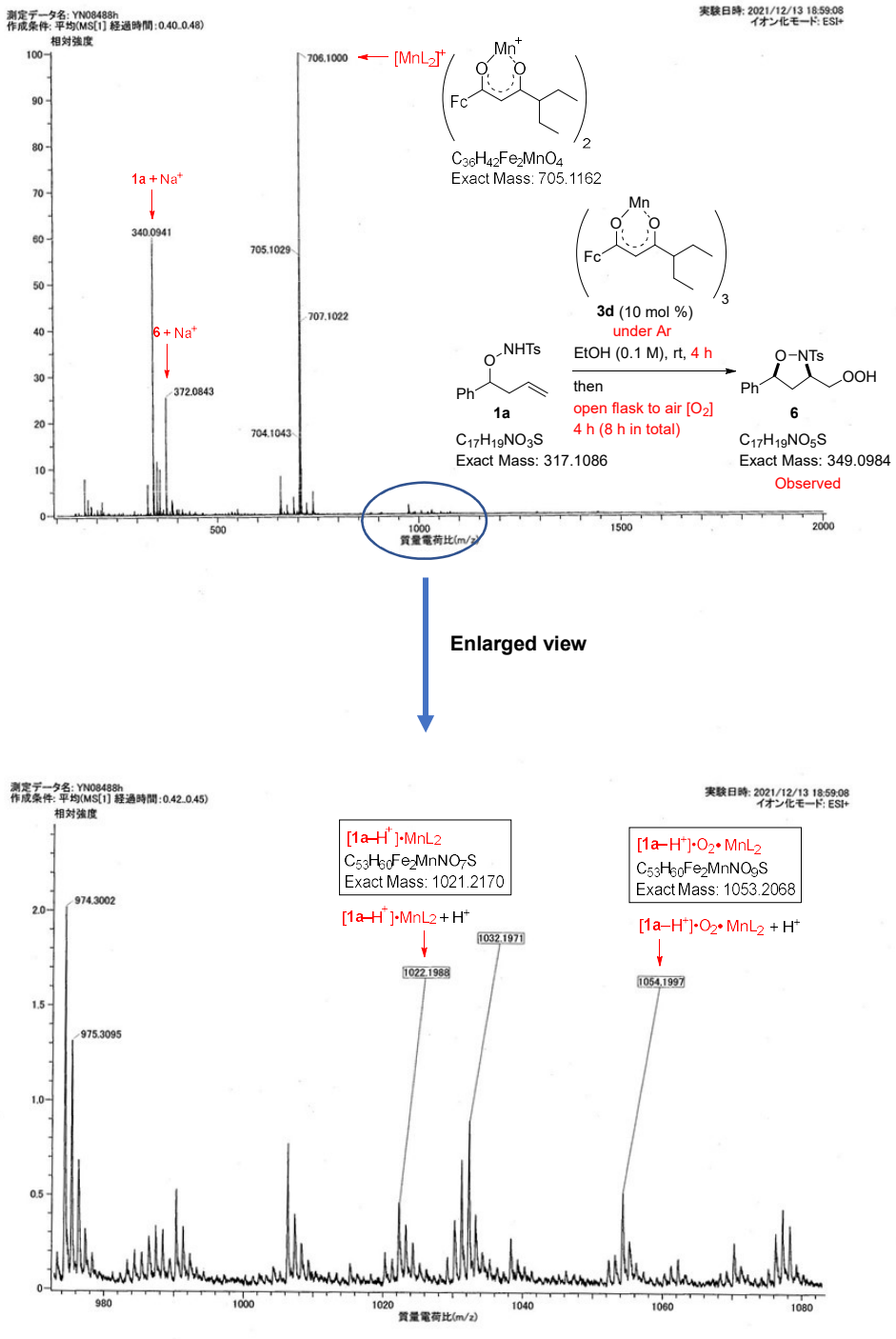


Figure S11 ESI-MS analysis of the reaction mixture at 8 h in delayed air-expose experiment (4 h under Ar and then additional 4 h under air).

4) A possible mechanistic pathway

Based on the results of the standard experiment (**1-A**), the delayed addition experiment of **1a** (**2-A**), the delayed air-expose experiment (**2-B**), and detection of intermediates by ESI-MS (**3-A**, **B**), we hypothesized the following possible mechanism for this aminoperoxide reaction. (Figure S12). The reaction could be initiated via a ligand exchange of Mn(III)-complex **3d** with sulphonamide **1a** to generate intermediate [**I**]. Thereafter, the coordination of molecular oxygen present in air occurs, forming intermediate [**II**]. Furthermore, an isoxazolidine ring was formed via radical process, giving intermediate [**III**]. Finally, a ligand exchange of intermediate [**III**] with sulphonamide **1a** produced the desired hydroperoxide **6** and regenerated intermediate [**I**] for the next catalytic cycle. Further investigations to clarify the key active Mn(III)-complex are currently ongoing in our laboratory. [2]

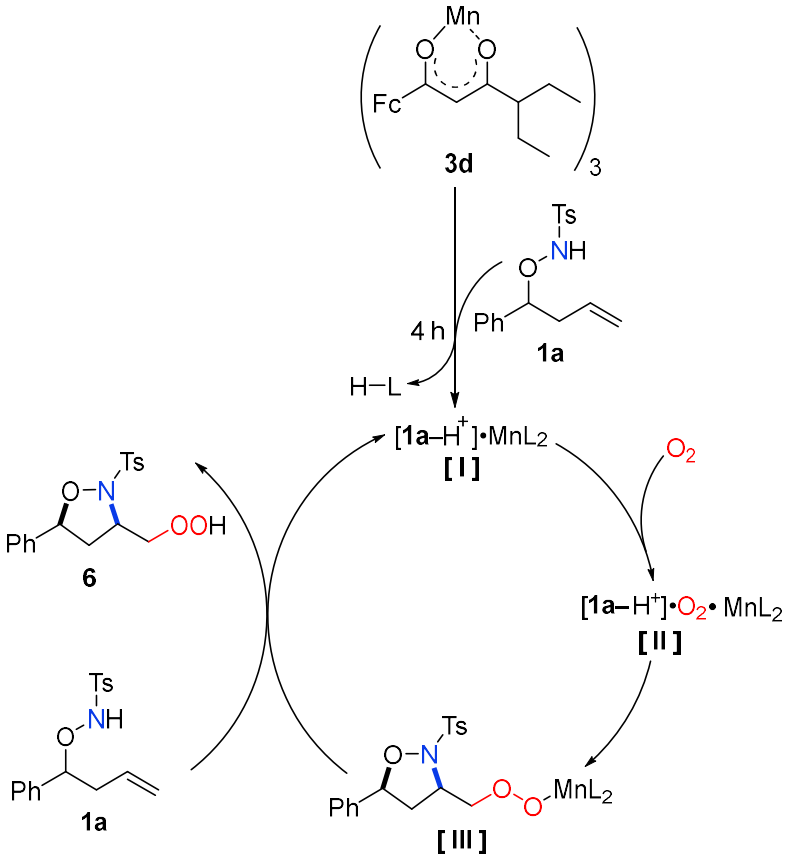
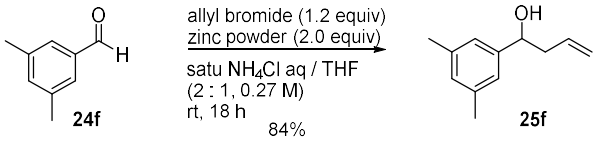


Figure S12 A possible mechanistic pathway.

III. Experimental procedures and characterization data

1. Preparation of the alcohols 25f, 25o and 25q

1-(3,5-dimethylphenyl)but-3-en-1-ol (**25f**)

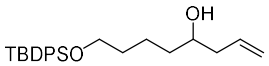


(Representative procedure[3])

To a stirred solution of 3,5-dimethylbenzaldehyde (**24f**) (3.00 g, 22.4 mmol) and allyl bromide (3.25 g, 26.9 mmol) in THF (28.0 mL) at room temperature were added zinc powder (2.93 g, 44.8 mmol) and saturated aqueous NH_4Cl solution (56.0 mL). After stirred for 18 h, the resulting mixture was diluted with water, extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layer was washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 10 : 1) to give alcohol **25f** (3.33 g, 18.9 mmol, 84% yield) as colorless oil.

TLC Rf = 0.37 (hexane / ethyl acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 6.98 (s, 2H), 6.92 (s, 1H), 5.88-5.77 (m, 1H), 5.21-5.15 (m, 1H), 5.16-5.13 (m, 1H), 4.67 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.56-2.44 (m, 2H), 2.32 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 144.0, 138.1, 134.9, 129.3, 123.7, 118.4, 73.5, 43.9, 21.5; IR (neat) 3374, 2978, 2732, 1736, 1461, 1346, 1209, 1055, 958, 804, 636, 504 cm^{-1}; HRMS (FAB, NBA) *m*/*z* calcd for $C_{12}H_{16}ONa$ $[M+Na]^+$ 199.1099 found 199.1105.

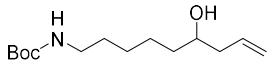
8-((*tert*-butyldiphenylsilyl)oxy)oct-1-en-4-ol (**25o**)



According to the representative procedure, the reaction gave **25o** (3.26 g, 8.51 mmol, 74% yield) as colorless oil from the corresponding aldehyde[4] (3.90 g, 11.5 mmol).

TLC Rf = 0.42 (hexane / ethyl acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.68-7.66 (m, 4H), 7.44-7.35 (m, 6H), 5.88-5.77 (m, 1H), 5.16-5.10 (m, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.64-3.59 (m, 1H), 2.32-2.25 (m, 1H), 2.16-2.08 (m, 1H), 1.63-1.38 (m, 6H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 135.7, 135.0, 134.2, 129.6, 127.7, 118.2, 70.7, 63.9, 42.0, 36.6, 32.6, 27.0, 22.0, 19.3; IR (neat) 3372, 3071, 2931, 2857, 1640, 1472, 1428, 1111, 997, 915, 823, 740, 701, 614, 503 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{34}NaO_2Si$ $[M+Na]^+$ 405.2226 found 405.2215.

tert-butyl (6-hydroxynon-8-en-1-yl)carbamate (**25q**)

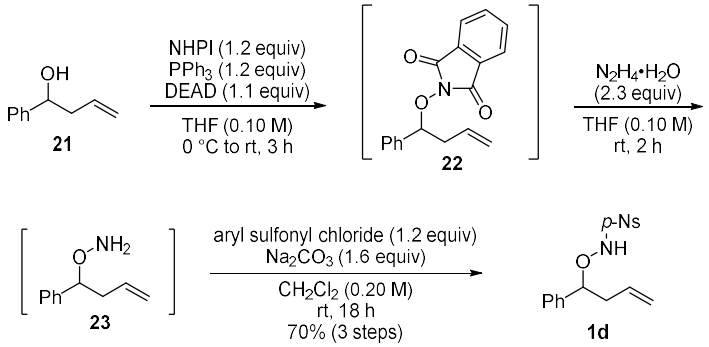


According to the representative procedure, the reaction gave **25q** (1.14 g, 4.42 mmol, 95% yield) as a yellow solid from the corresponding aldehyde[5] (860 mg, 4.65 mmol).

M.p. 41.5-43.2 ˚C; TLC Rf = 0.45 (hexane / ethyl acetate = 1 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.88-5.77 (m, 1H), 5.16-5.14 (m, 1H), 5.13-5.10 (m, 1H), 4.50 (br s, 1H), 3.67-3.61 (m, 1H), 3.14-3.08 (m, 2H), 2.33-2.26 (m, 1H), 2.18-2.10 (m, 1H), 1.50-1.44 (m, 15H), 1.40-1.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ :156.2, 135.0, 118.2, 79.2, 70.6, 42.1, 40.6, 36.8, 30.2, 28.6, 26.8, 25.4; IR (KBr) 3377, 2980, 2931, 2853, 1682, 1640, 1519, 1462, 1369, 1317, 1278, 1178, 1131, 1028, 1000, 966, 910, 873, 784, 717, 605 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{27}NNaO_3$ $[M+Na]^+$ 280.1889 found 280.1884.

2. Preparation of the substrates 1a–e and 4a–u

4-nitro-*N*-((1-phenylbut-3-en-1-yl)oxy)benzenesulphonamide (**1d**)



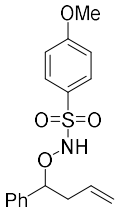
(Representative procedure[6])

A solution of diethyl azodicarboxylate (2.72 mL, 6.00 mmol, 40% in toluene, *ca*. 2.2 M) was added dropwise to a stirred solution of the alcohol **21** (740 mg, 5.00 mmol), triphenylphosphine (1.58 g, 6.00 mmol) and *N*-hydroxyphthalimide (0.978 g, 6.00 mmol) in THF (50.0 mL) under N_2 atmosphere at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h, and then hydrazine monohydrate (0.559 mL, 11.5 mmol) was added dropwise. After 2 h, the mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure to afford the corresponding amine **23**, which was directly used without further purification. A solution of the 4-nitrobenzensulphonyl chloride (1.33 g, 6.00 mmol) in CH_2Cl_2 (10.0 mL) was added dropwise over 15 min to a stirred suspension of crude amine **23** and Na_2CO_3 (0.954 g, 9.00 mmol) in CH_2Cl_2 (15.0 mL). The resulting mixture was stirred at room temperature for 18 h, monitoring the conversion by TLC analysis. The reaction was quenched by addition of water. The resulting mixture was extracted

with CH_2Cl_2 (3 x 20 mL) and the combined organic layer was washed with water (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 15 : 1 to 5 : 1) to give sulphonamide **1d** (1.22 g 3.51 mmol, 70% yield (3 steps)) as a white solid.
TLC Rf = 0.26 (hexane / ethyl acetate = 5 : 1); M.p. 124.9-128.7 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.37 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.11 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.38-7.31 (m, 3H), 7.29-7.24 (m, 2H), 6.82 (s, 1H, -NH), 5.84-5.74 (m, 1H), 5.14-5.05 (m, 3H), 2.68-2.61 (m, 1H), 2.53-2.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.4, 139.2, 133.7, 130.1, 128.70, 128.68, 127.2, 124.2, 118.1, 88.8, 39.8; IR (KBr) 3321, 3235, 3103, 1527, 1349, 1300, 1170, 1088, 849, 752, 702 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{15}N_2O_5S$ $[M-H]^-$ 347.0702 found 374.0685.

1a was prepared by a known procedure[7].

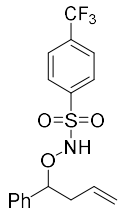
4-methoxy-*N*-((1-phenylbut-3-en-1-yl)oxy)benzenesulphonamide (**1b**)



According to the representative procedure, the reaction gave **1b** (766 mg, 2.30 mmol, 46% yield) as a white solid from the corresponding alcohol (740 mg, 5.00 mmol) and 4-methoxybenzenesulphonyl chloride (1.24 g, 6.00 mmol).

TLC Rf = 0.50 (hexane / ethyl acetate = 5 : 1); M.p. 126.4-136.2 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.86 (d, *J* = 8.8 Hz, 2H), 7.36-7.25 (m, 5H), 6.99 (d, *J* = 9.2 Hz, 2H), 6.63 (s, 1H, -N<u>H</u>), 5.81-5.71 (m, 1H), 5.10-5.06 (m, 2H), 5.01 (dd, *J* = 7.6, 6.4 Hz, 1H), 3.89 (s, 3H), 2.68-2.60 (m, 1H), 2.50-2.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 163.9, 139.8, 133.9, 131.0, 128.5, 128.4, 128.3, 127.3, 117.7, 114.3, 88.1, 55.8, 39.8; IR (KBr) 3213, 1596, 1497, 1327, 1269, 1153, 1091, 1020, 910, 825, 807, 740, 701, 557 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{19}NNaO_4S$ $[M+Na]^+$ 356.0932 found 356.0926.

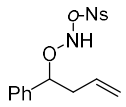
N-((1-phenylbut-3-en-1-yl)oxy)-4-(trifluoromethyl)benzenesulphonamide (**1c**)



According to the representative procedure, the reaction gave **1c** (928 mg, 2.50 mmol, 50% yield) as a white solid from the corresponding alcohol (740 mg, 5.00 mmol) and 4-(trifluoromethyl)benzenesulphonyl chloride (1.47 g, 6.00 mmol).

TLC Rf = 0.23 (hexane / ethyl acetate = 5 : 1); M.p. 116.3-119.9 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.05 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.37-7.25 (m, 5H), 6.79 (s, 1H, -NH), 5.83-5.73 (m, 1H), 5.13-5.08 (m, 2H), 5.06 (dd, *J* = 8.0, 6.0 Hz), 2.69-2.61 (m, 1H), 2.52-2.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 140.3 (q, $^{4}J_{F-C}$ = 1 Hz), 139.4, 135.5 (q, $^{2}J_{F-C}$ = 33 Hz), 133.8, 129.4, 128.7, 128.6, 127.3, 126.2 (q, $^{3}J_{F-C}$ = 4 Hz), 123.3 (q, $^{1}J_{F-C}$ = 271 Hz), 118.0, 88.6, 39.8; IR (KBr) 3224, 1408, 1328, 1169, 1123, 1092, 1064, 1017, 919, 840, 790, 740, 700, 595 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{15}F_3NO_3S$ $[M-H]^-$ 370.0725 found 370.0714.

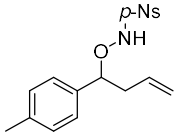
2-nitro-*N*-((1-phenylbut-3-en-1-yl)oxy)benzenesulphonamide (**1e**)



According to the representative procedure, the reaction gave **1e** (958 mg, 2.75 mmol, 55% yield) as a yellow solid from the corresponding alcohol (740 mg, 5.00 mmol) and 2-nitrobenzensulphonyl chloride (1.33 g, 6.00 mmol).

TLC Rf = 0.35 (hexane / ethyl acetate = 3 : 1); M.p. 93.8-100.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.24-8.22 (m, 1H), 7.90-7.88 (m, 1H), 7.83-7.76 (m, 2H), 7.40-7.29 (m, 5H), 5.82-5.72 (m, 1H), 5.14 (dd, *J* = 8.0, 6.0 Hz, 1H), 5.09-5.04 (m, 2H), 2.68-2.60 (m, 1H), 2.52-2.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 148.6, 139.4, 134.9,134.1, 133.8, 132.8, 130.6, 128.7, 128.6, 127.3, 125.6, 117.9, 88.5, 39.7; IR (KBr) 3261, 3042, 2936, 1644, 1537, 1494, 1441, 1407, 1357, 1174, 1121, 1003, 924, 854, 791, 747, 699, 655, 611, 579, 518; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{15}N_2O_5S$ $[M-H]^-$ 347.0702 found 374.0706.

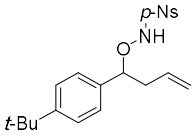
4-nitro-*N*-((1-(*p*-tolyl)but-3-en-1-yl)oxy)benzenesulphonamide (**4a**)



According to the representative procedure, the reaction gave **4a** (724 mg, 2.00 mmol, 40% yield) as a white solid from the corresponding alcohol (811 mg, 5.00 mmol).

TLC Rf = 0.16 (hexane / ethyl acetate = 2 : 1); M.p. 142.9-148.2 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.36 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.10 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.15 (br s, 4H), 6.79 (s, 1H, -NH), 5.83-5.73 (m, 1H), 5.13-5.09 (m, 2H), 5.03 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.68-2.60 (m, 1H), 2.51-2.44 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.5, 138.6, 136.1, 133.9, 130.2, 129.4, 127.3, 124.2, 118.0, 88.6, 39.6, 21.3; IR (KBr) 3248, 3094, 1529, 1351, 1172, 1088, 928, 858, 816, 753, 702, 602 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{17}N_2O_5S$ $[M-H]^-$ 361.0858 found 361.0843.

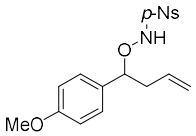
N-((1-(4-(*tert*-butyl)phenyl)but-3-en-1-yl)oxy)-4-nitrobenzenesulphonamide (**4b**)



According to the representative procedure, the reaction gave **4b** (606 mg, 1.50 mmol, 30% yield) as a white solid from the corresponding alcohol (1.02 g, 5.00 mmol).

TLC Rf = 0.75 (hexane / ethyl acetate = 2 : 1); M.p. 128.0-134.5 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.37 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.12 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.36 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.19 (dt, *J* = 8.8, 2.0 Hz, 2H), 6.78 (s, 1H, -NH), 5.87-5.76 (m, 1H), 5.16-5.11 (m, 2H), 5.06-5.03 (m, 1H), 2.67-2.60 (m, 1H), 2.53-2.45 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl3) δ : 151.8, 150.9, 142.6, 136.0, 134.1, 130.2, 127.0, 125.7, 124.3, 117.9, 88.7, 39.6, 34.8, 31.4; IR (KBr) 3234, 2961, 1533, 1406, 1348, 1312, 1174, 853, 761, 697, 589 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{20}H_{24}N_2NaO_5S$ $[M+Na]^+$ 427.1304 found 427.1301.

N-((1-(4-methoxyphenyl)but-3-en-1-yl)oxy)-4-nitrobenzenesulphonamide (**4c**)

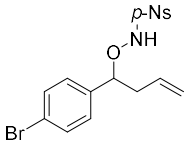


According to the representative procedure, the reaction gave **4c** (907 mg, 2.40 mmol, 48% yield) as a yellow solid from the corresponding alcohol (891 mg, 5.00 mmol).

TLC Rf = 0.68 (hexane / ethyl acetate = 2 : 1); M.p. 130.4-136.6 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.35 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.09 (dt, *J* = 9.2, 2.0 Hz, 2H), 7.21-7.18 (m, 2H), 6.87-6.85 (m, 2H), 6.80 (s, 1H, -NH), 5.82-5.72 (m, 1H), 5.14-5.08 (m, 2H), 5.01 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.80 (s, 3H),

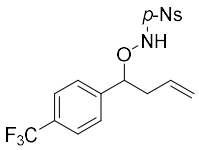
2.70-2.62 (m, 1H), 2.51-2.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 160.0, 150.9, 142.6, 133.9, 131.0, 130.2, 128.8, 124.3, 118.0, 114.1, 88.4, 55.4, 39.4; IR (KBr) 3243, 3102, 1614, 1530, 1353, 1170, 755, 705, 631, 591 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{17}N_2O_6S$ $[M-H]^-$ 377.0807 found 377.0790.

N-((1-(4-bromophenyl)but-3-en-1-yl)oxy)-4-nitrobenzenesulphonamide (**4d**)



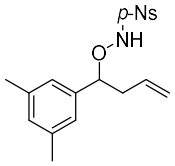
According to the representative procedure, the reaction gave **4d** (1.06 g, 2.50 mmol, 50% yield) as a white solid from the corresponding alcohol (1.13 g, 5.00 mmol).
TLC Rf = 0.63 (hexane / ethyl acetate = 2 : 1); M.p. 144.3-147.7 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.10 (dt, *J* = 9.2, 2.0 Hz, 2H), 7.48 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.14 (dt, *J* = 8.8, 2.0 Hz, 2H), 6.80 (s, 1H, -NH), 5.80-5.70 (m, 1H), 5.15-5.08 (m, 2H), 5.05 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.67-2.59 (m, 1H), 2.50-2.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.3, 138.2, 133.2, 131.9, 130.2, 129.0, 124.3, 122.8, 118.5, 88.1, 39.6; IR (KBr) 3247, 3099, 1528, 1415, 1351, 1317, 1173, 1084, 858, 818, 754, 706 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{14}BrN_2O_5S$ $[M-H]^-$ 424.9807 found 424.9794.

4-nitro-*N*-((1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)oxy)benzenesulphonamide (**4e**)



According to the representative procedure, the reaction gave **4e** (1.06 g, 2.55 mmol, 51% yield) as a white solid from the corresponding alcohol (1.08 g, 5.00 mmol).
TLC Rf = 0.63 (hexane / ethyl acetate = 2 : 1); M.p. 131.7-134.0 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.39 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.12 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H, -NH), 5.82-5.72 (m, 1H), 5.19-5.09 (m, 3H), 2.68-2.60 (m, 1H), 2.53-2.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.1, 143.20-143.19 (m), 142.3, 133.0, 131.3 (q, $^2J_{F-C}$ = 33 Hz, 1H), 130.2, 127.6, 125.8 (q, $^3J_{F-C}$ = 4 Hz, 1H), 124.4, 124.0 (q, $^1J_{F-C}$ = 271 Hz, 1H), 118.8, 88.2, 39.7; IR (KBr) 3250, 3119, 1608, 1525, 1326, 1186, 1134, 1067, 1010, 928, 857, 741, 684, 639, 590 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{14}F_3N_2O_5S$ $[M-H]^-$ 415.0576 found 415.0566.

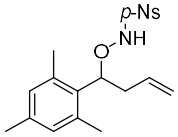
N-((1-(3,5-dimethylphenyl)but-3-en-1-yl)oxy)-4-nitrobenzenesulphonamide (**4f**)



According to the representative procedure, the reaction gave **4f** (1.37 g, 3.65 mmol, 73% yield) as a white solid from the corresponding alcohol (881 mg, 5.00 mmol).

TLC Rf = 0.45 (hexane / ethyl acetate = 3 : 1); M.p. 73.6-77.8 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.36 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.12 (dt, *J* = 8.8, 2.0 Hz, 2H), 6.95 (s, 1H), 6.86 (s, 2H), 6.80 (s, 1H, -NH), 5.85-5.75 (m, 1H), 5.14 (t, *J* = 1.2 Hz, 1H), 5.12-5.10 (m, 1H) 4.98 (dd, *J* = 8.4, 5.6 Hz, 1H), 2.64-2.56 (m, 1H), 2.49-2.42 (m, 1H) , 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.8, 142.4, 137.8, 134.3, 131.9, 130.1 x 2, 124.18, 124.17, 117.8, 85.9, 37.6, 20.9; IR (KBr) 3449, 2914, 1560, 1403, 1174, 925, 694 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{19}N_2O_5S$ $[M-H]^-$ 375.1015 found 375.1009.

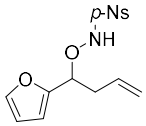
N-((1-mesitylbut-3-en-1-yl)oxy)-4-nitrobenzenesulphonamide (**4g**)



According to the representative procedure, the reaction gave **4g** (1.21 g, 3.10 mmol, 62% yield) as a white solid from the corresponding alcohol (951 mg, 5.00 mmol).

TLC Rf = 0.33 (hexane / ethyl acetate = 3 : 1); M.p. 109.3-117.6 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.34 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.08 (dt, *J* = 9.2, 2.0 Hz, 2H), 6.91 (s, 1H, -NH), 6.80 (s, 2H), 5.85-5.74 (m, 1H), 5.56 (dd, *J* = 8.4, 6.0 Hz, 1H), 5.15-5.10 (m, 2H), 2.82-2.74 (m, 1H), 2.53-2.46 (m, 1H), 2.28 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.5, 139.2, 138.3, 134.1, 130.3, 130.2, 125.0, 124.2, 117.9, 88.9, 39.9, 21.4 x 2; IR (KBr) 3230, 1642, 1405, 1174, 921, 684 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{22}N_2NaO_5S$ $[M+Na]^+$ 413.1147 found 413.1134.

N-((1-(furan-2-yl)but-3-en-1-yl)oxy)-4-nitrobenzenesulphonamide (**4h**)

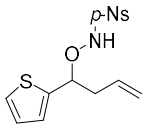


According to the representative procedure, the reaction gave **4h** (473 mg, 1.40 mmol, 28% yield) as a white solid from the corresponding alcohol (690 mg, 5.00 mmol).

TLC Rf = 0.25 (hexane / ethyl acetate = 5 : 1); M.p. 143.3-145.0 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.36 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.11 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.40 (dd, *J* =1.6, 0.8 Hz 1H), 6.92 (s, 1H, -NH), 6.42 (d, *J* = 3.2 Hz, 1H), 6.36 (dd, *J* = 3.2, 2.0 Hz 1H), 5.83-5.72 (m, 1H), 5.18-5.12 (m, 2H),

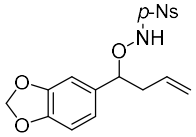
5.08 (t, *J* = 7.2 Hz, 1H), 2.79-2.71 (m, 1H), 2.68-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.3, 150.9, 143.3, 142.4, 133.1, 130.2, 124.3, 118.4, 110.6, 110.5, 81.2, 36.1; IR (KBr) 3232, 1525, 1349, 1170, 1087, 1011, 933, 855, 754, 596 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}N_2O_6S$ $[M-H]^-$ 337.0494 found 337.0492.

4-nitro-*N*-((1-(thiophen-2-yl)but-3-en-1-yl)oxy)benzenesulphonamide (**4i**)



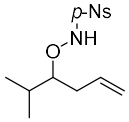
According to the representative procedure, the reaction gave **4i** (443 mg, 1.25 mmol, 25% yield) as a white solid from the corresponding alcohol (770 mg, 5.00 mmol).
TLC Rf = 0.32 (hexane / ethyl acetate = 5 : 1); M.p. 138.3-140.3 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.37 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.12 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.32 (ddd, *J* = 5.2, 1.2, 0.4 Hz, 1H), 7.09 (ddd, *J* = 3.6, 1.2, 0.4 Hz, 1H), 7.00 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.88 (s, 1H, -NH), 5.87-5.76 (m, 1H), 5.32 (dd, *J* = 7.6, 6.4 Hz, 1H), 5.19-5.14 (m, 2H), 2.79-2.71 (m, 1H), 2.66-2.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.4, 141.7, 133.3, 130.2, 127.6, 127.0, 126.4, 124.3, 118.5, 83.9, 39.7; IR (KBr) 3241, 1525, 1342, 1310, 1168, 1087, 936, 855, 816, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}N_2O_5S_2$ $[M-H]^-$ 353.0266 found 353.0274.

N-((1-(benzo[d][1,3]dioxol-5-yl)but-3-en-1-yl)oxy)-4-nitrobenzenesulfonamide (**4j**)



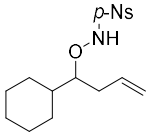
According to the representative procedure, the reaction gave **4j** (863 mg, 2.20 mmol, 73% yield) as a white solid from the corresponding alcohol (577 mg, 3.00 mmol).
TLC Rf = 0.50 (hexane / ethyl acetate = 2 : 1); M.p. 133.7-138.0 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.37 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.10 (dt, *J* = 8.8, 2.0 Hz, 2H), 6.84 (s, 1H, -NH), 6.78-6.73 (m, 2H), 6.709-6.706 (m, 1H), 5.96 (br s, 2H), 5.81-5.71 (m, 1H), 5.13-5.09 (m, 2H), 4.96 (dd, *J* = 8.0, 6.4Hz, 1H), 2.61 (dt, *J* = 14.4, 8.0 Hz, 1H), 2.47-2.40 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ : 150.9, 148.1, 148.0, 142.5, 133.7, 132.9, 130.2, 124.3, 121.5, 118.2, 108.4, 107.3, 101.4, 88.6, 39.6; IR (KBr) 3219, 2904, 2784, 1604, 1528, 1489, 1446, 1350, 1317, 1245, 1174, 1088, 1041, 926, 864, 818, 745, 686 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}N_2O_7S$ $[M-H]^+$ 391.0600 found 391.0600.

N-((2-methylhex-5-en-3-yl)oxy)-4-nitrobenzenesulphonamide (**4k**)



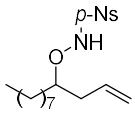
According to the representative procedure, the reaction gave **4k** (565 mg, 1.80 mmol, 36% yield) as a white solid from the corresponding alcohol (571 mg, 5.00 mmol).
TLC Rf = 0.36 (hexane / ethyl acetate = 5 : 1); M.p. 100.9-102.8 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.39 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.14 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.01 (s, 1H, -NH), 5.89-5.78 (m, 1H), 5.13-5.12 (m, 1H), 5.09-5.08 (m, 1H), 3.97 (dt, *J* = 6.8, 4.8 Hz, 1H), 2.41-2.35 (m, 1H), 2.30-2.23 (m, 1H), 2.05-1.97 (m, 1H), 0.90 (d, *J* = 6.8Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.7, 134.9, 130.2, 124.3, 117.5, 91.4, 33.6, 29.3, 18.3, 17.8; IR (KBr) 3242, 2970, 1529, 1351, 1172, 1089, 1013, 922, 859, 603 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}N_2O_5S$ $[M-H]^-$ 313.0858 found 313.0823.

N-((1-cyclohexylbut-3-en-1-yl)oxy)-4-nitrobenzenesulphonamide (**4l**)



According to the representative procedure, the reaction gave **4l** (567 mg, 1.60 mmol, 32% yield) as a white solid from the corresponding alcohol (771 mg, 5.00 mmol).
TLC Rf = 0.43 (hexane / ethyl acetate = 5 : 1); M.p. 121.7-124.4 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.39 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.14 (dt, *J* = 9.2, 2.0 Hz, 2H), 6.95 (s, 1H, -NH), 5.88-5.78 (m, 1H), 5.12 (br s, 1H), 5.07 (br s, 1H), 3.96 (dt, *J* = 6.8, 4.8 Hz, 1H), 2.45-2.39 (m, 1H), 2.31-2.23 (m, 1H), 1.75-1.58 (m, 5H), 1.27-0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.8, 134.9, 130.1, 124.3, 117.5, 90.9, 39.3, 33.9, 28.8, 28.3, 26.5, 26.24, 26.23; IR (KBr) 3244, 2934, 1533, 1347, 1178, 1090, 925, 857, 743, 692, 607 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{21}N_2O_5S$ $[M-H]^-$ 353.1171 found 353.1171.

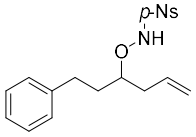
N-(dodec-1-en-4-yloxy)-4-nitrobenzenesulphonamide (**4m**)



According to the representative procedure, the reaction gave **4m** (1.13 g, 2.95 mmol, 59% yield) as a white solid from the corresponding alcohol (921 mg, 5.00 mmol).
TLC Rf = 0.43 (hexane / ethyl acetate = 5 : 1); M.p. 69.7-73.6 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.13 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.01 (s, 1H, -NH), 5.83-5.73 (m, 1H),

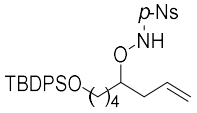
5.11-5.10 (m, 1H), 5.08-5.07 (m, 1H), 4.13 (quint., J = 6.0 Hz, 1H), 2.41-2.29 (m, 2H), 1.56-1.45 (m, 2H), 1.32-1.27 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.8, 142.6, 134.0, 130.1, 124.2, 117.8, 86.6, 37.0, 32.1, 31.9, 29.7, 29.6, 29.3, 25.3, 22.7, 14.2; IR (KBr) 3220, 2919, 2851, 1520, 1348, 1173, 1089, 1012, 934, 856, 762, 712, 597 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{27}N_2O_5S$ $[M-H]^-$ 383.1641 found 383.1637.

4-nitro-*N*-((1-phenylhex-5-en-3-yl)oxy)benzenesulphonamide (**4n**)



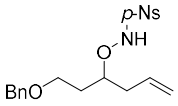
According to the representative procedure, the reaction gave **4n** (903 mg, 2.40 mmol, 48% yield) as a white solid from the corresponding alcohol (881 mg, 5.00 mmol).
TLC Rf = 0.63 (hexane / ethyl acetate = 2 : 1); M.p. 108.3-114.0 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.39 (dt, J = 8.8, 2.0 Hz, 2H), 8.12 (dt, J = 8.8, 2.0 Hz, 2H), 7.30-7.28 (m, 2H), 7.22-7.16 (m, 3H), 6.81 (s, 1H, -NH), 5.83-5.73 (m, 1H), 5.14-5.13 (m, 1H), 5.10-5.09 (m, 1H), 4.19 (quint, J = 6.0 Hz, 1H), 2.75-2.61 (m, 2H), 2.43-2.40 (m, 2H), 1.94-1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.8, 142.5, 141.6, 133.7, 130.0, 128.6, 128.4, 126.2, 124.3, 118.1, 86.1, 37.0, 33.8, 31.6; IR (KBr) 3224, 2927, 1525, 1343, 1311, 1170, 1088, 855, 760, 698, 598 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{19}N_2O_5S$ $[M-H]^-$ 375.1015 found 375.1007.

N-((8-((*tert*-butyldiphenylsilyl)oxy)oct-1-en-4-yl)oxy)-4-nitrobenzenesulphonamide (**4o**)



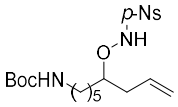
According to the representative procedure, the reaction gave **4o** (1.89 g, 3.25 mmol, 65% yield) as pale yellow oil from the corresponding alcohol (1.91 g, 5.00 mmol).
TLC Rf = 0.32 (hexane / ethyl acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$); δ : 8.33 (dt, J = 9.2, 2.0 Hz, 2H), 8.09 (dt, J = 9.2, 2.0 Hz, 2H), 7.68-7.65 (m, 4H), 7.44-7.36 (m, 6H), 6.87 (s, 1H, -NH), 5.82-5.72 (m, 1H), 5.11-5.07 (m, 2H), 4.16-4.10 (m, 1H), 3.67 (t, J = 6.0 Hz, 2H), 2.37-2.32 (m, 2H), 1.57-1.41 (m, 6H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.6, 135.7, 134.1, 134.0, 130.1, 129.7, 127.8, 124.3, 117.9, 86.6, 63.7, 37.1, 32.5, 31.8, 27.0, 21.6, 19.4; IR (neat) 2930, 2858, 1535, 1349, 1176, 1111, 744, 704 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{38}N_2NaO_6SSi$ $[M+Na]^+$ 605.2118 found 605.2106.

N-((1-(benzyloxy)hex-5-en-3-yl)oxy)-4-nitrobenzenesulfonamide (**4p**)



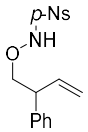
According to the representative procedure, the reaction gave **4p** (1.08 g, 2.65 mmol, 66% yield) as a colorless oil from the corresponding alcohol (827 mg, 4.00 mmol).
TLC Rf = 0.60 (hexane / ethyl acetate = 2 : 1);^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.27 (dt, *J* = 9.2, 2.0 Hz, 2H), 7.94 (dt, *J* = 9.2.0, 2.0 Hz, 2H), 7.39-7.27 (m, 5H), 5.84-5.74 (m, 1H), 5.11-5.07 (m, 2H), 4.50 (d, *J* = 12.0, 1H), 4.46 (d, *J* = 12.0, 1H), 4.21 (dt, *J* = 11.6, 6.4 Hz, 1H), 3.62-3.53 (m, 2H), 2.45-2.31 (m, 2H), 1.90-1.85 (m, 2H); ^{13}C NMR (100 MHz, CDCl3) δ : 150.7, 142.7, 138.1, 133.9, 129.9, 128.7, 128.0, 127.9, 124.2, 118.0, 84.4, 73.3, 67.0, 37.5, 32.5; IR (neat) 3234, 3106, 2917, 2849, 1606, 1532, 1349, 1312, 1175, 1090, 1013, 919, 855, 744, 699, 599 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{23}N_2O_6S$ $[M+H]^+$ 407.1277 found 407.1290.

tert-butyl (6-(((4-nitrophenyl)sulphonamido)oxy)non-8-en-1-yl)carbamate (**4q**)



According to the representative procedure, the reaction gave **4q** (892 mg, 1.95 mmol, 39% yield) as yellow oil from the corresponding alcohol (1.29 g, 5.00 mmol).
TLC Rf = 0.33 (hexane / ethyl acetate = 3 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.15 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.94 (br s, 1H, -N<u>H</u>), 5.85-5.75 (m, 1H), 5.11 (br s, 1H), 5.09-5.06 (m, 1H), 4.58 (br s, 1H, -N<u>H</u>), 4.19-4.13 (m, 1H), 3.19-3.12 (m, 1H), 3.03-2.97 (m, 1H), 2.38-2.26 (m, 2H), 1.55-1.46 (m, 2H), 1.45 (s, 9H), 1.39-1.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 156.5, 150.8, 143.1, 134.4, 130.1, 124.2, 117.7, 86.0, 79.6, 39.8, 36.9, 31.0, 29.4, 28.6, 25.9, 22.7; IR (neat) 3449, 3212, 1534, 1350, 1174, 1090, 925, 853, 752, 694 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{20}H_{31}N_3NaO_7S$ $[M+Na]^+$ 480.1780 found 480.1782.

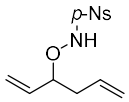
4-nitro-*N*-((2-phenylbut-3-en-1-yl)oxy)benzenesulphonamide (**4r**)



According to the representative procedure, the reaction gave **4r** (522 mg, 1.50 mmol, 30% yield) as a white solid from the corresponding alcohol (740 mg, 5.00 mmol).
TLC Rf = 0.24 (hexane / ethyl acetate = 5 : 1); M.p. 79.3-81.6 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.24 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.74 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.40-7.29 (m, 3H), 7.23-7.21(m, 2H),

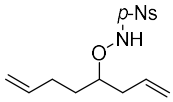
6.99 (s, 1H, -NH), 5.95 (ddd, J = 17.6, 10.4, 7.2, 1H), 5.19-5.09 (m, 2H), 4.41-4.31 (m, 2H), 3.68 (q, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ :150.8, 142.0, 140.3, 137.5, 130.1, 128.9, 128.2, 127.3, 124.2, 117.0, 80.4, 48.4; IR (KBr) 3249, 3101, 1531, 1348, 1170, 1088, 930, 857, 745, 703, 551 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{15}N_2O_5S$ $[M-H]^-$ 347.0702 found 347.0701.

N-(hexa-1,5-dien-3-yloxy)-4-nitrobenzenesulphonamide (**4s**)



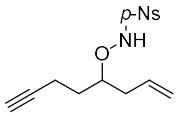
According to the representative procedure, the reaction gave **4s** (700 mg, 2.35 mmol, 47% yield) as a white solid from the corresponding alcohol (490 mg, 5.00 mmol).
TLC Rf = 0.43 (hexane / ethyl acetate = 3 : 1); M.p. 93.6-94.6 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.39 (dt, J = 8.8, 2.0 Hz, 2H), 8.13 (dt, J = 8.8, 2.0 Hz, 2H), 6.90 (s, 1H, -NH), 5.83-5.66 (m, 2H), 5.35-5.29 (m, 2H), 5.14-5.09 (m, 2H), 4.52 (q, J = 6.8 Hz, 1H), 2.45-2.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.5, 135.4, 133.3, 130.2, 124.3, 120.1, 118.2, 87.6, 37.9; IR (KBr) 3221, 3118, 2938, 1647, 1606, 1524, 1408, 1345, 1312, 1171, 1087, 987, 933, 856, 820, 761, 715, 687, 598, 542, 458; HRMS (ESI) m/z calcd for $C_{12}H_{13}N_2O_5S$ $[M-H]^-$ 297.0545 found 297.0547.

4-nitro-*N*-(octa-1,7-dien-4-yloxy)benzenesulphonamide (**4t**)



According to the representative procedure, the reaction gave **4t** (864 mg, 2.65 mmol, 53% yield) as a white solid from the corresponding alcohol (631 mg, 5.00 mmol).
TLC Rf = 0.4 (hexane / ethyl acetate = 3 : 1); M.p. 73.3-76.5 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.40 (dt, J = 8.8, 2.0 Hz, 2H), 8.13 (dt, J = 8.8, 2.0 Hz, 2H), 6.92 (s, 1H, -NH), 5.85-5.73 (m, 2H), 5.14-4.98 (m, 4H), 4.16 (quint., J = 6.0 Hz, 1H), 2.40-2.36 (m, 2H), 2.15-2.08 (m, 2H), 1.73-1.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.6, 137.8, 133.9, 130.1, 124.4, 118.1, 115.4, 86.2, 37.1, 31.4, 29.5; IR (KBr) 3216, 3123, 2938, 2857, 1931, 1642, 1607, 1524, 1454, 1412, 1343, 1312, 1170, 1107, 1088, 1042, 1010, 926, 855, 825, 762, 709, 680, 627, 597 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{17}N_2O_5S$ $[M-H]^-$ 325.0858 found 325.0847.

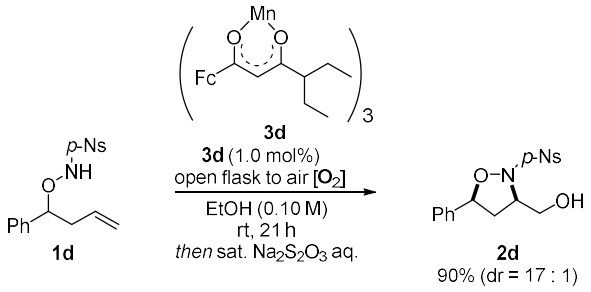
4-nitro-*N*-(oct-1-en-7-yn-4-yloxy)benzenesulphonamide (**4u**)



According to the representative procedure, the reaction gave **4u** (697 mg, 2.15 mmol, 43% yield) as a white solid from the corresponding alcohol (620 mg, 5.00 mmol).
TLC Rf = 0.24 (hexane / ethyl acetate = 5 : 1); M.p. 77.3-78.5 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.40 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.14 (dt, *J* = 9.2, 2.0 Hz, 2H), 7.00 (s, 1H, -NH), 5.83-5.72 (m, 1H), 5.15-5.10 (m, 2H), 4.25 (quint, *J* = 6.0 Hz, 1H), 2.47-2.34 (m, 2H), 2.27 (td, *J* = 7.2, 2.8 Hz, 2H), 1.98 (t, *J* = 2.8 Hz, 1H), 1.82-1.76(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.6, 133.5, 130.1, 124.4, 118.4, 85.1, 83.6, 69.2, 36.9, 30.9, 14.7; IR (KBr) 3288, 3208, 3105, 2937, 2114, 1606, 1525, 1413, 1348, 1313, 1171, 1089, 1002, 923, 857, 752, 682, 643, 593 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{15}N_2O_5S$ $[M-H]^-$ 323.0702 found 323.0696.

3. Representative procedure for the Mn(III)-catalysed oxygenative aminoperoxidation

(2-((4-nitrophenyl)sulphonyl)-5-phenylisoxazolidin-3-yl)methanol (**2d**)



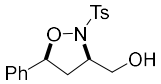
(Representative procedure)
To a stirred solution of sulphonamide **1d** (69.7 mg, 0.200 mmol) in EtOH (2.00 mL) at room temperature was added Mn(III)-complex **3d** (2.1 mg, 2.0 μmol) under air (open flask). The progress of the reaction was monitored by TLC analysis. After 21 h, saturated aqueous $Na_2S_2O_3$ solution (0.5 mL) was added and the mixture was stirred for 30 min. The resulting mixture was extracted with ethyl acetate (3 x 1 mL). The combined organic layer was washed with brine (2 x 1 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1) to give **2d** (65.4 mg, 0.180 mmol, 90% yield, dr = 17 : 1) as colorless oil. The diastereomeric ratio was determined by ^{1}H-NMR analysis of the crude product.

(Gram-scale synthesis)

To a stirred solution of sulphonamide **1d** (1.10 g, 3.15 mmol) in EtOH (31.5 mL) at room temperature was added Mn(III)-complex **3d** (32.4 mg, 31.5 μmol) under air (open flask). After 48 h, saturated aqueous $Na_2S_2O_3$ solution (8 mL) was added and the mixture was stirred for 30 min. The resulting mixture was extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with brine (2 x 10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1) to give **2d** (1.09 g, 3.00 mmol, 95% yield, dr = 17 : 1) as colorless oil. The diastereomeric ratio was determined by ^{1}H-NMR analysis of the crude product.

TLC Rf = 0.16 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.21 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.37-7.30 (m, 5H), 5.37 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.67-4.61 (m, 1H), 3.93-3.87 (m, 1H), 3.84-3.78 (m, 1H), 2.83 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 2.29 (ddd, *J* = 12.4, 10.4 , 7.6 Hz, 1H), 2.05 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.0, 135.8, 130.7, 129.3, 128.9, 127.1, 124.4, 84.2, 64.5, 62.0, 39.0; IR (neat) 3545, 3107, 2929, 1606, 1532, 1458, 1351, 1312, 1168, 1091, 855, 741, 619 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{16}N_2NaO_6S$ $[M+Na]^+$ 387.0627 found 387.0617.

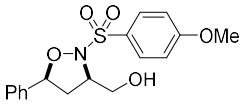
(5-phenyl-2-tosylisoxazolidin-3-yl)methanol (**2a**)



According to the representative procedure, the reaction gave **2a** (50.0 mg, 0.150 mmol, 75% yield, dr = 17 : 1) as colorless oil from **1a** (63.4 mg, 0.200 mmol).

TLC Rf = 0.13 (hexane / ethyl acetate = 3 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.85 (d, *J* = 8.0 Hz, 2H), 7.32-7.21 (m, 7H), 4.99 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.45-4.39 (m, 1H), 3.83-3.80 (m, 1H), 3.73 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.64 (ddd, *J* = 12.0, 8.0, 6.0 Hz, 1H), 2.40 (s, 3H), 2.16 (ddd, *J* = 12.0, 10.4, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 145.5, 136.3, 132.6, 130.0, 129.5, 129.1, 128.8, 127.1, 83.4, 64.7, 62.6, 39.2, 21.9; IR (neat) 3386, 2922, 2879, 1596, 1451, 1354, 1334, 1163, 1091, 815, 759, 699, 673, 590 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{19}NNaO_4S$ $[M+Na]^+$ 356.0933 found 356.0919.

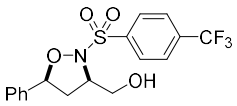
(2-((4-methoxyphenyl)sulphonyl)-5-phenylisoxazolidin-3-yl)methanol (**2b**)



According to the representative procedure, the reaction gave **2b** (50.3 mg, 0.144 mmol, 72% yield, dr = 17 : 1) as colorless oil from **1b** (66.6 mg, 0.200 mmol).

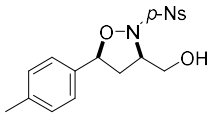
TLC Rf = 0.11 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.94 (d, *J* = 8.8 Hz, 2H), 7.34-7.27 (m, 5H), 7.03 (dt, *J* = 8.8 Hz, 2H), 5.08 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.49-4.23 (m, 1H), 3.89-3.84 (m, 4H), 3.80-3.74 (m, 1H), 2.70 (ddd, *J* = 12.0, 8.0, 6.0 Hz, 1H), 2.28 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>), 2.21 (ddd, *J* = 12.4, 10.4, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 164.4, 136.4, 131.7, 129.0, 128.8, 127.1, 126.8, 114.6, 83.3, 64.6, 62.7, 55.9, 39.2; IR (neat) 3527, 2944, 1595, 1497, 1459, 1353, 1264, 1159, 1093, 1025, 836, 805, 760, 699, 678, 591 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{19}NNaO_6S$ $[M+Na]^+$ 372.0882 found 372.0886.

(5-phenyl-2-((4-(trifluoromethyl)phenyl)sulphonyl)isoxazolidin-3-yl)methanol (**2c**)



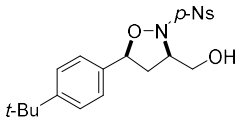
According to the representative procedure, the reaction gave **2c** (64.3 mg, 0.166 mmol, 83% yield, dr = 17 : 1) as colorless oil from **1c** (74.2 mg, 0.200 mmol).
TLC Rf = 0.11 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.15 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.36-7.29 (m, 5H), 5.31 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.64-4.58 (m, 1H), 3.92-3.87 (m, 1H), 3.83-3.77 (m, 1H), 2.80 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 2.27 (ddd, *J* = 12.4, 10.4, 7.6 Hz, 1H), 2.12 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 139.9 (q, $^4J_{F-C}$ = 2 Hz), 135.8 (q, $^2J_{F-C}$ = 33 Hz), 135.6, 129.9, 129.4, 128.9, 127.1, 126.4 (q, $^3J_{F-C}$ = 4 Hz), 123.2 (q, $^1J_{F-C}$ = 272 Hz), 83.9, 78.0, 57.2, 39.2; IR (neat) 3437, 2927, 1406, 1324, 1169, 1135, 1109, 1064, 1017, 845, 761, 715, 618 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{16}F_3NNaO_4S$ $[M+Na]^+$ 410.0650 found 410.0658.

(2-((4-nitrophenyl)sulphonyl)-5-(*p*-tolyl)isoxazolidin-3-yl)methanol (**5a**)



According to the representative procedure, the reaction gave **5a** (62.0 mg, 0.164 mmol, 82% yield, dr = 17 : 1) as colorless oil from **4a** (72.4 mg, 0.200 mmol).
TLC Rf = 0.12 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.20 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.32 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.66-4.59 (m, 1H), 3.93-3.87 (m, 1H), 3.84-3.77 (m, 1H), 2.79 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 2.36-2.24 (m, 1H), 2.33 (s, 3H), 2.07 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.0, 139.4, 132.6, 130.7, 130.0, 127.2, 124.3, 84.1, 64.5, 62.1, 38.7, 21.3; IR (neat) 3399, 2918, 2856, 1529, 1353, 1308, 1260, 1167, 1088, 1031, 814 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{18}N_2NaO_6S$ $[M+Na]^+$ 401.0783 found 401.0782.

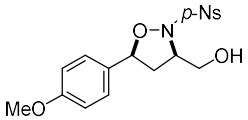
(5-(4-(*tert*-butyl)phenyl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5b**)



According to the representative procedure, the reaction gave **5b** (59.7 mg, 0.142 mmol, 71% yield, dr = 17 : 1) as yellow oil from **4b** (80.8 mg, 0.200 mmol).

TLC Rf = 0.21 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.20 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.37 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.26-7.24 (m, 2H), 5.34 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.66-4.60 (m, 1H), 3.93-3.88 (m, 1H), 3.84-3.78 (m, 1H), 2.80 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 2.29 (ddd, *J* = 12.4, 10.8, 8.0 Hz, 1H), 2.05 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 152.6, 151.0, 142.0, 132.6, 130.7, 127.0, 125.8, 124.3, 84.1, 64.5, 62.1, 38.7, 34.8, 31.3; IR (neat) 3547, 3412, 2963, 1607, 1534, 1350, 1312, 1168, 1092, 855, 831, 741, 685, 620, 573 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{20}H_{24}N_2NaO_6S$ $[M+Na]^+$ 443.1253 found 443.1247.

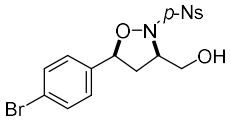
(5-(4-methoxyphenyl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5c**)



According to the representative procedure, the reaction gave **5c** (40.2 mg, 0.102 mmol, 51% yield, dr = 17 : 1) as yellow oil from **4c** (75.6 mg, 0.200 mmol).

TLC Rf = 0.14 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.20 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.24-7.23 (m, 2H), 6.89-6.85 (m, 2H), 5.31 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.66-4.60 (m, 1H), 3.94-3.88 (m, 1H), 3.84-3.78 (m, 1H), 3.79 (s, 3H), 2.77 (ddd, *J* = 12.4 , 8.4, 6.0 Hz, 1H), 2.29 (ddd, *J* = 12.4, 10.4, 8.0 Hz, 1H), 2.05 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 160.5, 151.0, 142.1, 130.7, 128.8, 127.3, 124.3, 114.3, 84.1, 64.6, 62.1, 55.5, 38.6; IR (neat) 3531, 3108, 2923, 1611, 1532, 1351, 1310, 1254, 1169, 1032, 855, 831, 741, 685, 620 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{19}N_2O_9S$ $[M+HCO_2]^-$ 439.0811 found 439.0793.

(5-(4-bromophenyl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5d**)

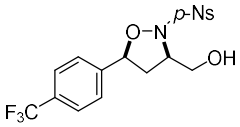


According to the representative procedure, the reaction gave **5d** (68.9 mg, 0.156 mmol, 78% yield, dr = 17 : 1) as brown oil from **4d** (85.1 mg, 0.200 mmol).

TLC Rf = 0.18 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0

Hz, 2H), 8.19 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.48 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.19 (dt, *J* = 8.8, 2.0 Hz, 2H), 5.35 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.68-4.61 (m, 1H), 3.89 (ddd, *J* = 11.6, 6.4, 4.0 Hz, 1H), 3.82-3.76 (m, 1H), 2.83 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 2.24 (ddd, *J* = 12.4, 10.4, 8.0 Hz, 1H), 2.02 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.1, 141.9, 135.0, 132.1, 130.7, 128.7, 124.4, 123.3, 83.4, 64.4, 61.9, 38.9; IR (neat) 3545, 3412, 1532, 1350, 1308, 1168, 1084, 1011, 863, 741, 619 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{14}BrN_2O_6S$ $[M-H]^-$ 440.9756 found 440.9745.

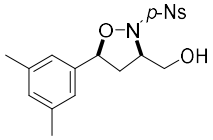
(2-((4-nitrophenyl)sulphonyl)-5-(4-(trifluoromethyl)phenyl)isoxazolidin-3-yl)methanol (**5e**)



According to the representative procedure, the reaction gave **5e** (46.7 mg, 0.108 mmol, 54% yield, dr = 17 : 1) as colorless oil from **4e** (83.2 mg, 0.200 mmol).

TLC Rf = 0.18 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.39 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.20 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 5.48 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.71-4.65 (m, 1H), 3.90 (ddd, *J* = 12.0, 6.4, 4.0 Hz, 1H), 3.83-3.77 (m, 1H), 2.90 (ddd, *J* = 12.4, 8.4, 6.4 Hz, 1H), 2.26 (ddd, *J* = 12.4, 10.0, 7.6 Hz, 1H), 2.01 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.2, 141.9, 140.1, 131.4 (q, $^2J_{F\text{-}C}$ = 32 Hz, 1H), 130.7, 127.2, 125.9 (q, $^1J_{F\text{-}C}$ = 275 Hz, 1H), 125.9 (q, $^3J_{F\text{-}C}$ = 4 Hz, 1H), 124.4, 83.3, 64.4, 61.8, 39.2; IR (neat) 3481, 3425, 3103, 2940, 1532, 1335, 1172, 1118, 1069, 1016, 840, 741, 619, 568, 460 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{14}F_3N_2O_6S$ $[M-H]^-$ 431.0525 found 431.0510.

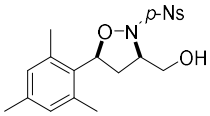
(5-(3,5-dimethylphenyl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5f**)



According to the representative procedure, the reaction gave **5f** (51.8 mg, 0.132 mmol, 66% yield, dr = >20 : 1) as colorless oil from **4f** (75.2 mg, 0.200 mmol).

TLC Rf = 0.33 (hexane / ethyl acetate = 3 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.37 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.20 (dt, *J* = 9.2, 2.0 Hz, 2H), 6.97 (s, 1H), 6.91 (s, 2H), 5.27 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.64-4.58 (m, 1H), 3.89 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.81 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.78 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 2.30-2.22 (m, 1H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.1, 138.6, 135.6, 131.0, 130.7, 124.9, 124.3, 84.3, 64.5, 62.1, 39.0, 21.4; IR (neat) 3579, 2919, 1604, 1403, 11183, 1011, 780, 686, 465 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{20}N_2NaO_6S$ $[M+Na]^+$ 415.0940 found 415.0934.

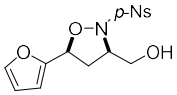
(5-mesityl-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5g**)



According to the representative procedure, the reaction gave **5g** (69.9 mg, 0.172 mmol, 86% yield, dr = >20 : 1) as a white solid from **4g** (78.0 mg, 0.200 mmol).

TLC Rf = 0.37 (hexane / ethyl acetate = 3 : 1); M.p. 153.3-156.5 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.37 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.19 (dt, *J* = 9.2, 2.0 Hz, 2H), 6.82 (s, 2H), 5.64 (dd, *J* = 11.6, 6.4 Hz,1H), 4.63-4.57 (m, 1H), 3.95 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.85 (dd, *J* = 11.6, 5.6 Hz, 1H), 2.60-2.49 (m, 2H), 2.29 (s, 6H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.2, 138.7, 137.5, 130.7, 130.5, 127.1, 124.3, 81.2, 64.6, 62.3, 35.2, 20.9, 20.8.; IR (KBr) 3368, 2924, 1544, 1365, 1261, 1038, 852, 703, 571 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{22}N_2NaO_6S$ $[M+Na]^+$ 429.1096 found 429.1084.

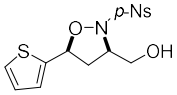
(5-(furan-2-yl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5h**)



According to the representative procedure, the reaction gave **5h** (58.1 mg, 0.164 mmol, 82% yield, dr = 7 : 1) as colorless oil from **4h** (67.6 mg, 0.200 mmol).

TLC Rf = 0.22 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$); δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.21 (dt, *J* =8.8, 2.0 Hz, 2H), 7.41 (dd, *J* = 2.0, 0.8 Hz, 1H), 6.45 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.35 (dd, *J* = 3.6, 2.0 Hz, 1H), 5.53 (dd, *J* = 9.2, 7.6 Hz, 1H), 4.72-4.66 (m, 1H), 3.84 (br s, 2H), 2.77 (ddd, *J* = 12.4, 8.4, 7.2 Hz, 1H), 2.51 (ddd, *J* = 12.8, 9.2, 6.0 Hz, 1H), 2.05 (br t, *J* = 6.4 Hz, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.1, 148.0, 144.1, 142.0, 130.7, 124.3, 111.5, 110.8, 77.1, 64.1, 61.6, 34.6; IR (neat) 3544, 3108, 2930, 1536, 1352, 1168, 1013, 855, 741, 619 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{14}N_2NaO_7S$ $[M+Na]^+$ 377.0419 found 377.0417.

(2-((4-nitrophenyl)sulphonyl)-5-(thiophen-2-yl)isoxazolidin-3-yl)methanol (**5i**)

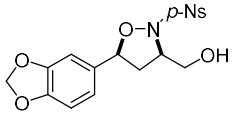


According to the representative procedure, the reaction gave **5i** (61.4 mg, 0.166 mmol, 83% yield, dr = 8 : 1) as colorless oil from **4i** (70.9 mg, 0.200 mmol).

TLC Rf = 0.24 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.21 (dt, *J* = 9.2, 2.0 Hz, 2H), 7.34 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.11 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.98 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.71 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.71-4.64 (m, 1H), 3.88 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.82 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.90 (ddd, *J* = 12.4, 8.4, 6.4 Hz, 1H), 2.36 (ddd, *J* = 12.4, 10.0, 7.2 Hz, 1H), 1.84 (br s, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.1, 142.0, 138.1, 130.7,

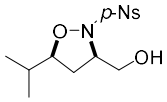
127.9, 127.2, 127.1, 124.4, 79.8, 64.4, 61.9, 39.0; IR (neat) 3544, 3107, 2939, 1607, 1538, 1350, 1166, 1091, 855, 742, 619 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{14}N_2NaO_6S_2$ $[M+Na]^+$ 393.0191 found 393.0182.

(5-(benzo[d][1,3]dioxol-5-yl)-2-((4-nitrophenyl)sulfonyl)isoxazolidin-3-yl)methanol (**5j**)



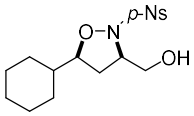
According to the representative procedure, the reaction gave **5j** (53.4 mg, 0.131 mmol, 65% yield, dr = > 20 : 1) as yellow oil from **4j** (78.5 mg, 0.200 mmol).
TLC Rf = 0.17 (hexane / ethyl acetate = 2 : 1); ^1H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.20 (dt, *J* = 8.8, 2.0 Hz, 2H), 6.81-6.75 (m, 3H), 5.95-5.94 (m, 2H), 5.28 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.65-4.59 (m, 1H), 3.90 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.80 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.77 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 2.25 (ddd, *J* = 12.4, 10.4, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 148.5, 148.2, 142.0, 130.7, 129.2, 124.4, 121.5, 108.5, 107.3, 101.5, 84.2, 64.5, 61.9, 38.7; IR (neat) 3389, 2916, 2849, 1533, 1505, 1446, 1350, 1311, 1250, 1166, 1090, 1037, 931, 855, 741, 684, 618. cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{16}N_2NaO_8S$ $[M+Na]^+$ 431.0525 found 431.0531.

(5-isopropyl-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5k**)



According to the representative procedure, the reaction gave **5k** (48.2 mg, 0.146 mmol, 73% yield, dr = >20 : 1) as a white solid from **4k** (62.8 mg, 0.200 mmol).
TLC Rf = 0.26 (hexane / ethyl acetate = 2 : 1); M.p. 113.0-116.6 ˚C; ^1H NMR (400 MHz, $CDCl_3$) δ : 8.40 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.17 (dt, *J* = 8.8, 2.0 Hz, 2H), 4.46-4.39 (m, 1H), 3.99 (ddd, *J* = 10.4, 8.0, 6.0 Hz, 1H), 3.81-3.76 (m, 1H), 3.70-3.65 (m, 1H), 2.44 (ddd, *J* = 12.0, 8.0, 6.0 Hz, 1H), 2.05-2.01 (m, 1H, -O<u>H</u>), 1.85 (ddd, *J* = 12.0, 10.4, 7.6 Hz, 1H), 1.77-1.65 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.1, 142.1, 130.7, 124.3, 87.9, 64.5, 61.8, 34.8, 31.3, 19.5, 18.8; IR (KBr) 3536, 3105, 2966, 2871, 1525, 1353, 1064, 940, 743, 617 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{18}N_2NaO_6S$ $[M+Na]^+$ 353.0783 found 353.0778.

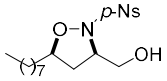
(5-cyclohexyl-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5l**)



According to the representative procedure, the reaction gave **5l** (61.4 mg, 0.166 mmol, 83% yield, dr = >20 : 1) as a white solid from **4l** (70.8 mg, 0.200 mmol).

TLC Rf = 0.32 (hexane / ethyl acetate = 2 : 1); M.p. 166.2-168.0 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.41 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.17 (dt, *J* = 8.8, 2.0 Hz, 2H), 4.43-4.37 (m, 1H), 3.97 (ddd, *J* = 10.4, 8.0, 5.6 Hz, 1H), 3.80-3.77 (m, 1H), 3.68-3.64 (m, 1H), 2.43 (ddd, *J* = 12.0, 8.0, 5.6 Hz, 1H), 2.02 (br t, *J* = 6.0 Hz, 1H, -O<u>H</u>), 1.85 (ddd, *J* = 12.0, 10.0, 8.0 Hz, 1H), 1.79-1.52 (m, 4H), 1.46-1.36 (m, 1H), 1.28-1.11 (m, 4H), 1.01-0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.1, 130.7, 124.3, 86.9, 64.6, 61.7, 40.9, 34.7, 30.0, 29.1, 26.2, 25.8, 25.5; IR (KBr) 3569, 3111, 2924, 2852, 1531, 1353, 1179, 1056, 856, 741, 641, 741 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}N_2NaO_6S$ $[M+Na]^+$ 393.1096 found 393.1084.

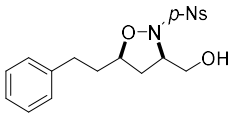
(2-((4-nitrophenyl)sulphonyl)-5-octylisoxazolidin-3-yl)methanol (**5m**)



According to the representative procedure, the reaction gave **5m** (68.8 mg, 0.172 mmol, 86% yield, dr = >20 : 1) as a white solid from **4m** (76.8 mg, 0.200 mmol).

TLC Rf = 0.26 (hexane / ethyl acetate = 2 : 1); M.p. 48.0-51.2 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.40 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.18 (dt, *J* = 8.8, 2.0 Hz, 2H), 4.47-4.40 (m, 1H), 4.31-4.27 (m, 1H), 3.80-3.76 (m, 1H), 3.70-3.65 (m, 1H), 2.50 (ddd, *J* = 12.0, 8.0, 6.0 Hz, 1H), 2.02 (br t, *J* = 6.0 Hz, 1H, -O<u>H</u>), 1.80 (ddd, *J* = 12.0, 10.0, 7.6 Hz, 1H), 1.57-1.46 (m, 2H), 1.33-1.25 (s, 12H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.2, 130.6, 124.3, 82.9, 64.5, 61.7, 36.8, 32.7, 31.9, 29.6, 29.5, 29.3, 26.2, 22.8, 14.2; IR (KBr) 3246, 2923, 2853, 1543, 1354, 1167, 1092, 854, 743, 617 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{28}N_2NaO_6S$ $[M+Na]^+$ 423.1566 found 423.1573.

(2-((4-nitrophenyl)sulphonyl)-5-phenethylisoxazolidin-3-yl)methanol (**5n**)

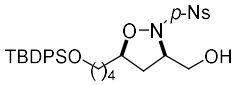


According to the representative procedure, the reaction gave **5n** (70.6 mg, 0.180 mmol, 90% yield, dr = 7 : 1) as brown oil from **4n** (75.2 mg, 0.200 mmol).

TLC Rf = 0.18 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.35 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.13 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.31-7.28 (m, 2H), 7.23-7.20 (m, 1H), 7.14-7.11 (m, 2H),

4.43-4.37 (m, 1H), 4.25-4.16 (m, 1H), 3.82-3.76 (m, 1H), 3.72-3.66 (m, 1H), 2.71-2.56 (m, 2H), 2.47 (ddd, *J* = 12.0, 8.4 , 6.0 Hz, 1H), 2.00 (t, *J* = 6.4, 1H, -O<u>H</u>), 1.96-1.79 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.0, 140.5, 130.6, 128.7, 128.4, 126.5, 124.4, 81.9, 64.5, 61.9, 36.7, 34.3, 32.3; IR (neat) 3545, 3382, 2934, 1605, 1532, 1455, 1351, 1173, 1090, 855, 741, 685, 619, 574, 462 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{20}N_2NaO_6S$ $[M+Na]^+$ 415.0940 found 415.0922.

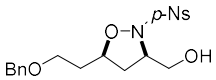
(5-(4-((*tert*-butyldiphenylsilyl)oxy)butyl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5o**)



According to the representative procedure, the reaction gave **5o** (93.3 mg, 0.156 mmol, 78% yield, dr = 17 : 1) as colorless oil from **4o** (116 mg, 0.200 mmol).

TLC Rf = 0.34 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.36 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.16 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.66-7.63 (m, 4H), 7.43-7.35 (m, 6H), 4.47-4.41 (m, 1H), 4.33-4.25 (m, 1H), 3.80-3.75 (m, 1H), 3.70-3.62 (m, 3H), 2.49 (ddd, *J* = 12.4, 8.4, 6.0, 1H), 2.05-1.98 (m, 1H, -O<u>H</u>), 1.78 (ddd, *J* = 12.0, 10.0, 7.6 Hz, 1H), 1.58-1.36 (m, 5H), 1.26 (s, 1H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.2, 135.7, 134.0, 130.6, 129.8, 127.8, 124.3, 82.9, 64.5, 63.6, 61.7, 36.7, 32.4, 32.3, 27.0, 22.7, 19.4; IR (neat) 3413, 2918, 2857, 1536, 1350, 1217, 1168, 1109, 759 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{38}N_2NaO_7SSi$ $[M+Na]^+$ 621.2067 found 621.2056.

(5-(2-(benzyloxy)ethyl)-2-((4-nitrophenyl)sulfonyl)isoxazolidin-3-yl)methanol (**5p**)



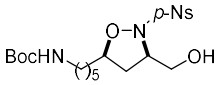
According to the representative procedure, the reaction gave **5p** (63.4 mg, 0.150 mmol, 75% yield, dr = 7 : 1) as colorless oil from **4p** (81.2 mg, 0.200 mmol).

The following physical data were measured as an inseparable diastereomeric mixture (*syn*-**5p** : *anti*-**5p** = 7 : 1).

TLC Rf = 0.13 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) *syn*-**5p** δ : 8.27 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.11 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.40-7.29 (m, 5H), 4.52-4.36 (m, 2H), 4.488-4.485 (m, 2H), 3.78 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.67 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.50 (t, *J* = 6.0 Hz, 2H), 2.51 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 1.95-1.81 (m, 3H), 1.66 (br s, 1H, -O<u>H</u>); *anti*-**5p** δ : 8.33 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.11 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.40-7.29 (m, 5H), 4.52-4.36 (m, 2H), 4.488-4.485 (m, 2H), 3.73 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.67 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.50 (t, *J* = 6.0 Hz, 2H), 2.31-2.26 (m, 1H), 1.95-1.81 (m, 3H), 1.66 (br s, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) *syn*-**5p** δ : 151.0, 141.8, 138.1, 130.6, 128.7, 128.0, 127.8, 124.3, 80.2, 73.3, 66.8, 64.4, 61.9, 36.9, 33.0; *anti*-**5p** δ :

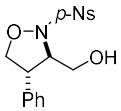
151.0, 141.0, 138.1, 130.9, 128.6, 127.9, 127.7, 124.1, 80.9, 73.2, 66.9, 63.8, 62.5, 37.1, 34.5; IR (neat) 3403, 2916, 2846, 1532, 1455, 1349, 1311, 1168, 1091, 1025, 855, 740, 684, 619 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{22}N_2NaO_7S$ $[M+Na]^+$ 445.1045 found 445.1028.

tert-butyl (5-(3-(hydroxymethyl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-5-yl)pentyl)carbamate (**5q**)



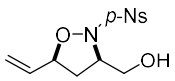
According to the representative procedure, the reaction gave **5q** (56.8 mg, 0.120 mmol, 60% yield, dr = >20 : 1) as yellow oil from **4q** (91.4 mg, 0.200 mmol).
TLC Rf = 0.45 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.41 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.17 (dt, *J* = 9.2, 2.0 Hz, 2H), 4.50 (br s, 1H, -NH), 4.47-4.41 (m, 1H), 4.33-4.26 (m, 1H), 3.77 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.67 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.07 (br t, *J* = 6.4 Hz, 2H), 2.50 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 1.84-1.77 (m, 3H), 1.59-1.51 (m, 2H), 1.43 (s, 9H), 1.36-1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 156.2, 151.0, 142.2, 130.6, 124.4, 82.7, 79.4, 64.5, 61.6, 40.5, 36.7, 32.6, 30.0, 28.5, 26.6, 25.8; IR (neat) 3416, 2932, 1694, 1535, 1351, 1090, 856, 741, 620, 575 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{20}H_{31}N_3NaO_8S$ $[M+Na]^+$ 496.1730 found 496.1729.

(2-((4-nitrophenyl)sulphonyl)-4-phenylisoxazolidin-3-yl)methanol (**5r**)



According to the representative procedure, the reaction gave **5r** (47.3 mg, 0.130 mmol, 65% yield, dr = 17 : 1) as colorless oil from **4r** (69.6 mg, 0.200 mmol).
TLC Rf = 0.36 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.43 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.25 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.39-7.28 (m, 5H), 4.34 (ddd, *J* = 8.4, 5.2, 3.2 Hz, 1H), 4.28 (d, *J* = 9.6 Hz, 2H), 3.95-3.90 (m, 1H), 3.79-3.71 (m, 2H), 2.08 (br t, *J* = 6.4 Hz, 1H, -OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.1, 141.9, 135.4, 130.8, 129.4, 128.4, 128.1, 124.4, 76.4., 68.4, 62.8, 50.5; IR (neat) 3563, 3107, 2927, 1537, 1351, 1168, 1089, 856, 743, 619 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{16}N_2NaO_6S$ $[M+Na]^+$ 387.0626 found 387.0619.

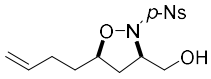
(2-((4-nitrophenyl)sulphonyl)-5-vinylisoxazolidin-3-yl)methanol (**5s**)



According to the representative procedure, the reaction gave **5s** (46.5 mg, 0.148 mmol, 74% yield, dr = 17 : 1) as a yellow solid from **4s** (59.6 mg, 0.200 mmol).

TLC Rf = 0.10 (hexane / ethyl acetate = 3 : 1); M.p. 96.9-98.3 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.40 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.19 (dt, *J* = 9.2, 2.0 Hz, 2H), 5.70 (ddd, *J* = 17.6, 10.0, 7.2 Hz, 1H), 5.36 (dt, *J* = 17.6, 0.8 Hz, 1H), 5.29 (d, *J* = 10.0 Hz, 1H), 4.86-4.80 (m, 1H), 4.56-4.50 (m, 1H), 3.82-3.77 (m, 1H), 3.73-3.67 (m, 1H), 2.66-2.59 (m, 1H), 2.03-1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.1, 142.0, 133.3, 130.7, 124.3, 121.1, 83.7, 64.4, 61.7, 37.0; IR (KBr) 3497, 3103, 2920, 1607, 1531, 1350, 1178, 1055, 995, 943, 867, 854, 740, 686, 641, 577, 458; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{14}N_2NaO_6S$ $[M+Na]^+$ 337.0470 found 337.0462.

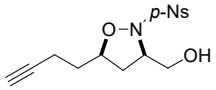
(5-(but-3-en-1-yl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5t**)



According to the representative procedure, the reaction gave **5t** (58.2 mg, 0.170 mmol, 85% yield, dr = 17 : 1) as brown oil from **4t** (65.2 mg, 0.200 mmol).

TLC Rf = 0.21 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.41 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.18 (dt, *J* = 9.2, 2.0 Hz, 2H), 5.79-5.69 (m, 1H), 5.05-4.98 (m, 2H), 4.48-4.41 (m, 1H), 4.35-4.27 (m, 1H), 3.79 (dd, *J* = 7.6, 4.0 Hz, 1H), 3.68 (dd, *J* = 11.6, 6.4 Hz, 1H), 2.52 (ddd, *J* = 12.0, 8.4, 6.0 Hz, 1H), 2.15-2.01 (m, 2H), 1.82 (ddd, *J* = 12.0, 10.0, 7.6 Hz, 1H), 1.75-1.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.1, 142.1, 137.1, 130.7, 124.3, 115.8, 82.2, 64.5, 61.7, 36.7, 32.0, 30.4; IR (neat) 3542, 3106, 2917, 1731, 1641, 1607, 1536, 1448, 1351, 1169, 1090, 919, 856, 741, 685, 619, 576 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{18}N_2NaO_6S$ $[M+Na]^+$ 365.0927 found 365.0917.

(5-(but-3-yn-1-yl)-2-((4-nitrophenyl)sulphonyl)isoxazolidin-3-yl)methanol (**5u**)



According to the representative procedure, the reaction gave **5u** (50.3 mg, 0.148 mmol, 74% yield, dr = 5 : 1) as colorless oil from **4u** (64.8 mg, 0.200 mmol).

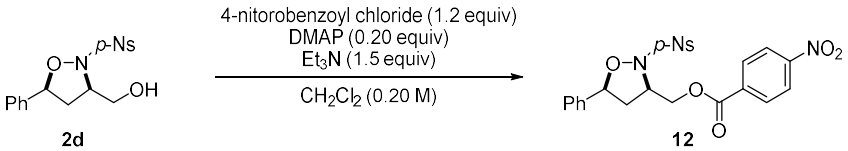
The following physical data were measured as an inseparable diastereomeric mixture (*syn*-**5u** : *anti*-**5u** = 5 : 1).

TLC Rf = 0.21 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) *syn*-**5u** δ : 8.41 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.20 (dt, *J* = 9.2, 2.0 Hz, 2H), 4.45-4.35 (m, 2H), 3.80 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.69 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.54 (ddd, *J* = 14.0, 8.0, 6.0 Hz, 1H), 2.28-2.23 (m, 2H), 1.98 (t, *J* = 2.4 Hz, 1H), 1.87 (ddd, *J* = 12.0, 10.0, 7.6 Hz, 1H), 1.77 (q, *J* = 6.8 Hz, 2H and 1H, -O<u>H</u>); *anti*-**5u** δ : 8.41 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.16 (dt, *J* = 9.2, 2.0 Hz, 2H), 4.45-4.35 (m, 2H), 3.77-3.72 (m, 2H), 2.36 (ddd, *J* = 12.8, 6.8, 2.4 Hz, 1H), 2.28-2.23 (m, 2H), 1.96 (t, *J* = 2.4 Hz, 1H), 1.91-1.84 (m, 1H), 1.77 (q, *J* = 6.8 Hz, 2H and 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) *syn*-**5u** δ : 151.0, 141.6, 130.7, 124.4, 82.6, 80.8, 69.7, 64.3, 62.0, 36.5, 31.4, 15.5; *anti*-**5u** δ : 151.0, 141.0, 130.8, 124.2, 81.7, 77.4,

69.6, 63.7, 62.5, 36.7, 32.9, 15.7; IR (neat) 3535, 3292, 3106, 2938, 2118, 1725, 1607, 1534, 1351, 1312, 1173, 1090, 1051, 856, 741, 685, 620, 575 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{16}N_2NaO_6S$ $[M+Na]^+$ 363.0627 found 363.0617.

4. Synthesis of 4-nitrobenzoate 12 and 13

2-((4-nitrophenyl)sulphonyl)-5-phenylisoxazolidin-3-yl)methyl 4-nitrobenzoate (**12**)

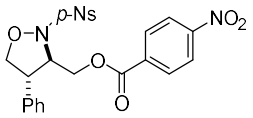


(Representative procedure)

To a solution of **2d** (67.3 mg, 0.185 mmol), DMAP (4.5 mg, 0.037 mmol) and Et_3N (39.3 μL, 0.278 mmol) in CH_2Cl_2 (930 μL) at 0 °C was added 4-nitorobenzoyl chloride (41.2 mg, 0.222 mmol). The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with H_2O (5 mL). The resulting mixture was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layer was washed with brine (3 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 5 : 1 to 3 : 1) to give **12** (61.1 mg, 0.134 mmol, 72% yield) as a white solid.

TLC Rf = 0.20 (hexane / ethyl acetate = 3 : 1); M.p. 164.7-171.7 ˚C; ^1H NMR (400 MHz, $CDCl_3$) δ : 8.37-8.27 (m, 6H), 8.14 (dt, *J* = 9.2, 2.0 Hz, 2H), 7.39-7.30 (m, 5H), 5.51 (dd, *J* = 10.0, 6.0 Hz, 1H), 5.03-4.95 (m, 1H), 4.61 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.54 (dd, *J* = 11.2, 7.6 Hz, 1H), 3.01 (ddd, *J* = 12.8, 8.4, 6.0 Hz, 1H), 2.20 (ddd, *J* = 12.8, 10.0 , 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 164.5, 151.0, 150.9, 142.2, 135.6, 135.1, 131.1, 130.5, 129.4, 129.0, 126.9, 124.3, 123.8, 83.9, 66.5, 58.3, 39.6; IR (KBr) 3110, 2965, 1730, 1606, 1531, 1348, 1276, 1167, 1122, 962, 857, 722, 699, 618, 567, 458 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}N_3NaO_9S$ $[M+Na]^+$ 536.0740 found 536.0732.

(2-((4-nitrophenyl)sulphonyl)-4-phenylisoxazolidin-3-yl)methyl 4-nitrobenzoate (**13**)



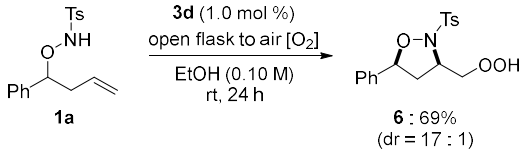
According to the representative procedure, the reaction gave **13** (307 mg, 0.60 mmol, 60% yield) as a white solid from **5r** (364 mg, 1.00 mmol).

TLC Rf = 0.36 (hexane / ethyl acetate = 3 : 1); M.p. 184.7-187.5 ˚C; ^1H NMR (400 MHz, $CDCl_3$) δ : 8.40 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.25 (dt, *J* = 9.2, 2.0 Hz, 2H), 8.20 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.10 (dt, *J* = 9.2, 2.0 Hz, 2H), 7.39-7.33 (m, 5H), 4.79-4.74 (m, 1H), 4.64-4.56 (m, 2H), 4.42 (dd, *J* = 10.8,

8.4 Hz, 1H), 4.34 (t, *J* = 8.0 Hz, 1H), 3.65 (dt, *J* = 11.2 ,8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 164.4, 151.1, 150.9, 142.1, 134.95, 134.94, 131.0, 130.7, 129.6, 128.6, 128.1, 124.4, 123.7, 76.7, 66.0, 64.4, 52.7; IR (KBr) 3110, 2909, 1724, 1524, 1348, 1277, 1168, 951, 854, 744, 619, 557 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{19}N_3NaO_9S$ $[M+Na]^+$ 536.0739 found 536.0749.

5. Synthesis of peroxide 6

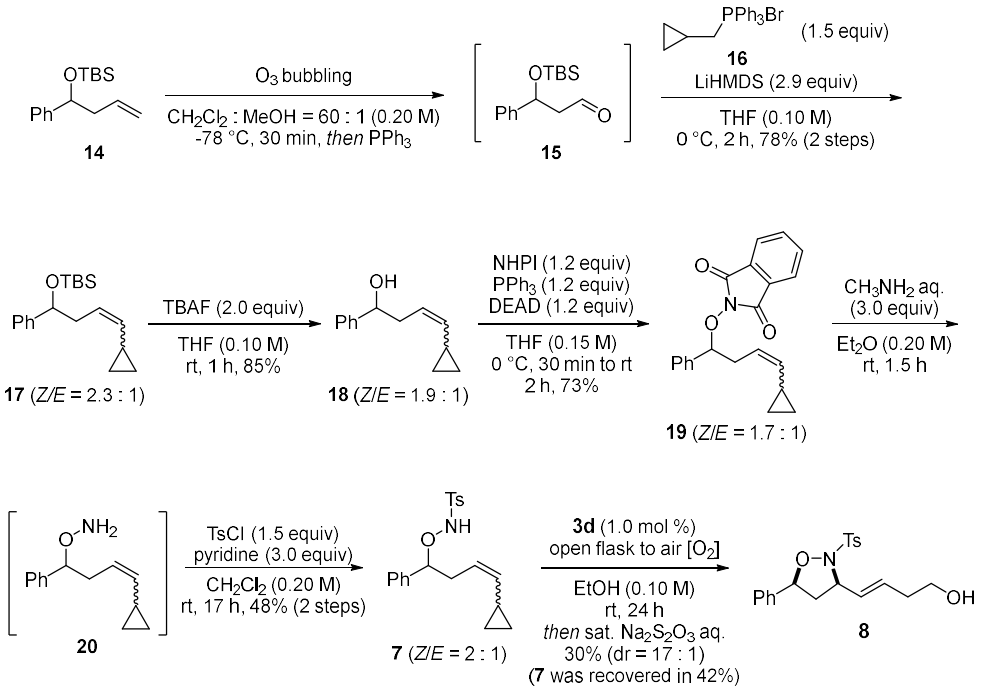
3-(hydroperoxymethyl)-5-phenyl-2-tosylisoxazolidine (**6**)



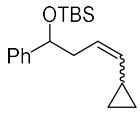
To a stirred solution of **1a** (63.4 mg, 0.200 mmol) in EtOH (2.00 mL) at room temperature was added Mn(III)-complex **3d** (2.1 mg, 2.0 μmol) under air (open flask). The progress of the reaction was monitored by TLC analysis. The reaction was quenched with saturated aqueous NaCl solution (0.5 mL). The resulting mixture was extracted with ethyl acetate (3 x 1 mL). The combined organic layers were washed with brine (2 x 1 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1) to give **6** (48.2 mg, 0.138 mmol, 69% yield, dr = 17 : 1) as colorless oil.

TLC Rf = 0.50 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 9.46 (br s, 1 H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.36-7.27 (m, 7H), 5.29 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.94 (m, 1H), 4.25 (dd, *J* = 13.2, 4.0 Hz, 1H), 4.03 (dd, *J* = 12.8, 8.8 Hz, 1H), 2.81 (ddd, *J* = 12.0, 8.0, 5.6 Hz, 1H), 2.44 (s, 3H), 2.00 (ddd, *J* = 12.0, 10.4, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 145.5, 135.9, 132.8, 130.0, 129.4, 129.1, 128.8, 127.0, 83.3, 78.0, 57.5, 39.3, 21.8; IR (neat) 3421, 2923, 2850, 1596, 1455, 1355, 1163, 1088, 889, 758, 672, 589 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{19}NNaO_5S$ $[M+Na]^+$ 372.0882 found 372.0873.

6. Synthesis of 8



(*Z*)-*tert*-butyl((4-cyclopropyl-1-phenylbut-3-en-1-yl)oxy)dimethylsilane (**17**)



(*Z*/*E* = 2.3 : 1)

A stirred solution of **14** (495 mg, 1.88 mmol) in CH_2Cl_2 (9.25 mL) and MeOH (0.150 mL) at –78 °C was treated with O_3 for 30 min. After N_2 was passed through the solution for 1 h to remove excess of O_3, PPh_3 (542 mg, 2.07 mmol) was added. The solution was allowed to warm up to room temperature. After 1 h, the mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure to afford the corresponding aldehyde **15**, which was directly used without further purification.

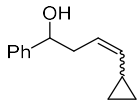
To a stirred solution of triphenylphosphonium bromide **16** (596 mg, 1.50 mmol) in THF (10.0 mL) at 0 °C was added LiHMDS (2.23 mL, 2.90 mmol, 1.30 M in THF) under N_2 atmosphere. The resulting mixture was stirred at 0 °C for 30 min, and then a solution of aldehyde **15** in THF (5.00 mL) was added. The resulting mixture was stirred at 0 °C for 2 h, and the reaction was quenched with saturated aqueous NH_4Cl (5 mL). The resulting mixture was extracted with EtOAc (10 mL x 3). The combined organic layer was washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 50 : 1) to give **17** (444 mg, 1.47 mmol, *Z*/*E* = 2.3 : 1, 78% yield (2 steps)) as

colorless oil.

The following physical data were measured as a mixture of the geometric isomers (*Z*/*E* = 2.3 : 1).

TLC Rf = 0.4 (hexane / ethyl acetate = 40 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (*Z)*-major isomer δ : 7.34-7.28 (m, 4H), 7.24-7.19 (m, 1H), 5.34-5.27 (m, 1H), 4.82-4.76 (m, 1H), 4.70 (dd, *J* = 7.2, 5.2 Hz, 1H), 2.63-2.55 (m, 1H), 2.52-2.45 (m, 1H), 1.50-1.41 (m, 1H), 0.88 (s, 9H), 0.68-0.61 (m, 2H), 0.31-0.23 (m, 2H), 0.03 (s, 3H), -0.12 (s, 3H) ; (*E)*-minor isomer δ : 7.34-7.28 (m, 4H), 7.24-7.19 (m, 1H), 5.45 (dt, *J* = 15.2, 7.2 Hz, 1H), 4.98 (ddt, *J* = 15.2, 8.8, 1.2 Hz, 1H), 4.61 (dd, *J* = 7.8, 5.2 Hz, 1H), 2.39-2.25 (m, 2H), 1.35-1.28 (m, 1H), 0.88 (s, 9H), 0.68-0.61 (m, 2H), 0.31-0.23 (m, 2H), 0.03 (s, 3H), -0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z)*-major isomer δ : 145.6, 135.9, 128.1, 127.0, 126.1, 124.2, 75.3, 39.4, 26.0, 18.4, 9.9, 7.0, 6.9, -4.5, -4.7; (*E)*-minor isomer δ : 145.6, 136.5, 128.1, 126.9, 126.0, 124.5, 75.6, 44.4, 26.0, 18.4, 13.7, 6.5, 6.4, -4.5, -4.7; IR (neat) 3082, 3005, 2929, 2857, 1654, 1602, 1492, 1471, 1388, 1361, 1255, 1090, 1004, 946, 835, 776, 699, 628 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{30}NaOSi$ $[M+Na]^+$ 325.2139 found 325.2149.

(*Z*)-4-cyclopropyl-1-phenylbut-3-en-1-ol (**18**)



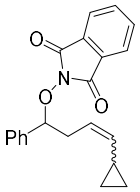
(*Z*/*E* = 1.9 : 1)

To a stirred solution of **17** (302 mg, 1.00 mmol) in THF (16.0 mL) at room temperature was added TBAF (2.00 mL, 2.00 mmol, 1.0 M in THF). After stirred for 1 h, the reaction was quenched with saturated aqueous NH_4Cl (5 mL), and the resulting mixture was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 15 : 1) to give **18** (160 mg, 0.851 mmol, *Z*/*E* = 1.9 : 1, 85% yield) as colorless oil.

The following physical data measured as a mixture of the geometric isomers (*Z*/*E* = 1.9 : 1).

TLC Rf = 0.36 (hexane / ethyl acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (*Z)*-major isomer δ: 7.41-7.34 (m, 4H), 7.30-7.26 (m, 1H), 5.37-5.30 (m, 1H), 4.97-4.91 (m, 1H), 4.76 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.74-2.66 (m, 1H), 2.63-2.56 (m, 1H), 1.61-1.52 (m, 1H), 0.79-0.66 (m, 2H), 0.38-0.29 (m, 2H); (*E)*-minor isomer δ : 7.41-7.34 (m, 4H), 7.30-7.26 (m, 1H), 5.53-5.46 (m, 1H), 5.13 (ddt, *J* = 15.2, 8.8, 1.2 Hz, 1H), 4.68 (dd, *J* = 8.0, 4.4 Hz, 1H), 2.50-2.35 (m, 2H), 1.43-1.34 (m, 1H), 0.79-0.66 (m, 2H), 0.38-0.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z)*-major isomer δ : 144.2, 138.0, 128.5, 127.6, 126.0, 123.0, 74.0, 37.8, 9.9, 7.2 x 2; (*E)*-minor isomer δ : 144.2, 138.7, 128.5, 127.5, 125.9, 123.2, 73.6, 42.9, 13.8, 6.8, 6.7; IR (neat) 3374, 3081, 3004, 2915, 1653, 1601, 1493, 1454, 1197, 1047, 964, 884, 809, 757, 700 cm^{-1}; HRMS (FAB) *m*/*z* calcd for $C_{13}H_{16}NaO$ $[M+Na]^+$ 211.1099 found 211.1107.

(*Z*)-2-((4-cyclopropyl-1-phenylbut-3-en-1-yl)oxy)isoindoline-1,3-dione (**19**)



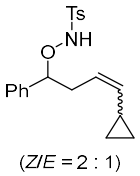
(*Z*/*E* = 1.7 : 1)

A solution of diethyl azodicarboxylate (90.5 μL, 1.99 mmol, 40% in toluene, ca. 2.2 M) was added dropwise to a solution of the alcohol **18** (150 mg, 0.797 mmol), triphenylphosphine (251 mg, 0.956 mmol) and *N*-hydroxyphthalimide (156 mg, 0.956 mmol) in THF (5.30 mL) under N_2 at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 12 : 1) to give **19** (194 mg, 0.583 mmol, *Z*/*E* = 1.7 : 1, 73% yield) as yellow oil.

The following physical data measured as a mixture of the geometric isomers (*Z*/*E* = 1.7 : 1).

TLC Rf = 0.30 (hexane / ethyl acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (*Z)*-major isomer δ : 7.75-7.70 (m, 2H), 7.69-7.65 (m, 2H), 7.51-7.45 (m, 2H), 7.35-7.28 (m, 3H), 5.46-5.38 (m, 1H), 5.36-5.26 (m, 1H), 4.85-4.79 (m, 1H), 3.13-3.06 (m, 1H), 2.91-2.80 (m, 1H), 1.53-1.44 (m, 1H), 0.76-0.58 (m, 2H), 0.33-0.21 (m, 2H); (*E)*-minor isomer δ : 7.75-7.70 (m, 2H), 7.69-7.65 (m, 2H), 7.51-7.45 (m, 2H), 7.35-7.28 (m, 3H), 5.46-5.38 (m, 1H), 5.36-5.26 (m, 1H), 5.07 (ddt, *J* = 15.2, 8.4, 1.2 Hz, 1H), 2.91-2.80 (m, 1H), 2.69-2.61 (m, 1H), 1.33-1.24 (m, 1H), 0.76-0.58 (m, 2H), 0.33-0.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z)*-major isomer δ : 163.9, 137.9, 137.0, 134.4, 129.1, 129.0, 128.4 x 2, 123.5, 121.8, 88.9, 33.4, 9.9, 7.1, 7.0; (*E)*-minor isomer δ : 163.8, 137.80, 137.76, 134.4, 129.1, 129.0, 128.4 x 2, 123.5, 121.8, 88.9, 38.1, 13.7, 6.64, 6.56; IR (neat) 3005, 2917, 1789, 1732, 1466, 1374, 1186, 1126, 1081, 1015, 974, 877, 759, 700 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{19}NNaO_3$ $[M+Na]^+$ 356.1263 found 356.1256.

(*Z*)-*N*-((4-cyclopropyl-1-phenylbut-3-en-1-yl)oxy)-4-methylbenzenesulphonamide (**7**)



(*Z*/*E* = 2 : 1)

To a stirred solution of *N*-alkoxyphthalimide **19** (194 mg, 0.543 mmol) in Et_2O (2.90 mL) at room temperature was added aqueous methylamine (140 μL, 1.74 mmol, 40 wt% in H_2O). After 30 min, the mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The saturated aqueous $NaHCO_3$ (1 mL) was added to the residue and extracted with Et_2O (3 × 5 mL). The combined organic layer was washed with brine (2 mL), dried over Na_2SO_4, filtered,

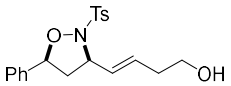
and concentrated under reduced pressure to afford the corresponding hydroxylamine **20**, which was used without further purification.

A solution of TsCl (166 mg, 0.871 mmol) and pyridine (210 μL, 1.74 mmol) in CH_2Cl_2 (1.90 mL) was added dropwise to a stirred solution of the crude hydroxylamine **20** in CH_2Cl_2 (1.00 mL) at room temperature. The resulting mixture was stirred at room temperature for 17 h. The reaction was quenched with water. The resulting mixture was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic layer was washed with water (5 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 15 : 1) to give sulphonamide **7** (100 mg 0.280 mmol, *Z*/*E* = 2 : 1, 48% yield (2 steps)) as a white solid.

The following physical data measured as a mixture of the geometric isomers (*Z*/*E* = 2 : 1).

TLC Rf = 0.25 (hexane / ethyl acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (*Z*)-major isomer δ : 7.84-7.81 (m, 2H), 7.35-7.23 (m, 7H), 6.68 (br s, 1H, -NH), 5.28 (dt, *J* = 10.8, 7.2 Hz, 1H), 5.04-5.01 (m, 1H), 4.87-4.81 (m, 1H), 2.83-2.76 (m, 1H), 2.59-2.49 (m, 1H), 2.45 (s, 3H), 1.45-1.35 (m, 1H), 0.73-0.63 (m, 2H), 0.34-0.24 (m, 2H); (*E*)-minor isomer δ : 7.84-7.81 (m, 2H), 7.35-7.23 (m, 7H), 6.63 (br s, 1H, -NH), 5.49-5.41 (m, 1H), 5.04-5.01 (m, 1H), 4.99-4.95 (m, 1H), 2.59-2.49 (m, 1H), 2.45 (s, 3H), 2.41-2.34 (m, 1H), 1.45-1.35 (m, 1H), 0.73-0.63 (m, 2H), 0.34-0.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z*)-major isomer δ : 144.9, 140.0, 136.3, 134.0, 129.8, 128.9, 128.5, 128.3, 127.3, 122.6, 88.6, 33.7, 21.8, 9.8, 7.1, 7.0; (*E*)-minor isomer δ : 144.9, 140.1, 137.2, 134.0, 129.8, 128.8, 128.5, 128.3, 127.3, 122.9, 88.6, 38.7, 21.8, 13.7, 6.7, 6.5; IR (KBr) 3224, 3000, 2919, 2850, 1597, 1451, 1345, 1167, 1092, 919, 814, 701 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{20}H_{23}NNaO_3S$ $[M+Na]^+$ 380.1296 found 380.1302.

(*E*)-4-(5-phenyl-2-tosylisoxazolidin-3-yl)but-3-en-1-ol (**8**)

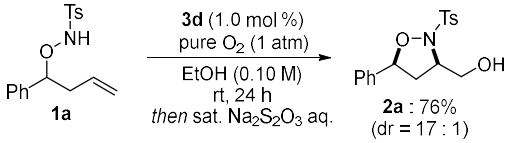


To a stirred solution of sulphonamide **7** (35.7 mg, 0.100 mmol) in EtOH (1.00 mL) at room temperature was added Mn(III)-complex **3d** (1.0 mg, 1.0 μmol) under air (open flask). After 24 h, saturated aqueous $Na_2S_2O_3$ solution (0.5 mL) was added and the mixture was stirred for 30 min. The resulting mixture was extracted with ethyl acetate (3 x 1 mL). The combined organic layer was washed with brine (2 x 1 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by preparative thin layer chromatography (silica gel, hexane / ethyl acetate = 2 : 1) to give **8** (11.2 mg, 0.0300 mmol, 30% yield, dr = 17 : 1) as colorless oil.

TLC Rf = 0.2 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.89 (dt, *J* = 8.0, 6.0 Hz, 2H), 7.35-7.27 (m, 7H), 5.82 (dt, *J* = 15.6, 8.8 Hz, 1H), 5.73 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.10 (dd, *J* = 10.0, 6.4 Hz, 1H), 4.84-4.78 (m, 1H), 3.70 (t, *J* = 6.4 Hz, 2H), 2.79 (ddd, *J* = 12.4, 6.4, 5.6 Hz,

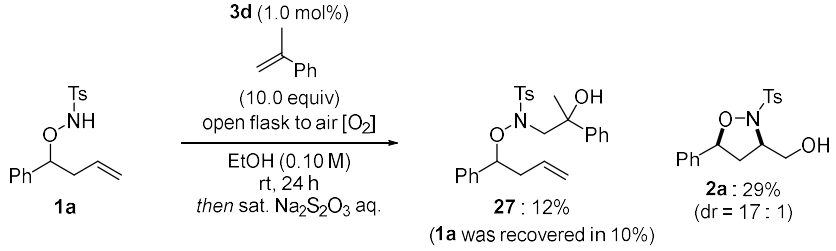
1H), 2.45 (s, 3H), 2.39-2.34 (m, 2H), 2.19 (ddd, J = 12.4, 10.0, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 145.2, 136.7, 133.0, 131.8, 130.3, 129.9, 129.5, 128.9, 128.7, 127.1, 83.2, 62.5, 61.8, 44.0, 35.7, 21.9; IR (neat) 3403, 2924, 2854, 1728, 1597, 1494, 1456, 1360, 1261, 1163, 1091, 968, 893, 804, 760, 700, 673, 593 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{23}NNaO_4S$ $[M+Na]^+$ 396.1245 found 396.1254.

(5-phenyl-2-tosylisoxazolidin-3-yl)methanol (**2a**)



To a stirred solution of sulphonamide **1a** (63.4 mg, 0.200 mmol) in EtOH (2.00 mL) at room temperature was added Mn(III)-complex **3d** (2.1 mg, 2.0 μmol) under pure O_2 (balloon, 1 atm). After 24 h, saturated aqueous $Na_2S_2O_3$ solution (0.5 mL) was added and the mixture was stirred for 30 min. The resulting mixture was extracted with ethyl acetate (3 x 1 mL). The combined organic layer was washed with brine (2 x 1 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1) to give **2a** (50.6 mg, 0.152 mmol, 76% yield, dr = 17 : 1) as colorless oil.

N-(2-hydroxy-2-phenylpropyl)-4-methyl-*N*-((1-phenylbut-3-en-1-yl)oxy)benzenesulphonamide (**27**)



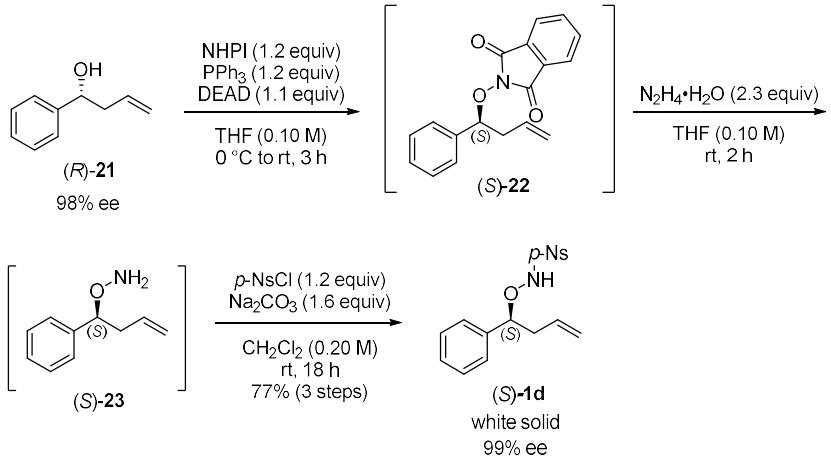
To a stirred solution of sulphonamide **1a** (31.7 mg, 0.100 mmol) and α-methylstyrene (130 μL, 1.00 mmol) in EtOH (1.00 mL) at room temperature was added Mn(III)-complex **3d** (1.0 mg, 1.0 μmol) under air (open flask). After 24 h, saturated aqueous $Na_2S_2O_3$ solution (0.5 mL) was added and the mixture was stirred for 30 min. The resulting mixture was extracted with ethyl acetate (3 x 1 mL). The combined organic layer was washed with brine (2 x 1 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by preparative thin layer chromatography (silica gel, hexane / ethyl acetate = 2 : 1) to give **27** (5.6 mg, 0.0124 mmol, 12% yield) as colorless oil and **2a** (9.7 mg, 0.0291 mmol, 29% yield, dr = 17 : 1) as colorless oil.

Data of **27**: TLC Rf = 0.53 (hexane / ethyl acetate = 3 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.83 (d, J = 0.8 Hz, 1H), 7.40-7.31 (m, 7H), 7.24-7.12 (m, 5H), 5.76-5.65 (m, 1H), 5.21(t, J = 7.2 Hz, 1H), 5.07-

5.03 (m, 2H), 3.98 (s, 1H, -OH), 3.14-3.04 (m, 2H), 2.74-2.66 (m, 1H), 2.48-2.41 (m, 4H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 146.1, 145.4 140.0, 133.9, 130.2, 129.7, 129.2, 128.78, 128.76, 128.3, 128.1, 127.0, 125.1, 117.9, 86.6, 73.4, 67.7, 40.0, 27.0, 21.8; IR (neat) 3514, 2916, 2848, 1577, 1538, 1444, 1380, 1348, 1165, 1027, 914, 818, 768, 700, 649, 566, 464 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{26}H_{29}NNaO_4S$ $[M+Na]^+$ 474.1715 found 474.1716.

7. Synthesis of HPA-12

(*S*)-4-nitro-*N*-((1-phenylbut-3-en-1-yl)oxy)benzenesulphonamide ((*S*)-**1d**)

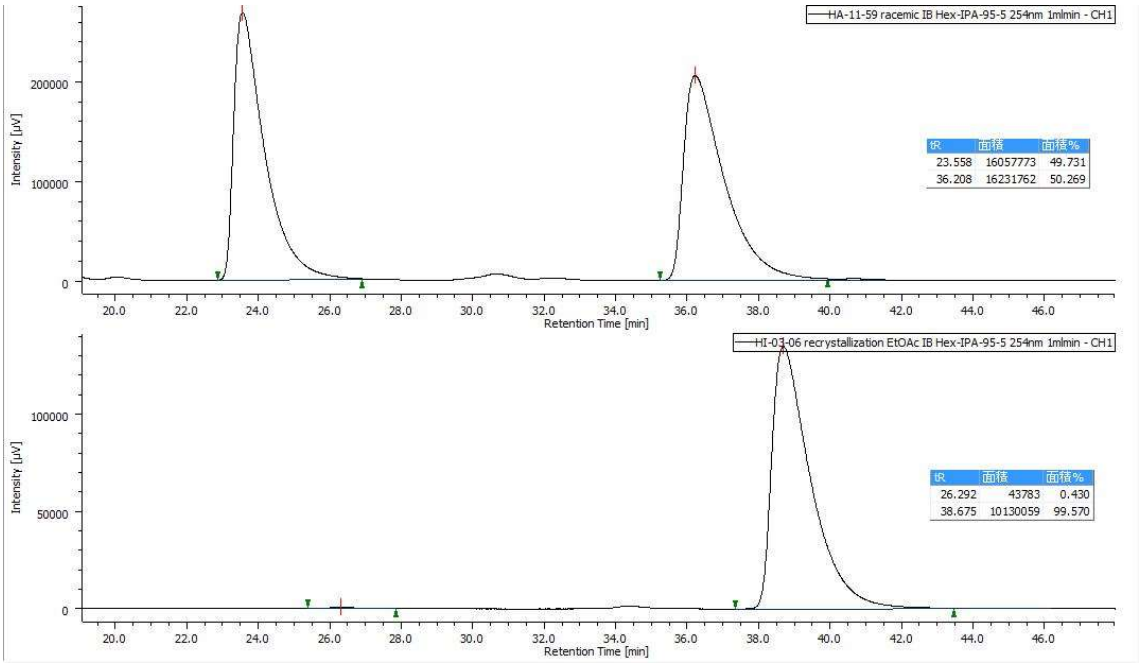


A solution of diethyl azodicarboxylate (7.48 mL, 16.4 mmol, 40% in toluene, *ca*. 2.2 M) was added dropwise to a stirred solution of the alcohol (*R*)-**21**[8] (2.03 g, 13.7 mmol), triphenylphosphine (4.30 g, 16.4 mmol) and *N*-hydroxyphthalimide (2.68 g, 16.4 mmol) in THF (137 mL) under N_2 at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h, and then hydrazine monohydrate (1.53 mL, 31.5 mmol) was added dropwise. After 2 h, the mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure to afford the corresponding amine (*S*)-**23**, which was used without further purification. A solution of the 4-nitrobenzensulphonyl chloride (3.35 g, 15.1 mmol) in CH_2Cl_2 (30.0 mL) was added dropwise over 15 min to a stirred suspension of crude amine (*S*)-**23** and Na_2CO_3 (2.32 g, 21.9 mmol) in CH_2Cl_2 (38.5 mL). The resulting mixture was stirred at room temperature for 18 h, monitoring the conversion by TLC analysis. The reaction was quenched by addition of water. Then, the resulting mixture was extracted with CH_2Cl_2 (3 x 30 mL) and the combined organic layer was washed with water (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 15 : 1 to 5 : 1) to give sulphonamide (*S*)-**1d** (3.67 g, 10.5 mmol, 77% yield (3 steps), 99% ee) as a white solid.

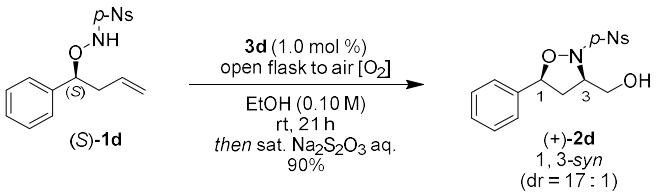
TLC Rf = 0.26 (hexane / ethyl acetate = 5 : 1); M.p. 124.9-128.7 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.37 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.11 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.38-7.31 (m, 3H), 7.29-7.24 (m, 2H),

6.82 (s, 1H, -NH), 5.84-5.74 (m, 1H), 5.14-5.05 (m, 3H), 2.68-2.61 (m, 1H), 2.53-2.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.9, 142.4, 139.2, 133.7, 130.1, 128.70, 128.68, 127.2, 124.2, 118.1, 88.8, 39.8; IR (KBr) 3321, 3235, 3103, 1527, 1349, 1300, 1170, 1088, 849, 752, 702 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2O_5S$ $[M-H]^-$ 347.0702 found 374.0685; $[\alpha]^{27}_D$ +74.0 (*c* 0.20, $CHCl_3$) for 99% ee.

HPLC (CHIRALPAK® IB, ϕ 0.46 cm × 25 cm, hexane/*i*-PrOH = 95:5, detected at 254 nm, flow rate 1.0 mL/min, t_R = 26.2 min (minor), 38.7 min (major).



((3*R*,5*S*)-2-((4-nitrophenyl)sulphonyl)-5-phenylisoxazolidin-3-yl)methanol ((+)-**2d**)



To a stirred solution of sulphonamide (*S*)-**1d** (69.7 mg, 0.200 mmol) in EtOH (2.00 mL) at room temperature was added Mn(III)-complex **3d** (2.1 mg, 2.0 μmol) under air (open flask). The progress of the reaction was monitored by TLC analysis. After 21 h, saturated aqueous $Na_2S_2O_3$ solution (0.5 mL) was added and the mixture was stirred for 30 min. The resulting mixture was extracted with ethyl acetate (3 x 1 mL). The combined organic layer was washed with brine (2 x 1 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1) to give (+)-**2d** (65.4 mg, 0.180 mmol, 90%

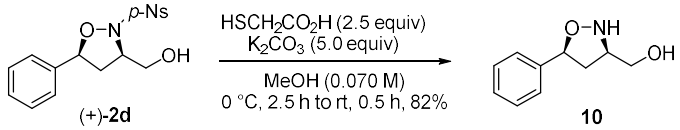
yield, dr = 17 : 1) as colorless oil.

TLC Rf = 0.16 (hexane / ethyl acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.21 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.37-7.30 (m, 5H), 5.37 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.67-4.61 (m, 1H), 3.93-3.87 (m, 1H), 3.84-3.78 (m, 1H), 2.83 (ddd, *J* = 12.4, 8.0, 6.0 Hz, 1H), 2.29 (ddd, *J* = 12.4, 10.4 , 7.6 Hz, 1H), 2.05 (t, *J* = 6.4 Hz, 1H, -O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.0, 142.0, 135.8, 130.7, 129.3, 128.9, 127.1, 124.3, 84.1, 64.5, 62.0, 38.9; IR (neat) 3545, 3107, 2929, 1606, 1532, 1458, 1351, 1312, 1168, 1091, 855, 741, 619 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{16}N_2NaO_6S$ $[M+Na]^+$ 387.0627 found 387.0617; $[\alpha]^{27}_D$ +87.2 (*c* 0.20, $CHCl_3$).

(2 mmol Scale Reaction)

To a stirred solution of sulphonamide (*S*)-**1d** (697 mg, 2.00 mmol) in EtOH (20.0 mL) at room temperature was added Mn(III)-complex **3d** (18.9 mg, 0.0200 mmol) under air (open flask). The progress of the reaction was monitored by TLC analysis. After 48 h, saturated aqueous $Na_2S_2O_3$ solution (5 mL) was added and the mixture was stirred for 30 min. The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine (2 x 10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1) to give (+)-**2d** (690 mg, 1.90 mmol, 95% yield, dr = 17 : 1) as colorless oil.

((3*R*,5*S*)-5-phenylisoxazolidin-3-yl)methanol (**10**)

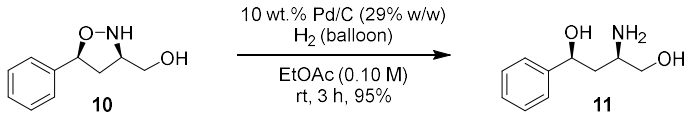


To a stirred solution of (+)-**2d** (200 mg, 0.549 mmol) in MeOH (7.85 mL) at 0 °C was dropwise added thioglycolic acid (94.0 μL, 1.38 mmol) under N_2. Anhydrous potassium carbonate (253 mg, 2.75 mmol) was added portionwise. The resulting mixture was stirred at 0 °C for 2.5 h and gradually warmed up to room temperature. After 0.5 h, the mixture was concentrated under reduced pressure. The residue was dissolved in aqueous 9% Na_2CO_3 (10 mL), and the resulting mixture was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layer was washed with aqueous 9% Na_2CO_3 (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, $CHCl_3$: MeOH = 100 : 1) to give **10** (80.6 mg, 0.450 mmol, 82% yield) as colorless oil.

TLC Rf = 0.48 ($CHCl_3$: MeOH = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.37-7.28 (m, 5H), 4.81 (t, *J* = 8.4 Hz, 1H), 3.77-3.70 (m, 1H), 3.62 (dd, *J* = 11.2, 8.8 Hz, 1H), 3.54 (dd, *J* = 11.2, 4.4 Hz, 1H), 2.74 (dt, *J* = 12.8, 8.0 Hz, 1H), 1.80 (ddd, *J* = 13.2, 9.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 138.7, 128.7, 128.3, 126.6, 85.4, 64.3, 62.5, 40.0; IR (neat) 3372, 2918, 2881, 1637, 1489, 1454,

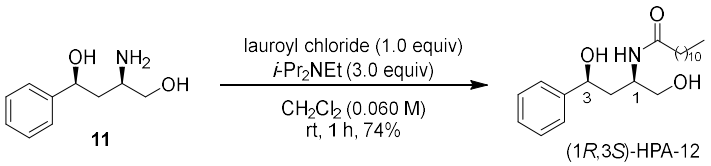
1379, 1262, 1061, 1022, 944, 904, 799, 759, 700 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{13}NNaO_2$ $[M+Na]^+$ 202.0844 found 202.0836; $[\alpha]^{27}_D$ -111.8 (*c* 0.80, $CHCl_3$)

(1*S*,3*R*)-3-amino-1-phenylbutane-1,4-diol (**11**)



A mixture of **10** (20.0 mg, 0.112 mmol) and 10% Pd/C (5.80 mg) in ethyl acetate (1.10 mL) was stirred for 3 h under H_2 atmosphere (balloon, 1 atm). The catalyst was filtered off and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, $CHCl_3$: MeOH = 10 : 1) to give **11** (19.3 mg, 0.10 mmol, 95% yield) as colorless oil.
TLC Rf = 0.13 ($CHCl_3$ / MeOH = 10 : 1); ^{1}H NMR (400 MHz, CDOD) δ : 7.39-7.31 (m, 4H), 7.26-7.23 (m, 1H), 4.84-4.81 (m, 1H), 3.59 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.47 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.15-3.09 (m, 1H), 1.87-1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 146.3, 129.4, 128.4, 126.8, 73.9, 65.8, 53.2, 41.9; IR (neat) 3357, 2923, 2845, 1561, 1495, 1454, 1407, 1204, 1054, 912, 849, 760, 702, 563 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{16}NO_2$ $[M+H]^+$ 182.1181 found 182.1180; $[\alpha]^{27}_D$ -43.2 (*c* 0.90, MeOH)

(1*R*,3*S*)-HPA-12 (*N*-((2*R*,4*S*)-1,4-dihydroxy-4-phenylbutan-2-yl)dodecanamide)

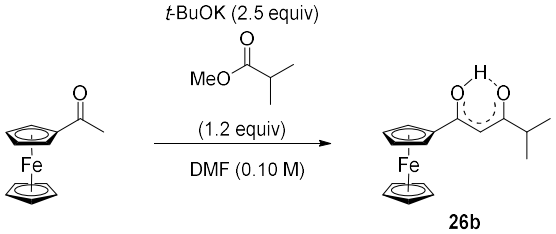


To a stirred solution of amine **11** (19.3 mg, 0.100 mmol) and *N,N*-diisopropylethylamine (55.0 µL, 0.300 mmol) in dichloromethane (1.67 mL) at 0 °C was added dropwise lauroyl chloride (25.3 µL, 0.100 mmol). After stirred for 20 min at this temperature, the mixture was gradually warmed to room temperature and stirred for additional 30 min. The reaction was quenched by slowly addition of ice-cold 1 M HCl solution (2 mL) at 0 °C. The resulting mixture was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layer was washed with aqueous saturated $NaHCO_3$ solution (5 mL), brine (5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1 to $CHCl_3$: MeOH = 7 : 1) to give (1*R*,3*S*)-HPA-12 (26.9 mg, 0.074 mmol, 74% yield) as a white solid.
TLC Rf = 0.47 ($CHCl_3$: MeOH = 10 : 1); M.p. 87.2-89.0 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.35-7.34 (m, 4H), 7.31-7.27 (m, 1H), 6.56 (br d, 1.6 Hz, 1H), 4.83 (dd, *J* = 8.8, 3.2 Hz, 1H), 4.09-4.06 (m, 1H), 3.70 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.67 (dd, *J* = 11.6, 4.0 Hz, 1H), 2.96 (br s, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 2.06 (ddd, *J* = 14.4, 5.2, 3.2 Hz, 2H), 1.94 (ddd, *J* = 14.4 8.8 7.2 Hz, 2H), 1.65-1.58 (m,

2H), 1.33-1.26 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ :174.6, 144.4, 128.7, 127.9, 125.7, 72.1, 65.8, 50.7, 40.9, 36.9, 32.1, 29.78, 29.76, 29.7, 29.51, 29.48, 29.4, 25.9, 22.8, 14.3; IR (KBr) 3360, 3055, 2927, 2854, 1647, 1521, 1422, 1265, 743 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{37}NNaO_3$ $[M+Na]^+$ 386.2671 found 386.2660; $[\alpha]^{25}_D$ -35.4 (c 0.2, $CHCl_3$) for 99% ee.

8. Preparation of the (ferrocenyl)butane-1,3-dione derivatives (26b−e, g, h)

5-ferrocenyl-5-hydroxy-1-methylpent-4-en-3-one (**26b**)[9]

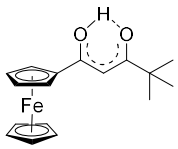


(Representative procedure)

To a stirred solution of *t*-BuOK (7.50 mL, 7.50 mmol, solution 1.00 M in THF) in DMF (15.0 mL) at 50 °C under N_2 atmosphere was added dropwise a solution of acetylferrocene (684 mg, 3.00 mmol) in DMF (5.00 mL). After 10 min, methyl isobutyrate (413 μL, 3.60 mmol) was added slowly. The progress of the reaction was monitored by TLC analysis. The reaction was quenched with brine (10 mL). The resulting mixture was extracted with Et_2O (3 x 10 mL) and the combined organic layer was washed with HCl (10 mL, 3.0 M in H_2O), water (10 mL), and brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : ethyl acetate = 20 : 1) to give **26b** (823 mg, 2.76 mmol, 92% yield, enol form : diketone form = 8 : 1) as a dark-orange solid.

TLC Rf = 0.52 (hexane : ethyl acetate = 5 : 1); M.p. 55.4-59.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) (enol form) δ : 5.72 (s, 1H), 4.78 (t, J = 2.0 Hz, 2H), 4.49 (t, J = 2.0 Hz, 2H), 4.18 (s, 5H), 2.50 (q, J = 6.8 Hz, 1H), 1.21 (d, J = 6.8 Hz, 6H). (diketone form) δ : 4.78 (t, J = 2.0 Hz, 2H), 4.56 (t, J = 2.0 Hz, 2H), 4.24 (s, 5H), 3.89 (s, 2H), 2.50 (q, J = 6.8 Hz, 1H), 1.15 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (enol form) δ : 194.1, 193.0, 94.3, 78.1, 72.0, 70.4, 68.7, 36.1, 19.8. (diketone form) δ : 208.3, 197.9, 79.0, 73.0, 70.1, 69.9, 52.8, 41.3, 18.1; IR (neat) 3374, 3097, 2969, 2929, 2871, 2335, 1710, 1603, 1326, 1026, 925, 820, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{18}{}^{56}FeNaO_2$ $[M+Na]^+$ 321.0554 found 321.0538.

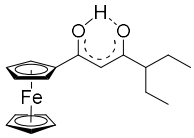
2,2-dimethyl-5-ferrocenyl-5-hydroxypent-4-en-3-one (**26c**)[10]



According to the representative procedure, the reaction gave **26c** (655 mg, 2.10 mmol, 70% yield, enol form : diketone form = 12.5 : 1) as dark-orange amorphous material from acetylferrocene (684 mg, 3.00 mmol) and methyl pivalate (475 μL, 3.60 mmol).

TLC Rf = 0.52 (hexane : ethyl acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (enol form) δ : 5.82 (s, 1H), 4.79 (t, *J* = 2.0 Hz, 2H), 4.49 (t, *J* = 2.0 Hz, 2H), 4.18 (s, 5H), 1.24 (s, 9H). (diketone form) δ : 4.76 (t, *J* = 2.0 Hz, 2H), 4.54 (t, *J* = 2.0 Hz, 2H), 4.26 (s, 5H), 3.93 (s, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (enol form) δ : 195.9, 193.5, 92.5, 78.4, 72.0, 70.4, 68.7, 38.5, 27.7. (diketone form) δ : 209.8, 198.5, 79.1, 72.8, 70.1, 69.9, 48.8, 45.2, 26.3; IR (KBr) 3449, 2964, 2873, 1654, 1560, 1293, 1105, 1032, 824, 502 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{20}{}^{56}FeO_2$ $[M]^+$ 312.0813 found 312.0806.

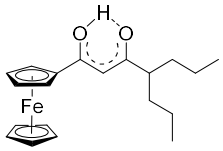
3-ethyl-6-ferrocenyl-6-hydroxyhex-5-en-4-one (**26d**)



According to the representative procedure, the reaction gave **26d** (186 mg, 0.570 mmol, 19% yield, enol form : diketone form = 9.3 : 1) as a dark-red solid from acetylferrocene (684 mg, 3.00 mmol) and methyl 2-ethylbutanoate (469 mg, 3.60 mmol).

TLC Rf = 0.76 (hexane : ethyl acetate = 3 : 1); M.p. 64.9-66.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) (enol form) δ : 5.71 (s, 1H), 4.80 (t, *J* = 2.0 Hz, 2H), 4.50 (t, *J* = 2.0 Hz, 2H), 4.18 (s, 5H), 2.05-1.98 (m, 1H), 1.72-1.47 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 6H). (diketone form) δ : 4.79 (t, *J* = 2.0 Hz, 2H), 4.55 (t, *J* = 2.0 Hz, 2H), 4.18 (s, 5H), 2.05-1.98 (m, 1H), 1.72-1.43 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (enol form) δ : 193.5, 191.1, 97.5, 72.16, 72.15, 70.4, 68.8, 51.3, 25.8, 12.2. (diketone form) δ : 209.1, 199.6, 78.1, 73.1, 70.1, 70.0, 55.3, 54.4, 23.5, 11.7; IR (KBr) 3426, 2964, 2929, 2873, 1622, 1558, 1476, 1274, 1105, 998, 936, 820, 500 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{22}{}^{56}FeNaO_2$ $[M+Na]^+$ 349.0867 found 349.0857.

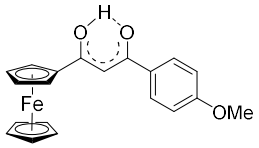
7-ferrocenyl-7-hydroxy-4-propylsept-6-en-5-one (**26e**)



According to the representative procedure, the reaction gave **26e** (266 mg, 0.751 mmol, 25% yield, enol form : diketone form = 12.6 : 1) as dark-orange oil from acetylferrocene (684 mg, 3.00 mmol) and methyl 2-propylpentanoate (569 mg, 3.60 mmol).

TLC Rf = 0.62 (hexane : ethyl acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (enol form) δ: 5.70 (s,1H), 4.80 (br s, 2H), 4.50 (br s, 2H), 4.18 (s, 5H), 2.24-2.17 (m, 1H), 1.69-1.60 (m, 2H), 1.49-1.25 (m, 6H), 0.92 (t, *J* = 7.2, 6H). (diketone form) δ: 4.78 (br s, 2H), 4.55 (br s, 2H), 4.25 (s, 5H), 3.85 (s, 2H), 2.24-2.17 (m, 1H), 1.69-1.60 (m, 2H), 1.49-1.25 (m, 6H), 0.90 (t, *J* = 7.2, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (only enol form) δ: 193.3, 191.7, 97.3, 72.17, 72.16, 70.4, 68.8, 47.5, 35.4, 20.9, 14.3. (diketone form) δ: 208.2, 199.6, 78.1, 73.1, 70.1, 70.0, 54.2, 52.2, 33.3, 20.7, 14.4; IR (neat) 3374, 2957, 2929, 2869, 1713, 1608, 1356, 1272, 1104, 1024, 923, 818, 694 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{26}{}^{56}FeNaO_2$ $[M+Na]^+$ 377.1180 found 377.1169.

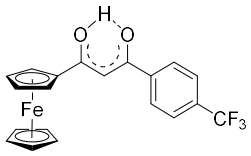
3-ferrocenyl-3-hydroxy-1-(4-methoxyphenyl)prop-2-en-1-one (**26g**)



According to the representative procedure, the reaction gave **26g** (988 mg, 2.73 mmol, 91% yield, enol form : diketone form = 1.6 : 1) as a dark-red solid from acetylferrocene (684 mg, 3.00 mmol) and methyl *p*-anisate (598 mg, 3.60 mmol).

TLC Rf = 0.36 (hexane : ethyl acetate = 5 : 1); M.p. 102.4-108.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) (only enol form) δ: 7.92 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.34 (s,1H), 4.87 (br s, 2H), 4.53 (br s, 2H), 4.21 (s, 5H), 3.88 (s, 3H). (diketone form) δ : 8.11 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.88 (br s, 2H), 4.55 (br s, 2H), 4.30 (s, 5H), 4,13 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (enol form) δ: 192.7, 180.6, 162.9, 131.7, 128.8, 114.1, 92.8, 78.4, 72.1, 70.4, 68.7, 55.6. (diketone form) δ : 197.7, 191.7, 164.1, 129.8, 127.9, 114.1, 79.2, 73.0, 70.3, 70.2, 55.7, 52.9; IR (KBr) 3855, 3449, 3083, 2995, 2934, 2244, 1603, 1524, 1261, 1032, 996, 815, 713, 495 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{18}{}^{56}FeNaO_3$ $[M+Na]^+$ 385.0503 found 385.0492.

3-ferrocenyl-3-hydroxy-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**26h**)

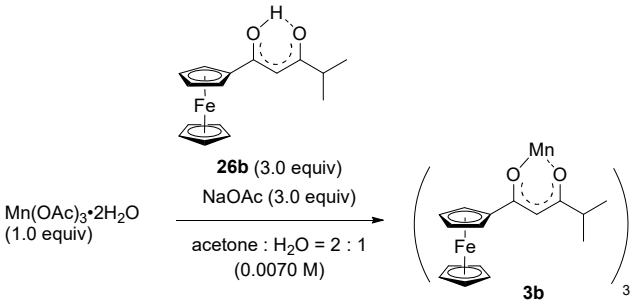


According to the representative procedure, the reaction gave **26h** (1.07 g, 2.67 mmol, 89% yield, only enol form) as a dark-red solid from acetylferrocene (684 mg, 3.00 mmol) and methyl 4-(trifluoromethyl)benzoate (565 μL, 3.60 mmol).

TLC Rf = 0.51 (hexane : ethyl acetate = 5 : 1); M.p. 135-137.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) (only enol form) δ: 8.03 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 6.38 (s,1 H), 4.91 (br s, 2H), 4.61 (br s, 2H), 4.24 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) (only eno l form) δ: 195.3, 177.3, 138.7, 133.3 (q, J_{F-C} = 32 Hz), 127.1, 125.8 (q, J_{F-C} = 4 Hz) 123. 9 (q, J_{F-C} = 271 Hz), 94.7, 78.1, 72.8, 70.6, 69.1; IR (KBr) 3855, 3442, 3083, 2225, 1610, 1507, 1326, 1125, 1013, 855, 729, 485 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{15}F_3{}^{56}FeNaO_2$ $[M+Na]^+$ 423.0271 found 423.0262.

9. Preparation of the Mn(III)-complexes (3a−i)

tris(1-ferrocenyl-4-methylpentane-1,3-dionato)manganese(III) (**3b**)



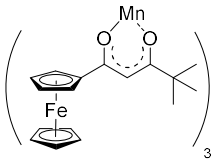
(Representative procedure)

To a stirred solution of ligand **26b** (293 mg, 0.900 mmol) in acetone (30.0 mL) at room temperature was added an aqueous solution of $Mn(OAc)_3$•$2H_2O$ (80.0 mg, 0.300 mmol) in H_2O (9.00 mL). After the dropwise addition of a solution of NaOAc (73.8 mg, 0.900 mmol) in H_2O (6.00 mL), the reaction mixture was allowed to stir under ambient conditions for 16 h. The resulting precipitate was collected by filtration and washed first with plenty of water and then with MeOH. Dried under vacuum at room temperature to afford **3b** (503 mg, 0.532 mmol, 73% yield) as a brown solid.

M.p. 170.3-175.9 ºC; IR (KBr) 2959, 2925, 2867, 1654, 1509, 1411, 1087, 485 cm^{-1}; HRM S (APCI+) *m/z* calcd for $C_{48}H_{52}{}^{56}Fe_3{}^{55}MnO_6$ $[M+H]^+$ 947.1193 found 947.1154.

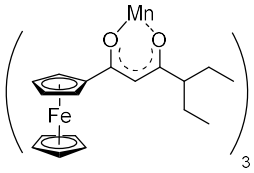
3a, **f**, and **i** were prepared by a known procedure[11].

tris(1-ferrocenylpentane-1,3-dionato)manganese(III) (**3c**)



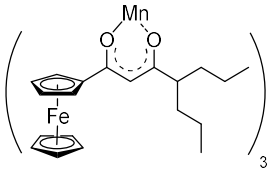
According to the representative procedure, the reaction gave **3c** (702 mg, 0.711 mmol, 79% yield) as a brown solid from $Mn(OAc)_3•2H_2O$ (80.0 mg, 0.300 mmol) and **26c** (281 mg, 0.900 mmol).
M.p. 172.3-178.1 ºC; IR (KBr) 2961, 1560, 1509, 1401, 1287, 1111, 951, 715, 488 cm^{-1}; HRMS (APCI+) *m/z* calcd for $C_{51}H_{58}{}^{56}Fe_3{}^{55}MnO_6$ $[M+H]^+$ 989.1662 found 989.1621.

tris(4-ethyl-1-ferrocenylhexane-1,3-dionato)manganese(III) (**3d**)



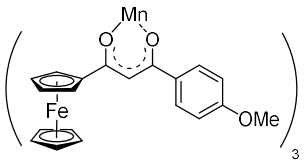
According to the representative procedure, the reaction gave **3d** (238 mg, 0.231 mmol, 77% yield) as a brown solid from $Mn(OAc)_3•2H_2O$ (80.0 mg, 0.300 mmol) and **26d** (293 mg, 0.900 mmol).
M.p. 155.5-158.9 ºC; IR (KBr) 2960, 2925, 2869, 1561, 1509, 1412, 1273, 1105, 951, 732, 503 cm^{-1}; HRMS (APCI+) *m/z* calcd for $C_{54}H_{64}{}^{56}Fe_3{}^{55}MnO_6$ $[M+H]^+$ 1031.2132 found 1031. 2046.

tris(1-ferrocenyl-4-propylseptane-1,3-dionato)manganese(III) (**3e**)



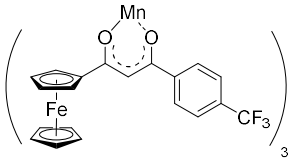
According to the representative procedure, the reaction gave **3e** (298 mg, 0.267 mmol, 89% yield) as a brown solid from $Mn(OAc)_3•2H_2O$ (80.0 mg, 0.300 mmol) and **26e** (319 mg, 0.900 mmol).
M.p. 144.8-155.4 ºC; IR (KBr) 2953, 2925, 2864, 1561, 1509, 1410, 1270, 1058, 734, 479 cm^{-1}; HRMS (APCI+) *m/z* calcd for $C_{60}H_{76}{}^{56}Fe_3{}^{55}MnO_6$ $[M+H]^+$ 1115.3071 found 1115.2908.

tris(1-ferrocenyl-3-(4-methoxyphenyl)propane-1,3-dionato)manganese(III) (**3g**)



According to the representative procedure, the reaction gave **3g** (297 mg, 0.261 mmol, 87% yield) as a red solid from $Mn(OAc)_3 \bullet 2H_2O$ (80.0 mg, 0.300 mmol) and **26g** (326 mg, 0.900 mmol).
M.p. 242.2-249.2 ºC; IR (KBr) 3090, 2959, 2836, 1522, 1497, 1374, 1233, 1172, 1026, 786, 496 cm^{-1}; HRMS (APCI+) *m*/*z* calcd for $C_{60}H_{52}{}^{56}Fe_3{}^{55}MnO_9$ $[M+H]^+$ 1139.1040 found 1139.0980.

tris(1-ferrocenyl-3-(4-(trifluoromethyl)phenyl)propane-1,3-dionato)manganese(III) (**3h**)

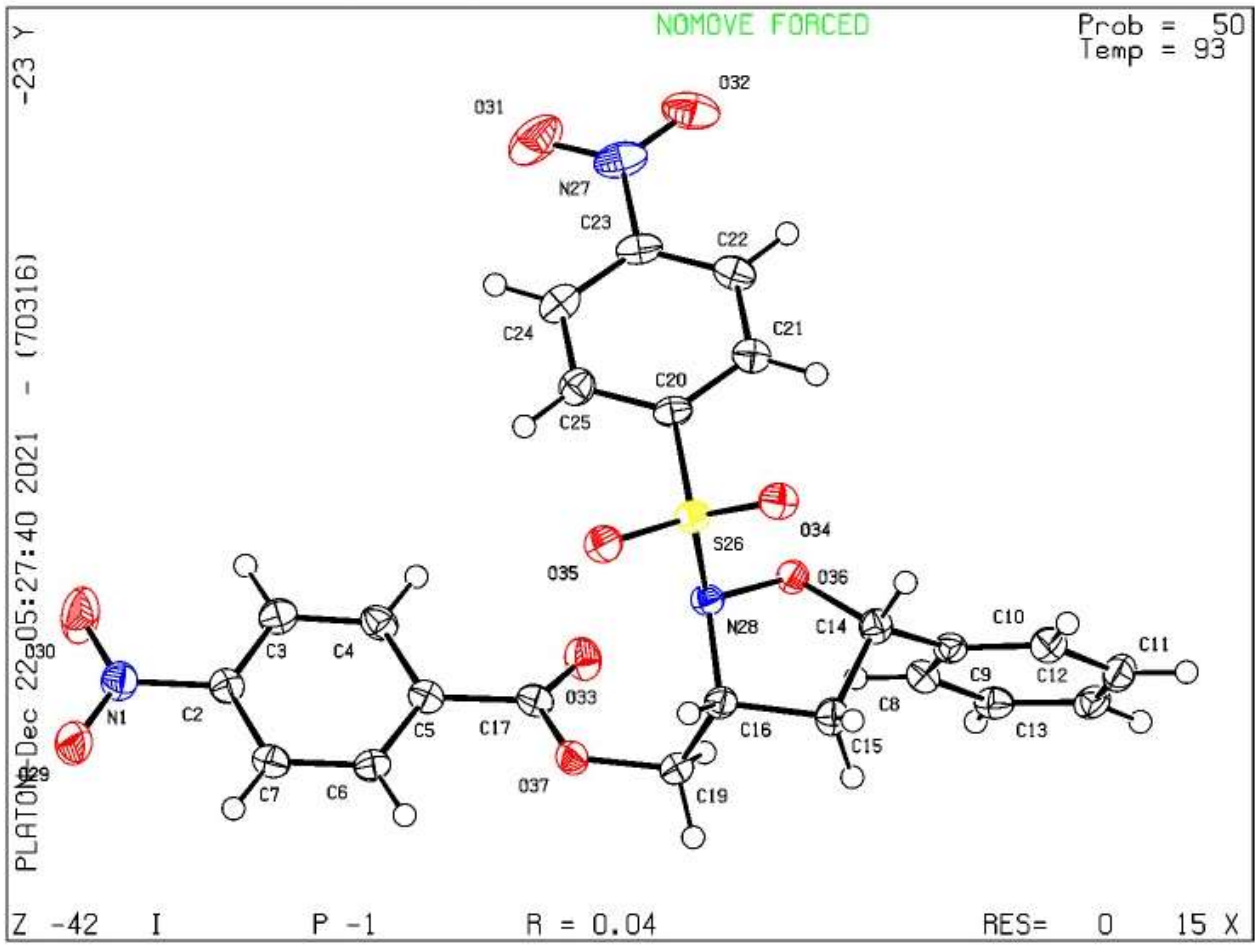


According to the representative procedure, the reaction gave **3h** (364 mg, 0.291 mmol, 97% yield) as a black solid from $Mn(OAc)_3 \bullet 2H_2O$ (80.0 mg, 0.300 mmol) and **26h** (360 mg, 0.900 mmol).
M.p. 197.2-208.6 ºC; IR (KBr) 3097, 1528, 1500, 1322, 938, 785, 484 cm^{-1}; HRMS (APCI+) *m*/*z* calcd for $C_{60}H_{43}F_9{}^{56}Fe_3{}^{55}MnO_6$ $[M+H]^+$ 1253.0345 found 1253.0118.

10. X-ray structure of 12, 13 and 3d

All the crystals were obtained by the slow diffusion method from the mixture of AcOEt/*n*-hexane at room temperature. A suitable single crystal was selected and mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Cu-Ka radiation.

Figure S13. X-ray crystallography of **12**



The detail of the obtained data is available as a crystallographic information file (CIF), which is available from CCDC (2131101).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{23}H_{19}N_3O_9S$
Formula Weight	513.48
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.300 X 0.300 X 0.100 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.23789(13) Å b = 12.2345(2) Å c = 13.6811(3) Å α = 72.142(5) ^{o} β = 82.584(6) ^{o} γ = 80.322(6) ^{o} V = 1132.82(5) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.505 g/cm^3
F_{000}	532.00
μ(CuKα)	18.214 cm^{-1}

B. Intensity Measurements

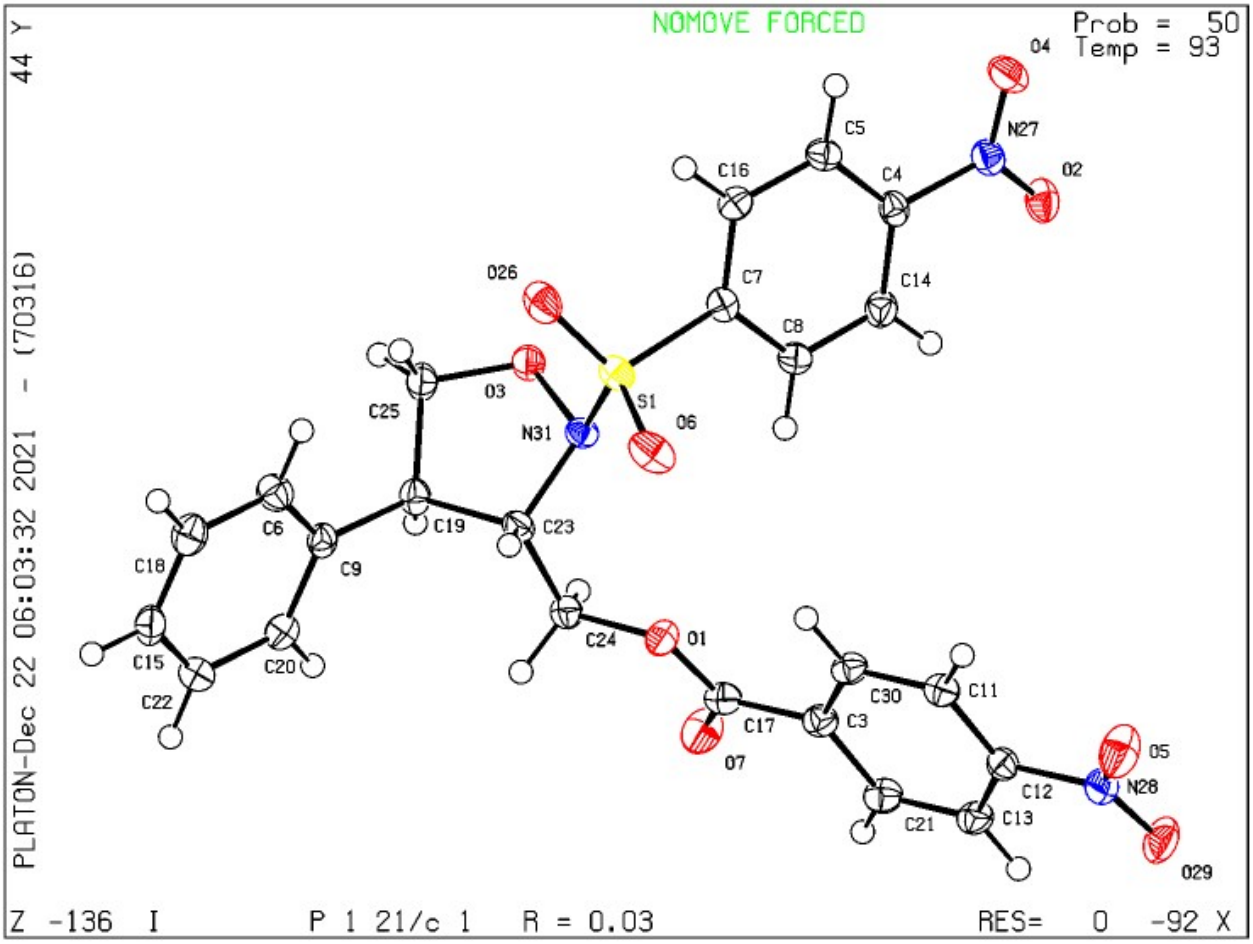
Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-180.0^{o}C
Detector Aperture	460.0 x 256.0 mm
Data Images	90 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=90.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=270.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
ω oscillation Range (χ=0.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
Detector Position	127.40 mm

Pixel Size	0.100 mm
$2\theta_{max}$	136.4°
No. of Reflections Measured	Total: 12761 Unique: 4072 (R_{int} = 0.0302)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.591 - 0.833) Secondary Extinction (coefficient: 6.10000e-004)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS2013)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0385 \cdot P)^2 + 0.7575 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.4^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	4072
No. Variables	326
Reflection/Parameter Ratio	12.49
Residuals: R1 (I>2.00σ(I))	0.0394
Residuals: R (All reflections)	0.0462
Residuals: wR2 (All reflections)	0.0963
Goodness of Fit Indicator	1.036
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.45 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.33 $e^-/Å^3$

Figure S14. X-ray crystallography of **13**



The detail of the obtained data is available as a crystallographic information file (CIF), which is available from CCDC (2132840).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{23}H_{19}N_3O_9S$
Formula Weight	513.48
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.300 X 0.200 X 0.200 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 15.7934(3) Å b = 6.97062(13) Å c = 20.9252(4) Å α = 90.0000 ^{o} β = 106.862(8) ^{o} γ = 90.0000 ^{o} V = 2204.60(11) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.547 g/cm^3
F_{000}	1064.00
μ(CuKα)	18.718 cm^{-1}

B. Intensity Measurements

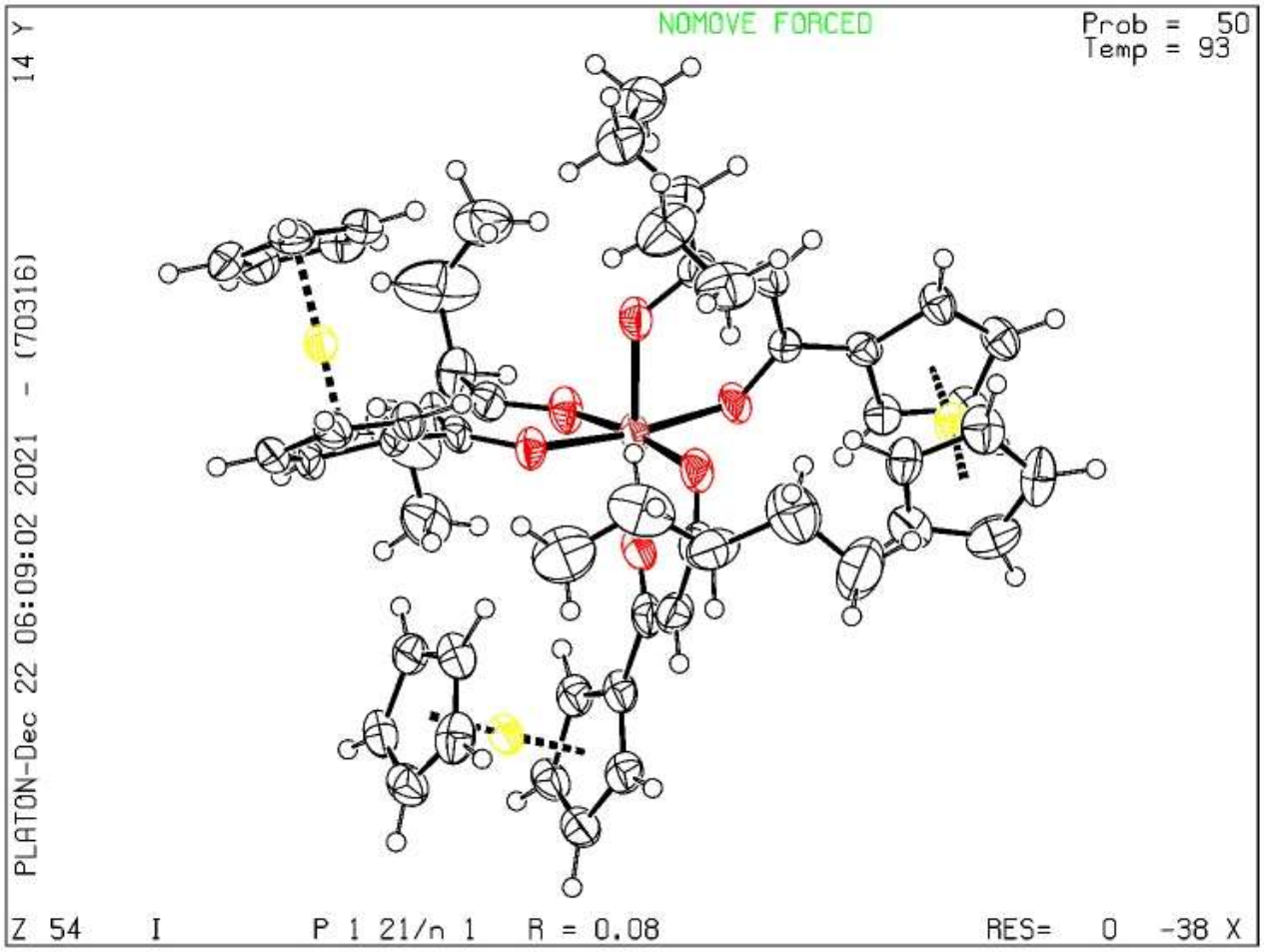
Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-180.0^{o}C
Detector Aperture	460.0 x 256.0 mm
Data Images	180 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	60.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=90.0)	80.0 - 260.0^{o}
Exposure Rate	60.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	80.0 - 260.0^{o}
Exposure Rate	60.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=270.0)	80.0 - 260.0^{o}
Exposure Rate	60.0 sec./^{o}
ω oscillation Range (χ=10.0, ϕ=60.0)	80.0 - 260.0^{o}
Exposure Rate	60.0 sec./^{o}
Detector Position	127.40 mm

Pixel Size	0.100 mm
$2\theta_{max}$	136.4°
No. of Reflections Measured	Total: 24080 Unique: 4006 (R_{int} = 0.0283)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.515 - 0.688) Secondary Extinction (coefficient: 1.20000e-004)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR2008)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0376 \cdot P)^2 + 1.5675 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.4°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	4006
No. Variables	326
Reflection/Parameter Ratio	12.29
Residuals: R1 (I>2.00σ(I))	0.0340
Residuals: R (All reflections)	0.0385
Residuals: wR2 (All reflections)	0.0852
Goodness of Fit Indicator	1.040
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.27 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.41 $e^-/Å^3$

Figure S15. X-ray crystallography of **3d**



The detail of the obtained data is available as a crystallographic information file (CIF), which is available from CCDC (2132912).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{54}H_{63}Fe_3MnO_6$
Formula Weight	1030.57
Crystal Color, Habit	black, platelet
Crystal Dimensions	0.500 X 0.300 X 0.300 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 11.5777(2) Å b = 23.2895(4) Å c = 17.4903(3) Å α = 90.0000 ^{o} β = 92.923(7) ^{o} γ = 90.0000 ^{o} V = 4709.91(15) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.453 g/cm^3
F_{000}	2152.00
μ(CuKα)	97.983 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-180.0^{o}C
Detector Aperture	460.0 x 256.0 mm
Data Images	90 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	120.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=90.0)	80.0 - 260.0^{o}
Exposure Rate	120.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	80.0 - 260.0^{o}
Exposure Rate	120.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=270.0)	80.0 - 260.0^{o}
Exposure Rate	120.0 sec./^{o}
ω oscillation Range (χ=0.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	120.0 sec./^{o}
Detector Position	127.40 mm

Pixel Size	0.100 mm
$2\theta_{max}$	136.5°
No. of Reflections Measured	Total: 51218 Unique: 8583 (R_{int} = 0.1000)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.026 - 0.053)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS2013)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.1004 \cdot P)^2 + 6.0496 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.5^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	8583
No. Variables	577
Reflection/Parameter Ratio	14.88
Residuals: R1 (I>2.00σ(I))	0.0785
Residuals: R (All reflections)	0.1145
Residuals: wR2 (All reflections)	0.2166
Goodness of Fit Indicator	1.081
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.77 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.84 $e^-/Å^3$

11. Reference

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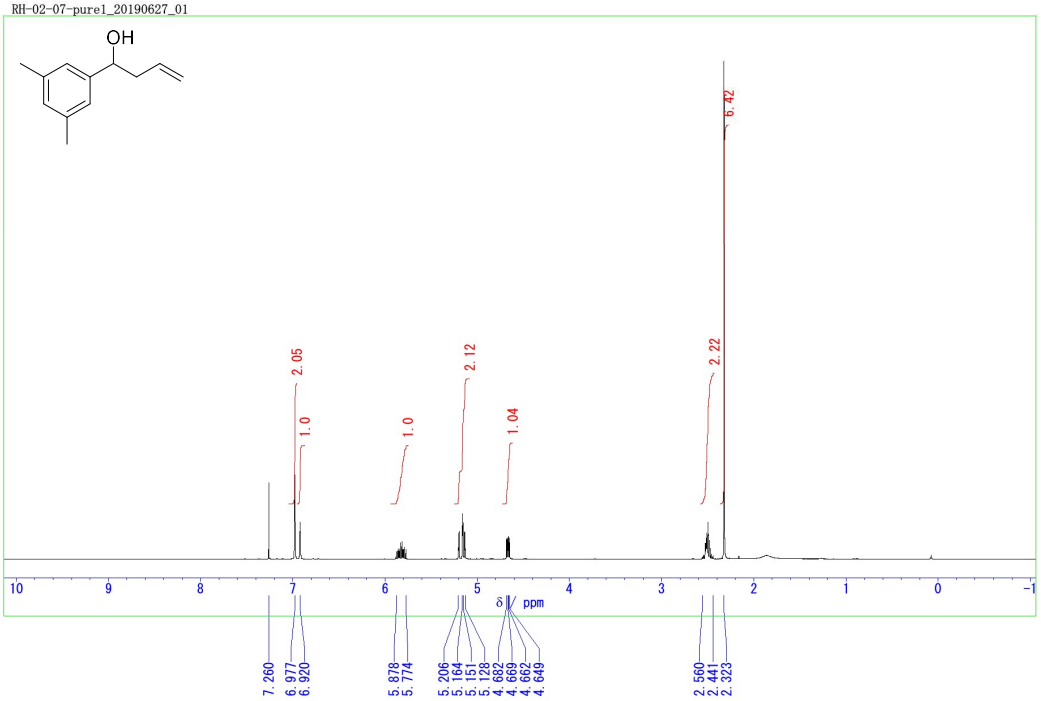

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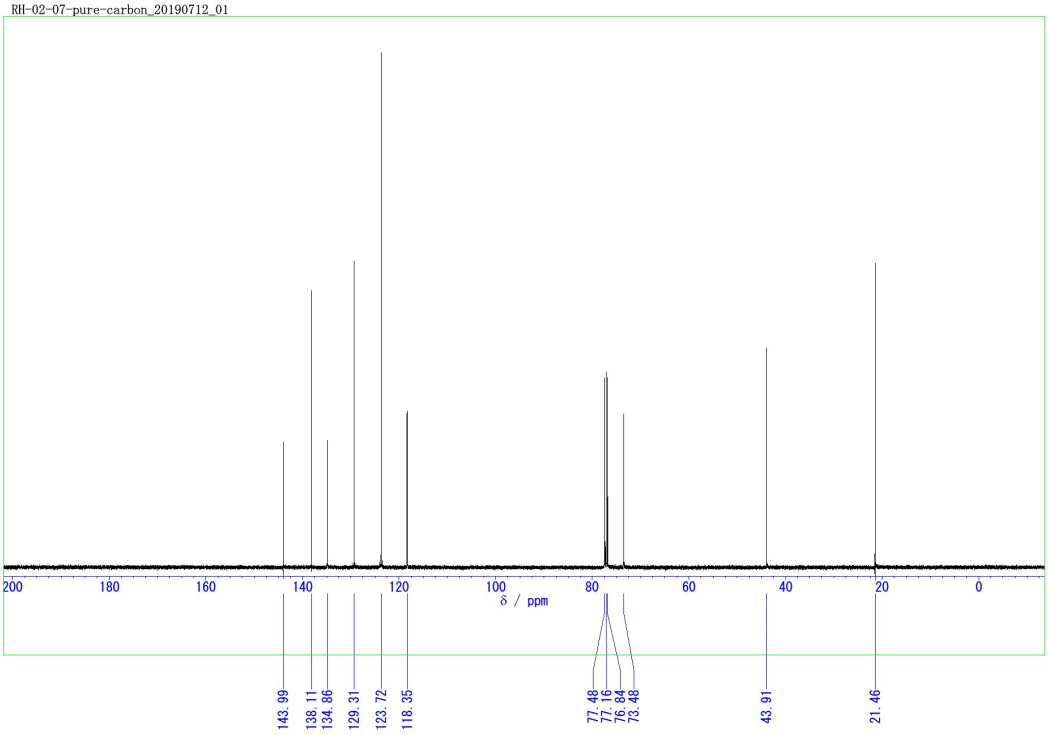

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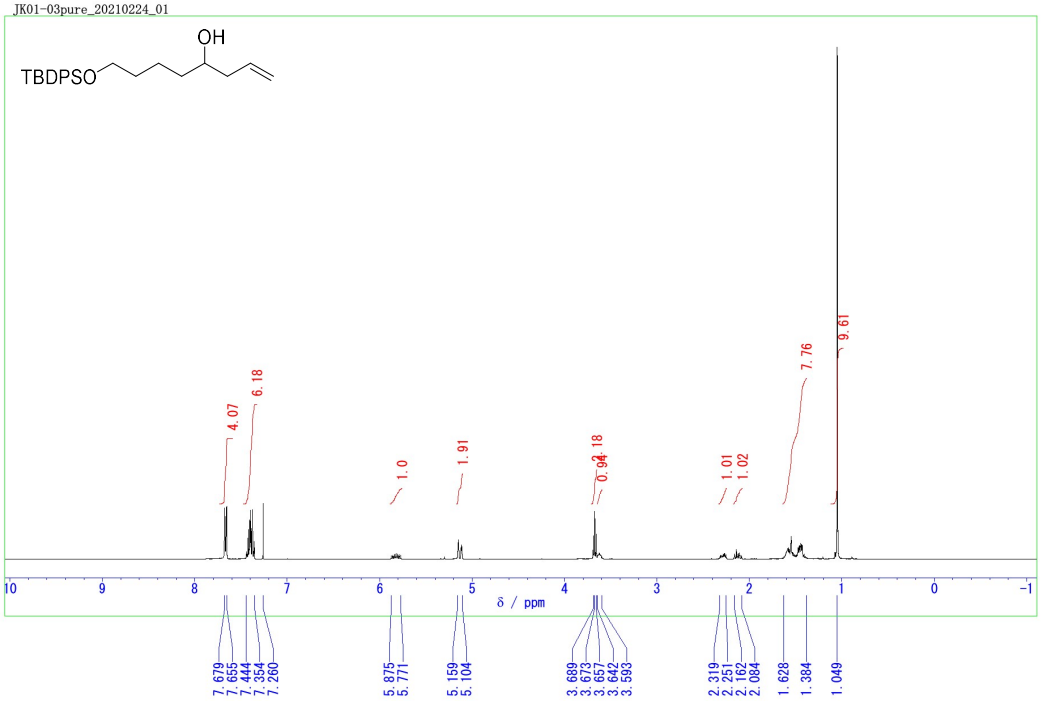

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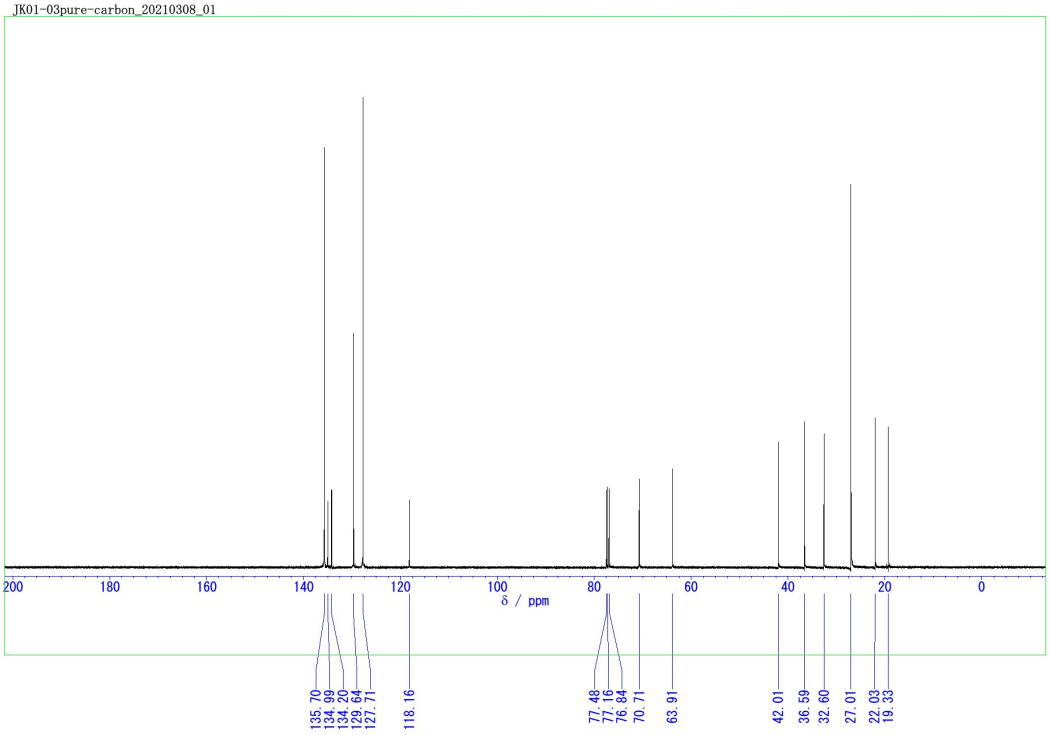

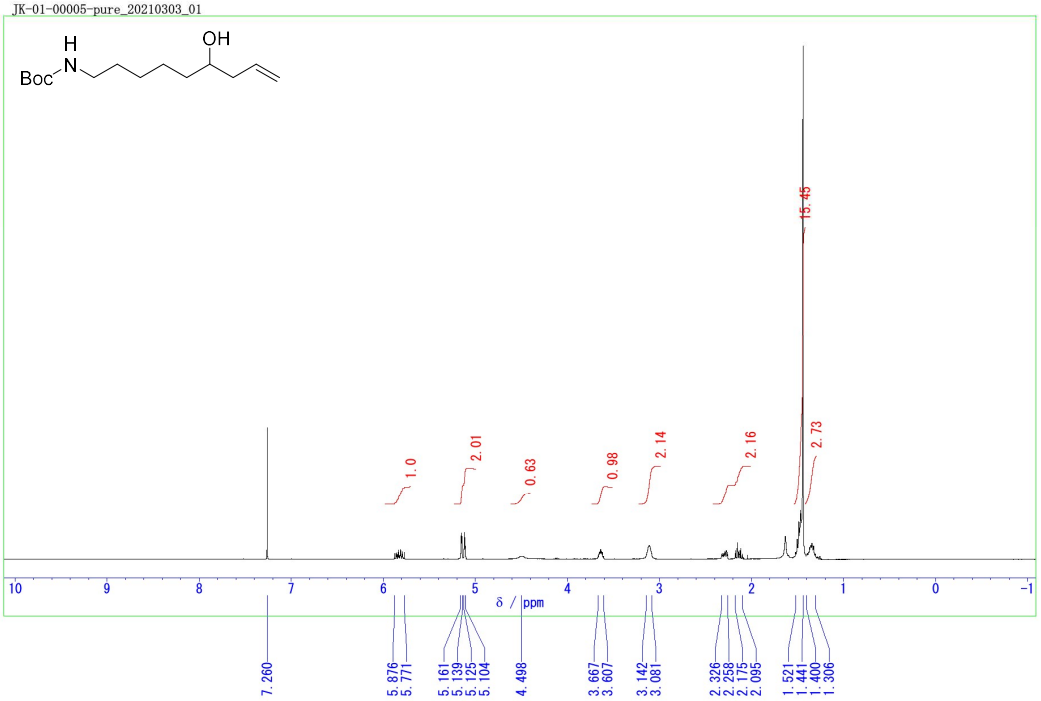
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Boc
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2.16
2.73
10
9
8
7
6
5
4
3
2
1
0
-1
δ / ppm
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5.771
5.161
5.139
5.125
5.104
4.498
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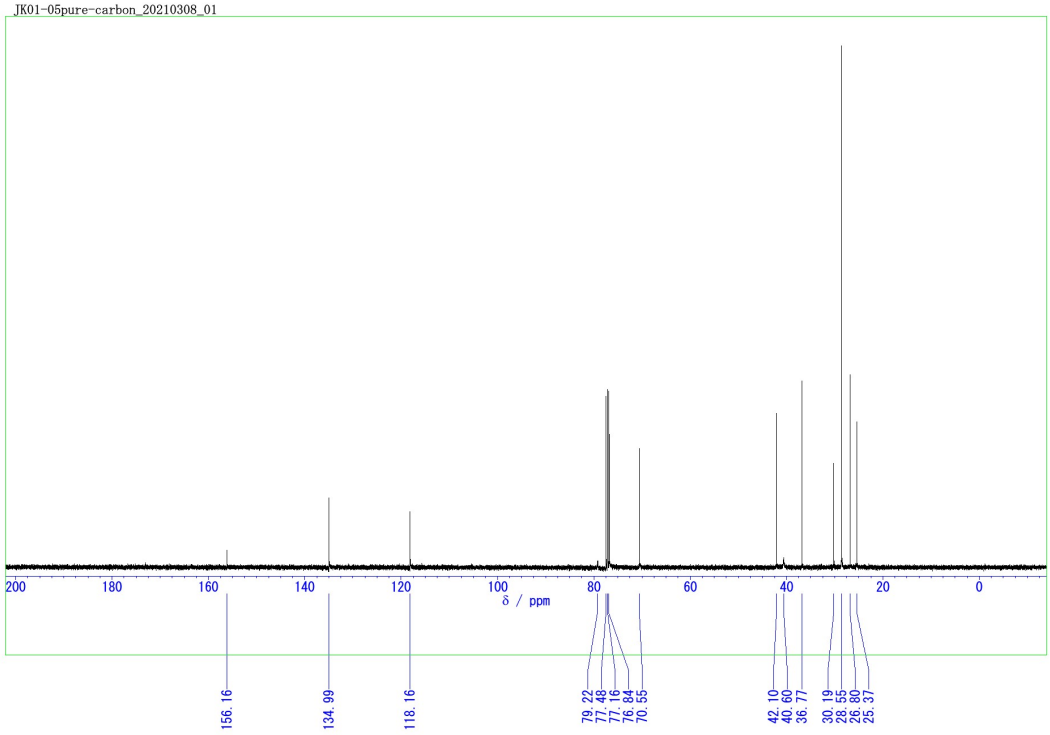
1.306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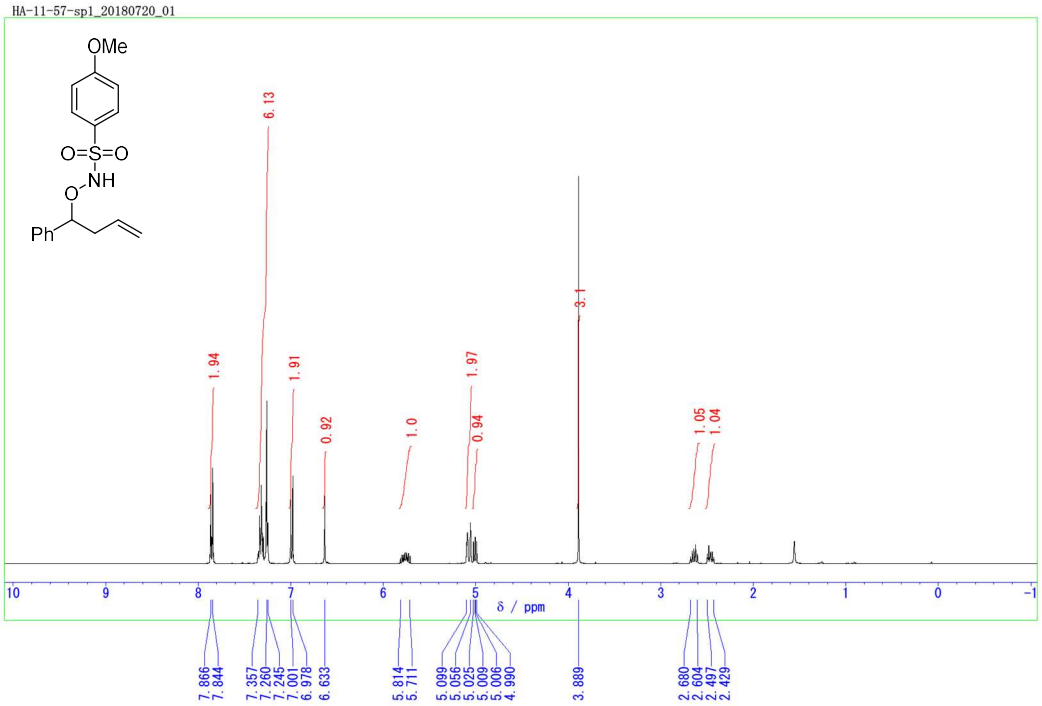
26.80
25.37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O
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1.0
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1.04
δ / ppm
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7.357
7.260
7.245
7.001
6.978
6.633
5.814
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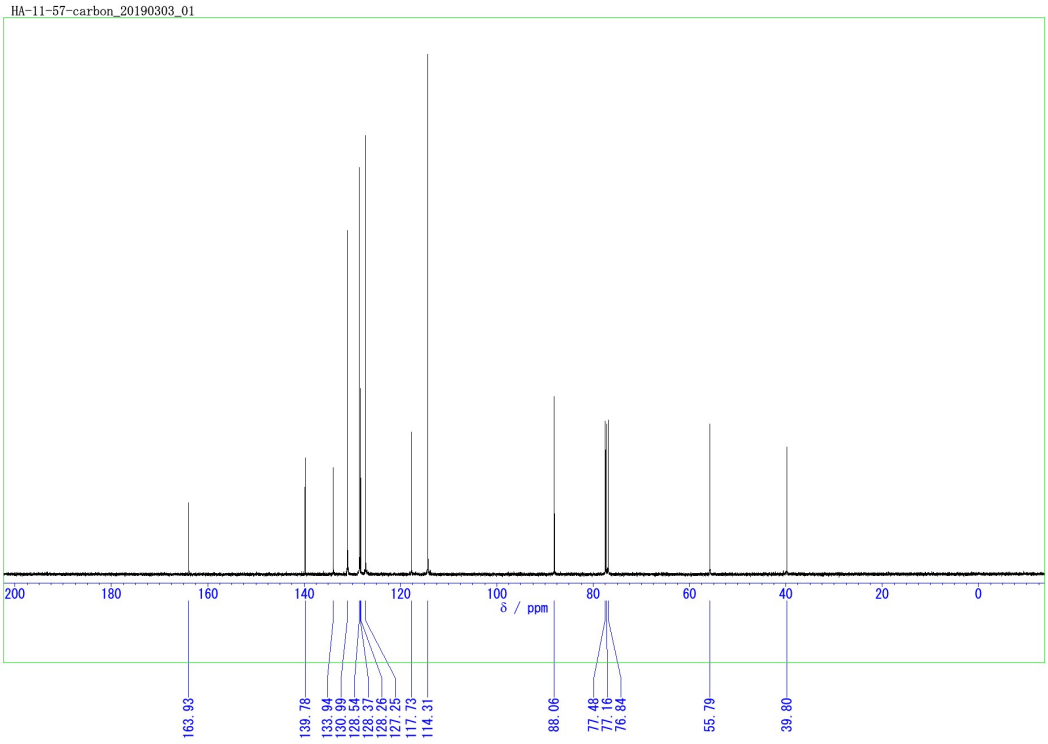
2.429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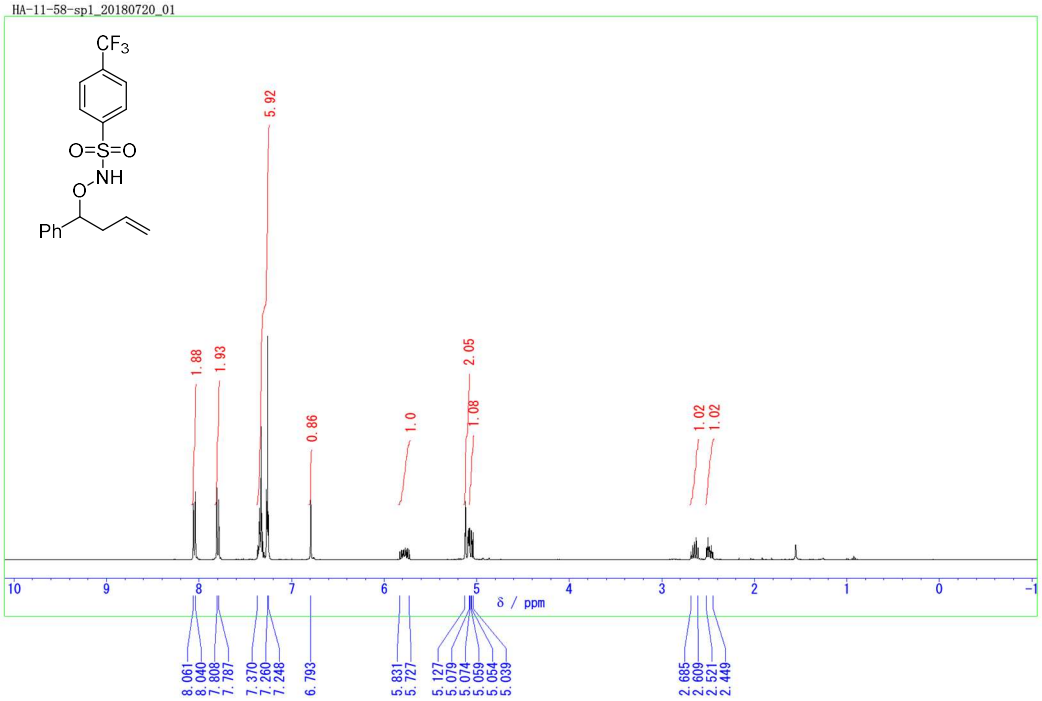
76.84
55.79
39.80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1.02
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7.787
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7.260
7.248
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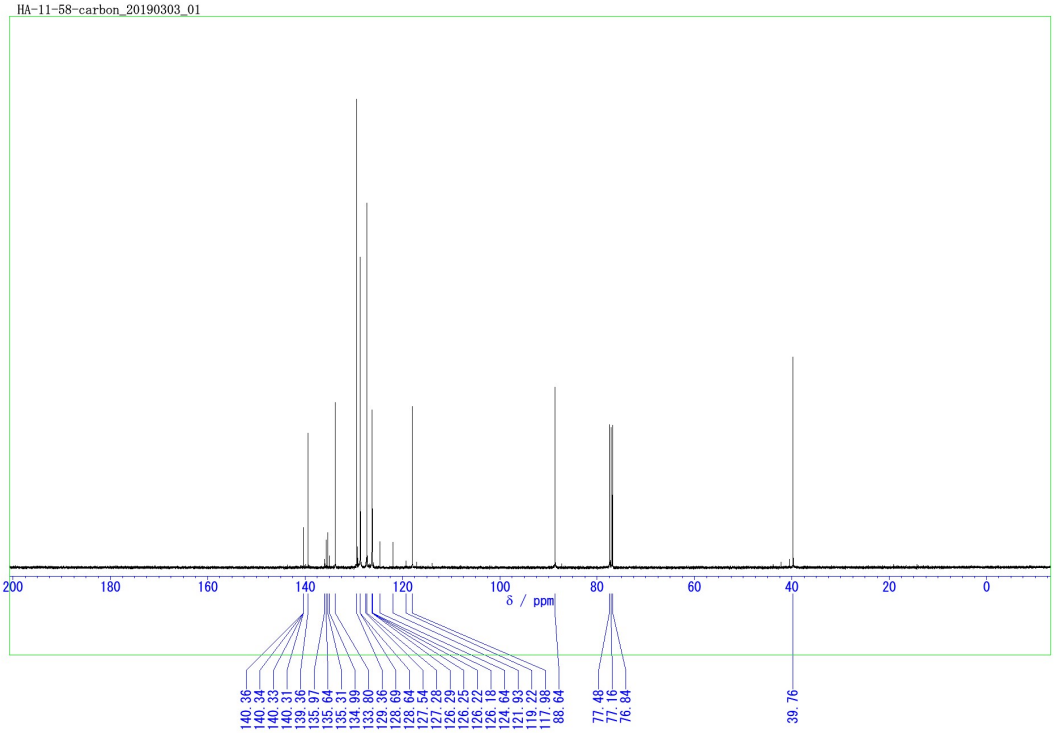
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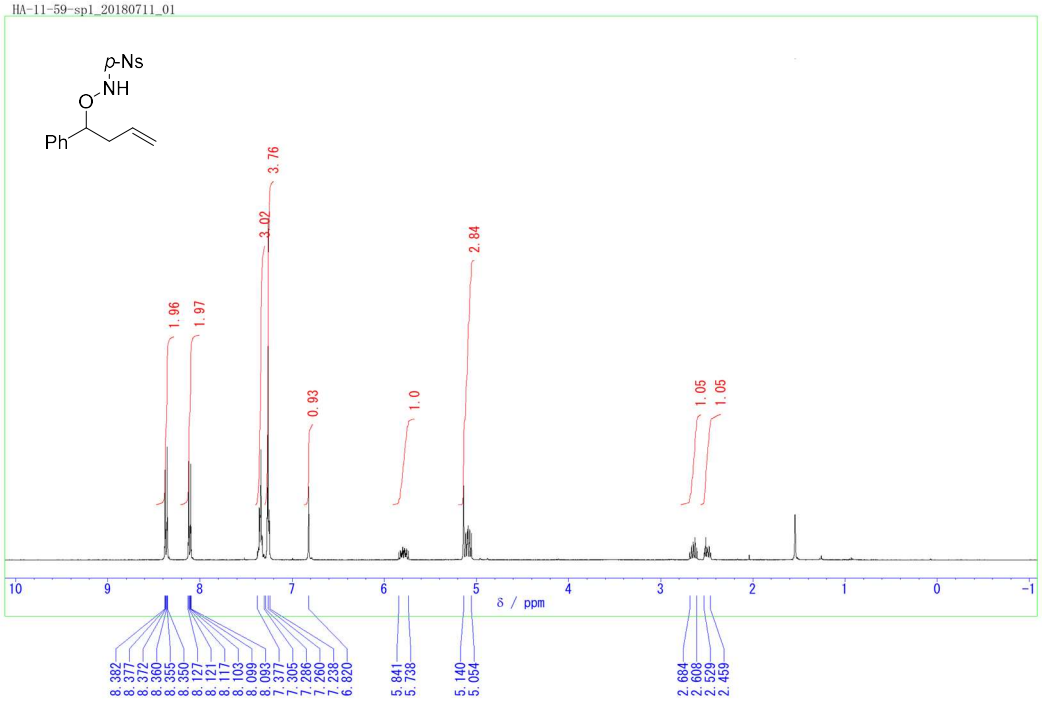
39.76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1.05
1.05
δ / ppm
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8.377
8.372
8.360
8.355
8.350
8.127
8.121
8.117
8.103
8.099
8.093
7.377
7.305
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5.054
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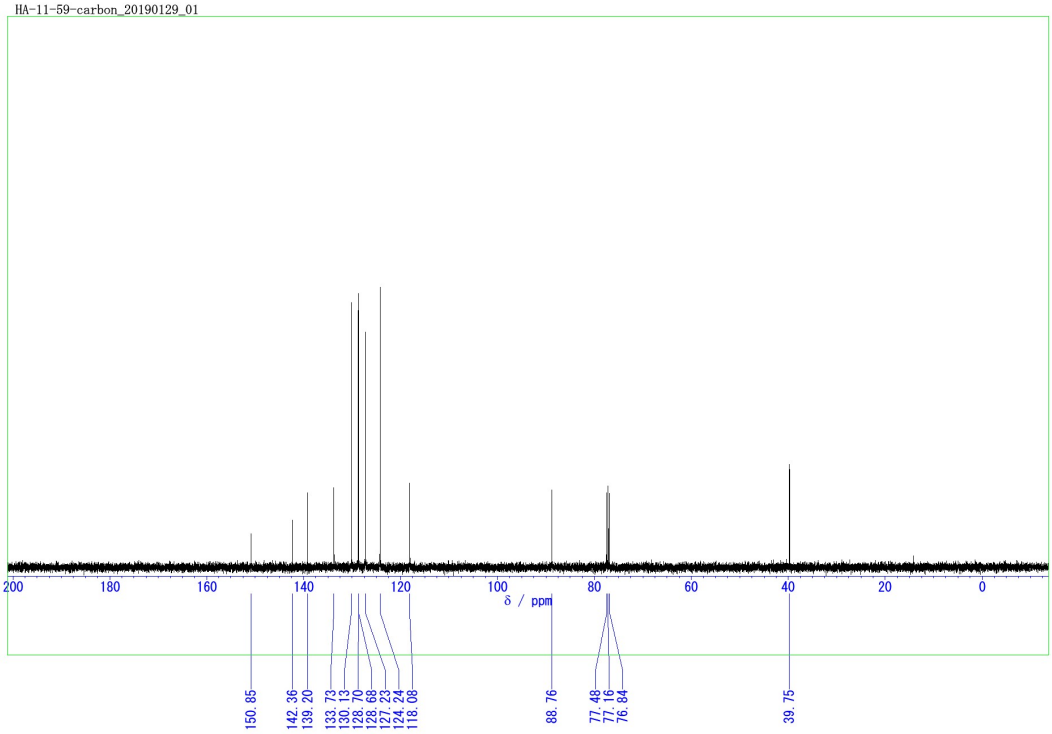
2.608
2.529
2.459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77.16
76.84
39.75

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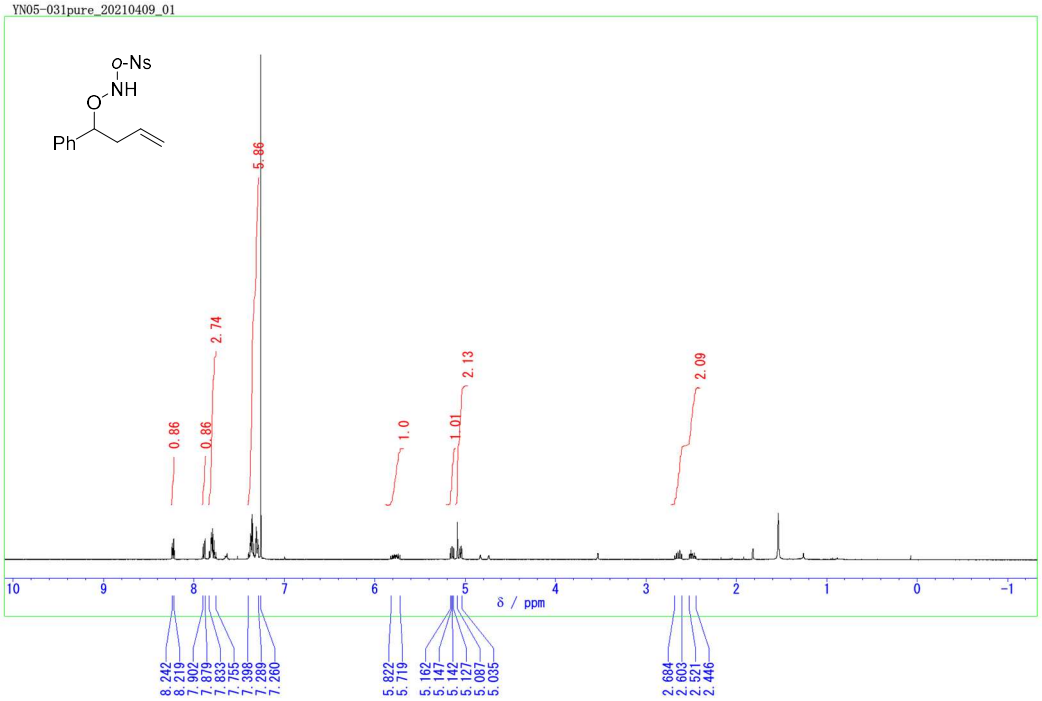

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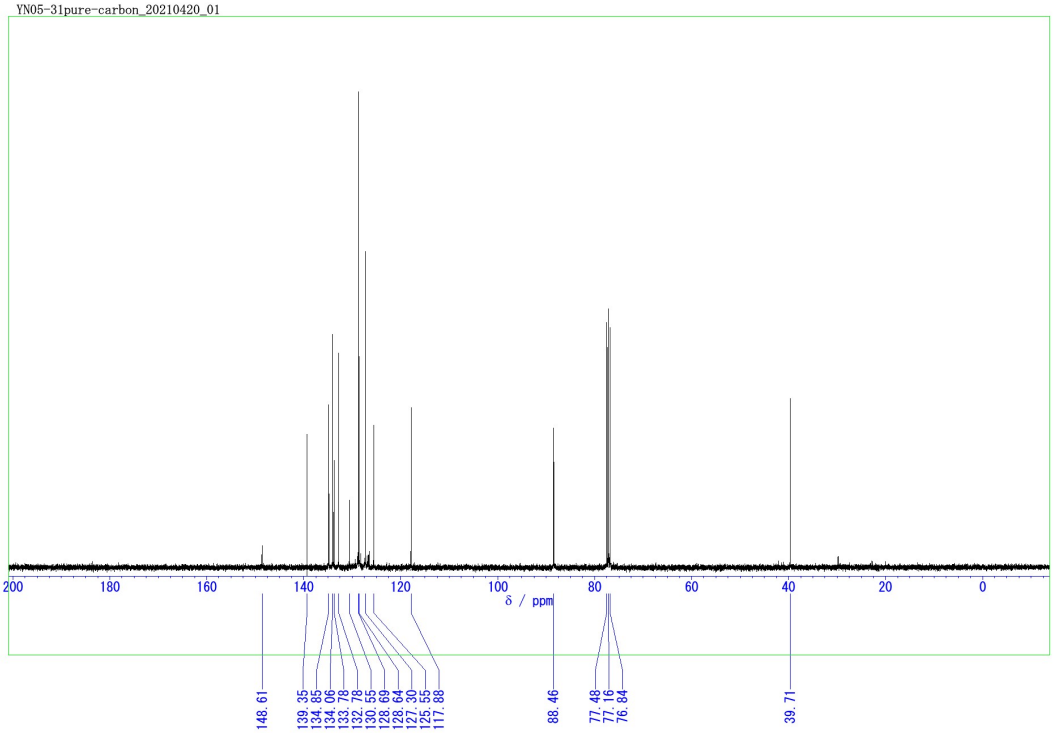

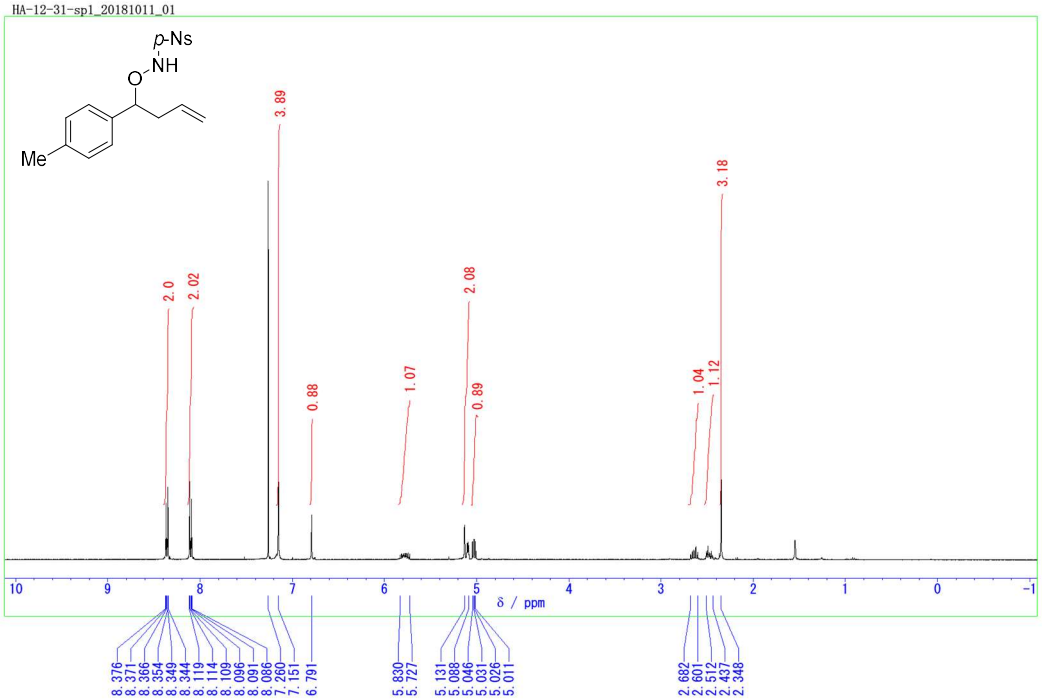
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1.12
δ / ppm
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8.366
8.354
8.349
8.344
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8.114
8.109
8.096
8.091
8.086
7.260
7.151
6.791
5.830
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5.026
5.011
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2.601
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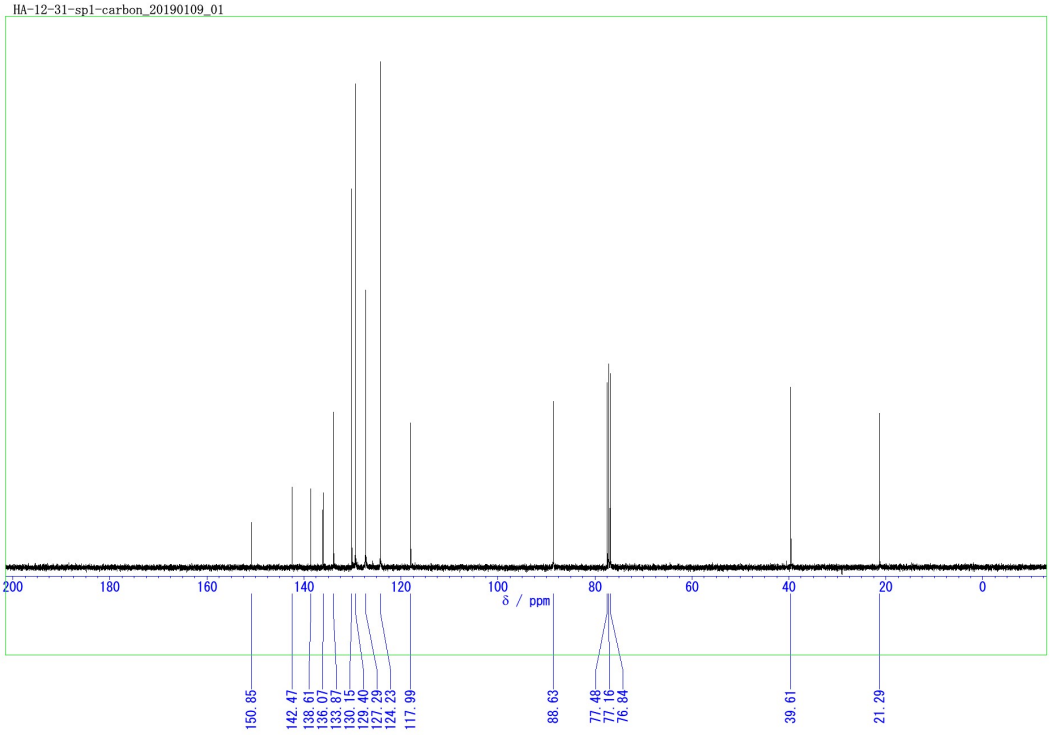
2.437
2.348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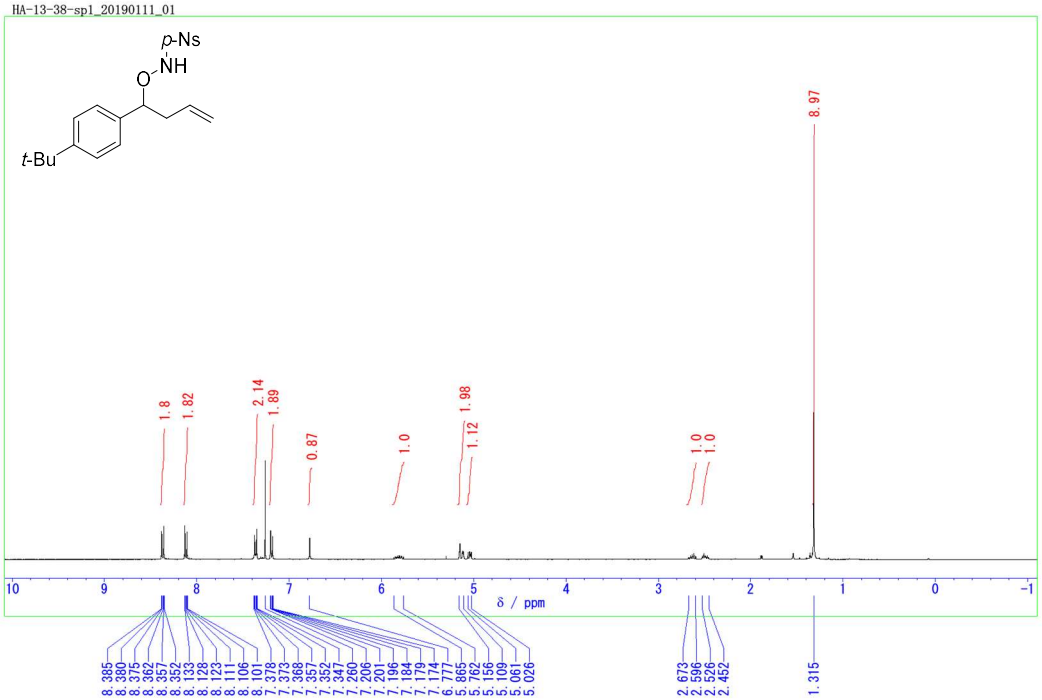
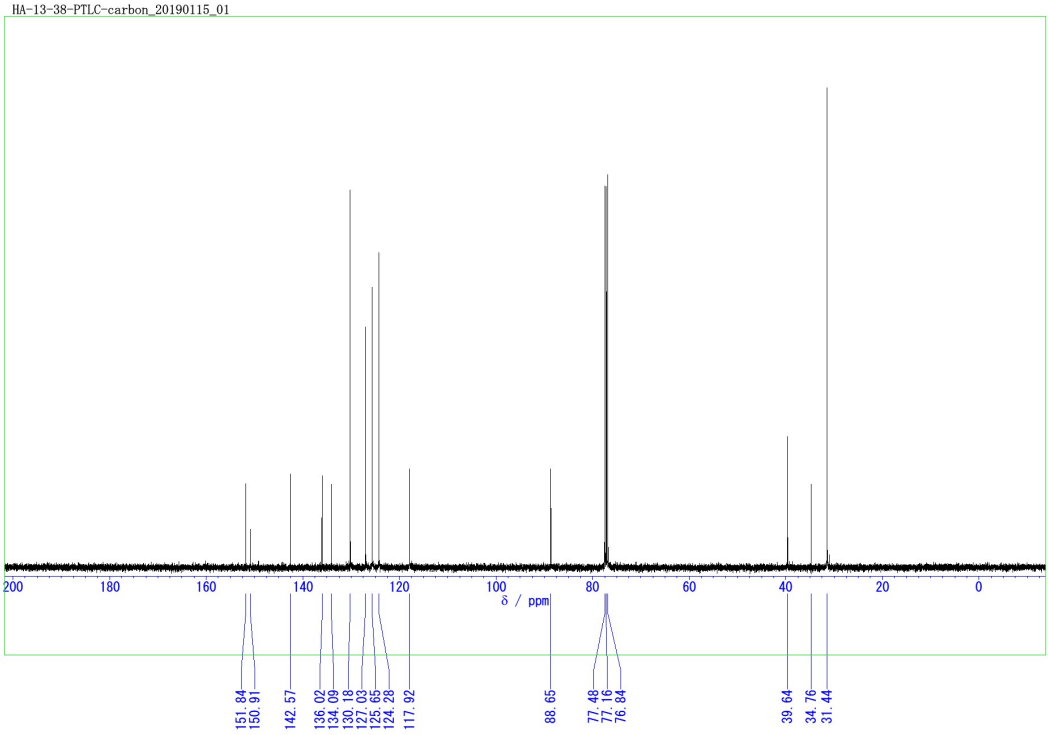
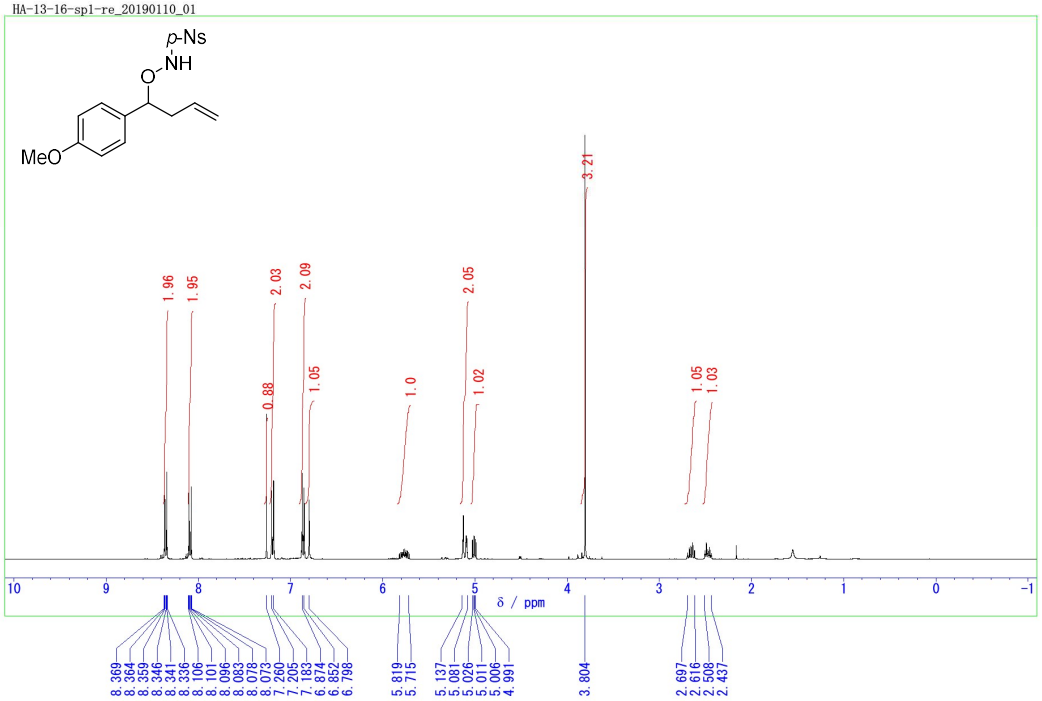
77.16
76.84
39.61
21.29

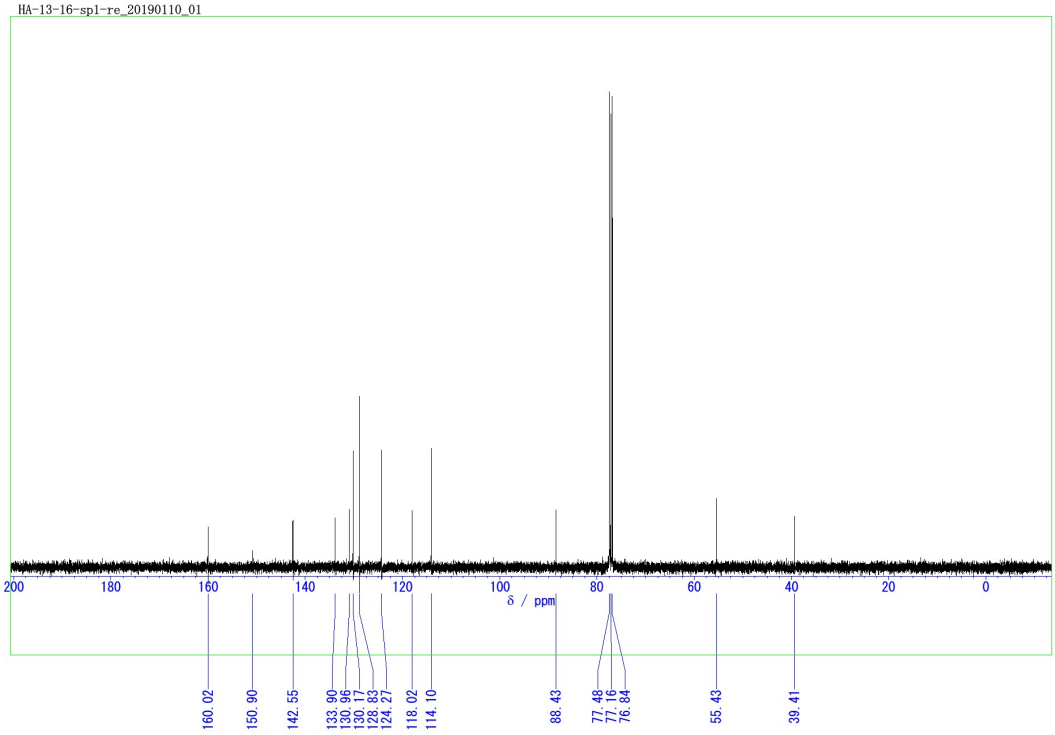
HA-13-38-sp1_20190111_01

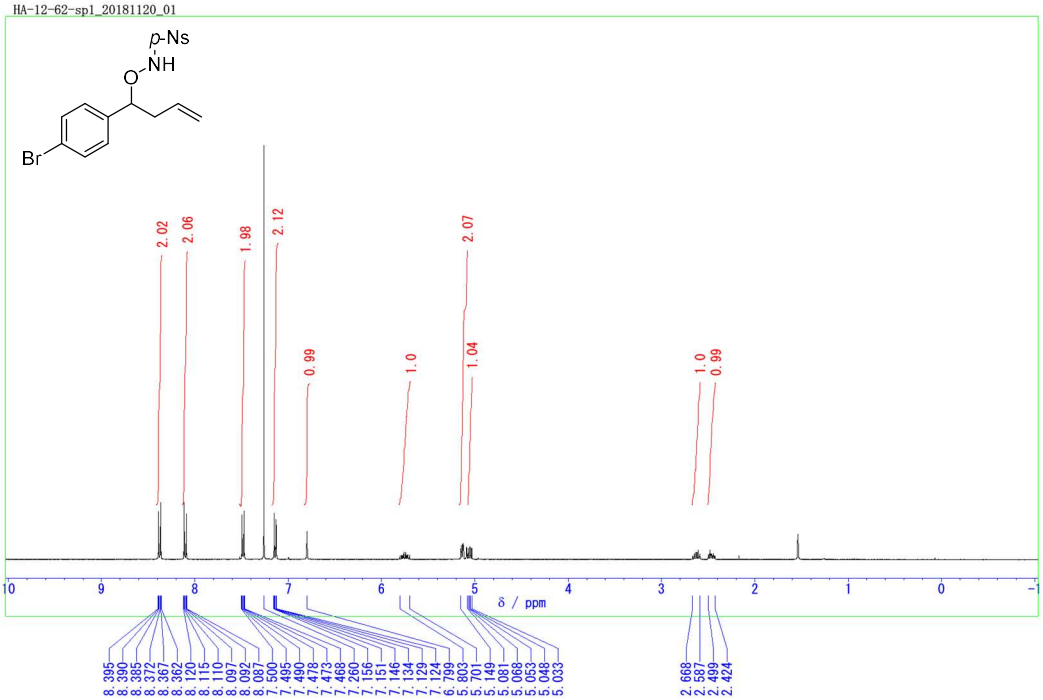


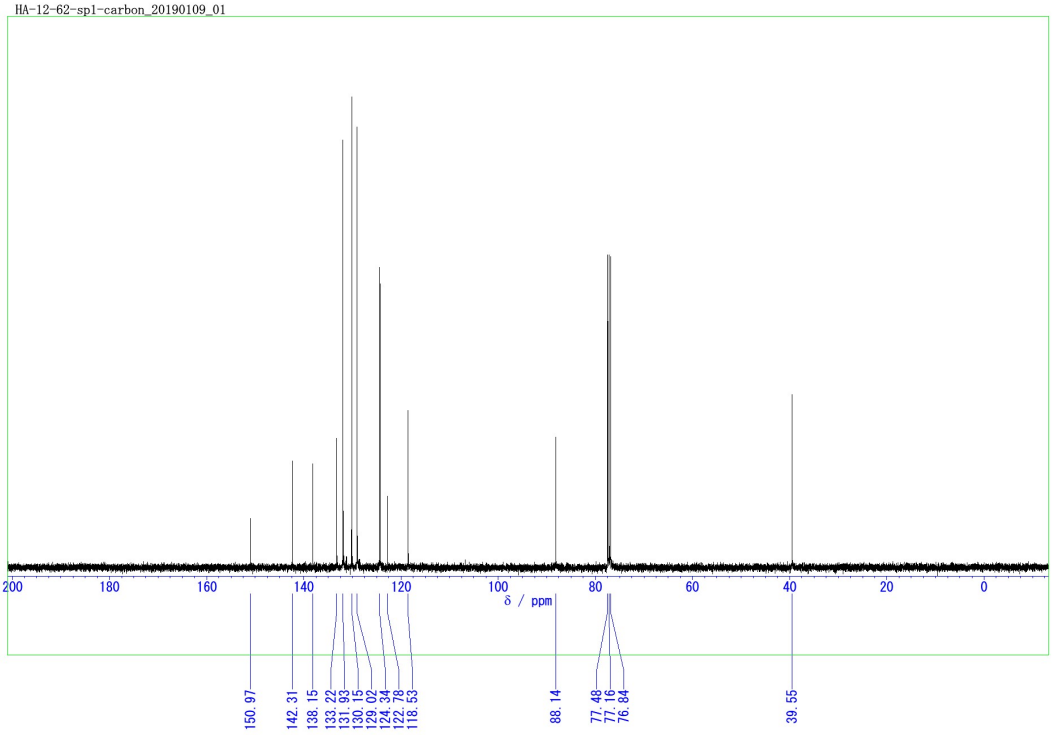
HA-13-38-PTLC-carbon_20190115_01

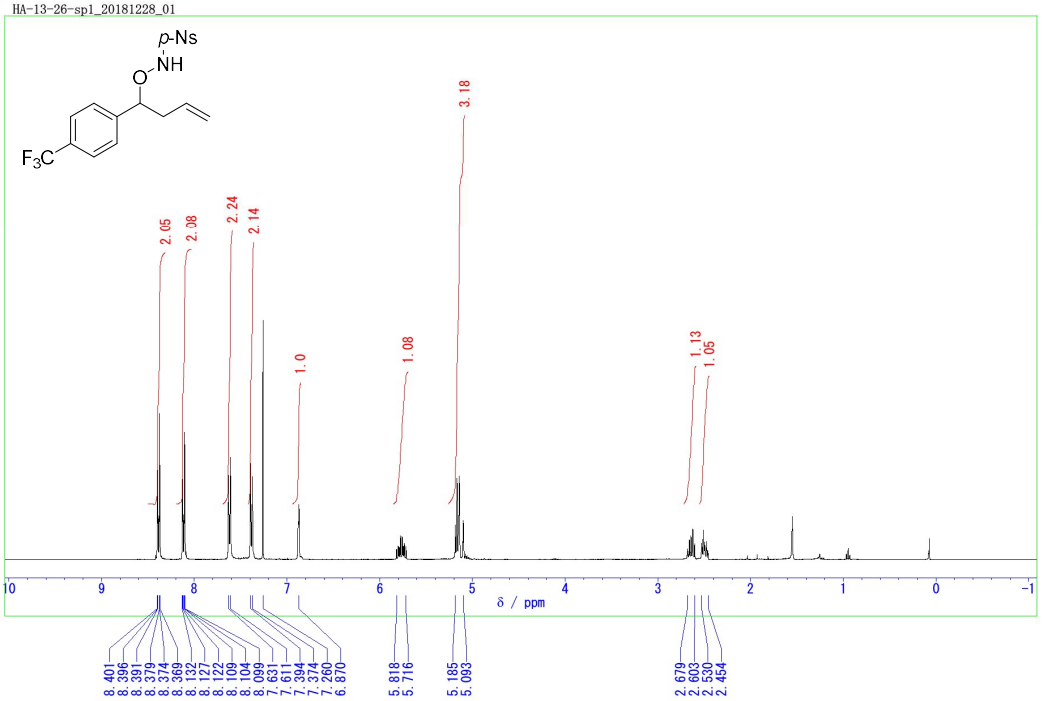


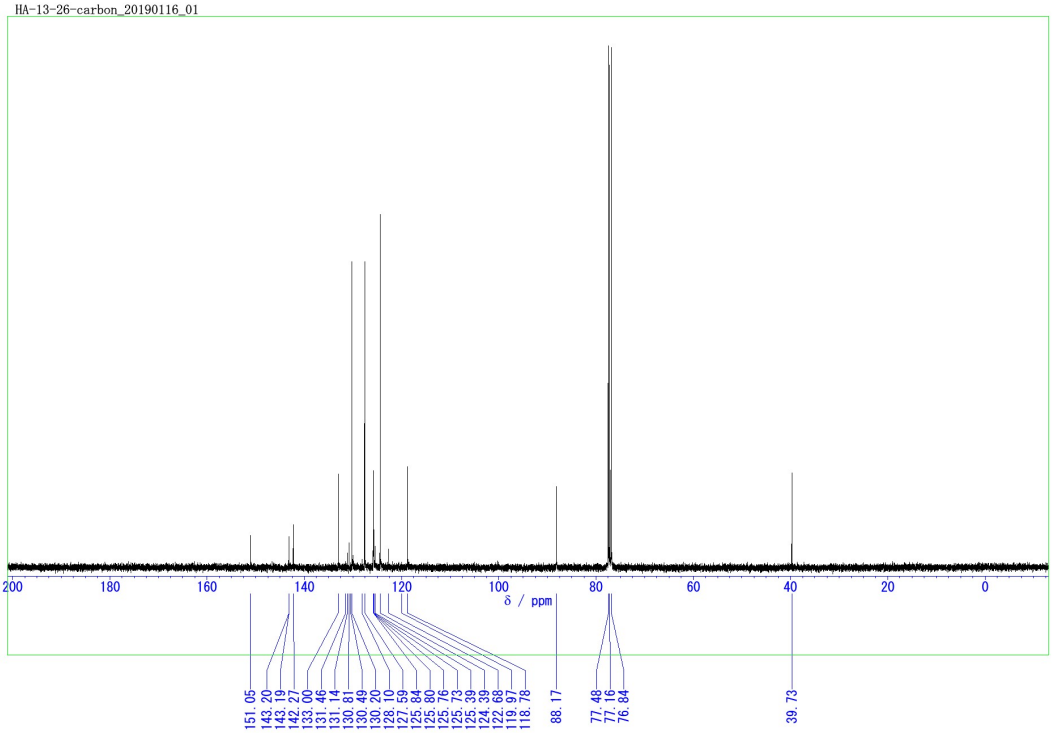

HA-13-16-sp1-re_20190110_01
p-Ns
NH
O
MeO
1.96
1.95
2.03
2.09
0.88
1.05
1.0
2.05
1.02
3.21
1.05
1.03
δ / ppm
8.369
8.364
8.359
8.346
8.341
8.336
8.106
8.101
8.096
8.078
8.073
7.260
7.205
7.183
6.874
6.852
6.798
5.819
5.715
5.137
5.081
5.026
5.011
5.006
4.991
3.804
2.697
2.616
2.508
2.437


HA-13-16-sp1-re_20190110_01
δ / ppm
160.02
150.90
142.55
133.90
130.96
130.17
128.83
124.27
118.02
114.10
88.43
77.48
77.16
76.84
55.43
39.41

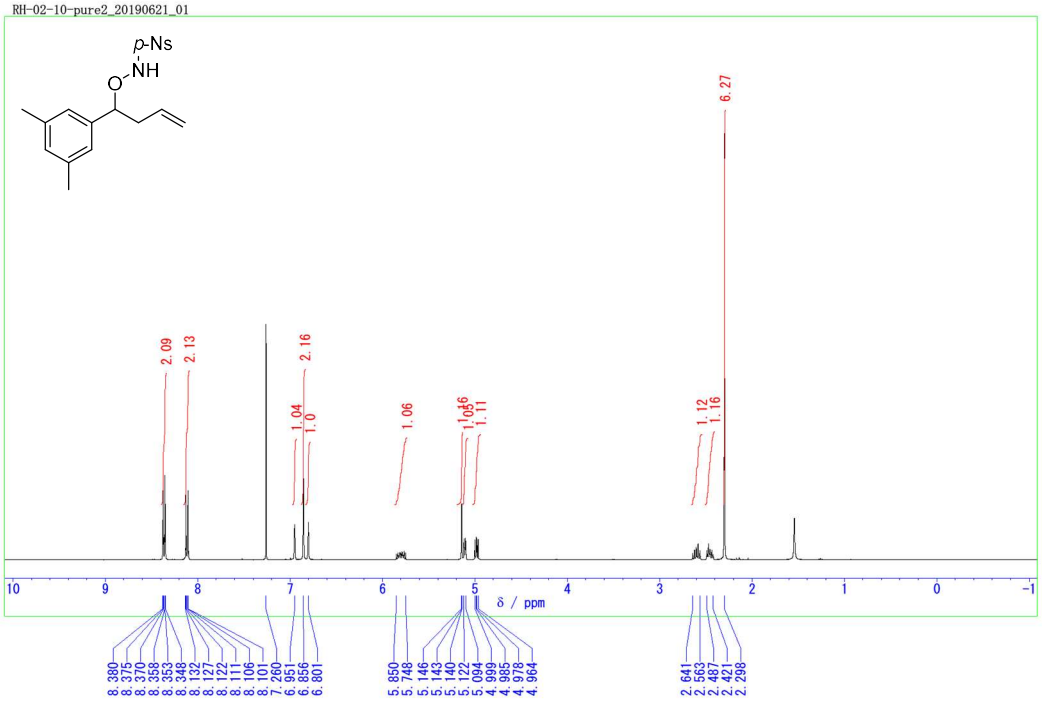

HA-12-62-sp1_20181120_01
p-Ns
NH
O
Br
2.02
2.06
1.98
2.12
0.99
1.0
2.07
1.04
1.0
0.99
δ / ppm
8.395
8.390
8.385
8.372
8.367
8.362
8.120
8.115
8.110
8.097
8.092
8.087
7.500
7.495
7.490
7.478
7.473
7.468
7.260
7.156
7.151
7.146
7.134
7.129
7.124
7.799
6.803
5.701
5.149
5.081
5.068
5.053
5.048
5.033
2.668
2.587
2.499
2.424


HA-12-62-sp1-carbon_20190109_01
δ / ppm
150.97
142.31
138.15
133.22
131.93
130.15
129.02
124.34
122.78
118.53
88.14
77.48
77.16
76.84
39.55

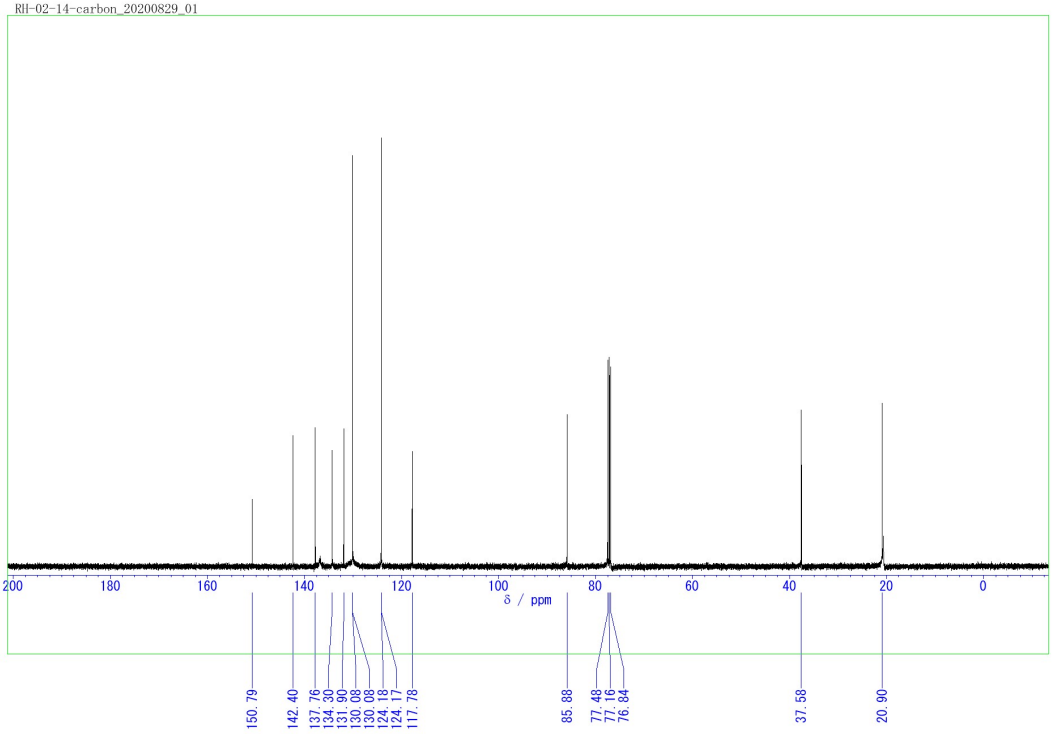

HA-13-26-sp1_20181228_01
p-Ns
NH
O
F3C
2.05
2.08
2.24
2.14
1.0
1.08
3.18
1.13
1.05
δ / ppm
8.401
8.396
8.391
8.379
8.374
8.369
8.132
8.127
8.122
8.109
8.104
8.099
7.631
7.611
7.394
7.374
7.260
6.870
5.818
5.716
5.185
5.093
2.679
2.603
2.530
2.454

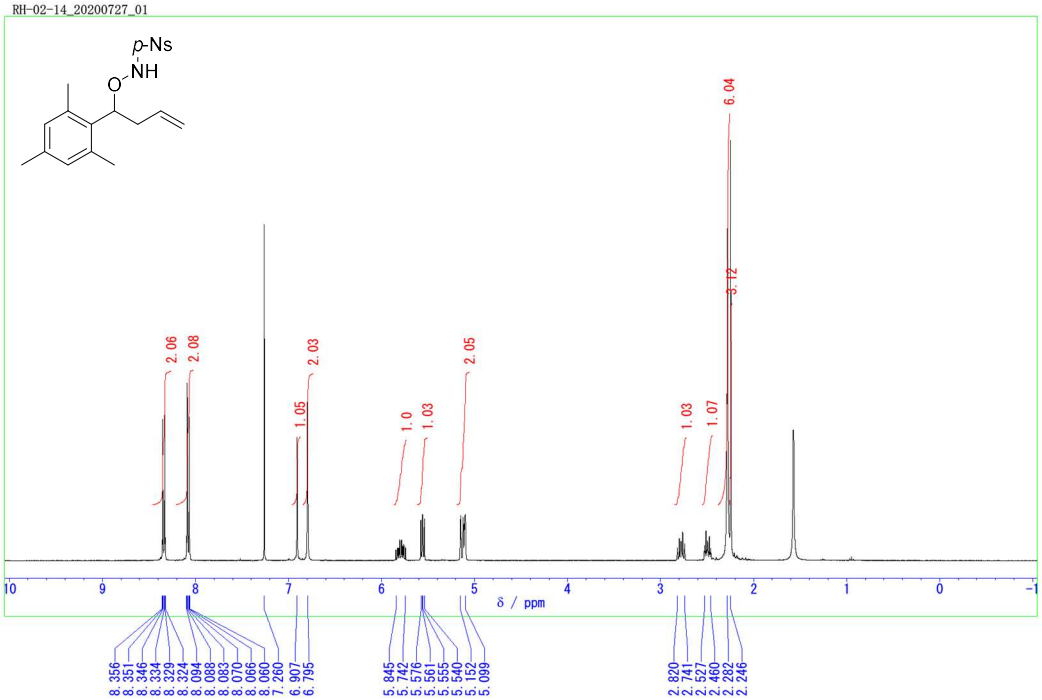

HA-13-26-carbon_20190116_01
δ / ppm
151.05
143.20
143.19
142.27
133.00
131.46
131.14
130.81
130.49
130.20
128.10
127.59
125.84
125.80
125.76
125.73
125.39
124.39
122.68
119.97
118.78
88.17
77.48
77.16
76.84
39.73

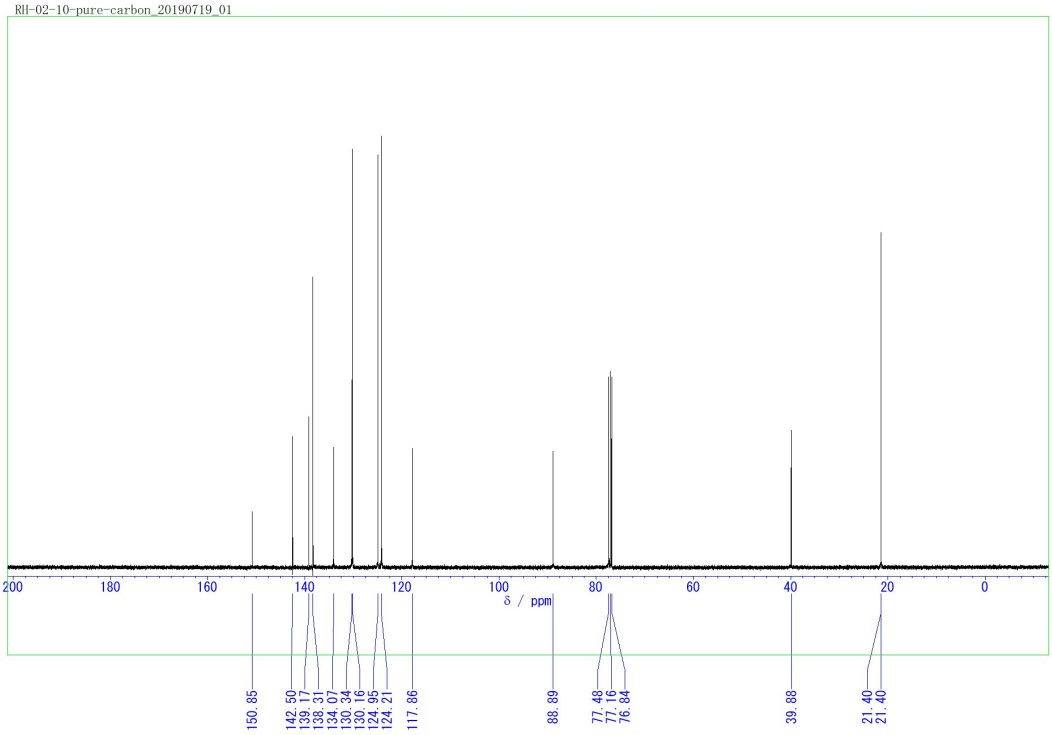
RH-02-10-pure2_20190621_01

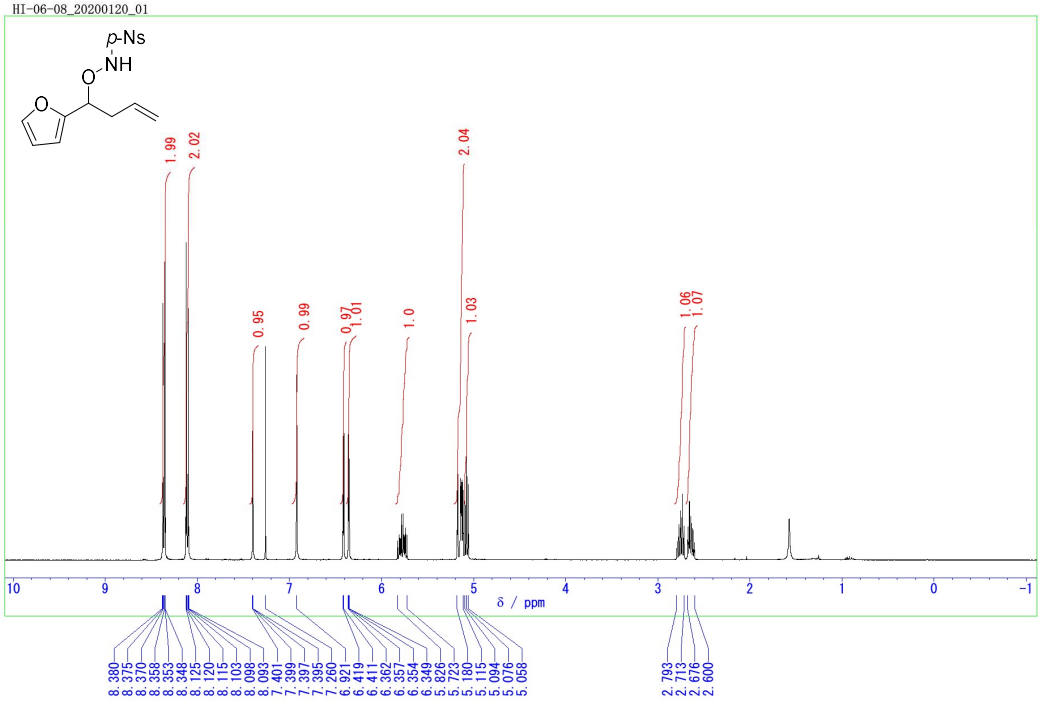


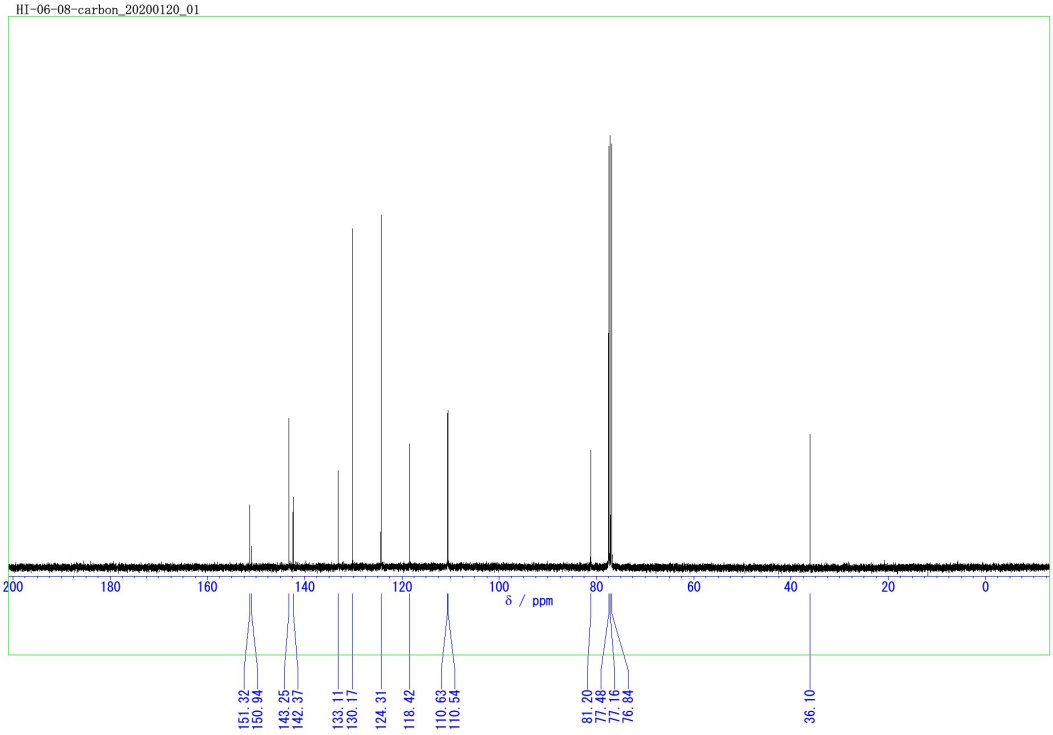
RH-02-14-carbon_20200829_01

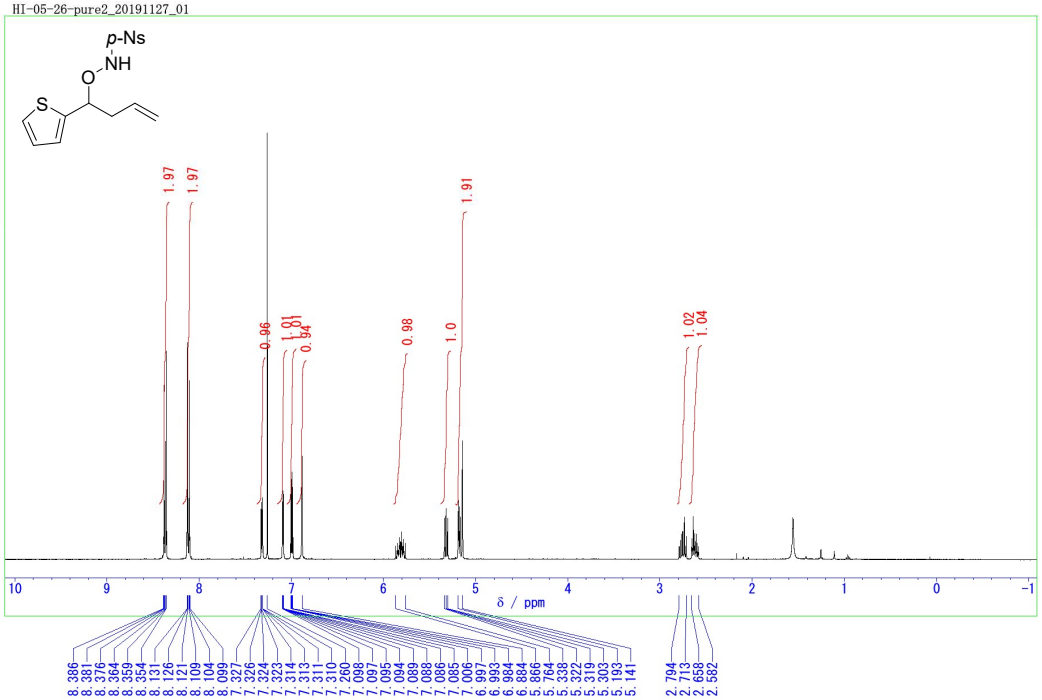


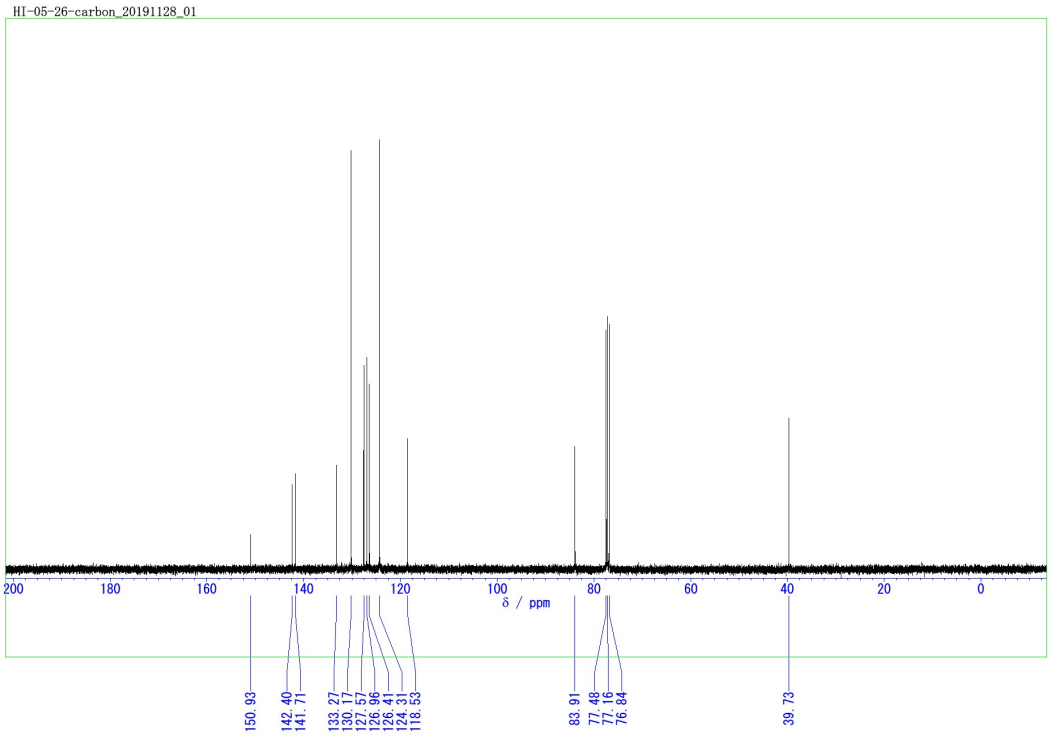

RH-02-14_20200727_01
p-Ns
NH
O
6.04
3.12
2.06
2.08
2.03
2.05
1.05
1.0
1.03
1.03
1.07
δ / ppm
8.356
8.351
8.346
8.334
8.329
8.324
8.084
8.083
8.070
8.066
8.060
7.260
6.907
6.795
5.845
5.742
5.576
5.561
5.555
5.540
5.152
5.099
2.820
2.741
2.727
2.467
2.282
2.246


RH-02-10-pure-carbon_20190719_01
δ / ppm
150.85
142.50
139.17
138.31
134.07
130.34
130.16
124.95
124.21
117.86
88.89
77.48
77.16
76.84
39.88
21.40
21.40

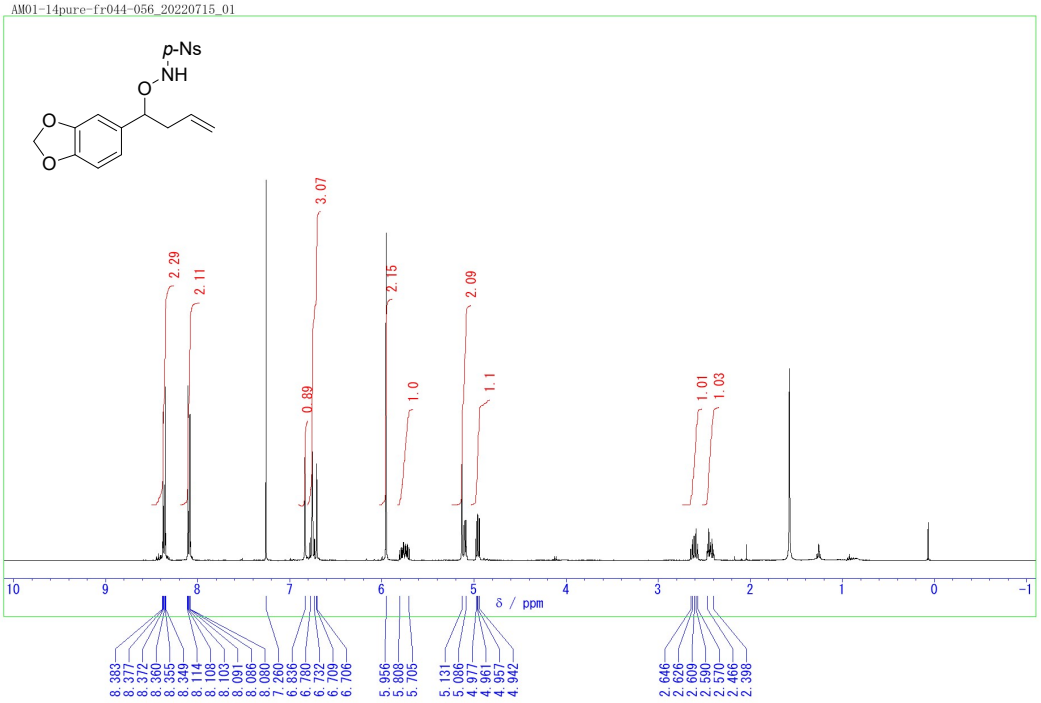

HI-06-08_20200120_01
p-Ns
NH
O
O
1.99
2.02
2.04
0.95
0.99
0.97
1.01
1.0
1.03
1.06
1.07
δ / ppm
8.380
8.375
8.370
8.358
8.353
8.348
8.125
8.120
8.115
8.103
8.098
8.093
7.401
7.399
7.397
7.395
7.260
6.921
6.419
6.411
6.362
6.357
6.354
6.349
5.826
5.723
5.180
5.115
5.094
5.076
5.058
2.793
2.713
2.676
2.600


HI-06-08-carbon_20200120_01
δ / ppm
151.32
150.94
143.25
142.37
133.11
130.17
124.31
118.42
110.63
110.54
81.20
77.48
77.16
76.84
36.10

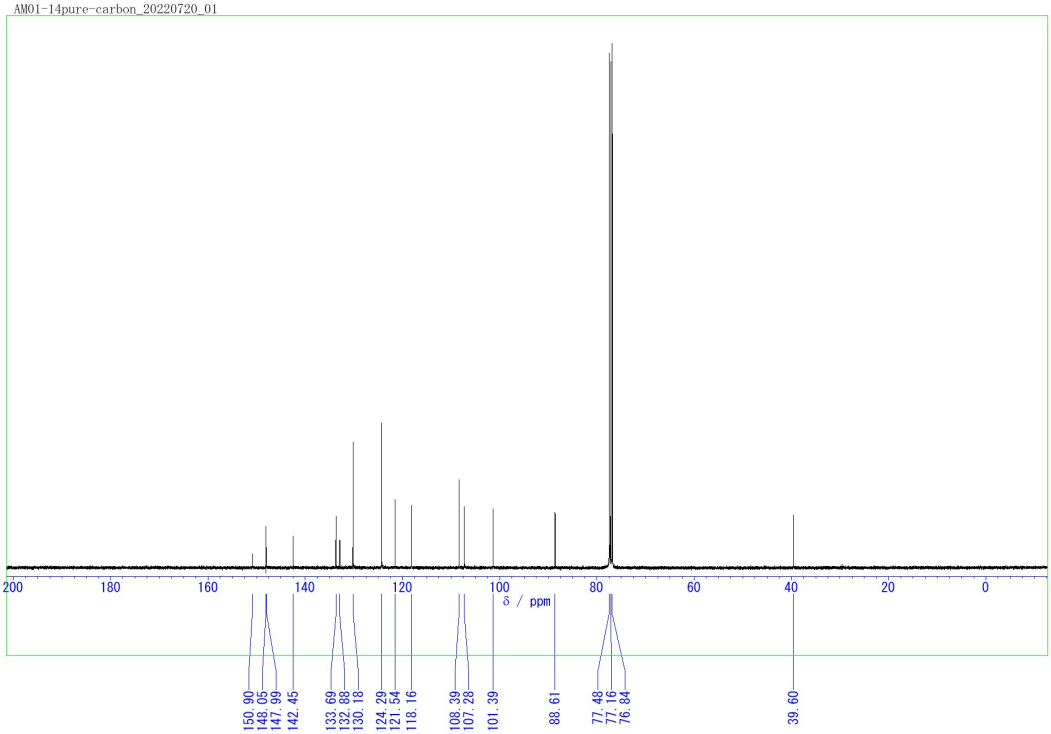

HI-05-26-pure2_20191127_01
p-Ns
NH
O
S
1.97
1.97
0.96
1.01
0.94
0.98
1.0
1.91
1.02
1.04
δ / ppm
8.386
8.381
8.376
8.364
8.359
8.354
8.131
8.126
8.121
8.109
8.104
8.099
7.327
7.326
7.324
7.323
7.314
7.313
7.311
7.310
7.260
7.098
7.097
7.095
7.094
7.089
7.088
7.086
7.085
7.006
6.997
6.993
6.984
6.884
5.866
5.764
5.338
5.322
5.319
5.303
5.193
5.141
2.794
2.713
2.658
2.582

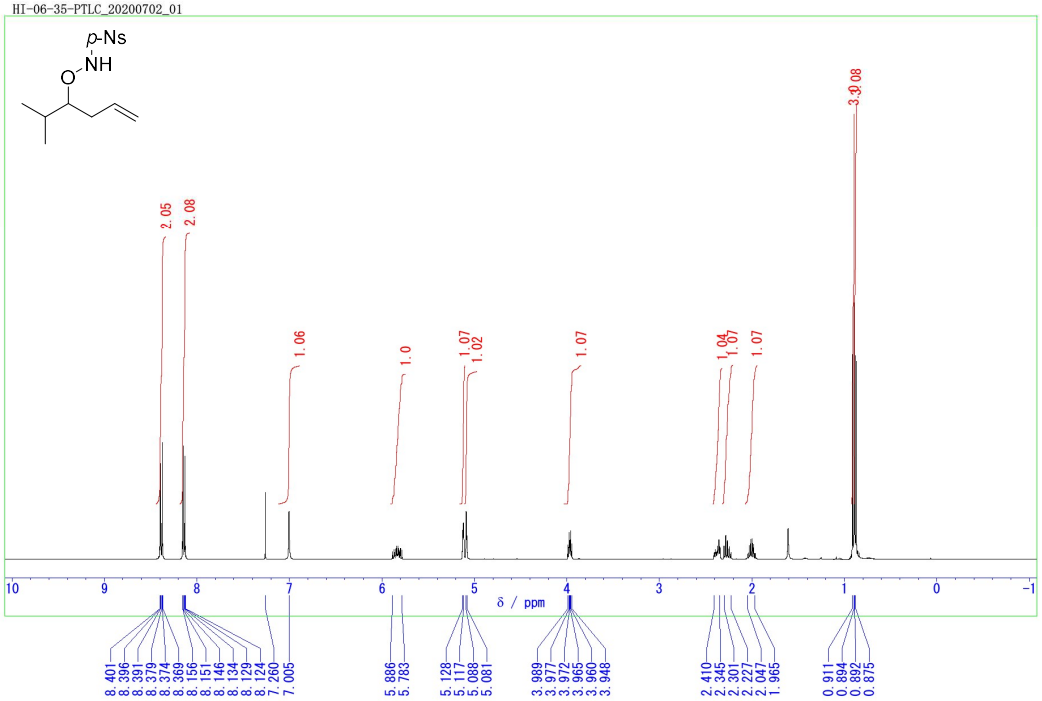

HI-05-26-carbon_20191128_01
δ / ppm
150.93
142.40
141.71
133.27
130.17
127.57
126.96
126.41
124.31
118.53
83.91
77.48
77.16
76.84
39.73

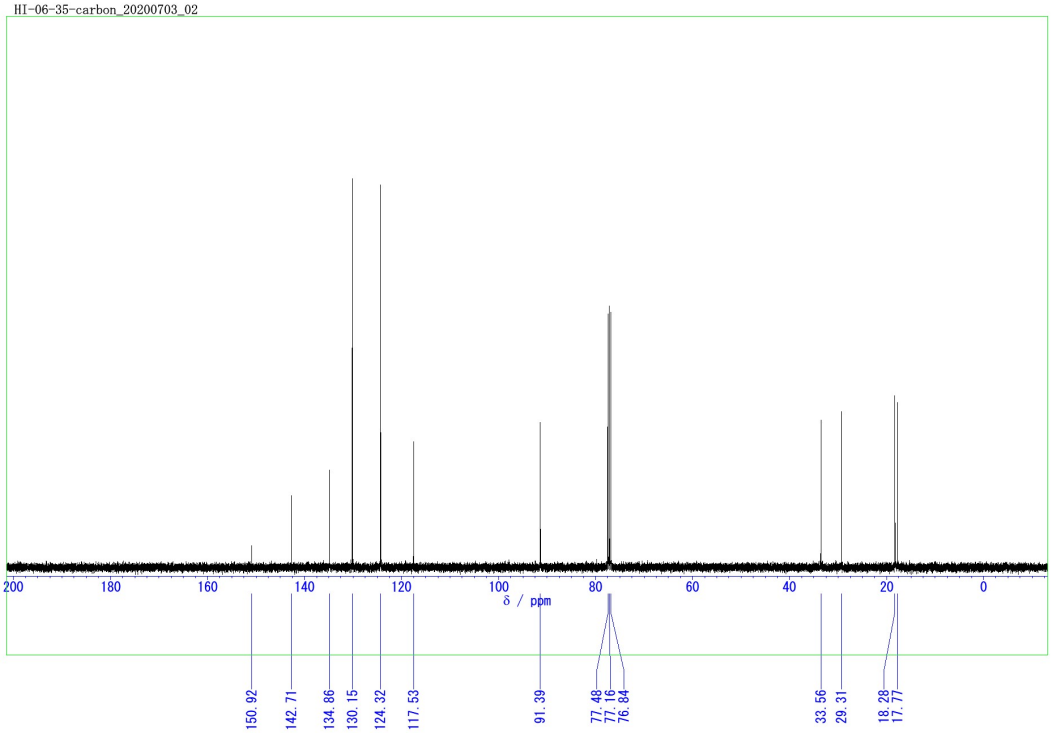
AM01-14pure-fr044-056_20220715_01



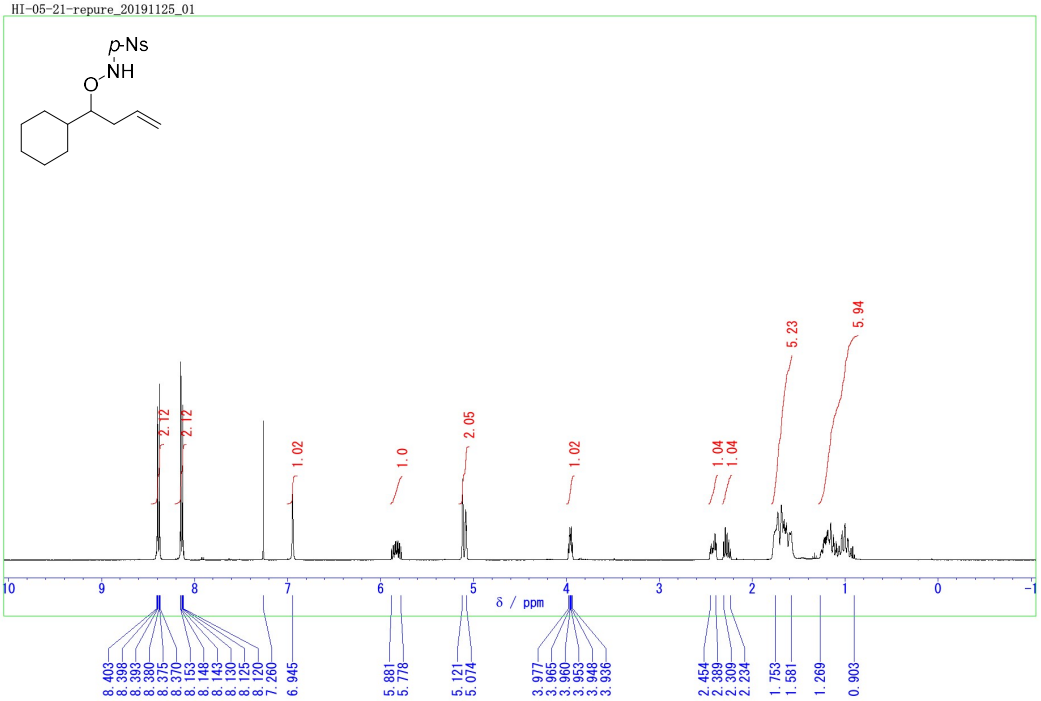
AM01-14pure-carbon_20220720_01



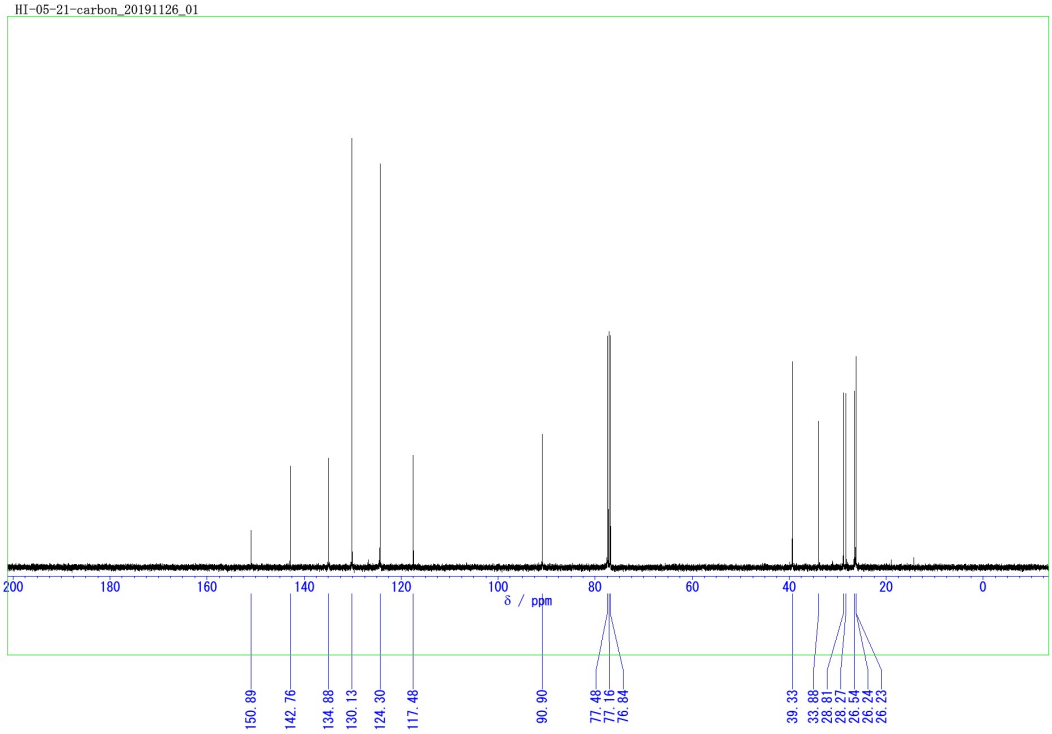

HI-06-35-PTLC_20200702_01
p-Ns
NH
O
δ / ppm


HI-06-35-carbon_20200703_02
δ / ppm

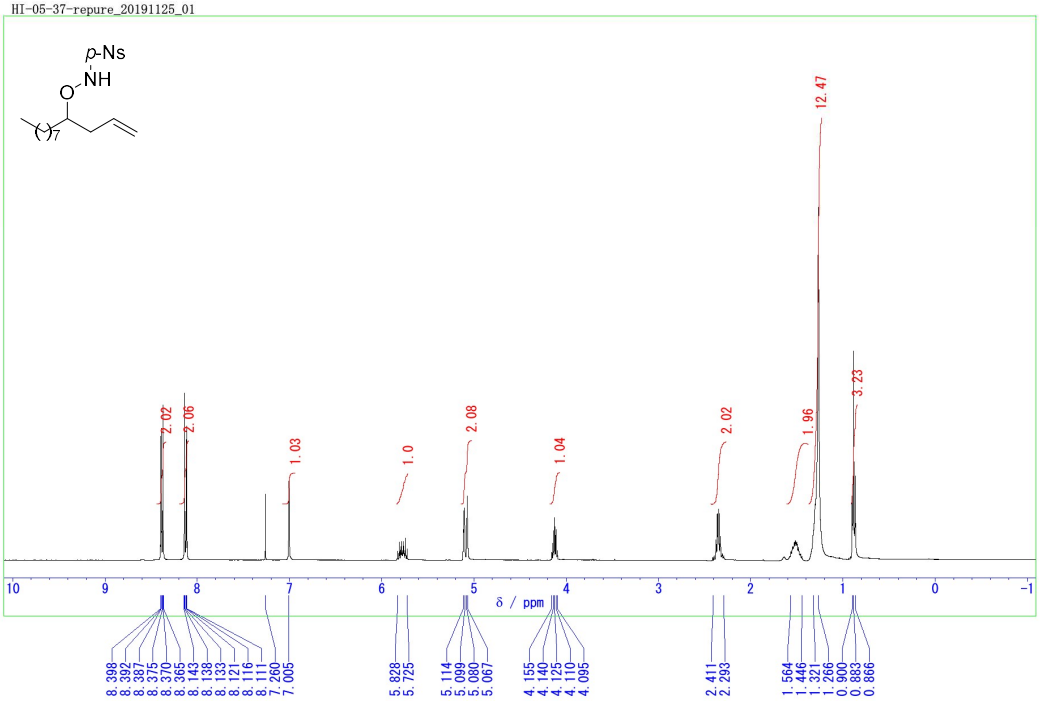
HI-05-21-repure_20191125_01



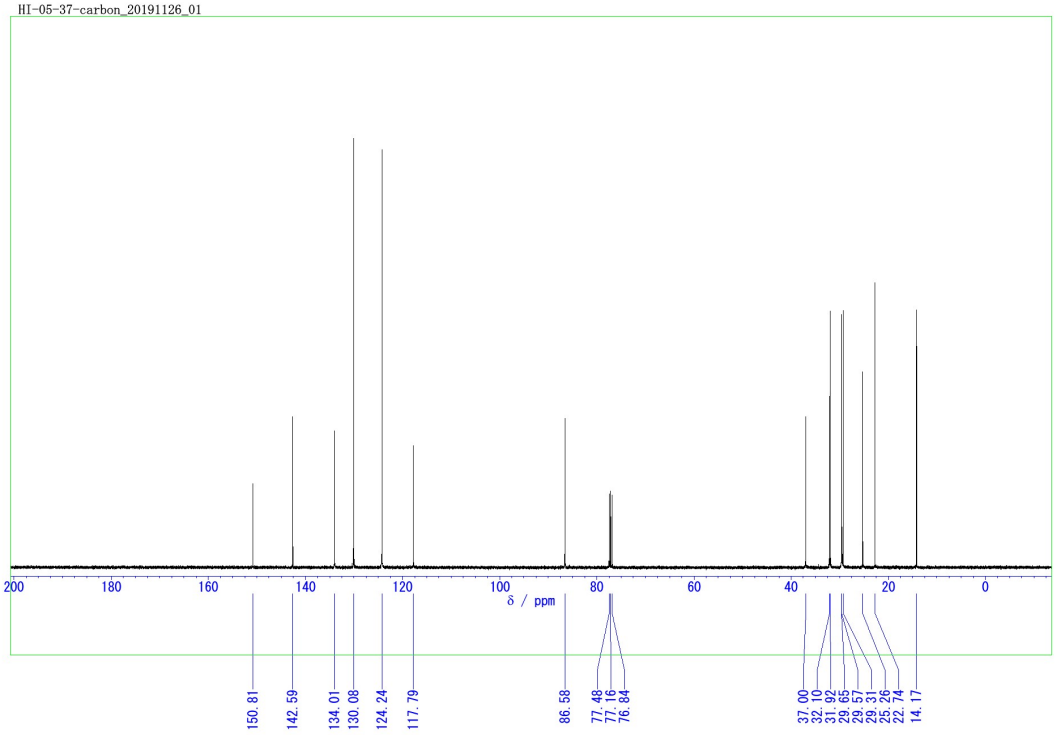
HI-05-21-carbon_20191126_01



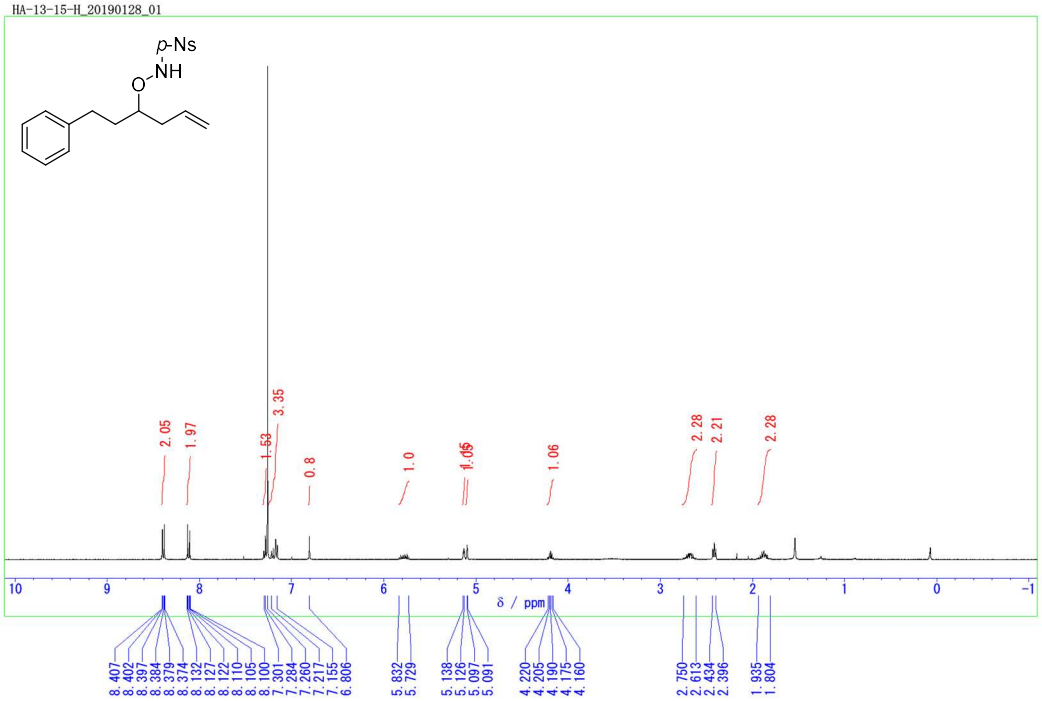
HI-05-37-repure_20191125_01



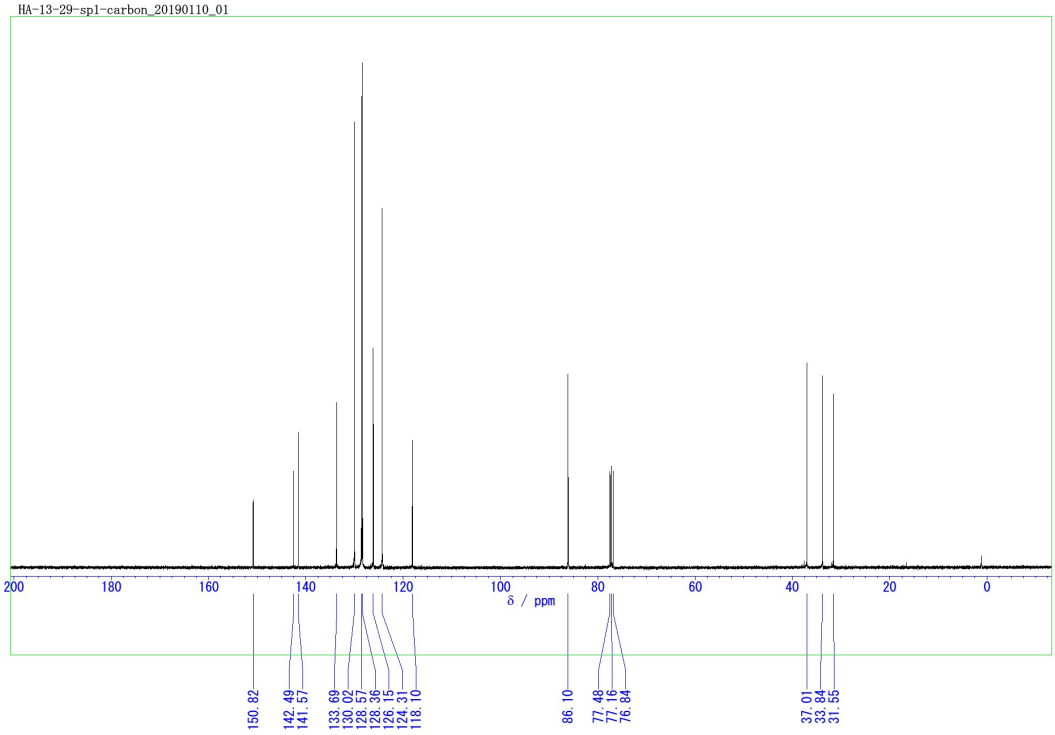
HI-05-37-carbon_20191126_01

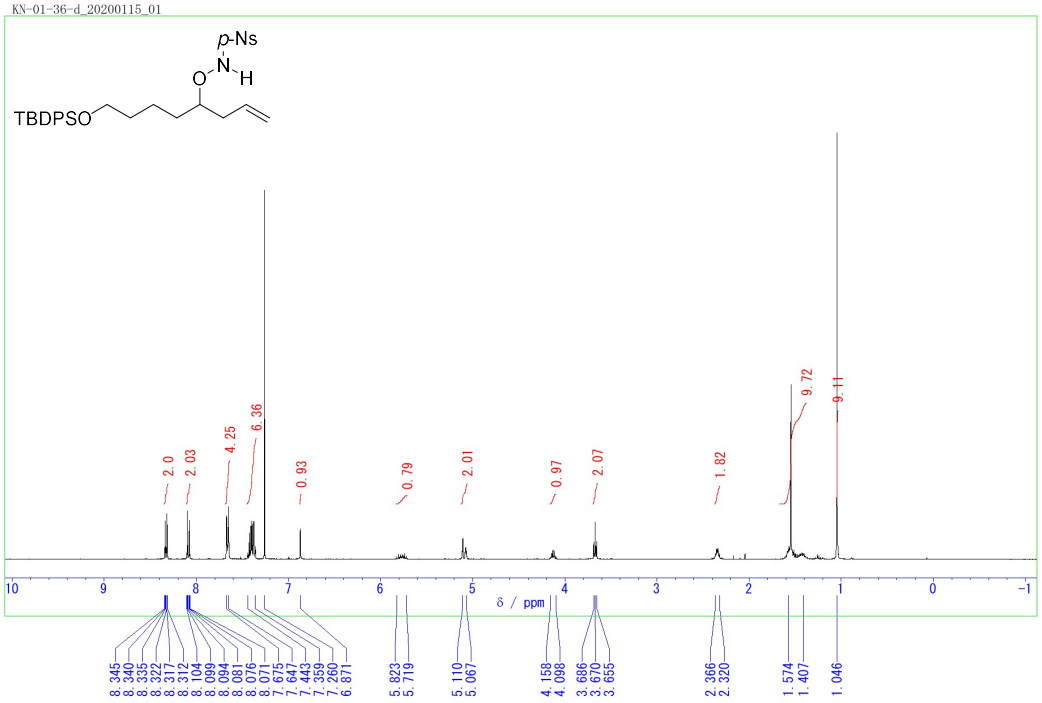


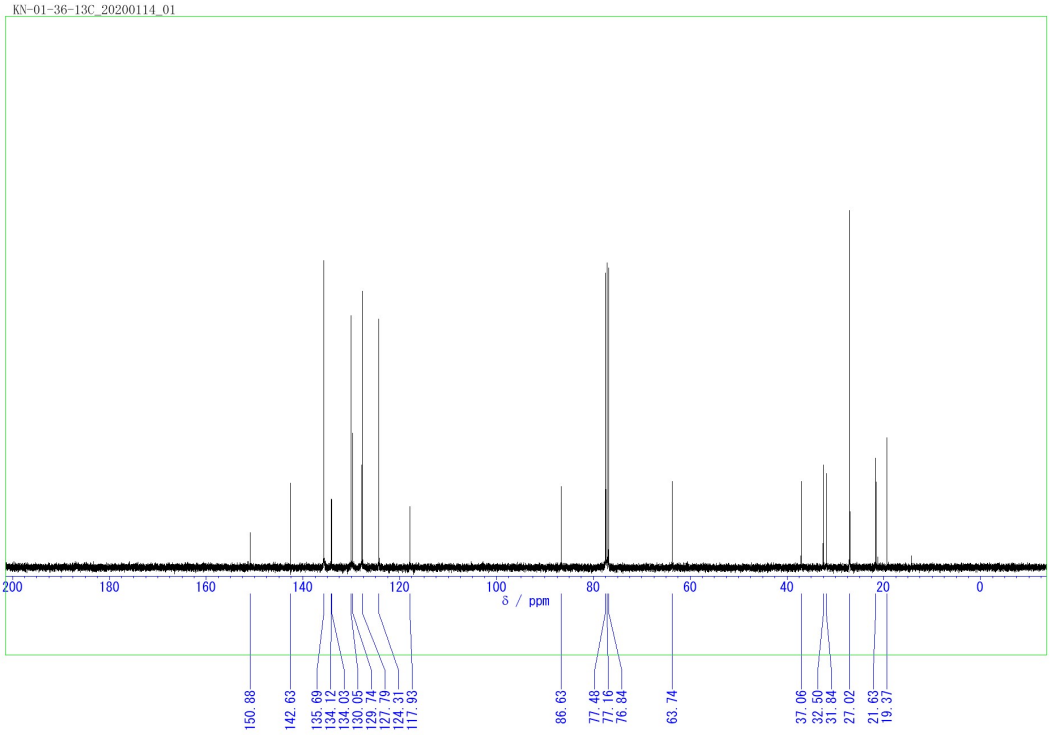
HA-13-15-H_20190128_01



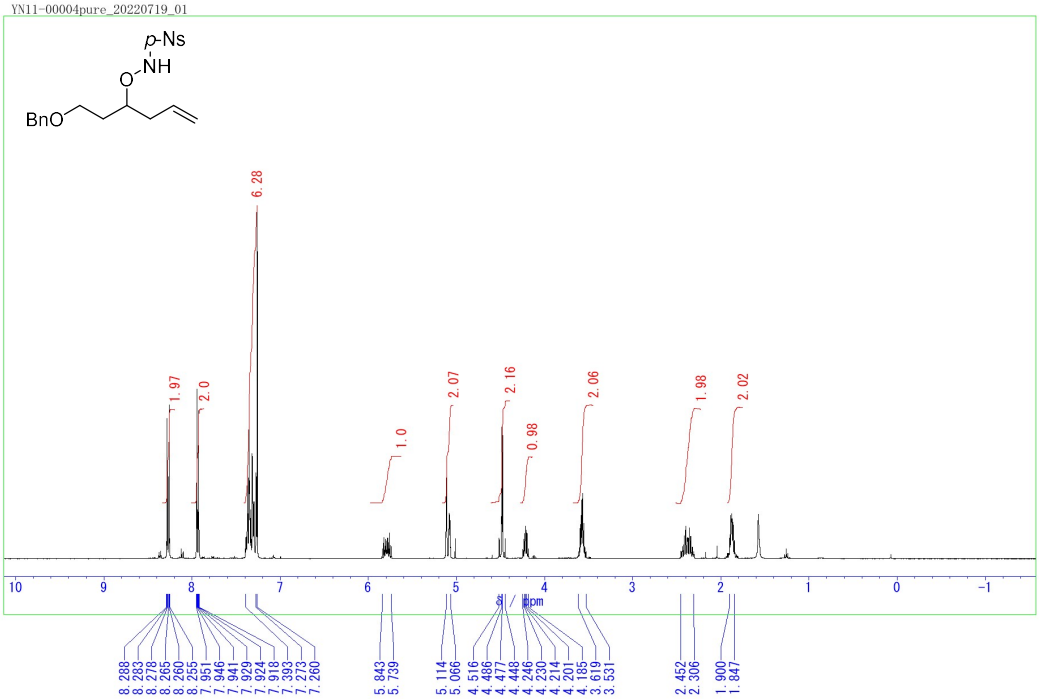
HA-13-29-sp1-carbon_20190110_01



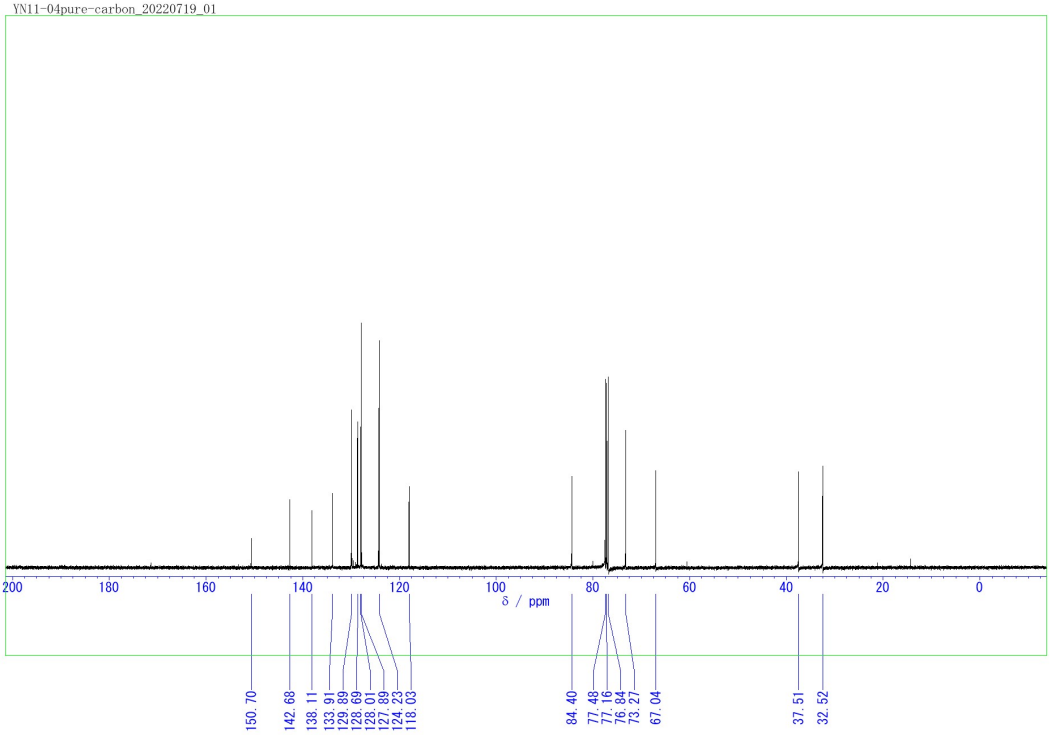

KN-01-36-d_20200115_01
p-Ns
N
H
O
TBDPSO
2.0
2.03
4.25
6.36
0.93
0.79
2.01
0.97
2.07
1.82
9.72
9.11
δ / ppm
8.345
8.340
8.335
8.322
8.317
8.312
8.104
8.094
8.081
8.076
8.071
7.675
7.647
7.443
7.359
7.260
6.871
5.823
5.719
5.110
5.067
4.158
4.098
3.686
3.670
3.655
2.366
2.320
1.574
1.407
1.046

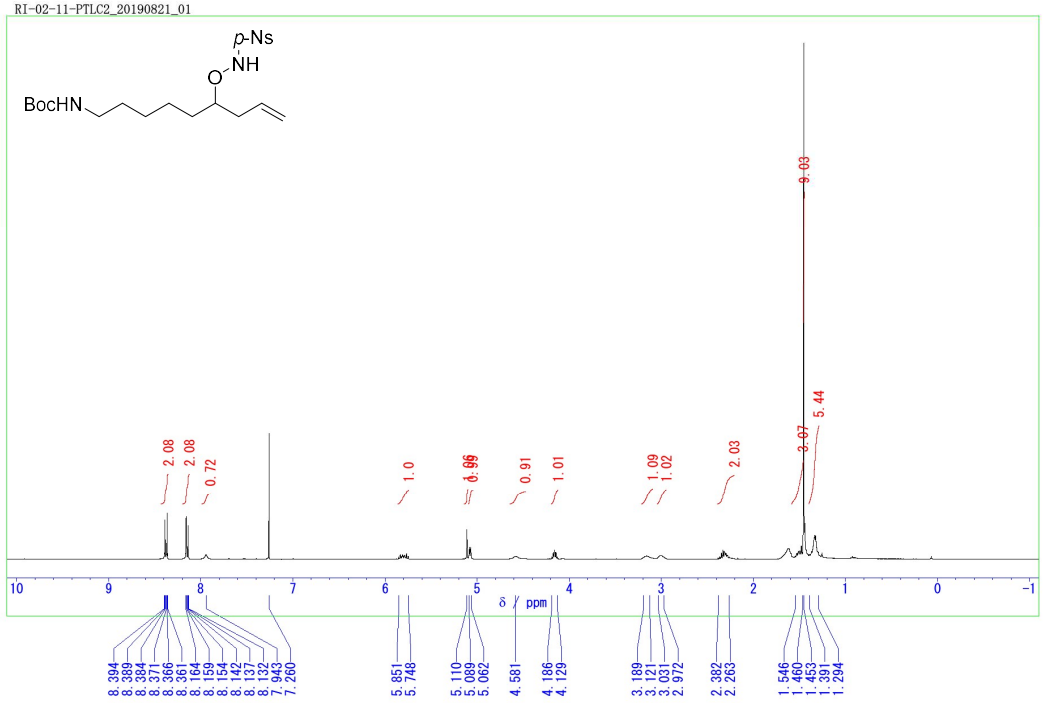

KN-01-36-13C_20200114_01
δ / ppm
150.88
142.63
135.69
134.12
134.03
130.05
129.74
127.79
124.31
117.93
86.63
77.48
77.16
76.84
63.74
37.06
32.50
31.84
27.02
21.63
19.37

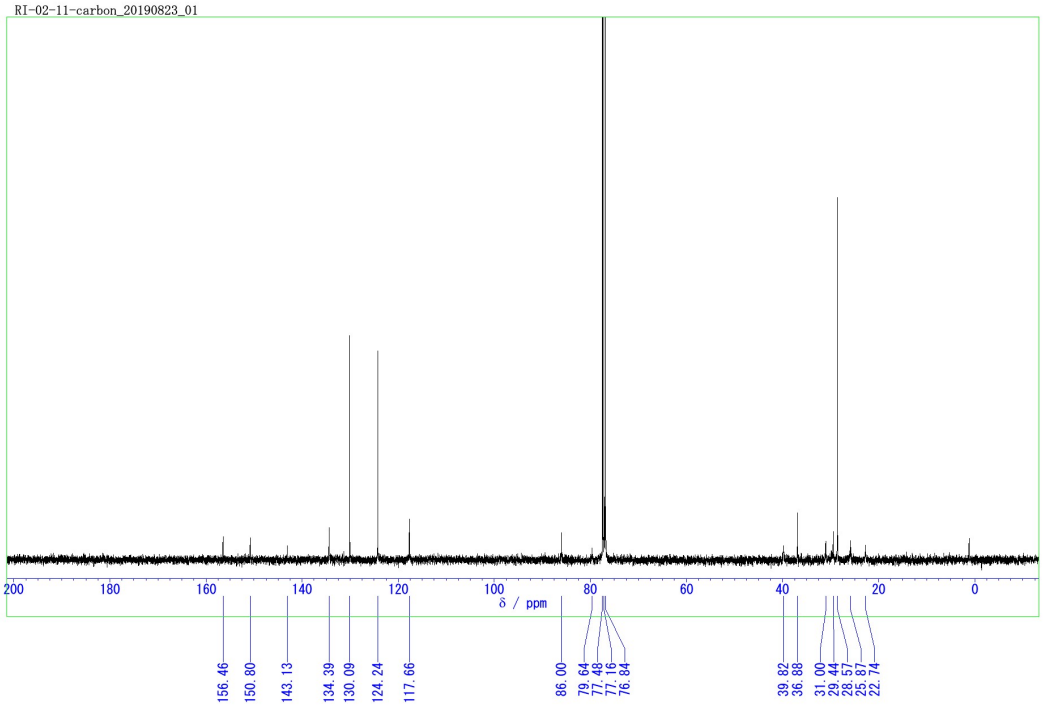
YN11-00004pure_20220719_01

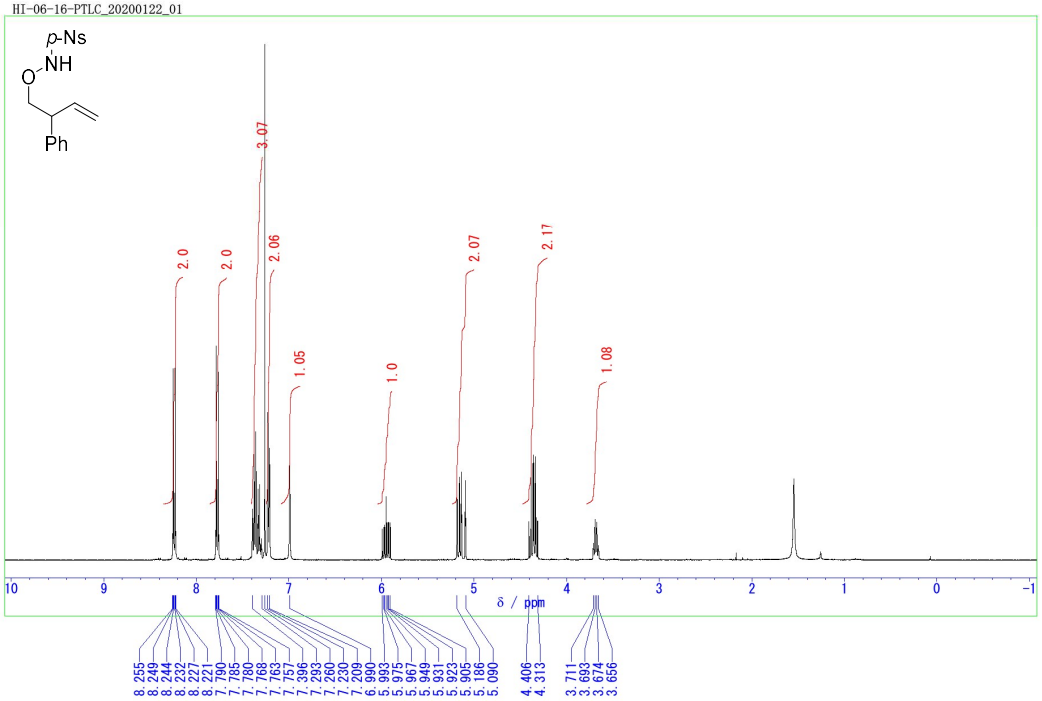


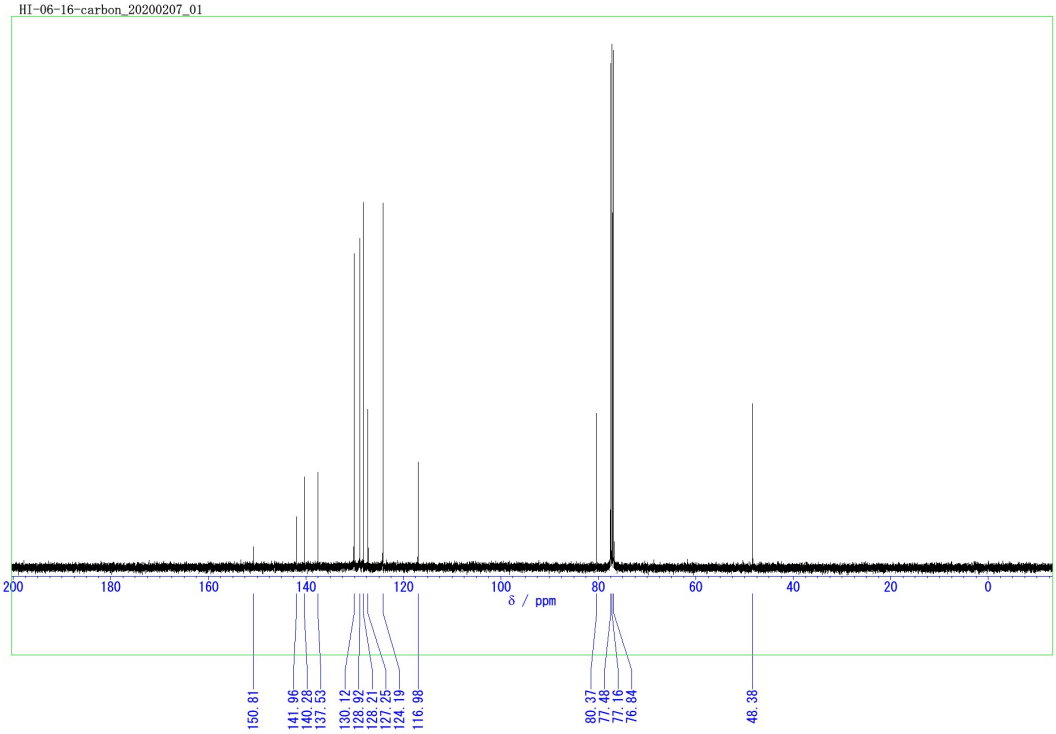
YN11-04pure-carbon_20220719_01



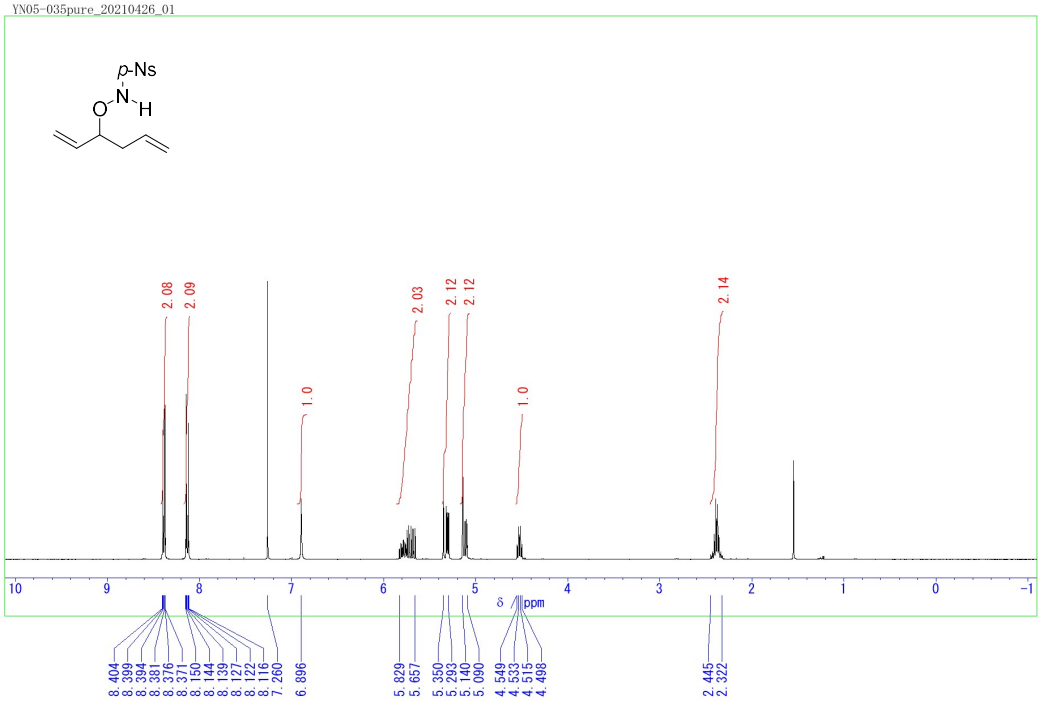

RI-02-11-PTLC2_20190821_01
p-Ns
NH
O
BocHN
9.03
5.44
3.07
2.08
2.08
0.72
1.0
0.91
1.01
1.09
1.02
2.03
δ / ppm
8.394
8.389
8.384
8.371
8.366
8.361
8.164
8.159
8.154
8.142
8.137
8.132
7.943
7.260
5.851
5.748
5.110
5.089
5.062
4.581
4.186
4.129
3.189
3.121
3.031
2.972
2.382
2.263
1.546
1.460
1.453
1.391
1.294


RI-02-11-carbon_20190823_01
δ / ppm
156.46
150.80
143.13
134.39
130.09
124.24
117.66
86.00
79.64
77.48
77.16
76.84
39.82
36.88
31.00
29.44
28.57
25.87
22.74

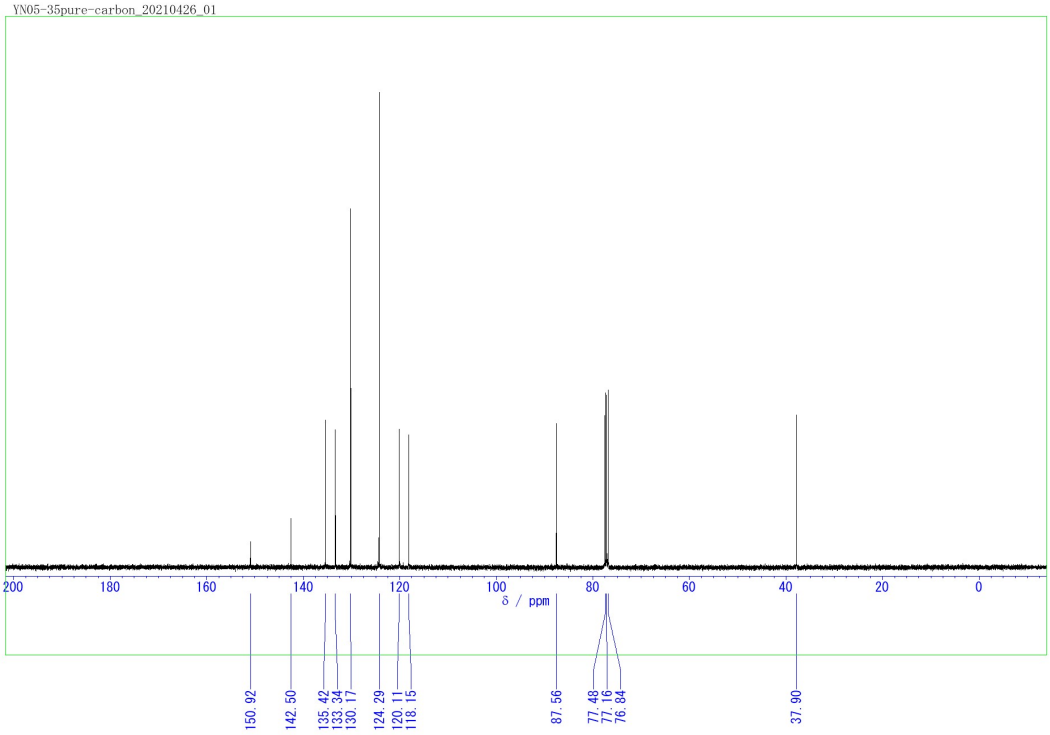

HI-06-16-PTLC_20200122_01
p-Ns
NH
O
Ph
3.07
2.0
2.0
2.06
1.05
1.0
2.07
2.17
1.08
δ / ppm
8.255
8.249
8.244
8.232
8.227
8.221
7.790
7.785
7.780
7.768
7.763
7.757
7.396
7.293
7.260
7.230
7.209
6.990
5.993
5.975
5.967
5.949
5.931
5.923
5.905
5.186
5.090
4.406
4.313
3.711
3.693
3.674
3.656


HI-06-16-carbon_20200207_01
δ / ppm
150.81
141.96
140.28
137.53
130.12
128.92
128.21
127.25
124.19
116.98
80.37
77.48
77.16
76.84
48.38

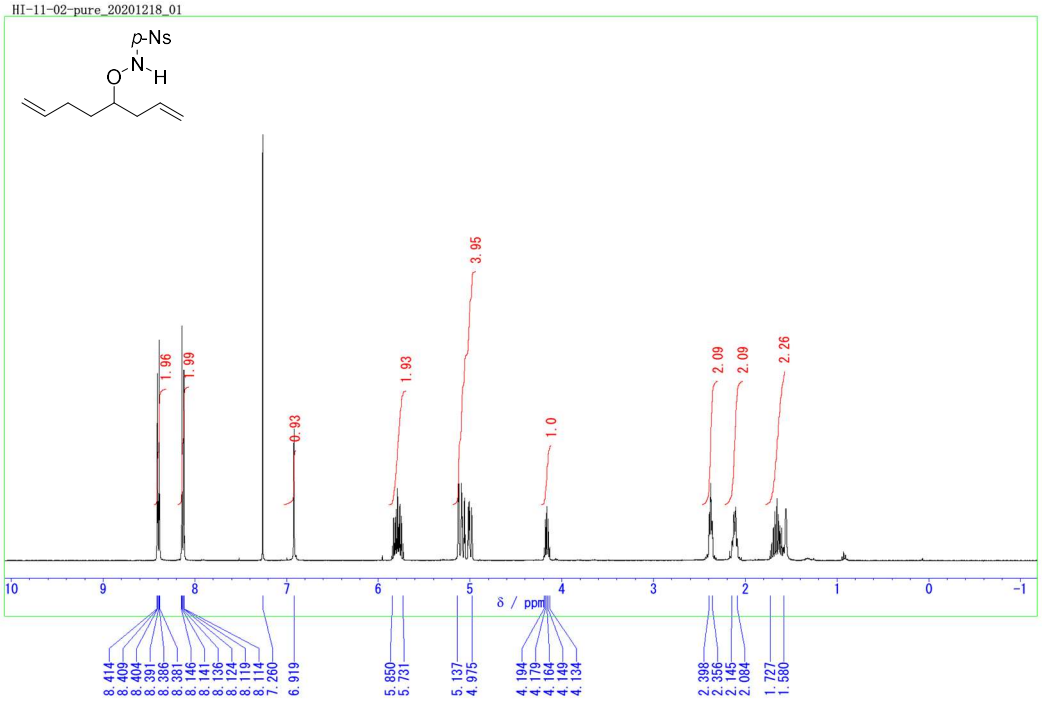
YN05-035pure_20210426_01



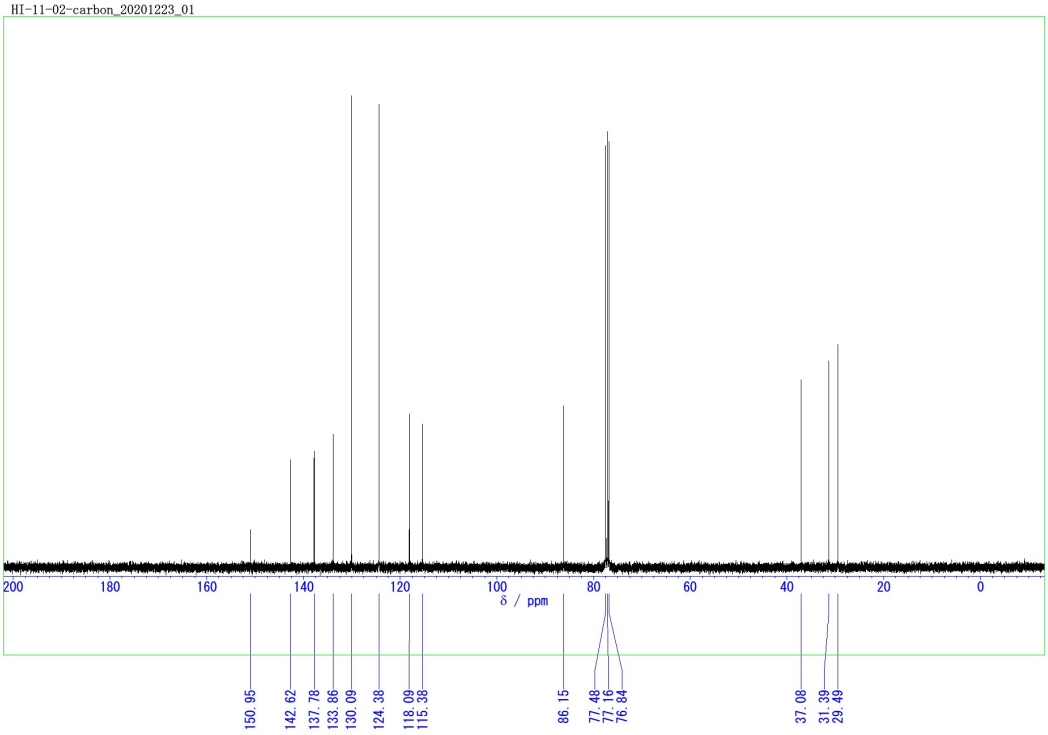
YN05-35pure-carbon_20210426_01

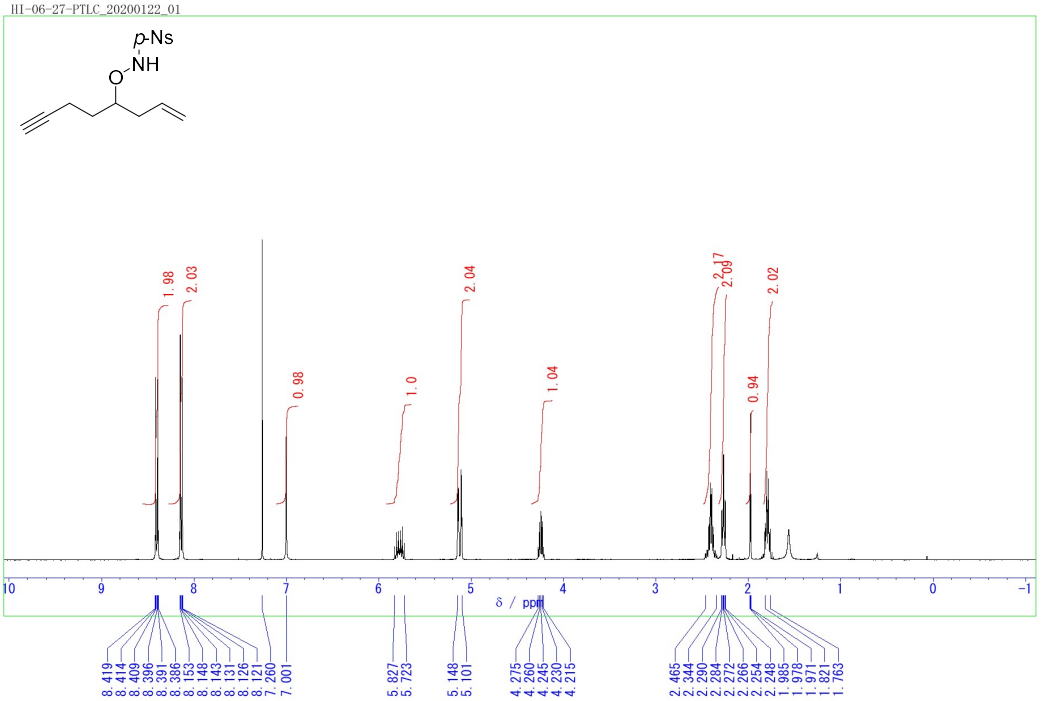


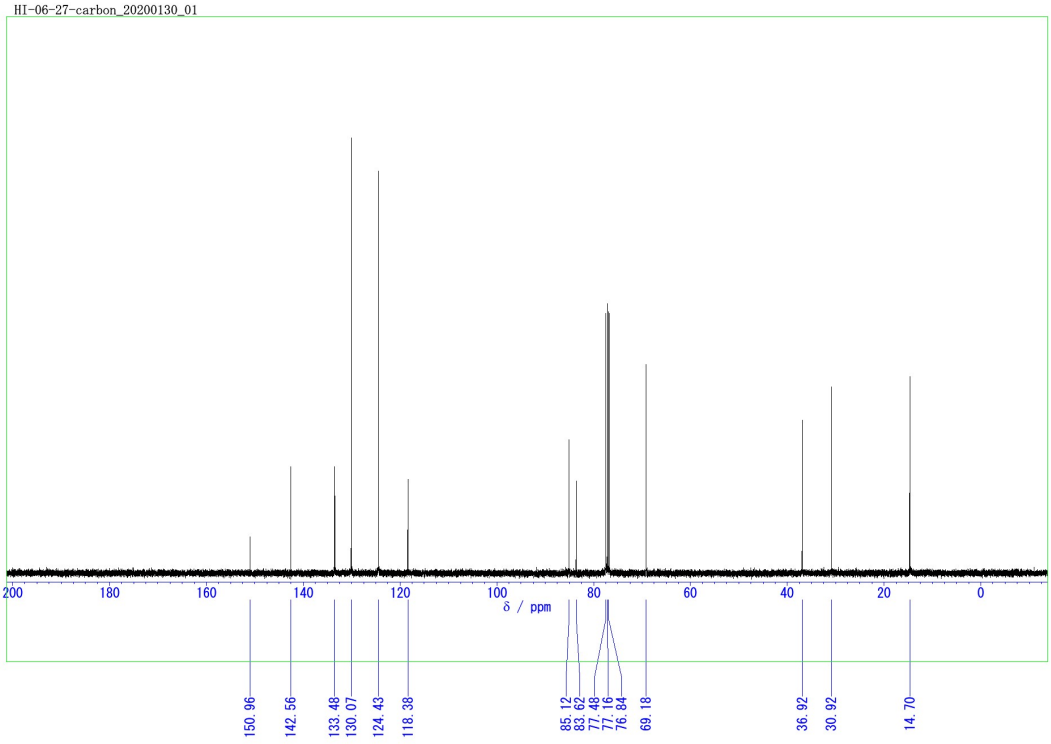
HI-11-02-pure_20201218_01

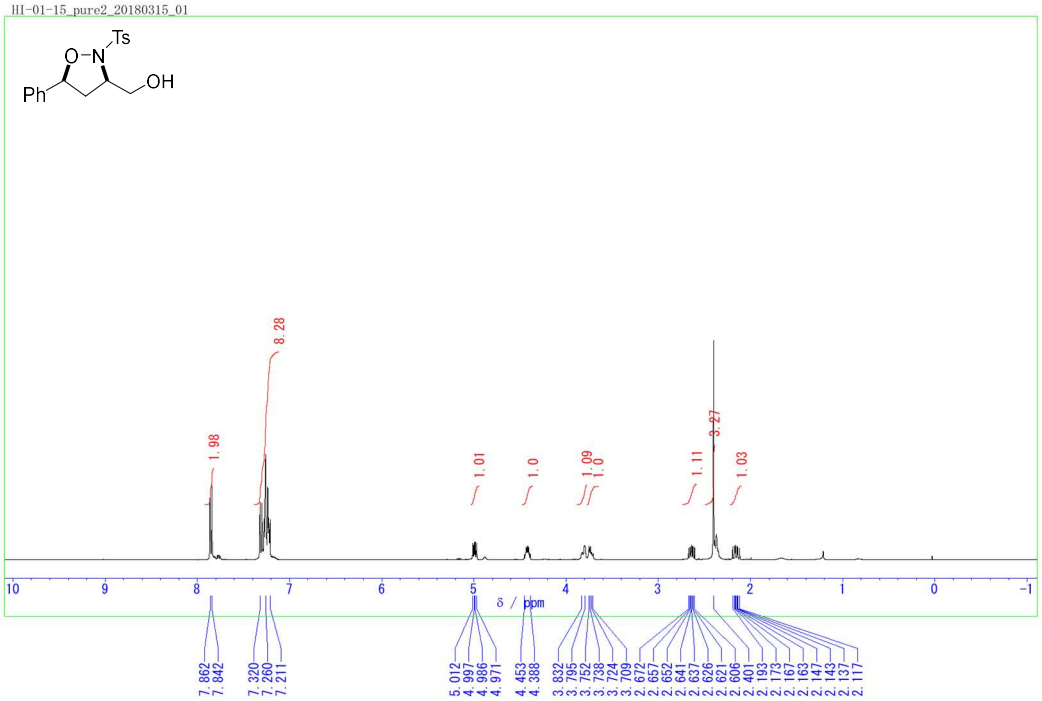


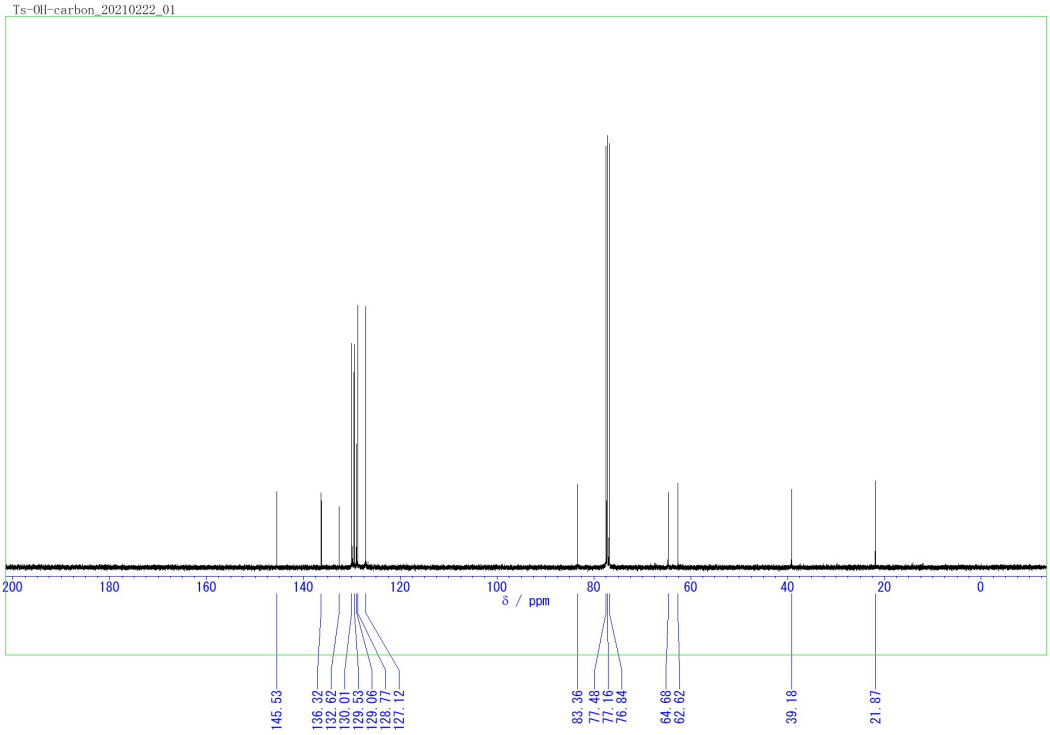
HI-11-02-carbon_20201223_01

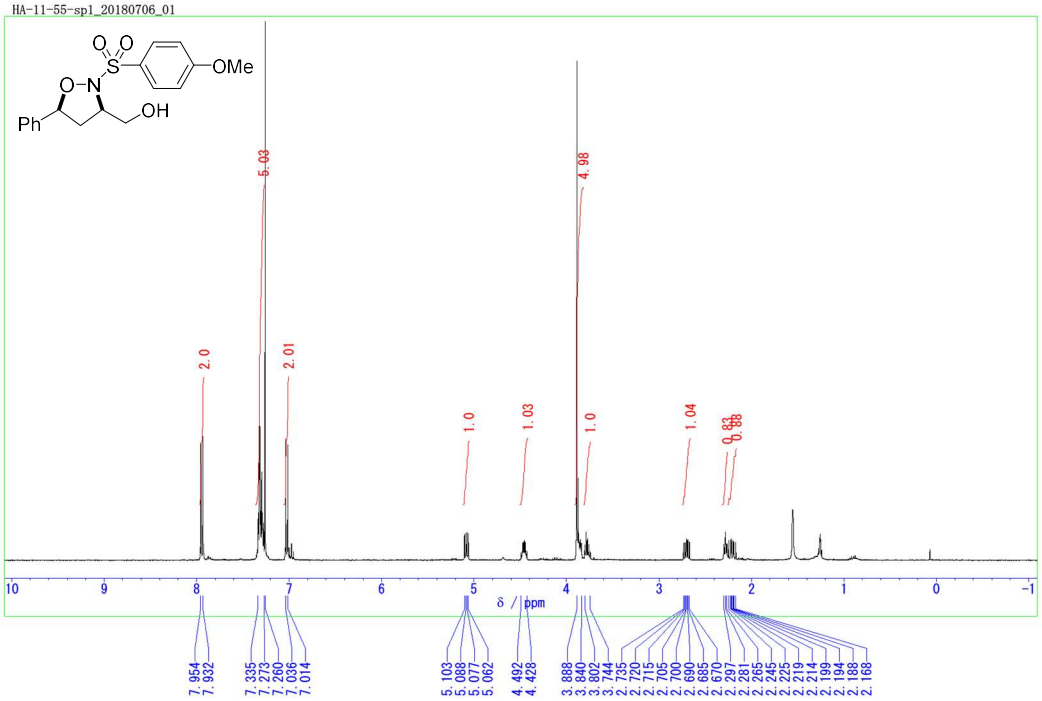


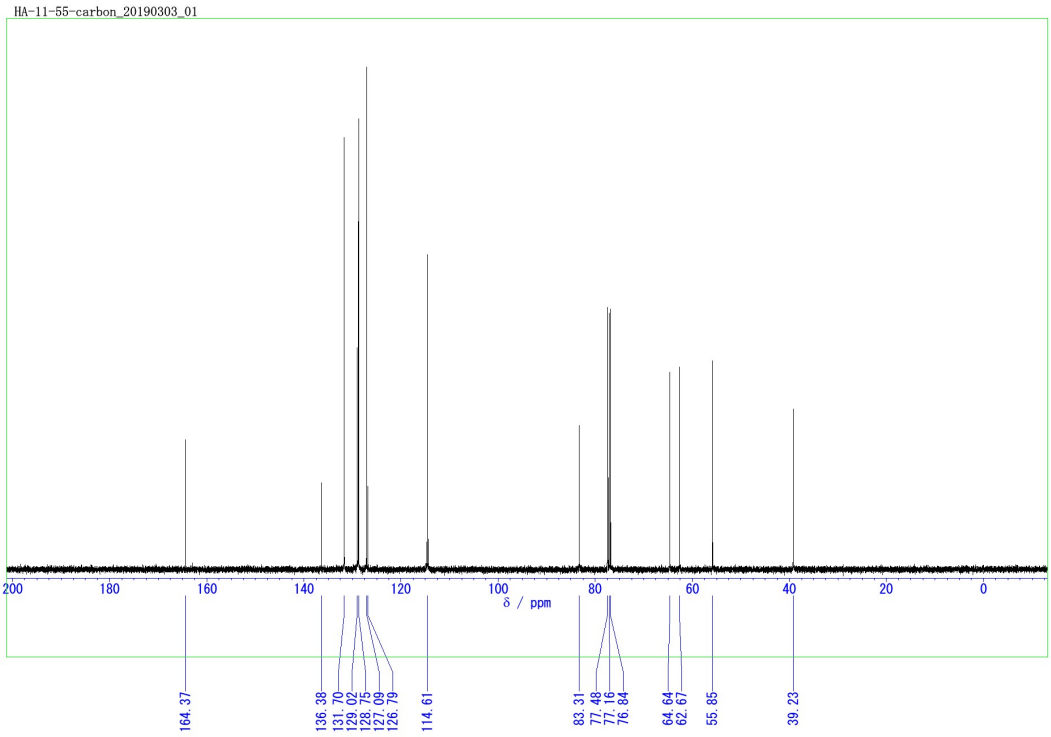

HI-06-27-PTLC_20200122_01
p-Ns
NH
O
1.98
2.03
0.98
1.0
2.04
1.04
2.17
2.09
0.94
2.02
δ / ppm
8.419
8.414
8.409
8.396
8.391
8.386
8.153
8.148
8.143
8.131
8.126
8.121
7.260
7.001
5.827
5.723
5.148
5.101
4.275
4.260
4.245
4.230
4.215
2.465
2.344
2.290
2.284
2.272
2.266
2.254
2.248
1.978
1.971
1.821
1.763

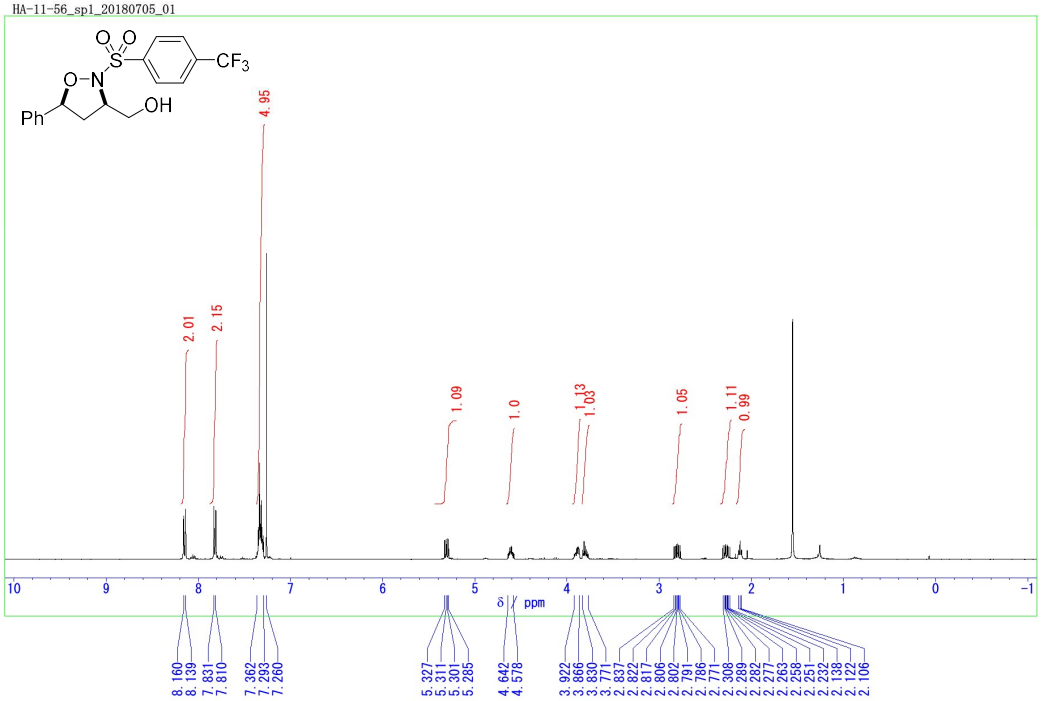

HI-06-27-carbon_20200130_01
δ / ppm
150.96
142.56
133.48
130.07
124.43
118.38
85.12
83.62
77.48
77.16
76.84
69.18
36.92
30.92
14.70

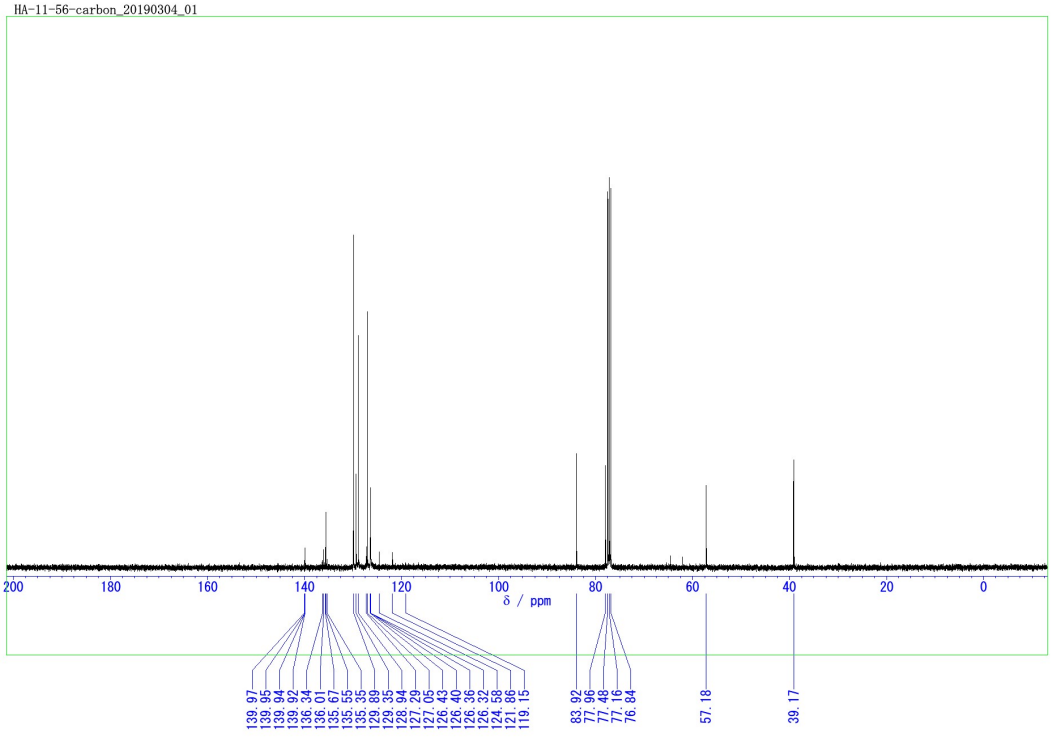

HH-01-15_pure2_20180315_01
Ts
O
N
Ph
OH
1.98
8.28
1.01
1.0
1.09
1.0
1.11
3.27
1.03
δ / ppm
7.862
7.842
7.320
7.260
7.211
5.012
4.997
4.986
4.971
4.453
4.388
3.832
3.795
3.752
3.738
3.724
3.709
2.672
2.657
2.652
2.641
2.637
2.626
2.621
2.606
2.401
2.193
2.173
2.167
2.163
2.147
2.143
2.137
2.117

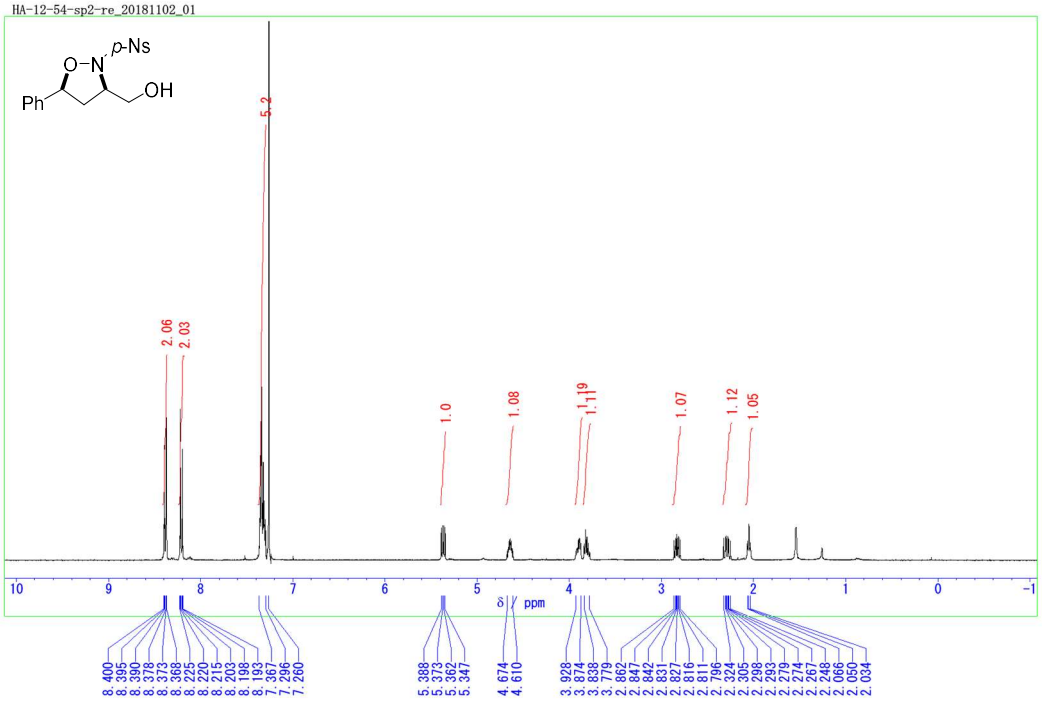

Ts-OH-carbon_20210222_01
δ / ppm
145.53
136.32
132.62
130.01
129.53
129.06
128.77
127.12
83.36
77.48
77.16
76.84
64.68
62.62
39.18
21.87

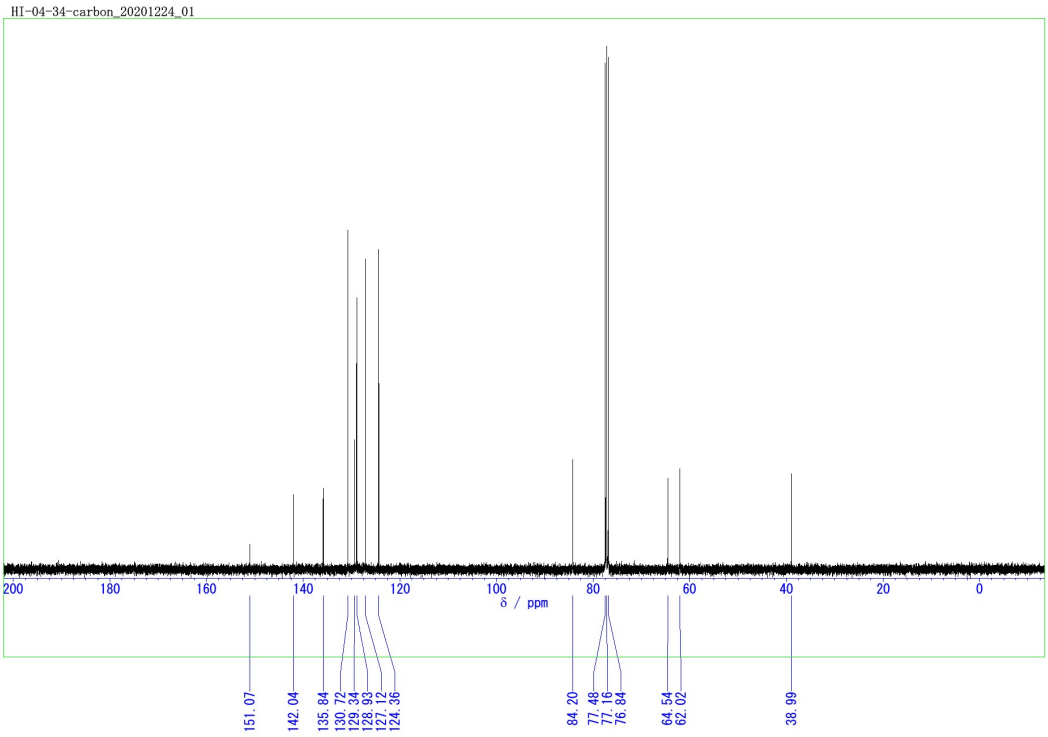

HA-11-55-sp1_20180706_01
OMe
OH
Ph
δ / ppm


HA-11-55-carbon_20190303_01
δ / ppm

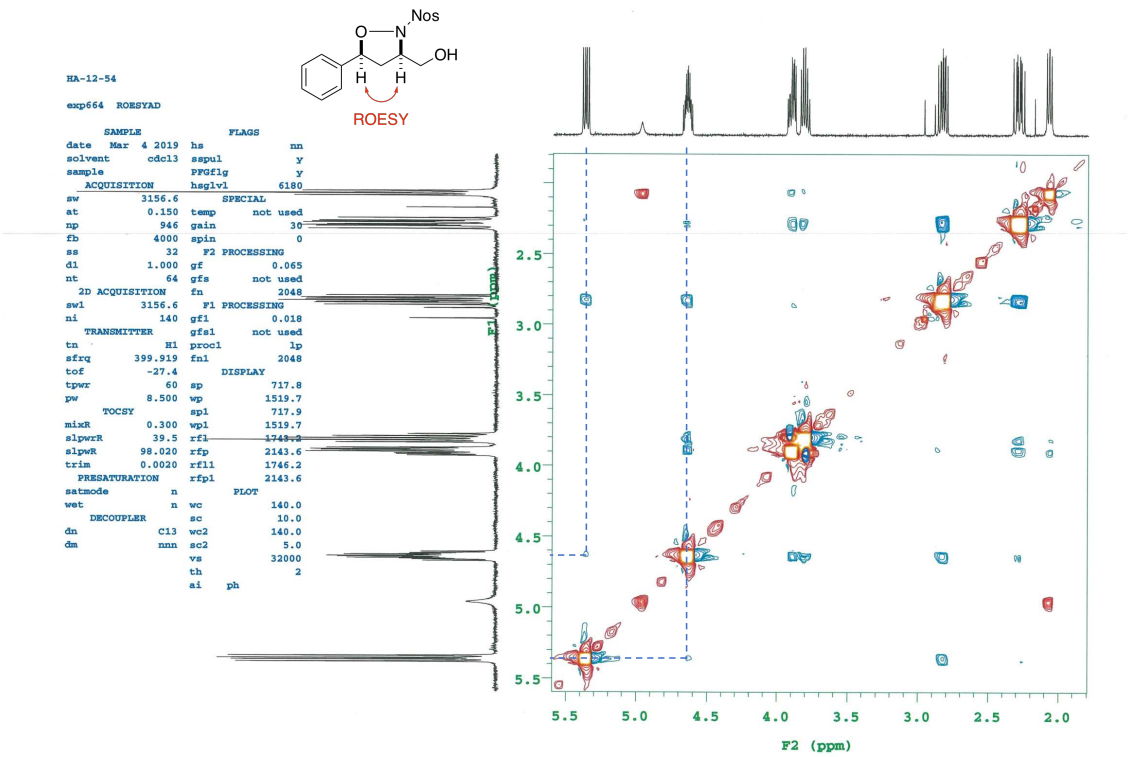

HA-11-56_sp1_20180705_01
Ph
OH
CF3
4.95
2.01
2.15
1.09
1.0
1.13
1.03
1.05
1.11
0.99
δ / ppm
8.160
8.139
7.831
7.810
7.362
7.293
7.260
5.327
5.311
5.301
5.285
4.642
4.578
3.922
3.866
3.830
3.771
2.837
2.822
2.817
2.806
2.802
2.791
2.786
2.771
2.308
2.289
2.282
2.277
2.263
2.258
2.251
2.232
2.138
2.122
2.106


HA-11-56-carbon_20190304_01
δ / ppm
139.97
139.95
139.94
139.92
136.34
136.01
135.67
135.55
135.35
129.89
129.35
128.94
127.29
127.05
126.43
126.40
126.36
126.32
121.58
121.86
119.15
83.92
77.96
77.48
77.16
76.84
57.18
39.17

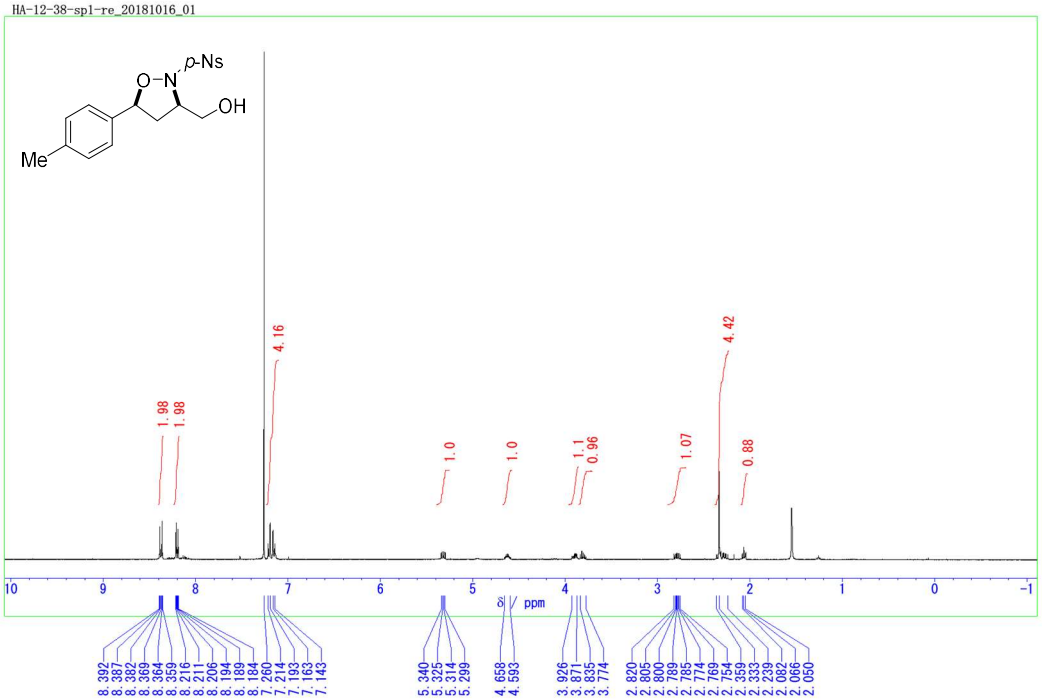

HA-12-54-sp2-re_20181102_01
p-Ns
O
N
Ph
OH
5.2
2.06
2.03
1.0
1.08
1.19
1.11
1.07
1.12
1.05
δ / ppm
8.400
8.395
8.390
8.378
8.373
8.368
8.225
8.220
8.215
8.203
8.198
8.193
7.367
7.296
7.260
5.388
5.373
5.362
5.347
4.674
4.610
3.928
3.874
3.838
3.779
2.862
2.847
2.842
2.831
2.827
2.816
2.811
2.796
2.324
2.305
2.298
2.293
2.274
2.267
2.248
2.066
2.050
2.034


HI-04-34-carbon_20201224_01
δ / ppm
151.07
142.04
135.84
130.72
129.34
129.03
127.12
124.36
84.20
77.48
77.16
76.84
64.54
62.02
38.99

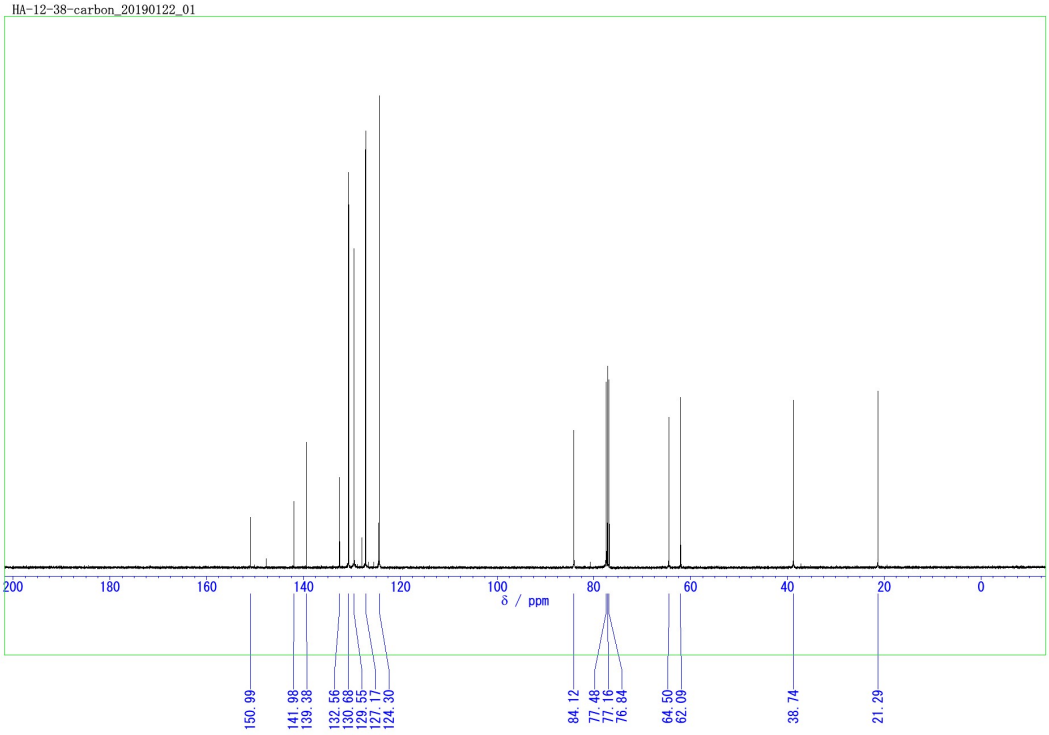
ROESY analysis.

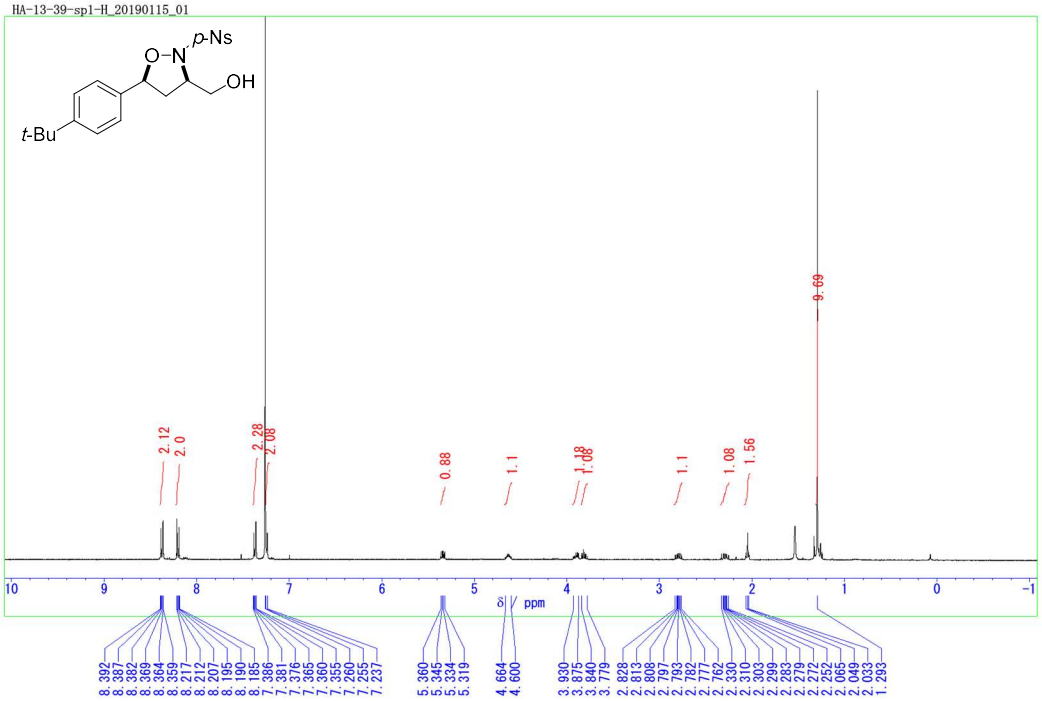


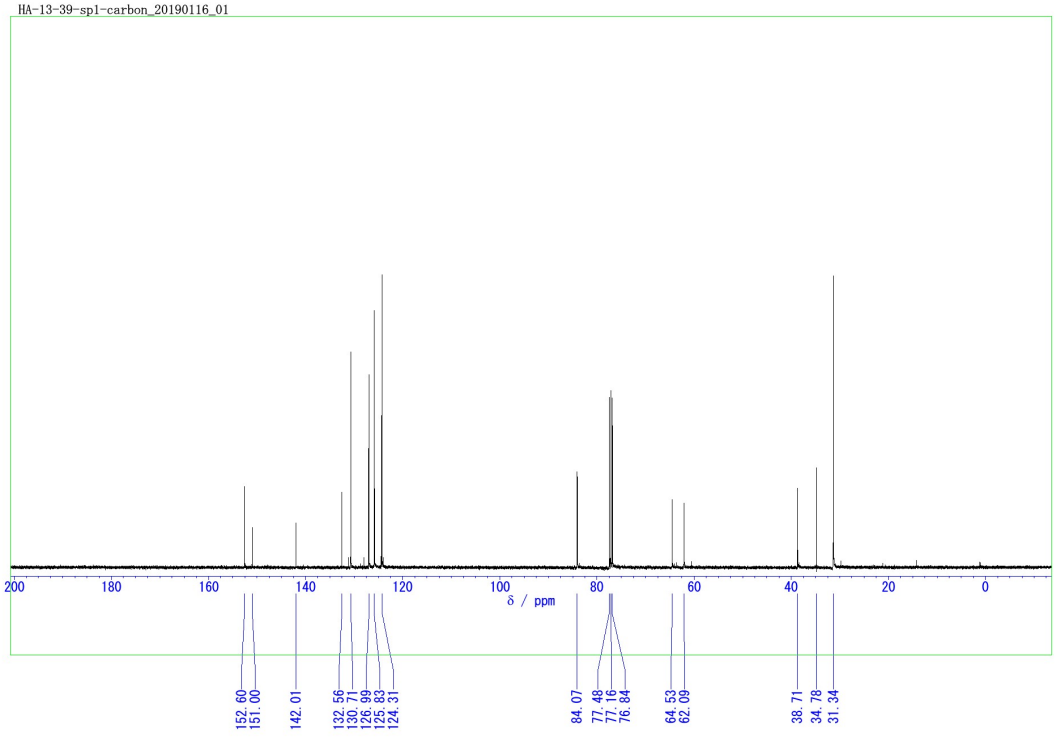
HA-12-38-sp1-re_20181016_01

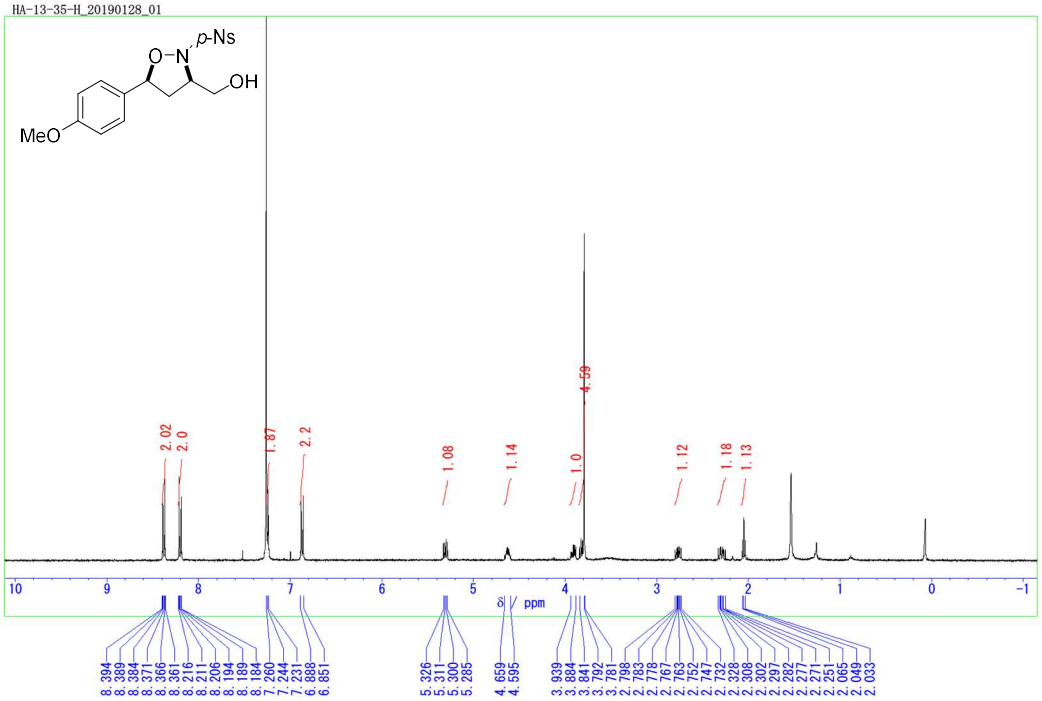


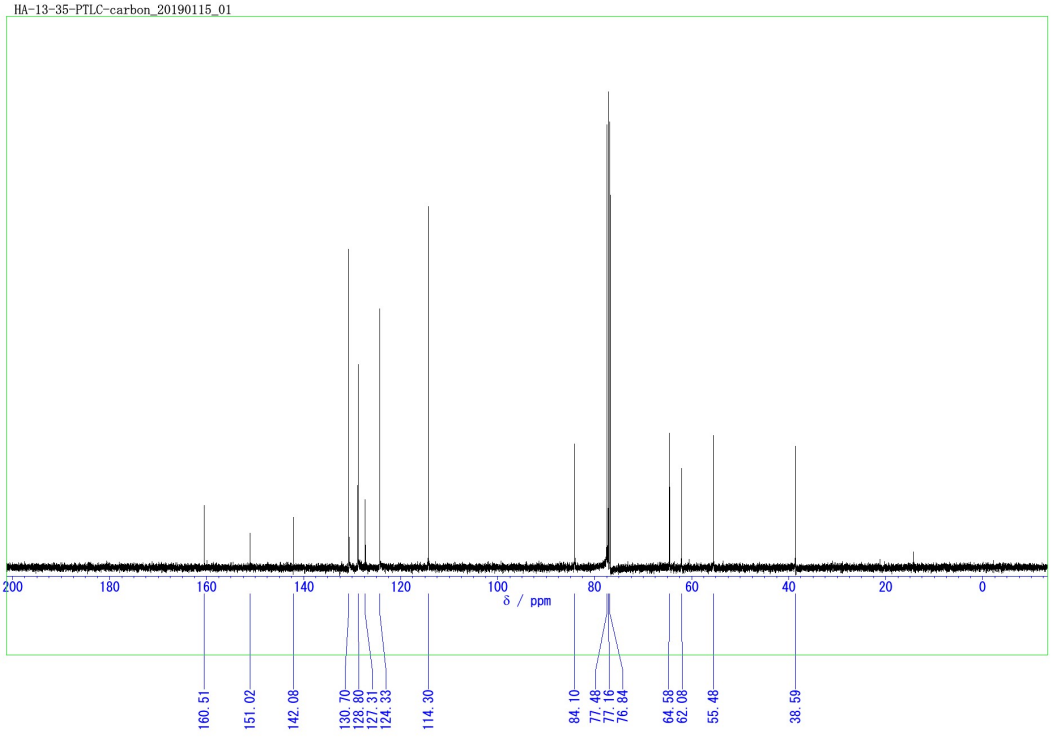
HA-12-38-carbon_20190122_01

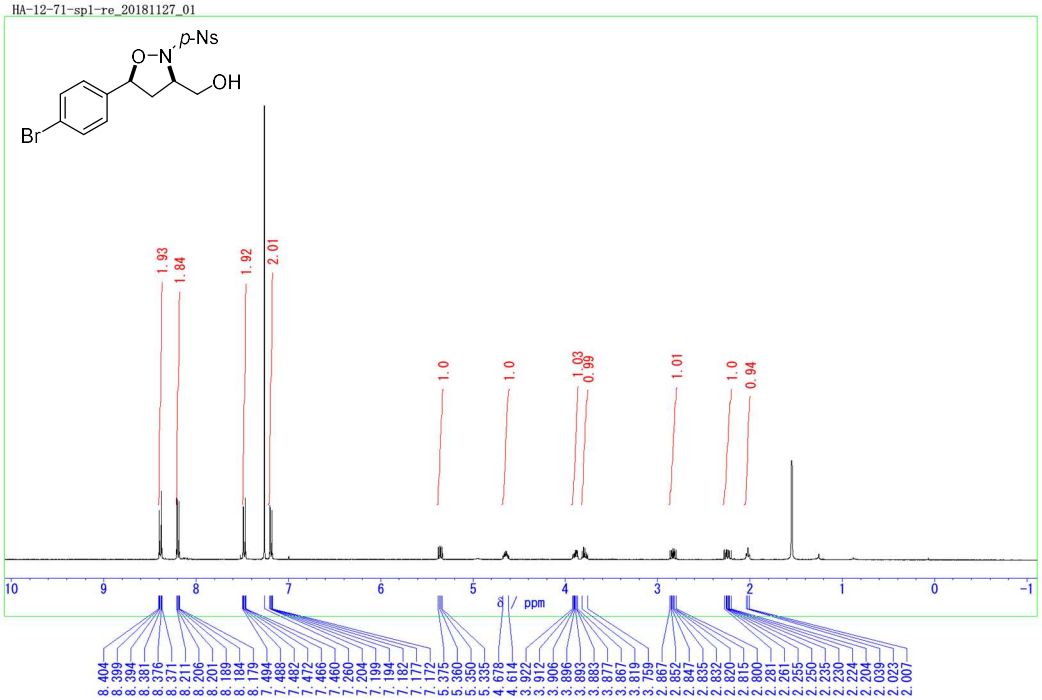


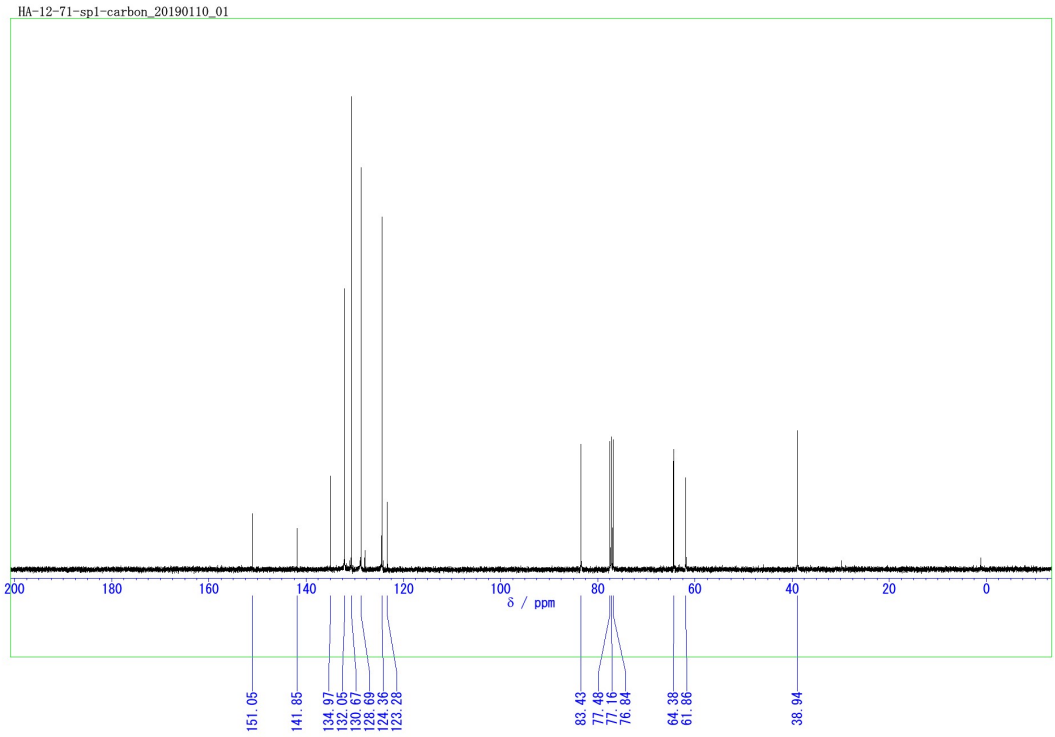

HA-13-39-sp1-H_20190115_01
p-Ns
O-N
OH
t-Bu
9.69
2.12
2.0
2.28
2.08
0.88
1.1
1.08
1.08
1.1
1.08
1.56
δ / ppm
8.392
8.387
8.382
8.369
8.364
8.359
8.217
8.212
8.207
8.195
8.190
8.185
7.386
7.381
7.376
7.365
7.360
7.355
7.260
7.255
7.237
5.360
5.345
5.334
5.319
4.664
4.600
3.930
3.875
3.840
3.779
2.828
2.813
2.808
2.797
2.793
2.782
2.777
2.762
2.330
2.310
2.303
2.299
2.283
2.279
2.272
2.252
2.065
2.049
2.033
1.293

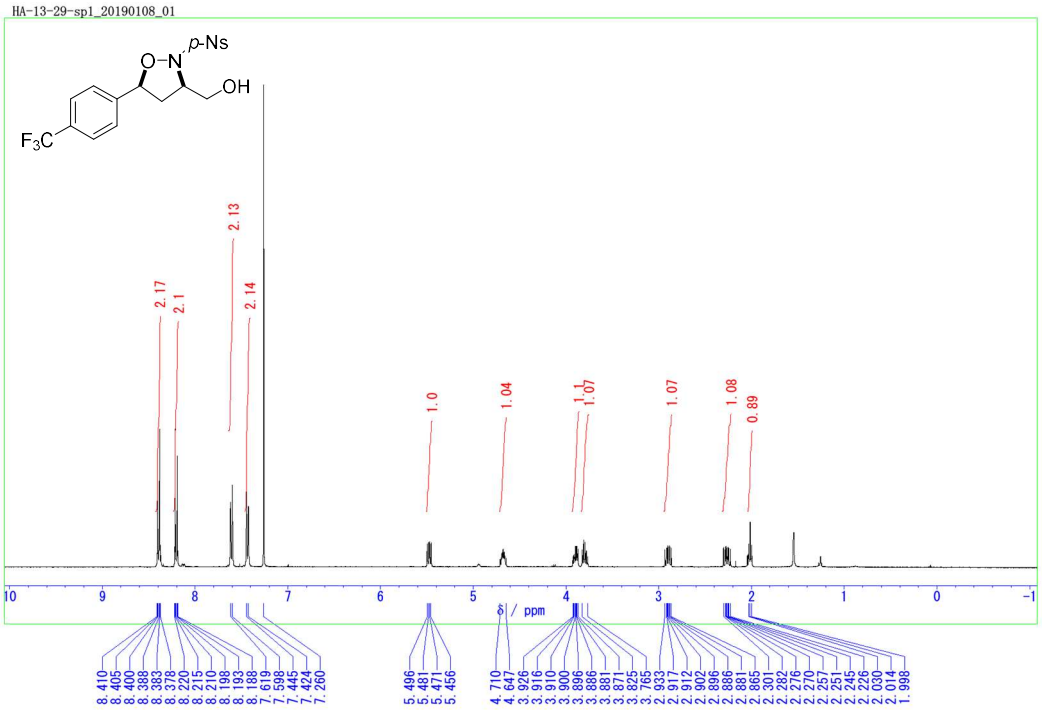

HA-13-39-sp1-carbon_20190116_01
δ / ppm
152.60
151.00
142.01
132.56
130.71
126.99
125.83
124.31
84.07
77.48
77.16
76.84
64.53
62.09
38.71
34.78
31.34

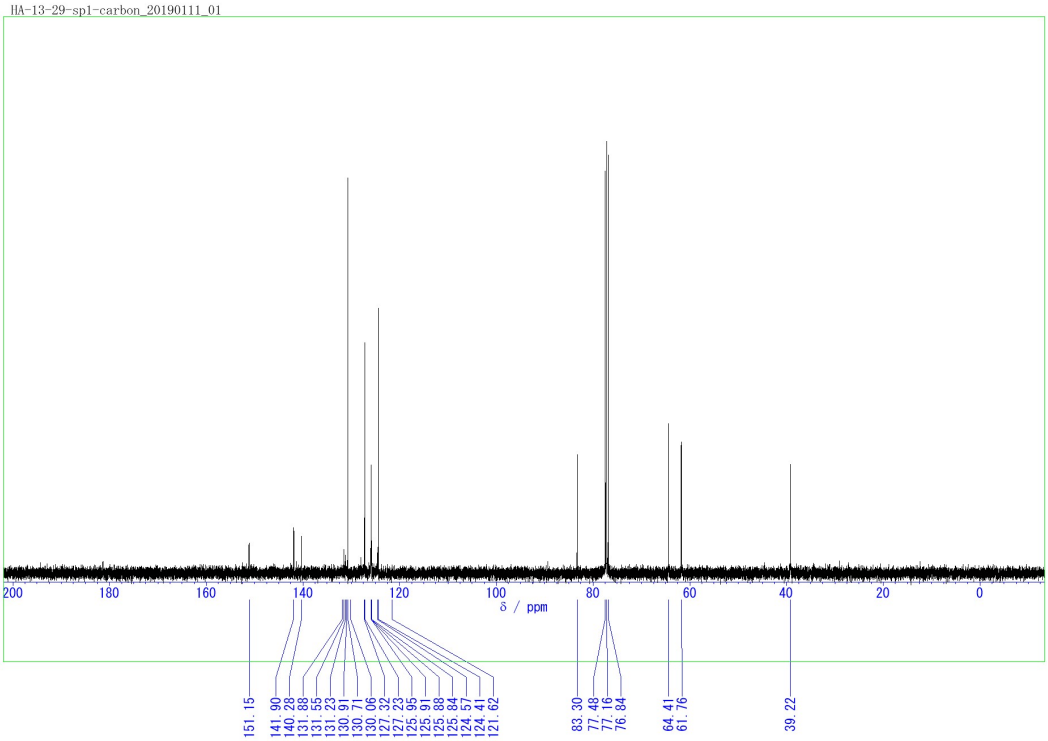

HA-13-35-H_20190128_01
p-Ns
O
N
OH
MeO
2.02
2.0
1.87
2.2
1.08
1.14
1.0
4.59
1.12
1.18
1.13
δ / ppm
8.394
8.389
8.384
8.371
8.366
8.361
8.216
8.211
8.206
8.194
8.189
8.184
7.260
7.244
7.231
6.888
6.851
5.326
5.311
5.300
5.285
4.659
4.595
3.939
3.884
3.841
3.792
3.781
2.798
2.783
2.778
2.767
2.763
2.752
2.747
2.732
2.328
2.308
2.302
2.297
2.282
2.277
2.271
2.251
2.065
2.049
2.033

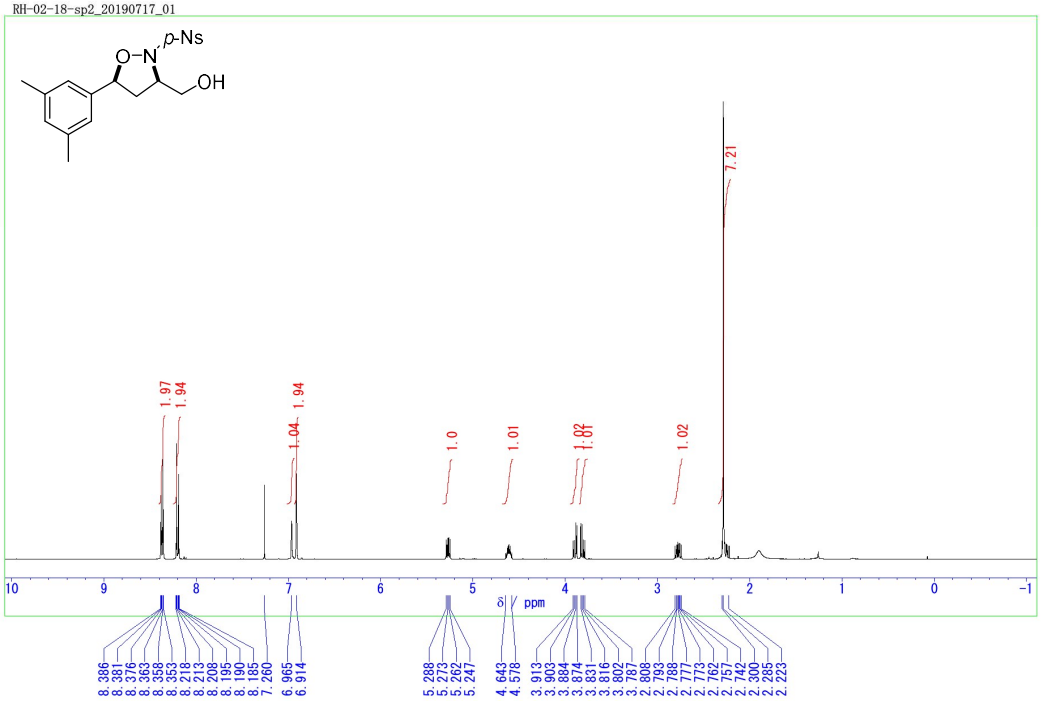

HA-13-35-PTLC-carbon_20190115_01
δ / ppm
160.51
151.02
142.08
130.70
128.80
127.31
124.33
114.30
84.10
77.48
77.16
76.84
64.58
62.08
55.48
38.59

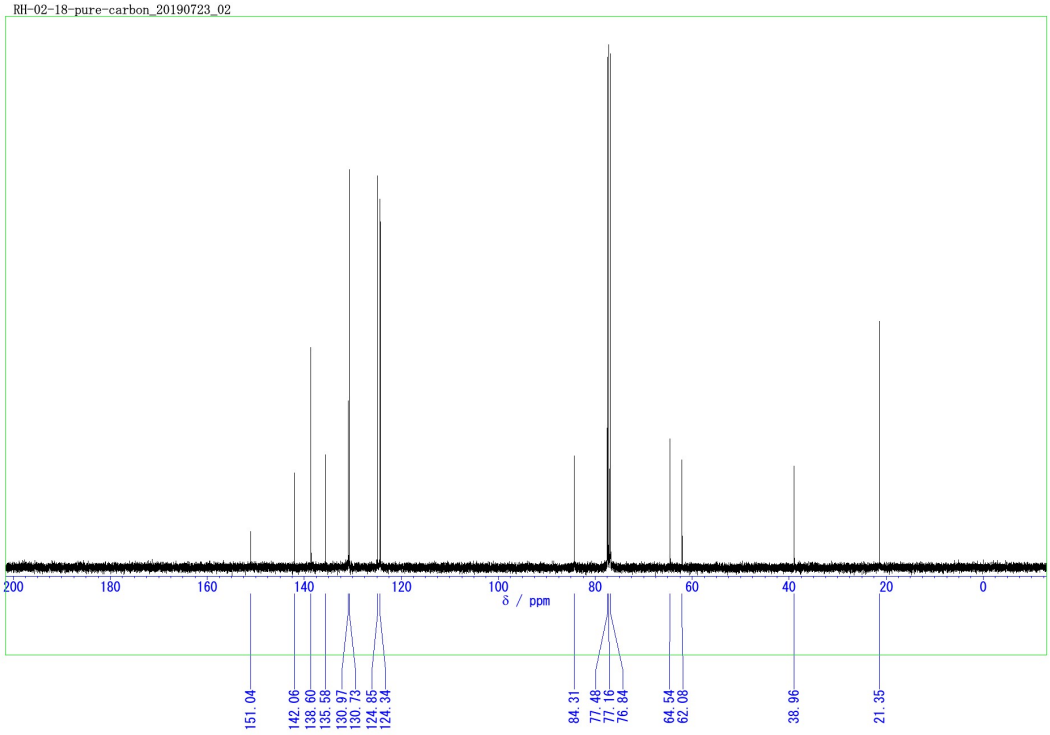

HA-12-71-sp1-re_20181127_01
p-Ns
O
N
OH
Br
1.93
1.84
1.92
2.01
1.0
1.0
1.03
0.99
1.01
1.0
0.94
δ / ppm

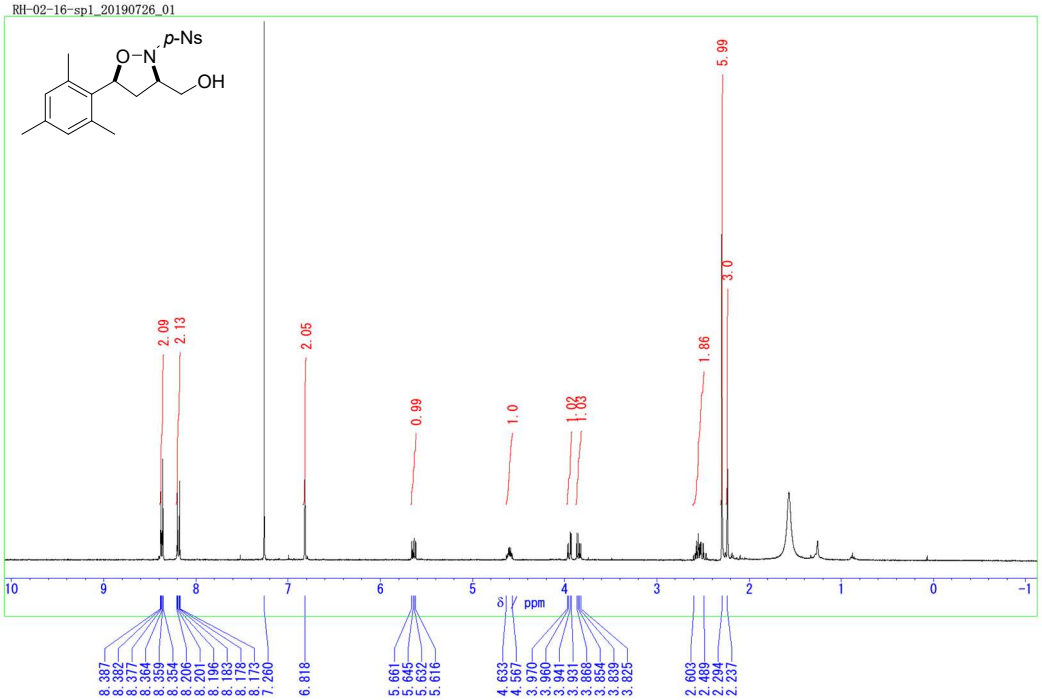

HA-12-71-sp1-carbon_20190110_01
δ / ppm

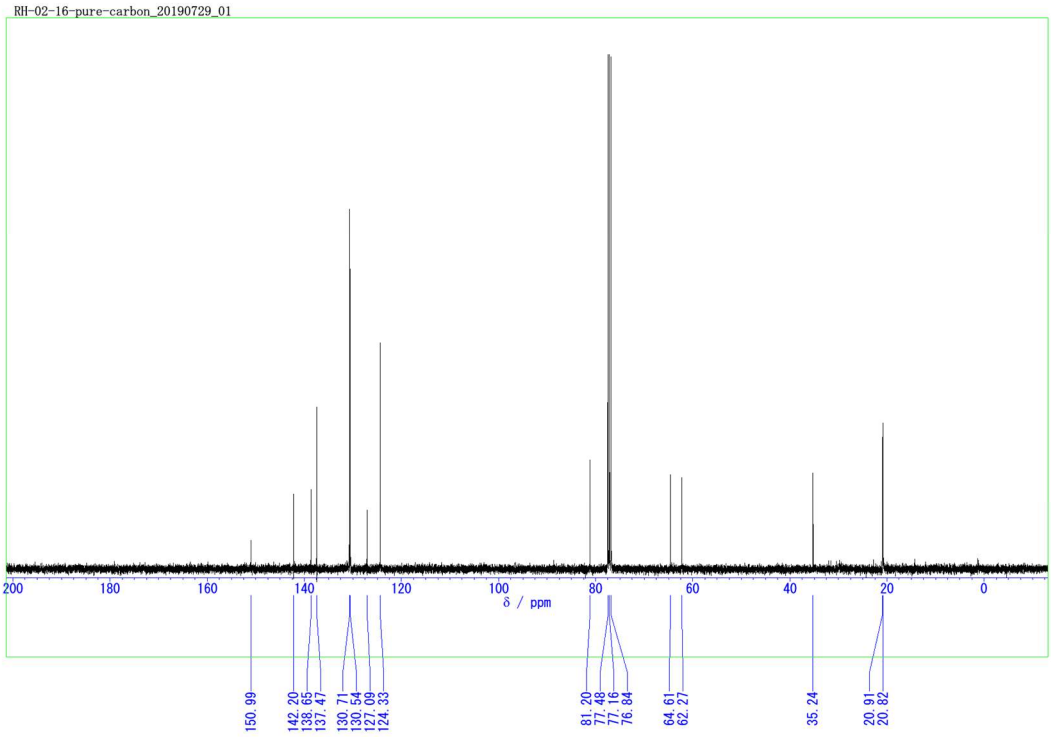

HA-13-29-sp1_20190108_01
p-Ns
O-N
OH
F3C
2.17
2.1
2.13
2.14
1.0
1.04
1.1
1.07
1.07
1.08
0.89
δ / ppm
8.410
8.405
8.400
8.388
8.383
8.378
8.220
8.215
8.210
8.198
8.193
8.188
7.619
7.598
7.445
7.424
7.260
5.496
5.481
5.471
5.456
4.710
4.647
3.926
3.916
3.910
3.900
3.896
3.886
3.881
3.871
3.825
3.765
2.933
2.917
2.912
2.902
2.896
2.886
2.881
2.865
2.301
2.282
2.276
2.270
2.257
2.251
2.245
2.226
2.030
2.014
1.998


HA-13-29-sp1-carbon_20190111_01
δ / ppm
151.15
141.90
140.28
131.88
131.55
131.23
130.91
130.71
130.06
127.32
127.23
125.95
125.91
125.88
125.84
124.57
124.41
121.62
83.30
77.48
77.16
76.84
64.41
61.76
39.22

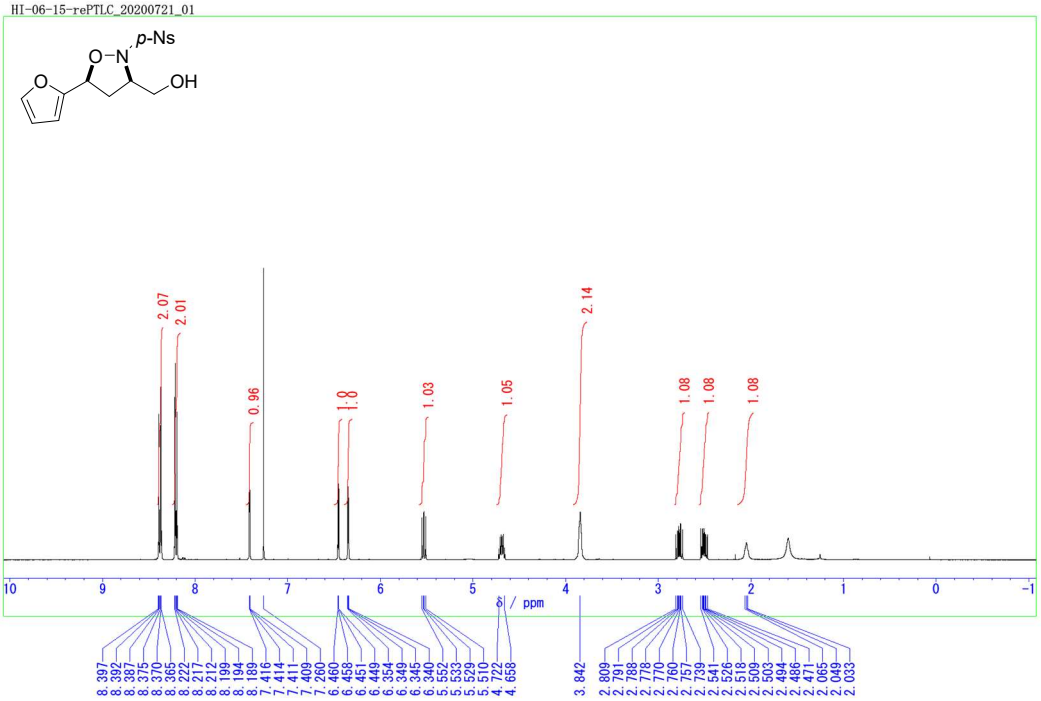

RH-02-18-sp2_20190717_01
p-Ns
O
N
OH
1.97
1.94
1.04
1.94
1.0
1.01
1.02
1.02
1.01
7.21
δ / ppm
8.386
8.381
8.376
8.363
8.358
8.353
8.218
8.213
8.208
8.195
8.190
8.185
7.260
6.965
6.914
5.288
5.273
5.262
5.247
4.643
4.578
3.913
3.903
3.884
3.874
3.831
3.816
3.802
3.787
2.808
2.788
2.783
2.777
2.773
2.762
2.757
2.742
2.300
2.285
2.223


RH-02-18-pure-carbon_20190723_02
δ / ppm
151.04
142.06
138.60
135.58
130.97
130.73
124.85
124.34
84.31
77.48
77.16
76.84
64.54
62.08
38.96
21.35

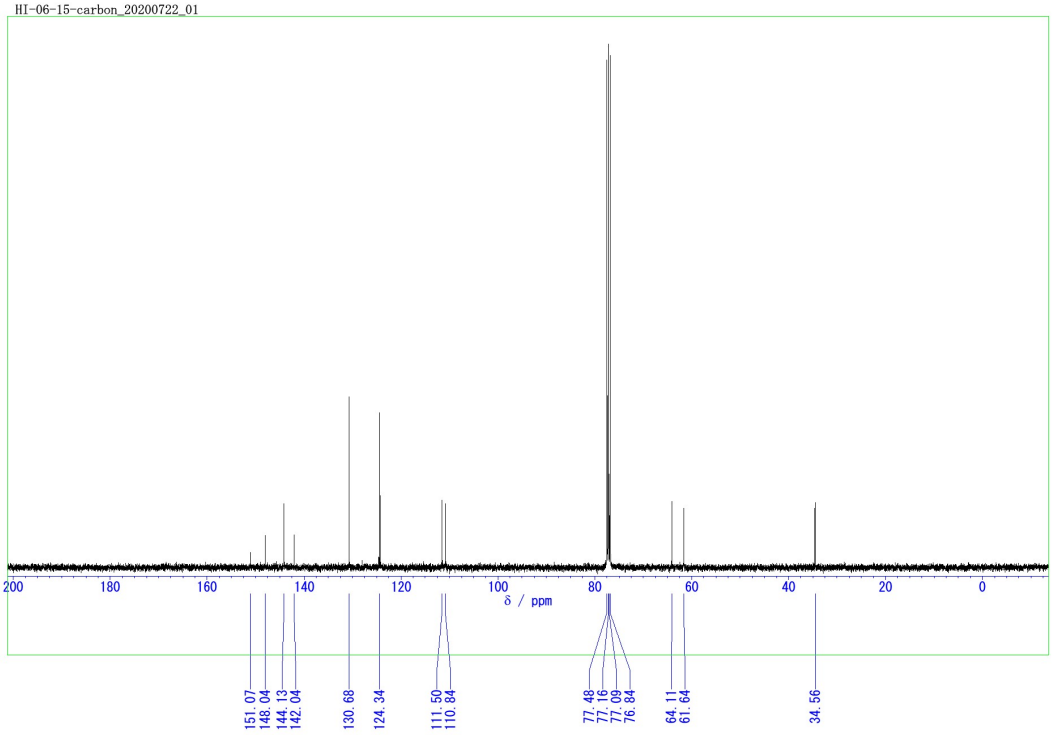

RH-02-16-sp1_20190726_01
p-Ns
O
N
OH
5.99
3.0
2.09
2.13
2.05
1.86
0.99
1.0
1.02
1.03
δ / ppm
8.387
8.382
8.377
8.364
8.359
8.354
8.206
8.201
8.196
8.183
8.178
8.173
7.260
6.818
5.661
5.645
5.632
5.616
4.633
4.567
3.970
3.960
3.941
3.931
3.868
3.854
3.839
3.825
2.603
2.489
2.294
2.237

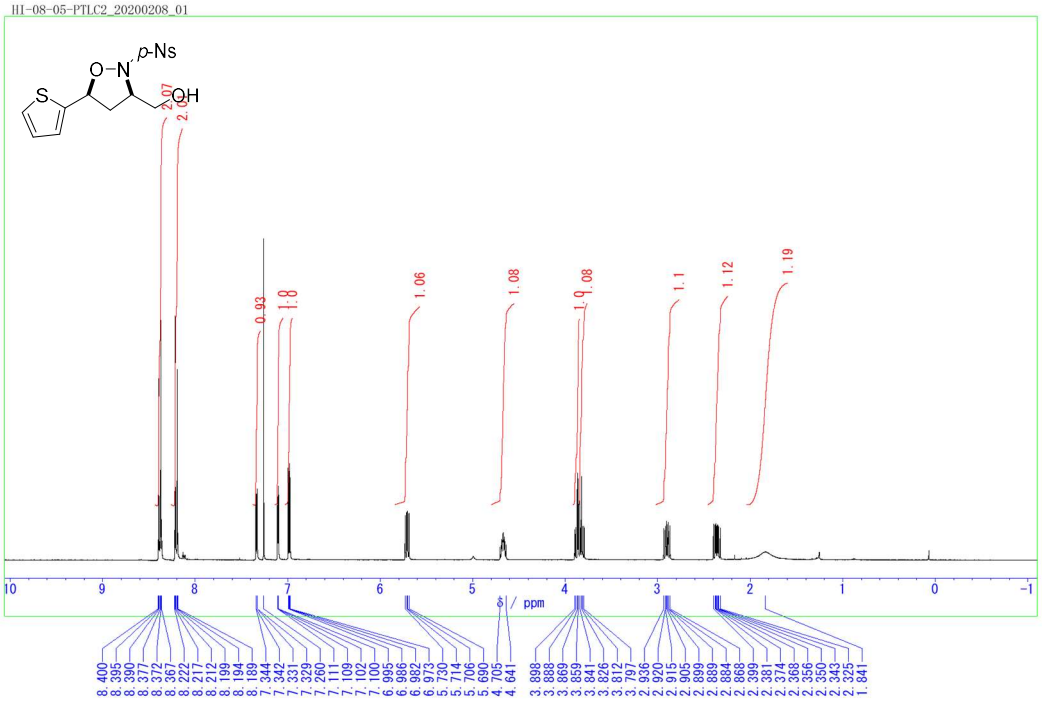

RH-02-16-pure-carbon_20190729_01
δ / ppm
150.99
142.20
138.65
137.47
130.71
130.54
127.09
124.33
81.20
77.48
77.16
76.84
64.61
62.27
35.24
20.91
20.82

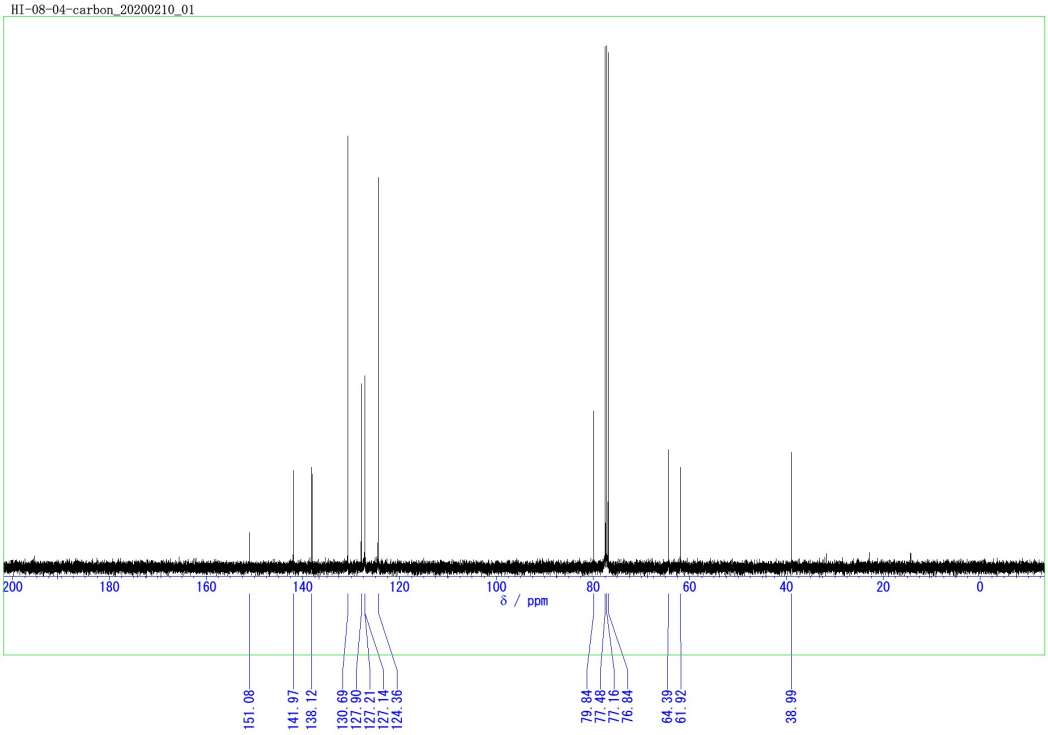
HI-06-15-rePTLC_20200721_01



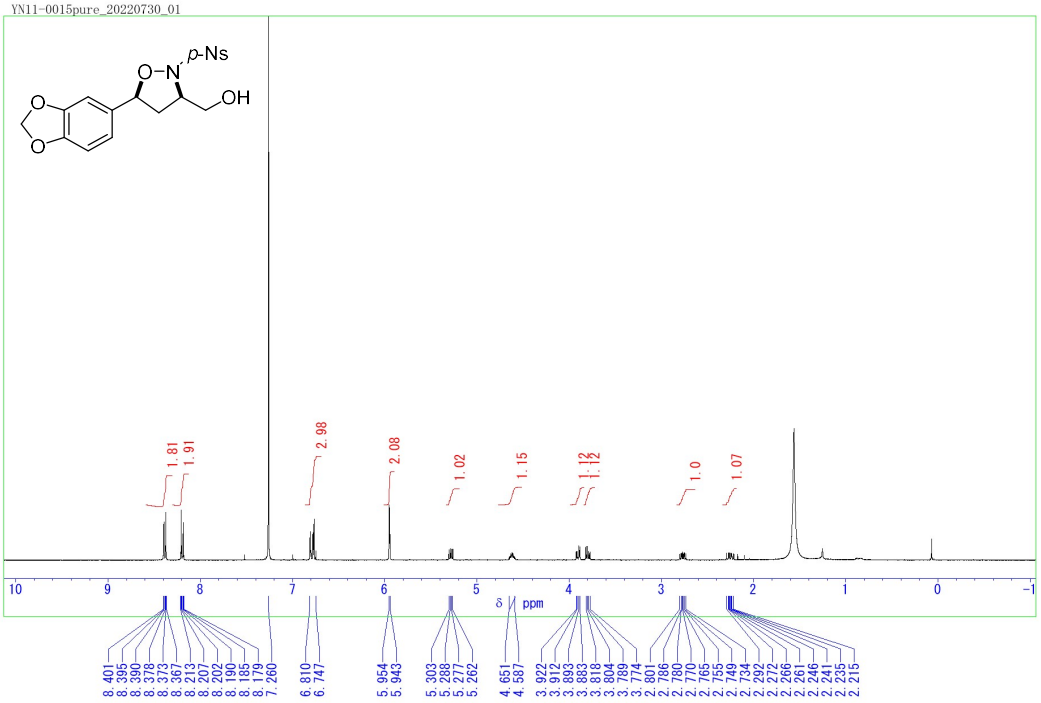
HI-06-15-carbon_20200722_01



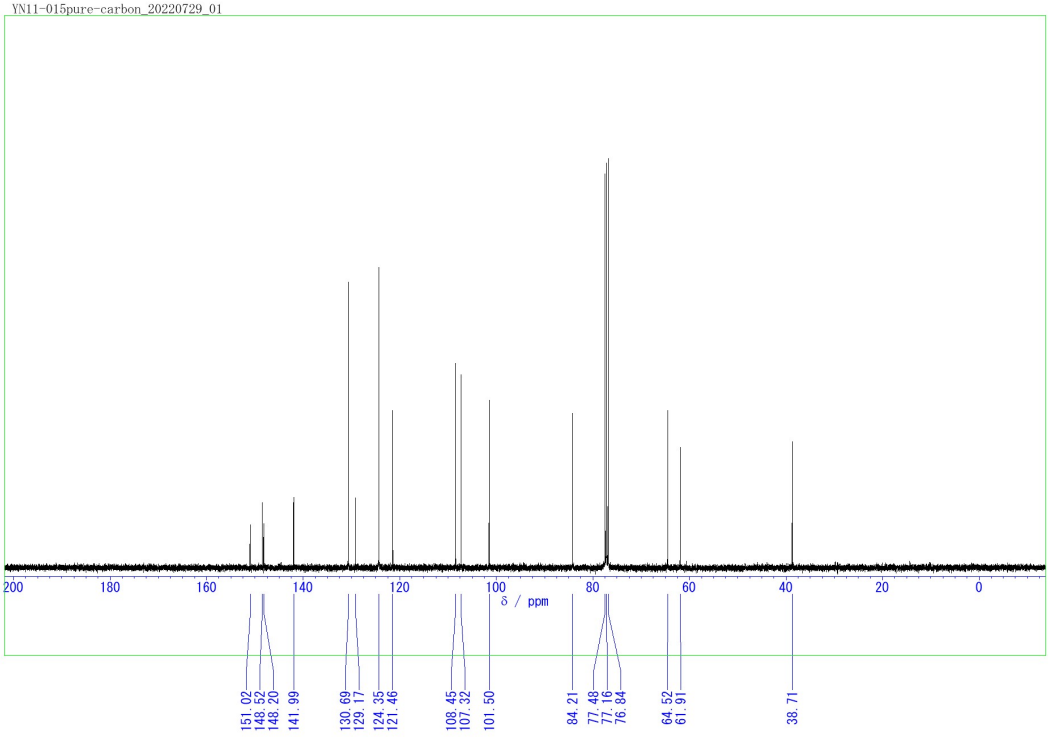

HI-08-05-PTLC2_20200208_01
p-Ns
O
N
S
OH
2.07
2.00
0.93
1.8
1.06
1.08
1.9
1.08
1.1
1.12
1.19
δ / ppm
8.400
8.395
8.390
8.377
8.372
8.367
8.222
8.217
8.212
8.199
8.194
8.189
7.344
7.342
7.331
7.329
7.260
7.111
7.109
7.102
7.100
6.995
6.986
6.982
6.973
5.730
5.714
5.706
5.690
4.705
4.641
3.898
3.888
3.869
3.859
3.841
3.826
3.812
3.036
2.920
2.915
2.905
2.899
2.889
2.884
2.868
2.399
2.381
2.374
2.368
2.356
2.350
2.343
2.325
1.841

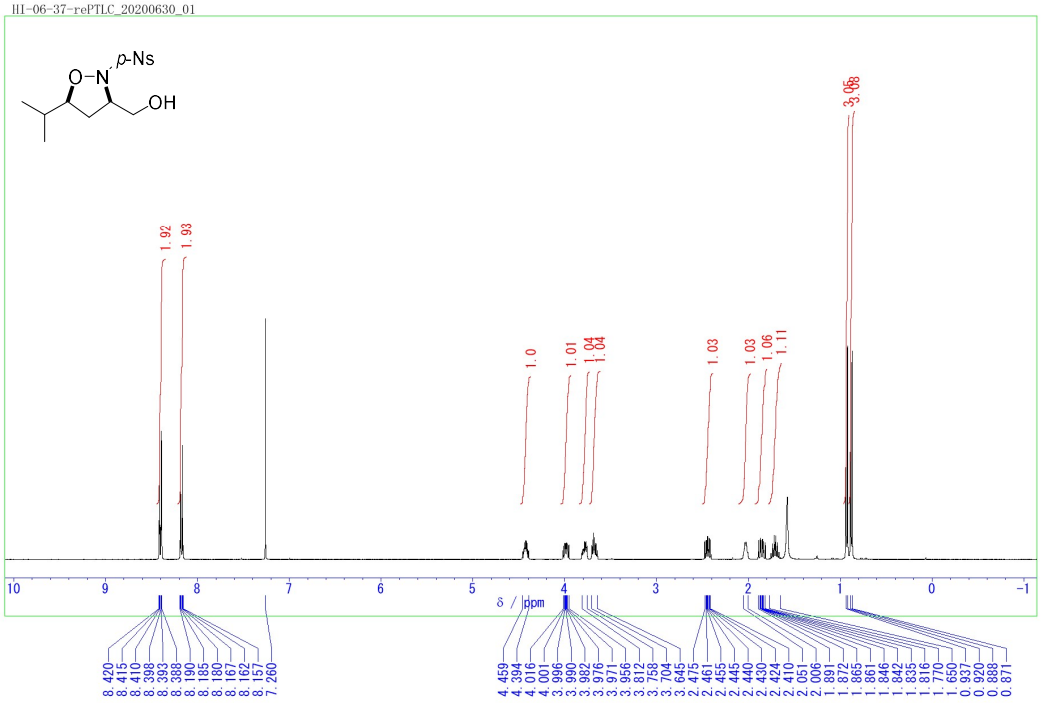

HI-08-04-carbon_20200210_01
δ / ppm
151.08
141.97
138.12
130.69
127.90
127.21
127.14
124.36
79.84
77.48
77.16
76.84
64.39
61.92
38.99

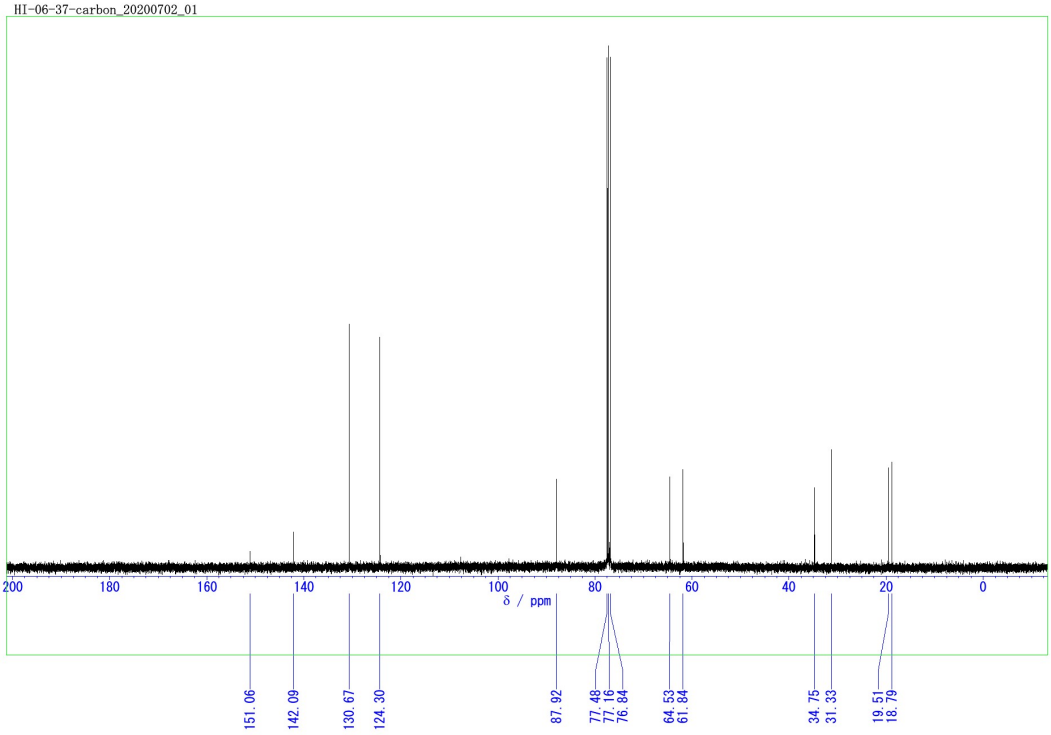
YN11-0015pure_20220730_01

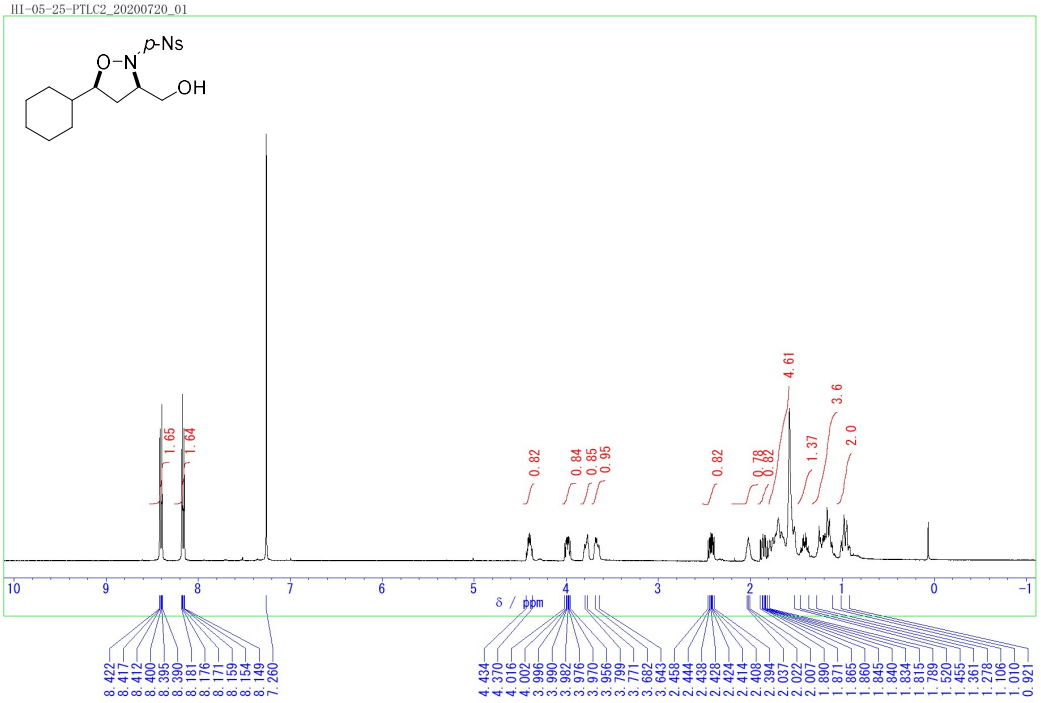


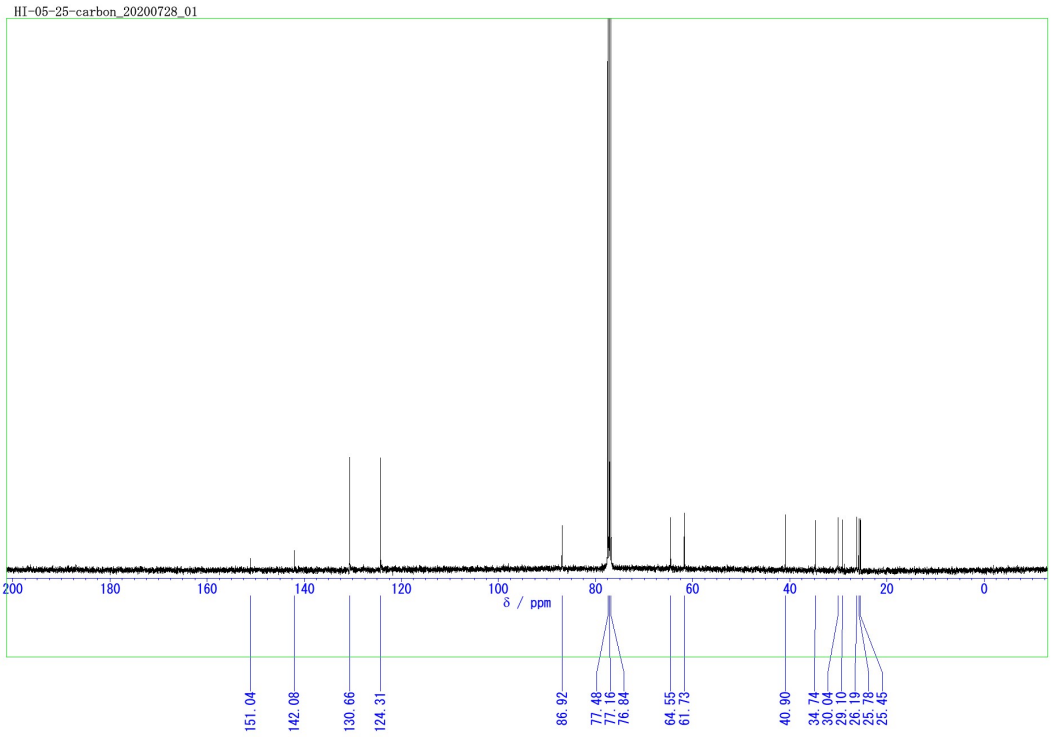
YN11-015pure-carbon_20220729_01

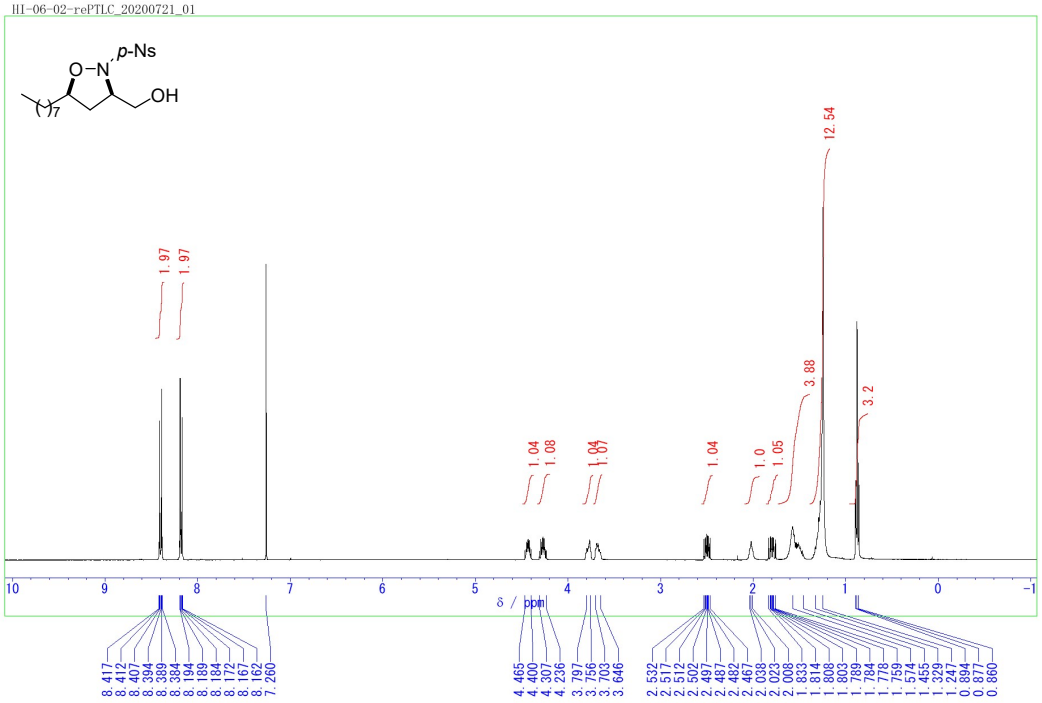


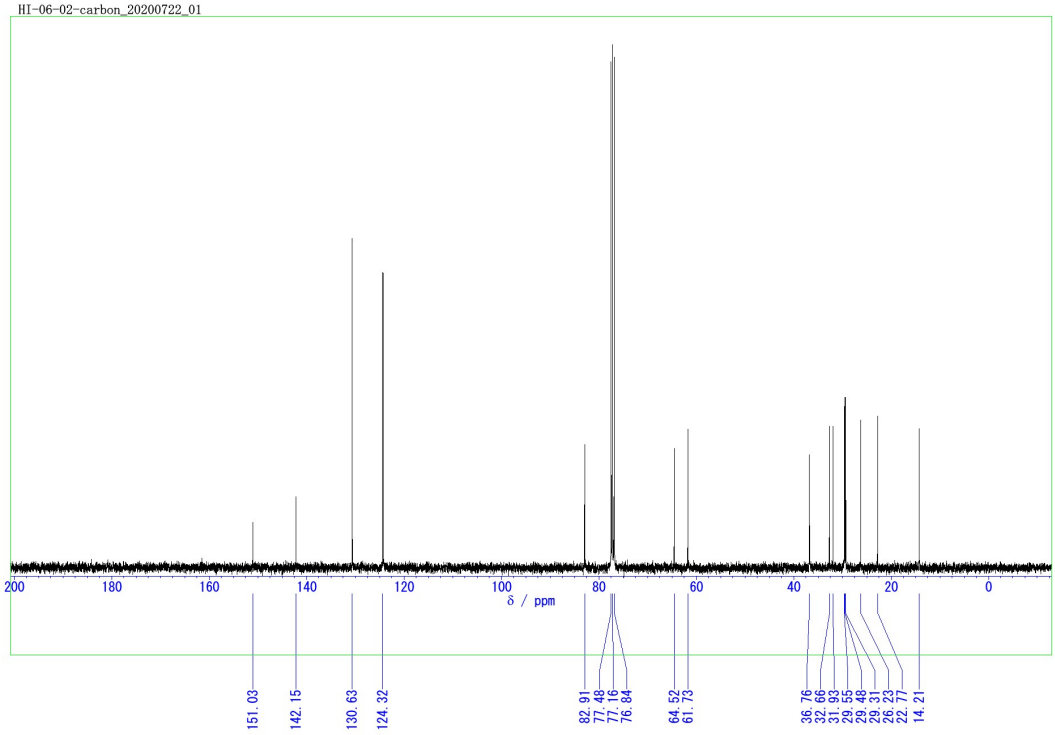

HI-06-37-rePTLC_20200630_01
p-Ns
O
N
OH
δ / ppm

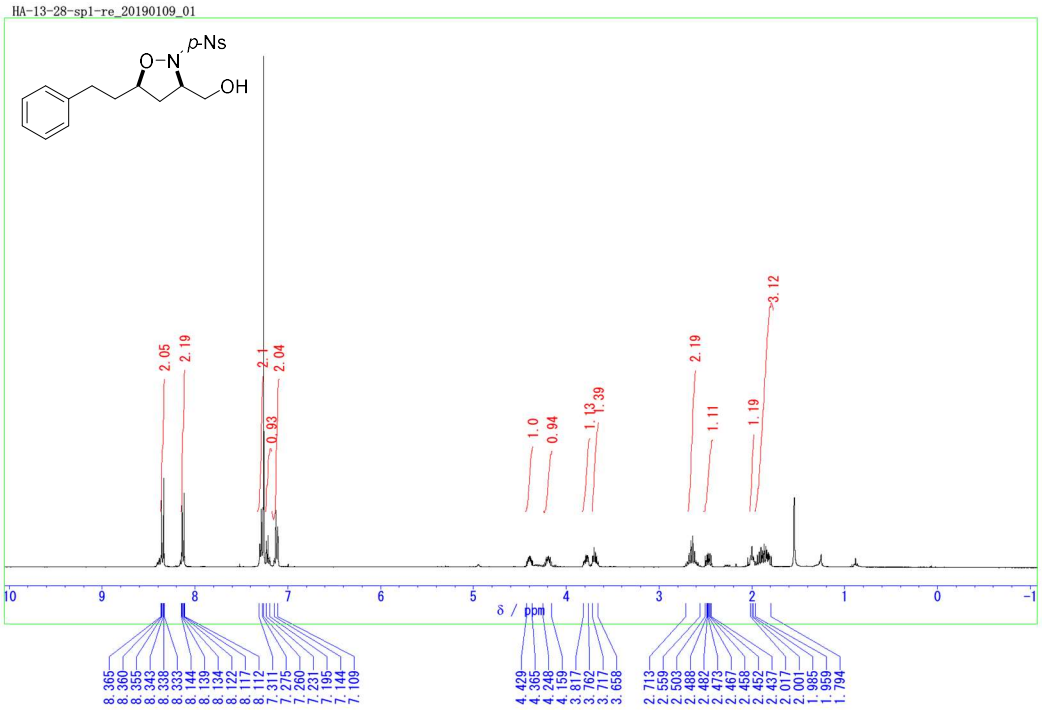

HI-06-37-carbon_20200702_01
δ / ppm

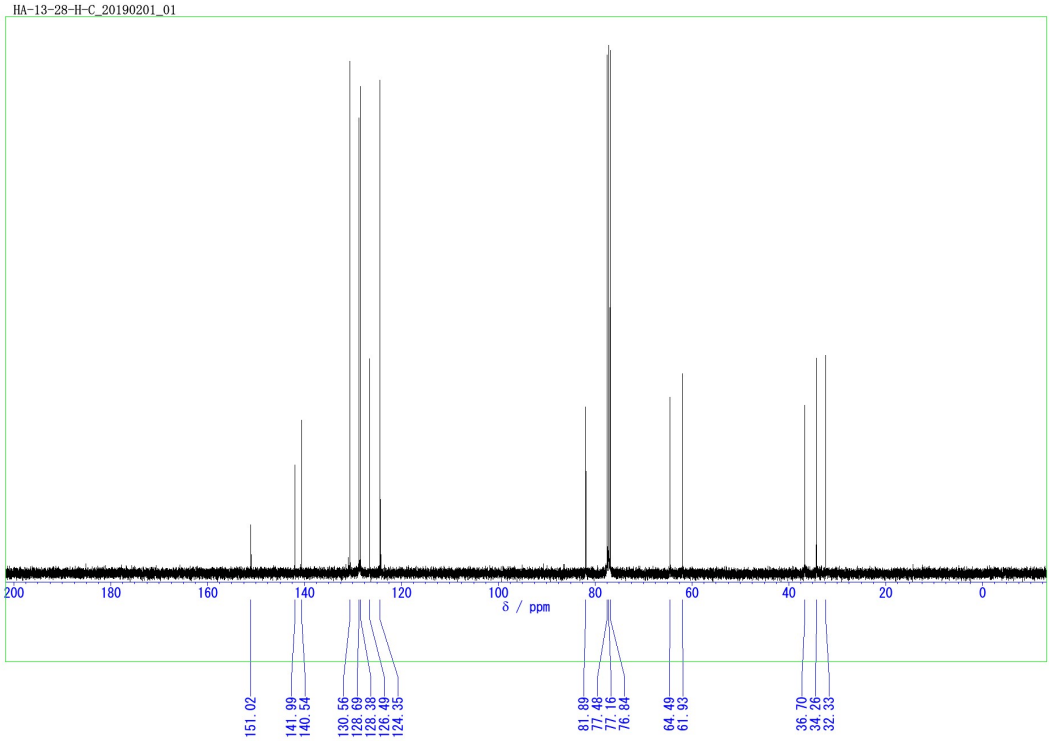

HI-05-25-PTLC2_20200720_01
p-Ns
O-N
OH
4.61
3.6
2.0
1.37
1.65
1.64
0.82
0.84
0.85
0.95
0.82
0.78
0.82
δ / ppm

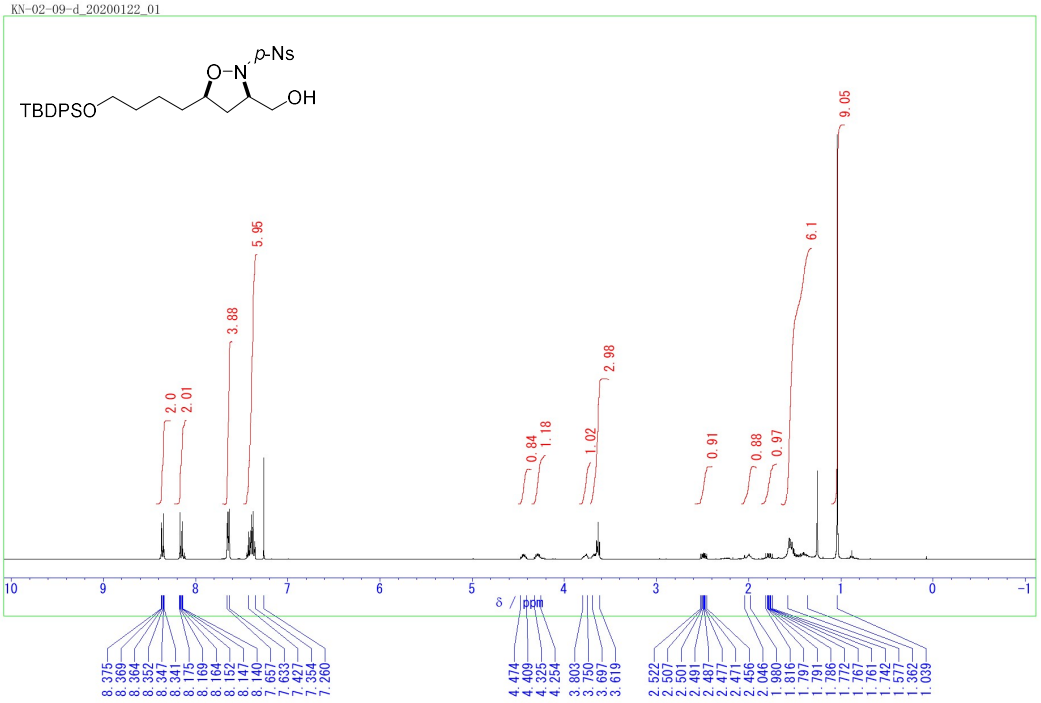

HI-05-25-carbon_20200728_01
δ / ppm
151.04
142.08
130.66
124.31
86.92
77.48
77.16
76.84
64.55
61.73
40.90
34.74
30.04
29.10
26.19
25.78
25.45

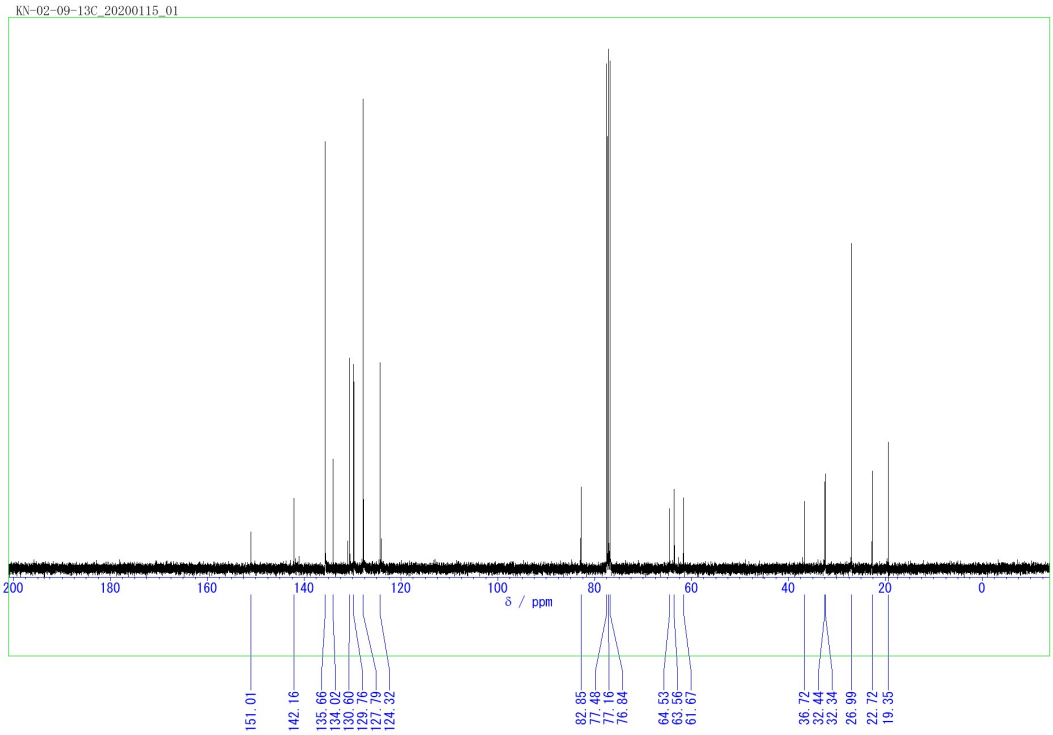

HI-06-02-rePTLC_20200721_01
p-Ns
O–N
OH
7
12.54
3.88
3.2
1.97
1.97
1.04
1.08
1.04
1.07
1.04
1.0
1.05
δ / ppm


HI-06-02-carbon_20200722_01
δ / ppm

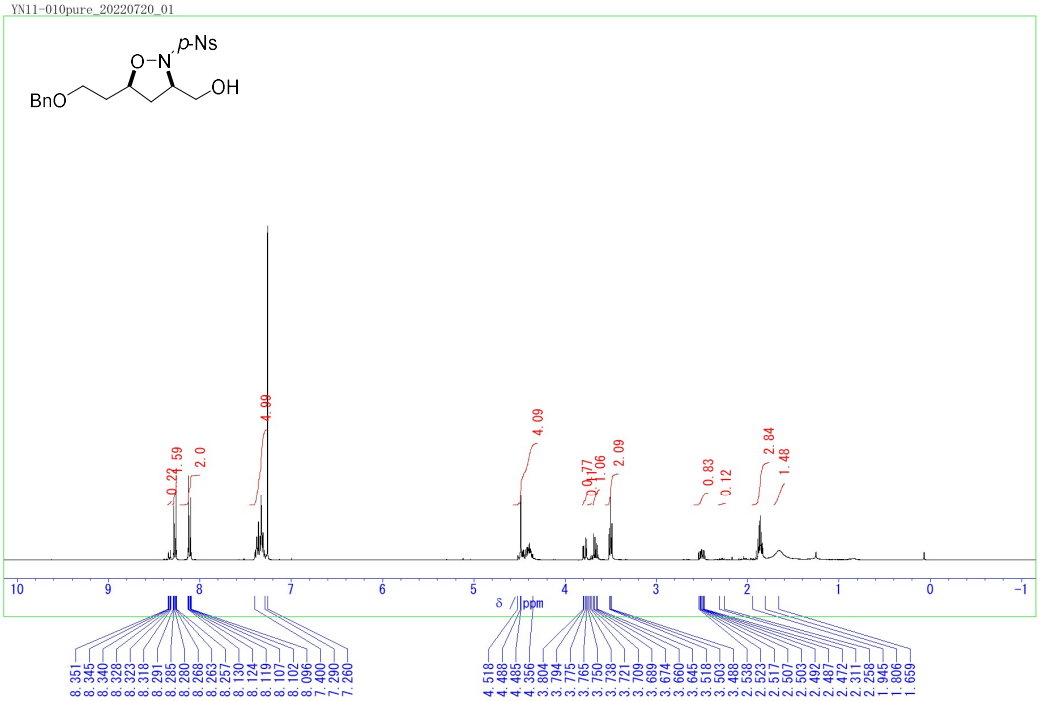

HA-13-28-sp1-re_20190109_01
p-Ns
O-N
OH
2.05
2.19
2.1
2.04
0.93
1.0
0.94
1.13
1.39
2.19
1.11
1.19
3.12
δ / ppm
8.365
8.360
8.355
8.343
8.338
8.333
8.144
8.139
8.134
8.122
8.117
8.112
7.311
7.275
7.260
7.231
7.195
7.144
7.109
4.429
4.365
4.248
4.159
3.817
3.762
3.717
3.658
2.713
2.559
2.503
2.488
2.482
2.473
2.467
2.458
2.452
2.437
2.017
2.001
1.965
1.959
1.794


HA-13-28-H-C_20190201_01
δ / ppm
151.02
141.99
140.54
130.56
128.69
128.38
126.49
124.35
81.89
77.48
77.16
76.84
64.49
61.93
36.70
34.26
32.33

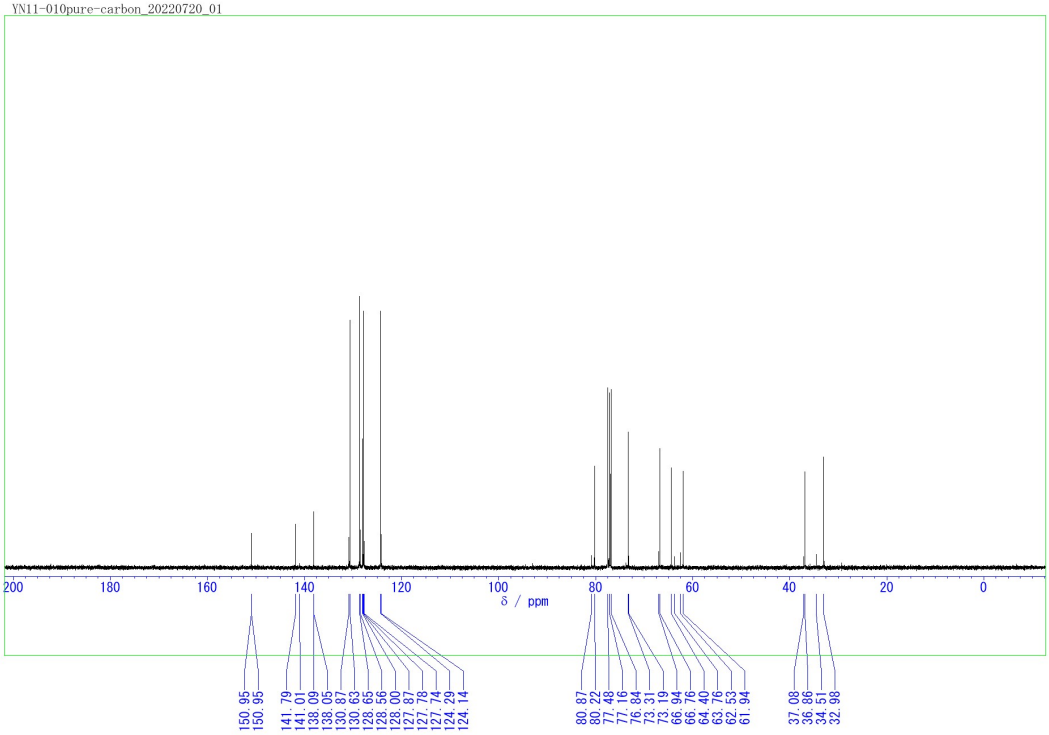

KN-02-09-d_20200122_01
p-Ns
O–N
TBDPSO
OH
9.05
6.1
5.95
3.88
2.98
2.0
2.01
0.84
1.18
1.02
0.91
0.88
0.97
δ / ppm


KN-02-09-13C_20200115_01
δ / ppm

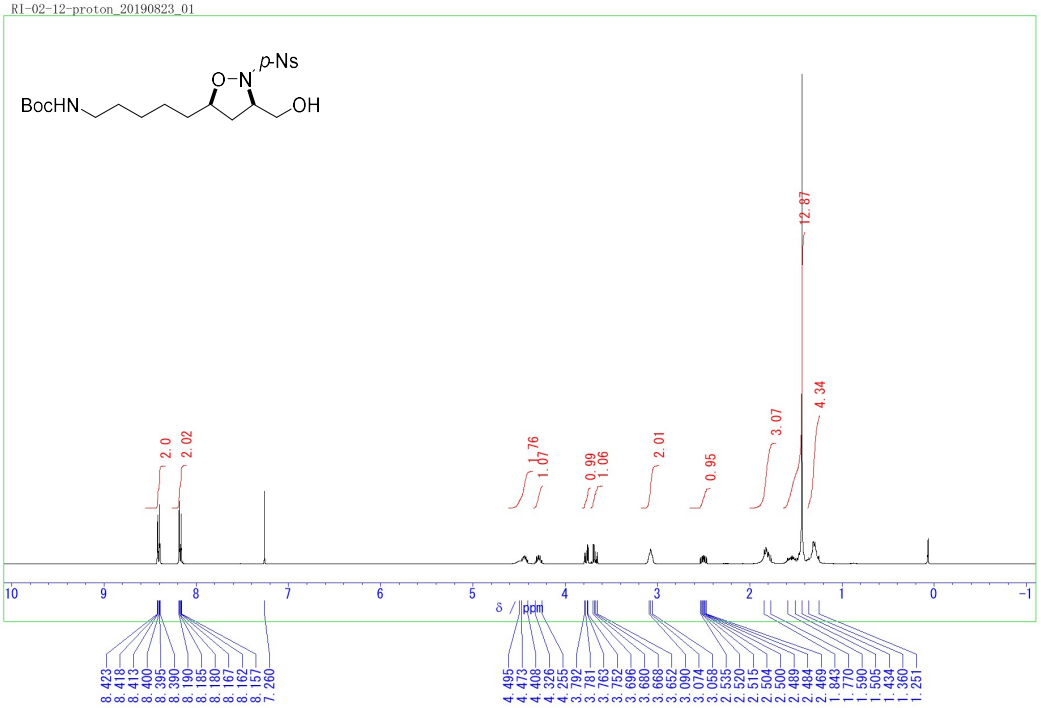
YN11-010pure_20220720_01



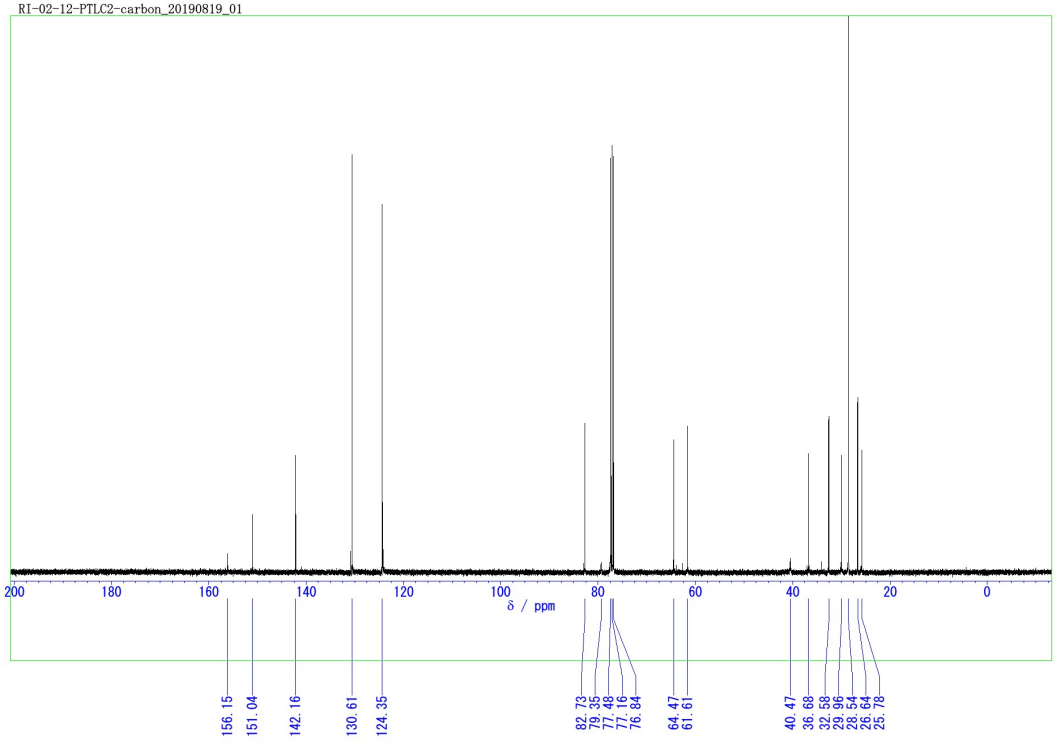
YN11-010pure-carbon_20220720_01



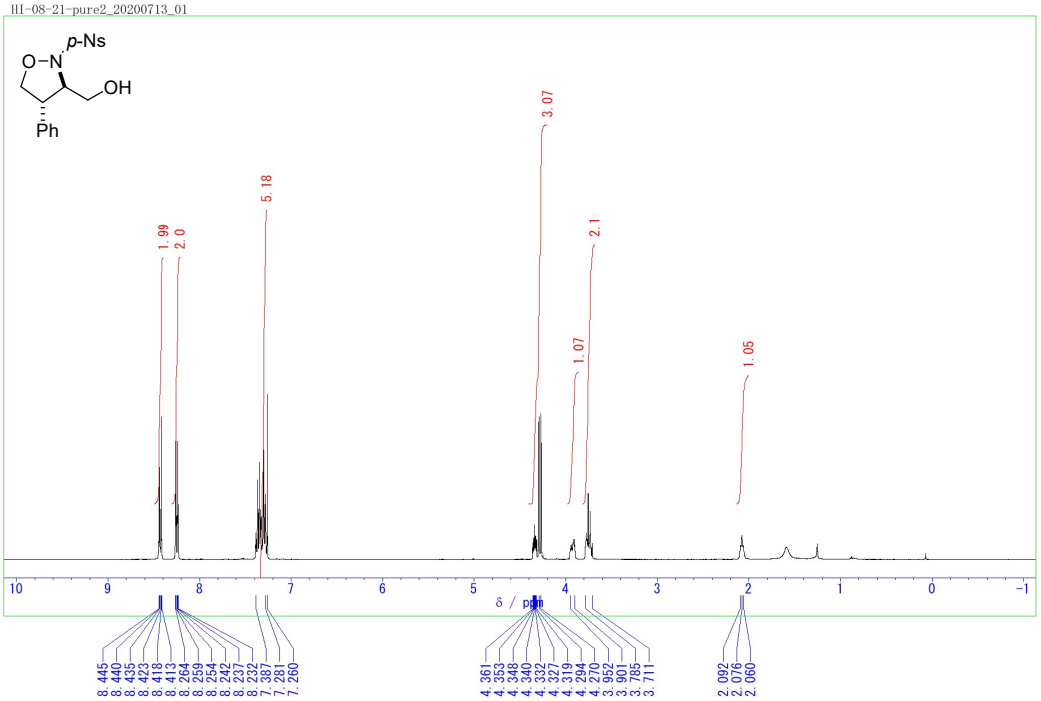
RI-02-12-proton_20190823_01



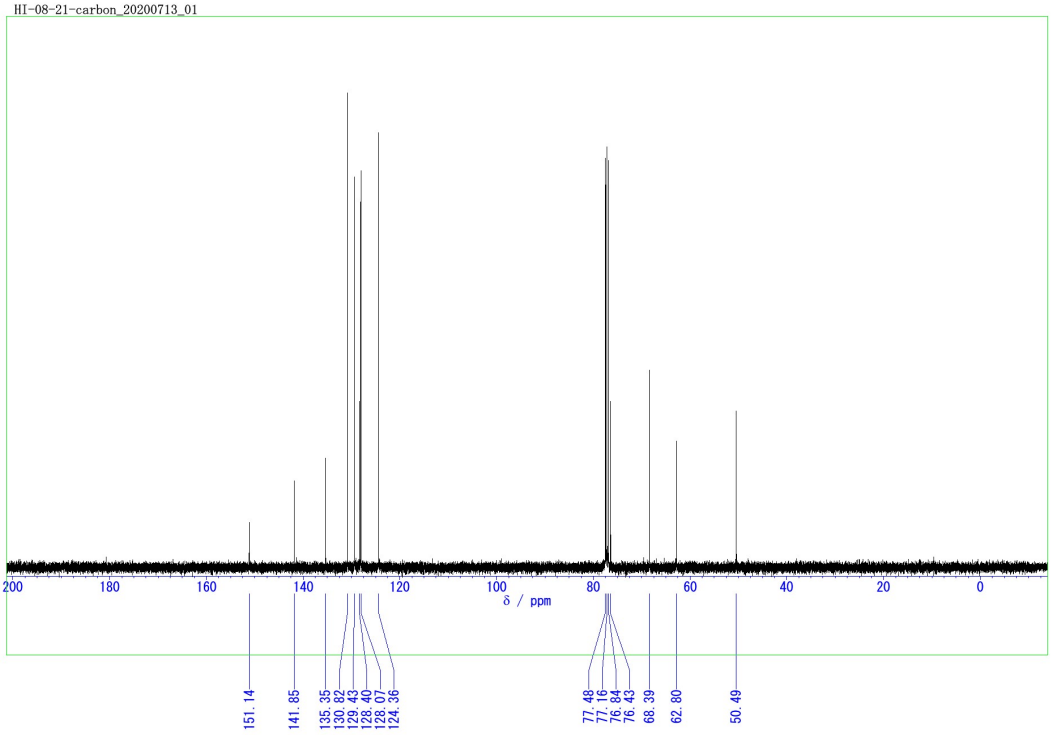
RI-02-12-PTLC2-carbon_20190819_01

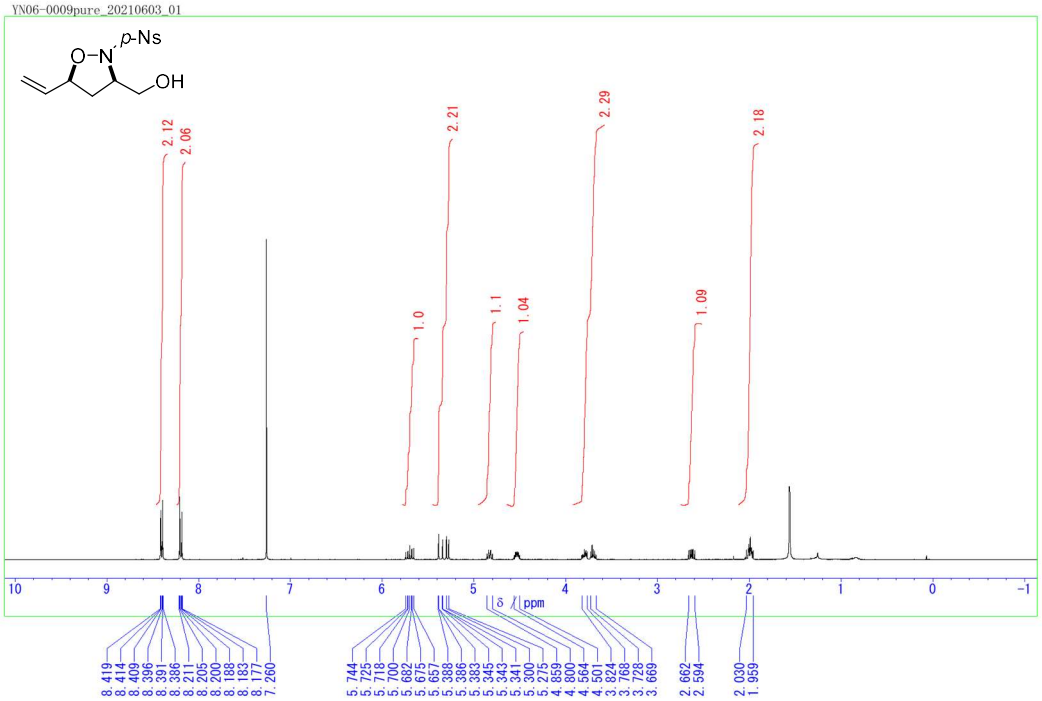


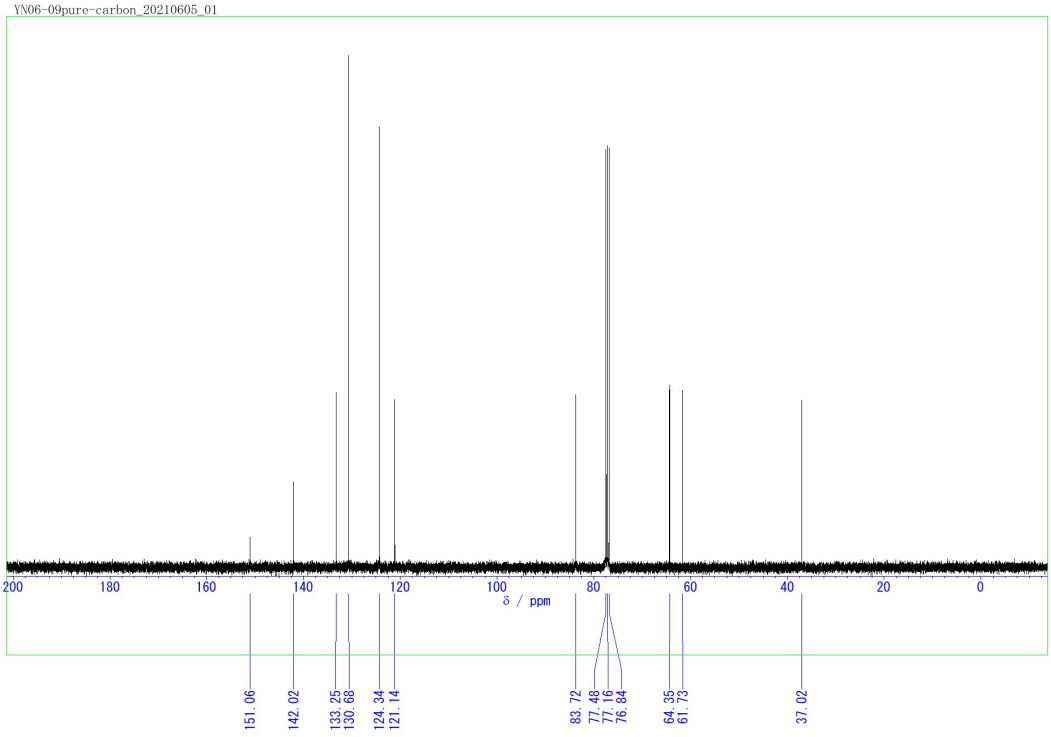
HI-08-21-pure2_20200713_01

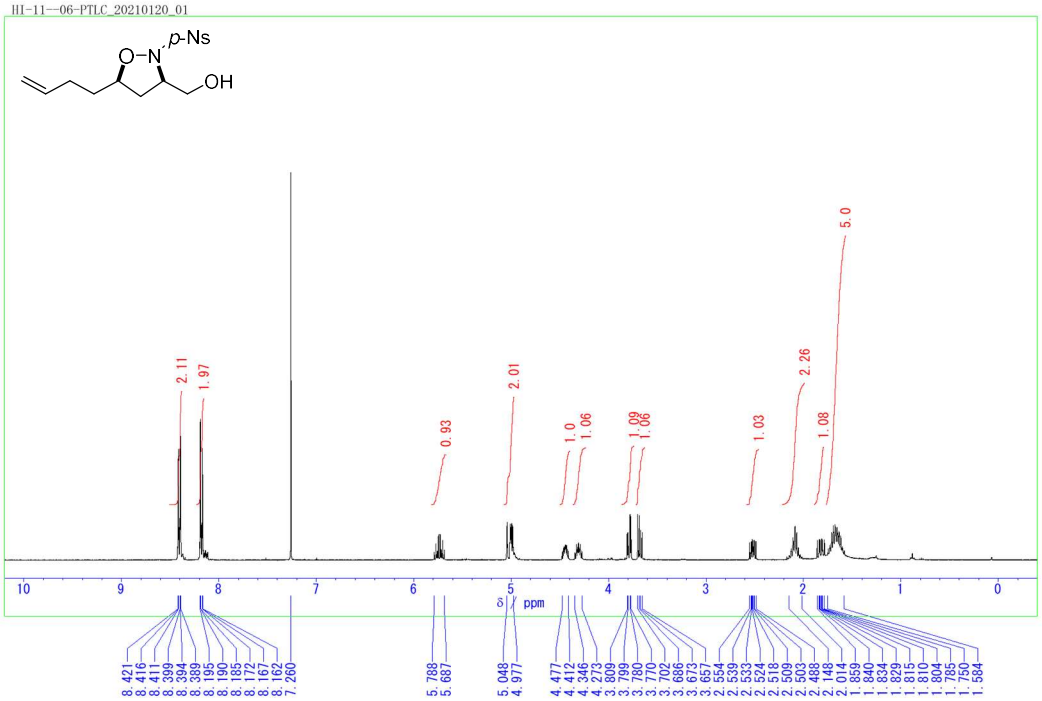


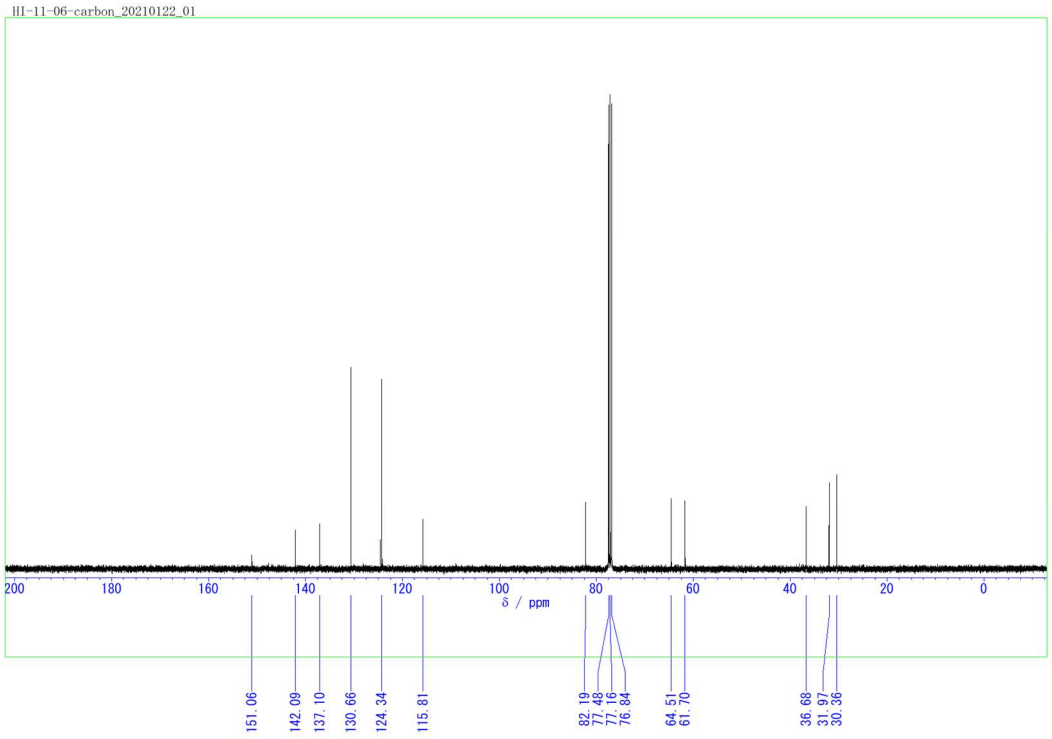
HI-08-21-carbon_20200713_01

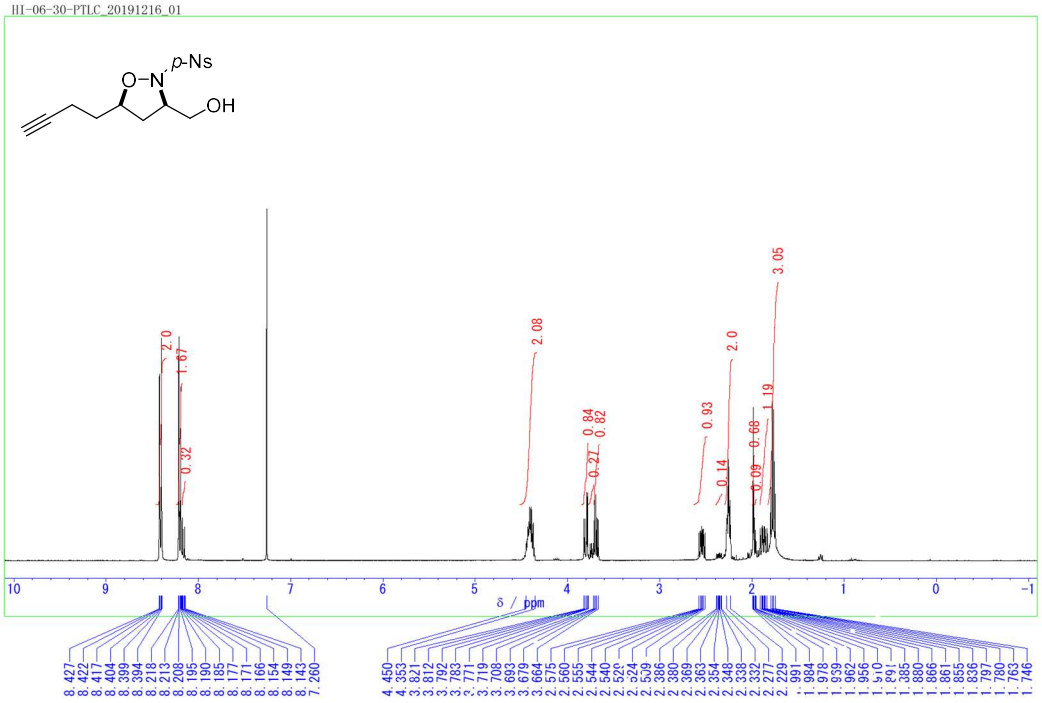


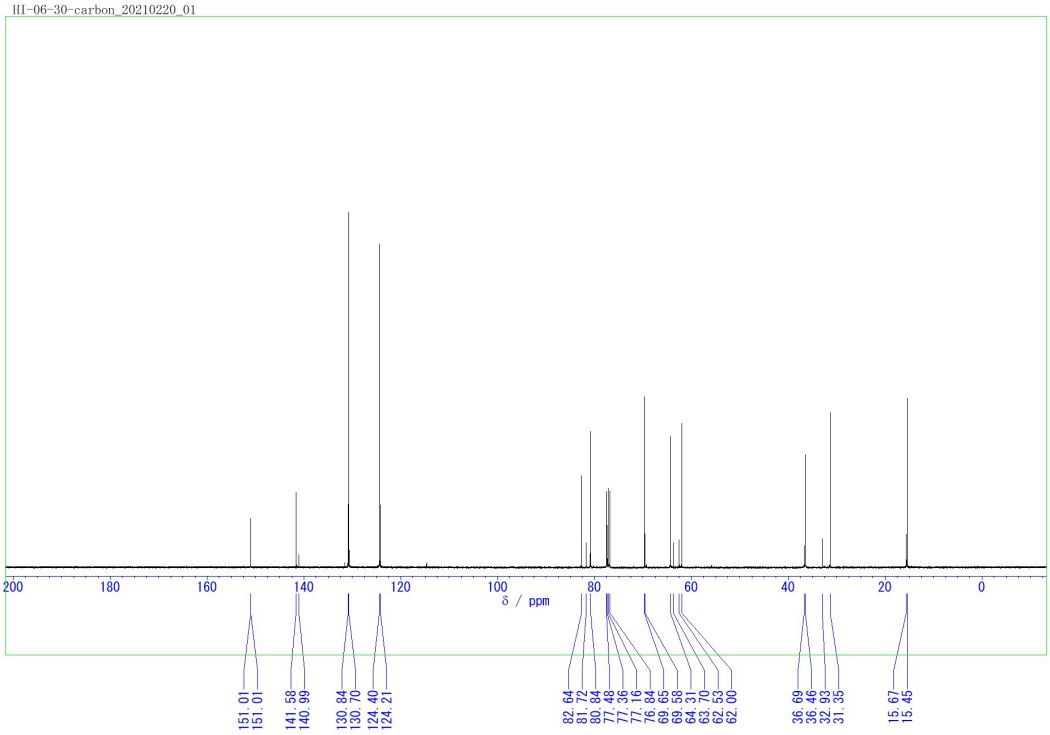

YN06-0009pure_20210603_01
p-Ns
O
N
OH
2.12
2.06
2.21
2.29
2.18
1.0
1.1
1.04
1.09
10
9
8
7
6
5
4
3
2
1
0
-1
δ / ppm
8.419
8.414
8.409
8.396
8.391
8.386
8.211
8.205
8.200
8.188
8.183
8.177
7.260
5.744
5.725
5.718
5.700
5.682
5.657
5.388
5.386
5.383
5.345
5.343
5.341
5.300
5.275
4.859
4.800
4.564
4.501
3.824
3.768
3.728
3.669
2.662
2.594
2.030
1.959

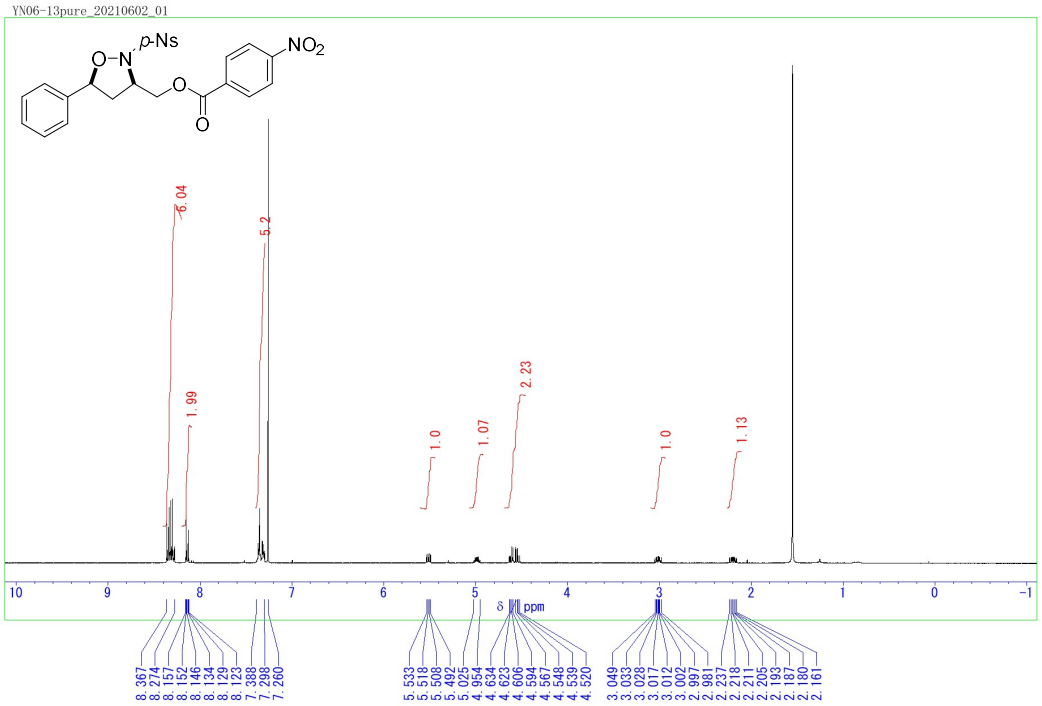

YN06-09pure-carbon_20210605_01
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
151.06
142.02
133.25
130.68
124.34
121.14
83.72
77.48
77.16
76.84
64.35
61.73
37.02

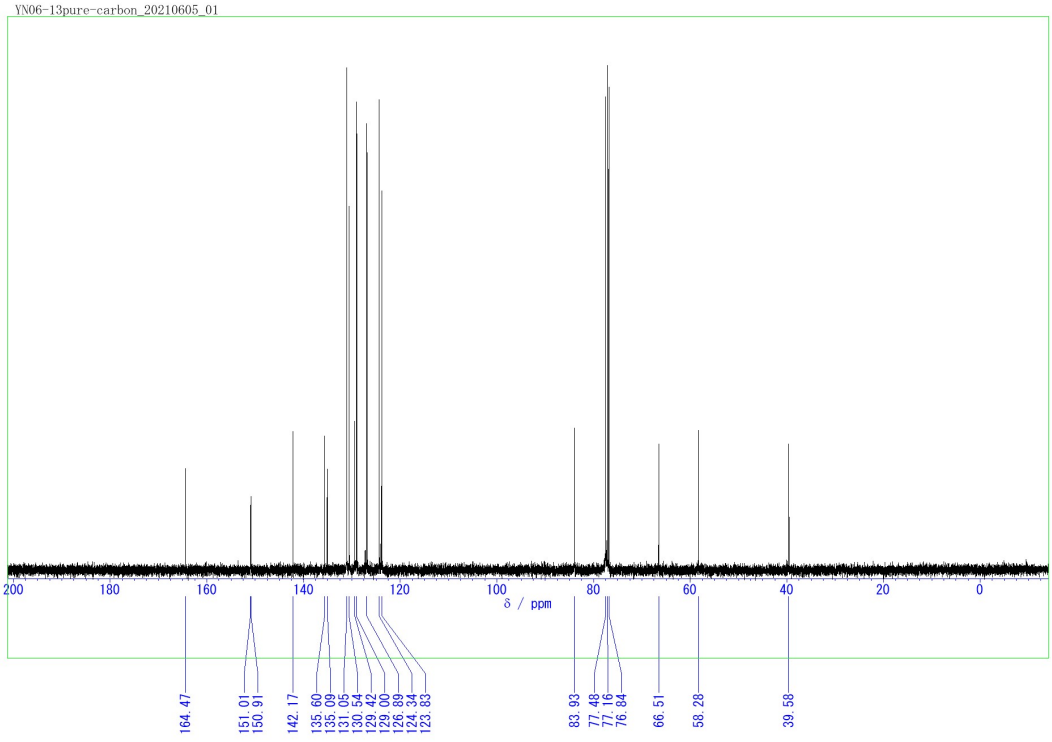

III-11--06-PTLC_20210120_01
p-Ns
O
N
OH
2.11
1.97
0.93
2.01
1.0
1.06
1.09
1.06
1.03
2.26
1.08
5.0
10
9
8
7
6
5
4
3
2
1
0
δ / ppm
8.421
8.416
8.411
8.399
8.394
8.389
8.195
8.190
8.185
8.172
8.167
8.162
7.260
5.788
5.687
5.048
4.977
4.477
4.412
4.346
4.273
3.809
3.799
3.780
3.770
3.702
3.686
3.673
3.657
2.554
2.539
2.533
2.524
2.518
2.509
2.503
2.488
2.148
2.014
1.858
1.840
1.829
1.815
1.810
1.804
1.785
1.750
1.584

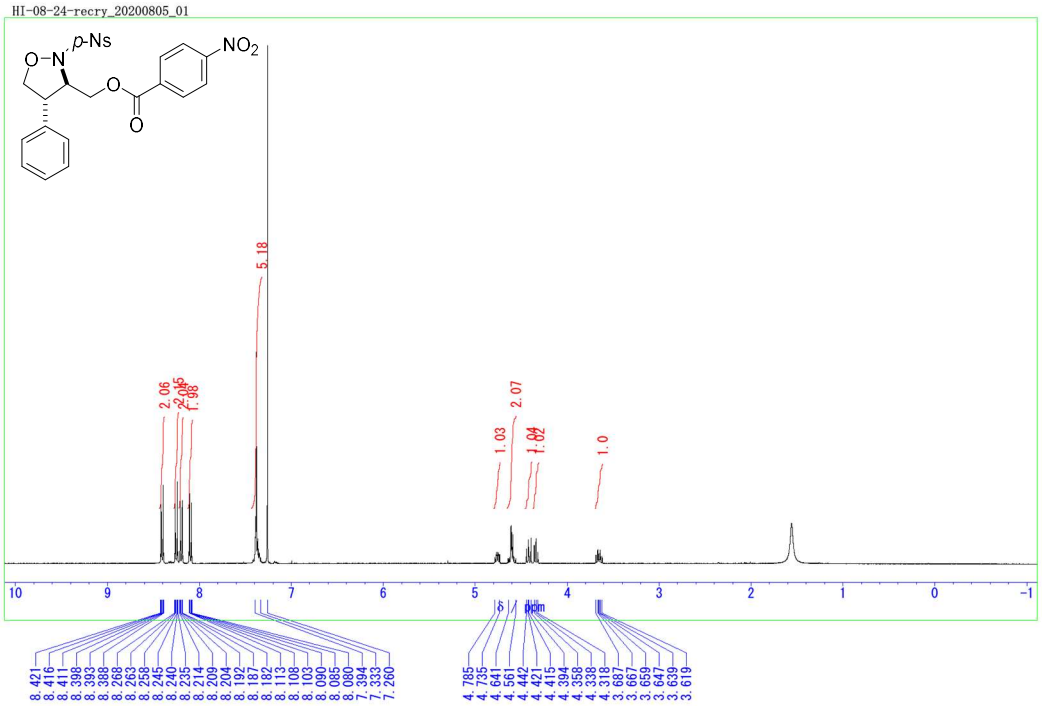

III-11-06-carbon_20210122_01
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
151.06
142.09
137.10
130.66
124.34
115.81
82.19
77.48
77.16
76.84
64.51
61.70
36.68
31.97
30.36

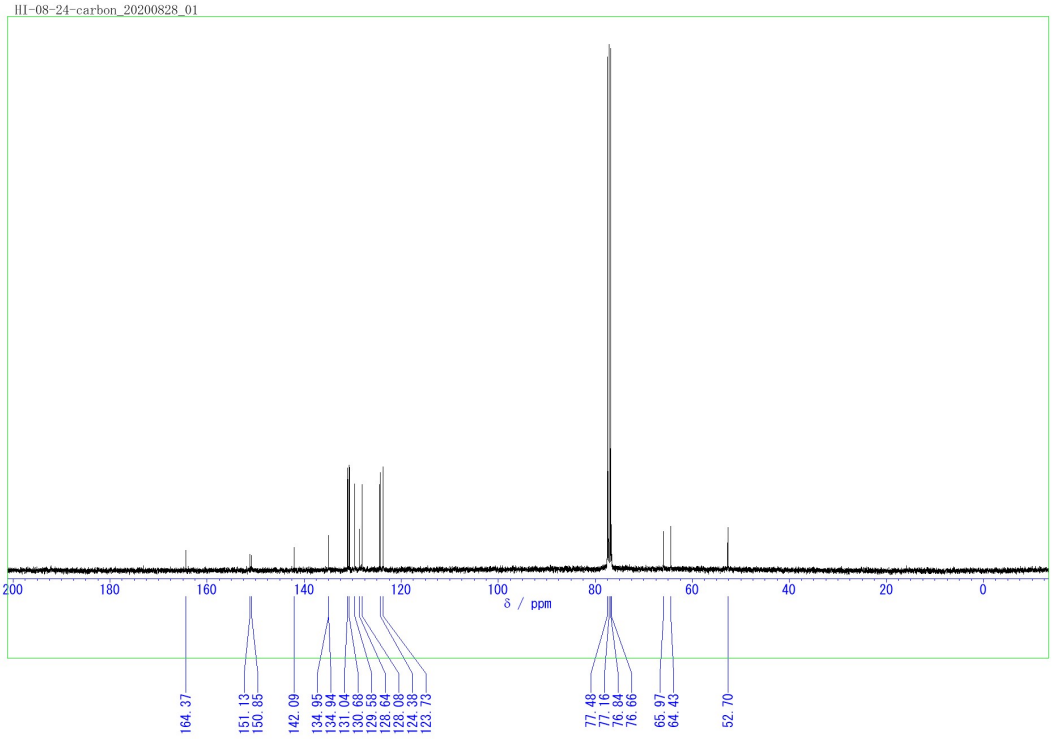

HI-06-30-PTLC_20191216_01
p-Ns
O-N
OH
δ / ppm


HI-06-30-carbon_20210220_01
δ / ppm

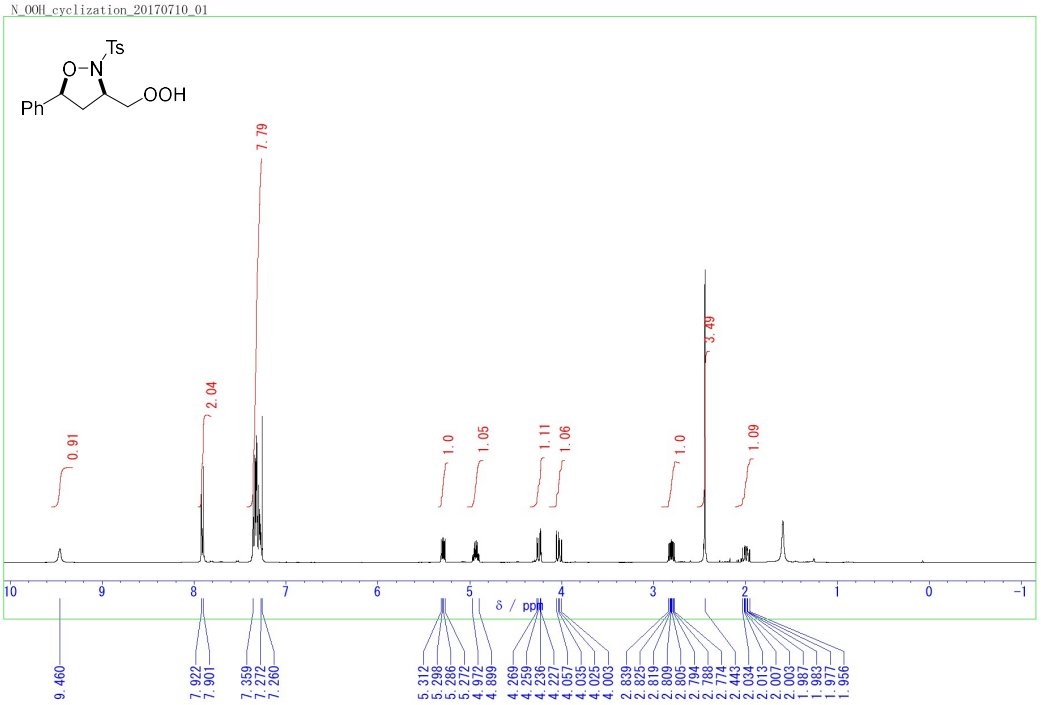

YN06-13pure_20210602_01
p-Ns
NO2
6.04
5.2
1.99
1.0
1.07
2.23
1.0
1.13
δ / ppm


YN06-13pure-carbon_20210605_01
δ / ppm

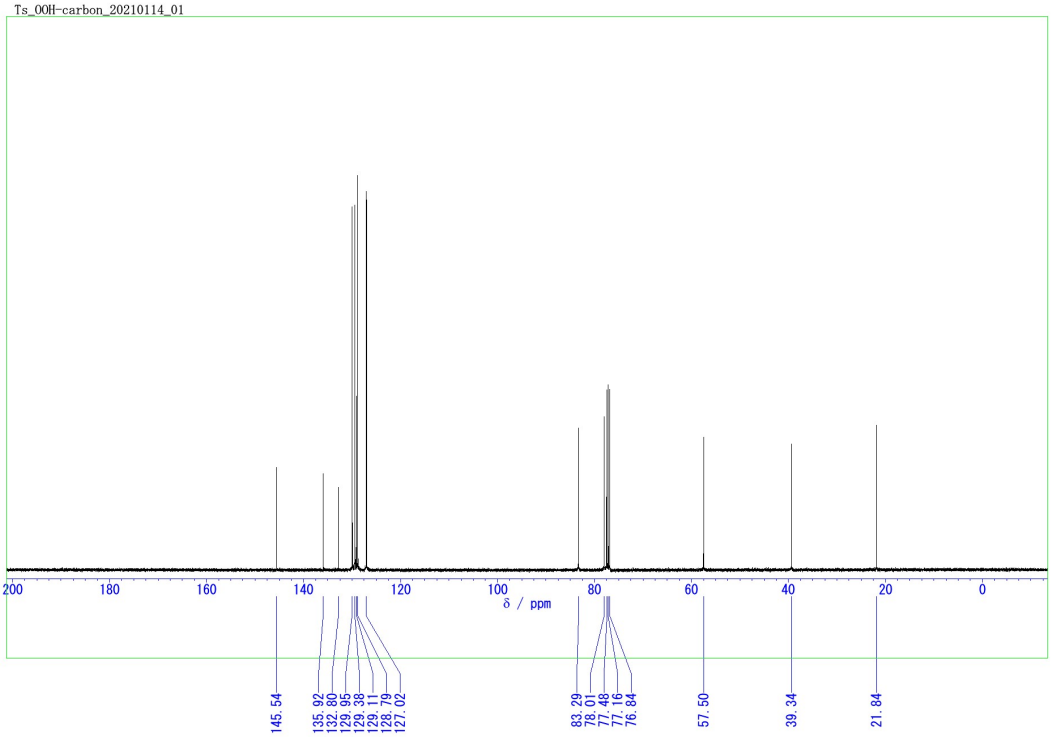

HI-08-24-recry_20200805_01
p-Ns
NO2
5.18
2.06
2.07
1.03
1.0
δ / ppm


HI-08-24-carbon_20200828_01
δ / ppm

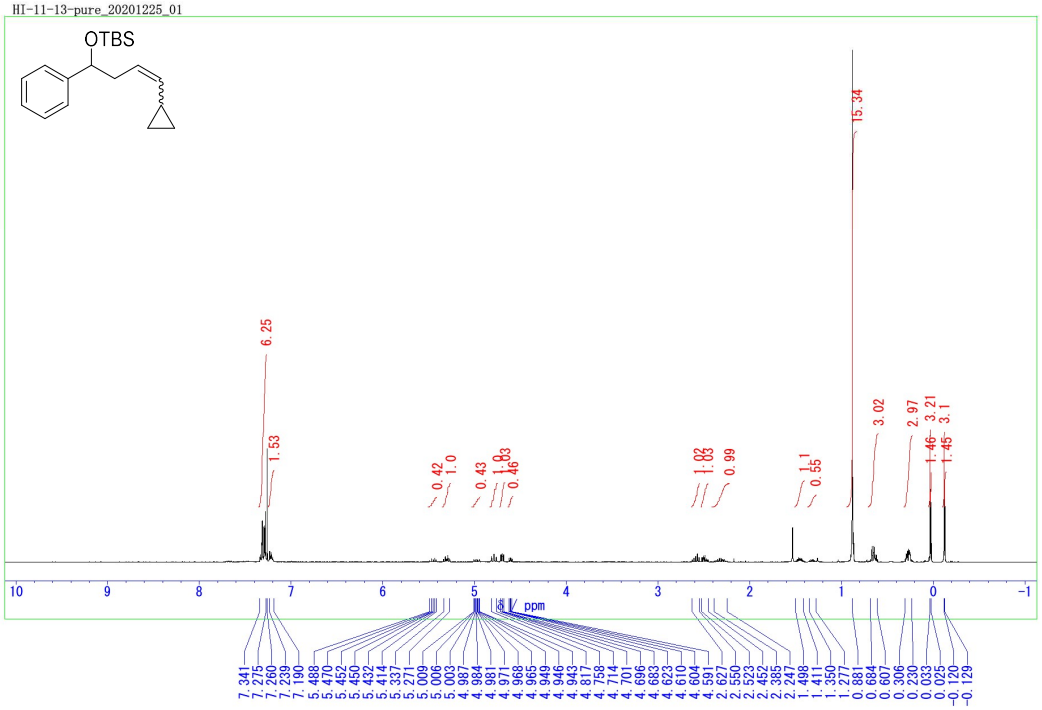
N_OOH_cyclization_20170710_01



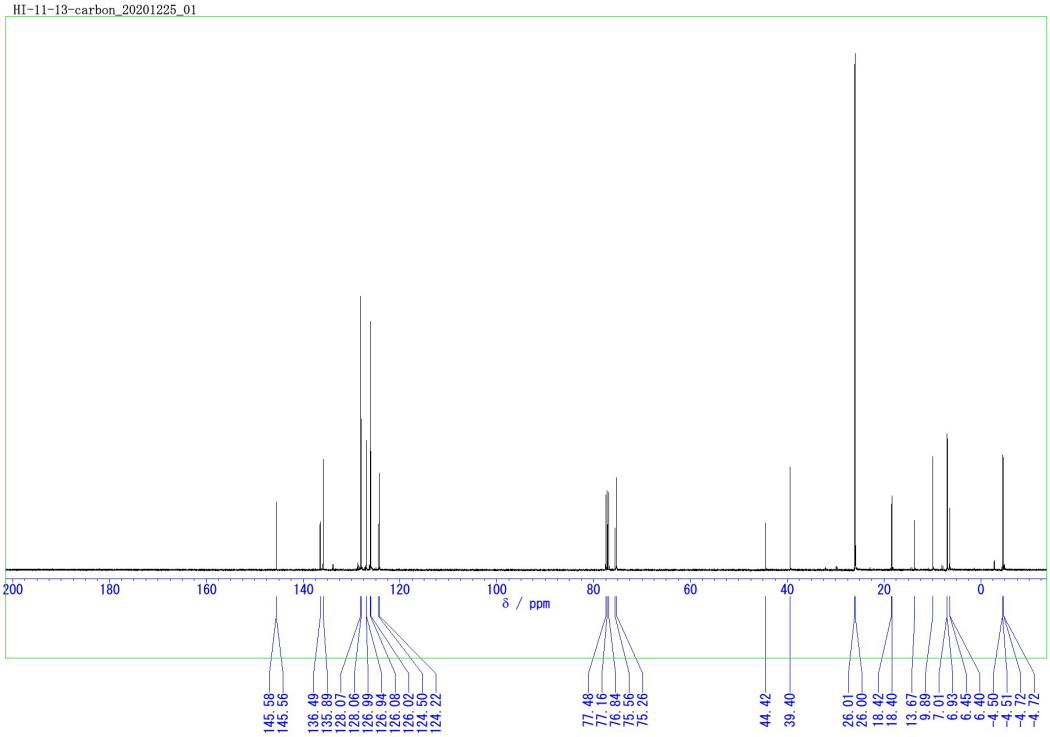
Ts_OOH-carbon_20210114_01



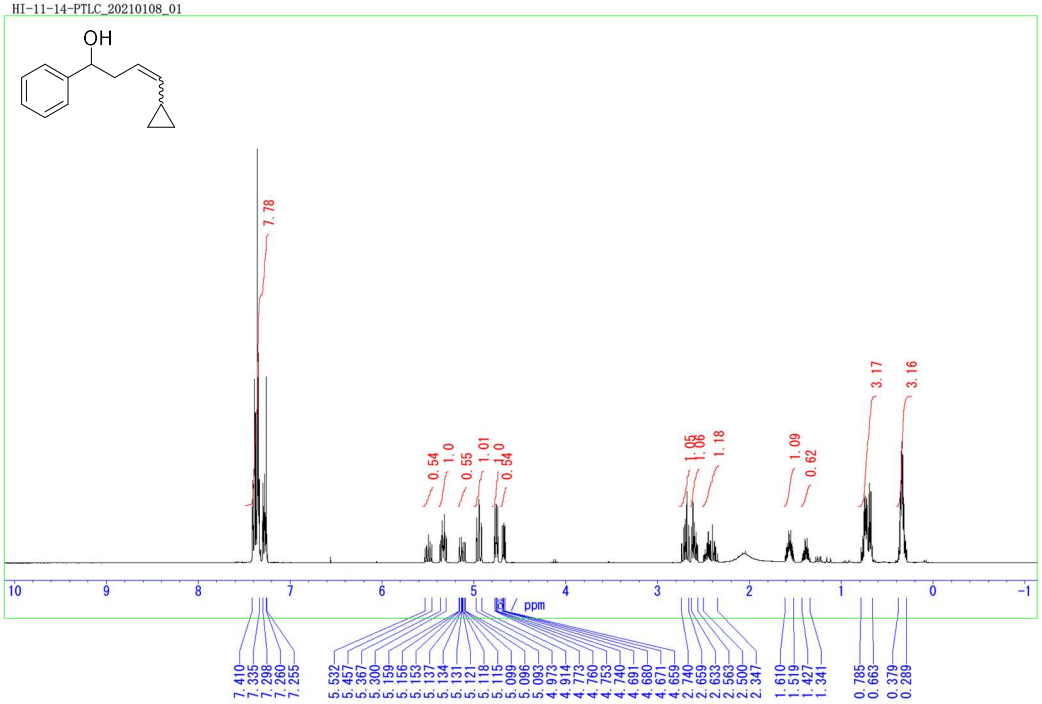
HI-11-13-pure_20201225_01



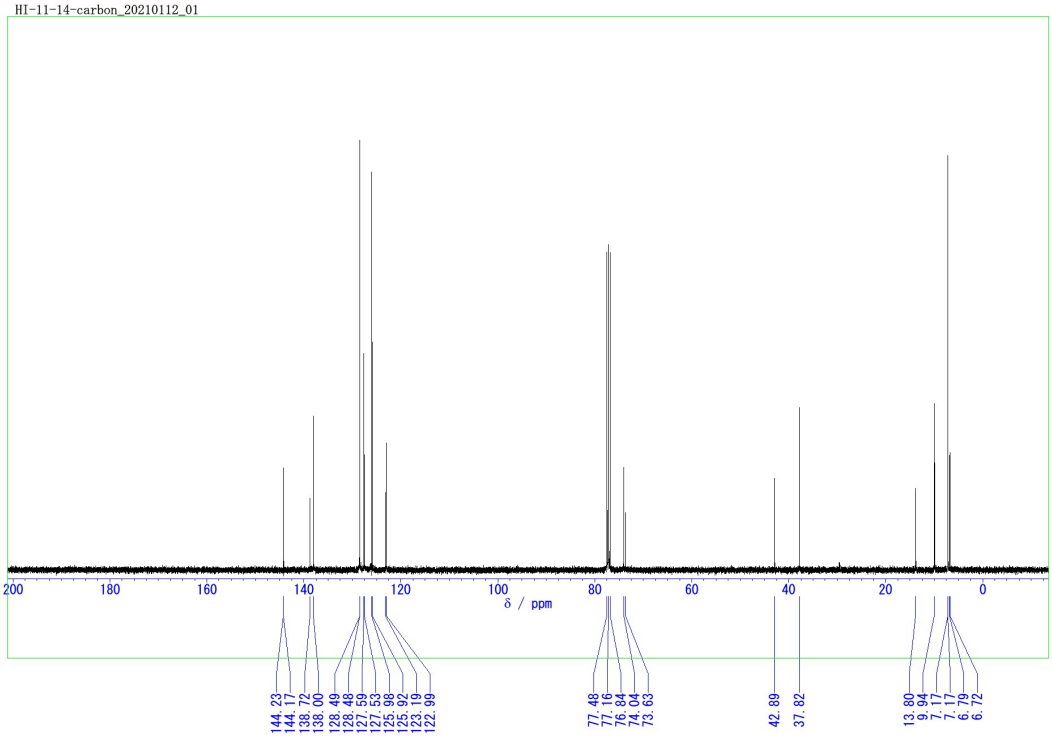
HI-11-13-carbon_20201225_01

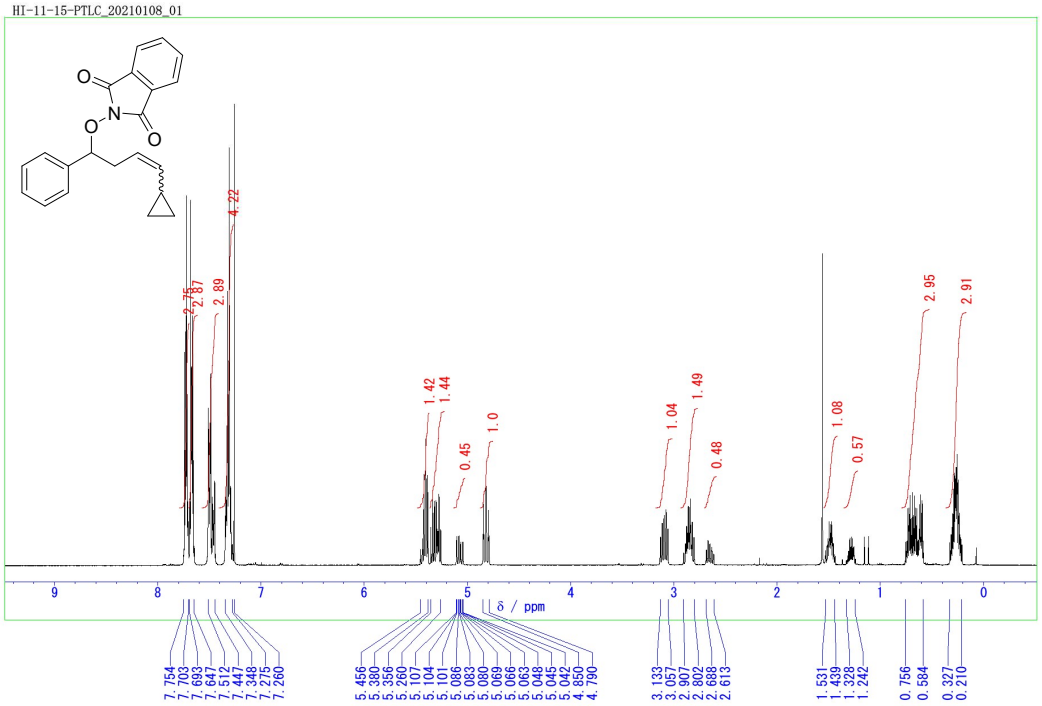


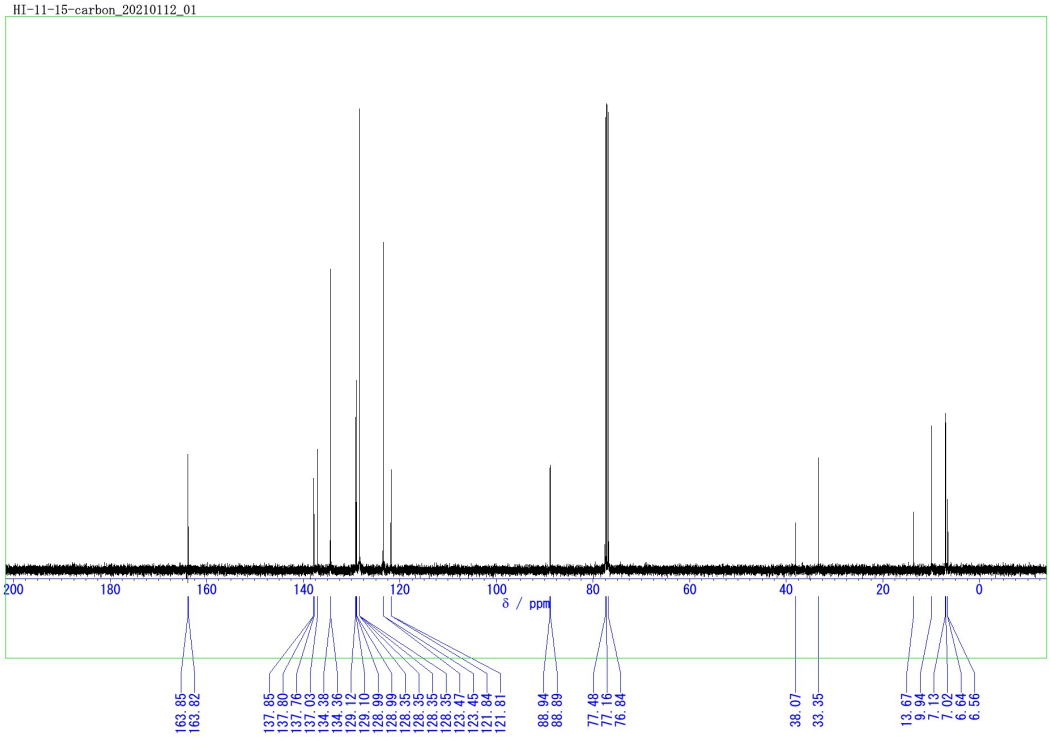
HI-11-14-PTLC_20210108_01

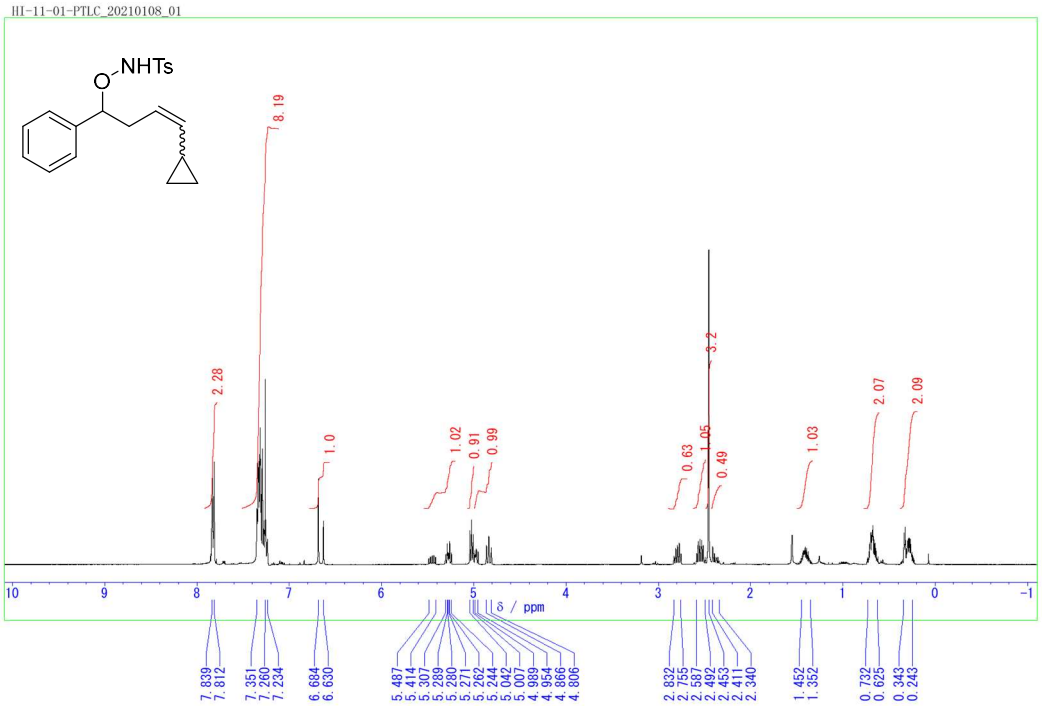


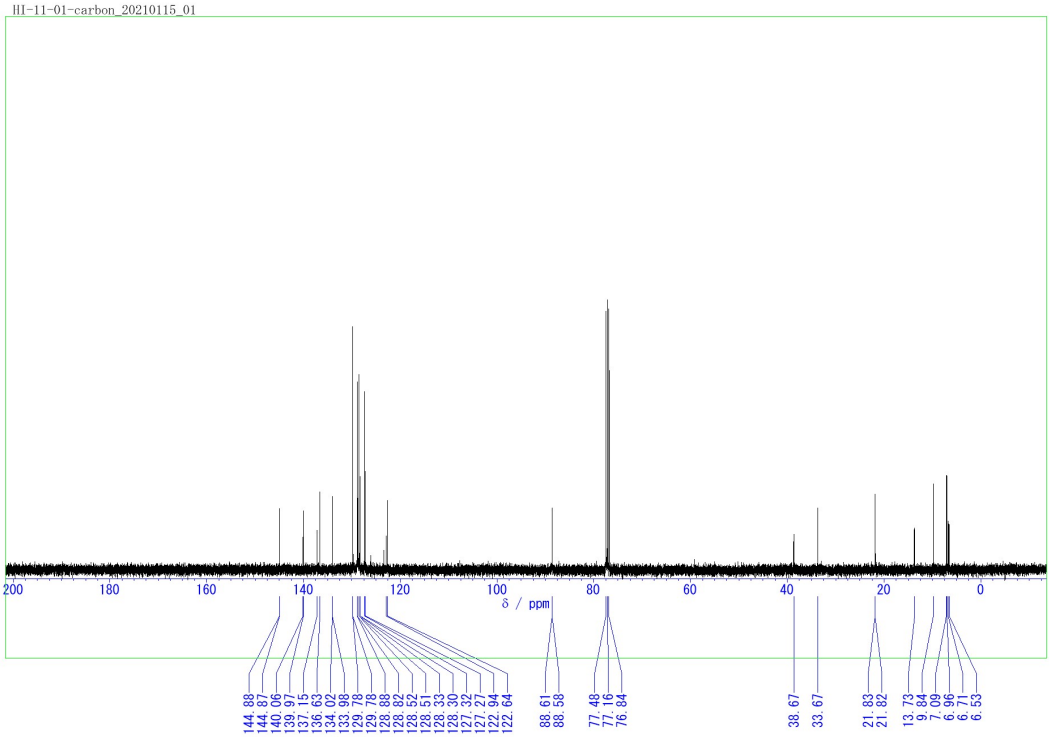
HI-11-14-carbon_20210112_01

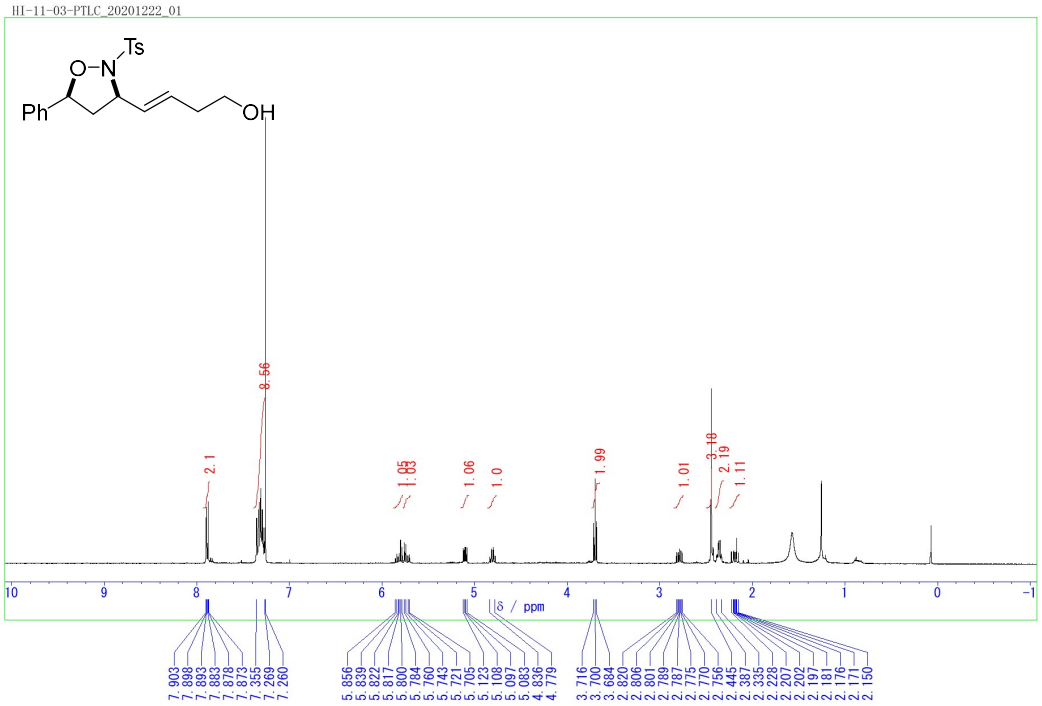


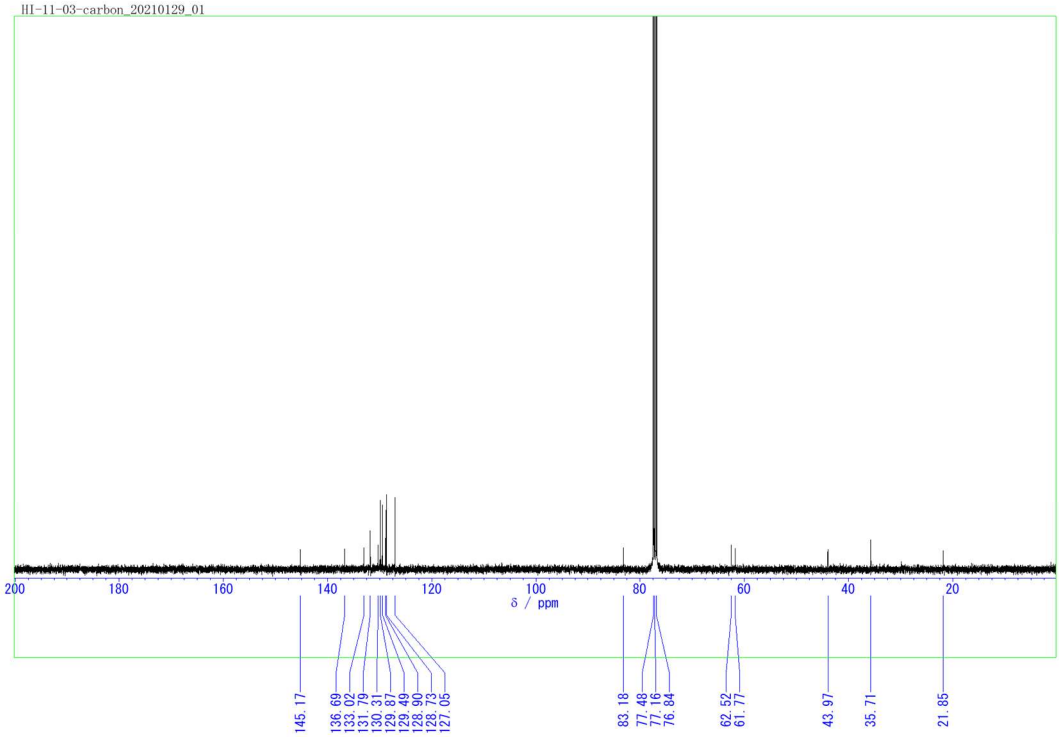

HI-11-15-PTLC_20210108_01
O
N
O
O
O
4.22
2.75
2.87
2.89
1.42
1.44
0.45
1.0
1.04
1.49
0.48
1.08
0.57
2.95
2.91
δ / ppm
7.754
7.703
7.693
7.647
7.517
7.447
7.348
7.275
7.260
5.456
5.380
5.356
5.260
5.107
5.104
5.101
5.086
5.083
5.080
5.069
5.066
5.063
5.048
5.045
5.042
4.850
4.790
3.133
3.057
2.907
2.802
2.688
2.613
1.531
1.439
1.328
1.242
0.756
0.584
0.327
0.210


HI-11-15-carbon_20210112_01
δ / ppm
163.85
163.82
137.85
137.80
137.76
137.03
134.38
134.36
129.12
129.10
128.99
128.99
128.35
128.35
128.35
128.35
123.47
123.45
121.84
121.81
88.94
88.89
77.48
77.16
76.84
38.07
33.35
13.67
9.94
7.13
7.02
6.64
6.56

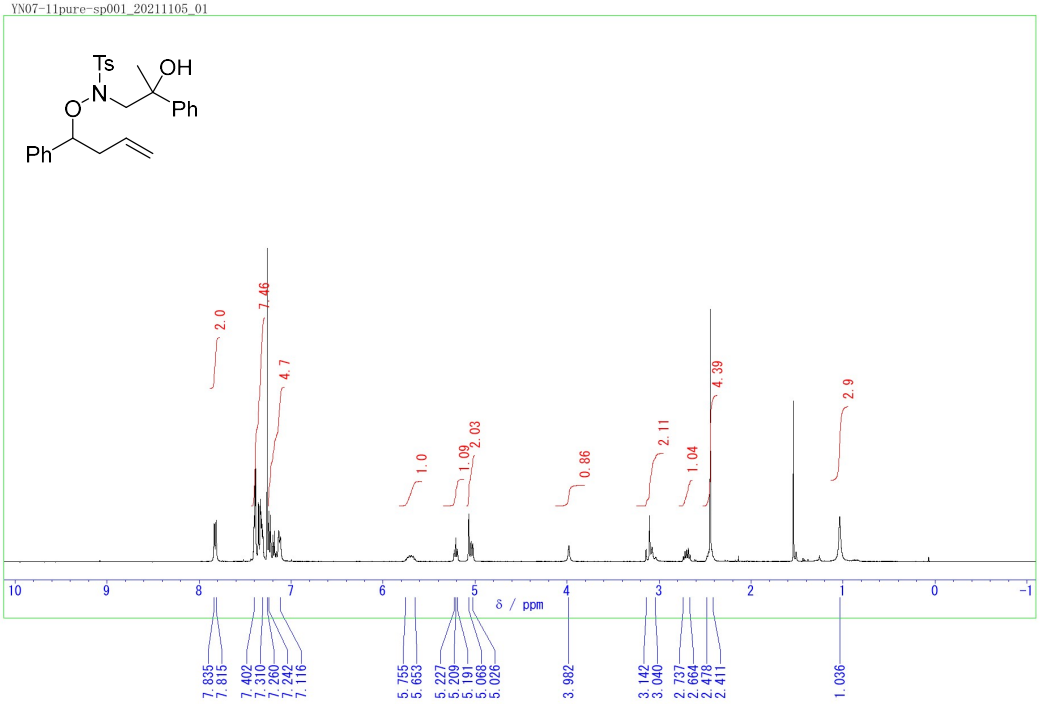

HI-11-01-PTLC_20210108_01
NHTs
8.19
2.28
1.0
1.02
0.91
0.99
0.63
1.05
3.2
0.49
1.03
2.07
2.09
δ / ppm
7.839
7.812
7.351
7.260
7.234
6.684
6.630
5.487
5.414
5.307
5.289
5.280
5.271
5.262
5.244
5.042
5.007
4.989
4.964
4.866
4.806
2.832
2.755
2.587
2.492
2.453
2.411
2.340
1.452
1.352
0.732
0.625
0.343
0.243


HI-11-01-carbon_20210115_01
δ / ppm
144.88
144.87
140.06
139.97
137.15
136.63
134.02
133.98
129.78
129.78
128.88
128.82
128.52
128.51
128.33
127.32
127.27
122.94
122.64
88.61
88.58
77.48
77.16
76.84
38.67
33.67
21.83
21.82
13.73
9.84
7.09
6.96
6.71
6.53

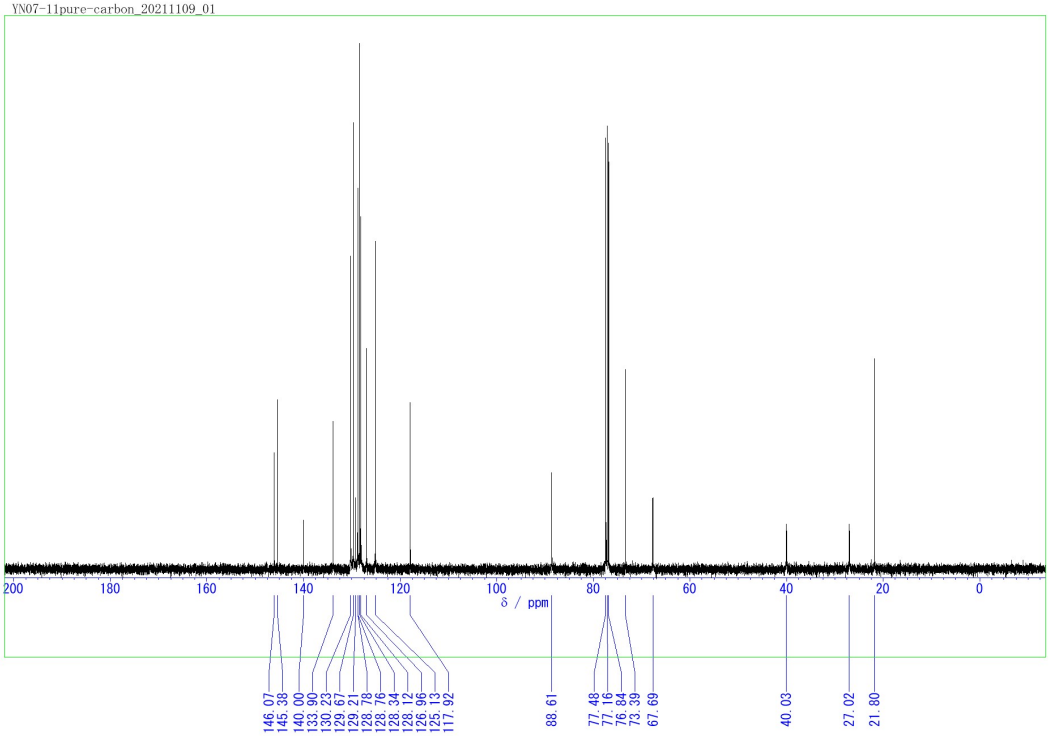

HI-11-03-PTLC_20201222_01
Ts
O
N
Ph
OH
8.56
2.1
1.05
1.03
1.06
1.0
1.99
1.01
3.10
2.19
1.11
δ / ppm
7.903
7.898
7.893
7.883
7.878
7.873
7.355
7.269
7.260
5.856
5.839
5.822
5.817
5.800
5.784
5.760
5.743
5.721
5.705
5.123
5.108
5.097
5.083
4.836
4.779
3.716
3.700
3.684
2.820
2.806
2.801
2.789
2.787
2.775
2.770
2.756
2.445
2.387
2.335
2.228
2.207
2.202
2.197
2.181
2.176
2.171
2.160

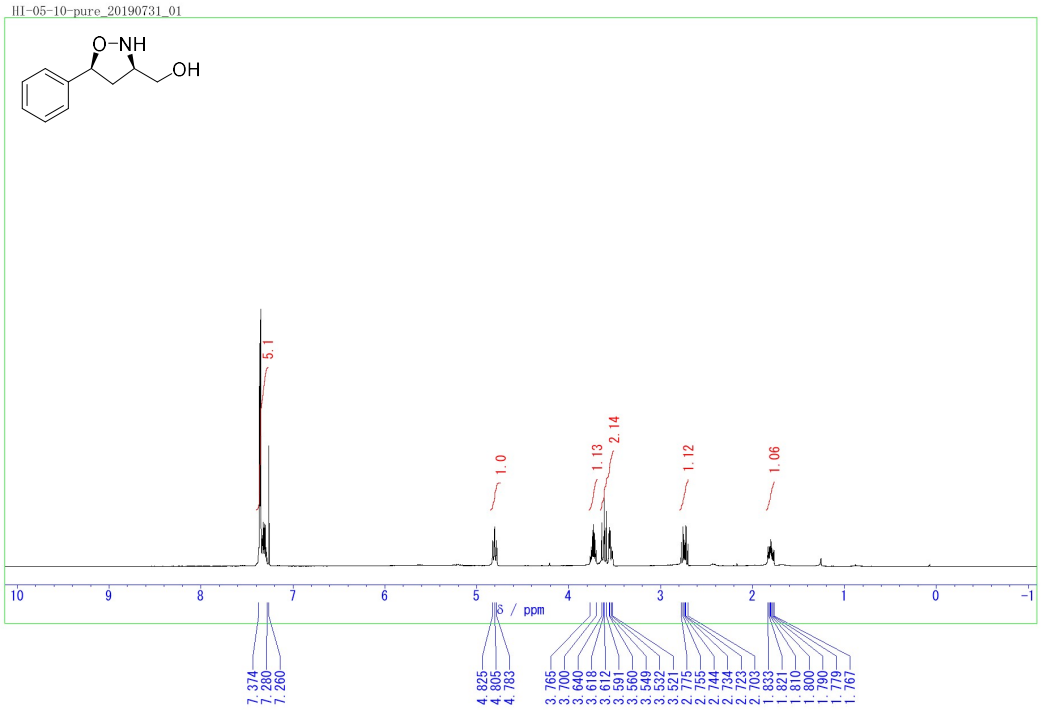

HI-11-03-carbon_20210129_01
δ / ppm
145.17
136.69
133.02
131.79
130.31
129.87
129.49
128.90
128.73
127.05
83.18
77.48
77.16
76.84
62.52
61.77
43.97
35.71
21.85

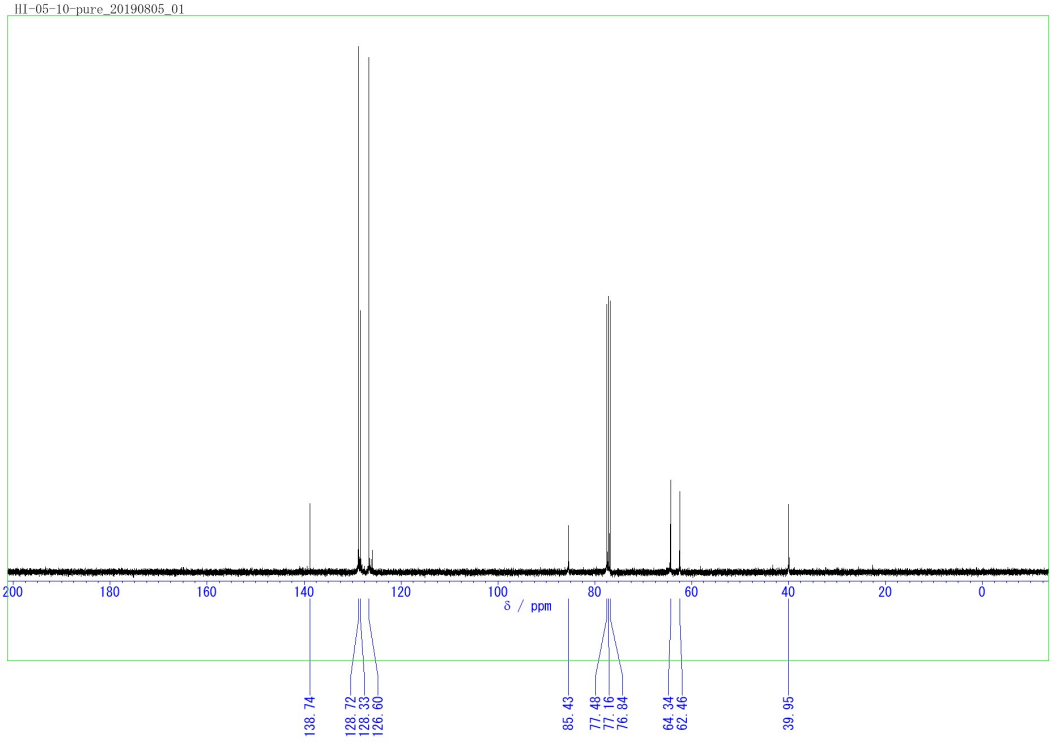
YN07-11pure-sp001_20211105_01



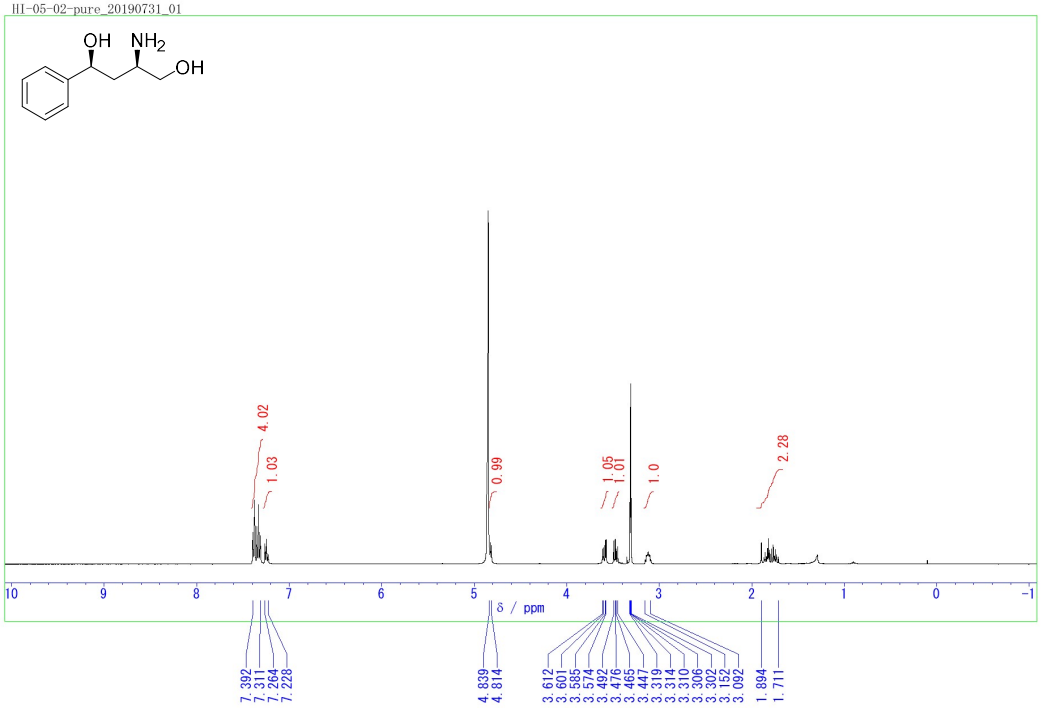
YN07-11pure-carbon_20211109_01



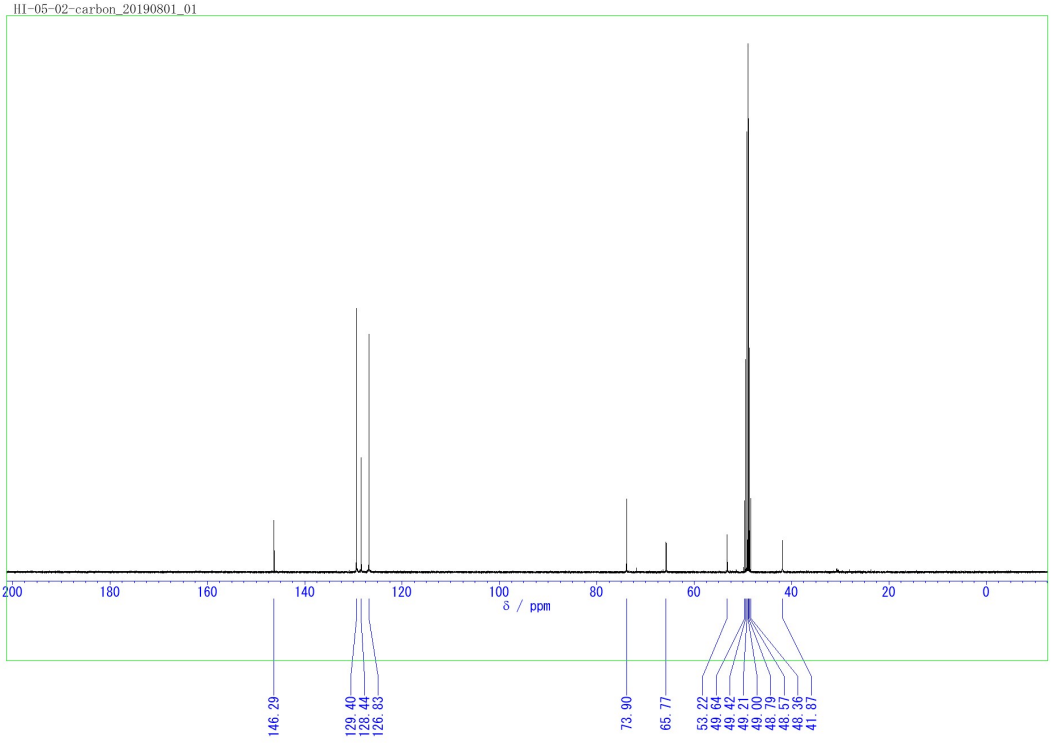

HI-05-10-pure_20190731_01
O-NH
OH
5.1
1.0
1.13
2.14
1.12
1.06
δ / ppm
7.374
7.280
7.260
4.825
4.805
4.783
3.765
3.700
3.640
3.618
3.612
3.591
3.560
3.549
3.532
3.571
2.755
2.744
2.734
2.723
2.703
1.833
1.821
1.810
1.800
1.790
1.779
1.767

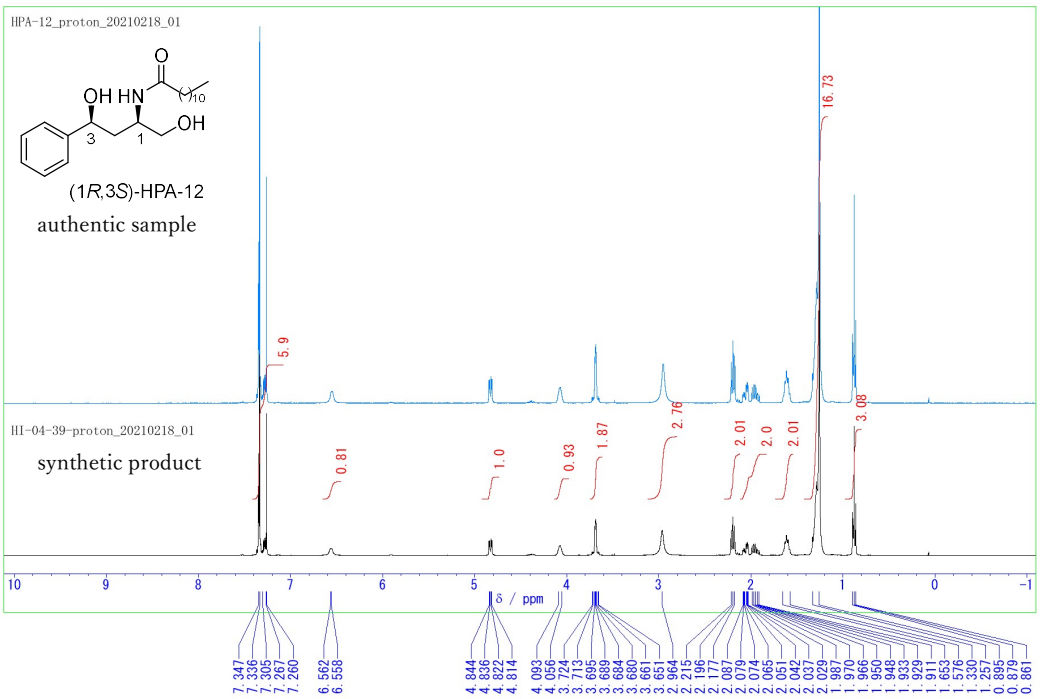

HI-05-10-pure_20190805_01
δ / ppm
138.74
128.72
128.33
126.60
85.43
77.48
77.16
76.84
64.34
62.46
39.95

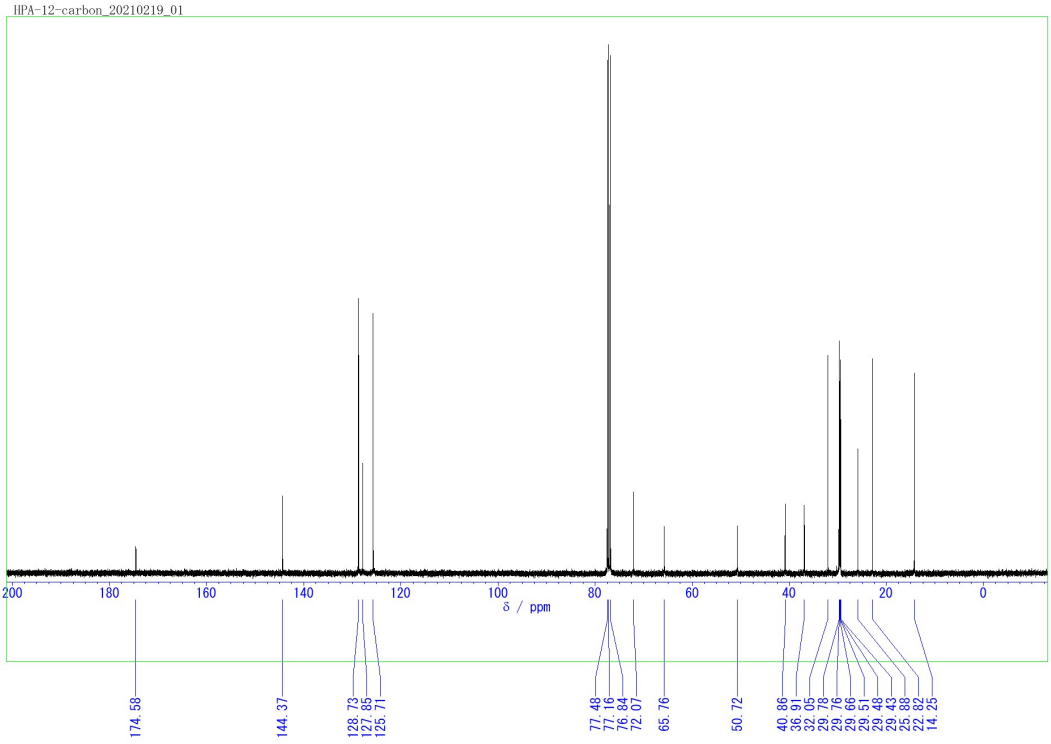
HI-05-02-pure_20190731_01

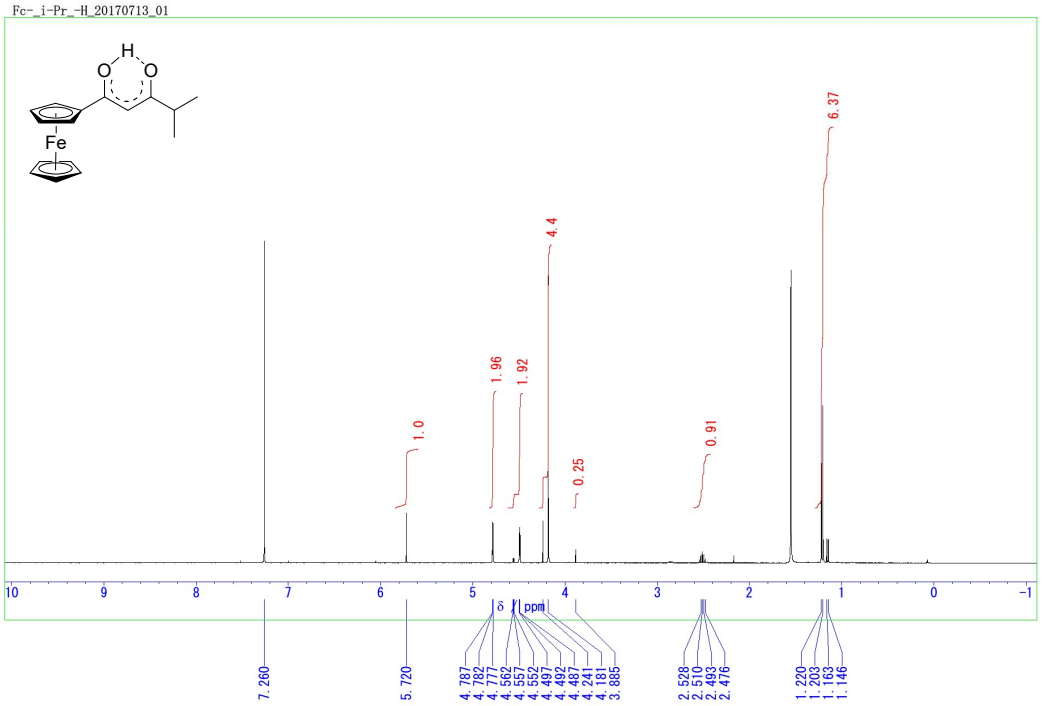


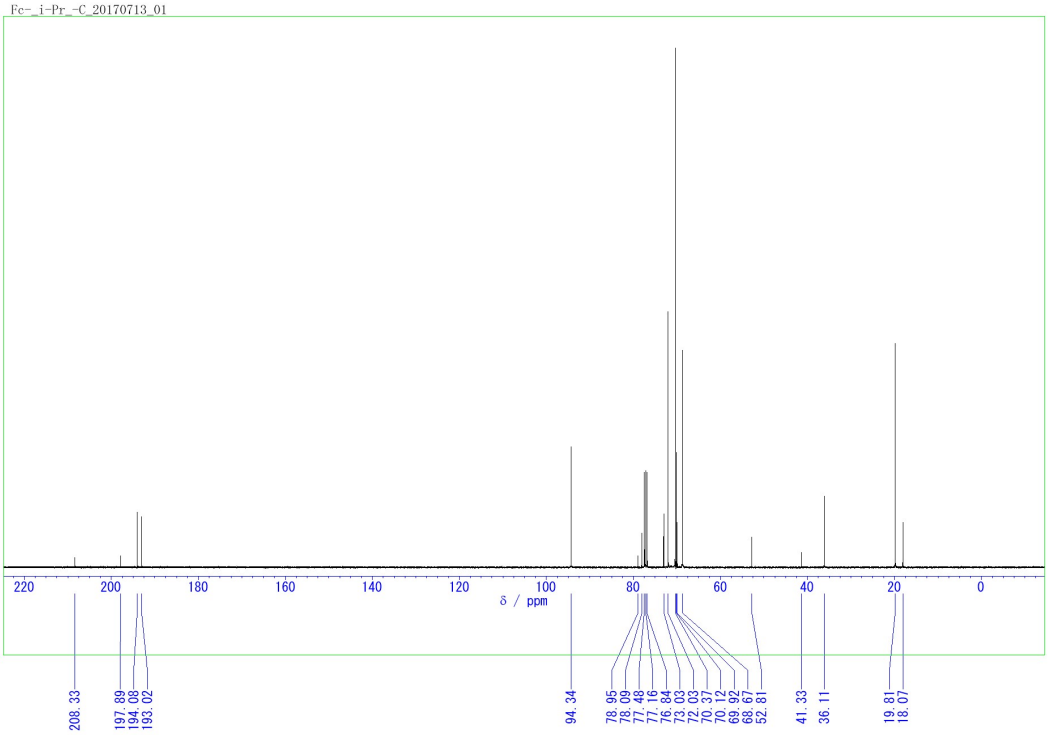
HI-05-02-carbon_20190801_01

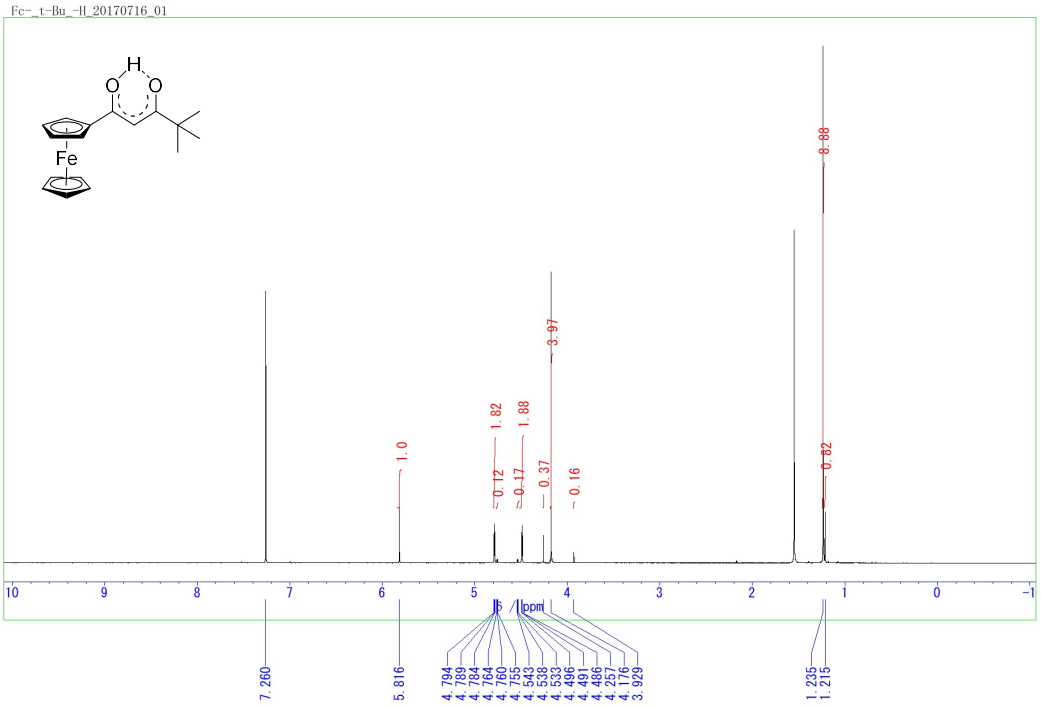


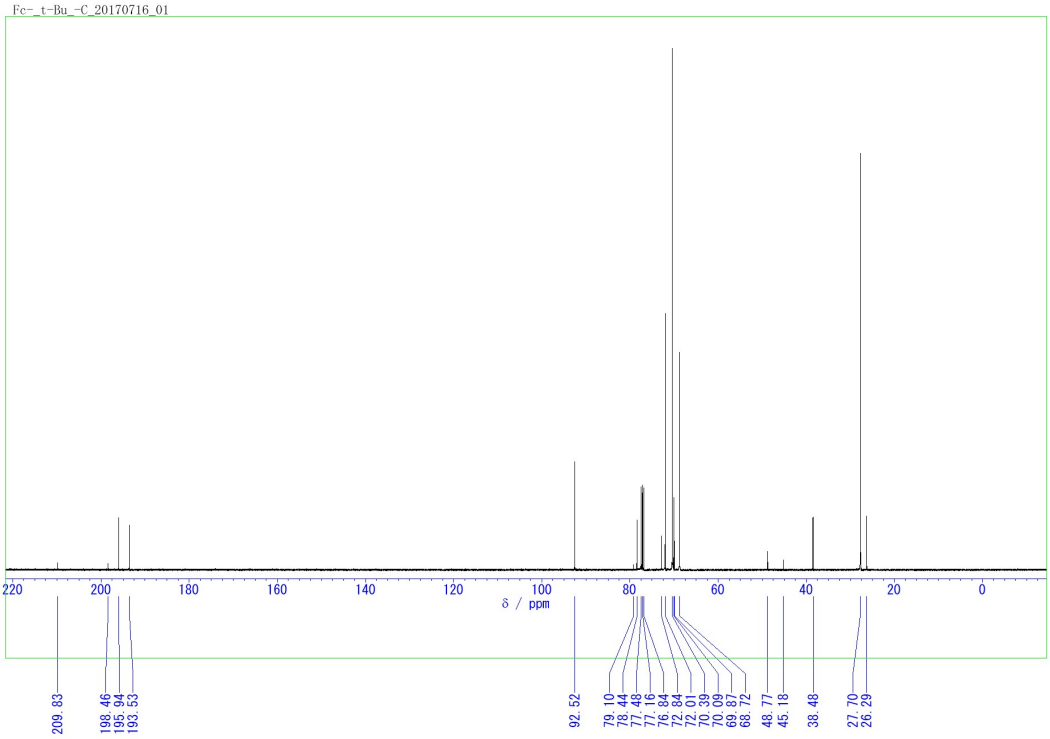

HPA-12_proton_20210218_01
(1R,3S)-HPA-12
authentic sample
HI-04-39-proton_20210218_01
synthetic product
δ / ppm


HPA-12-carbon_20210219_01
δ / ppm

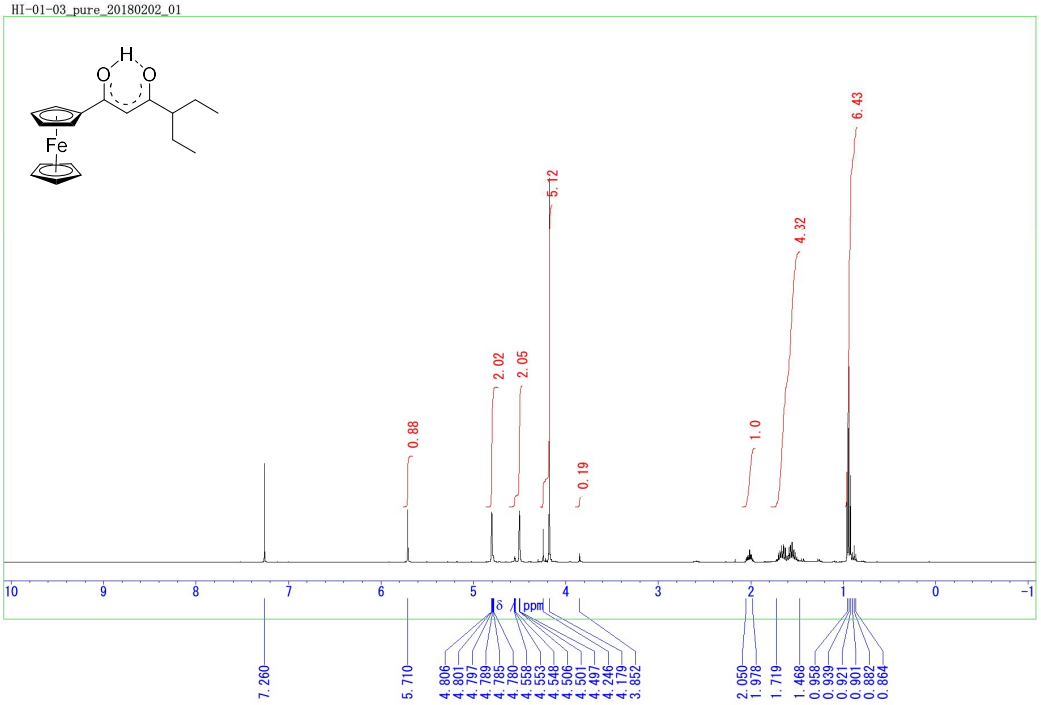

Fc-_i-Pr_-H_20170713_01
H
O
O
Fe
6.37
4.4
1.96
1.92
1.0
0.91
0.25
10
9
8
7
6
5
4
3
2
1
0
-1
δ / ppm
7.260
5.720
4.787
4.782
4.777
4.562
4.557
4.552
4.492
4.487
4.241
4.181
3.885
2.528
2.510
2.493
2.476
1.220
1.203
1.163
1.146


Fc-_i-Pr_-C_20170713_01
220
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
208.33
197.89
194.08
193.02
94.34
78.95
78.09
77.48
77.16
76.84
73.03
72.03
70.37
70.12
69.92
68.67
52.81
41.33
36.11
19.81
18.07

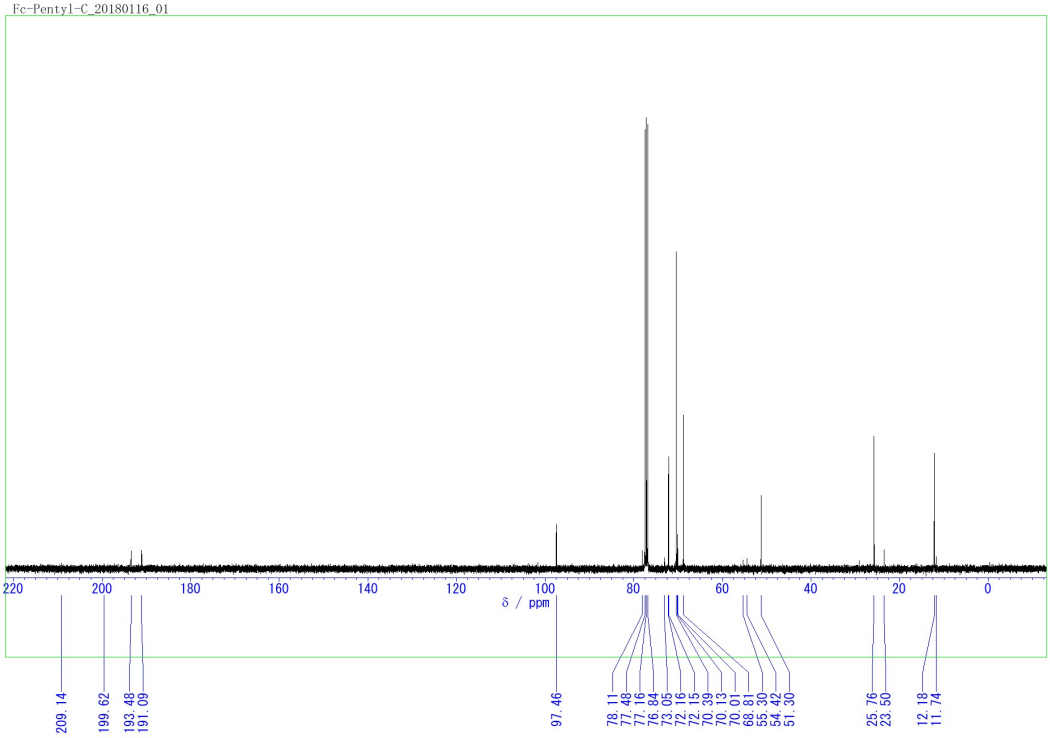

Fc-_t-Bu_-H_20170716_01
H
O
O
Fe
8.88
3.97
1.82
1.88
1.0
0.82
0.12
0.17
0.37
0.16
10
9
8
7
6
5
4
3
2
1
0
−1
δ / ppm
7.260
5.816
4.794
4.789
4.784
4.764
4.760
4.755
4.543
4.538
4.533
4.496
4.491
4.486
4.257
4.176
3.929
1.235
1.215

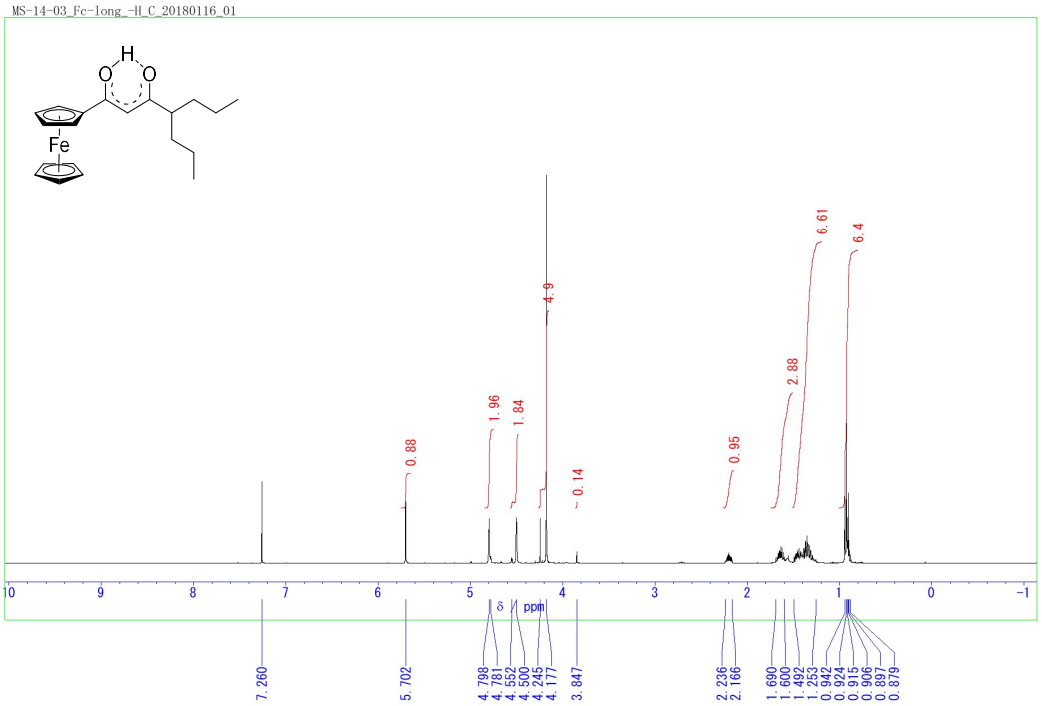

Fc-_t-Bu_-C_20170716_01
220
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
209.83
198.46
195.94
193.53
92.52
79.10
78.44
77.48
77.16
76.84
72.01
70.39
70.09
69.87
68.72
48.77
45.18
38.48
27.70
26.29

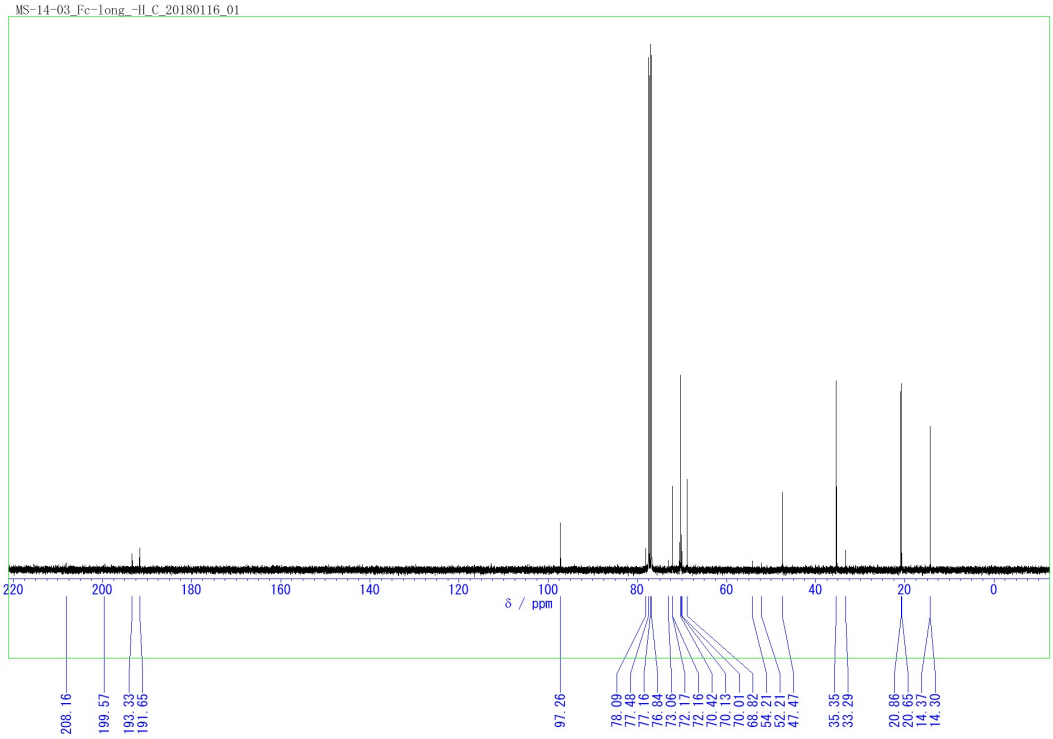
HI-01-03_pure_20180202_01

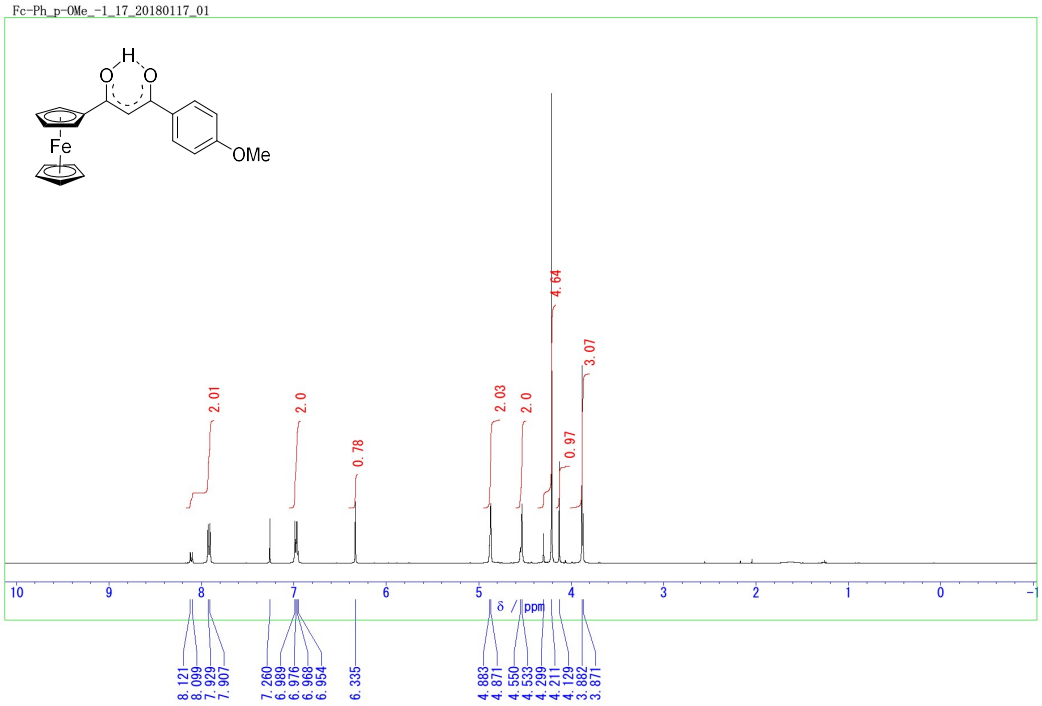


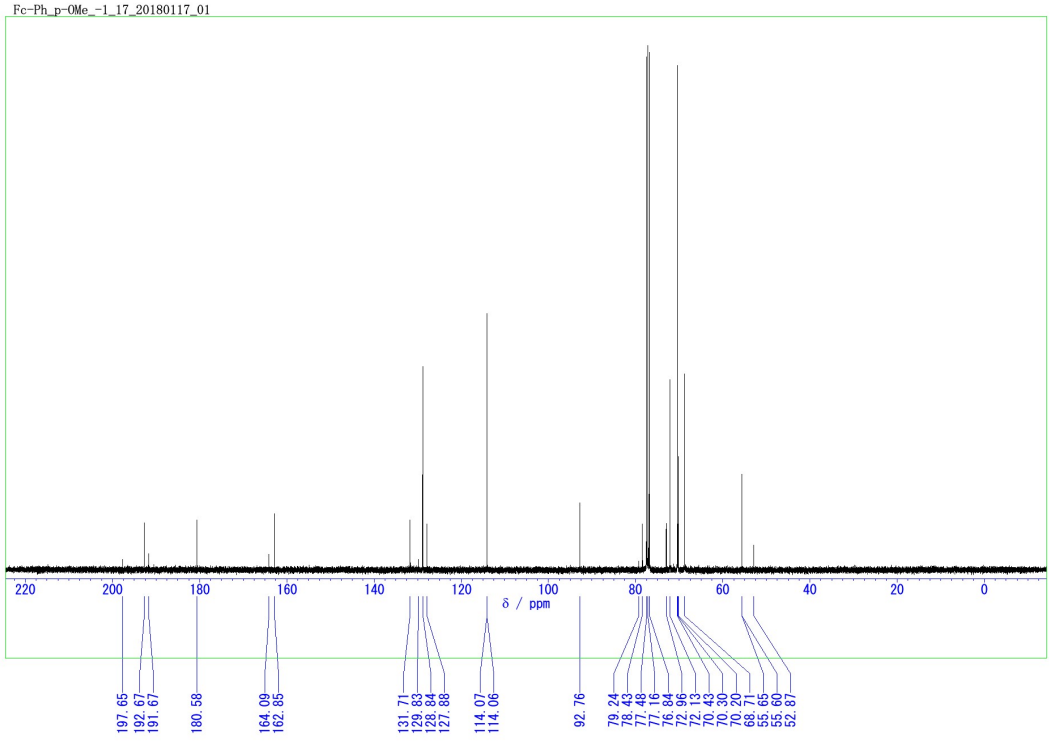
Fc-Pentyl-C_20180116_01

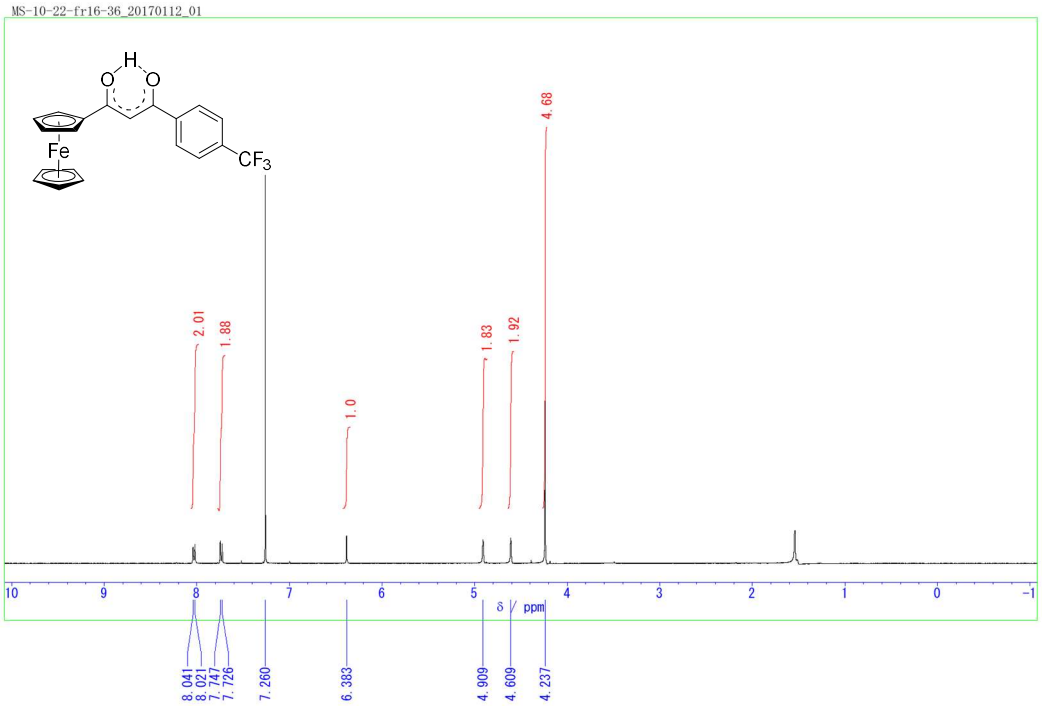


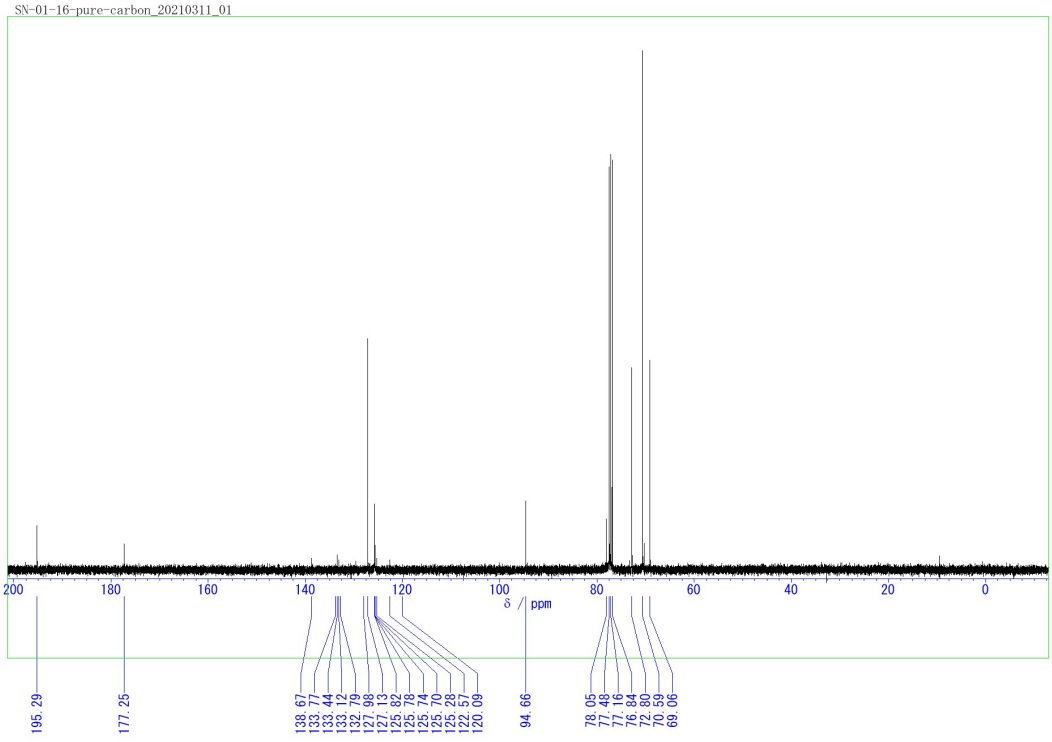

MS-14-03_Fc-long_-H_C_20180116_01
H
O
O
Fe
0.88
1.96
1.84
4.9
0.14
0.95
2.88
6.61
6.4
δ / ppm
7.260
5.702
4.798
4.781
4.552
4.500
4.245
4.177
3.847
2.236
2.166
1.690
1.600
1.492
1.252
1.043
0.924
0.915
0.906
0.897
0.879


MS-14-03_Fc-long_-H_C_20180116_01
δ / ppm
208.16
199.57
193.33
191.65
97.26
78.09
77.48
77.16
76.84
73.06
72.17
72.16
70.42
70.13
70.01
68.82
54.21
52.21
47.47
35.35
33.29
20.86
20.65
14.37
14.30


Fc-Ph_p-OMe_-1_17_20180117_01
H
O
O
Fe
OMe
2.01
2.0
0.78
2.03
2.0
4.64
0.97
3.07
10
9
8
7
6
5
4
3
2
1
0
−1
δ / ppm
8.121
8.090
7.929
7.907
7.260
6.980
6.976
6.968
6.954
6.335
4.883
4.871
4.550
4.533
4.299
4.211
4.129
3.882
3.871


Fc-Ph_p-OMe_-1_17_20180117_01
220
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
197.65
192.67
191.67
180.58
164.09
162.85
131.71
129.83
128.84
127.88
114.07
114.06
92.76
79.24
78.43
77.48
77.16
76.84
72.96
72.13
70.43
70.30
70.20
68.71
55.65
55.60
52.87


MS-10-22-fr16-36_20170112_01
H
O
O
Fe
CF3
4.68
2.01
1.88
1.0
1.83
1.92
10
9
8
7
6
5
4
3
2
1
0
−1
δ / ppm
8.041
8.021
7.747
7.726
7.260
6.383
4.909
4.609
4.237


SN-01-16-pure-carbon_20210311_01
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
195.29
177.25
138.67
133.77
133.44
133.12
132.79
127.98
127.13
125.82
125.78
125.74
125.70
125.28
122.57
120.09
94.66
78.05
77.48
77.16
76.84
72.80
70.59
69.06