Supporting Information

Chemoselective Oxidative Spiroetherification and Spiroamination of Arenols Using I^+/Oxone Catalysis

Muhammet Uyanik, Naoto Sahara, Outa Katade, Kazuaki Ishihara*

Graduate School of Engineering, Nagoya University
Furo-cho, Chikusa, Nagoya 464-8603, Japan
E-mail: ishihara@cc.nagoya-u.ac.jp

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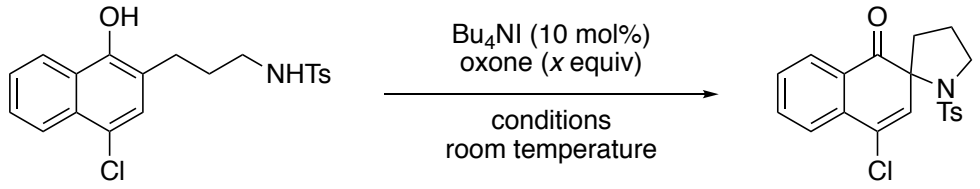
Materials and Methods

Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) and Bruker AVANCE III HD (500 MHz) spectrometers at ambient temperature. Chemical shifts are reported in ppm from the solvent resonance (CD_3CN; 1.94 ppm, DMSO-d_6; 2.50 ppm) or Me_4Si resonance (0.00 ppm; $CDCl_3$) as internal standard. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; quin = quintet; sept = septet; m = multiplet; brs = broad singlet), coupling constant (Hz), and integration. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) and Bruker AVANCE III HD (125 MHz) spectrometers at ambient temperature. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$; 77.00 ppm, CD_3CN; 1.32 ppm, C_6D_6; 128.00 ppm, CD_2Cl_2; 53.84 ppm, DMSO-d_6; 39.00 ppm). High-resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700 (FAB). For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm) were used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385).

In experiments that required dry solvents, diethyl ether (Et_2O), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF) and dichloromethane (CH_2Cl_2), were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. as the "anhydrous" and stored over 4Å molecular sieves. Pure (deionized)-water, *tert*-butyl methyl ether (MTBE) and ethyl acetate (EtOAc) were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. and used without further purification. Other solvents were purchased from Aldrich Chemical Co., Inc., FUJIFILM Wako Pure Chemical Industries, Ltd. or Tokyo Chemical Industry Co., Ltd., and used without further purification. Tetrabutylammonium iodide (Bu_4NI), tetrabutylammonium triiodide (Bu_4NI_3) and cumene hydroperoxide (CHP, contains ca. 20% aromatic hydrocarbon) were purchased from Tokyo Chemical Industry Co. Ltd. and used without further purification. 30-wt% Aqueous hydrogen peroxide and 70% aqueous *tert*-butyl hydroperoxide (TBHP) were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. Oxone and anhydrous TBHP (5.5 *M* nonane solution) were purchased from Aldrich Chemical Co., Inc., and used without further purification. Other simple chemicals were analytical-grade and obtained commercially and used without further purification.

Additional Optimization of Reaction Conditions and Control Experiments

Table S1. Optimization of Conditions for Oxidative Spiroamination of 3b

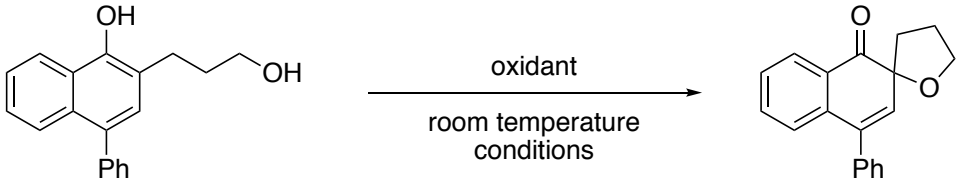


3b **4b**

entry	*x* (equiv)	solvent	time (h)	**3b**, conv. (%)[a]	**4b**, yield (%)[a]
1[b]	0.6	toluene (0.1 *M*)/H_2O (2/1)	12	<5	<5
2	0.6	CH_3CN (0.1 *M*)/H_2O (2/1)	3	>95	49
3	0.6	CH_3CN (0.02 *M*)/H_2O (10/1)	12	80	55
4	1	CH_3CN (0.02 *M*)/H_2O (10/1)	6	>95	65
5	1	CH_3CN (0.05 *M*)/H_2O (5/1)	6	>95	61

[a] ^1H NMR analysis. [b] **3b** did not dissolved in a toluene–water biphasic solvent. Other arenols **3**, except **3a**, tethered to amides were found to be less soluble in toluene–water biphasic solvent.

Table S2. Control Experiments Using 1a

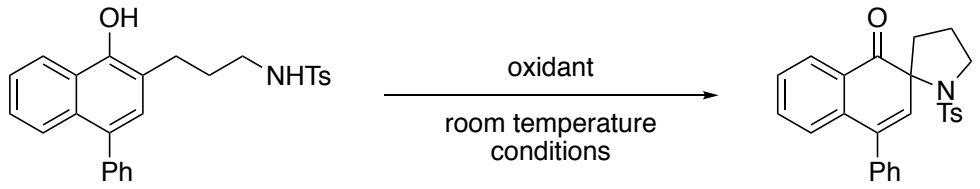


1a **2a**

entry	oxidant (equiv)	solvent[a]	time (h)	**1a**, conv. (%)[b]	**2a**, yield (%)[b]
1	I_2 (1)	CH_3CN/H_2O	1	40	35
2	I_2 (1)	toluene/H_2O	8	35	33
3	I_2 (1) + AcOH (1)	toluene/H_2O	1	30	30
4[c]	I_2 (1) + Bu_4NOH (2)	CH_3CN/H_2O	1	74	55
5[c]	I_2 (1) + K_2CO_3 (2)	toluene/H_2O	1	>95	>95
6	Bu_4NI_3 (1)	CH_3CN/H_2O	1	<5	<1
7[c]	Bu_4NI_3 (1) + K_2CO_3 (2)	CH_3CN/H_2O	1	75	7
8	$NaIO_3$ (1)	CH_3CN/H_2O	24	<5	<1
9[d]	$NaIO_4$ (1)	CH_3CN/H_2O	12	>95	40

[a] Solvent (0.1 *M*)/H_2O (2/1, *v*/*v*). [b] ^1H NMR analysis. [c] Hypoiodite species might be generated *in situ* under these conditions (see: Uyanik, M.; Hayashi, H.; Ishihara, K. *Science* **2014**, 345, 291). Notably, with the use of I_2, compared to strong alkali conditions with Bu_4NOH, cleaner reactions were observed under mild basic conditions with K_2CO_3 (entry 5 versus entry 4). On the other hand, although oxidation of **1a** proceeded with the use of Bu_4NI_3 in the presence of K_2CO_3, a complex reaction mixture was observed and **2a** was obtained in only 7% yield (entry 7). [d] Although oxidation of **1a** proceeded with the use of $NaIO_4$ to give **2a** in moderate yield along with several unidentified side products, according to the Raman analysis, high valent species ($[IO_4]^-$ or $[IO_3]^-$) were not generated under the present Bu_4NI/oxone catalytic conditions (see: Uyanik, M.; Kato, T.; Sahara, N.; Katade, O.; Ishihara, K. *ACS Catal.* **2019**, *9*, 11619).

Table S3. Control Experiments Using 3a

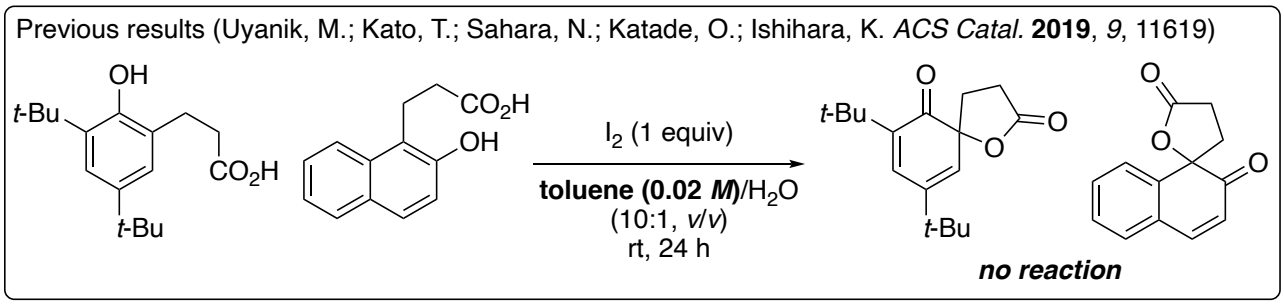


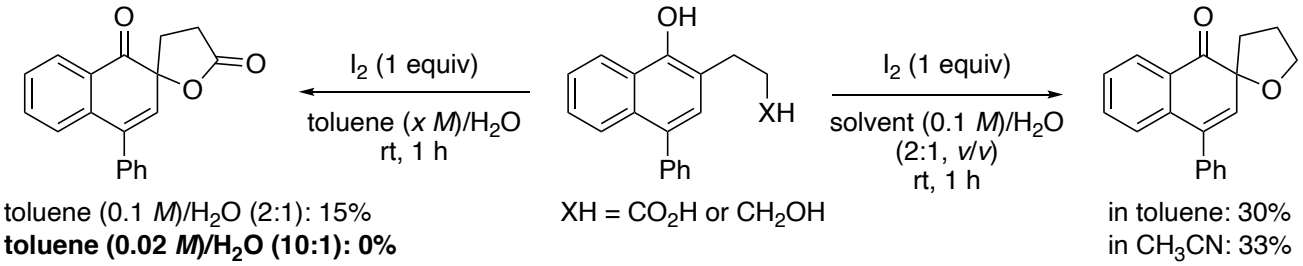
3a **4a**

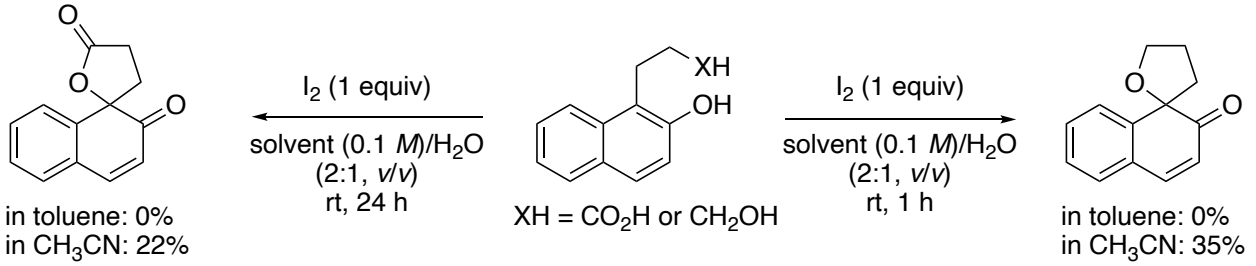
entry	oxidant (equiv)	solvent[a]	time (h)	**1a**, conv. (%)[b]	**2a**, yield (%)[b]
1	I_2 (1)	toluene/H_2O	1	30	30
2[c]	I_2 (1) + Bu_4NOH (2)	toluene/H_2O	1	>95	<5
3[c]	I_2 (1) + K_2CO_3 (2)	toluene/H_2O	1	>95	>95
4[c]	I_2 (1) + K_2CO_3 (2)	toluene	1	30	30
5	Bu_4NI_3 (1)	toluene/H_2O	1	<5	<1
6[c]	Bu_4NI_3 (1) + K_2CO_3 (2)	toluene/H_2O	1	40	<5
7	$NaIO_3$ (1)	toluene/H_2O	24	<5	<1
8	$NaIO_4$ (1)	toluene/H_2O	12	>5	<1

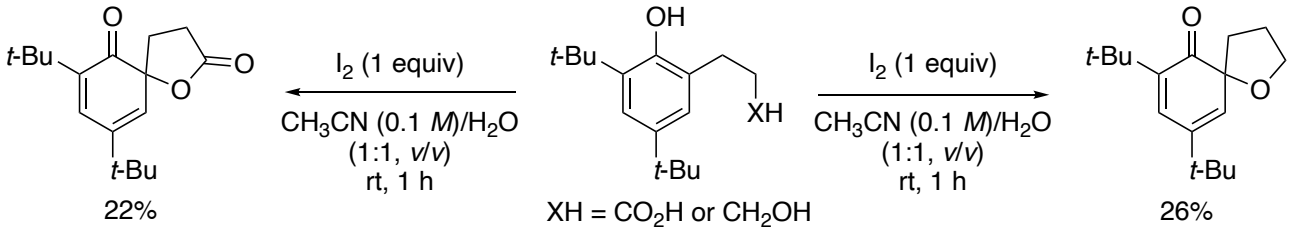
[a] Toluene (0.1 *M*)/H_2O (2/1, *v*/*v*). [b] ^1H NMR analysis. [c] Hypoiodite species might be generated *in situ* under these conditions (see: Uyanik, M.; Hayashi, H.; Ishihara, K. *Science* **2014**, 345, 291). Notably, compared to strong alkali conditions with Bu_4NOH, cleaner reactions were observed with the use of I_2 under mild basic conditions with K_2CO_3 (entries 3 and 4 versus entry 2). On the other hand, although oxidation of **3a** proceeded with the use of Bu_4NI_3 in the presence of K_2CO_3, a complex reaction mixture was observed and **4a** was obtained in less than 5% yield (entry 6).

Scheme S1. Additional Control Experiments for Spirolactonization and Comparison

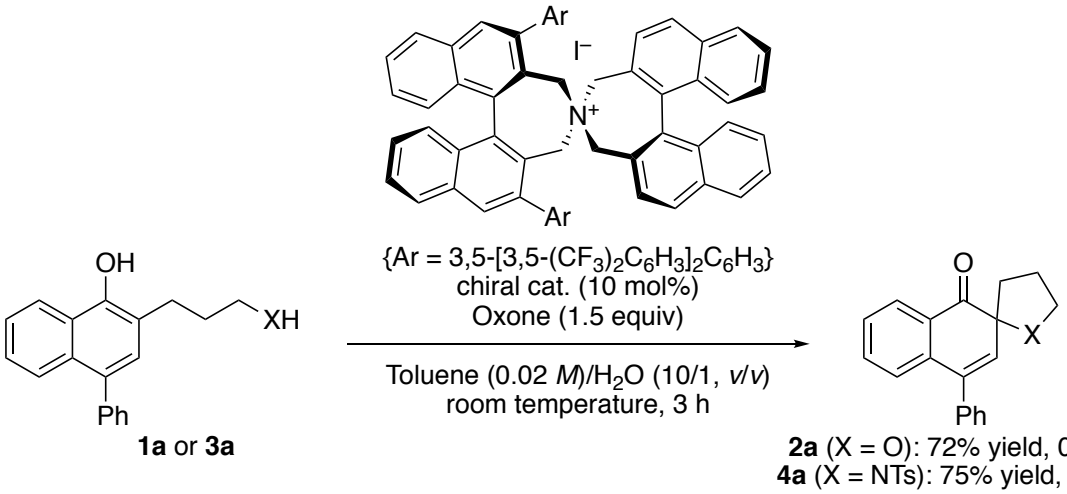






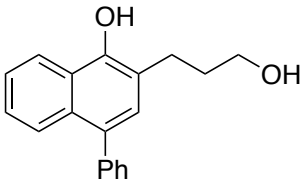


Scheme S2. Enantioselective Oxidative Spiroetherification and Spiroamination Reactions

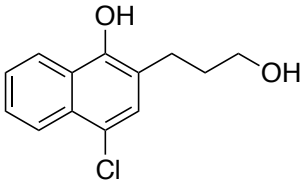


Synthesis and Characterization of Substrates

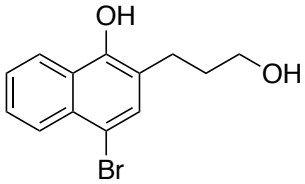
Substrates **1a**,[1] **1b–1d**,[2] **1e**,[3] **1i**,[4] **1j**,[4] **1l**,[3] **1m**,[3] **3aa**[1] and **3ea**[5] were known compounds and prepared by following the literature procedures.



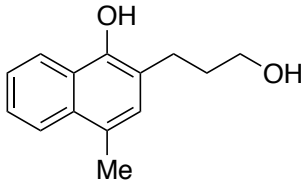
2-(3-Hydroxypropyl)-4-phenylnaphthalen-1-ol (1a):[1] White solid; **TLC**, R_f = 0.52 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.94–2.03 (m, 3H), 2.98 (t, *J* = 6.6 Hz, 2H), 3.69–3.72 (m, 2H), 7.17 (s, 1H), 7.37–7.42 (m, 2H), 7.44–7.49 (m, 5H), 7.83–7.87 (m, 2H), 8.35 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.1, 31.4, 60.3, 119.2, 122.4, 125.0, 125.5, 125.6, 125.7, 126.8, 128.2, 129.7, 130.2, 131.5, 132.6, 140.9, 149.8.



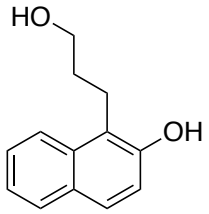
4-Chloro-2-(3-hydroxypropyl)naphthalen-1-ol (1b):[2] White solid; **TLC**, R_f = 0.48 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.93–2.00 (m, 3H), 2.92–2.95 (m, 2H), 3.68 (t, *J* = 5.7 Hz, 2H), 7.31 (s, 1H), 7.50–7.58 (m, 2H), 7.99 (brs, 1H), 8.14–8.16 (m, 1H), 8.29–8.31 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 24.9, 31.1, 60.1, 120.3, 122.6, 122.7, 124.0, 125.8, 126.5, 126.6, 128.3, 130.3, 149.4.



4-Bromo-2-(3-hydroxypropyl)naphthalen-1-ol (1c):[2] White solid; **TLC**, R_f = 0.48 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.93–2.05 (m, 3H), 2.91–2.95 (m, 2H), 3.67 (t, *J* = 5.7 Hz, 2H), 7.49–7.57 (m, 3H), 8.03 (brs, 1H), 8.09–8.12 (m, 1H), 8.28–8.31 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 24.8, 31.1, 60.1, 112.7, 120.8, 122.7, 125.8, 126.6, 126.7, 126.9, 131.6, 131.9, 150.3

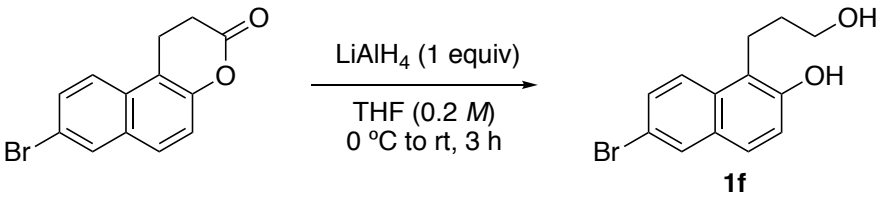


2-(3-Hydroxypropyl)-4-methylnaphthalen-1-ol (1d):[2] White solid; R_f = 0.50 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.92–1.98 (m, 3H), 2.59 (s, 3H), 2.91–2.94 (m, 2H), 3.66 (q, *J* = 5.2 Hz, 2H), 7.04 (s, 1H), 7.47–7.49 (m, 2H), 7.59 (s, 1H), 7.87–7.90 (m, 1H), 8.28–8.30 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 18.7, 25.0, 31.4, 60.3, 119.4, 122.5, 123.9, 124.8, 125.3, 125.5, 126.1, 129.0, 132.3, 148.3.



1-(3-Hydroxypropyl)naphthalen-2-ol (1e):[3] White solid; R_f = 0.35 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.01–2.07 (m, 2H), 2.43 (s, 1H), 3.24 (t, *J* = 6.6 Hz, 2H), 3.63 (t, *J* = 5.5 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.33 (td, *J* = 7.4, 1.2 Hz, 1H), 7.46–7.50 (m, 1H), 7.65–7.67 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.0, 30.2, 60.5, 117.8, 118.7, 122.6, 122.9, 126.3, 128.1, 128.6, 129.5, 133.2, 152.3.

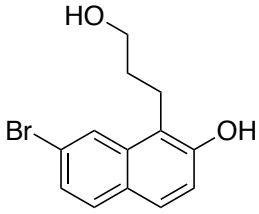
Synthesis of 1f:



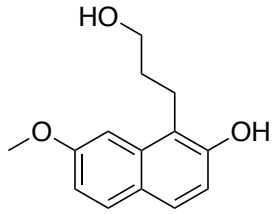
1f

To a solution of 8-bromo-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one[6] (0.415 g, 1.50 mmol) in THF (8.00 mL) was added $LiAlH_4$ (0.0569 g, 1.50 mmol) at 0 ºC. After stirring for 3 h at room temperature, resulting mixture was cooled at 0 ºC and sequentially quenched by saturated aqueous Rochelle salt (15 mL). After stirring for 30 min at room temperature, the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 3:1) to give **1f** (0.240 g, 1.10 mmol, 73% yield).

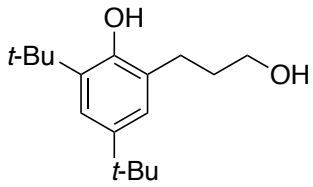
6-Bromo-1-(3-hydroxypropyl)naphthalen-2-ol (1f): White solid; R_f = 0.32 (Hexane–EtOAc = 1:1); **IR** (KBr) 3358, 3112, 1585, 1499, 1348, 1232, 1048, 890 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.99–2.05 (m, 2H), 2.36 (brs, 1H), 3.20 (t, *J* = 6.4 Hz, 2H), 3.62 (t, *J* = 5.5 Hz, 2H), 7.17 (d, *J* = 9.2 Hz, 1H), 7.51–7.57 (m, 2H), 7.75 (d, *J* = 9.2 Hz, 2H), 7.92 (d, *J* = 1.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.0, 30.2, 60.4, 116.6, 118.2, 119.9, 124.5, 127.2, 129.4, 130.5, 130.7, 131.8, 152.7; **HRMS** (FAB) m/z calcd for $[C_{13}H_{13}{}^{79}BrO_2]^+$/$[C_{13}H_{13}{}^{81}BrO_2]^+$ 280.0099/282.0078, found 280.0087/282.0078.



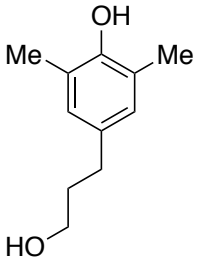
7-Bromo-1-(3-hydroxypropyl)naphthalen-2-ol (1g): This compound was synthesized from 9-bromo-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one[6] as in **1f** in 76% yield (0.371 g, 1.32 mmol). White solid; R_f = 0.39 (Hexane–EtOAc = 1:1); **IR** (KBr) 3396, 3127, 1502, 1342, 1083, 977, 827 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.00–2.06 (m, 2H), 2.67 (brs, 1H), 3.18 (t, *J* = 6.4 Hz, 2H), 3.63 (t, *J* = 5.5 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.39 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.62 (t, *J* = 9.2 Hz, 2H), 8.01 (brs, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.0, 30.1, 60.4, 117.2, 119.2, 120.9, 125.0, 126.2, 127.8, 128.1, 130.3, 134.6, 153.2; **HRMS** (FAB) m/z calcd for $[C_{13}H_{13}{}^{79}BrO_2]^+$/$[C_{13}H_{13}{}^{81}BrO_2]^+$ 280.0099/282.0078, found 280.0098/282.0076.



1-(3-Hydroxypropyl)-7-methoxynaphthalen-2-ol (1g): This compound was synthesized from 9-methoxy-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one[6] as in **1f** in 75% yield (0.262 g, 1.13 mmol). Pale yellow solid; R_f = 0.33 (Hexane–EtOAc = 1:1); **IR** (KBr) 3435, 3140, 2937, 1631, 1513, 1462, 1227, 1029, 828 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.02–2.08 (m, 3H), 3.20 (t, *J* = 6.4 Hz, 2H), 3.64–3.64 (m, 2H), 3.93 (s, 3H), 7.00–7.02 (m, 2H), 7.18 (d, *J* = 2.7 Hz, 1H), 7.33 (s, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 9.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.2, 29.9, 55.3, 60.5, 102.1, 114.8, 116.0, 117.0, 124.8, 127.8, 130.2, 134.5, 152.7, 158.2; **HRMS** (FAB) m/z calcd for $[C_{14}H_{16}O_3]^+$ 232.1099, found 232.1093.

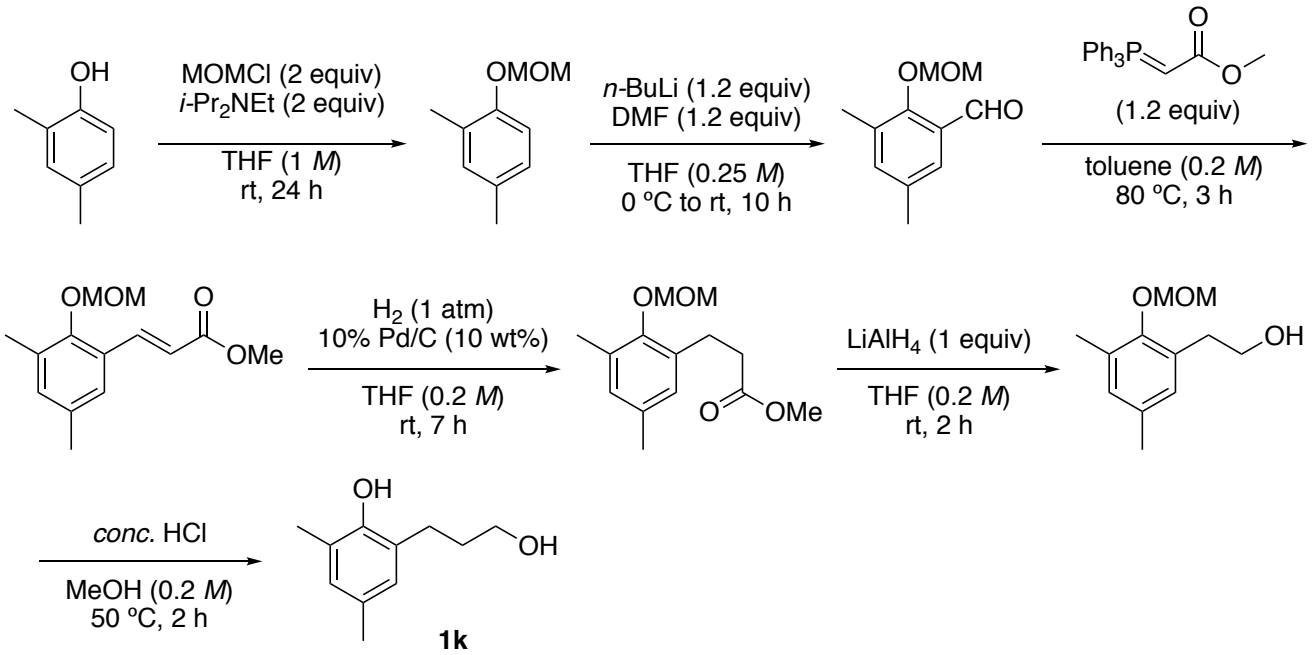


2,4-Di-tert-butyl-6-(3-hydroxypropyl)phenol (1i):[4] White solid; **TLC**, R_f = 0.31 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.29 (s, 9H), 1.42 (s, 9H), 1.85–1.91 (m, 2H), 2.01 (brs, 1H), 2.76 (t, *J* = 6.9 Hz, 2H), 3.65–3.68 (m, 2H), 6.73 (s, 1H), 6.97 (d, *J* = 2.7 Hz, 1H), 7.18 (d, *J* = 2.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.7, 29.9, 31.6, 32.2, 34.2, 34.9, 60.9, 122.1, 124.9, 126.6, 135.9, 142.0, 151.1.



4-(3-Hydroxypropyl)-2,6-dimethylphenol (1j):[4] White solid; **TLC**, R_f = 0.78 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.26 (t, J = 5.0 Hz, 1H), 1.81–1.88 (m, 2H), 2.22 (s, 6H), 2.58 (t, J = 7.6 Hz, 2H), 3.67 (q, J = 5.8 Hz, 2H), 4.51 (s, 1H), 6.81 (s, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 16.0, 31.3, 34.6, 62.5, 123.1, 128.6, 133.4, 150.4.

Synthesis of 1k:



To a solution of 2,4-dimethylphenol (1.19 g, 10.0 mmol) in THF (10.0 mL) was added diisopropylamine (3.49 mL, 20.0 mmol) and chloromethyl methyl ether (1.52 mL, 20.0 mmol) at 0 ºC. After stirring for 24 h at room temperature, resulting mixture was poured into H_2O (20 mL), and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 20:1) to give 1-(methoxymethoxy)-2,4-dimethylbenzene (1.21 g, 7.27 mmol, 73% yield).

To a solution of this MOM ether (1.21 g, 7.27 mmol) in THF (37.0 mL) was added *n*-BuLi (5.02 mL, 8.03 mmol, 1.6 *M* in hexane) dropwise at 0 ºC. After stirring for 1 h at room temperature, to the reaction mixture was added anhydrous DMF (1.14 mL, 14.6 mmol) at room temperature. After stirring for 12 h, the resulting mixture was quenched by saturated aqueous NH_4Cl (10 mL). The aqueous layers were extracted with Et_2O (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by

flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 20:1) to give 2-(methoxymethoxy)-3,5-dimethylbenzaldehyde (0.715 g, 3.68 mmol, 50% yield).

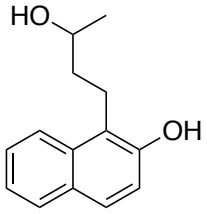
To a solution of this aldehyde (0.715 g, 3.68 mmol) in toluene (20.0 mL) was added methyl(triphenylphosphoranylidene)acetate (1.47 g, 4.44 mmol) at room temperature. After stirring for 3 h at 80 ºC, the resulting mixture was cooled to room temperature and diluted with water and EtOAc. The aqueous layers were separated and extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1) to give methyl (*E*)-3-(2-(methoxymethoxy)-3,5-dimethylphenyl)acrylate (0.908 g, 3.62 mmol, 98% yield).

To a solution of this olefin (0.908 g, 3.62 mmol) in THF (18.0 mL) was added 10% Pd/C (0.0908 g). The flask containing the mixture was then evacuated and purged with H_2 three times. In an H_2 gas environment, the resulting mixture was stirred at room temperature for 7 h. Upon the completion of the reaction, the mixture was filtered through celite with EtOAc and the crude product was obtained after removal of the solvent *in vacuo*.

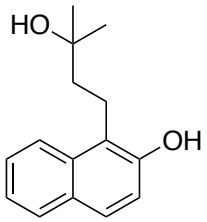
Without further purification, to a solution of this ester in THF (7.20 mL) was added $LiAlH_4$ (0.137 g, 3.62 mmol) at 0 ºC. After stirring for 3 h at room temperature, resulting mixture was cooled at 0 ºC and sequentially quenched by saturated aqueous Rochelle salt (15 mL). After stirring for 30 min at room temperature, the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 5:1) to give 3-(2-(methoxymethoxy)-3,5-dimethylphenyl)propan-1-ol (0.796 g, 3.55 mmol, 98% yield, 2 steps).

To a solution of this alcohol (0.308 g, 1.70 mmol) in MeOH (8.50 mL) was added *conc.* HCl aq. (ca. 0.100 mL). After stirring for 2 h at 50 ºC, the reaction mixture was cooled to room temperature, and to the mixture was added water (20 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 2:1) to give **1k** (0.256 g, 1.42 mmol, 84% yield).

2-(3-Hydroxypropyl)-4,6-dimethylphenol (1k): White solid; **TLC**, R_f = 0.49 (Hexane–EtOAc = 1:1); **IR** (KBr) 3467, 2949, 1482, 1325, 1193, 1054, 997, 864 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.83–1.89 (m, 2H), 2.18-2.29 (m, 1H), 2.22 (s, 6H), 2.73 (t, *J* = 6.9 Hz, 2H), 3.64 (t, *J* = 5.5 Hz, 2H), 6.59 (brs, 1H), 6.76 (s, 1H), 6.81 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 16.2, 20.4, 25.2, 32.1, 60.7, 124.4, 126.4, 128.6, 129.3, 129.5, 150.5; **HRMS** (FAB) m/z calcd for $[C_{11}H_{16}O_2]^+$ 180.1150, found 180.1144.

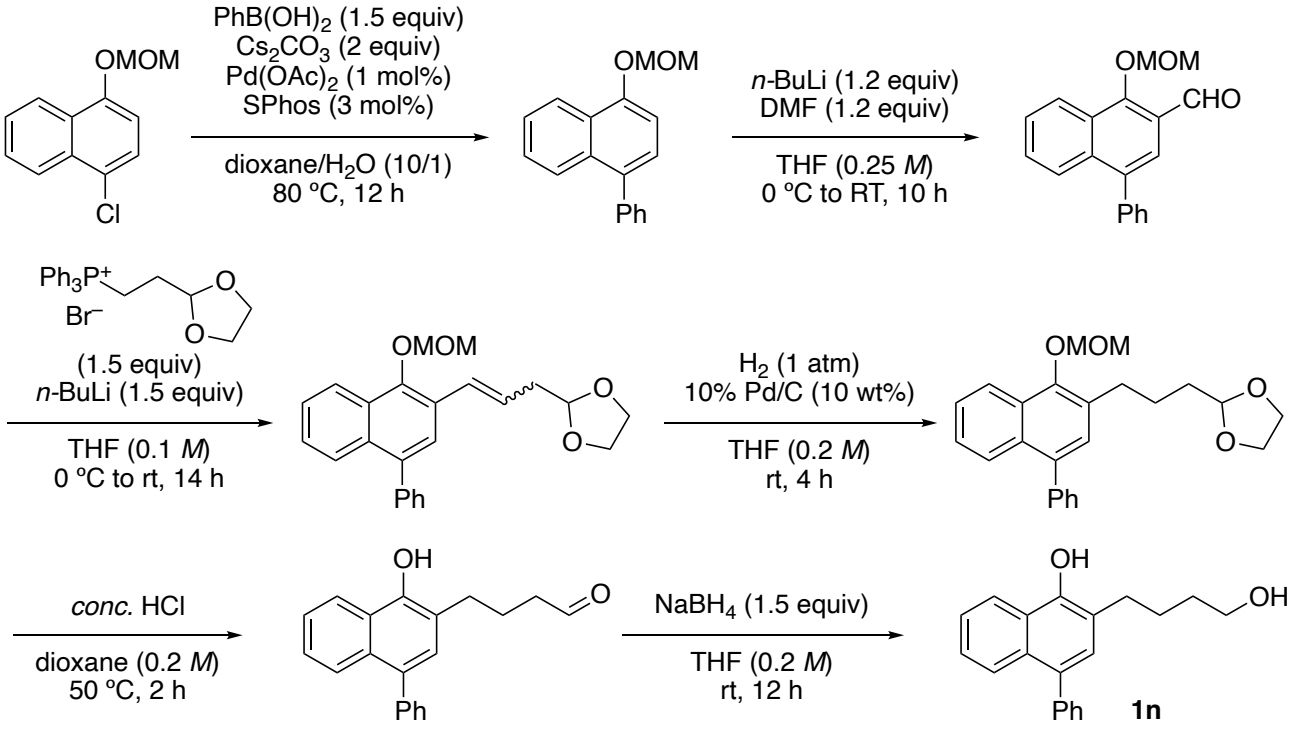


1-(3-Hydroxybutyl)naphthalen-2-ol (1l):[3] Pale yellow solid; **TLC**, R_f = 0.46 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.21 (d, J = 6.0 Hz, 3H), 1.81–1.89 (m, 1H), 1.92–2.00 (m, 1H), 2.29 (brs, 1H), 3.18–3.28 (m, 2H), 3.70 (brs, 1H), 7.17 (d, J = 9.2 Hz, 1H), 7.31–7.35 (m, 1H), 7.46–7.50 (m, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.93 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.8, 23.8, 37.3, 66.7, 118.3, 118.9, 122.6, 122.9, 126.2, 128.0, 128.7, 129.4, 133.2, 152.4.



1-(3-Hydroxy-3-methylbutyl)naphthalen-2-ol (1m):[3] White solid; **TLC**, R_f = 0.44 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.33 (s, 6H), 1.91 (t, J = 7.1 Hz, 2H), 2.14 (brs, 1H), 3.15 (t, J = 7.3 Hz, 2H), 7.15 (d, J = 8.7 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.45–7.52 (m, 2H), 7.63 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.3, 29.7, 42.2, 72.1, 119.0, 120.7, 122.6, 122.8, 126.2, 127.7, 128.6, 129.3, 133.0, 151.3.

Synthesis of 1n:



To a solution of 1-chloro-4-(methoxymethoxy)naphthalene[7] (2.22 g, 10.0 mmol),Cs_2CO_3 (6.51 g, 20.0 mmol) and phenylboronic acid (1.83 g, 15.0 mmol) in degassed dioxane (50.0 mL) and H_2O (5.00 mL) were added $Pd(OAc)_2$ (0.0224 g, 0.100 mmol) and SPhos (0.123 g, 0.300 mmol) at room temperature. After stirring for 12 h at 80 ºC, resulting mixture was poured into H_2O (20 mL), and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 20:1) to give 1-(methoxymethoxy)-2,4-dimethylbenzene (2.46 g, 9.31 mmol, 93% yield).

To a solution of this MOM ether (1.32 g, 5.00 mmol) in THF (20.0 mL) was added *n*BuLi (3.75 mL, 6.00 mmol, 1.6 *M* in hexane) dropwise at 0 ºC. After stirring for 1 h at room temperature, to the reaction mixture was added anhydrous DMF (0.777 mL, 10.0 mmol) at room temperature. After stirring for 10 h, the resulting mixture was quenched by saturated aqueous NH_4Cl (10 mL). The aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 10:1) to give 2-(methoxymethoxy)-3,5-dimethylbenzaldehyde (0.925 g, 3.16 mmol, 63% yield).

To a solution of 2-(1,3-dioxolan-2-yl)ethyltriphenylphosphonium bromide (2.32 g, 5.25 mmol) in THF (17.5 mL) was added *n*BuLi (3.28 mL, 5.25 mmol, 1.6 *M* in hexane) dropwise at 0 ºC. After stirring for 1 h at 0 ºC, to the resulting mixture was added aldehyde (0.925 g, 3.16 mmol) in THF (17.5 mL) dropwise at 0 ºC. After stirring for 14 h, the resulting mixture was quenched by saturated aqueous NH_4Cl (10 mL). The aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 10:1) to give 2-(3-(1-(methoxymethoxy)-4-phenylnaphthalen-2-yl)allyl)-1,3-dioxolane (1.20 g, 3.16 mmol, >99% yield).

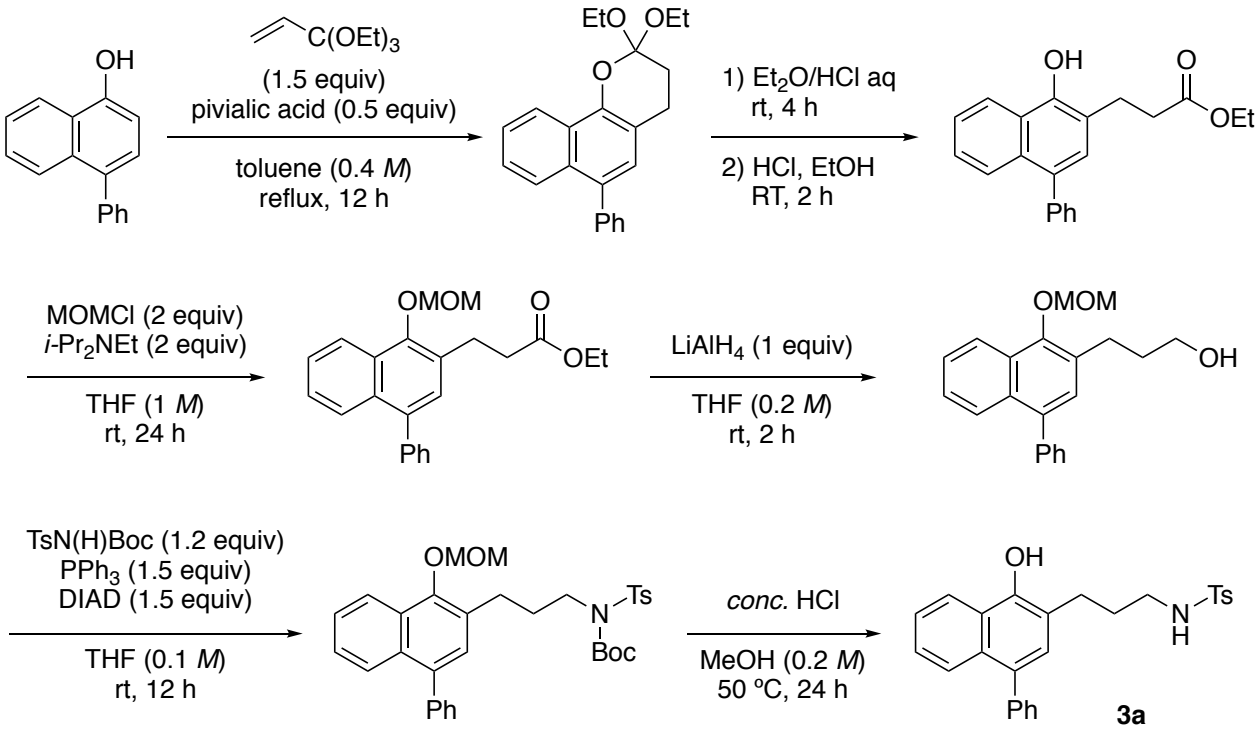
To a solution of this olefin (1.20 g, 3.16 mmol) in THF (15.8 mL) was added 10% Pd/C (0.120 g). The flask containing the mixture was then evacuated and purged with H_2 three times. In an H_2 gas environment, the resulting mixture was stirred at room temperature for 4 h. Upon the completion of the reaction, the mixture was filtered through celite with EtOAc and the crude product was obtained after removal of the solvent *in vacuo*.

Without further purification, to a solution of this acetal in dioxane (15.8 mL) was added *conc.* HCl aq. (ca. 0.100 mL). After stirring for 2 h at 50 ºC, the reaction mixture was cooled to room temperature, and to the mixture was added water (20 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*.

Without further purification, to a solution of this aldehyde in THF (15.8 mL) was added $NaBH_4$ (0.182 g, 4.80 mmol) at 0 ºC. After stirring for 12 h at room temperature, to the mixture was added water (10 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 4:1) to give **1m** (0.687g, 2.35 mmol, 74% yield, 3 steps).

2-(4-Hydroxybutyl)-4-phenylnaphthalen-1-ol (1m): White solid; **TLC**, R_f = 0.28 (hexane–EtOAc = 1:1); **IR** (KBr) 3500, 2948, 1578, 1415, 1226, 1067, 955, 701 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.62–1.68 (m, 2H), 1.79 (brs, 1H), 1.86–1.93 (m, 2H), 2.91–2.95 (m, 2H), 3.88–3.91 (m, 2H), 7.11 (s, 1H), 7.19 (s, 1H), 7.37–7.40 (m, 2H), 7.44–7.50 (m, 5H), 7.85 (d, *J* = 8.2 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** (C_6D_6, 100 MHz) δ 28.8, 29.1, 29.6, 64.2, 120.7, 122.9, 125.4, 126.0, 126.2, 126.4, 127.0, 128.6, 130.1, 130.8, 132.3, 133.0, 141.8, 149.9; **HRMS** (EI) *m*/*z* calcd for $[C_{20}H_{20}O_2]^+$ 292.1463, found 292.1458.

Synthesis of 3a:



To a solution of 4-phenylnaphthalen-1-ol[8] (0.770 g, 3.50 mmol) and 3,3,3-triethoxyprop-1-ene[9] (0.653 mL, 5.25 mmol) in toluene (9.00 ml) was added pivalic acid (0.179 g, 1.75 mmol) at room temperature. After stirring for 12 h at 130 °C, the resulting mixture was poured into 2 *M* NaOH (10 mL), and the aqueous layers were extracted with Et_2O (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then solvents were removed *in vacuo*.

Without further purification, to a solution of this acetal in Et_2O (15.0 mL) was added 1 *M* HCl *aq.* (15.0 mL) at room temperature. After stirring for 4 h at room temperature, the resulting mixture was

poured into H_2O (10 mL) and the aqueous layers were extracted with Et_2O (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then solvents were removed *in vacuo*. To a solution of this residue in EtOH (10.0 mL) was added *conc.* HCl aq. (15.0 mL) at room temperature. After stirring for 2 h at 50 ºC, the resulting mixture was poured into H_2O (10 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then solvents were removed *in vacuo*.

Without further purification, to a solution of this phenol in THF (3.50 mL) was added diisopropylamine (1.22 mL, 7.00 mmol) and chloromethyl methyl ether (0.532 mL, 7.00 mmol) at 0 ºC. After stirring for 24 h at room temperature, resulting mixture was poured into H_2O (20 mL), and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*.

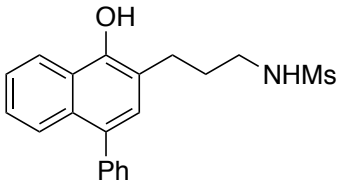
Without further purification, to a solution of this ether in THF (7.00 mL) was added $LiAlH_4$ (0.154 g, 3.50 mmol) at 0 ºC. After stirring for 3 h at room temperature, resulting mixture was cooled at 0 ºC and sequentially quenched by saturated aqueous Rochelle salt (15 mL). After stirring for 30 min at room temperature, the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*.

To a solution of this alcohol, *N*-(*tert*-butoxycarbonyl)-*para*-toluenesulfonamide (1.14 g, 4.20 mmol) and PPh_3 (1.38 g, 5.25 mmol) in THF (35.0 mL) was added diisopropyl azodicarboxylate (2.78 mL, 5.25 mmol, 1.9 *M* in toluene) dropwise at 0 ºC. After stirring for 12 h at room temperature, resulting mixture was poured into H_2O (20 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 10:1) to give *ter*t-butyl (3-(1-(methoxymethoxy)-4-phenylnaphthalen-2-yl)propyl)(tosyl)carbamate (1.37 g, 2.38 mmol, 68% yield, 5 steps).

To a solution of this amide (1.37 g, 2.38 mmol) in MeOH (11.9 mL) was added *conc.* HCl aq. (ca. 0.100 mL). After stirring for 24 h at 50 ºC, the reaction mixture was cooled to room temperature, and to the mixture was added water (20 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 2:1) to give **3a** (0.772 g, 1.79 mmol, 75% yield).

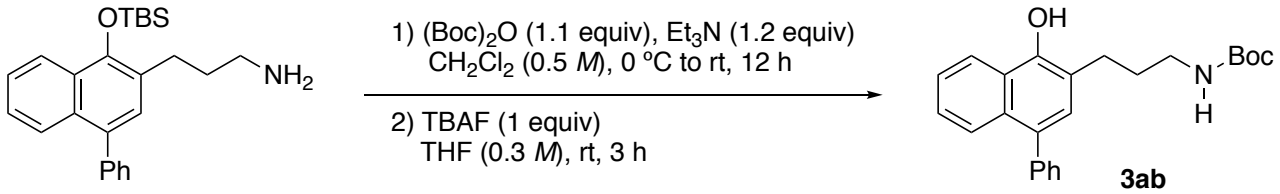
***N*-(3-(1-Hydroxy-4-phenylnaphthalen-2-yl)propyl)-4-methylbenzenesulfonamide (3a)**: White solid; **TLC**, R_f = 0.56 (Hexane–EtOAc = 1:1); **IR** (KBr) 3465, 3262, 1392, 1321, 1159, 1139, 1091, 763, 705 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.8–1.93 (m, 2H), 2.38 (s, 3H), 2.88 (t, *J* = 7.3 Hz, 2H),

2.97 (q, J = 6.1 Hz, 2H), 4.85 (s, 1H), 5.82 (s, 1H), 7.11 (s, 1H), 7.25 (d, J = 7.8 Hz, 3H), 7.38–7.52 (m, 7H), 7.74 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 8.7 Hz, 1H), 8.15 (d, J = 8.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 26.2, 29.7, 42.2, 120.1, 121.2, 124.9, 125.3, 125.7, 126.0, 126.9, 127.1, 128.2, 129.1, 129.7, 130.2, 131.3, 133.2, 136.2, 140.6, 143.6, 148.0; **HRMS** (FAB) m/z calcd for $[C_{26}H_{25}NO_3S]^+$ 431.1555, found 431.1562.



***N*-(3-(1-Hydroxy-4-phenylnaphthalen-2-yl)propyl)methanesulfonamide (3aa)**:[1] White solid; **TLC**, R_f = 0.44 (hexane–EtOAc = 1:2); **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 1.81 (quin, J = 7.3 Hz, 2H), 2.81–2.85 (m, 2H), 2.88 (s, 3H), 2.99–3.03 (m, 2H), 7.01 (brs, 1H), 7.22 (s, 1H), 7.38–7.52 (m, 7H), 7.74 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 8.2 Hz, 1H), 9.20 (brs, 1H); **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 27.0, 30.3, 39.3, 42.4, 121.8, 122.4, 124.8, 125.0, 125.5, 125.6, 126.9, 128.4, 129.8, 130.0, 130.6, 131.0, 140.4, 149.1.

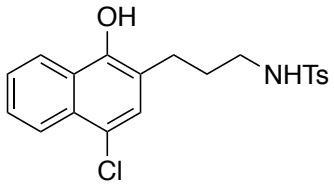
Synthesis of 3ab:



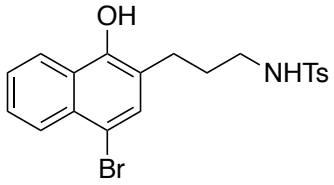
To a solution of 3-(1-((*tert*-butyldimethylsilyl)oxy)-4-phenylnaphthalen-2-yl)propan-1-amine[1] (0.392 g, 1.00 mmol) in CH_2Cl_2 (2.00 mL) were added triethylamine (0.167 mL, 1.20 mmol) and $(Boc)_2O$ (0.240 mL, 1.10 mmol) at 0 ºC. The reaction mixture was allowed to warm to room temperature. After stirring for 12 h, the resulting mixture was quenched by saturated aqueous NH_4Cl (10 mL). The aqueous layers were extracted with CH_2Cl_2 (twice) and the organic layers were washed with brine. The combined organic layers were dried over anhydrous Na_2SO_4, then he solvents were removed in *vacuo*. Without further purification, to a solution of this residue in THF (3.00 mL) was added TBAF (1.00 mL, 1.00 mmol, 1 *M* in THF) at room temperature. After stirring for 3 h, the resulting mixture was poured into H_2O (10 mL). The aqueous layers were extracted with EtOAc (twice) and the organic layers were washed with brine. The combined organic layers were dried over anhydrous $MgSO_4$. The solvents were removed in *vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1) to give **3ab** (0.347 g, 0.920 mmol, 92% yield).

***tert*-Butyl (3-(1-hydroxy-4-phenylnaphthalen-2-yl)propyl)carbamate (3ab)**: White solid; **TLC**, R_f = 0.66 (Hexane–EtOAc = 1:1); **IR** (neat) 3414, 2976, 1684, 1510, 1392, 1367, 1163, 757 cm^{-1}; **^{1}H**

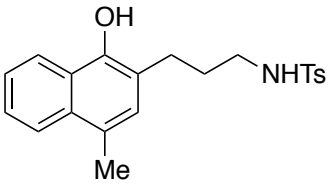
NMR ($CDCl_3$, 400 MHz) δ 1.50 (s, 9H), 1.88–1.94 (m, 2H), 2.87 (t, *J* = 6.6 Hz, 2H), 3.17 (q, *J* = 6.0 Hz, 2H), 4.86 (brs, 1H), 7.16 (d, *J* = 1.4 Hz, 1H), 7.37–7.50 (m, 7H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.97 (brs, 1H), 8.37 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.7, 28.4, 32.7, 39.3, 80.1, 120.4, 120.5, 122.4, 125.0, 125.6, 125.7, 126.7, 128.1, 129.6, 130.2, 131.3, 132.6, 140.9, 149.0, 157.5; **HRMS** (FAB) m/z calcd for $[C_{24}H_{27}NO_3]^+$ 377.1991, found 377.1987.



***N*-(3-(4-Chloro-1-hydroxynaphthalen-2-yl)propyl)-4-methylbenzenesulfonamide (3b)**: This compound was synthesized from 4-chloronaphthalen-1-ol as in **3a** in 43% yield (6 steps, 0.538 g, 1.38 mmol). Pale yellow solid; **TLC**, R_f = 0.51 (Hexane–EtOAc = 1:1); **IR** (KBr) 3447, 3278, 1595, 1449, 1314, 1264, 1243, 1153, 1139, 758, 673 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.82–1.89 (m, 2H), 2.39 (s, 3H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.94 (q, *J* = 6.3 Hz, 2H), 5.10 (t, *J* = 6.0 Hz, 1H), 6.12 (s, 1H), 7.23–7.27 (m, 3H), 7.50–7.58 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 8.12–8.16 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 26.0, 29.5, 42.1, 121.0, 121.7, 123.3, 124.3, 126.0, 126.1, 126.6, 127.1, 127.7, 129.8, 130.2, 136.0, 143.8, 147.8.; **HRMS** (FAB) m/z calcd for $[C_{20}H_{20}{}^{35}ClNO_3S]^+$/$[C_{20}H_{20}{}^{37}ClNO_3S]^+$ 389.0852/391.0823, found 389.0837/391.0836.

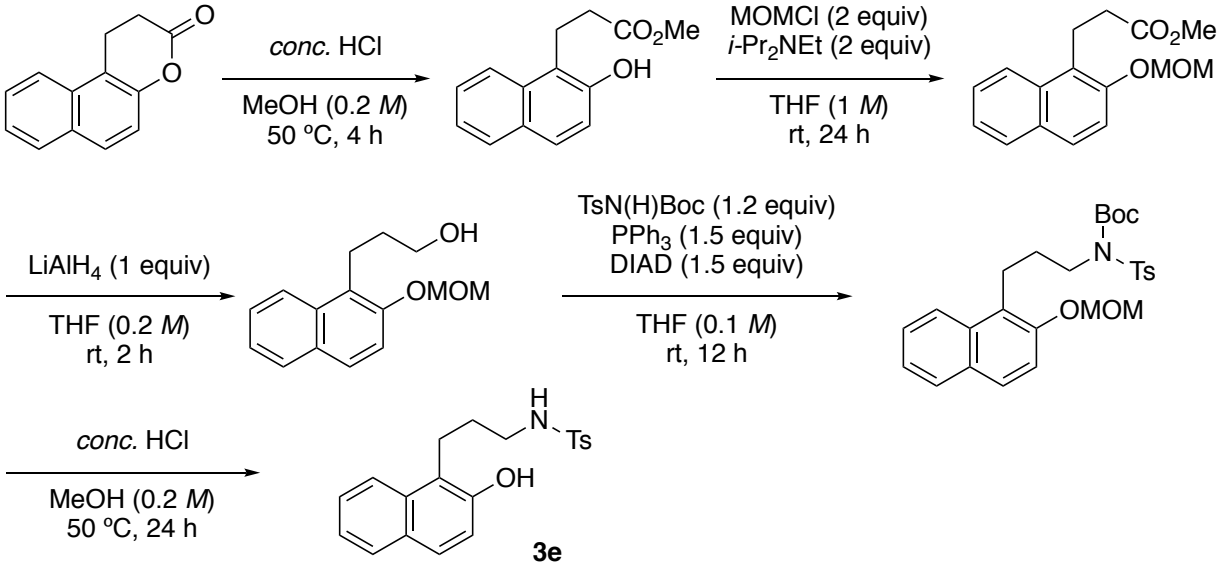


***N*-(3-(4-Bromo-1-hydroxynaphthalen-2-yl)propyl)-4-methylbenzenesulfonamide (3c)**: This compound was synthesized from 4-bromonaphthalen-1-ol as in **3a** in 40% yield (6 steps, 0.256 g, 0.598 mmol). Orange solid; **TLC**, R_f = 0.51 (Hexane–EtOAc = 1:1); **IR** (KBr)3477, 3267, 1595, 1447, 1376, 1319, 1151, 1030, 907, 755, 668 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.84–1.91 (m, 2H), 2.41 (s, 3H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.95 (q, *J* = 6.3 Hz, 2H), 4.81 (t, *J* = 6.0 Hz, 1H), 5.99 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.46 (s, 1H), 7.51–7.59 (m, 2H), 7.73–7.75 (m, 2H), 8.11–8.15 (m, 2H); **^{13}C NMR** (CD_2Cl_2, 100 MHz) δ 21.6, 26.4, 30.0, 42.7, 113.5, 122.1, 122.3, 126.5, 126.6, 127.2, 127.4, 127.4, 130.2, 131.7, 131.9, 136.4, 144.4, 149.0; **HRMS** (FAB) m/z calcd for $[C_{20}H_{20}{}^{79}BrNO_3S+H]^+$/$[C_{20}H_{20}{}^{81}BrNO_3S+H]^+$ 434.0426/436.0405, found 434.0412/436.0413.



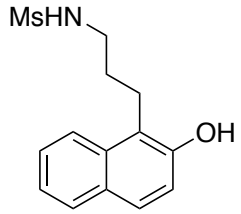
***N*-(3-(1-Hydroxy-4-methylnaphthalen-2-yl)propyl)-4-methylbenzenesulfonamide (3d)**: This compound was synthesized from 4-chloronaphthalen-1-ol as in **3a** in 47% yield (6 steps, 0.733 g, 1.98 mmol). Pale yellow solid; **TLC**, R_f = 0.58 (Hexane–EtOAc = 1:1); **IR** (KBr) 3485, 3281, 2923, 1582, 1442, 1315, 1140, 1075, 762, 673 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.82–1.88 (m, 2H), 2.39 (s, 3H), 2.56 (s, 3H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.92 (q, *J* = 6.3 Hz, 2H), 4.98 (s, 1H), 5.61 (s, 1H), 6.98 (s, 1H), 7.25 (d, *J* = 9.2 Hz, 2H), 7.47–7.52 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.87–7.91 (m, 1H), 8.06–8.10 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 18.7, 21.5, 26.0, 29.7, 42.1, 120.2, 121.4, 124.2, 125.0, 125.1, 125.3, 126.7, 127.1, 128.5, 129.7, 132.1, 136.3, 143.5, 146.8.; **HRMS** (FAB) m/z calcd for $[C_{21}H_{23}NO_3S]^+$ 369.1399, found 369.1391.

Synthesis of 3e:

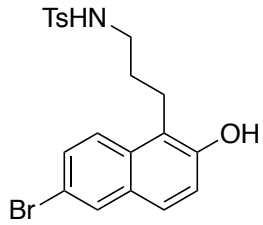


To a solution of 1,2-dihydro-3*H*-benzo[*f*]chromen-3-one[6] (0.793 g, 4.00 mmol) in MeOH (20.0 mL) was added *conc.* HCl aq. (ca. 0.100 mL). After stirring for 4 h at 50 ºC, the reaction mixture was cooled to room temperature, and to the mixture was added water (20 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo* to give methyl 3-(2-hydroxynaphthalen-1-yl)propanoate. **3e** was synthesized from this compound as in **3a** in 66% yield (4 steps, 0.941 g, 2.64 mmol).

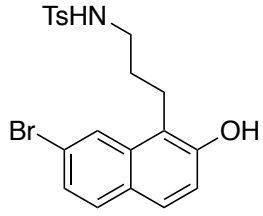
***N*-(3-(2-Hydroxynaphthalen-1-yl)propyl)-4-methylbenzenesulfonamide (3e)**: White solid; **TLC**, R_f = 0.51 (Hexane–EtOAc = 1:1); **IR** (KBr) 3388, 3238, 1439, 1316, 1287, 1154, 1088, 814 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.83–1.89 (m, 2H), 2.38 (s, 3H), 2.89 (q, *J* = 6.3 Hz, 2H), 3.11 (t, *J* = 6.9 Hz, 2H), 5.61 (s, 1H), 6.20 (s, 1H), 7.06 (d, *J* = 9.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.42–7.46 (m, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.72–7.80 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.7, 21.4, 28.2, 41.8, 117.6, 117.9, 122.7, 123.0, 126.3, 127.0, 128.0, 128.6, 129.4, 129.7, 133.0, 136.5, 143.4, 150.8.; **HRMS** (FAB) m/z calcd for $[C_{20}H_{21}NO_3S+H]^+$ 356.1320, found 356.1311.



***N*-(3-(2-Hydroxynaphthalen-1-yl)propyl)methanesulfonamide (3ea)**:[10] White solid; **TLC**, R_f = 0.48 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.99–2.05 (m, 2H), 2.94 (s, 3H), 3.08 (q, *J* = 6.3 Hz, 2H), 3.21 (t, *J* = 6.9 Hz, 2H), 5.49 (t, *J* = 6.2 Hz, 1H), 6.45 (s, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.47–7.51 (m, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.8, 29.0, 40.1, 41.9, 117.5, 118.0, 122.7, 123.2, 126.6, 128.2, 128.7, 129.5, 133.1, 150.8.

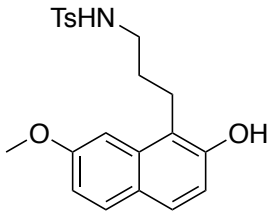


***N*-(3-(6-Bromo-2-hydroxynaphthalen-1-yl)propyl)-4-methylbenzenesulfonamide (3f)**: This compound was synthesized from 8-bromo-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one[6] as in **3e** in 53% yield (5 steps, 0.619 g, 1.42 mmol). White solid; **TLC**, R_f = 0.27 (Hexane–EtOAc = 1:1); **IR** (KBr) 3439, 3285, 1499, 1431, 1318, 1282, 1154, 812 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.79–1.85 (m, 2H), 2.39 (s, 3H), 2.90 (q, *J* = 6.3 Hz, 2H), 3.08 (q, *J* = 7.0 Hz, 2H), 5.55 (t, *J* = 6.4 Hz, 1H), 6.41 (s, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.46–7.51 (m, 2H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.70–7.74 (m, 2H), 7.89 (d, *J* = 2.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.8, 21.5, 28.4, 41.9, 116.8, 118.5, 118.7, 124.6, 127.0, 127.1, 129.6, 129.7, 130.5, 130.6, 131.6, 136.5, 143.6, 151.0.; **HRMS** (FAB) m/z calcd for $[C_{20}H_{20}{}^{79}BrNO_3S+H]^+$/$[C_{20}H_{20}{}^{81}BrNO_3S+H]^+$ 434.0426/436.0405, found 434.0418/436.0389.



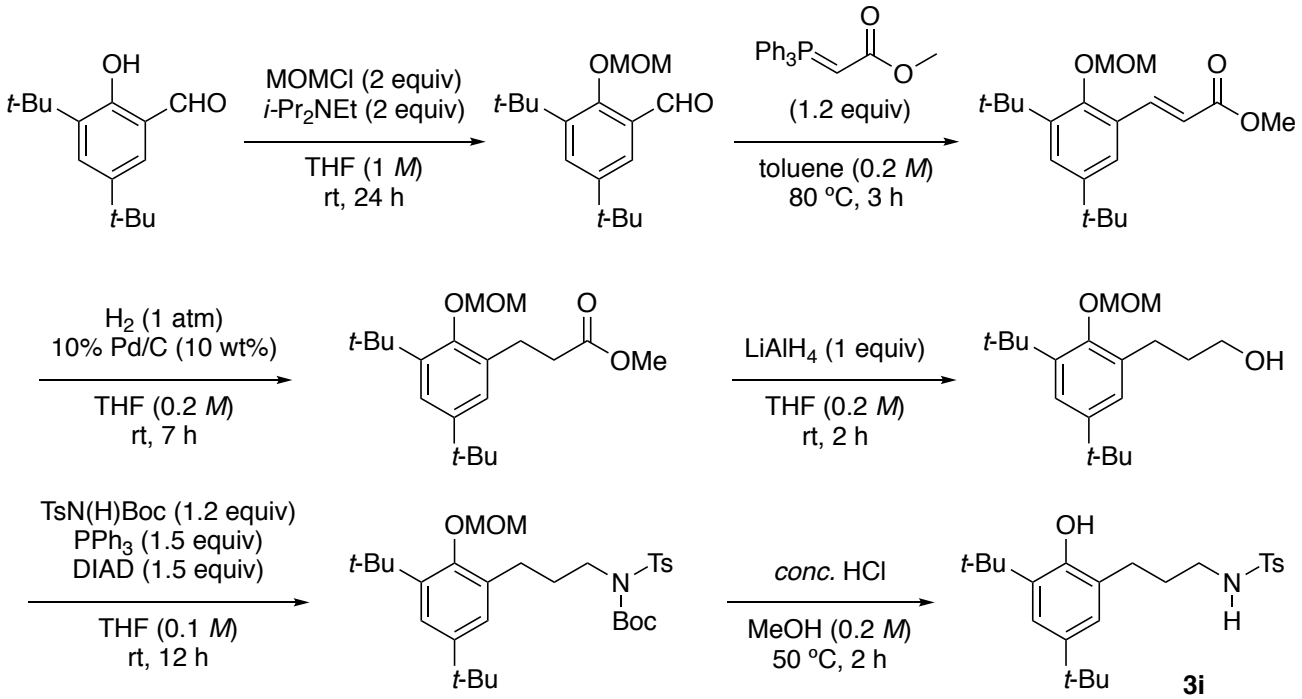
***N*-(3-(7-Bromo-2-hydroxynaphthalen-1-yl)propyl)-4-methylbenzenesulfonamide (3g)**: This compound was synthesized from 9-bromo-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one[6] as in **3e** in 43% yield (5 steps, 0.564 g, 1.30 mmol). White solid; **TLC**, R_f = 0.48 (Hexane–EtOAc = 1:1); **IR** (KBr) 3419, 3307, 1626, 1501, 1320, 1262, 1152, 1080, 830 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.79–1.86 (m, 2H), 2.39 (s, 3H), 2.91 (q, *J* = 6.3 Hz, 2H), 3.04 (t, *J* = 6.9 Hz, 2H), 5.64 (t, *J* = 6.4 Hz, 1H), 6.65 (s, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 7.24 (s, 1H), 7.38 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.55 (d, J = 8.7 Hz, 1H),

7.60 (d, J = 8.7 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 1.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.8, 21.5, 28.3, 41.9, 117.5, 118.0, 121.1, 125.0, 126.5, 127.0, 127.8, 128.0, 129.8, 130.3, 134.4, 136.5, 143.6, 151.6; **HRMS** (FAB) m/z calcd for $[C_{20}H_{20}{}^{79}BrNO_3S+H]^+$/$[C_{20}H_{20}{}^{81}BrNO_3S+H]^+$ 434.0426/436.0405, found 434.0431/436.0407.



***N*-(3-(2-Hydroxy-7-methoxynaphthalen-1-yl)propyl)-4-methylbenzenesulfonamide (3h)**: This compound was synthesized from 9-methoxy-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one[6] as in **3e** in 40% yield (5 steps, 0.381 g, 0.989 mmol). Pale yellow solid; **TLC**, R_f = 0.57 (Hexane–EtOAc = 1:1); **IR** (KBr) 3398, 3349, 1628, 1514, 1291, 1221, 1146, 828, 659 cm^{-1}; **^{1}H NMR** (CD_3CN, 500 MHz) δ 1.69–1.75 (m, 2H), 2.38 (s, 3H), 2.87 (q, J = 6.8 Hz, 2H), 2.96 (t, J = 7.5 Hz, 2H), 3.88 (s, 3H), 5.59 (t, J = 6.1 Hz, 1H), 6.93–6.97 (m, 2H), 7.00 (s, 1H), 7.13–7.14 (m, 1H), 7.29–7.32 (m, 2H), 7.54 (d, J = 8.9 Hz, 1H), 7.61–7.64 (m, 2H), 7.67 (d, J = 9.2 Hz, 1H); **^{13}C NMR** (CD_3CN, 125 MHz) δ 21.5, 22.4, 29.7, 43.8, 55.9, 102.7, 115.9, 115.9, 119.0, 125.4, 127.8, 128.3, 130.6, 131.0, 135.5, 138.3, 144.3, 153.1, 159.3; **HRMS** (FAB) m/z calcd for $[C_{21}H_{23}NO_4S+H]^+$ 386.1426, found 386.1419.

Synthesis of 3i:



To a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.17 g, 5.00 mmol) in THF (5.00 mL) were added diisopropylamine (1.74 mL, 10.0 mmol) and chloromethyl methyl ether (0.759 mL, 10.0 mmol) at 0 ºC. After stirring for 24 h at room temperature, resulting mixture was poured into H_2O (20

mL), and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*.

Without further purification, to a solution of this aldehyde in toluene (25.0 mL) was added methyl(triphenylphosphoranylidene)acetate (2.01g, 6.00 mmol) at room temperature. After stirring for 3 h at 80 ºC, the resulting mixture was cooled to room temperature and diluted with water and EtOAc. The aqueous layers were separated and extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1) to give methyl (*E*)-3-(3,5-di-*tert*-butyl-2-(methoxymethoxy)phenyl)acrylate (1.66 g, 5.00 mmol, >99% yield).

To a solution of this olefin (1.66 g, 5.00 mmol) in THF (25.0 mL) was added 10% Pd/C (0.166 g). The flask containing the mixture was then evacuated and purged with H_2 three times. In an H_2 gas environment, the resulting mixture was stirred at room temperature for 7 h. Upon the completion of the reaction, the mixture was filtered through celite with EtOAc and the crude product was obtained after removal of the solvent *in vacuo*.

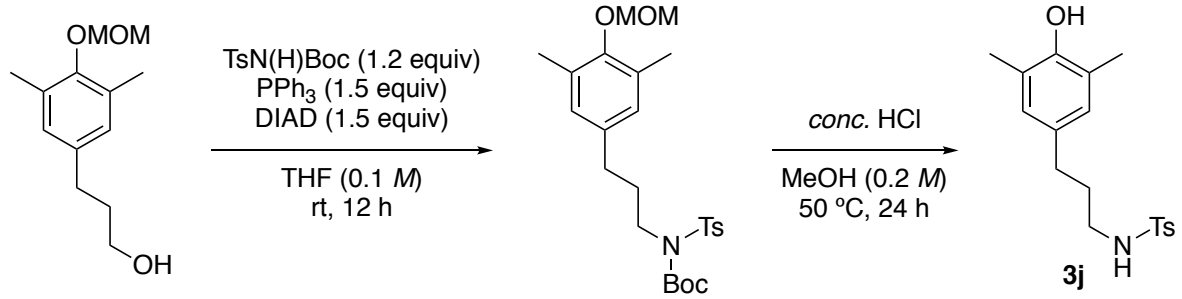
Without further purification, to a solution of this ester in THF (25.0 mL) was added $LiAlH_4$ (0.190 g, 5.00 mmol) at 0 ºC. After stirring for 3 h at room temperature, resulting mixture was cooled at 0 ºC and sequentially quenched by saturated aqueous Rochelle salt (15 mL). After stirring for 30 min at room temperature, the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*.

Without further purification, to a solution of this alcohol, *N*-(*tert*-Butoxycarbonyl)-*para*-toluenesulfonamide (1.67 g, 6.00 mmol) and PPh_3 (1.97 g, 7.50 mmol) in THF (50.0 mL) was added diisopropyl azodicarboxylate (3.94 mL, 7.50 mmol, 1.9 *M* in toluene) dropwise at 0 ºC. After stirring for 12 h at room temperature, resulting mixture was poured into H_2O (30 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 10:1) to give *N*-(3-(3,5-di-tert-butyl-2-hydroxyphenyl)propyl)-4-methylbenzenesulfonamide (2.51 g, 4.47 mmol, 89% yield, 3 steps).

To a solution of this amide (2.51 g, 4.47 mmol) in MeOH (22.4 mL) was added *conc.* HCl aq. (ca. 0.100 mL). After stirring for 24 h at 50 ºC, the reaction mixture was cooled to room temperature, and to the mixture was added water (20 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 2:1) to give **3i** (1.44 g, 3.44 mmol, 79% yield).

***N*-(3-(3,5-Di-tert-butyl-2-hydroxyphenyl)propyl)-4-methylbenzenesulfonamide (3i)**: White solid; **TLC**, R_f = 0.76 (Hexane–EtOAc = 1:1); **IR** (KBr) 3529, 3308, 2957, 2866, 1597, 1480, 1288, 1148, 813, 665 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.26 (s, 9H), 1.40 (s, 9H), 1.75–1.82 (m, 2H), 2.42 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.98 (q, *J* = 6.0 Hz, 2H), 4.82–4.94 (m, 2H), 6.92 (d, *J* = 2.5 Hz, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 27.2, 29.8, 30.0, 31.6, 34.2, 34.6, 42.6, 122.1, 124.7, 126.5, 127.1, 129.7, 135.2, 136.6, 142.5, 143.5, 149.9.; **HRMS** (FAB) m/z calcd for $[C_{24}H_{35}NO_3S]^+$ 417.2338, found 417.2342.

Synthesis of 3j:



To a solution of 3-(4-(methoxymethoxy)-3,5-dimethylphenyl)propan-1-ol (0.561 g, 2.50 mmol), *N*-(*tert*-Butoxycarbonyl)-*para*-toluenesulfonamide (0.814 g, 3.00 mmol) and PPh_3 (0.983 g, 3.75 mmol) in THF (25.0 mL) was added diisopropyl azodicarboxylate (1.97 mL, 3.75 mmol, 1.9 *M* in toluene) dropwise at 0 ºC. After stirring for 12 h at room temperature, resulting mixture was poured into H_2O (30 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 10:1) to give *tert*-butyl (3-(4-(methoxymethoxy)-3,5-dimethylphenyl)propyl)(tosyl)carbamate (1.19 g, 2.50 mmol, >99%).

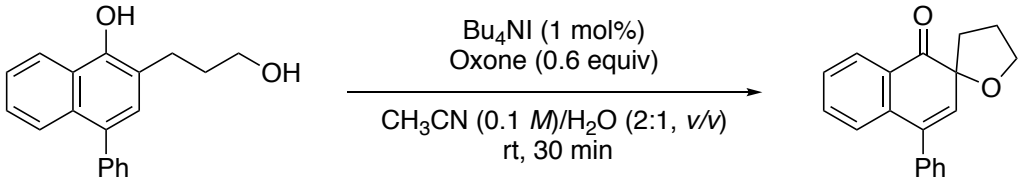
To a solution of this amide (1.19 g, 2.50 mmol) in MeOH (12.5 mL) was added *conc.* HCl aq. (ca. 0.100 mL). After stirring for 24 h at 50 ºC, the reaction mixture was cooled to room temperature, and to the mixture was added water (20 mL) and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane-EtOAc = 2:1) to give **3j** (0.653 g, 1.95 mmol, 78% yield).

***N*-(3-(4-Hydroxy-3,5-dimethylphenyl)propyl)-4-methylbenzenesulfonamide (3j)**: White solid; **TLC**, R_f = 0.64 (Hexane–EtOAc = 1:1); **IR** (KBr) 3467, 3260, 2924, 1598, 1487, 1427, 1315, 1208, 1149, 1093, 815, 690 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.68–1.75 (m, 2H), 2.19 (s, 6H), 2.43–2.48 (m, 2H), 2.43 (s, 3H), 2.95 (q, *J* = 6.7 Hz, 2H), 4.35 (brs, 1H), 4.50 (s, 1H), 6.69 (s, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 15.9, 21.5, 31.3, 31.8, 42.6, 76.7,

77.0, 77.3, 122.9, 127.1, 128.4, 129.6, 132.3, 136.8, 143.3, 150.4.; **HRMS** (FAB) m/z calcd for $[C_{18}H_{23}NO_3S+H]^+$ 334.1477, found 334.1469.

Procedures for Oxidation and Characterization of Products

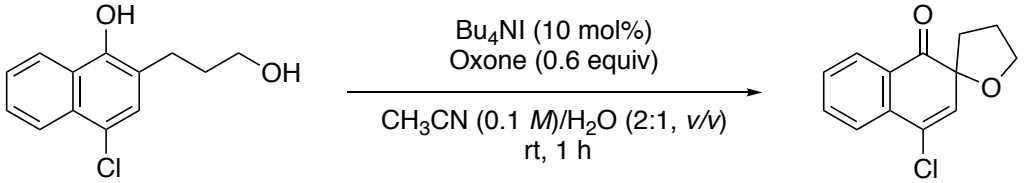
Representative Procedures for Oxidative Dearomative Spiroetherification of Arenols 1



1a **2a** (90%)

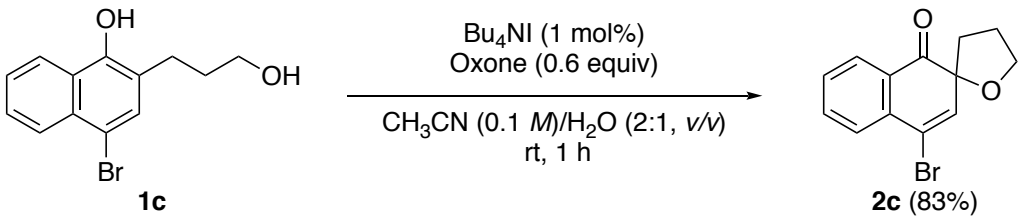
To a solution of **1a** (0.278 g, 1.00 mmol) and Bu_4NI (0.00369 g, 0.0100 mmol, 1 mol%) in CH_3CN (10.0 mL) and H_2O (5.00 mL) was added oxone (0.368 g, 0.600 mmol) at room temperature. The reaction was monitored by TLC analysis. After stirring for 30 min, the reaction was quenched by saturated aqueous $Na_2S_2O_3$ (10 mL) at 0 °C. The aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1) to give **2a** (0.252 g, 0.913 mmol) in 91% yield.

4'-Phenyl-4,5-dihydro-1'*H*,3*H*-spiro[furan-2,2'-naphthalen]-1'-one (2a):[1] White solid; **TLC**, R_f = 0.36 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.97–2.12 (m, 2H), 2.20–2.37 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 1H), 4.30–4.35 (m, 1H), 6.11 (s, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.34–7.50 (m, 7H), 8.04 (dd, *J* = 7.6, 1.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.3, 36.6, 70.4, 84.3, 126.6, 127.4, 127.8, 128.0, 128.4, 128.8, 129.1, 134.2, 135.0, 137.4, 137.7, 138.5, 201.5.



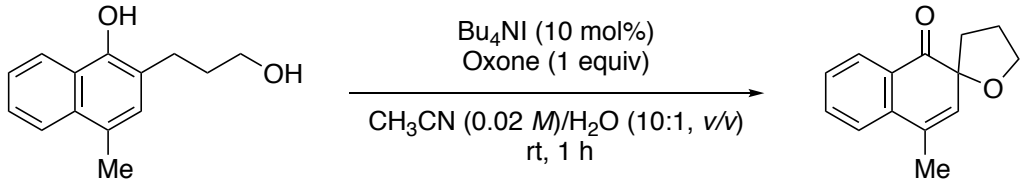
1b **2b** (71%)

4'-Chloro-4,5-dihydro-1'*H*,3*H*-spiro[furan-2,2'-naphthalen]-1'-one (2b):[2] 0.0166 g, 0.0701 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). Pale yellow solid; **TLC**, R_f = 0.46 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.93–2.10 (m, 2H), 2.19–2.30 (m, 2H), 4.12–4.18 (m, 1H), 4.26–4.31 (m, 1H), 6.36 (s, 1H), 7.45 (td, *J* = 7.4, 1.3 Hz, 1H), 7.65–7.72 (m, 2H), 8.01 (dd, *J* = 7.4, 1.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.3, 36.5, 70.6, 84.6, 125.4, 127.4, 128.8, 129.1, 129.2, 133.3, 134.8, 134.9, 199.5.



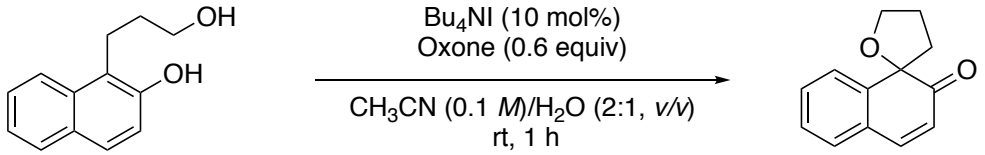
1c **2c** (83%)

4'-Bromo-4,5-dihydro-1'*H*,3*H*-spiro[furan-2,2'-naphthalen]-1'-one (2c):[2] 0.0231 g, 0.0827 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). Brwon oil; **TLC**, R_f = 0.45 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.94–2.12 (m, 2H), 2.18–2.29 (m, 2H), 4.12–4.18 (m, 1H), 4.26–4.31 (m, 1H), 6.63 (s, 1H), 7.41–7.45 (m, 1H), 7.64–7.69 (m, 2H), 7.98 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.2, 36.3, 70.6, 85.5, 119.7, 127.3, 128.1, 128.8, 129.2, 134.8, 135.5, 137.7, 199.6.



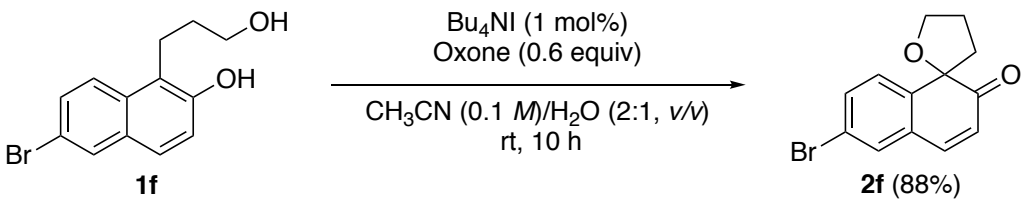
1d **2d** (78%)

4'-Methyl-4,5-dihydro-1'*H*,3*H*-spiro[furan-2,2'-naphthalen]-1'-one (2d):[2] 0.0167 g, 0.0780 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). Pale yellow oil; **TLC**, R_f = 0.35 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.84–1.93 (m, 1H), 1.99–2.08 (m, 1H), 2.13 (d, *J* = 1.2 Hz, 3H), 2.18–2.27 (m, 2H), 4.11–4.17 (m, 1H), 4.25–4.31 (m, 1H), 5.99 (d, *J* = 1.2 Hz, 1H), 7.32-7.37 (m, 2H), 7.60 (td, *J* = 7.8, 1.4 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.2, 25.3, 36.3, 70.3, 83.9, 124.2, 127.2, 127.8, 128.9, 130.5, 133.1, 134.5, 138.4, 201.9.



1e **2e** (95%)

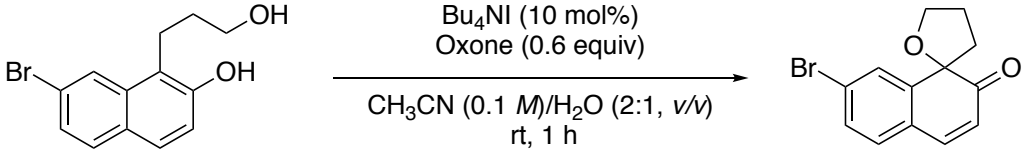
4,5-Dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalen]-2'-one (2e):[3] 0.0191 g, 0.0950 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). Yellow oil; **TLC**, R_f = 0.58 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.84–1.91 (m, 1H), 2.03–2.22 (m, 2H), 2.41–2.47 (m, 1H), 4.35–4.45 (m, 2H), 6.10 (d, *J* = 10.1 Hz, 1H), 7.26–7.32 (m, 2H), 7.35–7.41 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 24.5, 40.6, 71.9, 87.8, 124.0, 125.3, 127.7, 129.0, 129.6, 130.2, 144.5, 145.4, 203.7.



1f **2f** (88%)

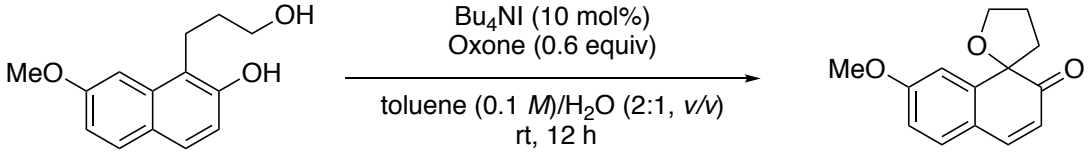
6'-Bromo-4,5-dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalen]-2'-one (2f): 0.0246 g, 0.0881 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent:

hexane–EtOAc = 4:1). Yellow oil; **TLC**, R_f = 0.65 (hexane–EtOAc = 1:1); **IR** (neat) 2952, 1682, 1554, 1479, 1225, 1201, 1064, 816 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1 1.81–1.88 (m, 1H), 2.01–2.21 (m, 2H), 2.40–2.46 (m, 1H), 4.33–4.44 (m, 2H), 6.14 (d, *J* = 10.1 Hz, 1H), 7.28 (d, *J* = 10.1 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.49–7.51 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 24.5, 40.4, 71.9, 87.6, 121.5, 125.2, 127.1, 131.4, 131.5, 132.8, 142.9, 144.1, 202.8; **HRMS** (FAB) m/z calcd for $[C_{13}H_{11}{}^{79}BrO_2+H]^+$/$[C_{13}H_{11}{}^{81}BrO_2+H]^+$ 279.0021/281.0001, found 279.0021/281.0003.



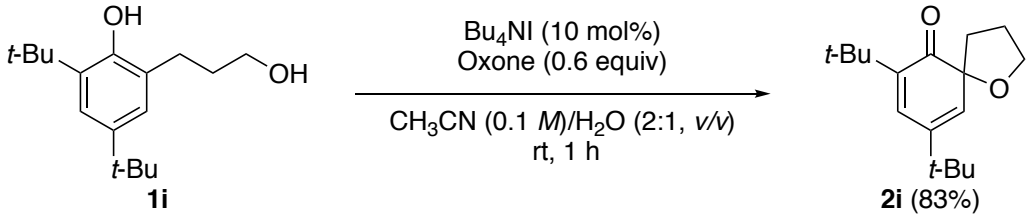
1g **2g** (84%)

7'-Bromo-4,5-dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalen]-2'-one (2g): 0.0234 g, 0.0838 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 4:1). Yellow oil; **TLC**, R_f = 0.65 (hexane–EtOAc = 1:1); **IR** (neat) 2975, 1682, 1584, 1384, 1129, 1078, 1061, 838 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.84–1.91 (m, 1H), 2.03–2.22 (m, 2H), 2.41–2.48 (m, 1H), 4.36–4.45 (m, 2H), 6.12 (d, *J* = 10.1 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 10.1 Hz, 1H), 7.43 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 24.4, 40.5, 72.0, 87.4, 124.3, 125.0, 128.5, 128.6, 130.3, 131.0, 143.4, 147.2, 202.6; **HRMS** (FAB) m/z calcd for $[C_{13}H_{11}{}^{79}BrO_2+H]^+$/$[C_{13}H_{11}{}^{81}BrO_2+H]^+$ 279.0021/281.0001, found 279.0024/281.0005.

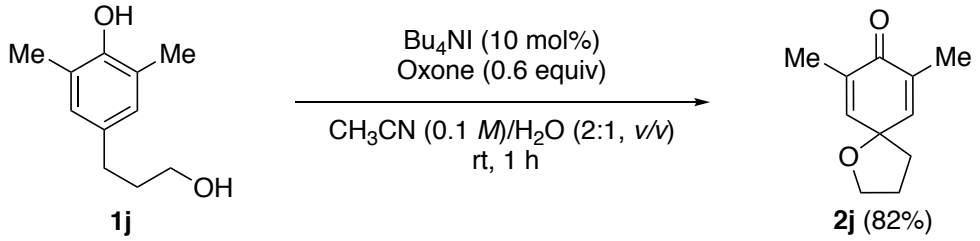


1h **2h** (70%)

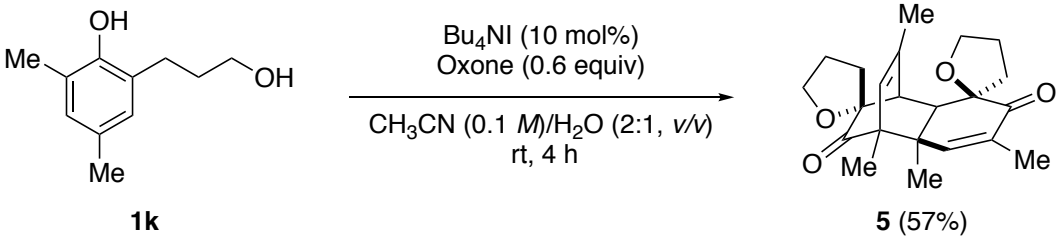
7'-Methoxy-4,5-dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalen]-2'-one (2h): 0.0161 g, 0.0699 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 4:1). Yellow oil; **TLC**, R_f = 0.60 (hexane–EtOAc = 1:1); **IR** (neat) 2950, 1675, 1602, 1321, 1284, 1227, 1061, 833 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.83–1.90 (m, 1H), 2.02–2.21 (m, 2H), 2.40–2.47 (m, 1H), 3.86 (s, 3H), 4.34–4.46 (m, 2H), 5.97 (d, *J* = 9.8 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 9.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 24.4, 40.9, 55.4, 71.9, 88.0, 111.6, 112.6, 121.4, 122.8, 130.8, 144.4, 147.9, 161.5, 203.7; **HRMS** (FAB) m/z calcd for $[C_{14}H_{14}O_3+H]^+$ 231.1021, found 231.1021.



4'-Methyl-4,5-dihydro-1'*H*,3*H*-spiro[furan-2,2'-naphthalen]-1'-one (2i): 0.0218 g, 0.0832 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). Yellow oil; **TLC**, R_f = 0.43 (hexane–EtOAc = 4:1); **IR** (KBr) 2960, 1680, 1459, 1366, 1272, 1030 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.11 (s, 9H), 1.22 (s, 9H), 1.70–1.78 (m, 1H), 1.91–2.01 (m, 1H), 2.05–2.18 (m, 2H), 4.08–4.14 (m, 1H), 4.22–4.27 (m, 1H), 5.96 (d, *J* = 2.7 Hz, 1H), 6.80 (d, *J* = 2.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 24.7, 28.6, 29.2, 34.1, 34.3, 35.7, 70.5, 86.7, 132.0, 134.8, 141.4, 143.4, 204.9; **HRMS** (FAB+) *m/z* calcd for $[C_{17}H_{26}O_2+H]^+$ 263.2011, found 263.2001.

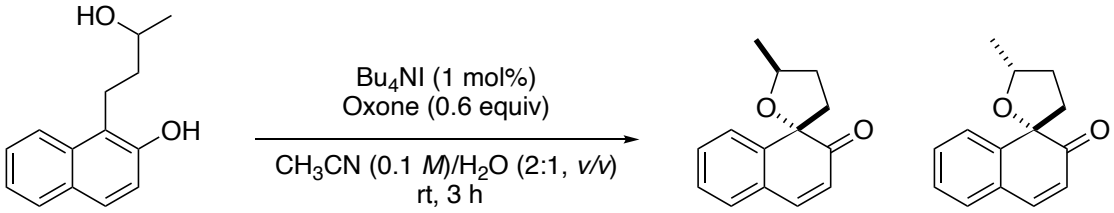


7,9-Dimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (2j): 0.0146 g, 0.0819 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 4:1). Colorless oil; **TLC**, R_f = 0.30 (hexane–EtOAc = 4:1); **IR** (neat) 2952, 1675, 1642, 1447, 1373, 1032. 762 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.87 (s, 6H), 1.99–2.03 (m, 2H), 2.11–2.18 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.56 (s, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 15.8, 26.8, 36.7, 68.8, 77.5, 133.5, 144.7, 186.9; **HRMS** (FAB) m/z calcd for $[C_{11}H_{14}O_2+H]^+$ 179.1072, found 179.1073.



(1'*R,2*R**,4'*R**,4a'*R**,10'*R**)-2',4',4a',6'-Tetramethyl-1',4,4',4a',4'',5,5'',8a'-octahydro-3*H*,3''*H*,7'*H*-dispiro[furan-2,8'-[1,4]ethanonaphthalene-10',2''-furan]-7',9'-dione (5)**: 0.0101 g, 0.0285 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). White solid; **TLC**, R_f = 0.20 (hexane–EtOAc = 1:1); **IR** (neat) 3406, 1722, 1691, 1451, 1375, 1032 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.16 (s, 3H), 1.26 (s, 3H), 1.59–1.66 (m, 1H), 1.78 (d, *J* = 1.5 Hz, 3H), 1.79 (d, *J* = 1.5 Hz, 3H), 1.80–1.98 (m, 6H), 2.05–

2.13 (m, 1H), 2.54 (d, J = 1.5 Hz, 1H), 2.93 (t, J = 2.1 Hz, 1H), 3.93–4.07 (m, 4H), 5.04 (t, J = 1.8 Hz, 1H), 5.94 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 12.5, 16.7, 21.7, 23.9, 24.9, 26.2, 34.8, 39.8, 45.5, 48.6, 49.9, 58.3, 68.6, 69.6, 82.1, 85.7, 128.1, 135.5, 143.4, 145.2, 199.8, 213.1; **HRMS** (FAB) m/z calcd for $[C_{22}H_{28}O_4+H]^+$357.2066, found 358.2063.

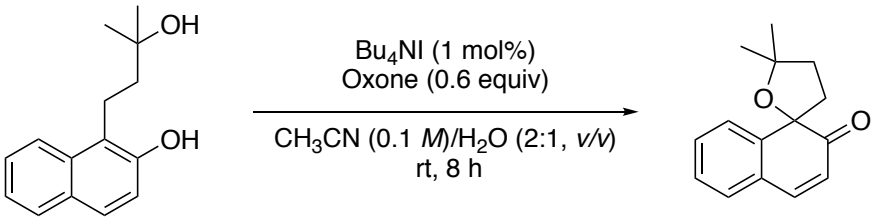


1l **2l** *(major)* **2l** *(minor)*

2l (95%), d.r. 4:1

(2*S,5*S**)-5-Methyl-4,5-dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalen]-2'-one (major) (2l)**:[3] 0.0169 g, 0.0789 mmol. The diastereomer ratio (d.r. 4:1) was determined by crude ^{1}H NMR. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 20:1 to 15:1). Yellow oil; **TLC**, R_f = 0.32 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.49 (d, J = 6.4 Hz, 3H), 1.64–1.73 (m, 1H), 1.89–1.95 (m, 1H), 2.14–2.22 (m, 1H), 2.38–2.45 (m, 1H), 4.66–4.74 (m, 1H), 6.09 (d, J = 10.1 Hz, 1H), 7.26–7.41 (m, 4H), 7.60 (d, J = 7.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.9, 31.9, 40.6, 78.8, 88.1, 124.0, 125.4, 127.7, 129.1, 129.5, 130.1, 144.6, 145.4, 204.2.

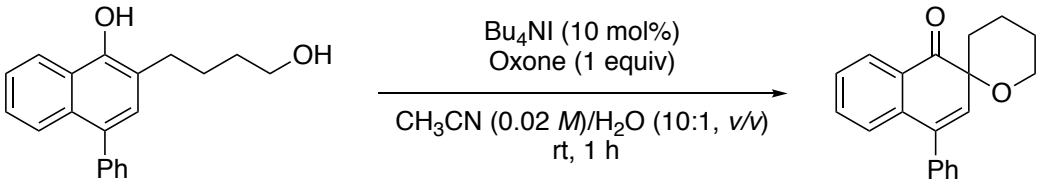
(2*S,5*R**)-5-Methyl-4,5-dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalen]-2'-one (minor)**: 0.00345 g, 0.0161 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 15:1 to 10:1). Yellow oil; **TLC**, R_f = 0.35 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.55 (d, J = 6.1 Hz, 3H), 1.81–1.95 (m, 2H), 2.03–2.08 (m, 1H), 2.47–2.51 (m, 1H), 4.64–4.70 (m, 1H), 6.10 (d, J = 10.1 Hz, 1H), 7.24–7.31 (m, 2H), 7.33 (d, J = 10.1 Hz, 1H), 7.39 (td, J = 7.4, 1.5 Hz, 1H), 7.58–7.59 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 20.8, 31.4, 41.3, 79.8, 88.6, 124.0, 125.4, 127.6, 128.9, 129.6, 130.2, 144.1, 146.1, 202.8.



1m **2m** (83%)

5,5-Dimethyl-4,5-dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalen]-2'-one (2m):[3] 0.0189 g, 0.0827 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 20:1). Yellow oil; **TLC**, R_f = 0.70 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.55 (s, 3H), 1.64 (s, 3H), 1.79–1.86 (m, 1H), 1.96–2.06 (m, 2H), 2.45–2.54 (m, 1H), 6.08 (d, J = 10.1 Hz, 1H), 7.24–7.32 (m, 3H), 7.39 (td, J = 7.5, 1.7 Hz, 1H), 7.66 (d, J = 7.5 Hz,

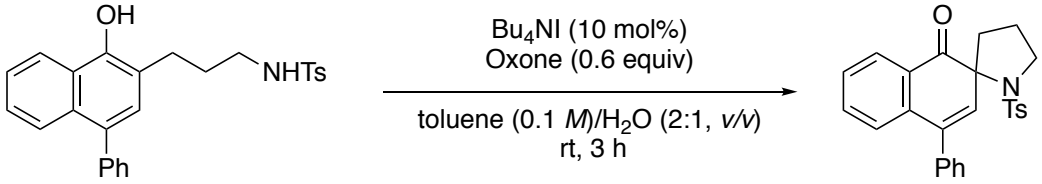
1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 28.0, 28.8, 35.9, 40.1, 84.8, 89.9, 124.1, 125.4, 127.6, 129.0, 129.8, 130.1, 144.0, 145.7, 203.4.



1n **2n** (68%)

4-Phenyl-3',4',5',6'-tetrahydro-1*H*-spiro[naphthalene-2,2'-pyran]-1-one (2n): 0.0197 g, 0.0678 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 15:1). Pale yellow solid; **TLC**, R_f = 0.49 (hexane–EtOAc = 4:1); **IR** (neat) 2935, 1693, 1592, 1443, 1274, 1199, 1078, 775 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.59–2.01 (m, 6H), 3.94–4.00 (m, 1H), 4.29–4.34 (m, 1H), 6.39 (s, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 7.32–7.49 (m, 7H), 7.99 (dd, *J* = 7.3, 1.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.1, 25.2, 33.8, 63.2, 77.7, 126.4, 127.5, 127.9, 128.2, 128.4, 128.9, 130.0, 132.5, 134.0, 136.9, 137.5, 138.8, 201.5; **HRMS** (FAB) m/z calcd for $[C_{20}H_{18}O_2+H]^+$ 291.1385, found 291.1384.

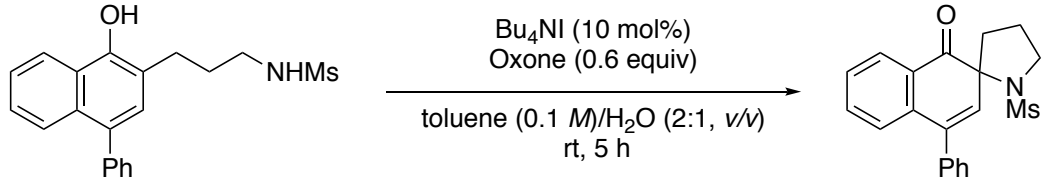
Representative Procedures for Oxidative Dearomative Spiroamination of Arenols 3



3a **4a** (84%)

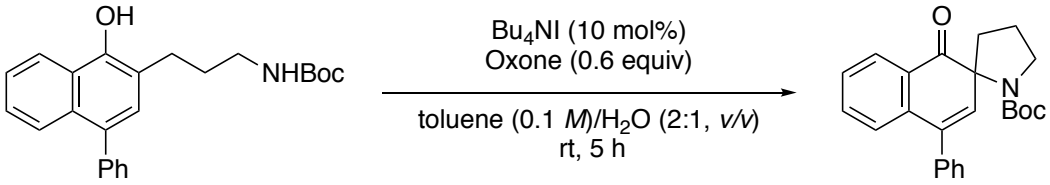
To a solution of **3a** (0.0431 g, 0.100 mmol) and Bu_4NI (0.00369 g, 0.0100 mmol, 10 mol%) in toluene (1.00 mL) and H_2O (0.500 mL) was added oxone (0.0368 g, 0.0600 mmol) at room temperature. The reaction was monitored by TLC analysis. After stirring for 3 h, the reaction was quenched by saturated aqueous $Na_2S_2O_3$ (1 mL) at 0 °C. The aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1) to give **4a** (0.0361 g, 0.0842 mmol) in 84% yield.

4-Phenyl-1'-tosyl-1*H*-spiro[naphthalene-2,2'-pyrrolidin]-1-one (4a): White solid; **TLC**, R_f = 0.17 (hexane–EtOAc =4:1); **IR** (neat) 2924, 1687, 1593, 1339, 1154 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.98–2.12 (m, 2H), 2.18–2.29 (m, 2H), 2.37 (s, 3H), 3.58–3.64 (m, 1H), 3.66–3.72 (m, 1H), 6.11 (s, 1H), 7.16–7.20 (m, 3H), 7.36–7.52 (m, 7H), 7.70 (d, *J* = 8.2 Hz, 2H), 8.12 (d, *J* = 7.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 23.2, 39.8, 48.9, 70.7, 126.8, 127.6, 127.8, 127.9, 128.0, 128.4, 128.8, 129.0, 129.2, 134.4, 135.3, 136.1, 137.2, 137.6, 138.5, 143.1, 198.3; **HRMS** (FAB) m/z calcd for $[C_{26}H_{23}NO_3S+H]^+$ 430.1477, found 430.1475.



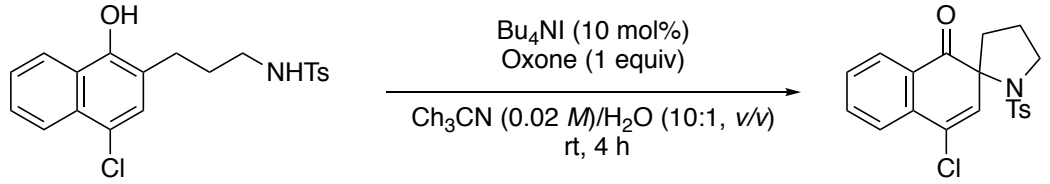
3aa **4aa** (71%)

1'-(Methylsulfonyl)-4-phenyl-1*H*-spiro[naphthalene-2,2'-pyrrolidin]-1-one (4aa):[1] 0.0250 g, 0.0710 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). White solid; **TLC**, R_f = 0.49 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.04–2.12 (m, 1H), 2.16–2.34 (m, 3H), 3.03 (s, 3H), 3.70–3.76 (m, 2H), 6.27 (s, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.36–7.44 (m, 6H), 7.51 (t, J = 7.6 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 23.0, 39.6, 39.9, 49.3, 72.1, 126.8, 127.8(2C), 127.9, 128.4, 128.6, 129.1, 134.8, 135.3, 136.4, 138.1, 138.4, 199.3.



3ab **4ab** (73%)

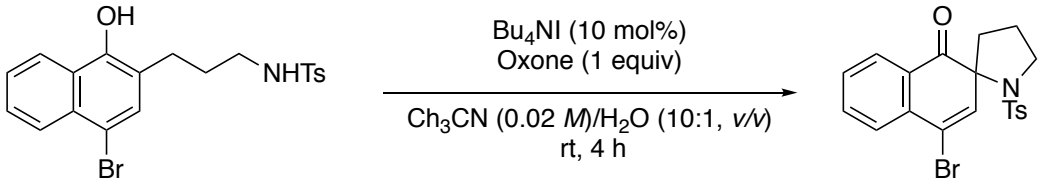
***tert*-Butyl 1-oxo-4-phenyl-1*H*-spiro[naphthalene-2,2'-pyrrolidine]-1'-carboxylate (4ab)**: 0.0274 g, 0.0732 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). Pale yellow solid; **TLC**, R_f = 0.34 (hexane–EtOAc = 4:1); **IR** (neat) 2974, 1698, 1593, 1388, 1365, 1156, 775 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz, two rotamers) δ 1.13 (s, 7.4H), 1.43 (s, 1.6H), 1.90–1.98 (m, 1H), 2.03–2.29 (m, 3H), 3.58–3.67 (m, 1H), 3.78–3.80 (m, 0.2H), 3.84–3.90 (m, 0.8H), 6.08 (s, 0.8H), 6.11 (s, 0.2H), 7.15 (q, J = 3.5 Hz, 1H), 7.31–7.52 (m, 8H), 8.11–8.12 (m, 0.2H), 8.16 (dd, J = 7.6, 1.1 Hz, 0.8H); **^{13}C NMR** ($CDCl_3$, 100 MHz, two rotamers) δ 22.4, 22.8, 28.0, 28.4, 38.1, 39.1, 47.9, 48.3, 67.9, 68.9, 76.7, 77.0, 77.3, 79.8, 80.1, 126.5, 127.5, 127.8, 127.8, 128.3, 128.5, 128.9, 129.2, 129.3, 134.0, 134.2, 135.3, 136.8, 137.1, 137.9, 138.0, 138.9, 139.0, 153.6, 199.5; **HRMS** (FAB) m/z calcd for $[C_{24}H_{25}NO_3+H]^+$ 376.1913, found 376.1920.



3b **4b** (64%)

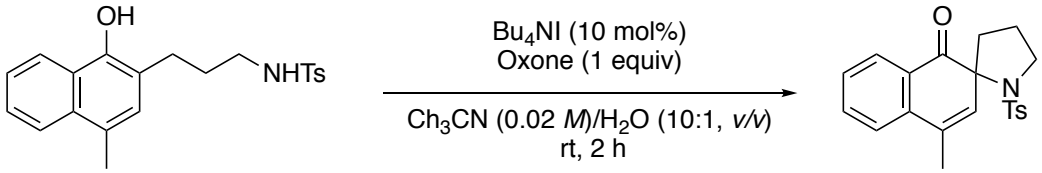
4-Chloro-1'-tosyl-1*H*-spiro[naphthalene-2,2'-pyrrolidin]-1-one (4b): 0.0248 g, 0.0639 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). Pale yellow solid; **TLC**, R_f = 0.19 (hexane–EtOAc = 4:1); **IR** (neat) 2954, 1692, 1593, 1340, 1154, 1096, 664 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.96–2.07 (m, 2H), 2.17–2.27

(m, 2H), 2.43 (s, 3H), 3.53–3.59 (m, 1H), 3.69–3.74 (m, 1H), 6.28 (s, 1H), 7.30 (d, J = 7.8 Hz, 2H), 7.46–7.50 (m, 1H), 7.69–7.72 (m, 3H), 7.78 (d, J = 7.3 Hz, 1H), 8.11 (dd, J = 7.8, 0.9 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 23.3, 39.7, 48.8, 71.0, 125.6, 127.6, 127.8, 128.4, 128.7, 129.3, 129.4, 133.0, 134.8, 134.9, 137.0, 143.4, 196.7; **HRMS** (FAB) m/z calcd for $[C_{20}H_{18}{}^{35}ClNO_3S+H]^+$/$[C_{20}H_{18}{}^{37}ClNO_3S+H]^+$ 388.0774/390.0745, found 388.0780/390.0747.



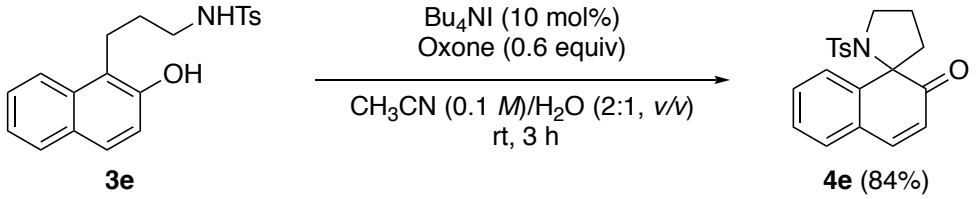
3c **4c** (73%)

4-Bromo-1'-tosyl-1*H*-spiro[naphthalene-2,2'-pyrrolidin]-1-one (4c): 0.0317 g, 0.0733 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). White solid; **TLC**, R_f = 0.19 (hexane–EtOAc = 4:1); **IR** (neat) 2918, 1692, 1590, 1341, 1155, 1096, 663 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.94–2.07 (m, 2H), 2.16–2.27 (m, 2H), 2.43 (s, 3H), 3.52–3.58 (m, 1H), 3.73 (td, J = 7.9, 5.0 Hz, 1H), 6.51 (s, 1H), 7.30 (d, J = 8.7 Hz, 2H), 7.46 (td, J = 7.5, 1.1 Hz, 1H), 7.67–7.76 (m, 4H), 8.09 (dd, J = 7.5, 1.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 23.3, 39.4, 48.8, 71.8, 119.1, 127.5, 127.7, 128.3, 128.8, 129.3, 129.4, 134.9, 135.3, 137.0, 137.2, 143.4, 196.6; **HRMS** (FAB) m/z calcd for $[C_{20}H_{18}{}^{79}BrNO_3S+H]^+$/$[C_{20}H_{18}{}^{81}BrNO_3S+H]^+$ 432.0269/434.0249, found 432.0266/434.0235.



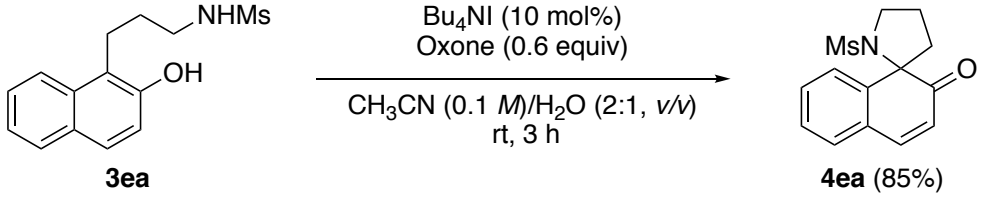
3d **4d** (43%)

4-Methyl-1'-tosyl-1*H*-spiro[naphthalene-2,2'-pyrrolidin]-1-one (4d): 0.0158 g, 0.0429 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). White solid; **TLC**, R_f = 0.19 (hexane–EtOAc = 4:1); **IR** (neat) 2951, 1687, 1596, 1339, 1154, 1097, 671 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.93–2.02 (m, 2H), 2.12–2.21 (m, 2H), 2.42 (d, J = 1.4 Hz, 3H), 3.56–3.67 (m, 2H), 6.00 (d, J = 1.4 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.36–7.40 (m, 2H), 7.63 (td, J = 7.6, 1.2 Hz, 1H), 7.69–7.72 (m, 2H), 8.08 (dd, J = 8.2, 1.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.3, 21.5, 23.1, 39.9, 48.8, 70.7, 124.5, 127.7, 127.7, 127.8, 128.7, 128.9, 129.2, 133.2, 134.7, 137.3, 138.3, 143.1, 198.7; **HRMS** (FAB) m/z calcd for $[C_{21}H_{21}NO_3S+H]^+$ 368.1820, found 368.1324.



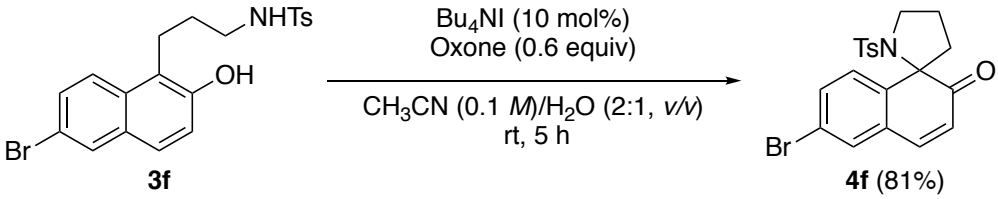
3e **4e** (84%)

1'-Tosyl-2*H*-spiro[naphthalene-1,2'-pyrrolidin]-2-one (4e): 0.0298 g, 0.0843 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 4:1). Pale white solid; **TLC**, R_f = 0.52 (hexane–EtOAc = 1:1); **IR** (neat) 2926, 1675, 1337, 1154, 1094, 1006, 754 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.94–2.00 (m, 1H), 2.04–2.21 (m, 2H), 2.29–2.36 (m, 1H), 2.42 (s, 3H), 3.70–3.81 (m, 2H), 6.22 (d, *J* = 9.6 Hz, 1H), 7.25–7.27 (m, 2H), 7.29–7.41 (m, 4H), 7.46 (d, *J* = 10.1 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.7, 23.1, 44.2, 49.7, 75.1, 124.1, 126.5, 127.8, 127.9, 129.1, 129.2, 129.8, 130.3, 137.3, 143.2, 145.4, 145.8, 200.0; **HRMS** (FAB) m/z calcd for $[C_{20}H_{19}NO_3S+H]^+$ 354.1164, found 354.1163.



3ea **4ea** (85%)

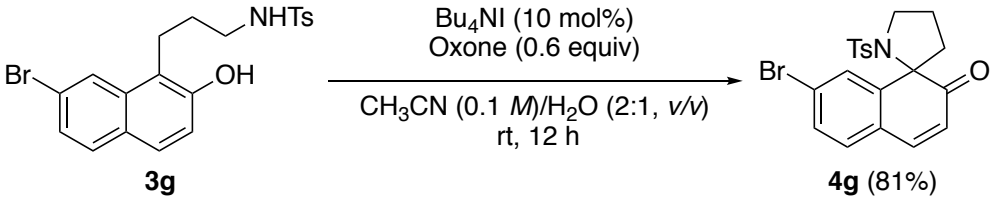
1'-(Methylsulfonyl)-2*H*-spiro[naphthalene-1,2'-pyrrolidin]-2-one (4ea):[10] 0.0235 g, 0.0847 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 4:1). White solid; **TLC**, R_f = 0.33 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.99–2.05 (m, 1H), 2.14–2.20 (m, 2H), 2.34–2.41 (m, 1H), 3.10 (s, 3H), 3.73–3.78 (m, 1H), 3.93–3.98 (m, 1H), 6.17 (d, *J* = 10.1 Hz, 1H), 7.28–7.33 (m, 2H), 7.42–7.47 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 22.7, 39.9, 44.1, 49.9, 75.8, 123.7, 125.8, 127.7, 128.4, 129.8, 130.6, 145.9, 146.5, 200.5.



3f **4f** (81%)

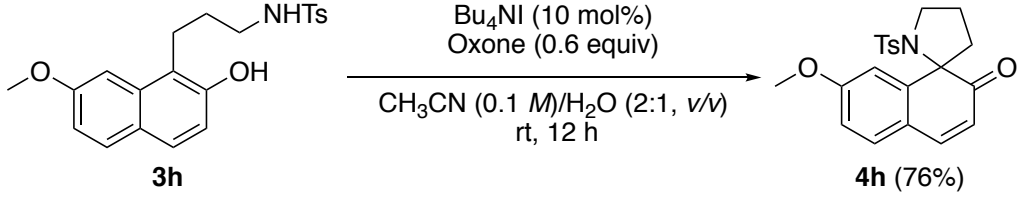
6-Bromo-1'-tosyl-2*H*-spiro[naphthalene-1,2'-pyrrolidin]-2-one (4f): 0.0352 g, 0.0814 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 4:1). White solid; **TLC**, R_f = 0.57 (hexane–EtOAc = 1:1); **IR** (neat) 2916, 1678, 1337, 1154, 1096, 815, 754 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.91–1.97 (m, 1H), 2.00–2.10 (m, 1H), 2.12–2.20 (m, 1H), 2.28–2.34 (m, 1H), 2.43 (s, 3H), 3.68–3.80 (m, 2H), 6.25 (d, *J* = 9.6 Hz, 1H), 7.27–7.33 (m, 3H), 7.34–7.39 (m, 1H), 7.44–7.48 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 22.9, 43.8, 49.5, 74.6, 121.4, 125.2, 127.8, 128.1, 129.2, 130.8, 132.0, 132.8, 136.9, 143.3,

143.6, 144.5, 199.0; **HRMS** (FAB) m/z calcd for$[C_{20}H_{18}{}^{79}BrNO_3S+H]^+/[C_{20}H_{18}{}^{81}BrNO_3S+H]^+$ 432.0269/434.0249, found 432.0251/434.0255.



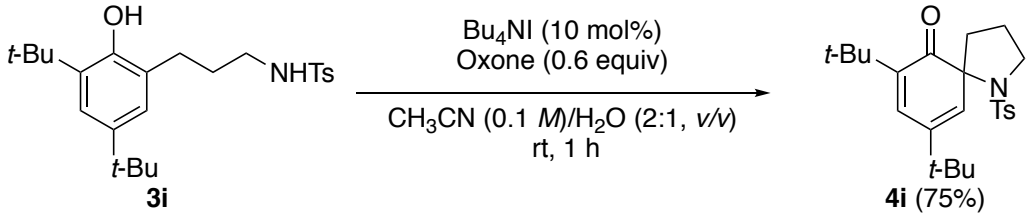
3g **4g** (81%)

7-Bromo-1'-tosyl-2*H*-spiro[naphthalene-1,2'-pyrrolidin]-2-one (4g): 0.0349 g, 0.0807 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 4:1). White solid; **TLC**, R_f = 0.53 (hexane–EtOAc = 1:1); **IR** (neat) 3025, 1678, 1585, 1338, 1155, 1095, 673 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.91–2.06 (m, 2H), 2.23–2.38 (m, 2H), 2.43 (s, 4H), 3.67–3.73 (m, 1H), 3.90–3.95 (m, 1H), 6.25 (d, *J* = 10.1 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.26–7.28 (m, 3H), 7.38–7.45 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 22.8, 43.7, 49.6, 74.1, 124.3, 124.8, 127.2, 128.2, 129.4, 129.7, 130.8, 130.9, 137.3, 143.2, 143.9, 146.8, 198.9; **HRMS** (FAB) m/z calcd for$[C_{20}H_{18}{}^{79}BrNO_3S+H]^+/[C_{20}H_{18}{}^{81}BrNO_3S+H]^+$ 432.0269/434.0249, found 432.0266/434.0235.



3h **4h** (76%)

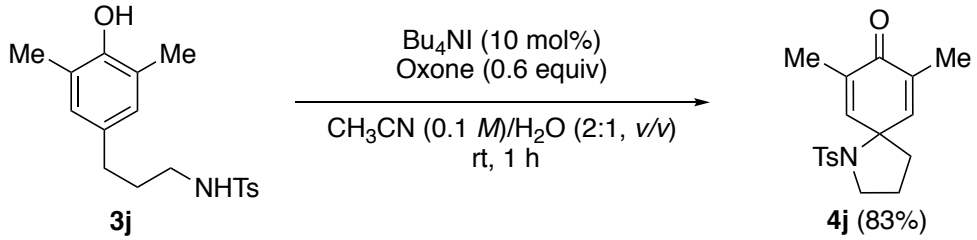
7-Methoxy-1'-tosyl-2*H*-spiro[naphthalene-1,2'-pyrrolidin]-2-one (4h): 10.0291 g, 0.0758 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 4:1). White solid; **TLC**, R_f = 0.48 (hexane–EtOAc = 1:1); **IR** (neat) 2953, 1671, 1602, 1336, 1286, 1232, 1154, 1094, 673, cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.93–2.02 (m, 1H), 2.03–2.13 (m, 1H), 2.14–2.23 (m, 1H), 2.29–2.36 (m, 1H), 2.41 (s, 3H), 3.73–3.77 (m, 2H), 3.73 (s, 3H), 6.09 (d, *J* = 9.8 Hz, 1H), 6.79–6.82 (m, 1H), 6.87 (d, *J* = 2.3 Hz, 1H), 7.25–7.27 (m, 3H), 7.40 (d, *J* = 9.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 22.8, 44.1, 49.6, 55.2, 75.0, 112.5, 112.9, 121.3, 122.3, 127.7, 129.0, 131.3, 137.3, 143.0, 145.2, 147.8, 161.3, 199.8; **HRMS** (FAB) m/z calcd for $[C_{21}H_{21}NO_4S+H]^+$ 384.1270, found 384.1269.



3i **4i** (75%)

7,9-Di-tert-butyl-1-tosyl-1-azaspiro[4.5]deca-7,9-dien-6-one (4i): 0.0311 g, 0.0749 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent:

hexane–EtOAc = 10:1). Brown solid; **TLC**, R_f = 0.76 (hexane–EtOAc = 1:1); **IR** (neat) 2959, 1672, 1652, 1343, 1157, 1104, 665 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.15 (s, 9H), 1.21 (s, 9H), 1.82–1.92 (m, 2H), 2.00–2.10 (m, 2H), 2.40 (s, 3H), 3.62–3.68 (m, 2H), 6.04 (d, *J* = 2.5 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (CD_2Cl_2, 100 MHz) δ 21.6, 22.7, 28.8, 29.3, 34.5, 34.7, 39.4, 49.8, 73.3, 127.7, 129.6, 133.0, 135.8, 138.6, 140.5, 143.3, 143.4, 200.4; **HRMS** (FAB) m/z calcd for $[C_{24}H_{33}NO_3S+H]^+$ 415.2181, found 415.2174.



3j **4j** (83%)

7,9-Dimethyl-1-tosyl-1-azaspiro[4.5]deca-6,9-dien-8-one (4j): 0.0276 g, 0.0832 mmol. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–EtOAc = 10:1). White solid; **TLC**, R_f = 0.57 (hexane–EtOAc = 1:1); **IR** (neat) 2919, 1643, 1336, 1155, 1006, 664 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.82 (s, 6H), 1.98–2.05 (m, 4H), 2.43 (s, 3H), 3.67–3.70 (m, 2H), 6.38 (s, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 15.9, 21.5, 23.2, 40.0, 49.0, 63.4, 127.7, 129.3, 133.9, 136.4, 143.5, 144.8, 186.4; **HRMS** (FAB) m/z calcd for $[C_{18}H_{21}NO_3S+H]^+$ 332.1320, found 332.1325.

Procedures for Control Experiments

Control Experiments to Probe Active Species

Using I_2 and Bu_4NOH (Scheme 3b, Entries 1 and 8): To a solution of **1a** (0.0139 g, 0.0500 mmol) and 40% aqueous tetrabutylammonium hydroxide (0.0650 mL, 0.100 mmol) in CH_3CN (0.500 mL) and H_2O (0.250 mL) were added iodine (0.0129 g, 0.0500 mmol) at room temperature. After stirring for 1 h, small amount of reaction mixture was sampled *via* syringe and poured into saturated aqueous $Na_2S_2O_3$ to quench the reaction. The volatiles were removed under reduced pressure, and the residue was dissolved into $CDCl_3$ to measure the conversion yield, which was determined by ^{1}H NMR analysis. Similar control experiment was also performed using **3a** instead of **1a** and similar results were obtained.

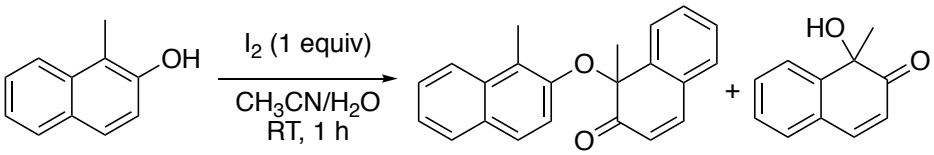
Using I_2 and K_2CO_3 (Scheme 3b, Entries 2 and 9): To a solution of **1a** (0.0139 g, 0.0500 mmol) and K_2CO_3 (0.0138 g, 0.100 mmol) in toluene (0.500 mL) and H_2O (0.250 mL) were added iodine (0.0129 g, 0.0500 mmol) at room temperature. After stirring for 1 h, small amount of reaction mixture was sampled *via* syringe and poured into saturated aqueous $Na_2S_2O_3$ to quench the reaction. The volatiles were removed under reduced pressure, and the residue was dissolved into $CDCl_3$ to measure the conversion yield, which was determined by ^{1}H NMR analysis. Similar control experiment was also performed using **3a** instead of **1a** and similar results were obtained.

Using Bu_4NI_3 (Scheme 3b, Entries 3 and 10): To a solution of **1a** (0.0139 g, 0.0500 mmol) in CH_3CN (0.500 mL) and H_2O (0.250 mL) was added Bu_4NI_3 (0.0311 g, 0.0500 mmol) at room temperature. After stirring for 24 h, small amount of reaction mixture was sampled *via* syringe and poured into saturated aqueous $Na_2S_2O_3$ to quench the reaction. The volatiles were removed under reduced pressure, and the residue was dissolved into $CDCl_3$ to measure the conversion yield, which was determined by ^1H NMR analysis. Similar control experiments were also performed using **3a** instead of **1a**.

Using I_2 (Scheme 3b, Entries 4, 5, 7 and 11): To a solution of **1a** (0.0139 g, 0.0500 mmol) in CH_3CN (0.500 mL) and H_2O (0.250 mL) was added iodine (0.0129 g, 0.0500 mmol) at room temperature. After stirring for 1 h, small amount of reaction mixture was sampled *via* syringe and poured into saturated aqueous $Na_2S_2O_3$ to quench the reaction. The volatiles were removed under reduced pressure, and the residue was dissolved into $CDCl_3$ to measure the conversion yield, which was determined by ^1H NMR analysis. Similar control experiments were also performed using **3a** instead of **1a**.

Using I_2 and AcOH (Scheme 3b, Entry 6): To a solution of **1a** (0.0139 g, 0.0500 mmol) and AcOH (3.00 μL, 0.0500 mmol) in toluene (0.500 mL) and H_2O (0.250 mL) was added iodine (0.0129 g, 0.0500 mmol) at room temperature. After stirring for 1 h, small amount of reaction mixture was sampled *via* syringe and poured into saturated aqueous $Na_2S_2O_3$ to quench the reaction. The volatiles were removed under reduced pressure, and the residue was dissolved into $CDCl_3$ to measure the conversion yield, which was determined by ^1H NMR analysis.

Control Experiments to Probe the Influence of Tethers (Scheme 3c)



6 **7**: 35% **8**: 7%

To a solution of **6** (0.00791 g, 0.0500 mmol) in CH_3CN (0.500 mL) and H_2O (0.0250 mL) was added iodine (0.0129 g, 0.0500 mmol) at room temperature. After stirring for 1 h, small amount of reaction mixture was sampled *via* syringe and poured into saturated aqueous $Na_2S_2O_3$ to quench the reaction. The volatiles were removed under reduced pressure, and the residue was dissolved into $CDCl_3$ to measure the conversion yield, which was determined by ^1H NMR analysis. **7**[5,11] and **8**[12] were known compounds.

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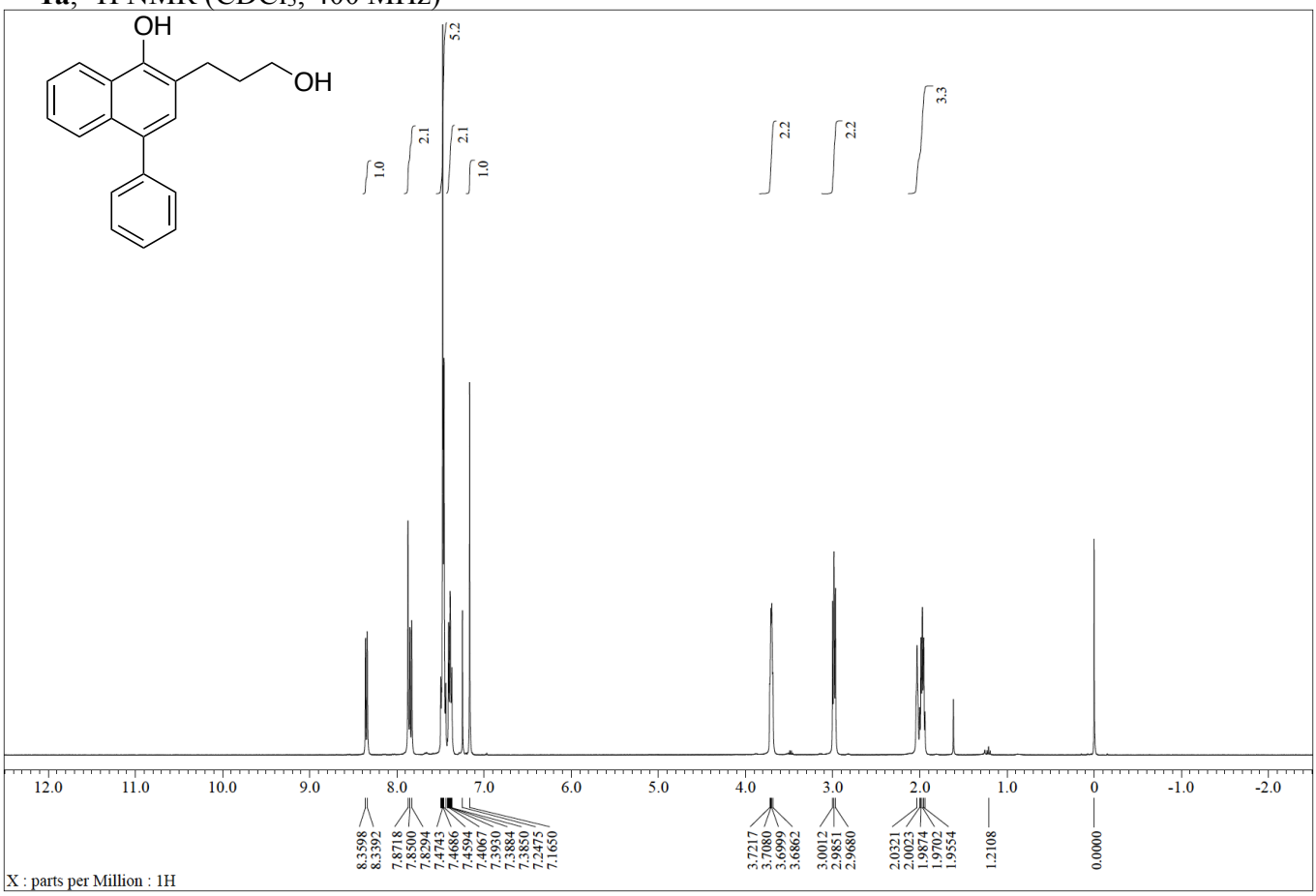
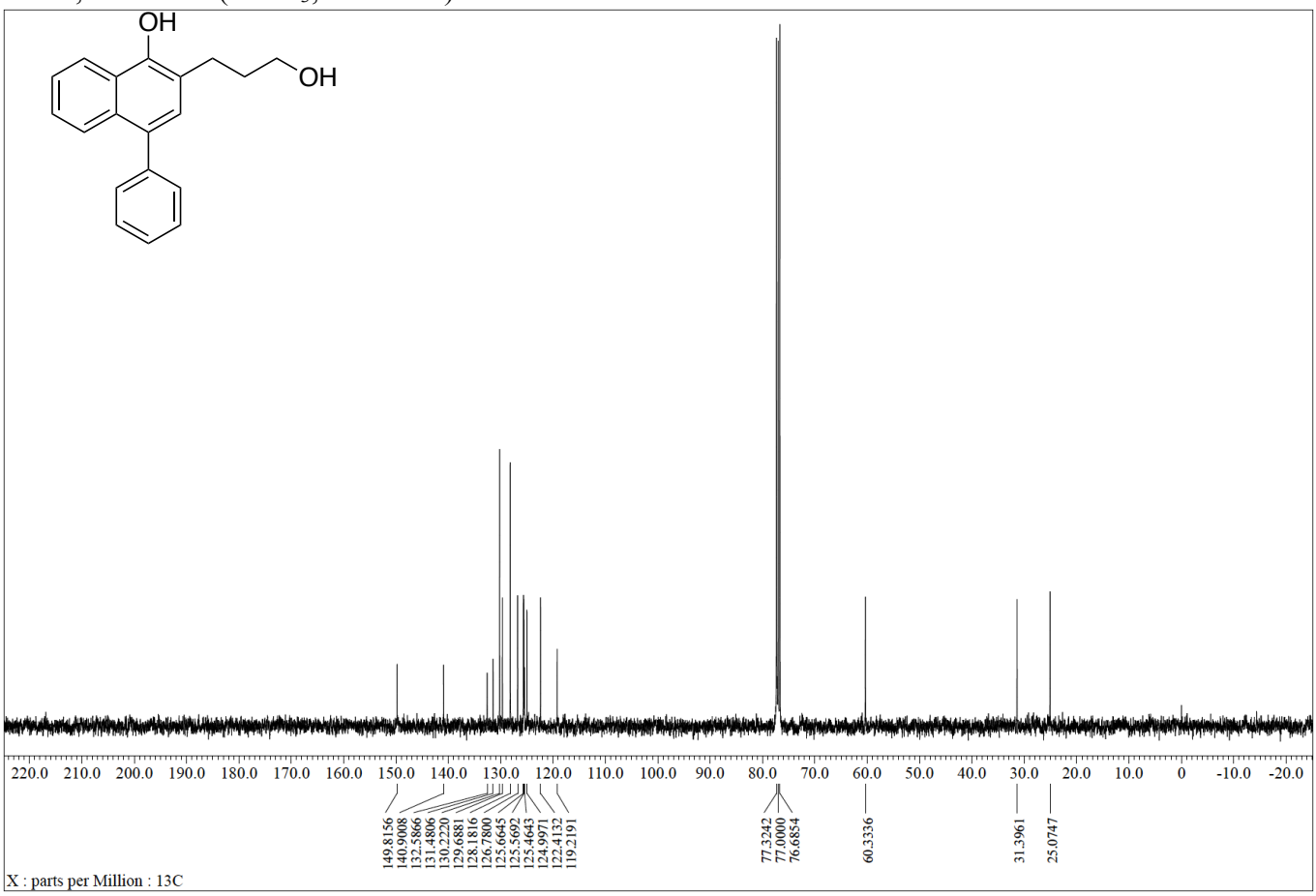
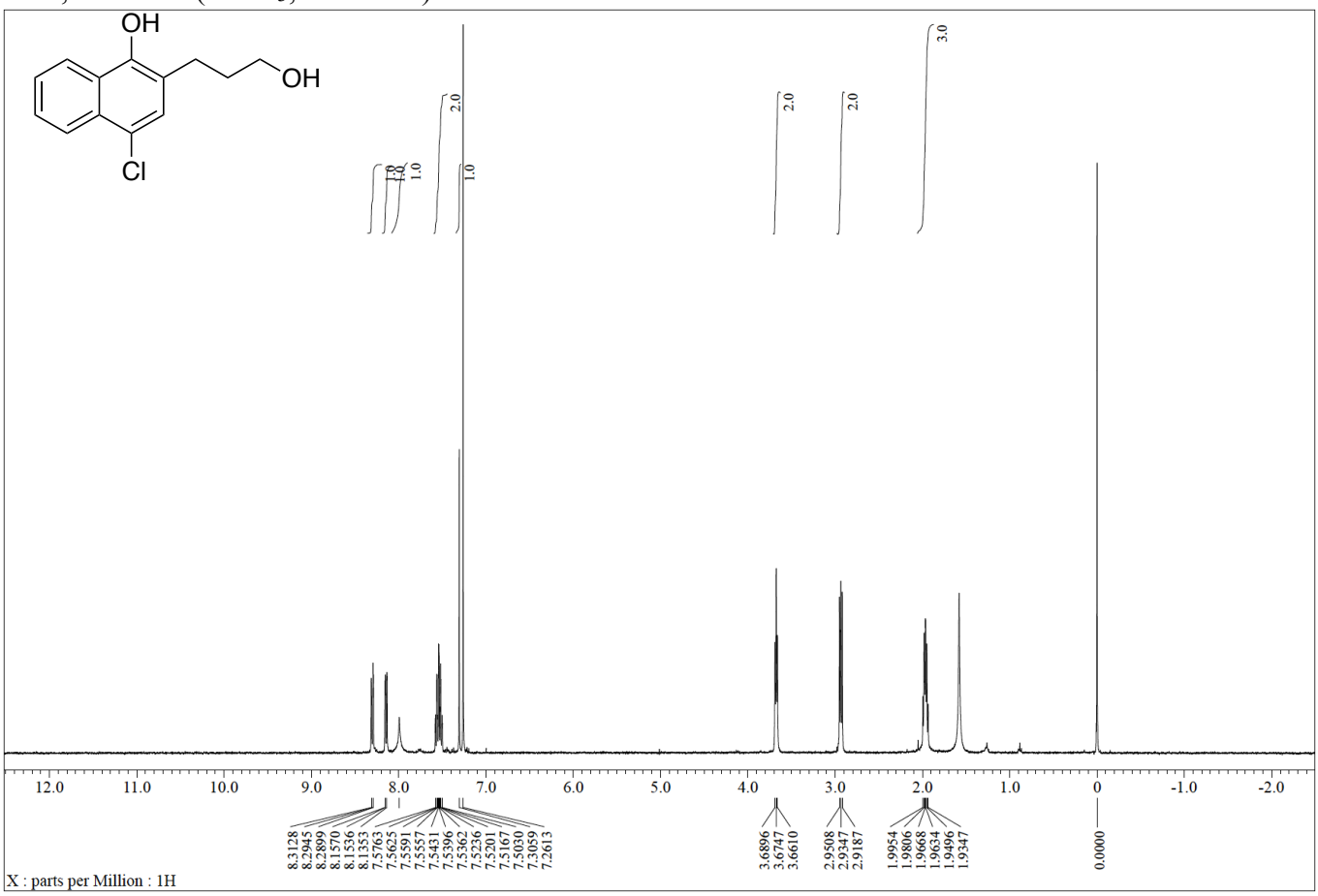
1a, ^{1}H NMR ($CDCl_3$, 400 MHz)



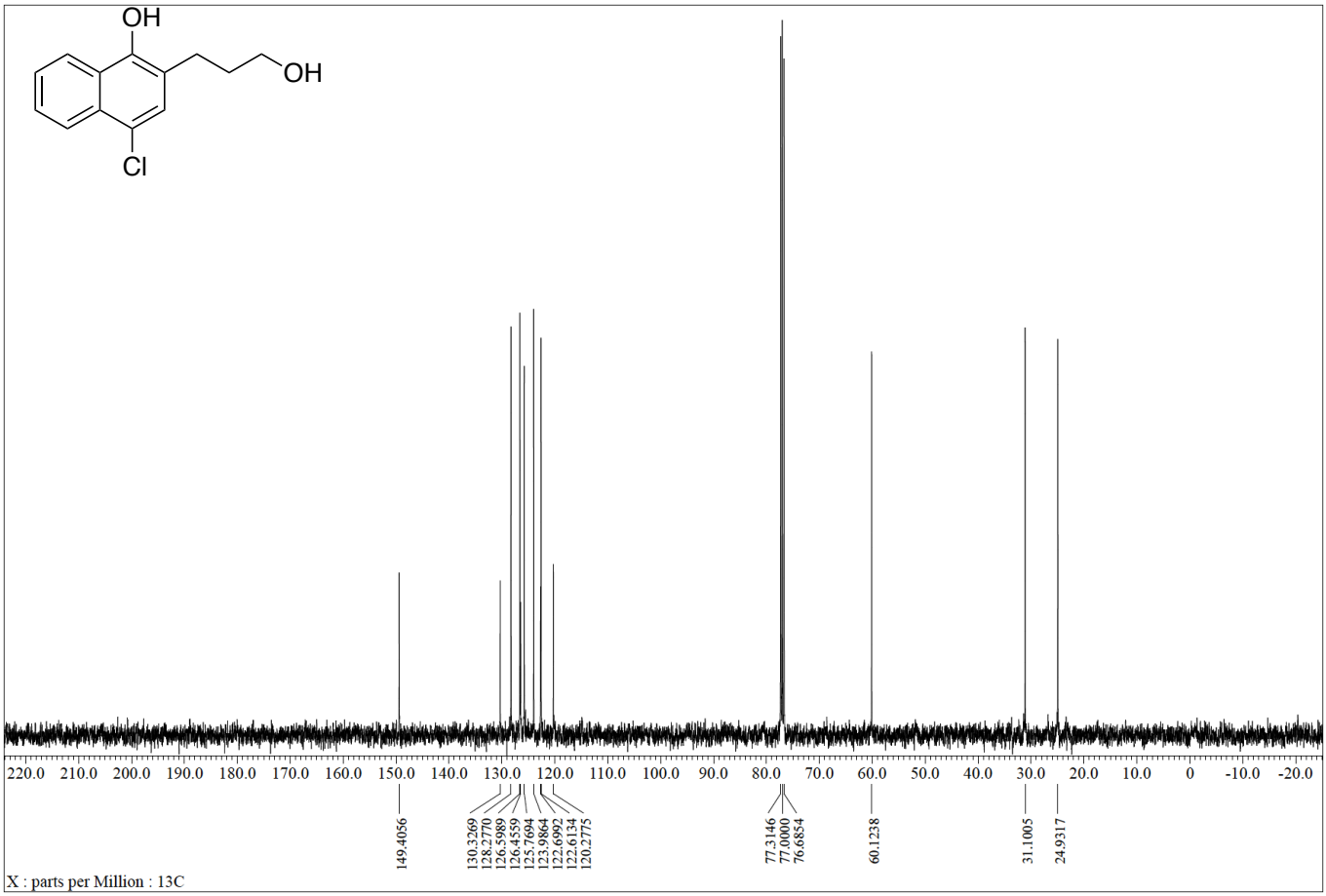
1a, ^{13}C NMR ($CDCl_3$, 100 MHz)



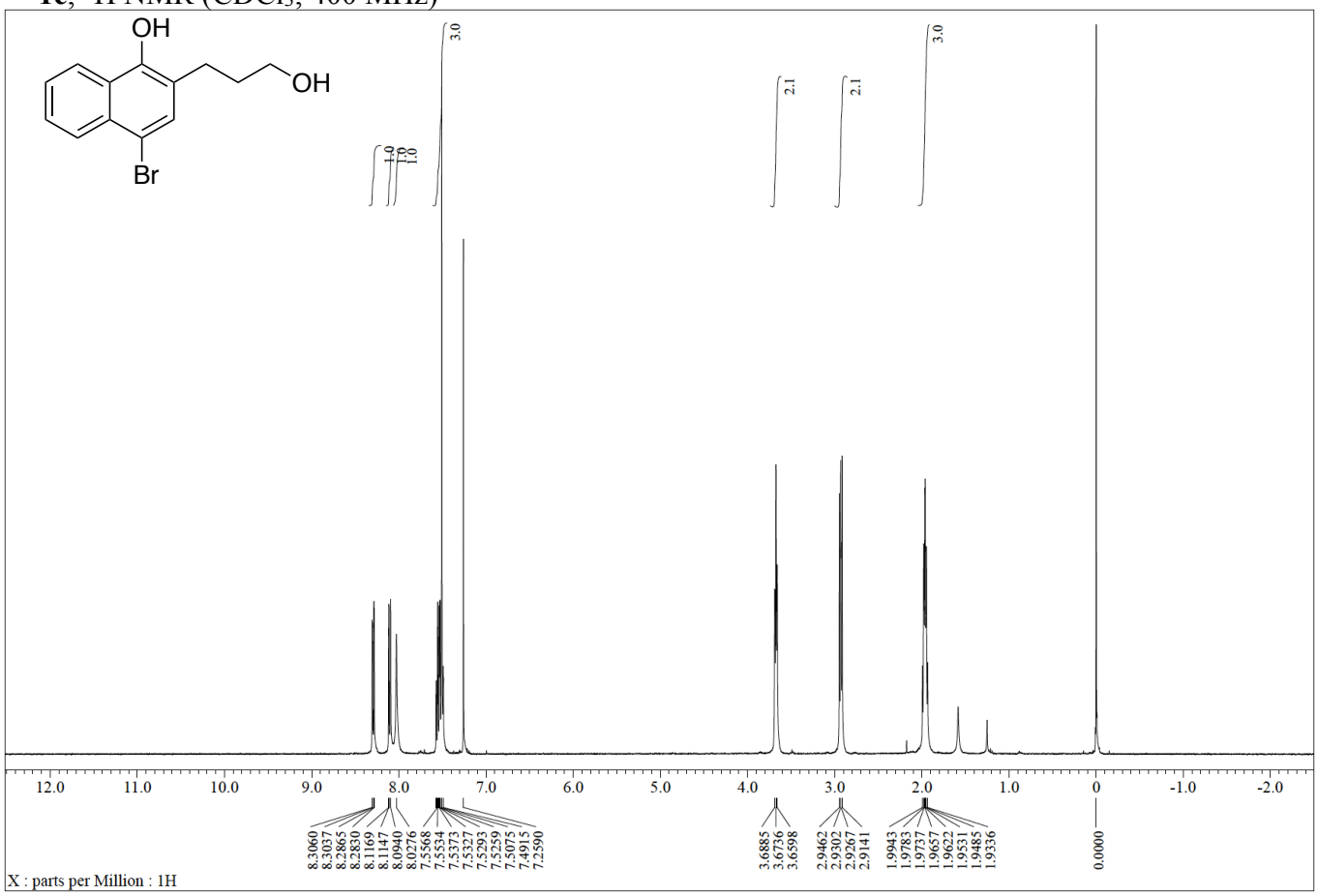
1b, ^{1}H NMR ($CDCl_3$, 400 MHz)



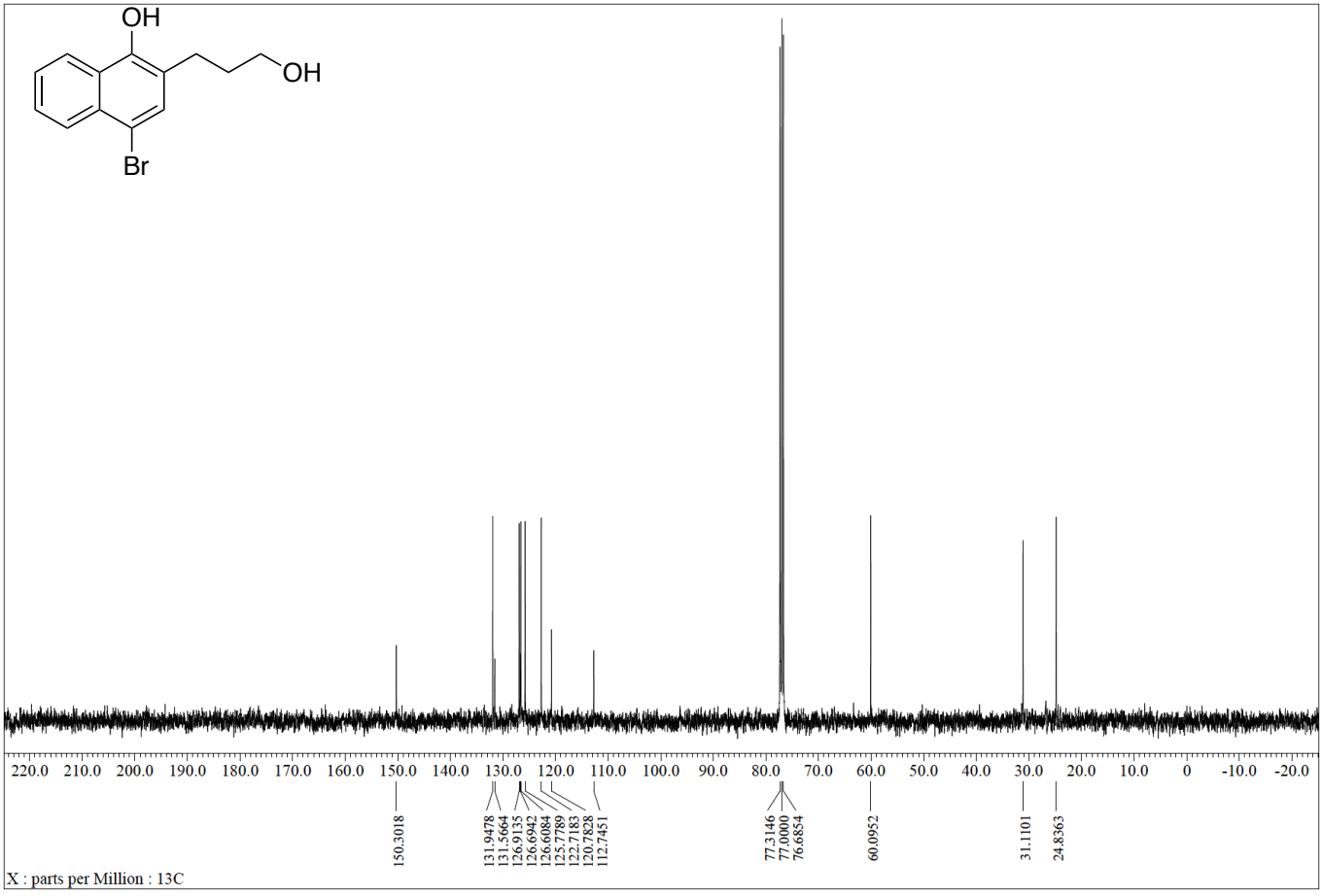
1b, ^{13}C NMR ($CDCl_3$, 100 MHz)



1c, ^{1}H NMR ($CDCl_3$, 400 MHz)



1c, ^{13}C NMR ($CDCl_3$, 100 MHz)



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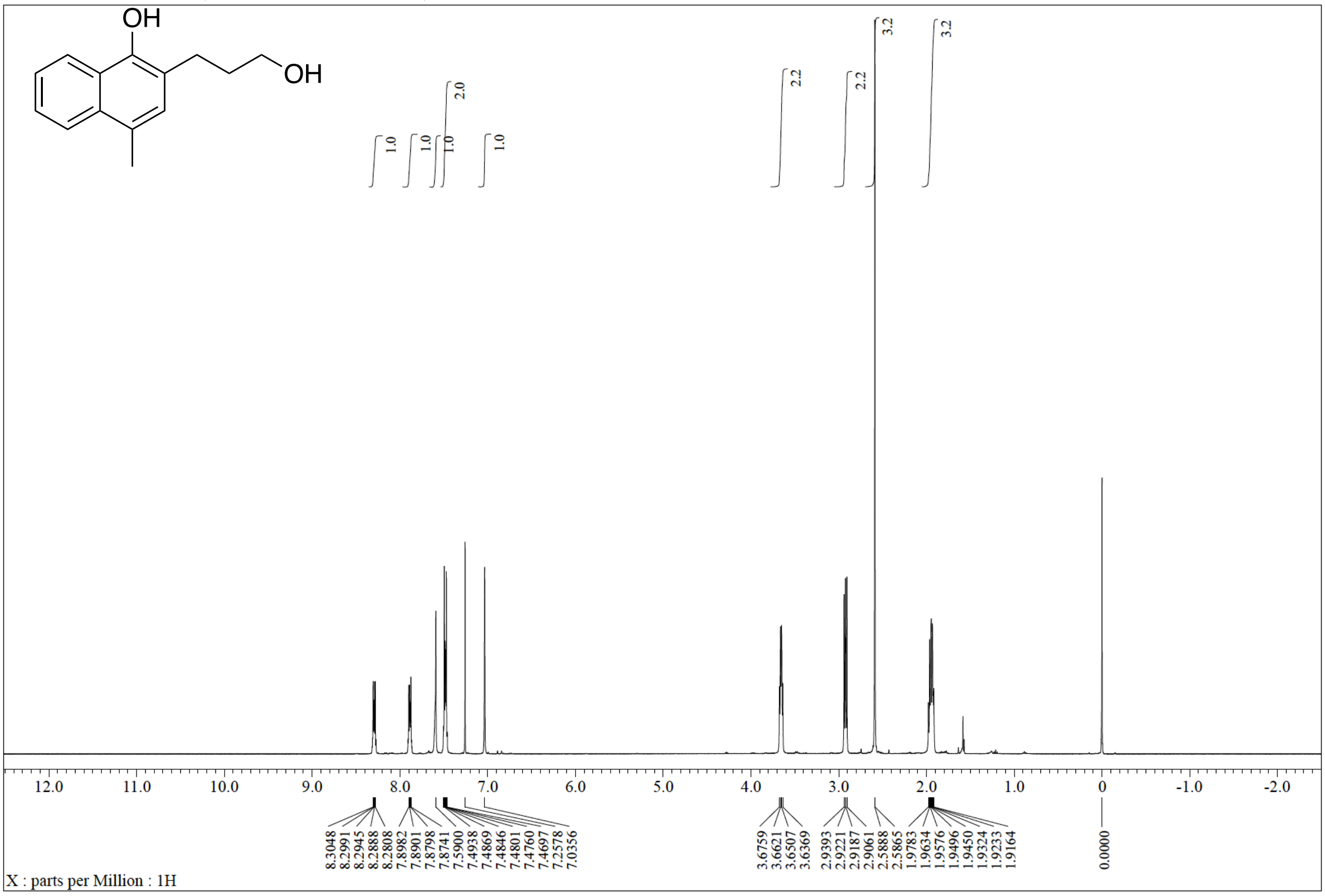

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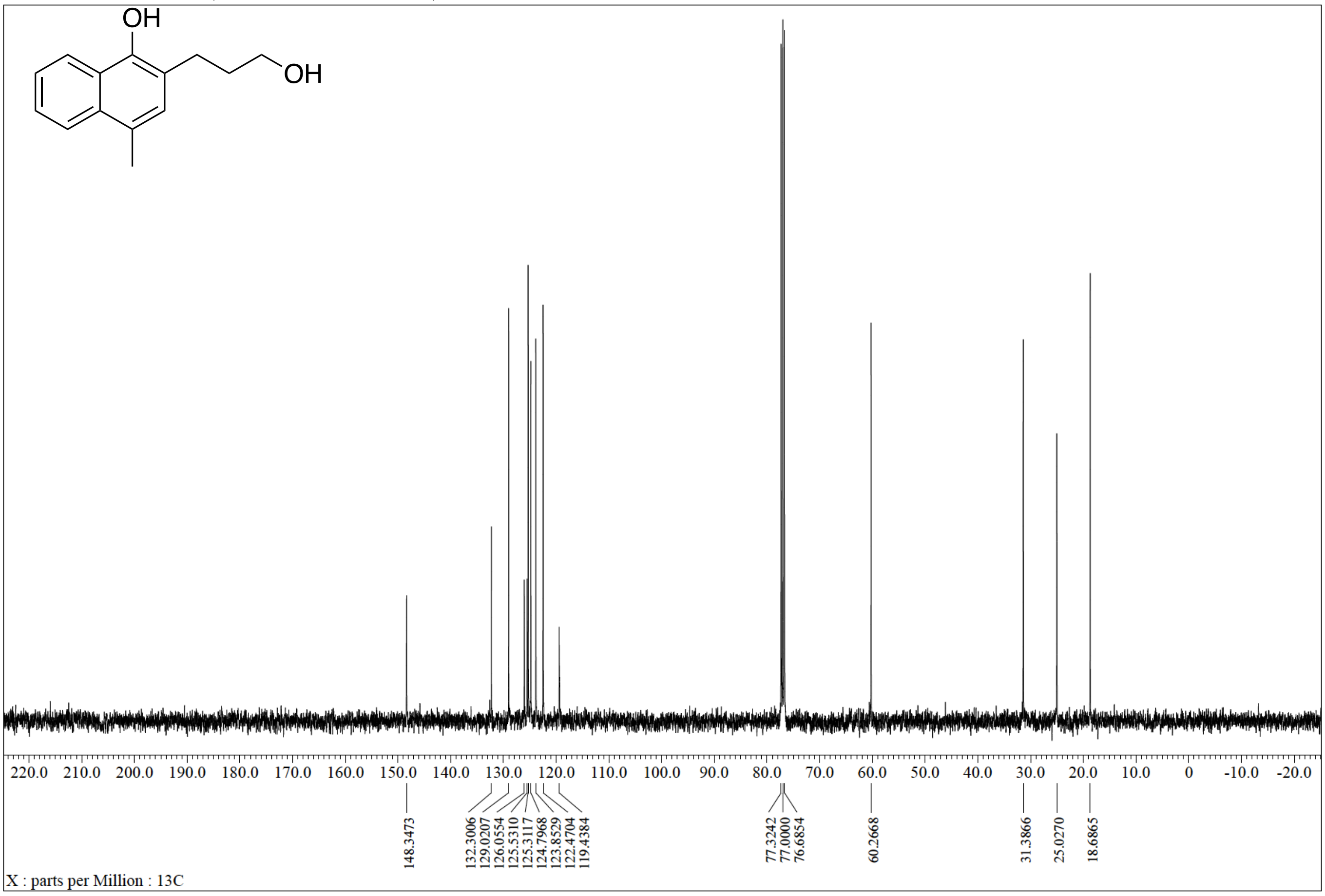
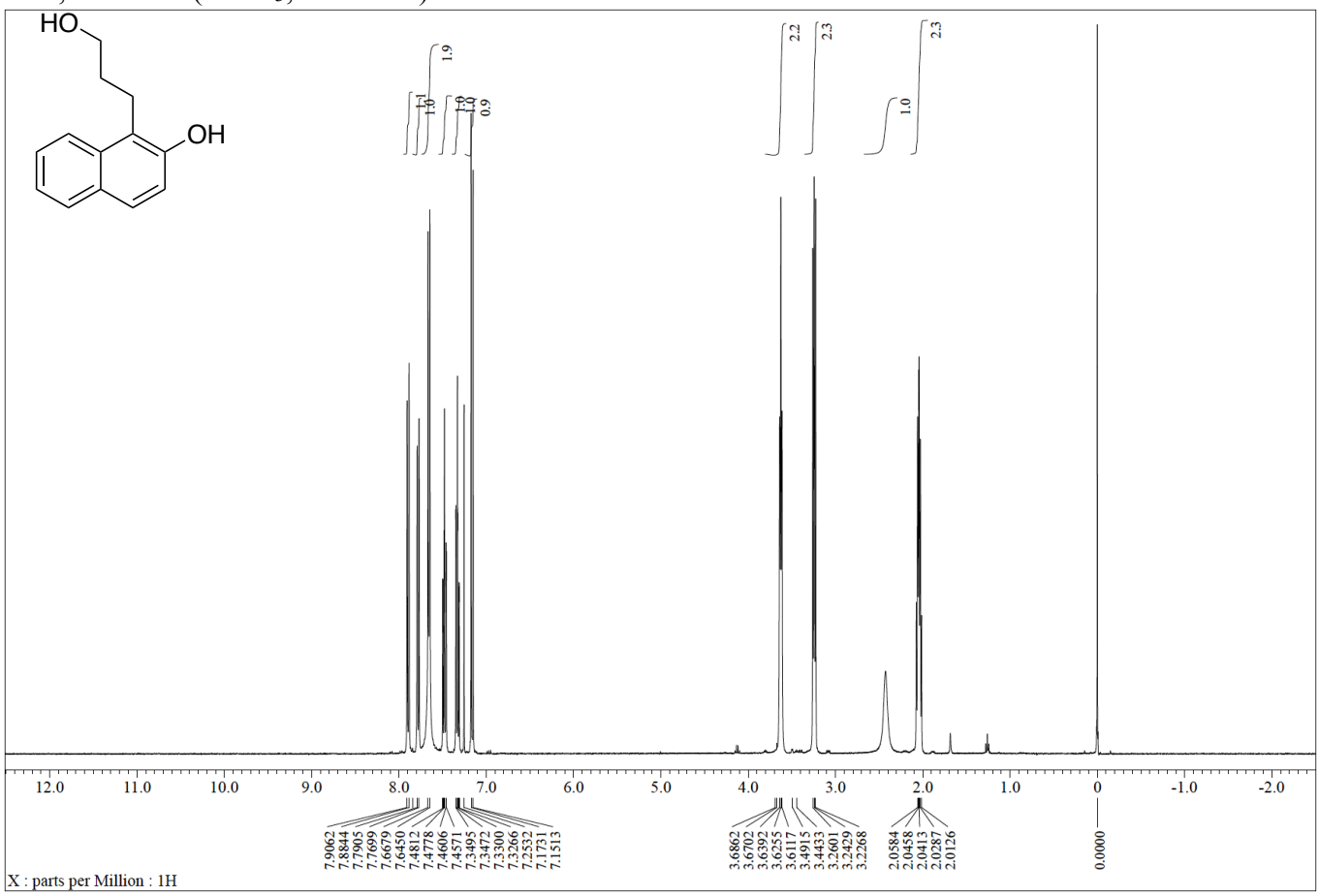


1e, ^{1}H NMR ($CDCl_3$, 400 MHz)



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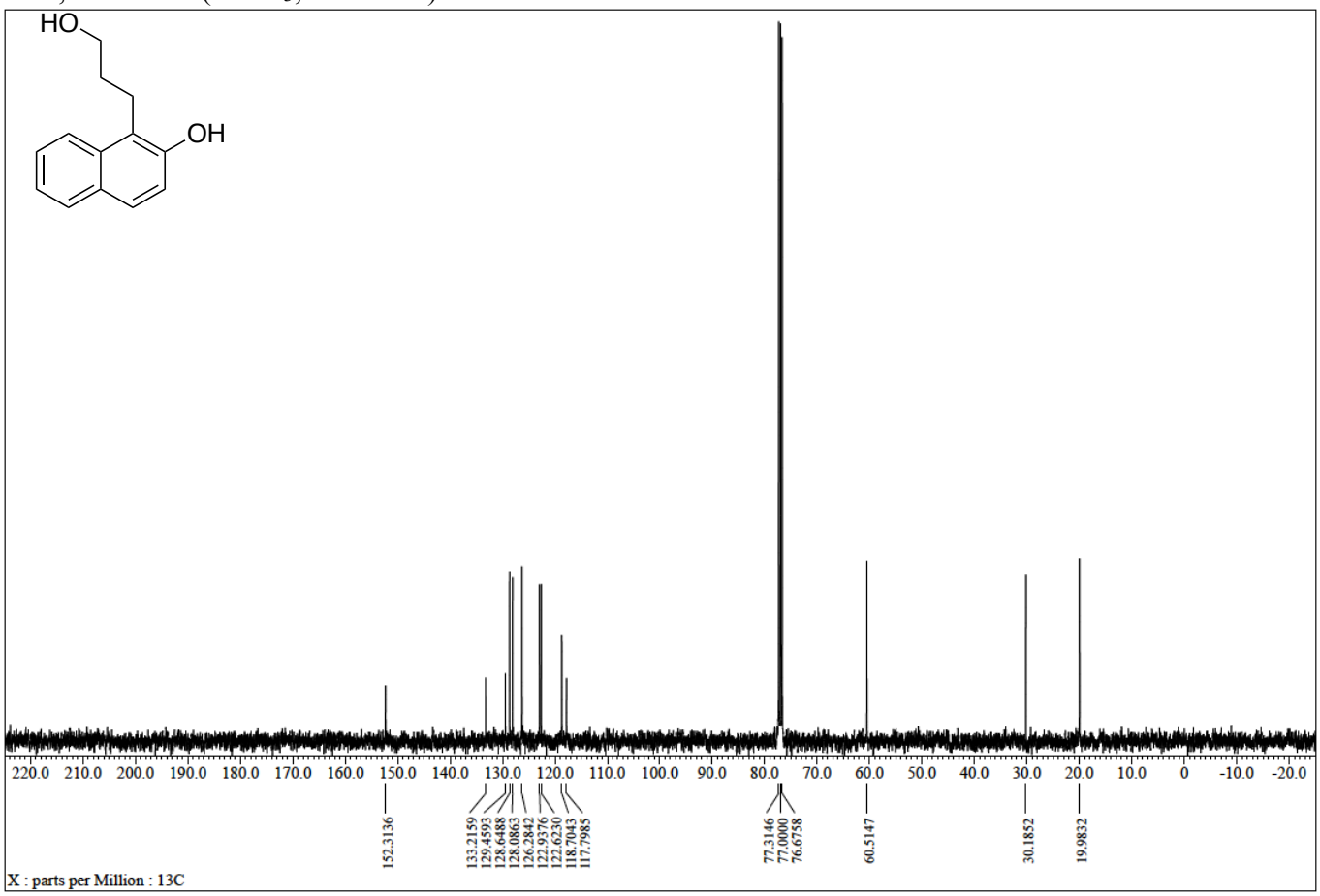
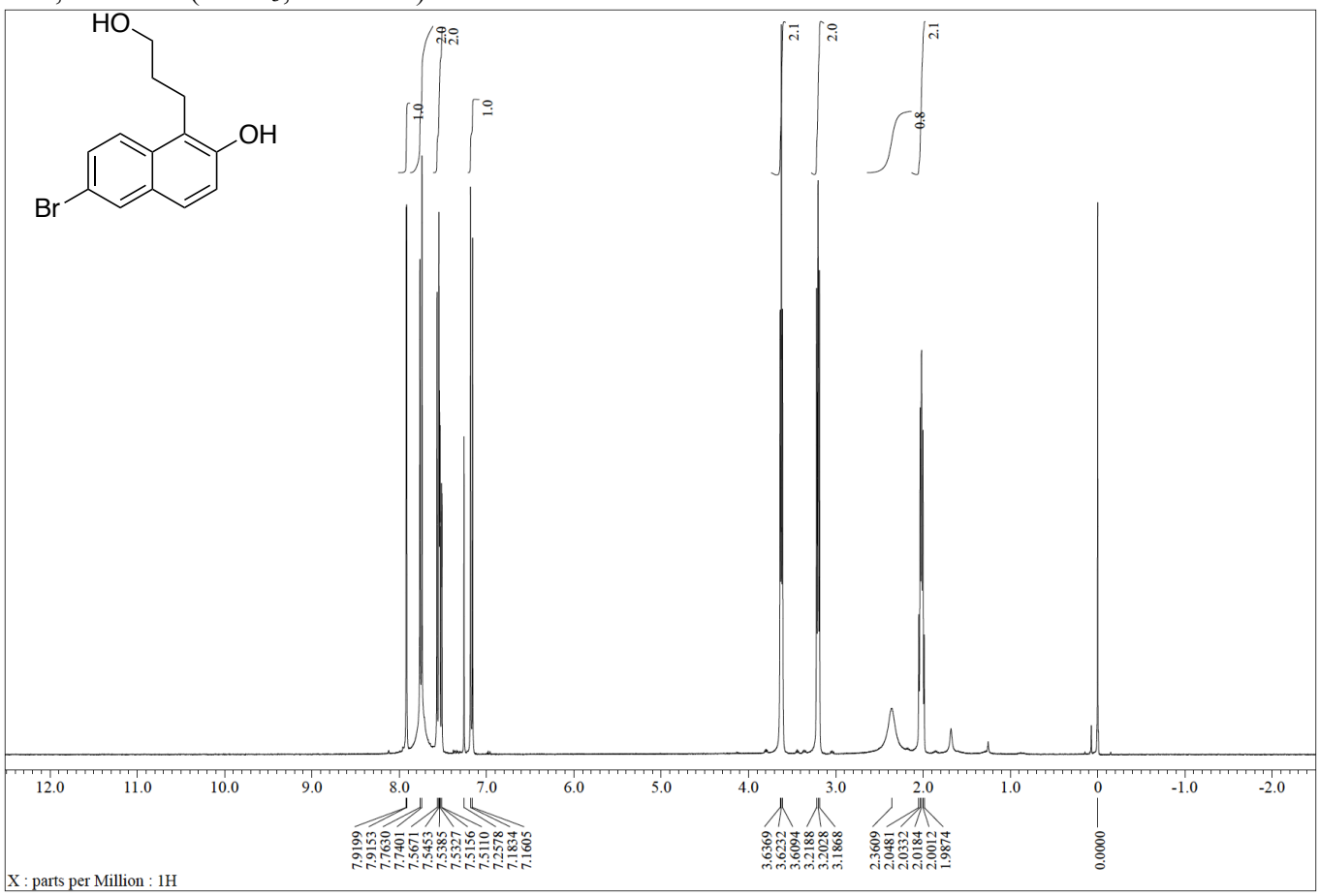


1f, ^{1}H NMR ($CDCl_3$, 400 MHz)



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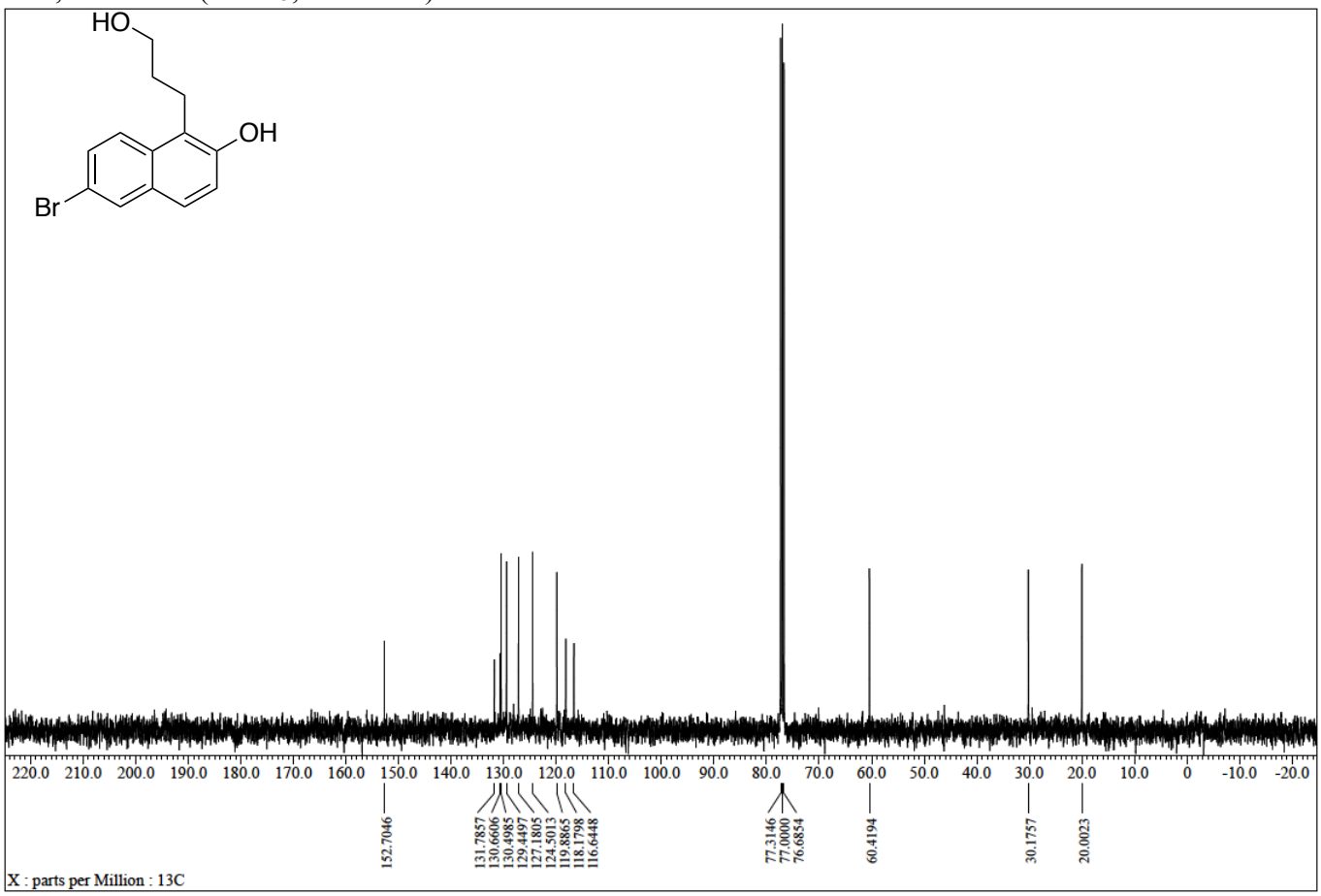

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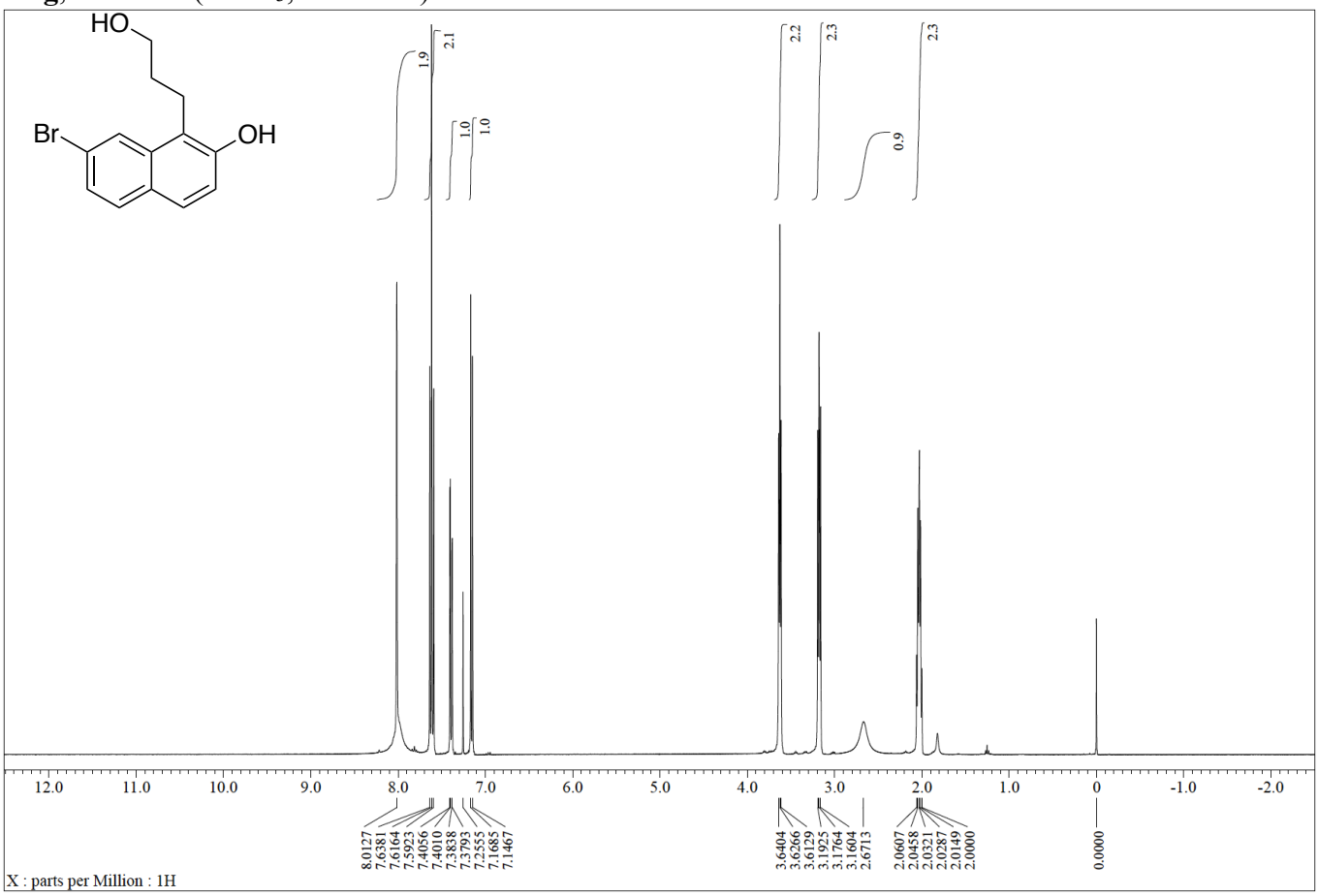

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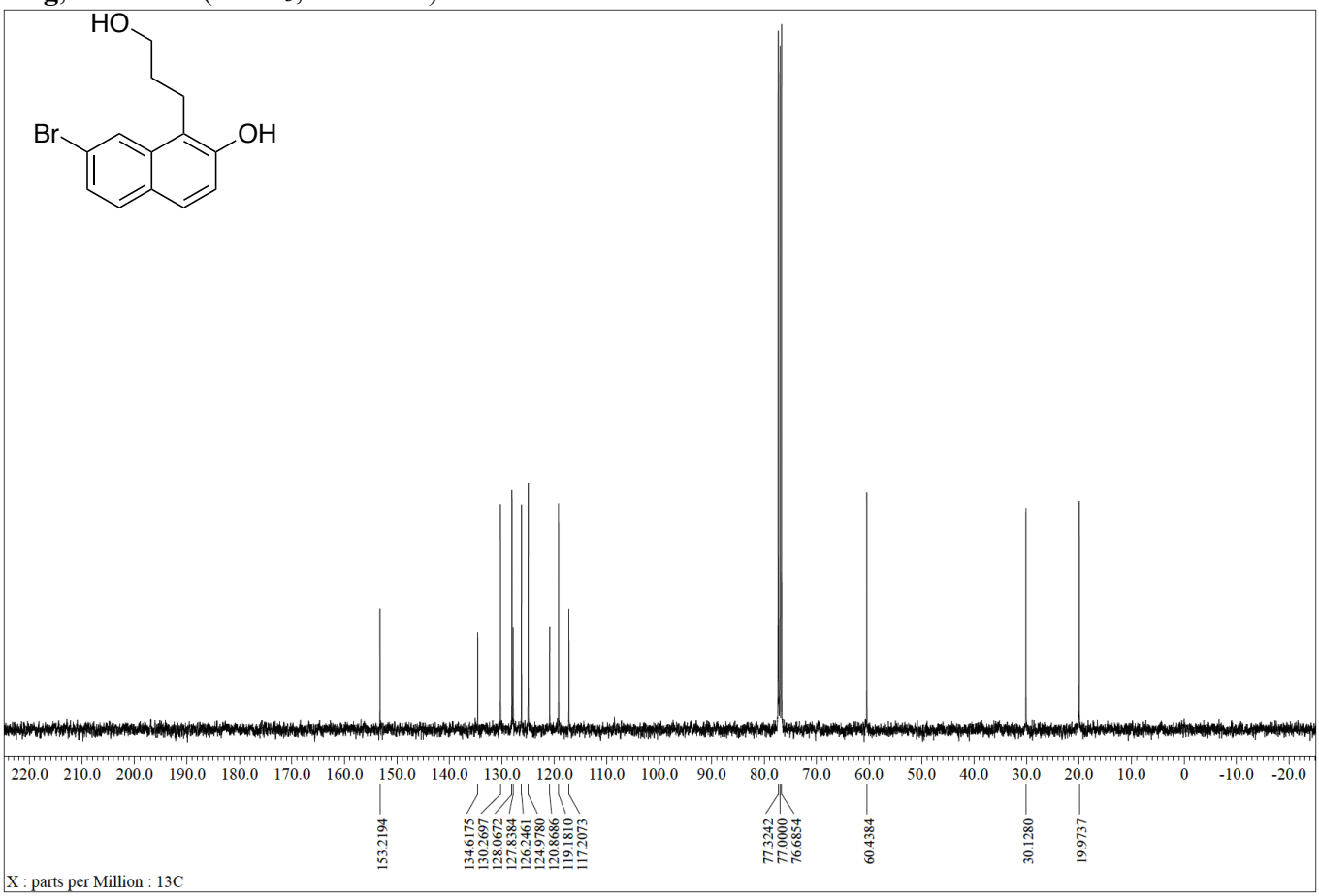
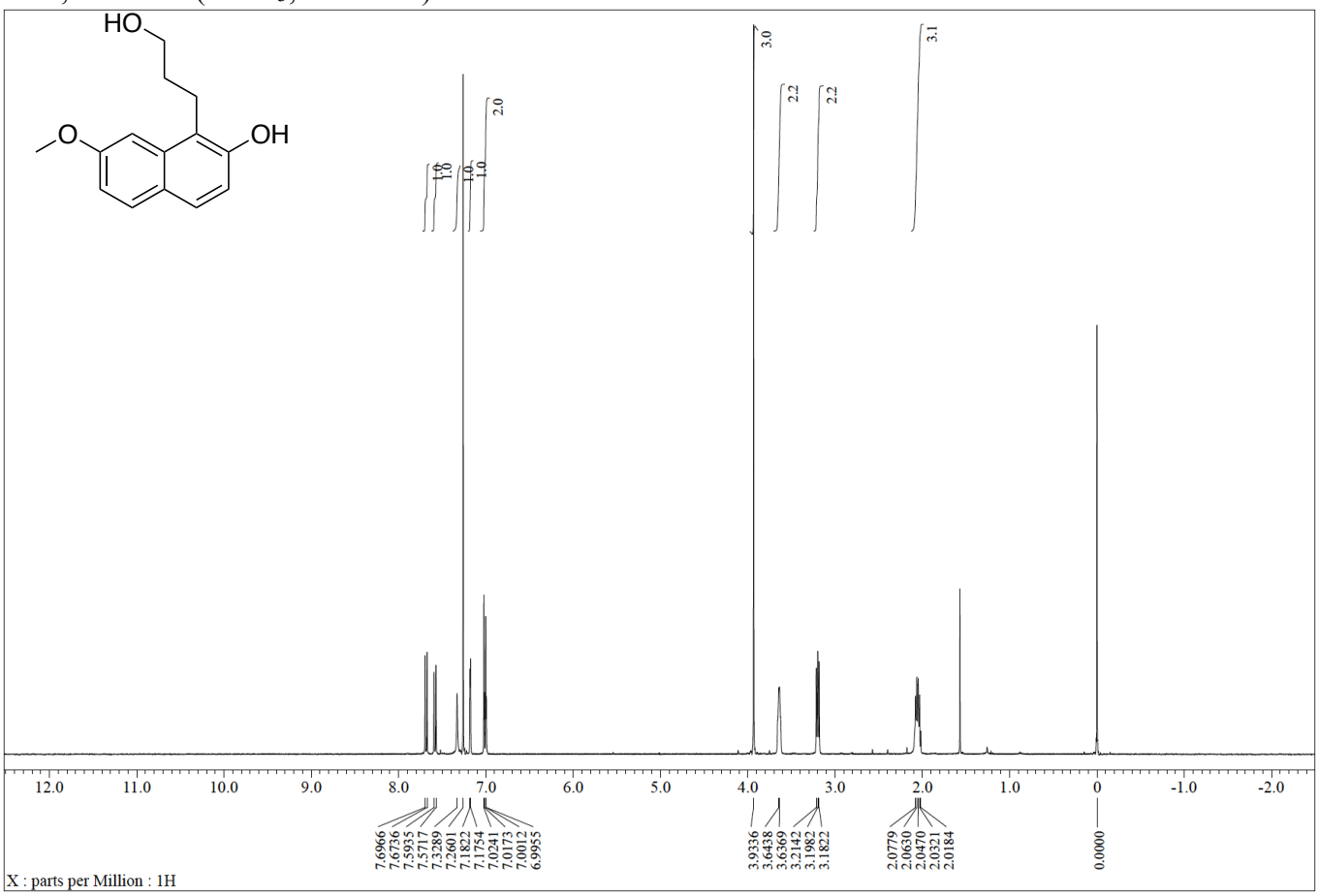


1h, ^{1}H NMR ($CDCl_3$, 400 MHz)



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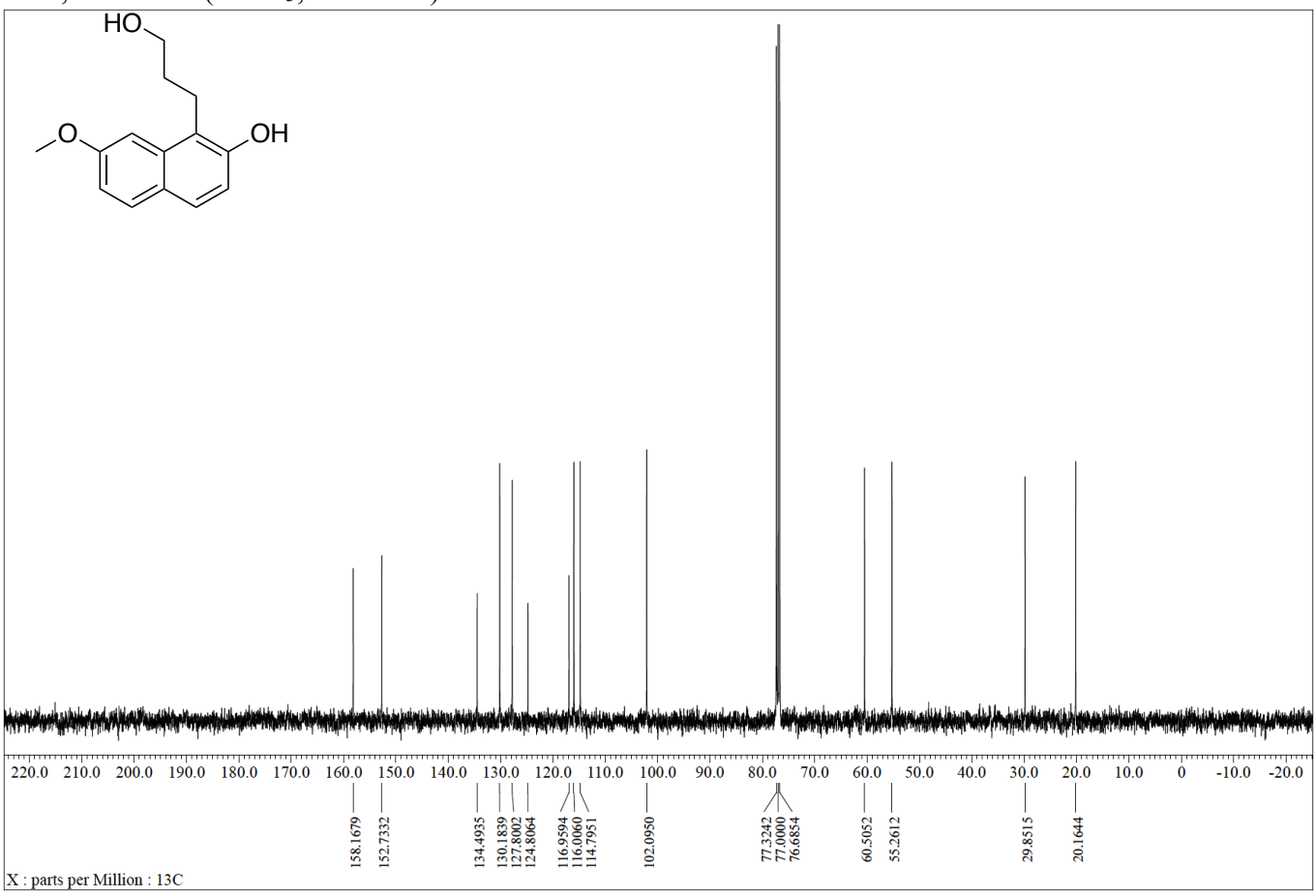
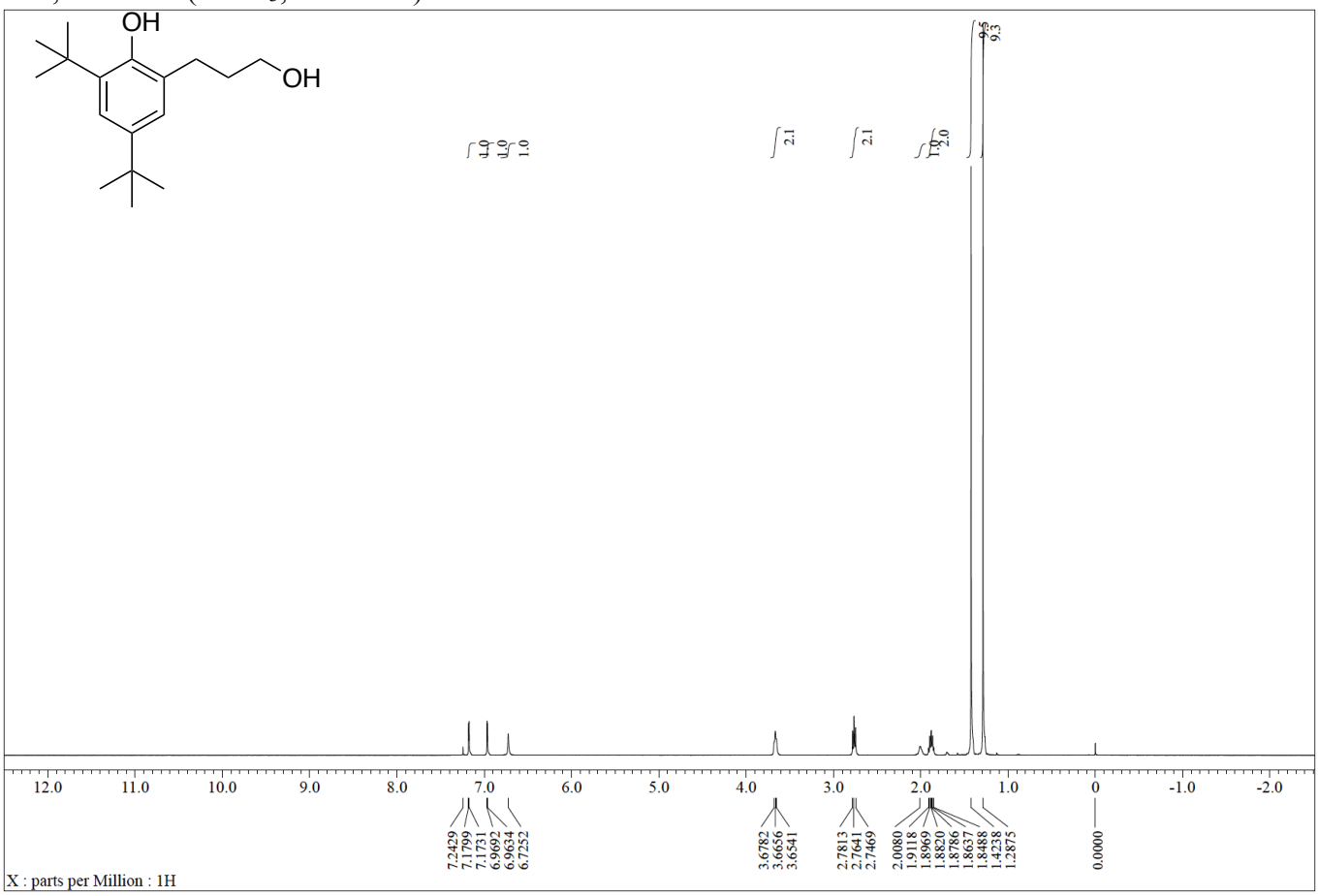
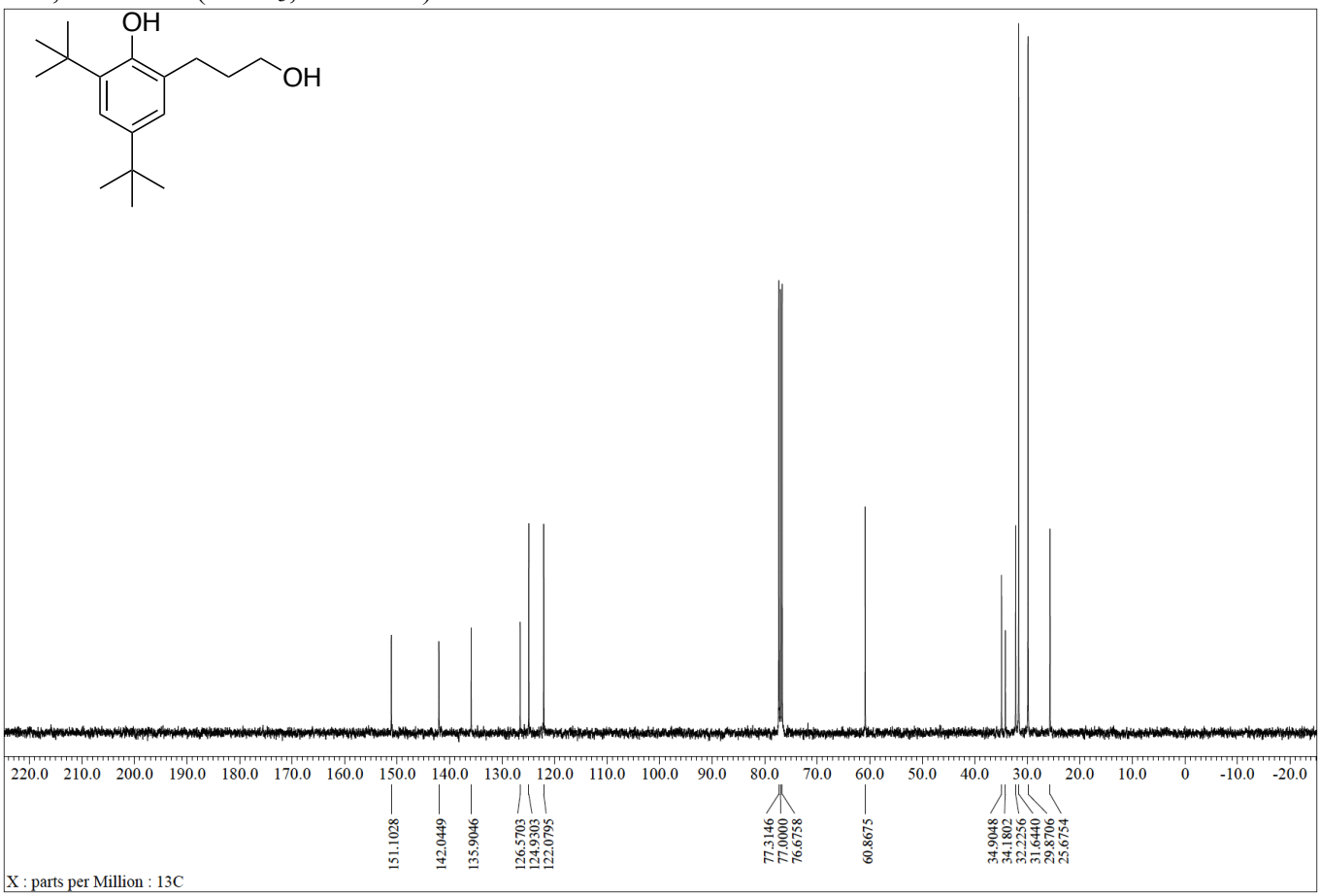


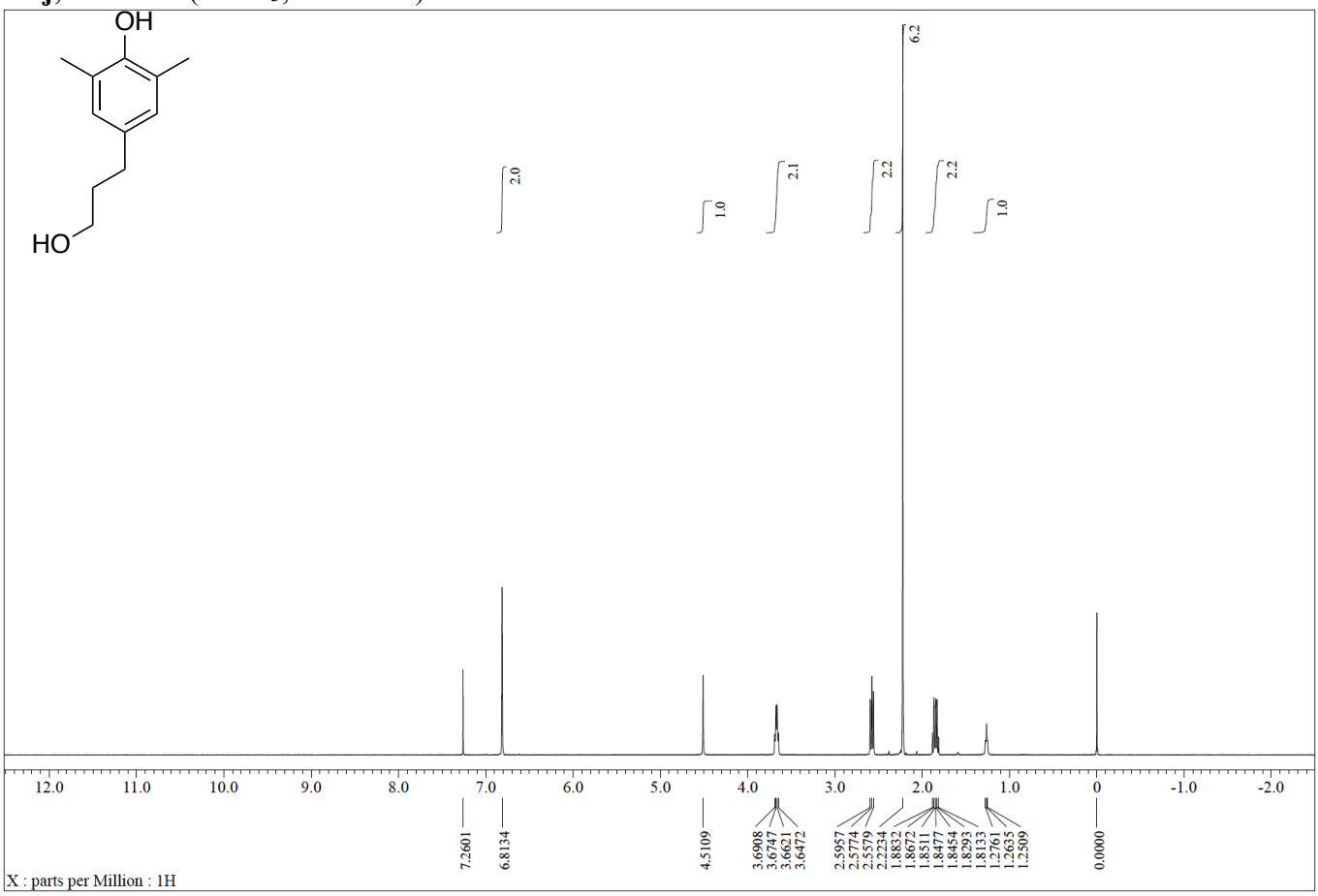
1i, ^{1}H NMR ($CDCl_3$, 400 MHz)



1i, ^{13}C NMR ($CDCl_3$, 100 MHz)



1j, ^{1}H NMR ($CDCl_3$, 400 MHz)



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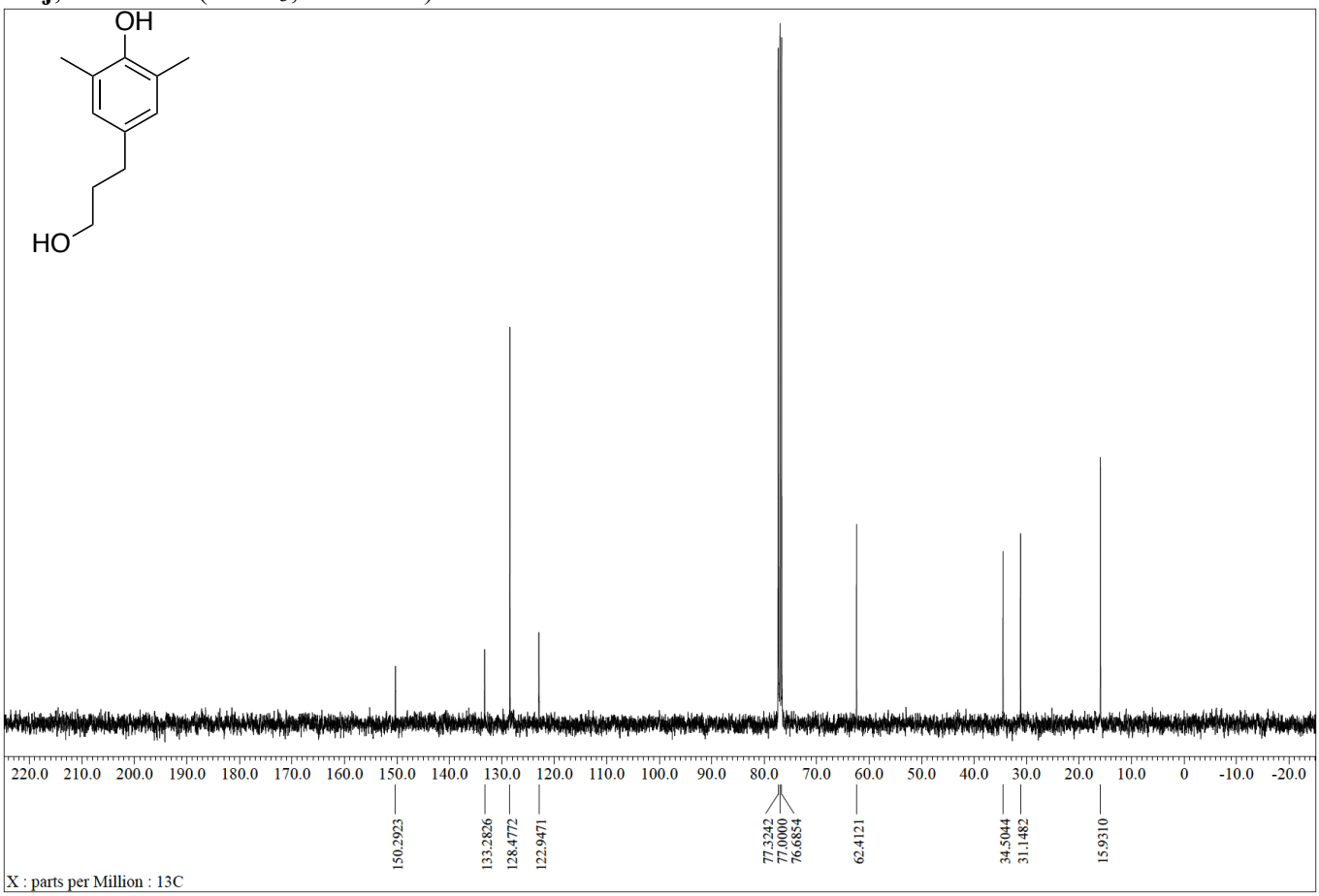
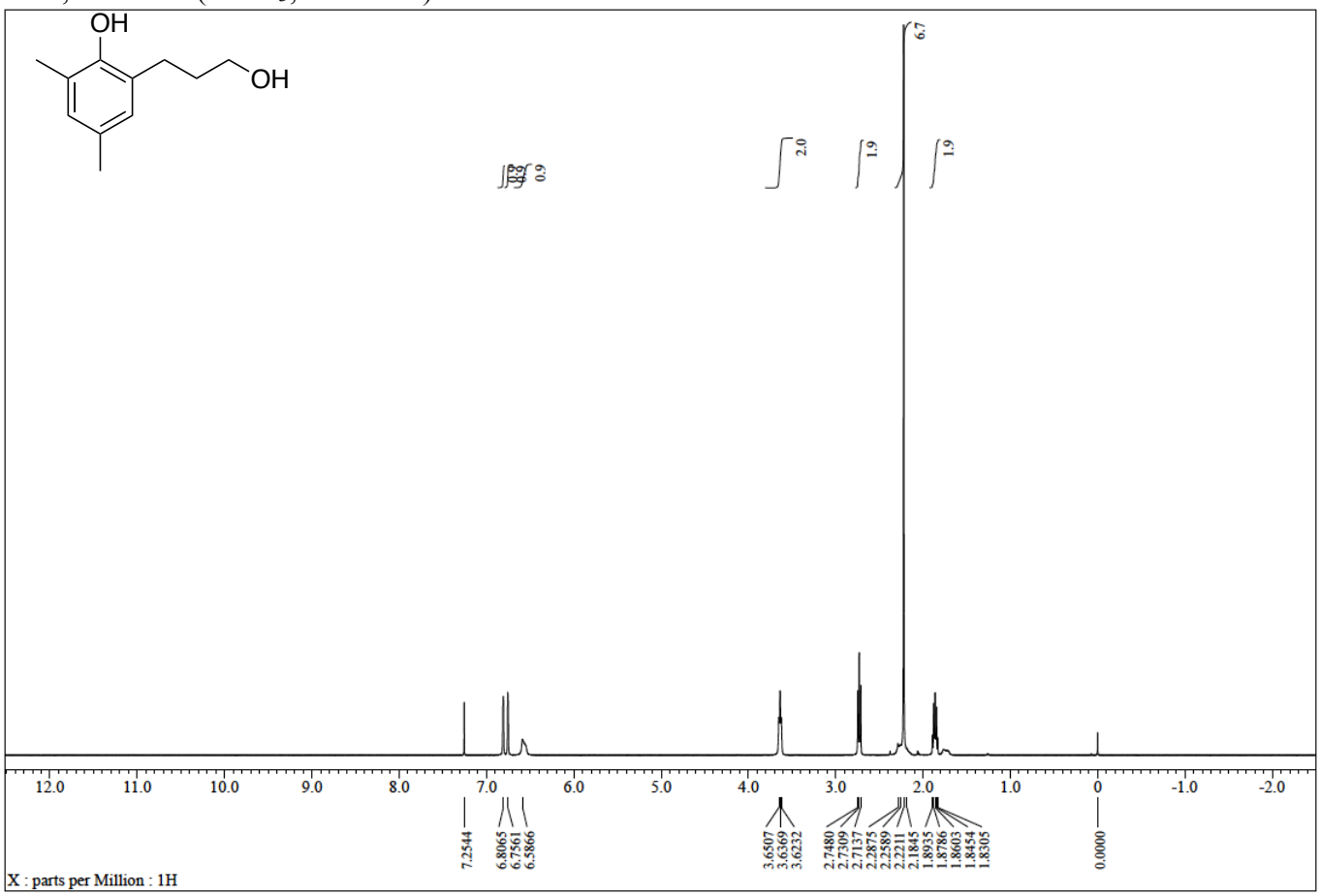
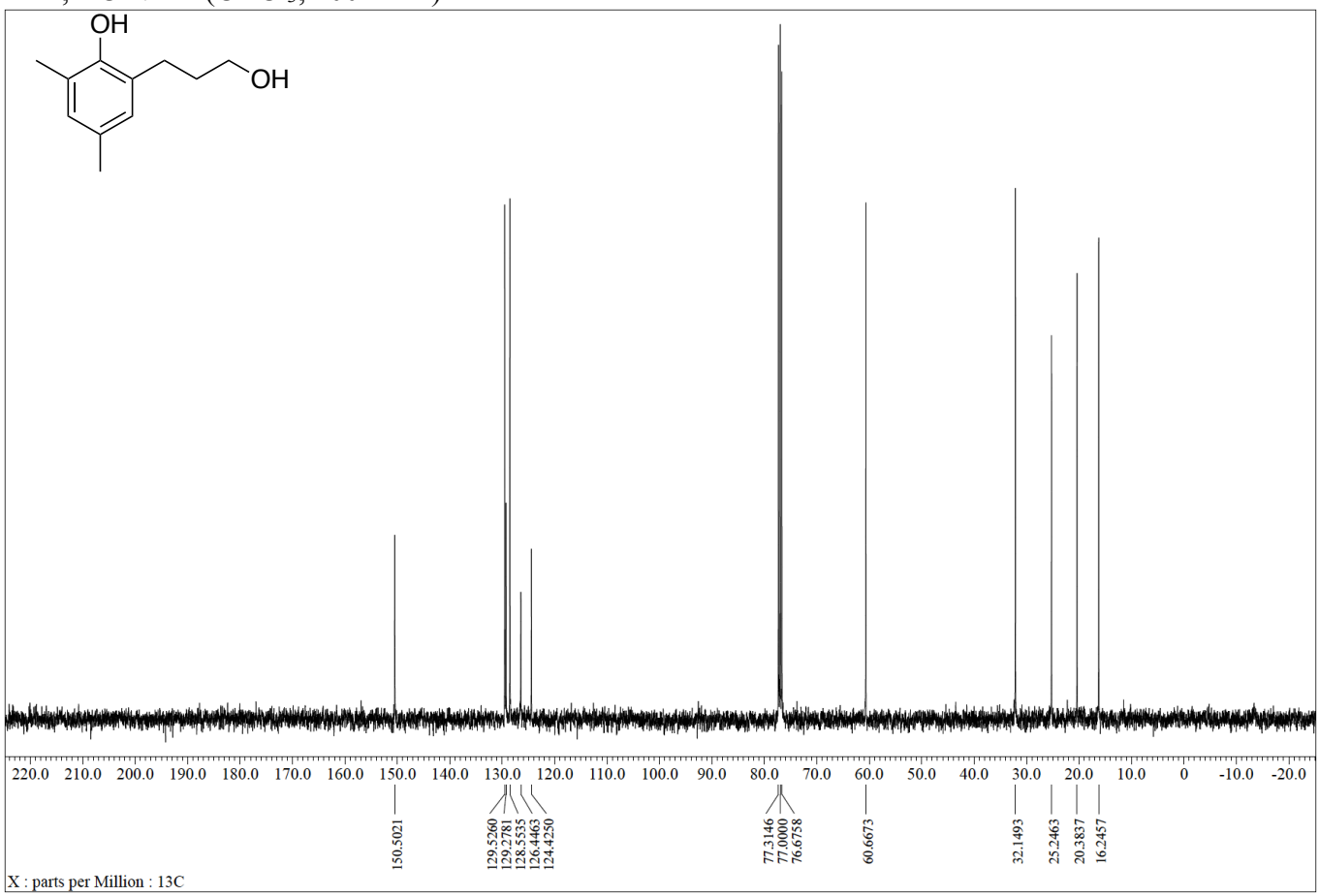


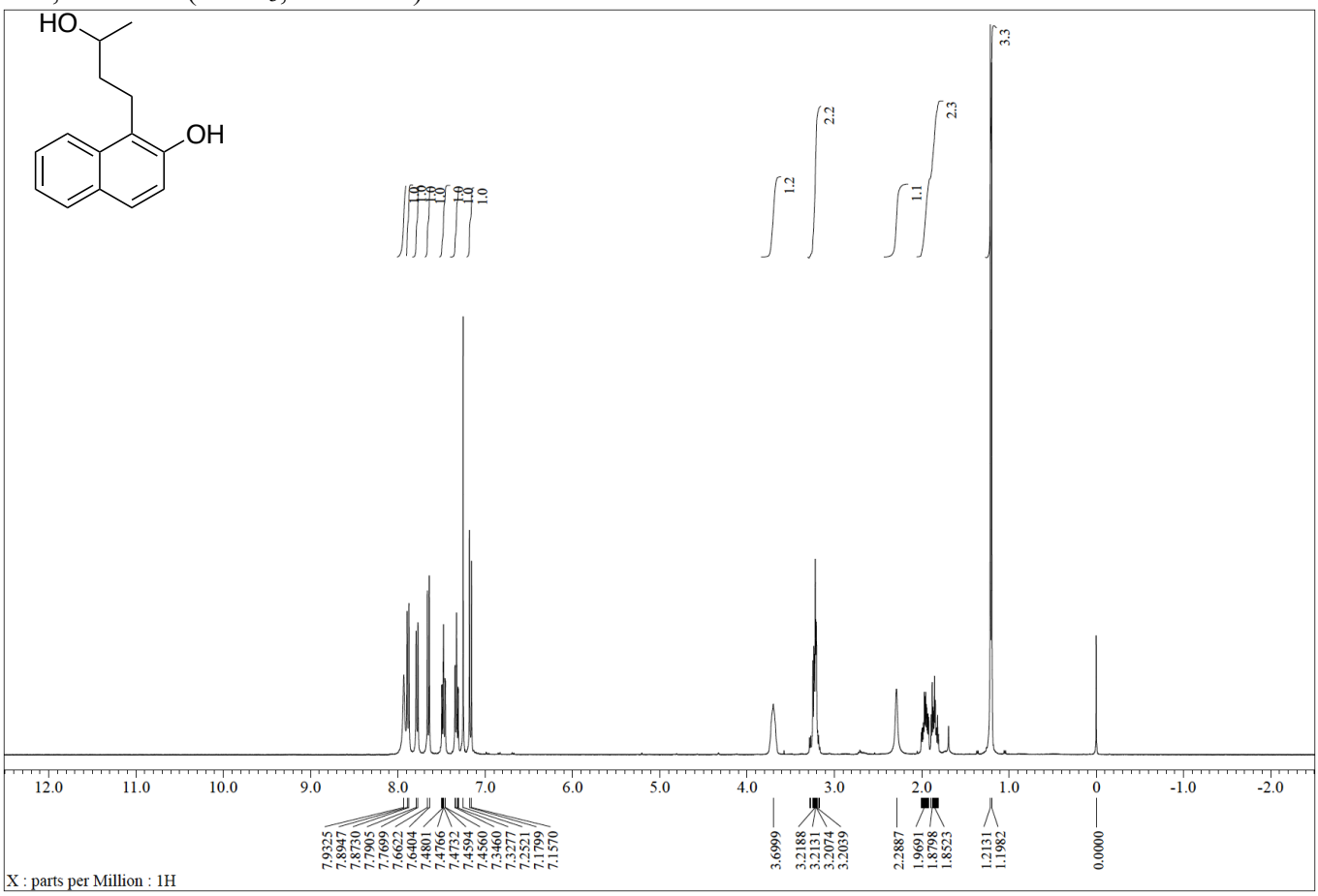
1k, ^{1}H NMR ($CDCl_3$, 400 MHz)



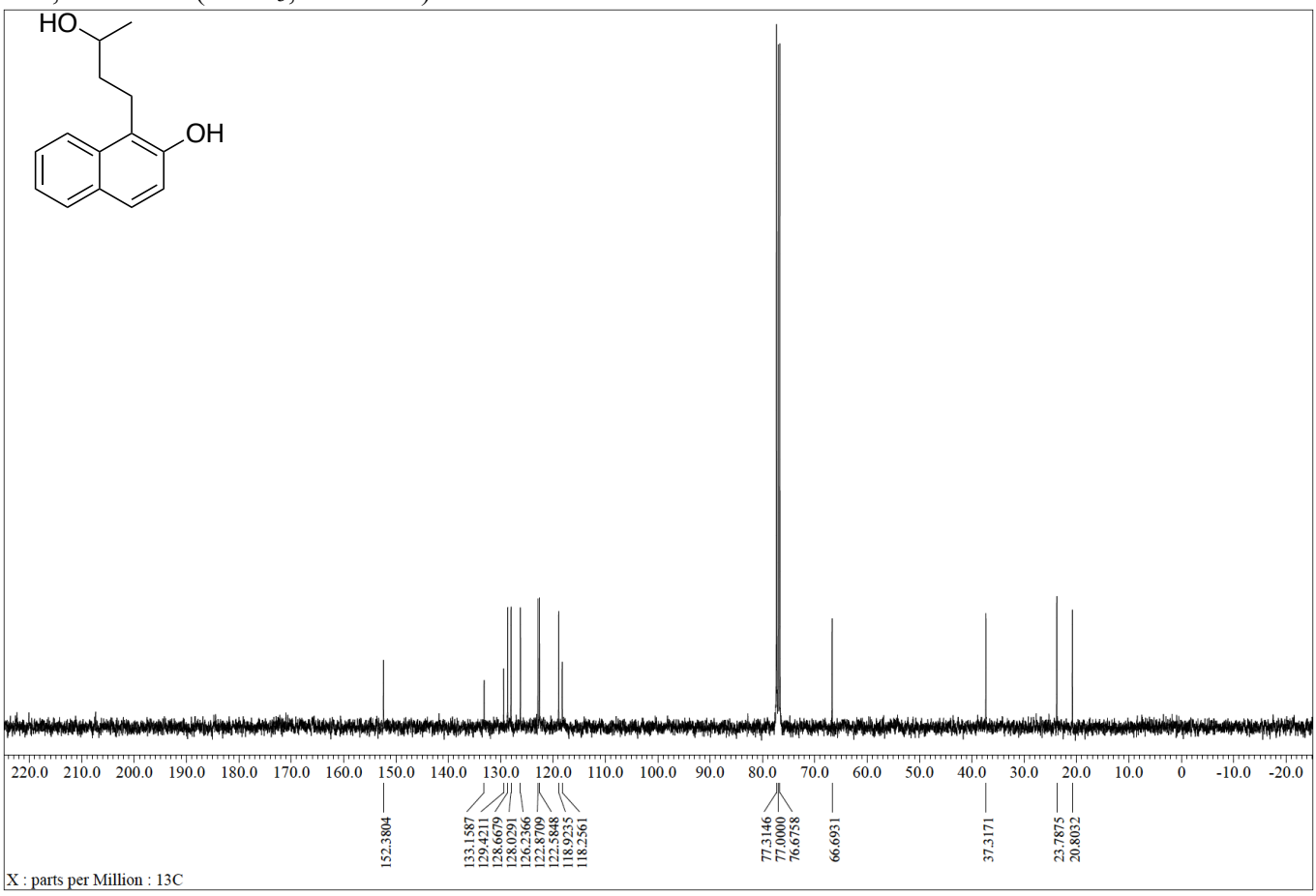
1k, ^{13}C NMR ($CDCl_3$, 100 MHz)



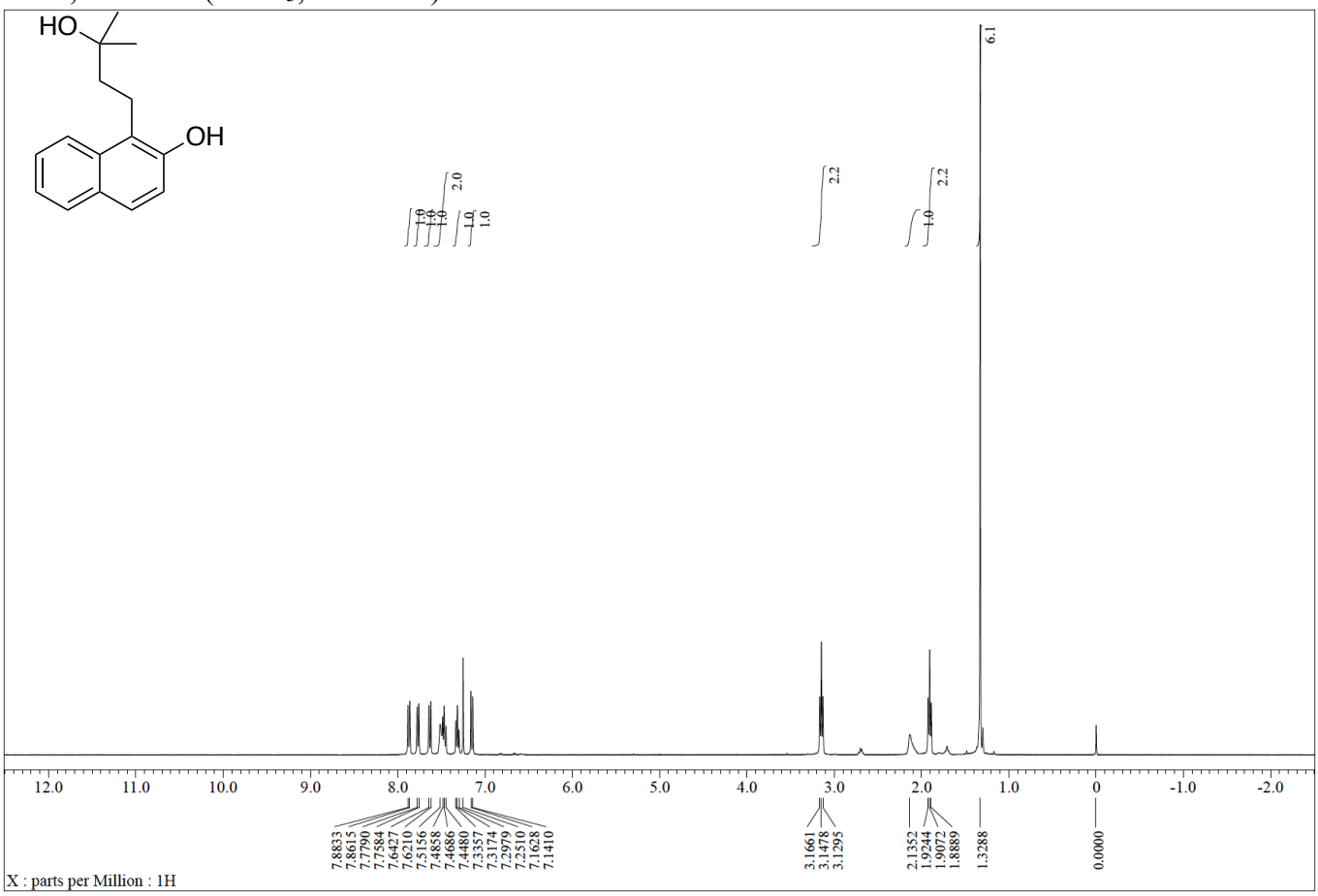
1l, ^{1}H NMR ($CDCl_3$, 400 MHz)



1l, ^{13}C NMR ($CDCl_3$, 100 MHz)



1m, ^{1}H NMR ($CDCl_3$, 400 MHz)



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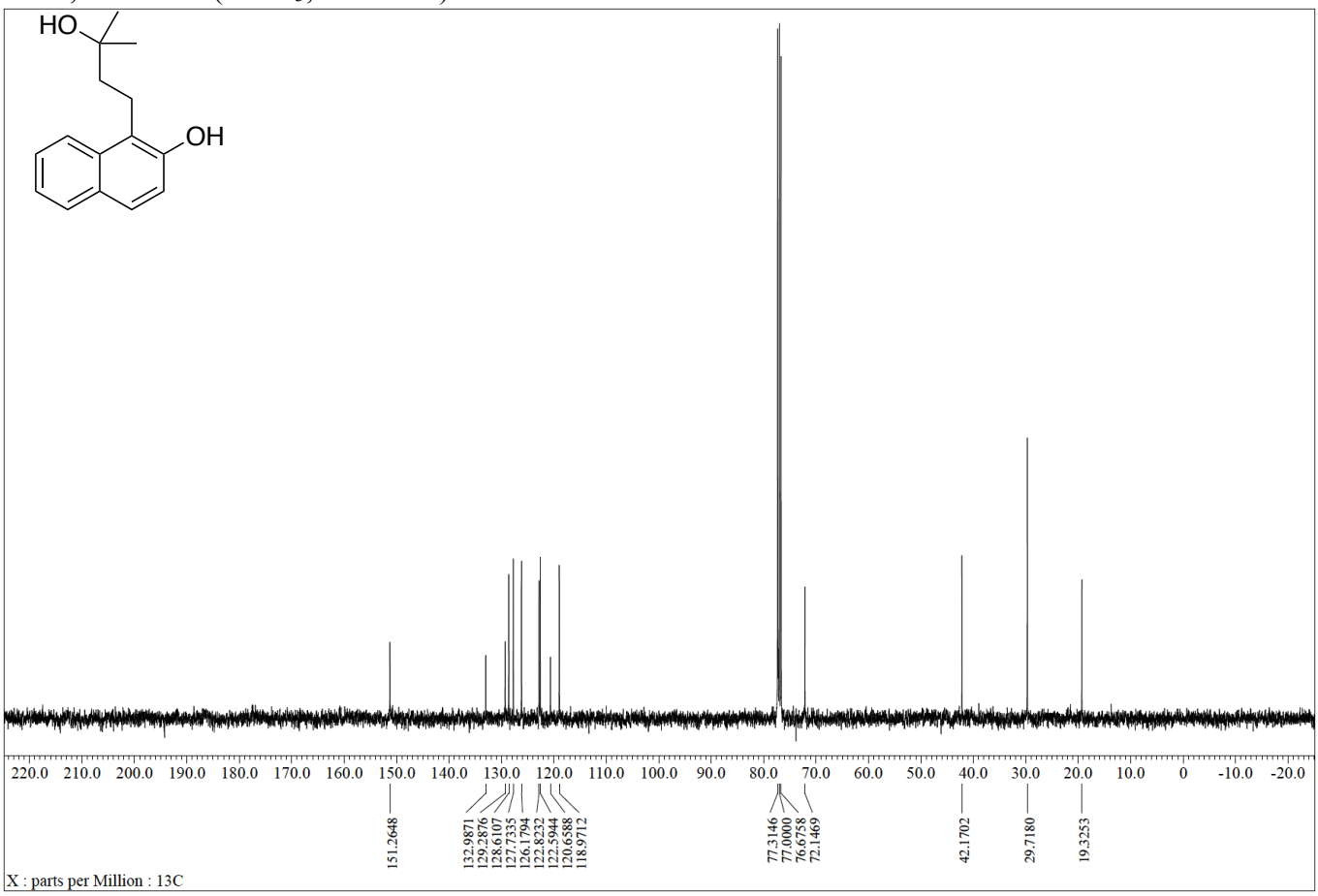
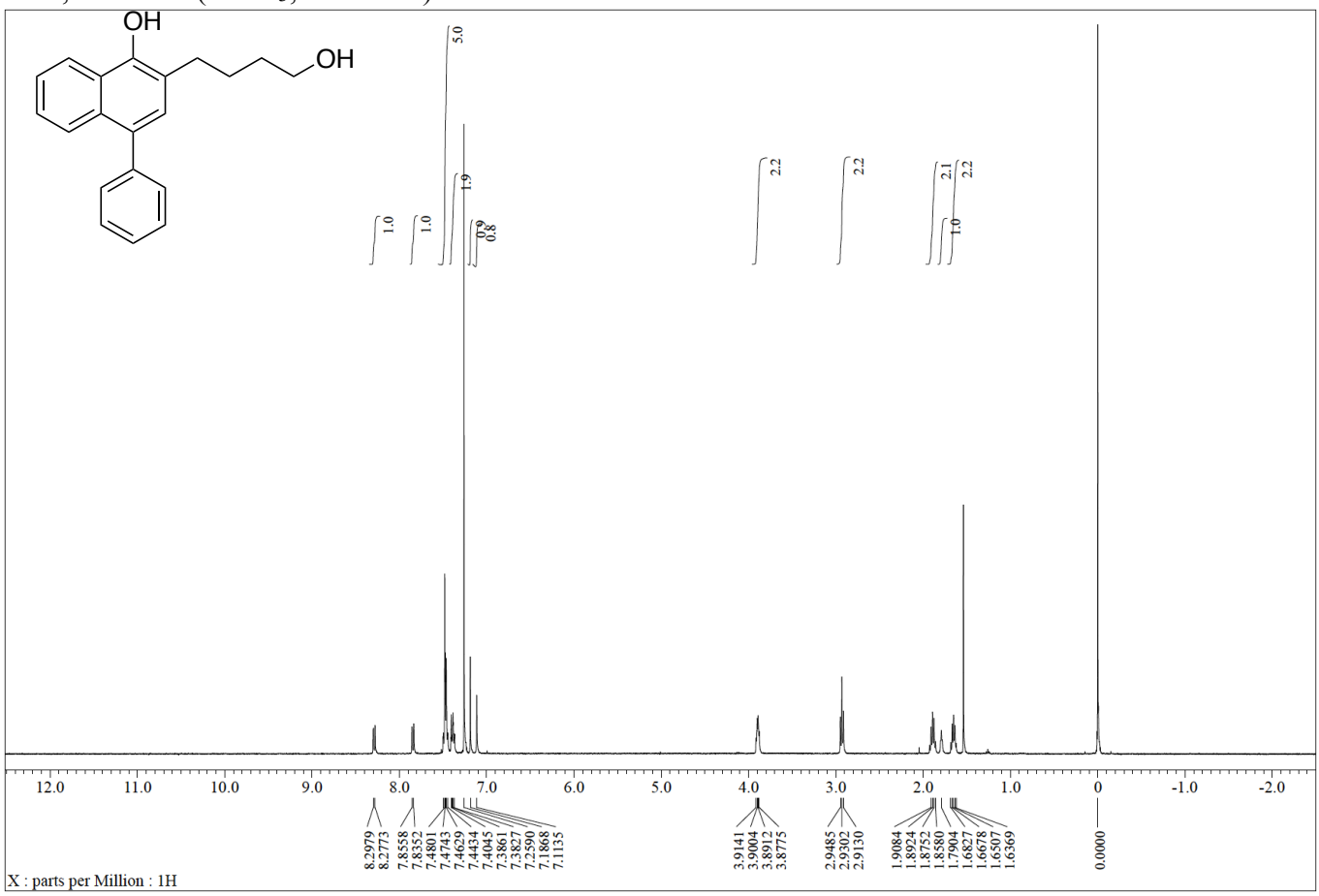
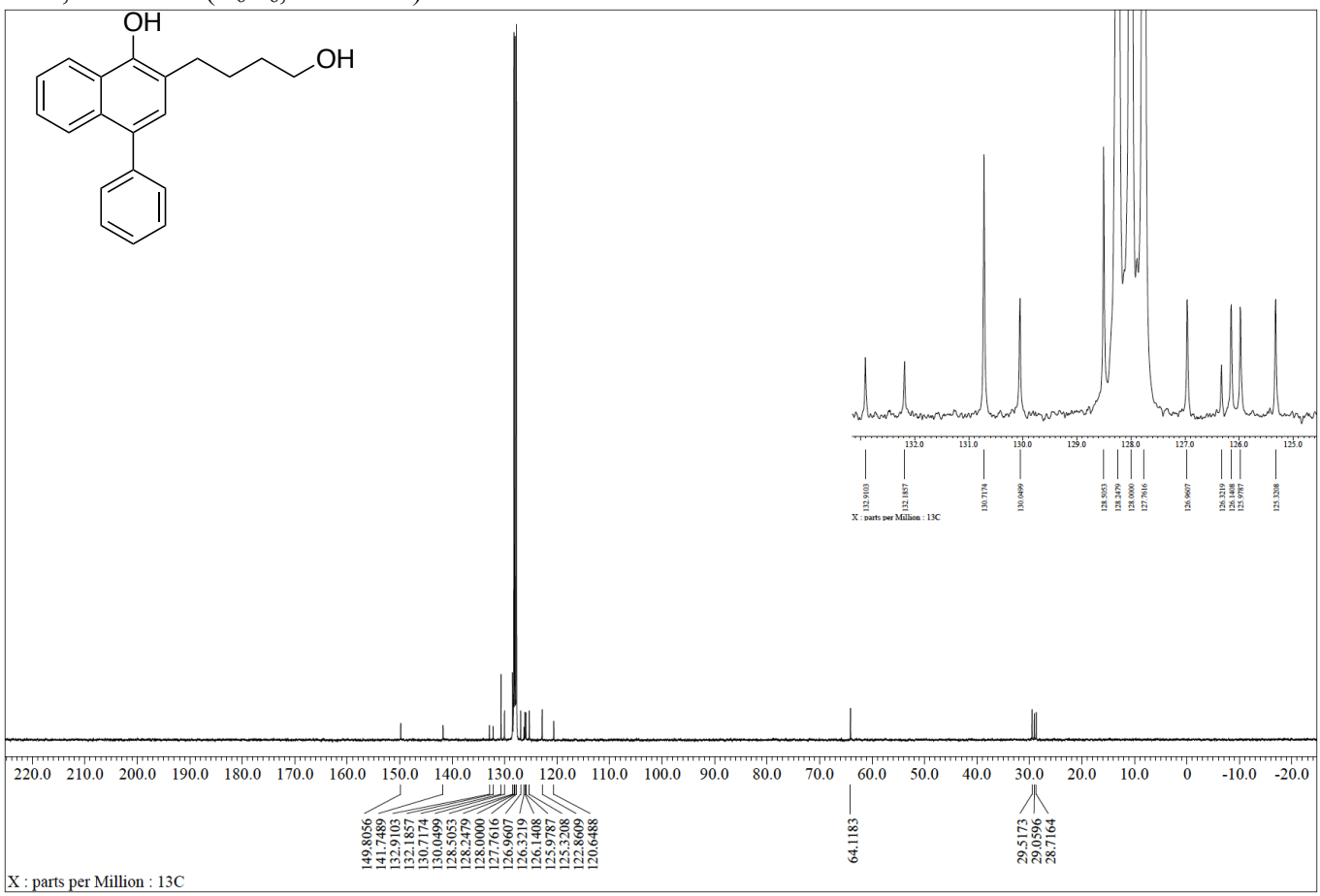


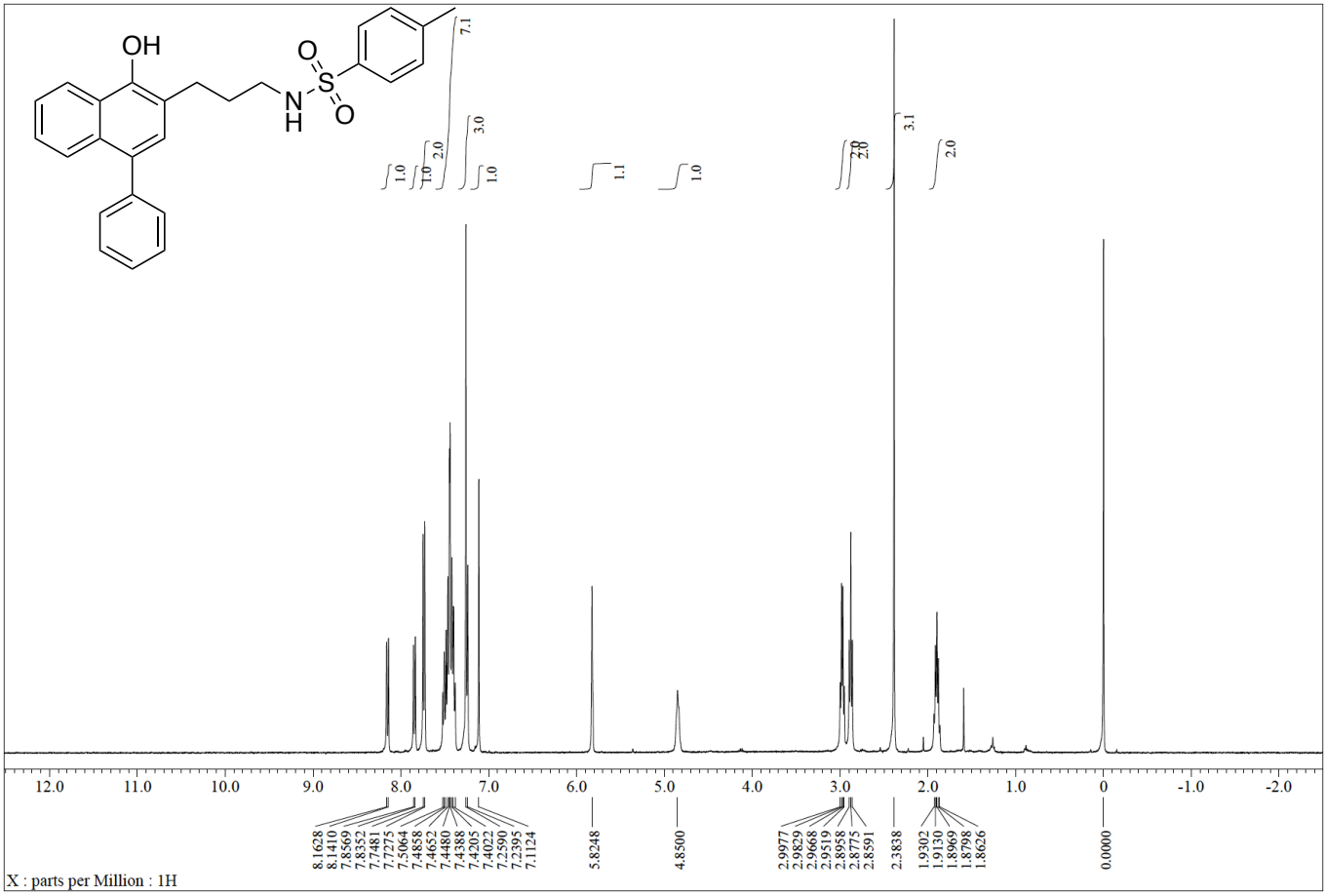
1n, ^{1}H NMR ($CDCl_3$, 400 MHz)



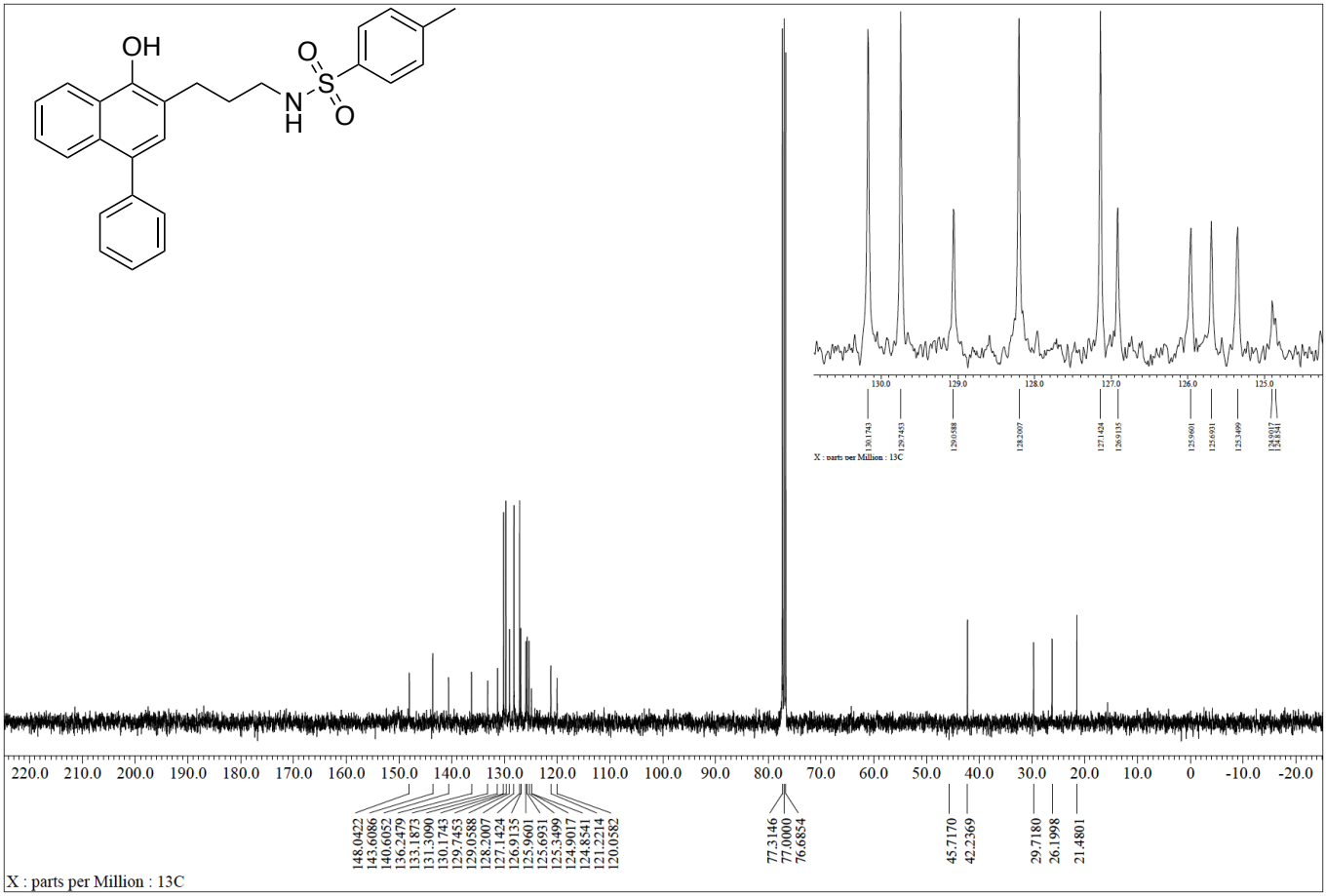
1n, ^{13}C NMR (C_6D_6, 100 MHz)



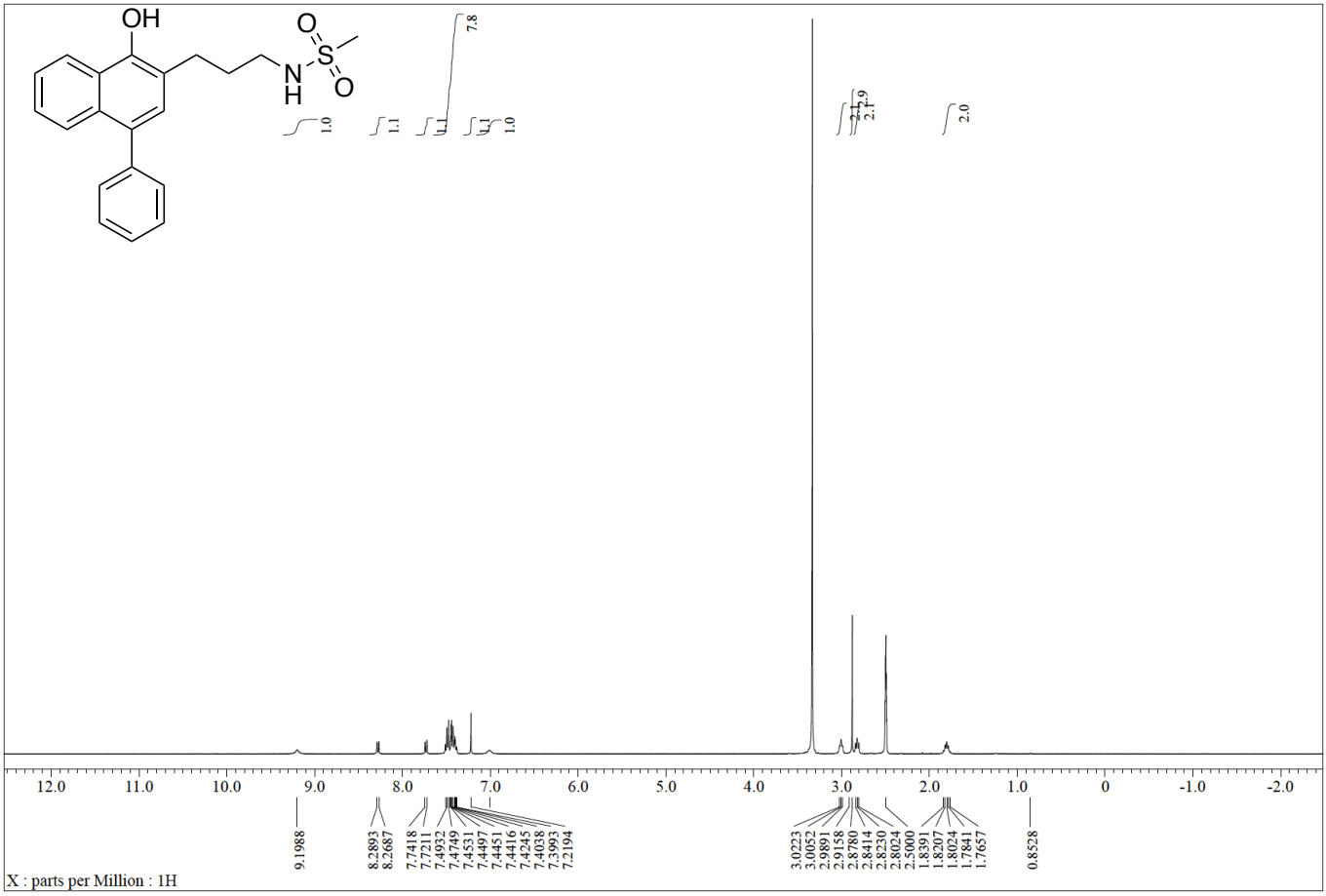
3a, ^{1}H NMR ($CDCl_3$, 400 MHz)



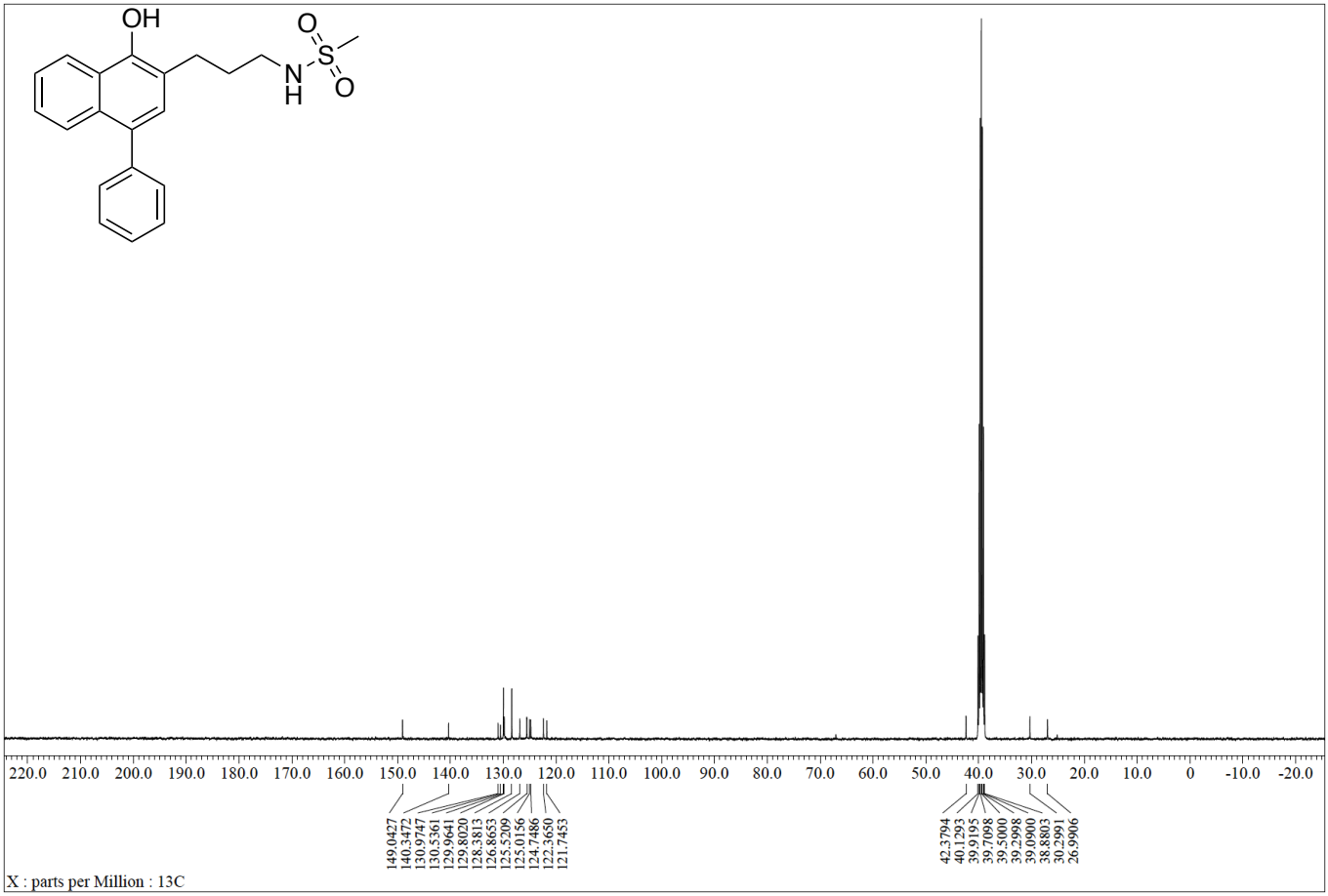
3a, ^{13}C NMR ($CDCl_3$, 100 MHz)



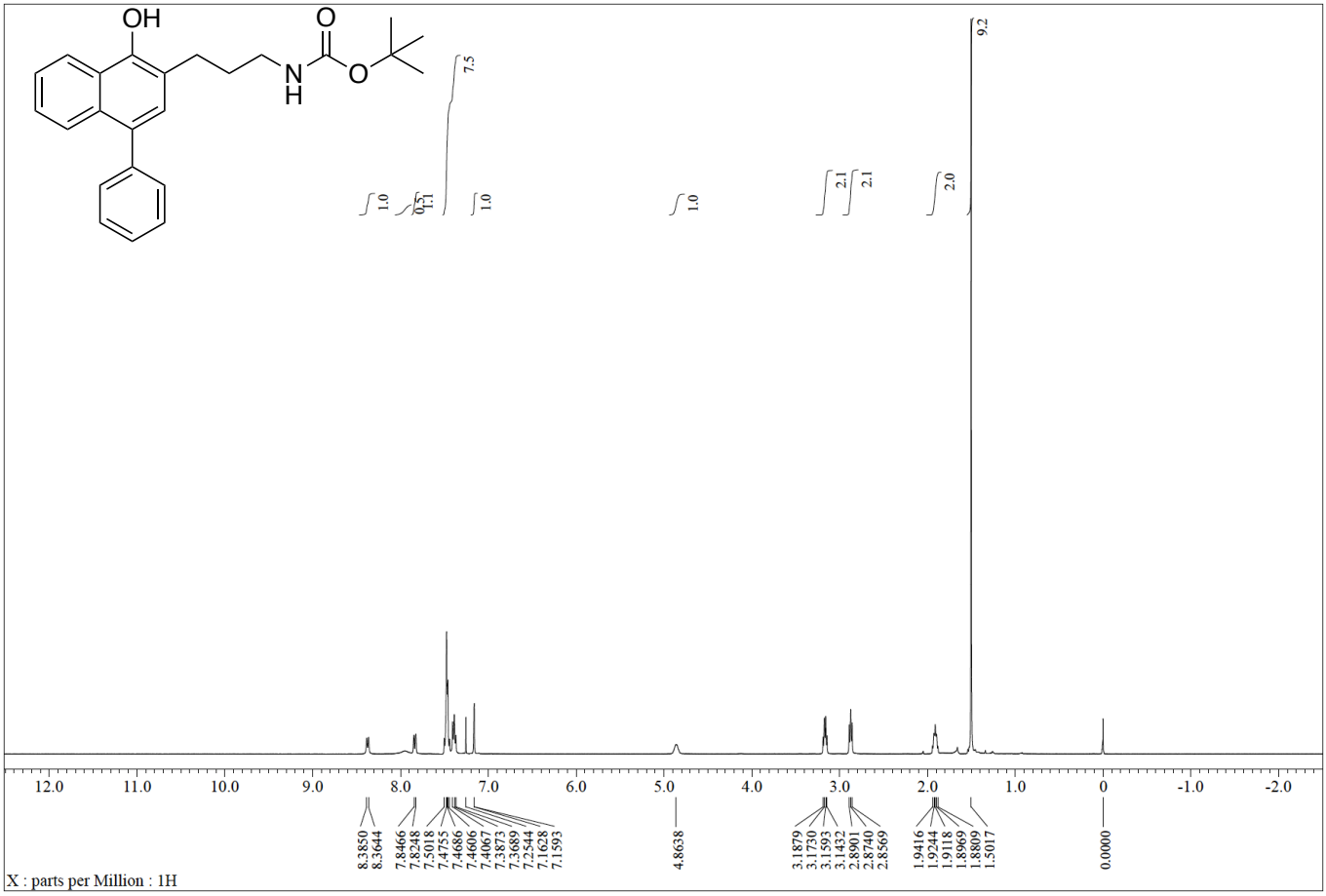
3aa, ^{1}H NMR (DMSO-d_6, 400 MHz)



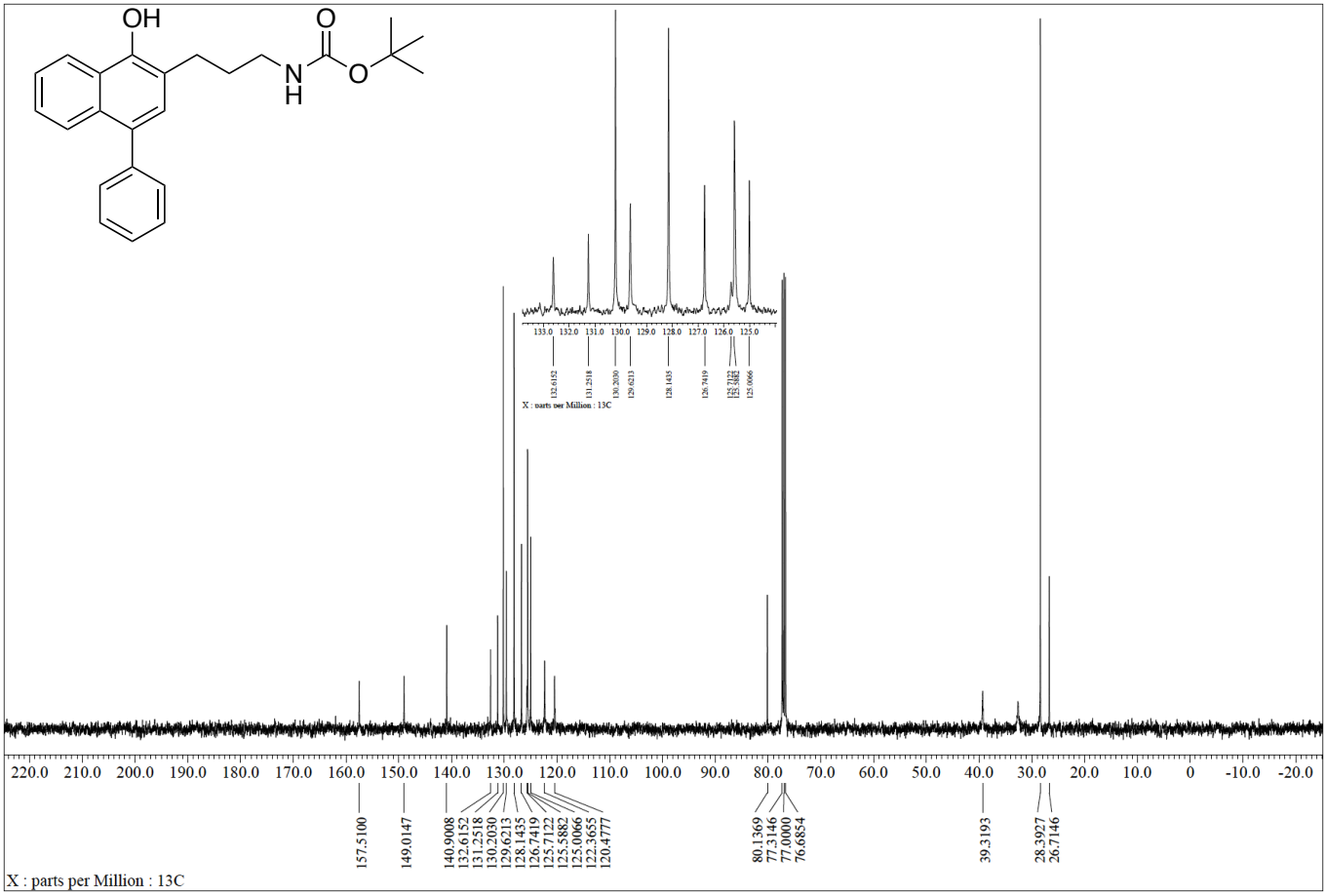
3aa, ^{13}C NMR (DMSO-d_6, 100 MHz)



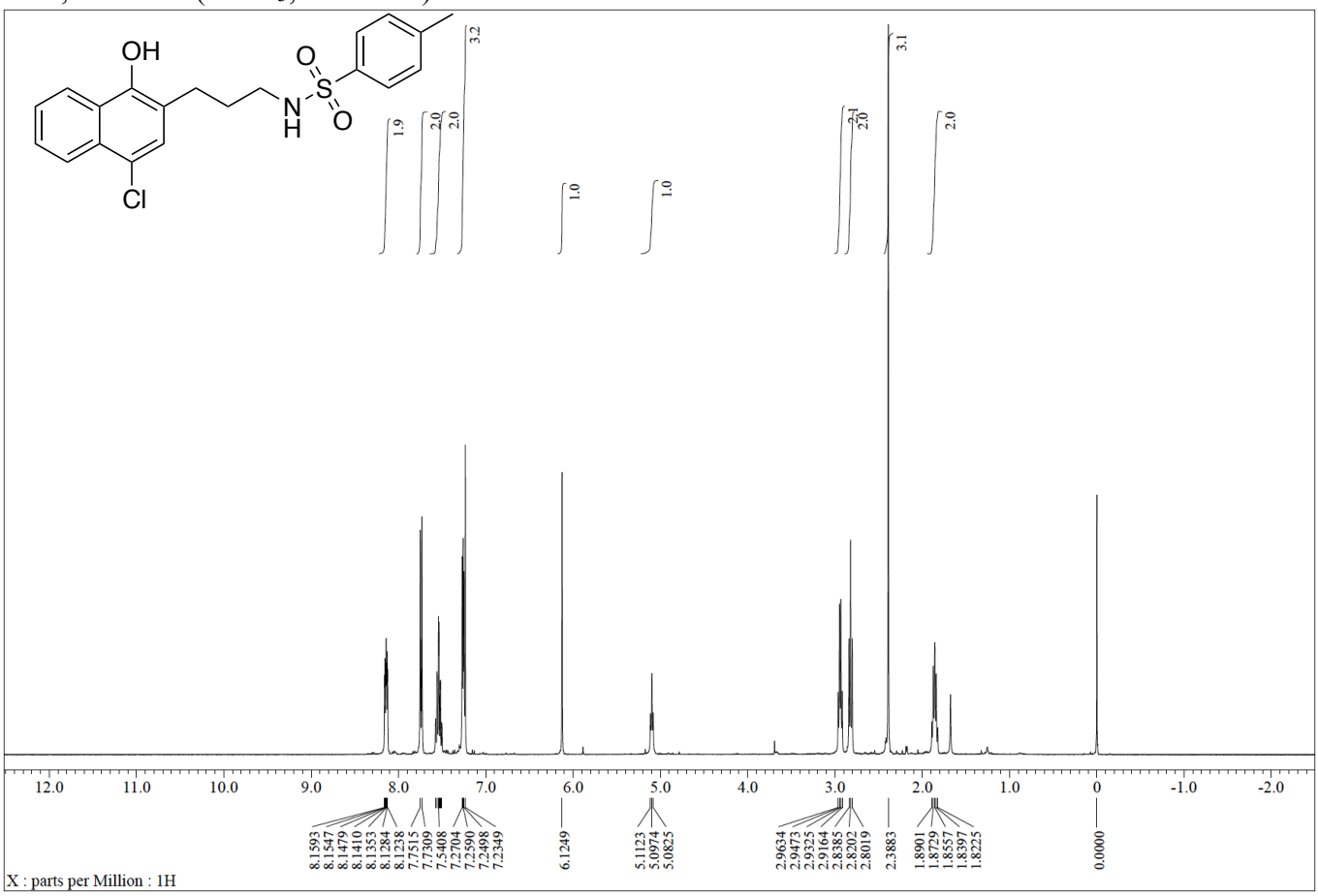
3ab, ^{1}H NMR ($CDCl_3$, 400 MHz)



3ab, ^{13}C NMR ($CDCl_3$, 100 MHz)



3b, ^{1}H NMR ($CDCl_3$, 400 MHz)



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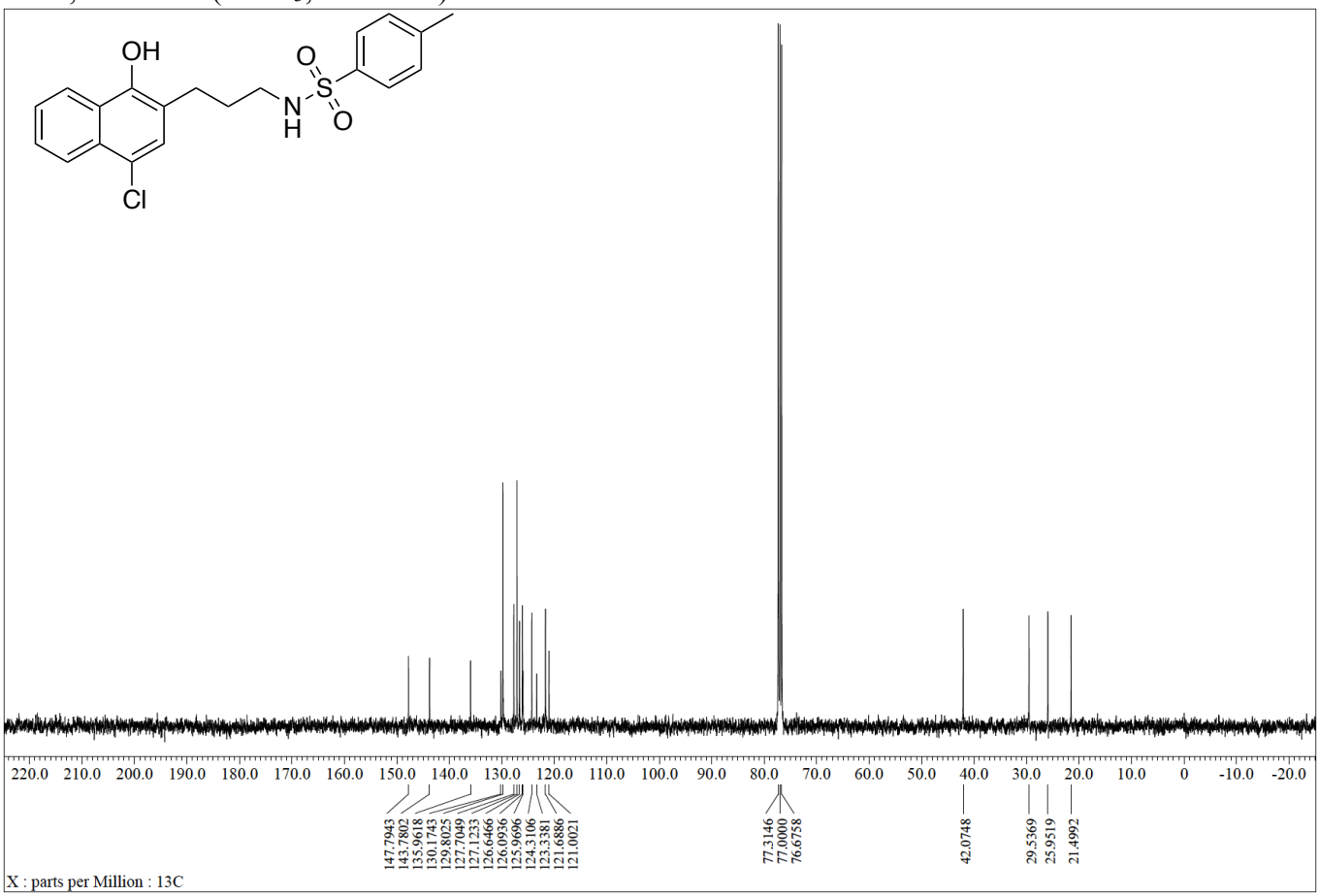
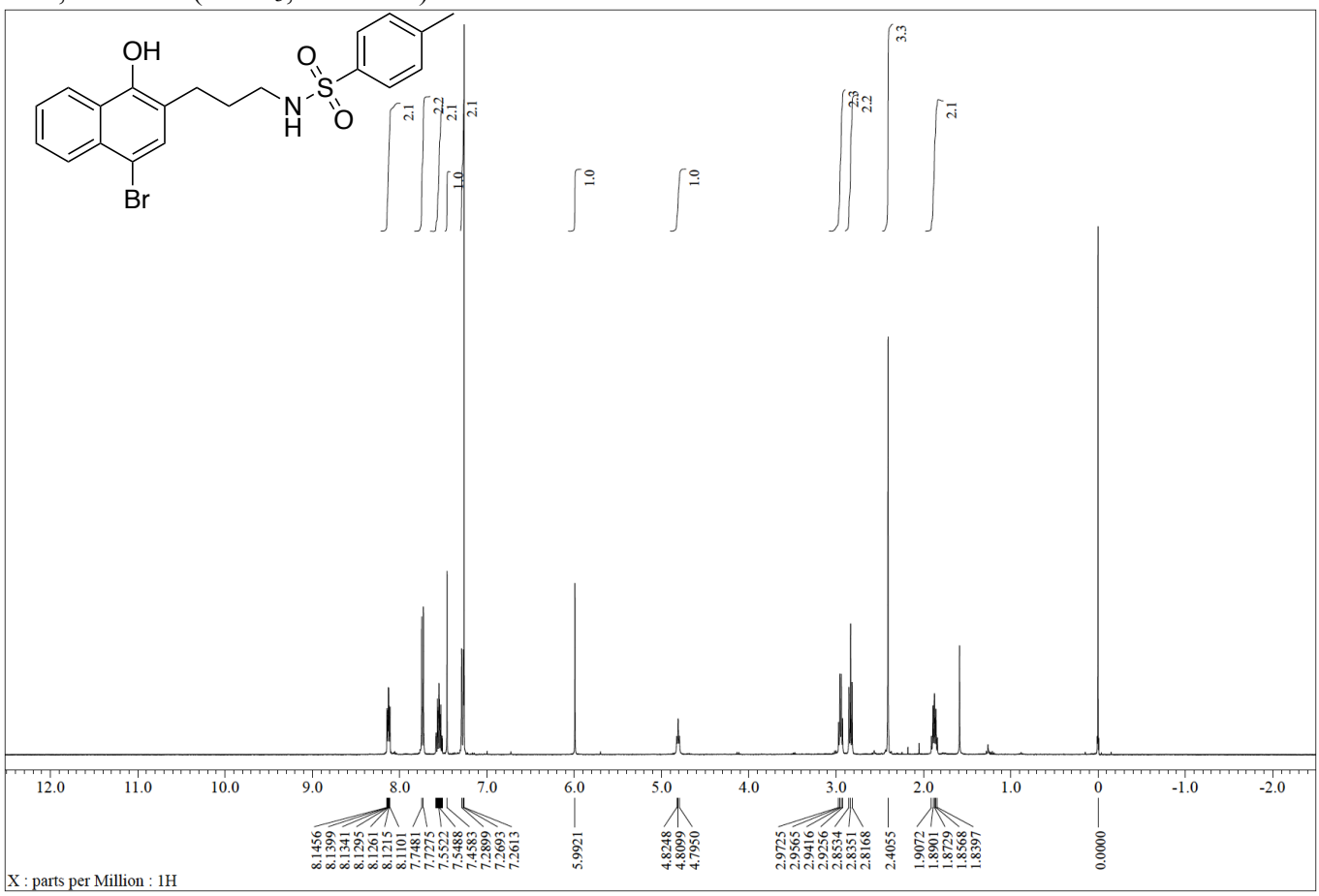
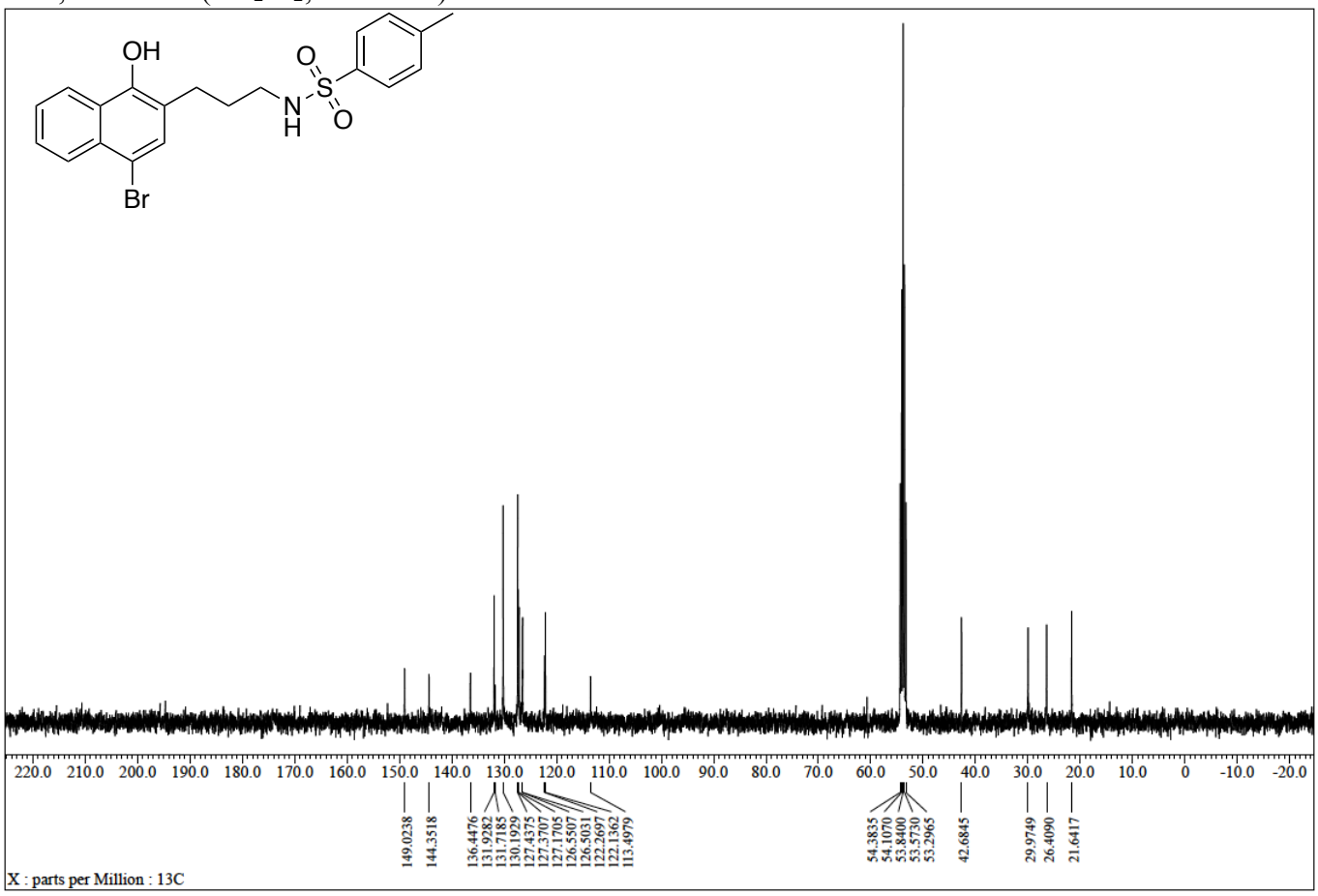


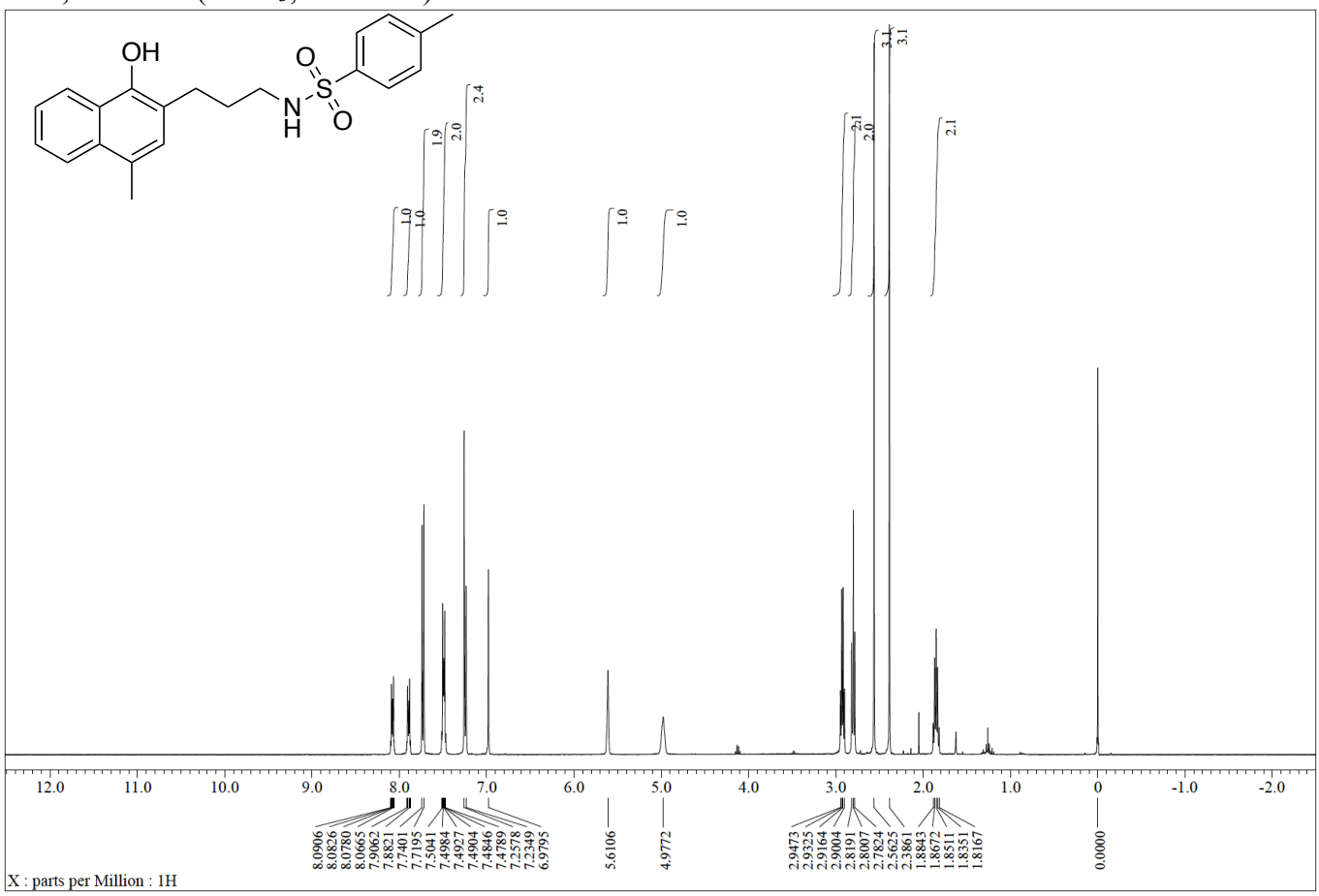
3c, ^{1}H NMR ($CDCl_3$, 400 MHz)



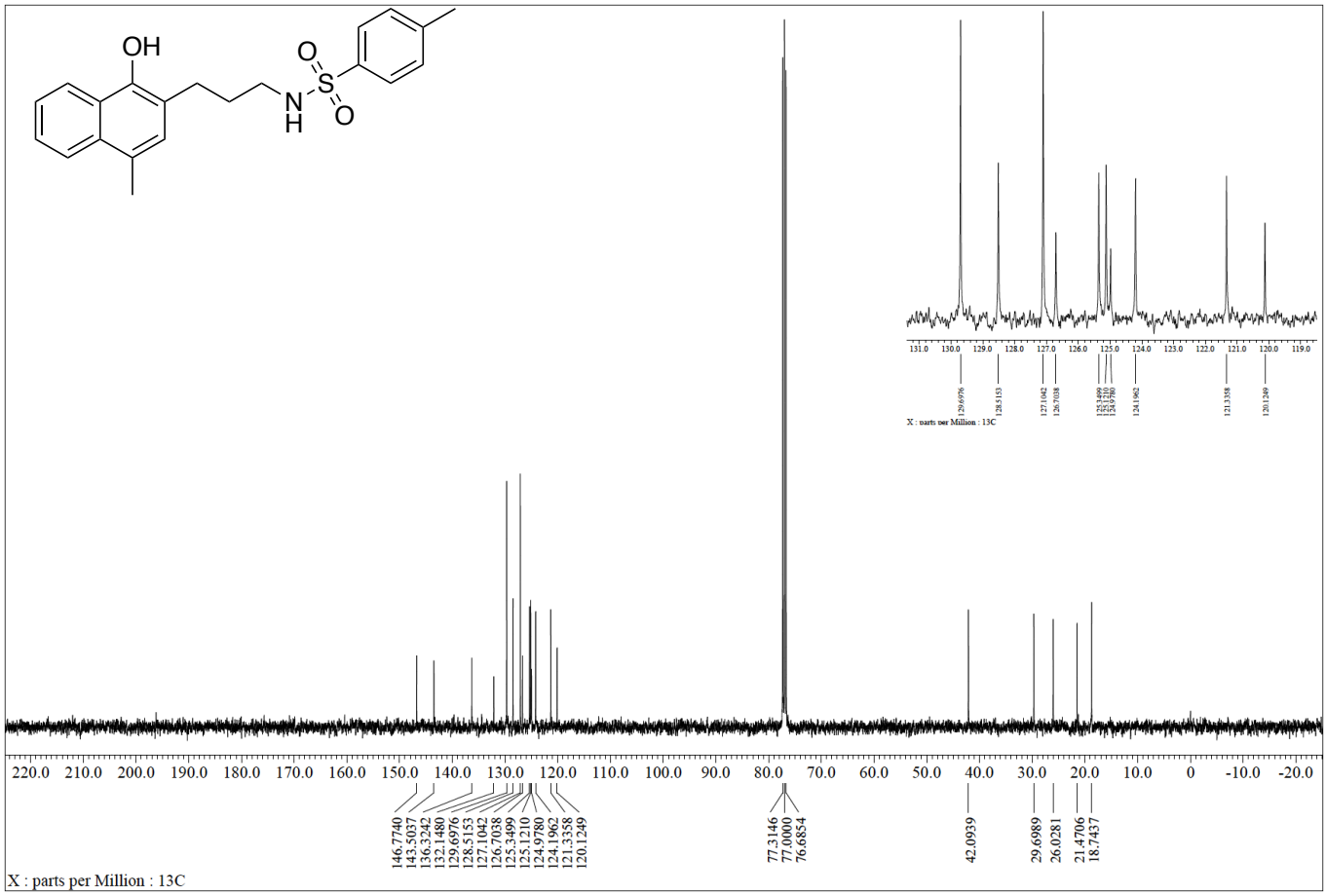
3c, ^{13}C NMR (CD_2Cl_2, 100 MHz)



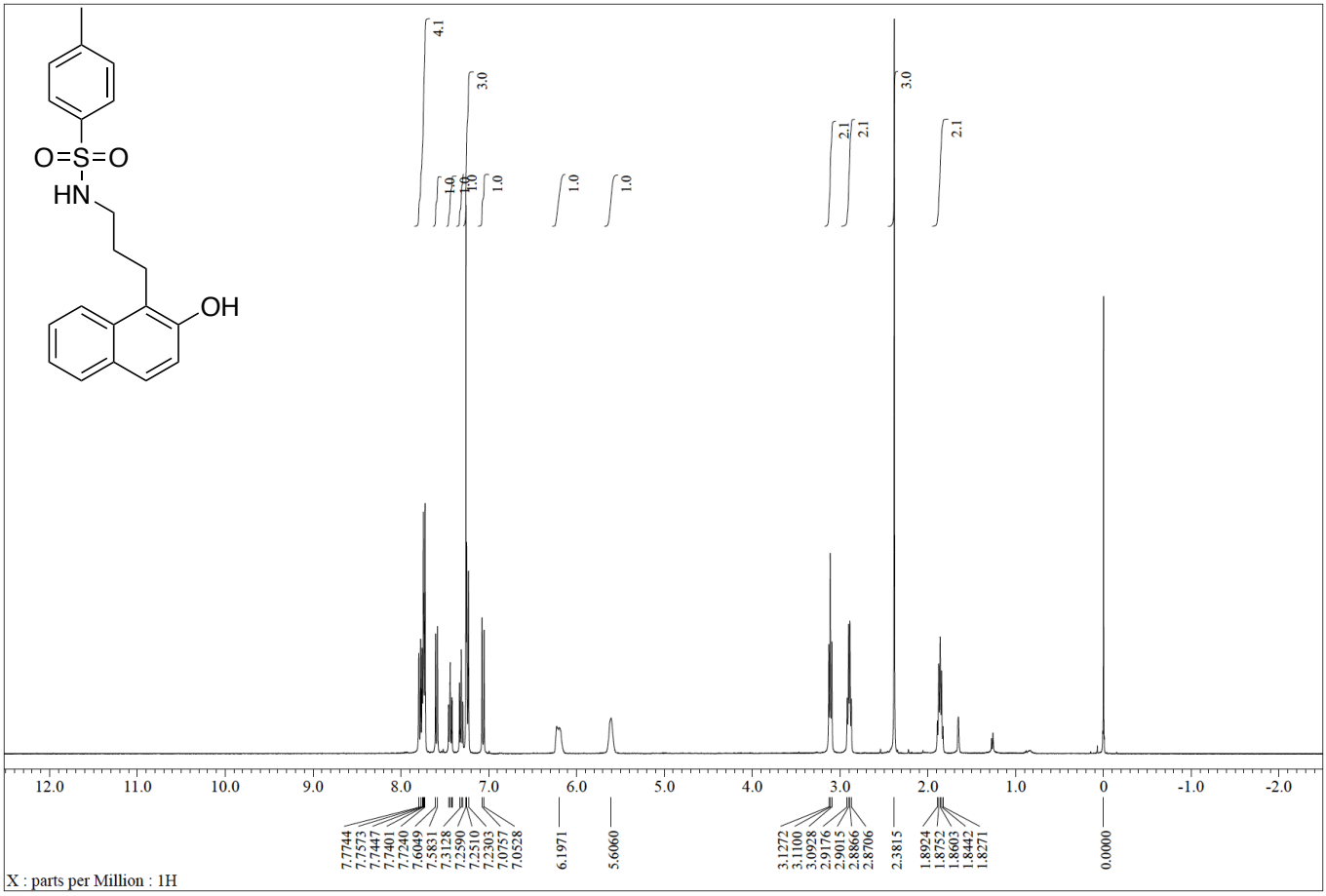
3d, ^{1}H NMR ($CDCl_3$, 400 MHz)



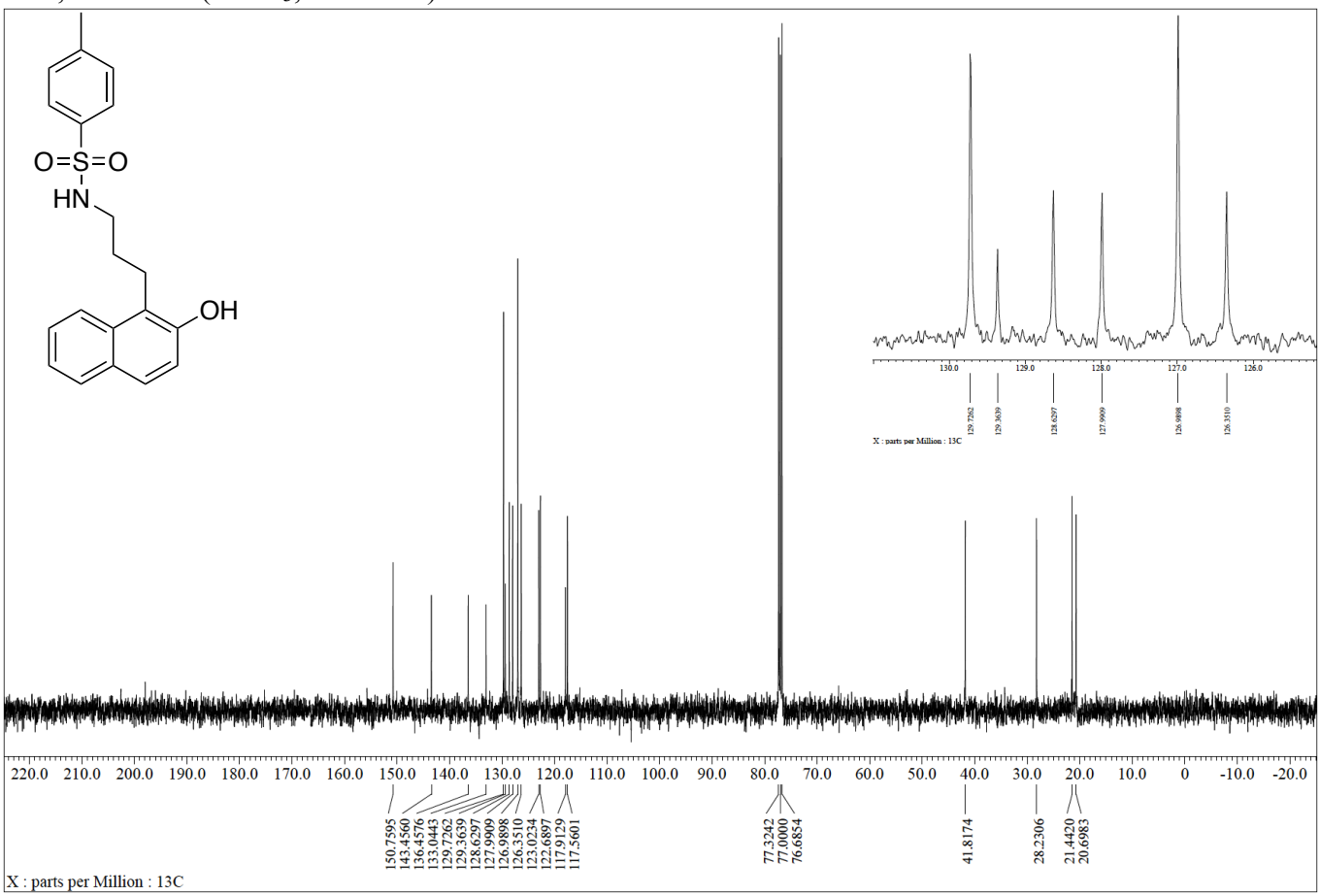
3d, ^{13}C NMR ($CDCl_3$, 100 MHz)



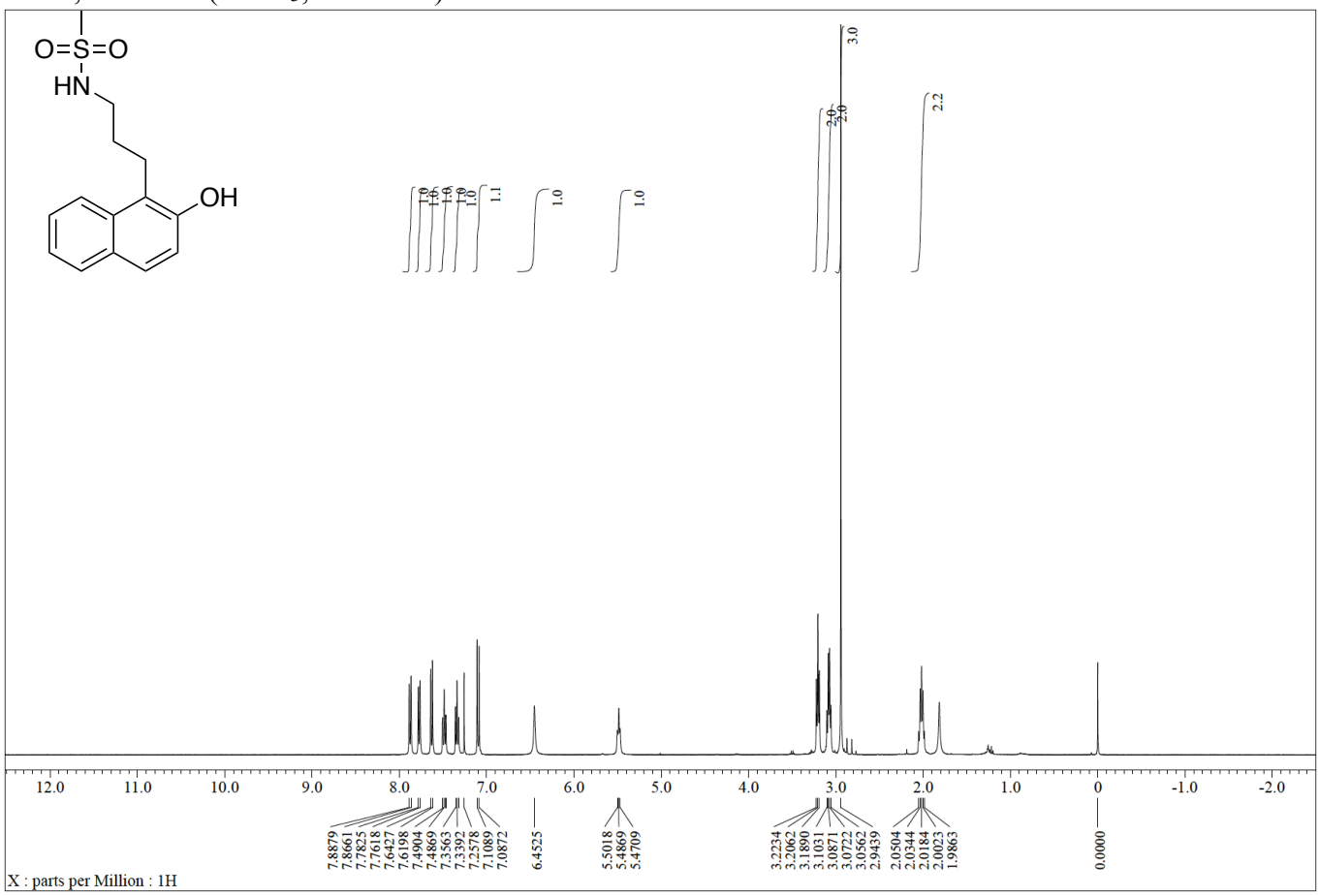
3e, ^{1}H NMR ($CDCl_3$, 400 MHz)



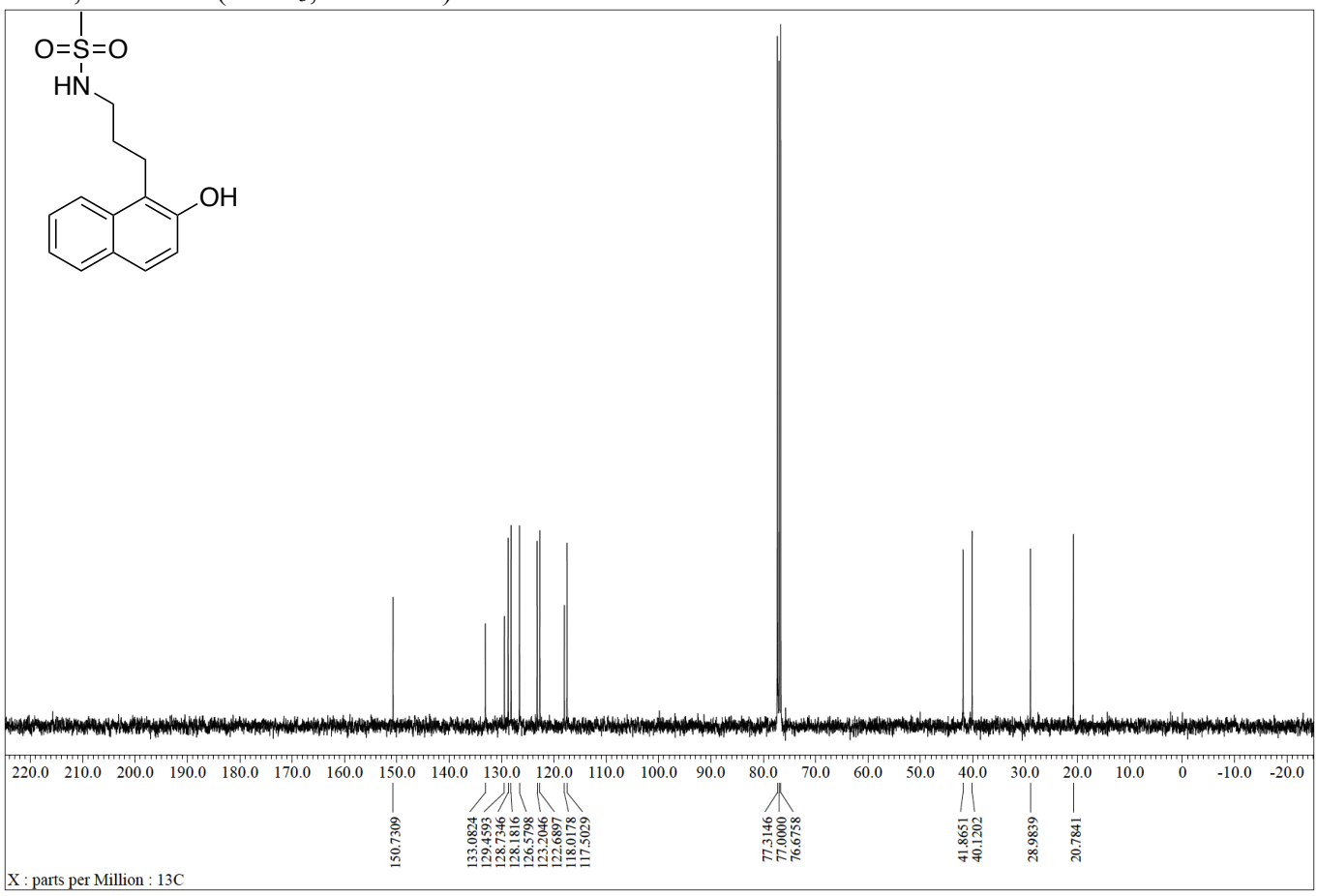
3e, ^{13}C NMR ($CDCl_3$, 100 MHz)



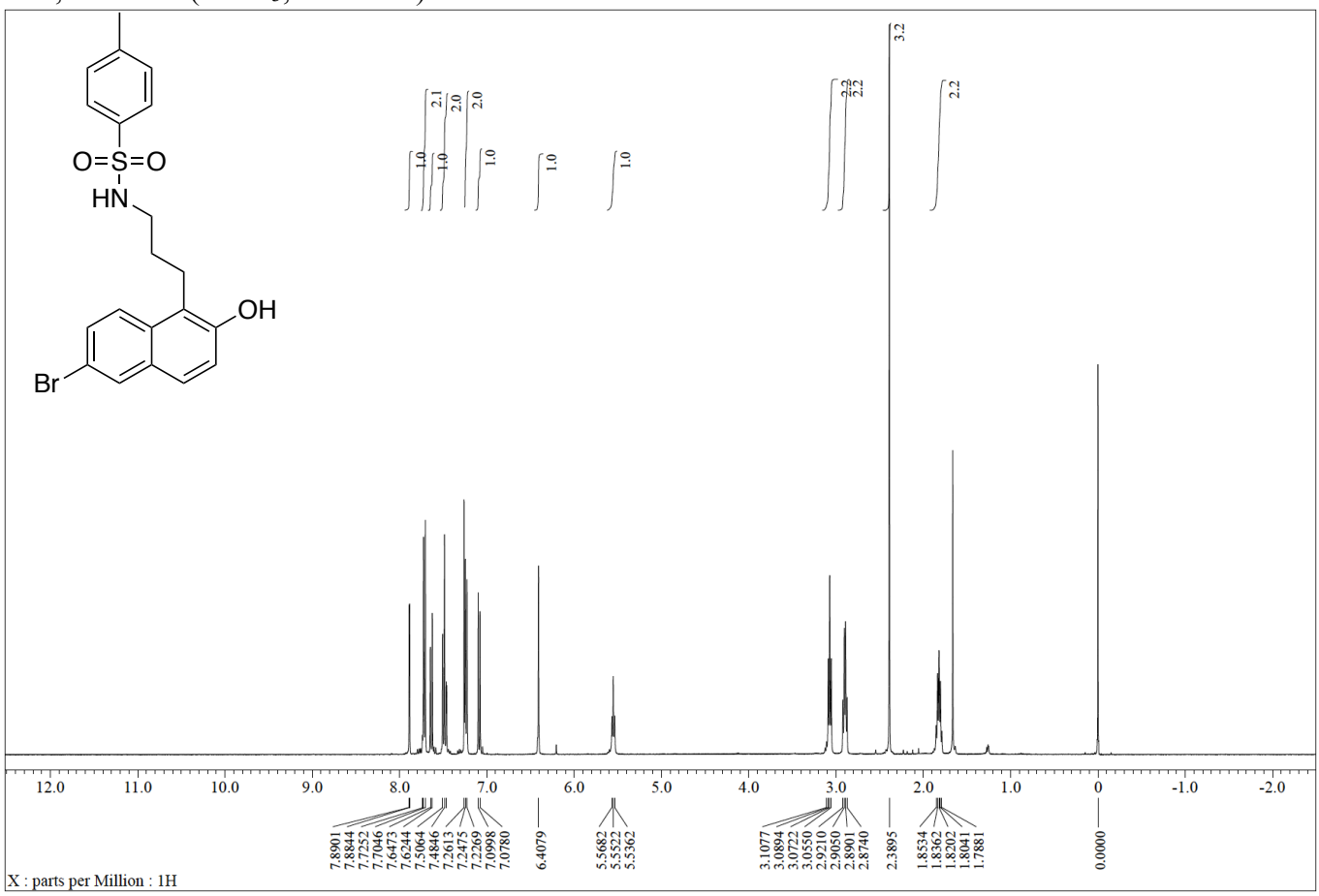
3ea, ^{1}H NMR ($CDCl_3$, 400 MHz)



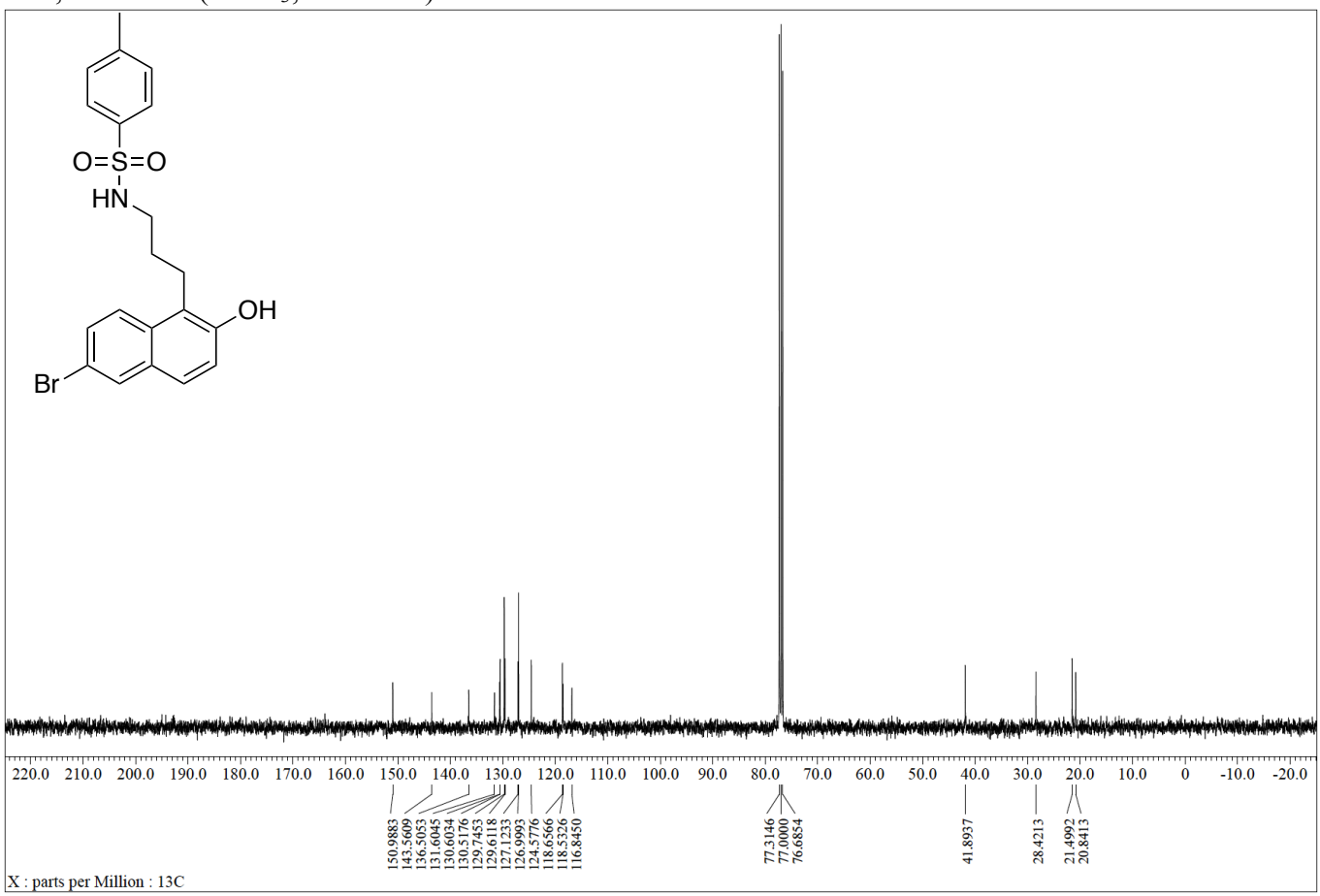
3ea, ^{13}C NMR ($CDCl_3$, 100 MHz)



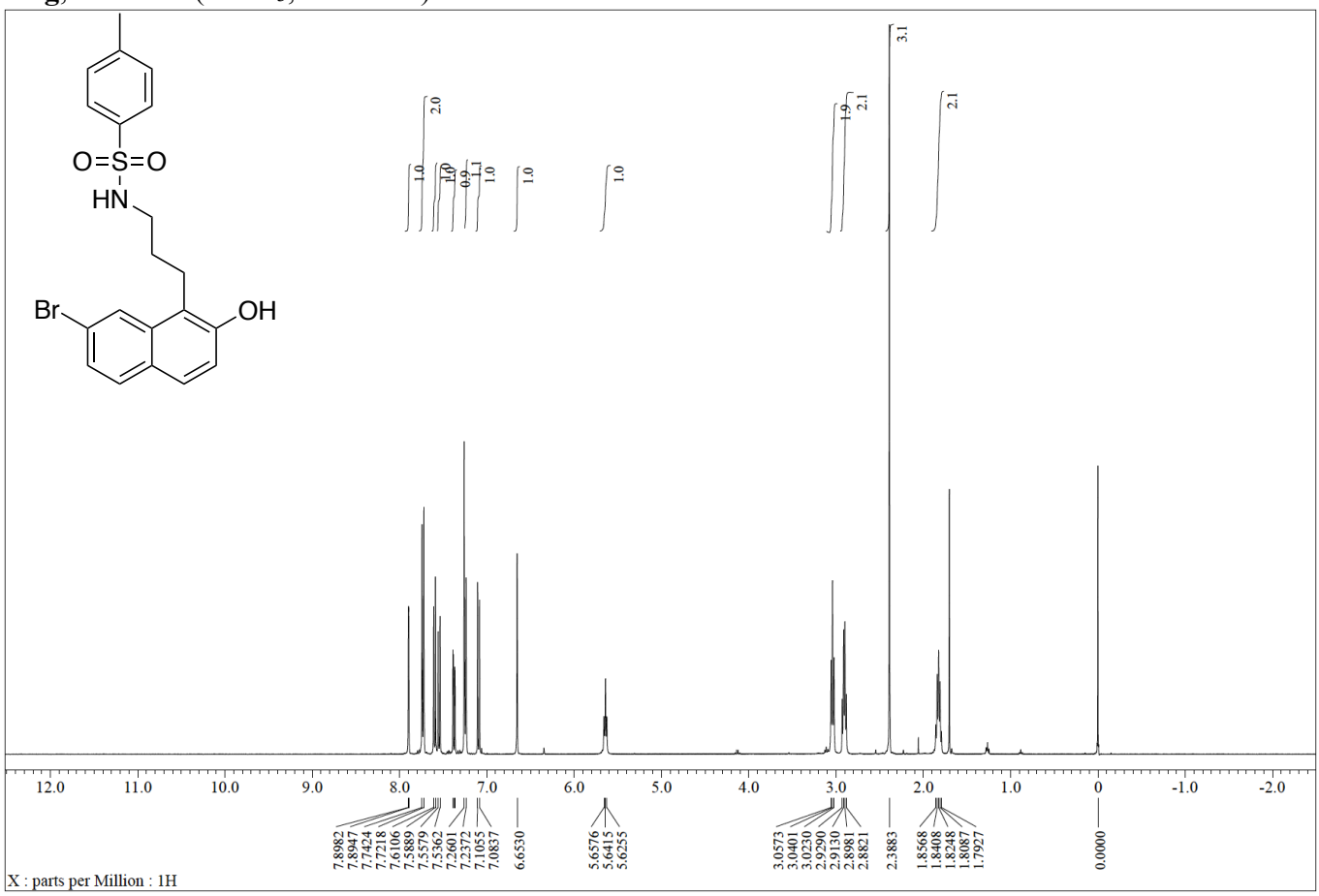
3f, ^{1}H NMR ($CDCl_3$, 400 MHz)



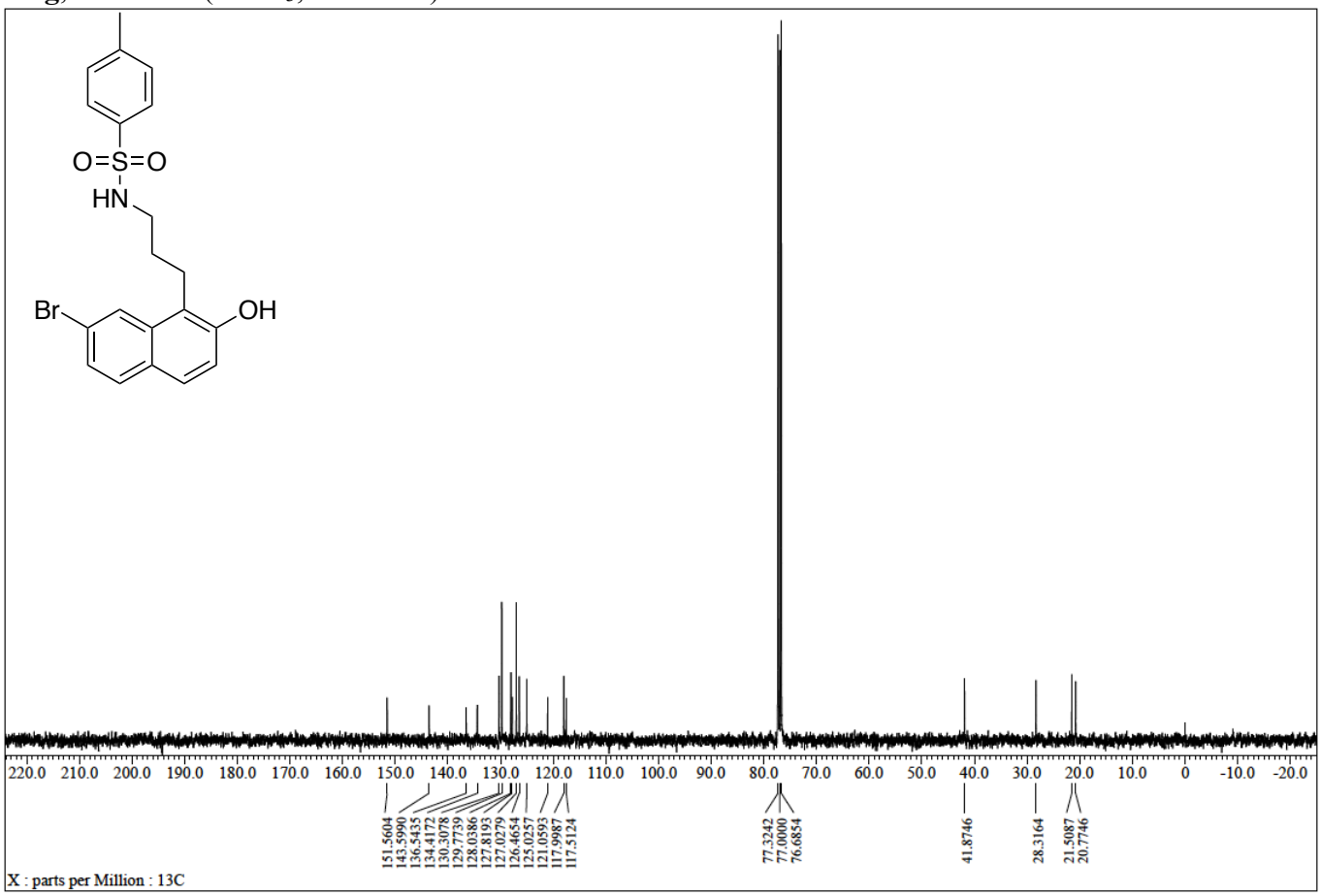
3f, ^{13}C NMR ($CDCl_3$, 100 MHz)



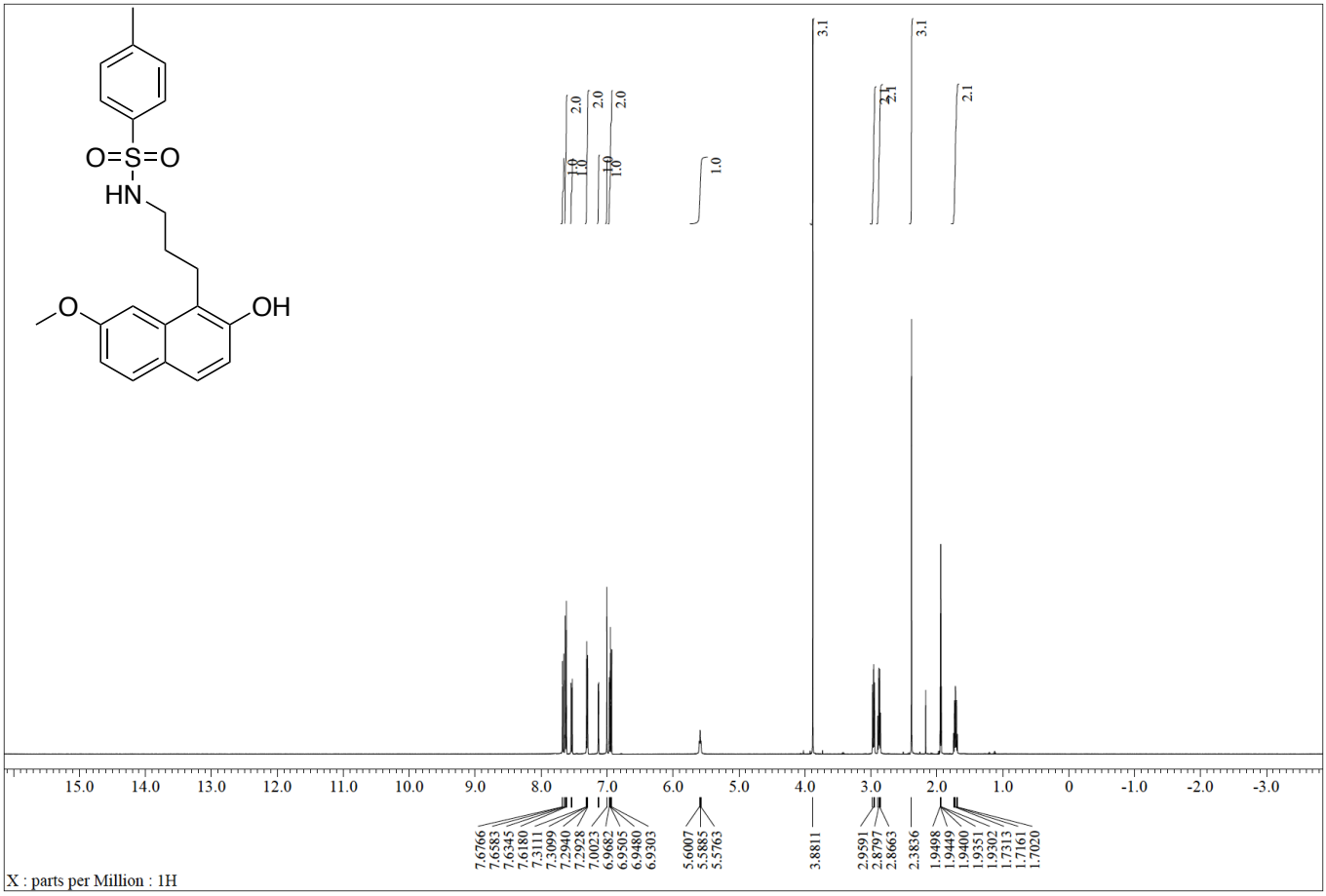
3g, ^{1}H NMR ($CDCl_3$, 400 MHz)



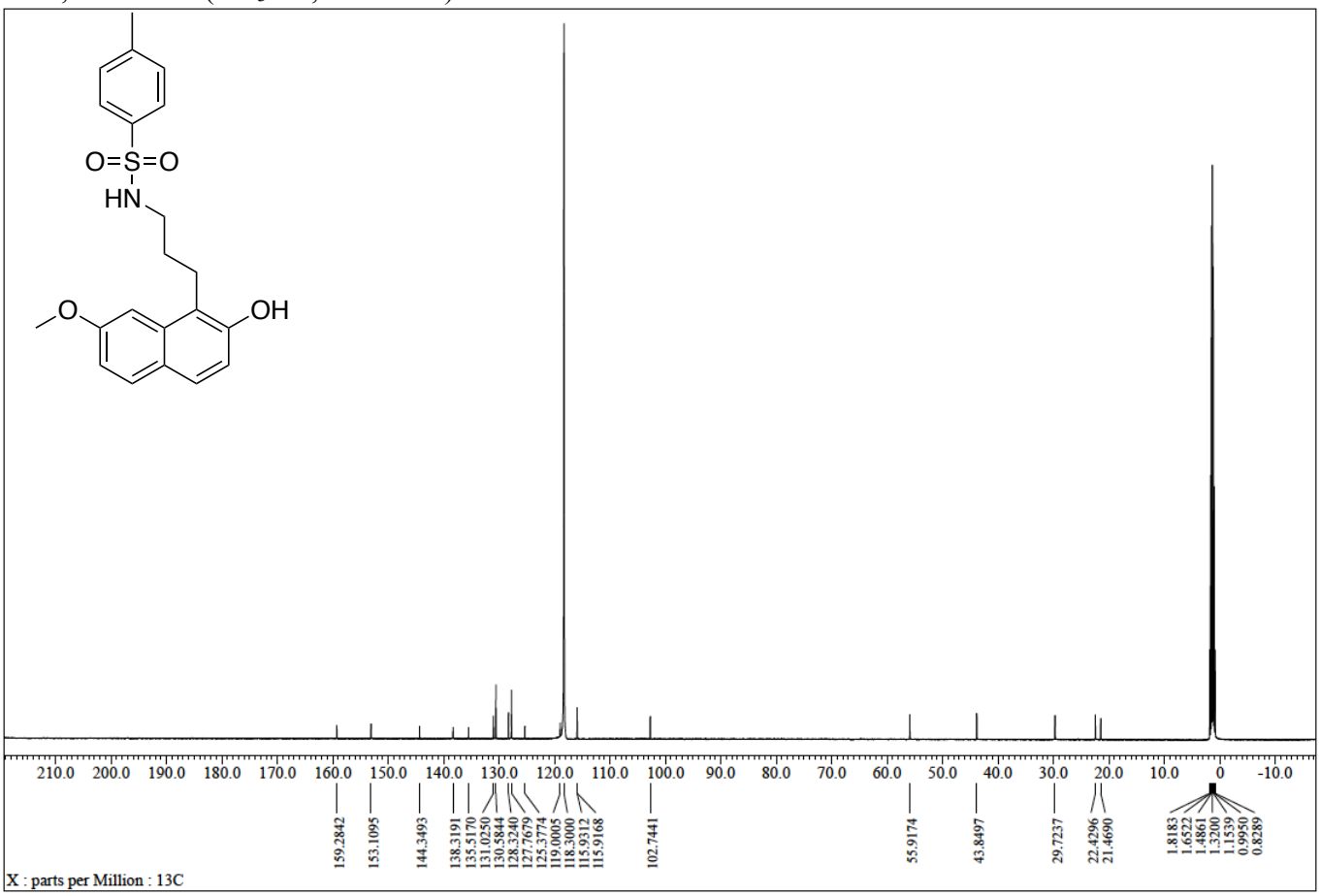
3g, ^{13}C NMR ($CDCl_3$, 100 MHz)



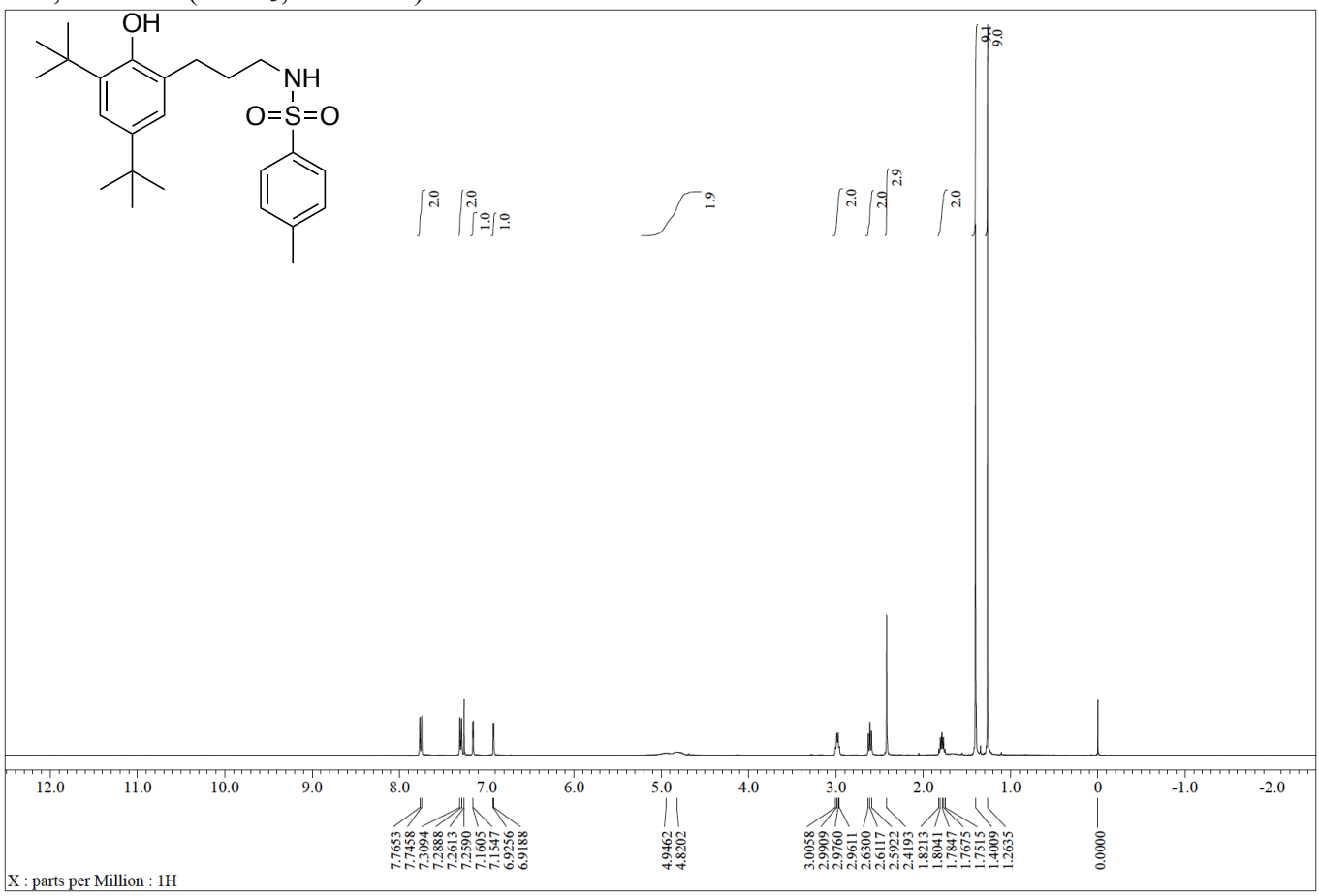
3h, ^{1}H NMR (CD_3CN, 500 MHz)



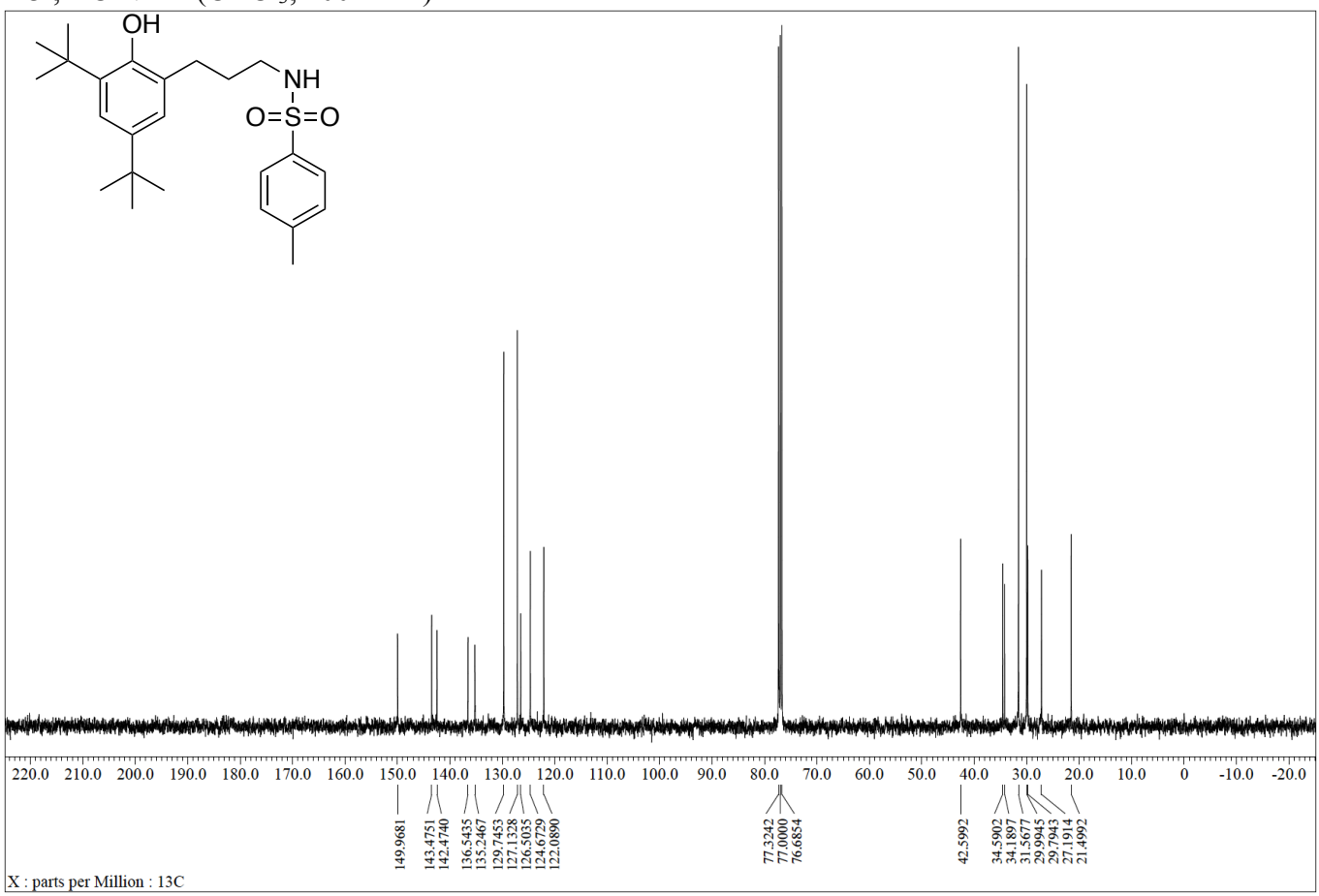
3h, ^{13}C NMR (CD_3CN, 125 MHz)



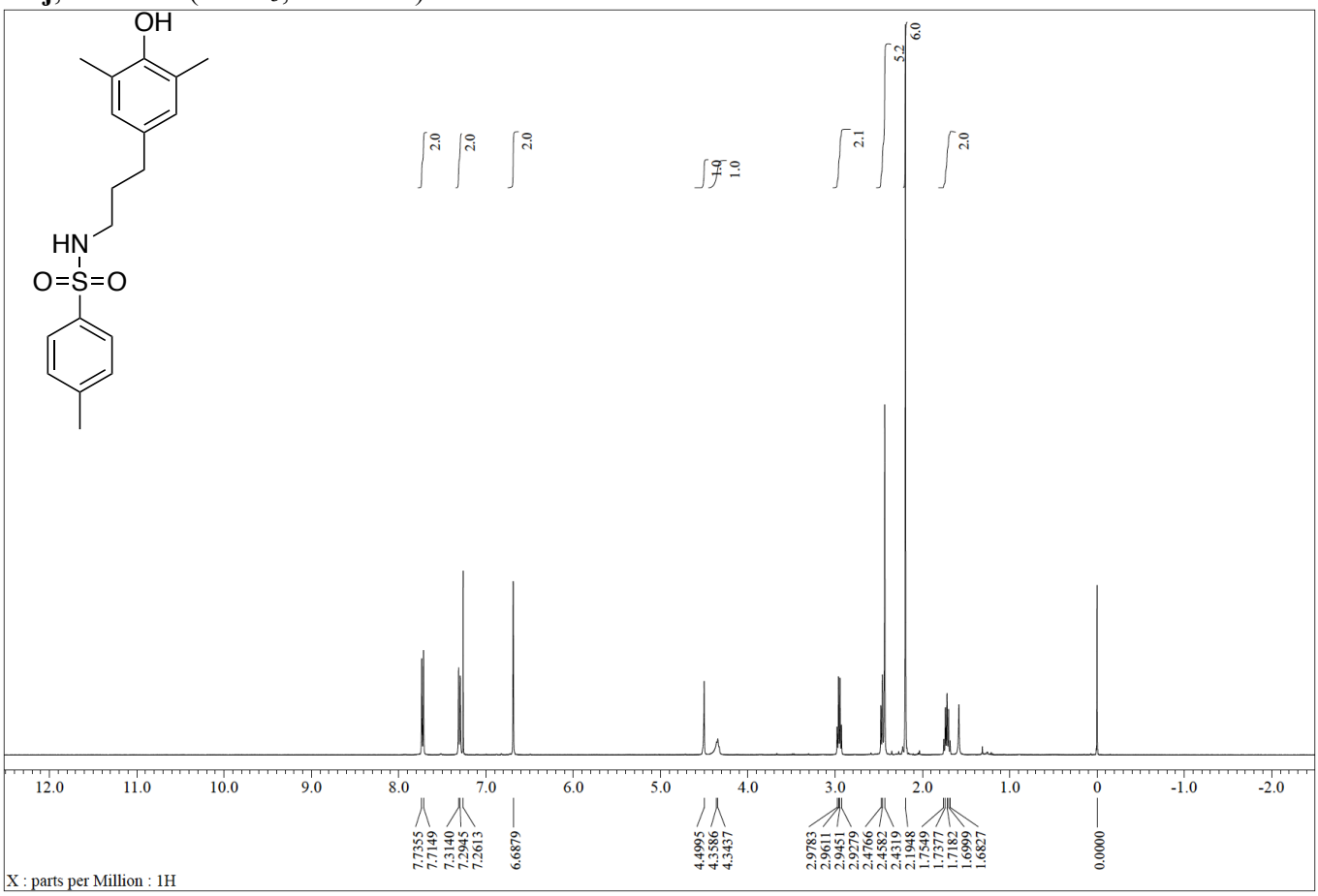
3i, ^{1}H NMR ($CDCl_3$, 400 MHz)



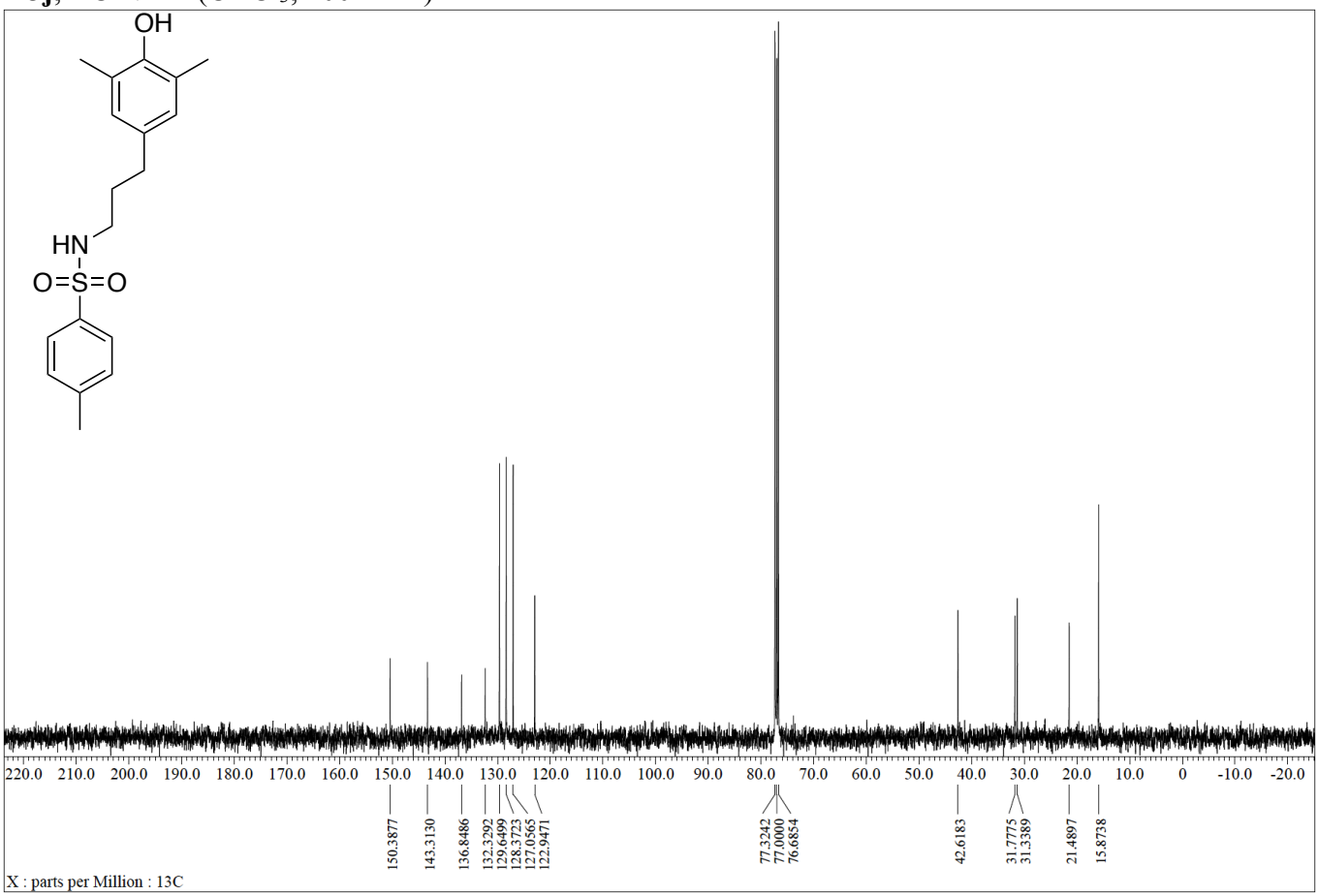
3i, ^{13}C NMR ($CDCl_3$, 100 MHz)



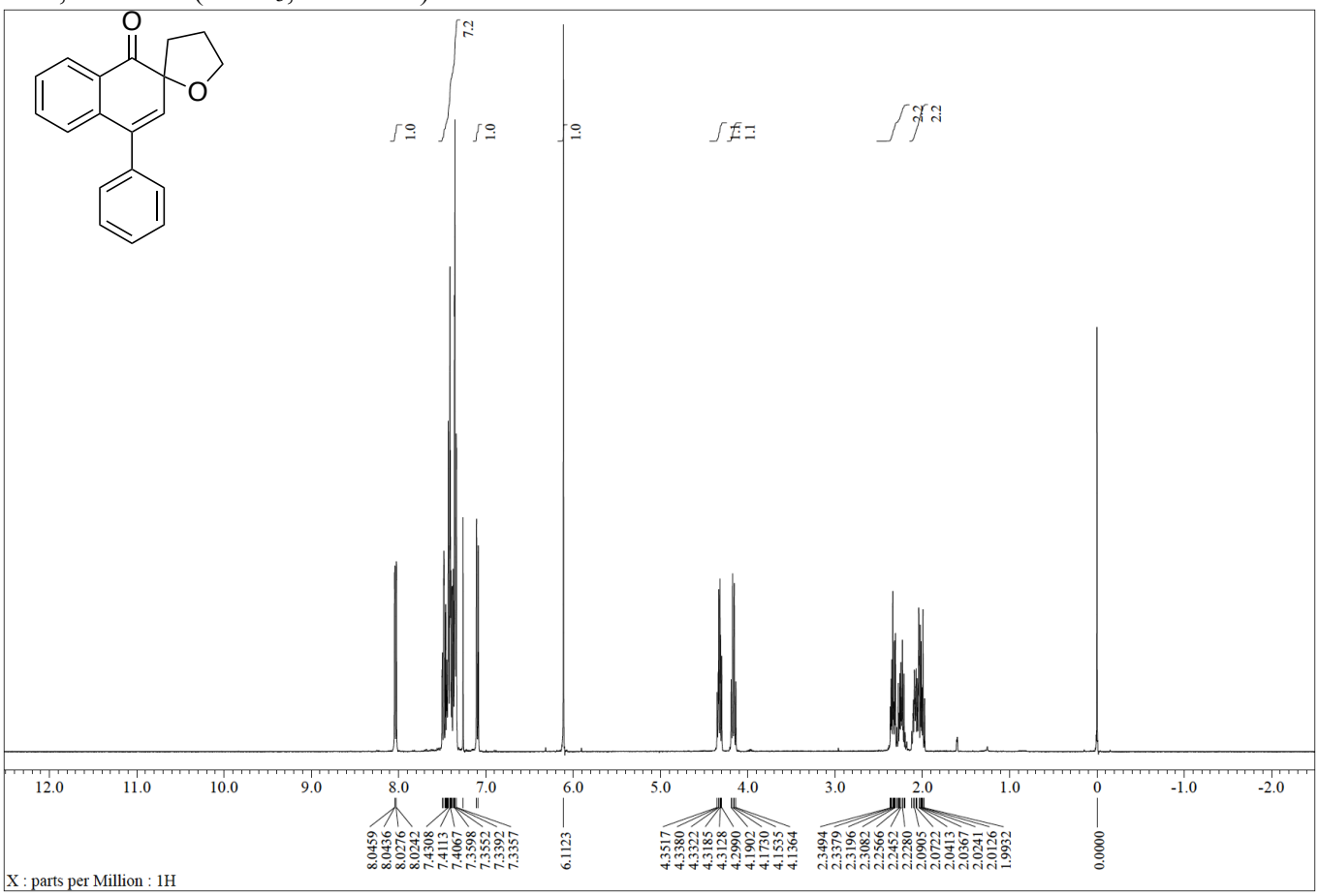
3j, ^{1}H NMR ($CDCl_3$, 400 MHz)



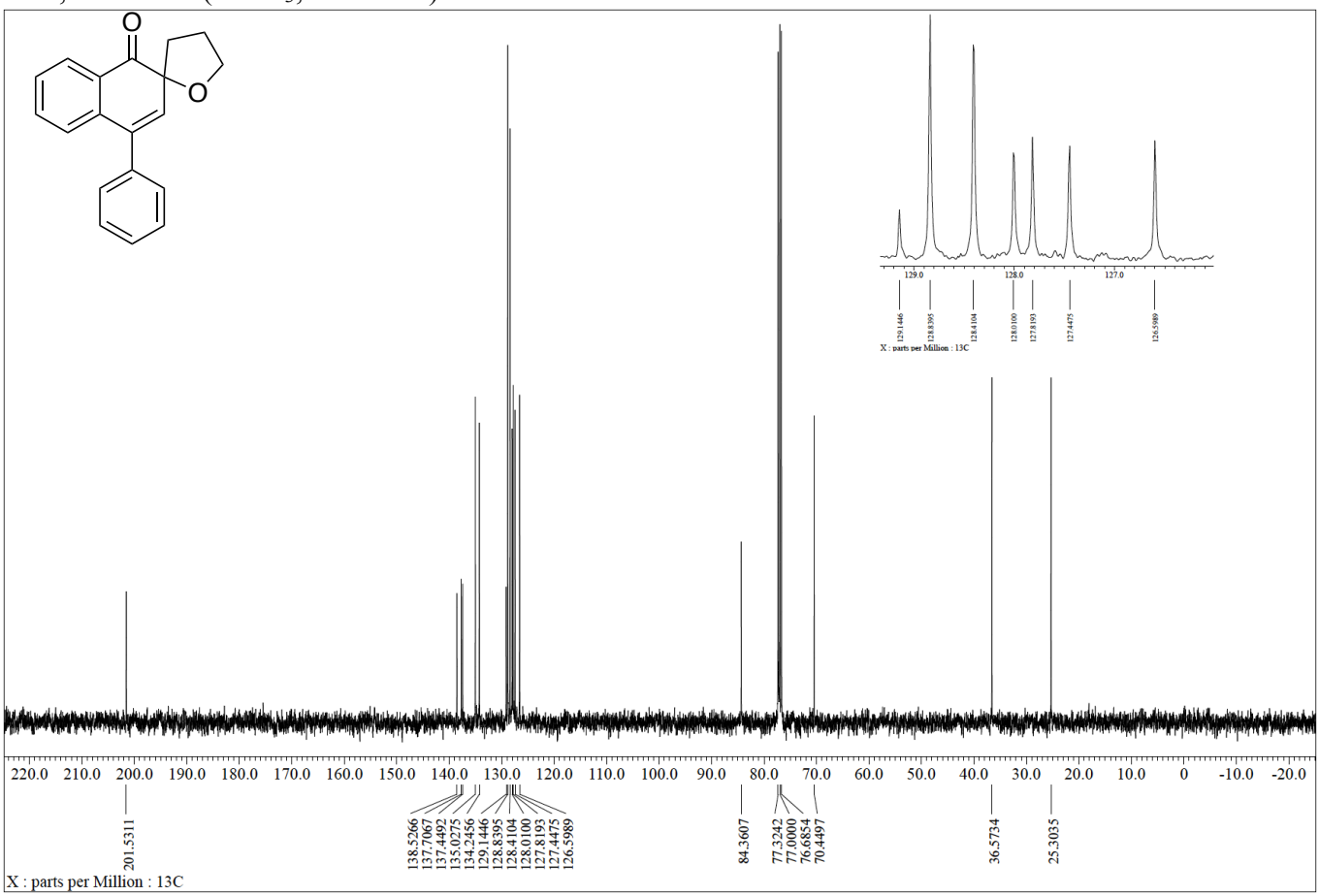
3j, ^{13}C NMR ($CDCl_3$, 100 MHz)



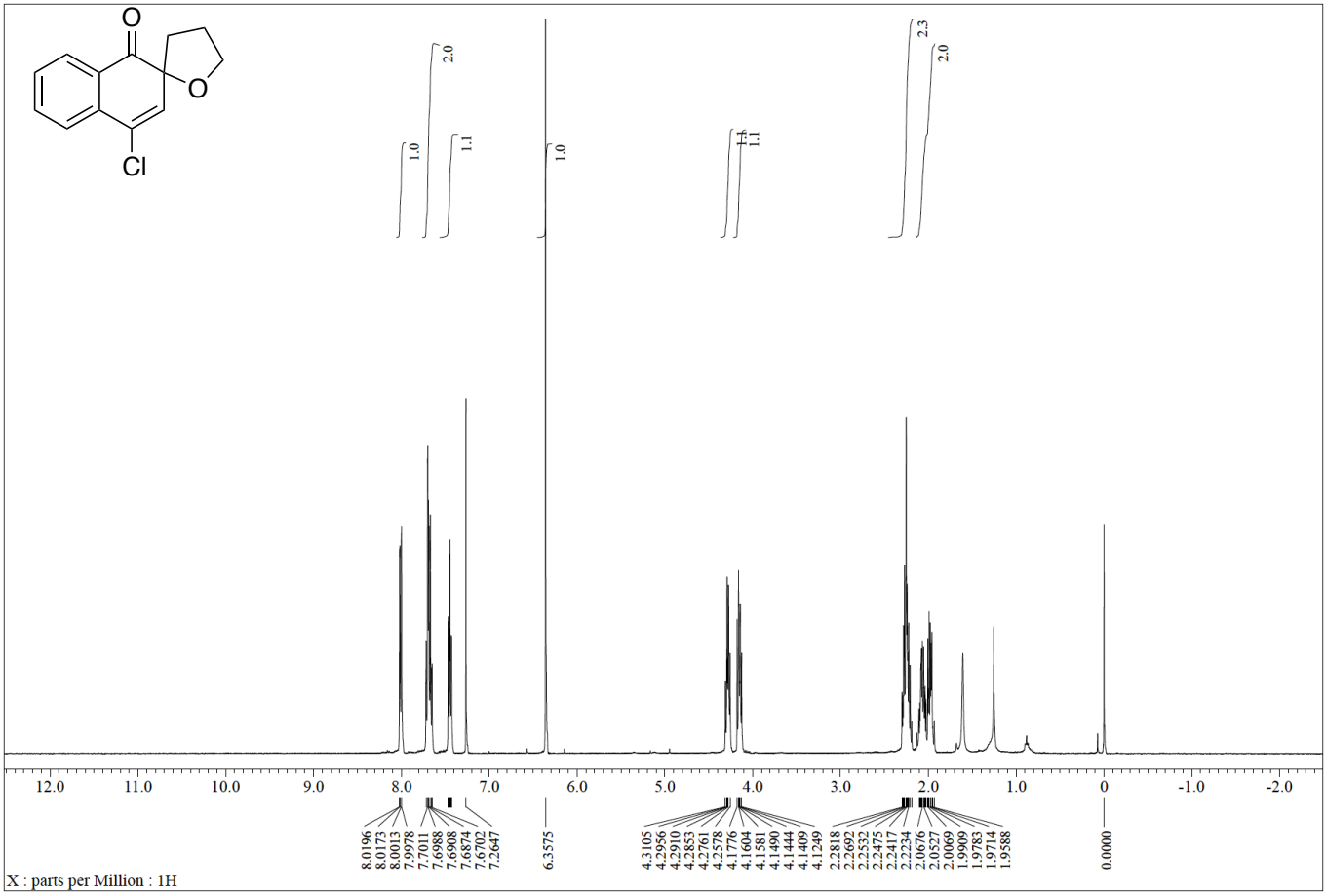
2a, ^{1}H NMR ($CDCl_3$, 400 MHz)



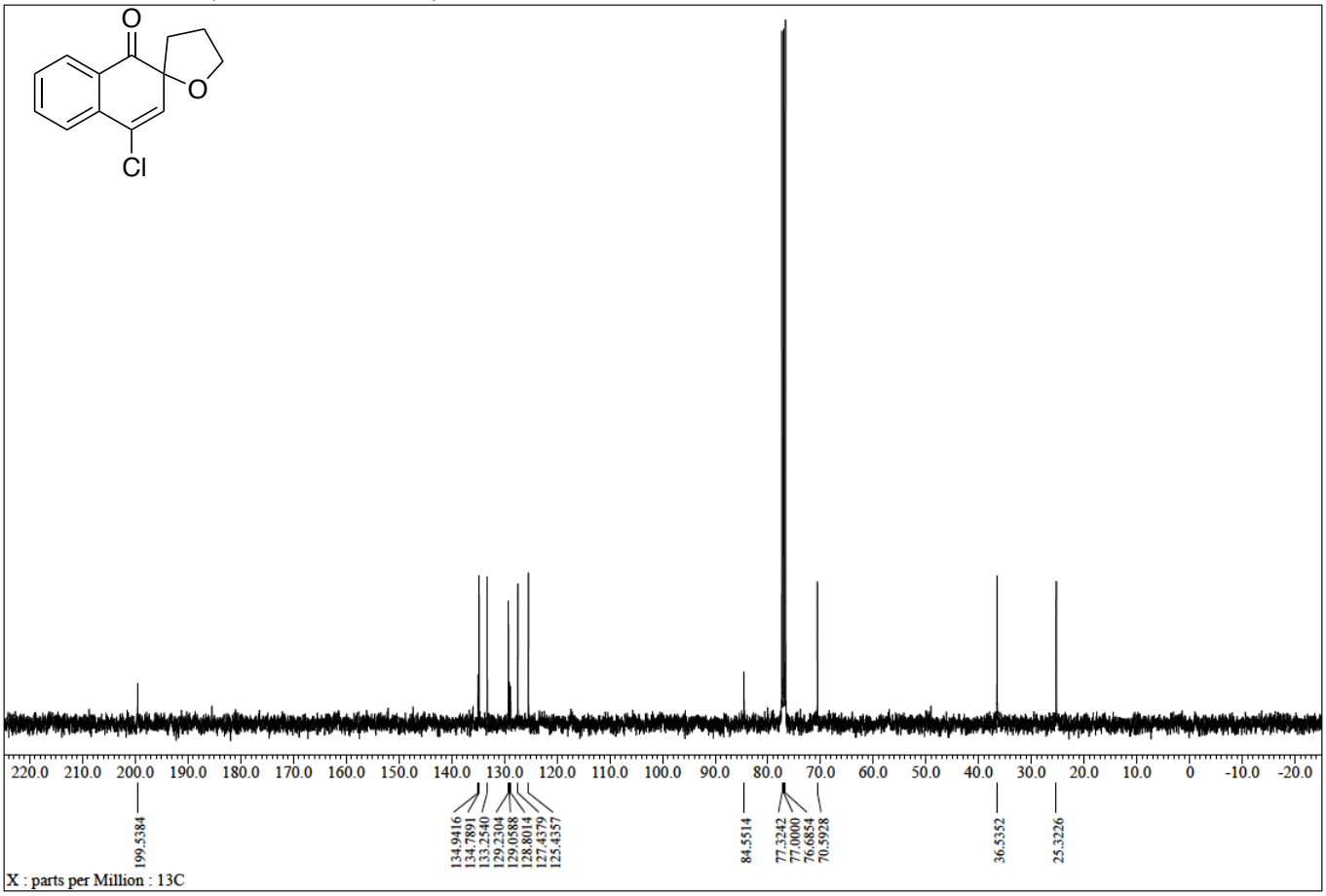
2a, ^{13}C NMR ($CDCl_3$, 100 MHz)



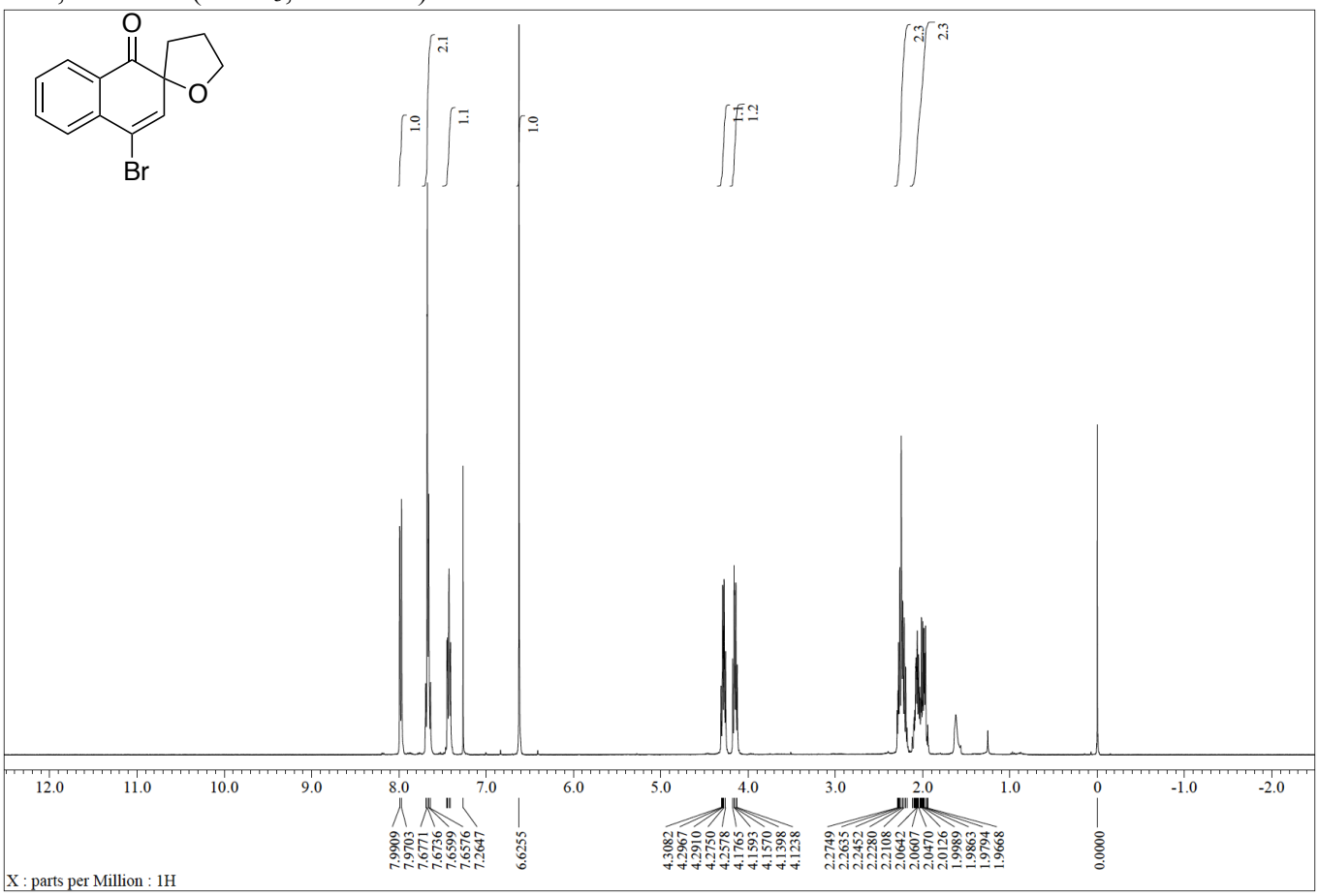
2b, ^{1}H NMR ($CDCl_3$, 400 MHz)



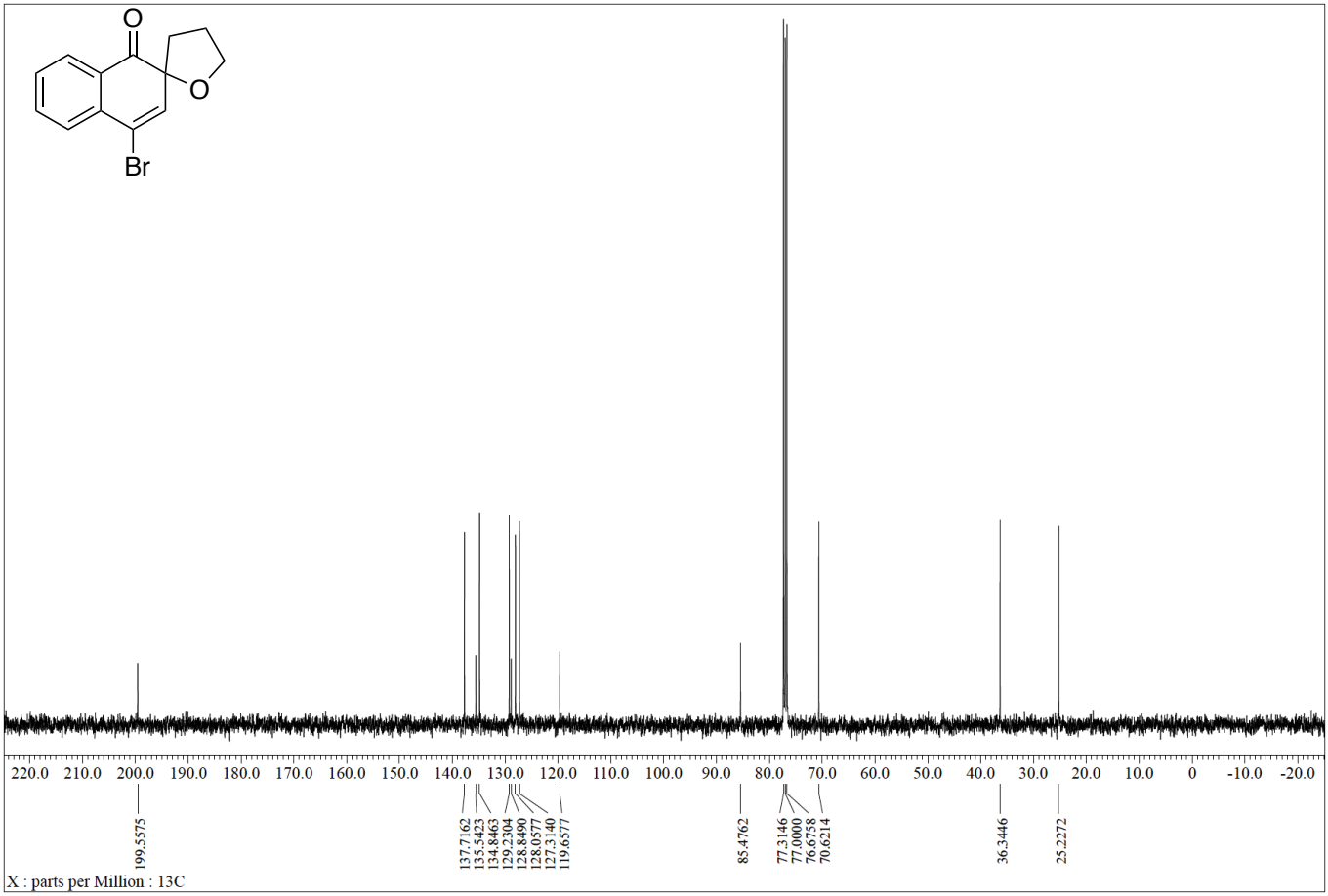
2b, ^{13}C NMR ($CDCl_3$, 100 MHz)



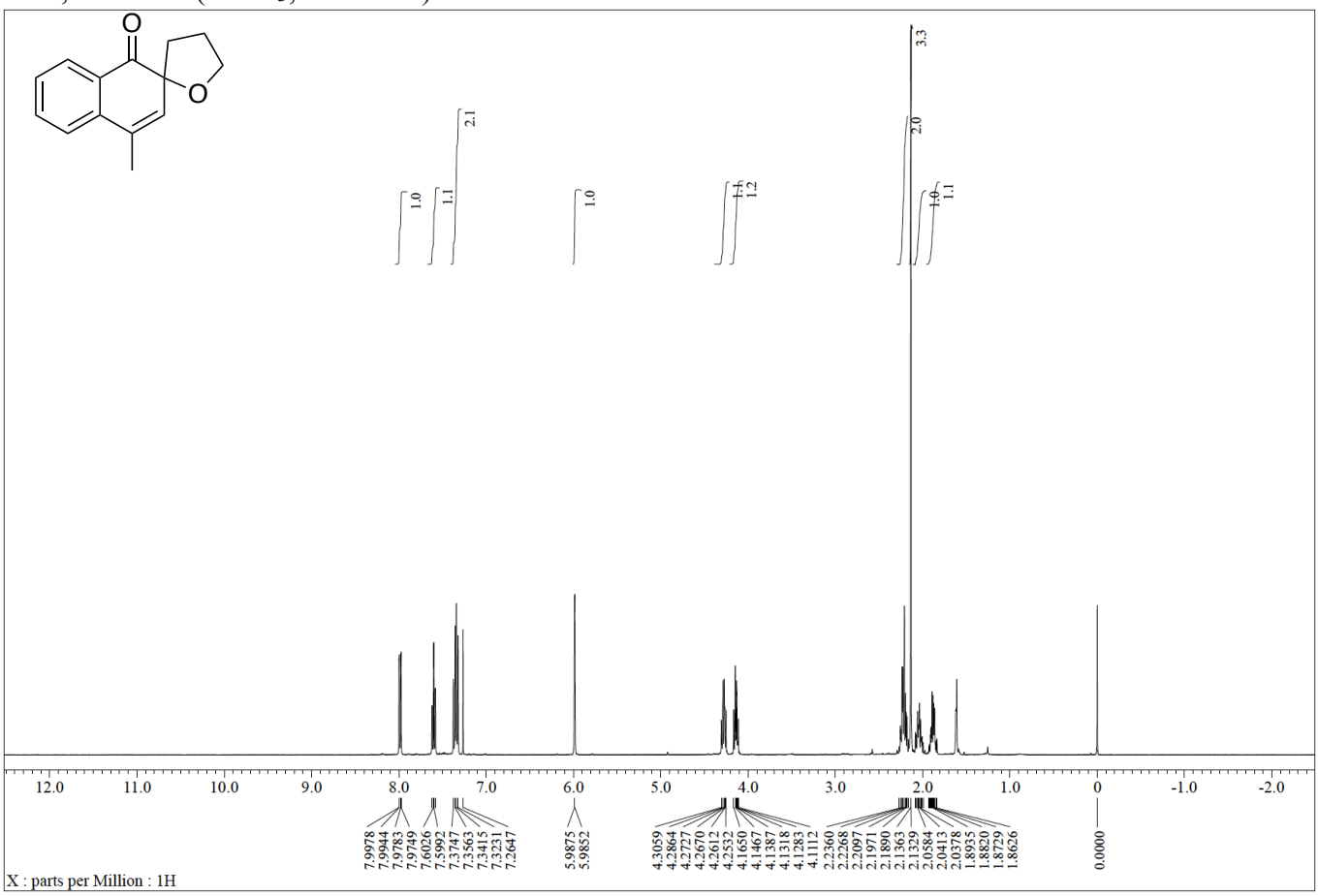
2c, ^{1}H NMR ($CDCl_3$, 400 MHz)



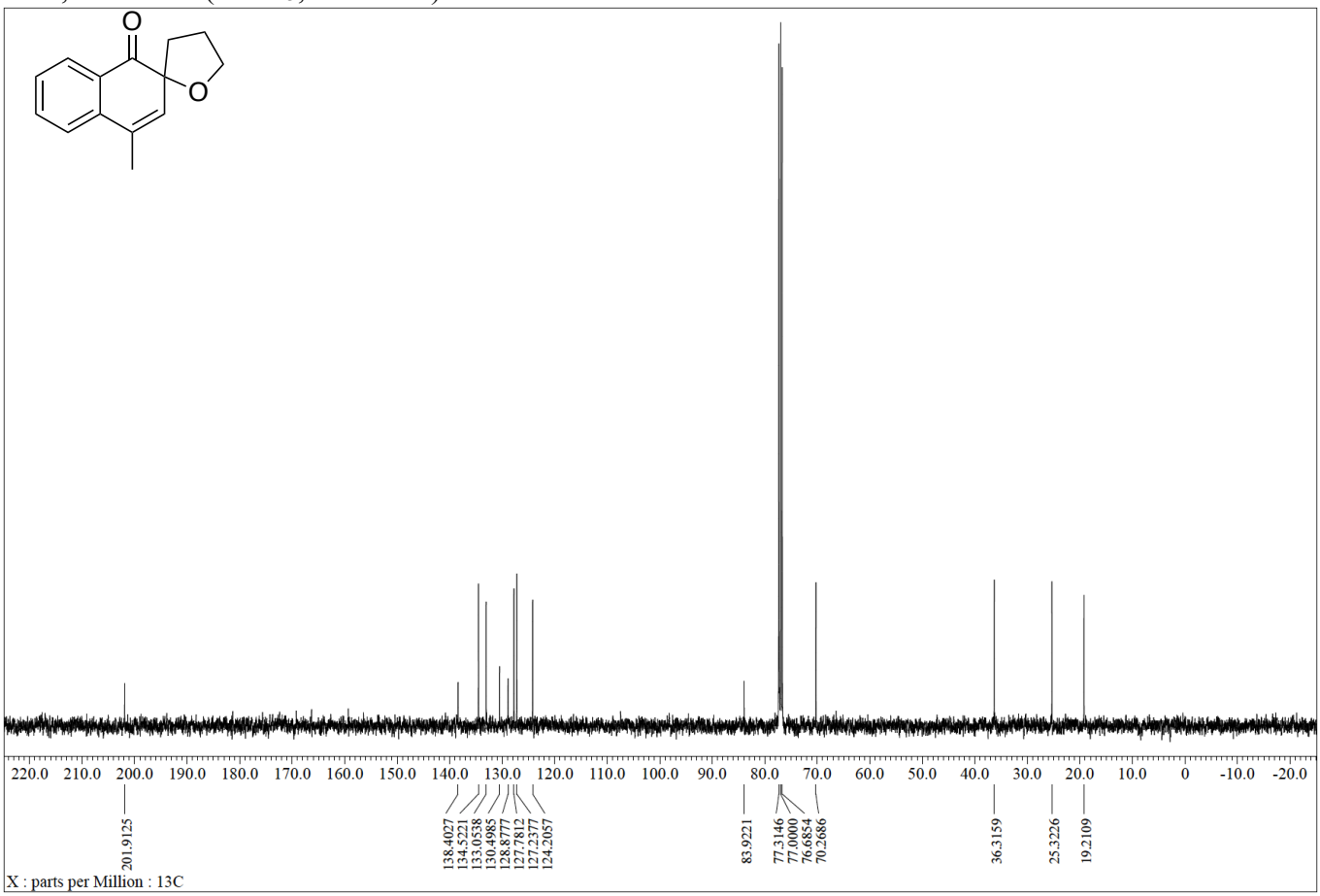
2c, ^{13}C NMR ($CDCl_3$, 100 MHz)



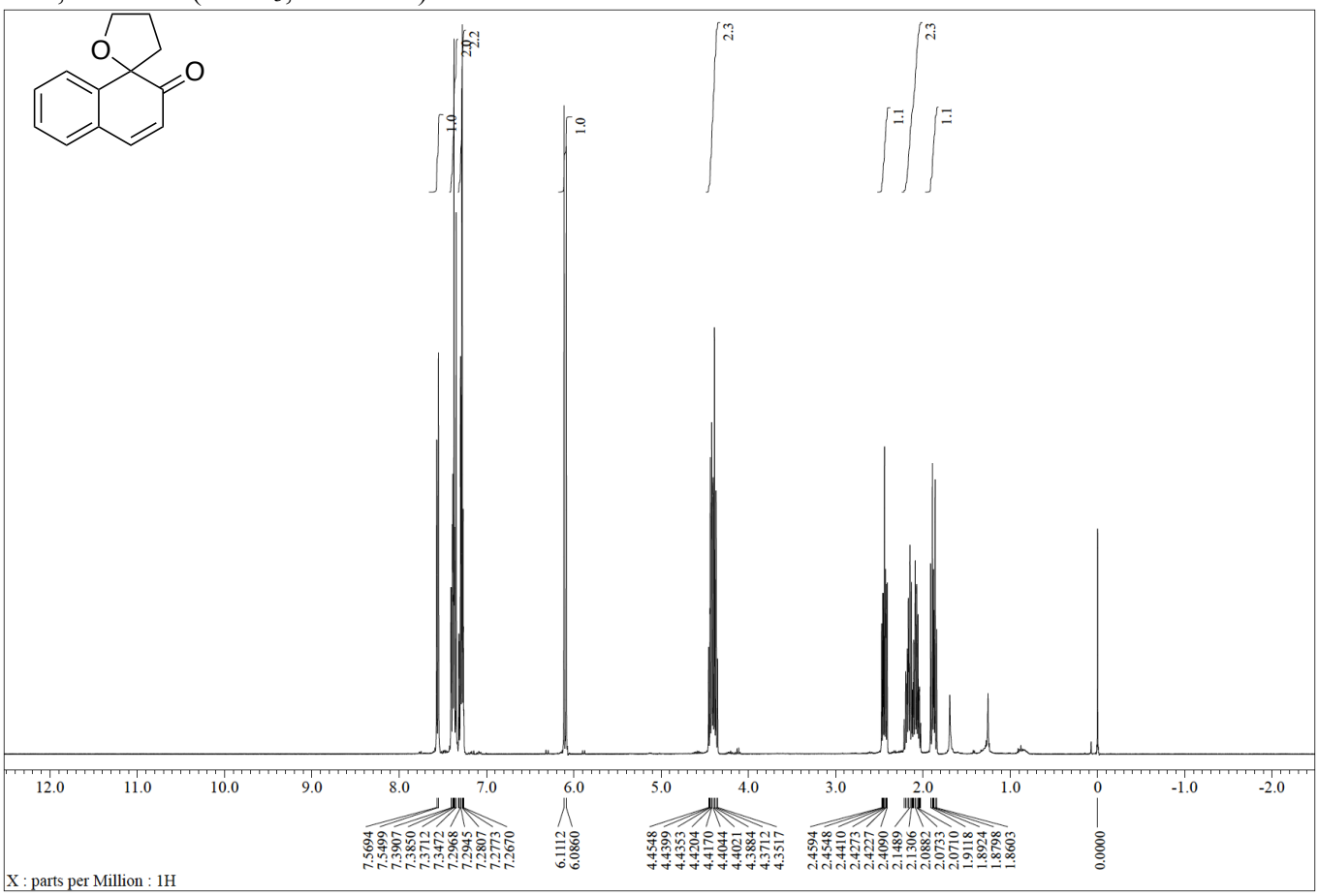
2d, ^{1}H NMR ($CDCl_3$, 400 MHz)



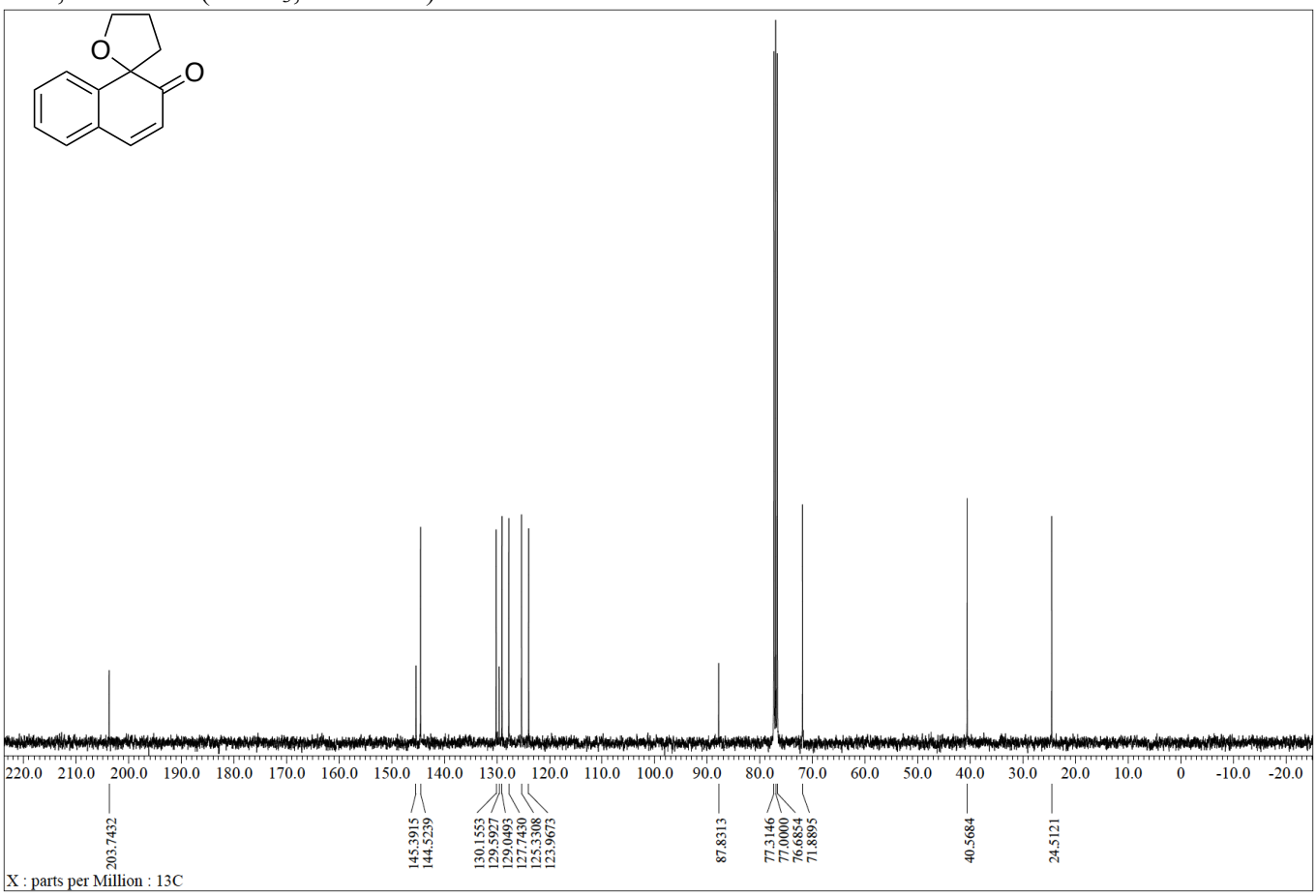
2d, ^{13}C NMR ($CDCl_3$, 100 MHz)



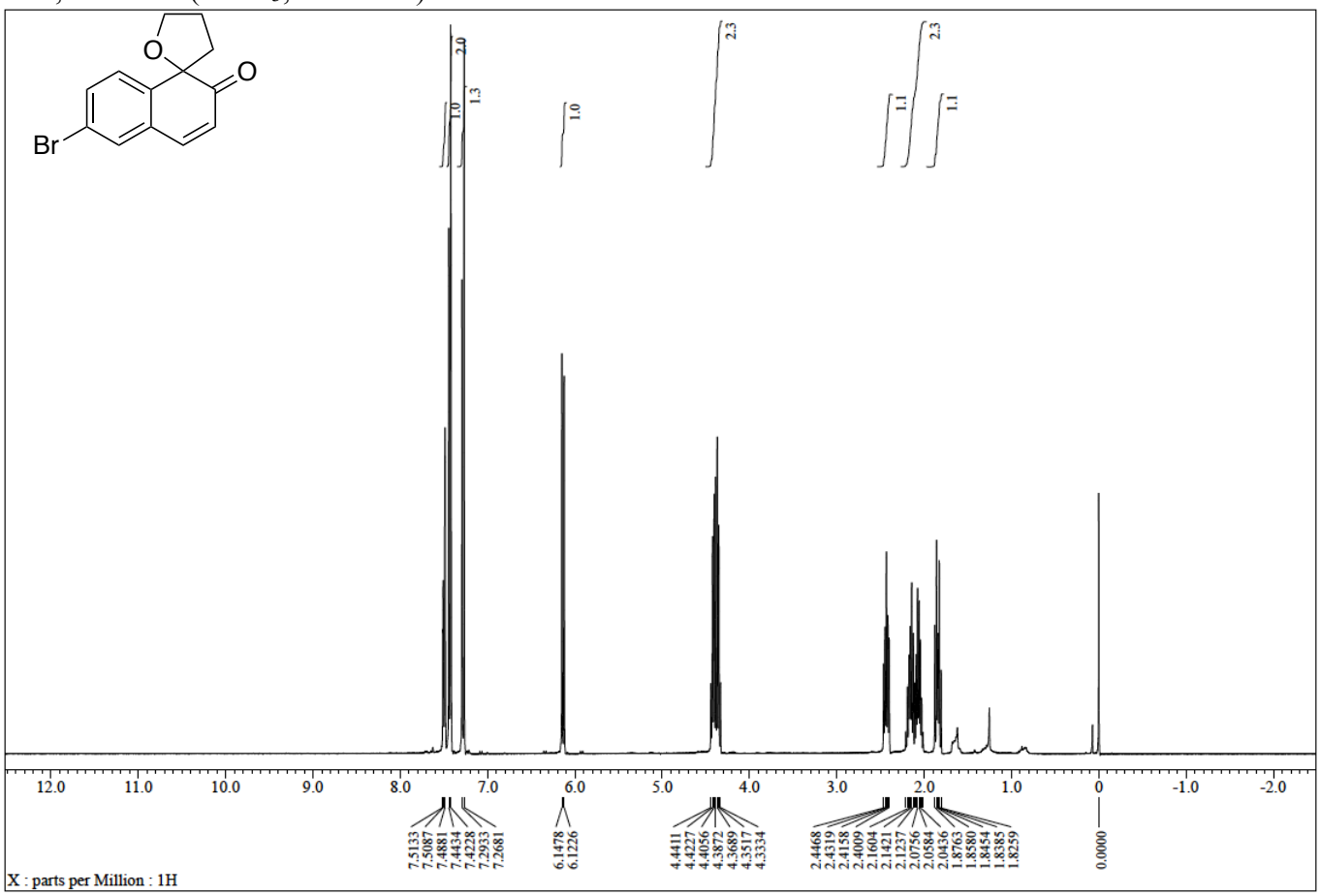
2e, ^{1}H NMR ($CDCl_3$, 400 MHz)



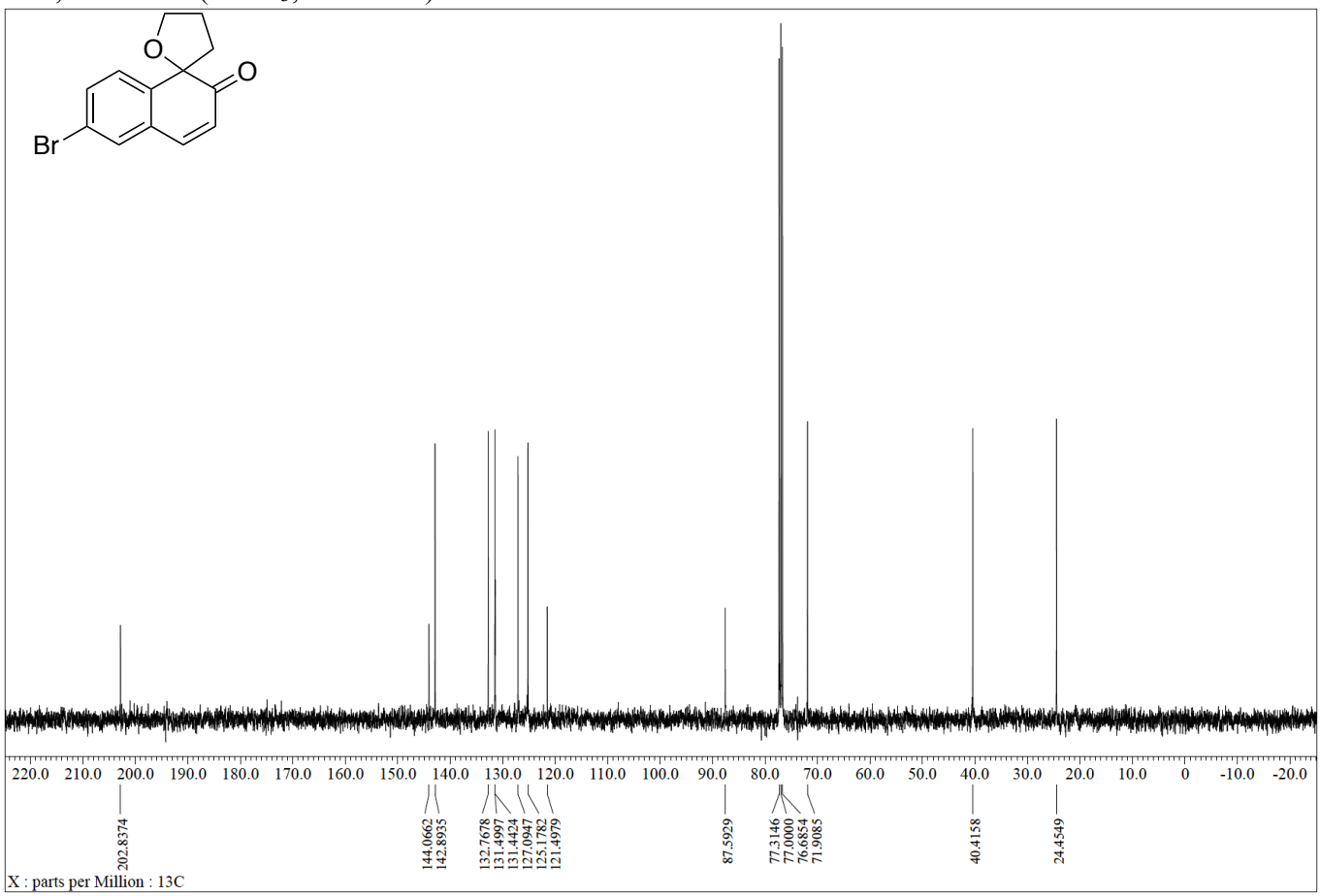
2e, ^{13}C NMR ($CDCl_3$, 100 MHz)



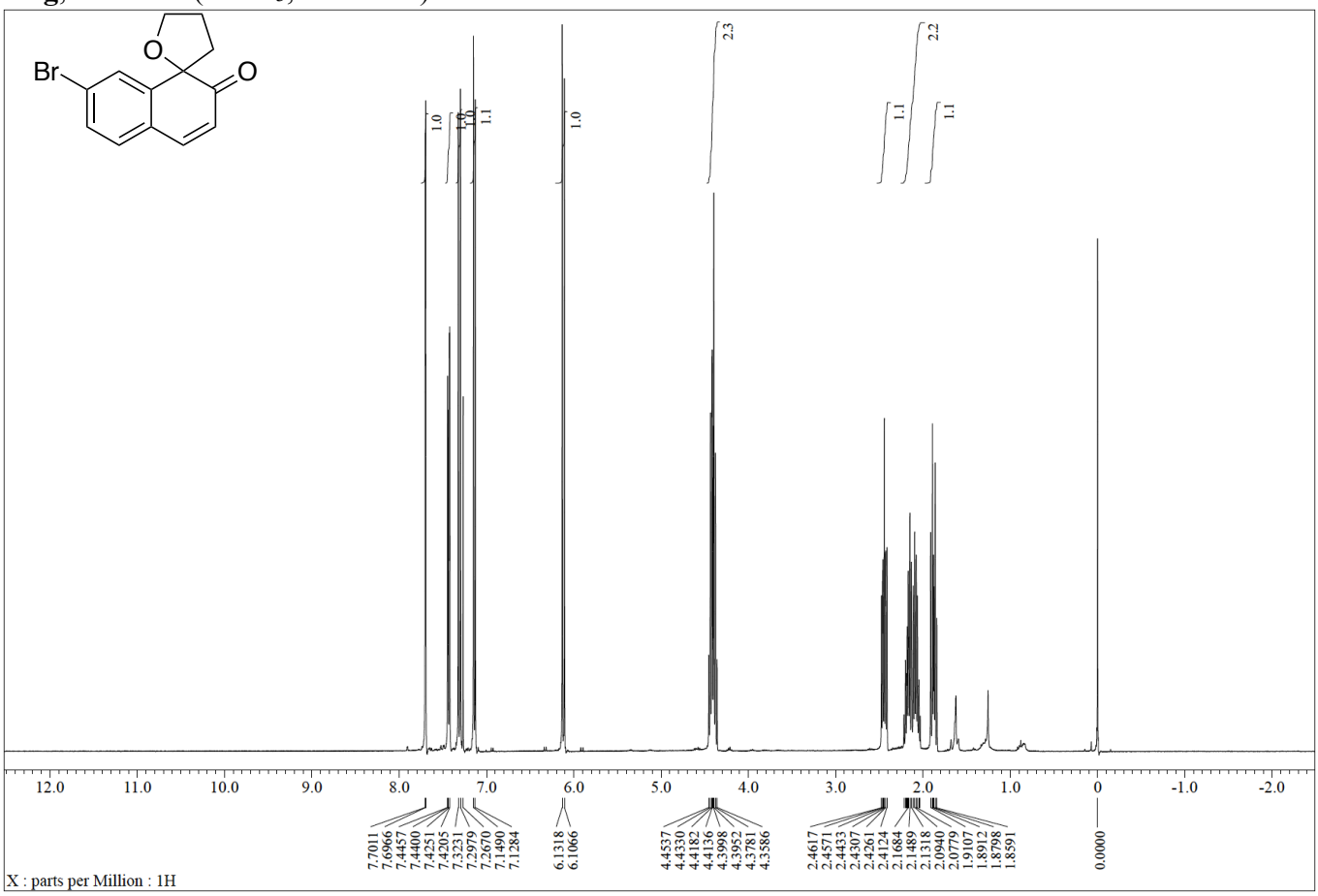
2f, ^{1}H NMR ($CDCl_3$, 400 MHz)



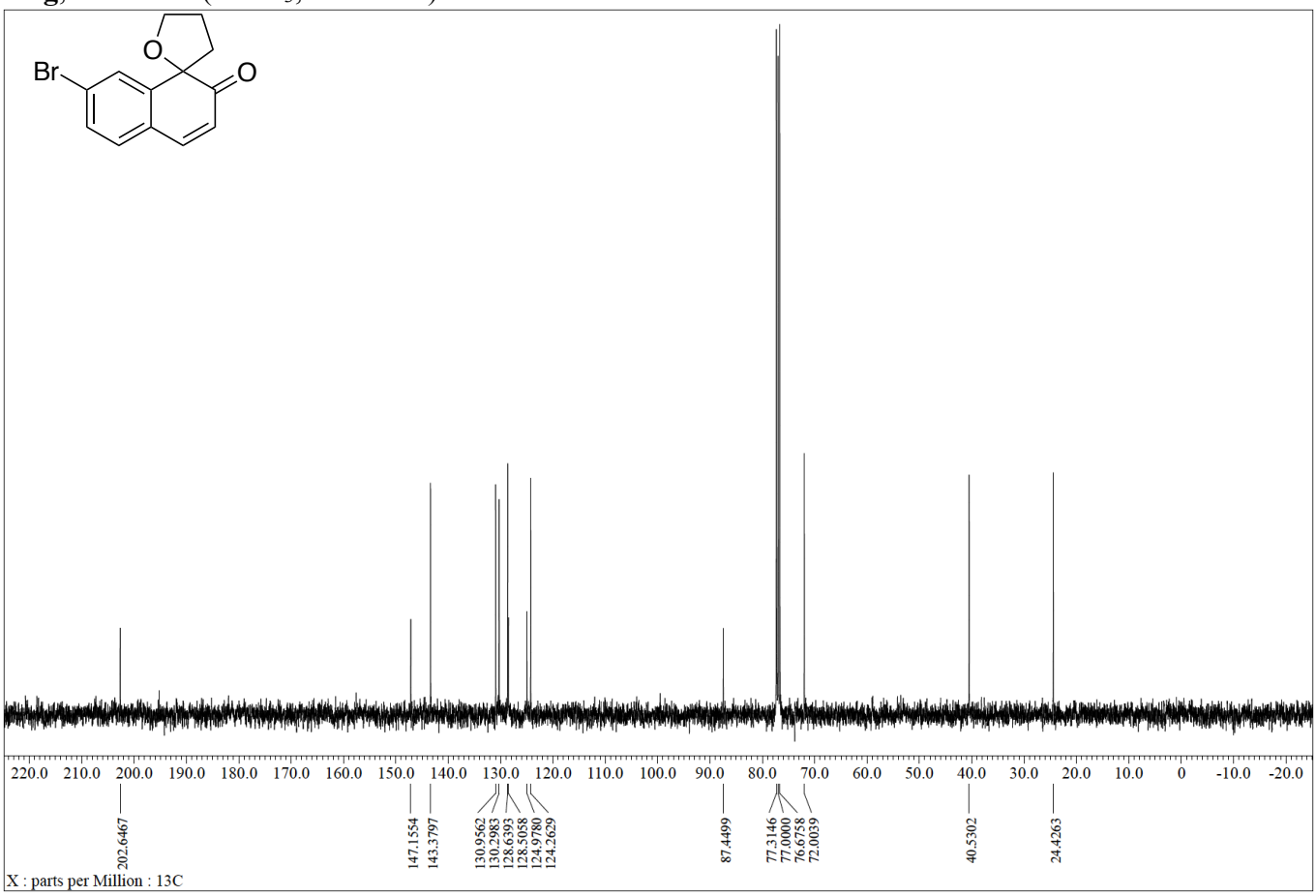
2f, ^{13}C NMR ($CDCl_3$, 100 MHz)



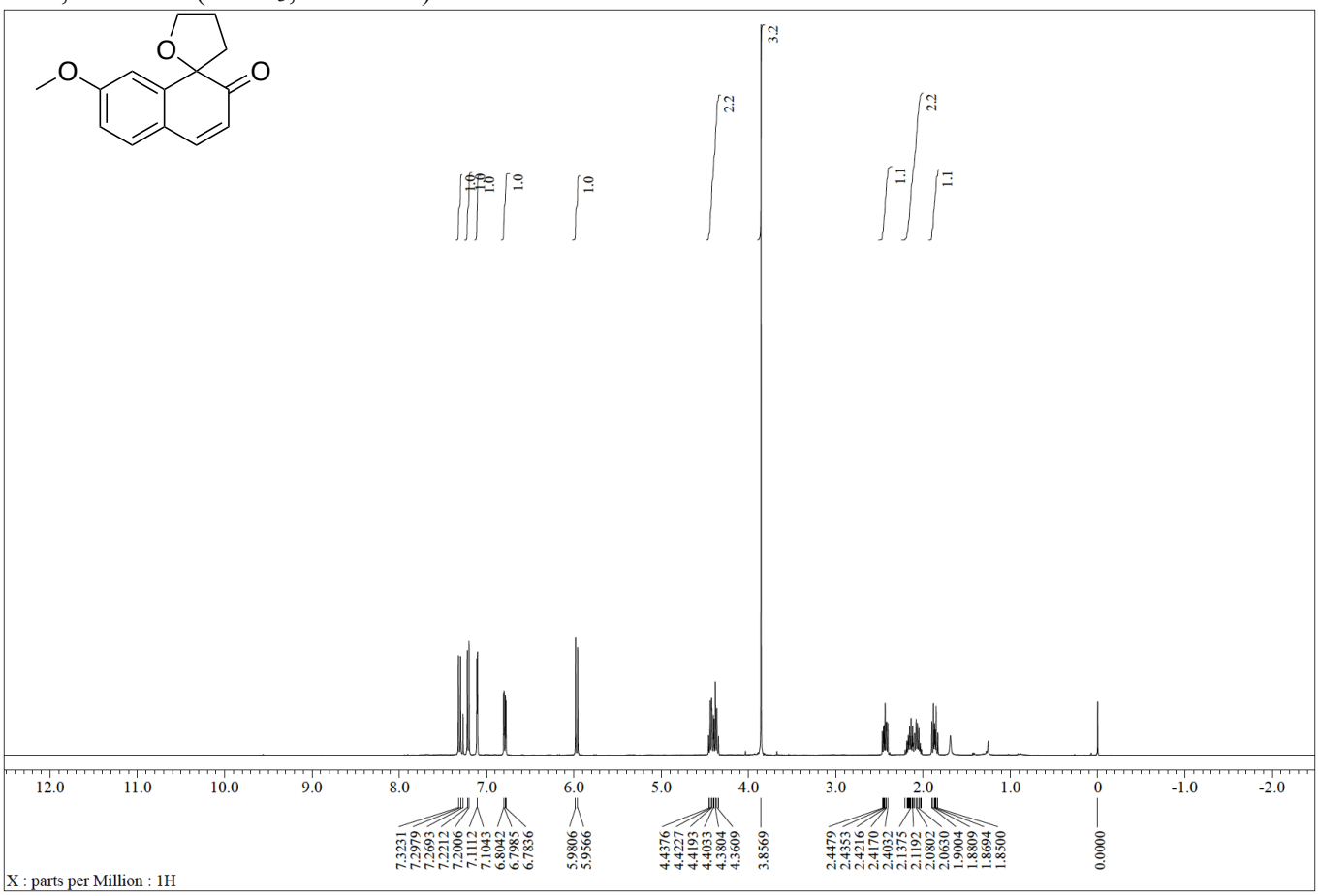
2g, ^{1}H NMR ($CDCl_3$, 400 MHz)



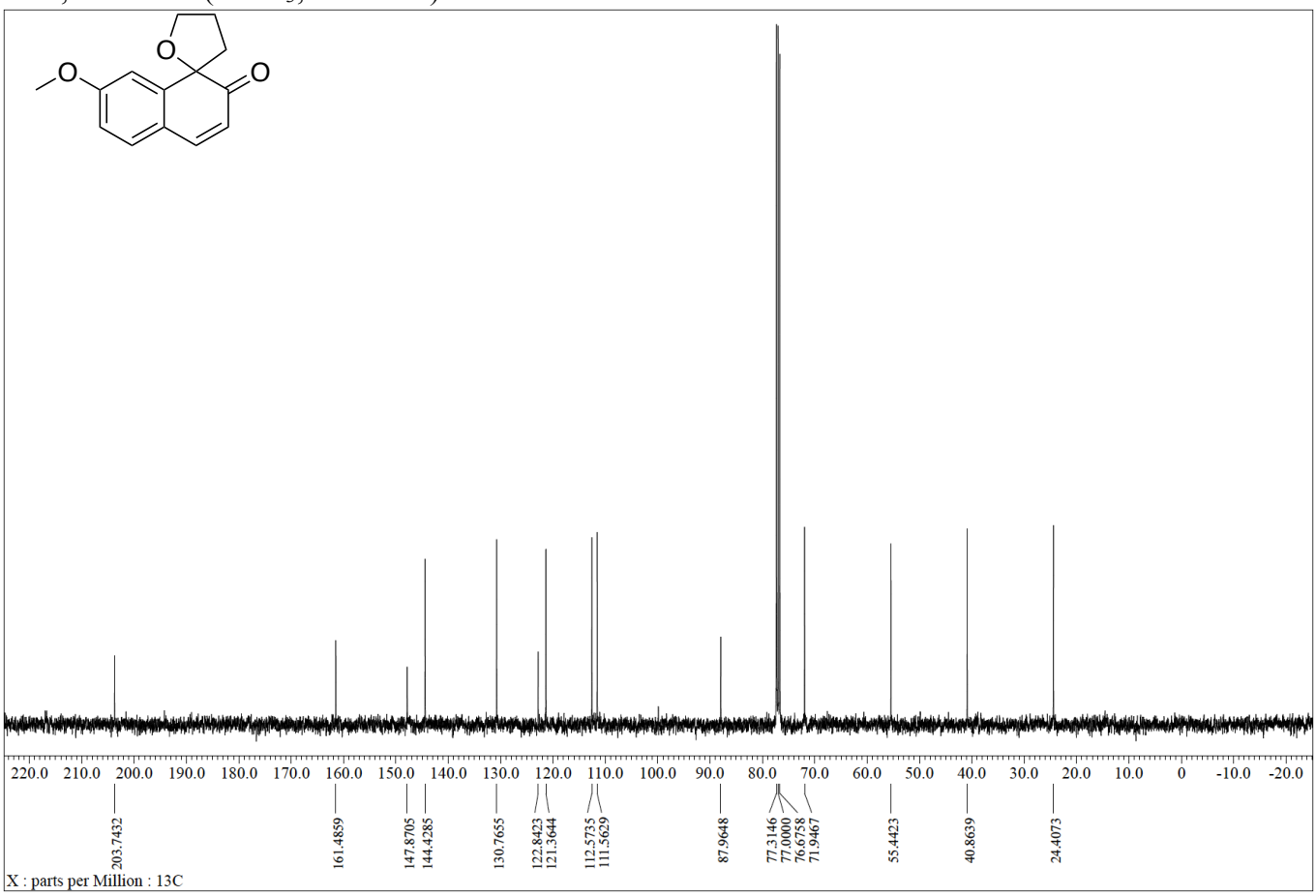
2g, ^{13}C NMR ($CDCl_3$, 100 MHz)



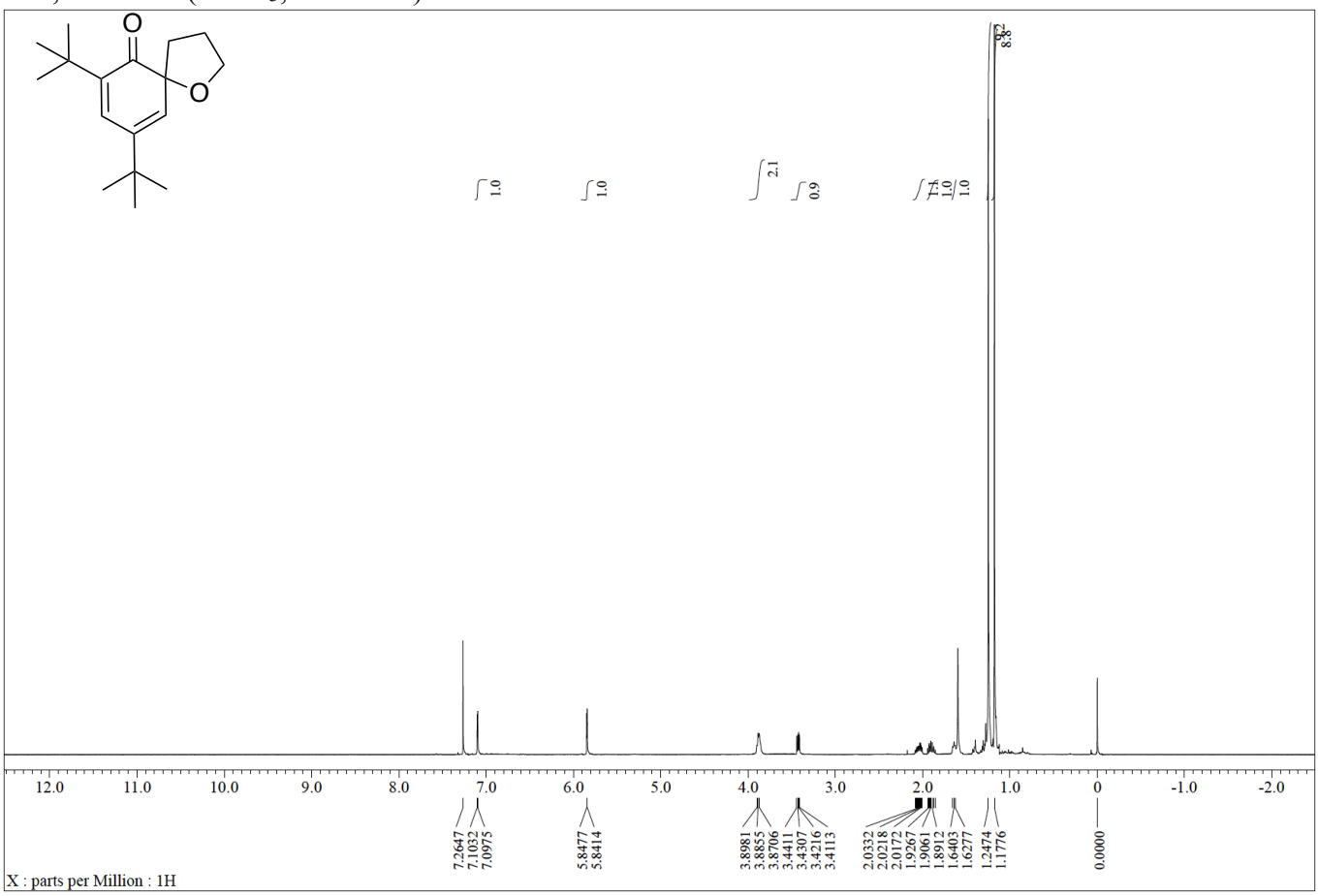
2h, ^{1}H NMR ($CDCl_3$, 400 MHz)



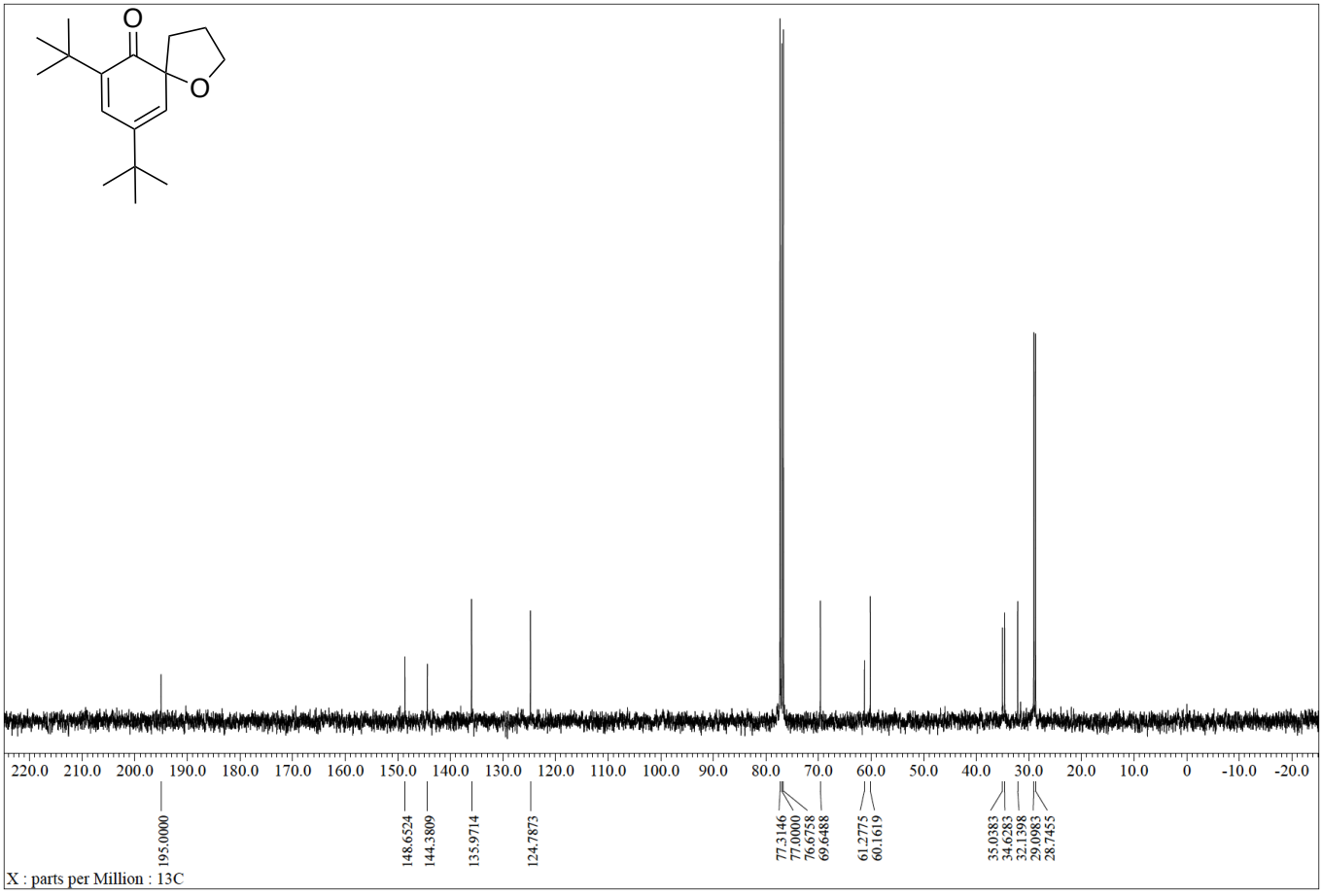
2h, ^{13}C NMR ($CDCl_3$, 100 MHz)



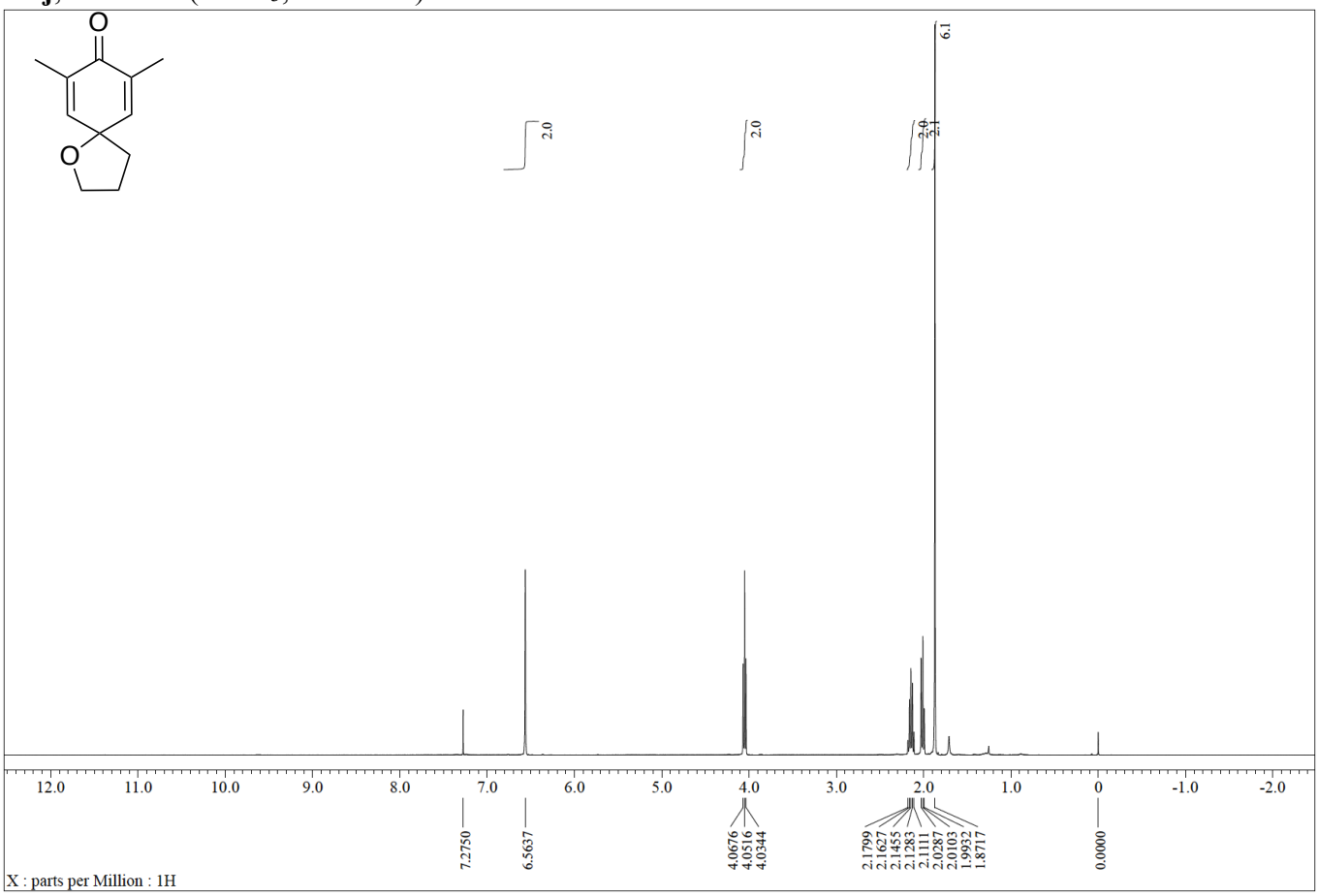
2i, ^{1}H NMR ($CDCl_3$, 400 MHz)



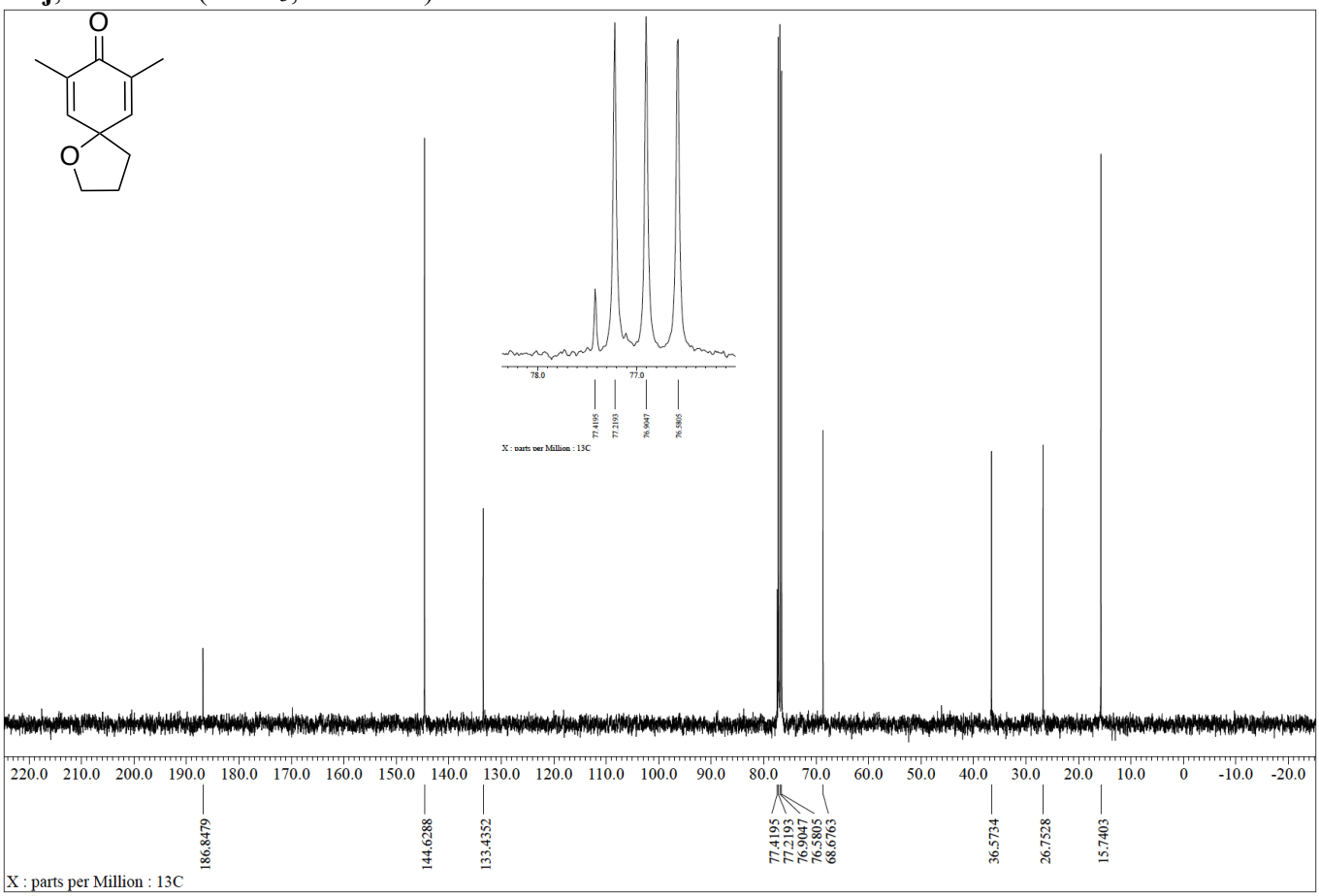
2i, ^{13}C NMR ($CDCl_3$, 100 MHz)



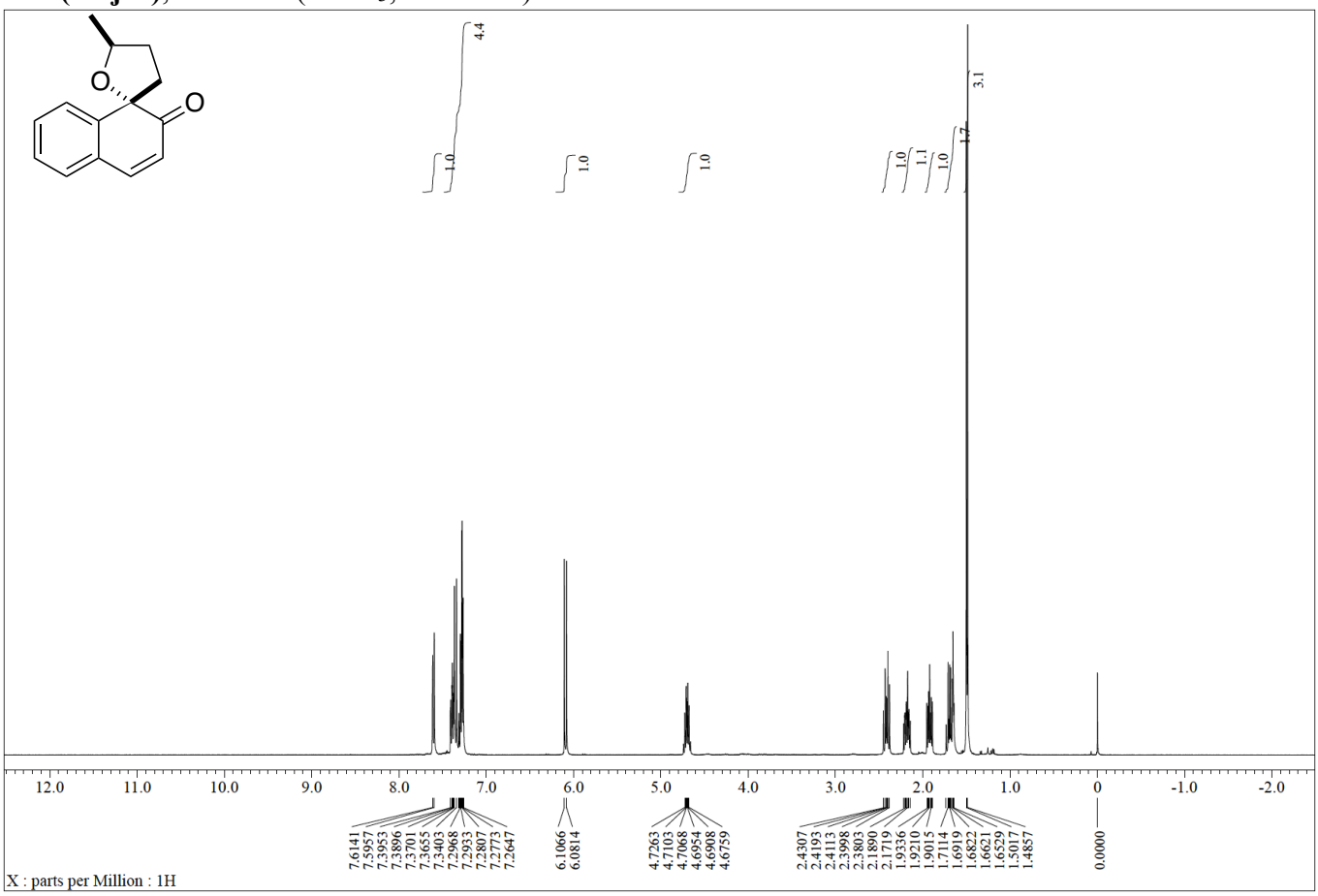
2j, ^{1}H NMR ($CDCl_3$, 400 MHz)



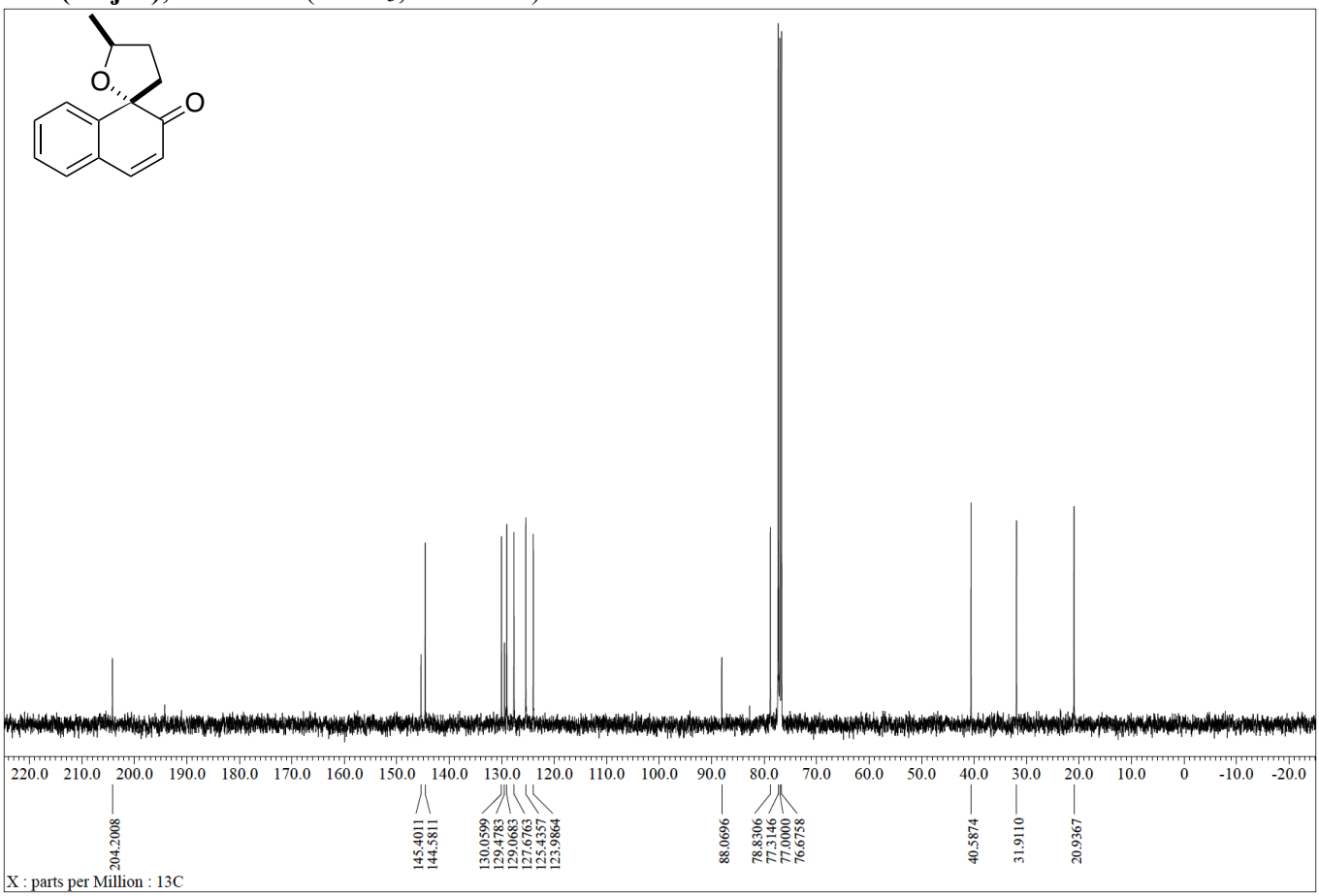
2j, ^{13}C NMR ($CDCl_3$, 100 MHz)



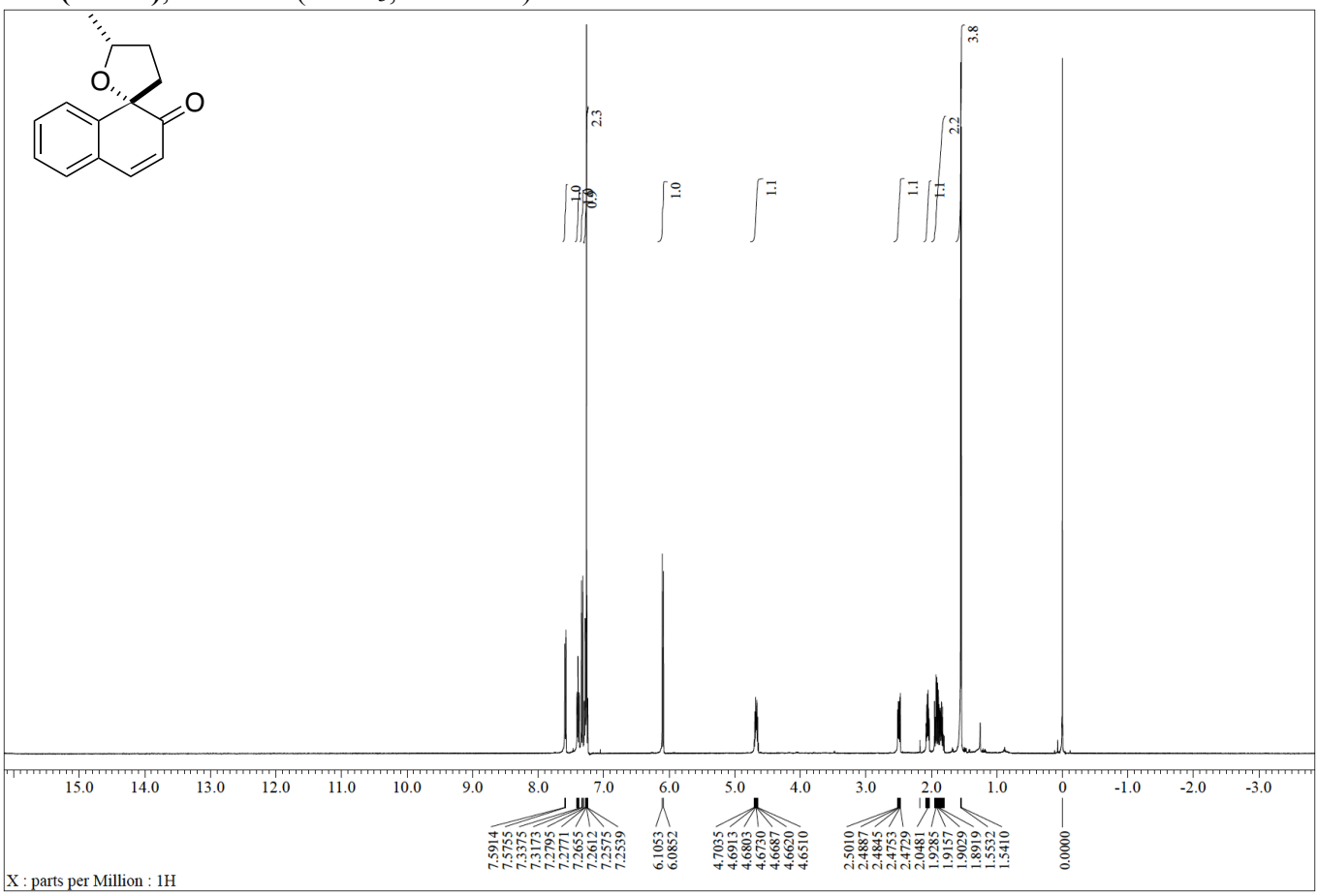
2l (major), ^{1}H NMR ($CDCl_3$, 400 MHz)



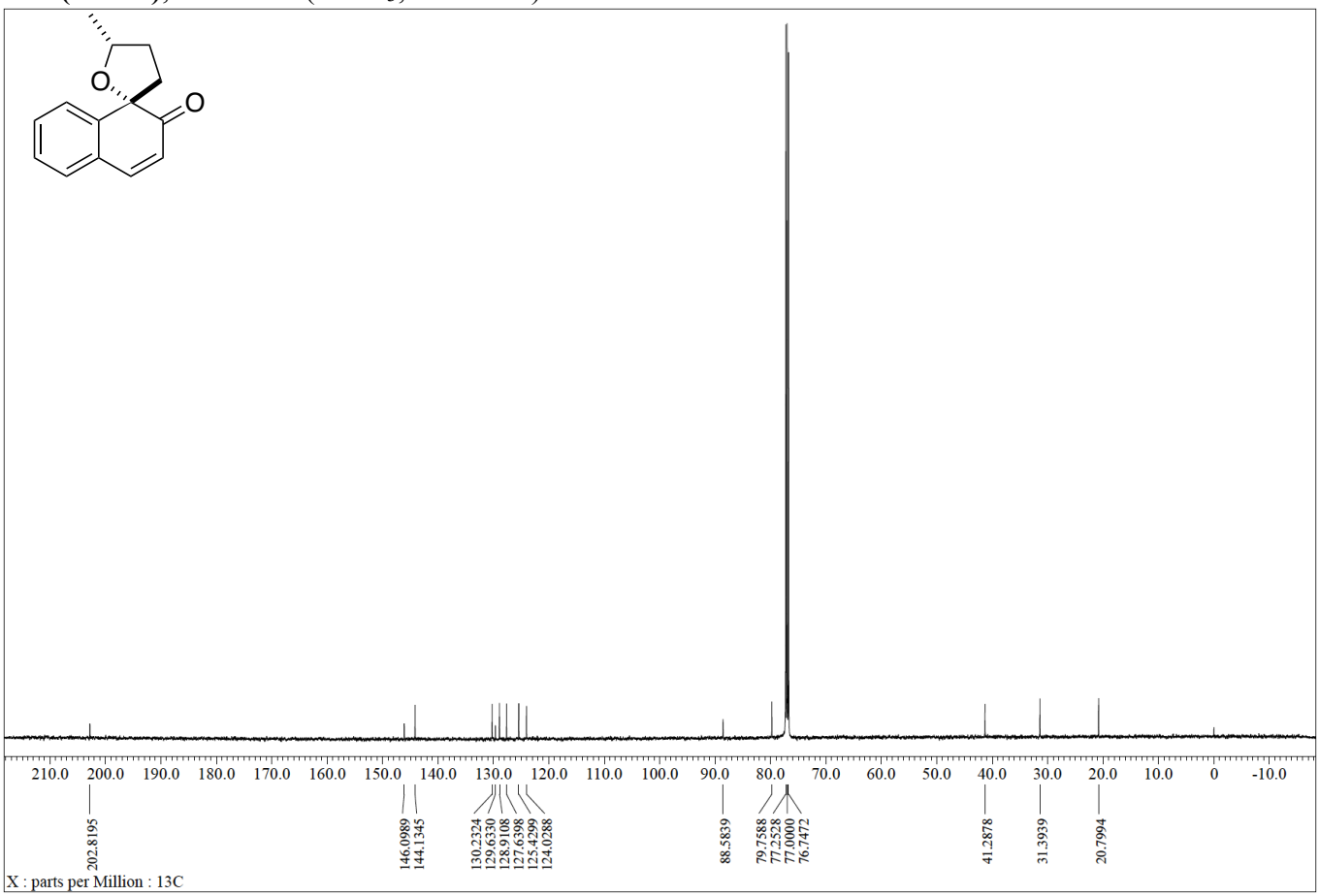
2l (major), ^{13}C NMR ($CDCl_3$, 100 MHz)



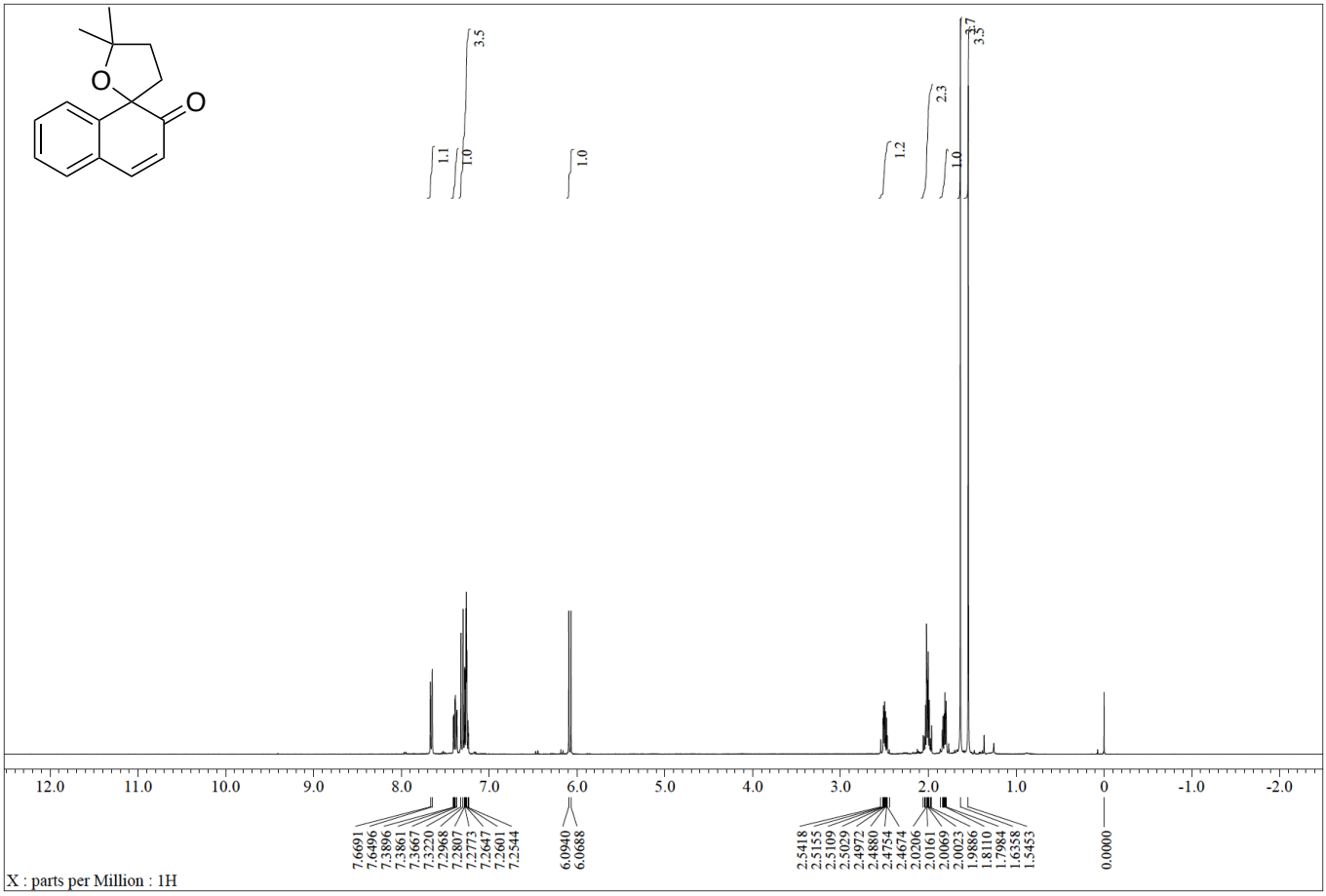
2l (minor), ^{1}H NMR ($CDCl_3$, 500 MHz)



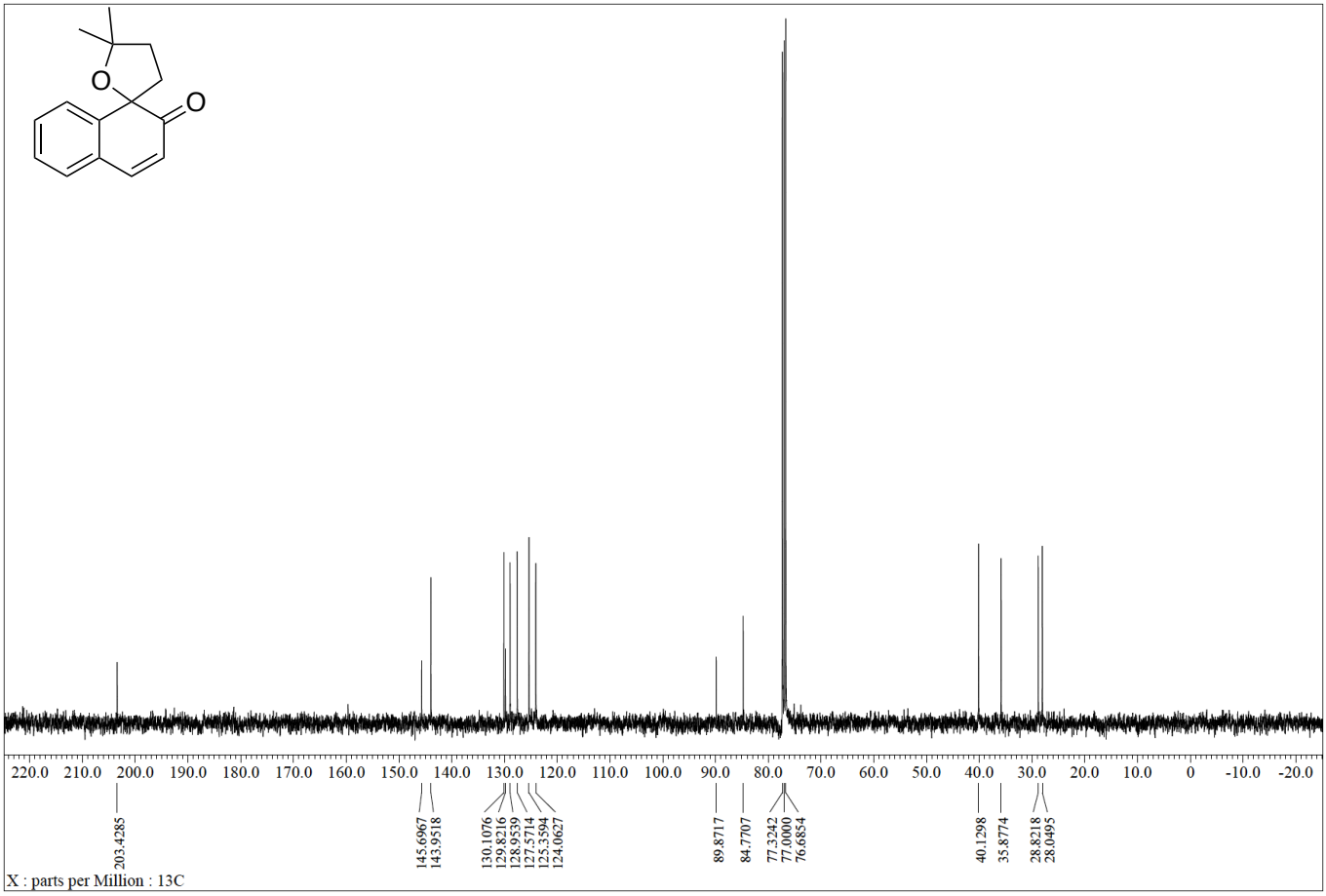
2l (minor), ^{13}C NMR ($CDCl_3$, 125 MHz)



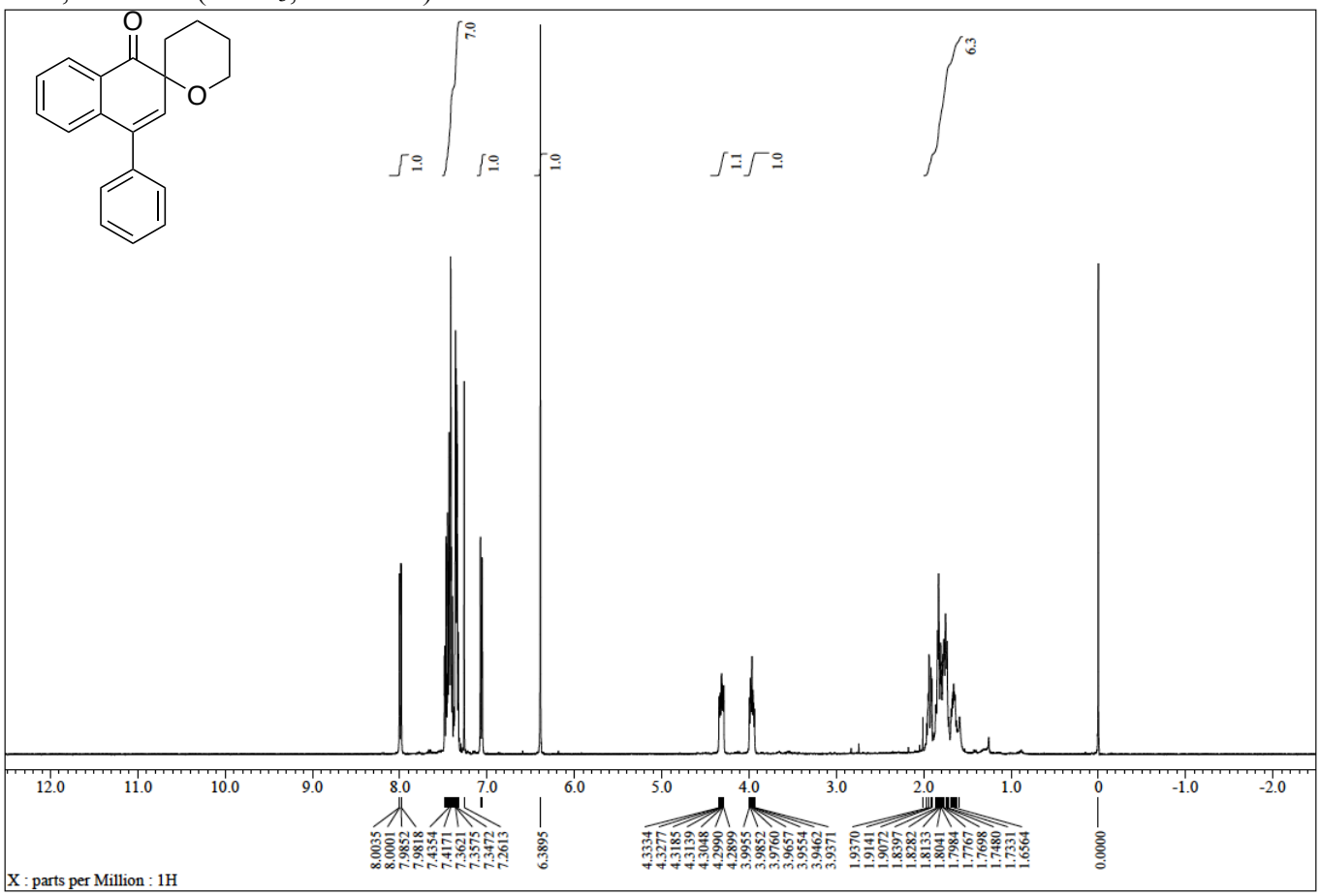
2m, ^{1}H NMR ($CDCl_3$, 400 MHz)



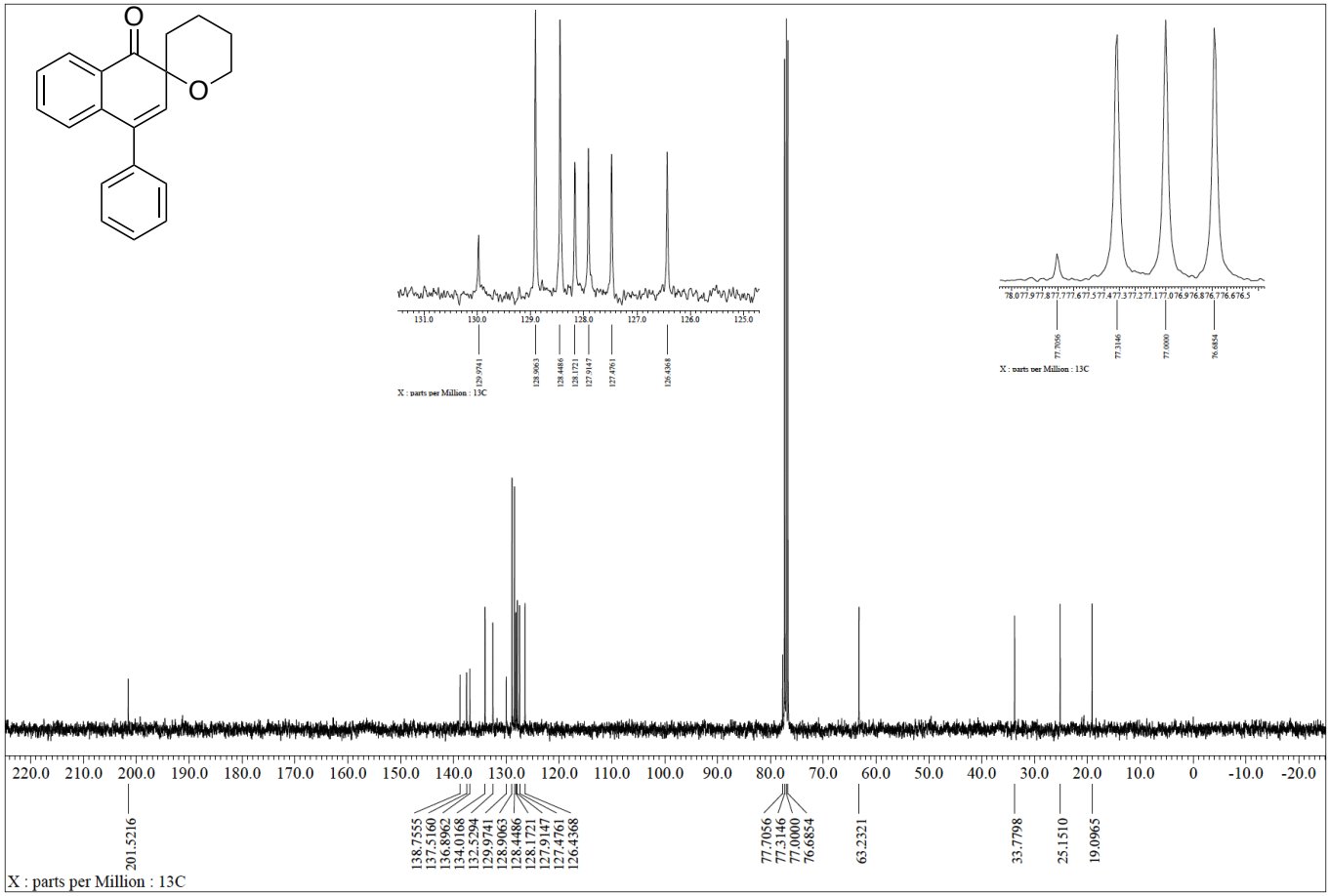
2m, ^{13}C NMR ($CDCl_3$, 100 MHz)



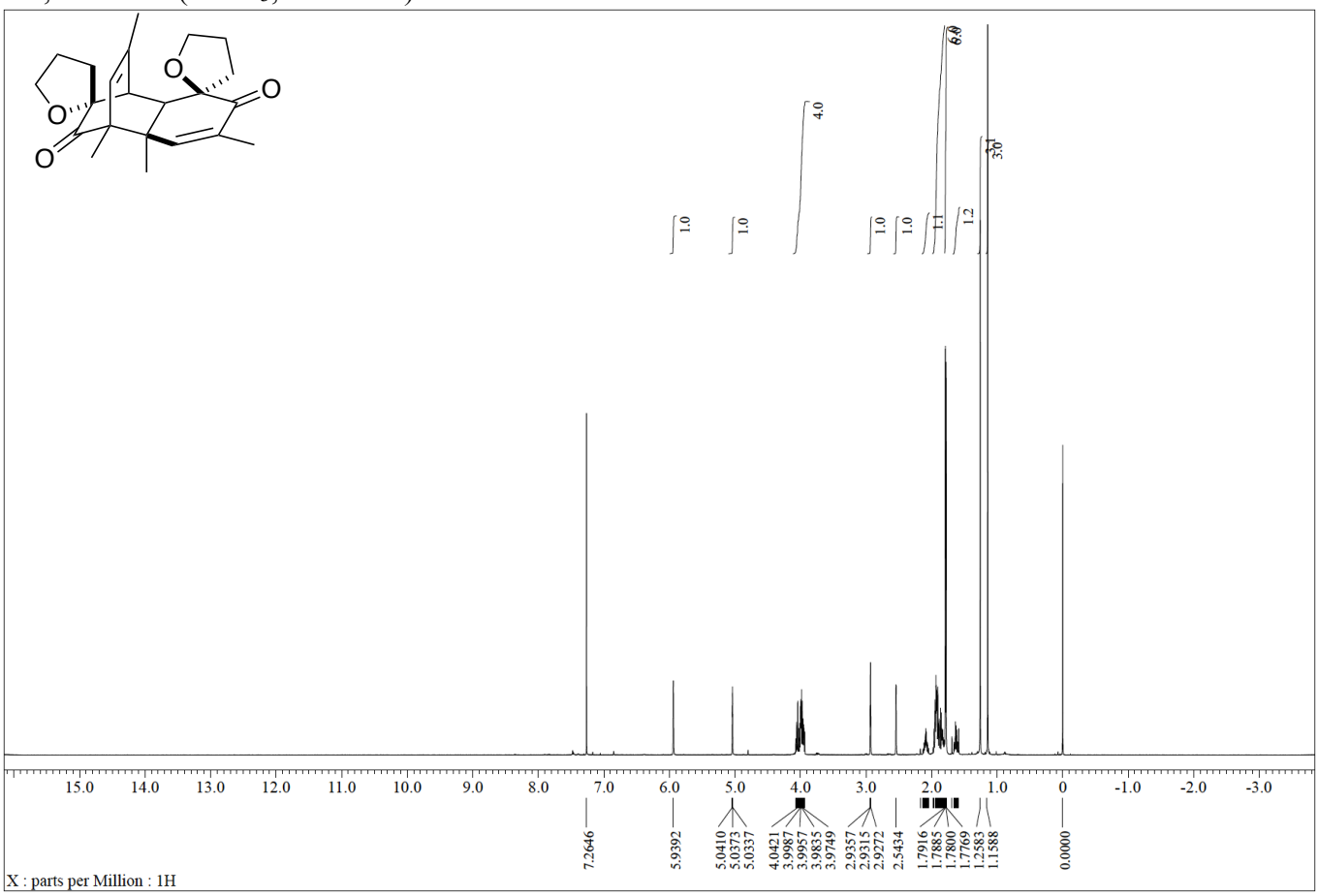
2n, ^{1}H NMR ($CDCl_3$, 400 MHz)



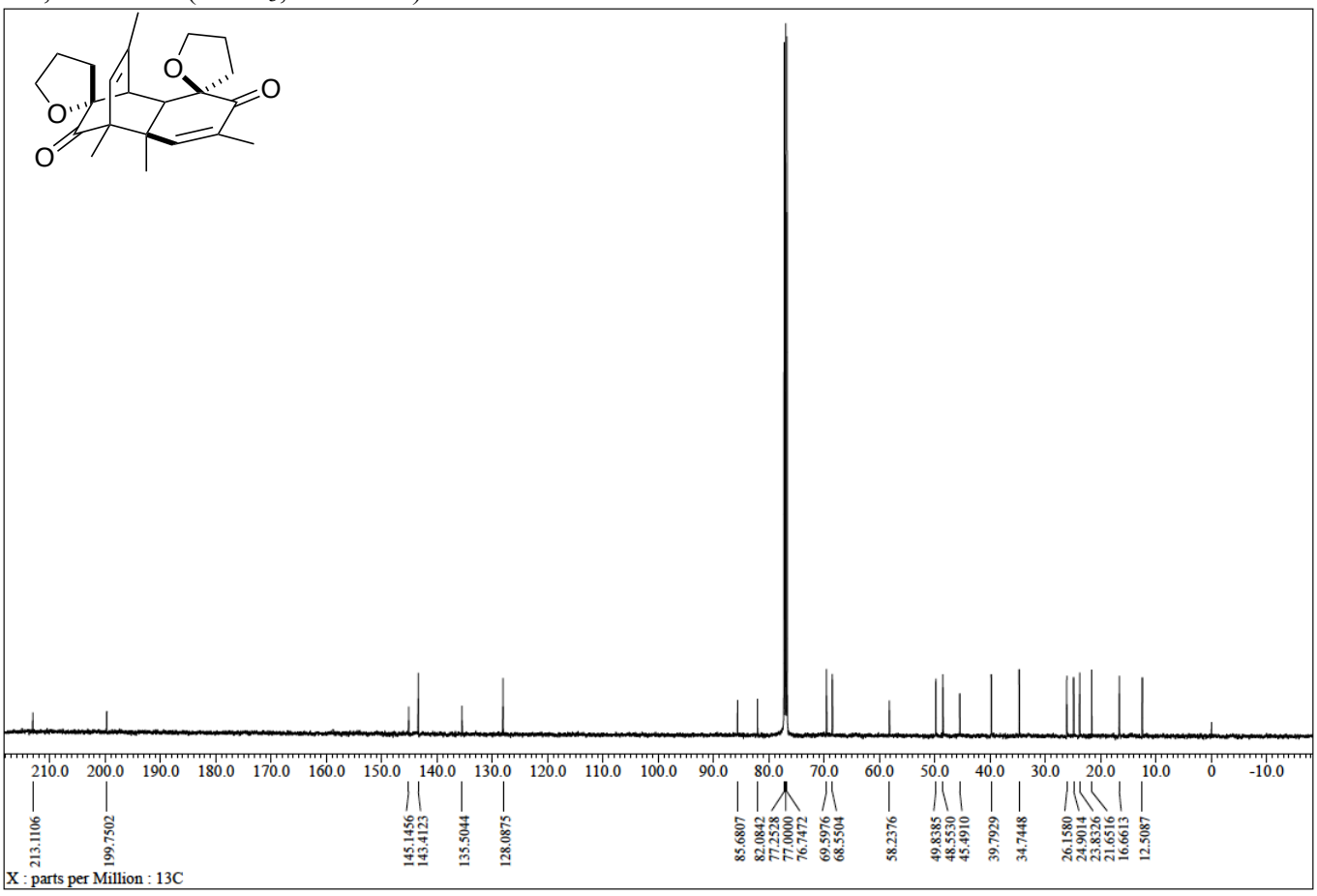
2n, ^{13}C NMR ($CDCl_3$, 100 MHz)



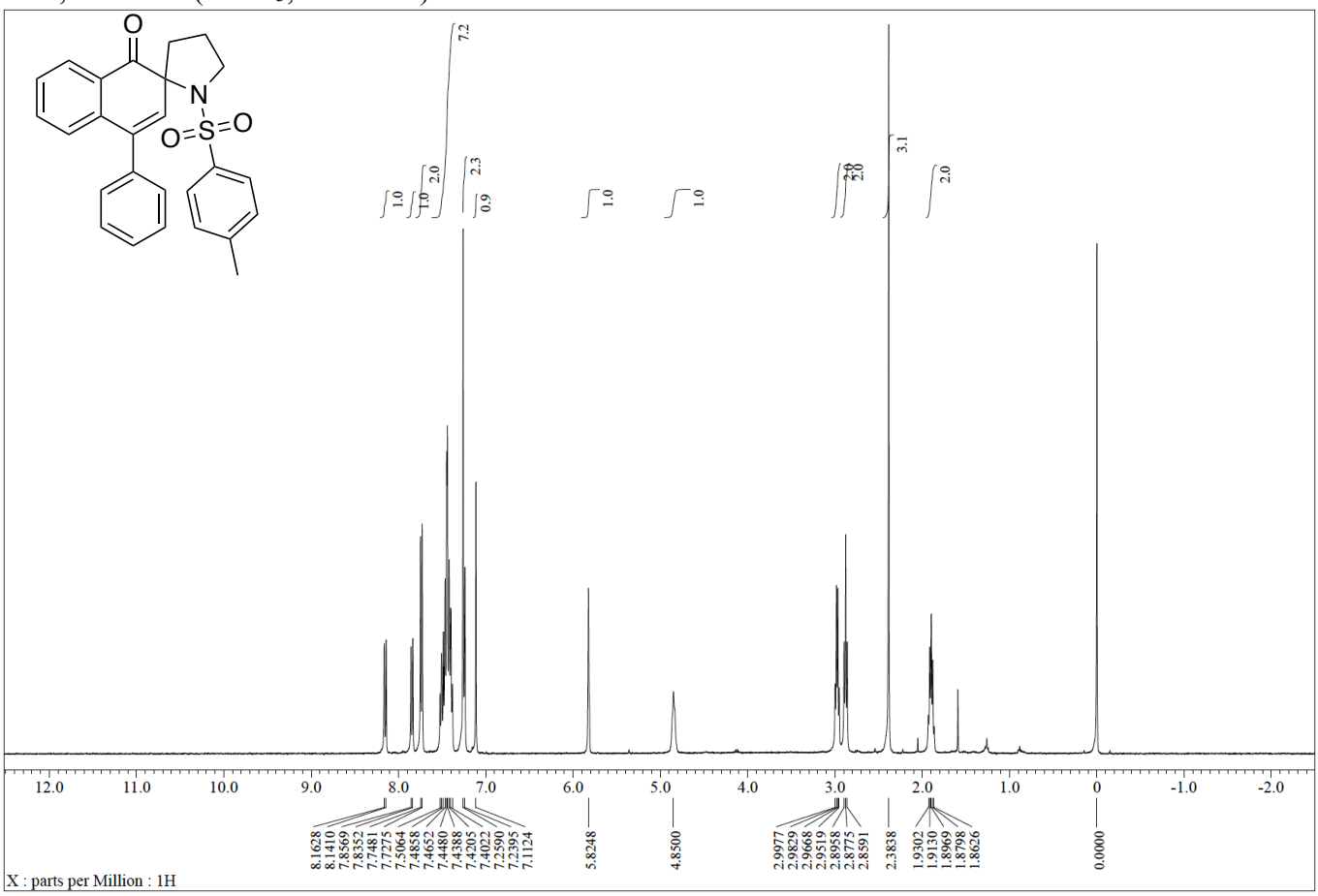
5, ^{1}H NMR ($CDCl_3$, 500 MHz)



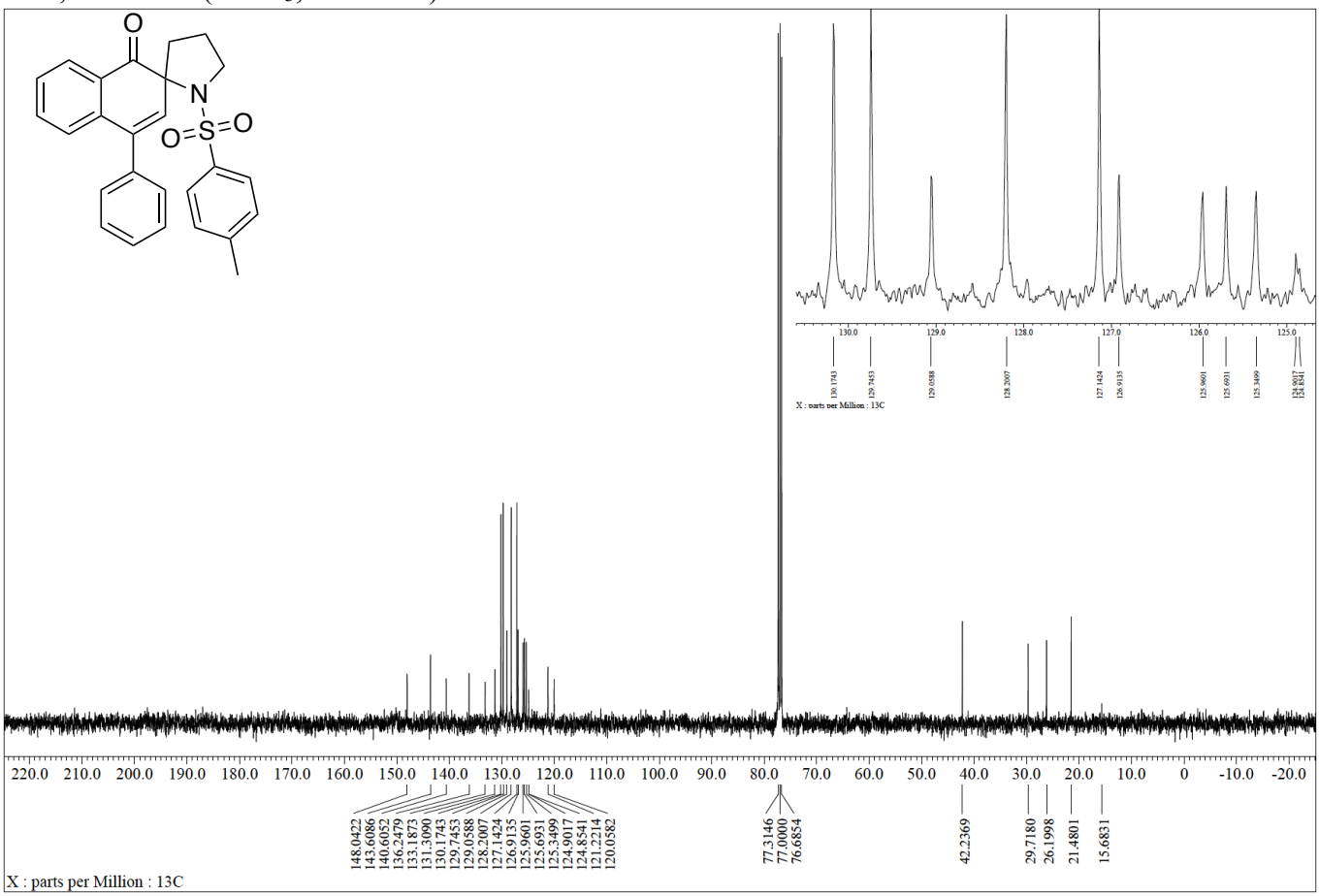
5, ^{13}C NMR ($CDCl_3$, 125 MHz)



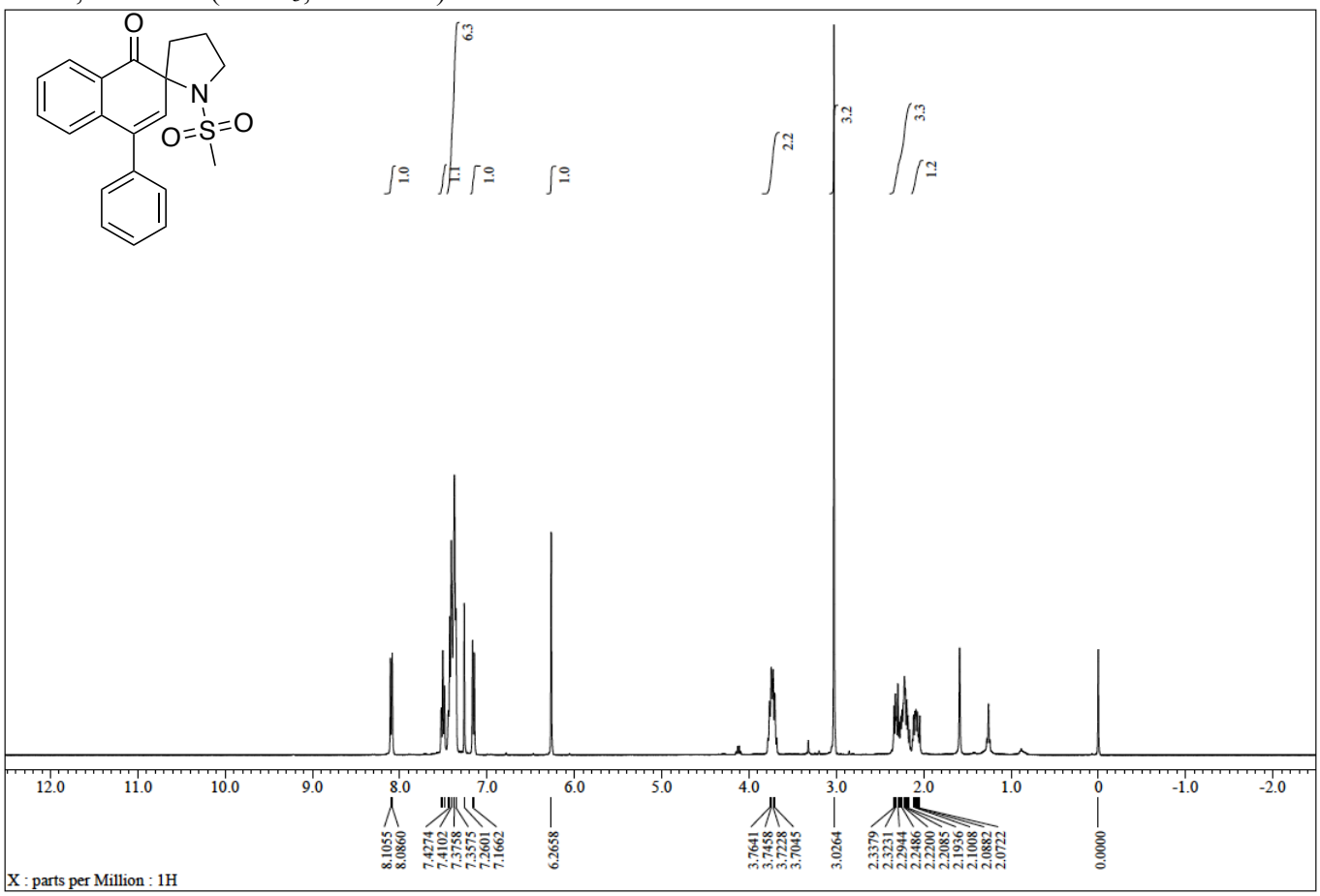
4a, ^{1}H NMR ($CDCl_3$, 400 MHz)



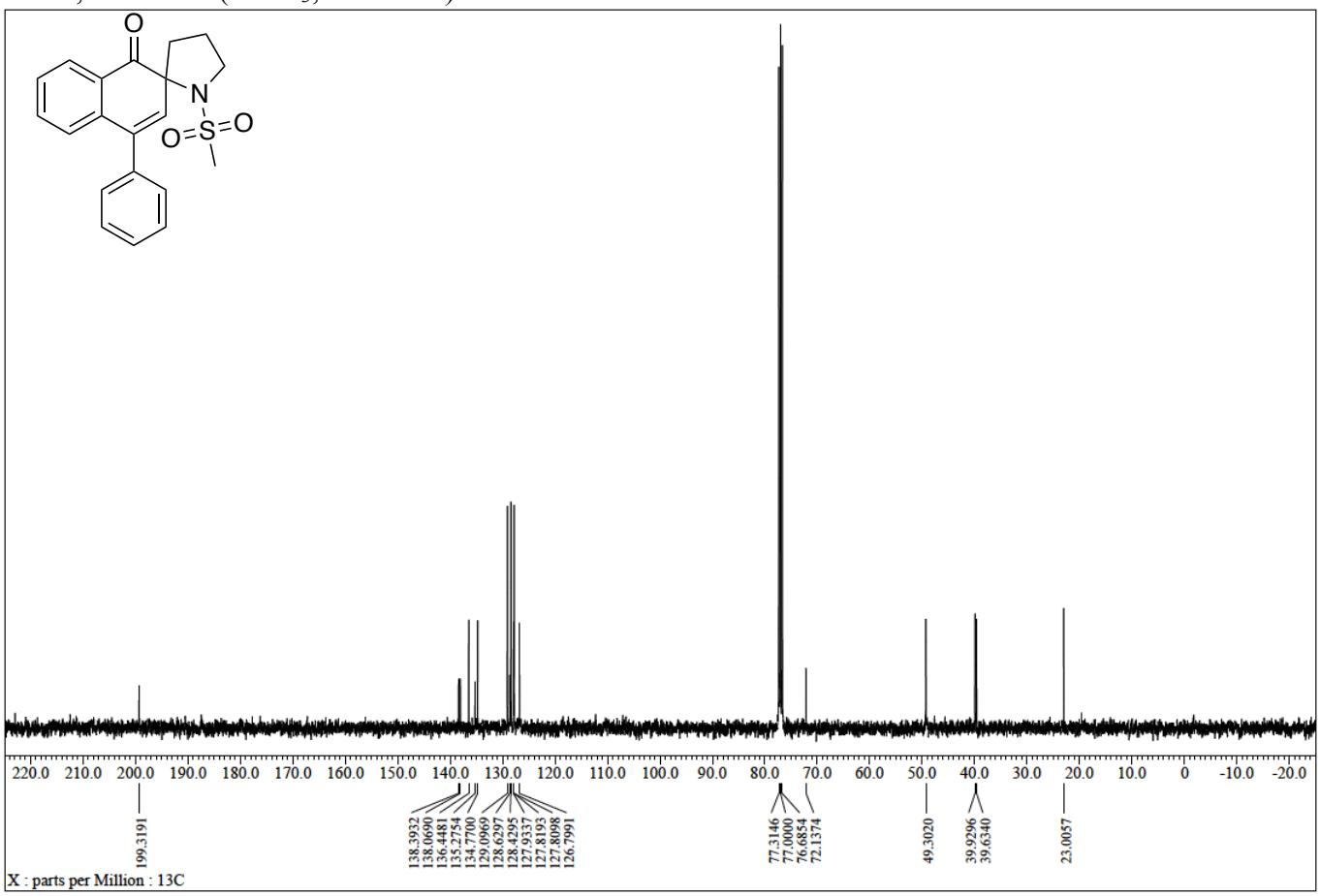
4a, ^{13}C NMR ($CDCl_3$, 100 MHz)



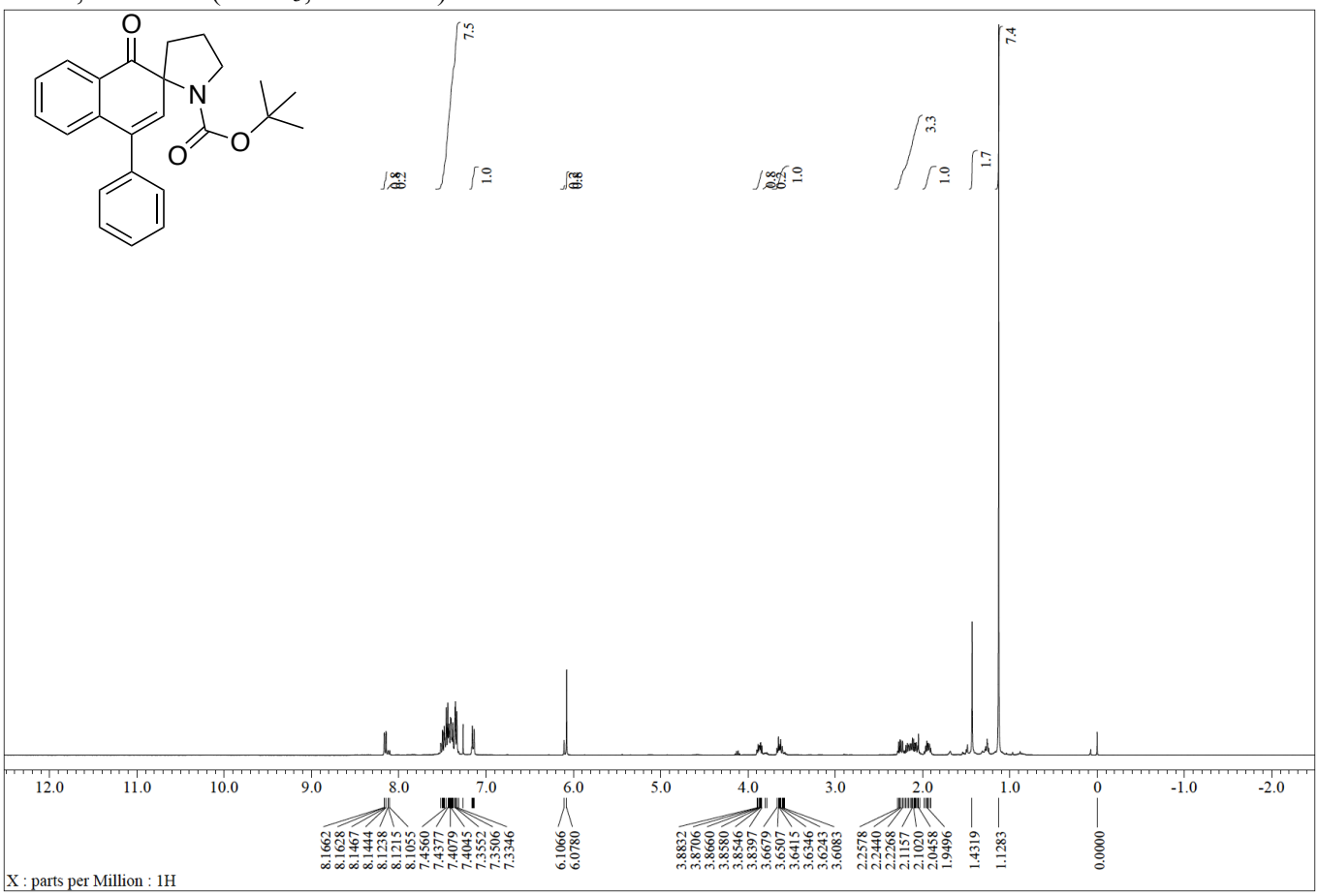
4aa, ^{1}H NMR ($CDCl_3$, 400 MHz)



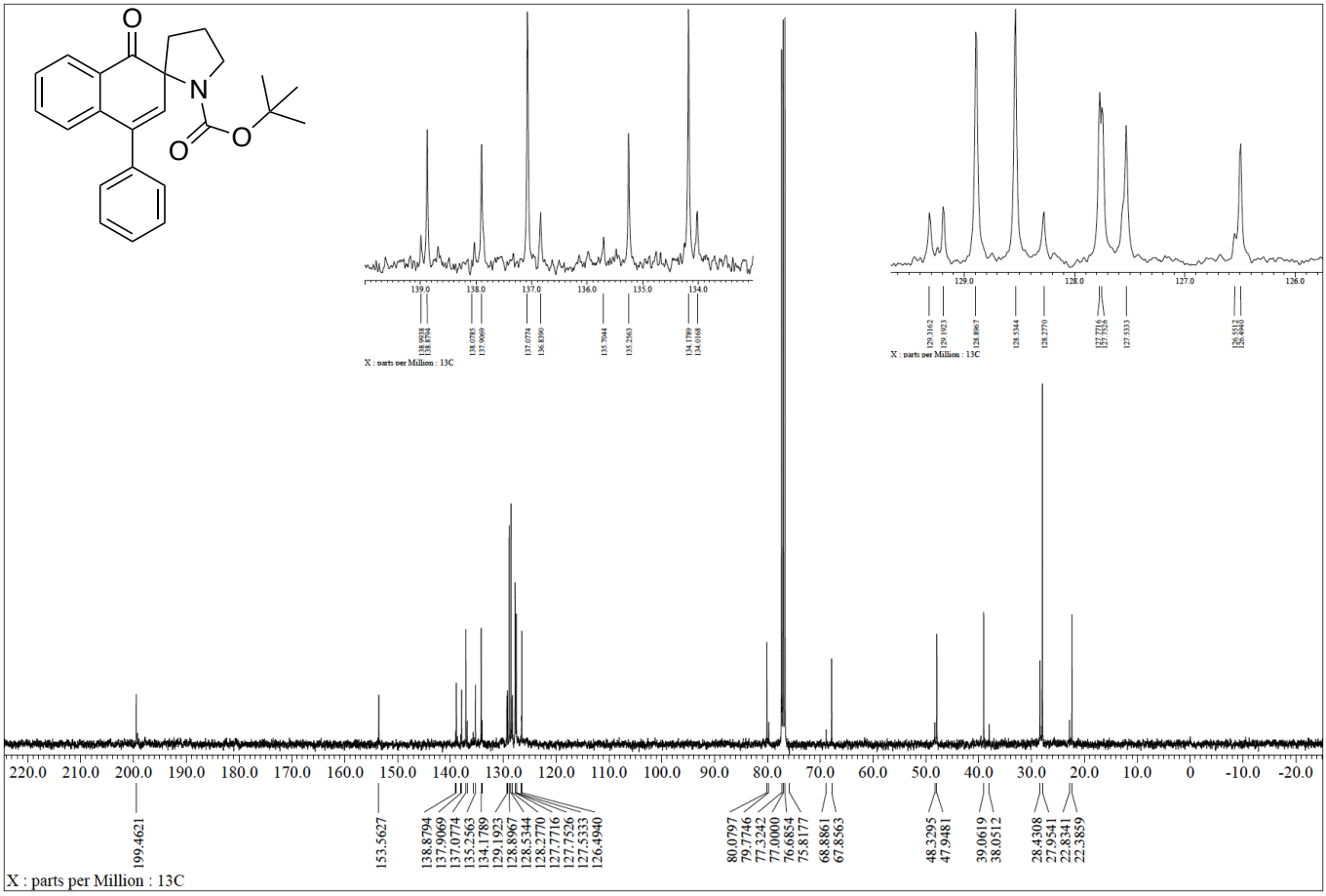
4aa, ^{13}C NMR ($CDCl_3$, 100 MHz)



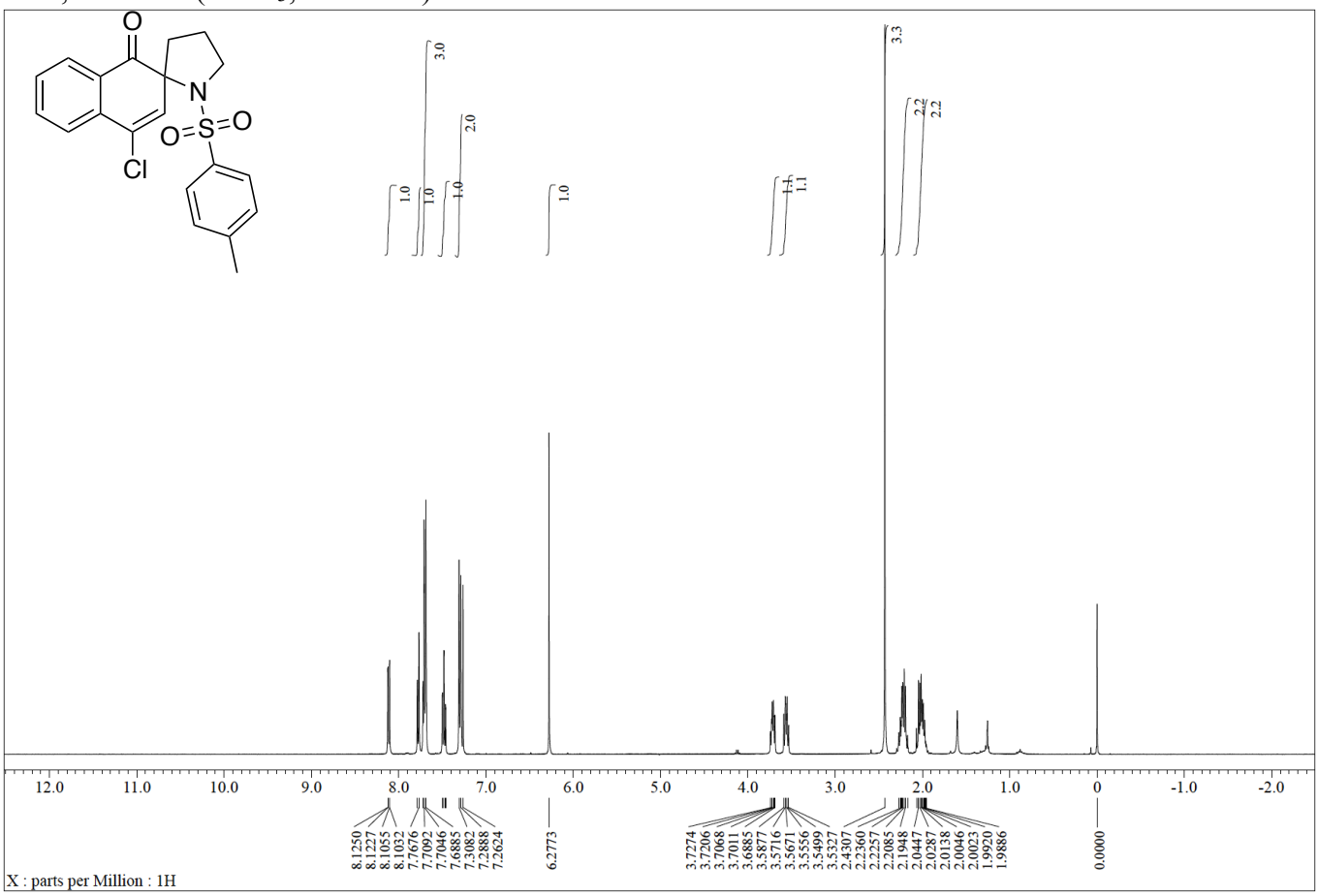
4ab, ^{1}H NMR ($CDCl_3$, 400 MHz)



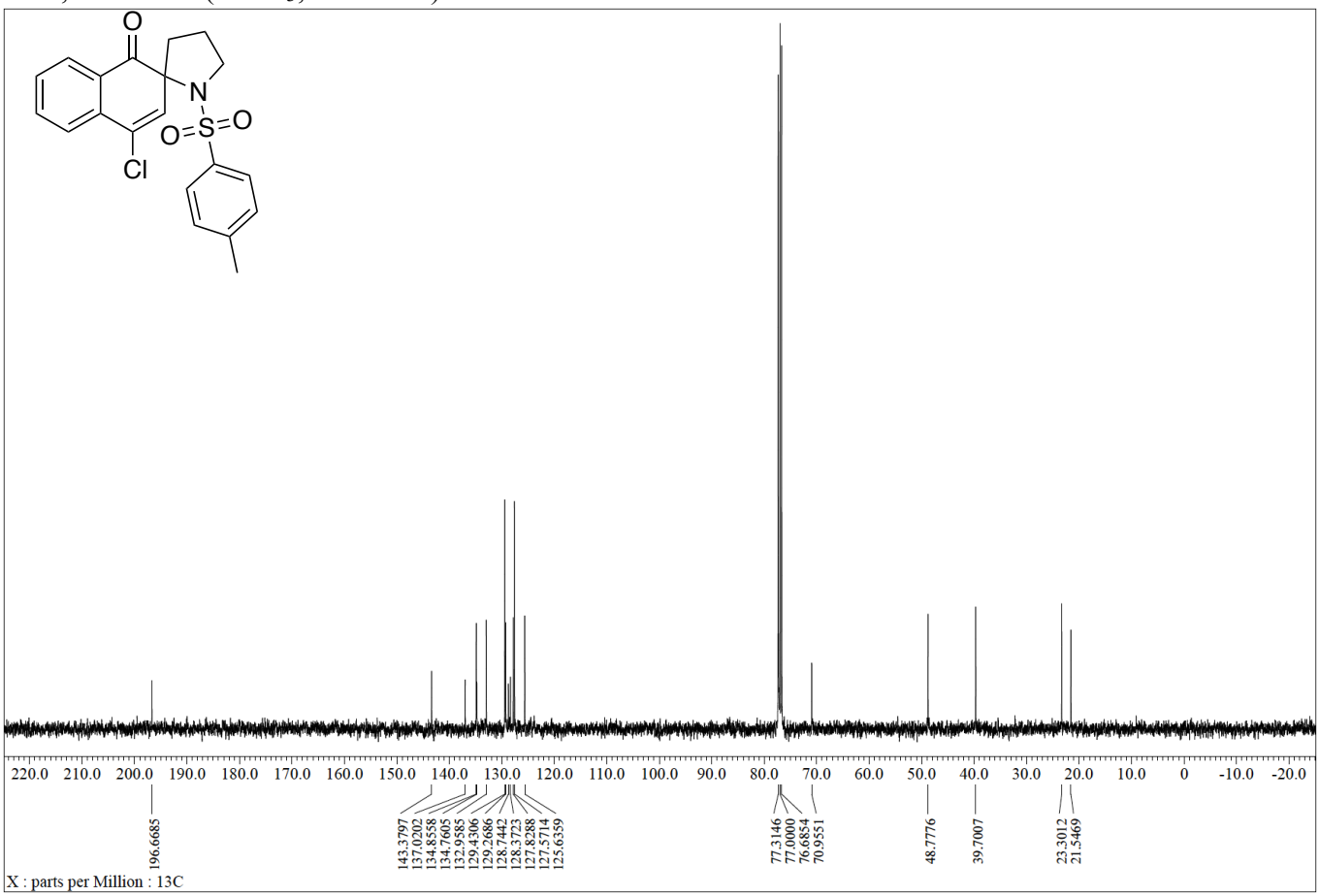
4ab, ^{13}C NMR ($CDCl_3$, 100 MHz)



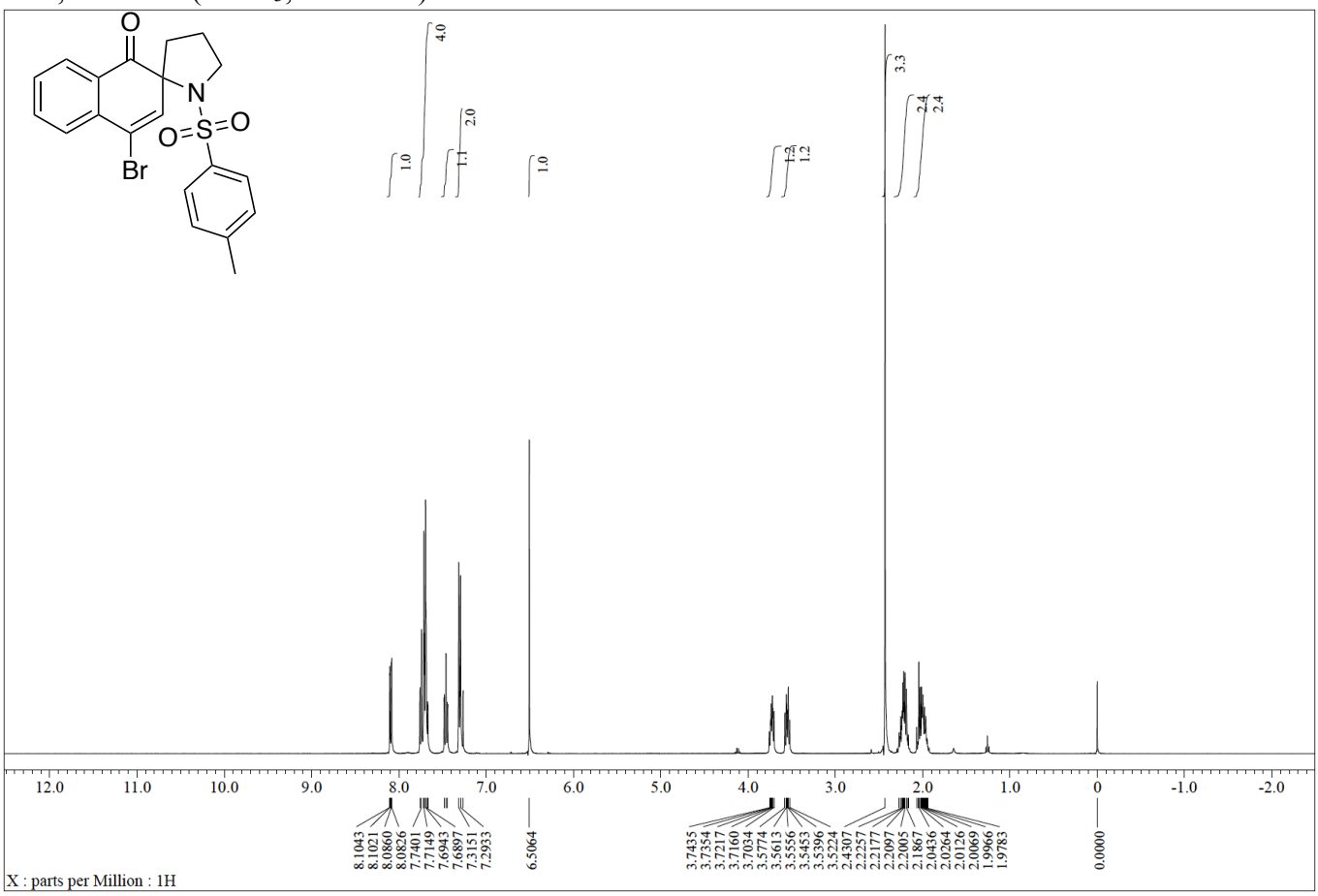
4b, ^{1}H NMR ($CDCl_3$, 400 MHz)



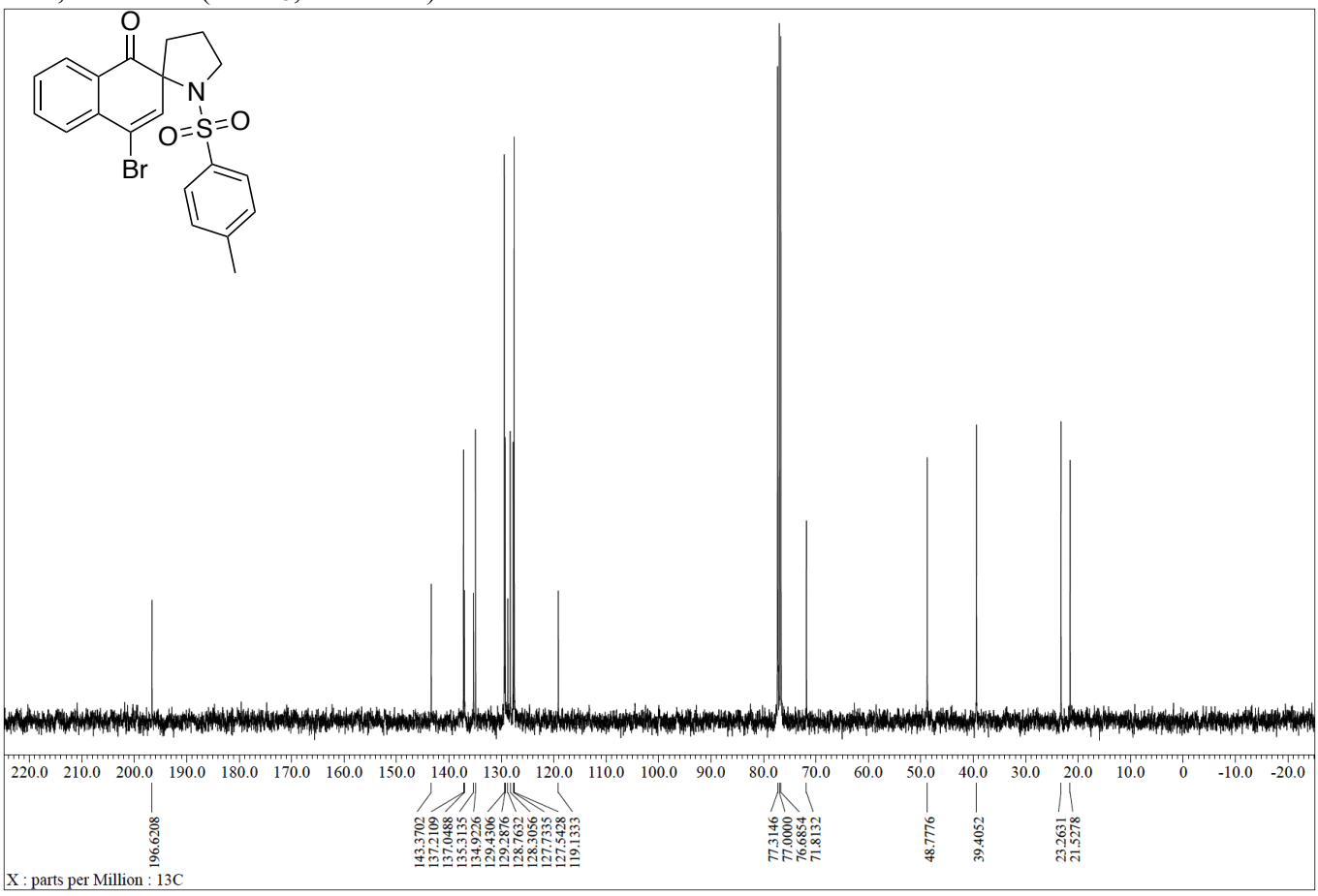
4b, ^{13}C NMR ($CDCl_3$, 100 MHz)



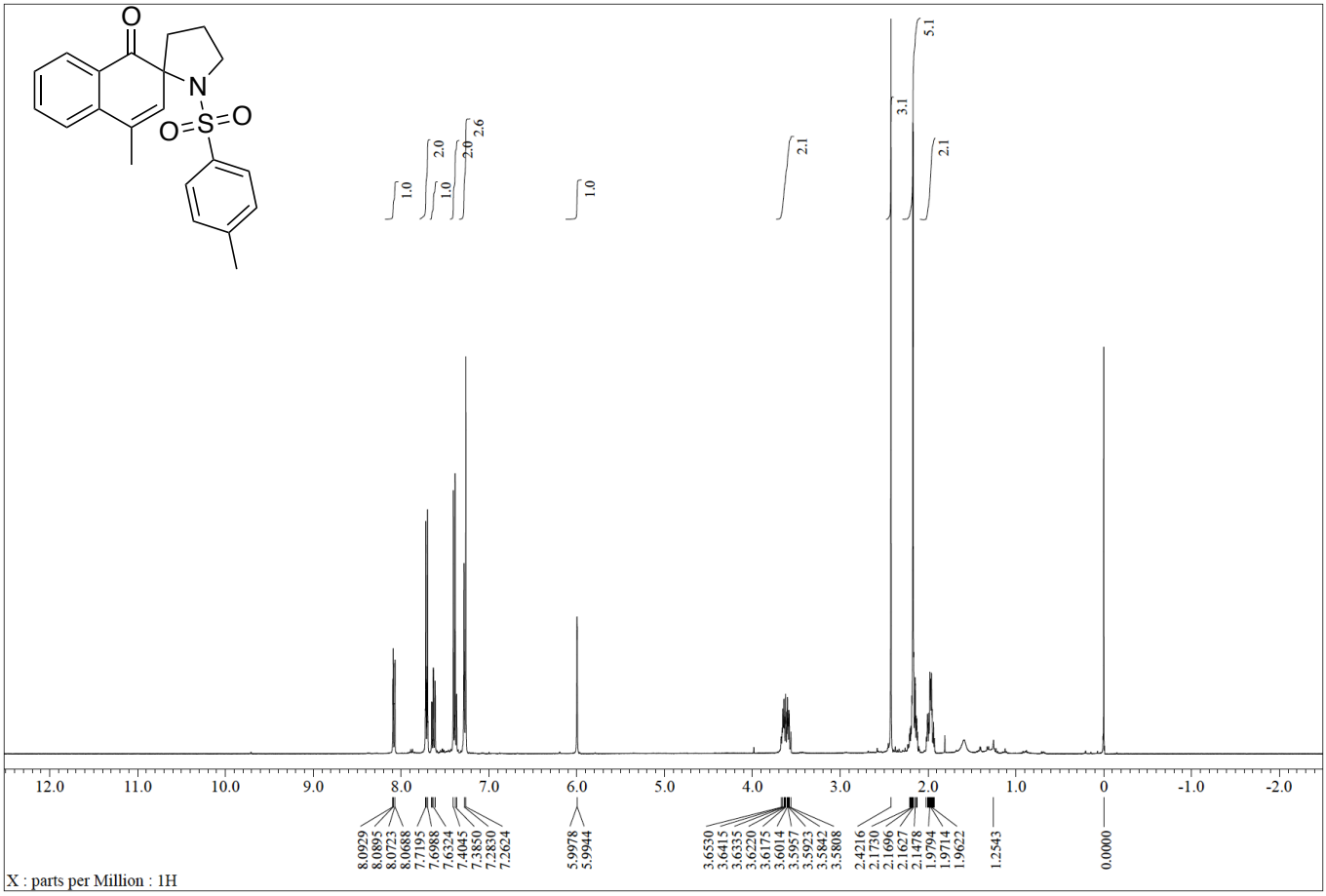
4c, ^{1}H NMR ($CDCl_3$, 400 MHz)



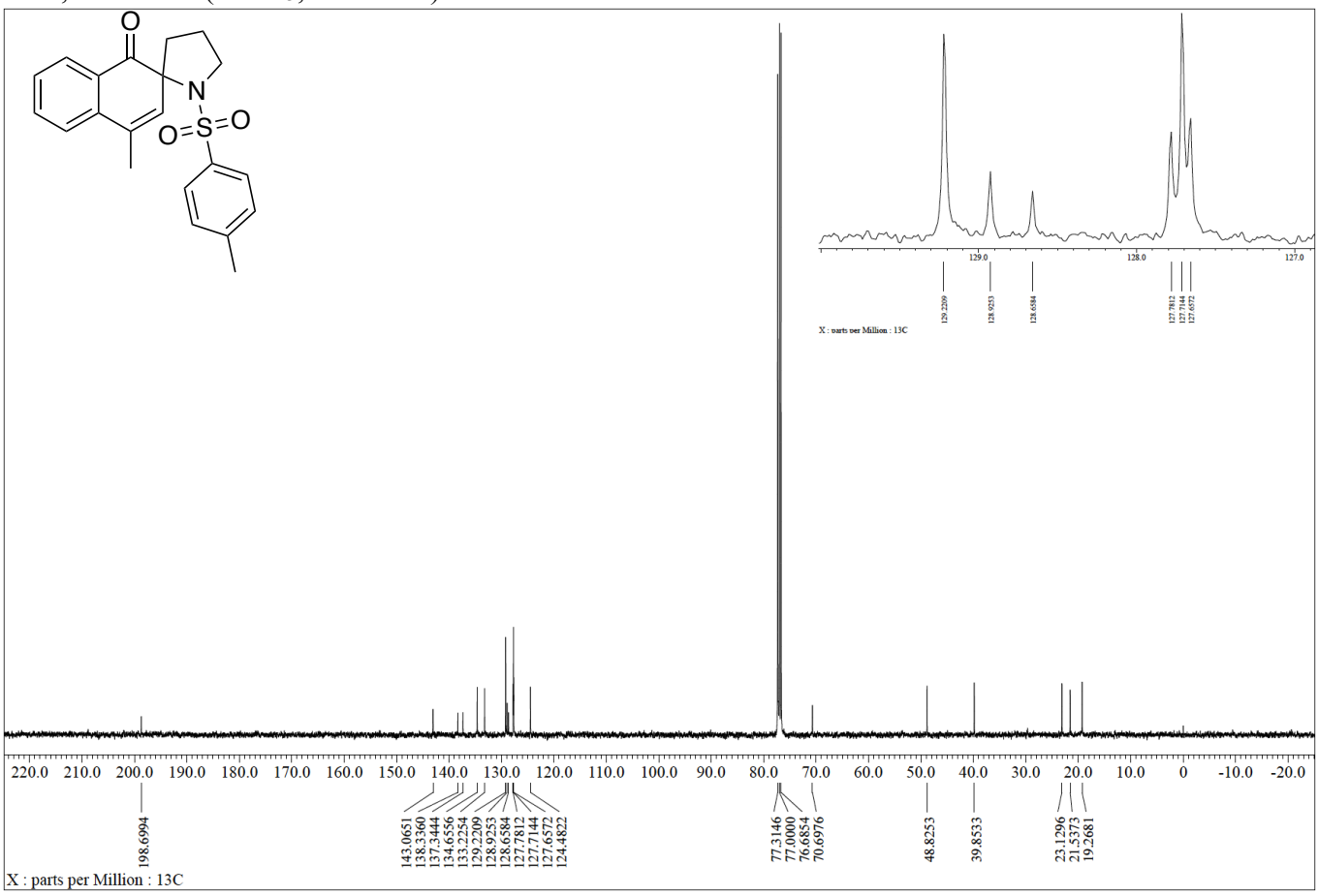
4c, ^{13}C NMR ($CDCl_3$, 100 MHz)



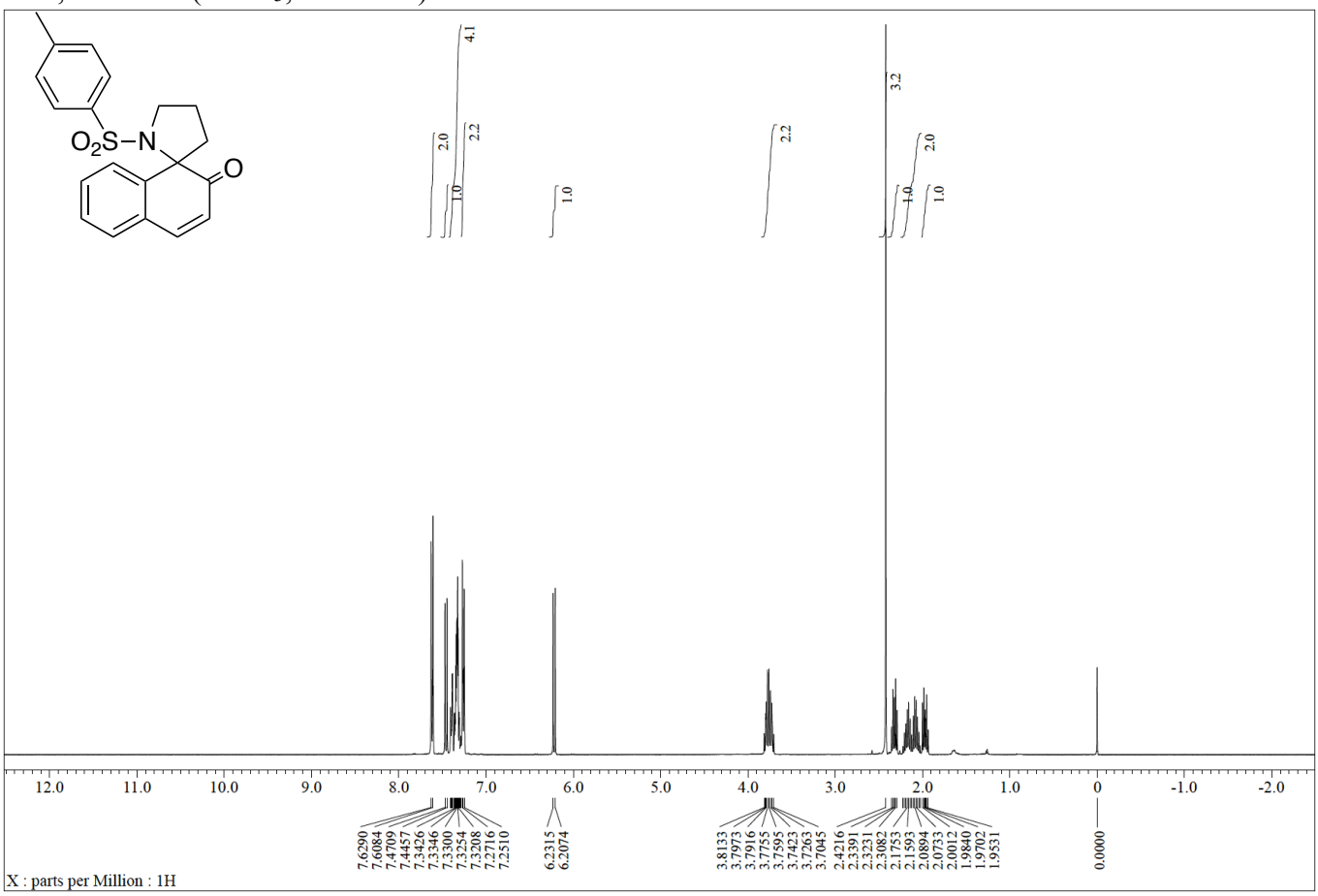
4d, ^{1}H NMR ($CDCl_3$, 400 MHz)



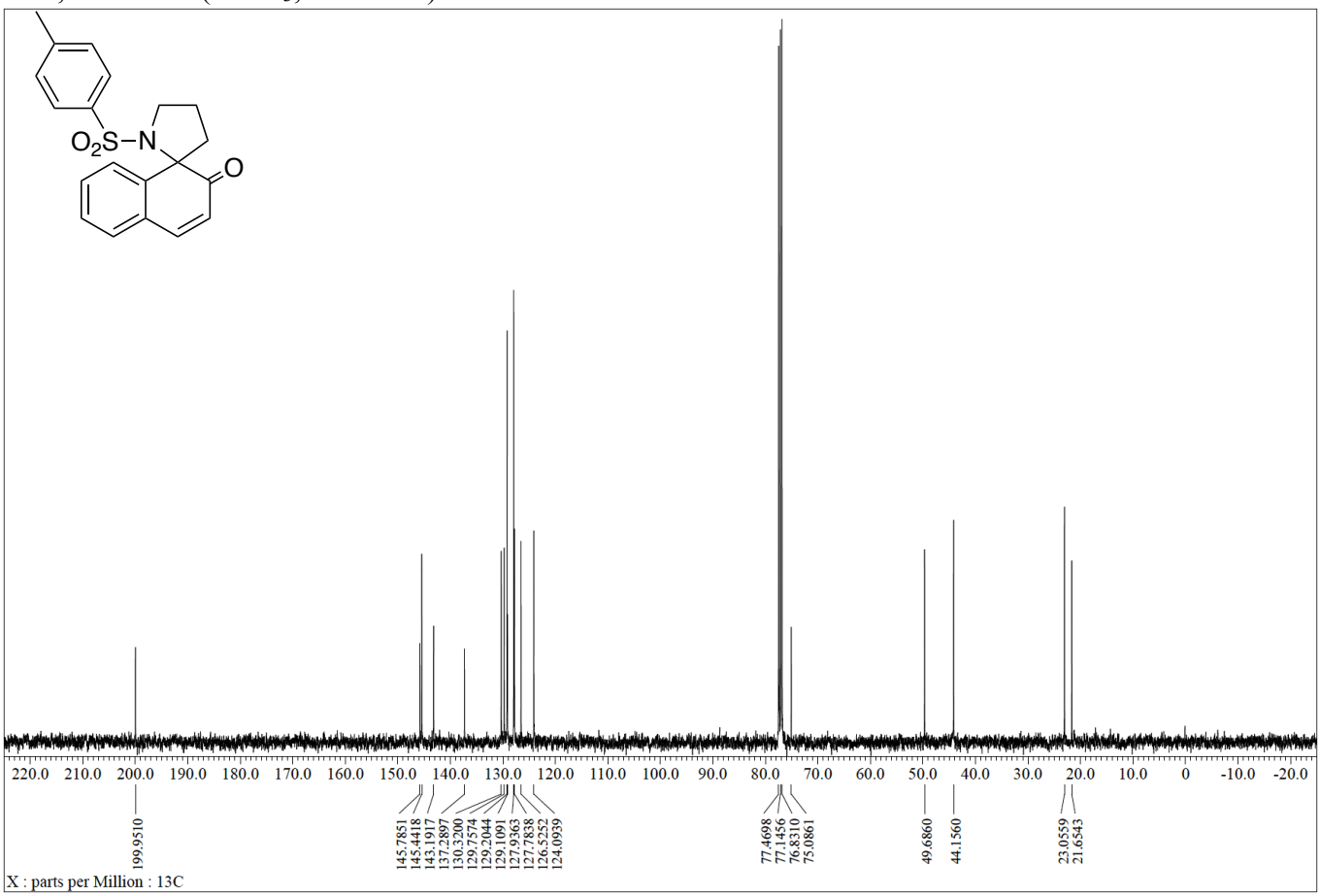
4d, ^{13}C NMR ($CDCl_3$, 100 MHz)



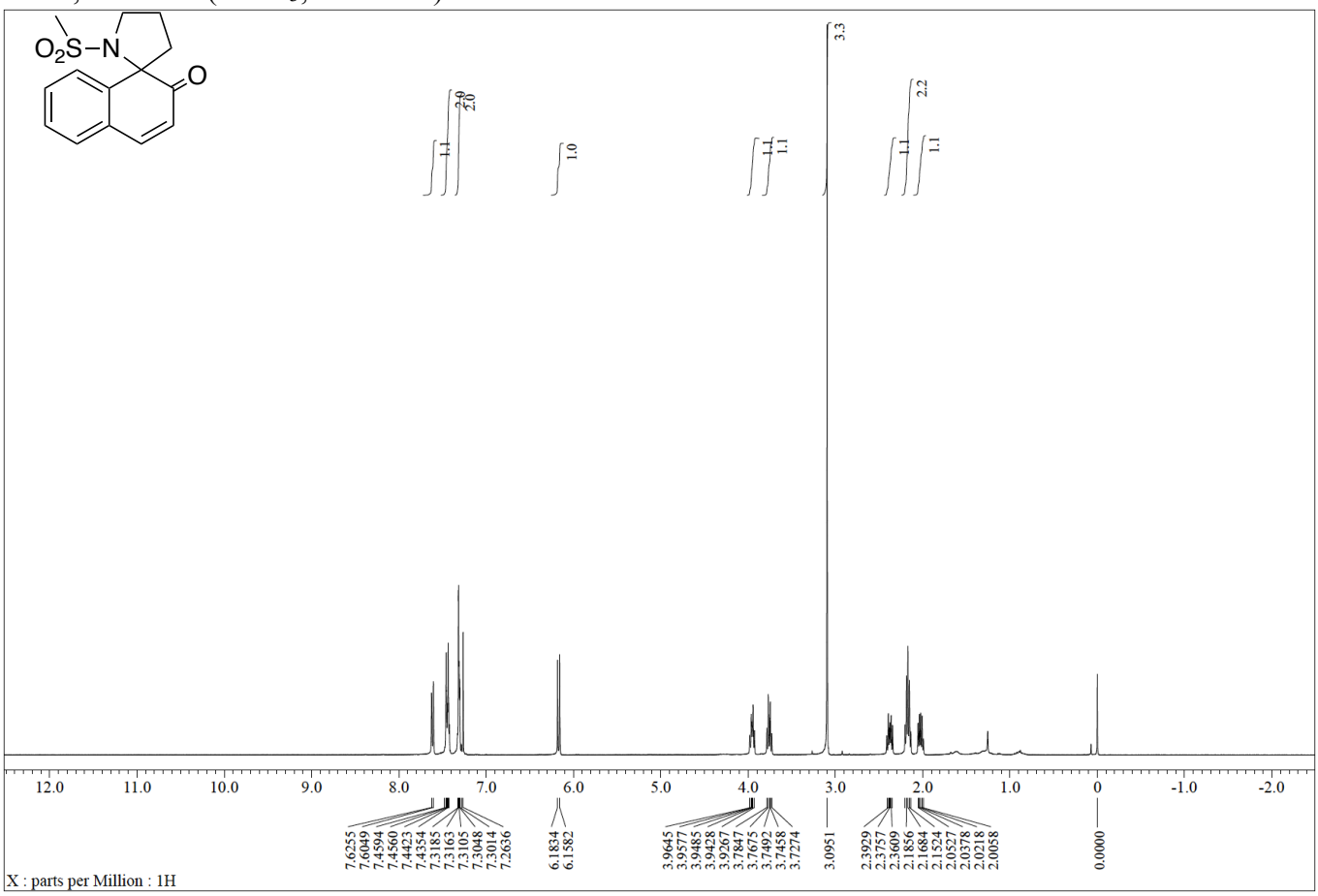
4e, ^{1}H NMR ($CDCl_3$, 400 MHz)



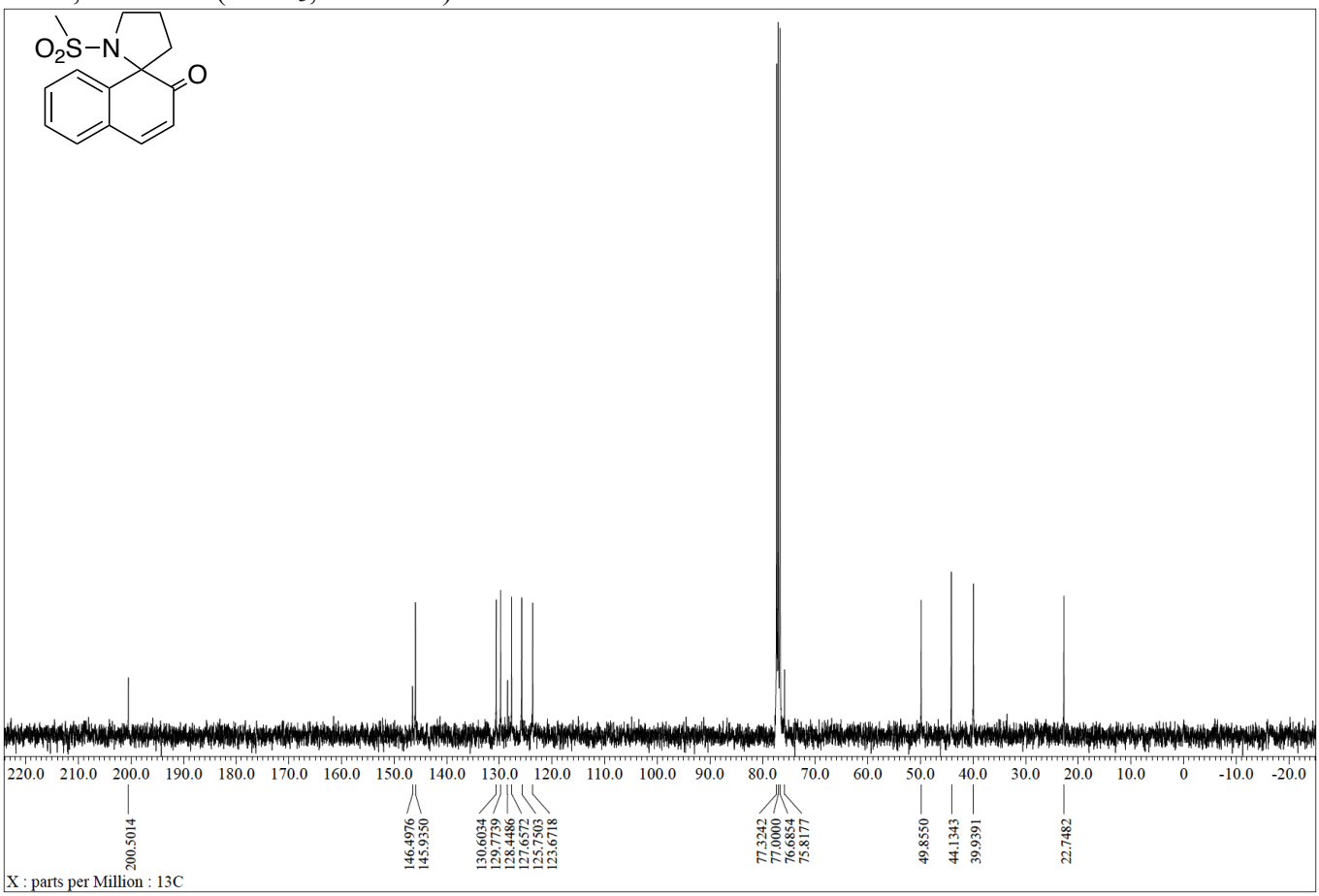
4e, ^{13}C NMR ($CDCl_3$, 100 MHz)



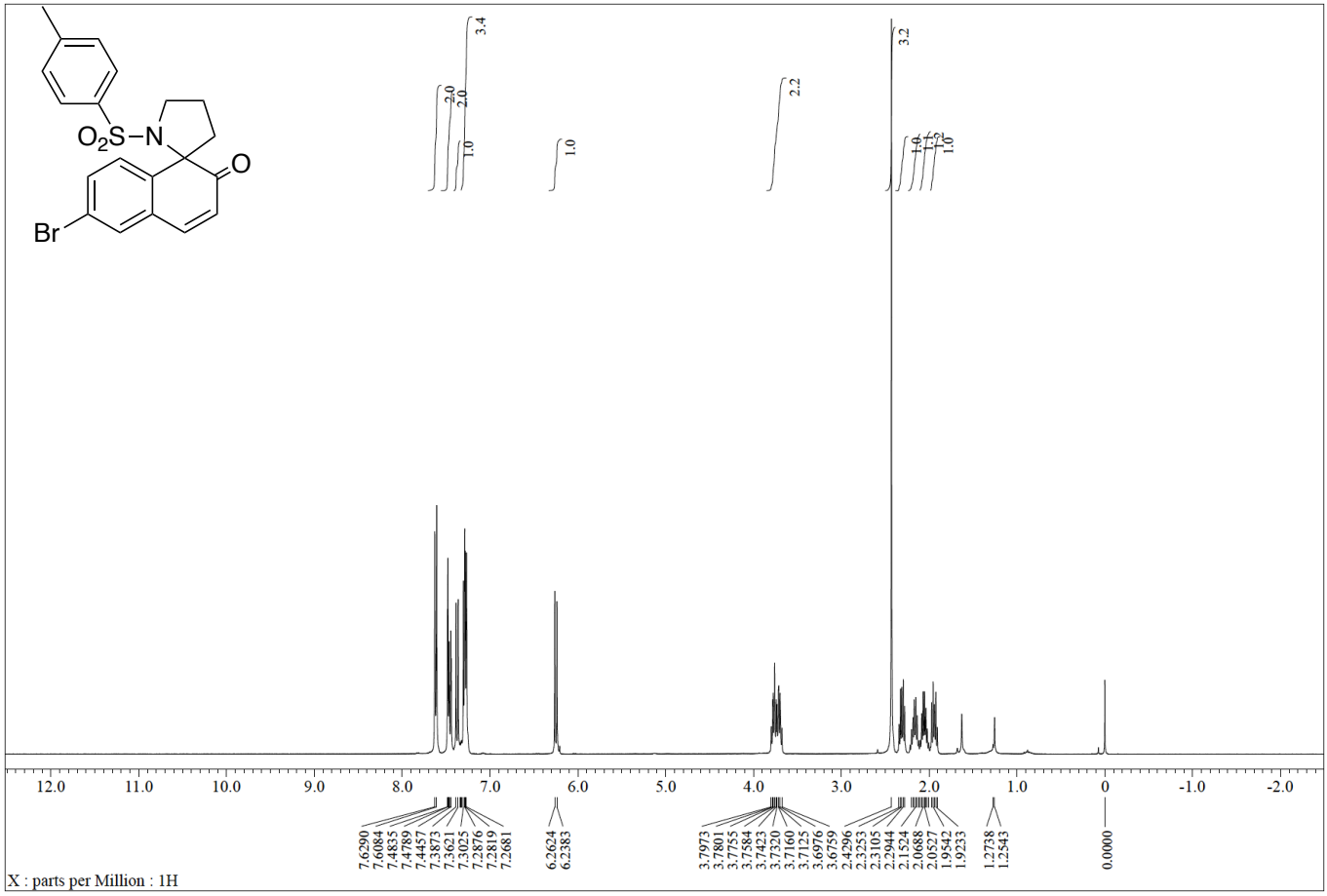
4ea, ^{1}H NMR ($CDCl_3$, 400 MHz)



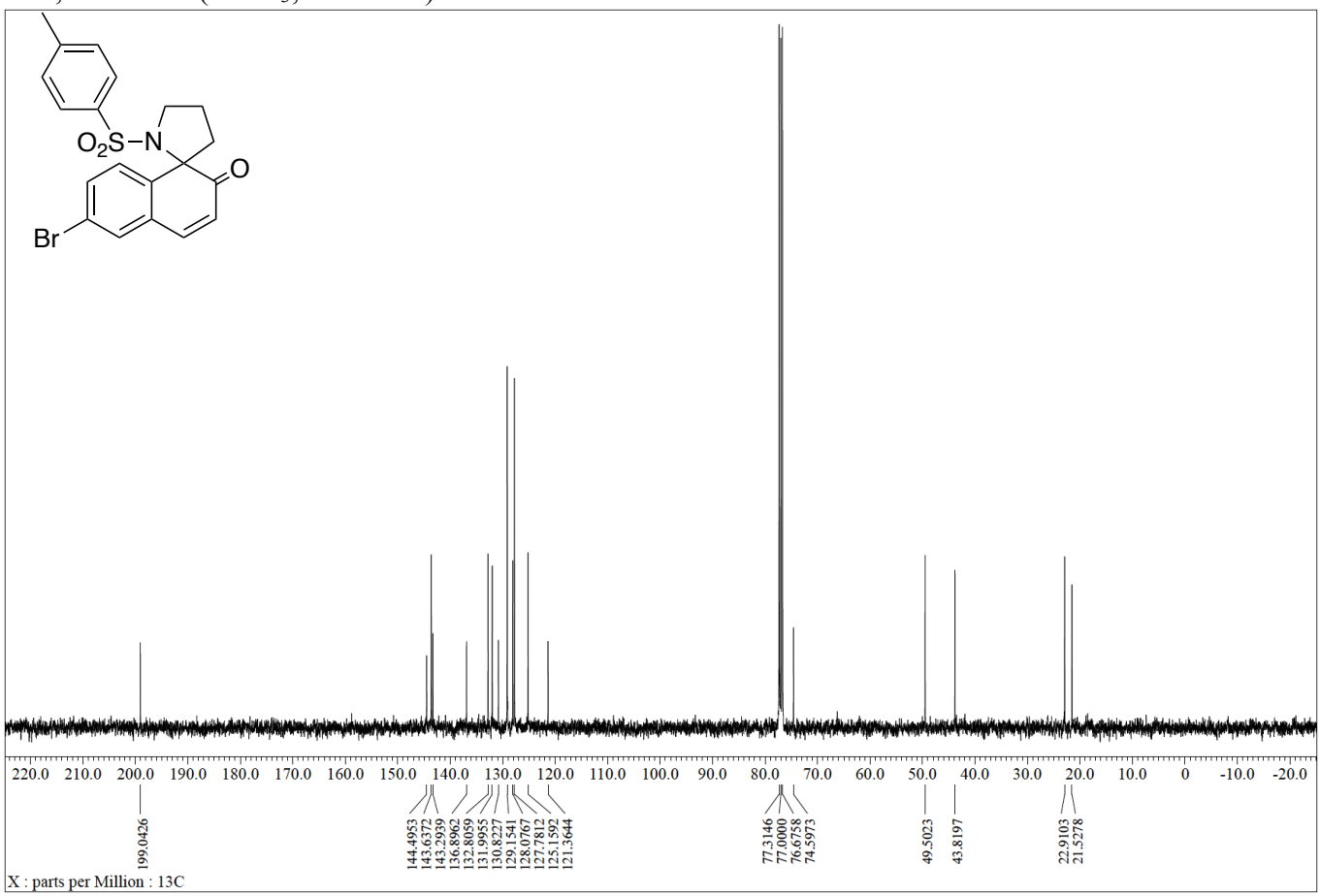
4ea, ^{13}C NMR ($CDCl_3$, 100 MHz)



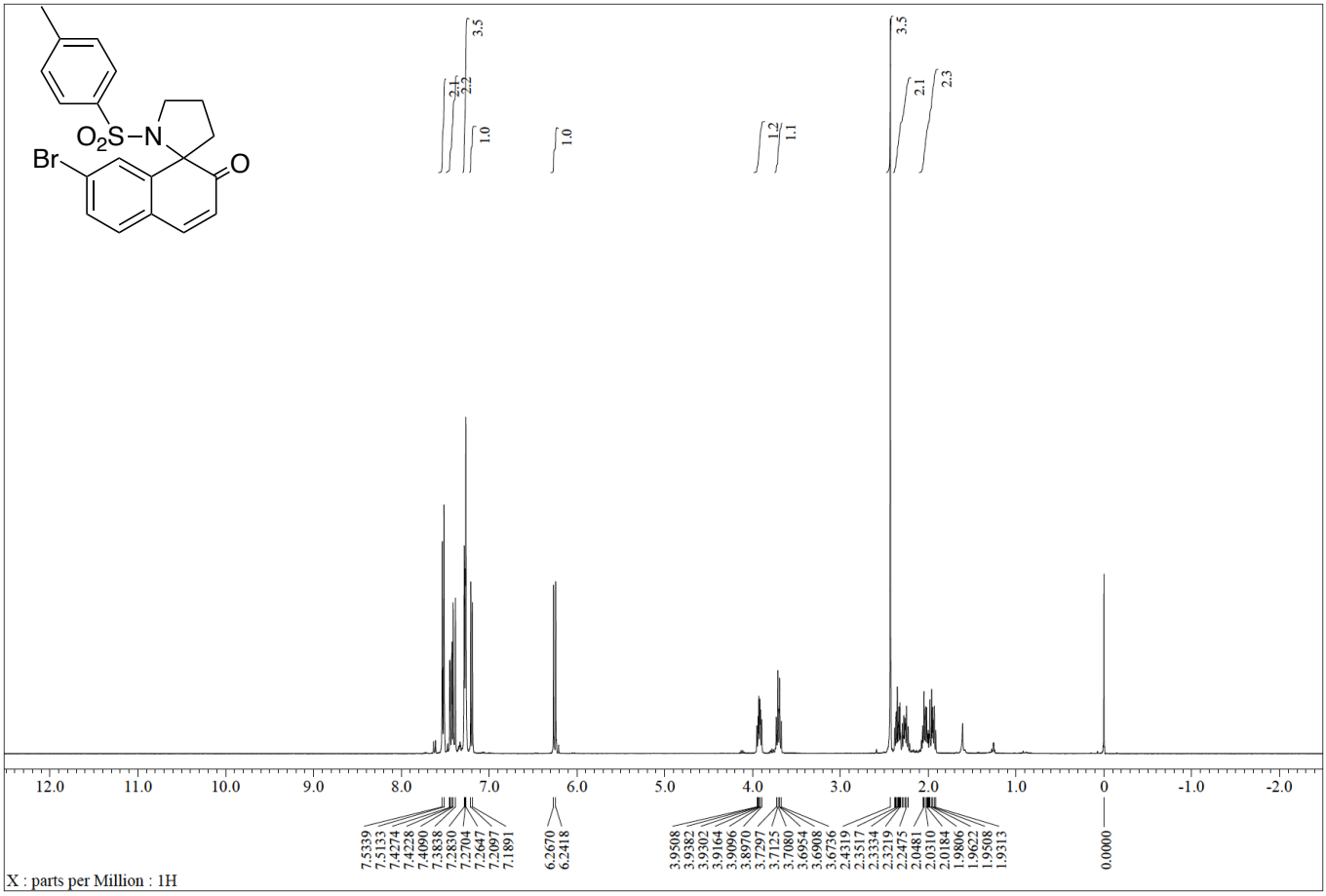
4f, ^{1}H NMR ($CDCl_3$, 400 MHz)



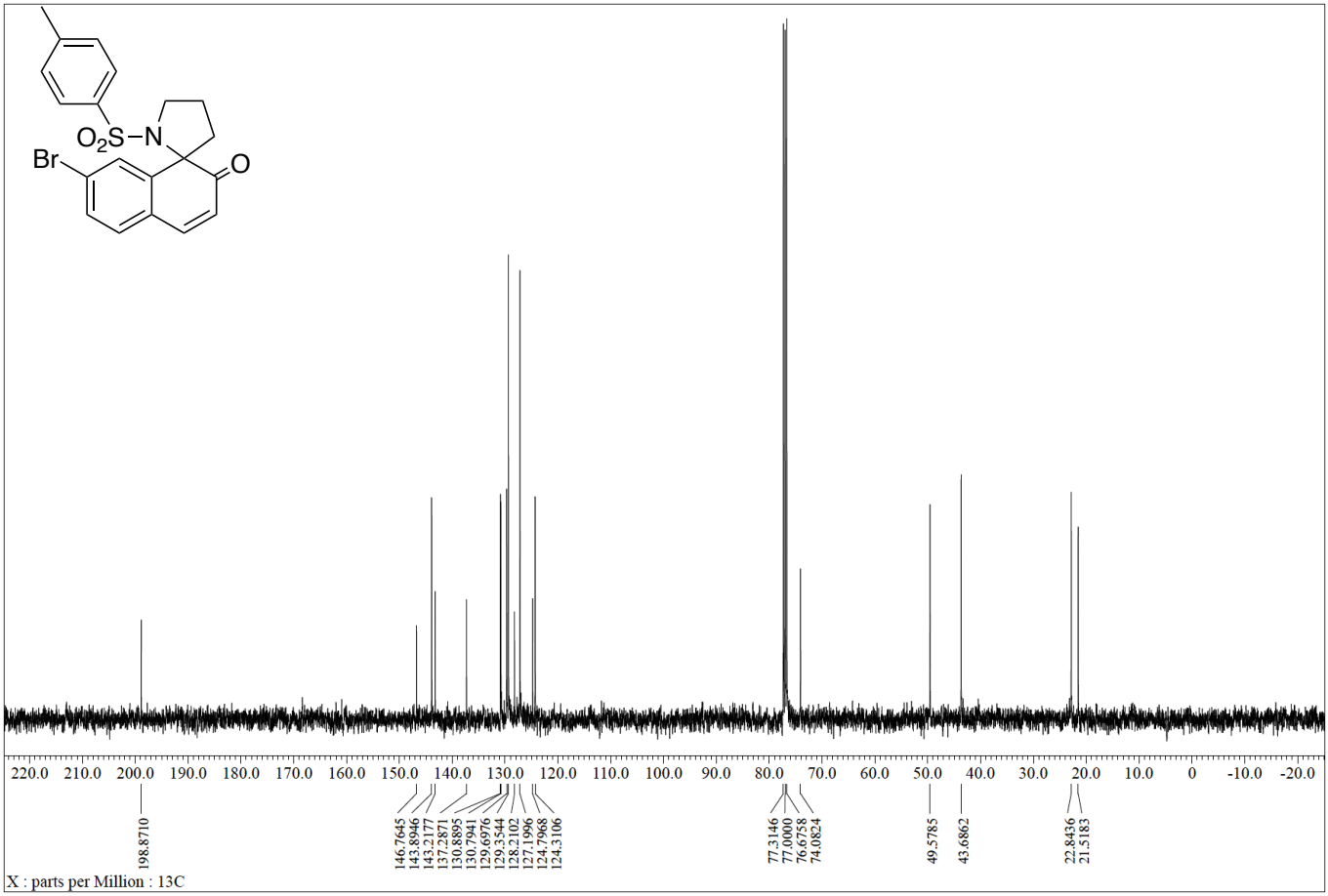
4f, ^{13}C NMR ($CDCl_3$, 100 MHz)



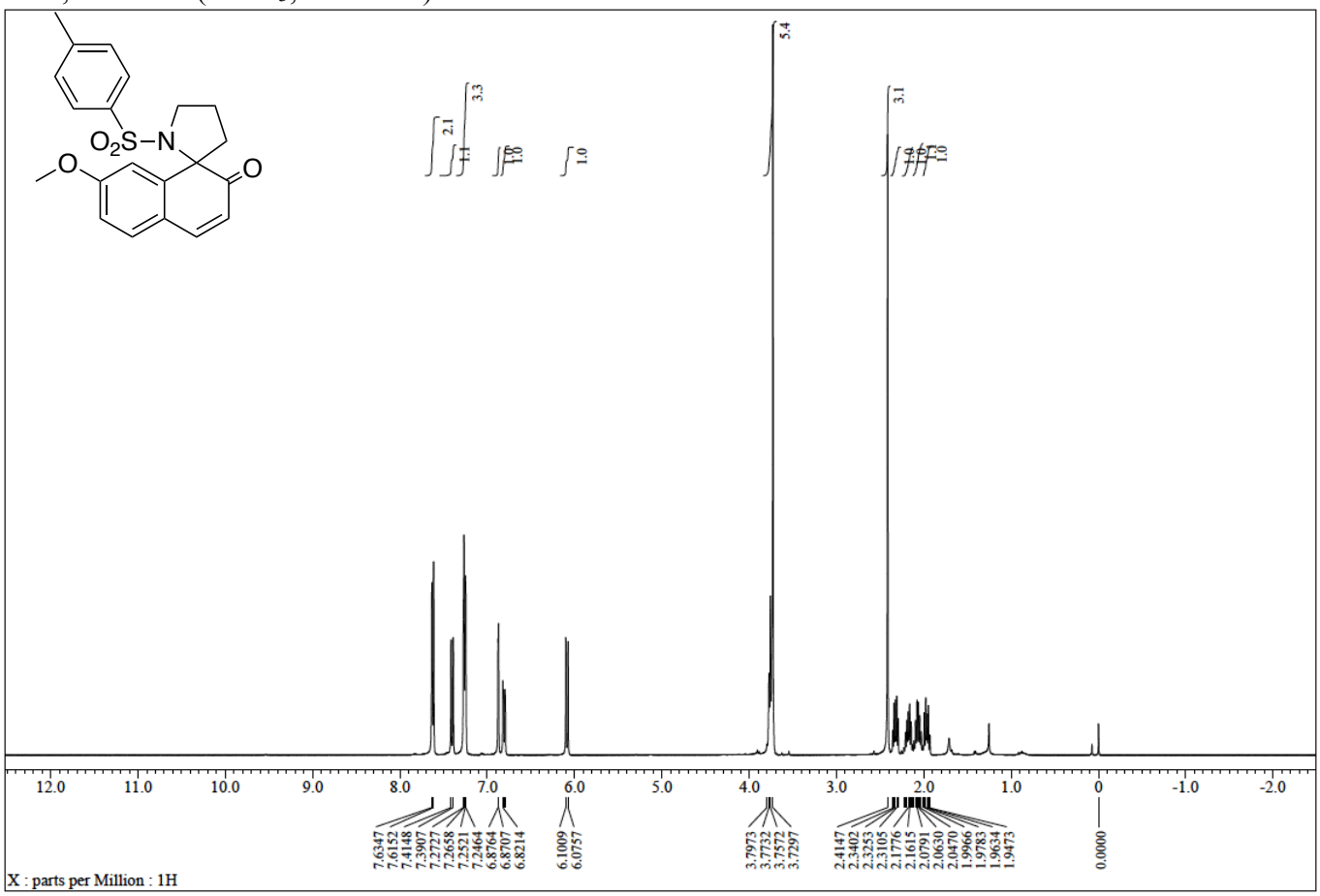
4g, ^{1}H NMR ($CDCl_3$, 400 MHz)



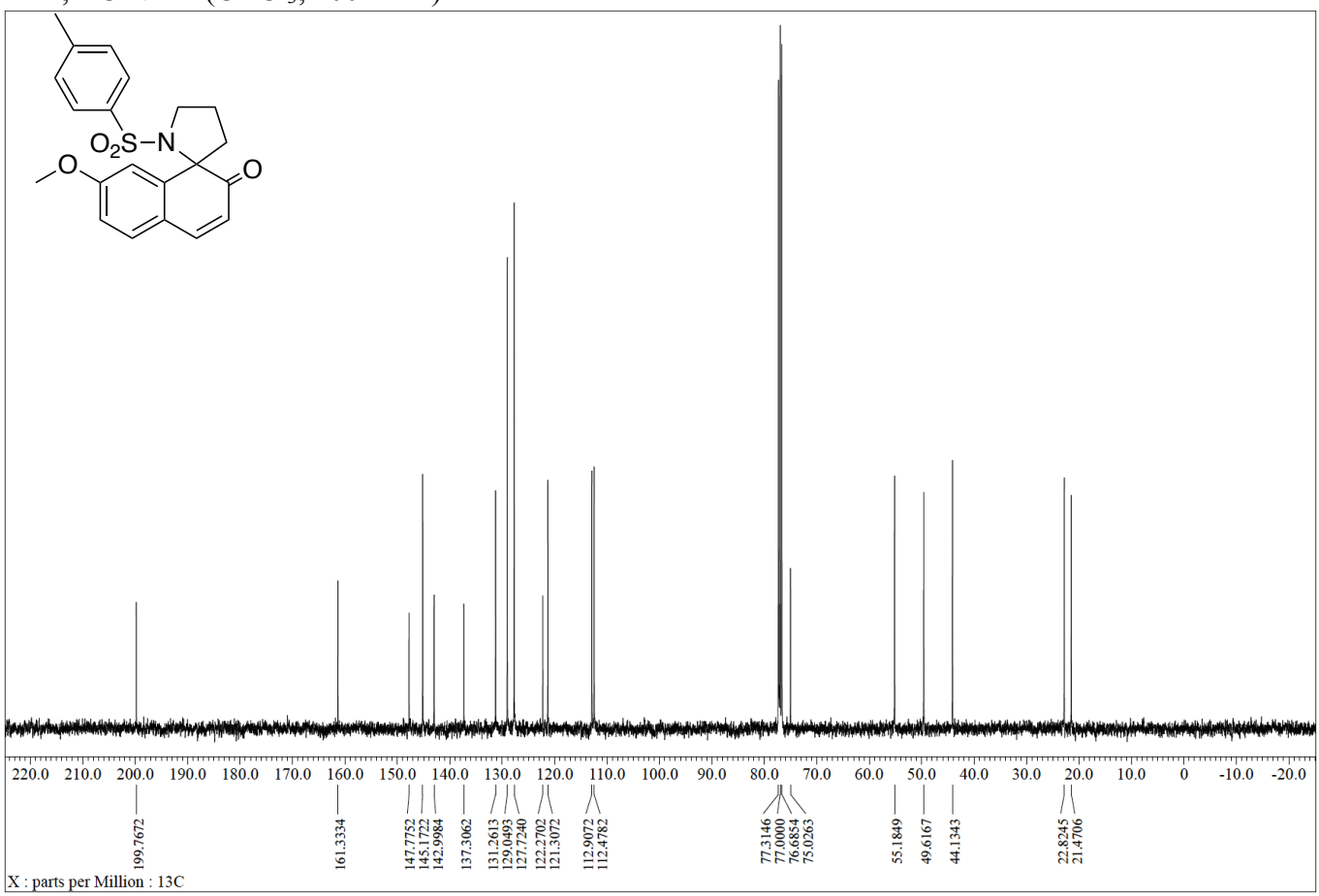
4g, ^{13}C NMR ($CDCl_3$, 100 MHz)



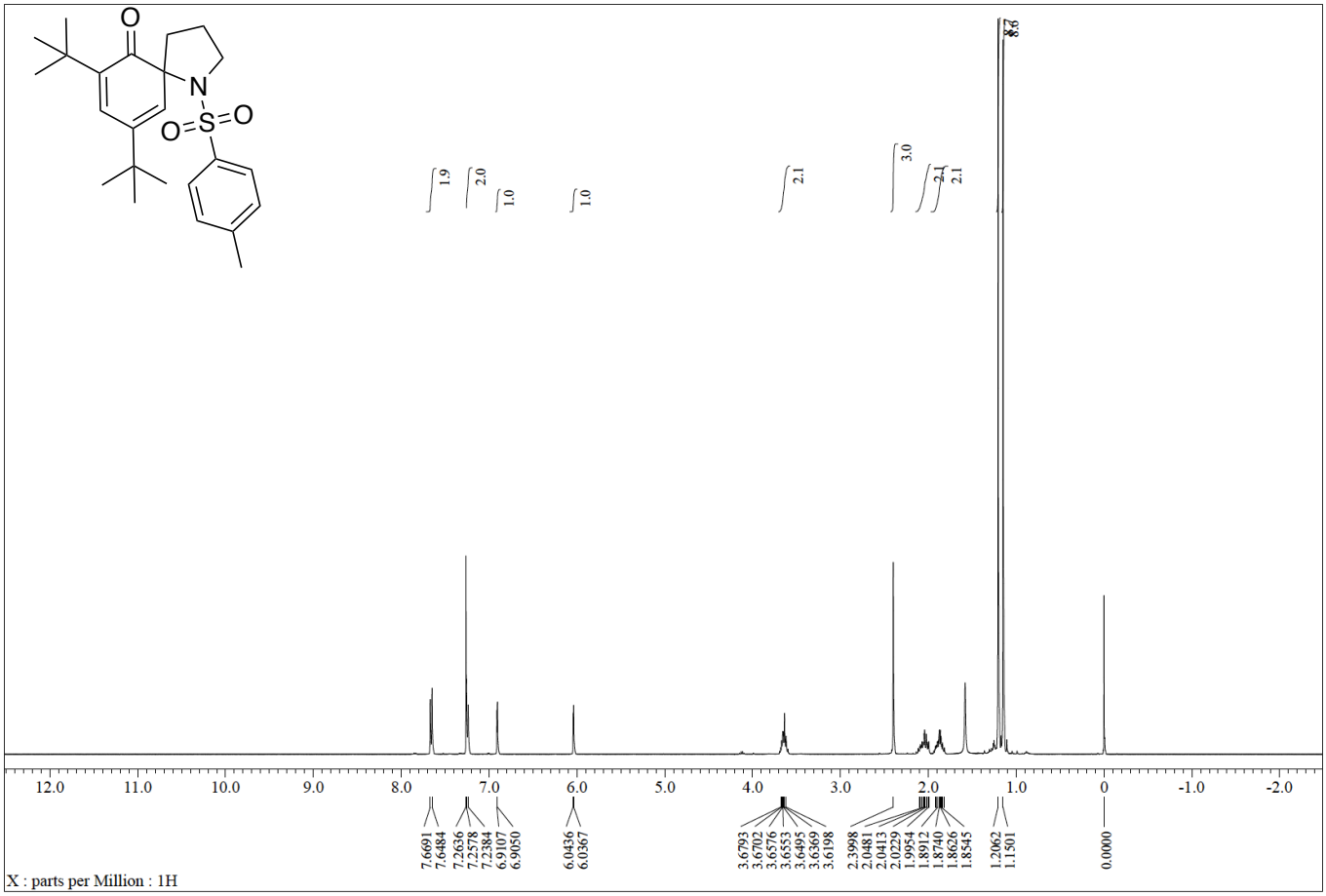
4h, ^{1}H NMR ($CDCl_3$, 400 MHz)



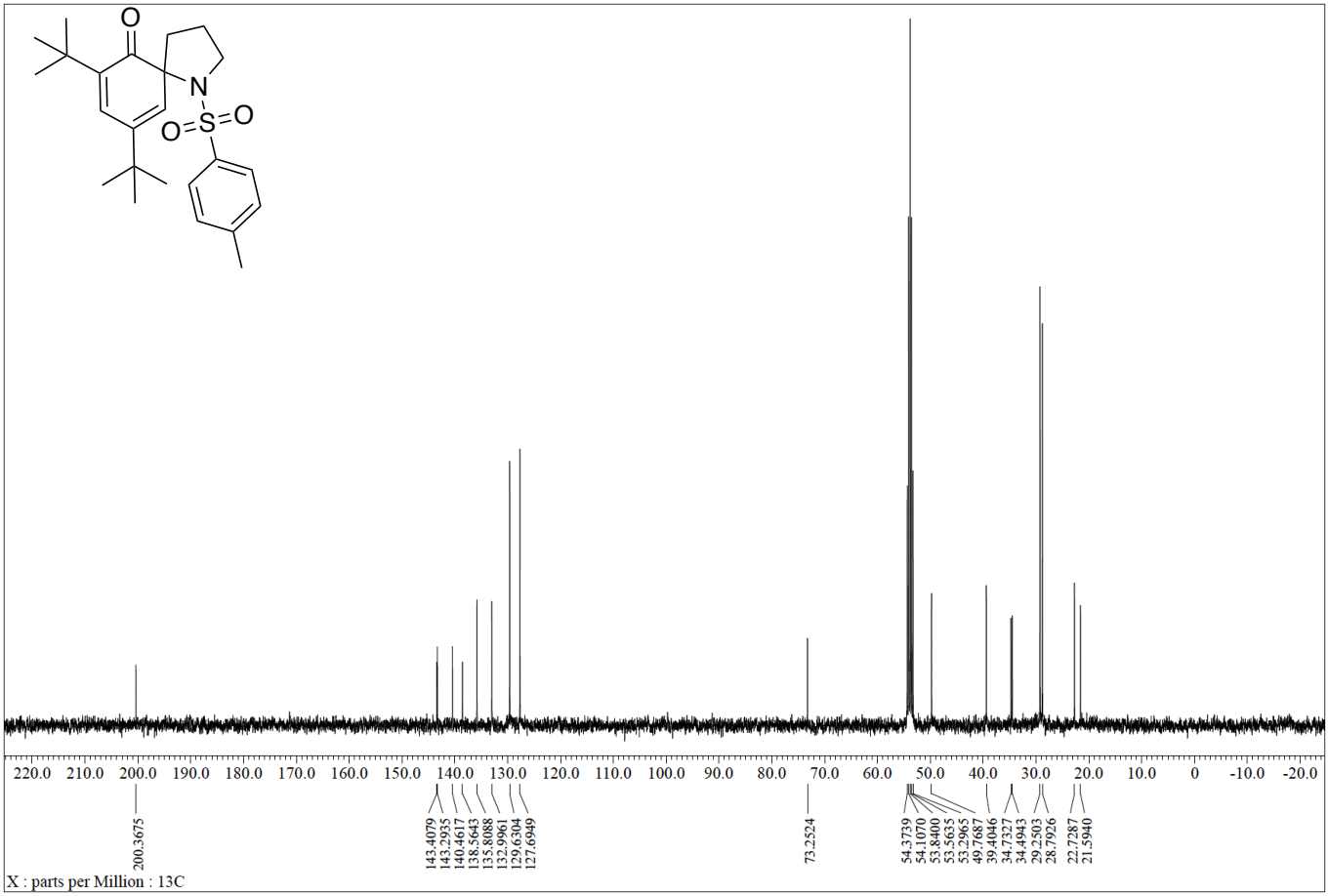
4h, ^{13}C NMR ($CDCl_3$, 100 MHz)



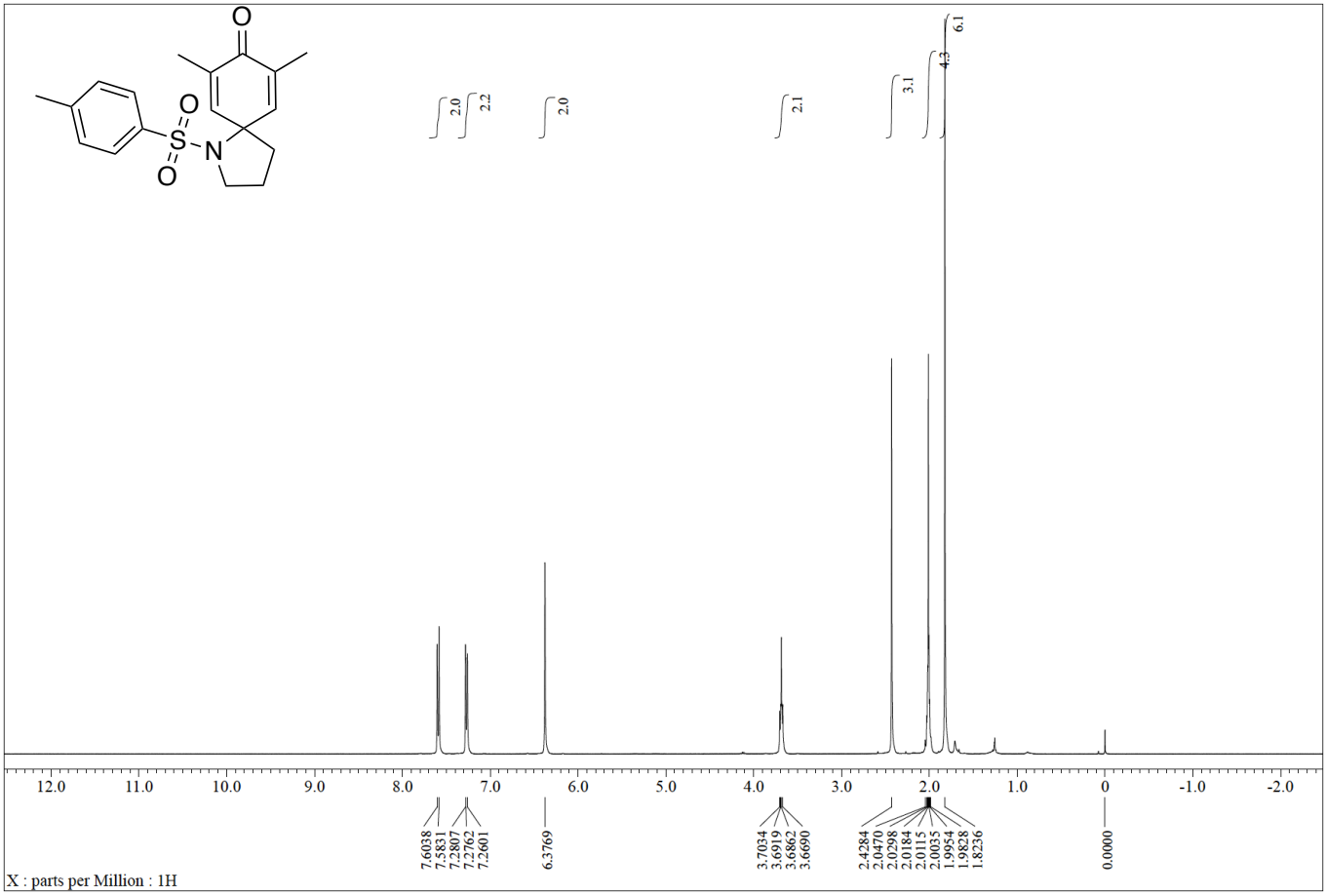
4i, ^{1}H NMR ($CDCl_3$, 400 MHz)



4i, ^{13}C NMR (CD_2Cl_2, 100 MHz)



4j, ^{1}H NMR ($CDCl_3$, 400 MHz)



4j, ^{13}C NMR ($CDCl_3$, 100 MHz)