Supplementary information

Contents

1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Tetrahydrofuran, diethyl ether, 1,2-dimethoxyethane and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane, 1,2-dichloroethane and acetonitrile were distilled from CaH_2 prior to use. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) and Bruker AVANCE 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz) nuclear magnetic resonance spectrometers. ^{1}H-NMR spectra are reported relative to Me_4Si (0.00 ppm) or residual solvent signals (C_6D_6: 7.16 ppm, CD_2Cl_2: 5.32 ppm). Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, s = singlet, br. = broad, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplet, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm, CD_2Cl_2: 53.8 ppm). Infrared spectra were recorded on Bruker Tensor 27 fourier transform infrared spectrometer (FT-IR) and were reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS mass spectrometer (ESI). Crystallographic data were recorded on RAPID-S Image Plate X-Ray Diffractameter made by Rigaku Denki Co., Ltd.

Abbreviations:

Bs = *p*-bromo-benzenesulfonyl
DCE = 1,2-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodicarboxylate
DME = 1,2-dimethoxyethane
DMF = *N*,*N*-dimethylformamide
EA = ethyl acetate

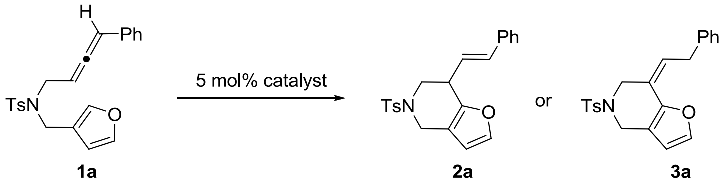
MS = molecular sieve
PE = petroleum ether
PTLC = preparative thin layer chromatography
Tf = trifluoromethanesulfonyl
THF = tetrahydrofuran
TLC = thin layer chromatography
Ts = *p*-toluenesulfonyl

IPr = 1,3-bis(2,6-diisopropylphenyl) imidazole-2-ylidene
JohnPhos = 2-(di-tert-butylphosphino)biphenyl
XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbipheny

2. Experimental Procedures and Characterization Data

2.1 Screening Reaction Conditions

Table S1 Optimization studies on the hydroarylation of β-allenyl-furans

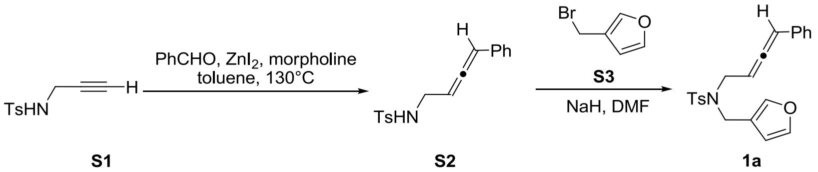


entry	solvent[a]	catalyst	temp	time [h]	product	yield[%][b]
1	DME	$[Au(NCMe)JohnPhos]SbF_6$	rt	60	**2a**	65
2	DME	$[Au(NCMe)JohnPhos]SbF_6$	50°C	7	**2a**	86
3	DME	Au(JohnPhos)Cl	50°C	12	-	no reaction
4	DME	$Au(JohnPhos)Cl/AgSbF_6$[c]	50°C	8	**2a**	81
5	DME	$Au(PPh_3)Cl/AgSbF_6$[c]	50°C	24	**2a**	49[d]
6	DME	$Au(IPr)Cl/AgSbF_6$[c]	50°C	4	**2a**	83
7	DME	$Au[P(OPh\text{-}2,4\text{-}t\text{-}Bu)_3]Cl/AgSbF_6$[c]	50°C	15	**2a**	71
8	DME	$Au(XPhos)NTf_2$	50°C	48	**2a**	48[e]
9	DME	AuCl	50°C	20	**2a**	trace
10	DME	$AuCl_3$	50°C	20	**2a**	trace
11	DME	$AgSbF_6$	50°C	7	-	no reaction
12	DME	TfOH	50°C	7	-	no reaction
13	DME	$AlCl_3$	50°C	7	-	no reaction
14	DME	$BF_3{\cdot}OEt_2$	50°C	7	-	no reaction
15	dioxane	$InCl_3$	50°C	7	-	no reaction
16	MeCN	$[Au(NCMe)JohnPhos]SbF_6$	50°C	7	-	no reaction
17	DCE	$[Au(NCMe)JohnPhos]SbF_6$	50°C	42	**2a**	76[f]
18	toluene	$[Au(NCMe)JohnPhos]SbF_6$	50°C	13	**2a**	88
19	THF	$[Au(NCMe)JohnPhos]SbF_6$	50°C	9	**2a**	36
20	dioxane	$[Au(NCMe)JohnPhos]SbF_6$	50°C	6	**2a**	91
21	dioxane	$[Au(NCMe)JohnPhos]SbF_6$	60°C	3	**2a**	72
22	dioxane	$[Au(NCMe)JohnPhos]SbF_6$[g]	50°C	1.2	**2a**	64
23	dioxane	$[Au(NCMe)JohnPhos]SbF_6$[h]	50°C	7	-	no reaction
24	DME	$PtCl_2$	50°C	17	**3a**	73%
25	DME	$PtCl_4$	50°C	2	**3a**	74
26	CH_3CN	$PtCl_4$	50°C	3	-	no reaction
27	dioxane	$PtCl_4$	50°C	2	**3a**	76
28	DCE	$PtCl_4$	50°C	4	-	no reaction
29	toluene	$PtCl_4$	50°C	4	**3a**	40[i]
30	THF	$PtCl_4$	50°C	2	**3a**	92

[a] Concentration: 0.05M. [b] Isolated yield, the Z/E ratio of **3a** was above 20/1. [c] Gold and silver salts were added at radio of 1:1. [d] 27% **1a** was recovered. [e] 28% **1a** was recovered. [f] 4% **1a** was recovered. [g] Carried out using the microwave apparatus. [h] 4Å molecular sieve was added. [i] Yield based on NMR.

2.2 Synthesis of Substrates

β-allenyl-furan (1a)



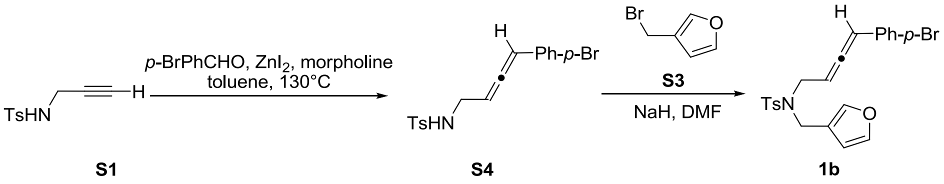
S1[1] to **S2**[2]: To a dried reaction tube was added ZnI_2 (256 mg, 0.8 mmol) and alkyne **S1** (208 mg, 1.0 mmol). Then aldehyde (192 mg, 1.8 mmol), morpholine (122 mg, 1.4 mmol), and toluene (3 mL) were added sequentially into this dried reaction tube equipped with a reflux condenser under an argon atmosphere and the resulting mixture was stirred at 130 ℃. After 3.5 h, the reaction mixture was cooled to room temperature and then filtered through a short silica gel column. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1 then 5:1) to afford allene **S2** (144 mg, 48%).

S2: Yellow oil: TLC R_f (PE/EA 5:1) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.3, 2H), 7.26-7.31 (m, 4H), 7.17-7.24 (m, 3H), 6.17-6.23 (m, 1H), 5.49-5.56 (m, 1H), 4.68 (br. s, 1H), 3.66-3.73 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.6, 143.5, 136.9, 133.2, 129.7, 128.7, 127.5, 127.2, 126.9, 97.8, 92.0, 41.6, 21.5. IR (neat): v 3281, 2923, 1723, 1598, 1424, 1327, 1159, 1091 m^{-1}. HRMS (ESI): Calcd for $C_{17}H_{18}NO_2S$ (M + H$^+$): 300.1053; found: 300.1057.

S2 to **1a**: To a suspension of NaH (60% purity, 30 mg, 0.75 mmol) in DMF (10 mL) was added allene **S2** (149 mg, 0.5 mmol) at 0 ℃. After stirred for 30 min, a solution of bromide **S3**[3] (1 mmol) in THF (2 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1 then 5:1) to afford β-allenyl-furan **1a** (156 mg, 82%).

1a: Yellow oil: TLC R_f (PE/EA 10:1) = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.3 Hz, 2H), 7.27-7.33 (m, 5H), 7.15-7.24 (m, 4H), 6.20-6.26 (m, 1H), 6.08-6.13 (m, 1H), 5.29-5.37 (m, 1H), 4.22-4.35 (m, 2H), 3.87-3.93 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.3, 143.5, 143.4, 141.2, 137.6, 133.4, 129.7, 128.7, 127.4, 127.2, 126.8, 119.9, 110.6, 95.9, 90.3, 45.2, 41.0, 21.5. IR (neat): v 2978, 2921, 1597, 1497, 1451, 1340, 1158, 1091, 1068 cm^{-1}. HRMS (ESI): Calcd for $C_{22}H_{22}NO_3S$ (M + H$^+$): 380.1315; found: 380.1324.

β-allenyl-furan (1b)



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[1] M.-C. P. Yeh, M.-N. Lin, C.-H. Hsu and C.-J. Liang. *J. Org. Chem.*, 2013, **78**, 12381.

[2] The synthesis of allene **S2**, **S4**, **S14** followed the procedure reported by Ma: J. Kuang and S. Ma. *J. Am. Chem. Soc.*, 2010, **132**, 1786.

[3] **S3** was synthesized using this method without distillation and used directly: V. K. Aggarwal and J.-L. Vasse. *Org. Lett.*, 2003, **5**, 3987.

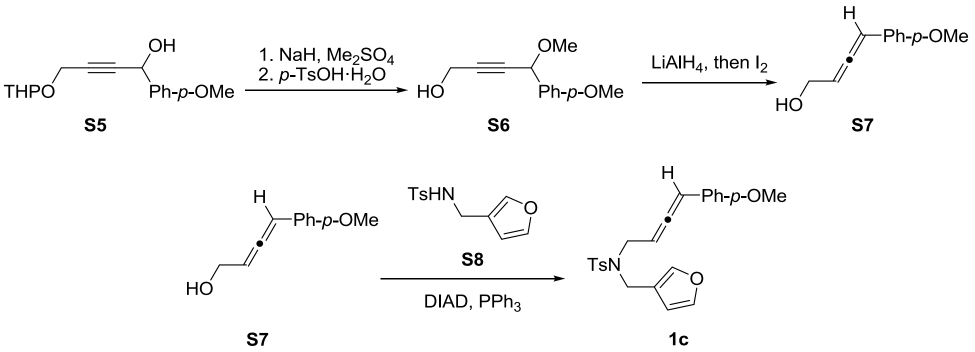
S1 to **S4**[2]: To a dried reaction tube was added ZnI_2 (511 mg, 1.6 mmol) and alkyne **S1** (416 mg, 2.0 mmol). Then aldehyde (666 mg, 3.6 mmol), morpholine (244 mg, 2.8 mmol), and toluene (6 mL) were added sequentially into this dried reaction tube equipped with a reflux condenser under an argon atmosphere and the resulting mixture was stirred at 130 ℃. After 3 h, the reaction mixture was cooled to room temperature and then filtered through a short silica gel column. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1 then 5:1) to afford allene **S4** (247 mg, 33%).

S4: Yellow solid: TLC R_f (PE/EA 5:1) = 0.35, m.p. = 120-123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.11-6.18 (m, 1H), 5.48-5.56 (m, 1H), 4.69 (t, J = 5.6 Hz, 1H), 3.66-3.74 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.7, 143.6, 136.8, 132.2, 131.7, 129.7, 128.4, 127.1 121.1, 97.0, 92.5, 41.5, 21.5. IR (neat): v 3278, 2924, 1953, 1595, 1487, 1425, 1326, 1158, 1093, 1067 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{17}BrNO_2S$ (M + H$^+$): 378.0158; found: 378.0163.

S4 to **1b**: To a suspension of NaH (60% purity, 35 mg, 0.87 mmol) in DMF (5 mL) was added allene **S4** (208.5 mg, 0.5 mmol) at 0 ℃. After stirred for 30 min, a solution of bromide **S3** (1 mmol) in THF (5 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford β-allenyl-furan **1b** (194 mg, 77%).

1b: Yellow oil: TLC R_f (PE/EA 3:1) = 0.66. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.31-7.33 (m, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.18 (s, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.20-6.23 (m, 1H), 6.03-6.09 (m, 1H), 5.31-5.39 (m, 1H), 4.23-4.29 (m, 2H), 3.90 (dd, J = 6.9 and 2.3 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.2, 143.6, 143.4, 141.1, 137.4, 132.5, 131.8, 129.8, 128.3, 127.2, 121.0, 119.9, 110.6, 95.2, 91.0, 45.1, 41.2, 21.5. IR (neat): v 2979, 2921, 1950, 1596, 1490, 1341, 1158, 1093, 1069, 1017 cm^{-1}. HRMS (ESI): Calcd for $C_{22}H_{21}BrNO_3S$ (M + H$^+$): 458.0420; found: 458.0412.

β-allenyl-furan (1c)



S5[4] to **S7**[5]: To a suspension of NaH (60% purity, 400 mg, 10 mmol) in THF (20 mL) was added propargyl alcohol **S5** (1.85 g, 6.7 mmol) at 0 ℃. After stirred for 10 min, dimethyl sulfate

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[4] S. Ghosal, M. Nirmal, J. C. Medina and K. S. Kyler. *Synthetic Commun.*, 1987, **17**, 1683.

[5] The synthesis of allene **S7** followed the procedure reported by Welker: N. A. Vinson, C. S. Day and M. E. Welker. *Organometallics*, 2000, **19**, 4356.

(0.9 mL, 9.5 mmol) was added slowly and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was dissolved in MeOH (16 mL) at 0 ℃. Then TsOH·H_2O (59 mg, 4.5 mol %) was added and the reaction mixture was stirred for 2 h at 0 ℃. Saturated $NaHCO_3$ solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 3:1 then 2:1) to afford alcohol **S6** (998 mg, 72% for 2 steps).

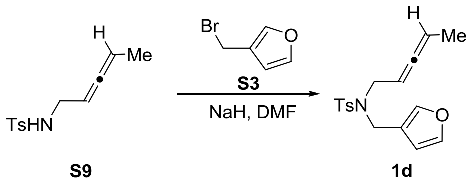
Then lithium aluminum hydride (368 mg, 9.7 mmol) was added to diethyl ether (170 mL) and cooled to -15 ℃. Compound **S6** (500 mg, 2.42 mmol) in ether (10 mL) was added dropwise, and the reaction mixture was stirred for 20 min as it warmed to -12 ℃. The solution was cooled to -78 ℃, iodine was added (1.85 g, 7.27 mmol), and the mixture was stirred for 2 h. After warming to 0 ℃, saturated aqueous potassium sodium tartrate (10 mL) and saturated aqueous sodium thiosulfate (10 mL) were added. After stirring 1 h, the water layer was extracted four times with ether. The ether layers were combined and dried with anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with pentane/ether 3:1) to afford allene **S7** (326 mg, 76%)

S7: Colorless oil: TLC R_f (PE/EA 2:1) = 0.43. ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.25-6.30 (m, 1H), 5.72-5.79 (m, 1H), 4.20-4.26 (m, 2H), 3.79 (s, 3H), 1.80 (br. s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.6, 159.0, 127.9, 126.0, 114.2, 96.6, 95.8, 60.5, 55.3. IR (neat): v 3382, 2934, 2837, 1606, 1512, 1301, 1248, 1174, 1032 cm^{-1}. HRMS (ESI): Calcd for $C_{11}H_{13}O_2$ (M + H$^+$): 177.0910; found: 177.0906.

S7 to **1c**: To a stirred solution of allene **S7** (240 mg, 1.36 mmol), tosylamide **S8**[6] (535 mg, 2.13 mmol), and PPh_3 (745 mg, 3.29 mmol) in anhydrous THF (10 mL) was added DIAD (632 mg, 3.12 mmol) at 0 ℃. The mixture was then stirred for 2 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford β-allenyl-furan **1c** (213 mg, 39%). **1c** is not stable which should be kept at -20 ℃ and used quickly.

1c: Colorless oil: TLC R_f (PE/EA 3:1) = 0.46. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.3 Hz, 2H), 7.28-7.32 (m, 3H), 7.16-7.19 (m, 1H), 7.11 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.21-6.25 (m, 1H), 6.04-6.10 (m, 1H), 5.25-5.34 (m, 1H), 4.24-4.32 (m, 2H), 3.86-3.92 (m, 2H), 3.80 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9, 159.0, 143.5, 143.3, 141.2, 137.6, 129.7, 128.0, 127.2, 125.6, 119.9, 114.2, 110.6, 95.4, 90.2, 55.3, 45.4, 40.9, 21.5. IR (neat): v 2931, 2838, 1606, 1460, 1344, 1249, 1159, 1092, 1032 cm^{-1}. HRMS (ESI): Calcd for $C_{23}H_{24}NO_4S$ (M + H$^+$): 410.1421; found: 410.1417.

β-allenyl-furan (1d)



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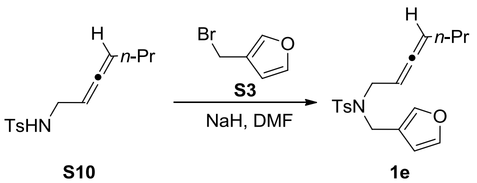
[6] Z. Dong, C.-H. Liu, Y. Wang, M. Lin and Z.-X. Yu. *Angew. Chem. Int. Ed.*, 2013, **52**, 14157.

S9[7] to **1d**: To a suspension of NaH (60% purity, 40 mg, 1 mmol) in DMF (8 mL) was added allene **S9** (155.2 mg, 0.65 mmol) at 0 °C. After stirred for 30 min, a solution of bromide **S3** (1 mmol) in THF (3 mL) was added and the reaction mixture was stirred for 1 h. Then saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1 then 10:1) to afford β-allenyl-furan **1d** (193.5 mg, 93%).

1d: Colorless oil: TLC R_f (PE/EA 5:1) = 0.68. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.70 (d, J = 8.3 Hz, 2H), 7.35-7.38 (m, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.27-7.30 (m, 1H), 6.24-6.29 (m, 1H), 5.01-5.14 (m, 1H), 4.73-4.83 (m, 1H), 4.24 (s, 2H), 3.72-3.78 (m, 2H), 2.43 (s, 3H), 1.60 (dd, J = 7.1, 3.1 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 206.4, 143.9, 143.8, 141.6, 138.1, 130.1, 127.4, 120.7, 111.1, 87.4, 85.8, 46.1, 41.0, 21.6, 14.2. IR (neat): v 2925, 1598, 1501, 1442, 1344, 1159, 1094, 1020 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}NO_3S$ (M + H^+): 318.1158; found: 318.1166.

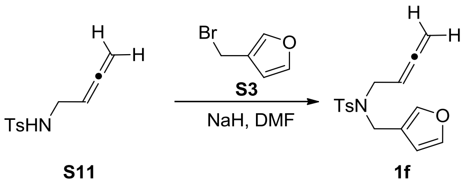
β-allenyl-furan (1e)



S10[8] to **1e**: To a suspension of NaH (60% purity, 55 mg, 1.37 mmol) in DMF (10 mL) was added allene **S10** (239.3 mg, 0.90 mmol) at 0 °C. After stirred for 30 min, a solution of bromide **S3** (1.33 mmol) in THF (4 mL) was added and the reaction mixture was stirred for 1 h. Then saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1 then 10:1) to afford β-allenyl-furan **1e** (256.5 mg, 82%).

1e: Colorless oil: TLC R_f (PE/EA 10:1) = 0.46. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.70 (d, J = 8.3 Hz, 2H), 7.35-7.37 (m, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.26-7.30 (m, 1H), 6.25-6.29 (m, 1H), 5.06-5.16 (m, 1H), 4.76-4.86 (m, 1H), 4.25 (s, 2H), 3.73-3.80 (m, 2H), 2.43 (s, 3H), 1.88-1.97 (m, 2H), 1.32-1.43 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 205.7, 143.9, 143.8, 141.6, 138.1, 130.1, 127.4, 120.8, 111.0, 92.6, 86.3, 46.3, 41.0, 31.0, 22.7, 21.6, 13.7. IR (neat): v 2960, 2930, 2871, 1962, 1502, 1453, 1346, 1160, 1094, 1021 cm^{-1}. HRMS (ESI): Calcd for $C_{19}H_{24}NO_3S$ (M + H^+): 346.1471; found: 346.1474.

β-allenyl-furan (1f)



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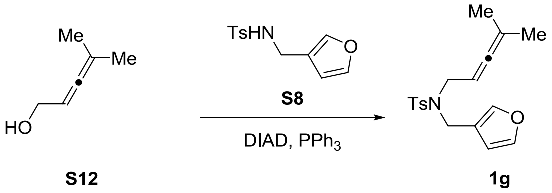
[7] A. Horváth and J.-E. Bäckvall. *Chem. Commun.*, 2004, 964.
[8] J. Kuang, H. Luo and S. Ma. *Adv. Synth. Catal.*, 2012, **354**, 933.

S11[9] to **1f**: To a suspension of NaH (60% purity, 65 mg, 1.6 mmol) in DMF (6 mL) was added allene **S11** (244.1 mg, 1.10 mmol) at 0 ℃. After stirred for 30 min, a solution of bromide **S3** (2.0 mmol) in THF (5 mL) was added and the reaction mixture was stirred overnight. Then saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford β-allenyl-furan **1f** (245.9 mg, 74%).

1f: Colorless oil: TLC R_f (PE/EA 3:1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.3 Hz, 2H), 7.33-7.36 (m, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.27-7.28 (m, 1H), 6.23-6.29 (m, 1H), 4.80-4.92 (m, 1H), 4.64-4.73 (m, 2H), 4.26 (s, 2H), 3.77-3.85 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 209.6, 143.4, 143.3, 141.2, 137.6, 129.7, 127.2, 119.9, 110.7, 85.5, 76.1, 45.1, 40.7, 21.5. IR (neat): v 2924, 1955, 1597, 1499, 1443, 1337, 1158, 1093, 967 cm^{-1}. HRMS (ESI): Calcd for $C_{16}H_{18}NO_3S$ (M + H$^+$): 304.1002; found: 304.1005.

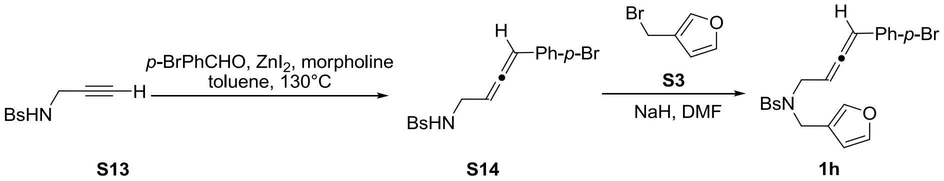
β-allenyl-furan (1g)



S12[10] to **1g**: To a stirred solution of allene **S12** (146 mg, 1.5 mmol), tosylamide **S8** (253.2 mg, 1.0 mmol), and PPh_3 (526 mg, 2.0 mmol) in anhydrous THF (10 mL) was added DIAD (440 mg, 2.2 mmol) at 0 ℃. The mixture was then stirred overnight at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1 then 10:1) to afford β-allenyl-furan **1g** (237.5 mg, 71%).

1g: Light yellow oil: TLC R_f (PE/EA 10:1) = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.32-7.35 (m, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.24-7.26 (m, 1H), 6.24-6.28 (m, 1H), 4.62-4.75 (m, 1H), 4.27 (s, 2H), 3.75 (d, J = 7.0 Hz, 2H), 2.43 (s, 3H), 1.64 (d, J = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.4, 143.3, 143.1, 141.0, 137.8, 129.6, 127.1, 120.2, 110.7, 96.6, 84.0, 46.0, 40.4, 21.5, 20.3. IR (neat): v 2980, 2923, 2859, 1598, 1501, 1446, 1343, 1159, 1094, 1020 cm^{-1}. HRMS (ESI): Calcd for $C_{18}H_{22}NO_3S$ (M + H$^+$): 332.1315; found: 332.1321.

β-allenyl-furan (1h)



S13[11] to **S14**[2]: To a dried reaction tube was added ZnI_2 (511 mg, 1.6 mmol) and alkyne **S13** (548 mg, 2.0 mmol). Then aldehyde (666 mg, 3.6 mmol), morpholine (244 mg, 2.8 mmol), and toluene (6 mL) were added sequentially into this dried reaction tube equipped with a reflux

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[9] R. Kumareswaran, S. Shin, I. Gallou and T. V. RajanBabu. *J. Org. Chem.*, 2004, **69**, 7157.

[10] A. Boutier, C. Kammerer-Pentier, N. Krause, G. Prestat and G. Poli. *Chem. Eur. J.*, 2012, **18**, 3840.

[11] H. M. Peng, J. Zhao and X. Li. *Adv. Synth. Catal.*, 2009, **351**, 1371.

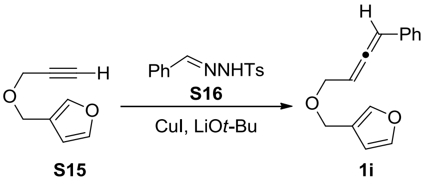
condenser under an argon atmosphere and the resulting mixture was stirred at 130 ℃. After 3 h, the reaction mixture was cooled to room temperature and then filtered through a short silica gel column. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 5:1) to afford allene **S14** (323 mg, 36%).

S14: Light yellow solid: TLC R_f (PE/EA 3:1) = 0.39, m.p. = 144-145 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.11-6.21 (m, 1H), 5.49-5.59 (m, 1H), 4.81 (br. s, 1H), 3.67-3.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.7, 139.0, 132.4, 132.0, 131.8, 128.6, 128.4, 127.8 121.4, 97.3, 92.4, 41.4. IR (neat): v 3270, 2360, 2340, 1574, 1487, 1424, 1389, 1323, 1160, 1091, 1068, 1009 cm^{-1}. HRMS (ESI): Calcd for $C_{16}H_{14}Br_2NO_2S$ (M + H$^+$): 441.9106; found: 441.9104.

S14 to **1h**: To a suspension of NaH (60% purity, 35 mg, 0.87 mmol) in DMF (10 mL) was added allene **S14** (233 mg, 0.52 mmol) at 0 ℃. After stirred for 30 min, a solution of bromide **S3** (1 mmol) in THF (2 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford β-allenyl-furan **1h** (234 mg, 85%).

1h: White solid: TLC R_f (PE/EA 3:1) = 0.63, m.p. = 103-105 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.32-7.36 (m, 1H), 7.21-7.23 (m, 1H), 7.05 (d, J = 8.5 Hz, 2H), 6.21-6.24 (m, 1H), 6.03-6.08 (m, 1H), 5.33-5.40 (m, 1H), 4.28 (s, 2H), 3.89-3.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.2, 143.7, 141.2, 139.5, 132.4, 132.3, 131.8, 128.6, 128.3, 127.6, 121.2, 119.6, 110.5, 95.5, 90.8, 45.1, 41.2. IR (neat): v 3090, 2925, 1951, 1574, 1487, 1440, 1389, 1348, 1161, 1092, 1069, 1010 cm^{-1}. HRMS (ESI): Calcd for $C_{21}H_{18}Br_2NO_3S$ (M + H$^+$): 521.9369; found: 521.9355.

β-allenyl-furan (1i)



S15[12] to **1i**[13]: Under a nitrogen atmosphere, a solution of alkyne **S15** (163.4 mg, 1.2 mmol) in 1,4-dioxane (5 mL) was added to a mixture of CuI (45.7 mg, 0.24 mmol), LiO*t*-Bu (336.2 mg, 5.2 mmol), and the N-tosylhydrazone **S16**[14] (724 mg, 2.6 mmol) in 1,4-dioxane (10 mL). The solution was stirred at 90 ℃ for 1 h. The mixture was cooled to room temperature and was filtered through a short silica gel column eluting with EtOAc. The solvent was removed in vacuum to leave a crude mixture, which was purified by column chromatography on silica gel (eluting with PE/EA 100:1 then 50:1) to afford β-allenyl-furan **1i** (175.3 mg, 64%).

1i: Light yellow oil: TLC R_f (PE/EA 50:1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.40 (m, 2H), 7.27-7.32 (m, 4H), 7.17-7.23 (m, 1H), 6.39-6.44 (m, 1H), 6.23-6.28 (m, 1H), 5.63-5.72 (m,

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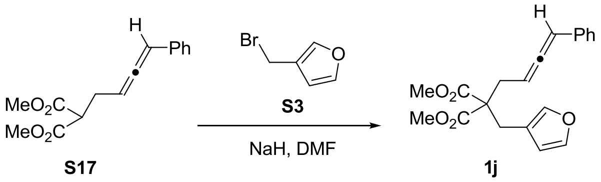
[12] S. J. Pastine, S. W. Youn and D. Sames. *Tetrahedron*, 2003, **59**, 8859.

[13] The synthesis of compound **1i** followed the procedure reported by Wang: M. L. Hossain, F. Ye, Y. Zhang and J. Wang. *J. Org. Chem.*, 2013, **78**, 1236.

[14] F. Ye, M. L. Hossain, Y. Xu, X. Ma, Q. Xiao, Y. Zhang and J. Wang. *Chem. Asian J.*, 2013, **8**, 1404.

1H), 4.45 (s, 2H), 4.14 (dd, *J* = 6.8 and 2.3 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 206.1, 143.4, 140.8, 133.9, 128.7, 127.2, 126.9, 122.0, 110.4, 95.6, 92.4, 67.5, 63.0. IR (neat): v 3031, 2858, 1951, 1626, 1598, 1498, 1458, 1350, 1159, 1085, 1065, 1021 cm^{-1}. HRMS (ESI): Calcd for $C_{15}H_{15}O_2$ (M + H$^+$): 227.1067; found: 227.1066.

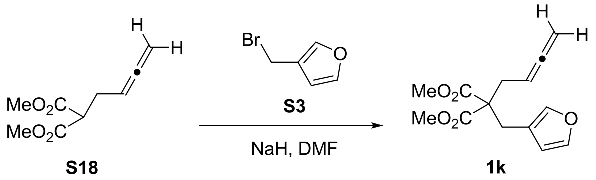
β-allenyl-furan (1j)



S17[15] to **1j**: To a suspension of NaH (60% purity, 49 mg, 1.23 mmol) in DMF (5 mL) was added allene **S17** (187.5 mg, 0.72 mmol) at 0 °C. After stirred for 1 h, a solution of bromide **S3** (1.5 mmol) in THF (3 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for 3 h. Then saturated NH$_4$Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over MgSO$_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford β-allenyl-furan **1j** (172.7 mg, 70%).

1j: Colorless oil: TLC R_f (PE/EA 5:1) = 0.52. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.26-7.34 (m, 5H), 7.16-7.22 (m, 2H), 6.15-6.21 (m, 1H), 6.12-6.15 (m, 1H), 5.38-5.46 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.16 (s, 2H), 2.70 (dd, *J* = 7.9 and 2.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 207.0, 171.0, 170.9, 142.9, 141.0, 133.9, 128.6, 127.1, 126.8, 118.6, 111.5, 94.8, 89.1, 58.3, 52.6, 52.5, 31.9, 27.8. IR (neat): v 2953, 1735, 1498, 1437, 1290, 1260, 1235, 1202, 1181, 1074, 1025 cm^{-1}. HRMS (ESI): Calcd for $C_{20}H_{20}NaO_5$ (M + Na$^+$): 363.1203; found: 363.1205.

β-allenyl-furan (1k)



S18[16] to **1k**: To a suspension of NaH (60% purity, 95 mg, 2.38 mmol) in DMF (8 mL) was added allene **S18** (292.4 mg, 1.59 mmol) at 0 °C. After stirred for 1 h, a solution of bromide **S3** (3 mmol) in THF (4 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for 3 h. Then saturated NH$_4$Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over MgSO$_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford β-allenyl-furan **1k** (325.4 mg, 78%).

1k: Light yellow oil: TLC R_f (PE/EA 5:1) = 0.51. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31-7.35 (m, 1H), 7.19-7.23 (m, 1H), 6.15-6.18 (m, 1H), 4.91-5.00 (m, 1H), 4.70-4.75 (m, 2H), 3.73 (s, 6H),

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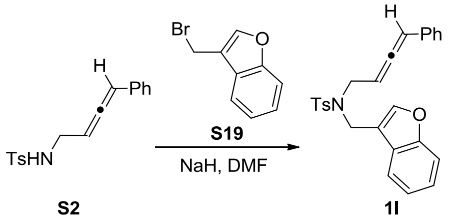
[15] P. Cérat, P. J. Gritsch, S. R. Goudreau and A. B. Charette. *Org. Lett.*, 2010, **12**, 564.

[16] Z. Zhang and R. A. Widenhoefer. *Org. Lett.*, 2008, **10**, 2079.

3.09 (s, 2H), 2.55-2.59 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 210.2, 170.9, 142.8, 141.1, 118.6, 111.6, 84.3, 74.8, 58.4, 52.4, 31.5, 27.6. IR (neat): ν 2954, 1956, 1736, 1502, 1438, 1289, 1261, 1236, 1203, 1181, 1076, 1026 cm^{-1}. HRMS (ESI): Calcd for $C_{14}H_{16}NaO_5$ (M + Na$^+$): 287.0890; found: 287.0890.

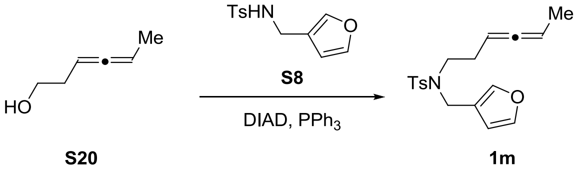
β-allenyl-furan (1l)



S2 to **1l**: To a suspension of NaH (60% purity, 45 mg, 1.1 mmol) in DMF (6 mL) was added allene **S2** (201 mg, 0.67 mmol) at 0 ℃. After stirred for 15 min, a solution of bromide **S19**^{6} (1 mmol) in THF (4 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted four times with ether and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford β-allenyl-furan **1l** (239 mg, 83%).

1l: Yellow oil: TLC R_f (PE/EA 3:1) = 0.62. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.65-7.70 (m, 1H), 7.41-7.46 (m, 1H), 7.26-7.36 (m, 6H), 7.17-7.24 (m, 2H), 7.11-7.16 (m, 2H), 5.99-6.05 (m, 1H), 5.21-5.30 (m, 1H), 4.47-4.62 (m, 2H), 3.86-3.98 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 206.3, 155.5, 143.7, 143.6, 137.2, 133.3, 129.8, 128.7, 127.4, 127.3, 126.8, 126.7, 124.7, 122.9, 120.4, 115.1, 111.4, 95.8, 89.8, 45.4, 40.4, 21.5. IR (neat): ν 1948, 1597, 1541, 1453, 1344, 1159, 1092 cm^{-1}. HRMS (ESI): Calcd for $C_{26}H_{24}NO_3S$ (M + H$^+$): 430.1471; found: 430.1472.

β-allenyl-furan (1m)



S20^{17} to **1m**: To a stirred solution of allene **S20** (392 mg, 4.0 mmol), tosylamide **S8** (502 mg, 2.0 mmol), and PPh$_3$ (1.05 g, 4.0 mmol) in anhydrous THF (25 mL) was added DIAD (809 mg, 4.0 mmol) at 0 ℃. The mixture was then stirred overnight at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford β-allenyl-furan **1m** (514 mg, 78%).

1m: Colorless oil: TLC R_f (PE/EA 5:1) = 0.49. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.32-7.35 (m, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.26-7.28 (m, 1H), 6.20-6.25 (m, 1H), 4.97-5.05 (m, 1H), 4.82-4.95 (m, 1H), 4.22 (s, 2H), 3.13-3.22 (m, 2H), 2.43 (s, 3H), 2.06-2.15 (m, 2H), 1.60 (dd, J = 7.0, 3.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 205.2, 143.5, 143.2, 140.9, 137.3, 129.7, 127.2, 120.6, 110.6, 86.7, 86.3, 46.7, 42.3, 27.8, 21.5, 14.3. IR (neat): ν 2926, 2858, 1964, 1598, 1502, 1453,

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[17] X. Jiang, C. Fu and S. Ma. *Chem. Eur. J.*, 2008, **14**, 9656.

1336, 1158, 1097, 1021, 960 cm^{-1}. HRMS (ESI): Calcd for $C_{18}H_{22}NO_3S$ (M + H$^+$): 332.1315; found: 332.1321.

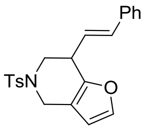
2.3 Experimental Details for Gold(I)- and Platinum(IV)-Catalyzed Intramolecular Cyclization of β-Allenyl-furans

General procedure: A solution of β-allenyl-furan substrate and catalyst (5 mol% or 10 mol%, [Au(NCMe)JohnPhos]SbF_6 or $PtCl_4$) in anhydrous solvent (dioxane or THF, 0.05 M) was stirred under an argon atmosphere at 50 ℃ (or 80 ℃). When TLC indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the corresponding product.

We observed that, when substrates 1 used for the intramolecular cyclization was not pure, low reaction conversion was observed. Therefore, we suggest that for the present reactions, all used substrates should be pure.

Experimental Data for Gold(I)- and Platinum(IV)-Catalyzed Intramolecular Cyclization of β-Allenyl-furans:

Product (2a)

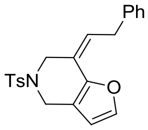


2a

Following the general procedure, β-allenyl-furan **1a** (43.0 mg, 0.11 mmol) was converted to product **2a** (39.3 mg, 91%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 4.2 mg, 5 mol%, temperature: 50 ℃, volume of dioxane: 2.1 mL, reaction time: 6 h.

2a: White solid: TLC R_f (PE/EA 5:1) = 0.42, m.p. = 53-55 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.26-7.36 (m, 7H), 7.18-7.25 (m, 1H), 6.56 (d, J = 15.9 Hz, 1H), 6.20-6.24 (m, 1H), 6.10 (dd, J = 15.9, 8.0 Hz, 1H), 4.14-4.20 (m, 1H), 4.03-4.09 (m, 1H), 3.70-3.78 (m, 1H), 3.62 (dd, J = 12.0, 5.0 Hz, 1H), 3.21 (dd, J = 12.0, 6.5 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 143.7, 142.3, 136.6, 134.0, 133.1, 129.7, 128.5, 127.6, 127.5, 126.4, 126.3, 113.9, 108.1, 49.1, 43.5, 38.7, 21.5. IR (neat): v 2977, 2904, 1597, 1497, 1453, 1346, 1164, 1087, 1040, 945 cm^{-1}. HRMS (ESI): Calcd for $C_{22}H_{22}NO_3S$ (M + H^+): 380.1315, found: 380.1316.

Product (3a)



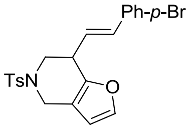
3a

Following the general procedure, β-allenyl-furan **1a** (32.5 mg, 0.09 mmol) was converted to product **3a** (29.8 mg, 92%). Catalyst: $PtCl_4$, 1.4 mg, 5 mol%, temperature: 50 ℃, volume of THF: 1.7 mL, reaction time: 2 h.

3a: Colorless oil: TLC R_f (PE/EA 3:1) = 0.60. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.61 (d, J = 8.2 Hz, 2H), 7.35-7.39 (m, 1H), 7.27-7.33 (m, 2H), 7.18-7.26 (m, 5H), 6.27-6.33 (m, 1H), 5.48 (t, J = 7.8 Hz, 1H), 4.30 (s, 2H), 3.97 (s, 2H), 3.79 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz,

CD_2Cl_2): δ 148.2, 144.1, 143.0, 141.0, 134.8, 129.7, 128.8, 128.7, 127.8, 126.4, 123.6, 121.3, 118.5, 109.0, 51.1, 44.5, 35.0, 21.6. IR (neat): v 3027, 2968, 2918, 1598, 1493, 1452, 1346, 1162, 1088, 1037, 940 cm^{-1}. HRMS (ESI): Calcd for $C_{22}H_{22}NO_3S$ ($M + H^+$): 380.1315, found: 380.1316.

Product (2b)

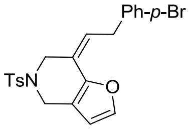


2b

Following the general procedure, β-allenyl-furan **1b** (80.0 mg, 0.17 mmol) was converted to product **2b** (62.3 mg, 78%). Catalyst: $[Au(NCMe)JohnPhos]SbF_6$, 6.7 mg, 5 mol%, temperature: 50 ℃, volume of dioxane: 3.5 mL, reaction time: 7 h.

2b: White solid: TLC R_f (PE/EA 3:1) = 0.60, m.p. = 49-51 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.28-7.33 (m, 3H), 7.20 (d, J = 8.5 Hz, 2H), 6.49 (d, J = 15.9 Hz, 1H), 6.21-6.25 (m, 1H), 6.11 (dd, J = 15.9 and 7.9 Hz, 1H), 4.08-4.14 (m, 2H), 3.68-3.77 (m, 1H), 3.57 (dd, J = 12.1 and 4.9 Hz, 1H), 3.28 (dd, J = 12.1 and 6.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 143.7, 142.4, 135.5, 134.0, 131.9, 131.6, 129.7, 128.0, 127.5, 127.3, 121.4, 114.1, 108.2, 49.0, 43.5, 38.7, 21.5. IR (neat): v 2969, 2919, 1594, 1482, 1455, 1401, 1346, 1239, 1164, 1083, 1040, 946 cm^{-1}. HRMS (ESI): Calcd for $C_{22}H_{21}BrNO_3S$ ($M + H^+$): 458.0420, found: 458.0422.

Product (3b)

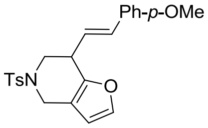


3b

Following the general procedure, β-allenyl-furan **1b** (29.7 mg, 0.07 mmol) was converted to product **3b** (23.6 mg, 79%). Catalyst: $PtCl_4$, 1.1 mg, 5 mol%, temperature: 50 ℃, volume of THF: 1.3 mL, reaction time: 2.5 h.

3b: White solid: TLC R_f (PE/EA 3:1) = 0.52, m.p. = 170-172 ℃. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.59 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.33-7.37 (m, 1H), 7.21 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.27-6.31 (m, 1H), 5.42 (t, J = 7.9 Hz, 1H), 4.29 (s, 2H), 3.95 (s, 2H), 3.73 (d, J = 7.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 148.0, 144.1, 143.1, 140.2, 134.7, 131.8, 130.6, 129.7, 127.8, 122.7, 121.9, 120.0, 118.8, 109.0, 51.0, 44.4, 34.4, 21.6. IR (neat): v 2966, 2920, 1596, 1488, 1452, 1345, 1161, 1087, 1039, 939 cm^{-1}. HRMS (ESI): Calcd for $C_{22}H_{21}BrNO_3S$ ($M + H^+$): 458.0420, found: 458.0426.

Product (2c)

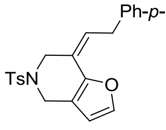


2c

Following the general procedure, β-allenyl-furan **1c** (40.2 mg, 0.1 mmol) was converted to product **2c** (27.0 mg, 67%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 3.8 mg, 5 mol%, temperature: 50 ℃, volume of dioxane: 2 mL, reaction time: 3 h.

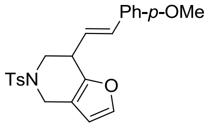
2c: Colorless oil: TLC R_f (PE/EA 5:1) = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H), 7.26-7.32 (m, 5H), 6.83 (d, J = 8.7 Hz, 2H), 6.51 (d, J = 15.8 Hz, 1H), 6.19-6.24 (m, 1H), 5.95 (dd, J = 15.8, 8.0 Hz, 1H), 4.15-4.23 (m, 1H), 4.00-4.07 (m, 1H), 3.80 (s, 3H), 3.70-3.76 (m, 1H), 3.64 (dd, J = 11.9, 5.0 Hz, 1H), 3.16 (dd, J = 11.9, 6.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 149.2, 143.6, 142.3, 134.0, 132.6, 129.7, 129.4, 127.6, 127.5, 124.0, 113.9, 113.8, 108.1, 55.3, 49.3, 43.5, 38.8, 21.5. IR (neat): v 2959, 2929, 2838, 1721, 1606, 1511, 1461, 1347, 1300, 1250, 1170, 1154, 1090, 1034 cm^{-1}. HRMS (ESI): Calcd for $C_{23}H_{24}NO_4S$ (M + H$^+$): 410.1421, found: 410.1420.

Product (3c) + Product (2c)



3c

+



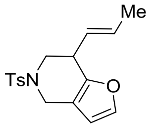
2c

Following the general procedure, β-allenyl-furan **1c** (48.4 mg, 0.19 mmol) was converted to the mixture of product **3c** and **2c** (28.1 mg, 58%, **3c**:**2c** = 4.3:1 based on the integral of ^{1}H-NMR of β-H in furan rings). Catalyst: $PtCl_4$, 2 mg, 5 mol%, temperature: 50 ℃, volume of THF: 2.4 mL, reaction time: 2 h. Products **3c** and **2c** are hard to separate.

Mixture of 3c and 2c: Colorless oil: TLC R_f (PE/EA 5:1) = 0.29. IR (neat): v 2956, 2836, 1609, 1511, 1458, 1346, 1302, 1247, 1166, 1089, 1035, 941 cm^{-1}. HRMS (ESI): Calcd for $C_{23}H_{24}NO_4S$ (M + H$^+$): 410.1421, found: 410.1417.

3c: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.60 (d, J = 8.3 Hz, 2H), 7.35-7.38 (m, 1H), 7.22 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.27-6.31 (m, 1H), 5.45 (t, J = 7.8 Hz, 1H), 4.28 (s, 2H), 3.93-3.97 (m, 2H), 3.77 (s, 3H), 3.71 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 158.5, 148.3, 144.1, 143.0, 134.8, 133.0, 129.7, 129.6, 127.9, 124.2, 121.0, 118.4, 114.2, 109.0, 55.6, 51.1, 44.5, 34.1, 21.6.

Product (2d)

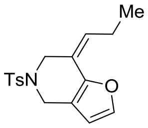


2d

Following the general procedure, β-allenyl-furan **1d** (41.1 mg, 0.13 mmol) was converted to product **2d** (32.6 mg, 79%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 5.0 mg, 5 mol%, temperature: 50 ℃, volume of dioxane: 2.6 mL, reaction time: 5 h.

2d: Colorless oil: TLC R_f (PE/EA 5:1) = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.26-7.28 (m, 1H), 6.14-6.22 (m, 1H), 5.68 (m, 1H), 5.30-5.41 (m, 1H), 4.10-4.18 (m, 1H), 3.92-4.00 (m, 1H), 3.48-3.60 (m, 2H), 2.98-3.05 (m, 1H), 2.42 (s, 3H), 1.70 (dd, J = 6.5, 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 143.6, 142.0, 134.0, 129.7, 129.4, 127.6, 127.5, 113.5, 108.0, 49.3, 43.5, 38.6, 21.5, 18.0. IR (neat): v 2969, 2918, 1458, 1347, 1169, 1090, 1041, 966, 944 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}NO_3S$ (M + H$^+$): 318.1158, found: 318.1161.

Product (3d)

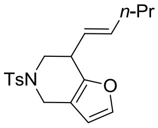


3d

Following the general procedure, β-allenyl-furan **1d** (41.1 mg, 0.13 mmol) was converted to product **3d** (33.1 mg, 80%). Catalyst: $PtCl_4$, 2.2 mg, 5 mol%, temperature: 50 ℃, volume of THF: 2.6 mL, reaction time: 1 h.

3d: Colorless oil: TLC R_f (PE/EA 3:1) = 0.53. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.60 (d, J = 8.3 Hz, 2H), 7.29-7.33 (m, 1H), 7.23 (d, J = 8.3 Hz, 2H), 6.23-6.27 (m, 1H), 5.30 (t, J = 8.0 Hz, 1H), 4.26 (s, 2H), 3.89-3.93 (m, 2H), 2.38-2.44 (m, 2H), 2.37 (s, 3H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 148.4, 144.0, 142.8, 134.8, 129.7, 127.9, 127.4, 120.2, 117.6, 108.8, 51.2, 44.5, 22.2, 21.5, 14.2. IR (neat): ν 2966, 2930, 2873, 1598, 1493, 1458, 1346, 1158, 1089, 1040, 945 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}NO_3S$ (M + H$^+$): 318.1158, found: 318.1159.

Product (2e)

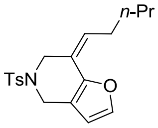


2e

Following the general procedure, β-allenyl-furan **1e** (42.9 mg, 0.12 mmol) was converted to product **2e** (39.2 mg, 91%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 4.8 mg, 5 mol%, temperature: 50 ℃, volume of dioxane: 2.5 mL, reaction time: 4 h.

2e: Colorless oil: TLC R_f (PE/EA 3:1) = 0.59. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 1.5 Hz, 1H), 6.23 (d, J = 1.5 Hz, 1H), 5.61-5.72 (m, 1H), 5.30-5.38 (m, 1H), 4.07-4.14 (m, 1H), 3.93-4.01 (m, 1H), 3.49-3.51 (m, 2H), 3.00-3.08 (m, 1H), 2.42 (s, 3H), 1.97-2.05 (m, 2H), 1.34-1.45 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 150.1, 144.2, 142.4, 134.8, 134.4, 130.1, 127.8, 127.1, 114.0, 108.5, 49.8, 43.9, 38.9, 34.9, 22.7, 21.6, 13.8. IR (neat): ν 2959, 2922, 2971, 1503, 1460, 1349, 1170, 1156, 1091, 1044, 969, 949 cm^{-1}. HRMS (ESI): Calcd for $C_{19}H_{24}NO_3S$ (M + H$^+$): 346.1471, found: 346.1473.

Product (3e)

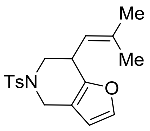


3e

Following the general procedure, β-allenyl-furan **1e** (41.6 mg, 0.12 mmol) was converted to product **3e** (33.5 mg, 80%). Catalyst: $PtCl_4$, 2.0 mg, 5 mol%, temperature: 50 ℃, volume of THF: 2.4 mL, reaction time: 2 h.

3e: Colorless oil: TLC R_f (PE/EA 3:1) = 0.62. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.60 (d, J = 8.3 Hz, 2H), 7.29-7.33 (m, 1H), 7.23 (d, J = 8.3 Hz, 2H), 6.23-6.27 (m, 1H), 5.31 (t, J = 7.6 Hz, 1H), 4.26 (s, 2H), 3.90-3.94 (m, 2H), 2.38-2.43 (m, 2H), 2.37 (s, 3H), 1.31-1.40 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 148.5, 144.0, 142.7, 134.9, 129.7, 127.9, 126.0, 120.7, 117.6, 108.8, 51.2, 44.5, 32.2, 28.5, 22.8, 21.6, 14.1. IR (neat): v 2957, 2926, 2858, 1597, 1493, 1457, 1347, 1160, 1090, 1036, 940 cm^{-1}. HRMS (ESI): Calcd for $C_{19}H_{24}NO_3S$ (M + H$^+$): 346.1471, found: 346.1475.

Product (2g)

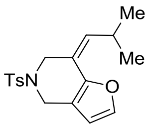


2g

Following the general procedure, β-allenyl-furan **1g** (41.9 mg, 0.13 mmol) was converted to product **2g** (40.5 mg, 97%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 4.6 mg, 5 mol%, temperature: 50 ℃, volume of dioxane: 2.5 mL, reaction time: 4 h.

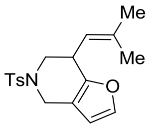
2g: Colorless oil: TLC R_f (PE/EA 10:1) = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.22-7.26 (m, 1H), 6.15-6.20 (m, 1H), 5.00 (d, J = 9.1 Hz, 1H), 4.21-4.28 (m, 1H), 3.87-3.95 (m, 1H), 3.72-3.82 (m, 1H), 3.65 (dd, J = 12.0 and 5.2 Hz, 1H), 2.84 (dd, J = 12.0 and 7.7 Hz, 1H), 2.42 (s, 3H), 1.76 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 143.6, 141.8, 136.4, 134.1, 129.7, 127.5, 120.6, 113.1, 108.0, 49.0, 43.6, 34.5, 25.8, 21.5, 18.2. IR (neat): v 2972, 2918, 2857, 1598, 1503, 1446, 1347, 1168, 1090, 1049, 1022, 943 cm^{-1}. HRMS (ESI): Calcd for $C_{18}H_{22}NO_3S$ (M + H$^+$): 332.1315, found: 332.1323.

Product (3g) + Product (2g)



3g

+

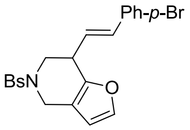


2g

Following the general procedure, β-allenyl-furan **1g** (43.0 mg, 0.13 mmol) was converted to the mixture of product **3g** and **2g** (37.9 mg, 88%, **3g**:**2g** = 1:2.4 based on the integral of ^{1}H-NMR of β-H in furan rings). Catalyst: $PtCl_4$, 2.4 mg, 5 mol%, temperature: 50 ℃, volume of THF: 2.5 mL, reaction time: 4 h. The pure product **3g** can be achieved by PTLC.

3g: Colorless oil: TLC R_f (PE/EA 10:1) = 0.24. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.59 (d, J = 8.3 Hz, 2H), 7.29-7.32 (m, 1H), 7.23 (d, J = 8.3 Hz, 2H), 6.22-6.26 (m, 1H), 5.12 (d, J = 9.6 Hz, 1H), 4.27 (s, 2H), 3.90-3.93 (m, 2H), 3.06-3.18 (m, 1H), 2.36 (s, 3H), 0.97 (d, J = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 148.3, 144.0, 142.8, 135.1, 133.0, 129.8, 127.9, 118.8, 117.7, 108.9, 51.2, 44.5, 28.0, 23.1, 21.6. IR (neat): v 2962, 2925, 2866, 1597, 1493, 1459, 1345, 1160, 1090, 1034 cm^{-1}. HRMS (ESI): Calcd for $C_{18}H_{22}NO_3S$ (M + H$^+$): 332.1315, found: 332.1321.

Product (2h)

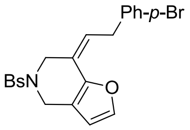


2h

Following the general procedure, β-allenyl-furan **1h** (52.4 mg, 0.10 mmol) was converted to product **2h** (48.6 mg, 93%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 3.8 mg, 5 mol%, temperature: 50 ℃, volume of dioxane: 2 mL, reaction time: 8 h.

2h: White solid: TLC R_f (PE/EA 5:1) = 0.39, m.p. = 65-67 ℃. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.60-7.75 (m, 4H), 7.44 (d, J = 8.5 Hz, 2H), 7.31-7.36 (m, 1H), 7.23 (d, J = 8.5 Hz, 2H), 6.48 (d, J = 15.9 Hz, 1H), 6.24-6.31 (m, 1H), 6.13 (dd, J = 15.9 and 7.8 Hz, 1H), 4.08-4.19 (m, 2H), 3.67-3.77 (m, 1H), 3.56 (dd, J = 12.2 and 4.9 Hz, 1H), 3.34 (dd, J = 12.2 and 5.9 Hz, 1H).^{13}C NMR (100 MHz, CD_2Cl_2): δ 149.0, 142.9, 136.7, 136.0, 132.8, 132.2, 132.0, 129.3, 128.3, 128.2, 127.9, 121.7, 114.5, 108.5, 49.3, 43.9, 38.9. IR (neat): v 2853, 1574, 1486, 1469, 1389, 1352, 1172, 1154, 1089, 1070, 1041, 1009, 951 cm^{-1}. HRMS (ESI): Calcd for $C_{21}H_{21}Br_2N_2O_3S$ (M + NH_4^+): 538.9634, found: 538.9625.

Product (3h)

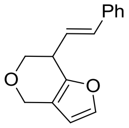


3h

Following the general procedure, β-allenyl-furan **1h** (51.8 mg, 0.10 mmol) was converted to product **3h** (43.4 mg, 84%). Catalyst: $PtCl_4$, 1.8 mg, 5 mol%, temperature: 50 ℃, volume of THF: 2 mL, reaction time: 2 h.

3h: White soid: TLC R_f (PE/EA 5:1) = 0.41, m.p. = 169-172 ℃. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.34-7.38 (m, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.27-6.32 (m, 1H), 5.42 (t, J = 7.9 Hz, 1H), 4.38 (s, 2H), 4.02-4.05 (m, 2H), 3.70 (d, J = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 148.0, 143.3, 140.0, 137.4, 132.3, 131.9, 130.6, 129.3, 127.9, 123.0, 121.4, 120.1, 118.6, 109.0, 51.0, 44.6, 34.4. IR (neat): v 2361, 2340, 1573, 1487, 1389, 1348, 1165, 1087, 1069, 1034, 1010, 936 cm^{-1}. HRMS (ESI): Calcd for $C_{21}H_{17}Br_2KNO_3S$ (M + K^+): 559.8928, found: 559.8928.

Product (2i)



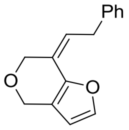
2i

Following the general procedure, β-allenyl-furan **1i** (41.2 mg, 0.18 mmol) was converted to product **2i** (34.3 mg, 83%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 13.6 mg, 10 mol%, temperature: 80 ℃, volume of dioxane: 3.5 mL, reaction time: 8 h.

2i: Colorless oil: TLC R_f (PE/EA 10:1) = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.39 (m, 2H), 7.31-7.33 (m, 1H), 7.25-7.31 (m, 2H), 7.18-7.23 (m, 1H), 6.57 (d, J = 15.9 Hz, 1H), 6.23-6.26 (m, 1H), 6.15-6.23 (m, 1H), 4.57-4.69 (m, 2H), 4.05 (dd, J = 11.0 and 4.8 Hz, 1H), 3.78

(dd, *J* = 11.0 and 5.9 Hz, 1H), 3.65-3.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.9, 141.7, 136.8, 132.7, 128.5, 127.5, 126.9, 126.3, 116.1, 107.2, 70.1, 64.6, 39.6. IR (neat): *ν* 3026, 2961, 2851, 1498, 1450, 1230, 1122, 1078, 1034, 966 cm^{-1}. HRMS (ESI): Calcd for $C_{15}H_{15}O_2$ (M + H$^+$): 227.1067, found: 227.1065.

Product (3i)

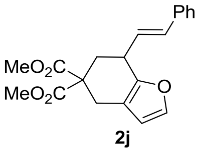


3i

Following the general procedure, β-allenyl-furan **1i** (40.0 mg, 0.18 mmol) was converted to product **3i** (26.8 mg, 67%). Catalyst: $PtCl_4$, 6 mg, 10 mol%, temperature: 80 ℃, volume of dioxane: 3.5 mL, reaction time: 4 h.

3i: Colorless oil: TLC *R*$_f$ (PE/EA 10:1) = 0.54. ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 7.42-7.47 (m, 1H), 7.23-7.32 (m, 4H), 7.15-7.22 (m, 1H), 6.30-6.36 (m, 1H), 5.37 (t, *J* = 7.9 Hz, 1H), 4.67 (s, 2H), 4.24-4.29 (m, 2H), 3.90 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): *δ* 147.9, 142.7, 141.5, 128.8, 128.7, 126.3, 124.7, 121.2, 120.6, 108.2, 71.1, 65.0, 35.1. IR (neat): *ν* 3026, 2960, 2830, 1602, 1493, 1453, 1342, 1284, 1148, 1112, 1089, 1030 cm^{-1}. HRMS (ESI): Calcd for $C_{15}H_{15}O_2$ (M + H$^+$): 227.1067, found: 227.1066.

Product (2j)

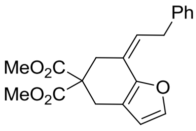


2j

Following the general procedure, β-allenyl-furan **1j** (39.7 mg, 0.12 mmol) was converted to product **2j** (34.2 mg, 86%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 4.5 mg, 5 mol%, temperature: 50 ℃, volume of dioxane: 2 mL, reaction time: 4 h.

2j: Colorless oil: TLC *R*$_f$ (PE/EA 5:1) = 0.49. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.34-7.39 (m, 2H), 7.26-7.32 (m, 3H), 7.16-7.24 (m, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.22-6.28 (m, 1H), 6.14 (dd, *J* = 15.8 and 7.8 Hz, 1H), 3.65-3.79 (m, 7H), 3.17-3.25 (m, 1H), 2.93-3.01 (m, 1H), 2.72 (ddd, *J* = 13.5, 6.0, 1.5 Hz, 1H), 2.15 (dd, *J* = 13.5, 9.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 171.7, 170.8, 149.4, 142.0, 136.9, 131.9, 129.3, 128.5, 127.4, 126.3, 115.2, 110.2, 54.3, 52.9, 52.8, 36.1, 35.7, 28.4. IR (neat): *ν* 3027, 2953, 2849, 1736, 1496, 1448, 1435, 1292, 1255, 1176, 1146, 967 cm^{-1}. HRMS (ESI): Calcd for $C_{20}H_{21}O_5$ (M + H$^+$): 341.1384, found: 341.1383.

Product (3j)

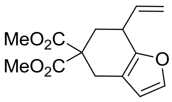


3j

Following the general procedure, β-allenyl-furan **1j** (29.6 mg, 0.09 mmol) was converted to product **3j** (26.4 mg, 89%, *Z*:*E* = 10:1 based on the integral of ^{1}H-NMR of β-H in furan rings). Catalyst: $PtCl_4$, 1.5 mg, 5 mol%, temperature: 50 ℃, volume of THF: 1.8 mL, reaction time: 2 h.

3j: Colorless oil: TLC R_f (PE/EA 5:1) = 0.49. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.38-7.42 (m, 1H), 7.15-7.36 (m, 5H), 6.33-6.39 (m, 1H), 5.45 (t, *J* = 7.9 Hz, 1H), 3.89 (d, *J* = 7.9 Hz, 2H), 3.67 (s, 6H), 3.13 (s, 2H), 2.96-3.00 (m, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.2, 149.1, 142.7, 141.8, 128.8, 128.7, 126.2, 124.3, 122.1, 120.1, 111.1, 55.7, 53.0, 38.8, 35.1, 29.4. IR (neat): *v* 3026, 3001, 2954, 2919, 1737, 1494, 1436, 1307, 1255, 1200, 1151, 1106, 1070 cm^{-1}. HRMS (ESI): Calcd for $C_{20}H_{21}O_5$ (M + H$^+$): 341.1384, found: 341.1384.

Product (2k)

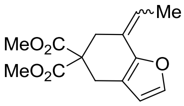


2k

Following the general procedure, β-allenyl-furan **1k** (43.2 mg, 0.16 mmol) was converted to product **2k** (27.1 mg, 63%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 12.6 mg, 10 mol%, temperature: 80 ℃, volume of dioxane: 3.3 mL, reaction time: 3 h.

2k: Colorless oil: TLC R_f (PE/EA 5:1) = 0.58. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.29 (m, 1H), 6.20-6.25 (m, 1H), 5.71-5.83 (m, 1H), 5.13-5.28 (m, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 3.48-5.60 (m, 1H), 3.16-3.25 (m, 1H), 2.88-2.96 (m, 1H), 2.61-2.70 (m, 1H), 2.01-2.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 170.8, 149.3, 141.8, 137.7, 116.7, 114.9, 110.1, 54.3, 52.8, 52.7, 36.8, 35.4, 28.4. IR (neat): *v* 2955, 2360, 1736, 1504, 1435, 1293, 1253, 1194, 1180, 1148, 1063 cm^{-1}. HRMS (ESI): Calcd for $C_{14}H_{17}O_5$ (M + H$^+$): 265.1070, found: 265.1068.

Product (3k)



3k

Following the general procedure, β-allenyl-furan **1k** (43.4 mg, 0.16 mmol) was converted to product **3k** (31.3 mg, 72%, *Z*:*E* = 1.3:1 based on the integral of ^{1}H-NMR of vinyl hydrogen). Catalyst: $PtCl_4$, 5.5 mg, 10 mol%, temperature: 80 ℃, volume of dioxane: 3.3 mL, reaction time: 2 h.

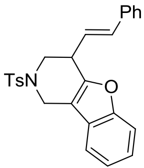
Mixture of (*Z*)-3k and (*E*)-3k: Colorless oil: TLC R_f (PE/EA 5:1) = 0.61. IR (neat): *v* 2955, 2917, 2360, 1737, 1494, 1436, 1310, 1295, 1254, 1198, 1180, 1156, 1106, 1069 cm^{-1}. HRMS (ESI): Calcd for $C_{14}H_{17}O_5$ (M + H$^+$): 265.1070, found: 265.1069.

(*Z*)-3k: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.35-7.42 (m, 1H), 6.29-6.34 (m, 1H), 5.36 (q, *J* = 7.4 Hz, 1H), 3.68 (s, 6H), 3.09 (s, 2H), 2.92 (s, 2H), 2.02 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.3, 149.6, 142.4, 122.2, 120.3, 119.2, 110.9, 55.6, 53.0, 38.7, 29.3, 14.6.

(*E*)-3k: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.21-7.29 (m, 1H), 6.25-6.29 (m, 1H), 5.90 (q, *J* = 7.2 Hz, 1H), 3.68 (s, 6H), 3.10 (s, 2H), 2.99 (s, 2H), 1.80 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.3, 149.5, 141.9, 123.7, 116.6, 116.2, 111.2, 55.7, 53.0, 31.4, 29.0, 12.8.

The assignment of the ^{13}C-NMR of **(*Z*)-3k** and **(*E*)-3k** is based on the relative change of *Z*/*E* mixture with different ratios.

Product (2l)

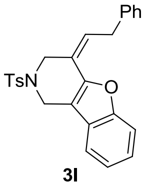


2l

Following the general procedure, β-allenyl-furan **1l** (34.8 mg, 0.08 mmol) was converted to product **2l** (29.2 mg, 85%). Catalyst: [Au(NCMe)JohnPhos]SbF_6, 6.3 mg, 10 mol%, temperature: 80 ℃, volume of dioxane: 1.6 mL, reaction time: 5 h.

2l: White solid: TLC R_f (PE/EA 5:1) = 0.41, m.p. = 158-160 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.3 Hz, 2H), 7.38-7.43 (m, 2H), 7.32-7.37 (m, 2H), 7.27-7.32 (m, 4H), 7.19-7.26 (m, 3H), 6.63 (d, J = 15.9 Hz, 1H), 6.17 (dd, J = 15.9, 8.0 Hz, 1H), 4.26-4.43 (m, 2H), 3.84-3.94 (m, 1H), 3.70 (dd, J = 12.0, 5.1 Hz, 1H), 3.37 (dd, J = 12.0, 6.2 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 151.9, 143.8, 136.4, 134.0, 133.6, 129.8, 128.5, 127.8, 127.6, 126.5, 125.9, 125.6, 124.2, 122.8, 118.5, 111.4, 110.1, 49.1, 42.5, 39.0, 21.5. IR (neat): ν 3059, 3028, 2921, 2852, 1597, 1494, 1452, 1347, 1306, 1159, 1091, 964 cm^{-1}. HRMS (ESI): Calcd for $C_{26}H_{24}NO_3S$ (M + H$^+$): 430.1471, found: 430.1474.

Product (3l)

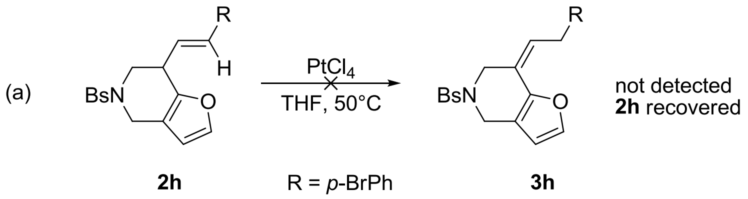


3l

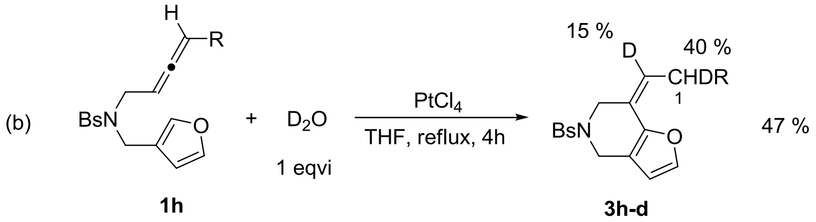
Following the general procedure, β-allenyl-furan **1l** (42.3 mg, 0.10 mmol) was converted to product **3l** (35.1 mg, 83%, Z:E = 8:1 based on the integral of ^{1}H-NMR of vinyl hydrogen). Catalyst: $PtCl_4$, 3.3 mg, 10 mol%, temperature: 80 ℃, volume of dioxane: 2 mL, reaction time: 1 h.

3l: White solid: TLC R_f (PE/EA 5:1) = 0.55, m.p. = 138-139 ℃. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.64 (d, J = 8.3 Hz, 2H), 7.45-7.50 (m, 2H), 7.22-7.37 (m, 7H), 7.17 (d, J = 8.3 Hz, 2H), 5.71 (t, J = 7.9 Hz, 1H), 4.52 (s, 2H), 4.09 (s, 2H), 3.97 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 155.0, 150.0, 144.2, 140.8, 134.6, 129.8, 128.9, 128.8, 127.8, 127.5, 126.5, 125.8, 125.6, 123.5, 121.4, 119.4, 113.8, 111.7, 51.2, 43.5, 35.4, 21.6. IR (neat): ν 3060, 3028, 2921, 2850, 1599, 1494, 1451, 1346, 1166, 1091, 1042, 952 cm^{-1}. HRMS (ESI): Calcd for $C_{26}H_{24}NO_3S$ (M + H$^+$): 430.1471, found: 430.1473.

3. Preliminary Mechanistic Study

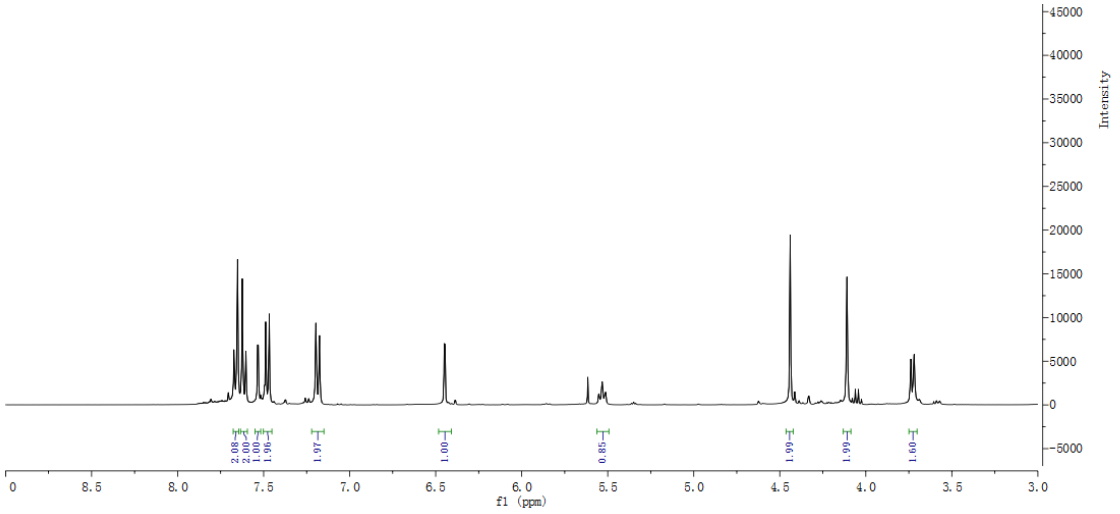


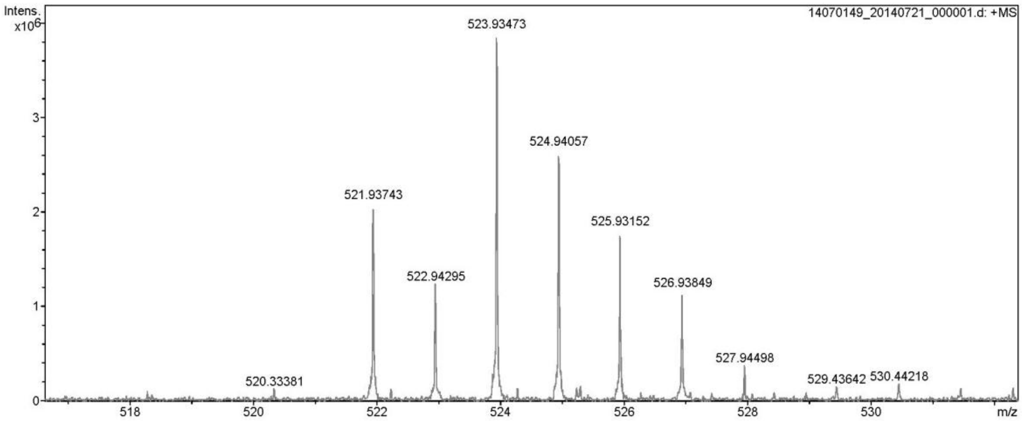
Following the general procedure, a solution of **2h** (42.6 mg, 0.08 mml) and $PtCl_4$ (1.4 mg, 5 mol%) in anhydrous THF (0.05 M, 1.6 mL) was stirred under an argon atmosphere at 50 ℃ for 2 h, and no product **3h** was detected, showing that compound **3h** was not generated through olefin isomerization from **2h**.



Compound **1h** (90.6 mg, 0.17 mmol) and $PtCl_4$ (3.5 mg, 5 mol%) were dissolved in anhydrous THF (0.05 M, 3.5 mL), then D_2O (3.5 mg, 0.17mmol) was added. The resulting mixture was refluxed under an argon atmosphere for 4 h. When TLC indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was filtered through a short silica gel column quickly to afford the product **3h-d**.

^{1}H-NMR (400 MHz, CD_3COCD_3) and HRMS for the product **3h-d** are shown below.





Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
521.93743	2108725	C 21 H 18 Br 2 N O 3 S	521.93687	-0.57	-1.09	187.6	12.5	even	ok
522.94295	1245102	C 21 H 17 Br 2 D N O 3 S	522.94314	0.20	0.37	101.8	12.5	even	ok

4. Crystallographic Data of Compound 3h

Table S2 Crystal data and structure refinement for **3h**.

Identification code	3
Empirical formula	$C_{21}H_{17}Br_2NO_3S$
Formula weight	523.24
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.4812(7)
b/Å	8.1107(6)
c/Å	13.3671(9)
α/°	90
β/°	106.900(7)
γ/°	90
Volume/Å^3	983.53(12)
Z	2
ρ_{calc}mg/mm^3	1.767
m/mm^{-1}	4.250
F(000)	520.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
2Θ range for data collection	5.948 to 52.04 °
Index ranges	$-11 \le h \le 11$, $-7 \le k \le 9$, $-16 \le l \le 12$
Reflections collected	3819
Independent reflections	2860[R(int) = 0.0673]
Data/restraints/parameters	2860/1/253
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	$R_1 = 0.0628$, $wR_2 = 0.1638$
Final R indexes [all data]	$R_1 = 0.0816$, $wR_2 = 0.1843$
Largest diff. peak/hole / e Å^{-3}	0.86/-0.76
Flack parameter	-0.04(3)

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3h**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	681.6(17)	5465(2)	-4833.9(11)	51.5(5)
Br2	13842.4(19)	-2423(2)	4219.6(12)	56.1(5)
C1	9010(12)	3807(16)	2467(9)	26(3)
C2	7417(13)	3935(17)	2402(9)	28(3)

C3	6763(15)	4605(18)	3156(10)	34(3)
C4	5277(15)	4470(20)	2710(12)	41(4)
C5	6328(12)	3440(16)	1573(9)	24(3)
C6	6521(13)	2650(16)	629(8)	24(2)
C7	8137(11)	2219(15)	824(10)	25(3)
C8	5506(12)	2291(17)	-240(10)	29(3)
C9	3870(13)	2520(20)	-486(9)	33(3)
C10	3124(12)	3227(16)	-1546(10)	27(3)
C11	3878(13)	4199(16)	-2085(10)	30(3)
C12	3175(15)	4880(17)	-3047(12)	37(3)
C13	1663(14)	4526(17)	-3534(10)	31(3)
C14	921(14)	3550(18)	-2984(10)	35(3)
C15	1627(14)	2906(18)	-2038(11)	37(3)
C16	11745(12)	1947(15)	2066(10)	24(3)
C17	11766(12)	403(17)	1644(9)	26(3)
C18	12395(13)	-923(16)	2273(11)	30(3)
C19	13003(13)	-623(18)	3332(10)	30(3)
C20	12991(13)	910(20)	3772(9)	37(3)
C21	12365(12)	2190(16)	3125(10)	29(3)
N1	9116(10)	3534(12)	1370(7)	22(2)
O1	5000(9)	3730(13)	1728(7)	33(2)
O2	11460(10)	5091(11)	1778(8)	34(2)
O3	10715(9)	3265(13)	217(6)	35(2)
S1	10804(3)	3591(4)	1301(2)	28.0(7)

Table S4 Anisotropic Displacement Parameters (Å^2×10^3) for **3h**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	49.1(8)	67.5(11)	31.3(7)	6.7(7)	1.4(6)	1.5(8)
Br2	63.7(10)	57.3(10)	48.4(9)	22.0(8)	18.1(7)	27.6(9)
C1	27(6)	30(7)	19(6)	-7(5)	2(5)	0(5)
C2	30(6)	31(7)	25(6)	-2(5)	12(5)	4(6)
C3	39(7)	40(8)	25(7)	12(6)	14(6)	3(6)
C4	31(7)	51(9)	47(9)	-2(7)	20(6)	4(7)
C5	22(6)	30(7)	20(6)	1(5)	6(5)	1(5)
C6	35(6)	20(6)	22(6)	0(5)	14(5)	-2(6)
C7	17(5)	28(7)	32(7)	-1(5)	7(5)	-1(5)
C8	20(6)	34(8)	31(7)	-4(6)	3(5)	0(5)
C9	26(6)	41(8)	29(6)	-11(7)	7(5)	-6(6)

C10	18(5)	30(7)	34(7)	2(5)	7(5)	-1(5)
C11	18(6)	36(7)	35(7)	-12(6)	5(5)	-3(5)
C12	37(7)	29(8)	50(9)	11(6)	18(7)	-7(6)
C13	38(7)	30(7)	23(7)	2(6)	5(6)	-2(6)
C14	30(6)	35(8)	37(7)	-16(7)	4(6)	2(6)
C15	34(7)	33(8)	41(8)	6(7)	5(6)	-3(6)
C16	19(5)	28(7)	22(6)	0(5)	0(5)	-3(5)
C17	24(6)	31(7)	20(6)	-5(6)	0(4)	-6(6)
C18	21(6)	27(7)	43(8)	7(6)	10(6)	10(5)
C19	18(6)	45(8)	24(7)	6(6)	-1(5)	8(6)
C20	28(6)	61(10)	20(6)	3(7)	5(5)	-6(7)
C21	15(5)	27(7)	42(8)	9(6)	5(5)	0(5)
N1	27(5)	22(5)	19(5)	4(4)	6(4)	0(4)
O1	27(4)	47(6)	27(5)	-2(4)	9(4)	-3(4)
O2	30(5)	26(5)	46(6)	5(4)	11(4)	-1(4)
O3	27(4)	50(6)	30(5)	8(4)	12(4)	8(4)
S1	23.0(14)	30.2(17)	30.5(16)	1.8(14)	7.1(12)	-0.3(13)

Table S5 Bond Lengths for **3h**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	C13	1.877(13)	C10	C15	1.404(17)
Br2	C19	1.904(13)	C11	C12	1.380(19)
C1	C2	1.491(16)	C12	C13	1.421(18)
C1	N1	1.514(14)	C13	C14	1.40(2)
C2	C3	1.434(18)	C14	C15	1.352(19)
C2	C5	1.338(17)	C16	C17	1.376(19)
C3	C4	1.365(19)	C16	C21	1.380(18)
C4	O1	1.396(17)	C16	S1	1.758(12)
C5	C6	1.473(16)	C17	C18	1.388(18)
C5	O1	1.355(14)	C18	C19	1.386(19)
C6	C7	1.519(16)	C19	C20	1.37(2)
C6	C8	1.308(16)	C20	C21	1.372(18)
C7	N1	1.462(15)	N1	S1	1.631(10)
C8	C9	1.501(16)	O2	S1	1.429(10)
C9	C10	1.501(18)	O3	S1	1.450(9)
C10	C11	1.396(19)			

Table S6 Bond Angles for **3h**.

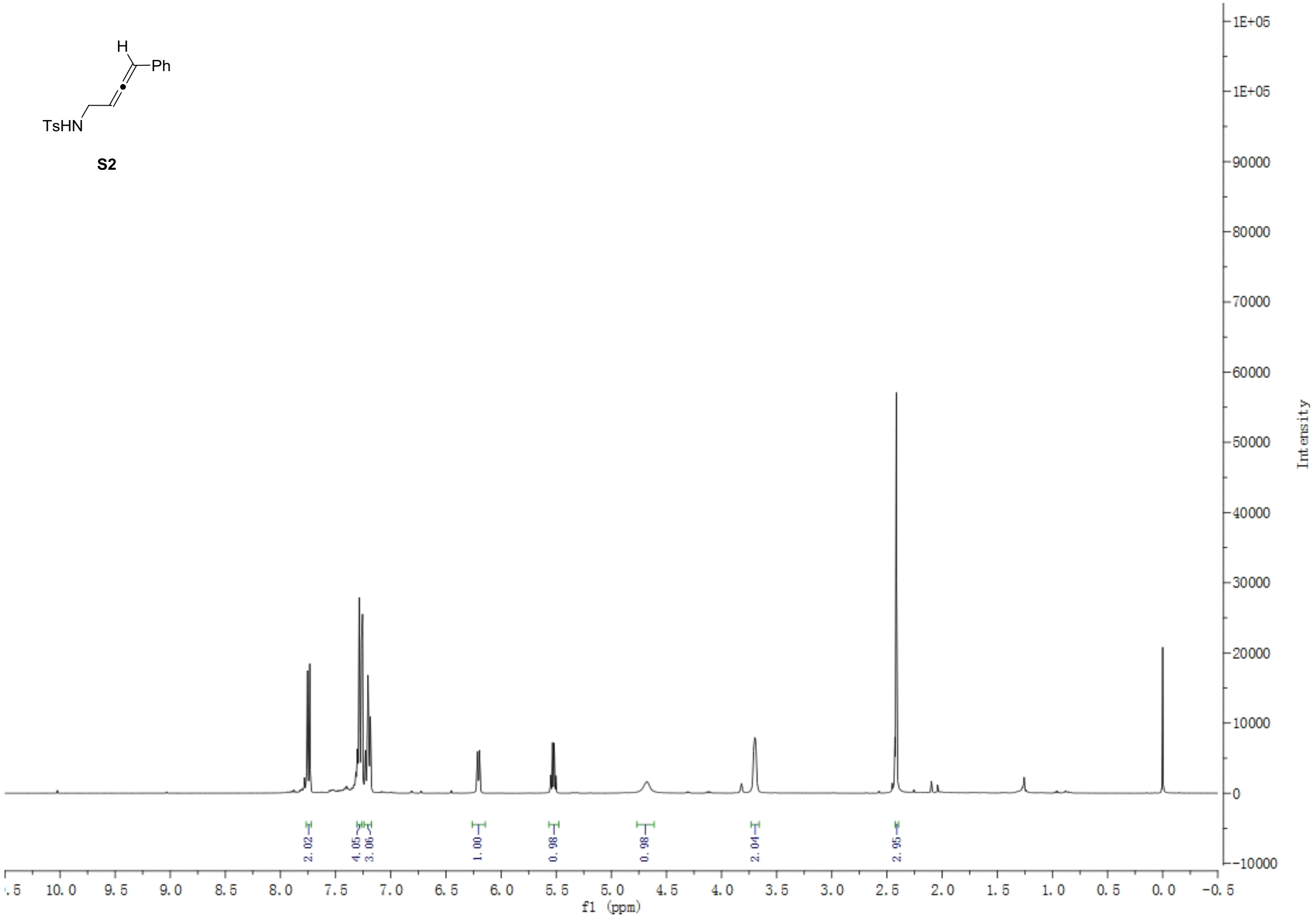
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	N1	107.7(9)	C15	C14	C13	121.4(12)
C3	C2	C1	128.5(11)	C14	C15	C10	121.6(13)
C5	C2	C1	123.5(11)	C17	C16	C21	119.8(11)
C5	C2	C3	108.0(11)	C17	C16	S1	121.1(9)
C4	C3	C2	105.3(12)	C21	C16	S1	118.8(9)
C3	C4	O1	109.5(11)	C16	C17	C18	120.8(11)
C2	C5	C6	125.6(11)	C17	C18	C19	117.4(12)
C2	C5	O1	110.5(10)	C18	C19	Br2	118.5(10)
O1	C5	C6	123.9(10)	C20	C19	Br2	118.6(9)
C5	C6	C7	108.9(10)	C20	C19	C18	122.9(12)
C8	C6	C5	128.0(11)	C19	C20	C21	118.1(12)
C8	C6	C7	123.1(11)	C20	C21	C16	121.0(12)
N1	C7	C6	112.3(10)	C1	N1	S1	113.1(7)
C6	C8	C9	127.8(12)	C7	N1	C1	112.3(9)
C8	C9	C10	115.3(10)	C7	N1	S1	118.9(8)
C11	C10	C9	122.0(10)	C5	O1	C4	106.7(9)
C11	C10	C15	117.6(12)	N1	S1	C16	106.6(5)
C15	C10	C9	120.4(12)	O2	S1	C16	107.7(6)
C12	C11	C10	121.7(11)	O2	S1	N1	107.8(5)
C11	C12	C13	119.7(12)	O2	S1	O3	119.5(6)
C12	C13	Br1	120.3(10)	O3	S1	C16	108.4(6)
C14	C13	Br1	121.7(10)	O3	S1	N1	106.1(5)
C14	C13	C12	117.9(12)				

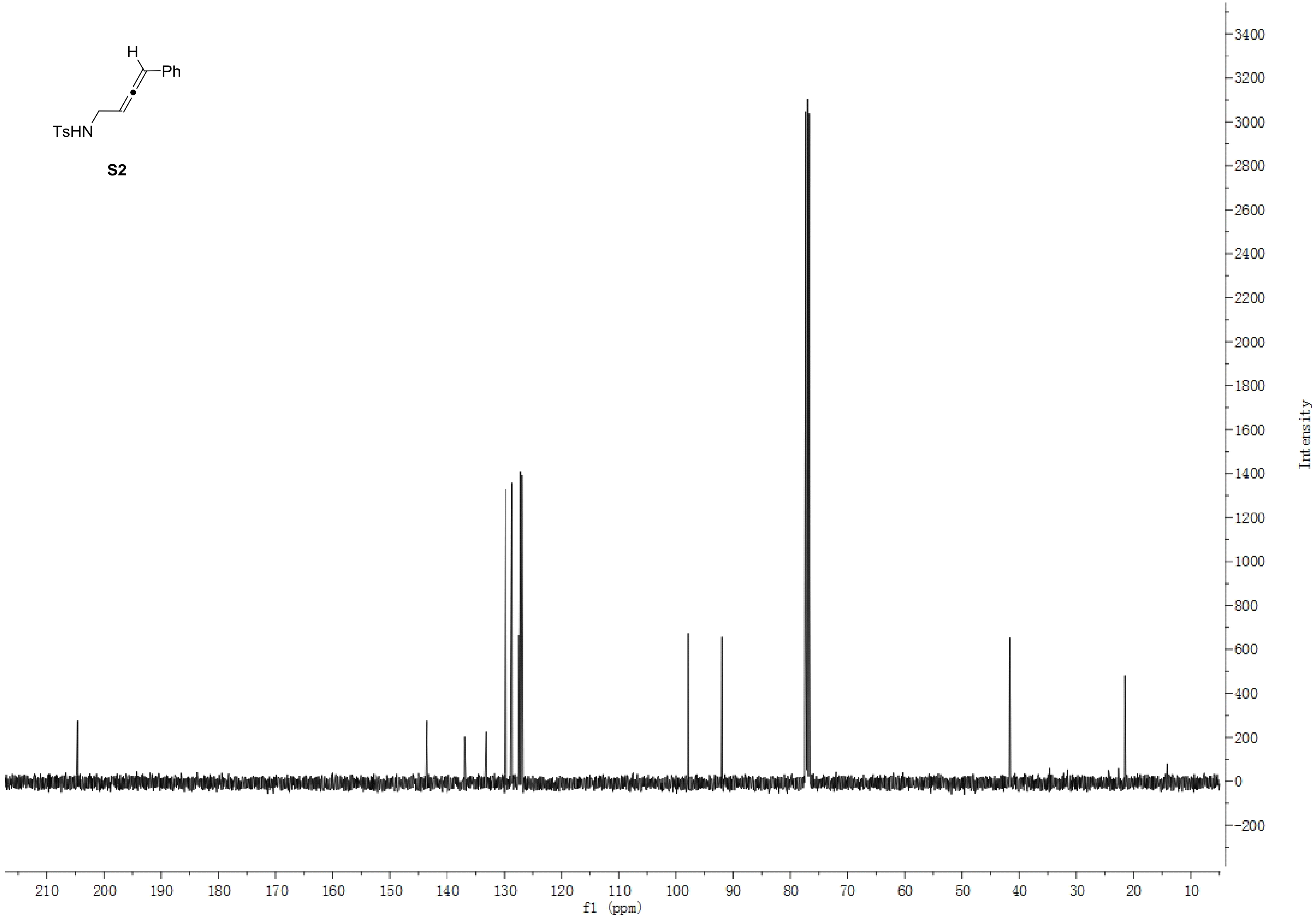
Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3h**.

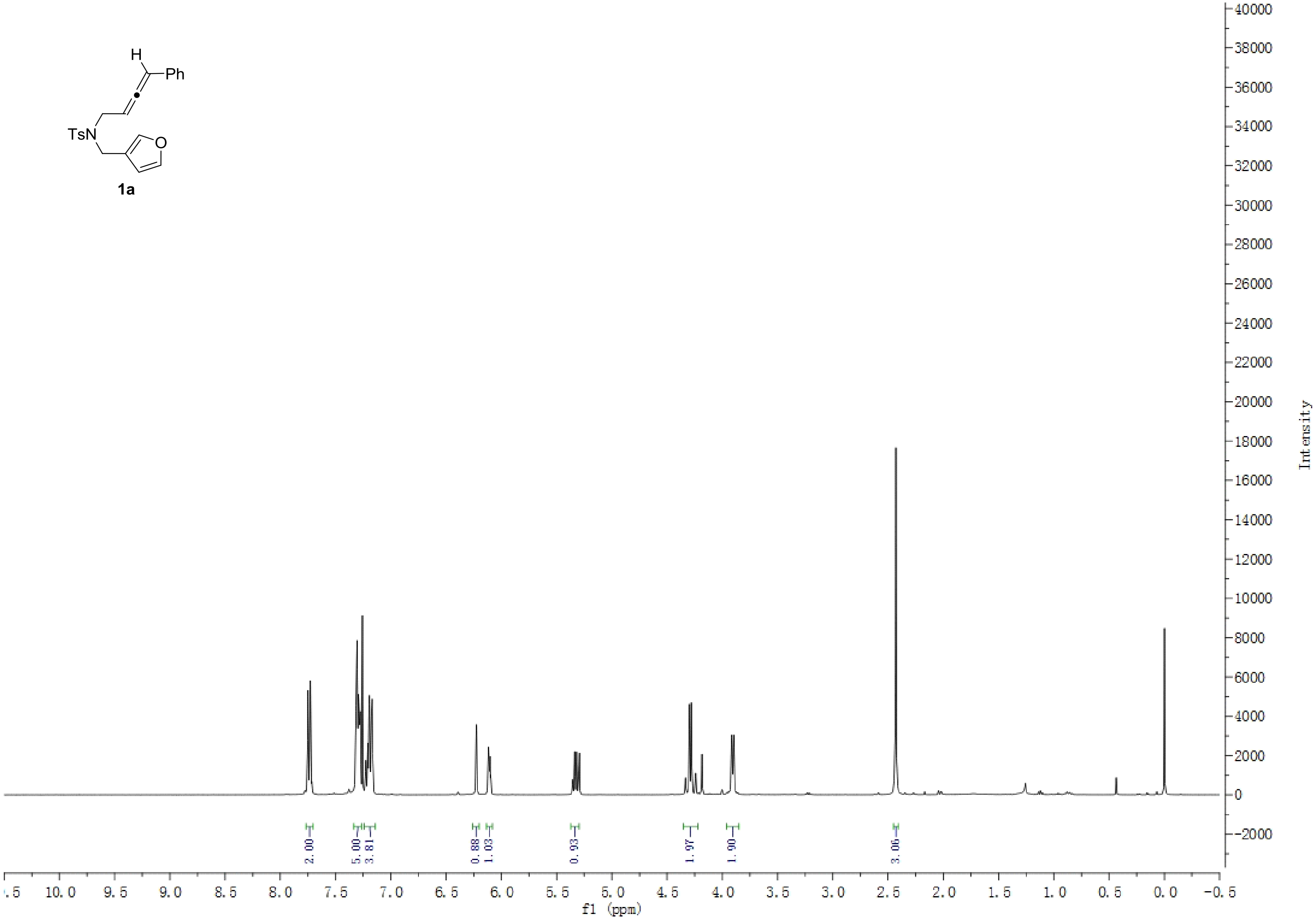
Atom	*x*	*y*	*z*	U(eq)
H1A	9469	2874	2924	31
H1B	9532	4833	2763	31
H3	7259	5050	3823	40
H4	4545	4816	3021	49
H7A	8360	1197	1246	31
H7B	8328	2002	147	31
H8	5845	1829	-781	35
H9A	3674	3260	49	39
H9B	3417	1441	-426	39
H11	4901	4397	-1781	36

H12	3700	5582	-3382	45
H14	-101	3336	-3282	42
H15	1098	2219	-1697	45
H17	11345	243	914	31
H18	12409	-1994	1988	36
H20	13404	1071	4502	44
H21	12360	3262	3411	35

5. ^{1}H and ^{13}C-NMR Spectra for New Compounds

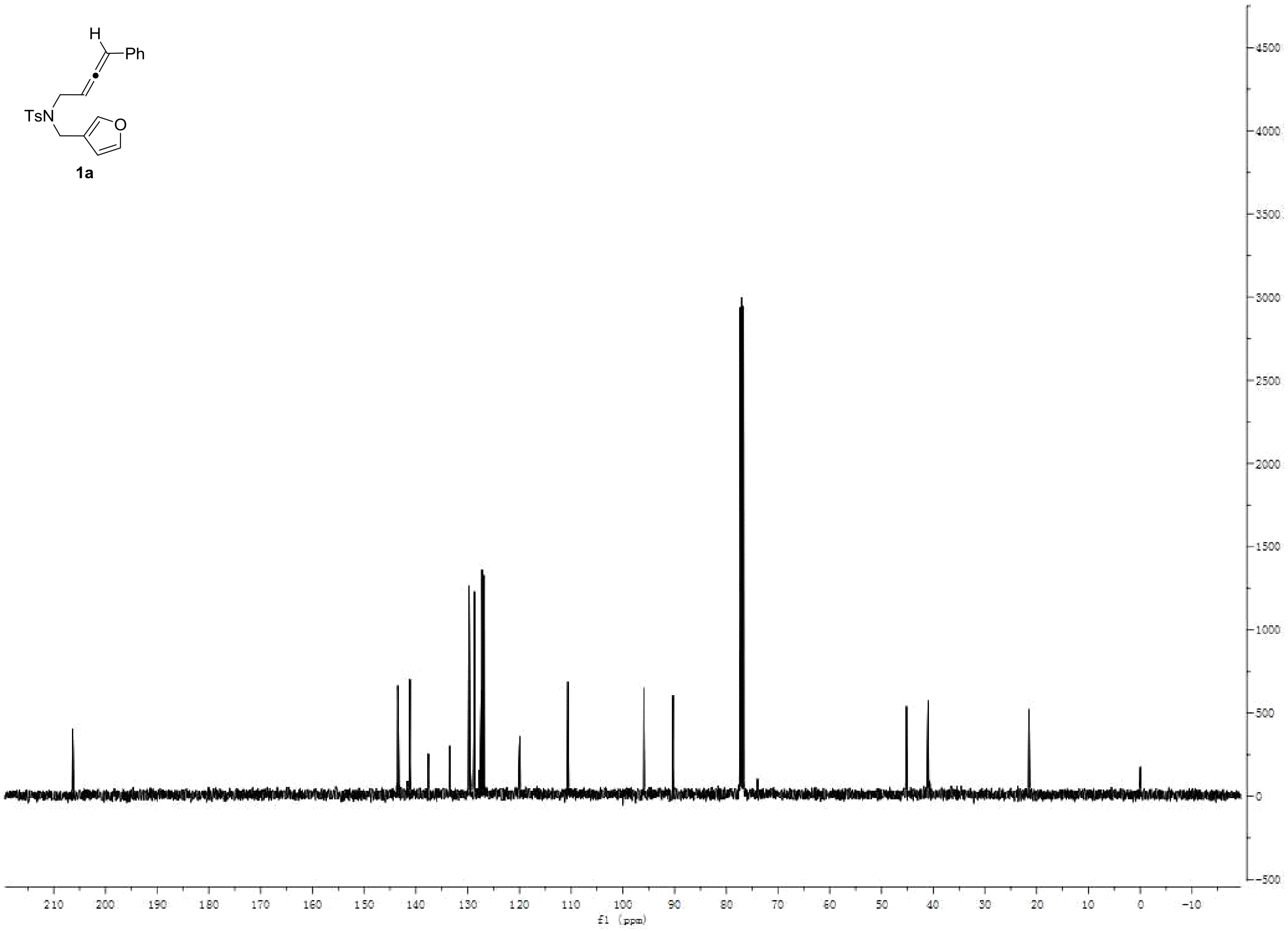

S2


H
Ph
TsHN
S2
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

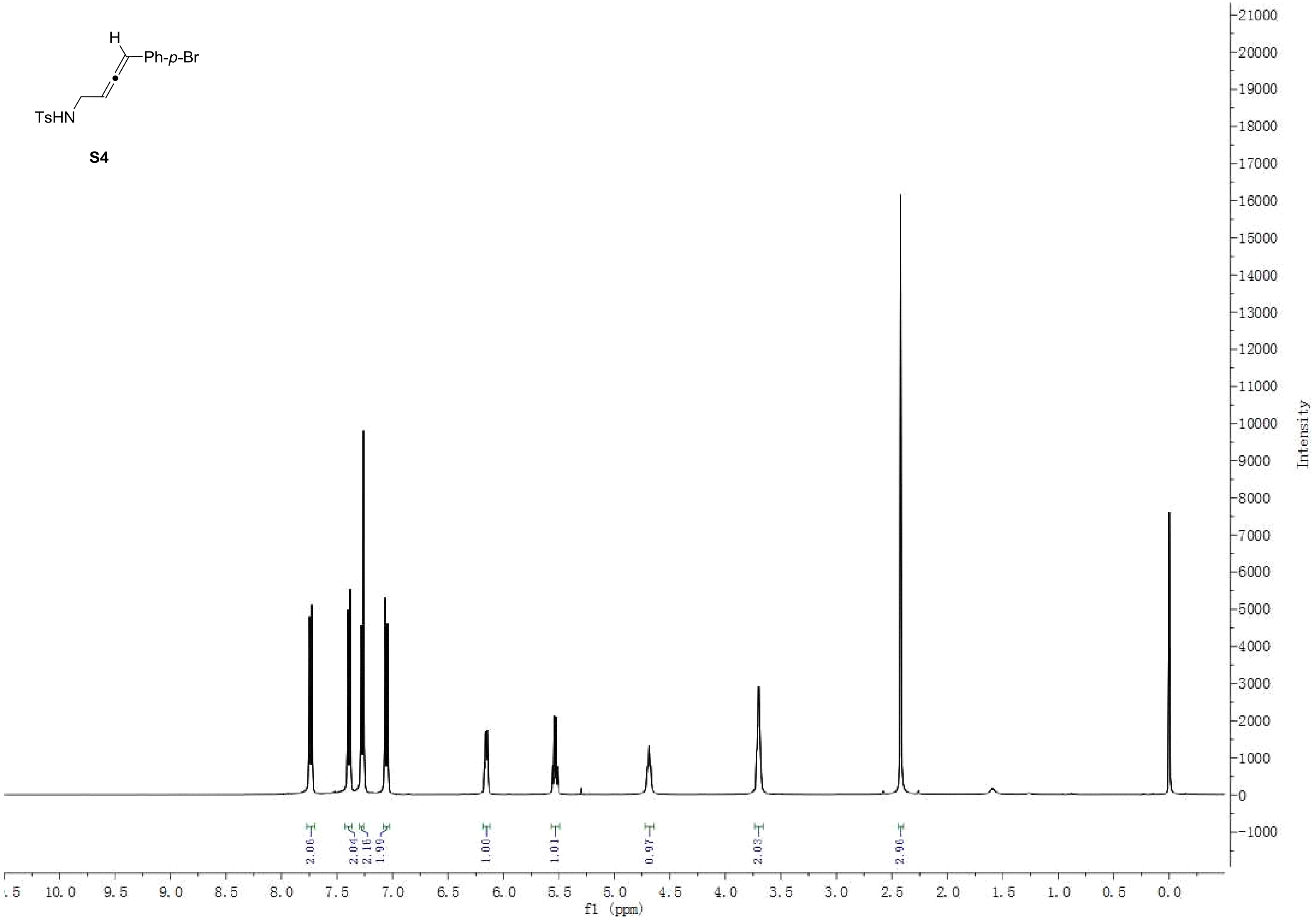

H
Ph
TsN
O

1a

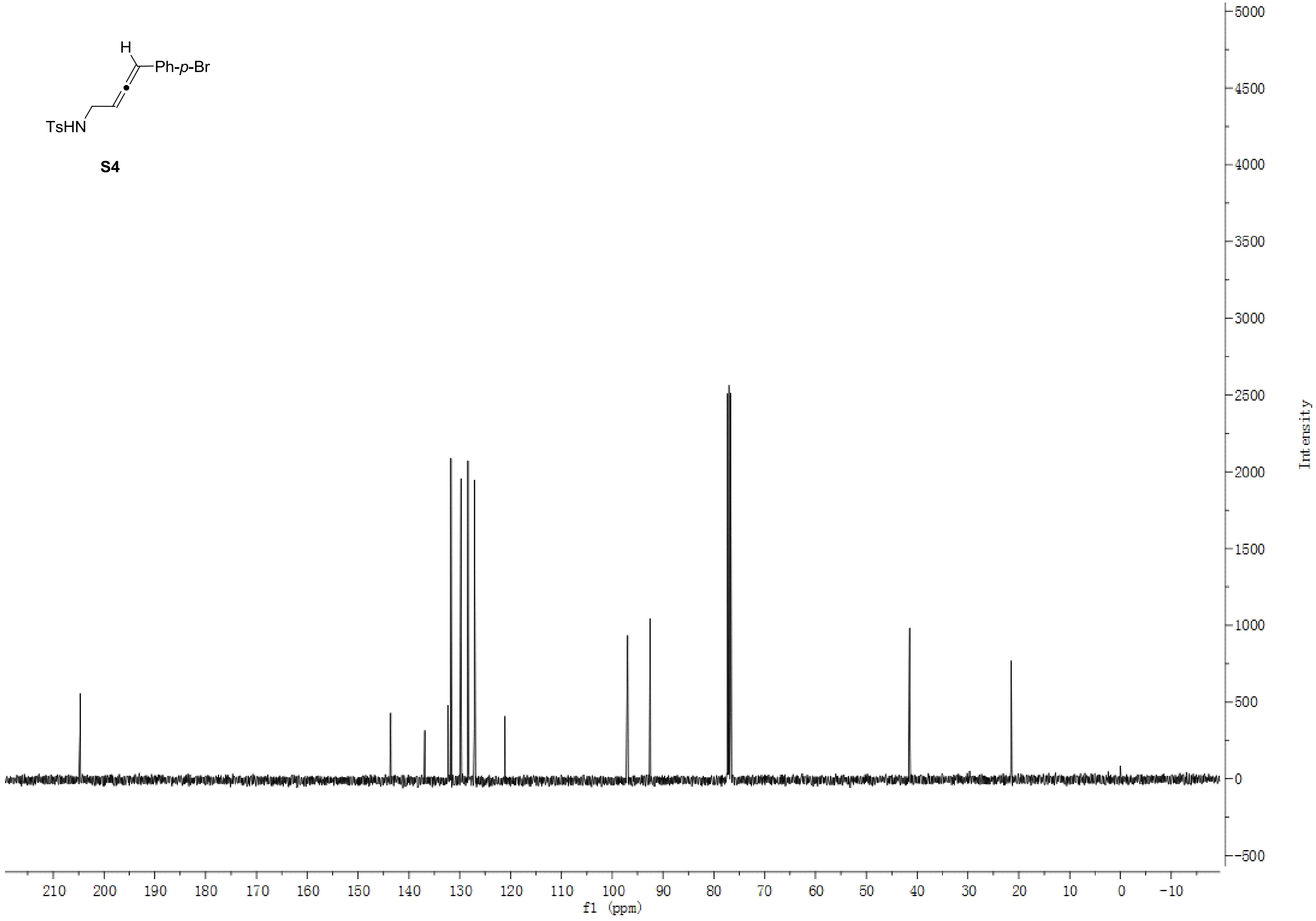
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
Intensity
2.00
5.00
3.81
0.88
1.03
0.93
1.97
1.90
3.06
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


1a

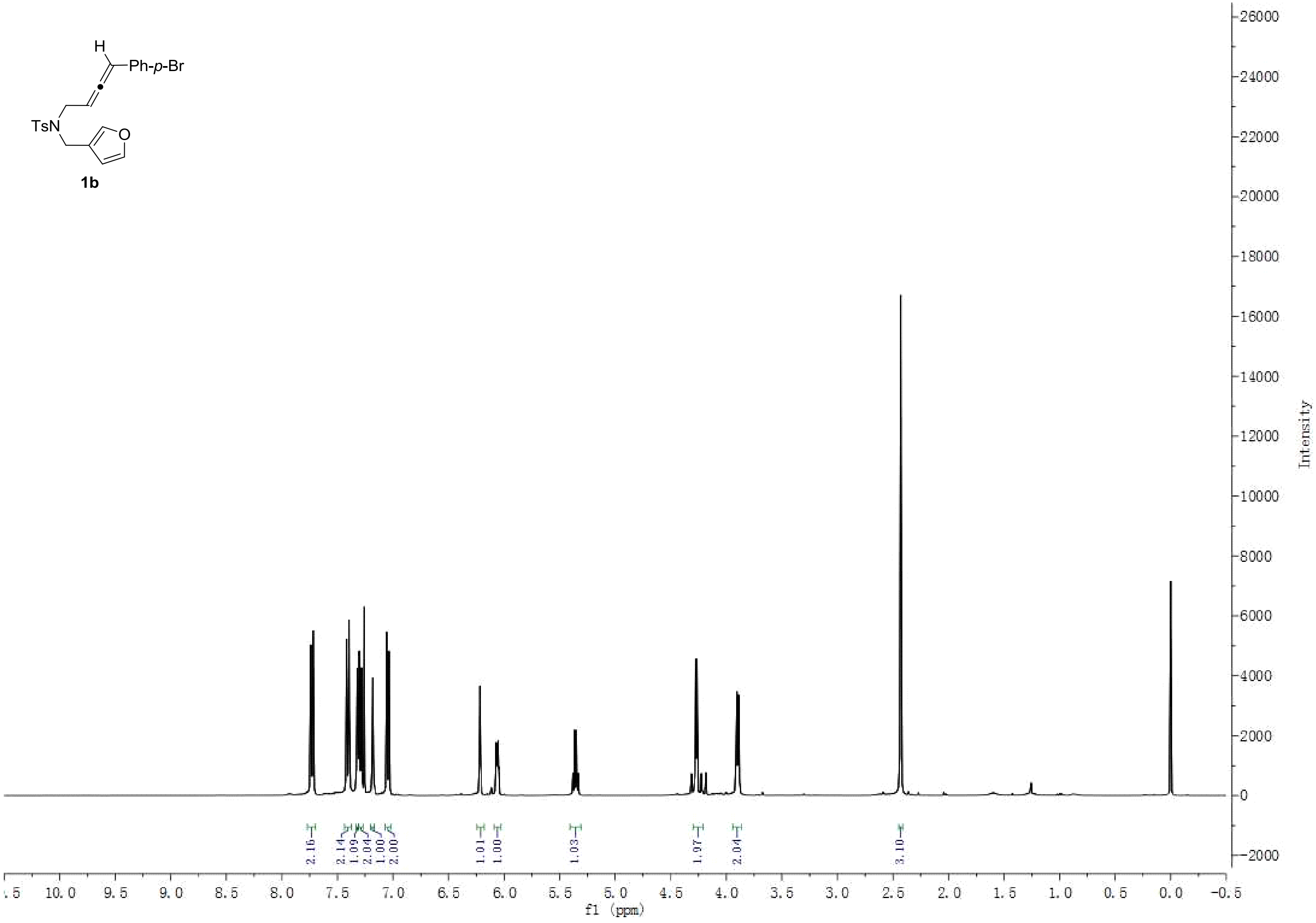
H
Ph
TsN
O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

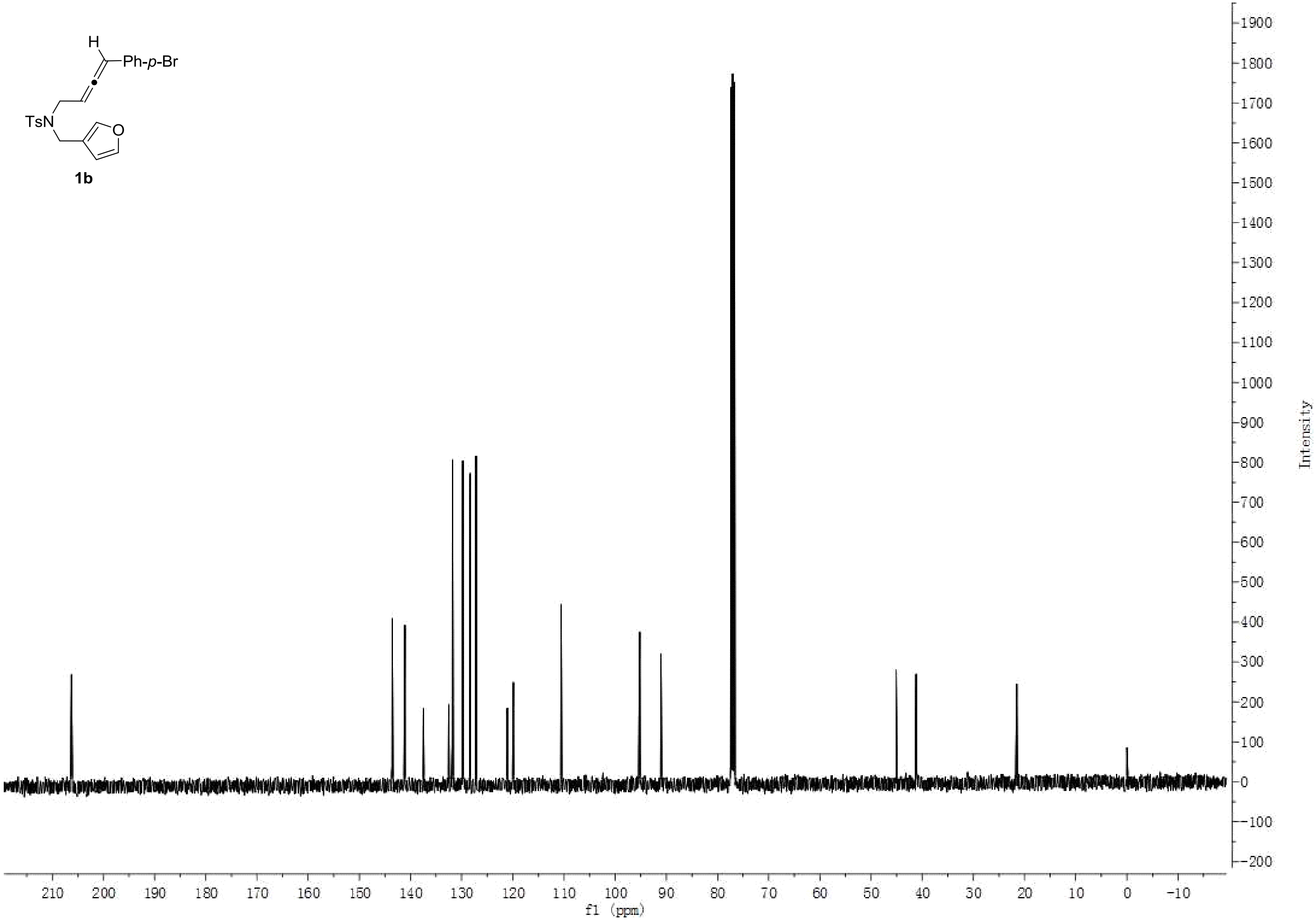

S4

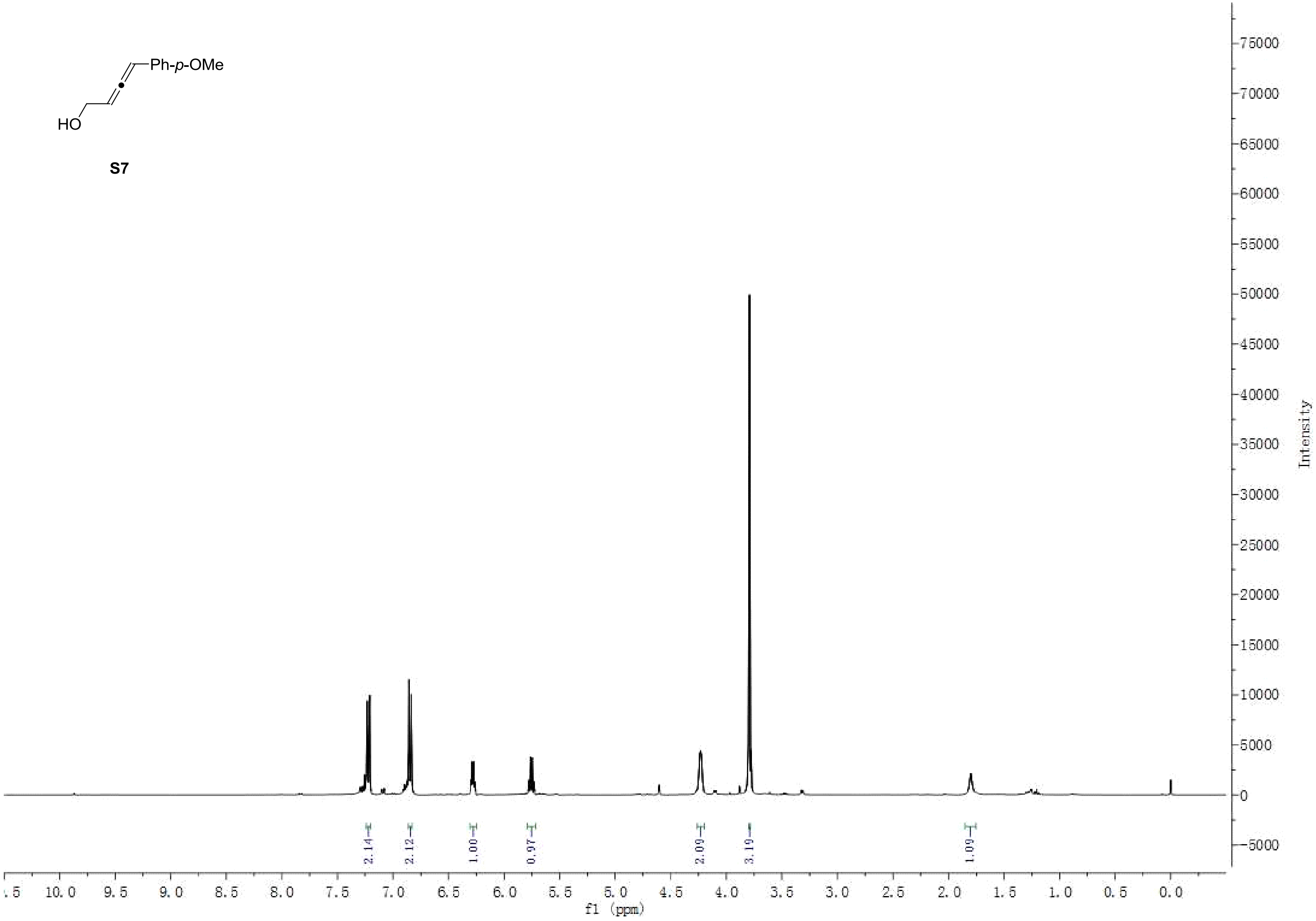
H
Ph-p-Br
TsHN
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
2.06
2.04
2.16
1.99
1.00
1.01
0.97
2.03
2.96
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

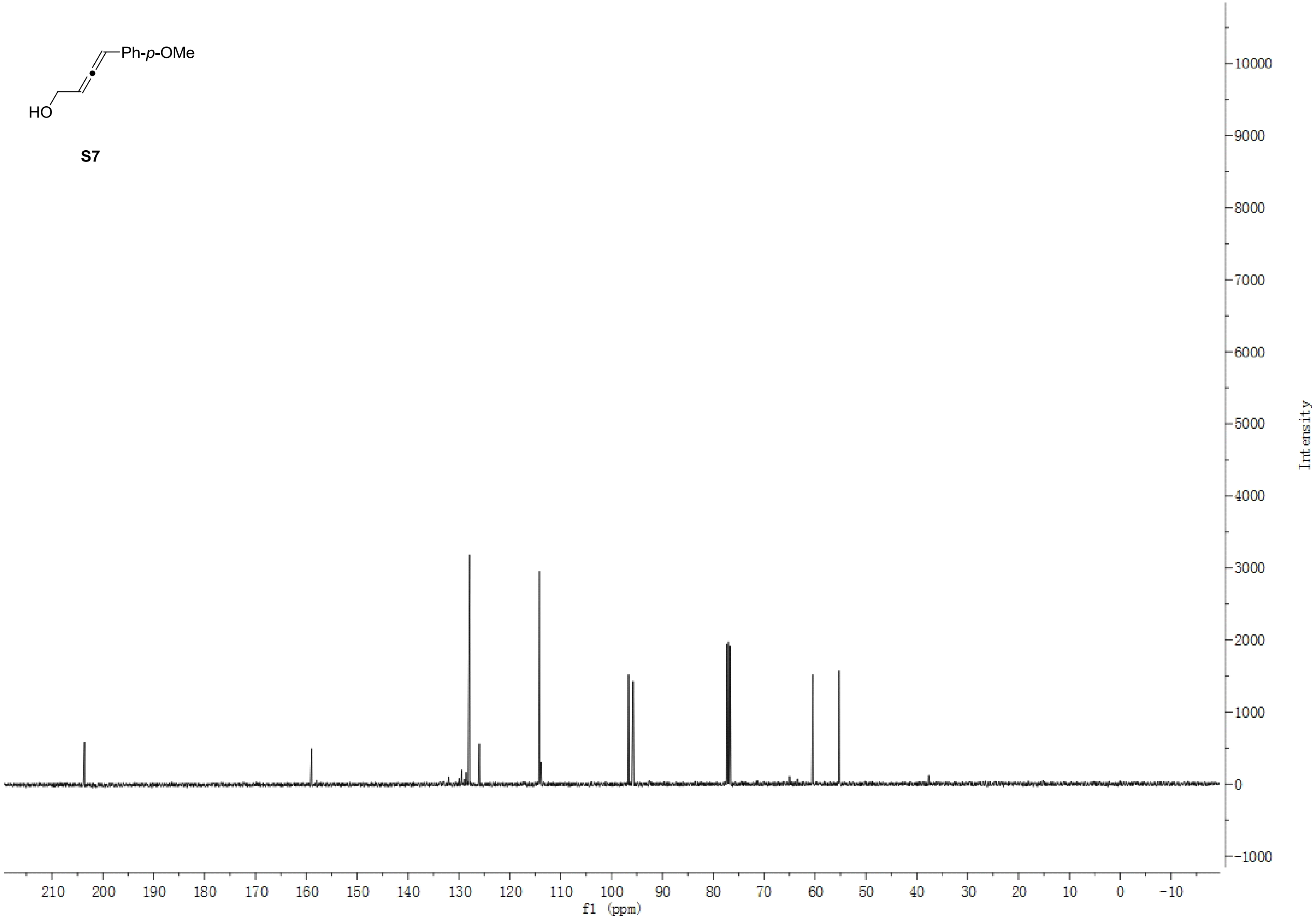

H
Ph-p-Br
TsHN
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

S4


H
Ph-p-Br
TsN
O
1b
2.16
2.14
1.09
2.04
1.00
2.00
1.01
1.00
1.03
1.97
2.04
3.10
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity

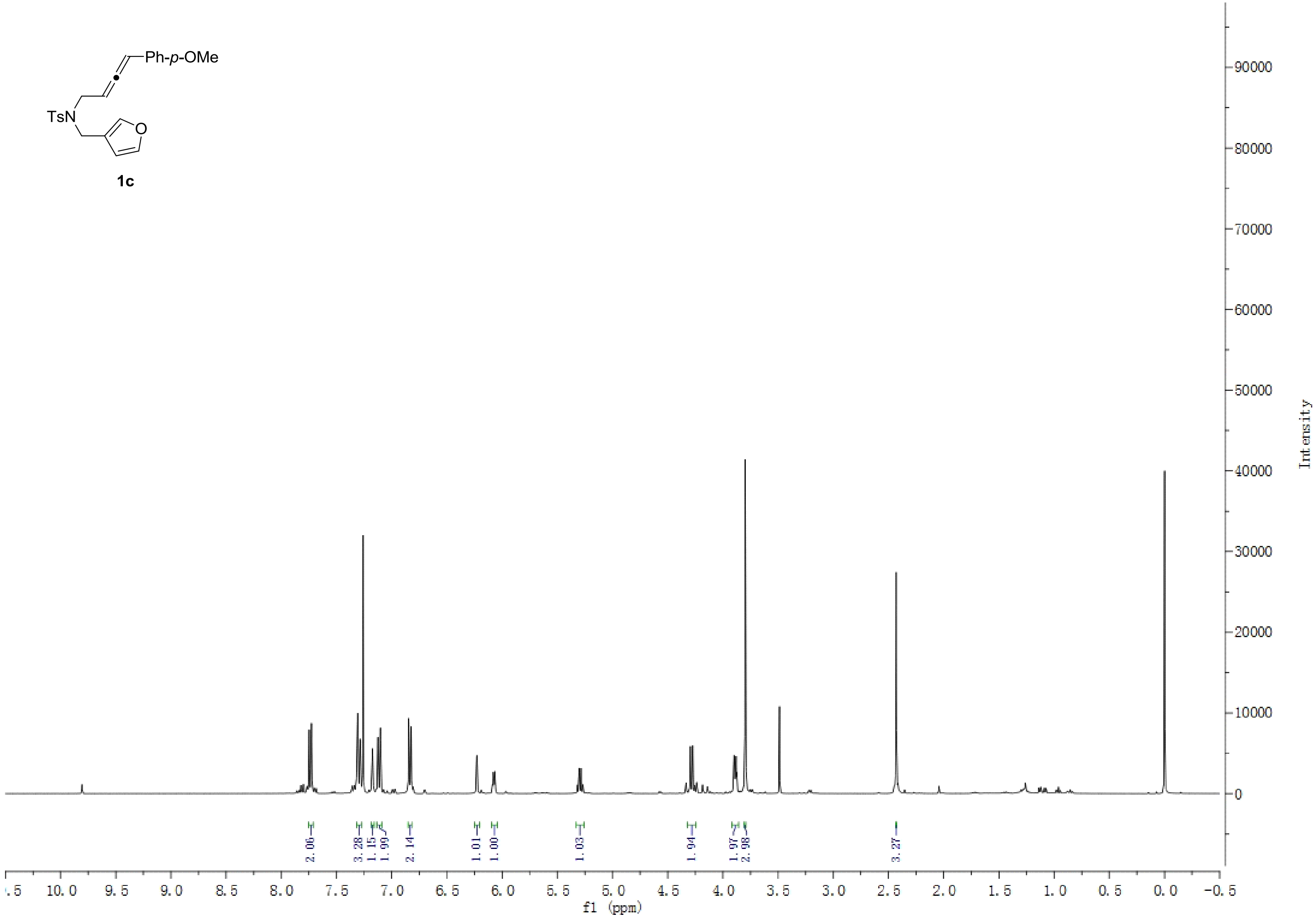

H
Ph-p-Br
TsN
O
1b
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

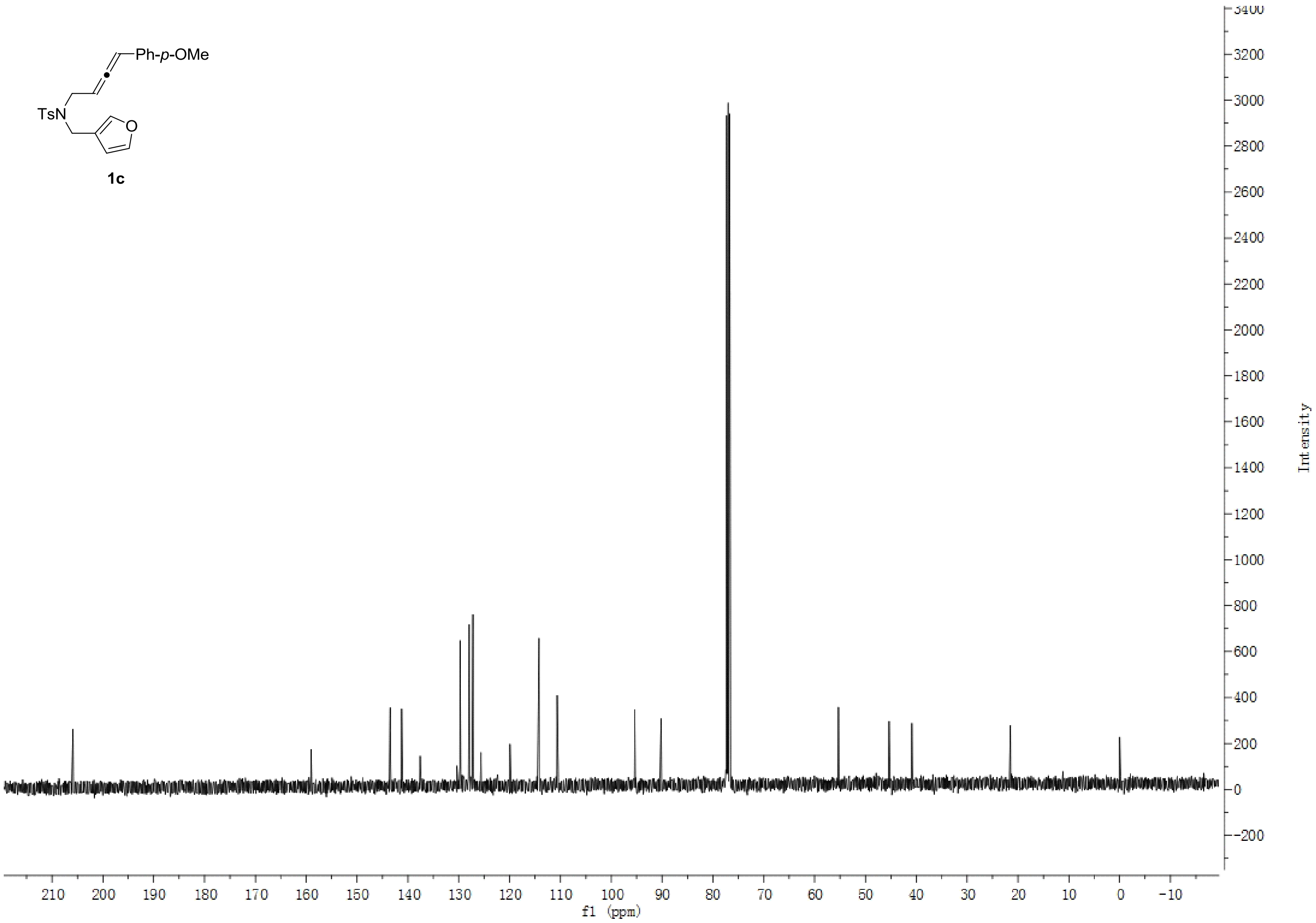

Ph-p-OMe
HO
S7
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
Intensity
2.14
2.12
1.00
0.97
2.09
3.19
1.09
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



S7

Ph-*p*-OMe
HO
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

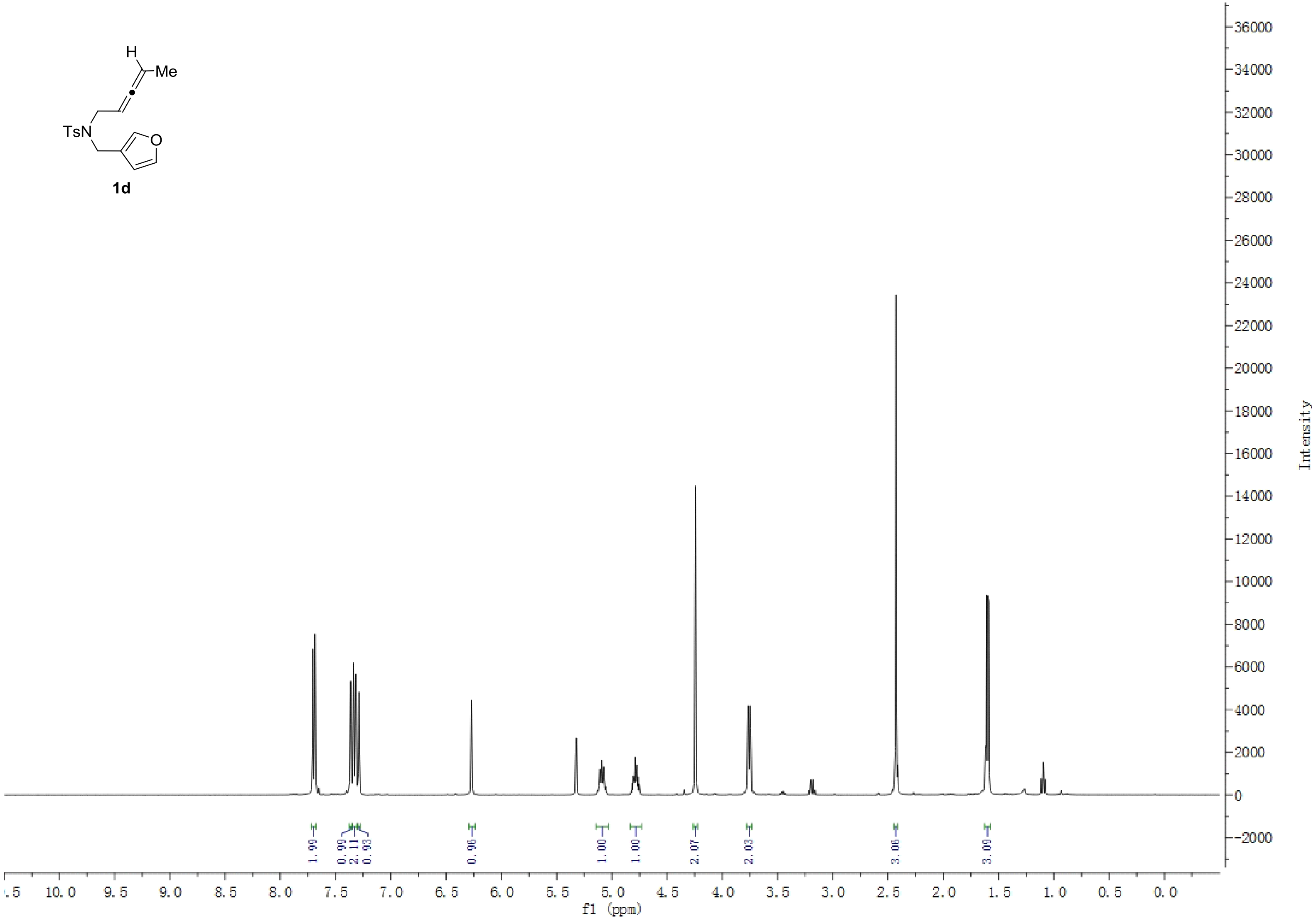

Ph-p-OMe
TsN
O
1c
2.06
3.28
1.15
1.99
2.14
1.01
1.00
1.03
1.94
1.97
2.98
3.27
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Intensity

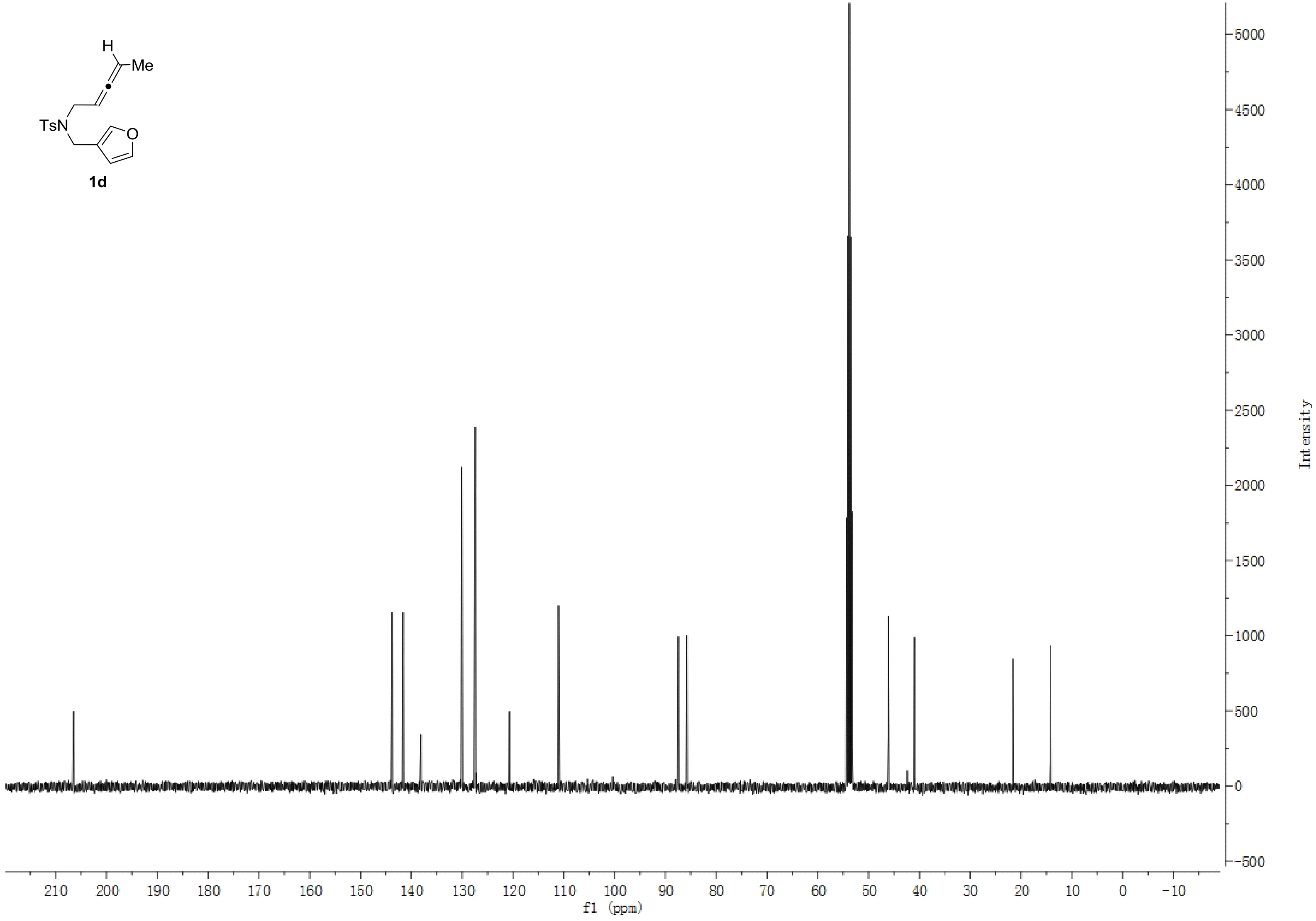

Ph-*p*-OMe
TsN
O
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

1c

H
Me
TsN
O

1d


1.99
0.99
2.11
0.93
0.96
1.00
1.00
2.07
2.03
3.06
3.09
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity

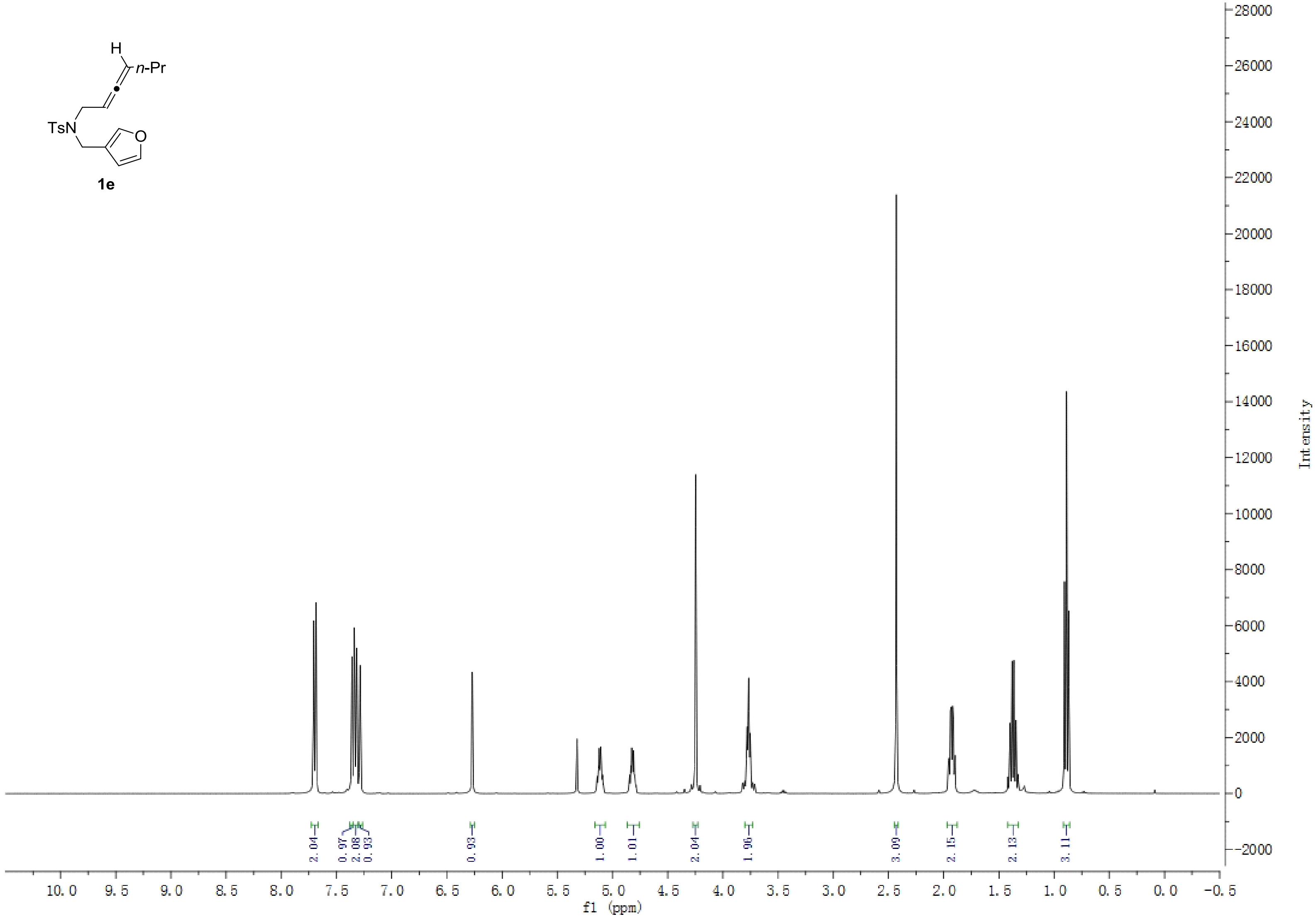


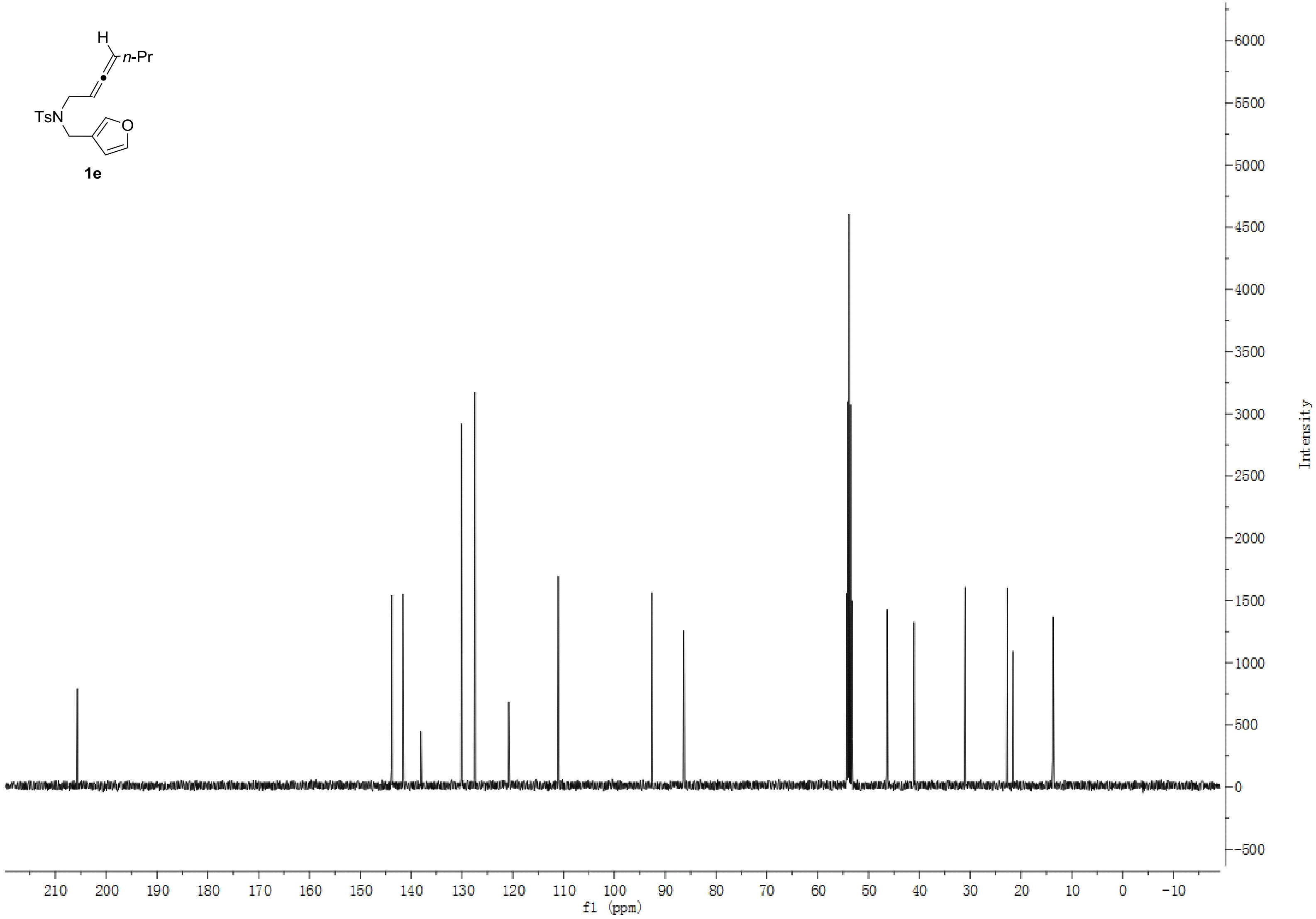
1d

TsN
O
H
Me
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

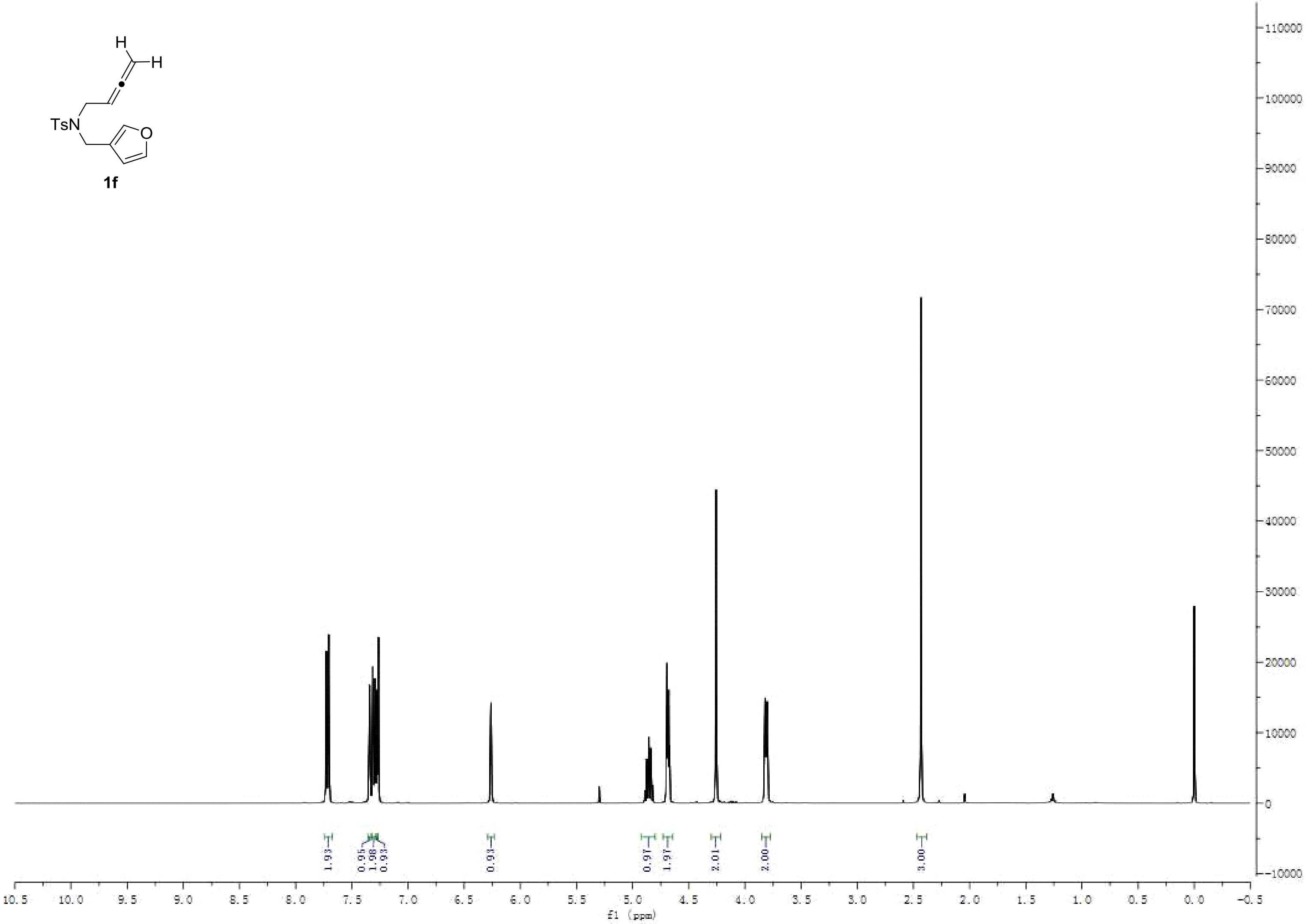
H
n-Pr
TsN
O

1e

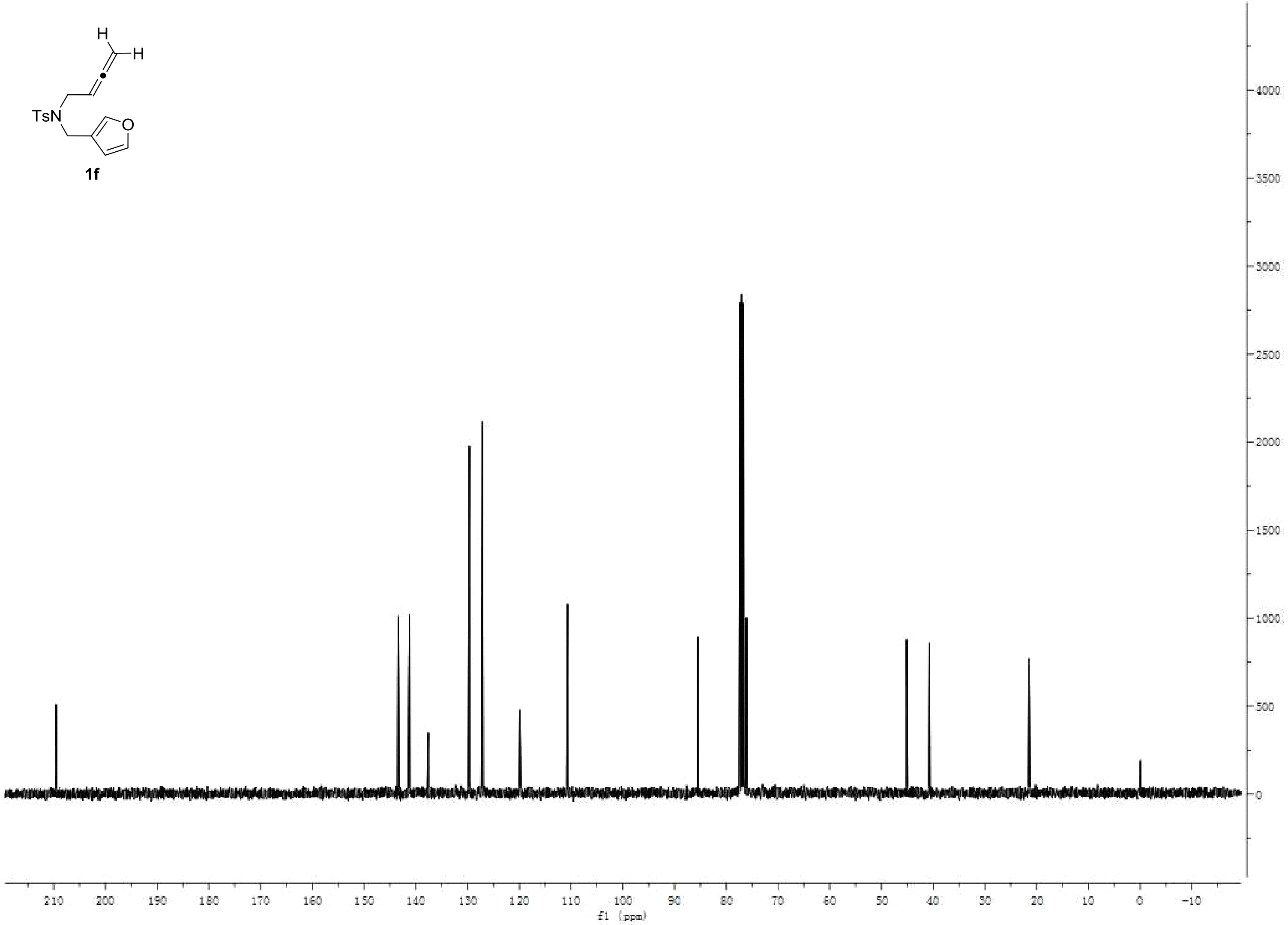

28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
Intensity
2.04
0.97
2.08
0.93
0.93
1.00
1.01
2.04
1.96
3.09
2.15
2.13
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


1e

H
n-Pr
TsN
O
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

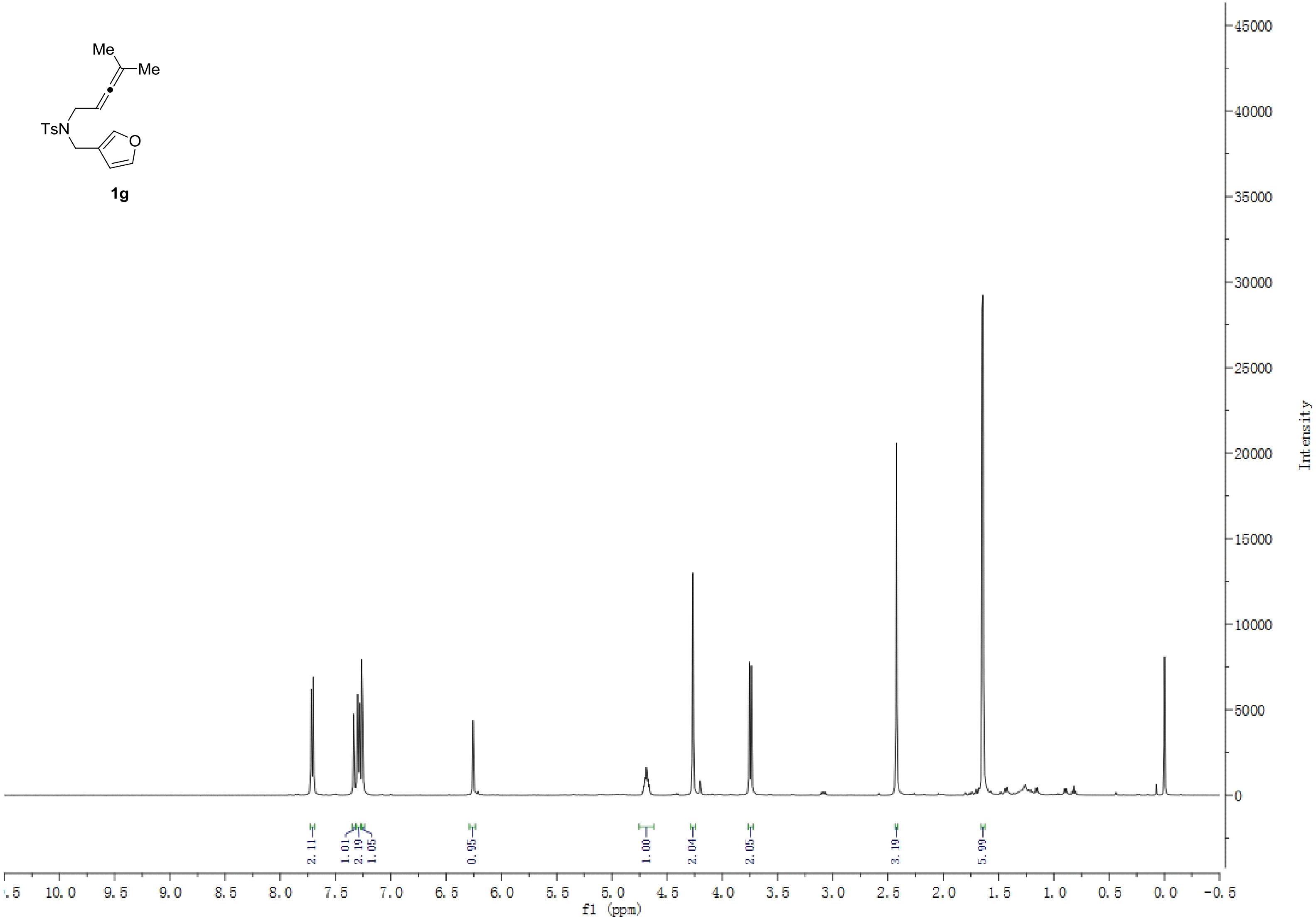

H
H
TsN
O
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
1.93
0.95
1.98
0.93
0.93
0.97
1.97
2.01
2.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

1f


H
H
TsN
O

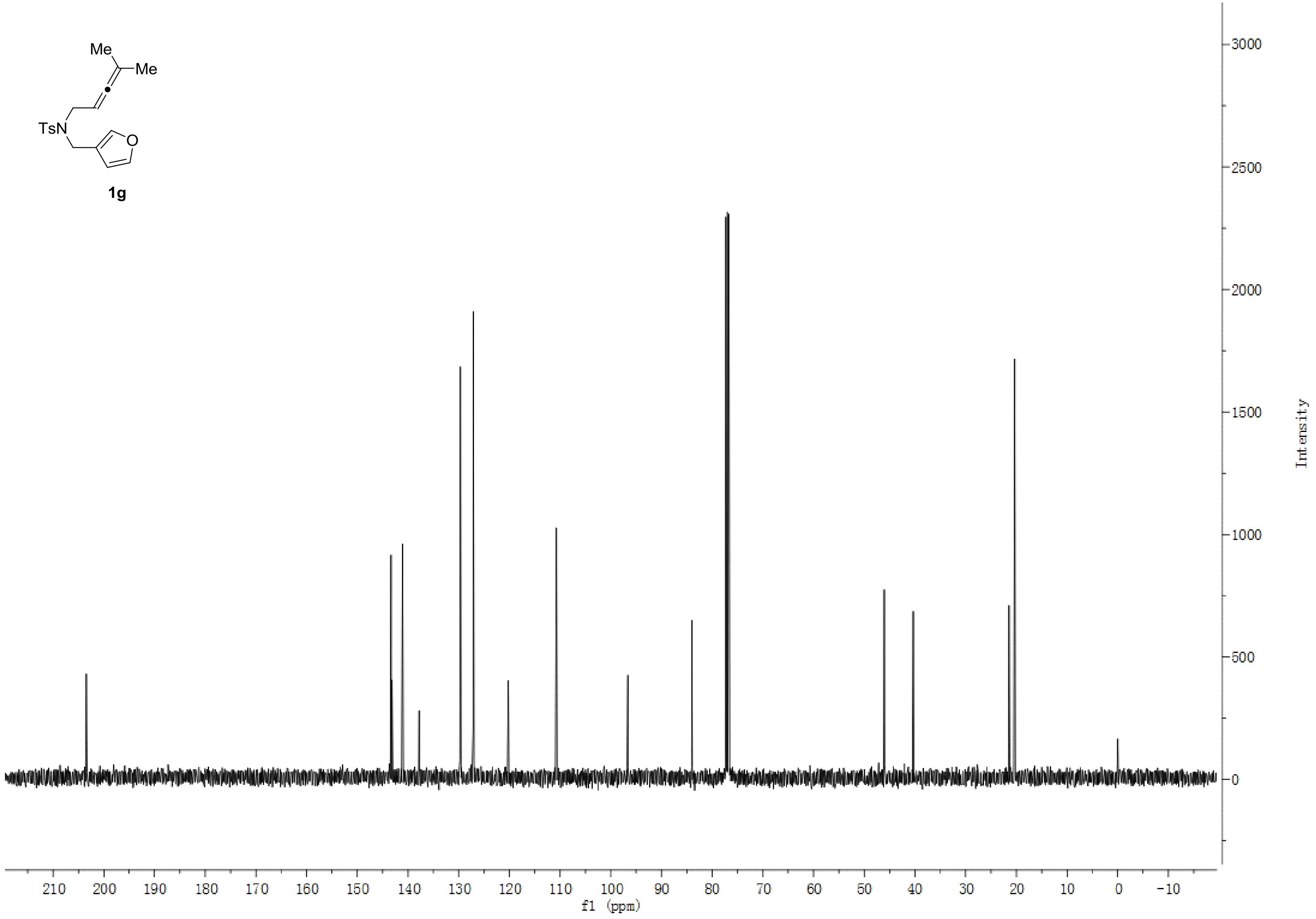
1f

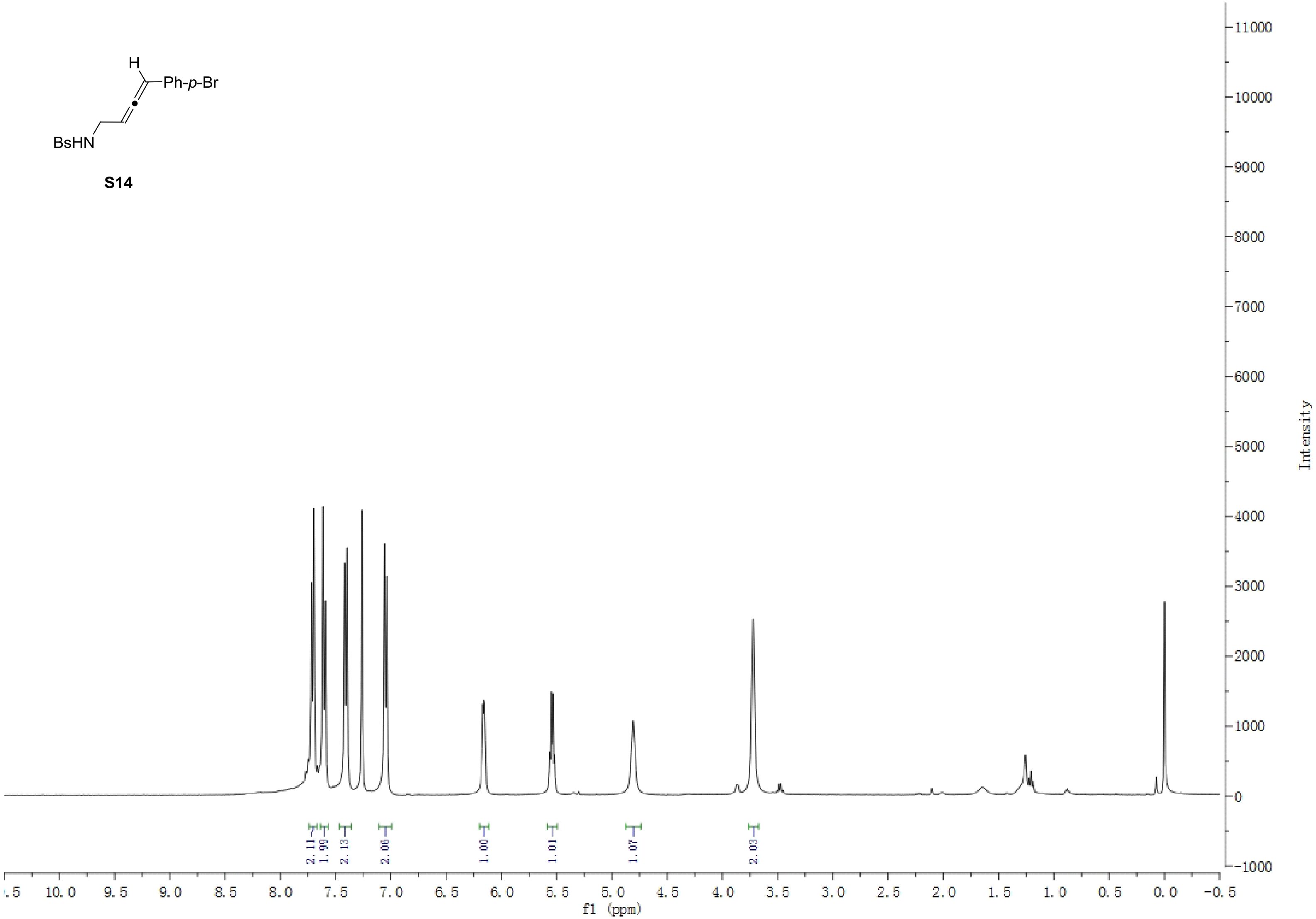
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

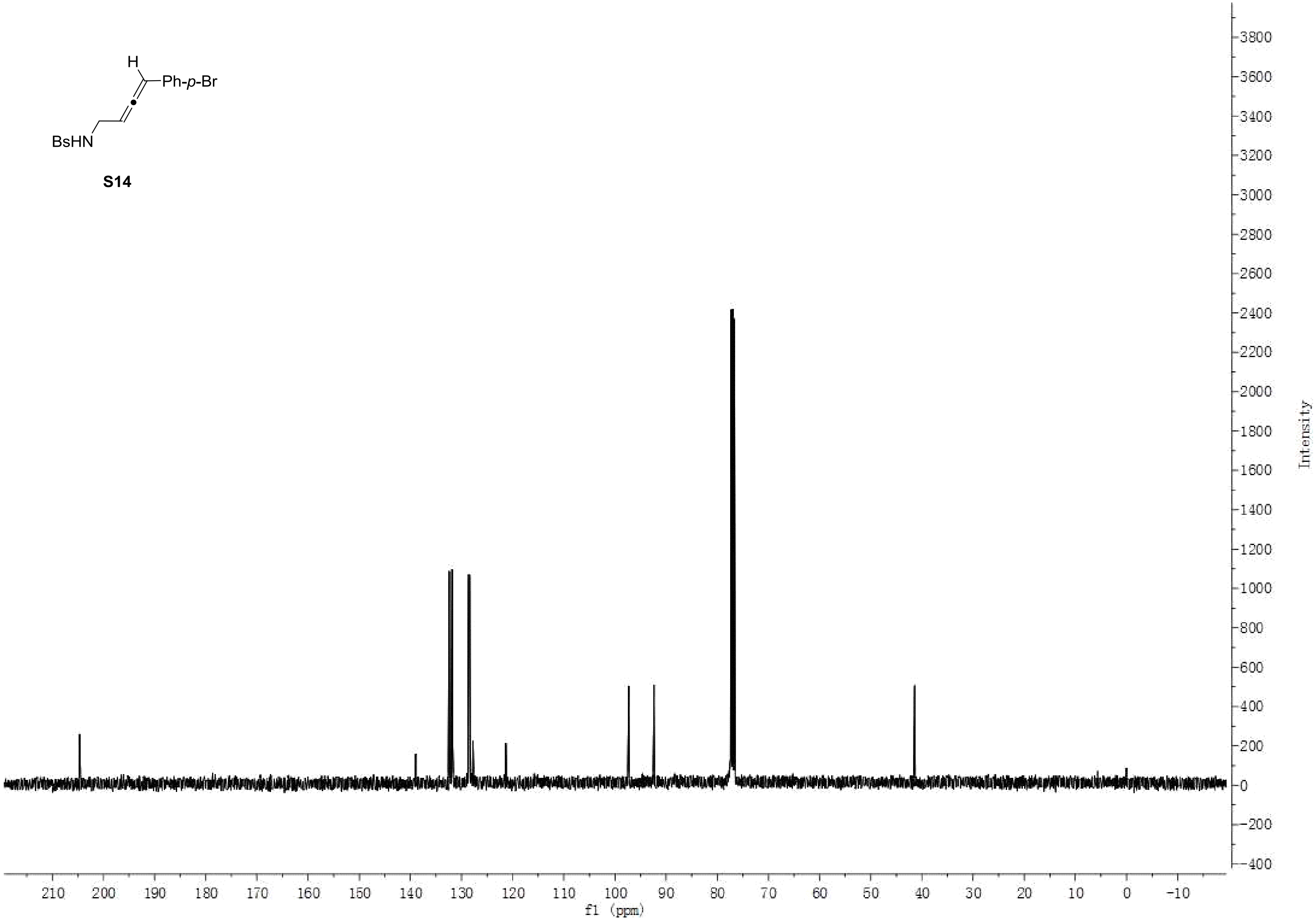


1g

Me
Me
TsN
O
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
2.11
1.01
2.19
1.05
0.95
1.00
2.04
2.05
3.19
5.99
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

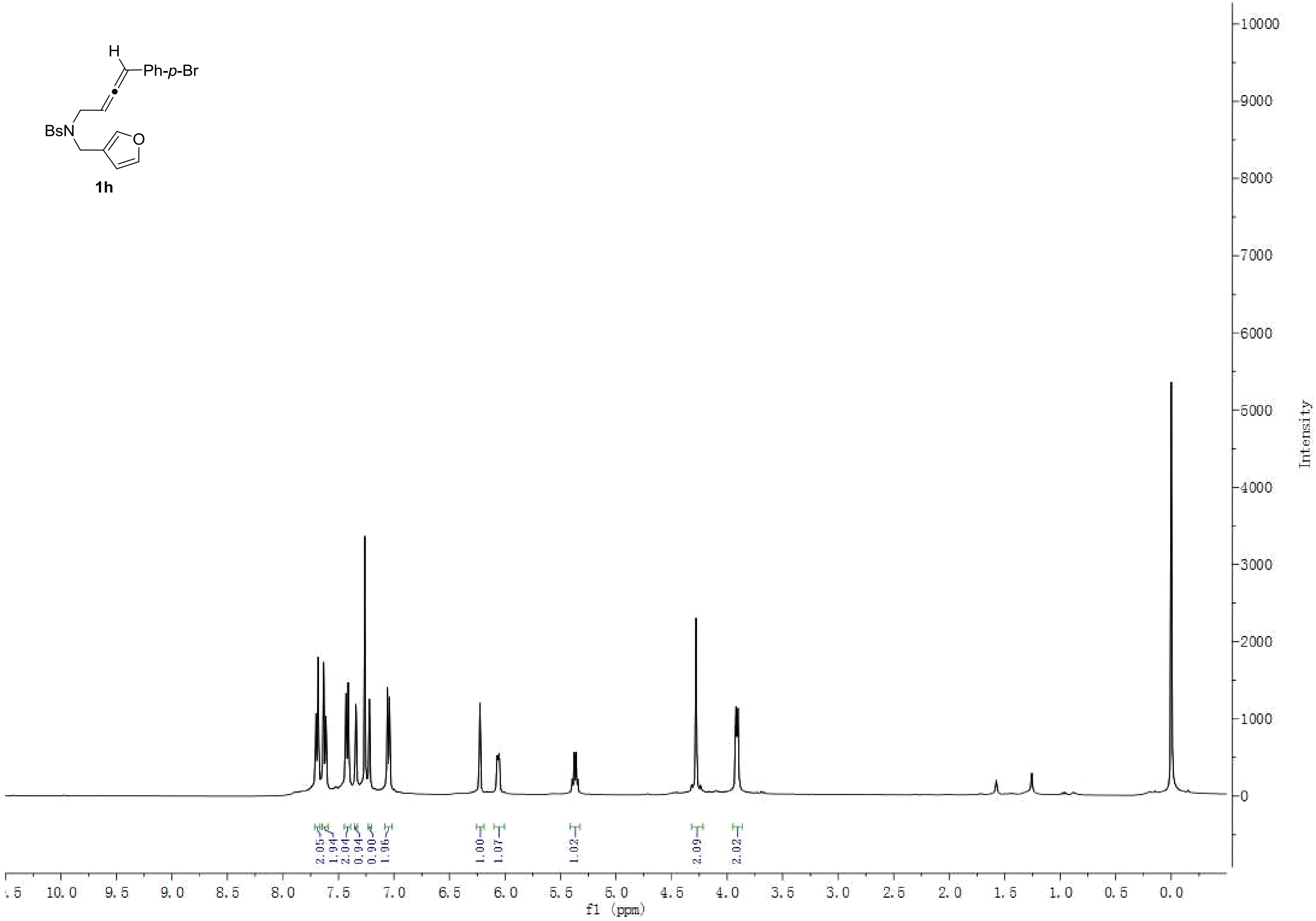

Me
Me
TsN
O
1g
3000
2500
2000
1500
1000
500
0
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

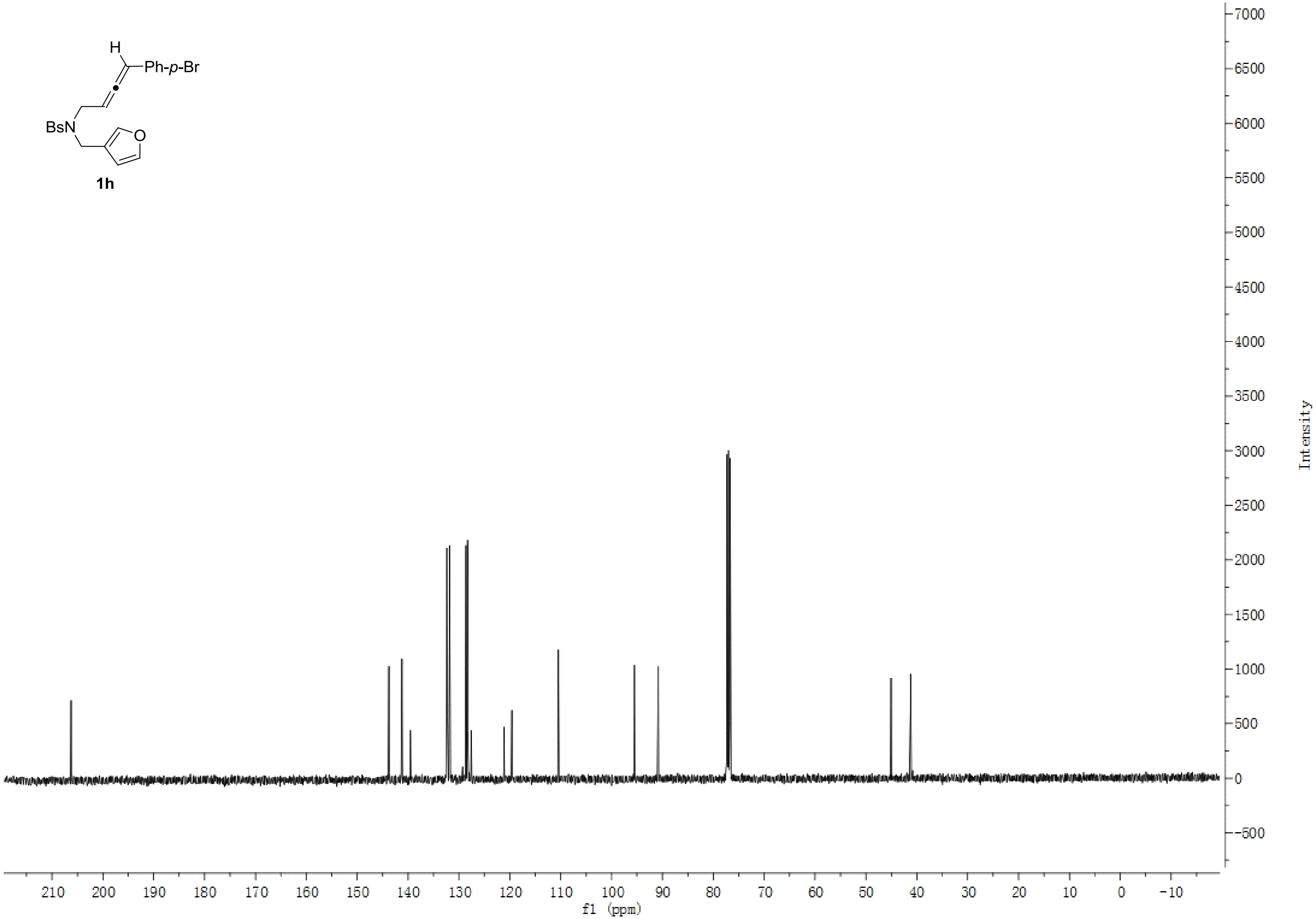

H
Ph-p-Br
BsHN
S14
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
2.11
1.99
2.13
2.06
1.00
1.01
1.07
2.03
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


H
Ph-p-Br
BsHN
S14
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

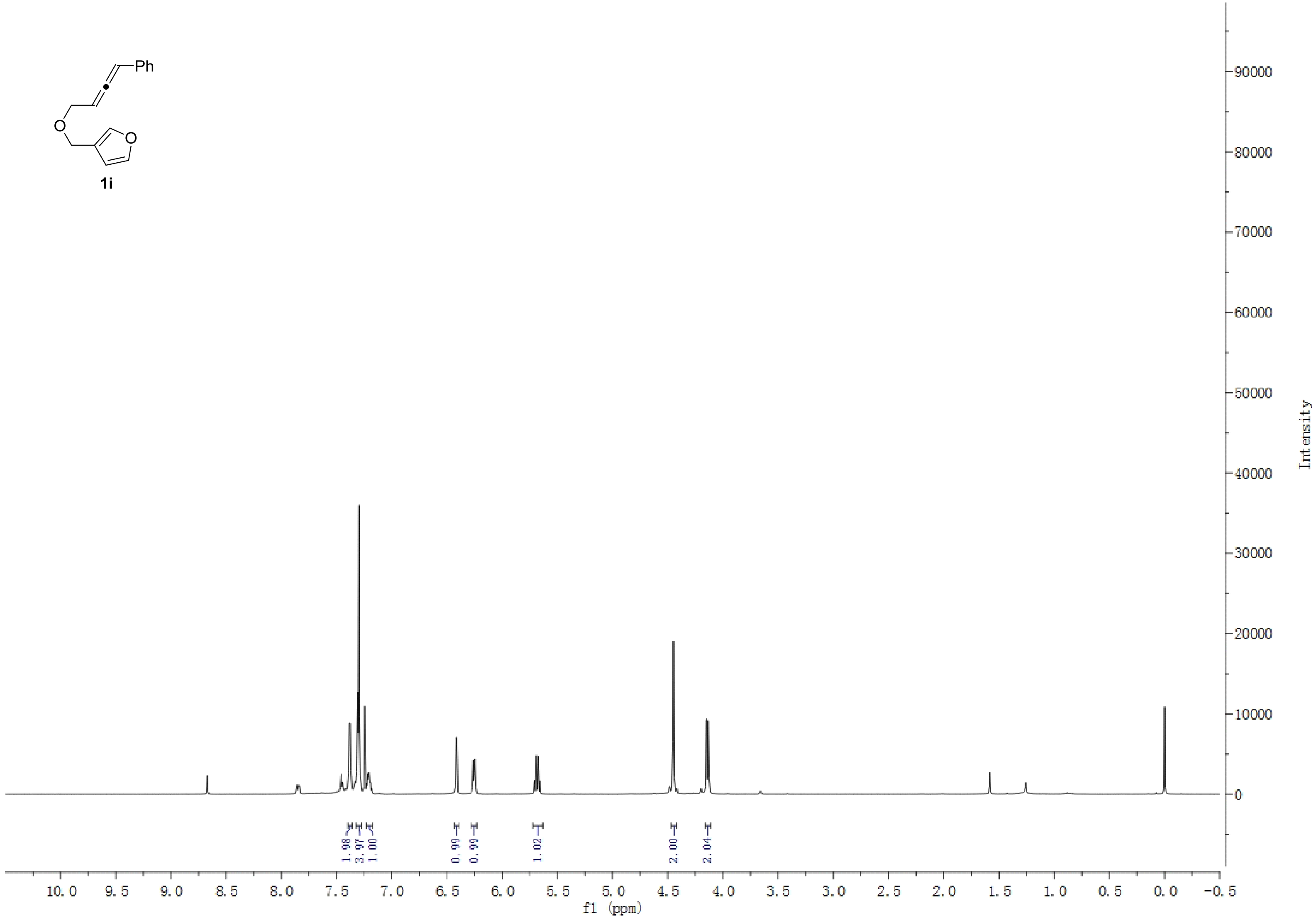
H
Ph-p-Br
BsN
O

1h


2.05
1.94
2.04
0.94
0.90
1.96
1.00
1.07
1.02
2.09
2.02
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Intensity

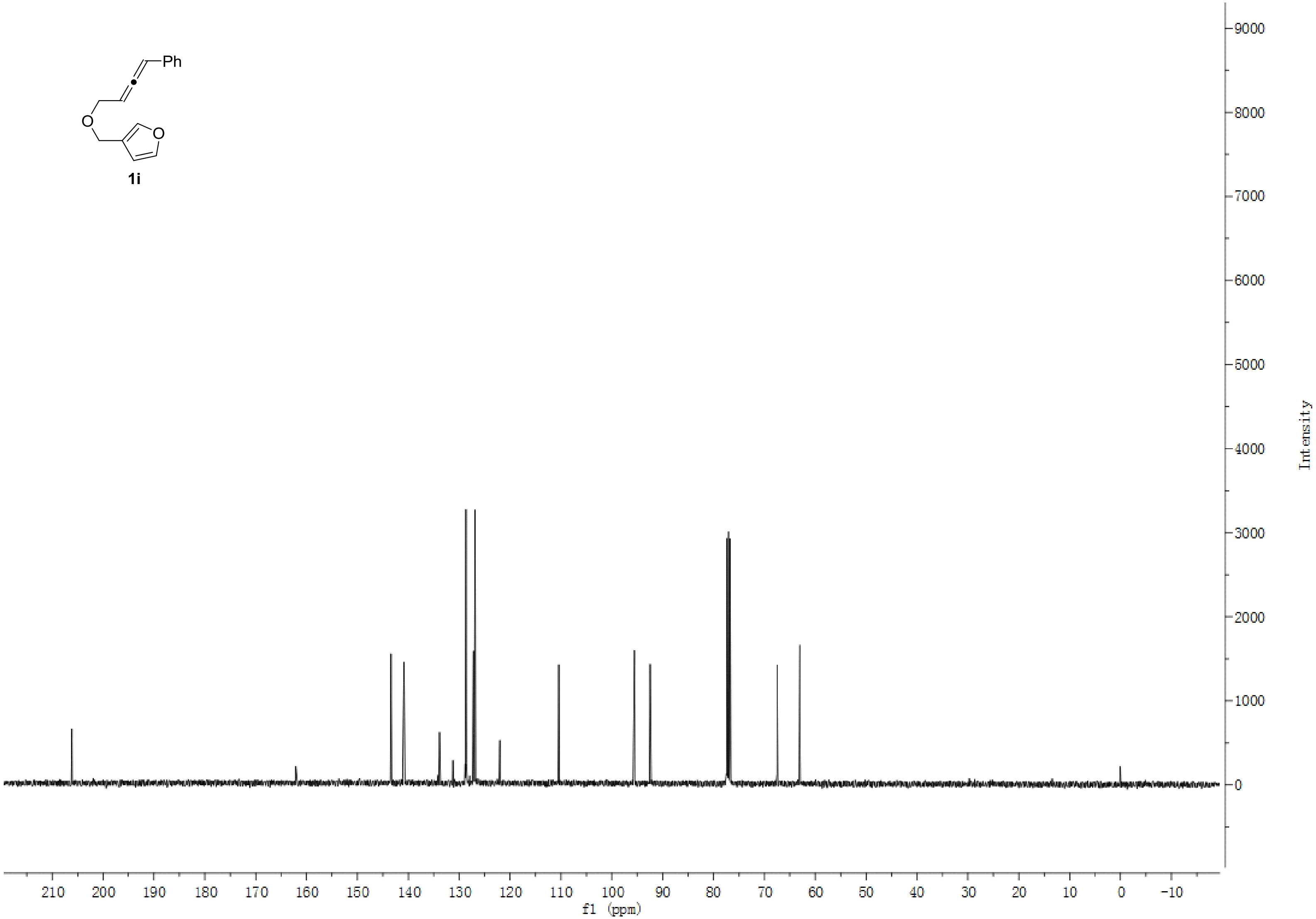

H
Ph-p-Br
BsN
O
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

1h


Ph
O
O

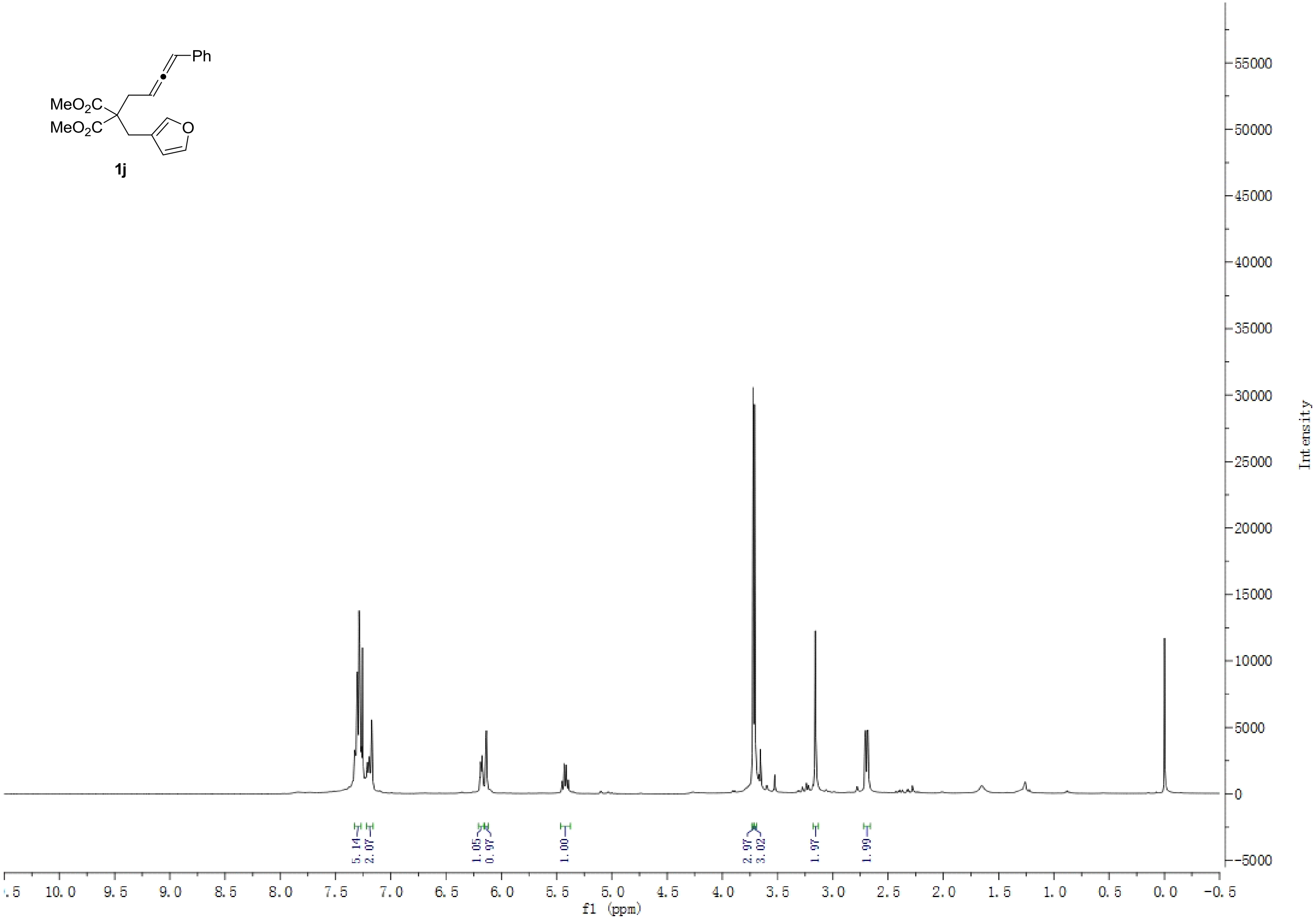
1i

1.98
3.97
1.00
0.99
0.99
1.02
2.00
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Intensity

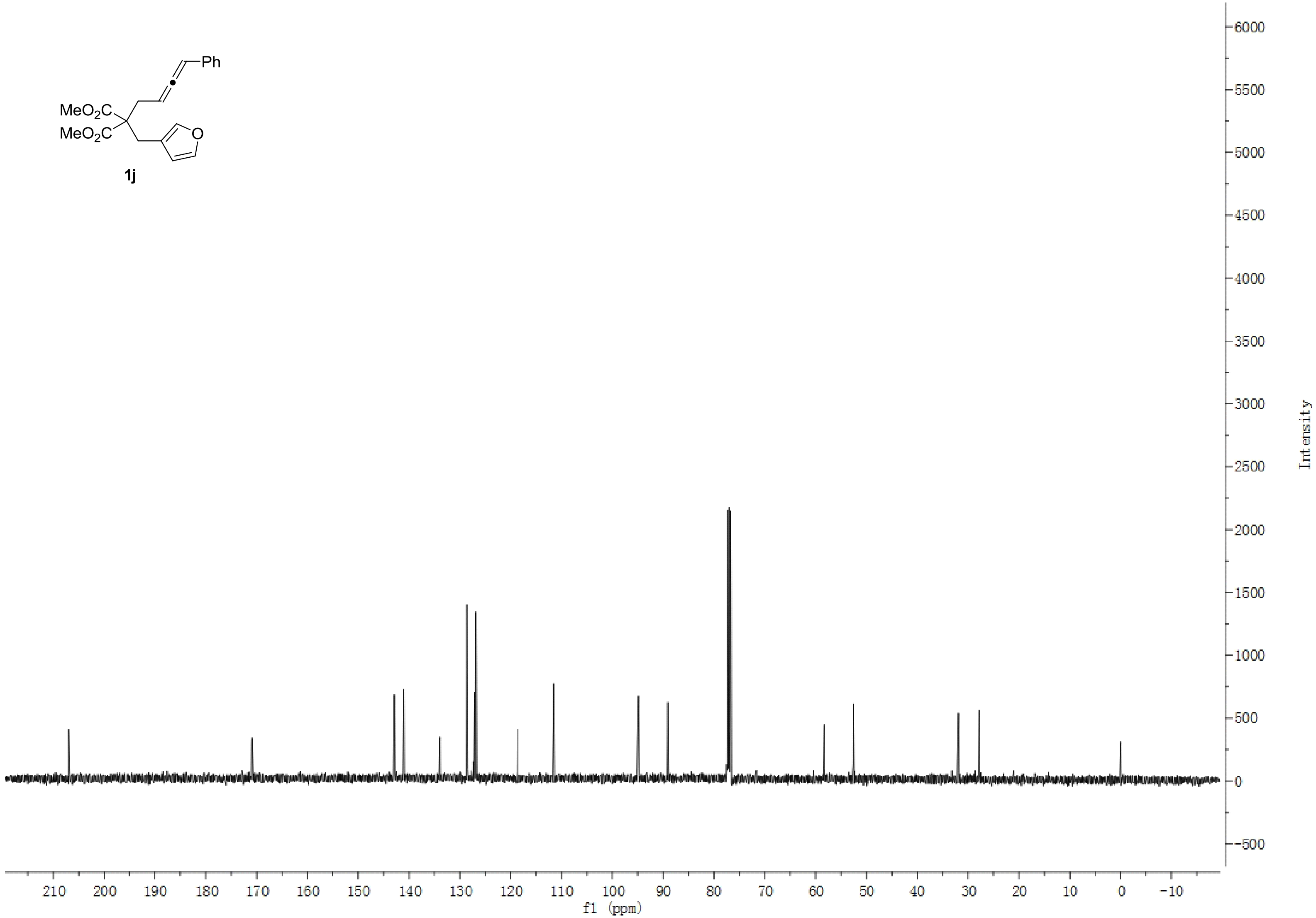


1i

Ph
O
O
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

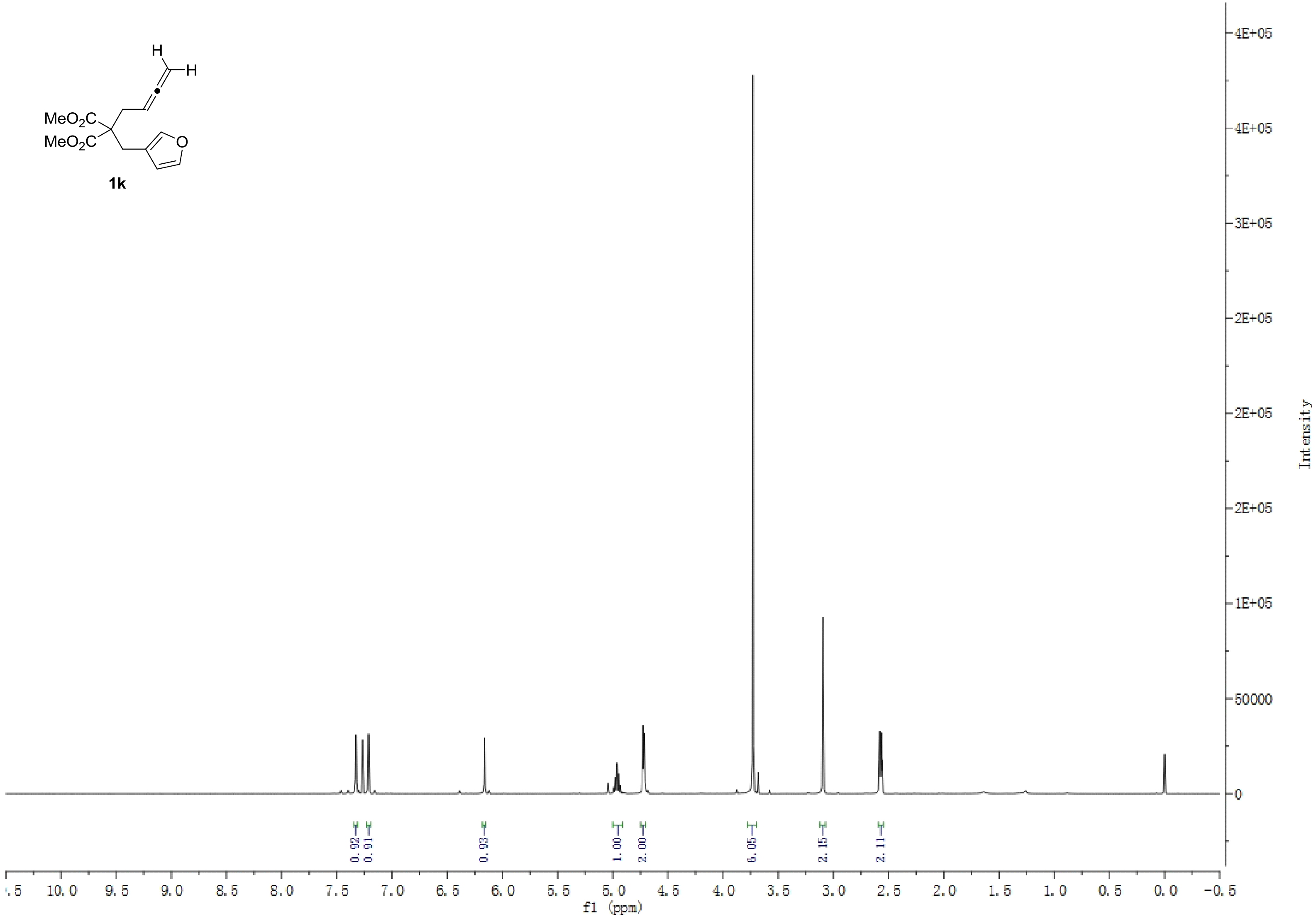


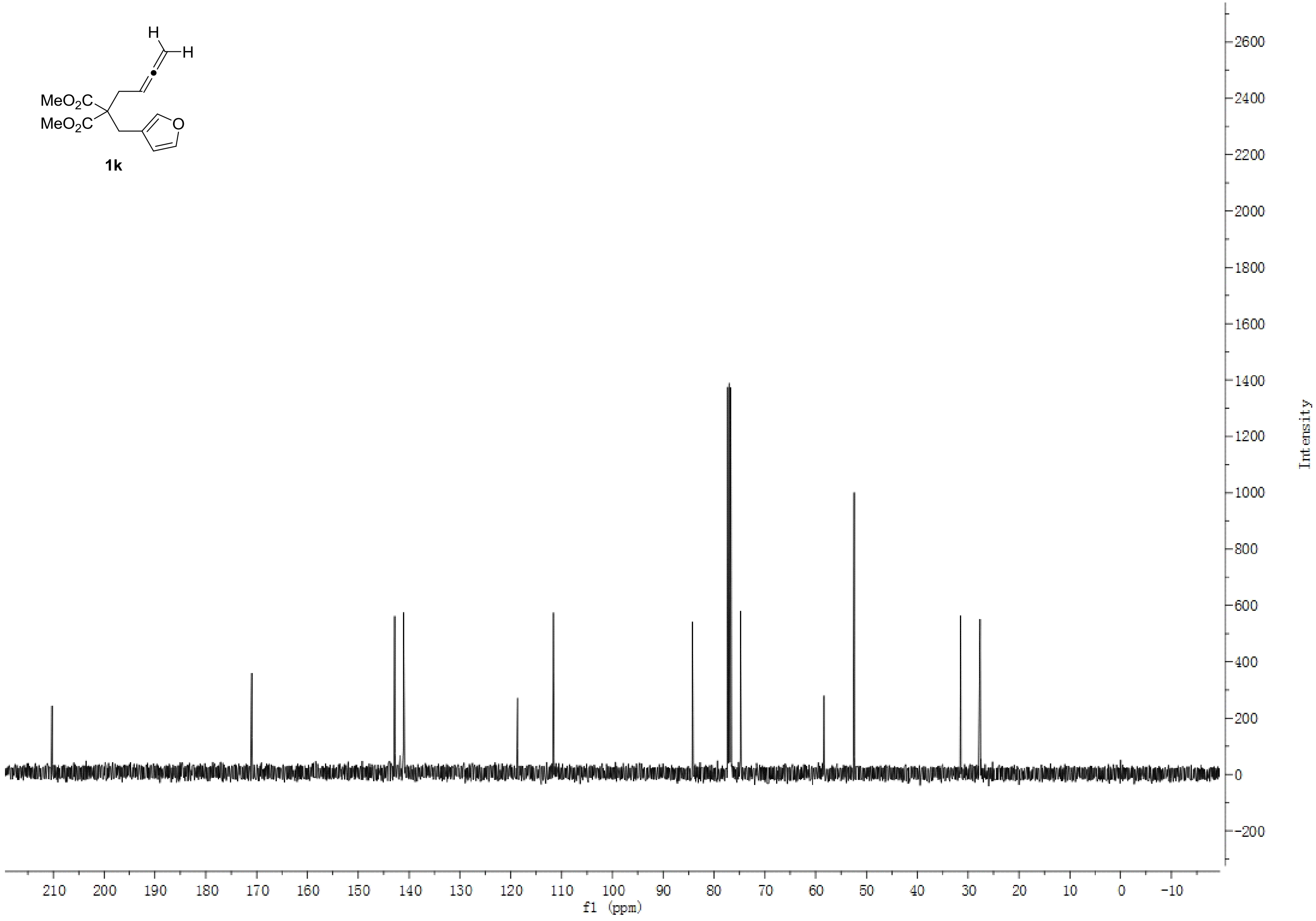
Ph
MeO2C
MeO2C
O
1j
5.14
2.07
1.05
0.97
1.00
2.97
3.02
1.97
1.99
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
Intensity

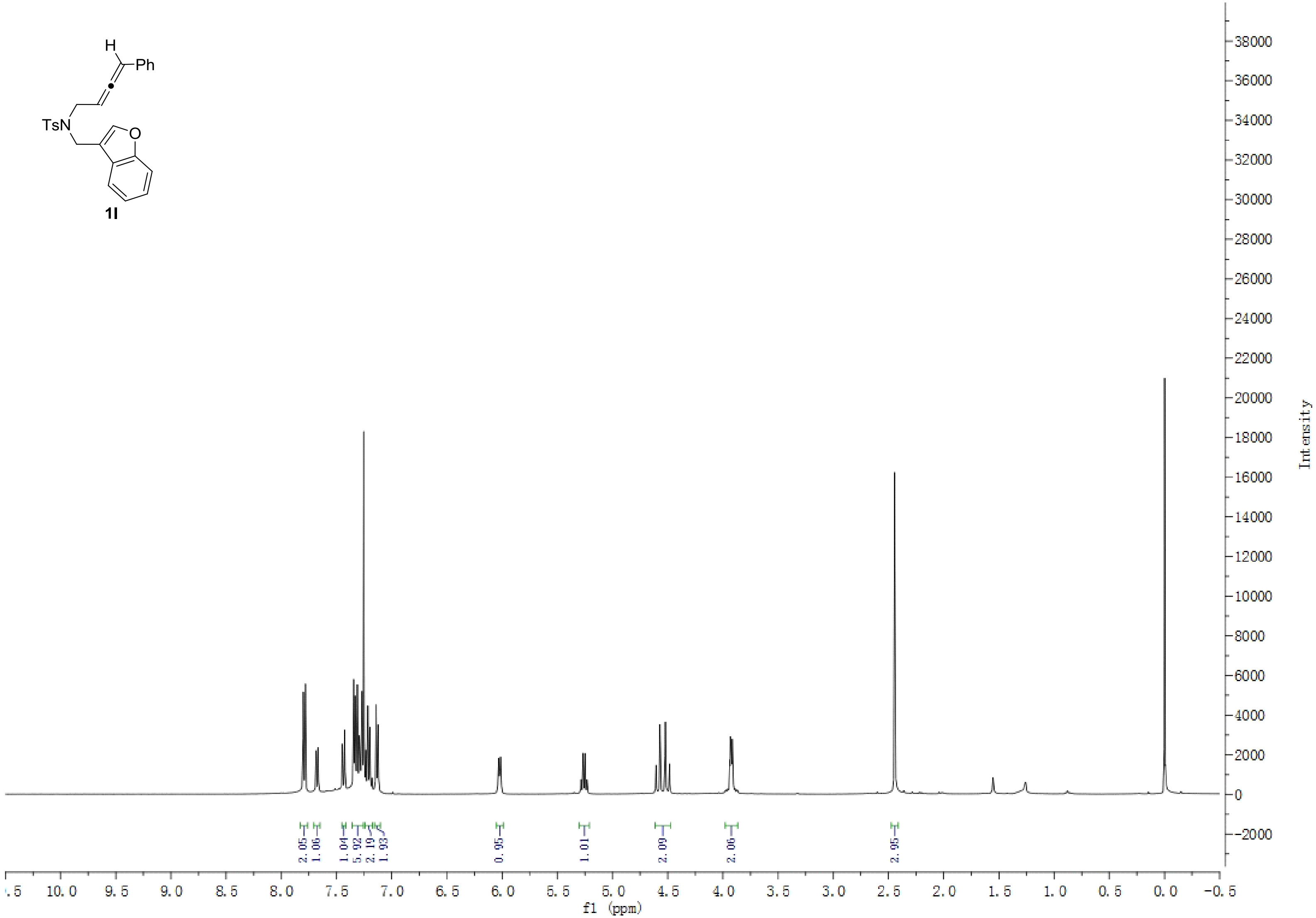

Ph
MeO2C
MeO2C
O
1j
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

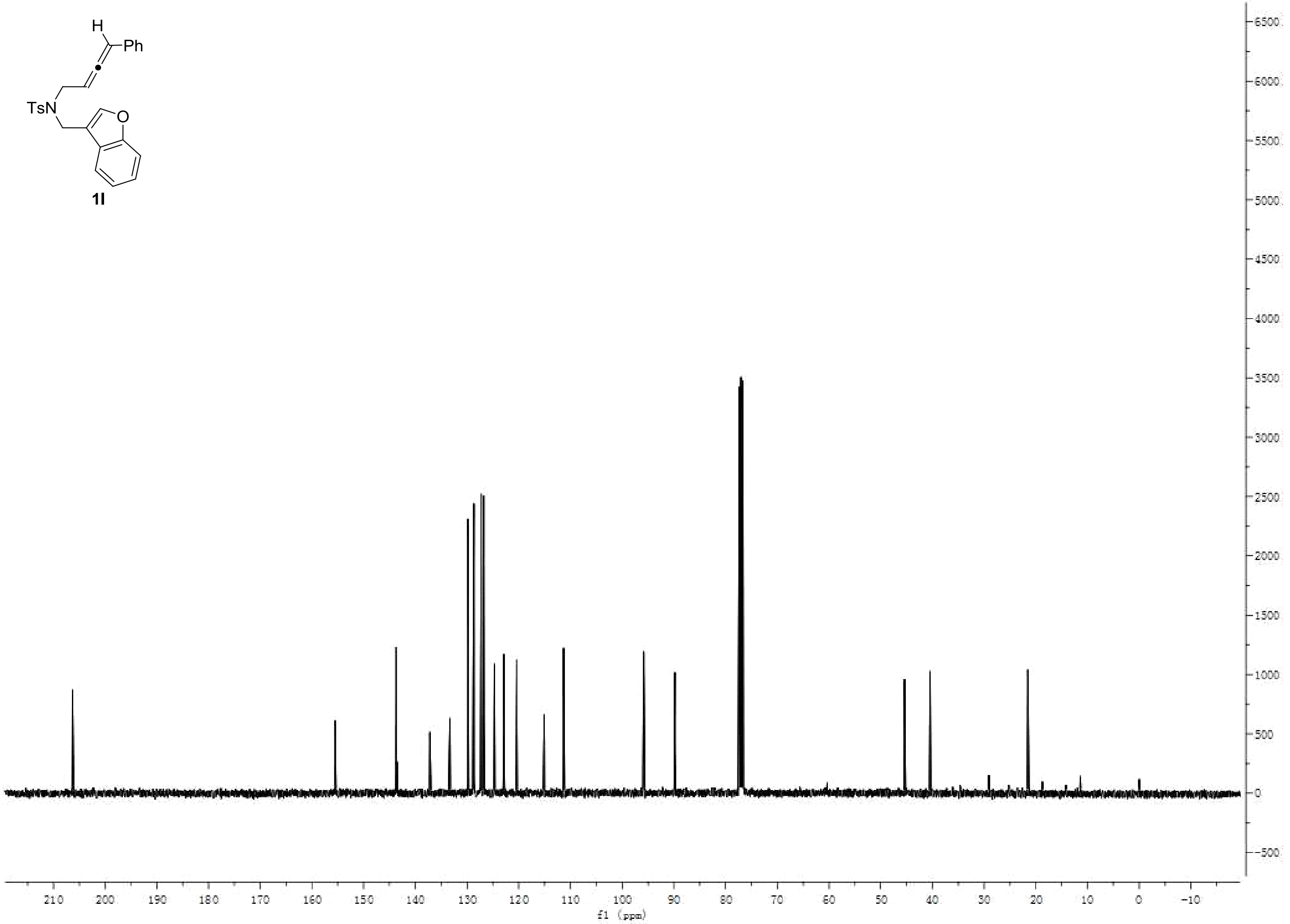
H
H
MeO2C
MeO2C
O

1k

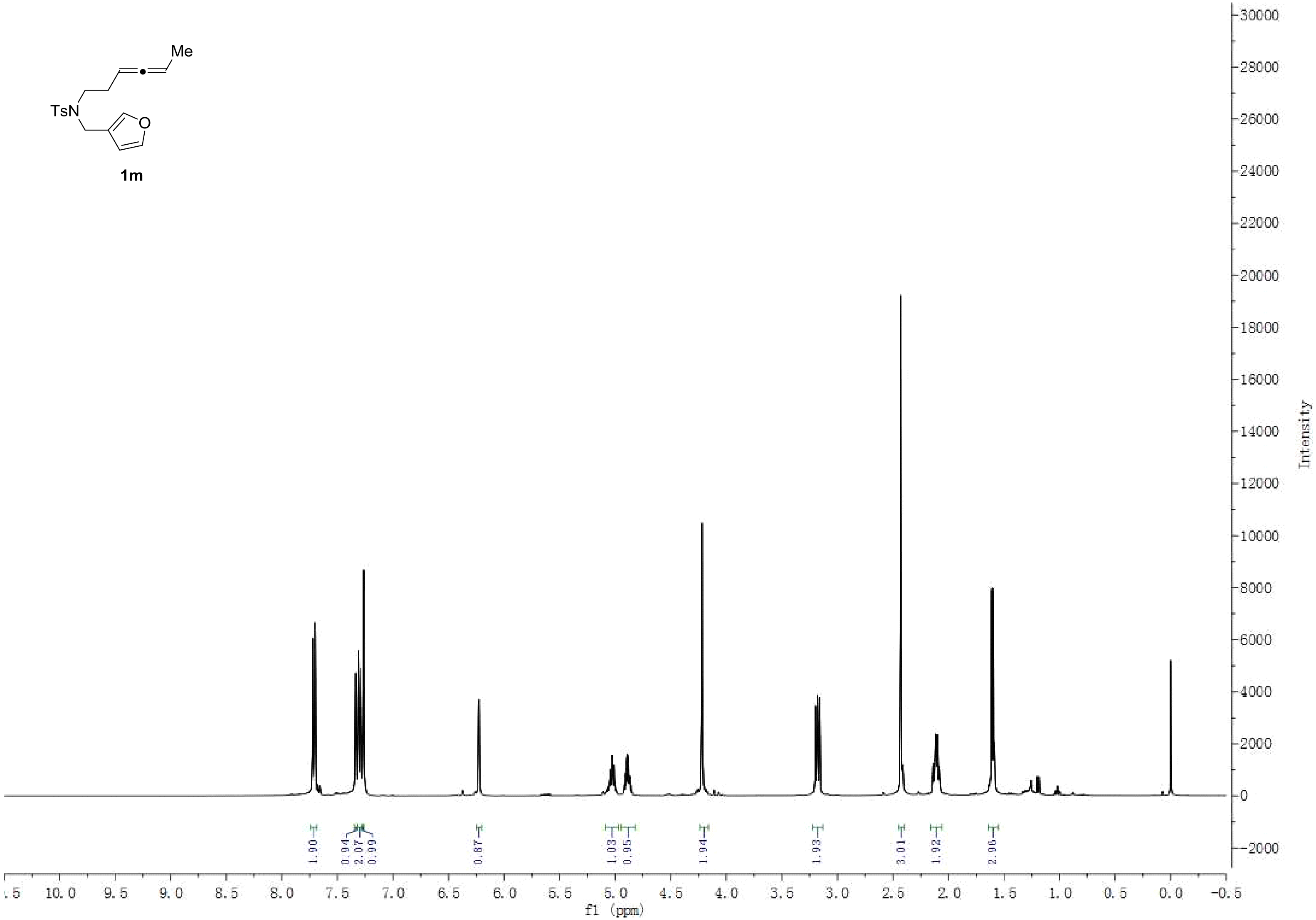

4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
Intensity
0.92
0.91
0.93
1.00
2.00
6.05
2.15
2.11
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


H
H
MeO2C
MeO2C
O
1k
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

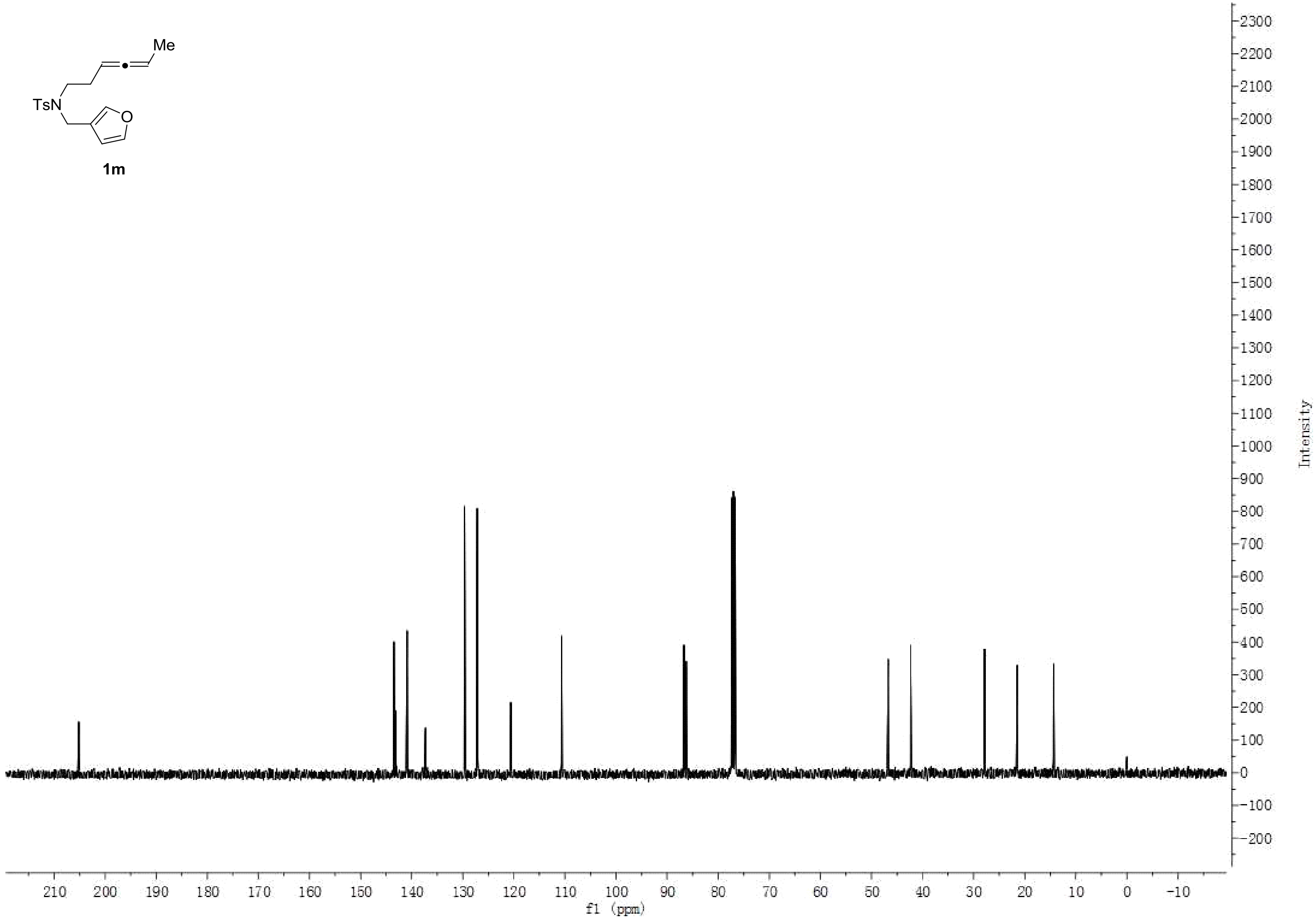

1l
H
Ph
TsN
O
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
Intensity
2.05
1.06
1.04
5.92
2.19
1.93
0.95
1.01
2.09
2.06
2.95
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


H
Ph
TsN
O
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1l

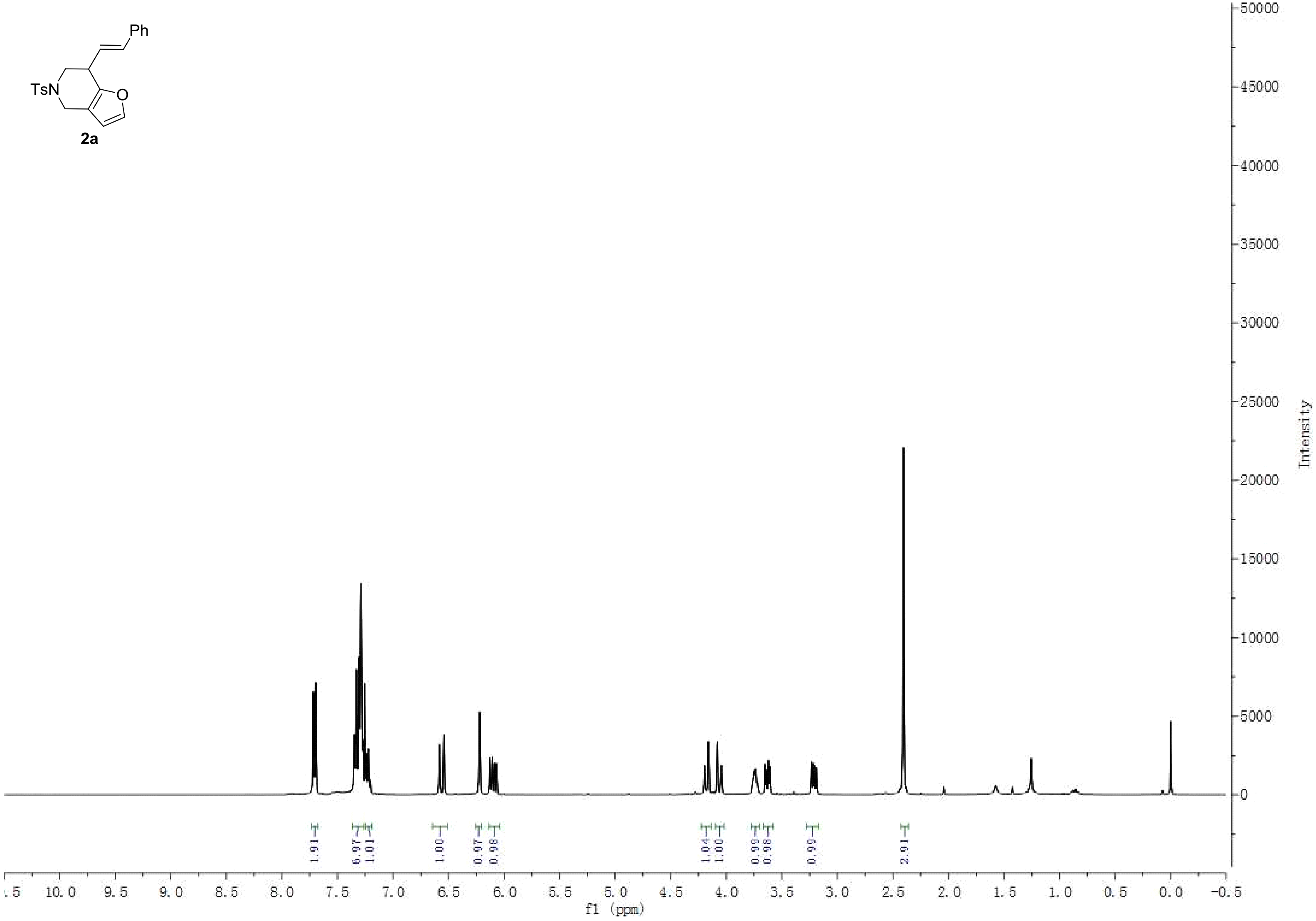

Me
TsN
O
1.90
0.94
2.07
0.99
0.87
1.03
0.95
1.94
1.93
3.01
1.92
2.96
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity

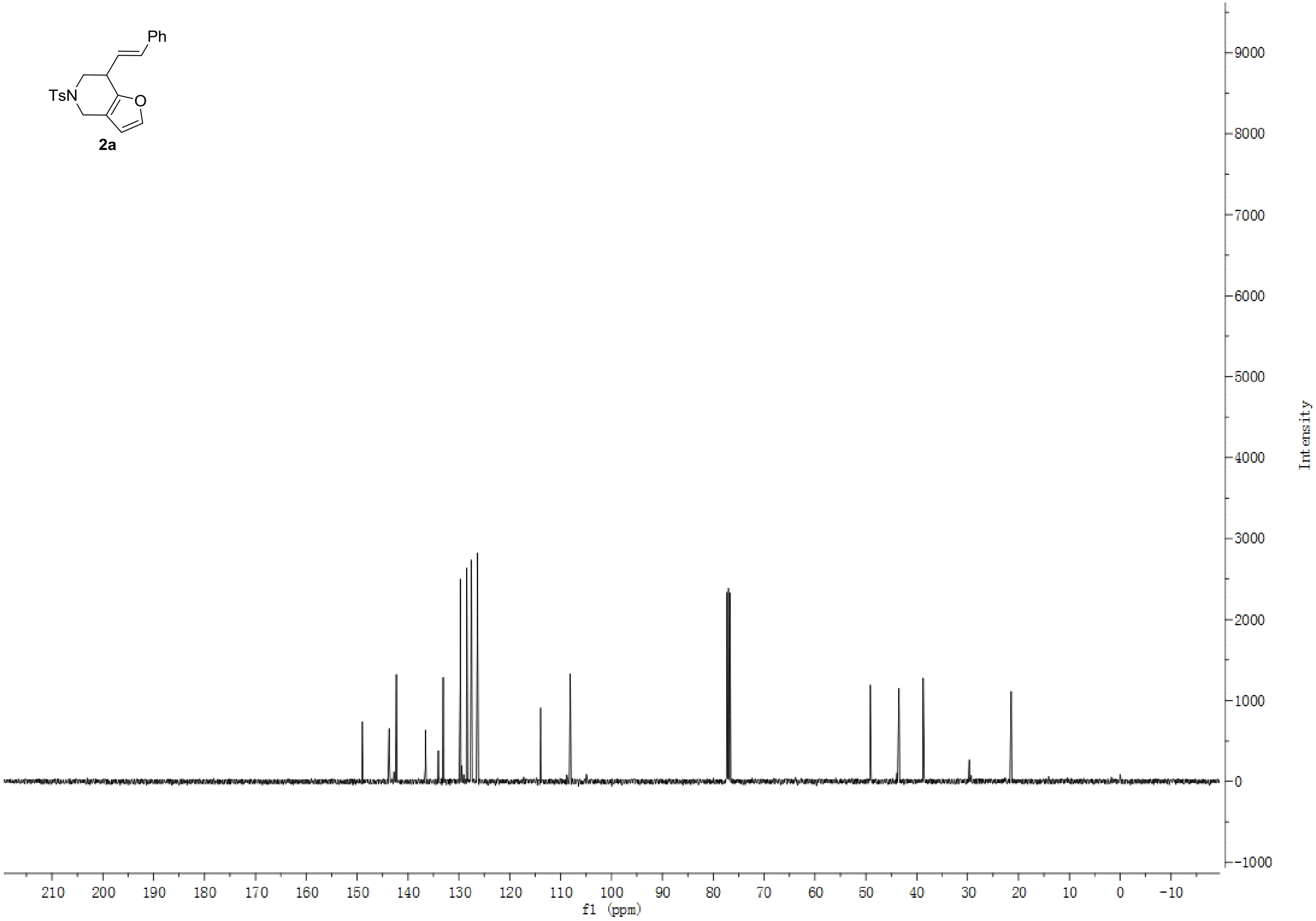
1m


Me
TsN
O

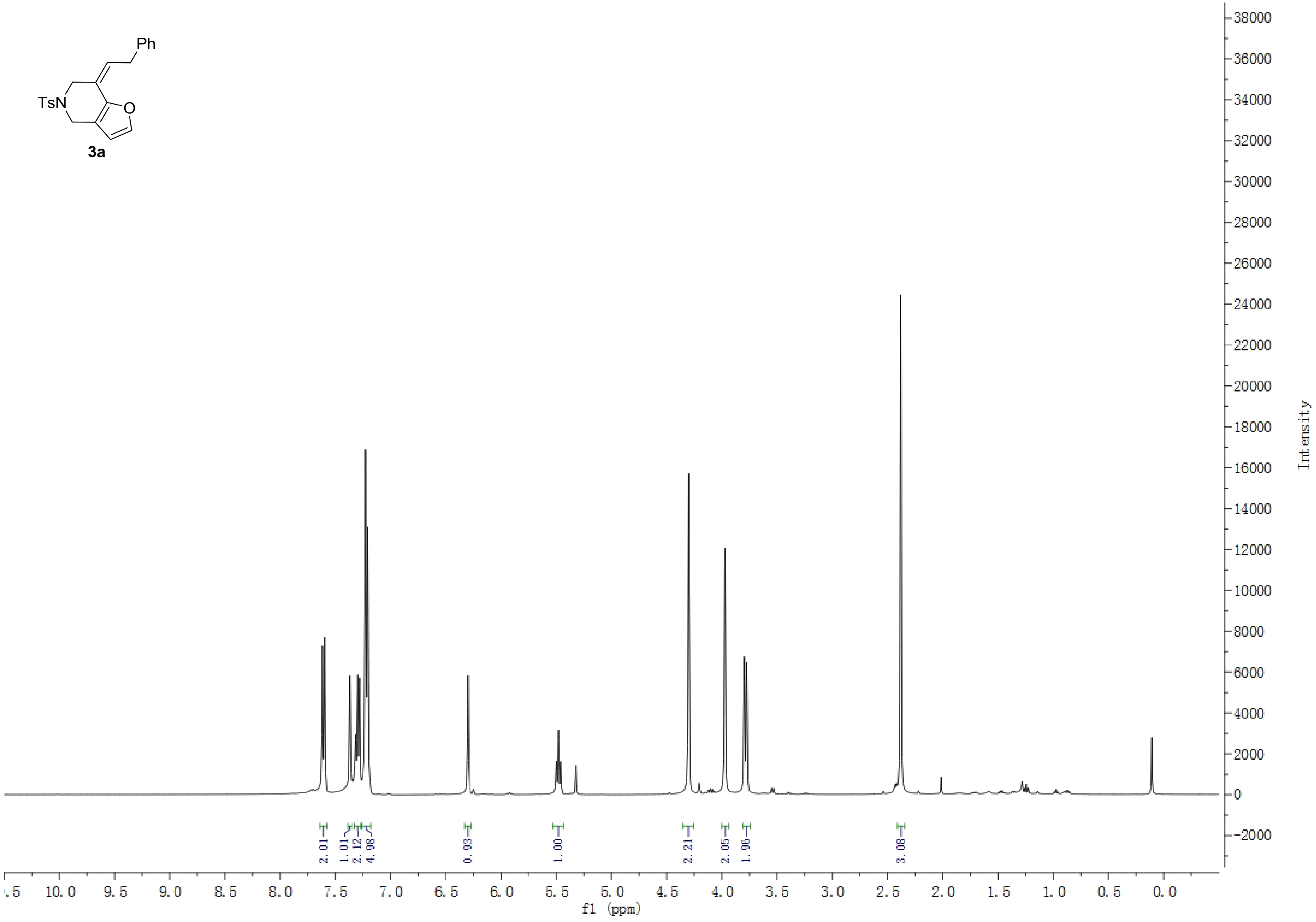
1m

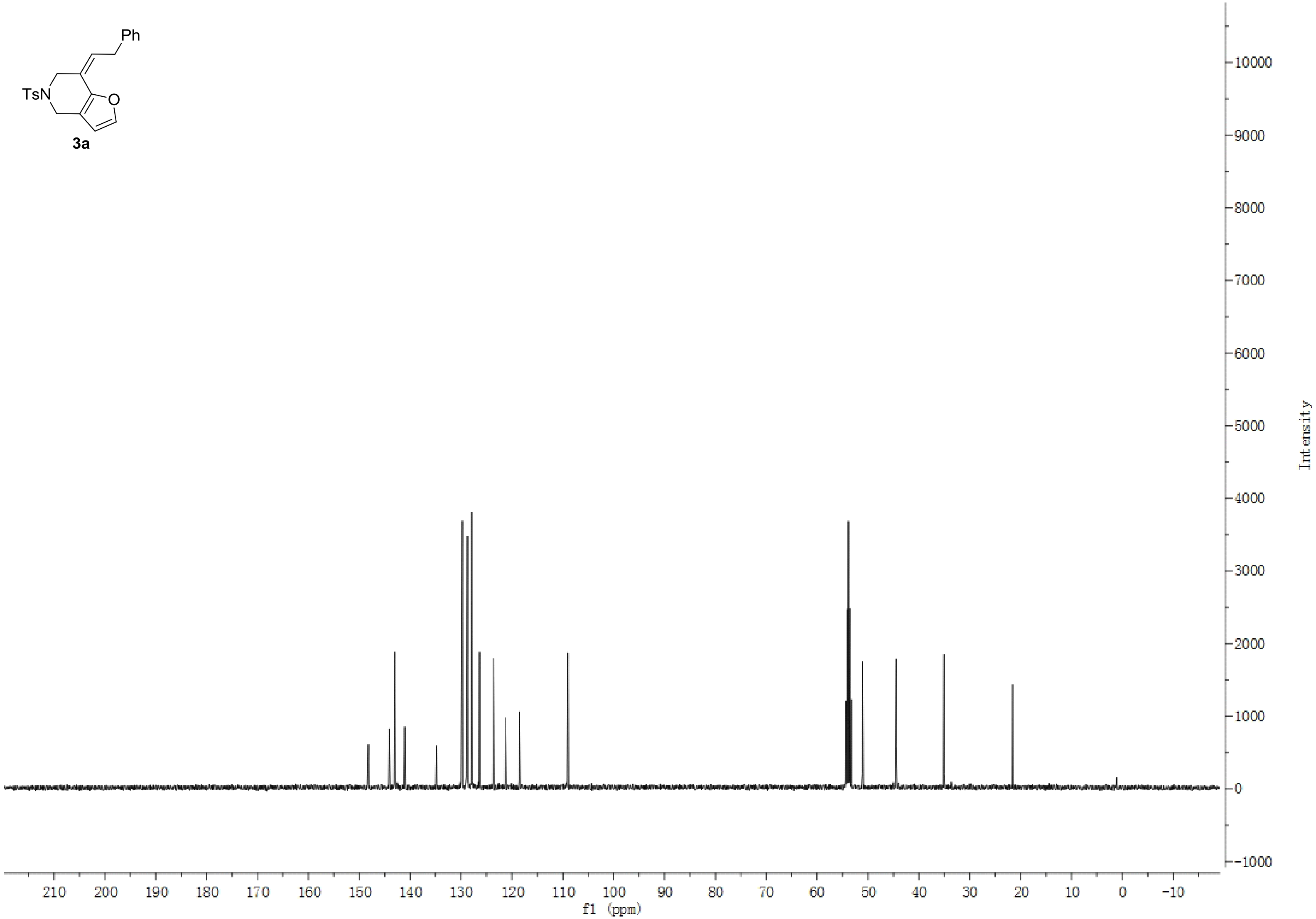
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
TsN
O
2a
1.91
6.97
1.01
1.00
0.97
0.98
1.04
1.00
0.99
0.98
0.99
2.91
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity


Ph
TsN
O
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

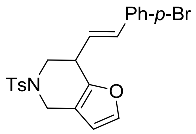
2a


Ph
TsN
O
3a
2.01
1.01
2.12
4.98
0.93
1.00
2.21
2.05
1.96
3.08
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity

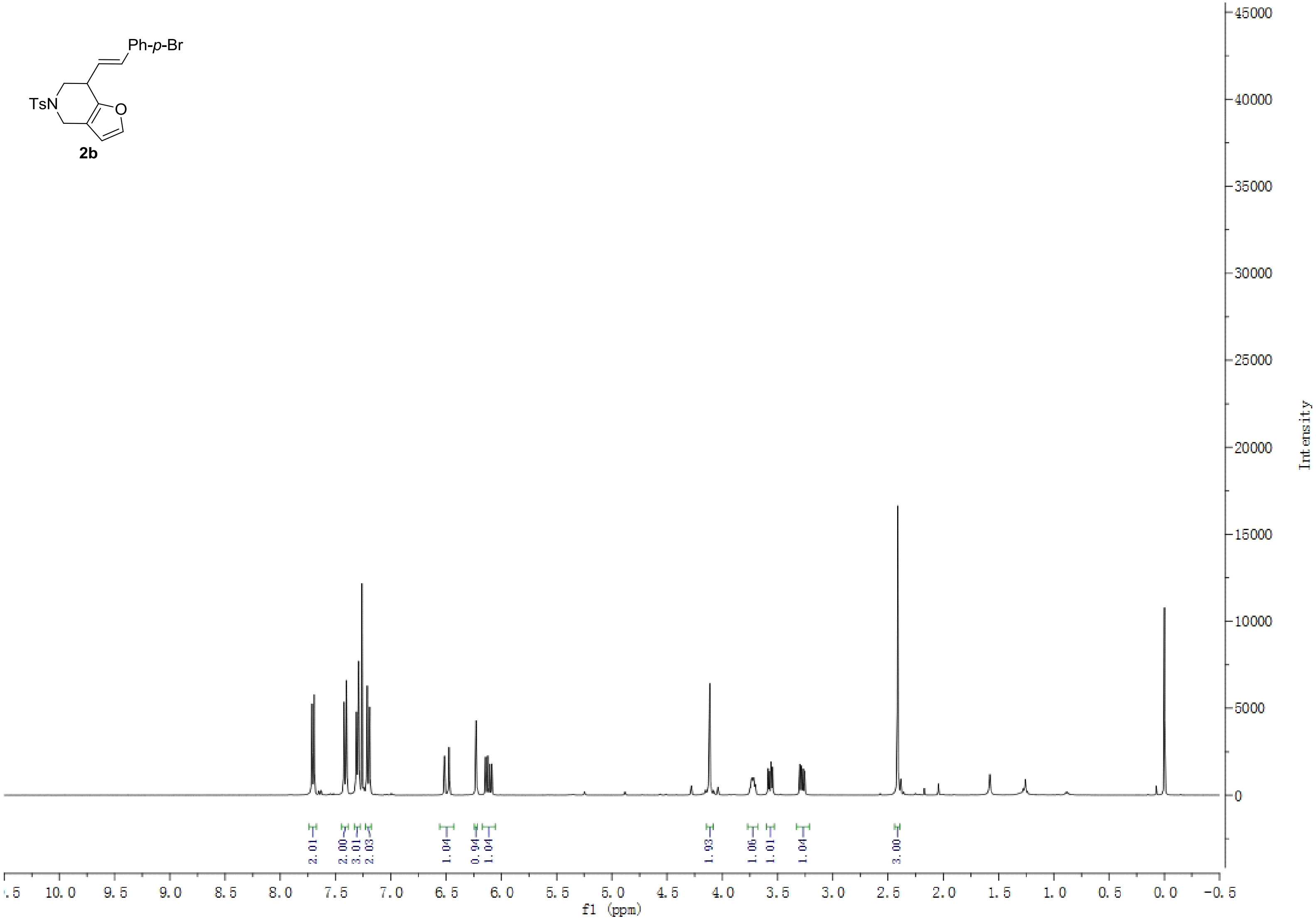

Ph
TsN
O

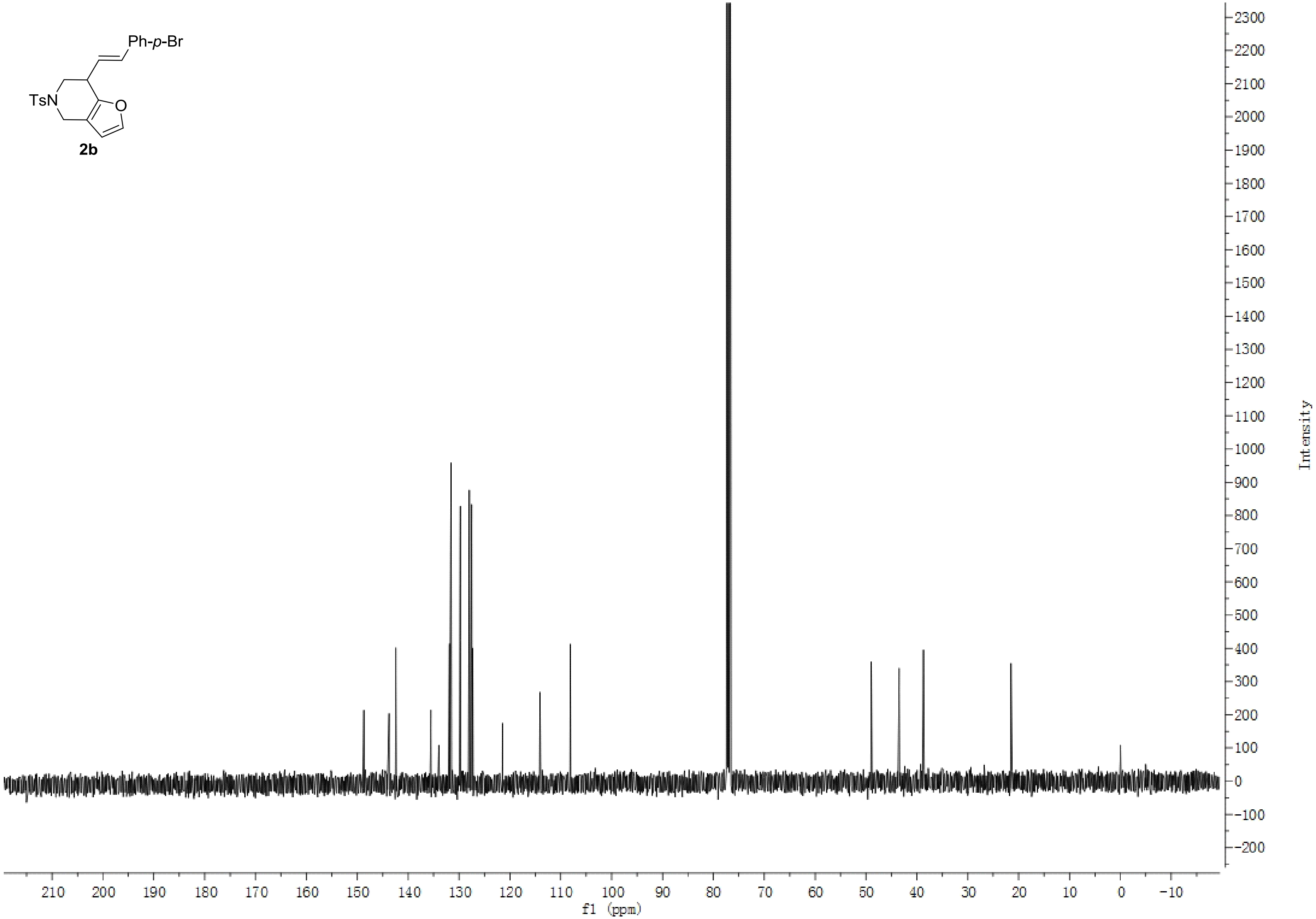
3a

10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Ph-p-Br
TsN
O

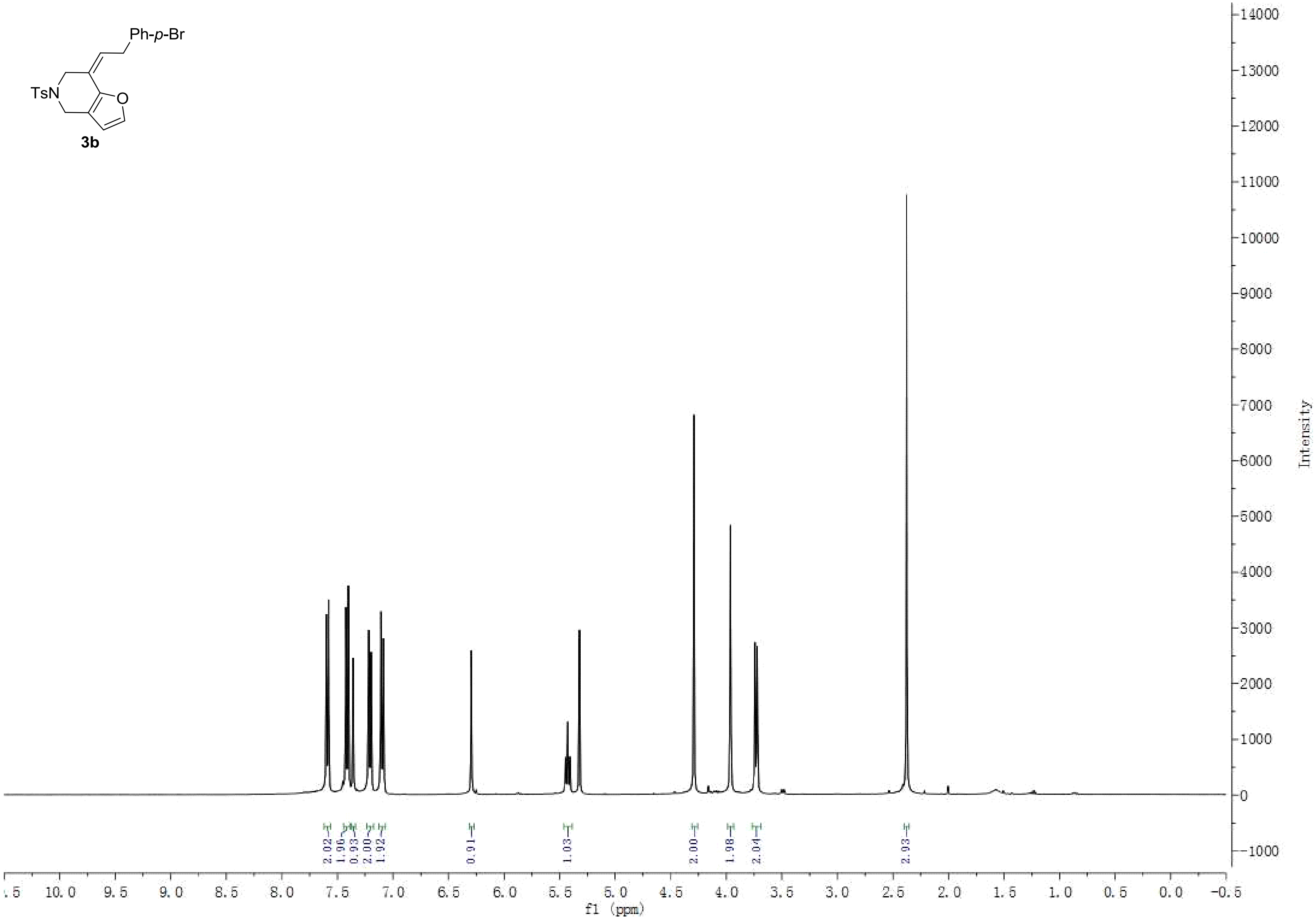
2b

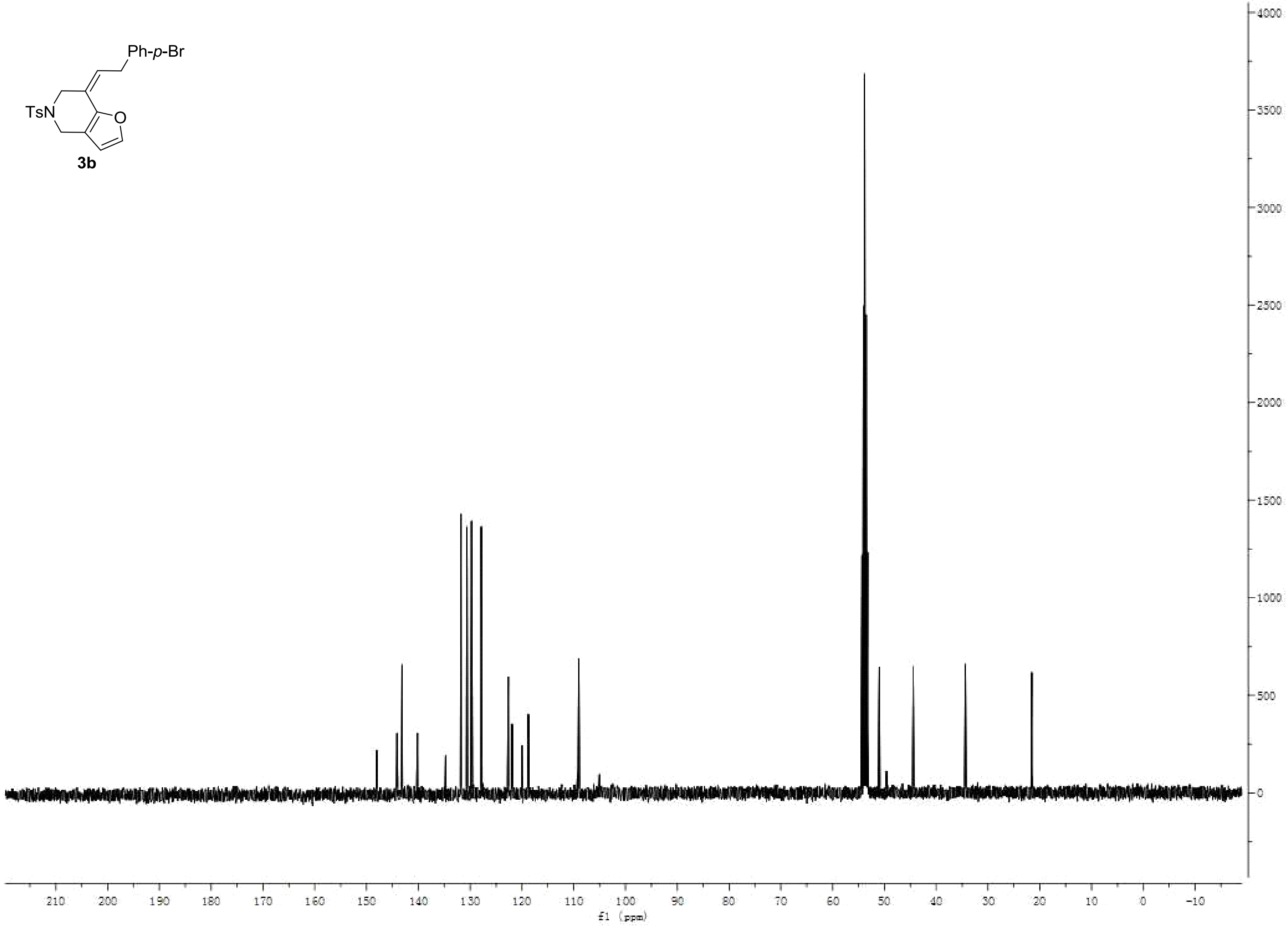

45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
2.01
2.00
3.01
2.03
1.04
0.94
1.04
1.93
1.06
1.01
1.04
3.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

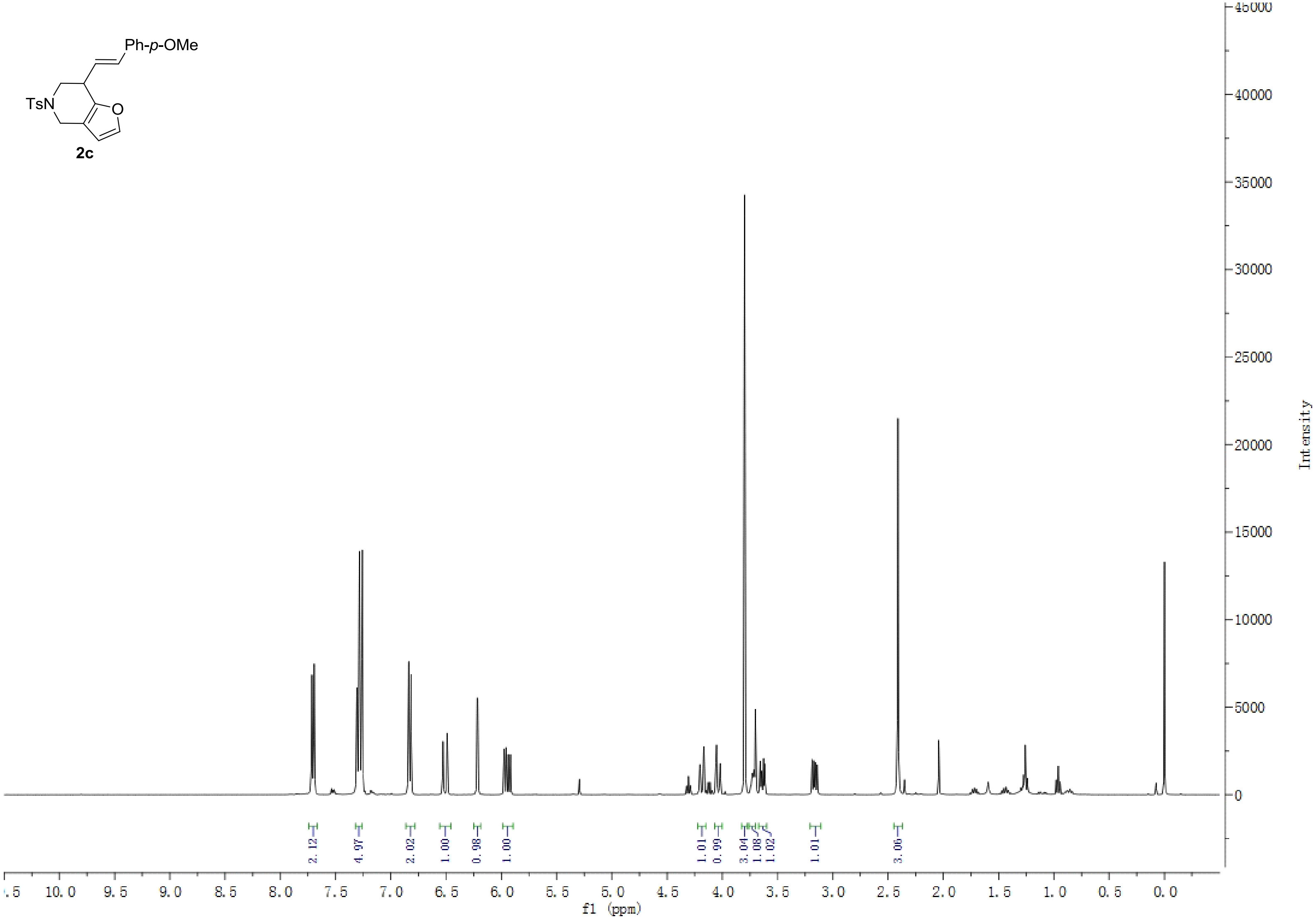


2b

Ph-*p*-Br
TsN
O
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

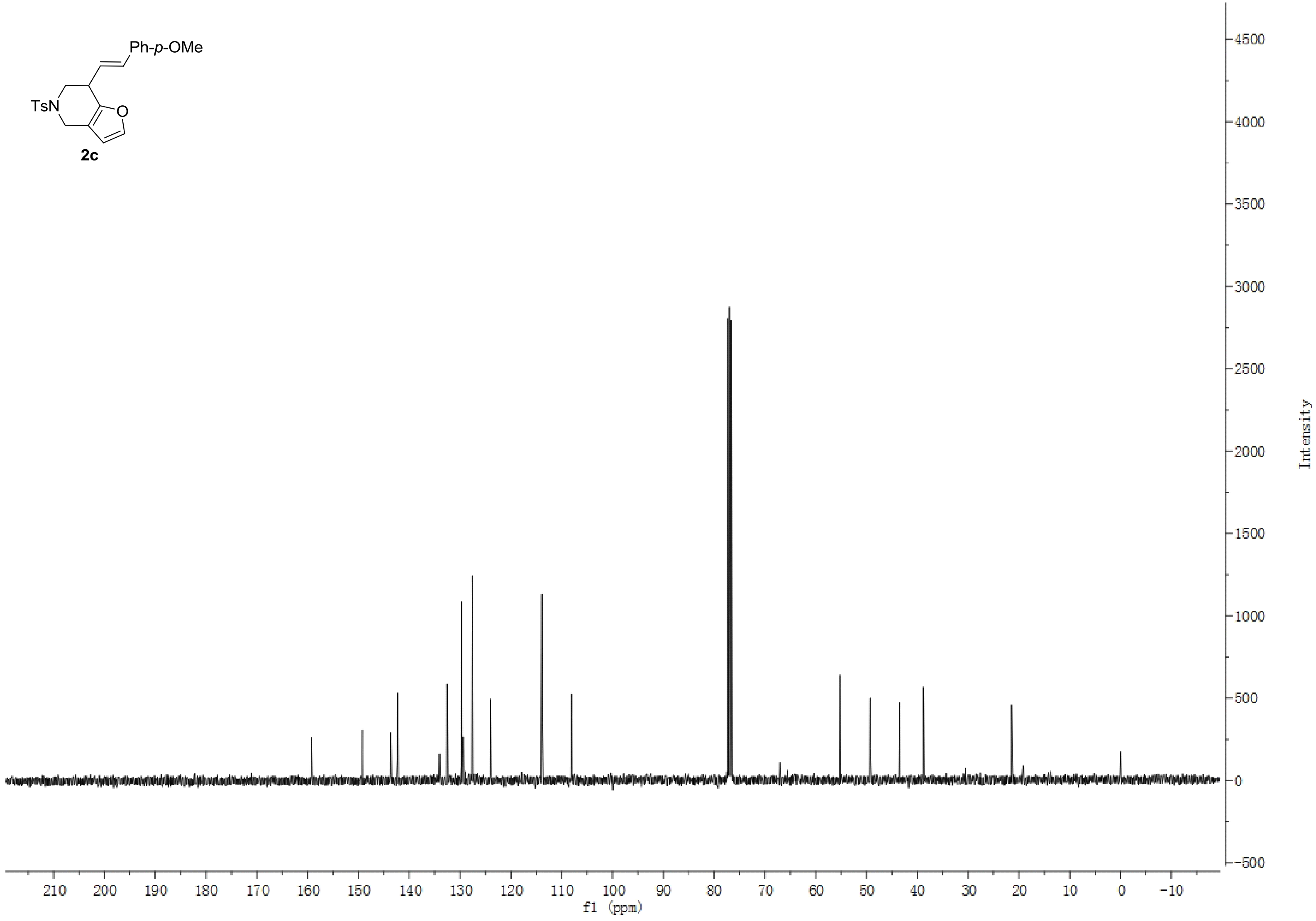

Ph-p-Br
TsN
O
3b
2.02
1.96
0.93
2.00
1.92
0.91
1.03
2.00
1.98
2.04
2.93
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

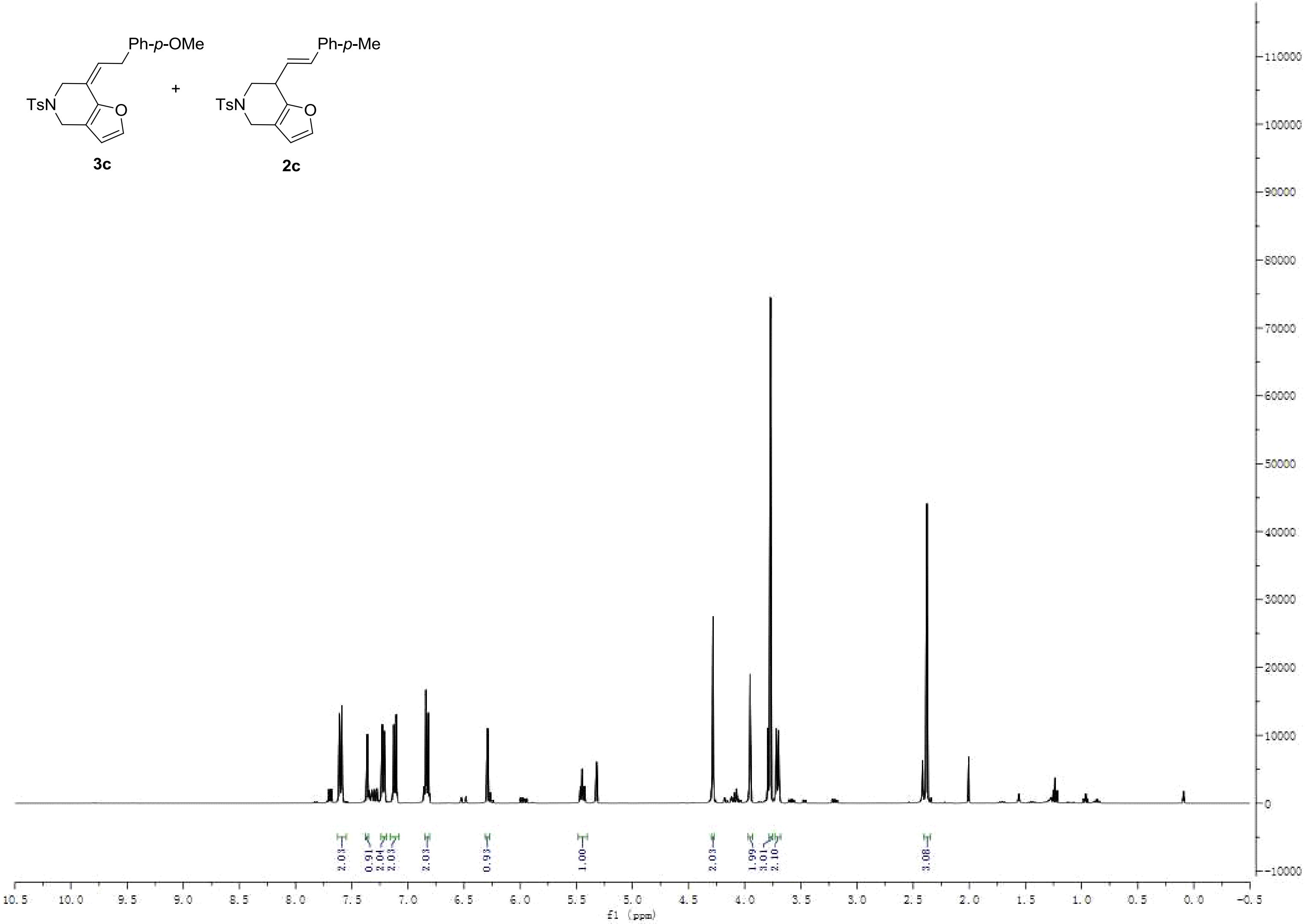

Ph-*p*-Br
TsN
O
3b
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

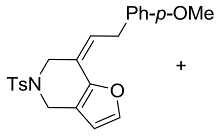


2c

Ph-p-OMe
TsN
O
2.12
4.97
2.02
1.00
0.98
1.00
1.01
0.99
3.04
1.08
1.02
1.01
3.06
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity

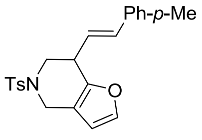

Ph-*p*-OMe
TsN
O
2c
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Ph-p-OMe
TsN
O
3c
+
Ph-p-Me
TsN
O
2c
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
2.03
0.91
2.04
2.03
2.03
0.93
1.00
2.03
1.99
3.01
2.10
3.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

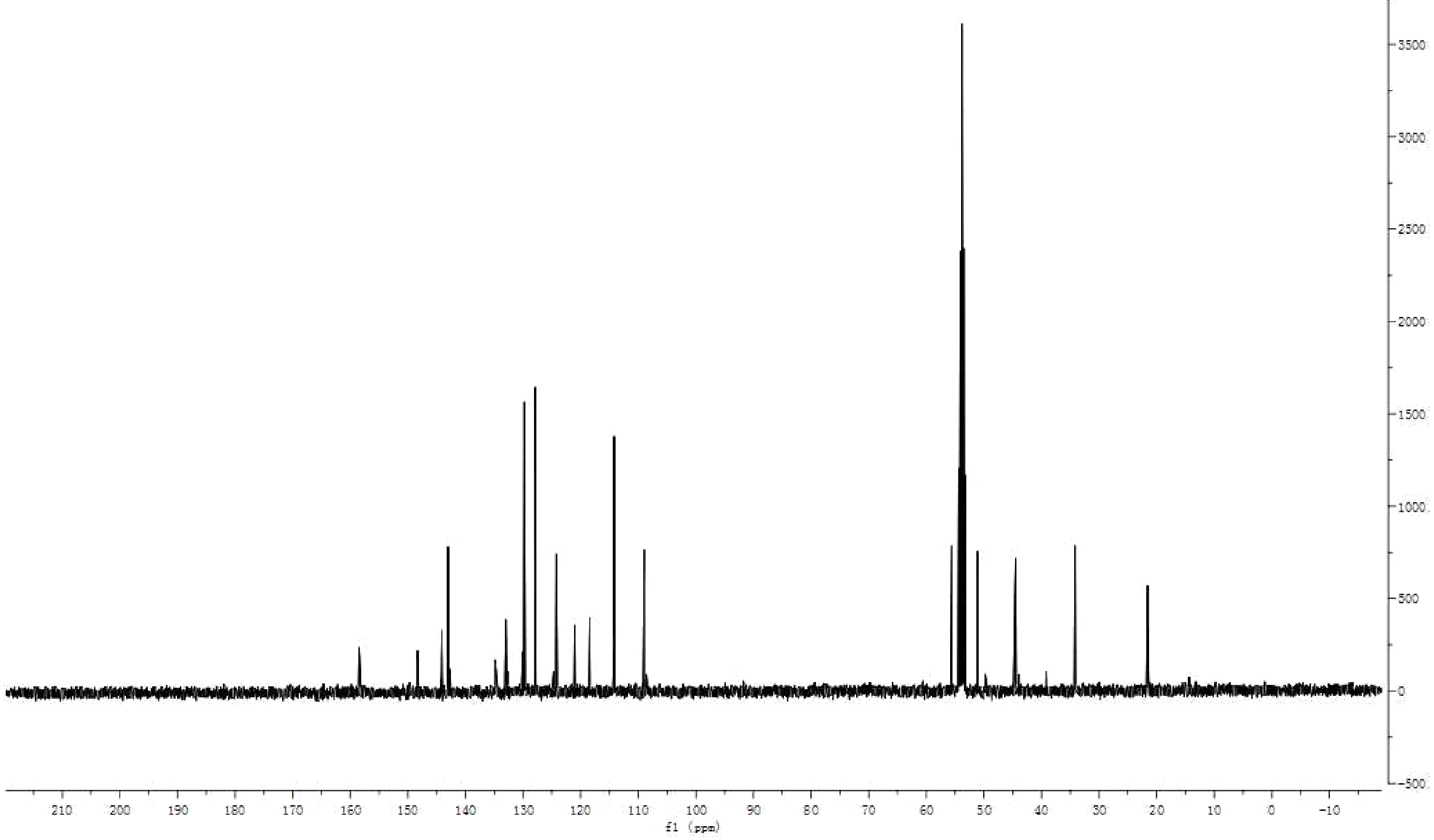

Ph-*p*-OMe
TsN
O

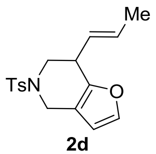
3c

+

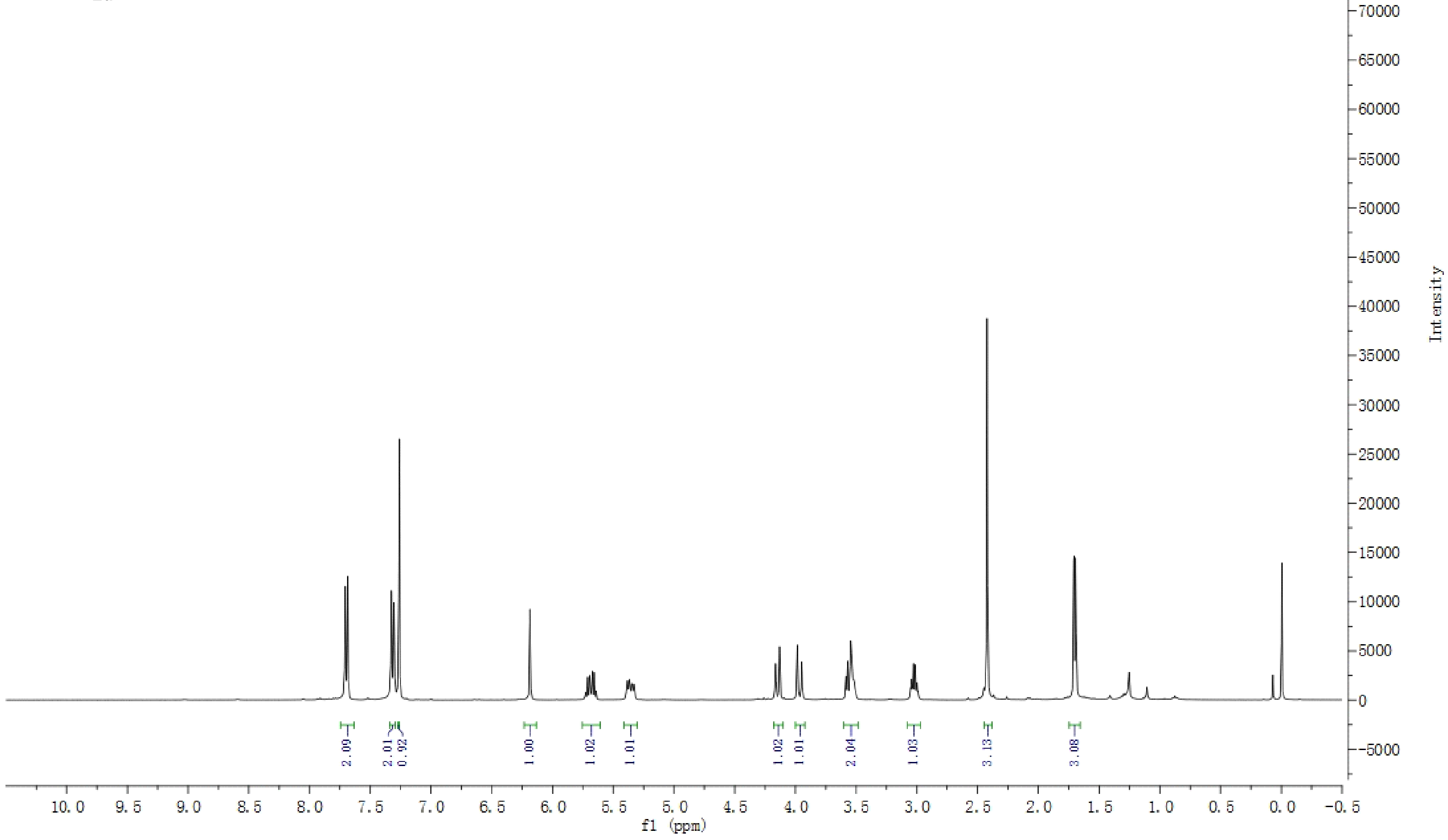

Ph-*p*-Me
TsN
O

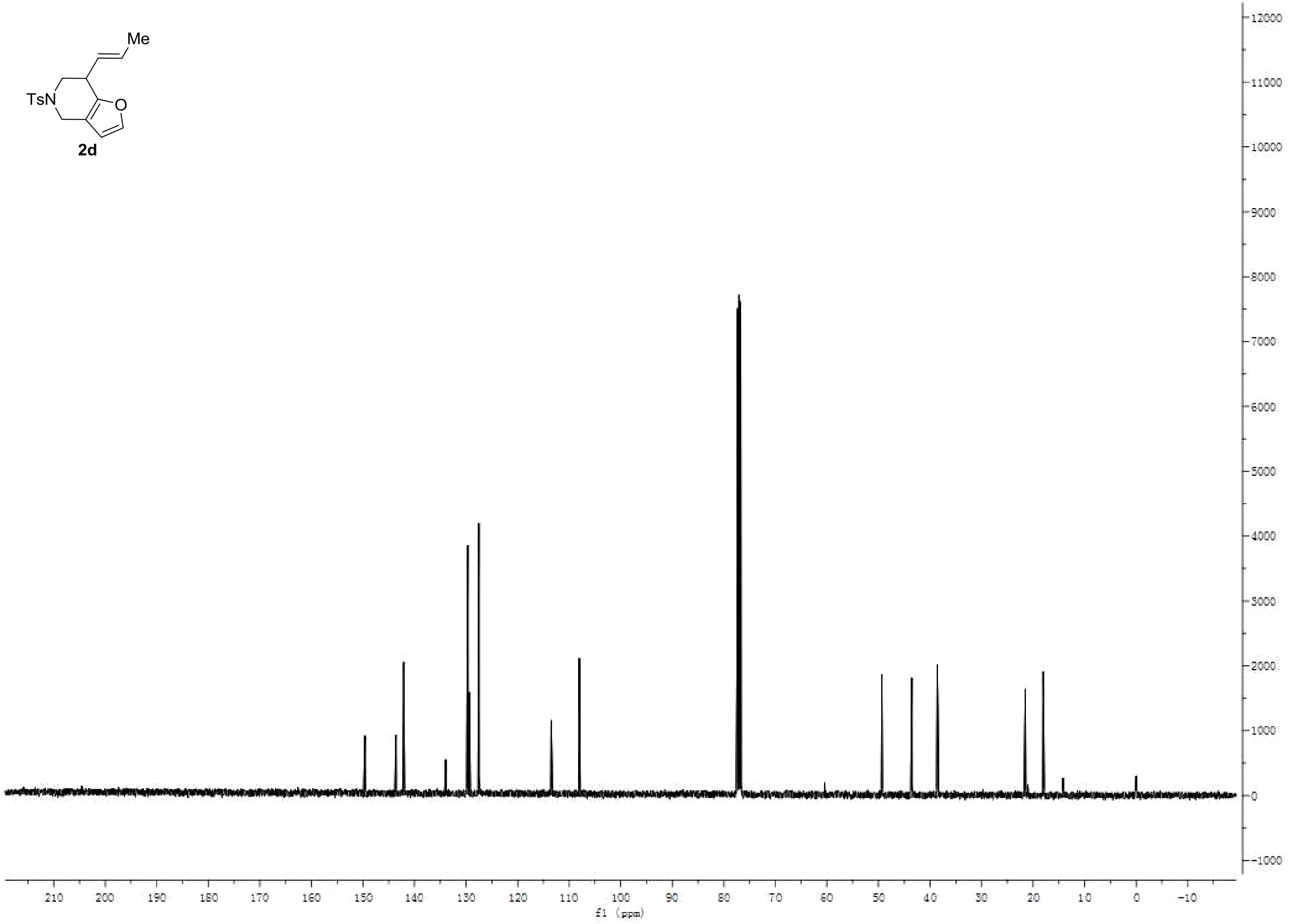
2c

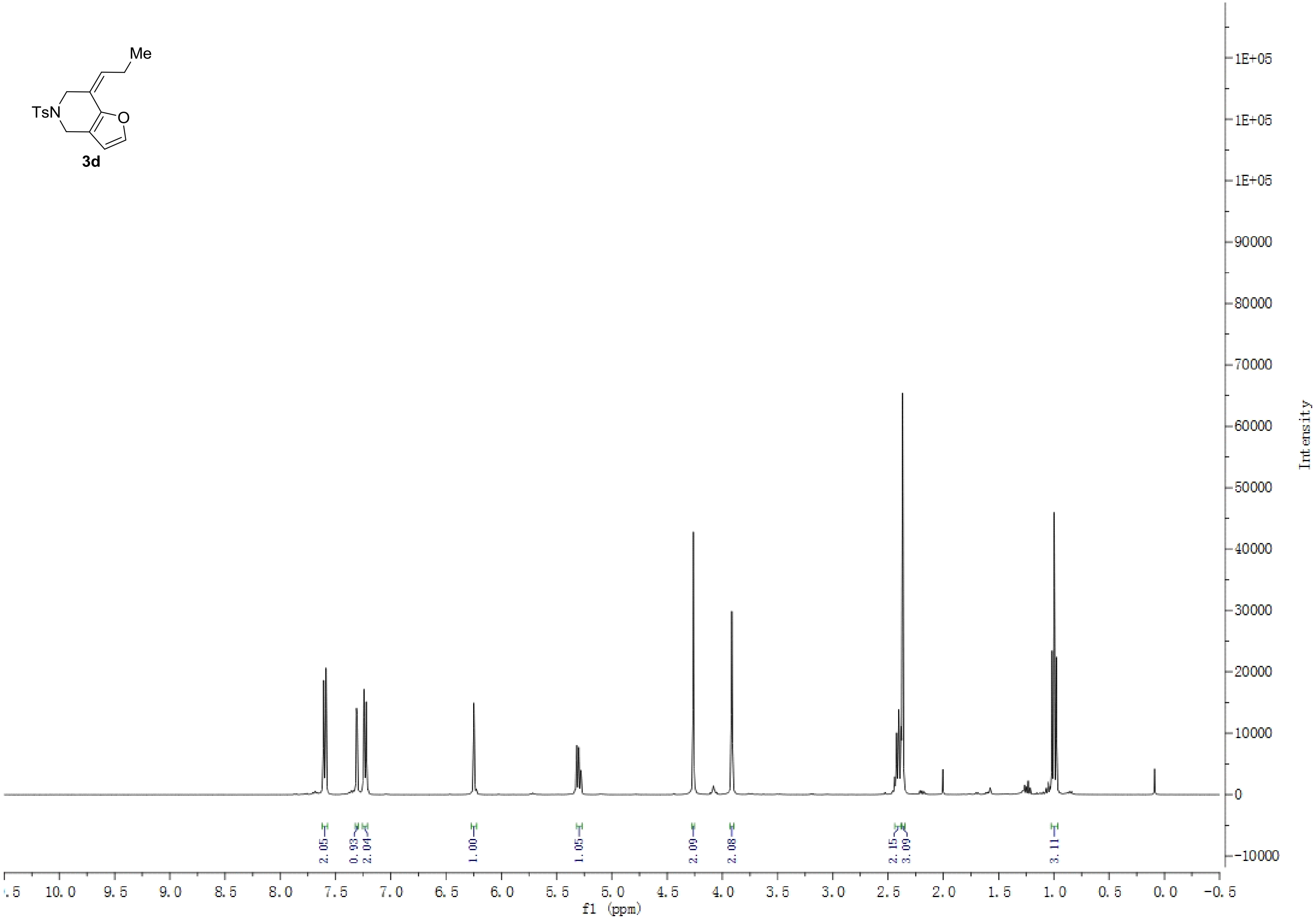

4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

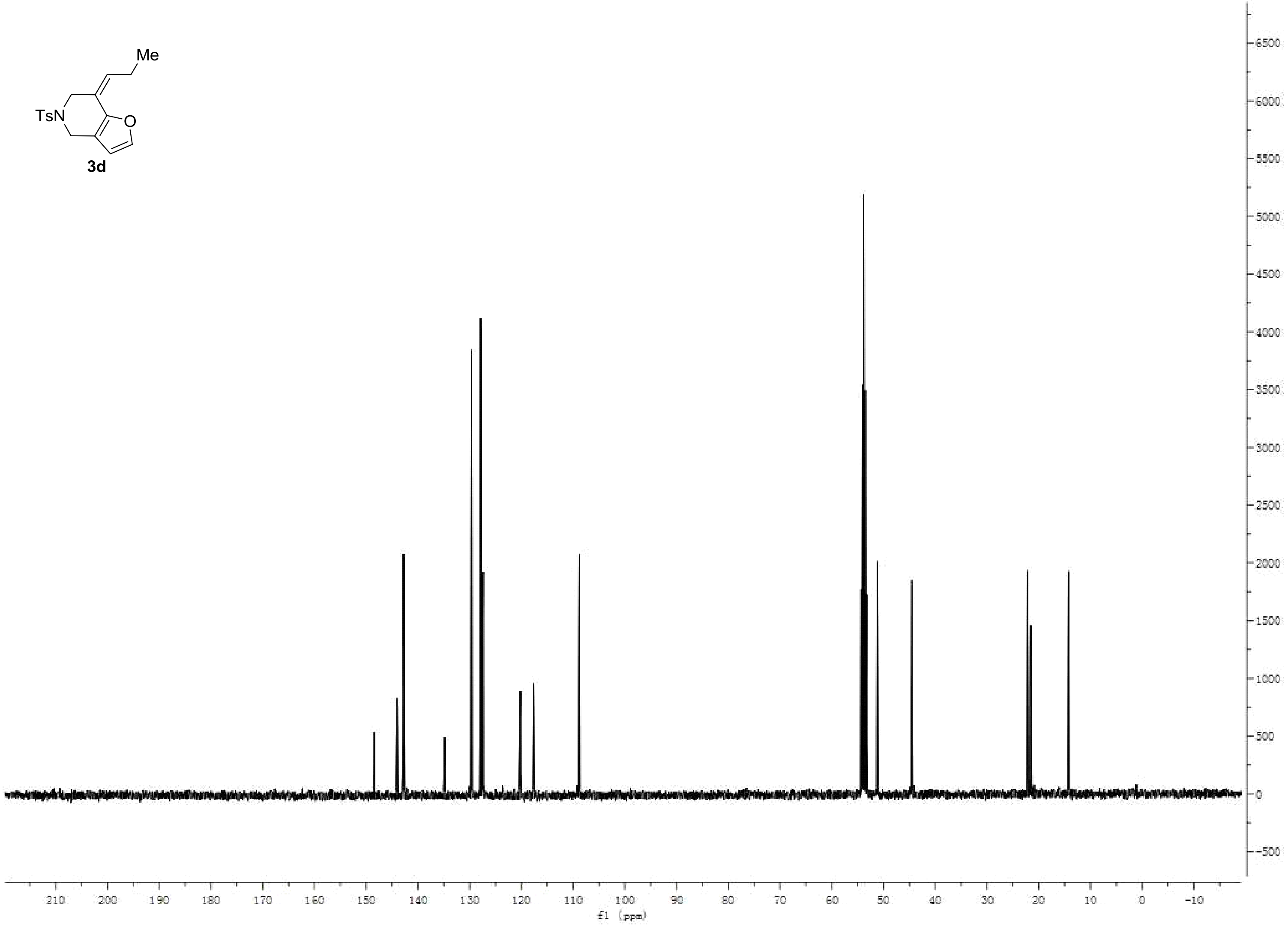

Me
TsN
O

2d

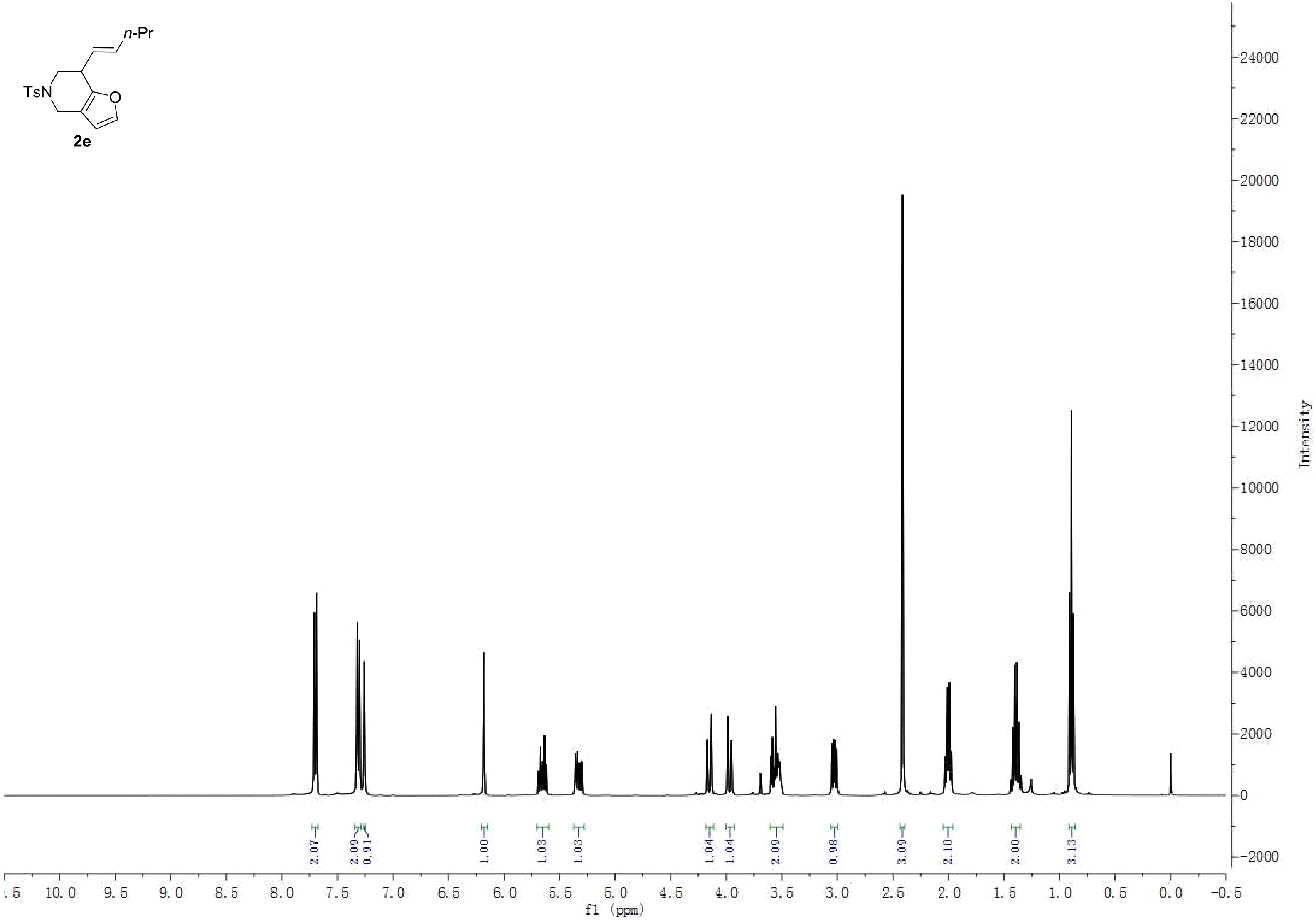

2.09
2.01
0.92
1.00
1.02
1.01
1.02
1.01
2.04
1.03
3.13
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
Intensity

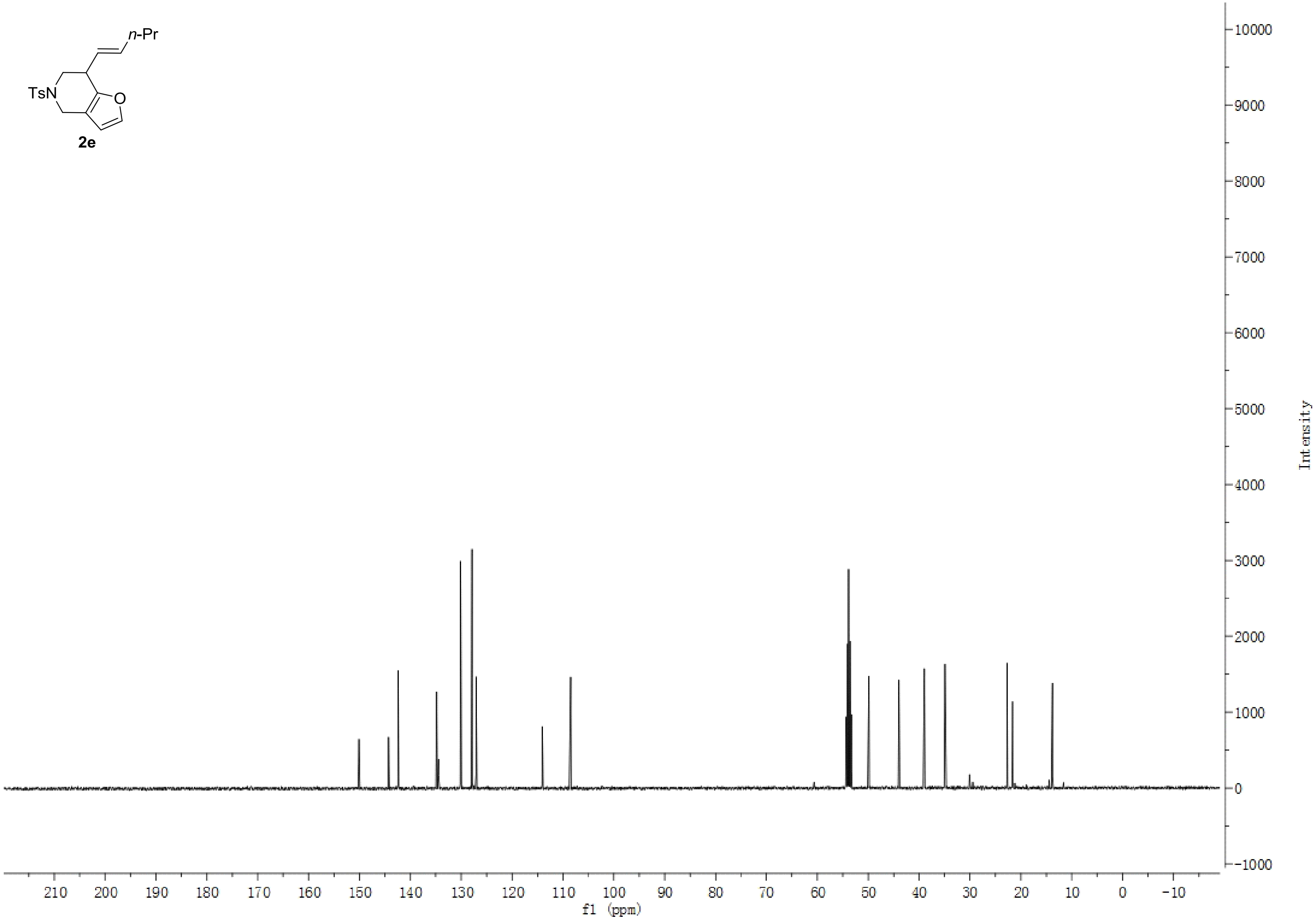

Me
TsN
O
2d
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Me
TsN
O
3d
2.05
0.93
2.04
1.00
1.05
2.09
2.08
2.15
3.09
3.11
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
Intensity
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


Me
TsN
O
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3d

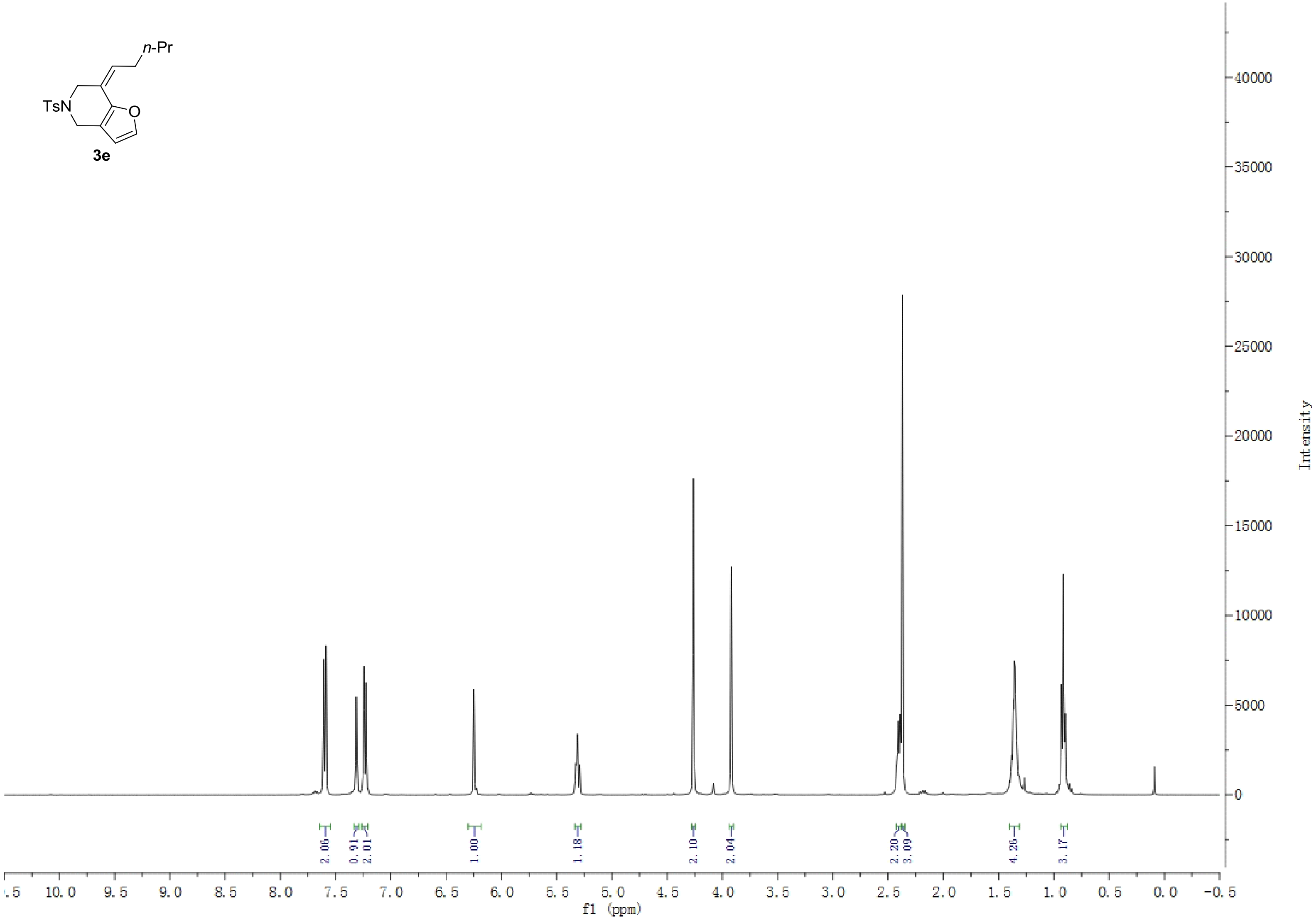

n-Pr
TsN
O
2e
2.07
2.09
0.91
1.00
1.03
1.03
1.04
1.04
2.09
0.98
3.09
2.10
2.00
3.13
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity

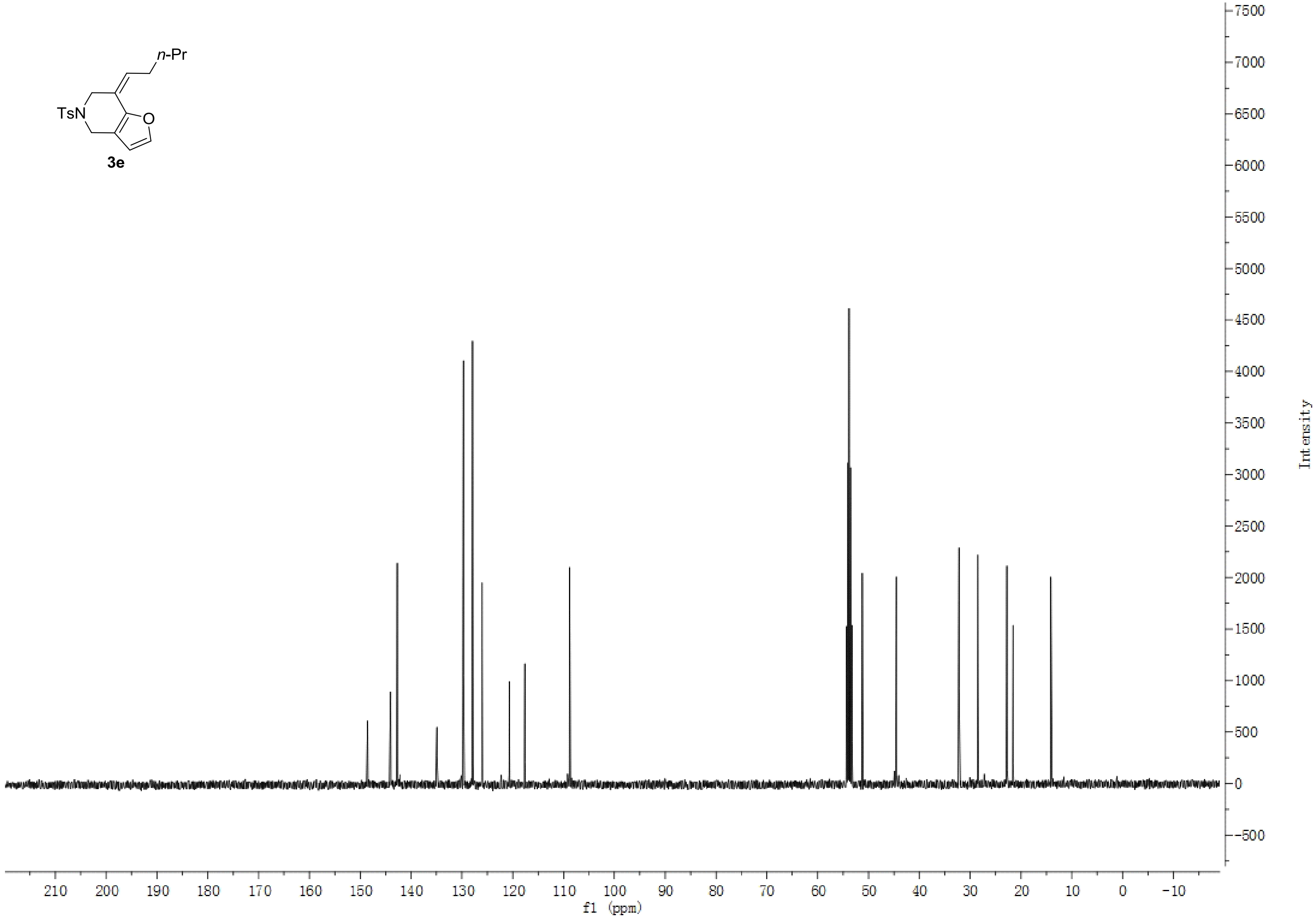

2e

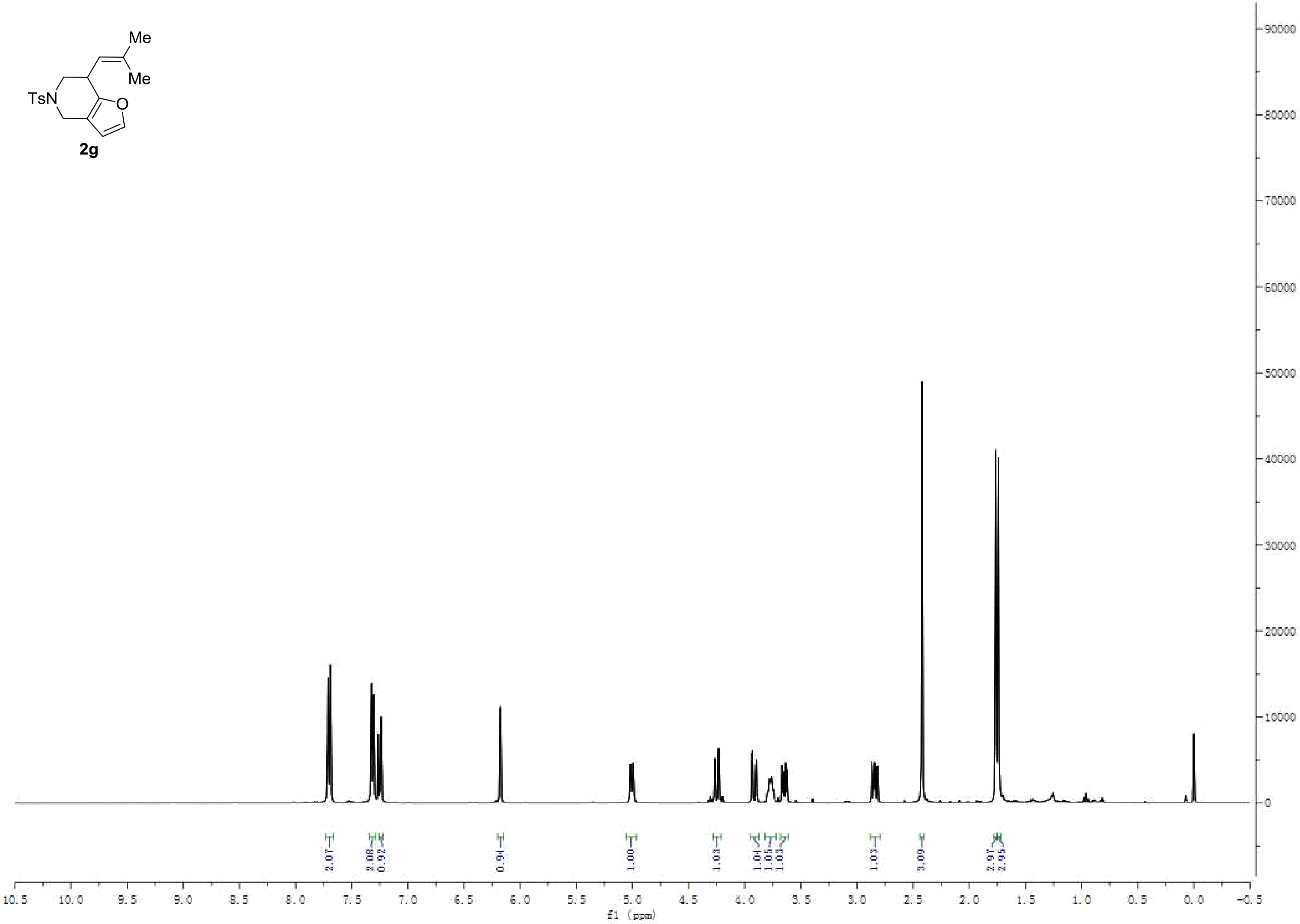
n-Pr
TsN
O
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

n-Pr
TsN
O

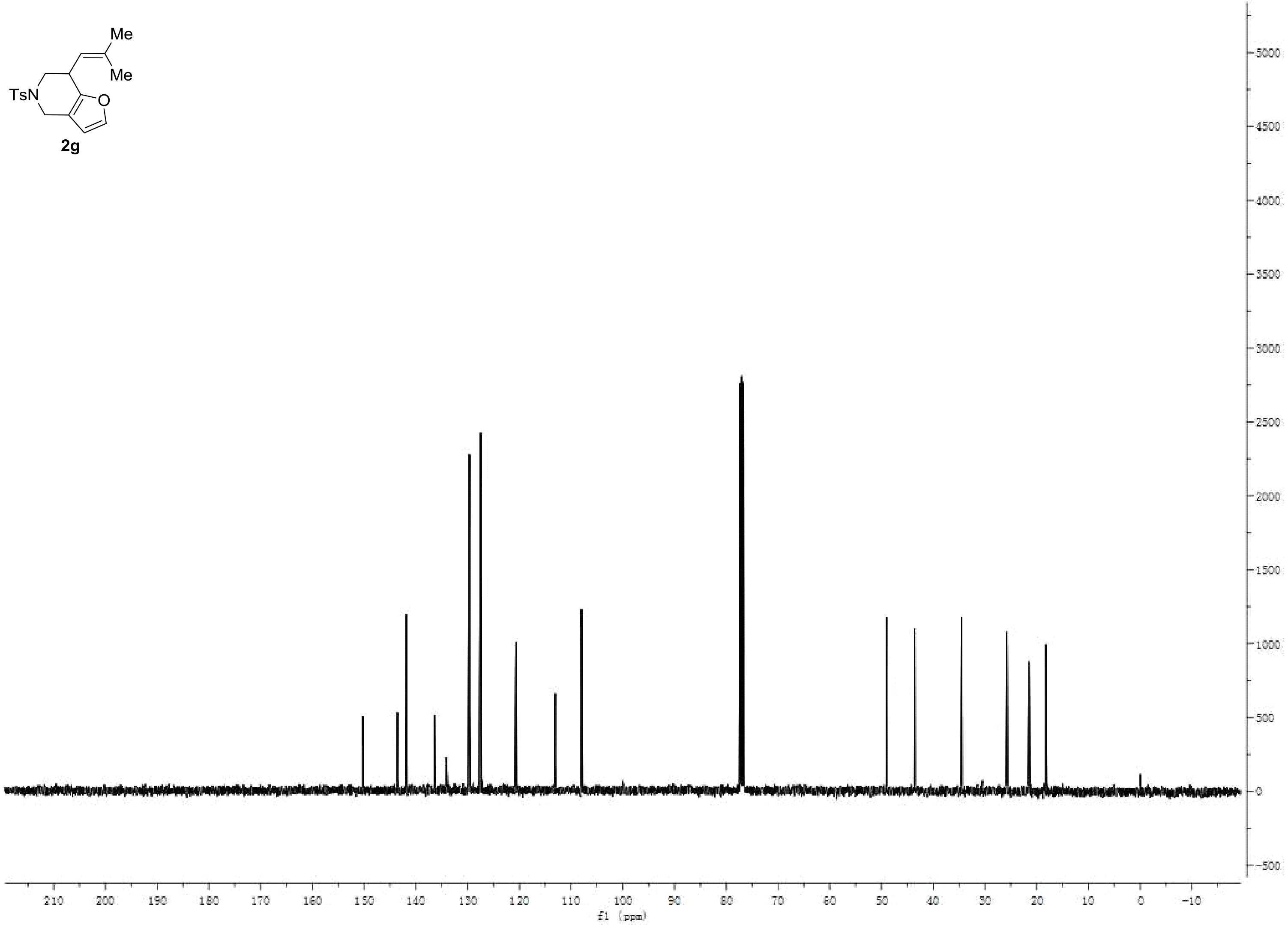
3e


40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
2.06
0.91
2.01
1.00
1.18
2.10
2.04
2.20
3.09
4.26
3.17
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

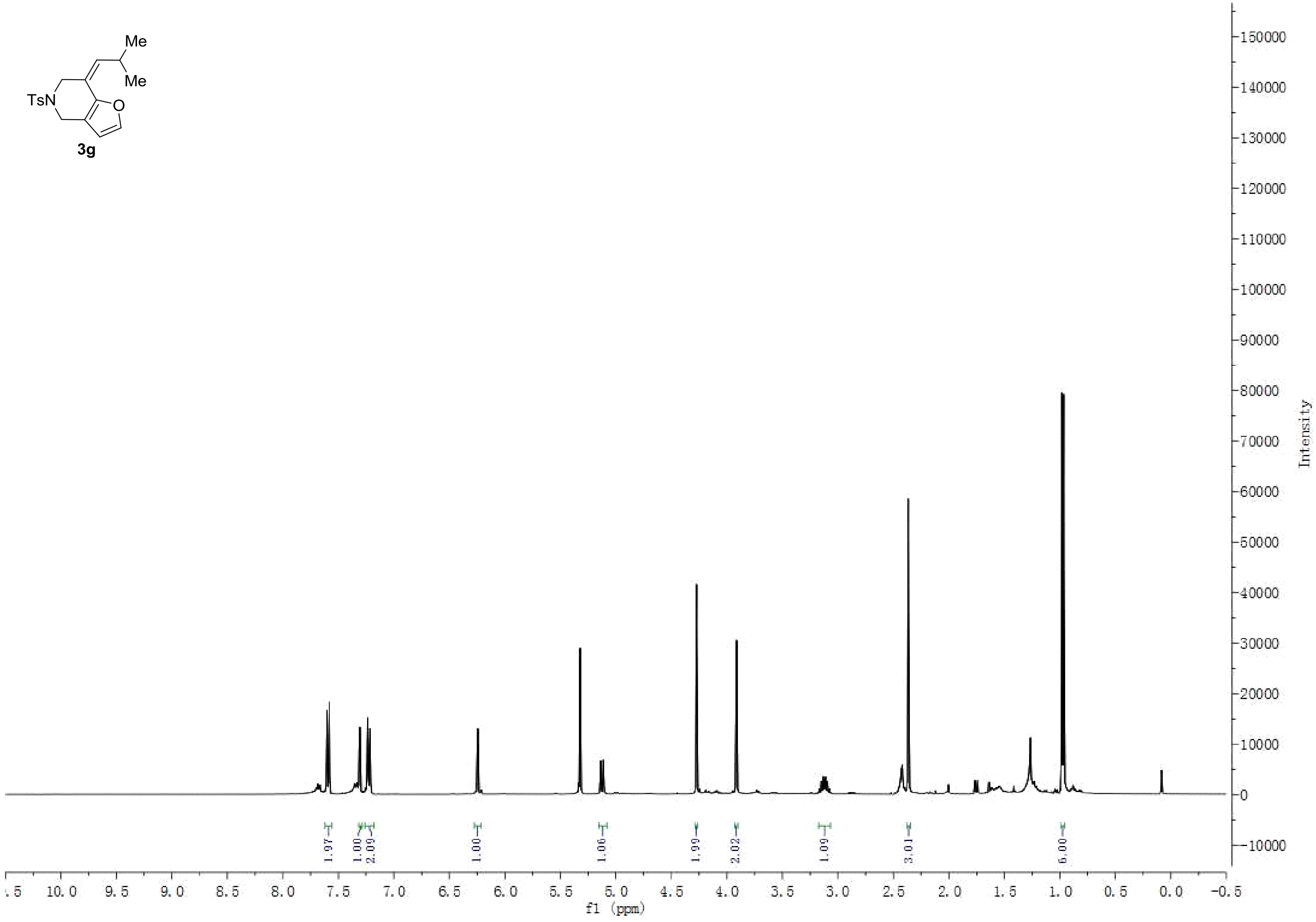

n-Pr
TsN
O
3e
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

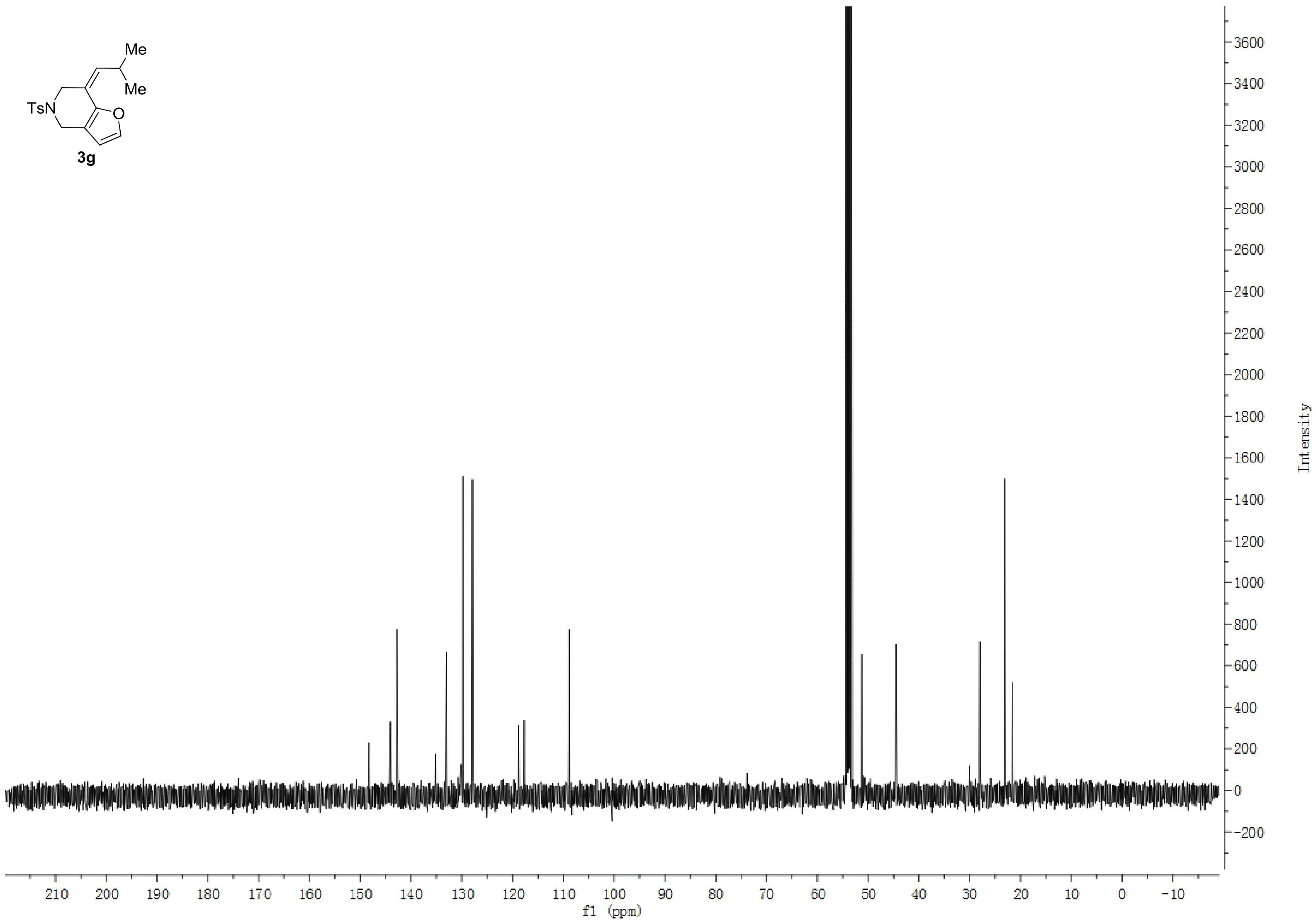

Me
Me
TsN
O
2.07
2.08
0.92
0.94
1.00
1.03
1.04
1.05
1.03
1.03
3.09
2.97
2.95
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

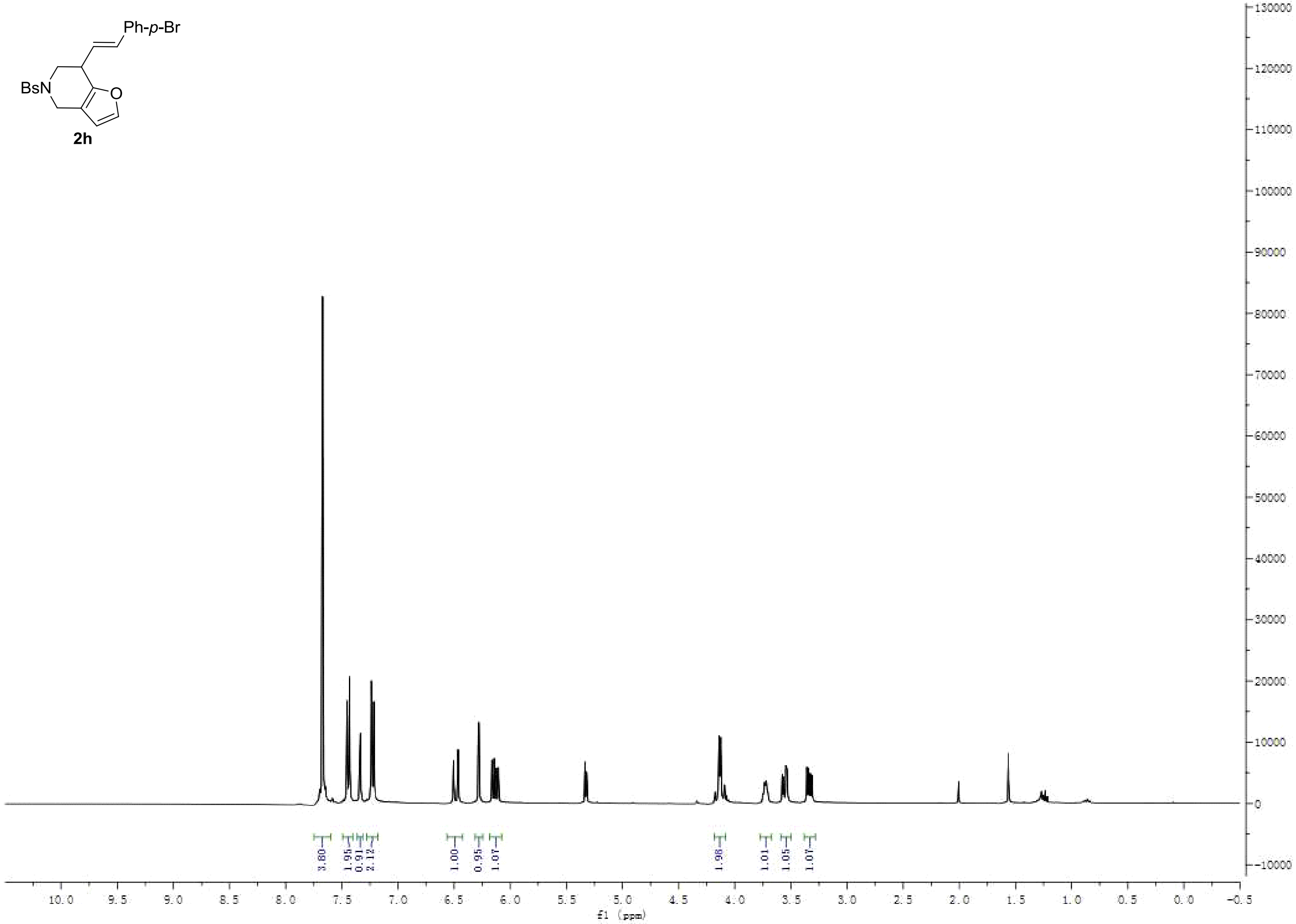
2g


Me
Me
TsN
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

2g


3g
Me
Me
TsN
O
1.97
1.00
2.09
1.00
1.06
1.99
2.02
1.09
3.01
6.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
Intensity

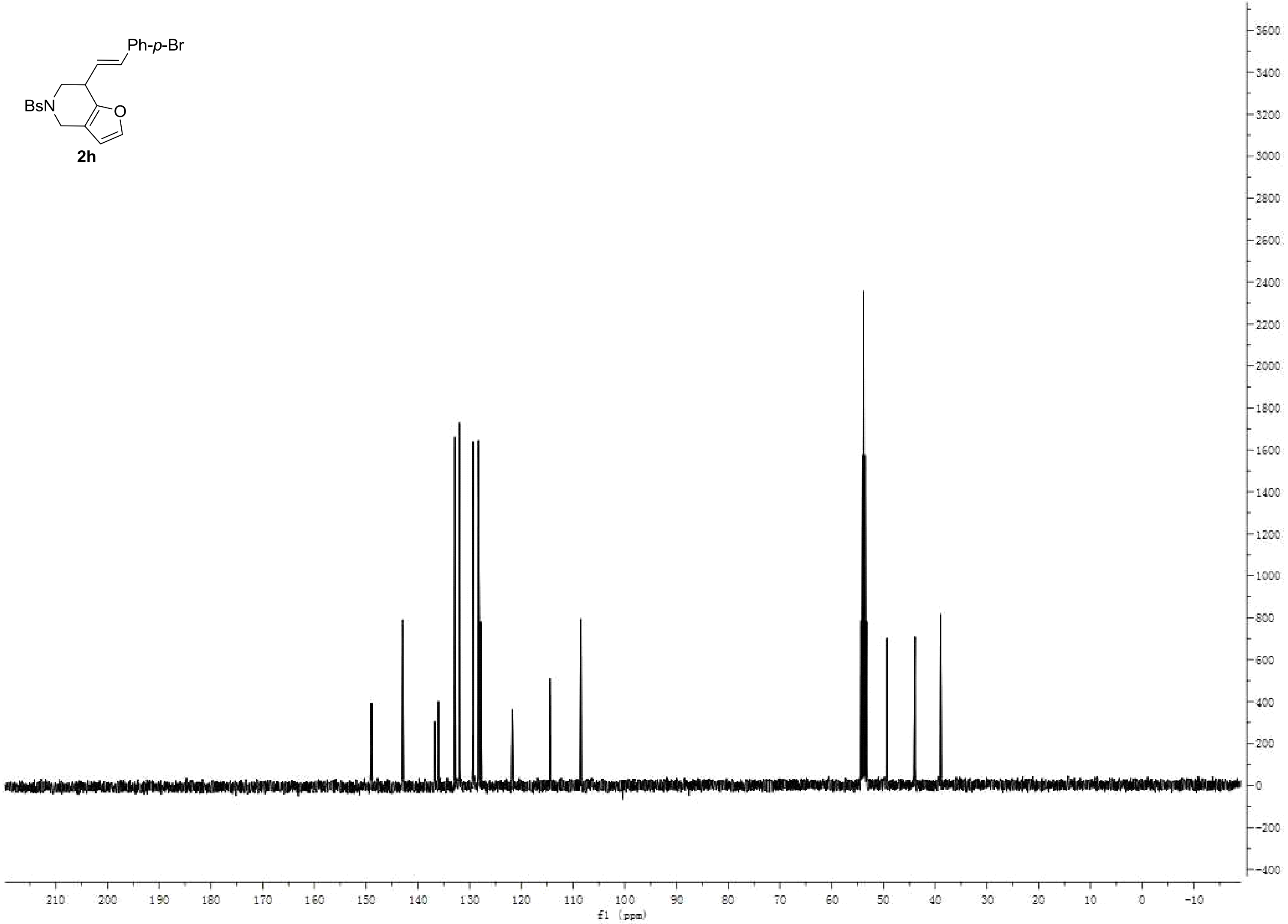

Me
Me
TsN
O
3g
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

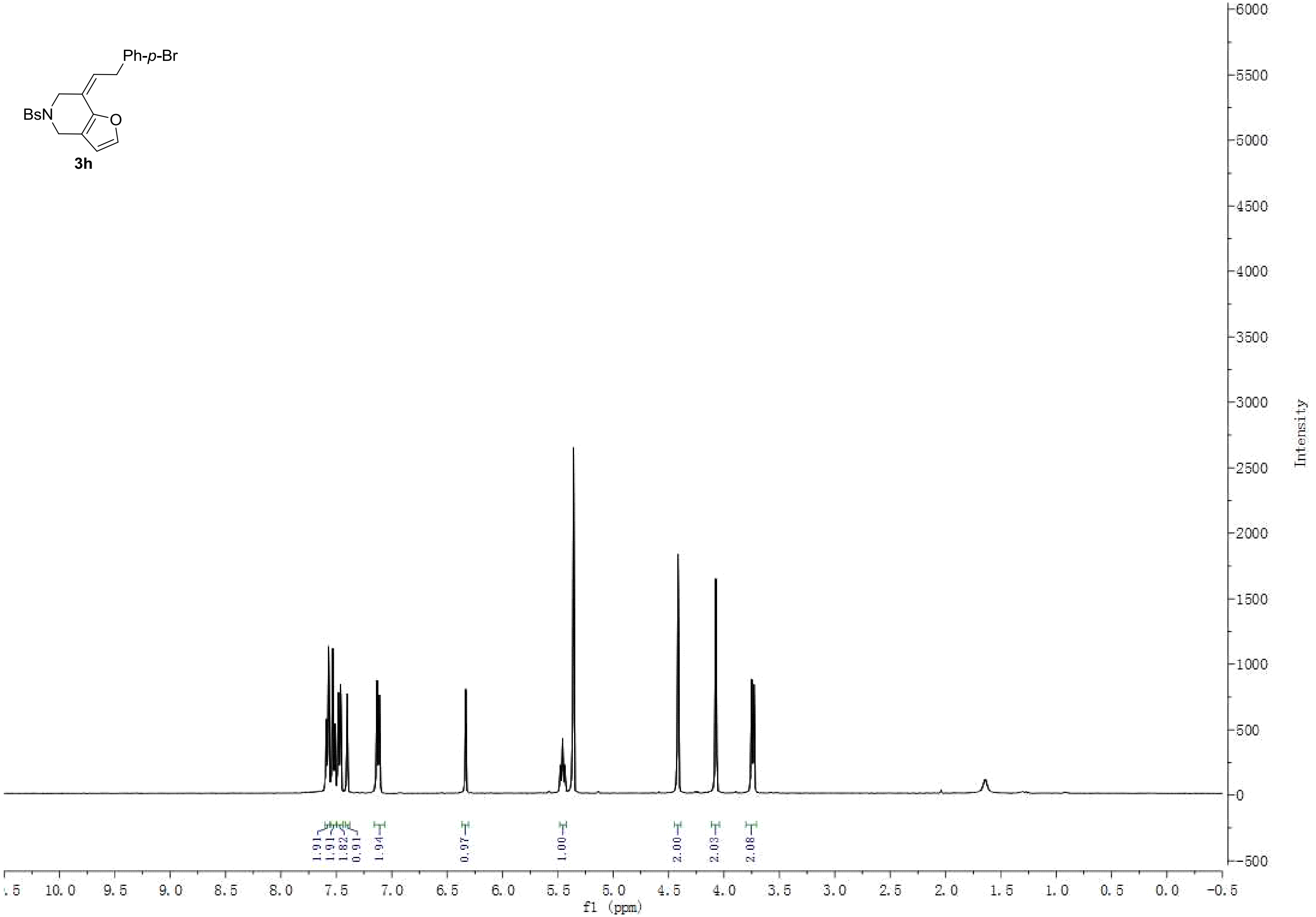

2h

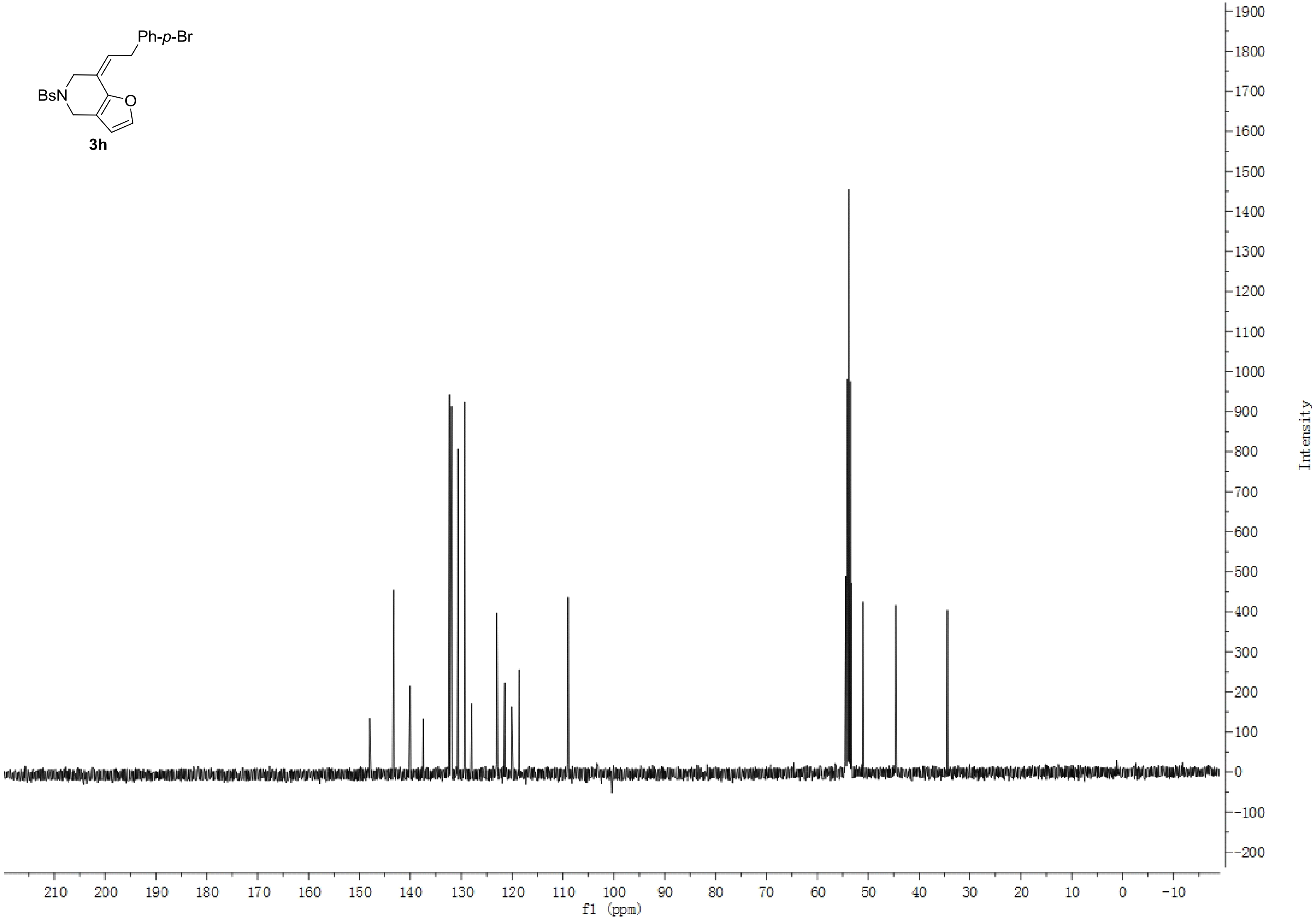
Ph-p-Br
BsN
O
3.80
1.95
0.91
2.12
1.00
0.95
1.07
1.98
1.01
1.05
1.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000

Ph-*p*-Br
BsN
O

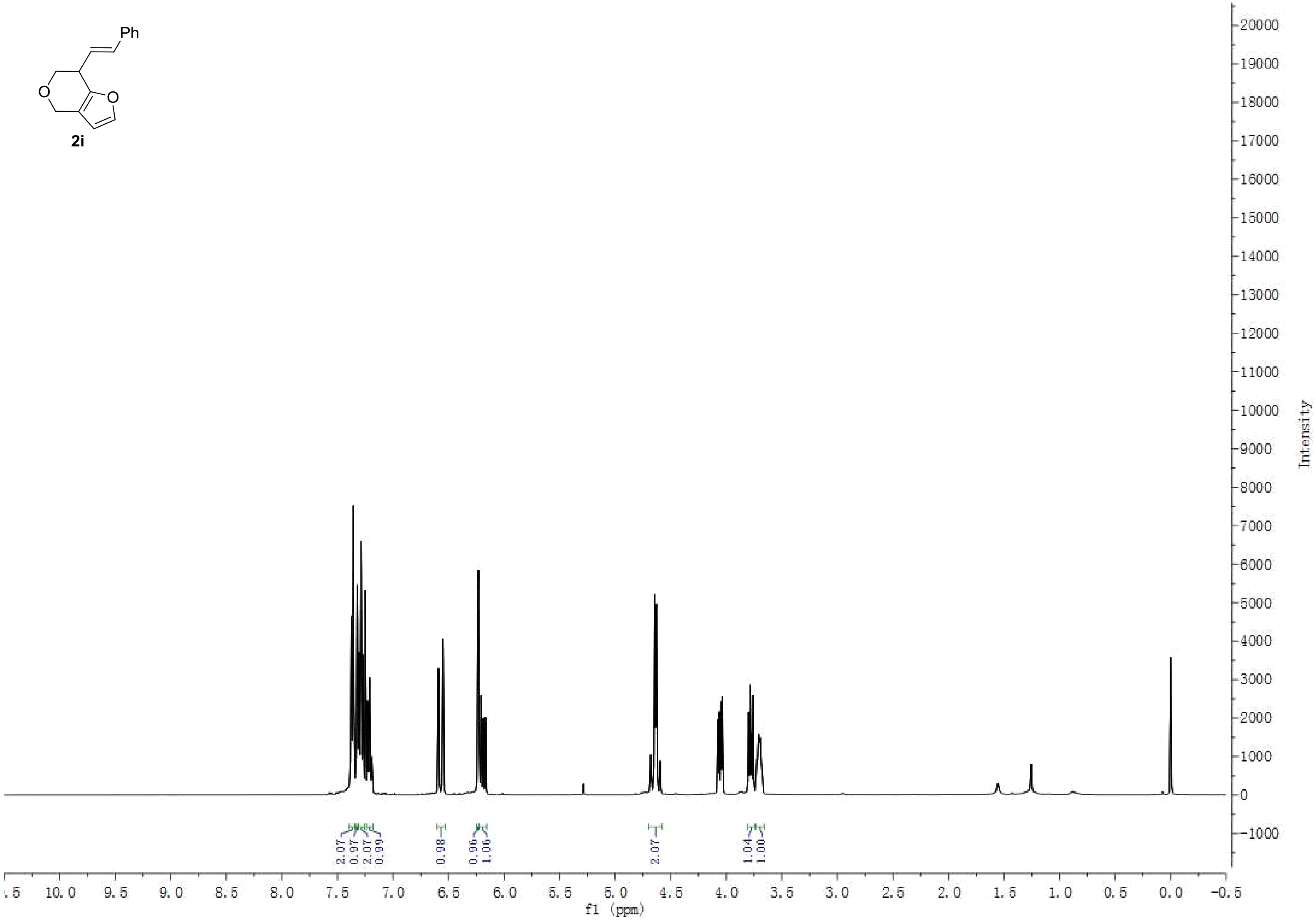
2h


3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
−400
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

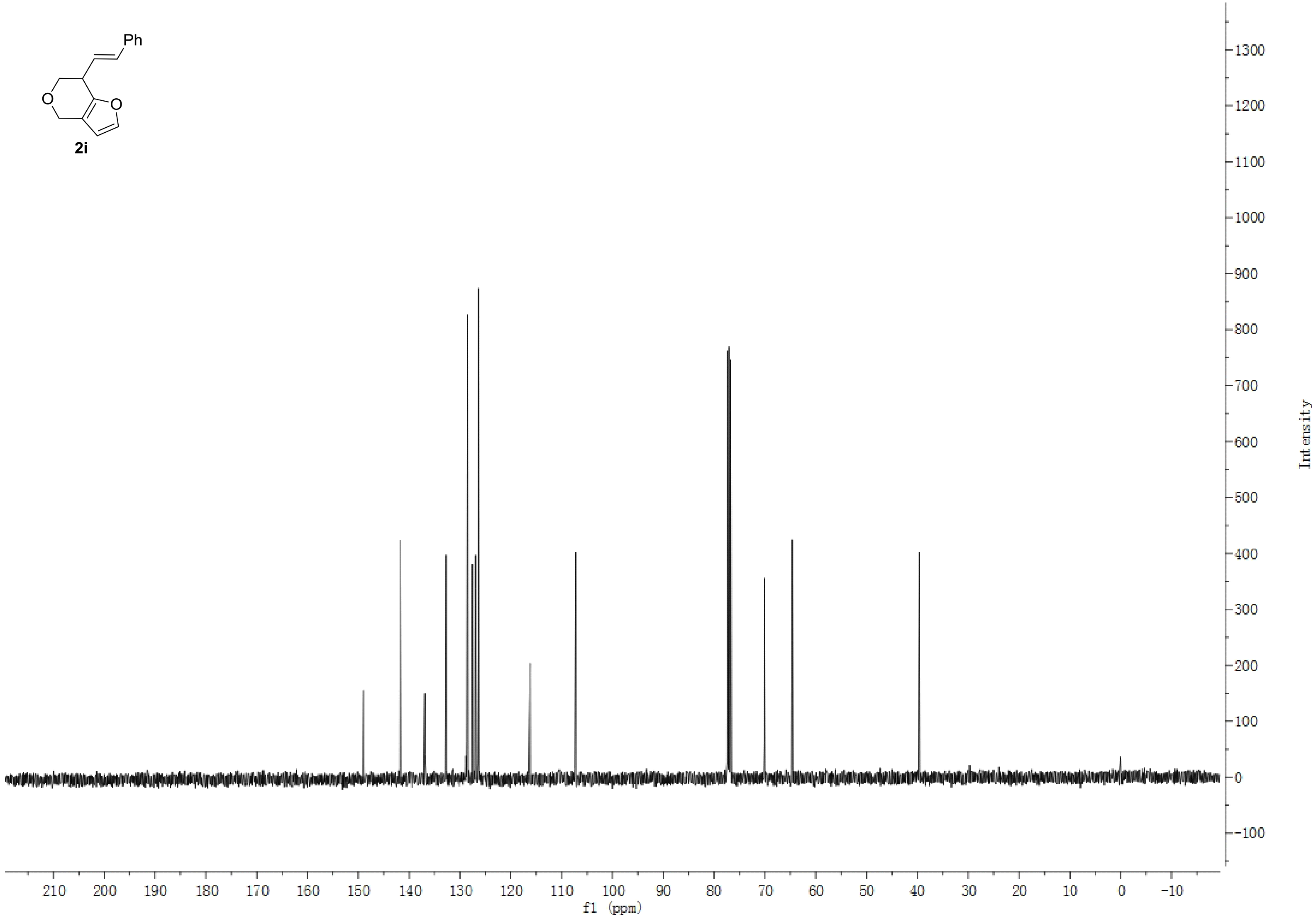

Ph-p-Br
BsN
O
3h
1.91
1.91
1.82
0.91
1.94
0.97
1.00
2.00
2.03
2.08
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
Intensity


Ph-*p*-Br
BsN
O
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3h

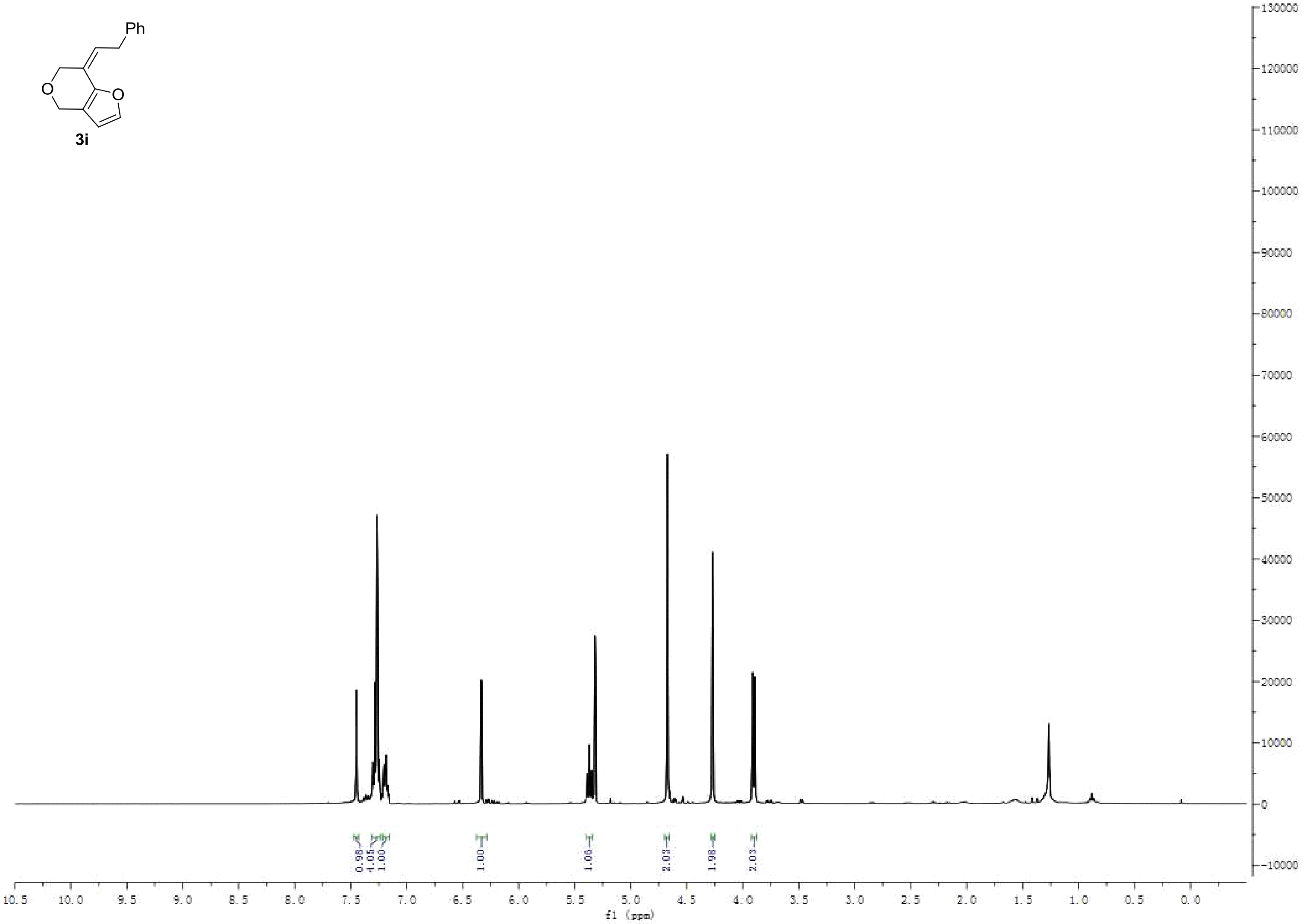

Ph
O
O
2.07
0.97
2.07
0.99
0.98
0.96
1.00
2.07
1.04
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

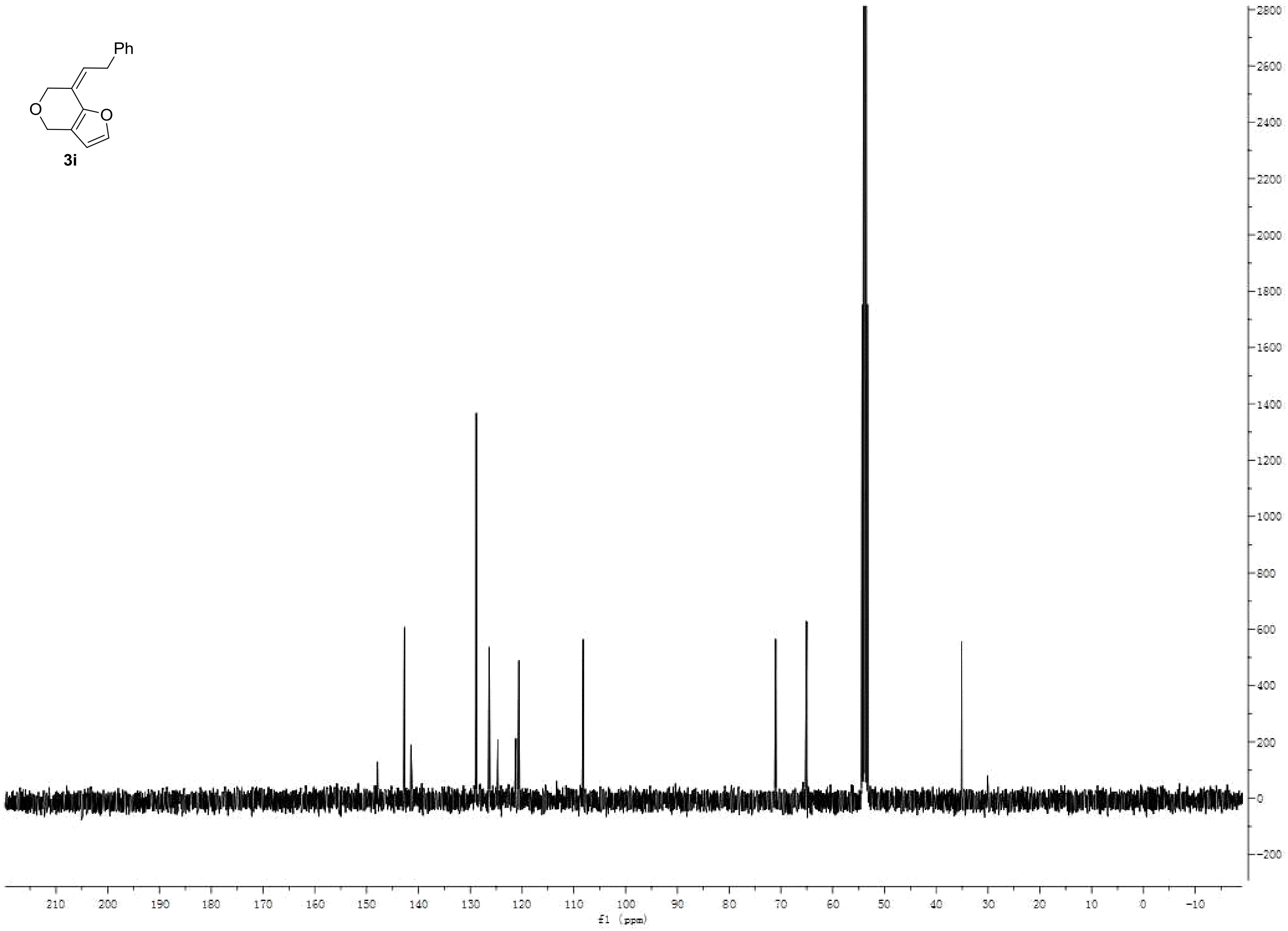
2i



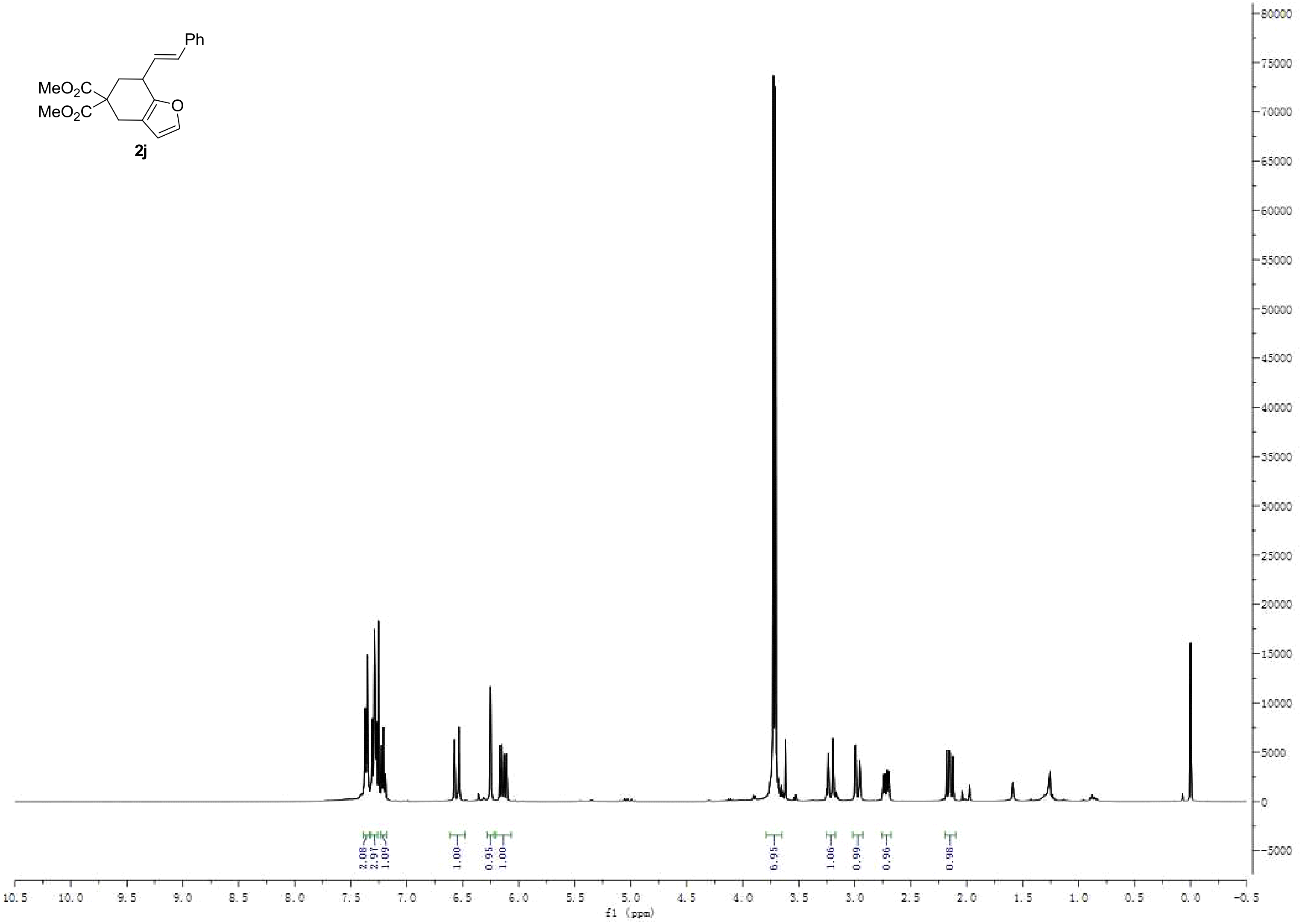
2i

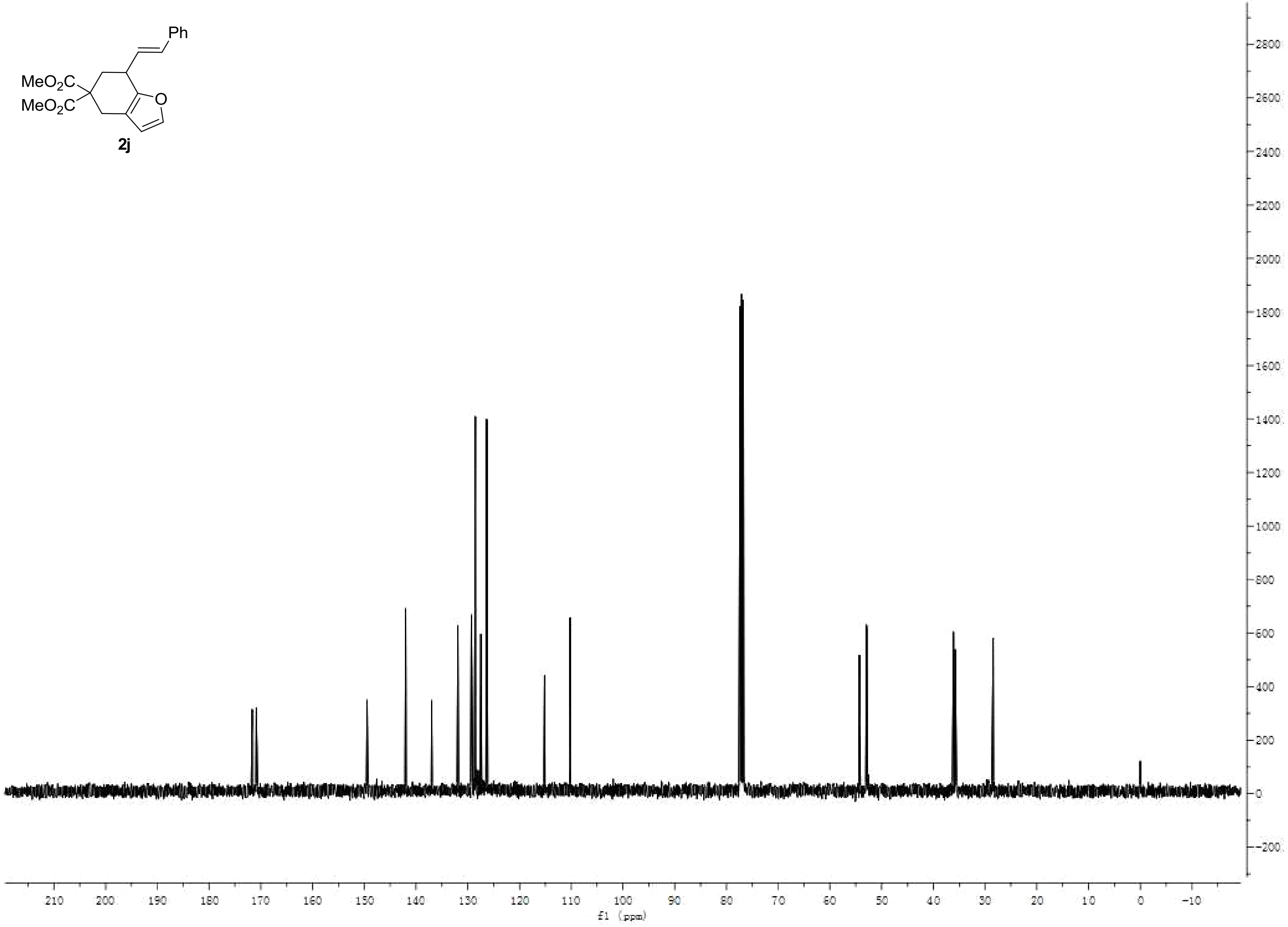
Ph
O
O
Intensity
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Ph
O
O
3i
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
0.98
4.05
1.00
1.00
1.06
2.03
1.98
2.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

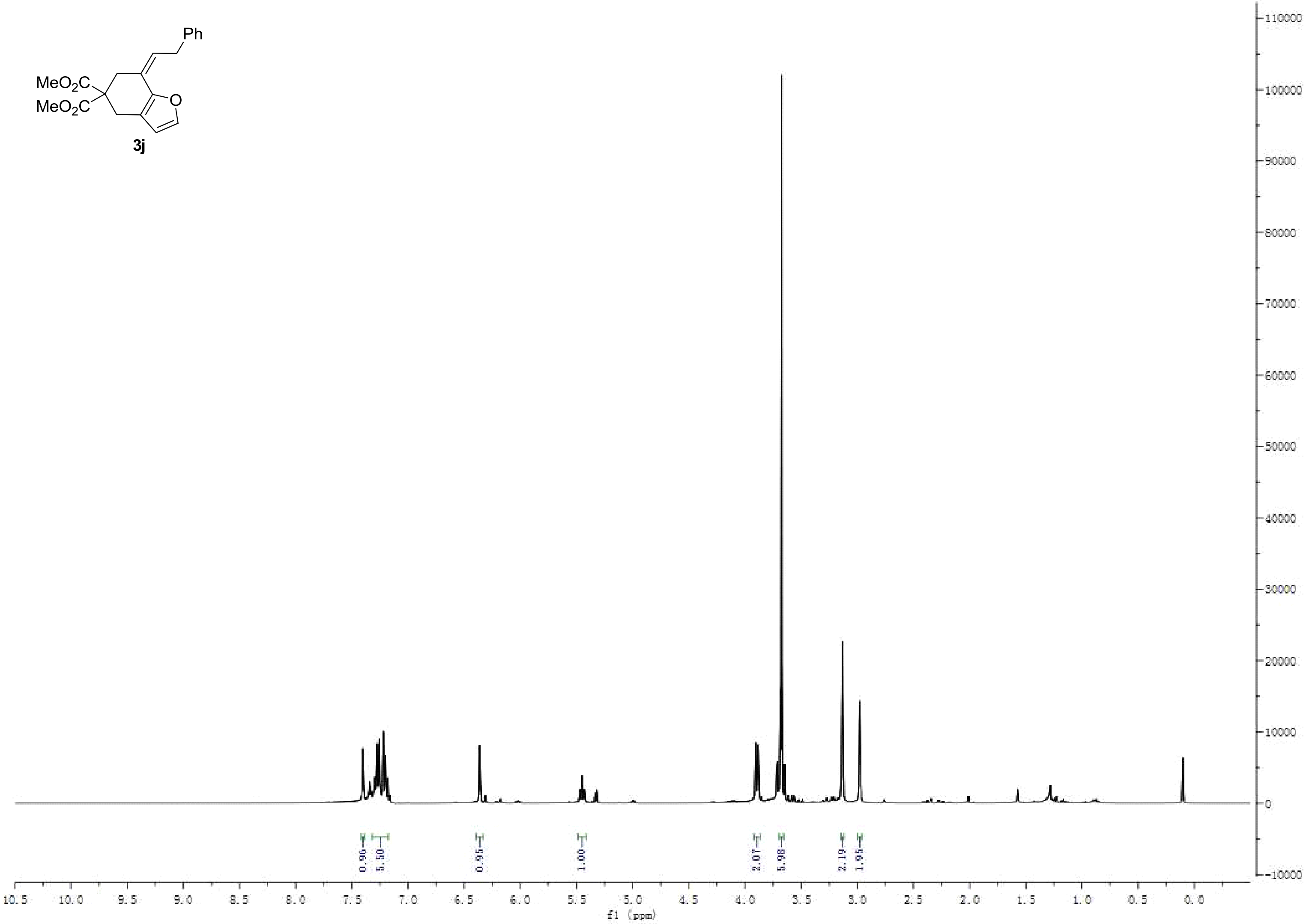

3i

Ph
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

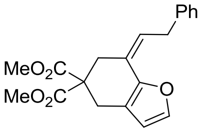

Ph
MeO$_2$C
MeO$_2$C
O
2j
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
2.08
2.97
1.09
1.00
0.95
1.00
6.95
1.06
0.99
0.96
0.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Ph
MeO$_2$C
MeO$_2$C
O
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

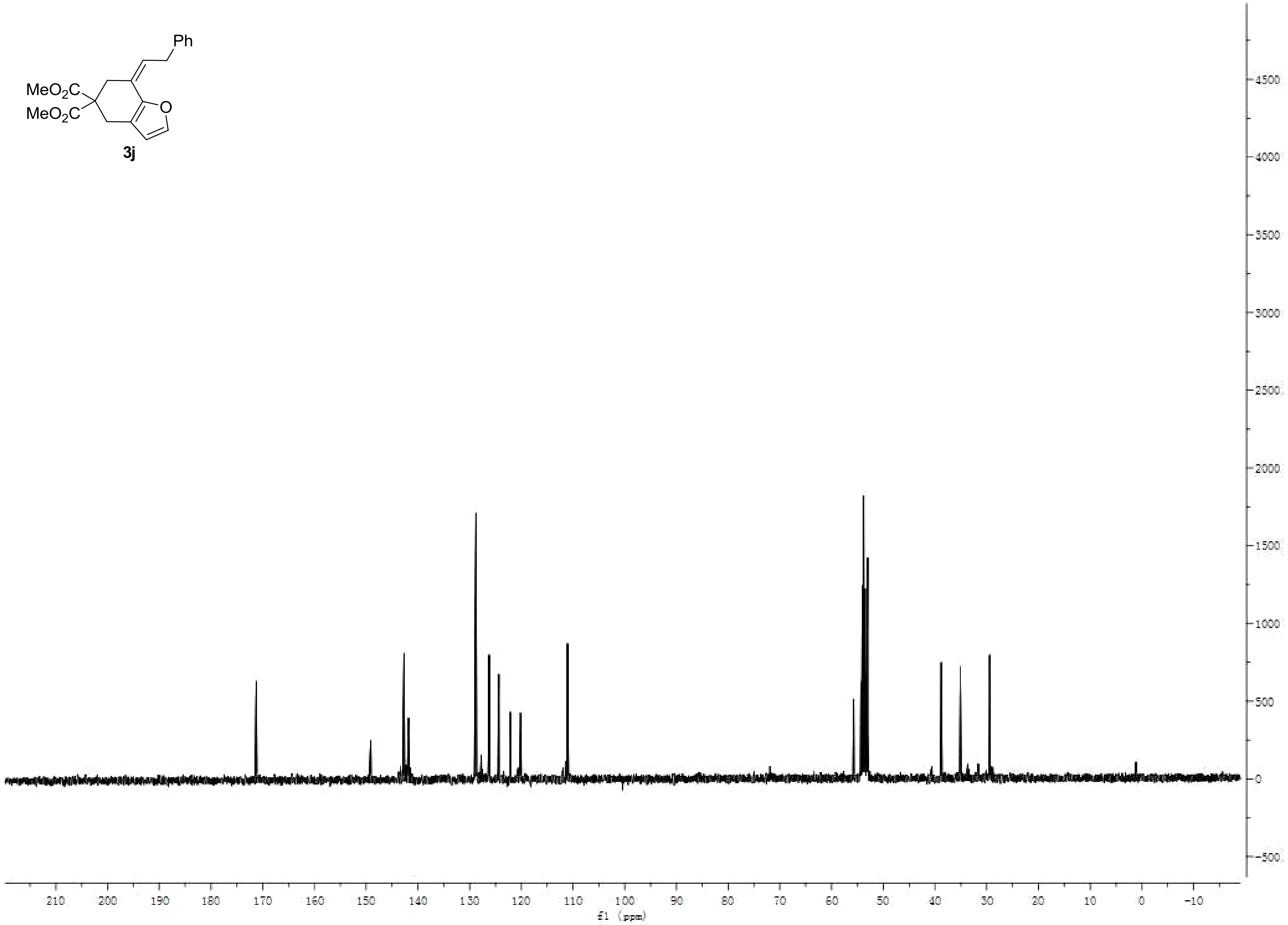
2j

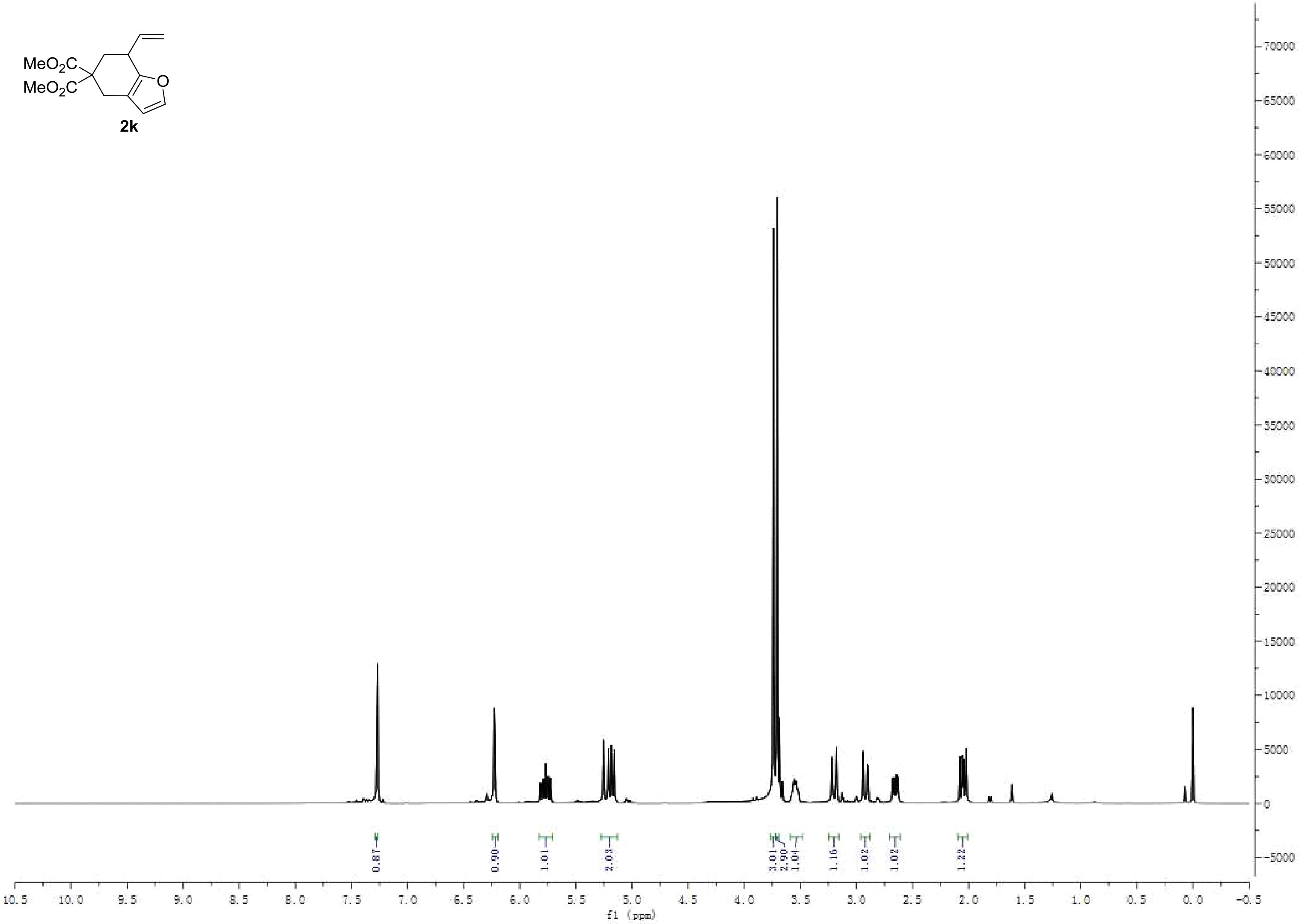

Ph
MeO2C
MeO2C
O
0.96
5.50
0.95
1.00
2.07
5.98
2.19
1.95
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

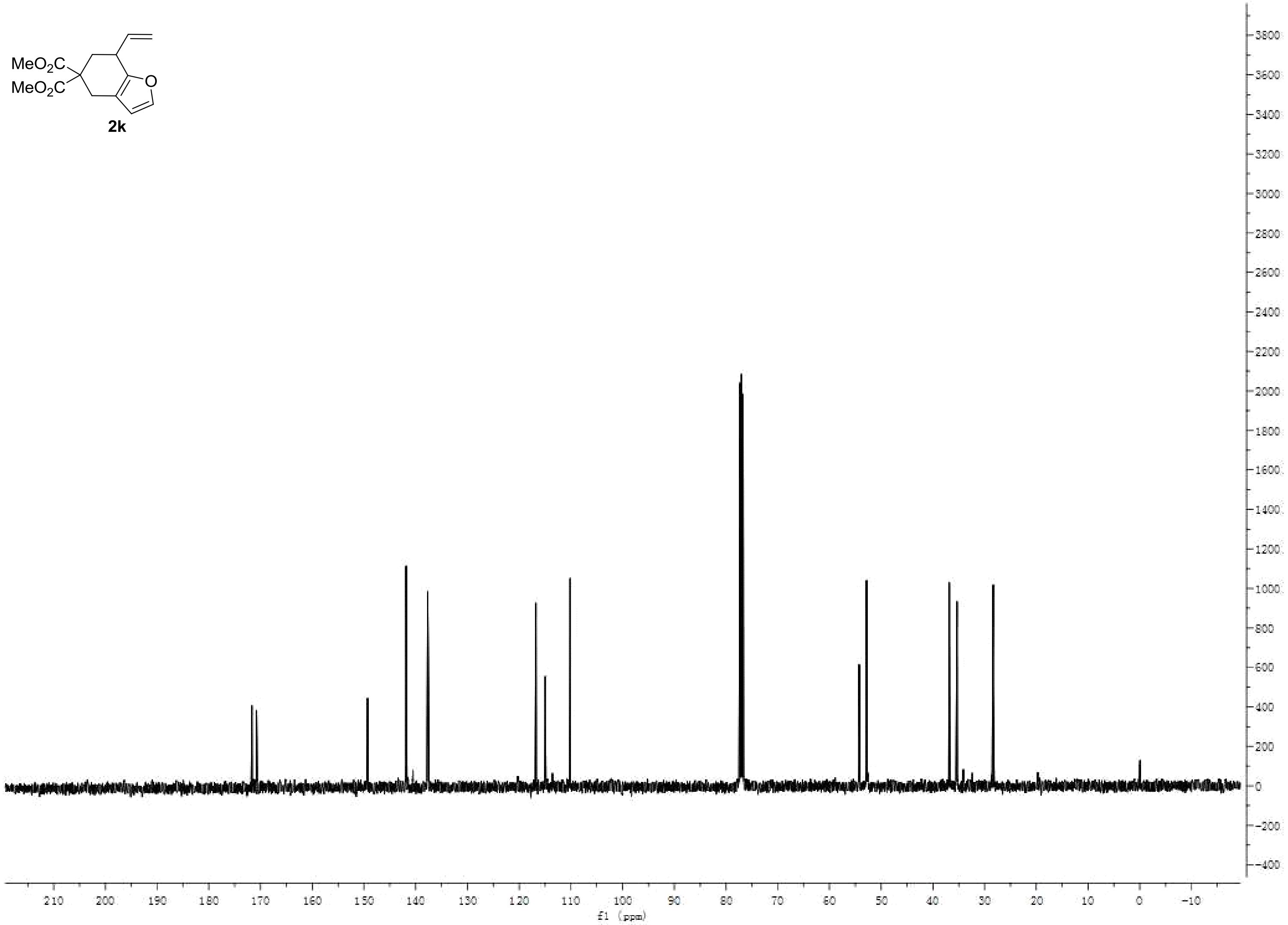
3j


Ph
MeO2C
MeO2C
O

3j

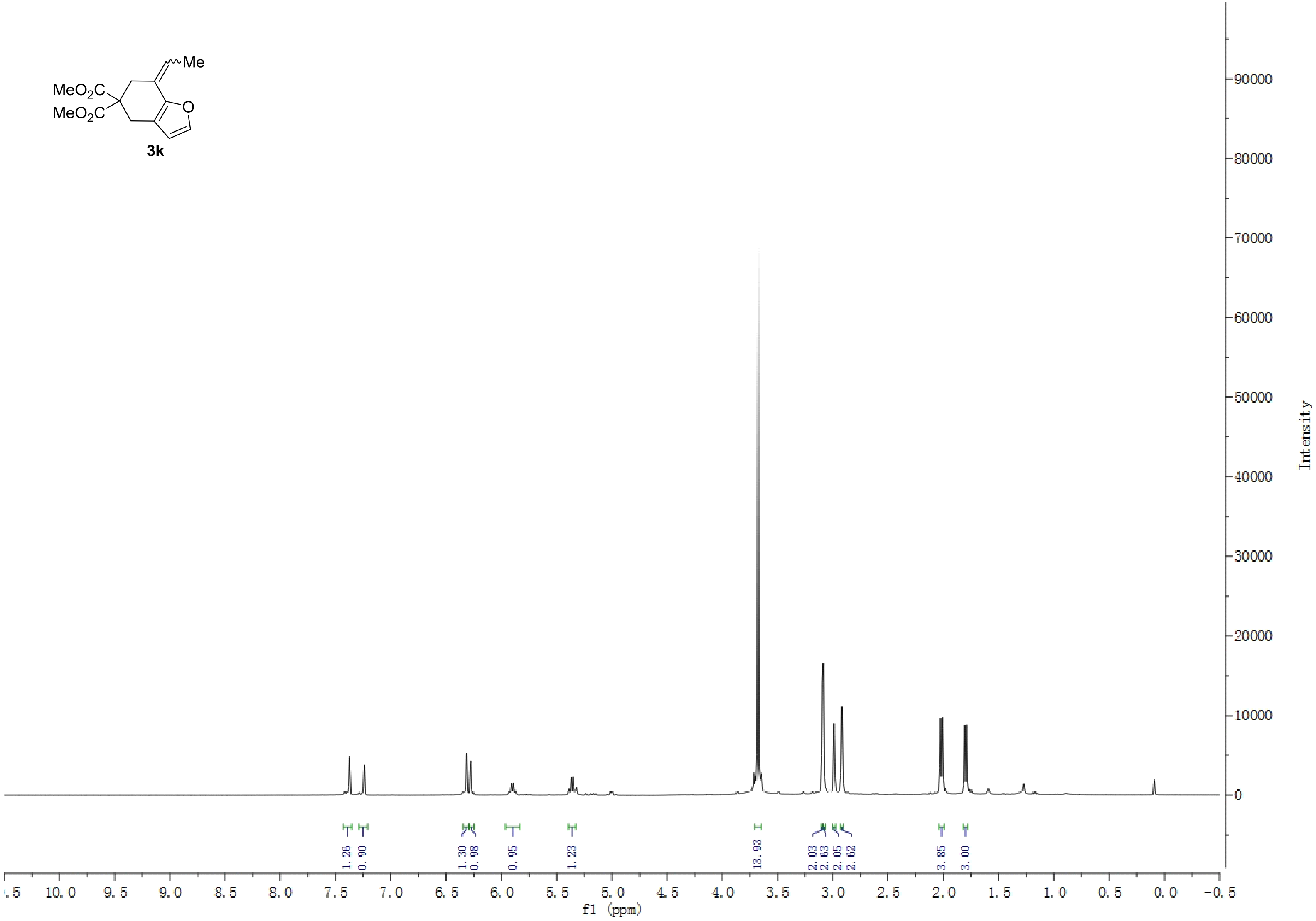

4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


MeO2C
MeO2C
O
2k
0.87
0.90
1.01
2.03
3.01
2.90
1.04
1.16
1.02
1.02
1.22
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


MeO2C
MeO2C
O
2k
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

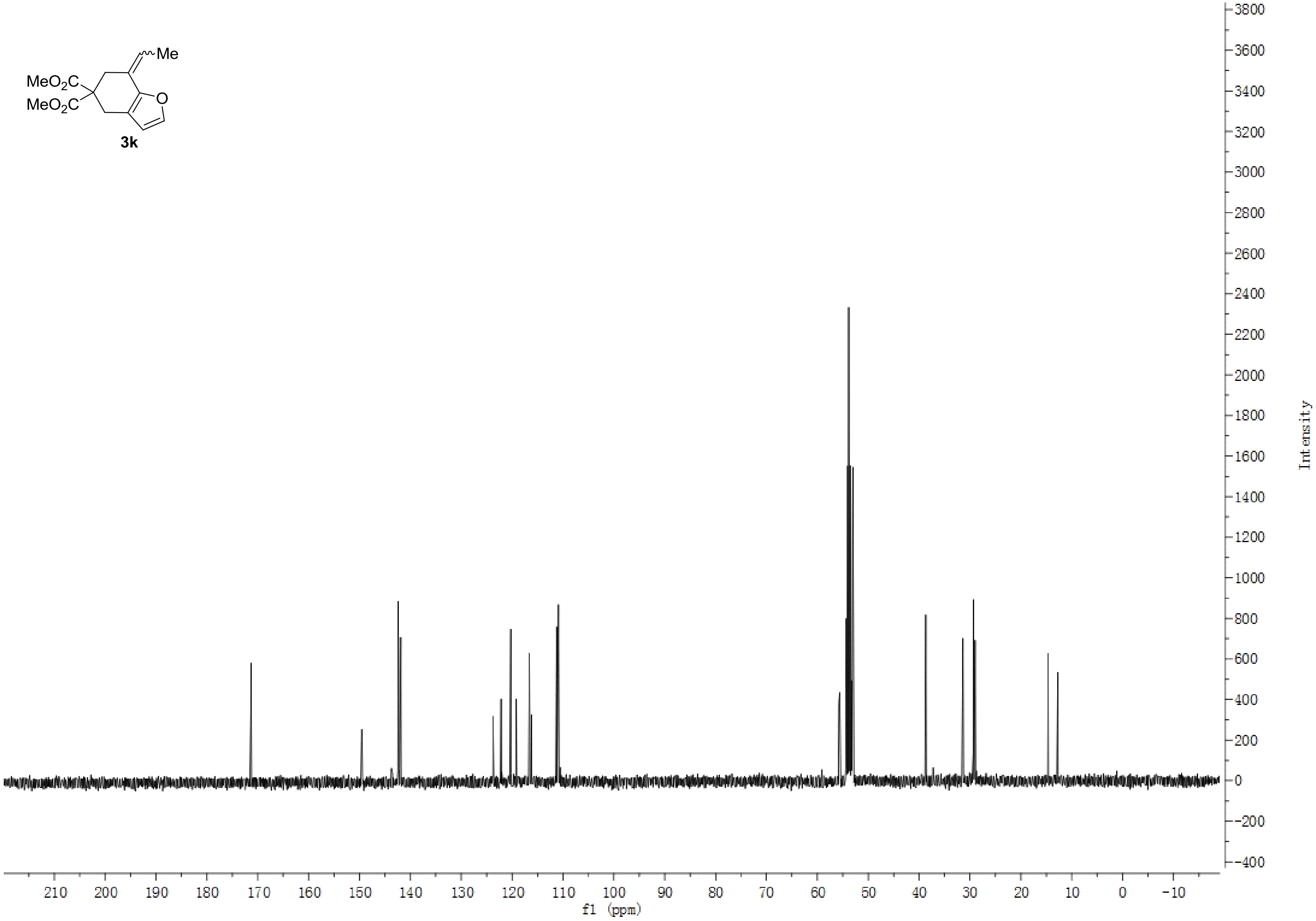
Me
MeO2C
MeO2C
O

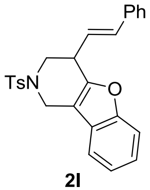
3k


90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Intensity
1.26
0.90
1.30
0.98
0.95
1.23
13.93
2.03
2.03
2.05
2.02
3.85
3.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

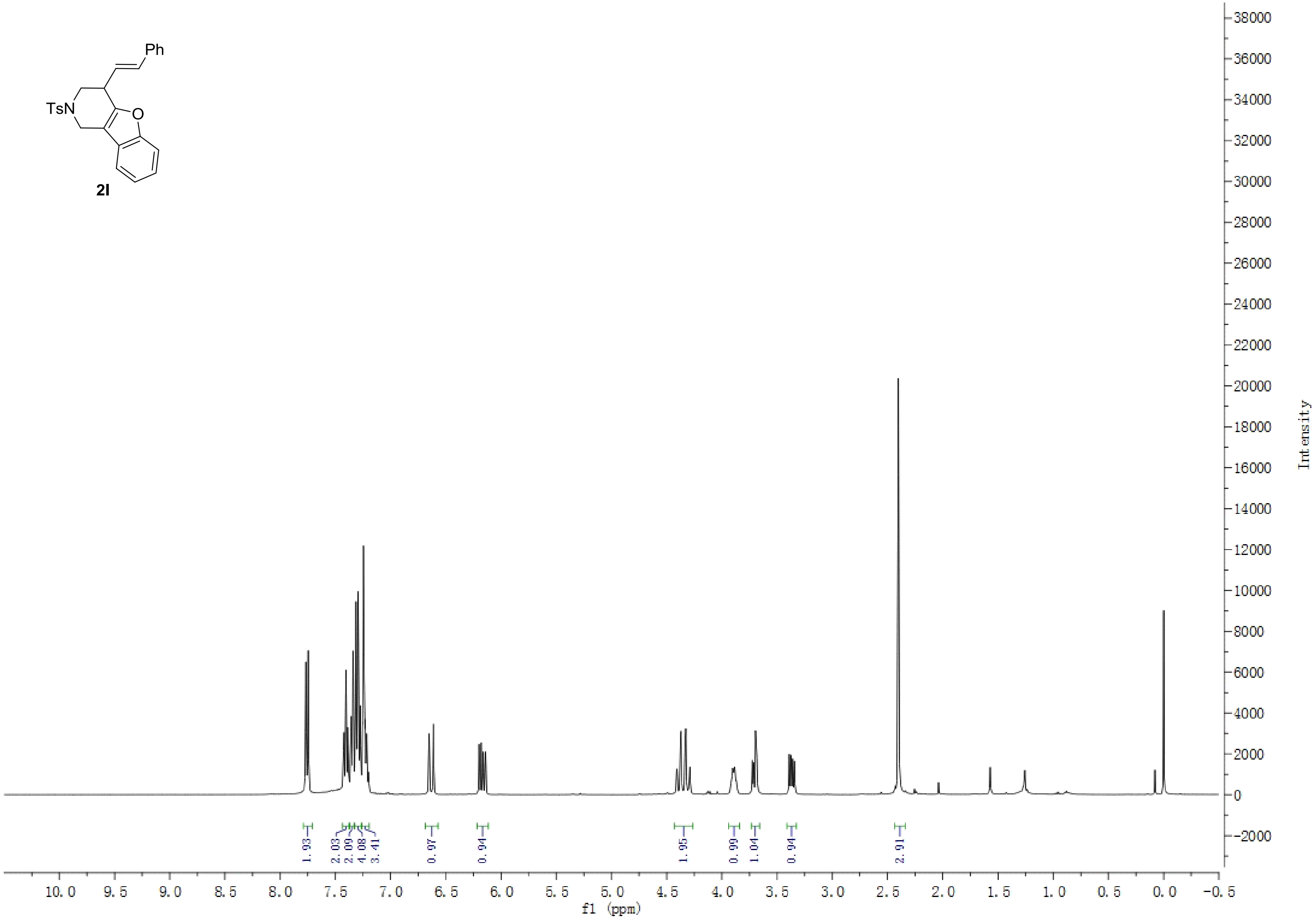
Me
MeO2C
MeO2C
O

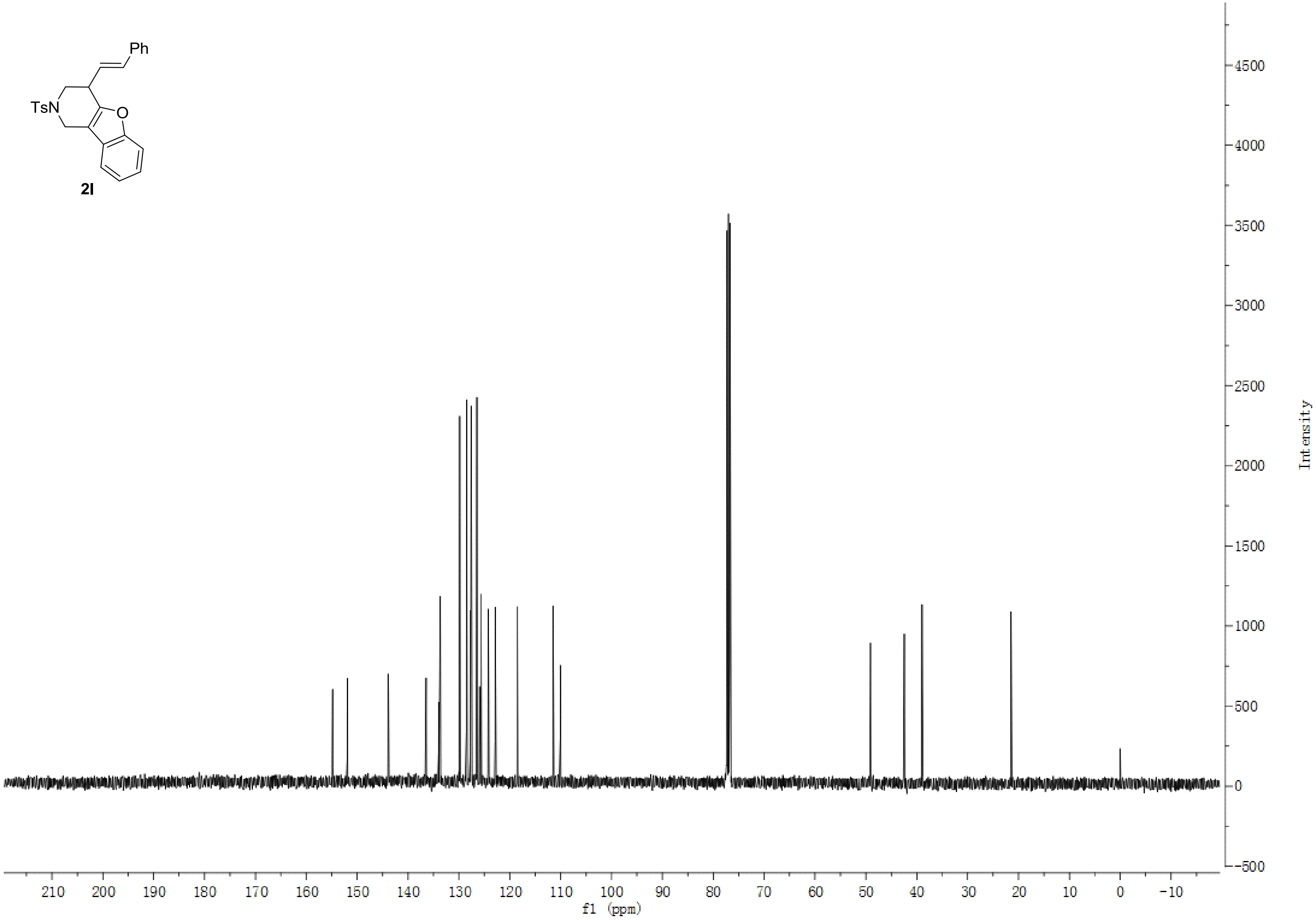
3k


3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
−400
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Ph
TsN
O

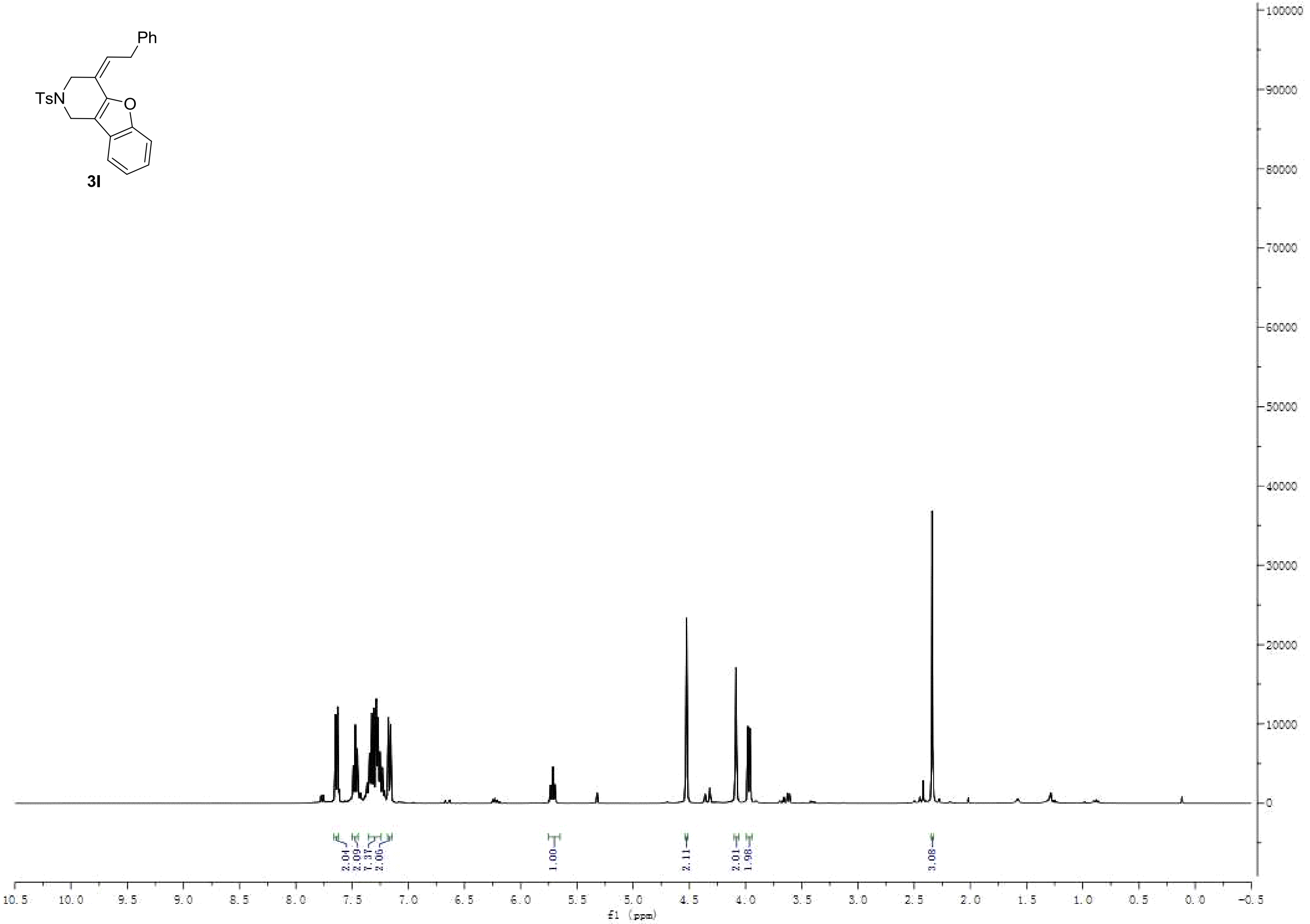
2l


38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
1.93
2.03
2.09
4.08
3.41
0.97
0.94
1.95
0.99
1.04
0.94
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



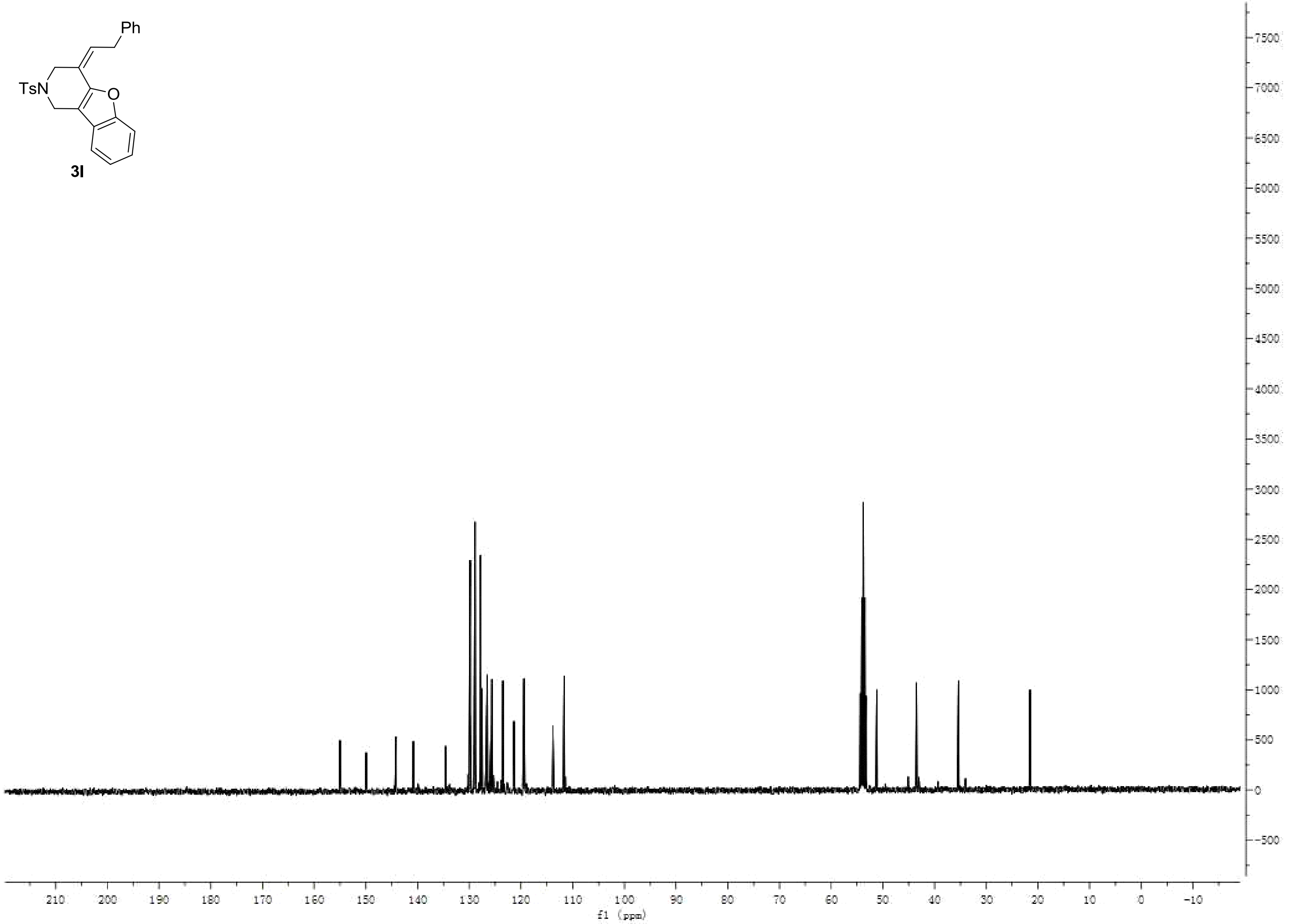
2l

Ph
TsN
O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3l

100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
2.04
2.09
7.31
2.06
1.00
2.11
2.01
1.98
3.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



3l

Ph
TsN
O
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)