Electronic Supplementary Information

Pd-catalyzed [4+2] cycloaddition of methylene cyclic carbamates with dihydropyrazolone-derived alkenes: Synthesis of spiropyrazolones

Biming Mao,[ab] Jiaqing Xu,[a] Wangyu Shi,[a] Wei Wang,[c] Yongjun Wu,[c] Yumei Xiao,*[a] and Hongchao Guo*[a]

[a] Department of Chemistry and Innovation Center of Pesticide Research, P. R. China Agricultural University, Beijing 100193, China

[b] Institute of Materia Medica, Shandong First Medical University & Shandong Academy of Medical Sciences, Jinan 250117, Shandong, P. R. China

[c] College of Public Health, Zhengzhou University, Zhengzhou 450001, P. R. China

E-mail: hchguo@cau.edu.cn, xiaoyumei23@126.com

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General Information

All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 300, 400 or 600 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on a Perkin-Elmer 343 polarimeter. Melting points were determined by an X-4 digital micro melting point apparatus. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. X-ray crystallographic data were collected using a Gemini E Rigaku.

Starting materials and reagents were purchased directly from commercial suppliers and used without further purifications. All solvents used as reaction medium were distilled before the use. The *N*-tosyl carbamate **1a**[1], unsaturated pyrazolones **2**[2], were synthesized using known literature procedures.

General Procedure for Pd-Catalyzed [4+2] Cycloaddition

Under argon atmosphere, to a mixture of *N*-tosyl carbamate **1a** (0.15 mmol) , unsaturated pyrazolones **2** (0.10 mmol) and catalyst $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol%, 0.0025 mmol) / Xantphos (7.5 mol %, 0.0075 mmol) in a Schlenk tube, 1 mL of DCM were added at room temperature. The resulting mixture was stirred until the starting material were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (11.1% EtOAc / PE) to afford the corresponding cycloaddition product **3**.

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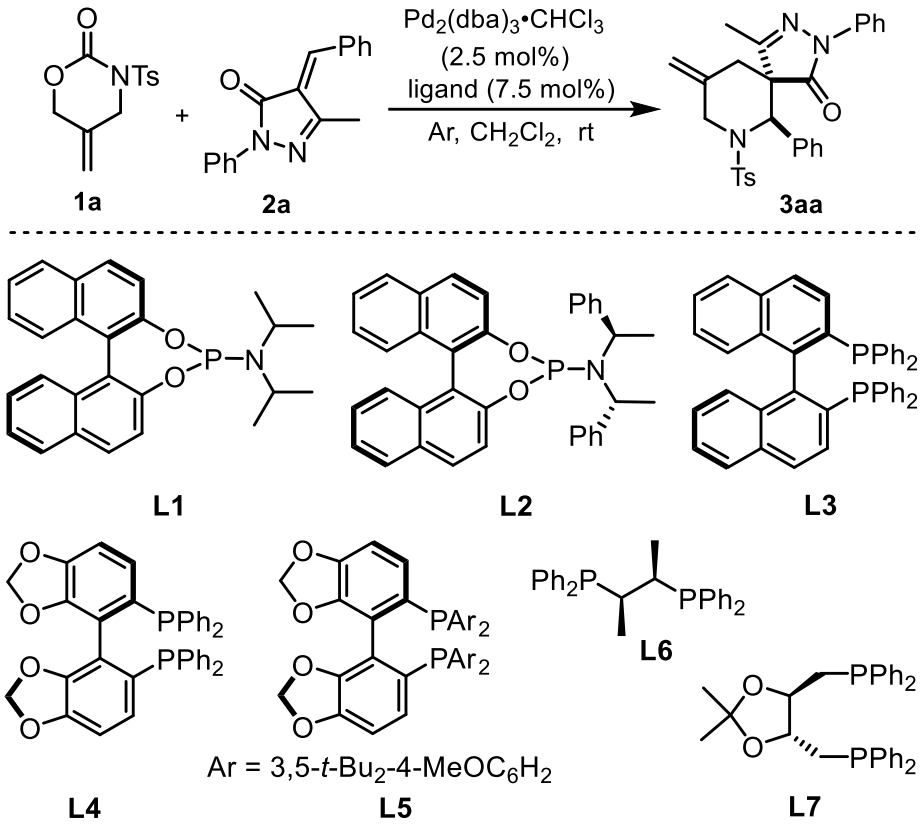
[1] Allen, B. D. W.; Connolly, M. J.; Harrity, J. P. A. *Chem. Eur. J.* **2016**, *22*, 13000.

[2] Malerich, J. P.; Hagihara, K.; Rawal, V. H. *J. Am. Chem. Soc.* **2008**, *130*, 14416.

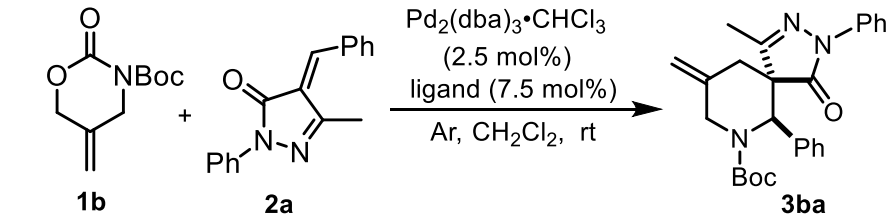
Table S1. Screening Reaction Conditions for Asymmetric Reaction of N-Tosyl Methylene Cyclic Carbamate 1a

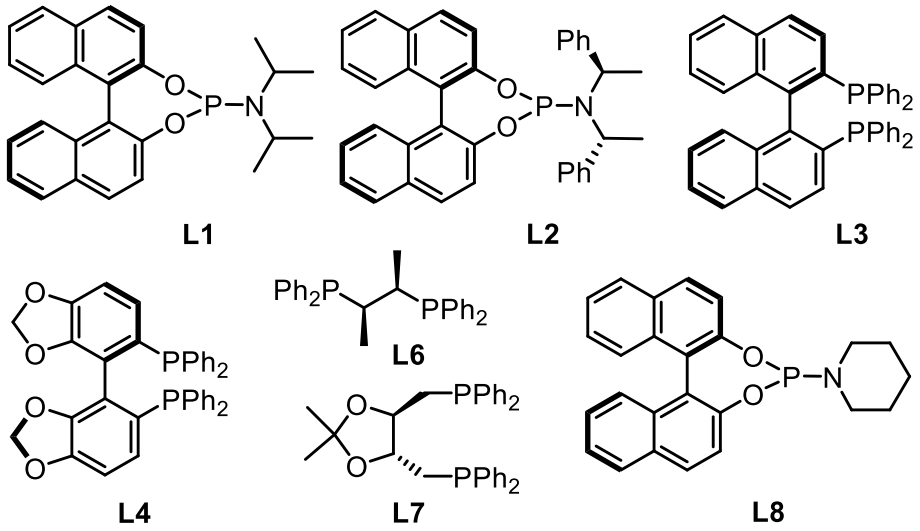


entry	ligand	t/h	yield (%)[b]	ee (%)[c]
1	**L1**	24	NR	-
2	**L2**	24	NR	-
3	**L3**	24	NR	-
4	**L4**	24	NR	-
5	**L5**	24	NR	-
6	**L6**	24	NR	-
7	**L7**	24	51	5

[a] All reactions were carried out with N-tosyl methylene cyclic carbamate **1a** (0.15 mmol) and alkene **2a** (0.10 mmol) in 1 mL of CH_2Cl_2. [b] Isolated yield and dr is >20:1, determined by ^1H NMR analysis of the crude product. [c] Determined by chiral HPLC analysis.

Table S2. Screening Reaction Conditions for Asymmetric Reaction of N-Boc Methylene Cyclic Carbamate 1b



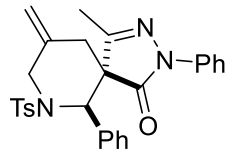


entry	ligand	t/h	yield (%)[b]	ee (%)[c]
1	**L1**	72	17	44
2	**L2**	72	21	39
3	**L3**	48	NR	-
4	**L4**	48	NR	-
5	**L6**	48	NR	-
6	**L7**	24	14	6
7	**L8**	72	15	50

[a] All reactions were carried out with N-Boc cyclic carbamate **1b** (0.15 mmol) and alkene **2a** (0.10 mmol) in 1 mL of CH_2Cl_2. [b] Isolated yield, and dr is >20:1, determined by ^1H NMR analysis of the crude product. [c] Determined by chiral HPLC analysis.

Characterization Data of the Products 3

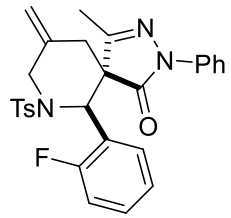
4-methyl-9-methylene-2,6-diphenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3aa)



3aa

Prepared according to the general procedure as described above in 84% yield (40.7 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 187 – 190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 2H), 7.53 – 7.43 (m, 2H), 7.30 – 7.07 (m, 10H), 5.29 (s, 1H), 5.12 (s, 1H), 4.91 (d, *J* = 2.3 Hz, 1H), 4.75 (s, 2H), 2.58 – 2.10 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 160.0, 143.3, 136.9, 136.5, 136.3, 136.1, 129.2, 128.3, 128.1, 127.7, 126.9, 125.7, 124.9, 118.9, 111.8, 57.9, 57.5, 47.2, 33.5, 21.2, 14.2; IR (film) ν_{max} 3063, 2923, 1708, 1596, 1499, 1452, 1397, 1347, 1285, 1257, 1183, 1119, 1092, 1053, 1008, 984, 936, 840, 811, 758, 736, 691, 638 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{28}N_3O_3S^+$ $[M+H]^+$ 486.1846, found 486.1851.

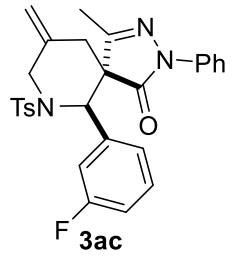
6-(2-fluorophenyl)-4-methyl-9-methylene-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ab)



3ab

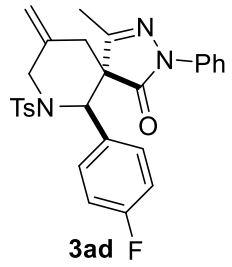
Prepared according to the general procedure as described above in 98% yield (49.3 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 166 – 169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.50 (m, 3H), 7.43 – 6.88 (m, 10H), 5.55 (s, 1H), 5.16 (s, 1H), 5.00 – 4.70 (m, 3H), 2.48 – 2.12 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 160.6, 159.2 (d, *J* = 245.4 Hz), 143.7, 137.2, 136.3, 135.9, 129.8 (d, *J* = 2.1 Hz), 129.7, 129.5, 129.3 (d, *J* = 3.4 Hz), 128.6, 127.2, 125.2, 124.1 (d, *J* = 3.6 Hz), 119.2, 114.9 (d, *J* = 22.6 Hz), 112.5, 57.2, 52.0, 48.0, 33.8, 21.6, 14.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ –116.29; IR (film) ν_{max} 3065, 2925, 1708, 1615, 1596, 1499, 1456, 1435, 1396, 1349, 1306, 1286, 1226, 1184, 1120, 1091, 1054, 1009, 989, 932, 840, 807, 754, 735, 690, 660 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FN_3NaO_3S^+$ $[M+Na]^+$ 526.1571, found 526.1572.

6-(3-fluorophenyl)-4-methyl-9-methylene-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ac)



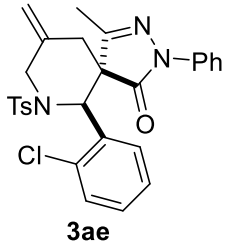
Prepared according to the general procedure as described above in 84% yield (42.3 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 147 – 150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.46 (m, 4H), 7.40 – 7.07 (m, 6H), 6.86 (tdt, *J* = 6.0, 4.3, 1.9 Hz, 3H), 5.28 (s, 1H), 5.14 (d, *J* = 2.2 Hz, 1H), 4.93 (s, 1H), 4.75 (s, 2H), 2.51 – 2.06 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 162.6 (d, *J* = 246.9 Hz), 160.1, 143.9, 139.5 (d, *J* = 6.7 Hz), 137.2, 136.2 (d, *J* = 4.1 Hz), 130.1 (d, *J* = 8.2 Hz), 129.7, 129.5, 128.6, 127.2, 127.1, 125.4, 121.6 (d, *J* = 3.0 Hz), 119.2, 115.1 (d, *J* = 21.0 Hz), 113.4 (d, *J* = 23.0 Hz), 112.4, 57.7, 57.6, 47.4, 33.9, 21.5, 14.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ –112.01; IR (film) ν_{max} 3065, 2923, 2853, 1709, 1615, 1594, 1500, 1490, 1448, 1398, 1348, 1306, 1283, 1267, 1250, 1159, 1120, 1093, 1054, 1008, 984, 932, 874, 811, 770, 737, 690, 661 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FN_3NaO_3S^+$ $[M+Na]^+$ 526.1571, found 526.1575.

6-(4-fluorophenyl)-4-methyl-9-methylene-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ad)



Prepared according to the general procedure as described above in 81% yield (40.7 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a light yellow solid. mp = 194 – 197 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.41 (m, 4H), 7.32 – 6.86 (m, 9H), 5.25 (s, 1H), 5.14 (s, 1H), 4.93 (d, *J* = 1.7 Hz, 1H), 4.75 (s, 2H), 2.54 – 2.11 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 162.3 (d, *J* = 247.4 Hz), 160.2, 143.8, 137.1, 136.2 (d, *J* = 4.2 Hz), 132.8, 132.7, 129.5, 128.7, 127.9 (d, *J* = 8.3 Hz), 127.2, 125.4, 119.1, 115.3 (d, *J* = 21.7 Hz), 112.5, 57.7, 57.6, 47.4, 33.7, 21.5, 14.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ –113.68; IR (film) ν_{max} 3064, 2924, 1707, 1596, 1509, 1500, 1435, 1398, 1365, 1306, 1284, 1197, 1160, 1119, 1091, 1053, 1008, 983, 931, 857, 811, 777, 735, 706, 689, 659 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FN_3NaO_3S^+$ $[M+Na]^+$ 526.1571, found 526.1575.

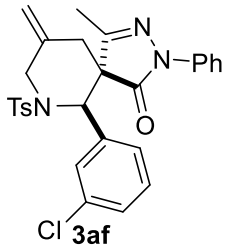
6-(2-chlorophenyl)-4-methyl-9-methylene-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ae)



3ae

Prepared according to the general procedure as described above in 99% yield (51.4 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 160 – 163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.57 (m, 3H), 7.51 – 6.92 (m, 10H), 5.80 (s, 1H), 5.31 – 4.54 (m, 4H), 2.75 – 1.76 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 161.1, 143.4, 137.4, 135.8, 134.2, 133.1, 129.6, 129.4, 129.3, 129.2, 129.1, 128.8, 128.6, 127.6, 127.0, 126.4, 125.1, 119.2, 119.0, 113.3, 56.3, 53.9, 48.0, 33.3, 21.4, 16.2; IR (film) ν_{max} 3065, 2924, 1712, 1596, 1500, 1474, 1438, 1397, 1366, 1324, 1289, 1185, 1161, 1120, 1093, 1038, 989, 933, 838, 814, 758, 690, 660 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClN_3NaO_3S^+$ $[M+Na]^+$ 542.1276, found 542.1274.

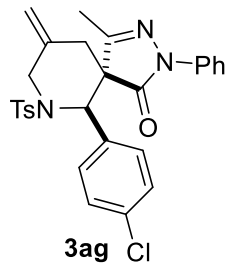
6-(3-chlorophenyl)-4-methyl-9-methylene-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3af)



3af

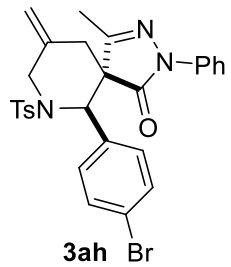
Prepared according to the general procedure as described above in 99% yield (51.4 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 116 – 119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.46 (m, 4H), 7.34 – 6.94 (m, 9H), 5.25 (s, 1H), 5.15 (s, 1H), 4.94 (s, 1H), 4.80 – 4.67 (m, 2H), 2.49 – 2.13 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 160.1, 143.9, 138.8, 137.2, 136.2, 136.2, 134.4, 129.6, 129.5, 128.6, 128.2, 127.1, 126.4, 125.4, 124.3, 119.2, 112.5, 57.7, 57.5, 47.5, 33.8, 21.5, 14.5; IR (film) ν_{max} 3065, 2924, 1708, 1596, 1575, 1499, 1435, 1399, 1365, 1306, 1282, 1256, 1198, 1161, 1119, 1092, 1054, 984, 939, 881, 811, 790, 755, 689, 660 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClN_3NaO_3S^+$ $[M+Na]^+$ 542.1276, found 542.1274.

6-(4-chlorophenyl)-4-methyl-9-methylene-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ag)



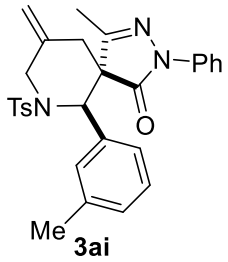
Prepared according to the general procedure as described above in 85% yield (44.1 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 205 – 208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.48 (m, 4H), 7.36 – 7.04 (m, 9H), 5.24 (s, 1H), 5.14 (d, *J* = 2.2 Hz, 1H), 4.93 (s, 1H), 4.74 (s, 2H), 2.52 – 2.10 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 160.2, 143.9, 137.2, 136.2, 136.2, 135.5, 133.9, 129.5, 128.7, 128.5, 127.6, 127.2, 125.4, 119.2, 112.5, 57.7, 57.6, 47.5, 33.8, 21.5, 14.5; IR (film) ν_{max} 2924, 2854, 1708, 1596, 1492, 1436, 1399, 1365, 1348, 1306, 1282, 1183, 1162, 1119, 1092, 1054, 1013, 984, 934, 850, 813, 758, 679, 661 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClN_3NaO_3S^+$ $[M+Na]^+$ 542.1276, found 542.1273.

6-(4-bromophenyl)-4-methyl-9-methylene-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ah)



Prepared according to the general procedure as described above in 79% yield (44.5 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 194 – 197 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.46 (m, 4H), 7.39 – 6.93 (m, 9H), 5.22 (s, 1H), 5.14 (s, 1H), 4.93 (s, 1H), 4.73 (d, *J* = 3.6 Hz, 2H), 2.53 – 2.07 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 159.2, 142.9, 136.1, 135.2, 135.1, 135.0, 130.5, 128.5, 127.7, 126.9, 126.2, 124.4, 121.1, 118.2, 111.5, 56.7, 56.5, 46.4, 32.8, 20.5, 13.5; IR (film) ν_{max} 3066, 2924, 1708, 1596, 1490, 1457, 1435, 1398, 1365, 1348, 1306, 1281, 1183, 1163, 1119, 1092, 1075, 1054, 1009, 983, 934, 849, 813, 758, 690, 663, 634 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}BrN_3NaO_3S^+$ $[M+Na]^+$ 586.0770, found 586.0770.

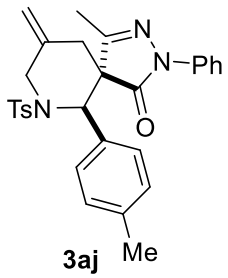
4-methyl-9-methylene-2-phenyl-6-(m-tolyl)-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ai)



3ai

Prepared according to the general procedure as described above in 82% yield (40.9 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 138 – 140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.45 (m, 4H), 7.37 – 6.79 (m, 9H), 5.27 (s, 1H), 5.13 (d, *J* = 2.0 Hz, 1H), 4.93 (s, 1H), 4.74 (s, 2H), 2.47 – 2.08 (m, 11H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 160.5, 143.5, 137.9, 137.4, 136.7, 136.5, 129.4, 128.8, 128.6, 128.3, 127.3, 126.7, 125.2, 123.2, 119.3, 112.2, 58.3, 57.8, 47.6, 33.9, 21.4, 21.3, 14.5; IR (film) ν_{max} 3063, 2923, 1706, 1596, 1499, 1457, 1435, 1399, 1364, 1346, 1306, 1284, 1158, 1119, 1092, 1053, 1008, 984, 947, 930, 856, 811, 754, 733, 690, 659 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}N_3NaO_3S^+$ $[M+Na]^+$ 522.1822, found 522.1825.

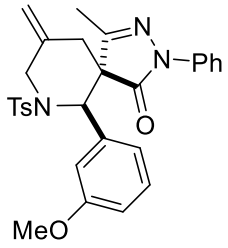
4-methyl-9-methylene-2-phenyl-6-(p-tolyl)-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3aj)



3aj

Prepared according to the general procedure as described above in 62% yield (30.9 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 160 – 163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.44 (m, 4H), 7.36 – 7.07 (m, 5H), 6.99 (s, 4H), 5.26 (s, 1H), 5.13 (s, 1H), 4.99 – 4.86 (m, 1H), 4.72 (s, 2H), 2.48 – 2.13 (m, 11H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 160.6, 143.5, 137.7, 137.4, 136.7, 136.4, 133.9, 129.4, 129.1, 128.6, 127.3, 126.1, 125.2, 119.3, 112.3, 58.2, 57.8, 47.6, 33.9, 21.5, 20.9, 14.6; IR (film) ν_{max} 3031, 2923, 1707, 1596, 1514, 1499, 1436, 1398, 1364, 1346, 1306, 1283, 1230, 1185, 1160, 1119, 1092, 1073, 1054, 1019, 1008, 983, 933, 851, 813, 755, 690, 660, cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}N_3NaO_3S^+$ $[M+Na]^+$ 522.1822, found 522.1822.

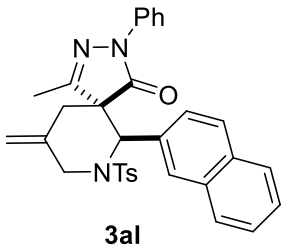
6-(3-methoxyphenyl)-4-methyl-9-methylene-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ak)



3ak

Prepared according to the general procedure as described above in 80% yield (41.2 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 171 – 174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.47 (m, 4H), 7.39 – 7.04 (m, 7H), 6.80 – 6.51 (m, 2H), 5.30 (s, 1H), 5.13 (s, 1H), 4.92 (s, 1H), 4.73 (s, 2H), 3.65 (s, 3H), 2.48 – 2.15 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 160.5, 159.5, 143.6, 138.4, 137.3, 136.5, 136.4, 129.8, 129.6, 129.5, 128.6, 127.2, 127.1, 125.2, 119.2, 118.2, 113.6, 112.2, 111.7, 58.1, 57.7, 55.0, 47.5, 34.0, 21.5, 14.5; IR (film) ν_{max} 3064, 2924, 1709, 1654, 1597, 1491, 1457, 1436, 1398, 1364, 1346, 1306, 1285, 1274, 1256, 1158, 1092, 1050, 1008, 984, 930, 867, 812, 756, 736, 691 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}N_3NaO_4S^+$ $[M+Na]^+$ 538.1771, found 538.1772.

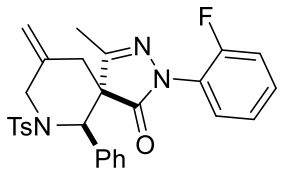
4-methyl-9-methylene-6-(naphthalen-2-yl)-2-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3al)



3al

Prepared according to the general procedure as described above in 87% yield (46.5 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 186 – 189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.39 (m, 10H), 7.28 – 7.00 (m, 6H), 5.49 (s, 1H), 5.18 (s, 1H), 4.97 (t, *J* = 1.7 Hz, 1H), 4.83 (s, 2H), 2.53 – 2.26 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 160.7, 143.6, 141.8, 137.3, 136.6, 136.4, 134.0, 132.9, 132.8, 129.7, 129.3, 128.5, 128.2, 128.1, 127.4, 127.1, 126.1, 125.9, 125.2, 123.7, 119.2, 118.1, 112.4, 58.5, 57.8, 53.0, 47.6, 34.2, 21.3, 14.7; IR (film) ν_{max} 3033, 2923, 1705, 1615, 1597, 1512, 1495, 1452, 1436, 1364, 1347, 1306, 1285, 1185, 1161, 1126, 1092, 1051, 1008, 984, 936, 841, 817, 789, 738, 697, 661 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{29}N_3NaO_3S^+$ $[M+Na]^+$ 558.1822, found 558.1825.

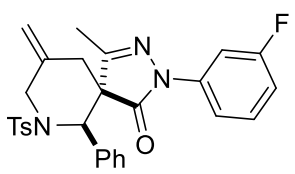
2-(2-fluorophenyl)-4-methyl-9-methylene-6-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3am)



3am

Prepared according to the general procedure as described above in 58% yield (29.2 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a light yellow solid. mp = 189 – 191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.31 – 6.74 (m, 11H), 5.32 (s, 1H), 5.12 (d, *J* = 2.3 Hz, 1H), 4.98 – 4.89 (m, 1H), 4.86 – 4.66 (m, 2H), 2.53 – 2.12 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 160.4, 156.5 (d, *J* = 253.7 Hz), 143.7, 136.9, 136.4, 136.3, 129.5, 129.3 (d, *J* = 7.7 Hz), 128.5, 128.1, 127.3, 126.8, 125.9, 124.1 (d, *J* = 3.8 Hz), 124.0, 123.9, 116.5 (d, *J* = 19.4 Hz), 112.3, 58.1, 56.6, 47.6, 33.6, 21.5, 14.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ –119.18; IR (film) ν_{max} 3064, 2925, 1716, 1614, 1596, 1506, 1461, 1435, 1370, 1347, 1306, 1283, 1269, 1227, 1197, 1161, 1121, 1092, 1030, 1007, 982, 936, 842, 812, 793, 759, 736, 697 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FN_3NaO_3S^+$ $[M+Na]^+$ 526.1571, found 526.1571.

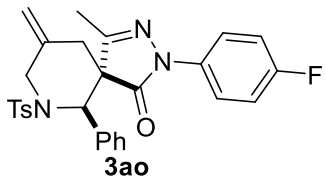
2-(3-fluorophenyl)-4-methyl-9-methylene-6-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3an)



3an

Prepared according to the general procedure as described above in 80% yield (40.2 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 163 – 166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 2H), 7.43 – 6.74 (m, 11H), 5.30 (s, 1H), 5.14 (d, *J* = 2.1 Hz, 1H), 4.94 (t, *J* = 1.7 Hz, 1H), 4.74 (s, 2H), 2.62 – 2.13 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 162.6 (d, *J* = 244.9 Hz), 160.7, 143.6, 136.7, 136.4, 136.3, 129.8 (d, *J* = 9.1 Hz), 129.4, 128.4, 128.1, 127.2, 126.0, 114.2 (d, *J* = 3.1 Hz), 112.4, 111.7 (d, *J* = 21.2 Hz), 106.3 (d, *J* = 26.8 Hz), 58.2, 58.0, 47.5, 33.8, 21.5, 14.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ –111.56; IR (film) ν_{max} 2925, 1714, 1611, 1594, 1492, 1453, 1348, 1306, 1283, 1210, 1185, 1162, 1115, 1093, 1010, 937, 905, 865, 843, 780, 680, 661 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FN_3NaO_3S^+$ $[M+Na]^+$ 526.1571, found 526.1572.

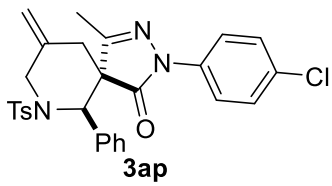
2-(4-fluorophenyl)-4-methyl-9-methylene-6-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ao)



3ao

Prepared according to the general procedure as described above in 74% yield (37.2 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 198 – 201 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.36 (m, 4H), 7.33 – 6.89 (m, 9H), 5.29 (s, 1H), 5.13 (d, *J* = 2.2 Hz, 1H), 4.93 (t, *J* = 1.7 Hz, 1H), 4.75 (s, 2H), 2.54 – 2.13 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 160.5, 160.0 (d, *J* = 245.0 Hz), 143.6, 136.8, 136.5, 136.3, 133.3 (d, *J* = 2.8 Hz), 129.7, 129.4, 128.4, 128.1, 127.2, 127.1, 126.0, 121.1 (d, *J* = 8.0 Hz), 115.3 (d, *J* = 22.5 Hz), 112.2, 58.2, 57.7, 47.5, 33.7, 21.5, 14.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ –116.62; IR (film) ν_{max} 2925, 1709, 1598, 1508, 1452, 1436, 1348, 1306, 1285, 1218, 1162, 1120, 1093, 1008, 983, 937, 869, 836, 765, 697, 661 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FN_3NaO_3S^+$ $[M+Na]^+$ 526.1571, found 526.1571.

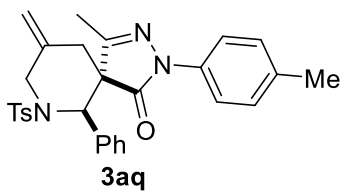
2-(4-chlorophenyl)-4-methyl-9-methylene-6-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ap)



3ap

Prepared according to the general procedure as described above in 98% yield (50.8 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 200 – 203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.45 (m, 4H), 7.26 – 7.01 (m, 9H), 5.29 (s, 1H), 5.14 (d, *J* = 2.2 Hz, 1H), 4.93 (d, *J* = 1.9 Hz, 1H), 4.74 (s, 2H), 2.53 – 2.17 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 160.7, 143.7, 136.7, 136.4, 136.3, 135.8, 129.5, 128.6, 128.4, 128.1, 127.2, 126.0, 120.2, 112.3, 58.2, 57.9, 47.5, 33.7, 21.5, 14.5; IR (film) ν_{max} 3064, 2925, 1709, 1596, 1492, 1451, 1436, 1416, 1397, 1363, 1349, 1324, 1306, 1285, 1202, 1184, 1160, 1123, 1092, 1052, 1011, 989, 937, 859, 830, 769, 738, 699, 679 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClN_3NaO_3S^+$ $[M+Na]^+$ 542.1276, found 542.1275.

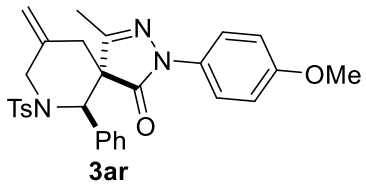
4-methyl-9-methylene-6-phenyl-2-(p-tolyl)-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3aq)



3aq

Prepared according to the general procedure as described above in 72% yield (35.9 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 187 – 189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.55 (m, 2H), 7.38 – 7.01 (m, 11H), 5.29 (s, 1H), 5.12 (d, *J* = 2.2 Hz, 1H), 4.92 (s, 1H), 4.77 (d, *J* = 3.7 Hz, 2H), 2.53 – 2.12 (m, 11H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 159.1, 142.6, 135.9, 135.6, 135.4, 133.9, 133.8, 128.4, 128.1, 127.3, 127.0, 126.2, 125.0, 118.3, 111.1, 57.2, 56.7, 46.5, 32.8, 20.4, 19.8, 13.4; IR (film) ν_{max} 3062, 2923, 1709, 1596, 1499, 1437, 1396, 1345, 1306, 1287, 1237, 1158, 1120, 1092, 1008, 984, 935, 892, 865, 780, 757, 689cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}N_3NaO_3S^+$ $[M+Na]^+$ 522.1822, found 522.1822.

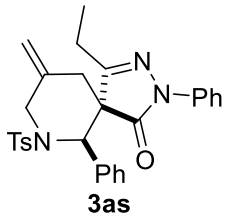
2-(4-methoxyphenyl)-4-methyl-9-methylene-6-phenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ar)



3ar

Prepared according to the general procedure as described above in 63% yield (32.4 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 120 – 123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.31 – 7.07 (m, 9H), 6.86 – 6.70 (m, 2H), 5.28 (s, 1H), 5.12 (s, 1H), 4.92 (s, 1H), 4.77 (d, *J* = 6.2 Hz, 2H), 3.77 (s, 3H), 2.51 – 2.10 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 160.0, 157.2, 143.6, 137.0, 136.6, 136.4, 130.5, 129.4, 128.3, 128.0, 127.3, 126.0, 121.3, 113.8, 112.0, 58.2, 57.5, 55.4, 47.6, 33.7, 21.5, 14.3; IR (film) ν_{max} 2929, 1703, 1597, 1509, 1440, 1401, 1369, 1347, 1298, 1285, 1246, 1183, 1161, 1122, 1093, 1031, 1007, 983, 937, 910, 832, 752, 739, 697 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{30}N_3O_4S^+$ $[M+H]^+$ 516.1952, found 516.1953.

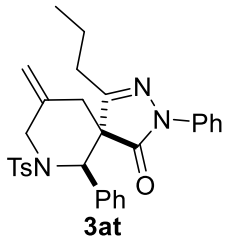
4-ethyl-9-methylene-2,6-diphenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3as)



3as

Prepared according to the general procedure as described above in 86% yield (42.9 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a light yellow solid. mp = 152 – 155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.45 (m, 4H), 7.33 – 7.06 (m, 10H), 5.34 (s, 1H), 5.11 (s, 1H), 4.91 (s, 1H), 4.83 – 4.69 (m, 2H), 2.86 – 2.69 (m, 1H), 2.53 – 2.18 (m, 6H), 1.44 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 163.0, 142.6, 136.4, 136.0, 135.8, 135.5, 128.4, 127.5, 127.3, 126.9, 126.2, 124.9, 124.1, 118.2, 110.9, 57.3, 57.0, 46.5, 33.1, 20.5, 20.4, 8.6; IR (film) ν_{max} 3064, 2925, 1707, 1597, 1499, 1456, 1386, 1347, 1285, 1236, 1183, 1161, 1122, 1092, 1053, 1007, 970, 933, 839, 812, 757, 737, 692, 669 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}N_3NaO_3S^+$ $[M+Na]^+$ 522.1822, found 522.1825.

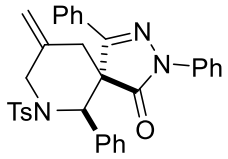
9-methylene-2,6-diphenyl-4-propyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3at)



3at

Prepared according to the general procedure as described above in 88% yield (45.1 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 171 – 174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.44 (m, 4H), 7.37 – 7.03 (m, 10H), 5.33 (s, 1H), 5.11 (d, J = 2.4 Hz, 1H), 4.90 (s, 1H), 4.84 – 4.69 (m, 2H), 2.68 (ddd, *J* = 17.1, 8.8, 6.4 Hz, 1H), 2.45 (s, 3H), 2.39 – 2.14 (m, 3H), 2.00 – 1.82 (m, 2H), 1.16 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.39, 162.9, 143.6, 137.4, 137.2, 136.8, 136.5, 129.5, 128.5, 128.4, 127.9, 127.3, 125.7, 125.1, 119.2, 111.8, 58.2, 58.1, 47.5, 34.1, 29.9, 21.5, 19.0, 14.0; IR (film) ν_{max} 3064, 2963, 1708, 1597, 1499, 1456, 1379, 1348, 1286, 1222, 1183, 1161, 1123, 1091, 987, 937, 840, 813, 757, 738, 691 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{31}N_3NaO_3S^+$ $[M+Na]^+$ 536.1978, found 536.1982.

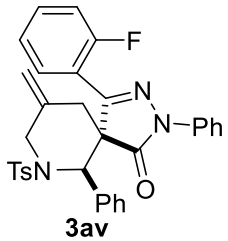
9-methylene-2,4,6-triphenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3au)



3au

Prepared according to the general procedure as described above in 80% yield (43.8 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 157 – 161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.86 (m, 2H), 7.68 – 6.98 (m, 17H), 5.85 (s, 1H), 5.22 – 4.79 (m, 4H), 3.17 (dd, *J* = 16.0, 2.6 Hz, 1H), 2.58 (d, *J* = 16.0 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 157.2, 143.2, 137.1, 137.0, 136.8, 136.6, 130.3, 129.5, 129.2, 128.8, 128.2, 127.9, 127.5, 127.0, 126.8, 125.2, 125.1, 119.4, 110.8, 58.0, 57.9, 47.4, 35.1, 21.1; IR (film) ν_{max} 3063, 2924, 1713, 1597, 1494, 1443, 1402, 1380, 1348, 1317, 1284, 1233, 1162, 1133, 1099, 1040, 970, 939, 838, 812, 757, 692 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{29}N_3NaO_3S^+$ $[M+Na]^+$ 570.1822, found 570.1825.

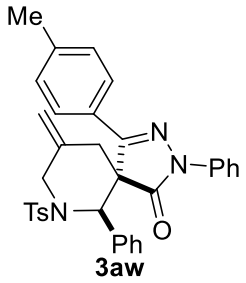
4-(2-fluorophenyl)-9-methylene-2,6-diphenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3av)



3av

Prepared according to the general procedure as described above in 95% yield (53.7 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 184 – 187 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.44 (m, 8H), 7.37 – 6.69 (m, 10H), 6.15 (s, 1H), 5.28 – 4.89 (m, 4H), 3.21 (dd, *J* = 15.7, 2.4 Hz, 1H), 2.58 (d, *J* = 16.1 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 158.0 (d, *J* = 247.1 Hz), 156.6, 142.6, 136.2, 136.1, 135.6, 129.4, 129.0 (d, *J* = 1.8 Hz), 128.6, 128.5, 128.0 (d, *J* = 3.6 Hz), 127.8, 127.6, 126.3, 125.8, 124.5, 123.6 (d, *J* = 14.0 Hz), 122.8 (d, *J* = 3.4 Hz), 118.5, 113.9 (d, *J* = 22.2 Hz), 110.2, 56.8, 51.8, 46.8, 34.7, 20.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ –114.38; IR (film) ν_{max} 3064, 2925, 2359, 1713, 1597, 1490, 1457, 1444, 1402, 1383, 1349, 1316, 1284, 1226, 1183, 1164, 1132, 1093, 1036, 970, 937, 859, 839, 755, 691 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{28}FN_3NaO_3S^+$ $[M+Na]^+$ 588.1728, found 588.1728.

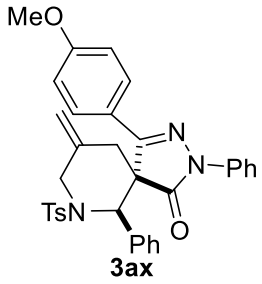
9-methylene-2,6-diphenyl-4-(p-tolyl)-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3aw)



3aw

Prepared according to the general procedure as described above in 99% yield (55.5 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 187 – 189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 7.89 (m, 2H), 7.75 – 7.60 (m, 2H), 7.60 – 7.49 (m, 5H), 7.36 – 7.12 (m, 6H), 7.00 – 6.85 (m, 4H), 5.81 (s, 1H), 5.23 – 4.79 (m, 4H), 3.14 (dd, *J* = 16.7, 2.6 Hz, 1H), 2.57 (d, *J* = 16.0 Hz, 1H), 2.46 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 156.6, 142.4, 136.5, 136.4, 136.2, 136.0, 133.5, 129.5, 128.9, 128.5, 128.1, 127.9, 127.5, 126.3, 126.2, 124.5, 124.4, 118.7, 110.1, 57.4, 57.2, 46.7, 34.5, 20.5, 19.9; IR (film) ν_{max} 3062, 2923, 2359, 1711, 1597, 1515, 1492, 1443, 1402, 1380, 1347, 1316, 1283, 1259, 1203, 1185, 1162, 1133, 1098, 1070, 1039, 1024, 970, 938, 852, 812, 765, 691 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{31}N_3NaO_3S^+$ $[M+Na]^+$ 584.1978, found 584.1978.

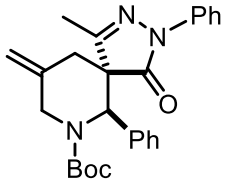
4-(4-methoxyphenyl)-9-methylene-2,6-diphenyl-7-tosyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one (3ax)



3ax

Prepared according to the general procedure as described above in 67% yield (38.7 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a white solid. mp = 174 – 177 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.87 (m, 2H), 7.71 – 7.49 (m, 7H), 7.37 – 7.11 (m, 6H), 6.96 – 6.89 (m, 2H), 6.71 – 6.57 (m, 2H), 5.76 (s, 1H), 5.24 – 4.81 (m, 4H), 3.69 (s, 3H), 3.14 (dd, *J* = 16.0, 2.3 Hz, 1H), 2.58 (d, *J* = 16.0 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 159.0, 157.5, 143.4, 137.4, 137.2, 137.0, 130.6, 129.9, 129.6, 129.5, 129.1, 128.6, 127.3, 127.1, 126.9, 125.6, 119.7, 113.6, 111.2, 58.6, 58.0, 55.1, 47.8, 35.4, 21.5; IR (film) ν_{max} 2932, 2837, 2360, 1712, 1611, 1597, 1513, 1493, 1458, 1443, 1380, 1347, 1306, 1284, 1250, 1178, 1162, 1134, 1099, 1070, 1035, 970, 939, 917, 854, 815, 765, 756, 691, 671 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{31}N_3NaO_4S^+$ $[M+Na]^+$ 600.1927, found 600.1923.

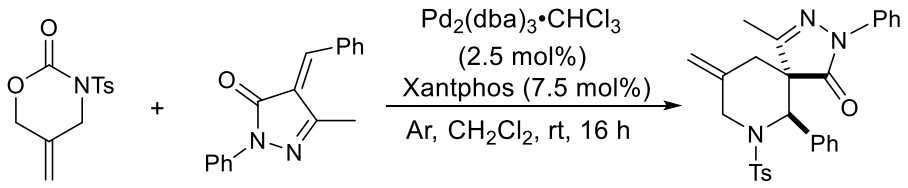
tert-butyl (5R,6R)-1-methyl-9-methylene-4-oxo-3,6-diphenyl-2,3,7-triazaspiro[4.5]dec-1-ene-7-carboxylate (3ba)



3ba

Prepared according to the general procedure as described above in 55 % yield (23.8 mg). It was purified by flash chromatography (11.1% EtOAc/PE) to afford a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.26 (d, *J* = 6.3 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.19 – 7.15 (m, 1H), 7.12 – 7.07 (m, 3H), 5.33 (s, 1H), 5.08 (s, 1H), 4.94 (s, 1H), 4.88 (d, *J* = 16.5 Hz, 1H), 4.62 (dd, *J* = 16.5, 2.2 Hz, 1H), 2.73 (dd, *J* = 15.5, 2.2 Hz, 1H), 2.57 (d, *J* = 15.5 Hz, 1H), 2.35 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (126 MHz, CDCl3) δ 171.60, 160.67, 154.95, 138.32, 137.89, 137.40, 128.63, 128.36, 127.81, 125.87, 125.21, 119.37, 111.32, 80.74, 57.82, 57.57, 45.98, 34.35, 28.25, 14.60; IR (film) ν_{max} 2977, 2929, 1691, 1596, 1499, 1453, 1394, 1363, 1304, 1278, 1244, 1156, 1117, 959, 892 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{30}N_3O_3^+$ $[M+H]^+$ 432.2287, found 432.2291.

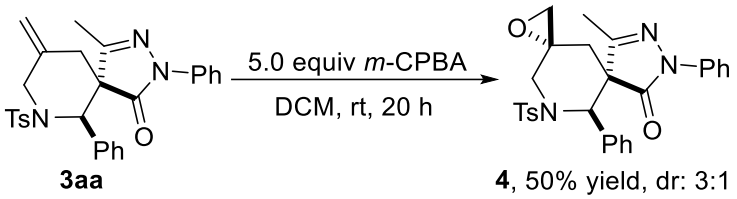
Scaled-up Synthesis of the Product 3aa



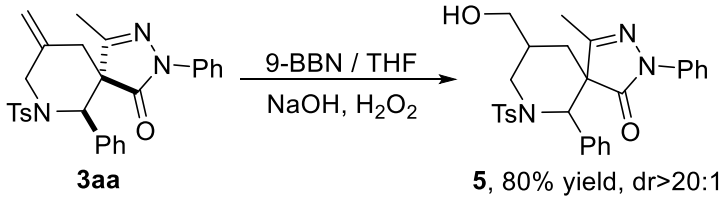
1a **2a** (2.0 mmol, 262 mg) **3aa** (802 mg) 83% yield, > 20:1 dr

Under argon atmosphere, to a mixture of *N*-tosyl carbamate **1a** (3.0 mmol) , unsaturated pyrazolones **2a** (2.0 mmol) and catalyst $Pd_2(dba)_3$·$CHCl_3$ (2.5 mol%, 0.05 mmol) / Xantphos (7.5 mol %, 0.15 mmol) in a Schlenk tube, 20 mL of DCM were added at room temperature. The resulting mixture was stirred until the starting material were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (11.1% EtOAc / PE) to afford the corresponding cycloaddition product **3aa** with 83% yield (802 mg) and dr> 20:1.

Transformations of the Product 3aa

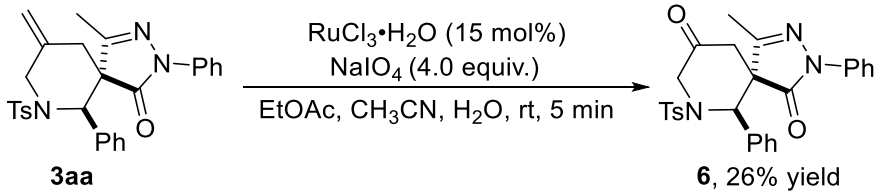


To a solution of **3aa** (0.10 mmol, 1.0 equiv.) in dichloromethane (3 mL) was added the dichloromethane solution of *m*-CPBA (0.50 mmol, 0.50 M, 1.0 mL) dropwise at 0 ℃ under room temperature. The reaction mixture was sealed under nitrogen and stirred for 12 hours. The reaction was then quenched with saturated $NaHCO_3$ solution and extracted with dichloromethane. The combined organic phase was collected and dried with Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (hexanes/EA = 6:1) to afford a white solid **4** (25.0 mg, 50% yield with dr: 3:1). mp = 123 – 125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.69 (m, 1H), 7.61 – 7.06 (m, 13H), 5.30 (s, 1H), 4.68 (d, *J* = 15.8 Hz, 1H), 4.00 (dd, *J* = 15.7, 1.4 Hz, 1H), 2.92 – 2.18 (m, 8H), 1.86 – 1.53 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 159.4, 143.5, 136.6, 136.2, 136.0, 129.2, 128.3, 128.1, 127.3, 125.5, 119.1, 58.0, 57.6, 53.8, 52.4, 48.2, 32.0, 21.2, 13.7; IR (film) ν_{max} 3063, 2923, 2359, 1706, 1596, 1499, 1456, 1436, 1399, 1366, 1346, 1307, 1287, 1199, 1184, 1161, 1120, 1091, 1051, 1007, 988, 961, 887, 860, 758, 693 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}N_3NaO_4S^+$ $[M+Na]^+$ 524.1614, found 524.1615.



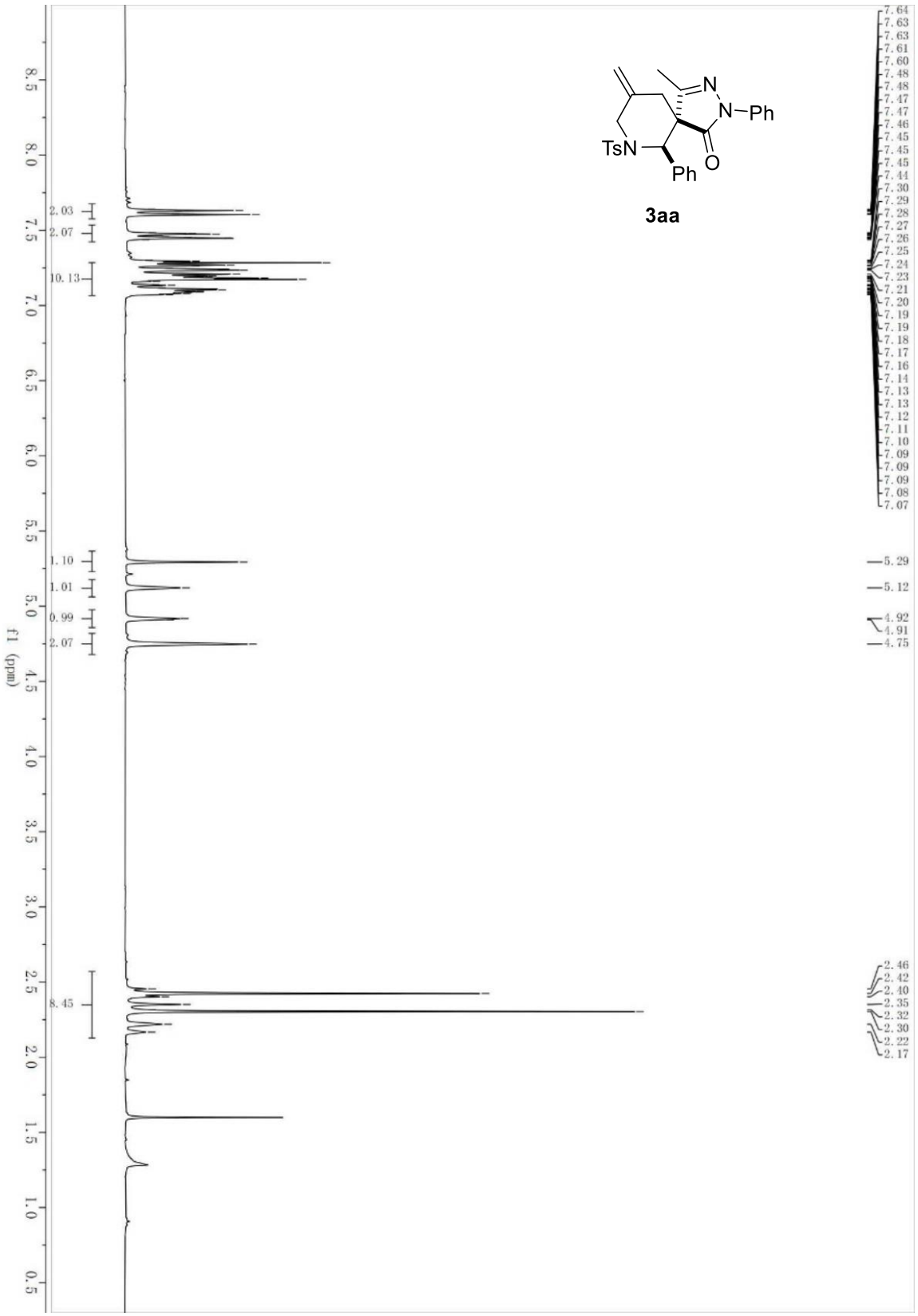
To 3 mL of 9-BBN (0.5 M in THF) solution at 0 °C under Ar atmosphere, a solution of the cycloaddition product **3aa** (0.2 M in THF, 0.1 mmol) was added dropwise. The resulting mixture was stirred at room temperature for 12 h and quenched with 2.0 mL of 2 N aqueous NaOH solution and 0.60 mL of 30% aqueous H_2O_2 solution. After stirring for 30 min, the aqueous layer was extracted with 15 mL portions of ether three times. The

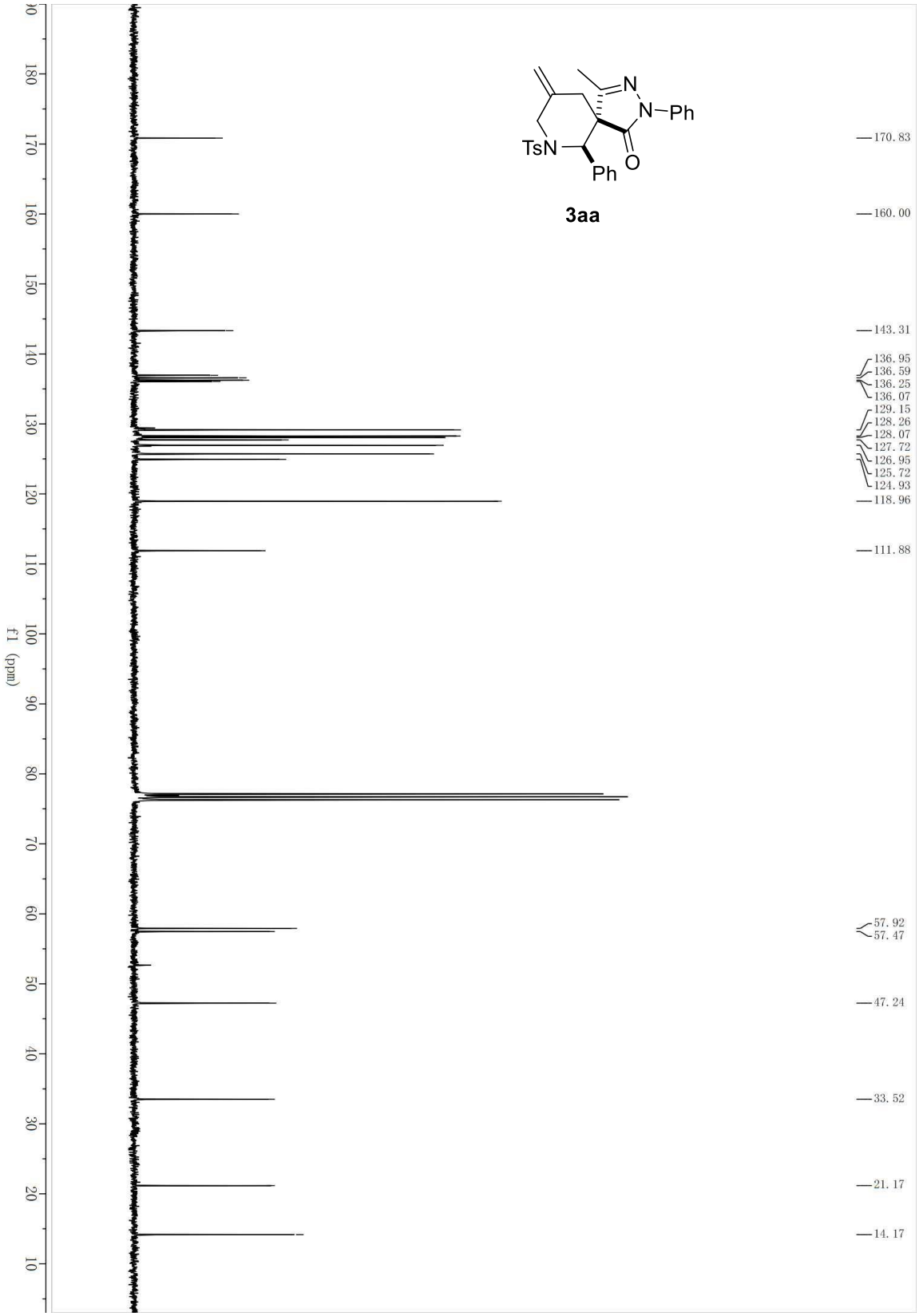
combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel (eluting with PE:EA = 2:1–1:2) to afford a colorless liquid **5** (40.2 mg, 80% yield and >20:1 dr). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 6.99 (m, 14H), 5.22 (s, 1H), 4.15 (dd, *J* = 13.3, 6.3 Hz, 1H), 3.74 – 3.47 (m, 3H), 2.68 – 2.19 (m, 8H), 2.15 – 1.75 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 162.1, 142.8, 137.1, 135.6, 135.3, 128.8, 128.3, 127.9, 127.8, 127.7, 126.7, 124.9, 118.9, 64.2, 58.5, 56.3, 42.8, 33.2, 26.7, 21.0, 16.4; IR (film) ν_{max} 3502, 3063, 2925, 2359, 1709, 1596, 1499, 1456, 1396, 1366, 1337, 1286, 1186, 1160, 1131, 1087, 1020, 1003, 924, 879, 834, 758, 734, 698 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_3NaO_4S^+$ $[M+Na]^+$ 526.1771, found 526.1771.



A solution of $NaIO_4$ (85mg, 0.4 mmol) in water (0.6 mL) was added to a solution of $RuCl_3$•H_2O (3.1mg, 15 mol%) in MeCN (0.8 mL). This mixture was stirred 2 minutes and then a solution of the **3aa** (0.1 mmol) in EA (0.8 mL) was added. The mixture was stirred for 10 minutes until TLC indicates complete consumption of the starting material. $MgSO_4$ was added and the resulting heterogeneous mixture was washed with EA, and finally evaporated under reduced pressure. Purified by flash chromatography on silica gel with PE/EA (8:1) as the solvent give a white solid **6** (12.7 mg, 26% yield). mp = 172 – 175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 6.97 (m, 14H), 5.65 (s, 1H), 4.87 – 4.47 (m, 2H), 2.54 (d, *J* = 16.0 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H), 2.26 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.5, 171.8, 157.7, 144.4, 136.5, 136.0, 135.9, 129.9, 128.7, 128.6, 128.5, 127.1, 125.8, 125.5, 119.4, 58.5, 57.9, 53.2, 40.3, 21.5, 13.9; IR (film) ν_{max} 2926, 1746, 1704, 1597, 1500, 1457, 1356, 1306, 1265, 1164, 1092, 1040, 1003, 975, 936, 903, 807, 731, 701, 691 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}N_3O_4S^+$ $[M+H]^+$ 488.1639, found 488.1639

^{1}H and ^{13}C NMR Spectra of All Products




N
N—Ph
TsN
O
Ph
3aa
170.83
160.00
143.31
136.95
136.59
136.25
136.07
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128.26
128.07
127.72
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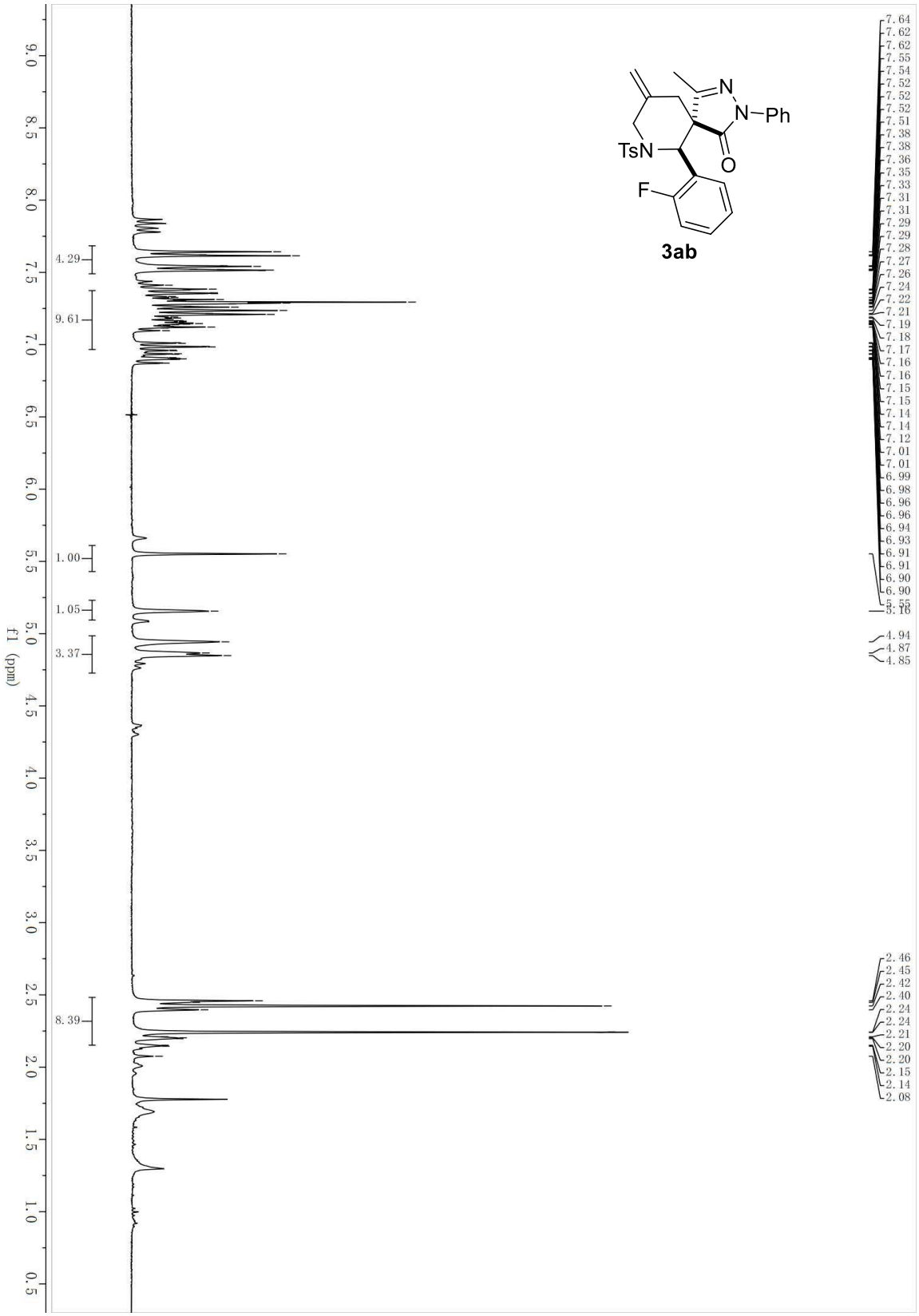
47.24
33.52
21.17
14.17
f1 (ppm)


3ab
TsN
N
N–Ph
O
F
f1 (ppm)
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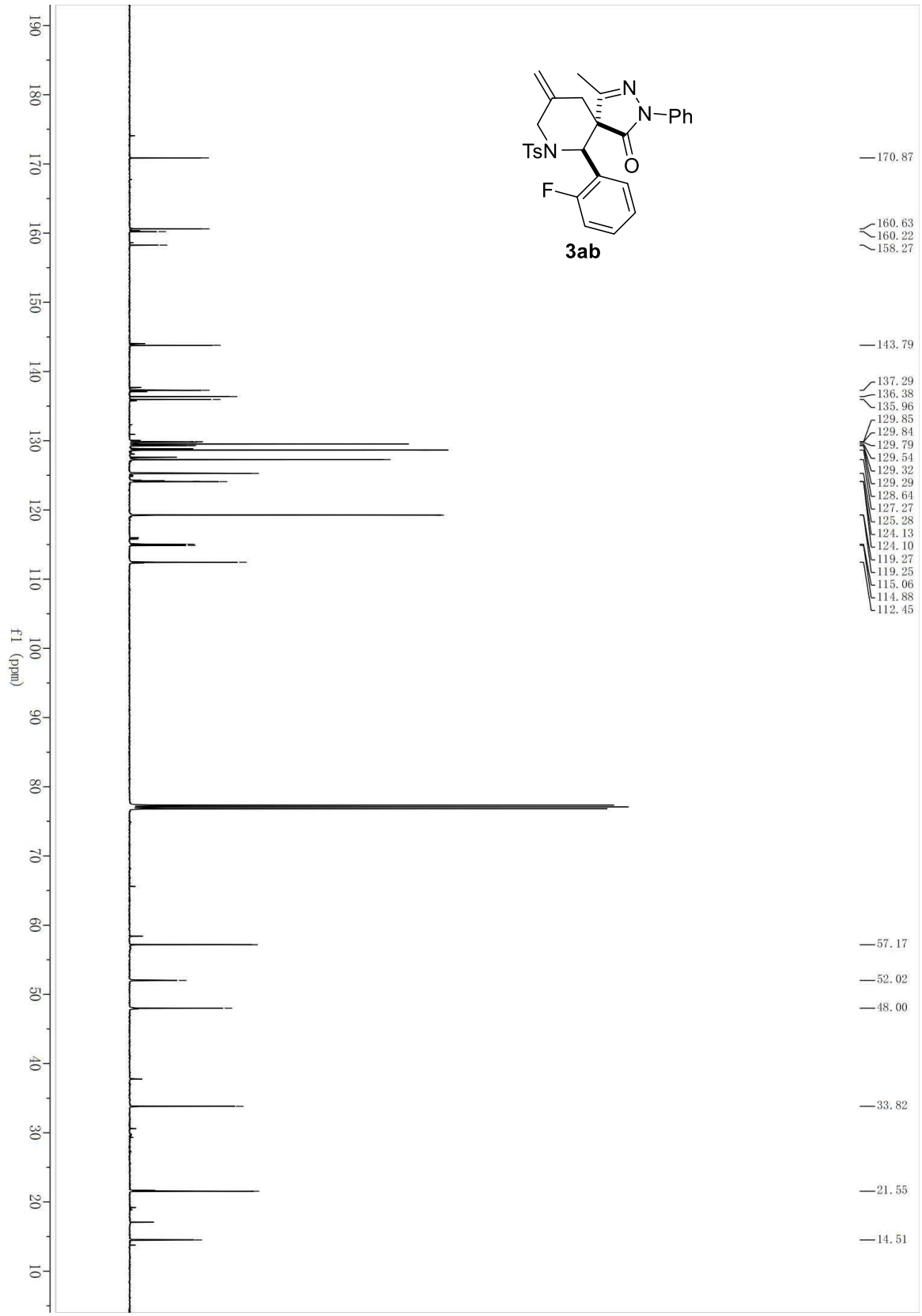
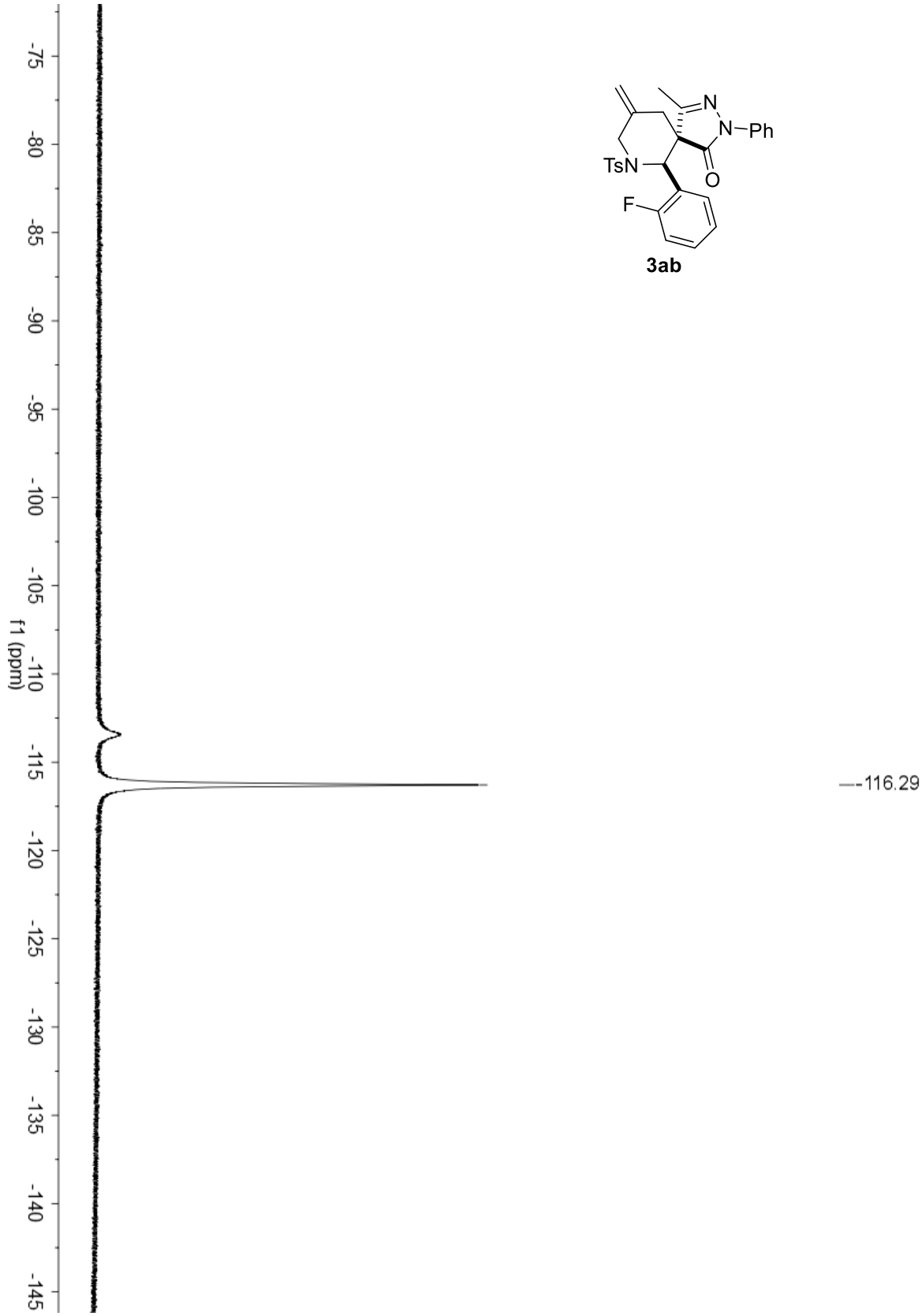
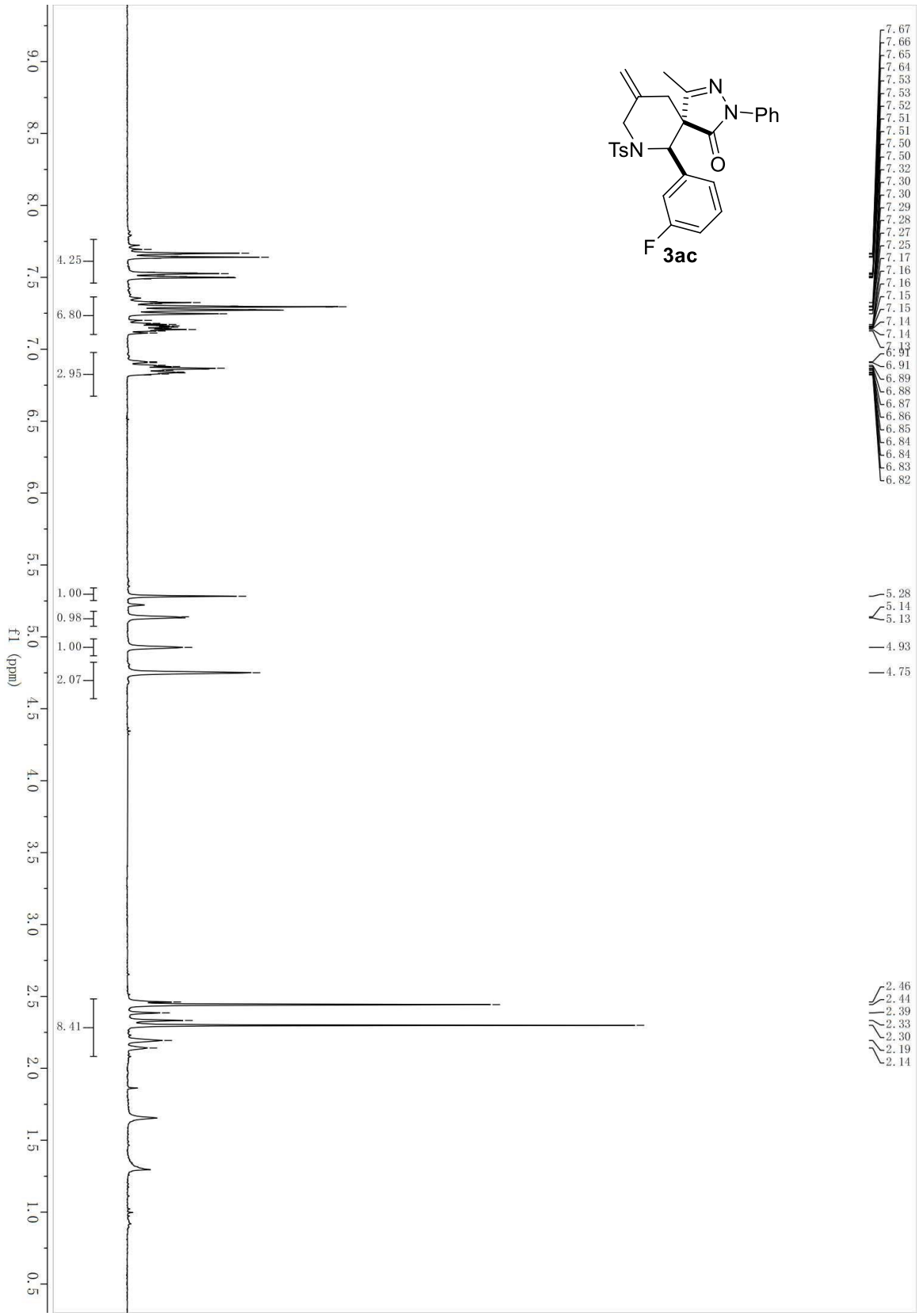
1.00
1.05
3.37
8.39


N
N–Ph
TsN
O
F
3ab
170.87
160.63
160.22
158.27
143.79
137.29
136.38
135.96
129.85
129.84
129.79
129.54
129.32
129.29
128.64
127.27
125.28
124.13
124.10
119.27
119.25
115.06
114.88
112.45
57.17
52.02
48.00
33.82
21.55
14.51
f1 (ppm)


-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)
-116.29
TsN
N
N
Ph
O
F

3ab


7.67
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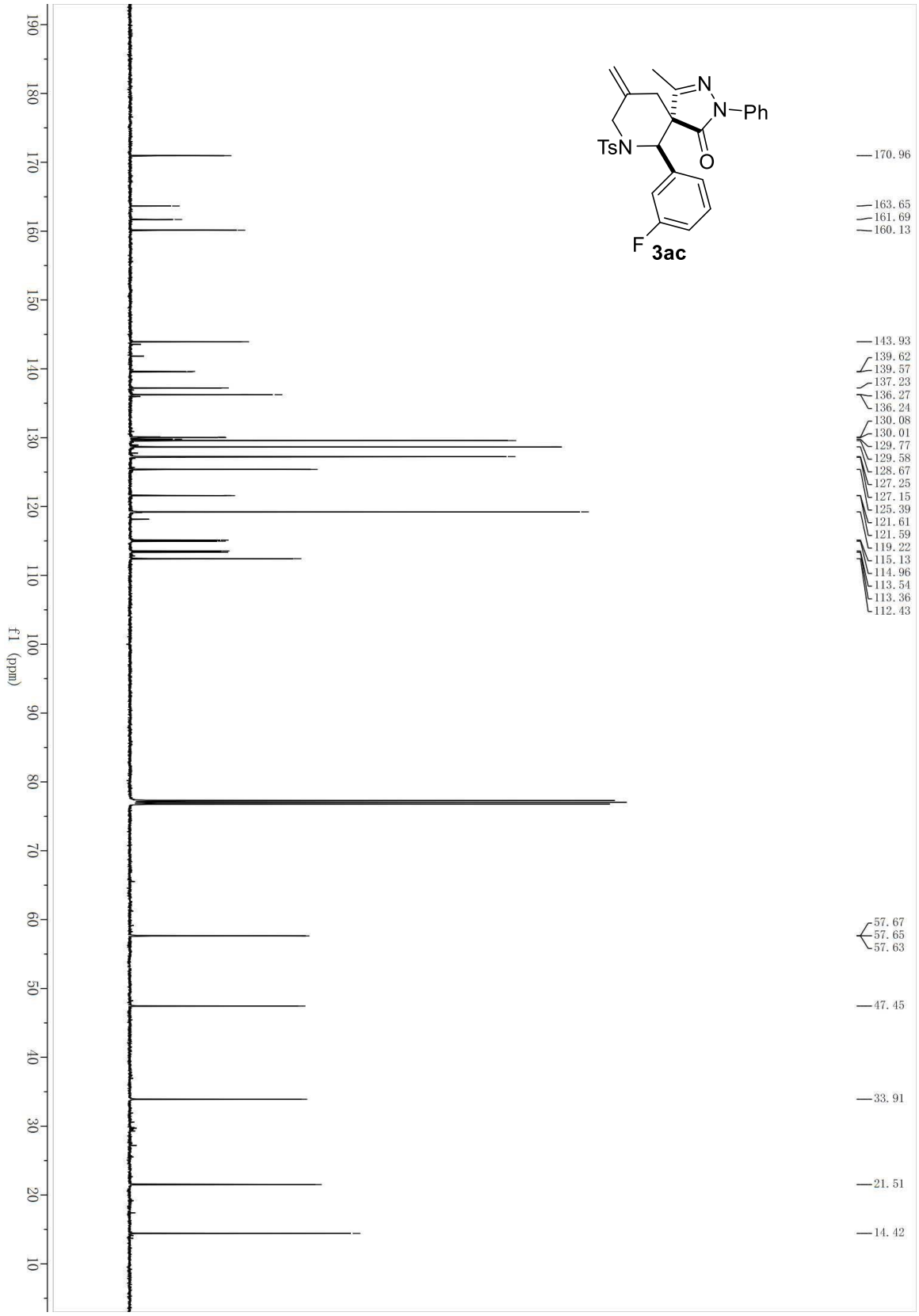
7.52
7.51
7.51
7.50
7.50
7.32
7.30
7.30
7.29
7.28
7.27
7.25
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.13
6.91
6.91
6.89
6.88
6.87
6.86
6.85
6.84
6.84
6.83
6.82
5.28
5.14
5.13
4.93
4.75
2.46
2.44
2.39
2.33
2.30
2.19
2.14
4.25
6.80
2.95
1.00
0.98
1.00
2.07
8.41
f1 (ppm)
TsN
N
N–Ph
O
F
3ac


N
N–Ph
TsN
O
F
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163.65
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139.62
139.57
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136.27
136.24
130.08
130.01
129.77
129.58
128.67
127.25
127.15
125.39
121.61
121.59
119.22
115.13
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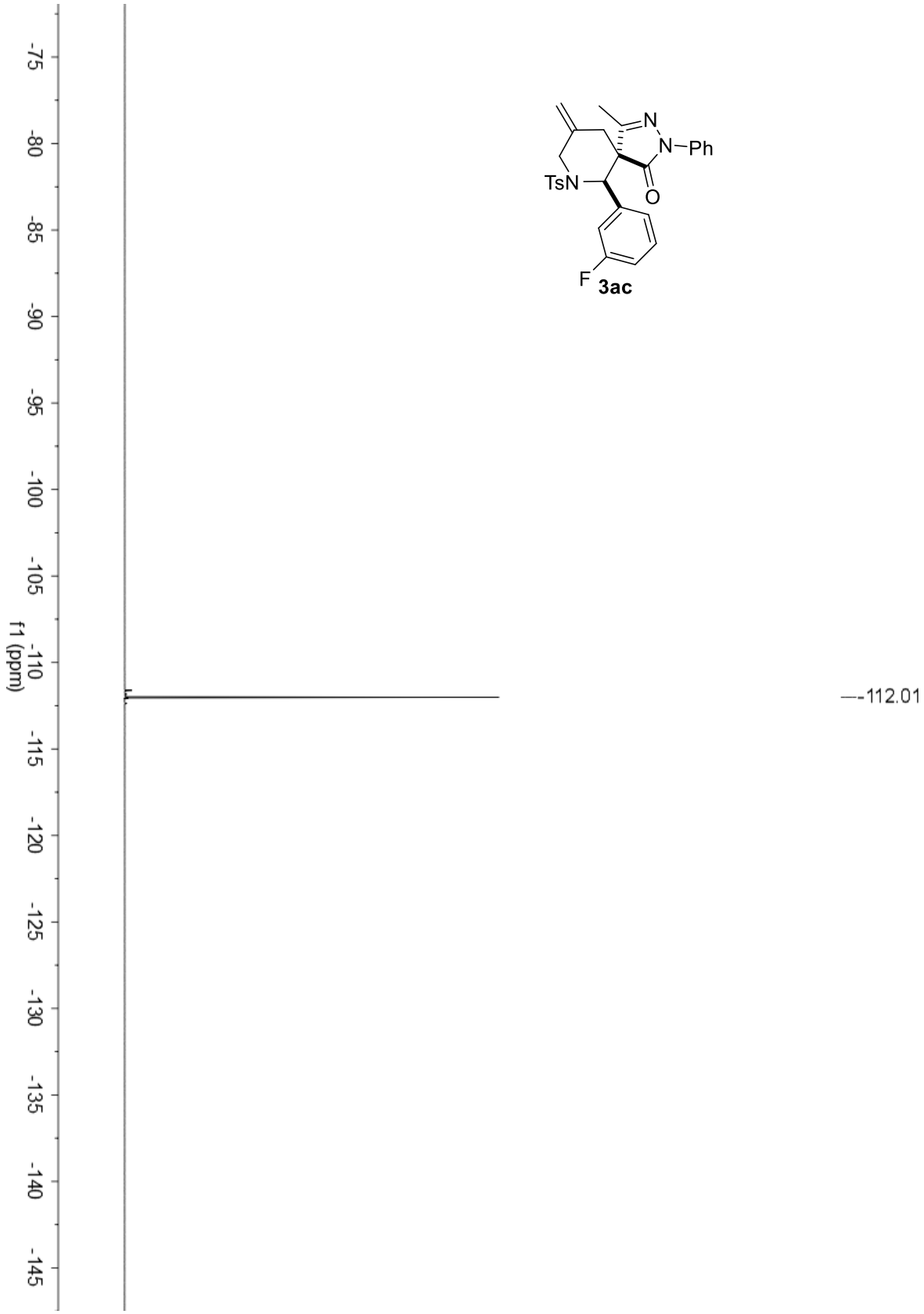
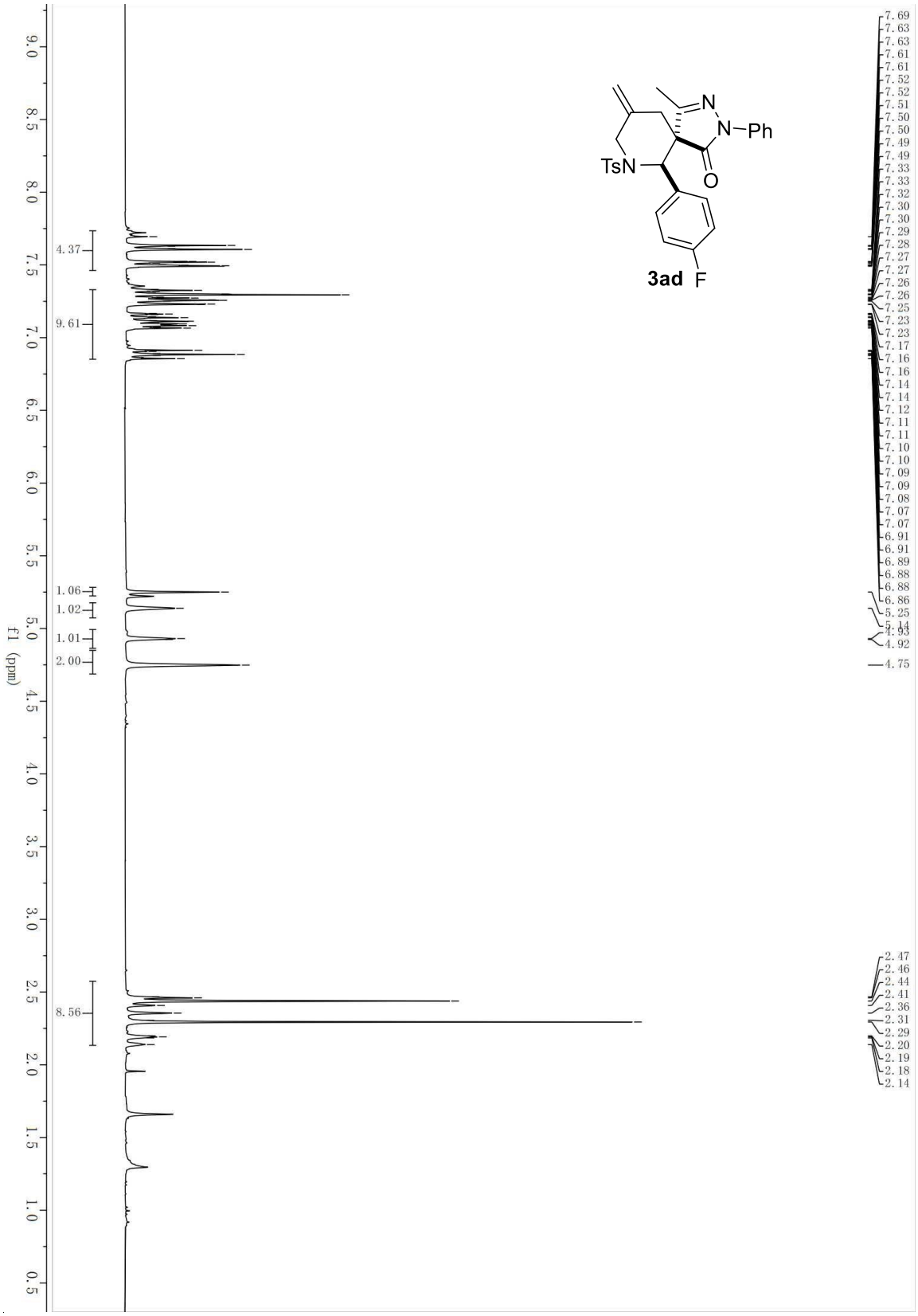
33.91
21.51
14.42
f1 (ppm)


-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)
-112.01
N
N–Ph
TsN
O
F
3ac


3ad
TsN
N
N–Ph
O
F
f1 (ppm)
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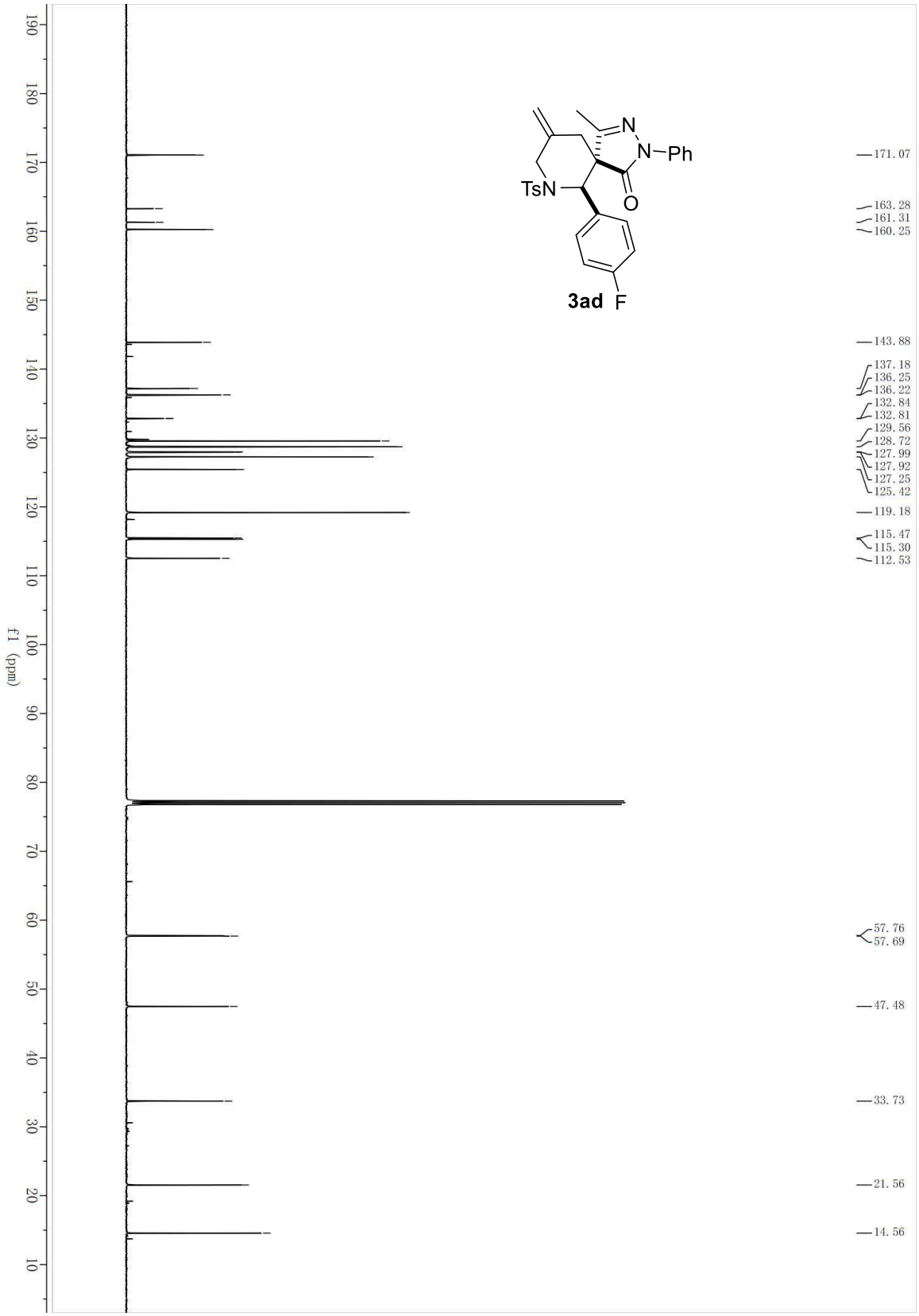
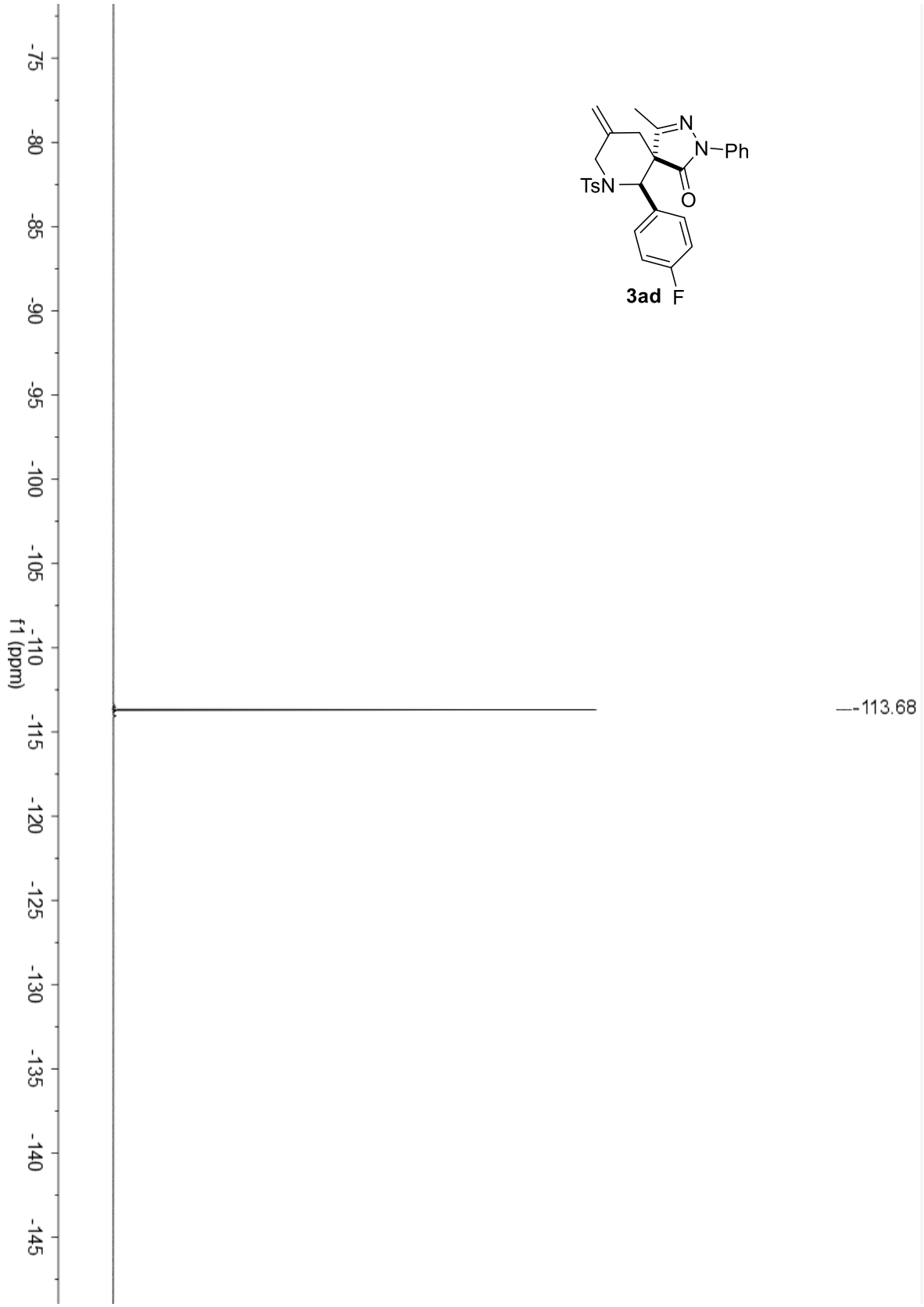
1.02
1.01
2.00
8.56


N
N–Ph
O
TsN
3ad F
f1 (ppm)
171.07
163.28
161.31
160.25
143.88
137.18
136.25
136.22
132.84
132.81
129.56
128.72
127.99
127.92
127.25
125.42
119.18
115.47
115.30
112.53
57.76
57.69
47.48
33.73
21.56
14.56


-75
-80
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-95
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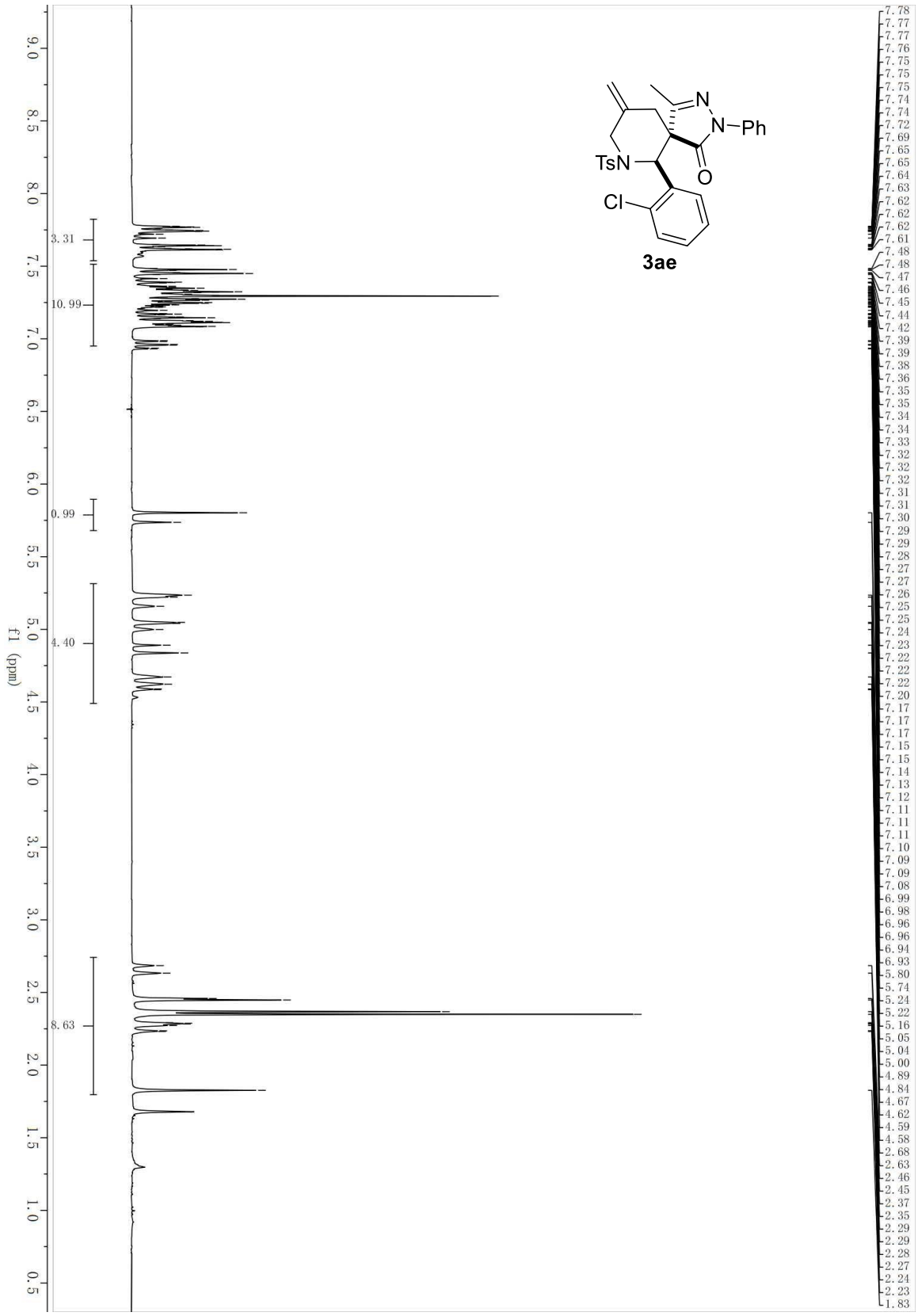
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)
-113.68
TsN
N
N–Ph
O
F
3ad


N
N–Ph
TsN
O
Cl
3ae
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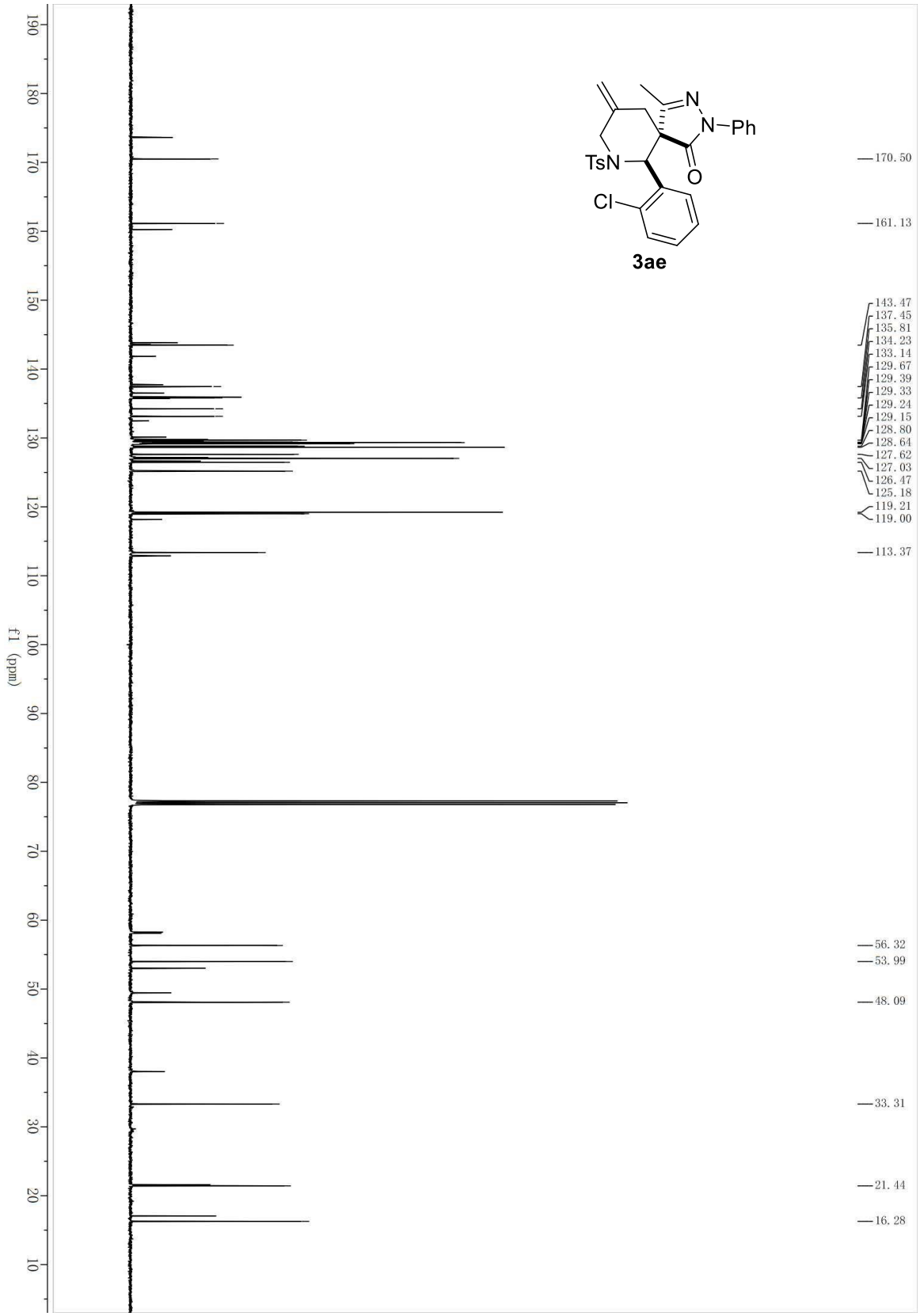
10.99
0.99
4.40
8.63
f1 (ppm)


N
N–Ph
TsN
O
Cl
3ae
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137.45
135.81
134.23
133.14
129.67
129.39
129.33
129.24
129.15
128.80
128.64
127.62
127.03
126.47
125.18
119.21
119.00
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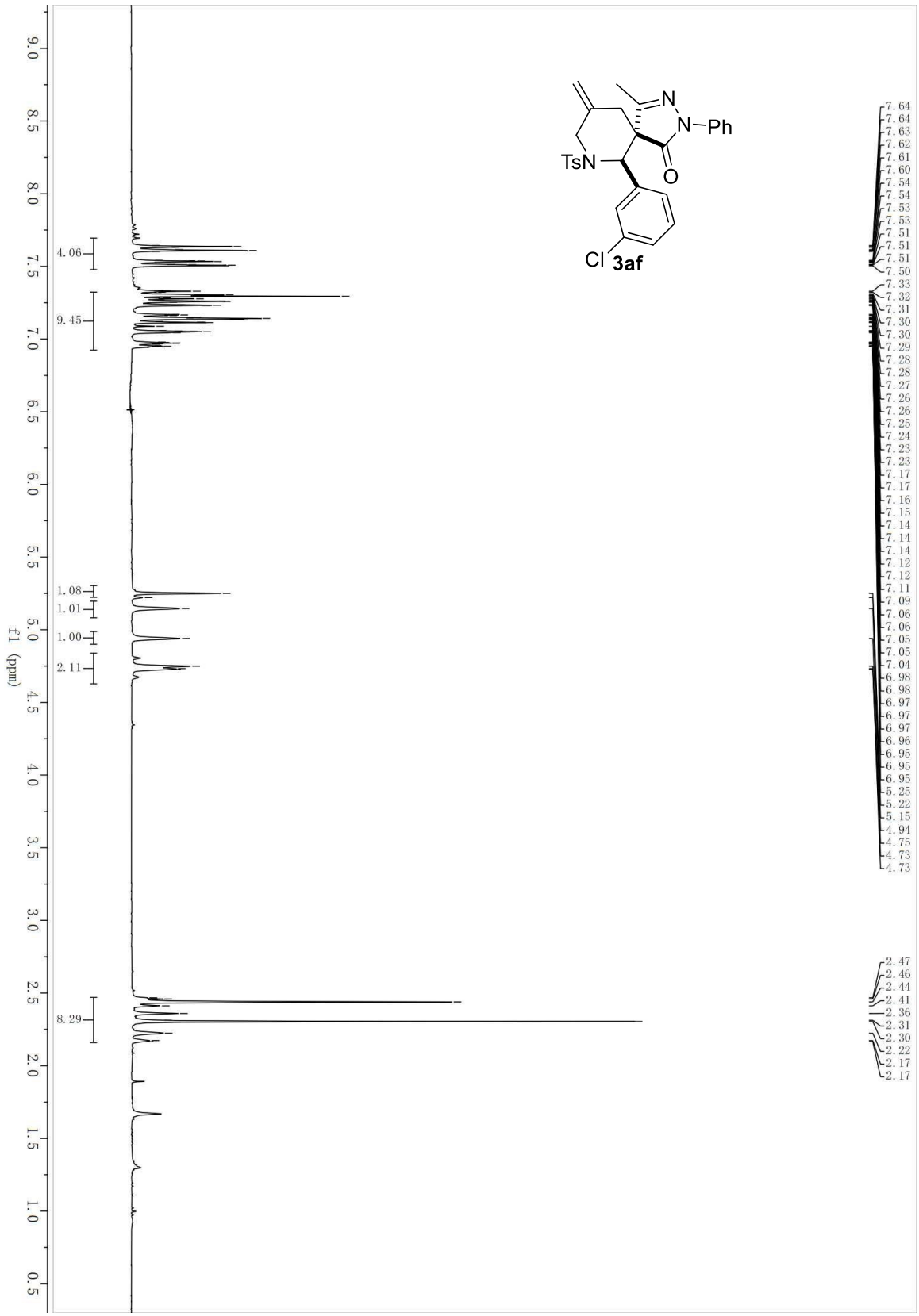
56.32
53.99
48.09
33.31
21.44
16.28
f1 (ppm)


N
N–Ph
TsN
O
Cl
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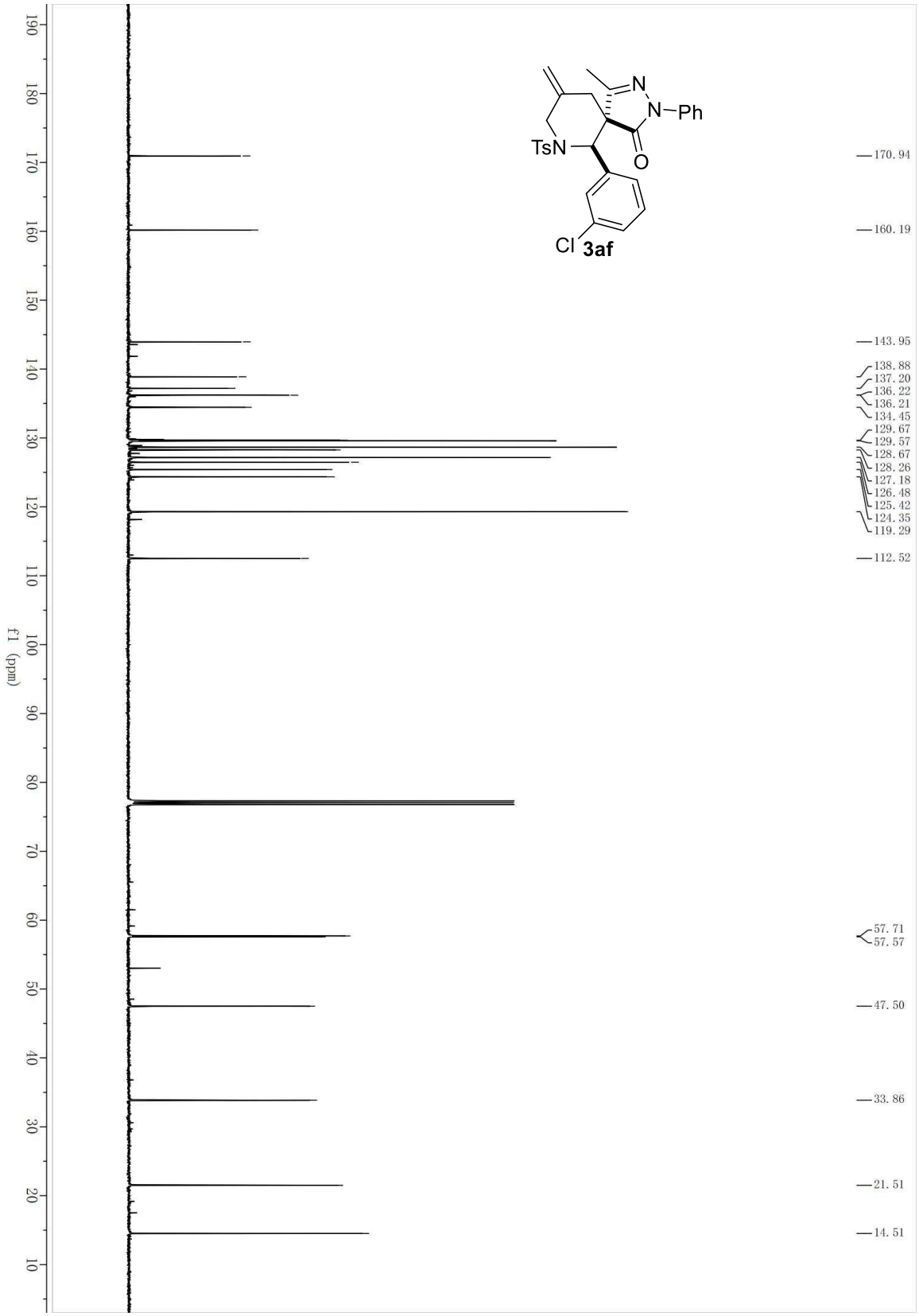
9.45
1.08
1.01
1.00
2.11
8.29
f1 (ppm)


N
N–Ph
TsN
O
Cl
3af
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160.19
143.95
138.88
137.20
136.22
136.21
134.45
129.67
129.57
128.67
128.26
127.18
126.48
125.42
124.35
119.29
112.52
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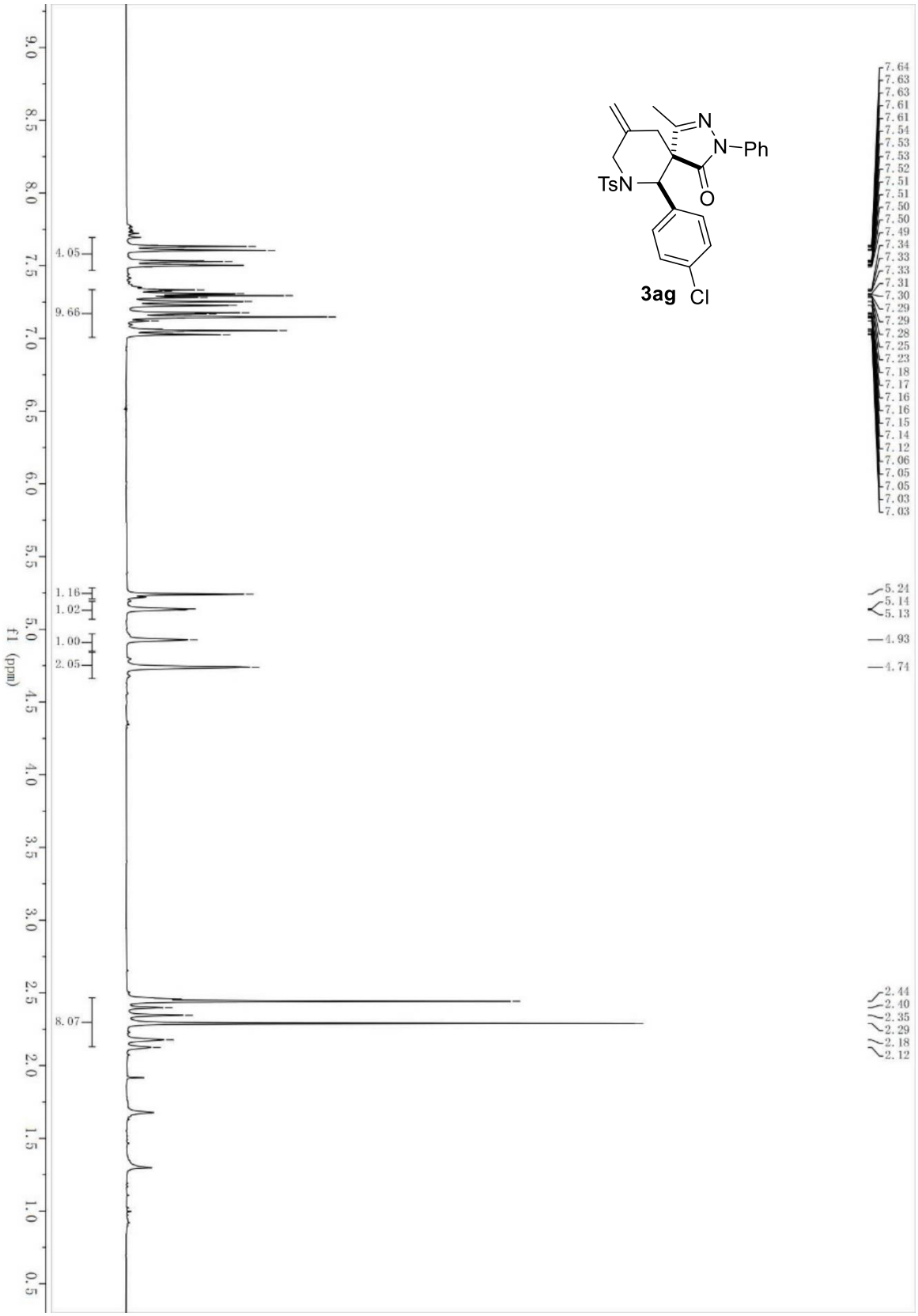
57.57
47.50
33.86
21.51
14.51
f1 (ppm)


3ag
TsN
N
N–Ph
O
Cl
f1 (ppm)
4.05
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1.16
1.02
1.00
2.05
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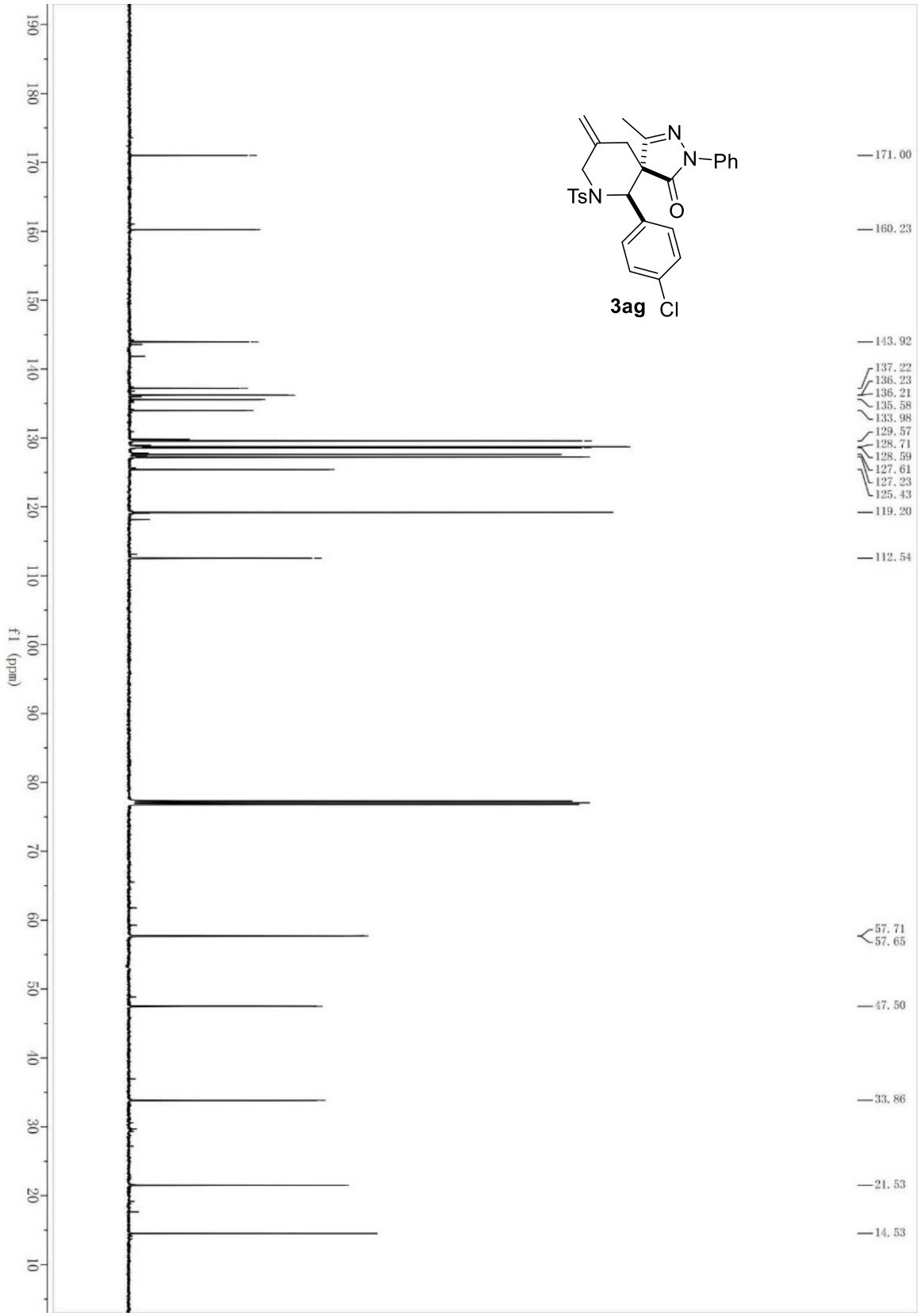
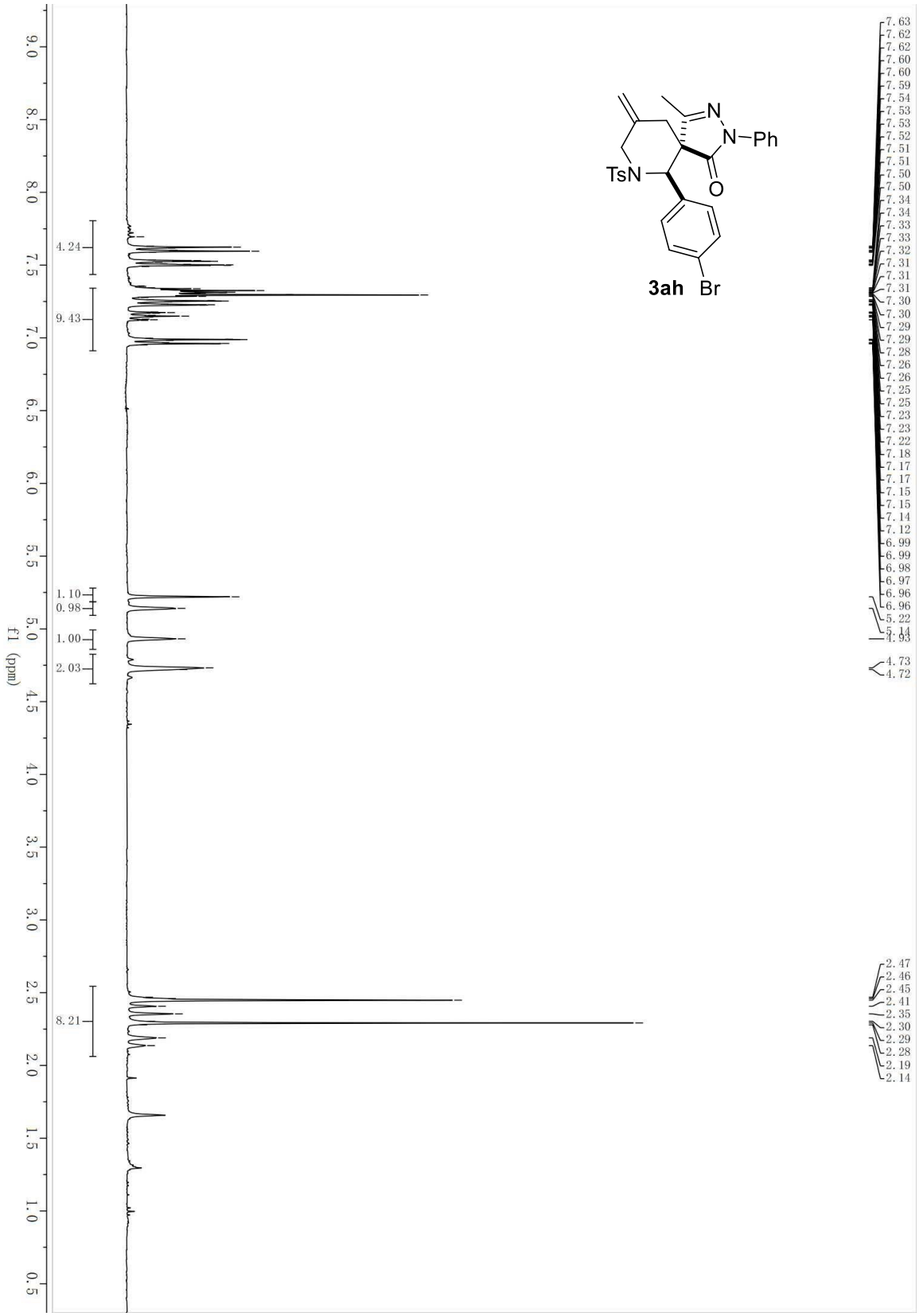
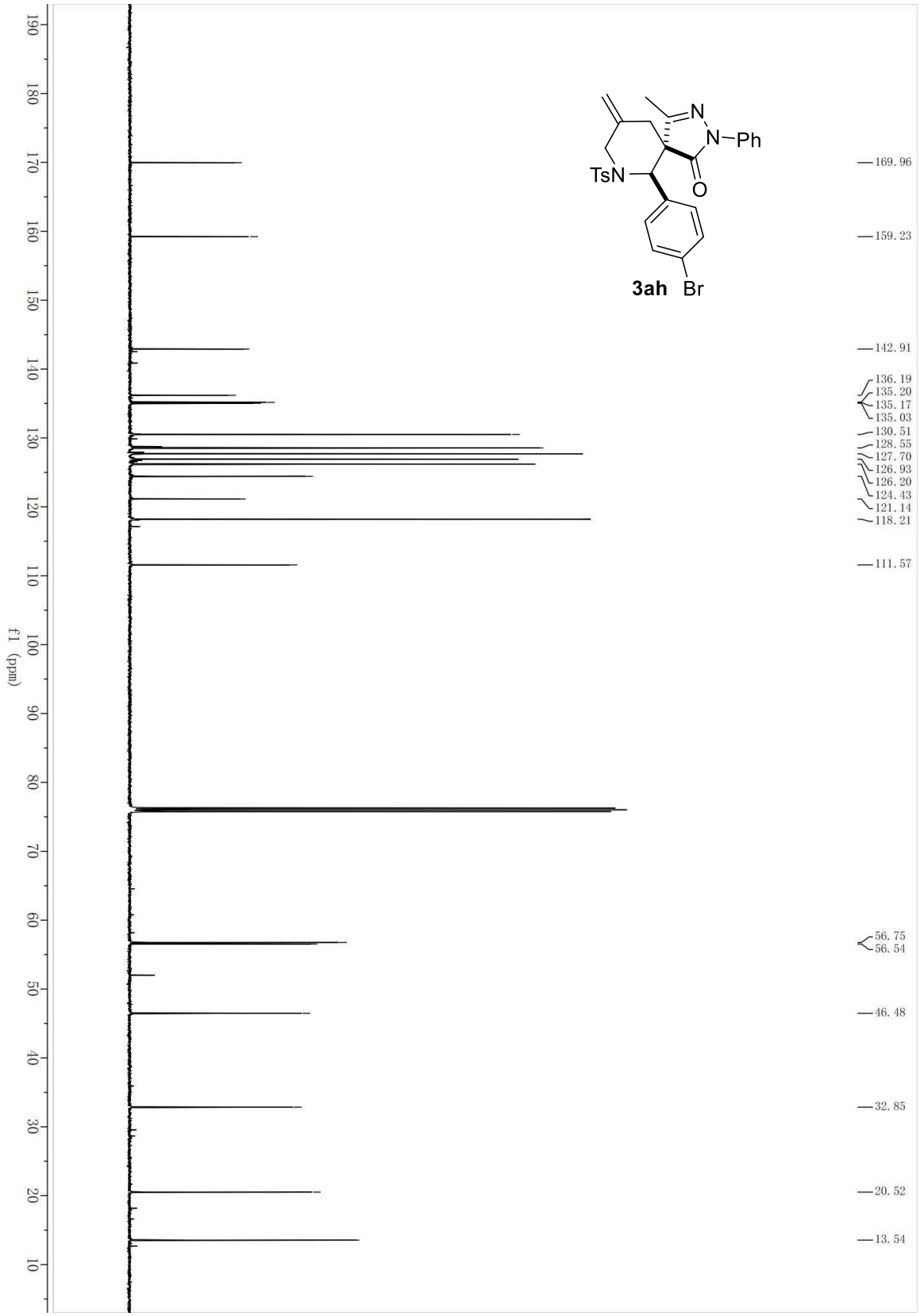
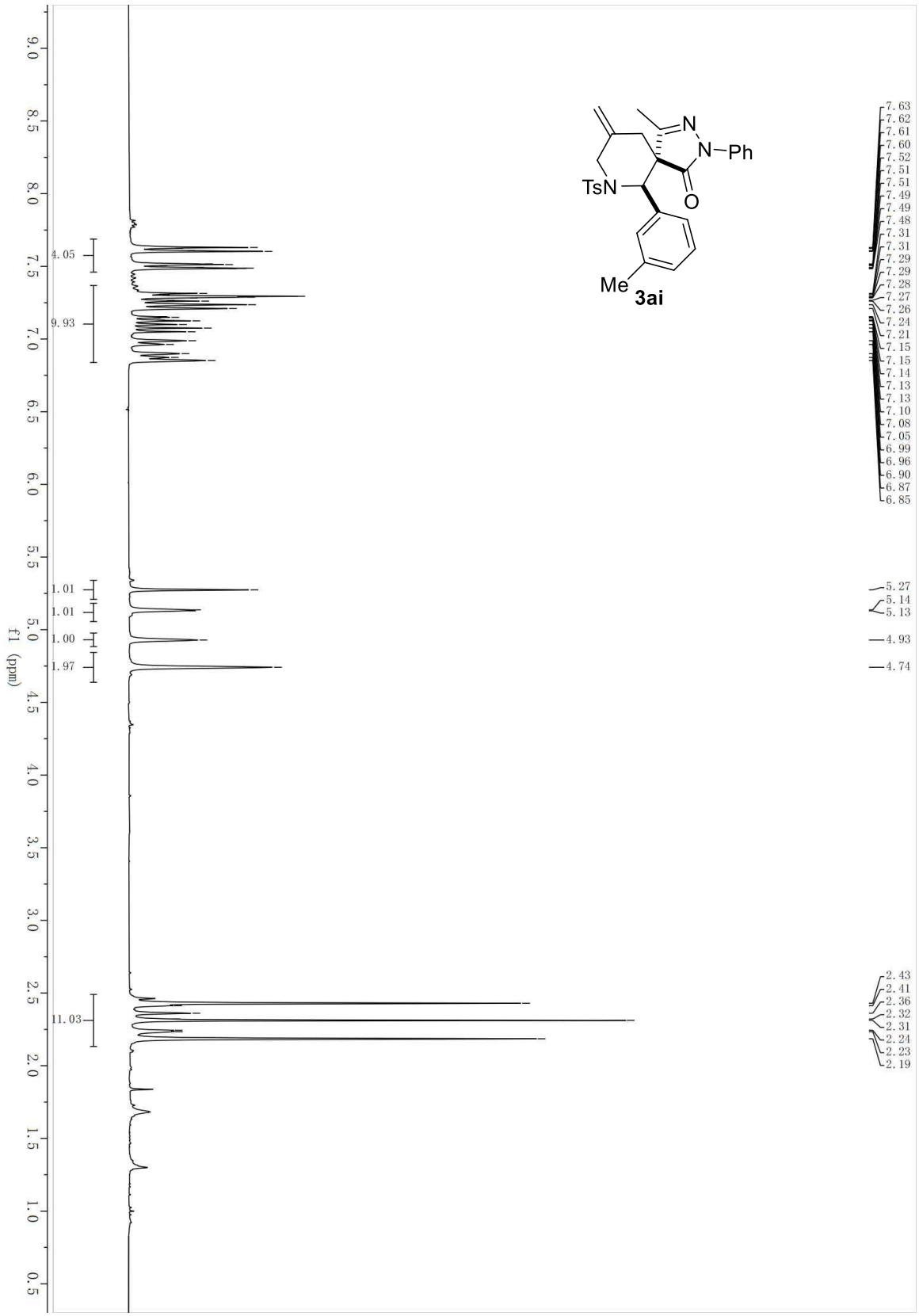
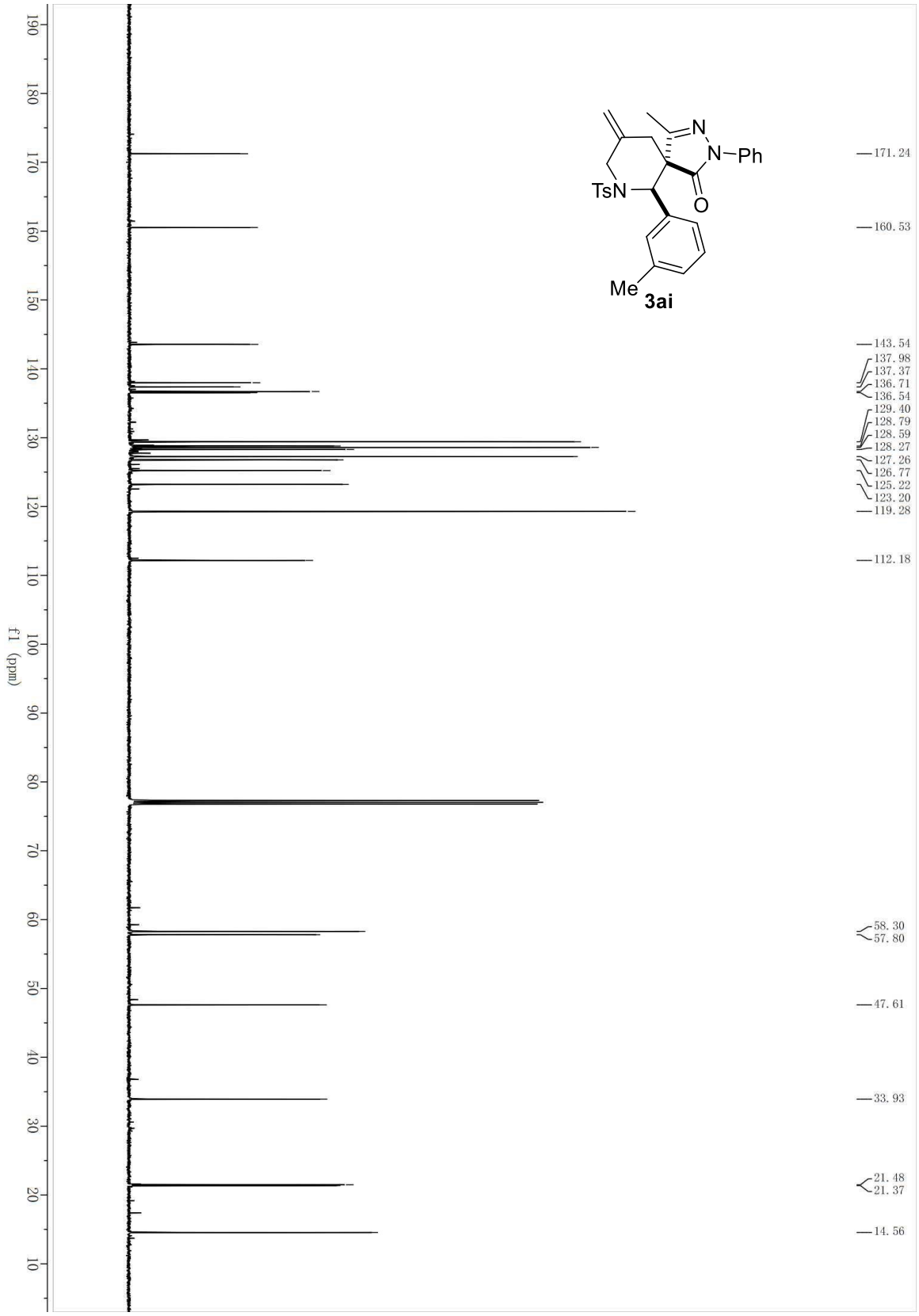
7.64
7.63
7.63
7.61
7.61
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.34
7.33
7.33
7.31
7.30
7.29
7.29
7.28
7.25
7.23
7.18
7.17
7.16
7.16
7.15
7.14
7.12
7.06
7.05
7.05
7.03
7.03
5.24
5.14
5.13
4.93
4.74
2.44
2.40
2.35
2.29
2.18
2.12

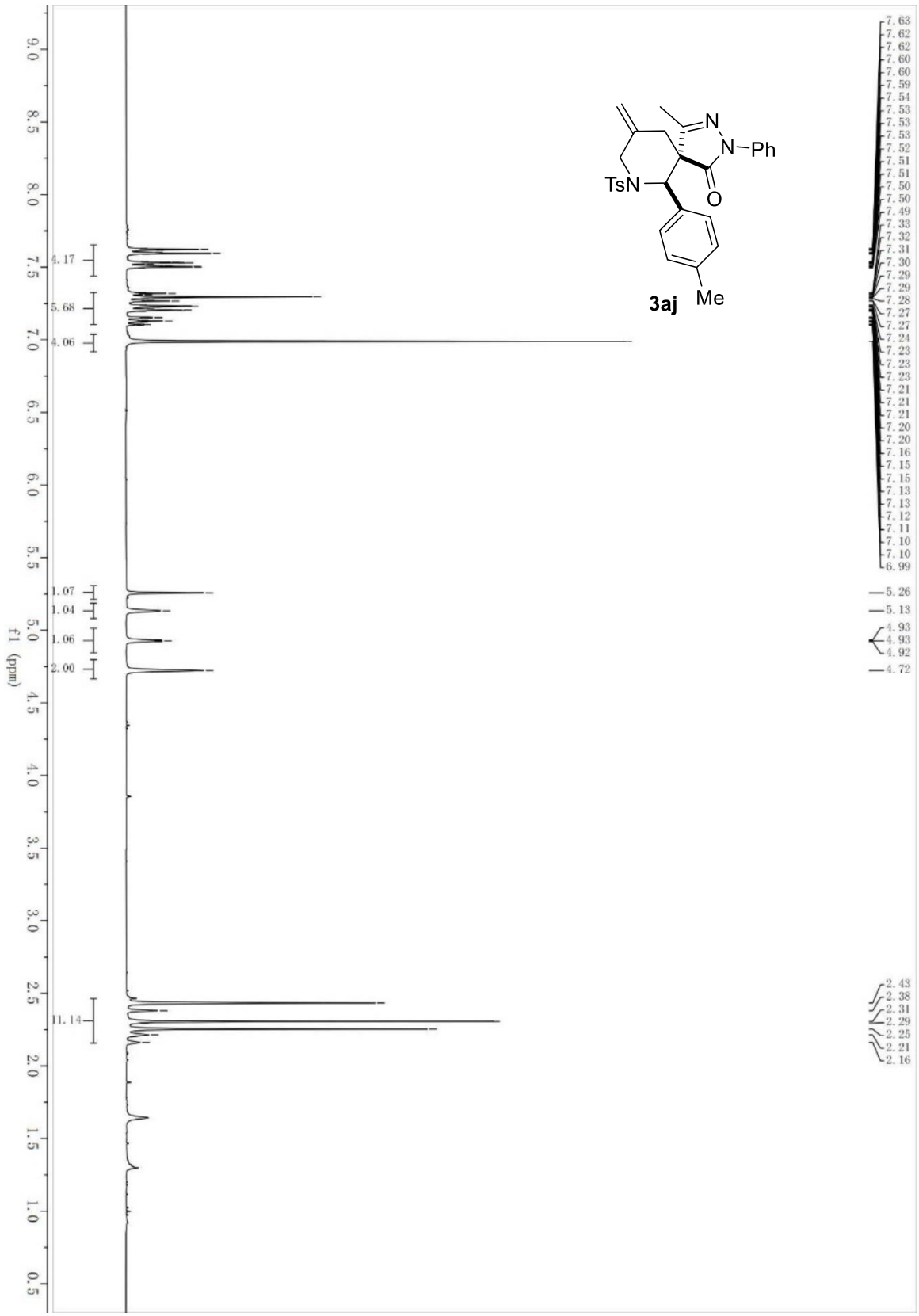

N
N–Ph
TsN
O
Cl
3ag
171.00
160.23
143.92
137.22
136.23
136.21
135.58
133.98
129.57
128.71
128.59
127.61
127.23
125.43
119.20
112.54
57.71
57.65
47.50
33.86
21.53
14.53
f1 (ppm)

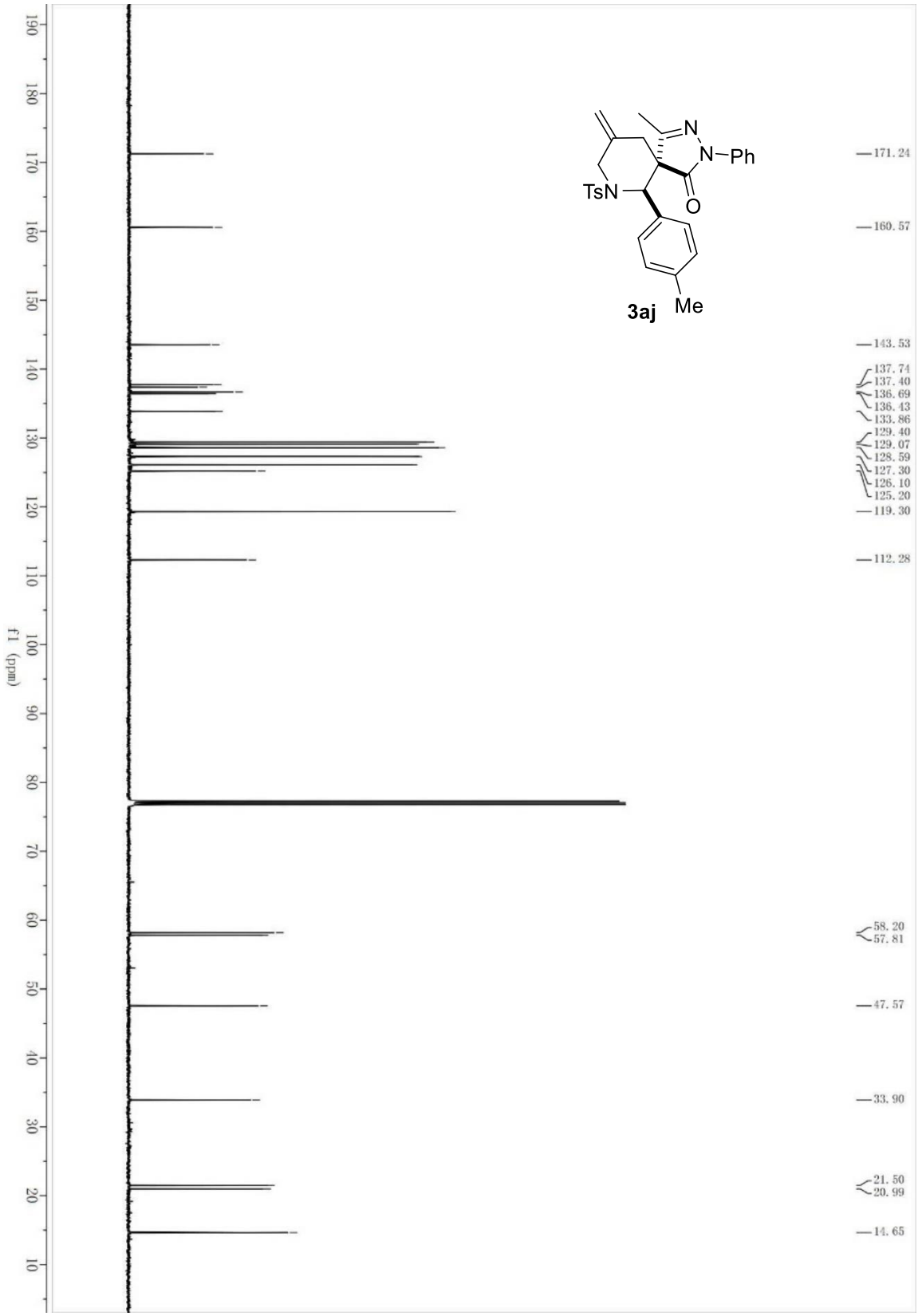

3ah
Br
TsN
N
N–Ph
O
f1 (ppm)
4.24
9.43
1.10
0.98
1.00
2.03
8.21

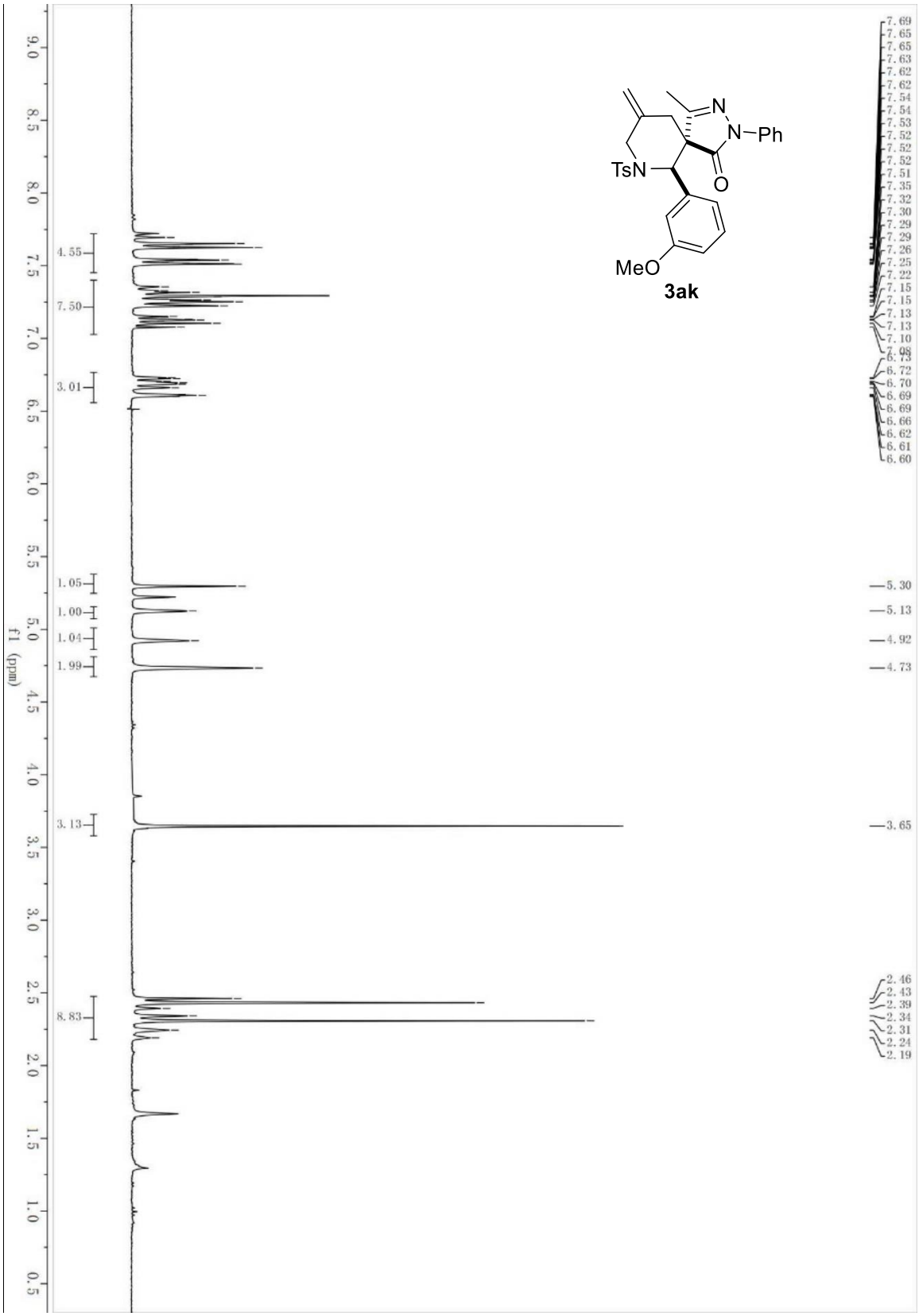

N
N–Ph
TsN
O
3ah Br
169.96
159.23
142.91
136.19
135.20
135.17
135.03
130.51
128.55
127.70
126.93
126.20
124.43
121.14
118.21
111.57
56.75
56.54
46.48
32.85
20.52
13.54
f1 (ppm)

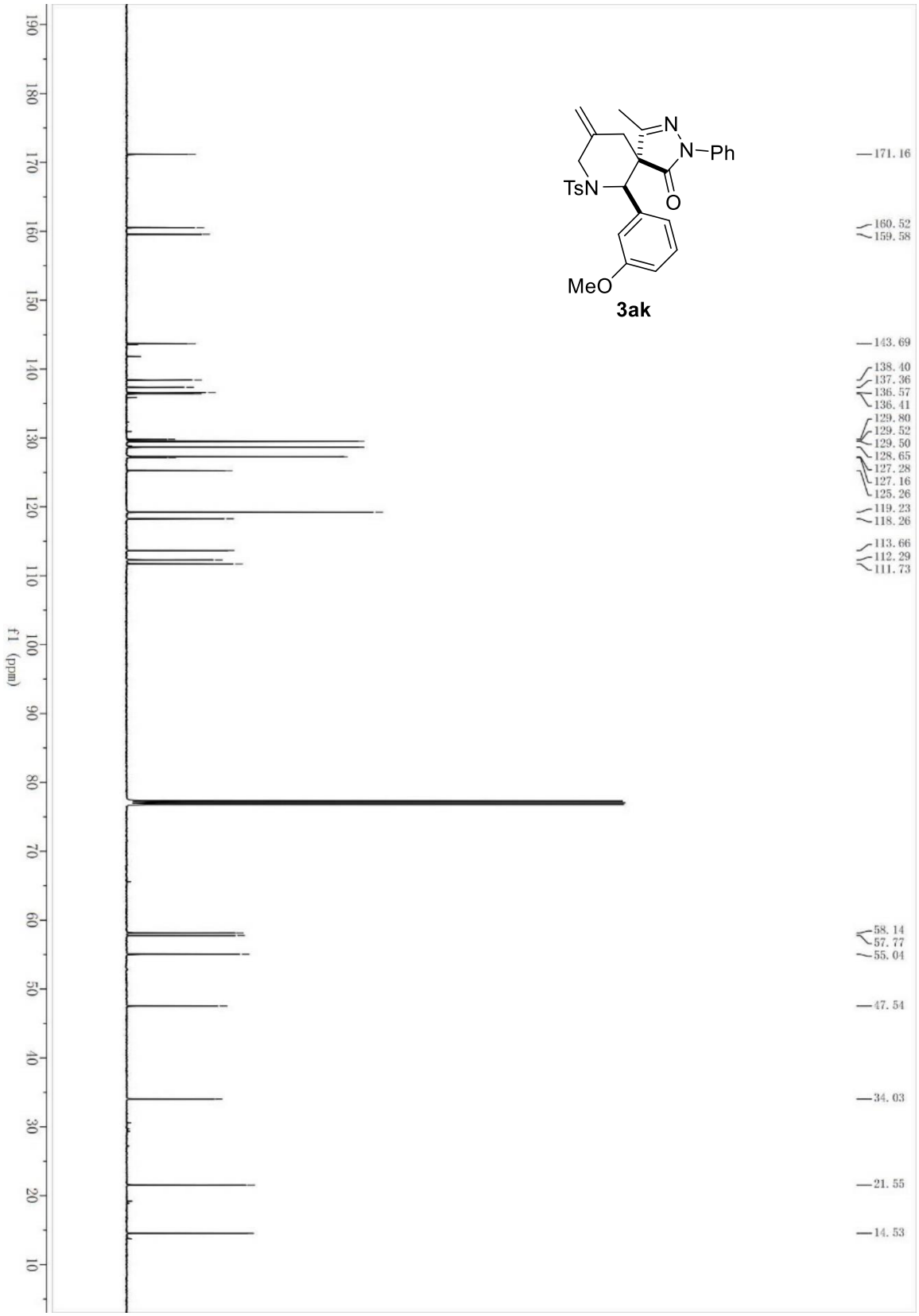

3ai
TsN
N
N–Ph
O
Me
f1 (ppm)
4.05
9.93
1.01
1.01
1.00
1.97
11.03
7.63
7.62
7.61
7.60
7.52
7.51
7.51
7.49
7.49
7.48
7.31
7.31
7.29
7.29
7.28
7.27
7.26
7.24
7.21
7.15
7.15
7.14
7.13
7.13
7.10
7.08
7.05
6.99
6.96
6.90
6.87
6.85
5.27
5.14
5.13
4.93
4.74
2.43
2.41
2.36
2.32
2.31
2.24
2.23
2.19

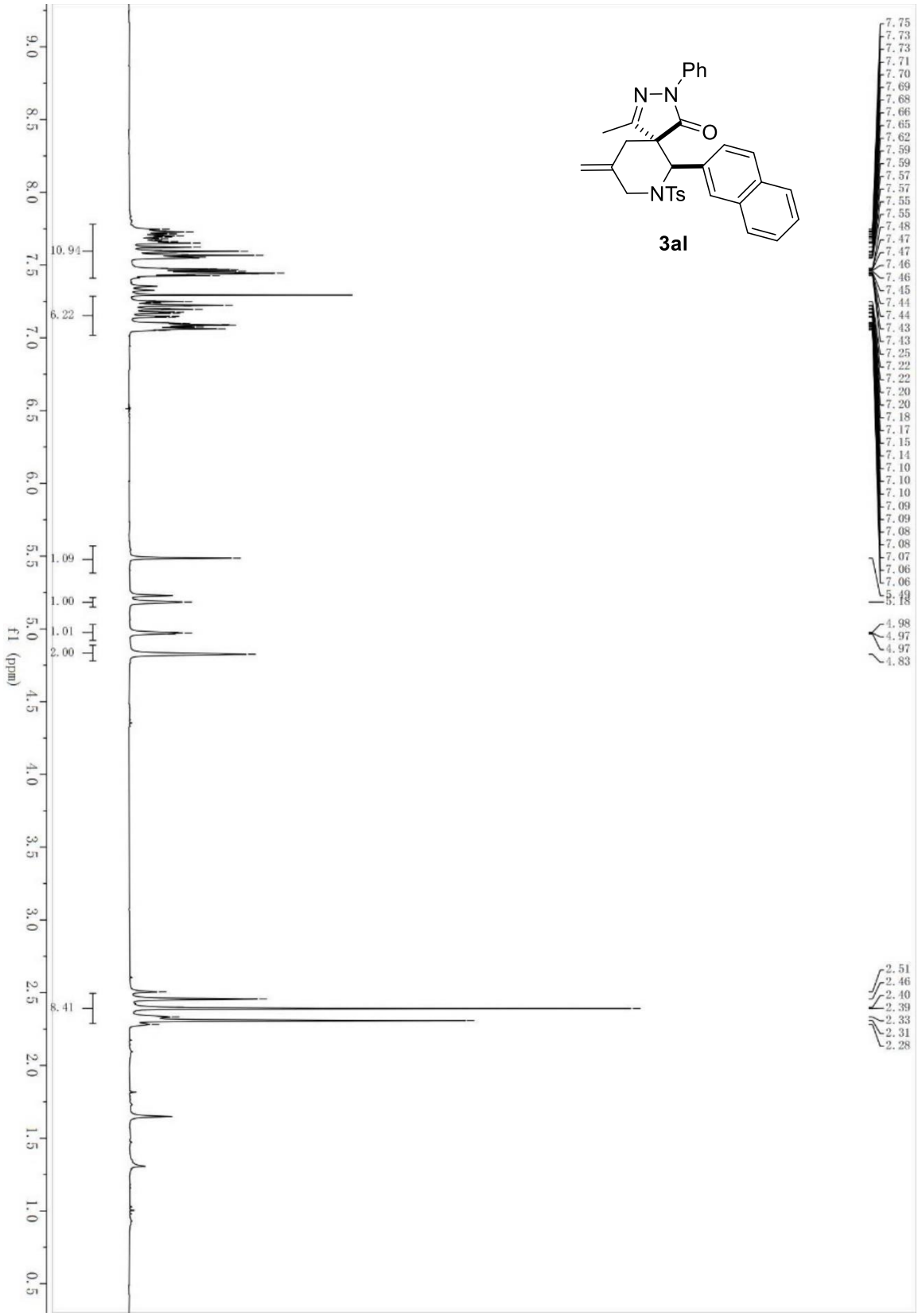

N
N–Ph
TsN
O
Me
3ai
171.24
160.53
143.54
137.98
137.37
136.71
136.54
129.40
128.79
128.59
128.27
127.26
126.77
125.22
123.20
119.28
112.18
58.30
57.80
47.61
33.93
21.48
21.37
14.56
f1 (ppm)

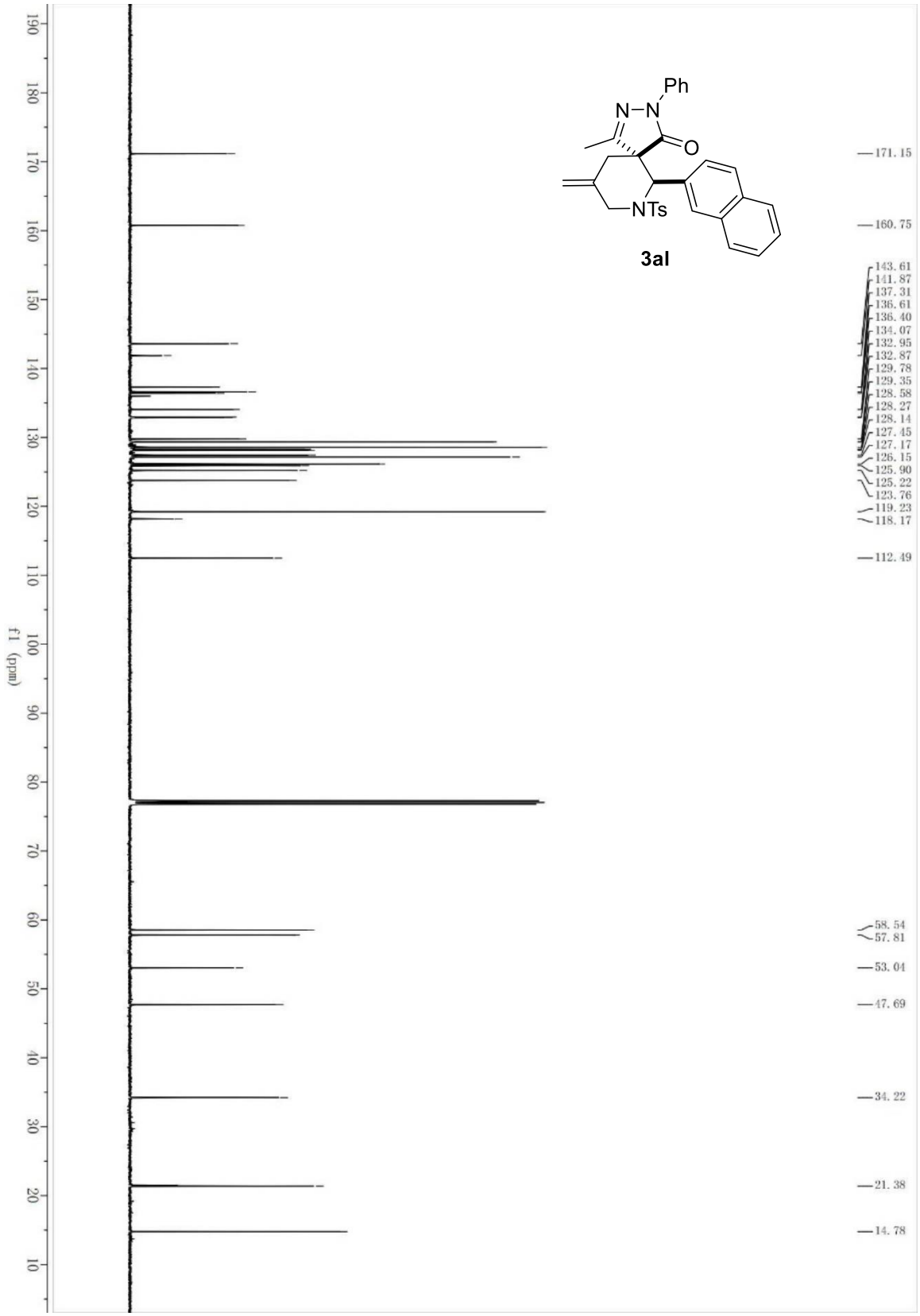

N
N–Ph
TsN
O
Me
3aj
f1 (ppm)
4.17
5.68
4.06
1.07
1.04
1.06
2.00
11.14
7.63
7.62
7.62
7.60
7.60
7.59
7.54
7.53
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.24
7.23
7.23
7.23
7.21
7.21
7.21
7.20
7.20
7.16
7.15
7.15
7.13
7.13
7.12
7.11
7.10
7.10
6.99
5.26
5.13
4.93
4.93
4.92
4.72
2.43
2.38
2.31
2.29
2.25
2.21
2.16

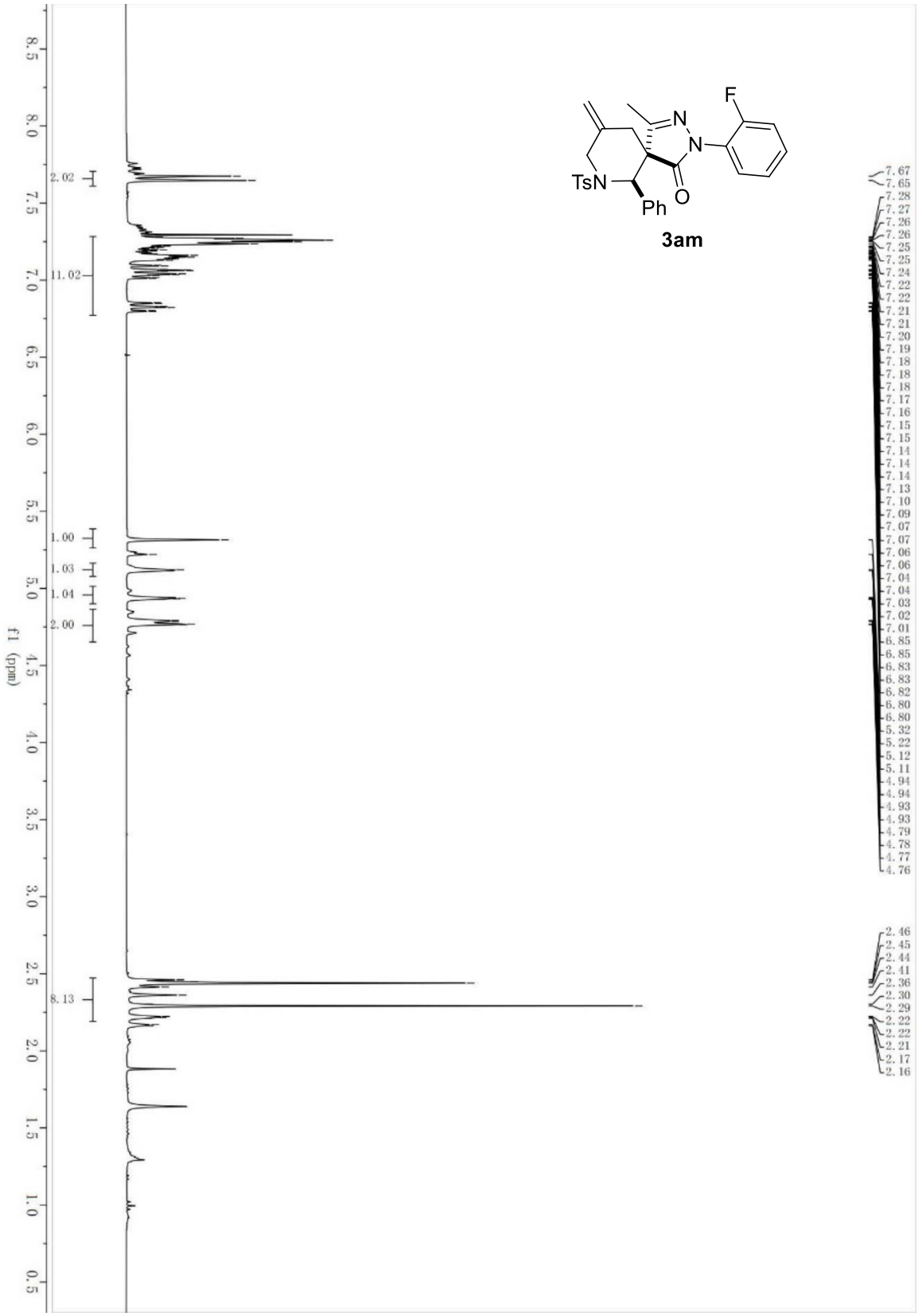

N
N–Ph
TsN
O
Me
3aj
171.24
160.57
143.53
137.74
137.40
136.69
136.43
133.86
129.40
129.07
128.59
127.30
126.10
125.20
119.30
112.28
58.20
57.81
47.57
33.90
21.50
20.99
14.65
f1 (ppm)

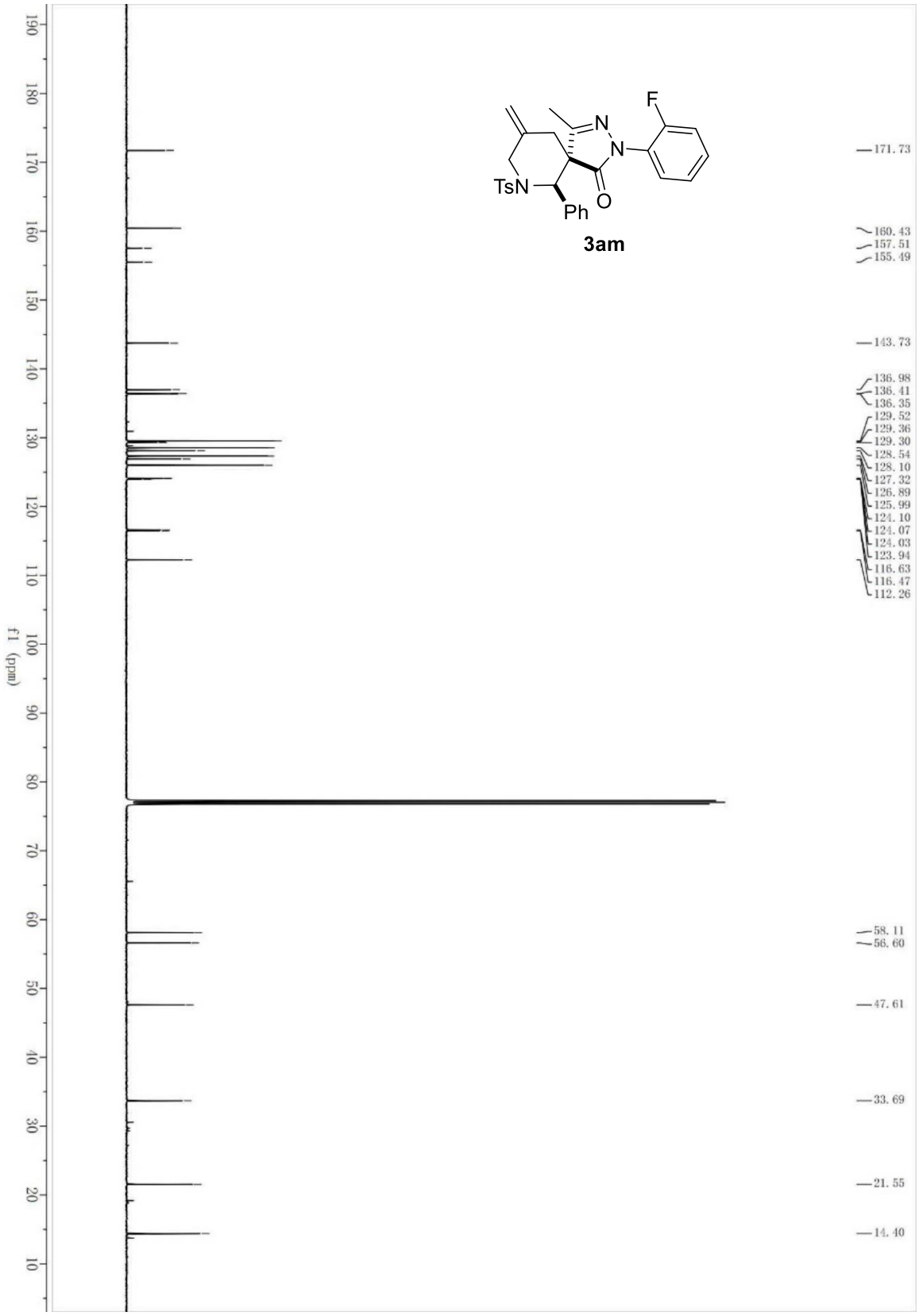

TsN
N
N–Ph
O
MeO
3ak
f1 (ppm)
4.55
7.50
3.01
1.05
1.00
1.04
1.99
3.13
8.83
7.69
7.65
7.65
7.63
7.62
7.62
7.54
7.54
7.53
7.52
7.52
7.52
7.51
7.35
7.32
7.30
7.29
7.29
7.26
7.25
7.22
7.15
7.15
7.13
7.13
7.10
7.08
6.73
6.72
6.70
6.69
6.69
6.66
6.62
6.61
6.60
5.30
5.13
4.92
4.73
3.65
2.46
2.43
2.39
2.34
2.31
2.24
2.19

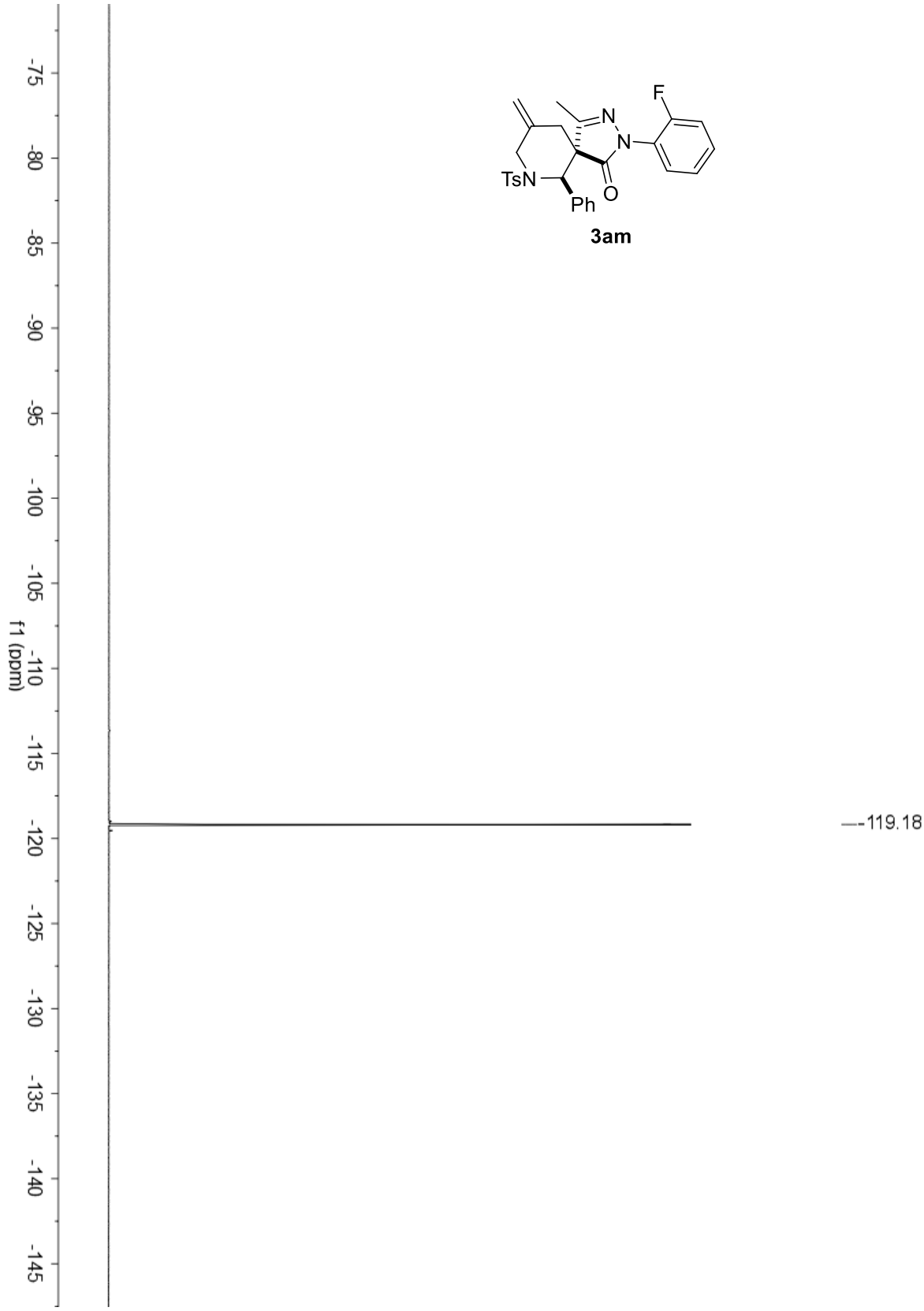

N
N–Ph
TsN
O
MeO
3ak
171.16
160.52
159.58
143.69
138.40
137.36
136.57
136.41
129.80
129.52
129.50
128.65
127.28
127.16
125.26
119.23
118.26
113.66
112.29
111.73
58.14
57.77
55.04
47.54
34.03
21.55
14.53
f1 (ppm)

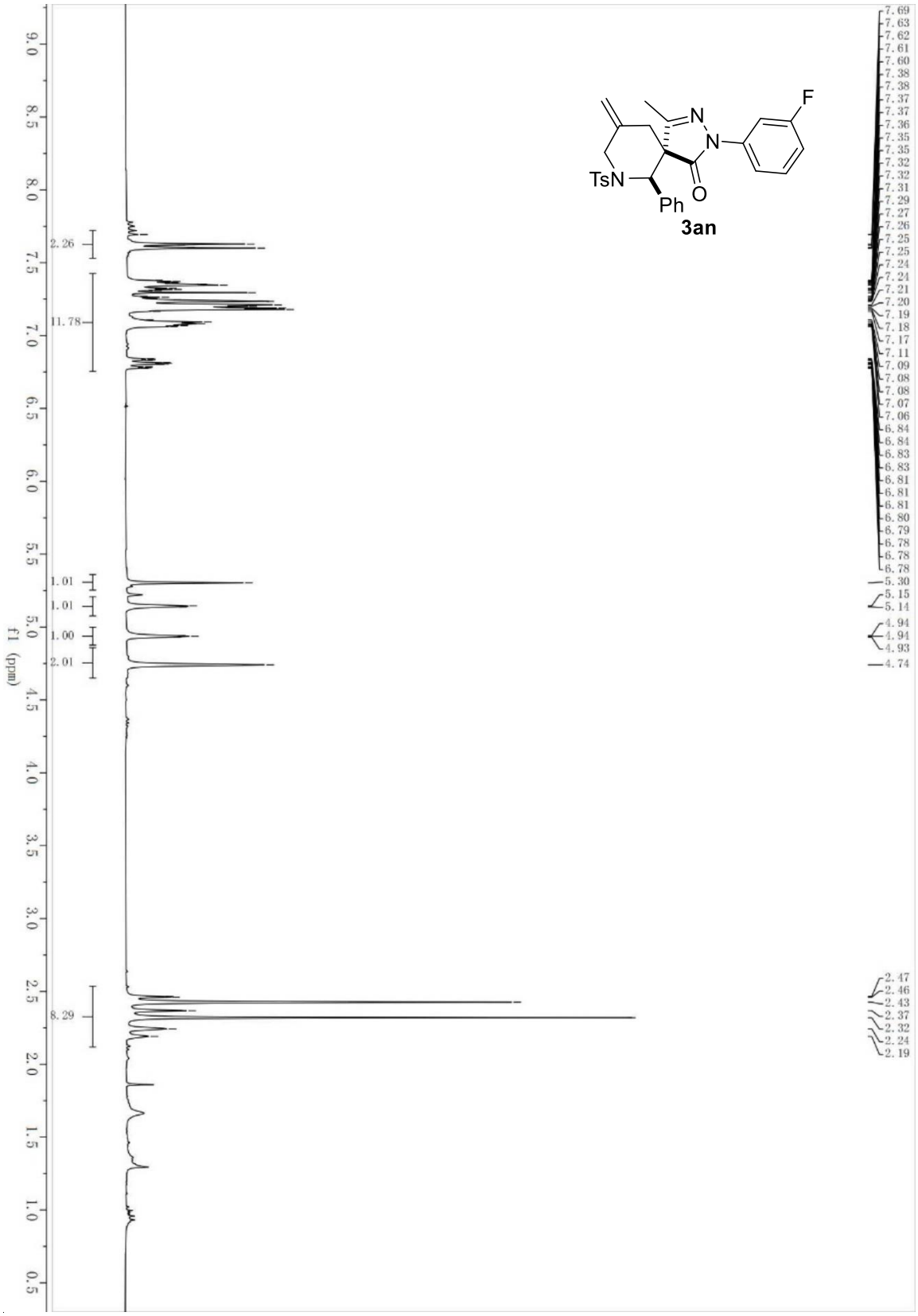

Ph
N–N
O
NTs
3al
f1 (ppm)
10.94
6.22
1.09
1.00
1.01
2.00
8.41
7.75
7.73
7.73
7.71
7.70
7.69
7.68
7.66
7.65
7.62
7.59
7.59
7.57
7.57
7.55
7.55
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.25
7.22
7.22
7.20
7.20
7.18
7.17
7.15
7.14
7.10
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.06
7.06
5.49
5.18
4.98
4.97
4.97
4.83
2.51
2.46
2.40
2.39
2.33
2.31
2.28

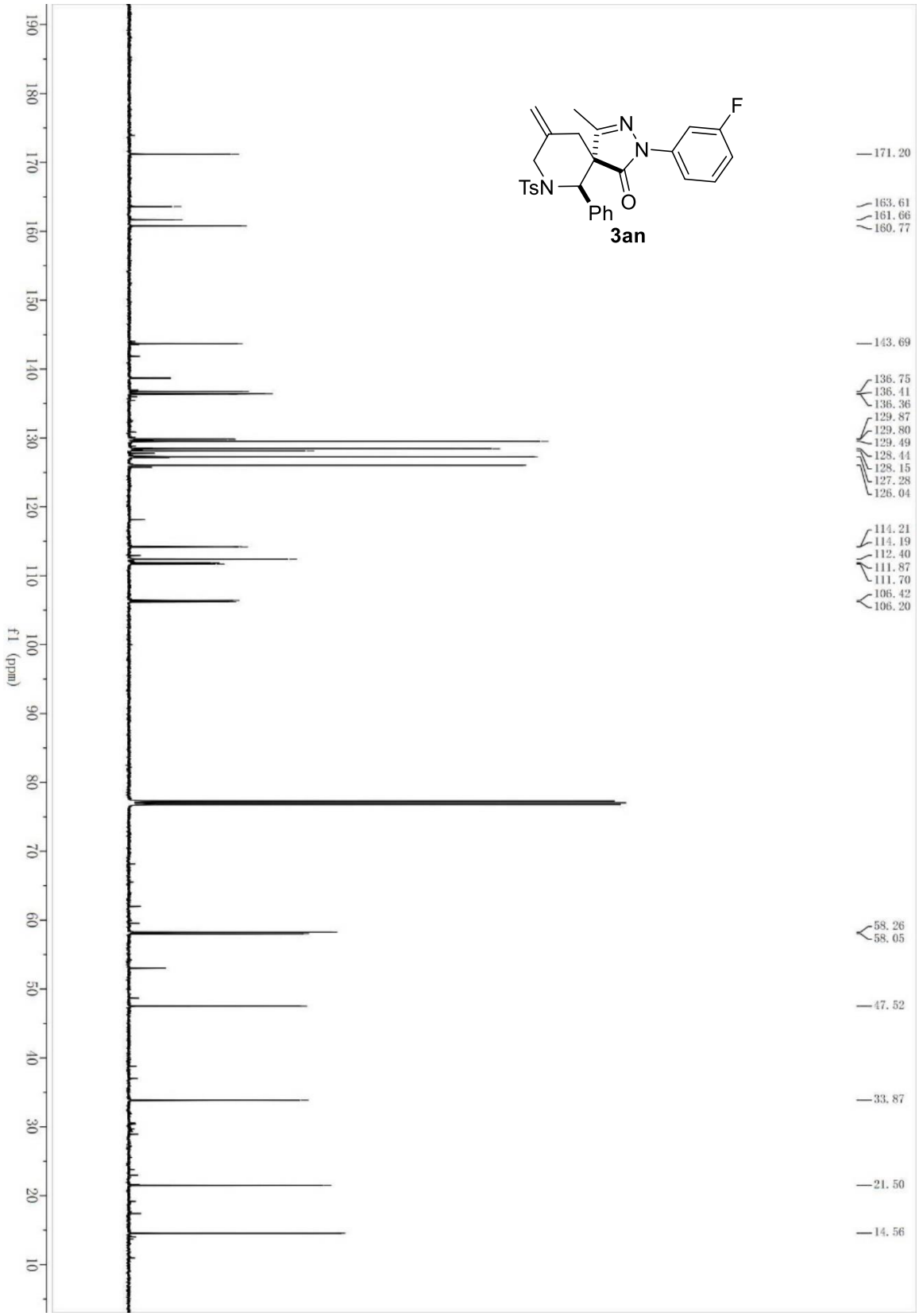

Ph
N–N
O
NTs
3al
171.15
160.75
143.61
141.87
137.31
136.61
136.40
134.07
132.95
132.87
129.78
129.35
128.58
128.27
128.14
127.45
127.17
126.15
125.90
125.22
123.76
119.23
118.17
112.49
58.54
57.81
53.04
47.69
34.22
21.38
14.78
f1 (ppm)

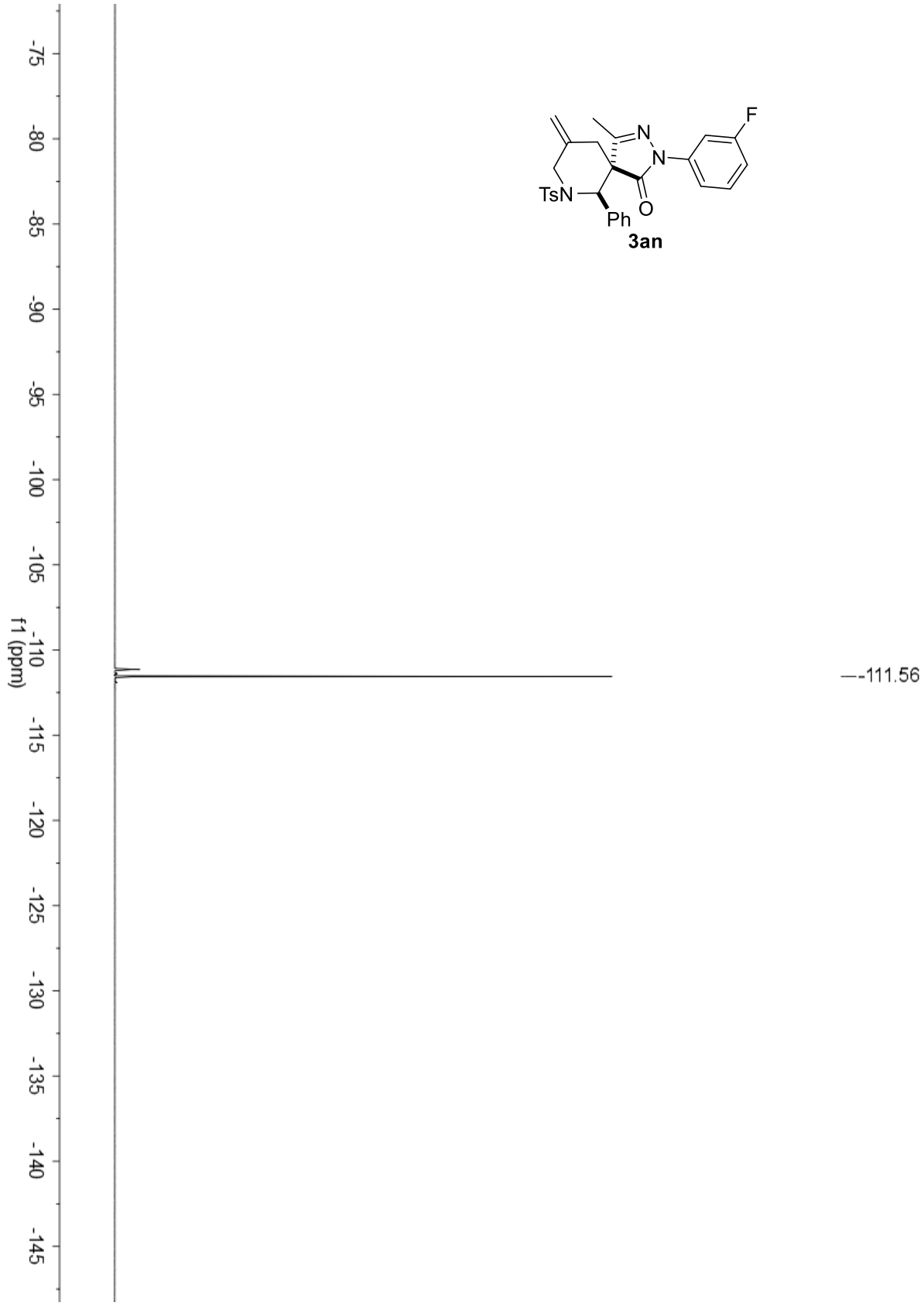

F
N
N
TsN
Ph
O
3am
f1 (ppm)
2.02
11.02
1.00
1.03
1.04
2.00
8.13

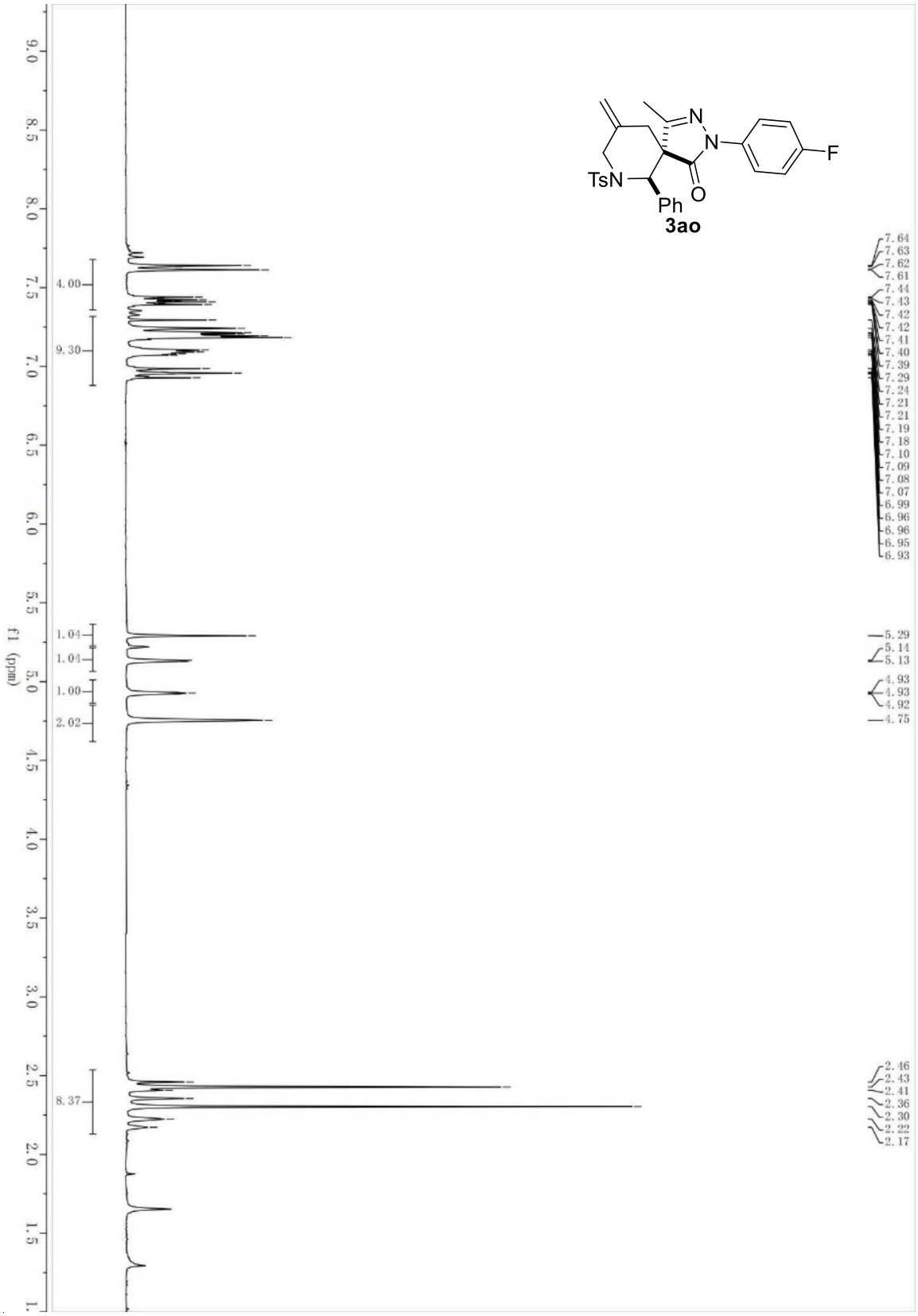

F
N
N
TsN
O
Ph
3am
171.73
160.43
157.51
155.49
143.73
136.98
136.41
136.35
129.52
129.36
129.30
128.54
128.10
127.32
126.89
125.99
124.10
124.07
124.03
123.94
116.63
116.47
112.26
58.11
56.60
47.61
33.69
21.55
14.40
f1 (ppm)

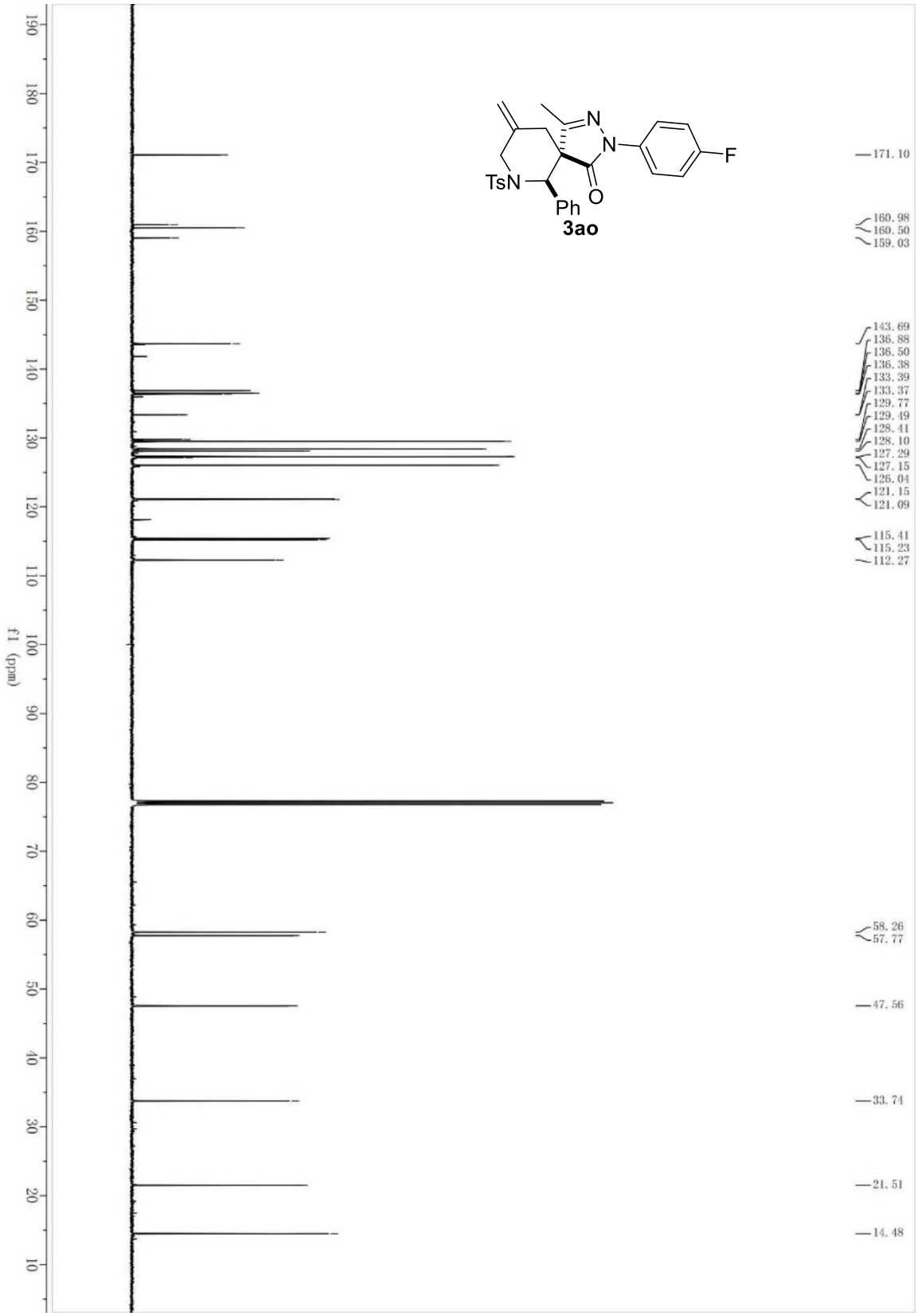

F
N
N
TsN
Ph
O
3am
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)
-119.18

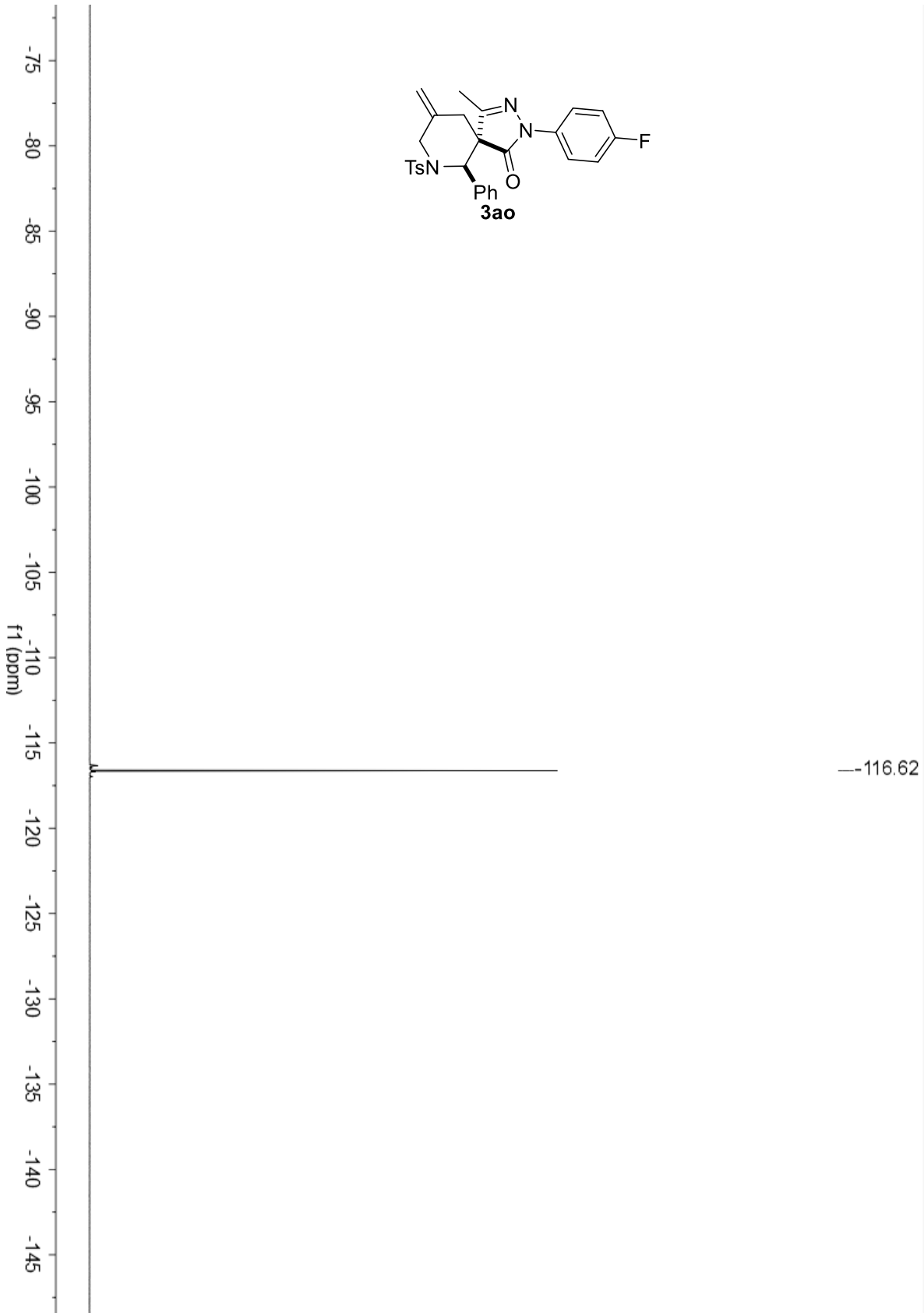

F
N
N
TsN
Ph
O
3an
f1 (ppm)
2.26
11.78
1.01
1.01
1.00
2.01
8.29
7.69
7.63
7.62
7.61
7.60
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.32
7.32
7.31
7.29
7.27
7.26
7.25
7.25
7.24
7.24
7.21
7.20
7.19
7.18
7.17
7.11
7.09
7.08
7.08
7.07
7.06
6.84
6.84
6.83
6.83
6.81
6.81
6.81
6.80
6.79
6.78
6.78
6.78
5.30
5.15
5.14
4.94
4.94
4.93
4.74
2.47
2.46
2.43
2.37
2.32
2.24
2.19

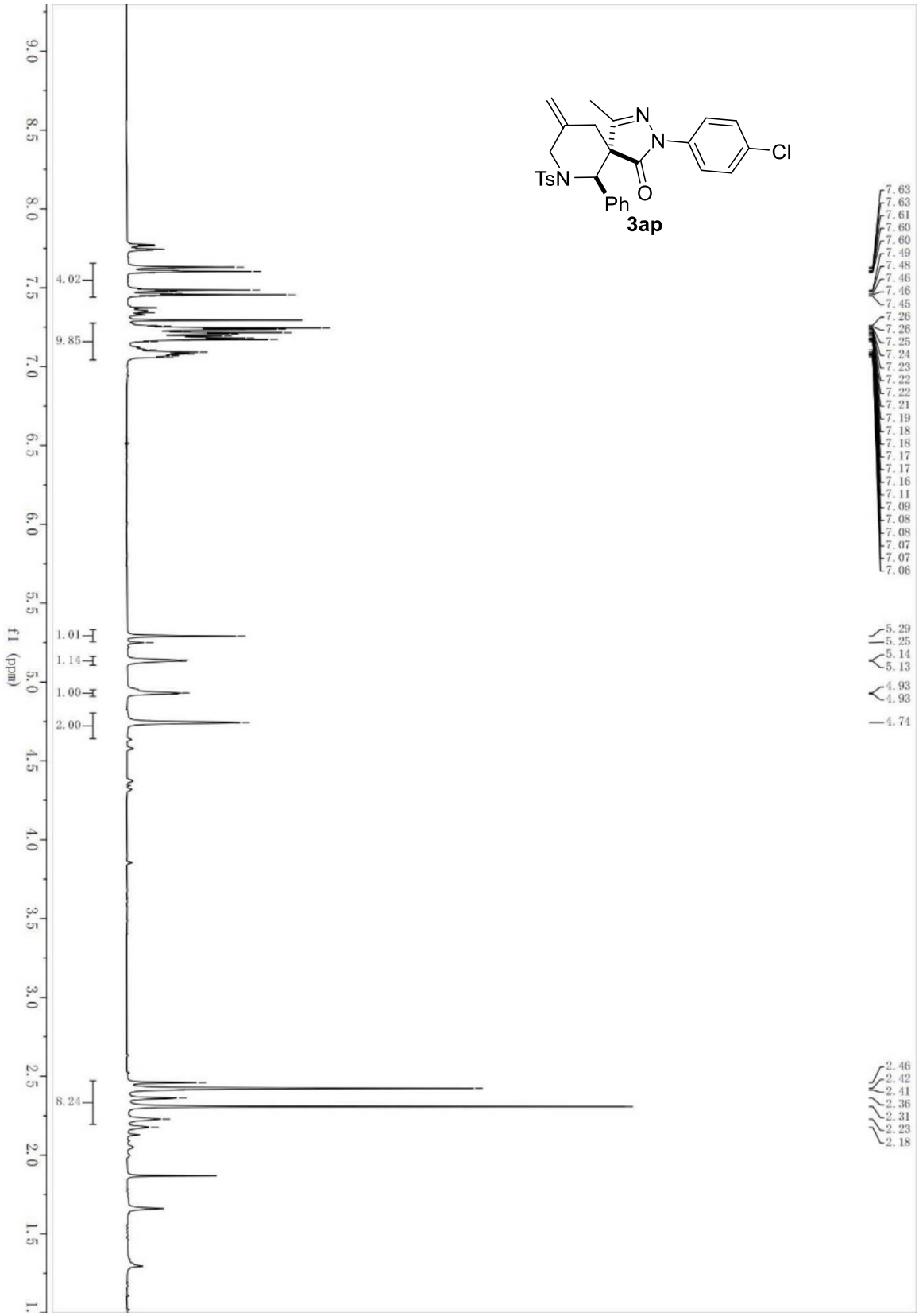

F
N
N
TsN
Ph
O
3an
171.20
163.61
161.66
160.77
143.69
136.75
136.41
136.36
129.87
129.80
129.49
128.44
128.15
127.28
126.04
114.21
114.19
112.40
111.87
111.70
106.42
106.20
58.26
58.05
47.52
33.87
21.50
14.56
f1 (ppm)

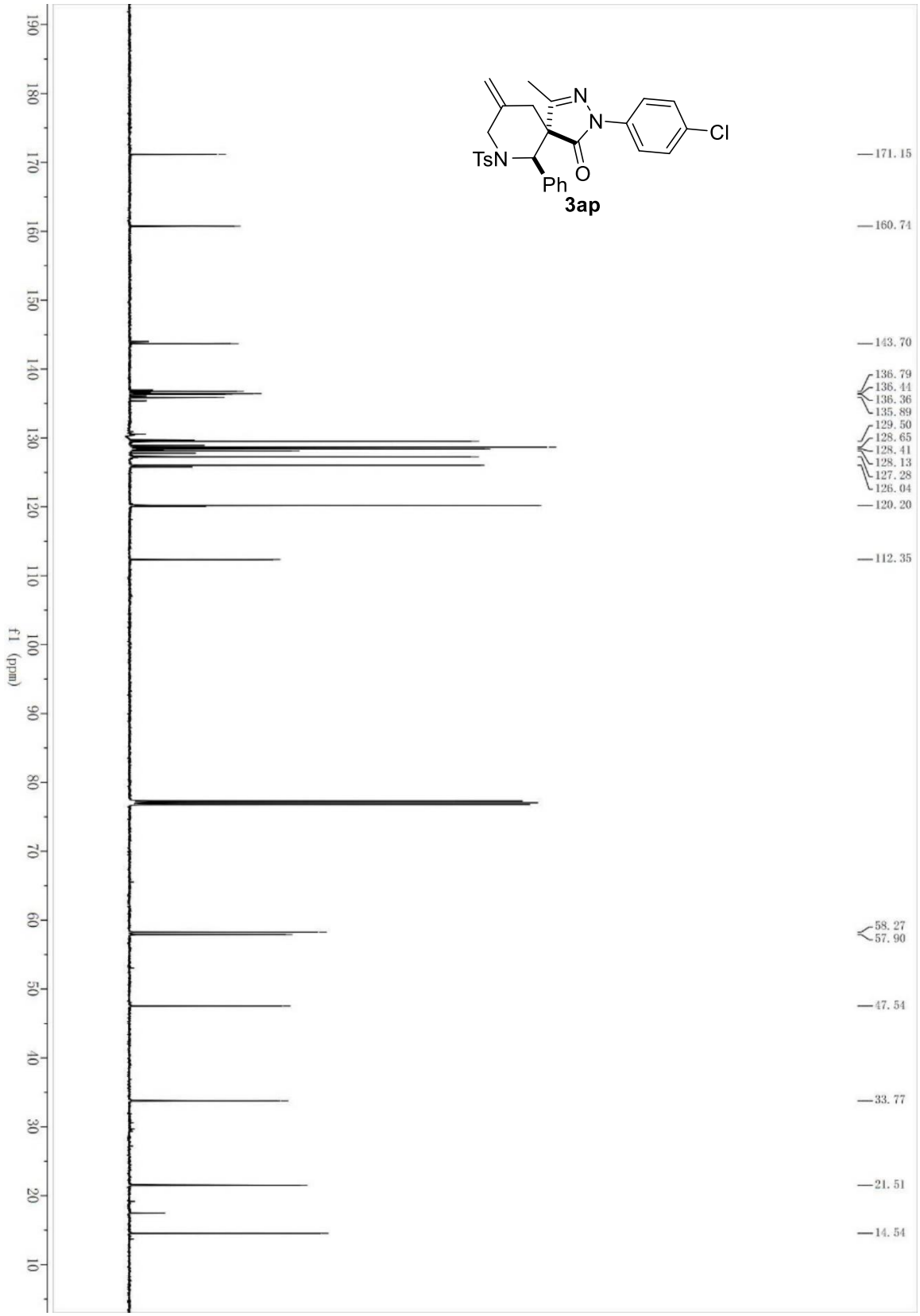

F
N
N
TsN
Ph
O
3an
-111.56
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

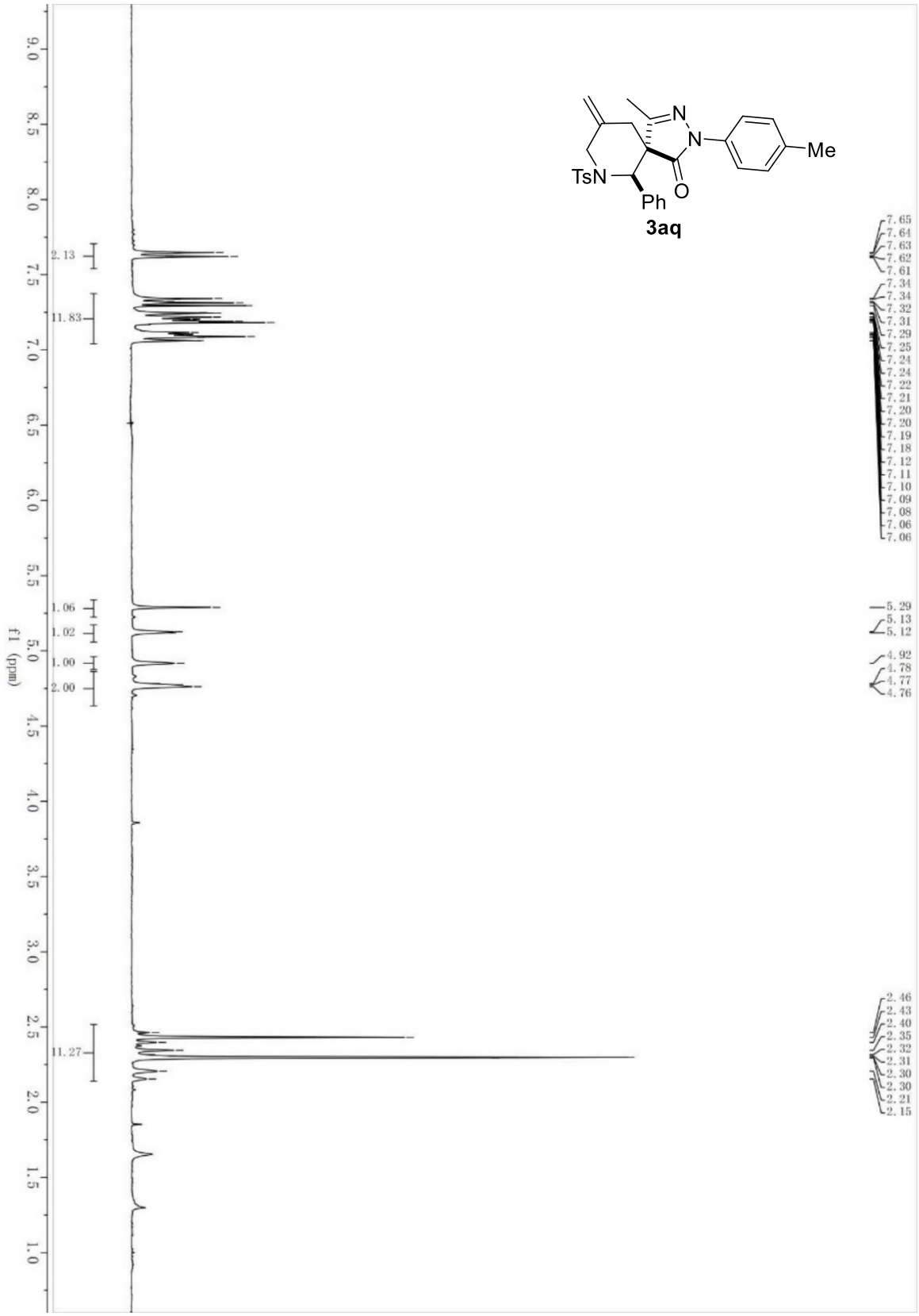

TsN
Ph
O
N
N
F
3ao
f1 (ppm)
4.00
9.30
1.04
1.04
1.00
2.02
8.37
7.64
7.63
7.62
7.61
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.29
7.24
7.21
7.21
7.19
7.18
7.10
7.09
7.08
7.07
6.99
6.96
6.96
6.95
6.93
5.29
5.14
5.13
4.93
4.93
4.92
4.75
2.46
2.43
2.41
2.36
2.30
2.22
2.17


TsN
Ph
O
N
N
F
3ao
f1 (ppm)
171.10
160.98
160.50
159.03
143.69
136.88
136.50
136.38
133.39
133.37
129.77
129.49
128.41
128.10
127.29
127.15
126.04
121.15
121.09
115.41
115.23
112.27
58.26
57.77
47.56
33.74
21.51
14.48


-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)
-116.62
TsN
Ph
O
N
N
F
3ao


TsN
Ph
O
N
N
Cl
3ap
f1 (ppm)
4.02
9.85
1.01
1.14
1.00
2.00
8.24
7.63
7.63
7.61
7.60
7.60
7.49
7.48
7.46
7.46
7.45
7.26
7.26
7.25
7.24
7.23
7.22
7.22
7.21
7.19
7.18
7.18
7.17
7.17
7.16
7.11
7.09
7.08
7.08
7.07
7.07
7.06
5.29
5.25
5.14
5.13
4.93
4.93
4.74
2.46
2.42
2.41
2.36
2.31
2.23
2.18


TsN
Ph
O
N
N
Cl
3ap
171.15
160.74
143.70
136.79
136.44
136.36
135.89
129.50
128.65
128.41
128.13
127.28
126.04
120.20
112.35
58.27
57.90
47.54
33.77
21.51
14.54
f1 (ppm)


3aq
TsN
Ph
O
N
N
Me
f1 (ppm)
2.13
11.83
1.06
1.02
1.00
2.00
11.27
7.65
7.64
7.63
7.62
7.61
7.34
7.34
7.32
7.31
7.29
7.25
7.24
7.24
7.22
7.21
7.20
7.20
7.19
7.18
7.12
7.11
7.10
7.09
7.08
7.06
7.06
5.29
5.13
5.12
4.92
4.78
4.77
4.76
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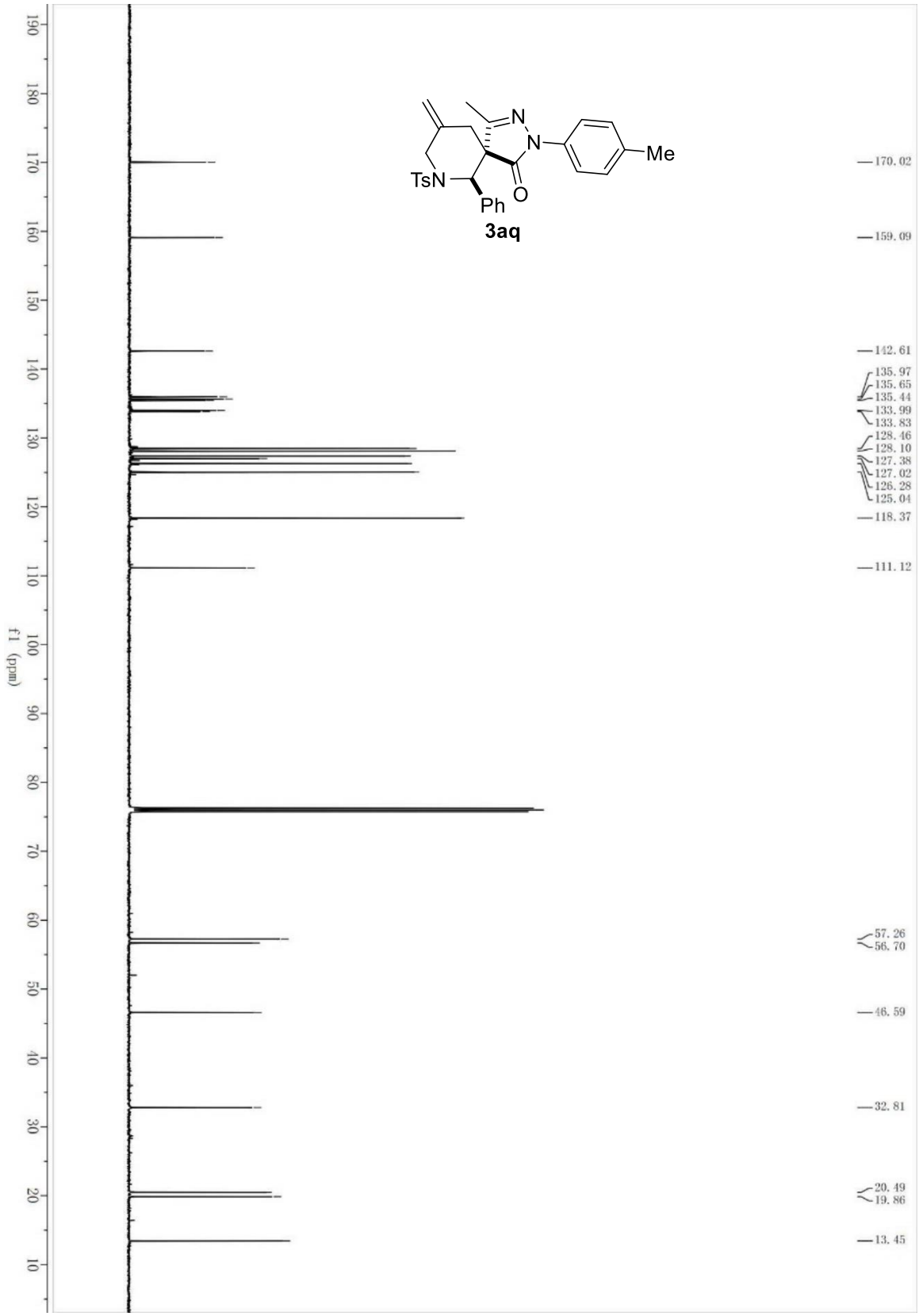
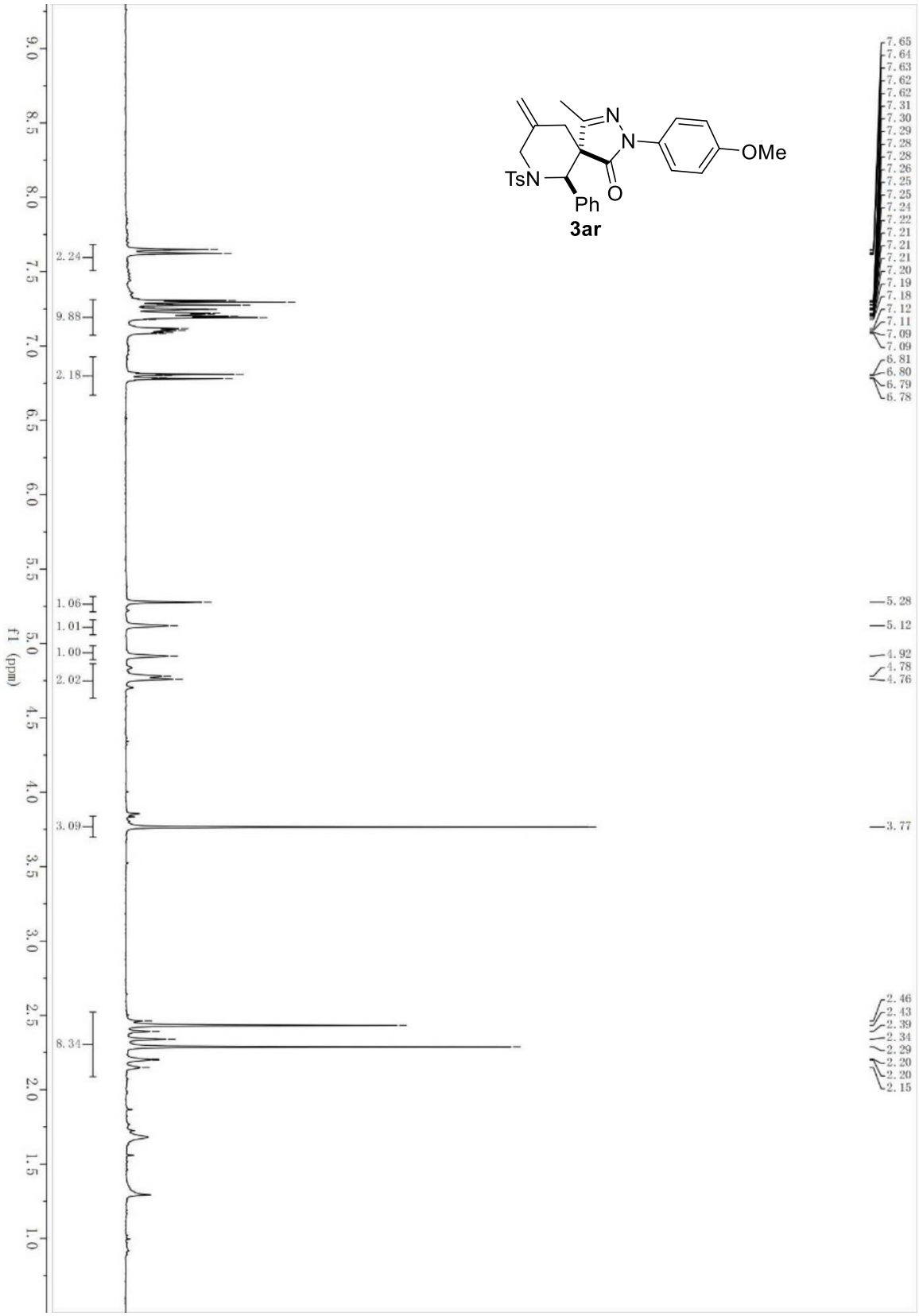
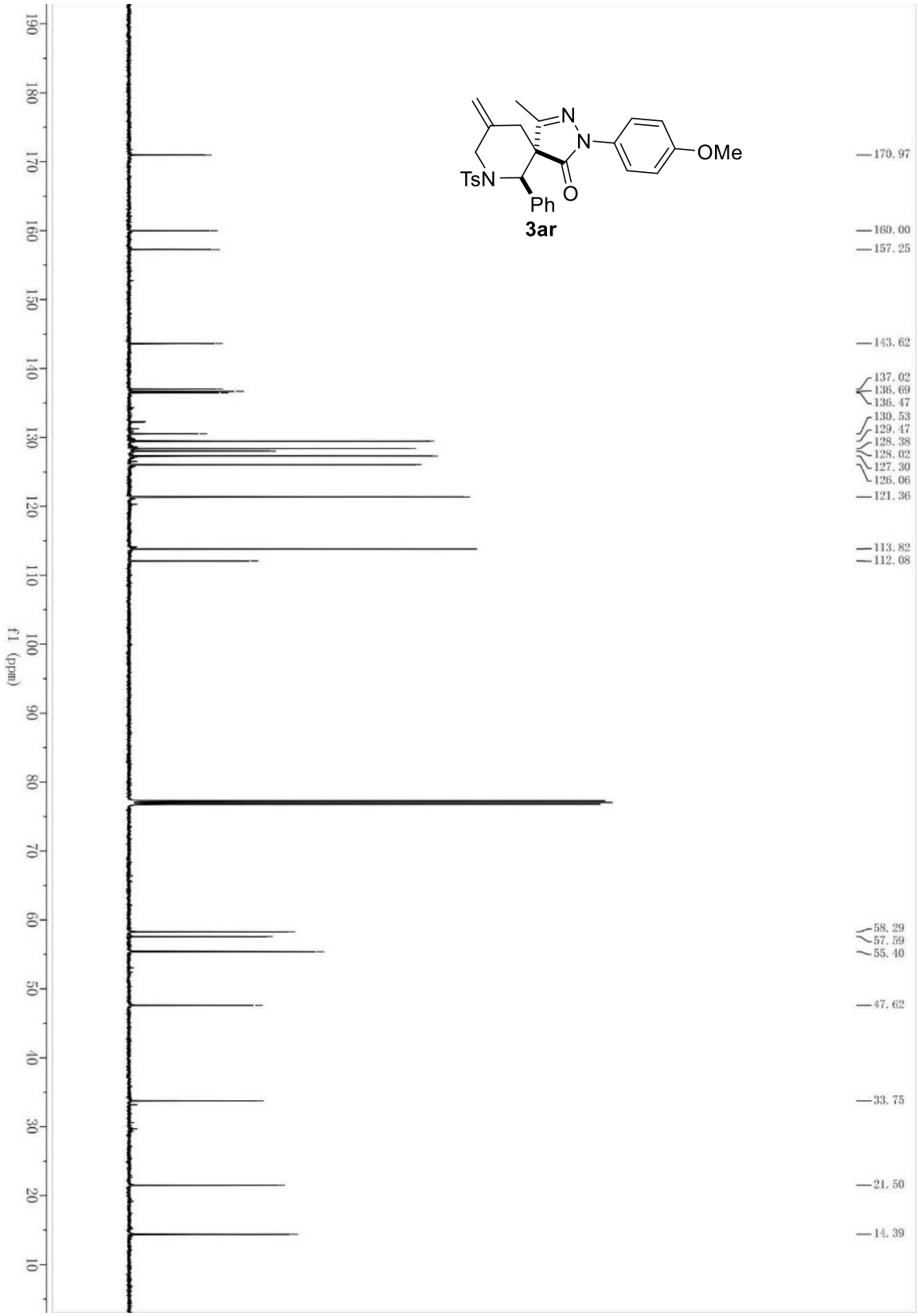
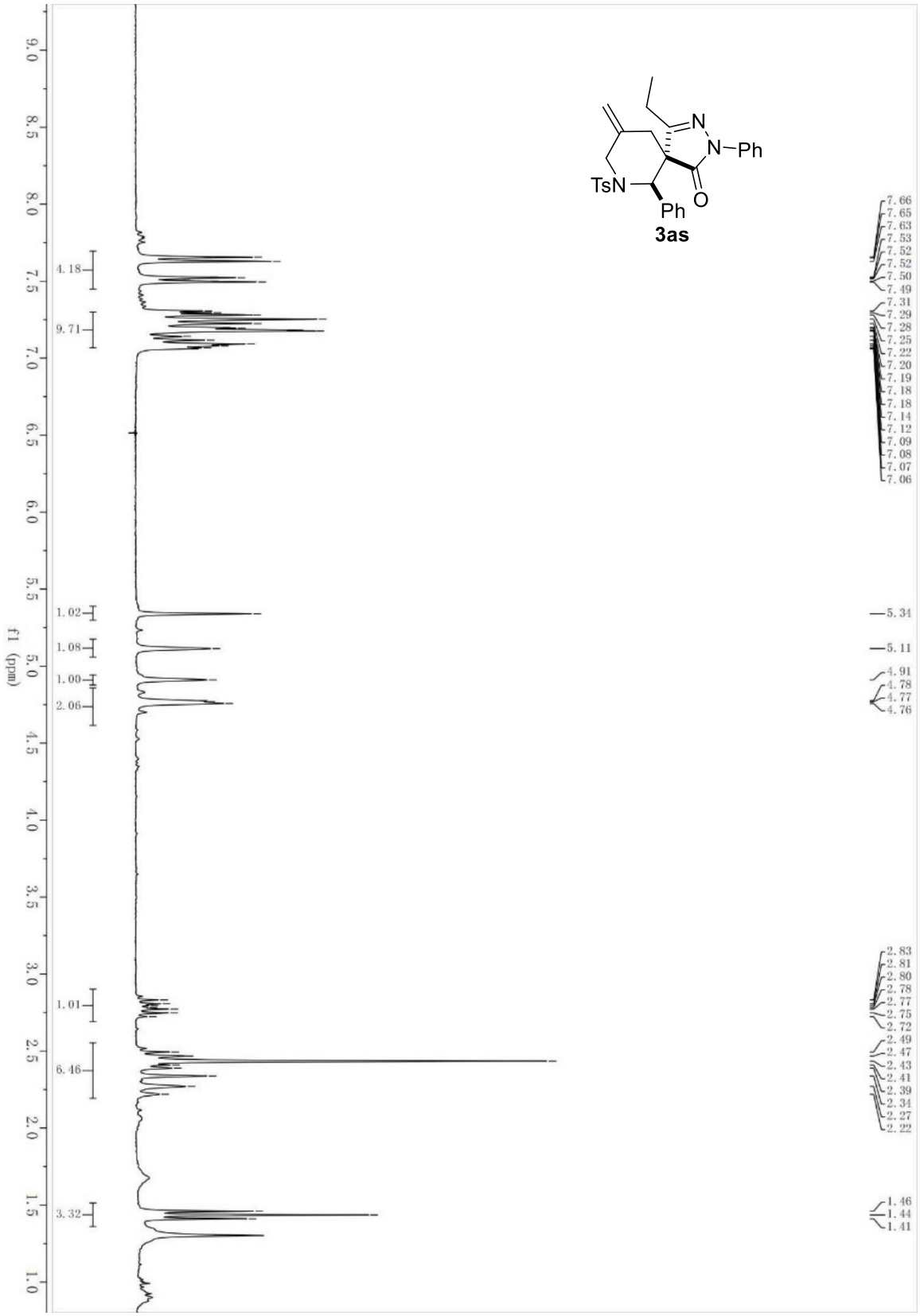
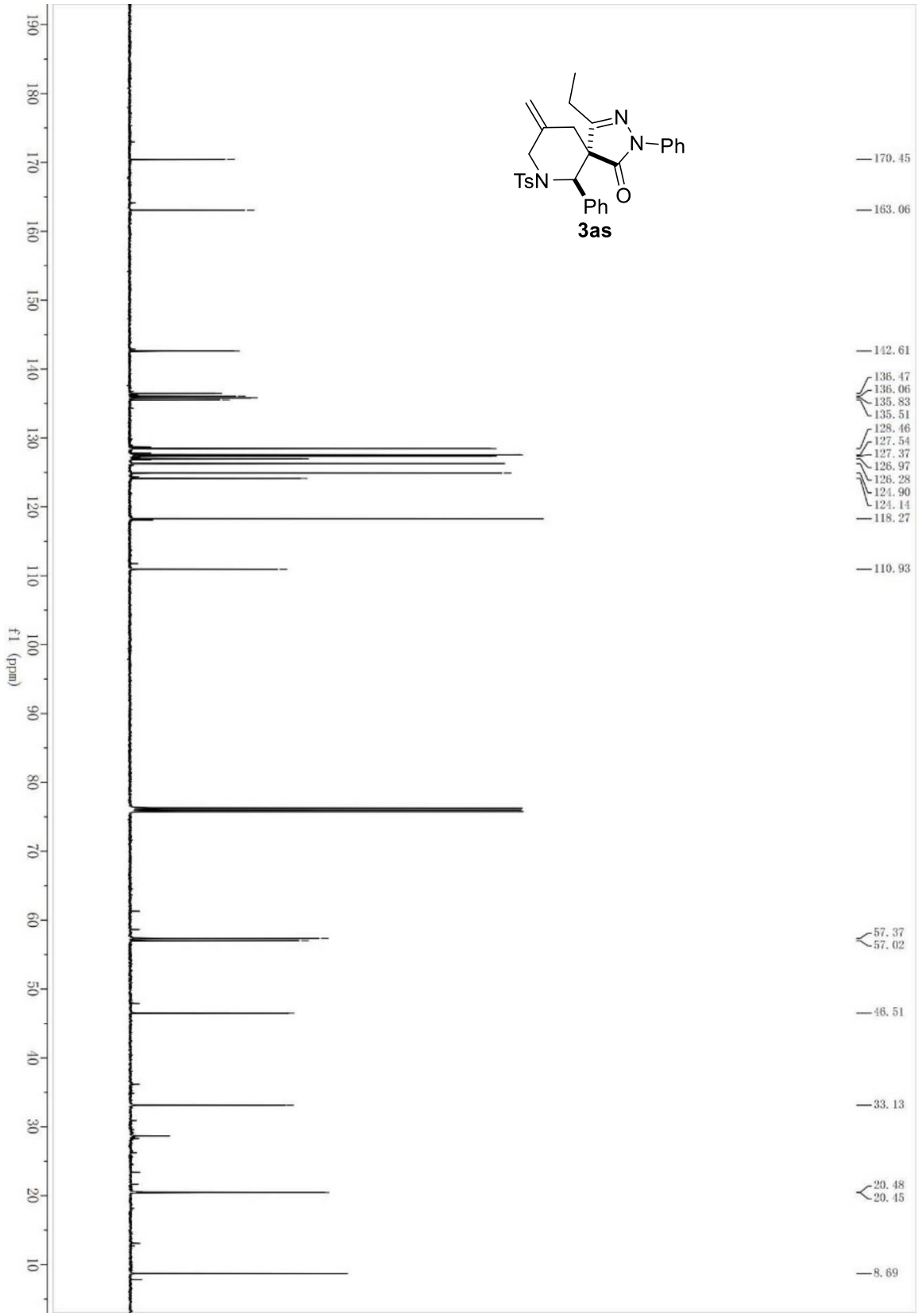
2.32
2.31
2.30
2.30
2.21
2.15

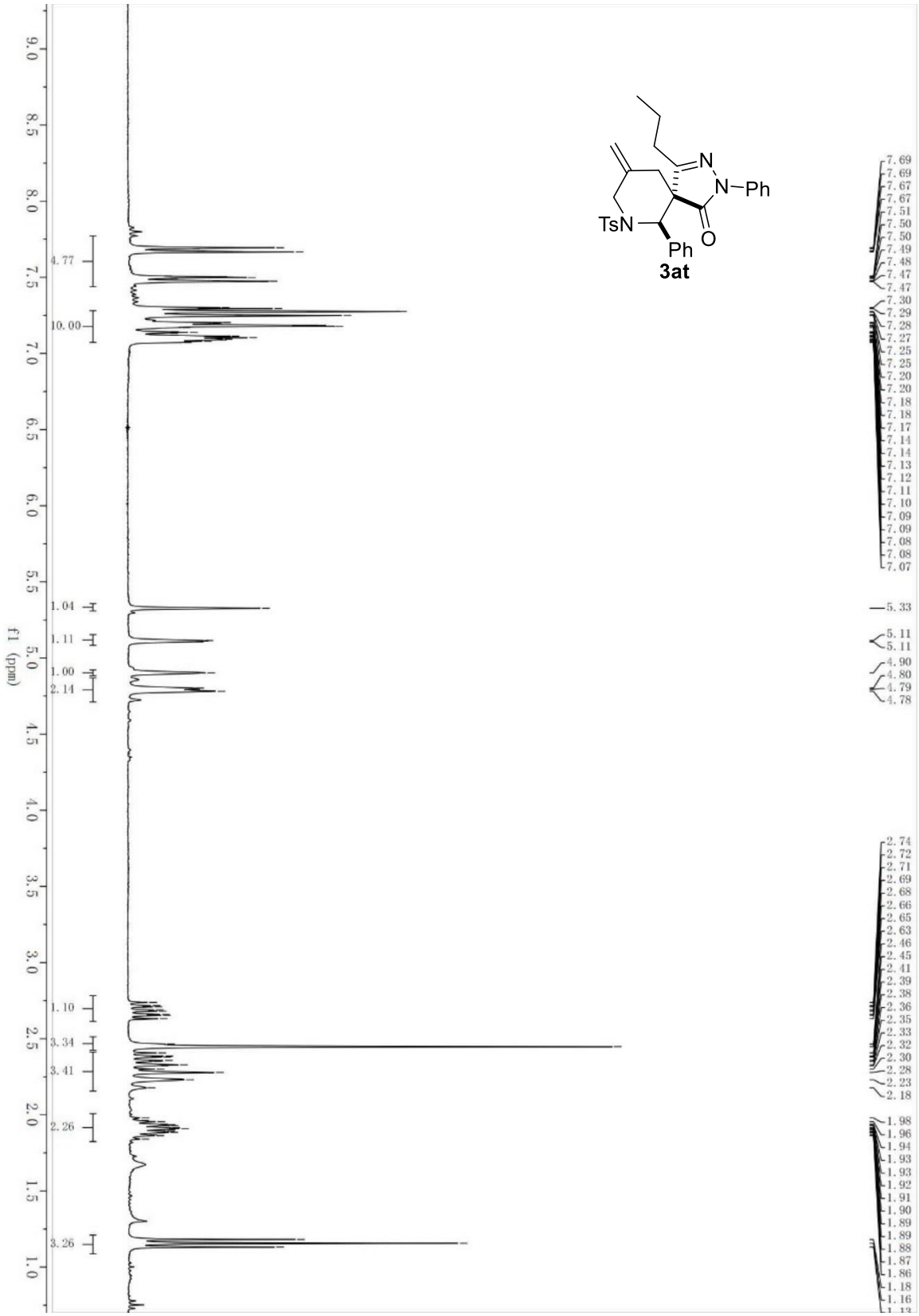

TsN
Ph
O
N
N
Me
3aq
f1 (ppm)
170.02
159.09
142.61
135.97
135.65
135.44
133.99
133.83
128.46
128.10
127.38
127.02
126.28
125.04
118.37
111.12
57.26
56.70
46.59
32.81
20.49
19.86
13.45

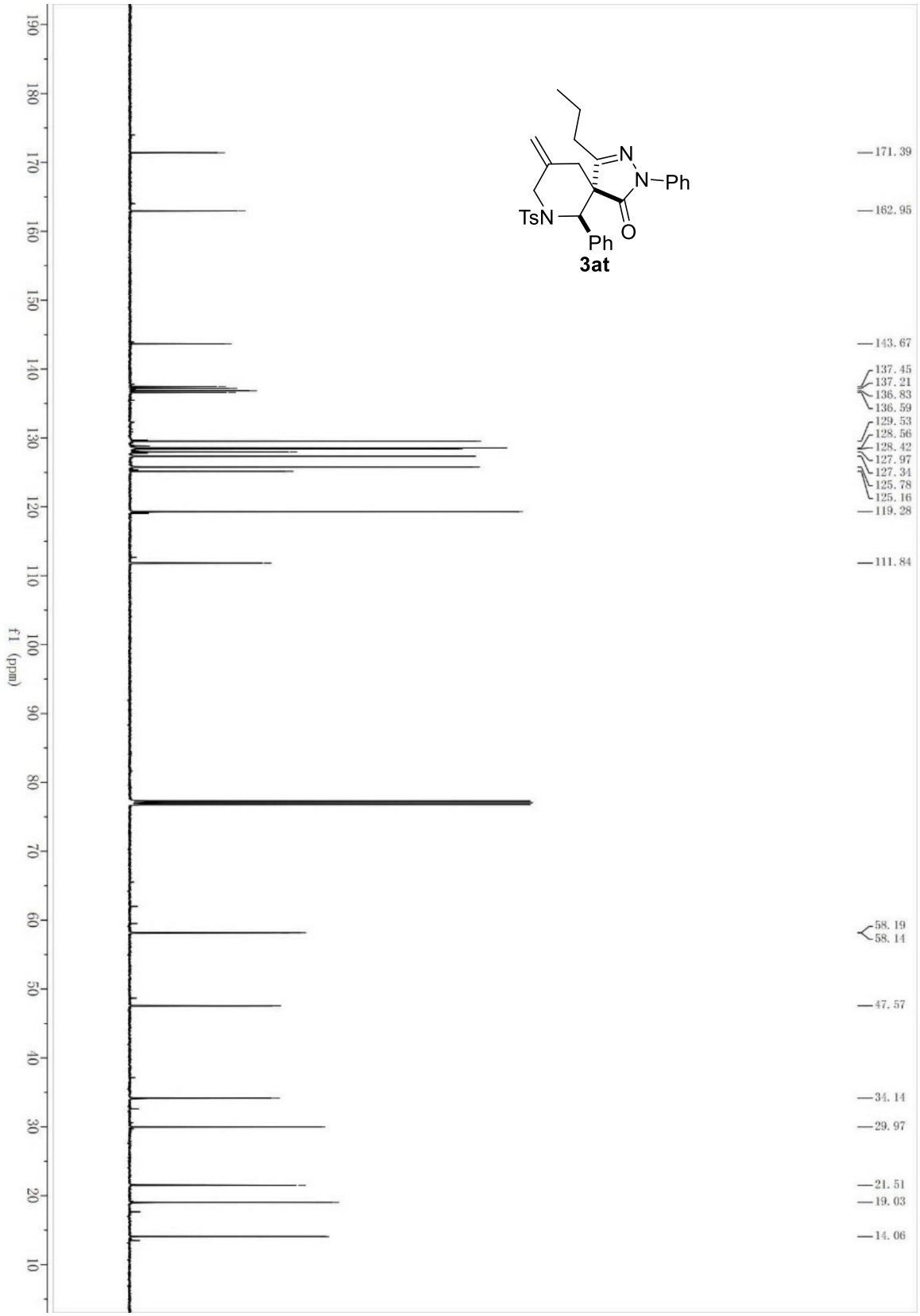

TsN
Ph
O
N
N
OMe
3ar
f1 (ppm)
2.24
9.88
2.18
1.06
1.01
1.00
2.02
3.09
8.34
7.65
7.64
7.63
7.62
7.62
7.31
7.30
7.29
7.28
7.28
7.26
7.25
7.25
7.24
7.22
7.21
7.21
7.21
7.20
7.19
7.18
7.12
7.11
7.09
7.09
6.81
6.80
6.79
6.78
5.28
5.12
4.92
4.78
4.76
3.77
2.46
2.43
2.39
2.34
2.29
2.20
2.20
2.15

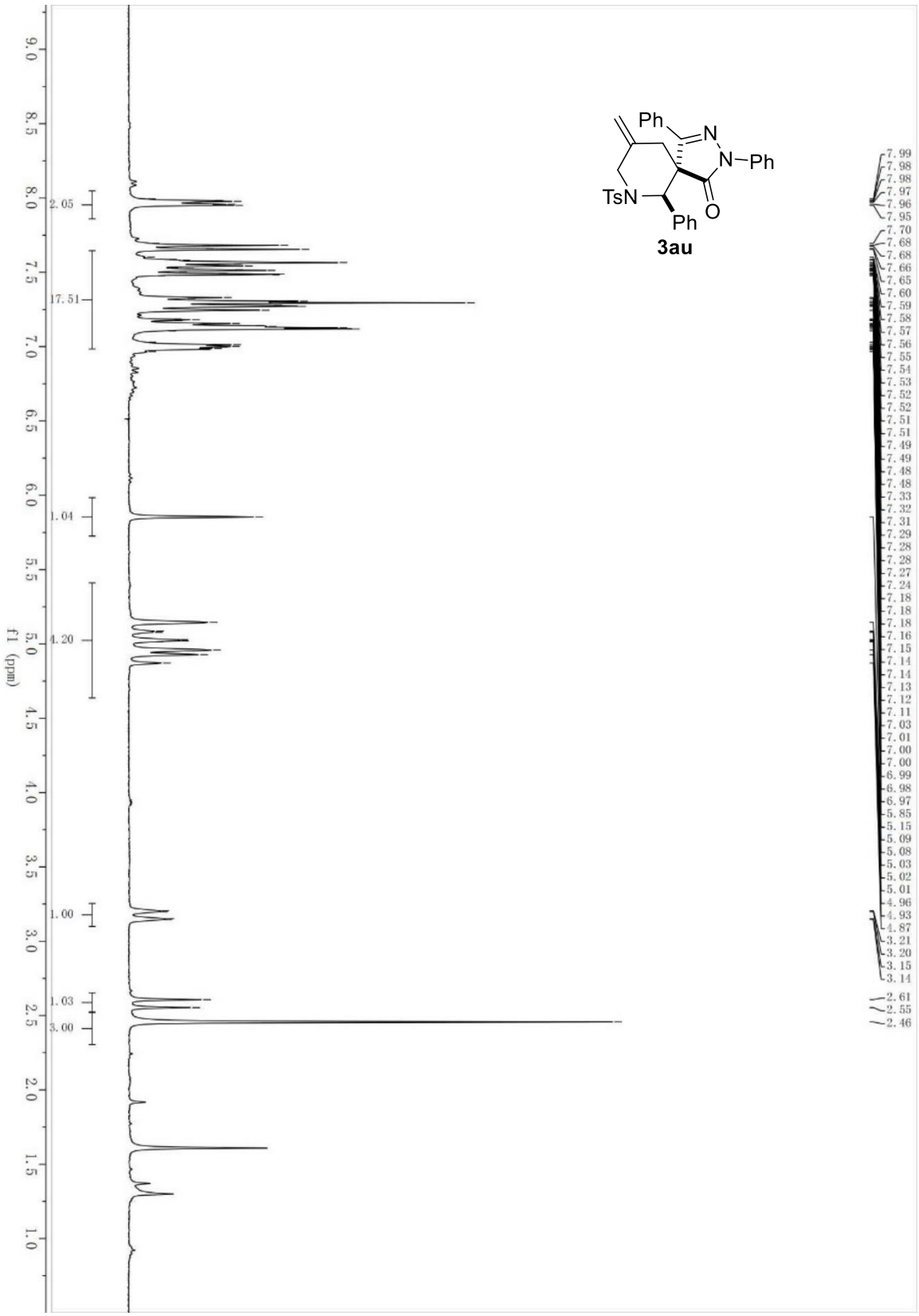

TsN
Ph
O
N
N
OMe
3ar
f1 (ppm)
170.97
160.00
157.25
143.62
137.02
136.69
136.47
130.53
129.47
128.38
128.02
127.30
126.06
121.36
113.82
112.08
58.29
57.59
55.40
47.62
33.75
21.50
14.39

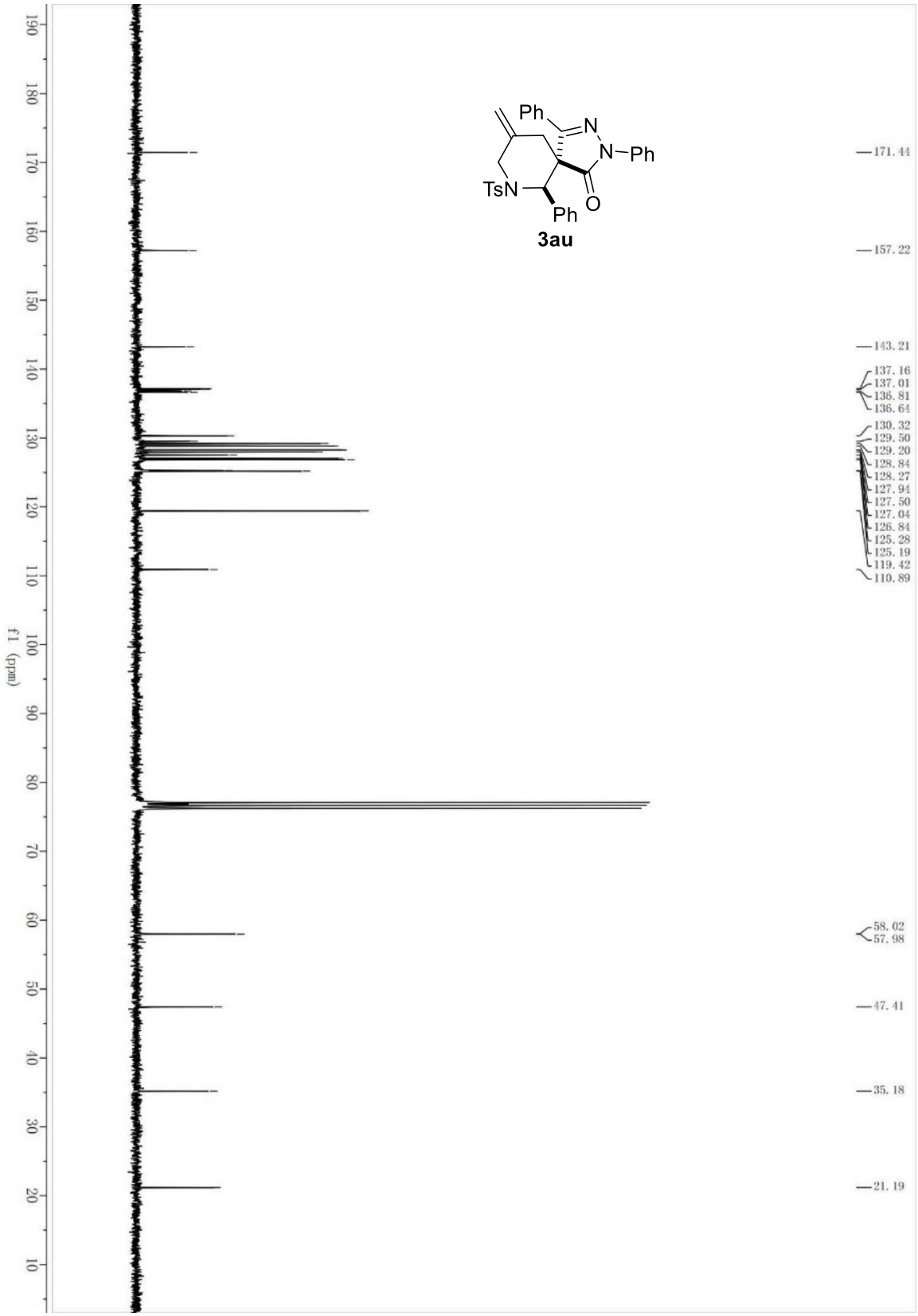

3as
TsN
Ph
N
N–Ph
O
f1 (ppm)
4.18
9.71
1.02
1.08
1.00
2.06
1.01
6.46
3.32
7.66
7.65
7.63
7.53
7.52
7.52
7.50
7.49
7.31
7.29
7.28
7.25
7.22
7.20
7.19
7.18
7.18
7.14
7.12
7.09
7.08
7.07
7.06
5.34
5.11
4.91
4.78
4.77
4.76
2.83
2.81
2.80
2.78
2.77
2.75
2.72
2.49
2.47
2.43
2.41
2.39
2.34
2.27
2.22
1.46
1.44
1.41

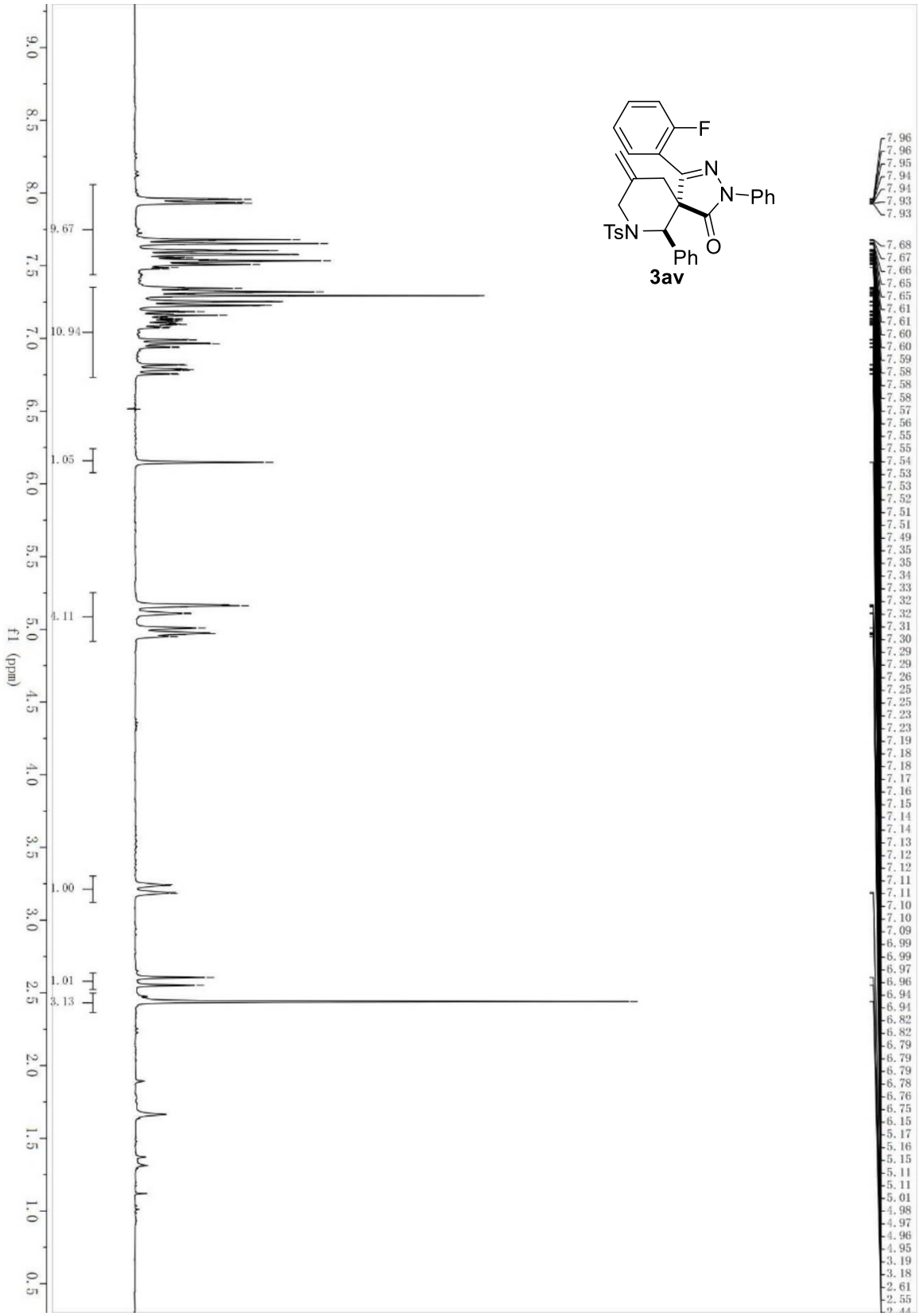

N
N–Ph
TsN
O
Ph
3as
170.45
163.06
142.61
136.47
136.06
135.83
135.51
128.46
127.54
127.37
126.97
126.28
124.90
124.14
118.27
110.93
57.37
57.02
46.51
33.13
20.48
20.45
8.69
f1 (ppm)

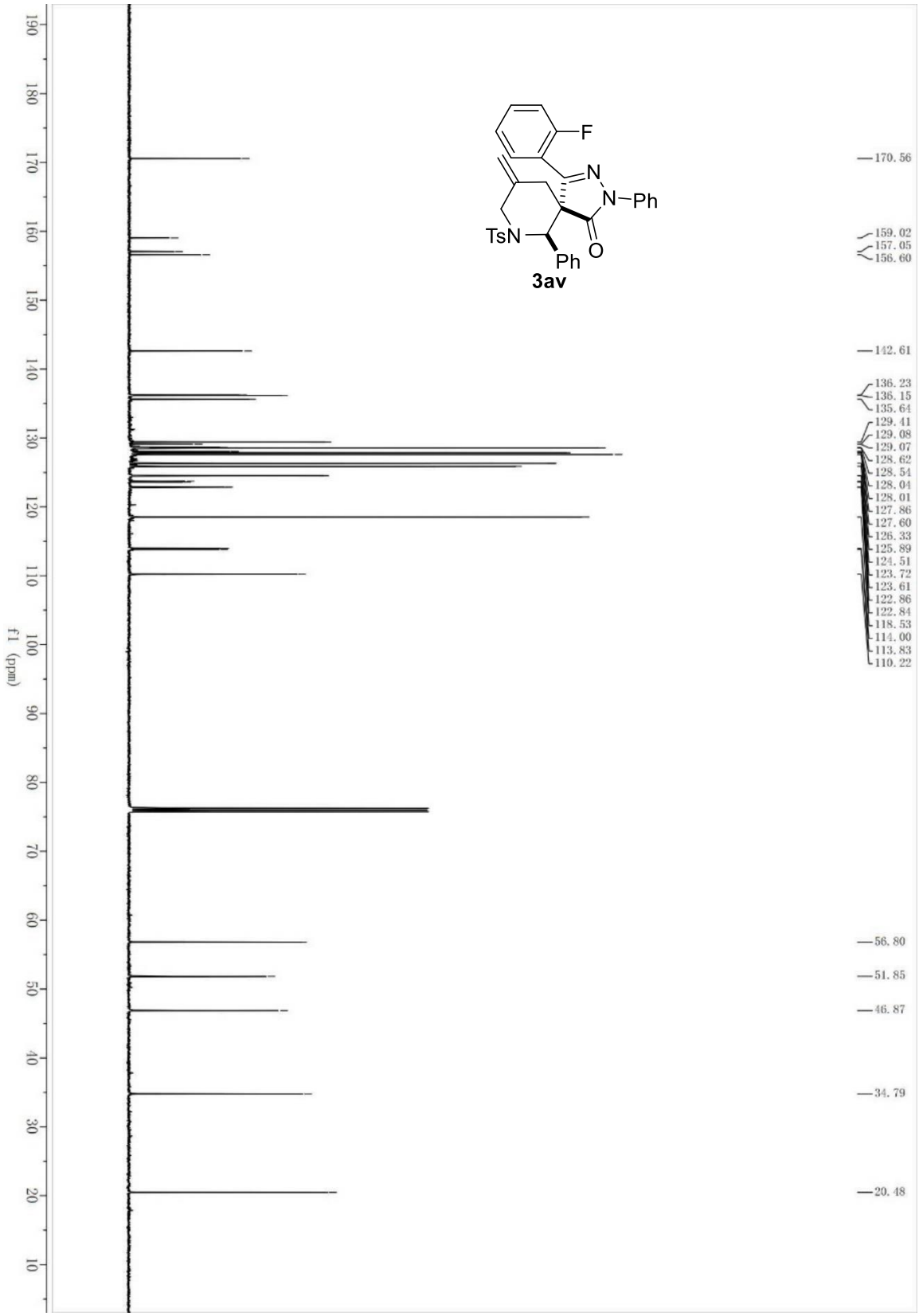

3at
f1 (ppm)

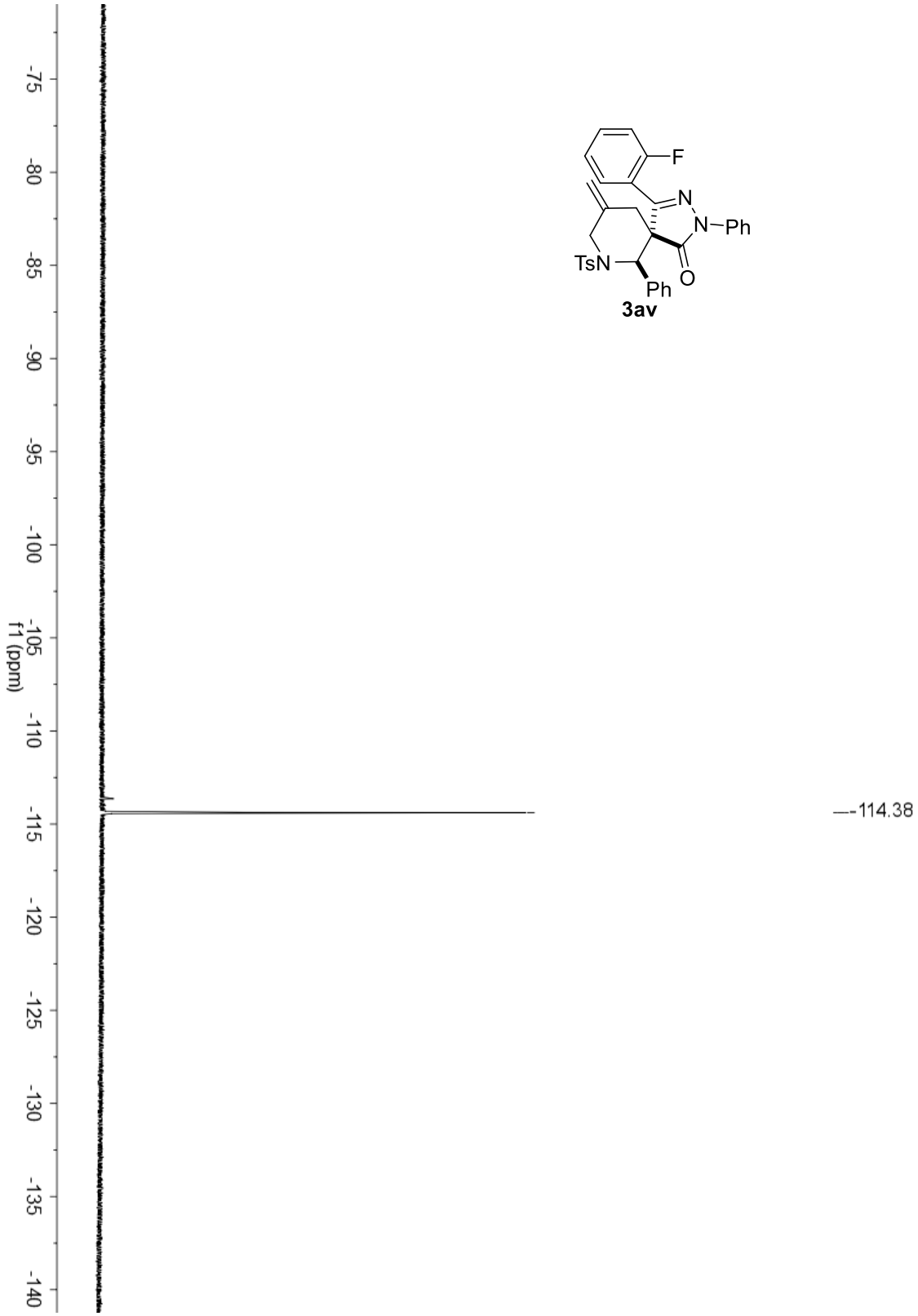

TsN
N
N–Ph
O
Ph
3at
f1 (ppm)
171.39
162.95
143.67
137.45
137.21
136.83
136.59
129.53
128.56
128.42
127.97
127.34
125.78
125.16
119.28
111.84
58.19
58.14
47.57
34.14
29.97
21.51
19.03
14.06

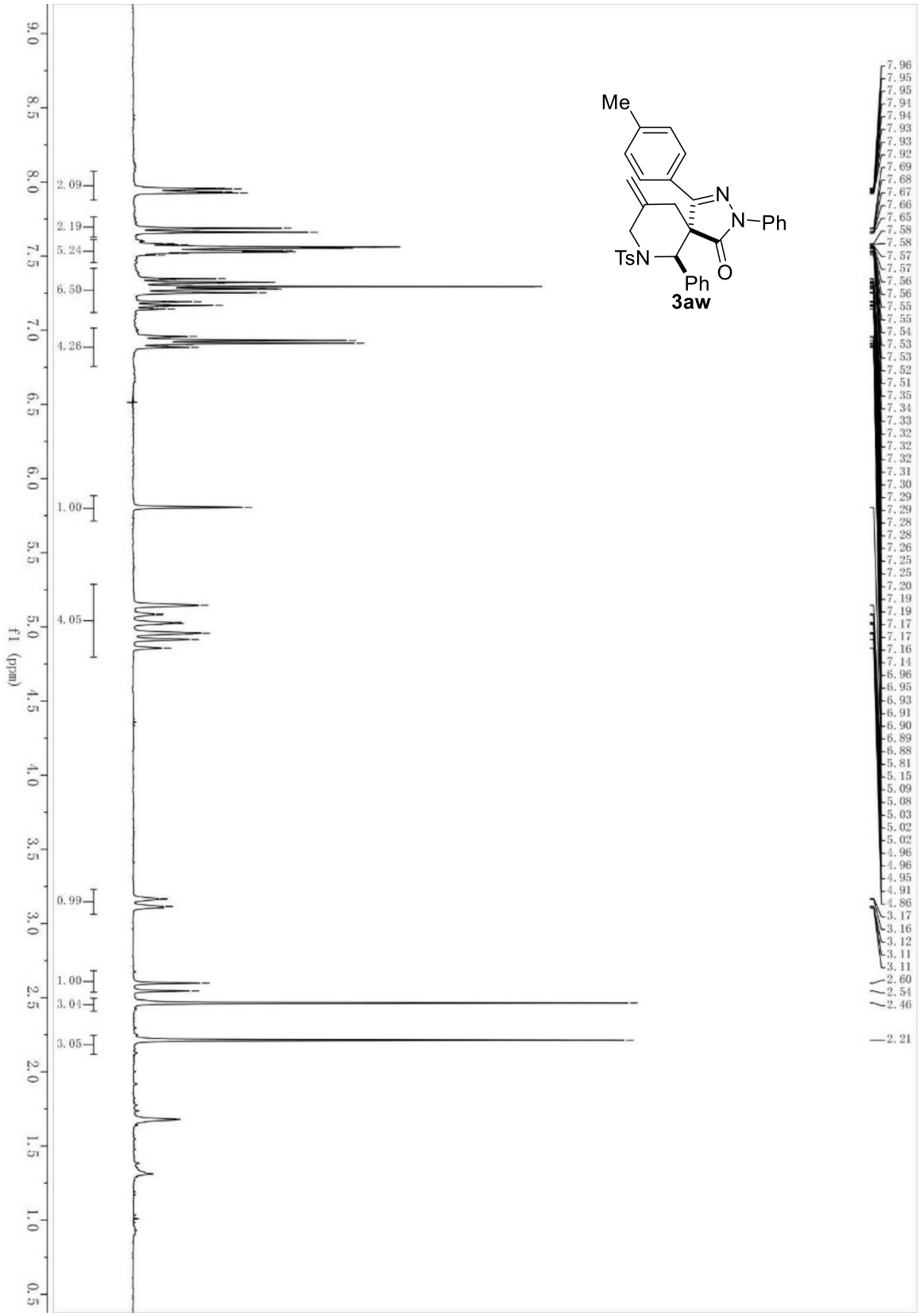

Ph
N
N–Ph
TsN
O
Ph
3au
f1 (ppm)
2.05
17.51
1.04
4.20
1.00
1.03
3.00

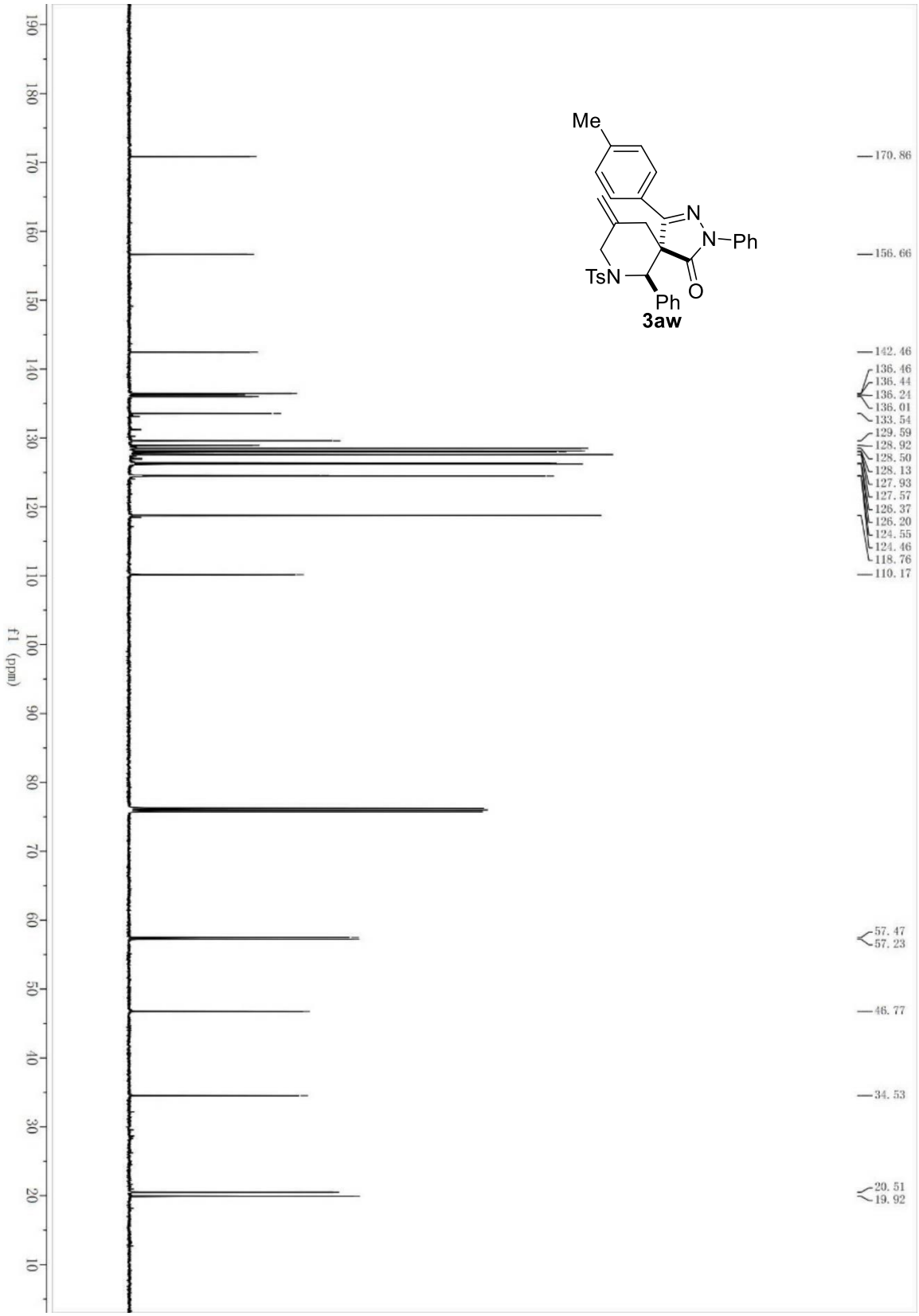

Ph
N
N
Ph
TsN
Ph
O
3au
f1 (ppm)
171.44
157.22
143.21
137.16
137.01
136.81
136.64
130.32
129.50
129.20
128.84
128.27
127.94
127.50
127.04
126.84
125.28
125.19
119.42
110.89
58.02
57.98
47.41
35.18
21.19

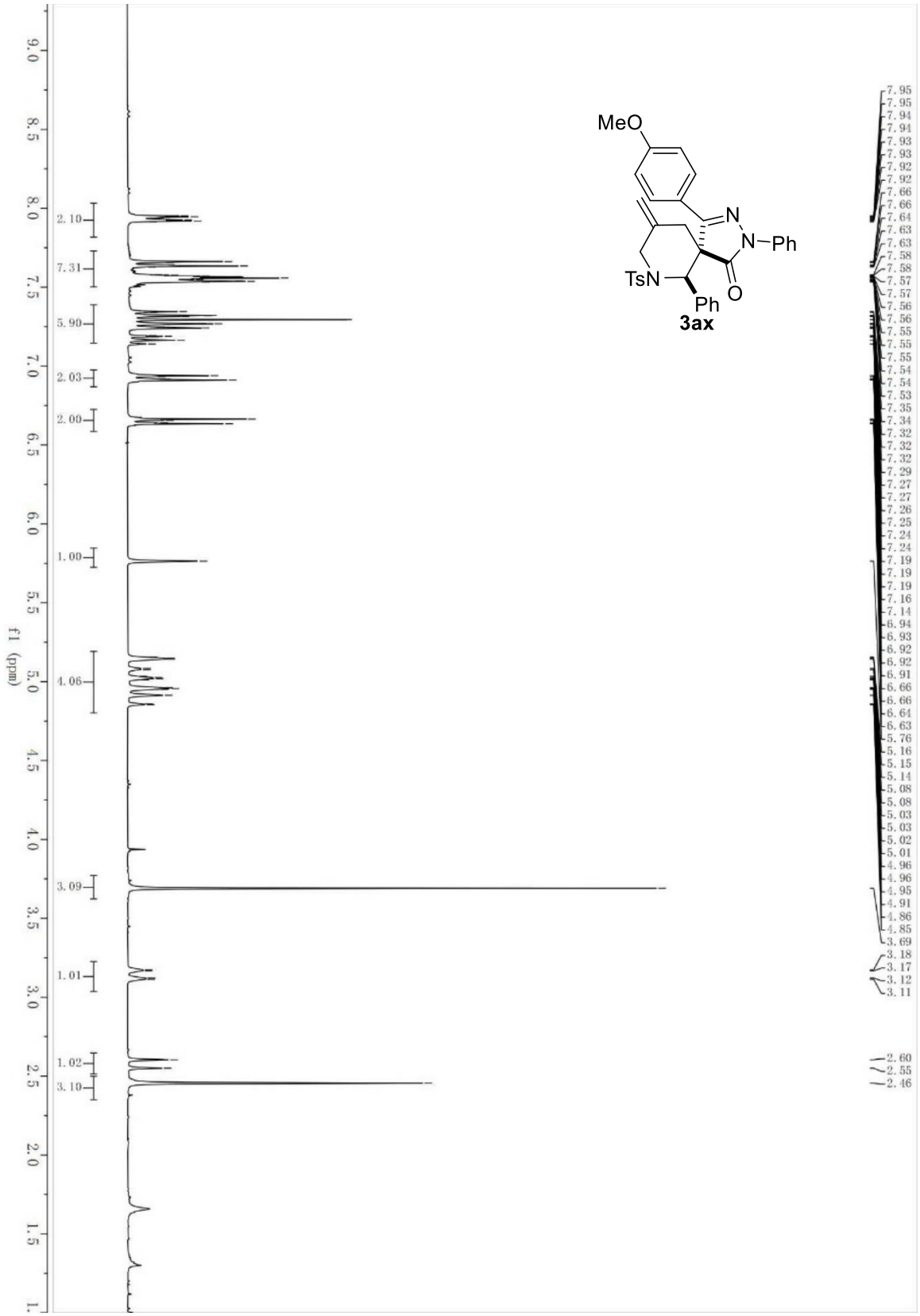

F
N
N–Ph
TsN
O
Ph
3av
f1 (ppm)
9.67
10.94
1.05
4.11
1.00
1.01
3.13

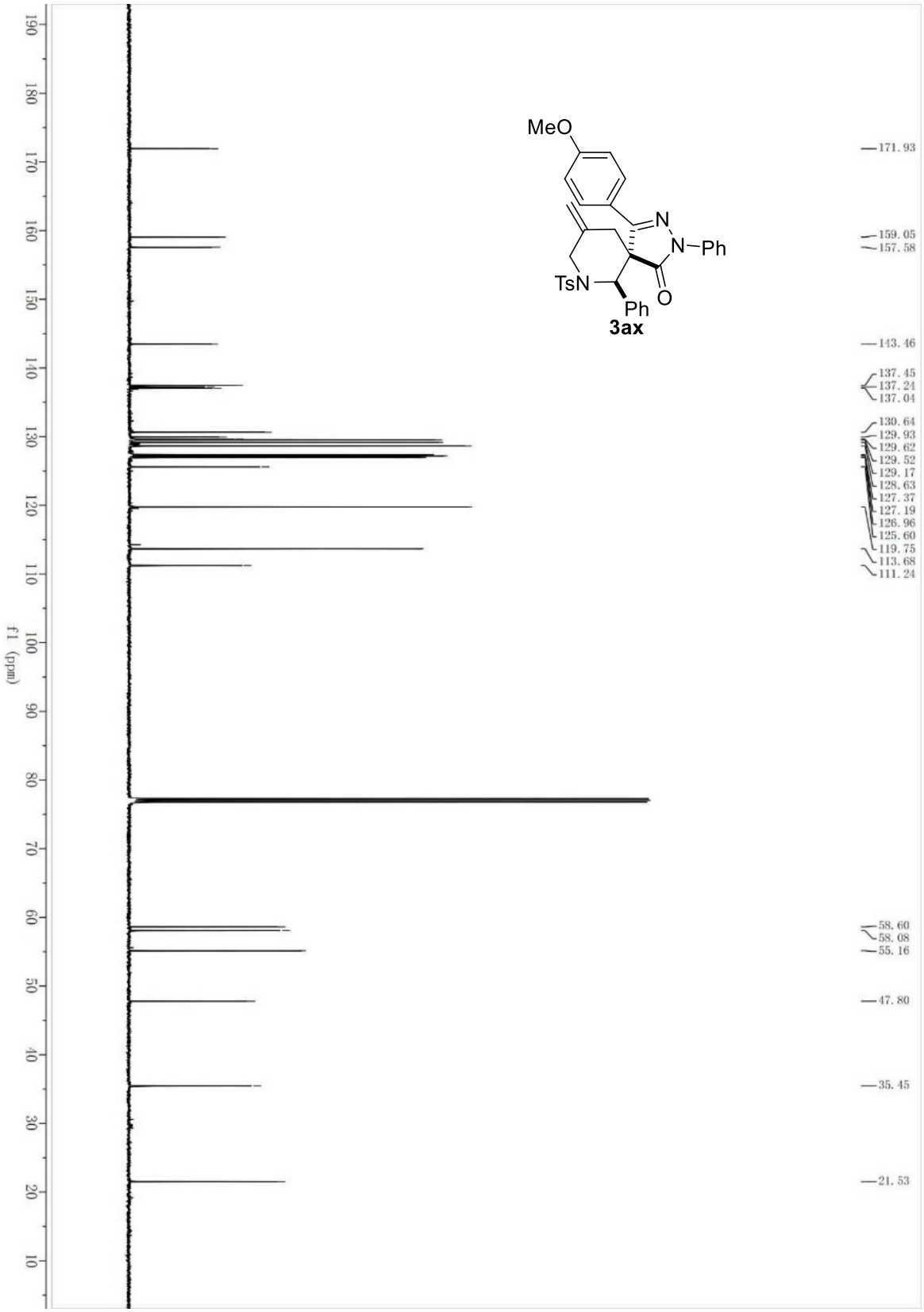

F
N
N–Ph
TsN
O
Ph
3av
170.56
159.02
157.05
156.60
142.61
136.23
136.15
135.64
129.41
129.08
129.07
128.62
128.54
128.04
128.01
127.86
127.60
126.33
125.89
124.51
123.72
123.61
122.86
122.84
118.53
114.00
113.83
110.22
56.80
51.85
46.87
34.79
20.48
f1 (ppm)

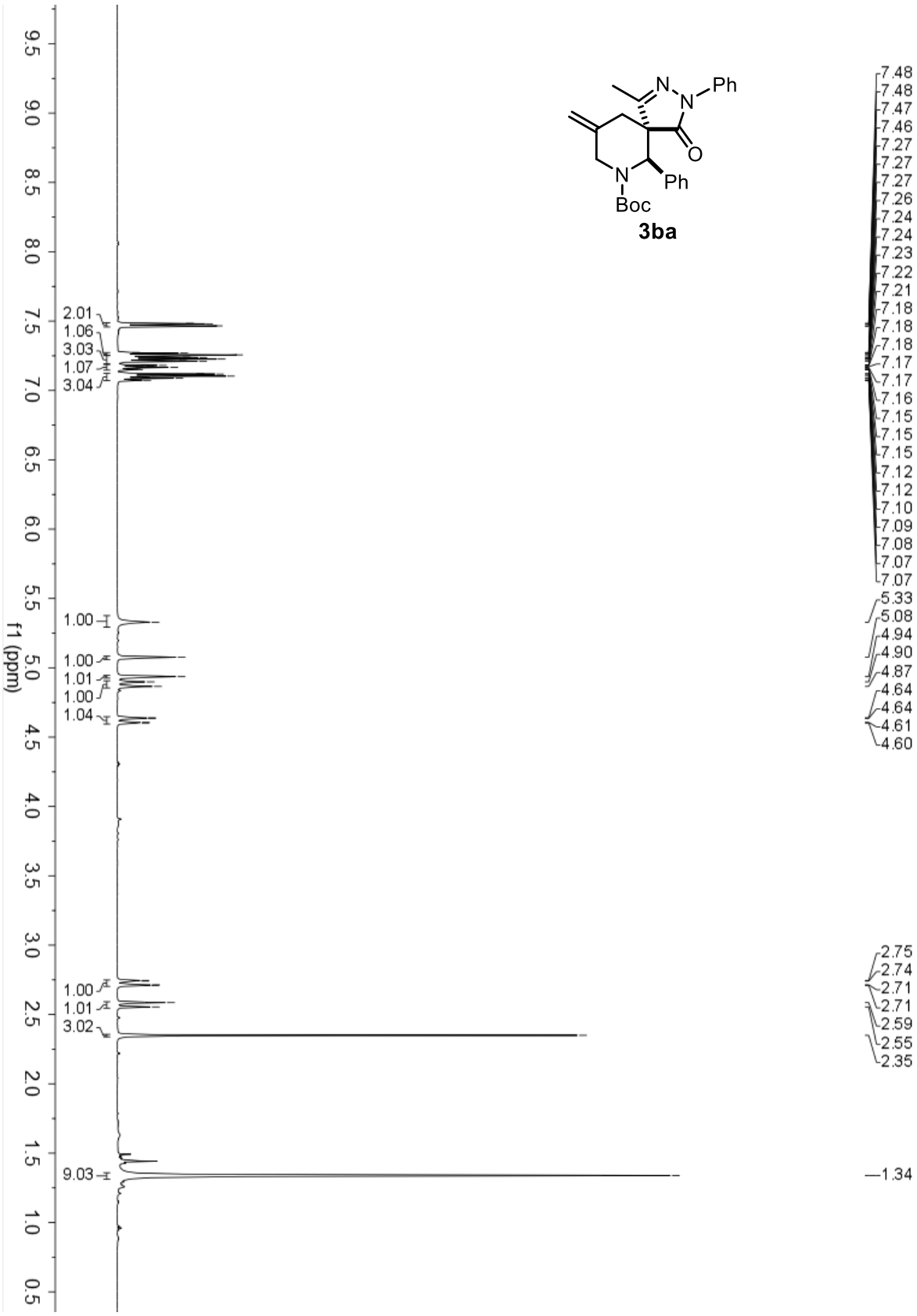

F
N
N–Ph
TsN
O
Ph
3av
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
f1 (ppm)
-114.38

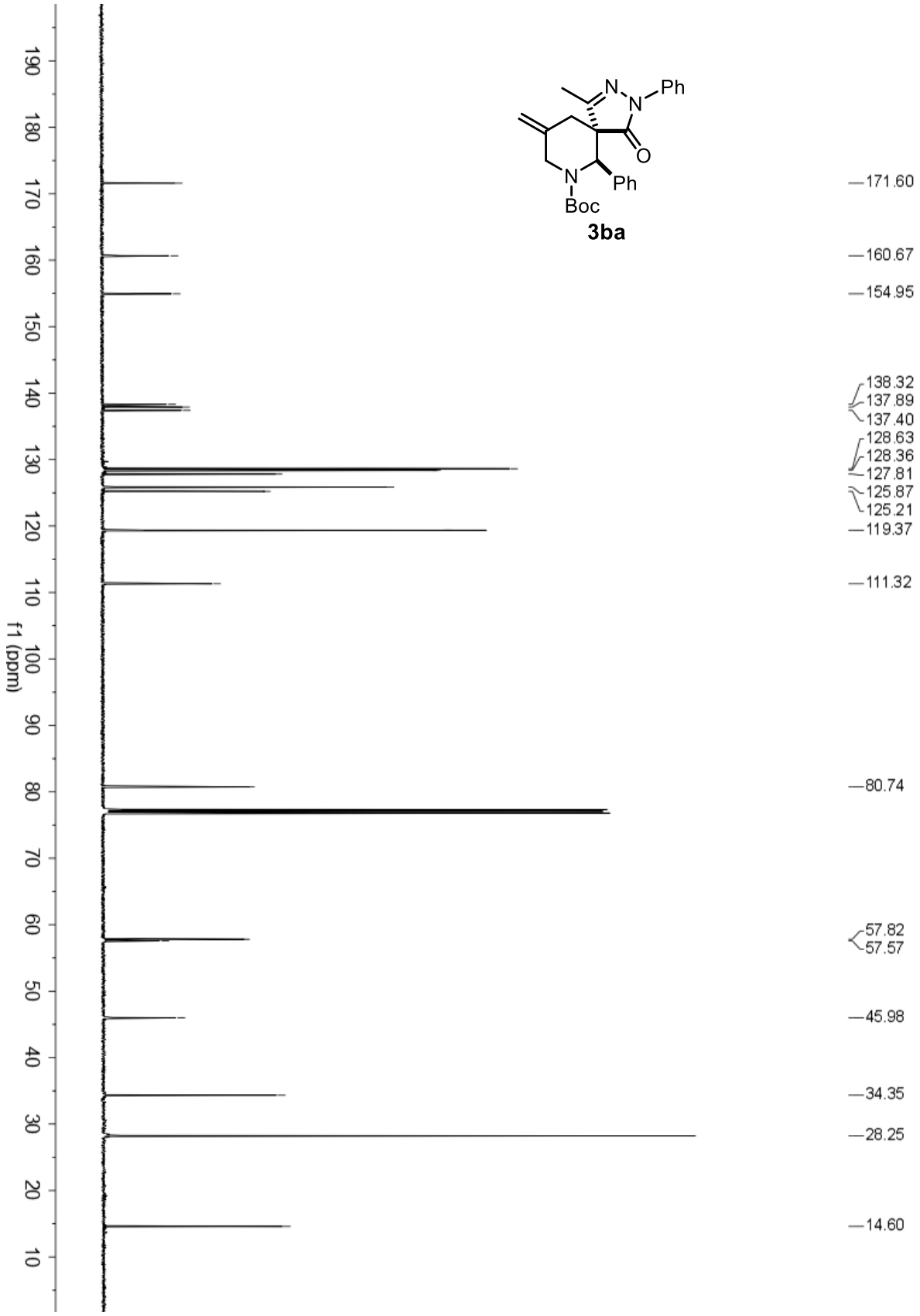

Me
N
N–Ph
TsN
O
Ph
3aw
f1 (ppm)
2.09
2.19
5.24
6.50
4.26
1.00
4.05
0.99
1.00
3.04
3.05
7.96
7.95
7.95
7.94
7.94
7.93
7.93
7.92
7.69
7.68
7.67
7.66
7.65
7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.35
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.26
7.25
7.25
7.20
7.19
7.19
7.17
7.17
7.16
7.14
6.96
6.95
6.93
6.91
6.90
6.89
6.88
5.81
5.15
5.09
5.08
5.03
5.02
5.02
4.96
4.96
4.95
4.91
4.86
3.17
3.16
3.12
3.11
3.11
2.60
2.54
2.46
2.21

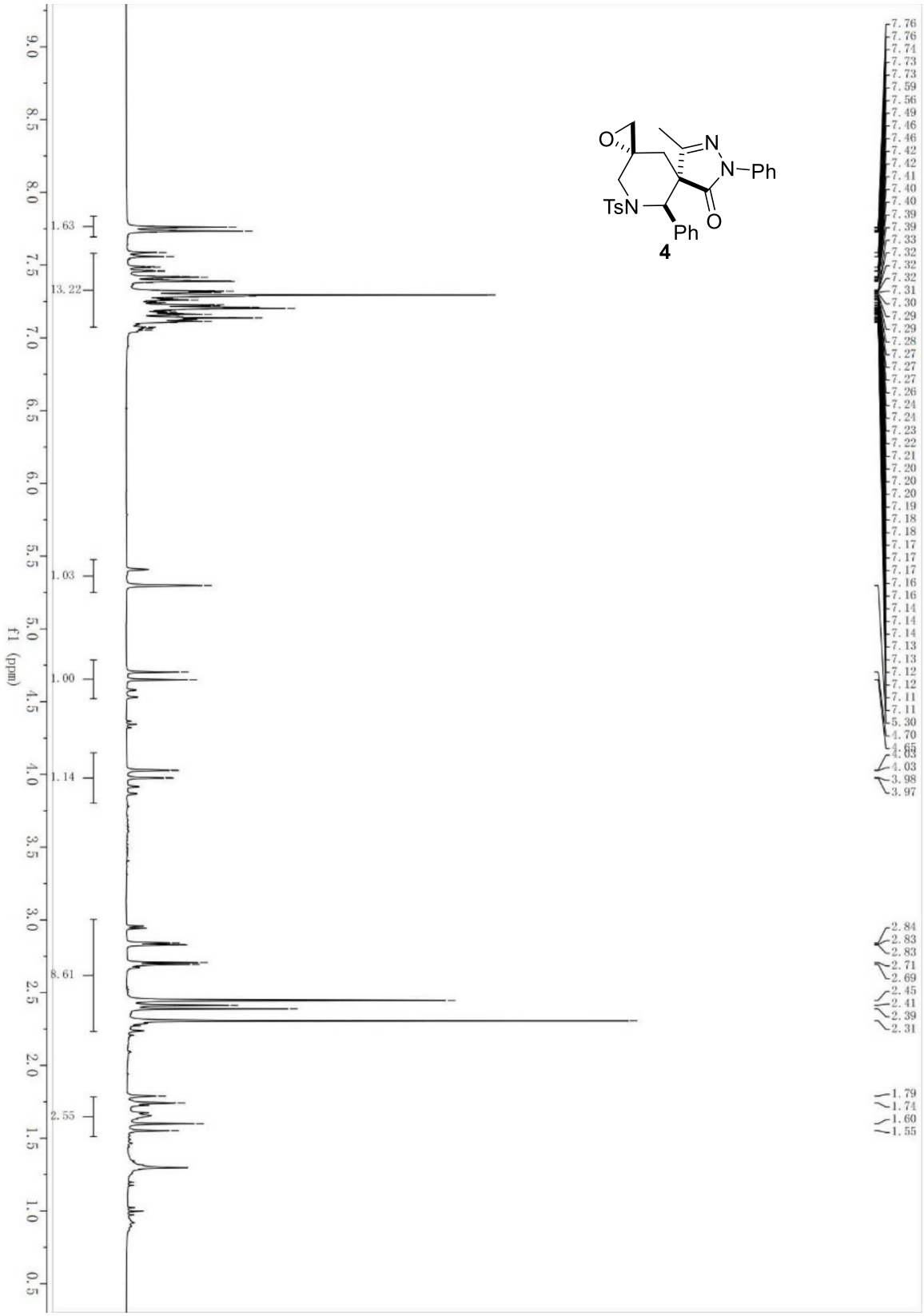

Me
N
N–Ph
TsN
O
Ph
3aw
170.86
156.66
142.46
136.46
136.44
136.24
136.01
133.54
129.59
128.92
128.50
128.13
127.93
127.57
126.37
126.20
124.55
124.46
118.76
110.17
57.47
57.23
46.77
34.53
20.51
19.92
f1 (ppm)

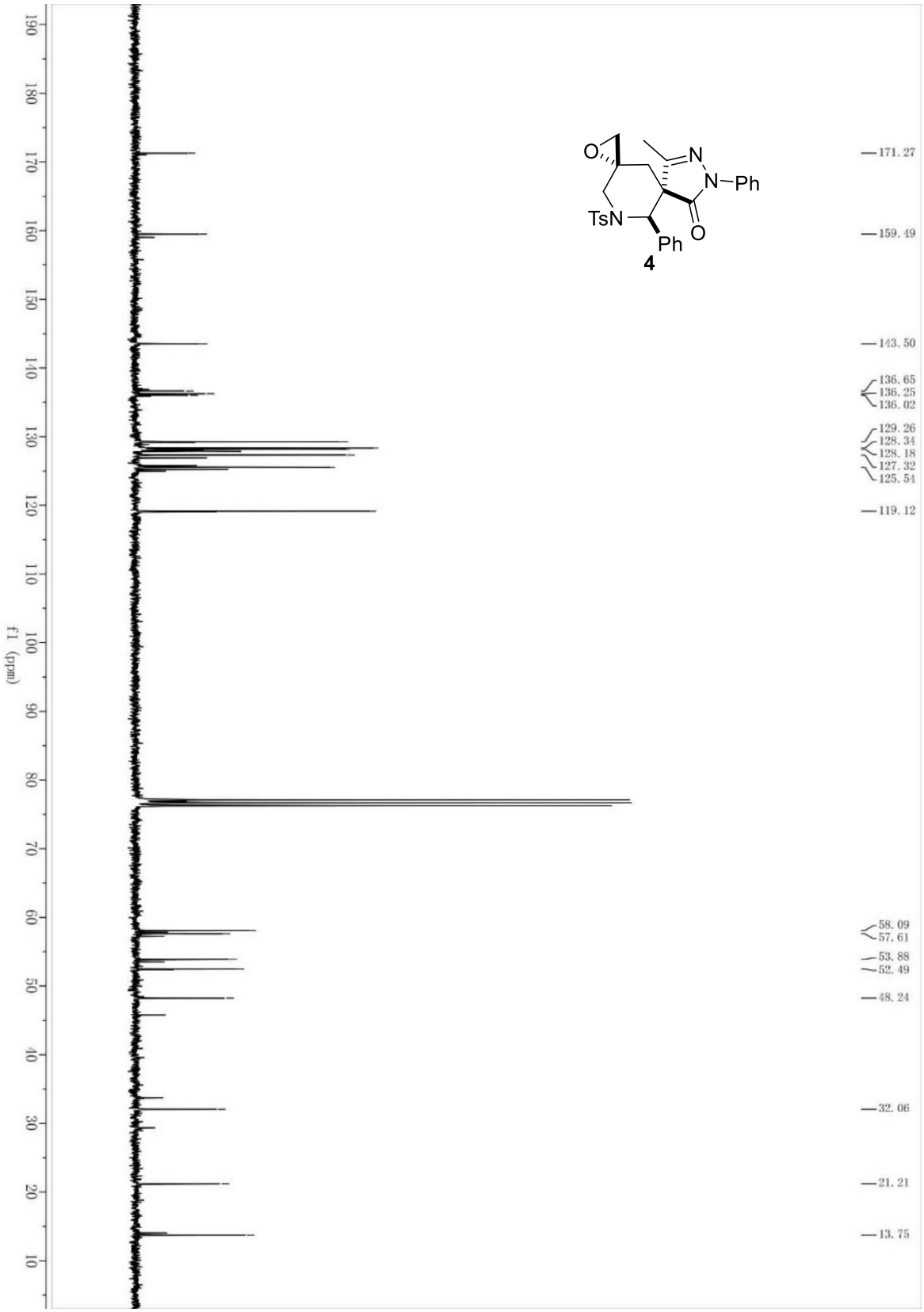

MeO
N
N–Ph
TsN
O
Ph
3ax
f1 (ppm)
2.10
7.31
5.90
2.03
2.00
1.00
4.06
3.09
1.01
1.02
3.10

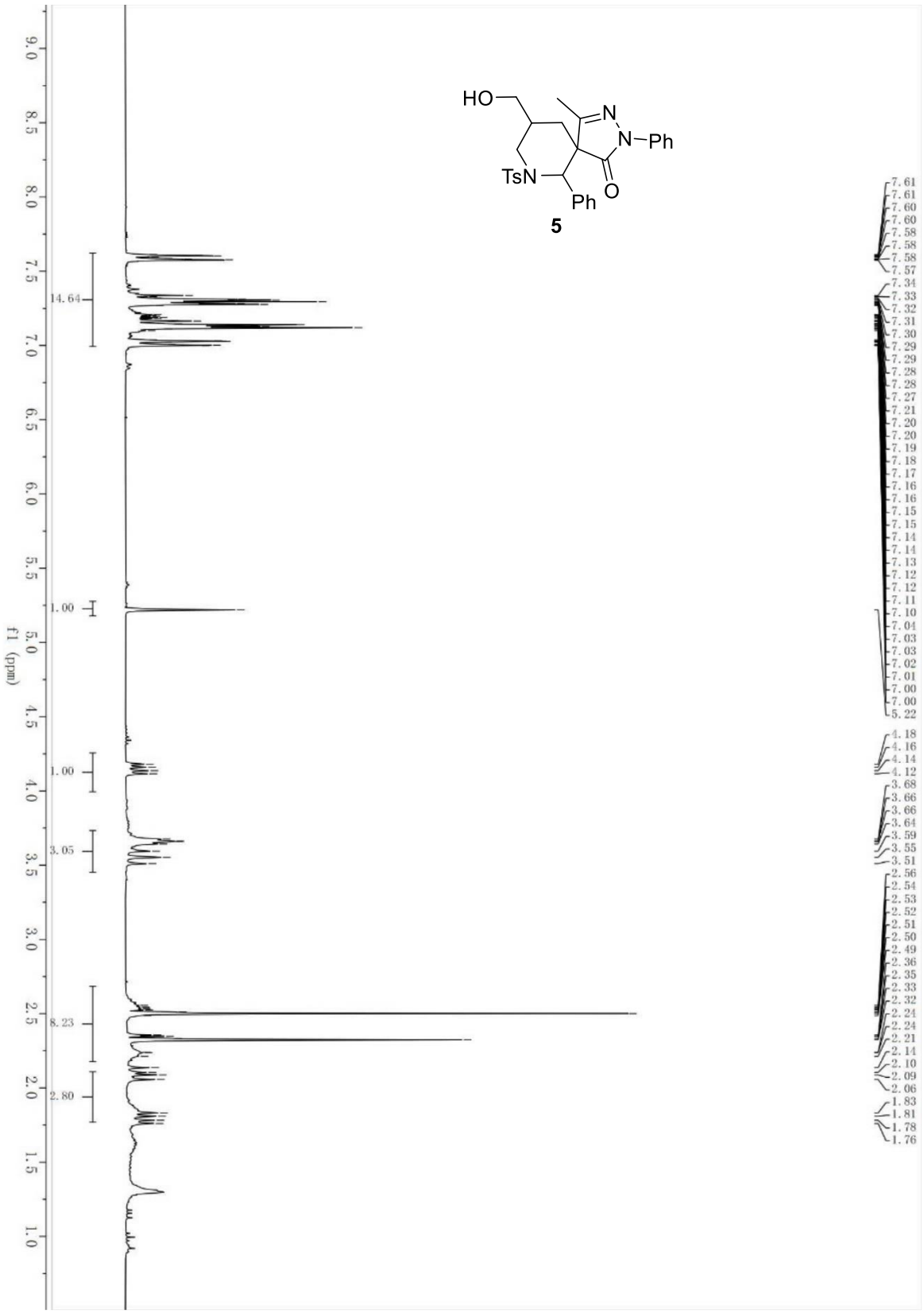

MeO
N
N–Ph
TsN
O
Ph
3ax
f1 (ppm)
171.93
159.05
157.58
143.46
137.45
137.24
137.04
130.64
129.93
129.62
129.52
129.17
128.63
127.37
127.19
126.96
125.60
119.75
113.68
111.24
58.60
58.08
55.16
47.80
35.45
21.53

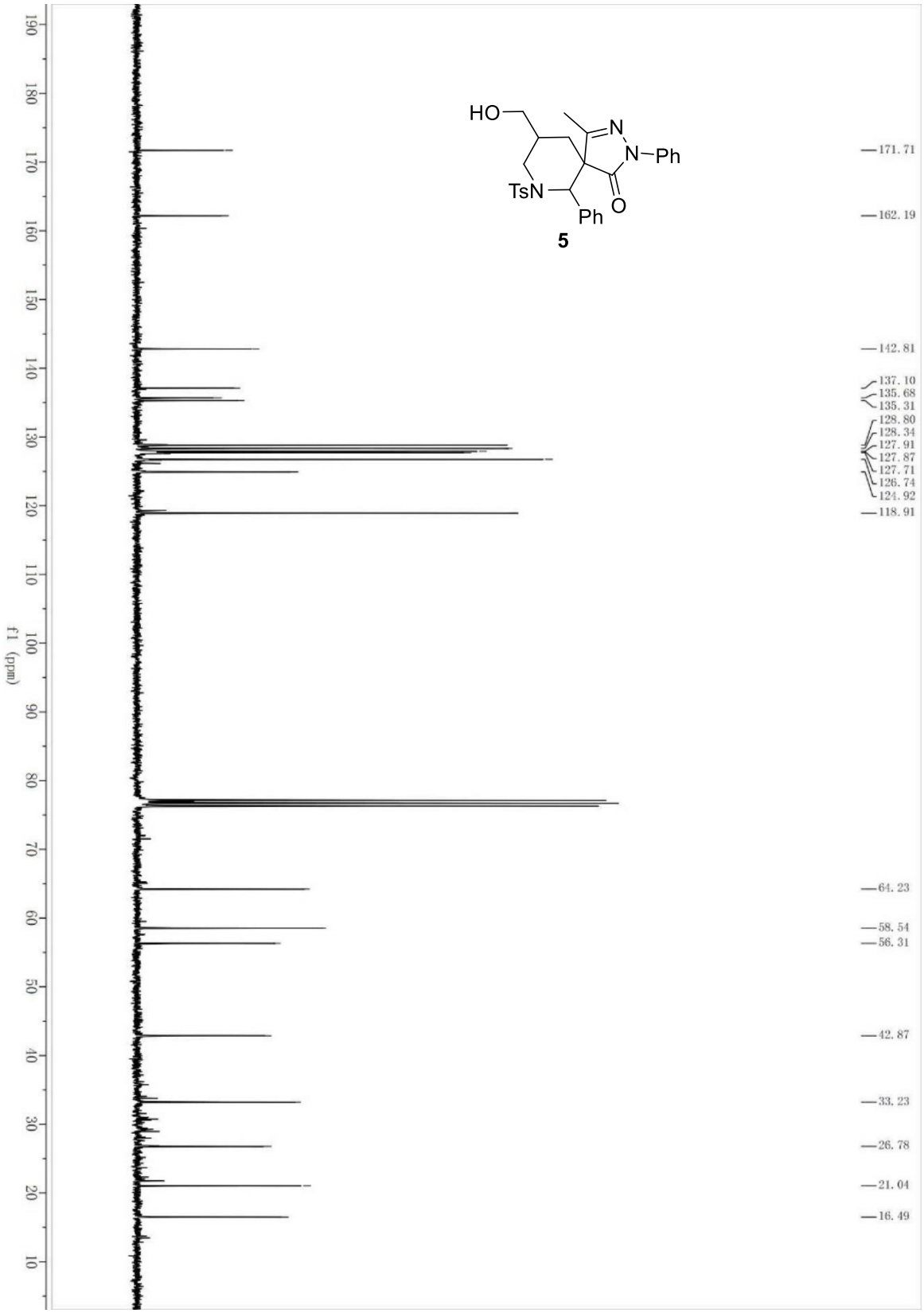

N
N
Ph
O
N
Ph
Boc
3ba
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.01
1.06
3.03
1.07
3.04
1.00
1.00
1.01
1.00
1.04
1.00
1.01
3.02
9.03
7.48
7.48
7.47
7.46
7.27
7.27
7.27
7.26
7.24
7.24
7.23
7.22
7.21
7.18
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.15
7.12
7.12
7.10
7.09
7.08
7.07
7.07
5.33
5.08
4.94
4.90
4.87
4.64
4.64
4.61
4.60
2.75
2.74
2.71
2.71
2.59
2.55
2.35
1.34

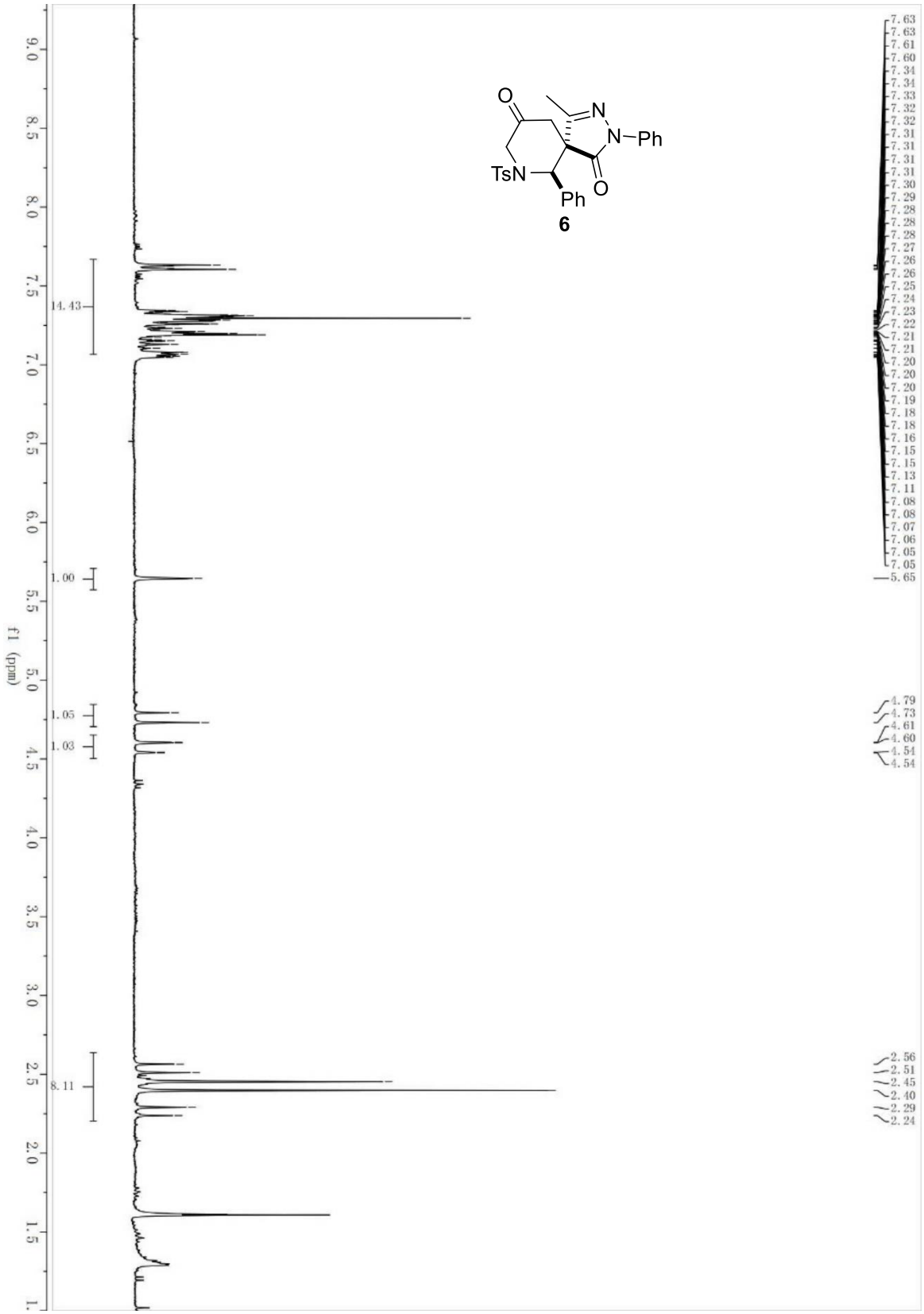

Ph
N
N
O
N
Ph
Boc
3ba
171.60
160.67
154.95
138.32
137.89
137.40
128.63
128.36
127.81
125.87
125.21
119.37
111.32
80.74
57.82
57.57
45.98
34.35
28.25
14.60
f1 (ppm)

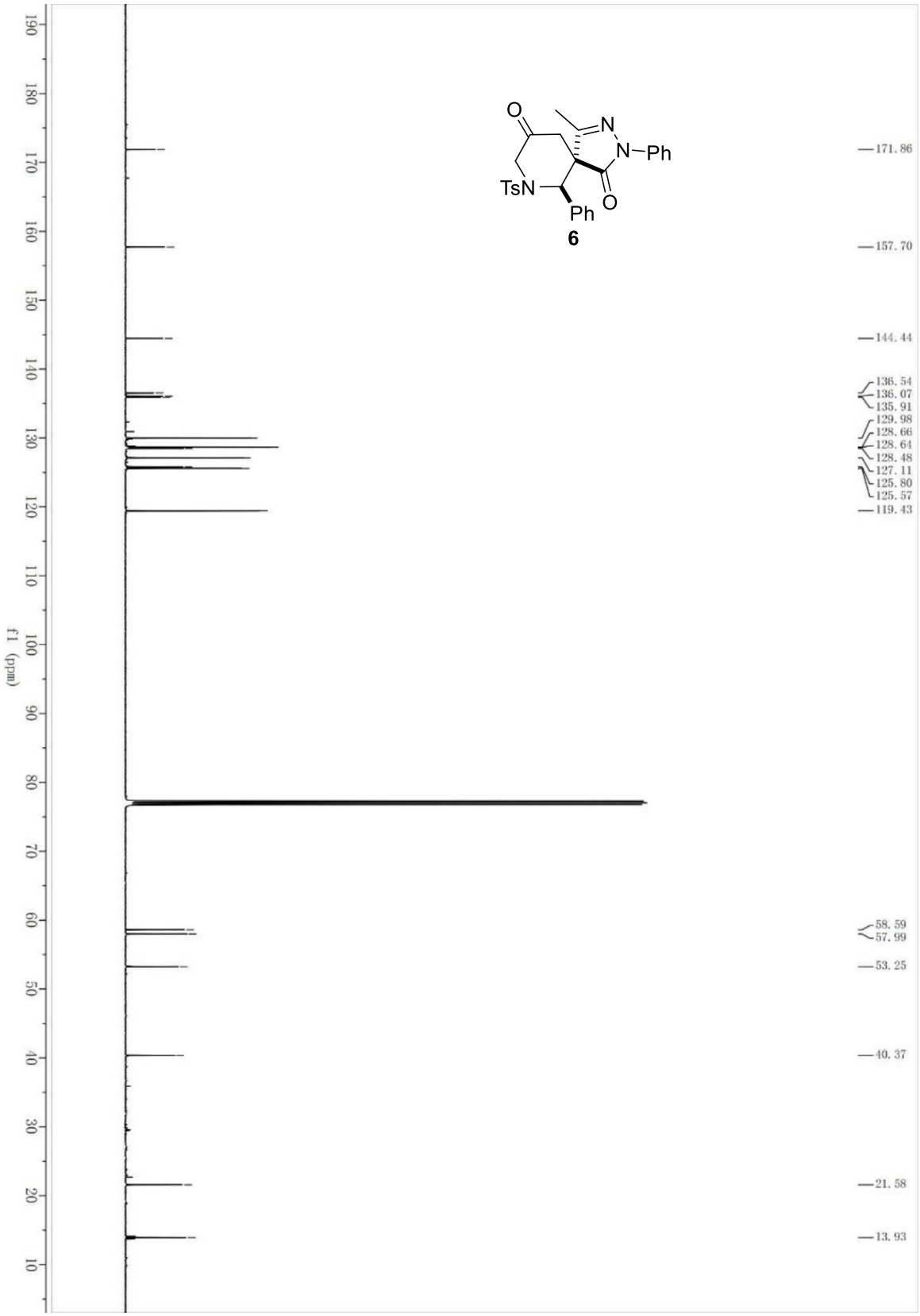

O
N
N–Ph
TsN
O
Ph
4
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.63
13.22
1.03
1.00
1.14
8.61
2.55
7.76
7.76
7.74
7.73
7.73
7.59
7.56
7.49
7.46
7.46
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.27
7.26
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.17
7.16
7.16
7.14
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
5.30
4.70
4.03
3.98
3.97
2.84
2.83
2.83
2.71
2.69
2.45
2.41
2.39
2.31
1.79
1.74
1.60
1.55


O
N
N–Ph
TsN
O
Ph
4
171.27
159.49
143.50
136.65
136.25
136.02
129.26
128.34
128.18
127.32
125.54
119.12
58.09
57.61
53.88
52.49
48.24
32.06
21.21
13.75
f1 (ppm)


HO
N
N
Ph
TsN
Ph
O
5
f1 (ppm)
14.64
1.00
1.00
3.05
8.23
2.80

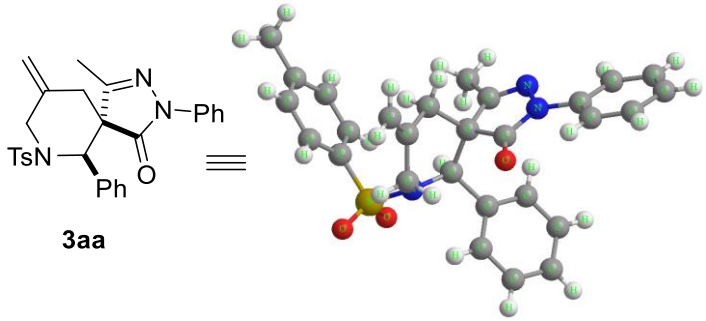

HO
N
N–Ph
TsN
O
Ph
5
f1 (ppm)
171.71
162.19
142.81
137.10
135.68
135.31
128.80
128.34
127.91
127.87
127.71
126.74
124.92
118.91
64.23
58.54
56.31
42.87
33.23
26.78
21.04
16.49


O
N
N–Ph
TsN
Ph
O
6
f1 (ppm)
14.43
1.00
1.05
1.03
8.11
7.63
7.63
7.61
7.60
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.31
7.30
7.29
7.28
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.20
7.20
7.19
7.18
7.18
7.16
7.15
7.15
7.13
7.11
7.08
7.08
7.07
7.06
7.05
7.05
5.65
4.79
4.73
4.61
4.60
4.54
4.54
2.56
2.51
2.45
2.40
2.29
2.24


O
N
N–Ph
TsN
O
Ph
6
171.86
157.70
144.44
136.54
136.07
135.91
129.98
128.66
128.64
128.48
127.11
125.80
125.57
119.43
58.59
57.99
53.25
40.37
21.58
13.93
f1 (ppm)

X-Ray Crystallographic Data of 3aa and 4

Crystallographic data for **3aa** have been deposited with the Cam-bridge Crystallographic Data Centre as deposition number CCDC 2023840. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



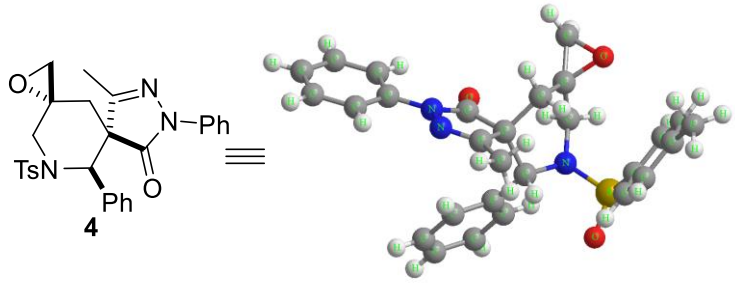
3aa

Table S3. Crystal data and structure refinement for 3aa.

Identification code	**3aa**
Empirical formula	$C_{62}H_{68}N_6O_6S_2$
Formula weight	1057.34
Temperature/K	163.15
Crystal system	triclinic
Space group	P-1
a/Å	9.868(2)
b/Å	11.707(2)
c/Å	12.318(3)
α/°	80.18(3)
β/°	82.46(3)
γ/°	76.91(3)
Volume/Å^3	1359.4(5)
Z	1
ρ_{calc}g/cm^3	1.292
μ/mm^{-1}	0.157
F(000)	562.0
Crystal size/mm^3	0.24 × 0.21 × 0.2

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.258 to 54.982
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	14219
Independent reflections	6130 [R_{int} = 0.0381, R_{sigma} = 0.0445]
Data/restraints/parameters	6130/0/346
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0696, wR_2 = 0.1819
Final R indexes [all data]	R_1 = 0.0760, wR_2 = 0.1877
Largest diff. peak/hole / e $Å^{-3}$	0.97/-0.49

Crystallographic data for **4** have been deposited with the Cam-bridge Crystallographic Data Centre as deposition number CCDC 2023841. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



4

Table S4. Crystal data and structure refinement for 4.

Identification code	**4**
Empirical formula	$C_{31}H_{34}N_3O_4S$
Formula weight	544.67
Temperature/K	163.15
Crystal system	triclinic
Space group	P-1

a/Å	9.928(2)
b/Å	11.674(2)
c/Å	12.353(3)
α/°	81.04(3)
β/°	82.19(3)
γ/°	78.40(3)
Volume/Å^3	1377.3(5)
Z	2
ρ_{calc}g/cm^3	1.313
μ/mm^{-1}	0.160
F(000)	578.0
Crystal size/mm^3	0.23 × 0.12 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.234 to 54.948
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	16681
Independent reflections	6250 [R_{int} = 0.0341, R_{sigma} = 0.0352]
Data/restraints/parameters	6250/0/355
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0575, wR_2 = 0.1410
Final R indexes [all data]	R_1 = 0.0635, wR_2 = 0.1452
Largest diff. peak/hole / e Å^{-3}	0.57/-0.34