Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Zinc-Catalyzed Oxidative Reaction of Ynamides with Phenols and Thiophenols: Highly Site-Selective Synthesis of Versatile α-Aryloxy Amides and α-Arylthio Amides

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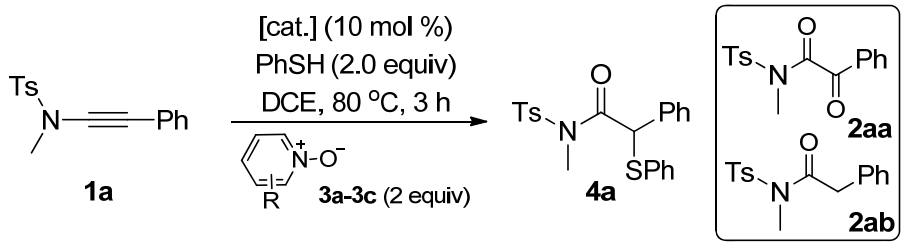
General Information. Ethyl acetate (ACS grade), hexanes (ACS grade) and anhydrous 1, 2-dichloroethane (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization.

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d_3. For ^{1}H NMR spectra, chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. For ^{13}C NMR spectra, chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

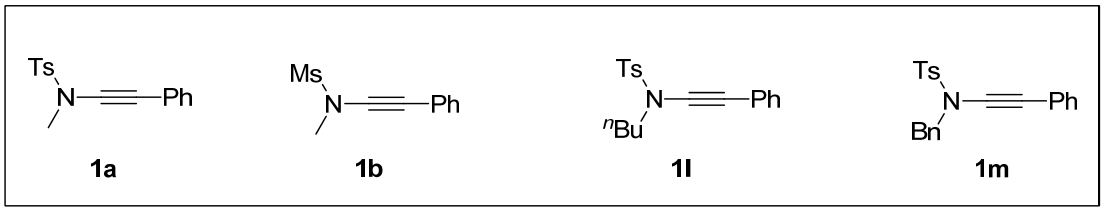
Table S1. Effects of catalyst and oxidant on the reaction of thiophenol with **1a**[a]



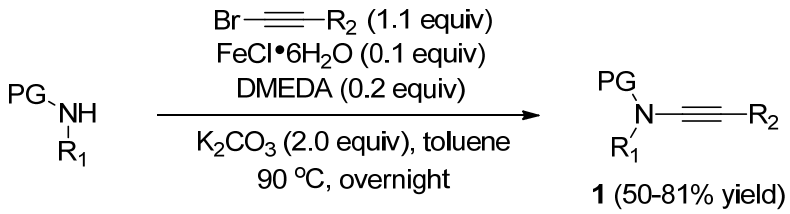
entry	catalyst	oxidant (R)	yield (%)[b]		
			4a	**2aa**	**2ab**
1	$Zn(OTf)_2$	**3a** (2,6-Br_2)	30	<1	<5
2	$Zn(OTf)_2$	**3b** (2,6-Me_2)	78	<1	<5
3	$Zn(OTf)_2$	**3c** (3,5-Cl_2)	69	<5	<5
4	$Sc(OTf)_3$	**3b** (2,6-Me_2)	67	<5	<5
5	$Y(OTf)_3$	**3b** (2,6-Me_2)	70	<1	8
6	$In(OTf)_3$	**3b** (2,6-Me_2)	72	<1	<5

[a] Reaction conditions: [**1a**] = 0.10 M. [b] Estimated by ^{1}H NMR using diethyl phthalate as internal reference.

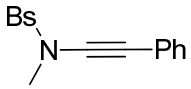
The data of the following ynamides **1** (**1a, 1b, 1l, 1m**) were reported in our previous work.[1,2]



Representative synthetic procedures for the preparation of ynamides 1:[3]



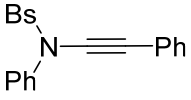
4-bromo-*N*-methyl-*N*-(phenylethynyl)benzenesulfonamide (1c)



1c

White solid (mp 79 – 81 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.76 – 7.69 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 3H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 132.4, 131.3, 129.0, 128.9, 128.2, 128.0, 122.1, 83.2, 69.2, 39.2; IR (neat): 2923, 2234, 2099, 1368, 1168, 756; MS (ESI, m/z) 372 (M + Na^+); HRESIMS Calcd for $[C_{15}H_{12}BrNNaO_2S]^+$ (M + Na^+) 371.9664, found 371.9661.

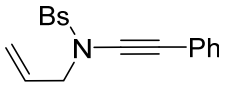
4-bromo-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide (1d)



1d

White solid (mp 100 – 101 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 2H), 7.59 – 7.57 (m, 2H), 7.40 – 7.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5 134.7, 132.2, 131.5, 129.6, 129.3, 129.2, 128.5, 128.3, 128.2, 126.2, 122.2, 82.3, 70.7; IR (neat): 3063, 2925, 2239, 1573, 1378, 1175, 741, 605; MS (ESI, m/z) 434 (M + Na^+); HRESIMS Calcd for $[C_{20}H_{14}BrNNaO_2S]^+$ (M + Na^+) 433.9821, found 433.9823.

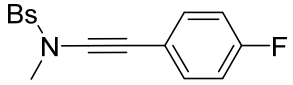
_N_-allyl-4-bromo-_N_-(phenylethynyl)benzenesulfonamide (1e)



1e

White solid (mp 85 – 86 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.71 – 7.69 (m, 2H), 7.36 – 7.33 (m, 2H), 7.29 – 7.25 (m, 3H), 5.84 – 5.74 (m, 1H), 5.33 – 5.24 (m, 2H), 4.07 (d, 2H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 136.1, 135.0, 132.5, 129.1, 129.0, 128.6, 128.4, 126.0, 106.9, 85.2, 68.9, 39.3; IR (neat): 3085, 2923, 2237, 1574, 1371, 1173, 740, 621; MS (ESI, m/z) 398 (M + Na^+); HRESIMS Calcd for $[C_{17}H_{14}BrNNaO_2S]^+$ (M + Na^+) 397.9821, found 397.9822.

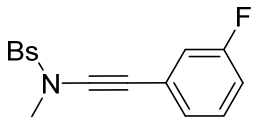
4-bromo-_N_-((4-fluorophenyl)ethynyl)-_N_-methylbenzenesulfonamide (1f)



1f

White solid (mp 105 – 106 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.74 – 7.72 (m, 2H), 7.36 – 7.32 (m, 2H), 7.02 – 6.97 (m, 2H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 249.6 Hz), 135.1, 133.6 (d, J = 8.4 Hz), 132.5, 129.2, 129.1, 118.3 (d, J = 3.4 Hz), 115.6 (d, J = 22.1 Hz), 82.8, 68.2, 39.3; IR (neat): 1933, 2240, 1509, 1371, 1169, 752, 566; MS (ESI, m/z) 390 (M + Na^+); HRESIMS Calcd for $[C_{15}H_{11}BrFNNaO_2S]^+$ (M + Na^+) 389.9570, found 389.9572.

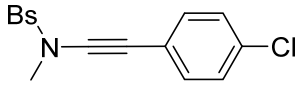
4-bromo-*N*-((3-fluorophenyl)ethynyl)-*N*-methylbenzenesulfonamide (1g)



1g

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.74 – 7.72 (m, 2H), 7.28 – 7.23 (m, 1H), 7.14 – 7.12 (m, 1H), 7.05 – 6.97 (m, 2H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.6 Hz), 135.1, 132.6, 129.9 (d, *J* = 8.8 Hz), 129.2, 129.1, 127.1 (d, *J* = 3.1 Hz), 124.2 (d, *J* = 9.7 Hz), 118.0 (d, *J* = 22.9 Hz), 115.3 (d, *J* = 21.2 Hz), 84.1, 68.4, 39.3; IR (neat): 2925, 2239, 1575, 1371, 1175, 750, 593; MS (ESI, m/z) 390 (M + Na^+); HRESIMS Calcd for $[C_{15}H_{11}BrFNNaO_2S]^+$ (M + Na^+) 389.9570, found 389.9572.

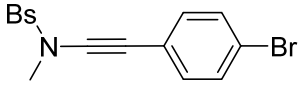
4-bromo-*N*-((4-chlorophenyl)ethynyl)-*N*-methylbenzenesulfonamide (1h)



1h

White solid (mp 120 – 121 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 2H), 7.74 – 7.72 (m, 2H), 7.30 – 7.25 (m, 4H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 134.0, 132.6, 132.5, 129.1, 128.6, 120.8, 84.1, 68.4, 39.3; IR (neat): 2930, 2236, 1574, 1372, 1170, 1010, 742, 596; MS (ESI, m/z) 406 (M + Na^+); HRESIMS Calcd for $[C_{15}H_{11}BrClNNaO_2S]^+$ (M + Na^+) 405.9275, found 405.9279.

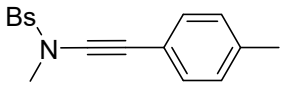
4-bromo-*N*-((4-bromophenyl)ethynyl)-*N*-methylbenzenesulfonamide (1i)



1i

White solid (mp 133 – 134 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 2H), 7.74 – 7.72 (m, 2H), 7.42 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 2H, *J* = 8.8 Hz), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 132.8, 132.6, 131.5, 129.1, 122.2, 121.3, 84.3, 68.5, 39.3; IR (neat): 2930, 2236, 1574, 1372, 1069, 742, 596; MS (ESI, m/z) 450 (M + Na^+); HRESIMS Calcd for $[C_{15}H_{11}Br_2NNaO_2S]^+$ (M + Na^+) 449.8769, found 449.8768.

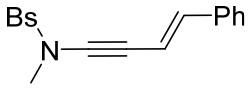
4-bromo-*N*-methyl-*N*-(*p*-tolylethynyl)benzenesulfonamide (1j)



1j

White solid (mp 83 – 84 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.73 – 7.70 (m, 2H), 7.25 (d, 2H, *J* = 8.0 Hz), 7.10 (d, 2H, *J* = 8.0 Hz), 3.16 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.1, 132.5, 131.6, 129.2, 129.1, 129.0, 119.1, 82.5, 69.3, 39.4, 21.4; IR (neat): 2923, 2237, 1574, 1370, 1182, 750, 565; MS (ESI, m/z) 386 (M + Na^+); HRESIMS Calcd for $[C_{16}H_{14}BrNNaO_2S]^+$ (M + Na^+) 385.9821, found 385.9819.

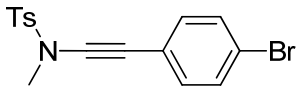
(*E*)-4-bromo-*N*-methyl-*N*-(4-phenylbut-3-en-1-yn-1-yl)benzenesulfonamide (1k)



1k

White solid (mp 109 – 111 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, *J* = 8.4 Hz), 7.71 (d, 2H, *J* = 8.4 Hz), 7.36 – 7.26 (m, 5H), 6.84 (d, 1H, *J* = 8.4 Hz), 6.20 (d, 1H, *J* = 8.4 Hz), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 136.1, 135.0, 132.5, 129.1, 129.0, 128.6, 128.4, 126.0, 106.9, 85.2, 68.9, 39.3; IR (neat): 3028, 2224, 1573, 1370, 745, 562; MS (ESI, m/z) 398 (M + Na^+); HRESIMS Calcd for $[C_{17}H_{14}BrNNaO_2S]^+$ (M + Na^+) 397.9821, found 397.9821.

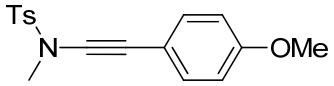
***N*-((4-bromophenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (1n)**



1n

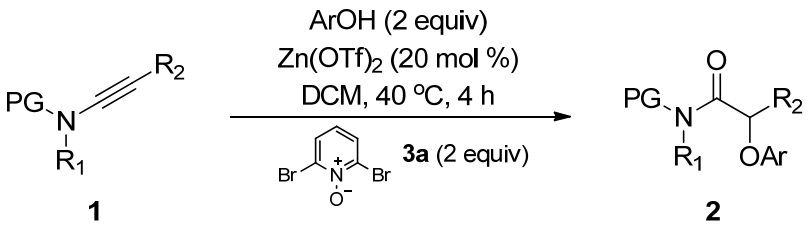
White solid (mp 116 – 118 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 2H, *J* = 8.4 Hz), 7.44 – 7.34 (m, 4H), 7.24 – 7.17 (m, 2H), 3.14 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 133.1, 132.6, 131.4, 129.8, 127.7, 121.8, 121.6, 85.0, 68.1, 39.1, 21.6; IR (neat): 2928, 2234, 2101, 1365, 1265, 1168, 739; MS (ESI, m/z) 386 (M + Na^+); HRESIMS Calcd for $[C_{16}H_{14}BrNNaO_2S]^+$ (M + Na^+) 385.9821, found 385.9823.

***N*-((4-methoxyphenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (1o)**



1o

White solid (mp 66 – 68 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, 2H, *J* = 8.0 Hz), 7.36 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 6.81 (d, 2H, *J* = 8.4 Hz), 3.79 (s, 3H), 3.12 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 144.6, 133.2, 132.9, 129.6, 127.6, 114.3, 113.8, 82.4, 68.5, 55.1, 39.2, 21.4; IR (neat): 2934, 2233, 1604, 1511, 1456, 1364, 1248, 1165, 727, 567; MS (ESI, m/z) 338 (M + Na^+); HRESIMS Calcd for $[C_{17}H_{17}NNaO_3S]^+$ (M + Na^+) 338.0821, found 338.0824.

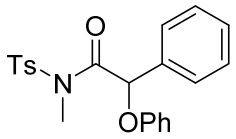


1 **2**

General procedure for the synthesis of 2:

2,6-dibromopyridine *N*-oxide (151.7 mg, 0.6 mmol), ArOH (0.6 mmol) and $Zn(OTf)_2$ (21.8 mg, 0.06 mmol) were added in this order to the ynamide **1** (0.30 mmol) in DCM (3.0 mL) at room temperature. The reaction mixture was stirred at 40 °C and the progress of the reaction was monitored by TLC. The reaction typically took 4 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product **2**.

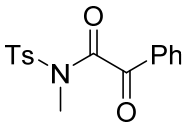
***N*-methyl-2-phenoxy-2-phenyl-*N*-tosylacetamide (2a)**



2a

Compound **2a** was prepared in 61% yield according to the general procedure (Table 2, entry 1). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 4H), 7.39 – 7.37 (m, 3H), 7.25 – 7.17 (m, 4H), 7.00 – 6.96 (m, 1H), 6.90 – 6.88 (m, 2H), 6.49 (s, 1H), 3.19 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 157.2, 145.0 135.0, 134.4, 129.7, 129.6, 129.1, 128.9, 127.9, 127.8, 122.0, 115.6, 79.5, 33.0, 21.6; IR (neat): 2921, 1709 (s), 1597, 1494, 1358, 1170, 751, 547; MS (ESI, m/z) 418 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{21}NNaO_4S]^+$ (M + Na^+) 418.1083, found 418.1084.

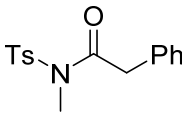
***N*-methyl-2-oxo-2-phenyl-N-tosylacetamide (2aa)**



2aa

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, 2H, *J* = 7.2 Hz), 7.88 (d, 2H, *J* = 8.0 Hz), 7.66 – 7.62 (m, 1H), 7.55 – 7.51 (m, 2H), 7.39 (d, 2H, *J* = 8.0 Hz), 3.24 (s, 3H), 2.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 167.2, 145.9, 134.4, 133.4, 132.7, 130.1, 129.6, 128.8, 128.3, 30.7, 21.7; IR (neat): 2922, 1681 (s), 1371, 1165, 947, 716, 663, 593; MS (ESI, m/z) 340 (M + Na^+); HRESIMS Calcd for $[C_{16}H_{15}NNaO_4S]^+$ (M + Na^+) 340.0614, found 340.0613.

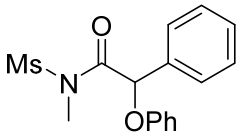
***N*-methyl-2-phenyl-*N*-tosylacetamide (2ab)**



2ab

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 2H, *J* = 8.4 Hz), 7.31 – 7.24 (m, 5H), 7.13 – 7.11 (m, 2H), 4.03 (s, 2H), 3.27 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 144.9, 135.9, 133.4, 129.8, 129.3, 128.5, 127.4, 127.1, 43.0, 33.2, 21.5; IR (neat): 2923, 1697 (s), 1357, 1167, 1075, 673, 583, 549; MS (ESI, m/z) 326 (M + Na^+); HRESIMS Calcd for $[C_{16}H_{17}NNaO_3S]^+$ (M + Na^+) 326.0821, found 326.0820.

***N*-methyl-*N*-(methylsulfonyl)-2-phenoxy-2-phenylacetamide (2b)**

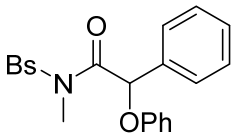


2b

Compound **2b** was prepared in 59% yield according to the general procedure (Table 2,

entry 2). White solid (mp 112 – 114 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.52 (m, 2H), 7.45 – 7.40 (m, 3H), 7.31 – 7.25 (m, 2H), 7.02 – 6.96 (m, 3H), 6.40 (s, 1H), 3.25 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 157.0, 133.9, 129.7, 129.4, 129.1, 127.9, 122.2, 115.5, 79.5, 40.6, 32.7; IR (neat): 3038, 2931, 1708 (s), 1597, 1494, 1354, 1225, 1168, 964, 755, 517; MS (ESI, m/z) 342 (M + Na^+); HRESIMS Calcd for $[C_{16}H_{17}NNaO_4S]^+$ (M + Na^+) 342.0770, found 342.0771.

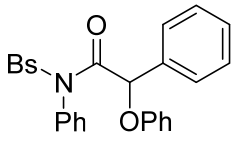
_N_-((4-bromophenyl)sulfonyl)-_N_-methyl-2-phenoxy-2-phenylacetamide (2c)



2c

Compound **2c** was prepared in 74% yield according to the general procedure (Table 2, entry 3). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.47 – 7.38 (m, 7H), 7.26 – 7.22 (m, 2H), 7.02 – 6.98 (m, 1H), 6.88 – 6.86 (m, 2H), 6.32 (s, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 157.0 136.9, 133.9, 132.2, 129.7, 129.4, 129.2, 129.1, 129.0, 127.5, 122.2, 115.5, 79.7, 33.0; IR (neat): 3064, 2925, 1710 (s), 1494, 1360, 1225, 1171, 750, 613; MS (ESI, m/z) 482 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{18}BrNNaO_4S]^+$ (M + Na^+) 482.0032, found 482.0038.

_N_-((4-bromophenyl)sulfonyl)-2-phenoxy-_N_,2-diphenylacetamide (2d)

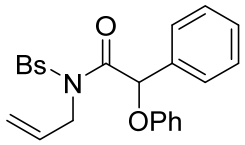


2d

Compound **2d** was prepared in 70% yield according to the general procedure (Table 2, entry 4). White solid (mp 123 – 124 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 2H, J = 8.4 Hz), 7.65 (d, 2H, J = 8.4 Hz), 7.49 – 7.46 (m, 1H), 7.38 – 7.19 (m, 5H), 7.18 –

7.14 (m, 2H), 7.00 – 6.91 (m, 5H), 6.66 (d, 2H, J = 8.0 Hz), 5.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 156.8, 137.3, 134.0, 133.7, 132.1, 130.8, 130.6, 130.5, 129.6, 129.5, 129.4, 128.7, 128.0, 122.1, 115.7, 79.0; IR (neat): 3065, 2924, 1717 (s), 1490, 1370, 1230, 1162, 747, 696, 601; MS (ESI, m/z) 544 (M + Na^+); HRESIMS Calcd for $[C_{26}H_{20}BrNNaO_4S]^+$ (M + Na^+) 544.0189, found 544.0188.

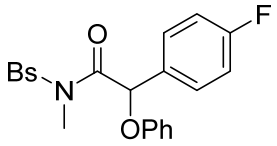
_N_-allyl-_N_-((4-bromophenyl)sulfonyl)-2-phenoxy-2-phenylacetamide (2e)



2e

Compound **2e** was prepared in 74% yield according to the general procedure (Table 2, entry 5). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 4H), 7.39 – 7.34 (m, 5H), 7.24 – 7.19 (m, 2H), 6.99 – 6.95 (m, 1H), 6.82 (d, 2H, J = 8.0 Hz), 6.18 (s, 1H), 5.74 – 5.64 (m, 1H), 5.21 – 5.17 (m, 2H), 4.46 – 4.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 157.0, 137.4, 133.8, 132.1, 131.9, 129.7, 129.5, 129.3, 129.1, 129.0, 127.7, 122.1, 119.0, 115.5, 79.4, 48.4; IR (neat): 3090, 1712 (s), 1574, 1494, 1362, 1226, 1171, 751, 610; MS (ESI, m/z) 508 (M + Na^+); HRESIMS Calcd for $[C_{23}H_{20}BrNNaO_4S]^+$ (M + Na^+) 508.0189, found 508.0187.

_N_-((4-bromophenyl)sulfonyl)-2-(4-fluorophenyl)-_N_-methyl-2-phenoxyacetamide (2f)

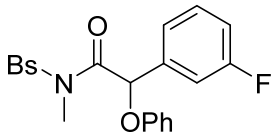


2f

Compound **2f** was prepared in 85% yield according to the general procedure (Table 2, entry 6). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.43 (m, 6H), 7.25 –

7.22 (m, 2H), 7.10 – 7.06 (m, 2H), 7.00 (t, 1H, *J* = 7.2 Hz), 6.85 (d, 2H, *J* = 8.0 Hz), 6.35 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 163.2 (d, *J* = 249.1 Hz), 156.8, 136.9, 132.4, 130.0 (d, *J* = 3.2 Hz), 129.7, 129.6 (d, *J* = 8.4 Hz), 129.3, 129.2, 122.4, 116.0 (d, *J* = 21.8 Hz), 115.6, 78.9, 33.1; IR (neat): 3091, 2918, 1711 (s), 1574, 1492, 1224, 1172, 1011, 752, 613; MS (ESI, m/z) 500 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{17}BrFNNaO_4S]^+$ (M + Na^+) 499.9938, found 499.9941.

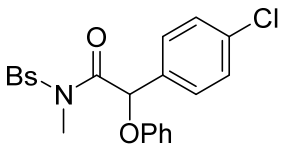
_N_-((4-bromophenyl)sulfonyl)-2-(3-fluorophenyl)-_N_-methyl-2-phenoxyacetamide (2g)



2g

Compound **2g** was prepared in 82% yield according to the general procedure (Table 2, entry 7). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 4H), 7.40 – 7.24 (m, 5H), 7.22 – 7.01 (m, 2H), 6.86 (d, 2H, *J* = 8.0 Hz), 6.33 (s, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 162.9 (d, *J* = 247.8 Hz), 156.7, 136.9, 136.5 (d, *J* = 7.5 Hz), 132.3, 130.6 (d, *J* = 8.1 Hz), 129.8, 129.3, 122.9 (d, *J* = 3.0 Hz), 122.5, 116.2 (d, *J* = 21.0 Hz), 115.5, 114.5 (d, *J* = 23.0 Hz), 79.1, 33.1; IR (neat): 2919, 1718 (s), 1574, 1011, 913, 747, 613; MS (ESI, m/z) 500 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{17}BrFNNaO_4S]^+$ (M + Na^+) 499.9938, found 499.9940.

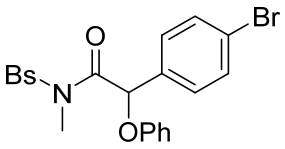
_N_-((4-bromophenyl)sulfonyl)-2-(4-chlorophenyl)-_N_-methyl-2-phenoxyacetamide (2h)



2h

Compound **2h** was prepared in 77% yield according to the general procedure (Table 2, entry 8). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 4H), 7.42 – 7.35 (m, 4H), 7.25 – 7.22 (m, 2H), 7.03 – 6.99 (m, 1H), 6.85 (d, 2H, *J* = 7.6 Hz), 6.34 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 156.7, 136.9, 135.4, 132.6, 132.4, 129.8, 129.3, 129.2, 129.1, 128.9, 122.4, 115.6, 79.0, 33.1; IR (neat): 2922, 1712 (s), 1510, 1362, 1225, 1011, 748, 614; MS (ESI, m/z) 516 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{17}BrClNNaO_4S]^+$ (M + Na^+) 515.9642, found 515.9644.

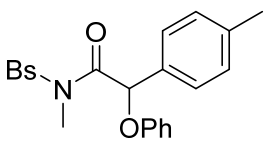
2-(4-bromophenyl)-*N*-((4-bromophenyl)sulfonyl)-*N*-methyl-2-phenoxyacetamide (2i)



2i

Compound **2i** was prepared in 75% yield according to the general procedure (Table 2, entry 9). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 6H), 7.33 (d, 2H, *J* = 8.4 Hz), 7.25 – 7.21 (m, 2H), 7.02 – 6.98 (m, 1H), 6.84 (d, 2H, *J* = 7.6 Hz), 6.32 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 156.7, 136.8, 133.1, 132.3, 132.1, 129.7, 129.3, 129.2, 129.1, 123.5, 122.4, 115.5, 79.0, 33.1; IR (neat): 2924, 1711 (s), 1596, 1489, 1365, 1223, 1070, 749, 614; MS (ESI, m/z) 560 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{17}Br_2NNaO_4S]^+$ (M + Na^+) 559.9137, found 559.9138.

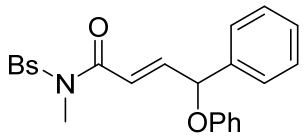
***N*-((4-bromophenyl)sulfonyl)-*N*-methyl-2-phenoxy-2-(*p*-tolyl)acetamide (2j)**



2j

Compound **2j** was prepared in 70% yield according to the general procedure (Table 2, entry 10). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 4H), 7.30 – 7.17 (m, 6H), 7.01 – 6.97 (m, 1H), 6.86 (d, 2H, *J* = 8.0 Hz), 6.26 (s, 1H) , 3.24 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 157.1, 139.3, 137.0, 132.2, 130.8, 129.7, 129.6, 129.4, 129.0, 127.5, 122.1, 115.5, 79.6, 33.0, 21.2; IR (neat): 2924, 1712 (s), 1574, 1488, 1363, 1226, 750, 613; MS (ESI, m/z) 496 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{20}BrNNaO_4S]^+$ (M + Na^+) 496.0189, found 496.0189.

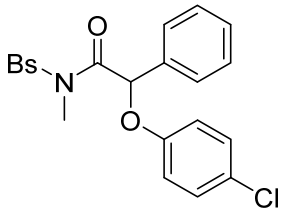
(*E*)-*N*-((4-bromophenyl)sulfonyl)-*N*-methyl-4-phenoxy-4-phenylbut-2-enamide (2k)



2k

Compound **2k** was prepared in 68% yield according to the general procedure (Table 2, entry 11). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.41 – 7.31 (m, 5H), 7.29 – 7.24 (m, 2H), 7.11 – 7.02 (m, 2H) , 6.99 – 6.91 (m, 3H), 5.79 (d, 1H, *J* = 3.2 Hz), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 157.3, 147.5, 138.0, 137.9, 132.6, 129.5, 129.0, 128.9, 128.8, 128.5, 126.8, 121.6, 121.0, 116.0, 78.9, 33.1; IR (neat): 2918, 1682 (s), 1493, 1365, 1166, 751, 1173, 614; MS (ESI, m/z) 508 (M + Na^+); HRESIMS Calcd for $[C_{23}H_{20}BrNNaO_4S]^+$ (M + Na^+) 508.0189, found 508.0191.

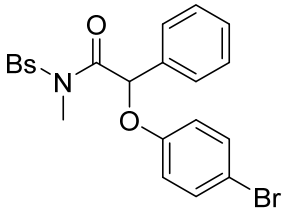
***N*-((4-bromophenyl)sulfonyl)-2-(4-chlorophenoxy)-*N*-methyl-2-phenylacetamide (2l)**



2l

Compound **2l** was prepared in 80% yield according to the general procedure (Table 2, entry 12). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2H, *J* = 8.8 Hz), 7.42 – 7.39 (m, 7H), 7.20 (d, 2H, *J* = 9.2 Hz), 6.81 (d, 2H, *J* = 9.2 Hz), 6.34 (s, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 155.5, 136.7, 133.4, 132.3, 129.5, 129.4, 129.2, 129.1, 127.7, 127.2, 116.9, 116.6, 79.9, 33.0; IR (neat): 2919, 1711 (s), 1489, 1229, 1010, 743, 613; MS (ESI, m/z) 516 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{17}BrClNNaO_4S]^+$ (M + Na^+) 515.9642, found 515.9643.

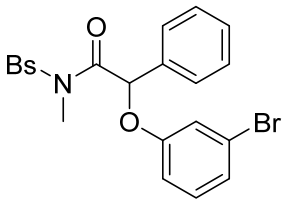
2-(4-bromophenoxy)-*N*-((4-bromophenyl)sulfonyl)-*N*-methyl-2-phenylacetamide (2m)



2m

Compound **2m** was prepared in 77% yield according to the general procedure (Table 2, entry 13). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2H, *J* = 8.8 Hz), 7.42 – 7.39 (m, 7H), 7.33 (d, 2H, *J* = 9.2 Hz), 6.76 (d, 2H, *J* = 9.2 Hz), 6.33 (s, 1H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 156.1, 136.7, 133.5, 132.5, 132.3, 129.5, 129.3, 129.2, 129.1, 127.8, 117.4, 114.6, 79.8, 33.1; IR (neat): 2918, 1710 (s), 1574, 1486, 1364, 1230, 821, 748, 613; MS (ESI, m/z) 560 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{17}Br_2NNaO_4S]^+$ (M + Na^+) 559.9137, found 559.9139.

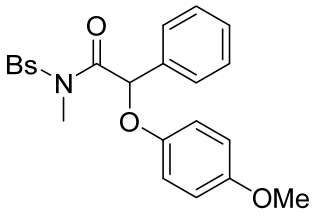
2-(3-bromophenoxy)-*N*-((4-bromophenyl)sulfonyl)-*N*-methyl-2-phenylacetamide (2n)



2n

Compound **2n** was prepared in 79% yield according to the general procedure (Table 2, entry 14). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.47 – 7.41 (m, 7H), 7.14 – 7.04 (m, 3H), 6.81 – 6.80 (m, 1H), 6.35 (s, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 157.7, 136.7, 133.4, 132.4, 130.8, 129.5, 129.3, 129.2, 129.1, 127.8, 125.3, 122.9, 119.1, 114.1, 79.7, 33.1; IR (neat): 3090, 2924, 1710 (s), 1574, 1473, 1364, 743, 613; MS (ESI, m/z) 560 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{17}Br_2NNaO_4S]^+$ (M + Na^+) 559.9137, found 559.9138.

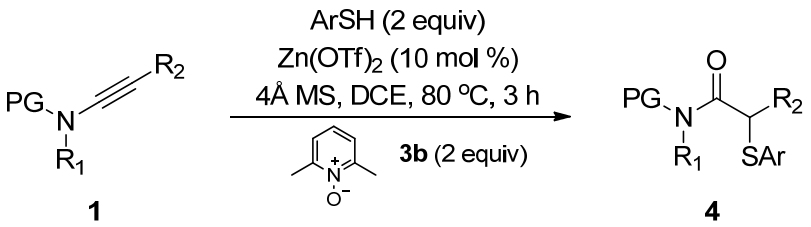
***N*-((4-bromophenyl)sulfonyl)-2-(4-methoxyphenoxy)-*N*-methyl-2-phenylacetamide (2o)**



2o

Compound **2o** was prepared in 81% yield according to the general procedure (Table 2, entry 15). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.47 – 7.83 (m, 7H), 6.83 – 6.75 (m, 4H), 6.21 (s, 1H), 3.77 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 154.9, 151.1, 137.0, 134.1, 132.2, 129.4, 129.2, 129.1, 129.0, 127.5, 117.0, 114.7, 80.9, 55.6, 33.0; IR (neat): 2922, 1711 (s), 1506, 1362,

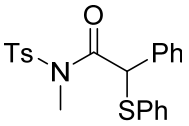
1222, 1040, 745, 613; MS (ESI, m/z) 512 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{20}BrNNaO_5S]^+$ (M + Na^+) 512.0138, found 512.0138.



General procedure for the synthesis of 4:

2,6-dimethylpyridine *N*-oxide (73.8 mg, 0.6 mmol), ArSH (0.6 mmol), 4Å MS (60.0 mg) and $Zn(OTf)_2$ (10.9 mg, 0.03 mmol) were added in this order to the ynamide **1** (0.30 mmol) in DCE (3.0 mL) at room temperature. The reaction mixture was stirred at 80 °C and the progress of the reaction was monitored by TLC. The reaction typically took 3 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product **4**.

***N*-methyl-2-phenyl-2-(phenylthio)-*N*-tosylacetamide (4a)**

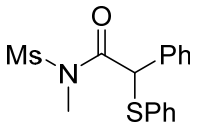


4a

Compound **4a** was prepared in 77% yield according to the general procedure (Table 3, entry 1). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, 2H, *J* = 8.4 Hz), 7.31 – 7.17 (m, 12H), 5.86 (s, 1H), 3.16 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 144.9, 135.5, 135.2, 133.4, 133.1, 129.7, 128.9, 128.8, 128.6, 128.2, 128.1, 127.5, 57.1, 33.4, 21.5; IR (neat): 3060, 2923, 1694 (s), 1359, 1168, 1070, 693, 548;

MS (ESI, m/z) 434 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{21}NNaO_3S_2]^+$ (M + Na^+) 434.0855, found 434.0857.

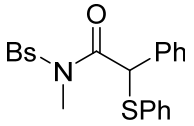
***N*-methyl-*N*-(methylsulfonyl)-2-phenyl-2-(phenylthio)acetamide (4b)**



4b

Compound **4b** was prepared in 66% yield according to the general procedure (Table 3, entry 2). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 10H), 5.67 (s, 1H), 3.22 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 135.0, 133.7, 133.0, 129.1, 128.9, 128.8, 128.5, 128.4, 57.2, 40.8, 33.1; IR (neat): 3059, 2927, 1692 (s), 1354, 1165, 1075, 964, 748, 517; MS (ESI, m/z) 358 (M + Na^+); HRESIMS Calcd for $[C_{16}H_{17}NNaO_3S_2]^+$ (M + Na^+) 358.0542, found 358.0546.

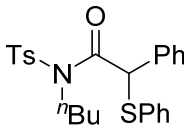
***N*-((4-bromophenyl)sulfonyl)-*N*-methyl-2-phenyl-2-(phenylthio)acetamide (4c)**



4c

Compound **4c** was prepared in 62% yield according to the general procedure (Table 3, entry 3). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.47 – 7.45 (m, 2H), 7.29 – 7.22 (m, 10H), 5.68 (s, 1H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 137.2, 135.0, 133.3, 133.2, 132.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.4, 128.3, 57.3, 33.5; IR (neat): 2922, 2851, 1693 (s), 1357, 1165, 748, 664, 593; MS (ESI, m/z) 498 (M + Na^+); HRESIMS Calcd for $[C_{21}H_{18}BrNNaO_3S_2]^+$ (M + Na^+) 497.9804, found 497.9805.

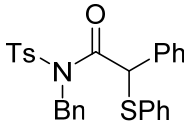
***N*-butyl-2-phenyl-2-(phenylthio)-*N*-tosylacetamide (4d)**



4d

Compound **4d** was prepared in 76% yield according to the general procedure (Table 3, entry 4). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, 2H, *J* = 8.4 Hz), 7.29 – 7.15 (m, 12H), 5.73 (s, 1H), 3.70 – 3.55 (m, 2H), 2.39 (s, 3H), 1.53 – 1.43 (m, 2H), 1.25 – 1.19 (m, 2H), 0.84 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 144.7, 136.0, 135.5, 133.6, 133.1, 129.6, 128.8, 128.7, 128.6, 128.2, 128.1, 127.6, 57.1, 47.0, 31.3, 21.5, 19.9, 13.5; IR (neat): 2956, 2873, 1693 (s), 1357, 1169, 1085, 1024, 910, 694, 590; MS (ESI, m/z) 476 (M + Na^+); HRESIMS Calcd for $[C_{25}H_{27}NNaO_3S_2]^+$ (M + Na^+) 476.1325, found 476.1327.

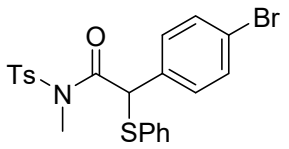
***N*-benzyl-2-phenyl-2-(phenylthio)-*N*-tosylacetamide (4e)**



4e

Compound **4e** was prepared in 64% yield according to the general procedure (Table 3, entry 5). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 2H, *J* = 8.0 Hz), 7.29 – 7.11 (m, 13H), 7.08 – 7.04 (m, 4H), 5.41 (s, 1H), 5.06 (d, 1H, *J* = 16.4 Hz), 4.78 (d, 1H, *J* = 16.8 Hz), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 144.9, 136.1, 135.7, 134.8, 133.3, 133.0, 129.5, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 127.7, 127.1, 57.0, 49.5, 21.6; IR (neat): 3062, 2924, 1699 (s), 1358, 1169, 748, 587; MS (ESI, m/z) 510 (M + Na^+); HRESIMS Calcd for $[C_{28}H_{25}NNaO_3S_2]^+$ (M + Na^+) 510.1168, found 510.1167.

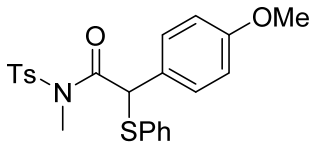
2-(4-bromophenyl)-*N*-methyl-2-(phenylthio)-*N*-tosylacetamide (4f)



4f

Compound **4f** was prepared in 70% yield according to the general procedure (Table 3, entry 6). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, 2H, *J* = 8.4 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 7.21 – 7.09 (m, 9H), 5.76 (s, 1H), 3.10 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 145.1, 135.2, 134.9, 133.4, 132.9, 131.6, 130.5, 129.8, 129.0, 128.4, 127.3, 122.4, 56.3, 33.5, 21.6; IR (neat): 3058, 2954, 2923, 1693 (s), 1596, 1486, 1359, 1168, 1011, 811, 590; MS (ESI, m/z) 512 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{20}BrNNaO_3S_2]^+$ (M + Na^+) 511.9960, found 511.9961.

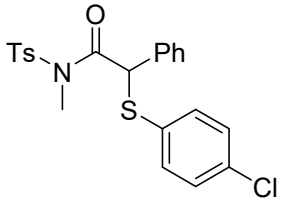
2-(4-methoxyphenyl)-*N*-methyl-2-(phenylthio)-*N*-tosylacetamide (4g)



4g

Compound **4g** was prepared in 83% yield according to the general procedure (Table 3, entry 7). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, 2H, *J* = 8.4 Hz), 7.23 – 7.21 (m, 9H), 6.81 – 6.78 (m, 2H), 5.81 (s, 1H), 3.79 (s, 3H), 3.16 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 159.5, 144.8, 135.2, 133.6, 133.1, 130.0, 129.7, 128.8, 128.0, 127.5, 127.3, 114.0, 56.4, 55.2, 33.4, 21.6; IR (neat): 2955, 2927, 1694 (s), 1510, 1359, 1169, 811, 591; MS (ESI, m/z) 464 (M + Na^+); HRESIMS Calcd for $[C_{23}H_{23}NNaO_4S_2]^+$ (M + Na^+) 464.0961, found 464.0961.

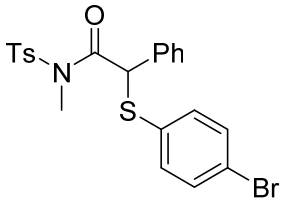
2-((4-chlorophenyl)thio)-*N*-methyl-2-phenyl-*N*-tosylacetamide (4h)



4h

Compound **4h** was prepared in 71% yield according to the general procedure (Table 3, entry 8). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, 2H, *J* = 8.4 Hz), 7.27 – 7.26 (m, 5H), 7.20 – 7.16 (m, 6H), 5.82 (s, 1H), 3.16 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 145.0, 135.1, 134.9, 134.5, 131.7, 129.7, 129.0, 128.8, 128.7, 128.3, 127.5, 57.2, 33.4, 21.5; IR (neat): 3063, 2924, 1694 (s), 1476, 1360, 1168, 1013, 813, 665, 548; MS (ESI, m/z) 468 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{20}ClNNaO_3S_2]^+$ (M + Na^+) 468.0465, found 468.0468.

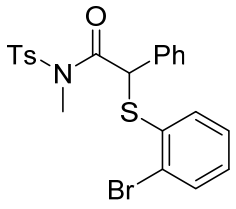
2-((4-bromophenyl)thio)-*N*-methyl-2-phenyl-*N*-tosylacetamide (4i)



4i

Compound **4i** was prepared in 73% yield according to the general procedure (Table 3, entry 9). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, *J* = 8.4 Hz), 7.33 – 7.31 (m, 2H), 7.28 – 7.26 (m, 5H), 7.19 (d, 2H, *J* = 8.0 Hz), 7.10 (d, 2H, *J* = 8.8 Hz), 5.83 (s, 1H), 3.16 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 145.0, 135.1, 135.0, 132.4, 132.0, 129.7, 128.8, 128.7, 128.4, 127.5, 122.7, 57.1, 33.5, 21.6; IR (neat): 3062, 2924, 1694 (s), 1473, 1359, 1168, 1009, 813, 665, 548; MS (ESI, m/z) 512 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{20}BrNNaO_3S_2]^+$ (M + Na^+) 511.9960, found 511.9961.

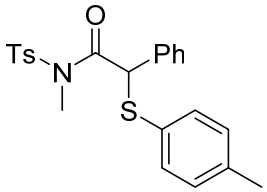
2-((2-bromophenyl)thio)-*N*-methyl-2-phenyl-*N*-tosylacetamide (4j)



4j

Compound **4j** was prepared in 62% yield according to the general procedure (Table 3, entry 10). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 1H), 7.50 – 7.47 (m, 2H), 7.32 – 7.26 (m, 5H), 7.17 – 7.15 (m, 3H), 7.14 – 7.07 (m, 2H), 6.00 (s, 1H), 3.20 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 145.0, 135.1, 134.9, 134.8, 133.3, 133.1, 129.7, 129.0, 128.8, 128.7, 128.4, 127.8, 127.6, 127.0, 55.7, 33.5, 21.6; IR (neat): 2924, 1693 (s), 1359, 1169, 1073, 1019, 665, 548; MS (ESI, m/z) 512 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{20}BrNNaO_3S_2]^+$ (M + Na^+) 511.9960, found 511.9961.

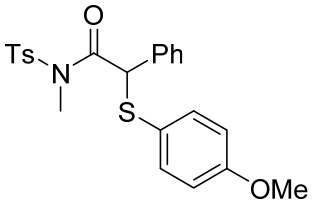
_N_-methyl-2-phenyl-2-(_p_-tolylthio)-_N_-tosylacetamide (4k)



4k

Compound **4k** was prepared in 72% yield according to the general procedure (Table 3, entry 11). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, J = 8.4 Hz), 7.27 – 7.25 (m, 5H), 7.19 (d, 2H, J = 8.0 Hz), 7.14 (d, 2H, J = 8.0 Hz), 7.01 (d, 2H, J = 8.0 Hz), 5.76 (s, 1H), 3.16 (s, 3H), 2.40 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 144.8, 138.4, 135.6, 135.2, 133.8, 129.6, 129.5, 128.8, 128.6, 128.1, 127.6, 57.4, 33.4, 21.5, 21.1; IR (neat): 2923, 1694 (s), 1493, 1359, 1168, 1071, 813, 665, 548; MS (ESI, m/z) 448 (M + Na^+); HRESIMS Calcd for $[C_{23}H_{23}NNaO_3S_2]^+$ (M + Na^+) 448.1012, found 448.1014.

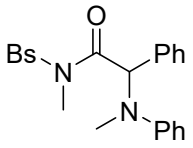
2-((4-methoxyphenyl)thio)-_N_-methyl-2-phenyl-_N_-tosylacetamide (4l)



4l

Compound **4l** was prepared in 75% yield according to the general procedure (Table 3, entry 12). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, 2H, *J* = 8.4 Hz), 7.26 – 7.16 (m, 9H), 6.73 (d, 2H, *J* = 8.4 Hz), 5.67 (s, 1H), 3.78 (s, 3H), 3.15 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 160.2, 144.8, 136.6, 135.6, 135.3, 129.7, 128.8, 128.5, 128.1, 127.6, 123.5, 114.4, 58.0, 55.2, 33.4, 21.6; IR (neat): 2955, 1694 (s), 1592, 1494, 1359, 1171, 813, 665, 548; MS (ESI, m/z) 464 (M + Na^+); HRESIMS Calcd for $[C_{23}H_{23}NNaO_4S_2]^+$ (M + Na^+) 464.0961, found 464.0961.

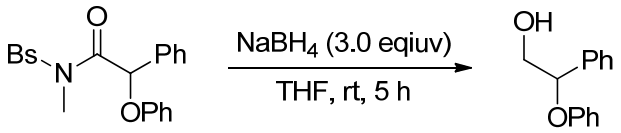
_N_-((4-bromophenyl)sulfonyl)-_N_-methyl-2-(methyl(phenyl)amino)-2-phenylaceta mide (5)



5

Compound **5** was prepared in 58% yield according to the general procedure except using 2-bromopyridine *N*-oxide as oxidant (eq 1). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 4H), 7.37 – 7.32 (m, 3H), 7.26 – 7.21 (m, 2H), 7.13 – 7.11 (m, 2H), 6.82 – 6.75 (m, 3H), 6.27 (s, 1H), 3.27 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 149.3, 137.4, 134.6, 132.2, 129.4, 129.3, 129.1, 129.0, 128.9, 128.5, 118.2, 113.2, 65.7, 34.5, 33.1; IR (neat): 2923, 1705 (s), 1598, 1504, 1360, 1172, 1069, 747, 611; MS (ESI, m/z) 495 (M + Na^+); HRESIMS Calcd for $[C_{22}H_{21}BrN_2NaO_3S]^+$ (M + Na^+) 495.0348, found 495.0353.

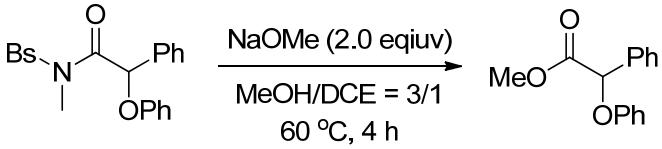
2-phenoxy-2-phenylethanol (6a)



2c 76% yield **6a**

Compound **6a** was prepared in 76% yield according to the known procedure.[4] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 7.21 – 7.17 (m, 2H), 6.91 – 6.86 (m, 3H), 5.28 – 5.25 (m, 1H), 3.95 – 3.81 (m, 2H), 2.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 137.8, 129.4, 128.7, 128.1, 126.3, 121.2, 115.9, 81.1, 67.5; IR (neat): 3400 (br), 2921, 1494, 1453, 1240, 1042, 750, 693; MS (ESI, m/z) 237 (M + Na^+); HRESIMS Calcd for $[C_{14}H_{14}NaO_2]^+$ (M + Na^+) 237.0886, found 237.0883.

methyl 2-phenoxy-2-phenylacetate (6b)



2c 80% yield **6b**

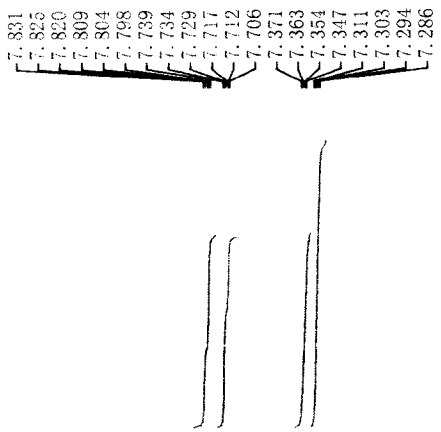
Compound **6b** was prepared in 80% yield according to the known procedure.[4] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.39 – 7.33 (m, 3H), 7.26 – 7.22 (m, 2H), 6.97 – 6.93 (m, 3H), 5.64 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 157.2, 135.4, 129.5, 128.9, 128.8, 127.0, 121.8, 115.4, 78.6, 52.6; IR (neat): 3033, 2953, 1759 (s), 1597, 1495, 1235, 1061, 754, 691; MS (ESI, m/z) 265 (M + Na^+); HRESIMS Calcd for $[C_{15}H_{14}NaO_3]^+$ (M + Na^+) 265.0835, found 265.0836.

Reference:

1. Li, L.; Shu, C.; Zhou, B.; Yu, Y.-F.; Xiao, X.-Y.; Ye, L.-W. *Chem. Sci.* **2014**, *5*, 4057.
2. Zhou, A.-H.; He, Q.; Shu, C.; Yu, Y.-F.; Liu, S.; Zhao, T.; Zhang, W.; Lu, X.; Ye,

L.-W. *Chem. Sci*. **2015**, *6*, 1265.

3. Yao, B.-B.; Liang, Z.-J.; Niu, T.-M.; Zhang, Y.-H. *J. Org. Chem.* **2009**, *74*, 4630.
4. Li, L.; Zhou, B.; Ye, L.-W. *Chin. J. Org. Chem.* **2015**, *35*, 655.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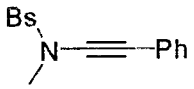
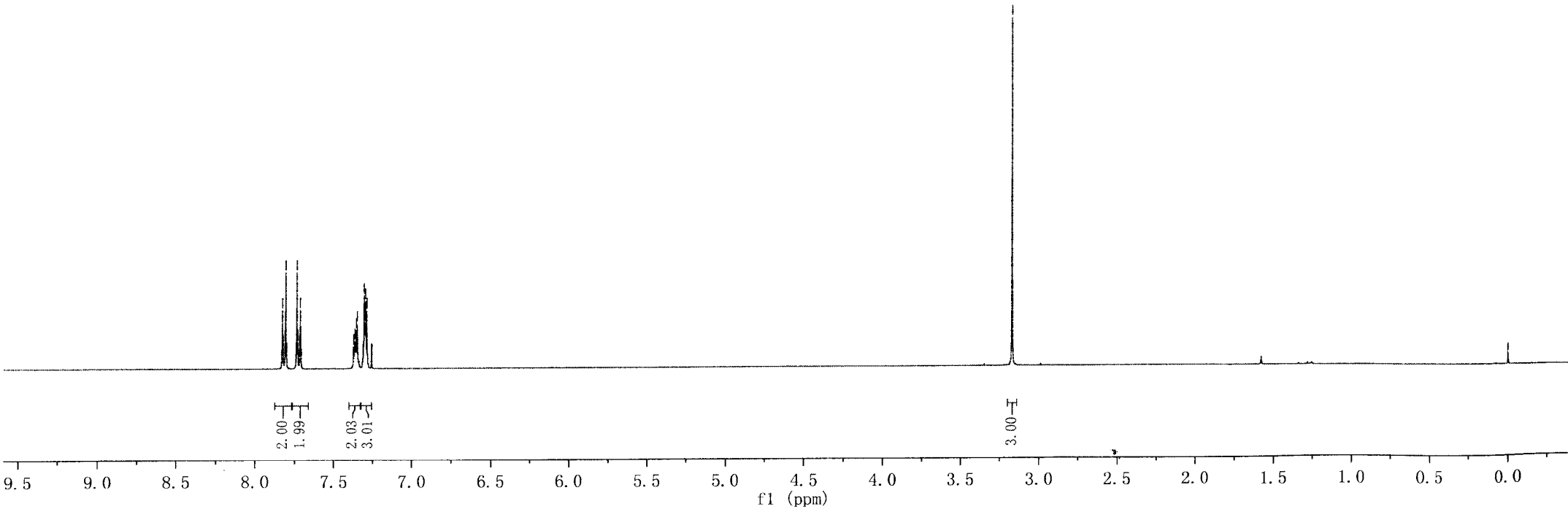
7.371
7.363
7.354
7.347
7.311
7.303
7.294
7.286


3.170


Bs
N
Ph

1c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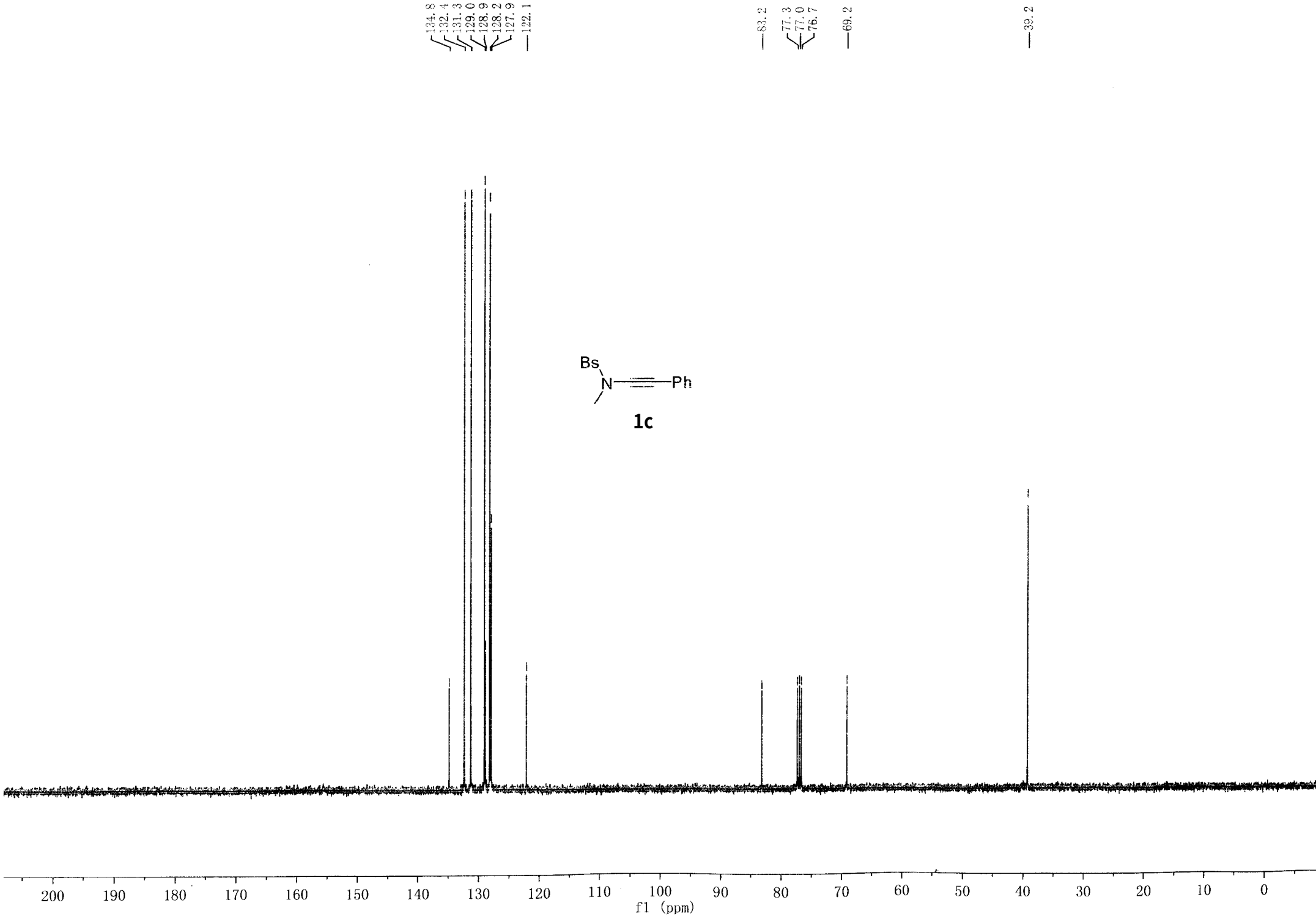
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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39.2
Bs
N
Ph
1c
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190
180
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90
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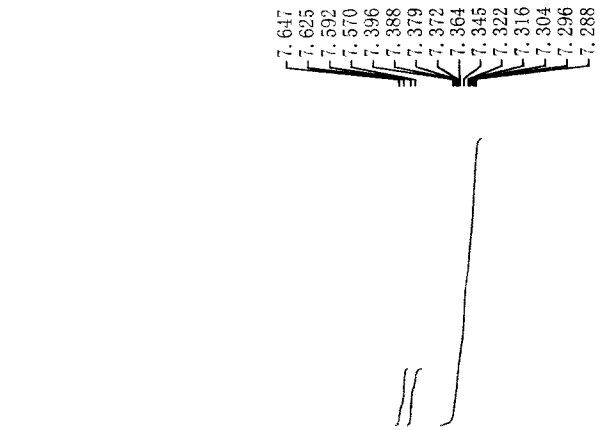
f1 (ppm)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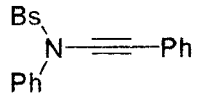
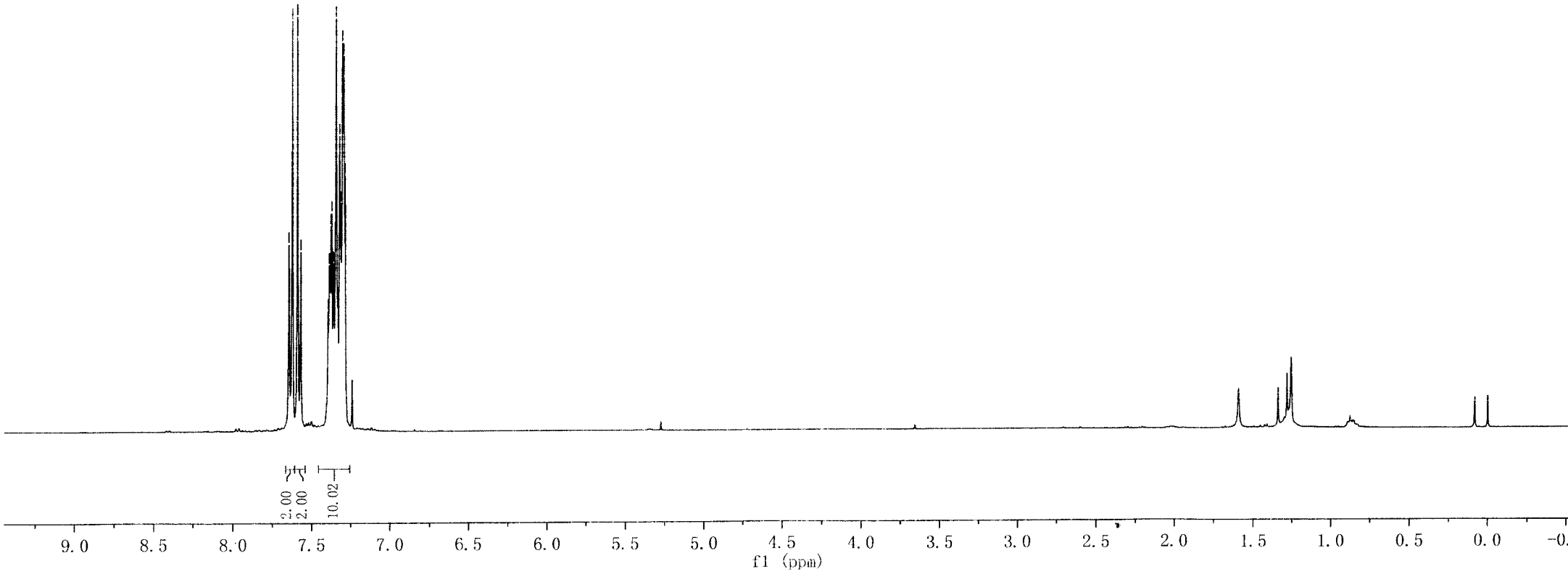
7.296
7.288


Bs
N
Ph
Ph

1d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1.0
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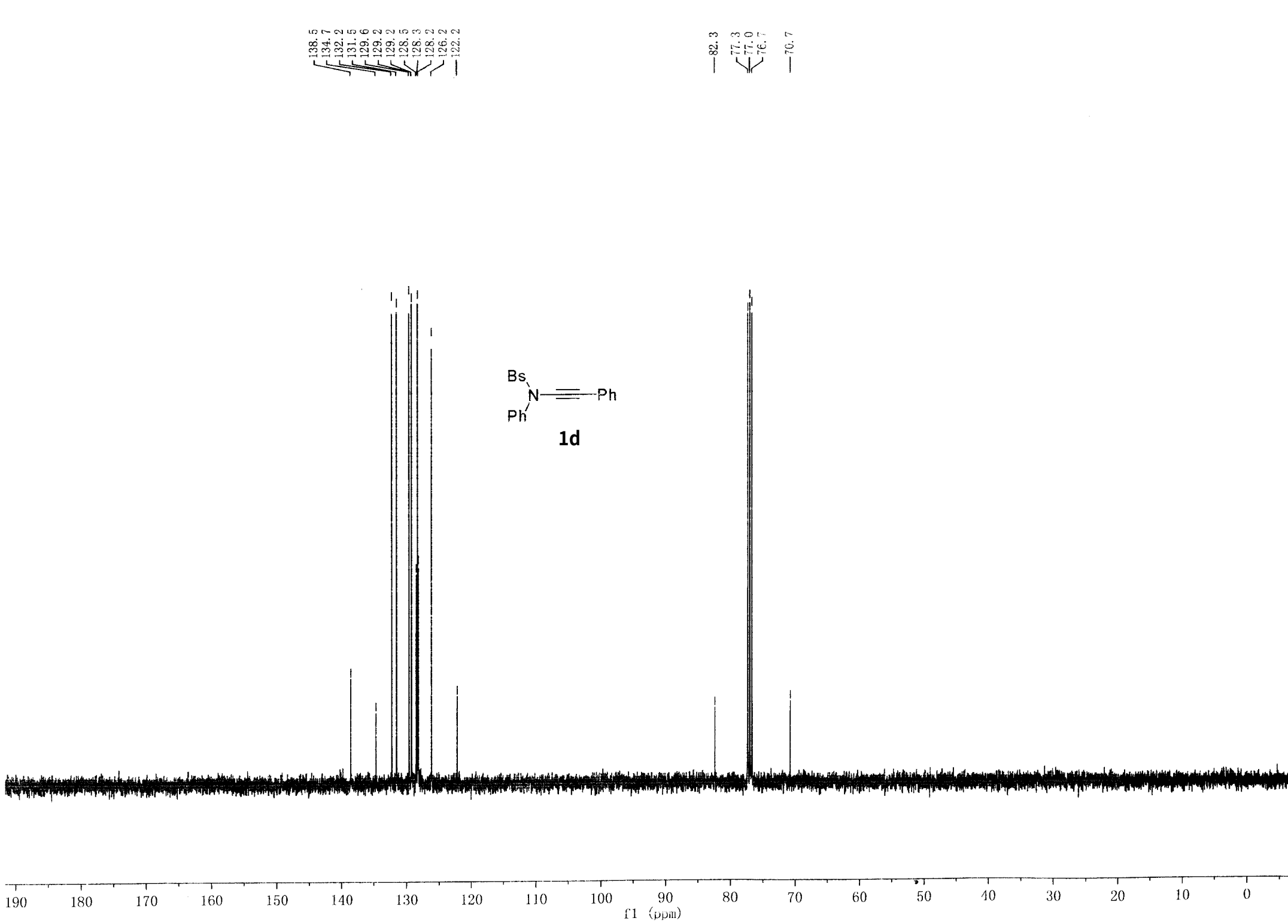
f1 (ppm)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128.2
126.2
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77.3
77.0
76.7
70.7
Bs
N
Ph
Ph
1d
190
180
170
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130
120
110
100
90
80
70
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50
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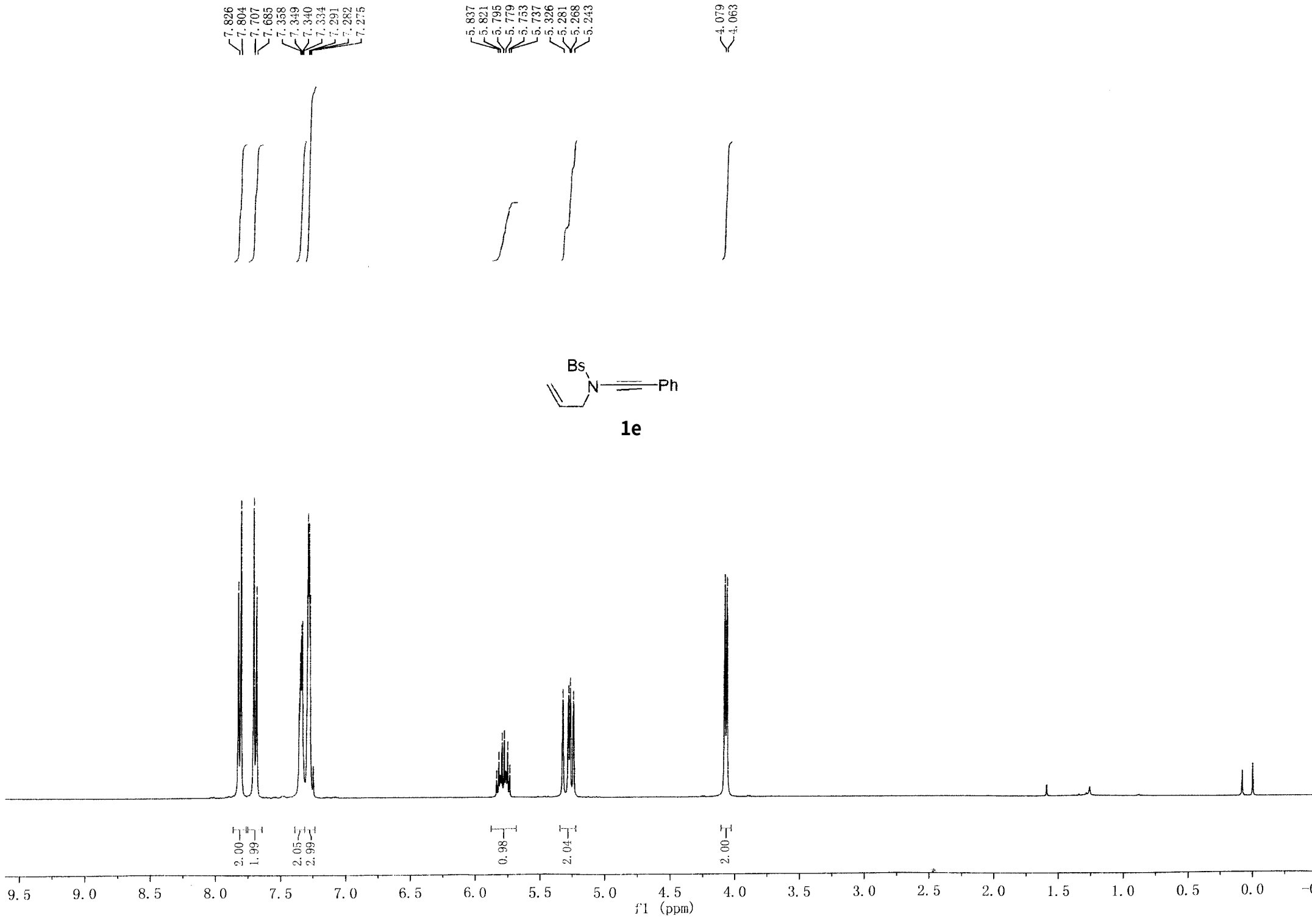
10
0
f1 (ppm)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5.821
5.795
5.779
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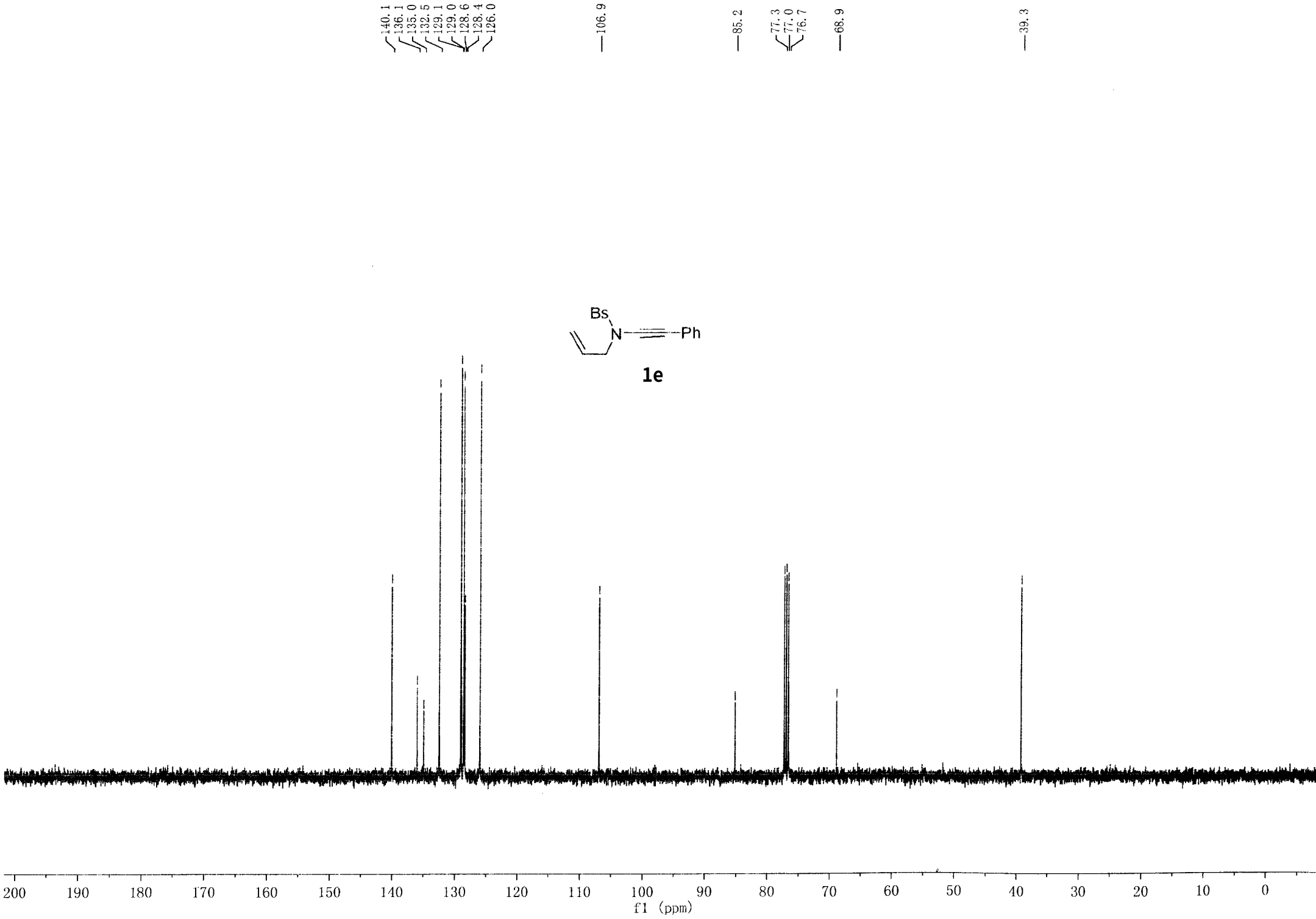
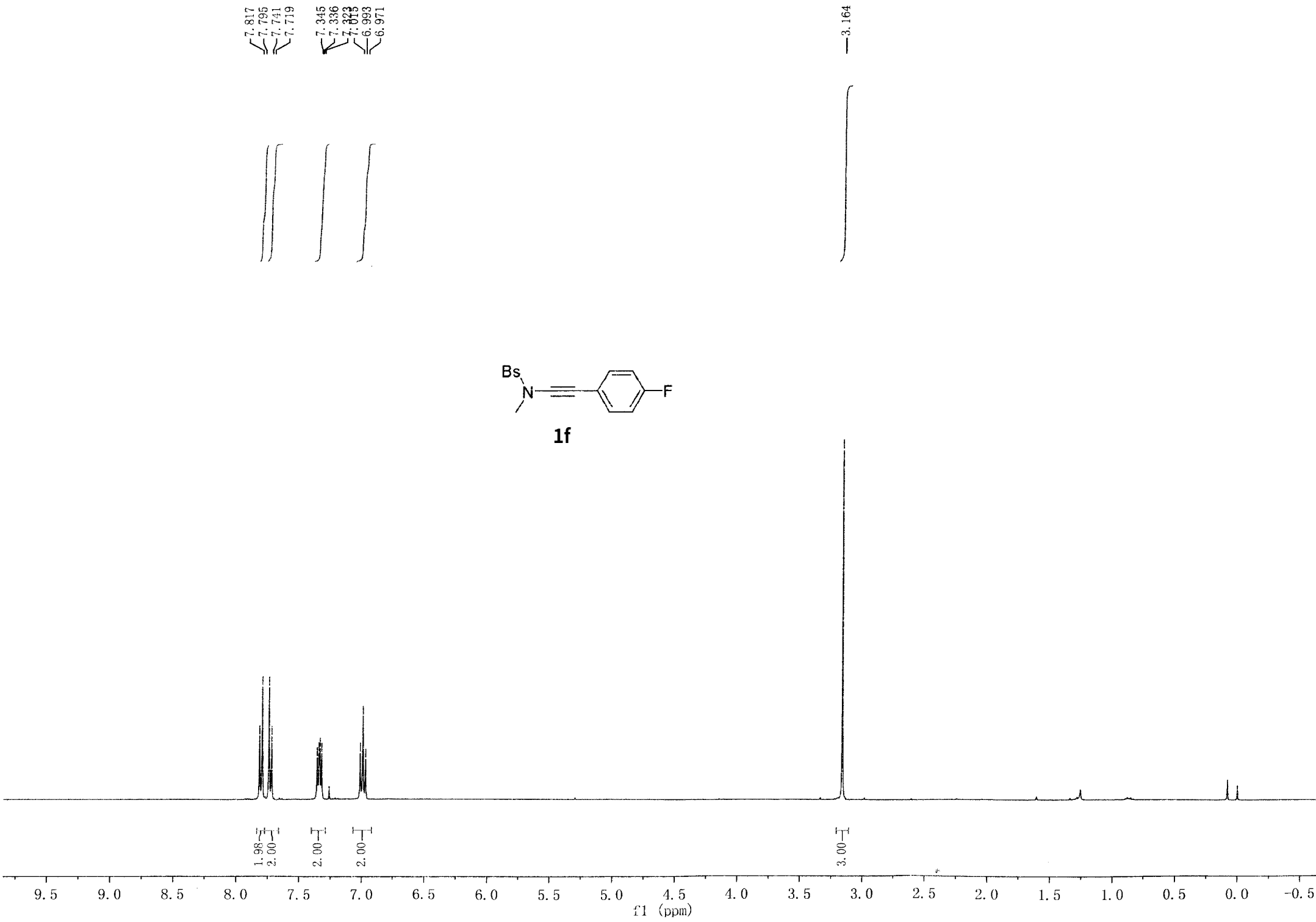
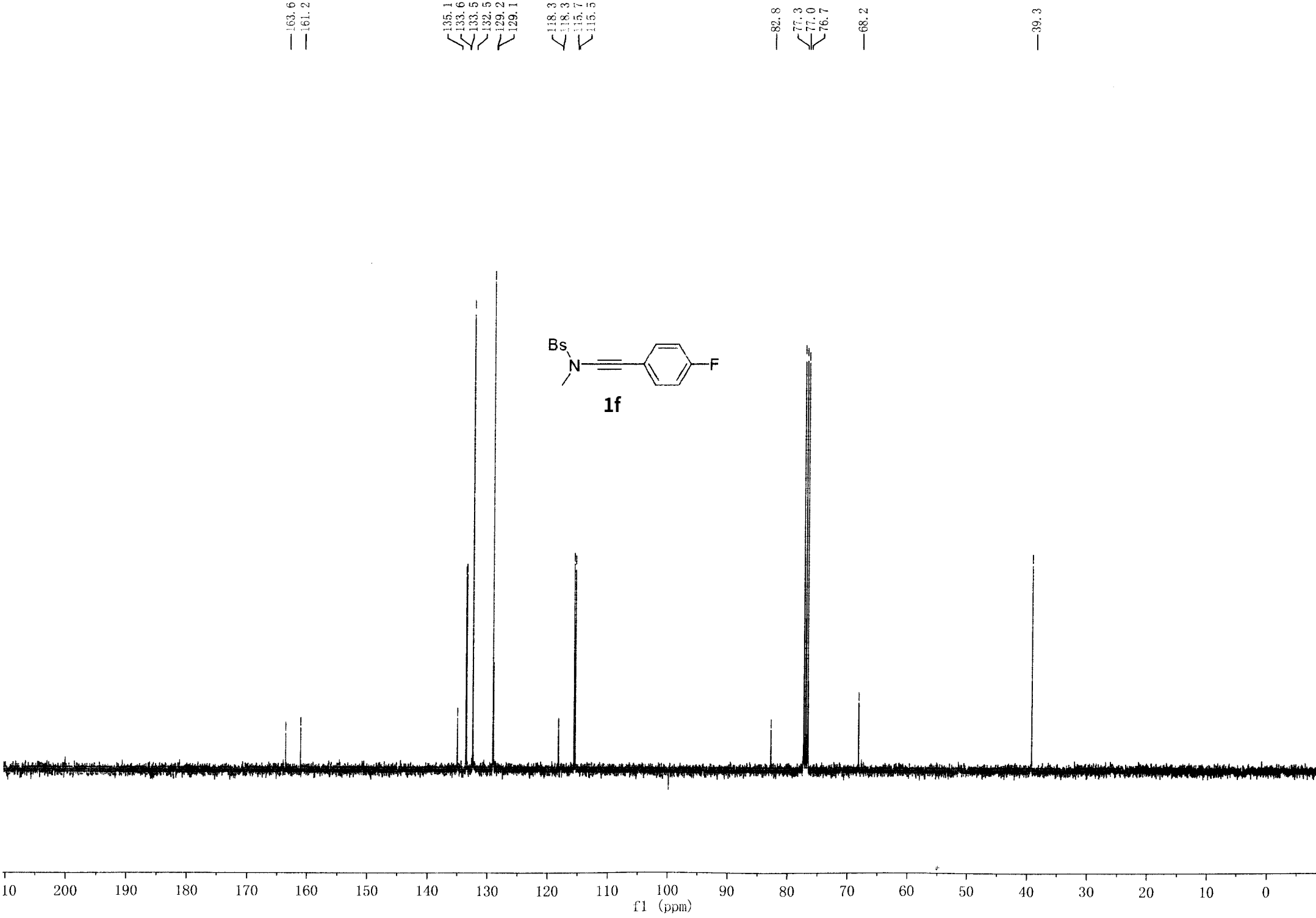
5.737
5.326
5.281
5.268
5.243
4.079
4.063
Bs
N
Ph
1e
2.00
1.99
2.05
2.99
0.98
2.04
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.1
136.1
135.0
132.5
129.1
129.0
128.6
128.4
126.0
106.9
85.2
77.3
77.0
76.7
68.9
39.3
Bs
N
Ph
1e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.817
7.795
7.741
7.719
7.345
7.336
6.993
6.971
3.164
Bs
N
F
1f
1.98
2.00
2.00
2.00
3.00
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)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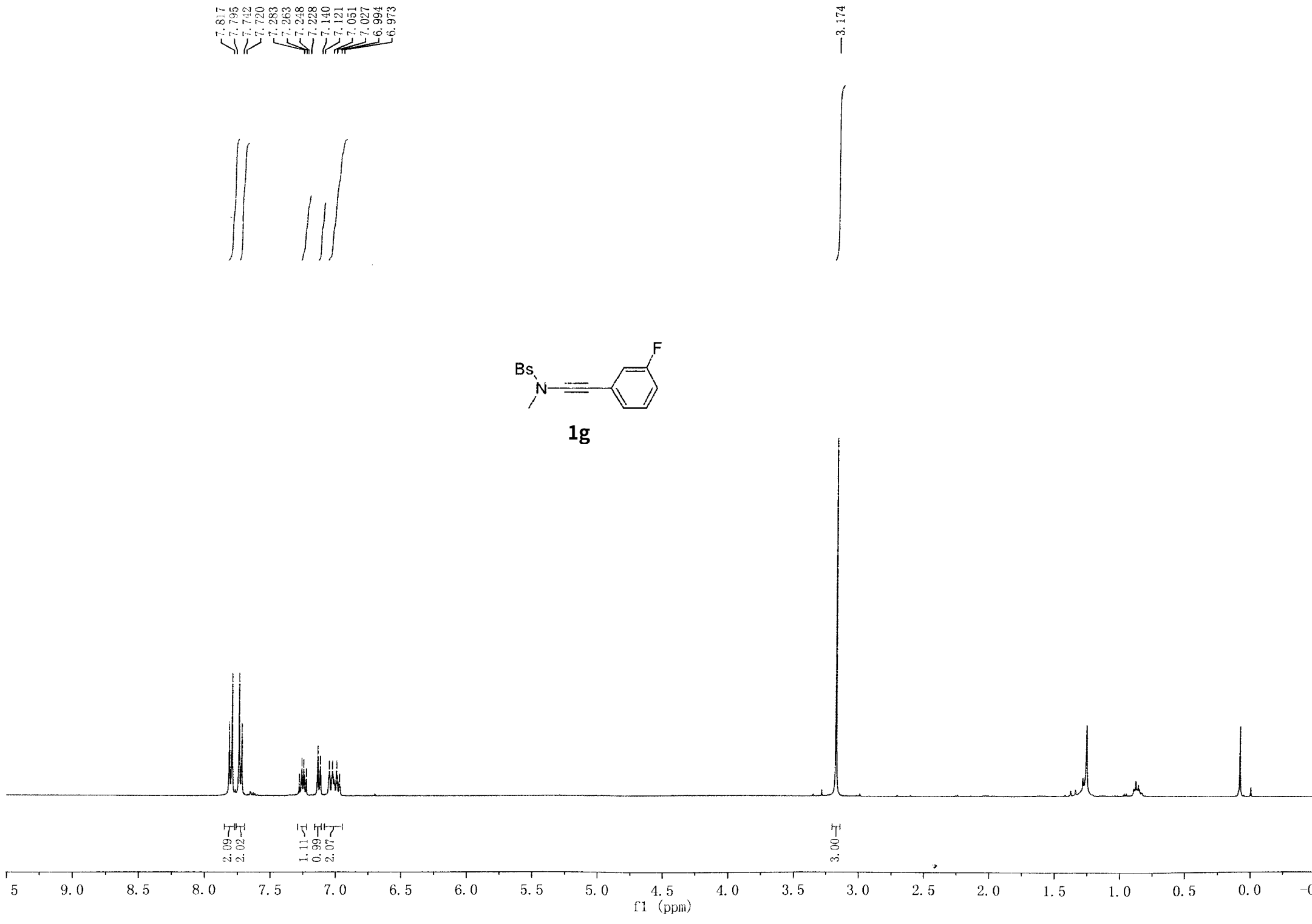
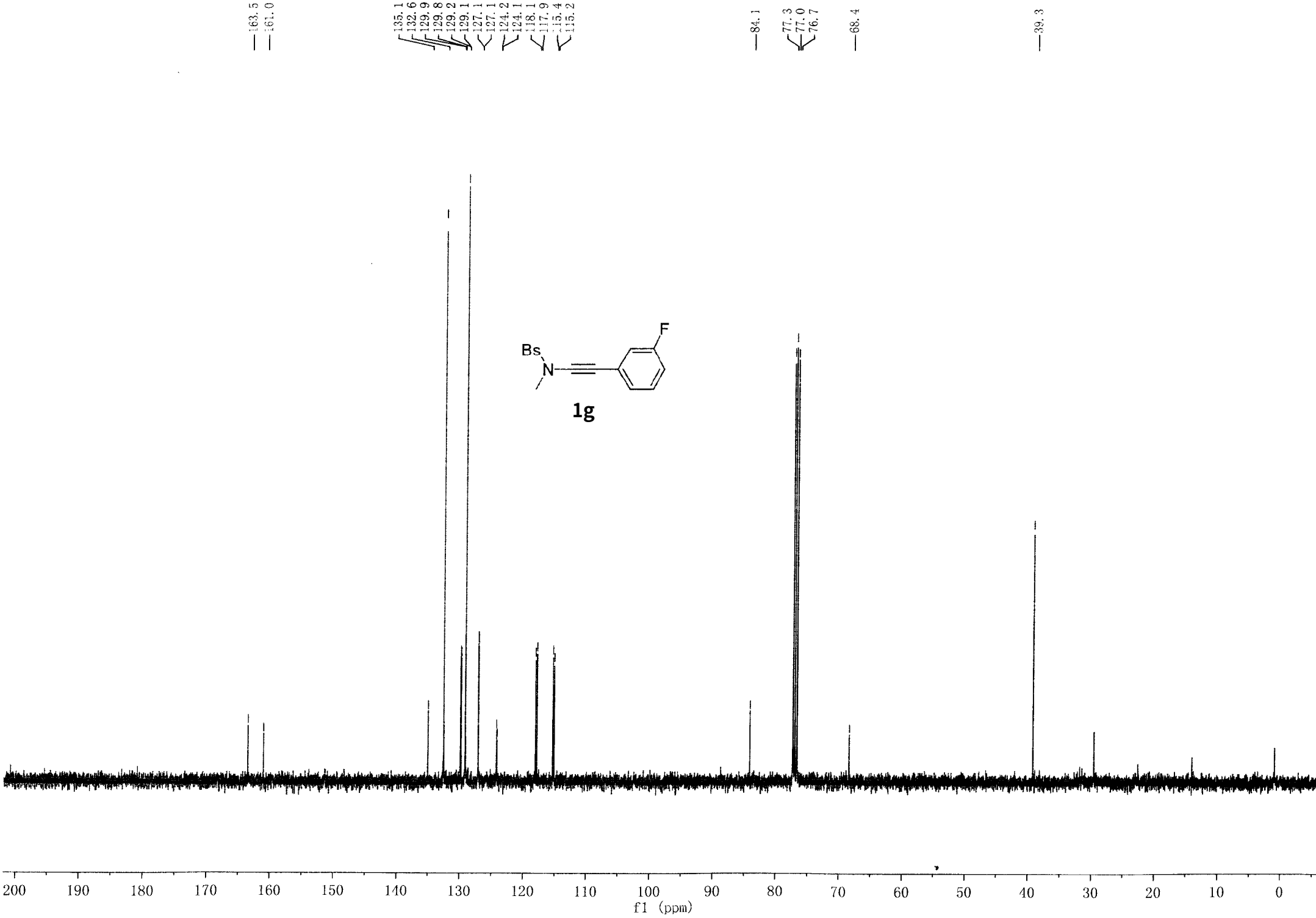
161.2
135.1
133.6
133.5
132.5
129.2
129.1
118.3
118.3
115.7
115.5
82.8
77.3
77.0
76.7
68.2
39.3
Bs
N
F
1f
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.817
7.795
7.742
7.720
7.283
7.263
7.248
7.228
7.140
7.121
7.051
7.027
6.994
6.973
3.174
Bs
N
F
1g
2.09
2.02
1.11
0.99
2.07
3.00
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)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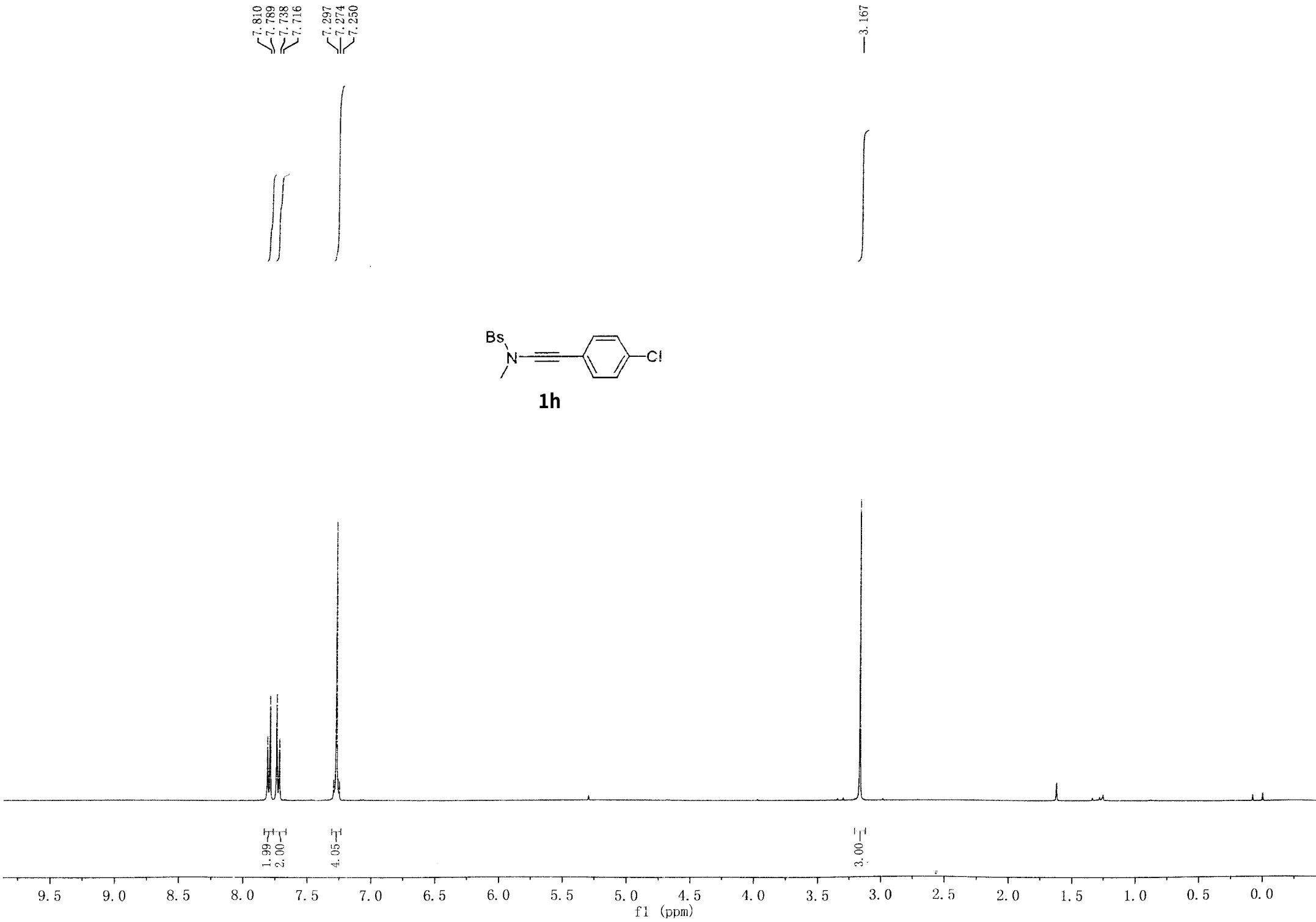
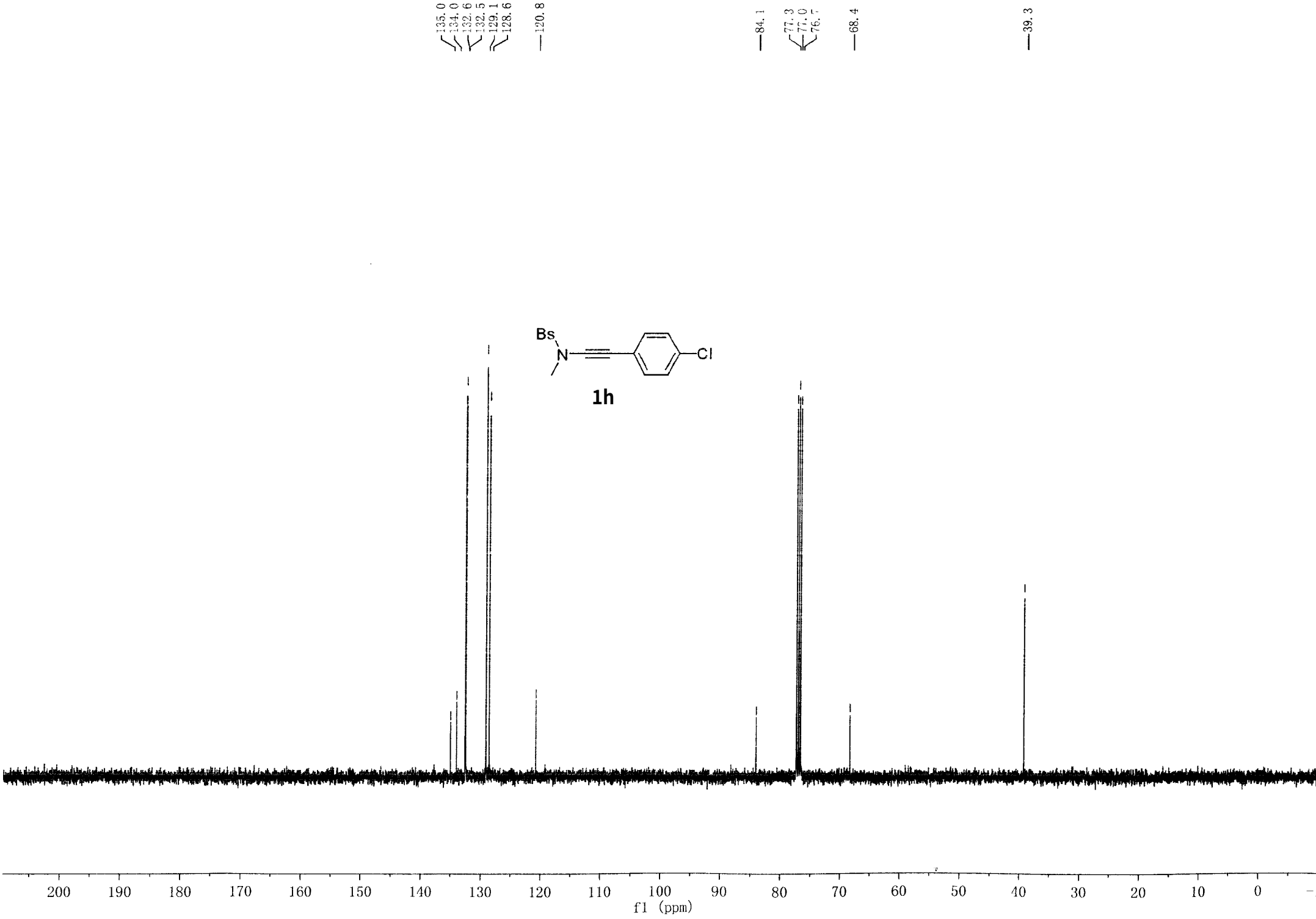
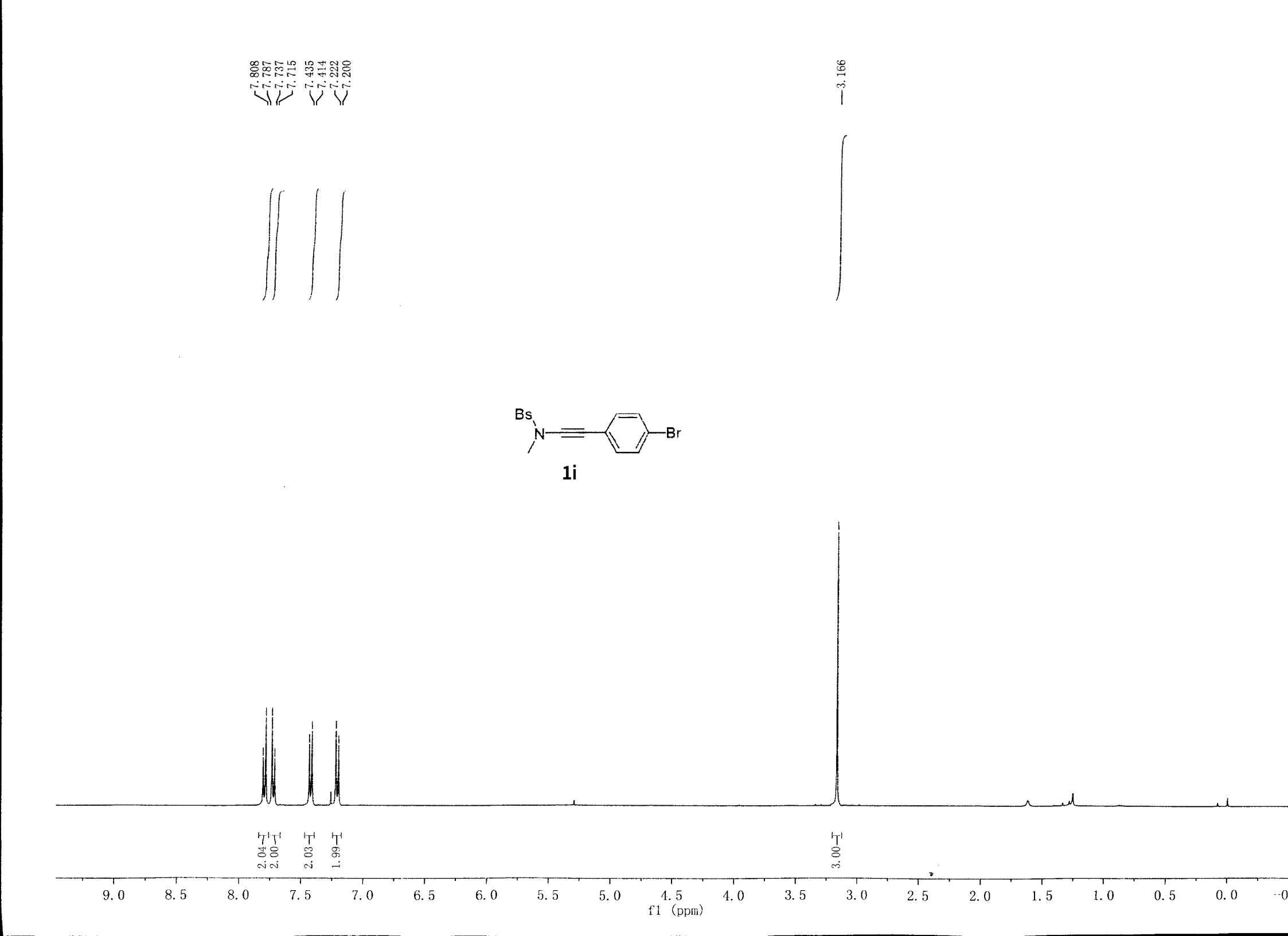
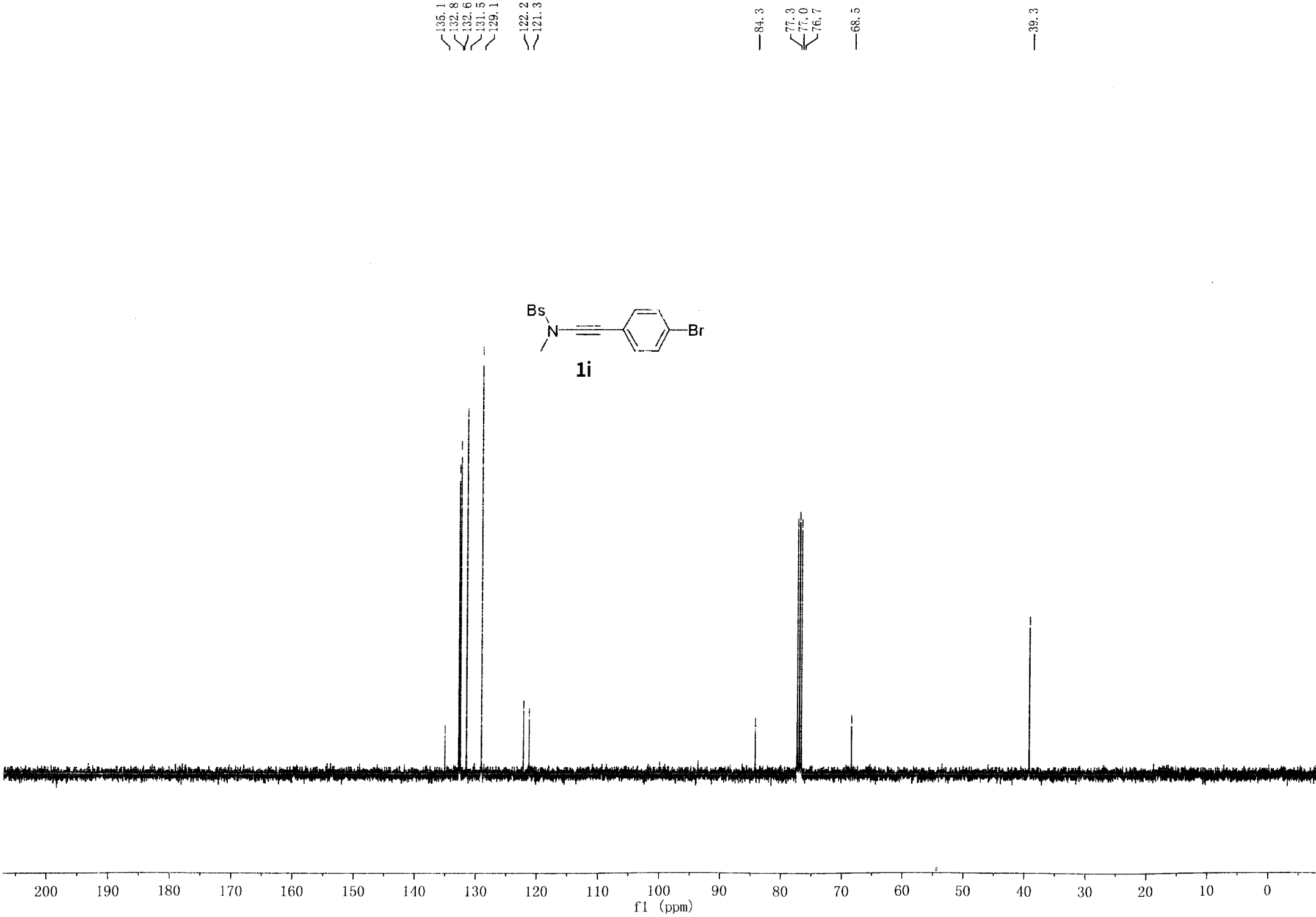
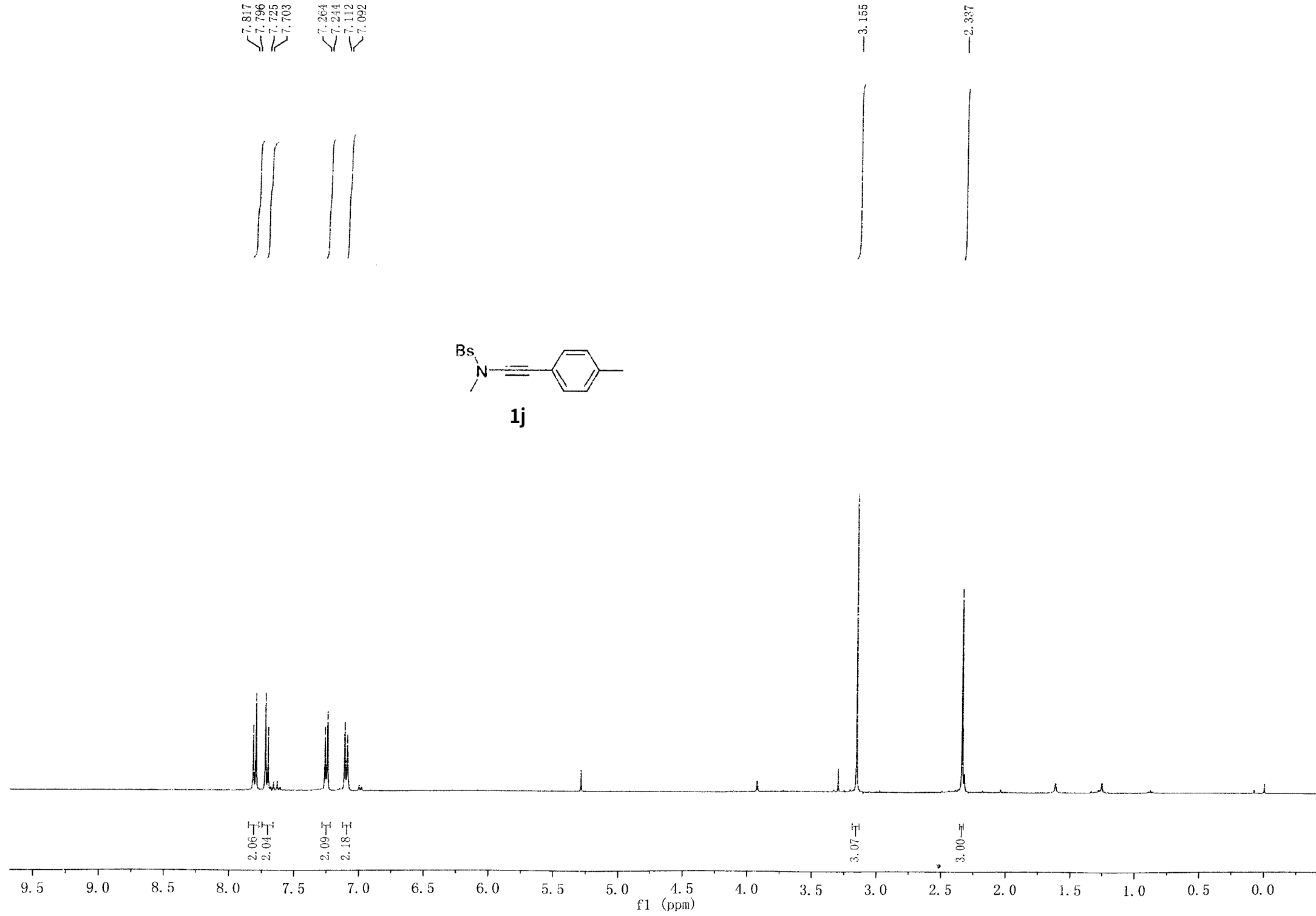
161.0
135.1
132.6
129.9
129.8
129.2
129.1
127.1
127.1
124.2
124.1
118.1
117.9
116.4
116.2
84.1
77.3
77.0
76.7
68.4
39.3
Bs
N
F
1g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.810
7.789
7.738
7.716
7.297
7.274
7.250
3.167
Bs
N
Cl
1h
1.99
2.00
4.05
3.00
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)

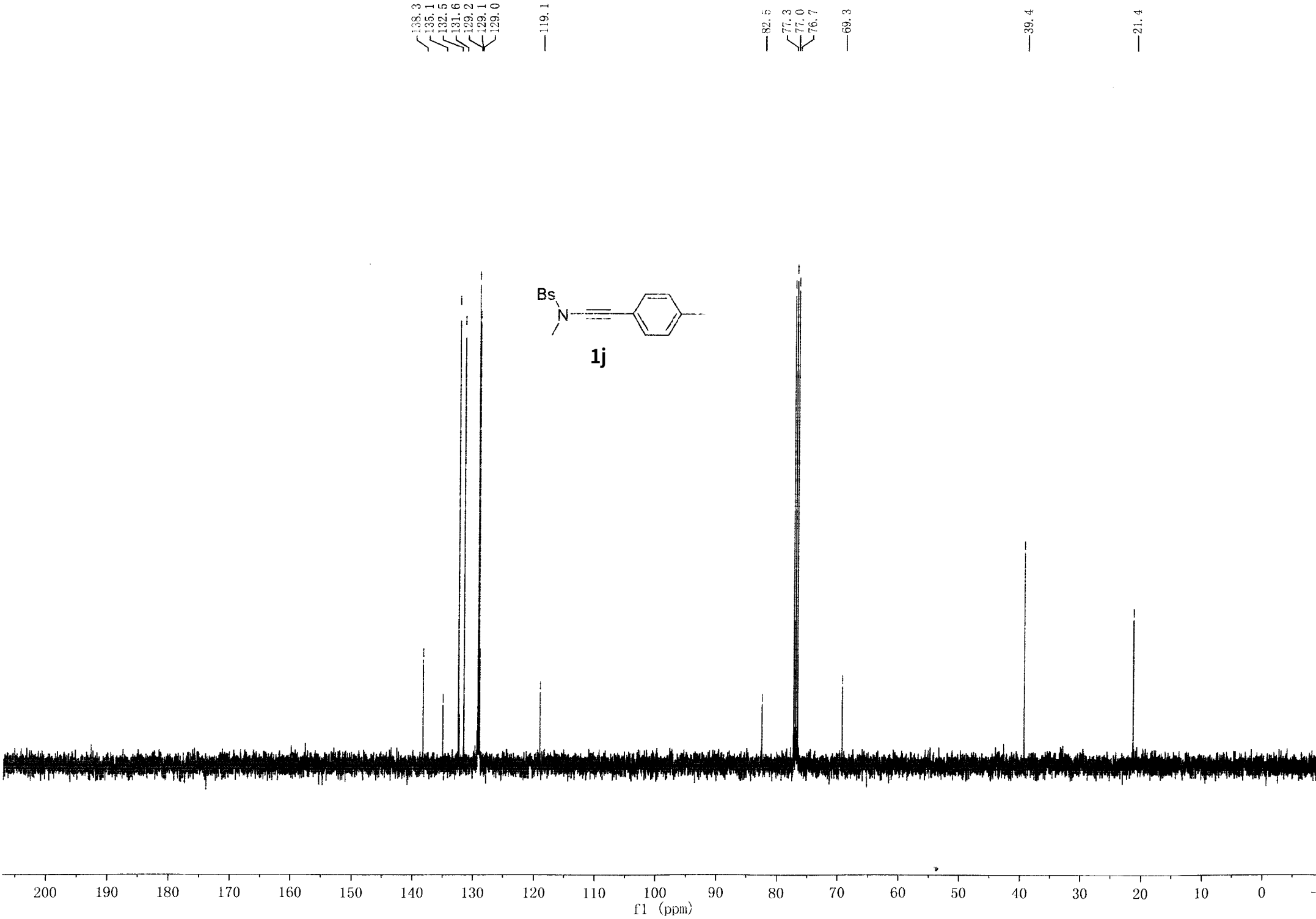

135.0
134.0
132.6
132.5
129.1
128.6
120.8
84.1
77.3
77.0
76.7
68.4
39.3
Bs
N
Cl
1h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

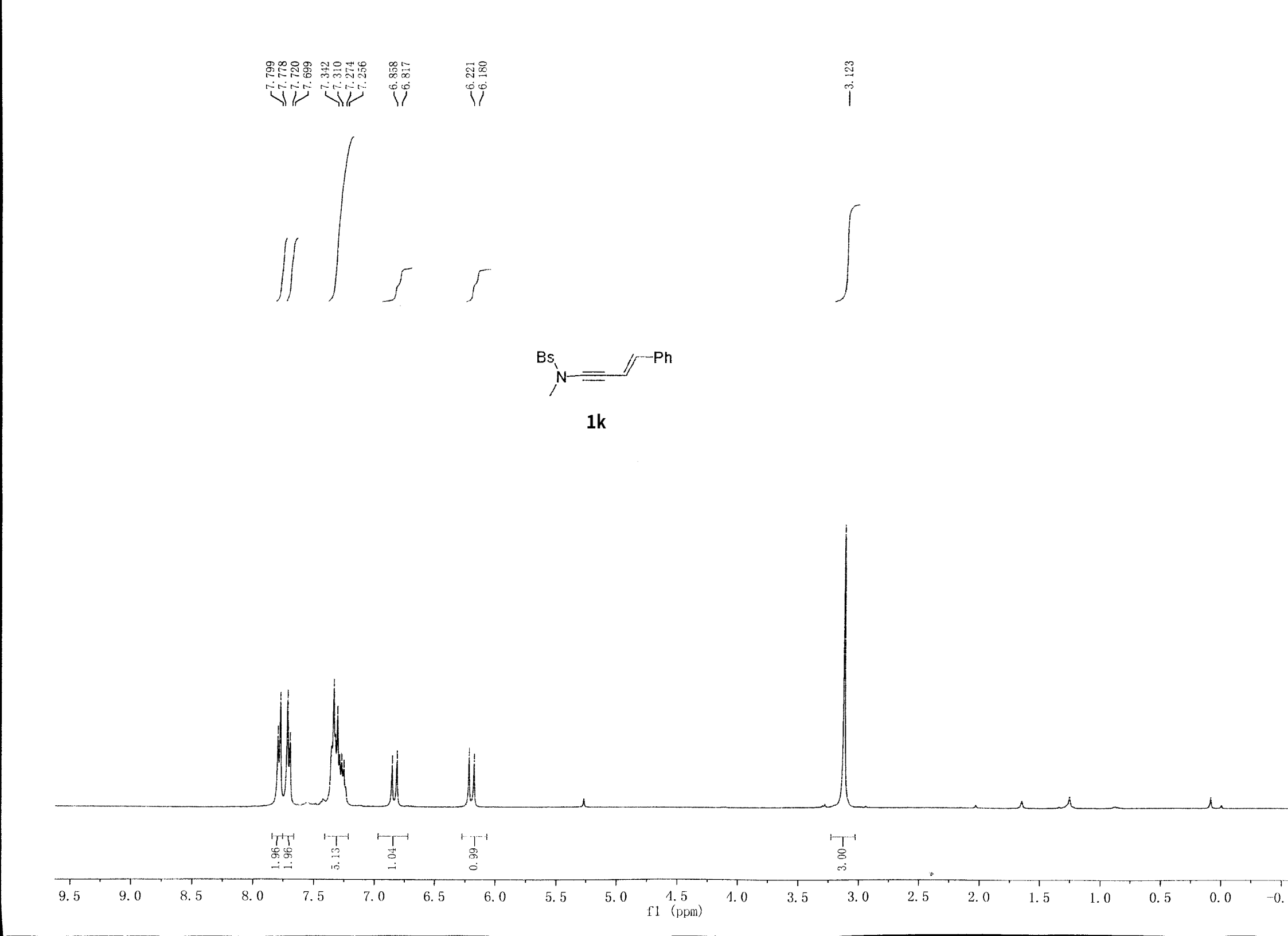

7.808
7.787
7.737
7.715
7.435
7.414
7.222
7.200
3.166
Bs
N
Br
1i
2.04
2.00
2.03
1.99
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


135.1
132.8
132.6
131.5
129.1
122.2
121.3
84.3
77.3
77.0
76.7
68.5
39.3
Bs
N
Br
1i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

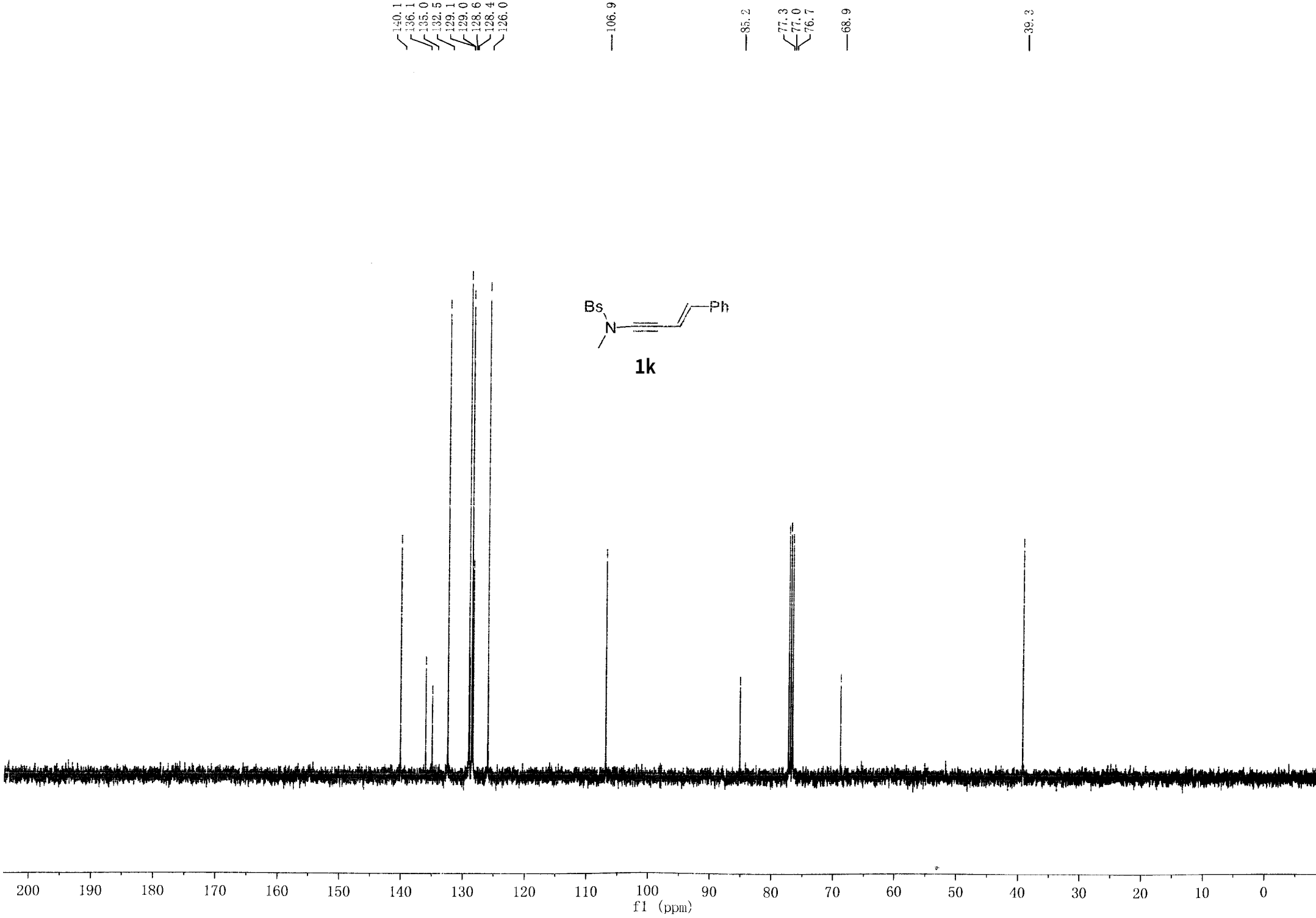

7.817
7.796
7.725
7.703
7.264
7.244
7.112
7.092
3.155
2.337
Bs
N
2.06
2.04
2.09
2.18
3.07
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

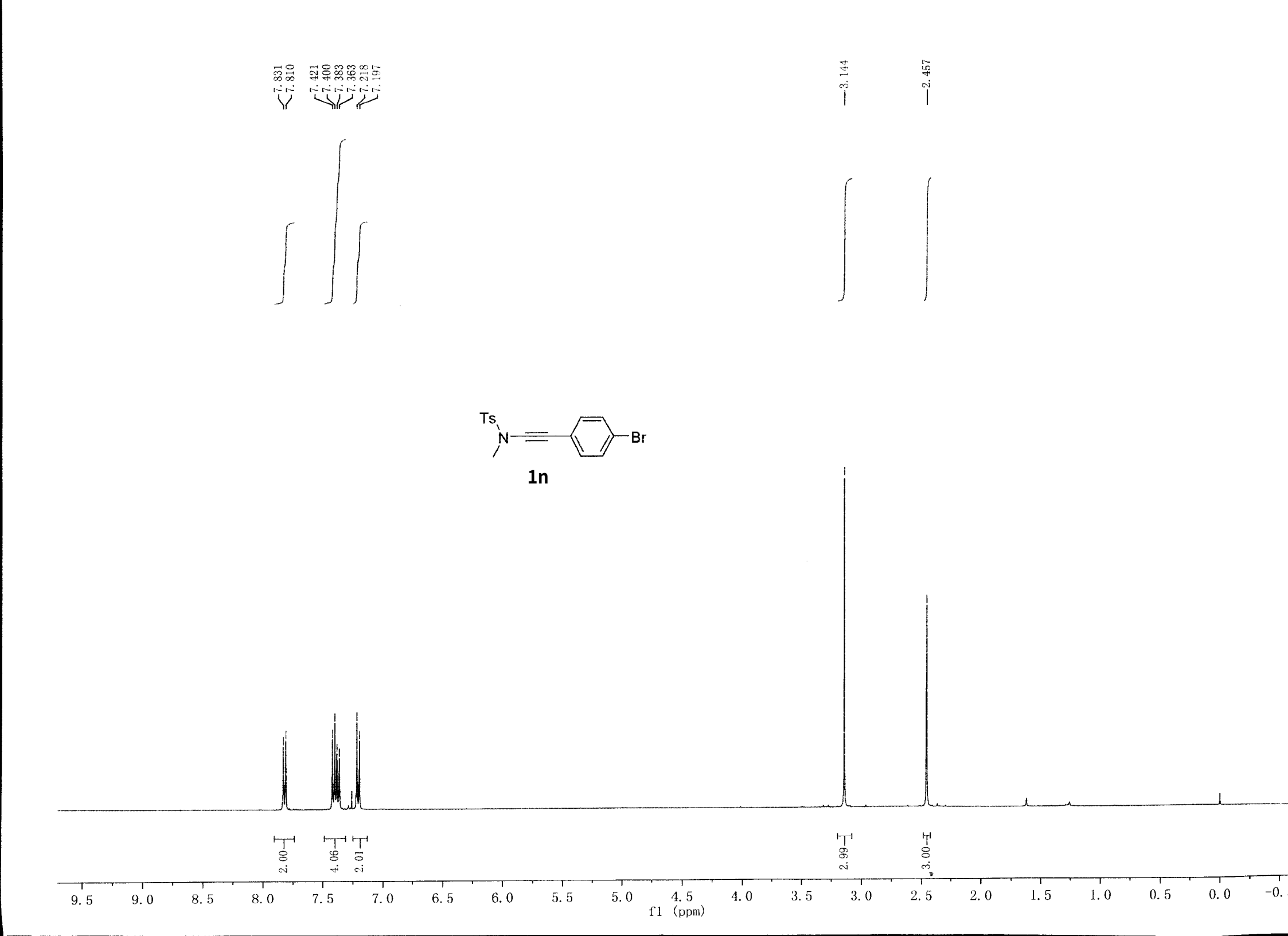
1j

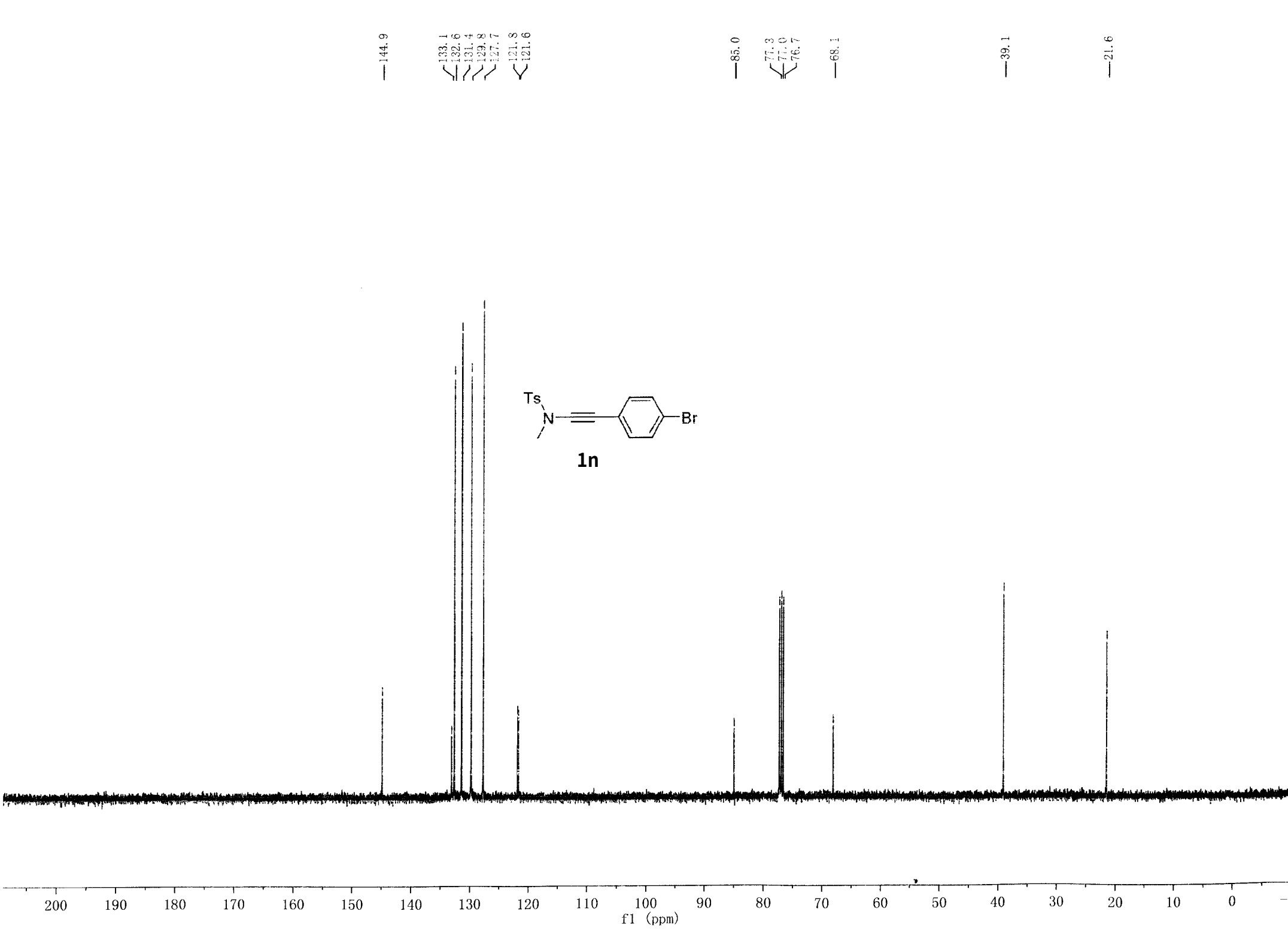

138.3
135.1
132.5
131.6
129.2
129.1
129.0
119.1
82.5
77.3
77.0
76.7
69.3
39.4
21.4
Bs
N
1j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

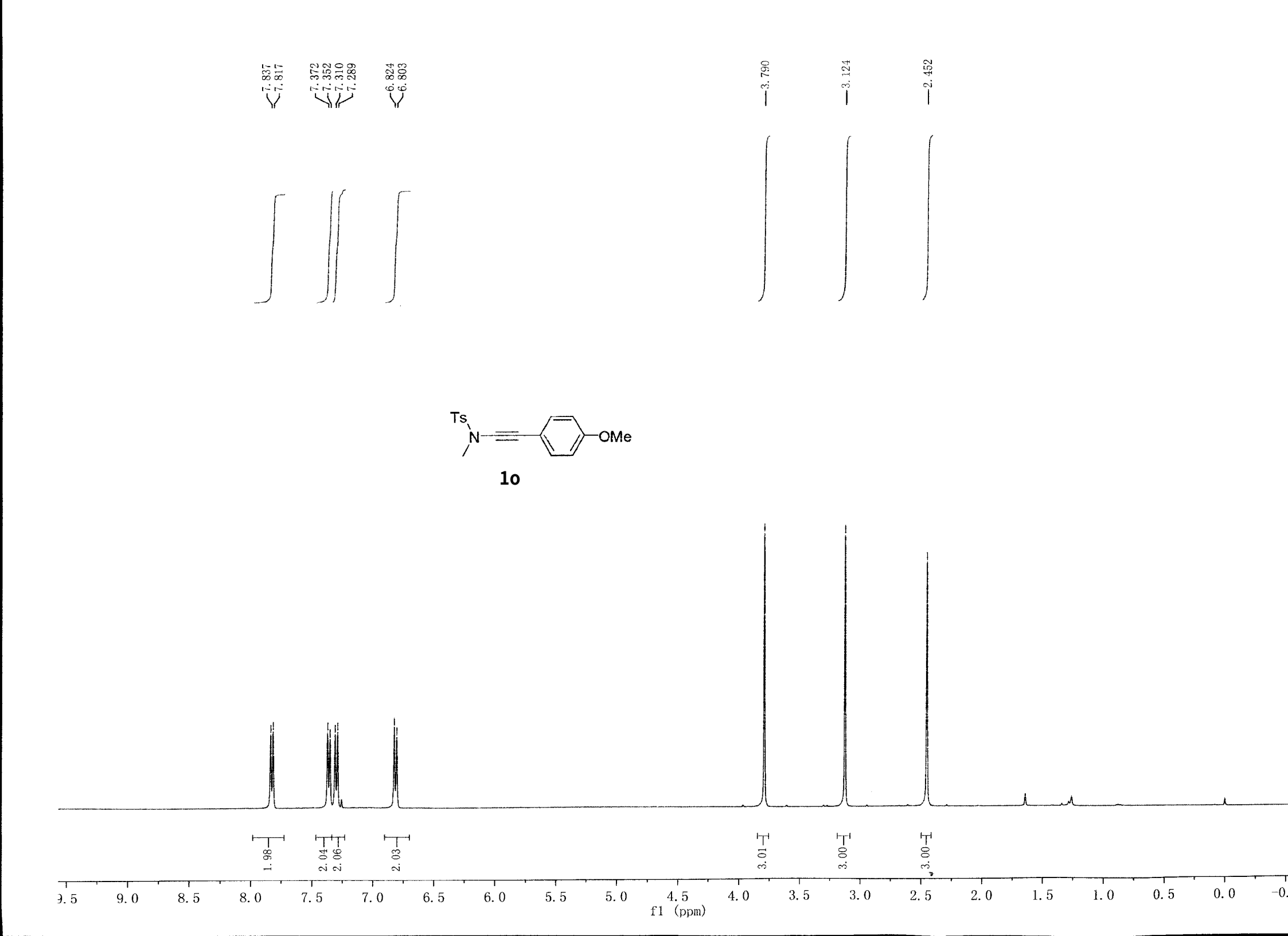

7.799
7.778
7.720
7.699
7.342
7.310
7.274
7.256
6.858
6.817
6.221
6.180
3.123
Bs
N
Ph
1.96
1.96
5.13
1.04
0.99
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

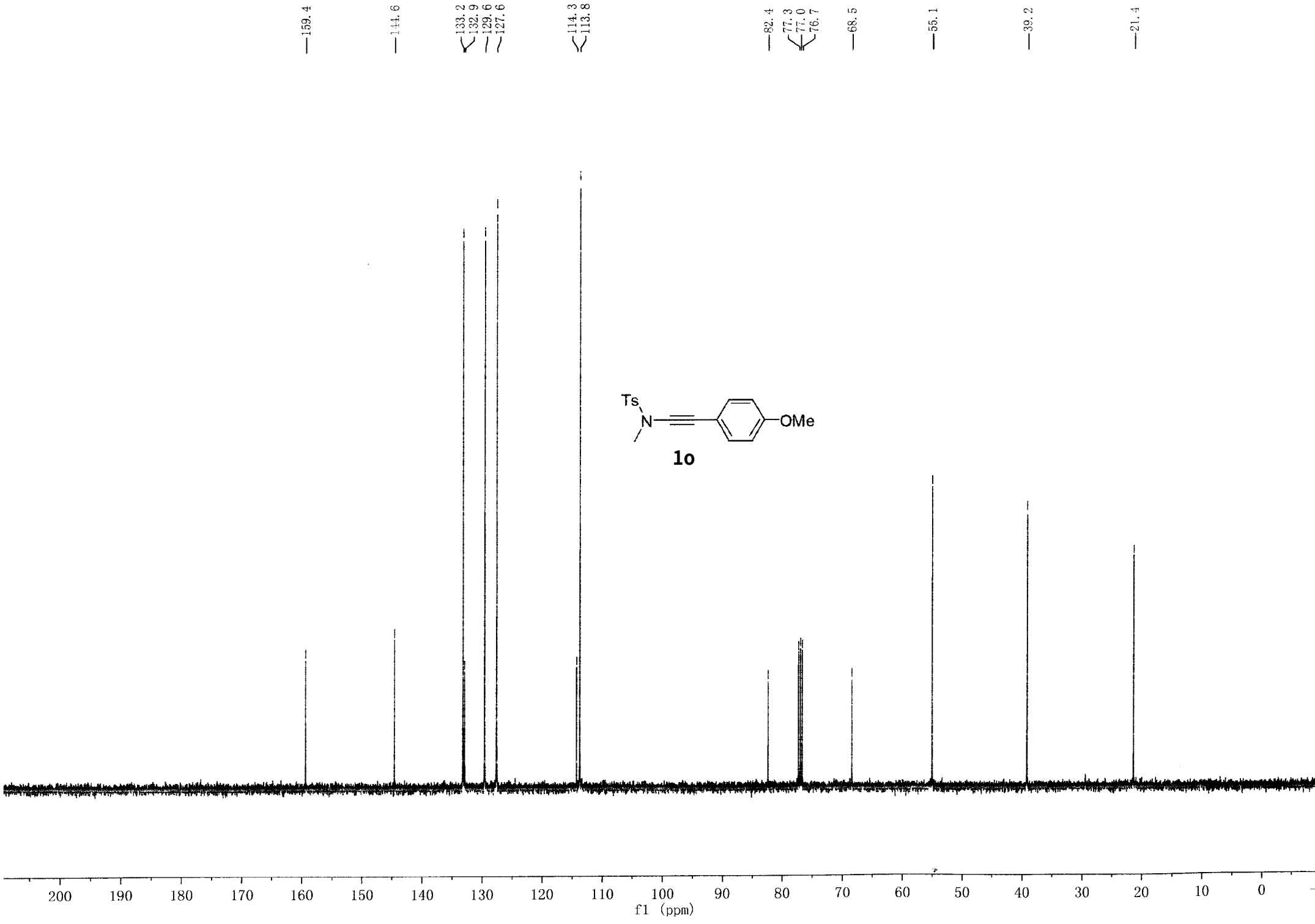
1k

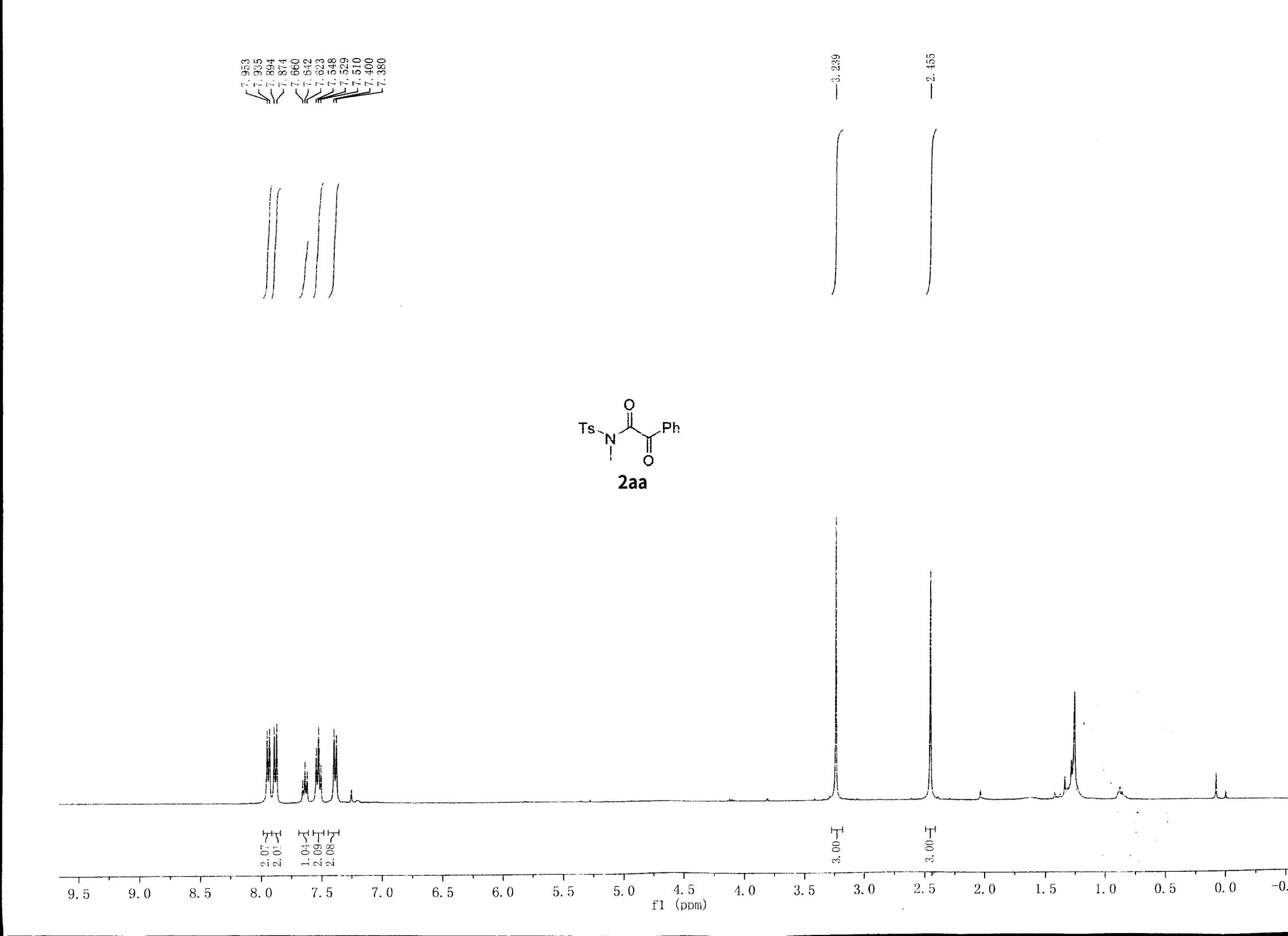

140.1
136.1
135.0
132.5
129.1
129.0
128.6
128.4
126.0
106.9
85.2
77.3
77.0
76.7
68.9
39.3
Bs
N
Ph
1k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

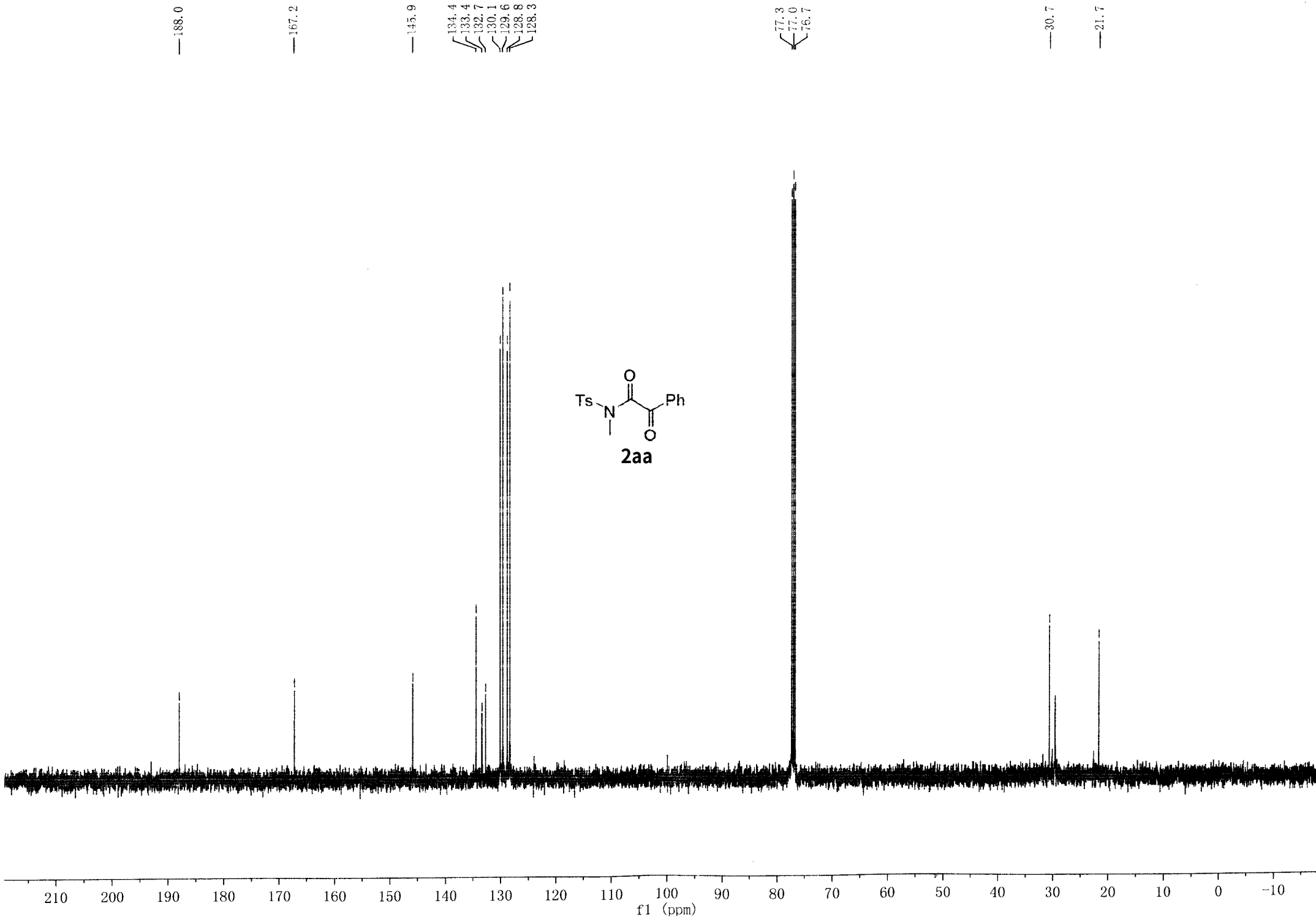

7.831
7.810
7.421
7.400
7.383
7.363
7.218
7.197
3.144
2.457
Ts
N
Br
1n
2.00
4.06
2.01
2.99
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

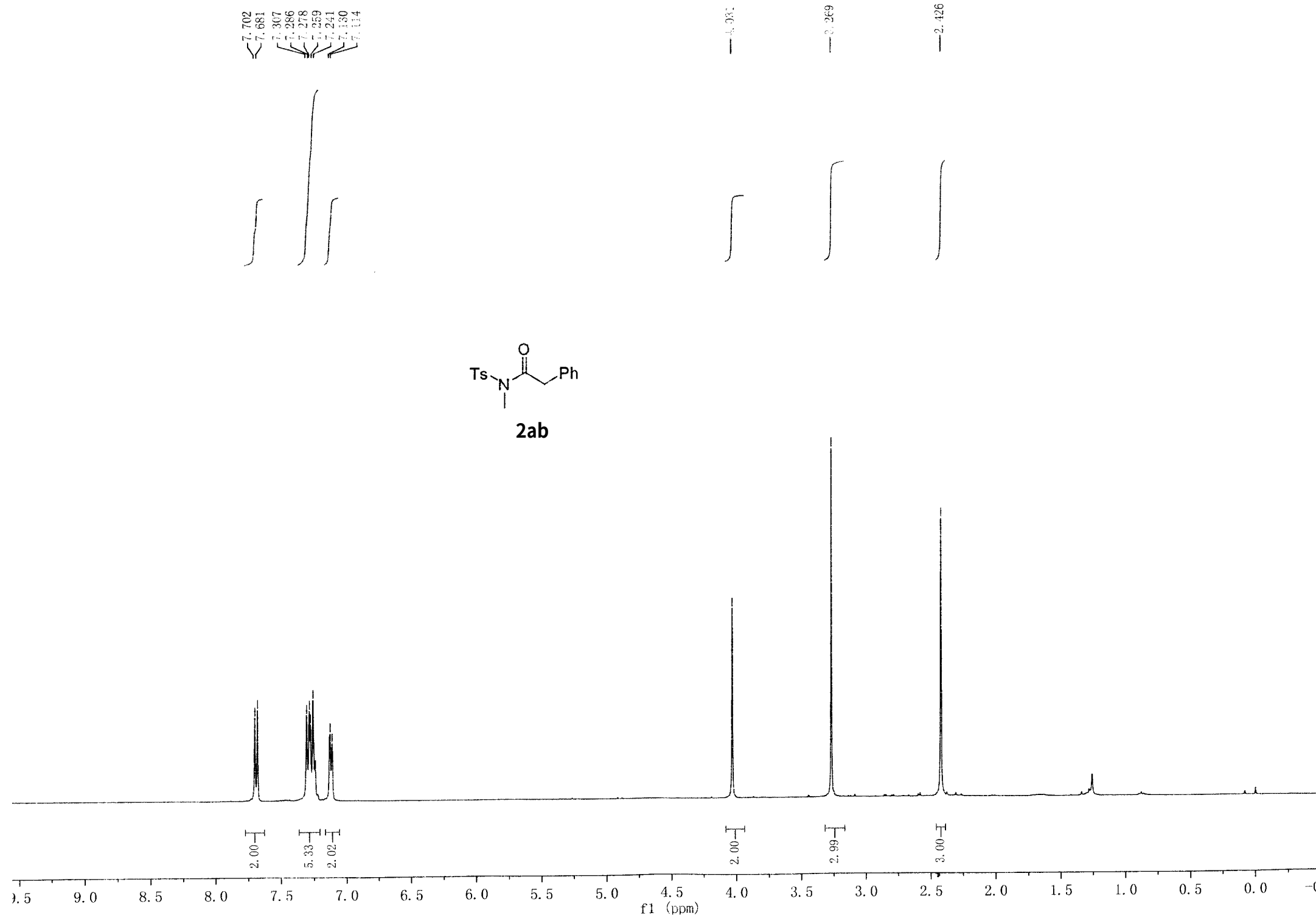

144.9
133.1
132.6
131.4
129.8
127.7
121.8
121.6
85.0
77.3
77.0
76.7
68.1
39.1
21.6
Ts
N
Br
1n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

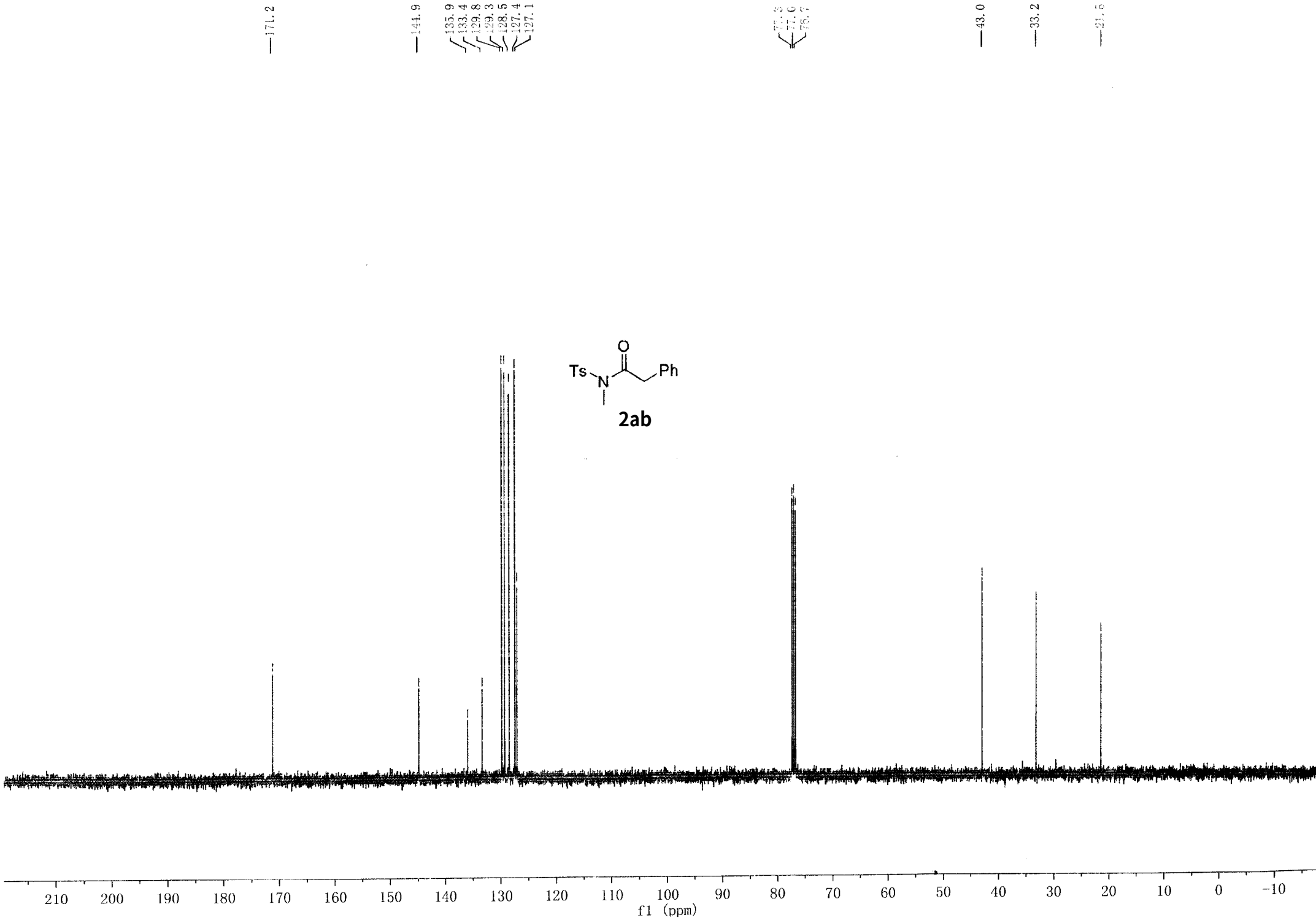

7.837
7.817
7.372
7.352
7.310
7.289
6.824
6.803
3.790
3.124
2.452
Ts
N
OMe
1o
1.98
2.04
2.06
2.03
3.01
3.00
3.00
f1 (ppm)

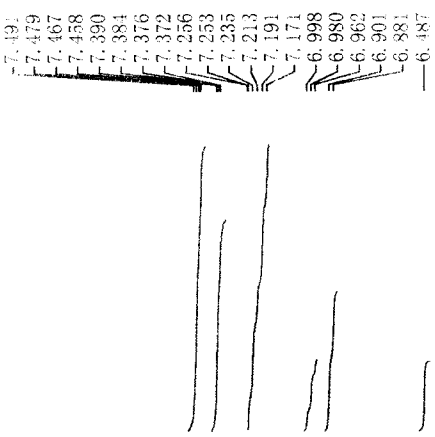

159.4
144.6
133.2
132.9
129.6
127.6
114.3
113.8
82.4
77.3
77.0
76.7
68.5
55.1
39.2
21.4
Ts
N
OMe
1o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.953
7.935
7.894
7.874
7.660
7.642
7.623
7.548
7.529
7.510
7.400
7.380
3.239
2.455
Ts
N
O
O
Ph
2aa
2.07
2.01
1.04
2.09
2.08
3.00
3.00
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)


188.0
167.2
145.9
134.4
133.4
132.7
130.1
129.6
128.8
128.3
77.3
77.0
76.7
30.7
21.7
Ts
N
O
O
Ph
2aa
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)


7.702
7.681
7.307
7.286
7.278
7.259
7.241
7.130
7.114
2.426
Ts
N
O
Ph
2ab
2.00
5.33
2.02
2.00
2.99
3.00
f1 (ppm)


171.2
144.9
135.9
133.4
129.8
129.3
128.5
127.4
127.1
77.3
77.0
76.7
43.0
33.2
21.5
Ts
N
O
Ph
2ab
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)


7.491
7.479
7.467
7.458
7.390
7.384
7.376
7.372
7.256
7.253
7.235
7.213
7.191
7.171
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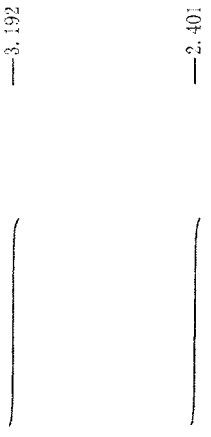
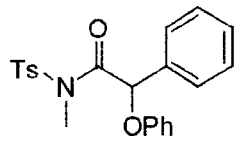
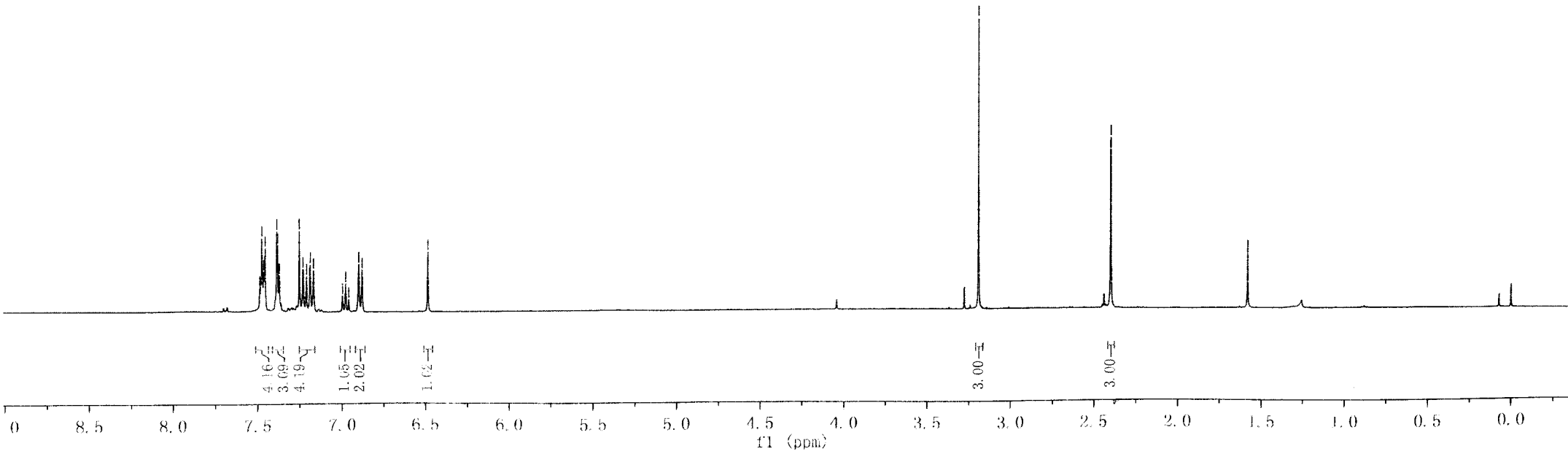
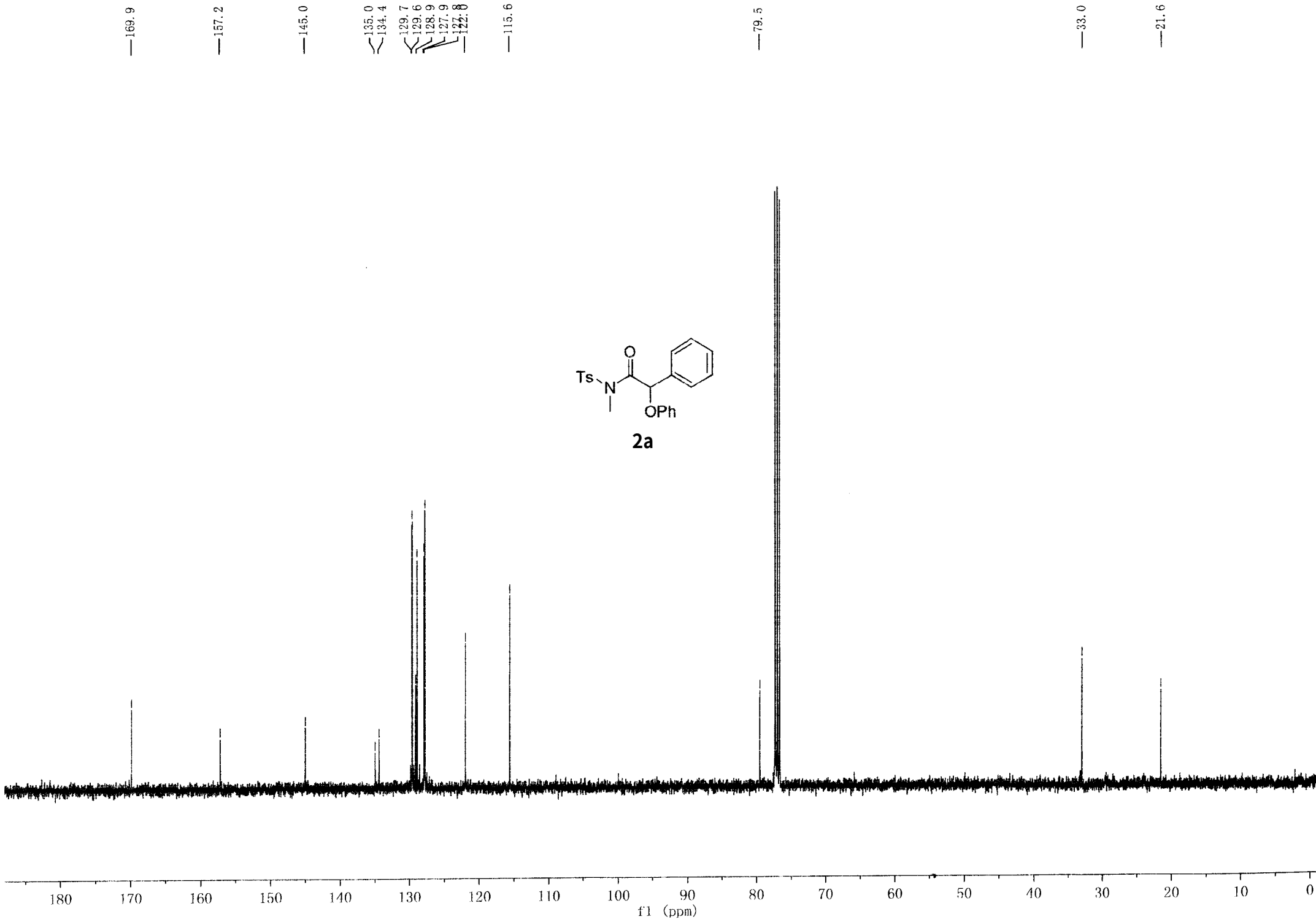
6.980
6.962
6.901
6.881
6.487

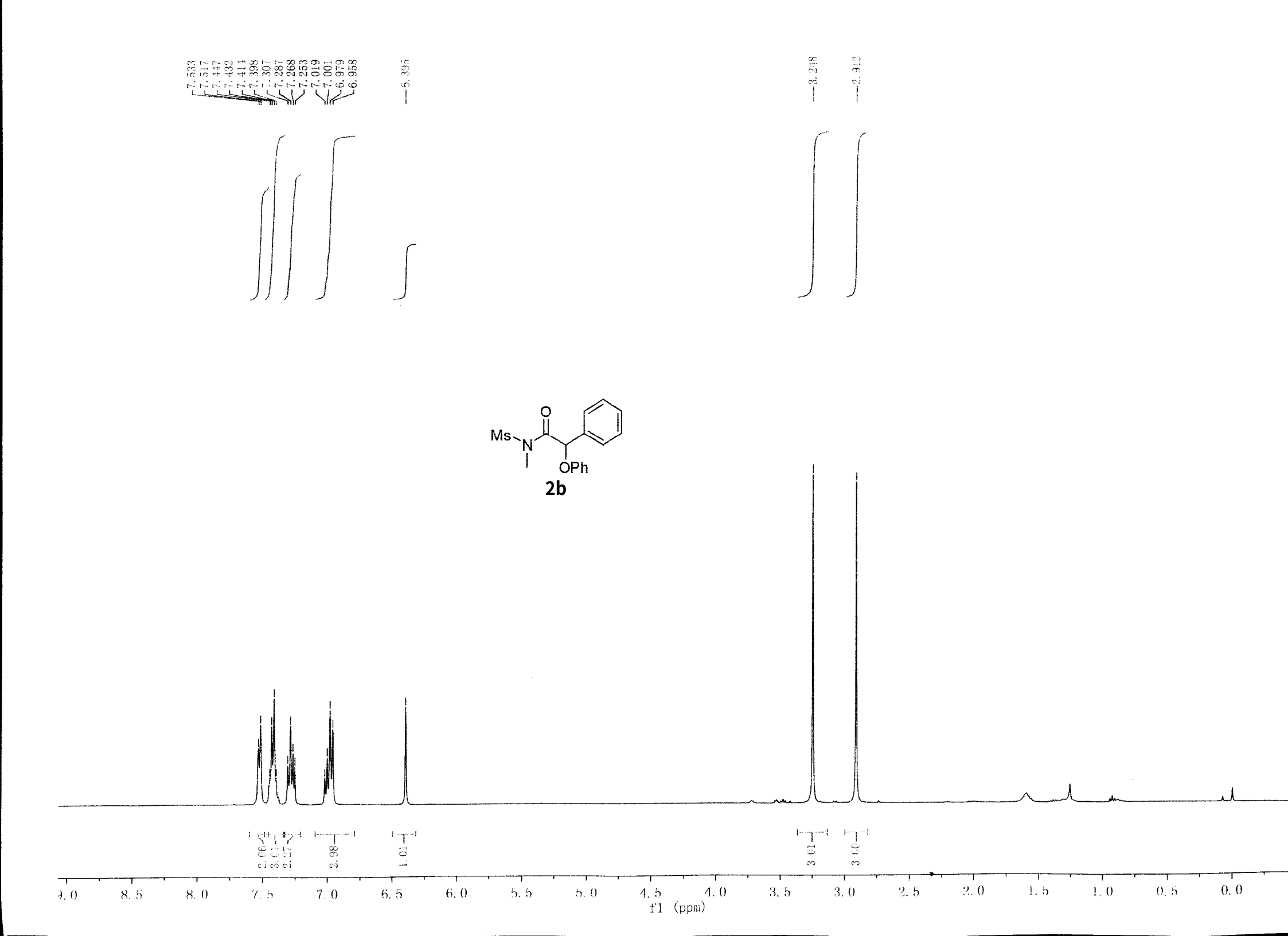

3.192
2.401

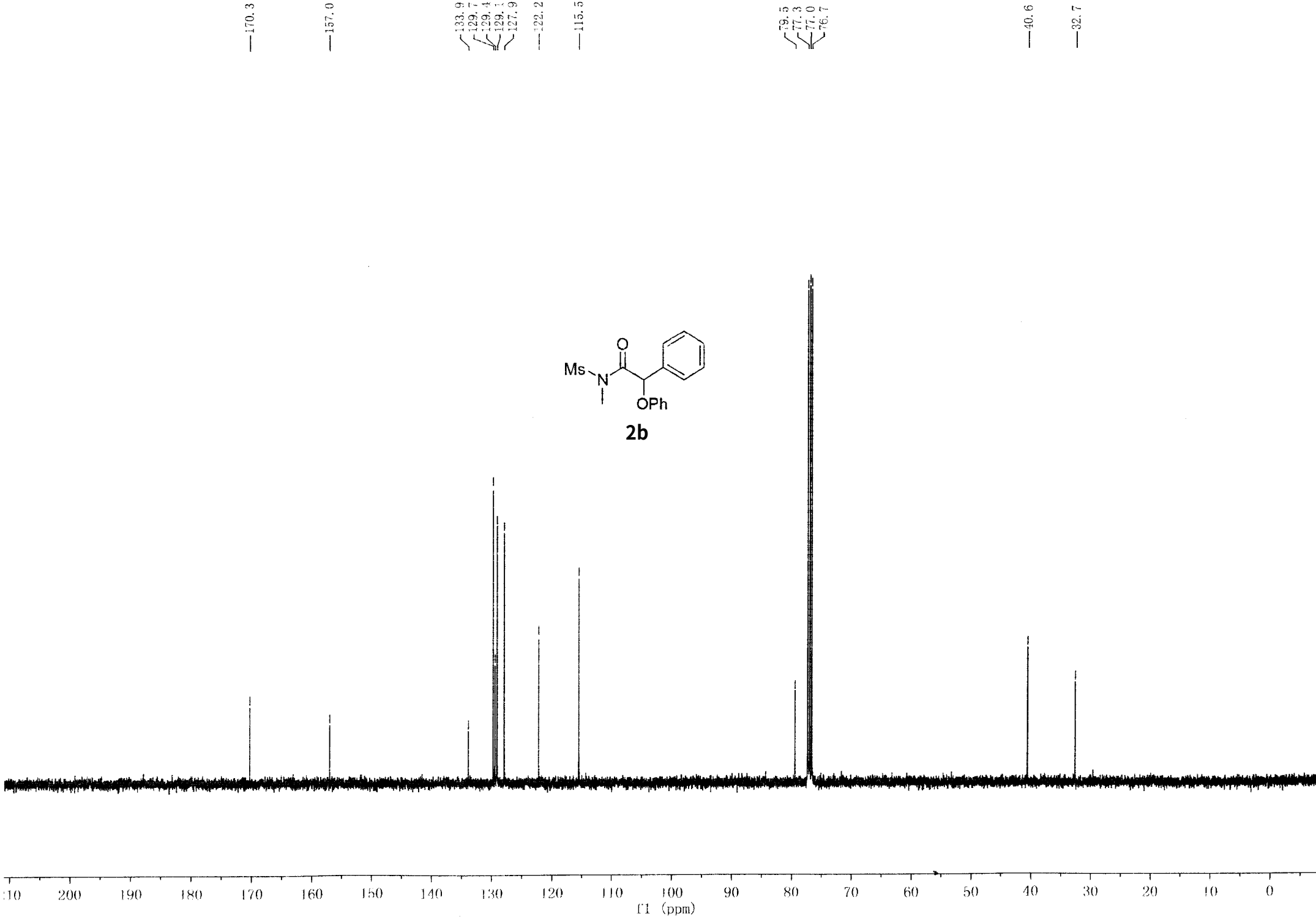

Ts
N
O
OPh

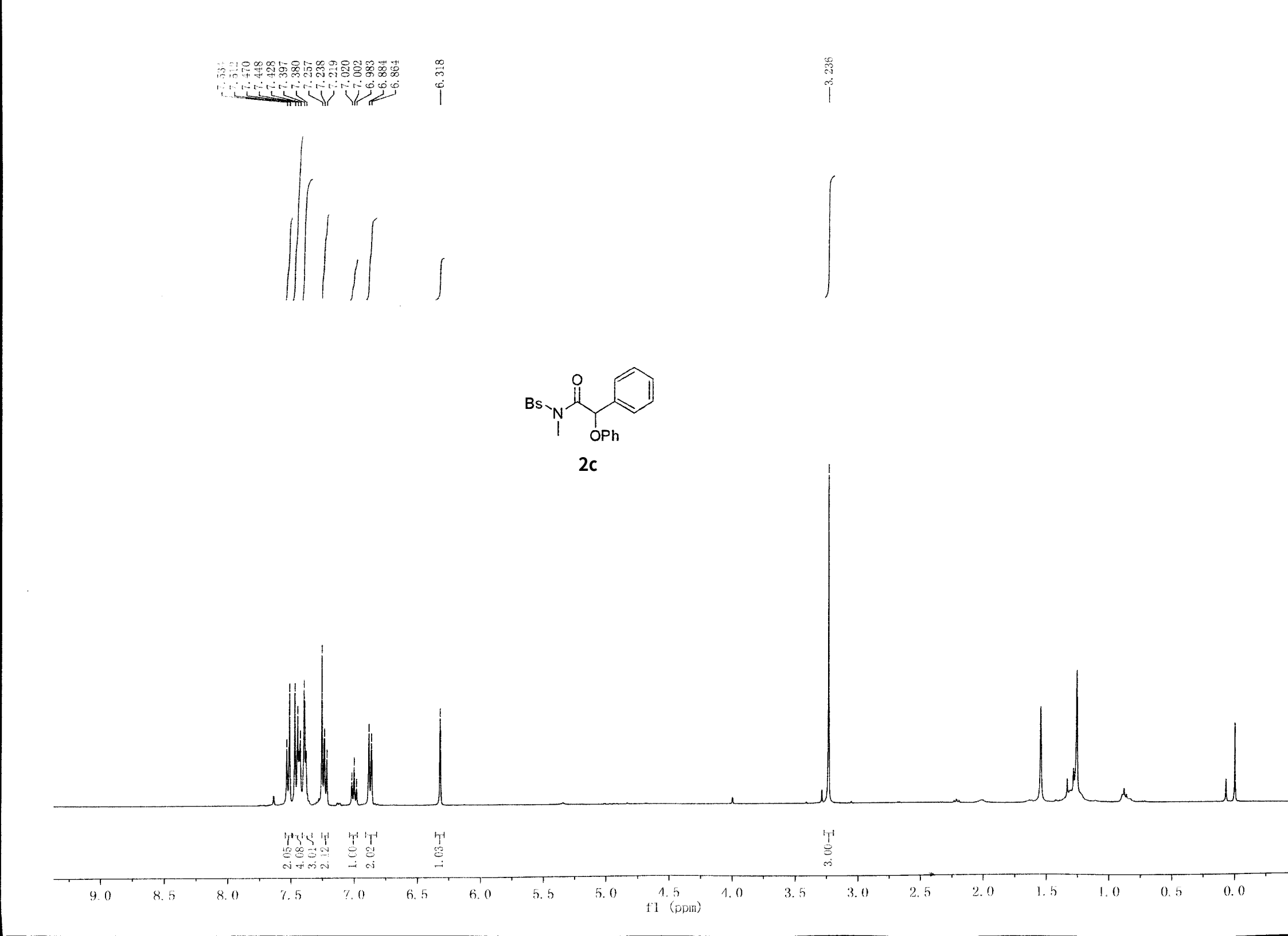
2a


4.16
3.09
4.19
1.05
2.02
1.02
3.00
3.00
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)


169.9
157.2
145.0
135.0
134.4
129.7
129.6
128.9
127.9
115.6
79.5
33.0
21.6
Ts
N
O
OPh
2a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.533
7.517
7.447
7.432
7.411
7.398
7.307
7.287
7.268
7.253
7.019
7.001
6.979
6.958
6.396
3.248
2.912
Ms
N
O
OPh
2b
2.98
1.01
3.01
3.00
f1 (ppm)


170.3
157.0
133.9
129.7
129.4
129.1
127.9
122.2
115.5
79.5
77.3
77.0
76.7
40.6
32.7
Ms
N
O
OPh
2b
f1 (ppm)


7.538
7.512
7.470
7.448
7.428
7.397
7.380
7.257
7.238
7.219
7.020
7.002
6.983
6.884
6.864
6.318
3.236
Bs
N
O
OPh
2c
2.05
4.08
3.01
2.12
1.00
2.02
1.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
2.0
1.5
1.0
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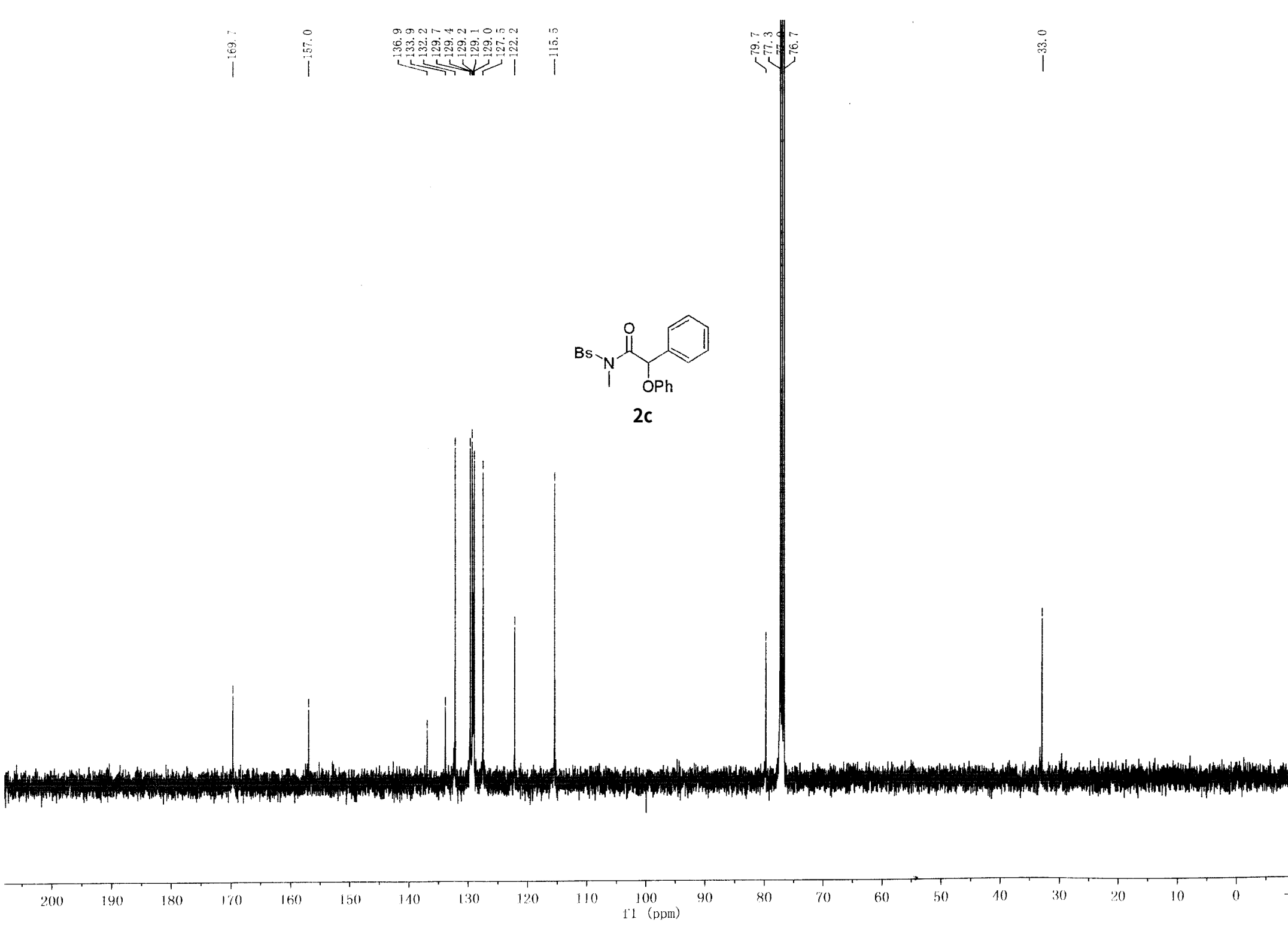
0.0
f1 (ppm)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133.9
132.2
129.7
129.4
129.2
129.1
129.0
127.5
122.2
115.5
79.7
77.3
76.7
33.0
Bs
N
O
OPh
2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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10
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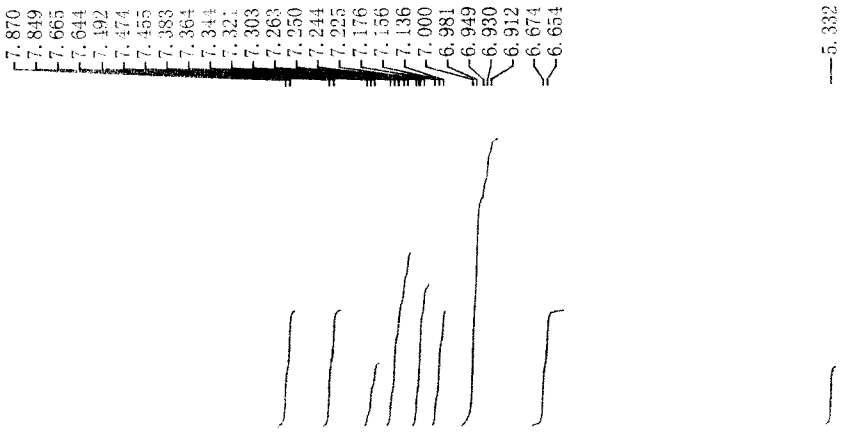
f1 (ppm)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7.383
7.364
7.344
7.321
7.303
7.263
7.250
7.244
7.225
7.176
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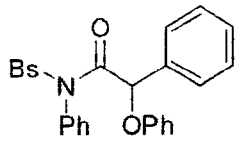
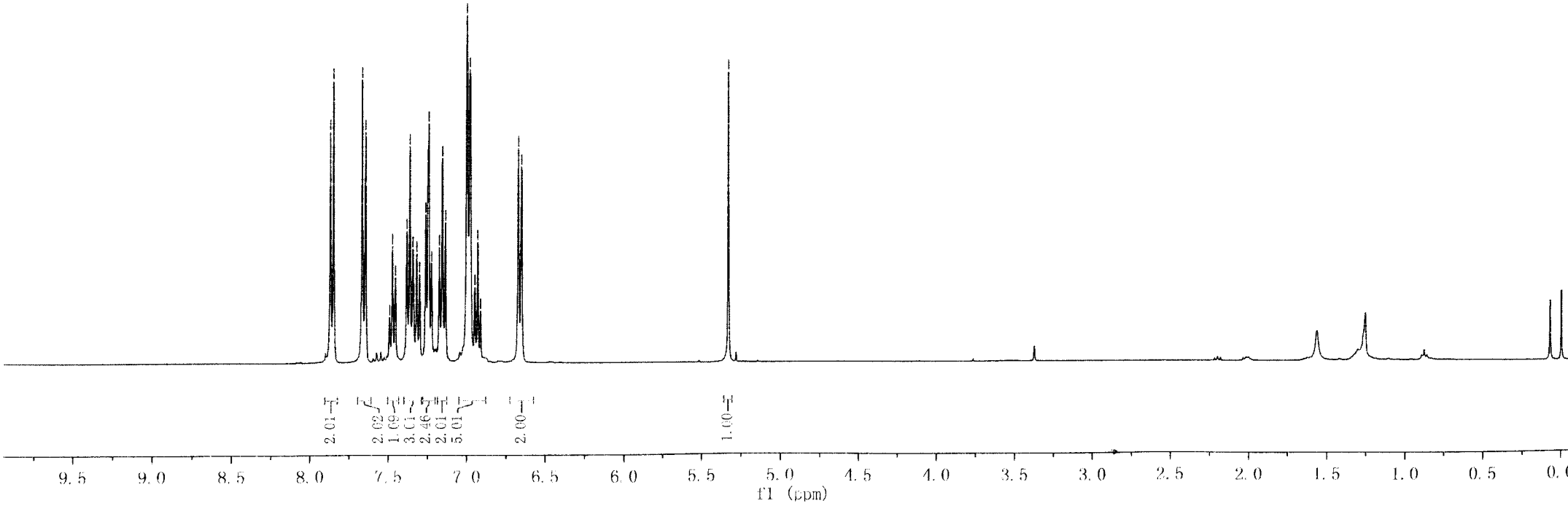
7.136
7.000
6.981
6.949
6.930
6.912
6.674
6.654
5.332


Bs
N
Ph
O
OPh

2d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2.62
1.09
3.01
2.46
2.01
5.01
2.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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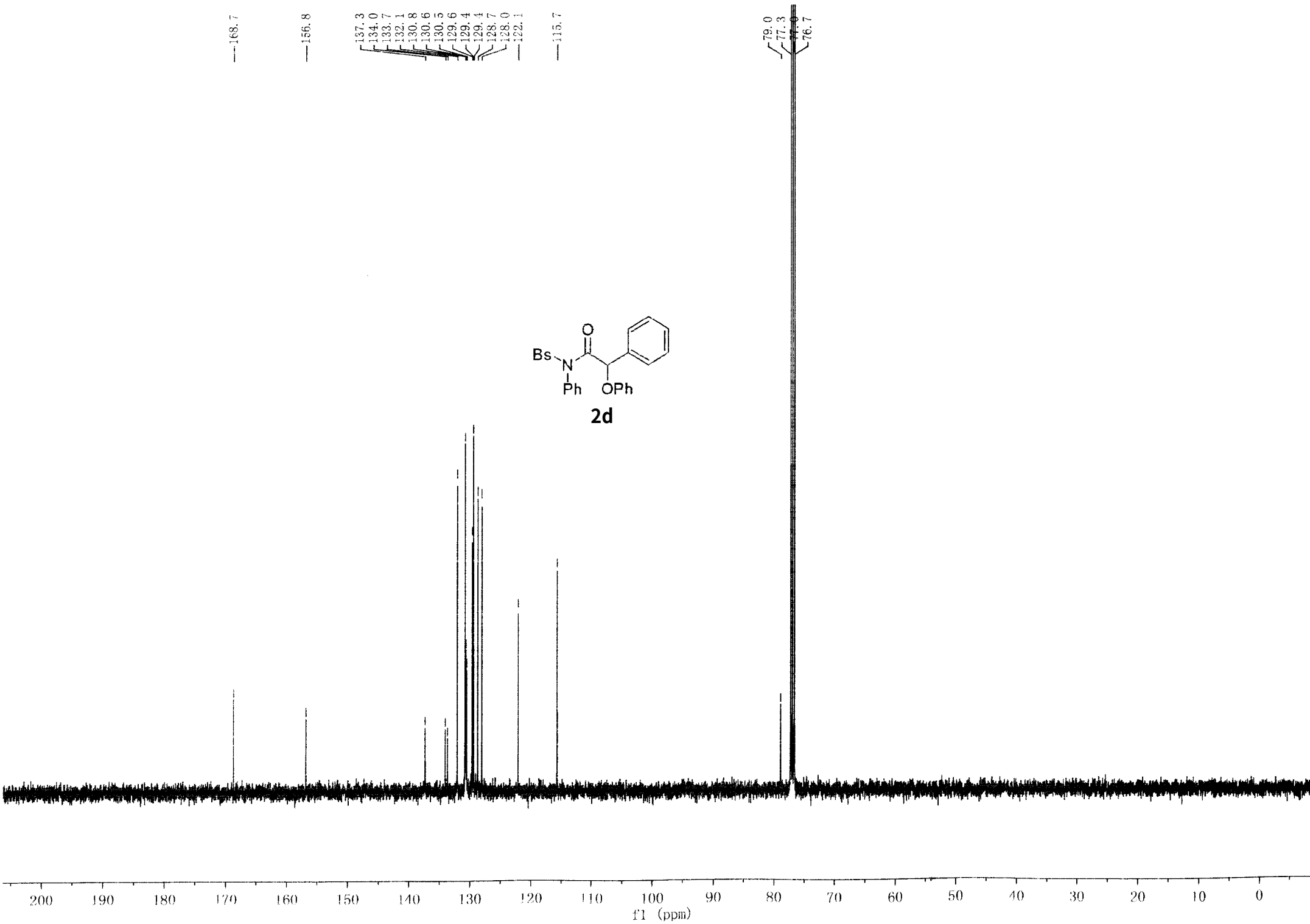
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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137.3
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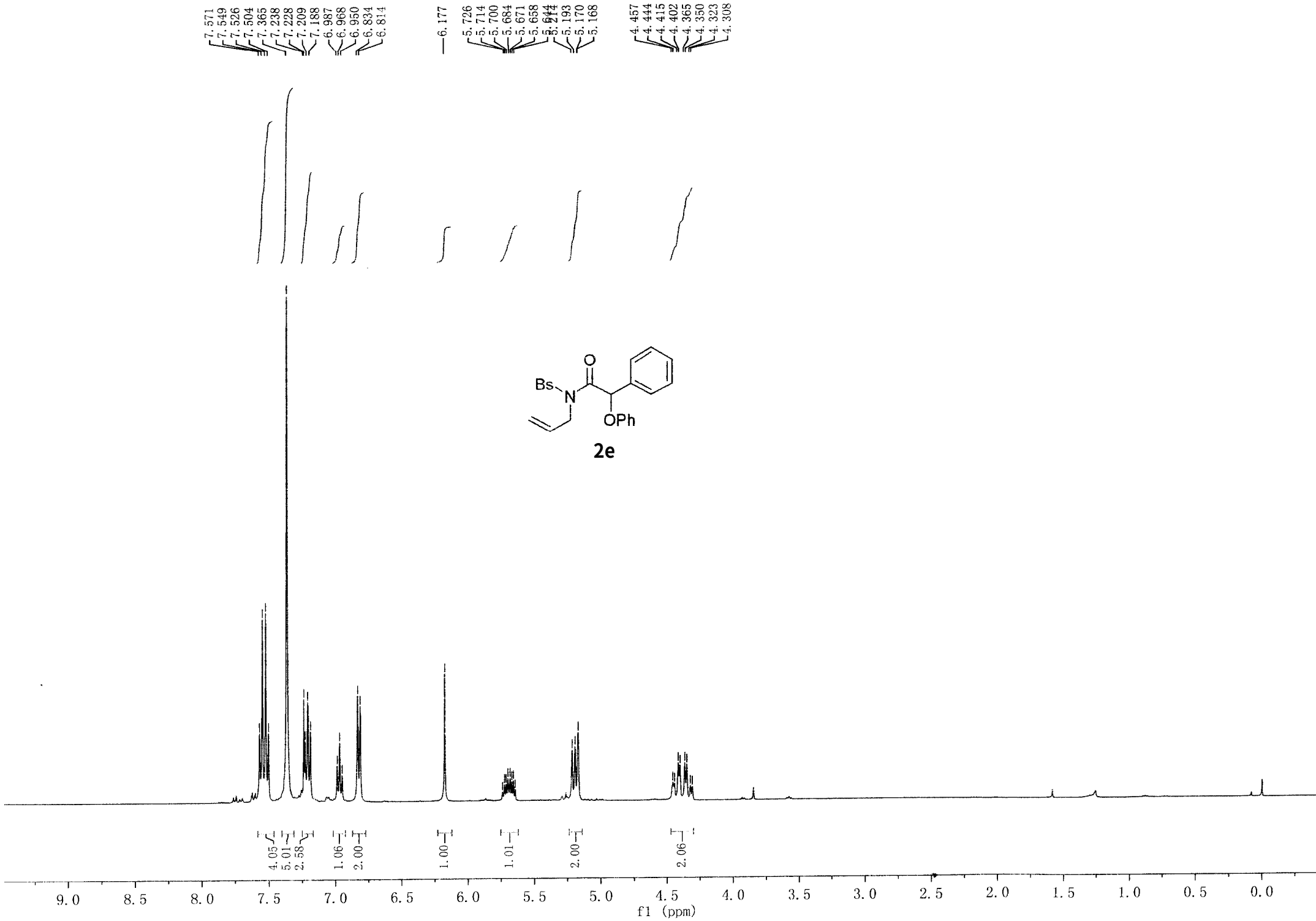
133.7
132.1
130.8
130.6
130.5
129.6
129.4
129.4
128.7
128.0
122.1
115.7
79.0
77.3
77.0
76.7
Bs
N
O
Ph
OPh
2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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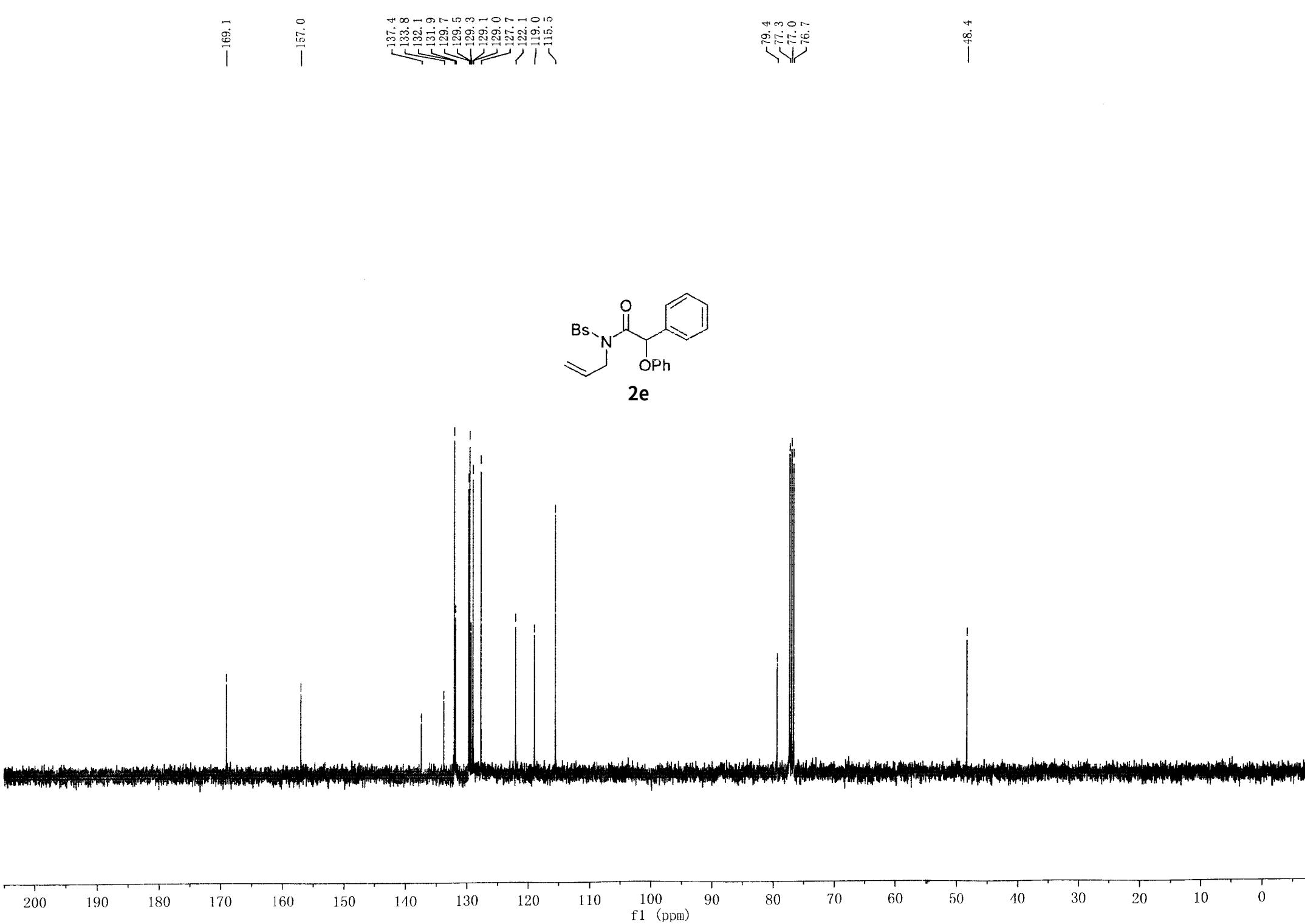
7.365
7.238
7.228
7.209
7.188
6.987
6.968
6.950
6.834
6.814
6.177
5.726
5.714
5.700
5.684
5.671
5.658
5.193
5.170
5.168
4.457
4.444
4.415
4.402
4.365
4.350
4.323
4.308
Bs
N
O
OPh
4.05
5.01
2.58
1.06
2.00
1.00
1.01
2.00
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2e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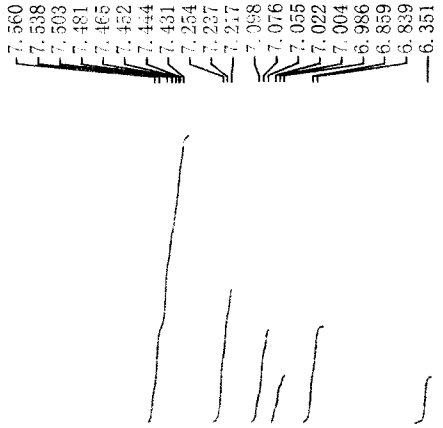
133.8
132.1
131.9
129.7
129.5
129.3
129.1
129.0
127.7
122.1
119.0
115.5
79.4
77.3
77.0
76.7
48.4
Bs
N
O
OPh
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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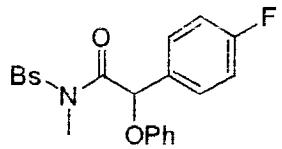
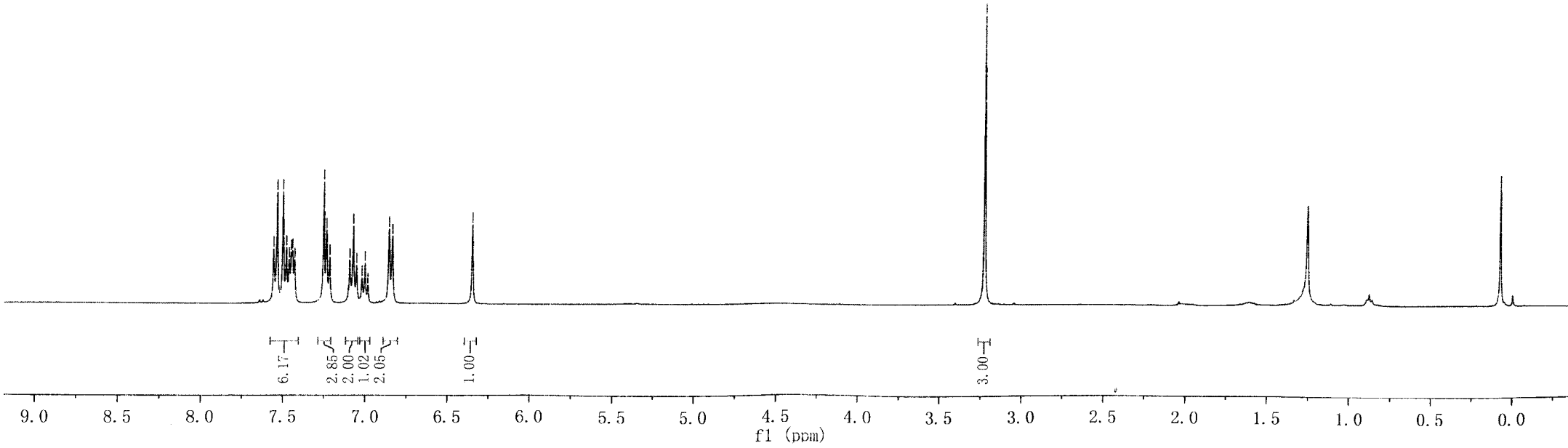
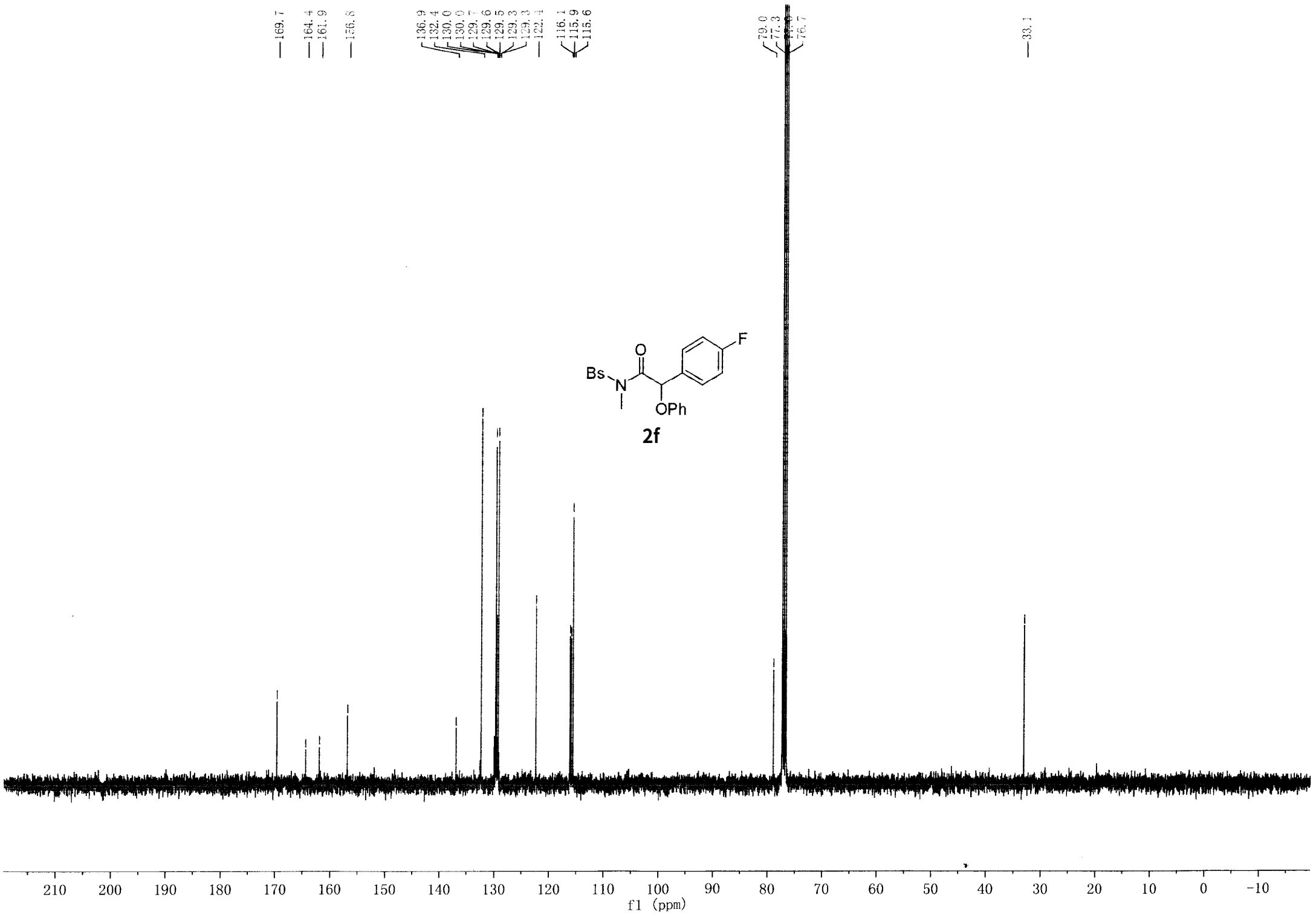
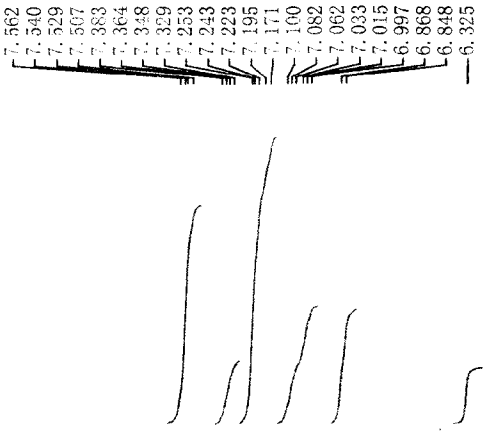
7.538
7.503
7.481
7.465
7.452
7.444
7.431
7.254
7.237
7.217
7.098
7.076
7.055
7.022
7.004
6.986
6.859
6.839
6.351
3.227


Bs
N
O
F
OPh

2f


6.17
2.85
2.00
1.02
2.05
1.00
3.00
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)


169.7
164.4
161.9
156.8
136.9
132.4
130.0
130.0
129.7
129.6
129.5
129.3
129.3
122.4
116.1
115.9
115.6
79.0
77.3
76.7
33.1
O
F
Bs
N
OPh
2f
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)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7.507
7.383
7.364
7.348
7.329
7.253
7.243
7.223
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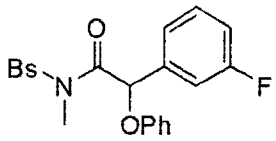
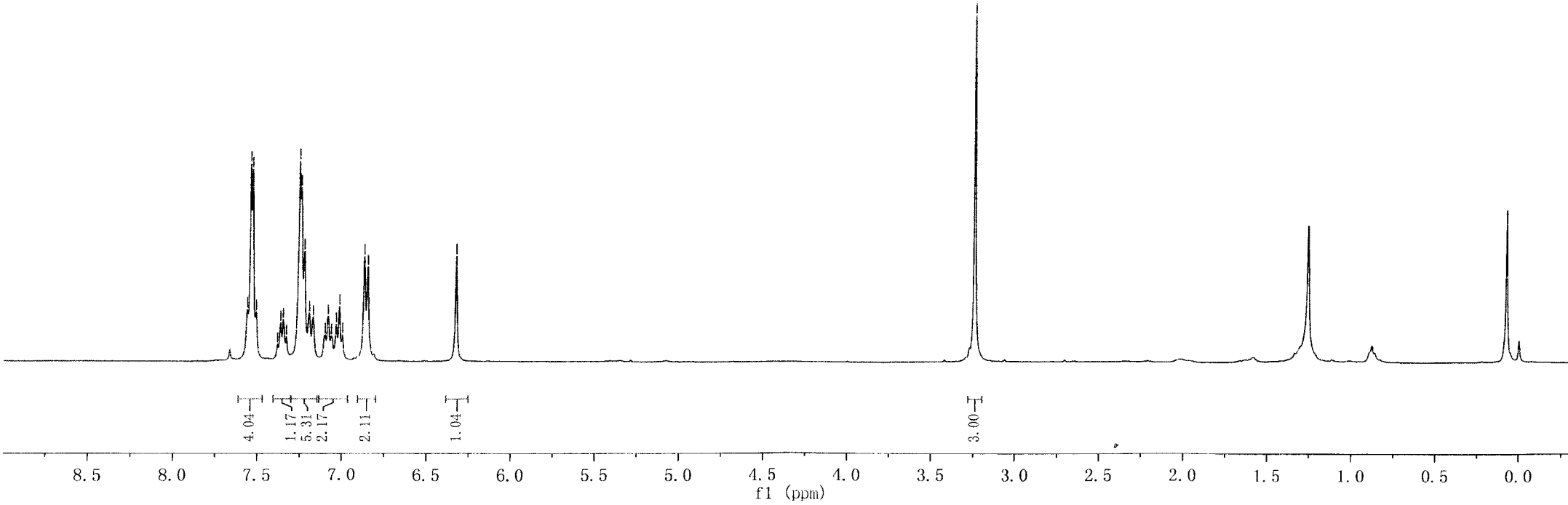
7.082
7.062
7.033
7.015
6.997
6.868
6.848
6.325


3.243


Bs
N
O
F
OPh

2g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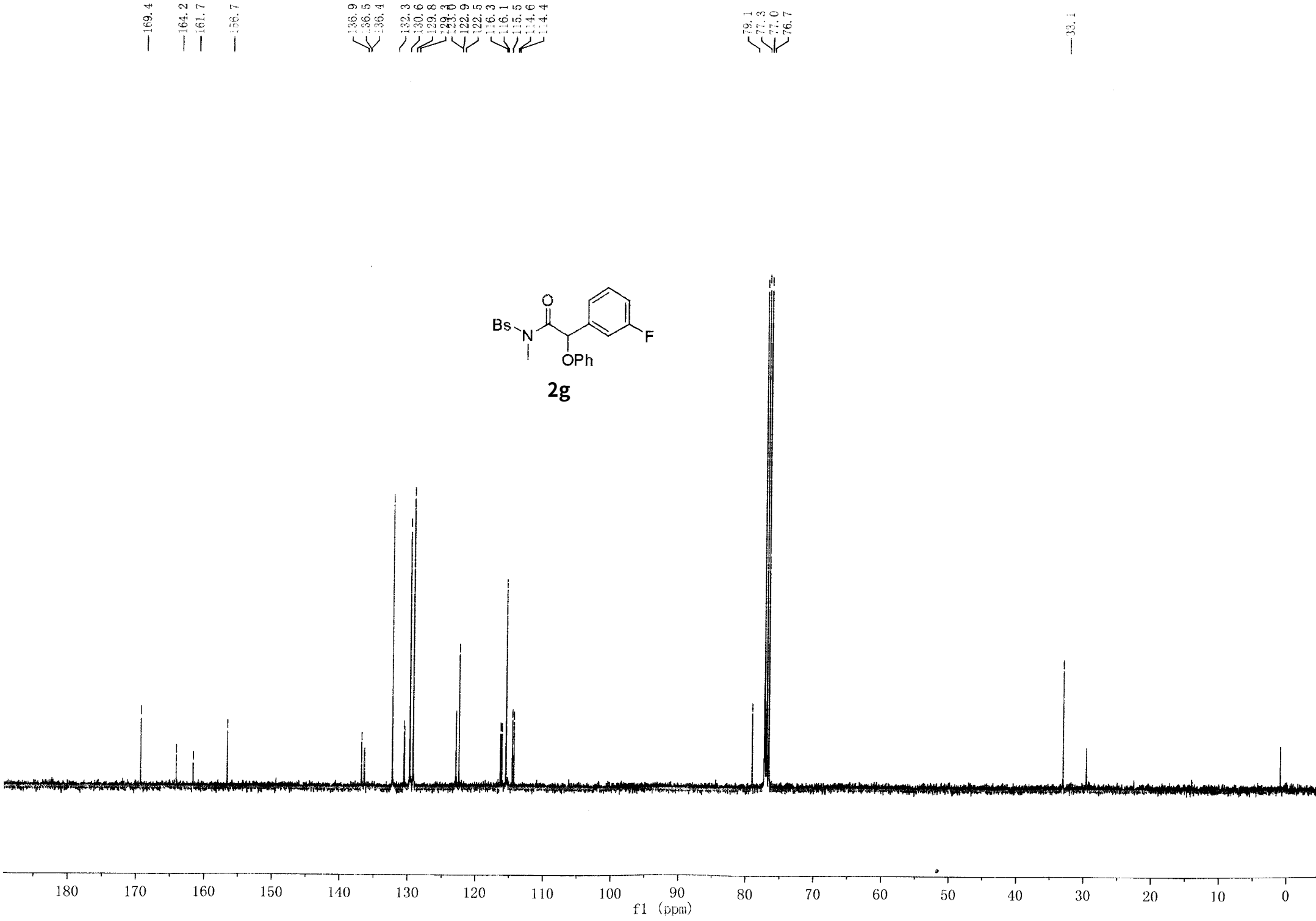
1.17
5.31
2.17
2.11
1.04
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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164.2
161.7
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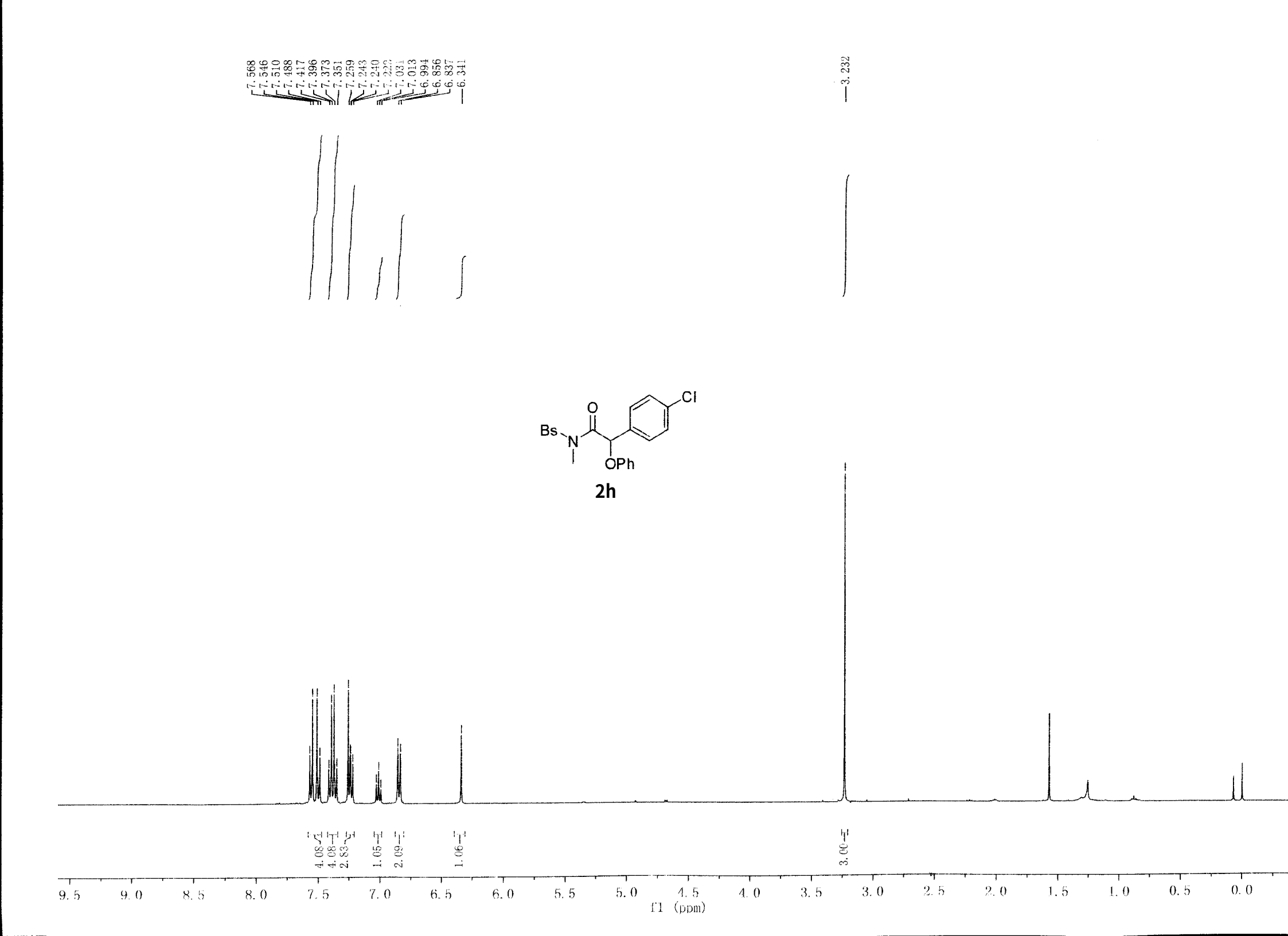
136.9
136.5
136.4
132.3
130.6
129.8
123.0
122.9
122.5
116.3
116.1
115.5
114.6
114.4
79.1
77.3
77.0
76.7
33.1
Bs
N
O
OPh
F
2g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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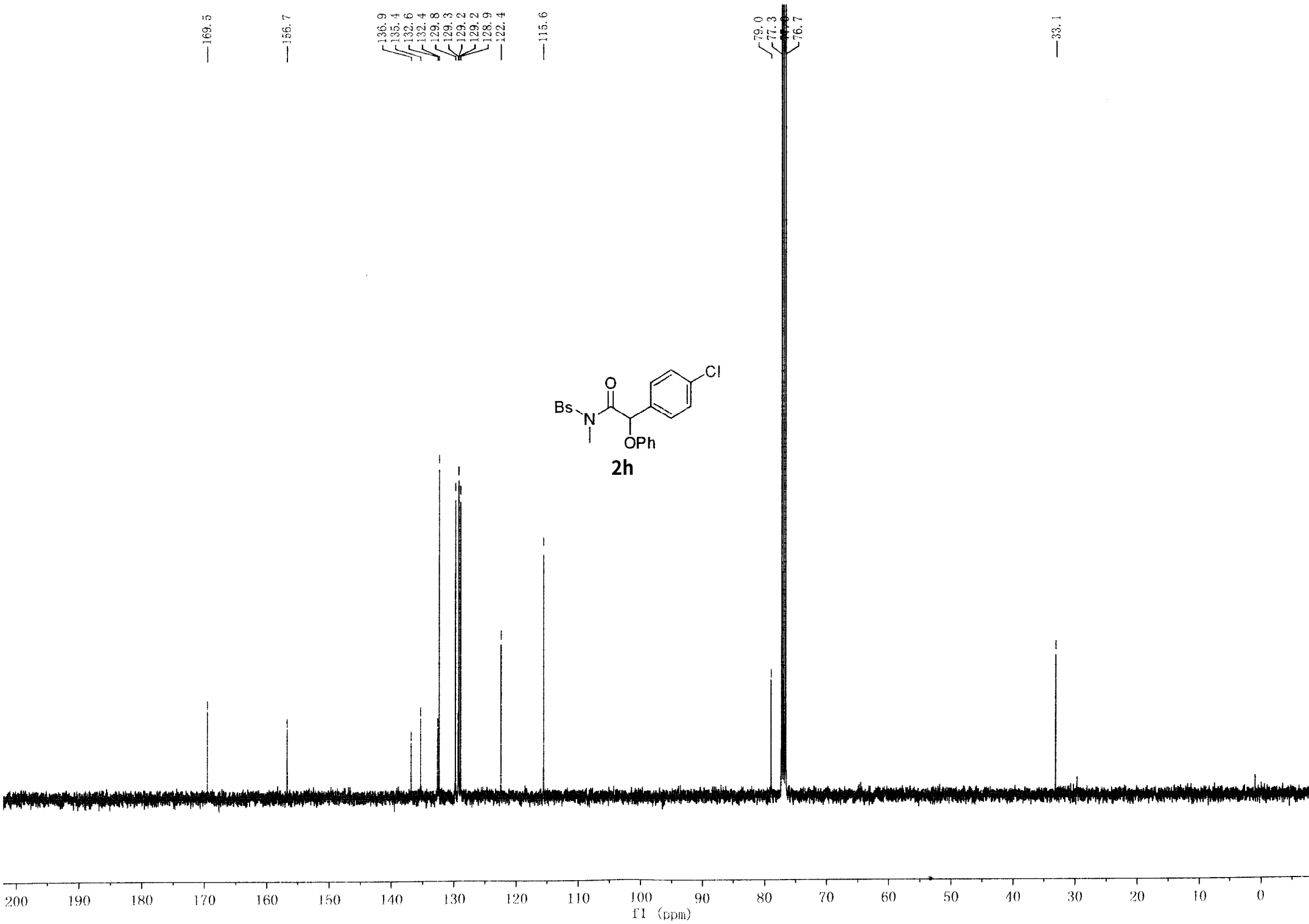
7.488
7.417
7.396
7.373
7.351
7.259
7.243
7.240
7.222
7.031
7.013
6.994
6.856
6.837
6.341
3.232
Bs
N
O
OPh
Cl
4.08
4.08
2.83
1.05
2.09
1.06
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2h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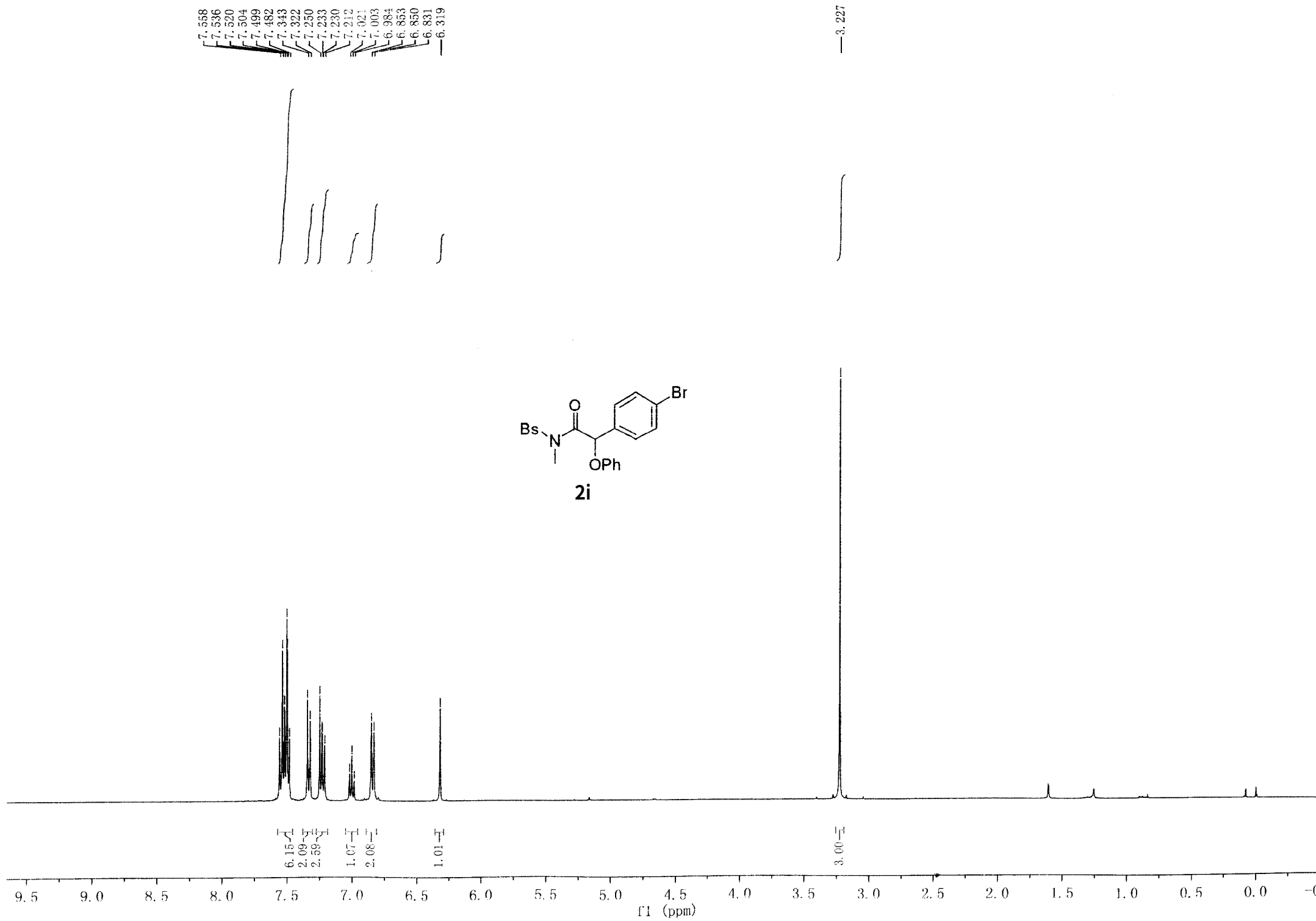
156.7
136.9
135.4
132.6
132.4
129.8
129.3
129.2
129.2
128.9
122.4
115.6
79.0
77.3
76.7
33.1
Cl
O
Bs
N
OPh
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.322
7.250
7.233
7.230
7.212
7.021
7.003
6.984
6.853
6.850
6.831
6.319
3.227
Br
O
Bs
N
OPh
6.15
2.09
2.59
1.07
2.08
1.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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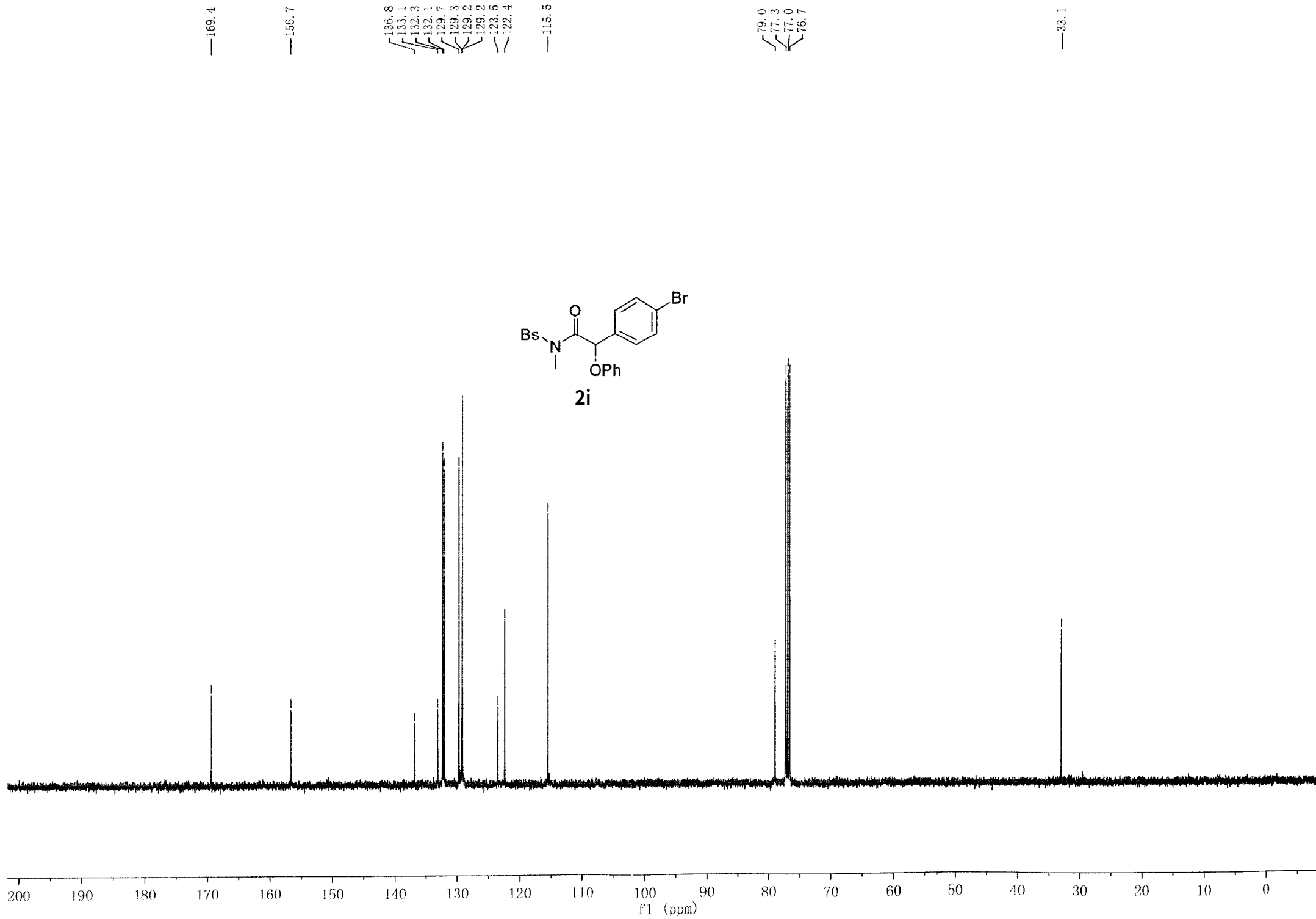
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2i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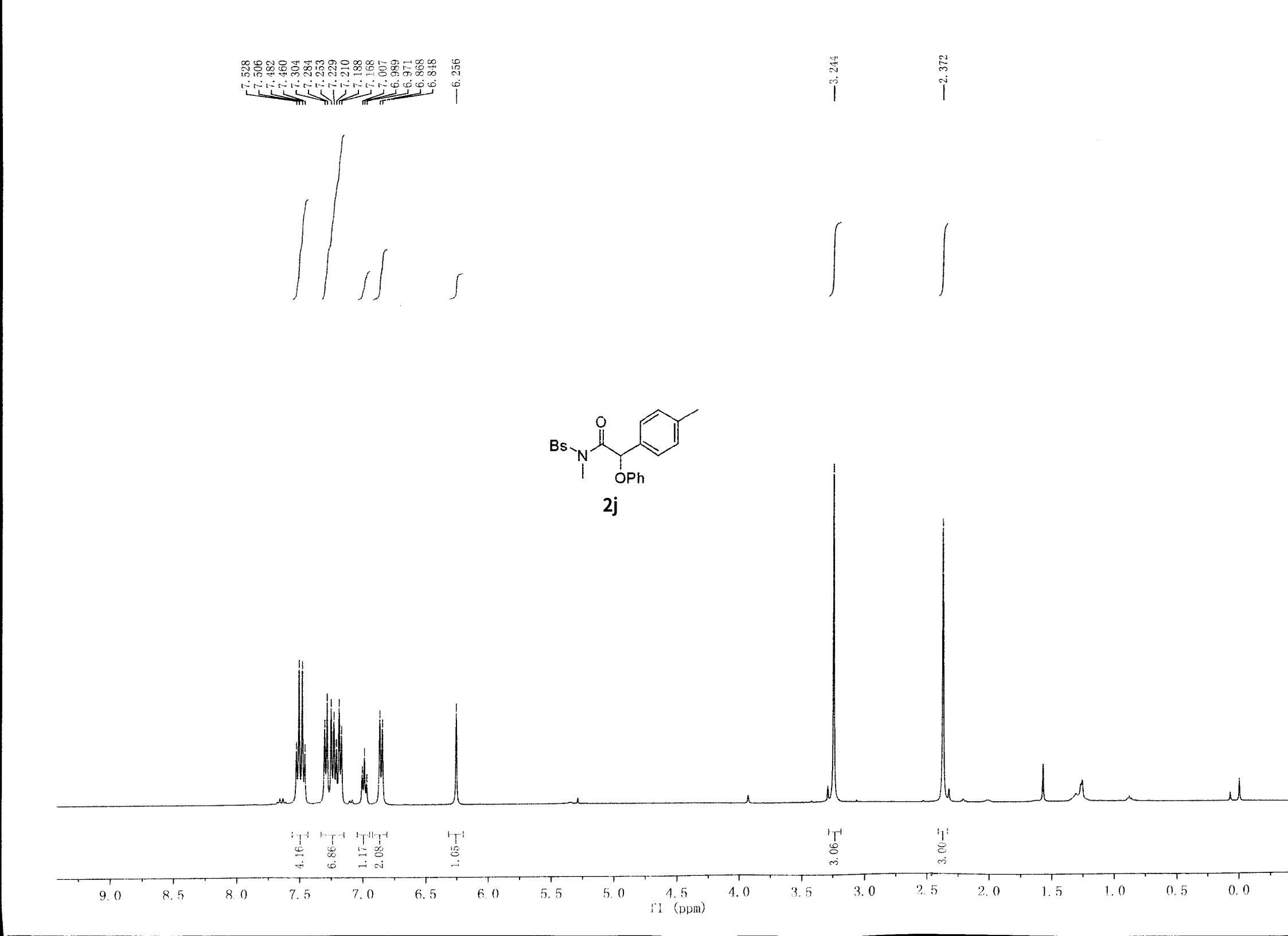
136.8
133.1
132.3
132.1
129.7
129.3
129.2
129.2
123.5
122.4
115.5
79.0
77.3
77.0
76.7
33.1
Br
O
Bs
N
OPh
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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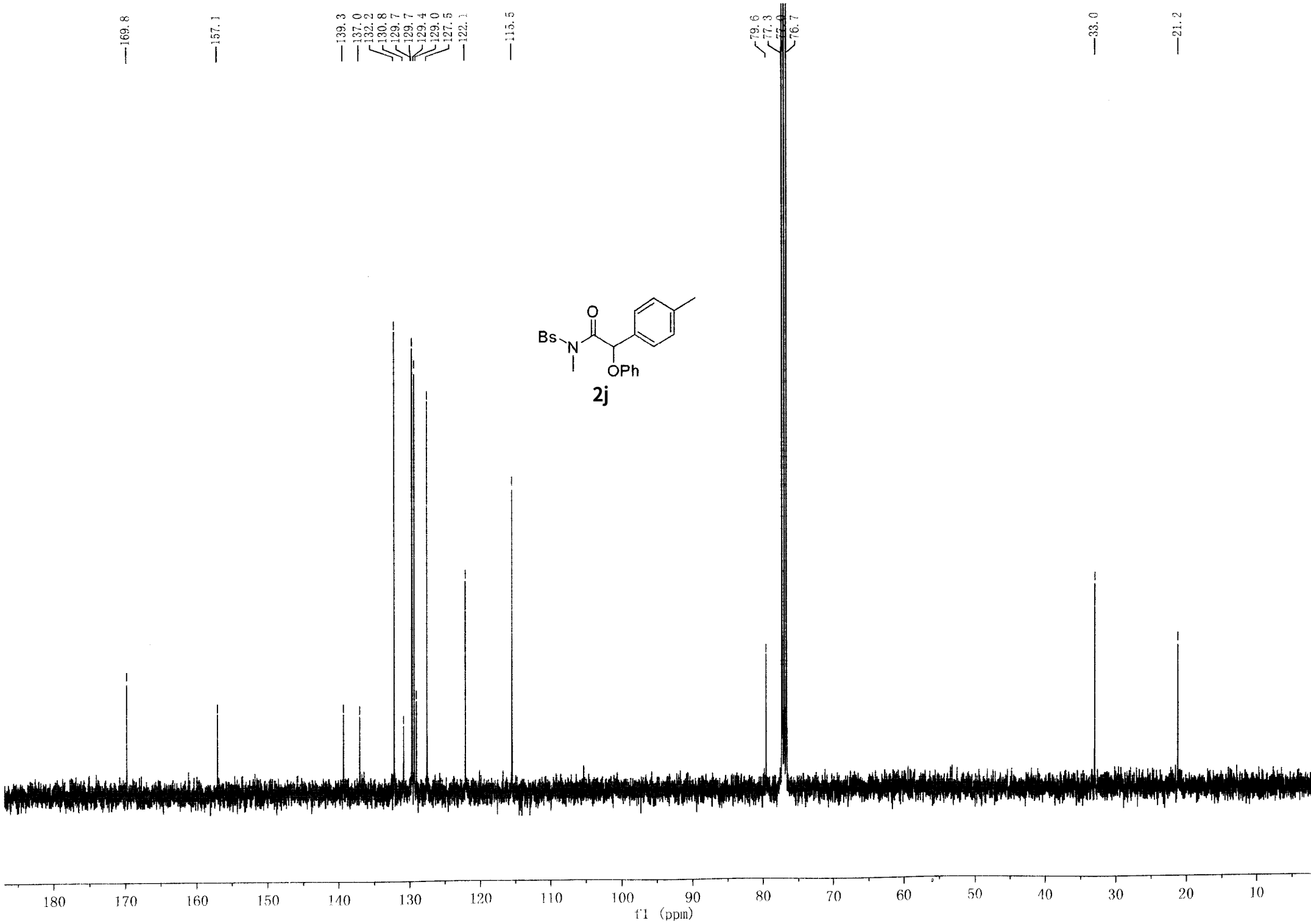
7.284
7.253
7.229
7.210
7.188
7.168
7.007
6.989
6.971
6.868
6.848
6.256
3.244
2.372
Bs
N
O
OPh
2j
4.16
6.86
1.17
2.08
1.05
3.06
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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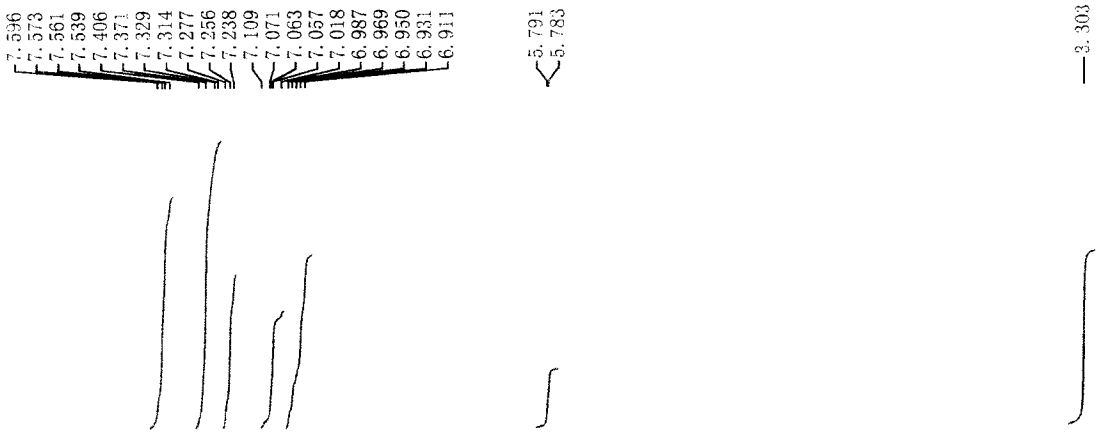
132.2
130.8
129.7
129.7
129.4
129.0
127.5
122.1
115.5
79.6
77.3
76.7
33.0
21.2
Bs
N
O
OPh
2j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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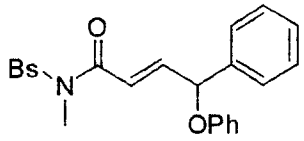
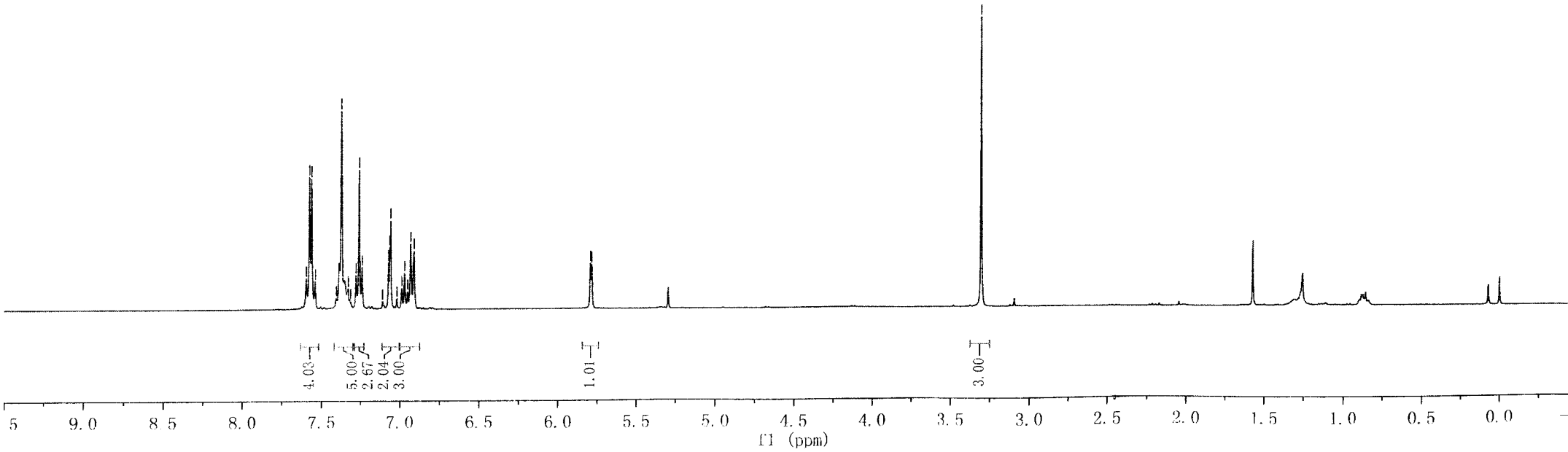
7.539
7.406
7.371
7.329
7.314
7.277
7.256
7.238
7.109
7.071
7.063
7.057
7.018
6.987
6.969
6.950
6.931
6.911
5.791
5.783
3.303


Bs
N
O
OPh

2k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5.00
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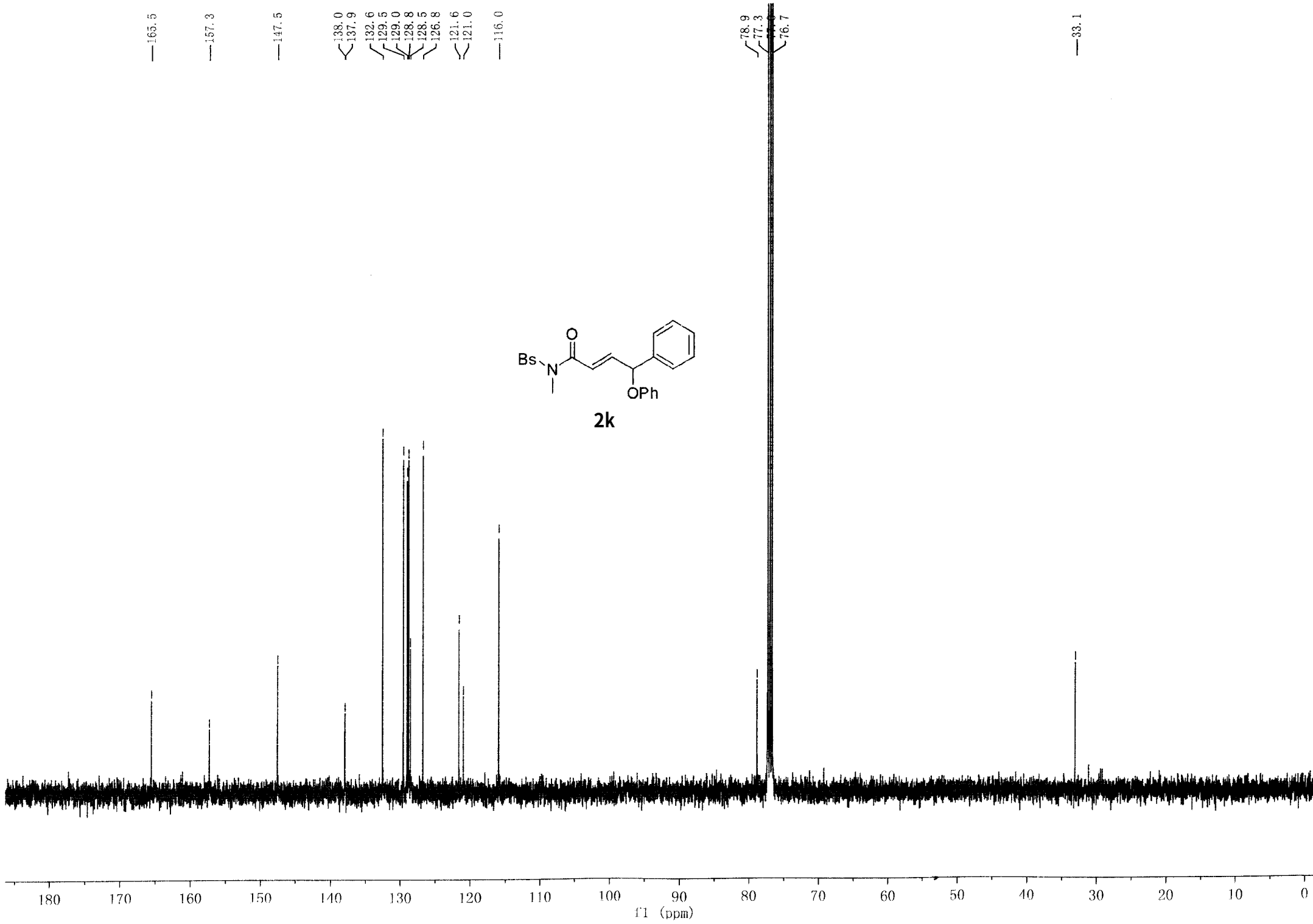
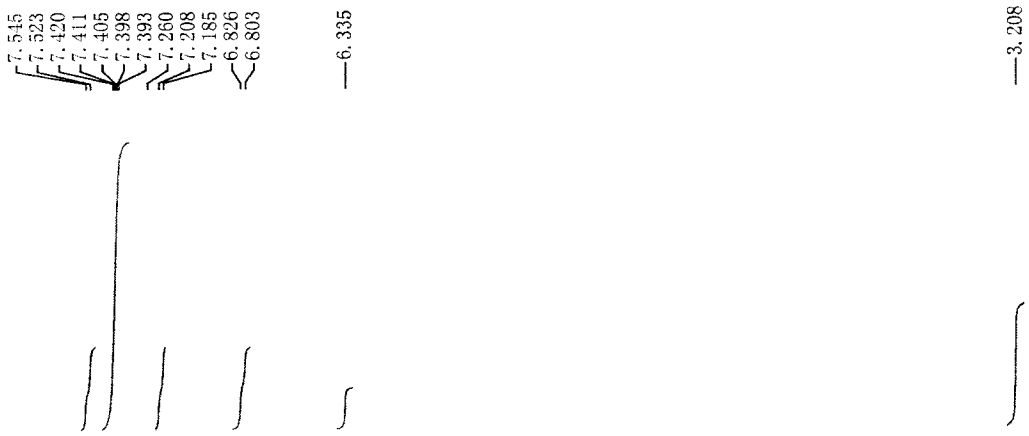
2.04
3.00
1.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.5
157.3
147.5
138.0
137.9
132.6
129.5
129.0
128.8
128.5
126.8
121.6
121.0
116.0
78.9
77.3
76.7
33.1
Bs
N
O
OPh
2k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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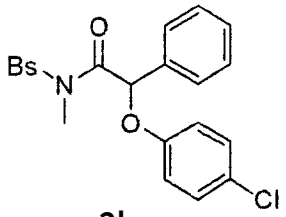
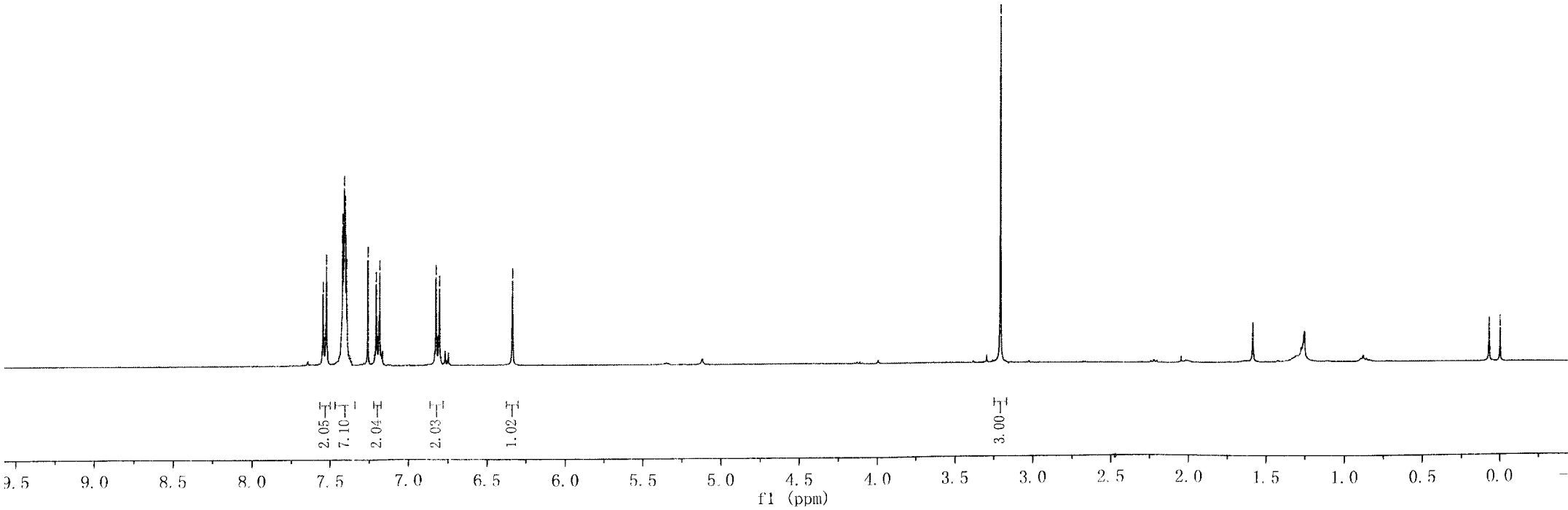
7.260
7.208
7.185
6.826
6.803
6.335
3.208


Bs
N
O
O
Cl

2l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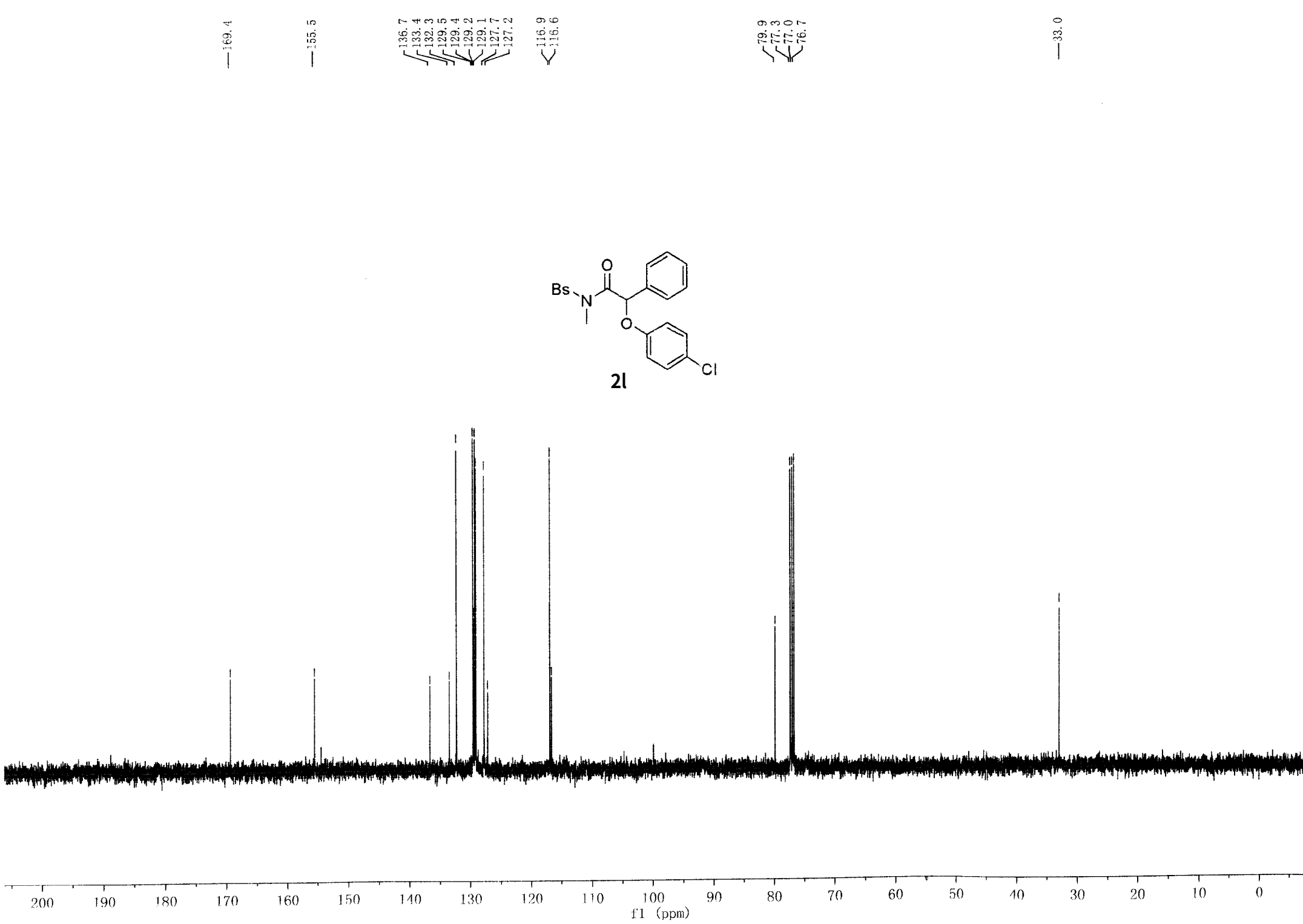
7.10
2.04
2.03
1.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.7
133.4
132.3
129.5
129.4
129.2
129.1
127.7
127.2
116.9
116.6
79.9
77.3
77.0
76.7
33.0
Bs
N
O
O
Cl
2l
200
190
180
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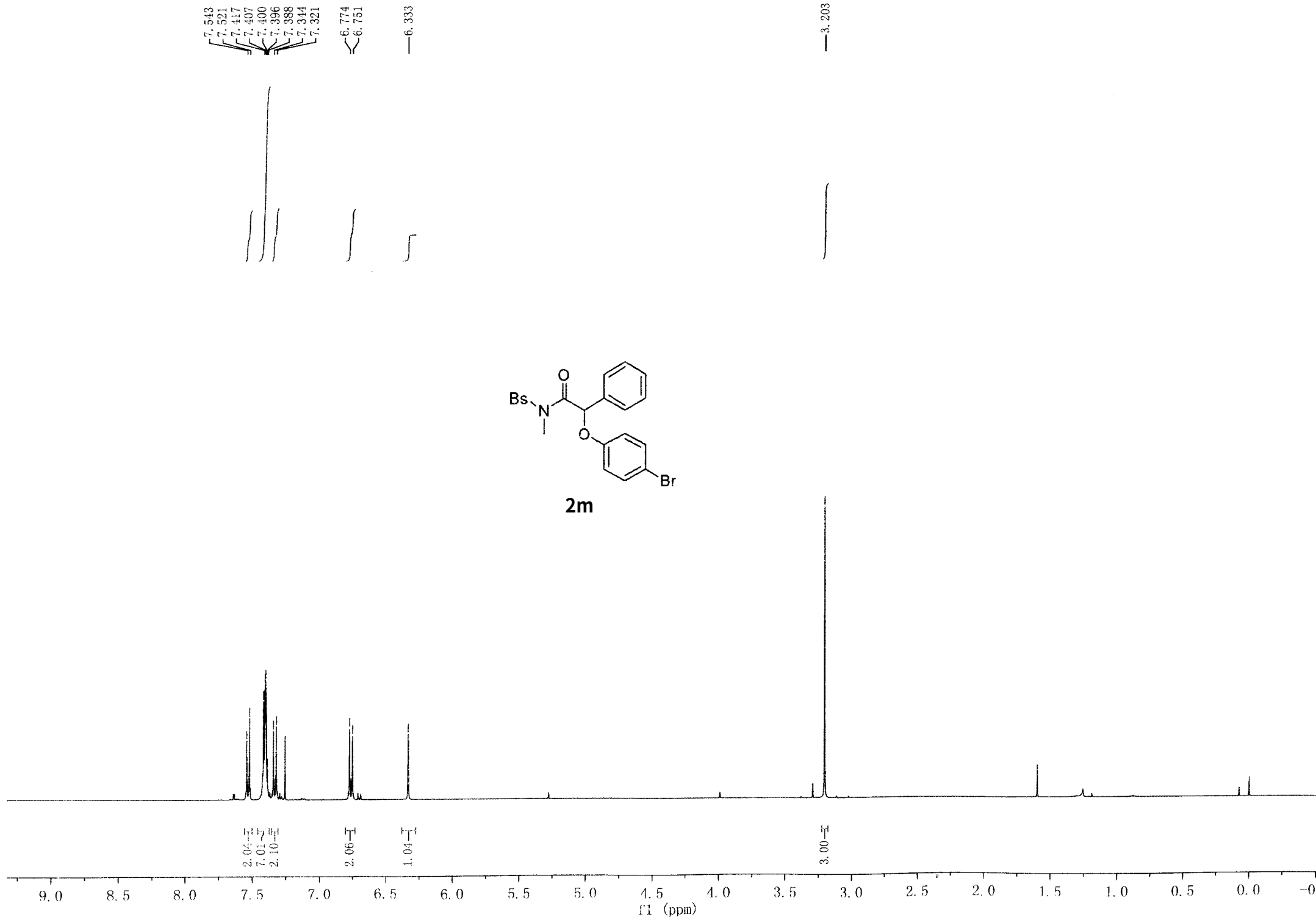
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6.751
6.333
3.203
Bs
N
O
O
Br
2m
2.04
7.01
2.10
2.06
1.04
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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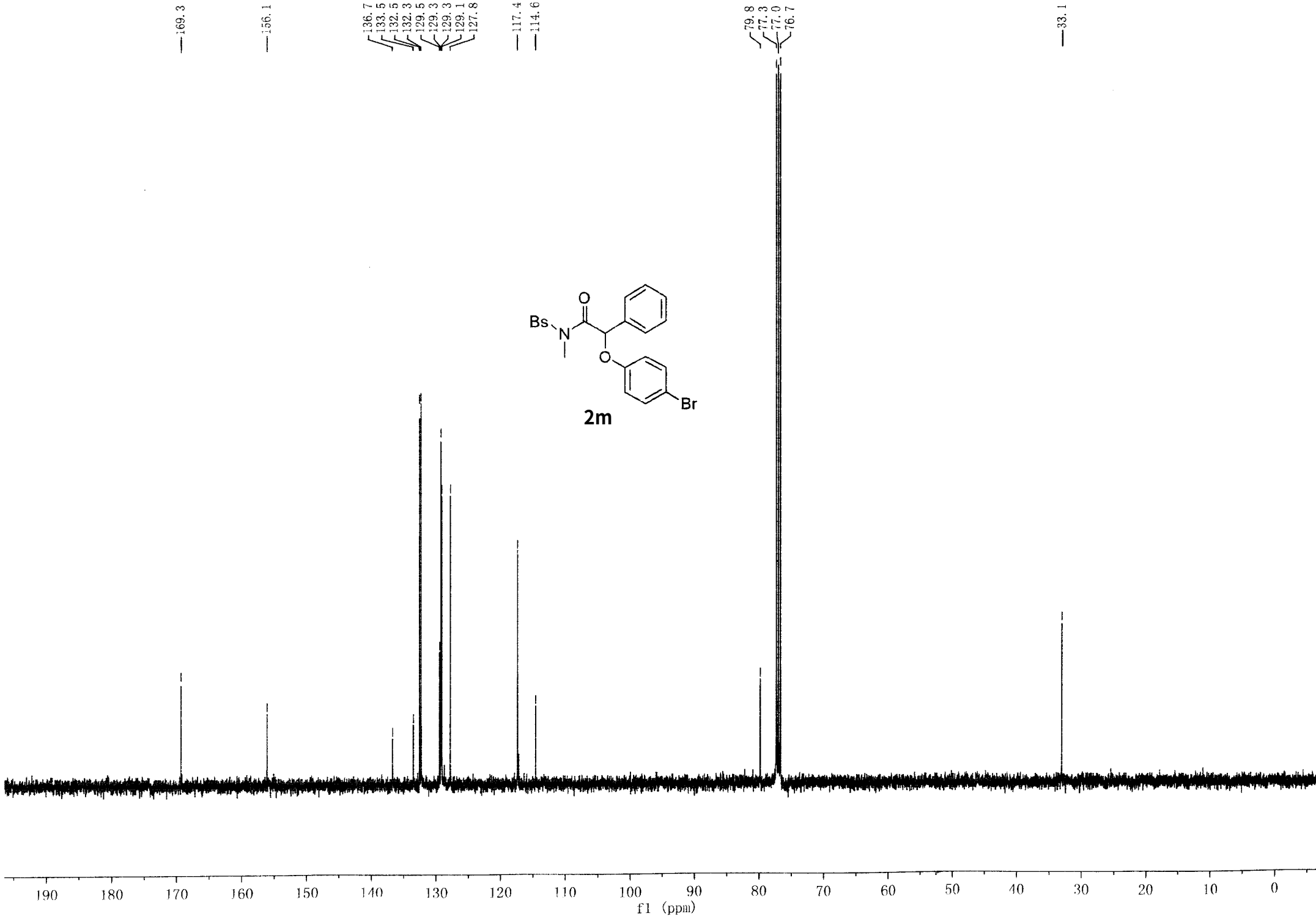
f1 (ppm)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129.3
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129.1
127.8
117.4
114.6
79.8
77.3
77.0
76.7
33.1
Bs
N
O
O
Br
2m
190
180
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130
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90
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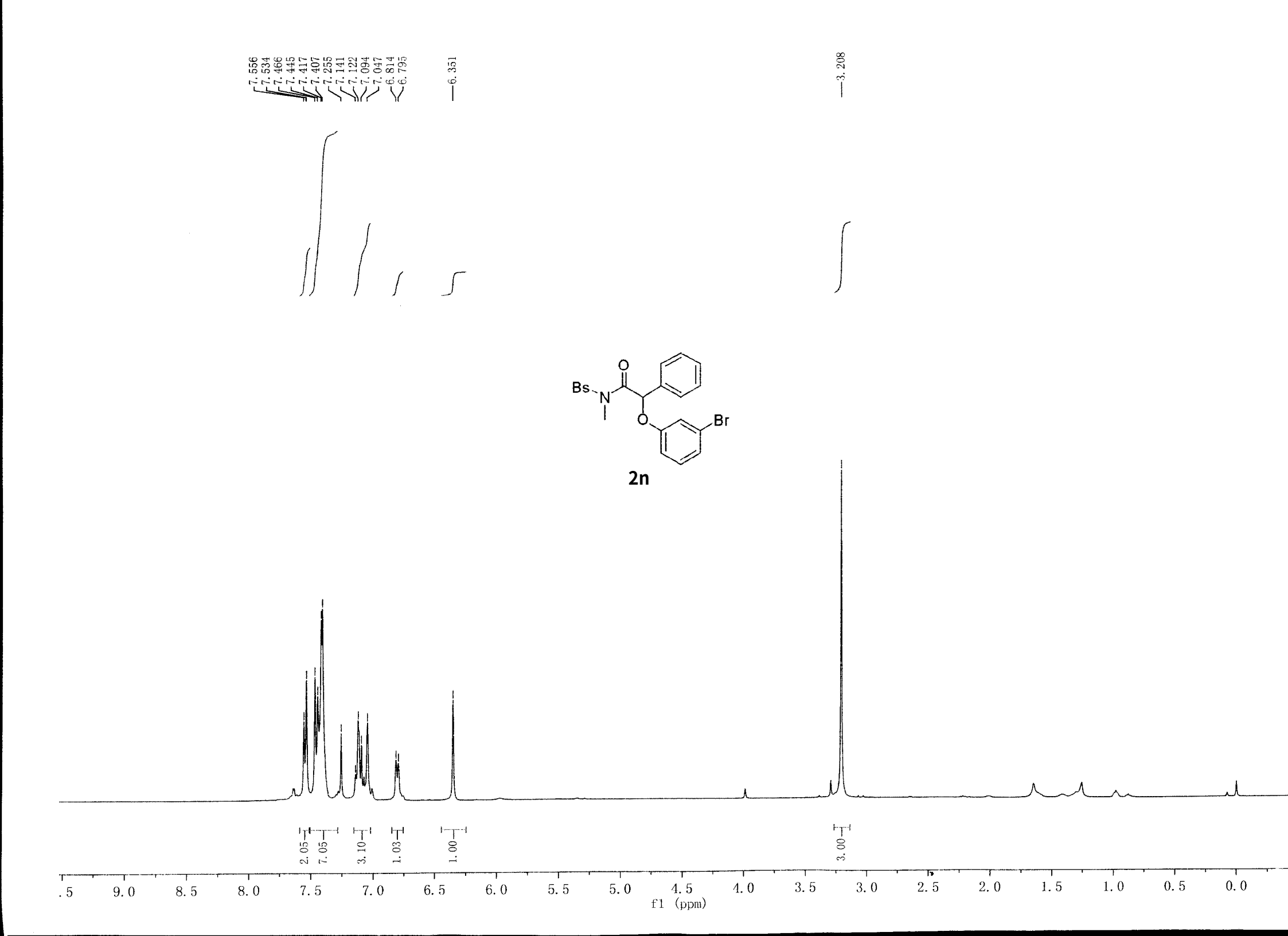
f1 (ppm)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6.795
6.351
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O
Br
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7.05
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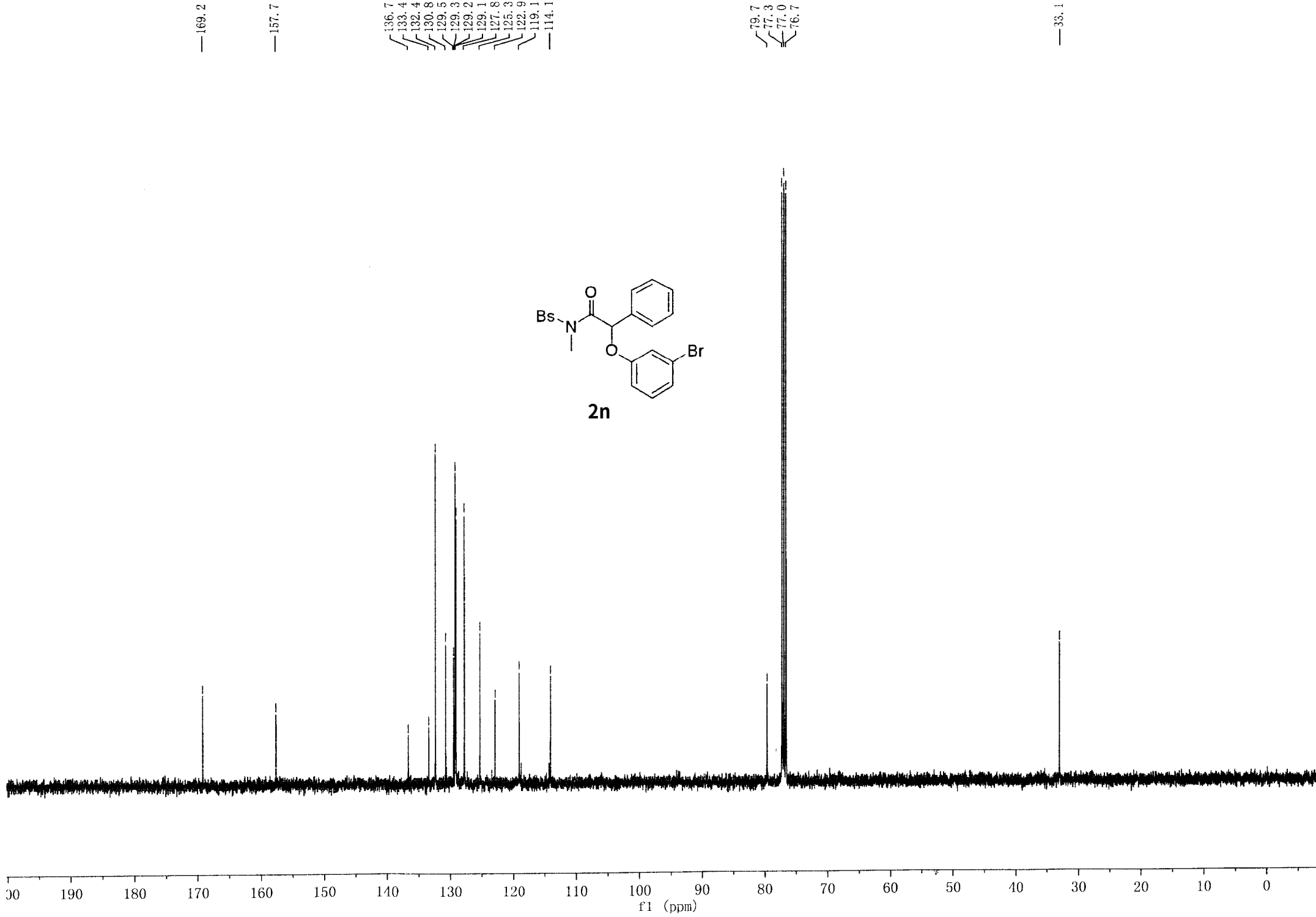
3.00
f1 (ppm)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122.9
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114.1
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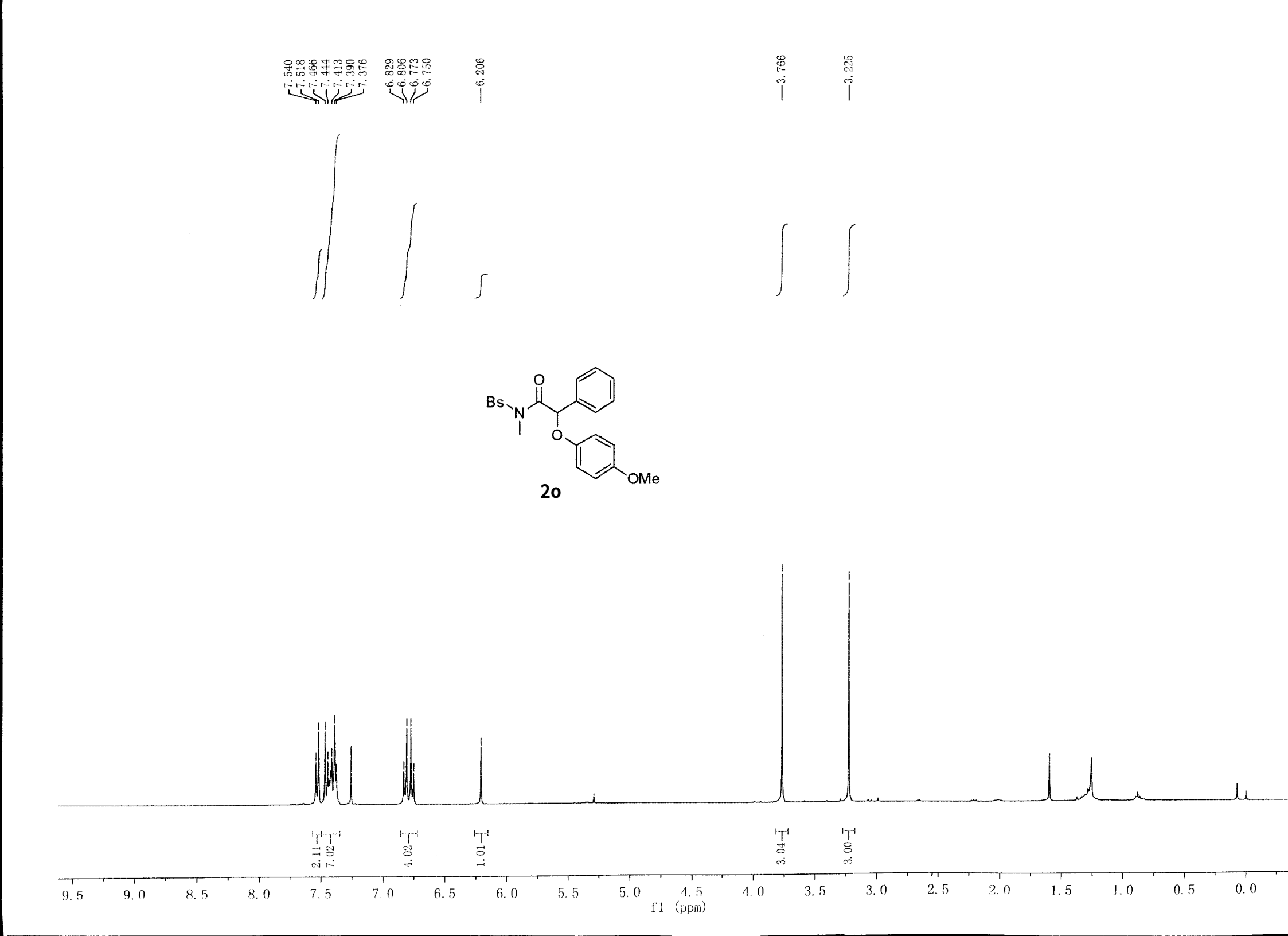
77.3
77.0
76.7
33.1
Bs
N
O
O
Br
2n
f1 (ppm)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6.750
6.206
3.766
3.225
Bs
N
O
O
OMe
2o
2.11
7.02
4.02
1.01
3.04
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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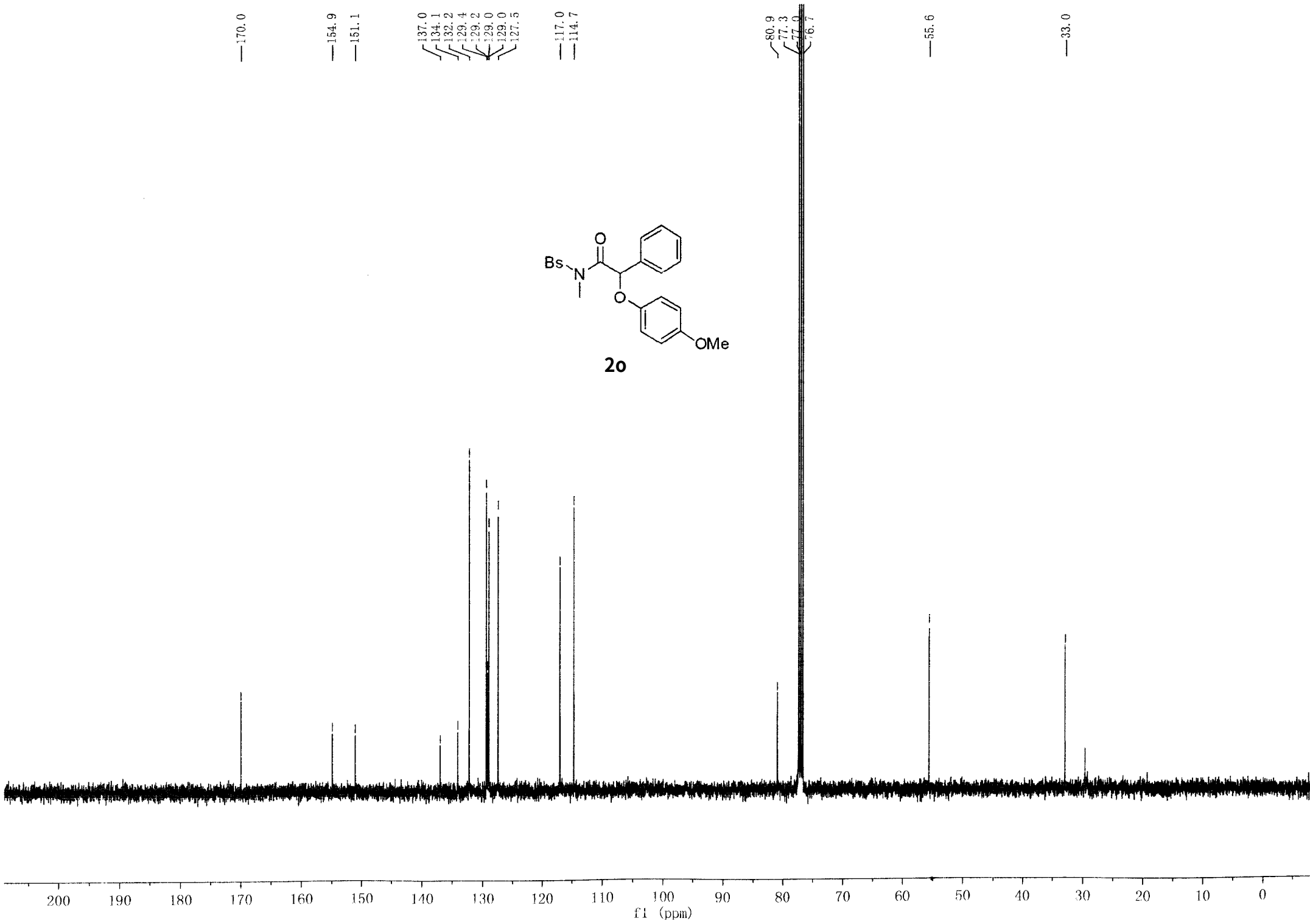
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129.2
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129.0
127.5
117.0
114.7
80.9
77.3
55.6
33.0
Bs
N
O
O
OMe
2o
200
190
180
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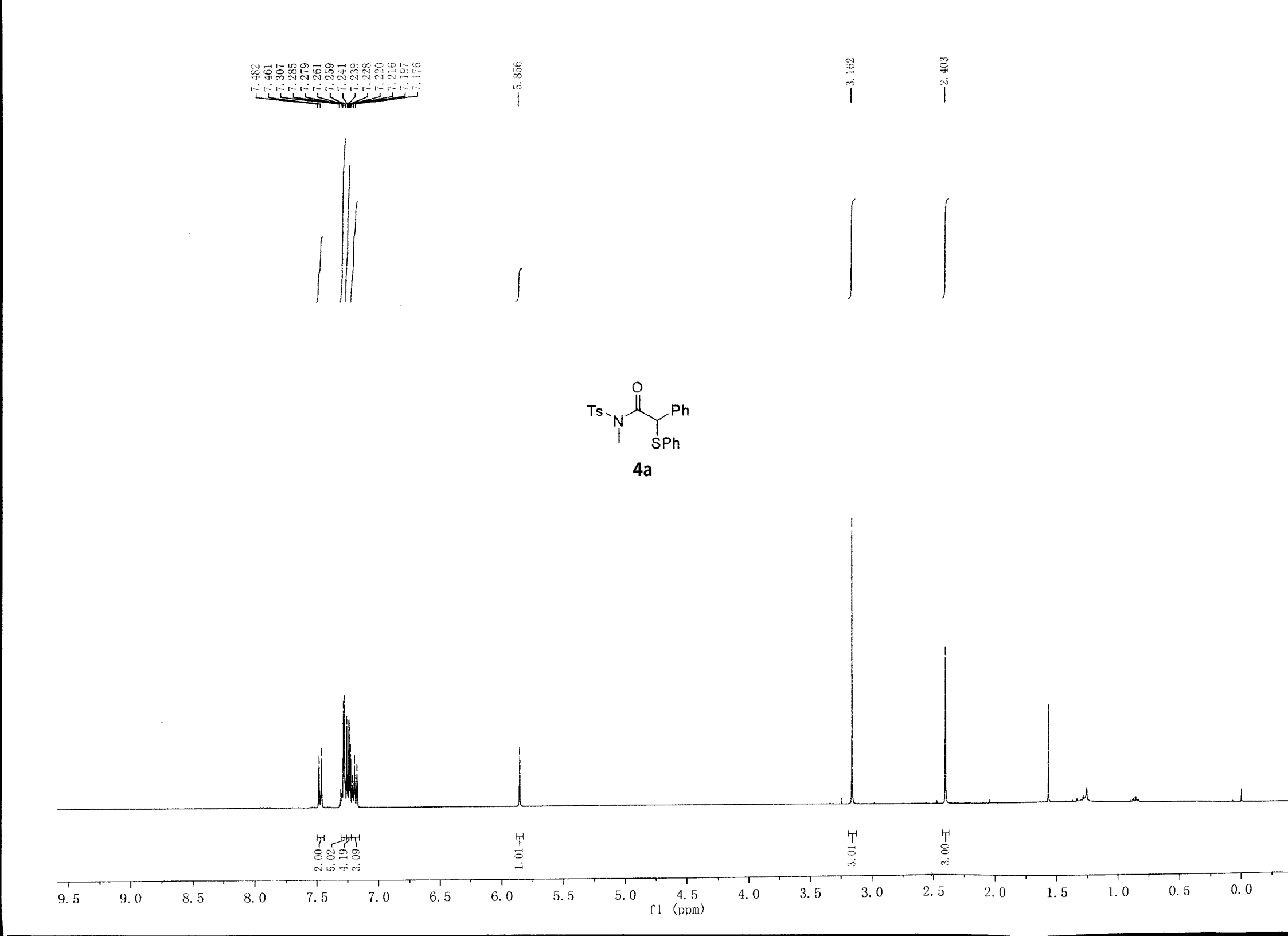
f1 (ppm)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7.225
7.220
7.216
7.197
7.176
5.856
3.162
2.403
Ts
N
O
Ph
SPh
4a
2.00
5.02
4.19
3.09
1.01
3.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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1.5
1.0
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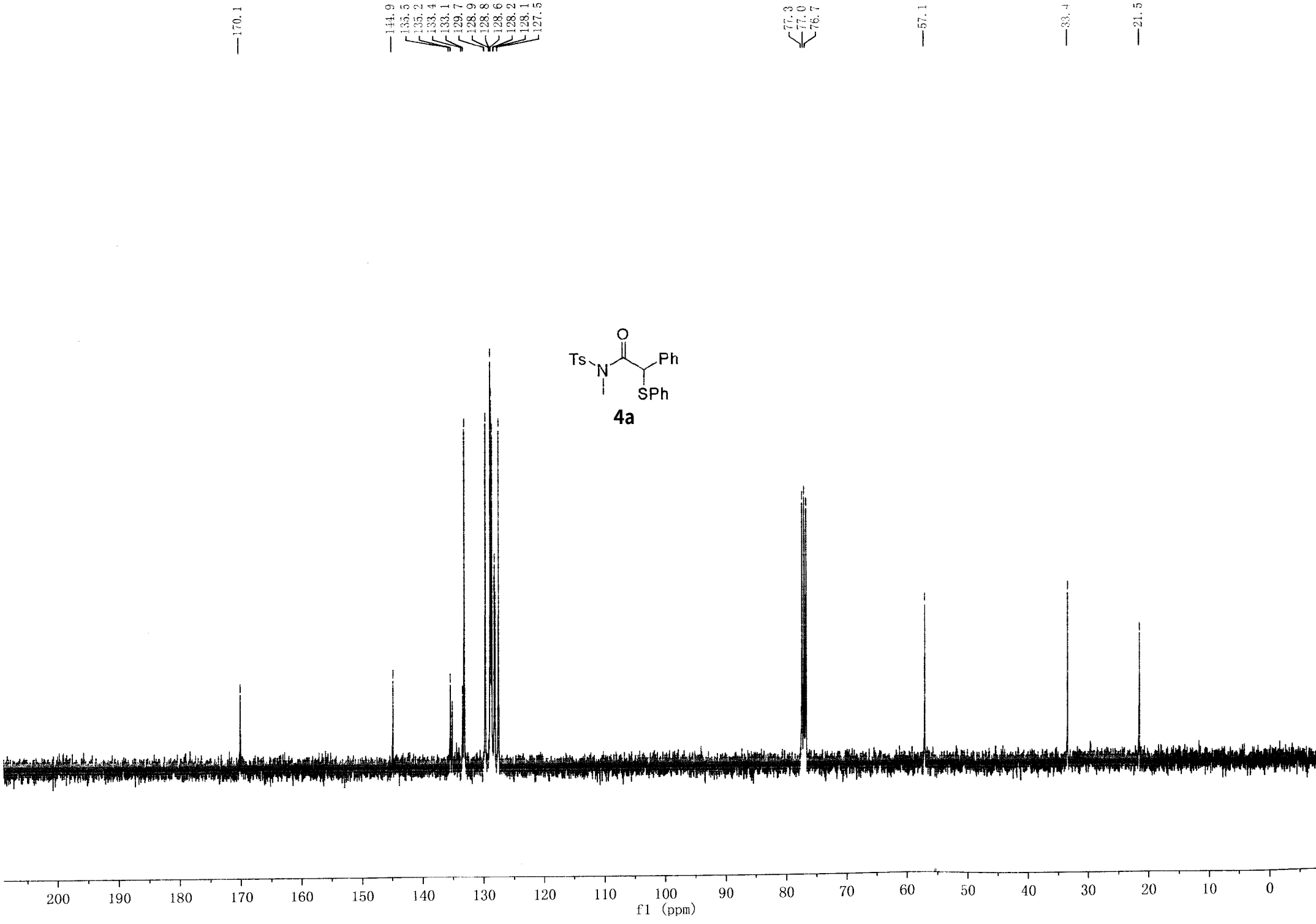
0.0
f1 (ppm)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135.2
133.4
133.1
129.7
128.9
128.8
128.6
128.2
128.1
127.5
77.3
77.0
76.7
57.1
33.4
21.5
Ts
N
O
Ph
SPh
4a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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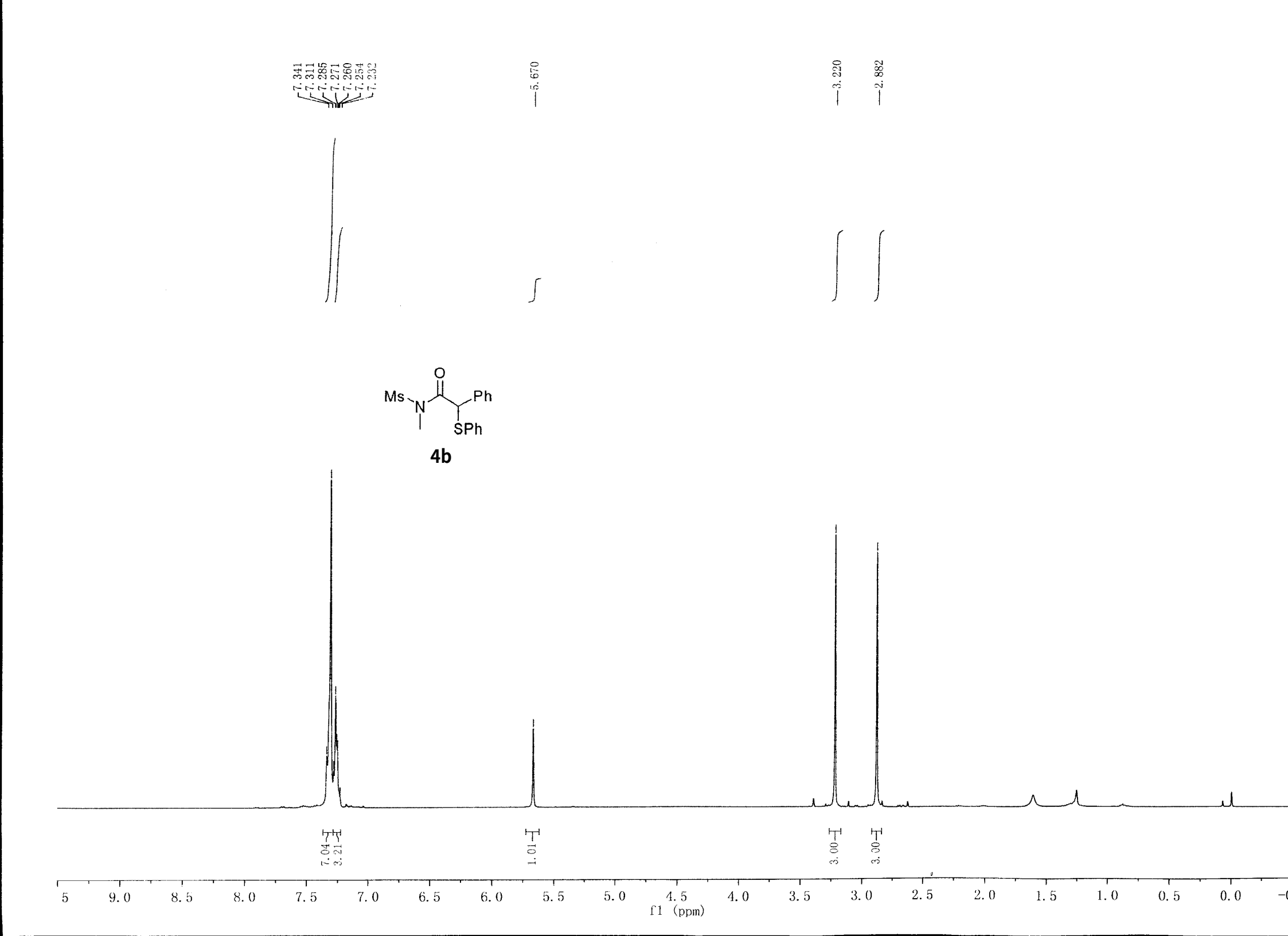
50
40
30
20
10
0
f1 (ppm)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7.254
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O
Ph
SPh
4b
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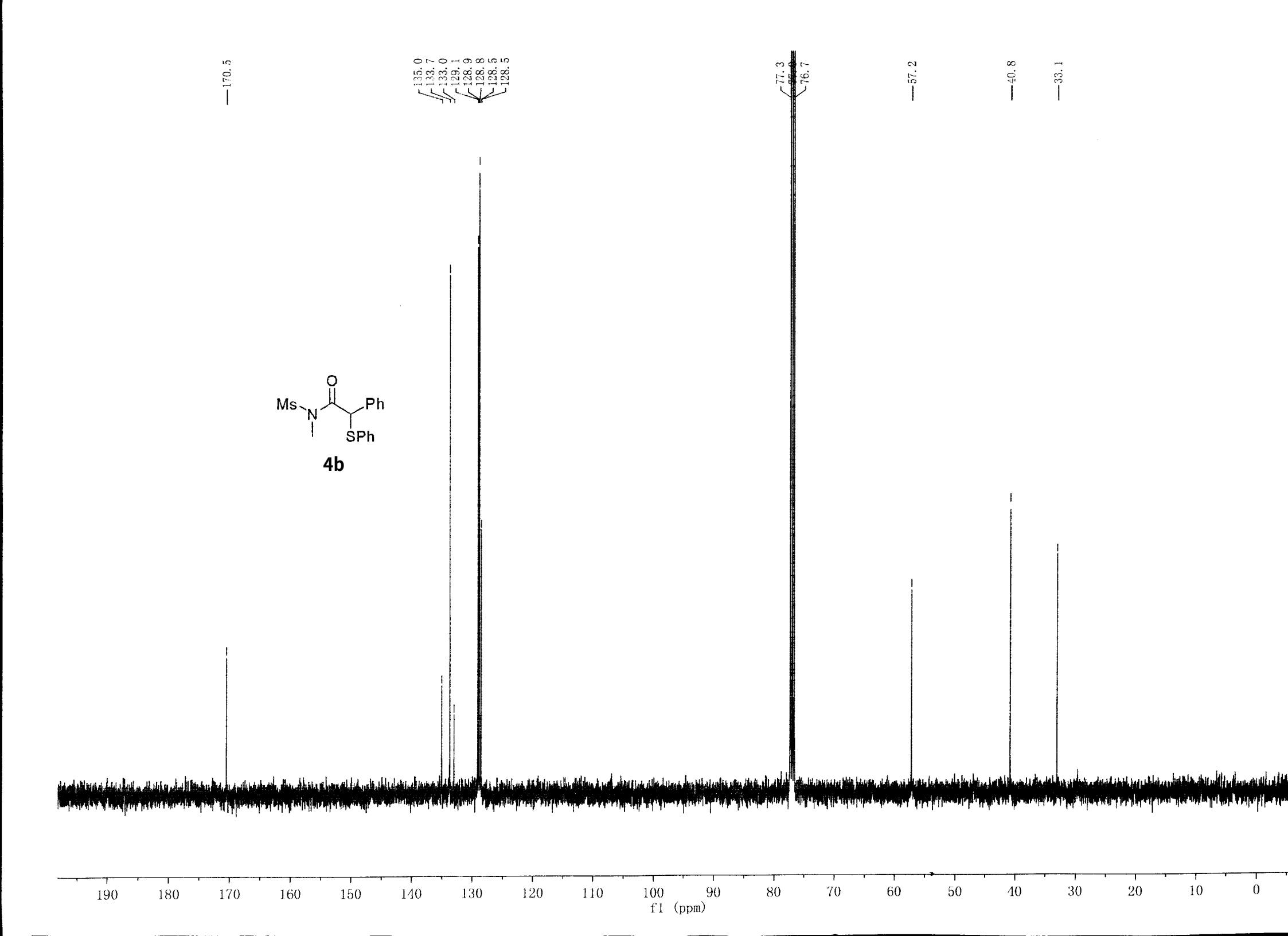
1.01
3.00
3.00
f1 (ppm)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135.0
133.7
133.0
129.1
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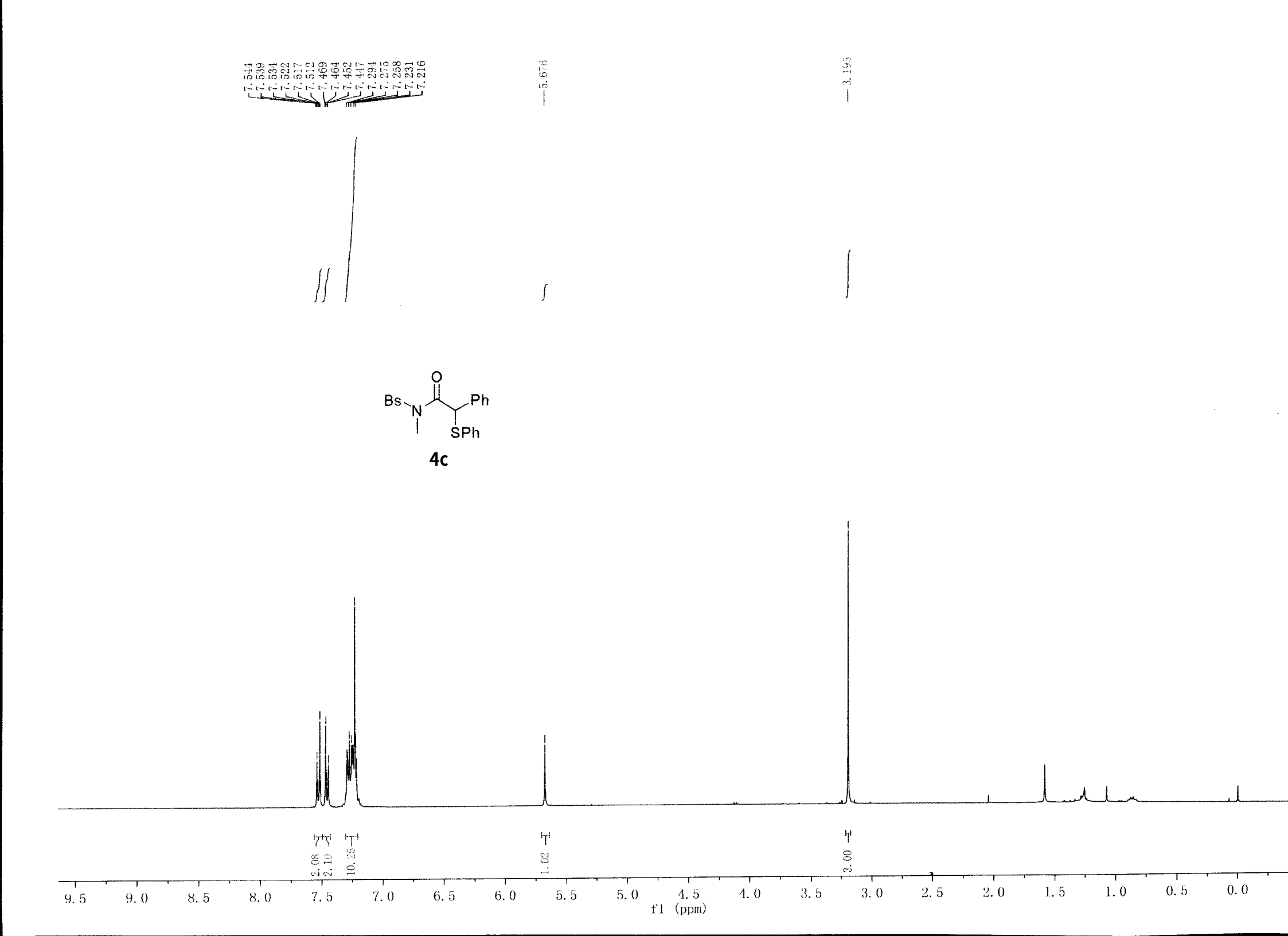
128.8
128.5
128.5
77.3
76.7
57.2
40.8
33.1
Ms
N
O
Ph
SPh
4b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.275
7.258
7.231
7.216
5.675
3.195
Bs
N
O
Ph
SPh
4c
2.08
2.10
10.25
1.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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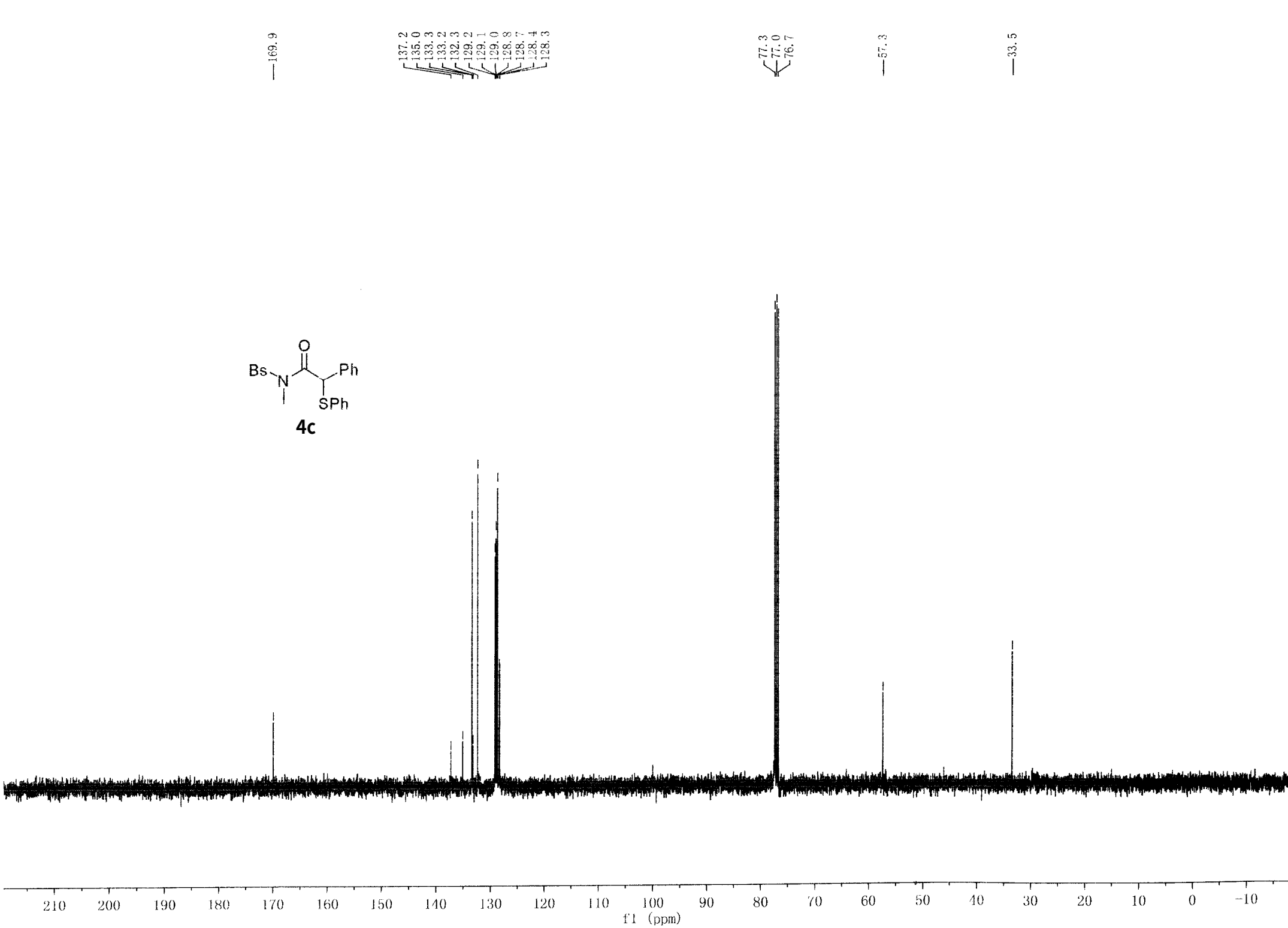
0.0
f1 (ppm)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129.1
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128.7
128.4
128.3
77.3
77.0
76.7
57.3
33.5
Bs
N
O
Ph
SPh
4c
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
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40
30
20
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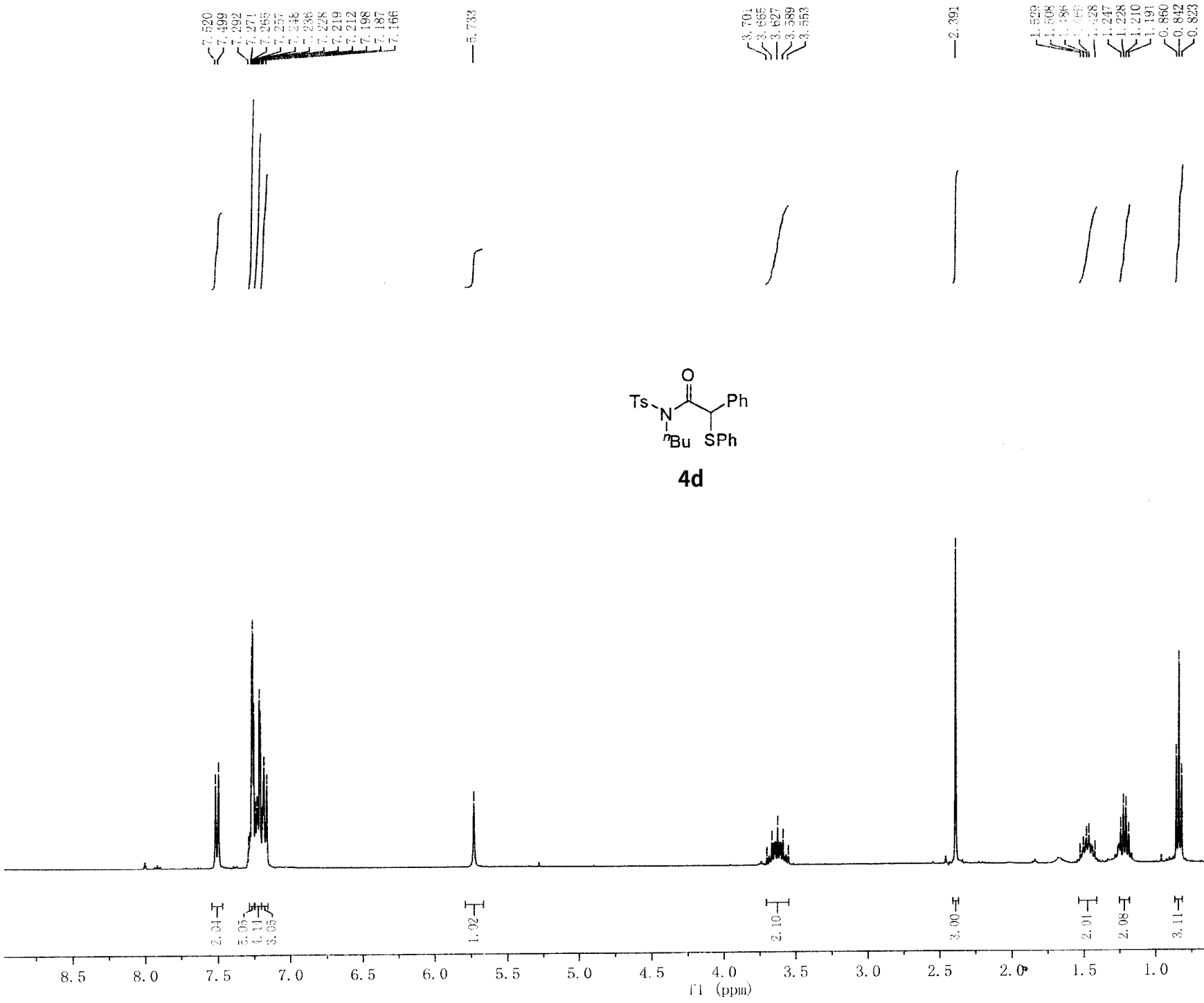
0
-10
f1 (ppm)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7.238
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7.212
7.198
7.187
7.166
5.733
3.701
3.665
3.627
3.589
3.553
2.391
1.529
1.508
1.247
1.228
1.210
1.191
0.860
0.842
0.823
O
Ts
N
Ph
nBu
SPh
4d
2.04
3.05
4.11
3.05
1.92
2.10
3.00
2.01
2.08
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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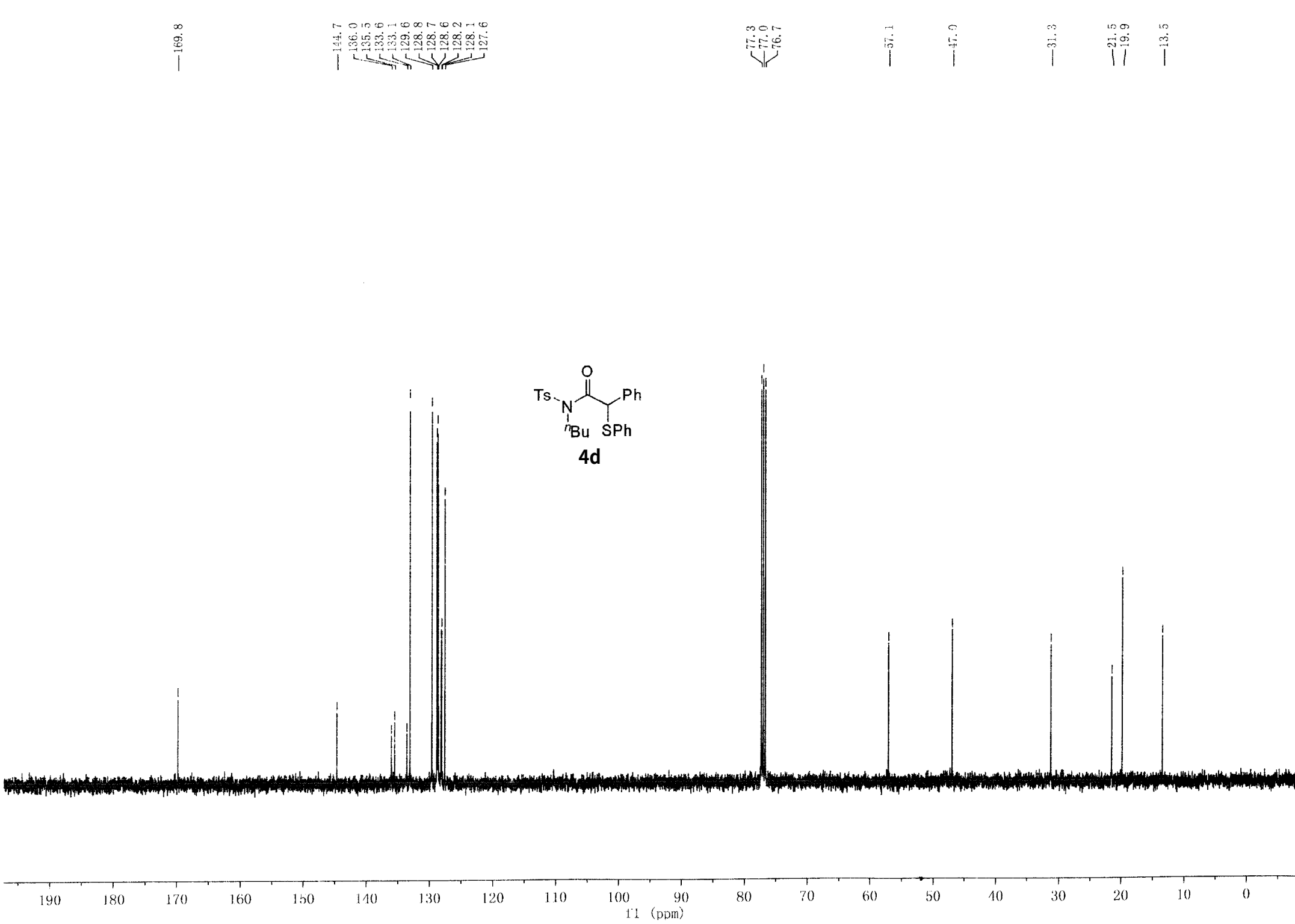
0.5
0.0
-0.5
f1 (ppm)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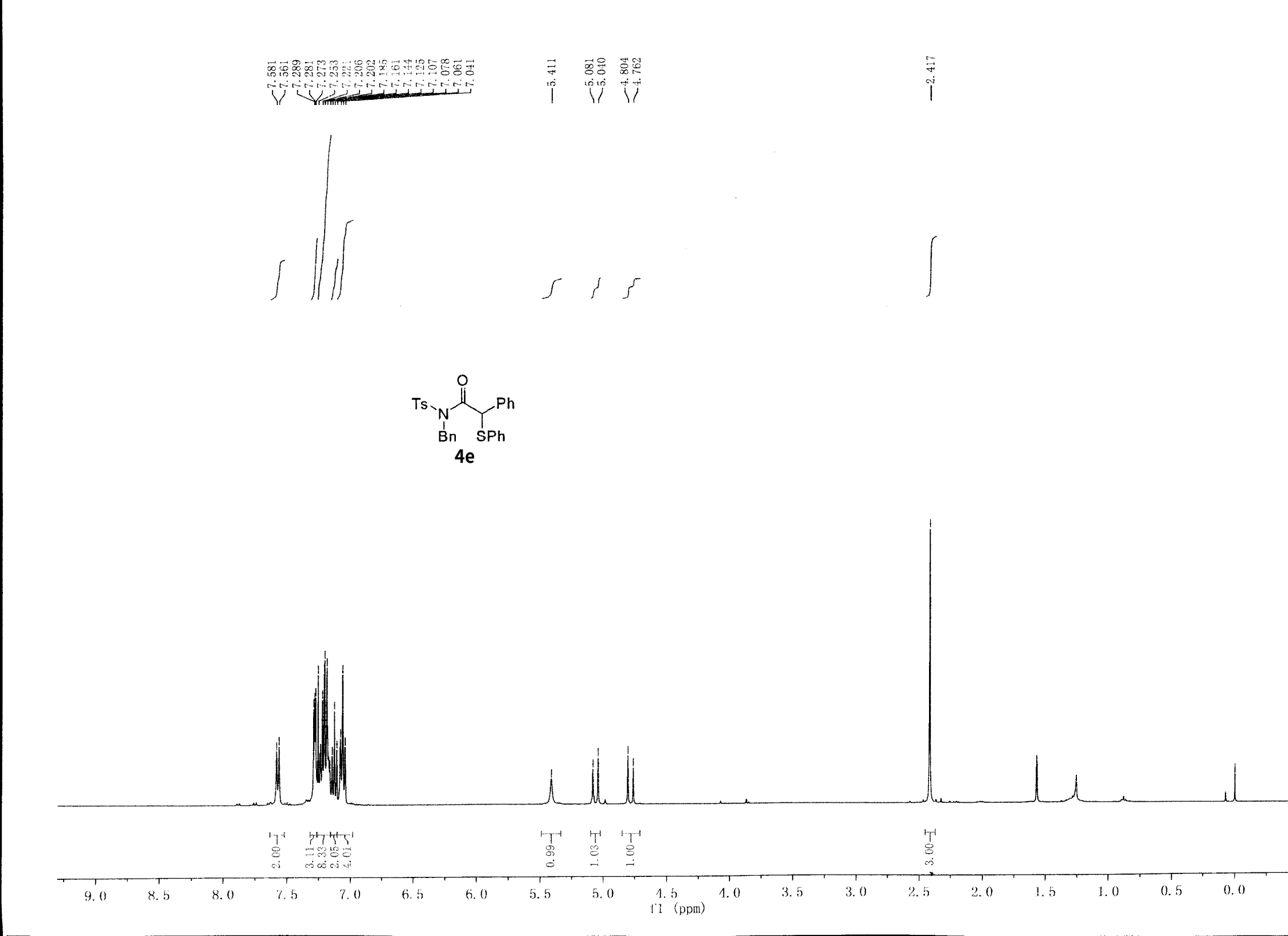
128.6
128.2
128.1
127.6
77.3
77.0
76.7
57.1
47.0
31.3
21.5
19.9
13.5
Ts
N
O
Ph
nBu
SPh
4d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.107
7.078
7.061
7.041
5.411
5.081
5.040
4.804
4.762
2.417
O
Ts
N
Ph
Bn
SPh
4e
2.00
3.11
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2.05
2.01
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1.03
1.00
3.00
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8.0
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7.0
6.5
6.0
5.5
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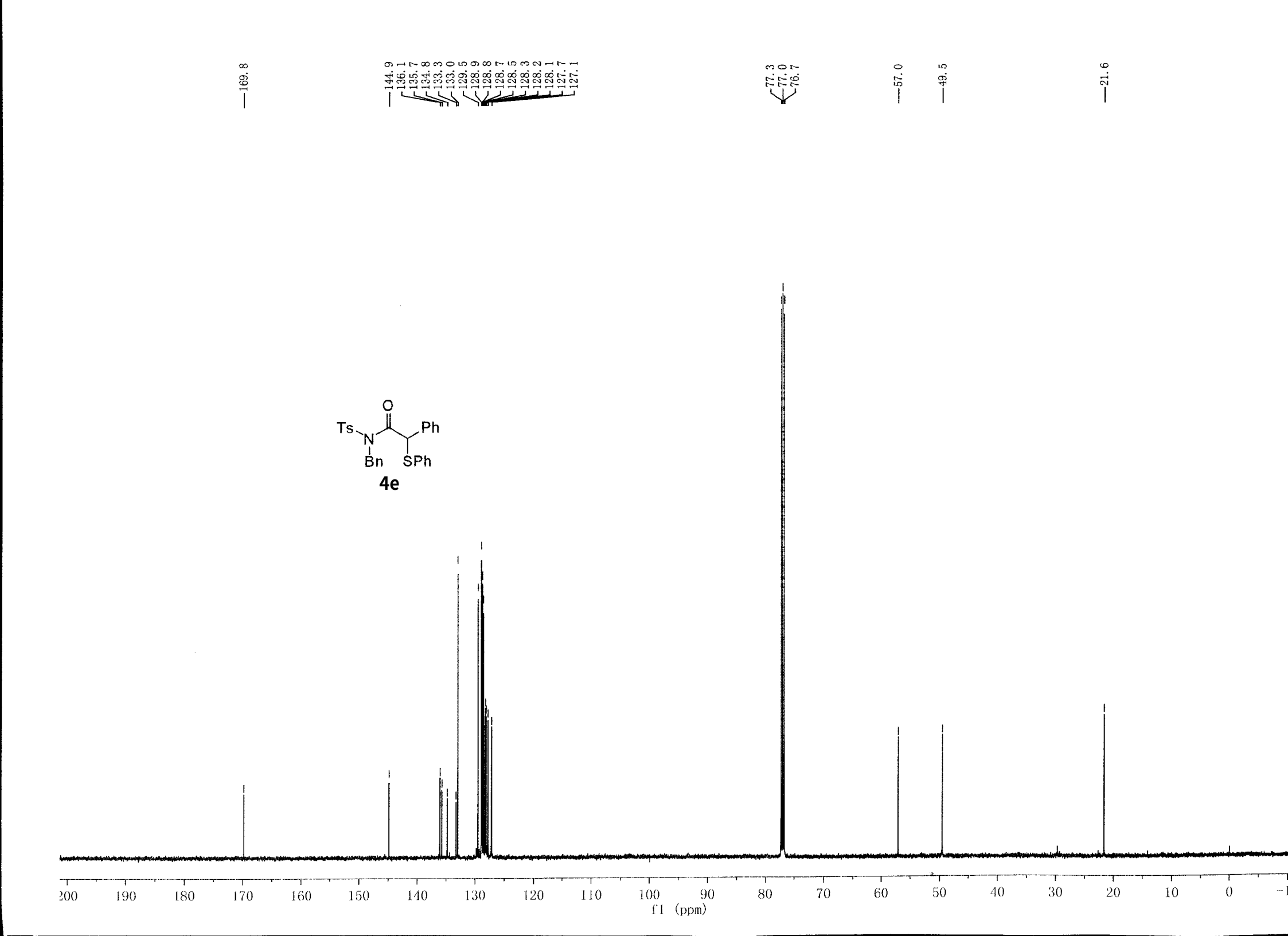
f1 (ppm)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128.5
128.3
128.2
128.1
127.7
127.1
77.3
77.0
76.7
57.0
49.5
21.6
Ts
N
Bn
O
Ph
SPh
4e
200
190
180
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130
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90
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50
40
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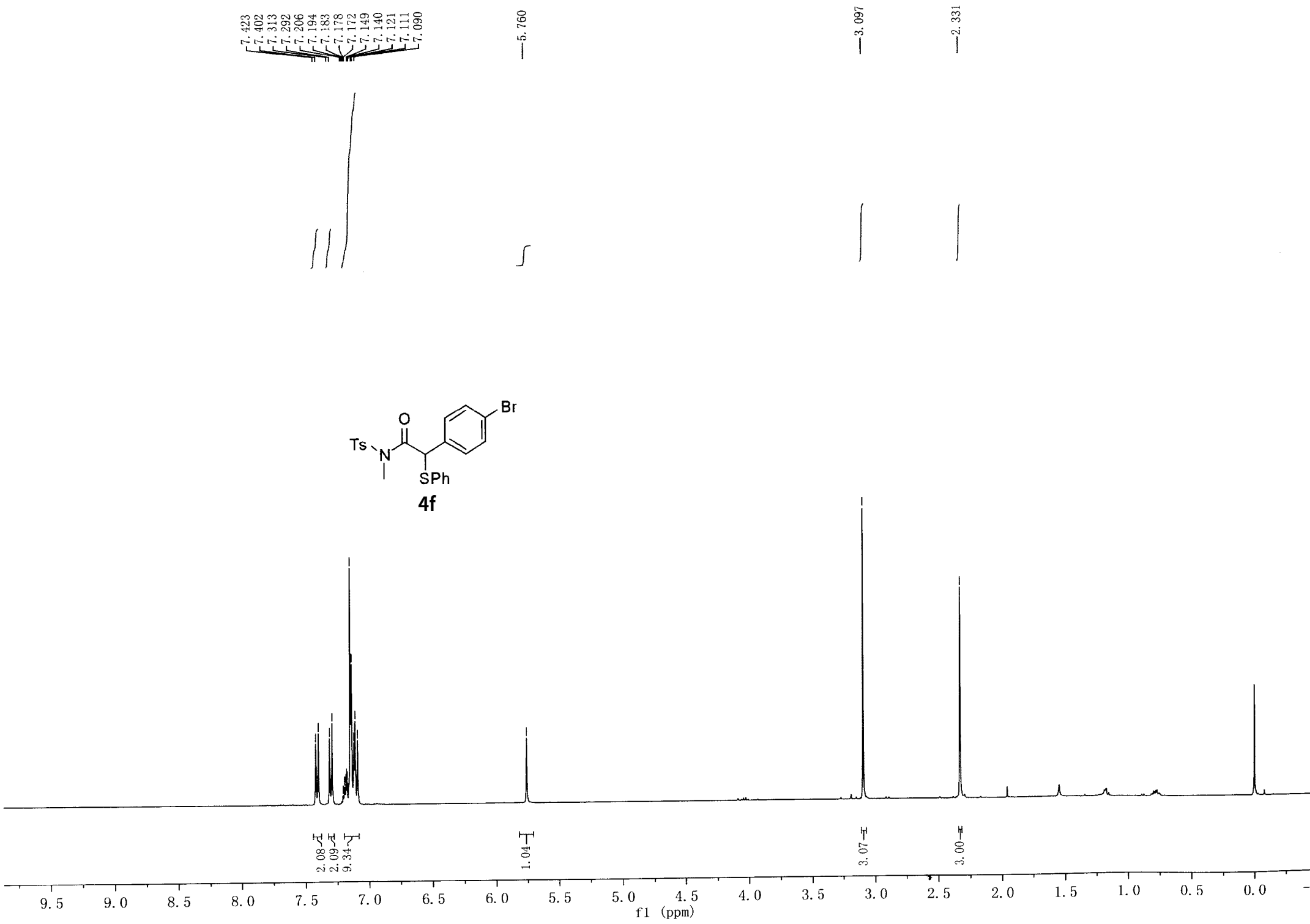
f1 (ppm)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3.097
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Br
O
Ts
N
SPh
4f
2.08
2.09
9.34
1.04
3.07
3.00
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6.0
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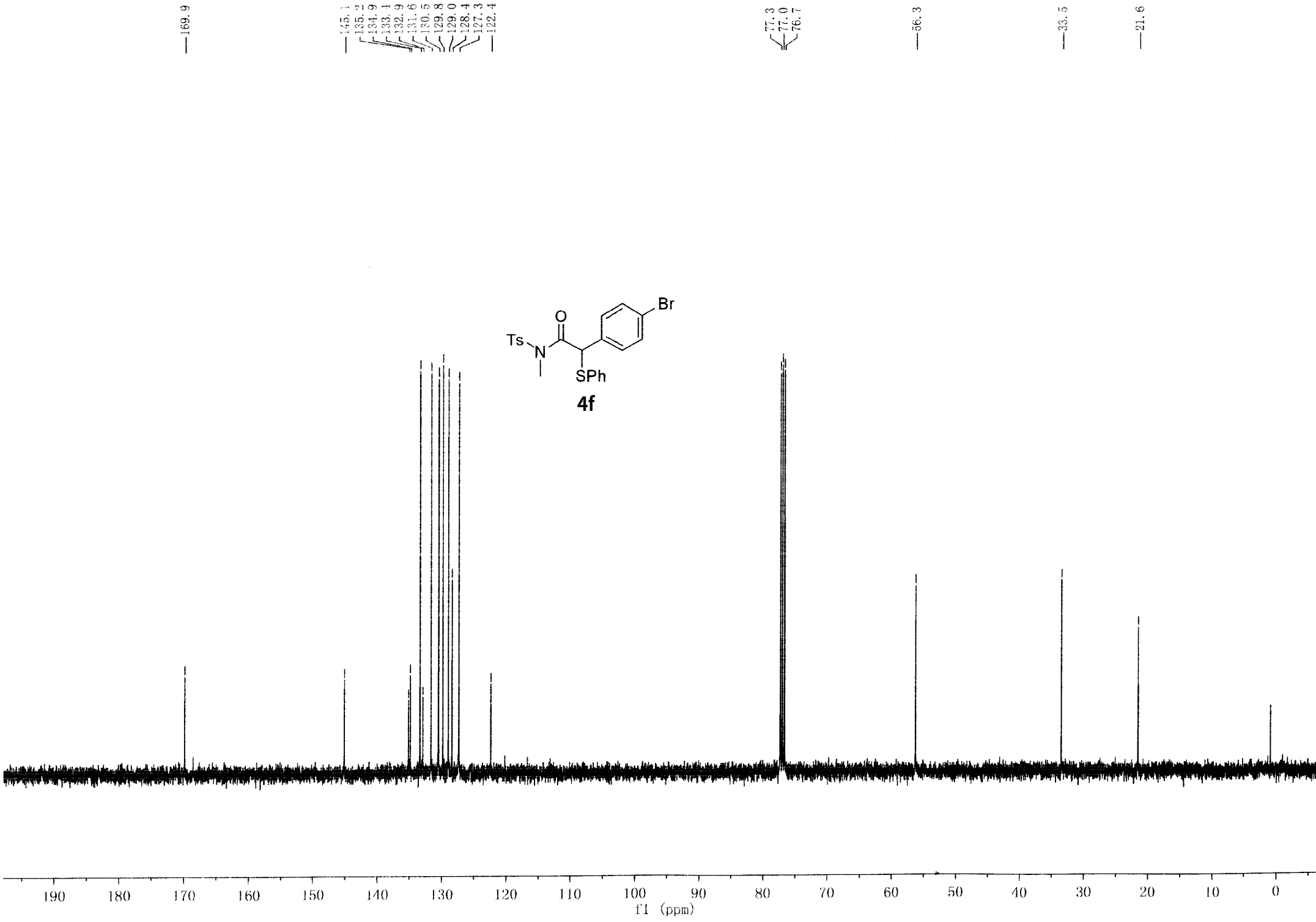
f1 (ppm)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122.4
77.3
77.0
76.7
56.3
33.5
21.6
Br
O
Ts
N
SPh
4f
190
180
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130
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110
100
90
80
70
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50
40
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10
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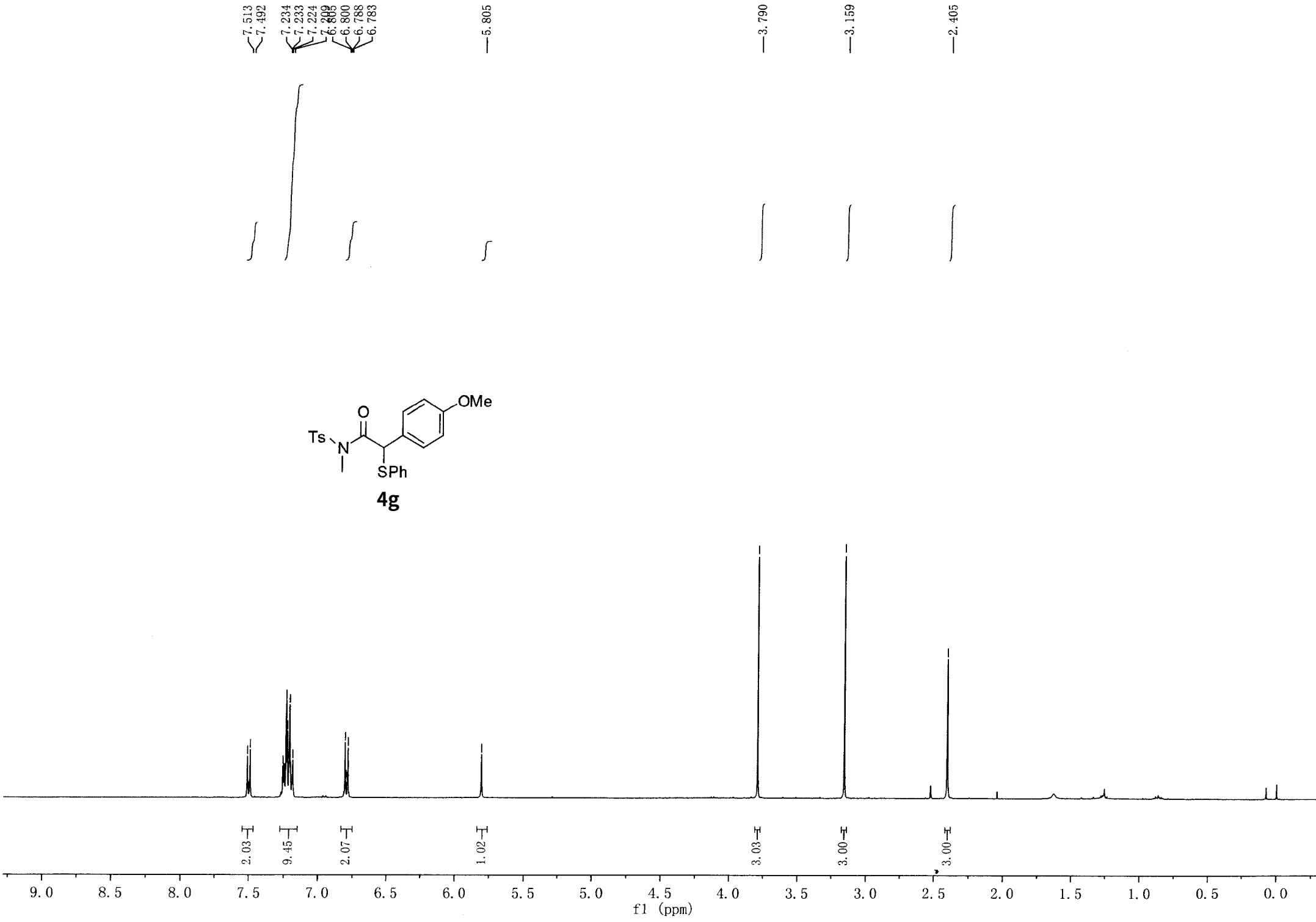
f1 (ppm)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OMe
O
Ts
N
SPh
4g
2.03
9.45
2.07
1.02
3.03
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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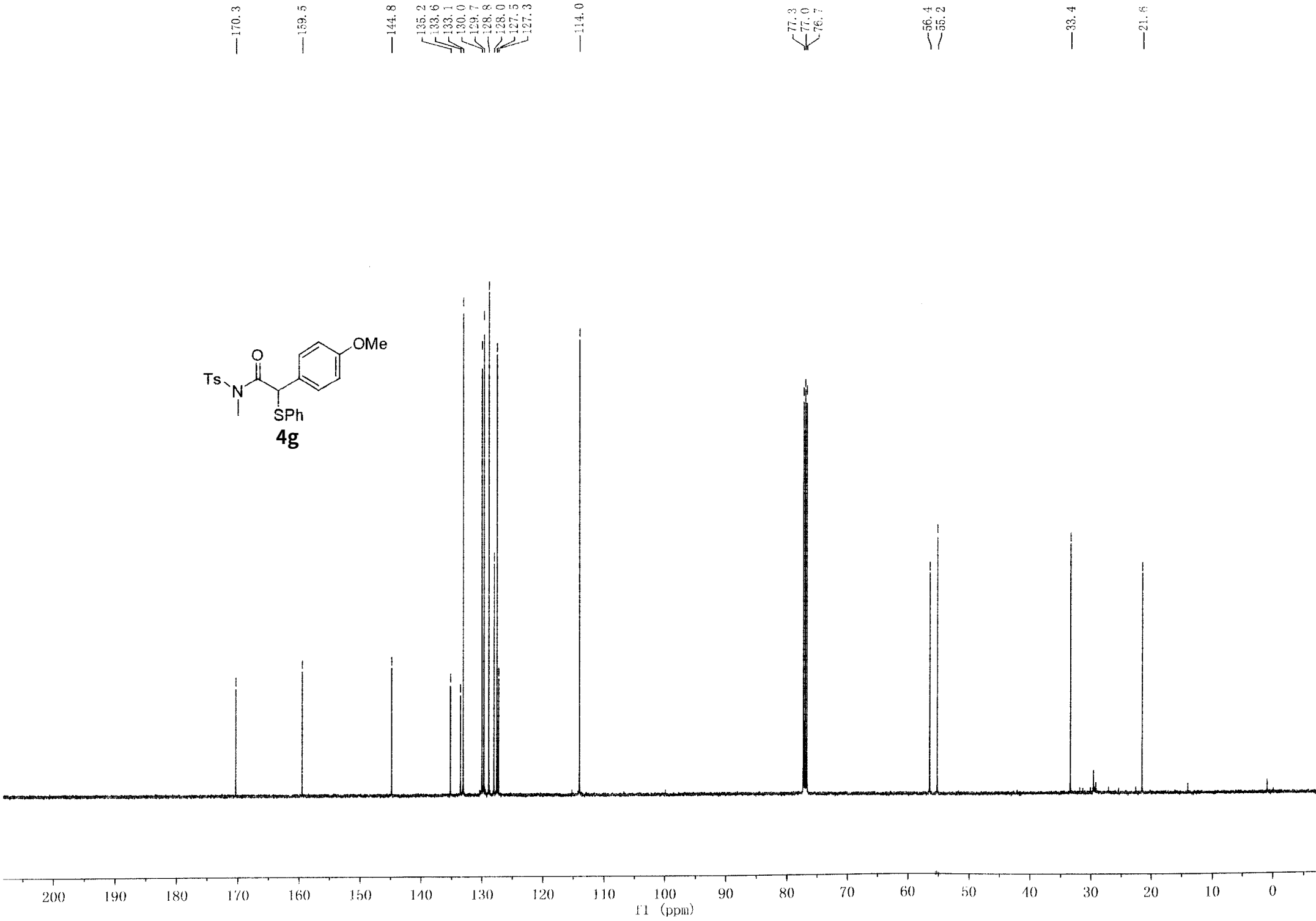
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127.5
127.3
114.0
77.3
77.0
76.7
56.4
55.2
33.4
21.6
OMe
O
Ts
N
SPh
4g
200
190
180
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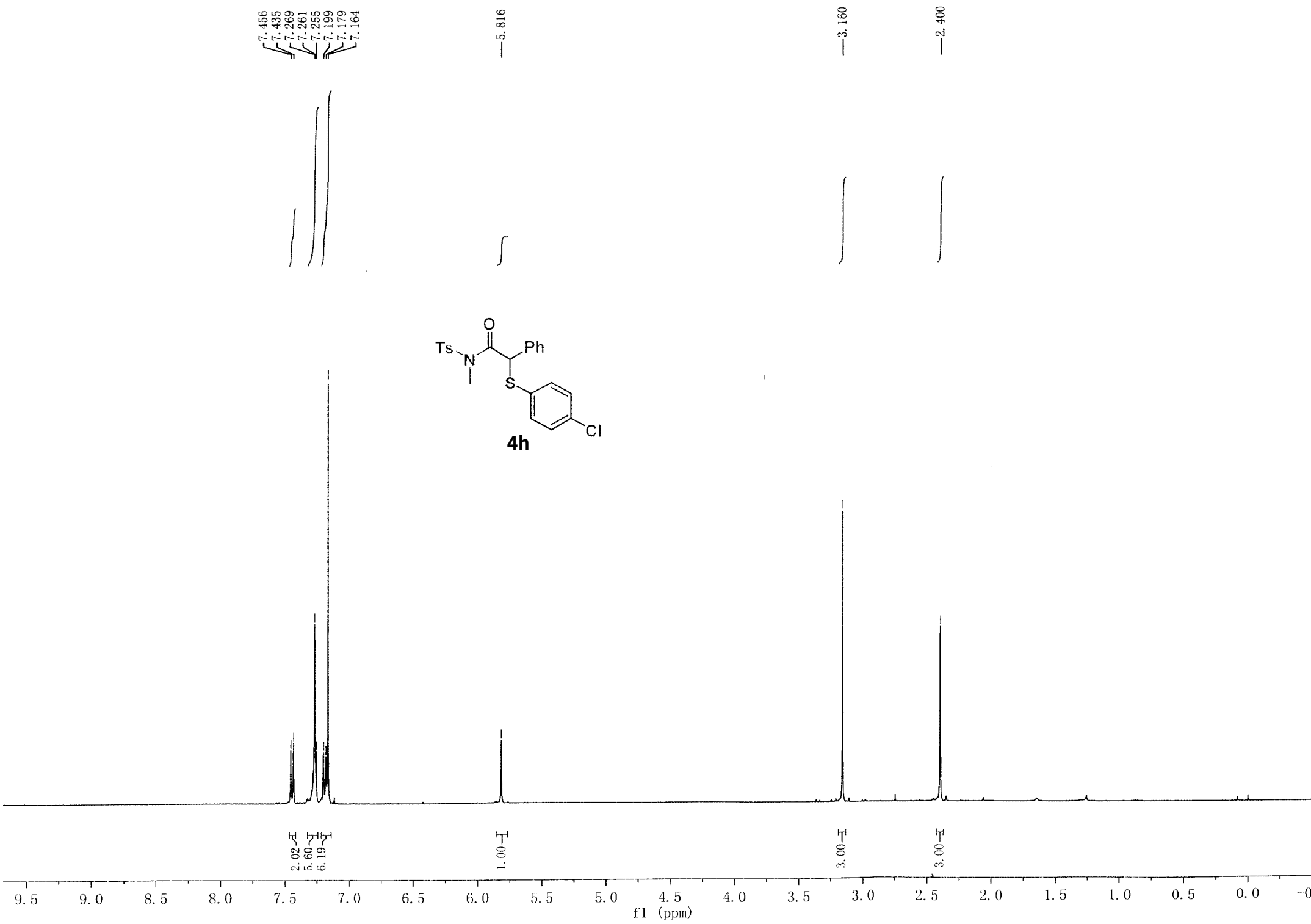
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O
Ts
N
Ph
S
Cl
4h
2.02
5.60
6.19
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3.00
3.00
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8.0
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7.0
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6.0
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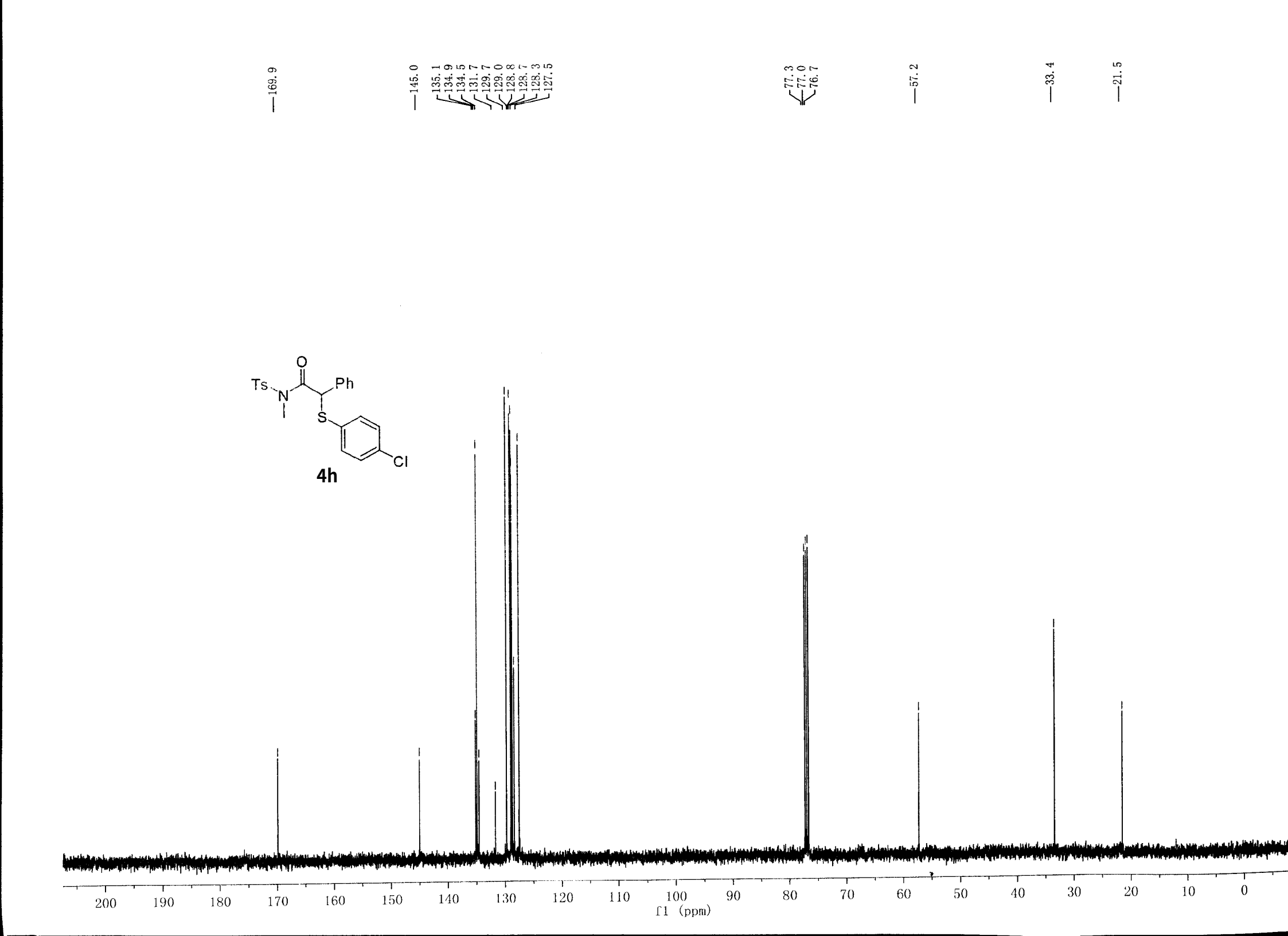
f1 (ppm)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77.3
77.0
76.7
57.2
33.4
21.5
O
Ts
N
Ph
S
Cl
4h
200
190
180
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110
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90
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10
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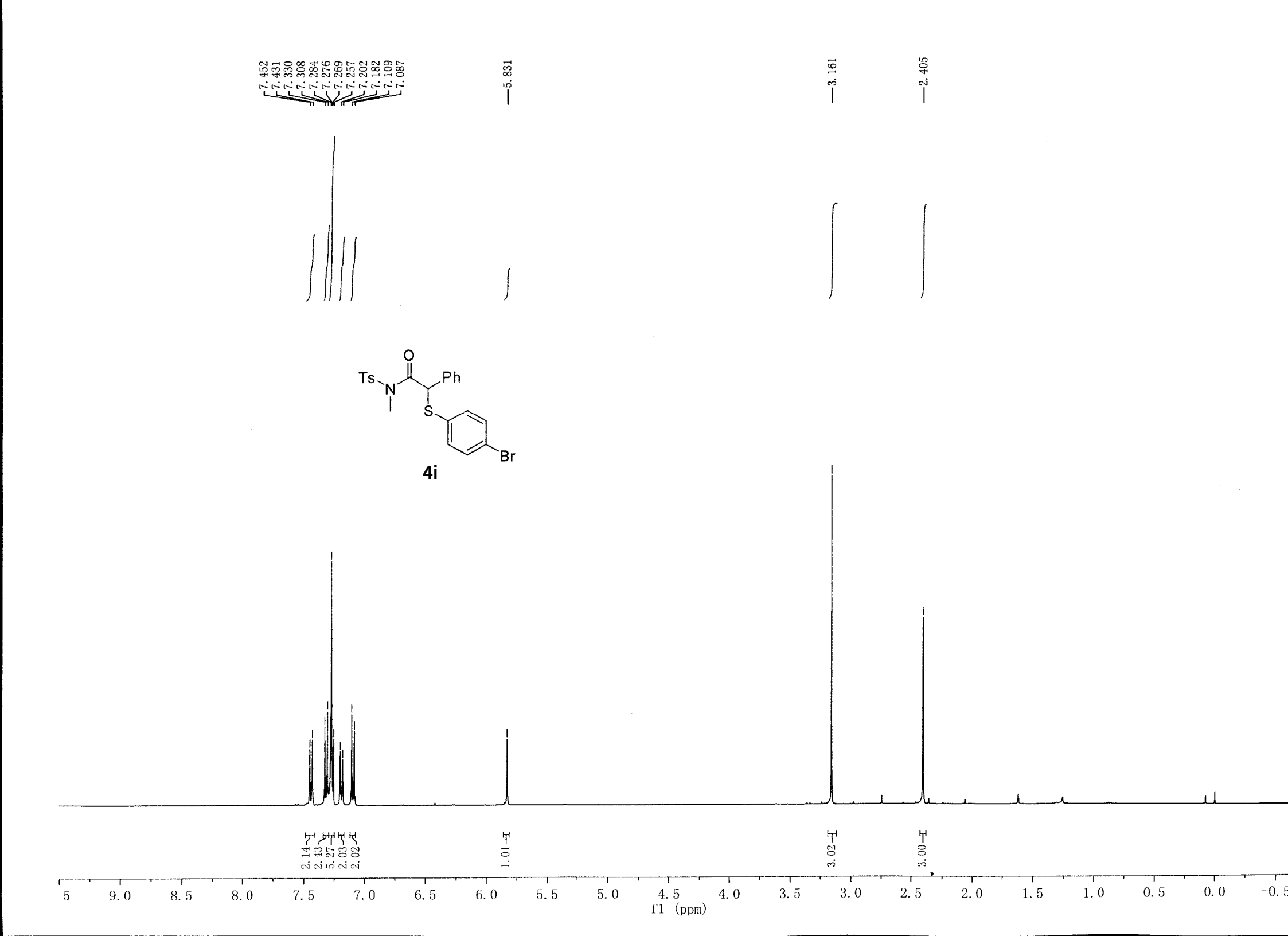
f1 (ppm)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3.161
2.405
O
Ts
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Ph
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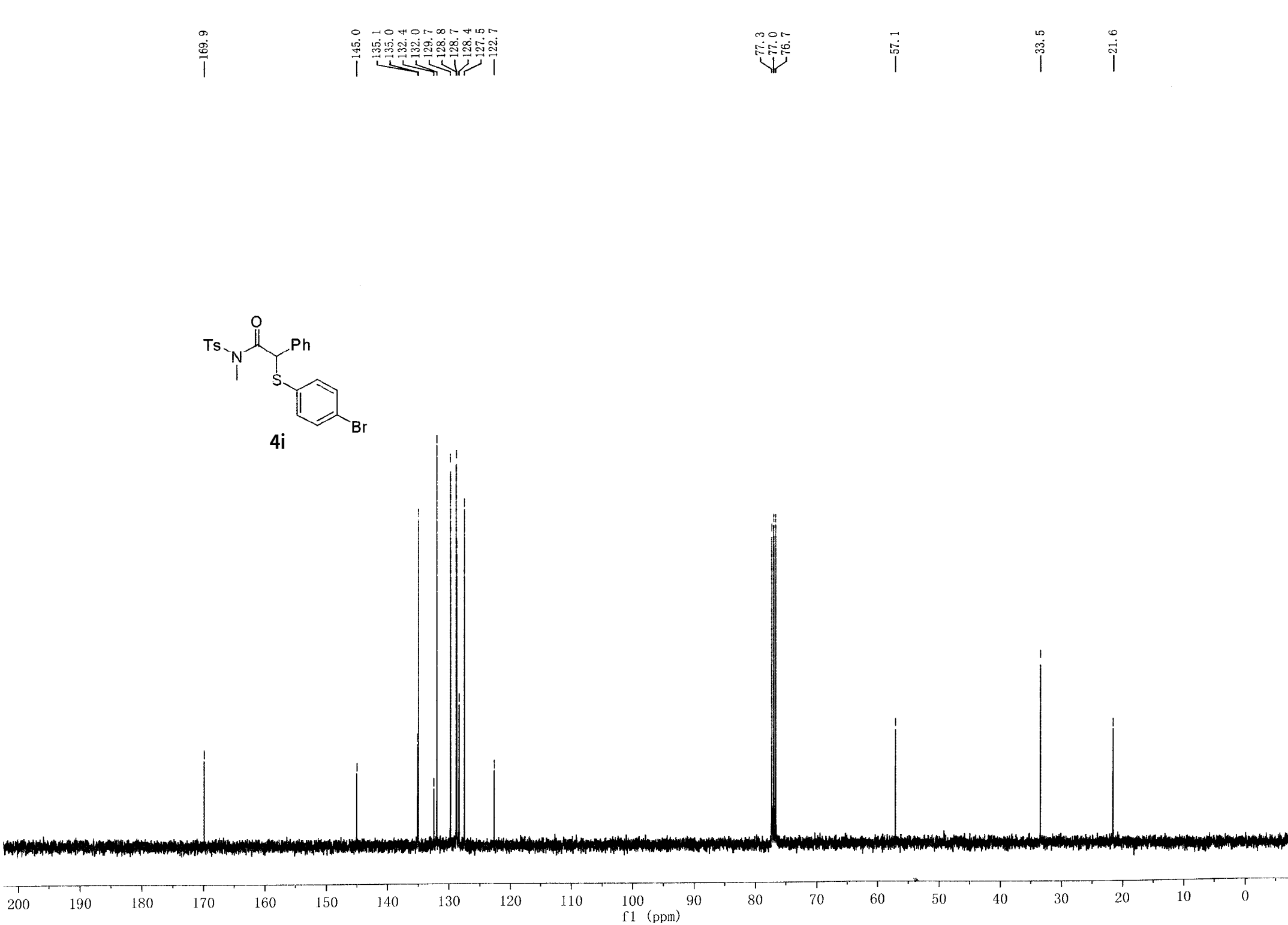
1.01
3.02
3.00
f1 (ppm)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77.3
77.0
76.7
57.1
33.5
21.6
O
Ts
N
Ph
S
Br
4i
200
190
180
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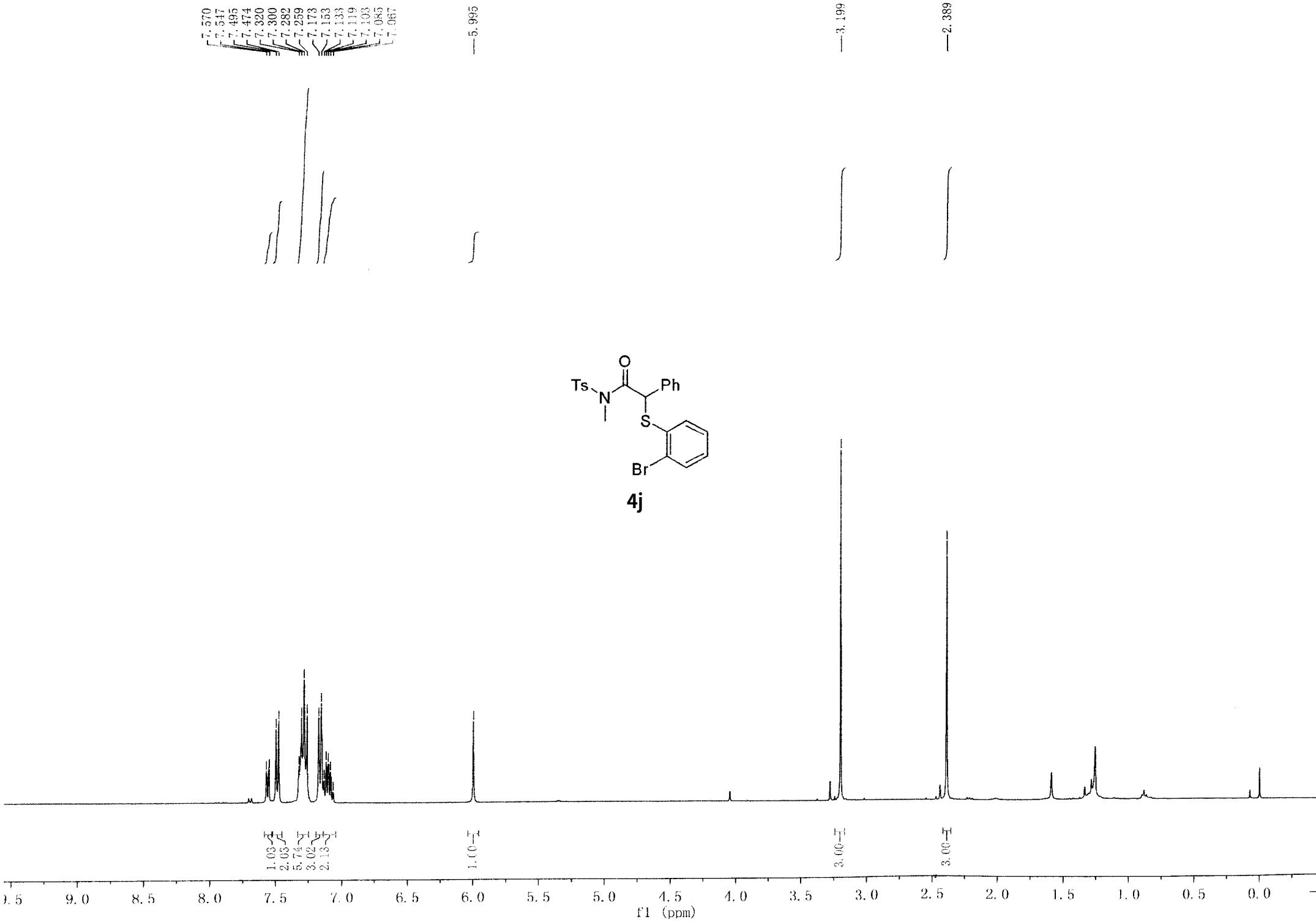
f1 (ppm)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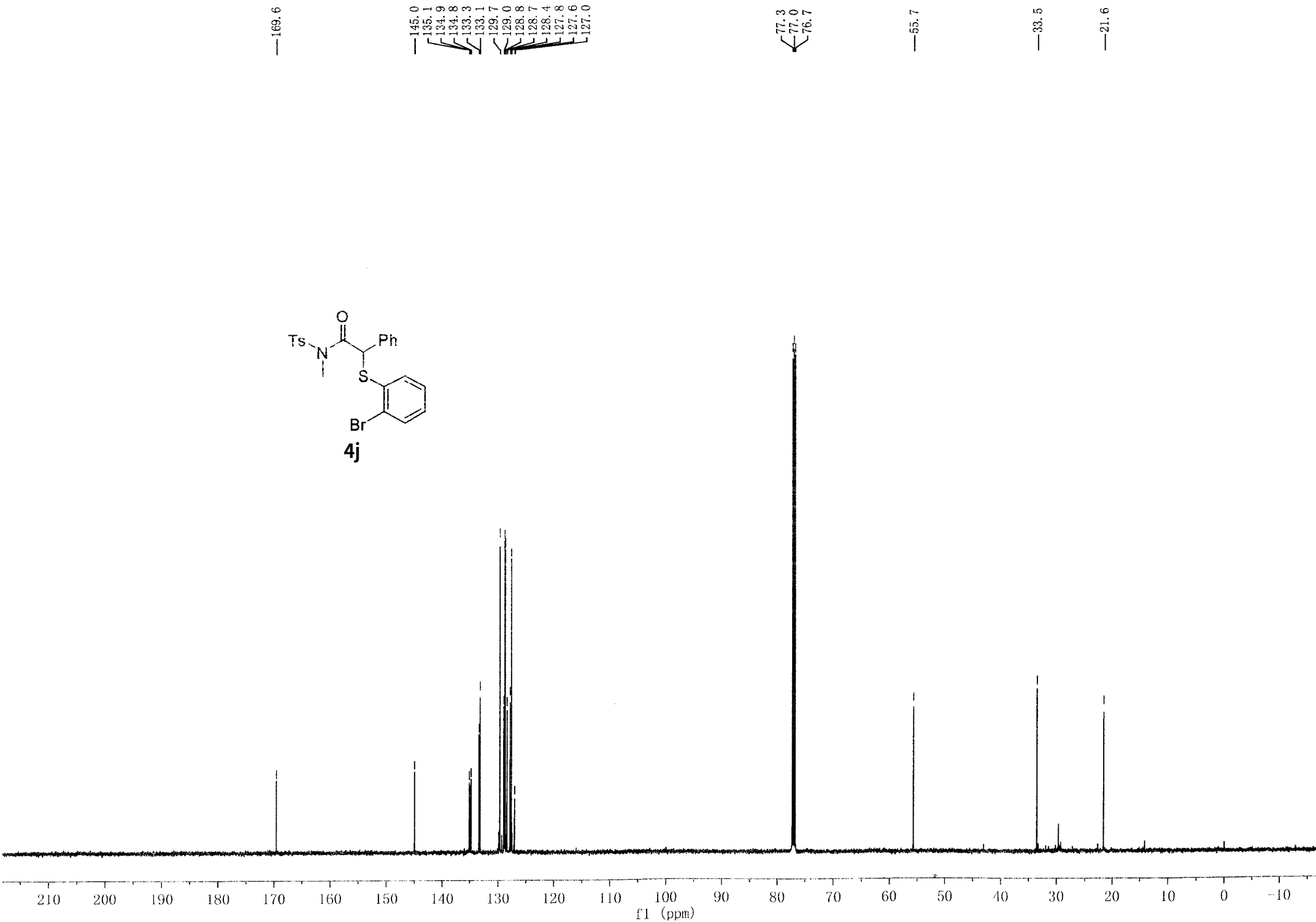
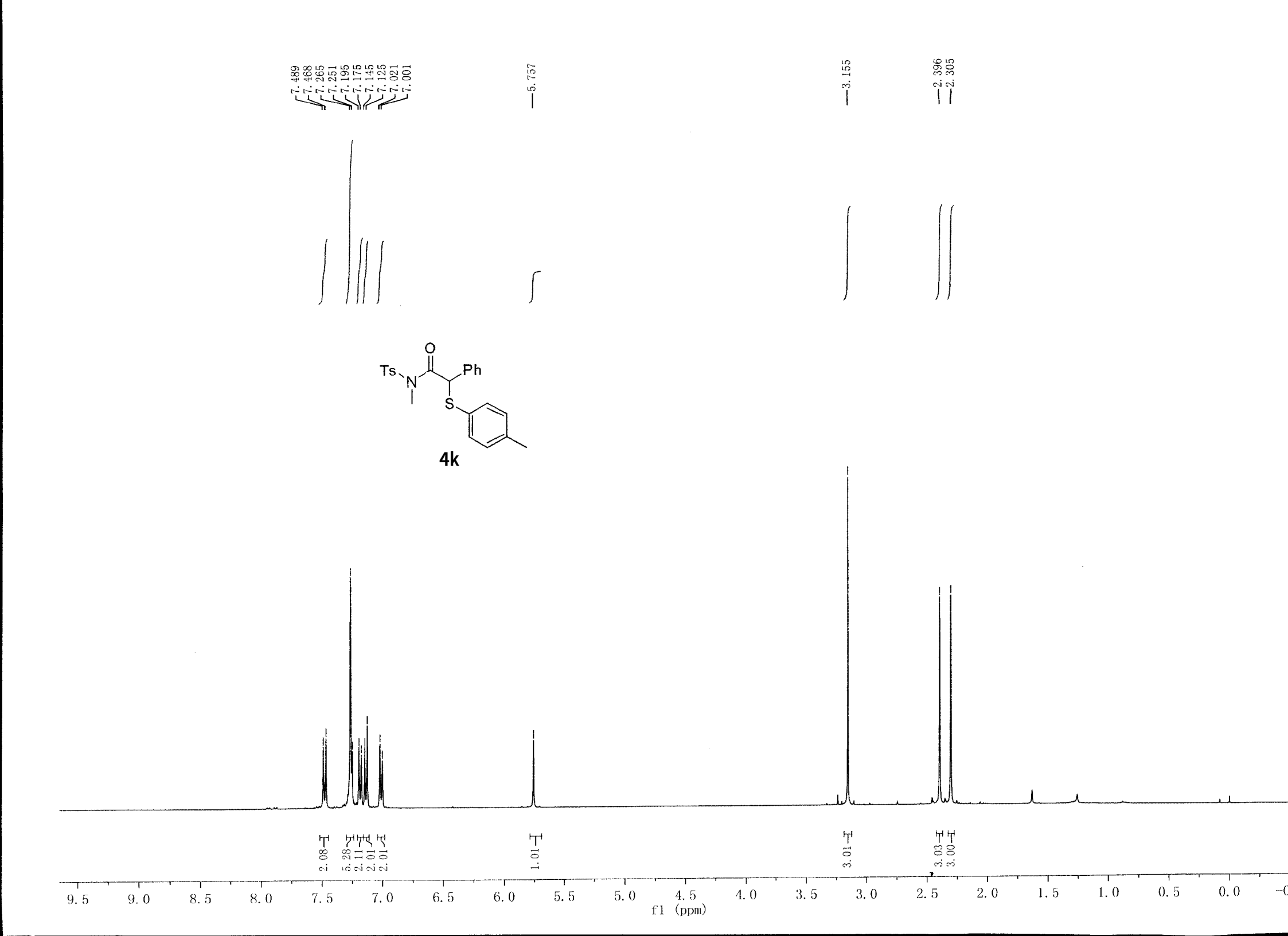
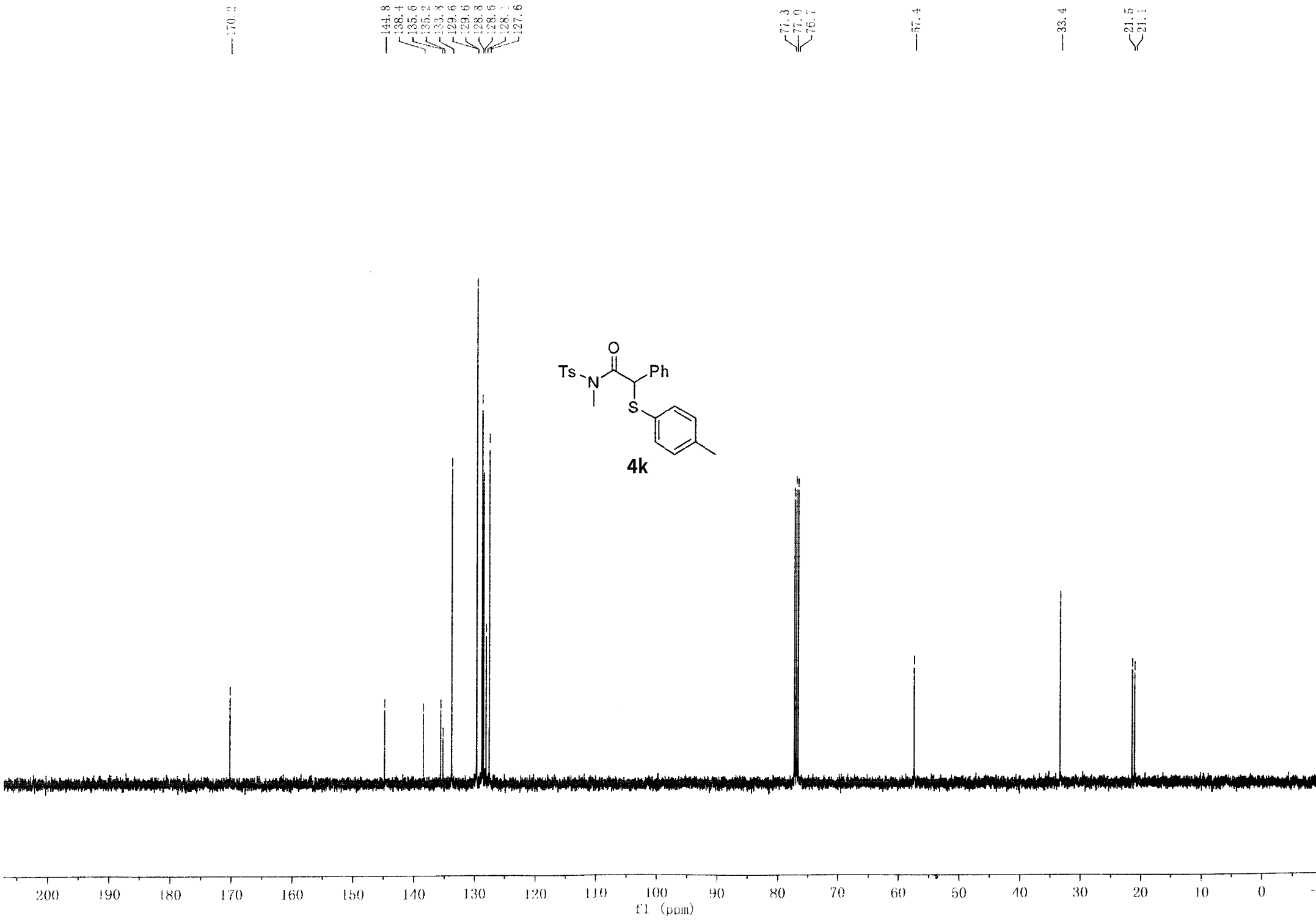
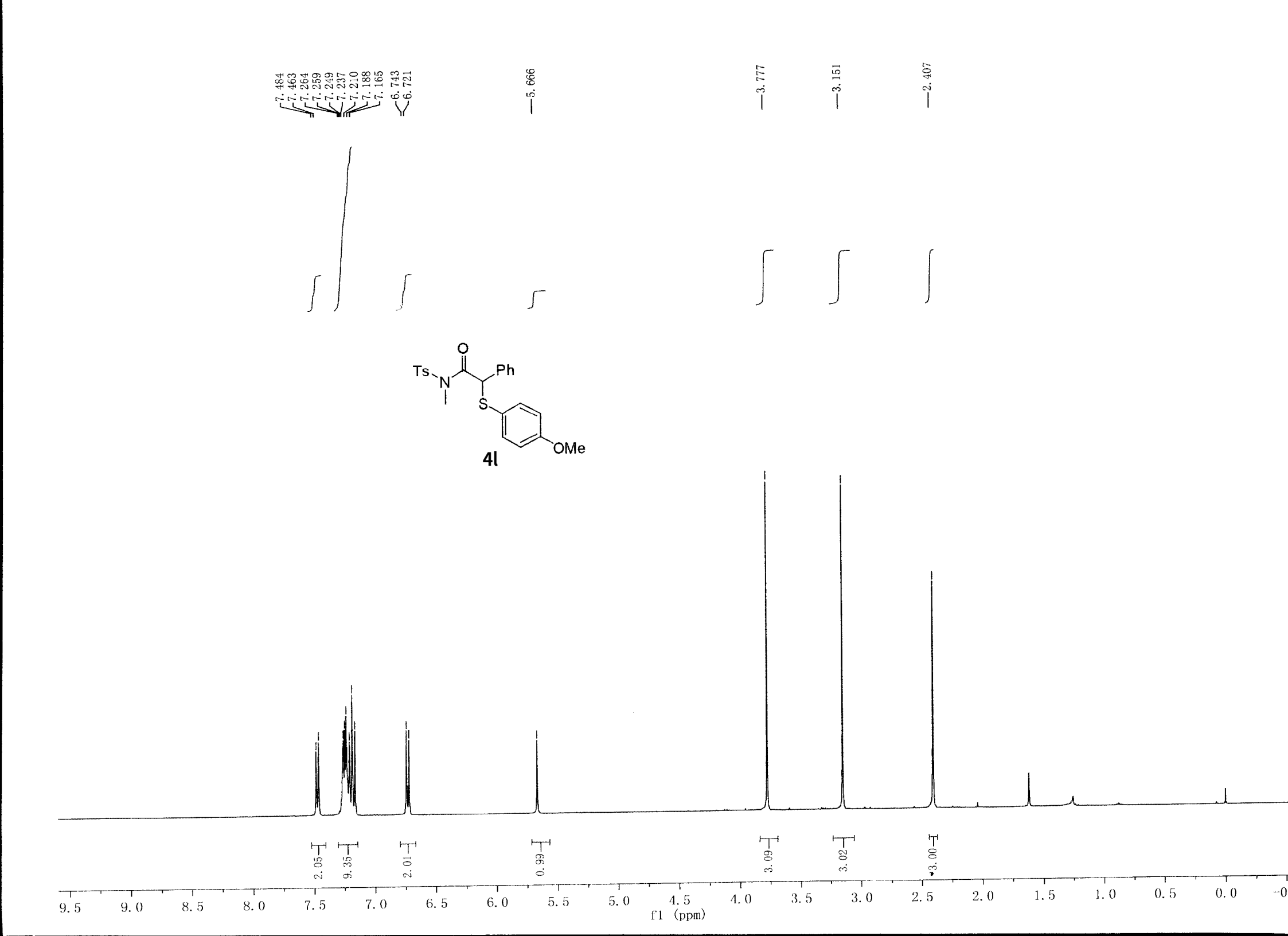
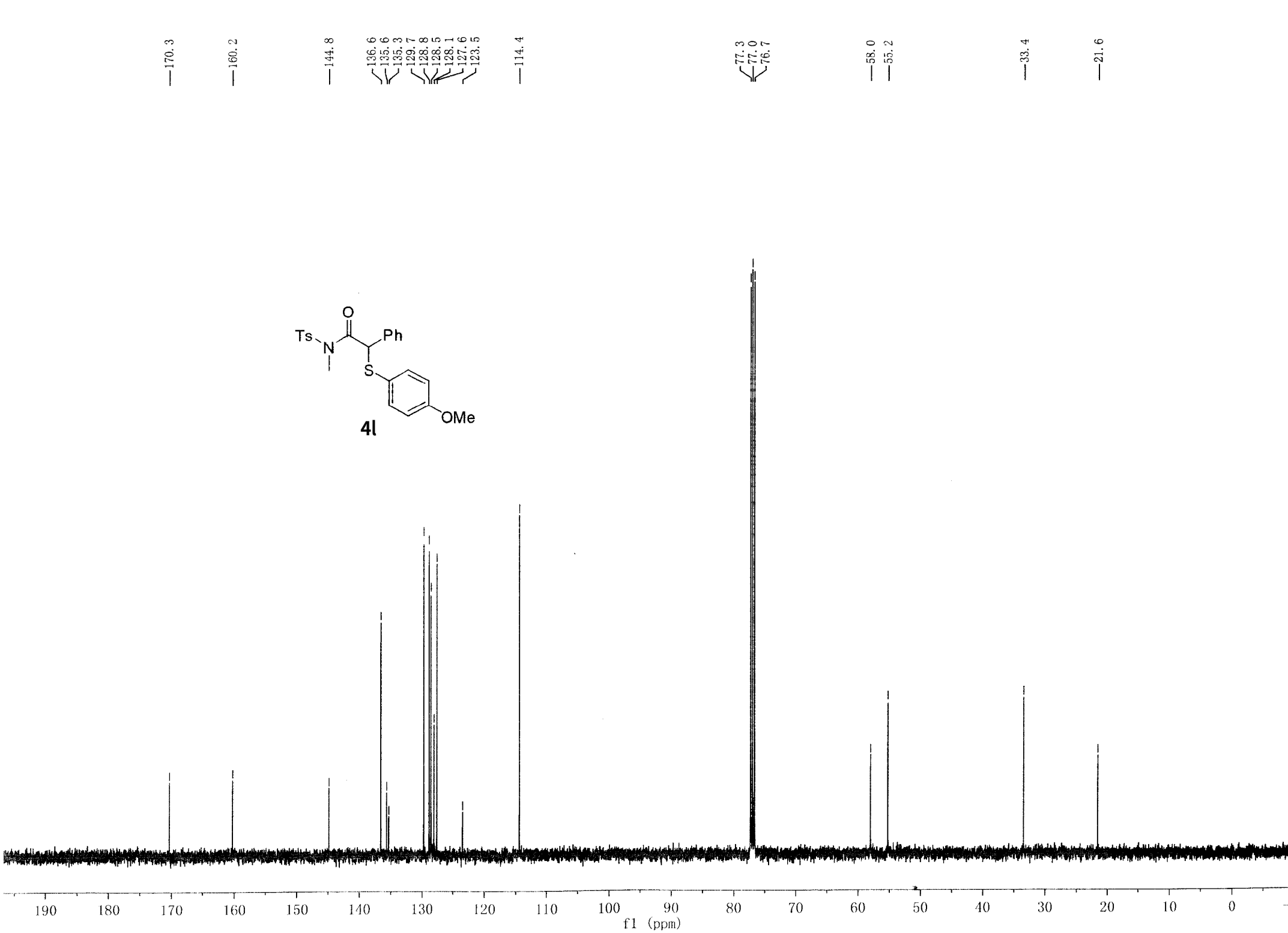
7.300
7.282
7.259
7.173
7.153
7.133
7.119
7.103
7.085
7.067
5.995
3.199
2.389
Ts
N
O
Ph
S
Br
4j
1.03
2.03
5.74
3.02
2.13
1.00
3.00
3.00
f1 (ppm)

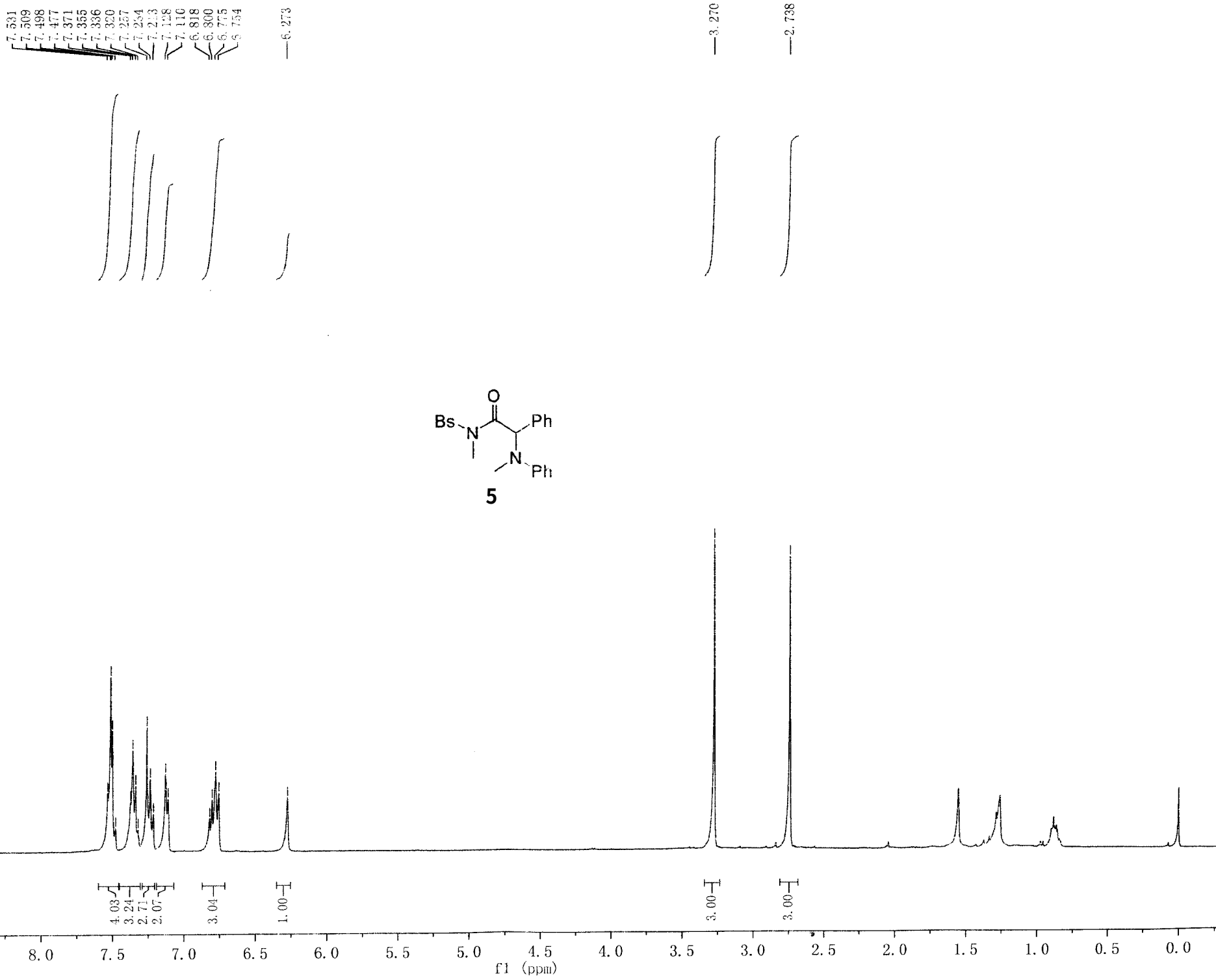

169.6
145.0
135.1
134.9
134.8
133.3
133.1
129.7
129.0
128.8
128.7
128.4
127.8
127.6
127.0
77.3
77.0
76.7
55.7
33.5
21.6
O
Ts
N
Ph
S
Br
4j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

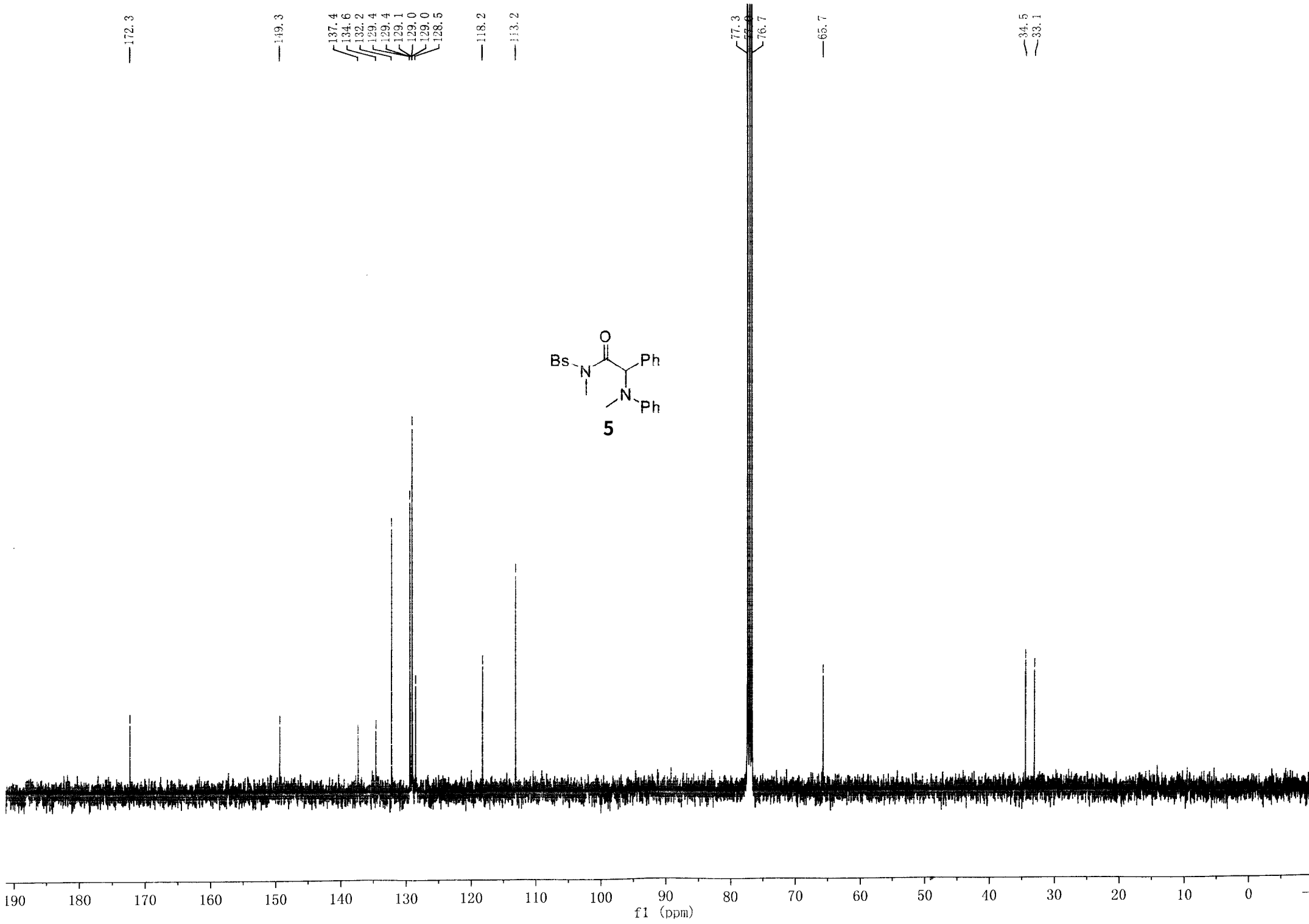

7.489
7.468
7.265
7.251
7.195
7.176
7.145
7.125
7.021
7.001
5.757
3.155
2.396
2.305
Ts
N
O
Ph
S
4k
2.08
5.28
2.11
2.01
2.01
1.01
3.01
3.03
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

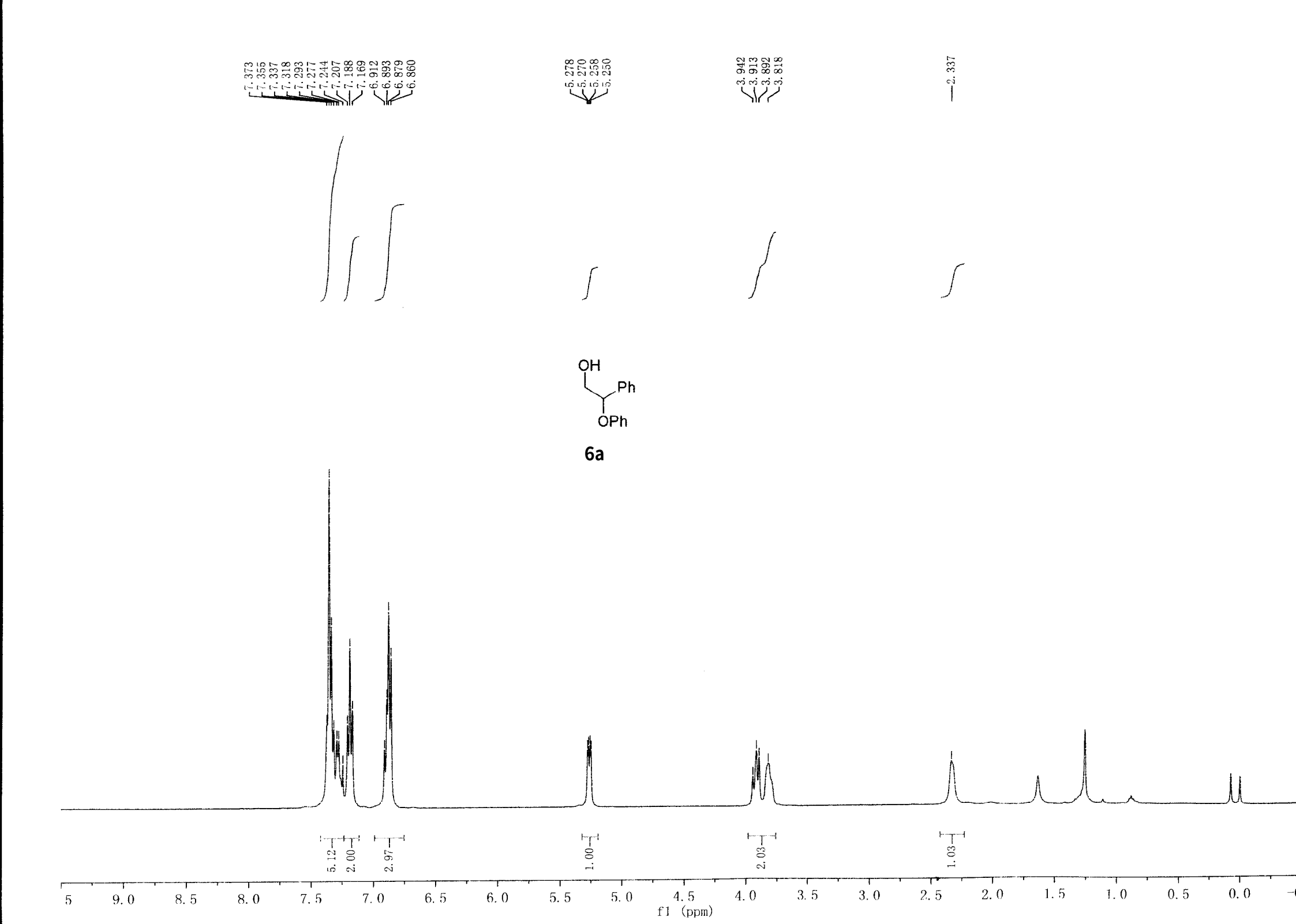

170.2
144.8
138.4
135.6
135.2
133.8
129.6
129.6
128.8
128.6
127.6
77.3
57.4
33.4
21.5
Ts
N
O
Ph
S
4k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.484
7.463
7.264
7.259
7.249
7.237
7.210
7.188
7.165
6.743
6.721
5.666
3.777
3.151
2.407
Ts
N
O
Ph
S
OMe
4l
2.05
9.35
2.01
0.99
3.09
3.02
3.00
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)

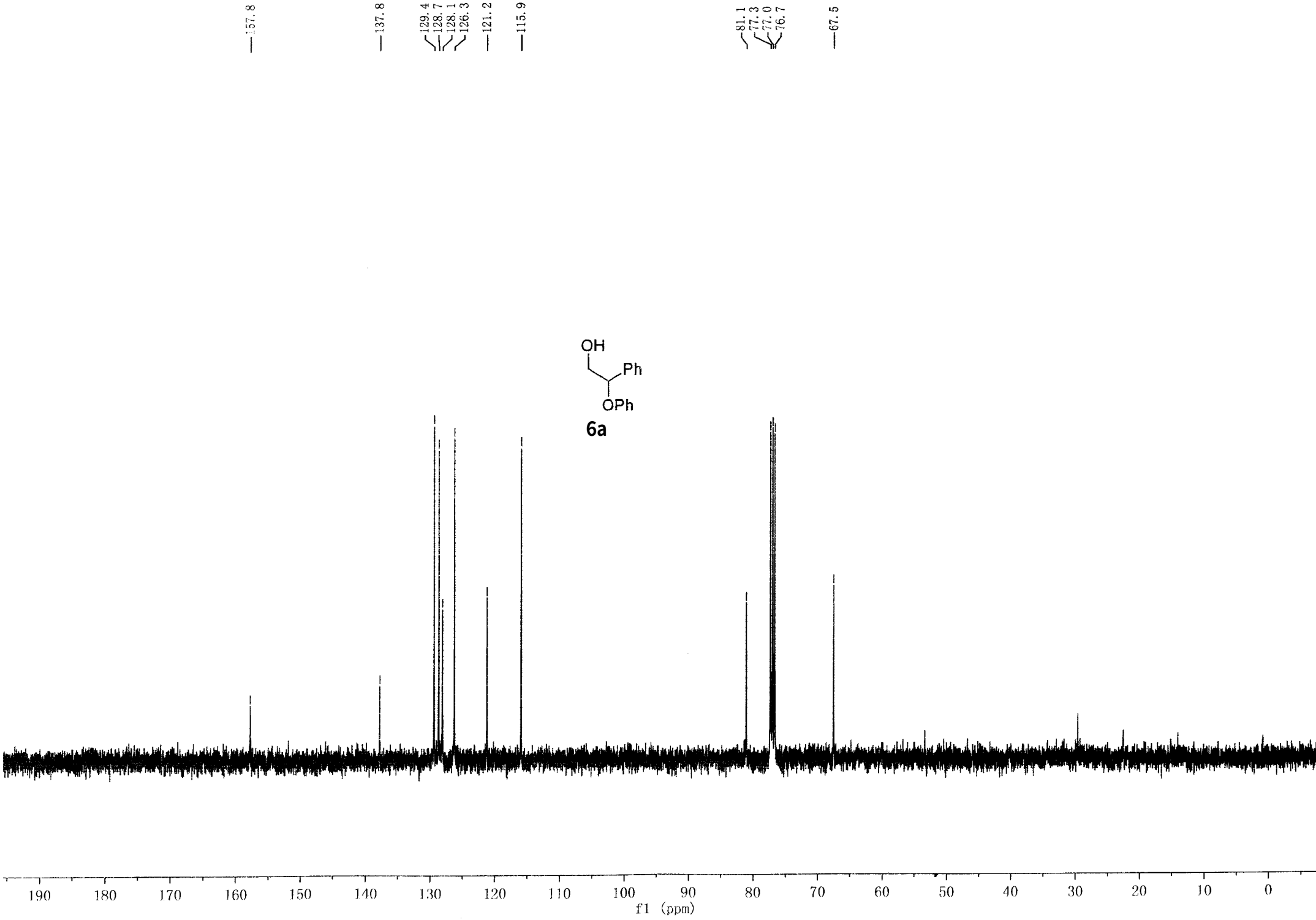

170.3
160.2
144.8
136.6
135.6
135.3
129.7
128.8
128.5
128.1
127.6
123.5
114.4
77.3
77.0
76.7
58.0
55.2
33.4
21.6
O
Ts
N
Ph
S
OMe
4l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

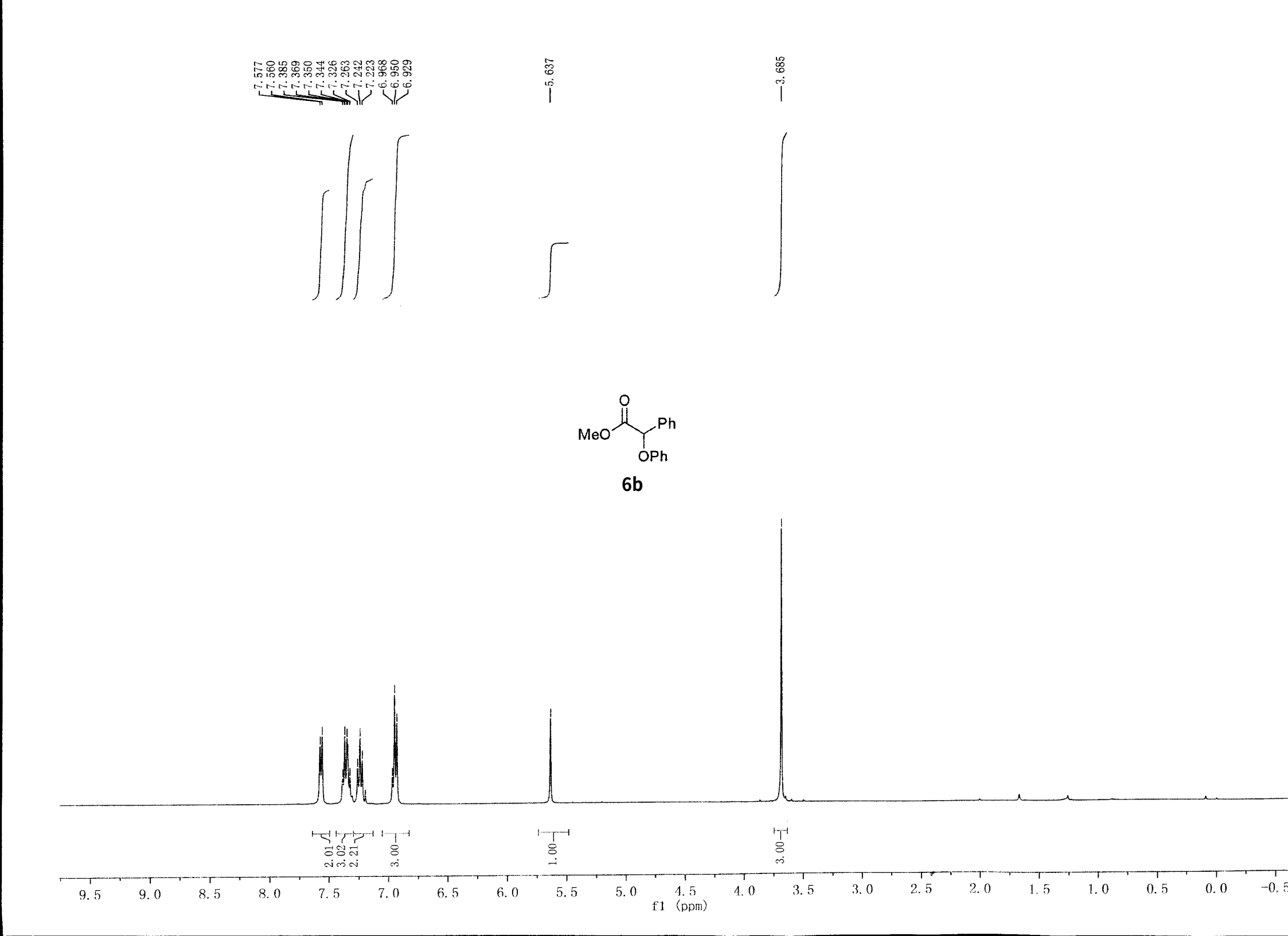

7.531
7.509
7.498
7.477
7.371
7.355
7.336
7.320
7.257
7.254
7.213
7.128
7.116
6.818
6.800
6.775
6.754
6.273
3.270
2.738
Bs
N
O
Ph
N
Ph
5
4.03
3.24
2.71
2.07
3.04
1.00
3.00
3.00
f1 (ppm)

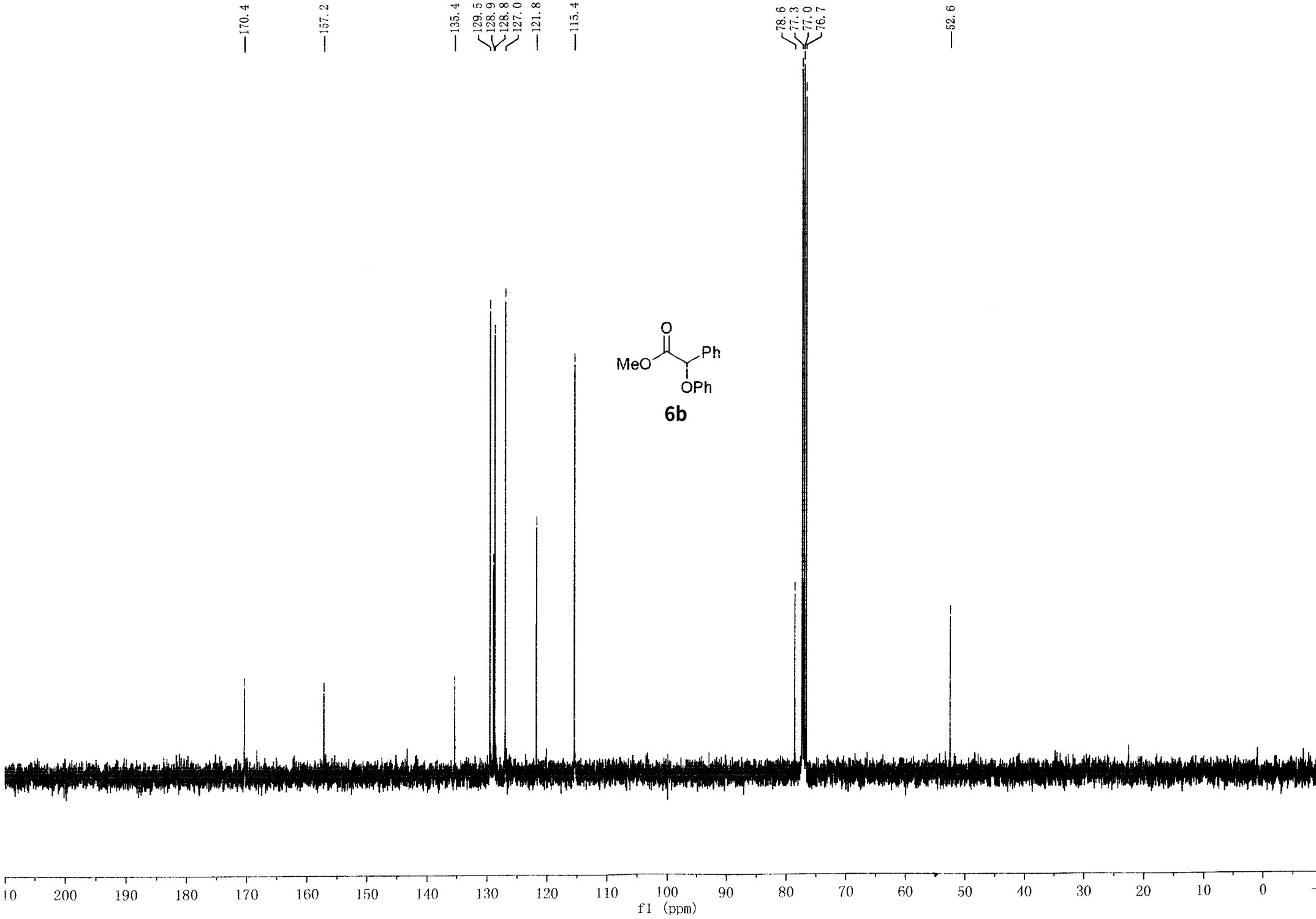

172.3
149.3
137.4
134.6
132.2
129.4
129.4
129.1
129.0
129.0
128.5
118.2
113.2
77.3
76.7
65.7
34.5
33.1
Bs
N
O
Ph
N
Ph
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.373
7.355
7.337
7.318
7.293
7.277
7.244
7.207
7.188
7.169
6.912
6.893
6.879
6.860
5.278
5.270
5.258
5.250
3.942
3.913
3.892
3.818
2.337
OH
Ph
OPh
5.12
2.00
2.97
1.00
2.03
1.03
f1 (ppm)

6a


157.8
137.8
129.4
128.7
128.1
126.3
121.2
115.9
81.1
77.3
77.0
76.7
67.5
OH
Ph
OPh
6a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.577
7.560
7.385
7.369
7.350
7.344
7.326
7.263
7.242
7.223
6.968
6.950
6.929
5.637
3.685
MeO
O
Ph
OPh
6b
2.01
3.02
2.21
3.00
1.00
3.00
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)


170.4
157.2
135.4
129.5
128.9
128.8
127.0
121.8
115.4
78.6
77.3
77.0
76.7
52.6
O
MeO
Ph
OPh
6b
f1 (ppm)