Supporting Information

Synthesis of α-Arylthioacetones using TEMPO as C_3 Synthons via a Reaction Cascade of Sequential Oxidization, Skeletal Rearrangement and C-S Bond Formation

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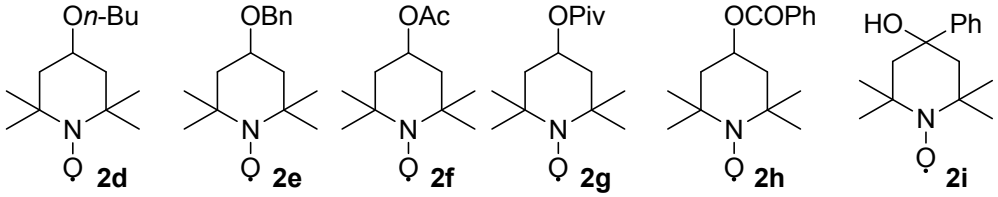
General Information

All reactions were carried out in a dry solvent under argon atmosphere unless otherwise noted. NMR spectra were recorded on Bruker 400 MHz or 600 MHz (400 MHz or 600 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR) spectrometers. Proton chemical shifts are reported relative to a residual solvent peak ($CDCl_3$ at 7.26 ppm). Carbon chemical shifts are reported relative to a residual solvent peak ($CDCl_3$ at 77.16 ppm). The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. Fourier transform infrared spectra (FT-IR) were recorded on an Agilent Cary 630 FT-IR instrument. High-resolution mass spectra (HRMS) were measured on a Brucker Daltonics Apex II 47e Specification (for HRMS). GC-MS spectra were recorded on an Agilent Technologies 7890B GC-system with an Agilent 5973C VL MSD and a HP-5MS column (0.25mm x 30 m, film: 0.25 μm). The major signals are quoted in m/z with the relative intensity in parentheses. The employed a method that starts with the injection temperature T0 (50 °C); after holding this temperature for 2 min, the column is heated by 40 °C/min to temperature T1 (200 °C) and this temperature is held for an additional time t (18 min).

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Substrates **1a-1o**, **2a**, **2b**, **2c** are commercially available. Nitroxyl radicals **2d-2i** were prepared according to the literature's procedures.

Experimental Section

Preparation of Nitroxyl radicals



Nitroxyl radicals **2d-2e**[1], **2f-2h**[2], were prepared according to the the literature. Nitroxyl radicals **2i** also were prepared according to the literature,[3] to a vigorously stirred solution of 170.2 mg (1 mmol) of 4-oxy-2,2,6,6-tetramethylpiperidinyl-1-oxy in 10 mL of anhydrous THF was added dropwise 1.33 mL (2 mmol) PhLi at -78 °C under argon. The reaction mixture was stirred at -78 °C about 4h, then quenched with saturated NH_4Cl. The resulting mixture was washed with water three times and separated, and the organic layer was dried with anhydrous magnesium sulfate. The organic solution was concentrated in vacuo to give a red liquid. Finally, the residue was purified by column chromatography on silica gel (hexane / EtOAc =5:1) to afford the desired product **2i** as orange solid in 50 % yield.

2d: IR (KBr, ν / cm^{-1}) 2973, 2939, 1463, 1377, 1243, 1180, 1101, 880; GC-MS (EI) m/z (%): 228.2 (21) (M^+), 214.2 (10), 172.2 (45), 142.2 (31), 127.2 (100), 116.1 (19), 98.1 (14), 85.1 (38), 71.1 (88), 57.1 (39); HRMS (ESI) Calcd for $C_{13}H_{26}NNaO_2^+$ ($M+Na^+$) 251.1856, Found 251.1852.

2e: IR (KBr, ν / cm^{-1}) 2984, 2941, 1465, 1374, 1359, 1247, 1191, 1178, 1094, 1031, 911, 747, 702, 688; GC-MS (EI) m/z (%): 262.2 (8) (M^+), 248.2 (3), 132.1 (6), 122.1 (17), 91.1 (100), 85.1 (13), 57.1 (11); HRMS (ESI) Calcd for $C_{16}H_{24}NNaO_2^+$ ($M+Na^+$) 285.1699, Found 285.1693.

2f: IR (KBr, ν / cm^{-1}) 2980, 2941, 1743, 1465, 1366, 1239, 1180, 1033, 736; GC-MS (EI) m/z (%): 214.2 (16) (M^+), 154.2 (9), 140.1 (29), 124.2 (50), 109.1 (100), 81.1 (19), 67.1 (25), 55.1 (17); HRMS (ESI) Calcd for $C_{11}H_{20}NNaO_3^+$ ($M+Na^+$) 237.1335, Found 237.1336.

2g: IR (KBr, ν / cm^{-1}) 2976, 2939, 1724, 1465, 1366, 1286, 1163, 738; GC-MS (EI) m/z (%): 256.2 (11) (M^+), 154.2 (10), 140.1 (98), 124.2 (68), 109.1 (100), 98.1 (15), 82.1 (20), 69.1 (23), 57.1 (92); HRMS (ESI) Calcd for $C_{14}H_{26}NNaO_3^+$ ($M+Na^+$) 279.1805, Found 279.1810.

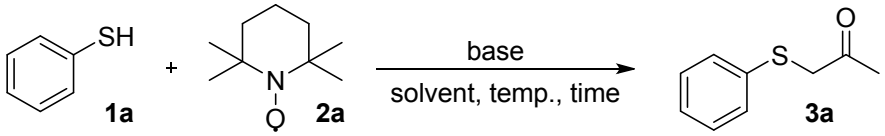
2h: IR (KBr, ν / cm^{-1}) 2980, 2941, 1716, 1465, 1364, 1280, 1180, 1118, 740, 716, 688; GC-MS (EI) m/z (%): 276.2 (6) (M^+), 262.2 (6), 154.2 (10), 140.1 (79), 124.2 (47), 109.1 (64), 105.1 (100), 98.1 (11), 77.1 (53), 67.1 (12), 51.1 (10); HRMS (ESI) Calcd for $C_{16}H_{22}NNaO_3^+$ ($M+Na^+$) 299.1492, Found 299.1506.

2i: IR (KBr, ν / cm^{-1}) 3429, 2974, 2932, 1446, 1362, 1243, 1224, 1185, 1057, 760, 701; GC-MS (EI) m/z (%): 248.2 (17) (M^+), 192.1 (11), 162.1 (42), 147.1 (100), 128.1 (10), 120.1 (21), 105.1 (80), 91.1 (12), 77.1 (36), 69.1 (14), 56.1 (11); HRMS (ESI) Calcd for $C_{15}H_{22}NNaO_2^+$ ($M+Na^+$) 271.1543, Found 271.1550.

Optimization of reaction conditions

A test tube equipped with a magnetic stir bar was charged with thiophenol **1a** (0.20 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) **2a** (0.40-0.50 mmol, 2.0-2.5 equiv), base (0-0.60 mmol, 0-3.0 equiv) and solvent (1.0-2.0 mL) under argon atmosphere. The resulting mixture was stirred for 3 min at room temperature, and then heated at indicated temperature for 1-24 h. The reaction solution was cooled to ambient temperature, quenched by 15 mL water and extracted with ethyl acetate (3*10mL). The combined organic extracts were dried with anhydrous magnesium sulfate, then concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (hexane / EtOAc= 15:1) to give **3a** as yellow oil.

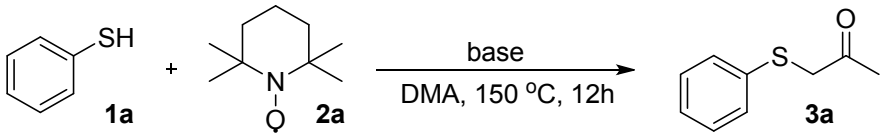
Table S1. Investigation of solvents for reaction



Entry	Base	Slovent	Temperature / °C	Time	Yield[b]/%
1	K_2CO_3	DMSO	150	12 h	70
2	K_2CO_3	DMF	150	12 h	66
3	K_2CO_3	DMA	150	12 h	82
4	K_2CO_3	NMP	150	12 h	76
5	K_2CO_3	CH_3CN	150	12 h	20
6	K_2CO_3	*n*-PrCN	150	12 h	trace
7	K_2CO_3	toluene	150	12 h	N.R.
8	K_2CO_3	dioxane	150	12 h	N.R.
9	K_2CO_3	MeOH	150	12 h	N.R.
10	K_2CO_3	THF	150	12 h	trace

[a]Reaction conditions: **1a** (0.20 mmol, 1.0 equiv), **2a** (0.40 mmol, 2.0 equiv), base (0.40 mmol, 2.0 equiv) , solvent (1.0 mL) at 150 °C for 12 h under argon atmosphere. [b]Isolated yields (the yield was calculated based on half of the sulfur source converted into products). *n*-PrCN = Butanenitrile. N.R. = no results.

Table S2. Investigation of bases for reaction

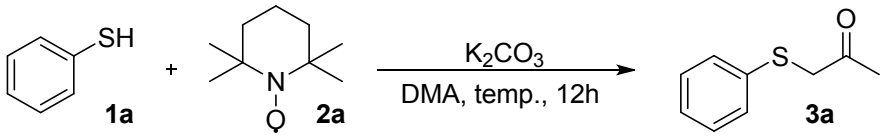


Entry	Base (2.0 equiv)	Yield [b]/%	Entry	K_2CO_3 (x equiv)	Yield [b]/%
1	K_2CO_3	82	10	0	N.R.
2	Cs_2CO_3	76	11	0.5 equiv	30
3	K_3PO_4•$3H_2O$	80	12	1.0 equiv	54
4	AcOK	N.R.	13	1.5 equiv	72
5	KO*t*-Bu	trace	14	2.0 equiv	82

6	NaOH	trace	15	3.0 equiv	80
7	DBU	trace	-	-	-
8	Pydine	trace	-	-	-
9	Et_3N	trace	-	-	-

[a]Reaction conditions: **1a** (0.20 mmol, 1.0 equiv), **2a** (0.40 mmol, 2.0 equiv), base (0-0.60 mmol, 0-3.0 equiv) , DMA (1.0 mL) at 150 °C for 12 h under argon atmosphere. [b]Isolated yields (the yield was calculated based on half of the sulfur source converted into products). N.R. = no results.

Table S3. Investigation of other factors (the amount of TEMPO, temperature, reaction time etc.) for reaction

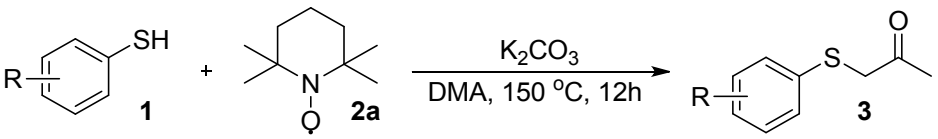


Entry	Changed parameters	Yield [b]/%	Entry	Changed parameters	Yield [b]/%
1	1.0 eq. TEMPO	trace	12	1h	30
2	1.5 eq. TEMPO	28	13	2h	48
3	2.5 eq. TEMPO	68	14	4 h	56
4	3.0 eq. TEMPO	60	15	7 h	70
5	4.0 eq. TEMPO	46	16	10 h	72
6	130 °C	64	17	24 h	60
7	110 °C	56	18	DMA 0.6mL	80
8	90 °C	52	19	DMA 2mL	68
9	70 °C	24	20	Air	42
10	50 °C	trace	21	O_2	N.R.
11	30 °C	trace	-	-	-

[a]Reaction conditions: **1a** (0.20 mmol, 1.0 equiv), **2a** (x mmol, x equiv), base (0.40mmol, 0.20 equiv) , DMA (x mL) at 30-130 °C for 1-24 h under argon atmosphere. [b]Isolated yields (the yield was calculated based on half of the sulfur source converted into products). N.R. = no results.

Investigation of substrate scopes

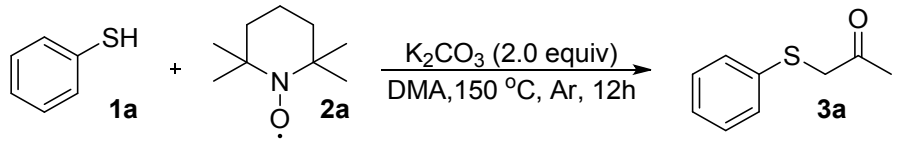
General procedure for the *C_3*-synthon form TEMPO coupling with thiols:



A test tube equipped with a magnetic stir bar was charged with thiols **1** (0.20 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) **2a** (0.40-0.50 mmol, 2.0-2.5 equiv), K_2CO_3 (0.40 mmol, 2.0 equiv) and DMA (1.0 mL) under argon atmosphere. The resulting mixture was stirred for 3 min at room temperature, and then heated at 150 °C for 12 h. The reaction solution was cooled to ambient

temperature, quenched by 15 mL water and extracted with ethyl acetate (3*10mL). The combined organic extracts were dried with anhydrous magnesium sulfate, then concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (hexane / EtOAc= 5:1 to 30:1) to give **3** as yellow oil.

General procedure for gram scale experiment:

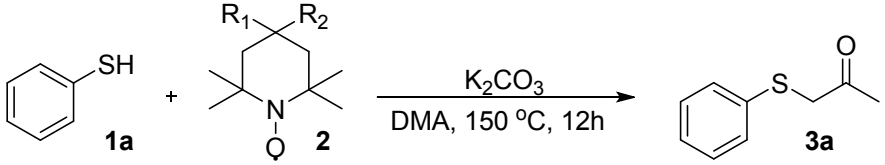


A round-bottom flask equipped with a magnetic stir bar was charged with thiophenol **1a** 1.10 g (10 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) **2a** 3.13 g (20 mmol, 2.0 equiv), K_2CO_3 2.76 g (20 mmol, 2.0 equiv) and DMA (30 mL) under argon atmosphere. The resulting mixture was stirred for 3 min at room temperature, and then heated at 150 °C for 12 h. The reaction solution was cooled to ambient temperature, quenched by 150 mL water and extracted with ethyl acetate (3*100 mL). The combined organic extracts were dried with anhydrous magnesium sulfate, then concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (hexane / EtOAc= 30:1) to give **3a** (0.574 g) in 69% yield as yellow oil.

General procedure for 1 mmol scale experiments:

A test tube equipped with a magnetic stir bar was charged with 4-(tert-butyl)benzenethiol **1g** 0.166 g (1.0 mmol, 1.0 equiv) or 2-chlorobenzenethiol **1j** 0.144 g (1.0 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) **2a** 0.313 g or 0.391 g (2.0-2.5 mmol, 2.0-2.5 equiv), K_2CO_3 0.276 g (2.0 mmol, 2.0 equiv) and DMA (3.0 mL) under argon atmosphere. The resulting mixture was stirred for 3 min at room temperature, and then heated at 150 °C for 12 h. The reaction solution was cooled to ambient temperature, quenched by 30 mL water and extracted with ethyl acetate (3*20mL). The combined organic extracts were dried with anhydrous magnesium sulfate, then concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (hexane / EtOAc= 5:1 to 40:1) to give **3g** in 74% yield (82.3 mg) and **3j** in 43% yield (43.2 mg), both as yellow oil.

General procedure for the *C_3*-synthon form nitroxyl radicals coupling with thiophenol **1a**:

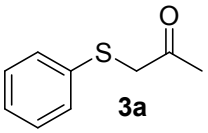


A test tube equipped with a magnetic stir bar was charged with thiophenol **1a** (0.20

mmol, 1.0 equiv), nitroxyl radicals **2a** (0.40 mmol, 2.0 equiv), K_2CO_3 (0.40 mmol, 2.0 equiv) and DMA (1.0 mL) under argon atmosphere. The resulting mixture was stirred for 3 min at room temperature, and then heated at 150 °C for 12 h. The reaction solution was cooled to ambient temperature, quenched by 15 mL water and extracted with ethyl acetate (3*10mL). The combined organic extracts were dried with anhydrous magnesium sulfate, then concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (hexane / EtOAc= 15:1) to give **3a** as yellow oil.

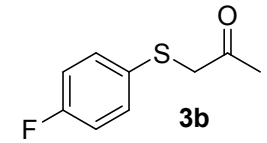
Characterization data for products

1-(phenylthio)propan-2-one (**3a**)



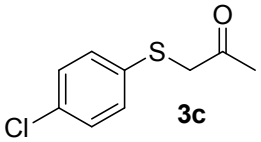
13.6 mg, 82 %, yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 4H), 7.24 – 7.18 (m, 1H), 3.66 (s, 2H), 2.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.6, 134.8, 129.6, 129.3, 127.0, 44.8, 28.1; IR (KBr, ν / cm^{-1}) 1709, 1584, 1482, 1441, 1357, 1232, 1150, 742, 691; GC-MS (EI) m/z (%): 166.1 (60) (M^+), 123.1 (100), 109.1 (19), 91.1 (6), 77.1 (22), 65.1 (15), 51.1 (20); HRMS (ESI) Calcd for $C_9H_{10}NaOS^+$ ($M+Na^+$) 189.0345, Found 189.0350.

1-((4-fluorophenyl)thio)propan-2-one (**3b**)



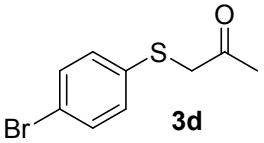
7.7 mg, 42 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.00 (dd, J = 12.0, 5.3 Hz, 2H), 3.60 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 163.7, 161.2, 133.0 (d, *J* = 8.2 Hz), 129.5 (d, *J* = 3.4 Hz), 116.6, 116.4, 45.9, 28.2; IR (KBr, ν / cm^{-1}) 1709, 1589, 1493, 1398, 1359, 1228, 1157, 1092, 1012, 829; GC-MS (EI) m/z (%): 184.1 (68) (M^+), 141.1 (100), 127.0 (24), 95.1 (9), 83.1 (30), 75.1 (15); HRMS (ESI) Calcd for $C_9H_9FNaOS^+$ ($M+Na^+$) 207.0250, Found 207.0259.

1-((4-chlorophenyl)thio)propan-2-one (**3c**)



10.0 mg, 50 %, yellow oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 4H), 3.64 (s, 2H), 2.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.2, 133.3, 131.2, 129.5, 44.9, 28.2; IR (KBr, ν / cm^{-1}) 1771, 1478, 1385, 1247, 1096, 1059, 915, 744; GC-MS (EI) m/z (%): 200.0 (65) (M^+), 157.0 (100), 143.0 (14), 121.0 (12), 108.0 (23), 75.1 (16); HRMS (ESI) Calcd for $C_9H_9ClNaOS^+$ ($M+Na^+$) 222.9955, Found 222.9963.

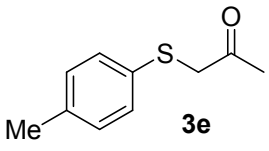
1-((4-bromophenyl)thio)propan-2-one (**3d**)



11.2 mg, 56 %, yellow oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 3.65 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 134.0, 132.4, 131.2, 121.1, 44.7, 28.1; IR (KBr, ν / cm^{-1}) 1705, 1476, 1387, 1116, 1096, 1008, 911, 811, 732; GC-MS (EI) m/z (%): 247.0 (6) ($M+3^+$), 246.0 (52)

(M+2$^+$), 245.1 (6) (M+1$^+$), 244.0 (51) (M$^+$), 204.0 (21) (M+3-43$^+$), 203.0 (62) (M+2-43$^+$), 202.0 (21) (M+1-43$^+$), 201.0 (61) (M-43$^+$), 122.1 (100), 108.0 (33); HRMS (ESI) Calcd for $C_9H_9BrNaOS^+$ (M+Na$^+$) 266.9450, Found 266.9453.

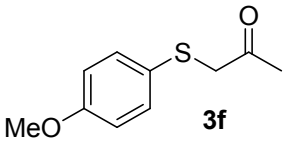
1-(p-tolylthio)propan-2-one (**3e**)



3e

8.6 mg, 48 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.10 (d, J = 8.0 Hz, 2H), 3.61 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 137.4, 130.9, 130.6, 130.1, 45.5, 28.1, 21.2; IR (KBr, ν / cm^{-1}) 1711, 1495, 1357, 1232, 1150, 1092, 913, 807, 744; GC-MS (EI) m/z (%): 180.1 (65) (M$^+$), 137.1 (100), 123.1 (11), 91.1 (28), 77.1 (15), 65.1 (13); HRMS (ESI) Calcd for $C_{10}H_{12}NaOS^+$ (M+Na$^+$) 203.0501, Found 203.0502.

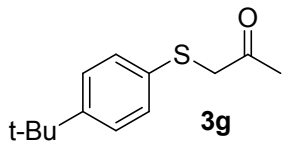
1-((4-methoxyphenyl)thio)propan-2-one (**3f**)



3f

13.7 mg, 70%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 3.55 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 159.7, 133.8, 124.7, 115.0, 55.5, 46.7, 28.2; IR (KBr, ν / cm^{-1}) 1709, 1593, 1497, 1357, 1288, 1247, 1180, 1031, 828, 747; GC-MS (EI) m/z (%): 196.1 (99) (M$^+$), 153.1 (100), 138.0 (42), 109.1 (42), 96.0 (13), 77.1 (12); HRMS (ESI) Calcd for $C_{10}H_{12}NaO_2S^+$ (M+Na$^+$) 219.0450, Found 219.0452.

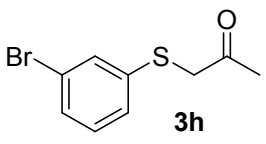
1-((4-(tert-butyl)phenyl)thio)propan-2-one (**3g**)



3g

18.2 mg, 82 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (q, J = 8.6 Hz, 4H), 3.63 (s, 2H), 2.28 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 150.5, 131.1, 130.0, 126.4, 45.3, 34.7, 31.4, 28.1; IR (KBr, ν / cm^{-1}) 1711, 1491, 1398, 1357, 1269, 1232, 1120, 1012, 822; GC-MS (EI) m/z (%): 222.2 (75) (M$^+$), 207.1 (100), 179.1 (29), 149.1 (23), 135.1 (11), 123.1 (54), 115.1 (17), 91.1 (20), 57.1 (47); HRMS (ESI) Calcd for $C_{13}H_{18}NaOS^+$ (M+Na$^+$) 245.0971, Found 245.0976.

1-((3-bromophenyl)thio)propan-2-one (**3h**)

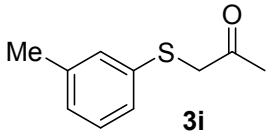


3h

12.2 mg, 50 %, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (t, J = 1.8 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.24 (dd, J = 7.1, 0.8 Hz, 1H), 7.15 (t, J = 7.9 Hz, 1H), 3.69 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 137.3, 131.8, 130.6, 129.9, 127.7, 123.1, 44.4, 28.2; IR (KBr, ν / cm^{-1}) 1711, 1558, 1577, 1461, 1396, 1357, 1232, 1152, 773, 753, 677; GC-MS (EI) m/z (%): 247.0 (5) (M+3$^+$), 246.0 (48) (M+2$^+$), 245.1 (6) (M+1$^+$), 244.0 (47) (M$^+$), 204.0 (28) (M+3-43$^+$), 203.0 (52) (M+2-43$^+$), 202.0 (28) (M+1-43$^+$), 201.0 (50) (M-43$^+$), 122.1 (100), 108.0 (35); HRMS (ESI) Calcd for $C_9H_9BrNaOS^+$ (M+Na$^+$) 266.9450, Found 266.9456.

1-(m-tolylthio)propan-2-one (**3i**)

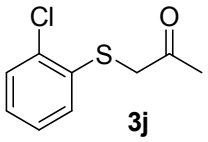
13.3 mg, 74 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, J = 9.3, 7.3 Hz, 3H), 7.03 (s, 1H), 3.66 (s, 2H), 2.32 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 139.2, 134.5, 130.3, 129.2, 127.9, 126.6, 44.8, 28.1, 21.5; IR (KBr, ν / cm^{-1}) 1771, 1709, 1593, 1476, 1357, 1241, 1059, 913, 744, 690; GC-MS (EI) m/z (%): 180.1 (67) (M^+), 137.1 (100), 123.1 (7), 91.1 (24), 77.1 (13), 65.1 (12); HRMS (ESI) Calcd for $C_{10}H_{12}NaOS^+$ (M+Na^+) 203.0501, Found 203.0503.



3i

1-((2-chlorophenyl)thio)propan-2-one (**3j**)

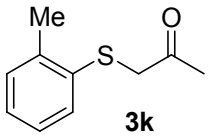
11.6 mg, 58 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.8 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.22 (dd, J = 10.6, 4.5 Hz, 1H), 7.16 (dd, J = 10.6, 4.5 Hz, 1H), 3.71 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 134.1, 130.1, 129.6, 127.7 (d, J = 18.5 Hz), 43.5, 28.2; IR (KBr, ν / cm^{-1}) 1713, 1454, 1433, 1357, 1232,1150, 1116, 1034, 913, 747; GC-MS (EI) m/z (%): 200.1 (62) (M^+), 157.0 (100), 143.0 (12), 121.1 (18), 108.0 (33), 75.1 (17); HRMS (ESI) Calcd for $C_9H_9ClNaOS^+$ (M+Na^+) 222.9955, Found 222.9960.



3j

1-(o-tolylthio)propan-2-one (**3k**)

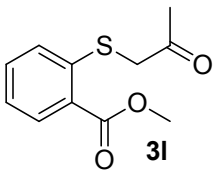
11.2 mg, 62 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 6.8, 4.8 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.13 (dt, J = 9.0, 5.9 Hz, 2H), 3.65 (s, 2H), 2.40 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 138.0, 134.0, 130.5, 128.9, 126.9, 44.0, 28.2, 20.4; IR (KBr, ν / cm^{-1}) 1713, 1590, 1470, 1357, 1280, 1232, 1150, 1068, 1049, 747; GC-MS (EI) m/z (%): 180.1 (71) (M^+), 137.1 (100), 121.1 (16), 91.1 (30), 77.1 (16), 65.1 (15); HRMS (ESI) Calcd for $C_{10}H_{12}NaOS^+$ (M+Na^+) 203.0501, Found 203.0502.



3k

Methyl 2-((2-oxopropyl)thio)benzoate (**3l**)

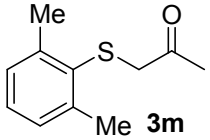
8.5 mg, 38 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 7.3 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 3.94 (s, 3H), 3.71 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 166.9, 140.1, 133.0, 131.7, 127.6, 125.9, 124.9, 52.4, 43.4, 28.1; IR (KBr, ν / cm^{-1}) 1711, 1465, 1435, 1277, 1254, 1144, 1064, 749; GC-MS (EI) m/z (%): 224.1 (57) (M^+), 193 (21), 181 (77), 167 (15), 150 (100), 136 (14), 121 (33), 108 (23); HRMS (ESI) Calcd for $C_{11}H_{12}NaO_3S^+$ (M+Na^+) 247.0399, Found 247.0401.



3l

1-((2,6-dimethylphenyl)thio)propan-2-one (**3m**)

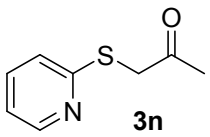
5.4 mg, 28 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.06 (m, 3H), 3.41 (s, 2H), 2.53 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 143.2, 132.0, 129.0, 128.5, 45.2, 28.7, 22.0; IR (KBr, ν / cm^{-1}) 1711, 1461, 1355, 1236, 1148, 915, 773, 747; GC-MS (EI) m/z (%): 194.1 (86) (M^+), 157.1 (100), 135.1 (26), 121.0 (8), 105.1 (39), 91.1 (24), 77.1 (24), 65.1 (7); HRMS (ESI) Calcd for $C_{11}H_{14}NaOS^+$ (M+Na^+)



3m

217.0658, Found 217.0656.

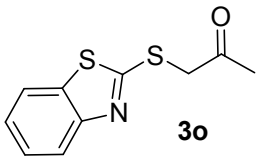
1-(pyridin-2-ylthio)propan-2-one (**3n**)



3n

5.0 mg, 30 %, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 4.4 Hz, 1H), 7.54 – 7.44 (m, 1H), 7.23 (d, J = 8.1 Hz, 1H), 6.99 (dd, J = 6.6, 5.3 Hz, 1H), 3.99 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 157.0, 149.5, 136.2, 122.2, 112.0, 40.3, 28.8; IR (KBr, ν / cm^{-1}) 1715, 1558, 1582, 1456, 1418, 1357, 1152, 1126, 913, 760, 732; GC-MS (EI) m/z (%): 167.1 (11) (M^+), 124.1 (100), 78.1 (40), 51.1 (13); HRMS (ESI) Calcd for $C_8H_{10}NOS^+$ ($M+H^+$) 168.0478, Found 168.0485.

1-(benzo[d]thiazol-2-ylthio)propan-2-one (**3o**)

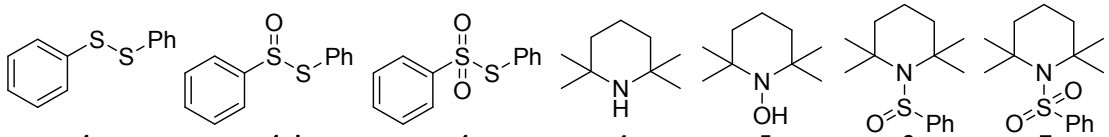


3o

7.6 mg, 34 %, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 4.23 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 165.0, 152.9, 135.7, 126.2, 124.6, 121.7, 121.3, 43.2, 29.0; IR (KBr, ν / cm^{-1}) 1716, 1461, 1429, 1357, 1277, 1239, 1154, 1079, 1021, 999, 759, 727; GC-MS (EI) m/z (%): 223.1 (35) (M^+), 181.0 (100), 148.0 (55), 136.0 (31), 122.0 (11), 108.0 (23); HRMS (ESI) Calcd for $C_{10}H_9NNaOS_2^+$ ($M+Na^+$) 246.0018, Found 246.0019.

Mechanism study

Firstly, we collected reaction samples at series of reaction time points (30 min, 1 h, 2 h, 3 h, 5 h) and analyzed every point in TLC by NMR or MS (HRMS, GC-MS and LC-MS).



1aa **1ab** **1ac** **4** **5** **6** **7**

1aa: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 129.2, 127.7, 127.3; GC-MS (EI) m/z: 218.0 (100) (M^+), 185.1 (21), 154.1 (21), 140.0 (5), 109.1(86). Data consistent with authentic sample.

1ab: LC-MS (ESI) t_R=11.937: 235.0 ($M+H^+$), 257.0 ($M+Na^+$).

1ac: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 3H), 7.47 (ddd, *J* = 6.9, 4.3, 2.0 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 136.7, 133.8, 131.6, 129.6, 128.9, 128.0, 127.7.

4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 – 1.49 (m, 2H), 1.24 – 1.17 (m, 4H), 1.01 (s, 12H); GC-MS (EI) m/z: 141.2 (2) (M^+), 126.1 (100), 109.1 (16), 98.1 (7); HRMS (ESI) Calcd for $C_9H_{20}N^+$ ($M+H^+$) 142.1590, Found 142.1592. Data consistent with authentic sample.

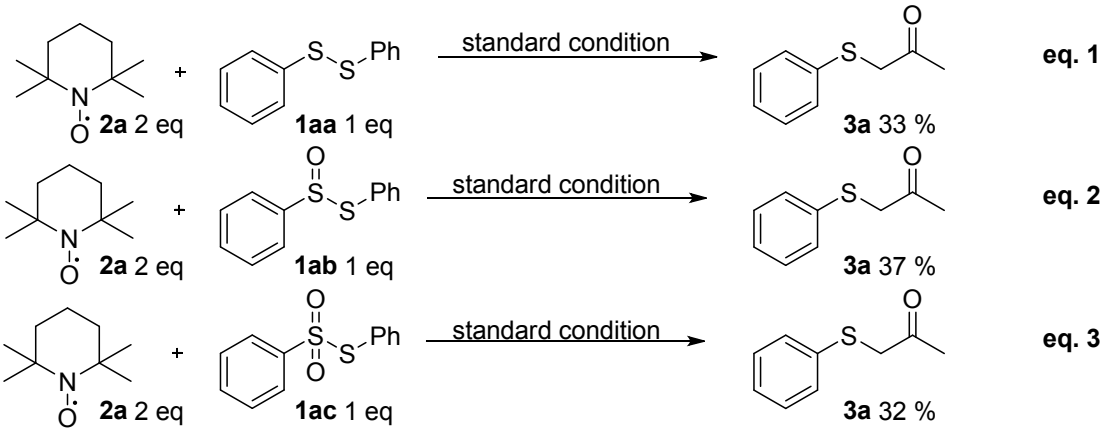
5 (unstable in air): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (s, 1H), 1.91 – 1.43 (m, 6H), 1.41 – 0.92 (m, 12H); GC-MS (EI) m/z: 157.1 (6) (M^+), 142.1 (100), 126.1 (8), 109.1 (18), 96.1 (9). HRMS (ESI) Calcd for $C_9H_{20}NO^+$ ($M+H^+$) 158.1539, Found 158.1538. Data consistent with literature values.[4]

6: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.3 Hz, 2H), 7.47 – 7.36 (m, 3H), 1.67 (s, 6H), 1.54 (d, J = 24.4 Hz, 10H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ150.4, 129.4, 128.6, 126.1, 61.4, 59.0, 43.6, 41.5, 35.5, 32.7, 28.9, 28.1, 17.4. IR (KBr, ν / cm^{-1}) 2973, 2932, 1771, 1243, 1085, 1059, 751, 699; GC-MS (EI) m/z (broken into two parts): 125.2 (58) ($PhSO^+$), 110.1 (39), 97.1 (100); 140.1 (92) ($C_9H_{18}N^+$), 125.1 (100), 109.1 (9), 97.1 (67); HRMS (ESI) Calcd for $C_{15}H_{23}NONaOS^+$ ($M+Na^+$) 288.1393, Found 288.1391.

7: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.38 (t, J = 6.2 Hz, 3H), 1.59 (s, 6H), 1.51 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 131.4, 128.7, 126.2, 61.0, 44.0, 31.2, 16.9; IR (KBr, ν / cm^{-1}) 2997, 1771, 1374, 1243, 1059, 915, 744; GC-MS (EI) m/z: 266.1 (61) ($M-15^+$), 198.1 (29), 158.0 (3), 141.0 (31), 124.1 (5), 109.1 (100); HRMS (ESI) Calcd for $C_{15}H_{23}NNaO_2S^+$ ($M+Na^+$) 304.1342, Found 304.1337.

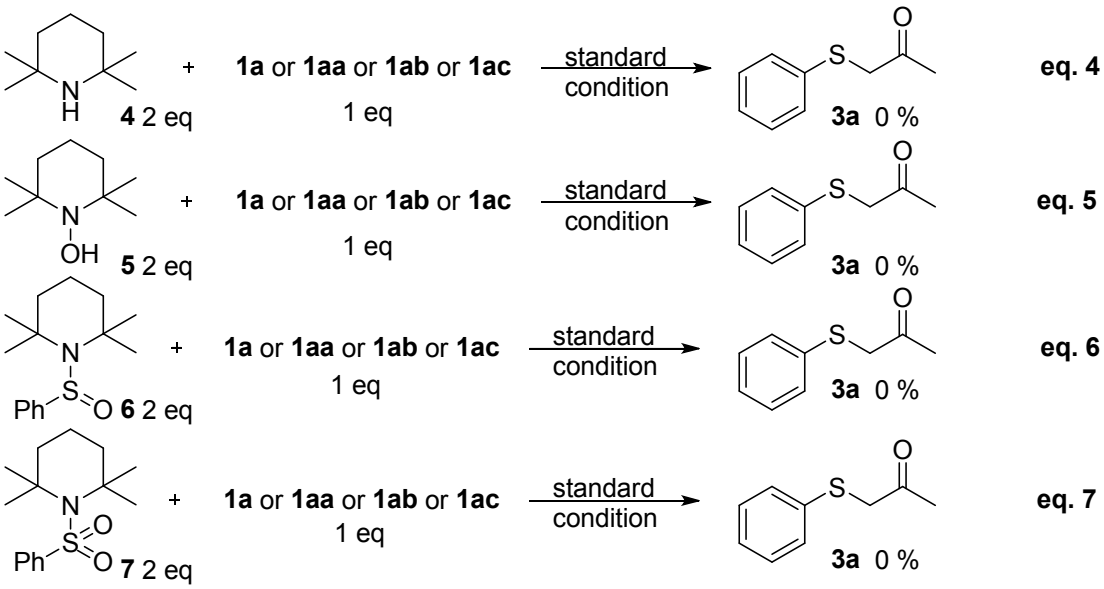
Based on above results of compounds and literature reports,[5] next, we examined the possibility of every compound as an intermediate.

a) Reaction in eq. 1-3



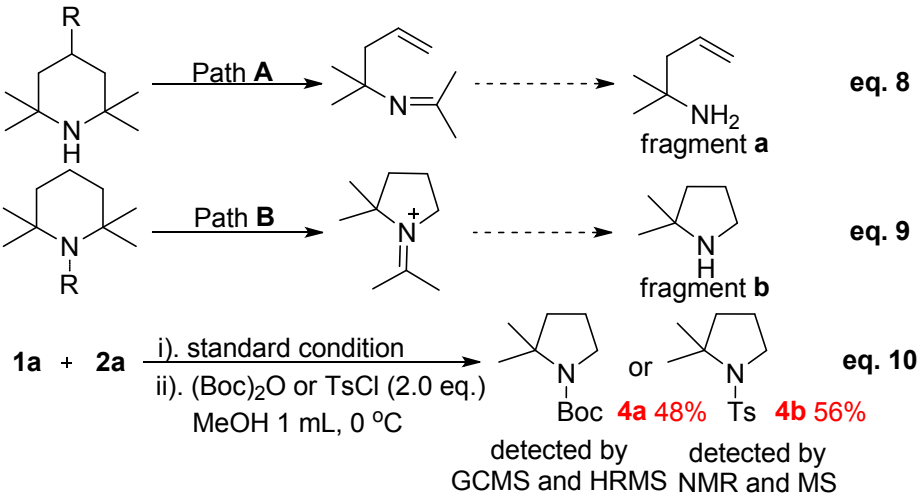
According to literature reports, compounds 1ab and 1ac were prepared. Next, **1aa**, **1ab** and **1ac** respectively reacted with TEMPO under standard condition, yielding the desired product **3a** in 33 %, 37 %, 32 %, respectively.

b) Reaction in eq. 4-7



We used compounds **4-7** to react with **1a**, **1aa**, **1ab** and **1ac** under standard condition, respectively. As showed in eq. **4-7**, compounds **4**, **5**, **6**, **7**as intermediates in this reaction process could be ruled out.

c) Reaction in eq. 8-10



According to literature reports, 2,2,6,6-tetarmethylpiperidine could support C_3-synthon via C-C bond cleavage through two possible pathways (eq. 8 and eq. 9). A test tube equipped with a magnetic stir bar was charged with thiophenols **1a** (0.20 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) **2a** (0.40 mmol, 2.0 equiv), K_2CO_3 (0.40 mmol, 2.0 equiv) and DMA (1.0 mL) under argon atmosphere. The resulting mixture was stirred for 3 min at room temperature, and then heated at 150 °C for 12 h. The reaction solution was cooled to 0 °C, then, dropwise adding 114 uL di-tert-butyl dicarbonate $(Boc)_2O$ (0.40 mmol, 2.0 equiv) or 76.3 mg 4-toluene sulfonyl chloride TsCl (0.40 mmol, 2.0 equiv) in 1.0 mL MeOH at 0 °C and stirred for 5 h at room temperature. The reaction solution was quenched by 15 mL water and extracted with ethyl acetate (3*10mL). The combined organic extracts were dried

with anhydrous magnesium sulfate, then concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (hexane / EtOAc= 30:1) to give **4b** as white solid.

4a: 48%, 9.6 mg; GC-MS (EI) m/z: 199.2 (M^+), 184.1, 124.1, 128.1, 98.1. HRMS (ESI^+) calcd for $C_{11}H_{21}NNaO_2^+$ (M + Na^+) 222.1465, Found 222.1468. Data consistent with literature values.[6]

4b: 56%, 14.17 mg; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 3.38 (t, J = 6.4 Hz, 2H), 2.41 (s, 3H), 1.84 – 1.73 (m, 4H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.7, 129.4, 127.1, 65.1, 49.4, 42.9, 28.3, 22.5, 21.5. IR (KBr, ν / cm^{-1}) 1599, 1459, 1331, 1154, 1100, 1010, 913, 818, 736, 680; GC-MS (EI) m/z: 253 (M^+), 238, 155, 139, 91; HRMS (ESI^+) calcd for $C_{13}H_{19}NNaO_2S^+$ (M + Na^+) 276.1029, Found 276.1033.

References

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[2] a) O. Bertrand, B. Ernould, F. Boujioui, A. Vlad, J.-F. Gohy, *Polymer Chemistry* **2015**, *6*, 6067-6072; b) E. G. Rozantsev, *Free Nitroxy Radicals*, Plenum Press, New York, **1971**.

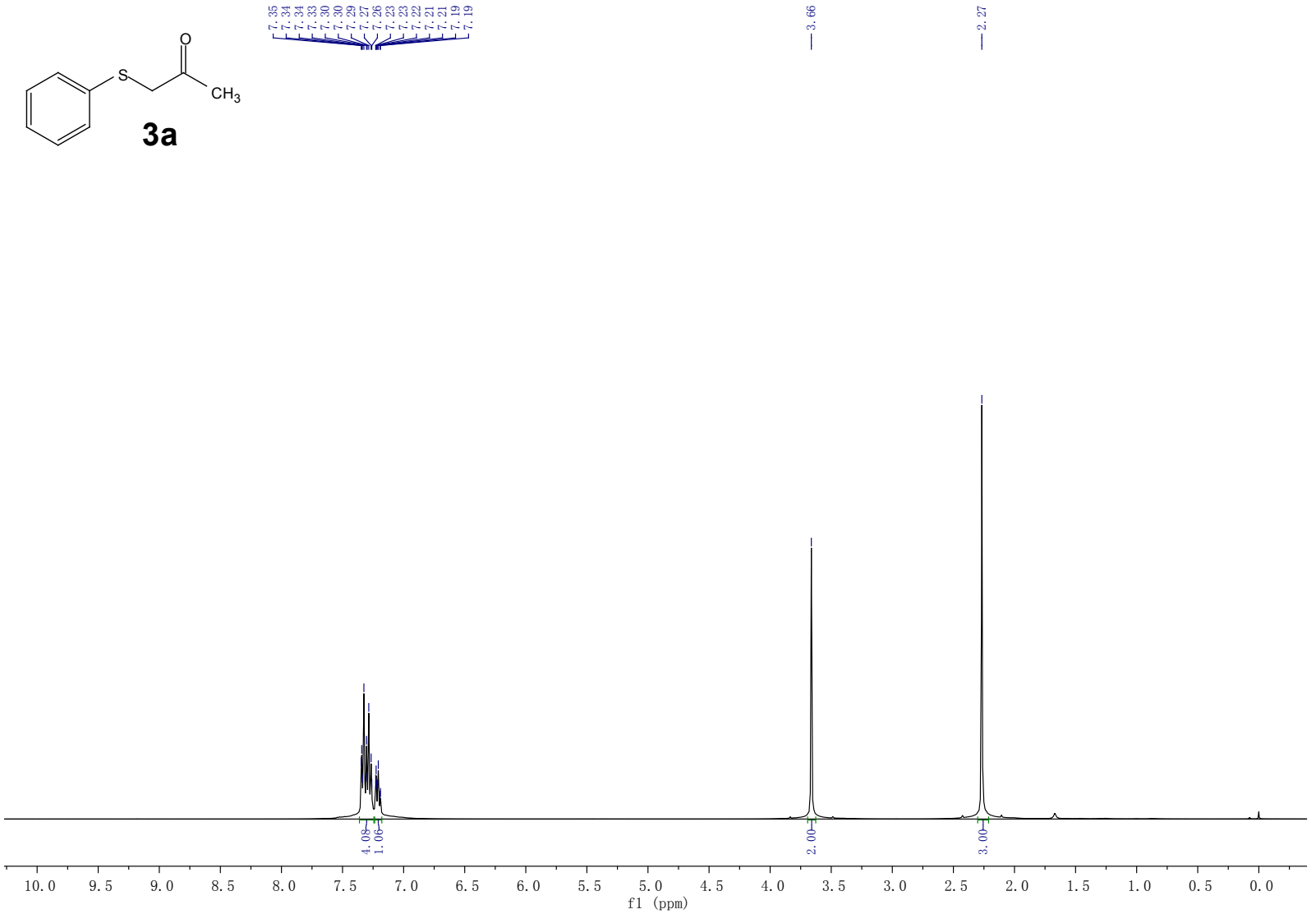
[3] N. J. Harper, A. H. Beckett, A. D. J. Balon, *J. Chem. Soc.* (Resumed) **1960**, 2704-2711.

[4] H. Henry-Riyad, T. T. Tidwell, J. Phys. *Org. Chem*. **2003**, *16*, 559-563.

[5] P. Carloni, E. Damiani, M. Iacussi, L. Greci, P. Stipa, D. Cauzi, C. Rizzoli, P. Sgarabotto, *Tetrahedron* **1995**, *51*, 12445-12452.

[6] E. T. Hennessy, T. A. Betley, *Science* **2013**, *340*, 591-595.

^{1}H NMR and ^{13}C NMR spectrum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7.19
7.19
3.66
2.27
O
S
CH3
3a
4.08
1.06
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
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3.5
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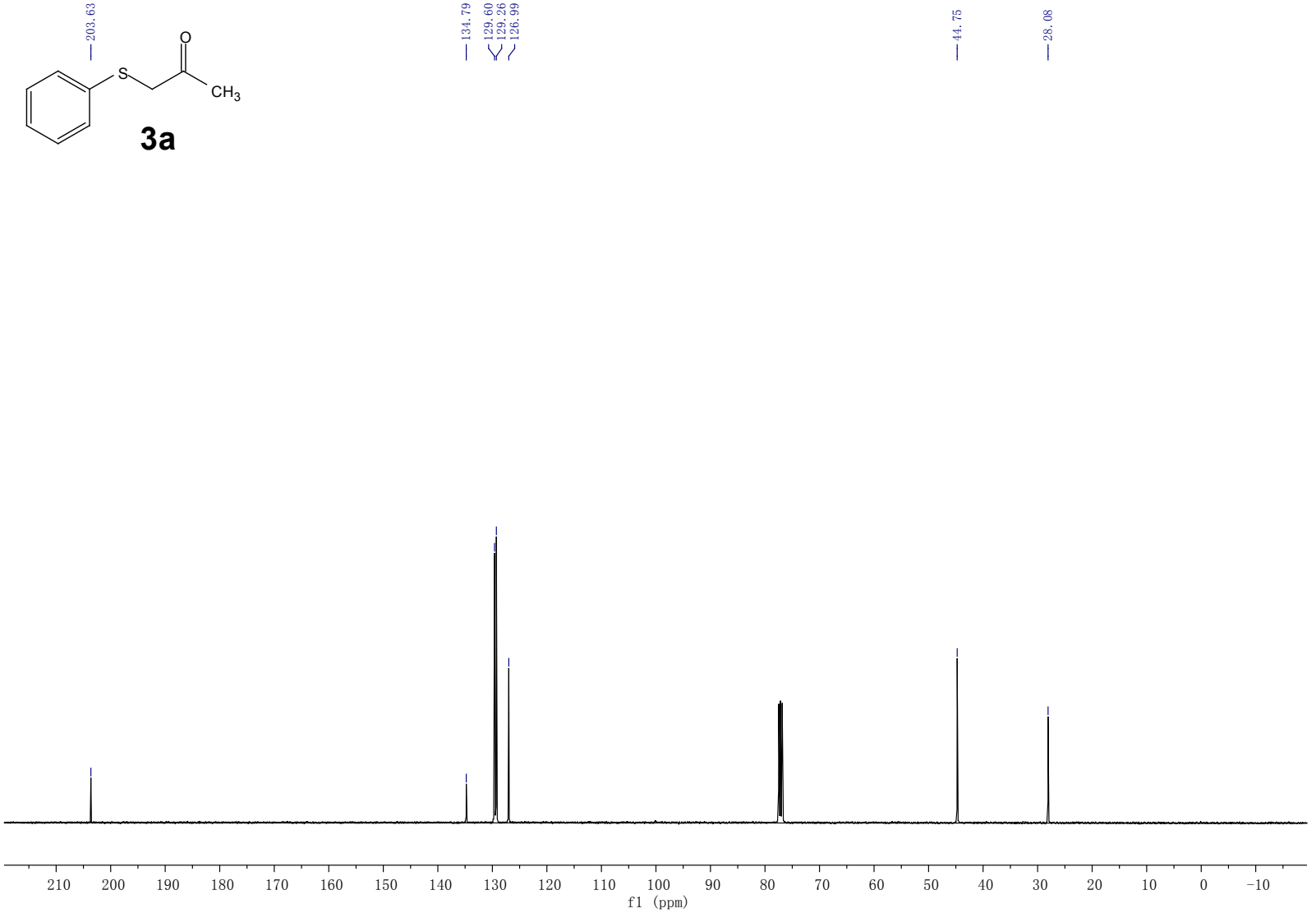
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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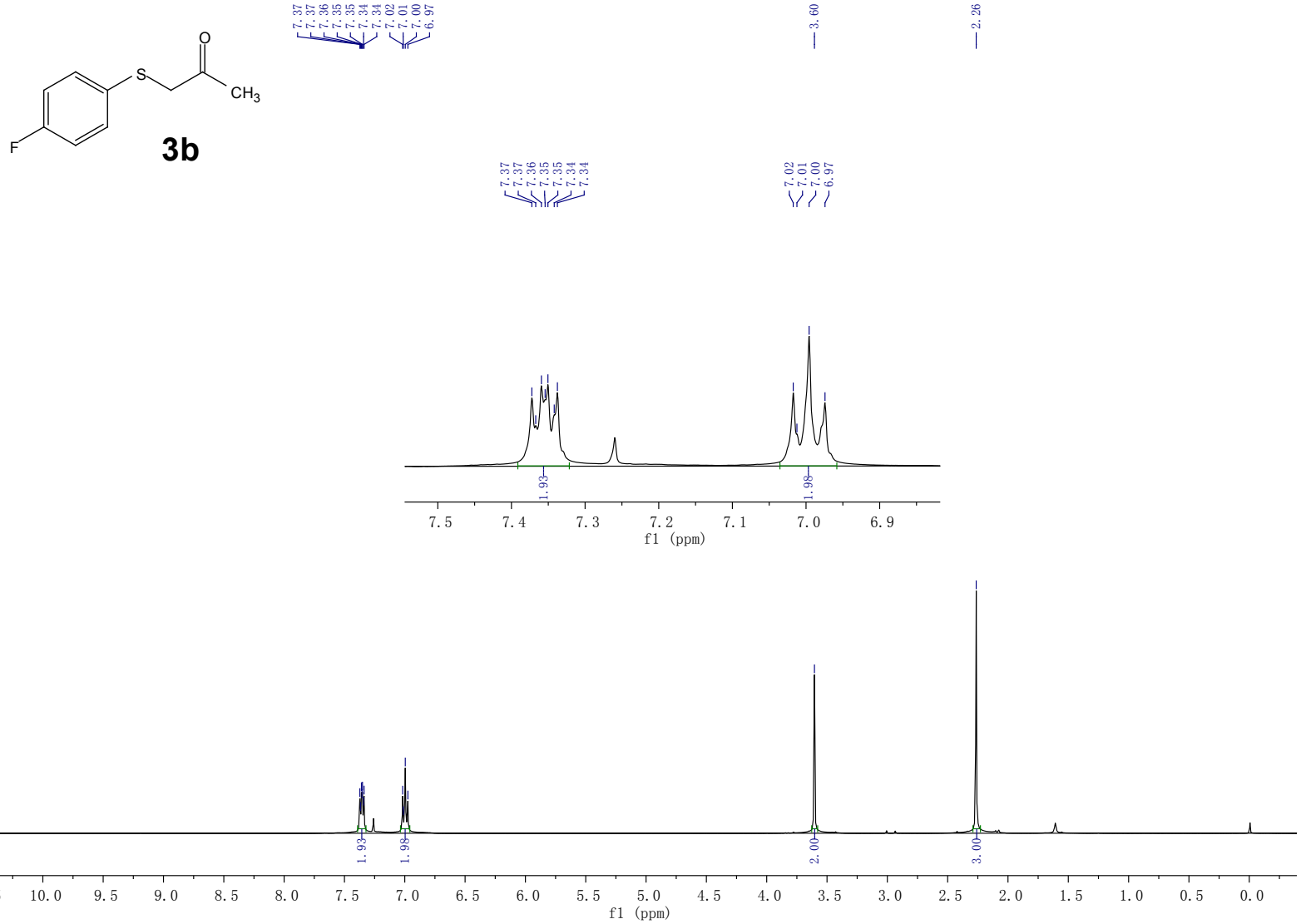
S
CH3
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.02
7.01
7.00
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2.26
O
S
CH3
F
3b
1.93
1.98
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
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1.98
2.00
3.00
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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1.0
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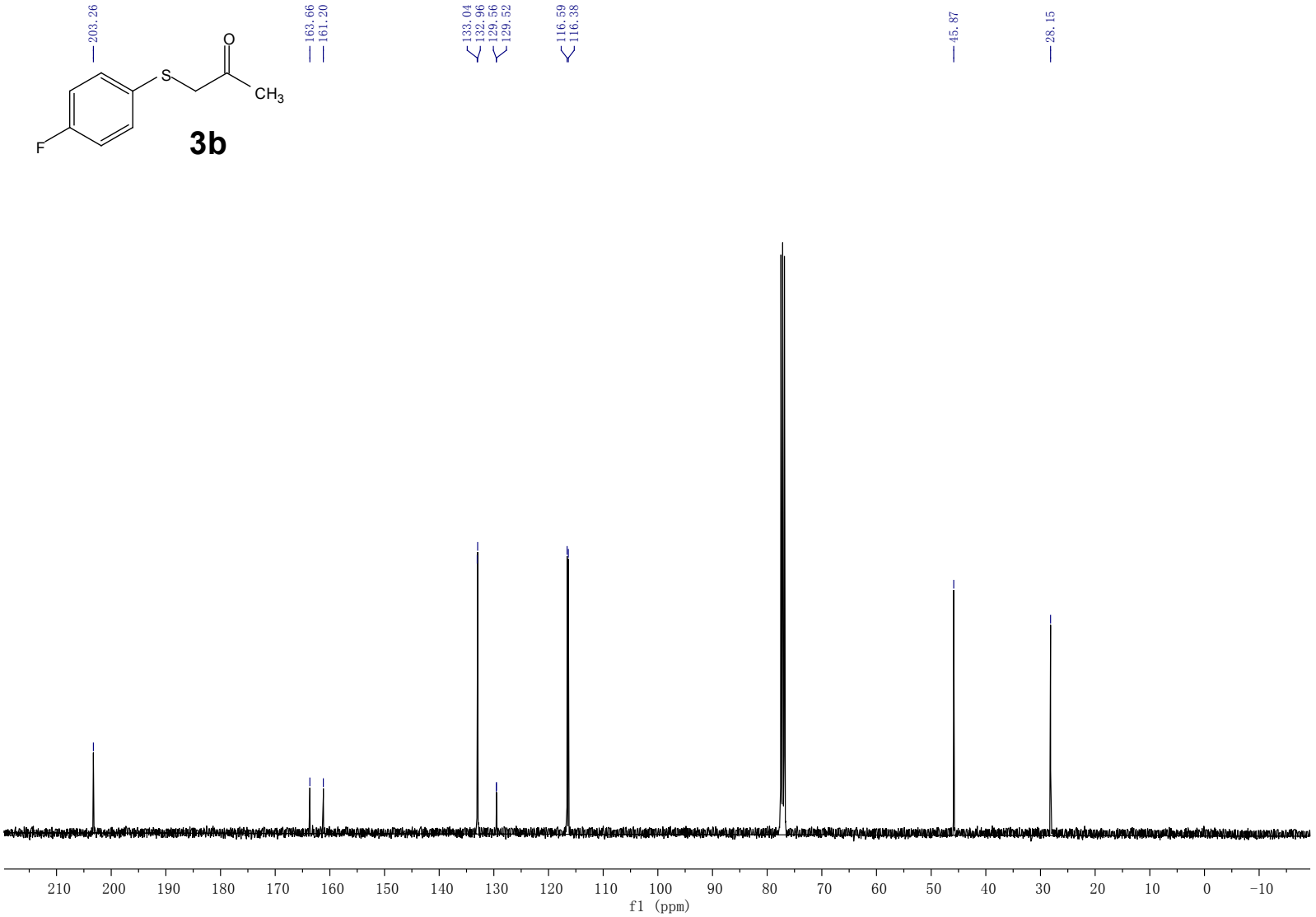
f1 (ppm)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129.56
129.52
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116.38
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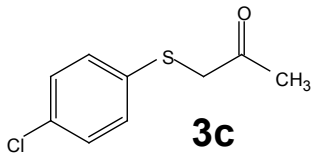
f1 (ppm)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S
CH3
Cl

3c

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2.00
2.95
10.0
9.5
9.0
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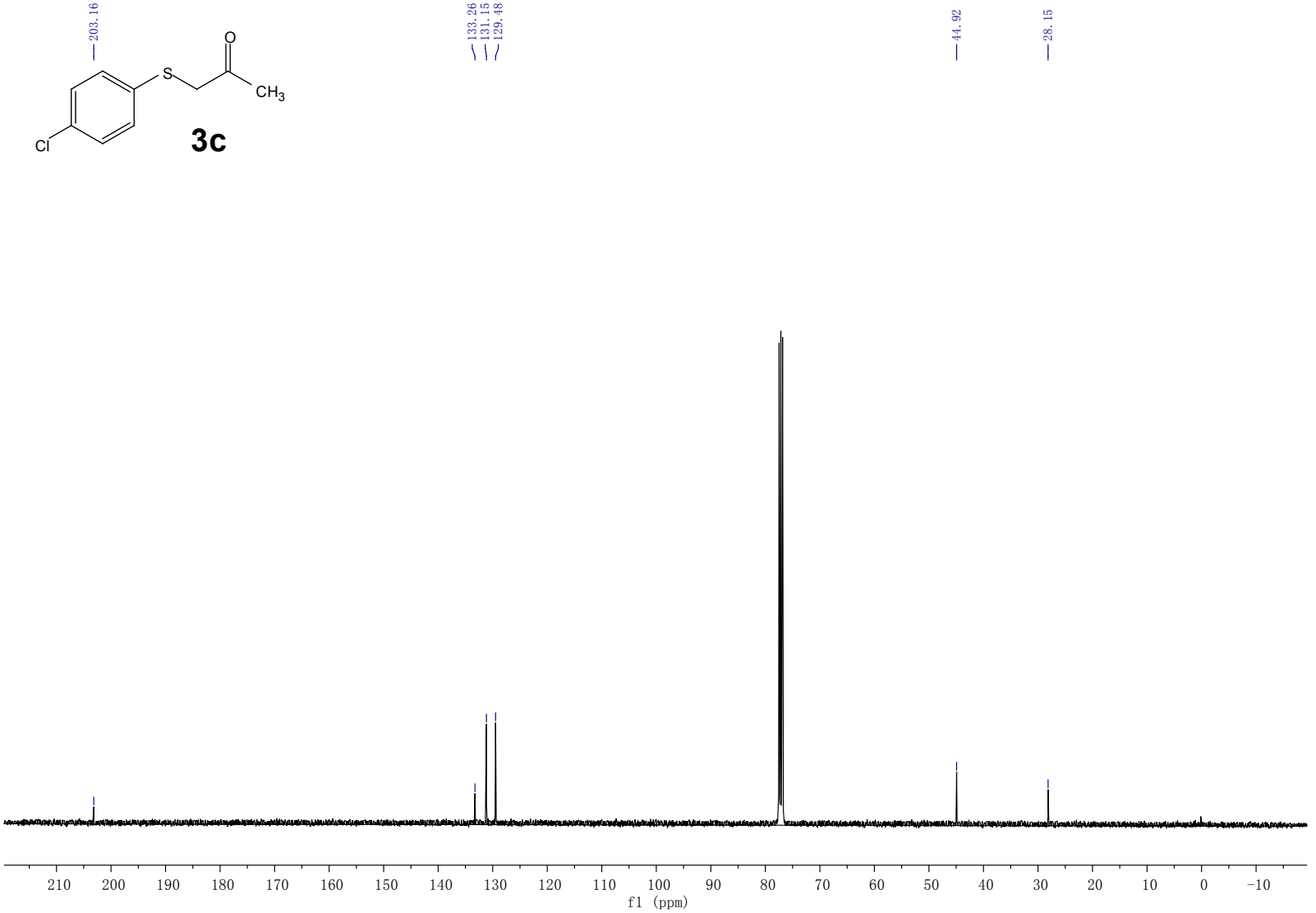
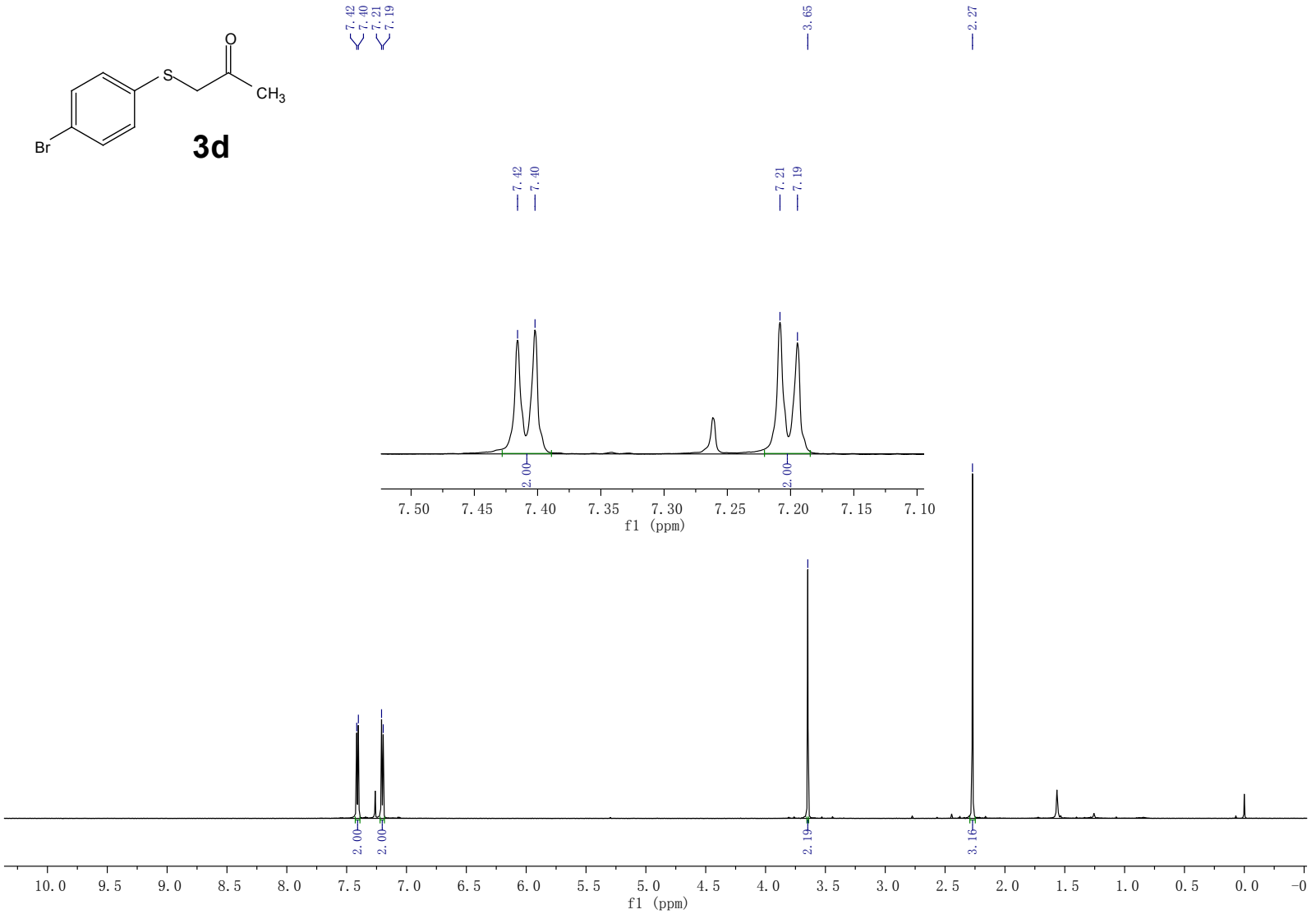
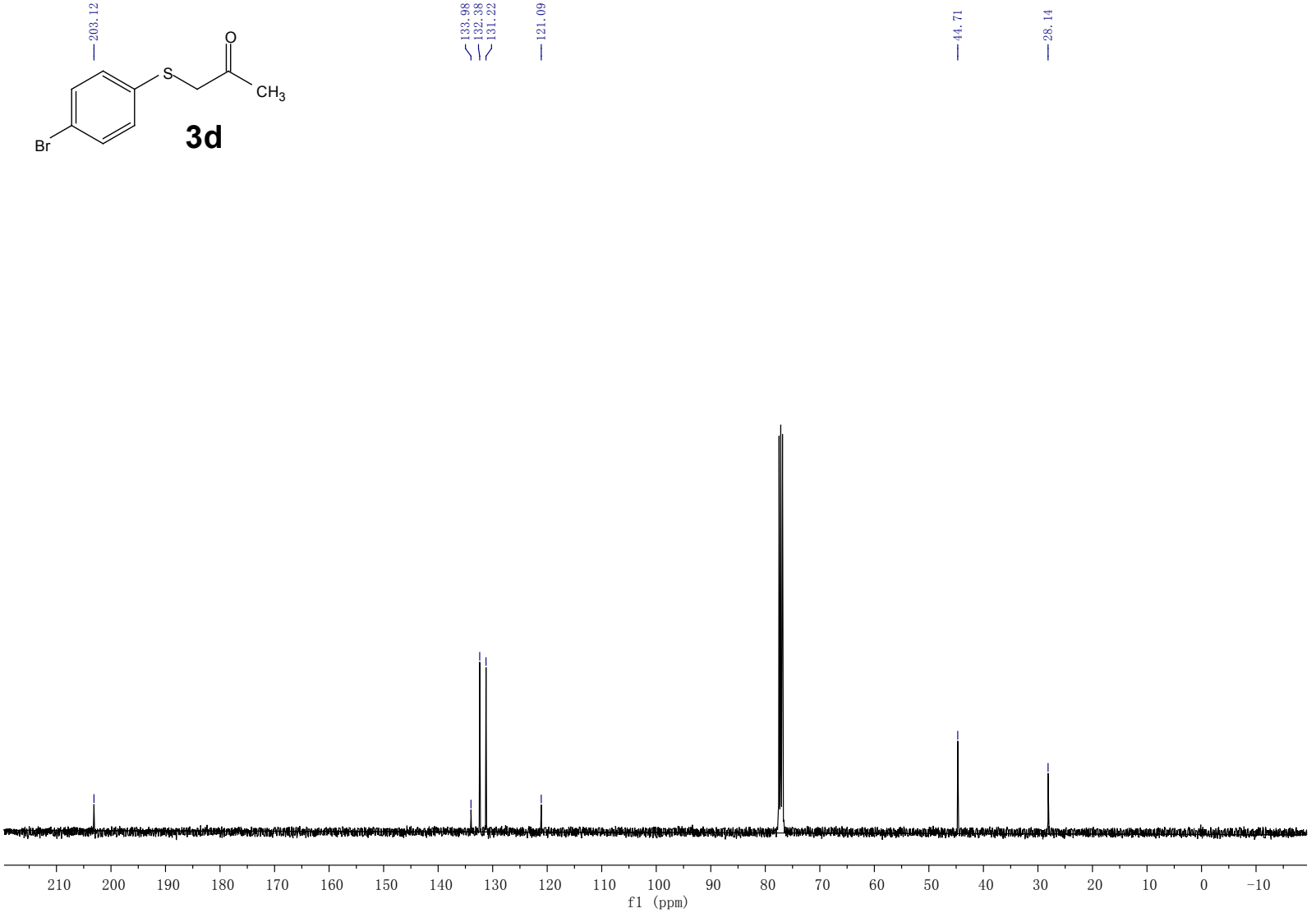
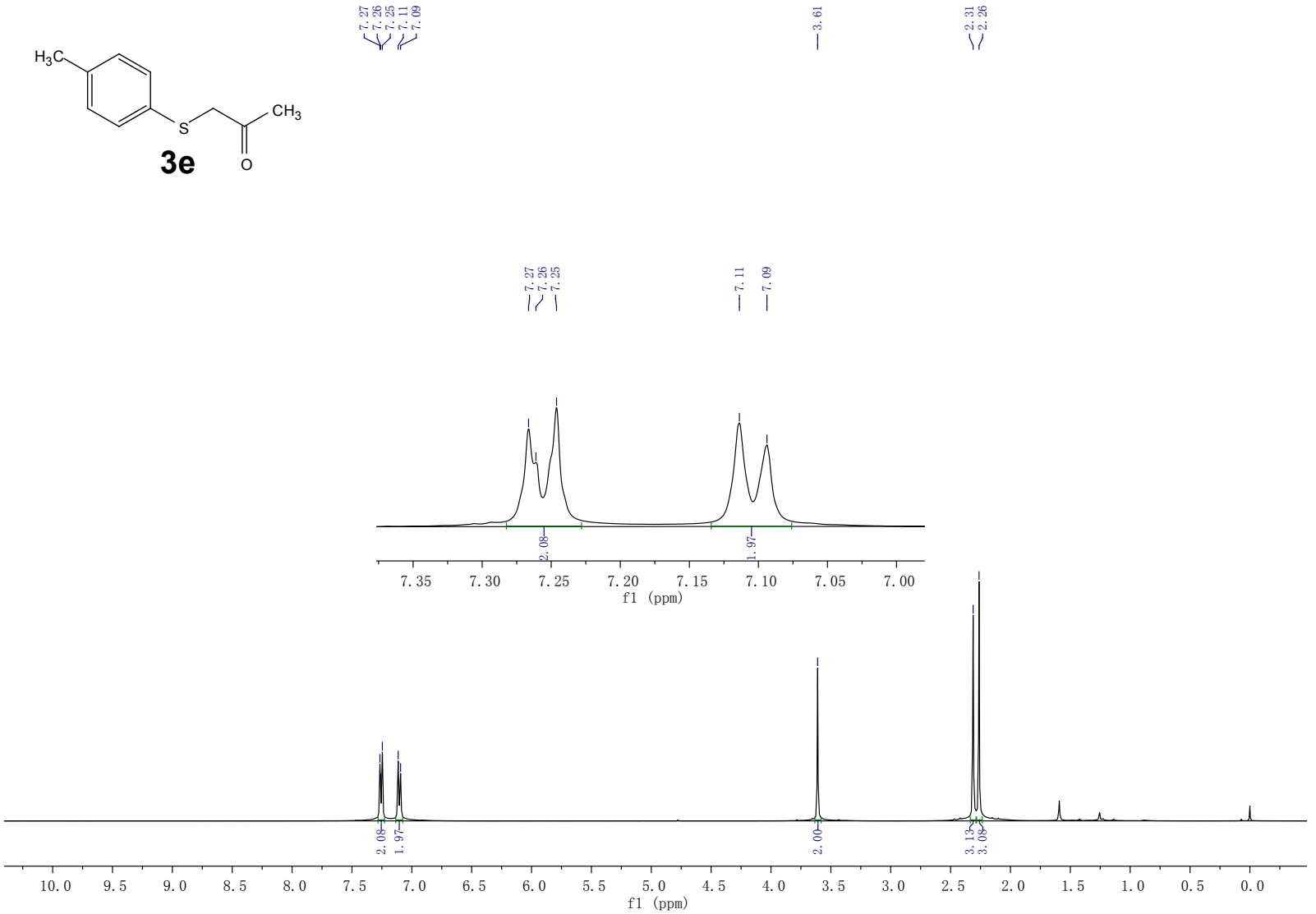
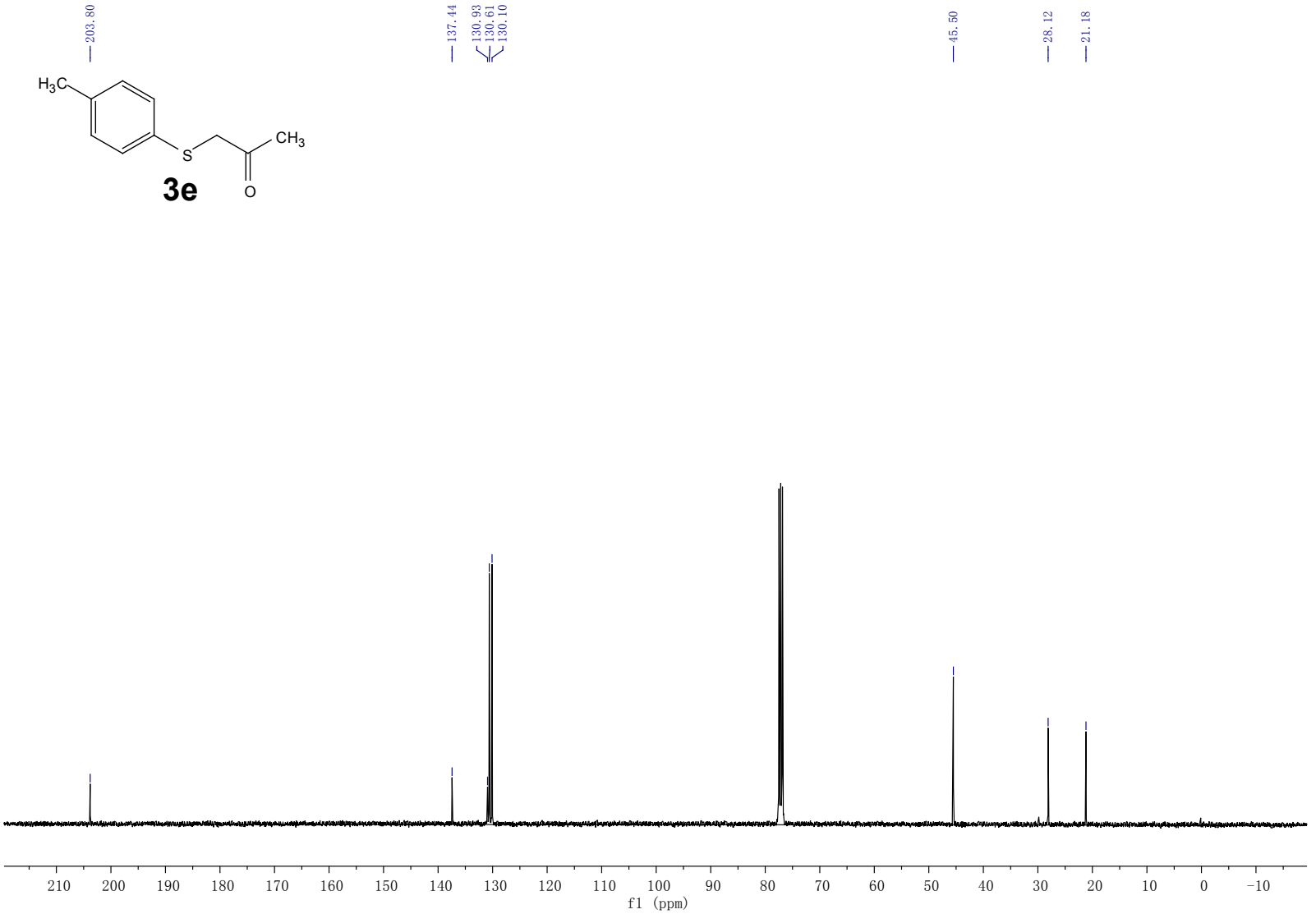
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

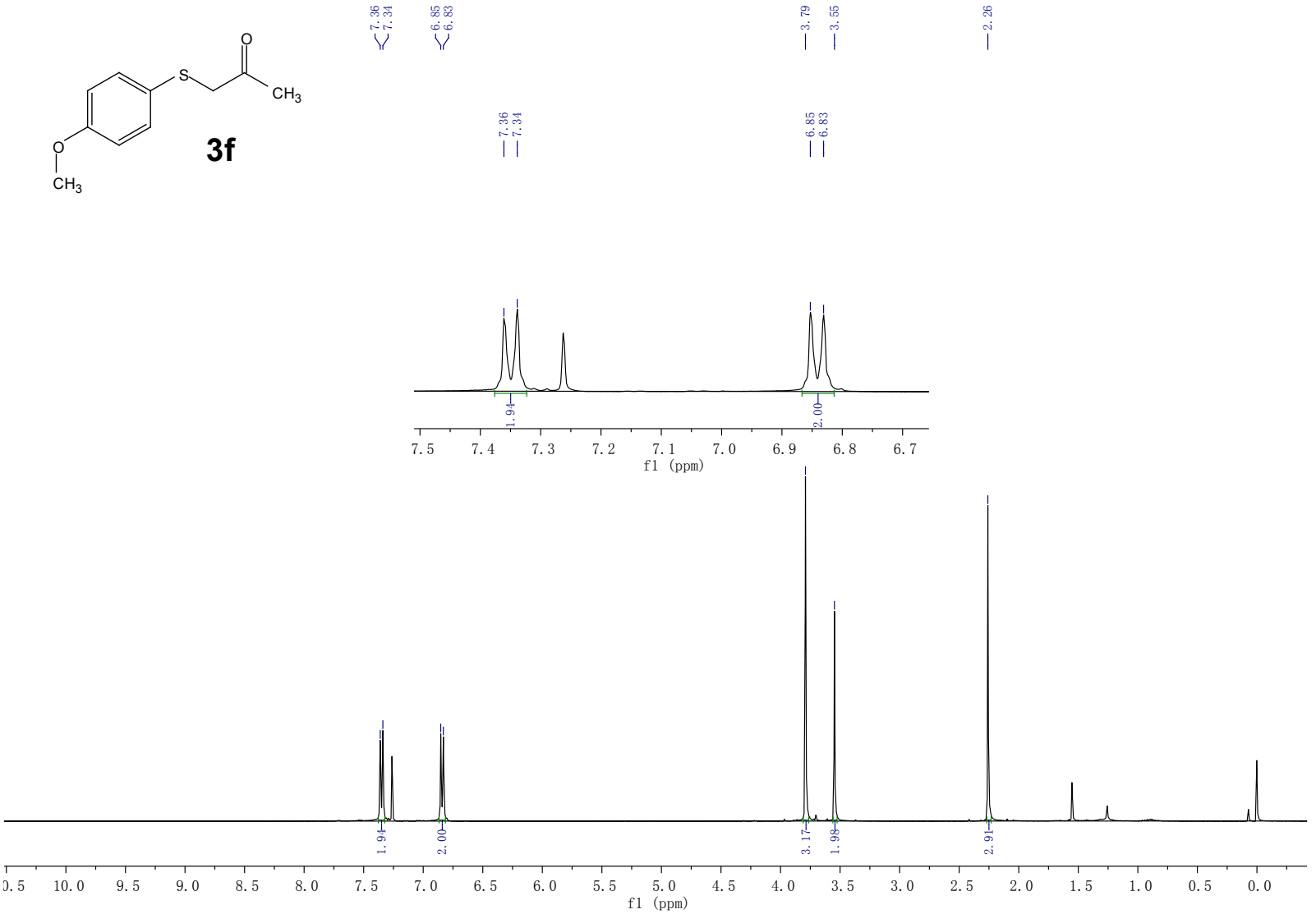

203.16
133.26
131.15
129.48
44.92
28.15
O
S
CH3
Cl
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

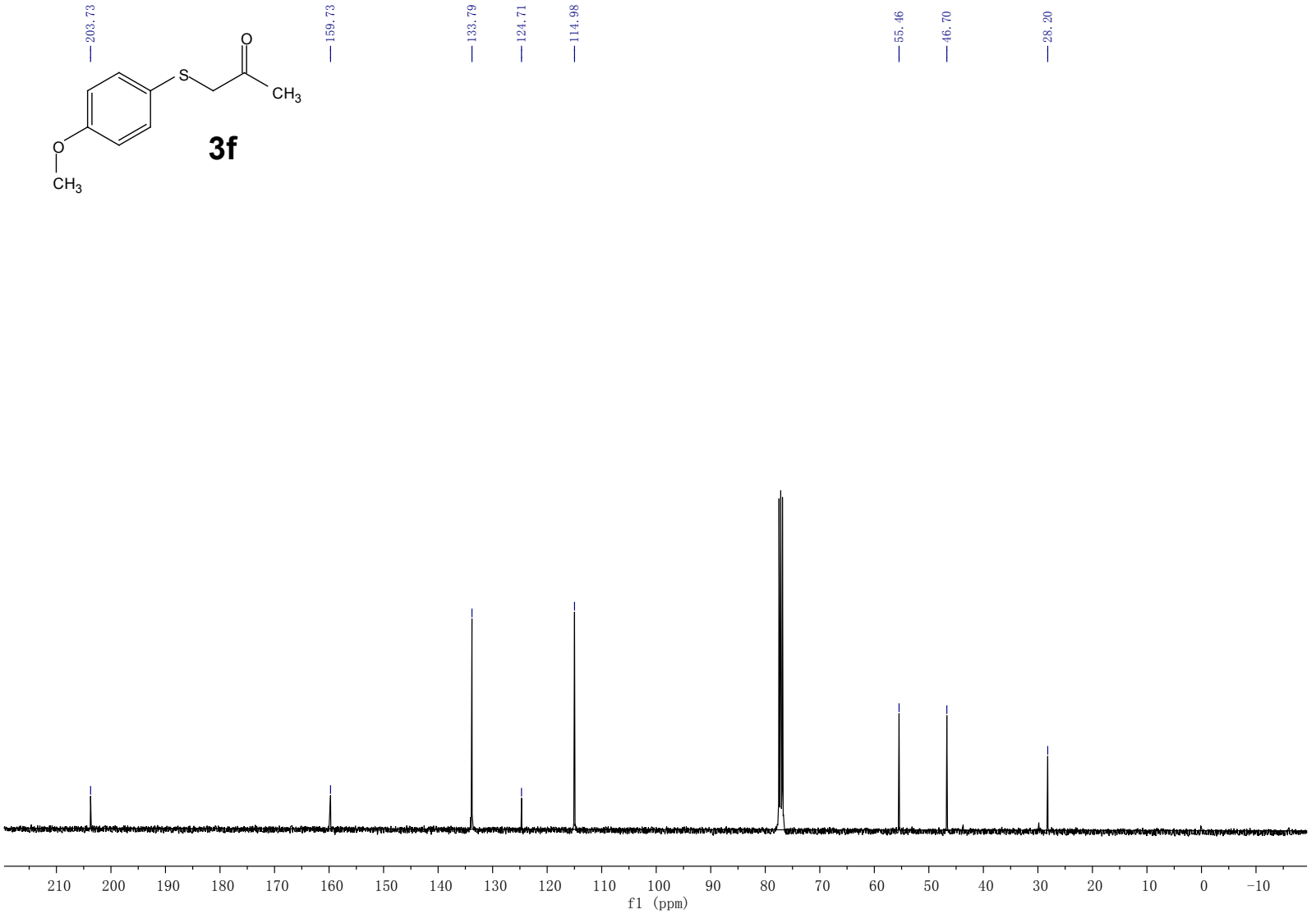

7.42
7.40
7.21
7.19
3.65
2.27
O
S
CH3
Br
3d
2.00
2.00
2.19
3.16
f1 (ppm)

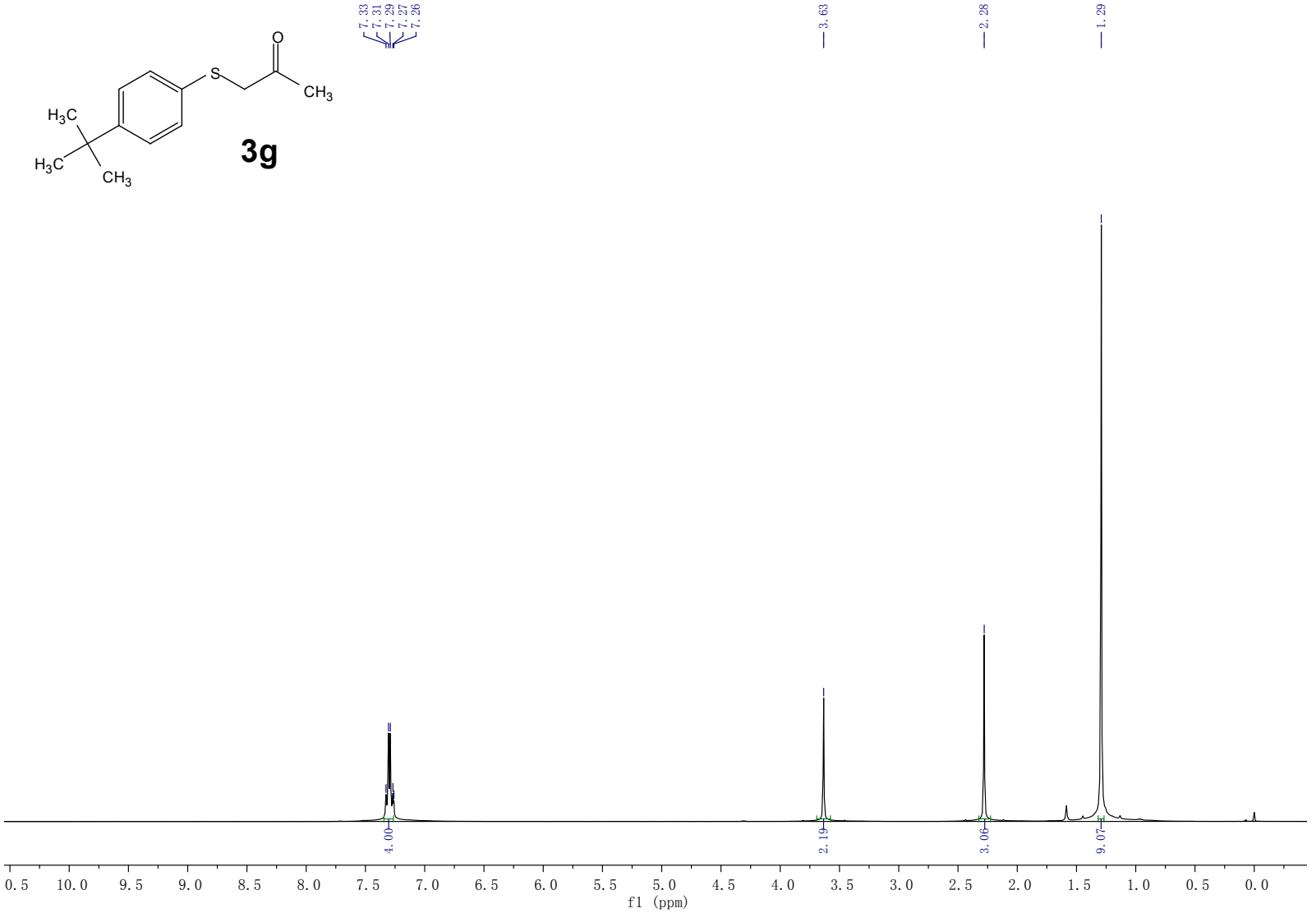

203.12
133.98
132.38
131.22
121.09
44.71
28.14
O
S
CH3
Br
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

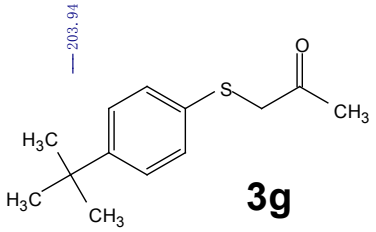

H3C
S
CH3
O
3e
7.27
7.26
7.25
7.11
7.09
3.61
2.31
2.26
2.08
1.97
2.00
3.13
3.08
f1 (ppm)


203.80
137.44
130.93
130.61
130.10
45.50
28.12
21.18
H3C
S
CH3
O
3e
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)


3f
7.36
7.34
6.85
6.83
3.79
3.55
2.26
1.94
2.00
3.17
1.98
2.91
f1 (ppm)

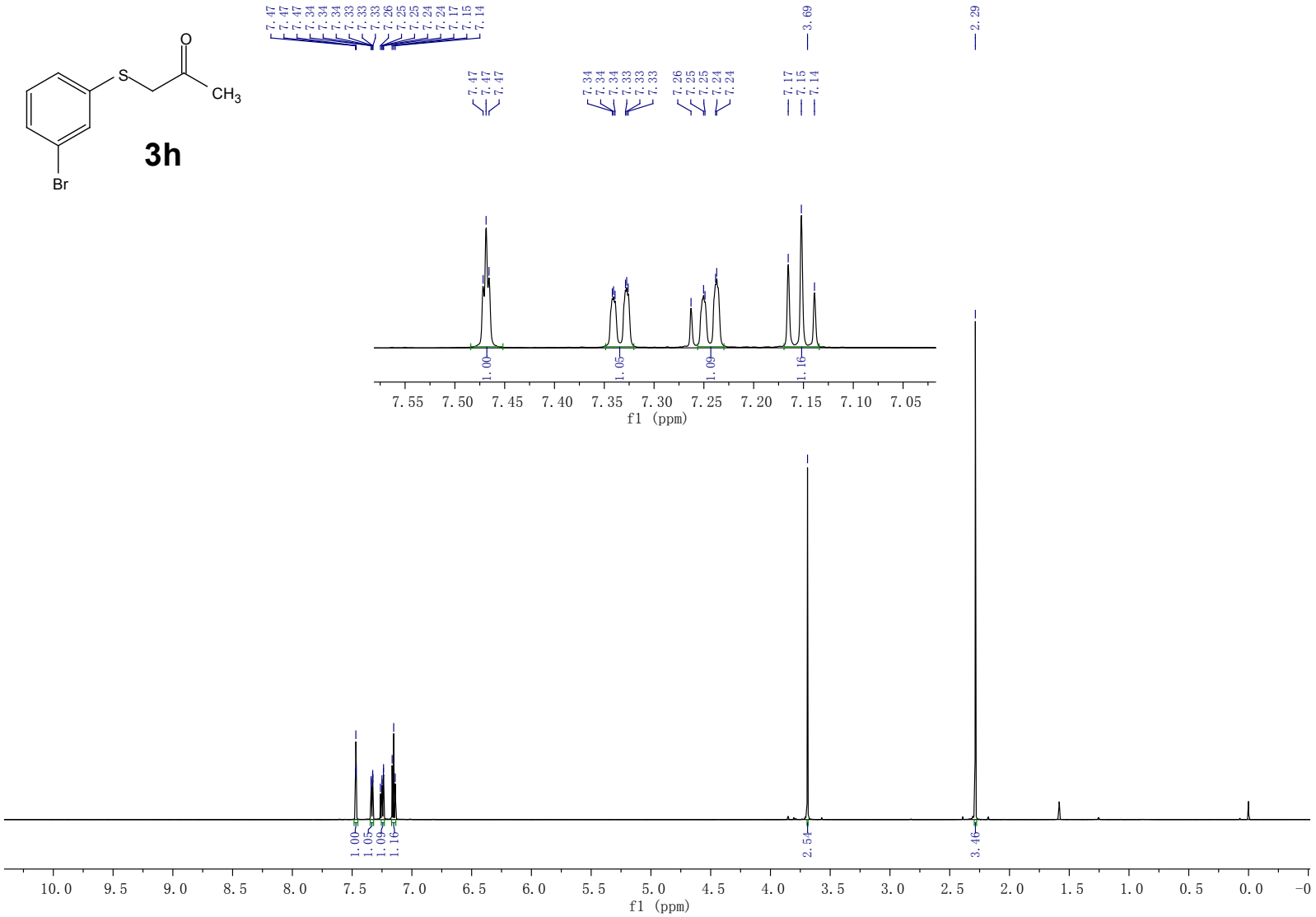

203.73
159.73
133.79
124.71
114.98
55.46
46.70
28.20
O
S
CH3
O
CH3
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

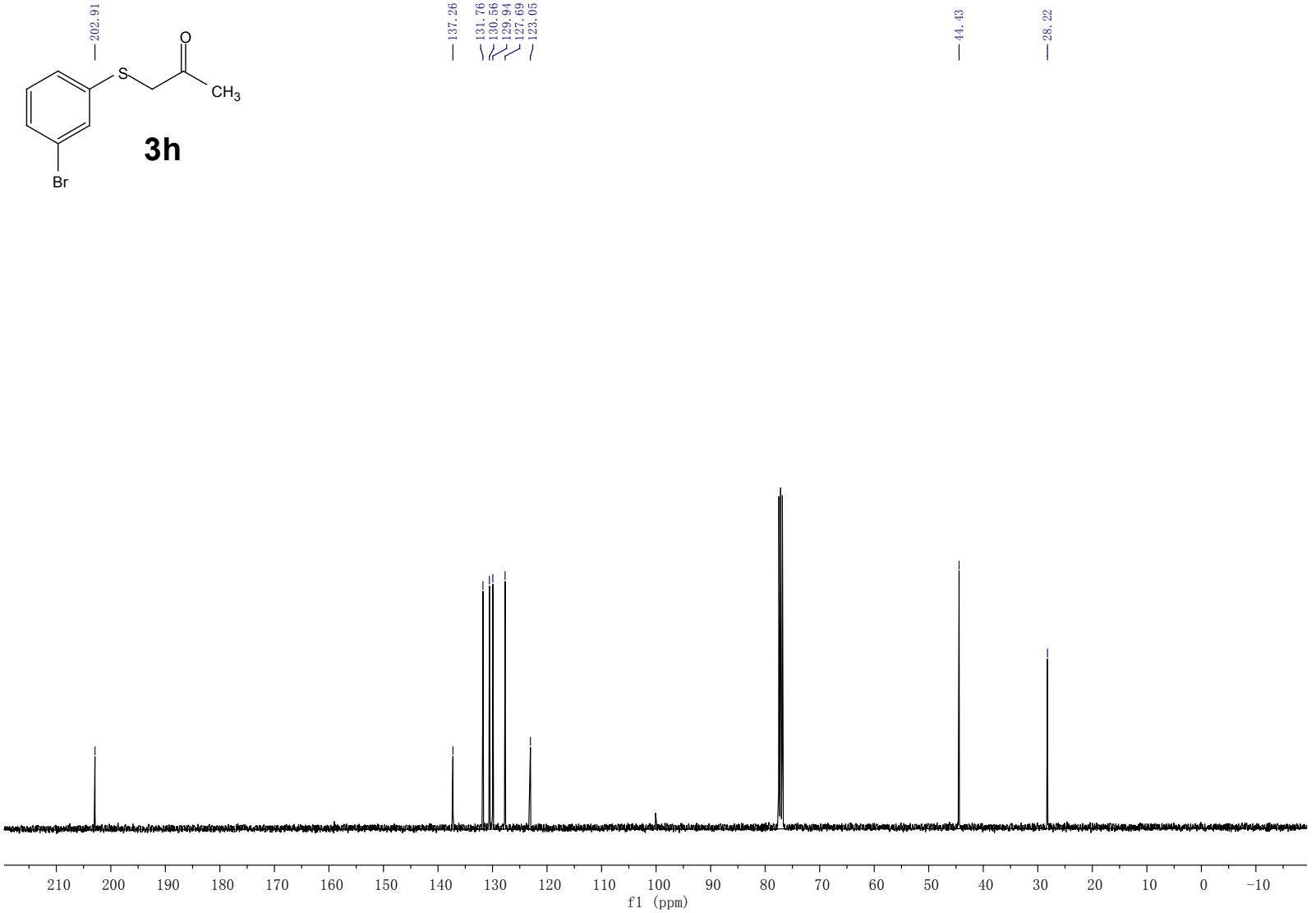

7.33
7.31
7.29
7.27
7.26
3.63
2.28
1.29
O
S
CH3
H3C
H3C
CH3
3g
4.00
2.19
3.06
9.07
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

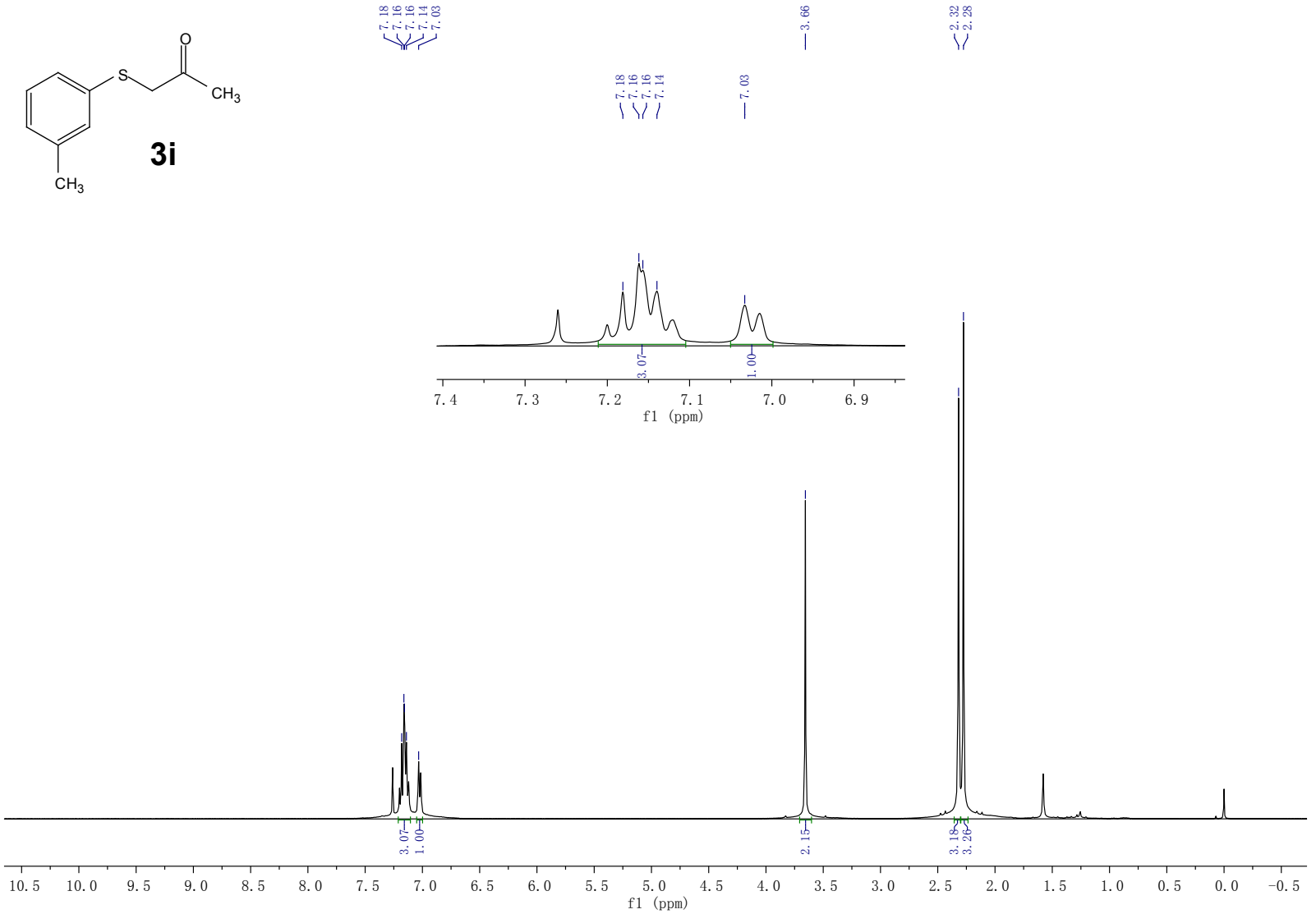

O
S
CH3
H3C
H3C
CH3

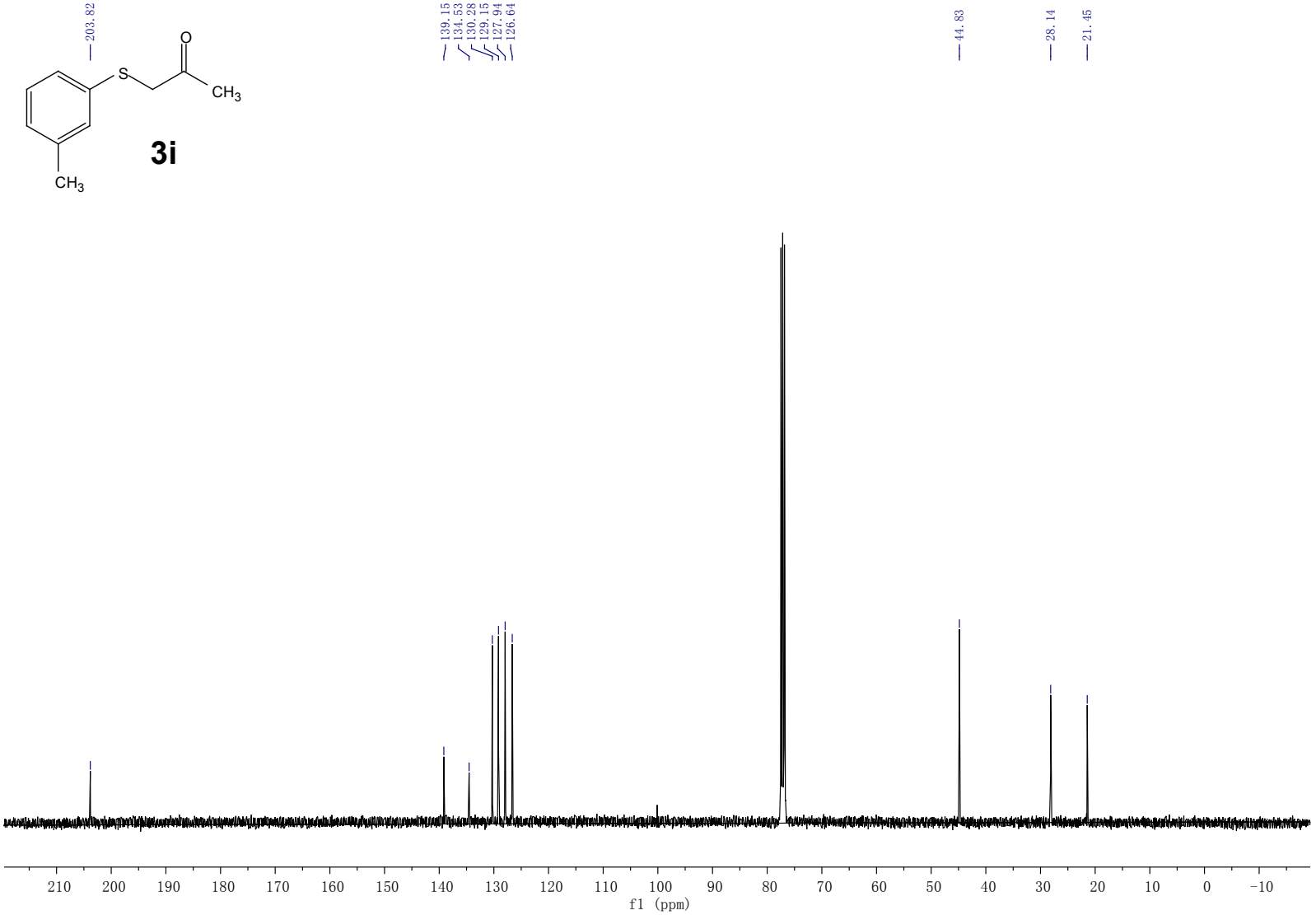
3g

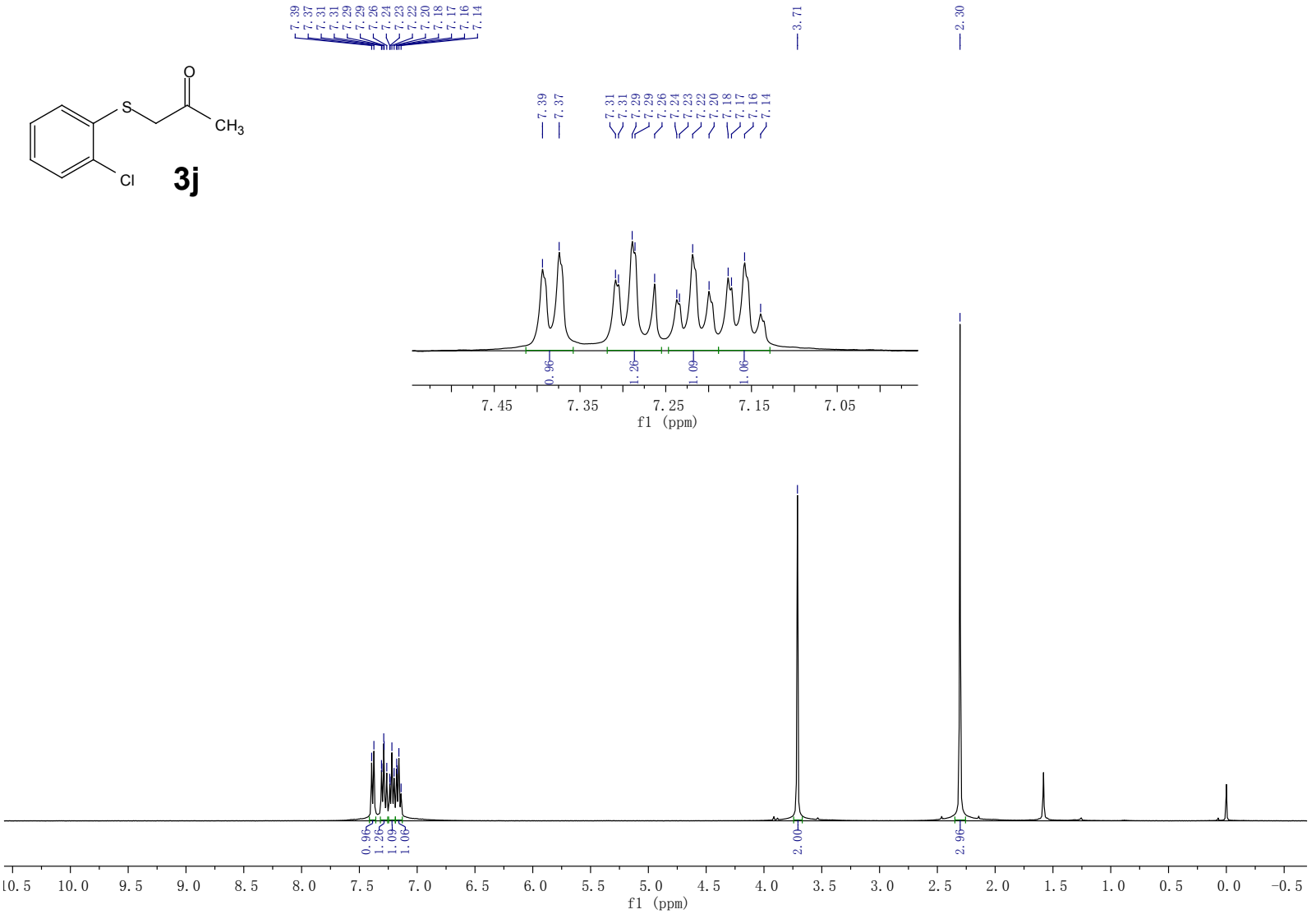
203.94
150.48
131.13
129.96
126.39
45.25
34.65
31.35
28.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

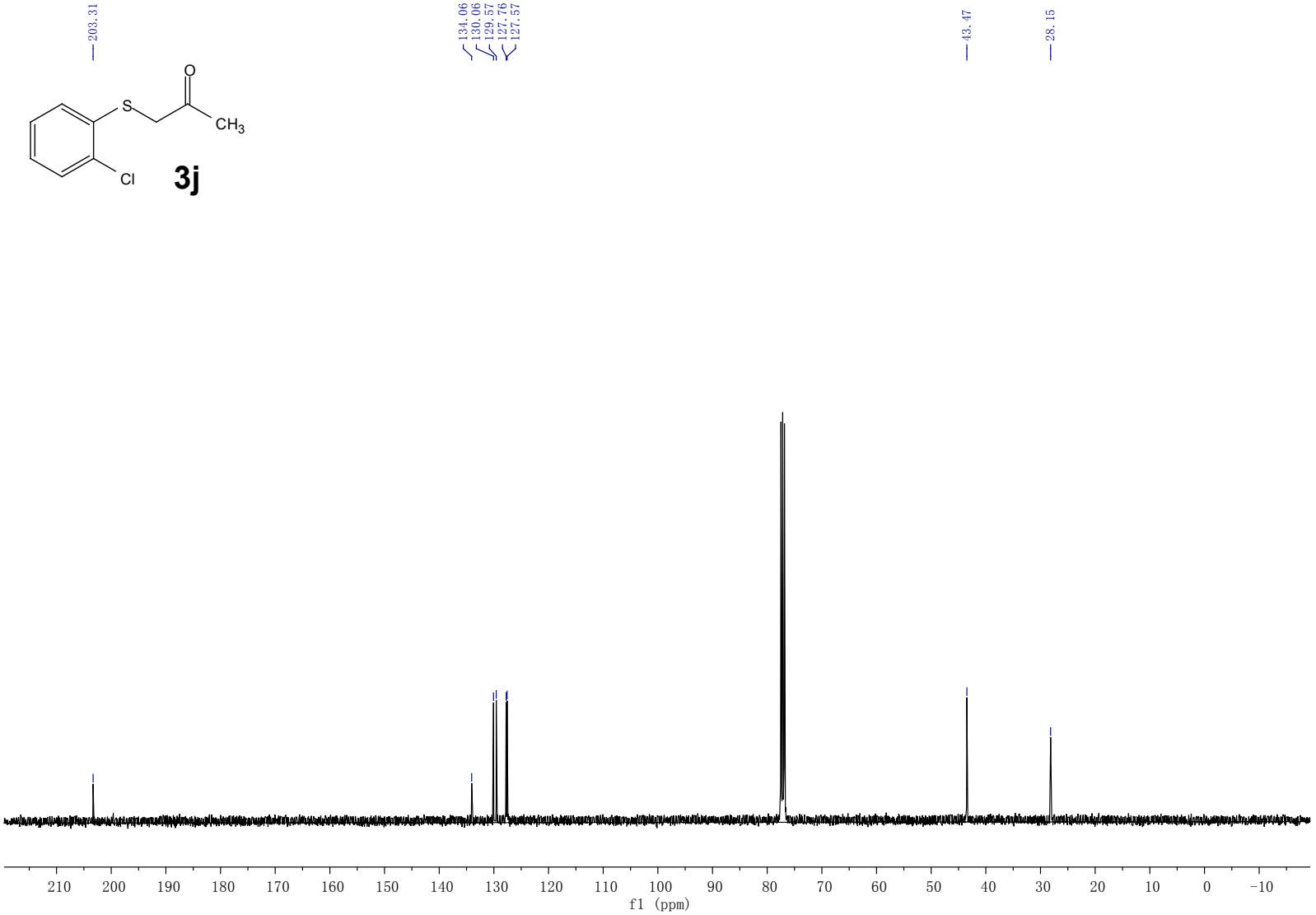

7.47
7.47
7.47
7.34
7.34
7.34
7.33
7.33
7.33
7.26
7.25
7.25
7.24
7.24
7.17
7.15
7.14
3.69
2.29
O
S
CH3
Br
3h
1.00
1.05
1.09
1.16
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)
2.54
3.46
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

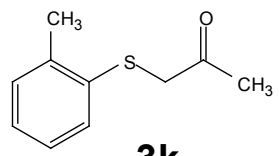

202.91
137.26
131.76
130.56
129.94
127.69
123.05
44.43
28.22
O
S
CH3
Br
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
S
CH3
CH3
3i
7.18
7.16
7.16
7.14
7.03
3.66
2.32
2.28
3.07
1.00
2.15
3.18
3.26
f1 (ppm)


203.82
139.15
134.53
130.28
129.15
127.94
126.64
44.83
28.14
21.45
O
S
CH3
CH3
3i
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)

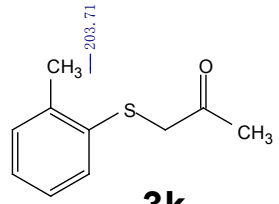

7.39
7.37
7.31
7.31
7.29
7.29
7.26
7.24
7.23
7.22
7.20
7.18
7.17
7.16
7.14
3.71
2.30
O
S
CH3
Cl
3j
0.96
1.26
1.09
1.06
7.45
7.35
7.25
7.15
7.05
f1 (ppm)
2.00
2.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


203.31
134.06
130.06
129.57
127.76
127.57
43.47
28.15
O
S
CH3
Cl
3j
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)


CH3
O
S
CH3

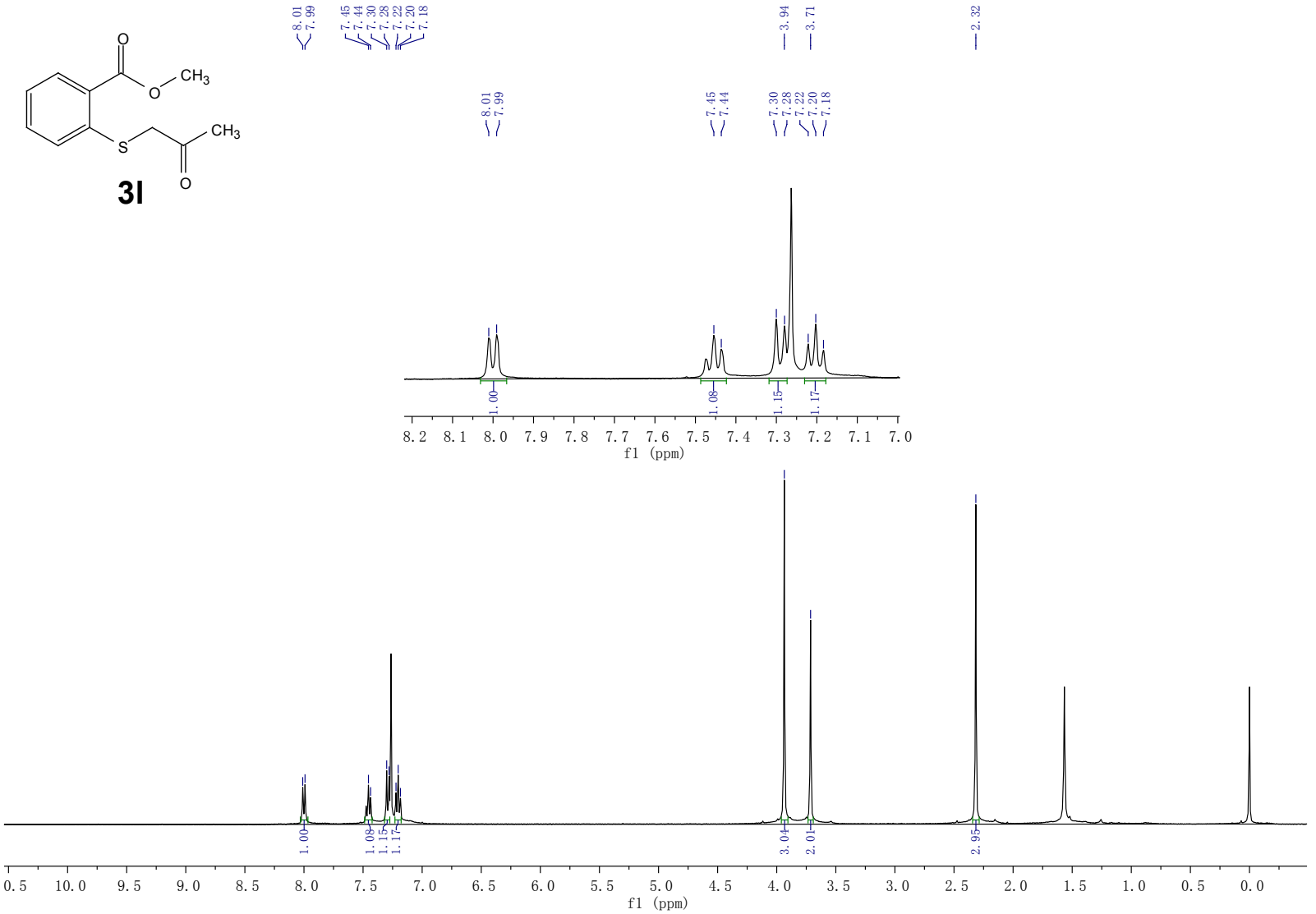
3k

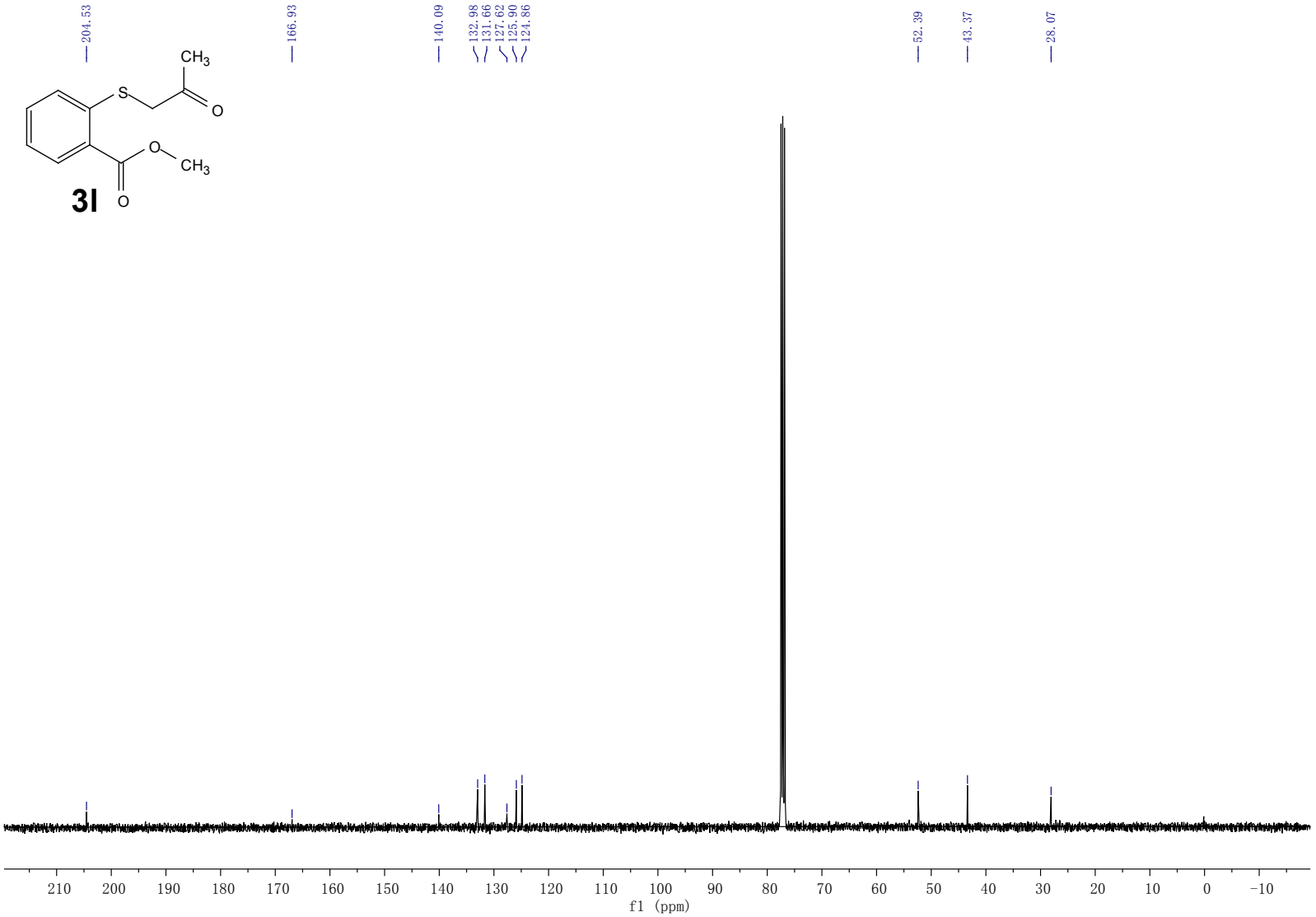
7.26
7.25
7.24
7.23
7.19
7.18
7.17
7.15
7.14
7.13
7.13
7.12
7.10
3.65
2.40
2.27
1.00
1.18
1.97
2.05
3.30
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

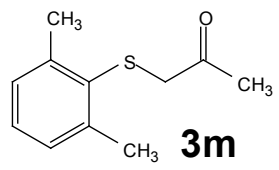

CH3
O
S
CH3

3k

203.71
138.02
134.02
130.52
128.88
126.85
44.04
28.16
20.44
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)

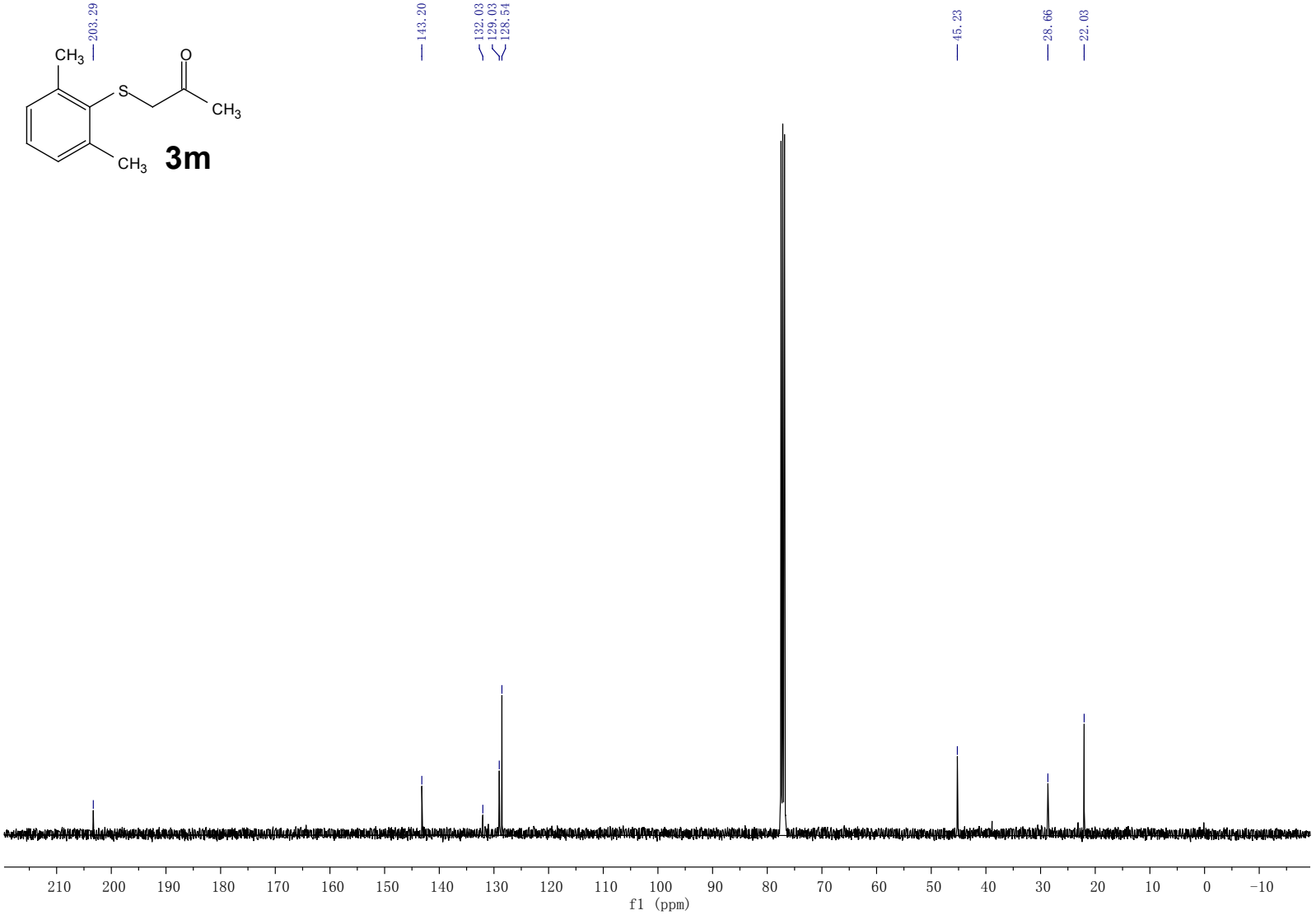

8.01
7.99
7.45
7.44
7.30
7.28
7.22
7.20
7.18
3.94
3.71
2.32
O
O
CH3
S
CH3
O
3l
1.00
1.08
1.15
1.17
3.04
2.01
2.95
f1 (ppm)

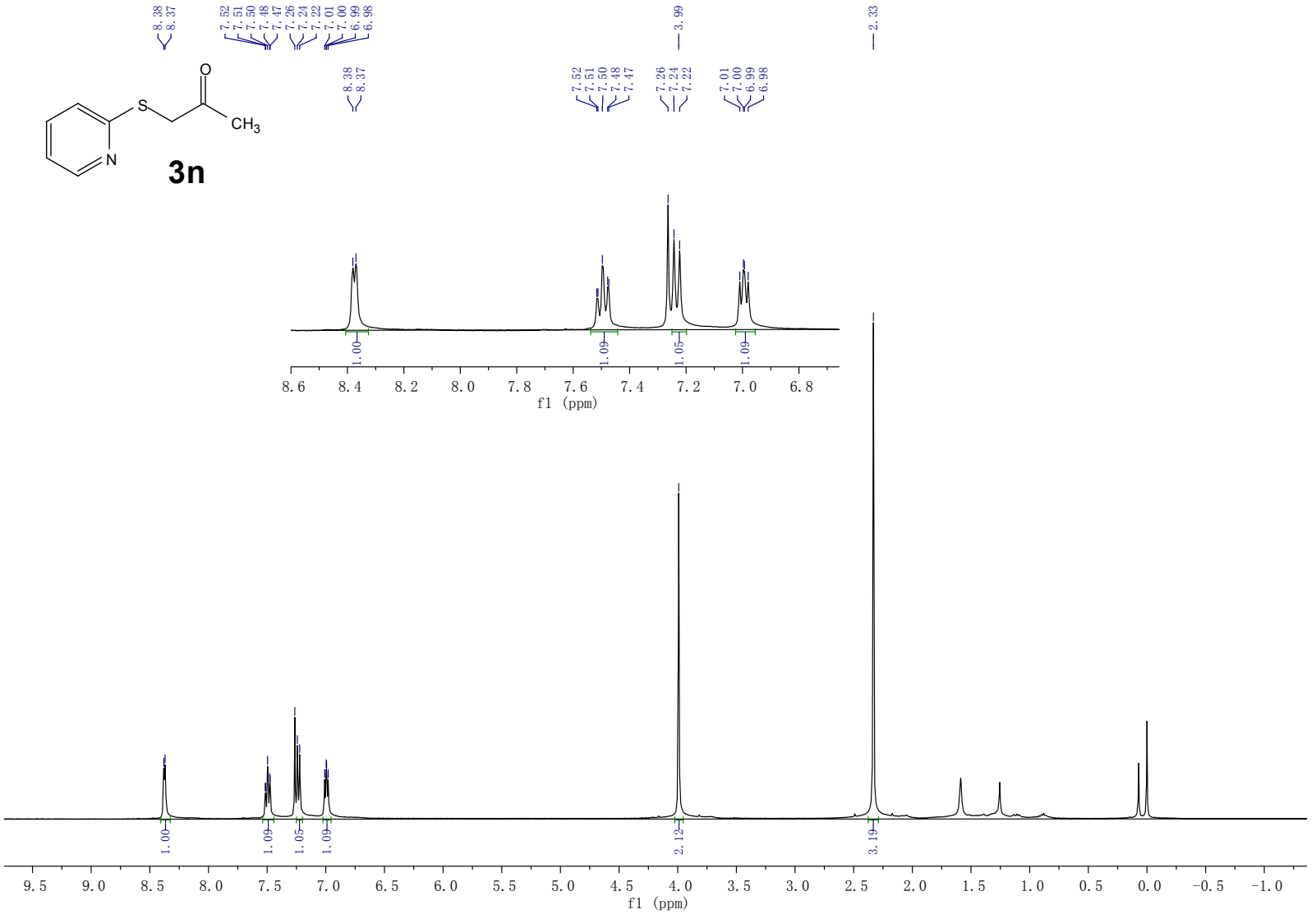

204.53
166.93
140.09
132.98
131.66
127.62
125.90
124.86
52.39
43.37
28.07
CH3
S
O
O
CH3
O
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

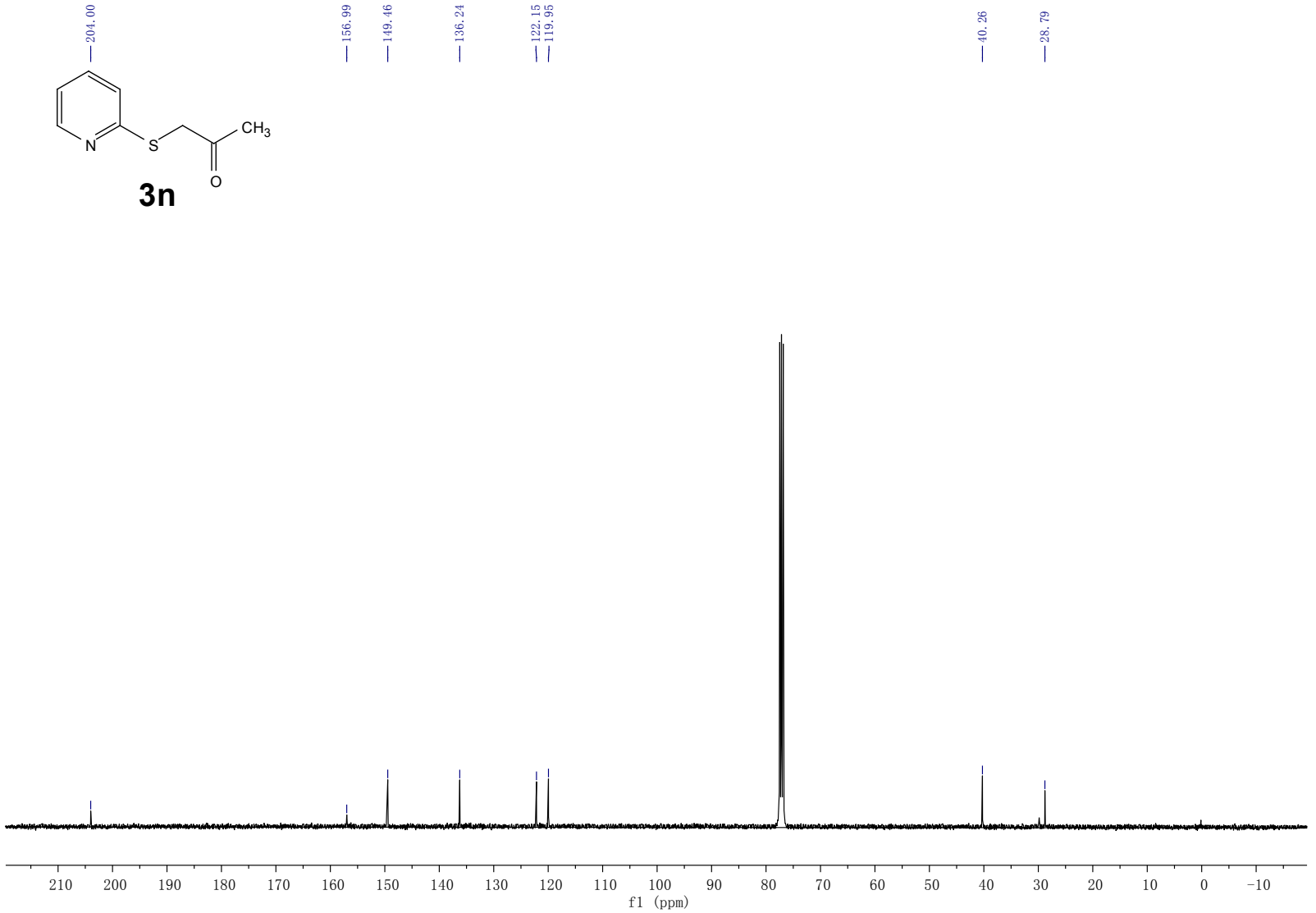

CH3
O
S
CH3
CH3

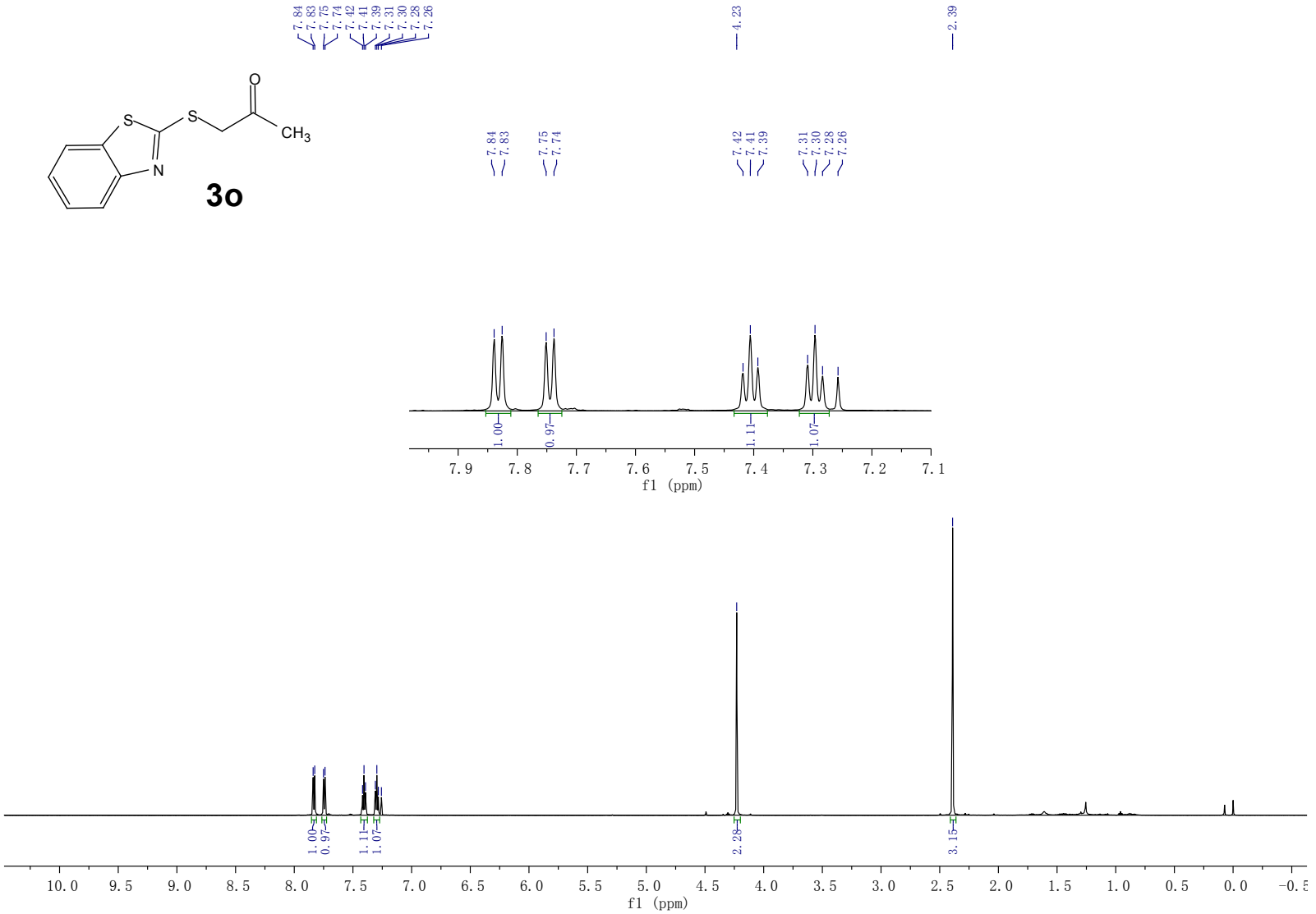
3m

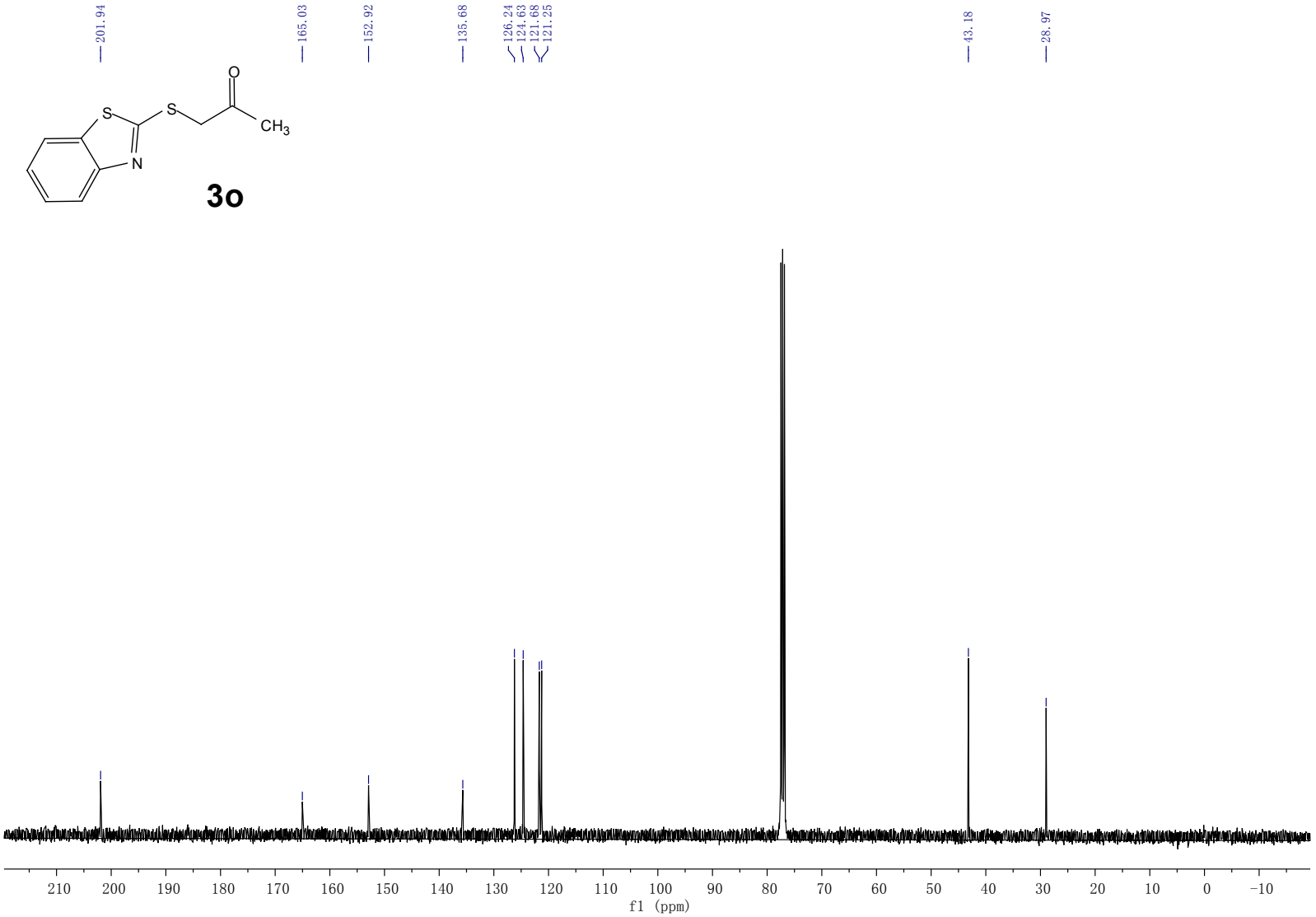
7.15
7.14
7.13
7.12
7.11
7.09
7.08
3.41
2.53
2.22
3.10
2.00
5.90
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

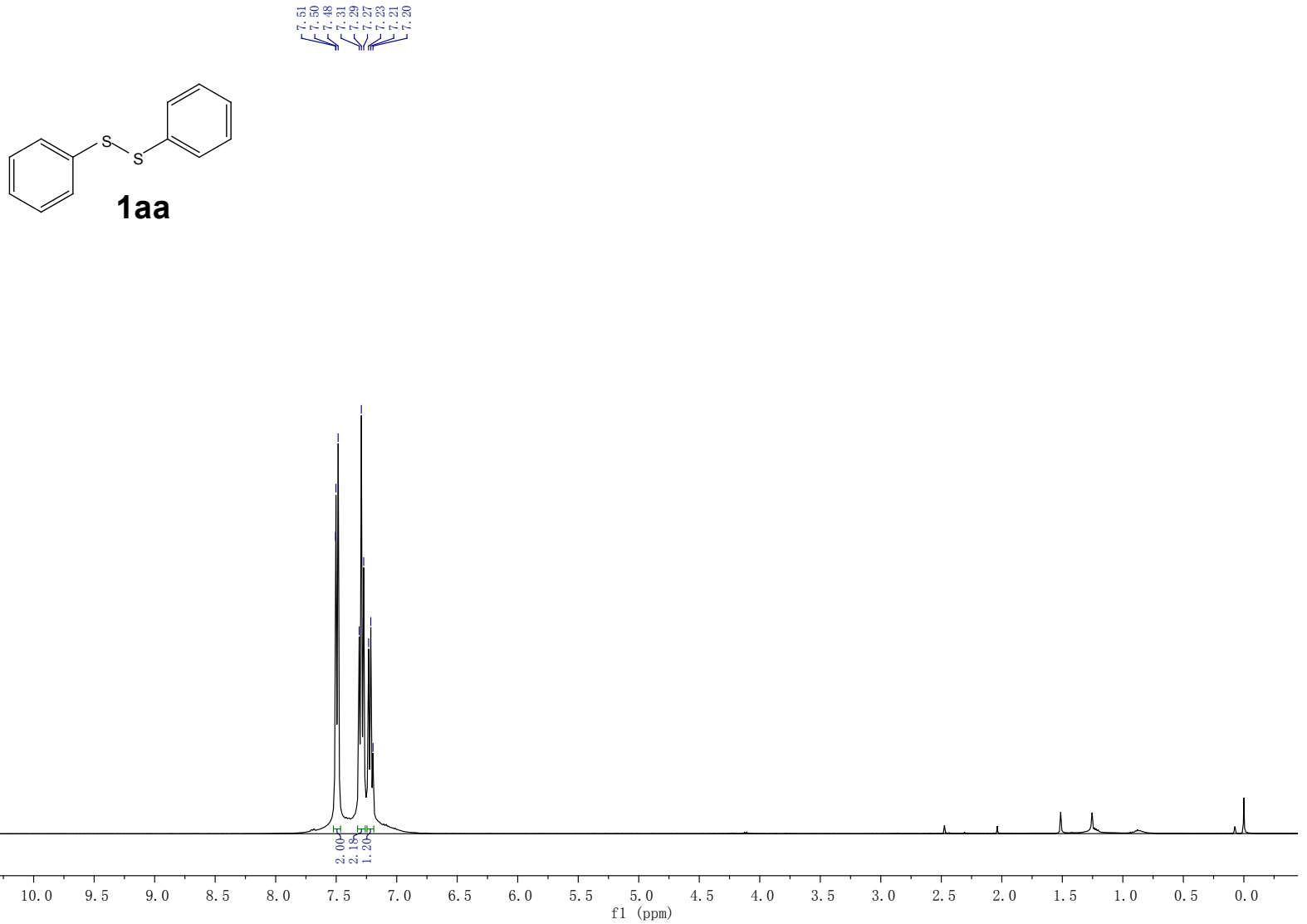

203.29
143.20
132.03
129.03
128.54
45.23
28.66
22.03
CH3
O
S
CH3
CH3
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

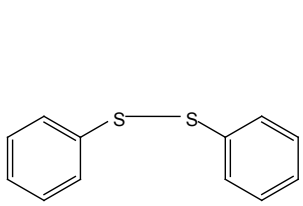

8.38
8.37
7.52
7.51
7.50
7.48
7.47
7.26
7.24
7.22
7.01
7.00
6.99
6.98
3.99
2.33
O
S
CH3
N
3n
1.00
1.09
1.05
1.09
2.12
3.19
f1 (ppm)


204.00
156.99
149.46
136.24
122.15
119.95
40.26
28.79
N
S
CH3
O
3n
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)


7.84
7.83
7.75
7.74
7.42
7.41
7.39
7.31
7.30
7.28
7.26
4.23
2.39
O
S
S
CH3
N
3o
1.00
0.97
1.11
1.07
2.28
3.15
f1 (ppm)

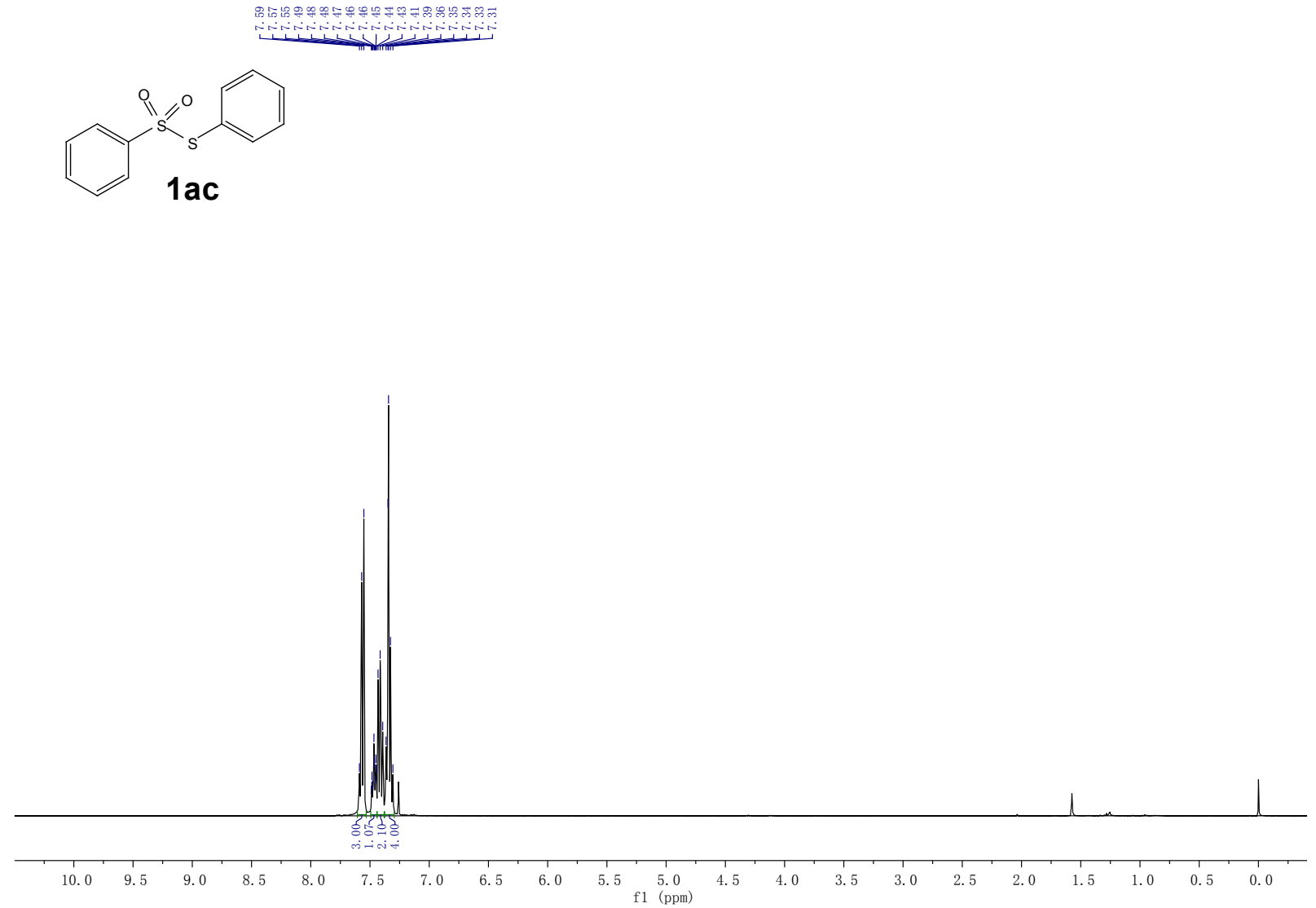

201.94
165.03
152.92
135.68
126.24
124.63
121.68
121.25
43.18
28.97
O
S
S
CH3
N
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

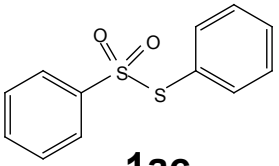

7.51
7.50
7.48
7.31
7.29
7.27
7.23
7.21
7.20
S
S
1aa
2.00
2.18
1.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


S
S

1aa

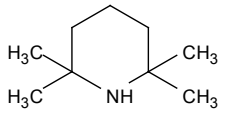
137.18
129.21
127.67
127.30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.59
7.57
7.55
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.41
7.39
7.36
7.35
7.34
7.33
7.31
O
O
S
S
1ac
3.00
1.07
2.10
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
S
S

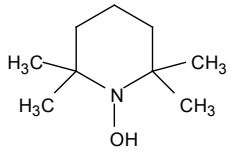
1ac

143.05
136.71
133.77
131.55
129.57
128.93
127.95
127.67
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)


H3C
CH3
H3C
NH
CH3

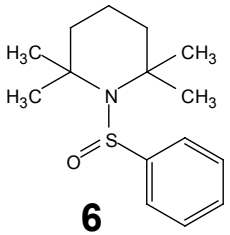
4

1.57
1.56
1.55
1.55
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.38
1.22
1.21
1.19
1.01
2.00
3.98
12.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


H3C
CH3
H3C
N
CH3
OH

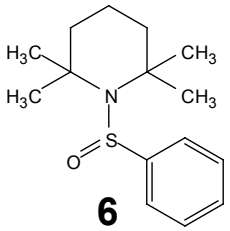
5

4.45
1.65
1.61
1.52
1.30
1.26
1.17
1.02
6.00
12.21
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H3C
CH3
H3C
CH3
N
S
O

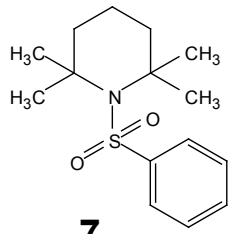
6

7.70
7.68
7.47
7.46
7.45
7.43
7.40
7.38
7.37
1.81
1.67
1.57
1.51
1.38
0.91
2.00
3.08
15.23
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


H3C
CH3
H3C
CH3
N
S
O

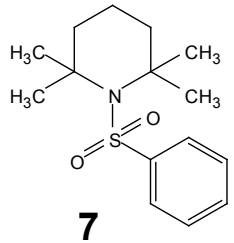
6

150.40
129.41
128.63
126.11
61.43
58.95
43.61
41.51
35.50
32.72
28.88
28.10
17.41
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)


H3C
CH3
H3C
CH3
N
O
S
O

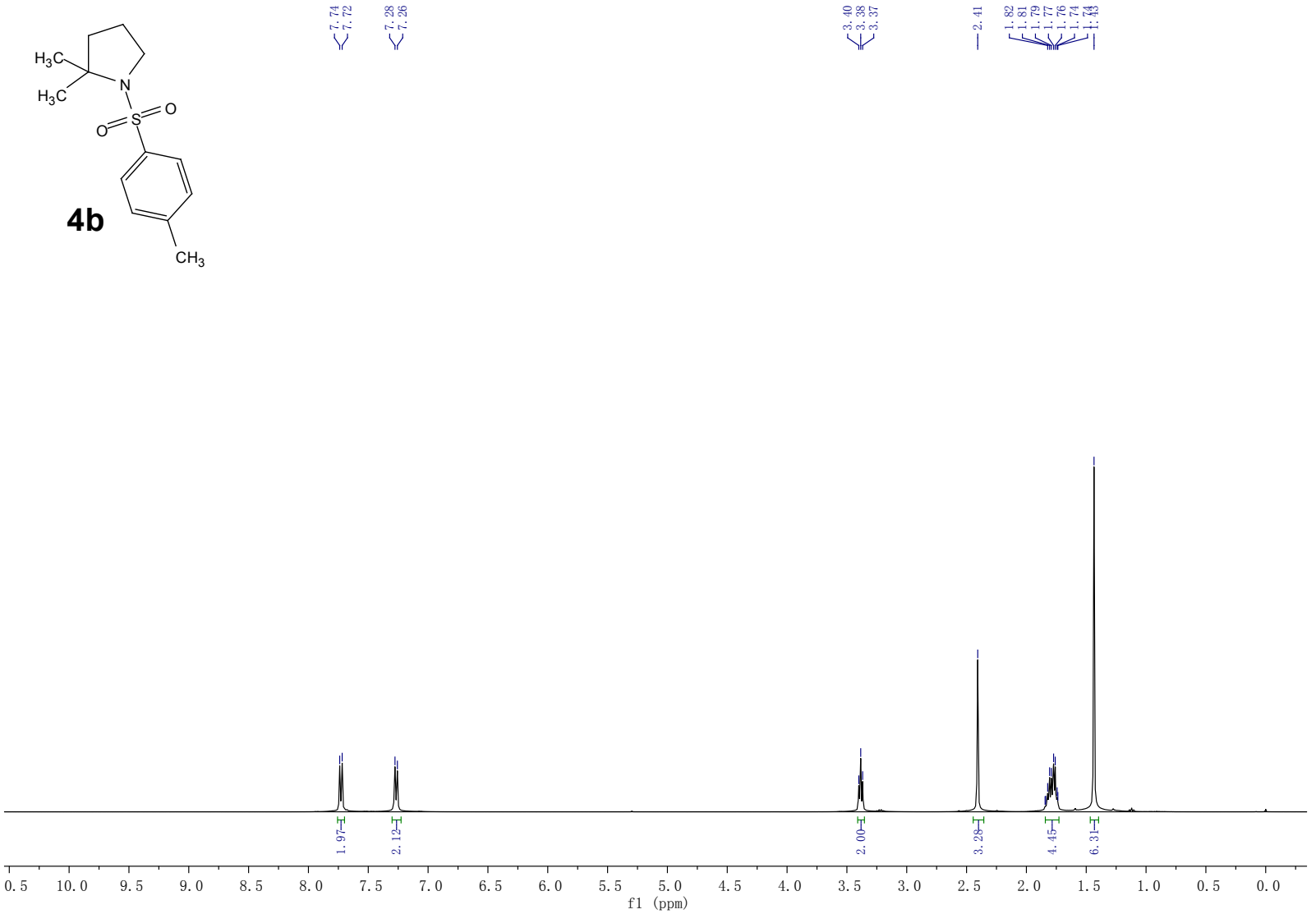
7

7.80
7.78
7.77
7.40
7.39
7.37
1.59
1.51
2.00
2.97
6.02
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

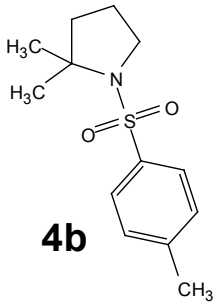

H3C
CH3
H3C
N
CH3
O
S
O

7

147.39
131.36
128.67
126.22
60.97
44.00
31.23
16.88
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)


7.74
7.72
7.28
7.26
3.40
3.38
3.37
2.41
1.82
1.81
1.79
1.77
1.76
1.74
1.43
1.97
2.12
2.00
3.28
4.45
6.31
f1 (ppm)

4b


H3C
H3C
N
S
O
O
CH3

4b

142.58
138.73
129.39
127.14
65.09
49.38
42.94
28.27
22.50
21.49
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)