Electronic Supplementary Material (ESI) for ChemComm.

Benzylic C(sp^3)-H Bond Sulfonylation of 4-Methylphenols with the Insertion of Sulfur Dioxide under Photocatalysis

Xinxing Gong, Jiahao Chen, Lifang Lai, Jiang Cheng, Jiangtao Sun, and Jie Wu*

Supporting Information

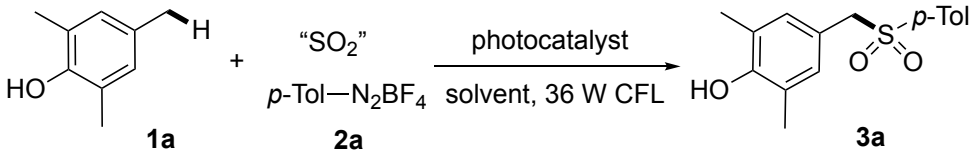
1. General experimental methods (S2-S3).
2. Optimization of reaction conditions, general experimental procedure, details for control experiments, and characterization data (S2-S12).
3. ^{1}H and ^{13}C NMR spectra of compounds **3** (S13-S56).

General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

Optimization of Reaction Conditions:

Table 1. Initial studies for the reaction of 2,4,6-trimethylphenol **1a**, sulfur dioxide, and *p*-tolyldiazonium tetrafluoroborate **2a**.



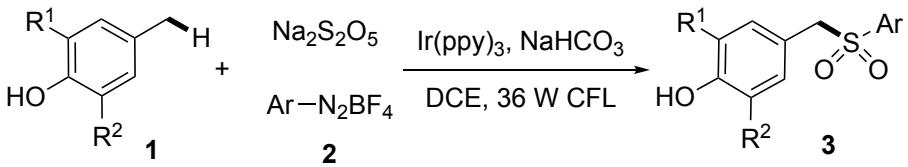
1a **2a** **3a**

Entry		"SO_2"	Base	Solvent	Yield (%)[b]
1	-	$K_2S_2O_5$	-	DCE	trace
2	$Ir(ppy)_3$	$K_2S_2O_5$	-	DCE	34
3	$Ru(ppy)_3Cl_2$	$K_2S_2O_5$	-	DCE	15
4	Eosin Y	$K_2S_2O_5$	-	DCE	25
5	Rodamin 6G	$K_2S_2O_5$	-	DCE	<10
6	Mes-Acr	$K_2S_2O_5$	-	DCE	<10
7[c]	$Ir(ppy)_3$	$K_2S_2O_5$	-	DCE	28
8	$Ir(ppy)_3$	$Na_2S_2O_5$	-	DCE	39
9	$Ir(ppy)_3$	$Na_2S_2O_5$	-	DMF	nd
10	$Ir(ppy)_3$	$Na_2S_2O_5$	-	DMSO	nd
11	$Ir(ppy)_3$	$Na_2S_2O_5$	-	1,4-dioxane	30
12	$Ir(ppy)_3$	$Na_2S_2O_5$	-	toluene	trace

13	$Ir(ppy)_3$	$Na_2S_2O_5$	-	DCE	trace
14[d]	$Ir(ppy)_3$	$Na_2S_2O_5$	-	DCE	50
15[d]	$Ir(ppy)_3$	$Na_2S_2O_5$	NaOAc	DCE	63
16[d]	$Ir(ppy)_3$	$Na_2S_2O_5$	$NaHCO_3$	DCE	68
17[d]	$Ir(ppy)_3$	$Na_2S_2O_5$	KH_2PO_4	DCE	66
18[d]	$Ir(ppy)_3$	$Na_2S_2O_5$	K_3PO_4	DCE	67
19[d,e]	$Ir(ppy)_3$	$Na_2S_2O_5$	$NaHCO_3$	DCE	75

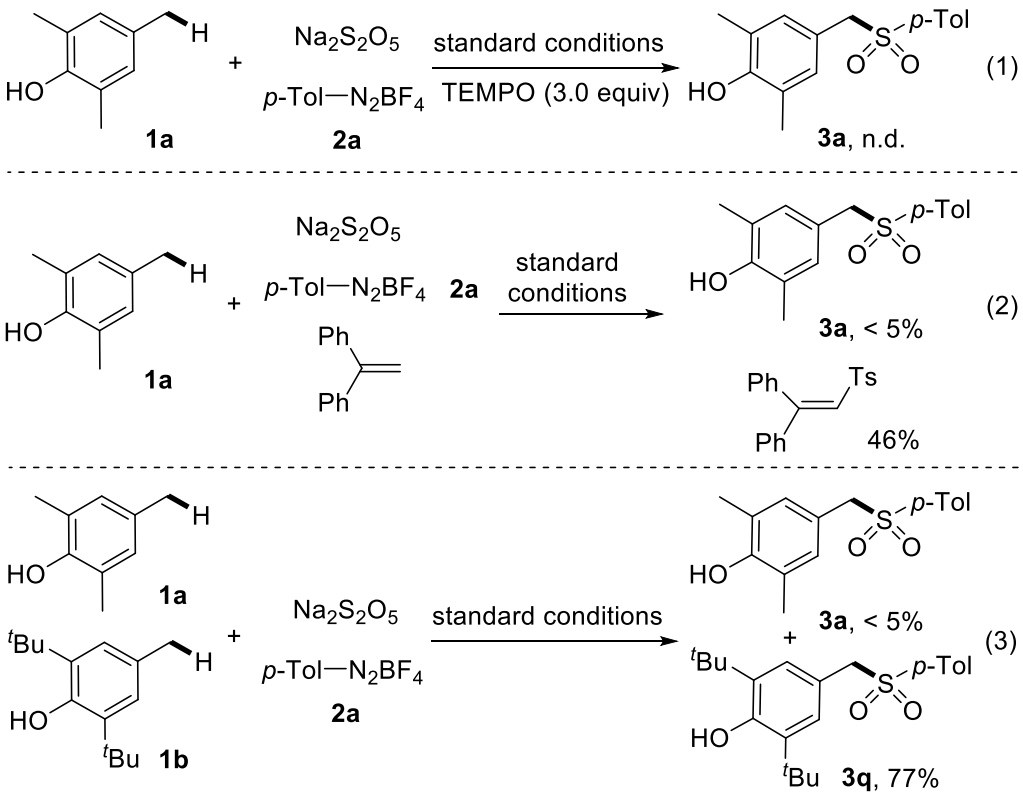
[a] Reaction conditions: 2,4,6-trimethylphenol **1a** (0.2 mmol), metabisulfite (0.4 mmol), *p*-tolyldiazonium tetrafluoroborate **2a** (0.4 mmol), photocatalyst (10 mol %), solvent (2.0 mL), N_2, 36 W CFL, rt, 12 h. [b] Isolated yield. [c] Blue LED was used instead of CFL. [d] The ratio was changed to **1a** (0.4 mmol), $Na_2S_2O_5$ (0.2 mmol), **2a** (0.4 mmol). [e] In the presence of $NaHCO_3$ (2.0 equiv).

*General experimental procedure for the photoinduced reaction of 4-methylphenols **1**, sodium metabisulfite, and aryldiazonium tetrafluoroborates **2***



4-Methylphenol **1** (0.40 mmol) in 1,2-dichloroethane (2.0 mL) was added to a mixture of aryldiazonium tetrafluoroborate **2** (0.40 mmol), $Ir(ppy)_3$ (2 mol %), $NaHCO_3$ (0.40 mmol) and $Na_2S_2O_5$ (0.20 mmol) at N_2 atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. After completion of reaction as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (*n*-hexane/EtOAc= 4:1 to 2:1) to give the corresponding pale yellow product **3**.

Experimental procedure for the control experiments.



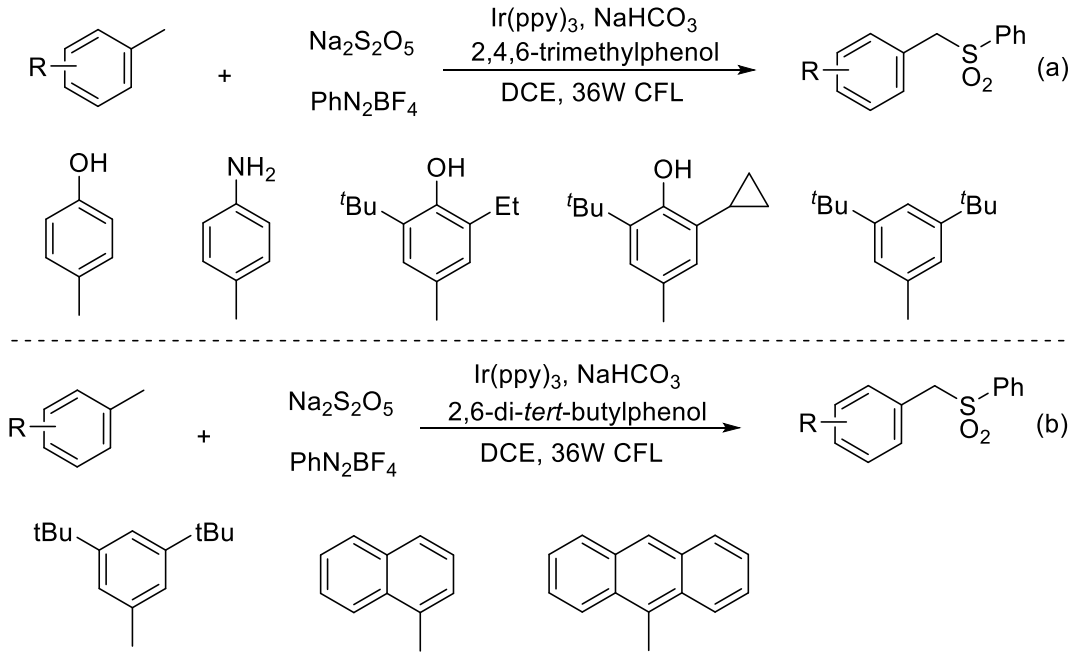
Eq (1): 2,4,6-Trimethylphenol **1a** (0.40 mmol) in 1,2-dichloroethane (2.0 mL) was added to a mixture of *p*-tolyldiazonium tetrafluoroborate **2a** (0.40 mmol), $Ir(ppy)_3$ (2 mol %), $NaHCO_3$ (0.40 mmol), TEMPO (0.6 mmol), and $Na_2S_2O_5$ (0.20 mmol) at N_2 atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. As indicated by TLC, no desired product was detected.

Eq (2): 2,4,6-Trimethylphenol **1a** (0.40 mmol) in 1,2-dichloroethane (2.0 mL) was added to a mixture of *p*-tolyldiazonium tetrafluoroborate **2a** (0.40 mmol), ethene-1,1-diyldibenzene (0.8 mmol), $Ir(ppy)_3$ (2 mol %), $NaHCO_3$ (0.40 mmol) and $Na_2S_2O_5$ (0.20 mmol) at N_2 atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. After consumption of 2,4,6-trimethylphenol **1a,** the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (*n*-hexane/EtOAc= 4:1 to 2:1) to give (2-tosylethene-1,1-diyl)dibenzene in 46% yield.

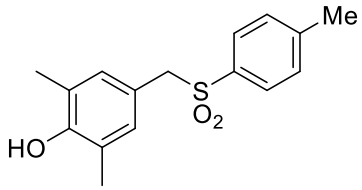
Eq (3): 2,4,6-trimethylphenol **1a** (0.4 mmol) and 2,6-di-*tert*-butyl-4-methylphenol **1b** (0.4 mmol) in 1,2-dichloroethane (2.0 mL) were added to a mixture of

p-tolyldiazonium tetrafluoroborate **2a** (0.40 mmol), $Ir(ppy)_3$ (2 mol %), $NaHCO_3$ (0.40 mmol) and $Na_2S_2O_5$ (0.20 mmol) at N_2 atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. After completion of reaction as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (*n*-hexane/EtOAc= 4:1 to 2:1) to give the corresponding pale yellow product **3q** in 77% yield.

General experimental procedure for the reactions employing other substituted toluenes.

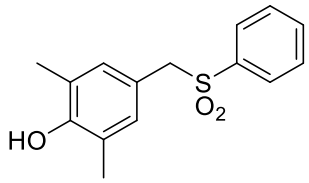


Substituted toluene (0.40 mmol) and 2,4,6-trimethylphenol or 2,6-di-*tert*-butylphenol (0.4 mmol) in 1,2-dichloroethane (2.0 mL) was added to a mixture of phenyldiazonium tetrafluoroborate **2a** (0.40 mmol), $Ir(ppy)_3$ (2 mol %), $NaHCO_3$ (0.40 mmol) and $Na_2S_2O_5$ (0.20 mmol) at N_2 atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. As indicated by TLC, no desired product was formed.



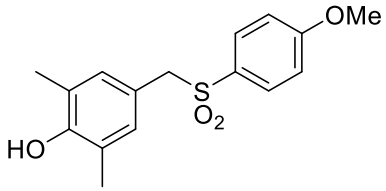
2, 6-Dimethyl-4-(tosylmethyl)phenol **(3a)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.16 (m, 2H), 6.70 (s, 2H), 4.83 (m, 1H), 4.15 (s, 2H), 2.43 (s, 3H), 2.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 144.5, 135.4, 131.1, 129.4, 128.7, 123.3, 119.3, 62.4, 21.6, 15.7. HRMS (ESI) calcd for $C_{16}H_{22}NO_3S^+$: 308.1315 ($M+NH_4^+$), found: 308.1333.



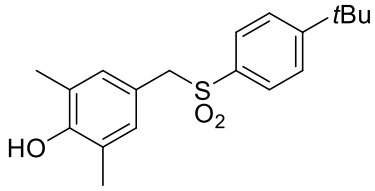
2, 6-Dimethyl-4-((phenylsulfonyl)methyl)phenol **(3b)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 2H), 7.61 (dd, *J* = 11.8, 4.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.68 (s, 2H), 4.91 (m, 1H), 4.17 (s, 2H), 2.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 138.2, 133.6, 131.1, 128.8, 128.7, 123.4, 119.1, 62.4, 15.7. HRMS (ESI) calcd for $C_{15}H_{20}NO_3S^+$: 294.1158 ($M+NH_4^+$), found: 294.1175.



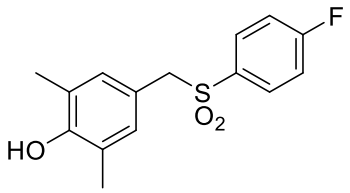
4-(((4-Methoxyphenyl)sulfonyl)methyl)-2,6-dimethylphenol **(3c)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.70 (s, 2H), 4.14 (s, 2H), 3.86 (s, 3H), 2.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 152.8, 131.1, 130.9, 129.9, 123.4, 119.5, 114.0, 62.6, 55.7, 15.8. HRMS (ESI) calcd for $C_{16}H_{22}NO_4S^+$: 324.1264 ($M+NH_4^+$), found: 324.1278.



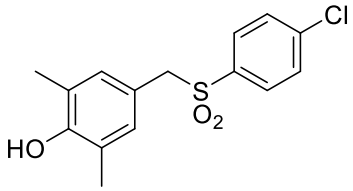
4-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-2,6-dimethylphenol **(3d)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 6.65 (s, 2H), 4.80 (m, 1H), 4.14 (s, 2H), 2.13 (s, 6H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 152.6, 134.9, 131.0, 128.5, 125.6, 123.1, 119.2, 62.3, 35.1, 30.95, 15.6. HRMS (ESI) calcd for $C_{19}H_{28}NO_3S^+$: 350.1784 ($M+NH_4^+$), found: 350.1786.



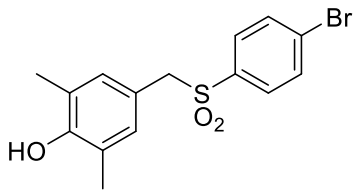
4-(((4-Fluorophenyl)sulfonyl)methyl)-2,6-dimethylphenol **(3e)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.52 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 6.68 (s, 2H), 4.94 (s, 1H), 4.17 (s, 2H), 2.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (d, $^1J_{CF}$= 256.1 Hz), 152.8, 134.0, 131.5 (d, $^3J_{CF}$ = 9.5 Hz), 130.9, 123.3, 118.9, 115.9 (d, $^2J_{CF}$ = 22.5 Hz), 62.4, 15.7. HRMS (ESI) calcd for $C_{15}H_{19}NFO_3S^+$: 312.1064 ($M+NH_4^+$), found: 312.1062.



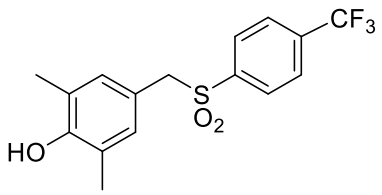
4-(((4-Chlorophenyl)sulfonyl)methyl)-2,6-dimethylphenol **(3f)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 6.70 (s, 2H), 4.78 (m, 1H), 4.17 (s, 2H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 140.4, 136.7, 131.1, 130.2, 129.1, 123.4, 118.9, 62.5, 15.7. HRMS (ESI) calcd for $C_{15}H_{19}NClO_3S^+$: 328.0769 ($M+NH_4^+$), found: 328.0774.



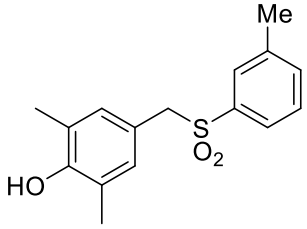
4-(((4-Bromophenyl)sulfonyl)methyl)-2,6-dimethylphenol **(3g)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 2H), 7.55 – 7.43 (m, 2H), 6.69 (s, 2H), 4.82 (s, 1H), 4.16 (s, 2H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 137.0, 132.0, 131.0, 130.2, 128.8, 123.3, 118.7, 62.3, 15.6. HRMS (ESI) calcd for $C_{15}H_{19}NBrO_3S^+$: 372.0264 ($M+NH_4^+$), found: 372.0246.



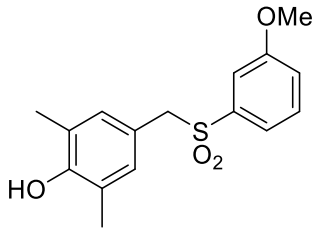
2, 6-Dimethyl-4-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)phenol **(3h)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 21.4, 8.4 Hz, 4H), 6.67 (s, 2H), 4.83 (m, 1H), 4.20 (s, 2H), 2.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 141.4, 130.9, 129.3, 125.8, 125.7, 123.4, 118.4, 62.3, 15.6. HRMS (ESI) calcd for $C_{16}H_{19}NF_3O_3S^+$: 362.1032 ($M+NH_4^+$), found: 362.1031.



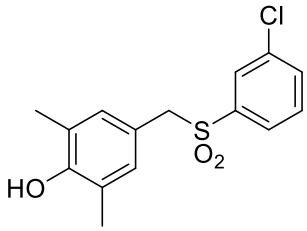
2, 6-Dimethyl-4-((m-tolylsulfonyl)methyl)phenol **(3i)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.43 – 7.32 (m, 2H), 6.70 (s, 2H), 4.98 (s, 1H), 4.15 (s, 2H), 2.37 (s, 3H), 2.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 139.0, 137.9, 134.2, 131.1, 128.9, 128.6, 125.7, 123.2, 118.9, 62.3, 21.1, 15.7. HRMS (ESI) calcd for $C_{16}H_{22}NO_3S^+$: 308.1315 ($M+NH_4^+$), found: 308.1331.



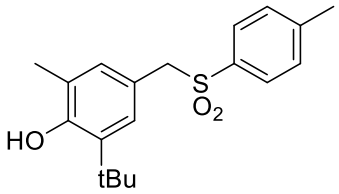
4-(((3-Methoxyphenyl)sulfonyl)methyl)-2,6-dimethylphenol **(3j)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.8 Hz, 1H), 7.30 (m, 1H), 7.13 (m, 2H), 6.71 (s, 2H), 4.81 (s, 1H), 4.16 (s, 2H), 3.76 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 152.8, 131.2, 129.9, 123.3, 120.9, 120.5, 119.2, 112.9, 62.4, 55.6, 15.7. HRMS (ESI) calcd for $C_{16}H_{22}NO_4S^+$: 324.1264 ($M+NH_4^+$), found: 324.1280.



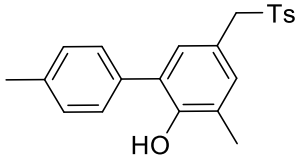
4-(((3-Chlorophenyl)sulfonyl)methyl)-2,6-dimethylphenol **(3k)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.36 (m, 4H), 6.70 (s, 2H), 4.75 (s, 1H), 4.17 (s, 2H), 2.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 139.8, 135.1, 133.7, 131.1, 130.0, 128.8, 126.8, 123.4, 118.7, 62.4, 15.7. HRMS (ESI) calcd for $C_{15}H_{19}NClO_3S^+$: 328.0769 ($M+NH_4^+$), found: 328.0775.



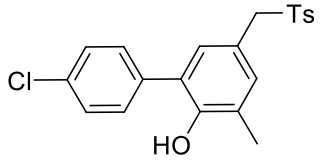
2-(*tert*-Butyl)-6-methyl-4-(tosylmethyl)phenol **(3l)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 1.8 Hz, 1H), 6.40 (d, *J* = 2.1 Hz, 1H), 5.15 – 4.88 (m, 1H), 4.17 (s, 2H), 2.41 (s, 3H), 2.20 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 144.5, 135.6, 134.9, 131.0, 129.4, 128.9, 127.8, 123.5, 119.2, 62.9, 34.3, 29.4, 21.6, 15.9. HRMS (ESI) calcd for $C_{19}H_{28}NO_3S^+$: 350.1784 ($M+NH_4^+$), found: 350.1786.



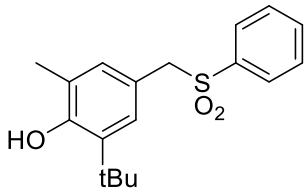
3, 4'-Dimethyl-5-(tosylmethyl)-[1, 1'-biphenyl]-2-ol **(3m)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.22 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 1.7 Hz, 1H), 6.60 (d, *J* = 2.1 Hz, 1H), 5.59 – 5.07 (m, 1H), 4.20 (s, 2H), 2.41 (m, 6H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 144.4, 137.9, 135.0, 133.3, 132.5, 130.1, 129.9, 129.4, 128.7, 127.5, 124.9, 119.4, 115.8, 62.3, 21.5, 21.1, 16.0. HRMS (ESI) calcd for $C_{22}H_{26}NO_3S^+$: 384.1628 ($M+NH_4^+$), found: 384.1623.



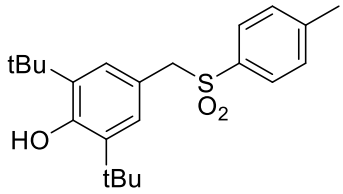
4'-Chloro-3-methyl-5-(tosylmethyl)-[1, 1'-biphenyl]-2-ol **(3n)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.95 (s, 1H), 6.63 (d, *J* = 1.9 Hz, 1H), 5.15 (s, 1H), 4.19 (s, 2H), 2.43 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 144.6, 135.3, 135.1, 133.2, 130.4, 130.3, 129.5, 129.4, 128.8, 126.6, 125.2, 119.9, 62.3, 21.6, 16.1. HRMS (ESI) calcd for $C_{21}H_{23}NClO_3S^+$: 404.1082 ($M+NH_4^+$), found: 404.1067.



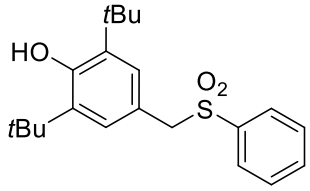
2-(*tert*-Butyl)-6-methyl-4-((phenylsulfonyl)methyl)phenol **(3o)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 3H), 7.50 – 7.38 (m, 2H), 6.93 (d, *J* = 1.8 Hz, 1H), 6.44 (d, *J* = 2.1 Hz, 1H), 4.91 (s, 1H), 4.20 (s, 2H), 2.20 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 137.7, 135.4, 133.4, 130.9, 128.8, 128.6, 127.7, 123.4, 118.9, 62.6, 34.1, 29.3, 15.8. HRMS (ESI) calcd for $C_{18}H_{26}NO_3S^+$: 336.1628 ($M+NH_4^+$), found: 336.1625.



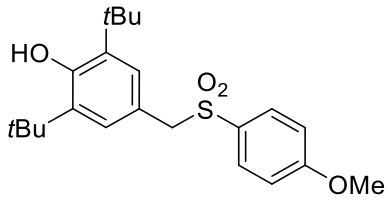
2, 6-Di-*tert*-butyl-4-(tosylmethyl)phenol **(3q)**[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 2H), 5.25 (s, 1H), 4.19 (s, 2H), 2.40 (s, 3H), 1.32 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 144.3, 136.0, 135.0, 129.3, 128.9, 127.7, 119.0, 63.3, 34.1, 30.1, 21.5.



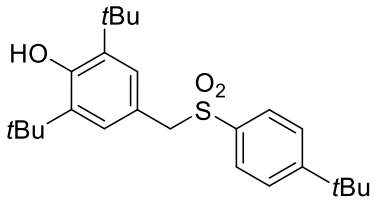
2, 6-Di-*tert*-butyl-4-((phenylsulfonyl)methyl)phenol **(3t)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.75 (s, 2H), 5.26 (s, 1H), 4.22 (s, 2H), 1.32 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 137.7, 135.9, 133.3, 128.8, 128.6, 127.6, 118.6, 63.0, 34.0, 30.0.



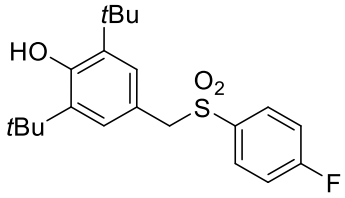
2, 6-Di-*tert*-butyl-4-(((4-methoxyphenyl)sulfonyl)methyl)phenol **(3u)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.75 (s, 2H), 5.26 (s, 1H), 4.19 (s, 2H), 3.84 (s, 3H), 1.33 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 154.1, 135.8, 130.9, 129.3, 127.5, 119.0, 113.7, 63.3, 55.5, 34.0, 30.0. HRMS (ESI) calcd for $C_{22}H_{34}NO_4S^+$: 408.2203 ($M+NH_4^+$), found: 408.2209.



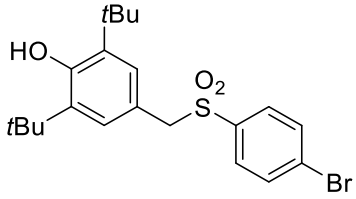
2, 6-Di-*tert*-butyl-4-(((4-(*tert*-butyl)phenyl)sulfonyl)methyl)phenol **(3v)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.1 Hz, 4H), 6.73 (s, 2H), 5.26 (s, 1H), 4.21 (s, 2H), 1.32 (d, *J* = 4.7 Hz, 27H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 154.1, 135.8, 134.6, 128.7, 127.6, 125.6, 118.8, 63.0, 34.0, 31.0, 30.0. HRMS (ESI) calcd for $C_{25}H_{40}NO_3S^+$: 434.2723 ($M+NH_4^+$), found: 434.2722.



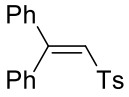
2, 6-Di-*tert*-butyl-4-(((4-fluorophenyl)sulfonyl)methyl)phenol **(3w)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.76 (s, 2H), 5.29 (s, 1H), 4.22 (s, 2H), 1.33 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, *J* = 256.1 Hz), 154.2, 136.1, 133.7, 131.6 (d, *J* = 9.5 Hz), 127.5, 118.5, 115.8 (d, *J* = 22.5 Hz), 34.0, 30.0. HRMS (ESI) calcd for $C_{21}H_{31}NO_3S^+$: 396.2003 ($M+NH_4^+$), found: 396.2026.



4-(((4-Bromophenyl)sulfonyl)methyl)-2,6-di-*tert*-butylphenol **(3x)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 6.74 (s, 2H), 5.29 (s, 1H), 4.21 (s, 2H), 1.33 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 136.6, 136.1, 131.8, 130.3, 128.7, 127.5, 118.3, 63.2, 34.0, 30.0. HRMS (ESI) calcd for $C_{21}H_{31}NBrO_3S^+$: 456.1203 ($M+NH_4^+$), found: 456.1201.

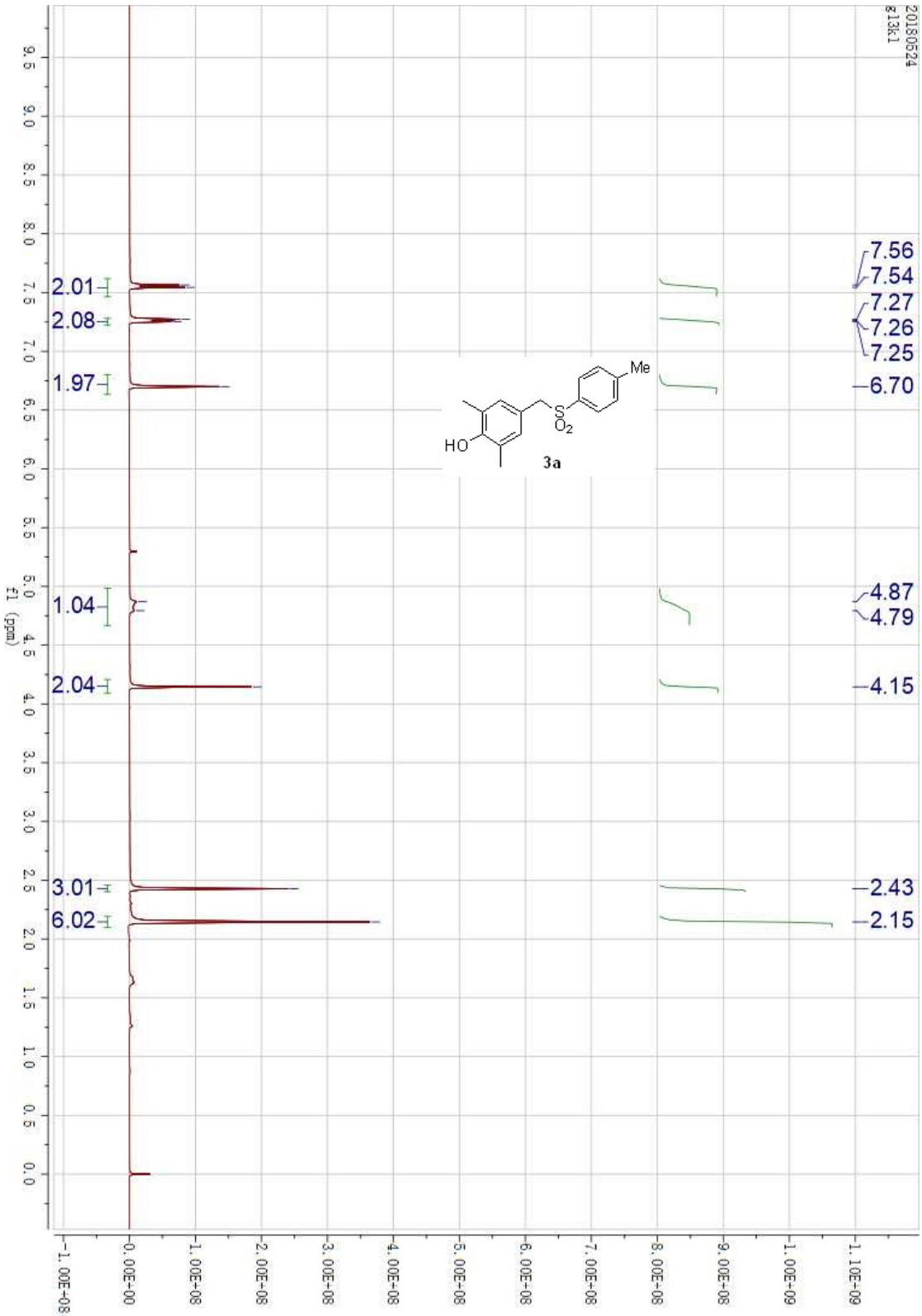


(2-Tosylethene-1,1-diyl)dibenzene [2]

^{1}H NMR (400 MHz, CDCl3) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 4H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 144.0, 139.4, 138.8, 135.8, 130.5, 123.0, 129.6, 129.2, 128.8, 128.4, 128.0, 21.8.

Reference:

1. W. Yang, P. Dai, K. Luo, L. Wu, *Adv. Synth. Catal.* **2016**, *358*, 184.
2. D. Zheng, J. Yu, J. Wu, *Angew. Chem. Int. Ed.* **2016**, *55*, 11925.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7.27
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6.70
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4.79
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2.43
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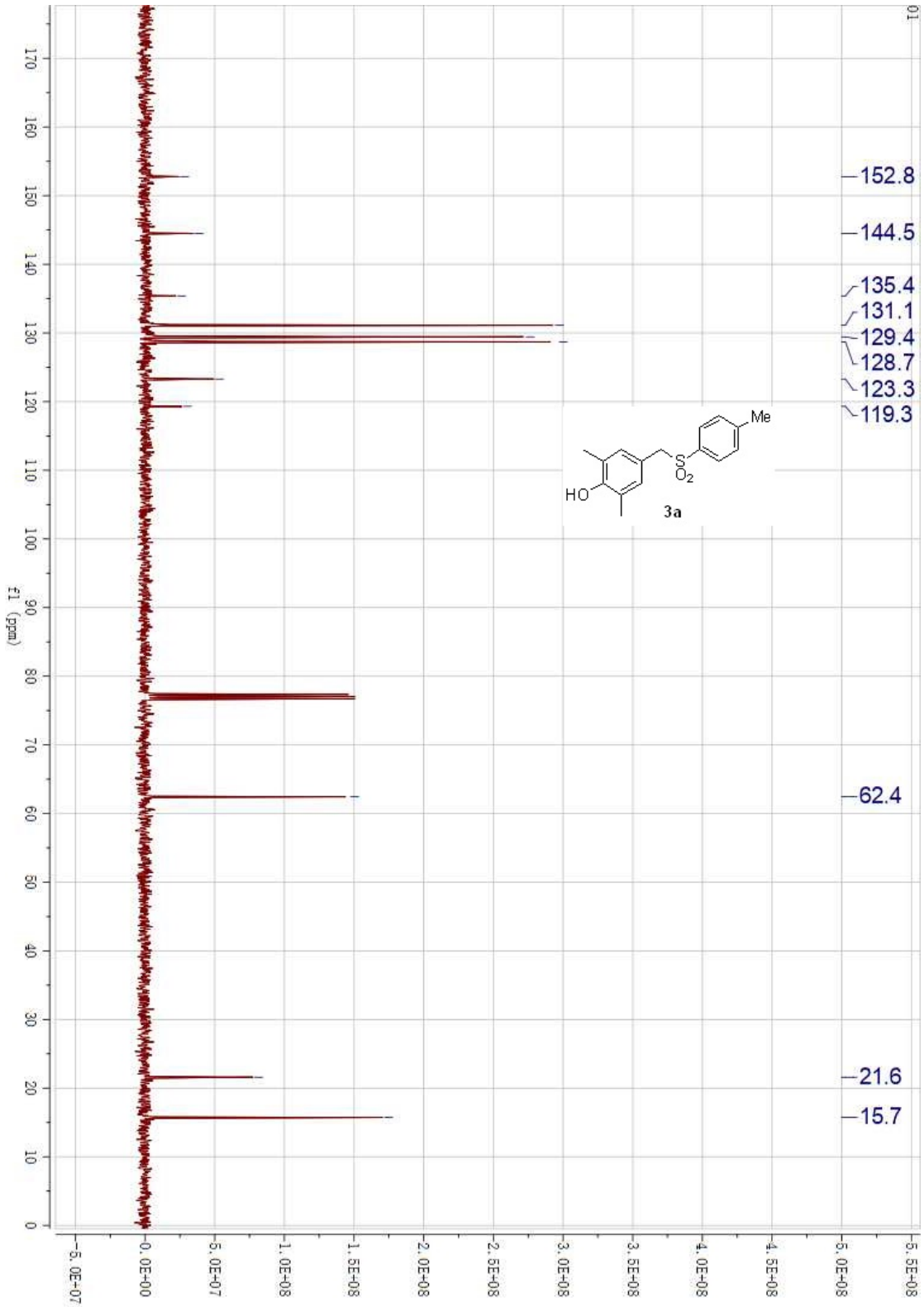
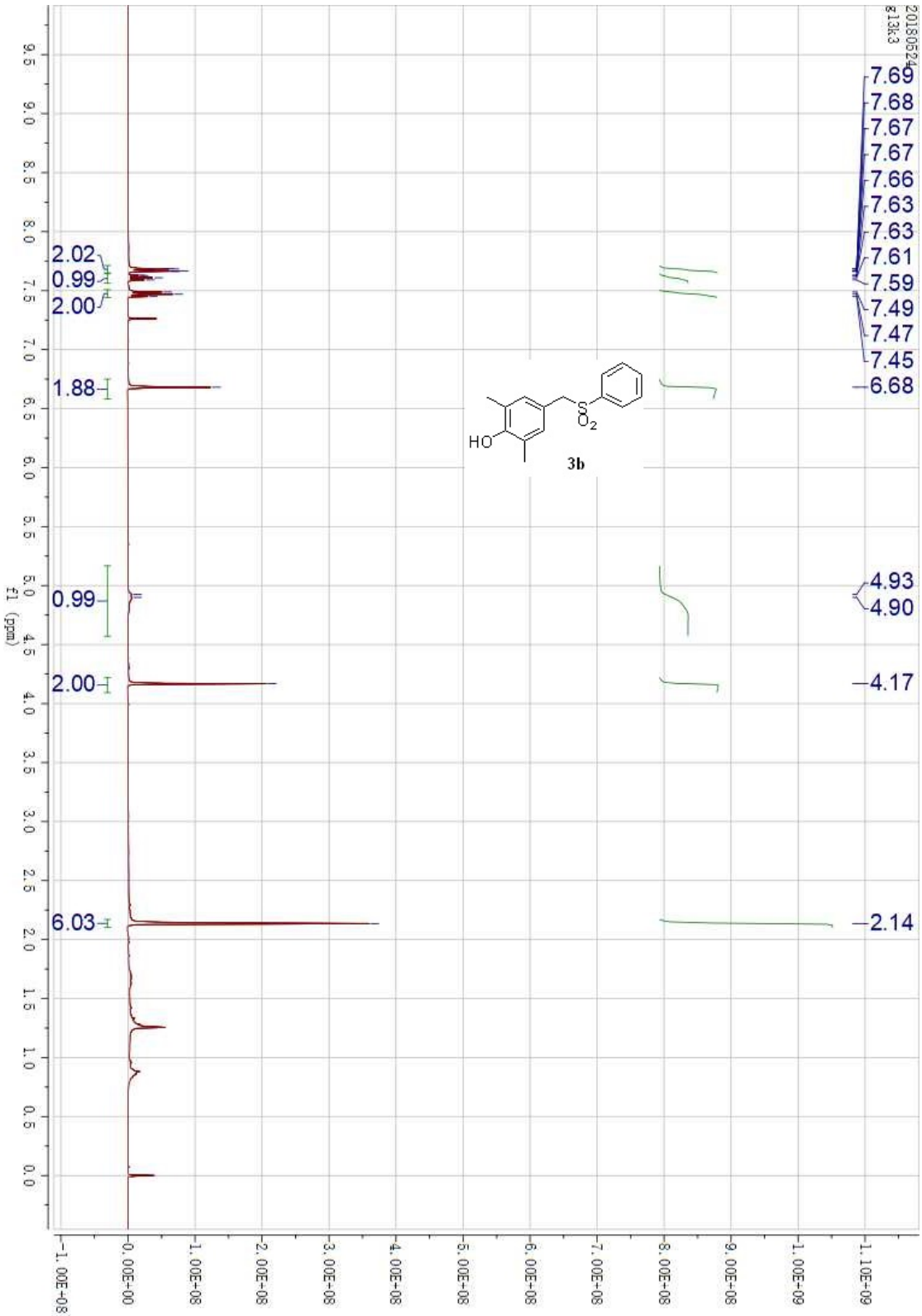
1.97
1.04
2.04
3.01
6.02
f1 (ppm)
HO
Me
SO2
3a


152.8
144.5
135.4
131.1
129.4
128.7
123.3
119.3
62.4
21.6
15.7
Me
HO
S
O2
3a
f1 (ppm)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7.47
7.45
6.68
4.93
4.90
4.17
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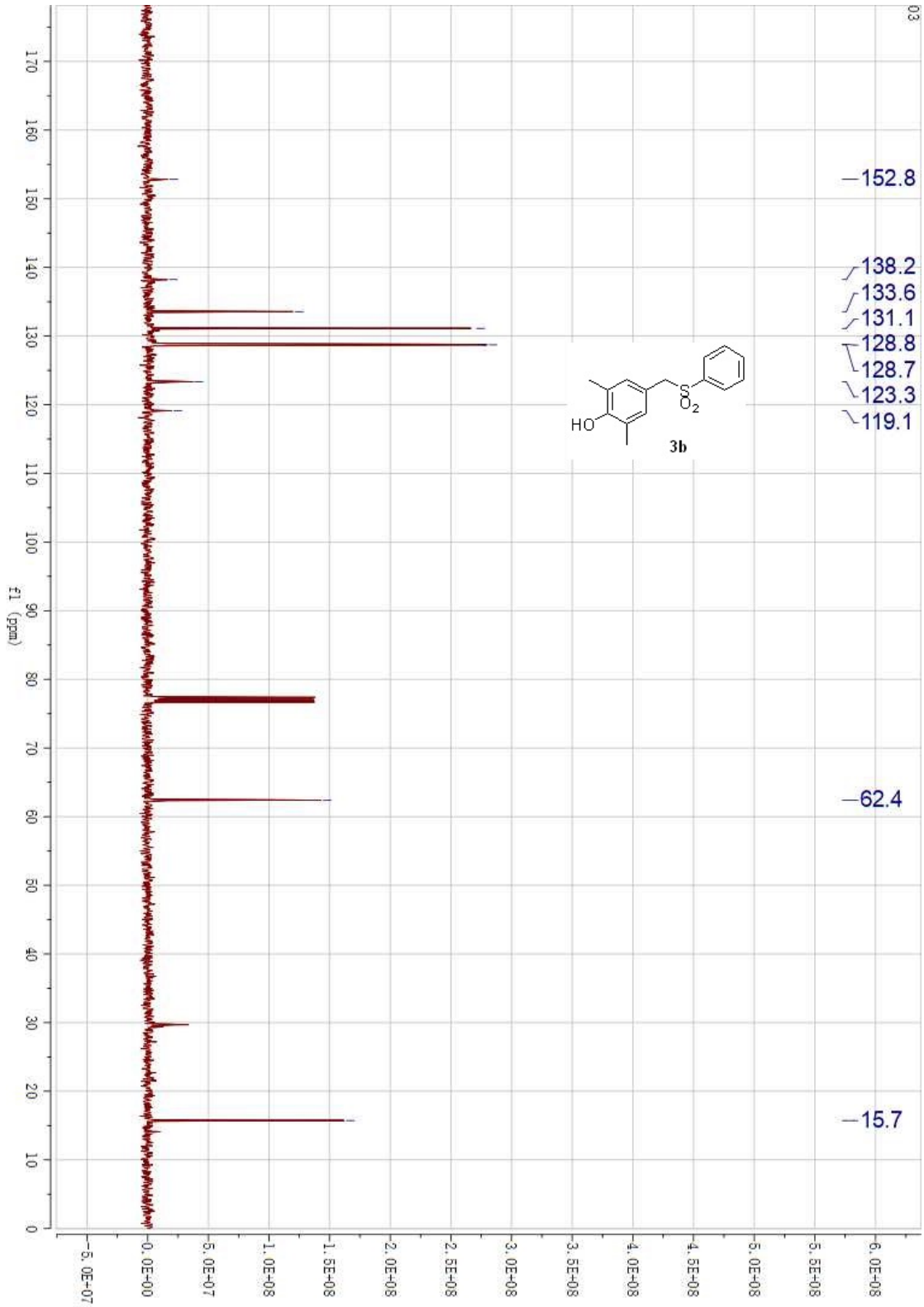
2.00
1.88
0.99
2.00
6.03
HO
S
O2
3b
f1 (ppm)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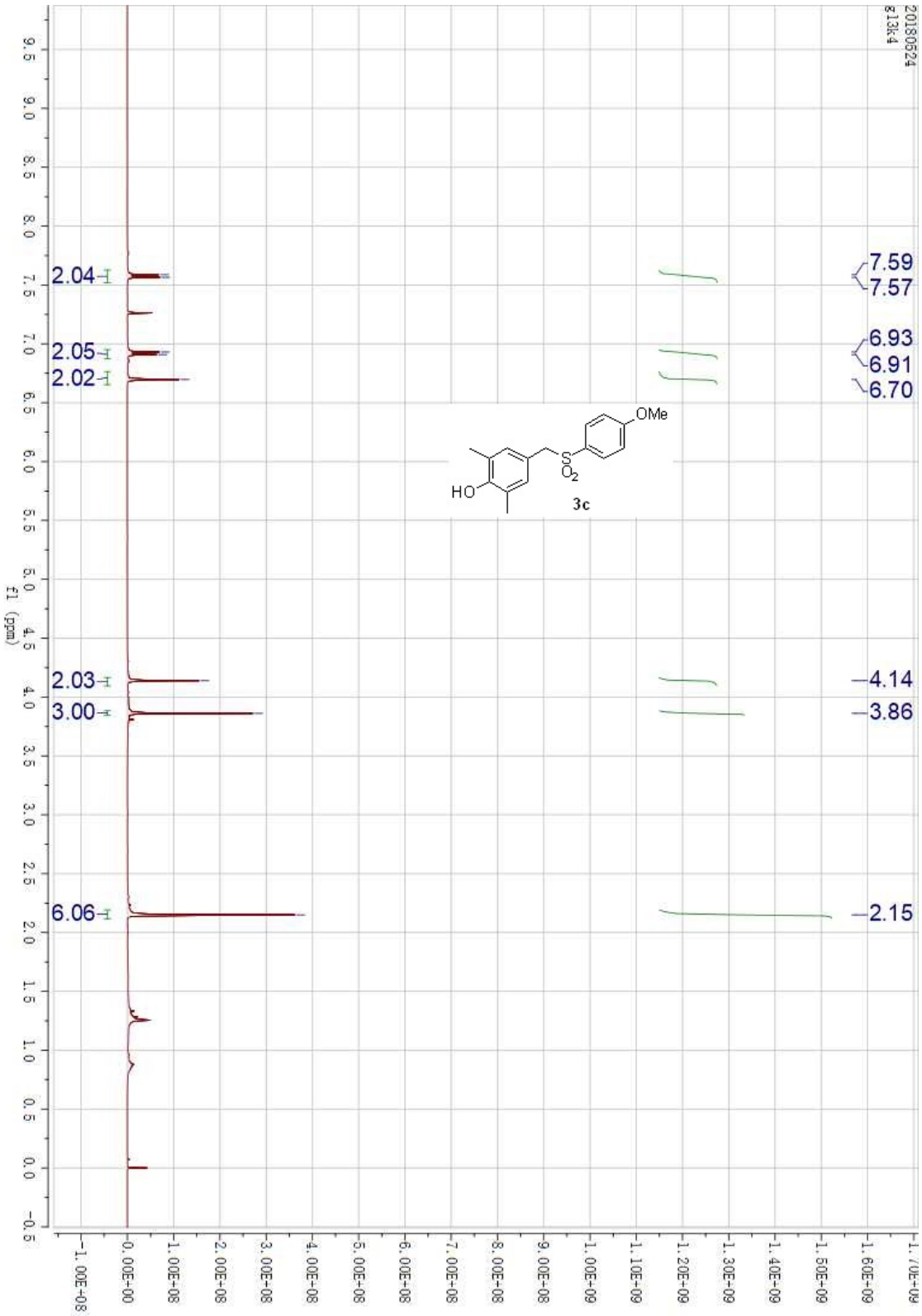
131.1
128.8
128.7
123.3
119.1
62.4
15.7
HO
O_2
S
3b
f1 (ppm)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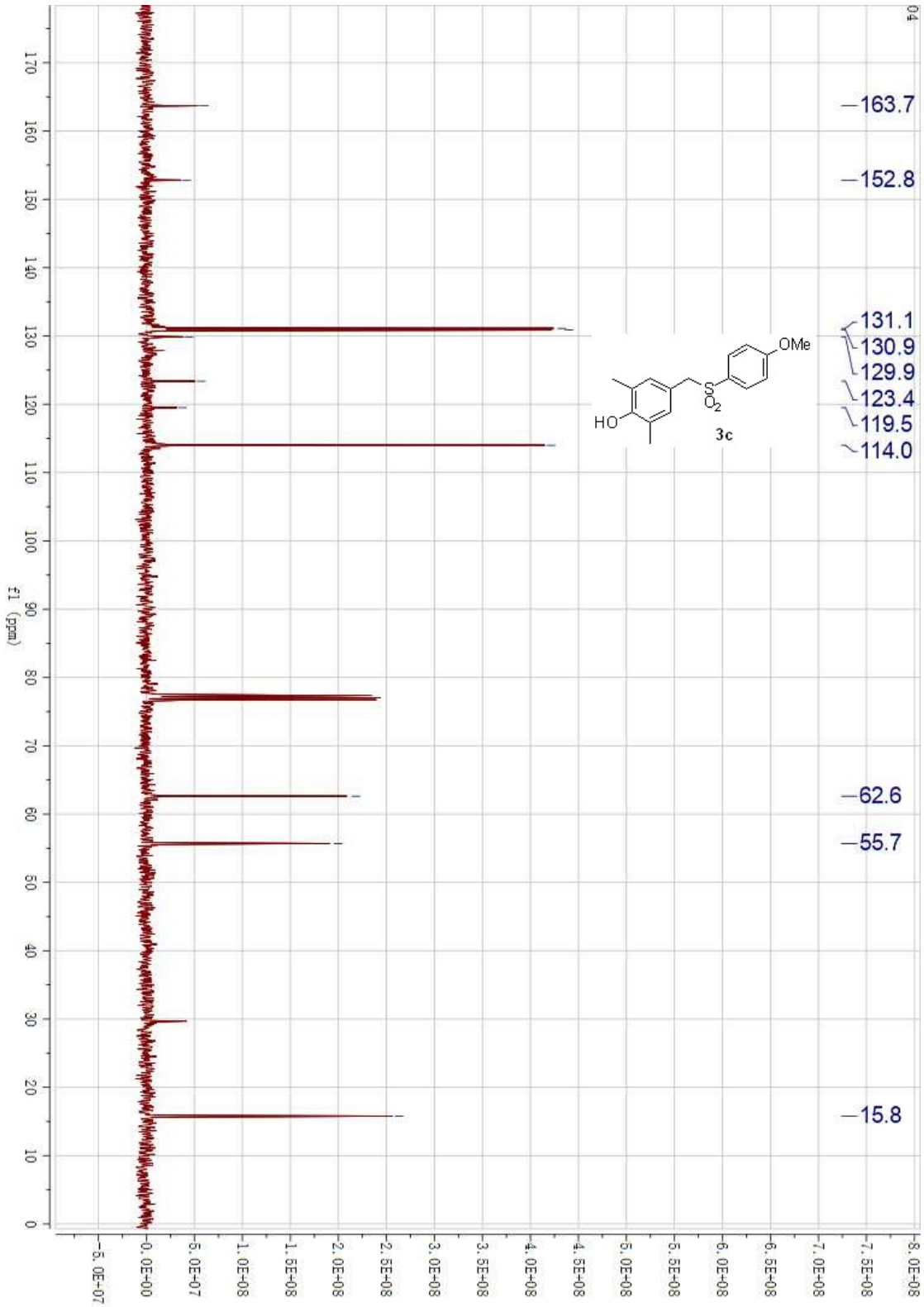
HO
3c
f1 (ppm)


163.7
152.8
131.1
130.9
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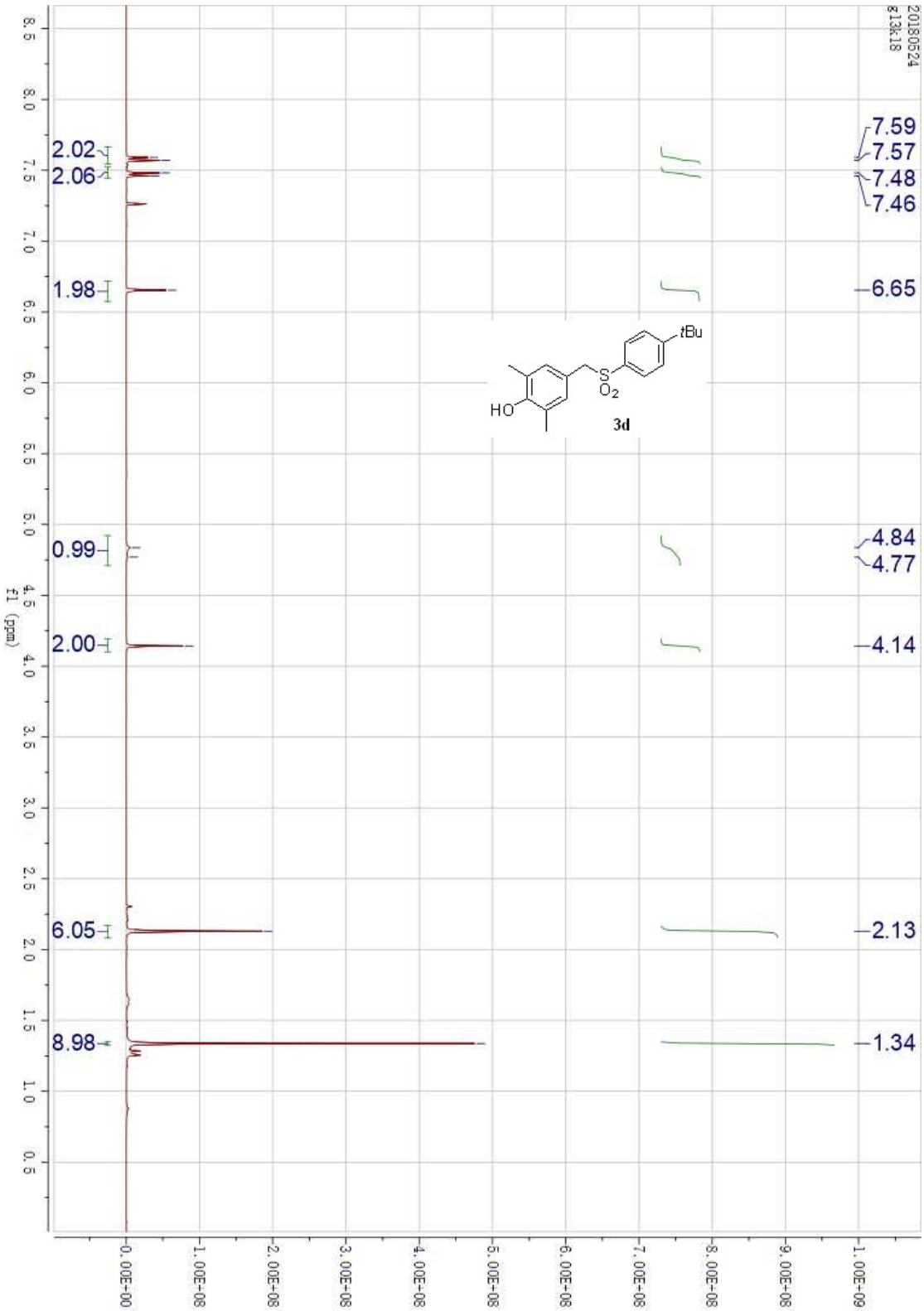
123.4
119.5
114.0
62.6
55.7
15.8
OMe
HO
3c
f1 (ppm)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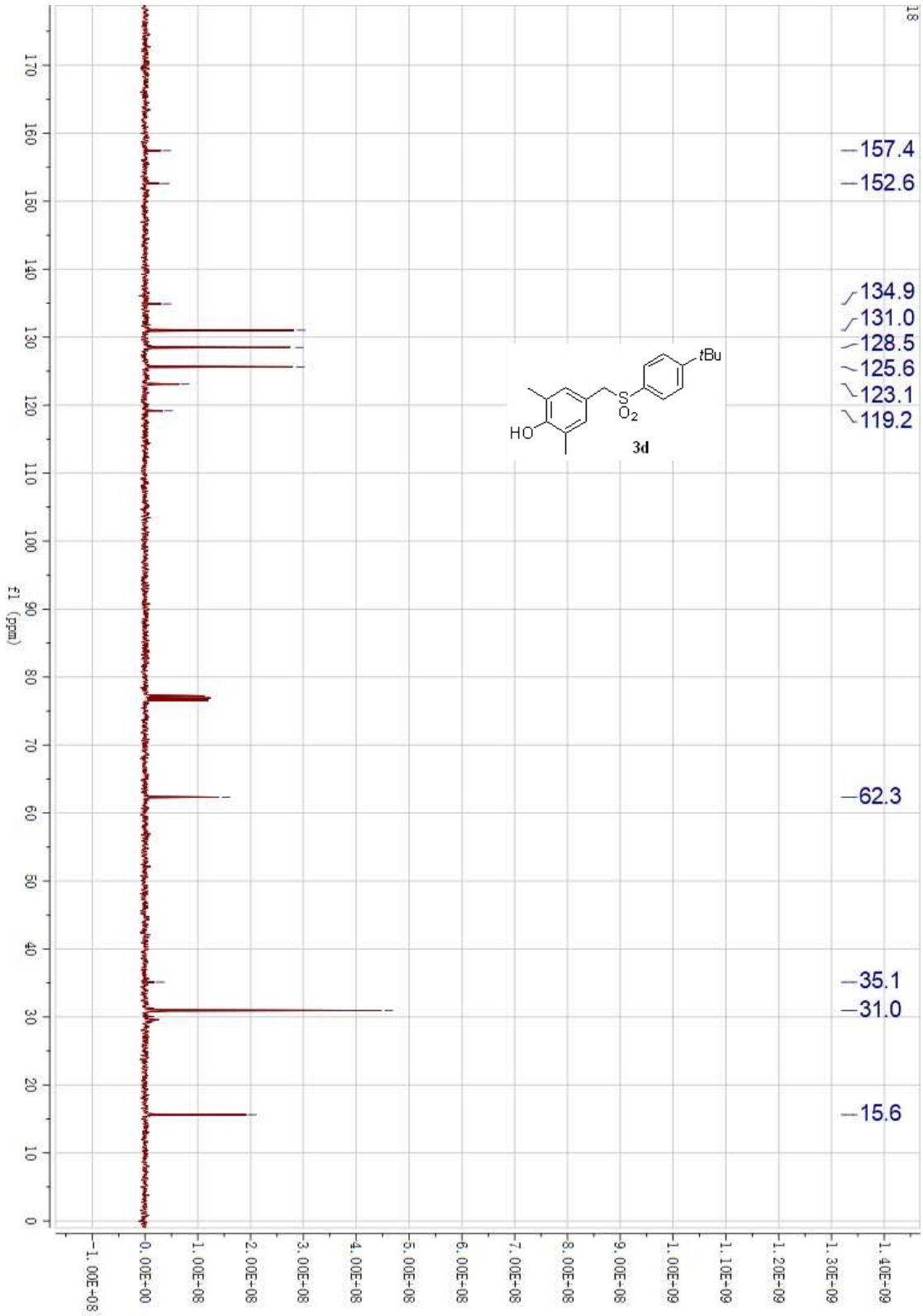
6.05
8.98
tBu
HO
O2
S
3d
f1 (ppm)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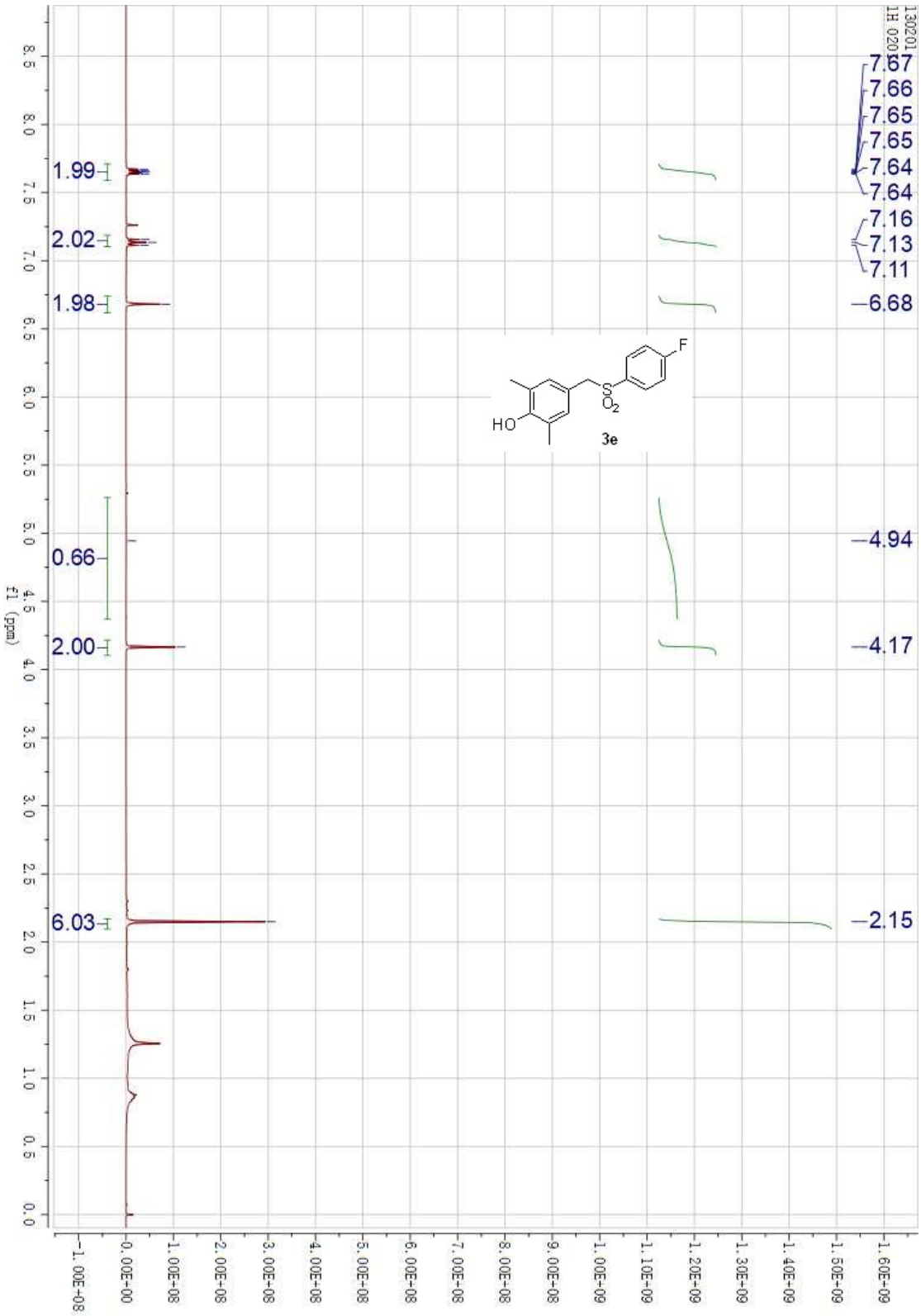
134.9
131.0
128.5
125.6
123.1
119.2
62.3
35.1
31.0
15.6
tBu
HO
S
O2
3d
f1 (ppm)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7.64
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4.17
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1.99
2.02
1.98
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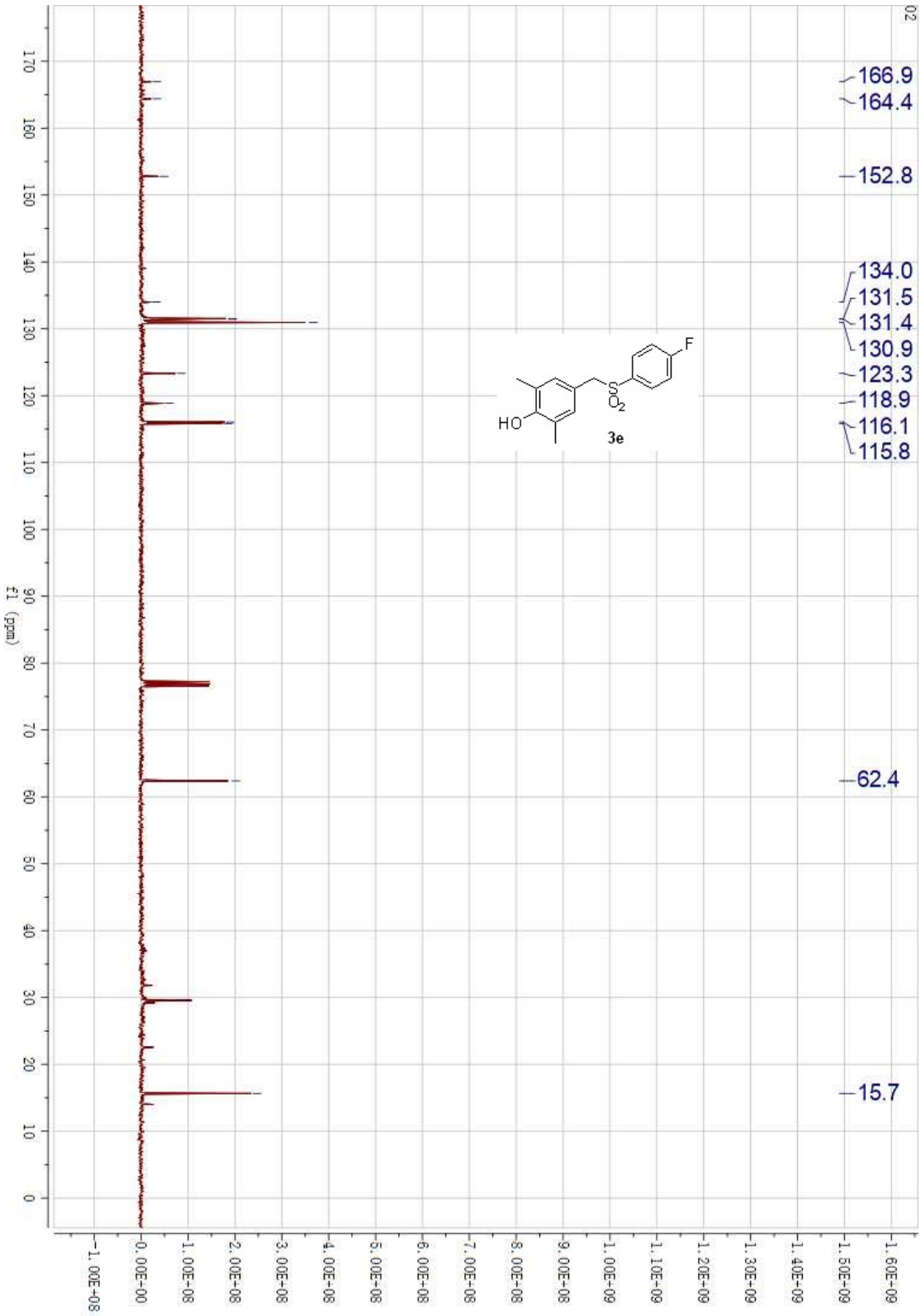
2.00
6.03
HO
F
3e
f1 (ppm)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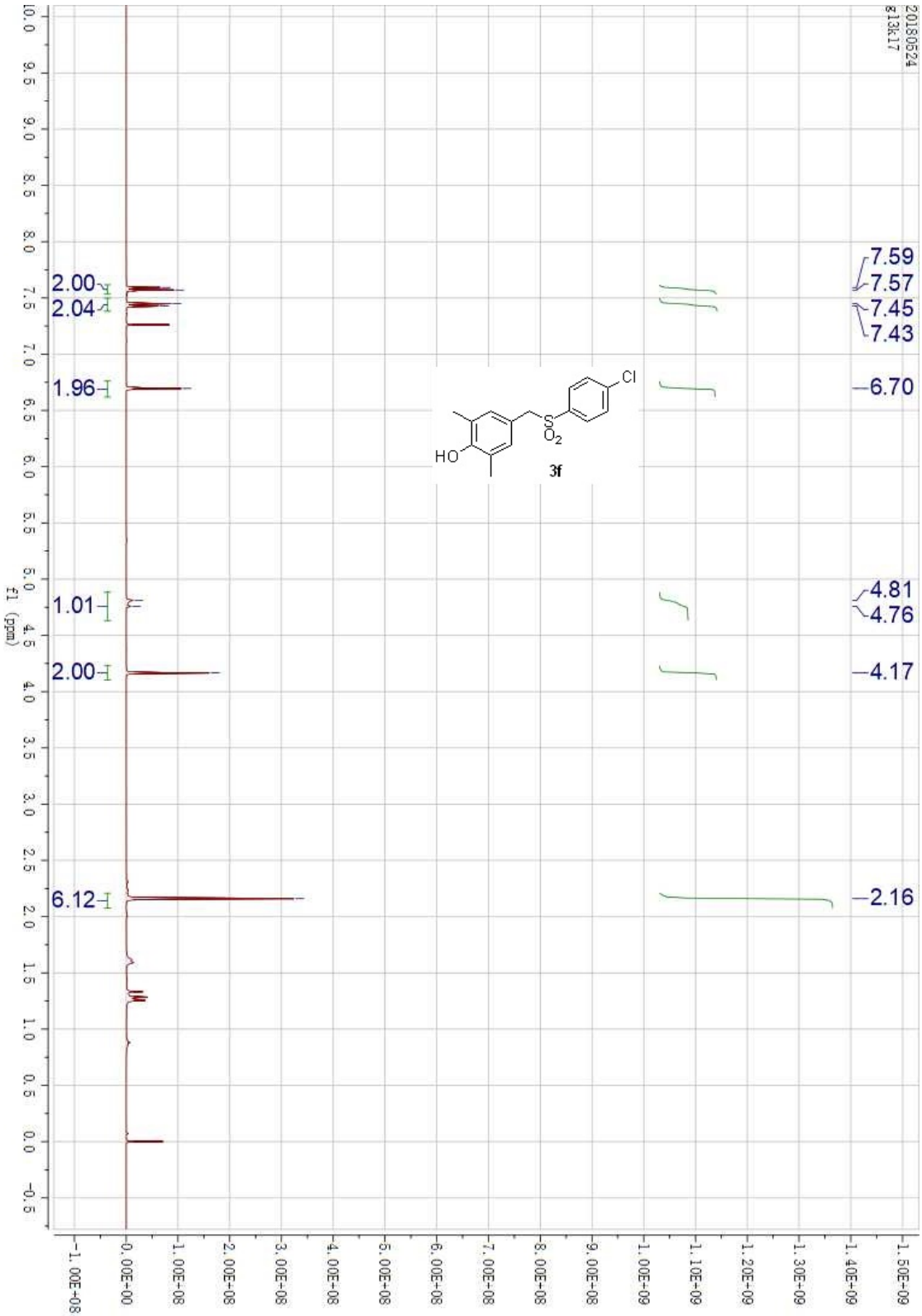
HO
F
3e
f1 (ppm)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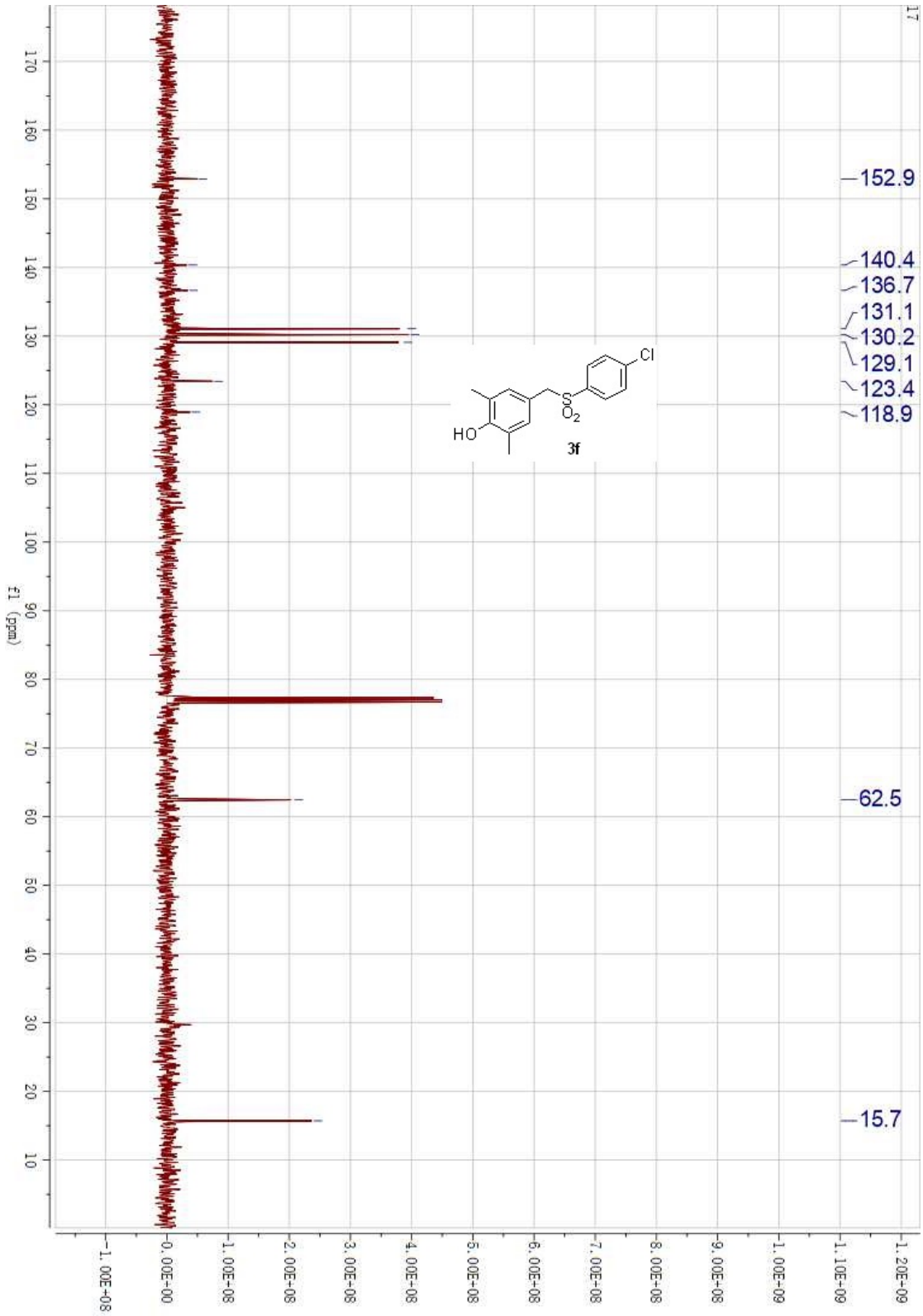
Cl
HO
O2
S
3f
f1 (ppm)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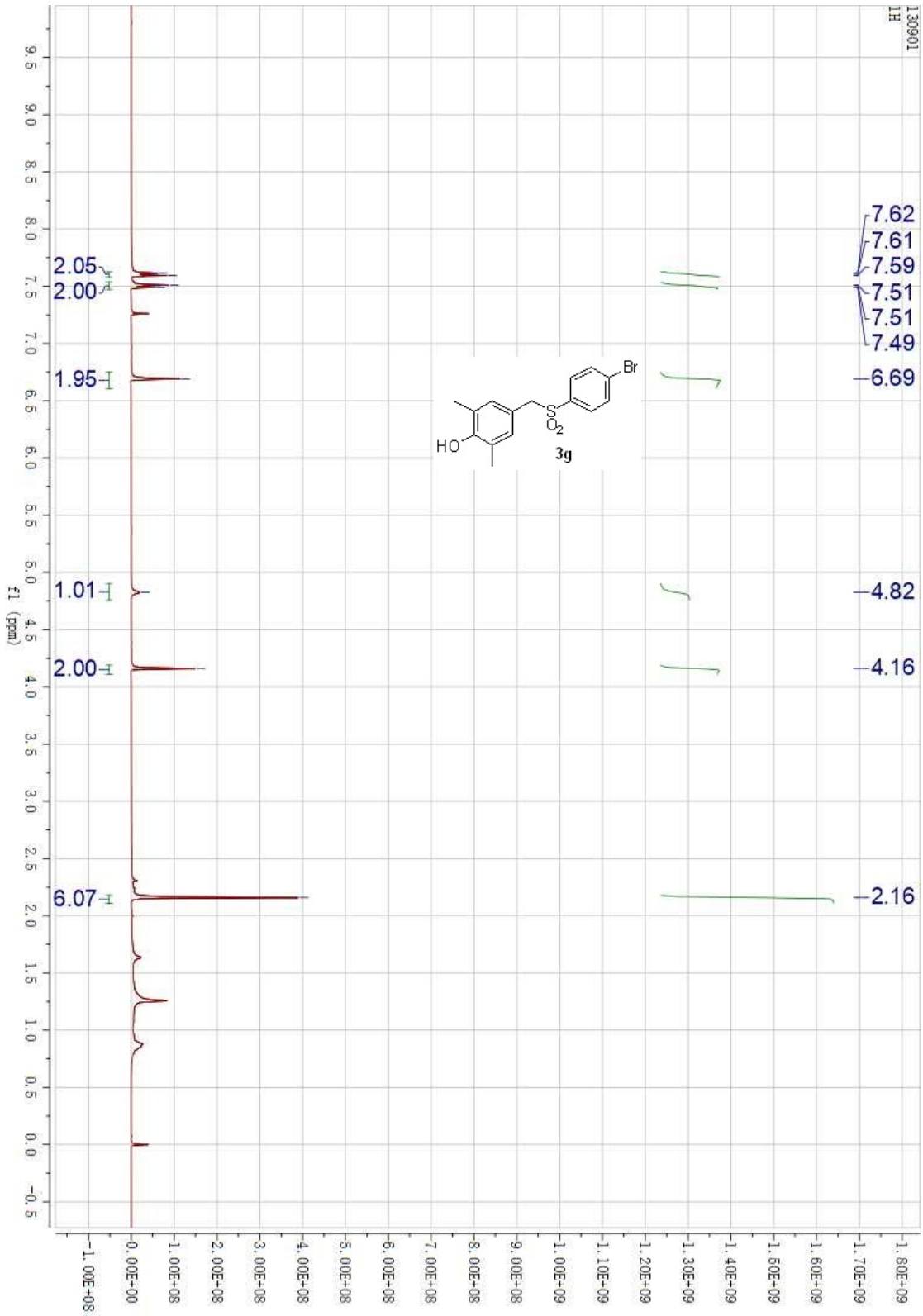
HO
Cl
O2
S
3f
f1 (ppm)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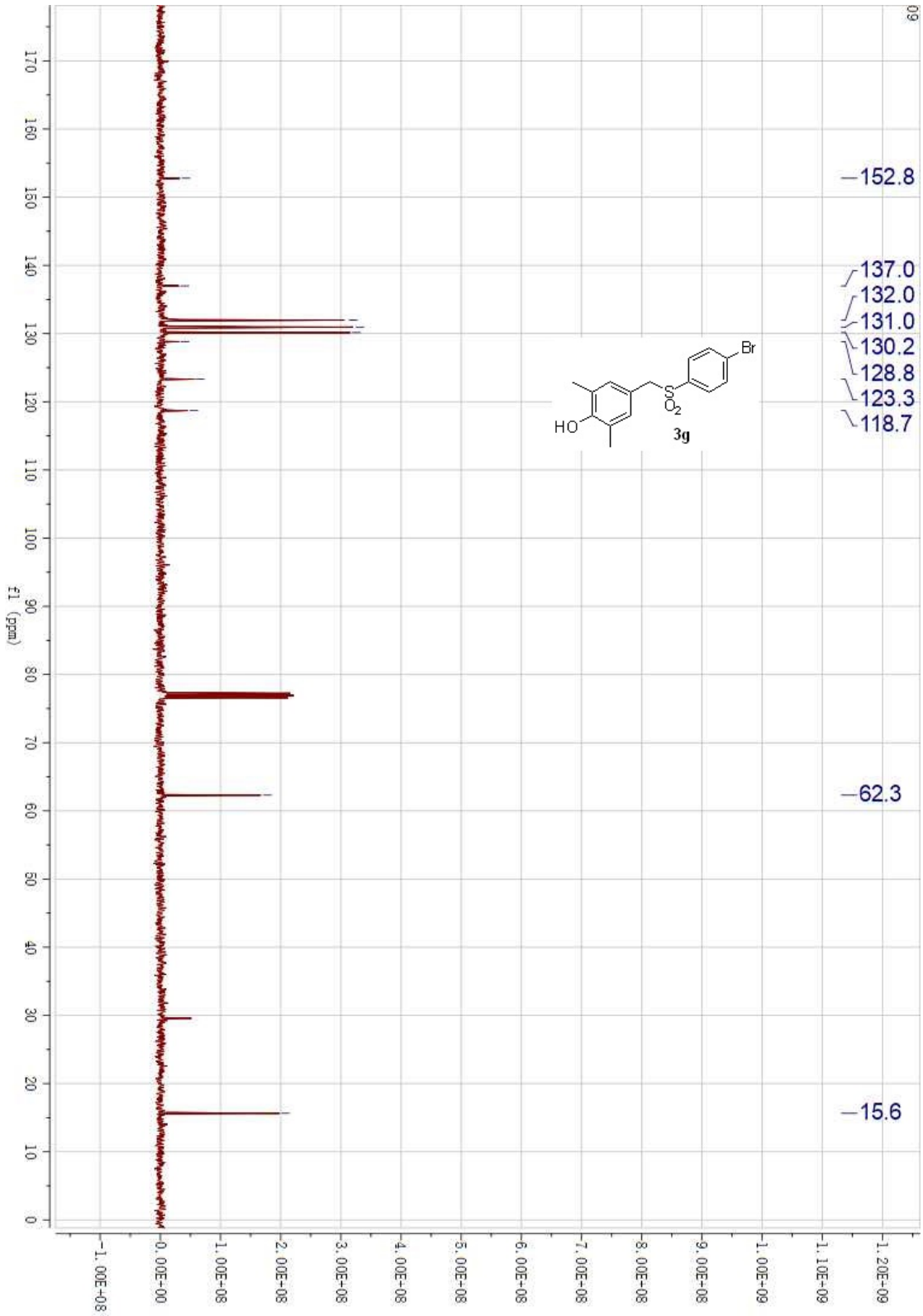
O2
3g
f1 (ppm)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Br
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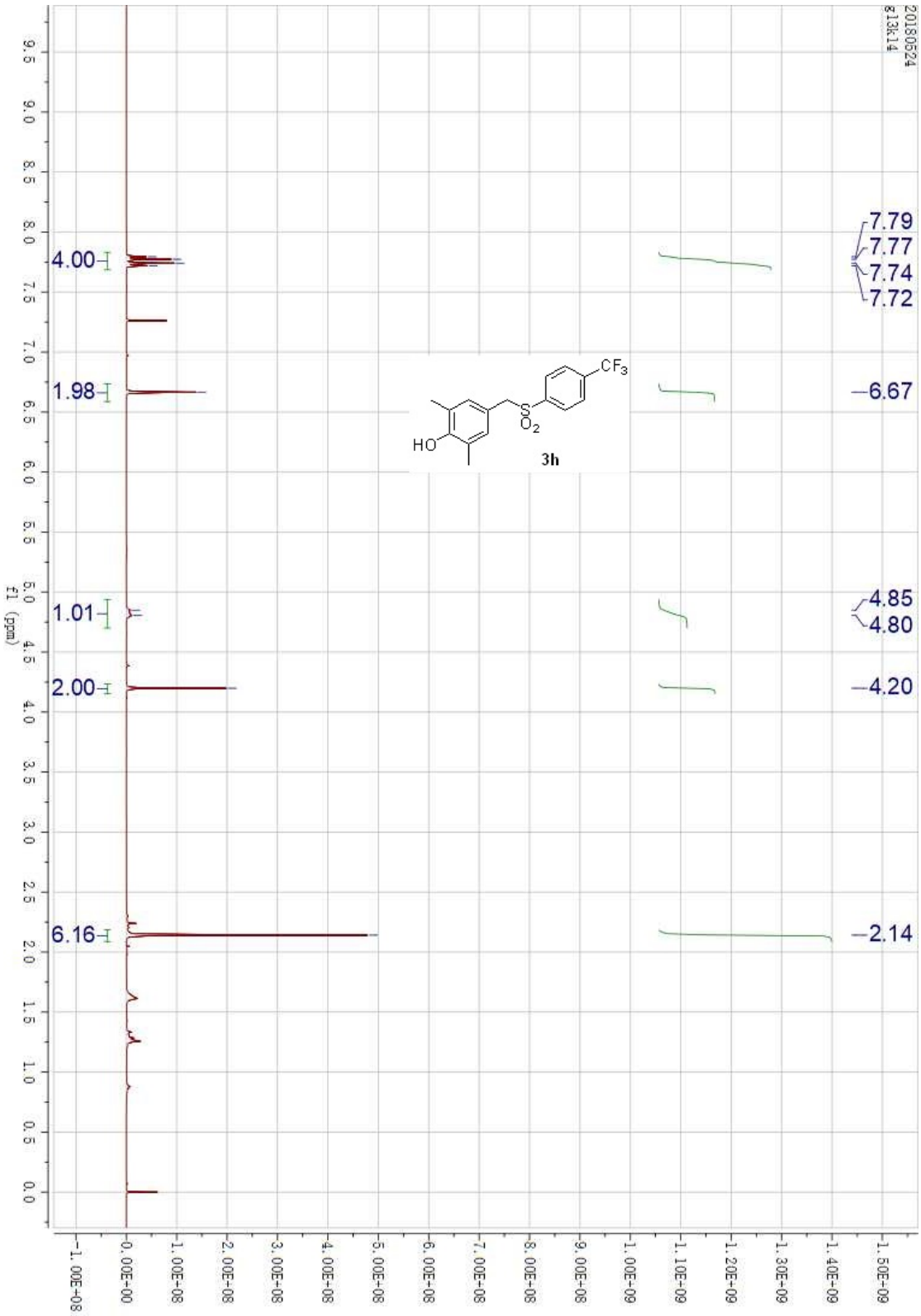
f1 (ppm)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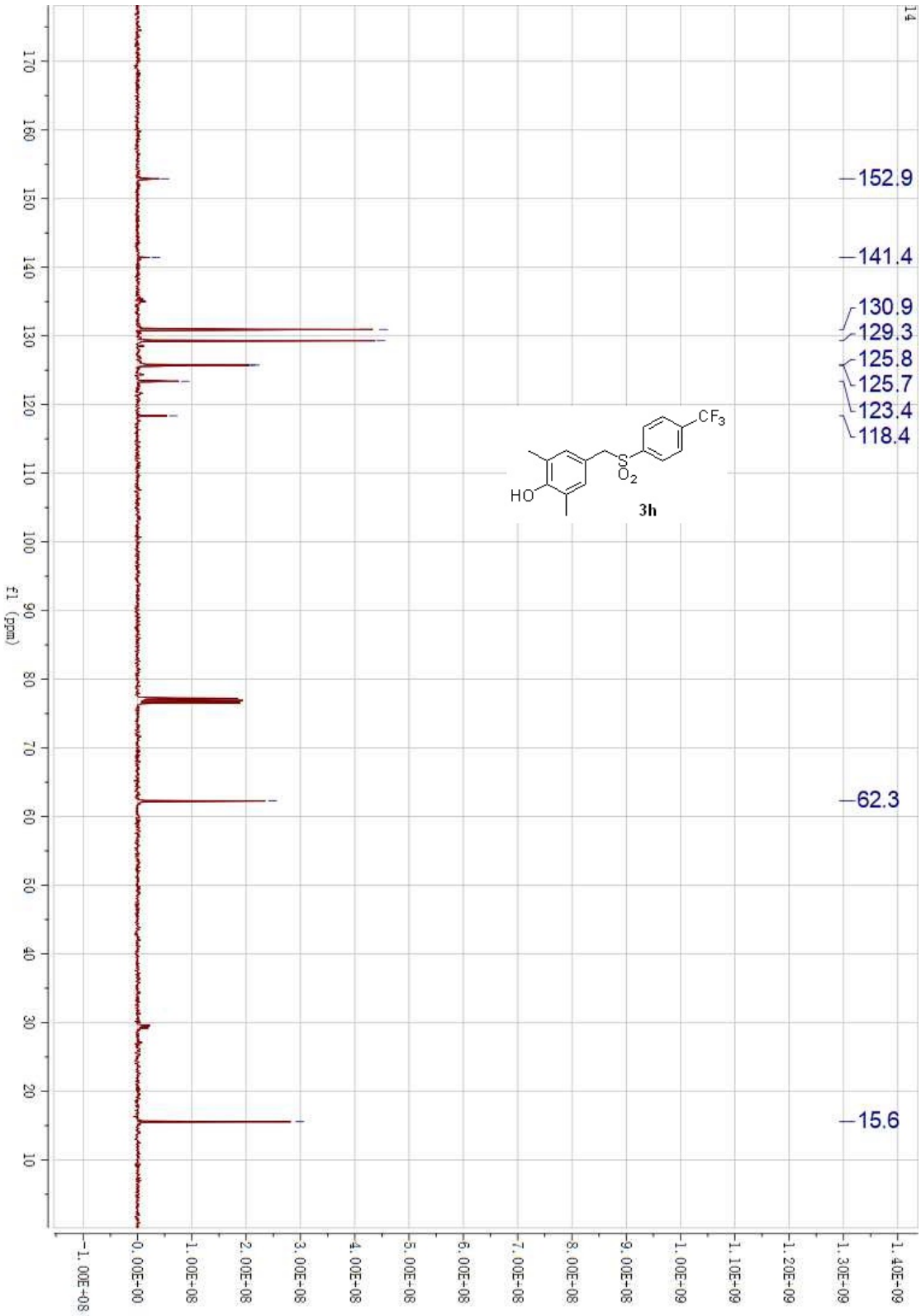
CF_3
SO_2
3h
f1 (ppm)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CF3
O2
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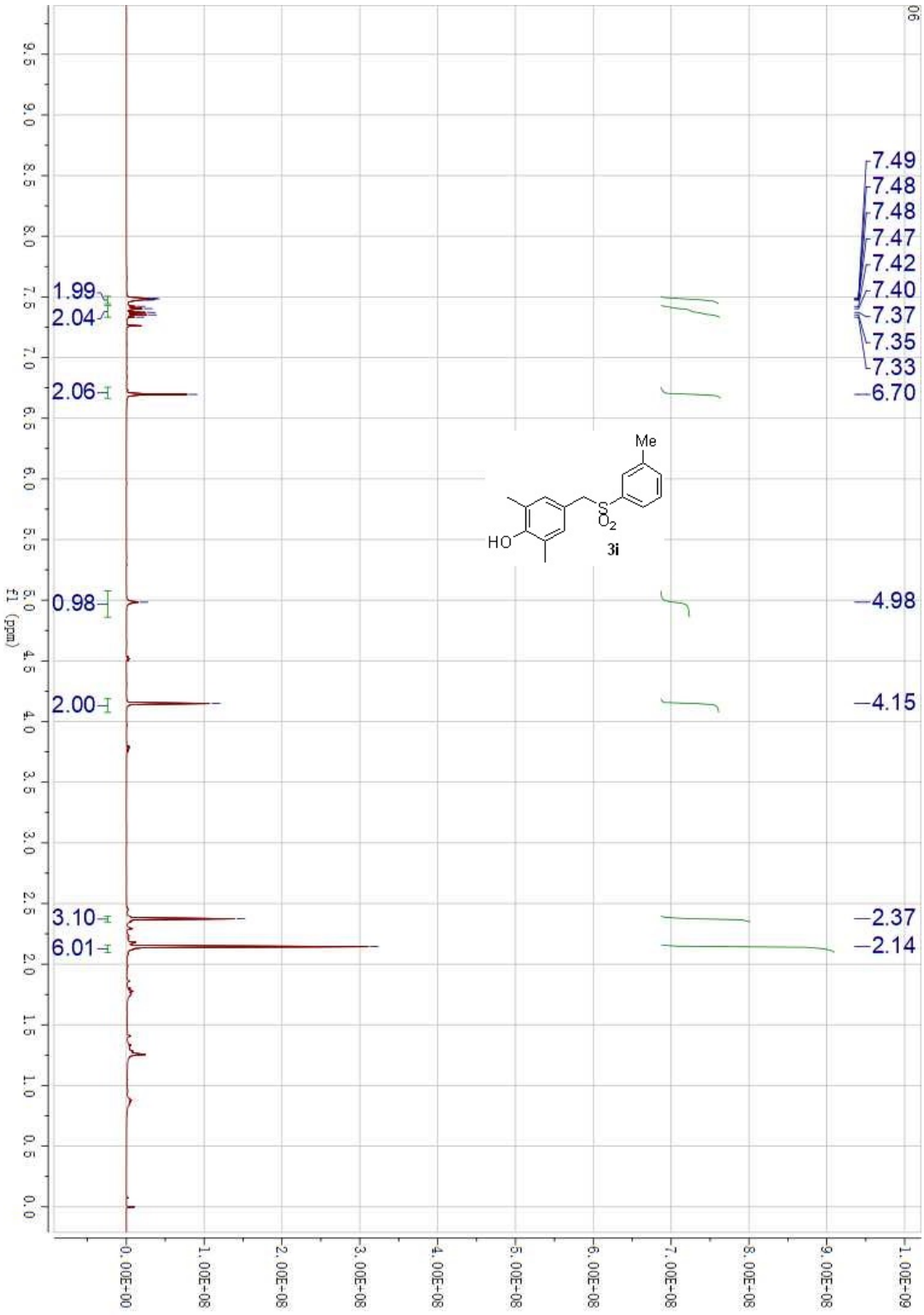
3h
f1 (ppm)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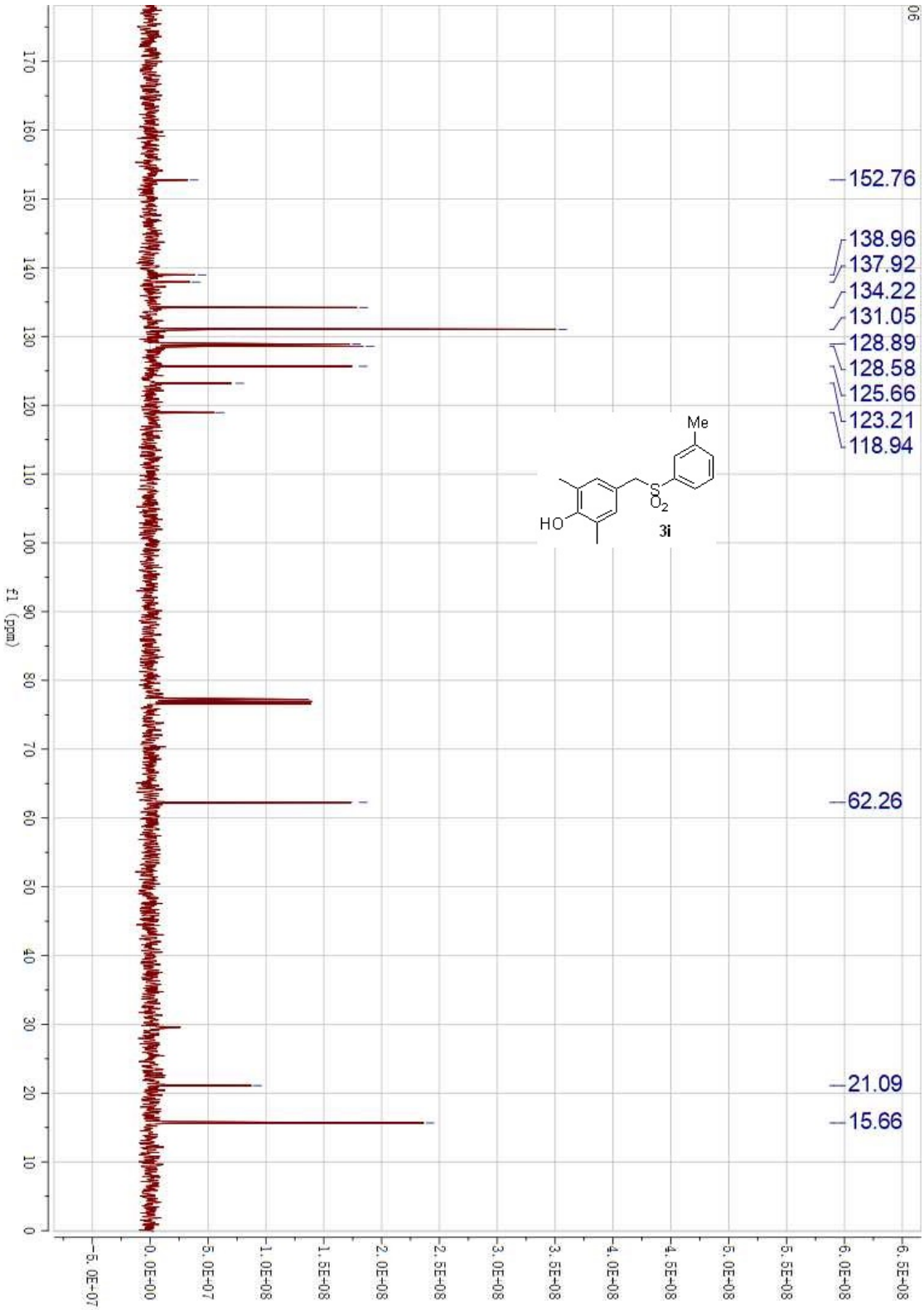
f1 (ppm)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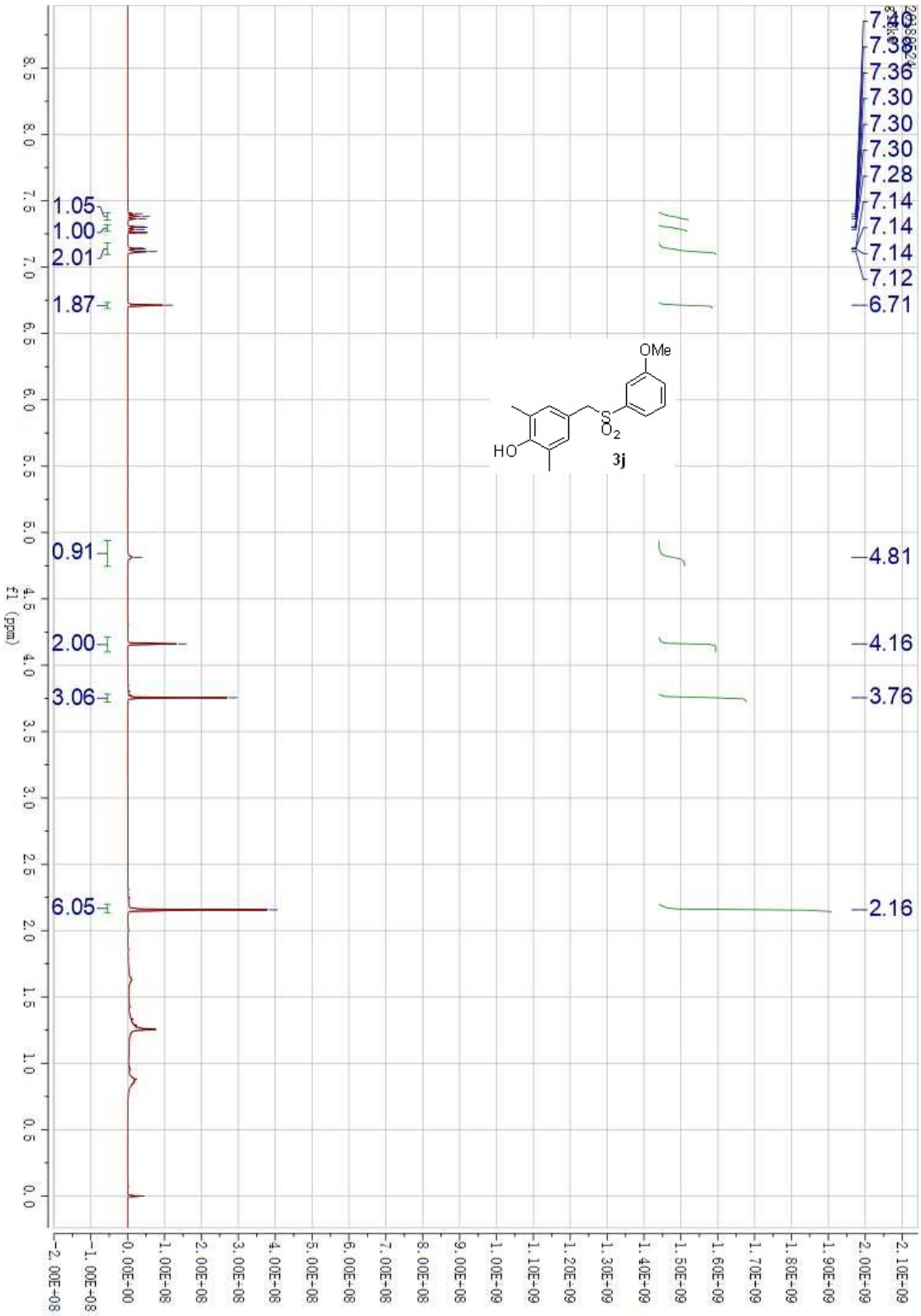
S
O2
3i
f1 (ppm)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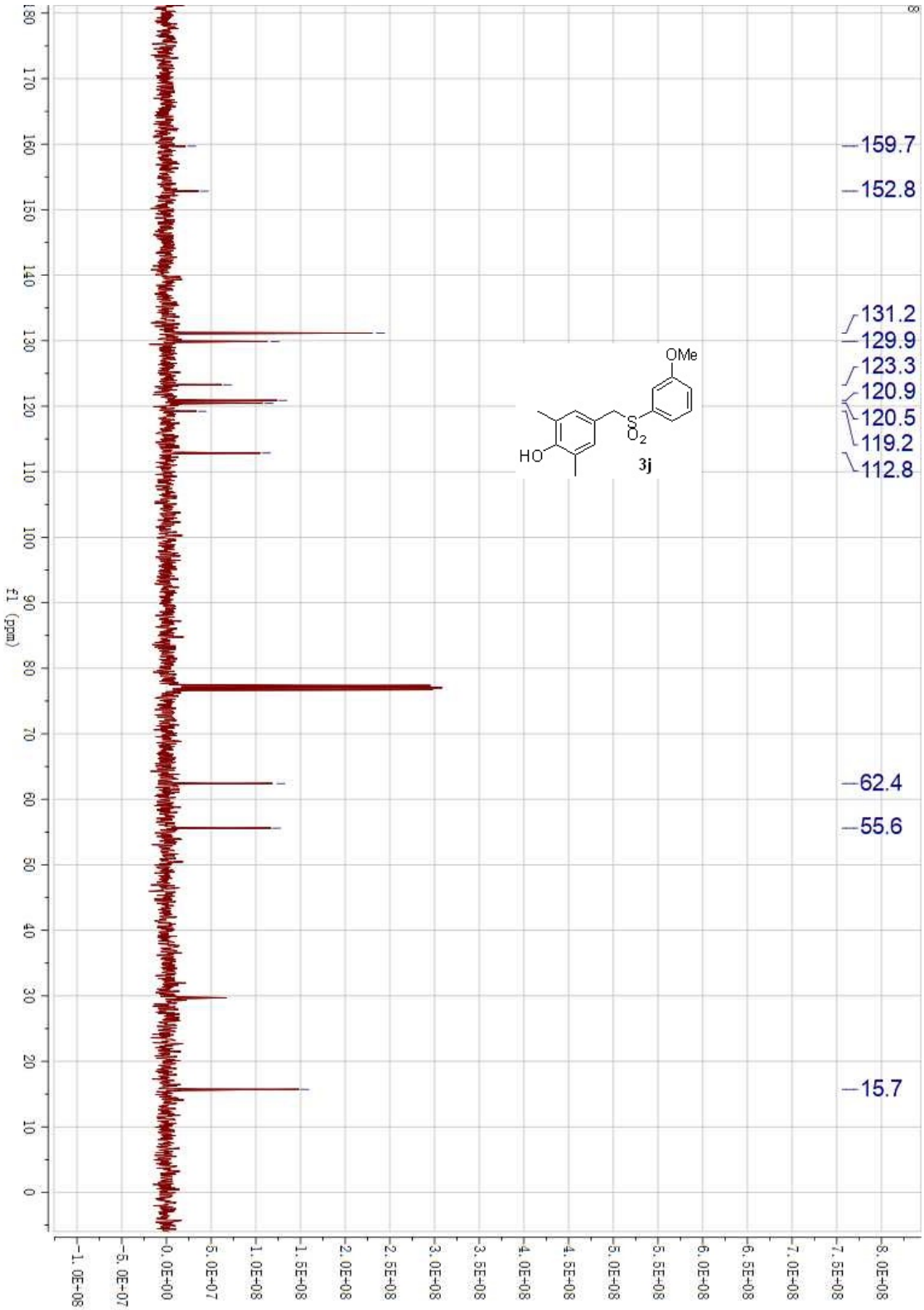
f1 (ppm)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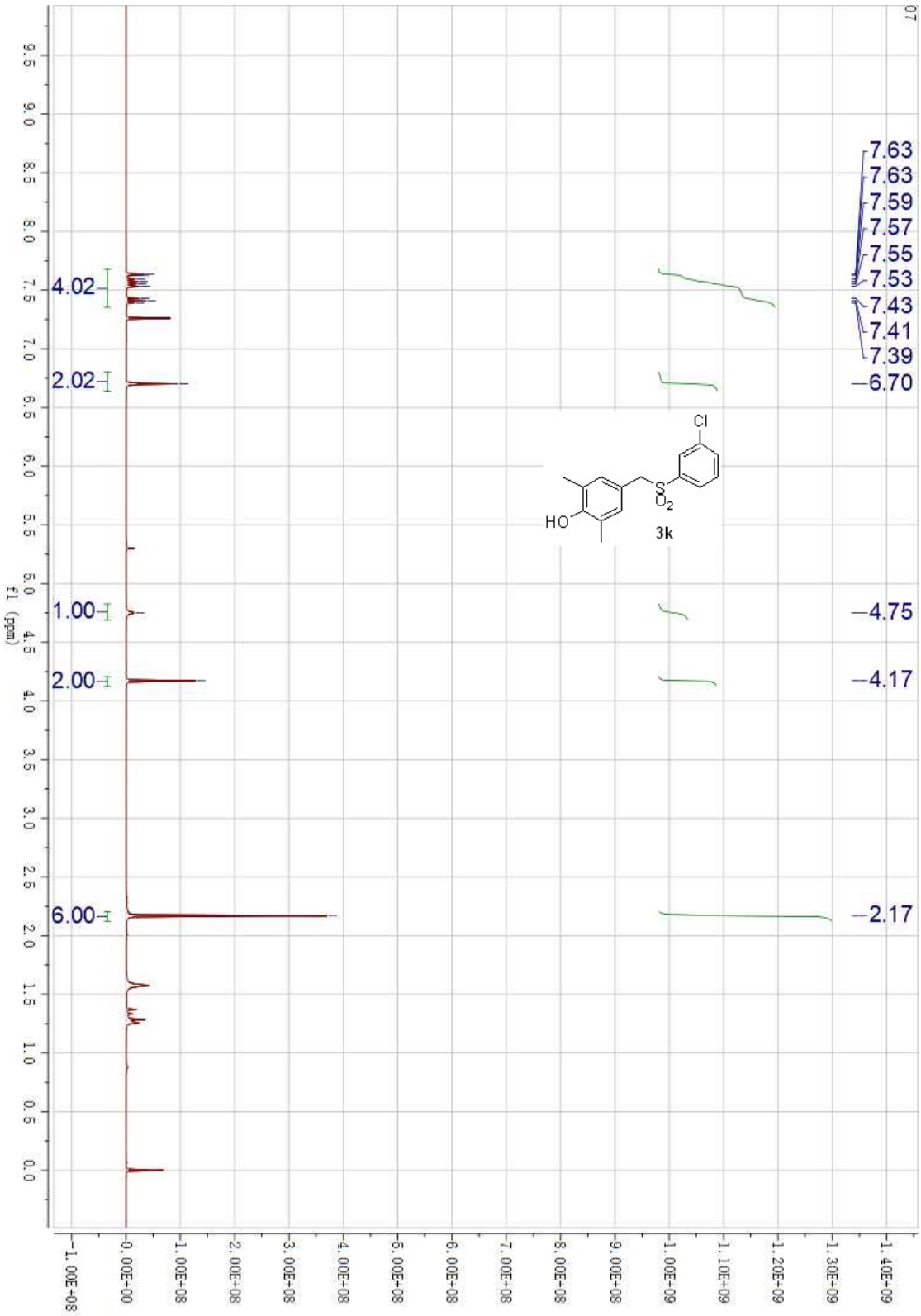
HO
S
O2
3j
f1 (ppm)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Cl
HO
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O2
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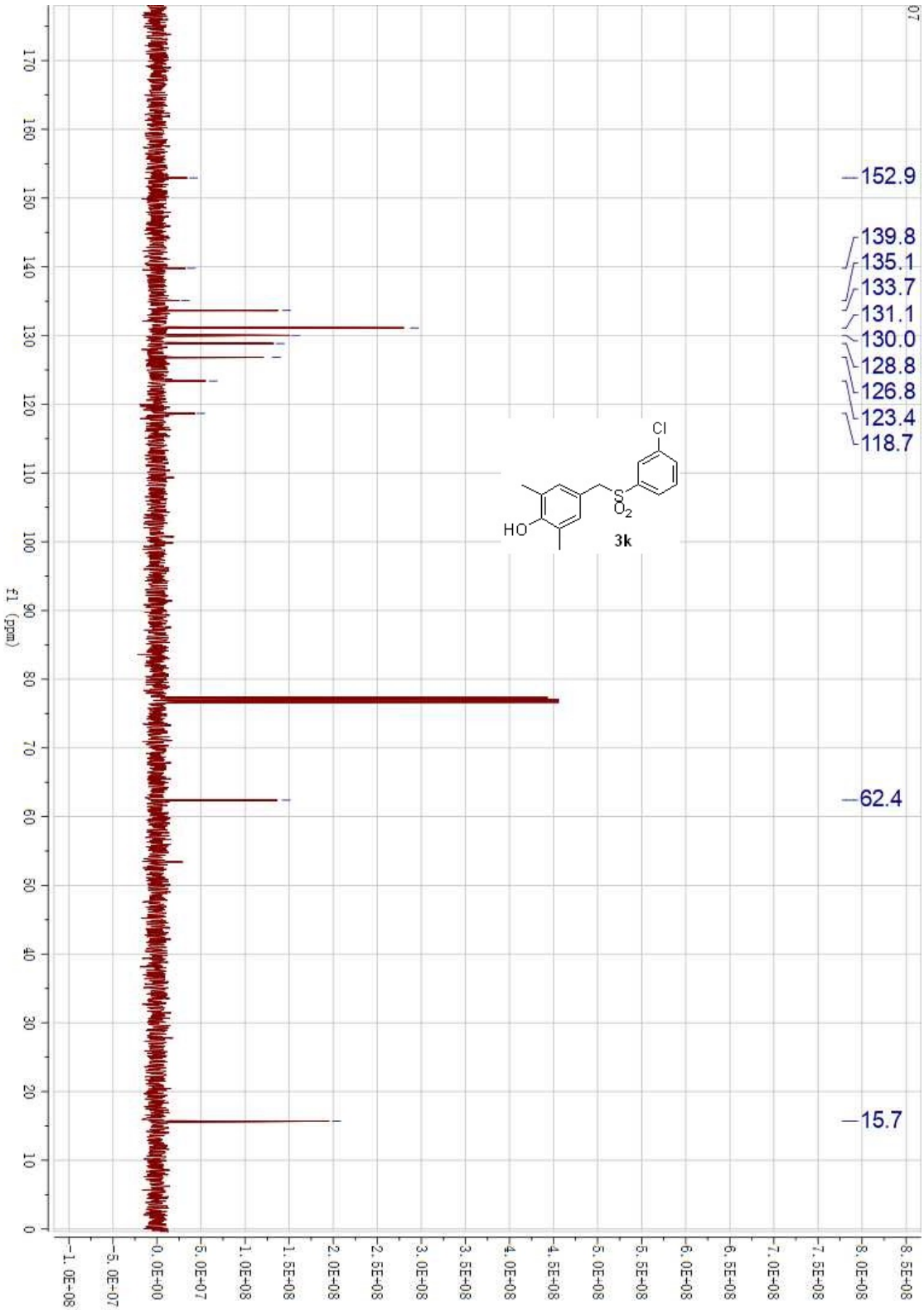
f1 (ppm)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118.7
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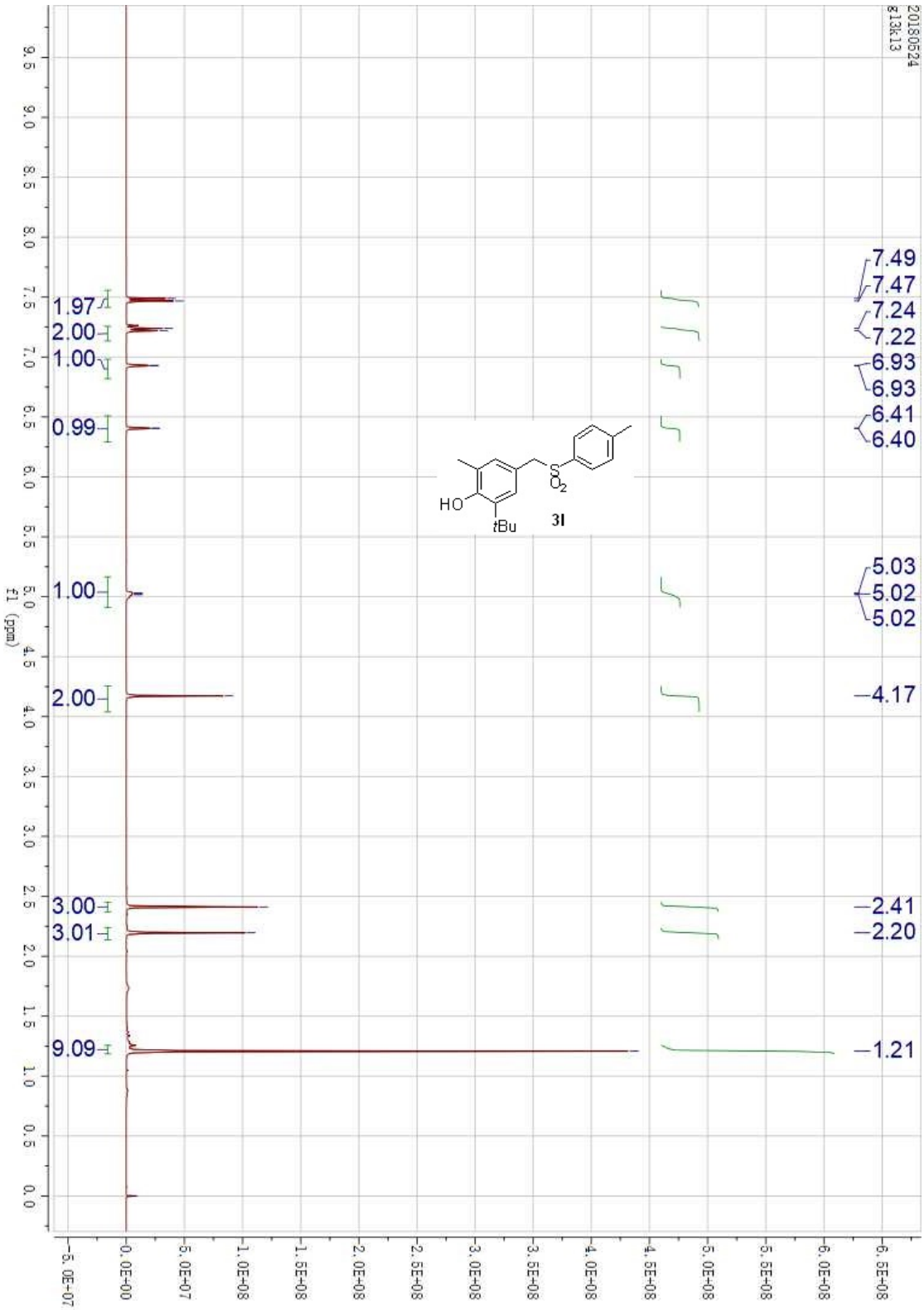
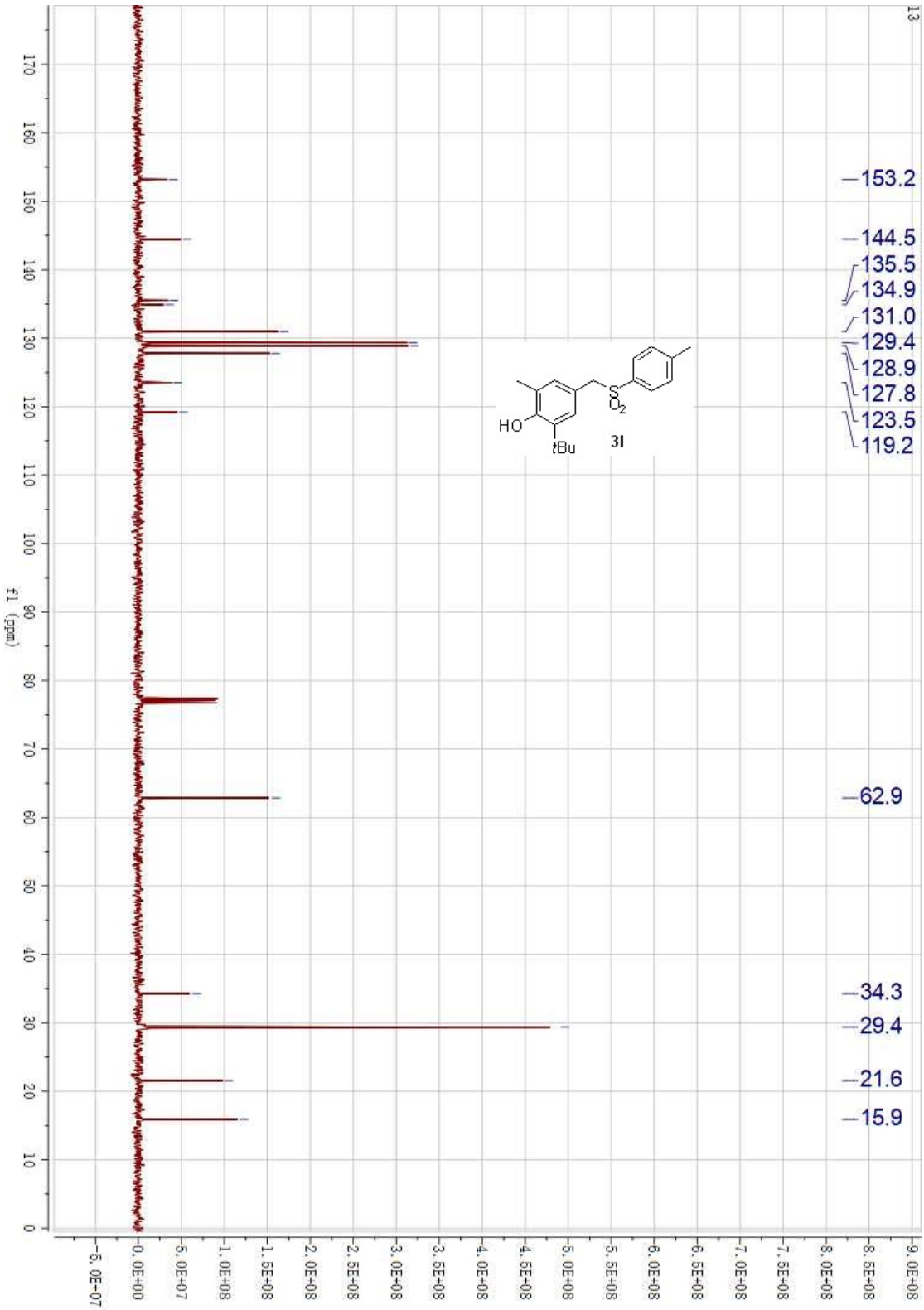
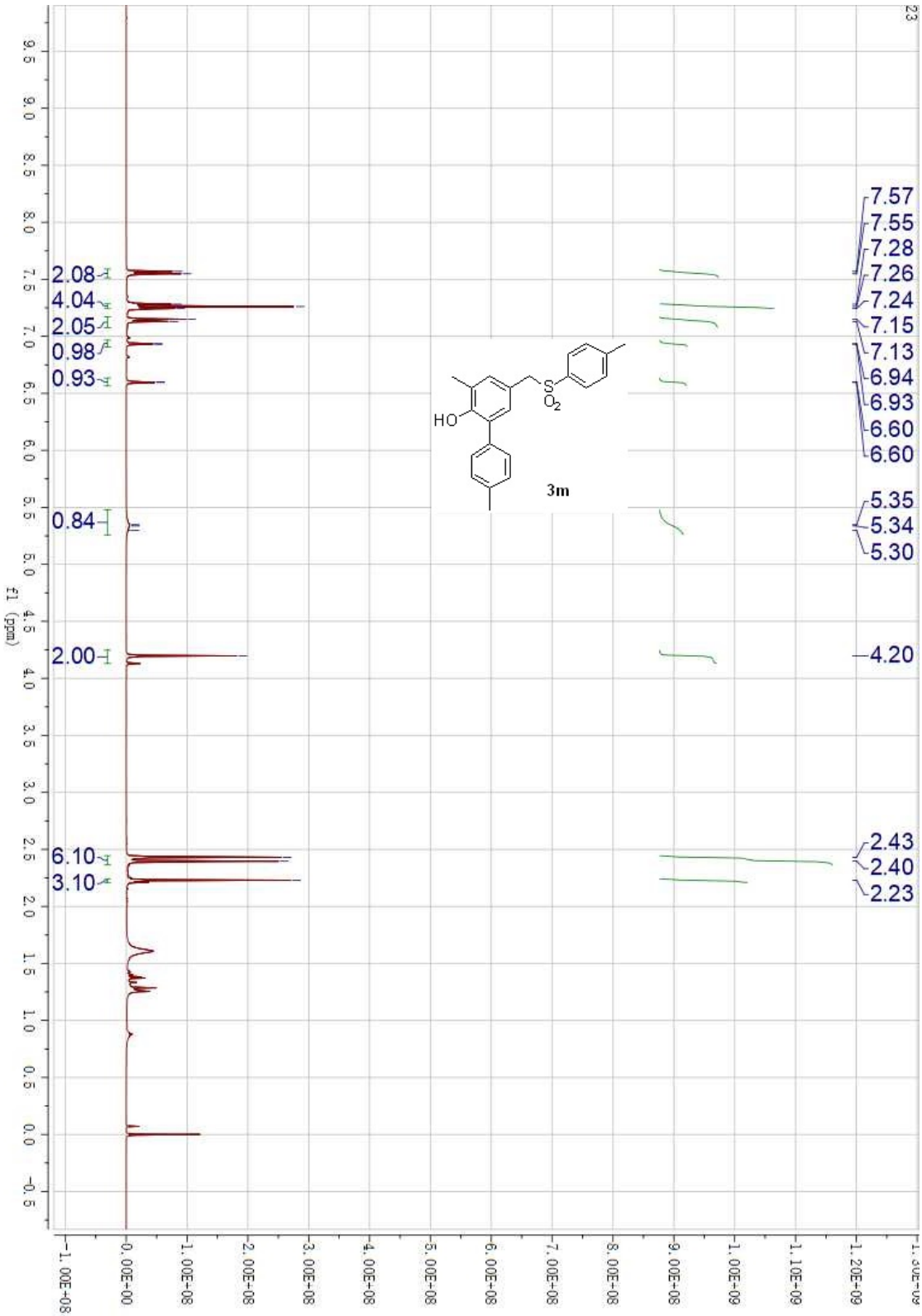
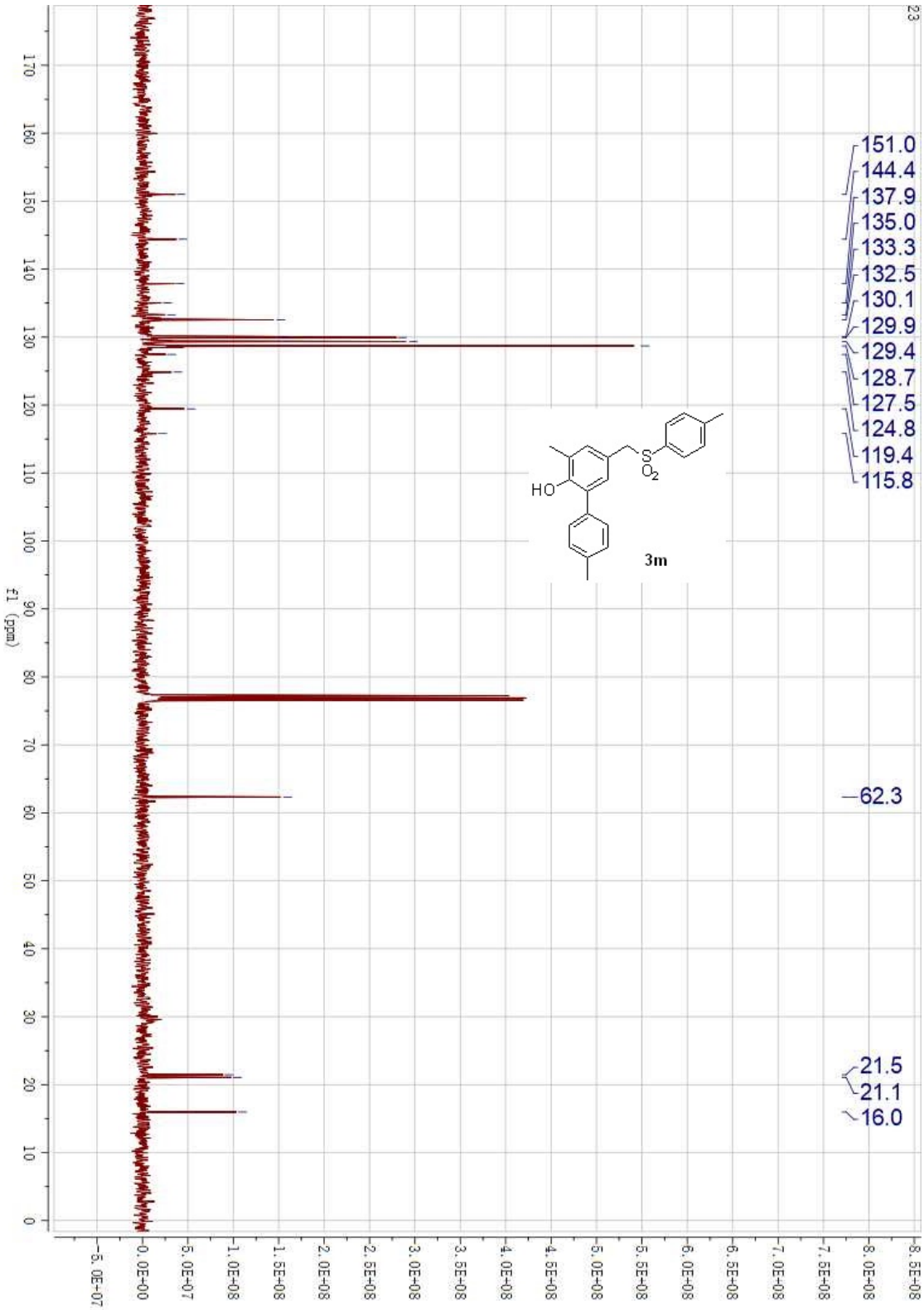
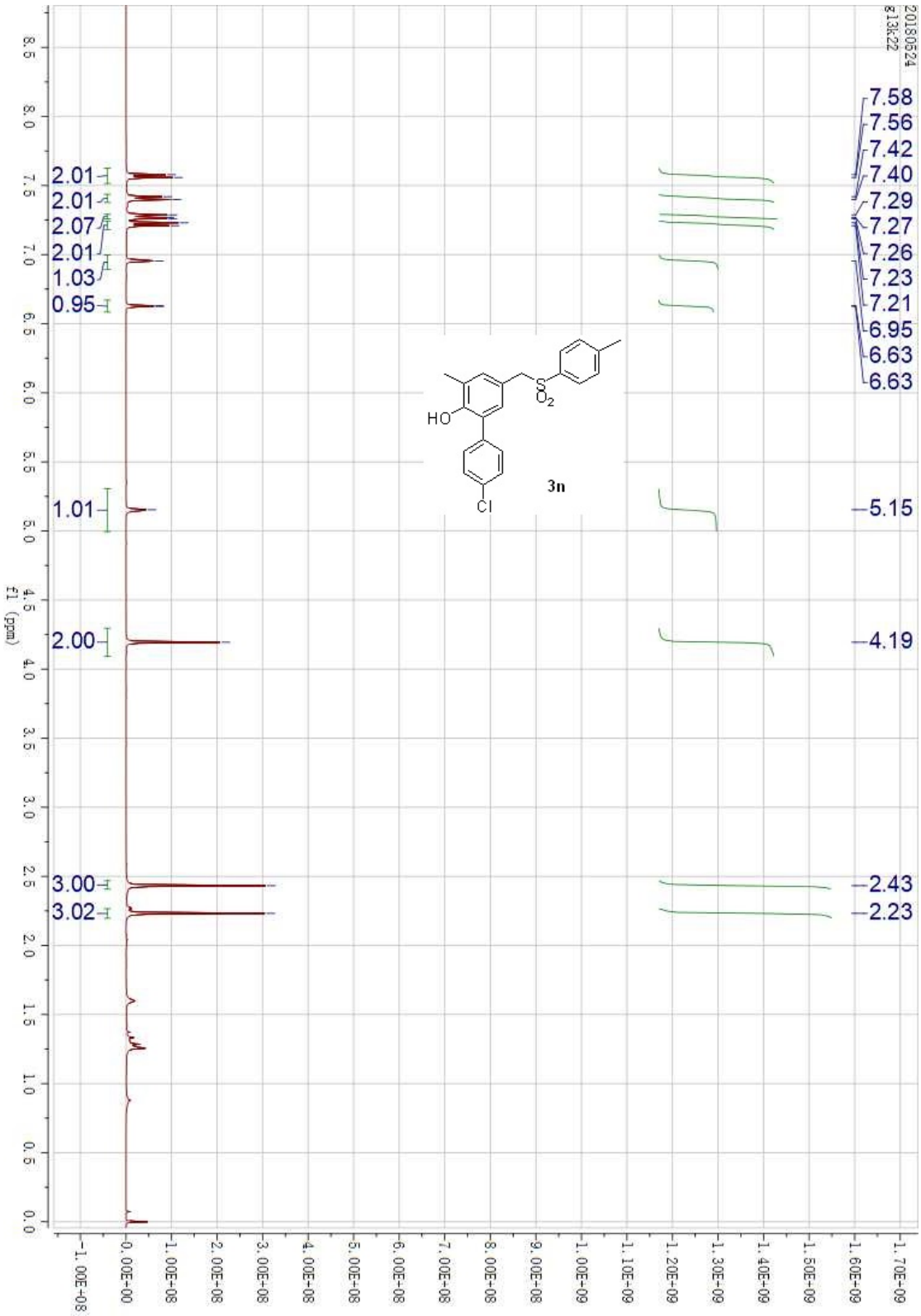
Cl
S
O2
HO
3k
f1 (ppm)

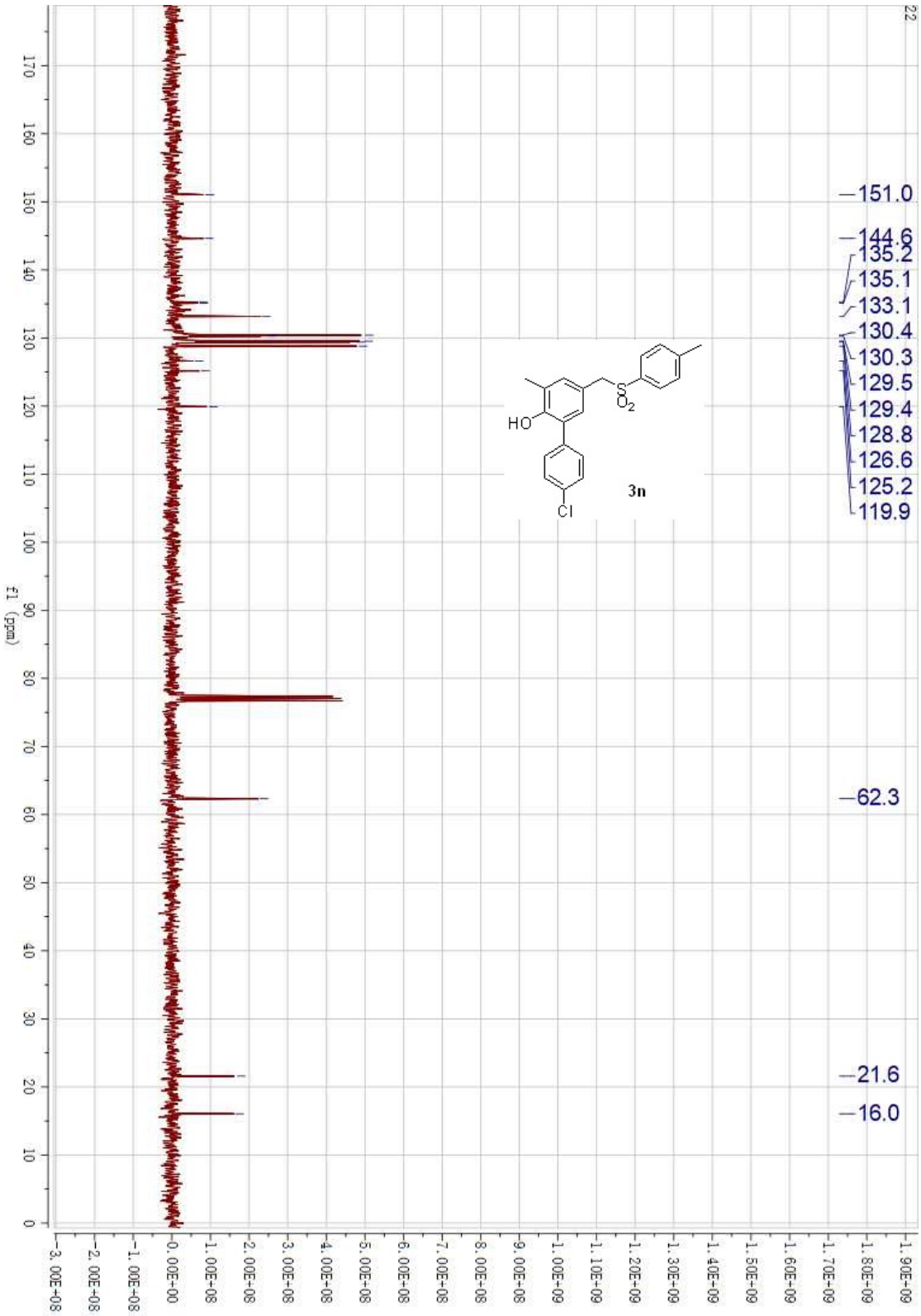

20180524
g13k13
7.49
7.47
7.24
7.22
6.93
6.93
6.41
6.40
5.03
5.02
5.02
4.17
2.41
2.20
1.21
1.97
2.00
1.00
0.99
1.00
2.00
3.00
3.01
9.09
HO
tBu
S
O2
3l
f1 (ppm)

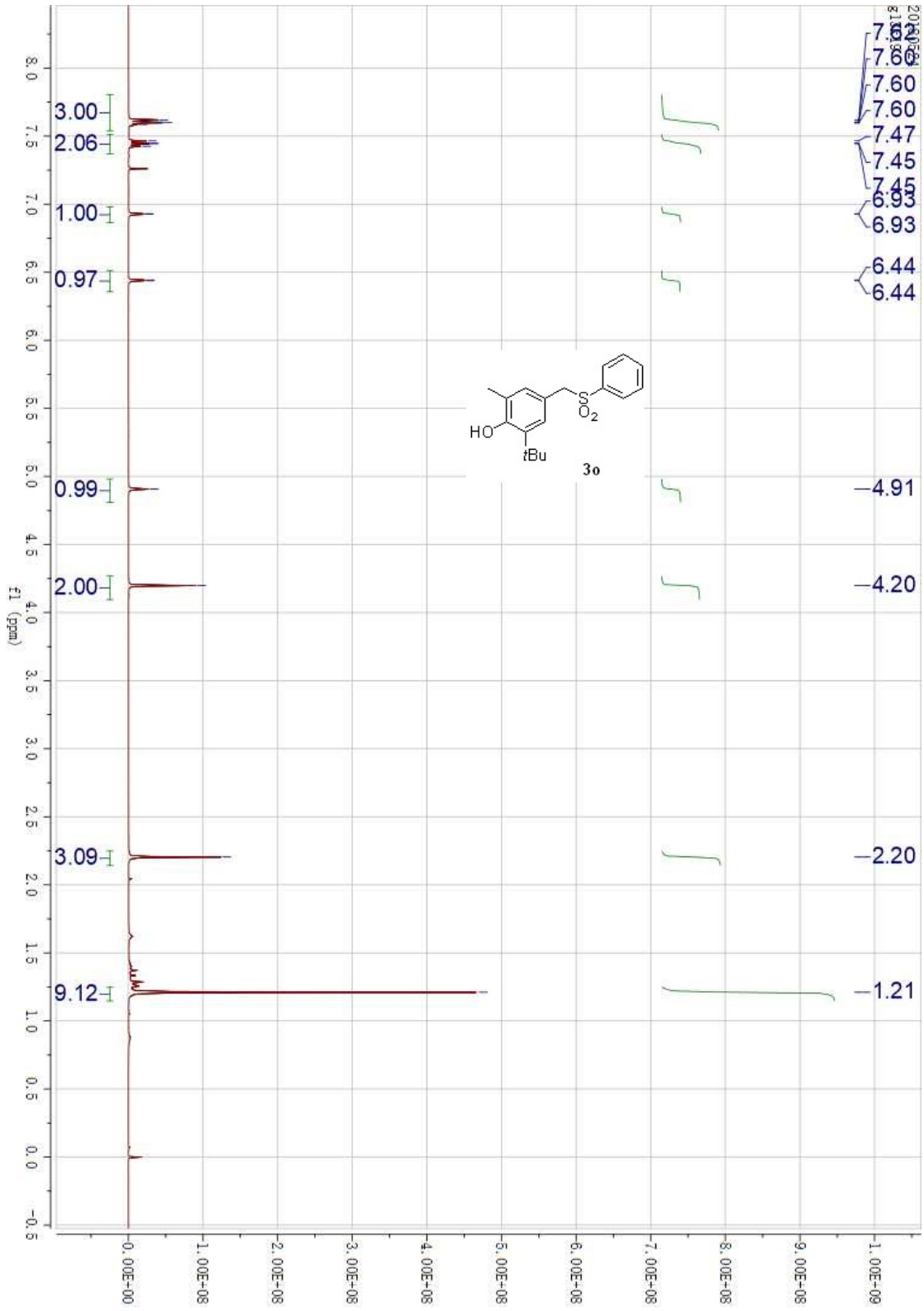

153.2
144.5
135.5
134.9
131.0
129.4
128.9
127.8
123.5
119.2
62.9
34.3
29.4
21.6
15.9
HO
tBu
3l
f1 (ppm)

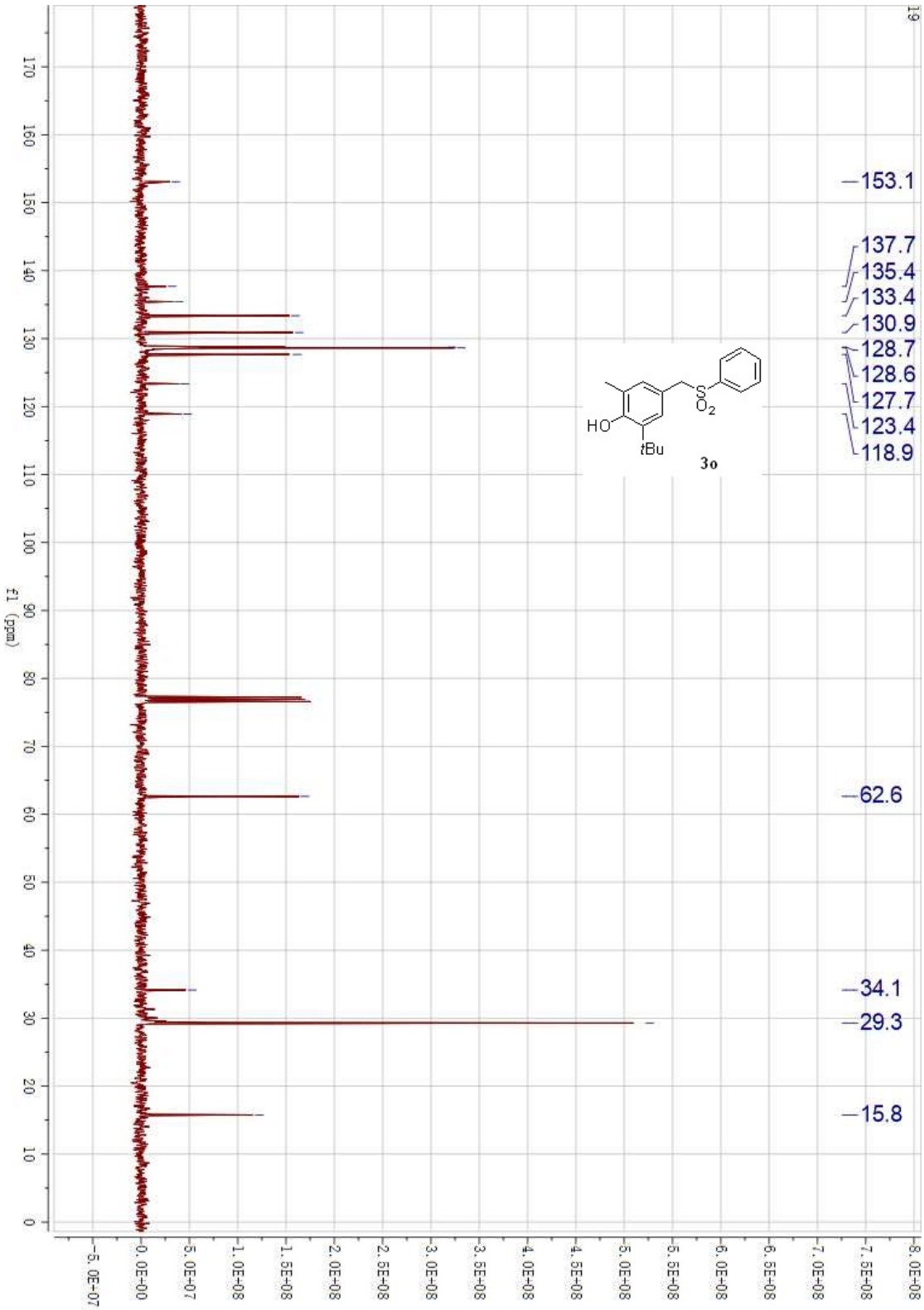

7.57
7.55
7.28
7.26
7.24
7.15
7.13
6.94
6.93
6.60
6.60
5.35
5.34
5.30
4.20
2.43
2.40
2.23
2.08
4.04
2.05
0.98
0.93
0.84
2.00
6.10
3.10
HO
3m
f1 (ppm)

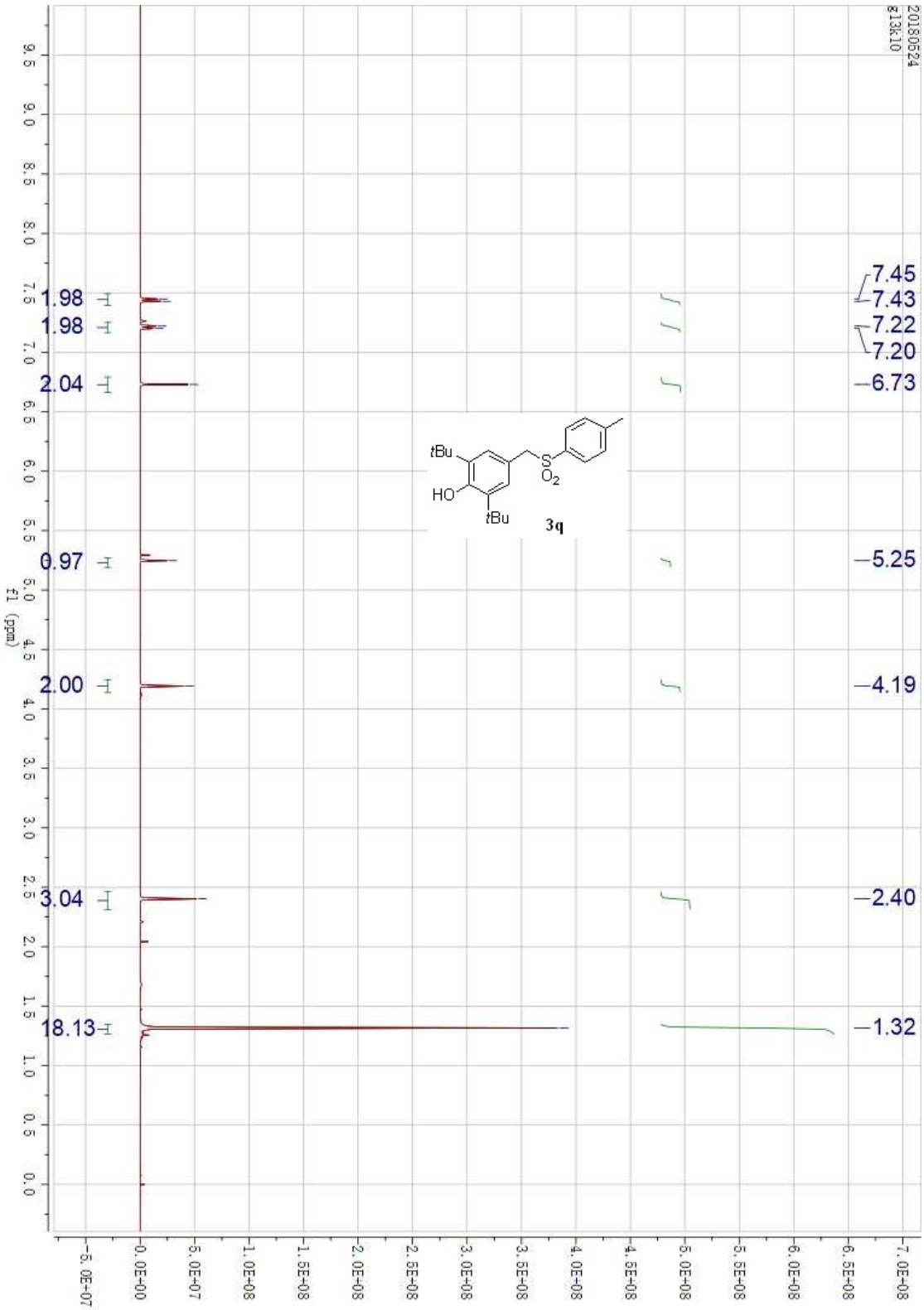

151.0
144.4
137.9
135.0
133.3
132.5
130.1
129.9
129.4
128.7
127.5
124.8
119.4
115.8
62.3
21.5
21.1
16.0
HO
S
O2
3m
f1 (ppm)

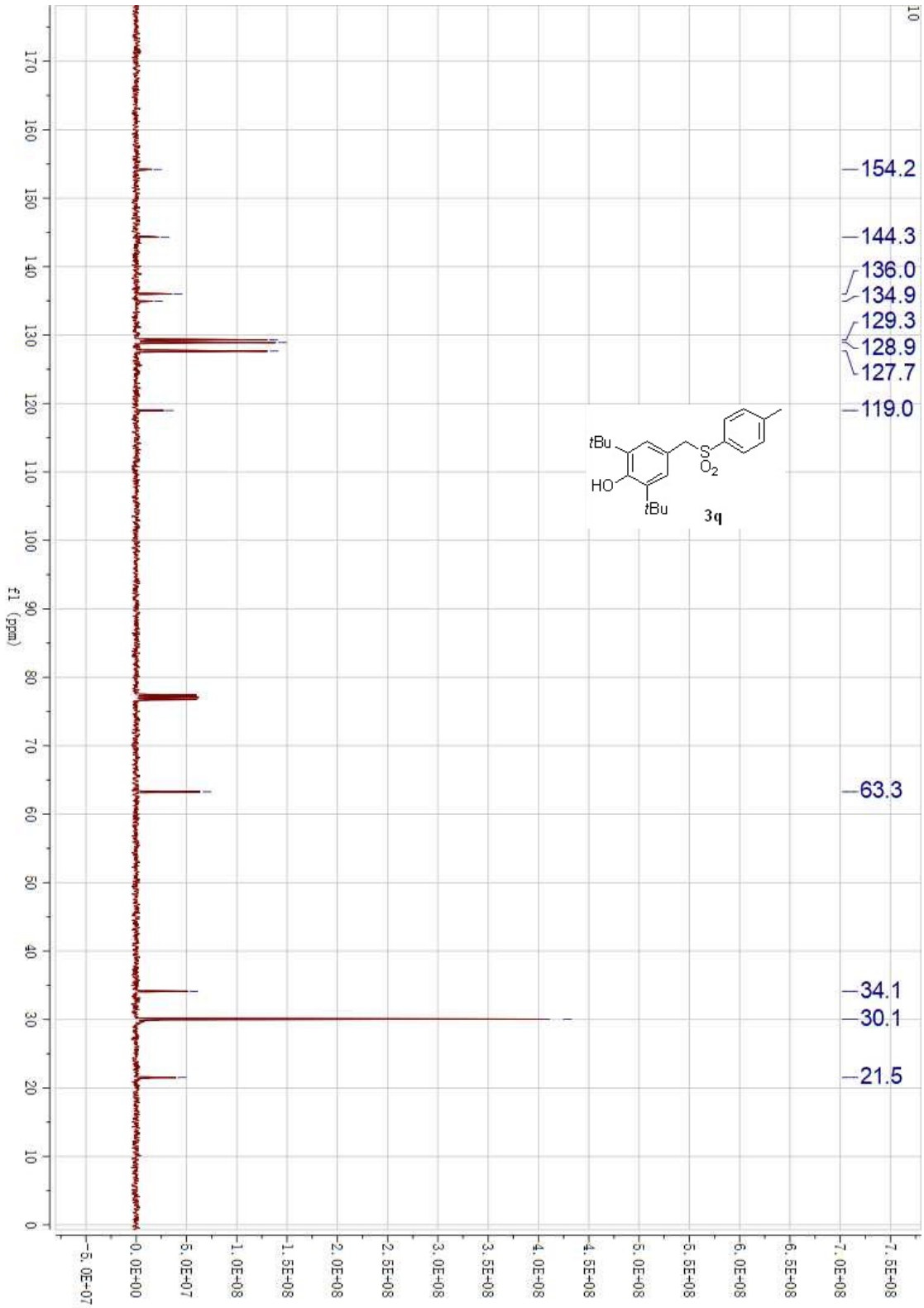

20180524
g13k22
7.58
7.56
7.42
7.40
7.29
7.27
7.26
7.23
7.21
6.95
6.63
6.63
5.15
4.19
2.43
2.23
2.01
2.01
2.07
2.01
1.03
0.95
1.01
2.00
3.00
3.02
HO
Cl
O2
S
3n
f1 (ppm)

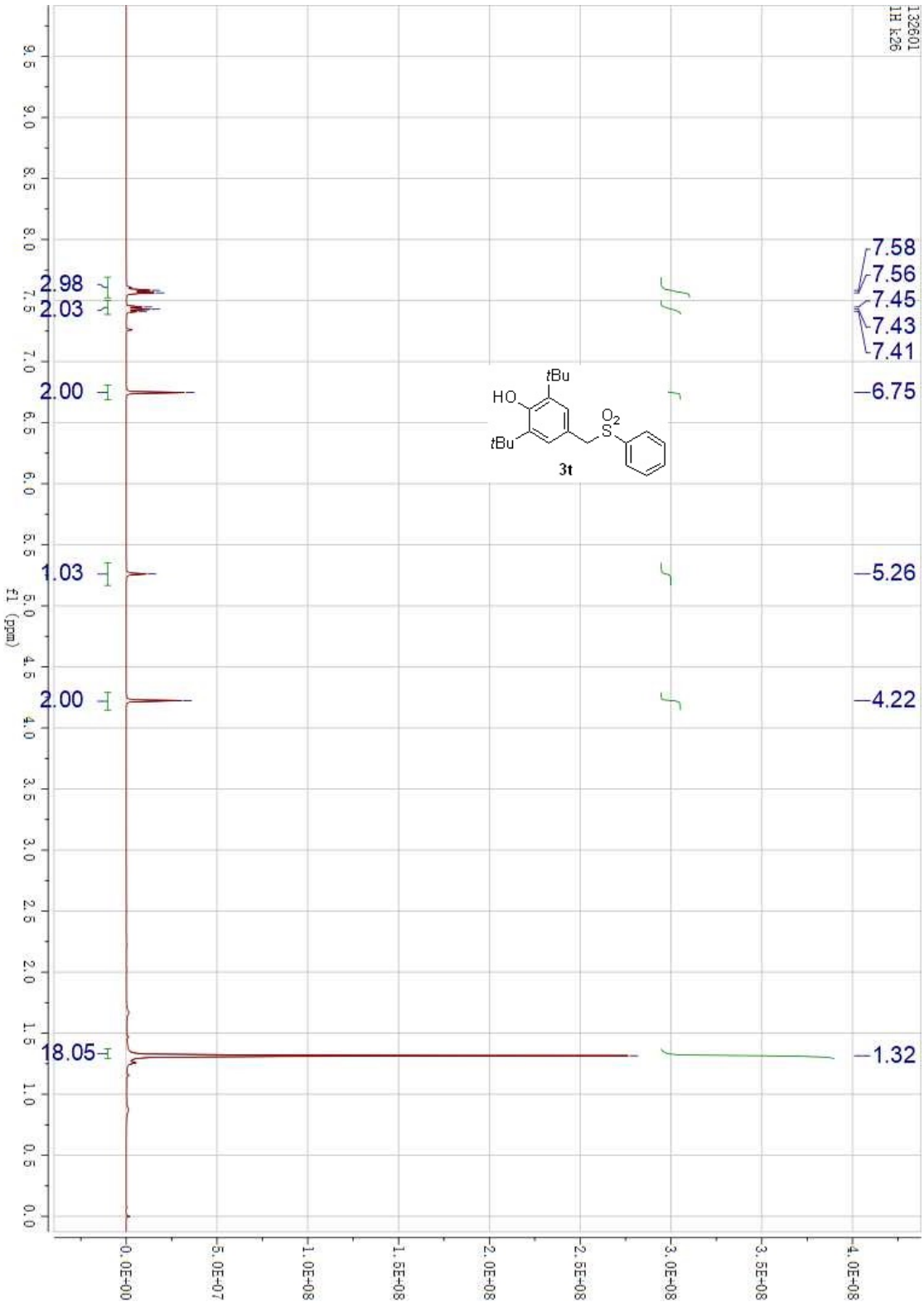

151.0
144.6
135.2
135.1
133.1
130.4
130.3
129.5
129.4
128.8
126.6
125.2
119.9
62.3
21.6
16.0
HO
O2S
Cl
3n
f1 (ppm)


3.00
2.06
1.00
0.97
0.99
2.00
3.09
9.12
7.60
7.60
7.60
7.47
7.45
7.45
6.93
6.93
6.44
6.44
4.91
4.20
2.20
1.21
HO
tBu
S
O2
3o
f1 (ppm)


153.1
137.7
135.4
133.4
130.9
128.7
128.6
127.7
123.4
118.9
62.6
34.1
29.3
15.8
HO
tBu
S
O2
3o
f1 (ppm)


20180524
g13k10
7.45
7.43
7.22
7.20
6.73
5.25
4.19
2.40
1.32
1.98
1.98
2.04
0.97
2.00
3.04
18.13
tBu
HO
tBu
S
O2
3q
f1 (ppm)


154.2
144.3
136.0
134.9
129.3
128.9
127.7
119.0
63.3
34.1
30.1
21.5
tBu
HO
tBu
S
O2
3q
f1 (ppm)


132601
1H k26
7.58
7.56
7.45
7.43
7.41
6.75
5.26
4.22
1.32
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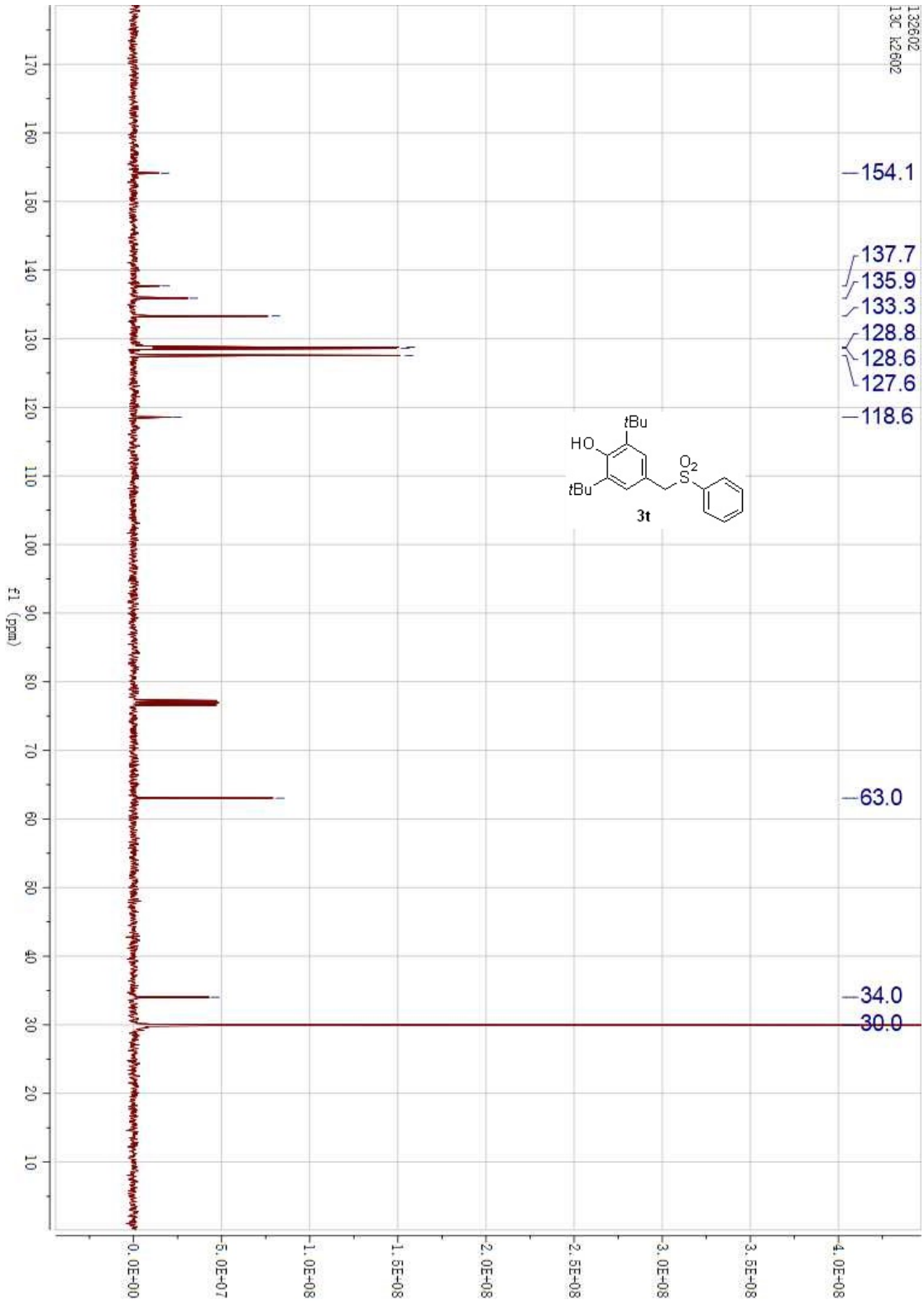
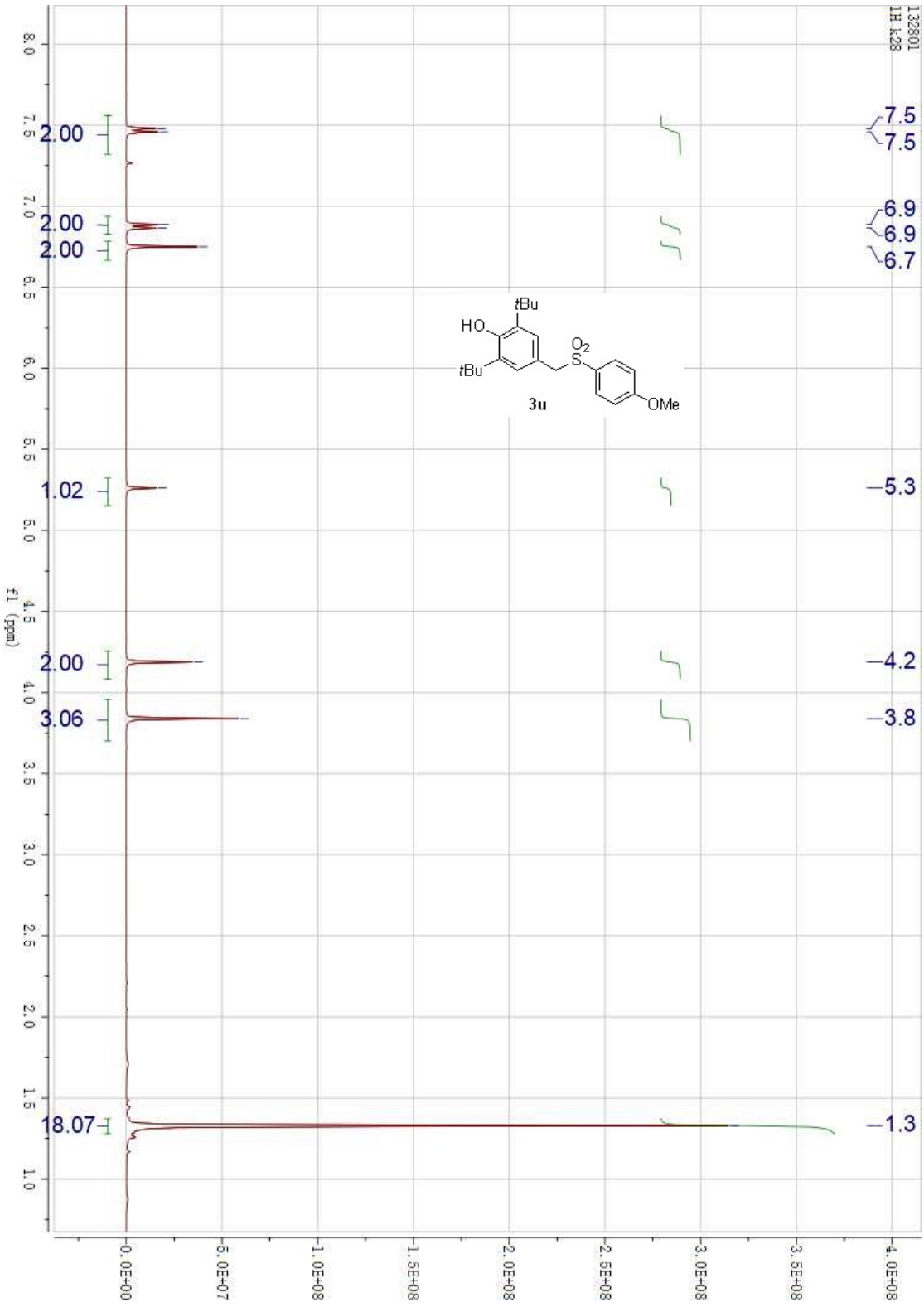
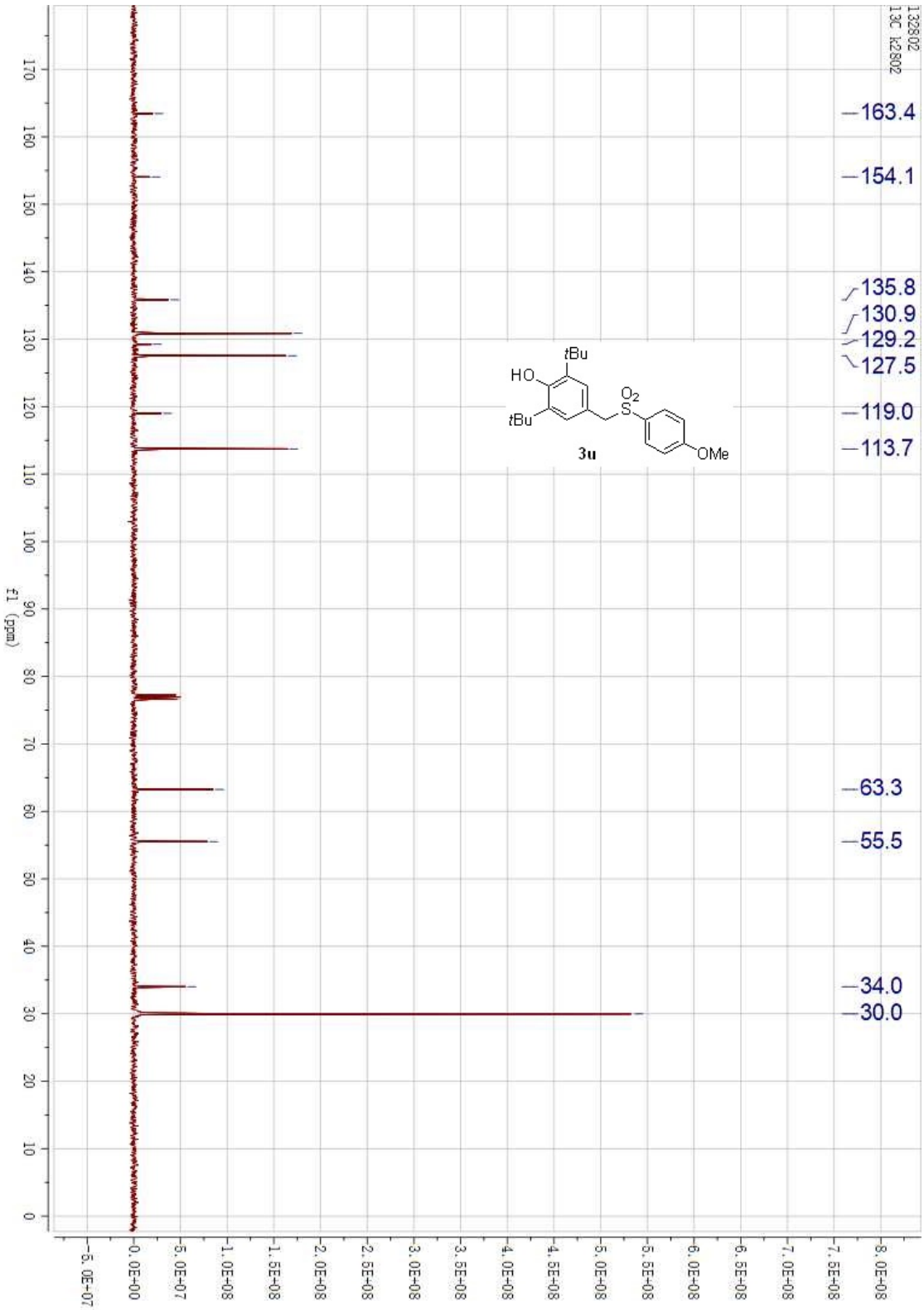
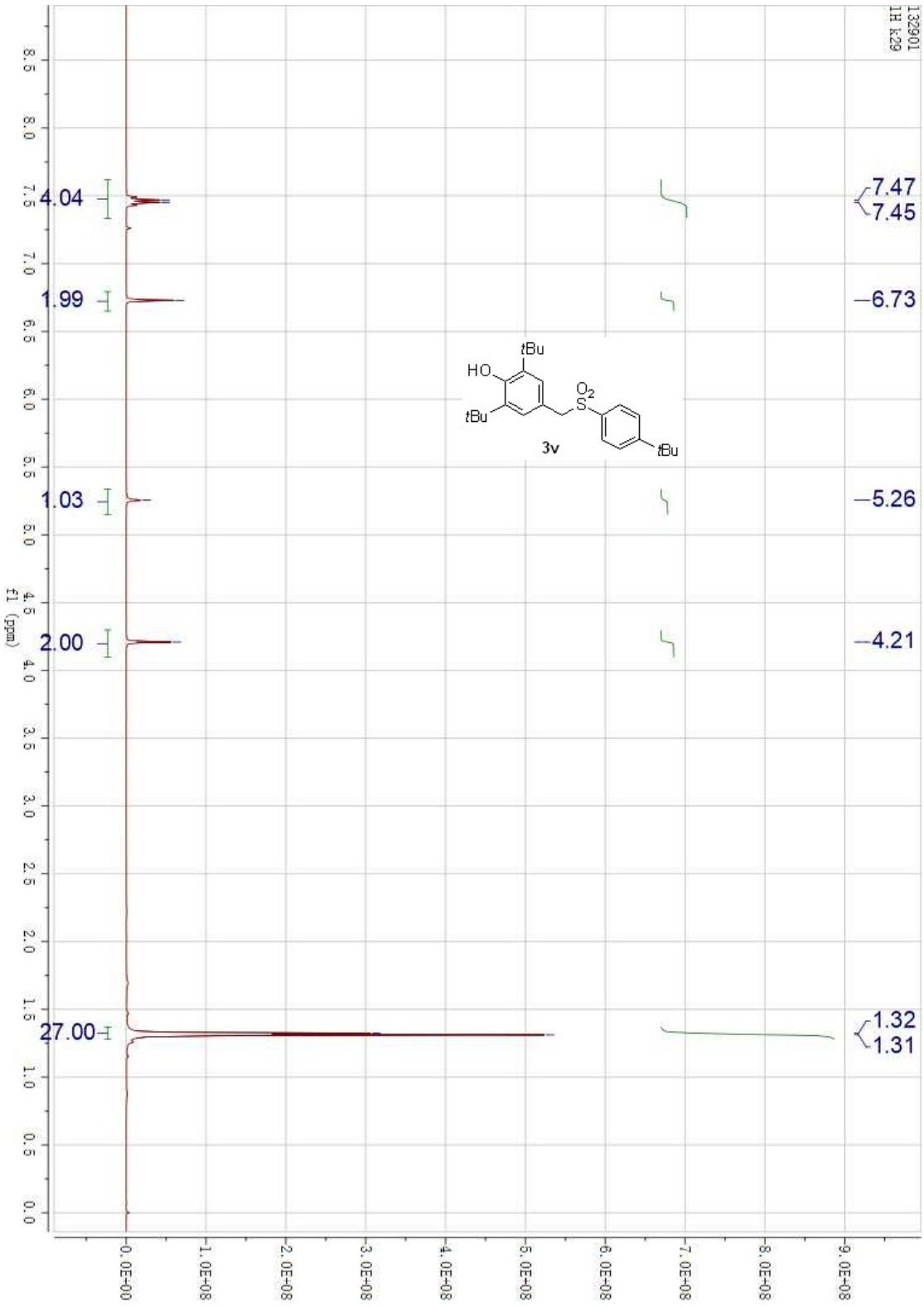
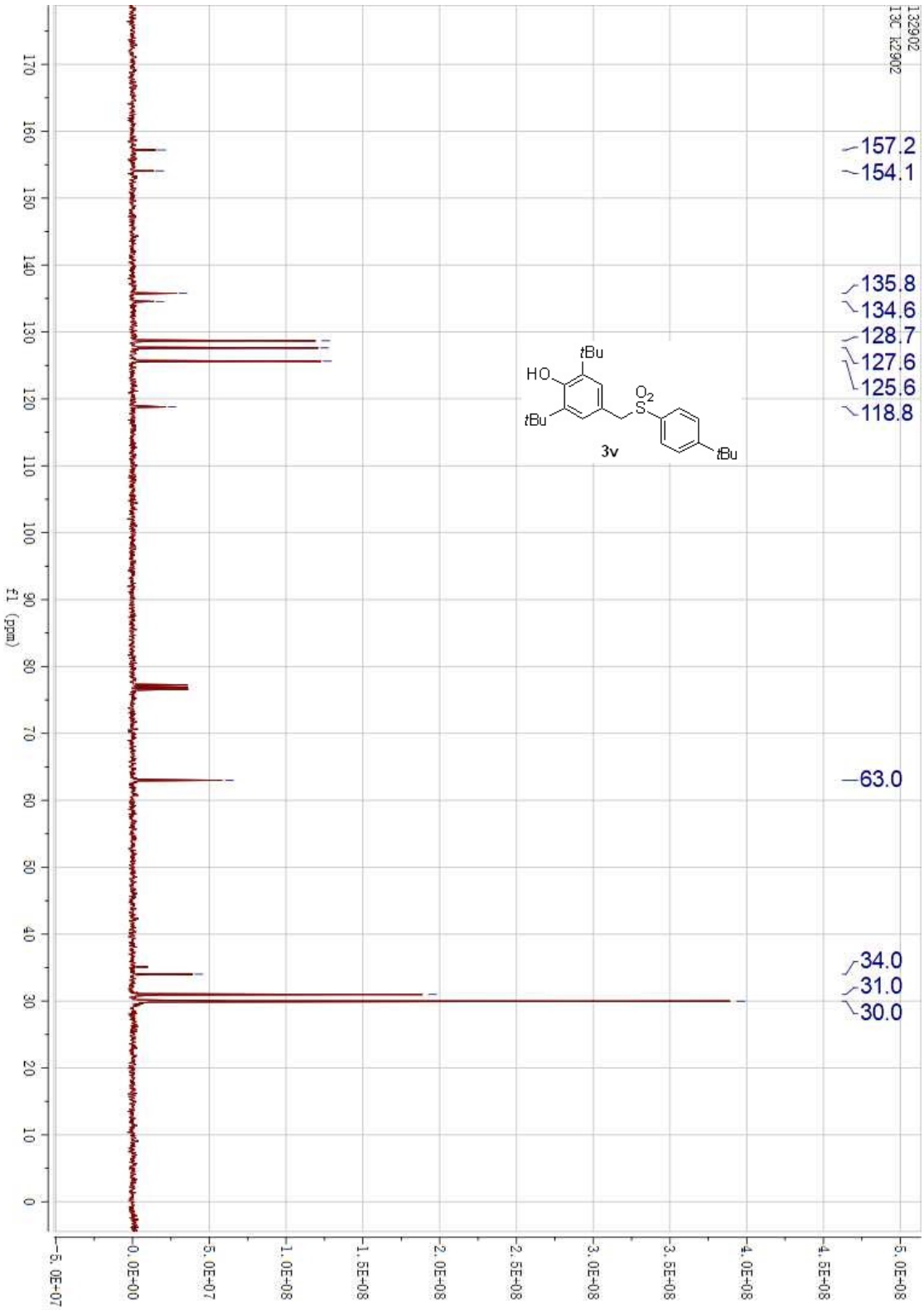
tBu
HO
tBu
O2
S
3t
f1 (ppm)

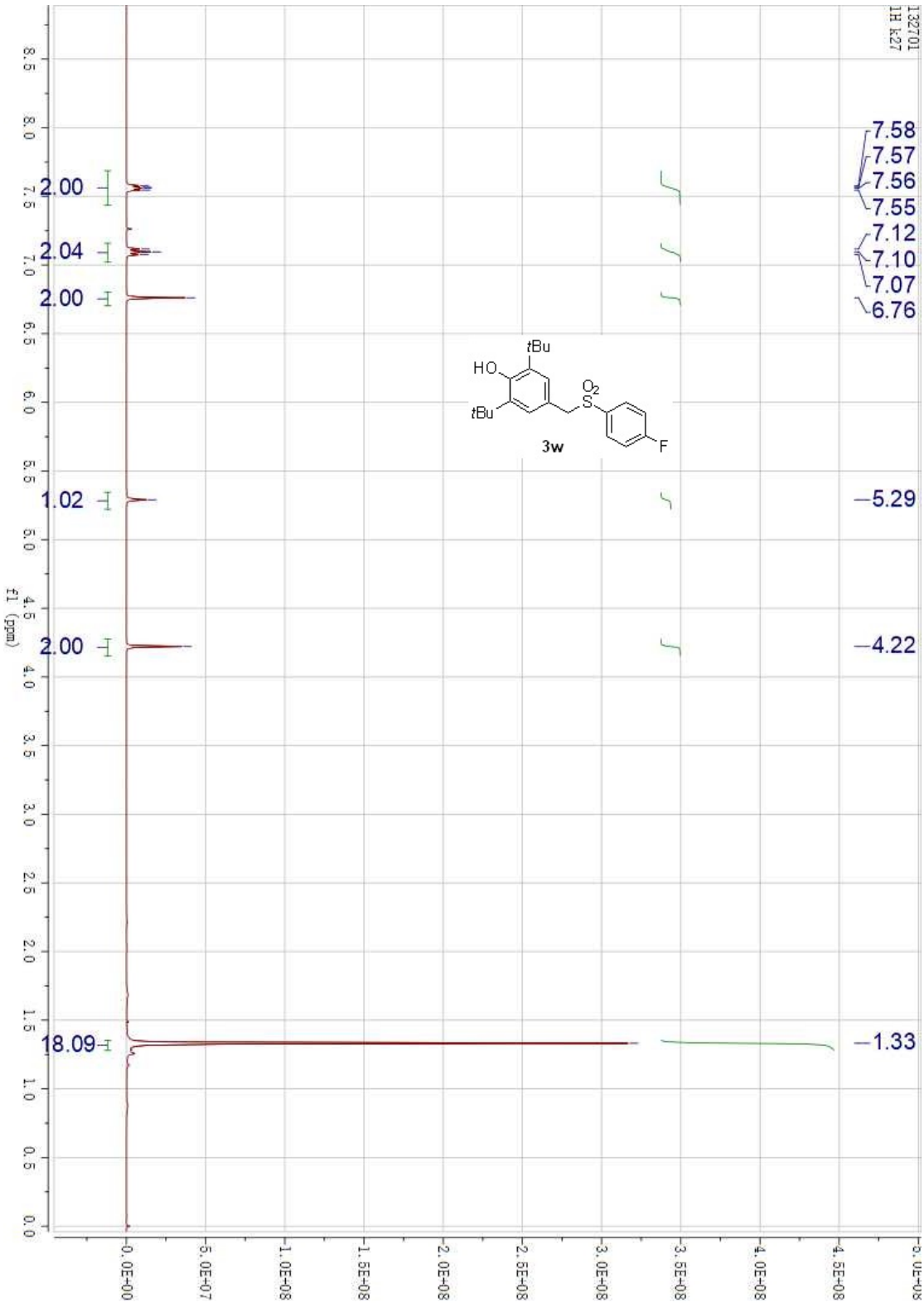

132602
13C h2602
154.1
137.7
135.9
133.3
128.8
128.6
127.6
118.6
63.0
34.0
30.0
tBu
HO
tBu
O2
S
3t
f1 (ppm)


132801
1H k28
7.5
7.5
6.9
6.9
6.7
5.3
4.2
3.8
1.3
2.00
2.00
2.00
1.02
2.00
3.06
18.07
tBu
HO
tBu
O2
S
OMe
3u
f1 (ppm)


132802
13C h2802
163.4
154.1
135.8
130.9
129.2
127.5
119.0
113.7
63.3
55.5
34.0
30.0
tBu
HO
tBu
O2
S
OMe
3u
f1 (ppm)


132901
1H k29
4.04
1.99
1.03
2.00
27.00
7.47
7.45
6.73
5.26
4.21
1.32
1.31
tBu
HO
tBu
O2
S
tBu
3v
f1 (ppm)


132902
13C h2902
157.2
154.1
135.8
134.6
128.7
127.6
125.6
118.8
63.0
34.0
31.0
30.0
tBu
HO
tBu
O2
S
tBu
3v
f1 (ppm)


132701
1H k27
7.58
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7.56
7.55
7.12
7.10
7.07
6.76
5.29
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1.33
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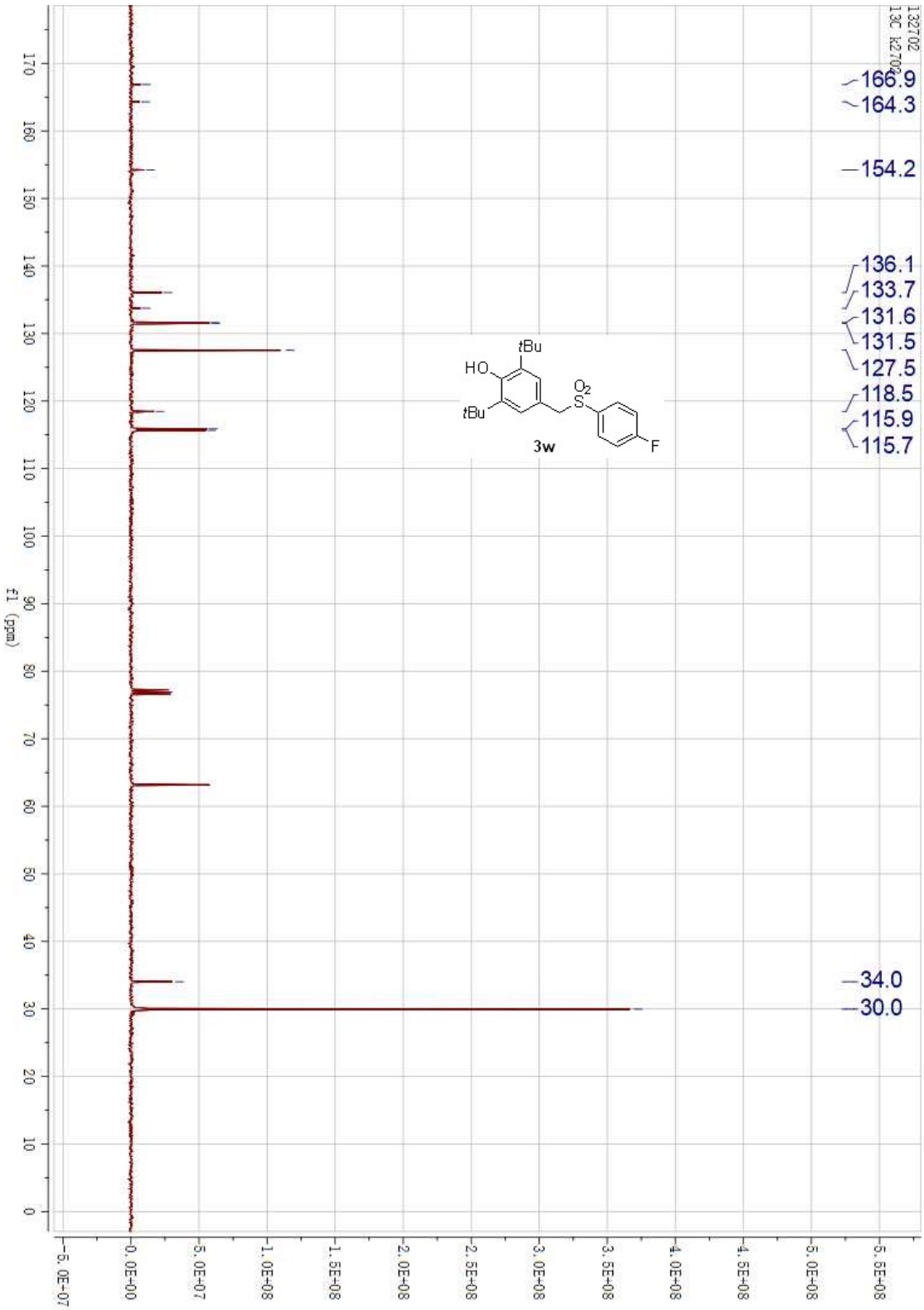
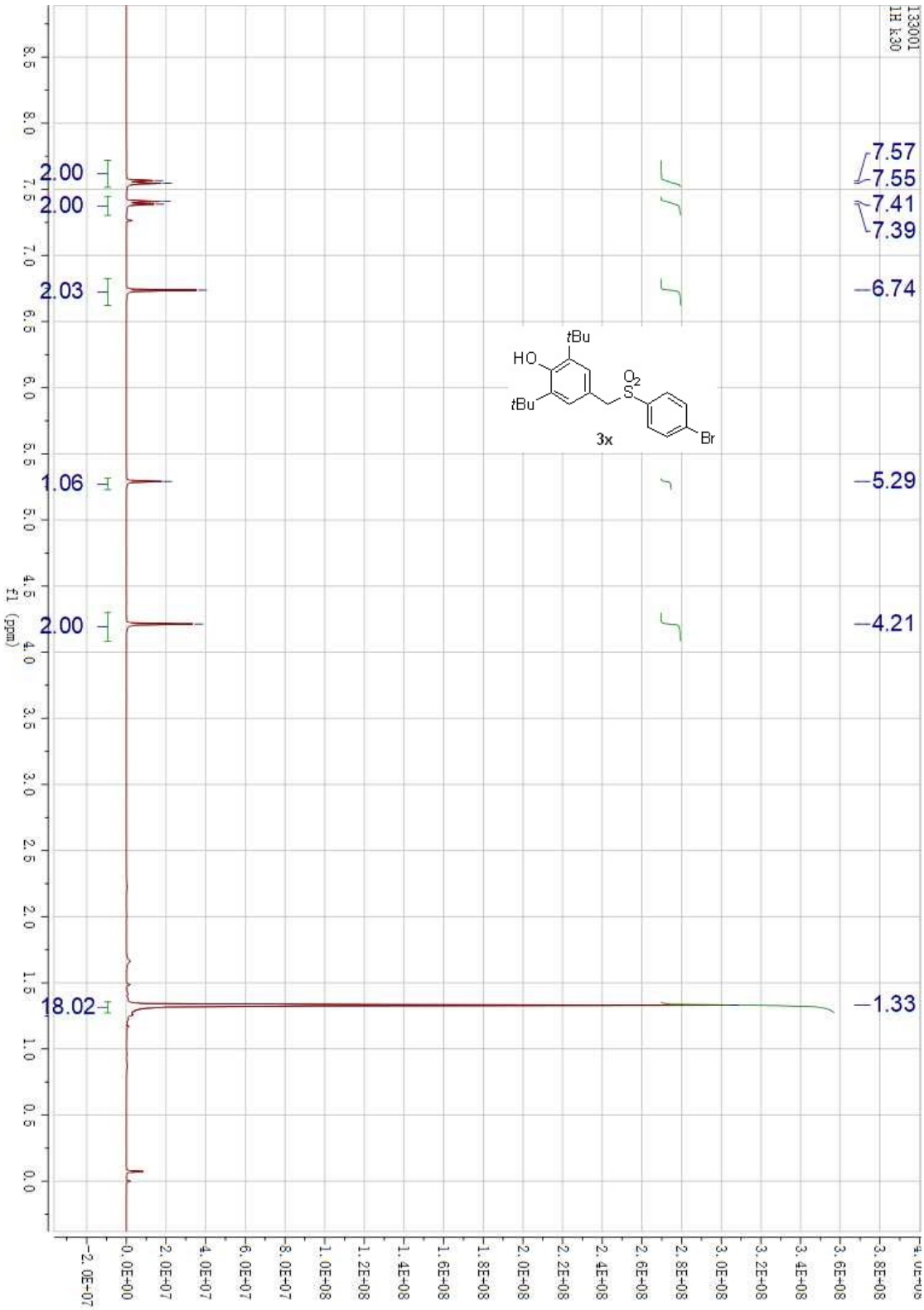
HO
tBu
O2
S
F
3w
f1 (ppm)


132702
13C h2702
166.9
164.3
154.2
136.1
133.7
131.6
131.5
127.5
118.5
115.9
115.7
34.0
30.0
tBu
HO
tBu
O2
S
F
3w
f1 (ppm)


133001
1H k30
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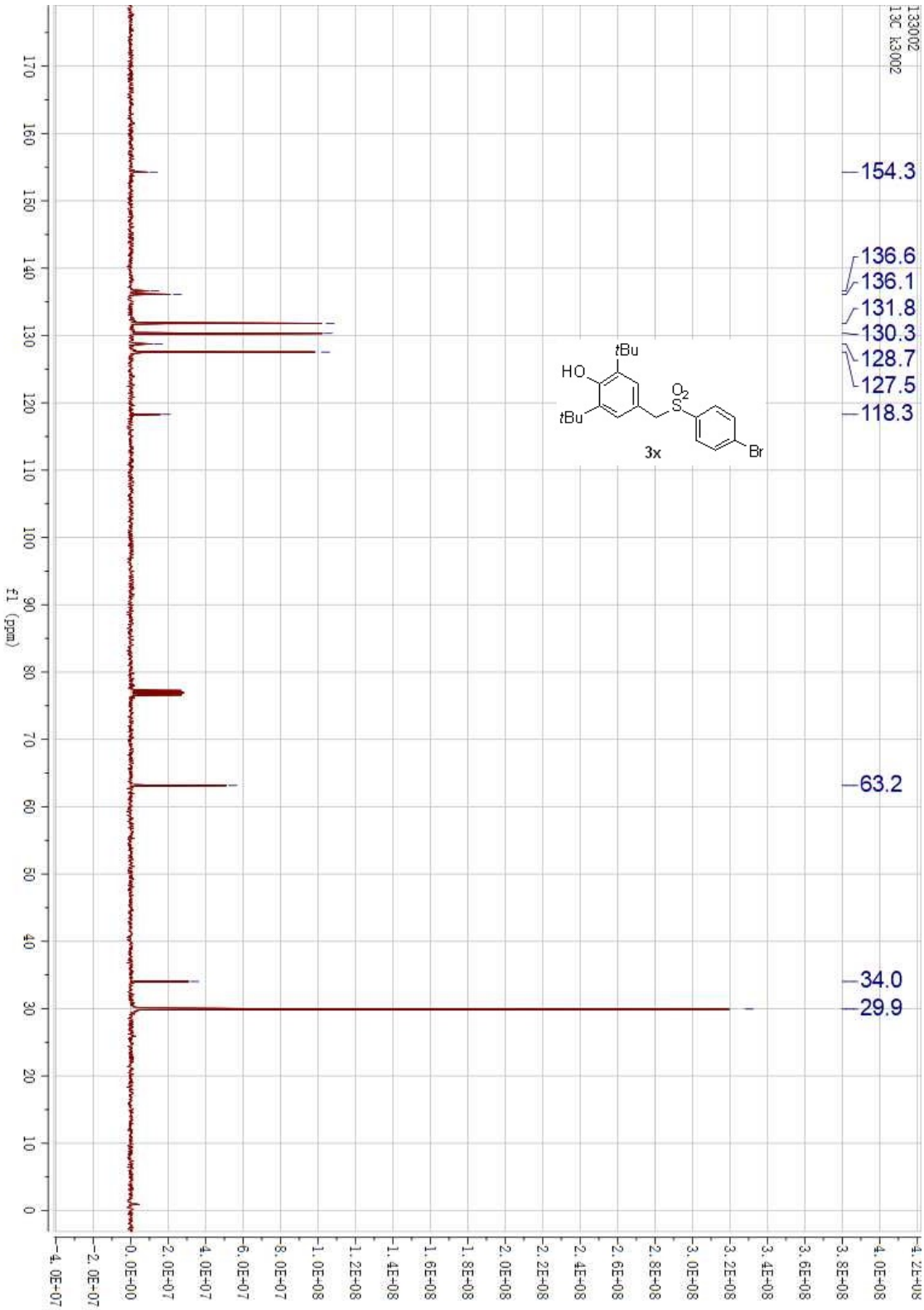
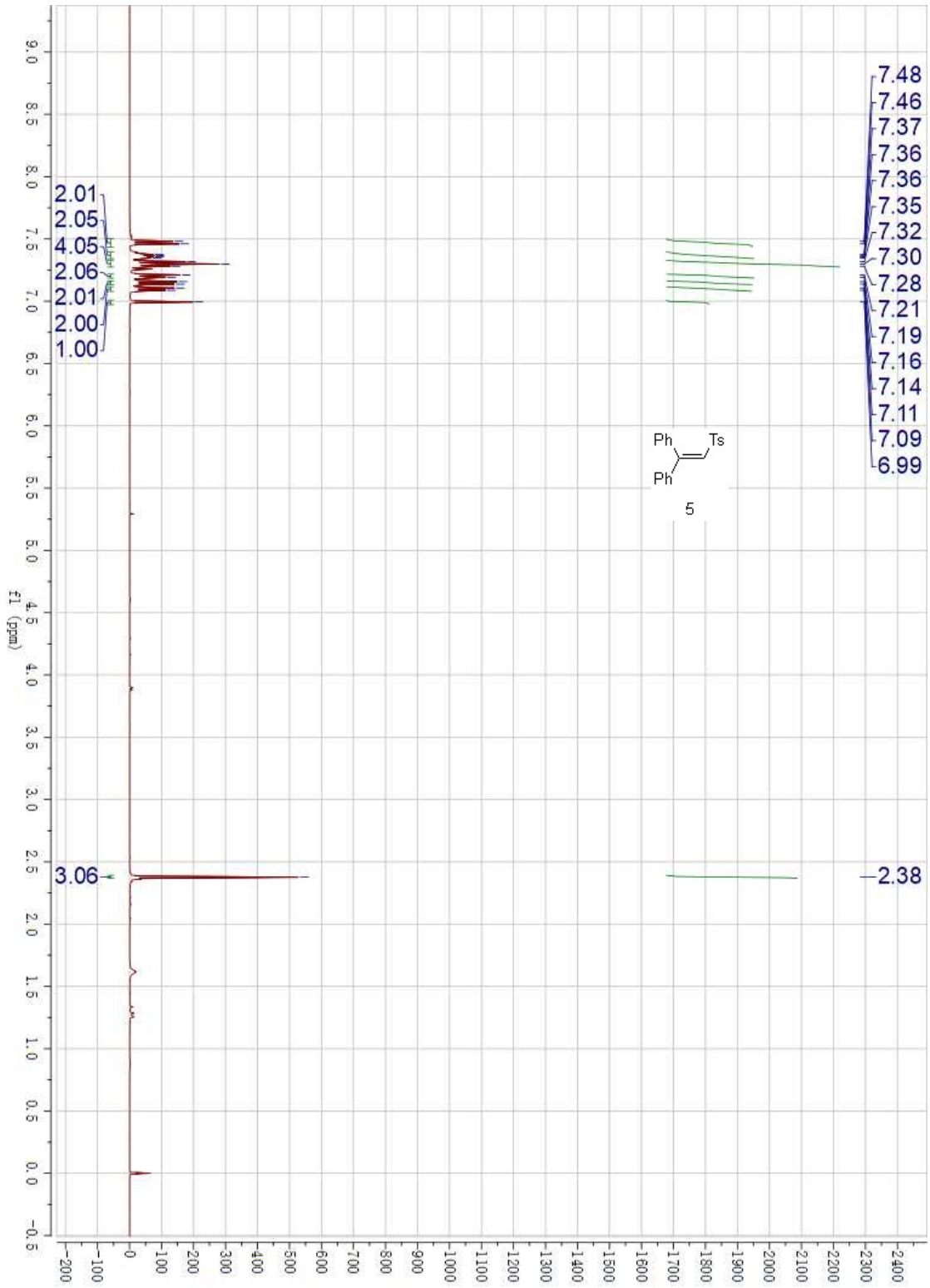
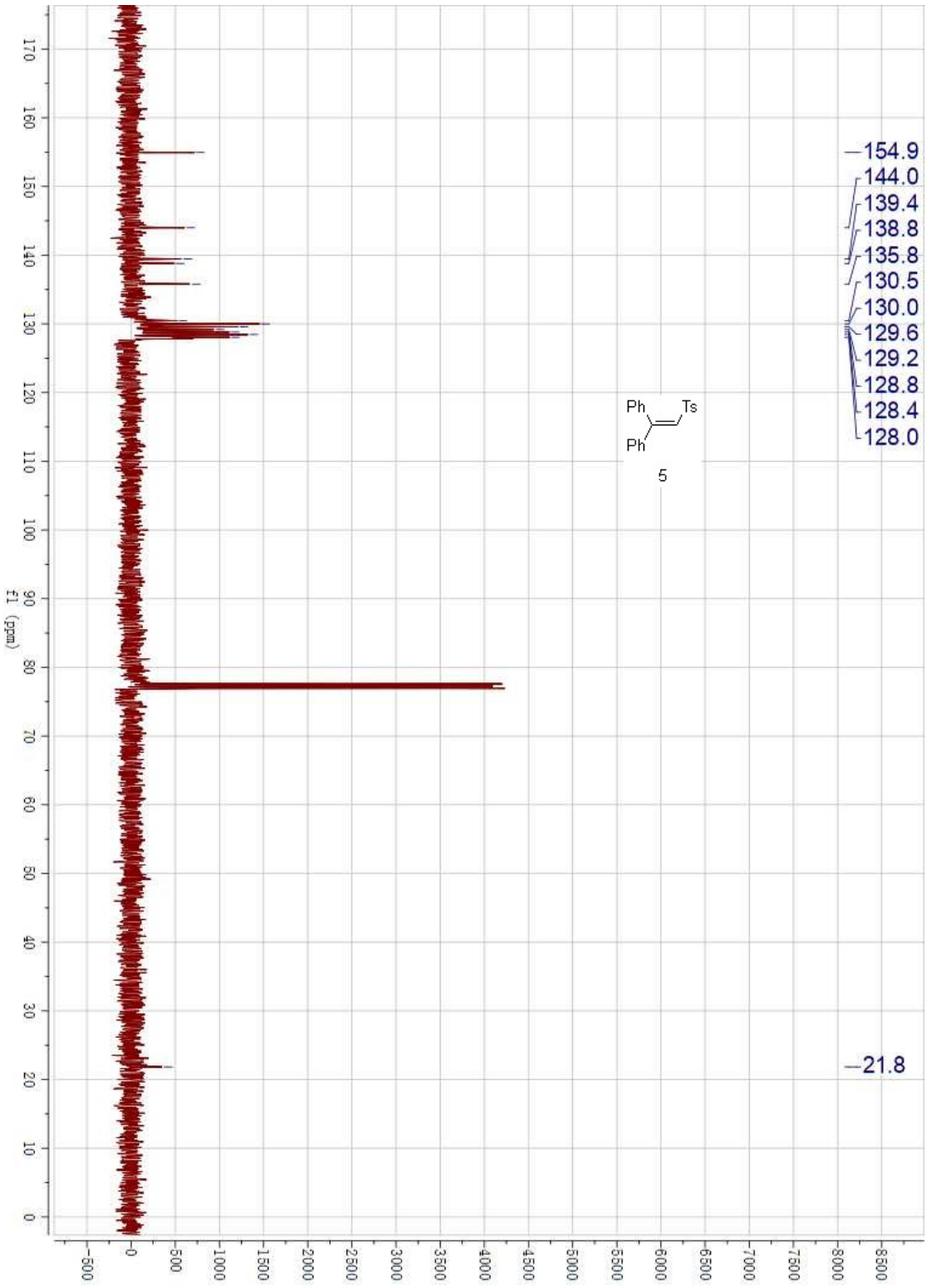
7.55
7.41
7.39
6.74
5.29
4.21
1.33
2.00
2.00
2.03
1.06
2.00
18.02
tBu
HO
tBu
O2
S
Br
3x
f1 (ppm)


133002
13C h3002
154.3
136.6
136.1
131.8
130.3
128.7
127.5
118.3
63.2
34.0
29.9
tBu
HO
tBu
O
O
S
Br
3x
f1 (ppm)


2.01
2.05
4.05
2.06
2.01
2.00
1.00
3.06
7.48
7.46
7.37
7.36
7.36
7.35
7.32
7.30
7.28
7.21
7.19
7.16
7.14
7.11
7.09
6.99
2.38
Ph
Ts
Ph
5
f1 (ppm)


154.9
144.0
139.4
138.8
135.8
130.5
130.0
129.6
129.2
128.8
128.4
128.0
21.8
Ph
Ts
Ph
5
f1 (ppm)