Supporting Information

$NbCl_5$-catalyzed sulfa-Michael addition to constructing quaternary centers on enones

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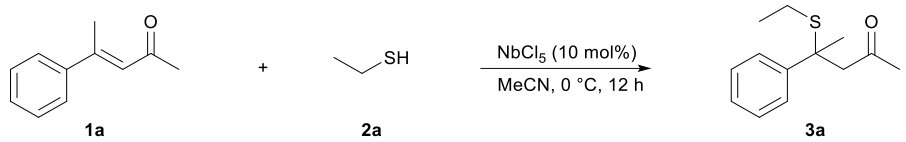
General Information

All commercially available reagents were used without further purification. Column chromatography was performed on silica gel (200-300 mesh). Thin-layer chromatography (TLC) was performed on silica gel plates.1H NMR (500 MHz), 13C NMR (126 MHz), and 19F NMR (471 MHz) spectra were recorded on a JEOL ECZ500R NMR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Micro TOF ESI mass spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (J) were given in Hertz (Hz). Data were reported as s – singlet, d – doublet, t – triplet, q – quartet, dd – doublet of doublets, m – multiplet, dm – doublet of multiplets. All of the liner tri-substituted enones were prepared according to literature procedures.[1] The 3-methylcyclohex-2-en-1-one, **1o**, and mercaptans were all commercially available reagents.

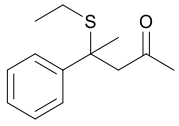
General procedure



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

Take the synthesis of **3a** as an example. To a dry and N_2-filled round-bottom flask was added (E)-4-phenylpent-3-en-2-one, **1a** (0.2 mmol, 32.0 mg), ethanethiol, **2a** (0.4 mmol, 24.9 mg), $NbCl_5$ (0.02 mmol, 5.4 mg), and 1.0 mL MeCN. The mixture was stirred at 0 °C for 12 hours. After the reaction was complete (monitored by TLC), the residual was extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4, and concentrated by rotary evaporation. The crude was further purified by silica gel column chromatography to afford 4-(ethylthio)-4-phenylpentan-2-one, **3a** as a light-yellow liquid (32.8 mg, 74%).

Characterization data



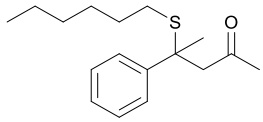
4-(ethylthio)-4-phenylpentan-2-one (3a)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and ethanethiol (24.8 mg, 0.4 mmol). The product was isolated as a light-yellow liquid (32.8 mg, 74%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.43 (m, 2H), 7.31 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.22 – 7.17 (m, 1H), 3.25 (d, *J* = 15.1 Hz, 1H), 2.92 (d, *J* = 15.1 Hz, 1H), 2.30 (dq, *J* = 11.5, 7.4 Hz, 1H), 2.12 (dq, *J* = 11.5, 7.5 Hz, 1H), 1.91 (s, 3H), 1.87 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.9, 144.2, 128.3 (2C), 126.8, 126.8 (2C), 55.4, 49.2, 31.9, 26.1, 23.0, 13.9.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{18}OS$: 245.0971; found: 245.0968.



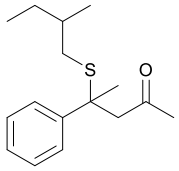
4-(hexylthio)-4-phenylpentan-2-one (3b)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and hexane-1-thiol (47.2 mg, 0.4 mmol). The product was isolated as a light-yellow liquid (35.8 mg, 64%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.22 – 7.17 (m, 1H), 3.25 (d, *J* = 15.0 Hz, 1H), 2.92 (d, *J* = 15.0 Hz, 1H), 2.28 (dt, *J* = 11.5, 7.3 Hz, 1H), 2.09 (dt, *J* = 11.5, 7.4 Hz, 1H), 1.90 (s, 3H), 1.86 (s, 3H), 1.34 (ddd, *J* = 14.6, 7.8, 4.6 Hz, 2H), 1.27 – 1.16 (m, 4H), 1.16 – 1.09 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.9, 144.2, 128.3 (2C), 126.8 (2C), 126.8, 55.5, 49.1, 31.9, 31.4, 28.93, 28.9, 28.8, 26.1, 22.6, 14.1.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{17}H_{26}OS$: 301.1597; found: 301.1597.



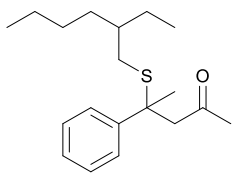
4-((2-methylbutyl)thio)-4-phenylpentan-2-one (3c)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and 2-methylbutane-1-thiol (41.6 mg, 0.4 mmol). The product was isolated as a light-yellow liquid (28.4 mg, 54%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 2H), 7.33 – 7.27 (m, 2H), 7.22 – 7.15 (m, 1H), 3.25 (dd, *J* = 15.0, 1.7 Hz, 1H), 2.92 (d, *J* = 14.9 Hz, 1H), 2.21 (dddd, *J* = 58.9, 11.7, 6.4, 1.2 Hz, 1H), 2.10 – 1.95 (m, 1H), 1.90 (d, *J* = 1.1 Hz, 3H), 1.86 (s, 3H), 1.38 – 1.26 (m, 2H), 1.13 – 1.00 (m, 1H), 0.82 (dt, *J* = 6.6, 1.8 Hz, 3H), 0.78 – 0.68 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.0, 144.2, 128.2 (2C), 126.9 (2C), 126.8, 55.6 (d, *J* = 2.7 Hz), 49.0, 35.6 (d, *J* = 9.8 Hz), 34.7 (d, *J* = 2.9 Hz), 32.0, 28.9 (d, *J* = 9.3 Hz), 26.1, 19.3 (d, *J* = 2.8 Hz), 11.3 (d, *J* = 11.9 Hz).

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{16}H_{24}OS$: 287.1440; found: 297.1429.



4-((2-ethylhexyl)thio)-4-phenylpentan-2-one (3d)

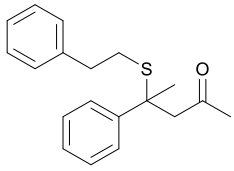
Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and 2-ethylhexane-1-thiol (58.4 mg, 0.4 mmol). The product was isolated as a light-yellow liquid (36.7 mg, 60%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.46 (m, 2H), 7.32 – 7.27 (m, 2H), 7.21 – 7.16 (m, 1H), 3.25 (d, *J* = 15.0 Hz, 1H), 2.92 (d, *J* = 14.9 Hz, 1H), 2.30 – 2.22 (m, 1H), 2.05 (ddd, *J* = 11.6, 5.7, 3.2

Hz, 1H), 1.90 (s, 3H), 1.85 (s, 3H), 1.27 – 1.21 (m, 3H), 1.17 (ddd, *J* = 9.3, 7.6, 4.8 Hz, 4H), 1.09 – 1.00 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H), 0.69 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.0, 144.2, 128.2 (2C), 127.0 (2C), 126.8, 55.5 (d, *J* = 3.5 Hz), 48.9 (d, *J* = 2.6 Hz), 39.2 (d, *J* = 2.6 Hz), 32.7 (d, *J* = 7.4 Hz), 32.6 (d, *J* = 5.1 Hz), 31.9, 28.9 (d, *J* = 17.2 Hz), 26.2 – 26.0 (m), 25.9 (d, *J* = 6.9 Hz), 23.0 (d, *J* = 4.6 Hz), 14.2, 10.9 (d, *J* = 13.6 Hz).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{30}OS$: 329.1910; found: 329.1900.



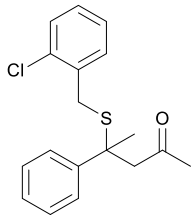
4-(phenethylthio)-4-phenylpentan-2-one (3f)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and 2-ethylhexane-1-thiol (55.2 mg, 0.4 mmol). The product was isolated as a light-yellow oil (42.4 mg, 71%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 2H), 7.36 – 7.28 (m, 2H), 7.23 (dd, *J* = 8.0, 6.4 Hz, 3H), 7.19 – 7.15 (m, 1H), 7.05 – 6.99 (m, 2H), 3.26 (d, *J* = 15.2 Hz, 1H), 2.92 (d, *J* = 15.2 Hz, 1H), 2.67 – 2.60 (m, 1H), 2.60 – 2.57 (m, 1H), 2.57 – 2.51 (m, 1H), 2.43 – 2.33 (m, 1H), 1.91 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.8, 144.0, 140.6, 128.5 (3C), 128.4 (2C), 127.0 (2C), 126.9 (2C), 126.4, 55.3, 49.5, 35.6, 31.9, 30.5, 26.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{22}OS$: 299.1464; found: 299.1464.



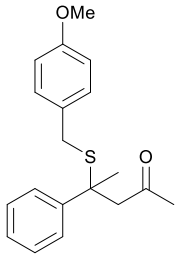
4-((2-chlorobenzyl)thio)-4-phenylpentan-2-one (3g)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and (2-chlorophenyl)methanethiol (63.2 mg, 0.4 mmol). The product was isolated as a light-yellow oil (52.1 mg, 82%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (dq, *J* = 6.9, 1.1 Hz, 2H), 7.34 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.25 – 7.21 (m, 1H), 7.10 (tt, *J* = 7.3, 5.3 Hz, 2H), 7.07 – 7.03 (m, 1H), 3.62 (d, *J* = 11.9 Hz, 1H), 3.40 (d, *J* = 11.9 Hz, 1H), 3.30 (d, *J* = 15.2 Hz, 1H), 2.96 (d, *J* = 15.2 Hz, 1H), 1.94 (s, 3H), 1.91 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.6, 143.5, 135.4, 134.1, 131.2, 129.7, 128.5, 128.4 (2C), 127.1, 127.0 (2C), 126.9, 55.0, 50.4, 31.9, 31.5, 26.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{19}ClOS$: 319.0918; found: 319.0916.



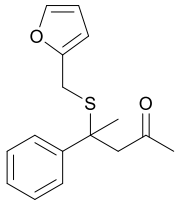
4-((4-methoxybenzyl)thio)-4-phenylpentan-2-one (3h)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and (4-methoxyphenyl)methanethiol (61.6 mg, 0.4 mmol). The product was isolated as a light-yellow oil (52.6 mg, 84%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.06 – 6.98 (m, 2H), 6.80 – 6.72 (m, 2H), 3.75 (s, 3H), 3.45 (d, *J* = 12.0 Hz, 1H), 3.30 – 3.19 (m, 2H), 2.93 (d, *J* = 15.1 Hz, 1H), 1.90 (s, 3H), 1.90 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.8, 158.6, 143.9, 130.2 (2C), 129.4, 128.4 (2C), 127.0, 127.0 (2C), 114.0 (2C), 55.4, 55.2, 50.2, 33.4, 31.9, 26.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{22}O_2S$: 315.1413; found: 315.1411.



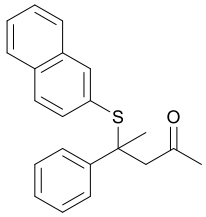
4-((furan-2-ylmethyl)thio)-4-phenylpentan-2-one (3i)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and furan-2-ylmethanethiol (45.6 mg, 0.4 mmol). The product was isolated as a light-yellow oil (14.8 mg, 27%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.48 (m, 2H), 7.33 (dd, *J* = 8.6, 7.1 Hz, 2H), 7.28 (dd, *J* = 2.0, 0.9 Hz, 1H), 7.24 – 7.20 (m, 1H), 6.22 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.95 (d, *J* = 3.2 Hz, 1H), 3.47 (d, *J* = 14.2 Hz, 1H), 3.35 (d, *J* = 14.2 Hz, 1H), 3.26 (d, *J* = 15.3 Hz, 1H), 2.93 (d, *J* = 15.3 Hz, 1H), 1.90 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.6, 151.2, 143.3, 142.0, 128.5 (2C), 127.1, 127.0(2C), 110.6, 107.5, 55.0, 50.1, 31.9, 26.4, 26.1.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{18}O_2S$: 297.0920; found: 297.0906.



4-(naphthalen-2-ylthio)-4-phenylpentan-2-one (3j)

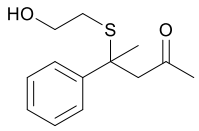
Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and naphthalene-2-thiol (64.0 mg, 0.4 mmol). The product was isolated as a light-yellow oil (52.5 mg,

82%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 – 7.76 (m, 1H), 7.70 – 7.62 (m, 3H), 7.51 – 7.43 (m, 2H), 7.38 (dq, *J* = 6.6, 1.8 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.13 (dq, *J* = 8.4, 1.8 Hz, 1H), 3.52 (d, *J* = 15.6 Hz, 1H), 3.01 – 2.93 (m, 1H), 1.92 (s, 3H), 1.87 – 1.82 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.6, 143.7, 137.1, 133.5, 133.3, 133.3, 128.9, 128.2 (2C), 128.1, 127.9, 127.7, 127.1, 127.0, 126.9 (2C), 126.4, 54.9, 52.9, 31.8, 25.7.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{20}OS$: 321.1308; found: 321.1308.



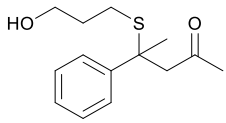
4-((2-hydroxyethyl)thio)-4-phenylpentan-2-one (3m)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and 2-mercaptoethan-1-ol (31.2 mg, 0.4 mmol). The product was isolated as a colorless oil (30.4 mg, 64%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.18 (m, 1H), 3.43 (dp, *J* = 20.2, 5.7 Hz, 2H), 3.29 (d, *J* = 15.3 Hz, 1H), 2.95 (d, *J* = 15.3 Hz, 1H), 2.49 (dt, *J* = 12.3, 6.2 Hz, 1H), 2.41 (dt, *J* = 12.4, 6.0 Hz, 1H), 1.93 (s, 3H), 1.89 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.6, 143.9, 128.5 (2C), 127.2, 126.8 (2C), 61.0, 55.3, 49.4, 32.5, 31.9, 26.3.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{18}O_2S$: 261.0920; found:261.0918.



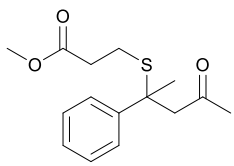
4-((3-hydroxypropyl)thio)-4-phenylpentan-2-one (3n)

Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol) and 3-mercaptopropan-1-ol (36.8 mg, 0.4 mmol). The product was isolated as a colorless oil (42.4 mg, 84%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.45 (m, 2H), 7.32 – 7.27 (m, 2H), 7.21 – 7.16 (m, 1H), 3.51 (t, *J* = 6.1 Hz, 2H), 3.26 (d, *J* = 15.2 Hz, 1H), 2.93 (d, *J* = 15.2 Hz, 1H), 2.38 (dt, *J* = 11.8, 7.1 Hz, 1H), 2.20 (dt, *J* = 11.8, 7.3 Hz, 1H), 1.90 (s, 3H), 1.86 (s, 3H), 1.75 (t, *J* = 11.9 Hz, 1H), 1.57 (dddd, *J* = 13.3, 8.4, 4.6, 1.7 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.0, 144.0, 128.4 (2C), 127.0, 126.8 (2C), 61.5, 55.2, 49.3, 31.9, 31.5, 26.1, 25.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{20}O_2S$: 253.1257; found: 253.1246.



methyl 3-((4-oxo-2-phenylpentan-2-yl)thio)propanoate (3o)

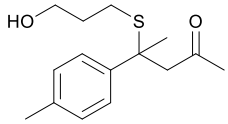
Prepared according to the general procedure from (E)-4-phenylpent-3-en-2-one **1a** (32.0 mg, 0.2 mmol)

and methyl 3-mercaptopropanoate (48.0 mg, 0.4 mmol). The product was isolated as a light-yellow oil (38.1 mg, 68%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.45 (m, 2H), 7.33 – 7.28 (m, 2H), 7.22 – 7.17 (m, 1H), 3.60 (d, *J* = 0.9 Hz, 3H), 3.26 (d, *J* = 15.3 Hz, 1H), 2.92 (d, *J* = 15.3 Hz, 1H), 2.57 – 2.49 (m, 1H), 2.44 – 2.37 (m, 1H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.90 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.6, 172.4, 143.7, 128.4 (2C), 127.1 (2C), 126.8, 55.1, 51.9, 49.5, 33.9, 31.9, 26.0, 23.9.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{20}O_3S$: 303.1025; found: 303.1017.



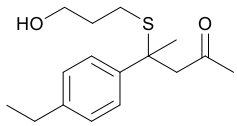
4-((3-hydroxypropyl)thio)-4-(p-tolyl)pentan-2-one (3q)

Prepared according to the general procedure from (E)-4-(p-tolyl)pent-3-en-2-one (34.8 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (38.5 mg, 72%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.34 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 3.53 (t, *J* = 6.1 Hz, 2H), 3.24 (d, *J* = 15.1 Hz, 1H), 2.91 (d, *J* = 15.0 Hz, 1H), 2.39 (dt, *J* = 11.8, 7.0 Hz, 1H), 2.29 (s, 3H), 2.21 (dt, *J* = 11.8, 7.2 Hz, 1H), 1.90 (s, 3H), 1.84 (s, 3H), 1.72 – 1.67 (m, 1H), 1.63 – 1.55 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.1, 141.0, 136.6, 129.1 (2C), 126.7 (2C), 61.6, 55.3, 49.2, 32.0, 31.5, 26.2, 25.4, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{22}O_2S$: 267.1413; found: 267.1383.



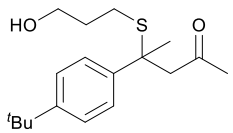
4-(4-ethylphenyl)-4-((3-hydroxypropyl)thio)pentan-2-one (3r)

Prepared according to the general procedure from (E)-4-(4-ethylphenyl)pent-3-en-2-one (37.6 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (34.3 mg, 61%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.53 (t, *J* = 6.1 Hz, 2H), 3.24 (d, *J* = 15.0 Hz, 1H), 2.92 (d, *J* = 15.0 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.39 (dt, *J* = 11.8, 7.0 Hz, 1H), 2.22 (dt, *J* = 11.8, 7.2 Hz, 1H), 1.91 (s, 3H), 1.84 (s, 3H), 1.64 (d, *J* = 6.1 Hz, 1H), 1.59 (dddd, *J* = 13.2, 7.2, 6.0, 2.5 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.2, 142.9, 141.2, 127.8 (2C), 126.7 (2C), 61.5, 55.3, 49.2, 32.0, 31.5, 28.4, 26.2, 25.4, 15.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{24}O_2S$: 303.1389; found: 303.1375.



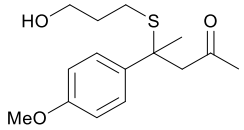
4-(4-(tert-butyl)phenyl)-4-((3-hydroxypropyl)thio)pentan-2-one (3s)

Prepared according to the general procedure from (E)-4-(4-(tert-butyl)phenyl)pent-3-en-2-one (43.2 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (18.9 mg, 31%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 8.9, 2.1 Hz, 2H), 7.35 – 7.29 (m, 2H), 3.56 (t, *J* = 6.0 Hz, 2H), 3.25 (d, *J* = 15.0 Hz, 1H), 2.94 (d, *J* = 15.1 Hz, 1H), 2.41 (dt, *J* = 11.5, 6.9 Hz, 1H), 2.25 (dt, *J* = 11.8, 7.2 Hz, 1H), 1.93 (s, 3H), 1.85 (s, 3H), 1.67 – 1.56 (m, 3H), 1.28 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.1, 149.8, 140.9, 126.4 (2C), 125.2 (2C), 61.5, 55.2, 49.1, 34.5, 32.0, 31.5, 31.4 (3C), 26.2, 25.4.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{18}H_{28}O_2S$: 331.1702; found: 331.1692.



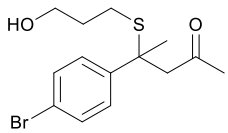
4-((3-hydroxypropyl)thio)-4-(4-methoxyphenyl)pentan-2-one (3t)

Prepared according to the general procedure from (E)-4-(4-methoxyphenyl)pent-3-en-2-one (38.0 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (34.2 mg, 61%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 6.86 – 6.79 (m, 2H), 3.76 (s, 3H), 3.54 (t, *J* = 6.1 Hz, 2H), 3.21 (d, *J* = 15.0 Hz, 1H), 2.89 (d, *J* = 15.0 Hz, 1H), 2.38 (dt, *J* = 11.8, 7.1 Hz, 1H), 2.20 (dt, *J* = 11.8, 7.2 Hz, 1H), 1.89 (s,3H), 1.83 (s, 3H), 1.75 (p, *J* = 7.3, 6.4 Hz, 1H), 1.59 (dddd, *J* = 13.3, 7.5, 6.1, 1.4 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.1, 158.3, 135.9, 128.0 (2C), 113.6 (2C), 61.7, 55.4, 55.3, 49.1, 32.0, 31.6, 26.3, 25.5.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{15}H_{22}O_3S$: 305.1182; found: 305.1174.



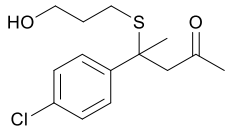
4-(4-bromophenyl)-4-((3-hydroxypropyl)thio)pentan-2-one (3u)

Prepared according to the general procedure from (E)-4-(4-bromophenyl)pent-3-en-2-one (47.6 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (46.3 mg, 70%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.39 (m, 2H), 7.36 – 7.29 (m, 2H), 3.55 (t, *J* = 6.1 Hz, 2H), 3.22 (d, *J* = 15.9 Hz, 1H), 2.93 (d, *J* = 15.9 Hz, 1H), 2.37 (dt, *J* = 11.7, 7.1 Hz, 1H), 2.18 (dt, *J* = 11.7, 7.2 Hz, 1H), 1.95 (s, 3H), 1.83 (s, 3H), 1.72 (s, 1H), 1.60 (p, *J* = 6.7 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.4, 143.4, 131.4 (2C), 128.7 (2C), 120.8, 61.6, 54.9, 48.8, 31.9, 31.5, 26.0, 25.4.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{14}H_{19}BrO_2S$: 353.0181; found: 353.0164.



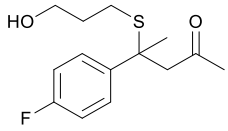
4-(4-chlorophenyl)-4-((3-hydroxypropyl)thio)pentan-2-one (3v)

Prepared according to the general procedure from (E)-4-(4-chlorophenyl)pent-3-en-2-one (38.8 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (48.0 mg, 84%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.28 – 7.21 (m, 2H), 3.57 – 3.47 (m, 2H), 3.22 (d, *J* = 15.8 Hz, 1H), 2.93 (d, *J* = 15.8 Hz, 1H), 2.36 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.18 (dt, *J* = 11.7, 7.2 Hz, 1H), 1.94 (s, 3H), 1.85 (s, 1H), 1.83 (s, 3H), 1.65 – 1.54 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.5, 142.8, 132.6, 128.4 (2C), 128.3 (2C), 61.6, 55.0, 48.8, 31.8, 31.5, 26.0, 25.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{19}ClO_2S$: 309.0686; found: 309.0672.



4-(4-fluorophenyl)-4-((3-hydroxypropyl)thio)pentan-2-one (3w)

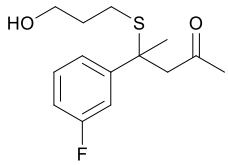
Prepared according to the general procedure from (E)-4-(4-fluorophenyl)pent-3-en-2-one (35.6 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (41.1 mg, 76%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 2H), 7.02 – 6.93 (m, 2H), 3.54 (t, *J* = 6.1 Hz, 2H), 3.22 (d, *J* = 15.6 Hz, 1H), 2.92 (d, *J* = 15.6 Hz, 1H), 2.38 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.19 (dt, *J* = 11.6, 7.2 Hz, 1H), 1.93 (s, 3H), 1.85 (s, 3H), 1.82 – 1.78 (m, 1H), 1.64 – 1.54 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.7, 161.5 (d, *J* = 246.4 Hz), 139.9 (d, *J* = 4.0 Hz), 128.6 (d, *J* = 8.5 Hz) (2C), 115.1 (d, *J* = 21.4 Hz) (2C), 61.6, 55.2, 48.8, 31.9, 31.5, 26.2, 25.4.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -115.7 (t, *J* = 6.8 Hz).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{19}FO_2S$: 293.0982; found: 293.0972.



4-(3-fluorophenyl)-4-((3-hydroxypropyl)thio)pentan-2-one (3x)

Prepared according to the general procedure from (E)-4-(3-fluorophenyl)pent-3-en-2-one (35.6 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (48.1 mg, 89%).

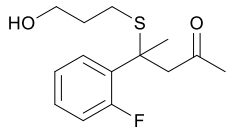
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 – 7.20 (m, 2H), 7.17 (dt, *J* = 10.7, 2.0 Hz, 1H), 6.91 – 6.84 (m, 1H), 3.56 – 3.45 (m, 2H), 3.22 (d, *J* = 15.8 Hz, 1H), 2.93 (d, *J* = 15.7 Hz, 1H), 2.38 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.20 (dt, *J* = 11.7, 7.3 Hz, 1H), 1.95 (s, 3H), 1.89 – 1.85 (m, 1H), 1.83 (s, 3H), 1.65 – 1.53 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.5, 162.8 (d, *J* = 245.2 Hz), 147.1 (d, *J* = 6.6 Hz), 129.7 (d, *J*

= 8.3 Hz), 122.5 (d, *J* = 2.8 Hz), 113.9 (dd, *J* = 31.8, 21.9 Hz) (2C), 61.5, 54.9, 48.9, 31.8, 31.5, 26.0, 25.4.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.6 (d, *J* = 8.8 Hz).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{19}FO_2S$: 293.0982; found: 293.0965.



4-(2-fluorophenyl)-4-((3-hydroxypropyl)thio)pentan-2-one (3y)

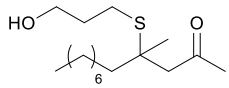
Prepared according to the general procedure from (E)-4-(2-fluorophenyl)pent-3-en-2-one (35.6 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (38.4 mg, 71%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (td, *J* = 8.2, 1.7 Hz, 1H), 7.20 (tdd, *J* = 7.7, 4.8, 1.7 Hz, 1H), 7.08 (td, *J* = 7.6, 1.4 Hz, 1H), 6.96 (ddd, *J* = 13.1, 8.1, 1.4 Hz, 1H), 3.70 (d, *J* = 17.0 Hz, 1H), 3.52 (t, *J* = 6.0 Hz, 2H), 2.93 (dd, *J* = 17.0, 2.5 Hz, 1H), 2.46 (dt, *J* = 11.7, 7.1 Hz, 1H), 2.28 (dt, *J* = 11.8, 7.1 Hz, 1H), 2.01 (s, 3H), 1.88 (s, 3H), 1.78 (s, 1H), 1.57 (p, *J* = 6.6 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.6, 160.8 (d, *J* = 248.4 Hz), 130.7 (d, *J* = 9.4 Hz), 129.0, 129.0 (d, *J* = 4.8 Hz), 124.0 (d, *J* = 3.2 Hz), 116.6 (d, *J* = 24.2 Hz), 61.6, 53.7 (d, *J* = 6.9 Hz), 47.1 (d, *J* = 2.9 Hz), 31.6, 31.1, 27.5, 25.5.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -108.3 (t, *J* = 10.3 Hz).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{19}FO_2S$: 293.0982; found: 293.0969.



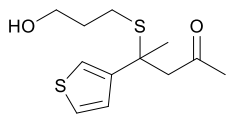
4-((3-hydroxypropyl)thio)-4-methylheptan-2-one (3z)

Prepared according to the general procedure from (E)-4-methyldodec-3-en-2-one (39.2 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (35.1 mg, 61%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.70 (t, *J* = 6.0 Hz, 2H), 2.65 (s, 2H), 2.61 – 2.50 (m, 2H), 2.16 (s, 3H), 1.77 (p, *J* = 6.7 Hz, 2H), 1.60 (dt, *J* = 9.5, 5.5 Hz, 2H), 1.35 (s, 5H), 1.24 (q, *J* = 6.7, 5.4 Hz, 11H), 0.84 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.4, 61.7, 52.7, 47.3, 40.0, 32.5, 31.9, 31.9, 30.0, 29.6, 29.4, 26.3, 24.5, 24.3, 22.8, 14.2.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{32}O_2S$: 311.2015; found: 311.2006.



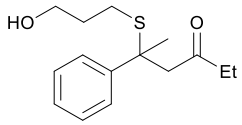
4-((3-hydroxypropyl)thio)-4-(thiophen-3-yl)pentan-2-one (3za)

Prepared according to the general procedure from (E)-4-(thiophen-2-yl)pent-3-en-2-one (33.2 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a yellow liquid (15.9 mg, 31%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.20 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.06 (dd, *J* = 3.0, 1.4 Hz, 1H), 3.58 (t, *J* = 6.1 Hz, 2H), 3.14 (d, *J* = 14.6 Hz, 1H), 2.90 (d, *J* = 14.5 Hz, 1H), 2.42 (dt, *J* = 11.9, 7.0 Hz, 1H), 2.26 (dt, *J* = 11.9, 7.2 Hz, 1H), 1.95 (s, 3H), 1.82 (s, 3H), 1.68 (dd, *J* = 7.5, 3.4 Hz, 1H), 1.62 (dddd, *J* = 13.3, 7.3, 6.1, 2.4 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.0, 146.2, 127.0, 126.3, 121.3, 61.7, 54.9, 47.2, 32.0, 31.6, 26.6, 25.5.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{12}H_{18}O_2S_2$: 281.0640; found: 281.0628.



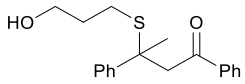
5-((3-hydroxypropyl)thio)-5-phenylhexan-3-one (3zb)

Prepared according to the general procedure from (E)-5-phenylhex-4-en-3-one (34.8 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (42.5 mg, 80%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 3.52 (t, *J* = 6.1 Hz, 2H), 3.22 (d, *J* = 15.2 Hz, 1H), 2.91 (d, *J* = 15.2 Hz, 1H), 2.39 (dt, *J* = 11.8, 7.0 Hz, 1H), 2.27 (dq, *J* = 18.1, 7.3 Hz, 1H), 2.19 (dt, *J* = 11.8, 7.2 Hz, 1H), 2.09 (dq, *J* = 18.0, 7.2 Hz, 1H), 1.87 (s, 3H), 1.70 (s, 1H), 1.62 – 1.52 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.4, 144.2, 128.3 (2C), 126.9, 126.8 (2C), 61.6, 54.1, 49.5, 37.8, 31.6, 26.2, 25.41, 7.6.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{22}O_2S$: 289.1233; found: 289.1223.



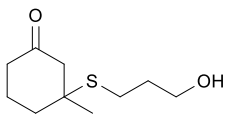
3-((3-hydroxypropyl)thio)-1,3-diphenylbutan-1-one (3zc)

Prepared according to the general procedure from (E)-1,3-diphenylbut-2-en-1-one (44.4 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a light-yellow oil (28.9 mg, 46%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (dt, *J* = 8.3, 1.1 Hz, 2H), 7.55 – 7.46 (m, 3H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.14 (m, 1H), 3.90 (d, *J* = 16.6 Hz, 1H), 3.61 – 3.43 (m, 3H), 2.43 (dt, *J* = 12.0, 7.0 Hz, 1H), 2.26 (dt, *J* = 12.1, 7.2 Hz, 1H), 1.98 (s, 3H), 1.68 – 1.52 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.8, 144.3, 137.6, 133.2, 128.6 (2C), 128.2 (2C), 128.1 (2C), 126.7 (d, *J* = 3.8 Hz) (3C), 61.6, 49.8, 49.7, 31.6, 26.4, 25.5.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{22}O_2S$: 337.1233; found: 337.1220.



3-((3-hydroxypropyl)thio)-3-methylcyclohexan-1-one (3zd)

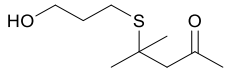
Prepared according to the general procedure from 3-methylcyclohex-2-en-1-one (22.0 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol). The product was isolated as a yellow liquid (11.3

mg, 28%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.70 (ddq, *J* = 16.5, 11.0, 5.8 Hz, 2H), 2.69 – 2.51 (m, 3H), 2.44 – 2.29 (m, 2H), 2.22 (dtd, *J* = 14.6, 6.3, 3.0 Hz, 1H), 2.17 – 2.05 (m, 1H), 2.00 – 1.85 (m, 3H), 1.85 – 1.76 (m, 2H), 1.76 – 1.69 (m, 1H), 1.38 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.7, 61.2, 53.1, 48.9, 40.4, 37.0, 31.7, 29.3, 23.8, 22.3.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{10}H_{18}O_2S$: 225.0920; found: 225.0905.



4-((3-hydroxypropyl)thio)-4-methylpentan-2-one (3ze)

Prepared according to the general procedure from 4-methylpent-3-en-2-one (19.6 mg, 0.2 mmol) and 3-mercaptopropan-1-ol **2l** (36.8 mg, 0.4 mmol) . The product was isolated as a light yellow liquid (33.7 mg, 89%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.69 (t, *J* = 6.0 Hz, 2H), 2.66 (s, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.15 (s, 4H), 1.83 – 1.73 (m, 2H), 1.38 (s, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.4, 61.6, 54.6, 43.6, 32.4, 32.0, 28.7 (2C), 24.8.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_9H_{18}O_2S$: 191.1100; found: 191.1079.

Theoretical Calculations

Computational Methods

All the calculations are performed in Gaussian 16 package.[2] The geometrical configurations are obtained by density functional theory (DFT) calculations, in which the PBE0 functional is used with Grimme's D3BJ dispersion[3, 4] at the def2-SV(P) basis set.[5] The effect of solvation was taken into account by using the IEFPCM model[6]. Vibrational frequencies were calculated at the same level of theory to obtain the thermal correction and confirm the optimized geometries as minima (no imaginary frequencies). Transition structures have also been verified by intrinsic reaction coordinate. More accurate electronic energies were obtained by single-point energy calculations at the PBE0-D3/def2-TZVP-SMD level of theory.[5, 7, 8] Molecular structure figures were prepared using CYLview.[9]

Table S1 DFT calculated free energy for $[NbCl_5(EtSH)]$ (**4a**) + solvent → $[NbCl_5(solvent)]$ + EtSH.

Entry	solvent	ΔG (kcal/mol)
1	THF	-8.4
2	DMF	-13.0

Cartesian coordinates of the species

In MeCN:

$NbCl_5$ dimer

Nb	2.00735700	-0.00000200	0.00033200
Nb	-2.00726800	-0.00000400	-0.00037700
Cl	0.00165600	0.00003100	1.62459600
Cl	-3.41126400	-0.00006400	-1.76598200
Cl	-1.72012800	2.28642400	-0.00162000
Cl	-3.39904800	0.00006800	1.77512600
Cl	-1.72011600	-2.28642800	-0.00151100
Cl	-0.00171900	-0.00002400	-1.62468500
Cl	3.41049900	0.00002700	1.76654600
Cl	3.40005200	-0.00001900	-1.77443500
Cl	1.71992400	2.28636700	0.00100400
Cl	1.71992700	-2.28636700	0.00107100

EtSH

C	-1.63116300	-0.33047000	0.00004800
H	-1.59959400	-0.97638200	-0.89092100
H	-1.59954400	-0.97637000	0.89102400
H	-2.59519400	0.19999500	0.00007200
C	-0.48789600	0.66567000	0.00000900
H	-0.53343200	1.31031600	-0.89011500
H	-0.53338300	1.31032900	0.89012500
S	1.10389100	-0.23290900	-0.00002900
H	1.91324400	0.84746400	-0.00006000

4a

Nb	0.64724700	-0.04493100	0.00100600
S	-1.89207000	0.94106500	-0.06698500
C	-3.08197700	-0.43972600	-0.15702700
H	-2.93717300	-0.84278100	-1.16915600
H	-2.76016600	-1.20359100	0.56435800
C	-4.50390400	0.02206700	0.07382700
H	-5.18038000	-0.83822400	-0.04175300
H	-4.64097300	0.42318700	1.08887800
H	-4.80336400	0.79289700	-0.65065200
Cl	0.80226100	1.45933800	1.77341500
Cl	-0.23904100	-1.63024800	1.46887300
Cl	-0.18879000	-1.26898300	-1.79629200
Cl	2.76669500	-0.88356800	0.04344400
Cl	1.07214100	1.71787300	-1.46006300
H	-2.05220800	1.25457100	1.23863300

$TS_{4a\text{-}5a}$

Nb	-0.60545100	0.18959300	-0.01025600
S	1.73672300	0.05820200	-0.89286100
C	2.99145200	0.49155500	0.36829300
H	2.82016800	1.53856900	0.65372800
H	2.81563900	-0.13771700	1.25189700
C	4.37908900	0.27793100	-0.20095300
H	5.12718100	0.55536900	0.55751600
H	4.54431200	-0.77505300	-0.47302800
H	4.55285700	0.89829800	-1.09243900
Cl	0.38634600	-2.37691500	0.46167200
Cl	0.33383300	0.72624300	2.02287600
Cl	-1.31902800	2.28331100	-0.46331700
Cl	-2.46032100	-0.81138500	0.89681700
Cl	-0.96210900	-0.63562300	-2.14732400
H	1.31426300	-1.55666800	-0.29776700

5a

Nb	0.56949300	0.05298100	0.07209900
S	-1.50234500	-0.84282700	-0.55413100
C	-2.90069600	0.31041800	-0.27093900
H	-2.78295400	0.74422200	0.73078400
H	-2.81067100	1.11868800	-1.01072700
C	-4.20584700	-0.44620200	-0.40292700
H	-5.04181700	0.25032000	-0.23530500
H	-4.32411400	-0.88576100	-1.40414500
H	-4.28108900	-1.25142300	0.34271000
Cl	1.25732900	-2.13099600	-0.39536400
Cl	-0.41124300	2.15222300	0.11732500
Cl	2.20849900	0.86052600	-1.38969700
Cl	0.62589800	-0.16694900	2.34596700

(E)-4-phenylpent-3-en-2-one

C	-0.46591000	0.52356700	-0.00002600
C	-1.42585900	-0.44135400	-0.00026400
H	-1.12962800	-1.49079300	-0.00046300
C	-2.88083700	-0.22565100	-0.00033800
O	-3.41151400	0.87547000	0.00024800
C	0.97509400	0.15038600	0.00001700
C	1.38968600	-1.19789700	0.00039000
C	1.98888400	1.12537700	-0.00032200
C	2.73370800	-1.54757300	0.00041000
H	0.65400200	-2.00214300	0.00071500

C	3.33880600	0.77783000	-0.00031100
H	1.73796800	2.18507300	-0.00063800
C	3.72114200	-0.56031100	0.00005300
H	3.01363500	-2.60360000	0.00071800
H	4.09495500	1.56626400	-0.00059500
H	4.77837800	-0.83541200	0.00007000
C	-3.71277700	-1.48525500	-0.00015500
H	-3.47723500	-2.09905500	-0.88410100
H	-3.47708300	-2.09886500	0.88388700
H	-4.77950200	-1.23044100	-0.00006900
C	-0.85435300	1.97314100	0.00017700
H	-1.48385500	2.19823200	-0.87199500
H	-1.48404200	2.19791900	0.87229800
H	-0.00098500	2.65550200	0.00040800

HCl

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Cl	0.00000000	0.00000000	0.07156800
H	0.00000000	0.00000000	-1.21665500

INTA1

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C	-2.94668800	-0.03745300	-0.09223200
C	-2.39314900	-1.00432800	0.72834600
H	-3.06319300	-1.62499900	1.32246100
C	-1.02143600	-1.32448500	0.86018000
O	-0.11272000	-0.67106800	0.24895100
C	-4.39690100	0.16901600	-0.04131500
C	-5.10370000	0.59191000	-1.18398800
C	-5.11850800	-0.05821400	1.14858300
C	-6.48334800	0.75612600	-1.14391600
H	-4.57614400	0.75801300	-2.12428000
C	-6.49286600	0.13439400	1.19182900
H	-4.59003500	-0.34778300	2.05852300
C	-7.18068800	0.53448300	0.04406200
H	-7.01793100	1.06198200	-2.04553100
H	-7.03250300	-0.02352600	2.12786500
H	-8.26302000	0.67837900	0.07783500
C	-0.58824900	-2.45153100	1.72015600
H	0.11939100	-2.07174400	2.47488300
H	-1.42972700	-2.95999700	2.20132000
H	-0.01273800	-3.15796900	1.09928100
Nb	1.79031600	-0.25904900	-0.24887600
S	1.10103900	1.95160100	0.30182900
C	2.50497000	3.11362500	0.47655300

H	3.17328700	2.95343400	-0.38130200
H	2.04870200	4.10969400	0.37939000
C	3.23558700	2.96794100	1.79420500
H	4.03110200	3.72732300	1.85470300
H	2.55758300	3.11499400	2.64791900
H	3.69799100	1.97526100	1.88688500
Cl	1.12925700	-0.11682300	-2.52514100
Cl	3.94595900	0.42288300	-0.76262900
Cl	2.46761500	-0.73359400	1.98981500
Cl	2.14159900	-2.60785200	-0.66571300
C	-2.13379100	0.79369800	-1.01832800
H	-1.45783300	1.43371500	-0.42621400
H	-1.47616600	0.17975300	-1.65002300
H	-2.74932700	1.44788600	-1.64312800

TS_{A1-B1}

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C	1.99101700	-1.23932600	0.40980600
C	1.41134000	-1.90777600	-0.70933700
H	2.06529400	-2.18494200	-1.53808500
C	0.07386900	-2.18300700	-0.87914300
O	-0.82738400	-1.62961200	-0.10143600
C	3.30230600	-0.59778800	0.23203900
C	4.18371500	-0.42865800	1.31379600
C	3.68763100	-0.11552700	-1.03346300
C	5.41606100	0.19074200	1.13121600
H	3.91595600	-0.79569400	2.30493200
C	4.91346900	0.51093300	-1.21117700
H	3.00431700	-0.21078100	-1.87982300
C	5.78309200	0.66392300	-0.12832200
H	6.09406500	0.30566700	1.97939500
H	5.19210600	0.88874300	-2.19704900
H	6.74787600	1.15696600	-0.26759800
C	-0.46212300	-2.99848500	-1.99873700
H	-1.09273300	-2.36531000	-2.64251800
H	0.34207400	-3.44871000	-2.59169500
H	-1.10636700	-3.79085700	-1.58741300
Nb	-1.76112700	0.06486200	0.14901900
S	0.51794000	0.80024400	0.61750800
C	1.05499100	2.44978200	0.07753200
H	0.37922700	3.15040400	0.59353900
H	2.05789600	2.56459600	0.51596800
C	1.06365900	2.67594200	-1.41714200
H	1.44847500	3.68689000	-1.62357200

H	1.71296700	1.95395800	-1.93197300
H	0.05414200	2.59625100	-1.84110400
Cl	-2.11070900	-0.53679400	2.40005700
Cl	-2.30279400	2.33074300	0.43460200
Cl	-1.49621400	0.36075300	-2.19998000
Cl	-4.01205200	-0.54604000	-0.29859600
C	1.57175100	-1.66446200	1.78362700
H	1.77452900	-0.90555700	2.54733600
H	0.51350700	-1.94490400	1.82090300
H	2.16029300	-2.56808900	2.02278700

INTB1

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C	1.73065100	0.24893500	-0.83498000
C	1.29994000	1.68462000	-0.74843900
H	2.06712900	2.45547300	-0.69443800
C	0.03445000	2.12906700	-0.82710800
O	-0.99741000	1.25506600	-0.88835200
C	3.18114900	-0.01801100	-0.43262600
C	3.63612000	-1.34577800	-0.39919800
C	4.09511100	0.99751200	-0.13391800
C	4.95396400	-1.64777000	-0.07209400
H	2.94295200	-2.16111300	-0.61999800
C	5.41920000	0.69649800	0.19032500
H	3.79812100	2.04588300	-0.14630500
C	5.85491000	-0.62468900	0.22515600
H	5.27769700	-2.69080300	-0.04874500
H	6.11109200	1.51012400	0.41948100
H	6.89022900	-0.85822300	0.48351700
C	-0.40231600	3.55219000	-0.81667100
H	-1.04787400	3.73743700	0.05592400
H	0.46191200	4.22610800	-0.77554600
H	-0.99099800	3.77515000	-1.71972200
Nb	-1.89210400	-0.14998000	-0.06297200
S	0.67156700	-0.84908800	0.26489700
C	1.25280400	-0.55543700	1.96819300
H	0.45844700	-1.03224000	2.56386100
H	2.15490800	-1.17706500	2.06435600
C	1.51417600	0.86853900	2.40279900
H	1.76703800	0.85802900	3.47423300
H	2.36486800	1.30557500	1.86504600
H	0.63751100	1.51190700	2.26409000
Cl	-1.70927500	-1.59911100	-1.90373500
Cl	-2.09755700	-2.02137800	1.36282800

Cl	-1.88930500	1.15399800	1.90733100
Cl	-4.11943900	0.28849800	-0.50600200
C	1.49969600	-0.26205000	-2.26762100
H	1.73859400	-1.33051600	-2.36020900
H	0.46234500	-0.10110700	-2.58634900
H	2.16214700	0.30354700	-2.93896800

$TS_{B1\text{-}3a}$

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C	1.95033400	0.63884300	-0.65910000
C	1.49183900	1.85427500	0.08698200
H	2.22861300	2.53116000	0.51580900
C	0.20789200	2.21238600	0.20607500
O	-0.77300800	1.42324900	-0.33599900
C	3.41324800	0.25715300	-0.45321000
C	3.90779400	-0.88651900	-1.10141500
C	4.29344700	0.99439900	0.34493100
C	5.23379900	-1.27937600	-0.95464500
H	3.24083700	-1.49180000	-1.71950200
C	5.62628300	0.60467300	0.48823200
H	3.96232700	1.88947100	0.87087300
C	6.10234600	-0.53236900	-0.15764900
H	5.59004200	-2.17621000	-1.46645900
H	6.29287600	1.20071300	1.11554300
H	7.14448000	-0.83802600	-0.04065300
C	-0.30233800	3.43987600	0.87633600
H	-0.97408800	3.17235800	1.70629700
H	0.52917600	4.03766300	1.26868200
H	-0.87711000	4.05843800	0.16878900
Nb	-1.68115400	-0.38381500	-0.01129500
S	0.96258700	-0.86181300	-0.10152600
C	1.65208300	-1.27313900	1.53637200
H	1.01607900	-2.11222500	1.85345800
H	2.64500700	-1.68668600	1.30616600
C	1.72588700	-0.18748800	2.58360500
H	2.08630700	-0.64263600	3.51891500
H	2.43141300	0.60521300	2.30586700
H	0.74711600	0.26705200	2.77979200
Cl	-1.53376300	-0.78926100	-2.29770000
Cl	-1.29116000	-2.60031900	0.65395500
Cl	-1.77935600	0.36337300	2.19910100
Cl	-3.91405900	-1.05600400	0.05192000
C	1.65113200	0.79843300	-2.15788800
H	1.89168600	-0.11152200	-2.72388300

H	0.59737900	1.05130300	-2.32618300
H	2.27345700	1.62055200	-2.54019100
Cl	-3.30404700	2.01876500	-0.90035100
H	-1.85755700	1.99629400	-0.66730300

3a

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C	-0.22749700	-0.57797300	0.48461100
C	-1.07283800	-1.19701600	-0.64081800
H	-0.78211100	-2.25348300	-0.76627400
C	-2.56989600	-1.18155800	-0.37505800
O	-3.06180900	-1.86654900	0.49663700
C	1.24510300	-0.46715200	0.10021300
C	2.12183200	0.25796900	0.92212600
C	1.77614000	-1.10277000	-1.02703900
C	3.47849500	0.34491700	0.62812300
H	1.72013400	0.78138000	1.79330000
C	3.13860900	-1.01710200	-1.32484700
H	1.13405200	-1.68035400	-1.69283200
C	3.99584600	-0.29437400	-0.50076500
H	4.13744400	0.92035600	1.28306600
H	3.52643200	-1.52237800	-2.21279300
H	5.06054800	-0.22463500	-0.73582600
C	-3.40779100	-0.31315100	-1.26815200
H	-3.07173600	0.73161500	-1.18045400
H	-3.26962900	-0.61072000	-2.32000300
H	-4.46652000	-0.39027800	-0.99163300
S	-0.90583600	1.09662600	0.89963800
C	-0.46272000	2.07055200	-0.56851500
H	0.62966100	2.02428300	-0.69813800
H	-0.92550700	1.62516700	-1.46301100
C	-0.92872000	3.50311200	-0.38577500
H	-0.65171800	4.10446600	-1.26449000
H	-2.02162800	3.55970000	-0.26754200
H	-0.46581100	3.96332200	0.50040500
C	-0.35030600	-1.38600200	1.78014900
H	0.24219200	-0.92486000	2.58263400
H	-1.39727700	-1.46470200	2.10067300
H	0.03221900	-2.40402600	1.61000800
H	-0.86042300	-0.68519500	-1.58991100

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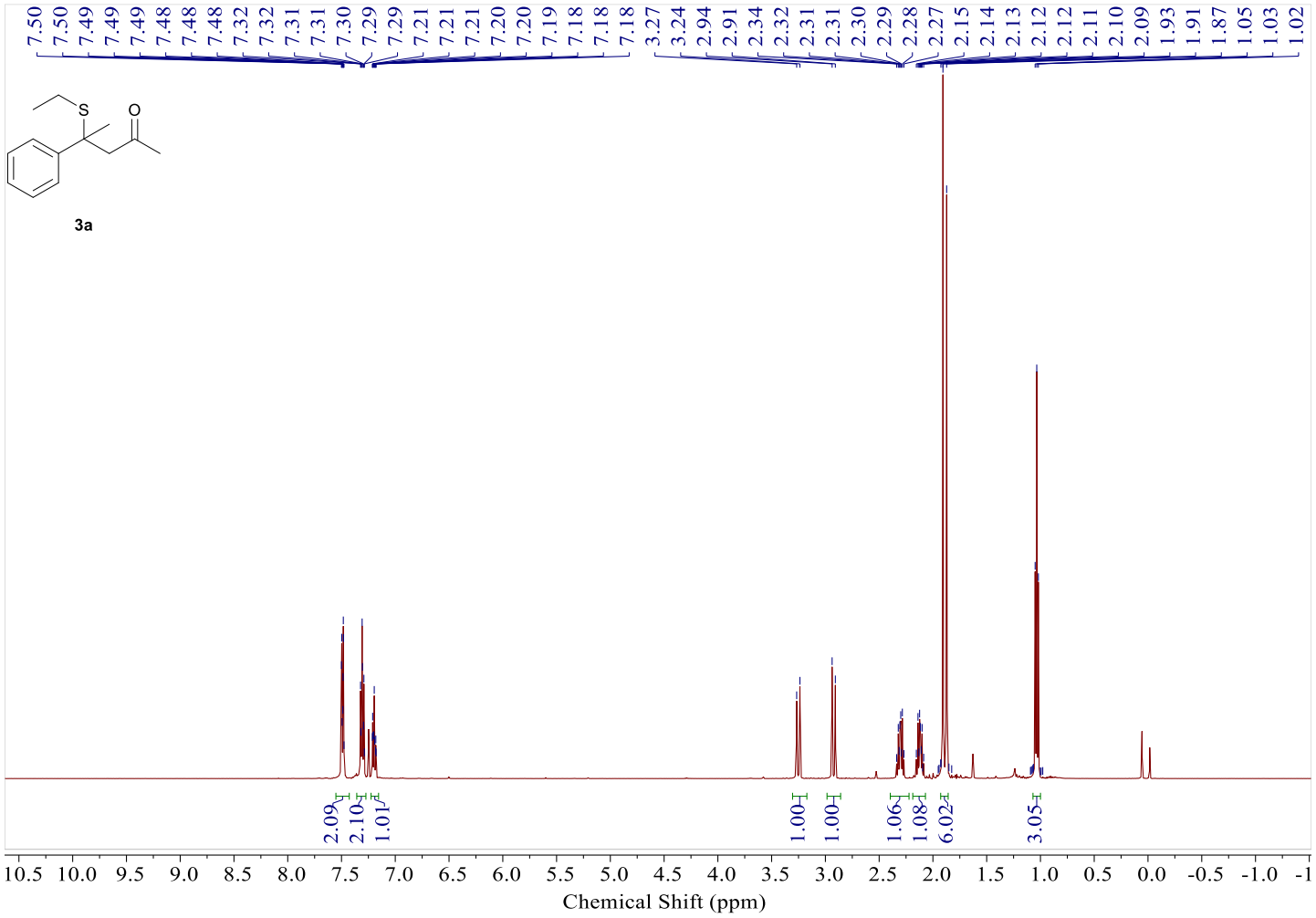
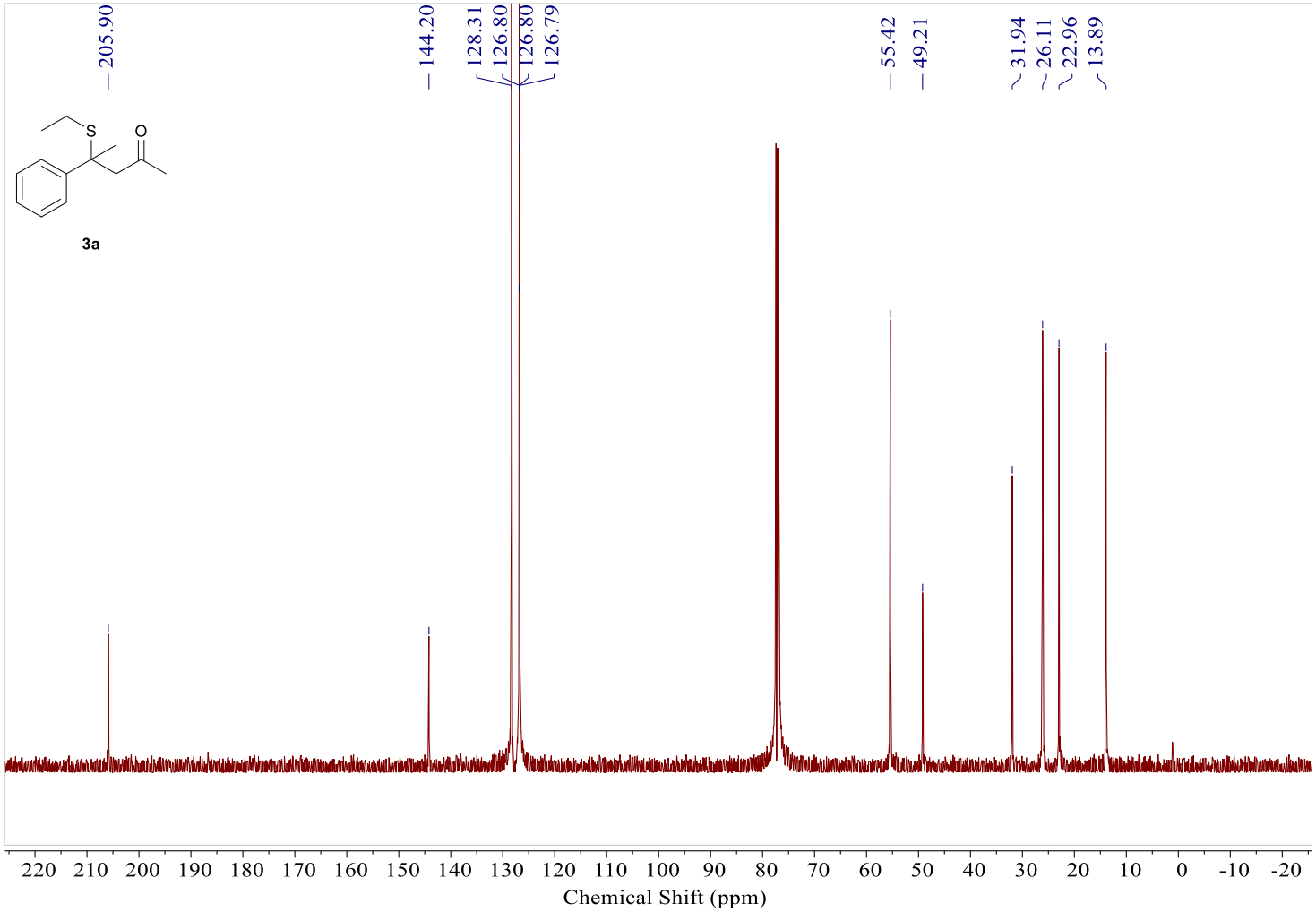
7. F. Weigend and R. Ahlrichs, *Physical Chemistry Chemical Physics*, 2005, **7**, 3297-3305.
8. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *The Journal of Physical Chemistry B*, 2009, **113**, 6378-6396.
9. C. Y. Legault, CYLview20, Université de Sherbrooke, 2020. (http://www.cylview.org

NMR Spectra of Compounds

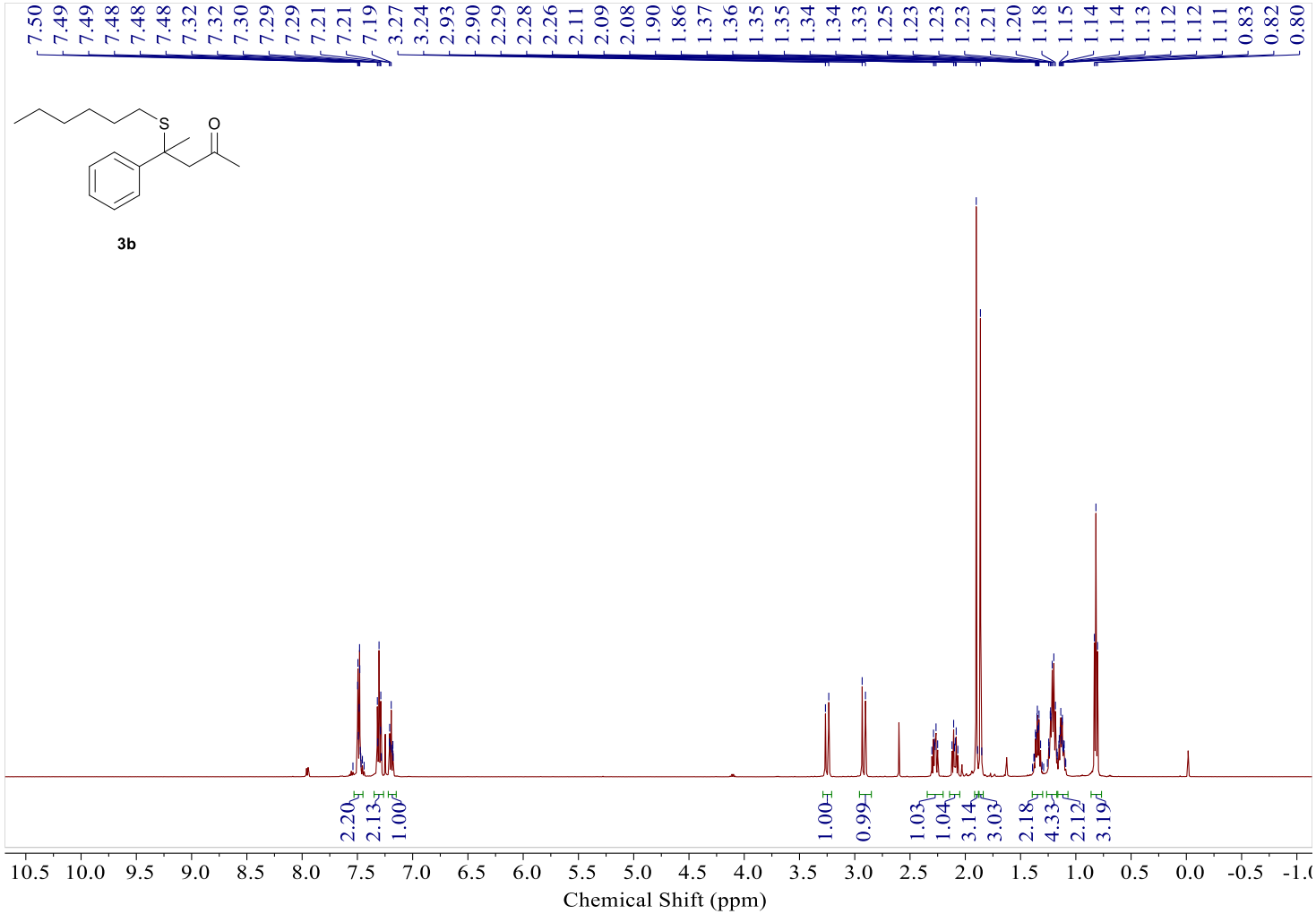
^{1}H NMR of compound **3a**



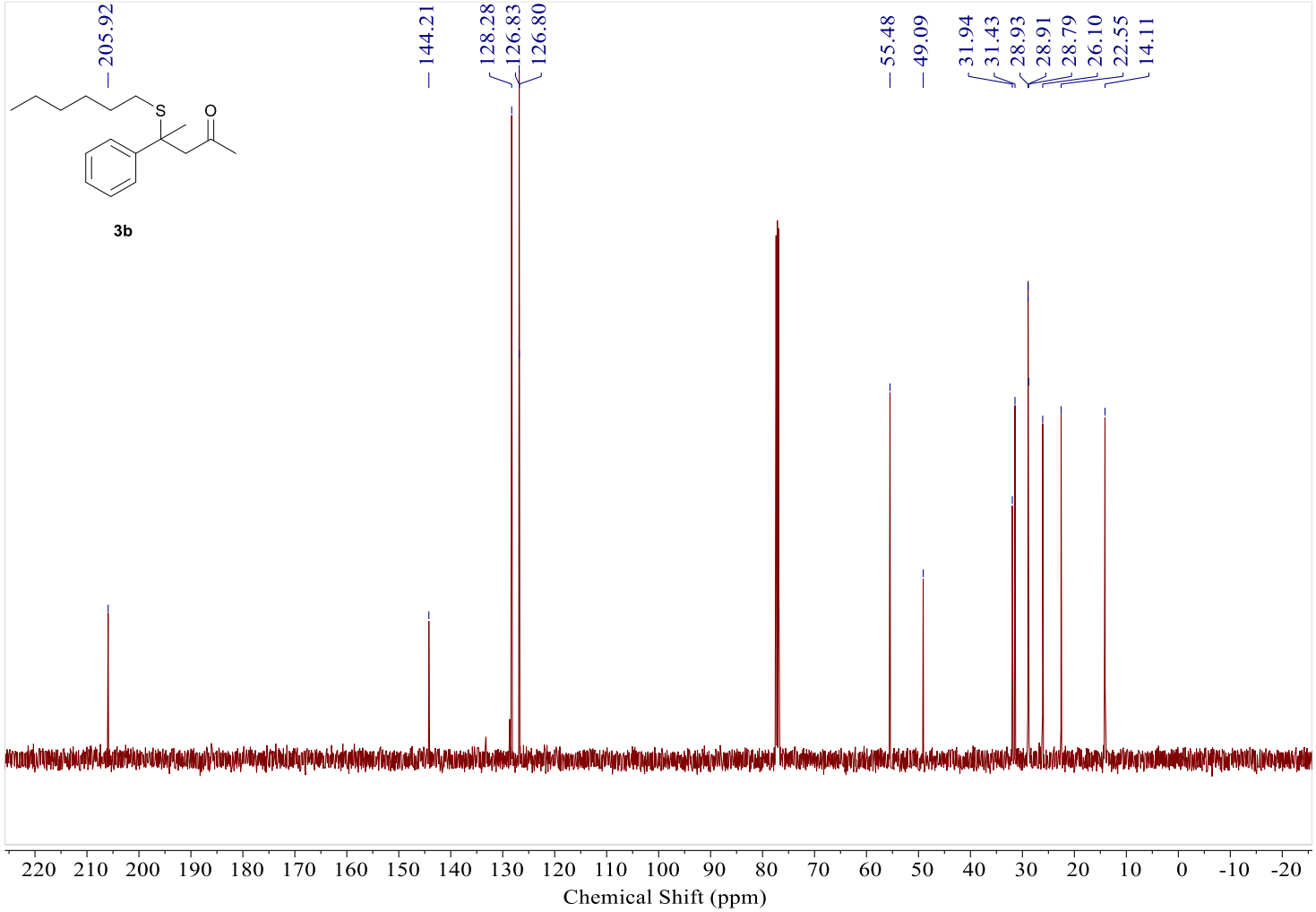
^{13}C NMR of compound **3a**



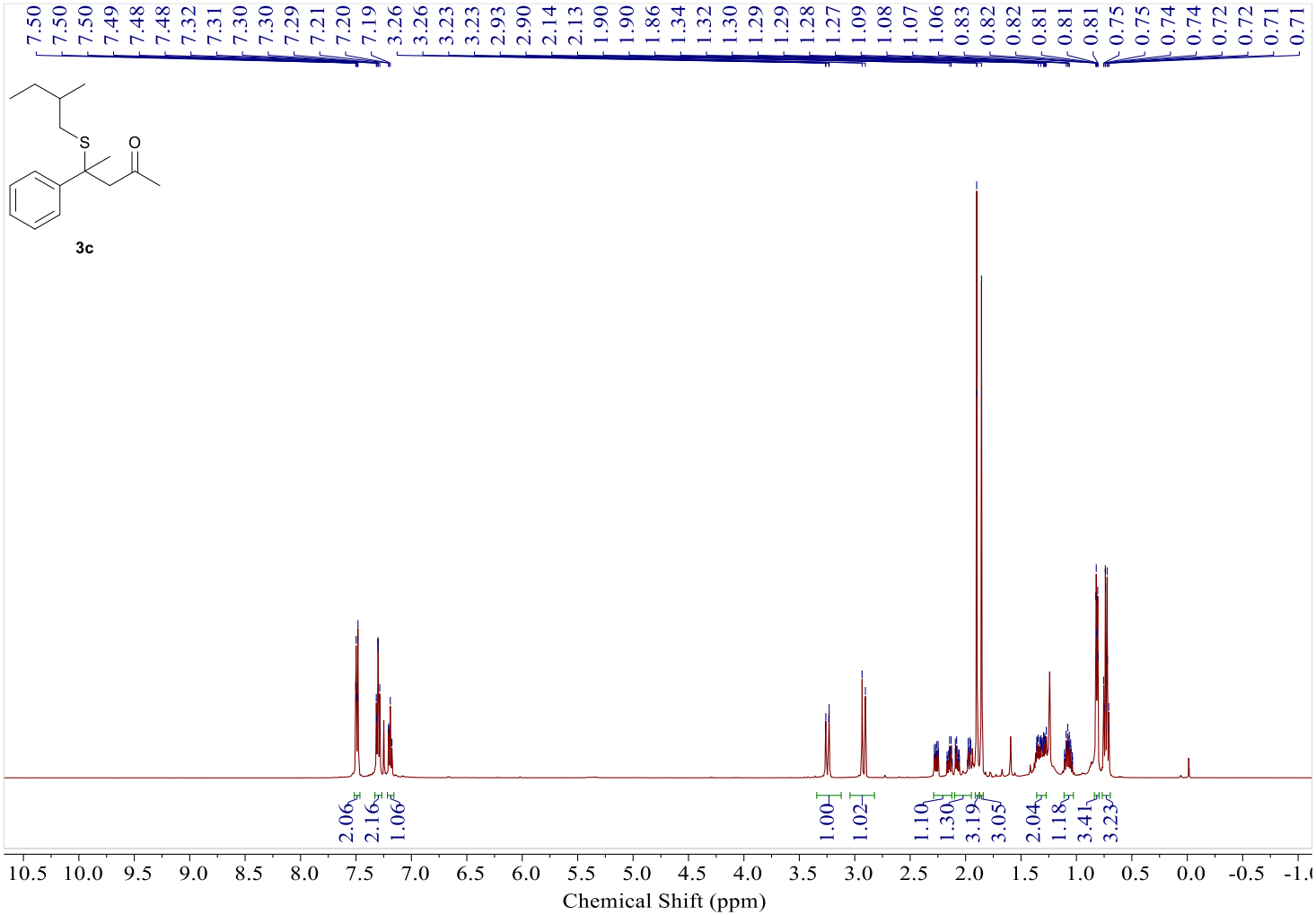
[1]H NMR of compound **3b**



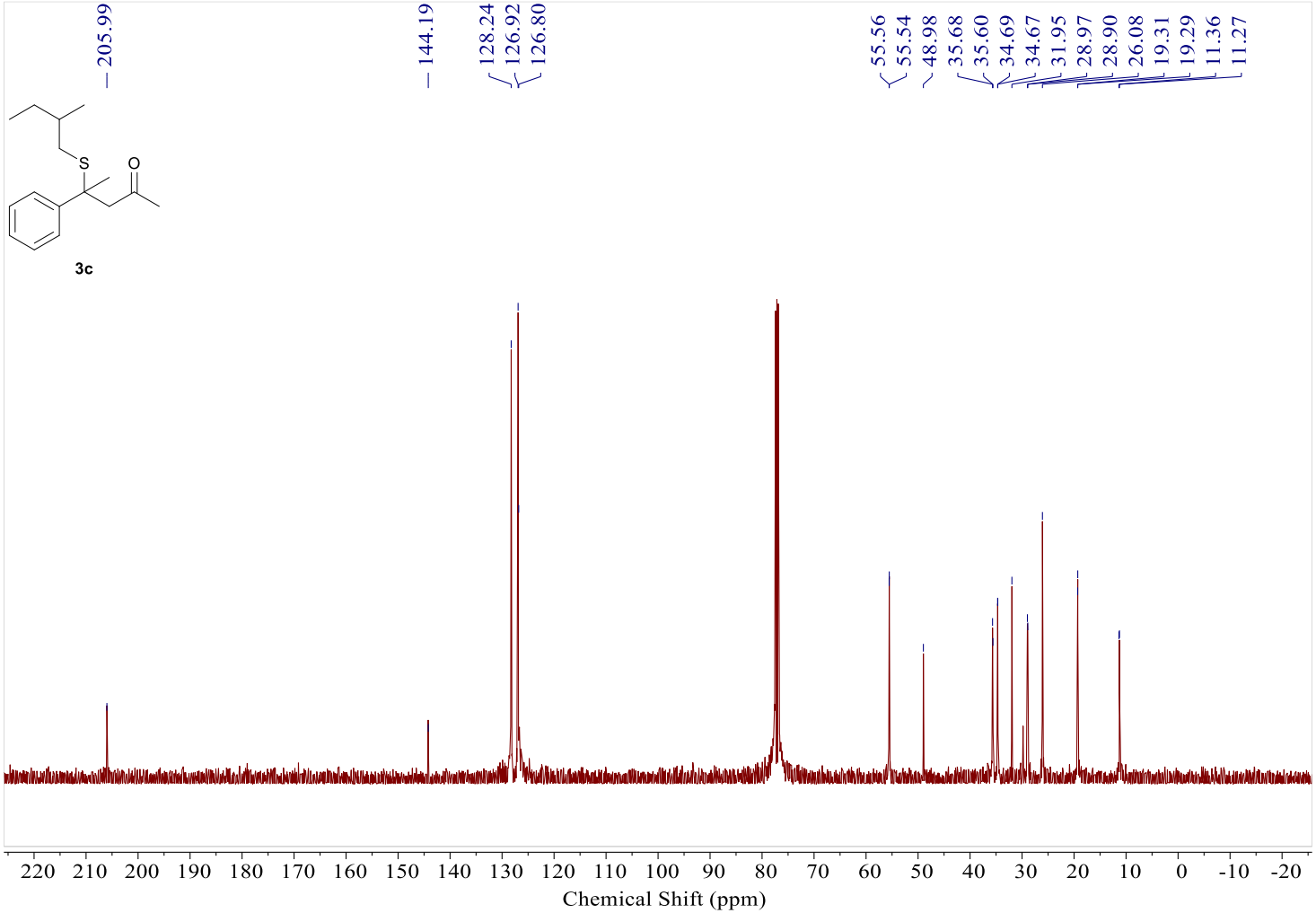
^{13}C NMR of compound **3b**



[1]H NMR of compound **3c**



^{13}C NMR of compound **3c**



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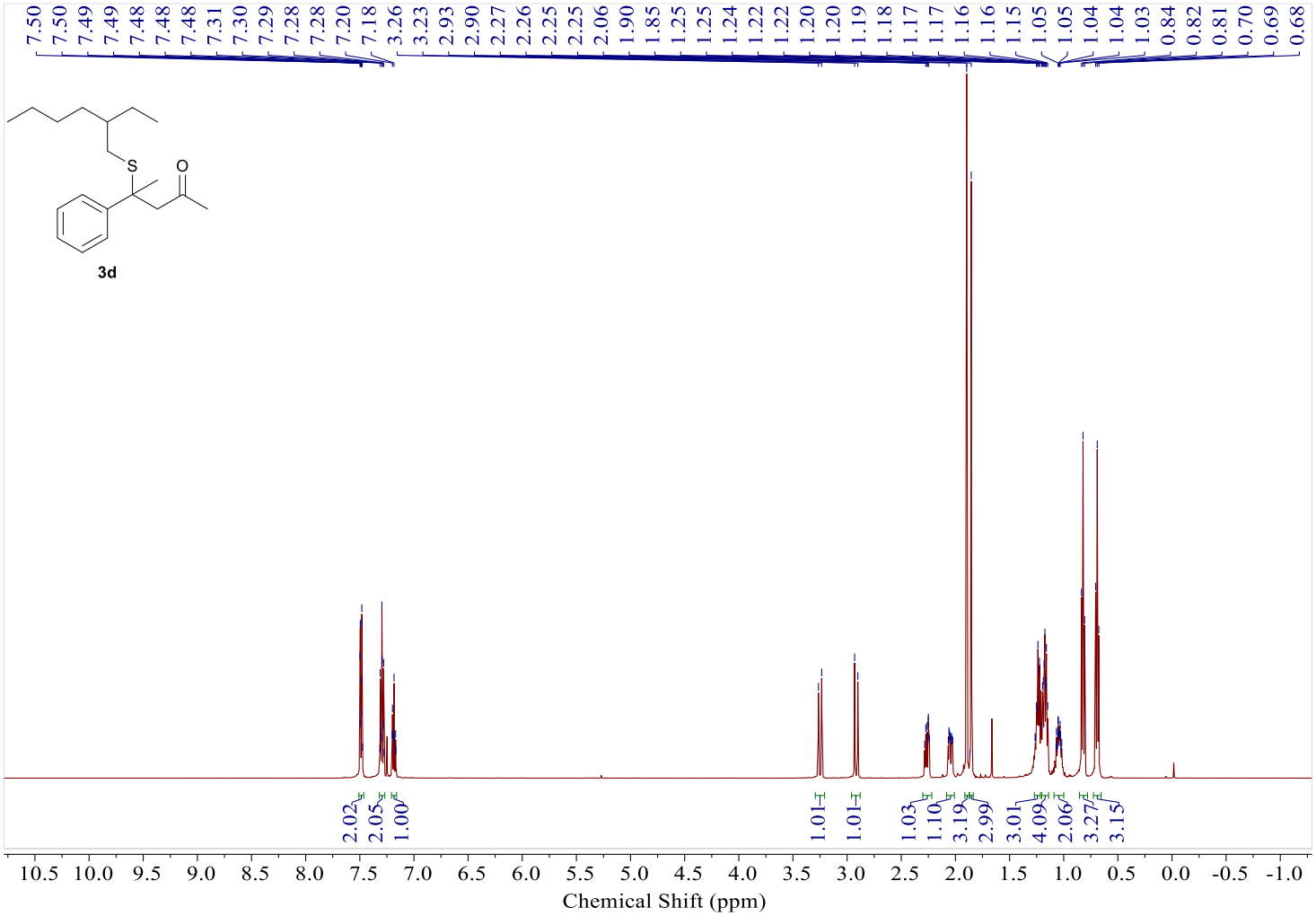
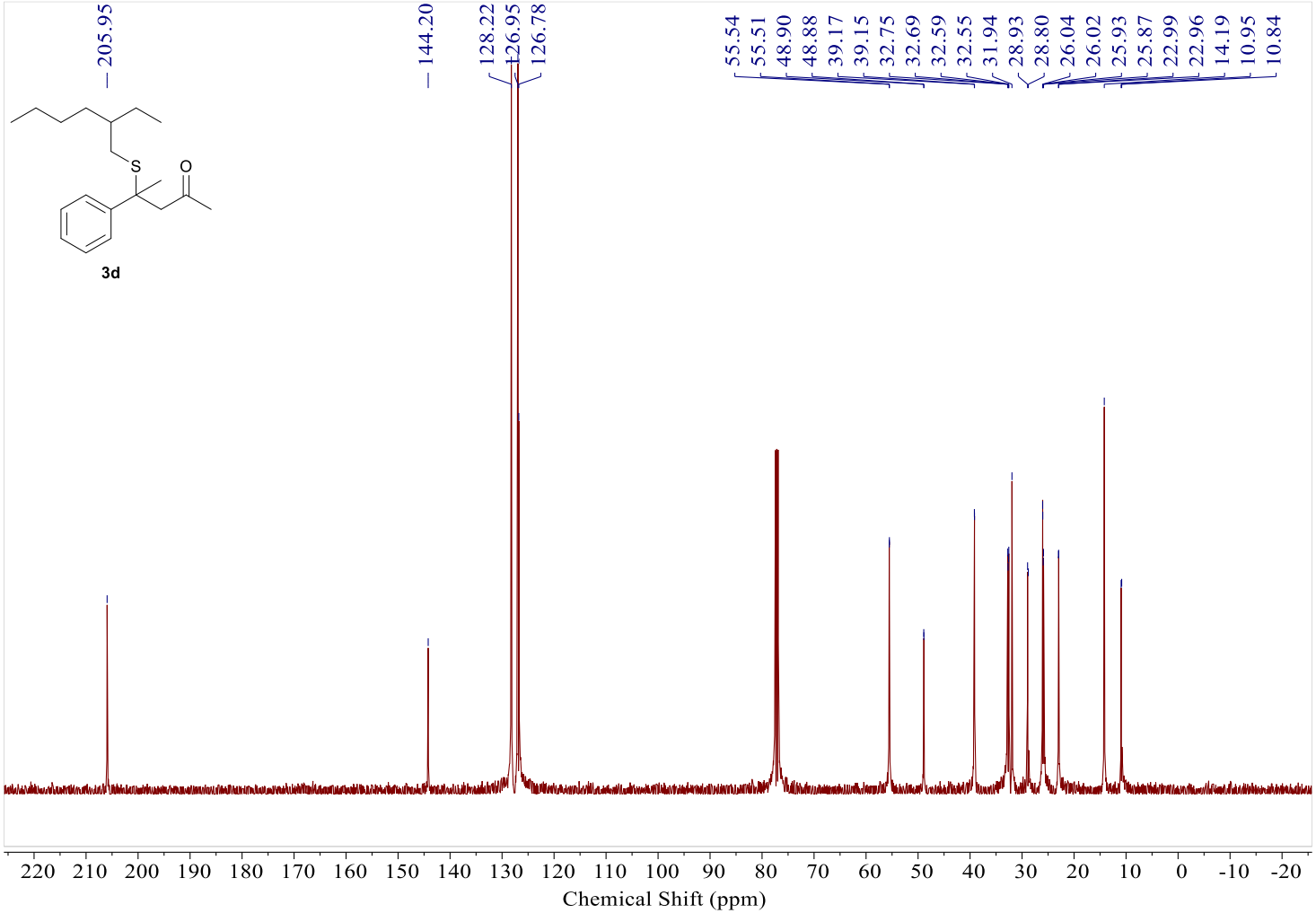


^{13}C NMR of compound **3d**



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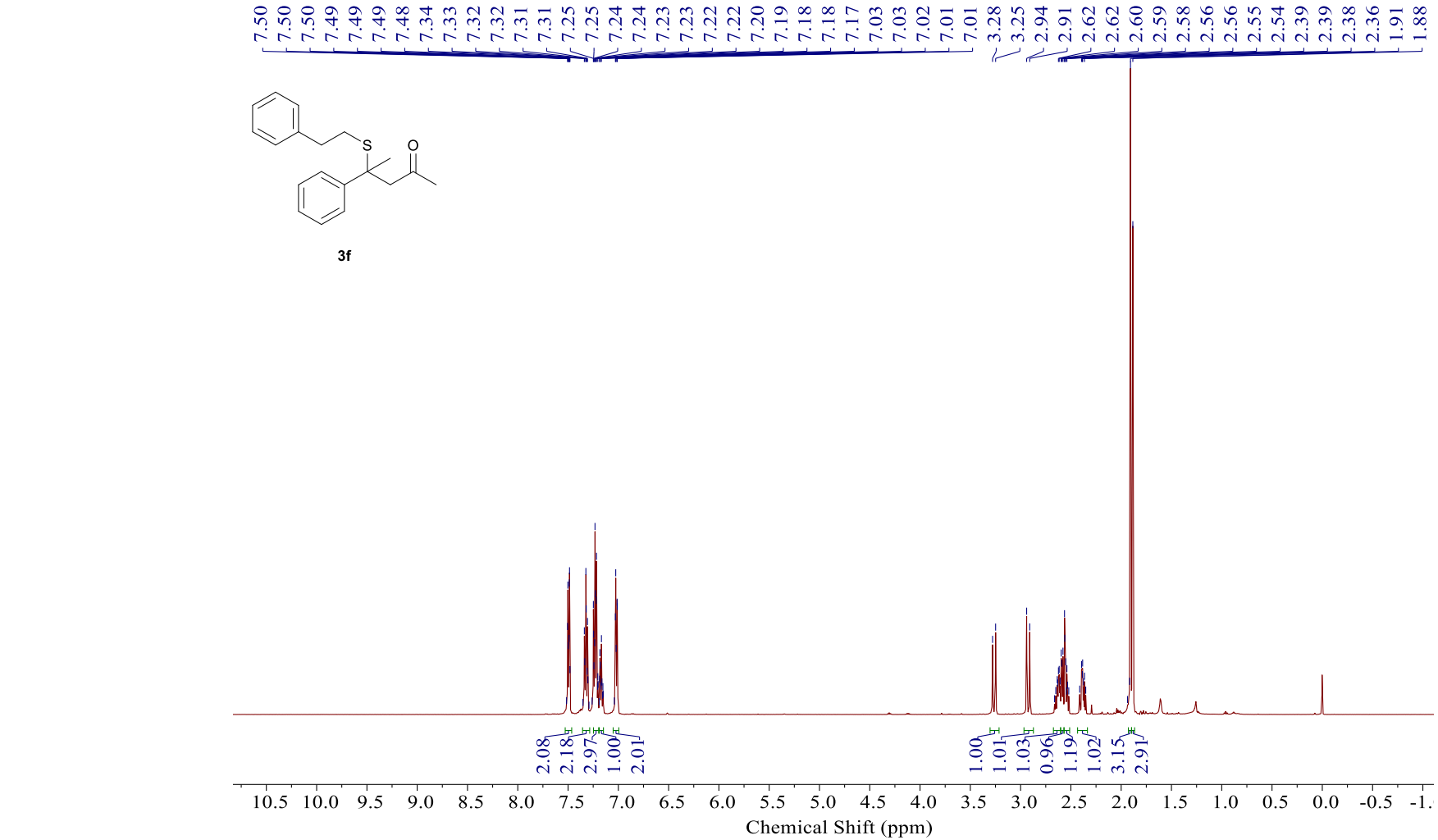

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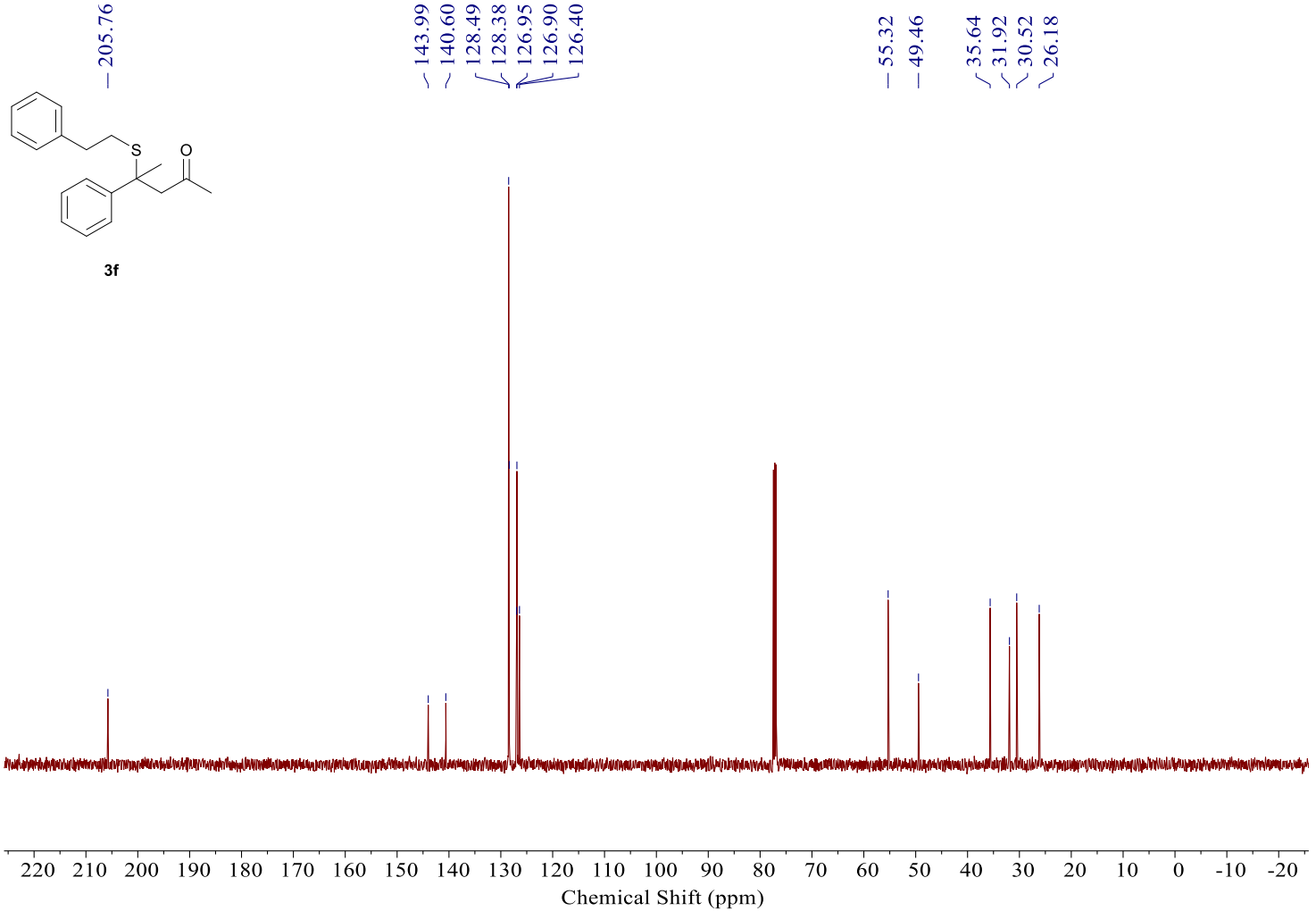
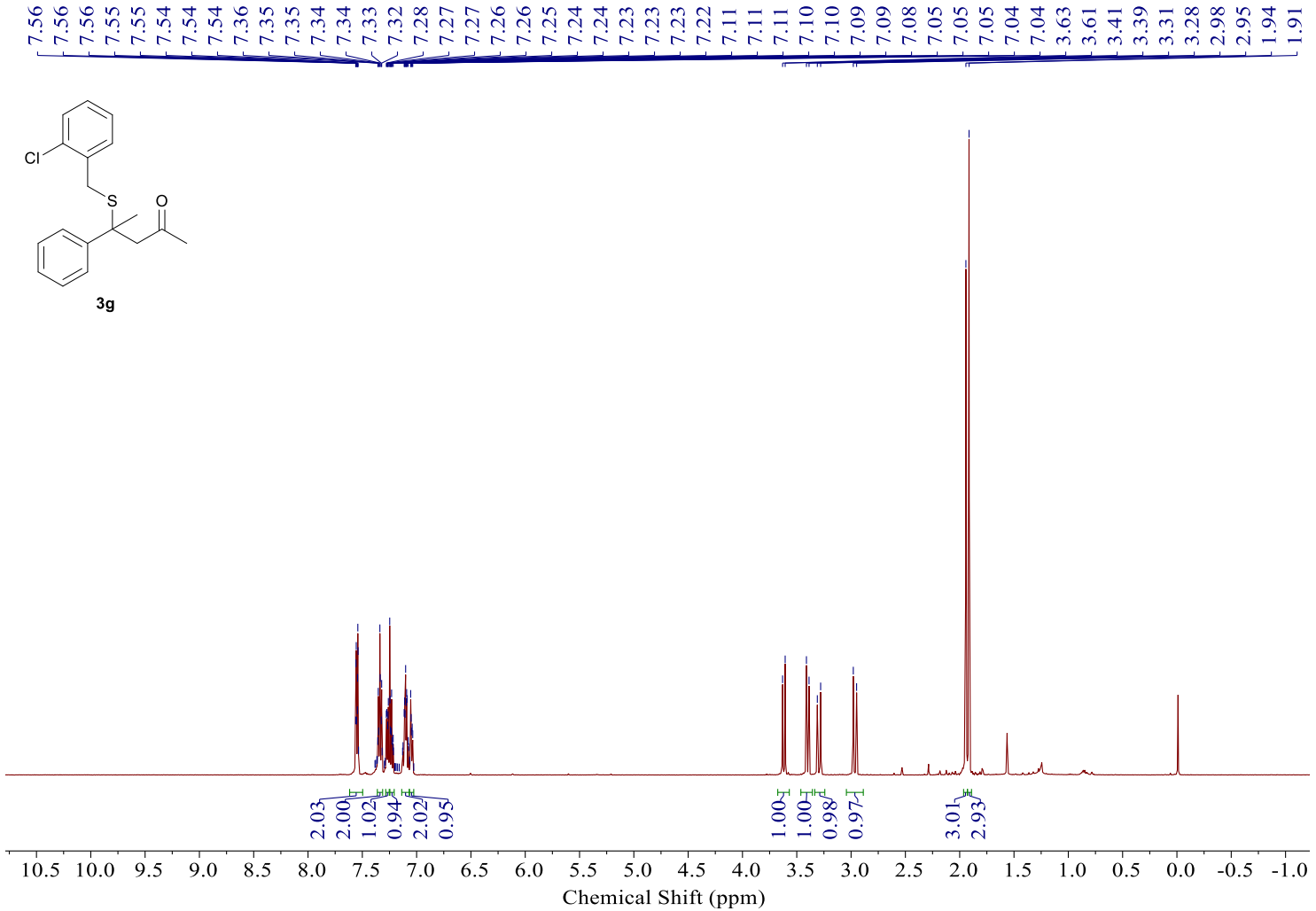
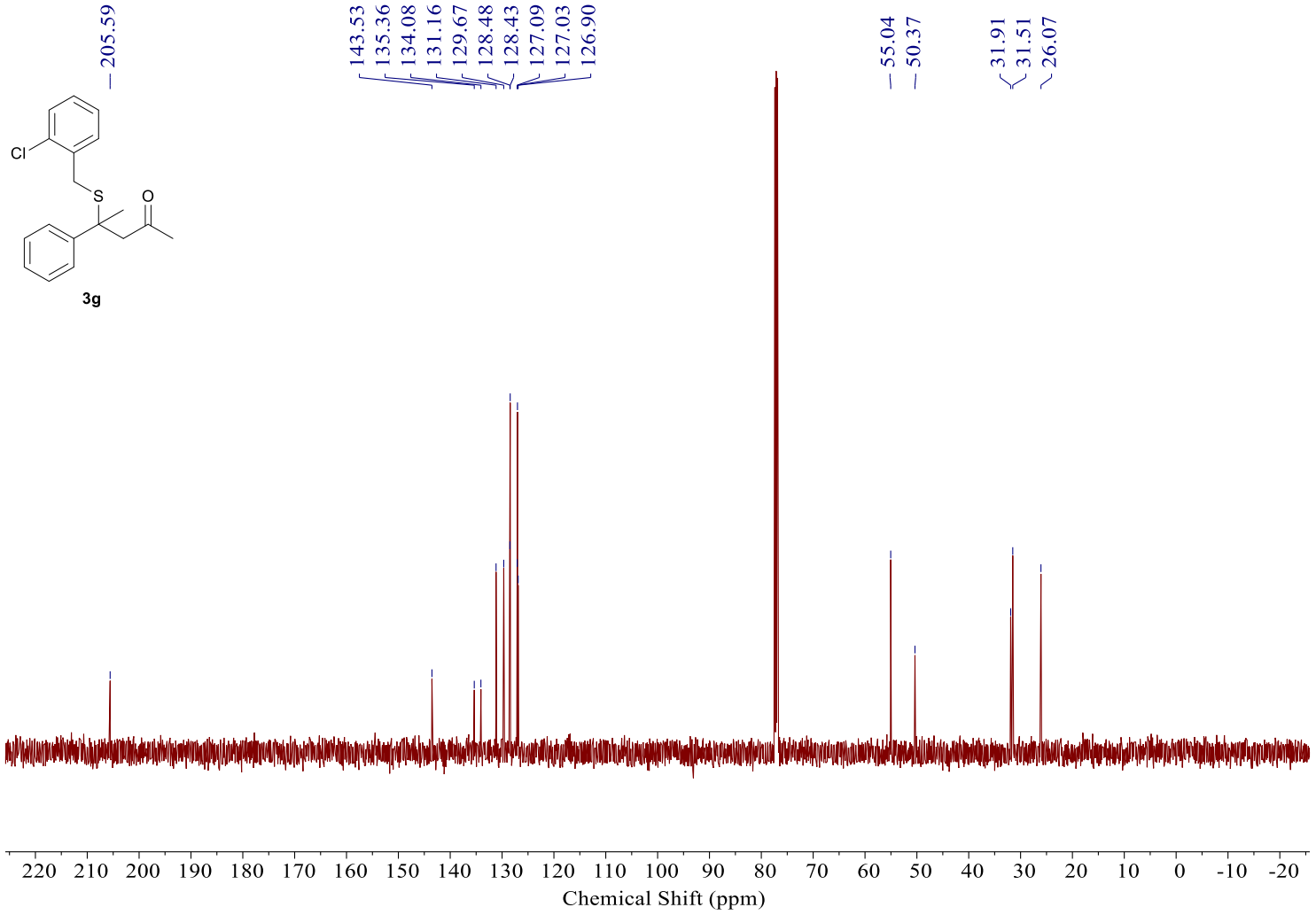


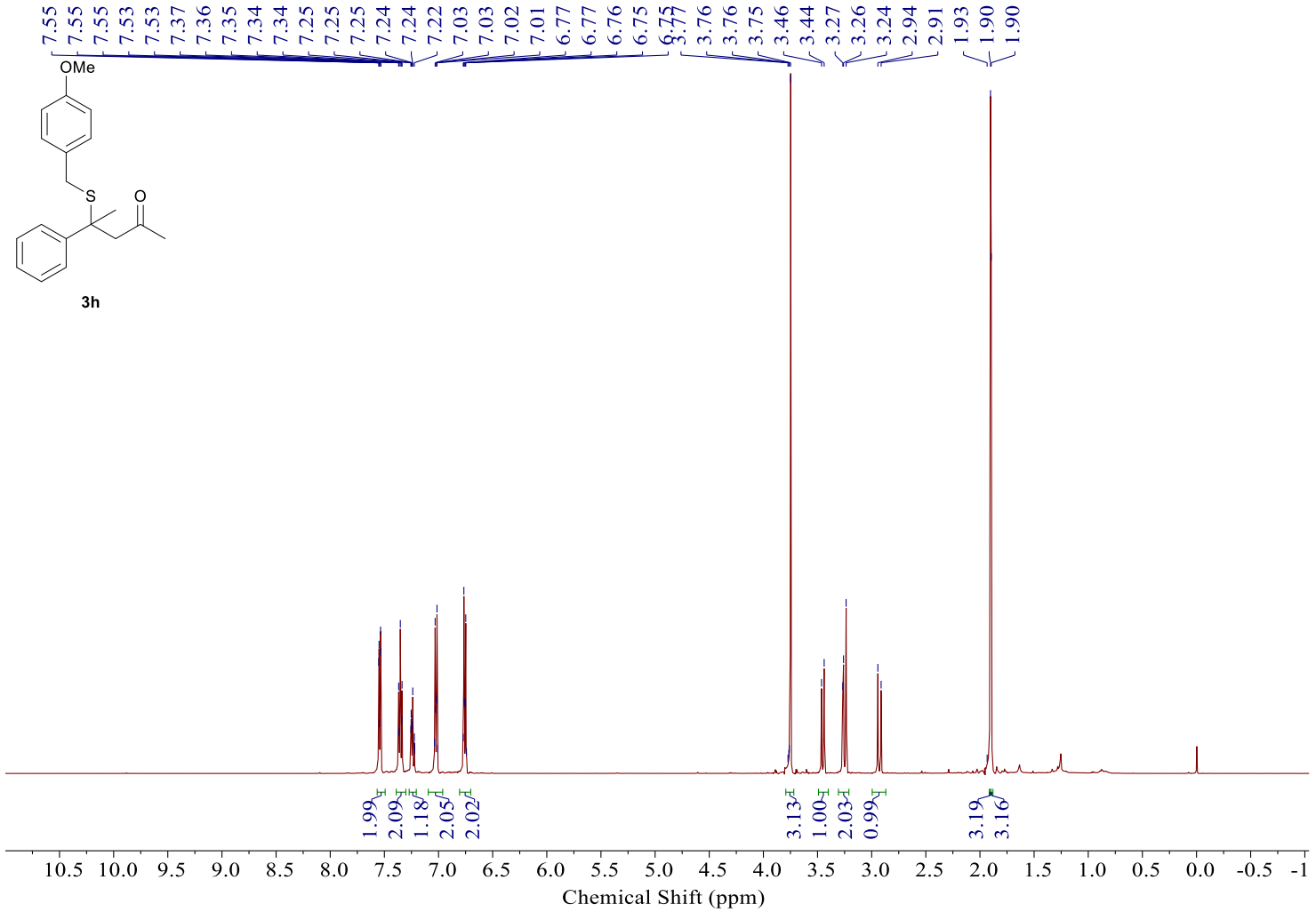
^{1}H NMR of compound **3g**



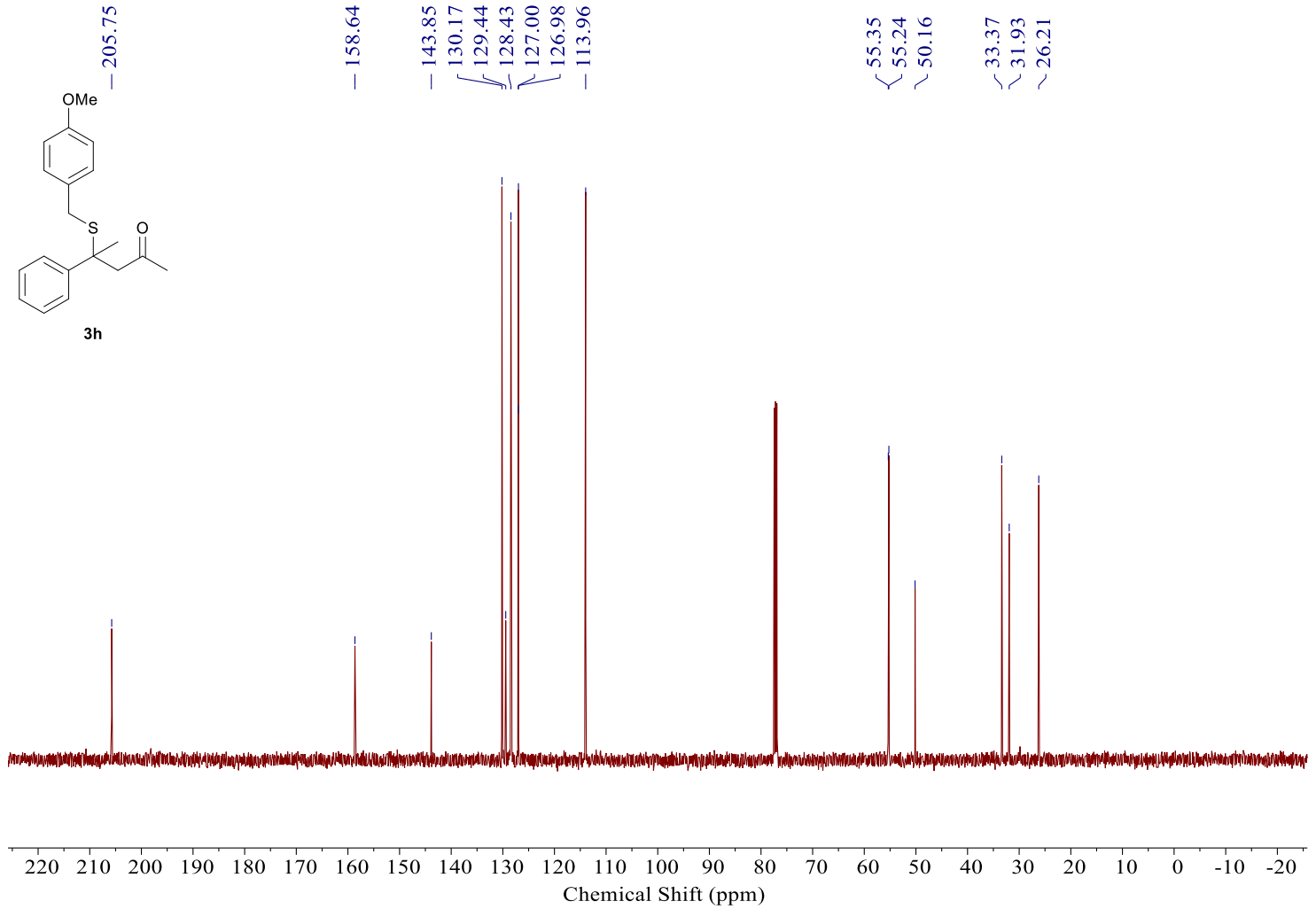
^{13}C NMR of compound **3g**



^{1}H NMR of compound **3h**



^{13}C NMR of compound **3h**



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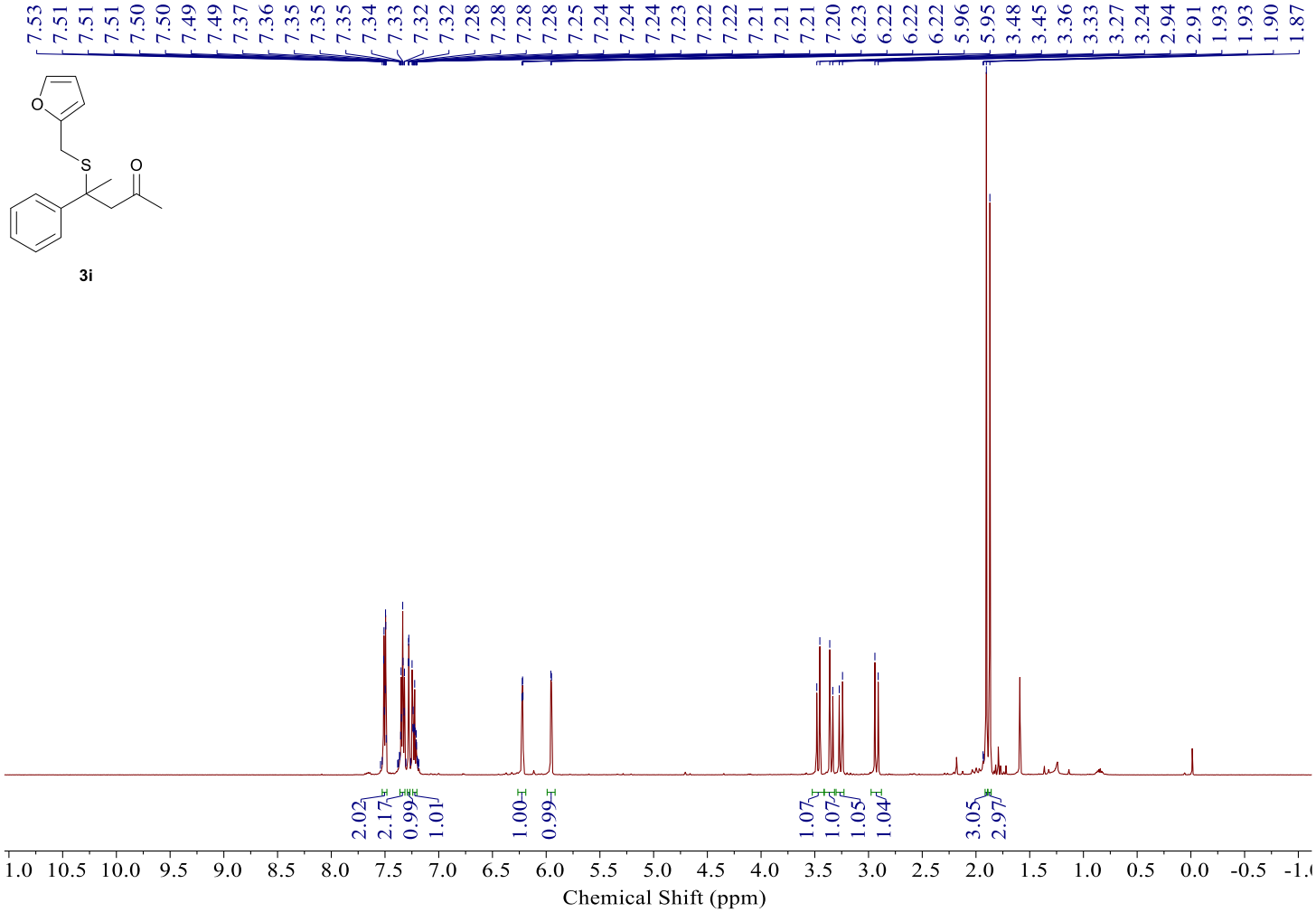

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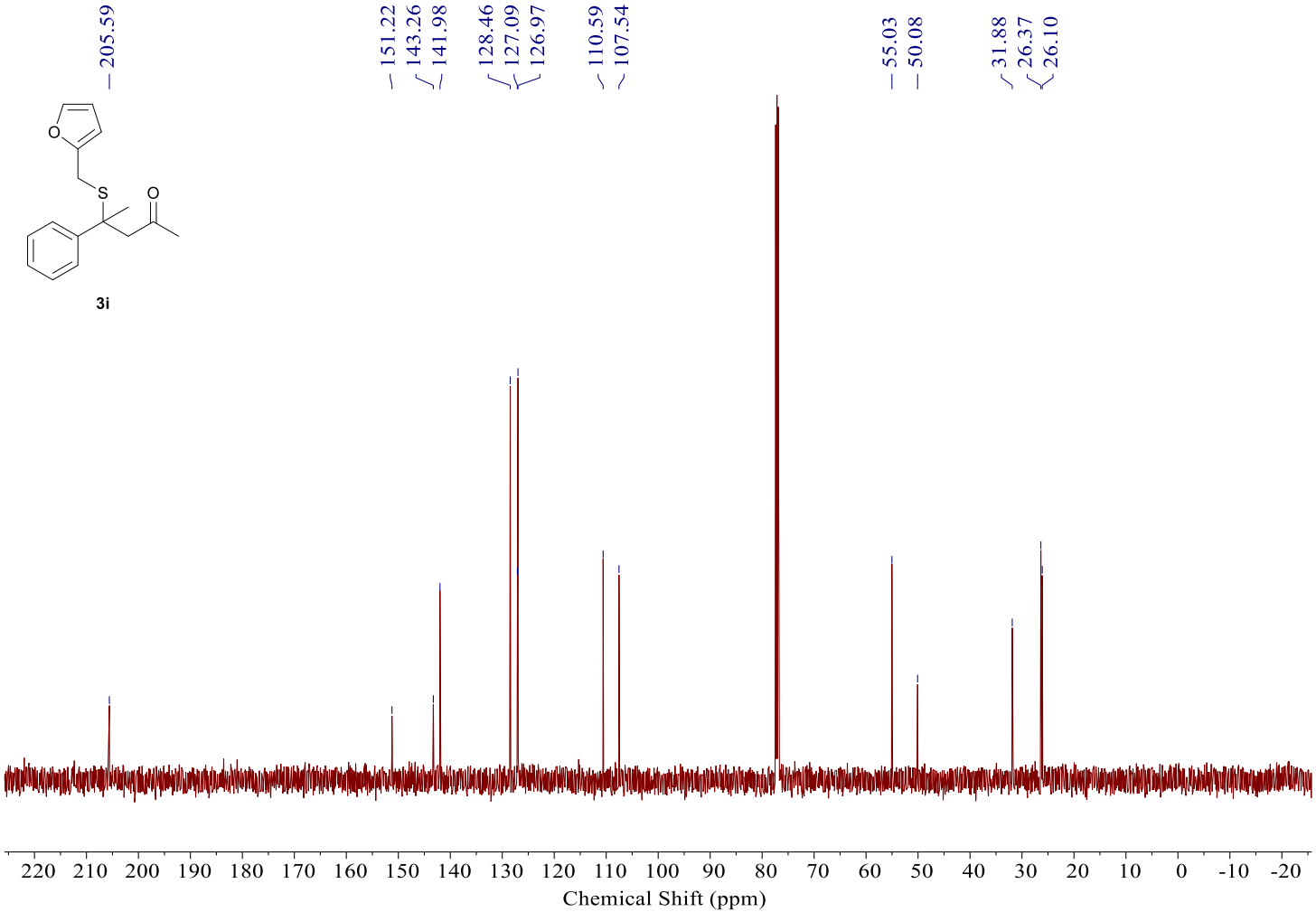

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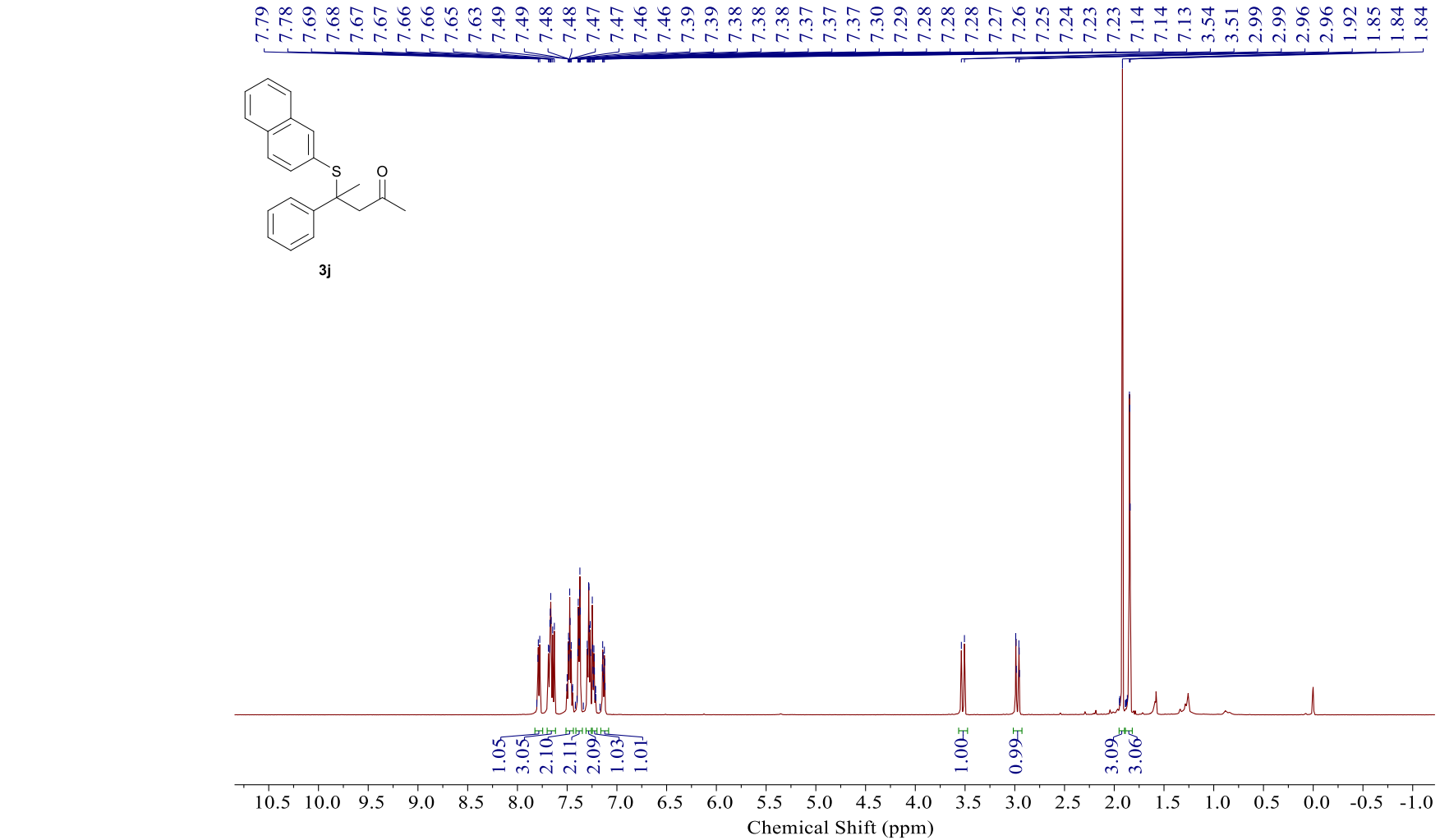

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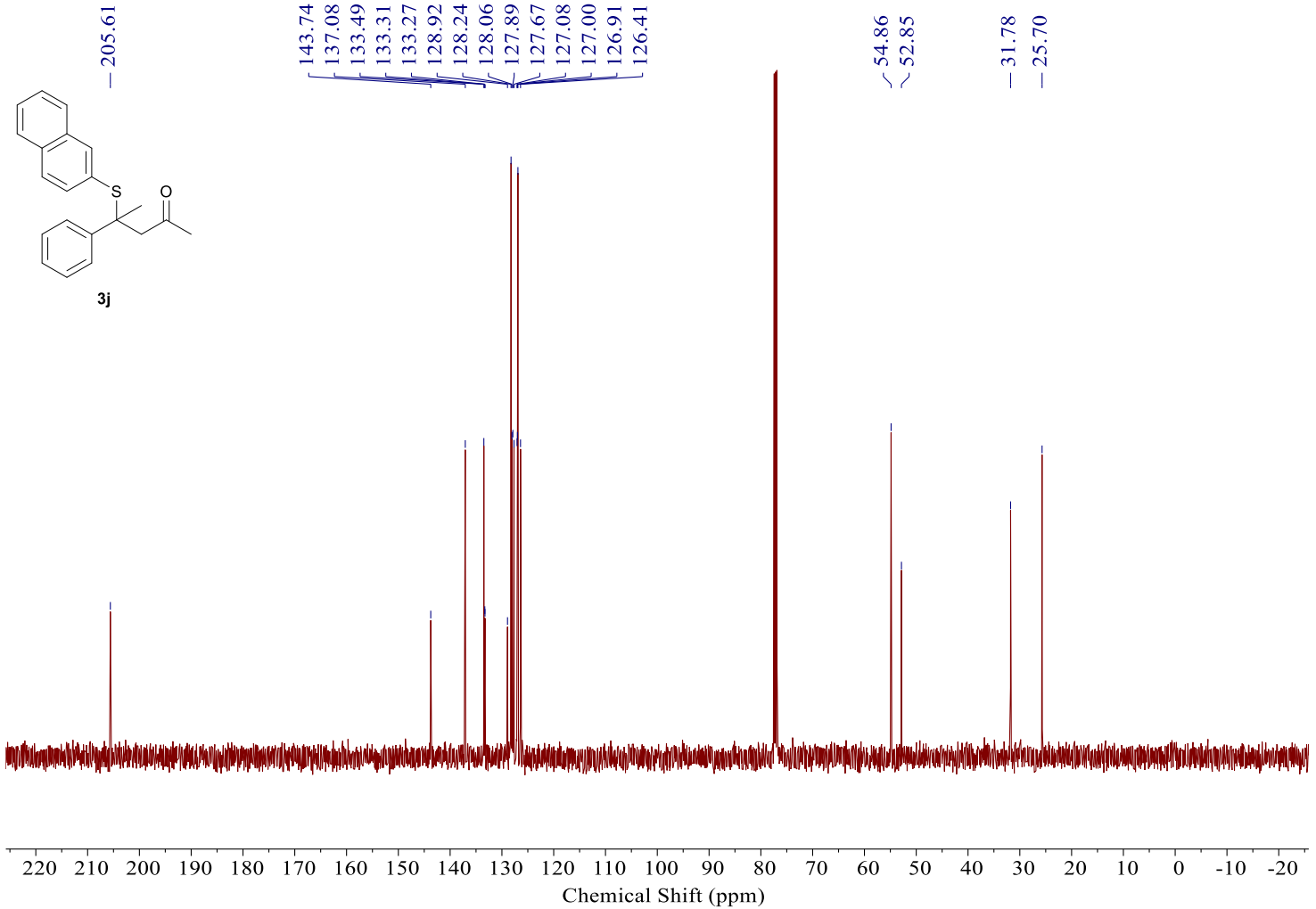

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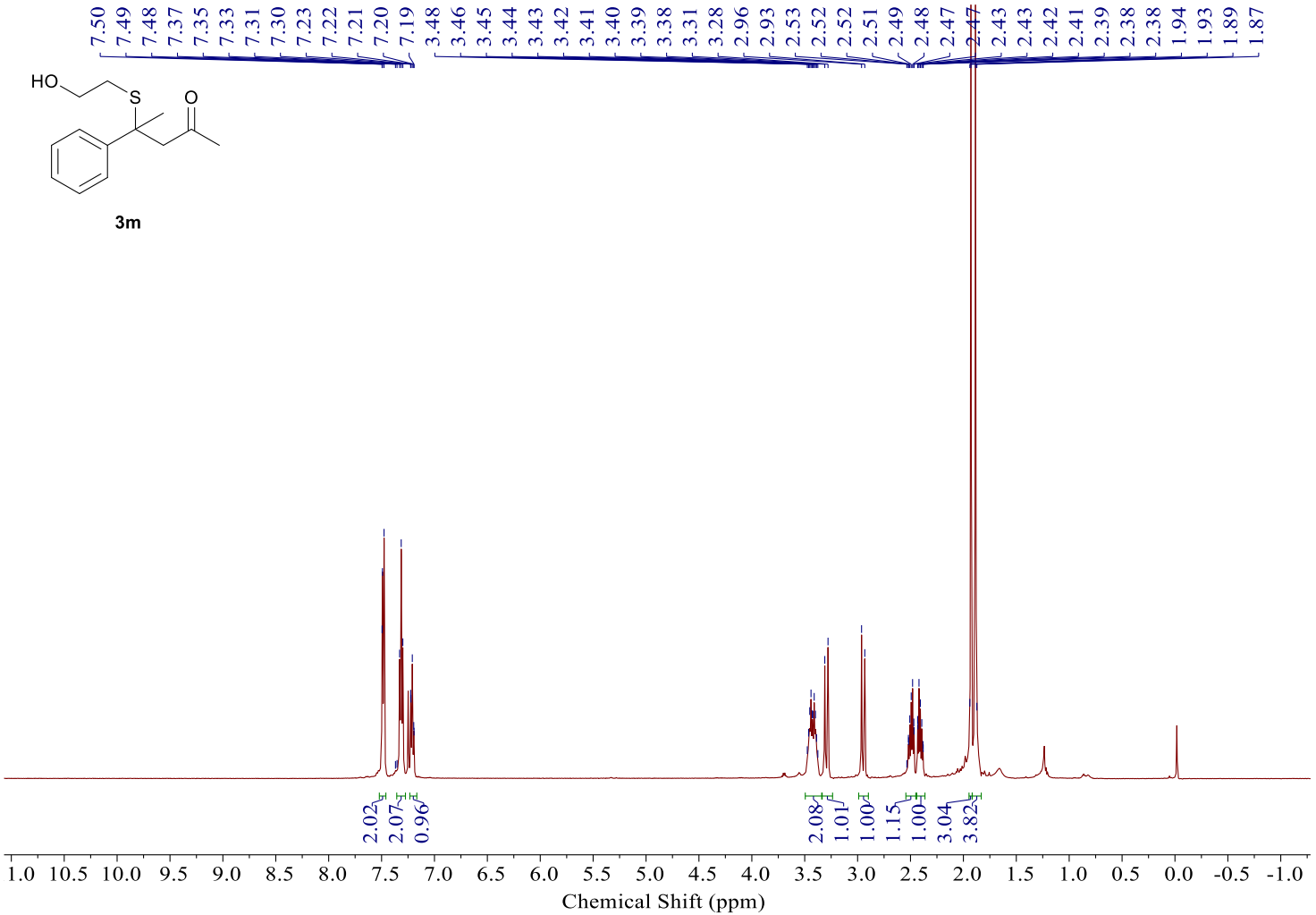
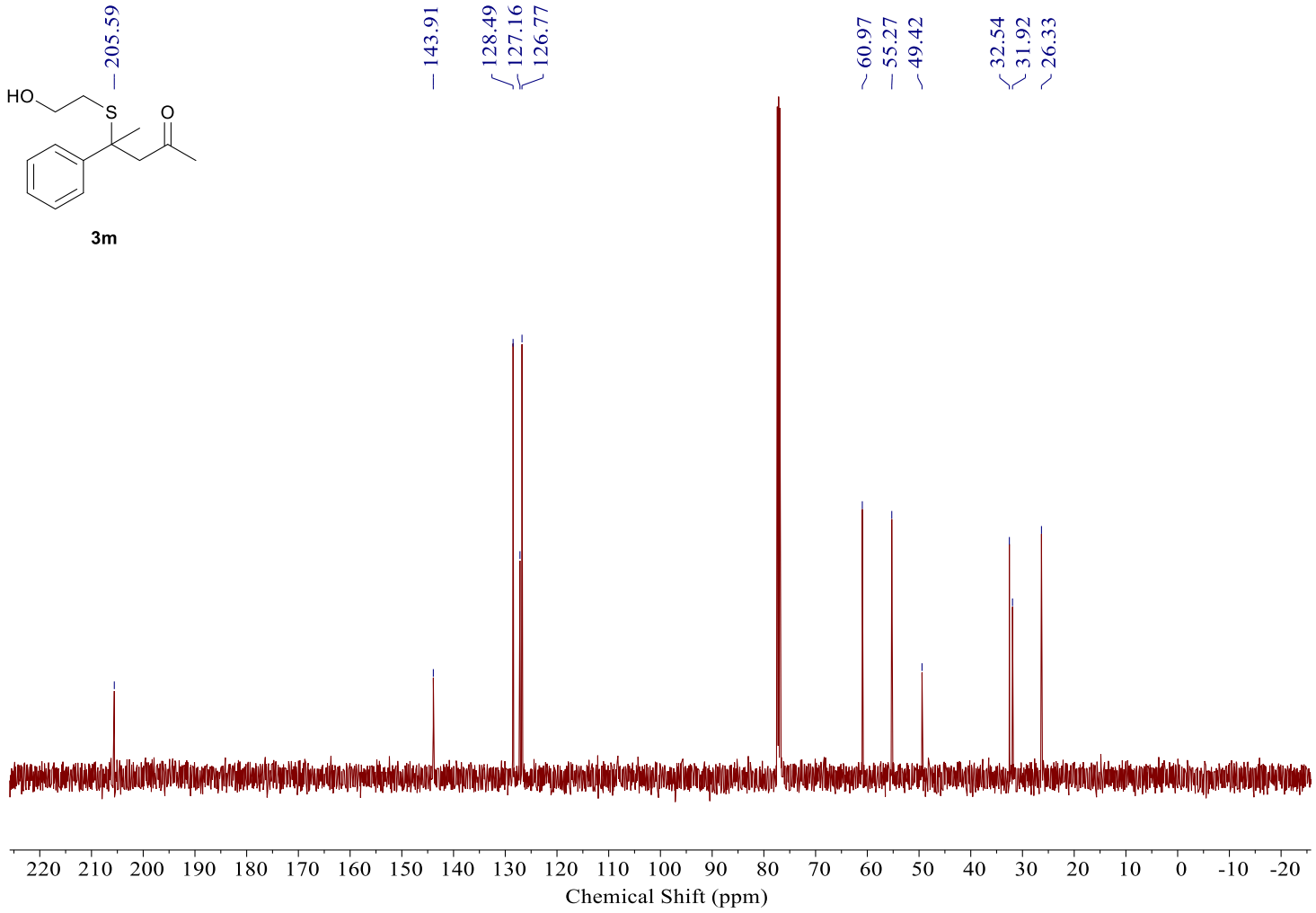


^{13}C NMR of compound **3m**



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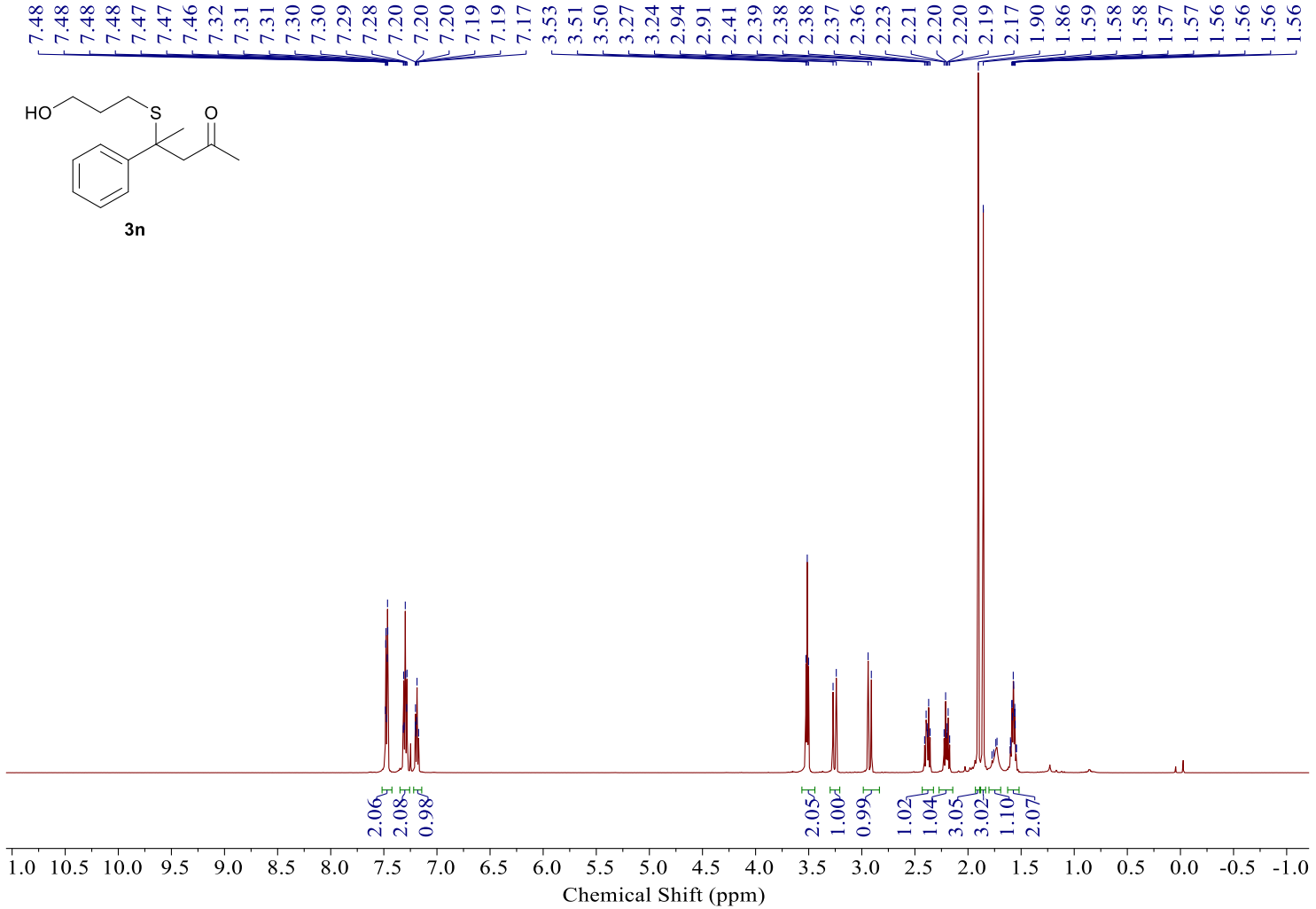

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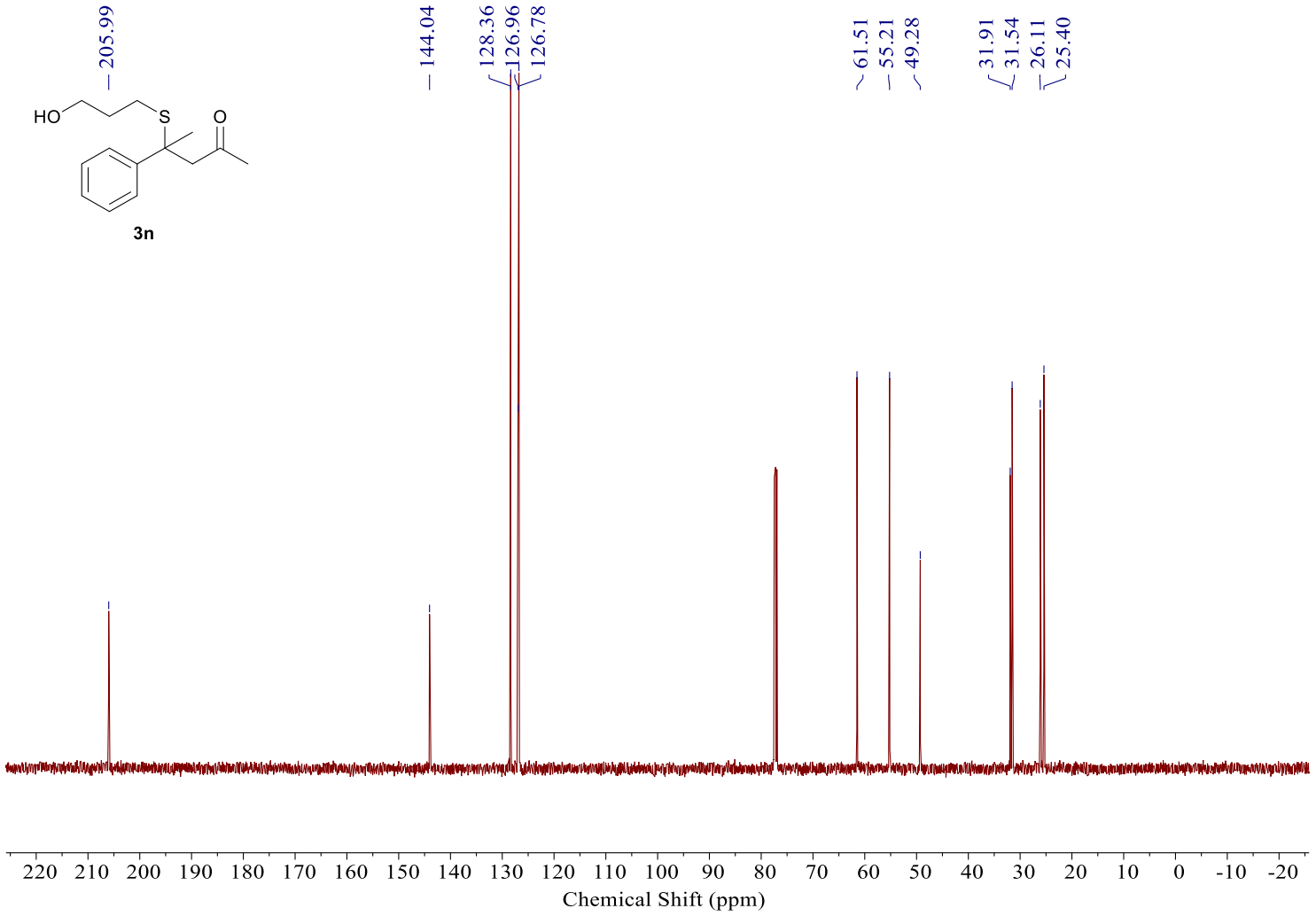
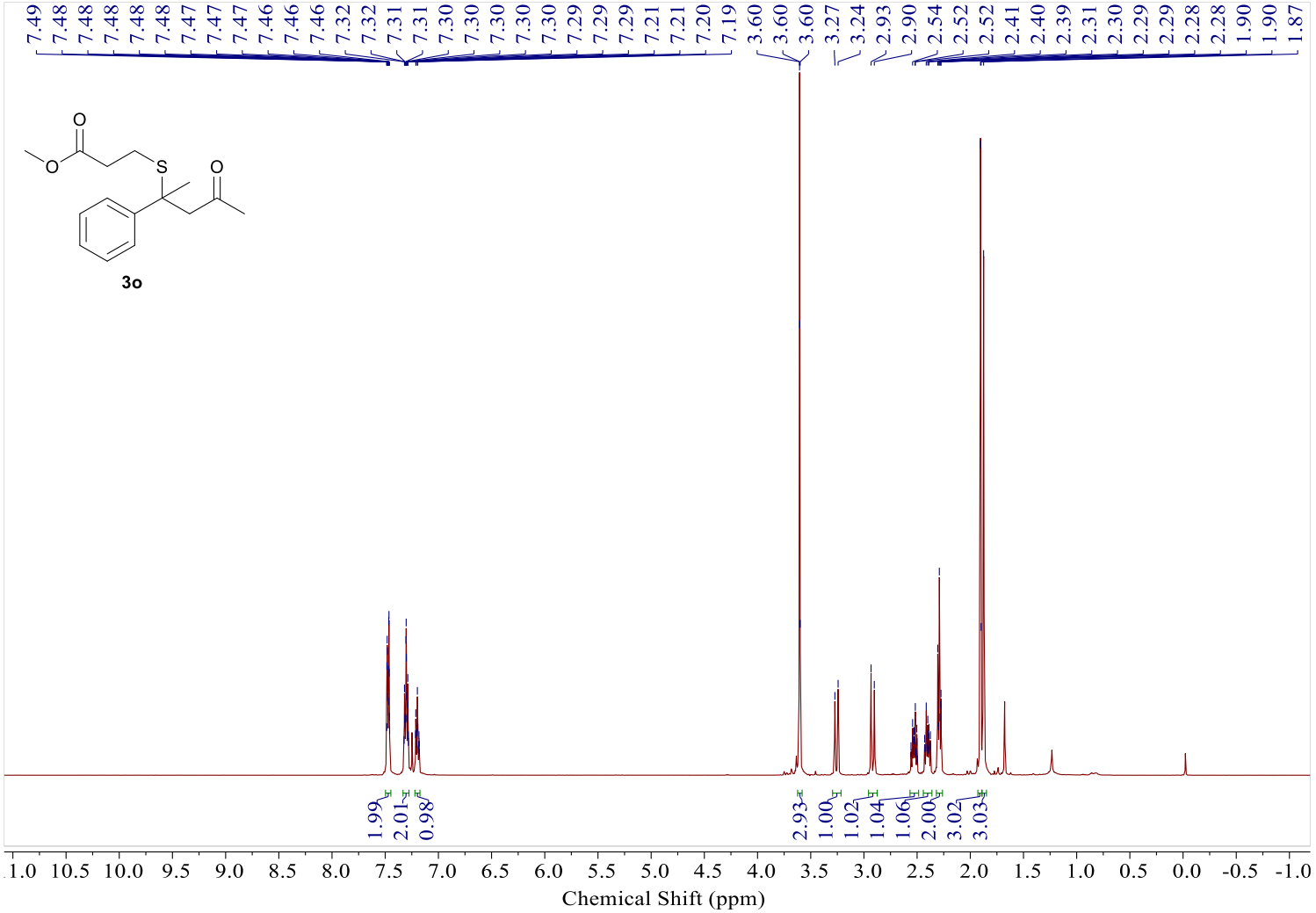


[1]H NMR of compound **3o**



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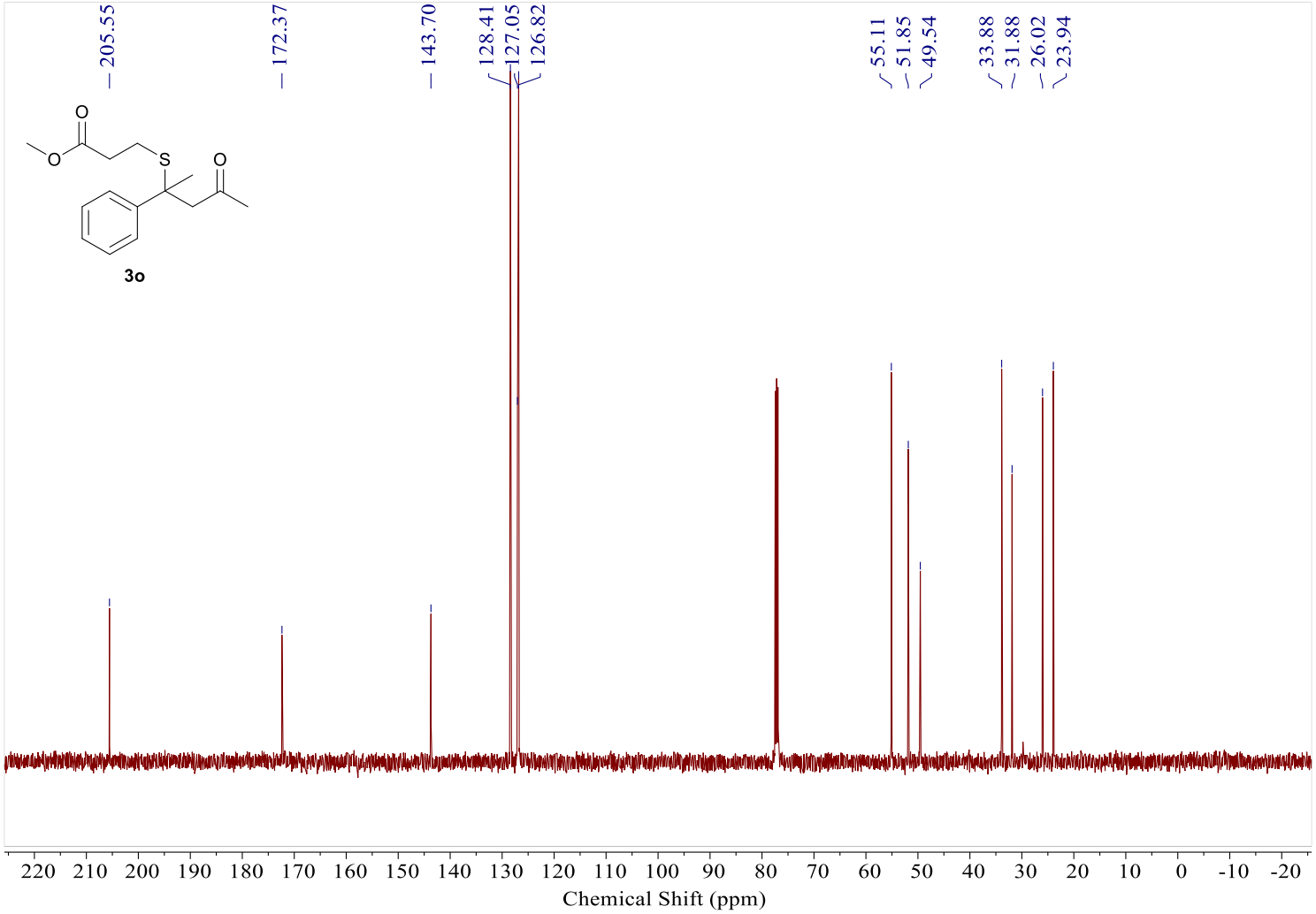

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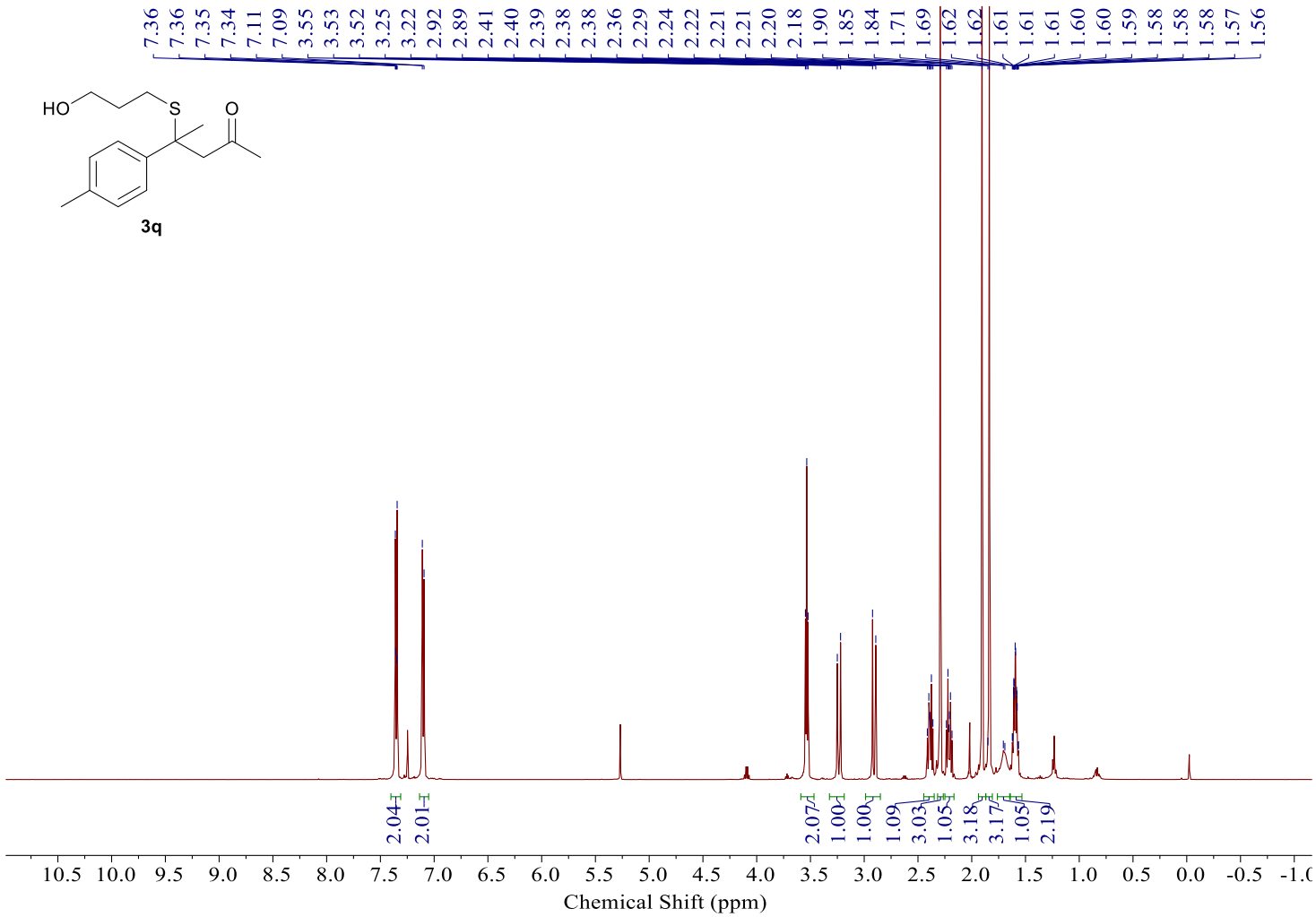
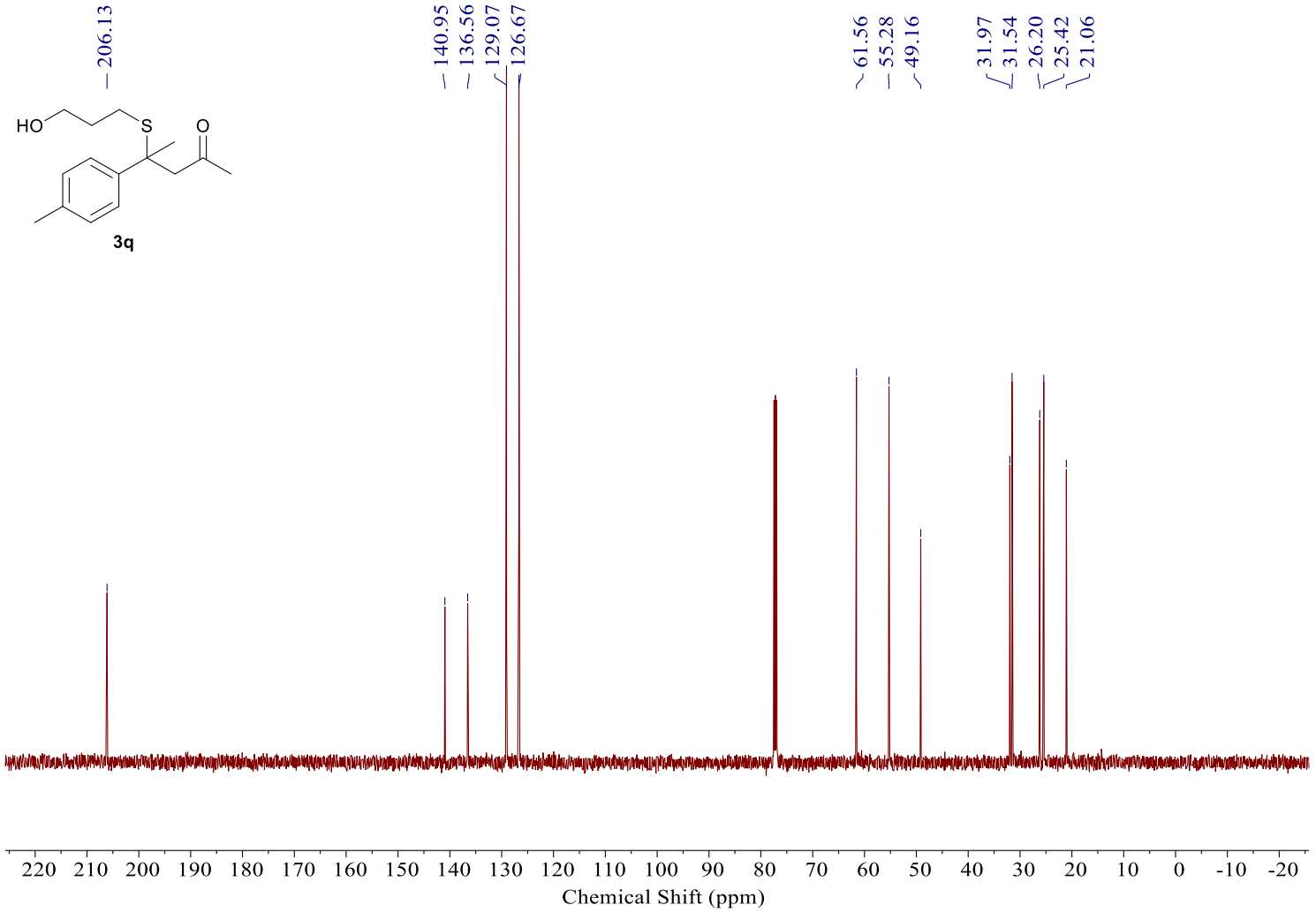
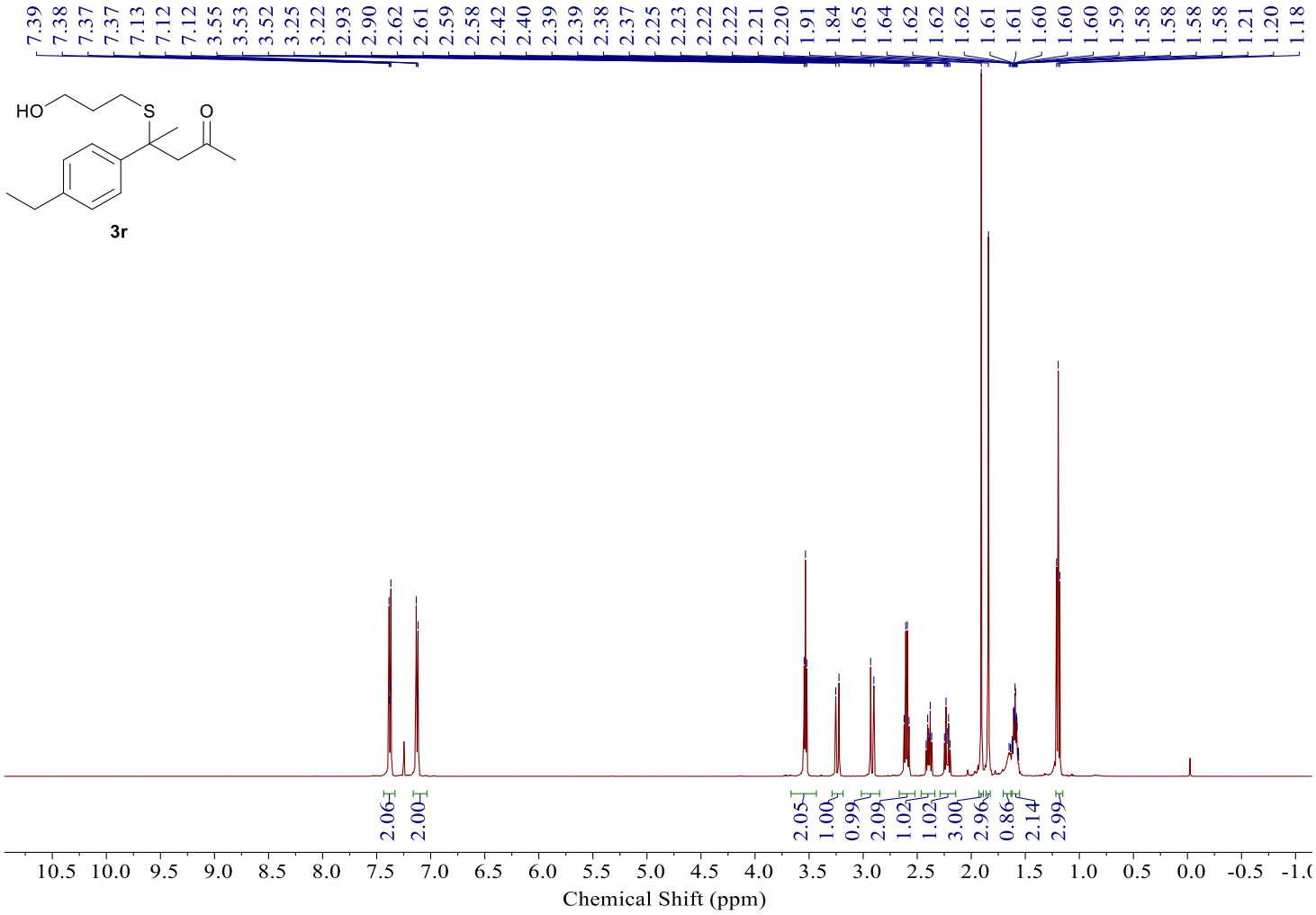


^{13}C NMR of compound **3q**



^{1}H NMR of compound **3r**



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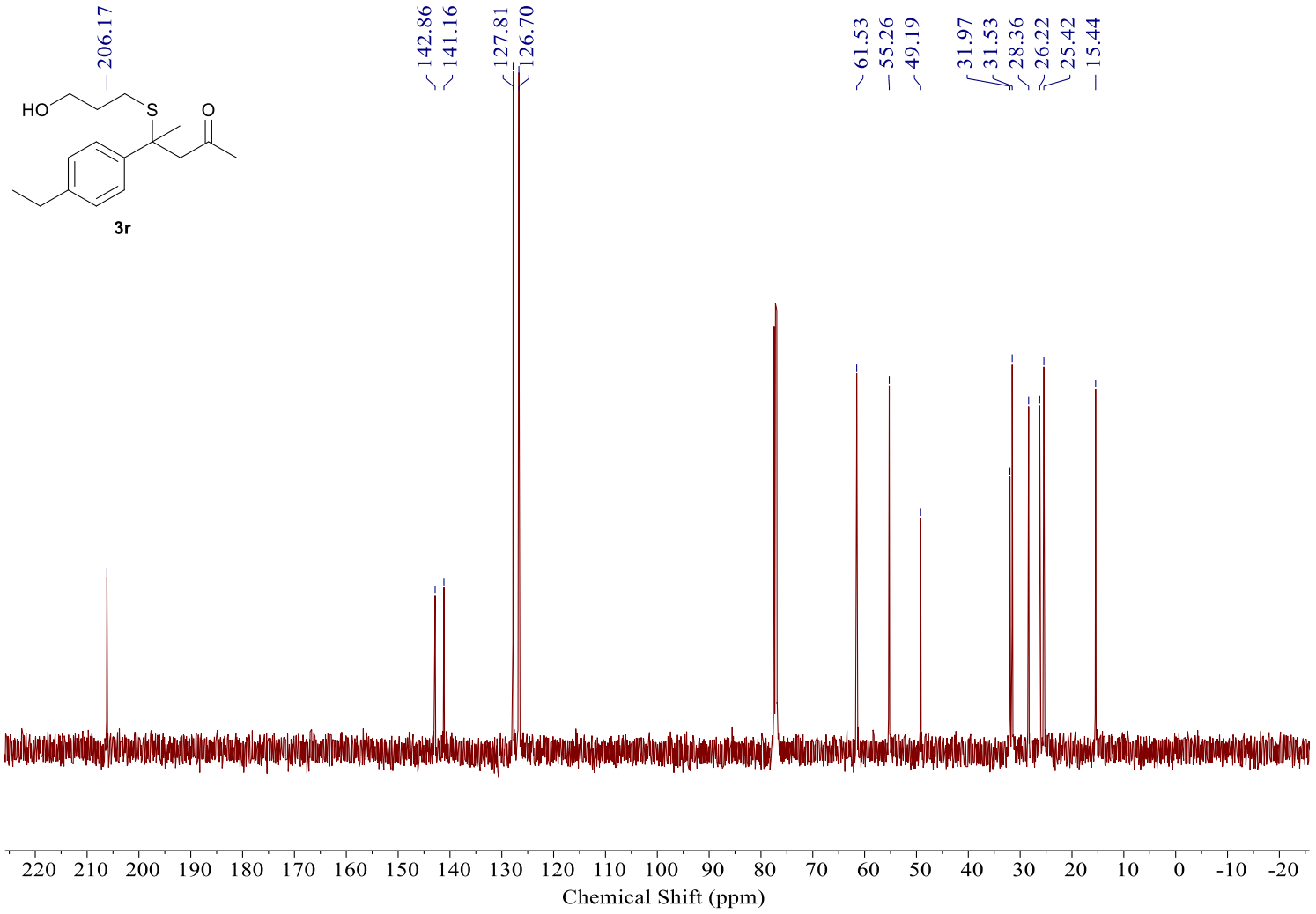

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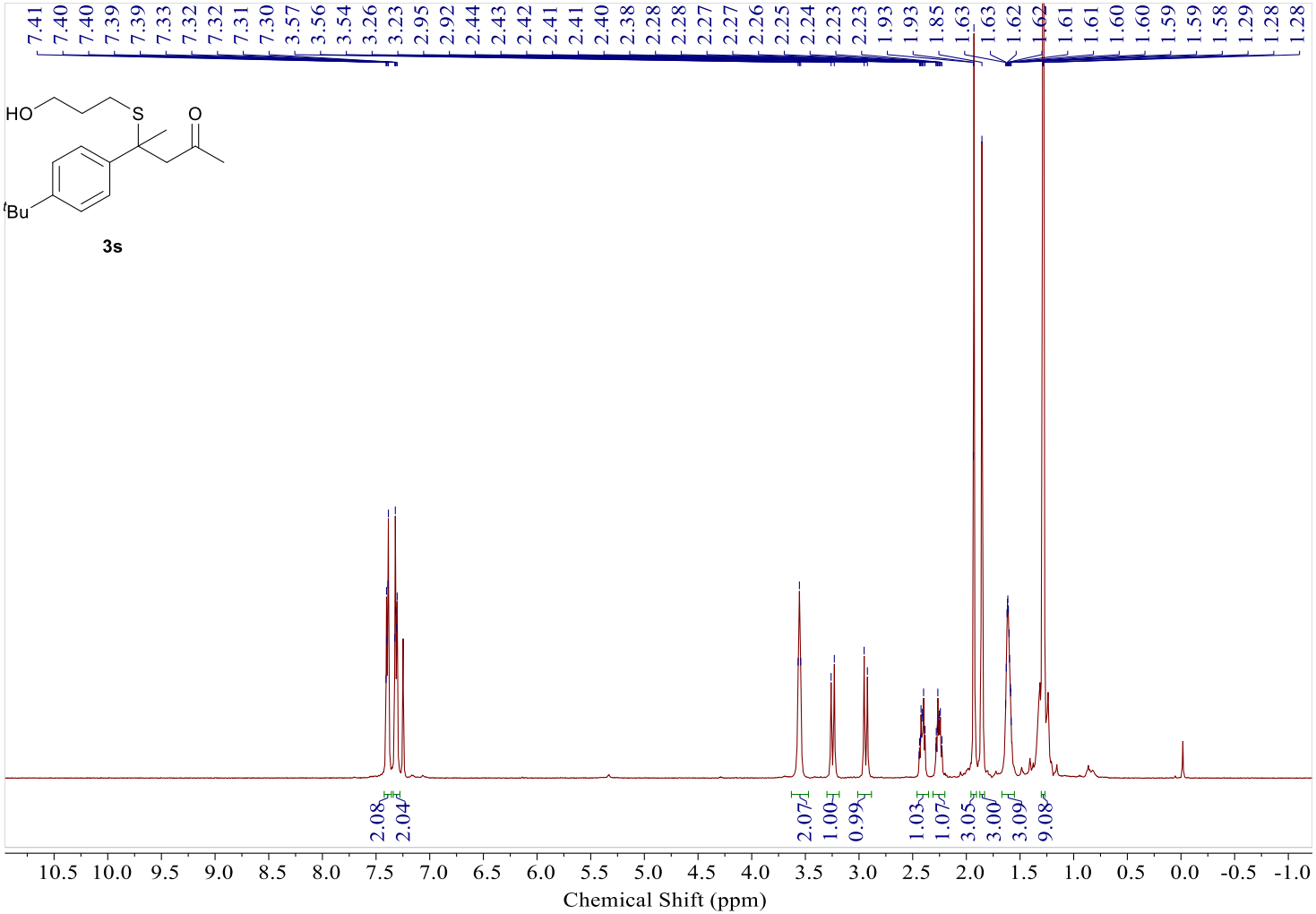

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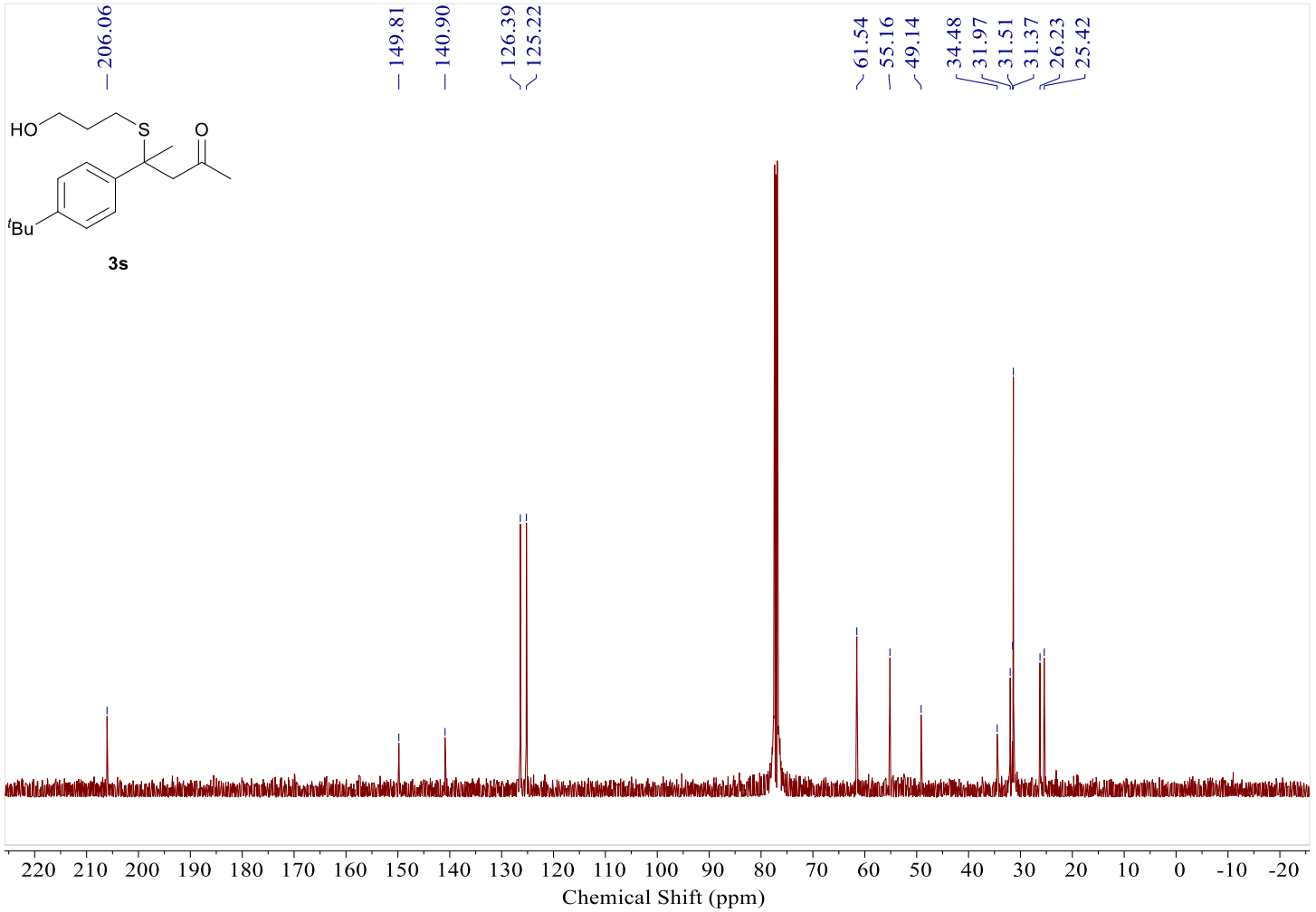

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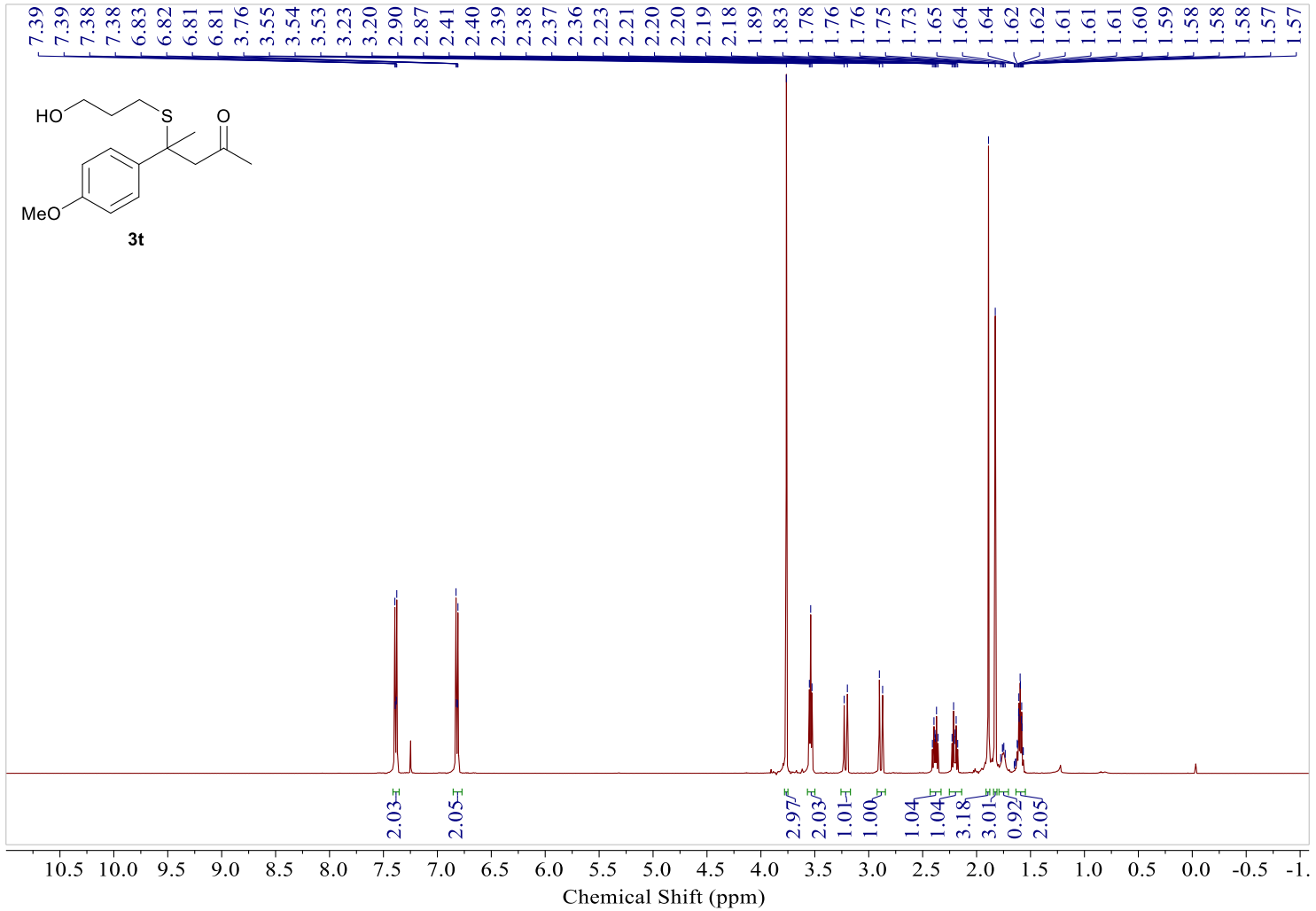

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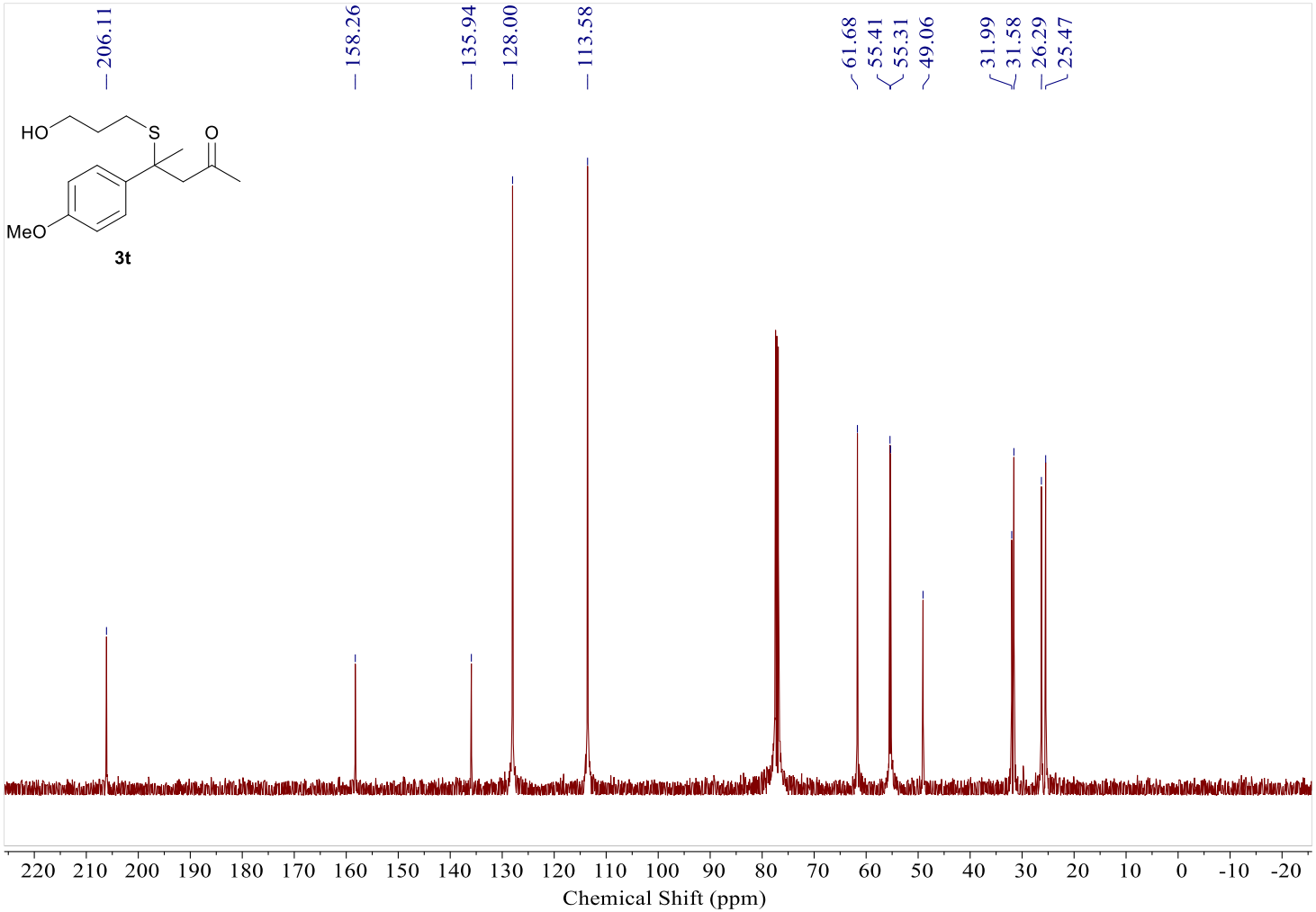

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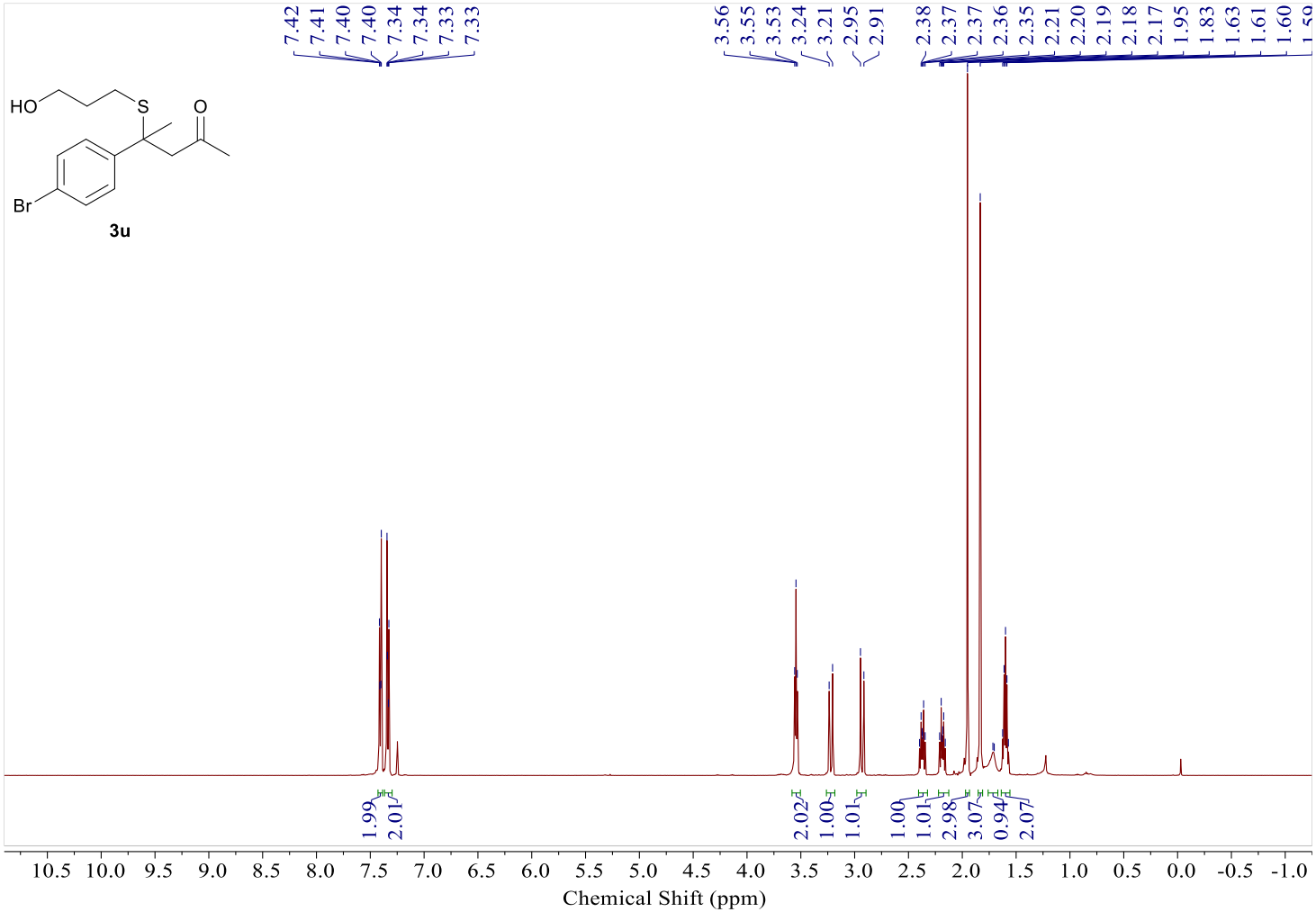

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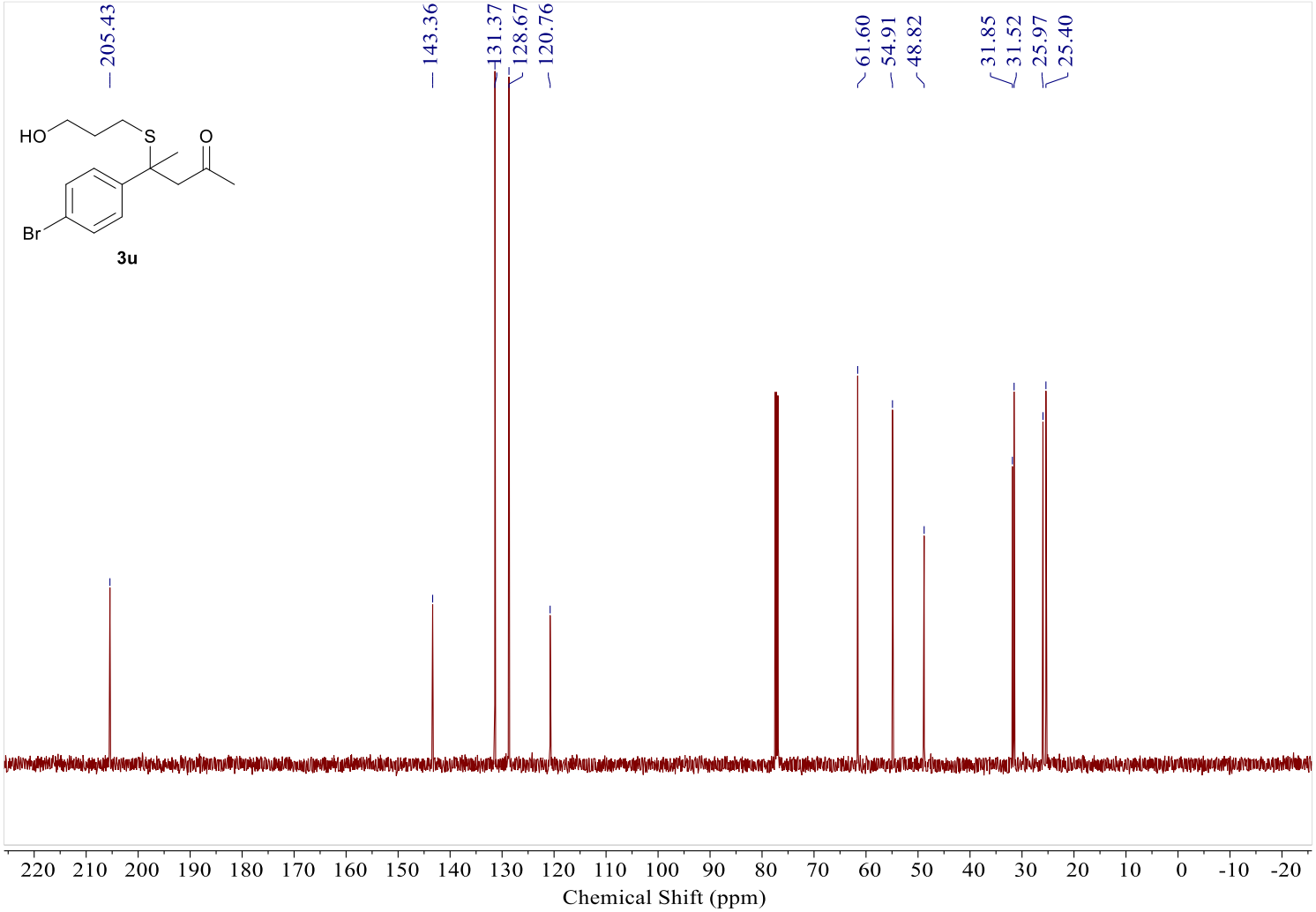

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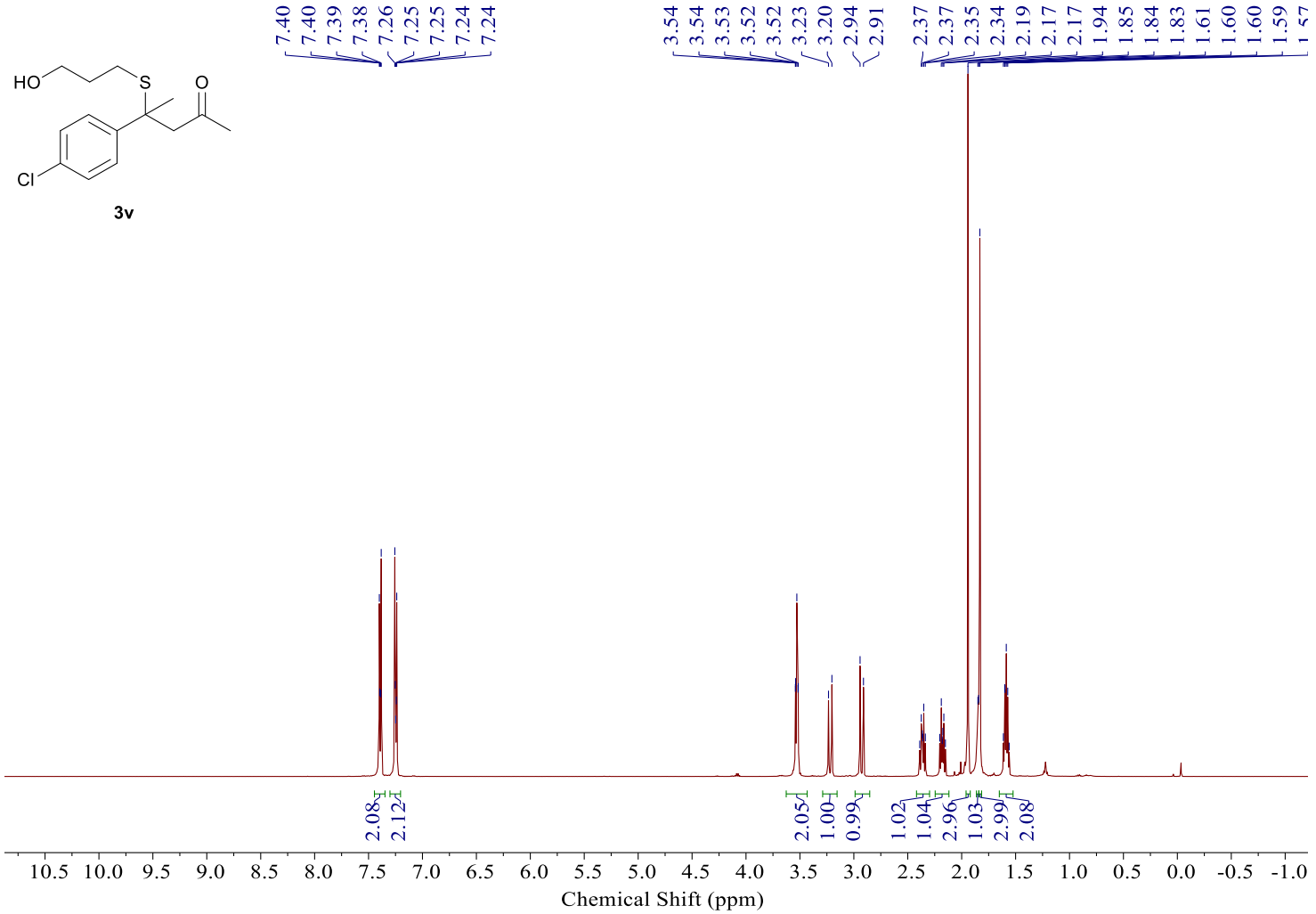
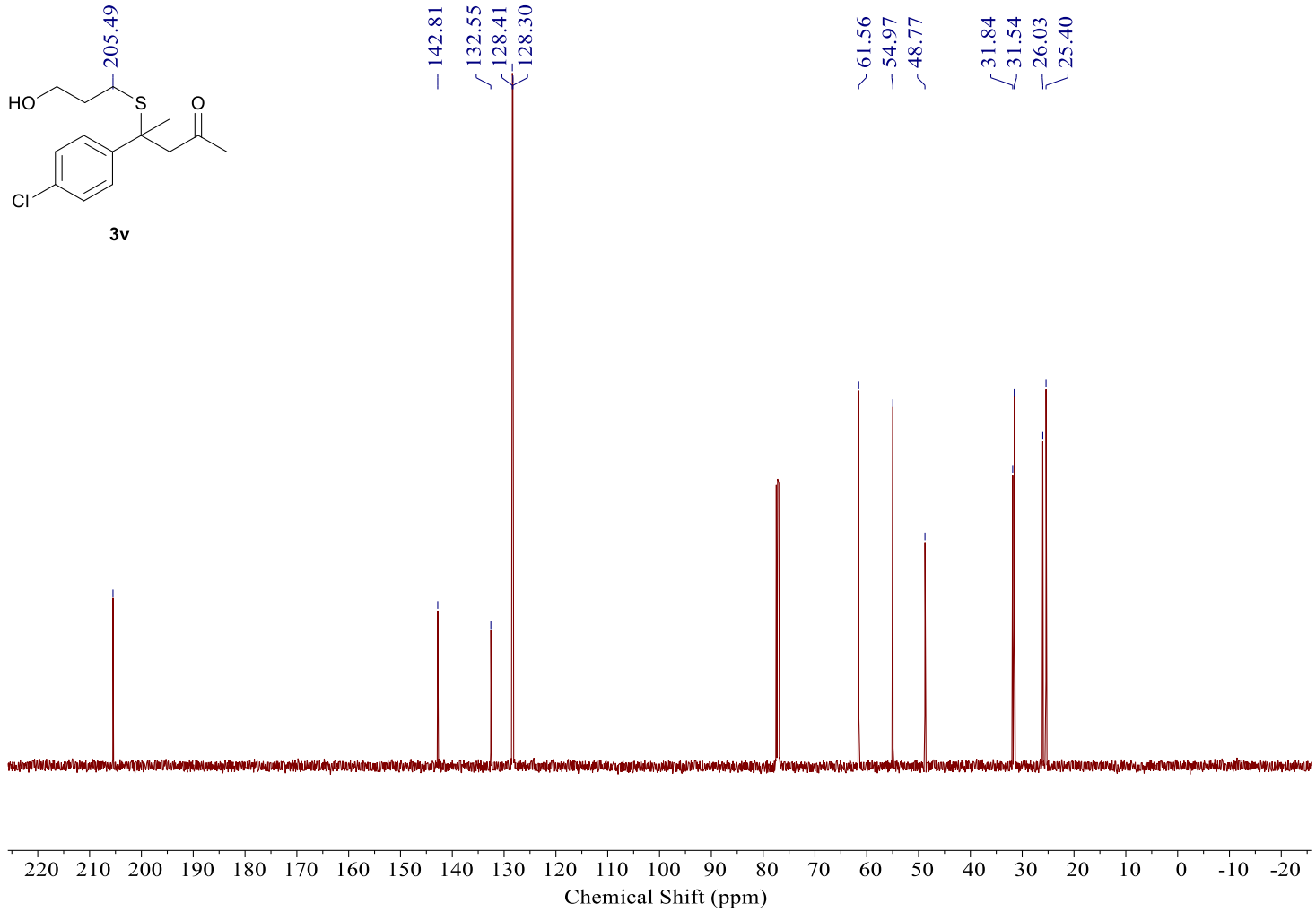


^{13}C NMR of compound **3v**



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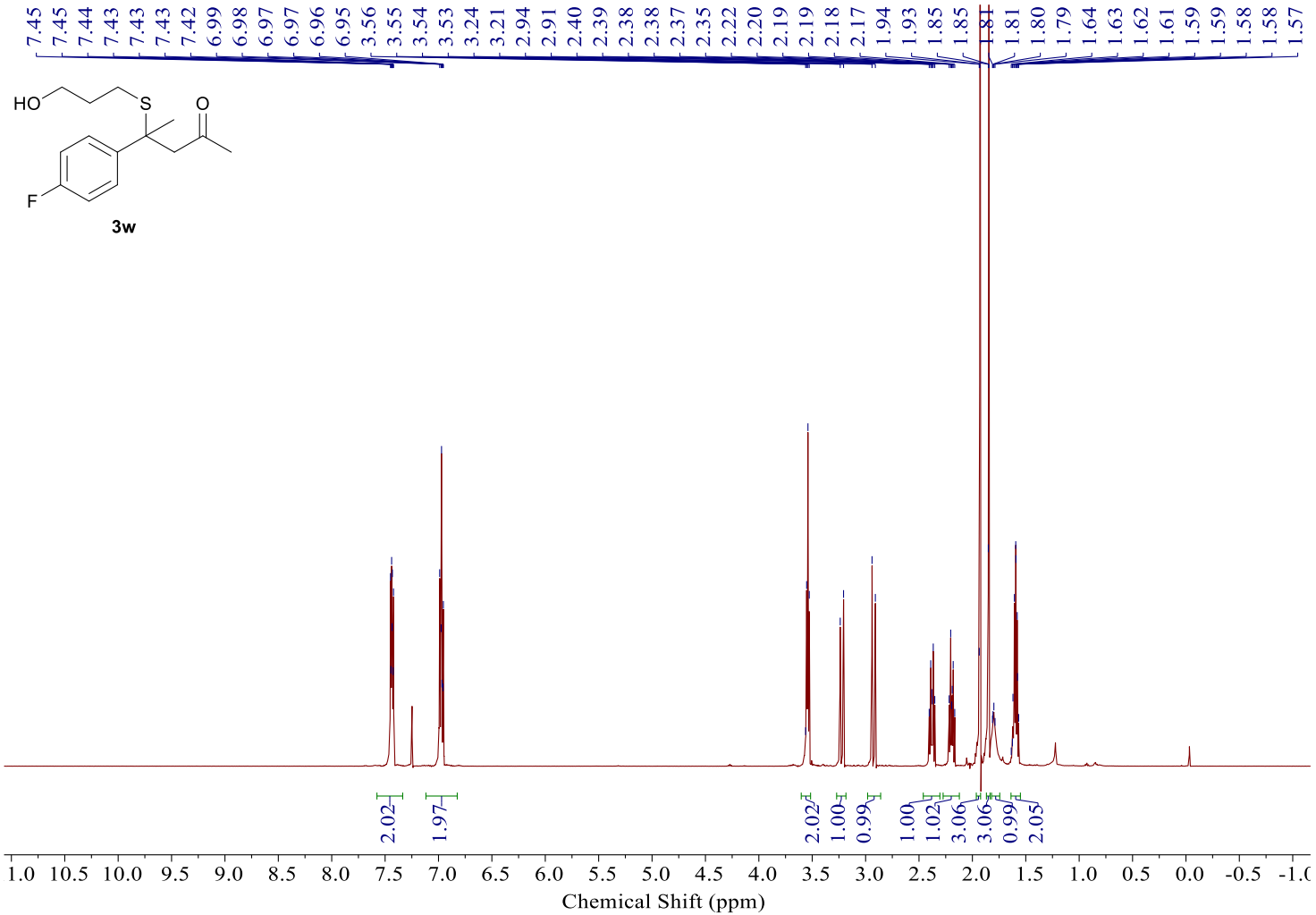

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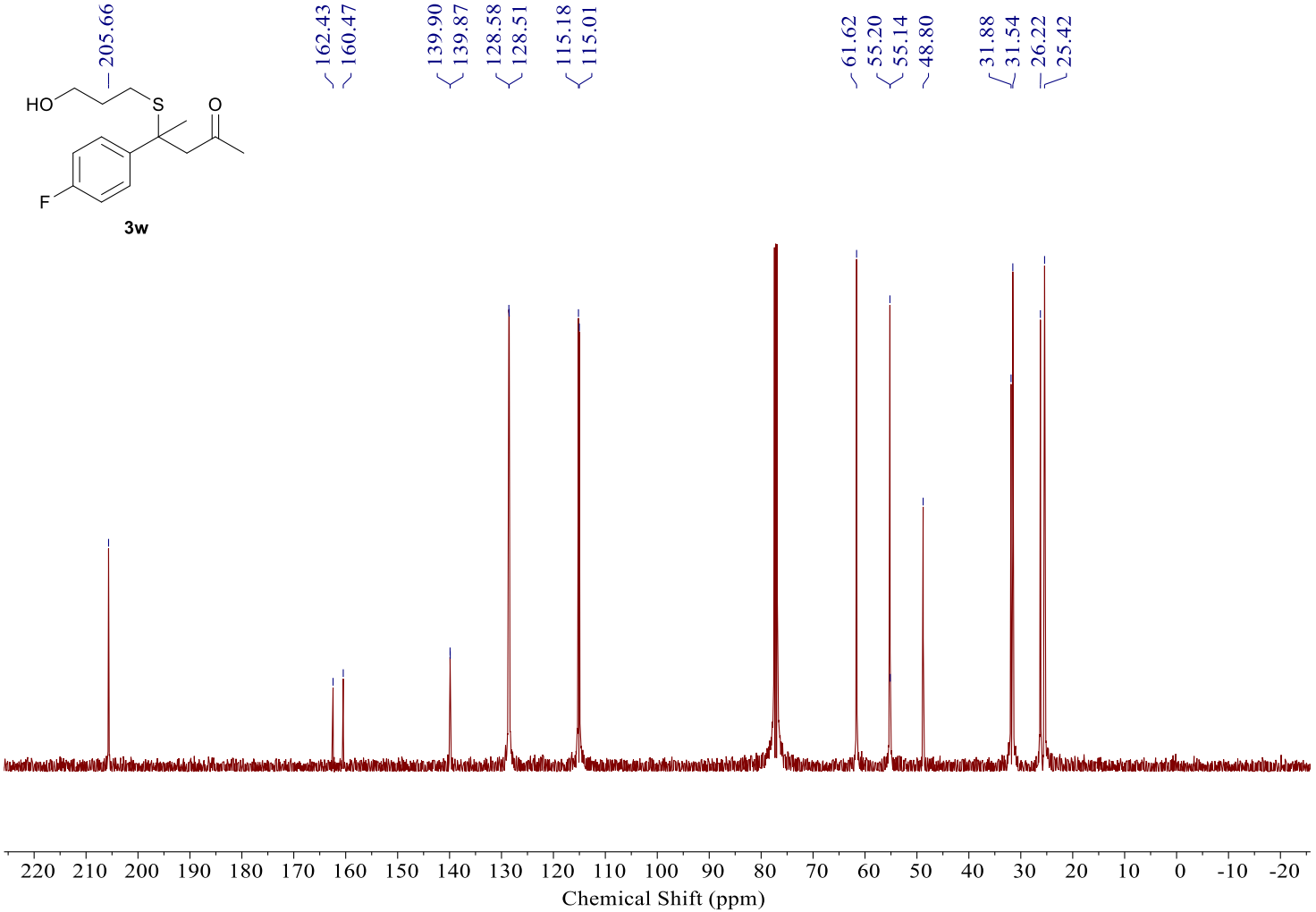
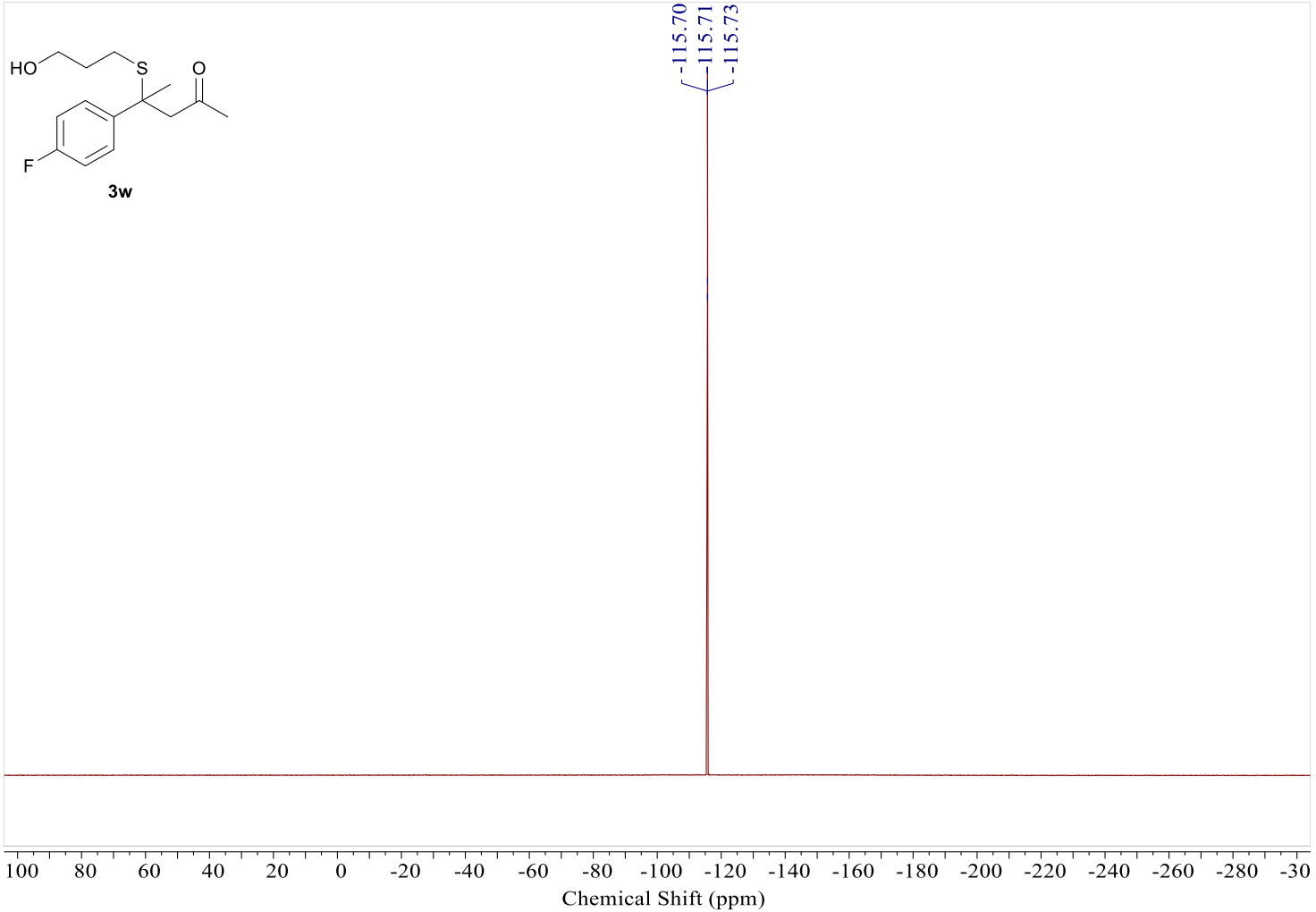
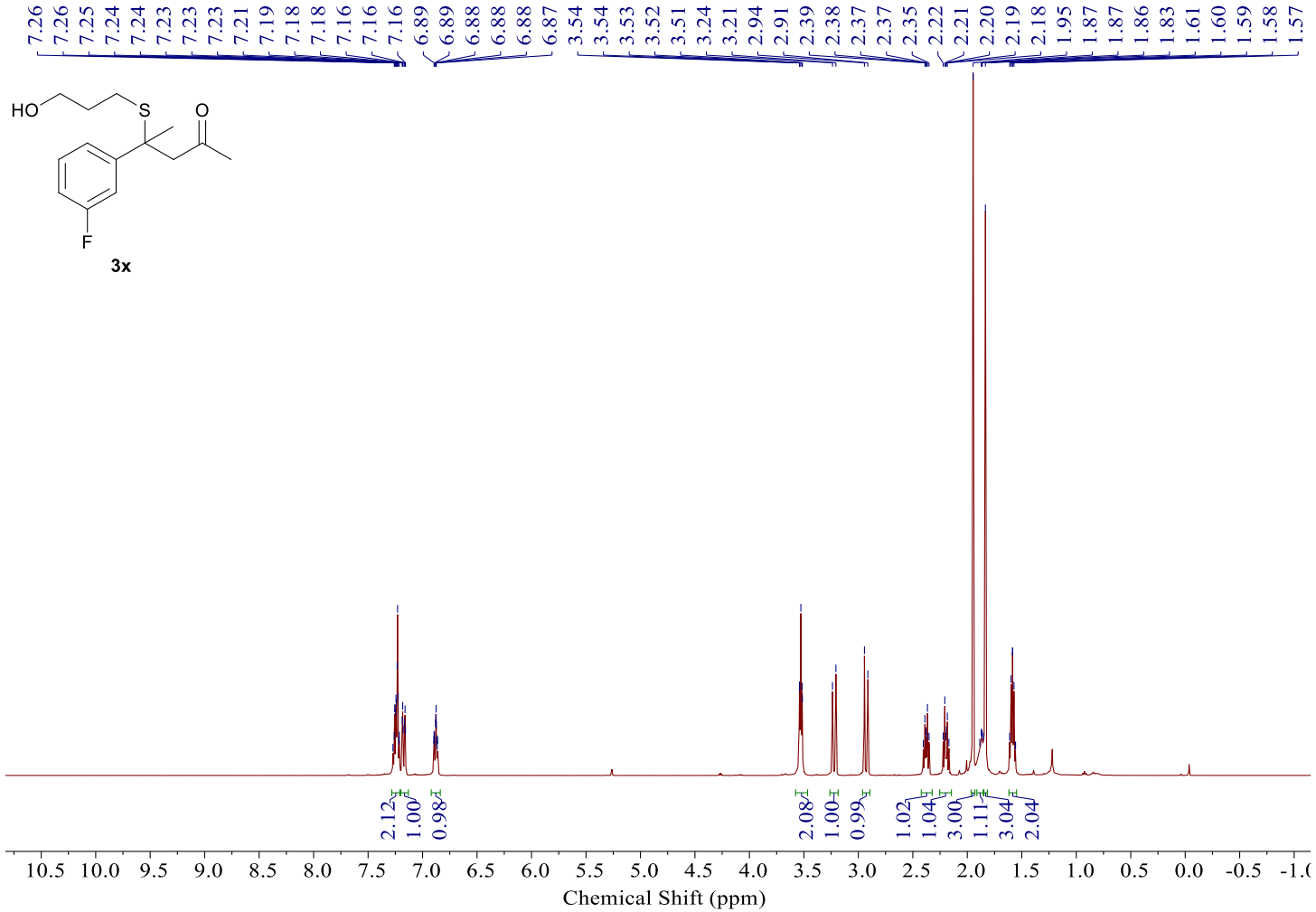


^{19}F NMR of compound **3w**



[1]H NMR of compound **3x**



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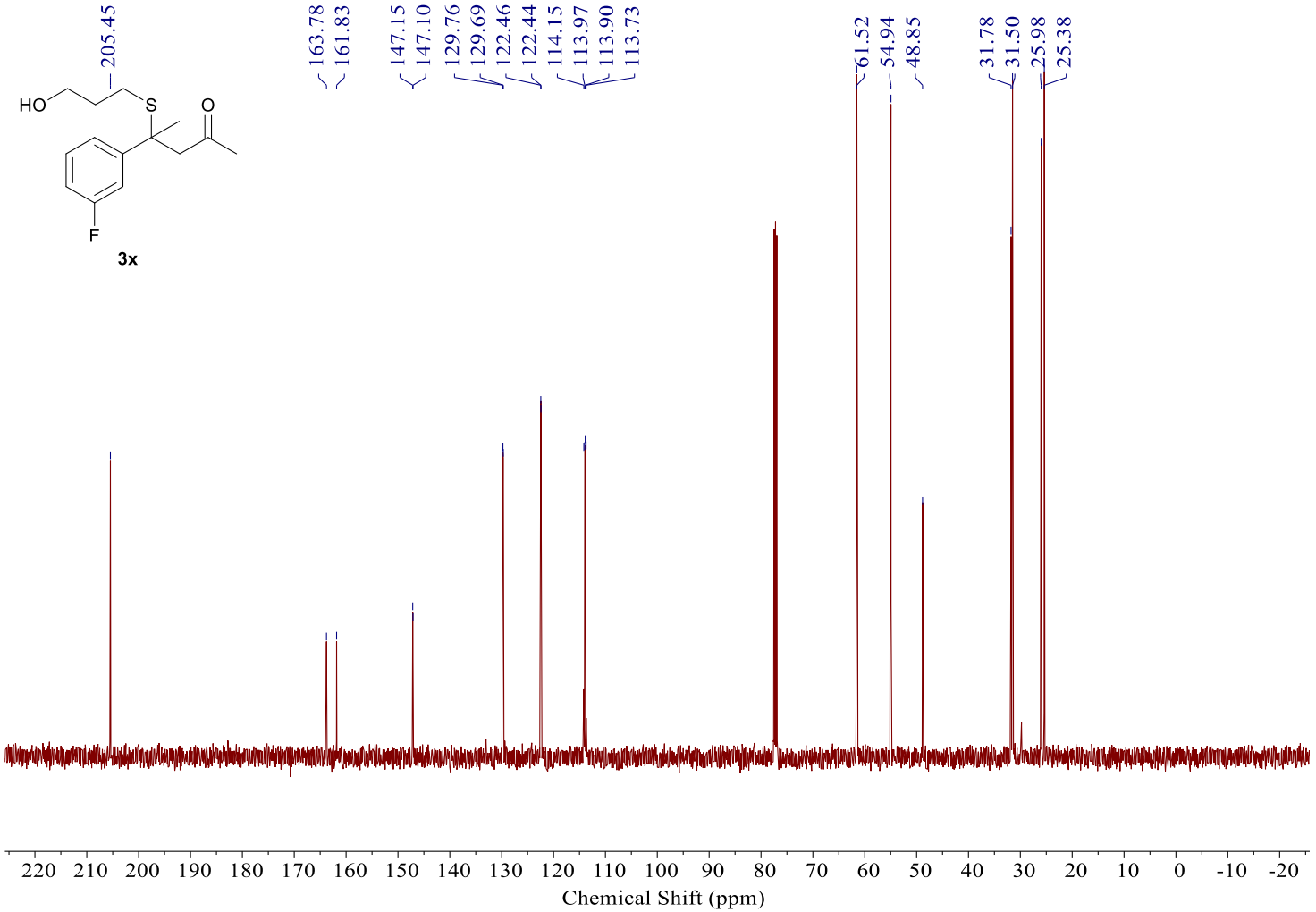

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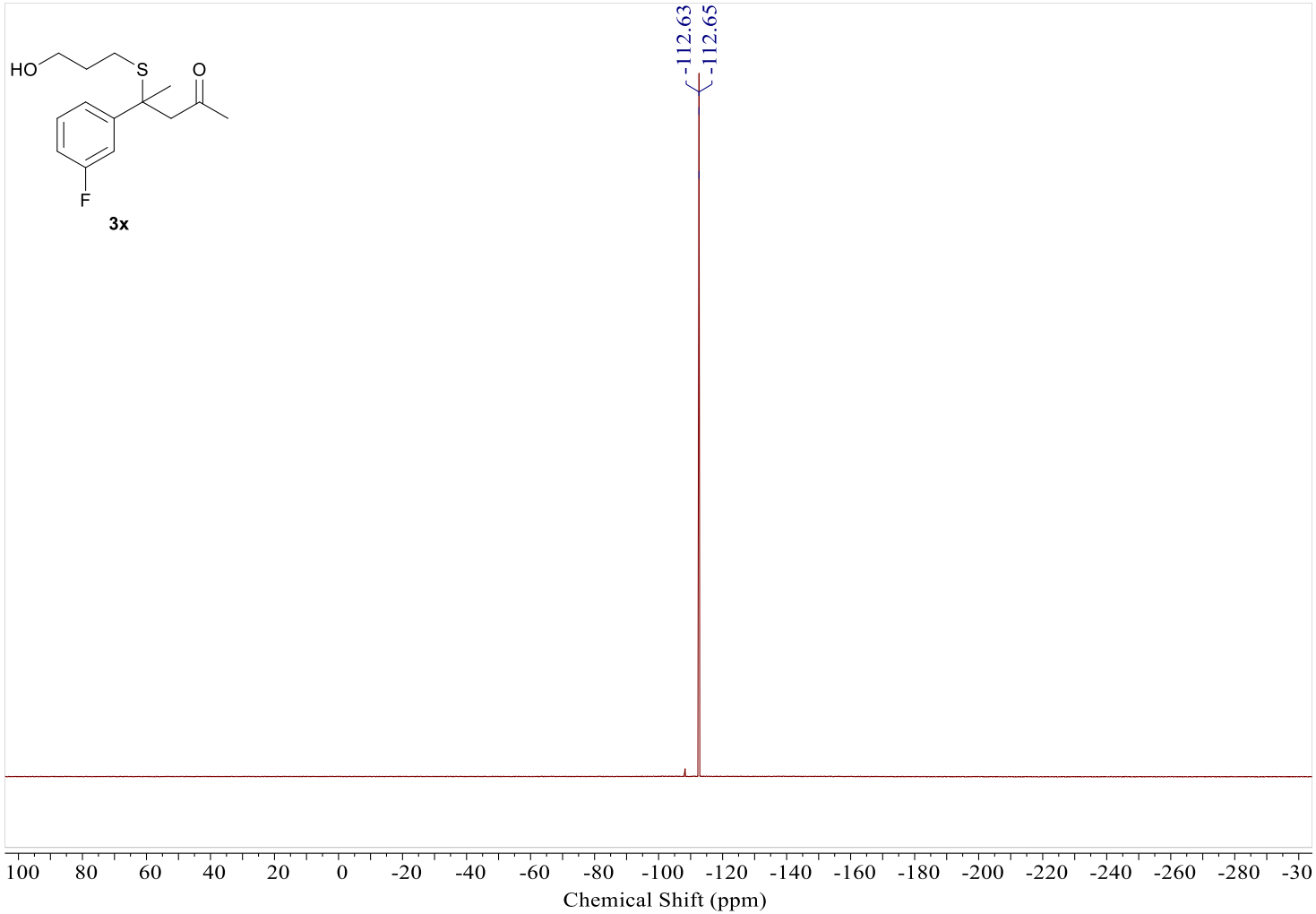
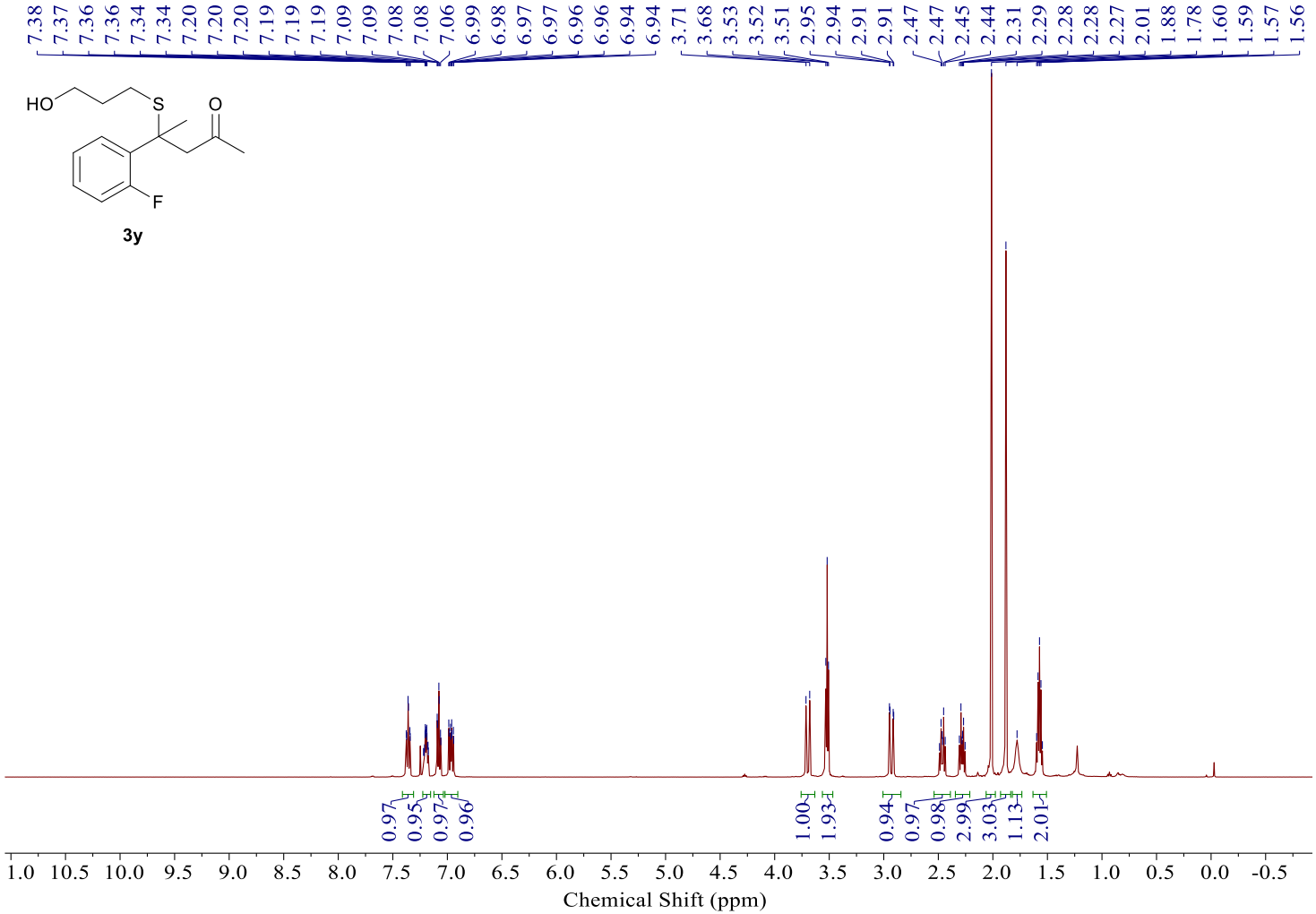


^{1}H NMR of compound **3y**



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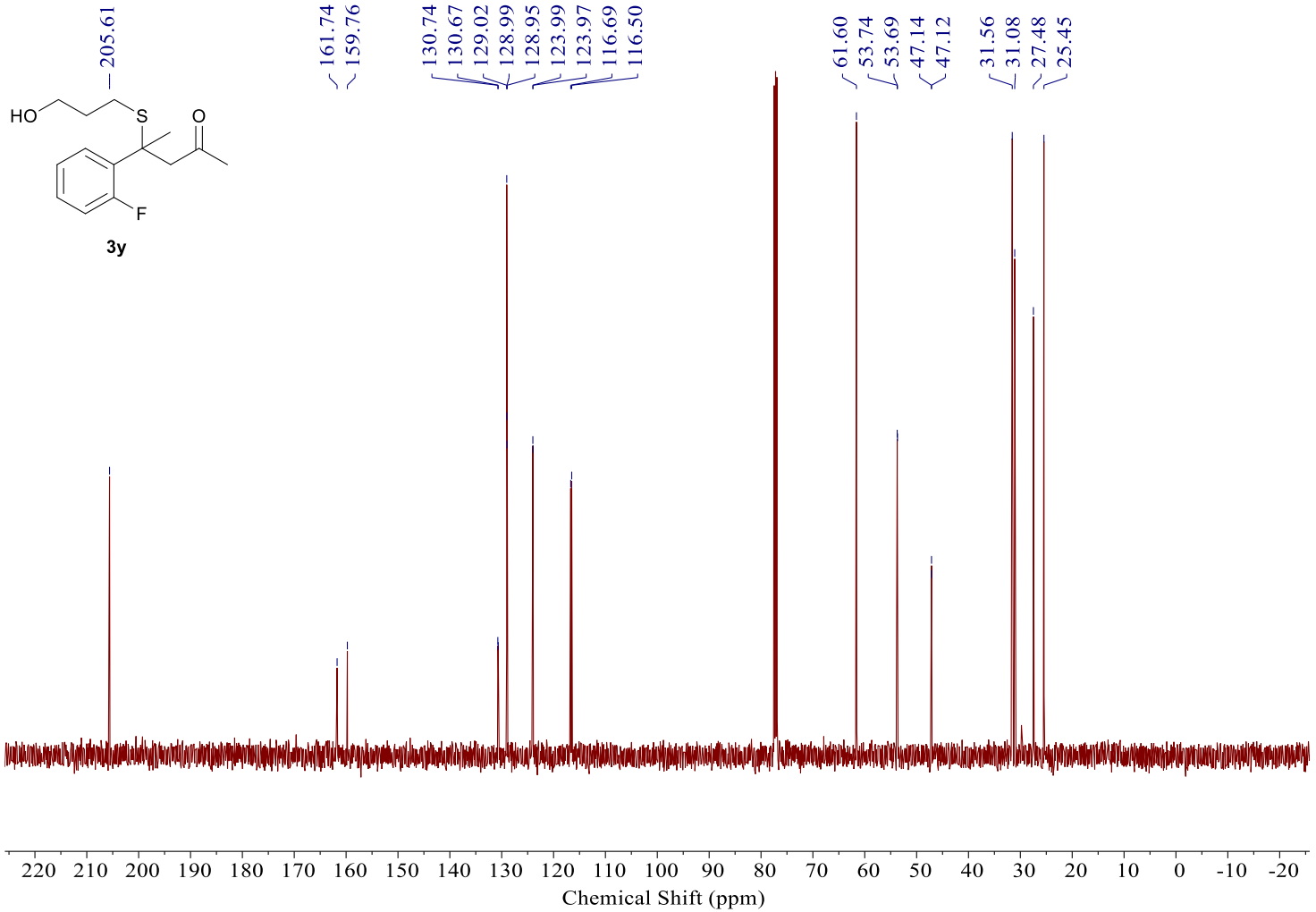

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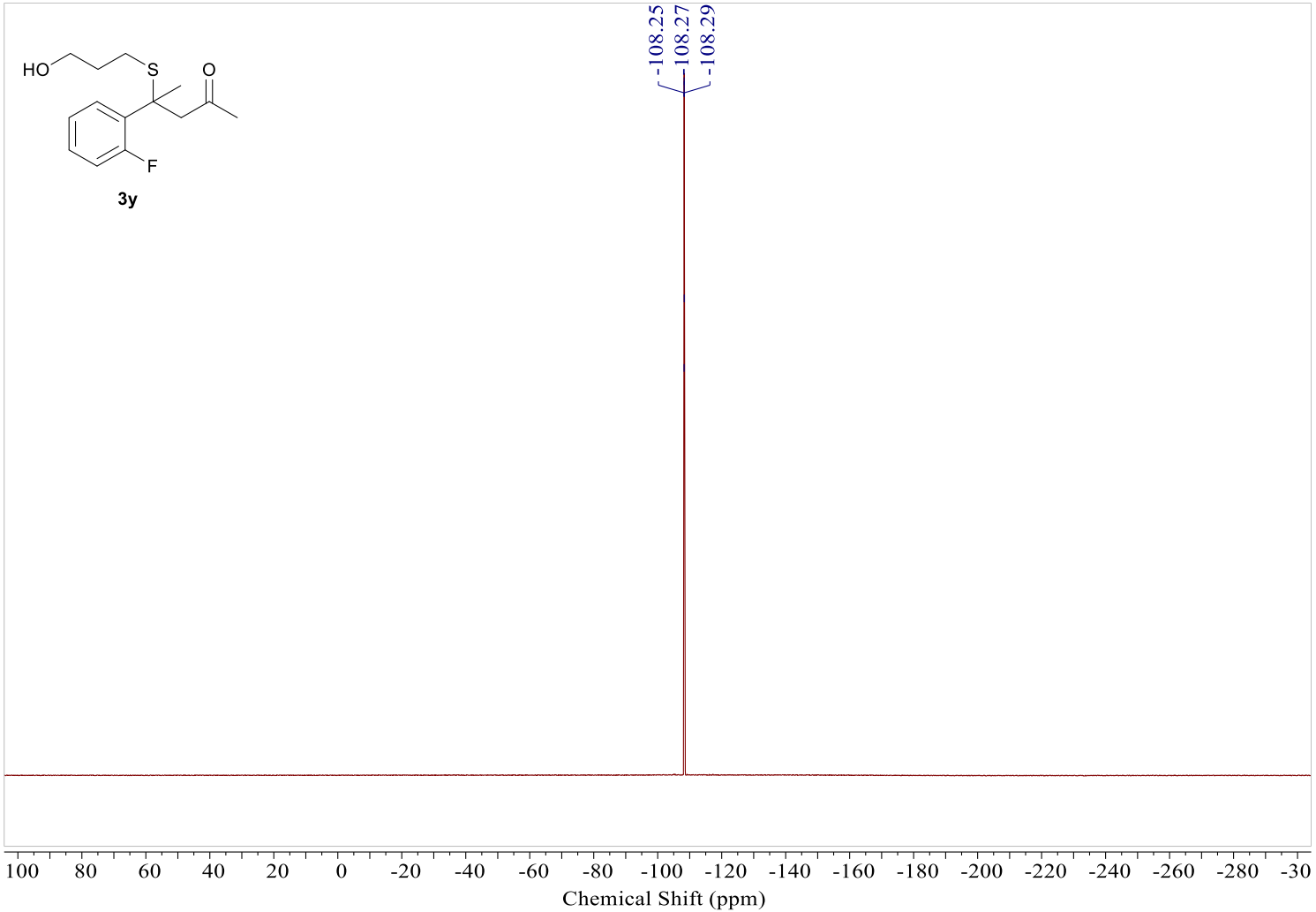

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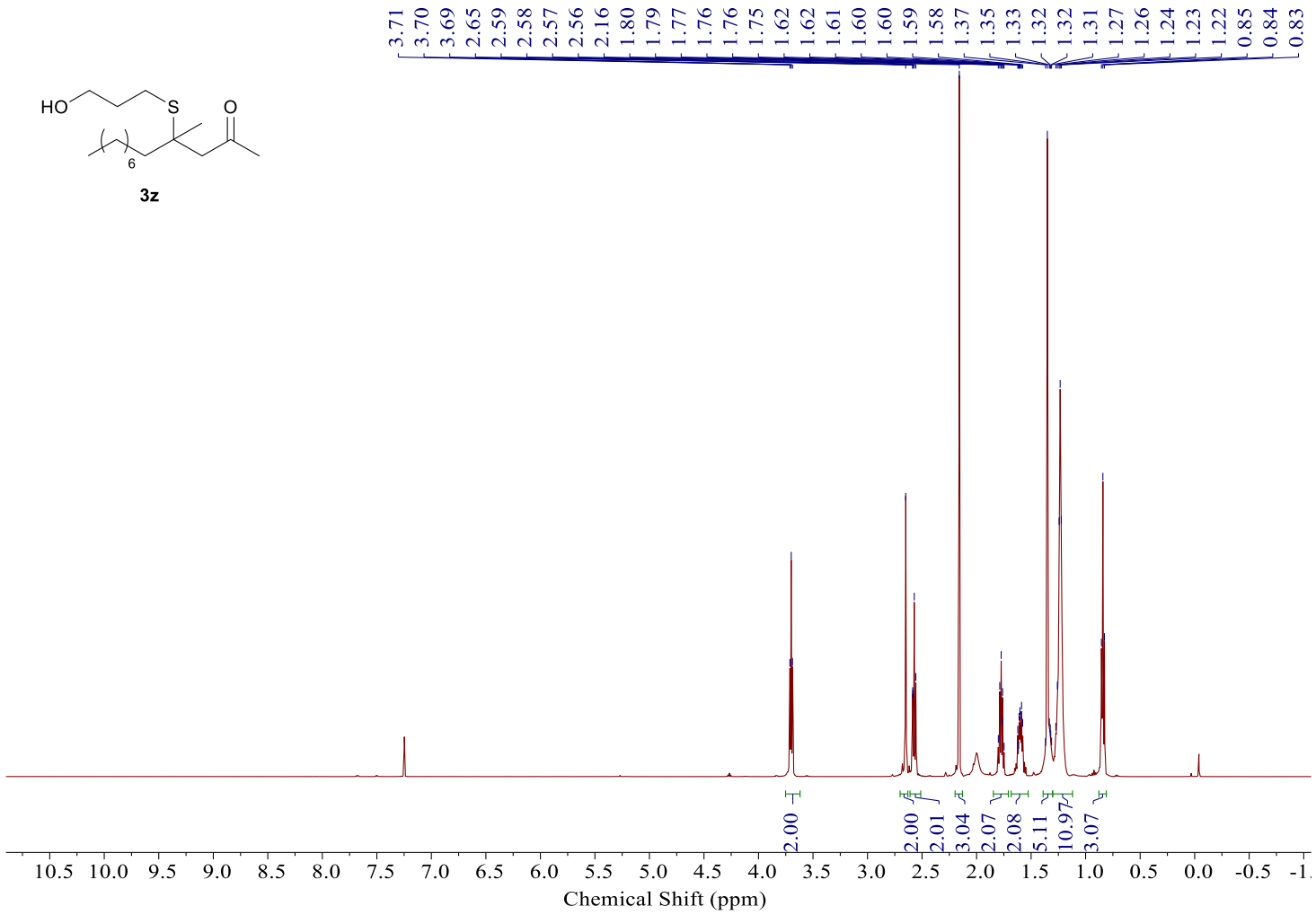

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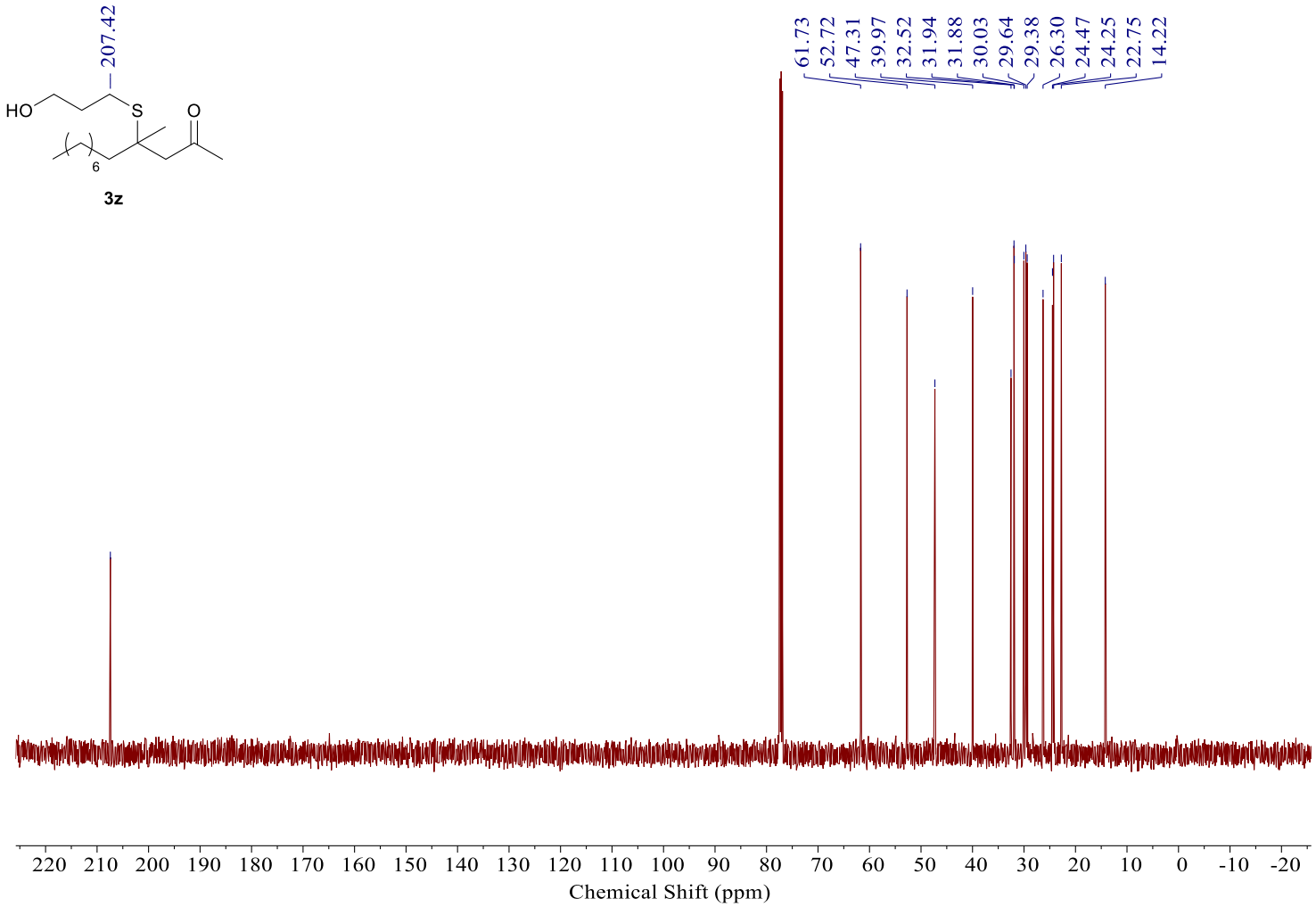

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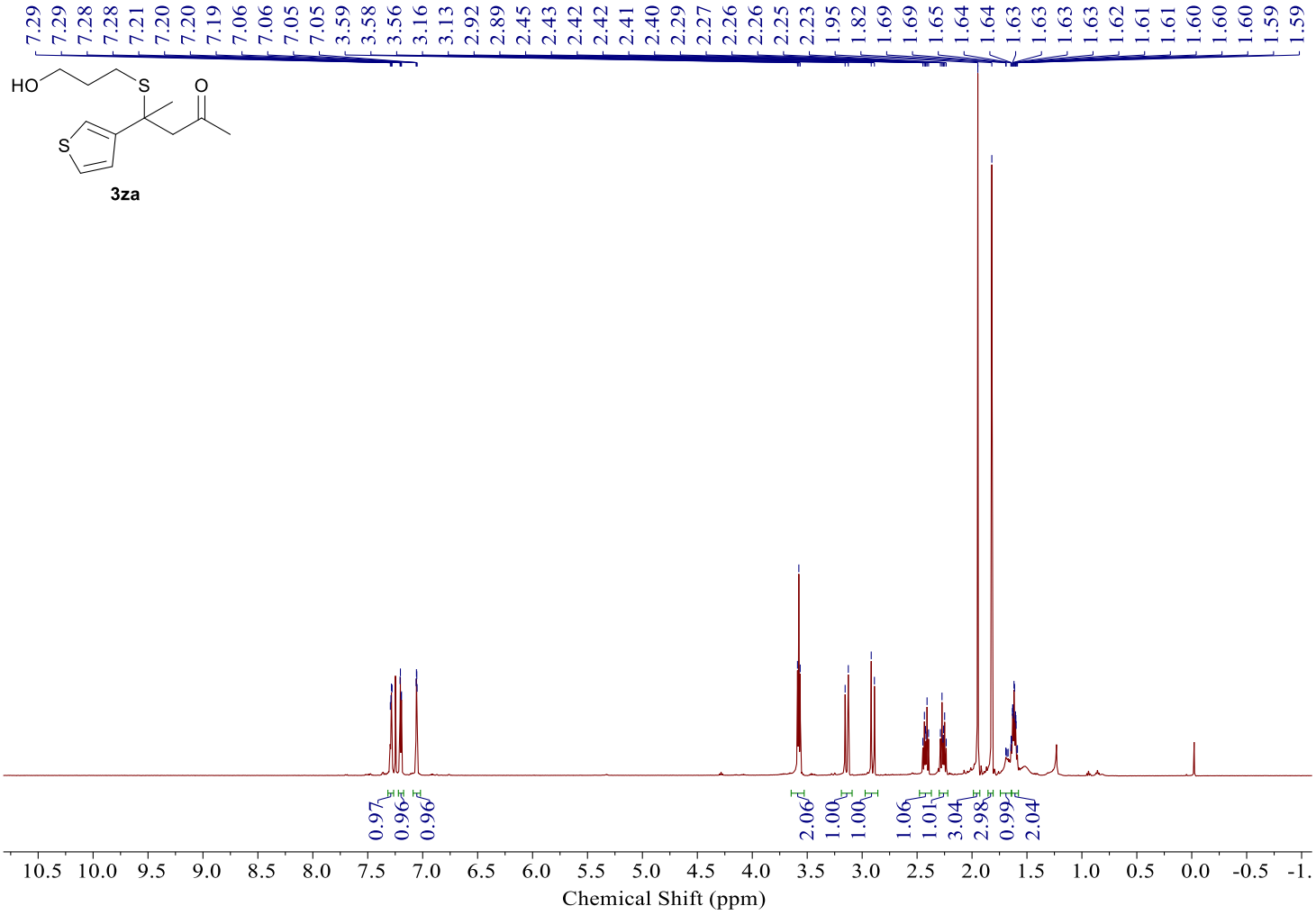

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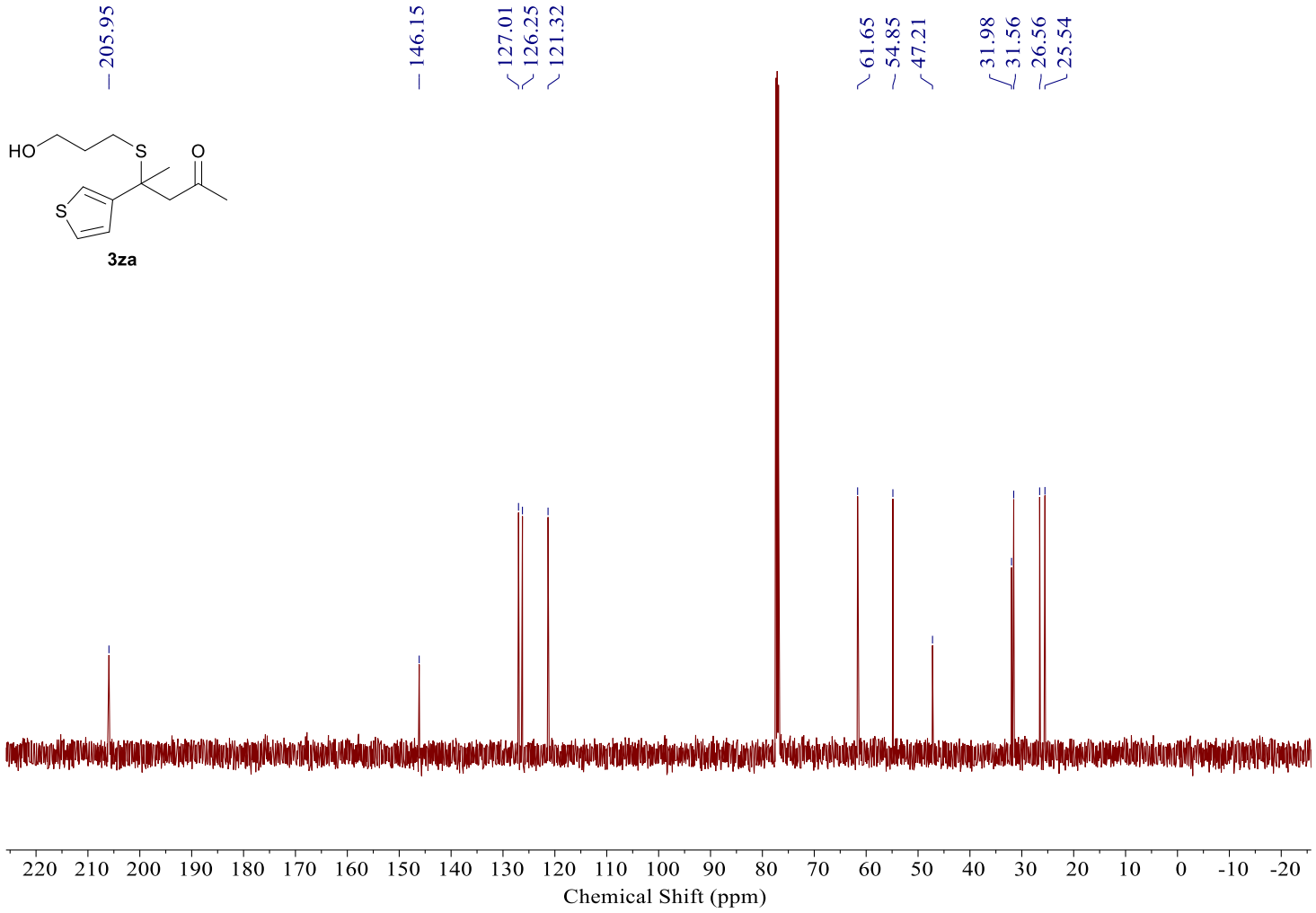

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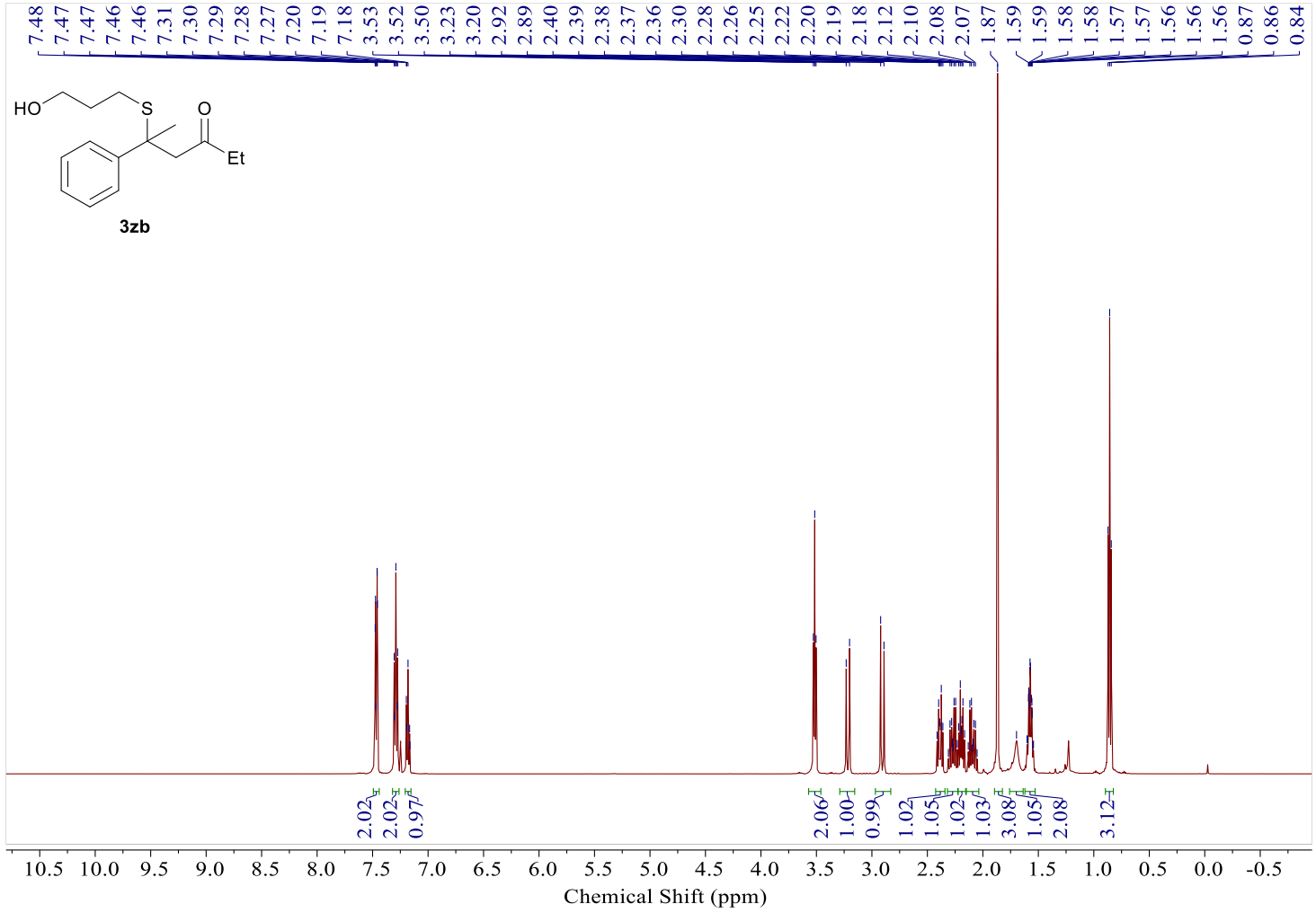

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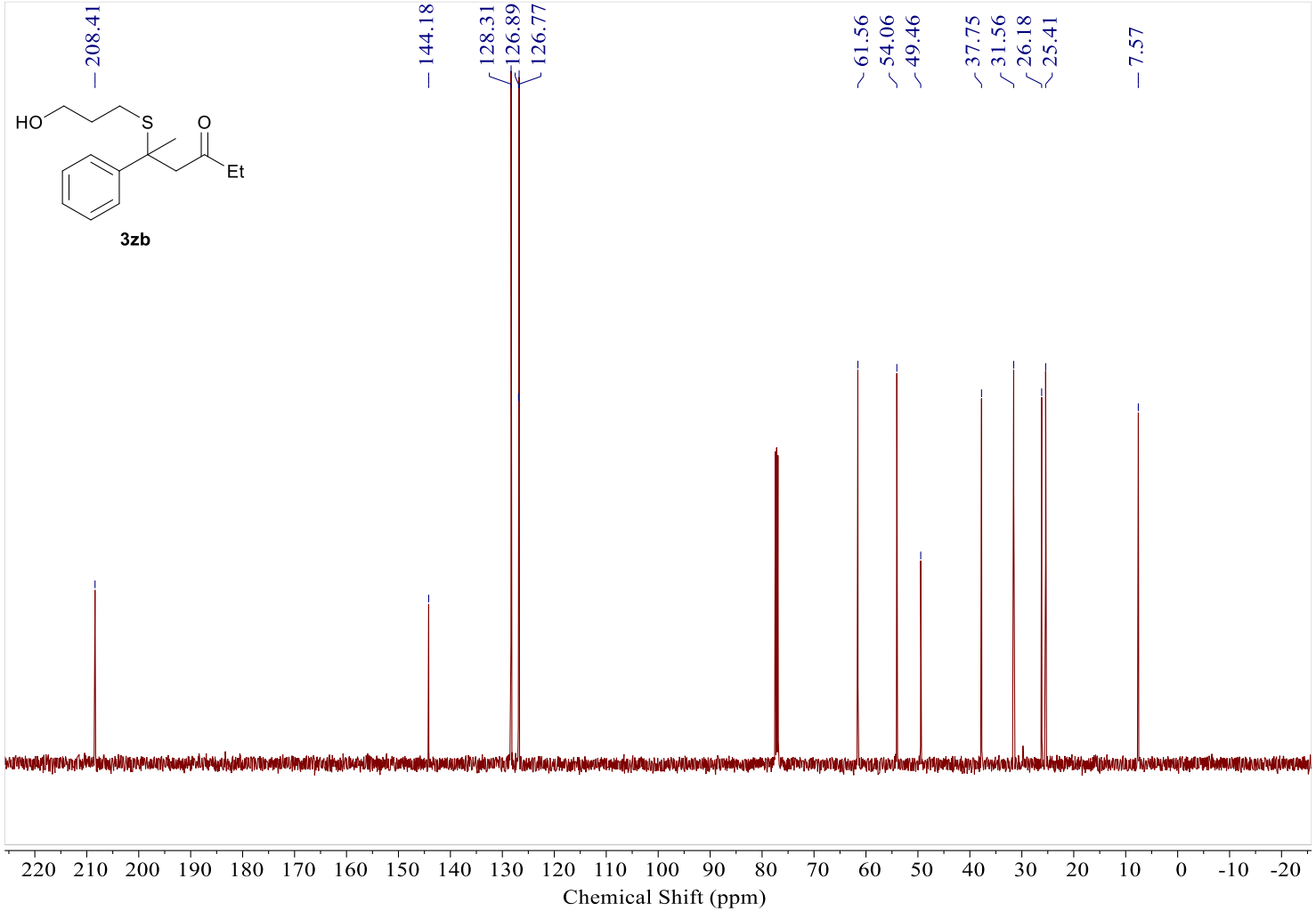

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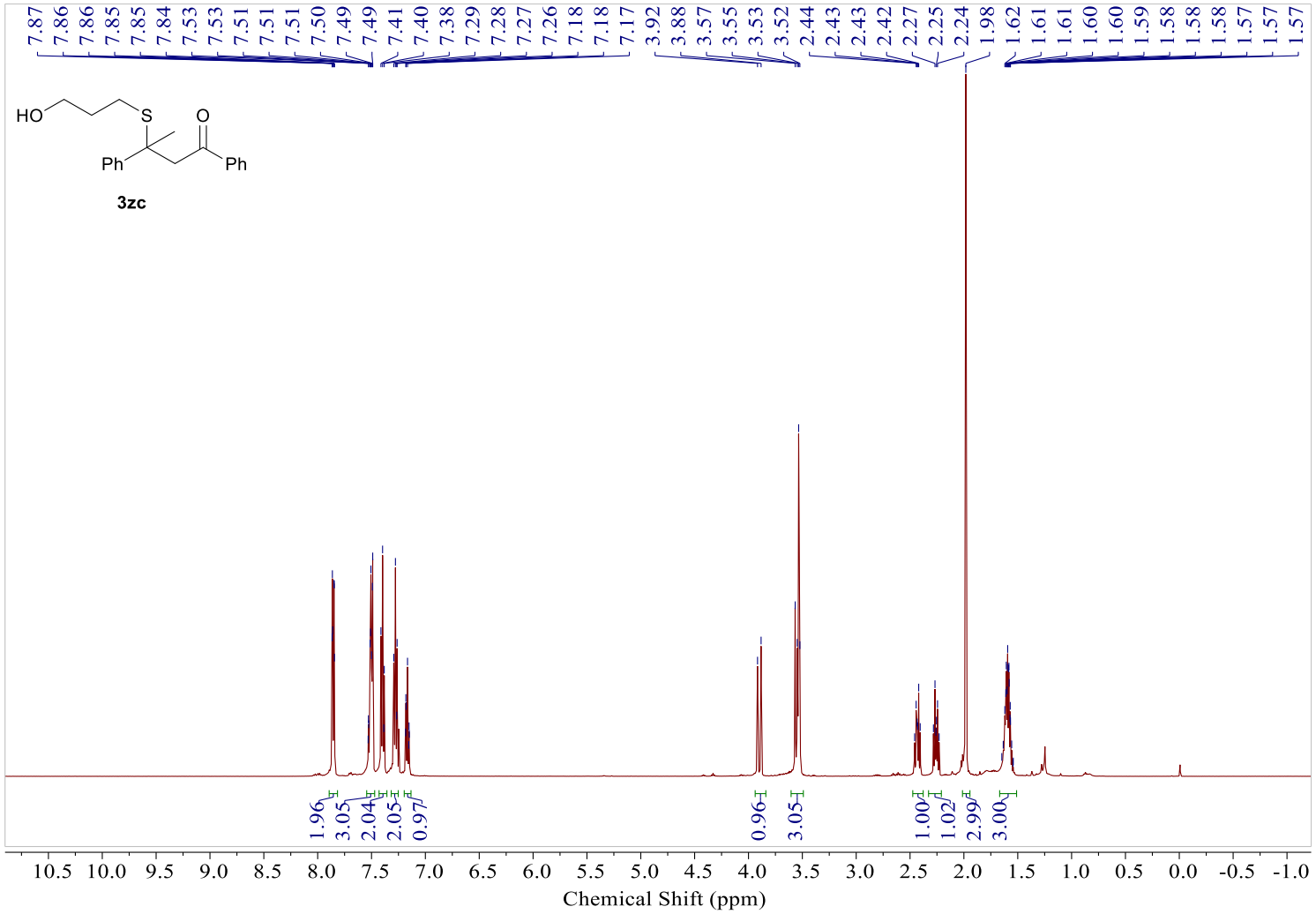

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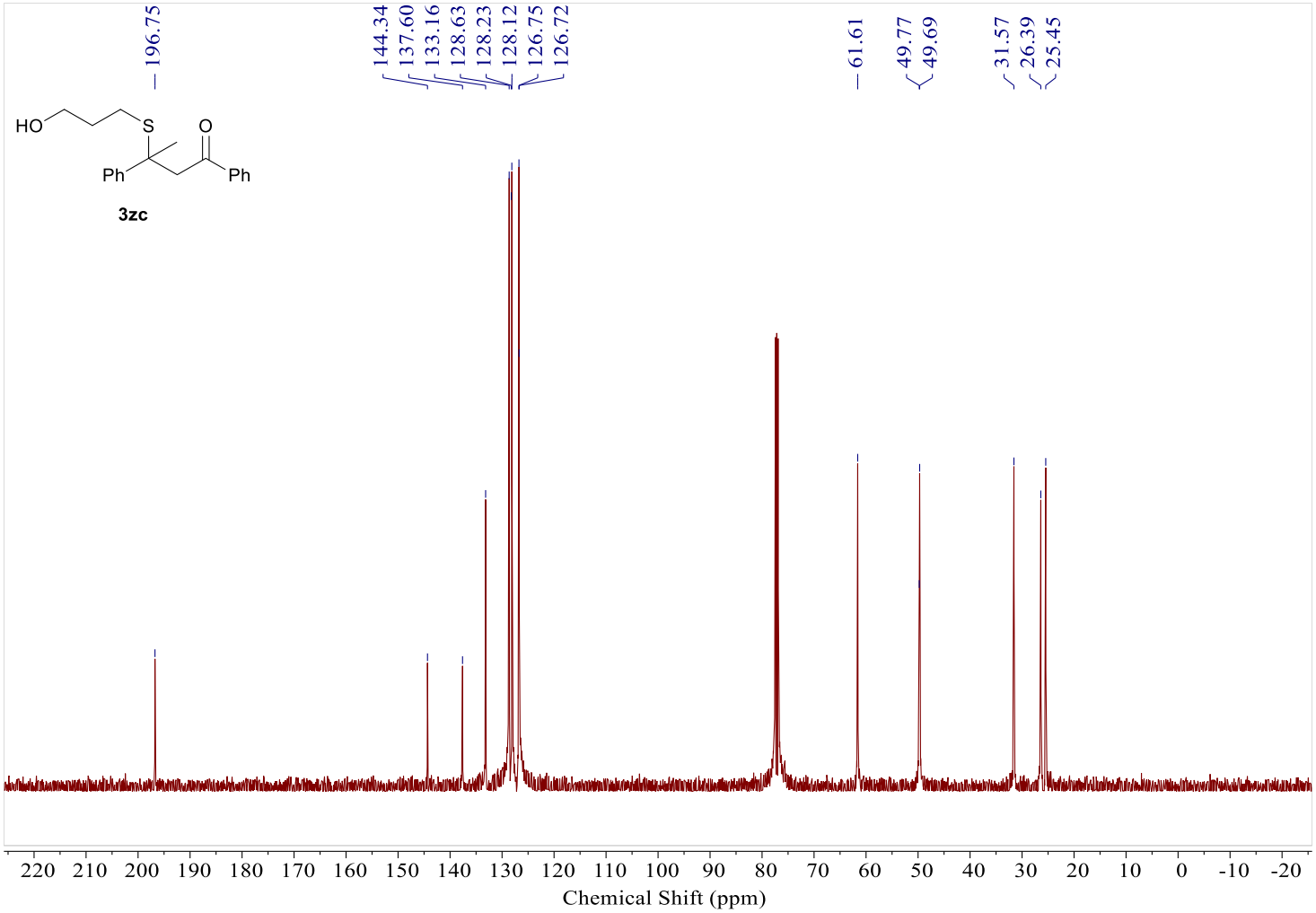

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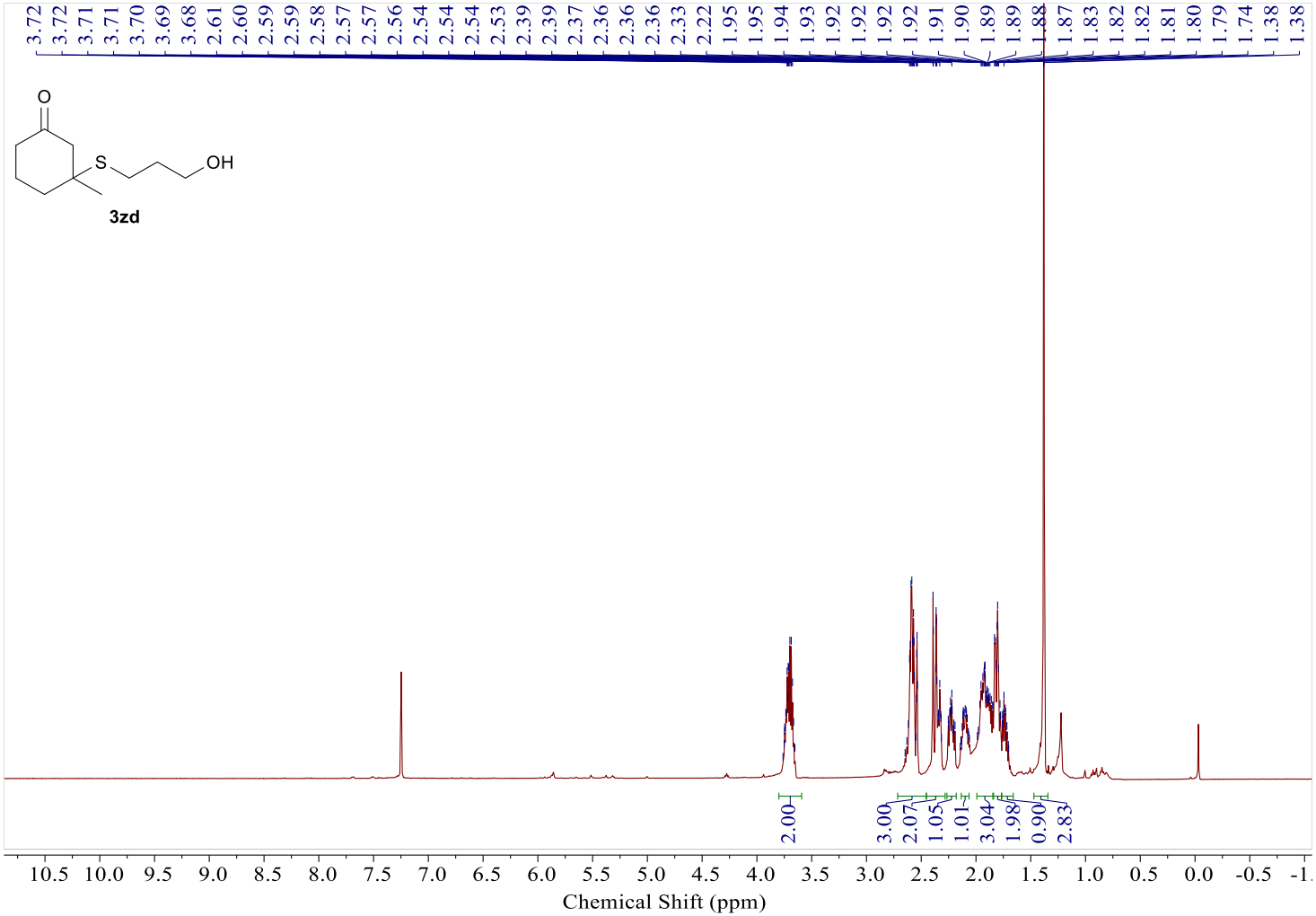

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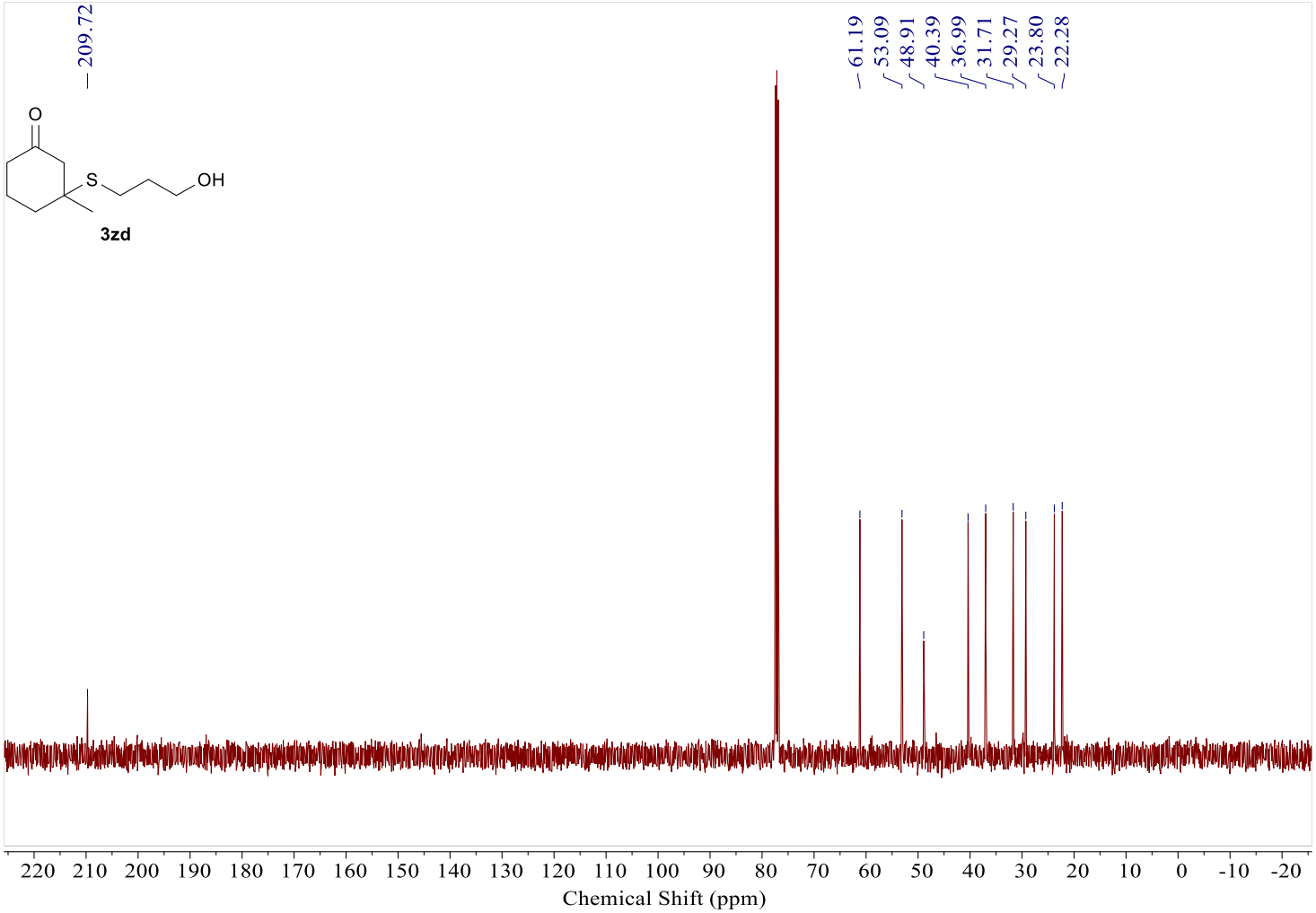
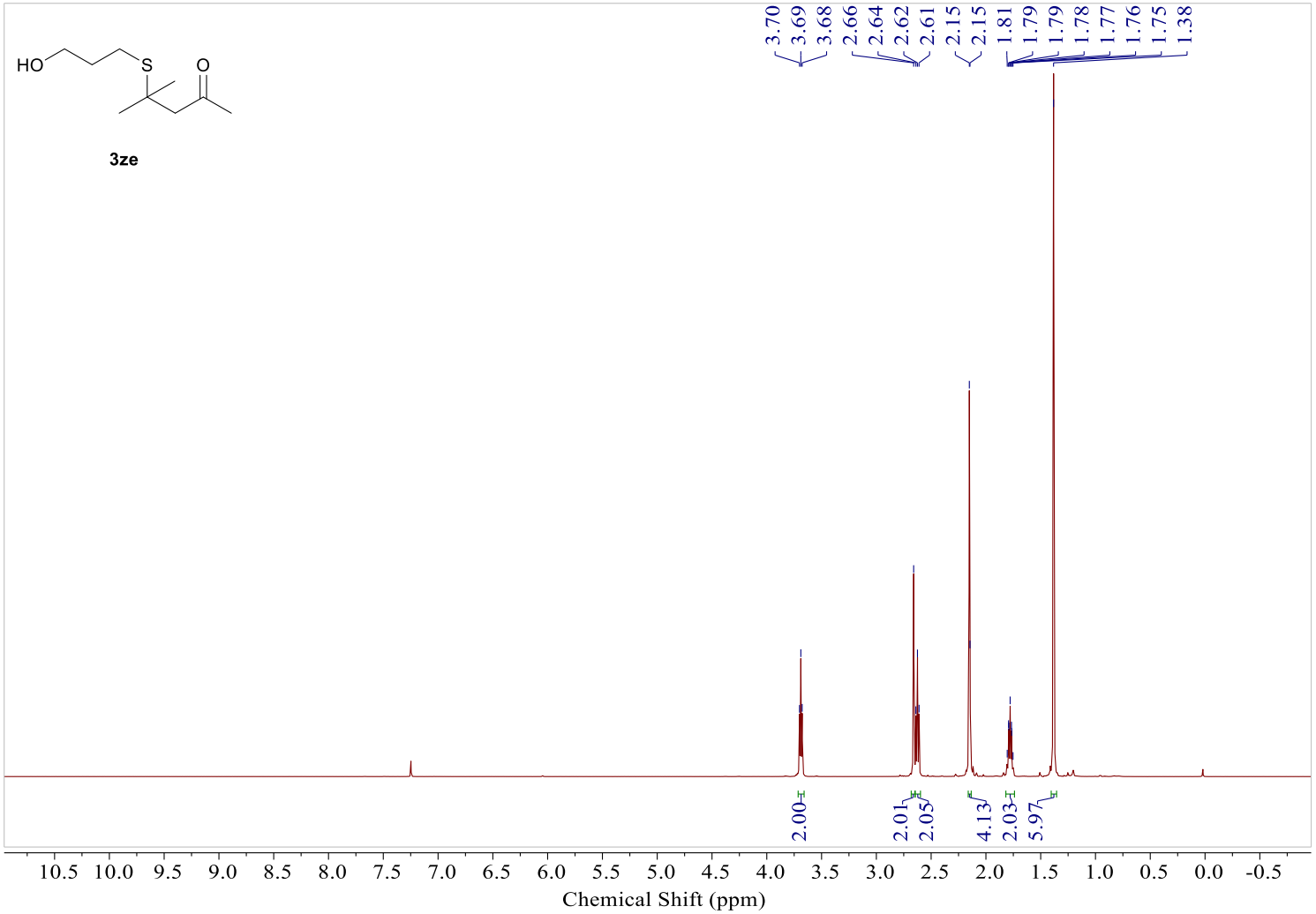


[1]H NMR of compound **3ze**



^{13}C NMR of compound **3ze**