Supporting Information

Rhodium-catalyzed Intra- and Intermolecular [5+2] Cycloaddition of 3-Acyloxy-1,4-enyne and Alkyne with Concomitant 1,2-Acyloxy Migration

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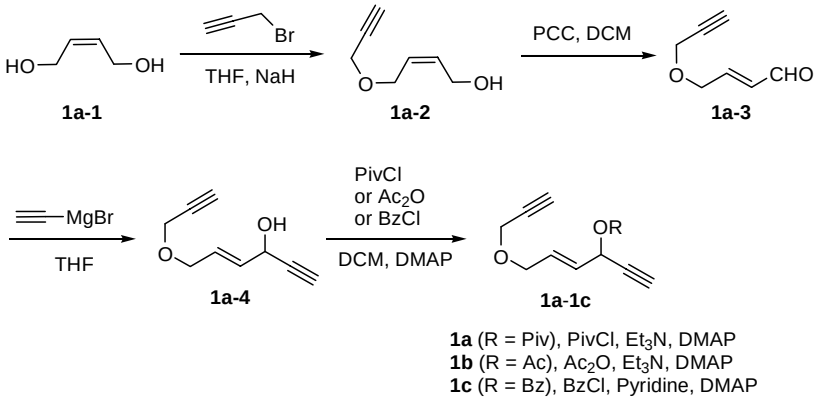


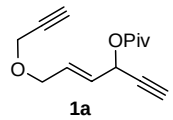
1a-1 **1a-2** **1a-3** **1a-4** **1a-1c**

1a (R = Piv), PivCl, Et_3N, DMAP
1b (R = Ac), Ac_2O, Et_3N, DMAP
1c (R = Bz), BzCl, Pyridine, DMAP

To a suspension of PCC (1.94 g, 9 mmol) and 4 Å MS (300 mg, 50mg/mmol) in CH_2Cl_2 (60 mL) was added a solution of known compound **1a-2**[1] (6 mmol) in dry CH_2Cl_2 (10 mL) at 0 ^oC under Ar. The mixture was stirred at room temperature for 1.5 h. It was then poured into Et_2O (70 mL). The mixed solution was filtered though silica gel and the filtrate was concentrated under reduced pressure to yield the crude aldehyde for next step without purification.

To a stirred solution of ethynylmagnesium bromide solution (12 mL, 1.2 equiv, 0.5 M in THF) was added a solution of crude aldehyde (5 mmol) in THF (20 mL) at room temperature. When the reaction was completed as determined by TLC analysis, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with ethyl ether (2×40 mL). The combined organic layers were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude propargylic alcohol **1a-4** for the next step without purification.

To a stirred solution of crude propargylic alcohol **1a-4** (4.6 mmol) in CH_2Cl_2 (40 mL) was added triethylamine (1.39 g, 13.8 mmol, 3.0 equiv), pivaloyl chloride (662 mg, 5.52 mmol, 1.2 equiv), and DMAP (5 mol %) at room temperature. The resulting mixture was stirred overnight, diluted with CH_2Cl_2 (40 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 20:1) to obtain the desired propargylic esters **1a** (940 mg) as an oil in 67% yield over 3 steps.

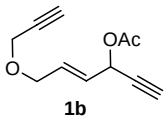


1a

(*E*)-6-(prop-2-ynyloxy)hex-4-en-1-yn-3-yl pivalate (**1a**).

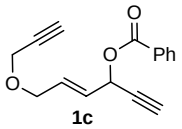
Oil. (940 mg) ^1H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9 H), 2.44 (t, *J* = 2.4 Hz, 1 H), 2.58 (d, *J* = 2.0 Hz, 1 H), 4.13 (td, *J* = 1.2, 5.2 Hz, 2 H), 4.17 (d, *J* = 2.4 Hz, 2 H), 5.79-5.87 (m, 2 H), 6.08 (dtd, *J* = 0.8, 5.6, 15.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$):

δ 26.9, 38.7, 57.4, 62.9, 68.7, 74.6, 74.8, 79.3, 79.4, 127.4, 130.5, 177.0. IR (film): ν 964, 1140, 1273, 1718, 2973, 3293 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{14}H_{18}O_3$ $(M+Na)^+$ 257.1148, found 257.1154.



1b

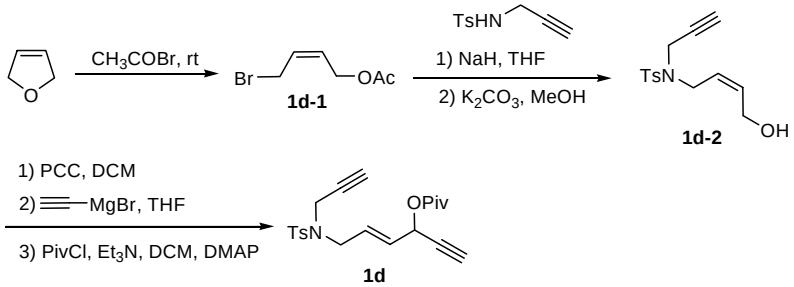
(*E*)-6-(prop-2-ynyloxy)hex-4-en-1-yn-3-yl acetate (**1b**).
Compound **1b** (721 mg) was prepared from alcohol **1a-2** (6 mmol) in 63% yield over 3 steps. Ac_2O (1.2 equiv), Et_3N (3 equiv), and DMAP (5%) were used for esterification. (silica gel, hexane/ethyl acetate 10:1), oil. ^1H NMR (400 MHz, $CDCl_3$): δ 2.09 (s, 3 H), 2.44 (t, *J* = 2.4 Hz, 1 H), 2.57 (d, *J* = 2.4 Hz, 1 H), 4.13 (ddd, *J* = 1.2, 1.6, 5.2 Hz, 2 H), 4.17 (d, *J* = 2.4 Hz, 2 H), 5.80-5.89 (m, 2 H), 6.06-6.12 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 57.4, 63.1, 68.6, 74.7, 75.2, 79.1, 79.3, 126.9, 131.2, 169.5. IR (film): ν 701, 965, 1082, 1371, 2855, 3292 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{11}H_{12}O_3$ $(M+Na)^+$ 215.0678, found 215.0680.



1c

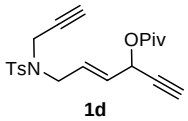
(*E*)-6-(prop-2-ynyloxy)hex-4-en-1-yn-3-yl benzoate (**1c**).
Compound **1c** (920 mg) was prepared from alcohol **1a-2** (6 mmol) in 61% yield over 3 steps. BzCl (1.1 equiv), pyridine (3 equiv), DMAP (5%) were used for esterification. (silica gel, hexane/ethyl acetate 10:1), oil. ^1H NMR (400 MHz, $CDCl_3$): δ 2.45 (t, *J* = 2.4 Hz, 1 H), 2.62 (d, *J* = 2.4 Hz, 1 H), 4.15 (td, *J* = 1.6, 5.2 Hz, 2 H), 4.18 (d, *J* = 2.4 Hz, 2 H), 5.97 (tdd, *J* = 1.6, 5.6, 15.6 Hz, 1 H), 6.14-6.23 (m, 2 H), 7.42-7.47 (m, 2 H), 7.55-7.60 (m, 1 H), 8.06-8.09 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 57.5, 63.7, 68.7, 74.7, 75.4, 79.1, 79.3, 127.1, 128.4, 129.5, 129.8, 131.2, 133.3, 165.2. IR (film): ν 713, 932, 1105, 1257, 1717, 3293 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{14}O_3$ $(M+Na)^+$ 277.0835, found 277.0841.

Preparation of substrate **1d**.



To a stirred solution of NaH (390 mg, 9.6 mmol, 60% in mineral oil) in THF (40 mL) was added sulfonamide (1.58 g, 8 mmol) at 0 °C under argon atmosphere. After stirring at rt for 0.5 h, known compound **1d-1**[2] (1.69 g, 8.8 mmol) in THF (10 mL) was added. The reaction mixture was allowed to stir overnight. The reaction was quenched with

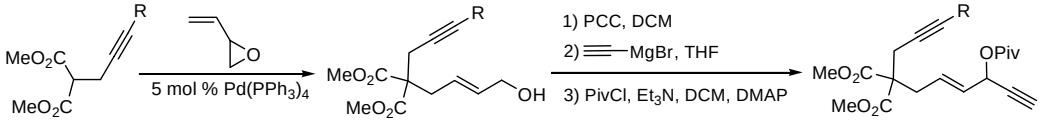
H_2O. The mixture was diluted with ethyl acetate, washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved with methanol (50 mL), and K_2CO_3 (4.4 g, 32 mmol) was added at room temperature. After stirring at room temperature for 1 h, most of solvent was removed under reduced pressure. The residue was diluted with ethyl acetate (70 mL), washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to afford **1d-2** (1.9 g) in 79% yield over 2 steps. Product **1d** (1.57 g) was obtained in 68% yield over three steps from **1d-2** according to procedures described for **1a**.



1d

(*E*)-6-(N-(prop-2-ynyl)-N-tosylamino)hex-4-en-1-yn-3-yl pivalate (**1d**).
(silica gel, hexane/ethyl acetate 10:1), oil. (1.57 g) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 9 H), 2.03 (t, *J* = 2.4 Hz, 1 H), 2.43 (s, 3 H), 2.55 (d, *J* = 2.0 Hz, 1 H), 3.83-3.93 (m, 2 H), 4.02-4.13 (m, 2 H), 5.76-5.84 (m, 2 H), 5.88-5.93 (m, 1 H), 7.28-7.31 (m, 2 H), 7.71-7.74 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 26.9, 35.9, 38.6, 47.3, 62.6, 73.9, 75.0, 76.2, 78.9, 127.7, 128.5, 129.5, 129.8, 135.7, 143.6, 176.8. IR (film): ν 742, 1091, 1159, 1348, 1733, 2974, 3290 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{21}H_{25}NO_4S$ $(M+Na)^+$ 410.1396, found 410.1398.

Preparation of substrate **1e** and **1i**.

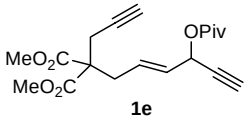


1e-1 R=H
1i-1 R=Me

1e-2 R=H
1i-2 R=Me

1e R=H
1i R=Me

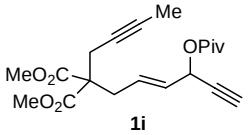
Compounds **1e-2** (1.13 g, 83% yield) and **1i-2** (1.62 g, 88% yield) were prepared in one step from corresponding malonates and vinyl epoxide according to the literature procedure.[3]
Products **1e** and **1i** were obtained in three steps from **1e-2** and **1i-2** respectively according to procedures described for **1a**.



1e

(E)-dimethyl 2-(4-(pivaloyloxy)hex-2-en-5-ynyl)-2-(prop-2-ynyl)malonate (**1e**).
Compound **1e** (980 mg) was prepared in 71% yield over 3 steps from **1e-2**. (silica gel, hexane/ethyl acetate 10:1), oil. ^{1}H NMR (400Mz, $CDCl_3$) δ 1.19 (s, 9H), 2.02 (t, *J*= 2.8 Hz, 1H), 2.51 (d, *J*= 2.0 Hz, 1H), 2.77 (d, *J*= 2.8 Hz, 2H), 2.82 (dd, *J*= 0.8, 7.6 Hz, 2H), 3.73 (s, 6H), 5.67 (tdd, *J*= 0.8, 6.0, 15.2 Hz, 1H), 5.75-5.85 (m, 2H); ^{13}C NMR (100Mz, $CDCl_3$) δ 23.1, 27.2, 35.0, 38.9, 53.1, 57.0, 63.4, 71.9, 74.9, 78.7, 79.7, 129.1, 130.0,

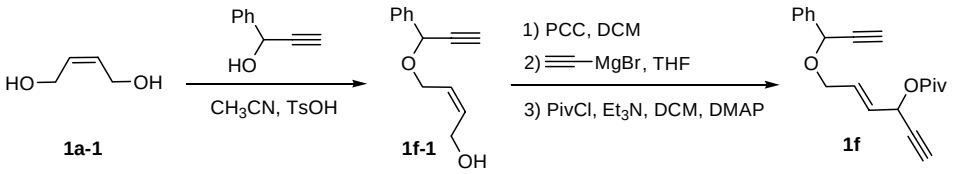
170.1, 177.1. IR (film): 933, 975, 1142, 1206, 1274, 1438, 1734, 2958, 3289 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{24}O_6$ $(M+Na)^+$ 371.1465, found 371.1459.



1i

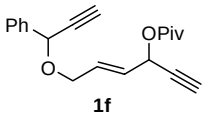
(E)-dimethyl 2-(but-2-ynyl)-2-(4-(pivaloyloxy)hex-2-en-5-ynyl)malonate (**1i**).
Compound **1i** (721 mg) was prepared in 50% yield over 3 steps from **1i-2**. (silica gel, hexane/ethyl acetate 10:1), oil. ^{1}H NMR (400Mz, $CDCl_3$) δ 1.20 (s, 9H), 1.75 (t, *J*= 2.4 Hz, 3H), 2.51 (d, *J*= 2.4 Hz, 1H), 2.71 (q, *J*= 2.4 Hz, 2H), 2.79 (d, *J*= 7.6 Hz, 2H), 3.72 (s, 6H), 5.65 (dd, *J*= 6.0, 15.2 Hz, 1H), 5.75-5.88 (m, 2H); ^{13}C NMR (100Mz, $CDCl_3$) δ 3.7, 23.5, 27.2, 35.1, 38.9, 52.9, 57.4, 63.4, 73.2, 74.8, 79.4, 79.8, 129.60, 129.64, 170.4, 177.2. IR (film): 738, 933, 972, 1031, 1059, 1142, 1207, 1274, 1438, 1480, 1735, 2958, 3275 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{26}O_6$ $(M+Na)^+$ 385.1622, found 385.1619.

Preparation of substrate **1f**



1a-1 **1f-1** **1f**

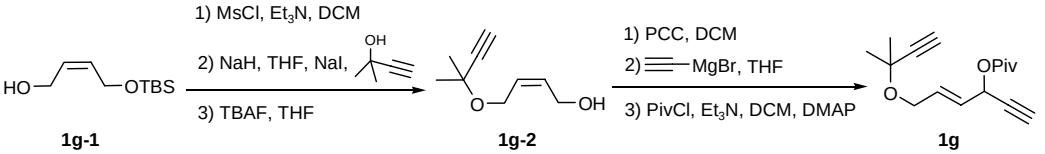
To a stirred solution of propargyl alcohol (1.98 g, 15 mmol) and *cis*-2-butene-1,4-diol **1a-1** (3.96 g, 45 mmol) in MeCN (80 mL) was added TsOH (258 mg, 10 mol %). The mixture was stirred at 80 °C for 8 h. The solvent was removed under reduced pressure and the residue was then purified by column chromatography (silica gel; hexane/ethyl acetate 2:1), affording the compound **1f-1** (1.8 g) in 60% yield. Product **1f** (1.13 g) was obtained in 61% yield over 3 steps from **1f-1** according to procedures described for **1a**.



1f

(*E*)-6-(1-phenylprop-2-ynyloxy)hex-4-en-1-yn-3-yl pivalate (**1f**).
(silica gel, hexane/ethyl acetate 20:1), oil. (two diastereomers, dr=1:1) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9 H), 2.53-2.54 (m, 1 H), 2.64-2.66 (m, 1 H), 4.12-4.26 (m, 2 H), 5.20 (d, *J* = 2.0 Hz, 1 H, one isomer), 5.21 (d, *J* = 2.0 Hz, 1 H, the other isomer), 5.81-5.88 (m, 2 H), 6.07-6.15 (m, 1 H), 7.33-7.40 (m, 3 H), 7.51-7.53 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0, 38.7, 63.01, 63.04, 67.3, 70.68, 70.74, 74.78, 74.81, 75.9, 79.4, 81.3, 127.2, 127.3, 127.4, 128.5, 128.6, 130.8, 130.9, 137.8, 177.0. IR (film): ν 966, 1030, 1140, 1272, 1717, 2972, 3291 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{22}O_3$ $(M+Na)^+$ 333.1461, found 333.1462.

Preparation of substrate **1g**

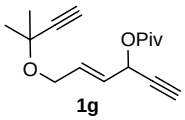


To a stirred solution of known compound **1g-1**[4] (3.03 g, 15 mmol) and Et_3N (1.67 g, 16.5 mmol) in DCM (70 mL) was slowly added MsCl (1.88 g, 16.5 mmol) dropwise at -10 °C. After stirring at the same temperature for 10 min, the reaction mixture was allowed to stir at room temperature for 30 min. The resulting mixture was diluted with DCM (60 mL), washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude methanesulfonate product for next step without purification.

To a stirred solution of NaH (672 mg, 16.8 mmol, 60% in mineral oil) in THF (60 mL) was added 2-methylbut-3-yn-2-ol (1.41 g, 16.8 mmol) at 0 °C under argon. After stirring at rt for 0.5 h, the above crude methanesulfonate product and NaI (1.05 g, 50 %) were added sequentially. The reaction mixture was allowed to stir overnight. The reaction was quenched with H_2O. The mixture was diluted with ethyl acetate, washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude propargyl ether for next step without purification.

To a stirred solution of the above crude propargyl ether (2.94 g, 11 mmol) in THF (50 mL) was added a solution of tetrabutylammonium fluoride (4.35 g, 16.5 mmol) in THF (20 mL) at 0 °C. The mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure, and the residue was diluted with ethyl acetate, washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 2:1) to afford **1g-2** (1.22 g) in 53% yield over 3 steps.

Compound **1g** (927 mg) was obtained in 59% yield over 3 steps from **1g-2** according to procedures described for **1a**.

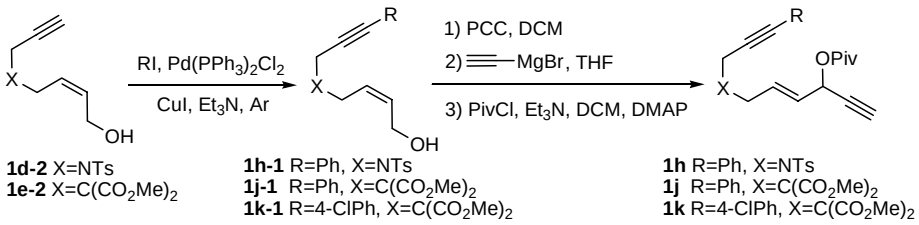


1g

(*E*)-6-(2-methylbut-3-yn-2-yloxy)hex-4-en-1-yn-3-yl pivalate (**1g**).

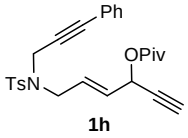
(silica gel, hexane/ethyl acetate 20:1), oil. (927 mg) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9 H), 1.49 (s, 6 H), 2.42 (s, 1 H), 2.52 (d, *J* = 2.0 Hz, 1 H), 4.16 (td, *J* = 1.2, 5.2 Hz, 2 H), 5.76-5.86 (m, 2 H), 6.11 (dtd, *J* = 1.2, 5.2, 15.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0, 28.7, 38.7, 63.2, 63.7, 70.3, 72.3, 74.6, 79.5, 85.7, 125.8, 132.2, 177.0. IR (film): ν 964, 1138, 1362, 1718, 2982, 3293 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_3$ $(M+Na)^+$ 285.1461, found 285.1466.

Preparation of substrate **1h**, **1j** and **1k**



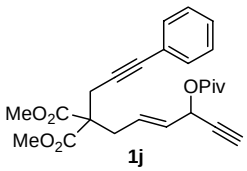
To a solution of compound **1d-2** (1.67 g, 6 mmol) and phenyl iodide (1.22 g, 6.0 mmol) in Et_3N (50 mL) was added CuI (11.5 mg, 1 mol %). The mixture was stirred for 5 min and $PdCl_2(PPh_3)_2$ (85 mg, 2 mol %) was added. The resulting mixture was then stirred under an argon atmosphere at room temperature for 24 h. The mixture was diluted with ethyl acetate (60 mL), washed with aqueous NH_4Cl, H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 2:1) to afford **1h-1** (1.9 g) in 89% yield.

Product **1h** (1.1 g) was obtained in 61% yield over 3 steps from **1h-1** according to procedures described for **1a**.



1h

(*E*)-6-(N-(3-phenylprop-2-ynyl)-N-tosylamino)hex-4-en-1-yn-3-yl pivalate (**1h**).
(silica gel, hexane/ethyl acetate 10:1), oil. (1.1 g) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 9 H), 2.34 (s, 3 H), 2.53 (d, *J* = 2.0 Hz, 1 H), 3.89-3.99 (m, 2 H), 4.24-4.34 (m, 2 H), 5.81-5.85 (m, 2 H), 5.96-6.01 (m, 1 H), 7.05-7.07 (m, 2 H), 7.22-7.29 (m, 5 H), 7.76-7.78 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 26.9, 37.0, 38.7, 47.7, 62.7, 75.1, 79.0, 81.4, 85.9, 122.1, 127.8, 128.1, 128.5, 128.8, 129.6, 129.8, 131.5, 135.8, 143.6, 176.9. IR (film): ν 1139, 1273, 1348, 1731, 2933, 2973, 3287 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{27}H_{29}NO_4S$ $(M+Na)^+$ 486.1709, found 486.1704.

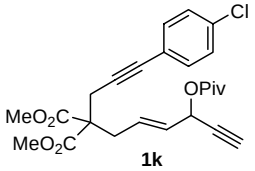


1j

(*E*)-dimethyl 2-(3-phenylprop-2-ynyl)-2-(4-(pivaloyloxy)hex-2-en-5-ynyl)-malonate **(1j).**

Product **1j** (270 mg) was obtained in 56% yield over 3 steps from **1j-1** (78% yield from **1e-2**) according to similar procedures. (silica gel, hexane/ethyl acetate 4:1), oil. ^{1}H NMR (400Mz, $CDCl_3$) δ 1.21 (s, 9H), 2.52 (d, *J*= 2.0 Hz, 1H), 2.89 (dd, *J*= 0.8, 7.6 Hz, 2H), 3.01 (s, 2H), 3.76 (s, 6H), 5.71 (tdd, *J*= 0.8, 6.0, 15.2 Hz, 1H), 5.81 (ddd, *J*= 0.8, 2.0, 6.0 Hz, 1H), 5.89 (dtd, *J*= 0.8, 7.6, 15.2 Hz, 1H), 7.25-7.31 (m, 3H), 7.33-7.40 (m, 2H); ^{13}C NMR (100Mz, $CDCl_3$) δ 24.1, 27.2, 35.3, 38.9, 53.1, 57.5, 63.4, 74.9, 79.8, 84.0, 84.1, 123.3, 128.3, 128.4, 129.4, 129.9, 131.9, 170.3, 177.2. IR (film): 757, 858,

971, 1140, 1204, 1274, 1437, 1479, 1490, 1733, 2957, 3287 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{28}O_6$ $(M+Na)^+$ 447.1778, found 447.1778.

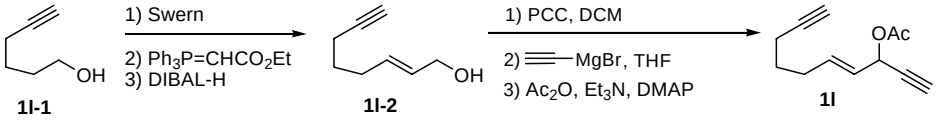


1k

(*E*)-dimethyl-2-(3-(4-chlorophenyl)prop-2-ynyl)-2-(4-(pivaloyloxy)hex-2-en-5-ynyl) malonate (**1k**).

Product **1k** (375 mg) was obtained in 60% yield over 3 steps from **1k-1** (93% yield from **1e-2**) according to similar procedures. (silica gel, hexane/ethyl acetate 4:1), oil. ^{1}H NMR (400Mz, $CDCl_3$) δ 1.21 (s, 9H), 2.53 (d, *J*= 2.4 Hz, 1H), 2.87 (d, *J*= 7.2 Hz, 2H), 3.00 (s, 2H), 3.76 (s, 6H), 5.66-5.74 (m, 1H), 5.78-5.83 (m, 1H), 5.88 (dtd, *J*= 1.2, 7.6, 15.2 Hz, 1H), 7.22-7.32 (m, 4H); ^{13}C NMR (100Mz, $CDCl_3$) δ 24.1, 27.2, 35.4, 38.9, 53.1, 57.4, 63.4, 74.9, 79.7, 83.0, 85.2, 121.7, 128.8, 129.3, 130.0, 133.1, 134.3, 170.2, 177.2. IR (film): 703, 736, 829, 933, 1060, 1090, 1141, 1205, 1268, 1398, 1436, 1490, 1733, 2957, 3299 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{27}ClO_6$ $(M+Na)^+$ 481.1388, found 481.1391.

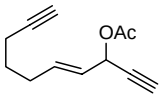
Preparation of substrate **1l**



1l-1 **1l-2** **1l**

Compound **1l-2** (907 mg, 73% yield from **1l-1**) was prepared in 3 steps according to literature procedure.[5]

Product **1l** (608 mg, 49% yield over 3 steps from **1l-2**) was obtained according to procedures described for **1a** and **1b**.

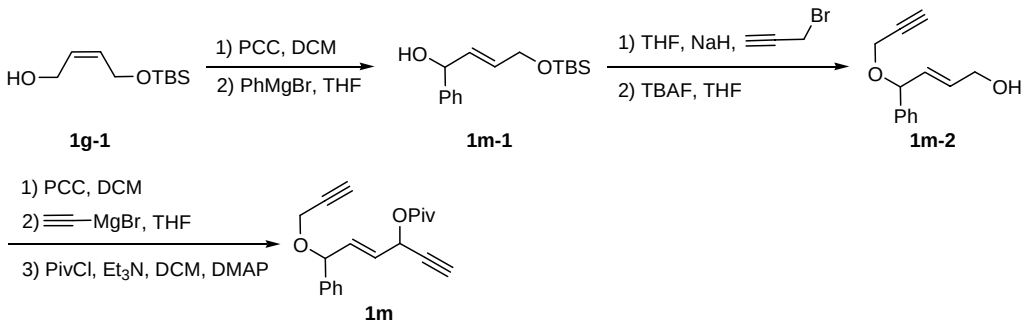


1l

(***E***)-deca-4-en-1,9-diyn-3-yl acetate (**1l**).

(silica gel, hexane/ethyl acetate 20:1), oil. (608 mg) ^{1}H NMR (400Mz, $CDCl_3$) δ 1.60-1.70 (m, 2H), 1.96 (t, *J*= 2.4 Hz, 1H), 2.10 (s, 3H), 2.17-2.25 (m, 4H), 2.57 (d, *J*= 2.0 Hz, 1H), 5.59 (dd, *J*= 6.4, 15.2 Hz, 1H), 5.84 (d, *J*= 6.0 Hz, 1H), 6.01 (td, *J*= 6.4, 15.2 Hz, 1H); ^{13}C NMR (100Mz, $CDCl_3$) δ 18.0, 21.2, 27.6, 31.0, 64.1, 68.9, 75.0, 79.9, 84.1, 125.5, 135.8, 169.8. IR (film): 800, 967, 1015, 1226, 1371, 1434, 1738, 2940, 3294 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{12}H_{14}O_2$ $(M+Na)^+$ 213.0886, found 213.0877.

Preparation of substrate **1m**



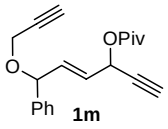
1g-1 **1m-1** **1m-2** **1m**

To a suspension of PCC (3.2 g, 15 mmol) and 4 Å MS (500 mg, 50mg/mmol) in CH_2Cl_2 (80 mL) was added known compound **1g-1**[4] (2.02 g, 10 mmol) in dry CH_2Cl_2 (20 mL) at 0 ^oC under Ar. The mixture was stirred at room temperature for 2.5 h. It was then poured into Et_2O (150 mL). The mixed solution was filtered though silica gel and the filtrate was concentrated under reduced pressure to yield the crude aldehyde for the next step without purification.

To a stirred solution of above crude aldehyde in THF (50 mL) was added a solution of phenylmagnesium bromide solution (4 mL, 1.2 equiv, 3 M in ether) at room temperature. When the reaction was completed as determined by TLC analysis, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with ethyl ether (2×50 mL). The combined organic layers were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 10:1) to afford **1m-1** (1.6 g) in 57% yield.

To a stirred solution of NaH (287 mg, 7.2 mmol, 60% in mineral oil) and 15-crown-5 (526 mg, 2.4 mmol) in toluene (50 mL) was added a solution of alcohol **1m-1** (1.33 g, 4.8 mmol) in toluene (10 mL) at 0 °C under argon atmosphere. After stirring at rt for 0.5 h, a solution of propargyl bromide (1.76 g, 12 mmol, 80% (w/w) solution in toluene) in toluene (10 mL) was added. The reaction mixture was allowed to stir overnight. The reaction was quenched with H_2O. The mixture was diluted with ethyl acetate, washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in THF (30 mL). A solution of TBAF (1.58 g, 5.98 mmol) in THF (10 mL) was added dropwise at 0 °C. When the reaction was completed as determined by TLC analysis, the reaction mixture was diluted with ether (60 mL), washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to afford **1m-2** (682 mg) in 56% yield.

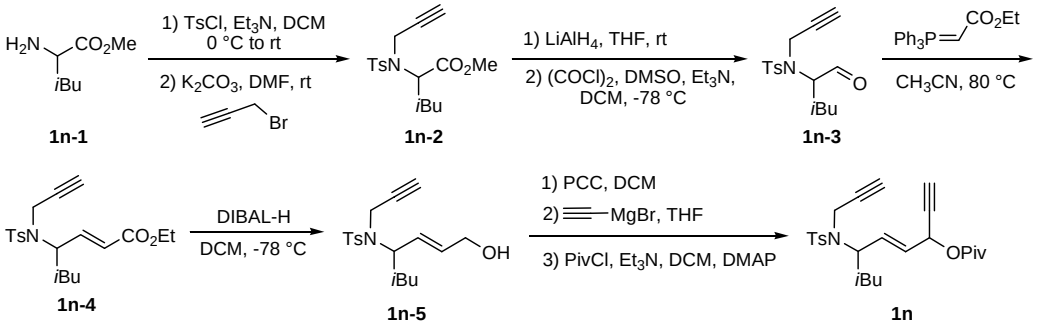
Product **1m** (511 mg, 52% yield over 3 steps from **1m-2**) was obtained according to procedures described for **1a**.



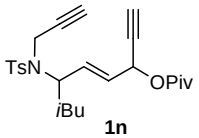
1m

(*E*)-6-phenyl-6-(prop-2-ynyloxy)hex-4-en-1-yn-3-yl pivalate (**1m**).
(silica gel, hexane/ethyl acetate 20:1), oil. (511 mg) (two diastereomers, dr=1:1) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 9 H), 2.43-2.45 (m, 1 H), 2.52 (t, *J* = 2.4 Hz, 1 H), 4.04-4.19 (m, 2 H), 5.10 (d, 6.4 Hz, 1 H), 5.83-5.91 (m, 2 H), 6.09-6.16 (m, 1 H), 7.29-7.39 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0, 38.7, 55.3, 55.4, 62.89, 62.91, 74.6, 74.9, 79.2, 79.41, 79.44, 79.5 126.86, 126.93, 127.3, 128.2, 128.6, 134.5, 139.2, 177.0. IR (film): ν 1067, 1138, 1272, 1456, 1718, 2972, 3292 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{22}O_3$ $(M+Na)^+$ 333.1461, found 333.1458.

Preparation of substrate **1n**



Compound **1n-3** was prepared in 4 steps according to literature procedure.[6]
To a stirred solution of aldehyde **1n-3**[6] (14 mmol) in CH_3CN (40.0 mL) was added (carbethoxymethylene)triphenylphosphorane (6.82 g, 19.6 mmol). The resulting mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to give the enoate **1n-4** (4.3 g) in 96% yield.
To a stirred solution of enoate **1n-4** (2.64 g, 7 mmol) in DCM (30 mL) at -78 °C was added DIBALH (1.0 M solution in hexane; 24 mL, 24 mmol) under argon. The reaction was quenched with NaOH (10% aqueous solution) after 3 h. The mixture was diluted with DCM, washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude alcohol **1n-5** for the next step without purification. Product **1n** (1.6 g) was obtained in 59% yield from **1n-4** over 4 steps according to procedures described for **1a** after DIBALH reduction.

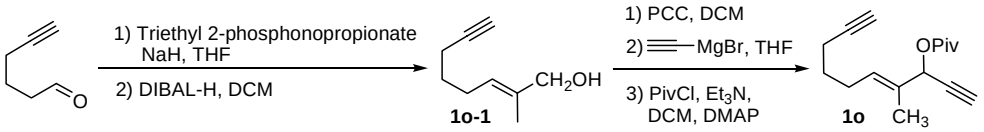


1n

(*E*)-6-(N-(prop-2-ynyl)-N-tosylamino)-8-methylnon-4-en-1-yn-3-yl pivalate (**1n**).
(silica gel, hexane/ethyl acetate 20:1), oil. (1.6 g) (two diastereomers, dr=1:1) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (m, 6 H), 1.19 (m, 9 H), 1.42-1.48 (m, 1 H), 1.57-1.64 (m, 2 H), 2.14-2.16 (m, 1 H), 2.41 (s, 3 H), 2.49 (d, *J* = 2.4 Hz, 1 H), 3.91-4.09 (m, 2 H), 4.48-4.53 (m, 1 H), 5.52-5.58 (m, 1 H), 5.69-5.74 (m, 1 H), 5.83-5.91 (m, 1 H), 7.26-7.29 (m, 2 H), 7.76-7.78 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 22.01, 22.04, 22.3, 22.4, 24.2, 26.8, 32.3, 32.4, 38.6, 40.8, 40.9, 56.5, 56.6, 62.6, 62.8, 72.43, 72.45, 74.7, 74.8, 78.9, 79.0, 79.57, 79.61, 127.48, 127.51, 129.3, 132.5, 132.8, 137.3,

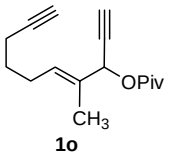
137.4, 143.2, 143.3, 176.7. IR (film): ν 863, 1092, 1140, 1338, 2959, 3275 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{33}NO_4S$ $(M+Na)^+$ 466.2022, found 466.2025.

Preparation of substrate **1o**



To a stirred solution of NaH (560 mg, 14 mmol, 60% in mineral oil) in THF (60 mL) was added a solution of triethyl 2-phosphonopropionate (3.33 g, 14 mmol) in THF (20 mL) at 0 °C under argon atmosphere. After stirring at rt for 0.5 h, a solution of 5-hexynal[5] (960 mg, 10 mmol) in THF (10 mL) was added. The reaction mixture was allowed to stir overnight. The reaction was quenched with H_2O. The mixture was diluted with ether, washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in DCM (50 mL). A solution of DIBAL-H (25 mL, 1 M solution in hexane) was added. After stirring at rt for 1 h, the reaction was carefully quenched with 10% NaOH aqueous solution. The mixture was diluted with DCM (100 mL), washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to give the alcohol **1o-1** (1.14 g) in 83% yield.

Product **1o** (693 mg) was obtained in 47% yield from **1o-1** over 3 steps according to procedures described for **1a**.

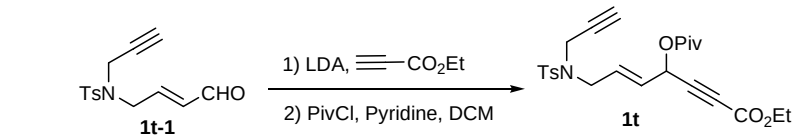


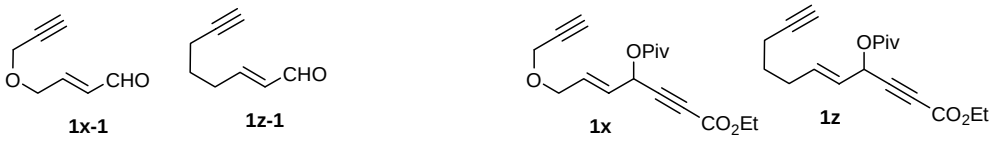
1o

(E)-4-methyldeca-4-en-1,9-diyn-3-yl pivalate (**1o**).

(silica gel, hexane/ethyl acetate 20:1), oil. (693 mg) ^1H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9 H), 1.59-1.66 (m, 2 H), 1.75 (s, 3 H), 1.96 (t, *J* = 2.8 Hz, 1 H), 2.17-2.22 (m, 4 H), 2.50 (d, *J* = 1.6 Hz, 1 H), 5.67 (tt, *J* = 1.2, 7.2 Hz, 1 H), 5.75 (d, *J* = 1.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 17.8, 26.6, 27.0, 27.8, 38.8, 68.45, 68.50, 74.2, 80.0, 84.1, 129.5, 131.5, 177.0. IR (film): ν 872, 1030, 1272, 1479, 1730, 2360, 2974, 3295 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_2$ $(M+Na)^+$ 269.1512, found 269.1513.

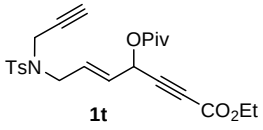
Preparation of substrates **1t**, **1x**, and **1z**.



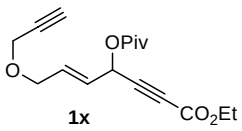


Procedure for **1t**: To a stirred solution of diisopropylamine (6.8 mmol, 1.7 equiv) in THF (20 mL) was added a solution of *n*-butyllithium (1.6 M in hexanes, 4.3 mL, 6.8 mmol, 1.7 equiv) slowly at -78 °C. The mixture was stirred at -78 °C for 15 min, warmed to 0 °C, and stirred for another 30 min at this temperature. The mixture was cooled to -78 °C and ethyl propiolate (6 mmol, 1.5 equiv) was added. After stirring for 30 min at -78 °C, a solution of aldehyde **1t-1** (4 mmol, 1.0 equiv, obtained according to procedures described for **1d**) in THF (10 mL) was added. After stirring at -78 °C for 3 h, the reaction mixture was added to a saturated ammonium chloride solution at 0 °C. The aqueous phase was extracted with Et_2O, the combined organic layer was washed with brine, dried over $MgSO_4$ and the solvents were removed under reduced pressure to give an oil.

To a solution of above oil (1.1 g, 3 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL), was added pyridine (711 mg, 3 equiv), DMAP (one crystal) and pivaloyl chloride (540 mg, 1.5 equiv) at 0°C. After stirring for overnight, the mixture was diluted with CH_2Cl_2 (30 mL) and washed with a 10% copper sulfate aqueous solution, brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate 4:1) to give **1t** (1.13 g, 62% yield over 2 steps).

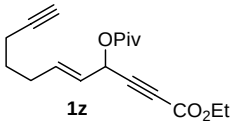


(*E*)-ethyl 7-(N-(prop-2-ynyl)-N-tosylamino)-4-(pivaloyloxy)hept-5-en-2-ynoate (**1t**). oil. (1.13 g) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H), 2.04 (t, *J* = 2.4 Hz, 1H), 2.43 (s, 3H), 3.83-3.94 (m, 2H), 4.01-4.13 (m, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 5.74-5.80 (m, 1H), 5.87-5.95 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 21.5, 26.9, 36.2, 38.8, 47.4, 62.2, 62.3, 74.1, 76.2, 77.9, 81.4, 127.7, 128.2, 129.6, 129.7, 135.7, 143.8, 152.8, 176.7. IR (film): ν 1092, 1132, 1160, 1247, 1349, 1713, 2244, 2935, 2978, 3277. HRMS (ESI) *m/z* calcd. For $C_{24}H_{29}NO_6S$ $(M+Na)^+$ 482.1607, found 482.1592.



(*E*)-ethyl 4-(pivaloyloxy)-7-(prop-2-ynyloxy)hept-5-en-2-ynoate (**1x**).

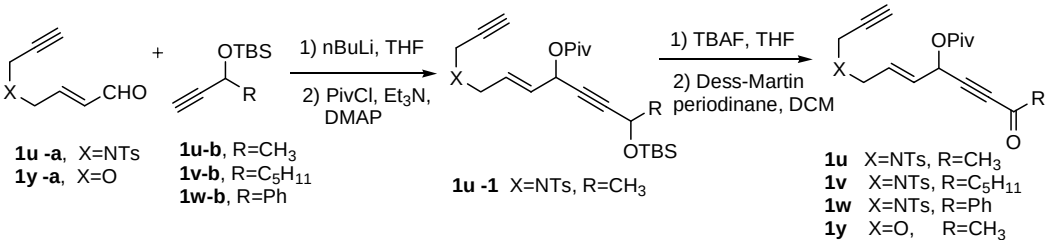
Compound **1x** (230 mg) was prepared in 47% yield from aldehyde **1x-1** (obtained according to procedures described for **1a**) according to procedures described for **1t**. (silica gel, hexane/ethyl acetate 10:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H), 2.45 (t, *J* = 2.4 Hz, 1H), 4.12 (dt, *J* = 5.2, 1.6 Hz, 2H), 4.17 (t, *J* = 2.4 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 5.82 (ddt, *J* = 15.2, 6.0, 1.6 Hz, 1H), 5.98 (dq, *J* = 6.0, 1.2 Hz, 1H), 6.07 (dtd, *J* = 15.2, 5.2, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 27.2, 39.0, 57.8, 62.5, 62.7, 68.8, 75.1, 78.0, 79.5, 82.1, 125.8, 131.9, 153.1, 177.0. IR (film): ν 2981, 2916, 2249, 1714, 1249, 1135, 1030, 961, 910, 731 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{17}H_{22}NaO_5$ $(M+Na)^+$ 329.1359, found 329.1367.



(*E*)-ethyl 4-(pivaloyloxy)undeca-5-en-2,10-diynoate (**1z**).

Compound **1z** (310 mg) was prepared in 53% yield from aldehyde **1z-1** (obtained according to procedures described for **1l**) according to procedures described for **1t**. (silica gel, hexane/ethyl acetate 10:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 9H), 1.30 (t, *J* = 6.8 Hz, 3H), 1.67-1.57 (m, 2H), 1.95 (t, *J* = 2.4 Hz, 1H), 2.24-2.15 (m, 4H), 4.23 (q, *J* = 6.8 Hz, 2H), 5.55 (tdd, *J* = 1.6, 6.4, 15.2, 1H), 5.90 (tdd, *J* = 0.8, 0.8, 6.4 Hz, 1H), 5.95 (tdd, *J* = 0.8, 7.2, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 18.0, 27.2, 27.4, 31.1, 39.0, 62.4, 63.4, 69.0, 77.8, 82.8, 84.0, 124.4, 136.6, 153.3, 177.1. IR (film): ν 1134, 1247, 1366, 1479, 1715, 1735, 2243, 2978. HRMS (ESI) *m/z* calcd. For $C_{18}H_{24}O_4$ $(M+Na)^+$ 327.1567, found 327.1577.

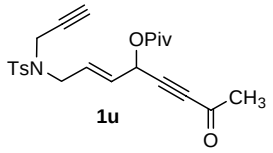
Preparation of substrates **1u**, **1v**, **1w** and **1y**.



Procedure for **1u**: To a stirred solution of terminal alkyne **1u-b** (883 mg, 4.8 mmol) in THF (30 mL) was added *n*BuLi (3 mL, 4.8 mmol, 1.6 M in hexane) at -78 °C. The mixture was stirred at -78 °C for 15 min, warmed to 0 °C, and stirred for another 20 min at this temperature. The mixture was cooled to -78 °C and a solution of aldehyde **1u-a** (831 mg, 3 mmol) in THF (10 mL) was added. After stirring for 1h at -78 °C, the reaction mixture was quenched with saturated ammonium chloride and extracted with diethyl ether. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The residue was dissolved in DCM (30 mL). To this solution was added Et_3N (1.2g, 12 mmol), PivCl (720 mg, 6 mmol) and DMAP (5%) at 0 °C. The solution was then warmed to rt. After stirring at rt for 2h, the reaction mixture was diluted with DCM (30 mL), washed with H_2O, brine, dried over anhydrous Na_2SO_4. The solvent was evaporated and the

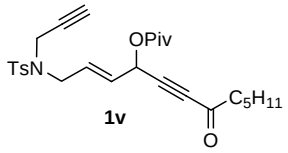
residue was purified by flash column chromatography (silica gel, Hexane/ ethyl acetate = 30:1) to provide product **1u-1** (1.09 g) in 67% yield.

To a solution of **1u-1** (1.09 g, 2 mmol) in THF (30 mL) was added a solution of TBAF (3 mL, 1M in THF) at 0 °C. After stirring at rt for 20 min, the reaction mixture was diluted with ether (60 mL), washed with H_2O, brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in DCM (30 mL). Dess-Martin Periodinane (715 mg, 2.6 mmol) was then added at 0 °C. After stirring at rt for 30 min, the reaction solution was filtered to remove the solid. The filtrate was washed with saturated aqueous Na_2SO_3 and $NaHCO_3$ solution, H_2O, brine and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 4:1) to give desired product **1u** (630 mg) in 74% yield as an oil.



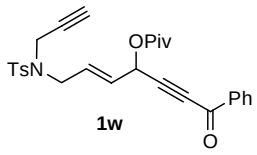
1u

(*E*)-1-(N-(prop-2-ynyl)-N-tosylamino)-7-oxooct-2-en-5-yn-4-yl pivalate (**1u**).
oil. (630 mg) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 9H), 2.04 (t, *J* = 2.4 Hz, 1H), 2.36 (s, 3H), 2.43 (s, 3H), 3.83-3.94 (m, 2H), 4.02-4.13 (m, 2H), 5.78 (tdd, *J* = 1.2, 5.6, 15.6 Hz, 1H), 5.91 (dtd, *J* = 1.2, 6.4, 15.6 Hz, 1H), 5.96 (dd, *J* = 0.8, 5.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.9, 32.6, 36.2, 38.8, 47.4, 62.3, 74.1, 76.2, 85.0, 85.5, 127.7, 128.2, 129.6, 129.7, 135.7, 143.8, 176.7, 183.6. IR (film): ν 1092, 1133, 1160, 1222, 1349, 1681, 1734, 2216, 2934, 2975, 3274. HRMS (ESI) *m/z* calcd. For $C_{23}H_{27}NO_5S$ $(M+Na)^+$ 452.1502, found 452.1498.



1v

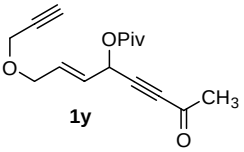
(*E*)-1-(N-(prop-2-ynyl)-N-tosylamino)-7-oxododec-2-en-5-yn-4-yl pivalate (**1v**).
Compound **1v** (625 mg) was prepared in 43% yield from aldehyde **1u-a** and alkyne **1v-b** according to procedures described for **1u**. (silica gel, hexane/ethyl acetate 10:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.22 (s, 9H), 1.22-1.38 (m, 4H), 1.62-1.70 (m, 2H), 2.03 (t, *J* = 2.4 Hz, 1H), 2.43 (s, 3H), 2.56 (t, *J* = 7.6 Hz, 2H), 3.83-3.93 (m, 2H), 4.02-4.12 (m, 2H), 5.78 (tdd, *J* = 1.2, 5.6, 15.2 Hz, 1H), 5.90 (dtd, *J* = 1.2, 6.4, 15.2 Hz, 1H), 5.96 (dd, *J* = 1.2, 5.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.5, 22.3, 23.5, 26.9, 31.0, 36.2, 38.8, 45.4, 47.4, 62.4, 74.1, 76.2, 84.7, 85.7, 127.7, 128.3, 129.6, 129.6, 135.7, 143.8, 176.7, 187.2. IR (film): ν 1092, 1132, 1160, 1271, 1349, 1678, 1735, 2219, 2872, 2932, 2959, 3274. HRMS (ESI) *m/z* calcd. For $C_{27}H_{35}NO_5S$ $(M+Na)^+$ 508.2128, found 508.2133.



1w

(*E*)-7-(N-(prop-2-ynyl)-N-tosylamino)-1-oxo-1-phenylhept-5-en-2-yn-4-yl pivalate (**1w**).

Compound **1w** (765 mg) was prepared in 52% yield from aldehyde **1u-a** and alkyne **1w-b** according to procedures described for **1u**. (silica gel, hexane/ethyl acetate 4:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 9H), 2.06 (t, *J* = 2.4 Hz, 1H), 2.41 (s, 3H), 3.87-3.97 (m, 2H), 4.04-4.15 (m, 2H), 5.88 (tdd, *J* = 1.2, 6.0, 15.2 Hz, 1H), 5.99 (dtd, *J* = 1.2, 6.4, 15.2 Hz, 1H), 6.08 (dd, *J* = 1.2, 5.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.61-7.65 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 8.08-8.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.0, 36.3, 38.9, 47.5, 62.6, 74.1, 76.3, 83.5, 88.2, 127.7, 128.3, 128.7, 129.6, 129.8, 134.4, 135.7, 136.3, 143.8, 176.8, 177.1. IR (film): ν 1092, 1132, 1159, 1261, 1348, 1597, 1646, 1734, 2225, 2332, 2975, 3277. HRMS (ESI) *m/z* calcd. For $C_{28}H_{29}NO_5S$ $(M+Na)^+$ 514.1659, found 514.1676.

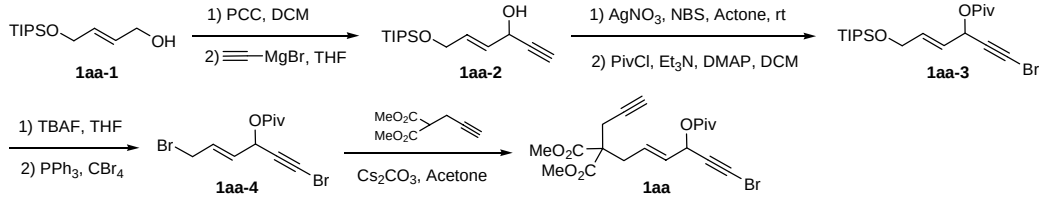


1y

(*E*)-7-oxo-1-(prop-2-ynyloxy)oct-2-en-5-yn-4-yl pivalate (**1y**).

Compound **1y** (192 mg) was prepared in 52% yield from aldehyde **1y-a** and alkyne **1u-b** according to procedures described for **1u**. (silica gel, hexane/ethyl acetate 10:1), oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.23 (s, 9H), 2.36 (s, 3H), 2.47 (t, *J* = 2.5 Hz, 1H), 4.13 (m, 2H), 4.17 (d, *J* = 2.5 Hz, 2H), 5.83 (m, 1H), 6.00 (m, 1H), 6.06 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.2, 32.9, 39.1, 57.9, 62.9, 68.9, 75.1, 79.5, 85.2, 86.3, 125.9, 131.9, 177.1, 183.9. IR (film): ν 2974, 2216, 1734, 1681, 1479, 1360, 1271, 1223, 1135, 1031, 956, 936 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{20}NaO_4$ $(M+Na)^+$ 299.1354, found 299.1364.

Preparation of substrate **1aa**.



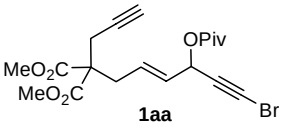
Compound **1aa-1** (3.44 g) was prepared in 86% yield from *cis*-2-butene-1,4-diol according to procedure described for **1g-1**. Propargyl alcohol **1aa-2** (2.26 g) was prepared in 63% yield from compound **1aa-1** (3.44 g) according to procedures described for **1a**.

To a solution of **1aa-2** (775 mg, 2.89 mmol) in dry acetone (24 ml) was added $AgNO_3$ (108 mg, 0.64 mmol) and NBS (771 mg, 4.33 mmol) at room temperature. The

mixture was stirred at room temperature for 30 min. After the addition of saturated $NaHCO_3$ (24 ml), the mixture was extracted with EtOAc. The combined extracts were dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL). To this solution was added triethylamine (0.95 mL, 6.80 mmol, 3.0 equiv), pivaloyl chloride (0.34 mL, 2.72 mmol, 1.2 equiv), and DMAP (5 mol %) at room temperature. The resulting mixture was stirred overnight, washed with water, brine, and dried over anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography to afford the desired propargylic ester **1aa-3** (894 mg) in 72% yield for 2 steps.

To a stirred solution of compound **1aa-3** (890 mg, 2.08 mmol) in THF (10 mL) was added a solution of tetrabutylammonium fluoride (3.12 mL, 3.12 mmol, 1.0M in THF) at 0 °C. The mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, and the residue was diluted with ethyl acetate, washed with H_2O, brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. To a solution of above residue in CH_2Cl_2 (20 mL) was added triphenylphosphine (786 mg, 3 mmol) and tetrabromomethane (981 mg, 3 mmol). The reaction mixture was stirred for 1 h at room temperature before silica was added and the solvents were removed under reduced pressure. The residue was purified through silica gel column chromatography to afford the corresponding bromide **1aa-4** (502 mg, 73% yield for 2 steps).

To a stirred solution of dimethylpropargyl malonate (23.0 mg, 0.12 mmol) and cesium carbonate (40.7 mg, 0.12 mmol) in dry acetone (3 mL) was added **1aa-4** (50.7 mg, 0.15 mmol). The resulting mixture was heated to 60°C and stirred overnight. The residue was filtered through a short pad of silica gel and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (20:1 Hex/EtOAc) to afford **1aa** (18 mg) in 35% yield as an oil.

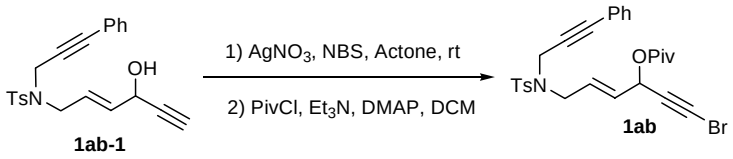


1aa

dimethyl 2-((E)-6-bromo-4-(pivaloyloxy)hex-2-en-5-ynyl)-2-(prop-2-ynyl)malonate (**1aa**).

Oil, (18 mg) ^{1}H NMR (400Mz, $CDCl_3$) δ 1.21 (s, 9H), 2.03 (brs, 1H), 2.78 (brs, 2H), 2.83 (d, *J*= 8.0 Hz, 2H), 3.75 (s, 6H), 5.66 (dd, *J*= 6.0, 14.0 Hz, 1H), 5.74-5.80 (m, 2H); ^{13}C NMR (100Mz, $CDCl_3$) δ 23.1, 27.2, 35.1, 39.0, 47.4, 53.1, 57.0, 64.3, 72.0, 76.2, 78.7, 129.2, 130.0, 170.1, 177.1. IR (film): 733, 912, 975, 1032, 1142, 1208, 1274, 1437, 1734, 2359, 2957, 3295 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{23}BrO_6$ $(M+Na)^+$ 449.0570, found 449.0576.

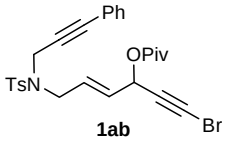
Preparation of substrate **1ab**.



Compound **1ab-1** was obtained during the preparation of **1h**.

To a solution of $AgNO_3$ (0.6 mmol, 10 %) in acetone (0.2 M) was added a propargyl alcohol **1ab-1** (2.27 g, 6 mmol). After stirring at rt for 10 min, NBS (7.2 mmol, 1.2 equiv) was added. The reaction mixture was stirred at rt until no starting material was left as indicated by TLC. The reaction mixture was filtered through a small pad of celite. The filtrate was concentrated under *vacuum* and the crude bromopropargyl alcohol was purified by silica gel flash column chromatography.

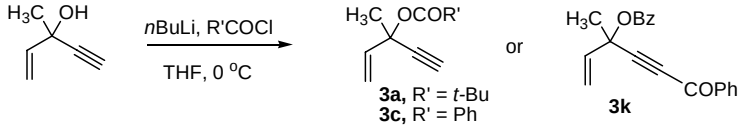
Product **1ab** (1.59 g) was obtained in 49% yield over two steps from **1ab-1** after esterification of the resulting alcohol following procedures described for the synthesis of **1a**.



(*E*)-6-(N-(3-phenylprop-2-ynyl)-N-tosylamino)-1-bromohex-4-en-1-yn-3-yl pivalate (**1ab**).

(silica gel, hexane/ethyl acetate 10:1), oil. (1.59 g) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 9 H), 2.34 (s, 3 H), 3.88-3.99 (m, 2 H), 4.23-4.34 (m, 2 H), 5.79 (tdd, *J* = 1.2, 5.6, 15.2 Hz, 1 H), 5.86 (dd, *J* = 1.2, 5.6 Hz, 1 H), 5.94 (dtd, *J* = 1.2, 6.4, 15.2 Hz, 1 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 7.22-7.29 (m, 5 H), 7.77 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 27.0, 37.0, 38.8, 47.7, 47.8, 63.5, 75.4, 81.4, 85.9, 122.0, 127.8, 128.1, 128.4, 128.8, 129.6, 129.7, 131.5, 135.8, 143.6, 176.9. IR (film): ν 1138, 1160, 1348, 1731, 2216, 2358, 2932, 2974, 3346 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{27}H_{28}BrNO_4S$ $(M+Na)^+$ 564.0814, found 564.0830.

Preparation of substrates **3a**, **3b**, **3c**, and **3k**.



For **3b,** R' = CH_3, Et_3N,/DMAP/AC_2O was used for esterification.
For **3k**, two equivalents of base (*n*-BuLi) and benzoyl chloride were used.

To a solution of commercially available 3-methyl-pent-1-en-4-yn-3-ol (1.92 g, 20 mmol) in THF (80 mL) was added *n*BuLi (12.5 mL, 20 mmol, 1.6 M in hexane) dropwise at 0 °C. After stirring for 20 min, a solution of pivaloyl chloride (2.4 g, 20 mmol) in THF (15 mL) was added. The reaction mixture was stirred at rt for 5 h. It was then quenched by saturated ammonium chloride and extracted with diethyl ether. The organic solution was washed with brine, dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 30:1) to provide the desired product **3a** (2.6 g) in 73% yield as an oil.

3a

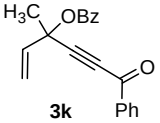
3-methylpent-1-en-4-yn-3-yl pivalate (**3a**).
oil. (2.6 g) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 9 H), 1.70 (s, 3 H), 2.65 (s, 1 H), 5.23 (dd, *J* = 0.8, 10.4 Hz, 1 H), 5.57 (dd, *J* = 0.8, 16.8 Hz, 1 H), 5.96 (dd, *J* = 10.4, 16.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0, 28.3, 39.0, 73.5, 74.4, 82.3, 115.3, 138.6, 176.3. IR (film): ν 928, 1062, 1136, 1281, 1367, 1479, 1738, 2971, 3271 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{11}H_{16}O_2$ $(M+Na)^+$ 203.1042 , found 203.1044.

3b

3-methylpent-1-en-4-yn-3-yl acetate (**3b**) is a known compound.[7]

3c

3-methylpent-1-en-4-yn-3-yl benzoate (**3c**).
Compound **3c** (760 mg) was prepared in 76% yield according to procedures described for **3a** by using benzoyl chloride instead of pivaloyl chloride. (silica gel, hexane/ethyl acetate 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (s, 3 H), 2.73 (s, 1 H), 5.31 (dd, *J* = 0.8, 10.4 Hz, 1 H), 5.69 (dd, *J* = 0.8, 17.2 Hz, 1 H), 6.11 (dd, *J* = 10.4, 17.2 Hz, 1 H), 7.41-7.45 (m, 2 H), 7.53-7.57 (m, 1 H), 8.02-8.04 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.6, 74.5, 75.1, 82.0, 115.9, 128.3, 129.6, 130.5, 133.0, 138.4, 164.5. IR (film): ν 707, 932, 1060, 1095, 1270, 1451, 1722, 2990, 3295 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{13}H_{12}O_2$ $(M+Na)^+$ 223.0729 , found 223.0732.

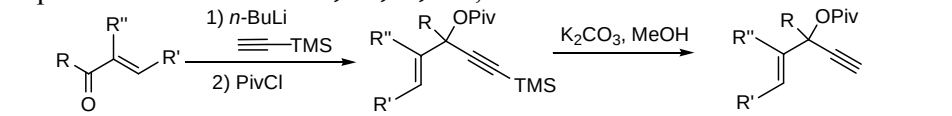


3k

3-methyl-6-oxo-6-phenylhex-1-en-4-yn-3-yl benzoate (**3k**).

Compound **3k** (360 mg) was prepared in 38% yield according to procedures described for **3a** by using benzoyl chloride (2 equiv) and ^{n}BuLi (2 equiv). (silica gel, hexane/ethyl acetate 4:1), oil. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.98 (s, 3H), 5.40 (d, *J*= 10.8 Hz, 1H), 5.74 (d, *J*= 17.2 Hz, 1H), 6.17 (dd, *J*= 10.4, 17.2 Hz, 1H), 7.44-7.50 (m, 4H), 7.56-7.62 (m, 2H), 8.04-8.10(m, 2H), 8.14-8.20 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 27.9, 74.0, 84.3, 91.5, 116.9, 128.4, 128.6, 129.68, 129.71, 130.1, 133.3, 134.2, 136.6, 137.3, 164.4, 177.6. IR (film): ν 700, 736, 850, 934, 1023, 1065, 1093, 1174, 1261, 1313, 1450, 1598, 1645, 1724 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{16}O_3$ $(M+Na)^+$ 327.0991, found 327.0993.

Preparation of substrates **3d, 3h, 3l, 3m**, and **3n.**



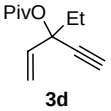
3d-1, R = Et, R' = R'' = H
3h-1, R = H, R' = R'' = H
3l-1, R = H, R' = Ph, R'' = H
3m-1, R = CH_3, R' = Ph, R'' = H
3n-1, R = CH_3, R' = H, R'' = CH_3

3d-2, R = Et, R' = R'' = H
3h-2, R = H, R' = R'' = H
3l-2, R = H, R' = Ph, R'' = H
3m-2, R = CH_3, R' = Ph, R'' = H
3n-2, R = CH_3, R' = H, R'' = CH_3

3d, R = Et, R' = R'' = H
3h, R = H, R' = R'' = H
3l, R = H, R' = Ph, R'' = H
3m, R = CH_3, R' = Ph, R'' = H
3n, R = CH_3, R' = H, R'' = CH_3

Procedure for the preparation of **3d**: To a stirred solution of trimethylsilylacetylene (1.41mL, 10 mmol) in THF (30 mL) was added *n*BuLi (6.25 mL, 10 mmol, 1.6 M in hexane) at -78 ^{o}C. The reaction mixture was warmed to 0 ^{o}C and stirred for 15 min. A solution of 1-penten-3-one **3d-1** (840 mg, 10 mmol) in THF (10 mL) was then added at -78 ^{o}C. The solution was stirred for 1 h. To this reaction mixture was added pivaloyl chloride (1.2 g, 10 mmol) and the solution was warmed to rt. The solution was stirred for another 3h, quenched with saturated ammonium chloride, and extracted with diethyl ether. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (silica gel, Hexane/ Et_3N = 60:1) to provide product **3d-2** (1.48 g) in 56% yield.

To a stirred solution of K_2CO_3 (221 mg, 1.6 mmol) in MeOH (16 mL) was added **3d-2** (425 mg, 1.6 mmol) and the solution was stirred for 2h at rt. The orgniac solvent was evaporated under reduced pressure and the residue was diluted with diethyl ether (30 mL). The solution was washed with H_2O, brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica gel, Hexane/Et_3N = 50:1) to provide the desired product **3d** (270 mg) in 87% yield as an oil.



3d

3-ethylpent-1-en-4-yn-3-yl pivalate (**3d**).

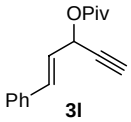
Oil. (270 mg) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (t, *J* = 7.2 Hz, 3 H), 1.20 (s, 9 H), 1.85 (m,1 H), 1.99 (m, 1 H), 2.65 (s, 1 H), 5.27 (dd, *J* = 0.8, 10.4 Hz, 1 H), 5.56 (dd, *J* = 0.8, 16.4 Hz, 1 H), 5.83 (dd, *J* = 10.4, 16.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.1, 27.0, 34.1, 39.1, 75.3, 77.4, 81.1, 116.3, 137.5, 176.2. IR (film): ν 936, 1152, 1278,

1479, 1740, 2360, 2976, 3286, cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{12}H_{18}O_2$ $(M+Na)^+$ 217.1199, found 217.1210.

3h

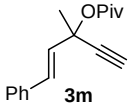
4-ethynyl-2,2-dimethylhex-5-en-3-one (**3h**).

Compound **3h** (1.05 g) was prepared in 63% yield from acrylaldehyde **3h-1** according to procedures described for **3d**. (silica gel, hexane/ethyl acetate 30:1), oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 9 H), 2.55 (d, J = 2.4 Hz, 1 H), 5.33 (dd, J = 1.2, 10.0 Hz, 1 H), 5.56 (dd, J = 1.2, 16.8 Hz, 1 H), 5.86-5.90 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0, 38.7, 63.7, 74.8, 79.3, 118.8, 132.6, 177.0. IR (film): ν 940, 966, 1004, 1139, 1273, 1479, 1731, 2975, 3296 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{10}H_{14}O_2$ $(M+Na)^+$ 189.0886 , found 189.0885.



3l

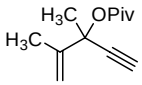
(*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate (**3l**) is a known compound.[7]



3m

(*E*)-3-methyl-1-phenylpent-1-en-4-yn-3-yl pivalate (**3m**).

Compound **3m** (330 mg) was prepared in 38% yield from (E)-4-phenylbut-3-en-2-one **3m-1** according to procedures described for **3d**. (silica gel, hexane/Et_3N 20:1), oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 9 H), 1.81 (s, 3 H), 2.72 (s, 1 H), 6.31 (d, J = 16.0 Hz, 1 H), 6.91 (d, J = 16.0 Hz, 1 H), 7.27-7.25 (m, 1 H), 7.34-7.30 (m, 2 H), 7.42-7.40 (m, 2 H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.2, 28.9, 39.3, 73.8, 74.9, 82.8, 127.1, 128.3, 128.8, 130.0, 131.1, 136.3, 176.6. IR (film): ν 1147, 1279, 1478, 1735, 2973, 3292 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{20}O_2$ $(M+Na)^+$ 279.1355, found 279.1356.

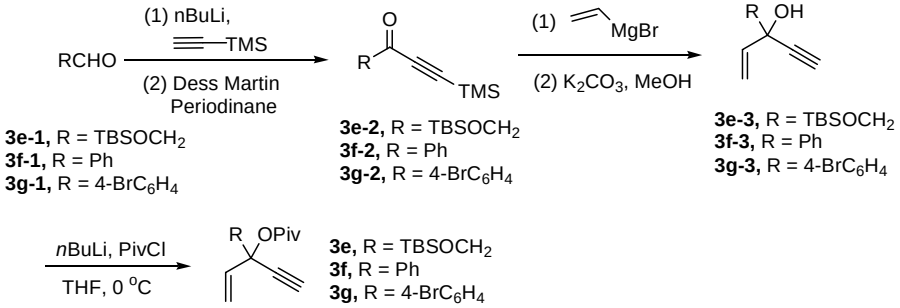


3n

2,3-dimethylpent-1-en-4-yn-3-yl pivalate (**3n**).

Compound **3n** (403 mg) was prepared in 52% yield from 3-methylbut-3-en-2-one **3n-1** according to procedures described for **3d**. (silica gel, hexane/Et_3N 30:1), oil. ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 9 H), 1.76 (s, 3 H), 1.85 (s, 3 H), 2.66 (s, 1 H), 5.00 (s, 1 H), 5.37 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.1, 27.2, 28.0, 39.2, 74.4, 76.0, 83.2, 112.4, 144.8, 176.3. IR (film): ν 1150, 1282, 1479, 1741, 2360, 2960, 3269 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{18}O_2$ $(M+Na)^+$ 217.1199, found 217.1198.

Preparation of substrates **3e**, **3f** and **3g**.



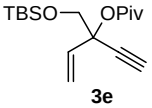
Procedure for substrate **3e**: To a stirred solution of trimethylsilylacetylene (280 mg, 2.8 mmol) in THF (14 mL, 0.2 M) at -78 °C, was added *n*BuLi (1.8 mL, 1.6 M in THF, 2.8 mmol). The reaction mixture was warmed to 0 °C and stirred for 15 min. A solution of aldehyde **3e-1** (2.8 mmol) in THF (6 mL) was then added at -78 °C. After stirring at -78 °C for 1h, the reaction mixture was diluted with Et_2O (10 mL), quenched by water (10 mL), and extracted with Et_2O (3x20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was used for the next step without purification.

To a solution of the above alcohol (2.8 mmol) in DCM (14 mL, 0.2 M) at 0 °C was added Dess-Martin periodinane (1.4 g, 3.4 mmol). The reaction was stirred at 0 °C for 1.5 h and was filtered to remove the solid. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane/ethyl acetate 20:1) to give a TMS-protected ynone **3e-2** in 71% yield for 2 steps.

To a solution of ketone **3e-2** (2 mmol) in THF (12 mL) was added vinyl Grignard reagent (2.86 mL, 2 mmol) dropwise at -78 °C. After stirring for 4 h, the reaction mixture was quenched by saturated ammonium chloride and extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was used for the next step without purification.

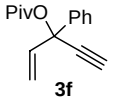
To a solution of the above crude product in MeOH (20 mL) was added K_2CO_3 (276 mg, 2 mmol). The reaction was stirred at rt for 1 h. The organic solvent was removed under reduced pressure. The resulting aqueous solution was extracted with diethyl ether, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to give product **3e-3** (375 g) in 83% yield over 2 steps.

To a solution of alcohol **3e-3** (375 g, 1.66 mmol) in THF was added *n*BuLi (1.1 mL, 1.66 mmol, 1.6 M in hexane) dropwise at 0 °C. After stirring for 20 min, pivaloyl chloride (200 mg, 1.66 mmol) was added. The reaction mixture was stirred at rt for 5 h before quenching by saturated ammonium chloride and extracted with diethyl ether. The solvent was evaporated and the residue was purified by flash column chromatography using neutral aluminum oxide (the aluminum oxide was treated by 20% Et_3N in hexane for 0.5h. Hexane/NEt_3/EtOAc = 30:2:1) to provide the desired product **3e** (442 mg) in 86% yield as an oil.



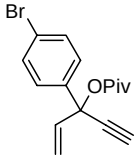
3e

3-((tert-butyldimethylsilyloxy)methyl)pent-1-en-4-yn-3-yl pivalate (**3e**).
oil. (442 mg) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.06 (s, 6 H), 0.89 (s, 9 H), 1.20 (s, 9 H), 2.63 (s, 1 H), 3.75 (d, *J* = 10.4 Hz, 1 H), 3.98 (d, *J* = 10.4 Hz, 1 H), 5.32 (d, *J* = 10.4 Hz, 1 H), 5.62 (d, *J* = 17.2 Hz, 1 H), 5.94 (dd, *J* = 10.8, 17.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.4, -5.5 18.2, 25.7, 27.0, 39.1, 68.7, 75.8, 79.9, 117.3, 135.3, 176.3. IR (film): ν 1136, 1255, 1477, 1742, 2957, 3270 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{30}O_3Si$ $(M+Na)^+$ 333.1856, found 333.1856.



3f

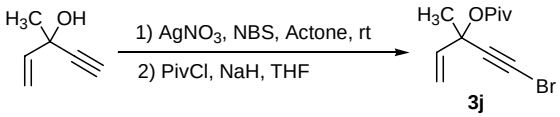
3-phenylpent-1-en-4-yn-3-yl pivalate (**3f**).
Compound **3f** (335 mg) was prepared in 46% yield from benzaldehyde **3f-1** according to procedures described for **3e**. (the aluminum oxide was treated by 20% Et_3N in hexane for 0.5h. Hexane/NEt_3/EtOAc = 30:2:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (s, 9 H), 2.90 (s, 1 H), 5.26 (dd, *J* = 0.8, 10.4 Hz, 1 H), 5.58 (dd, *J* = 0.8, 16.8 Hz, 1 H), 6.05 (dd, *J* = 10.4, 16.8 Hz, 1 H), 7.32 (m, 1 H), 7.35 (m, 2 H), 7.56 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0, 39.2, 77.5, 77.6, 80.6, 115.3, 125.6, 128.1, 128.3, 138.6, 140.2, 175.5. IR (film): ν 3284, 2973, 1742, 1277, 1132, 979, 934, 762, 696 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{18}O_2$ $(M+Na)^+$ 265.1199, found 265.1204.



3g

3-(4-bromophenyl)pent-1-en-4-yn-3-yl pivalate (**3g**).
Compound **3g** (512 mg) was prepared in 53% yield from 4-bromobenzaldehyde **3g-1** according to procedures described for **3e**. (the aluminum oxide was treated by 20% Et_3N in hexane for 0.5h. Hexane/NEt_3/EtOAc = 30:2:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 9 H), 2.91 (s, 1 H), 5.27 (d, *J* = 10.4 Hz, 1 H), 5.56 (d, *J* = 17.2 Hz, 1 H), 6.01 (dd, *J* = 10.4, 17.2 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 2 H), δ 7.48 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.9, 39.2, 77.9, 80.1, 115.7, 122.3, 127.5, 131.5, 138.2, 139.4, 175.4. IR (film): ν 1132, 1277, 1479, 1742, 2974, 3296 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{16}H_{17}BrO_2$ $(M+Na)^+$ 343.0304, found 343.0308.

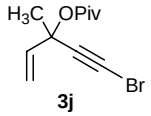
Preparation of substrate **3j**.



3j

To a solution of $AgNO_3$ (100 mg, 0.6 mmol, 10 %) in acetone (30 mL) was added commercially available 3-methyl-pent-1-en-4-yn-3-ol (576 mg, 6 mmol). After stirring at rt for 10 min, NBS (7.2 mmol, 1.2 equiv) was added. The reaction mixture was stirred at rt until no starting material was left as indicated by TLC. The reaction mixture was filtered through a small pad of celite. The filtrate was concentrated under reduced

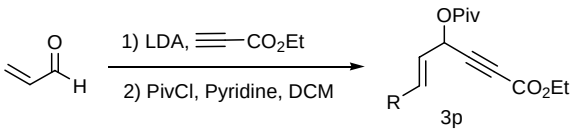
pressure and the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 4:1) to give bromopropargyl alcohol as an oil (887 mg, 85%).
To a solution of NaH (280 mg, 7 mmol) in THF (20 mL) was added a solution of the above bromopropargyl alcohol (870 mg, 5 mmol) in THF (10 mL). The mixture solution was stirred at rt for 30 min. To this solution was added pivaloyl chloride (840 mg, 7 mmol) in THF (10 mL). The reaction was stirred at rt overnight, quenched by H_2O, diluted with Et_2O (50 mL), washed with H_2O, brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (hexane/ethyl acetate 20:1) to give **3j** (1.05 g, 82%) as an oil.



3j

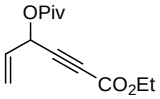
1-bromo-3-methylpent-4-en-1-yn-3-yl pivalate (**3j**).
oil. (1.05 g) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 9 H), 1.69 (s, 3 H), 5.21 (dd, J = 10.44, 0.73 Hz, 1 H), 5.51 (dd, J = 17.03, 0.70 Hz, 1 H), 5.93 (dd, J = 17.00, 10.44 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.3, 28.4, 39.3, 47.1, 74.6, 78.9, 115.6, 138.8, 176.4. IR (filv): ν 2981, 2935, 2873, 2360, 2341, 2216, 1736, 1479, 1460, 1397, 1368, 1281, 1136, 1062, 1029, 984, 923, 867, 819, 768, 735, 689 cm^{-1}. HRMS (ESI) for $C_{11}H_{15}BrO_2$ (M+Na), 281.0148 (calc.), found 281.0144.

Preparation of substrates **3p**.



3p

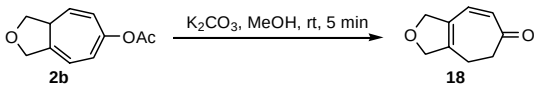
To a stirred solution of diisopropylamine (17 mmol, 1.7 equiv) in THF (40 mL) was added a solution of *n*-butyllithium (1.6 M in hexanes, 10.6 mL, 17 mmol, 1.7 equiv) slowly at -78 °C. The mixture was stirred at -78 °C for 15 min and then for 30 min at 0 °C. The mixture was cooled to -78 °C and ethyl propiolate (15 mmol, 1.5 equiv) was added. After stirring for 30 min at -78 °C, a solution of acrolein (10 mmol, 1.0 equiv) in THF (20 mL) was added. After stirring at -78 °C for 3 h, the reaction mixture was added to a saturated ammonium chloride solution at 0 °C. The aqueous phase was extracted with Et_2O, the combined organic layers were washed with brine, dried over $MgSO_4$ and the solvents were removed under reduced pressure to give an oil.
To a solution of above oil (770 mg, 5 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) was added pyridine (1.18 g, 3 equiv), DMAP (one crystal) and pivaloyl chloride (900 mg, 1.5 equiv) at 0°C. After stirring for overnight, the mixture was diluted with CH_2Cl_2 (30 mL), washed with a 10% copper sulfate aqueous solution and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (hexane/ethyl acetate 10:1) to give **3p** (840 mg, 71%).



3p

ethyl 4-(pivaloyloxy)hex-5-en-2-ynoate (**3p**).
oil. (840 mg) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (s, 9 H), 1.32 (t, *J* = 7.0 Hz, 3 H), 4.25 (q, *J* = 7.0 Hz, 2 H), 5.37 (d, *J* = 10.0 Hz, 1 H), 5.56 (d, *J* = 17 Hz, 1 H), 5.85-5.91 (m, 1 H), 5.97 (td, *J* = 1.0, 5.5 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 27.0, 38.8, 62.2, 63.2, 77.8, 81.9, 119.8, 131.2, 153.0, 176.8. IR (film): ν 975, 1131, 1244, 1462, 1715, 1737, 2244, 2978 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{13}H_{18}O_4$ $(M+Na)^+$ 261.1097, found 261.1103.

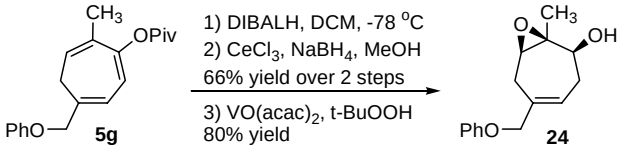
Hydrolysis of cycloheptatriene **2b** to dienone **18**.



2b **18**

To a solution of cycloheptatriene **2b** (0.2 mmol) in MeOH (6 mL) was added K_2CO_3 (41 mg, 0.3 mmol). After stirring at room temperature for 5 min, H_2O (30 mL) was added and extracted with ethyl acetate. The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to afford dienone **18** (25 mg, 83% yield) as an oil.
(7*Z*)-4,5-dihydro-1H-cyclohepta[c]furan-6(3H)-one (**18**).
Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (t, *J* = 6.4 Hz, 2 H), 2.73-2.77 (m, 2 H), 4.80 (s, 2 H), 4.81 (s, 2 H), 6.14 (d, *J* = 12.0 Hz, 1 H), 6.45 (d, *J* = 12.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 40.1, 78.0, 79.2, 129.8, 131.4, 131.7, 144.7, 199.9. IR (film): ν 793, 1058, 1595, 1644, 1662, 2840 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_9H_{10}O_2$ $(M+H)^+$ 151.0754, found 151.0753.

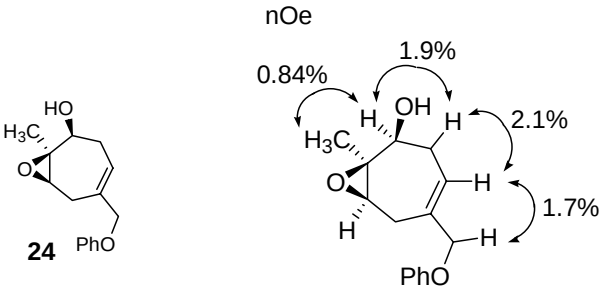
Procedure for the conversion of product **5g** to compound **24**.



5g **24**

To a stirred solution of **5g** (312 mg, 1 mmol) in DCM (20 mL) at -78 °C was added DIBALH (4 mL, 4 mmol, 1 M in hexane) dropwise. The reaction mixture was stirred at the same temperature for 30 min and was quenched with H_2O (200 mg, 11 mmol). When the temperature was reached at 0 °C, MeOH (20 mL) was added. To this solution, $CeCl_3$ (369 mg, 4.5 mmol) and $NaBH_4$ (111 mg, 12 mmol) was then added. The reaction mixture was stirred for 10 min and quenched with aqueous HCl solution (1M). The solution was diluted with DCM (40 mL), washed with H_2O, brine and dried with Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to give an allylic alcohol (152 mg, 66% yield).
To a solution of $VO(acac)_2$ (8 mg, 5 mol %) and the above allylic alcohol (143 mg, 0.62 mmol) in 20 mL of dry benzene at rt was added *t*-BuOOH (0.23 mL, 5.5 M in decane). The resulting solution was stirred for 24 h at 40 °C. The reaction mixture was quenched with $Na_2S_2O_3$ and filtered with celite. The solvent was removed under reduced pressure

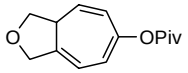
and the residue was purified by chromatography on silica gel to give epoxide **24** (121 mg, 80 %).



1-methyl-5-phenoxymethyl-8-oxa-bicyclo[5.1.0]oct-4-en-2-ol (**24**).
oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (s, 3 H), 2.12 (d, *J* = 6.0 Hz, 1 H), 2.38 (dd, *J* = 5.5, 5.5 Hz, 2 H), 2.70 (dd, *J* = 4.5, 16.5 Hz, 1 H), 2.76 (dd, *J* = 6.0, 16.0 Hz, 1 H), 3.19 (t, *J* = 6.0 Hz, 1 H), 3.83 (td, *J* = 5.5, 5.5 Hz, 1 H), 4.39 (s, 2 H), 5.73 (t, *J* = 6.0 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 2 H), 6.95 (t, *J* = 7.5 Hz, 1 H), 7.25-7.29 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.9, 28.6, 31.8, 61.9, 63.1, 69.4, 72.8, 114.9, 121.0, 124.7, 129.4, 135.1, 158.5. IR (film): ν 690, 753, 1027, 1238, 1454, 1493, 1597, 2360, 2850, 2918, 3418 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{18}O_3$ $(M+Na)^+$ 269.1148, found 269.1150.

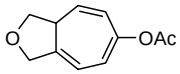
See procedures for the preparation of bicyclic products via Rh-catalyzed intramolecular [5+2] cycloaddition with concomitant 1,2-acyloxy migration in the experimental section of the manuscript.

Characterization data for products derived from intramolecular reaction:



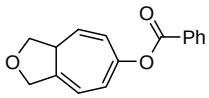
2a

3,8a-dihydro-1H-cyclohepta[c]furan-6-yl pivalate (**2a**).
Yield : 85%, 40 mg, oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (s, 9 H), 2.67-2.69 (m, 1 H), 4.09 (dd, *J* = 4.8, 9.2 Hz, 1 H), 4.29 (dd, *J* = 7.2, 9.2 Hz, 1 H), 4.41 (d, *J* = 14.4 Hz, 1 H), 4.47 (d, *J* = 14.4 Hz, 1 H), 5.22 (dd, *J* = 4.4, 9.6 Hz, 1 H), 5.91 (d, *J* = 9.6 Hz, 1 H), 6.06-6.09 (m, 1 H), 6.32 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.3, 39.1, 43.2, 71.0, 74.7, 112.3, 120.1, 123.7, 125.7, 139.5, 150.6, 177.7. IR (film): ν 912, 1124, 1277, 1480, 1742, 2872, 2972 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{14}H_{18}O_3$ $(M+Na)^+$ 257.1148, found 257.1145.



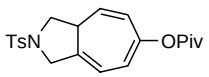
2b

3,8a-dihydro-1H-cyclohepta[c]furan-6-yl acetate (**2b**).
Yield : 81%, 31 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3 H), 2.64-2.67 (m, 1 H), 4.09 (dd, *J* = 4.8, 9.2 Hz, 1 H), 4.28 (dd, *J* = 7.2, 9.2 Hz, 1 H), 4.40 (d, *J* = 14.0 Hz, 1 H), 4.46 (d, *J* = 14.0 Hz, 1 H), 5.21 (dd, *J* = 4.8, 10.0 Hz, 1 H), 5.96 (d, *J* = 9.6 Hz, 1 H), 6.06-6.09 (m, 1 H), 6.34-6.36 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 42.9, 70.7, 74.5, 112.0, 120.1, 123.5, 125.3, 139.4, 150.0, 169.9. IR (film): ν 913, 1120, 1211, 1411, 1750, 2852, 2925 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{11}H_{12}O_3$ $(M+Na)^+$ 215.0678, found 215.0682.



2c

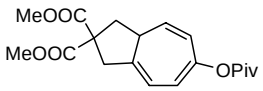
3,8a-dihydro-1H-cyclohepta[c]furan-6-yl benzoate (**2c**).
Yield : 83%, 42 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75-2.77 (m, 1 H), 4.13 (dd, *J* = 4.4, 8.8 Hz, 1 H), 4.32 (dd, *J* = 7.2, 8.8 Hz, 1 H), 4.45 (d, *J* = 14 Hz, 1 H), 4.50 (d, *J* = 14 Hz, 1 H), 5.27 (dd, *J* = 4.4, 9.6 Hz, 1 H), 6.08 (td, *J* = 1.2, 9.6 Hz, 1 H), 6.12-6.15 (m, 1 H), 6.50 (d, *J* = 6.8 Hz, 1 H), 7.47-7.51 (m, 2 H), 7.59-7.64 (m, 1 H), 8.12-8.15 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.0, 70.7, 74.5, 112.1, 120.3, 123.6, 125.5, 128.5, 129.6, 130.0, 133.4, 139.5, 150.3, 165.4. IR (film): ν 705, 914, 1122, 1314, 1729, 2360, 2854, 2941 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{14}O_3$ $(M+Na)^+$ 277.0835, found 277.0834.



2d

1,2,3,3a-tetrahydro-2-tosylcyclohepta[c]pyrrol-6-yl pivalate (**2d**).

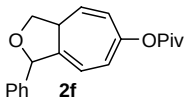
Yield : 96%, 74 mg, solid, mp: 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9 H), 2.45 (s, 3 H), 2.51-2.52 (m, 1 H), 3.50 (dd, *J* = 7.6, 10.0 Hz, 1 H), 3.57 (dd, *J* = 3.2, 10.0 Hz, 1 H), 3.86 (d, *J* = 14.4 Hz, 1 H), 3.99 (d, *J* = 14.8 Hz, 1 H), 5.16 (dd, *J* = 4.8, 10.0 Hz, 1 H), 5.87 (d, *J* = 9.6 Hz, 1 H), 6.03-6.05 (m, 1 H), 6.26 (d, *J* = 6.4 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.72-7.75 (m, 2 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 22.0, 27.8, 39.9, 43.0 53.2, 55.2, 116.2, 121.1, 124.9, 127.0, 129.6, 131.2, 133.7, 135.9, 145.4, 152.2, 177.7. IR (film): ν 814, 1137, 1161, 1347, 1742, 2974 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{21}H_{25}NO_4S$ $(M+Na)^+$ 410.1396, found 410.1392.



2e

Dimethyl 6-(pivaloyloxy)-3,3a-dihydroazulene-2,2(1H)-dicarboxylate (**2e**).

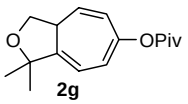
Yield : 75%, 52 mg, oil. (5 mol % of $[Rh(COD)_2]BF_4$) ^{1}H NMR (400Mz, $CDCl_3$) *δ* 1.27 (s, 9H), 2.43 (dd, *J*= 6.8, 13.2 Hz, 1H), 2.64-2.73 (m, 1H), 2.91 (dd, *J*= 8.4, 13.2 Hz, 1H), 3.14 (s, 2H), 3.73 (s, 3H), 3.74 (s, 3H), 5.15 (dd, *J*= 4.8, 9.6 Hz, 1H), 5.80 (td, *J*= 1.6, 10.0 Hz, 1H), 6.04-6.09 (m, 1H), 6.17-6.22 (m, 1H); ^{13}C NMR (100Mz, $CDCl_3$) *δ* 27.3, 39.1, 40.5, 41.0, 41.8, 53.1, 53.1, 61.0, 115.8, 120.0, 123.2, 128.4, 139.8, 150.5, 171.7, 171.8, 177.6. IR (film): 705, 738, 910, 1072, 1132, 1203, 1268, 1437, 1483, 1736, 2959 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{24}O_6$ $(M+Na)^+$ 371.1465, found 371.1484.



2f

3,3a-dihydro-1-phenyl-1H-cyclohepta[c]furan-6-yl pivalate (**2f**).

Yield : 90%, 56 mg, oil, (dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, one isomer): δ 1.29 (s, 9 H), 2.69 (m, 1 H), 4.25 (dd, *J* = 6.4, 9.2 Hz, 1 H), 4.35 (dd, *J* = 2.4, 9.2 Hz, 1 H), 5.38 (dd, *J* = 4.8, 9.6 Hz, 1 H), 5.46 (s, 1 H), 5.83 (d, *J* = 6.8 Hz, 1 H), 5.98 (d, *J* = 9.6 Hz, 1 H), 6.33 (d, *J* = 6.4, 1 H), 7.22-7.40 (m, 5 H). ^{1}H NMR (400 MHz, $CDCl_3$, the other isomer): δ 1.29 (s, 9 H), 3.01-3.06 (m, 1 H), 4.03 (dd, *J* = 7.2, 8.8 Hz, 1 H), 4.64 (dd, *J* = 8.8, 8.8 Hz, 1 H), 5.27 (dd, *J* = 4.4, 9.6 Hz, 1 H), 5.33 (s, 1 H), 5.64 (d, *J* = 6.8 Hz, 1 H), 5.93 (d, *J* = 9.6 Hz, 1 H), 6.19 (d, *J* = 6.8 Hz, 1 H), 7.22-7.40 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$, mixture): δ 27.0, 38.8, 43.5, 43.6, 73.0, 73.2, 83.2, 83.4, 114.8, 114.9, 119.5, 120.0, 123.6, 123.9, 125.3, 125.9, 127.6, 127.9, 128.1, 128.2, 128.4, 128.5, 139.9, 140.2, 141.8, 143.5, 150.4, 150.7, 177.4. IR (film): ν 908, 1055, 1134, 1275, 1746, 2872, 2973 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{22}O_3$ $(M+Na)^+$ 333.1461, found 333.1457.

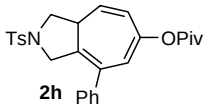


2g

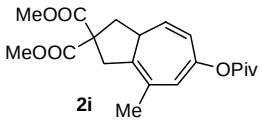
3,3a-dihydro-1,1-dimethyl-1H-cyclohepta[c]furan-6-yl pivalate (**2g**).

Yield : 90%, 47 mg, oil. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 1.08 (s, 3 H), 1.14 (s, 9 H), 1.26 (s, 3 H), 2.43-2.45 (m, 1 H), 3.92 (dd, *J* = 4.0, 9.2 Hz, 1 H), 4.12(dd, *J* = 7.2, 9.2 Hz,

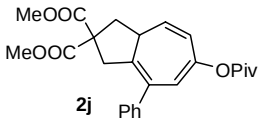
1 H), 5.16 (dd, *J* = 4.4, 9.6 Hz, 1 H), 5.77 (td, *J* = 1.6, 9.6 Hz, 1 H), 5.89 (dd, *J* = 1.6, 6.4 Hz, 1 H), 6.19-6.22 (m, 1 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 27.2, 27.9, 30.3, 39.9, 45.0, 71.2, 82.7, 113.1, 121.2, 124.6, 127.6, 149.5, 151.9, 177.8. IR (film): ν 841, 1125, 1279, 1750, 2872, 2974 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_3$ $(M+Na)^+$ 285.1461, found 285.1466.



1,2,3,3a-tetrahydro-8-phenyl-2-tosylcyclohepta[c]pyrrol-6-yl pivalate (**2h**).
Yield : 88%, 81 mg, solid, mp: 126-128 °C. (DCM, 0.025 M) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9 H), 2.46 (s, 3 H), 2.59 (m, 1 H), 3.38 (dd, *J* = 6.8, 9.6 Hz, 1 H), 3.72 (dd, *J* = 2.0, 9.6 Hz, 1 H), 3.79 (d, *J* = 15.2 Hz, 1 H), 3.95 (d, *J* = 15.2 Hz, 1 H), 5.38 (dd, *J* = 4.8, 9.6 Hz, 1 H), 5.93 (d, *J* = 10.0 Hz, 1 H), 6.37 (s, 1 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 7.27-7.38 (m, 5 H), 7.71 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 22.0, 27.8, 39.9, 43.3, 52.8, 55.0, 124.37, 124.41, 129.0, 129.58, 129.61, 129.64, 130.0, 130.3, 131.3, 132.9, 133.8, 141.0, 145.5, 152.4, 177.7. IR (film): ν 1028, 1127, 1162, 1348, 1700, 1747, 2973 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{27}H_{29}NO_4S$ $(M+Na)^+$ 486.1709, found 486.1699.

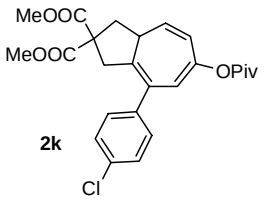


Dimethyl 8-methyl-6-(pivaloyloxy)-3,3a-dihydroazulene-2,2(1H)-dicarboxylate (**2i**).
Yield : 82%, 59 mg, oil. (DCM, 0.05 M. The amount of metal catalyst and ligand was doubled.) ^{1}H NMR (400Mz, $CDCl_3$) δ 1.27 (s, 9H), 1.86 (s, 3H), 2.50-2.62 (m, 2H), 2.72-2.84 (m, 1H), 3.09 (s, 2H), 3.72 (s, 6H), 5.23 (dd, *J*= 4.4, 9.6 Hz, 1H), 5.75 (d, *J*= 9.6 Hz, 1H), 6.17 (s, 1H); ^{13}C NMR (100Mz, $CDCl_3$) δ 19.5, 27.3, 39.0, 39.3, 40.1, 41.8, 53.07, 53.13, 60.9, 122.4, 123.3, 124.9, 129.6, 134.4, 149.6, 171.98, 172.03, 177.7. IR (film): 703, 736, 905, 1086, 1123, 1231, 1269, 1435, 1734, 2957 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{26}O_6$ $(M+Na)^+$ 385.1622, found 385.1610.



Dimethyl 8-phenyl-6-(pivaloyloxy)-3,3a-dihydroazulene-2,2(1H)-dicarboxylate (**2j**).
Yield : 70%, 59 mg, oil. (DCM, 0.05 M. The amount of metal catalyst and ligand was doubled.) ^{1}H NMR (400Mz, $CDCl_3$) δ 1.27 (s, 9H), 2.59 (dd, *J*= 5.2, 12.8 Hz, 1H), 2.74-2.82 (m, 1H), 2.90 (dd, *J*= 8.8, 12.8 Hz, 1H), 3.05 (d, *J*= 18.8 Hz, 1H), 3.18 (d, *J*= 17.6 Hz, 1H), 3.70 (s, 3H), 3.72 (s, 3H), 5.30 (dd, *J*= 4.4, 9.6 Hz, 1H), 5.85 (td, *J*= 1.6 , 9.6 Hz, 1H), 6.35 (s, 1H), 7.22-7.29 (m, 3H), 7.31-7.37 (m, 2H); ^{13}C NMR (100 Mz, $CDCl_3$) δ 27.3, 39.1, 40.2, 40.3, 42.2, 53.0, 53.1, 61.0, 122.8, 124.0, 127.2, 128.5, 128.8, 129.7, 130.0, 136.4, 141.0, 150.1, 171.7, 171.8, 177.6; IR (film): 704, 732,

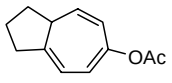
768, 911, 1072, 1124, 1201, 1266, 1436, 1736, 2958 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{28}O_6$ $(M+Na)^+$ 447.1778, found 447.1778.



2k

Dimethyl-8-(4-chlorophenyl)-6-(pivaloyloxy)-3,3a-dihydroazulene-2,2(1H)-dicarbox ylate (**2k**).

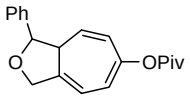
Yield : 60%, 55 mg, oil. (DCM, 0.05 M. The amount of metal catalyst and ligand was doubled.) ^{1}H NMR (400Mz, $CDCl_3$) δ 1.27 (s, 9H), 2.60 (dd, *J*= 4.8, 13.2 Hz, 1H), 2.72-2.80 (m, 1H), 2.89 (dd, *J*= 8.8, 13.2 Hz,1H), 3.01 (d, *J*= 18.0 Hz, 1H), 3.15 (d, *J*= 17.2 Hz, 1H), 3.70 (s, 3H), 3.71 (s, 3H), 5.30 (dd, *J*= 4.8, 9.6 Hz, 1H), 5.85 (td, *J*= 1.6 , 9.6 Hz, 1H), 6.28 (s, 1H), 7.17-7.21 (m, 2H), 7.29-7.35 (m, 2H); ^{13}C NMR (100 Mz, $CDCl_3$) δ 27.3, 39.1, 40.1, 40.2, 42.2, 53.1, 53.2, 60.9, 122.9, 123.5, 128.6, 128.7, 130.21, 130.24, 133.1, 136.8, 139.4, 150.4, 171.6, 171.7, 177.6. IR (film): 731, 831, 908, 1014, 1121, 1200, 1264, 1434, 1490, 1733, 2956 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{27}ClO_6$ $(M+Na)^+$ 481.1388, found 481.1386.



2l

1,2,3,3a-tetrahydroazulen-6-yl acetate (**2l**).

Yield : 76%, 29 mg, oil. (DCM, 0.05 M. The amount of metal catalyst and ligand was doubled.) ^{1}H NMR (400Mz, $CDCl_3$) δ 1.64-1.76 (m, 1H), 1.80-1.96 (m, 2H), 2.04-2.16 (m, 1H), 2.19 (s, 3H), 2.26-2.34 (m, 1H), 2.48 (t, *J*= 6.8 Hz, 2H), 5.10 (dd, *J*= 4.8, 9.6 Hz, 1H), 5.90 (d, *J*= 10.0 Hz, 1H), 6.06-6.12 (m, 1H), 6.30 (d, *J*= 6.4 Hz, 1H); ^{13}C NMR (100Mz, $CDCl_3$) δ 21.3, 27.2, 33.3, 33.4, 42.7, 114.4, 120.8, 122.6, 127.4, 144.7, 149.5, 170.1. IR (film): 732, 914, 1117, 1152, 1175, 1215, 1369, 1757, 2954 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{12}H_{14}O_2$ $(M+Na)^+$ 213.0886, found 213.0882.

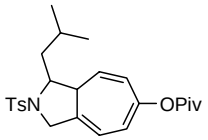


2m

3,8a-dihydro-1-phenyl-1H-cyclohepta[c]furan-6-yl pivalate (**2m**).

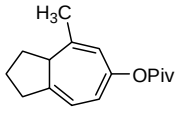
Yield : 76%, 47 mg, oil. (DCM, 0.025 M). ^{1}H NMR (400 MHz, CD_3COCD_3, one isomer): δ 1.11 (s, 9 H), 2.52-2.55 (m, 1 H), 4.47 (d, *J* = 14.4 Hz, 1 H), 4.52 (d, *J* = 14.0 Hz, 1 H), 4.67 (dd, *J* = 5.2, 10.0 Hz, 1 H), 5.21 (d, *J* = 5.6 Hz, 1 H), 5.66 (d, *J* = 10.0 Hz, 1 H), 6.08-6.10 (m, 1 H), 6.28 (d, *J* = 6.4 Hz, 1 H), 7.15-7.34 (m, 5H). ^{1}H NMR (400 MHz, CD_3COCD_3, the other isomer): δ 1.11 (s, 9 H), 2.48-2.50 (m, 1 H), 4.37 (d, *J* = 14.0 Hz, 1 H), 4.62 (d, *J* = 14.0 Hz, 1 H), 4.94 (d, *J* = 7.6 Hz, 1 H), 5.34 (dd, *J* = 4.0, 10.0 Hz, 1 H), 5.84 (d, *J* = 10.0 Hz, 1 H), 6.00-6.02 (m, 1 H), 6.14 (d, *J* = 6.8 Hz, 1 H), 7.15-7.34 (m, 5 H). ^{13}C NMR (100 MHz, CD_3COCD_3, mixture): δ 27.86, 27.88, 39.9, 48.1, 52.9, 70.9, 72.6, 83.9, 88.7, 113.6, 114.0, 121.1, 121.6, 121.8, 124.2, 125.9, 126.0,

127.3, 127.5, 128.7, 129.2, 129.7, 129.9, 139.9, 140.1, 141.9, 142.9, 151.9, 152.2, 177.7. IR (film): ν 814, 1028, 1039, 1130, 1161, 1348, 1746, 2871, 3058 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{22}O_3$ $(M+Na)^+$ 333.1461, found 333.1457.



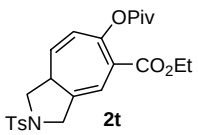
2n

1,2,3,8a-tetrahydro-1-isobutyl-2-tosylcyclohepta[c]pyrrol-6-yl pivalate (**2n**).
Yield : 80%, 71 mg, oil. (DCM, 0.025 M). ^{1}H NMR (400 MHz, $CDCl_3$, one isomer): δ 0.89-1.03 (m, 6 H), 1.26 (s, 9 H), 1.61-1.77 (m, 2 H), 1.82-1.89 (m, 1 H), 2.07-2.08 (m, 1 H), 2.41 (s, 3 H), 4.09-4.12 (m, 1 H), 4.26 (d, *J* = 16.4 Hz, 1 H), 4.29 (d, *J* = 16.4 Hz, 1 H), 4.56 (dd, *J* = 5.2, 9.6 Hz, 1 H), 5.68 (d, *J* = 10.0 Hz, 1 H), 6.05-6.07 (m, 1 H), 6.30 (d, *J* = 6.4 Hz, 1 H), 7.27-7.32 (m, 2 H), 7.70-7.73 (m, 2 H). ^{1}H NMR (400 MHz, $CDCl_3$, the other isomer): δ 0.89-1.03 (m, 6 H), 1.27 (s, 9 H), 1.61-1.77 (m, 2 H), 1.94-2.01 (m, 1 H), 2.12-2.15 (m, 1 H), 2.42 (s, 3 H), 3.61-3.67 (m, 1 H), 4.01 (d, *J* = 16.0 Hz, 1 H), 4.14 (d, *J* = 15.6 Hz, 1 H), 5.39 (dd, *J* = 5.2, 10.0 Hz, 1 H), 5.91 (d, *J* = 10.0 Hz, 1 H), 5.94-5.96 (m, 1 H), 6.18 (d, *J* = 6.4 Hz, 1 H), 7.27-7.32 (m, 2 H), 7.70-7.73 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, mixture): δ 21.5, 22.1, 22.3, 23.1, 23.3, 24.9, 25.2, 26.98, 27.0, 38.8, 39.0, 44.5, 44.6, 48.7, 51.0, 52.6, 60.7, 64.8, 114.3, 119.3, 119.4, 120.0, 122.6, 123.0, 124.7, 127.3, 127.9, 129.6, 129.7, 132.4, 133.0, 134.1, 135.9, 143.5, 143.9, 150.35, 150.44, 177.1, 177.3. IR (film): ν 731, 910, 1091, 1132, 1341, 1747, 2870, 2958 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{33}NO_4S$ $(M+Na)^+$ 466.2022, found 466.2025.



2o

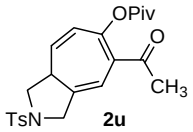
1,2,3,3a-tetrahydro-4-methylazulen-6-yl pivalate (**2o**).
Yield : 80%, 39 mg, oil. (DCM, 0.05 M. The mounts of metal catalyst and ligand were doubled.) ^{1}H NMR (400Mz, $CDCl_3$) δ1.28 (s, 9 H), 1.69-1.78 (m, 1 H), 1.80-1.86 (m, 1 H), 1.87-1.97 (m, 4 H), 2.16-2.23 (m, 1 H), 2.38-2.55 (m, 3 H), 5.71 (s, 1 H), 6.06 (d, *J* = 6.4 Hz, 1 H), 6.14 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 26.9, 27.1, 28.6, 32.9, 38.8, 45.3, 114.4, 118.7, 119.7, 135.5, 143.9, 149.0, 177.6. IR (film): ν 822, 907, 1277, 1395, 1745, 2959 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_2$ $(M+Na)^+$ 269.1512, found 269.1521.



2t

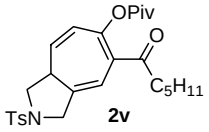
(3a*E*,5*Z*,7*Z*)-ethyl-1,2,3,8a-tetrahydro-6-(pivaloyloxy)-2-tosylcyclohepta[c]pyrrole-5-carboxylate (**2t**).
Yield : 83%, 76 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3 H), 1.29 (s, 9 H), 2.45 (s, 3 H), 2.47 (m, 1 H), 3.36 (dd, *J* = 7.2, 10.0 Hz, 1H), 3.68 (dd, *J* = 2.4, 10.0

Hz, 1H), 3.80 (dd, *J* = 2.0, 14.4 Hz, 1H), 4.05-4.12 (m, 1H), 4.16 (qd, *J* = 7.2, 10.8 Hz, 1H), 4.27 (qd, *J* = 7.2, 10.8 Hz, 1H), 5.50 (dd, *J* = 4.8, 9.6 Hz, 1H), 5.87 (dd, *J* = 2.0, 9.6 Hz, 1H), 6.47 (d, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.5, 27.0, 38.9, 41.3, 51.5, 53.2, 61.2, 114.9, 123.6, 124.2, 128.1, 129.8, 131.5, 131.6, 135.4, 144.1, 152.3, 165.5, 176.5. IR (film): ν 1092, 1134, 1161, 1227, 1275, 1348, 1720, 1749, 2341, 2360, 2872, 2978. HRMS (ESI) *m/z* calcd. For $C_{24}H_{29}NO_6S$ $(M+Na)^+$ 482.1607, found 482.1590.



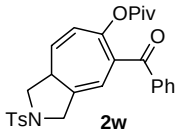
2u

(4*Z*,6*Z*,8*E*)-7-acetyl-1,2,3,3a-tetrahydro-2-tosylcyclohepta[c]pyrrol-6-yl pivalate (**2u**).
Yield : 83%, 71 mg, solid, mp: 115-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (s, 9H), 2.32 (s, 3H), 2.45 (s, 3 H), 2.48(m, 1 H), 3.39 (dd, *J* = 7.0, 10.0 Hz, 1H), 3.68 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.80 (dd, *J* = 1.5, 14.5 Hz, 1H), 4.08 (d, *J* = 14.5 Hz, 1H), 5.48 (dd, *J* = 5.0, 10.0 Hz, 1H), 5.82 (dd, *J* = 1.5, 10.0 Hz, 1H), 6.38 (d, *J* = 2.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 26.9, 30.6, 39.0, 41.4, 51.6, 53.2, 114.2, 123.3, 128.1, 129.8, 130.9, 131.6, 132.0, 135.7, 144.1, 150.8, 176.6, 199.6. IR (film): ν 1090, 1161, 1267, 1348, 1692, 1747, 2873, 2976. HRMS (ESI) *m/z* calcd. For $C_{23}H_{27}NO_5S$ $(M+Na)^+$ 452.1502, found 452.1513.



2v

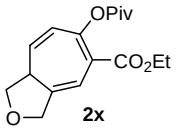
(4*Z*,6*Z*,8*E*)-7-hexanoyl-1,2,3,3a-tetrahydro-2-tosylcyclohepta[c]pyrrol-6-yl pivalate (**2v**).
Yield : 81%, 79 mg, oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.5 Hz, 3H), 1.28 (s, 9 H), 1.20-1.33 (m, 4H), 1.54-1.60 (m, 2H), 2.45 (s, 3H), 2.49 (m, 1H), 2.58 (qt, *J* = 7.5, 17.0 Hz, 2H), 3.41 (dd, *J* = 7.5, 10.0 Hz, 1H), 3.66 (dd, *J* = 2.5, 10.0 Hz, 1H), 3.81 (dd, *J* = 1.5, 14.5 Hz, 1H), 4.07 (d, *J* = 14.5 Hz, 1H), 5.41 (dd, *J* = 5.0, 10.0 Hz, 1H), 5.82 (dd, *J* = 1.5, 10.0 Hz, 1H), 6.30 (d, *J* = 1.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 21.5, 22.4, 23.7, 26.9, 31.3, 39.0, 41.4, 42.9, 51.6, 53.3, 114.1, 123.3, 128.1, 129.8, 131.6, 132.5, 135.6, 144.1, 149.4, 176.6, 202.9. IR (film): ν 1090, 1161, 1275, 1348, 1396, 1695, 1748, 2871, 2931, 2958. HRMS (ESI) *m/z* calcd. For $C_{27}H_{35}NO_5S$ $(M+Na)^+$ 508.2128, found 508.2136.



2w

(4*Z*,6*Z*,8*E*)-7-benzoyl-1,2,3,3a-tetrahydro-2-tosylcyclohepta[c]pyrrol-6-yl pivalate (**2w**).
Yield : 86%, 84 mg, solid, mp: 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (s, 9H), 2.41 (s, 3H), 2.68 (m, 1H), 3.56 (dd, *J* = 7.2, 10.0 Hz, 1H), 3.71 (dd, *J* = 3.2, 10.0 Hz, 1H), 3.87 (dd, *J* = 2.0, 14.8 Hz, 1H), 4.09 (td, *J* = 1.6, 14.8 Hz, 1H), 5.41 (dd, *J* = 4.4,

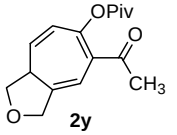
9.6 Hz, 1H), 5.89 (dd, *J* = 1.6, 9.6 Hz, 1H), 6.38 (d, *J* = 1.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.38-7.42 (m, 2H), 7.51-7.55 (m, 1H), 7.73- 7.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.2, 38.6, 41.8, 51.7, 53.5, 115.1, 123.4, 128.0, 128.1, 128.5, 129.2, 129.8, 130.3, 131.8, 133.5, 135.1, 136.8, 144.1, 149.0, 176.2, 195.5. IR (film): ν 1091, 1128, 1161, 1274, 1347, 1449, 1663, 1748, 2872, 2975. HRMS (ESI) *m/z* calcd. For $C_{28}H_{29}NO_5S$ $(M+Na)^+$ 514.1658, found 514.1678.



2x

6-(2,2-Dimethyl-propionyloxy)-3,8a-dihydro-1H-cyclohepta[c]furan-5-carboxylic acid ethyl ester (**2x**).

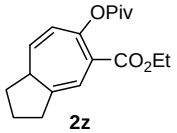
Yield: 72%, 44 mg, oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.31 (s, 9H), 1.32 (t, *J* = 7.5 Hz, 3H), 2.66 (m, 1H), 4.18 (m, 3H), 4.31 (qd, *J* = 7.0, 11.0 Hz, 1H), 4.46 (t, *J* = 1.5 Hz, 2H), 5.50 (dd, *J* = 4.5, 10.0 Hz, 1H), 5.89 (qd, *J* = 2.0, 10.0 Hz, 1H), 6.51 (q, *J* = 1.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 27.3, 39.2, 42.8, 61.4, 70.8, 74.4, 112.4, 123.9, 124.8, 131.6, 140.5, 152.1, 166.2, 176.8. IR (film): ν 2976, 1750, 1721, 1479, 1395, 1366, 1256, 1226, 1163, 1131, 1103, 1035, 924, 861, 730 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{17}H_{22}NaO_5$ $(M+Na)^+$ 329.1359, found 329.1368.



2y

(3a*E*,5*Z*,7*Z*)-5-acetyl-3,8a-dihydro-1H-cyclohepta[c]furan-6-yl pivalate (**2y**).

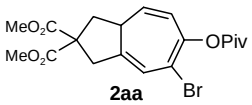
Yield: 60%, 33 mg, oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.31 (s, 9H), 2.38 (s, 3H), 2.66 (m, 1H), 4.15 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.23 (dd, *J* = 9.0, 6.5 Hz, 1H), 4.45 (t, *J* = 2.0 Hz, 2H), 5.49 (dd, *J* = 10.0, 5.0 Hz, 1H), 5.85 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.42 (q, *J* = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.2, 30.9, 39.3, 42.9, 70.8, 74.4, 111.8, 123.7, 131.0, 132.6, 140.7, 150.6, 176.9, 200.4. IR (film): ν 2975, 1747, 1690, 1479, 1396, 1355, 1265, 1101, 1026, 909, 728 cm^{-1}. For $C_{16}H_{20}NaO_4$ $(M+Na)^+$ 299.1354, found 299.1362.



2z

6-(2,2-Dimethyl-propionyloxy)-1,2,3,8a-tetrahydro-azulene-5-carboxylic acid ethyl ester (**2z**).

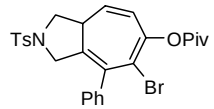
Yield: 64%, 39 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.72-1.61 (m, 1H), 1.97-1.83 (m, 2H), 2.13-2.01 (m, 1H), 2.39-2.30 (m, 1H), 2.50 (t, *J* = 6.4 Hz, 2H), 4.34-4.13 (m, 2H), 5.36 (dd, *J* = 4.8, 9.6 Hz, 1H), 5.81 (dd, *J* = 2.0, 9.6 Hz, 1H), 6.49 (dt, *J* = 1.6, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5, 27.0, 27.3, 33.0, 33.2, 39.1, 42.4, 61.2, 114.3, 122.8, 125.0, 133.1, 145.5, 151.2, 166.8, 176.9. IR (film): ν 1119, 1135, 1166, 1228, 1252, 1366, 1395, 1479, 1719, 1748, 2959. HRMS (ESI) *m/z* calcd. For $C_{18}H_{24}O_4$ $(M+Na)^+$ 327.1567, found 327.1576.



2aa

Dimethyl 7-bromo-6- (pivaloyloxy)-3,3a-dihydroazulene-2, 2(1H)-dicarboxylate (**2aa**).

Yield: 69%, 11 mg, oil. ^{1}H NMR (400Mz, $CDCl_3$) δ 1.32 (s, 9H), 2.42-2.49 (m, 1H), 2.83-2.89 (m, 2H), 3.15 (dd, *J*= 2.0, 17.2 Hz, 1H), 3.21 (d, *J*= 17.2 Hz, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 5.28 (dd, *J*= 4.0, 10.0 Hz, 1H), 5.79 (dd, *J*= 1.6, 9.6 Hz, 1H), 6.28 (td, *J*= 1.6, 4.0 Hz, 1H); ^{13}C NMR (100Mz, $CDCl_3$) δ 27.3, 39.4, 40.1, 40.5, 41.9, 53.2, 53.3, 61.0, 116.6, 120.6, 122.7, 130.7, 142.7, 147.1, 171.4, 176.2. IR (film): 729, 907, 1028, 1079, 1109, 1139, 1206, 1263, 1436, 1480, 1734, 2257, 2362, 2957 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{23}BrO_6$ $(M+Na)^+$ 449.0570, found 449.0577.



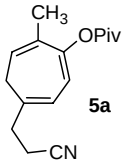
2ab

(4*Z*,6*Z*,8*E*)-7-bromo-1,2,3,3a-tetrahydro-8-phenyl-2-tosylcyclohepta[c]pyrrol-6-yl pivalate (**2ab**).

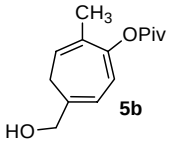
Yield : 75%, 81 mg, solid, mp: 178-180 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (s, 9 H), 2.46 (s, 3 H), 2.81-2.83 (m, 1 H), 3.21 (dd, *J* = 6.0, 9.5 Hz, 1 H), 3.64 (d, *J* = 15 Hz, 1 H), 3.80 (d, *J* = 9.5 Hz, 1 H), 3.82 (dd, *J* = 1.0, 15 Hz, 1 H), 5.68 (dd, *J* = 5.0, 9.5 Hz, 1 H), 5.95 (dd, *J* = 1.5, 9.5 Hz, 1 H), 7.07 (d, *J* = 8.5 Hz, 2 H), 7.32-7.38 (m, 5 H), 7.69 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6, 27.1, 39.2, 41.9, 51.3, 53.2, 77.3, 119.8, 122.4, 128.1, 128.5, 128.8, 129.8, 130.2, 131.5, 133.0, 136.2, 138.4, 144.2, 148.8, 175.8. IR (film): ν 1116, 1162, 1348, 1749, 2360, 2871, 2974 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{27}H_{28}BrNO_4S$ $(M+Na)^+$ 564.0814, found 564.0825.

See procedures for the preparation of seven-membered rings via Rh-catalyzed intermolecular [5+2] cycloaddition with concomitant 1,2-acyloxy migration in the experimental section of the manuscript.

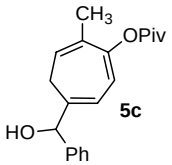
Characterization data for products derived from intermolecular reaction:



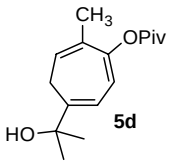
(1*E*,3*Z*,6*Z*)-4-(2-cyanoethyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5a**).
Yield : 81%, 42 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H), 1.77 (s, 3 H), 2.38 (d, *J* = 7.2 Hz, 2 H), 2.50 (dt, *J* = 1.2, 6.8 Hz, 2 H), 2.59 (t, *J* = 7.2 Hz, 2 H), 5.28 (t, *J* = 7.2Hz, 1 H), 5.95 (td, *J* = 1.2, 6.8 Hz, 1 H), 6.17 (d, *J* = 6.8 Hz, 1 H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.4, 17.5, 27.1, 31.5, 33.1, 38.9, 118.9, 119.1, 119.3, 120.2, 131.1, 133.5, 152.0, 176.9. IR (film): ν 912, 1057, 1277, 1479, 1741, 2250, 2972 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{21}NO_2$ $(M+Na)^+$ 282.1464 , found 282.1469.



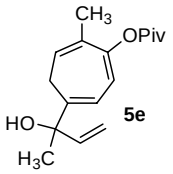
(1*E*,3*E*,6*Z*)-4-(hydroxymethyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5b**).
Yield : 81%, 38 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H), 1.77 (s, 3 H), 1.86 (s, 1 H), 2.42 (d, *J* = 7.2 Hz, 2 H), 4.23 (s, 2 H), 5.28 (t, *J* = 7.2 Hz, 1 H), 6.08 (td, *J* = 1.2, 6.4 Hz, 1 H), 6.19 (d, *J* = 6.4 Hz, 1 H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 27.1, 28.8, 38.9, 65.9, 118.1, 119.0, 120.2, 130.9, 136.9, 151.8, 177.0. IR (film): ν 800, 911, 1055, 1278, 1395, 1743, 2972, 3376 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{14}H_{20}O_3$ $(M+Na)^+$ 259.1304 , found 259.1308.



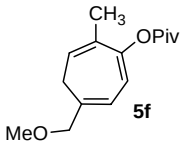
(1*E*,3*E*,6*Z*)-4-(hydroxy(phenyl)methyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5c**).
Yield : 83%, 52 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 9 H), 1.71 (s, 3 H), 2.18 (s, 1 H), 2.25 (dd, *J* = 7.2, 13.2 Hz, 1 H), 2.39 (dd, *J* = 7.2, 13.2 Hz, 1 H), 4.99 (t, *J* = 7.2 Hz, 1 H), 5.33 (s, 1 H), 6.20 (d, *J* = 6.4 Hz, 1 H), 6.24 (dd, *J* = 0.8, 6.4 Hz, 1 H), 7.25-7.37 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 27.1, 28.1, 38.9, 76.8, 118.7, 118.8, 121.4, 126.7, 127.7, 128.3, 130.6, 140.0, 142.2, 152.0, 177.0. IR (film): ν 730, 910, 1033, 1055, 1278, 1395, 1456, 1733, 2973, 3452 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}O_3$ $(M+Na)^+$ 335.1617 , found 335.1618.



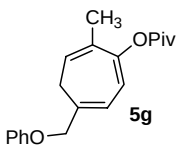
(1*E*,3*E*,6*Z*)-4-(2-hydroxypropan-2-yl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5d**).
Yield : 87%, 46 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 9 H), 1.39 (s, 6 H), 1.63 (s, 1 H), 1.75 (s, 3 H), 2.41 (d, *J* = 7.2 Hz, 2 H), 5.25 (t, *J* = 7.2 Hz, 1 H), 6.14 (d, *J* = 6.4 Hz, 1 H), 6.19 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.5, 27.2, 28.6, 29.7, 38.9, 72.7, 115.2, 119.1, 120.5, 130.5, 145.0, 151.4, 177.0. IR (film): ν 774, 912, 1051, 1278, 1479, 1743, 2973, 3397 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{24}O_3$ $(M+Na)^+$ 287.1617, found 287.1617.



(1*E*,3*E*,6*Z*)-4-(2-hydroxybut-3-en-2-yl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5e**).
Yield : 93%, 51 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H), 1.47 (s, 3 H), 1.76 (d, *J* = 1.6 Hz, 3 H), 1.77 (s, 1 H), 2.39 (d, *J* = 7.6 Hz, 2 H), 5.13 (dd, *J* = 1.2, 10.4 Hz, 1 H), 5.22 (qt, *J* = 1.6, 7.6 Hz, 1 H), 5.30 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.96 (dd, *J* = 10.4, 17.2 Hz, 1 H), 6.18-6.21 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.5, 27.1, 27.6, 28.5, 38.9, 75.1, 112.9, 116.7, 119.0, 121.2, 130.5, 142.3, 143.3, 151.6, 177.0. IR (film): ν 731, 839, 913, 1047, 1278, 1367, 1479, 1635, 1743, 2974, 3474 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{17}H_{24}O_3$ $(M+Na)^+$ 299.1617, found 299.1623.

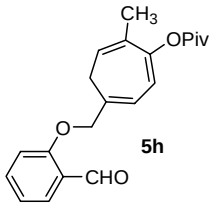


(1*E*,3*E*,6*Z*)-4-(methoxymethyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5f**).
Yield : 86%, 43 mg, (regioisomeric ratio = 8:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 9 H), 1.76 (s, 3 H), 2.41 (d, *J* = 7.2 Hz, 2 H), 3.31 (s, 3 H), 4.01 (s, 2 H), 5.27 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.05 (td, *J* = 1.2, 6.4 Hz, 1 H), 6.18 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 27.1, 28.7, 38.9, 57.7, 75.2, 118.9, 120.0, 120.3, 130.8, 133.8, 152.0, 176.9. IR (film): ν 732, 910, 1056, 1276, 1479, 1745, 2819, 2926, 2974 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_3$ $(M+Na)^+$ 273.1461, found 273.1461.



(1*E*,3*E*,6*Z*)-7-methyl-4-(phenoxymethyl)cyclohepta-1,3,6-trienyl pivalate (**5g**).

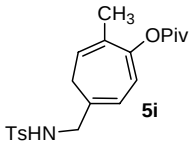
For 0.2 mmol scale, yield: 89%, 56 mg, (regioisomeric ratio = 17:1); for 3 mmol scale, yield: 81%, 758 mg, (regioisomeric ratio > 20:1). Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H), 1.78 (d, *J* = 1.2 Hz, 3 H), 2.50 (d, *J* = 7.2 Hz, 2 H), 4.62 (s, 2 H), 5.30 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.18 (td, *J* = 6.4 Hz, 1 H), 6.21 (d, *J* = 6.4 Hz, 1 H), 6.91-6.96 (m, 3 H), 7.24-7.29 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 27.1, 28.7, 38.9, 70.5, 114.9, 118.9, 120.1, 120.2, 120.9, 129.4, 131.0, 132.2, 152.2, 158.6, 176.9. IR (film): ν 730, 909, 1029, 1057, 1238, 1494, 1598, 1743, 2973 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}O_3$ $(M+Na)^+$ 335.1617, found 335.1619.



5h

(1*E*,3*E*,6*Z*)-4-((2-formylphenoxy)methyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5h**).

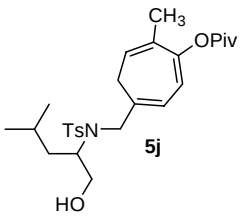
Yield : 89%, 61 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9 H), 1.79 (d, *J* = 1.2 Hz, 3 H), 2.52 (d, *J* = 7.2 Hz, 2 H), 4.75 (s, 2 H), 5.33 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.21-6.24 (m, 2 H), 6.97-7.05 (m, 2 H), 7.50-7.54 (m, 1 H), 7.84 (d, *J* = 7.6 Hz, 1 H), 10.54 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 27.1, 28.7, 38.9, 71.0, 112.9, 118.8, 120.1, 120.8, 121.0, 125.0, 128.4, 131.0, 131.3, 135.8, 152.6, 160.8, 176.9, 189.5. IR (film): ν 730, 757, 999, 1236, 1282, 1457, 1480, 1598, 1687, 1742, 2972 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{21}H_{24}O_4$ $(M+Na)^+$ 363.1566, found 363.1569.



5i

(1*E*,3*E*,6*Z*)-7-methyl-4-((tosylamino)methyl)cyclohepta-1,3,6-trienyl pivalate (**5i**).

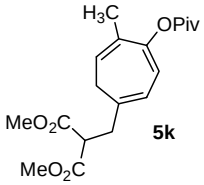
Yield : 91%, 71 mg, (regioisomeric ratio = 10:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 9 H), 1.73 (s, 3 H), 2.31 (d, *J* = 7.5 Hz, 2 H), 2.43 (s, 3 H), 3.69 (d, *J* = 6.0 Hz, 2 H), 4.63 (t, *J* = 6.5 Hz, 1 H), 5.20 (qt, *J* = 1.0, 7.0 Hz, 1 H), 5.92 (d, *J* = 6.5 Hz, 1 H), 6.07 (d, *J* = 6.5 Hz, 1 H), 7.30 (d, *J* = 8.5 Hz, 2 H), 7.74 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ17.6, 21.5, 27.1, 29.4, 38.9, 48.5, 118.7, 120.5, 120.7, 127.1, 129.7, 131.0, 131.7, 136.8, 143.5, 152.4, 176.8. IR (film): ν 730, 911, 1049, 1093, 1157, 1279, 1324, 1479, 1742, 2973, 3280 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{21}H_{27}NO_4S$ $(M+Na)^+$ 412.1553, found 412.1566.



5j

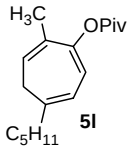
2,2-Dimethyl-propionic-acid-4-[(1-hydroxymethyl-3-methyl-butyl)-(toluene-4-sulfonyl)-amino]-methyl-7-methyl-cyclohepta-1,3,6-trienyl ester (**5j**).

Yield : 80%, 78 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.73-0.75 (m, 6 H), 1.14-1.38 (m, 3 H), 1.30 (s, 9 H), 1.77 (d, *J* = 1.2 Hz, 3 H), 2.03 (s, 1 H), 2.38 (dd, *J* = 7.2, 13.2 Hz, 1 H), 2.43 (s, 3 H), 2.51 (dd, *J* = 7.2, 13.2 Hz, 1 H), 3.48-3.58 (m, 2 H), 3.79-3.89 (m, 1 H), 3.90 (d, *J* = 16.4 Hz, 1H), 4.12 (d, *J* = 16.4 Hz, 1H), 5.29 (qt, *J* = 1.2, 7.2 Hz, 1H), 6.01 (d, *J* = 6.4 Hz, 1 H), 6.14 (d, *J* = 6.0 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 21.5, 22.3, 22.6, 24.7, 27.1, 28.7, 38.2, 38.9, 49.5, 58.4, 63.5, 118.7, 120.8, 121.0, 127.2, 129.6, 131.0, 133.2, 137.6, 143.4, 152.4, 176.8. IR (film): ν 728, 909, 1049, 1092, 1327, 1461, 1741, 2958, 3528 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{27}H_{39}NO_5S$ $(M+Na)^+$ 512.2441, found 512.2453.



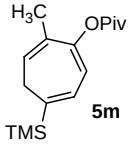
Dimethyl-2-(((1*E*,3*E*,5*Z*)-5-methyl-4-(pivaloyloxy)cyclohepta-1,3,5-trienyl)methyl)malonate (**5k**).

Yield : 85%, 60 mg, (regioisomeric ratio = 14:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 9 H), 1.73 (d, *J* = 1.2 Hz, 3 H), 2.33 (d, *J* = 7.2 Hz, 2 H), 2.82 (d, *J* = 8.0 Hz, 2 H), 3.58 (t, *J* = 7.6 Hz, 1 H), 3.68 (s, 6 H), 5.21 (qt, *J* = 1.2, 7.2 Hz, 1 H), 5.88 (td, *J* = 1.2, 6.4 Hz, 1 H), 6.10 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.5, 27.1, 31.6, 36.6, 38.9, 51.5, 52.5, 119.2, 119.5, 120.6, 130.6, 133.0, 151.6, 169.0, 176.9. IR (film): ν 730, 912, 1056, 1228, 1276, 1435, 1736, 2955 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{26}O_6$ $(M+Na)^+$ 373.1621, found 373.1622.



(1*E*,3*Z*,6*Z*)-7-methyl-4-pentylcyclohepta-1,3,6-trienyl pivalate (**5l**).

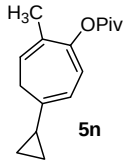
Yield : 81%, 45 mg, (regioisomeric ratio = 10:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 3 H), 1.26-1.32 (m, 4 H), 1.30 (s, 9 H), 1.42-1.50 (m, 2 H), 1.76 (d, *J* = 1.2 Hz, 3 H), 2.22 (t, *J* = 7.6 Hz, 2 H), 2.35 (d, *J* = 7.2 Hz, 2 H), 5.21 (qt, *J* = 1.2, 7.2 Hz, 1H), 5.84 (d, *J* = 1.2, 6.4 Hz, 1 H), 6.14 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 17.6, 22.5, 27.2, 28.9, 31.5, 32.1, 37.8, 38.9, 118.0, 119.4, 119.6, 130.3, 139.4, 150.7, 177.1. IR (film): ν 909, 1051, 1277, 1395, 1459, 1746, 2928, 2957 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{18}H_{28}O_2$ $(M+Na)^+$ 299.1981, found 299.1993.



(1*E*,3*E*,6*Z*)-7-methyl-4-(trimethylsilyl)cyclohepta-1,3,6-trienyl pivalate (**5m**).

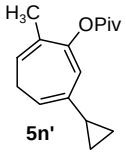
Yield : 53%, 29 mg, (regioisomeric ratio = 10:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.01 (s, 9 H), 1.19 (s, 9 H), 1.65 (s, 3 H), 2.21 (d, *J* = 7.2 Hz, 2 H), 5.10 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.18 (d, *J* = 6.0 Hz, 1 H), 6.20 (d, *J* = 6.0 Hz, 1 H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ -1.6, 17.7, 27.2, 30.2, 39.0, 120.0, 120.8, 130.2, 130.4, 139.4, 152.7, 177.0. IR (film): ν 751, 830, 1065, 1247, 1395, 1479, 1538, 1747, 2956 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{26}O_2Si$ $(M+Na)^+$ 301.1594, found 301.1601.



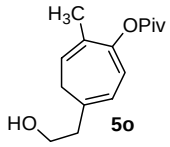
5n

(1*E*,3*E*,6*Z*)-4-cyclopropyl-7-methylcyclohepta-1,3,6-trienyl pivalate (**5n**).
Yield : 64%, 31 mg, oil. ^1H NMR (400 MHz, $CDCl_3$): δ 0.55-0.59 (m, 2 H), 0.75-0.80 (m, 2 H), 1.30 (s, 9 H), 1.56-1.63 (m, 1 H), 1.75 (d, *J* = 1.2 Hz, 3 H), 2.12 (d, *J* = 7.2 Hz, 2 H), 5.11 (qt, *J* = 1.2, 7.2 Hz, 1 H), 5.94 (d, *J* = 6.4 Hz, 1 H), 6.14 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.3, 16.8, 17.5, 27.2, 28.2, 38.9, 116.9, 118.6, 119.4, 130.6, 140.2, 150.5, 177.1. IR (film): ν 733, 911, 1037, 1278, 1395, 1479, 1745, 2359, 2973 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_2$ $(M+Na)^+$ 269.1512, found 269.1513.



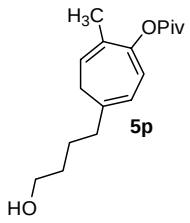
5n'

(1*E*,3*Z*,6*Z*)-3-cyclopropyl-7-methylcyclohepta-1,3,6-trienyl pivalate (**5n'**).
Yield : 13%, 6 mg, oil. ^1H NMR (400 MHz, $CDCl_3$): δ 0.45-0.49 (m, 2 H), 0.65-0.69 (m, 2 H), 1.31 (s, 9 H), 1.47-1.53 (m, 1 H), 1.76 (s, 3 H), 2.25 (dd, *J* = 7.2, 7.2 Hz, 2 H), 5.24 (t, *J* = 7.2 Hz, 1 H), 5.36 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.10 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 6.1, 15.5, 17.7, 26.8, 27.2, 38.9, 116.7, 120.4, 121.6, 130.0, 137.5, 151.9, 177.0. IR (film): ν 906, 1101, 1276, 1396, 1479, 1638, 1746, 2972 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_2$ $(M+Na)^+$ 269.1512, found 269.1514.



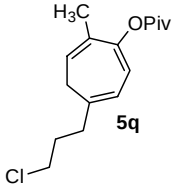
5o

(1*E*,3*E*,6*Z*)-4-(2-hydroxyethyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5o**).
Yield : 80%, 40 mg, (regioisomeric ratio = 10:1), oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H), 1.47 (s, 1 H), 1.77 (s, 3 H), 2.37 (d, *J* = 7.2 Hz, 2 H), 2.51 (t, *J* = 6.0 Hz, 2 H), 3.70 (m, 2 H), 5.26 (t, *J* = 7.2 Hz, 1 H), 5.95 (d, *J* = 6.0 Hz, 1 H), 6.18 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 27.1, 31.9, 38.9, 41.0, 61.4, 119.2, 119.5, 120.7, 130.9, 134.2, 151.5, 177.1. IR (film): ν 731, 911, 1057, 1278, 1479, 1635, 1744, 2874, 2958, 3357 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_3$ $(M+Na)^+$ 273.1461, found 273.1462.

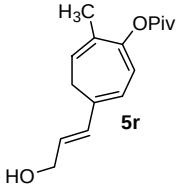


5p

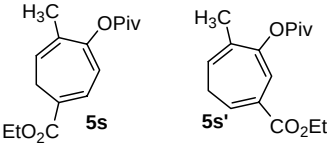
(1*E*,3*Z*,6*Z*)-4-(4-hydroxybutyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5p**).
Yield : 68%, 38 mg, (regioisomeric ratio = 8:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 9 H), 1.49-1.58 (m, 5 H), 1.76 (s, 3 H), 2.26 (t, *J* = 6.0 Hz, 2 H), 2.36 (d, *J* = 7.2 Hz, 2 H), 3.62-3.65 (m, 2 H), 5.21 (qt, *J* = 1.2, 7.2 Hz, 1 H), 5.85 (d, *J* = 6.4 Hz, 1 H), 6.14 (d, *J* = 6.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 25.3, 27.2, 32.0, 32.3, 37.5, 38.9, 62.7, 118.3, 119.4, 119.5, 130.4, 138.7, 150.9, 177.1. IR (film): ν 730, 910, 1062, 1278, 1479, 1743, 2871, 2933, 3353 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{17}H_{26}O_3$ $(M+Na)^+$ 301.1774, found 301.1774.



(1*E*,3*Z*,6*Z*)-4-(3-chloropropyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5q**).
Yield : 77%, 43 mg, (regioisomeric ratio = 8:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H), 1.77 (d, *J* = 1.2 Hz, 3 H), 1.91-1.97 (m, 2 H), 2.35-2.42 (m, 4 H), 3.51 (t, *J* = 6.4 Hz, 2 H), 5.22 (qt, *J* = 1.2, 7.2 Hz, 1 H), 5.89 (td, *J* = 1.2, 6.4 Hz, 1 H), 6.15 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 27.2, 31.85, 31.91, 34.7, 38.9, 44.2, 119.2, 119.3, 119.5, 130.7, 136.7, 151.2, 177.1. IR (film): ν 732, 911, 1058, 1277, 1395, 1479, 1743, 2958 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{23}ClO_2$ $(M+Na)^+$ 305.1278, found 305.1279.

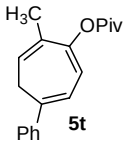


(1*E*,3*E*,6*Z*)-4-((*E*)-3-hydroxyprop-1-enyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5r**).
Yield : 74%, 39 mg, (regioisomeric ratio = 8:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H), 1.64 (s, 1 H), 1.77 (d, *J* = 1.2 Hz, 3 H), 2.64 (d, *J* = 7.2 Hz, 2 H), 4.25 (d, *J* = 6.0 Hz, 2 H), 5.30 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.06 (d, *J* = 6.8 Hz, 1 H), 6.11 (td, *J* = 6.0, 15.6 Hz, 1 H), 6.23 (d, *J* = 6.4 Hz, 1 H), 6.34 (d, *J* = 15.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 27.1, 27.5, 38.9, 63.5, 119.8, 121.0, 123.1, 129.3, 131.4, 132.0, 132.2, 152.2, 177.0. IR (film): ν 729, 909, 1054, 1277, 1395, 1479, 1739, 2974, 3415 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_3$ $(M+Na)^+$ 285.1461, found 285.1447.



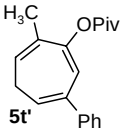
(1*E*,3*E*,5*Z*)-ethyl 5-methyl-4-(pivaloyloxy)cyclohepta-1,3,5-trienecarboxylate (**5s**).
(1*E*,4*Z*,6*E*)-ethyl 5-methyl-6-(pivaloyloxy)cyclohepta-1,4,6-trienecarboxylate (**5s'**).
Yield : 82%, 46 mg, (regioisomeric ratio = 1.4:1), oil. ^{1}H NMR (**5s**, 400 MHz, $CDCl_3$): δ 1.28-1.32 (m, 12 H), 1.78 (d, *J* = 1.2 Hz, 3 H), 2.68 (d, *J* = 7.2 Hz, 2 H), 4.19-4.25 (m, 2 H), 5.44 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.30 (d, *J* = 6.8 Hz, 1 H), 7.16 (d, *J* = 6.4 Hz, 1 H).

^{1}H NMR (**5s'**, 400 MHz, $CDCl_3$): δ 1.28-1.32 (m, 12 H), 1.76 (d, *J* = 1.2 Hz, 3 H), 2.42 (dd, *J* = 7.2, 7.2 Hz, 2 H), 4.19-4.25 (m, 2 H), 5.29 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.57 (t, *J* = 7.2 Hz, 1 H), 6.78 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 17.6, 17.7, 26.4, 27.09, 27.12, 27.3, 38.9, 39.0, 60.8, 117.3, 118.7, 119.2, 122.8, 123.6, 128.6, 130.4, 131.1, 131.4, 131.8, 152.9, 155.9, 165.8, 166.2, 176.5, 176.8. IR (film): ν 732, 762, 910, 1056, 1094, 1173, 1222, 1253, 1367, 1479, 1706, 1748, 2976 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_4$ $(M+Na)^+$ 301.1410, found 301.1425.



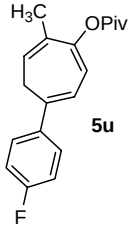
5t

(1*E*,3*E*,6*Z*)-7-methyl-4-phenylcyclohepta-1,3,6-trienyl pivalate (**5t**).
Yield : 58%, 33 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9 H), 1.81 (d, *J* = 1.2 Hz, 3 H), 2.84 (d, *J* = 7.2 Hz, 2 H), 5.35 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.36 (d, *J* = 6.8 Hz, 1 H), 6.41 (d, *J* = 6.8 Hz, 1 H), 7.23-7.27 (m, 1 H), 7.31-7.36 (m, 2 H), 7.47-7.50 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 27.2, 31.2, 39.0, 119.7, 120.1, 127.2, 127.3, 128.4, 131.1, 134.2, 140.5, 151.9, 177.0. IR (film): ν 758, 910, 1060, 1276, 1446, 1478, 1743, 2973 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{22}O_2$ $(M+Na)^+$ 305.1512, found 305.1516.



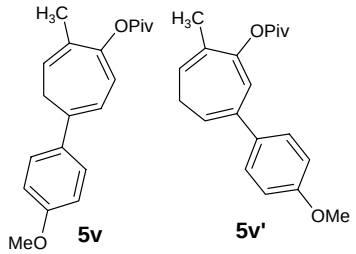
5t'

(1*E*,3*E*,6*Z*)-7-methyl-3-phenylcyclohepta-1,3,6-trienyl pivalate (**5t'**).
Yield : 17%, 10 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 9 H), 1.82 (d, *J* = 1.2 Hz, 3 H), 2.45 (dd, *J* = 7.2, 7.2 Hz, 2 H), 5.43 (qt, *J* = 1.6, 7.2 Hz, 1 H), 5.73 (t, *J* = 7.2 Hz, 1 H), 6.51 (s, 1 H), 7.24-7.28 (m, 1 H), 7.30-7.35 (m, 2 H), 7.37-7.40 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 27.2, 27.5, 39.0, 118.7, 120.8, 121.4, 127.1, 127.4, 128.3, 130.4, 136.8, 140.4, 152.9, 176.9. IR (film): ν 764, 906, 1100, 1276, 1446, 1746, 2973 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{22}O_2$ $(M+Na)^+$ 305.1512, found 305.1516.

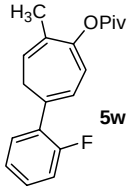


5u

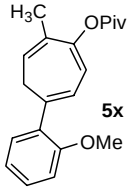
(1*E*,3*E*,6*Z*)-4-(4-fluorophenyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5u**).
Yield : 83%, 50 mg, (regioisomeric ratio = 6:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9 H), 1.81 (d, *J* = 1.2 Hz, 3 H), 2.80 (d, *J* = 7.6 Hz, 2 H), 5.34 (qt, *J* = 1.2, 7.6 Hz, 1 H), 6.33 (d, *J* = 6.8 Hz, 1 H), 6.35 (d, *J* = 6.8 Hz, 1 H), 6.99-7.04 (m, 2 H), 7.43-7.46 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 27.2, 31.3, 39.0, 115.3 (d, *J* = 21.3 Hz), 119.5, 119.6, 120.1, 128.8 (d, *J* = 7.7 Hz), 131.2, 133.0, 136.6, 151.9, 162.1 (d, *J* = 246 Hz), 177.0. IR (film): ν 651, 728, 907, 1130, 1510, 1602, 1741, 2978 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{21}FO_2$ $(M+Na)^+$ 323.1417, found 323.1421.



(1*E*,3*E*,6*Z*)-4-(4-methoxyphenyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5v**).
(1*E*,3*E*,6*Z*)-3-(4-methoxyphenyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5v'**).
Yield : 76%, 47 mg, (regioisomeric ratio = 3.6:1), oil. ^{1}H NMR (**5v**, 400 MHz, $CDCl_3$): δ 1.34 (s, 9 H), 1.81 (s, 3 H), 2.82 (d, *J* = 7.2 Hz, 2 H), 3.82 (s, 3 H), 5.31 (qt, *J* = 1.2, 7.6 Hz, 1 H), 6.33 (d, *J* = 6.8 Hz, 1 H), 6.36 (d, *J* = 6.8 Hz, 1 H), 6.86-6.89 (m, 2 H), 7.43-7.47 (m, 2 H). ^{1}H NMR (**5v'**, 400 MHz, $CDCl_3$): δ 1.35 (s, 9 H), 1.83 (s, 3 H), 2.43 (dd, *J* = 7.2 Hz, 2 H), 3.81 (s, 3 H), 5.43 (t, *J* = 7.2 Hz, 1 H), 5.64 (t, *J* = 7.2 Hz, 1 H), 6.49 (s, 1 H), 6.86-6.89 (m, 2 H), 7.31-7.33 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 27.2, 31.2, 38.9, 55.3, 113.6, 113.80, 113.84, 118.2, 119.3, 120.2, 126.2, 128.4, 128.6, 131.0, 132.9, 133.4, 151.4, 159.0, 177.1. IR (film): ν 824, 1034, 1178, 1247, 1278, 1460, 1509, 1605, 1743, 2971 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}O_3$ $(M+Na)^+$ 335.1617, found 335.1622.

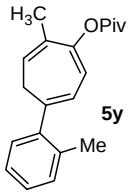


(1*E*,3*E*,6*Z*)-4-(2-fluorophenyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5w**).
Yield : 80%, 48 mg, (regioisomeric ratio = 11:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9 H), 1.83 (d, *J* = 1.2 Hz, 3 H), 2.76 (d, *J* = 7.6 Hz, 2 H), 5.44 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.32-6.35 (m, 2 H), 7.02-7.11 (m, 2 H), 7.20-7.26 (m, 1 H), 7.34 (dt, *J* = 1.6, 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6, 27.2, 32.3 (d, *J* = 3.8 Hz), 39.0, 115.8 (d, *J* = 22.9 Hz), 119.6, 120.7, 122.9 (d, *J* = 3.1 Hz), 124.0 (d, *J* = 3.0 Hz), 128.8 (d, *J* = 7.7 Hz), 129.5 (d, *J* = 13.0 Hz), 130.0 (d, *J* = 2.3 Hz), 130.5 (d, *J* = 3.8 Hz), 130.9, 152.4, 159.9 (d, *J* = 247 Hz), 177.0. IR (film): ν 754, 1060, 1275, 1450, 1484, 1744, 2973 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{21}FO_2$ $(M+Na)^+$ 323.1417, found 323.1418.

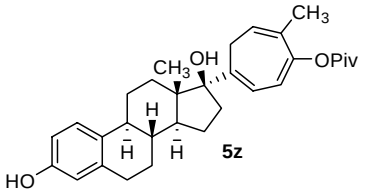


(1*E*,3*E*,6*Z*)-4-(2-methoxyphenyl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5x**).
Yield : 60%, 37 mg, (regioisomeric ratio = 5:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9 H), 1.82 (s, 3 H), 2.74 (d, *J* = 7.2 Hz, 2 H), 3.84 (s, 3 H), 5.38 (t, *J* = 7.2 Hz, 1 H), 6.22 (d, *J* = 6.4 Hz, 1 H), 6.30 (d, *J* = 6.4 Hz, 1 H), 6.87-6.93 (m, 2 H), 7.22-7.27 (m,

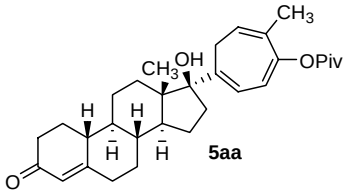
2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 27.2, 32.7, 38.9, 55.4, 110.7, 119.6, 120.4, 121.5, 121.8, 128.7, 130.4, 131.3, 134.6, 151.8, 156.5, 177.0. IR (film): ν 730, 909, 1027, 1248, 1280, 1491, 1745, 2972 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}O_3$ $(M+Na)^+$ 335.1617, found 335.1634.



(1*E*,3*E*,6*Z*)-7-methyl-4-o-tolylcyclohepta-1,3,6-trienyl pivalate (**5y**).
Yield : 32%, 19 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 9 H), 1.83 (d, *J* = 1.2 Hz, 3 H), 2.31 (s, 3 H), 2.69 (d, *J* = 7.2 Hz, 2 H), 5.32 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.04 (d, *J* = 6.4 Hz, 1 H), 6.32 (d, *J* = 6.4 Hz, 1 H), 7.12-7.15 (m, 2 H), 7.18-7.19 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 20.7, 27.2, 33.7, 39.0, 119.6, 119.8, 122.0, 125.5, 127.2, 129.5, 130.1, 130.9, 135.4, 136.4, 142.5, 151.6, 177.1. IR (film): ν 731, 910, 1057, 1276, 1457, 1480, 1745, 2972 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}O_2$ $(M+Na)^+$ 319.1668, found 319.1671.

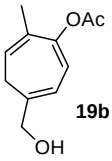


(1*E*,3*E*,6*Z*)-4-((8R,9S,13S,14S,17R)-7,8,9,11,12,13,14,15,16,17-decahydro-3,17-dihydroxy-13-methyl-6H-cyclopenta[a]phenanthren-17-yl)-7-methylcyclohepta-1,3,6-trienyl pivalate (**5z**).
Yield : 86%, 82 mg, (regioisomeric ratio > 20:1), soild, mp: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (s, 3 H), 1.11-1.19 (m, 1 H), 1.24-1.56 (m, 5 H), 1.32 (s, 9 H), 1.67-2.21 (m, 9 H), 1.78 (s, 3 H), 2.74-2.82 (m, 2 H), 2.99 (s, 1 H), 5.30 (t, *J* = 6.8 Hz, 1 H), 5.53 (s, 1 H), 5.90 (d, *J* = 2.4 Hz, 1 H), 6.27 (d, *J* = 6.4 Hz, 1 H), 6.50 (d, *J* = 2.4 Hz, 1 H), 6.59 (dd, *J* = 2.8, 8.4 Hz, 1 H), 7.06 (d, *J* = 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 17.5, 23.5, 26.4, 27.1, 27.4, 29.5, 30.6, 33.9, 38.7, 39.0, 39.4, 43.3, 47.4, 48.3, 86.3, 112.7, 115.1, 119.3, 120.1, 121.3, 126.3, 130.3, 132.3, 137.8, 144.2, 151.6, 153.5, 177.6. IR (film): ν 785, 909, 1052, 1283, 1378, 1450, 1500, 1611, 1726, 2360, 2872, 2930, 3441 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{31}H_{40}O_4$ $(M+Na)^+$ 499.2818, found 499.2834.



(1*E*,3*E*,6*Z*)-4-((8R,9S,10R,13S,14S,17R)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetrade cahydro-17-hydroxy-13-methyl-3-oxo-1H-cyclopenta[a]phenanthren-17-yl)-7-methyl cyclohepta-1,3,6-trienyl pivalate (**5aa**).

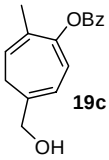
Yield : 92%, 88 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71-0.79 (m, 1 H), 1.01-1.11 (m, 2 H), 1.03 (s, 3 H), 1.20-1.33 (m, 1 H), 1.31 (s, 9 H), 1.35-1.55 (m, 4 H), 1.64-1.98 (m, 7 H), 1.76 (s, 3 H), 2.02-2.09 (m, 2 H), 2.18-2.31 (m, 3 H), 2.35-2.49 (m, 2 H), 2.96 (s, 1 H), 5.27 (t, *J* = 6.8 Hz, 1 H), 5.81 (s, 1 H), 5.85 (d, *J* = 6.4 Hz, 1 H), 6.22 (d, *J* = 6.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 17.5, 23.6, 26.3, 26.5, 27.1, 30.5, 30.7, 33.6, 35.4, 36.4, 38.5, 38.9, 41.1, 42.4, 47.1, 48.0, 49.0, 86.0, 119.1, 120.2, 121.2, 124.5, 130.4, 144.1, 151.7, 166.5, 177.1, 199.9. IR (film): ν 729, 911, 1007, 1027, 1053, 1208, 1261, 1332, 1395, 1452, 1478, 1661, 1742, 2869, 2930, 3454 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{31}H_{42}O_4$ $(M+Na)^+$ 501.2975, found 501.2990.



19b

(1*E*,3*E*,6*Z*)-4-(hydroxymethyl)-7-methylcyclohepta-1,3,6-trienyl acetate (**19b**).

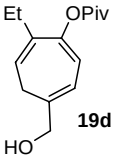
Yield : 71%, 28 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (s, 1 H), 1.79 (s, 3 H), 2.21 (s, 3 H), 2.43 (d, *J* = 7.50 Hz, 2 H), 4.25 (s, 2 H), 5.29 (qt, *J* = 1.00, 7.50 Hz, 1 H), 6.09 (td, *J* = 1.50, 7.50 Hz, 1 H), 6.24 (d, *J* = 6.50 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.7, 20.8, 28.9, 66.0, 118.2, 119.3, 120.3, 130.8, 137.0, 151.6, 169.3. IR (film) ν: 697, 804, 829, 884, 924, 1010, 1058, 1122, 1216, 1370,1436, 1637,1683,1746, 2926, 3422. HRMS (ESI) *m/z* calcd. For $C_{11}H_{14}O_3$ $(M+Na)^+$ 217.0835, found 217.0837.



19c

(1*E*,3*E*,6*Z*)-4-(hydroxymethyl)-7-methylcyclohepta-1,3,6-trienyl benzoate (**19c**).

Yield : 58%, 30 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (s, 1 H), 1.82 (d, *J* = 1.2 Hz, 3 H), 2.51 (d, *J* = 7.2 Hz, 2 H), 4.28 (s, 2 H), 5.34 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.15 (td, *J* = 1.2, 6.4 Hz, 1 H), 6.39 (d, *J* = 6.4 Hz, 1 H), 7.47-7.52 (m, 2 H), 7.60-7.64 (m, 1 H), 8.14-8.17 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 28.9, 66.0, 118.2, 119.5, 120.5, 128.5, 129.5, 130.0, 130.9, 133.4, 137.2, 151.8, 165.1. IR (film): ν 707, 908, 1023, 1133, 1456, 1724, 2923, 3319 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{16}O_3$ $(M+Na)^+$ 279.0991, found 279.0998.

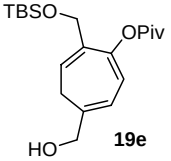


19d

(1*E*,3*E*,6*Z*)-7-ethyl-4-(hydroxymethyl)cyclohepta-1,3,6-trienyl pivalate (**19d**).

Yield : 87%, 44 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, *J* = 7.2 Hz, 3 H), 1.31 (s, 9 H), 1.85 (broad, 1 H), 2.10 (q, *J* = 7.2 Hz, 2 H), 2.43

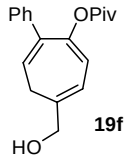
(d, J = 7.2 Hz, 2 H), 4.24 (s, 2 H), 5.28 (t, J = 7.2 Hz, 1 H), 6.06 (td, J = 1.2, 6.4 Hz, 1 H), 6.22 (d, J = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 25.0, 27.4, 29.0, 39.2, 66.1, 118.3, 119.3, 119.9, 136.9, 137.8, 151.7, 177.4. IR (film): ν 3361, 2967, 1745, 1278, 1125, 912 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_3$ $(M+Na)^+$ 273.1461, found 273.1473.



19e

(1*E*,3*E*,6*Z*)-7-((tert-butyldimethylsilyloxy)methyl)-4-(hydroxymethyl)cyclohepta-1,3,6-trienyl pivalate (**19e**).

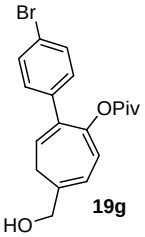
Yield : 92%, 67 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 6 H), 0.87 (s, 9 H), 1.30 (s, 9 H), 1.66-1.64 (m, 1 H), 2.49 (d, J = 7.6 Hz, 2 H), 4.20 (s, 2 H), 4.24 (d, J = 5.2 Hz, 2 H), 5.53 (t, J = 7.2 Hz, 1 H), 6.07 (d, J = 6.4 Hz, 1 H), 6.22 (d, J = 6.4 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ -5.3, 18.3, 25.8, 27.1, 28.5, 39.0, 62.0, 66.0, 118.3, 119.3, 120.1, 134.7, 137.0, 150.0, 176.9. IR (film): ν 1125, 1277, 1478, 1745, 2956, 3409, cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{34}O_4Si$ $(M+Na)^+$ 389.2118, found 389.2116.



19f

(1*E*,3*E*,6*Z*)-4-(hydroxymethyl)-7-phenylcyclohepta-1,3,6-trienyl pivalate (**19f**).

Yield : 81%, 48 mg, (regioisomeric ratio = 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (s, 9 H), 1.59 (broad, 1 H), 2.64 (d, J = 7.5 Hz, 2 H), 4.29 (d, J = 1.5 Hz, 2 H), 5.54 (t, J = 7.5 Hz, 1 H), 6.19 (td, J = 1.5, 6.5 Hz, 1 H), 6.49 (d, J = 6.5 Hz, 1 H), 7.21-7.34 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6, 29.3, 38.5, 65.9, 118.4, 120.8, 122.0, 127.4, 127.8, 129.2, 137.6, 137.8, 138.2, 150.1, 176.7. IR (film): ν 3356, 2966, 1744, 1278, 1130, 1013, 765, 731, 698 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{22}O_3$ $(M+Na)^+$ 321.1461, found 321.1468.

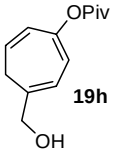


19g

(1*E*,3*E*,6*Z*)-7-(4-bromophenyl)-4-(hydroxymethyl)cyclohepta-1,3,6-trienyl pivalate (**19g**).

Yield : 76%, 57 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (s, 9 H), 1.58 (s, 1 H), 2.63 (d, J = 7.6 Hz, 2 H), 4.30 (s, 2 H), 5.53 (t, J = 7.6 Hz, 1 H), 6.19 (d, J = 6.0 Hz, 1 H), 6.49 (d, J = 6.0 Hz, 1 H), 7.12 (d, J = 8.0 Hz, 2 H), 7.41 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.7, 29.3, 38.6, 65.9, 118.4, 121.3, 121.5, 122.3, 130.8, 131.0, 136.5, 136.8, 138.3, 149.5, 176.6. IR (film): ν 1131,

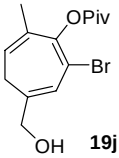
1263, 1484, 1742, 2967, 3386 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}BrO_3$ $(M+Na)^+$ 399.0566, found 399.0565.



19h

(1*E*,3*E*,6*Z*)-4-(hydroxymethyl)cyclohepta-1,3,6-trienyl pivalate (**19h**).

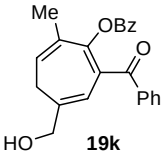
Yield : 16%, 7 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 9 H), 1.61 (s, 1 H), 2.52 (d, *J* = 7.2 Hz, 2 H), 4.25 (s, 2 H), 5.49 (td, *J* = 7.2, 9.6 Hz, 1 H), 5.95 (dd, *J* = 1.6, 9.6 Hz, 1 H), 6.16 (td, *J* = 1.2, 6.4 Hz, 1 H), 6.26 (dd, *J* = 1.6, 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.1, 29.2, 38.9, 66.3, 118.8, 119.2, 122.9, 124.4, 134.7, 151.0, 177.3. IR (film): ν 732, 907, 1053, 1112, 1278, 1410, 1478, 1747, 2971, 3365 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{13}H_{18}O_3$ $(M+Na)^+$ 245.1148, found 245.1160.



19j

2,2-Dimethyl-propionic acid 2-bromo-4-hydroxymethyl-7-methyl-cyclohepta-1,3,6-trienyl ester (**19j**).

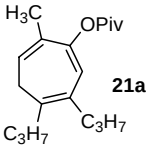
Yield : 34%, 21 mg, (regioisomeric ratio > 20:1), oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (s, 9 H), 1.76 - 1.83 (m, 3 H), 2.49 (br, 2 H), 4.26 (s, 2 H), 5.42 (tq, *J* = 7.10, 1.60 Hz, 1 H), 6.29 (t, *J* = 1.56 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125MHz): δ 18.3, 27.5, 29.0, 39.6, 65.2, 116.1, 122.6, 123.5, 131.0, 140.5, 148.8, 175.8. IR (film): ν 3448, 2975, 2933, 2873, 2360, 1750, 1632, 1479, 1460, 1397, 1368, 1276, 1242, 1140, 1107, 1089, 1026, 915, 887, 845, 808, 784, 759, 732 cm^{-1}. HRMS (ESI) for $C_{14}H_{19}BrO_3$ (M+Na), 337.0410 (calc.), found 337.0408.



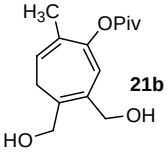
19k

2-benzoyl-4-(hydroxymethyl)-7-methylcyclohepta-1,3,6-trienyl benzoate (**19k**).

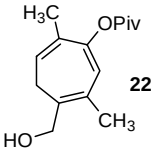
Yield : 62%, 45 mg, (regioisomeric ratio = 5:1), oil. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.80 (s, 3 H), 1.84 (s, 1 H), 2.70 (d, *J*= 6.8 Hz, 2 H), 4.34 (s, 2 H), 5.55 (t, *J*= 7.2 Hz, 1 H), 6.51 (s, 1 H), 7.22-7.32 (m, 5 H), 7.44-7.50(m, 1 H), 7.64-7.70 (m, 2 H), 7.76-7.82 (m, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 18.0, 29.4, 66.1, 118.7, 123.3, 128.4, 128.5, 128.6, 129.1, 129.9, 130.7, 131.1, 133.2, 133.6, 137.5, 138.4, 150.8, 164.3, 197.0. IR (film): ν 708, 735, 1023, 1058, 1115, 1144, 1177, 1264, 1316, 1450, 1597, 1661, 1735, 2924, 3409 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{23}H_{20}O_4$ $(M+Na)^+$ 383.1253, found 383.1254.



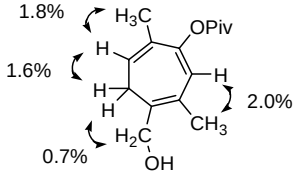
(1*E*,3*Z*,6*Z*)-7-methyl-3,4-dipropylcyclohepta-1,3,6-trienyl pivalate (**21a**).
Yield : 21%, 12 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 0.91 (t, *J* = 7.2 Hz, 3 H), 1.31 (s, 9 H), 1.35-1.48 (m, 4 H), 1.74 (s, 3 H), 2.12-2.19 (m, 4 H), 2.31 (d, *J* = 7.6 Hz, 2 H), 5.32 (t, *J* = 7.6 Hz, 1 H), 6.14 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.1, 17.3, 23.4, 23.6, 27.2, 33.2, 34.1, 36.1, 38.9, 121.4, 123.9, 129.4, 133.2, 150.1, 177.2. IR (film): ν 733, 908, 1066, 1277, 1396, 1746, 2871, 2958 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{30}O_2$ $(M+Na)^+$ 313.2138, found 313.2147.



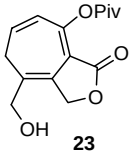
(1*E*,3*Z*,6*Z*)-7-methyl-3,4-dihydroxymethyl-1,3,6-trienyl pivalate (**21b**).
Yield : 80%, 43 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9 H), 1.77 (d, *J* = 1.2 Hz, 3 H), 2.43 (d, *J* = 7.2 Hz, 2 H), 2.73 (s, 2 H), 4.277 (s, 2 H), 4.283 (s, 2 H), 5.38 (qt, *J* = 1.2, 7.2 Hz, 1 H), 6.29 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.4, 27.2, 31.4, 39.0, 62.2, 62.8, 120.8, 122.2, 130.2, 131.7, 132.5, 152.2, 177.2. IR (film): ν 731, 908, 1002, 1076, 1278, 1396, 1479, 1744, 2874, 2971, 3338 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_4$ $(M+Na)^+$ 289.1410, found 289.1421.



nOe



(1*E*,3*E*,6*Z*)-4-(hydroxymethyl)-3,7-dimethylcyclohepta-1,3,6-trienyl pivalate (**22**).
Yield : 68%, 34 mg, (regioisomeric ratio = 5:1), oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H), 1.62 (broad, 1 H), 1.76 (d, *J* = 1.2 Hz, 3 H), 1.89 (s, 3 H), 2.47 (d, J = 7.6 Hz, 2 H), 4.25 (s, 2 H), 5.42 (qt, J = 1.2, 7.6 Hz, 1 H), 6.14 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.4, 17.6, 27.2, 30.3, 38.9, 62.8, 122.2, 124.2, 127.4, 129.90, 129.94, 151.2, 177.0. IR (film): ν 906, 1004, 1075, 1278, 1396, 1459, 1479, 1638, 1745, 2971, 3349 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_3$ $(M+Na)^+$ 273.1461, found 273.1469.



(3a*Z*,6*Z*,8*Z*)-3,5-dihydro-4-(hydroxymethyl)-1-oxo-1H-cyclohepta[c]furan-8-yl pivalatev(**23**).
Yield : 71%, 39 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 9 H), 2.54 (d, *J* = 7.2 Hz, 2 H), 2.80 (t, *J* = 5.6 Hz, 1 H), 4.29 (d, *J* = 4.8 Hz, 2 H), 5.00 (s, 2 H), 5.58 (td, *J* = 7.6, 9.6 Hz, 1 H), 6.16 (d, *J* = 9.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0, 28.8,

39.1, 63.6, 68.3, 116.6, 123.8, 124.8, 125.2, 130.0, 153.4, 168.7, 176.6. IR (film): ν 906, 1100, 1364, 1746, 2360, 2971, 3461 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{18}O_5$ $(M+Na)^+$ 301.1046 , found 301.1056.

References:

1) Zhao, L.; Lu, X.; Xu, W. *J. Org. Chem.* **2005**, *70*, 4059.
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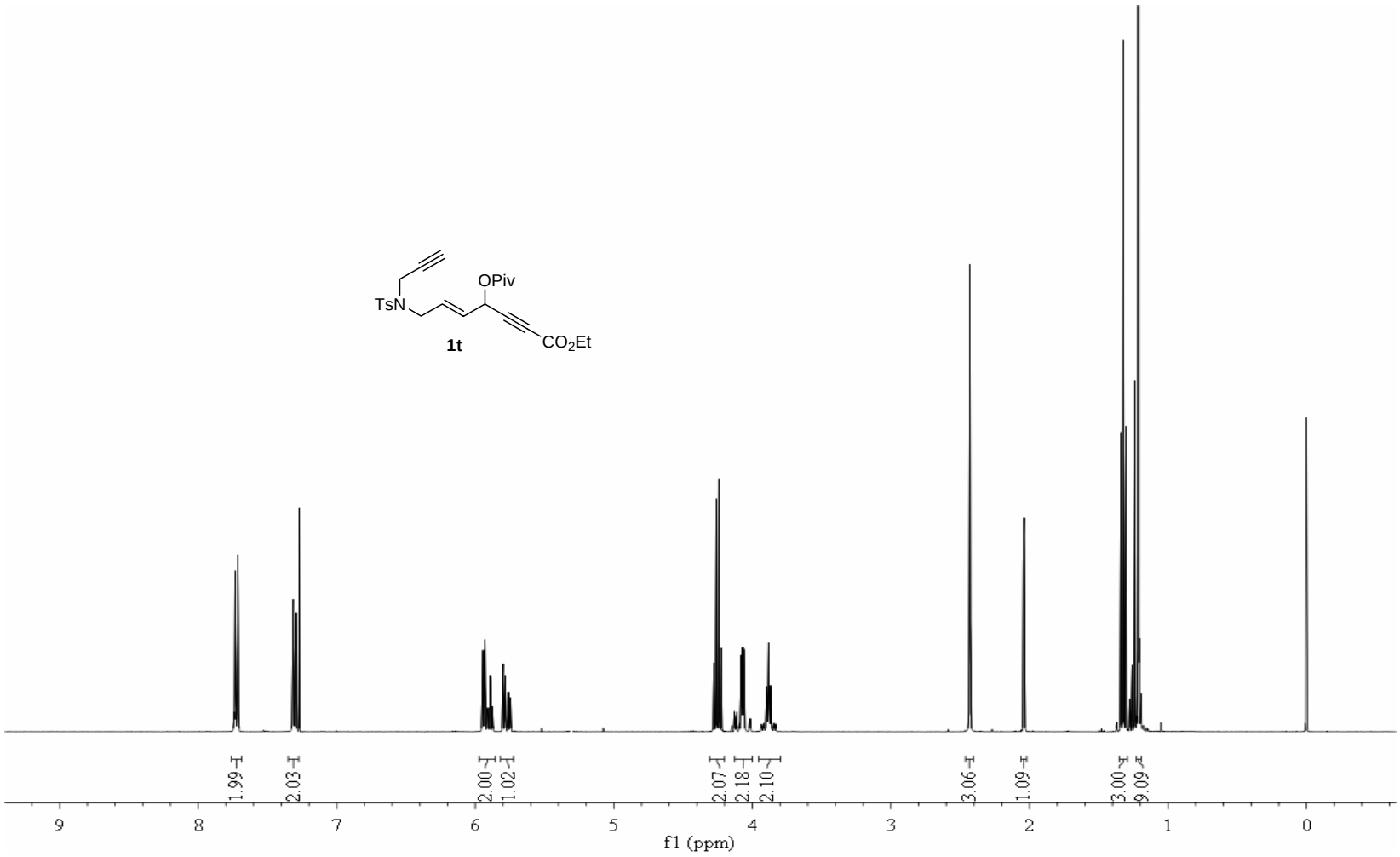
Copies of proton and carbon NMR spectra for substrates and products.

Note: See reference (*Angew. Chem. Int. Ed.*, **2011**, *50*, 8153-8156.) for ^{1}H and ^{13}C NMR spectra of compounds **1a-1o** and **2a-2o**.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9
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4
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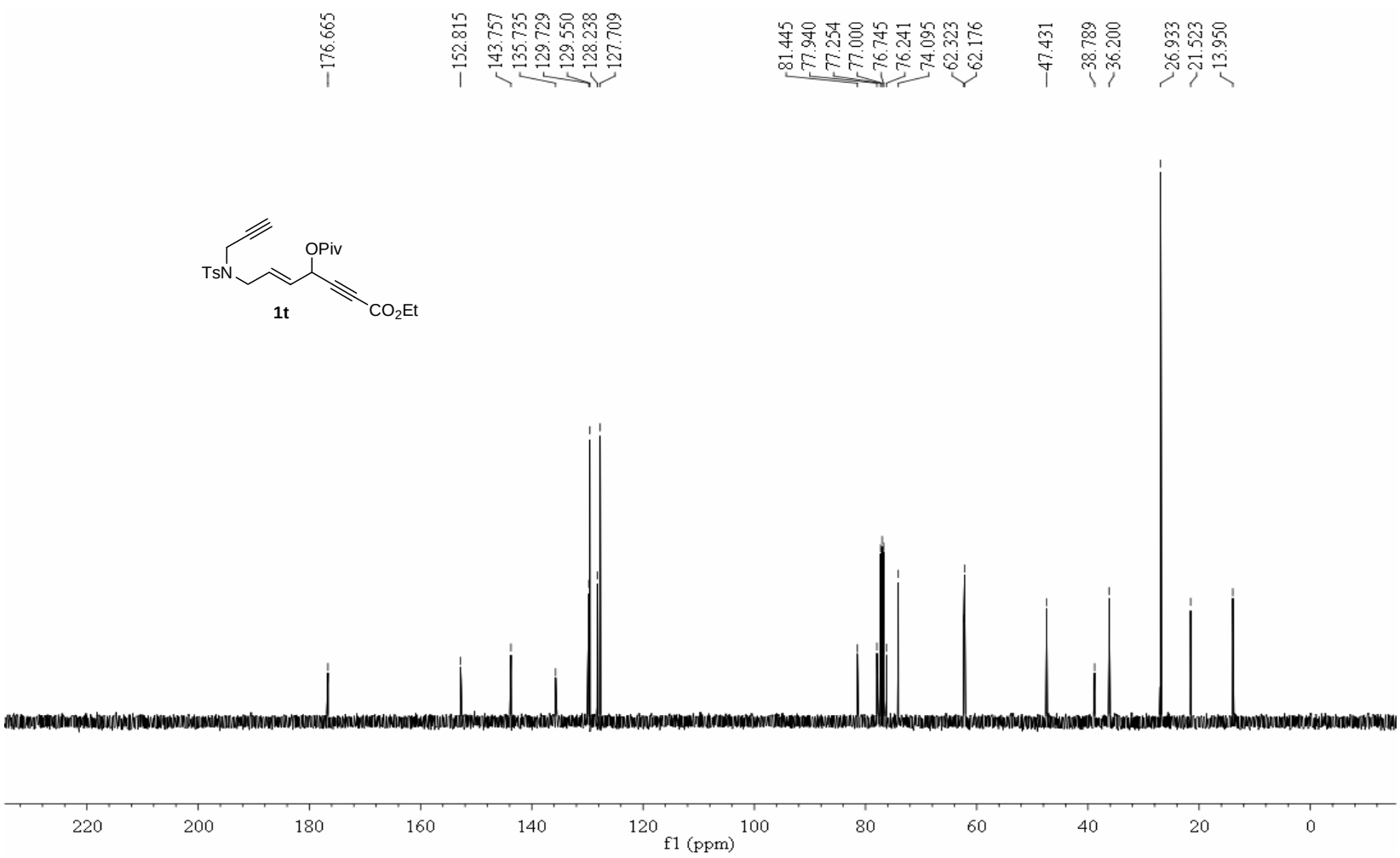
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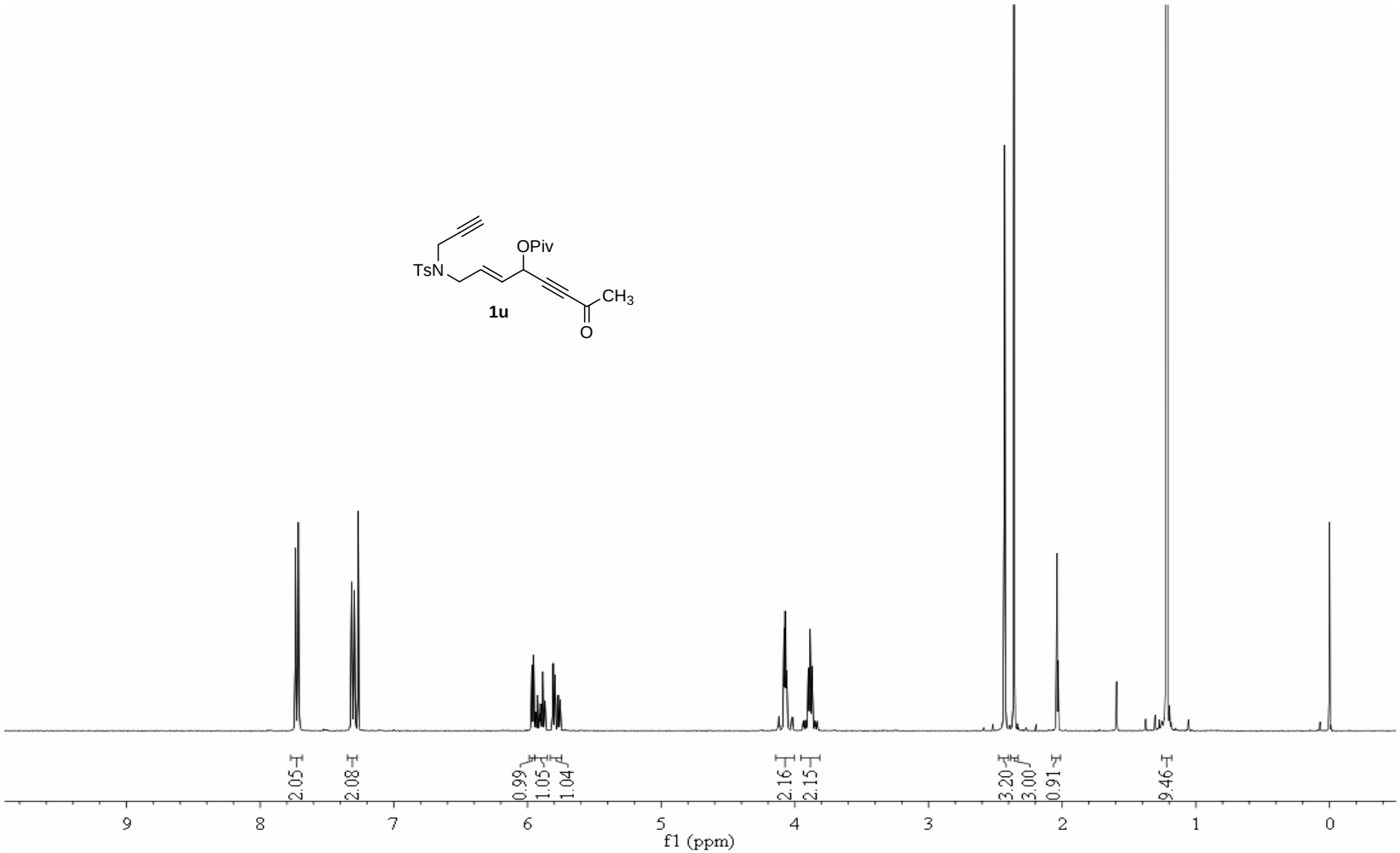
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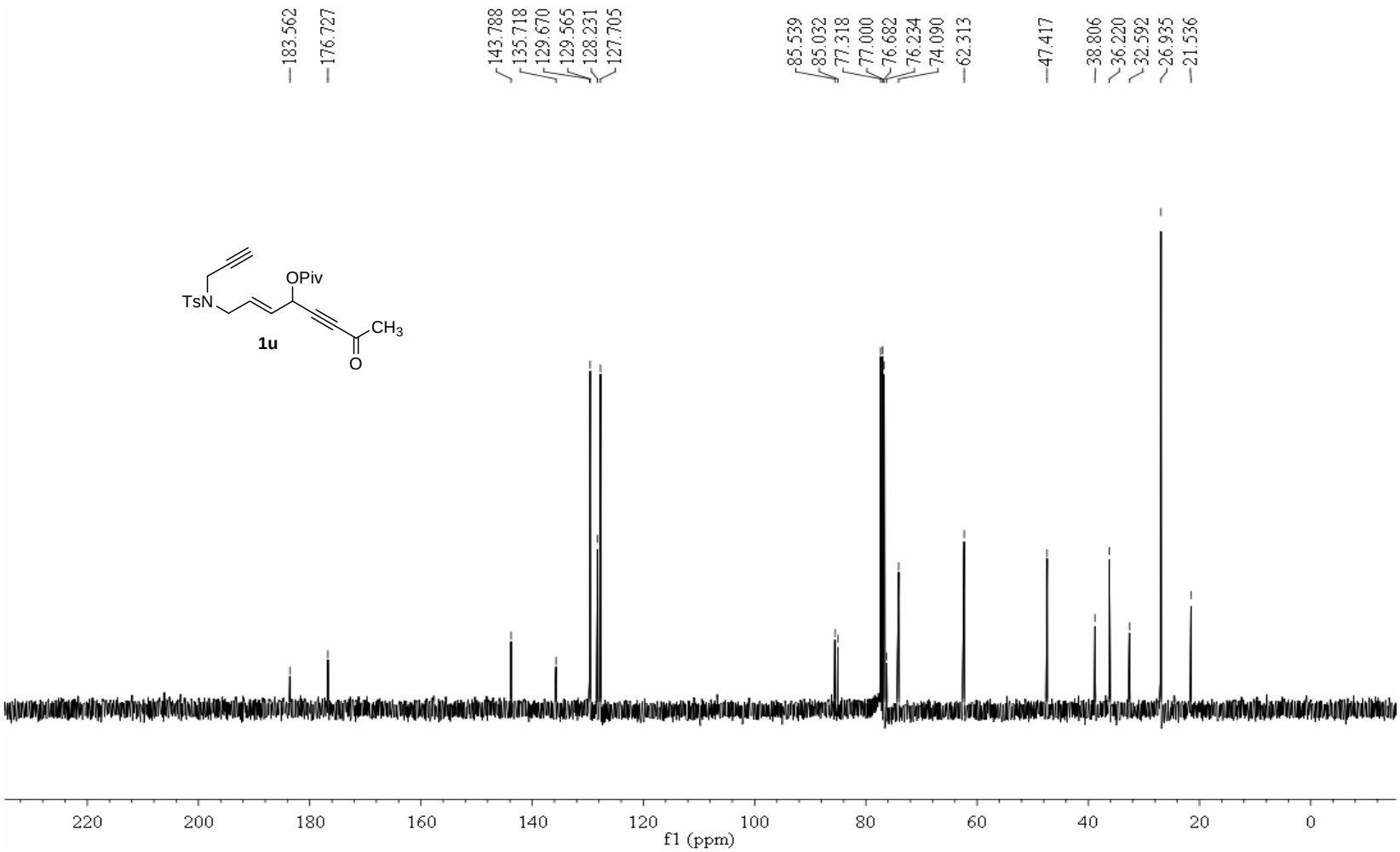
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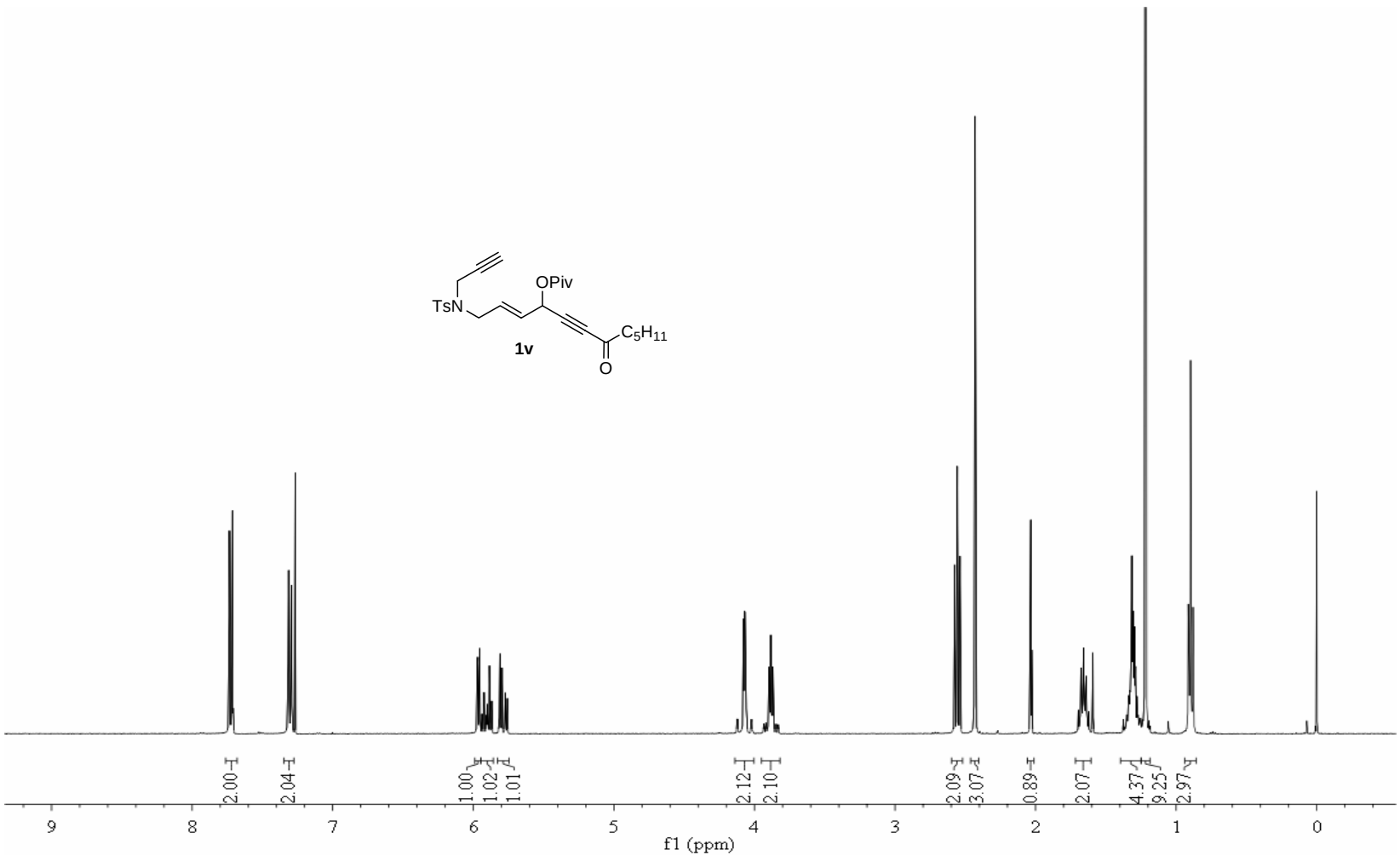
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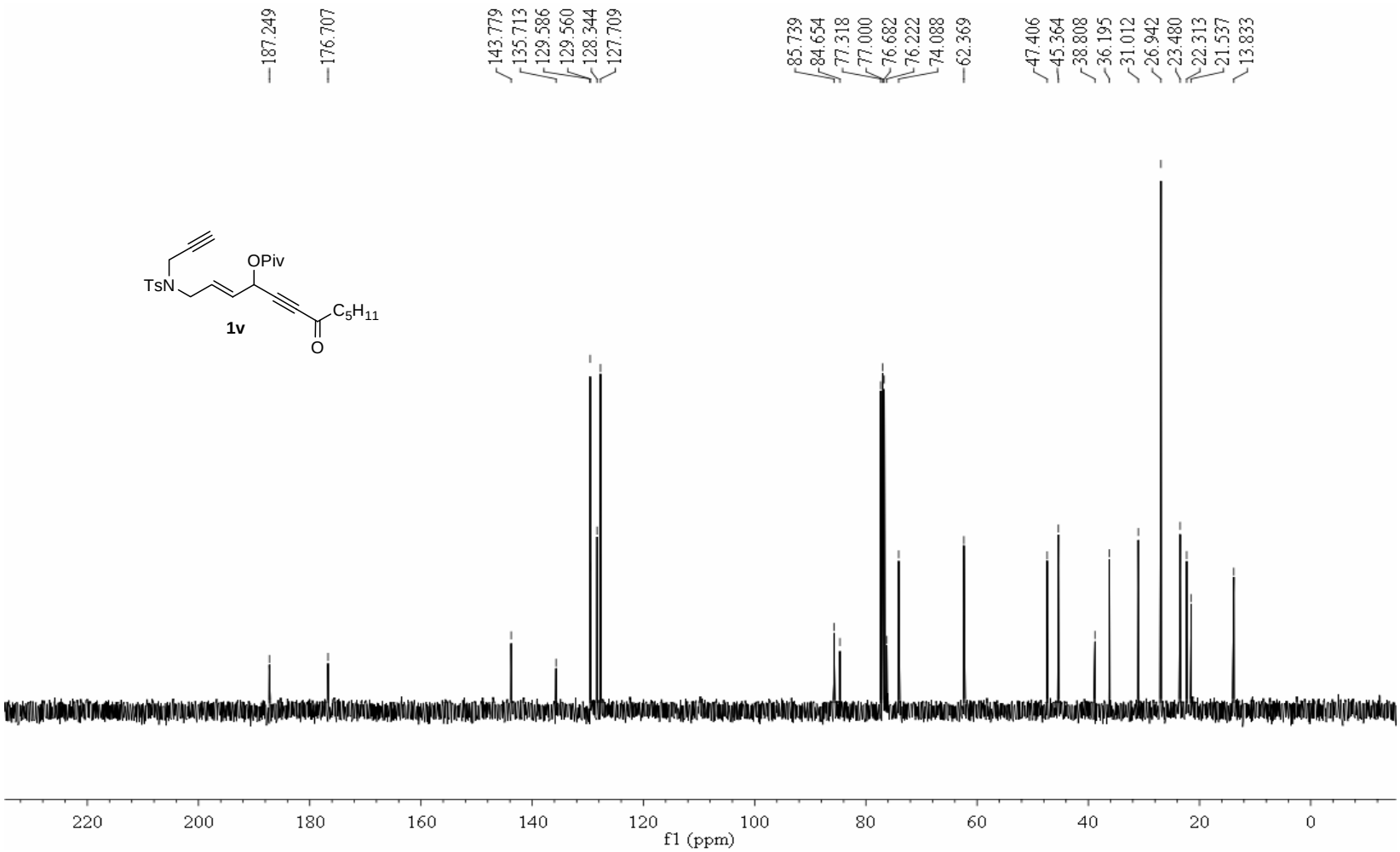
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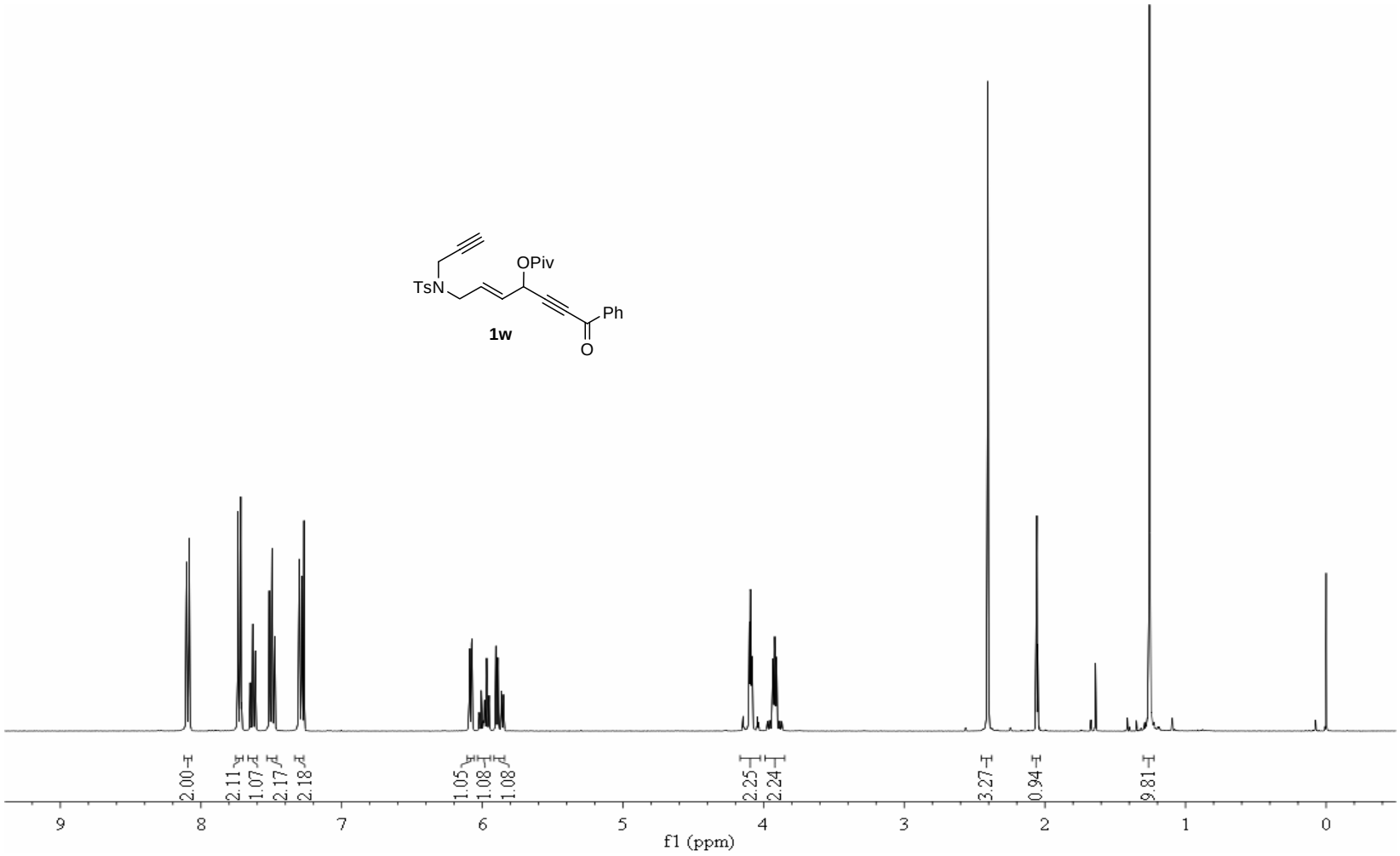
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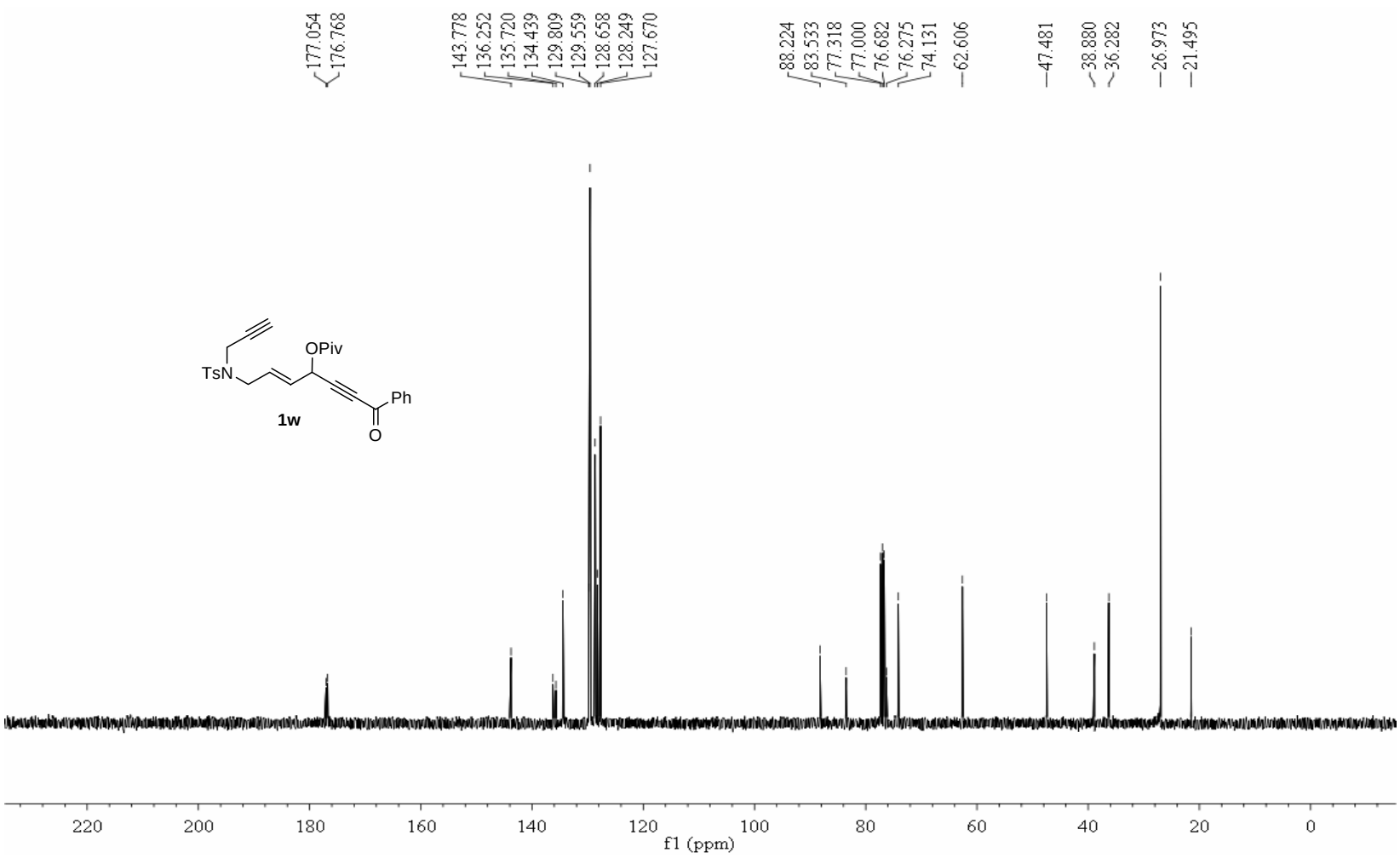
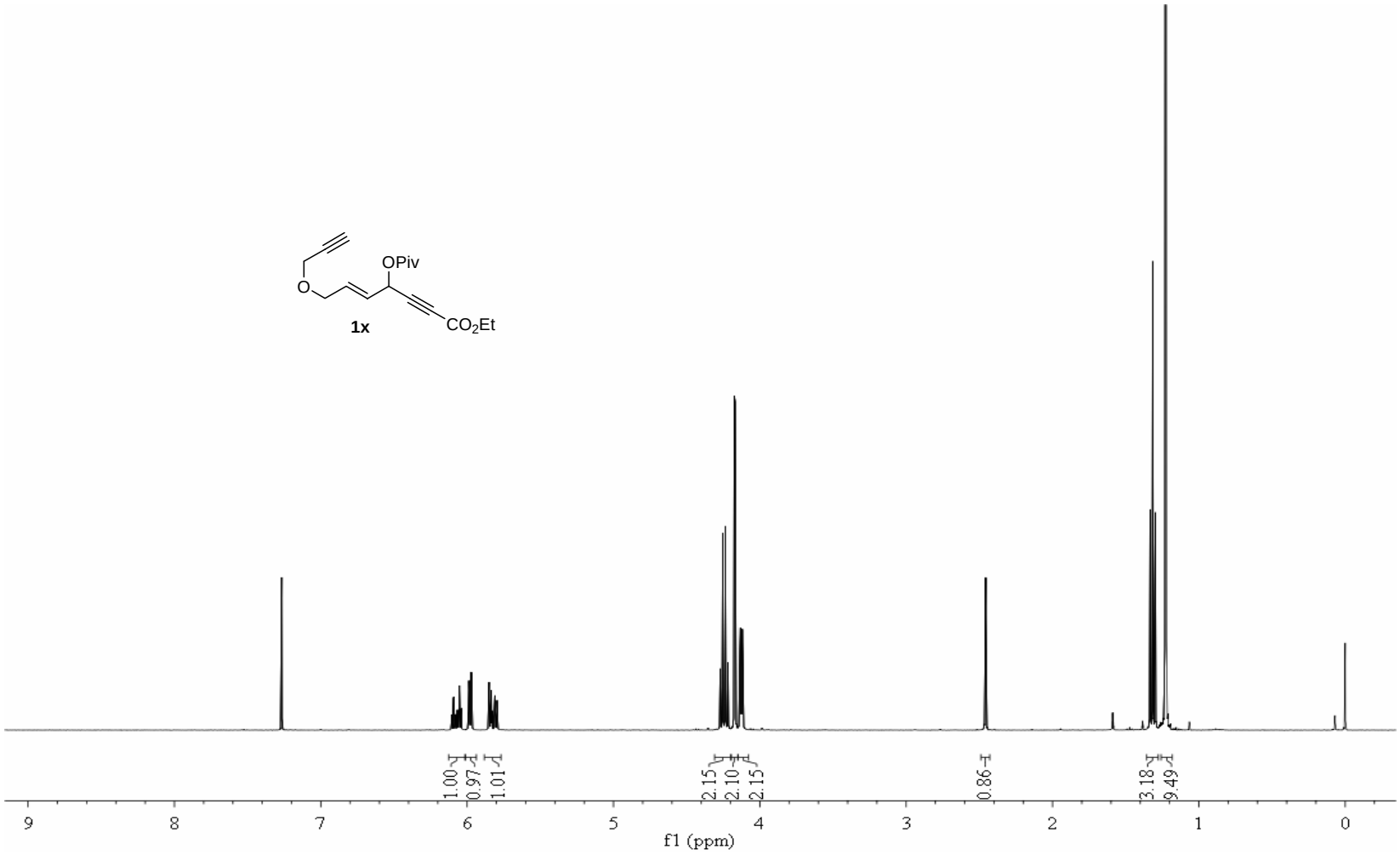
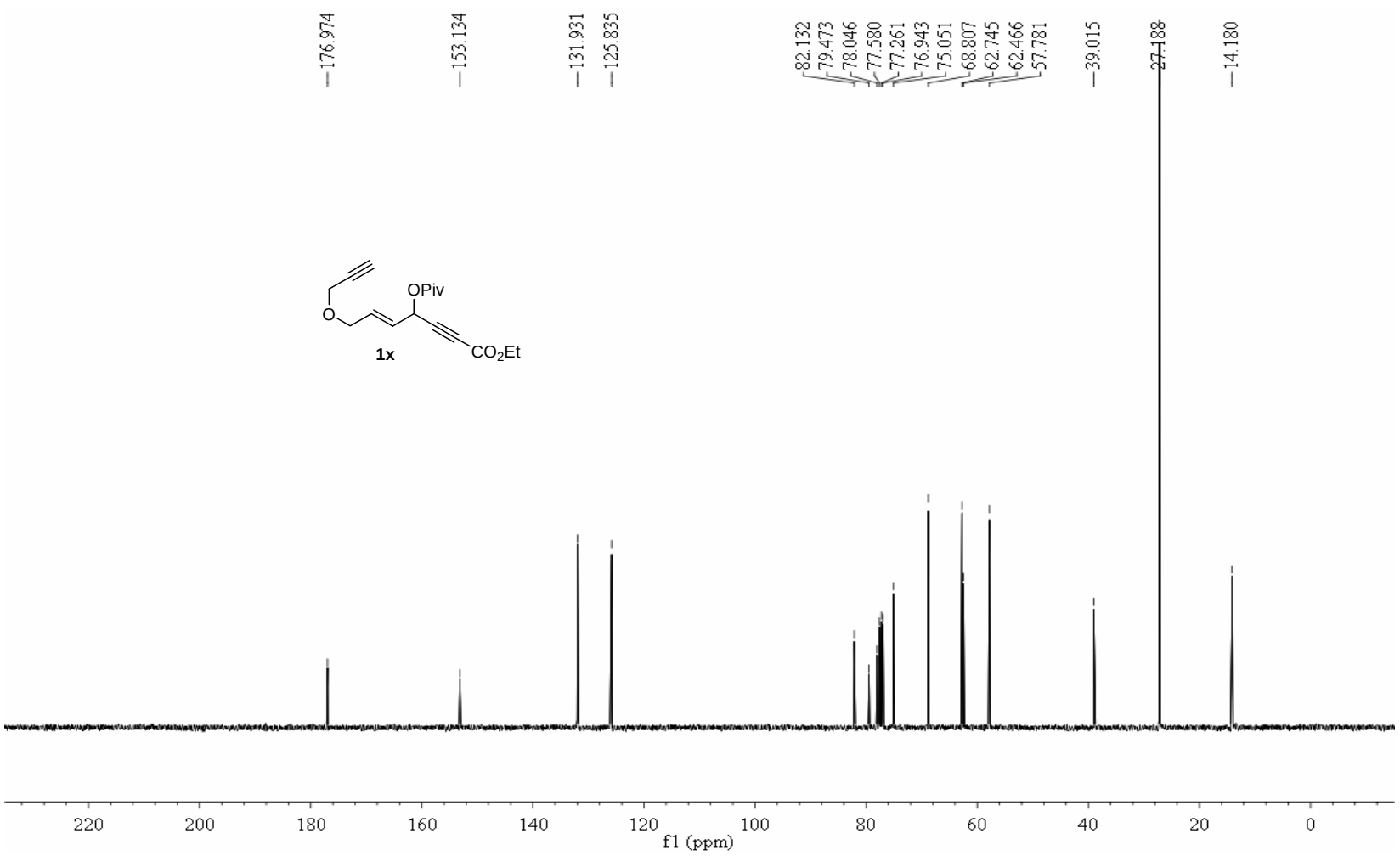
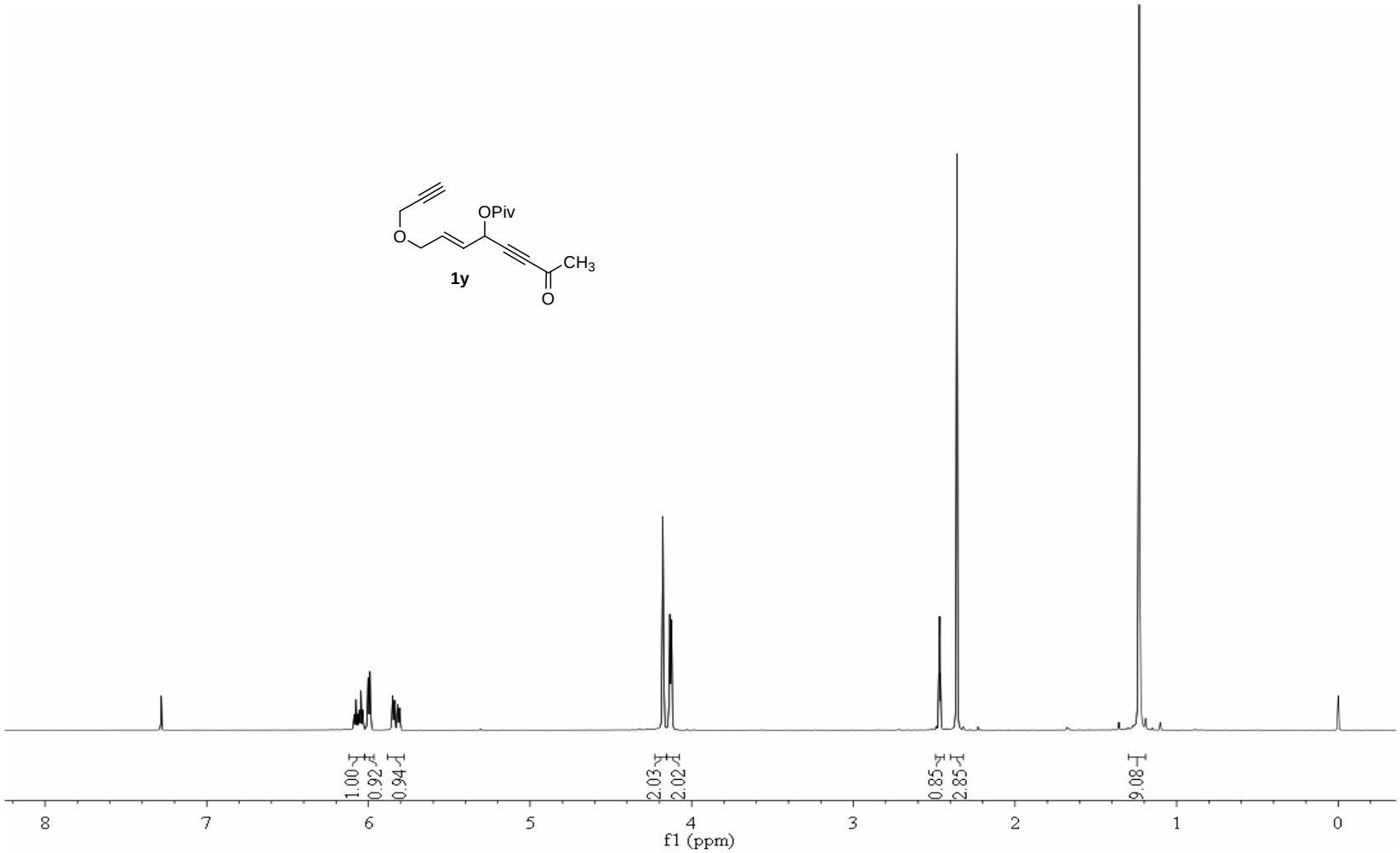
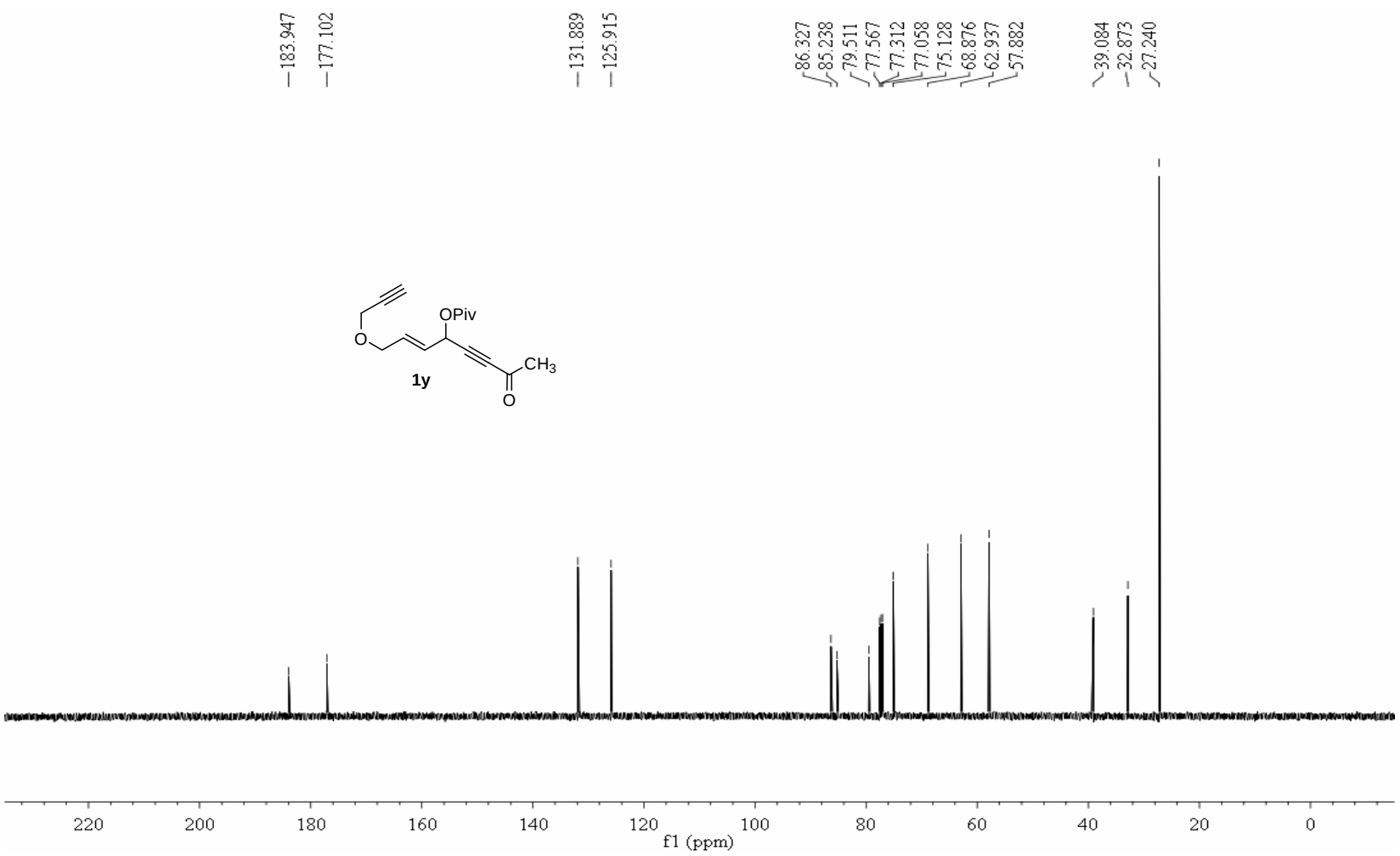
2.17
2.18
1.05
1.08
1.08
2.25
2.24
3.27
0.94
9.81
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

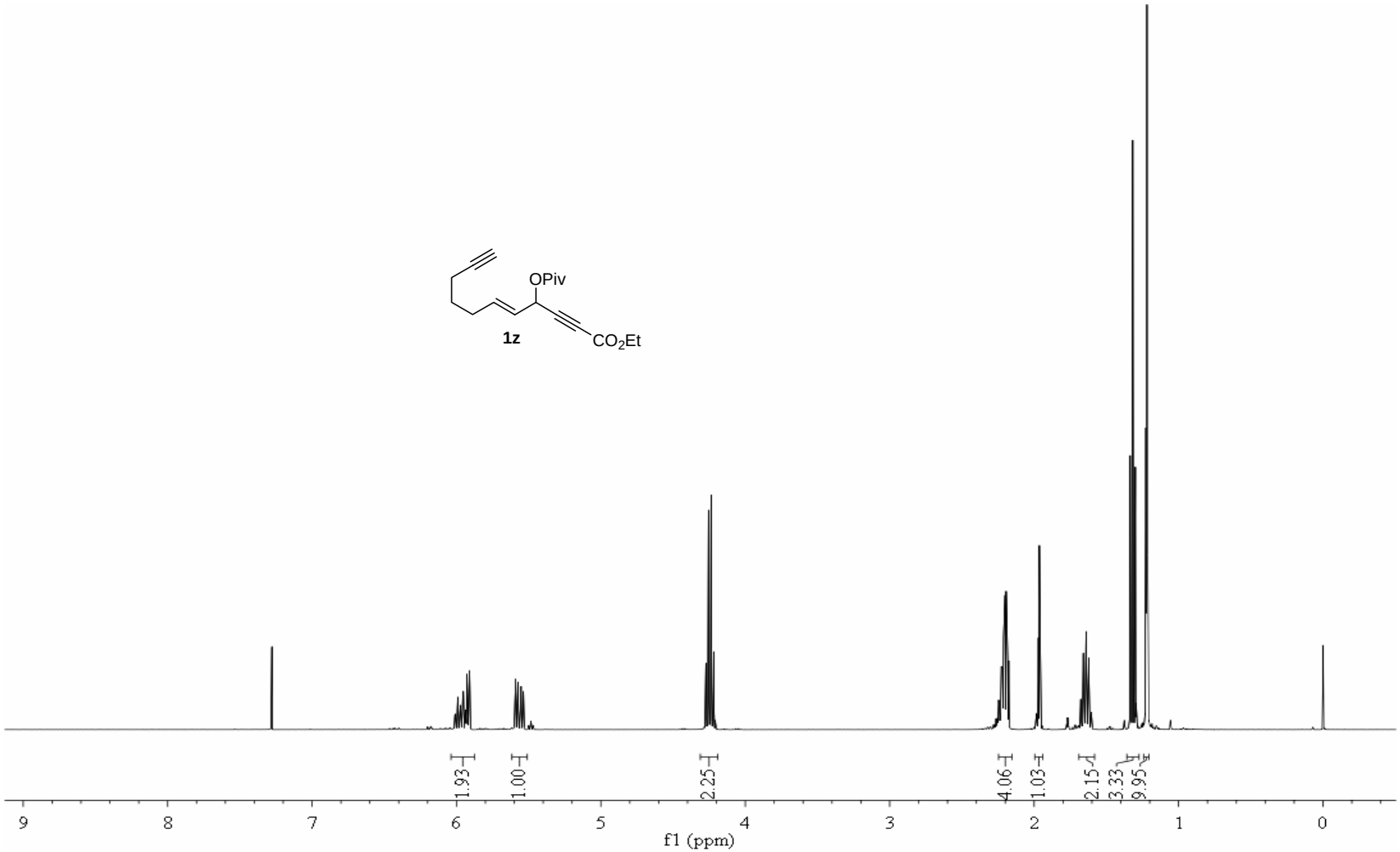

177.054
176.768
143.778
136.252
135.720
134.439
129.809
129.559
128.658
128.249
127.670
88.224
83.533
77.318
77.000
76.682
76.275
74.131
62.606
47.481
38.880
36.282
26.973
21.495
OPiv
TsN
Ph
O
1w
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

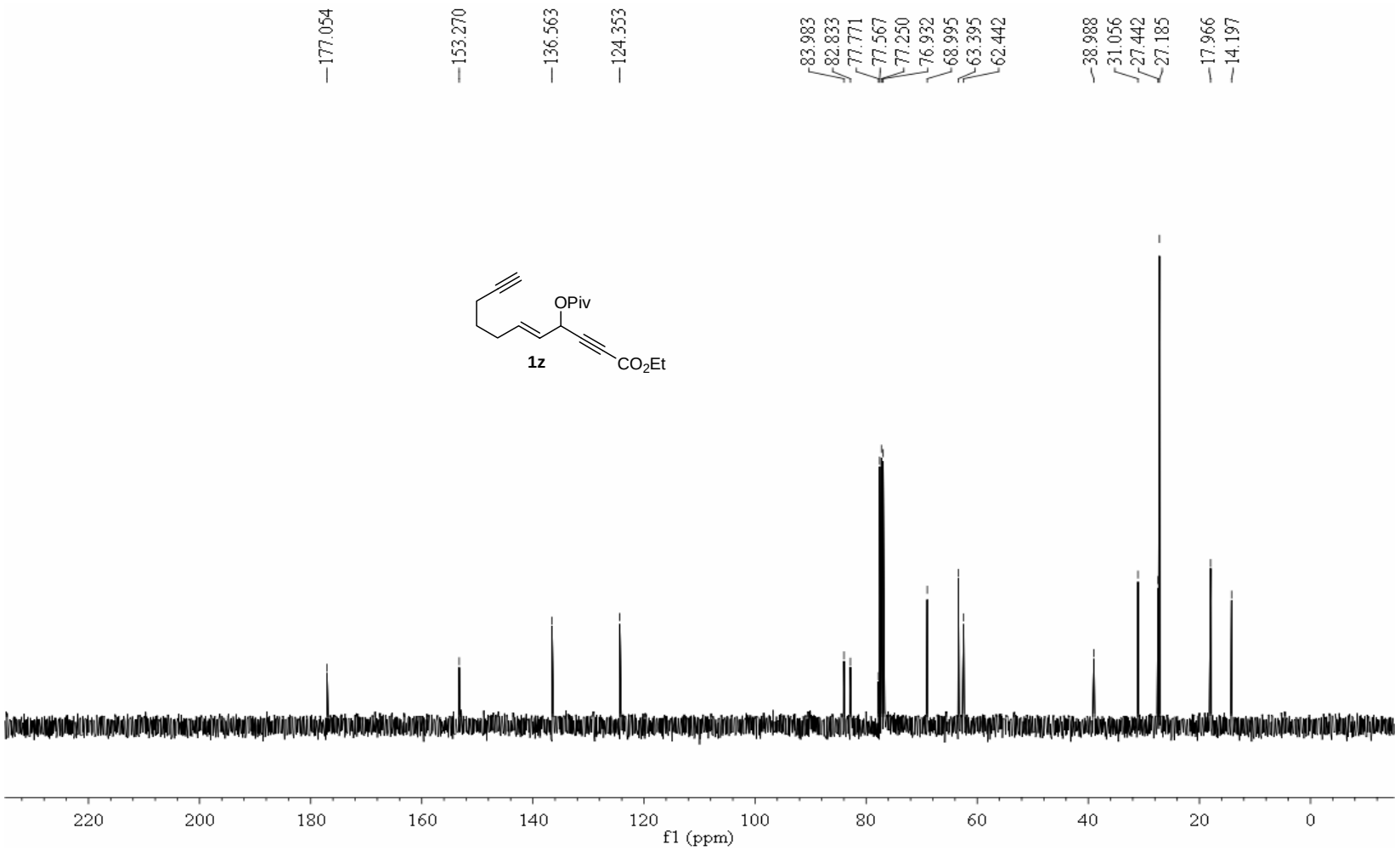

OPiv
O
CO2Et
1x
1.00
0.97
1.01
2.15
2.10
2.15
0.86
3.18
9.49
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

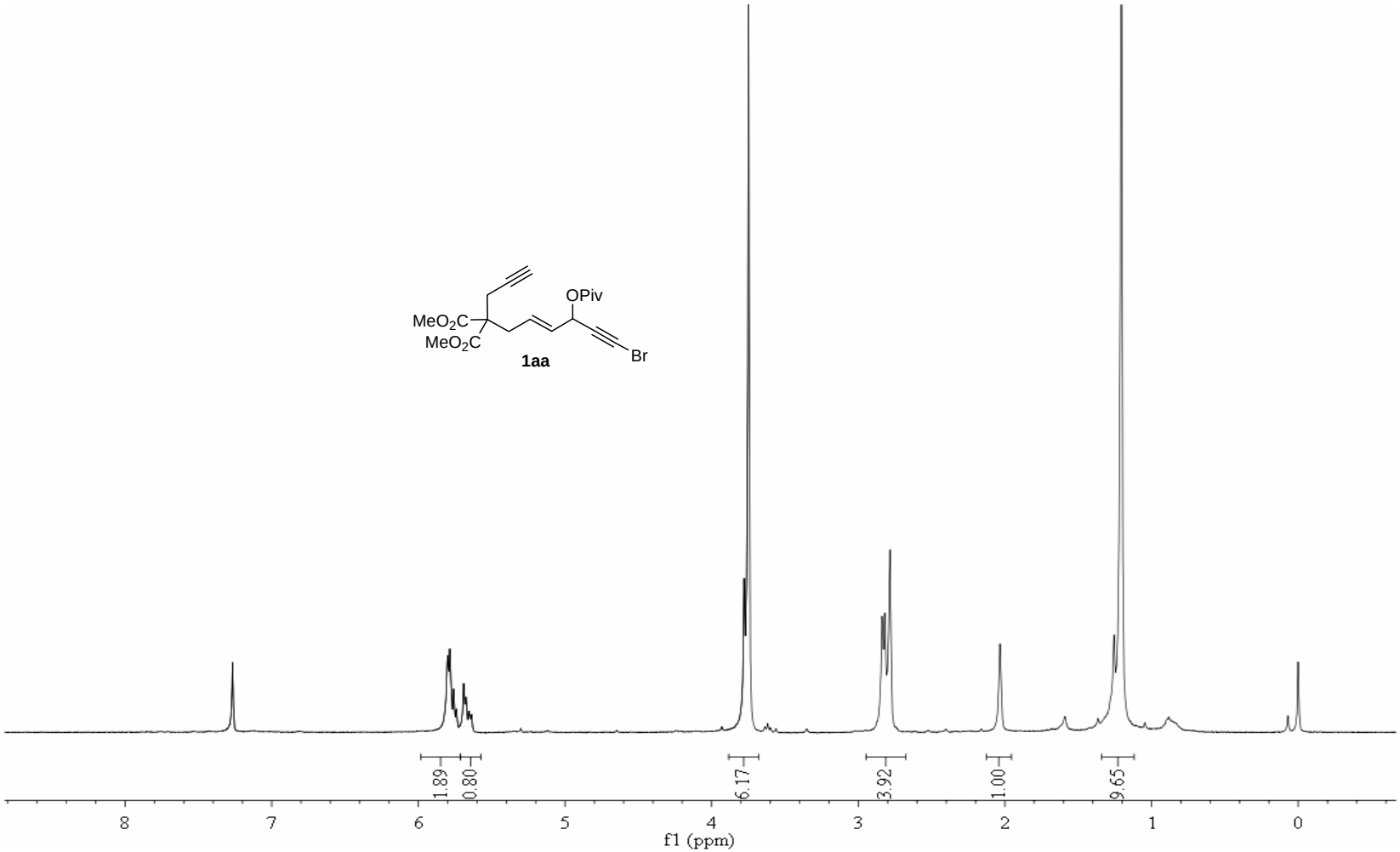

176.974
153.134
131.931
125.835
82.132
79.473
78.046
77.580
77.261
76.943
75.051
68.807
62.745
62.466
57.781
39.015
27.188
14.180
OPiv
O
CO2Et
1x
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

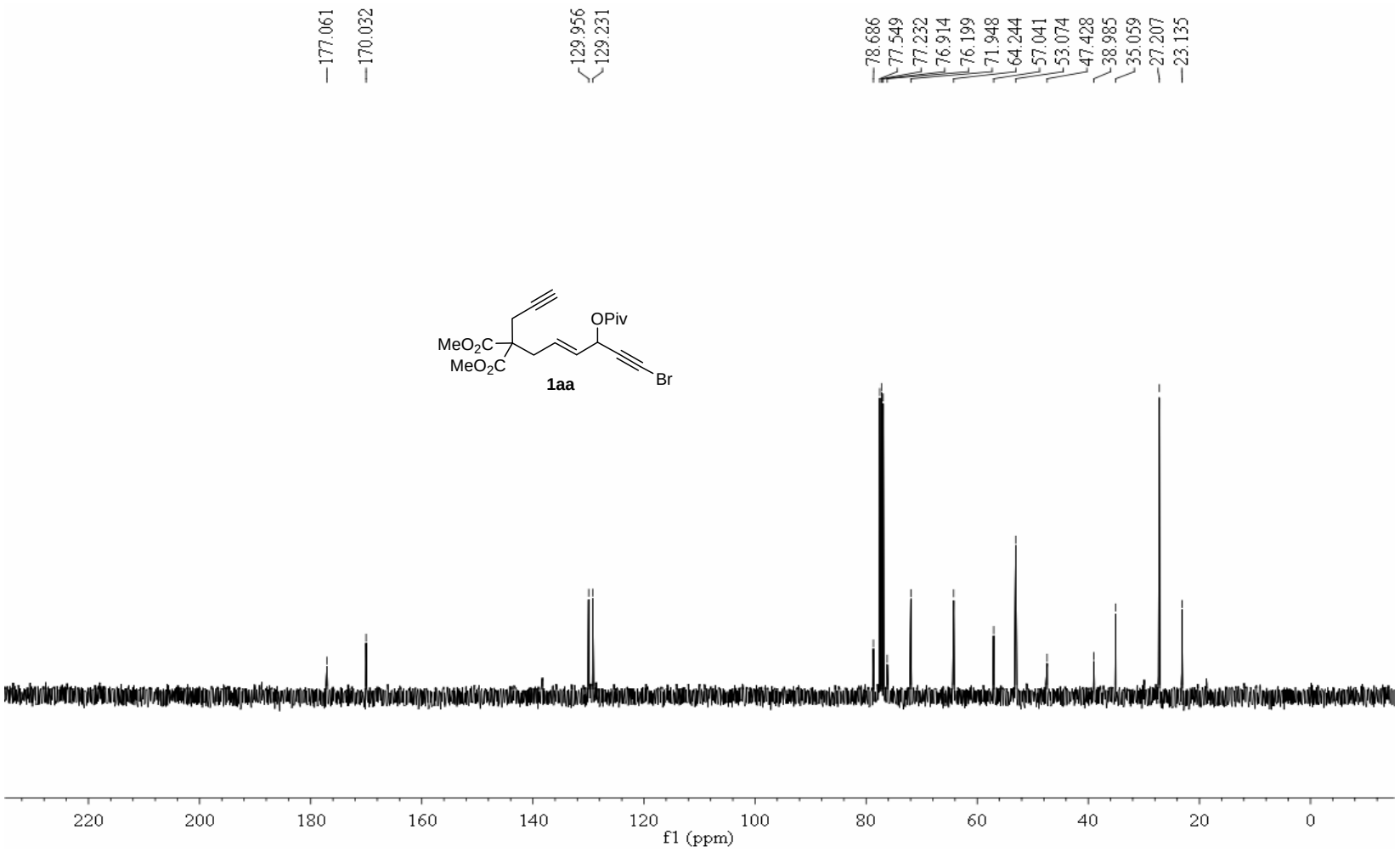

OPiv
O
CH3
O
1y
1.00
0.92
0.94
2.03
2.02
0.85
2.85
9.08
8
7
6
5
4
3
2
1
0
f1 (ppm)

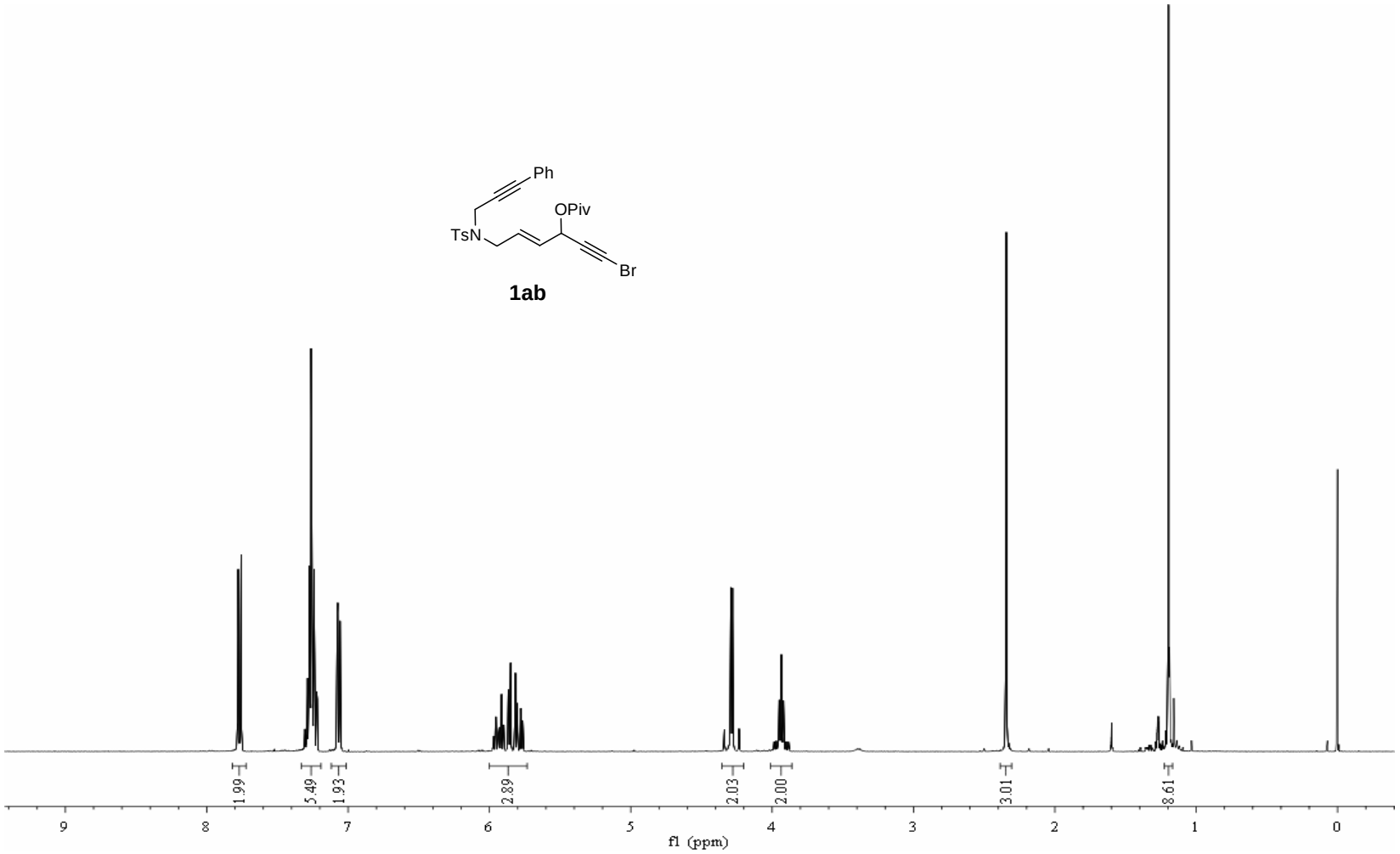

183.947
177.102
131.889
125.915
86.327
85.238
79.511
77.567
77.312
77.058
75.128
68.876
62.937
57.882
39.084
32.873
27.240
OPiv
O
CH3
O
1y
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

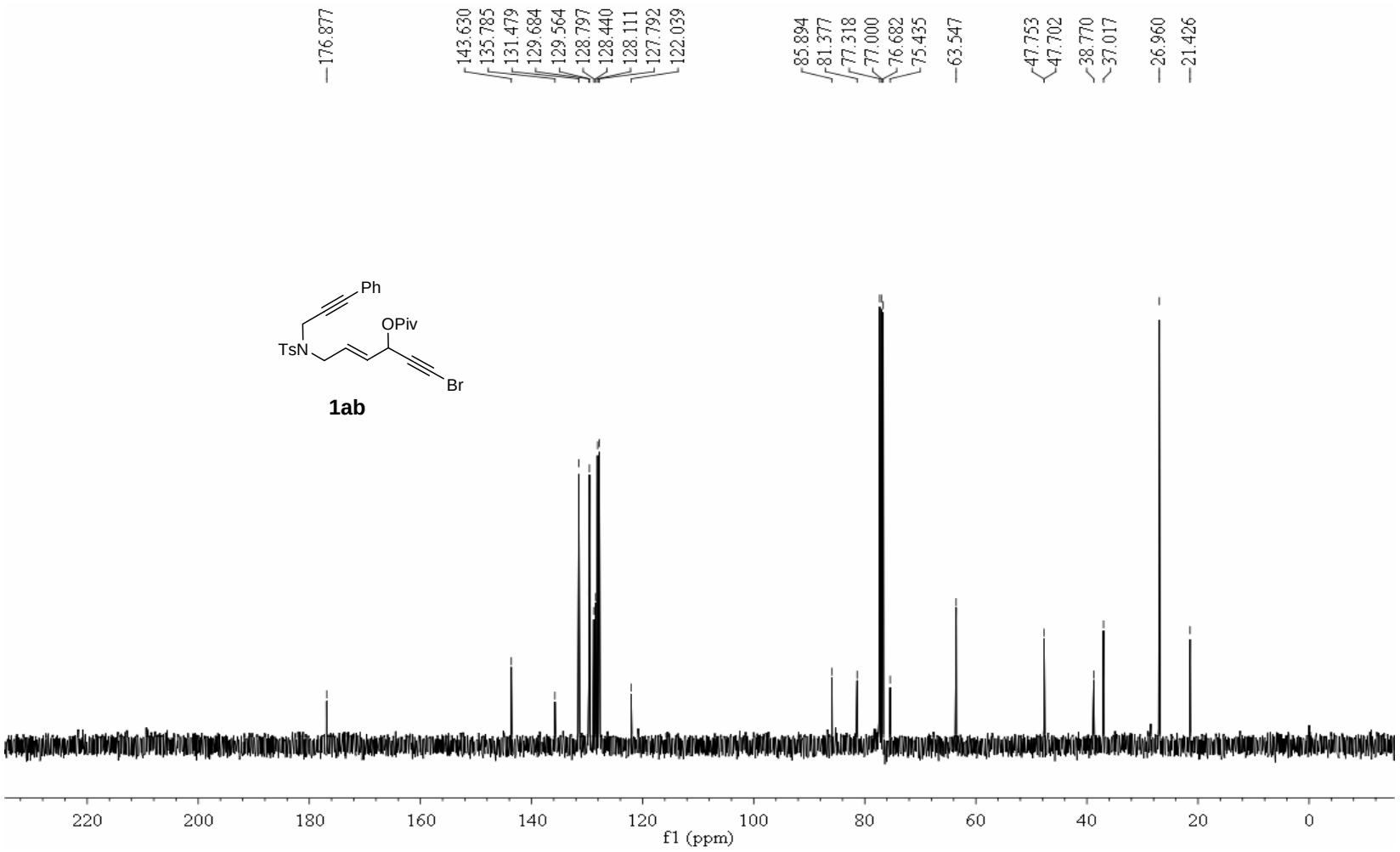

OPiv
1z
CO2Et
1.93
1.00
2.25
4.06
1.03
2.15
3.33
9.95
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

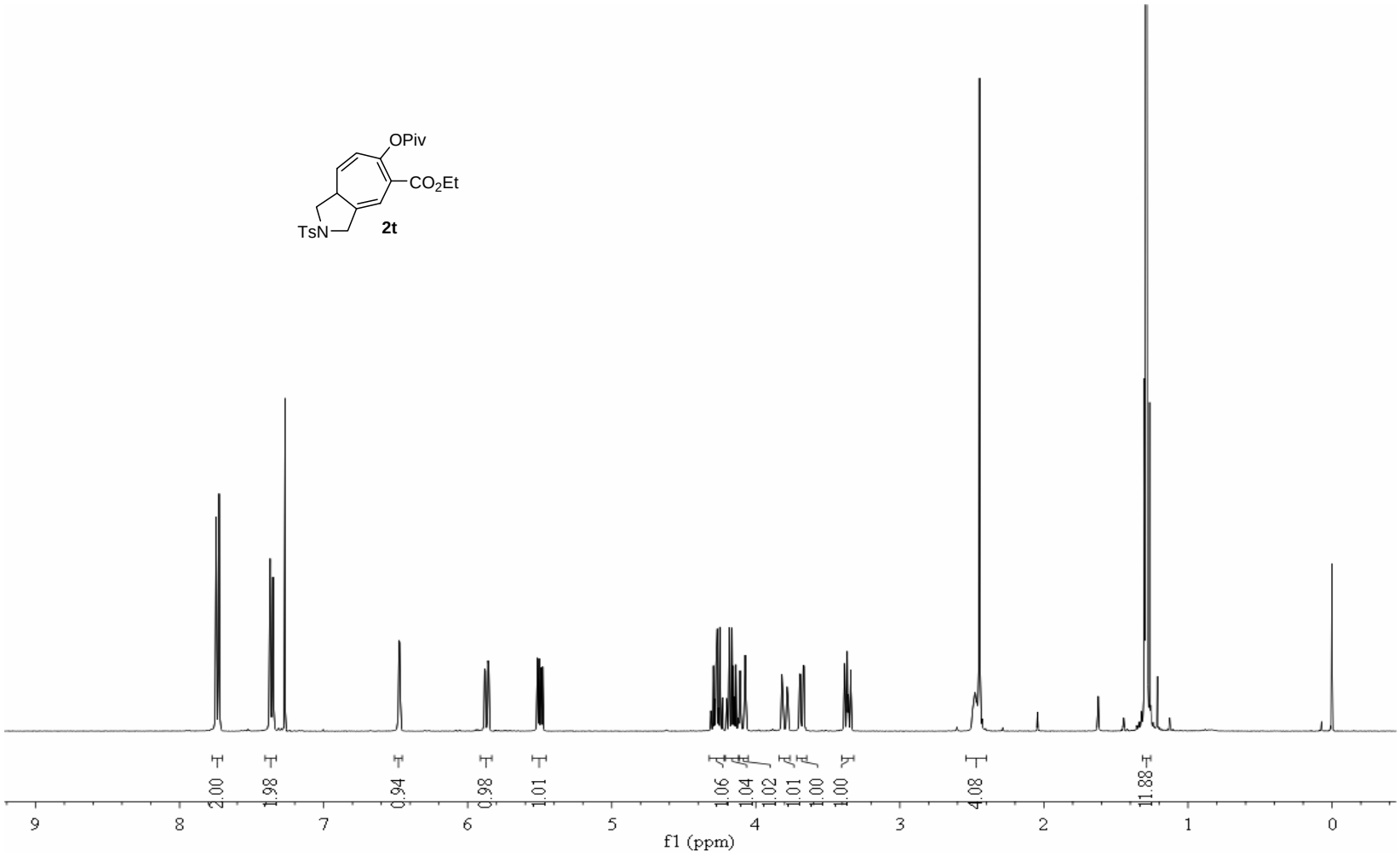

177.054
153.270
136.563
124.353
83.983
82.833
77.771
77.567
77.250
76.932
68.995
63.395
62.442
38.988
31.056
27.442
27.185
17.966
14.197
OPiv
1z
CO2Et
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

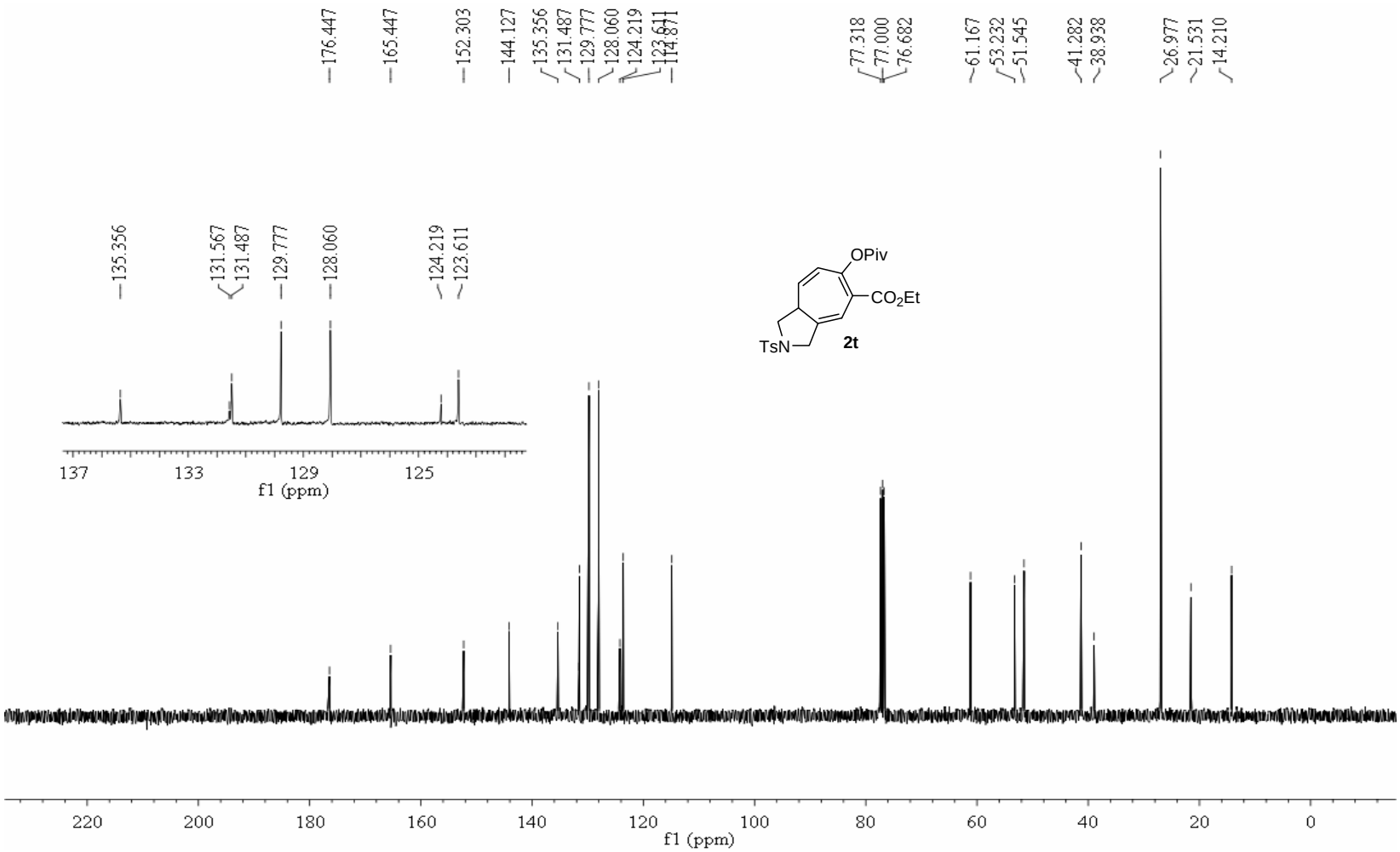

OPiv
MeO2C
MeO2C
Br
1aa
1.89
0.80
6.17
3.92
1.00
9.65
8
7
6
5
4
3
2
1
0
f1 (ppm)

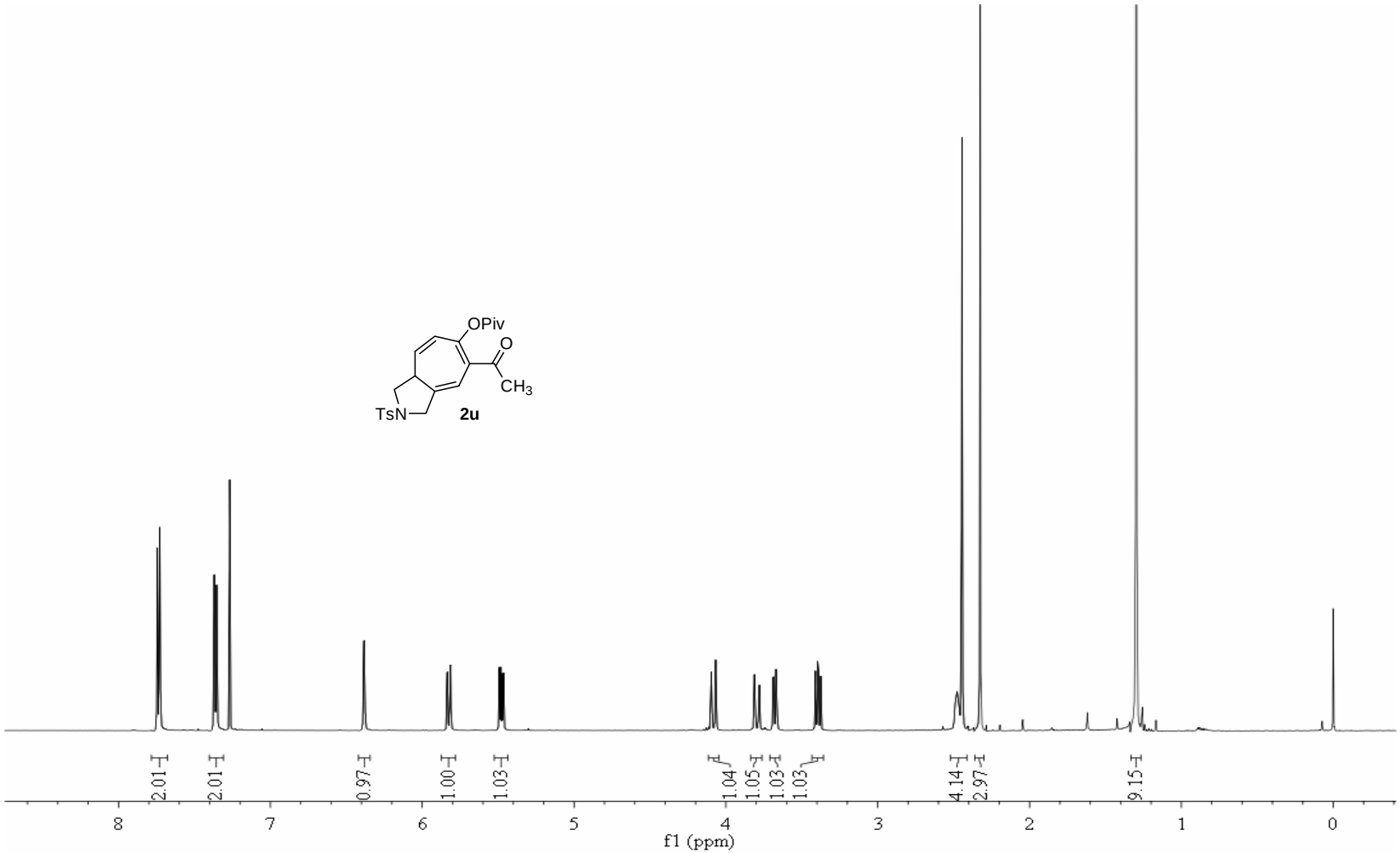

177.061
170.032
129.956
129.231
78.686
77.549
77.232
76.914
76.199
71.948
64.244
57.041
53.074
47.428
38.985
35.059
27.207
23.135
OPiv
MeO2C
MeO2C
Br
1aa
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

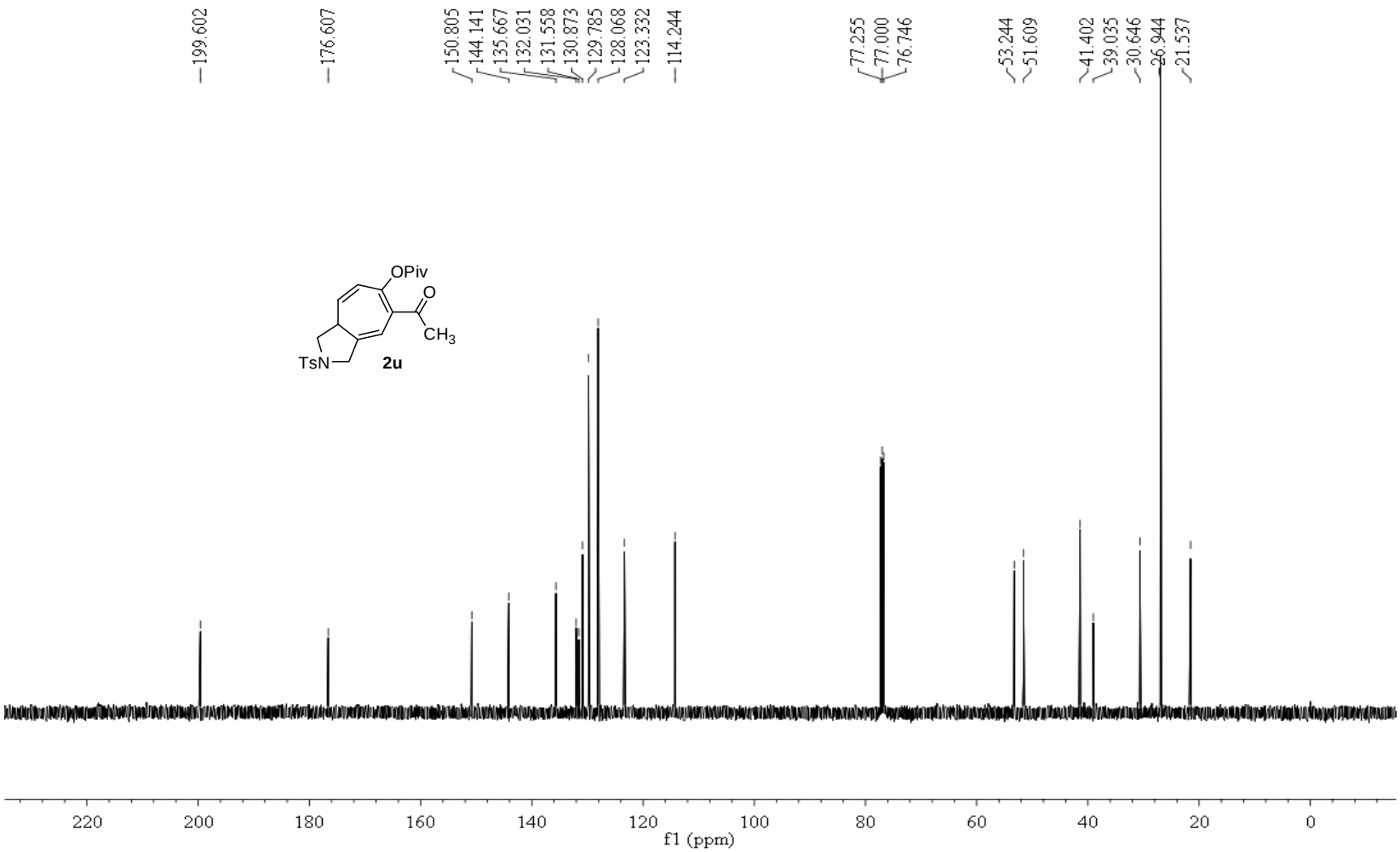

Ph
OPiv
TsN
Br
1ab
1.99
5.49
1.93
2.89
2.03
2.00
3.01
8.61
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

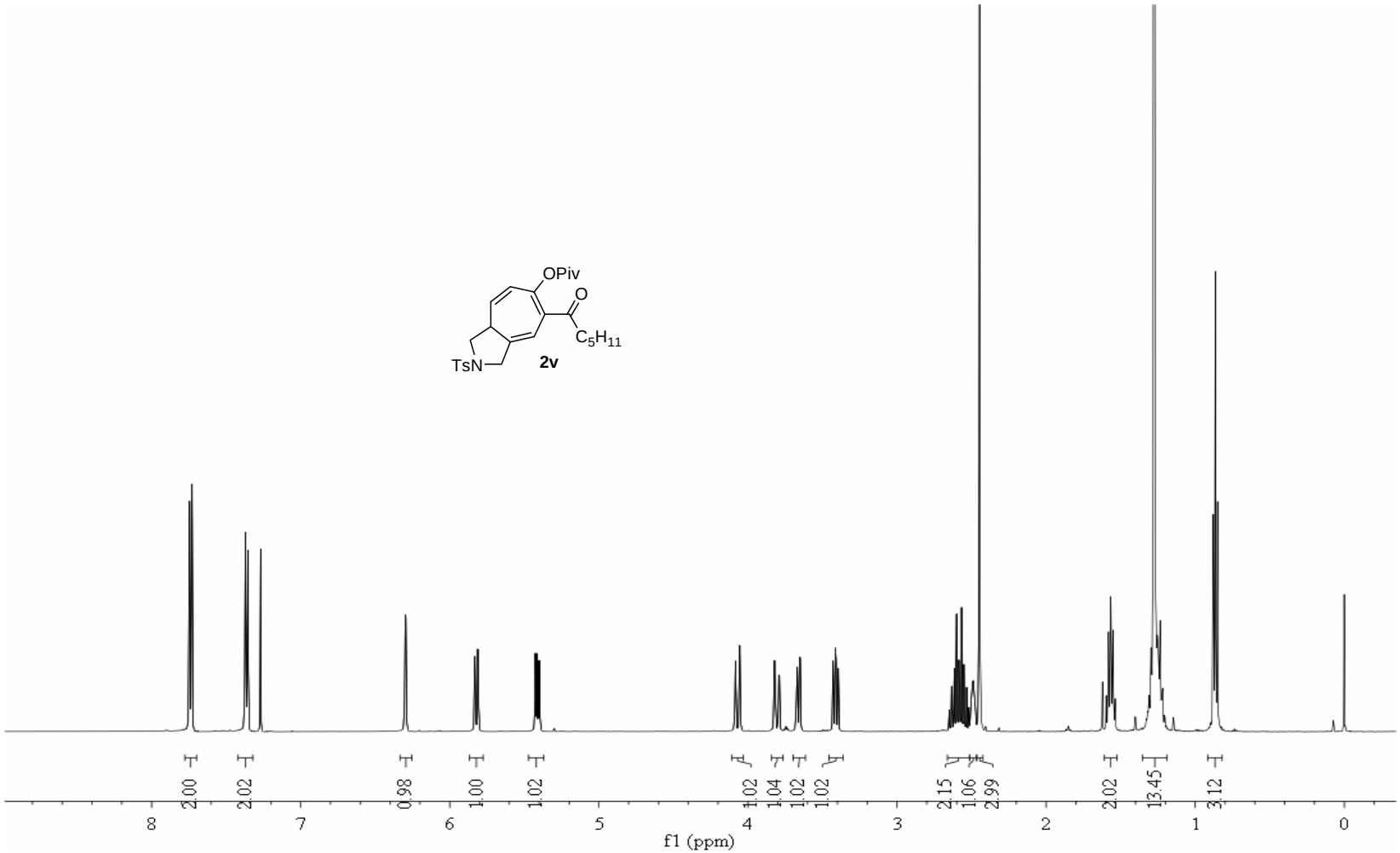

176.877
143.630
135.785
131.479
129.684
129.564
128.797
128.440
128.111
127.792
122.039
85.894
81.377
77.318
77.000
76.682
75.435
63.547
47.753
47.702
38.770
37.017
26.960
21.426
Ph
OPiv
TsN
Br
1ab
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

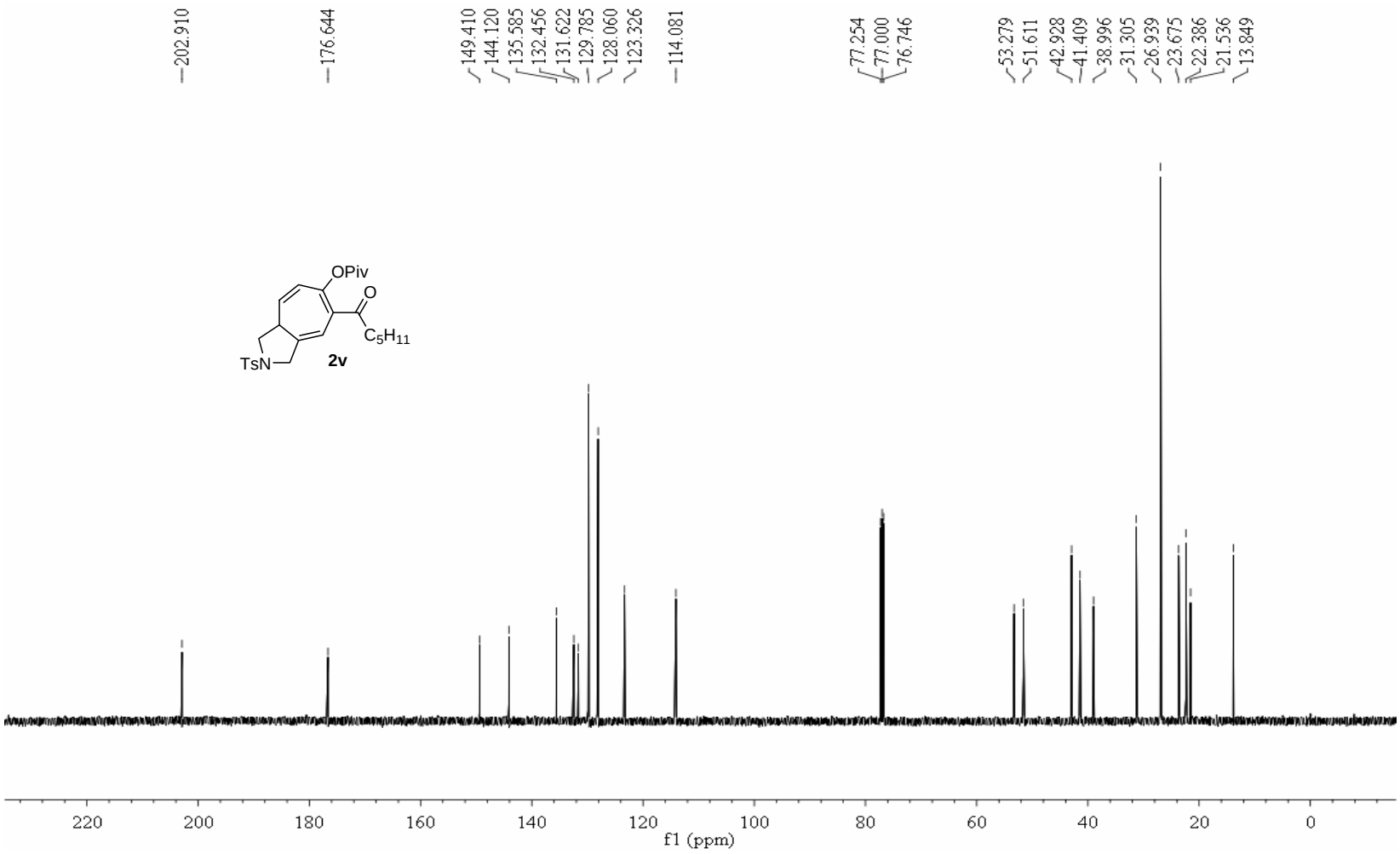

OPiv
CO2Et
TsN
2t
2.00
1.98
0.94
0.98
1.01
1.06
1.04
1.02
1.01
1.00
1.00
4.08
11.88
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

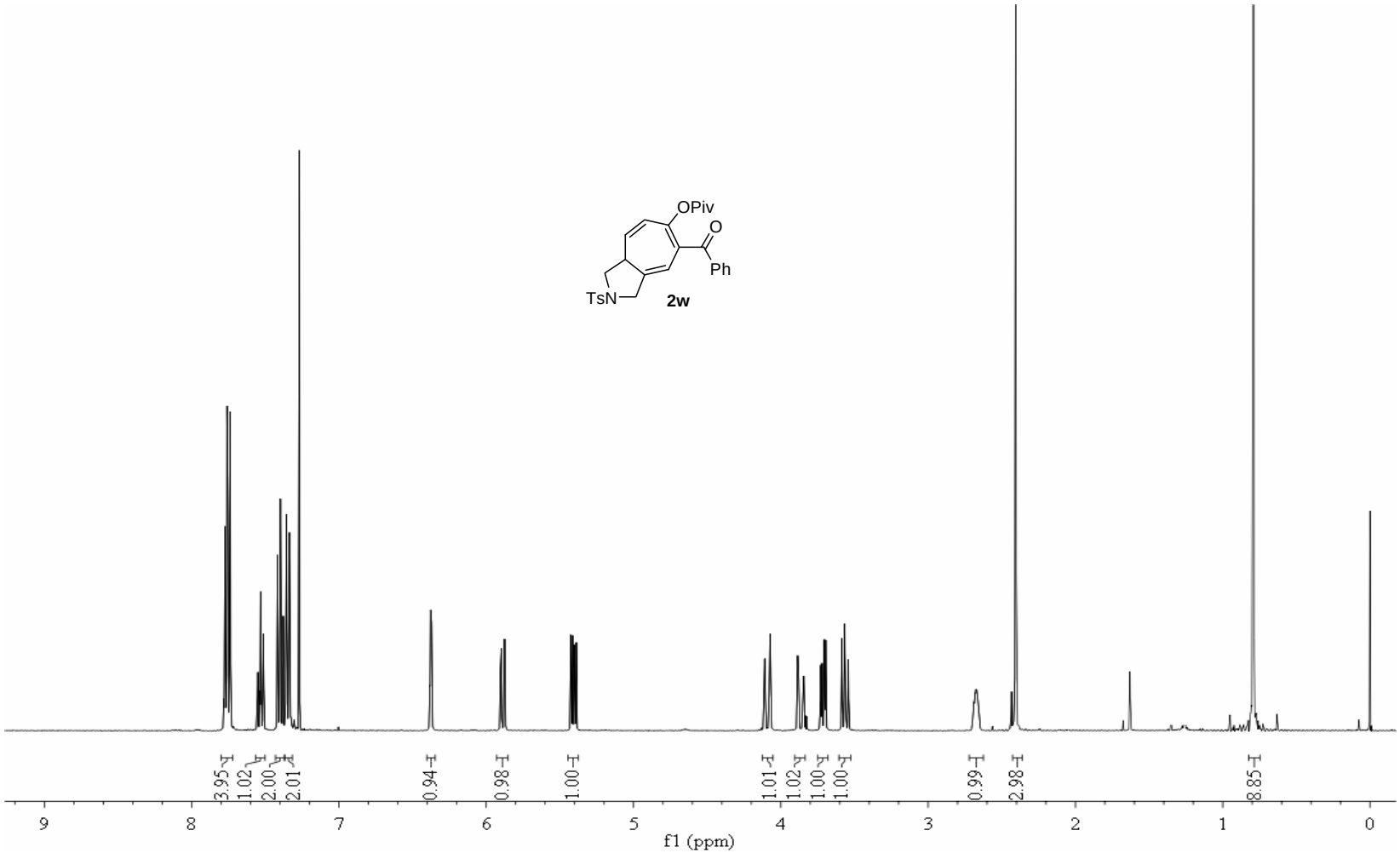

176.447
165.447
152.303
144.127
135.356
131.487
129.777
128.060
124.219
123.611
114.871
77.318
77.000
76.682
61.167
53.232
51.545
41.282
38.938
26.977
21.531
14.210
135.356
131.567
131.487
129.777
128.060
124.219
123.611
137
133
129
125
f1 (ppm)
OPiv
CO2Et
TsN
2t
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

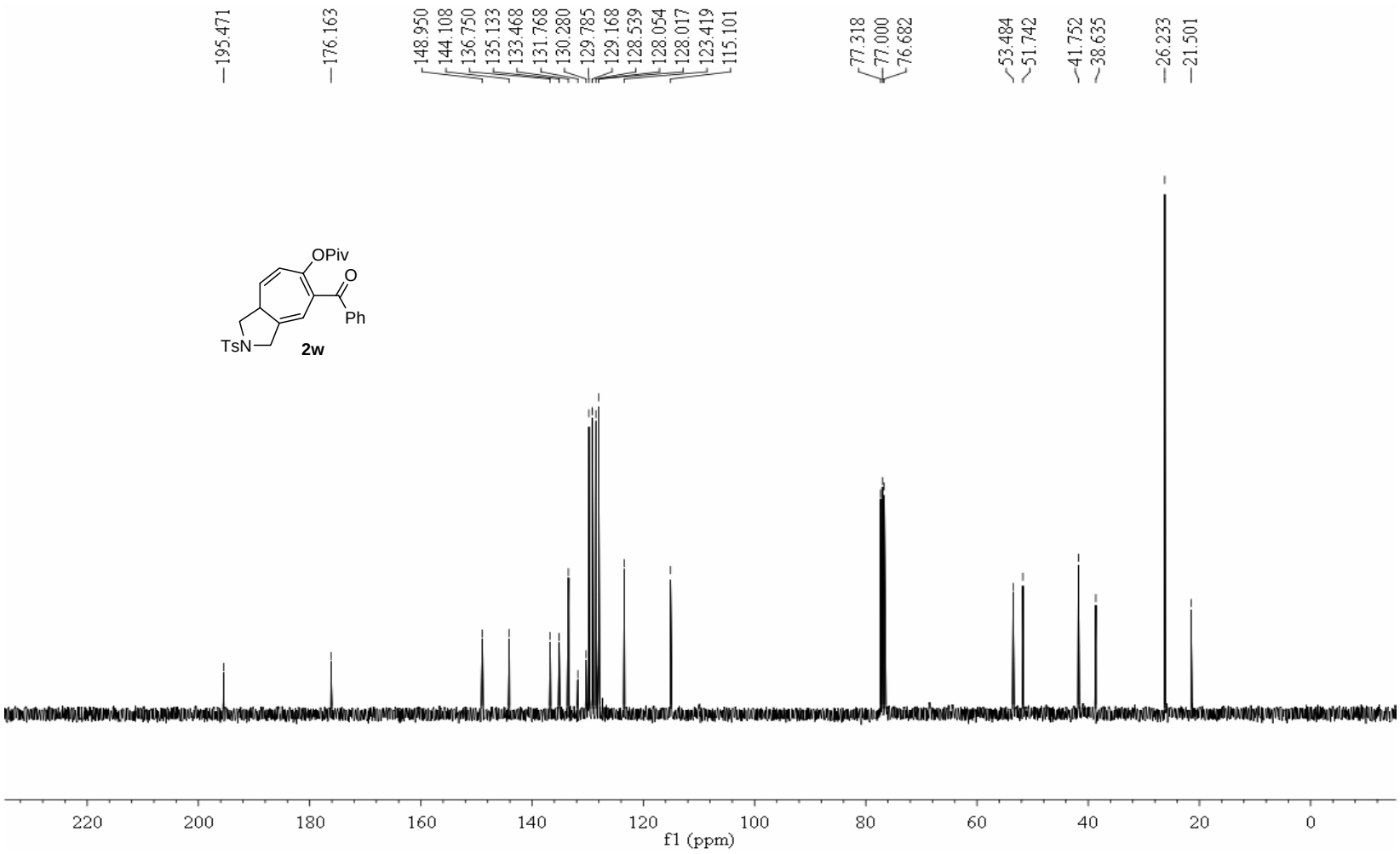

OPiv
O
CH3
TsN
2u
2.01
2.01
0.97
1.00
1.03
1.04
1.05
1.03
1.03
4.14
2.97
9.15
8
7
6
5
4
3
2
1
0
f1 (ppm)

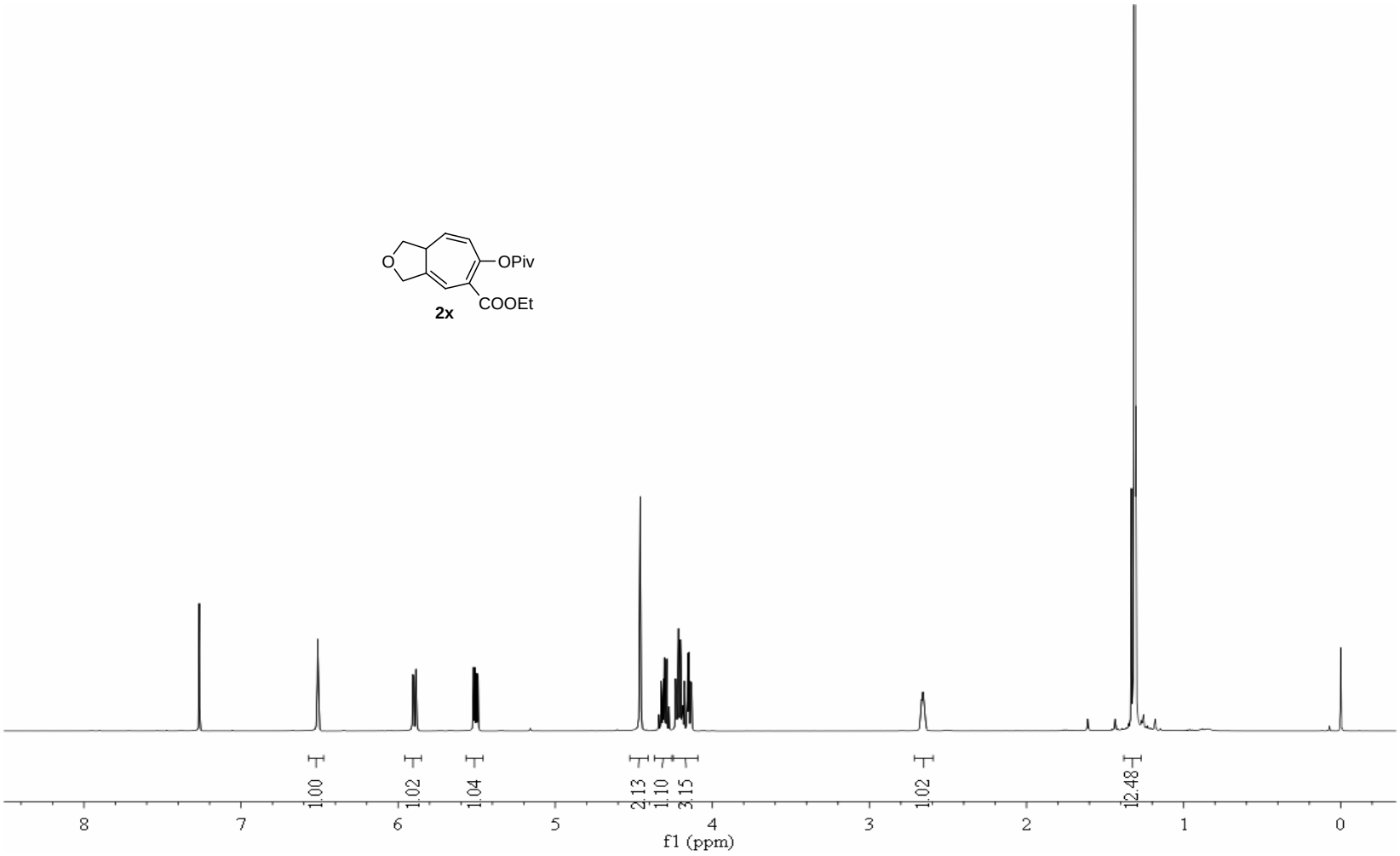

199.602
176.607
150.805
144.141
135.667
132.031
131.558
130.873
129.785
128.068
123.332
114.244
77.255
77.000
76.746
53.244
51.609
41.402
39.035
30.646
26.944
21.537
OPiv
O
CH3
TsN
2u
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

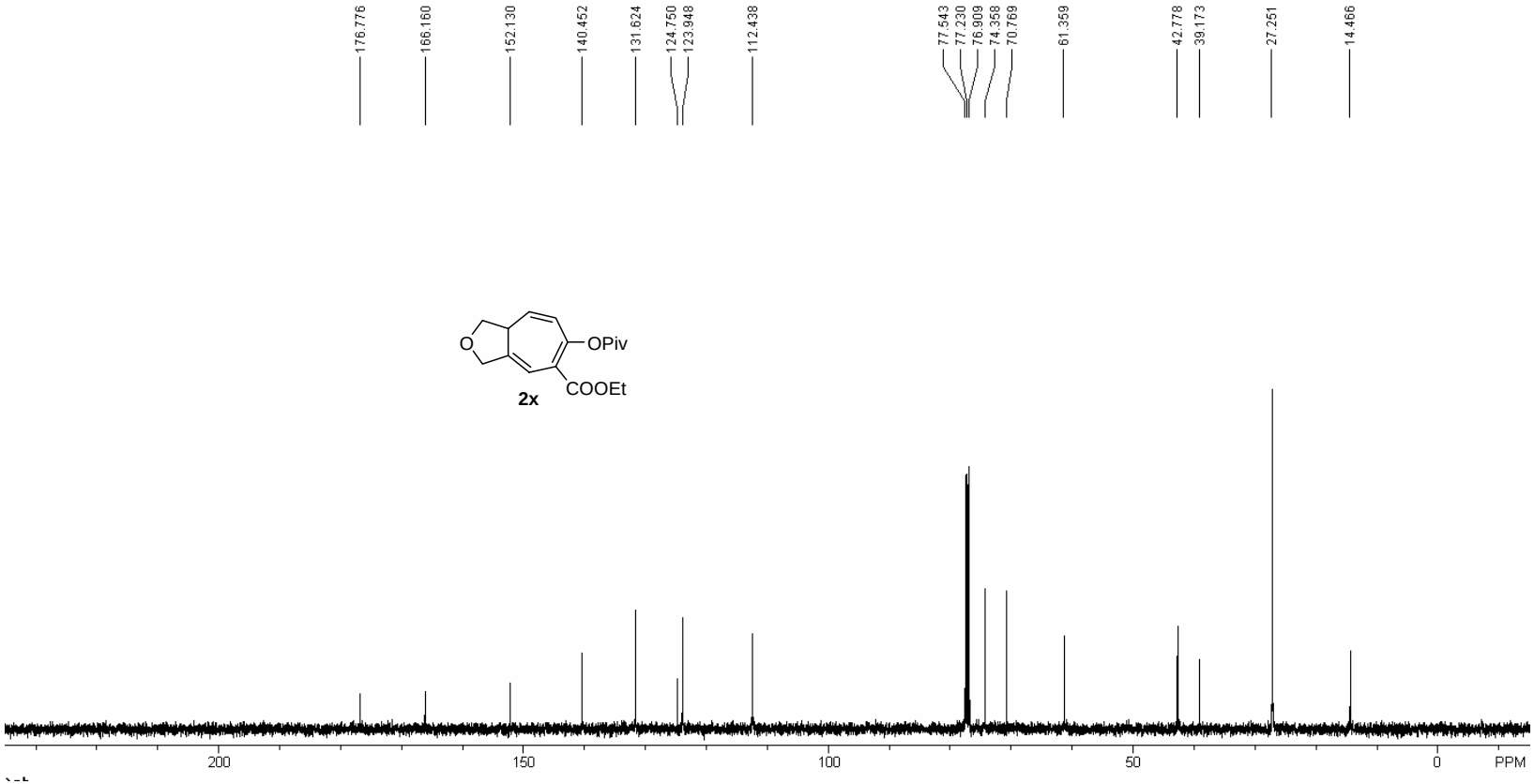

OPiv
O
C_5H_{11}
TsN
2v
2.00
2.02
0.98
1.00
1.02
1.02
1.04
1.02
1.02
2.15
1.06
2.99
2.02
13.45
3.12
8
7
6
5
4
3
2
1
0
f1 (ppm)

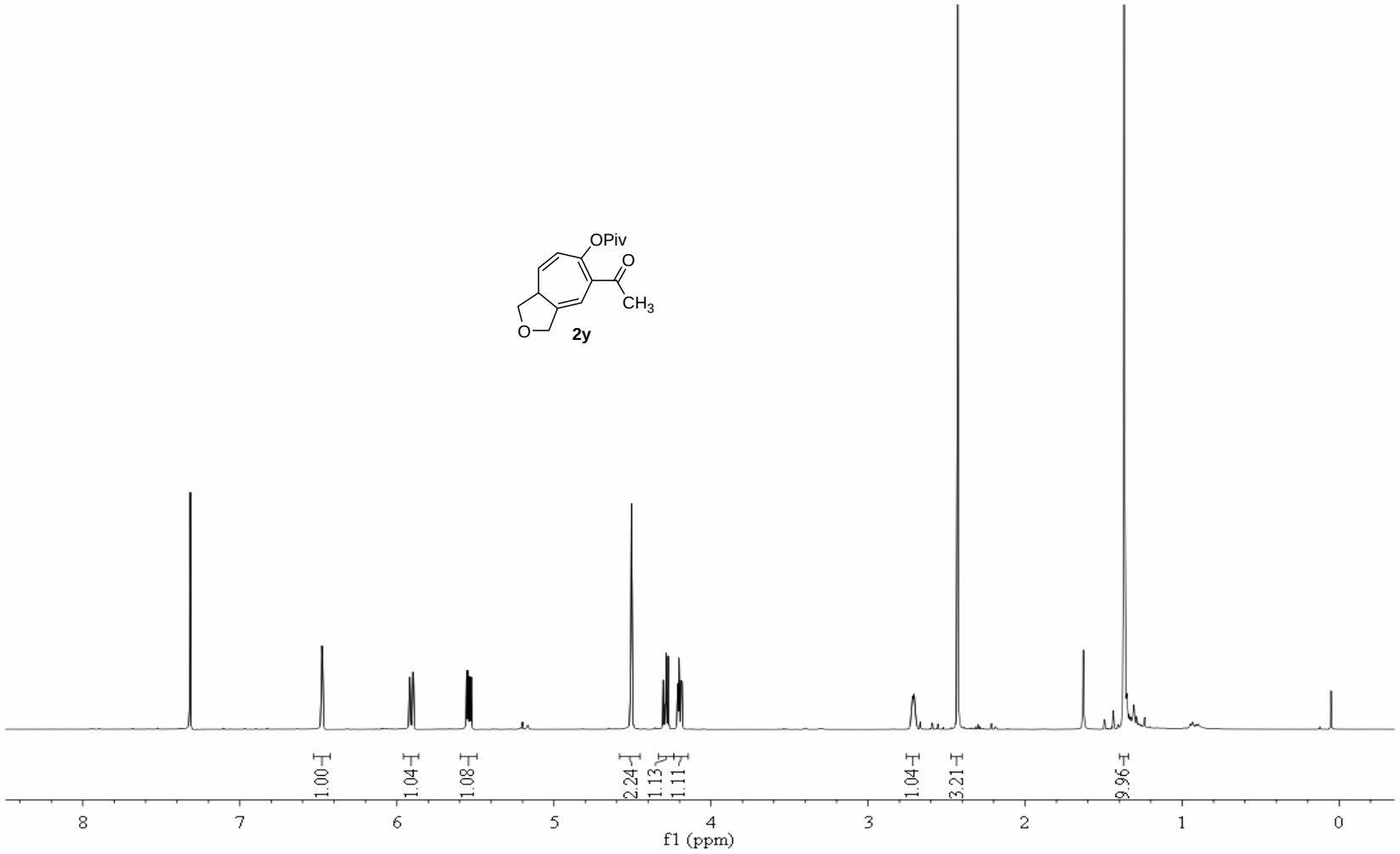

202.910
176.644
149.410
144.120
135.585
132.456
131.622
129.785
128.060
123.326
114.081
77.254
77.000
76.746
53.279
51.611
42.928
41.409
38.996
31.305
26.939
23.675
22.386
21.536
13.849
OPiv
O
C5H11
TsN
2v
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

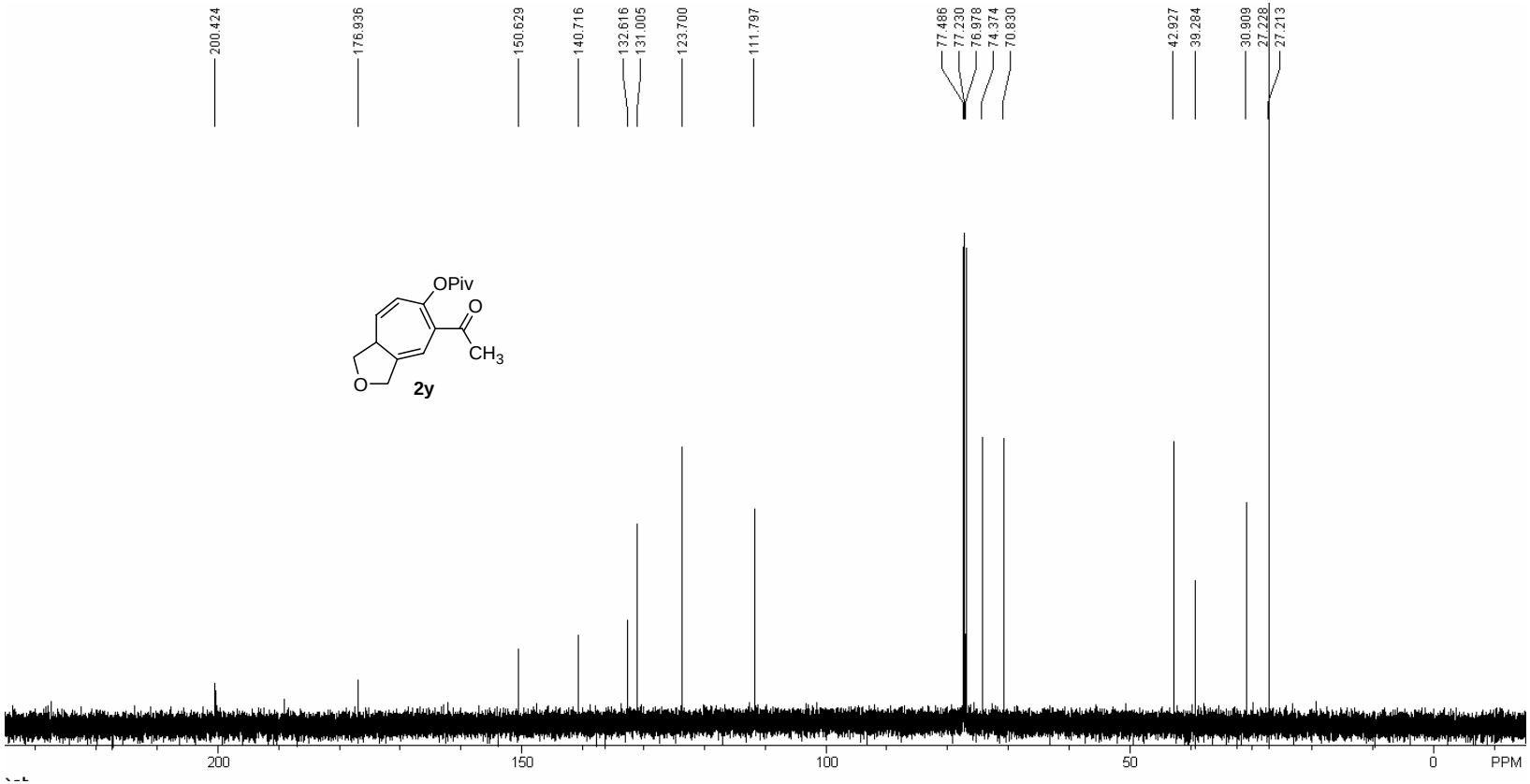

OPiv
O
Ph
TsN
2w
3.95
1.02
2.00
2.01
0.94
0.98
1.00
1.01
1.02
1.00
1.00
0.99
2.98
8.85
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

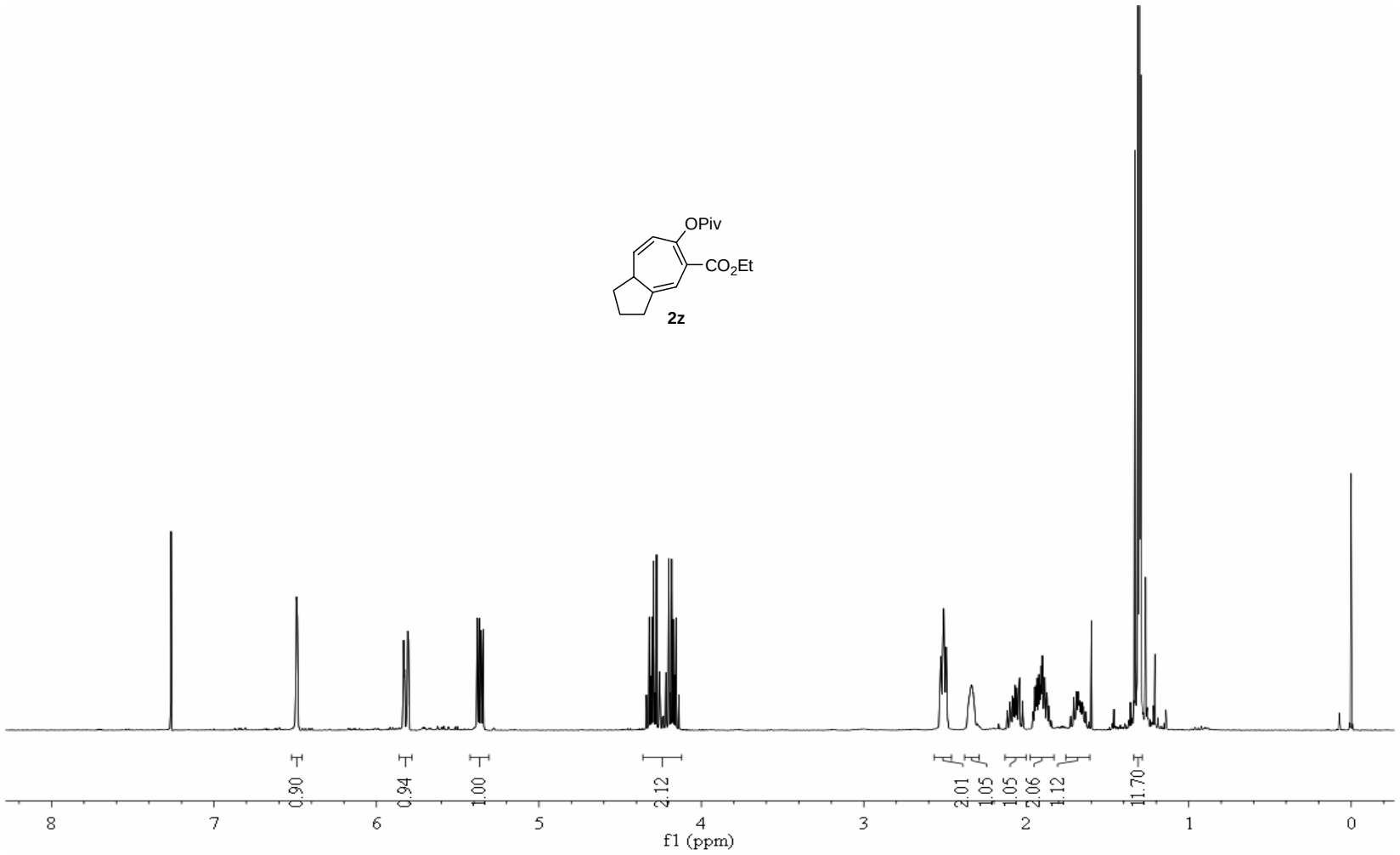

195.471
176.163
148.950
144.108
136.750
135.133
133.468
131.768
130.280
129.785
129.168
128.539
128.054
128.017
123.419
115.101
77.318
77.000
76.682
53.484
51.742
41.752
38.635
26.233
21.501
OPiv
O
Ph
TsN
2w
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

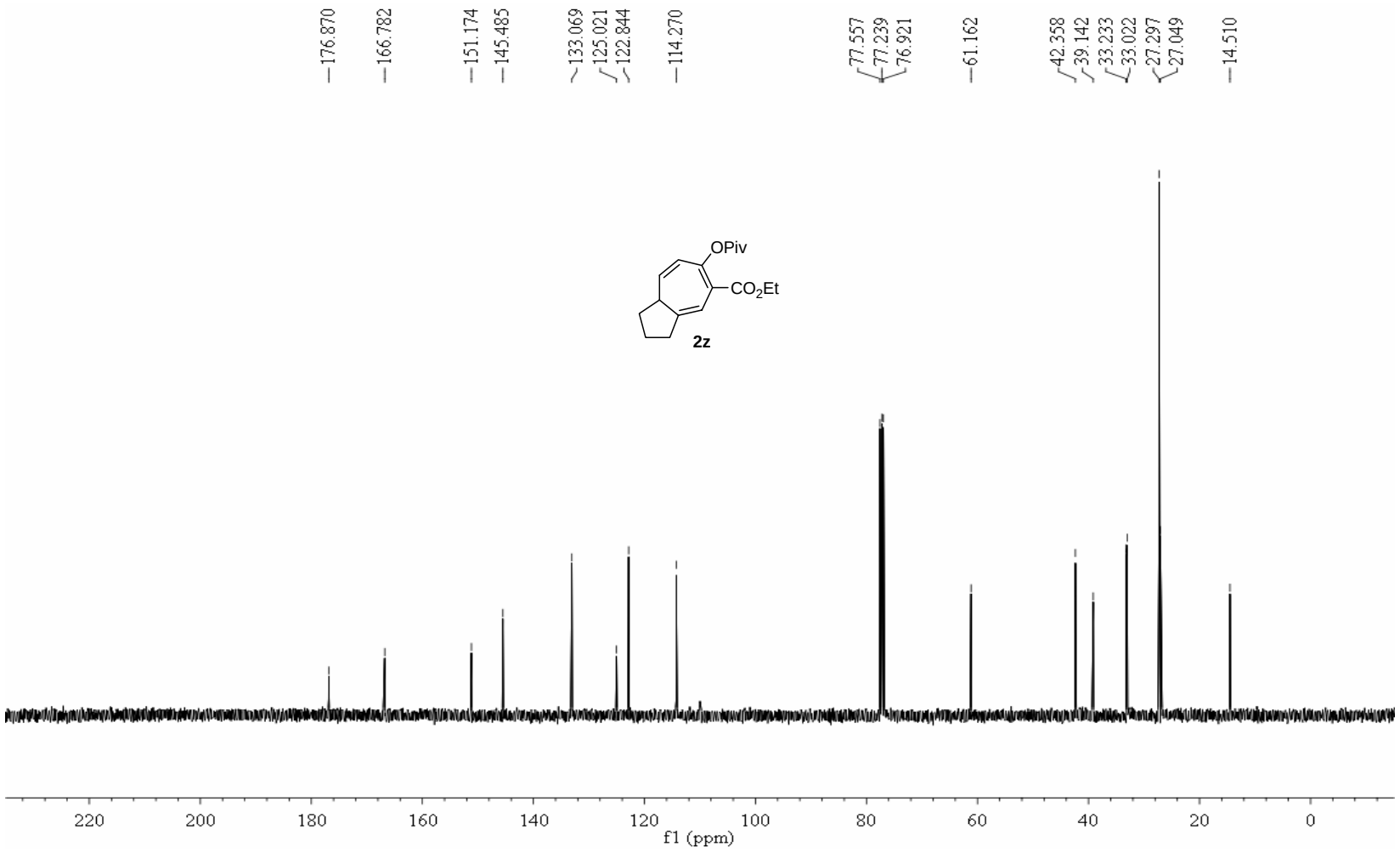

O
OPiv
COOEt
2x
1.00
1.02
1.04
2.13
1.10
3.15
1.02
12.48
8
7
6
5
4
3
2
1
0
f1 (ppm)

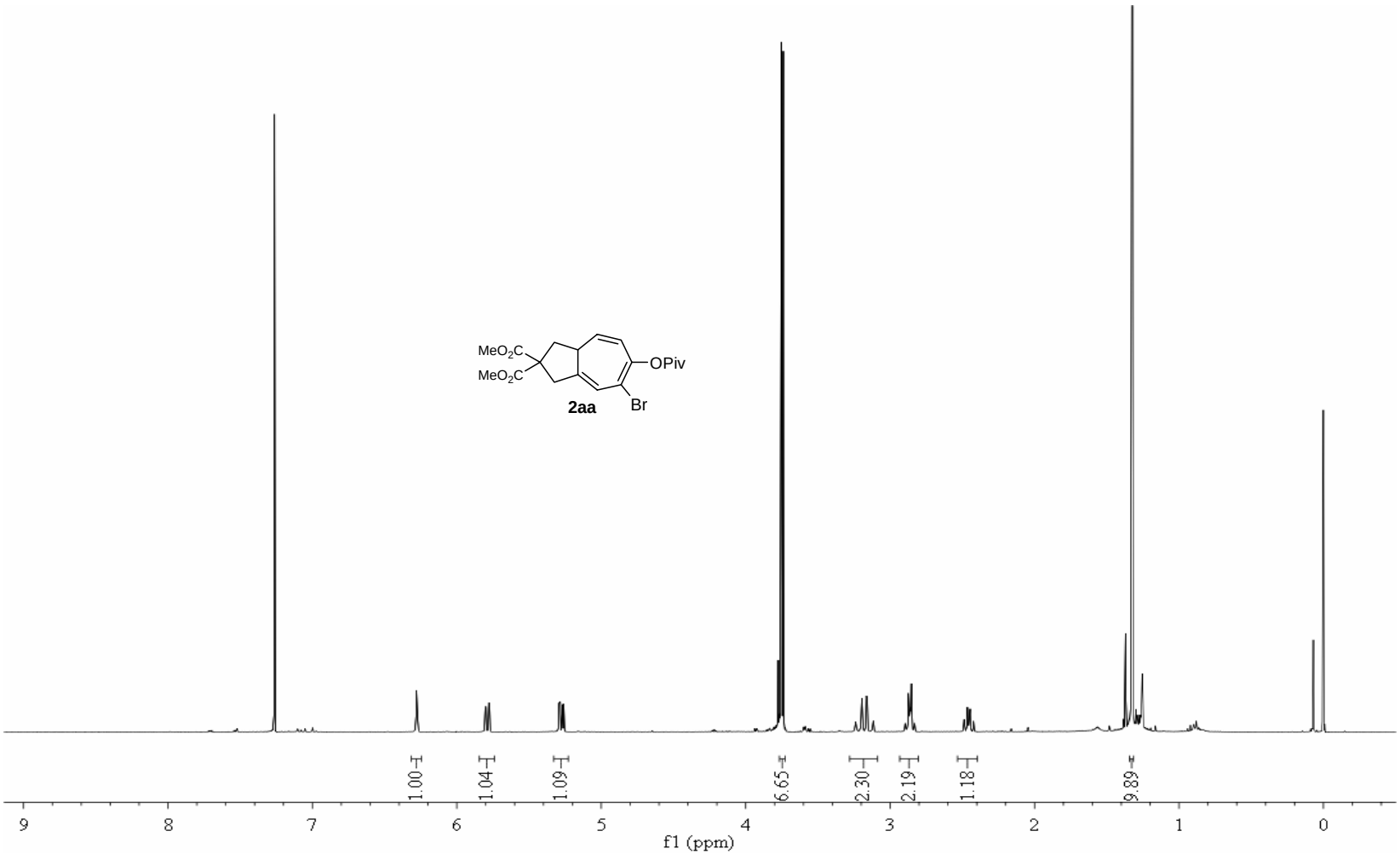

176.776
166.160
152.130
140.452
131.624
124.750
123.948
112.438
77.543
77.230
76.909
74.358
70.769
61.359
42.778
39.173
27.251
14.466
O
OPiv
COOEt
2x
200
150
100
50
0
PPM

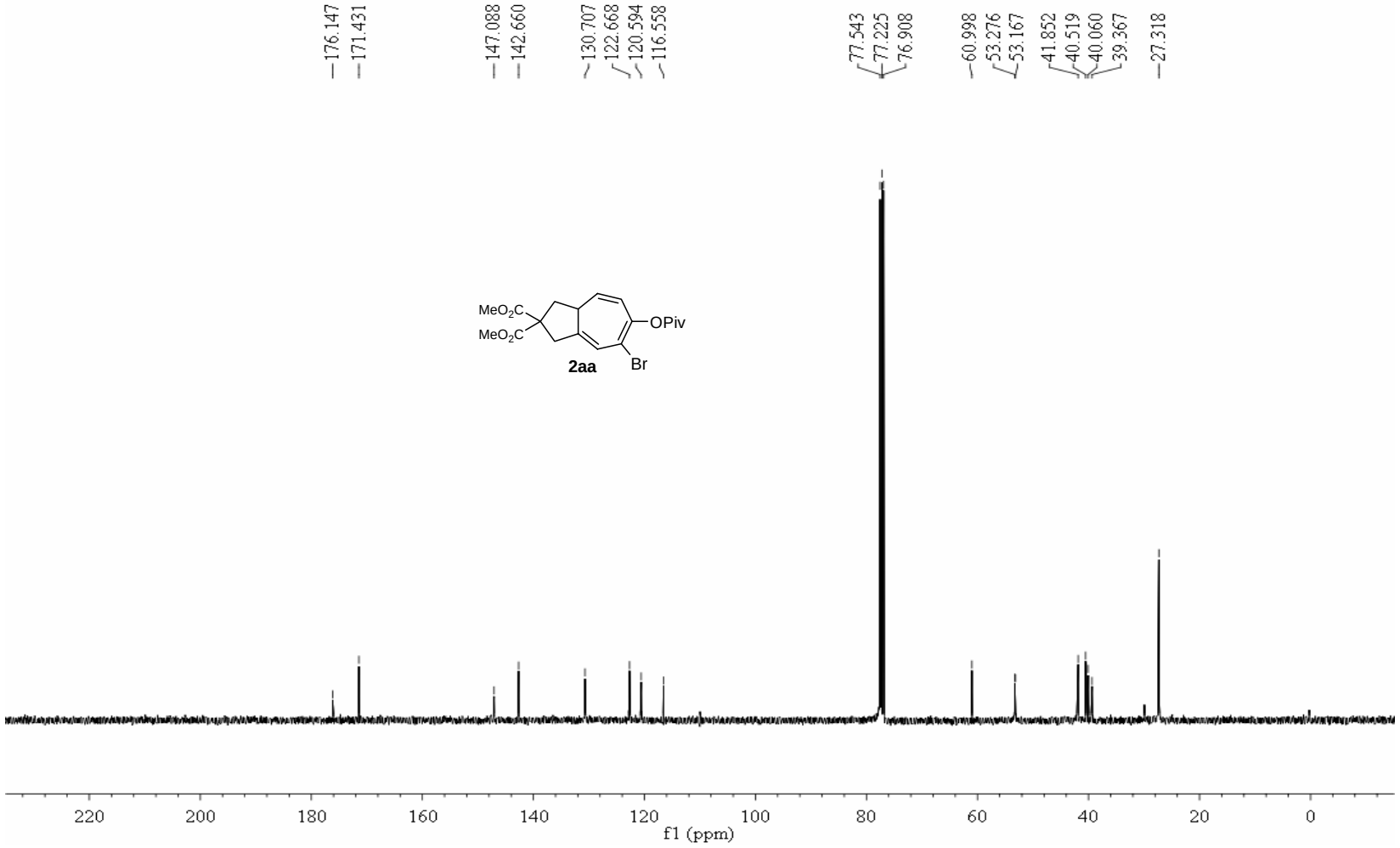

OPiv
O
CH3
O
2y
1.00
1.04
1.08
2.24
1.13
1.11
1.04
3.21
9.96
8
7
6
5
4
3
2
1
0
f1 (ppm)

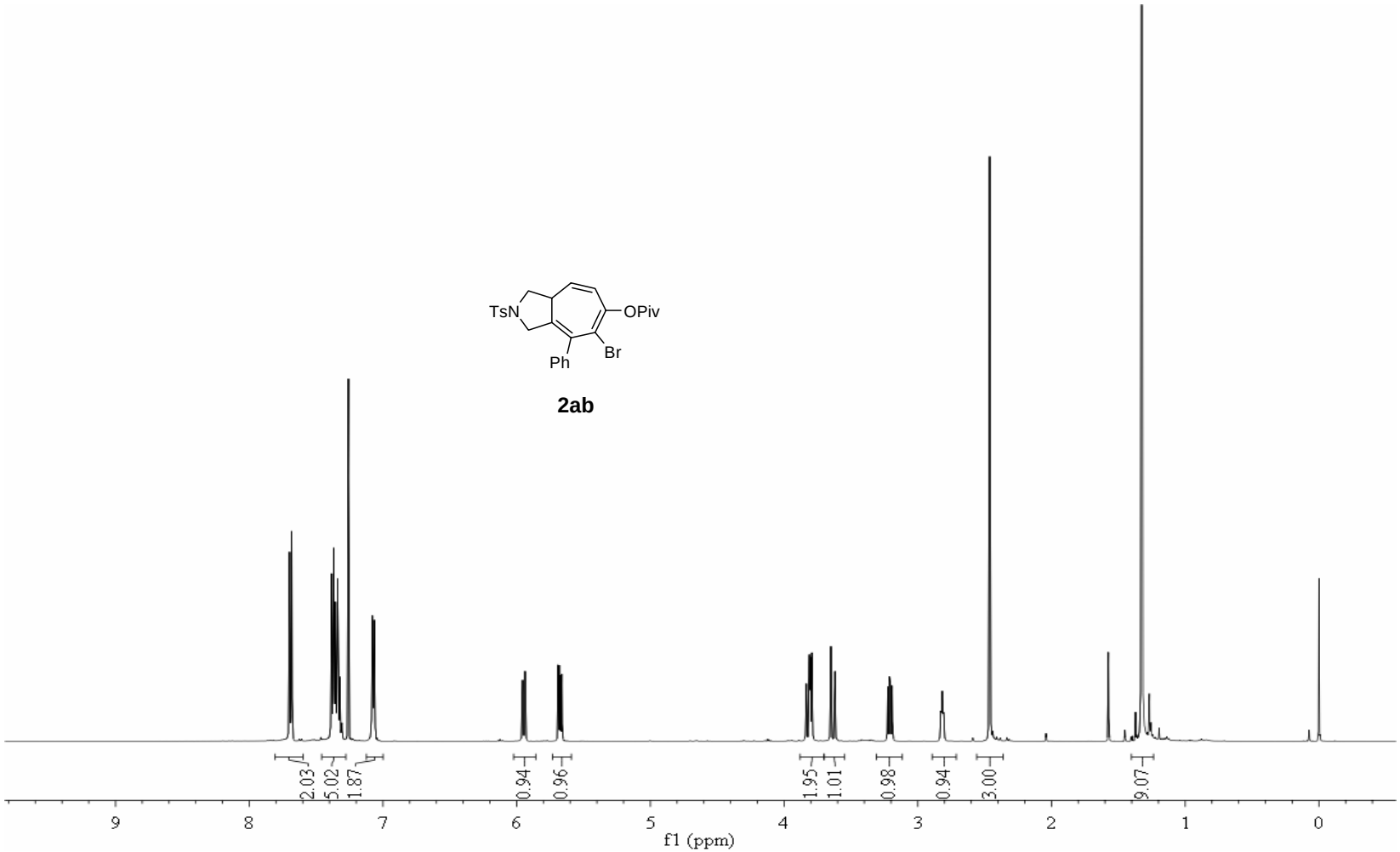

200.424
176.936
150.629
140.716
132.616
131.005
123.700
111.797
77.486
77.230
76.978
74.374
70.830
42.927
39.284
30.909
27.228
27.213
OPiv
O
CH3
O
2y
200
150
100
50
0
PPM

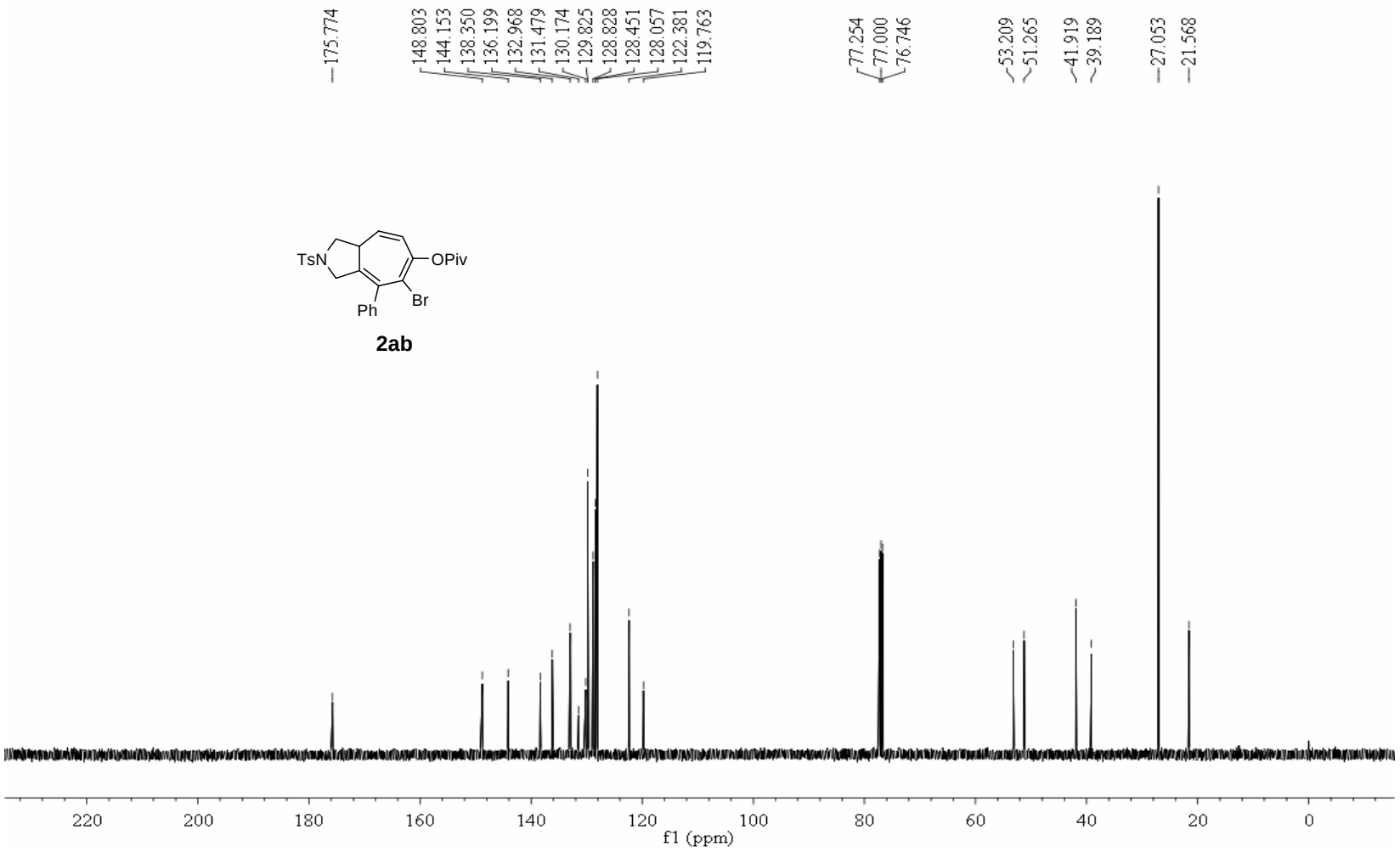

OPiv
CO2Et
2z
0.90
0.94
1.00
2.12
2.01
1.05
1.05
2.06
1.12
11.70
8
7
6
5
4
3
2
1
0
f1 (ppm)

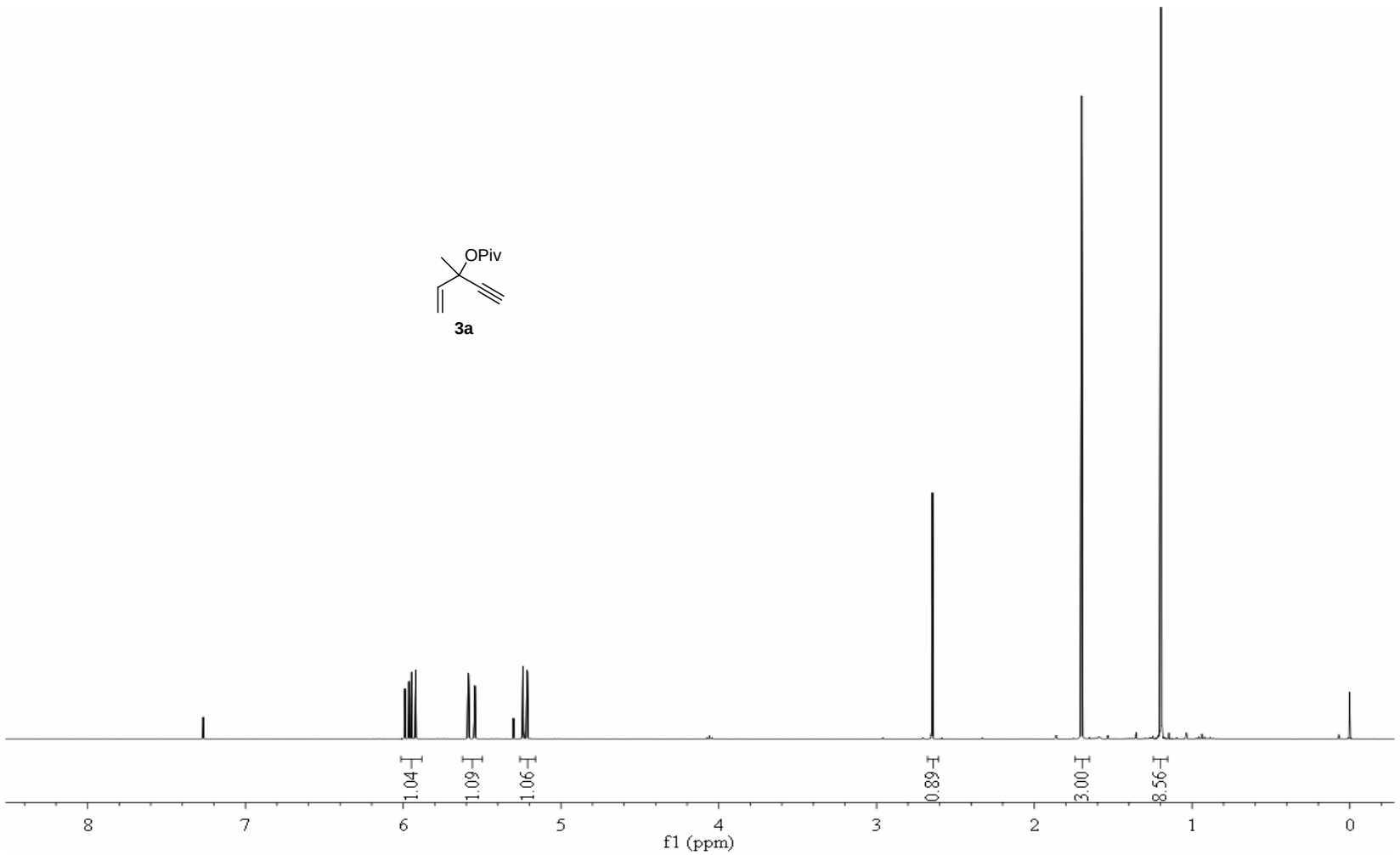

176.870
166.782
151.174
145.485
133.069
125.021
122.844
114.270
77.557
77.239
76.921
61.162
42.358
39.142
33.233
33.022
27.297
27.049
14.510
OPiv
CO2Et
2z
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

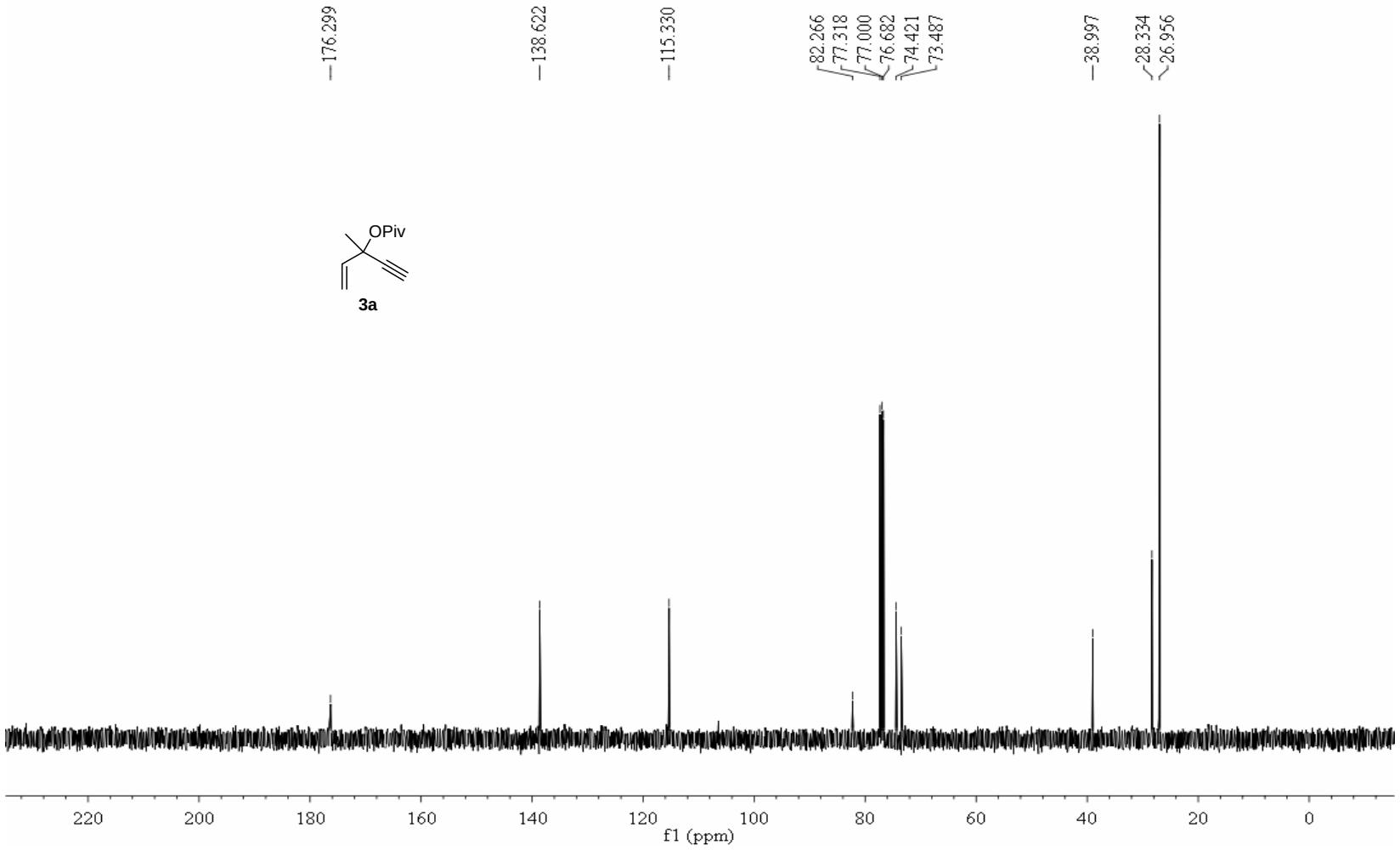

MeO2C
MeO2C
OPiv
Br
2aa
1.00
1.04
1.09
6.65
2.30
2.19
1.18
9.89
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


176.147
171.431
147.088
142.660
130.707
122.668
120.594
116.558
77.543
77.225
76.908
60.998
53.276
53.167
41.852
40.519
40.060
39.367
27.318
MeO2C
MeO2C
OPiv
Br
2aa
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


TsN
OPiv
Br
Ph
2ab
2.03
5.02
1.87
0.94
0.96
1.95
1.01
0.98
0.94
3.00
9.07
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


175.774
148.803
144.153
138.350
136.199
132.968
131.479
130.174
129.825
128.828
128.451
128.057
122.381
119.763
77.254
77.000
76.746
53.209
51.265
41.919
39.189
27.053
21.568
TsN
OPiv
Ph
Br
2ab
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


OPiv
3a
1.04
1.09
1.06
0.89
3.00
8.56
8
7
6
5
4
3
2
1
0
f1 (ppm)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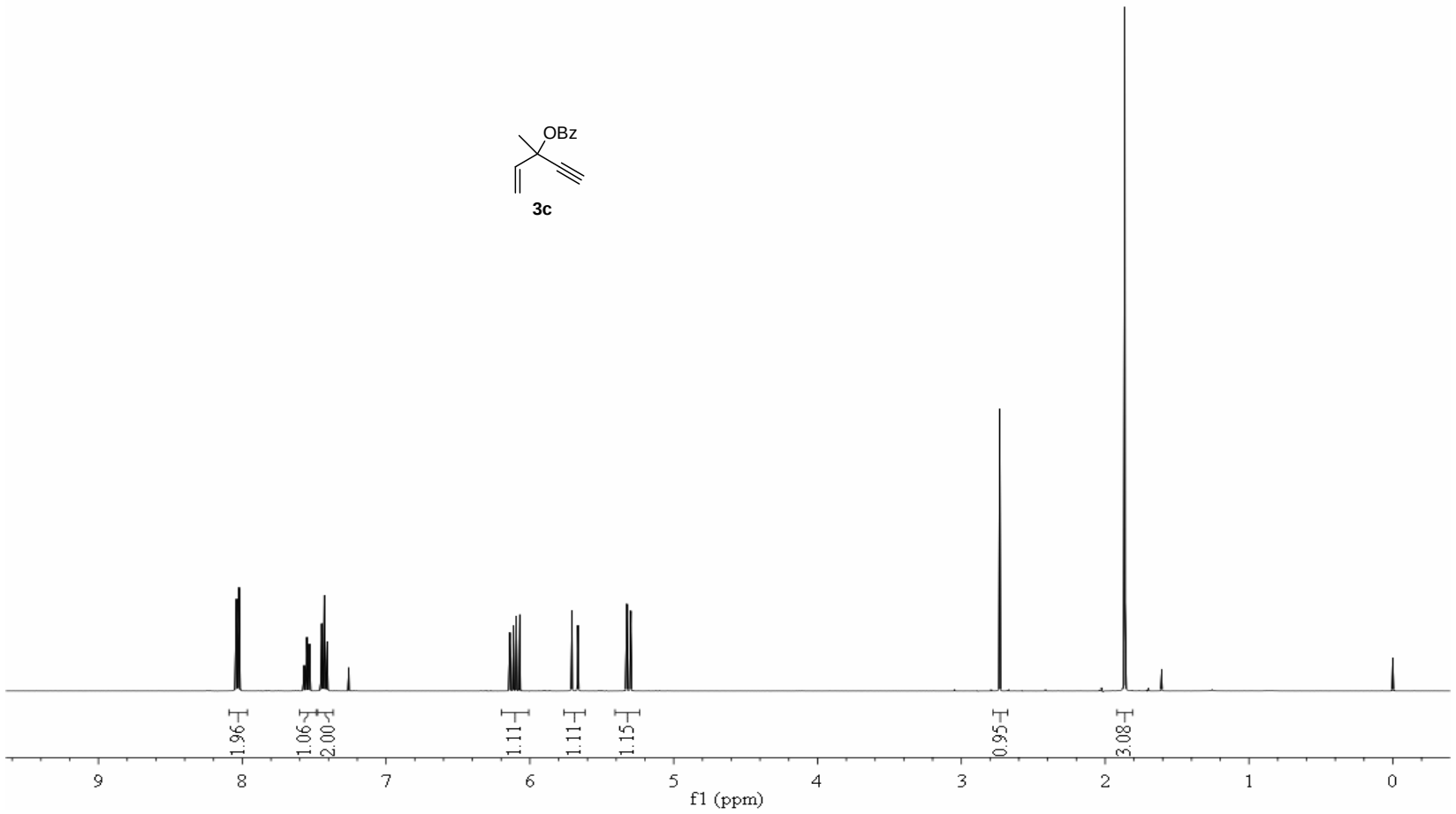
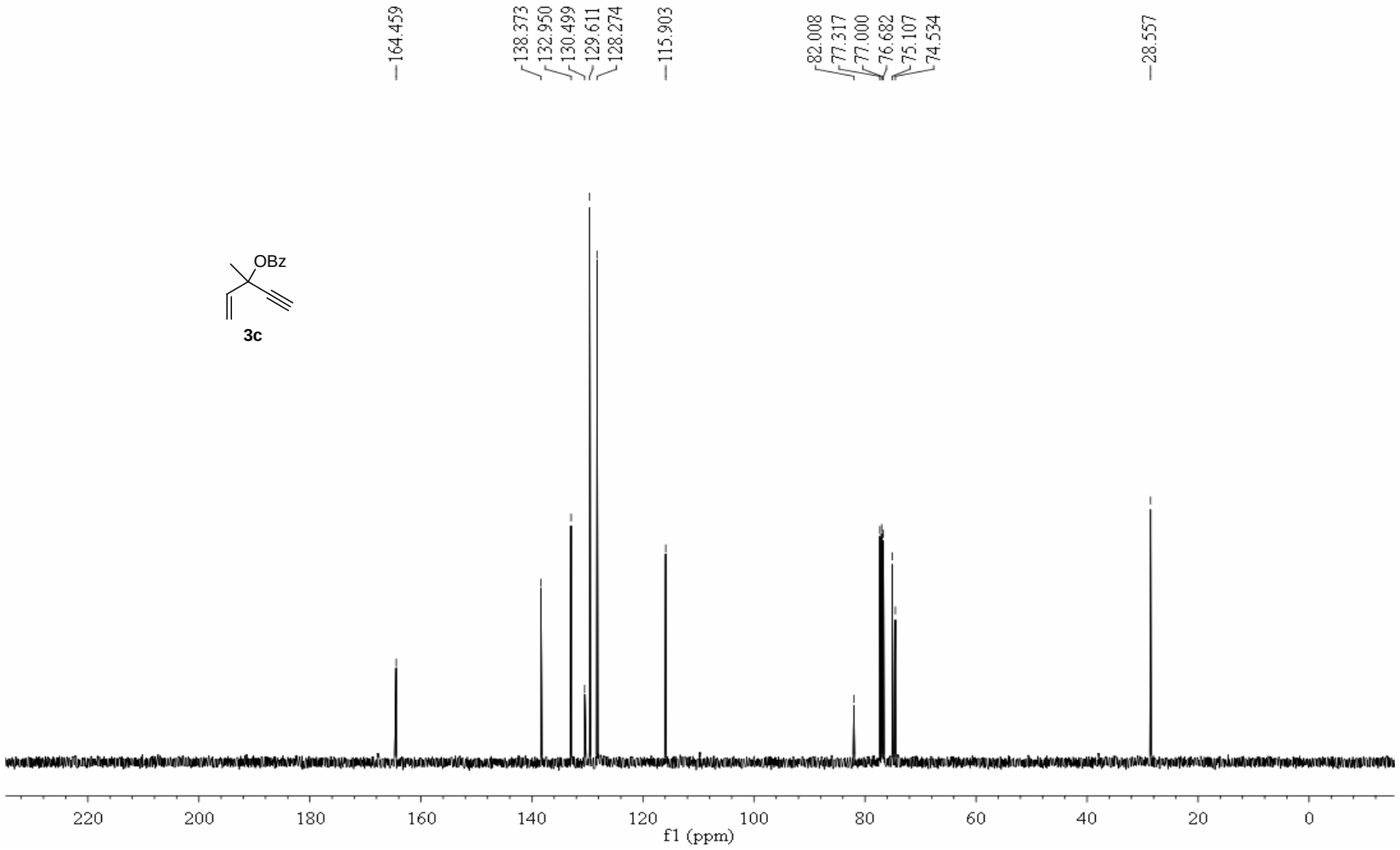
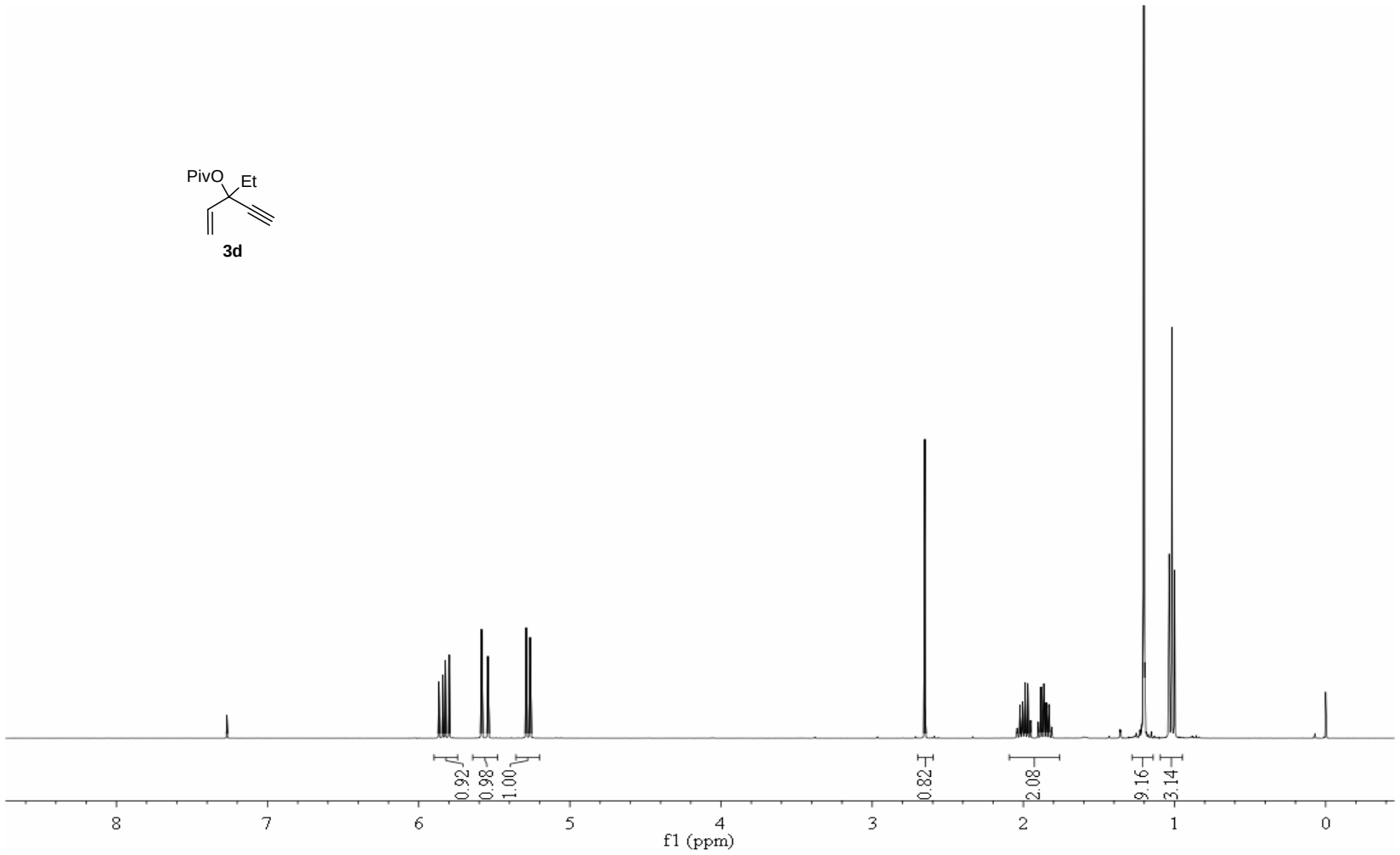
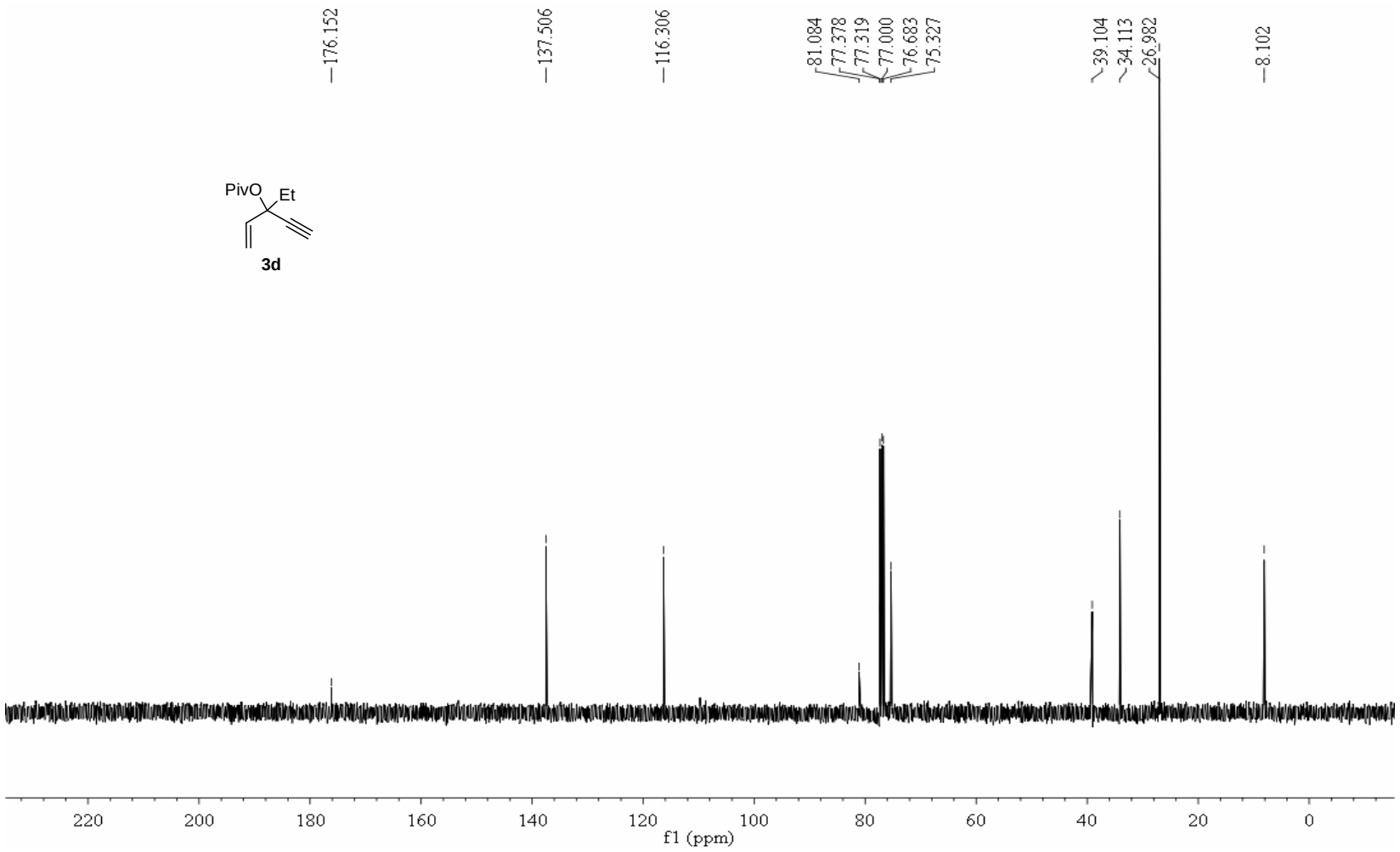
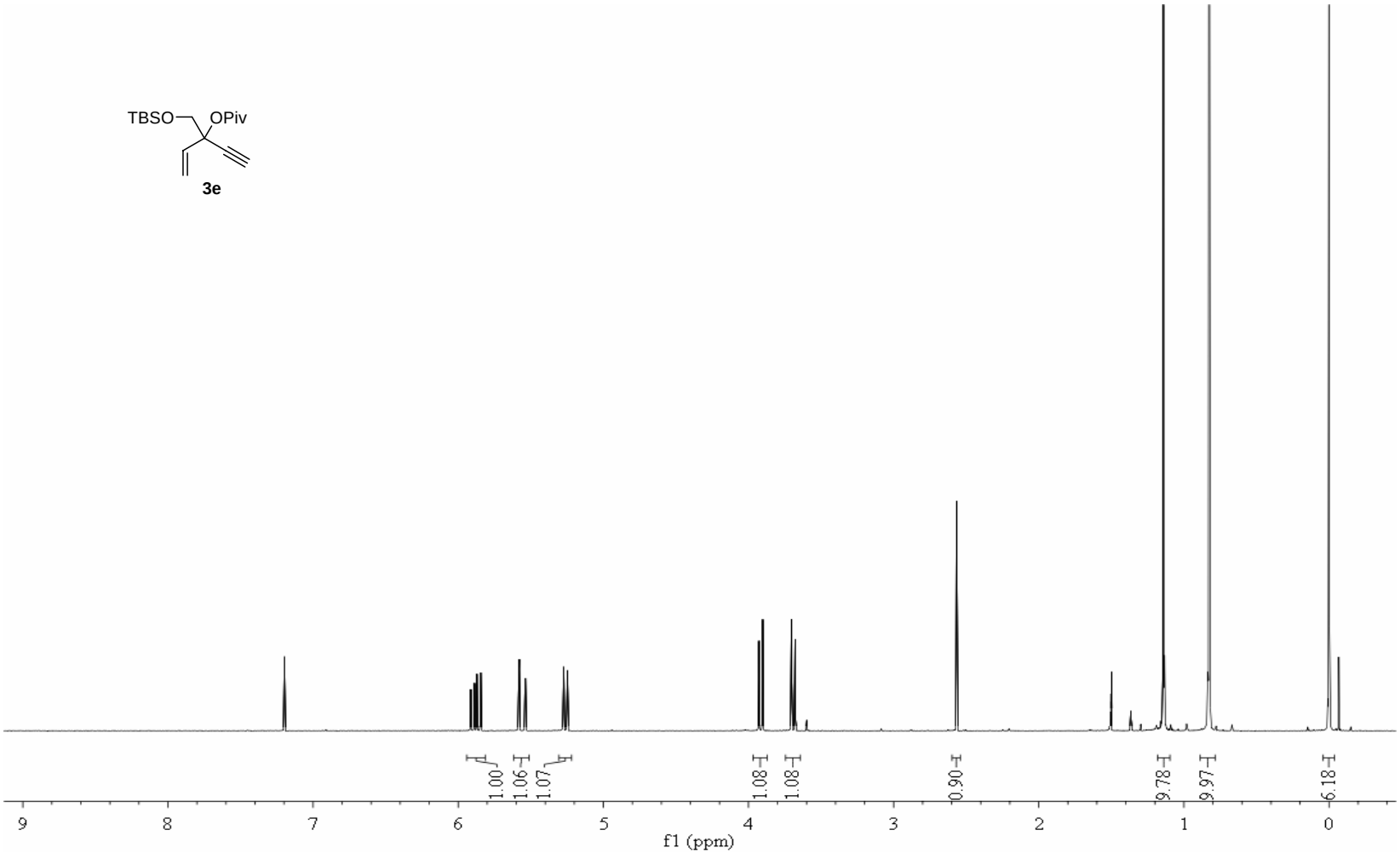
138.622
115.330
82.266
77.318
77.000
76.682
74.421
73.487
38.997
28.334
26.956
OPiv
3a
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

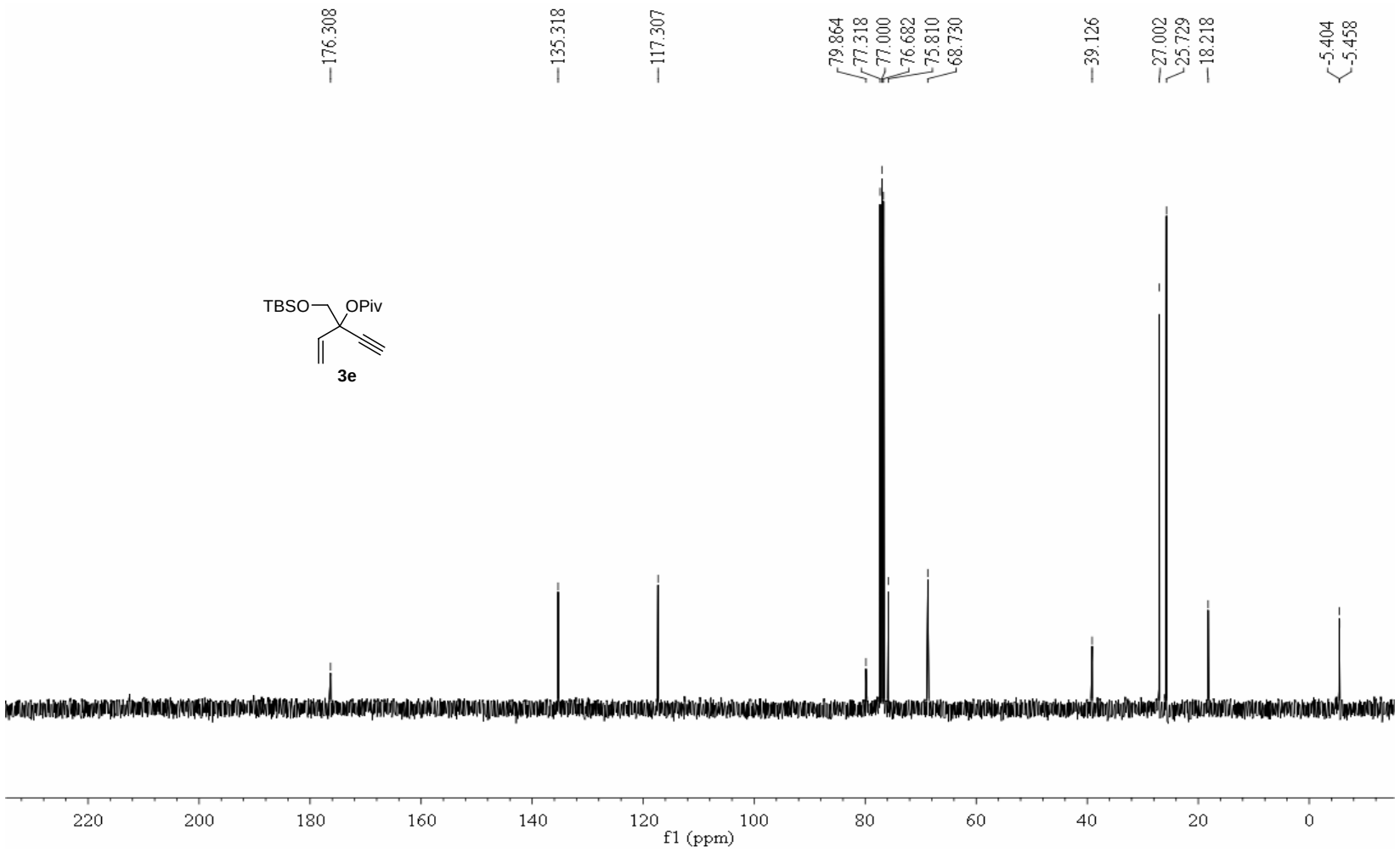

OBz
3c
1.96
1.06
2.00
1.11
1.11
1.15
0.95
3.08
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

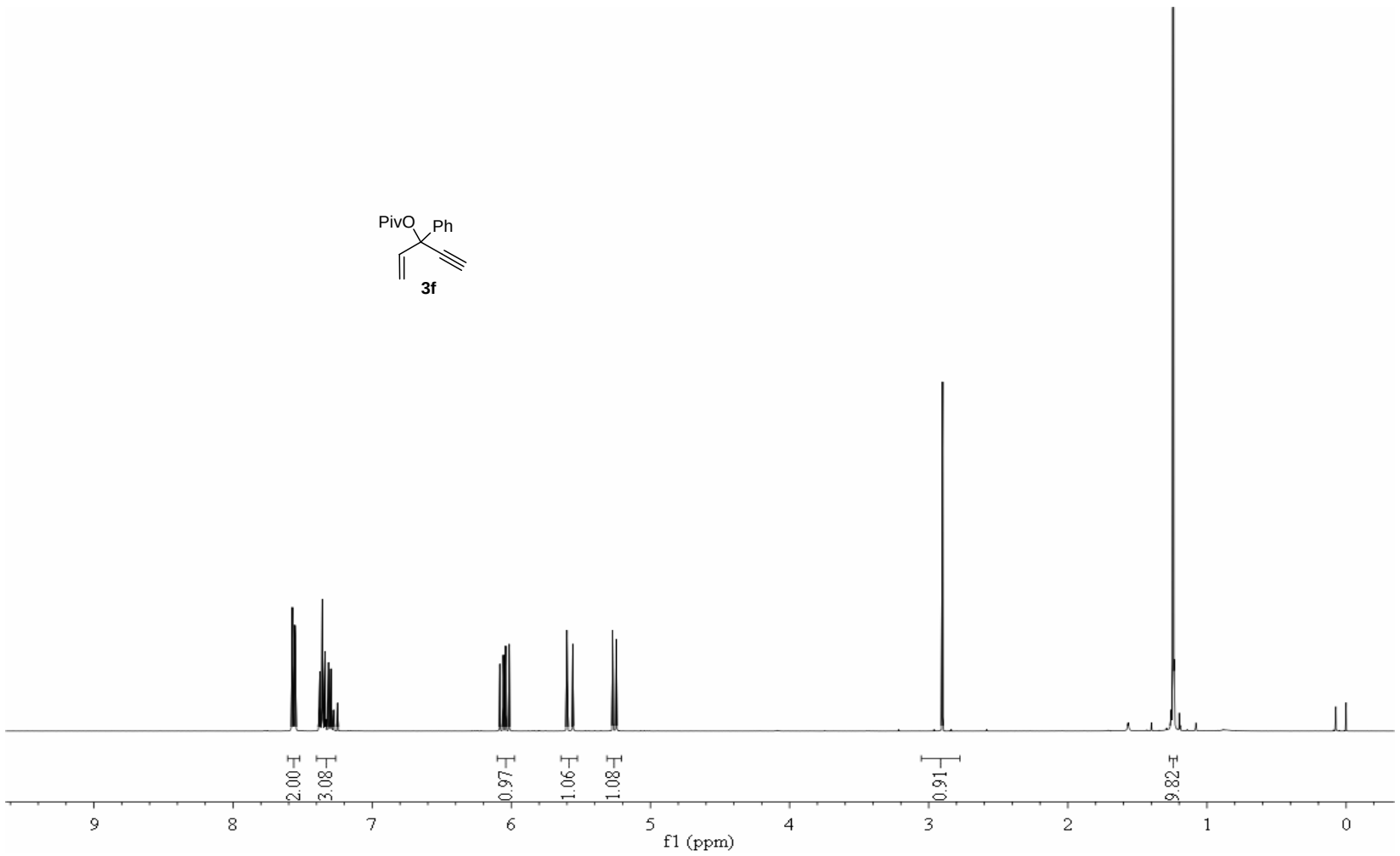

164.459
138.373
132.950
130.499
129.611
128.274
115.903
82.008
77.317
77.000
76.682
75.107
74.534
28.557
OBz
3c
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

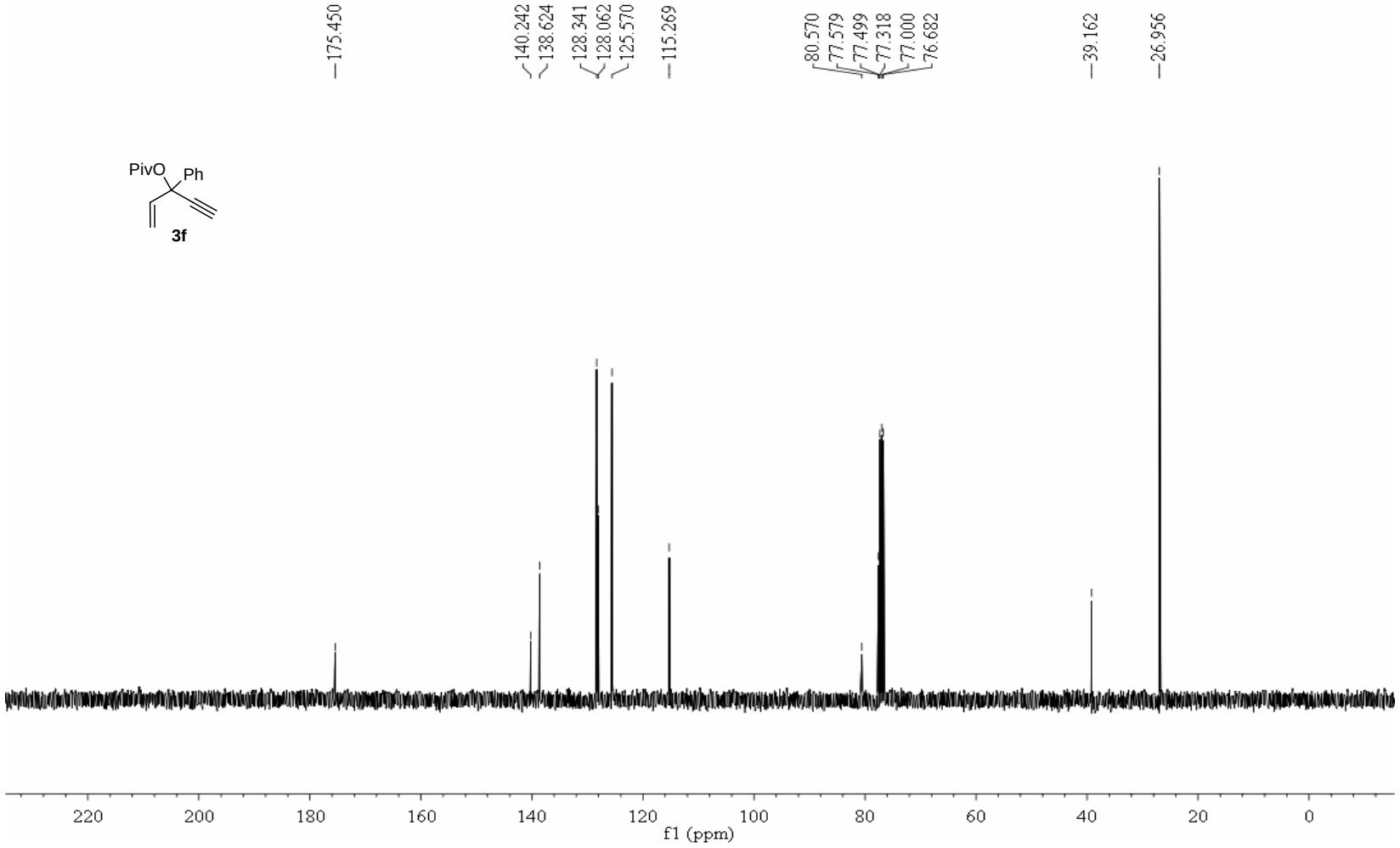

PivO
Et
3d
0.92
0.98
1.00
0.82
2.08
9.16
3.14
8
7
6
5
4
3
2
1
0
f1 (ppm)

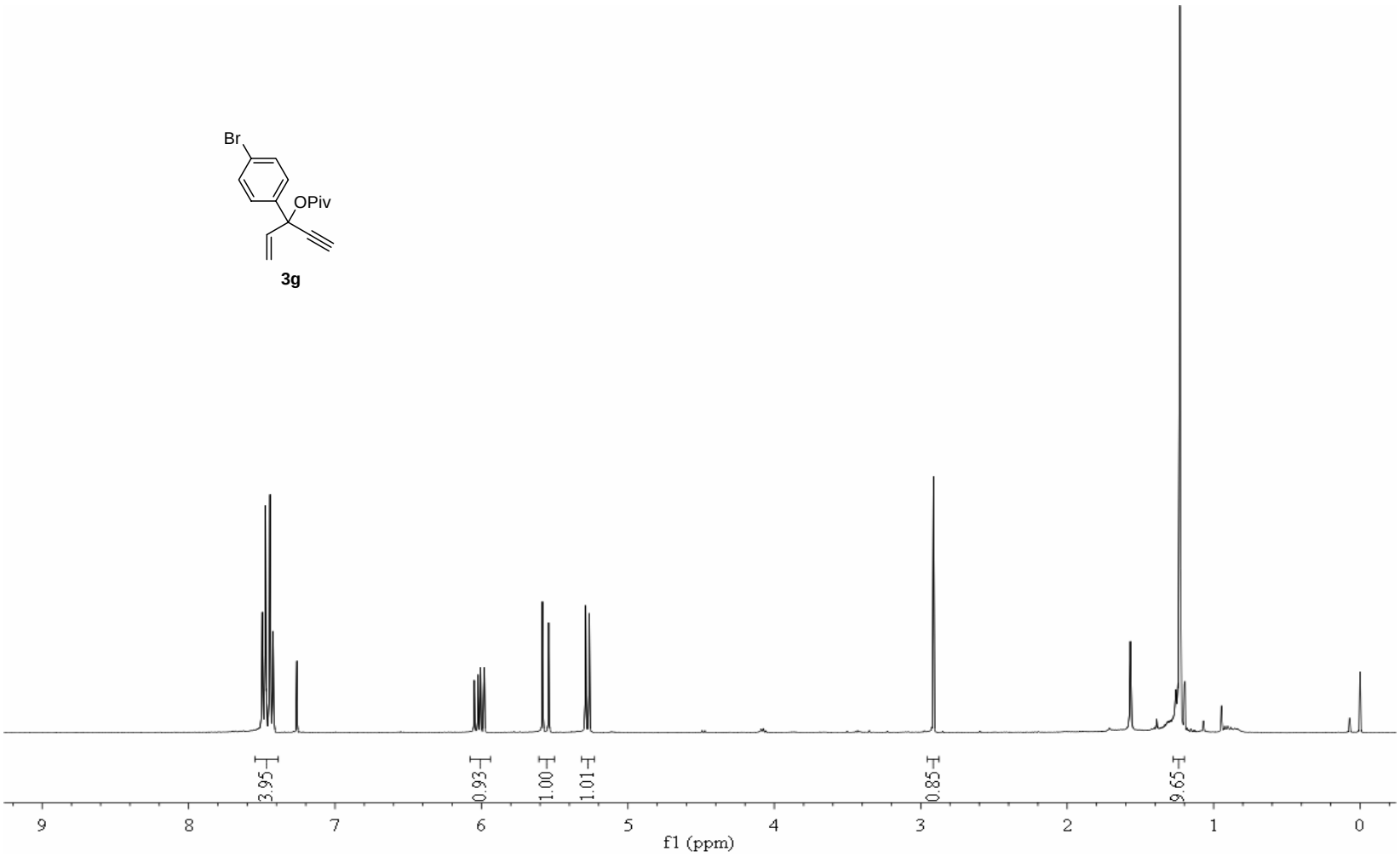

176.152
137.506
116.306
81.084
77.378
77.319
77.000
76.683
75.327
39.104
34.113
26.982
8.102
PivO
Et
3d
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

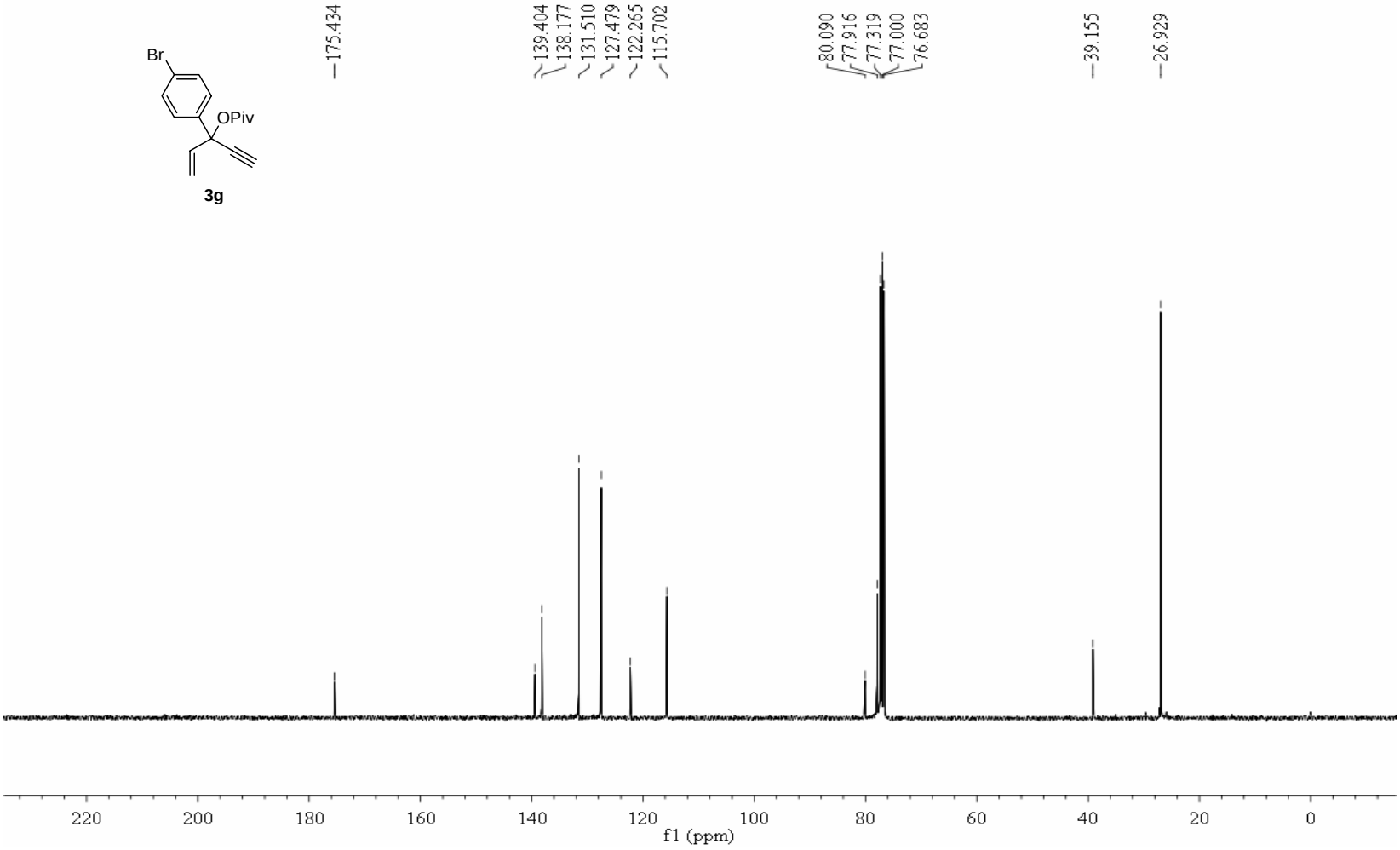

TBSO
OPiv
3e
1.00
1.06
1.07
1.08
1.08
0.90
9.78
9.97
6.18
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

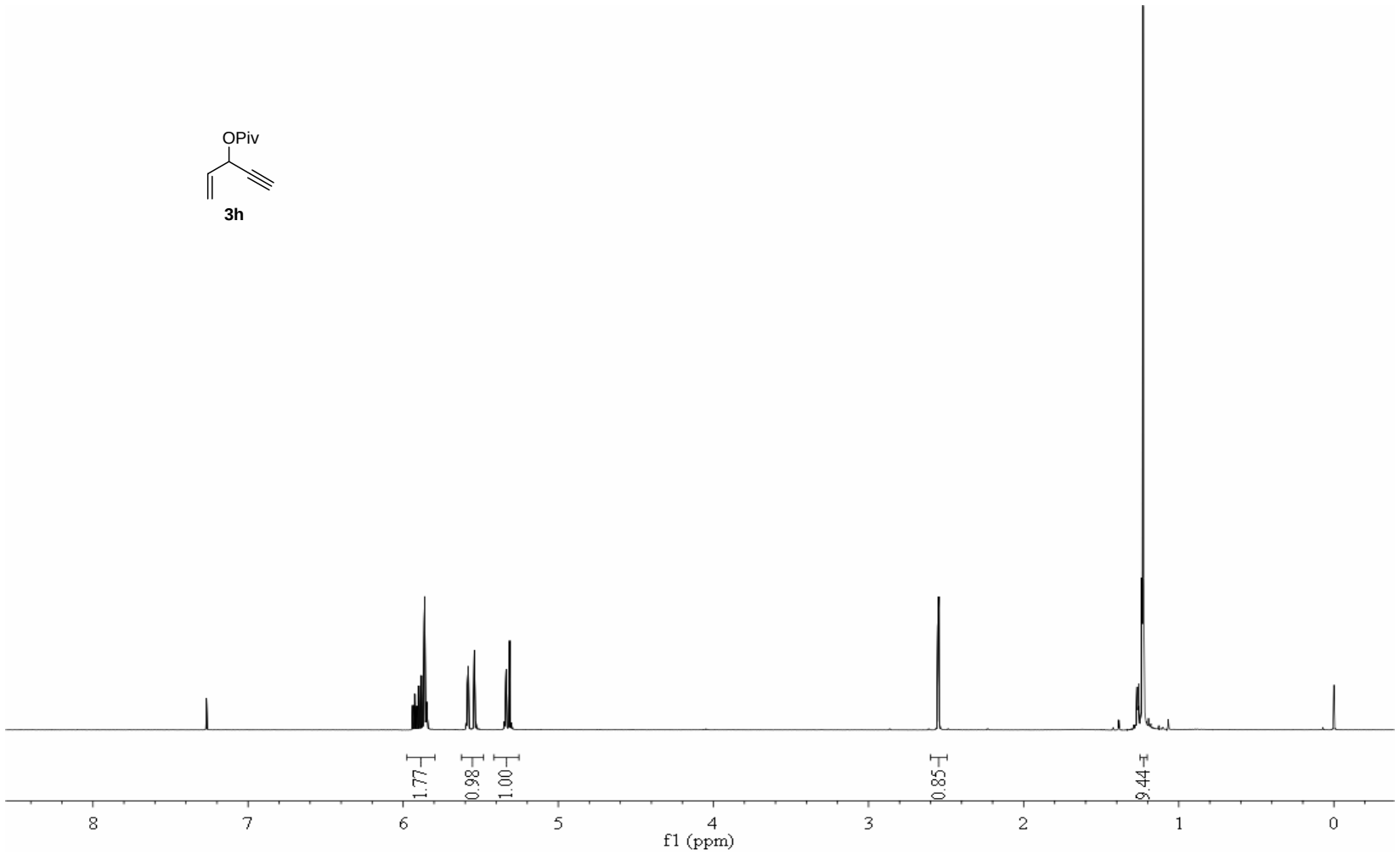

176.308
135.318
117.307
79.864
77.318
77.000
76.682
75.810
68.730
39.126
27.002
25.729
18.218
5.404
-5.458
TBSO
OPiv
3e
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

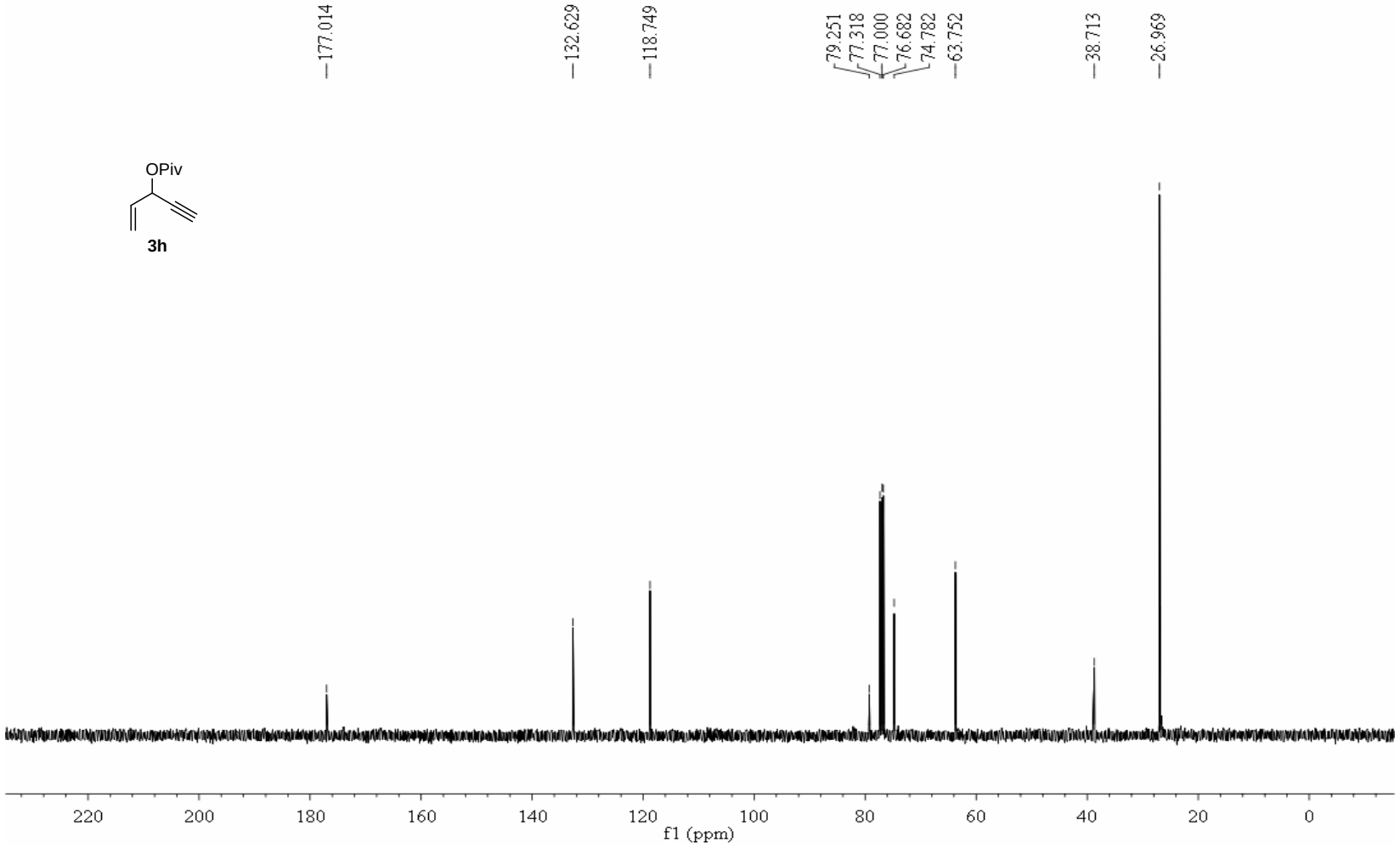

PivO
Ph
3f
2.00
3.08
0.97
1.06
1.08
0.91
9.82
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

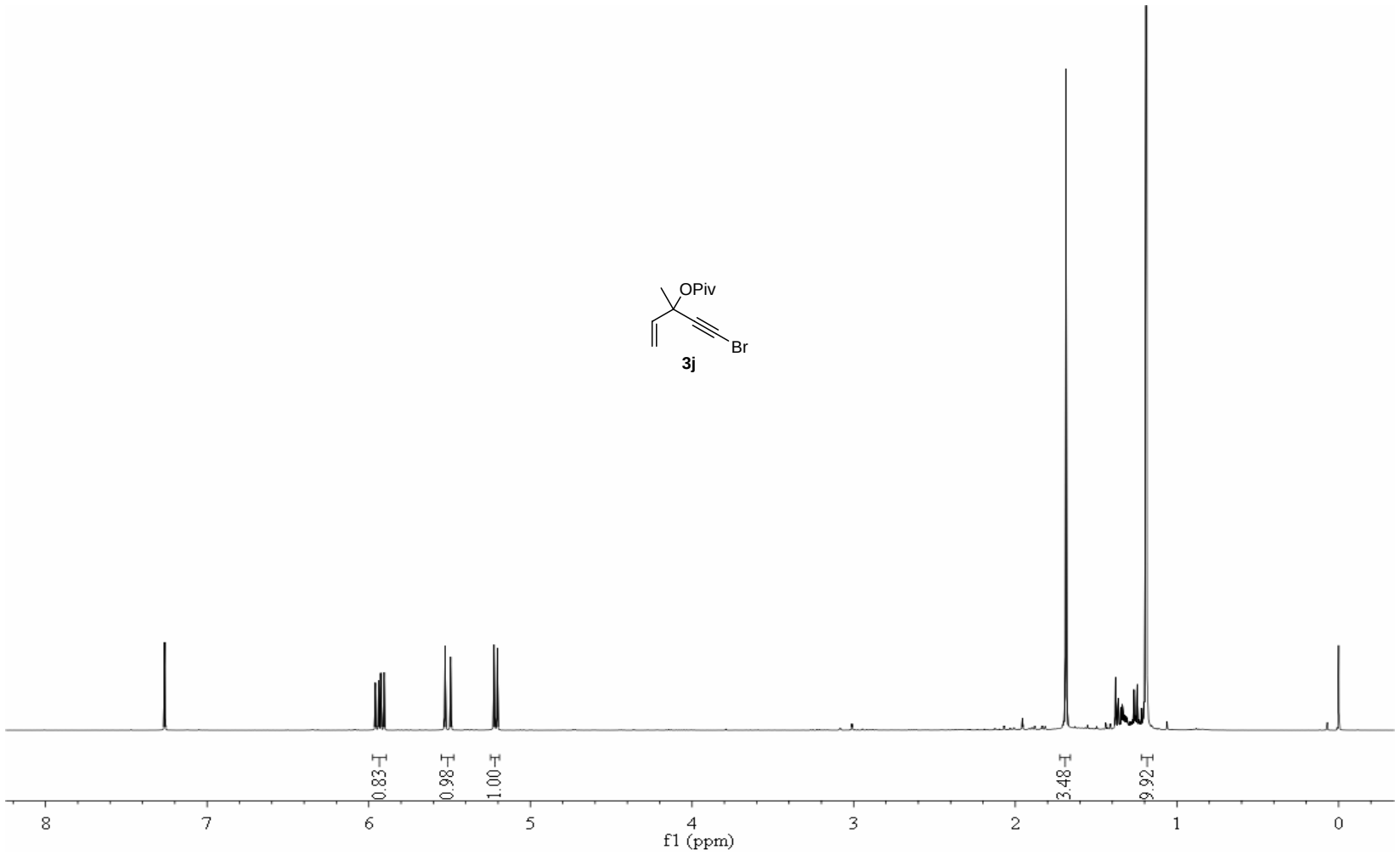

175.450
140.242
138.624
128.341
128.062
125.570
115.269
80.570
77.579
77.499
77.318
77.000
76.682
39.162
26.956
PivO
Ph
3f
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

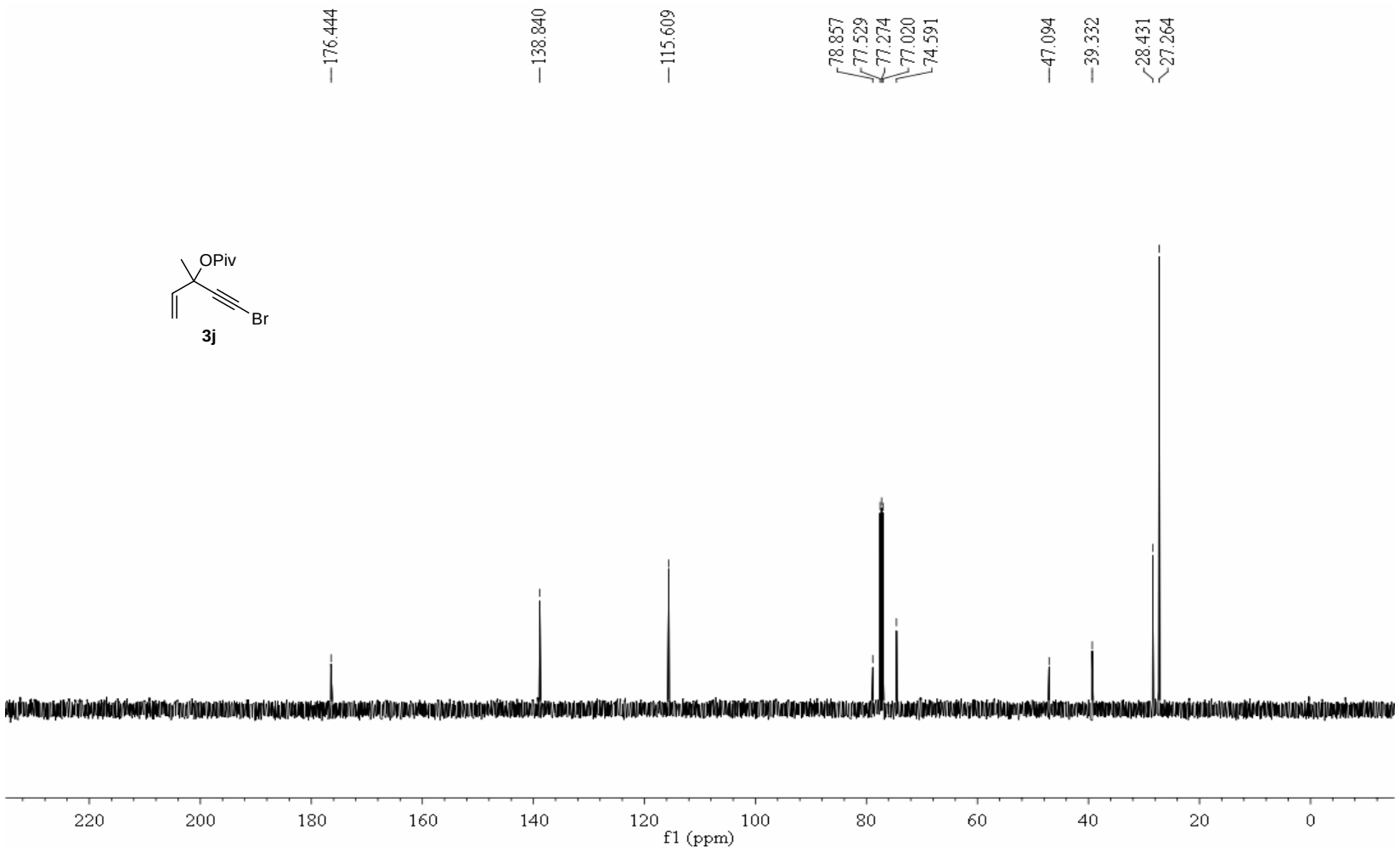

Br
OPiv
3g
3.95
0.93
1.00
1.01
0.85
9.65
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

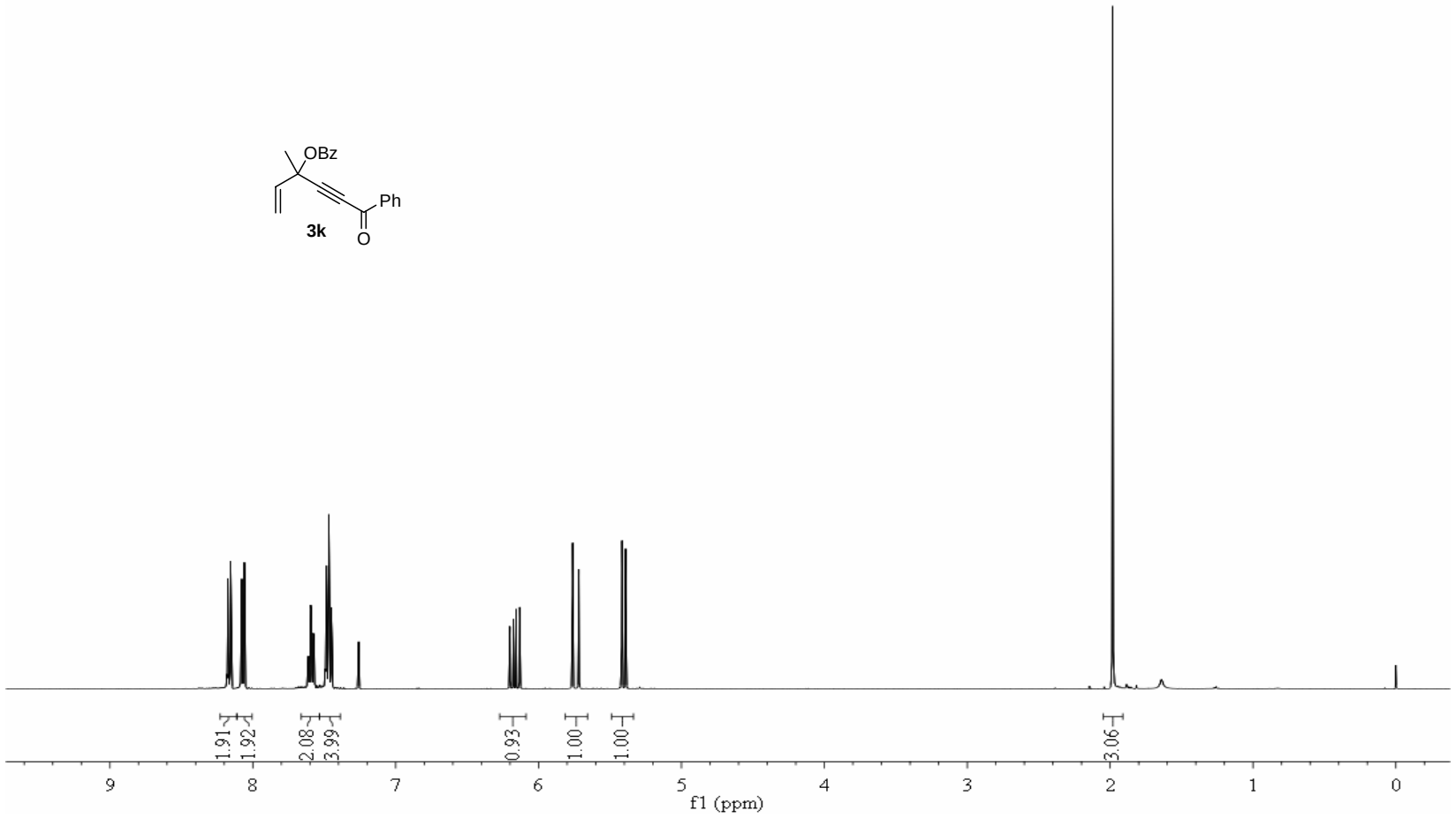

Br
OPiv
3g
175.434
139.404
138.177
131.510
127.479
122.265
115.702
80.090
77.916
77.319
77.000
76.683
39.155
26.929
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

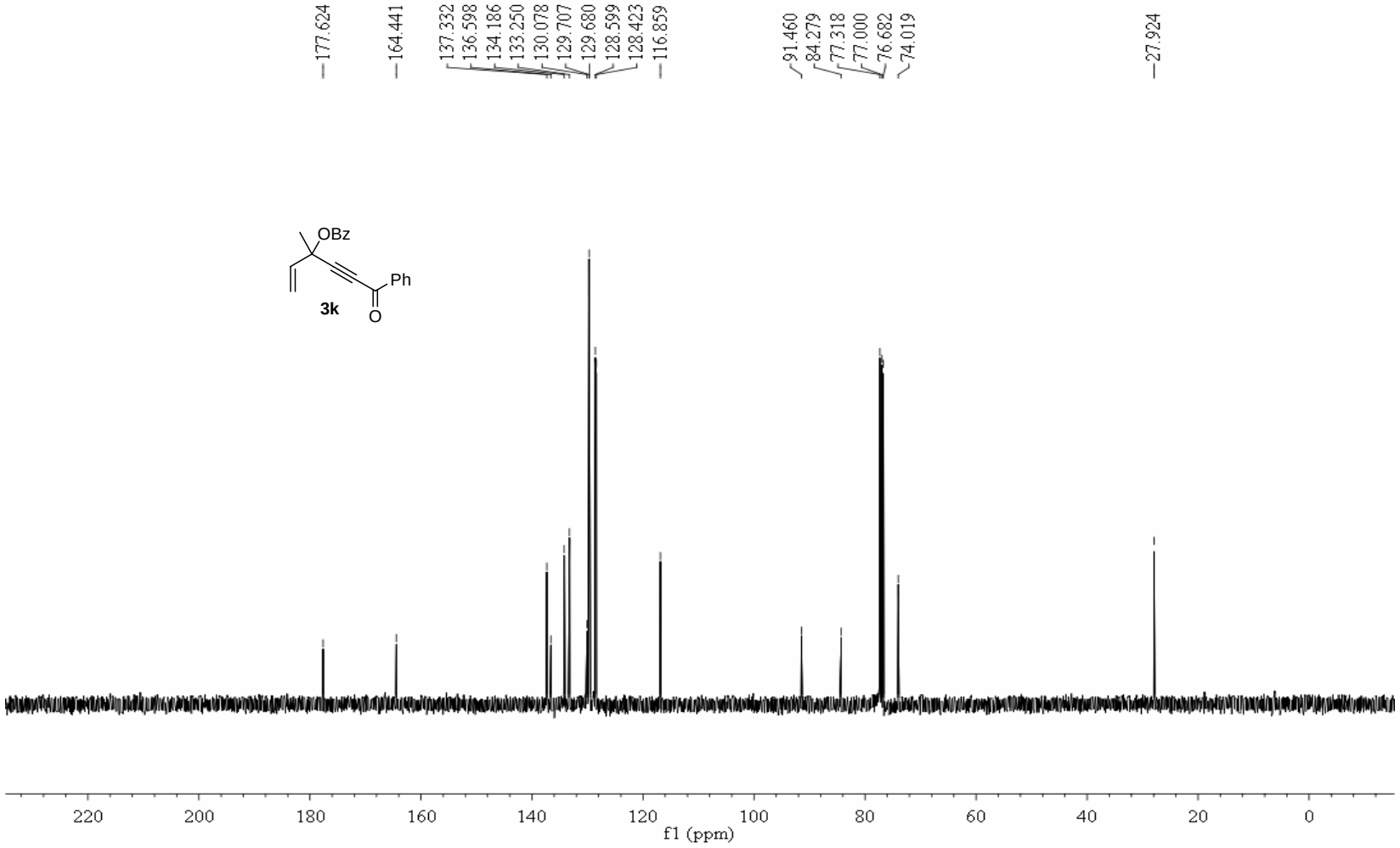

OPiv
3h
1.77
0.98
1.00
0.85
9.44
8
7
6
5
4
3
2
1
0
f1 (ppm)

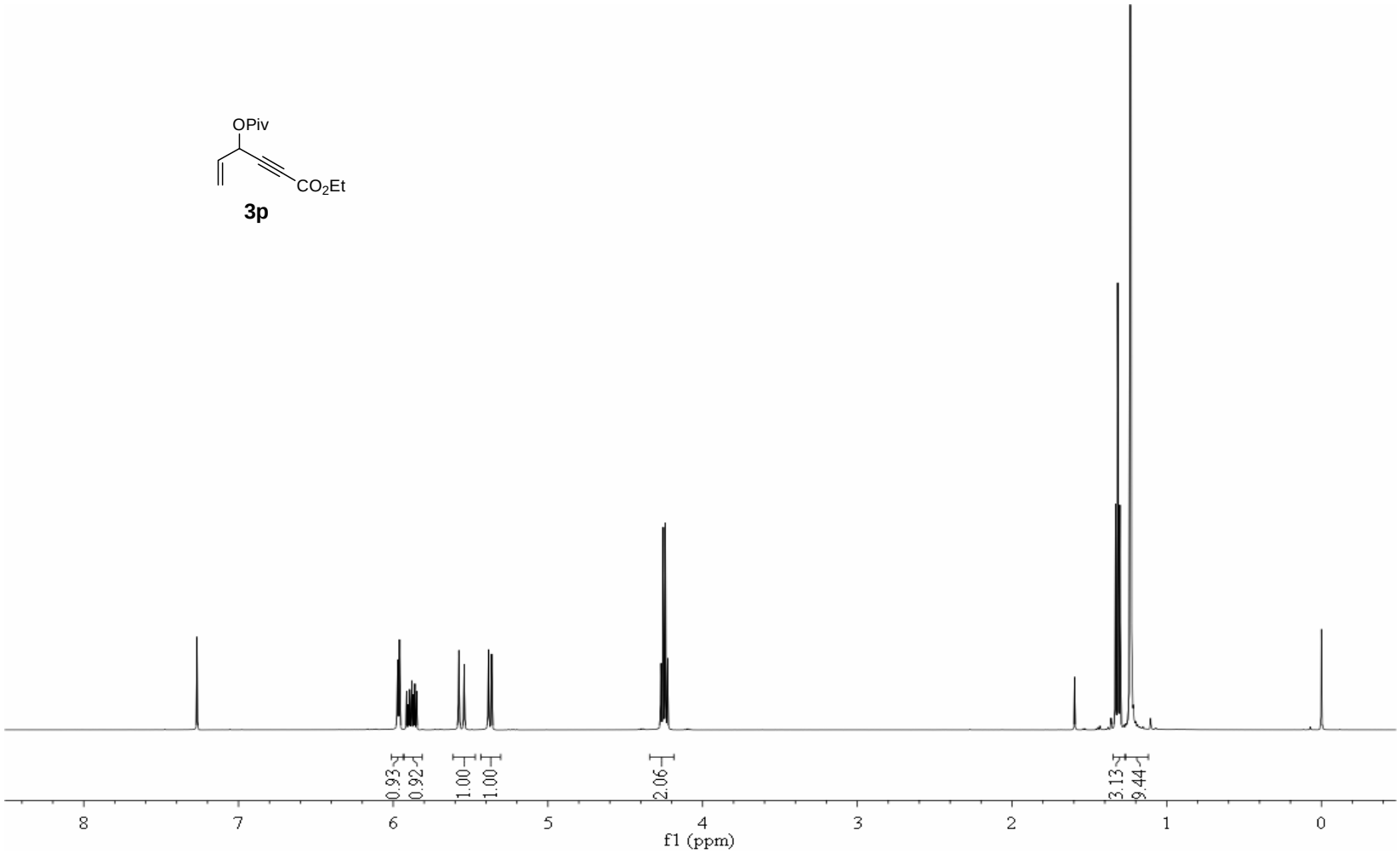

177.014
132.629
118.749
79.251
77.318
77.000
76.682
74.782
63.752
38.713
26.969
OPiv
3h
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

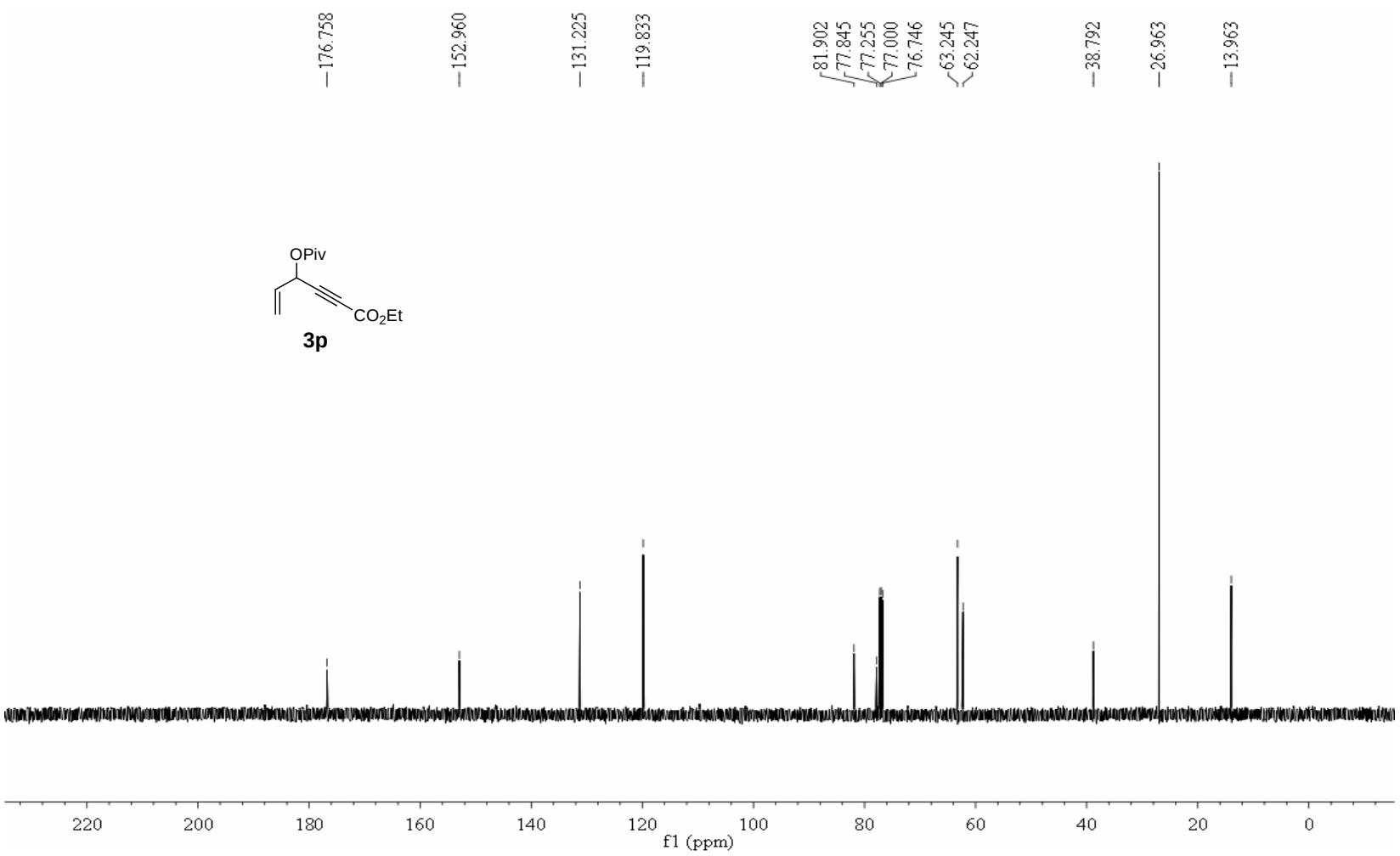

OPiv
Br
3j
0.83
0.98
1.00
3.48
9.92
8
7
6
5
4
3
2
1
0
f1 (ppm)

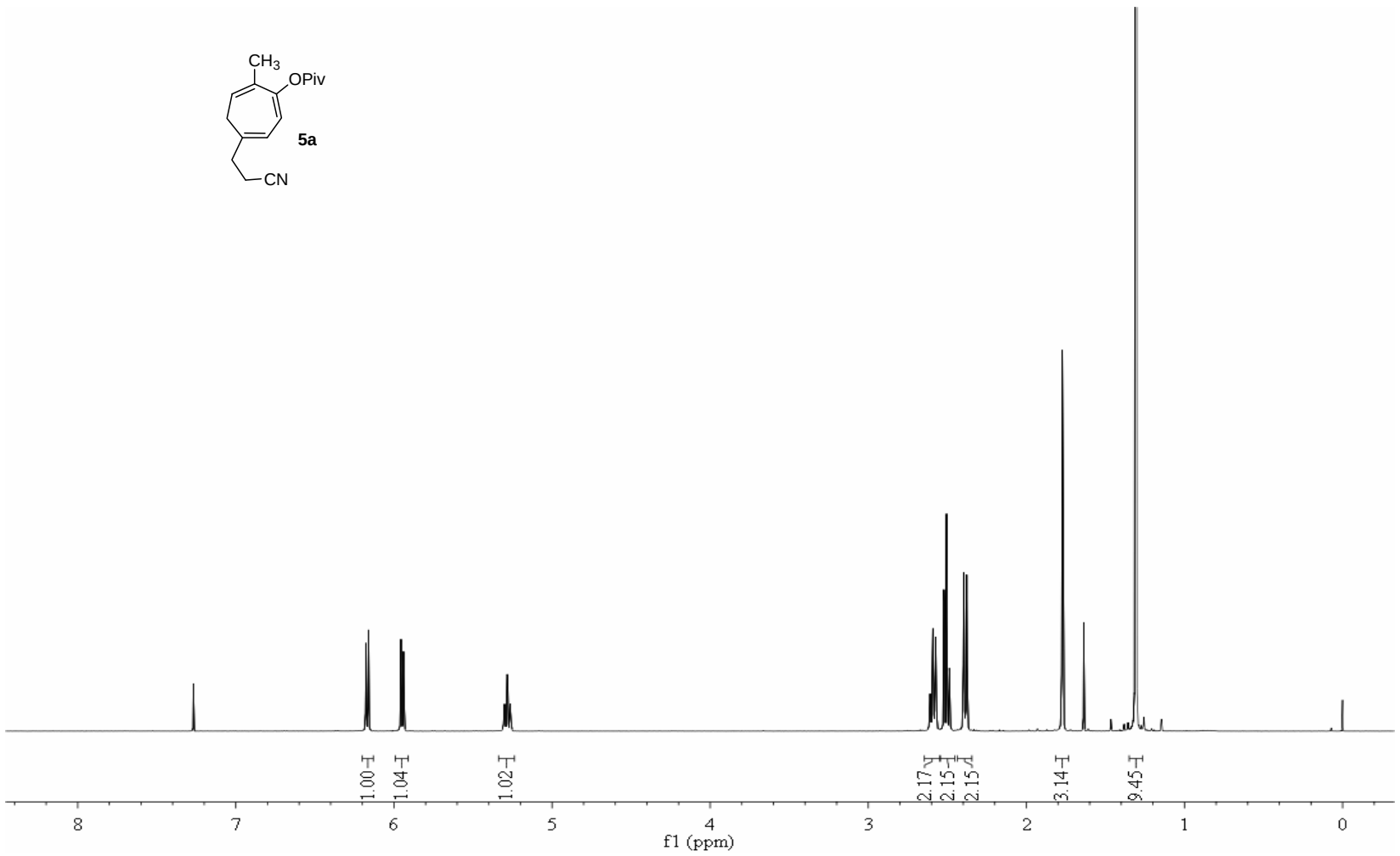

176.444
138.840
115.609
78.857
77.529
77.274
77.020
74.591
47.094
39.332
28.431
27.264
OPiv
Br
3j
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

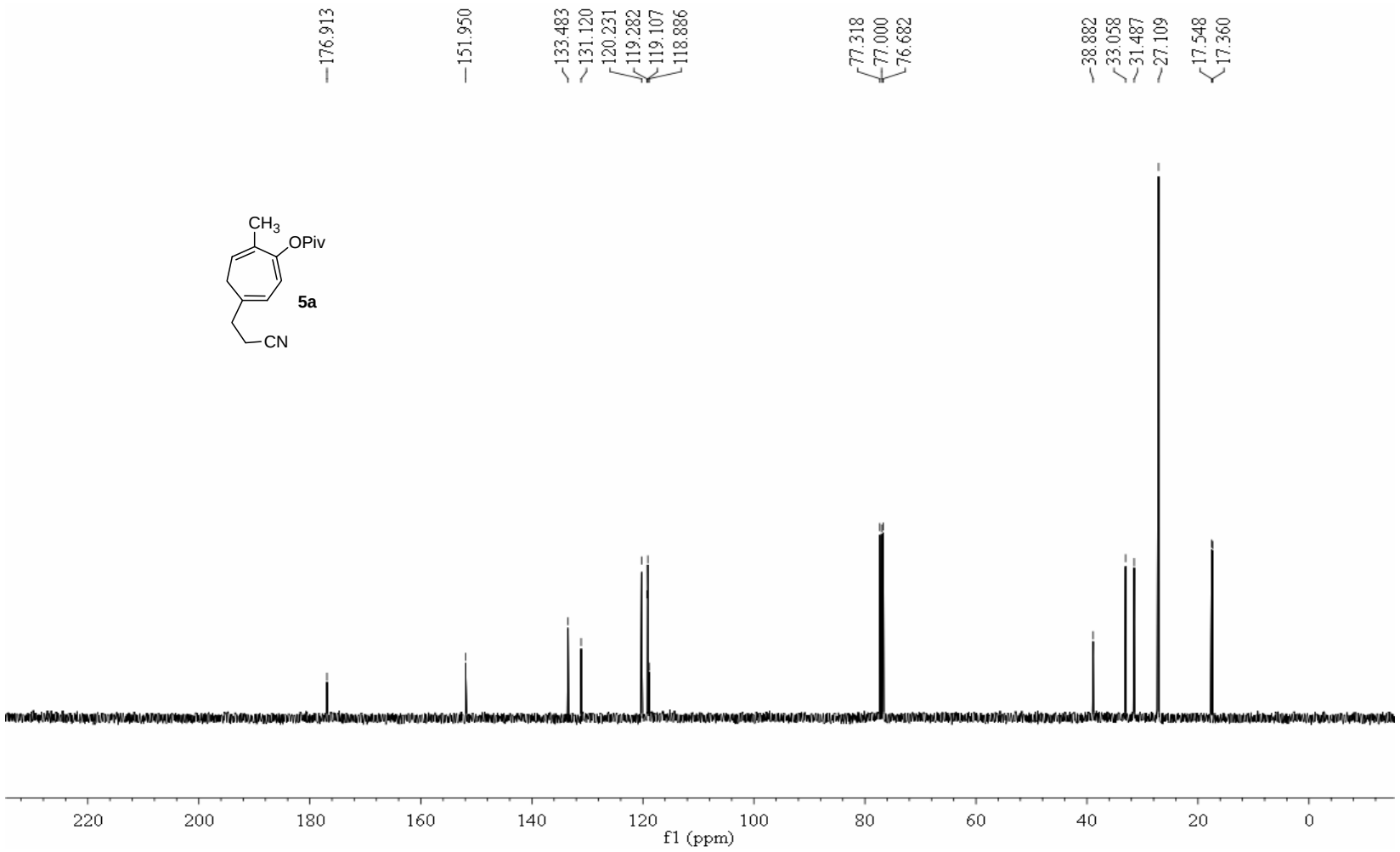

OBz
Ph
O
3k
1.91
1.92
2.08
3.99
0.93
1.00
1.00
3.06
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

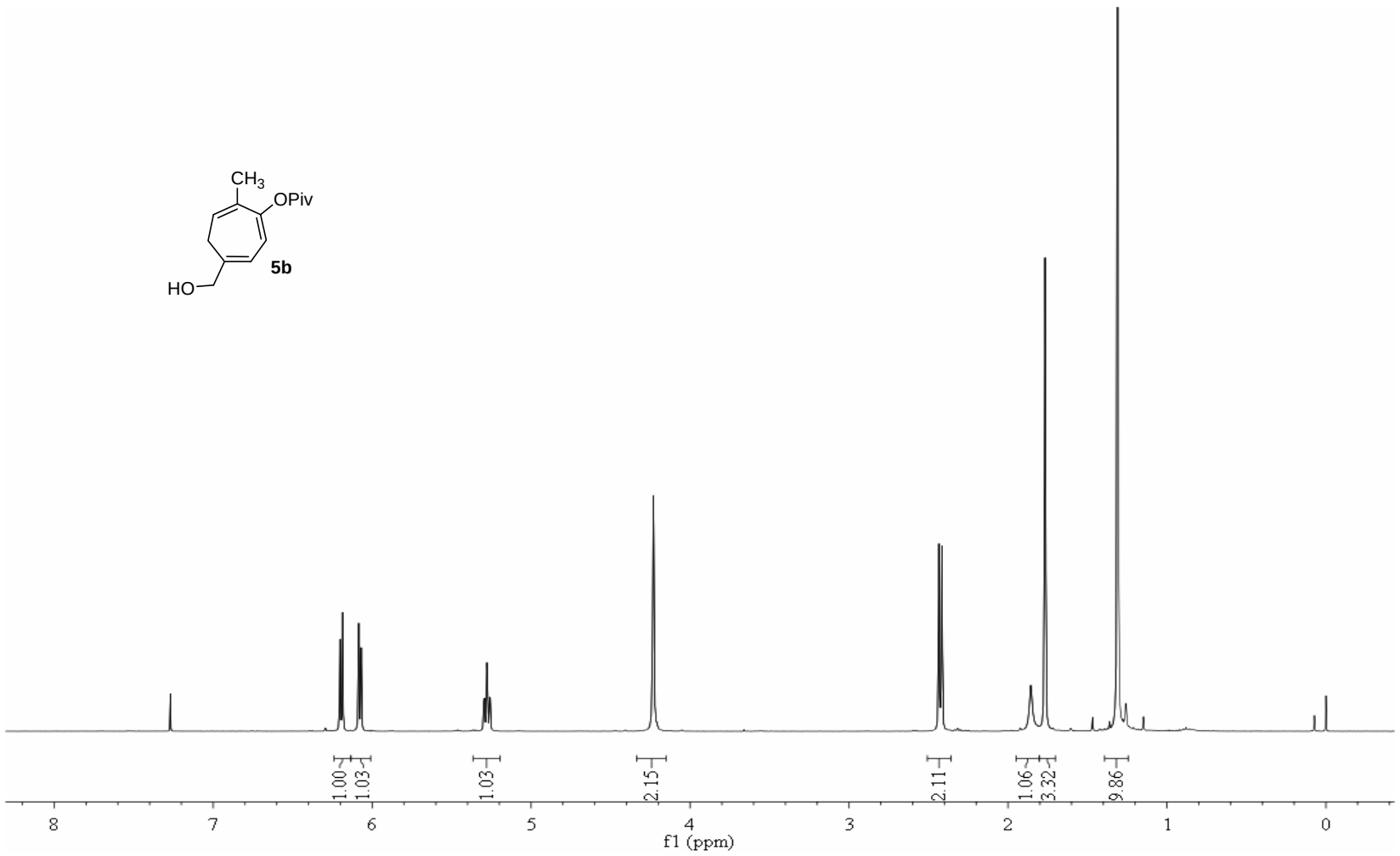

177.624
164.441
137.332
136.598
134.186
133.250
130.078
129.707
129.680
128.599
128.423
116.859
91.460
84.279
77.318
77.000
76.682
74.019
27.924
OBz
Ph
O
3k
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

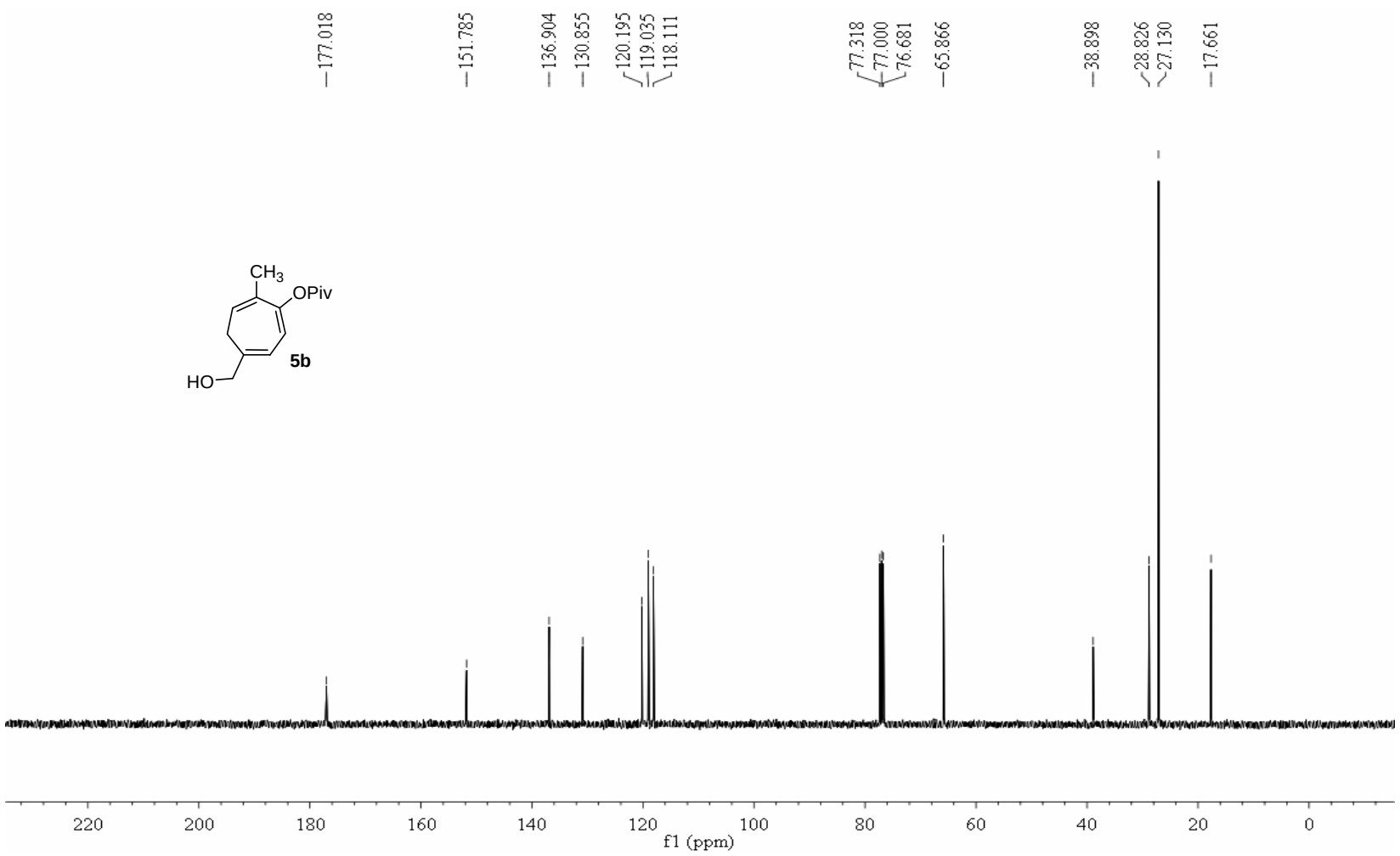

OPiv
CO2Et
3p
0.93
0.92
1.00
1.00
2.06
3.13
9.44
8
7
6
5
4
3
2
1
0
f1 (ppm)

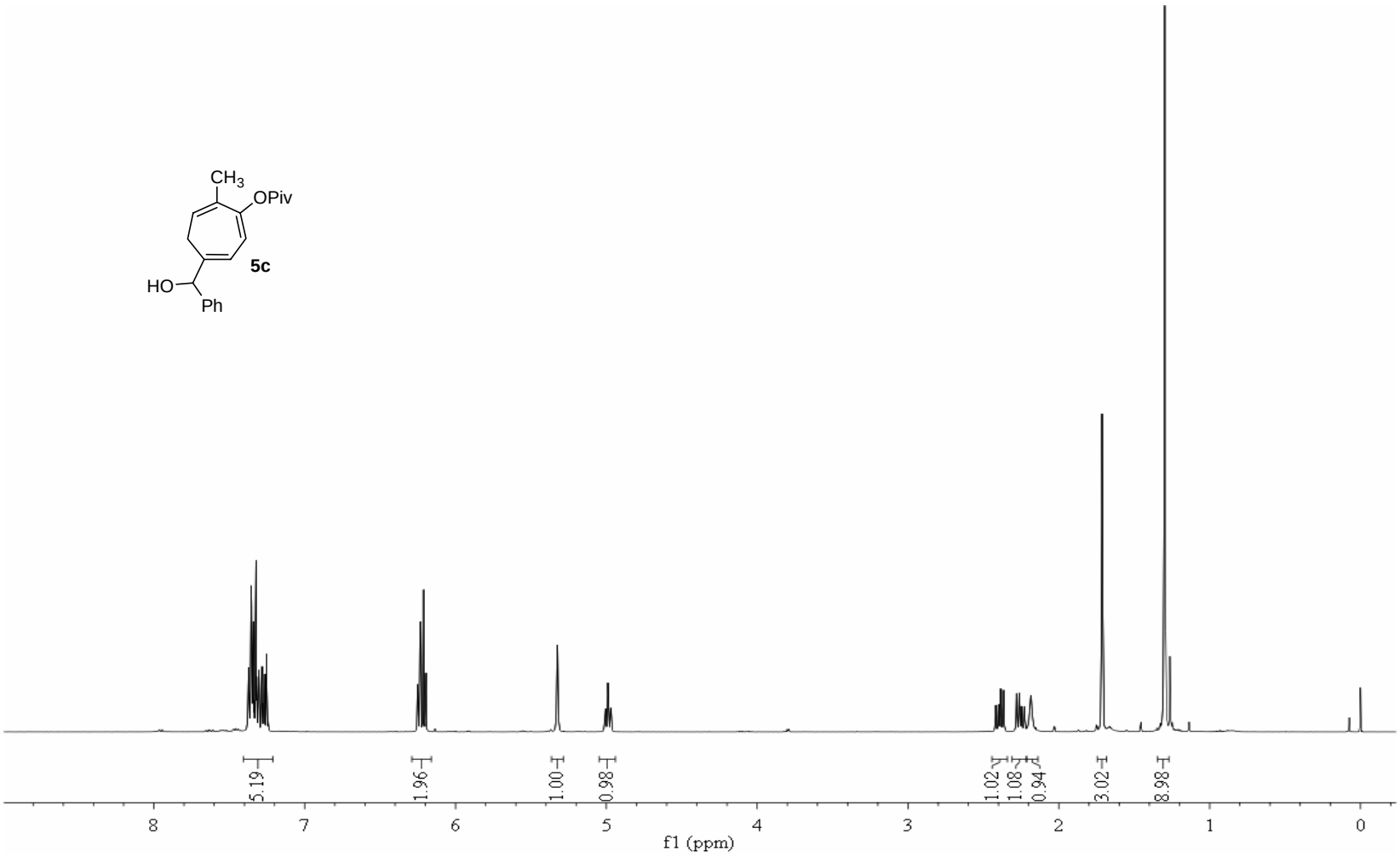

176.758
152.960
131.225
119.833
81.902
77.845
77.255
77.000
76.746
63.245
62.247
38.792
26.963
13.963
OPiv
CO2Et
3p
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

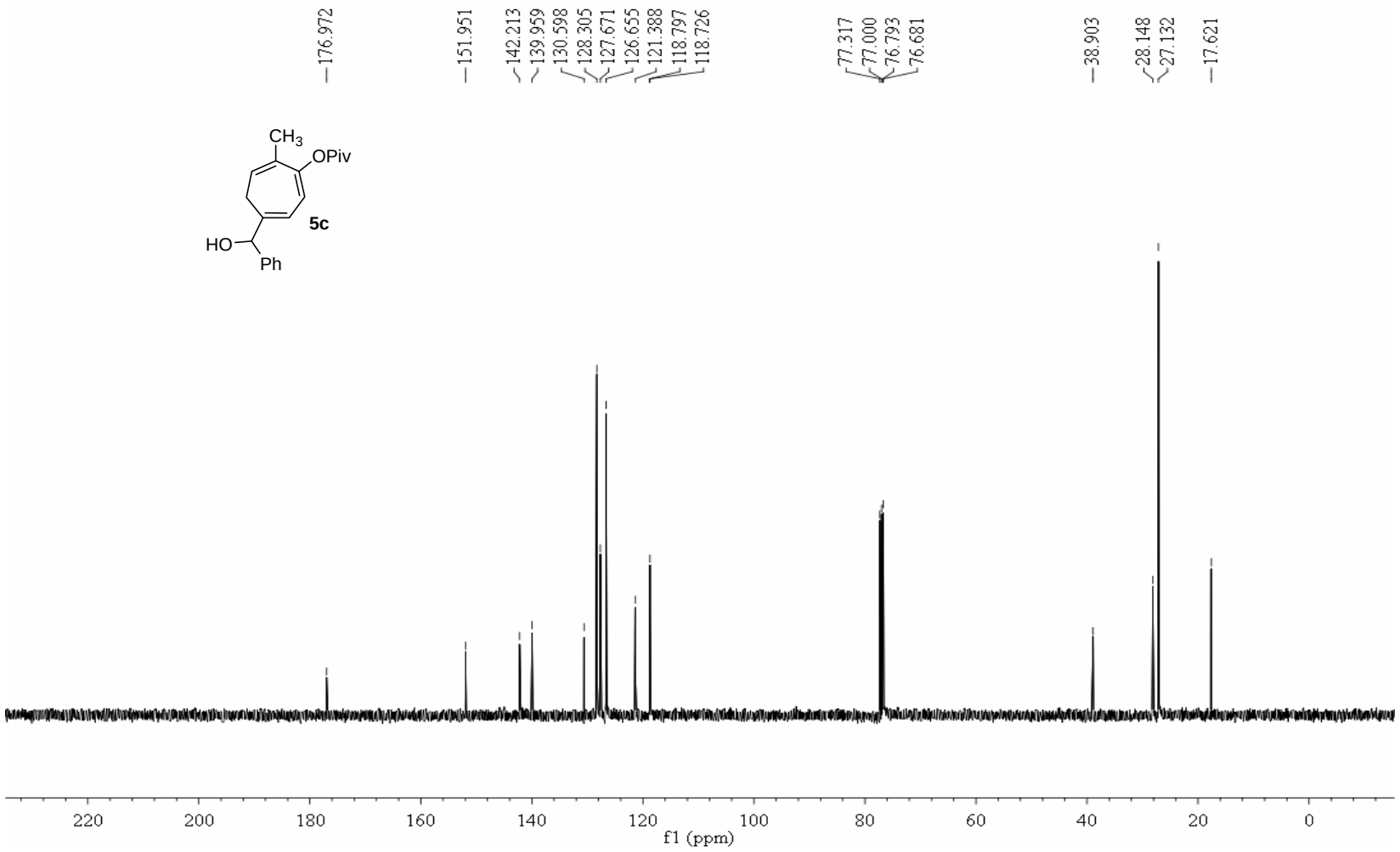

CH3
OPiv
5a
CN
1.00
1.04
1.02
2.17
2.15
2.15
3.14
9.45
8
7
6
5
4
3
2
1
0
f1 (ppm)

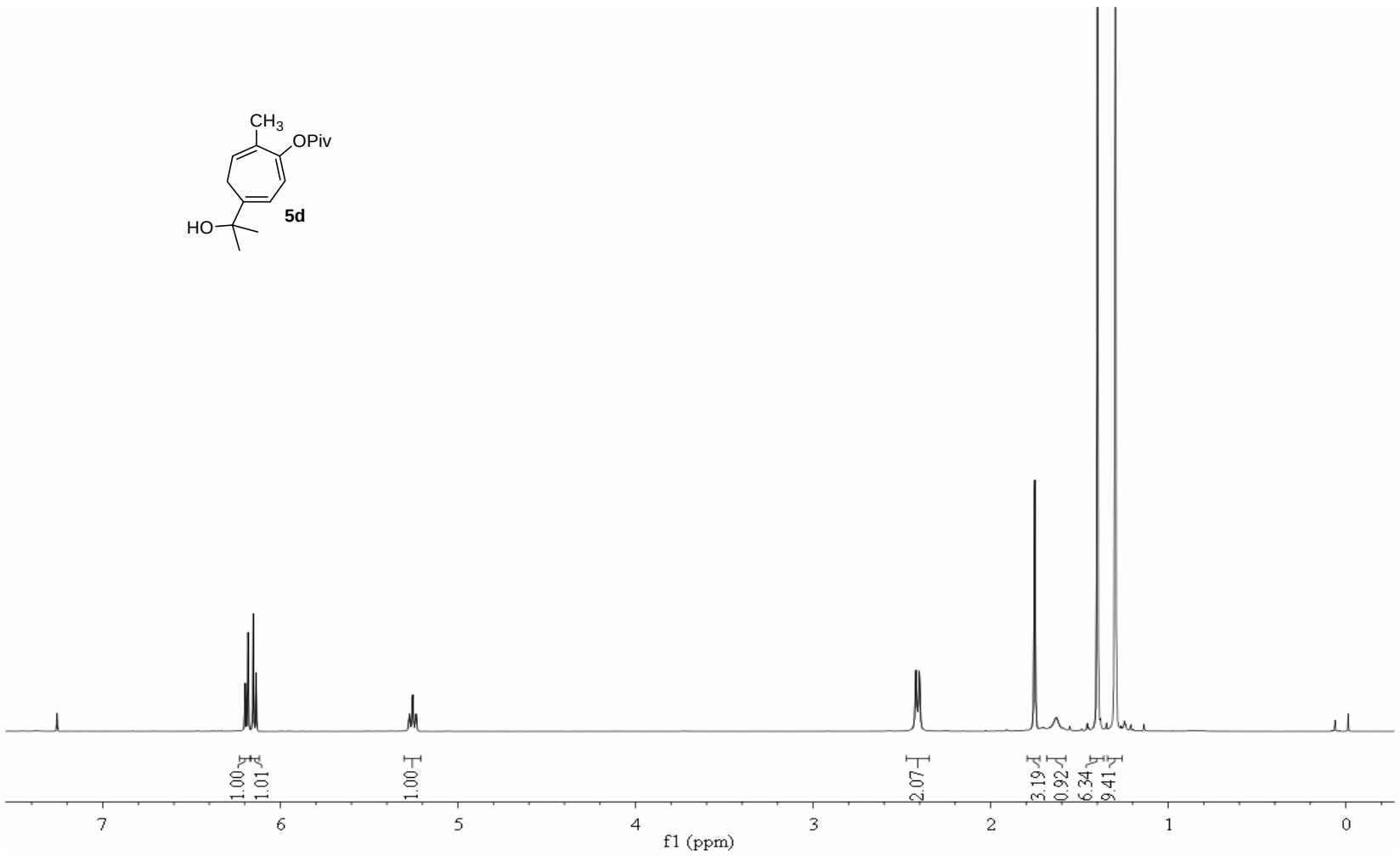

176.913
151.950
133.483
131.120
120.231
119.282
119.107
118.886
77.318
77.000
76.682
38.882
33.058
31.487
27.109
17.548
17.360
CH3
OPiv
5a
CN
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

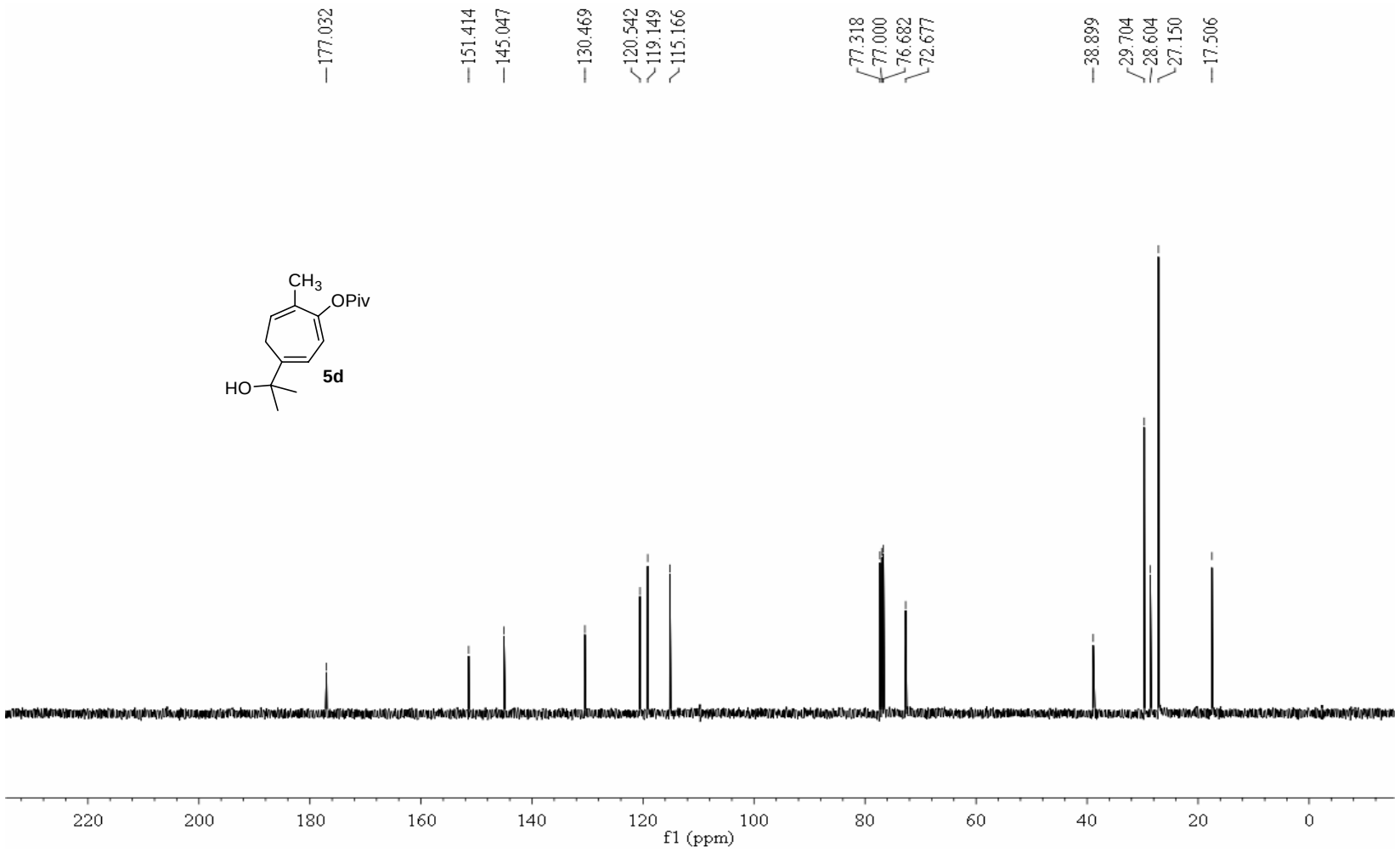

CH3
OPiv
HO
5b
1.00
1.03
1.03
2.15
2.11
1.06
3.32
9.86
8
7
6
5
4
3
2
1
0
f1 (ppm)

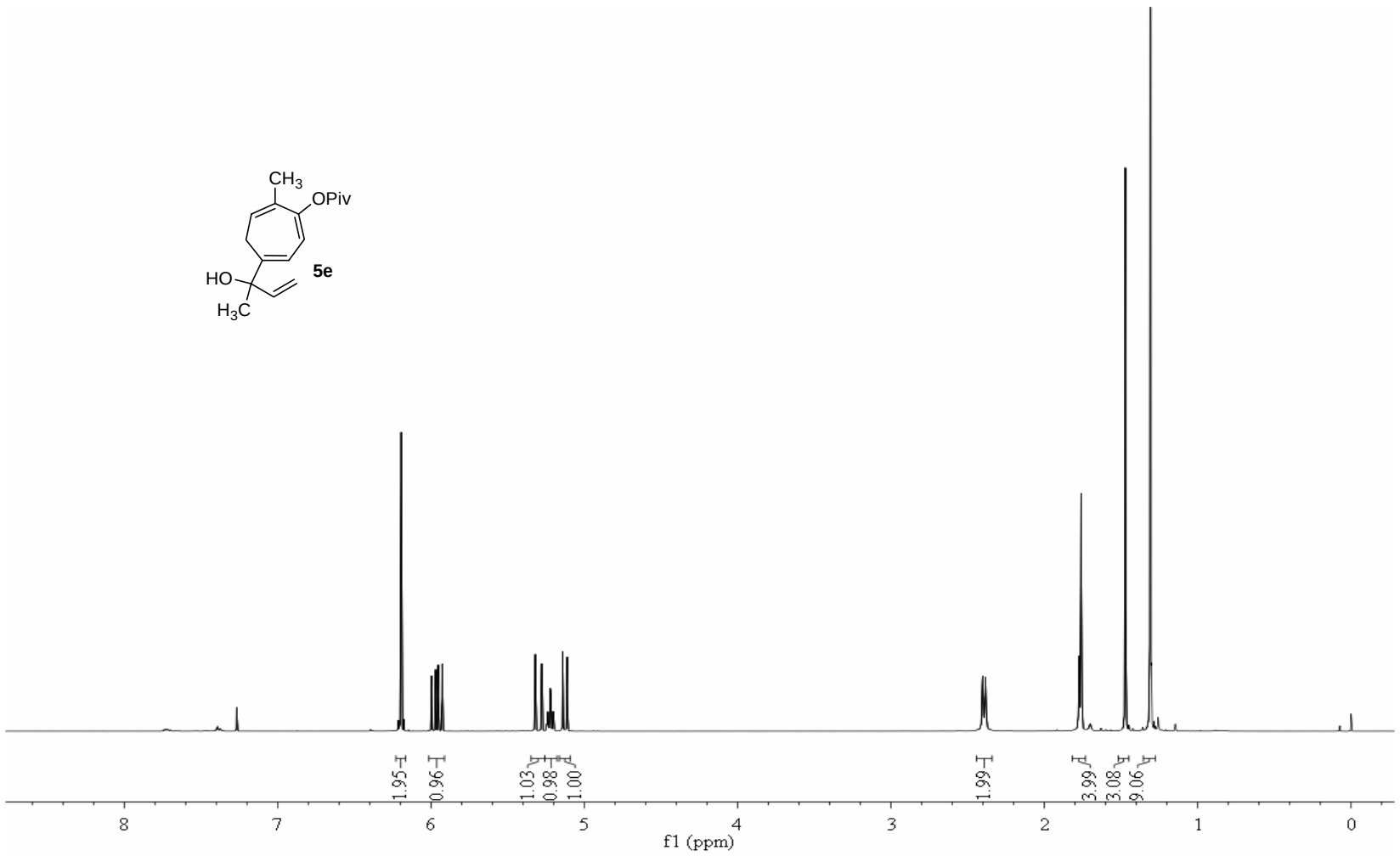

177.018
151.785
136.904
130.855
120.195
119.035
118.111
77.318
77.000
76.681
65.866
38.898
28.826
27.130
17.661
CH3
OPiv
HO
5b
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

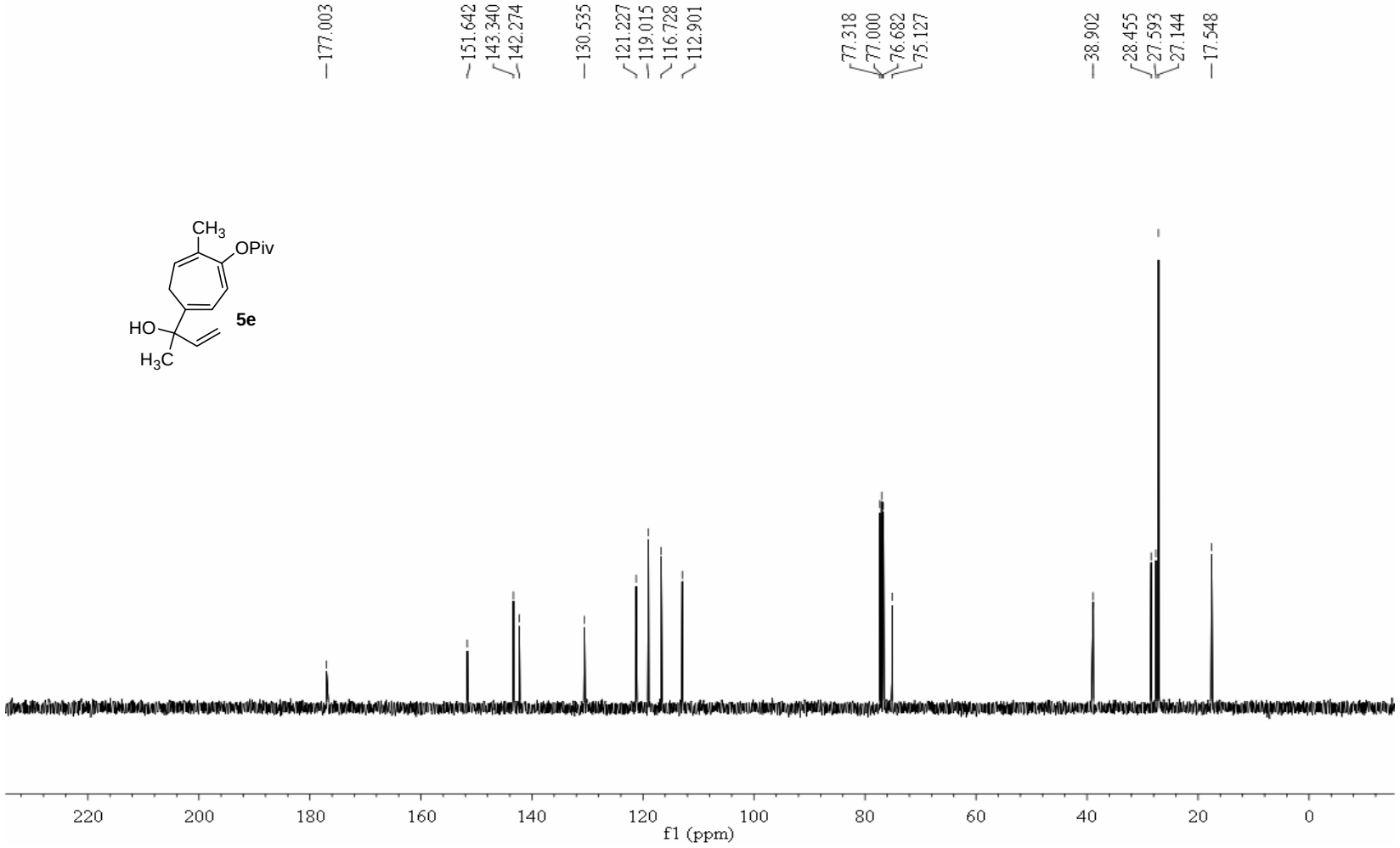

CH3
OPiv
HO
Ph
5c
5.19
1.96
1.00
0.98
1.02
1.08
0.94
3.02
8.98
8
7
6
5
4
3
2
1
0
f1 (ppm)

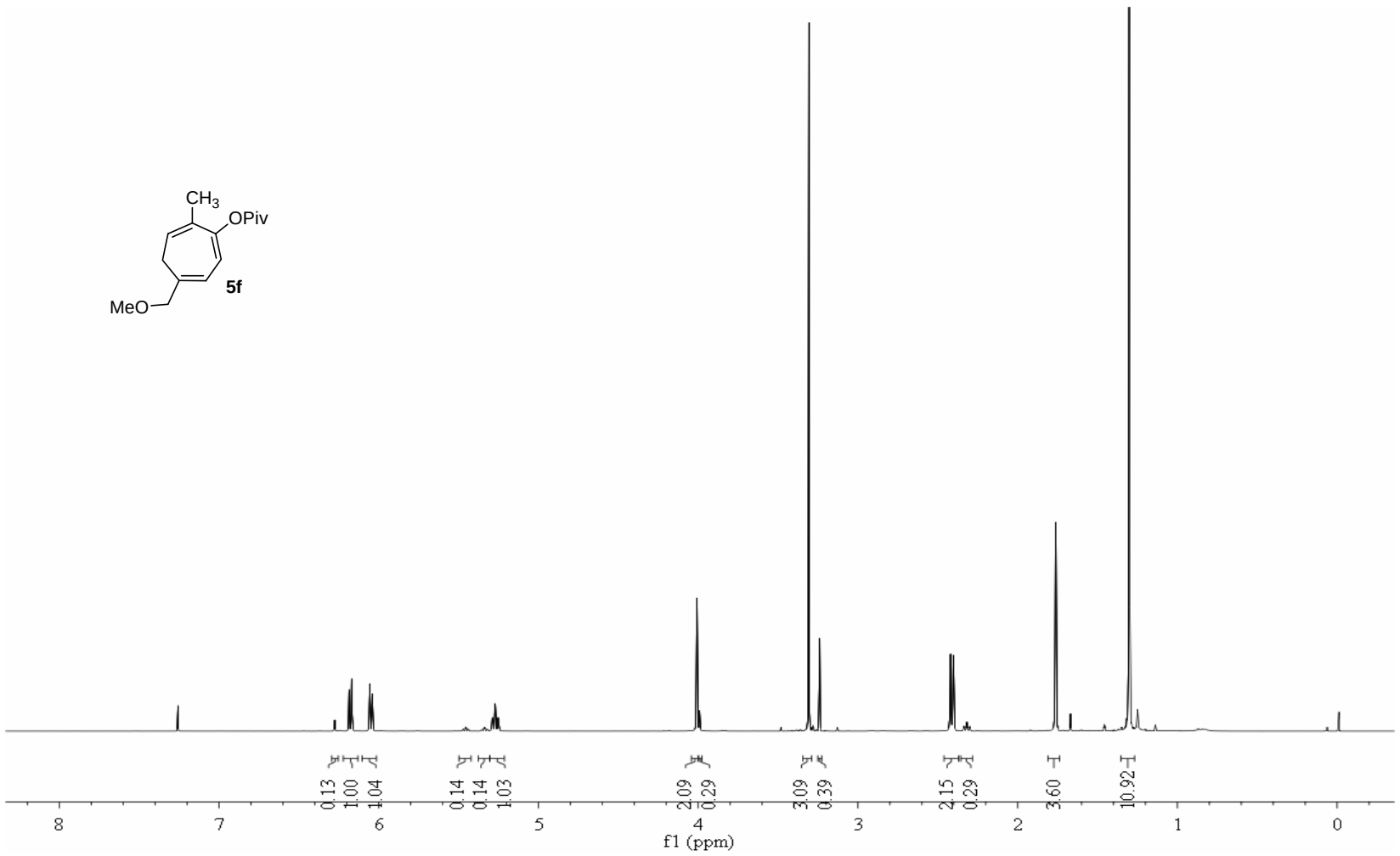

176.972
151.951
142.213
139.959
130.598
128.305
127.671
126.655
121.388
118.797
118.726
77.317
77.000
76.793
76.681
38.903
28.148
27.132
17.621
CH3
OPiv
HO
Ph
5c
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

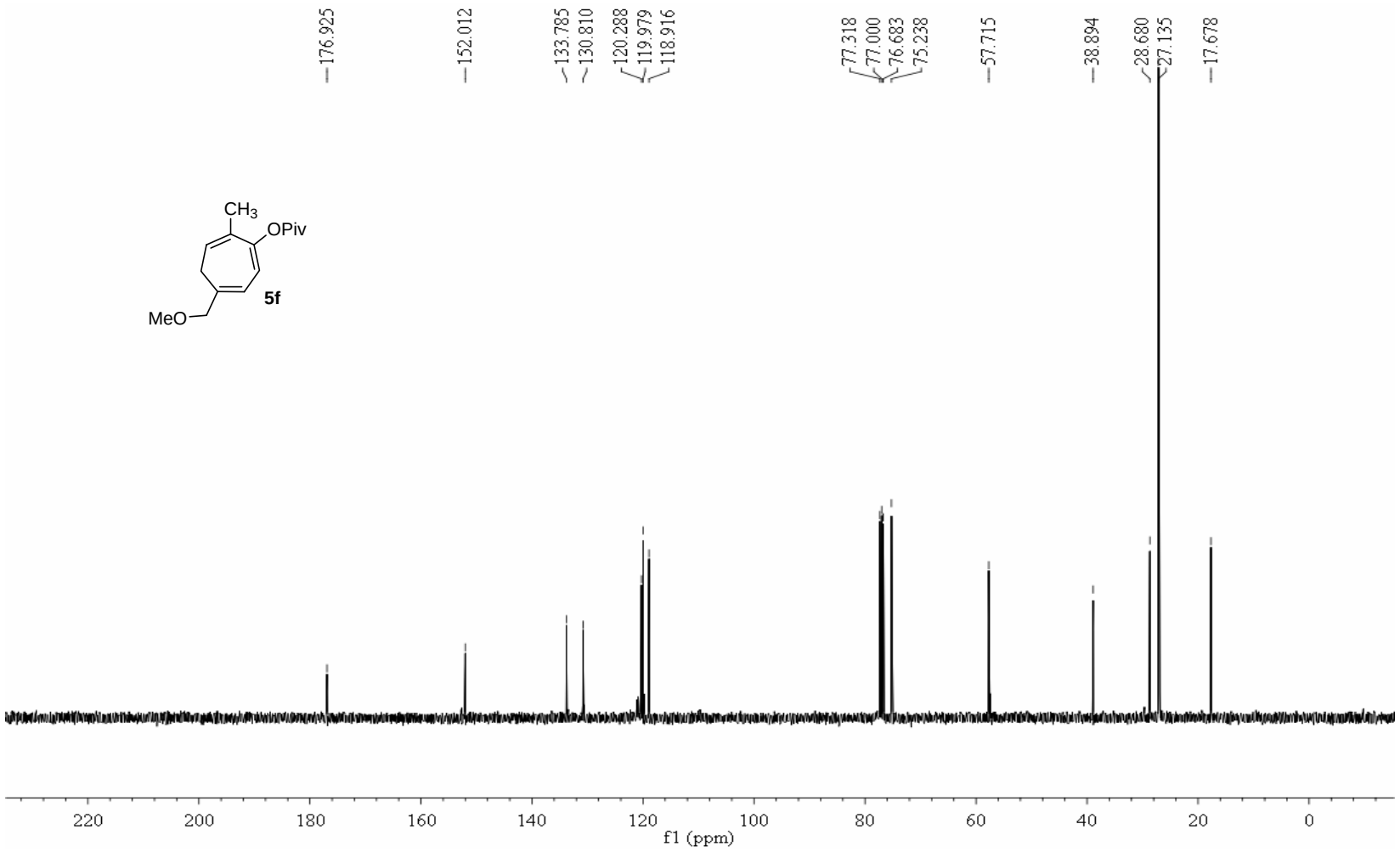

CH3
OPiv
HO
5d
1.00
1.01
1.00
2.07
3.19
0.92
6.34
9.41
7
6
5
4
3
2
1
0
f1 (ppm)

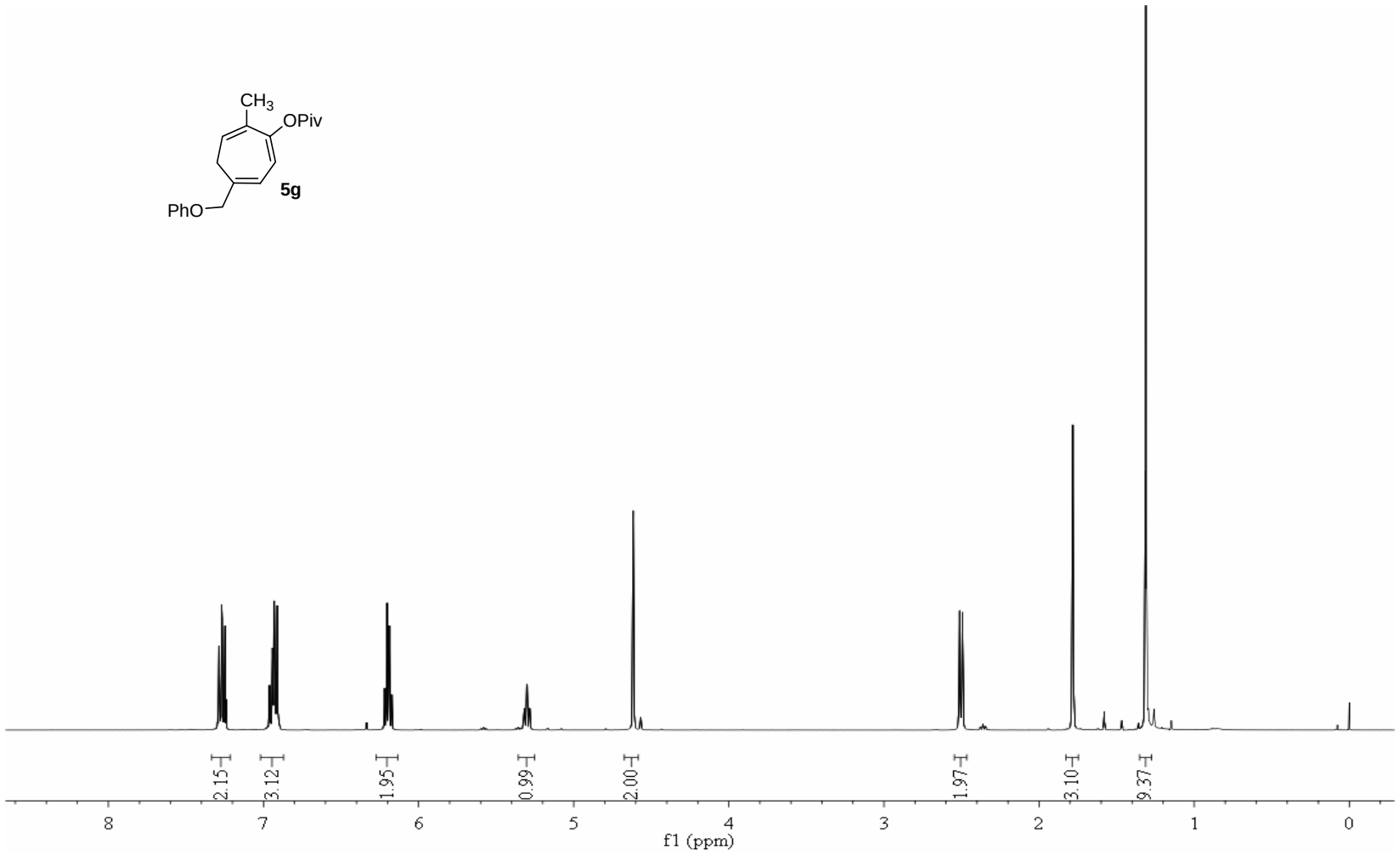

177.032
151.414
145.047
130.469
120.542
119.149
115.166
77.318
77.000
76.682
72.677
38.899
29.704
28.604
27.150
17.506
CH3
OPiv
HO
5d
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

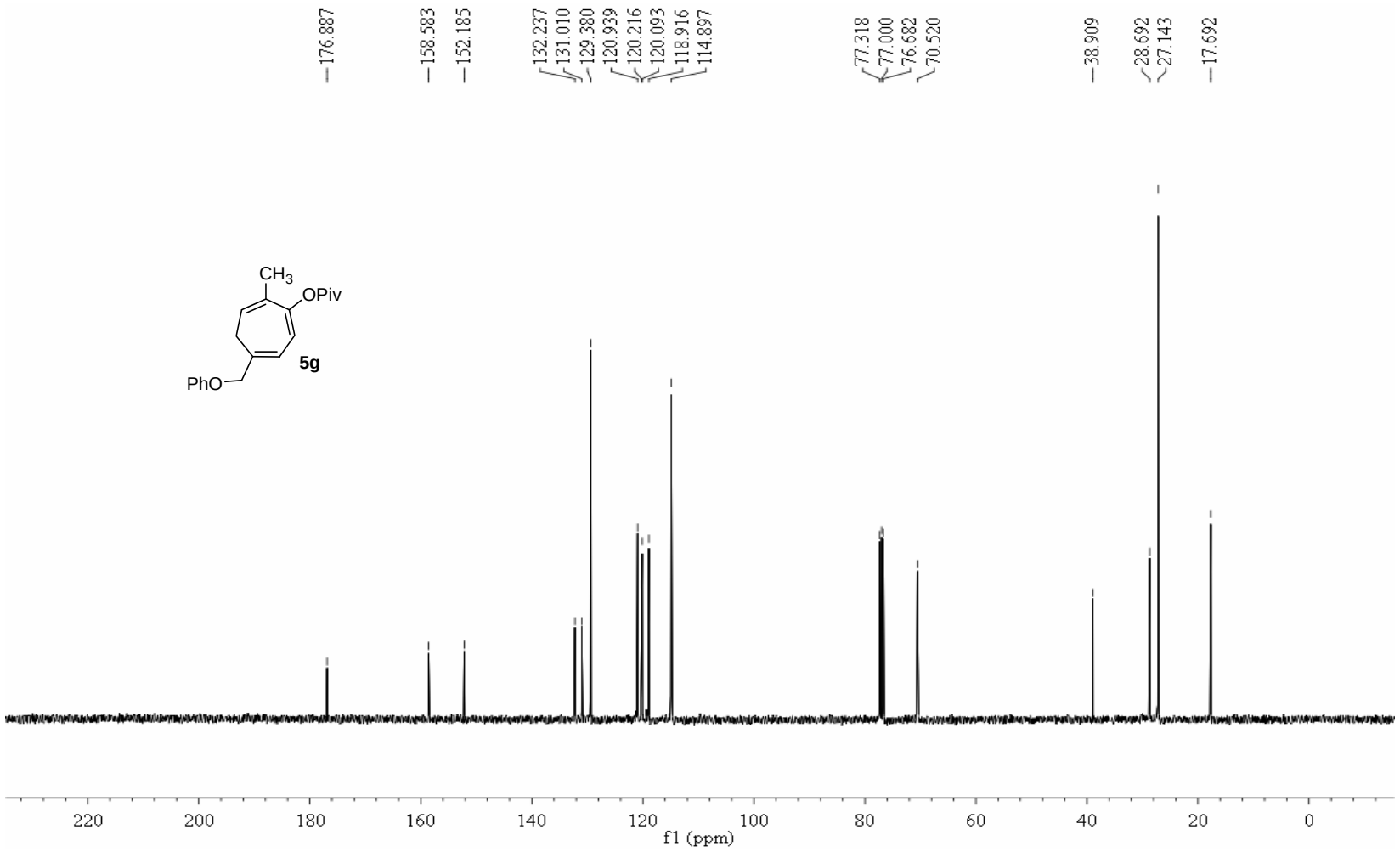

CH3
OPiv
HO
H3C
5e
1.95
0.96
1.03
0.98
1.00
1.99
3.99
3.08
9.06
8
7
6
5
4
3
2
1
0
f1 (ppm)

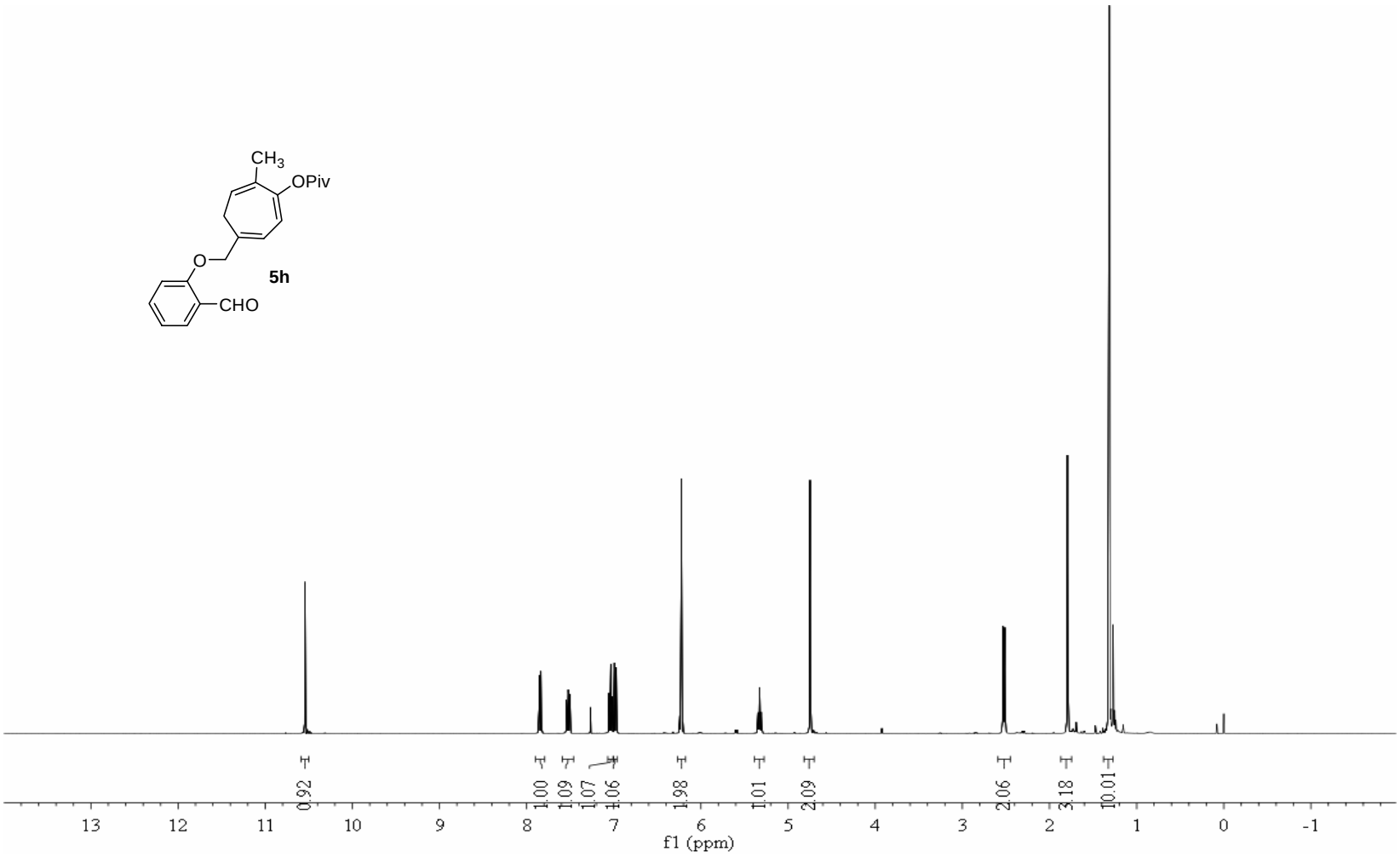

177.003
151.642
143.340
142.274
130.535
121.227
119.015
116.728
112.901
77.318
77.000
76.682
75.127
38.902
28.455
27.593
27.144
17.548
CH3
OPiv
HO
H3C
5e
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

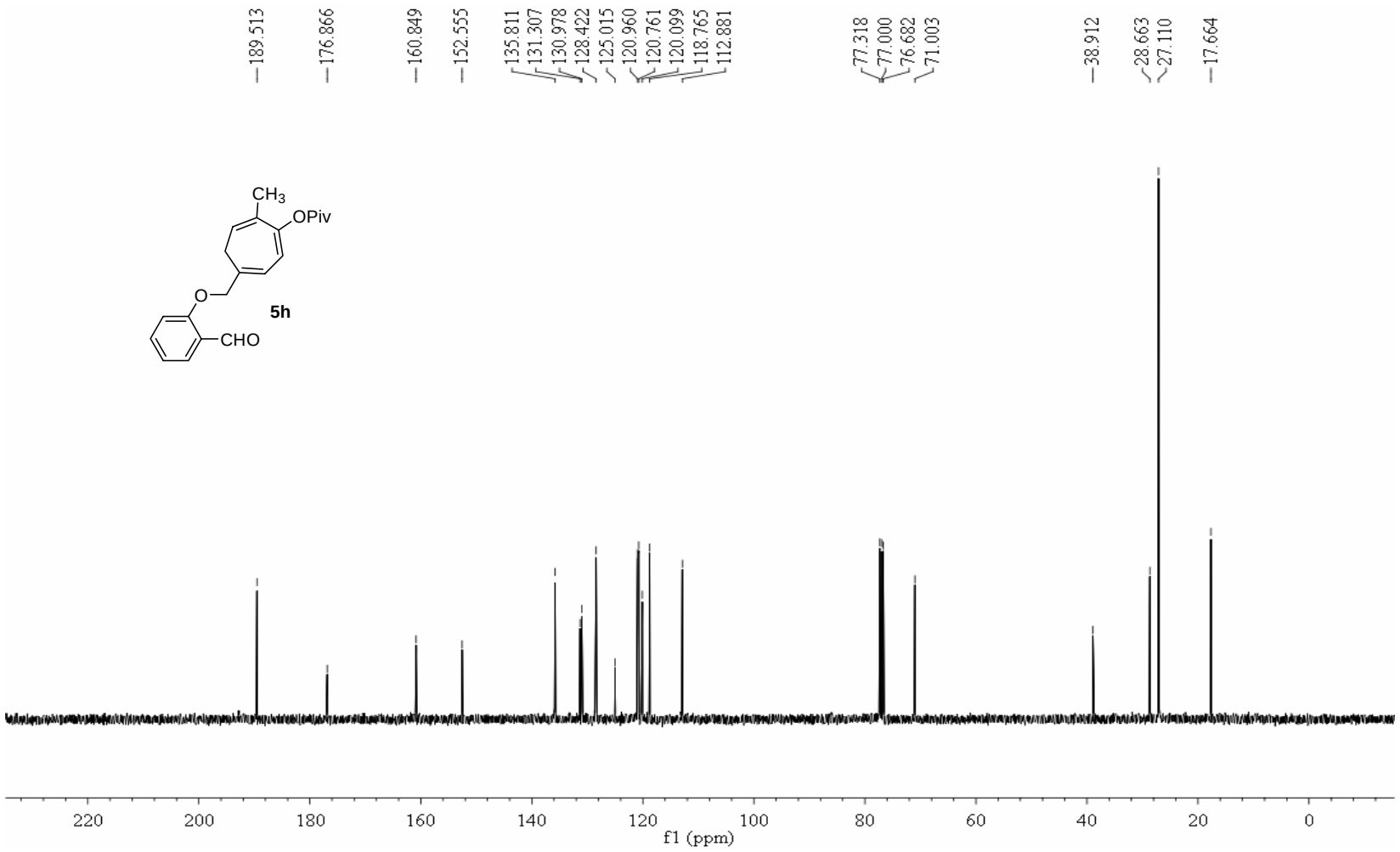

CH3
OPiv
MeO
5f
0.13
1.00
1.04
0.14
0.14
1.03
2.09
0.29
3.09
0.39
2.15
0.29
3.60
10.92
8
7
6
5
4
3
2
1
0
f1 (ppm)

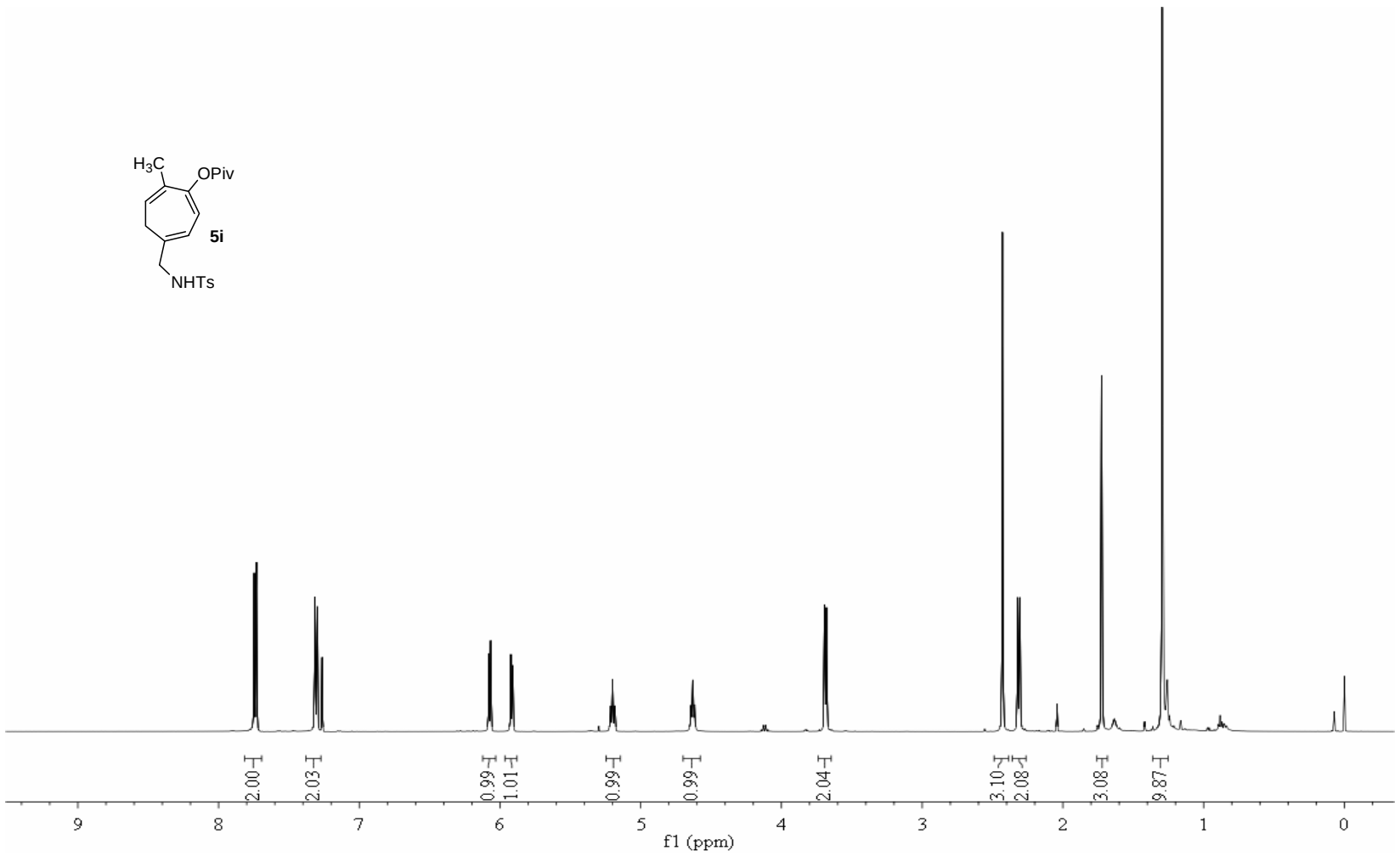

176.925
152.012
133.785
130.810
120.288
119.979
118.916
77.318
77.000
76.683
75.238
57.715
38.894
28.680
27.135
17.678
CH3
OPiv
MeO
5f
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

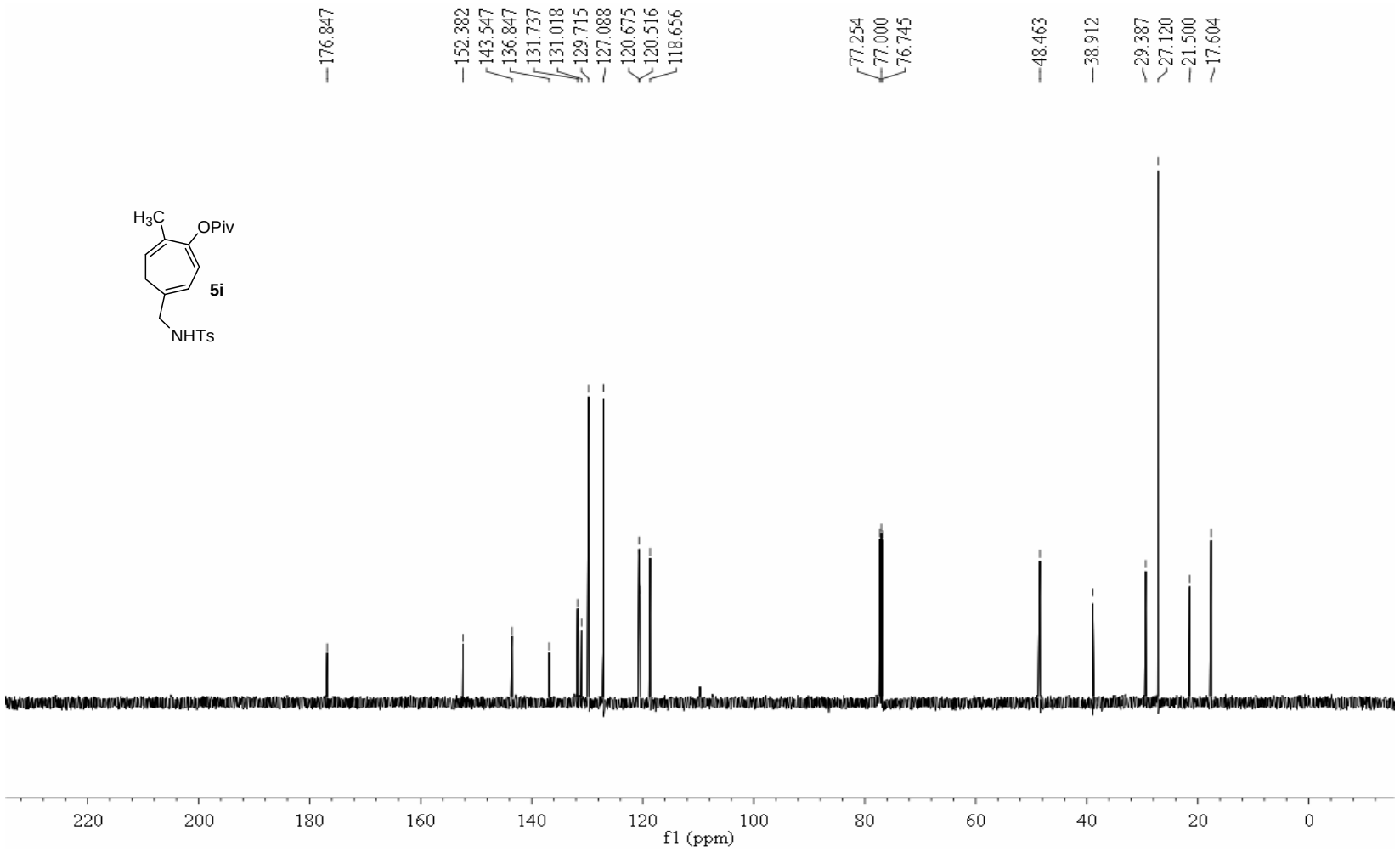

CH3
OPiv
PhO
5g
2.15
3.12
1.95
0.99
2.00
1.97
3.10
9.37
8
7
6
5
4
3
2
1
0
f1 (ppm)

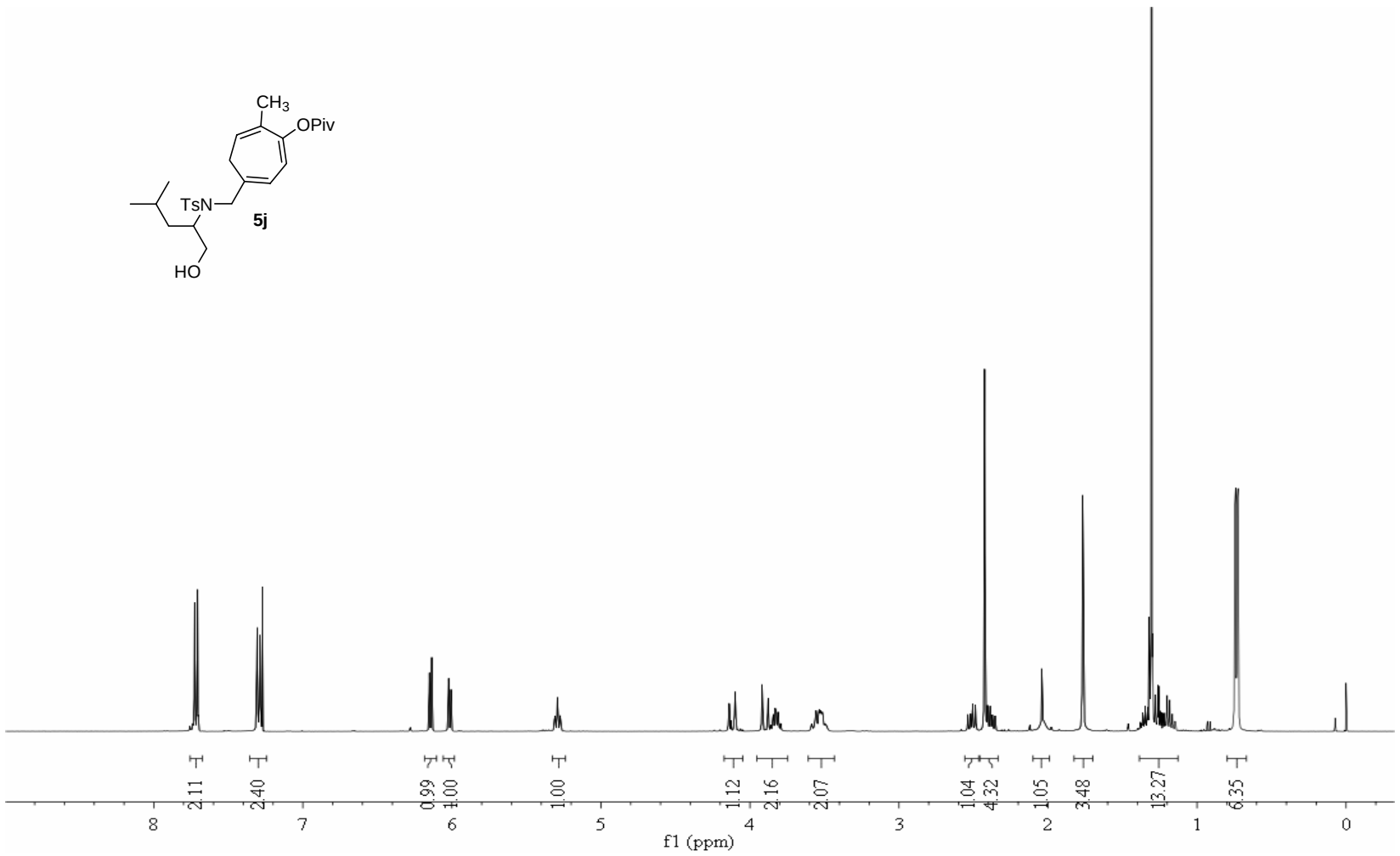

176.887
158.583
152.185
132.237
131.010
129.380
120.939
120.216
120.093
118.916
114.897
77.318
77.000
76.682
70.520
38.909
28.692
27.143
17.692
CH3
OPiv
PhO
5g
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

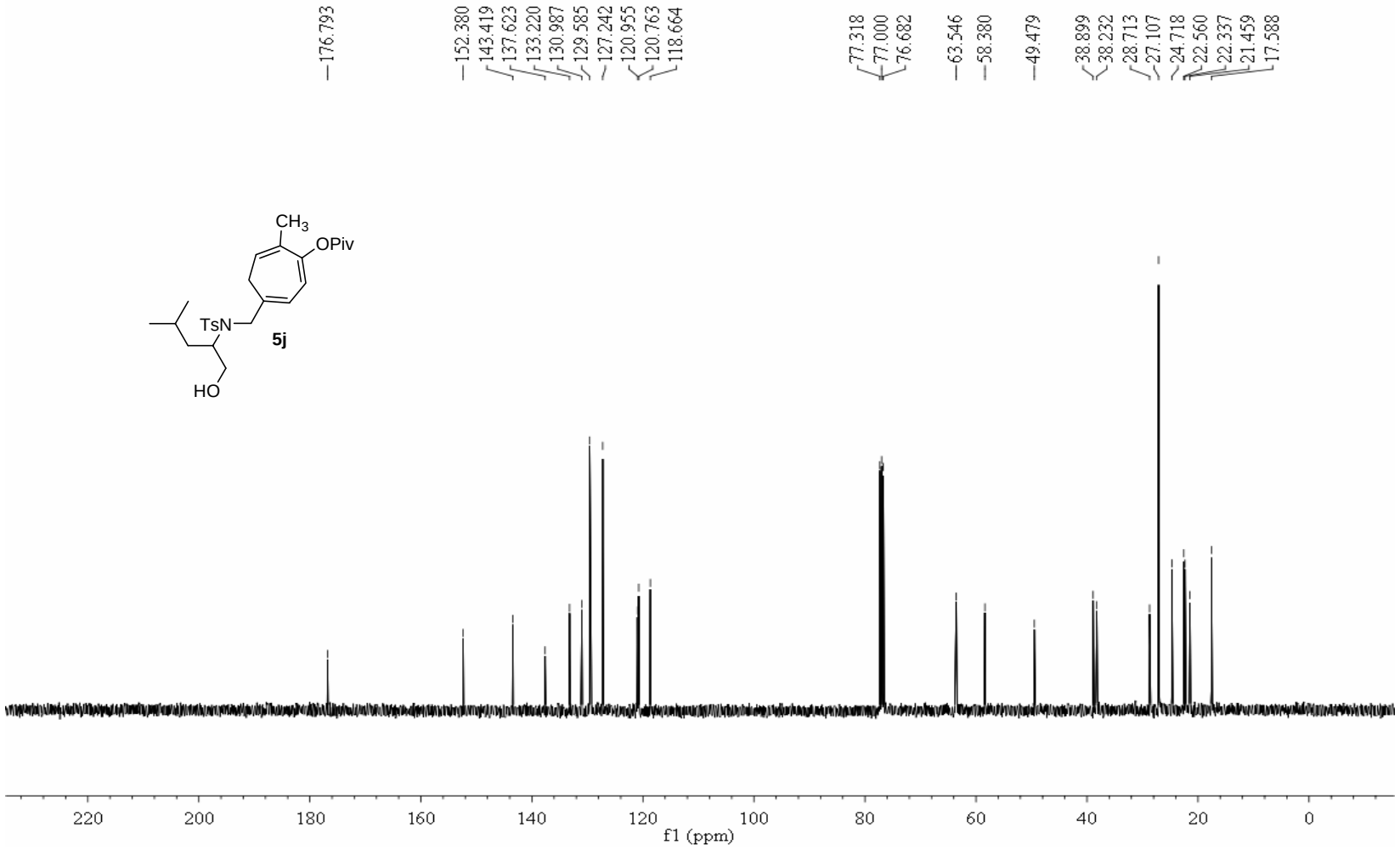

CH3
OPiv
O
5h
CHO
0.92
1.00
1.09
1.07
1.06
1.98
1.01
2.09
2.06
3.18
10.01
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

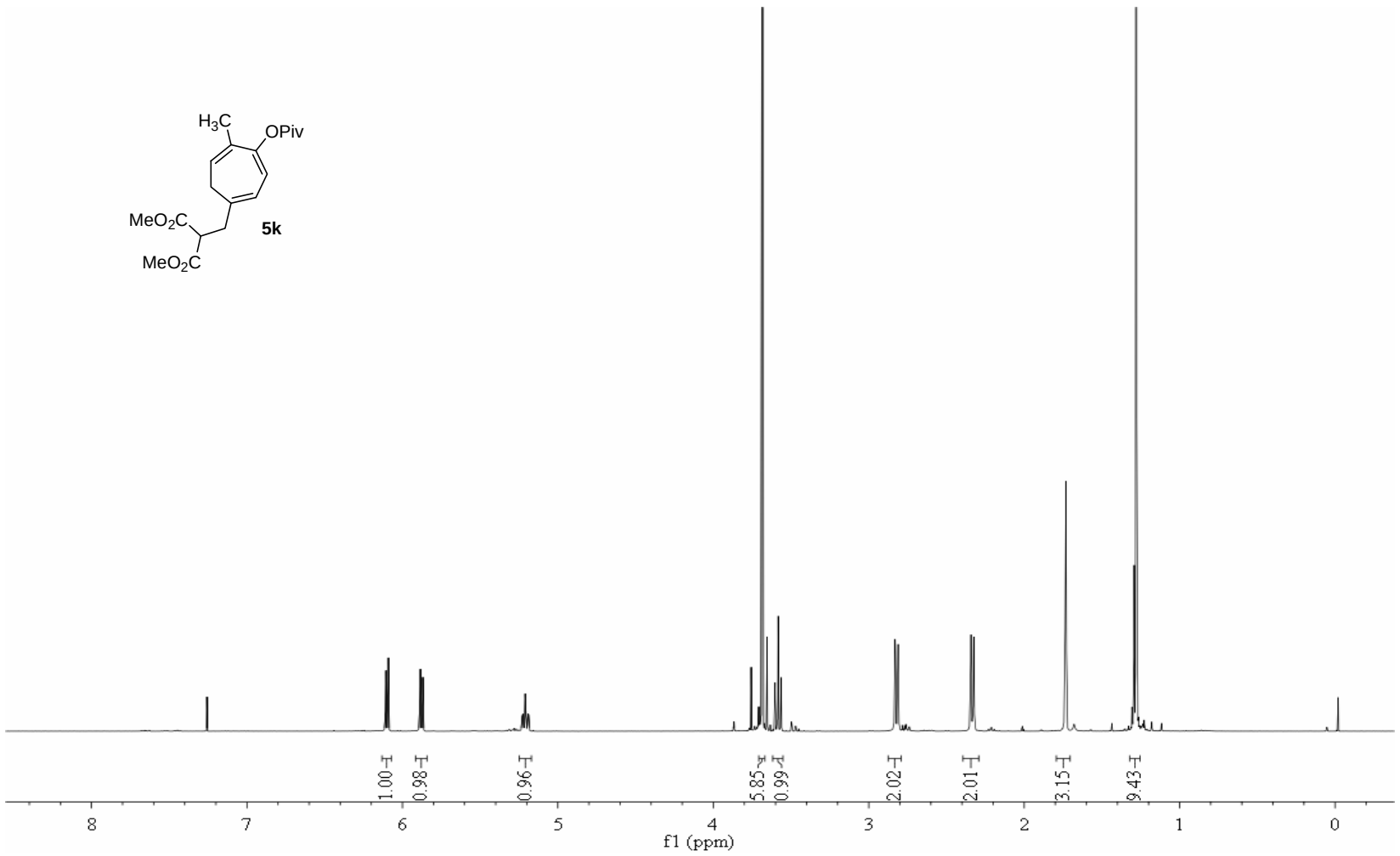

189.513
176.866
160.849
152.555
135.811
131.307
130.978
128.422
125.015
120.960
120.761
120.099
118.765
112.881
77.318
77.000
76.682
71.003
38.912
28.663
27.110
17.664
CH3
OPiv
O
CHO
5h
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

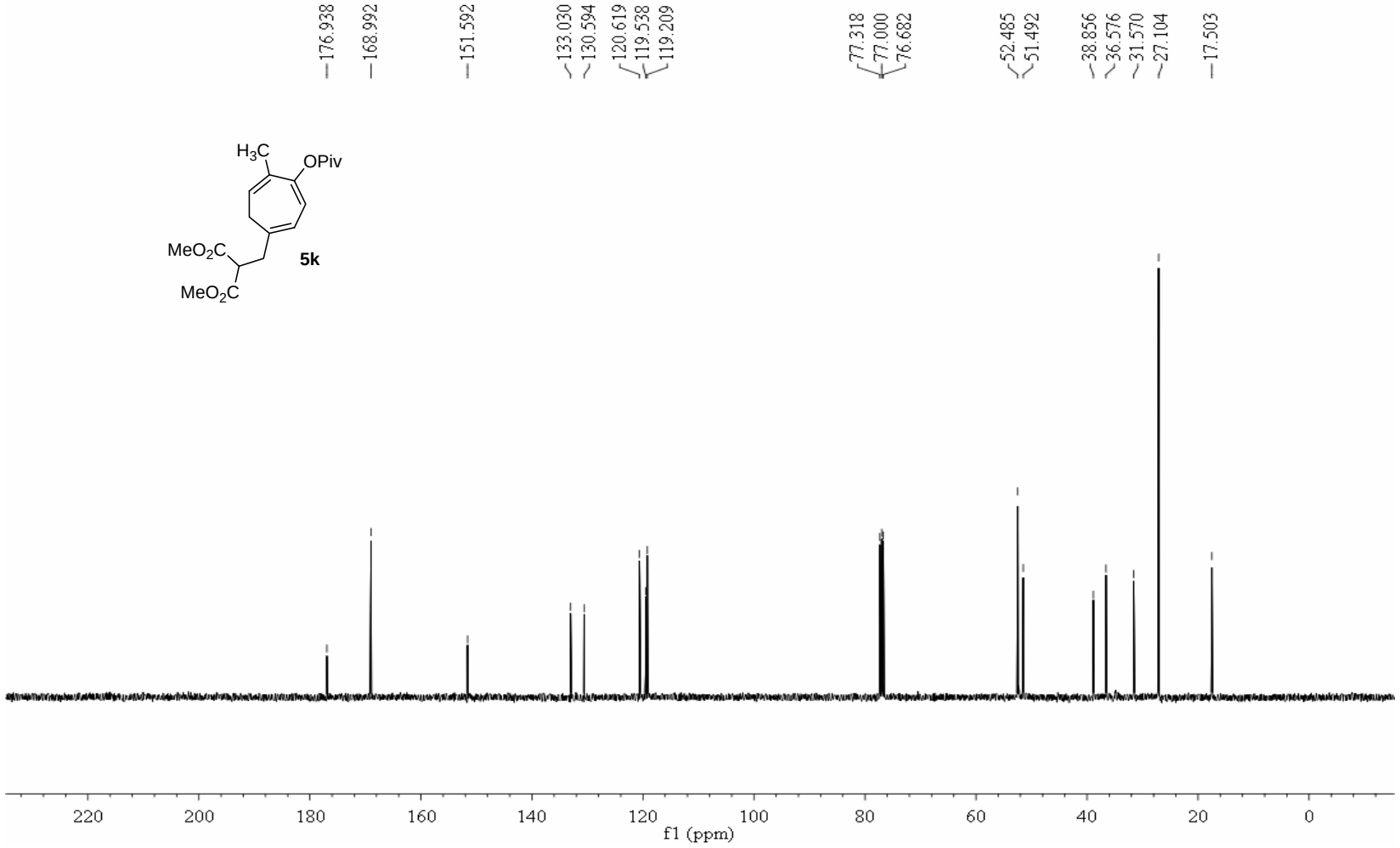

H3C
OPiv
5i
NHTs
2.00
2.03
0.99
1.01
0.99
0.99
2.04
3.10
2.08
3.08
9.87
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

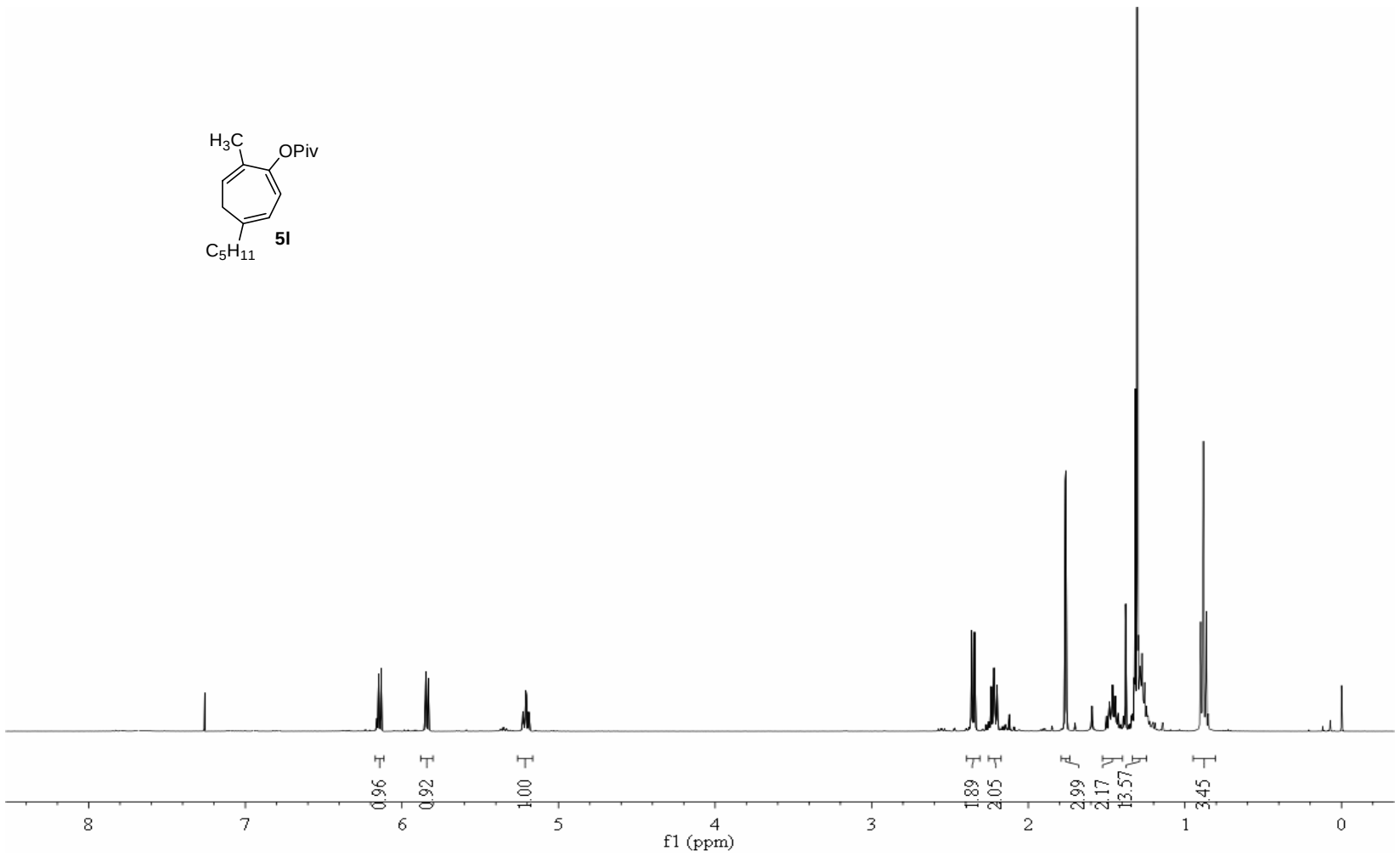

176.847
152.382
143.547
136.847
131.737
131.018
129.715
127.088
120.675
120.516
118.656
77.254
77.000
76.745
48.463
38.912
29.387
27.120
21.500
17.604
H3C
OPiv
5i
NHTs
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

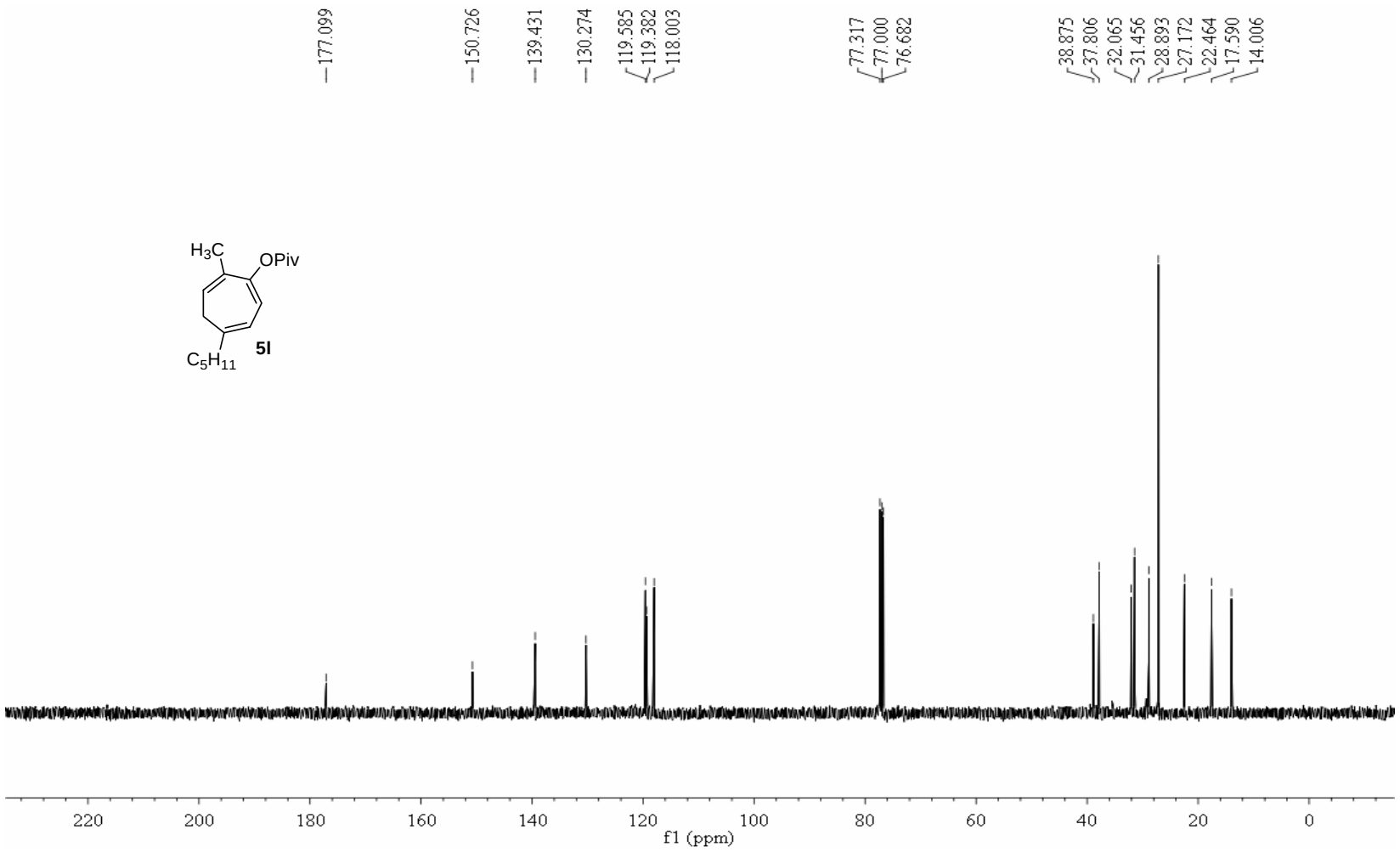

CH3
OPiv
TsN
5j
HO
2.11
2.40
0.99
1.00
1.00
1.12
2.16
2.07
1.04
4.32
1.05
3.48
13.27
6.35
8
7
6
5
4
3
2
1
0
f1 (ppm)

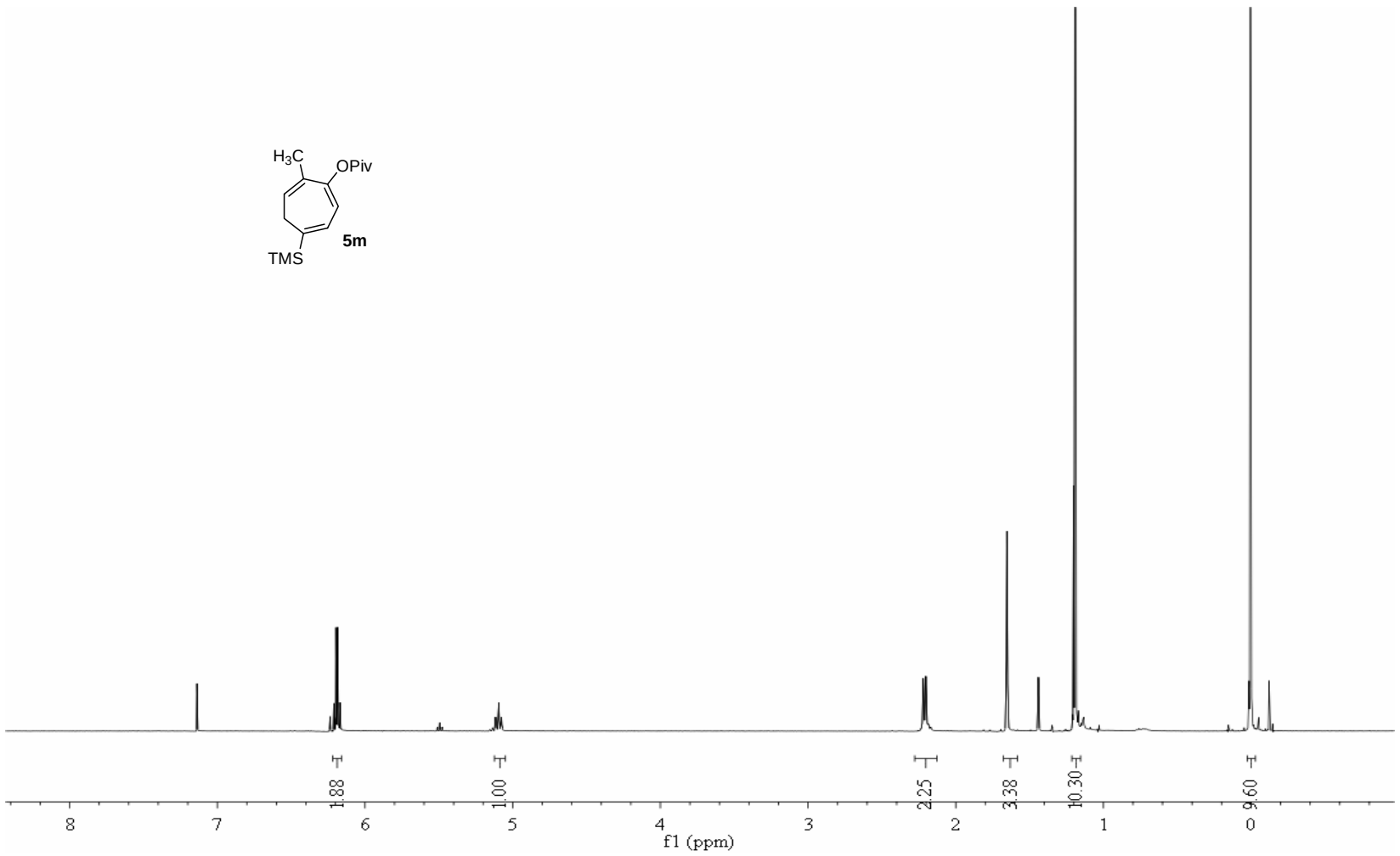

176.793
152.380
143.419
137.623
133.220
130.987
129.585
127.242
120.955
120.763
118.664
77.318
77.000
76.682
63.546
58.380
49.479
38.899
38.232
28.713
27.107
24.718
22.560
22.337
21.459
17.588
CH3
OPiv
TsN
HO
5j
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

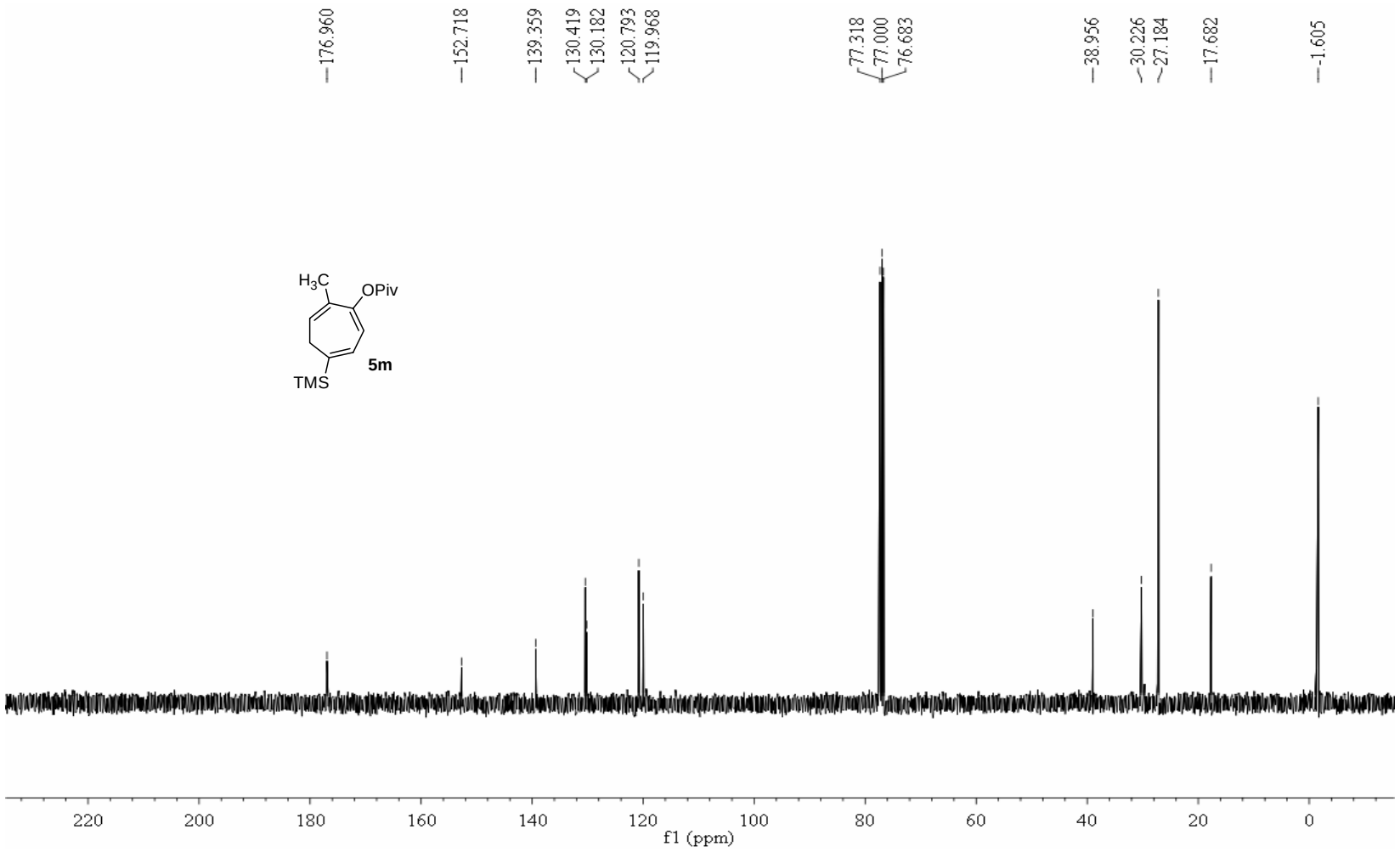

H3C
OPiv
MeO2C
MeO2C
5k
1.00
0.98
0.96
5.85
0.99
2.02
2.01
3.15
9.43
8
7
6
5
4
3
2
1
0
f1 (ppm)

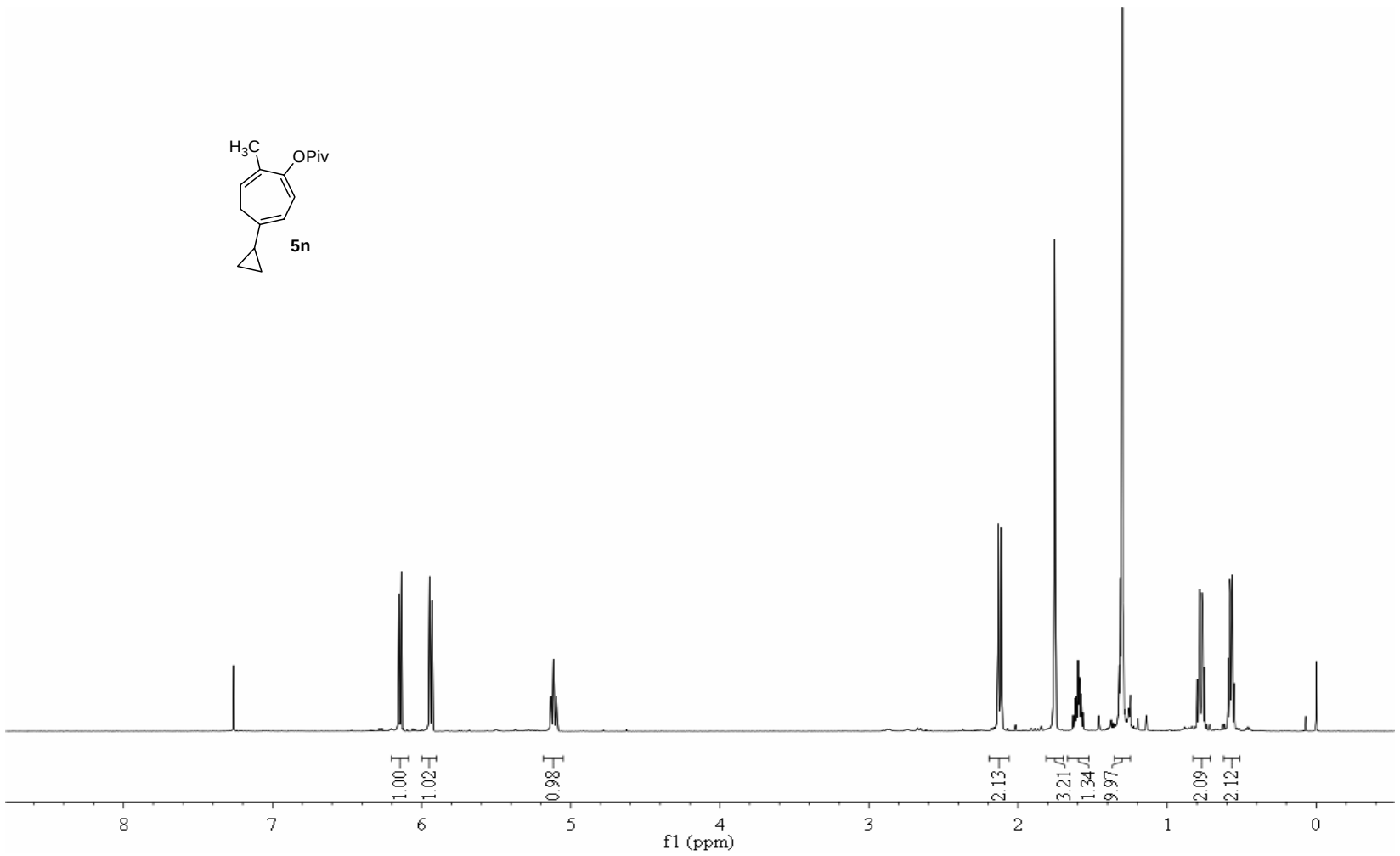

176.938
168.992
151.592
133.030
130.594
120.619
119.538
119.209
77.318
77.000
76.682
52.485
51.492
38.856
36.576
31.570
27.104
17.503
H3C
OPiv
MeO2C
MeO2C
5k
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

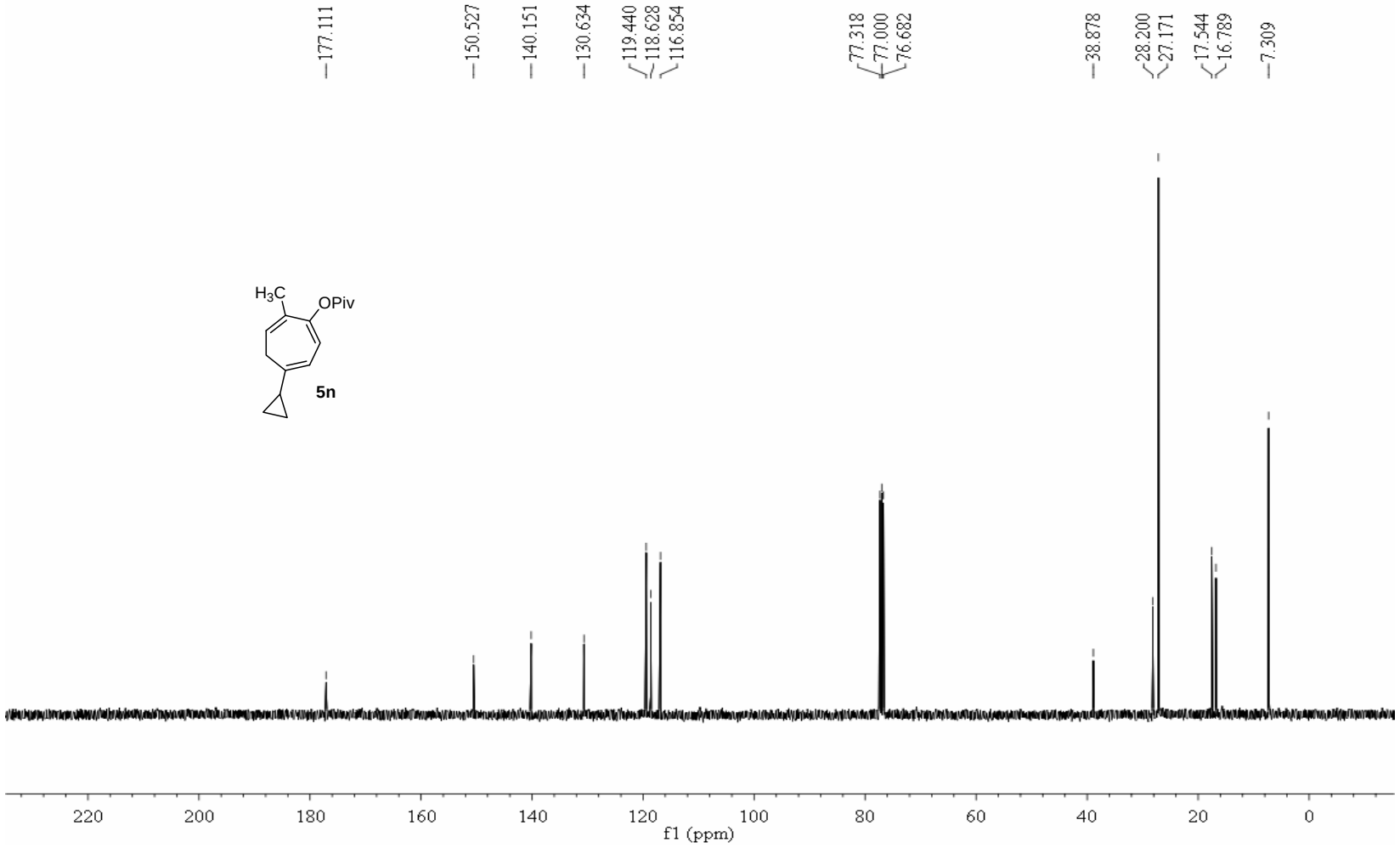

H3C
OPiv
C5H11
5l
0.96
0.92
1.00
1.89
2.05
2.99
2.17
13.57
3.45
8
7
6
5
4
3
2
1
0
f1 (ppm)

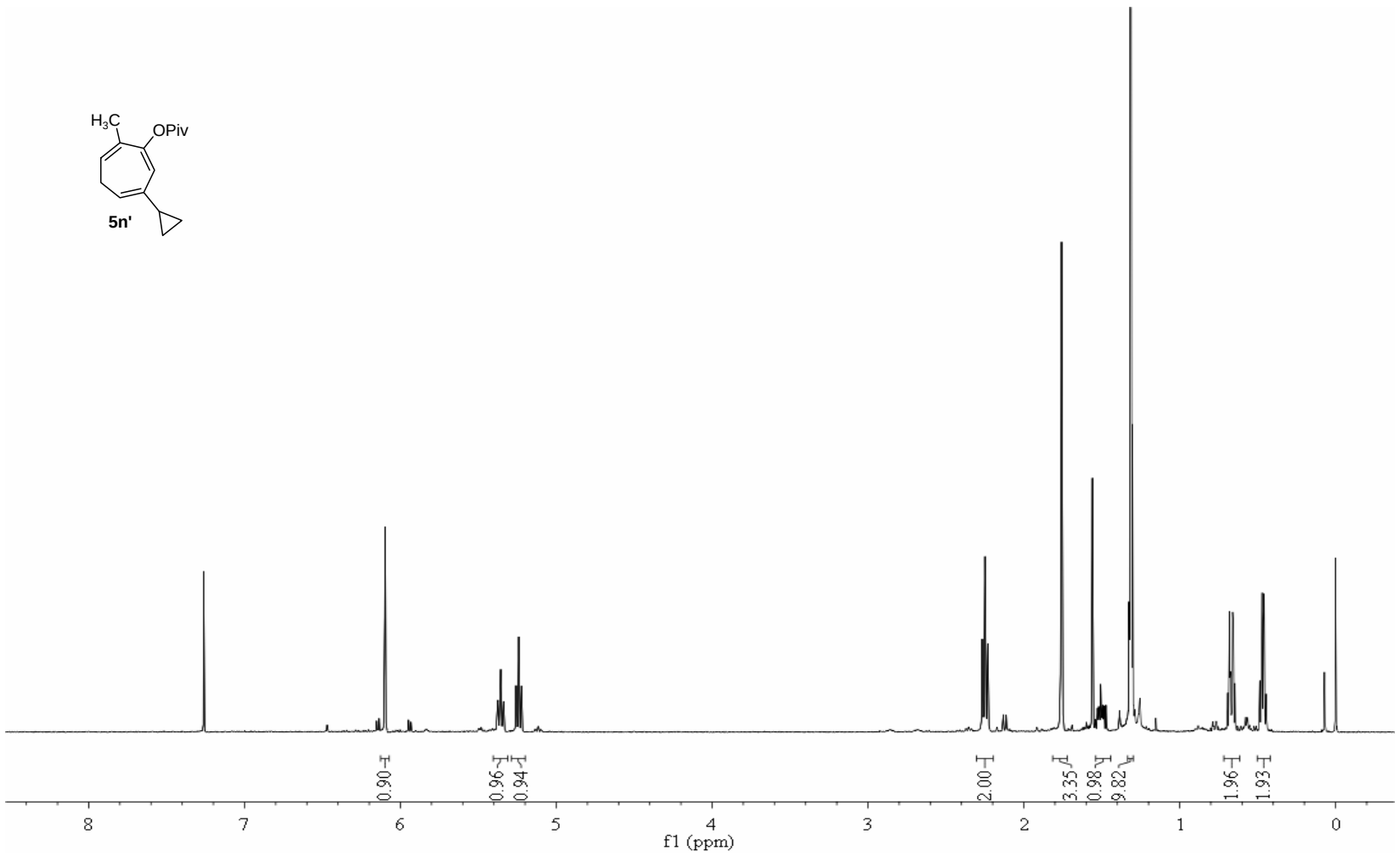

177.099
150.726
139.431
130.274
119.585
119.382
118.003
77.317
77.000
76.682
38.875
37.806
32.065
31.456
28.893
27.172
22.464
17.590
14.006
H3C
OPiv
C5H11
5l
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

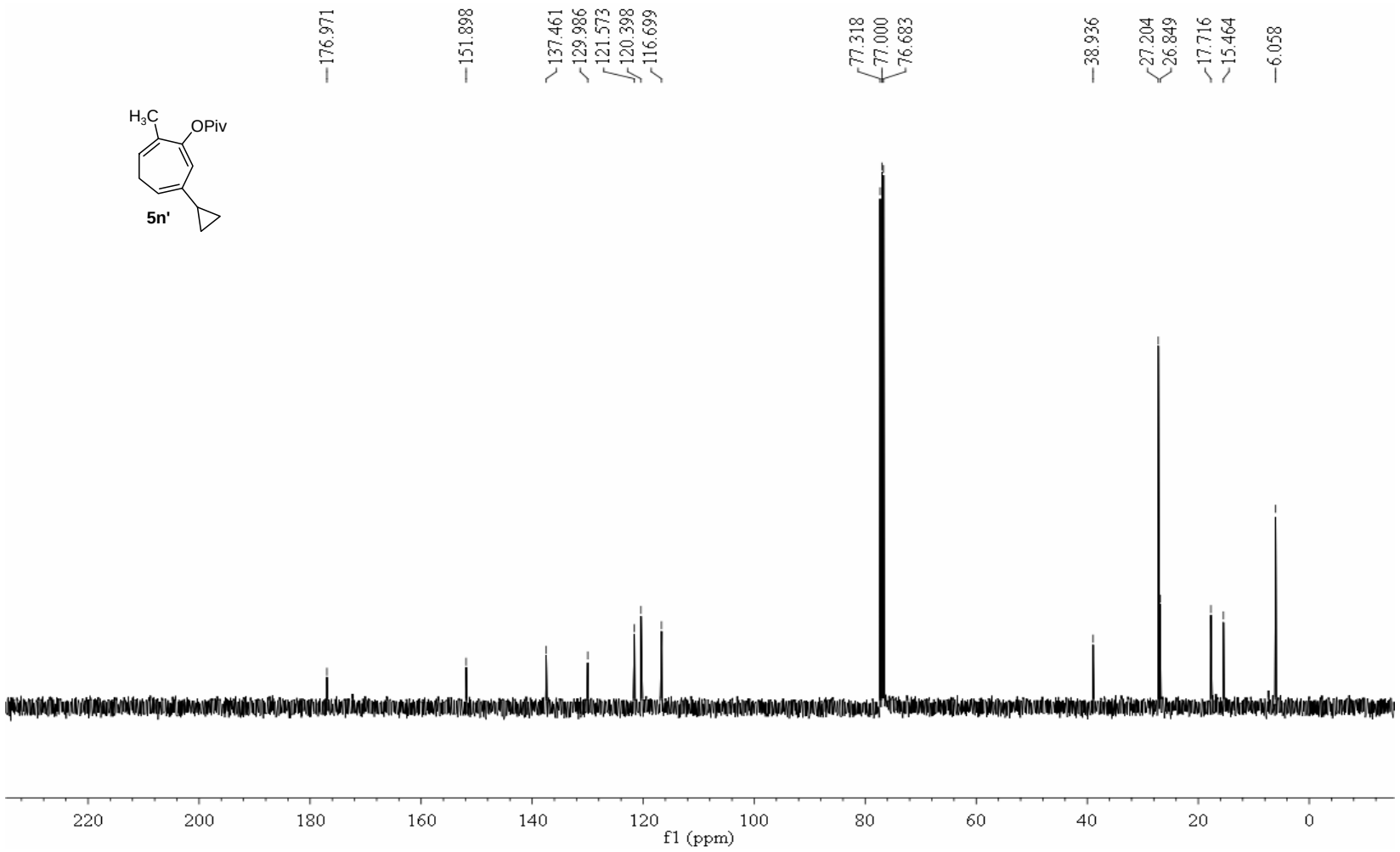

H3C
OPiv
5m
TMS
1.88
1.00
2.25
3.38
10.30
9.60
8
7
6
5
4
3
2
1
0
f1 (ppm)

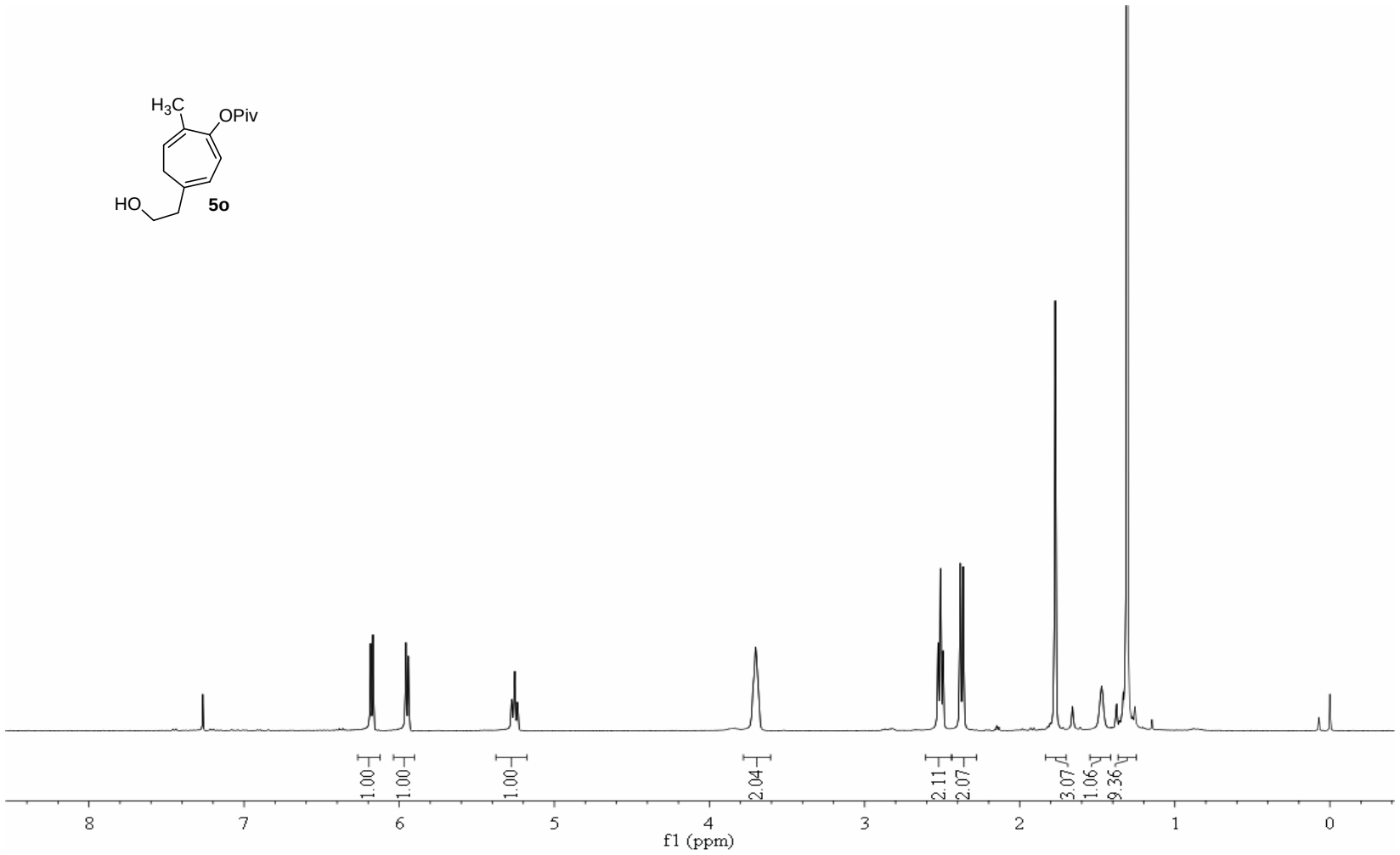

176.960
152.718
139.359
130.419
130.182
120.793
119.968
77.318
77.000
76.683
38.956
30.226
27.184
17.682
-1.605
H3C
OPiv
TMS
5m
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

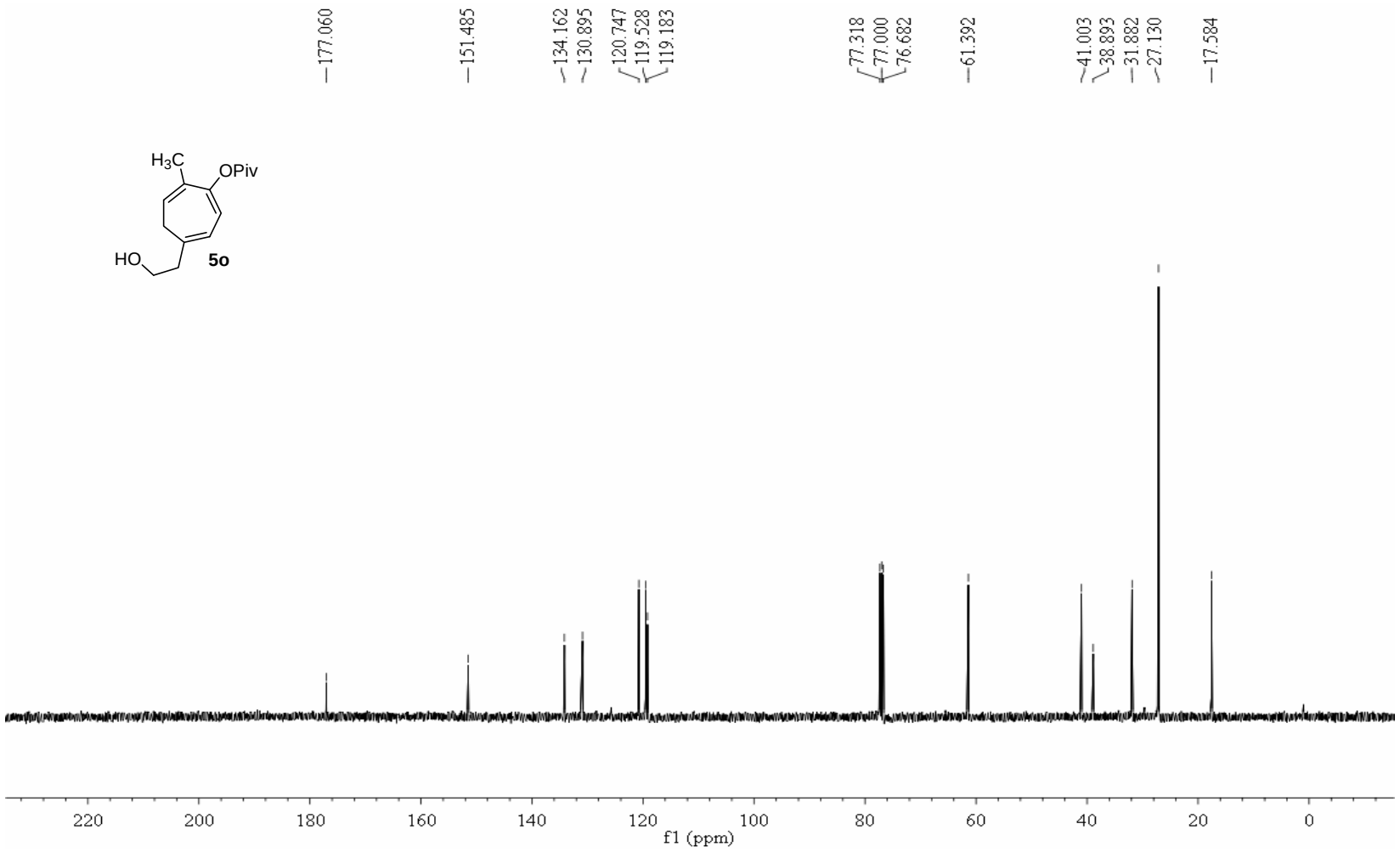

H3C
OPiv
5n
1.00
1.02
0.98
2.13
3.21
1.34
9.97
2.09
2.12
8
7
6
5
4
3
2
1
0
f1 (ppm)

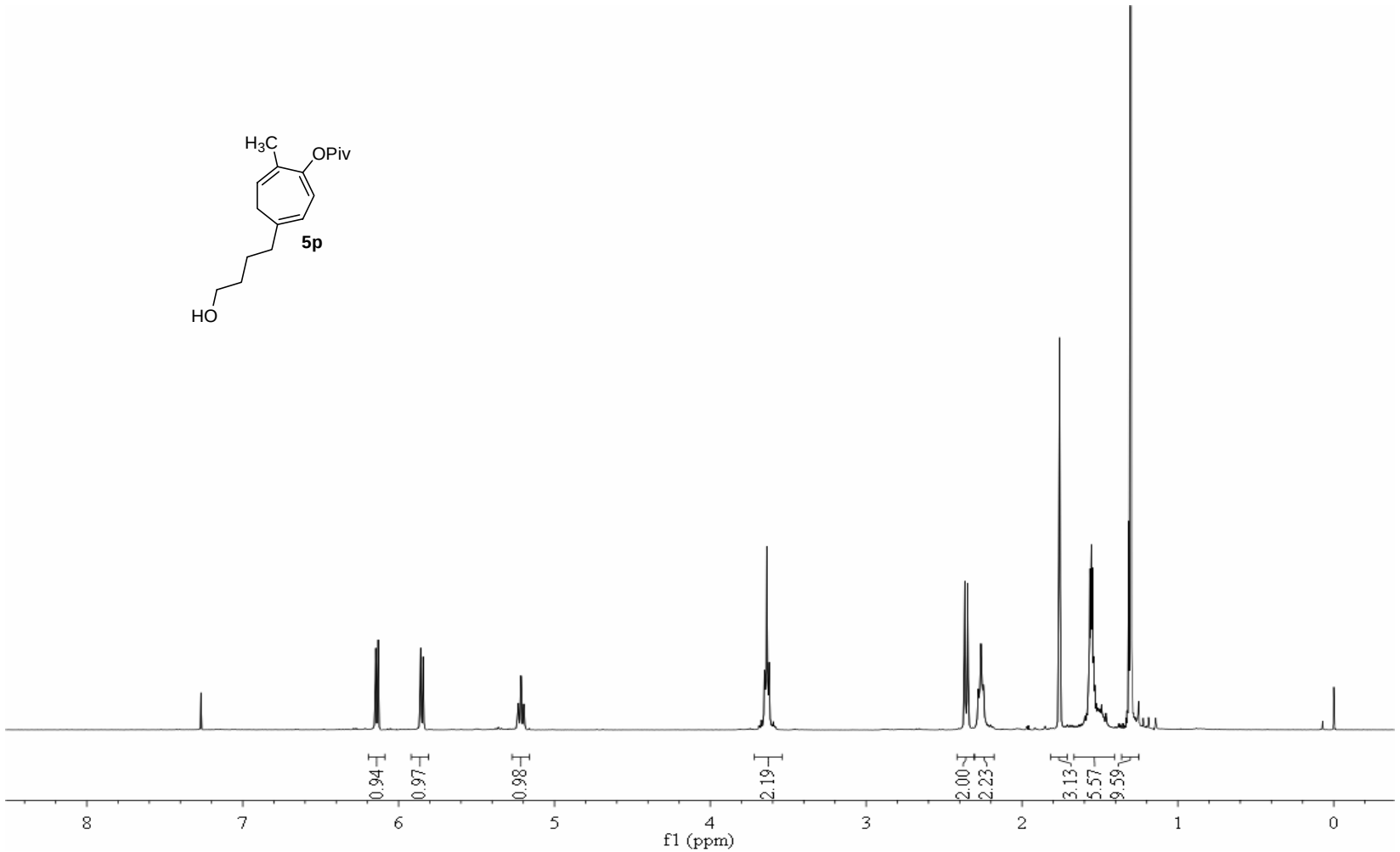

177.111
150.527
140.151
130.634
119.440
118.628
116.854
77.318
77.000
76.682
38.878
28.200
27.171
17.544
16.789
7.309
H3C
OPiv
5n
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

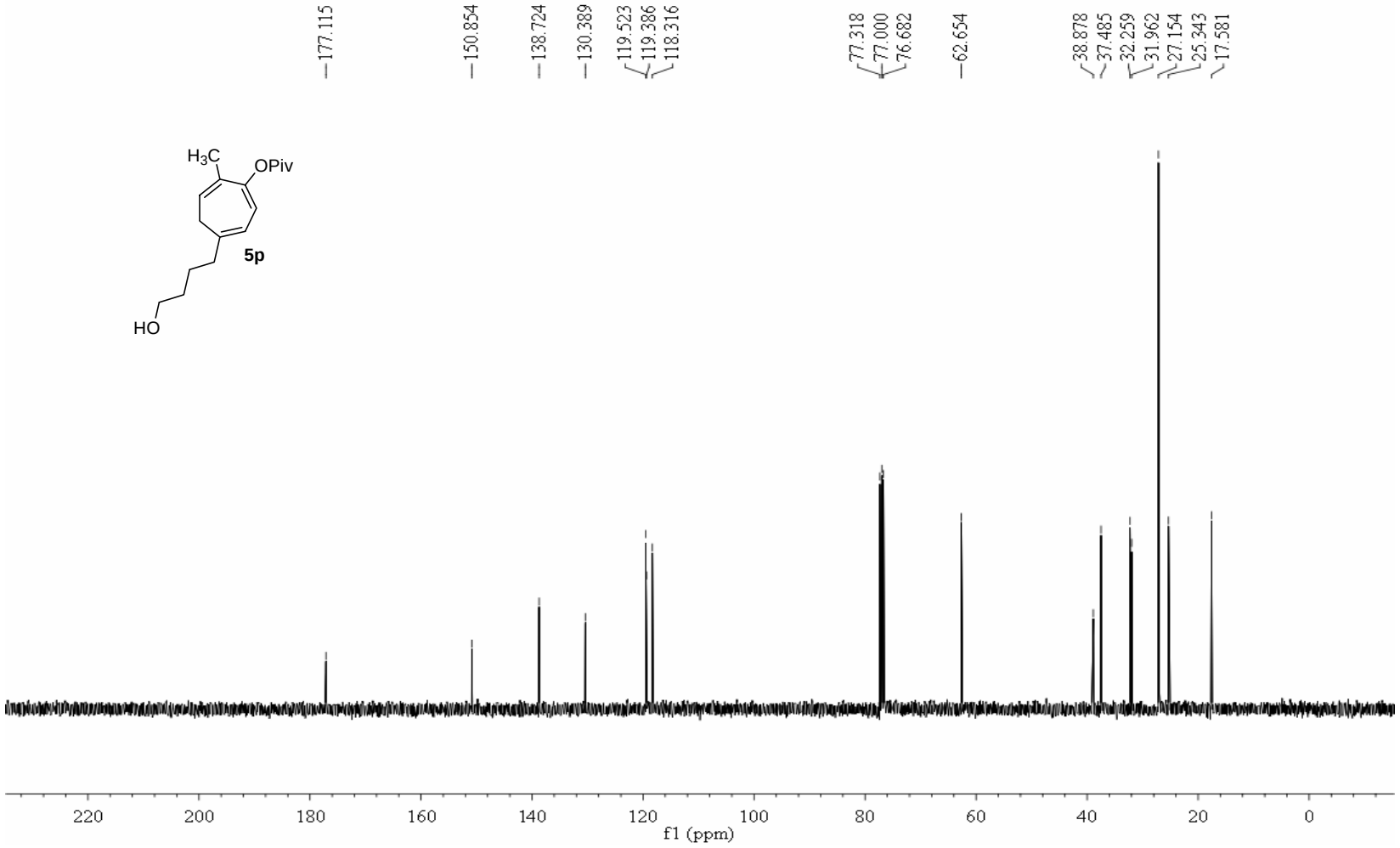

H3C
OPiv
5n'
0.90
0.96
0.94
2.00
3.35
0.98
9.82
1.96
1.93
8
7
6
5
4
3
2
1
0
f1 (ppm)

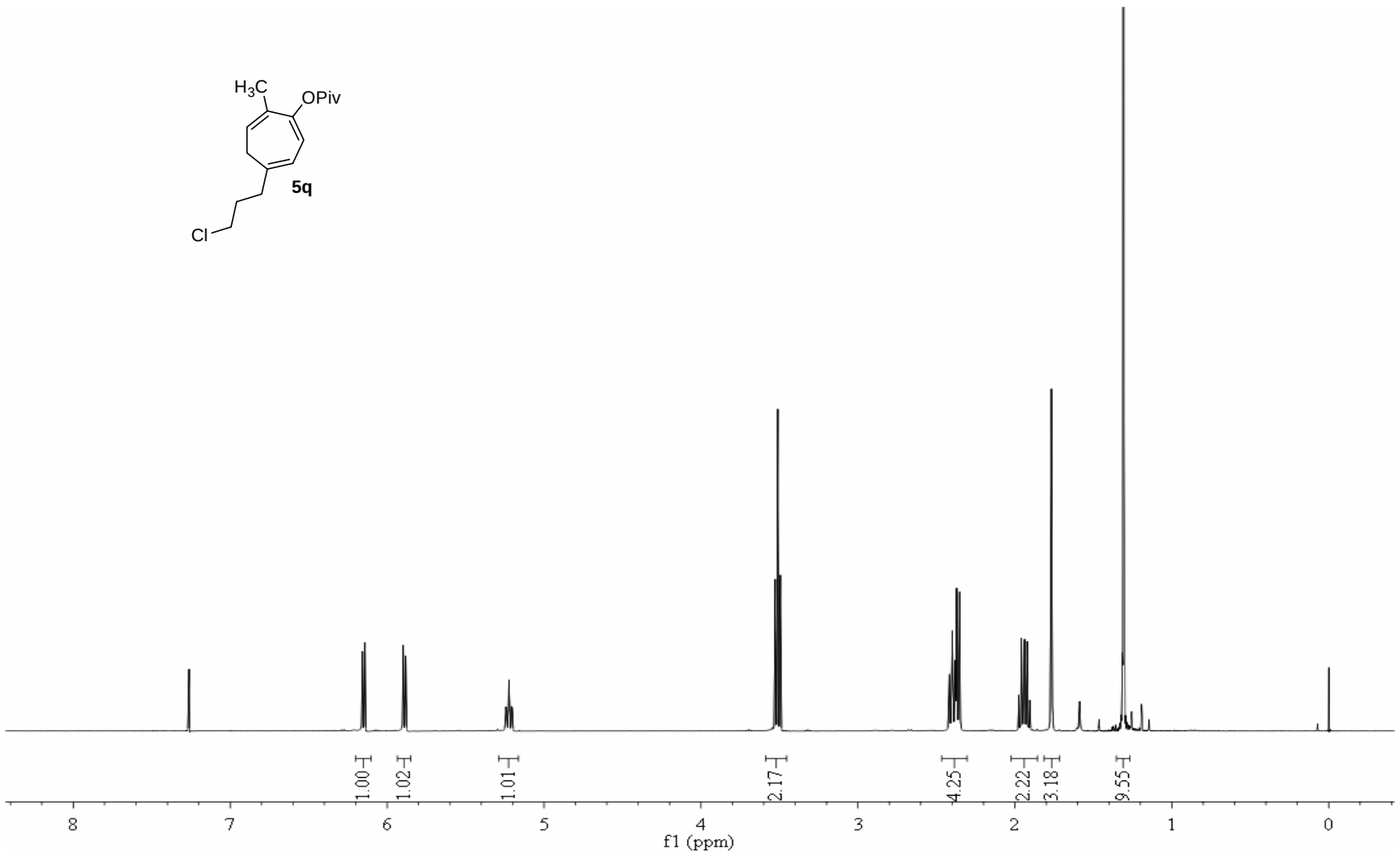

176.971
151.898
137.461
129.986
121.573
120.398
116.699
77.318
77.000
76.683
38.936
27.204
26.849
17.716
15.464
6.058
H3C
OPiv
5n'
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

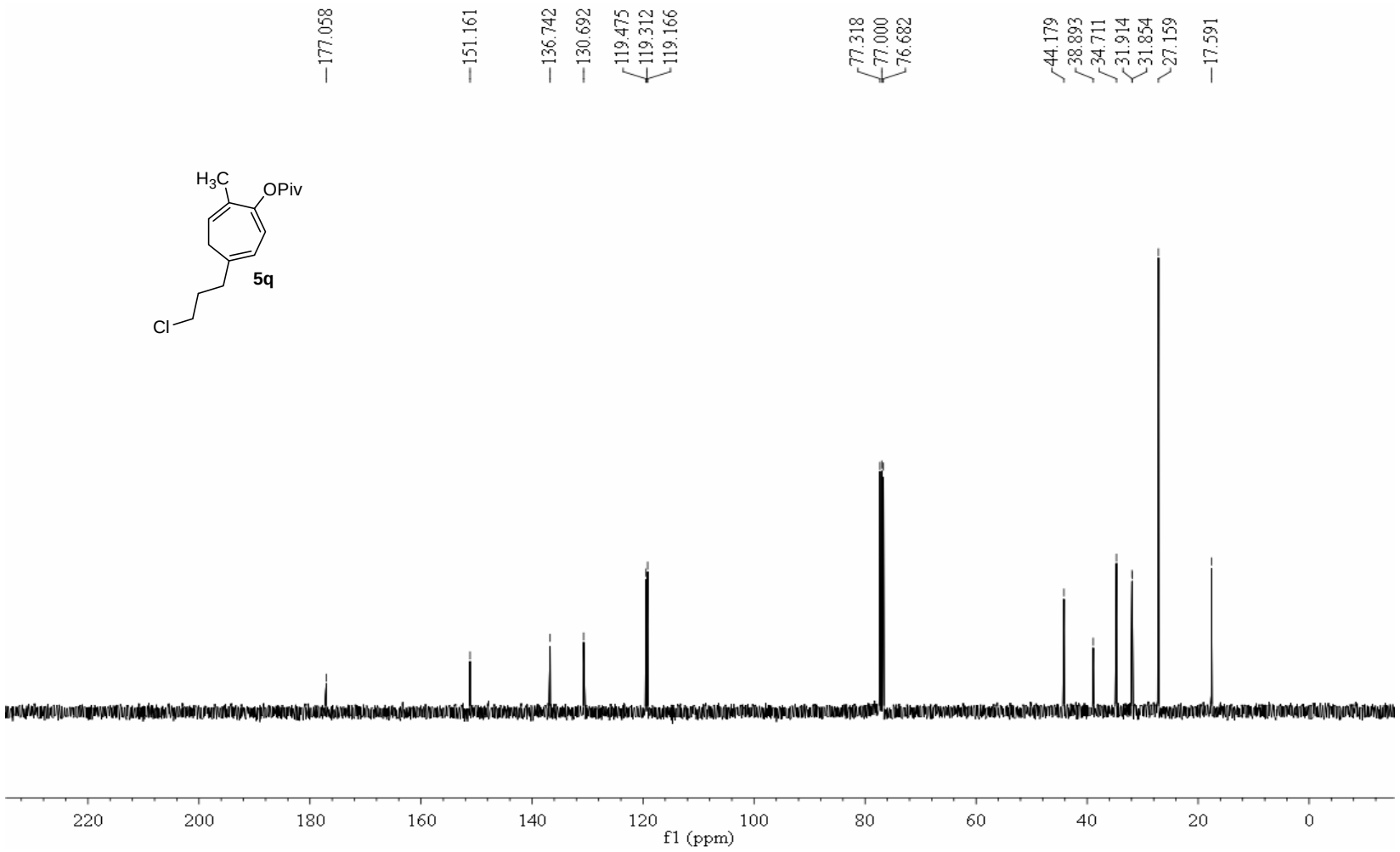

H3C
OPiv
HO
5o
1.00
1.00
1.00
2.04
2.11
2.07
3.07
1.06
9.36
8
7
6
5
4
3
2
1
0
f1 (ppm)

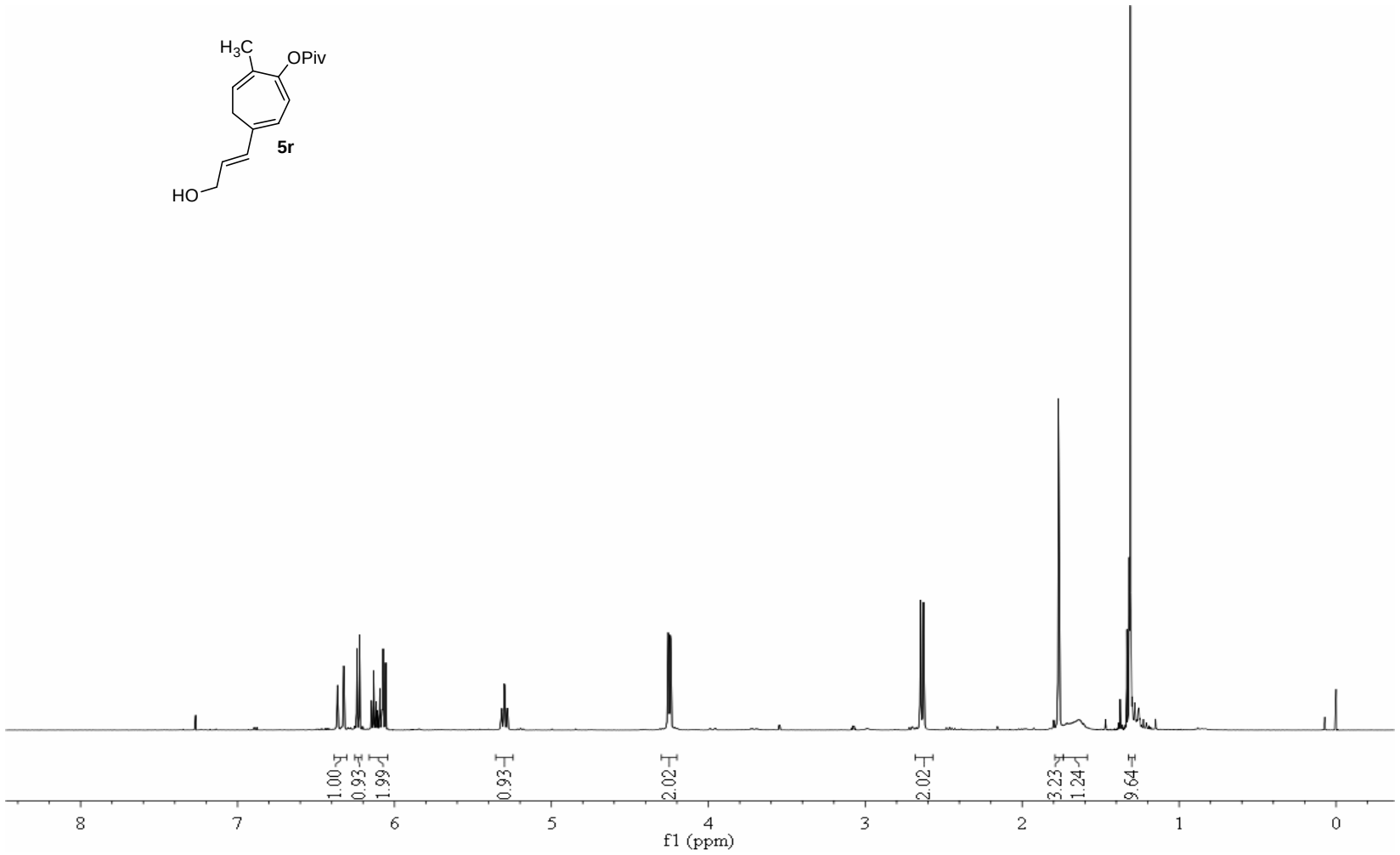

177.060
151.485
134.162
130.895
120.747
119.528
119.183
77.318
77.000
76.682
61.392
41.003
38.893
31.882
27.130
17.584
H3C
OPiv
HO
5o
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

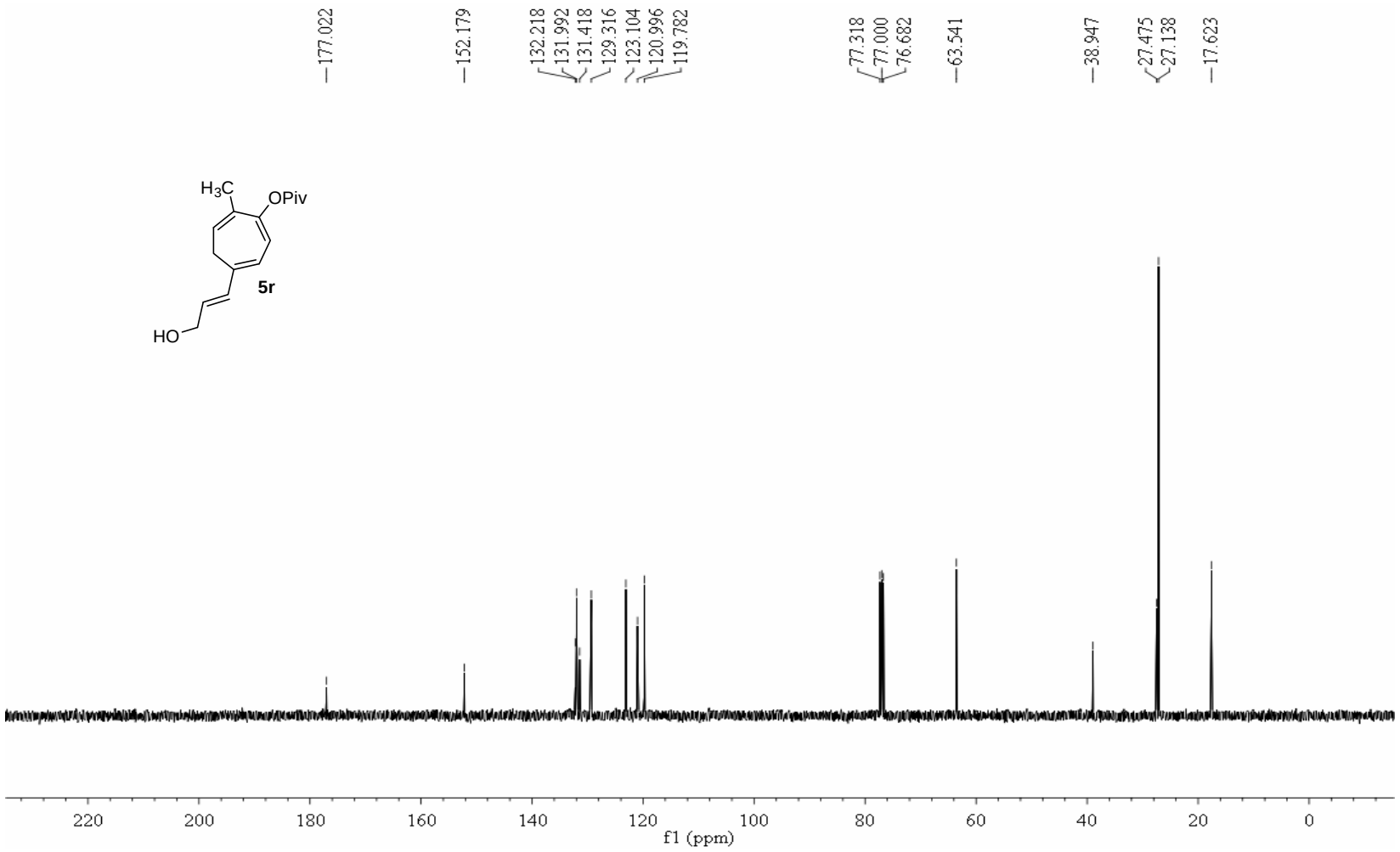

H3C
OPiv
5p
HO
0.94
0.97
0.98
2.19
2.00
2.23
3.13
5.57
9.59
8
7
6
5
4
3
2
1
0
f1 (ppm)

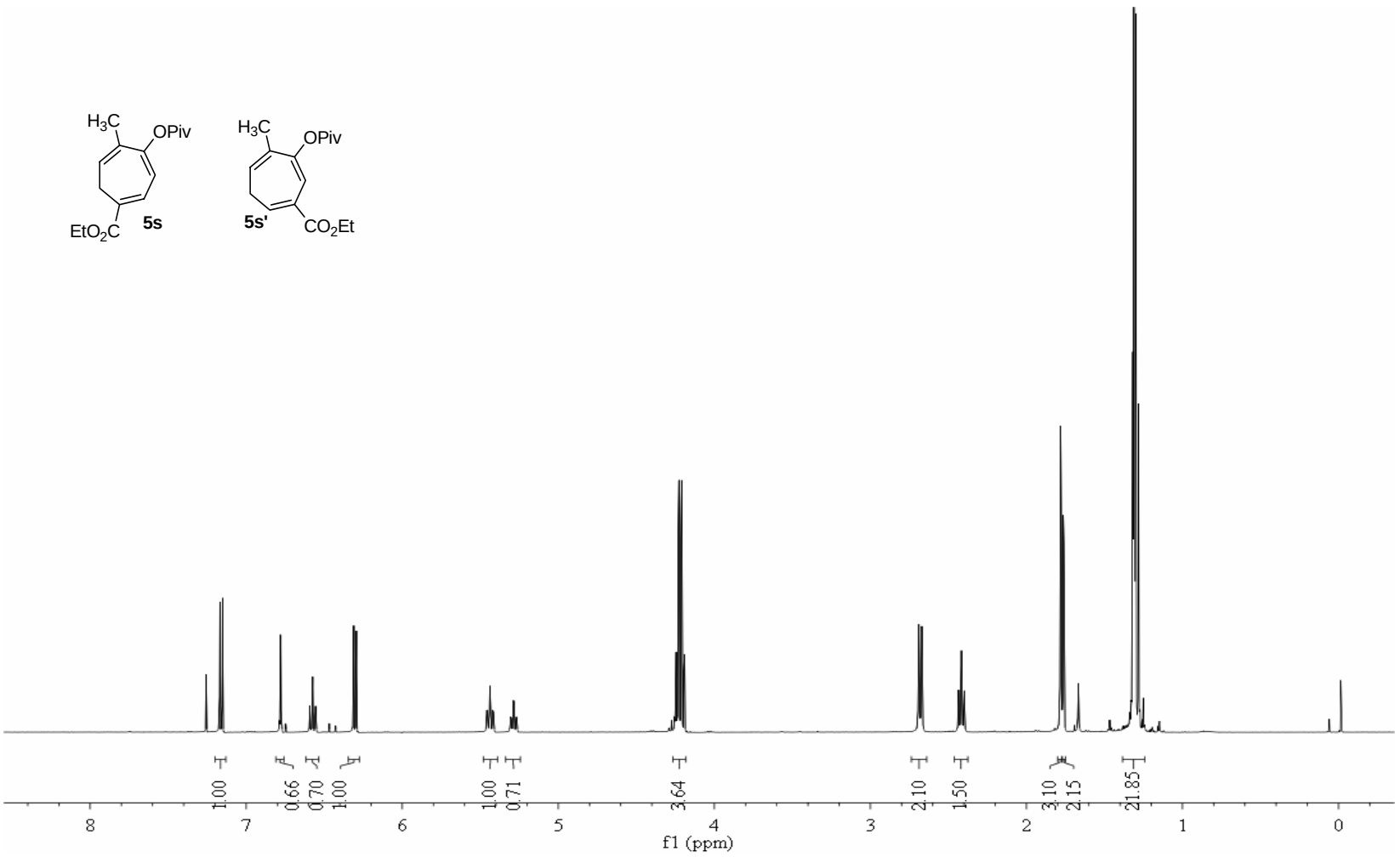

177.115
150.854
138.724
130.389
119.523
119.386
118.316
77.318
77.000
76.682
62.654
38.878
37.485
32.259
31.962
27.154
25.343
17.581
H3C
OPiv
HO
5p
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

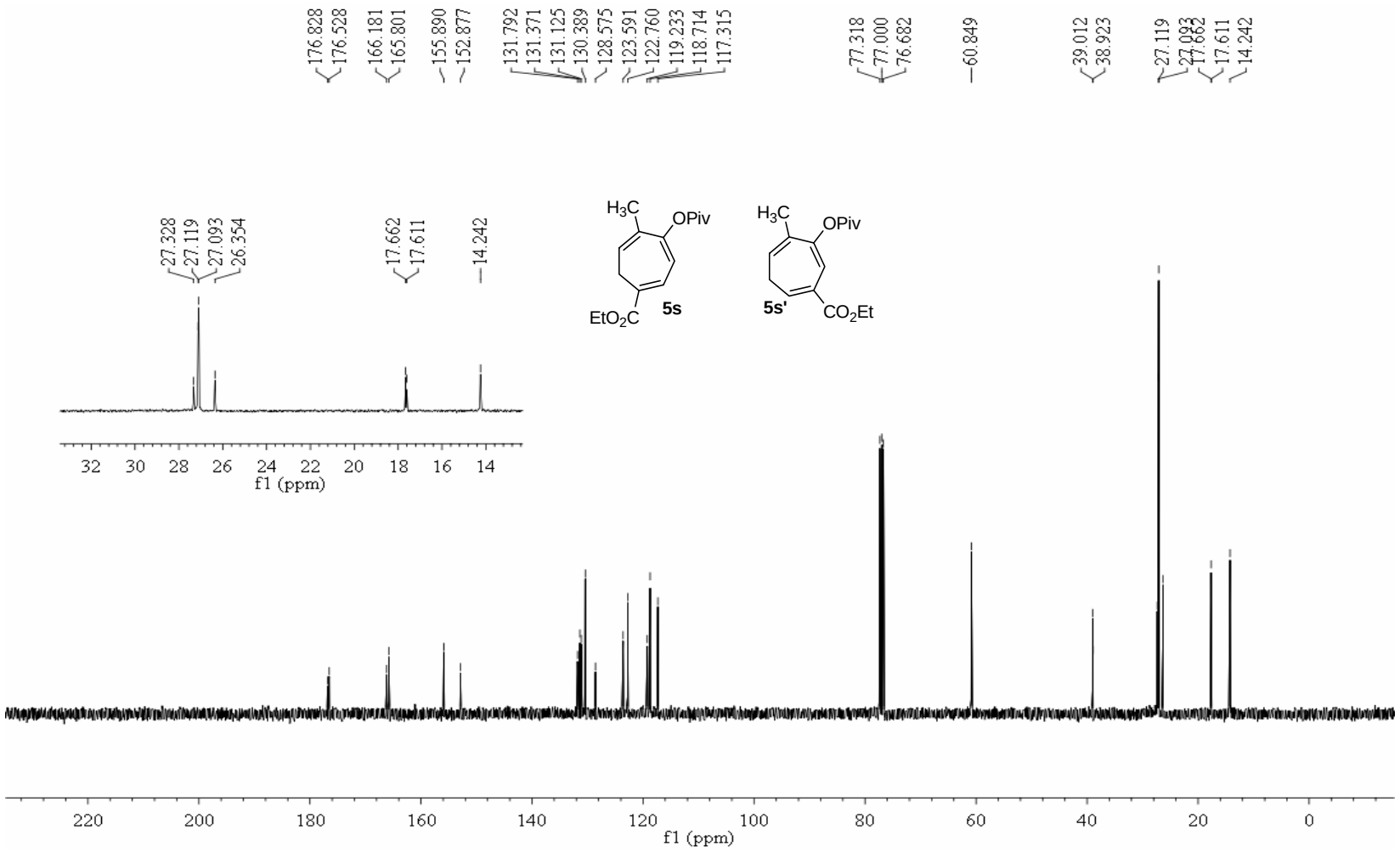

H3C
OPiv
5q
Cl
1.00
1.02
1.01
2.17
4.25
2.22
3.18
9.55
8
7
6
5
4
3
2
1
0
f1 (ppm)

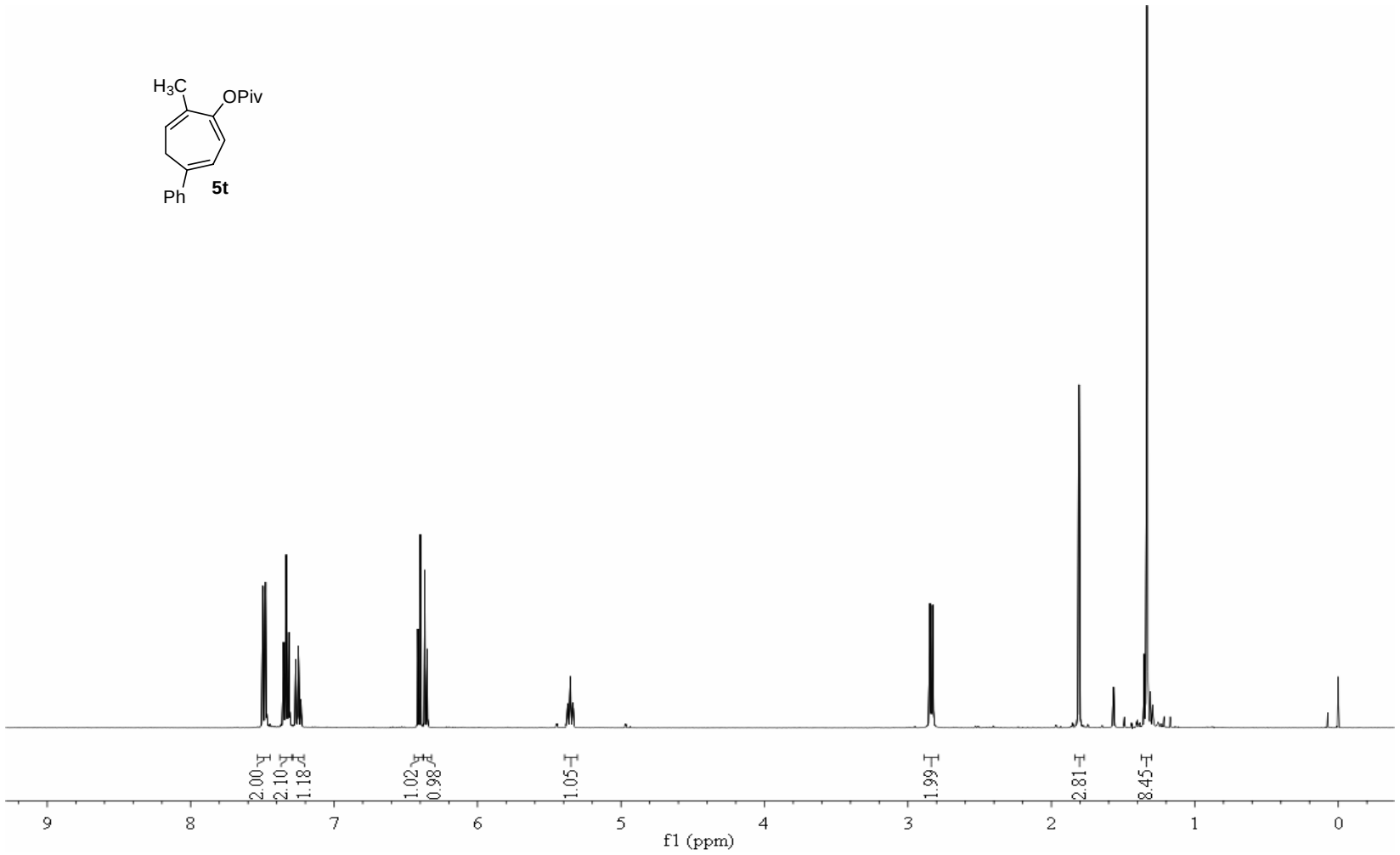

177.058
151.161
136.742
130.692
119.475
119.312
119.166
77.318
77.000
76.682
44.179
38.893
34.711
31.914
31.854
27.159
17.591
H3C
OPiv
Cl
5q
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

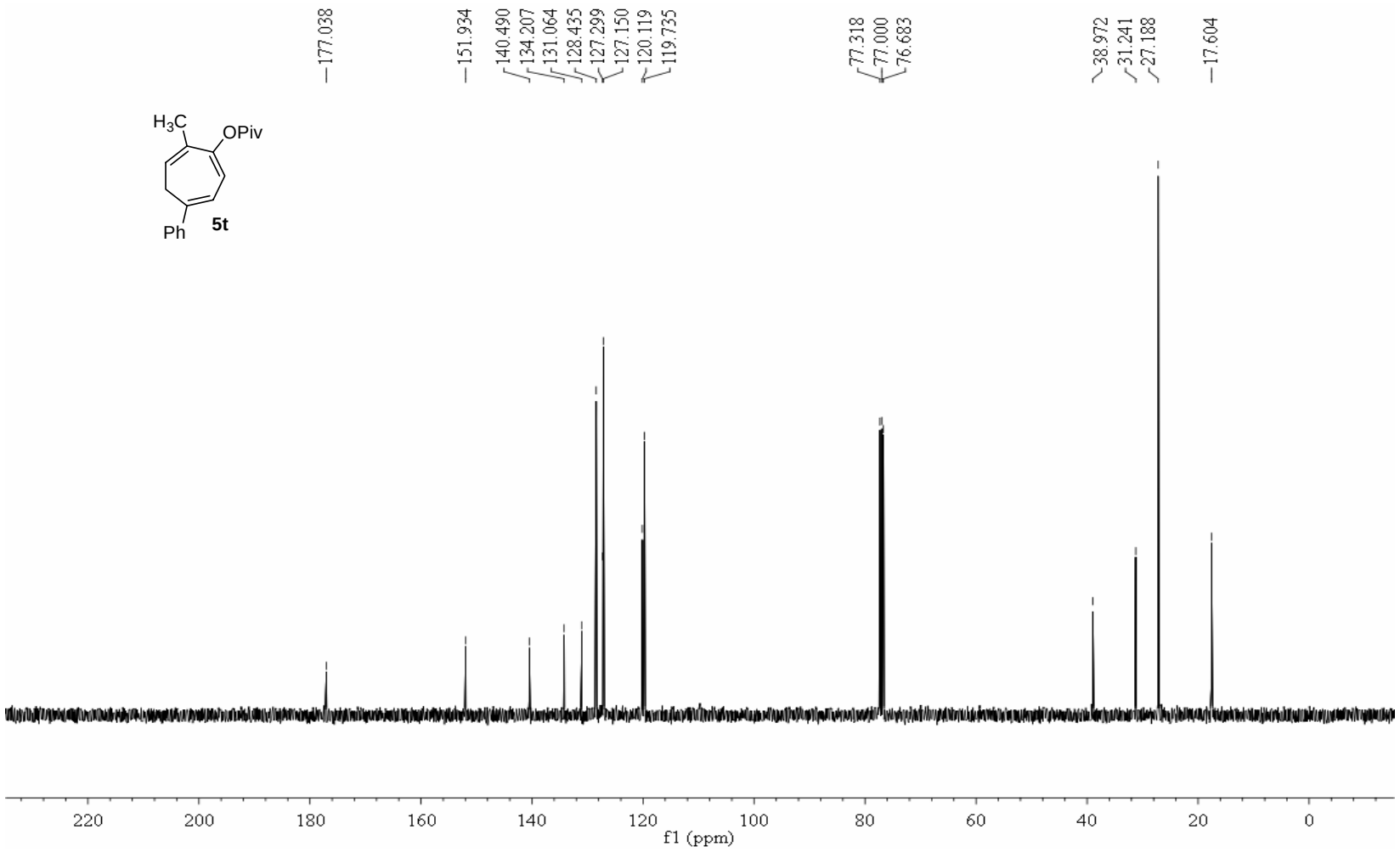

H3C
OPiv
5r
HO
1.00
0.93
1.99
0.93
2.02
2.02
3.23
1.24
9.64
8
7
6
5
4
3
2
1
0
f1 (ppm)

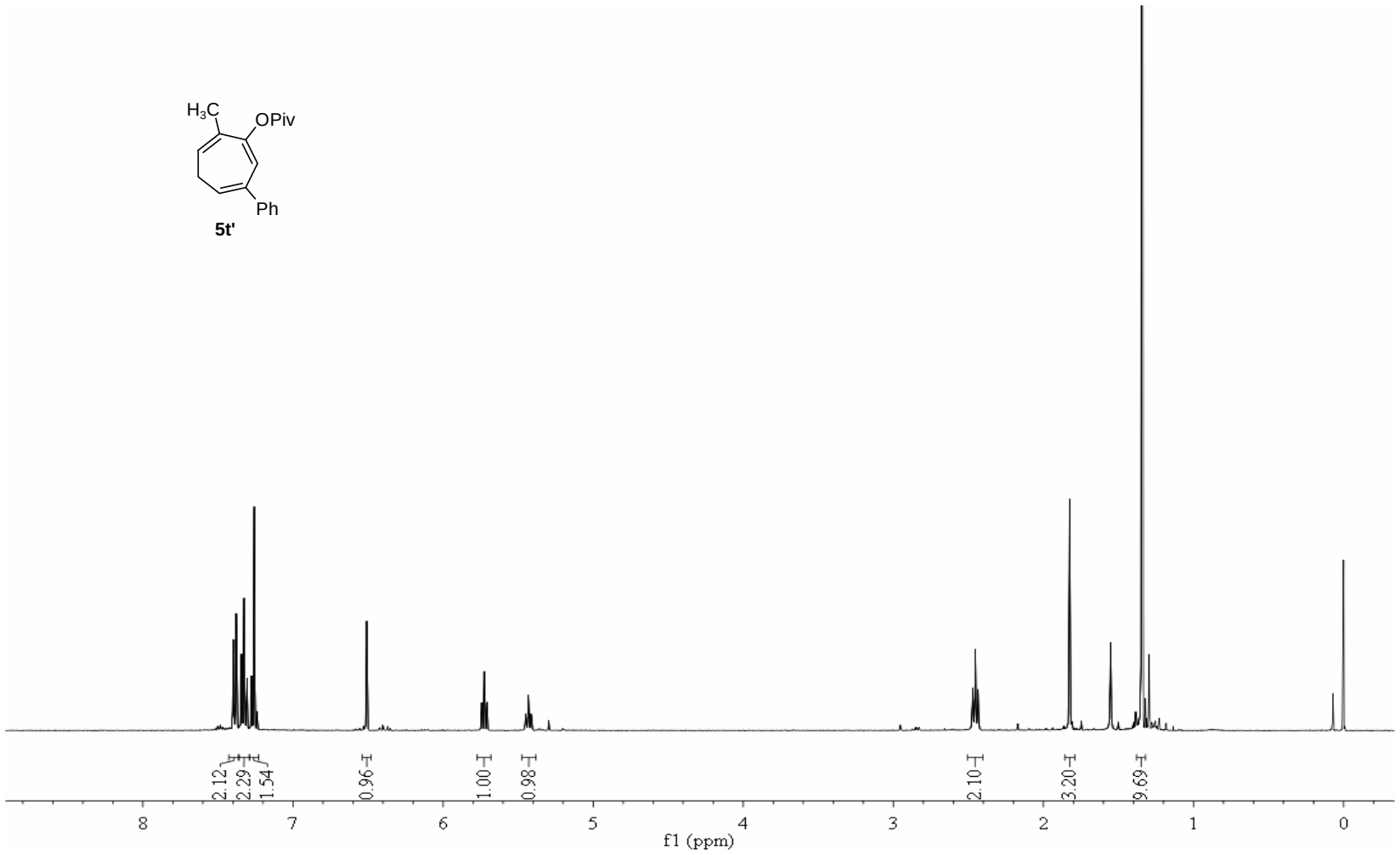

177.022
152.179
132.218
131.992
131.418
129.316
123.104
120.996
119.782
77.318
77.000
76.682
63.541
38.947
27.475
27.138
17.623
H3C
OPiv
5r
HO
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

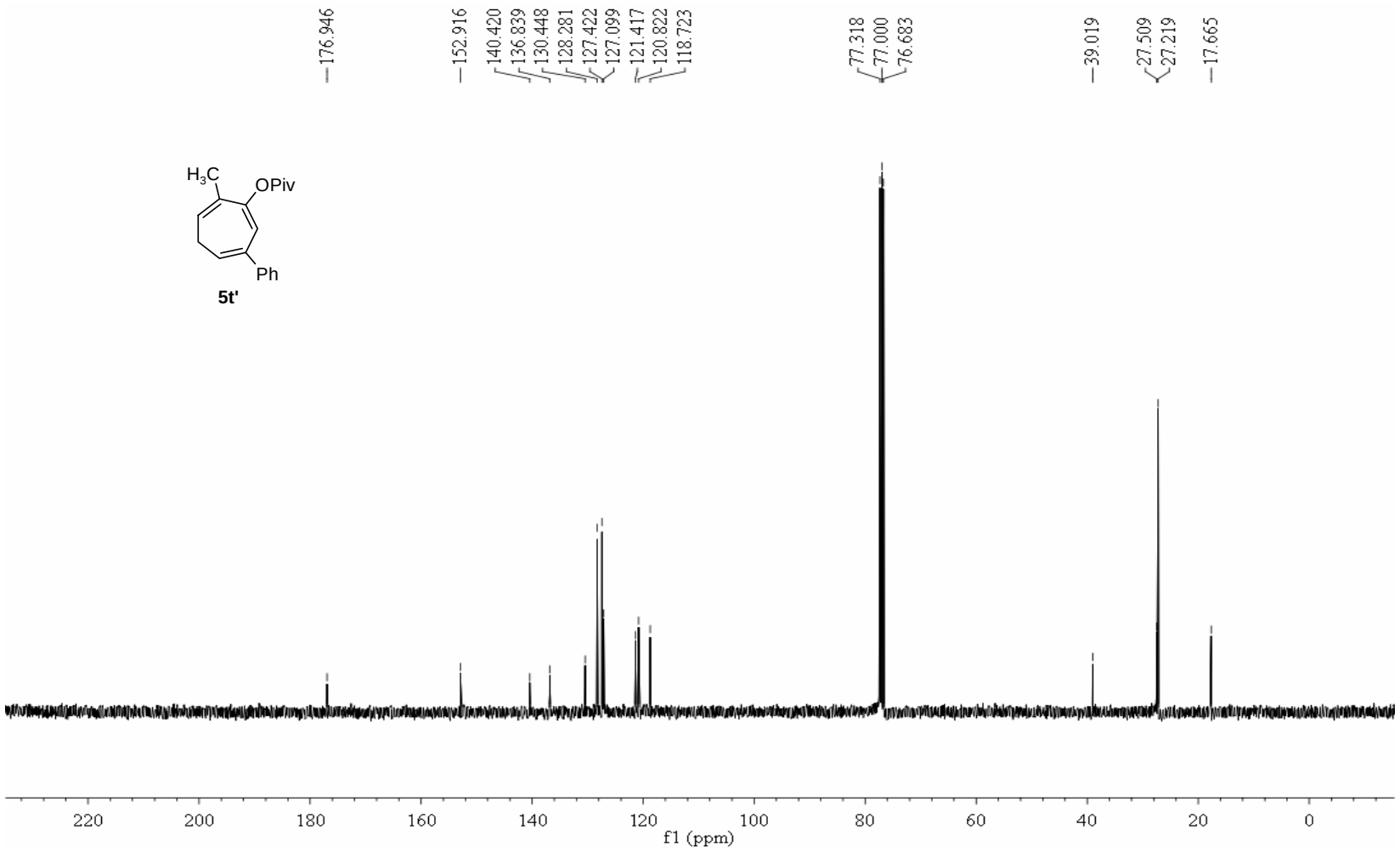

H3C
OPiv
EtO2C
5s
H3C
OPiv
5s'
CO2Et
1.00
0.66
0.70
1.00
1.00
0.71
3.64
2.10
1.50
3.10
2.15
21.85
8
7
6
5
4
3
2
1
0
f1 (ppm)

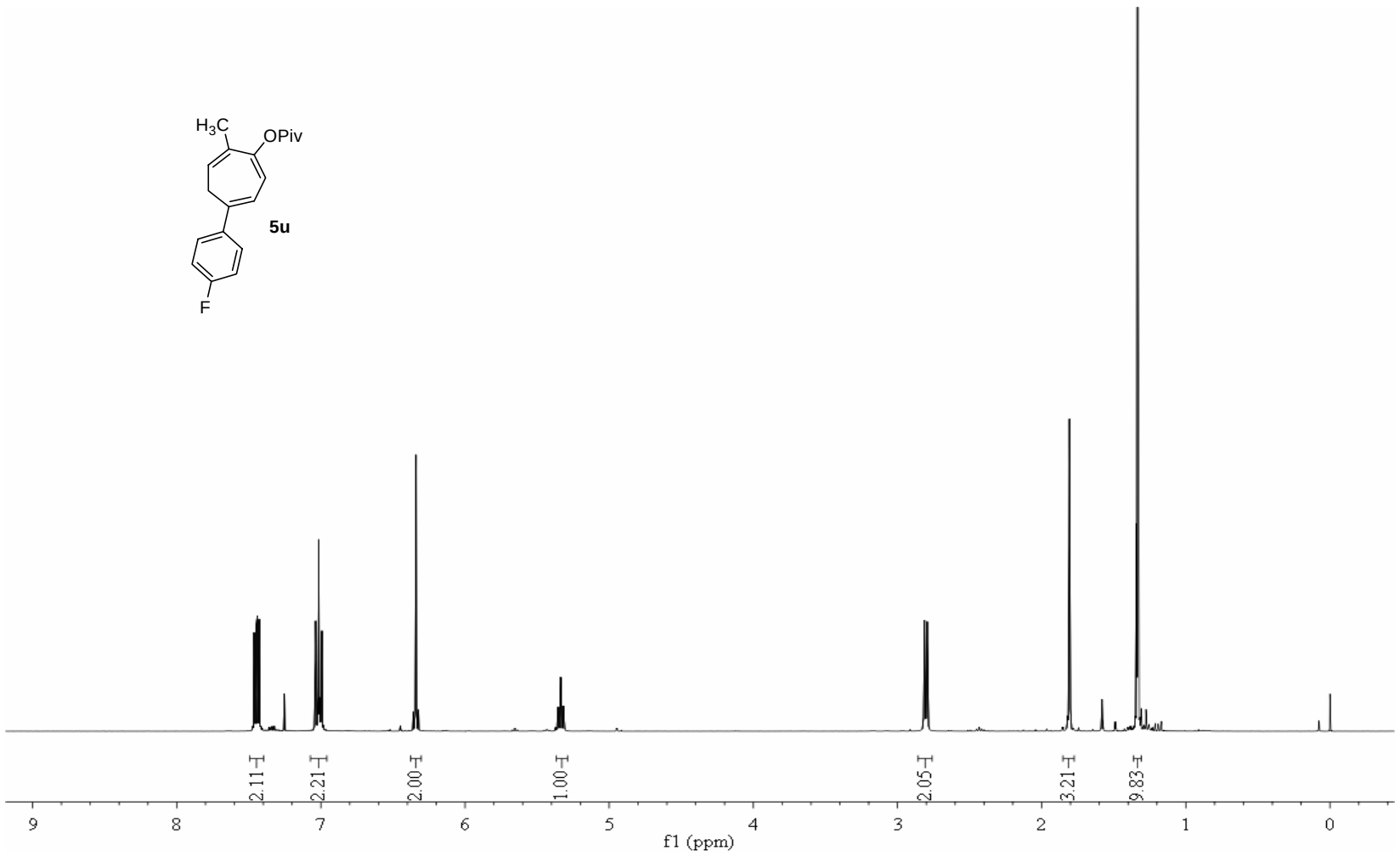

176.828
176.528
166.181
165.801
155.890
152.877
131.792
131.371
131.125
130.389
128.575
123.591
122.760
119.233
118.714
117.315
77.318
77.000
76.682
60.849
39.012
38.923
27.119
27.093
17.662
17.611
14.242
27.328
27.119
27.093
26.354
17.662
17.611
14.242
H3C
OPiv
EtO2C
5s
H3C
OPiv
5s'
CO2Et
f1 (ppm)
f1 (ppm)

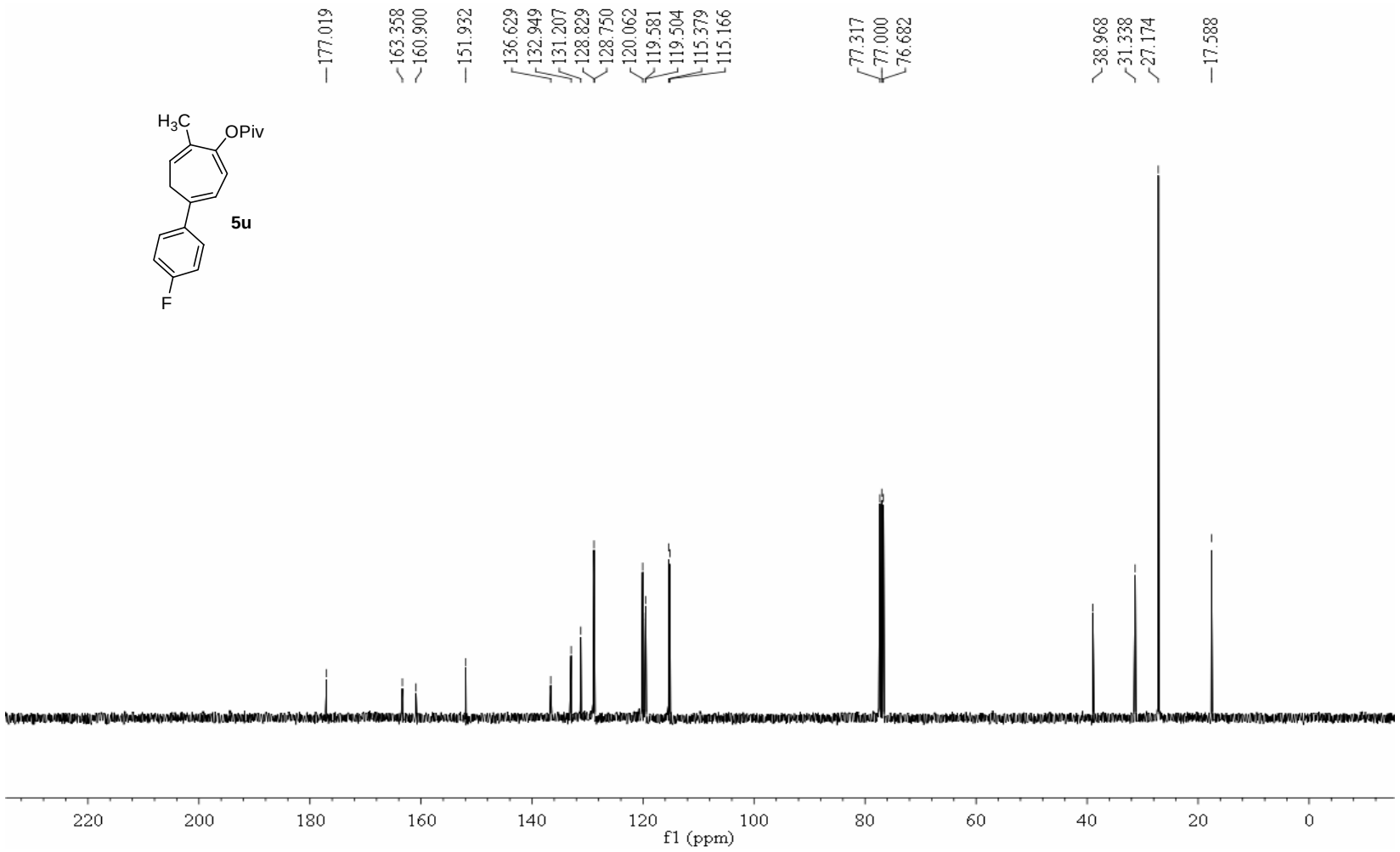

H3C
OPiv
Ph
5t
2.00
2.10
1.18
1.02
0.98
1.05
1.99
2.81
8.45
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

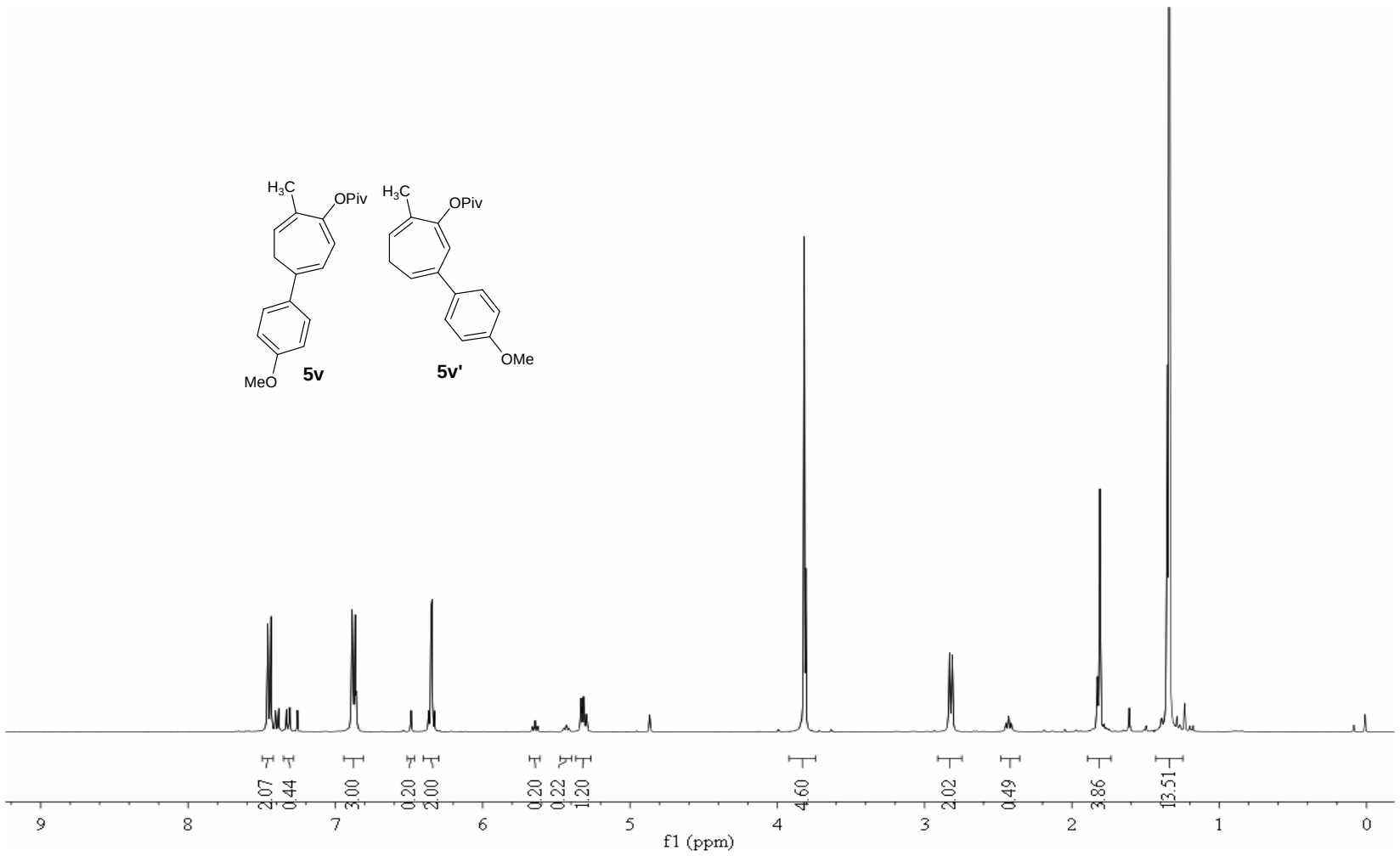

177.038
151.934
140.490
134.207
131.064
128.435
127.299
127.150
120.119
119.735
77.318
77.000
76.683
38.972
31.241
27.188
17.604
H3C
OPiv
Ph
5t
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

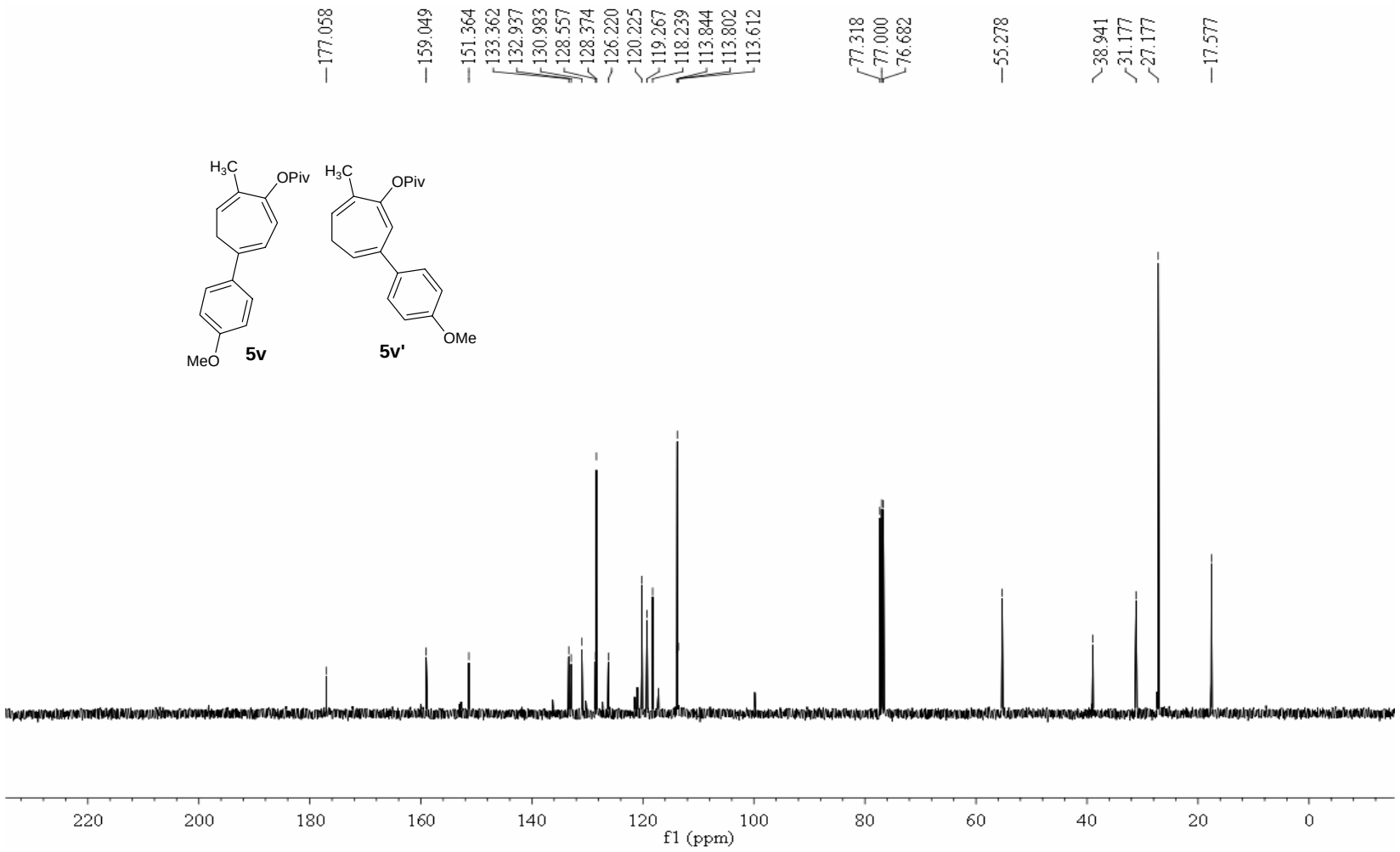

H3C
OPiv
Ph
5t'
2.12
2.29
1.54
0.96
1.00
0.98
2.10
3.20
9.69
8
7
6
5
4
3
2
1
0
f1 (ppm)

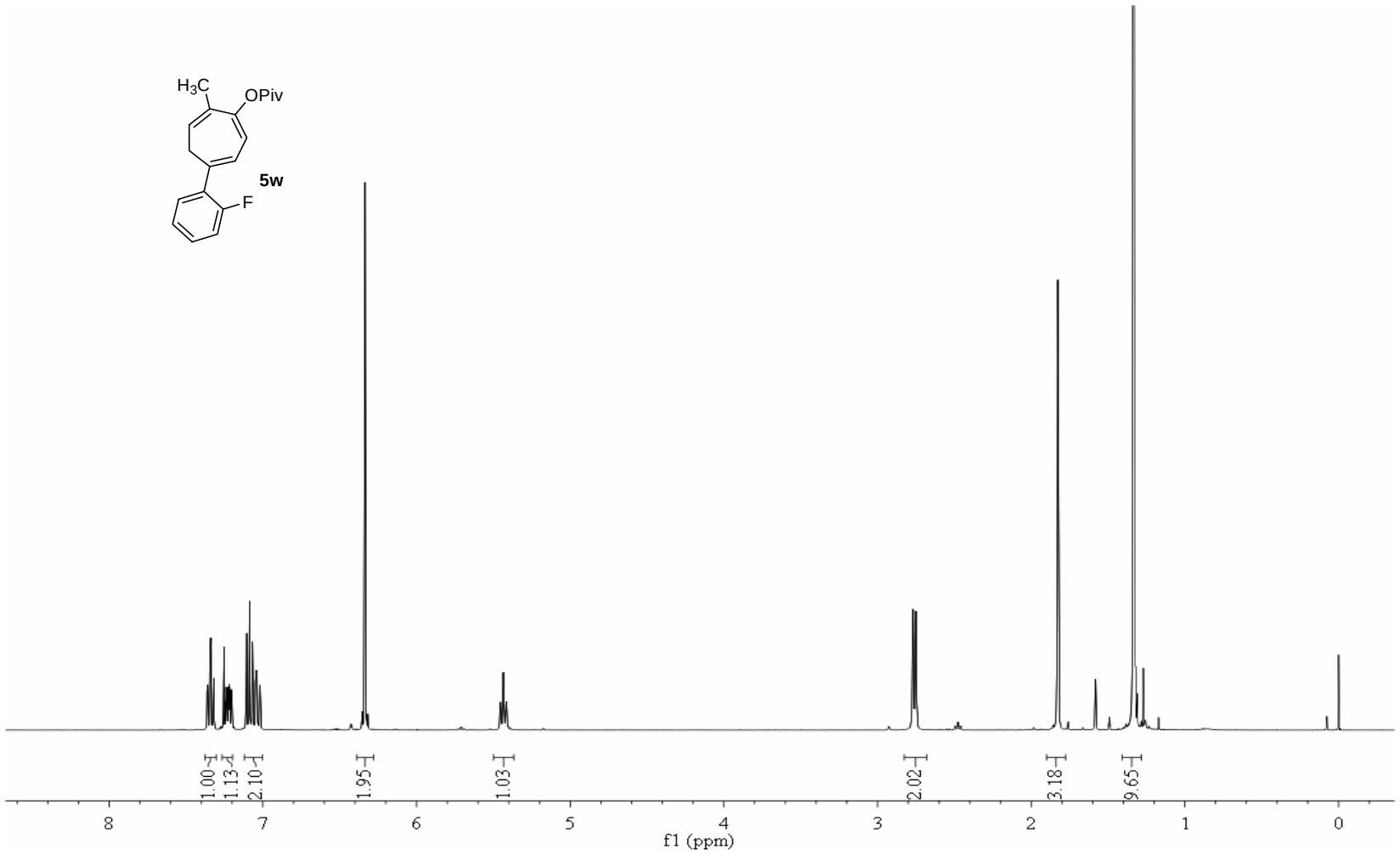

176.946
152.916
140.420
136.839
130.448
128.281
127.422
127.099
121.417
120.822
118.723
77.318
77.000
76.683
39.019
27.509
27.219
17.665
H3C
OPiv
Ph
5t'
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

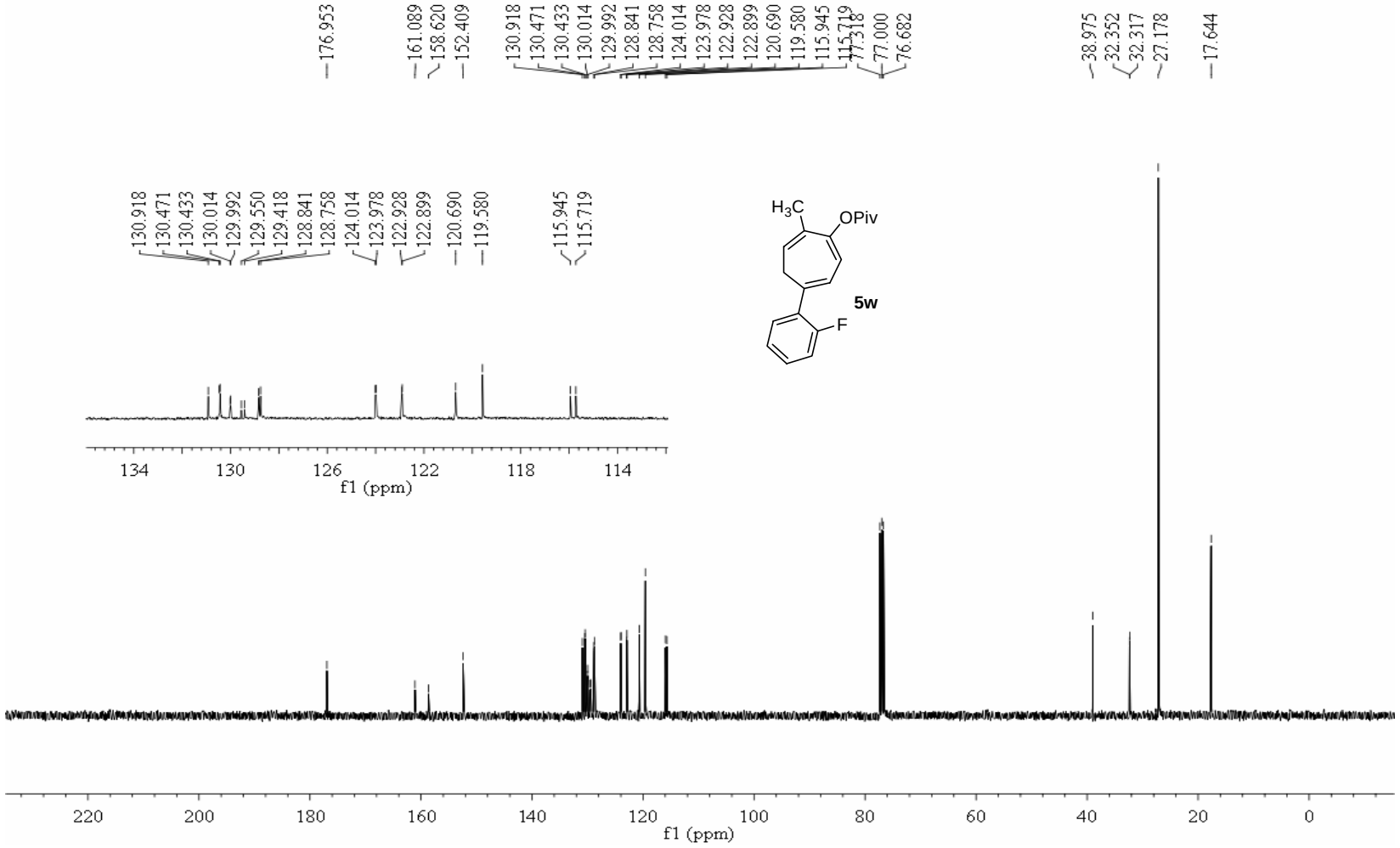

H3C
OPiv
5u
F
2.11
2.21
2.00
1.00
2.05
3.21
9.83
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

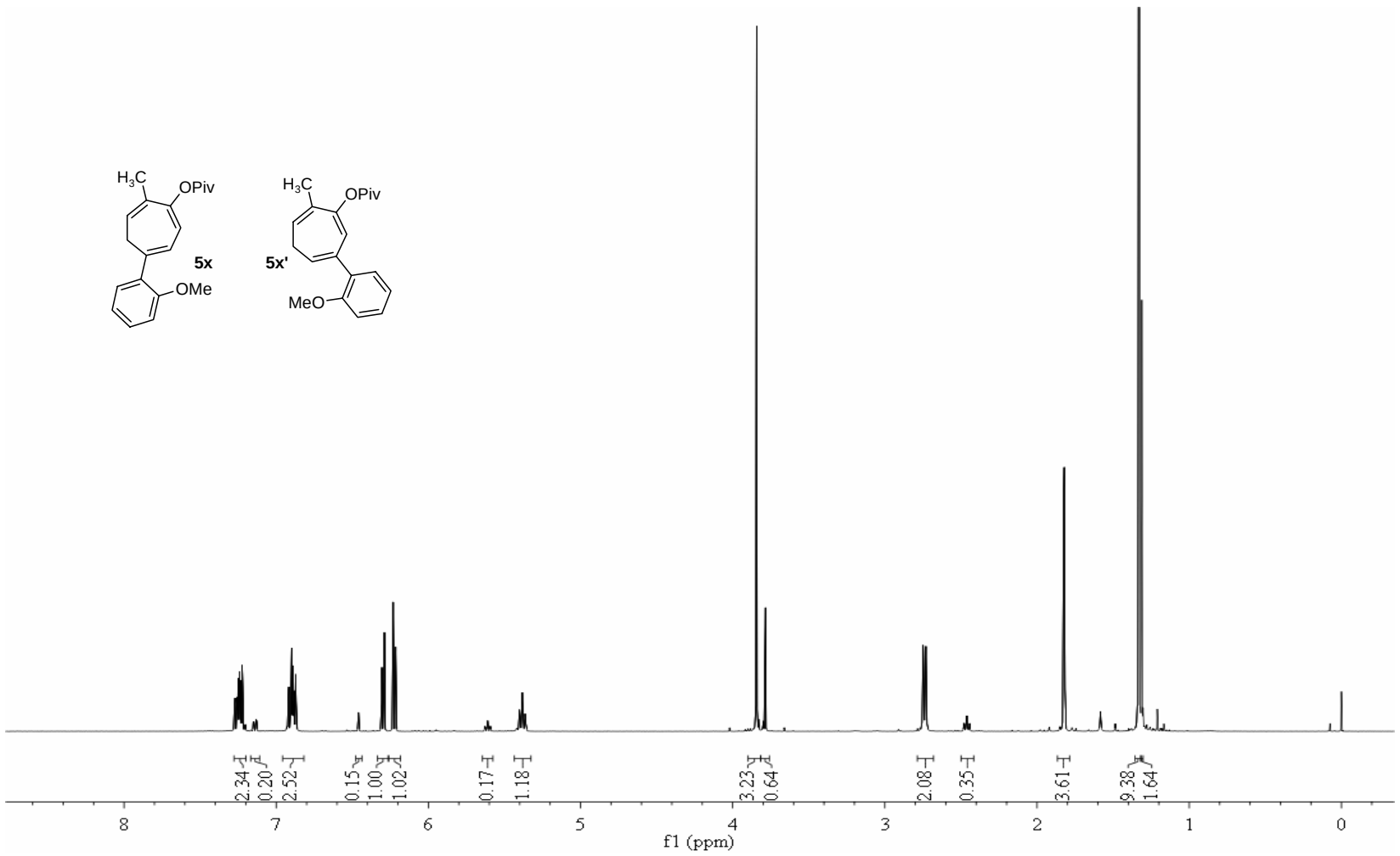

177.019
163.358
160.900
151.932
136.629
132.949
131.207
128.829
128.750
120.062
119.581
119.504
115.379
115.166
77.317
77.000
76.682
38.968
31.338
27.174
17.588
H3C
OPiv
5u
F
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

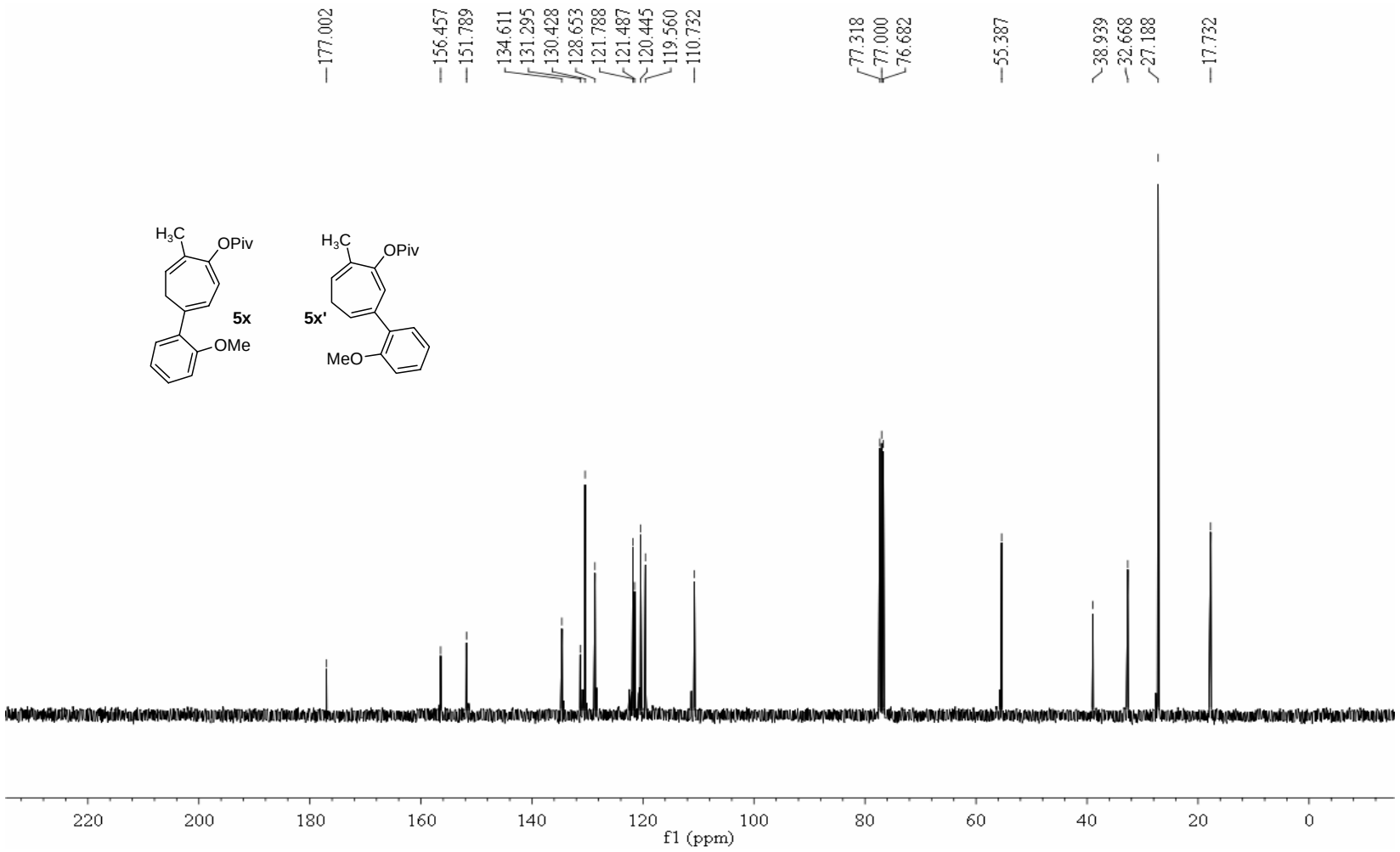

H3C
OPiv
MeO
5v
H3C
OPiv
OMe
5v'
2.07
0.44
3.00
0.20
2.00
0.20
0.22
1.20
4.60
2.02
0.49
3.86
13.51
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

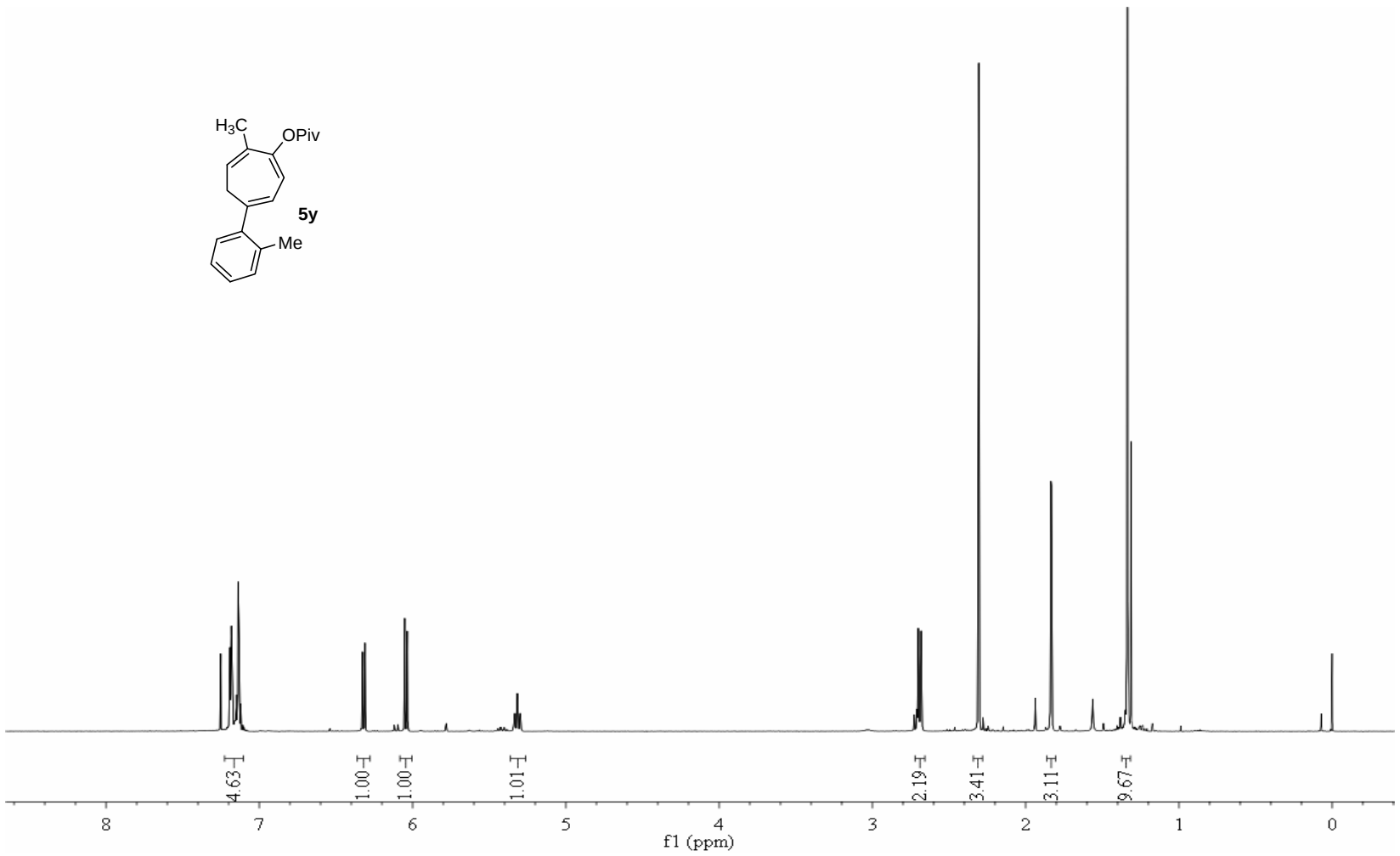

177.058
159.049
151.364
133.362
132.937
130.983
128.557
128.374
126.220
120.225
119.267
118.239
113.844
113.802
113.612
77.318
77.000
76.682
55.278
38.941
31.177
27.177
17.577
H3C
OPiv
MeO
5v
H3C
OPiv
OMe
5v'
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

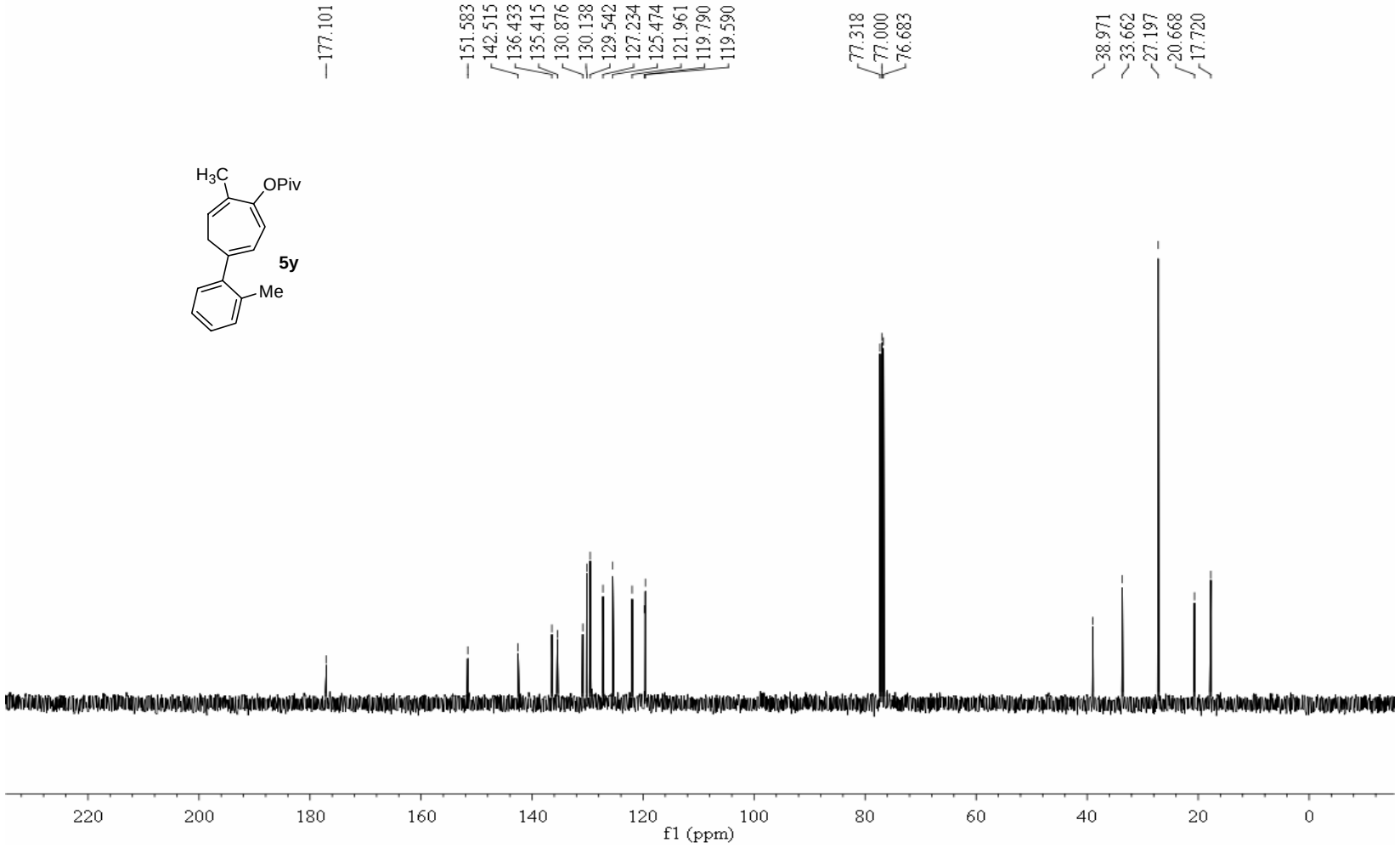

H3C
OPiv
5w
F
1.00
1.13
2.10
1.95
1.03
2.02
3.18
9.65
8
7
6
5
4
3
2
1
0
f1 (ppm)

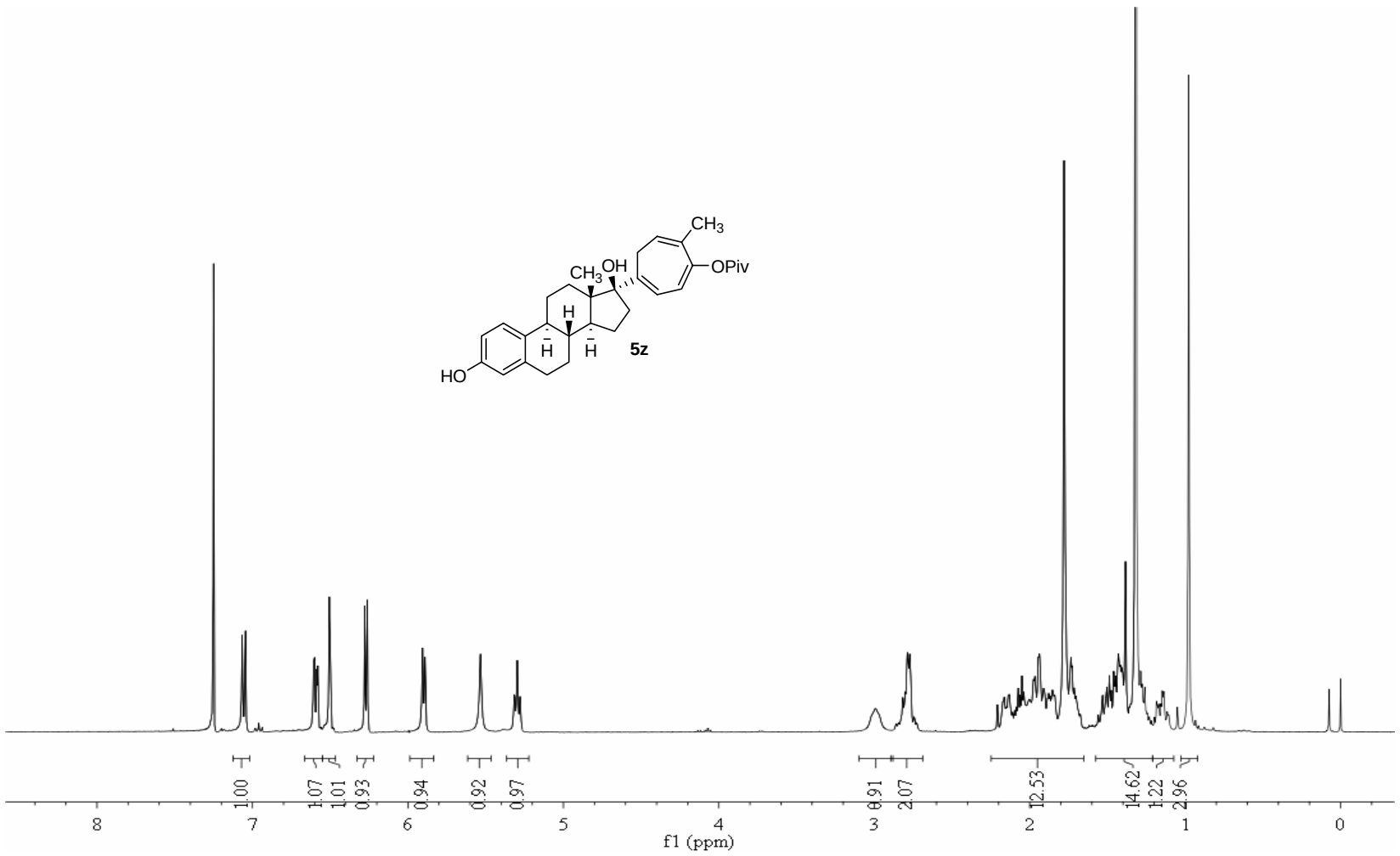

176.953
161.089
158.620
152.409
130.918
130.471
130.433
130.014
129.992
128.841
128.758
124.014
123.978
122.928
122.899
120.690
119.580
115.945
115.719
77.318
77.000
76.682
38.975
32.352
32.317
27.178
17.644
H3C
OPiv
5w
F
f1 (ppm)
f1 (ppm)

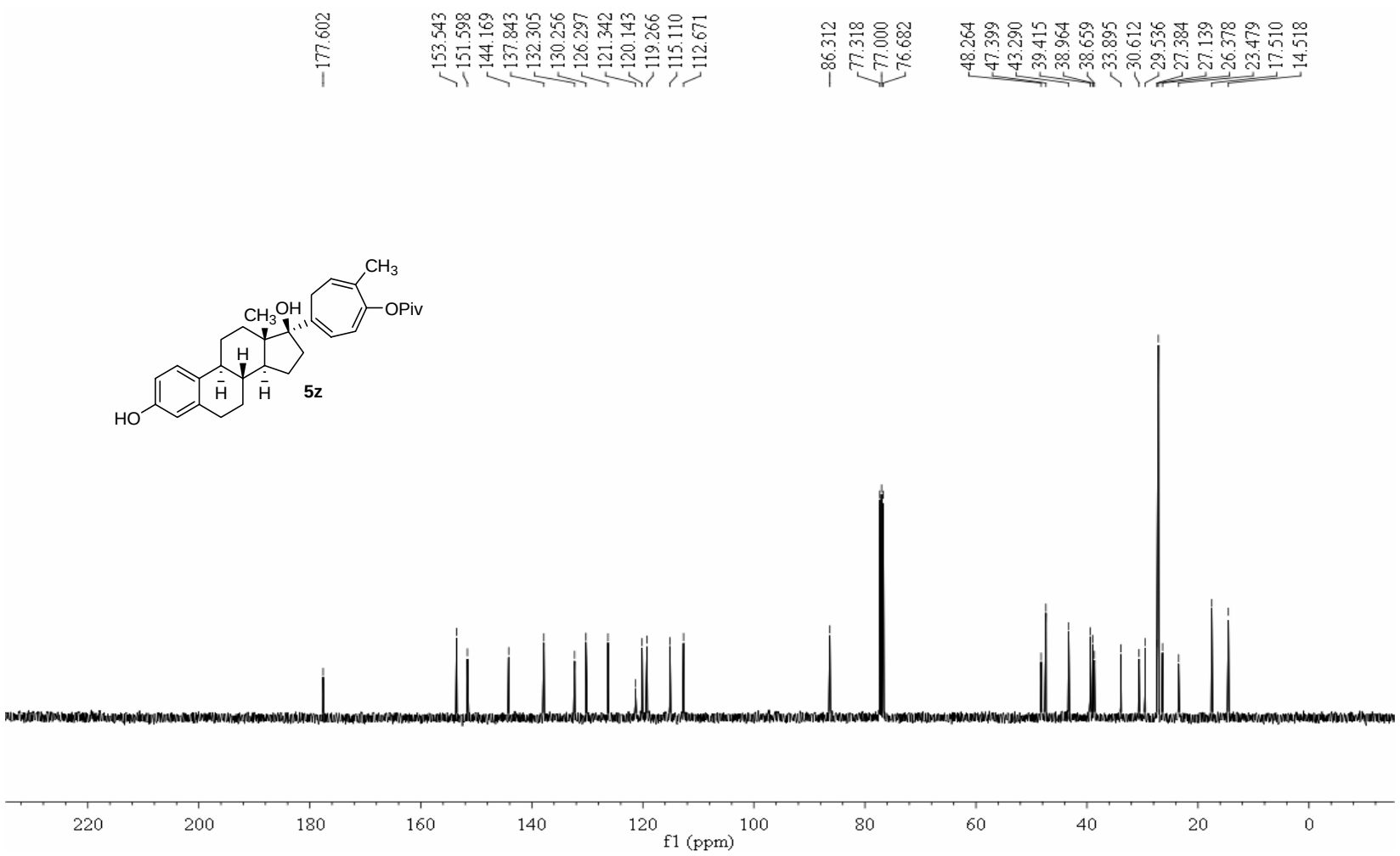

H3C
OPiv
5x
OMe
H3C
OPiv
5x'
MeO
2.34
0.20
2.52
0.15
1.00
1.02
0.17
1.18
3.23
0.64
2.08
0.35
3.61
9.38
1.64
8
7
6
5
4
3
2
1
0
f1 (ppm)

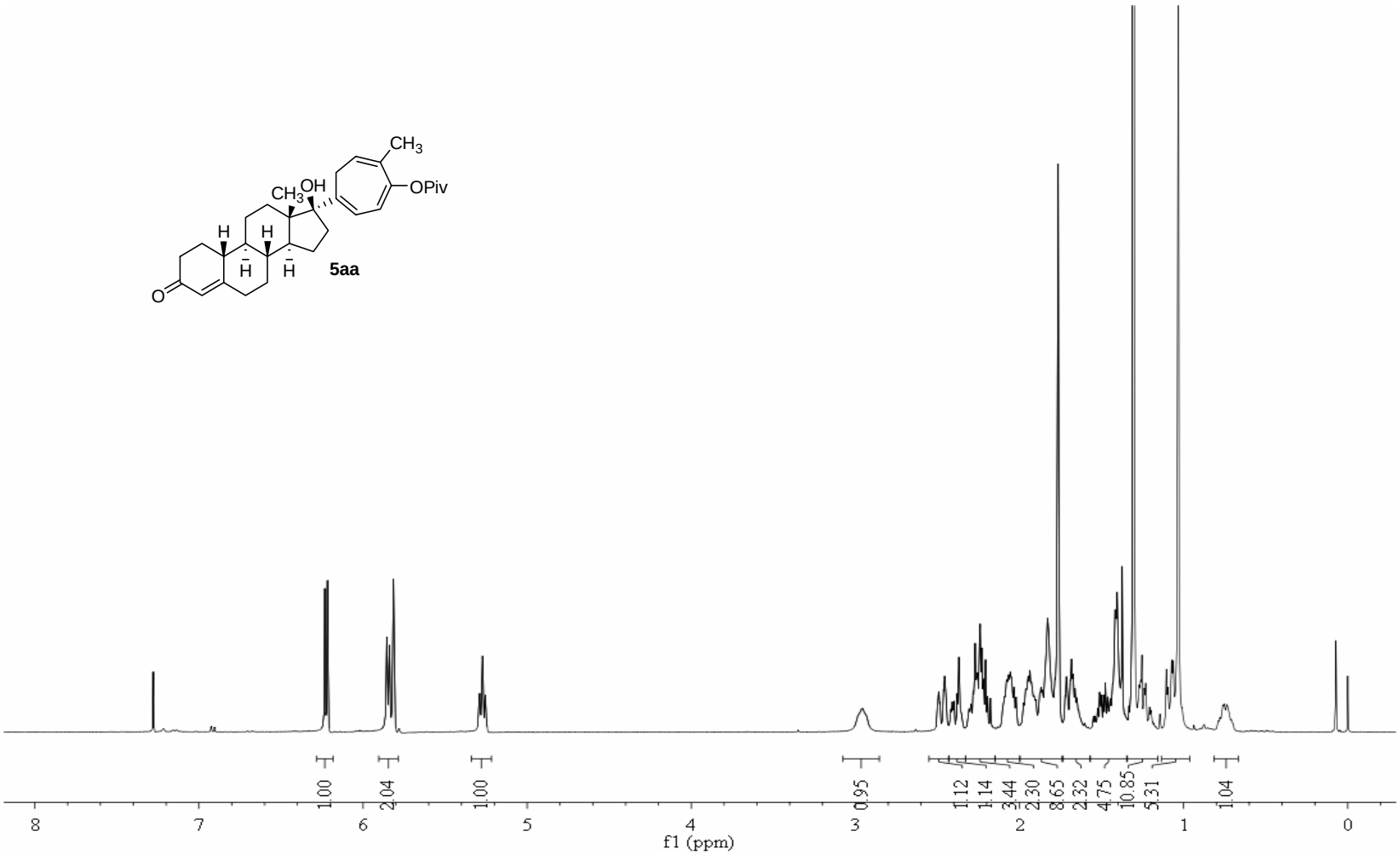

177.002
156.457
151.789
134.611
131.295
130.428
128.653
121.788
121.487
120.445
119.560
110.732
77.318
77.000
76.682
55.387
38.939
32.668
27.188
17.732
H3C
OPiv
5x
OMe
H3C
OPiv
5x'
MeO
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

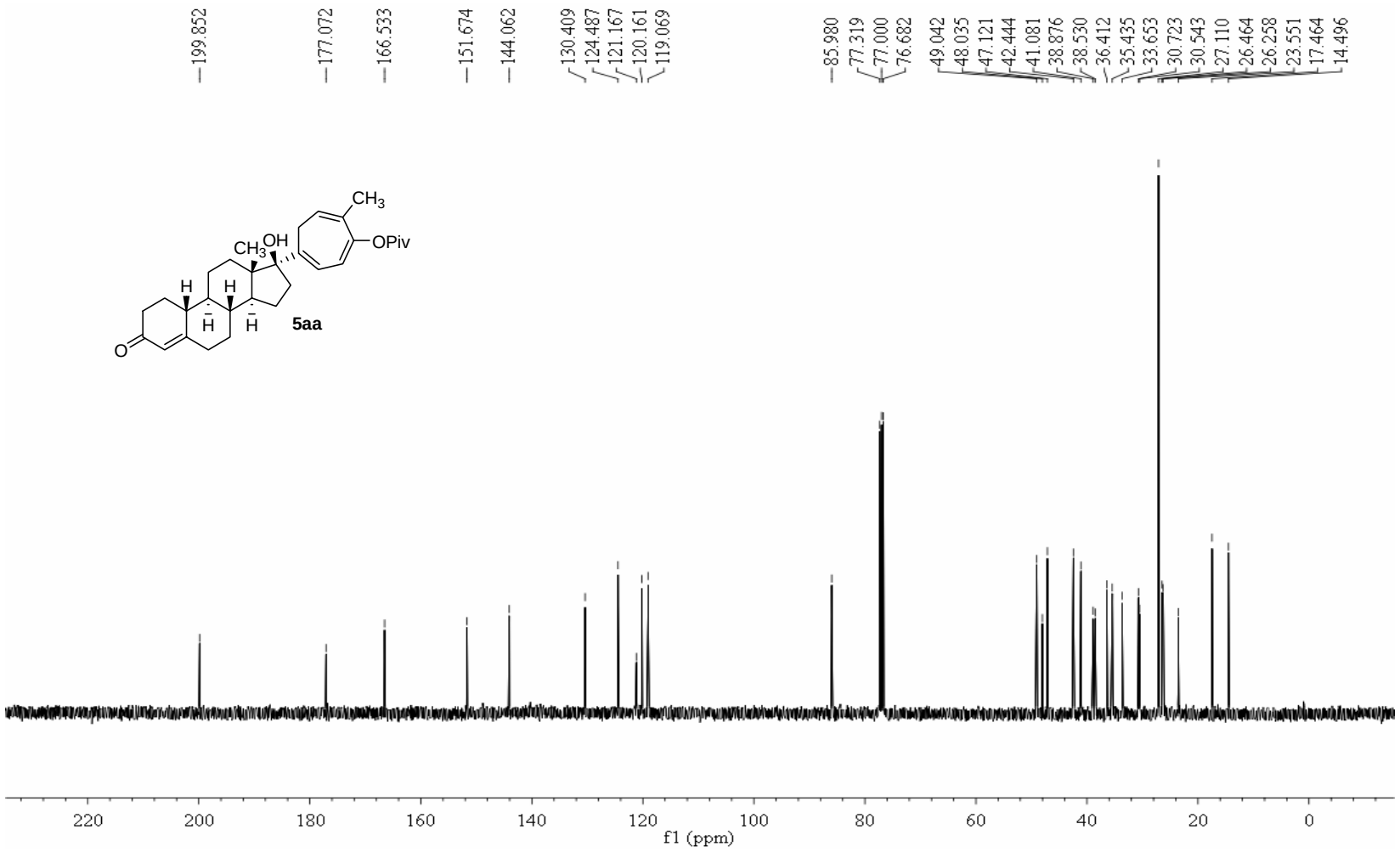

H3C
OPiv
5y
Me
4.63
1.00
1.00
1.01
2.19
3.41
3.11
9.67
8
7
6
5
4
3
2
1
0
f1 (ppm)

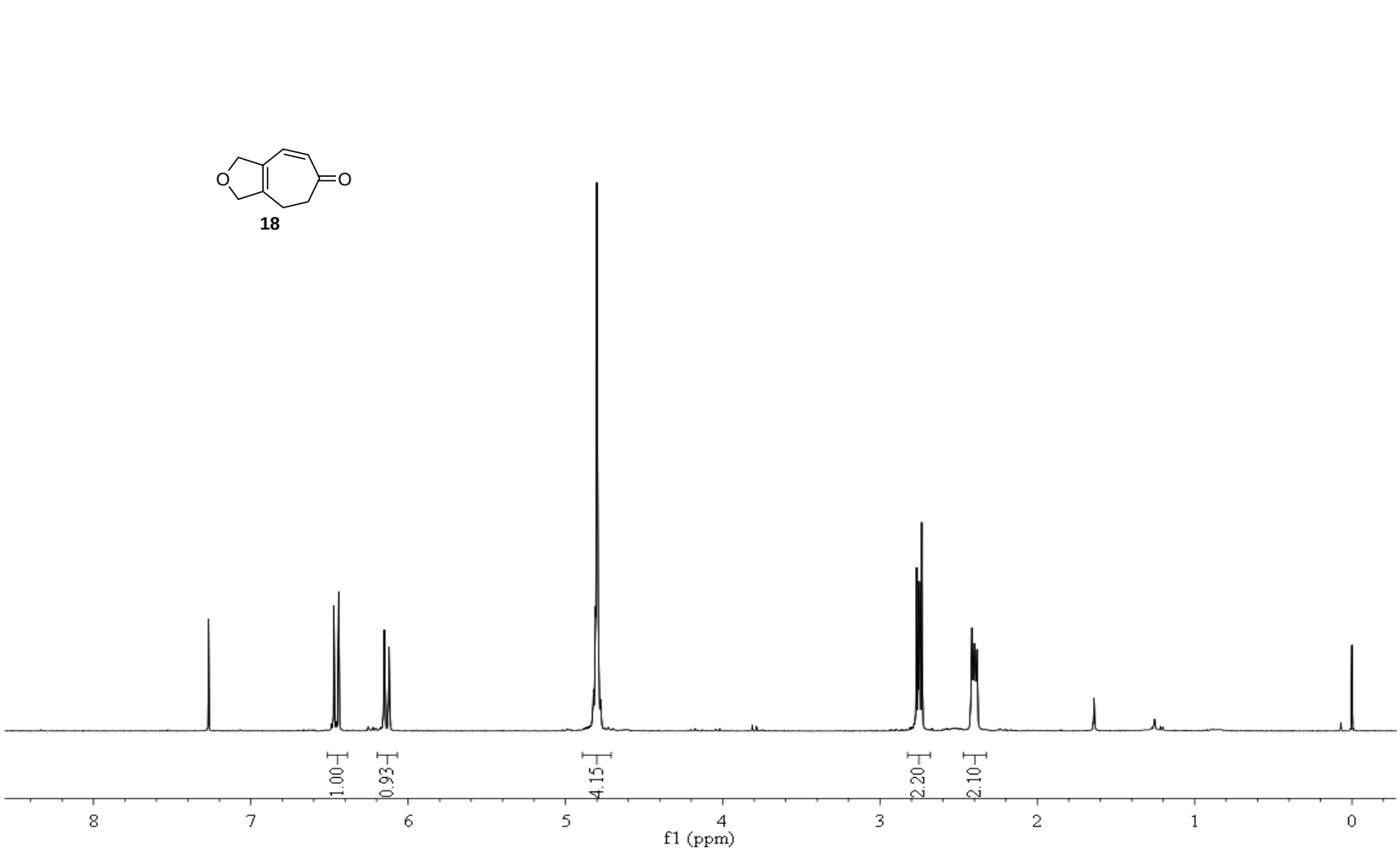

177.101
151.583
142.515
136.433
135.415
130.876
130.138
129.542
127.234
125.474
121.961
119.790
119.590
77.318
77.000
76.683
38.971
33.662
27.197
20.668
17.720
H3C
OPiv
5y
Me
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

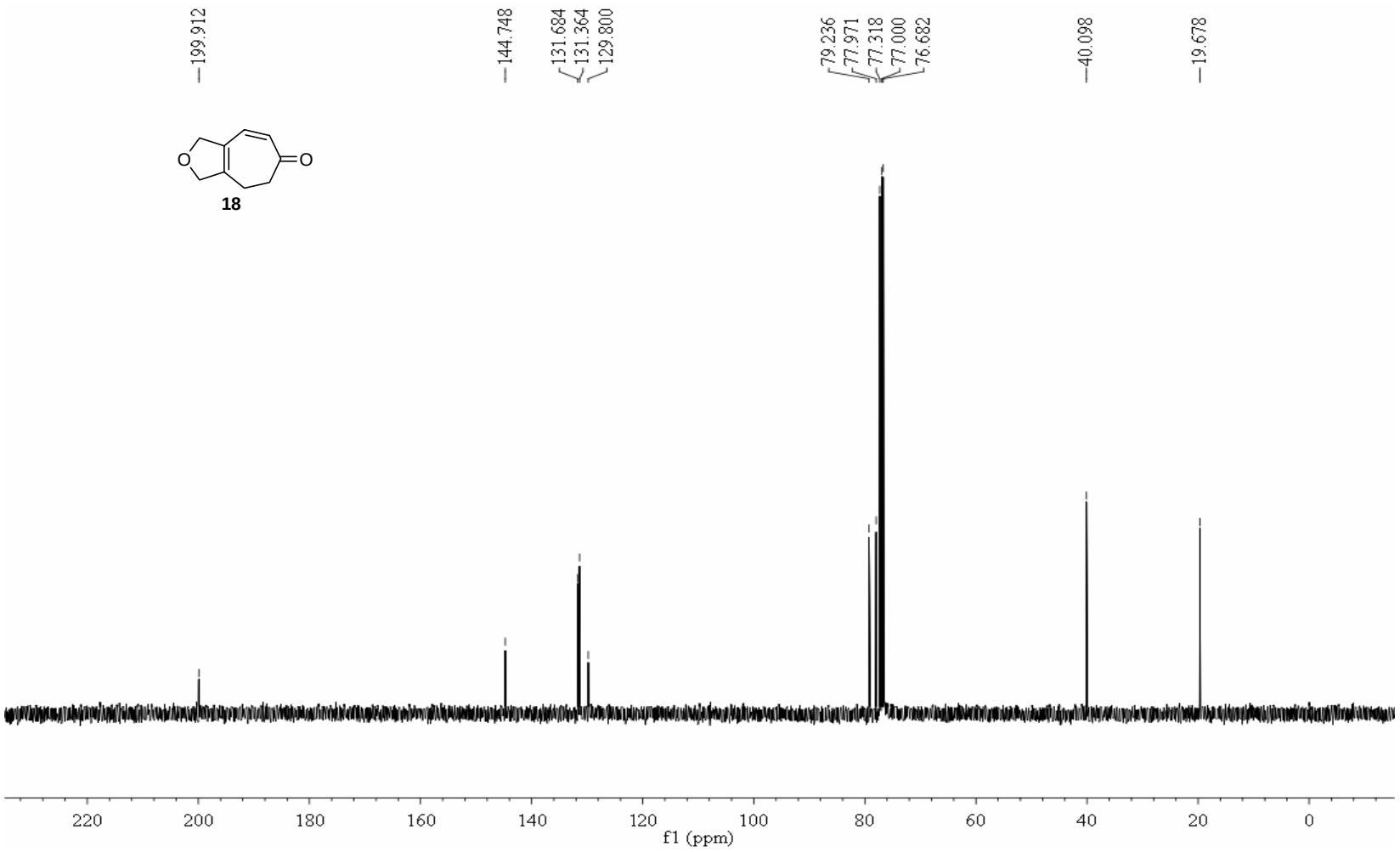

CH3
OH
CH3
OPiv
H
H
H
HO
5z
1.00
1.07
1.01
0.93
0.94
0.92
0.97
0.91
2.07
12.53
14.62
1.22
2.96
8
7
6
5
4
3
2
1
0
f1 (ppm)

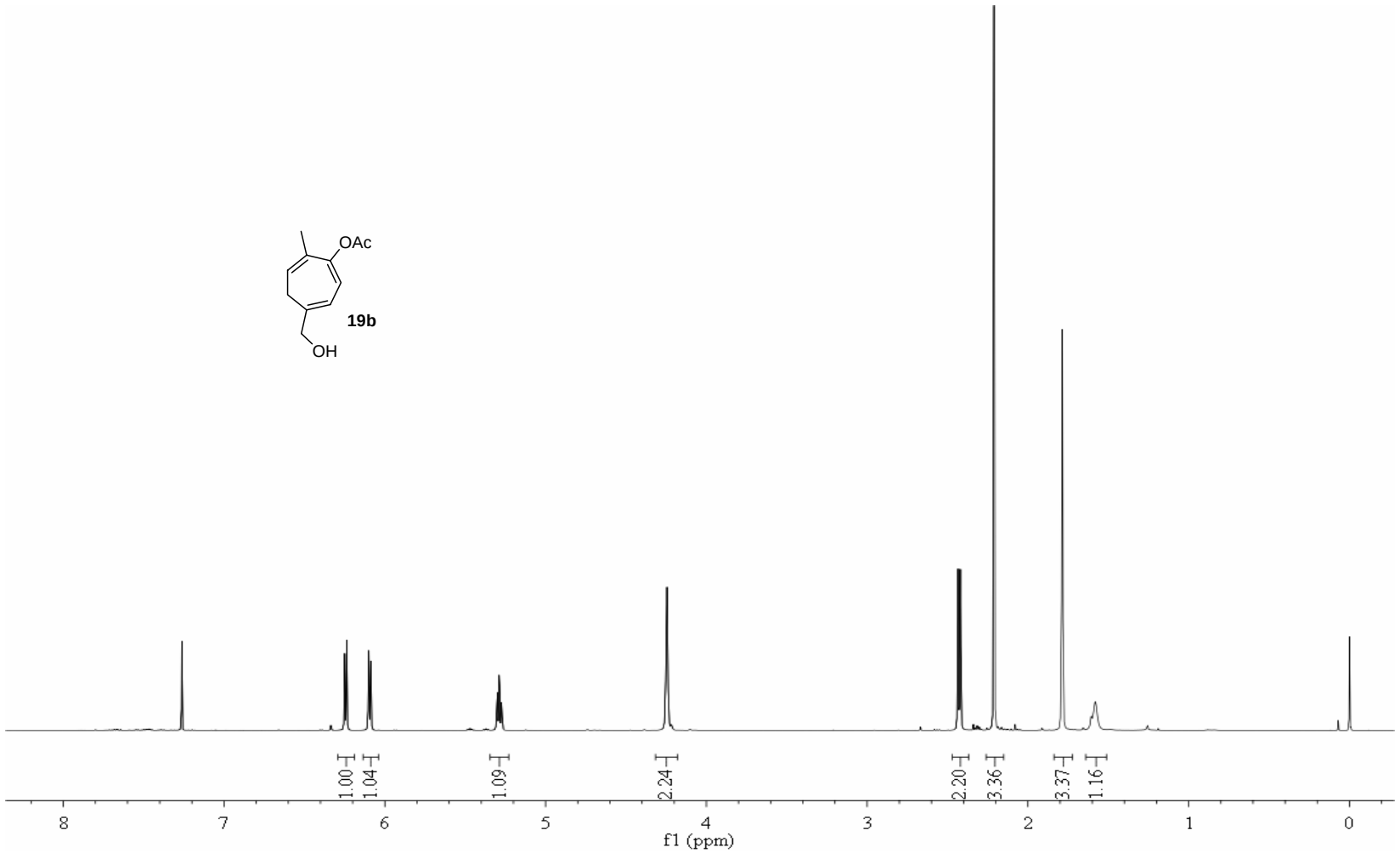

177.602
153.543
151.598
144.169
137.843
132.305
130.256
126.297
121.342
120.143
119.266
115.110
112.671
86.312
77.318
77.000
76.682
48.264
47.399
43.290
39.415
38.964
38.659
33.895
30.612
29.536
27.384
27.139
26.378
23.479
17.510
14.518
CH3
OPiv
CH3
OH
H
H
H
HO
5z
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

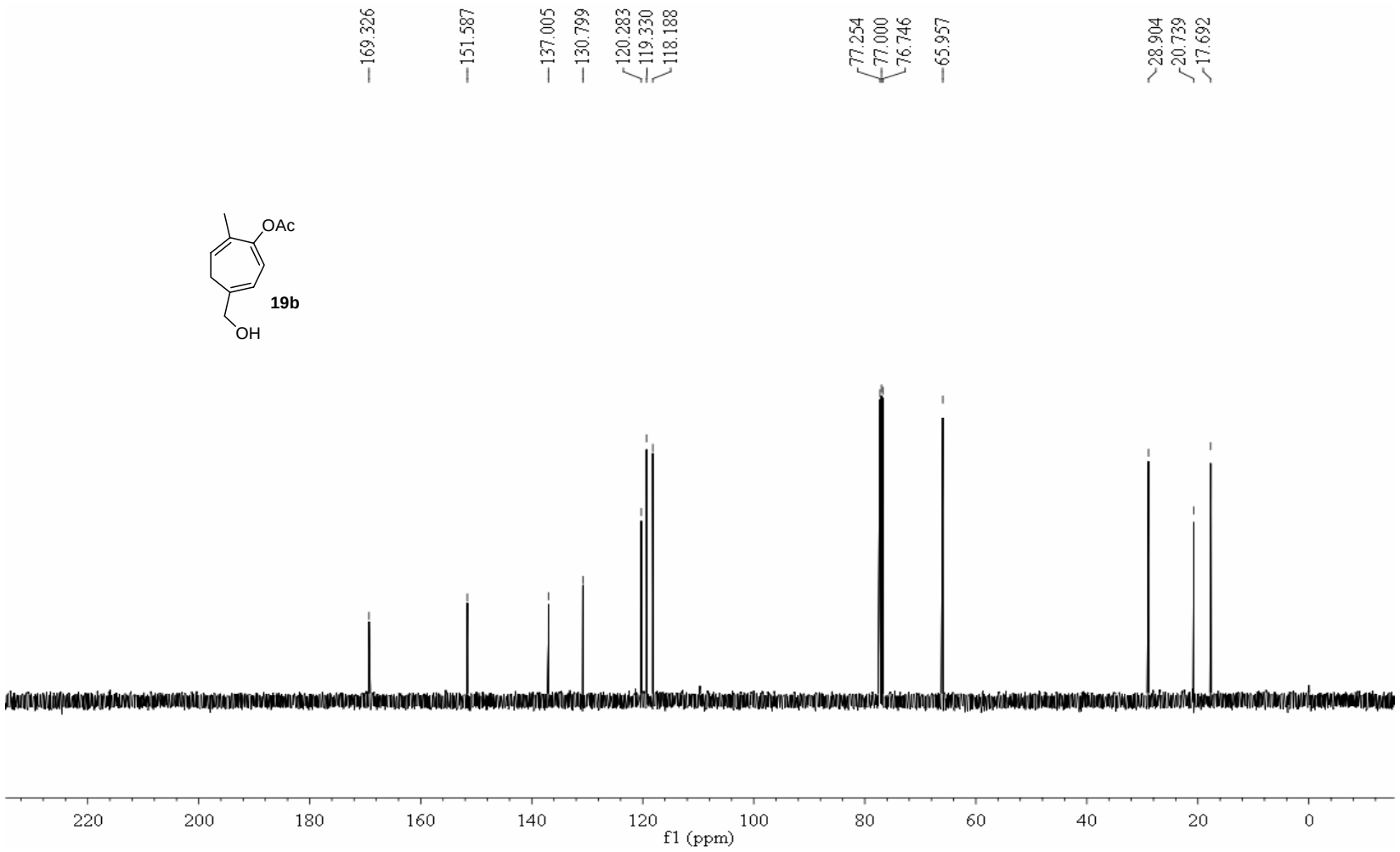

CH3
OH
CH3
OPiv
H
H
H
H
O
5aa
1.00
2.04
1.00
0.95
1.12
1.14
3.44
2.30
8.65
2.32
4.75
10.85
5.31
1.04
8
7
6
5
4
3
2
1
0
f1 (ppm)

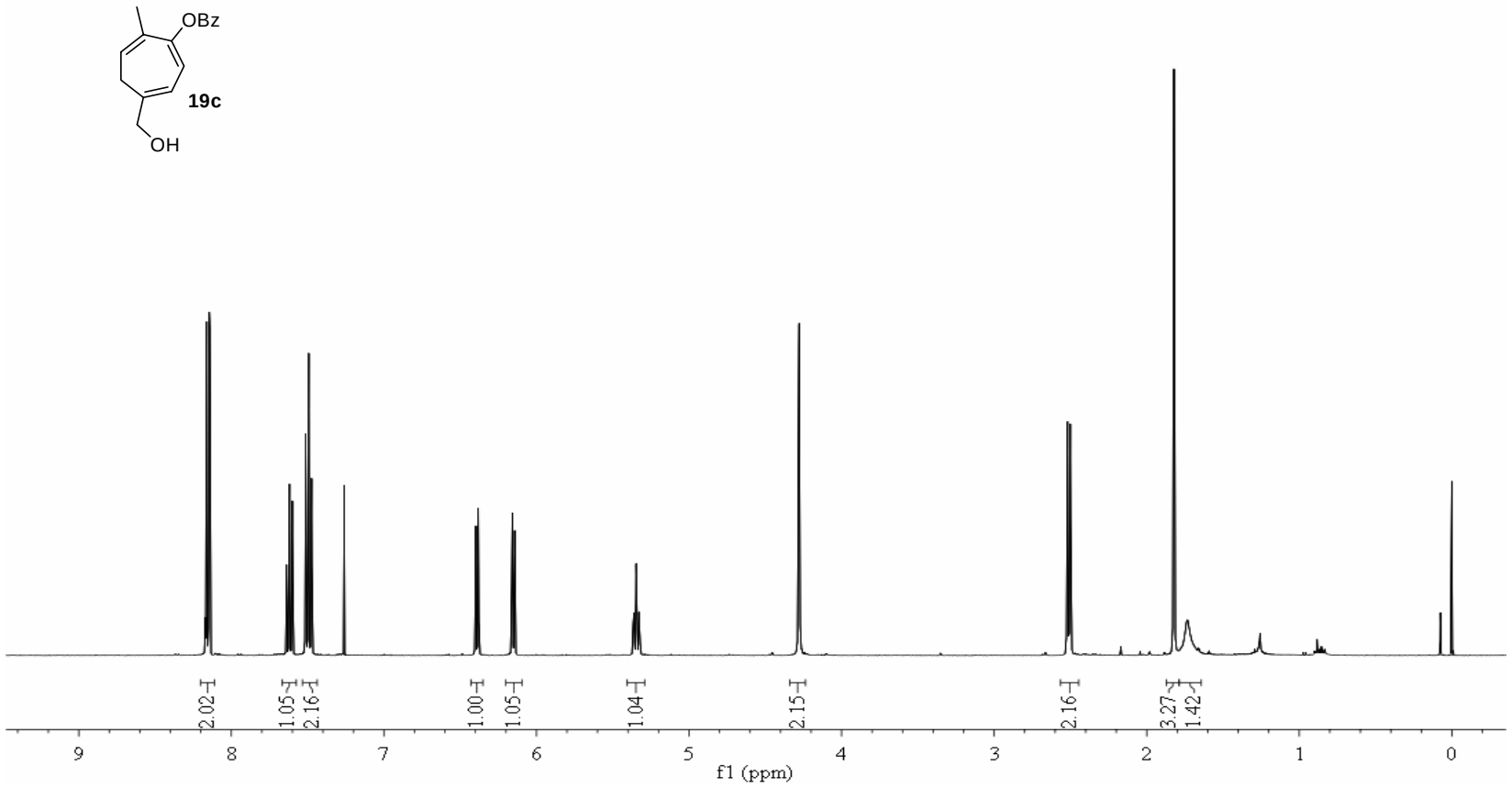

199.852
177.072
166.533
151.674
144.062
130.409
124.487
121.167
120.161
119.069
85.980
77.319
77.000
76.682
49.042
48.035
47.121
42.444
41.081
38.876
38.530
36.412
35.435
33.653
30.723
30.543
27.110
26.464
26.258
23.551
17.464
14.496
CH3
CH3
OH
OPiv
H
H
H
H
O
5aa
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

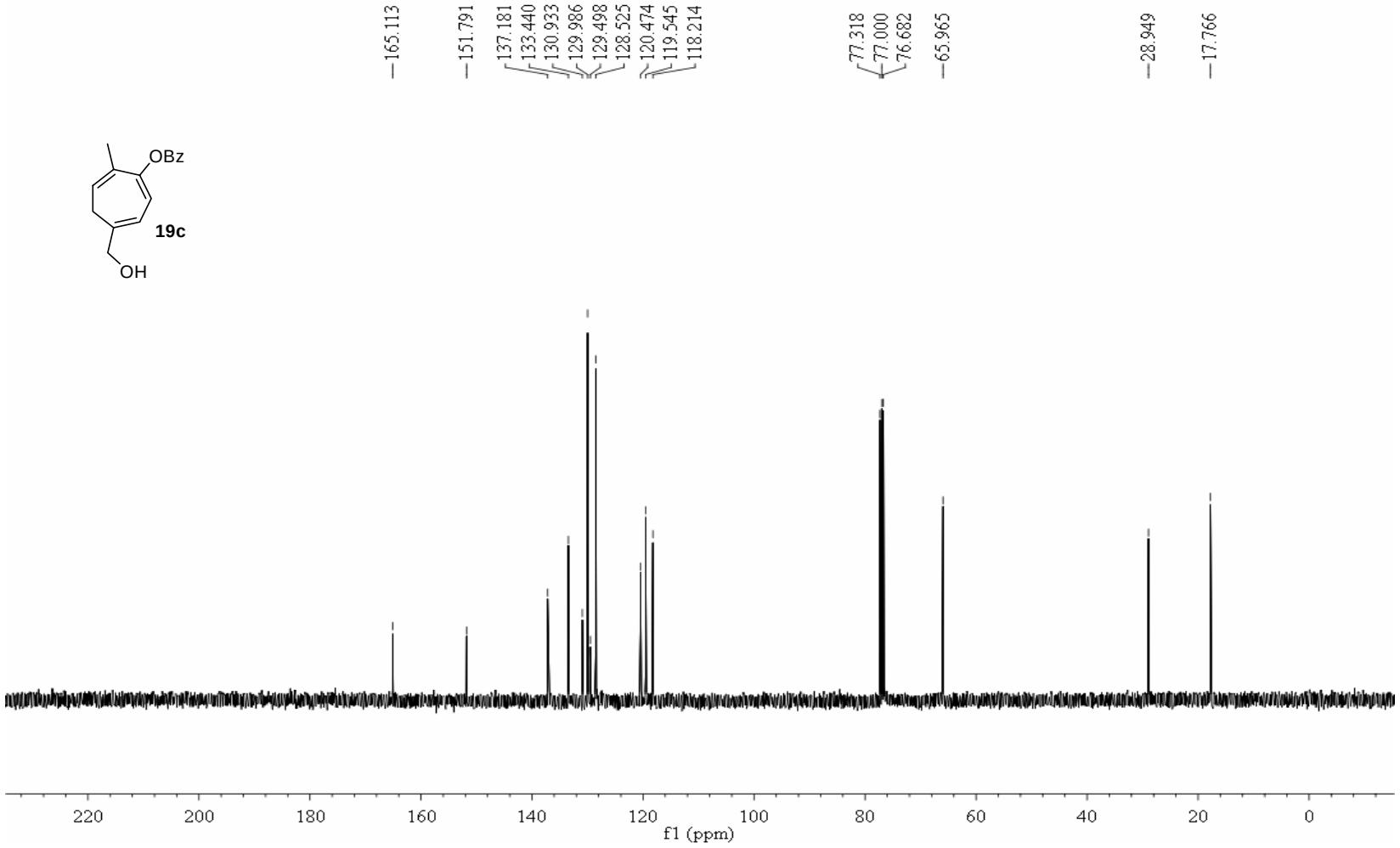

O
O
18
1.00
0.93
4.15
2.20
2.10
8
7
6
5
4
3
2
1
0
f1 (ppm)

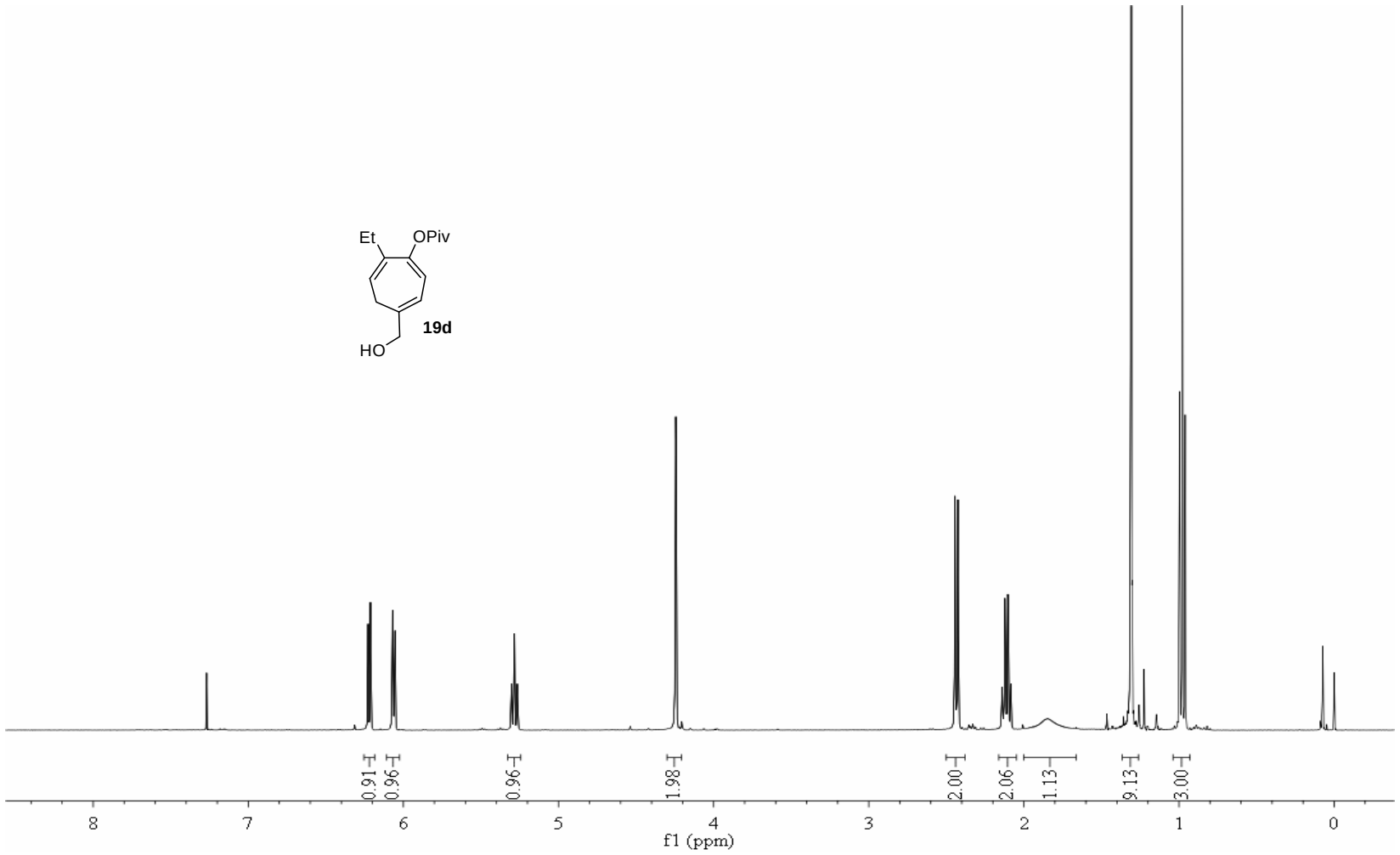

199.912
144.748
131.684
131.364
129.800
79.236
77.971
77.318
77.000
76.682
40.098
19.678
O
O
18
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

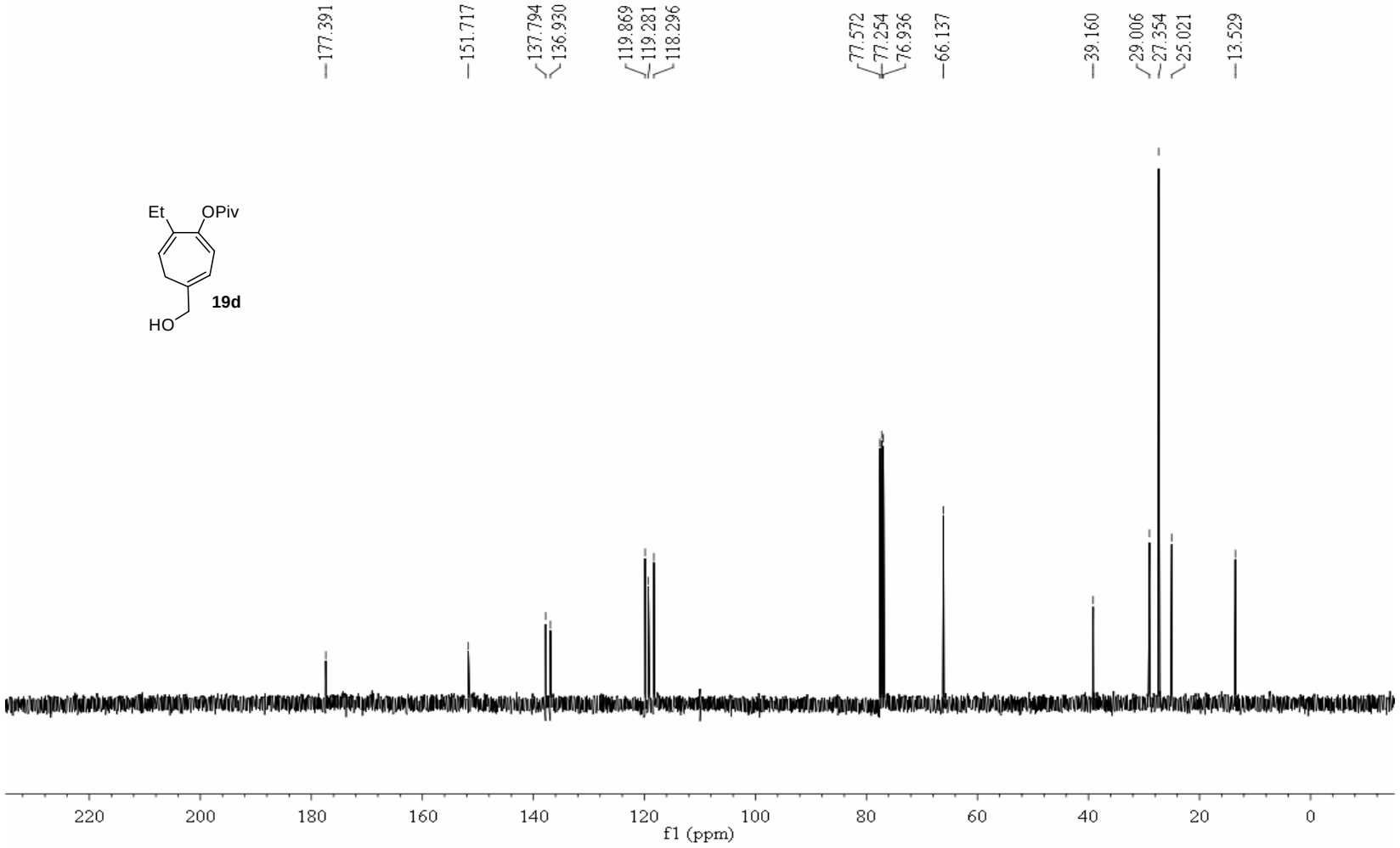

OAc
19b
OH
1.00
1.04
1.09
2.24
2.20
3.36
3.37
1.16
8
7
6
5
4
3
2
1
0
f1 (ppm)

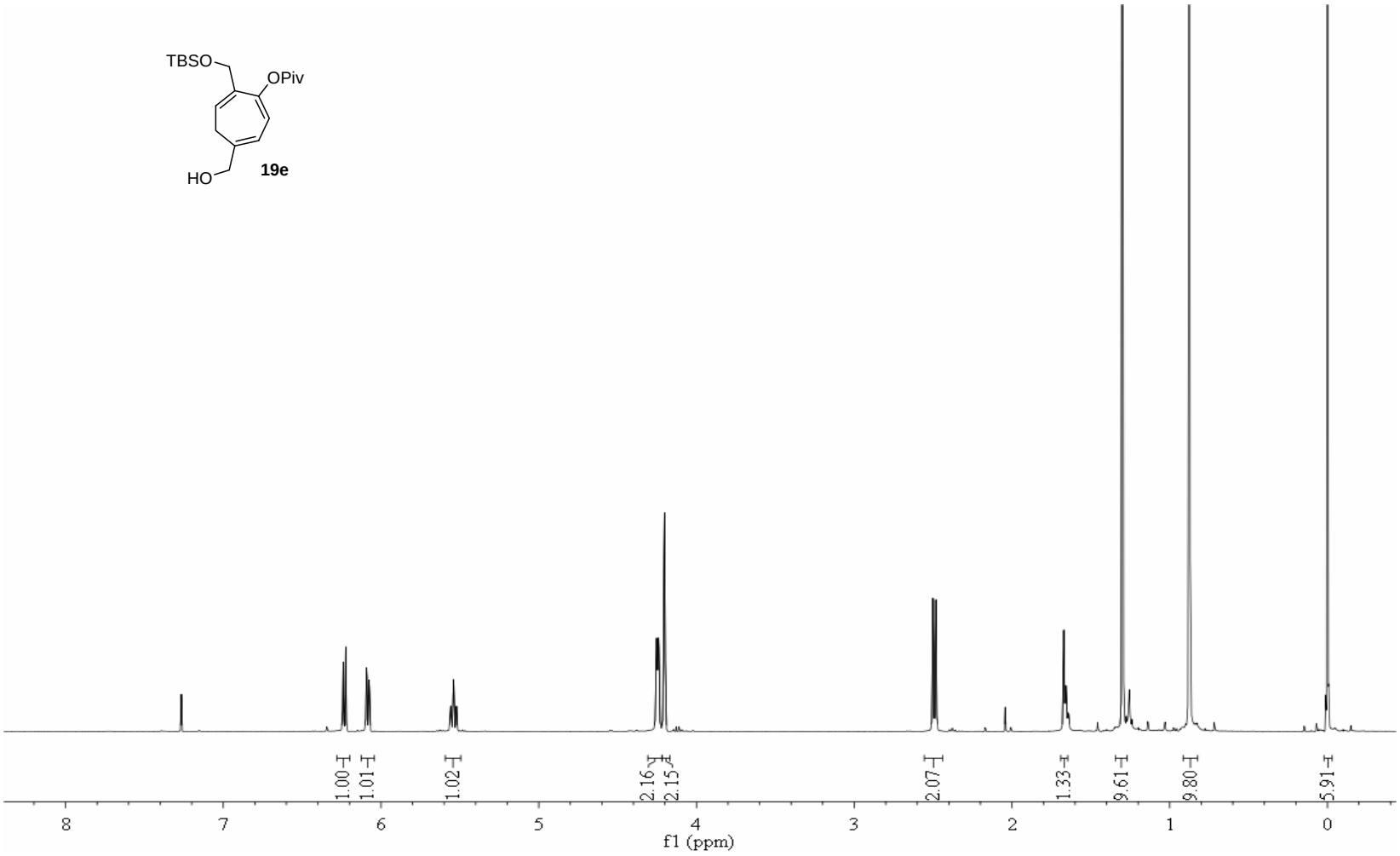

169.326
151.587
137.005
130.799
120.283
119.330
118.188
77.254
77.000
76.746
65.957
28.904
20.739
17.692
OAc
OH
19b
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

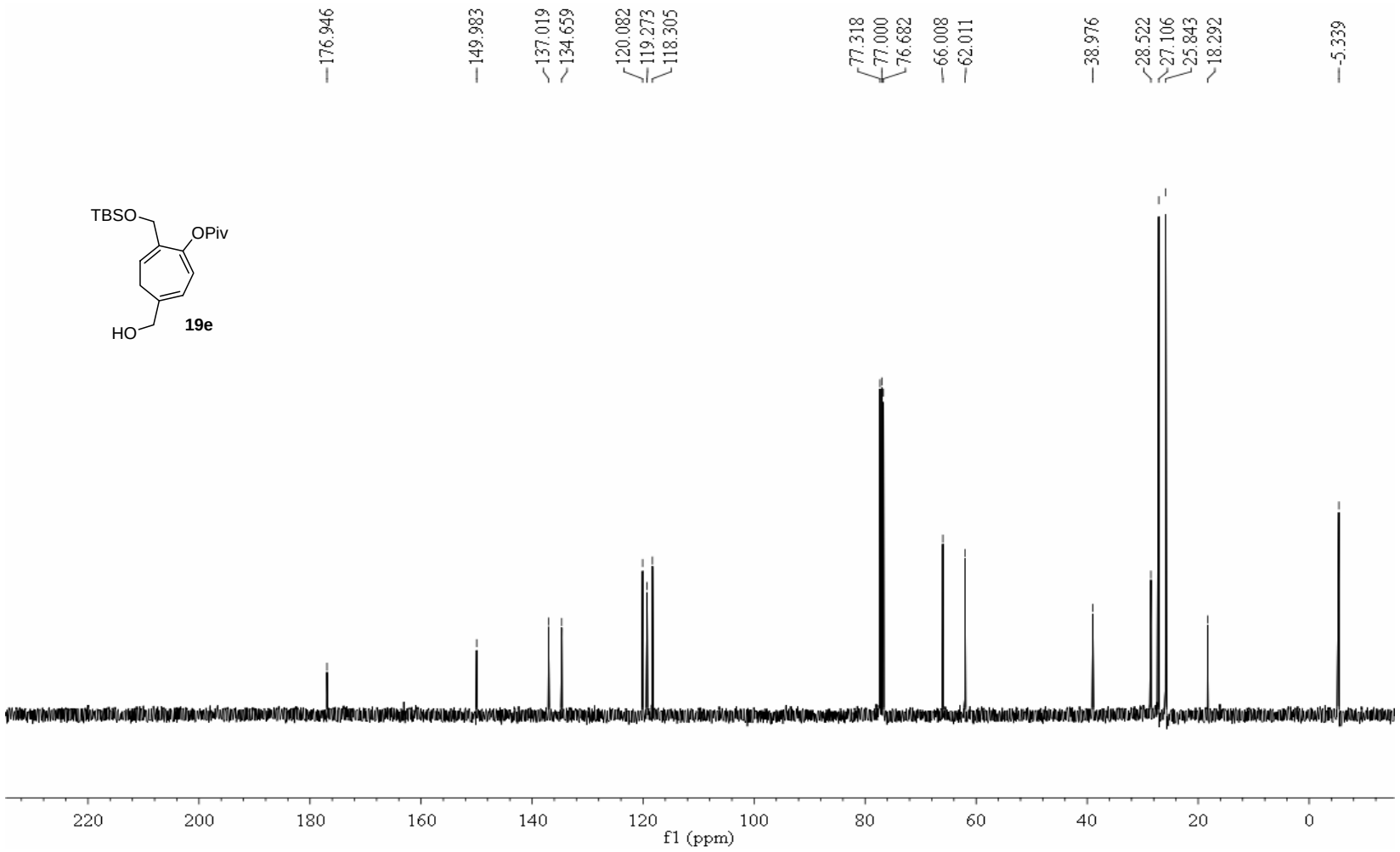

OBz
19c
OH
2.02
1.05
2.16
1.00
1.05
1.04
2.15
2.16
3.27
1.42
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

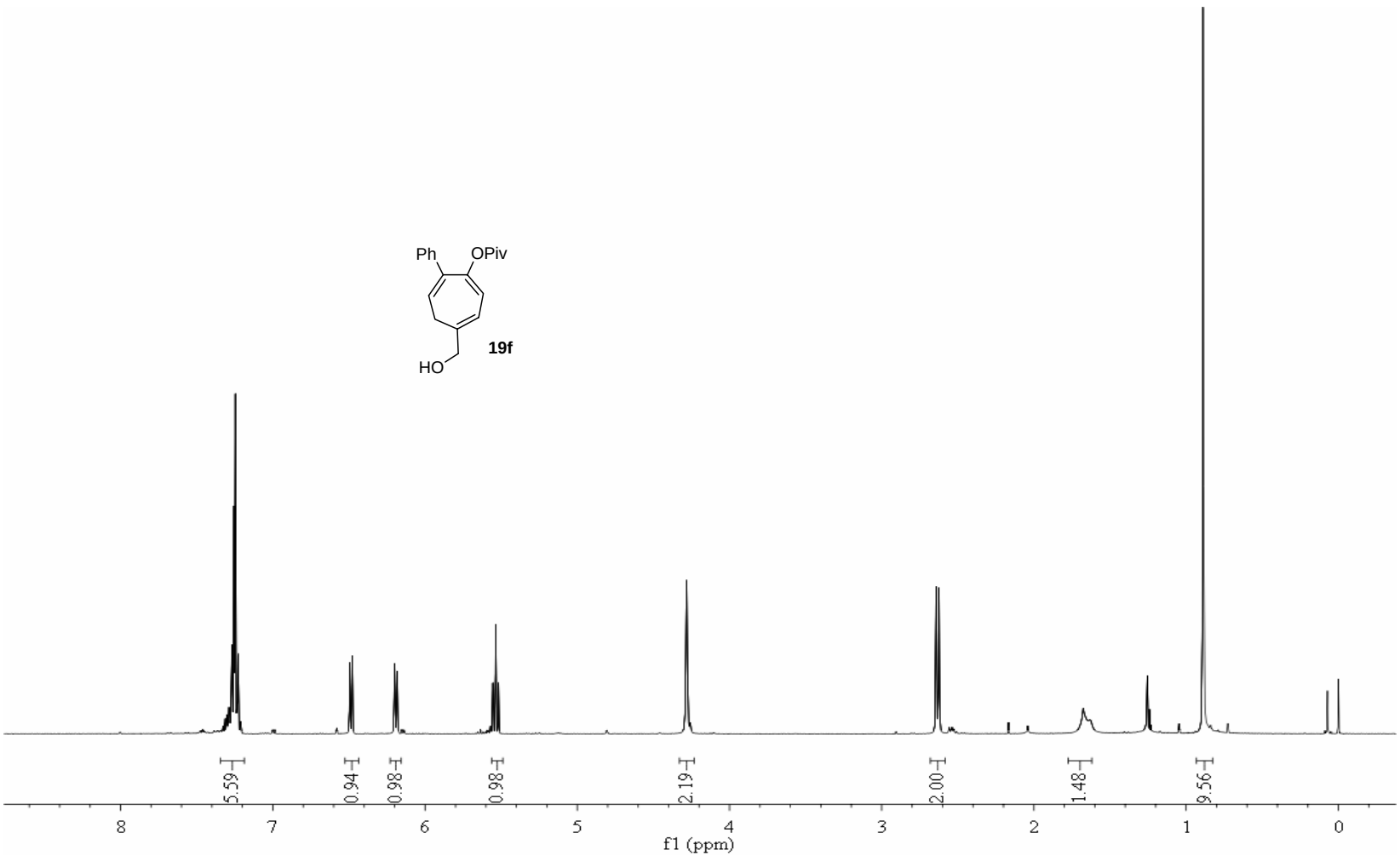

165.113
151.791
137.181
133.440
130.933
129.986
129.498
128.525
120.474
119.545
118.214
77.318
77.000
76.682
65.965
28.949
17.766
OBz
19c
OH
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

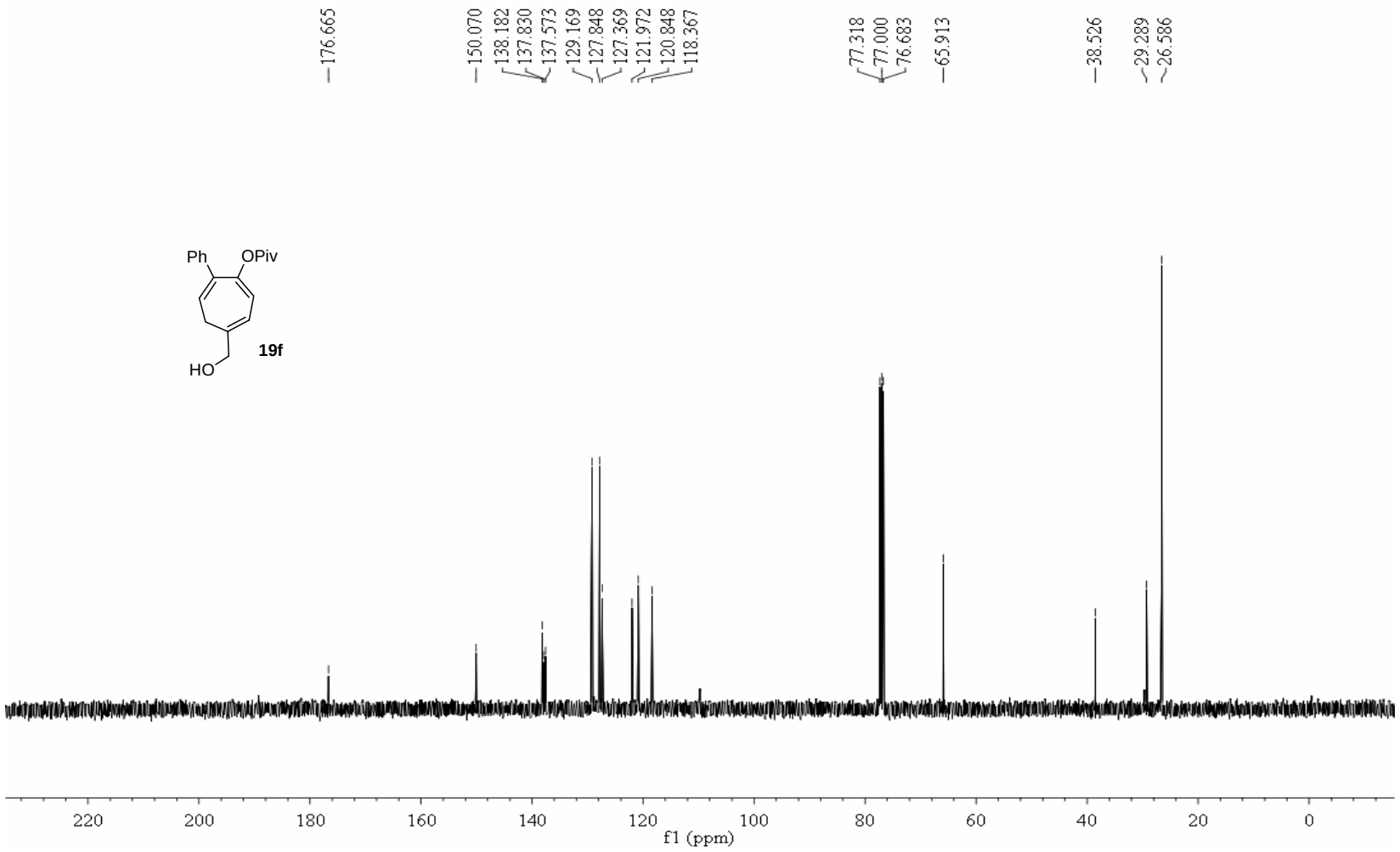

Et
OPiv
19d
HO
0.91
0.96
0.96
1.98
2.00
2.06
1.13
9.13
3.00
8
7
6
5
4
3
2
1
0
f1 (ppm)

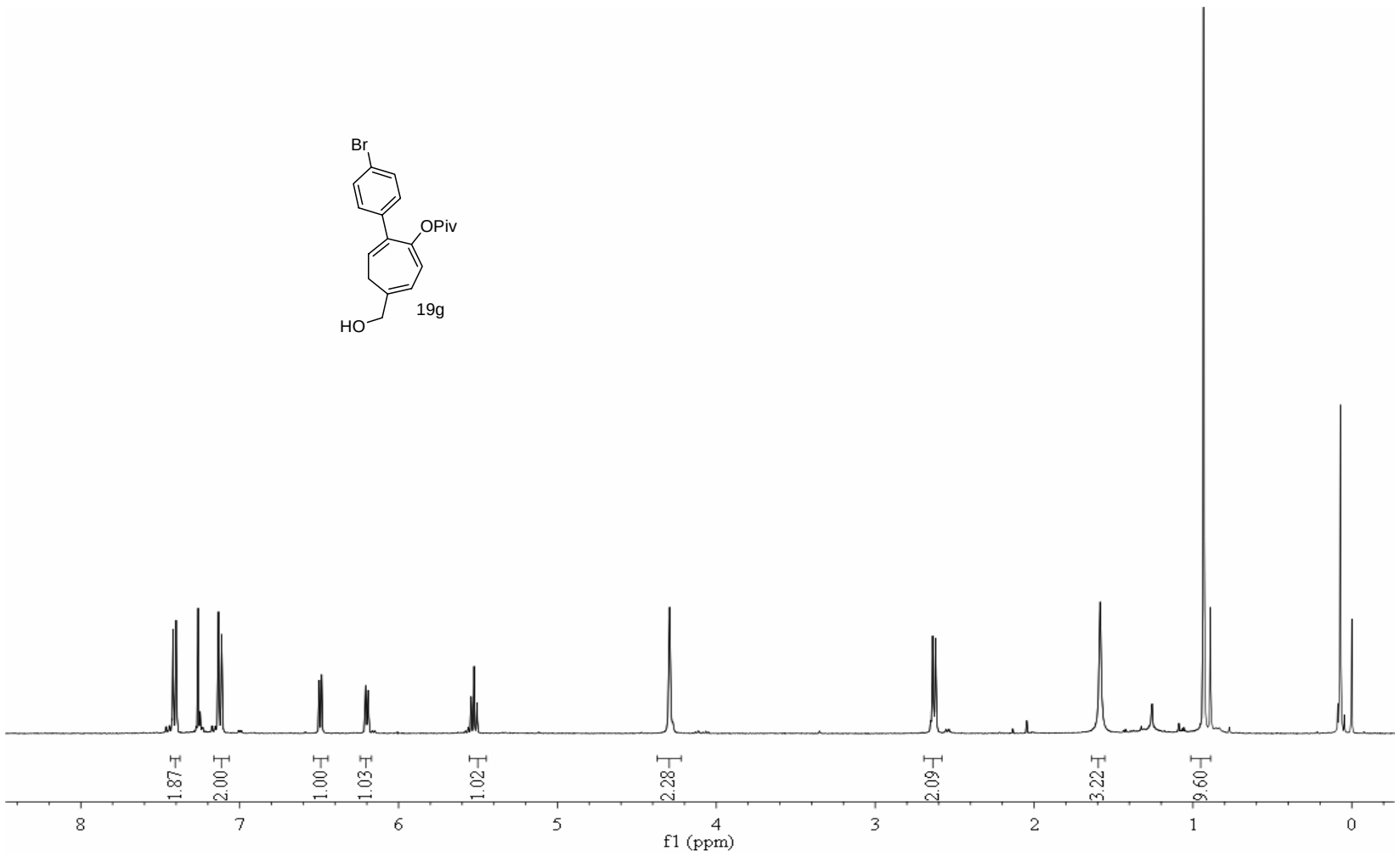

177.391
151.717
137.794
136.930
119.869
119.281
118.296
77.572
77.254
76.936
66.137
39.160
29.006
27.354
25.021
13.529
Et
OPiv
HO
19d
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

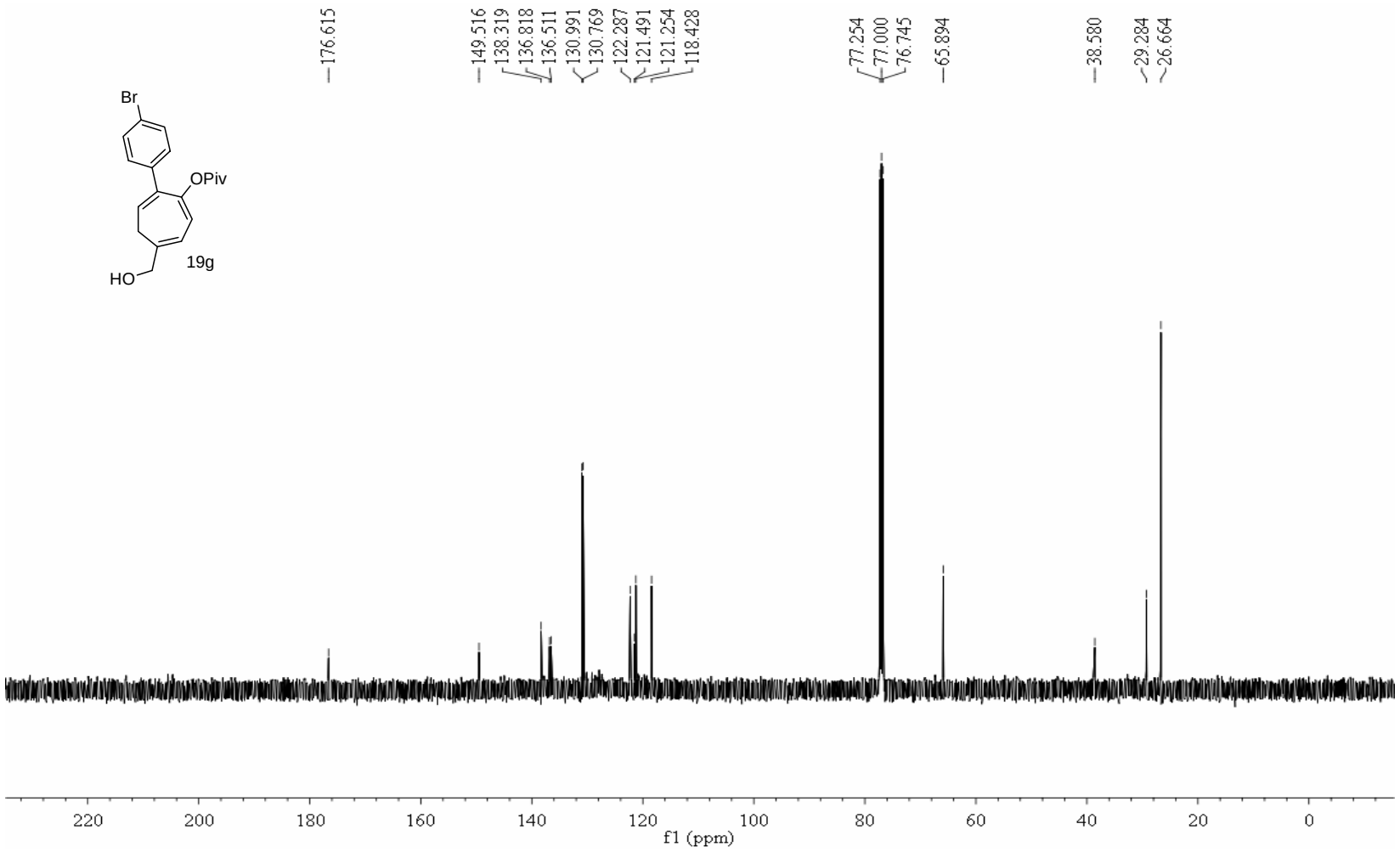

TBSO
OPiv
HO
19e
1.00
1.01
1.02
2.16
2.15
2.07
1.33
9.61
9.80
5.91
8
7
6
5
4
3
2
1
0
f1 (ppm)

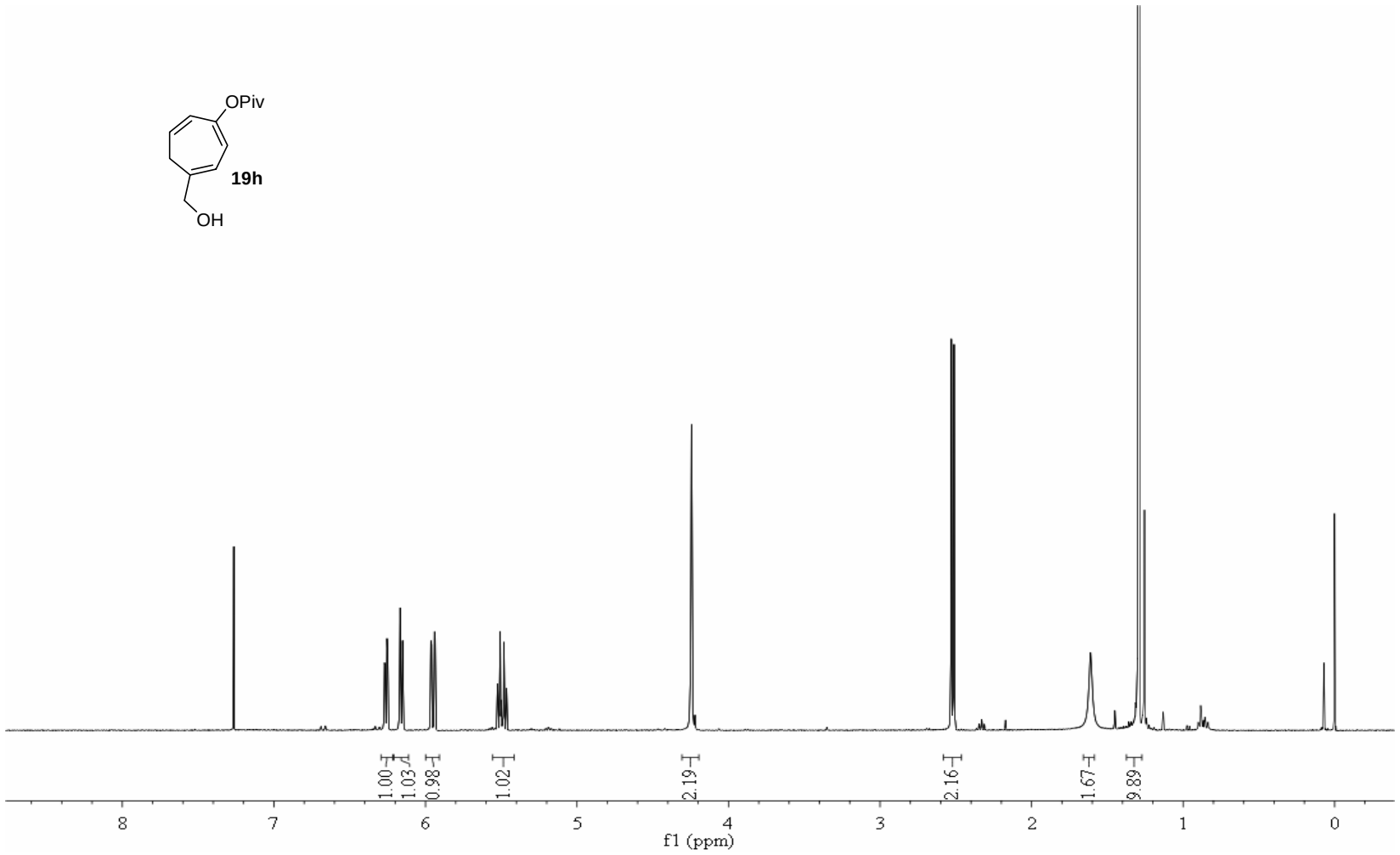

176.946
149.983
137.019
134.659
120.082
119.273
118.305
77.318
77.000
76.682
66.008
62.011
38.976
28.522
27.106
25.843
18.292
-5.339
TBSO
OPiv
HO
19e
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

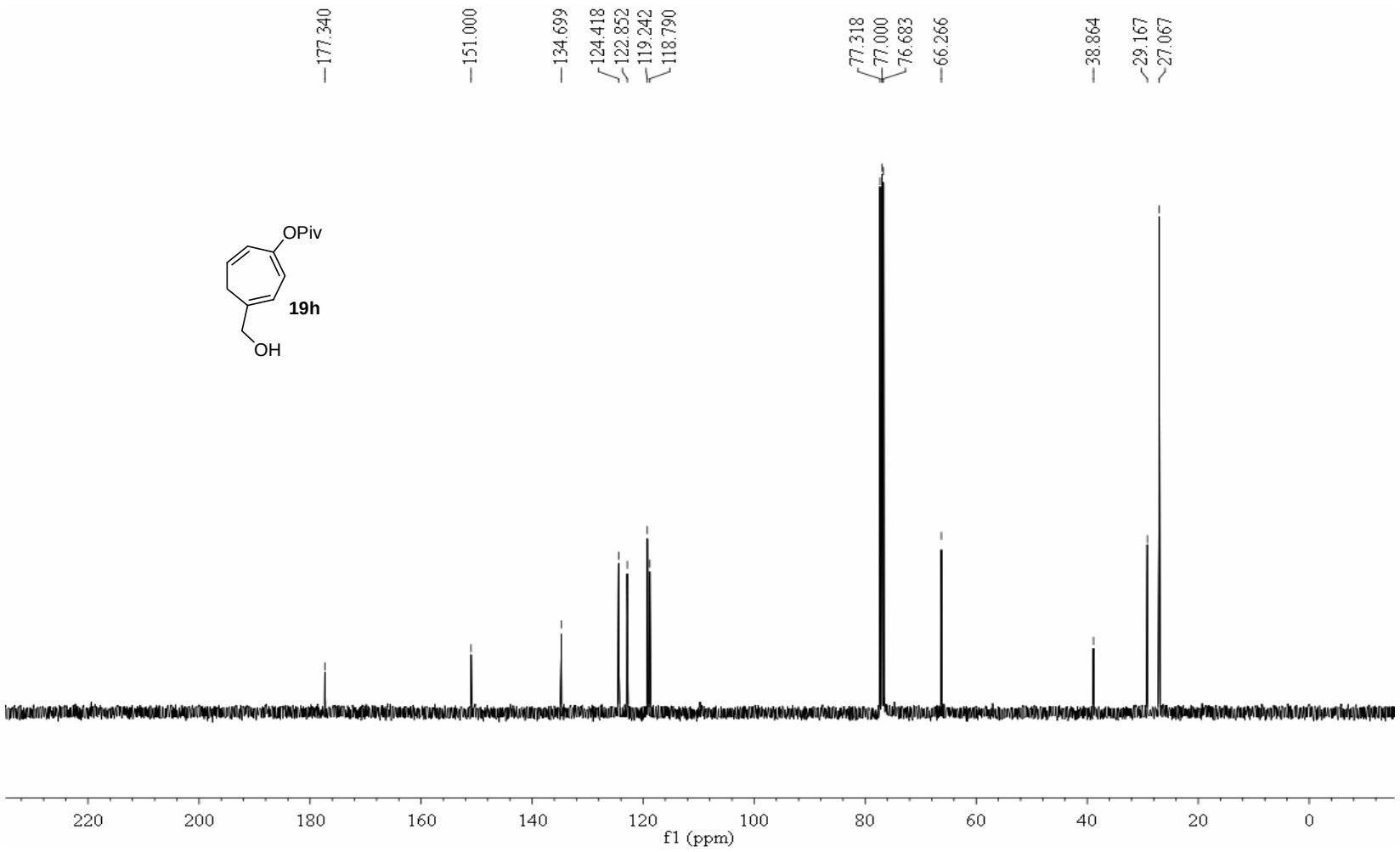

Ph
OPiv
HO
19f
5.59
0.94
0.98
0.98
2.19
2.00
1.48
9.56
8
7
6
5
4
3
2
1
0
f1 (ppm)

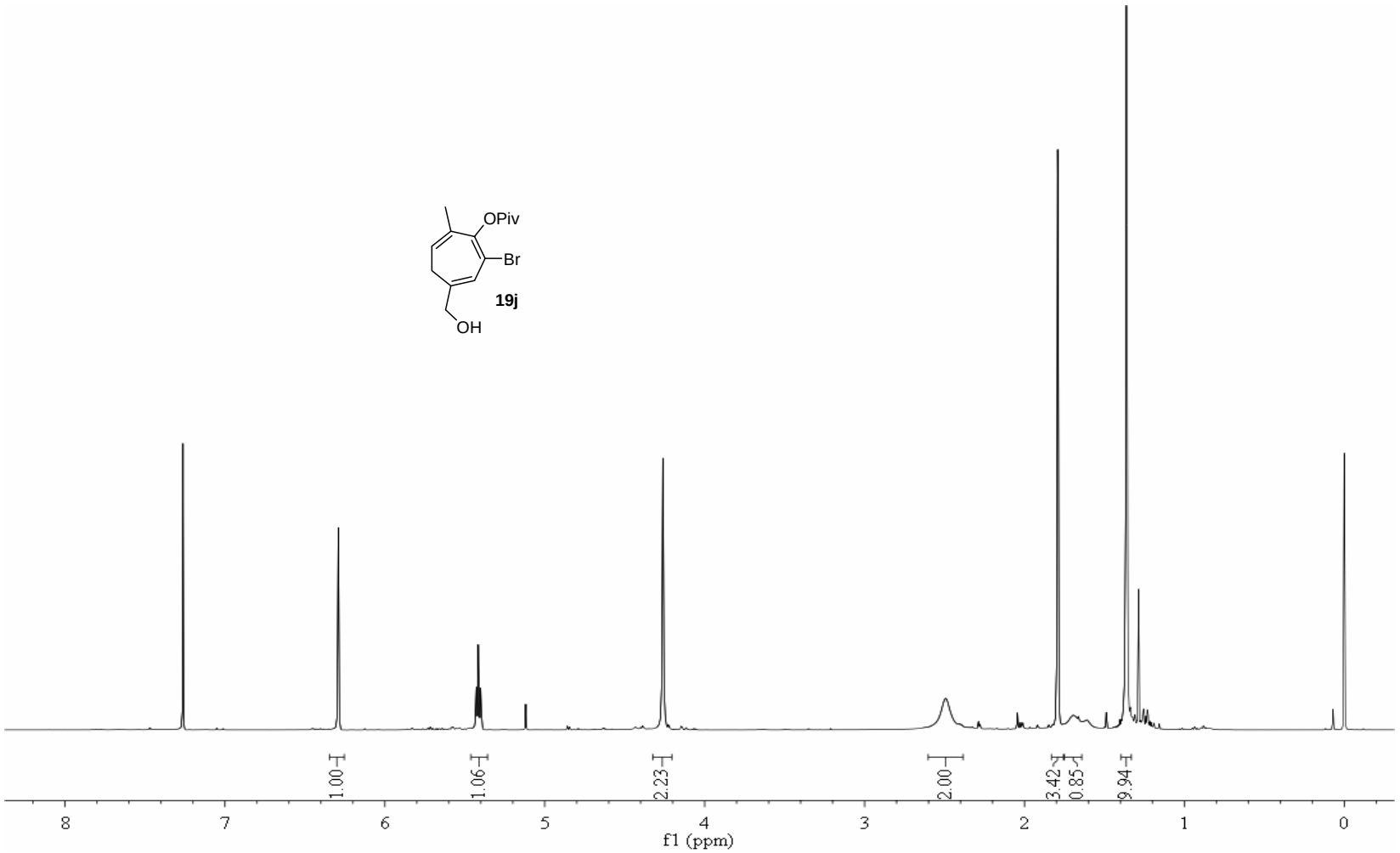

176.665
150.070
138.182
137.830
137.573
129.169
127.848
127.369
121.972
120.848
118.367
77.318
77.000
76.683
65.913
38.526
29.289
26.586
Ph
OPiv
HO
19f
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

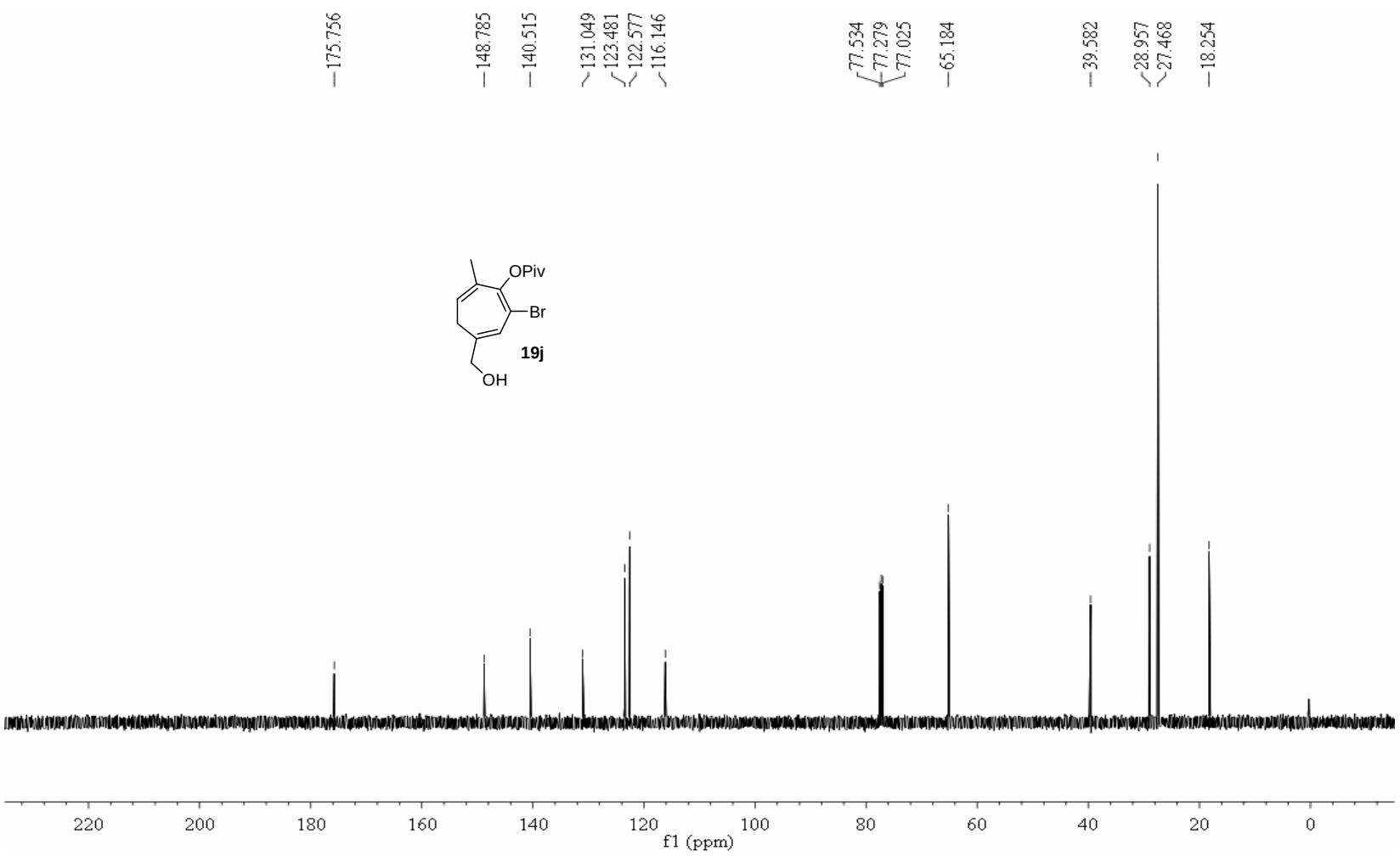

Br
OPiv
HO
19g
1.87
2.00
1.00
1.03
1.02
2.28
2.09
3.22
9.60
8
7
6
5
4
3
2
1
0
f1 (ppm)

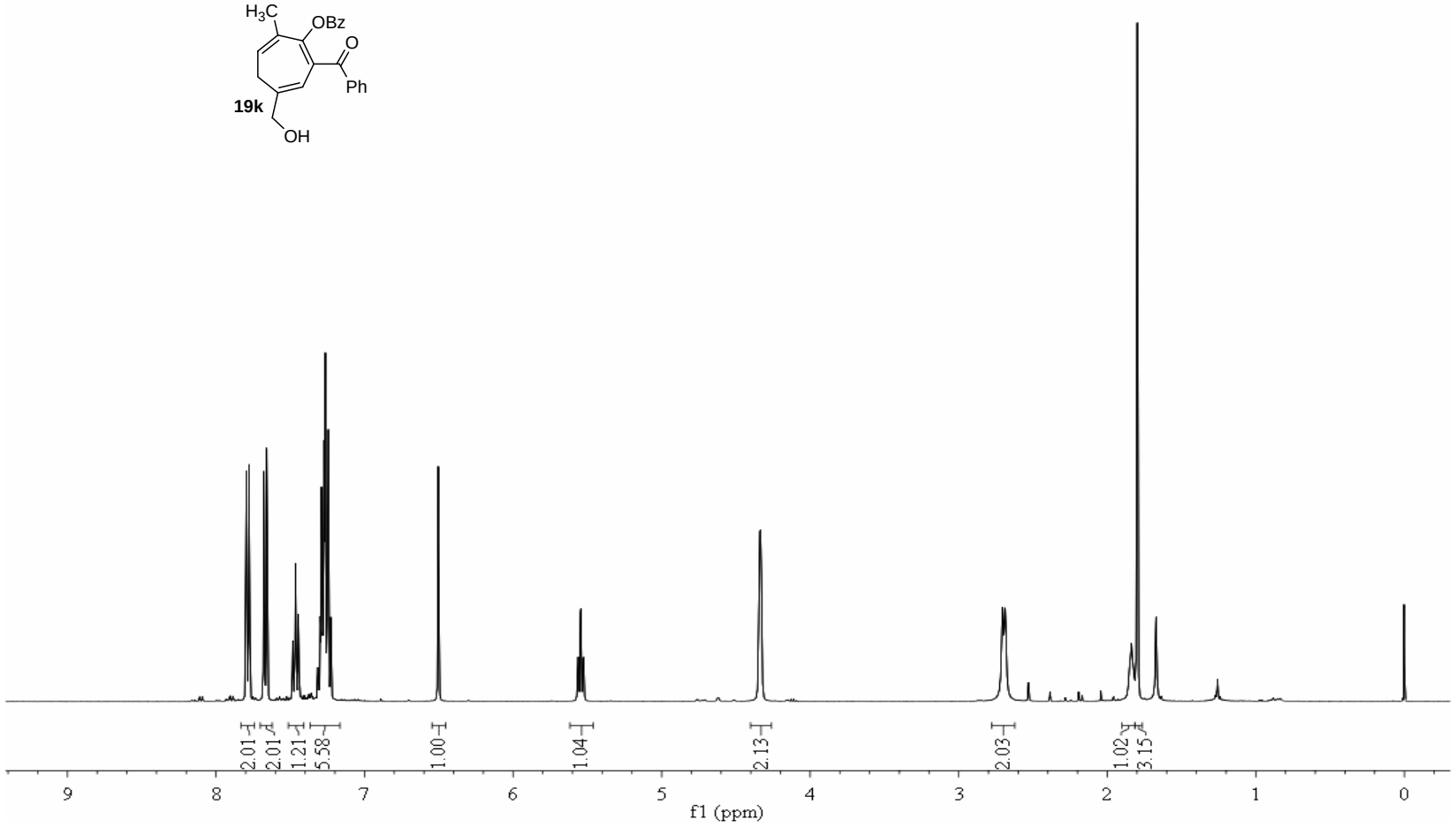

176.615
149.516
138.319
136.818
136.511
130.991
130.769
122.287
121.491
121.254
118.428
77.254
77.000
76.745
65.894
38.580
29.284
26.664
Br
OPiv
HO
19g
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

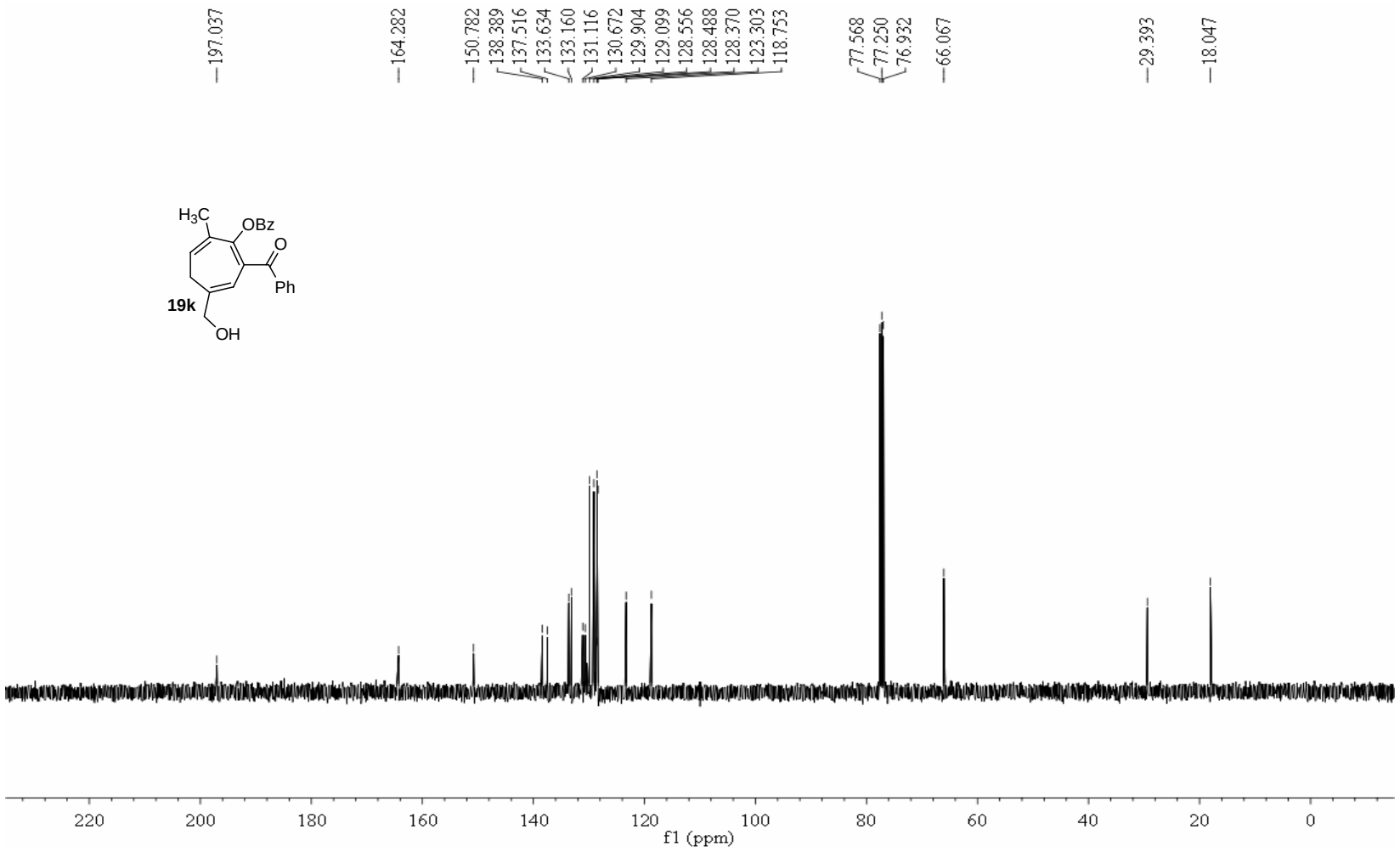

OPiv
19h
OH
1.00
1.03
0.98
1.02
2.19
2.16
1.67
9.89
8
7
6
5
4
3
2
1
0
f1 (ppm)

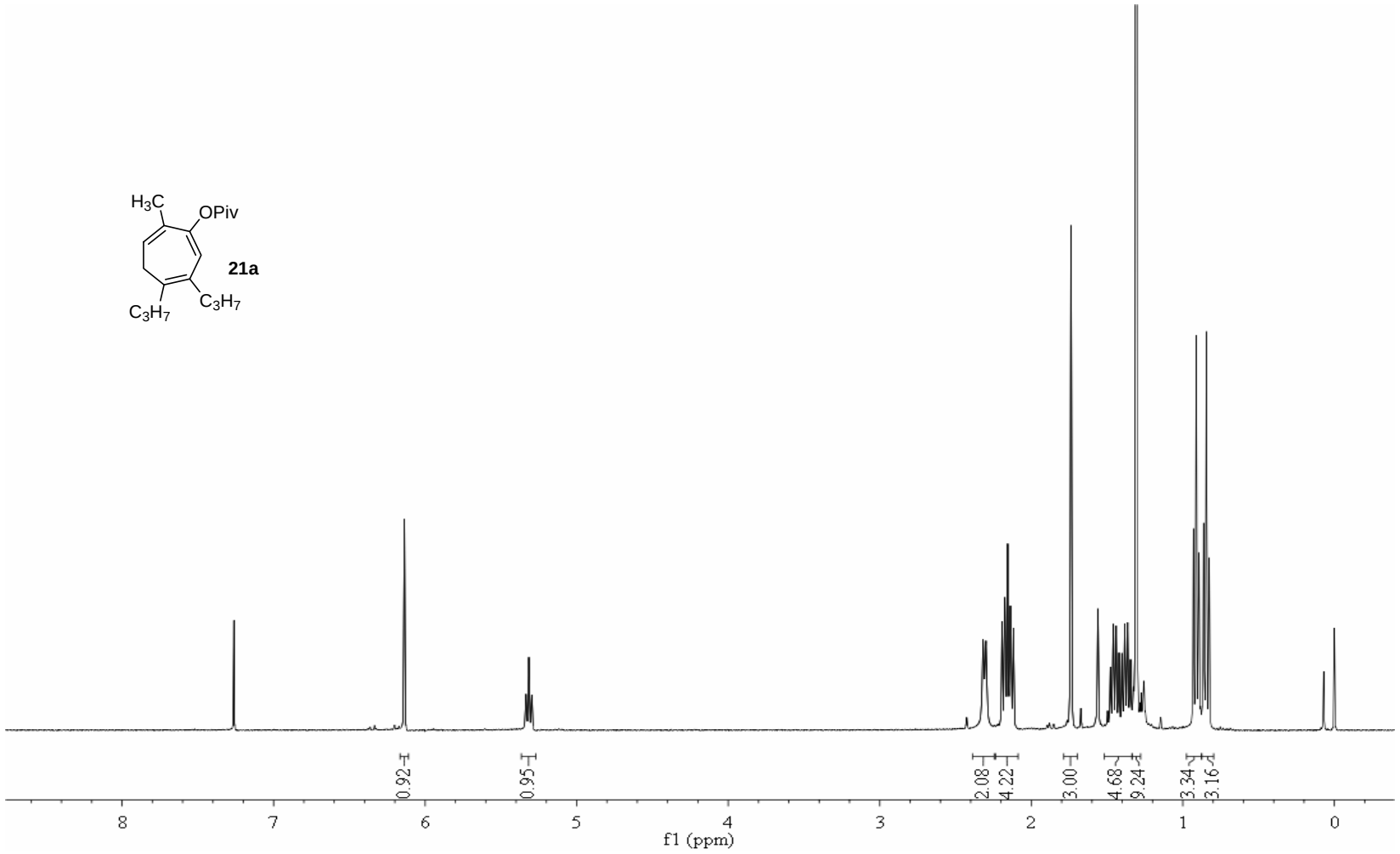

177.340
151.000
134.699
124.418
122.852
119.242
118.790
77.318
77.000
76.683
66.266
38.864
29.167
27.067
OPiv
19h
OH
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

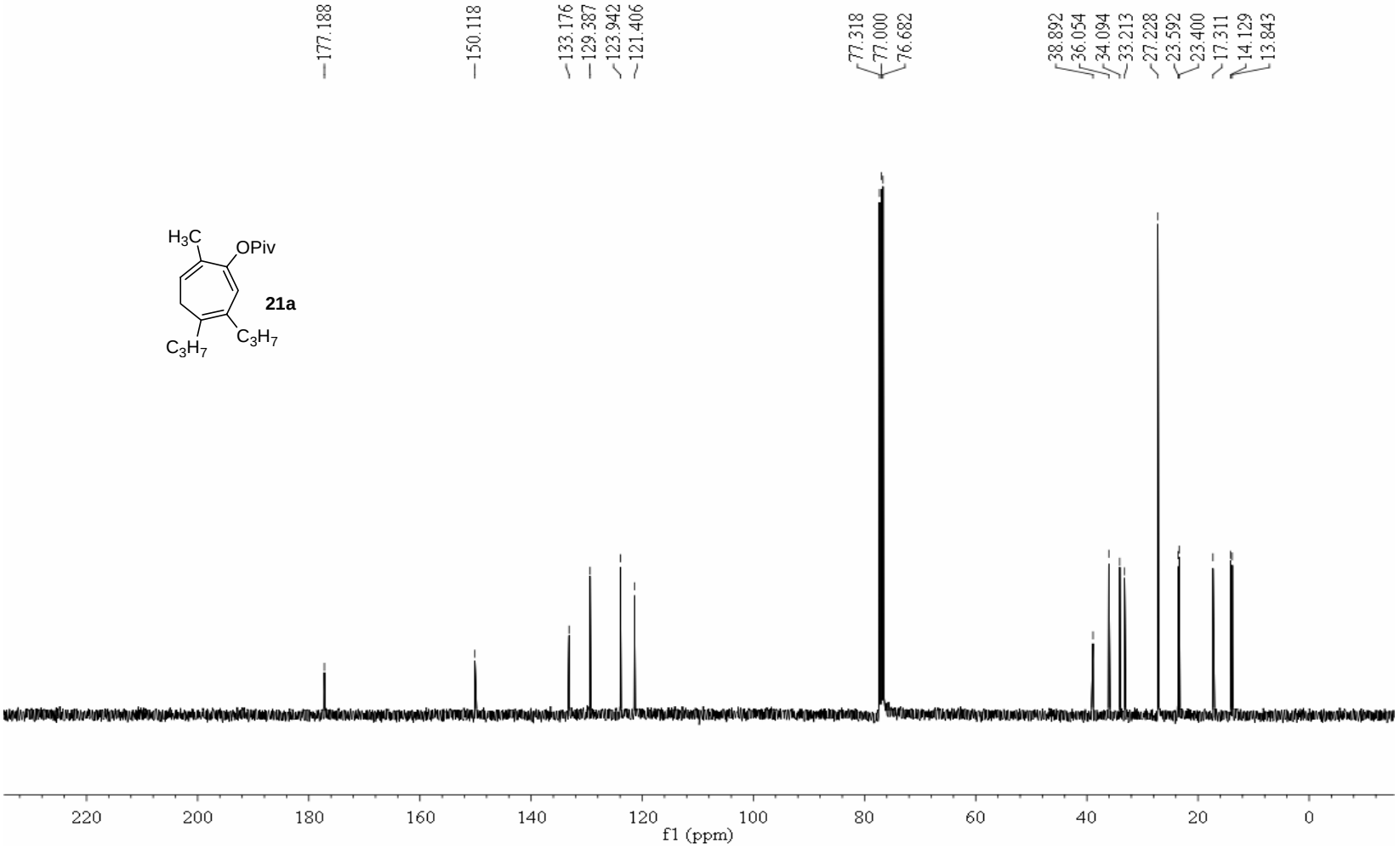

OPiv
Br
19j
OH
1.00
1.06
2.23
2.00
3.42
0.85
9.94
8
7
6
5
4
3
2
1
0
f1 (ppm)

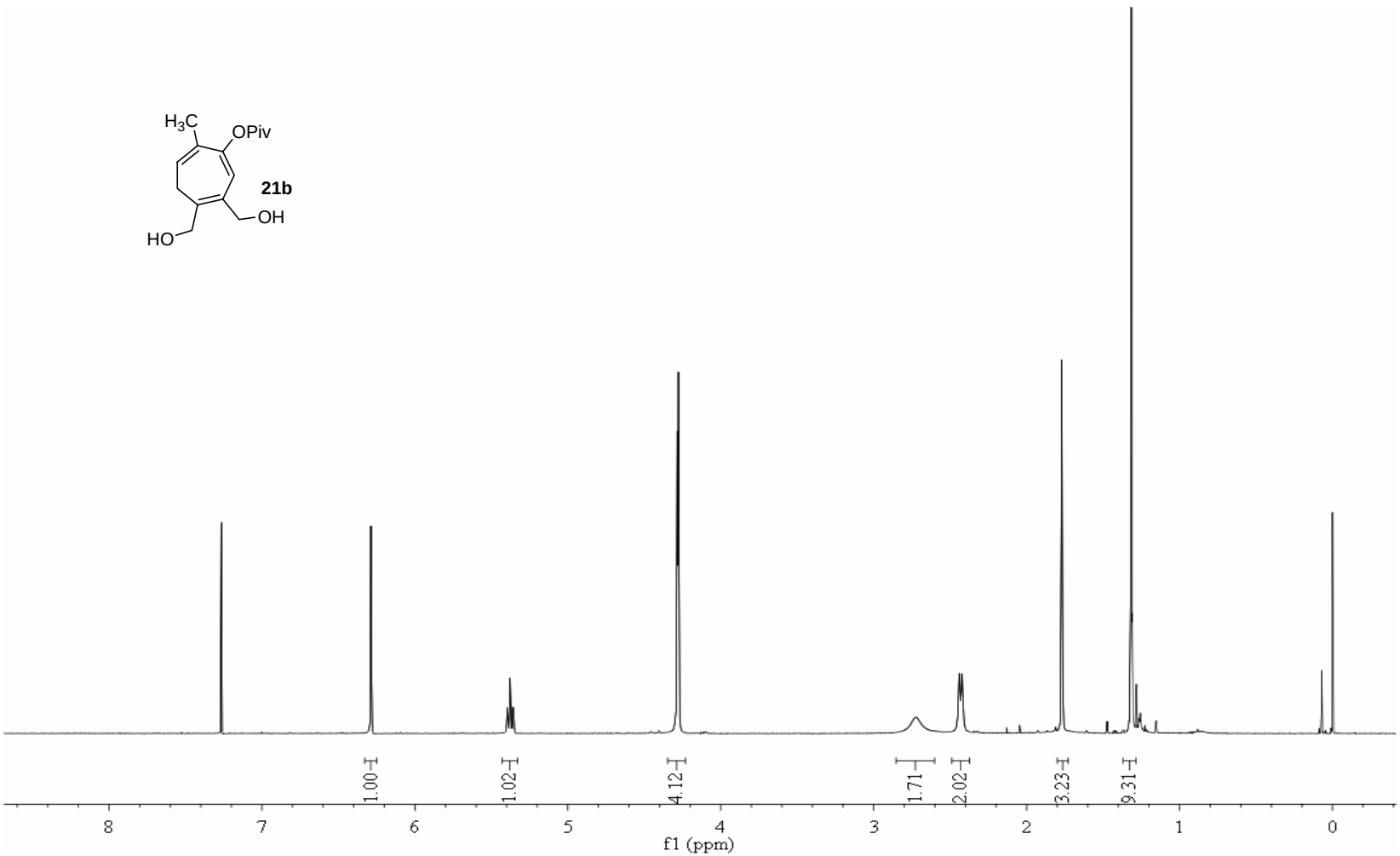

175.756
148.785
140.515
131.049
123.481
122.577
116.146
77.534
77.279
77.025
65.184
39.582
28.957
27.468
18.254
OPiv
Br
19j
OH
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

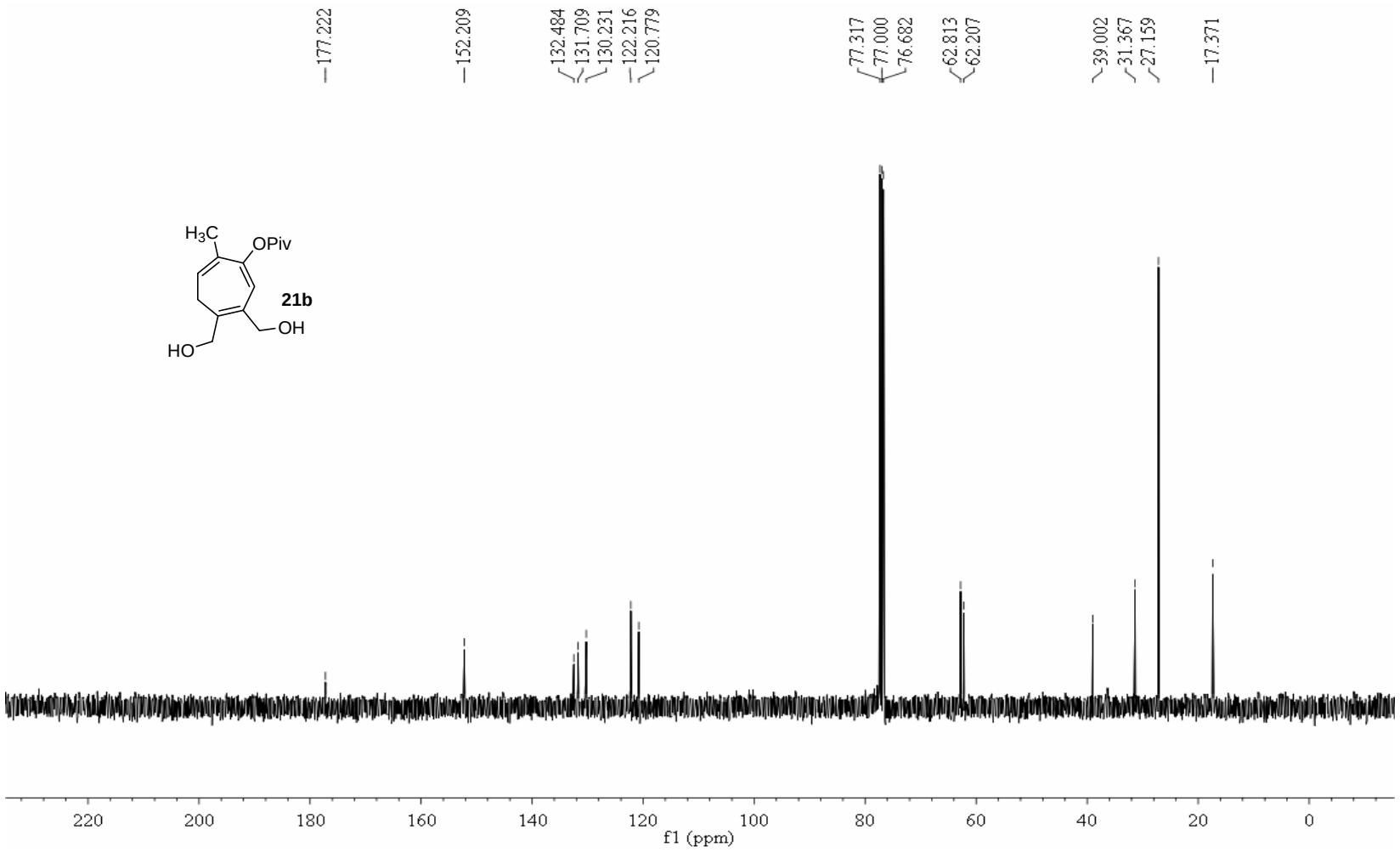

H3C
OBz
O
Ph
19k
OH
2.01
2.01
1.21
5.58
1.00
1.04
2.13
2.03
1.02
3.15
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

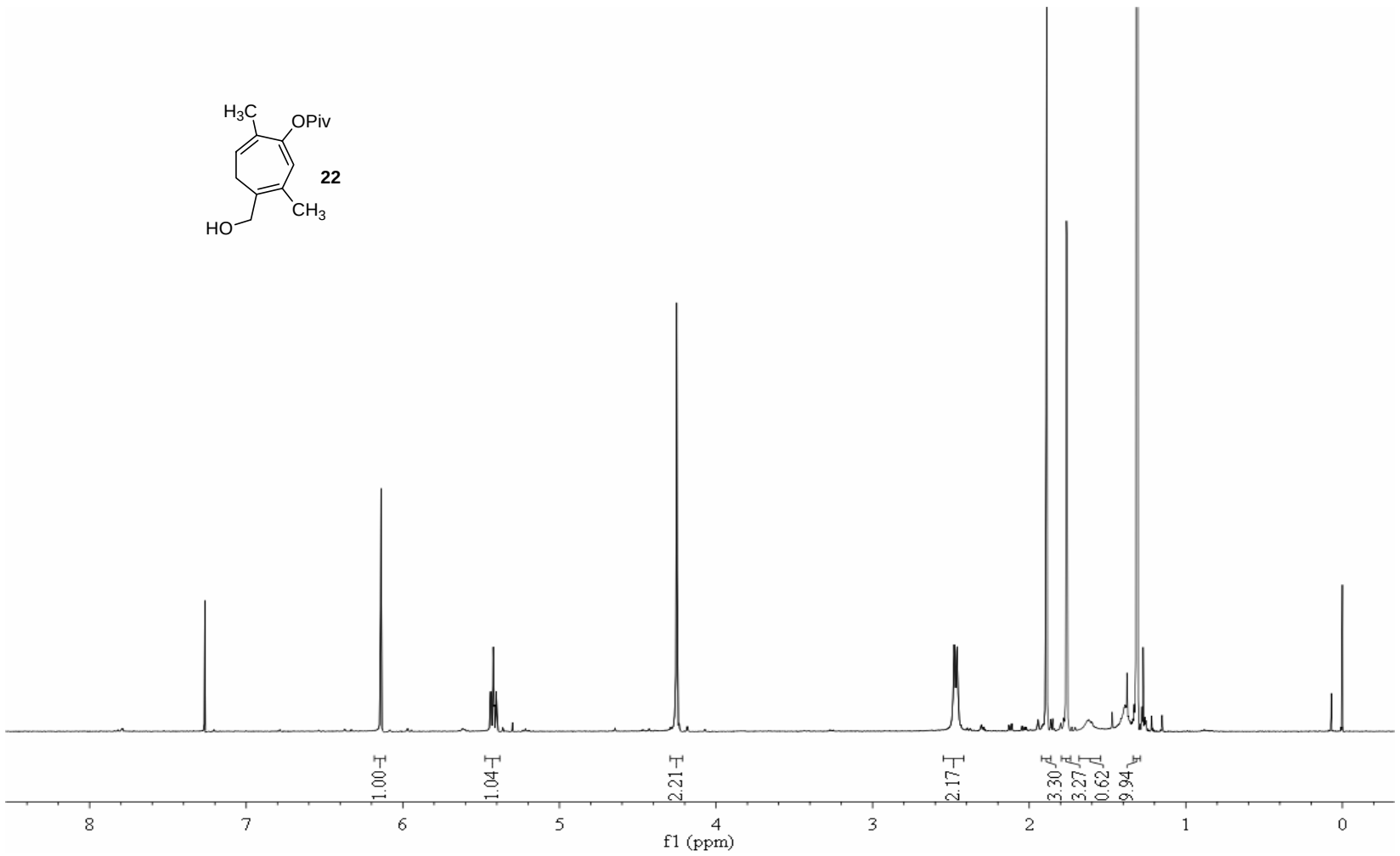

197.037
164.282
150.782
138.389
137.516
133.634
133.160
131.116
130.672
129.904
129.099
128.556
128.488
128.370
123.303
118.753
77.568
77.250
76.932
66.067
29.393
18.047
H3C
OBz
O
Ph
19k
OH
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

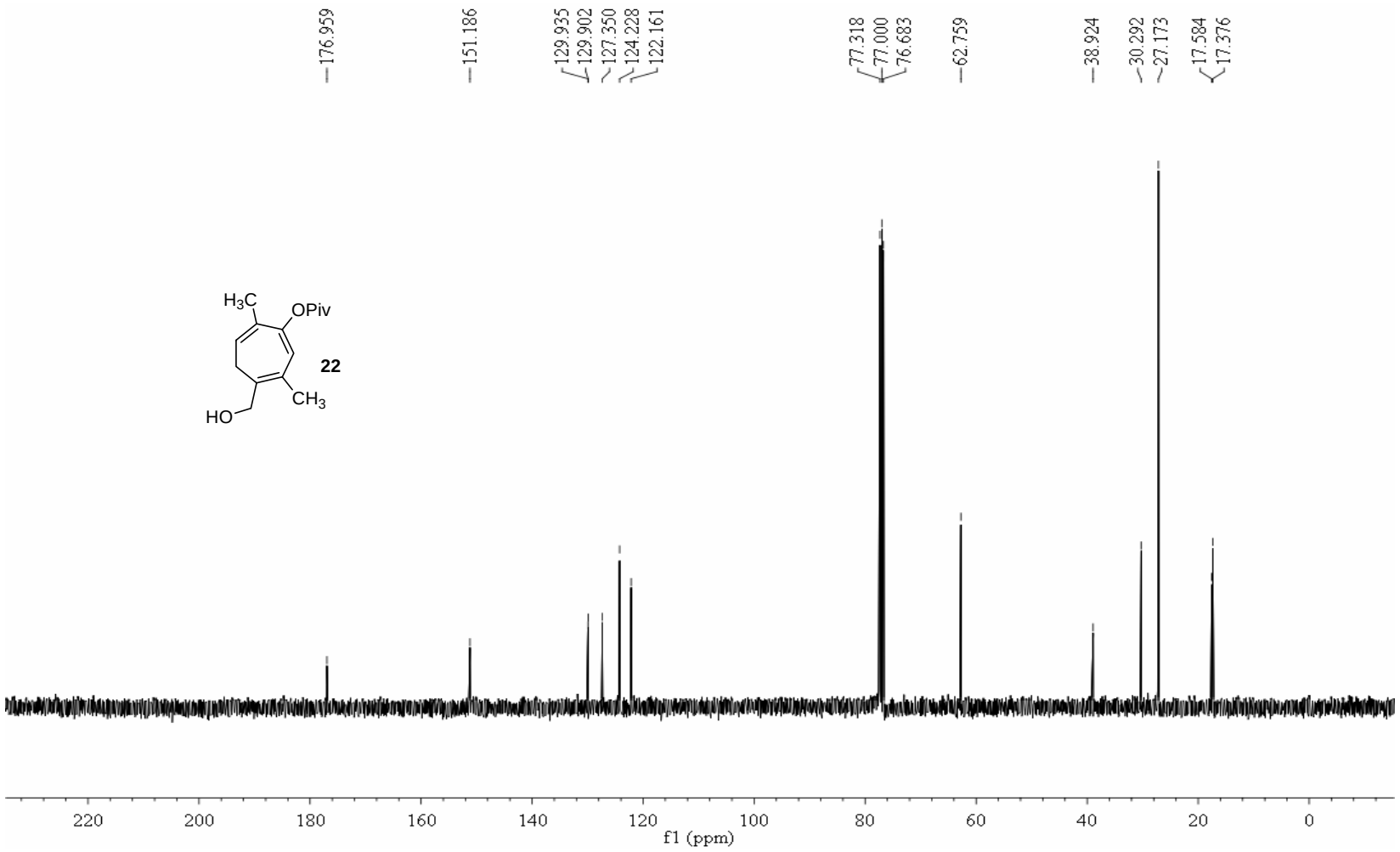

H3C
OPiv
21a
C3H7
C3H7
0.92
0.95
2.08
4.22
3.00
4.68
9.24
3.34
3.16
8
7
6
5
4
3
2
1
0
f1 (ppm)

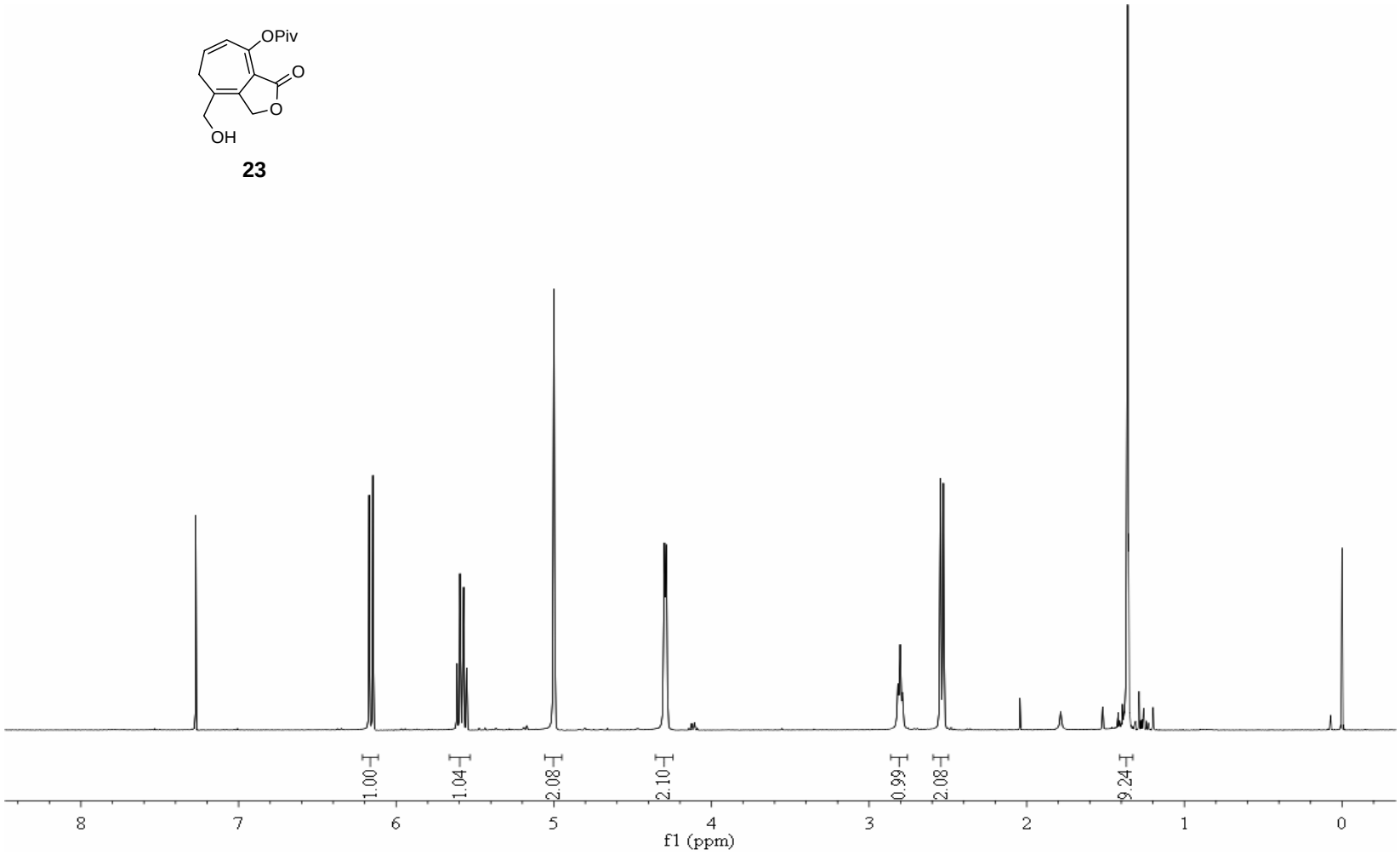

177.188
150.118
133.176
129.387
123.942
121.406
77.318
77.000
76.682
38.892
36.054
34.094
33.213
27.228
23.592
23.400
17.311
14.129
13.843
H3C
OPiv
21a
C3H7
C3H7
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

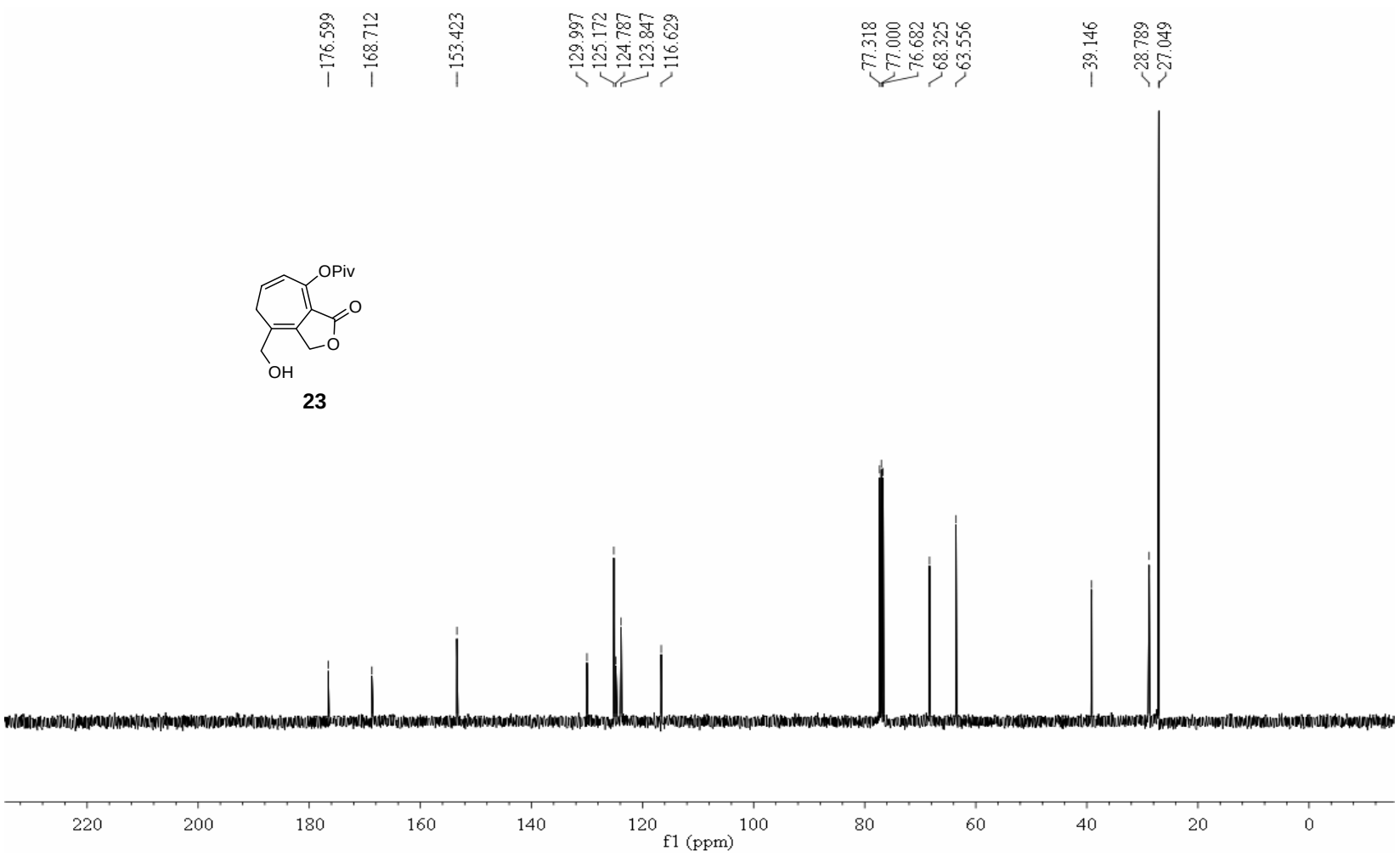

H3C
OPiv
21b
OH
HO
1.00
1.02
4.12
1.71
2.02
3.23
9.31
8
7
6
5
4
3
2
1
0
f1 (ppm)

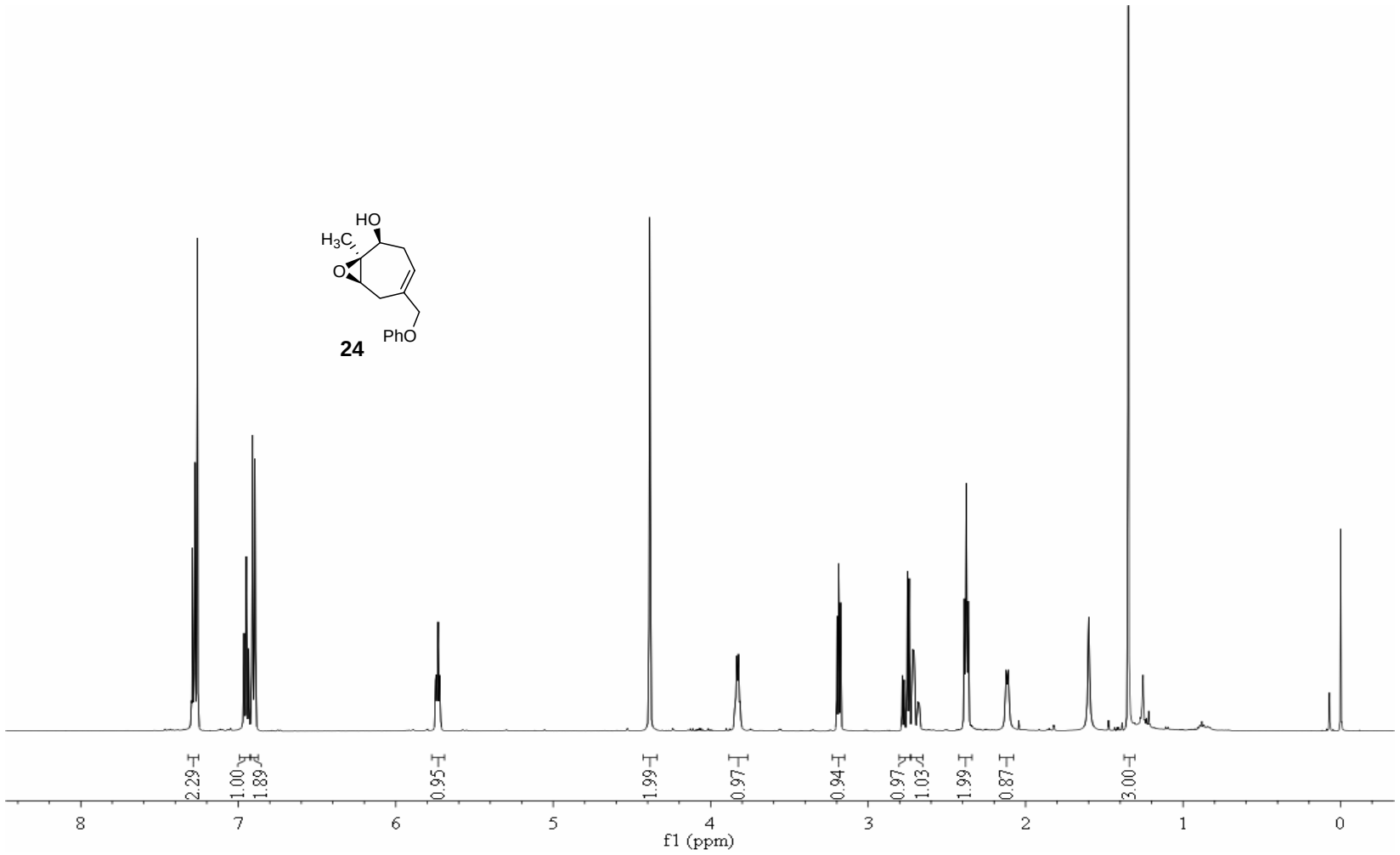

177.222
152.209
132.484
131.709
130.231
122.216
120.779
77.317
77.000
76.682
62.813
62.207
39.002
31.367
27.159
17.371
H3C
OPiv
21b
OH
HO
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

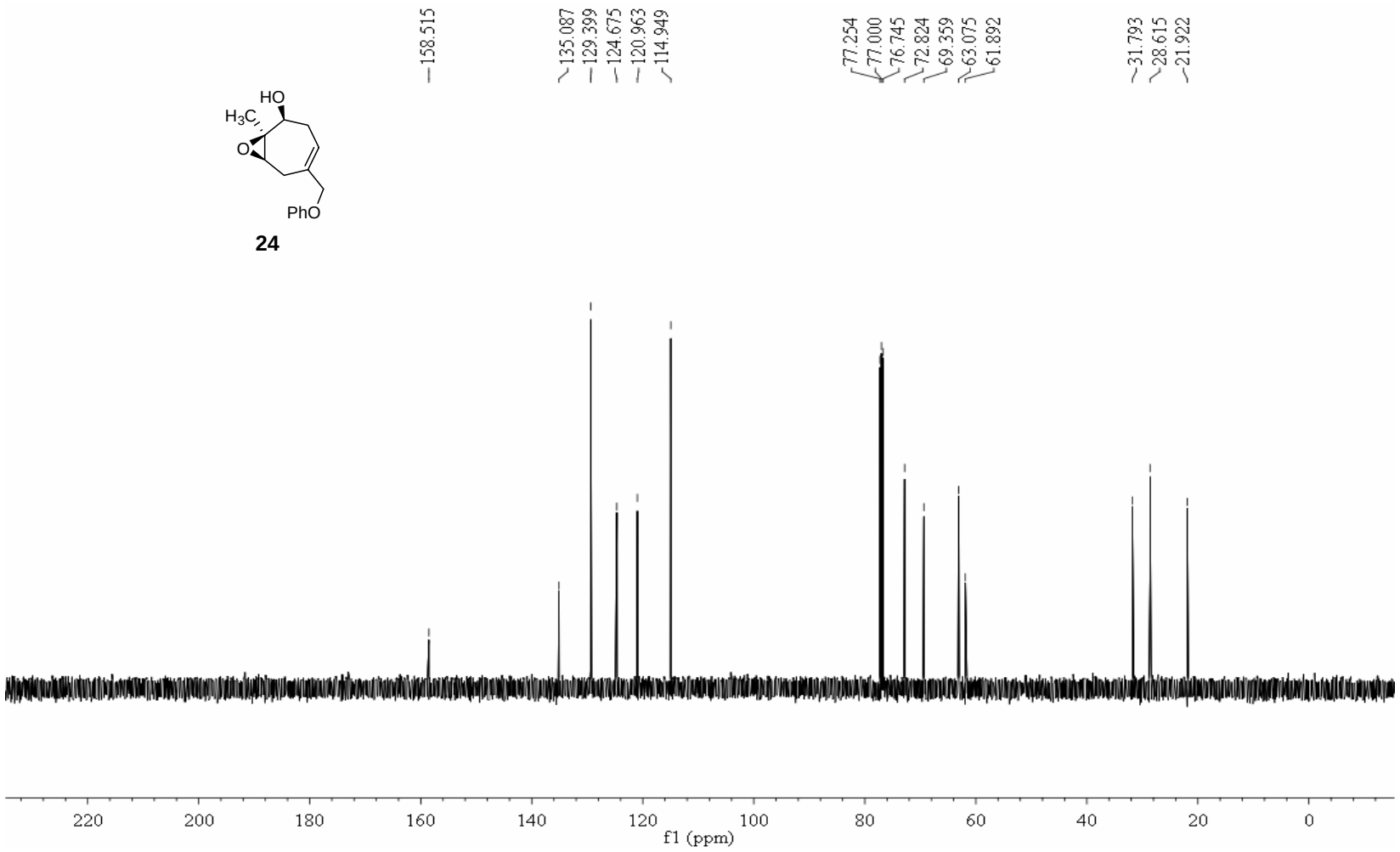

H3C
OPiv
22
CH3
HO
1.00
1.04
2.21
2.17
3.30
3.27
0.62
9.94
8
7
6
5
4
3
2
1
0
f1 (ppm)


176.959
151.186
129.935
129.902
127.350
124.228
122.161
77.318
77.000
76.683
62.759
38.924
30.292
27.173
17.584
17.376
H3C
OPiv
22
CH3
HO
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


OPiv
O
O
OH
23
1.00
1.04
2.08
2.10
0.99
2.08
9.24
8
7
6
5
4
3
2
1
0
f1 (ppm)


176.599
168.712
153.423
129.997
125.172
124.787
123.847
116.629
77.318
77.000
76.682
68.325
63.556
39.146
28.789
27.049
OPiv
O
O
OH
23
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


HO
H3C
O
PhO
24
2.29
1.00
1.89
0.95
1.99
0.97
0.94
0.97
1.03
1.99
0.87
3.00
8
7
6
5
4
3
2
1
0
f1 (ppm)


158.515
135.087
129.399
124.675
120.963
114.949
77.254
77.000
76.745
72.824
69.359
63.075
61.892
31.793
28.615
21.922
HO
H3C
O
PhO
24
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)