Supporting Information

Rhodium-Catalyzed Stereoselective Intramolecular [5 + 2] Cycloaddition of 3-Acyloxy-1,4-enyne and Alkene

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General Remarks:

All reactions were conducted under a positive pressure of dry argon in glassware that had been oven dried prior to use. Anhydrous solutions of reaction mixtures were transferred via an oven dried syringe or cannula. All solvents were dried prior to use unless noted otherwise. Thin layer chromatography (TLC) was performed using precoated silica gel plates. Flash column chromatography was performed with silica gel. Infrared spectra (IR) were obtained as neat oils. ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint),or multiplet (m), with coupling constants (*J*) in hertz. High resolution mass spectra (HRMS) were performed on an Electron Spray Injection (ESI) TOF mass spectrometer. Enantiomeric excess was determined by chiral HPLC analysis.

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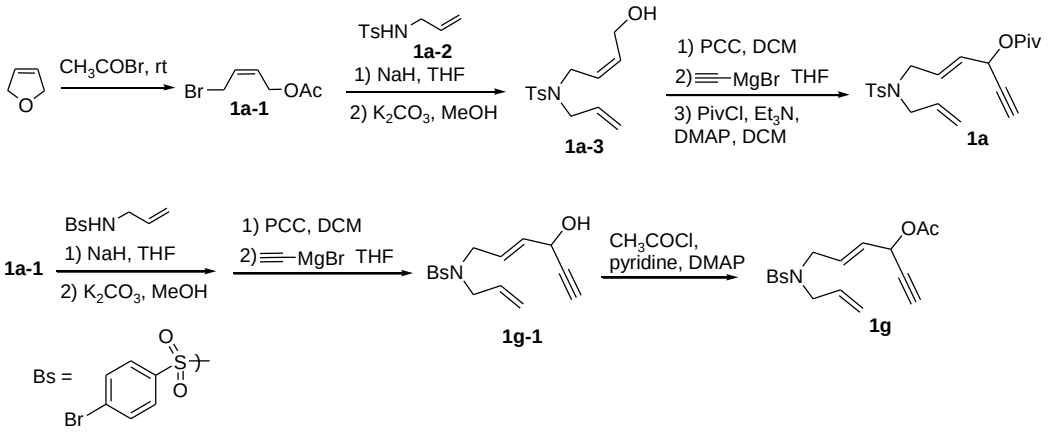
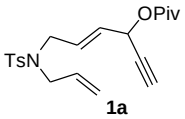
General procedure for the preparation of substrates with a nitrogen linker (1a and 1g)

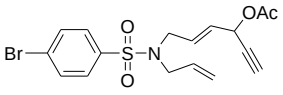


Bromide **1a-1** was prepared in one step according to the literature procedure.[1]
To a stirred solution of NaH (480 mg, 12.0 mmol, 60% in mineral oil) in THF (50 mL) at 0 °C was added sulfonamide **1a-2** (2.11 g, 10.0 mmol) under argon atmosphere. After stirring at rt for 0.5 h, compound **1a-1** (2.11 g, 11.0 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 (60 mL), and K_2CO_3 (4.14 g, 30 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 alcohol **1a-3** (2.14 g, 7.6 mmol) in 76% yield over 2 steps. Product **1a** (1.89 g, 4.86 mmol) was obtained in 64% yield over three steps from **1a-3** according to known procedures.[2]



1a

(*E*)-6-(N-allyl-N-tosylamino)hex-4-en-1-yn-3-yl pivalate (**1a**).
Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 9H), 2.43 (s, 3H), 2.51 (d, *J* = 2.0 Hz, 1H), 3.79 (d, *J* = 6.4 Hz, 2H), 3.85 (d, *J* = 6.0 Hz, 2H), 5.12-5.17 (m, 2H), 5.55-5.66 (m, 2H), 5.73-5.80 (m, 2H), 7.30 (dd, *J* = 0.8, 8.4 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 27.2, 38.9, 47.9, 49.9, 62.9, 75.1, 79.3, 119.5, 127.4, 129.2, 129.5, 130.0, 132.7, 137.4, 143.6, 177.1. IR (film): 3268, 2974, 2932, 1731, 1479, 1341, 1273, 1140, 1090, 1031, 970 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{21}H_{27}NO_4S$ $(M+Na)^+$ 412.1553, found 412.1546.



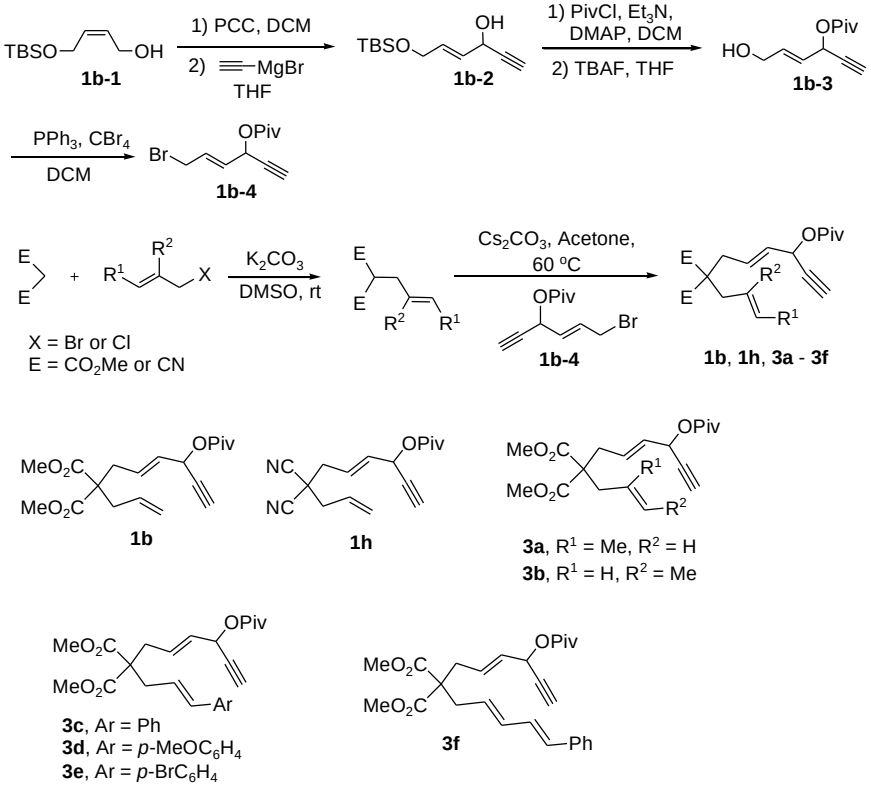
1g

(*E*)-Acetic acid 4-[allyl-(4-bromo-benzenesulfonyl)-amino]-1-ethynyl-but-2-enyl ester (**1g**).

Substrate **1g** was prepared in five steps (30.8 mg, 55% yield) according to procedures similar to **1a**.

Oil. ^{1}H NMR (500Mz, $CDCl_3$) δ 2.09 (s, 3H), 2.56 (d, J= 2.0 Hz, 1H), 3.81 (d, J= 6.0 Hz, 2H), 3.86 (d, J= 6.5 Hz, 2H), 5.16 (qd, J= 1.3, 16.8 Hz, 1H), 5.19 (qd, J= 1.3, 9.9 Hz, 1H), 5.61 (tdd, J= 6.0, 10.5, 17.0 Hz, 1H), 5.64 (tdd, J= 1.3, 5.7, 15.3 Hz, 1H), 5.76 (dtd, J= 1.2, 6.3, 15.3 Hz, 1H), 5.81-5.79 (m, 1H), 7.70-7.64 (m, 4H). ^{13}C NMR (125Mz, $CDCl_3$) δ 21.2, 47.8, 50.0, 63.1, 75.7, 79.0, 119.9, 127.8, 129.0, 129.3, 129.5, 132.4, 132.7, 139.7, 169.7. IR (film): 2918, 1738, 1574, 1389, 1370, 1343, 1224, 1161, 1089, 1069, 1009, 970, 908, 823, 763, 728, 669 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{17}H_{18}BrNO_4S$ $(M+Na)^+$ 434.0032, found 434.0022.

General procedure for the preparation of substrates with a gem-diester or gem-dinitrile linker (1b, 1h, 3a, 3b, 3c, 3d, 3e, and 3f).



Synthesis of bromide 1b-4.

To a suspension of PCC (6.46 g, 30 mmol) and 4 Å MS (1 g, 50mg/mmol) in CH_2Cl_2 (100 mL) was added a solution of compound **1b-1** (4.04 g, 20 mmol) in dry CH_2Cl_2 (40 mL) at 0 °C. 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 ethynylmagnesium bromide solution (48 mL, 24 mmol, 0.5 M in THF) was added a solution of above crude aldehyde in THF (40 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 (60 mL) and extracted with ethyl ether (2×60 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 flash column chromatography (silica gel, hexane/ethyl acetate 10:1) to obtain the desired propargylic alcohol **1b-2** (3.27 g, 14.5 mmol) in 72% yield for 2 steps.

To a stirred solution of propargylic alcohol **1b-2** (3.27 g, 14.5 mmol) in CH_2Cl_2 (80 mL) was added triethylamine (4.39 g, 43.5 mmol), pivaloyl chloride (2.09 g, 17.4 mmol), and DMAP (5 mol %) at room temperature. The resultant mixture was stirred overnight, washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude pivalate product for the next step without purification.

To a stirred solution of above pivalate compound in THF (60 mL) was added a solution of tetrabutylammonium fluoride (21 mL, 21 mmol, 1.0M in THF) at 0 °C. The mixture was stirred at room temperature for 2 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. The residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 4:1) to obtain the alcohol **1b-3** (2.29 g, 11.7 mmol) in 81% yield for 2 steps.

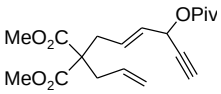
To a solution of alcohol **1b-3** (2.29 g, 11.7 mmol) in CH_2Cl_2 (80 mL) was added tetrabromomethane (5.72 g, 17.5 mmol) and triphenylphosphine (4.58 g, 17.5 mmol) at 0°C. The reaction mixture was stirred for 1 h at room temperature before silica was added and the solvents were removed under reduced pressure. The residue was purified through silica gel column chromatography (silica gel, hexane/ethyl acetate 20:1) to afford the corresponding bromide **1b-4** (2.73 g, 10.6 mmol) in 91% yield.

Synthesis of substrate 1b.

To a solution of dimethyl malonate (1.32 g, 10 mmol) in DMSO (50 mL), K_2CO_3 (2.07 g, 15 mmol) was added at 0 ºC and stirred for 10 min. Then allyl bromide (1.44 g, 12 mmol) was added slowly and the reaction mixture was stirred at rt overnight. Ethyl acetate was added to the reaction mixture. It was washed three times with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified through silica gel column chromatography (silica gel, hexane/ethyl acetate 10:1) to give 2-allylmalonate (1.44 g, 8.4 mmol) in 84% yield.

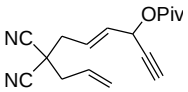
To a stirred solution of 2-allylmalonate (172 mg, 1 mmol) and cesium carbonate (650 mg, 2.0 mmol) in dry acetone (4 mL) was added bromide **1b-4** (387 mg, 1.5 mmol). The resulting mixture was heated to 60°C and stirred overnight. The residue was filtered

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 (10:1 Hex/EtOAc) to afford **1b** (304 mg, 0.87 mmol) in 87% yield as an oil.



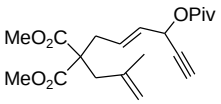
1b

Dimethyl 2-allyl-2-((*E*)-4-(pivaloyloxy)hex-2-en-5-ynyl)malonate (**1b**).
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 2.52 (d, *J* = 2.0 Hz, 1H), 2.62-2.67 (m, 4H), 3.72 (s, 6H), 5.09-5.14 (m, 2H), 5.59-5.66 (m, 2H), 5.77-5.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 35.4, 37.4, 38.9, 52.7, 57.7, 63.5, 74.8, 79.8, 119.7, 129.4, 129.7, 132.2, 171.1, 177.1. IR (film): 3275, 2975, 1730, 1437, 1274, 1212, 1138, 1031, 925 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{26}O_6$ $(M+Na)^+$ 373.1622, found 373.1617.



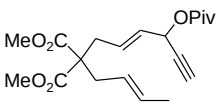
1h

(*E*)-7,7-dicyanodeca-4,9-dien-1-yn-3-yl pivalate (**1h**).
Compound **1h** (146 mg, 0.51 mmol) was prepared in two steps and 46% yield from malononitrile, allyl bromide, and bromide **1b-4** according to procedures described for **1b**. Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 2.60 (d, *J* = 2.0 Hz, 1H), 2.68 (d, *J* = 7.2 Hz, 2H), 2.73 (d, *J* = 7.2 Hz, 2H), 5.39-5.47 (m, 2H), 5.83-5.94 (m, 3H), 6.07 (dtd, *J* = 3.2, 7.6, 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 37.2, 39.0, 39.2, 41.0, 62.8, 75.7, 78.8, 114.7, 114.8, 123.8, 125.1, 128.4, 133.5, 177.1. IR (film): 3295, 2976, 2911, 1731, 1479, 1273, 1139, 969 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{17}H_{20}N_2O_2$ $(M+Na)^+$ 307.1417, found 307.1406.



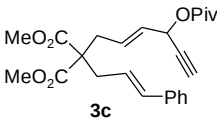
3a

Dimethyl 2-(2-methylallyl)-2-((*E*)-4-(pivaloyloxy)hex-2-en-5-ynyl)malonate (**3a**).
Compound **3a** (287 mg, 0.79 mmol) was prepared in two steps and 69% yield from dimethyl malonate and 3-bromo-2-methylprop-1-ene according to procedures described for **1b**. Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.65 (s, 3H), 2.52 (d, *J* = 2.4 Hz, 1H), 2.67-2.71 (m, 4H), 3.72 (s, 6H), 4.71-4.80 (m, 1H), 4.88-4.89 (m, 1H), 5.60 (tdd, *J* = 1.2, 6.4, 15.2 Hz, 1H), 5.77 (ddd, *J* = 1.2, 2.0, 6.0 Hz, 1H), 5.86 (dtd, *J* = 1.2, 7.6, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 27.2, 35.5, 38.9, 40.8, 52.66, 52.68, 57.4, 63.5, 74.8, 79.9, 116.2, 129.3, 130.1, 140.4, 171.5, 177.2. IR (film): 3271, 2973, 2361, 1731, 1436, 1272, 1201, 1178, 1140, 1063, 1031, 972 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{28}O_6$ $(M+Na)^+$ 387.1778, found 387.1762.



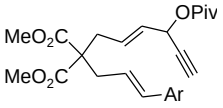
3b

Dimethyl 2-((*E*)-but-2-enyl)-2-((*E*)-4-(pivaloyloxy)hex-2-en-5-ynyl)malonate (**3b**).
Compound **3b** (299 mg, 0.82 mmol) was prepared in two steps and 75% yield from dimethyl malonate and (*E*)-1-bromobut-2-ene according to procedures described for **1b**. Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.61-1.67 (m, 3H), 2.52 (t, *J* = 2.0 Hz, 1H), 2.55-2.57 (m, 2H), 2.64 (t, *J* = 6.8 Hz, 2H), 3.71 (s, 6H), 5.18-5.26 (m, 1H), 5.48 -5.63 (m, 2H), 5.76-5.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 27.2, 35.4, 36.2, 38.9, 52.6, 58.0, 63.5, 74.8, 79.8, 124.4, 129.2, 130.0, 130.5, 171.3, 177.2. IR (film): 3290, 2956, 2360, 2341, 1731, 1437, 1271, 1203, 1140, 1031, 969 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{28}O_6$ $(M+Na)^+$ 387.1778, found 387.1766.



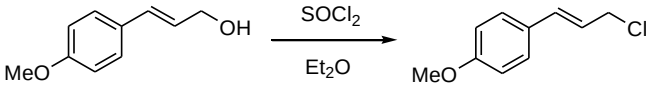
3c

Dimethyl 2-cinnamyl-2-((*E*)-4-(pivaloyloxy)hex-2-en-5-ynyl)malonate (**3c**).
Compound **3c** (215 mg, 0.5 mmol) was prepared in two steps and 57% yield from dimethyl malonate and (*trans*)-cinnamyl chloride according to procedures described for **1b**. Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 9H), 2.53 (d, *J* = 2.4 Hz, 1H), 2.71 (d, *J* = 7.6 Hz, 2H), 2.79 (dd, *J* = 1.2, 7.6 Hz, 2H), 3.74 (s, 6H), 5.64 (tdd, *J* = 1.2, 6.4, 15.2 Hz, 1H), 5.79-5.81 (m, 1H), 5.88 (dtd, *J* = 1.2, 7.6, 8.8 Hz, 1H), 6.00 (td, *J* = 7.6, 15.6 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 7.20-7.34 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.2, 35.8, 36.8, 39.0, 52.775, 52.783, 58.1, 63.5, 74.9, 79.9, 123.7, 126.5, 127.7, 128.8, 129.5, 129.8, 134.6, 137.2, 171.2, 177.2. IR (film): 3284, 2956, 1730, 1479, 1436, 1271, 1199, 1139, 1030, 967 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{30}O_6$ $(M+Na)^+$ 449.1935, found 449.1920.



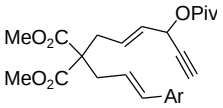
3d, Ar = *p*-$MeOC_6H_4$

Dimethyl 2-(4-methoxycinnamyl)-2-((*E*)-4-(pivaloyloxy)hex-2-en-5-ynyl)malonate (**3d**).



To a solution of (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol (328 mg, 2 mmol) in diethyl ether (2 ml, 1ml/mmol) at 0 ºC was slowly added $SOCl_2$ (283 mg, 2.4 mmol). The reaction mixture was stirred until completion, as determined by TLC. The resulting solution was then diluted with diethyl ether (30 ml), washed with a saturated solution of $NaHCO_3$, brine, dried over Na_2SO_4. The solvent was removed under reduced pressure to give crude allylic chloride for the next step without further purification.
Compound **3d** (355 mg, 0.78 mmol, 39% yield for 3 steps) was prepared from dimethyl malonate and the above chloride according to procedures described for **1b**. Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 9H), 2.53 (d, *J* = 2.0 Hz, 1H), 2.70 (d, *J* = 7.6 Hz, 2H), 2.76 (dd, *J* = 1.2, 7.6 Hz, 2H), 3.73 (s, 6H), 3.80 (s, 3H), 5.63 (dd, *J* = 6.4, 15.2 Hz, 1H), 5.79-5.91 (m, 3H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.25

(d, J = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 35.7, 36.8, 38.9, 52.7, 55.5, 58.1, 63.5, 74.9, 79.9, 114.2, 121.4, 127.6, 129.4, 129.9, 130.0, 134.0, 159.4, 171.2, 177.2. IR (film): 3286, 2956, 2359, 1730, 1607, 1510, 1438, 1272, 1246, 1200, 1174, 1140, 1032, 968 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{26}H_{32}O_7$ $(M+Na)^+$ 479.2040, found 479.2036.

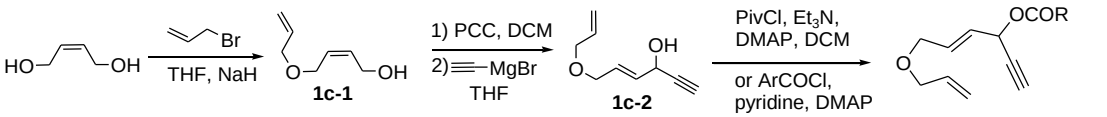


3e, Ar = *p*-BrC_6H_4

Dimethyl 2-(4-bromocinnamyl)-2-((*E*)-4-(pivaloyloxy)hex-2-en-5-ynyl)malonate (**3e**). Compound **3e** (215 mg, 0.43 mmol, 34% yield for 3 steps) was prepared according to above procedures described for **3d**.

Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 2.53 (d, J = 2.0 Hz, 1H), 2.69 (d, J = 7.6 Hz, 2H), 2.77 (dd, J = 1.2, 7.6 Hz, 2H), 3.73 (s, 6H), 5.60-5.66 (m, 1H), 5.78-5.81 (m, 1H), 5.86 (dtd, J = 1.2, 7.6, 8.4 Hz, 1H), 6.00 (td, J = 7.6, 15.6 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 35.9, 36.8, 39.0, 52.8, 58.0, 63.5, 74.9, 79.8, 121.5, 124.7, 128.0, 129.6, 129.7, 131.9, 133.4, 136.1, 171.1, 177.2. IR (film): 3277, 2956, 2360, 1731, 1486, 1434, 1275, 1233, 1200, 1141, 1072, 1030, 1008, 969 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{29}BrO_6$ $(M+Na)^+$ 527.1040, found 527.1048.

General procedure for the preparation substrates with an oxygen linker (1c and 1d).



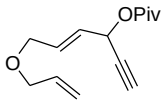
1c (R = *t*Bu)
1d (R = *p*-$Me_2NC_6H_4$)

To a suspension solution of sodium hydride (960 mg, 24 mmol, 60% suspension in mineral oil) in THF (80 mL) at 0 ºC was added a solution of cis-but-2-ene-1,4-diol (1.76g, 20 mmol) in dry THF (10 mL). The mixture was stirred at room temperature for 1 h, then allyl bromide (2.4 g, 20 mmol) in dry THF (10 mL) was quickly added and the reaction was refluxed overnight. Upon cooling, the reaction was quenched with H_2O, extracted with diethyl ether. The combined organic layers were washed with bine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 2:1) to give alcohol **1c-1** (2.10 g, 16.4 mmol) in 82% yield.

To a suspension of PCC (5.29 g, 24.6 mmol) and 4 Å MS (820 mg, 50mg/mmol) in CH_2Cl_2 (100 mL) was added a solution of alcohol **1c-1** (2.10 g, 16.4 mmol) in dry CH_2Cl_2 (20 mL) at 0 ºC under Ar. The mixture was stirred at room temperature for 2 h. It was then poured into diethyl ether (200 mL). The mixture solution was filtered though a pad of 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 (39.4 mL, 19.7 mmol, 0.5 M in THF) in THF was added a solution of the above crude aldehyde 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 (60 mL) and extracted with diethyl ether (2×60 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 flash column chromatography (silica gel, hexane/ethyl acetate 4:1) to give propargylic alcohol **1c-2** (1.82 g, 12.0 mmol) in 73% yield.

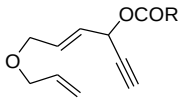
To a stirred solution of propargylic alcohol **1c-2** (608 mg, 4.0 mmol) in CH_2Cl_2 (40 mL) was added triethylamine (1.21 g, 12.0 mmol), pivaloyl chloride (624 mg, 5.2 mmol), and DMAP (5 mol %) at room temperature. The resulting mixture was stirred overnight, diluted with CH_2Cl_2 (40 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 20:1) to obtain the propargylic esters **1c** (849 mg, 3.6 mmol) in 90% yield as an oil.



1c

(*E*)-6-(allyloxy)hex-4-en-1-yn-3-yl pivalate (**1c**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 9H), 2.54 (d, *J* = 2.0 Hz, 1H), 4.00 (td, *J* = 1.6, 5.6 Hz, 2H), 4.03-4.05 (m, 2H), 5.18-5.32 (m, 2H), 5.78-5.97 (m, 3H), 6.09 (dtd, *J* = 1.2, 5.2, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 39.0, 63.3, 69.5, 71.6, 75.0, 79.7, 117.5, 126.8, 131.7, 134.7, 177.3. IR (film): 3294, 2957, 2854, 1731, 1479, 1273, 1139, 1030, 964 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{14}H_{20}O_3$ $(M+Na)^+$ 259.1305, found 259.1296.



1d (R = *p*-$Me_2NC_6H_4$)

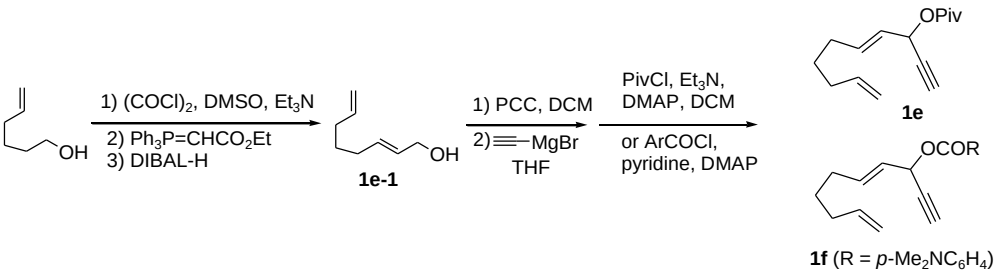
(*E*)-6-(allyloxy)hex-4-en-1-yn-3-yl 4-(dimethylamino)benzoate (**1d**).

To a stirred solution of propargylic alcohol **1c-2** (608 mg, 4.0 mmol) in pyridine (20 mL) at rt was added the hydrochloric salt of 4-(dimethylamino)benzoyl chloride (1.31 g, 6.0 mmol) and DMAP (48.8 mg, 0.4 mmol). The reaction mixture was stirred at rt overnight. Most volatile solvents were removed under reduced pressure and the residue was diluted with ethyl acetate (70 mL). The mixture solution was washed with an aqueous solution of $CuSO_4 \cdot 5H_2O$, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 10:1) to obtain the propargylic esters **1d** (741 mg, 2.48 mmol) in 62% yield as an oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.58 (d, *J* = 2.0 Hz, 1H), 3.04 (s, 6H), 4.01 (td, *J* = 1.5,

5.5 Hz, 2H), 4.05-4.06 (m, 2H), 5.18-5.21 (m, 1H), 5.27-5.31 (m, 1H), 5.88-5.96 (m, 2H), 6.12-6.19 (m, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 7.93 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3, 63.2, 69.6, 71.7, 75.0, 80.2, 110.9, 116.4, 117.5, 127.4, 131.6, 131.9, 134.8, 153.8, 165.8. IR (film): 3304, 2913, 2857, 1701, 1605, 1527, 1369, 1264, 1181, 1090, 946 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{18}H_{21}NO_3$ $(M+Na)^+$ 322.1414, found 322.1413.

General procedure for the preparation of substrates with an all carbon linker (1e and 1f).

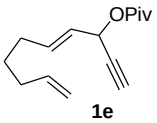


To a solution of $(COCl)_2$ (1.51 g, 12.0 mmol) in CH_2Cl_2 (60 ml) at –78 ºC was added a solution of DMSO (1.87 g, 24 mmol) in CH_2Cl_2 (10 ml). After 30 min, 5-hexen-1-ol (1.0 g, 10 mmol) in CH_2Cl_2 (10 ml) was added and the solution was stirred at –78 ºC for 1.5 h. Et_3N (5.05 g, 50 mmol) in CH_2Cl_2 (10 ml) was then added and the solution was warmed to rt. After 30 min the mixture solution was diluted with CH_2Cl_2 (50 ml), washed with saturated aqueous solution of sodium bicarbonate (50 ml), brine and dried over anhydrous Na_2SO_4. the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (70 ml).

To above crude aldehyde solution was added $Ph_3P=CHCO_2Et$ (5.22 g, 15 mmol). The reaction solution was stirred at rt overnight. Most of solvent was removed under reduced pressure and the residue was triturated with Et_2O (250 ml) to precipitate triphenylphosphine oxide. Concentration of the filtrate under reduced pressure gave crude ester for the next step without purification.

To a solution of above residue in CH_2Cl_2 (60 mL) at –78 ºC was added DIBALH (30 mL, 30 mmol, 1 M solution in hexane). The reaction mixture was stirred for 3 h, 10% aqueous solution of NaOH was then added carefully to quench the reaction. The mixture solution was filtered with a pad of silica gel and washed with CH_2Cl_2. The filtrate was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 4:1) to give compound **1e-1** (743 mg, 5.9 mmol) in 59% yied for 3 steps.

Product **1e** (295 mg, 1.26 mmol) was obtained in 63% yield over three steps from **1e-1** according to procedures described for the conversion of **1c-1** to **1c**.

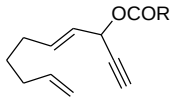


1e

(*E*)-deca-4,9-dien-1-yn-3-yl pivalate (**1e**).

Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.47-1.54 (m, 2H), 2.03-2.13 (m, 4H),

2.52 (d, *J* = 2.4 Hz, 1H), 4.94-5.04 (m, 2H), 5.54 (tdd, *J* = 1.6, 6.4, 15.2 Hz, 1H), 5.74-5.84 (m, 2H), 5.98 (dtd, *J* = 1.2, 6.8, 15.2 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 28.1, 31.6, 33.3, 38.9, 64.0, 74.6, 80.4, 115.0, 125.2, 136.3, 138.6, 177.4. IR (film): 3297, 2975, 2932, 1731, 1479, 1397, 1273, 1140, 1030, 966 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_2$ $(M+Na)^+$ 257.1512, found 257.1510.



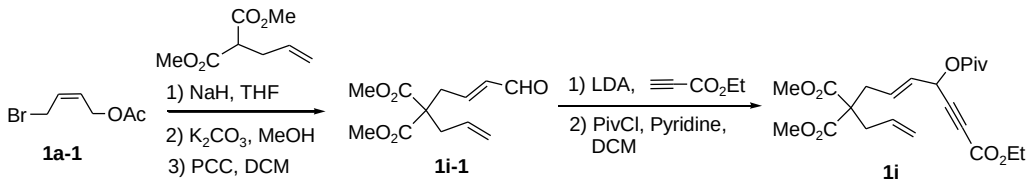
1f (R = *p*-$Me_2NC_6H_4$)

(*E*)-deca-4,9-dien-1-yn-3-yl 4-(dimethylamino)benzoate (**1f**).

Product **1f** (247 mg, 0.84 mmol) was obtained in 42% yield over three steps from **1e-1** according to procedures described for **1d**.

Oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49-1.55 (m, 2H), 2.05-2.14 (m, 4H), 2.56 (d, *J* = 2.0 Hz, 1H), 3.03 (s, 6H), 4.94-5.03 (m, 2H), 5.64-5.69 (m, 1H), 5.79 (tdd, *J* = 6.5, 10.0, 17.0 Hz, 1H), 6.03-6.09 (m, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 7.93 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 31.6, 33.4, 40.3, 63.8, 74.6, 80.8, 110.9, 115.0, 116.6, 125.6, 131.8, 136.1, 138.7, 153.7, 165.9. IR (film): 3295, 2927, 2857, 1701, 1605, 1525, 1368, 1317, 1262, 1180, 1089, 945 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{23}NO_2$ $(M+Na)^+$ 320.1621, found 320.1610.

Procedure for the preparation of ester substitued substrate 1i.



1a-1 **1i-1** **1i**

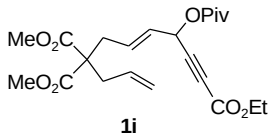
To a stirred solution of NaH (600 mg, 15 mmol, 60% in mineral oil) in THF (30 mL) at 0 °C was added allyl dimethylmalonate (2.84 g, 16.5 mmol) under argon atmosphere. After stirring at rt for 0.5 h, compound **1a-1** (2.86 g, 15 mmol) in THF (10 mL) was added. The reaction mixture was allowed to stir 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 in methanol (15 mL), and K_2CO_3 (2.28 g, 16.5 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 (20 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 an alcohol (2.18 g, 9 mmol) in 61% yield over 2 steps.

To a suspension of PCC (2.90 g, 13.5 mmol) in CH_2Cl_2 (20 mL) was added a solution of the above alcohol (2.18 g, 9 mmol) in dry CH_2Cl_2 (20 mL) at 0 ^{o}C under Ar. The mixture was stirred at room temperature for 4 h. It was then poured into Et_2O (60 mL). The mixed solution was filtered though silica gel and the filtrate was concentrated under

reduced pressure to yield the crude aldehyde**.** The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to afford aldehyde **1i-1** (1.94 g, 8.1 mmol) in 90% yield.

To a stirred solution of diisopropylamine (2 mmol, 2.0 equiv) in THF (5 mL) was added a solution of *n*-butyllithium (1.6 M in hexanes, 1.25 mL, 2 mmol, 2 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 (2 mmol, 2 equiv) was added. After stirring for 30 min at -78 °C, a solution of aldehyde **1i-1** (1 mmol, 1.0 equiv) in THF (5 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.

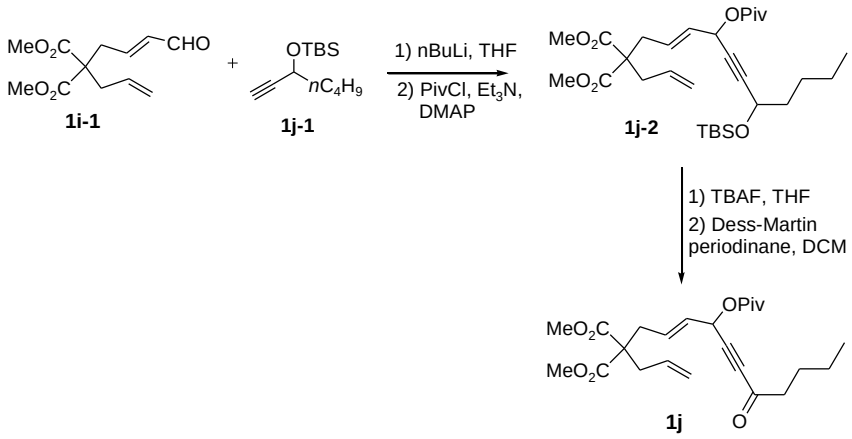
To a solution of above oil (0.31 g, 0.8 mmol, 1 equiv) in CH_2Cl_2 (10 mL), was added pyridine (253 mg, 4 equiv), DMAP (one crystal) and pivaloyl chloride (192 mg, 2 equiv) at 0°C. After stirring for overnight, the mixture was diluted with CH_2Cl_2 (20 mL) and washed with a 10% copper sulfate aqueous 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 **1i** (240 mg, 72% yield over 2 steps) as a yellow oil.



1i

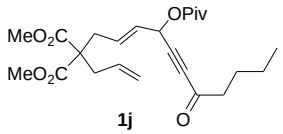
(E)-1-ethyl 7,7-dimethyl 3-(pivaloyloxy)deca-4,9-dien-1-yne-1,7,7-tricarboxylate (**1i**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.29 (t, *J* = 8.0 Hz, 3H), 2.61 (dd, *J* = 8.0, 12.0 Hz, 4H), 3.70 (s, 6H), 4.21 (q, *J* = 8.0, 2H), 5.07 -5.11 (m, 2H), 5.56-5.61 (m, 2H), 5.80-5.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 24.7, 33.0, 34.9, 36.5, 50.2, 55.1, 59.9, 60.5, 75.3, 79.9, 117.3, 125.4, 128.6, 129.6, 150.6, 168.5, 174.4. IR (film): ν 2979, 1730, 1200, 1096, 919, 859, 732 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{22}H_{30}O_8$ $(M+Na)^+$ 445.1832, found 445.1839.

Procedure for the preparation of ketone substitued substrate 1j.



To a stirred solution of terminal alkyne **1j-1** (422.7 mg, 2.5 mmol) in THF (10 mL) was added *n*BuLi (1 mL, 2.5 mmol, 2.5 M in hexane) at -78 ºC. 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 **1i-1** (480.5 mg, 2.0 mmol) in THF (5 mL) was added. After stirring for 4h 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 (10 mL). To this solution was added pyridine (400.0mg, 5.0 mmol), PivCl (301.5 mg, 2.5 mmol) and DMAP (10 mol%) at 0 °C. The solution was then warmed to rt. After stirring at rt for 2h, the reaction mixture was diluted with DCM (10 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 = 10:1) to provide product **1j-2** (834.9 mg) in 85% yield.

To a solution of **1j-2** (493.3 g, 1.0 mmol) in THF (2 mL) was added a solution of TBAF (2 mL, 1.0M in THF) at 0 °C. After stirring at rt for 60 min, the reaction mixture was diluted with ether (10 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 (5 mL). Dess-Martin periodinane (700 mg, 1.6 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 **1j** (304 mg) in 81% yield as an oil.

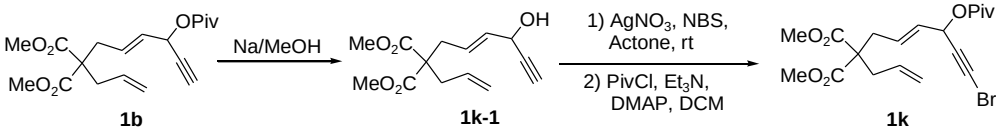


2-Allyl-2-[4-(2,2-dimethyl-propionyloxy)-7-oxo-undec-2-en-5-ynyl]-malonic acid dimethyl ester (**1j**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.3 Hz, 3H), 1.13 (s, 9H), 1.21-1.34 (m, 2H),

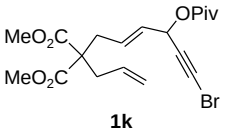
1.48-1.62 (m, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 2.56 (dd, *J* = 13.5, 7.4 Hz, 4H), 3.63 (s, 6H), 4.98-5.10 (m, 2H), 5.45-5.62 (m, 2H), 5.69-5.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.2, 26.1, 27.1, 35.4, 37.4, 38.9, 45.2, 52.6, 57.6, 63.1, 84.6, 86.6, 119.7, 127.9, 130.9, 132.1, 170.9, 176.8, 187.4. IR (film): 2959, 1733, 1680, 1437, 1214, 1134, 930 cm^{-1}. HRMS (ESI) m/z calcd. For $C_{24}H_{34}O_7$ $(M+Na)^+$ 457.2197, found 457.2198.

Procedure for the preparation of bromide substitued substrate 1k.



1b **1k-1** **1k**

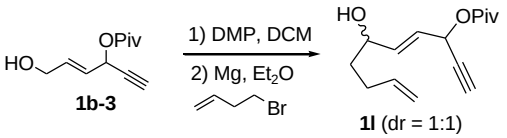
To a reaction tube filled with 6 mL of MeOH was added sodium (144 mg, 6 mmol). The mixture solution was stirred at rt for 10 min. It was then transferred to another tube filled with a solution of compound **1b** (700 mg, 2 mmol) in MeOH (10 mL). The reaction mixture was stirred at rt for 3 h and diluted with ethyl acetate (70 mL). The solution was washed with water, brine, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 2:1) to afford free alcohol **1k-1** (463 mg, 1.74 mmol) in 87% yield. To a solution of **1k-1** (463 mg, 1.74 mmol) in dry acetone (30 ml) was added $AgNO_3$ (58.4 mg, 0.35 mmol) and NBS (462 mg, 2.61 mmol) at room temperature. The mixture was stirred at room temperature for 30 min. A saturated aqueous solution of sodium bicarbonate (24 ml) was added and the mixture was extracted with ethyl acetate (2 X 50 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL). To this solution was added triethylamine (527 mg, 5.22 mmol), pivaloyl chloride (271 mg, 2.26 mmol) and DMAP (5 mol %) at room temperature. The resulting mixture was stirred overnight, 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 afford product **1k** (581 mg, 1.36 mmol) in 78% yied for 2 steps.



1k

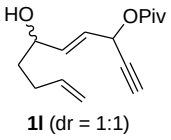
Dimethyl 2-allyl-2-((*E*)-6-bromo-4-(pivaloyloxy)hex-2-en-5-ynyl)malonate (**1k**).
Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 2.62-2.66 (m, 4H), 3.72 (s, 6H), 5.09-5.14 (m, 2H), 5.56-5.67 (m, 2H), 5.75-5.83 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 35.4, 37.4, 39.0, 47.4, 52.7, 57.7, 64.3, 76.3, 119.7, 129.4, 129.8, 132.2, 171.1, 177.1. IR (film): 3454, 2975, 2360, 1730, 1436, 1273, 1211, 1137, 1030, 972 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{25}BrO_6$ $(M+Na)^+$ 451.0727, found 451.0714.

General procedure for the preparation of substrate 1l.



To a solution of alcohol **1b-3** (784 mg, 4.0 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added Dess-Martin periodinane (1.65 g, 6.0 mmol). After stirring at rt for 1 h, the reaction solution was filtered to remove the solid. The filtrate was washed with saturated aqueous solution of Na_2SO_3 and $NaHCO_3$, H_2O, brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was used for the next step without purification.

To a dried two-neck round-bottom flask filled with a solution of magnesium turnings (240 mg, 10 mol) in Et_2O (40 mL) was added 2 mL of a solution of homoallyl bromide (1.61 g, 12 mmol) in Et_2O (8 mL). When the reaction was initiated, the rest of homoallyl bromide solution was slowly added. The reaction mixture was stirred at room temperature for 0.5 h and then heated to reflux for 1 h. Around 30 mL of this Grignard reagent solution was then transferred to the solution of above crude aldehyde in Et_2O (30 mL) at rt. The reaction mixture was stirred for 4 h, quenched with saturated aqueous solution of NH_4Cl and extracted with ethyl acetate (2 X 50 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 4:1) to afford product **1l** (750 mg, 3.0 mmol) in 75% yield for 2 steps.

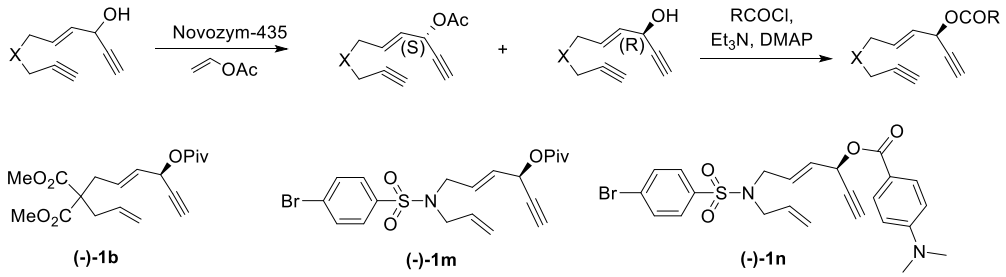


(*E*)-6-hydroxydeca-4,9-dien-1-yn-3-yl pivalate (**1l**).

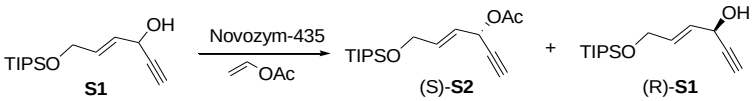
Oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (s, 9H), 1.63-1.69 (m, 3H), 2.17-2.17 (m, 2H), 2.55 (d, *J* = 2.0 Hz, 1H), 4.22 (m, 1H), 4.98-5.07 (m, 2H), 5.74-5.87 (m, 3H), 6.01-6.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.2, 29.8, 36.2, 39.0, 63.3, (71.4, 71.3 for two isomers), 75.1, 79.8, 115.4, (125.3, 125.4 for two isomers), 137.8, 138.2, 177.3. IR (film): 3411, 3296, 2975, 2935, 1727, 1479, 1460, 1397, 1367, 1273, 1141, 1030, 967 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_3$ $(M+Na)^+$ 273.1461, found 273.1473.

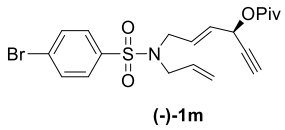
General procedure for the preparation of enantio-enriched substrates (-)-1b, (-)-1m and (-)-1n:

To a solution of Novozyme 435 from Aldrich (15 mg) in vinyl acetate (2.5 mL) was added a racemic propargylic alcohol (100 mg) at rt. After the solution was stirred for 10 h, it was filtered through a cotton pad. The resulting solution was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give (*S*)-acetates and (*R*)-alcohols in 40-45% yields. Substrates (-)-**1b**, (-)-**1m** and (-)-**1n** were then prepared by esterification according to known procedures.[2-3]



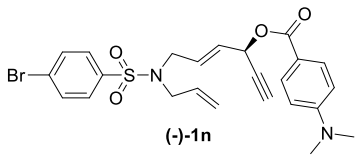
The absolute stereochemistry of the chiral alcohols and esters was determined by comparison to similar propargylic alcohols resolved by the same enzyme.[4] Known chiral alcohol (*R*)-**S1** was also prepared in 96% *ee*.[5] All of its spectroscopic data are identical to literature $[\alpha]_D$ = -8.5 (c 1.00, $CHCl_3$), (literature $[\alpha]_D$= -10.9 (c 1.00, $CHCl_3$).[5]





(R,*E*)-2,2-Dimethyl-propionic acid 4-[allyl-(4-bromo-benzenesulfonyl)-amino]-1-ethynyl-but-2-enyl ester (**1m**).

Oil, ^{1}H NMR (400Mz, $CDCl_3$) δ 1.20 (s, 9H), 2.53 (d, *J* = 2.4 Hz, 1H), 3.81 (d, *J* = 6.0 Hz, 2H), 3.87 (d, *J* = 6.4 Hz, 2H), 5.16 (qd, *J* = 1.2, 16.8 Hz, 1H), 5.19 (qd, *J* = 1.2, 10.0 Hz, 1H), 5.61 (tdd, *J* = 6.4, 10.0, 16.8 Hz, 1H), 5.64 (tdd, *J* = 1.2, 5.6, 15.6 Hz, 1H), 5.74 (dtd, *J* = 1.2, 6.4, 15.6 Hz, 1H), 5.80-5.77 (m, 1H), 7.71-7.64 (m, 4H). ^{13}C NMR (100Mz, $CDCl_3$) δ 27.2, 38.9, 47.9, 49.9, 62.8, 75.3, 79.1, 119.9, 127.8, 128.9, 129.0, 129.6, 132.3, 132.7, 139.6, 177.1. IR (film): 3300, 2975, 2930, 1733, 1575, 1478, 1389, 1348, 1267, 1144, 1090, 1067, 1010, 933, 909, 764, 736 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}BrNO_4S$ $(M+Na)^+$ 476.0501, found 476.0504.



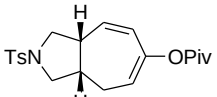
4-Dimethylamino-benzoic acid 4-[allyl-(4-bromo-benzenesulfonyl)-amino]-1-ethynyl- but-2-enyl ester (**1n**).

Oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.72-7.58 (m, 4H), 6.65 (d, *J* = 9.1 Hz, 2H), 6.03 (dd, *J* = 3.7, 2.1 Hz, 1H), 5.86-5.70 (m, 2H), 5.62 (ddt, *J* = 17.2, 9.8, 6.4 Hz, 1H), 5.22-5.12 (m, 2H), 3.90 (d, *J* = 4.8 Hz, 2H), 3.82 (d, *J* = 6.5 Hz, 2H), 3.05 (s, 6H), 2.56 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.59, 153.85, 139.68, 132.66, 132.37, 131.82, 130.22, 128.92, 128.64, 127.72, 119.88, 115.98, 110.93,

79.62, 75.25, 62.65, 49.84, 47.91, 40.27. IR (film): 2917, 2850, 2360, 2341, 1702, 1606, 1575, 1528, 1471, 1445, 1389, 1370, 1340, 1264, 1182, 1163, 1088, 1069, 1009, 944, 907, 827, 767, 727, 670, 669. cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{24}H_{25}BrN_2O_4S$ $(M+H)^+$ 517.0792, found 517.0780.

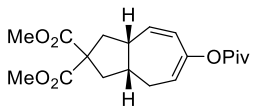
General procedure for the rhodium-catalyzed [5+2] reaction of ACE with alkene
Method A:
To a solution of $[Rh(coe)_2Cl]_2$ (5.4 mg, 5 mol %) in 1,2-dichloroethane (1.3 mL) at rt was added tris[3,5-bis(trifluoromethyl)phenyl]phosphine (30 mg, 30 mol %). The reaction solution was stirred at rt for 10 min, substrate **1** (0.15 mmol) was added. The reaction mixture was allowed to stir at 80 °C overnight. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the corresponding 7-membered ring product.

Method B:
To a solution of $[Rh(COD)Cl]_2$ (3.9 mg, 5 mol %) in 1,2-dichloroethane (1.3 mL) at rt was added tris[3,5-bis(trifluoromethyl)phenyl]phosphine (30 mg, 30 mol %). The reaction solution was stirred at rt for 10 min, substrate **1** (0.15 mmol) was added. The reaction mixture was allowed to stir at 80 °C overnight. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the corresponding 7-membered ring product.



2a

(5*E*,7*Z*)-1,2,3,3a,4,8a-hexahydro-2-tosylcyclohepta[c]pyrrol-6-yl pivalate (**2a**).
Oil, 47.8 mg, 82% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 9H), 1.76-1.83 (m, 1H), 1.97 (ddd, *J* = 2.8, 8.8, 14.8 Hz, 1H), 2.44 (s, 3H), 2.48-2.56 (m, 1H), 2.87-2.95 (m, 1H), 3.03 (dd, *J* = 8.8, 9.6 Hz, 1H), 3.11 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.54 (dd, *J* = 7.2, 10.0 Hz, 1H), 3.60 (dd, *J* = 7.2, 9.6 Hz, 1H), 5.57-5.61 (m, 2H), 5.74 (dd, *J* = 4.4, 12.4 Hz, 1H), 7.33 (dd, *J* = 0.4, 8.4 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 27.2, 27.6, 38.9, 43.8, 44.4, 53.2, 54.8, 119.2, 125.4, 127.8, 129.9, 133.0, 133.7, 143.8, 147.1, 177.6. IR (film): 2973, 2935, 2875, 2360, 2341, 1739, 1700, 1341, 1232, 1158, 901 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{21}H_{27}NO_4S$ $(M+Na)^+$ 412.1553, found 412.1545.

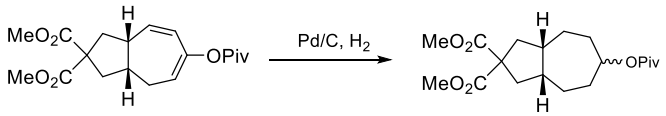


2b

(4*Z*,6*E*)-dimethyl 3,3a,8,8a-tetrahydro-6-(pivaloyloxy)azulene-2,2(1H)-dicarboxylate (**2b**).

Oil, 43.2 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 9H), 1.96-2.03 (m, 1H), 2.10-2.17 (m, 3H), 2.55-2.61 (m, 3H), 2.85-2.91 (m, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 5.58-5.66 (m, 2H), 5.93 (dd, *J* = 4.0, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 29.3, 38.9, 41.5, 41.6, 44.1, 46.0, 52.98, 53.02, 57.8, 119.3, 123.8, 136.9, 147.3, 172.7, 172.9, 177.6. IR (film): 3450, 2955, 2360, 1731, 1434, 1271, 1199, 1126, 1064, 905 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{26}O_6$ $(M+Na)^+$ 373.1622, found 373.1614.

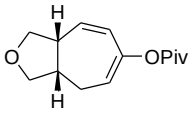
Hydrogenation of product **2b** led to the formation of two diastereomers (**2b-S**). This indicated that **2b** had cis-stereochemistry as discussed in the manuscript (**2b-S** = the 1:1 mixture of **2b-H$_4$a** and **2b-H$_4$b** in the manuscript).



2b **2b-S**

Dimethyl octahydro-6-(pivaloyloxy)azulene-2,2(1H)-dicarboxylate (**2b-S**).

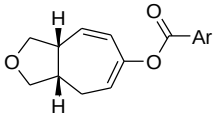
^{1}H NMR (one isomer, 400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.31-1.49 (m, 4H), 1.64-1.79 (m, 4H), 1.97-2.03 (m, 2H), 2.20-2.27 (m, 2H), 2.49-2.54 (m, 2H), 3.71 (s, 3H), 3.74 (s, 3H), 5.06-5.09 (m, 1H); ^{1}H NMR (the other isomer, 400 MHz, $CDCl_3$) δ 1.16 (s, 9H), 1.31-1.49 (m, 4H), 1.64-1.79 (m, 4H), 1.97-2.03 (m, 2H), 2.20-2.27 (m, 2H), 2.49-2.54 (m, 2H), 3.70 (s, 3H), 3.74 (s, 3H), 4.60-4.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.3, 26.8, 27.3, 27.4, 27.5, 33.2, 34.3, 38.8, 39.2, 41.2, 41.7, 42.3, 52.8, 52.9, 59.8, 60.6, 71.5, 75.8, 172.55, 172.61, 172.7, 172.7, 177.96, 178.02. IR (film): 2954, 2935, 2256, 1726, 1435, 1283, 1252, 1163, 1031, 1001, 909 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{30}O_6$ $(M+Na)^+$ 377.1935, found 377.1942.



2c

(4*Z*,6*E*)-3,3a,8,8a-tetrahydro-1H-cyclohepta[c]furan-6-yl pivalate (**2c**).

Oil, 21.9 mg, 61.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 9H), 2.04-2.20 (m, 2H), 2.62-2.69 (m, 1H), 2.99-3.07 (m, 1H), 3.54 (dd, *J* = 8.4, 9.2 Hz, 1H), 3.61 (dd, *J* = 4.8, 8.8 Hz, 1H), 4.05-4.13 (m, 2H), 5.68-5.75 (m, 2H), 5.94 (dd, *J* = 4.0, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 27.8, 39.0, 44.8, 46.3, 73.5, 75.4, 119.4, 124.7, 133.7, 147.5, 177.7. IR (film): 2972, 2934, 2870, 1742, 1479, 1396, 1278, 1128, 905 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{14}H_{20}O_3$ $(M+Na)^+$ 259.1305, found 259.1297.

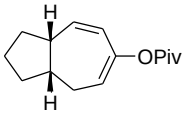


2d (Ar = *p*-Me_2N)

(4*Z*,6*E*)-3,3a,8,8a-tetrahydro-1H-cyclohepta[c]furan-6-yl 4-(dimethylamino)benzoate (**2d**).

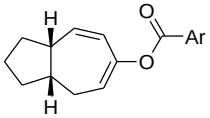
Solid, mp: 140-141 °C. 30.1 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.11-2.23 (m, 2H), 2.67-2.74 (m, 1H), 3.02-3.15 (m, 1H), 3.05 (s, 6 H), 3.58 (dd, *J* = 8.5, 8.5 Hz,

1H), 3.64 (dd, *J* = 4.5, 8.5 Hz, 1H), 4.08-4.14 (m, 2H), 5.85-5.87 (m, 1H), 5.86-5.88 (m, 1H), 5.96 (dd, *J* = 4.0, 12.0 Hz, 1H), 6.66 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 40.3, 44.9, 46.4, 73.7, 75.6, 111.0, 116.4, 119.7, 125.5, 132.0, 133.3, 147.8, 153.9, 166.1. IR (film): 2927, 2859, 1704, 1598, 1530, 1371, 1274, 1181, 1116, 1058, 908 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{18}H_{21}NO_3$ $(M+Na)^+$ 322.1414, found 322.1409.



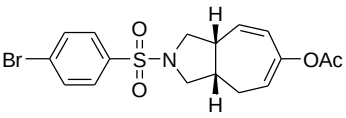
2e

(5*E*,7*Z*)-1,2,3,3a,4,8a-hexahydroazulen-6-yl pivalate (**2e**).
Oil, 19.0 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H), 1.39-1.50 (m, 3H), 1.59-1.64 (m, 1H), 1.88-2.00 (m, 3H), 2.07 (ddd, *J* = 2.8, 8.8, 14.4 Hz, 1H), 2.35-2.44 (m, 1H), 2.63-2.67 (m, 1H), 5.55 (td, *J* = 2.0, 12.0 Hz, 1H), 5.62 – 5.66 (m, 1H), 6.00 (dd, *J* = 4.0, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 27.3, 30.0, 34.0, 34.1, 39.0, 45.6, 46.3, 119.6, 122.5, 139.4, 147.3, 177.8. IR (film): 2955, 2870, 2360, 2340, 2255, 1742, 1478, 1395, 1279, 907 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_2$ $(M+Na)^+$ 257.1512, found 257.1507.



2f (Ar = *p*-Me_2N)

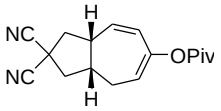
(5*E*,7*Z*)-1,2,3,3a,4,8a-hexahydroazulen-6-yl 4-(dimethylamino)benzoate (**2f**).
Solid, mp: 97-98 °C, 27.2 mg, 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.03 (dd, *J* = 4.0, 12.0 Hz, 1H), 5.71-5.79 (m, 2H), 3.05 (s, 6H), 2.68-2.71 (m, 1H), 2.42-2.49 (m, 1H), 2.11 (ddd, *J* = 2.5, 8.5 14.0 Hz, 1H), 1.93-2.03 (m, 3H), 1.60-1.66 (m, 1H), 1.39-1.53 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 30.2, 34.1, 34.2, 40.3, 45.6, 46.5, 110.9, 116.8, 119.9, 123.2, 131.9, 139.0, 147.6, 153.7, 166.1. IR (film): 3429, 2948, 1705, 1605, 1528, 1369, 1277, 1182, 1120, 905 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{23}NO_2$ $(M+Na)^+$ 320.1621, found 320.1613.



2g

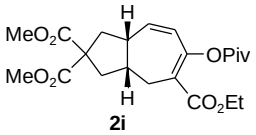
Acetic acid 2-(4-bromo-benzenesulfonyl)-1,2,3,3a,4,8a-hexahydrocyclohepta[c] pyrrol-6-yl ester (**2g**).
Solid, m.p. = 129-132 ºC. 25.9 mg, 84% yield. ^{1}H NMR (400Mz, $CDCl_3$) δ 1.85 (ddd, *J*= 5.2, 10.4, 15.2 Hz, 1H), 2.03 (ddd, *J*= 2.8, 8.7, 15.5 Hz, 1H), 2.12 (s, 3H), 2.60-2.53 (m, 1H), 2.97-2.91 (m, 1H), 3.05 (t, *J*= 9.2 Hz, 1H), 3.13 (dd, *J*= 4.4, 10.0 Hz, 1H), 3.54 (dd, *J*= 7.0, 10.2 Hz, 1H), 3.60 (dd, *J*= 7.4, 9.8 Hz, 1H), 5.66-5.61 (m, 2H), 5.73

(dd, *J*= 4.2, 12.2 Hz, 1H), 7.71-7.66 (m, 4H); ^{13}C NMR (100Mz, $CDCl_3$) δ 21.2, 27.5, 44.0, 44.2, 53.3, 54.7, 119.4, 125.6, 128.1, 129.3, 132.7, 132.9, 136.0, 146.9, 169.9. IR (film): 3058, 2975, 1740, 1575, 1479, 1389 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{17}H_{18}BrNO_4S$ $(M+Na)^+$ 434.0032, found 434.0022.



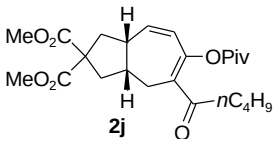
2h

(5*E*,7*Z*)-2,2-dicyano-1,2,3,3a,4,8a-hexahydroazulen-6-yl pivalate (**2h**).
Oil, 35.4 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H), 1.99-2.07 (m, 1H), 2.26-2.39 (m, 3H), 2.70-2.79 (m, 2H), 2.91-3.01 (m, 1H), 3.13-3.20 (m, 1H), 5.70-5.77 (m, 2H), 6.01 (dd, *J* = 4.8, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 28.4, 31.9, 39.0, 42.2, 44.5, 45.2, 48.1, 116.2, 116.6, 118.6, 126.5, 135.1, 147.9, 177.6. IR (film): 2976, 1740, 1660, 1479, 1279, 1126, 905 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{17}H_{20}N_2O_2$ $(M+Na)^+$ 307.1417, found 307.1405.

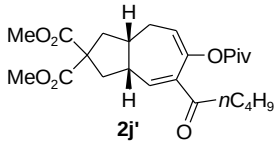


2i

4-methyl-2-tosyl-1,2,3,3a-tetrahydrocyclohepta[c]pyrrol-6-yl pivalate (**2i**)
Oil, 31.0 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23-1.30 (m, 3H), 1.28 (s, 9H), 1.99-2.07 (m, 2H), 2.11-2.16 (m, 1H), 2.58-2.66 (m, 2H), 2.73-2.77 (m, 2H), 2.91 (d, *J* = 4.0 Hz, 1H), 3.73 (s, 6H), 4.17-4.21 (m, 2H), 5.79 (d, *J* = 8.0, 1H), 6.20 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 24.8, 29.3, 36.6, 38.9, 39.1, 40.1, 47.4, 50.5, 56.3, 58.5, 120.2, 122.4, 140.5, 149.1, 163.6, 169.9, 170.0, 173.9. IR (film): ν 2980, 1731, 1274, 1253, 1124, 1026, 735 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{22}H_{30}O_8$ $(M+Na)^+$ 445.1832, found 445.1835.



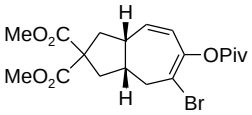
2j



2j'

6-(2,2-Dimethyl-propionyloxy)-5-pentanoyl-3,3a,4,8a-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**2j**). The ratio of **2j** : **2j'** is about 3:1.
Oil. 63.4 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.3 Hz, 3H), 1.25-1.40 (m, 10H), 1.50-1.75 (m, 3H), 1.91 (t, *J* = 13.1 Hz, 1H), 2.03 (dd, *J* = 13.4, 8.5 Hz, 1H), 2.14 (dd, *J* = 13.3, 9.7 Hz, 1H), 2.52-2.77 (m, 6H), 2.85-2.98 (m, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 5.67 (dd, *J* = 11.7, 2.2 Hz, 1H), 6.20 (dd, *J* = 11.8, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 26.5, 27.2, 31.1, 39.2, 41.3, 41.5, 42.5, 43.0, 50.0, 52.99, 53.04, 58.8, 122.7, 124.8, 130.6, 142.8, 172.4, 176.6, 201.3. IR (film): 2958, 1731, 1435, 1269, 1201, 1110 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{24}H_{34}O_7$ $(M+Na)^+$

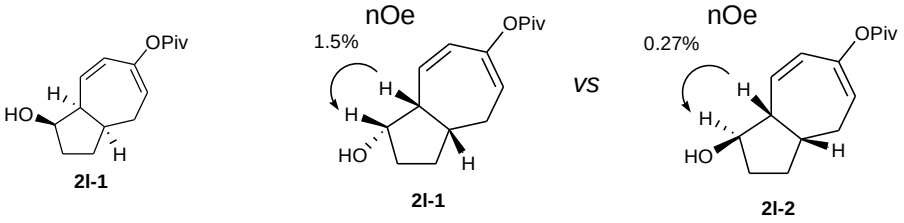
457.2197, found 457.2198.



2k

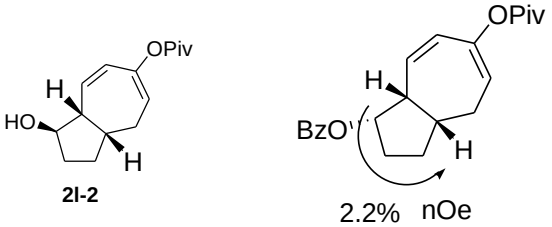
(4*Z*,6*Z*)-dimethyl 7-bromo-3,3a,8,8a-tetrahydro-6-(pivaloyloxy)azulene-2,2(1H)-dicarboxylate (**2k**).

Oil, 34.0 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.10 (td, *J* = 8.4, 13.6 Hz, 2H), 2.59-2.67 (m, 4H), 2.76-2.84 (m, 1H), 2.82-2.95 (m, 1H), 3.73 (s, 3H), 3.74 (s, 3H), 5.65 (dd, *J* = 2.4, 12.0 Hz, 1H), 6.01 (dd, *J* = 3.6, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 39.2, 41.1, 41.2, 41.3, 42.8, 47.4, 53.09, 53.13, 58.2, 114.7, 123.2, 137.9, 143.9, 172.4, 172.5, 176.0. IR (film): 2974, 1730, 1434, 1272, 1201, 1121, 1028, 912 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{25}BrO_6$ $(M+Na)^+$ 451.0727, found 451.0719.



(*trans*,*cis*)-2,2-Dimethyl-propionic acid 1-hydroxy-1,2,3,3a,4,8a-hexahydro-azulen-6-yl ester (**2l-1**)

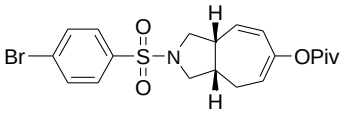
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H), 1.59-1.70 (m, 1H), 1.72-1.82 (m, 2H), 1.90-1.98 (m, 2H), 2.20-2.24 (m, 2H), 2.51-2.60 (m, 1H), 2.77-2.83 (m, 1H), 4.30-4.32 (m, 1H), 5.65-5.69 (m, 1H), 5.81 (td, *J* = 2.0, 12.0 Hz, 1H), 6.11 (dd, *J* = 5.0, 12.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.3, 31.0, 31.4, 33.2, 39.0, 46.7, 51.1, 76.9, 119.9, 127.2, 134.0, 147.0, 178.0. IR (film): 3416, 2958, 1729, 1479, 1396, 1280, 1131, 1047, 908 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}O_3$ $(M+Na)^+$ 273.1461, found 273.1448.



(*cis*,*cis*)-2,2-Dimethyl-propionic acid 1-hydroxy-1,2,3,3a,4,8a-hexahydro-azulen-6-yl ester (**2l-2**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H), 1.39-1.51 (m, 2H), 1.67 (s, 1H), 1.89-2.05 (m, 3H), 2.14 (ddd, *J* = 2.8, 8.0, 14.4, 1H), 2.51-2.55 (m, 1H), 2.64-2.70 (m, 1H), 4.01-4.07 (m, 1H), 5.63-5.68 (m, 2H), 6.13 (dd, *J* = 4.4, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 29.7, 30.6, 32.7, 39.0, 45.8, 53.1, 79.8, 119.4, 124.1, 136.7, 147.5, 177.8. IR (film): 3371, 2958, 2933, 1731, 1281, 1138, 906cm^{-1}. HRMS (ESI) *m/z* calcd. For

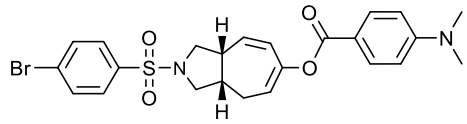
$C_{15}H_{22}O_3$ $(M+Na)^+$ 273.1461, found 273.1467.



(-)-2m

(*R*)-2,2-Dimethyl-propionic acid 2-(4-bromo-benzenesulfonyl)-1,2,3,3a,4,8a-hexahydro- cyclohepta[c]pyrrol-6-yl ester (**2m**).

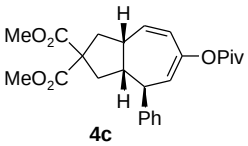
Solid, m.p. = 126-130 ^oC. 36 mg, 85% yield, ^1H NMR (400Mz, $CDCl_3$) δ 1.22 (s, 9H), 1.85 (ddd, *J*= 5.2, 10.4, 15.2 Hz, 1H), 2.03 (ddd, *J*= 2.6, 8.4, 14.8 Hz, 1H), 2.61-2.53 (m, 1H), 2.97-2.90 (m, 1H), 3.05 (t, *J*= 9.0 Hz, 1H), 3.11 (dd, *J*= 4.8, 10.0 Hz, 1H), 3.52 (dd, *J*= 7.2, 10.0 Hz, 1H), 3.58 (dd, *J*= 7.8, 9.4 Hz, 1H), 5.58-5.55 (m, 2H), 5.70 (dd, *J*= 4.2, 12.2 Hz, 1H), 7.70-7.65 (m, 4H); ^{13}C NMR (100Mz, $CDCl_3$) δ 27.2, 27.3, 38.9, 43.8, 44.5, 53.2, 54.4, 119.0, 125.6, 128.0, 129.2, 132.6, 132.9, 135.9, 147.1, 177.6. IR (film): 3058, 2975, 1740, 1575, 1479, 1389 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}BrNO_4S$ $(M+Na)^+$ 476.0501, found 476.0495.



(-)-2n

4-Dimethylamino-benzoic acid 2-(4-bromo-benzenesulfonyl)-1,2,3,3a,4,8a-hexahydro -cyclohepta[c]pyrrol-6-yl ester (**2n**).

Solid, m.p. = 199-202 ^oC. 24.3 mg, 72% yield, ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 7.74-7.65 (m, 4H), 6.65 (d, *J* = 9.0 Hz, 2H), 5.81-5.69 (m, 3H), 3.62 (dd, *J* = 9.6, 7.4 Hz, 1H), 3.56 (dd, *J* = 10.1, 6.9 Hz, 1H), 3.19-3.04 (m, 8H), 3.04-2.95 (m, 1H), 2.68-2.58 (m, 1H), 2.06 (ddd, *J* = 15.0, 8.6, 2.8 Hz, 1H), 1.90 (ddd, *J* = 15.4, 10.7, 5.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.98, 153.91, 147.43, 136.00, 132.67, 132.56, 132.02, 129.28, 128.06, 126.39, 119.27, 116.14, 110.99, 54.71, 53.37, 44.85, 43.91, 40.32, 27.61. IR (film): 2926, 2855, 2360, 1696, 1603, 1528, 1373, 1342, 1278, 1181, 1121, 1069, 1109, 907, 829, 764, 729 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{24}H_{25}BrN_2O_4S$ $(M+NH_4)^+$ 534.1057, found 534.1052.

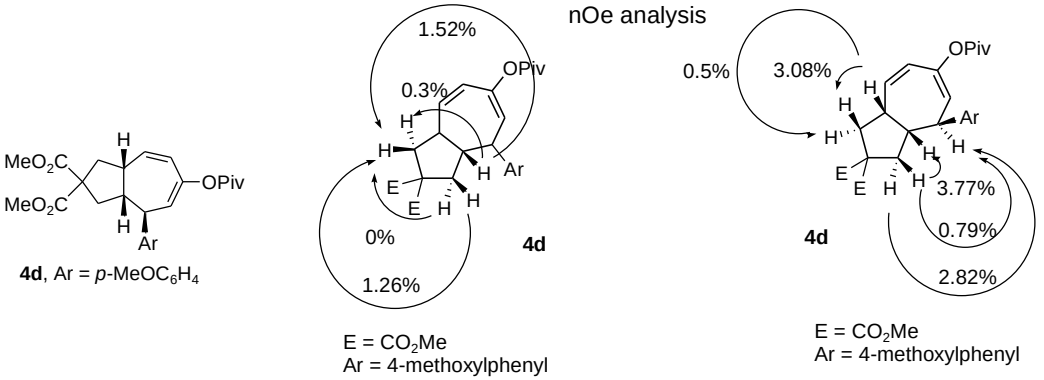


4c

(4*Z*,6*E*)-dimethyl-3,3a,8,8a-tetrahydro-8-phenyl-6-(pivaloyloxy)azulene-2,2(1H)-dicarboxylate (**4c**).

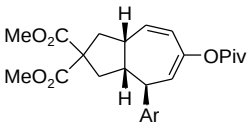
Oil, 33.2 mg, 52% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.95 (dd, *J* = 9.6, 13.6 Hz, 1H), 2.18 (dd, *J* = 6.4, 13.6 Hz, 1H), 2.34 (dd, *J* = 6.4, 13.6 Hz, 1H), 2.55 (dd, *J* = 7.2, 13.6 Hz, 1H), 2.93-2.99 (m, 2H), 3.21 (dd, *J* = 6.4, 10.0 Hz, 1H), 3.68 (s, 6H), 5.72-5.75 (m, 2H), 6.02 (dd, *J* = 2.8, 12.0 Hz, 1H), 7.22-7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 39.0, 39.6, 41.3, 42.1, 46.9, 52.95, 53.00, 57.4, 58.5, 124.4, 124.7,

126.8, 128.3, 128.9, 139.4, 144.0, 146.2, 172.6, 172.7, 177.7. IR (film): 3385, 2955, 1731, 1479, 1434, 1254, 1199, 1123, 909 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{30}O_6$ $(M+Na)^+$ 449.1935, found 449.1915.



(4*Z*,6*E*)-dimethyl-3,3a,8,8a-tetrahydro-8-(4-methoxyphenyl)-6-(pivaloyloxy)azulene-2,2(1H)- dicarboxylate (**4d**).

Oil, 34.9 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.95 (dd, *J* = 10.0, 13.6 Hz, 1H), 2.18 (dd, *J* = 6.8, 13.6 Hz, 1H), 2.34 (dd, *J* = 6.8, 13.6 Hz, 1H), 2.53 (dd, *J* = 7.2, 13.6 Hz, 1H), 2.86-2.96 (m, 2H), 3.17 (dd, *J* = 6.0, 9.6 Hz, 1H), 3.68 (s, 3H), 3.69 (s, 3H), 3.79 (s, 3H), 5.70-5.72 (m, 2H), 6.00 (dd, *J* = 3.2, 12.0 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 39.6, 41.3, 42.1, 46.0, 52.96, 53.01, 55.5, 57.3, 58.5, 114.3, 124.4, 124.9, 129.2, 136.1, 139.3, 146.0, 158.5, 172.7, 172.8, 177.7. IR (film): 2955, 2358, 1731, 1511, 1435, 1248, 1198, 1124, 1065, 1034, 906 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{26}H_{32}O_7$ $(M+Na)^+$ 479.2040, found 479.2040.

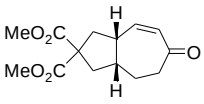


4e, Ar = *p*-BrC_6H_4

(4*Z*,6*E*)-dimethyl-8-(4-bromophenyl)-3,3a,8,8a-tetrahydro-6-(pivaloyloxy)azulene-2,2(1H)-dicarboxylate (**4e**).

Oil, 40.8 mg, 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.93 (dd, *J* = 10.0, 13.5 Hz, 1H), 2.16 (dd, *J* = 7.0, 13.5 Hz, 1H), 2.33 (dd, *J* = 6.5, 13.5 Hz, 1H), 2.54 (dd, *J* = 7.5, 13.5 Hz, 1H), 2.86-2.98 (m, 2H), 3.19 (dd, *J* = 6.0, 10.0 Hz, 1H), 3.69 (s, 6H), 5.67 (dd, *J* = 1.0, 6.0 Hz, 1H), 5.72 (d, *J* = 12.0 Hz, 1H), 6.00 (dd, *J* = 3.0, 11.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.3, 39.0, 39.5, 41.2, 42.1, 46.3, 53.0, 53.1, 57.2, 58.4, 120.7, 123.9, 124.4, 130.0, 132.0, 139.5, 142.9, 146.5, 172.5, 172.7, 177.7. IR (film): 2973, 1731, 1486, 1434, 1272, 1199, 1123, 1071 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{25}H_{29}BrO_6$ $(M+Na)^+$ 527.1040, found 527.1038.

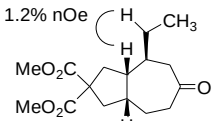
Procedures for the synthesis of compounds 5, 6, and 7



5

6-Oxo-3,3a,4,5,6,8a-hexahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**5**). To a solution of diene **2b** (35.0 mg, 0.1 mmol) in DCM (1 mL) was added TFA (0.5 mL) and MeOH (4 mg, 0.13 mmol). The reaction was stirred for 3-4 h at room temperature before the addition of saturated aqueous $NaHCO_3$. The mixture was extracted with EtOAc four times. The combined organic extracts were washed with brine, dried with Na_2SO_4 and concentrated under vacuum. Purification by flash column chromatography on silica gel (1:3 EtOAc/Hexane) gave compound **5** (22.0 mg, 83% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 – 1.71 (m, 1H), 1.86 – 2.00 (m, 2H), 2.31 (dd, *J* = 13.7, 7.9 Hz, 1H), 2.39 – 2.55 (m, 2H), 2.56 – 2.73 (m, 3H), 3.05 – 3.17 (m, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 5.92 (dt, *J* = 12.3, 2.0 Hz, 1H), 6.30 (dd, *J* = 12.3, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 40.9, 41.7, 42.3, 42.4, 43.0, 53.1, 53.2, 59.2, 131.0, 146.7, 172.4, 172.7, 204.3. IR (film): 2955, 1728, 1664, 1434, 1253, 1201, 1172, 1069, 939 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{14}H_{18}O_5$ $(M+Na)^+$ 289.1046, found 289.1046.

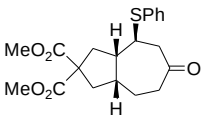


6

4-Ethyl-6-oxo-octahydro-azulene-2,2-dicarboxylic acid dimethyl ester (**6**).

To a solution of triethyl phosphite (1 mg, 0.006 mmol) in toluene (1.0 mL) was added $Cu(OTf)_2$ (1.1 mg, 0.003 mmol) under nitrogen atmoosphere. After the reaction mixture was stirred for 30 min at rt, Et_2Zn (1.0 M, 0.3 mL, 0.3 mmol) was added slowly under -20 ^{o}C, the resulting mixture was stirred for 15 min. Enone **5** (26.6 mg, 0.1 mmol) was added. The reaction was stirred for 3-4 h at rt before the addition of saturated aqueous $NaHCO_3$. The solution was extracted with EtOAc for four times. The combined organic extracts were washed with brine, dried with Na_2SO_4 and concentrated under vacuum. Purification by flash column chromatography on silica gel (1:3 EtOAc/Hexane) gave compound **6** (24.2.0 mg, 81% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.4 Hz, 3H), 1.21-1.34 (m, 1H), 1.46-1.62 (m, 2H), 1.64-1.83 (m, 2H), 1.97 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.01-2.17 (m, 2H), 2.26-2.40 (m, 3H), 2.47 (dd, *J* = 12.2, 5.7 Hz, 1H), 2.51-2.65 (m, 3H), 3.73 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9, 26.1, 27.8, 38.0, 38.8, 40.5, 42.0, 43.1, 46.5, 46.9, 53.0, 53.0, 58.7, 173.0, 173.0, 212.8. IR (film): 2956, 1731, 1699, 1434, 1360, 1254, 1220, 1196, 1173, 1149, 1071 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{24}O_5$ $(M+Na)^+$ 319.1516, found 319.1515.



7

6-Oxo-4-phenylsulfanyl-octahydro-azulene-2,2-dicarboxylic acid dimethyl ester (**7**).
To a solution of enone **5** (26.6 mg, 0.1 mmol) in $CHCl_3$ (0.5 mL) was added PhSH (11.1 mg, 0.1 mmol) and Et_3N (3 mg, 0.03 mmol). The reaction was stirred at room temperature for 2h. Purification by flash column chromatography on silica gel (1:3 EtOAc/Hexane) gave compound **7** (36.0 mg, 96% yield) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63-1.84 (m, 2H), 2.07 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.28-2.73 (m, 8H), 2.89 (dd, *J* = 15.4, 2.1 Hz, 1H), 3.34 (t, *J* = 7.7 Hz, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 7.18-7.37 (m, 3H), 7.37 – 7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 39.0, 41.0, 41.6, 42.4, 45.9, 47.0, 48.2, 53.1, 53.2, 58.3, 128.1, 129.4, 132.9, 133.3, 172.8, 172.9, 210.2. IR (film): 2952, 2358, 1729, 1702, 1435, 1253, 1200, 1164, 745, 693 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}O_5S$ $(M+Na)^+$ 399.1237, found 399.1246.

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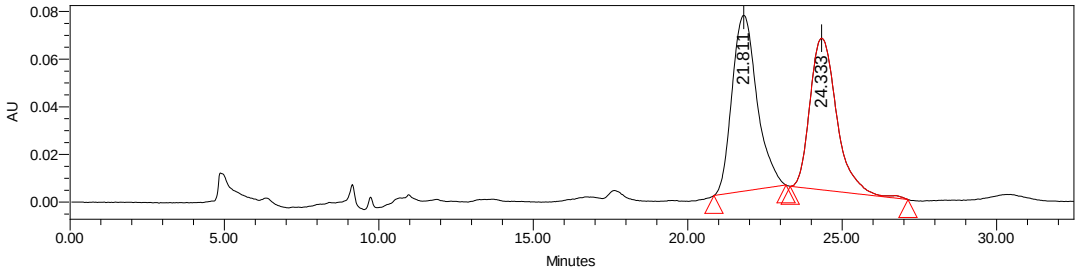
HPLC analysis for **1b**, **1m**, **1n**, **2b**, **2m**, and **2n**.

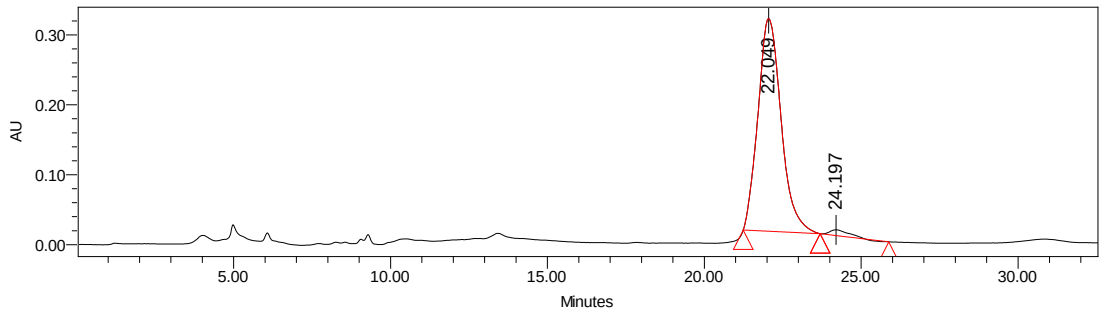
(-)-**1b**: 94% *ee* determined by HPLC analysis of the corresponding alcohol: AD-H column (hexane/iPrOH = 95/5), 0.7 mL/min, t-major = 22.0 min, and t-minor = 24.1 min. For alcohol: $[\alpha]_D$ = -20.3°(c 1.00, CH_2Cl_2); For **1b**: $[\alpha]_D$ = -16.7°(c 1.00, CH_2Cl_2).

Racemic sample **1b**:



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		21.811	4141767	51.90	73787	bb			Unknown	
2		24.333	3837972	48.10	63637	bb			Unknown	

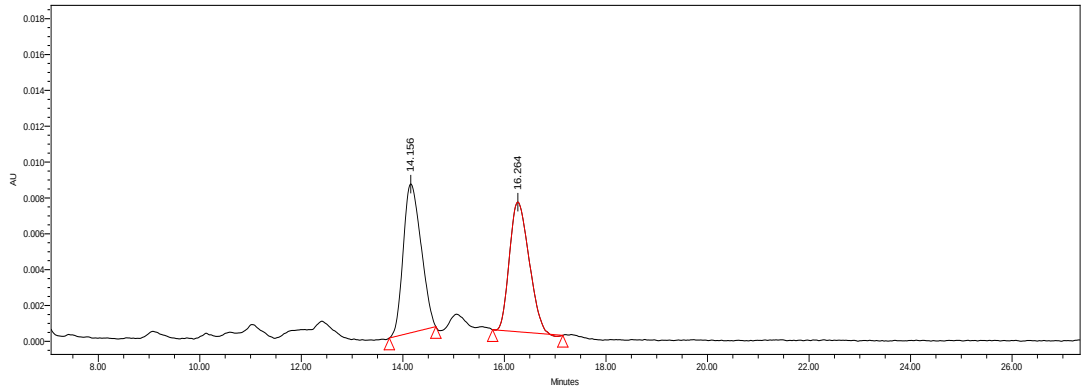
Enantio-enriched sample (-)-**1b**:



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		22.049	15620052	97.49	304043	bb			Unknown	
2		24.197	402202	2.51	8292	bb			Unknown	

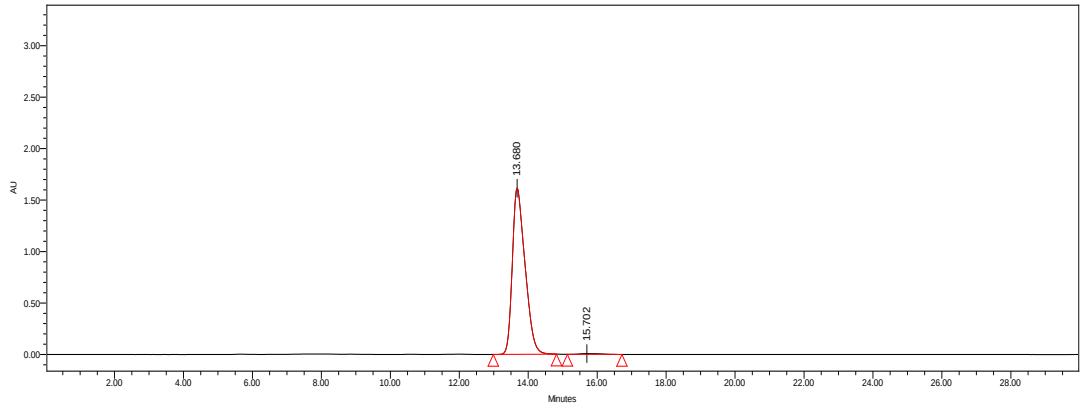
(-)-**1m**: 98% ee determined by HPLC analysis: AD-H column (hexane/iPrOH = 90/10), 0.7 mL/min, t-major = 13.7 min, and t-minor = 15.7 min. $[\alpha]_D$ = -10.9 (c 1.00, CH_2Cl_2).

Racemic sample **1m**:



	Retention Time	Area	% Area	Height	Int Type
1	14.156	198635	49.96	8303	bb
2	16.264	198953	50.04	7234	bb

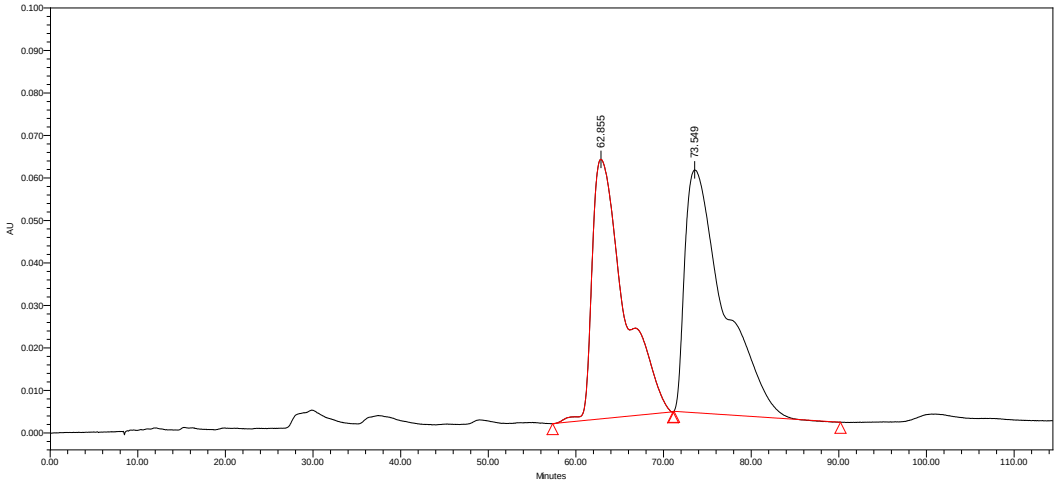
Enantio-enriched sample (-)-**1m**:



	Retention Time	Area	% Area	Height	Int Type
1	13.680	41313854	99.19	1615100	bb
2	15.702	335386	0.81	7481	bb

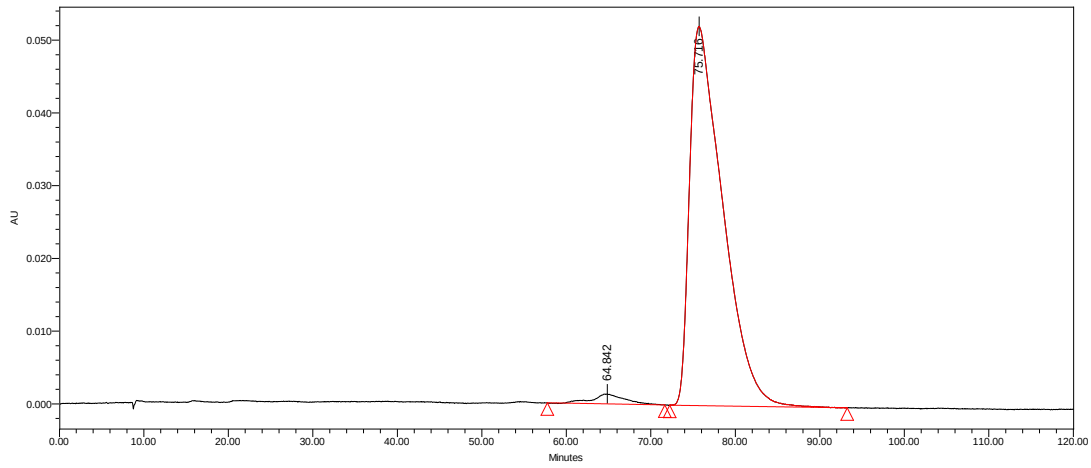
(-)-1n: 95% ee determined by HPLC analysis: Chiralpak 1A column (hexane/iPrOH = 85/15), 0.7 mL/min, t-major = 75.7 min, and t-minor = 64.8 min. $[\alpha]_D$ = -7.6 (c 1.00, CH_2Cl_2).

Raceimic sample **1n**:



	Retention Time	Area	% Area	Height
1	62.855	15554285	46.75	61078
2	73.549	17718337	53.25	57163

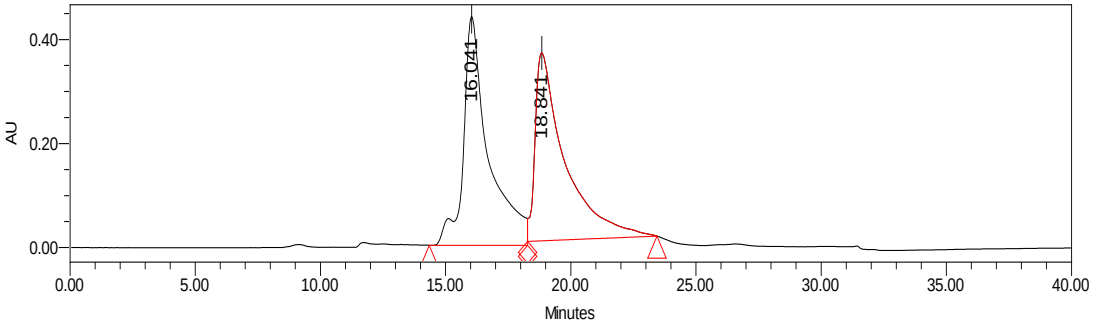
Enantio-enriched sample **(-)-1n**:



	Retention Time	Area	% Area	Height
1	64.842	367440	2.52	1374
2	75.716	14225197	97.48	52123

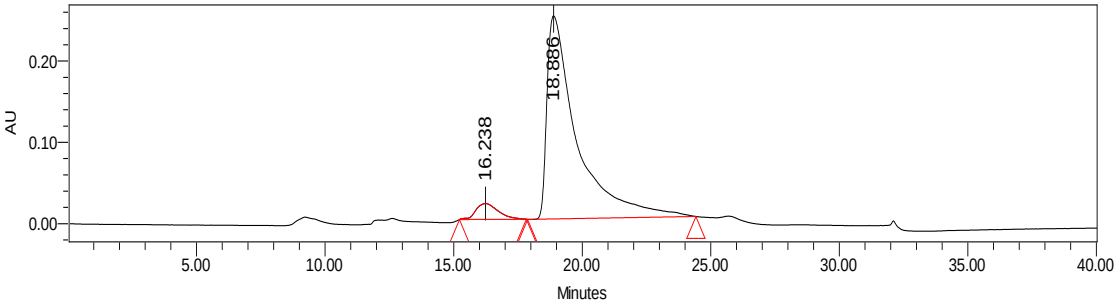
(-)-2b: 89% *ee* determined by HPLC analysis: AS-H column (hexane/iPrOH = 100/1), 0.6 mL/min, t-minor = 16.2 min, t-major = 18.9 min. $[\alpha]_D$ = -14.0°(c 1.00, CH_2Cl_2).

Racemic sample **2b**:



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.041	30473946	50.47	439757	bV			Unknown	
2		18.841	29905760	49.53	361029	Vb			Unknown	

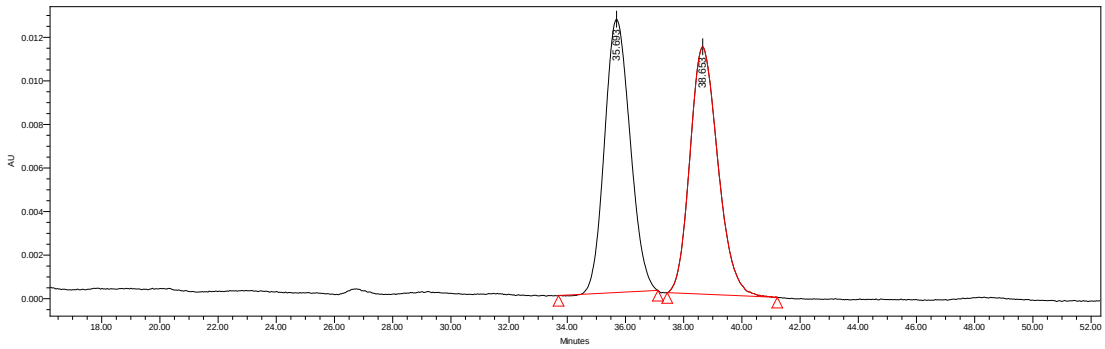
Enantio-enriched sample (-)-**2b**:



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.238	1176763	5.51	19652	bb			Unknown	
2		18.886	20199021	94.49	249740	bb			Unknown	

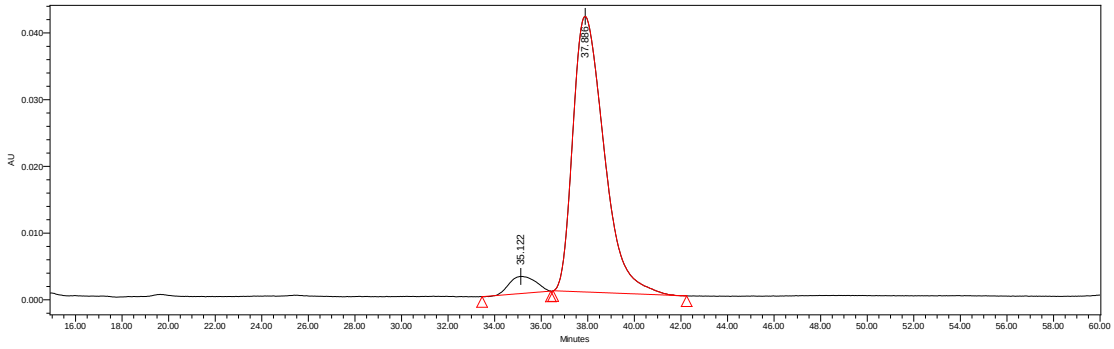
(-)-2m: 90% *ee* determined by HPLC analysis: AD-H column (hexane/iPrOH = 95/5), 0.7 mL/min, t-major = 37.9 min, and t-minor = 35.1 min. $[\alpha]_D^{25}$ = -35.3 (c 1.00, CH_2Cl_2).

Racemic sample **2m**:



	Retention Time	Area	% Area	Height	Int Type
1	35.693	769105	50.36	12545	Bb
2	38.653	758210	49.64	11354	bb

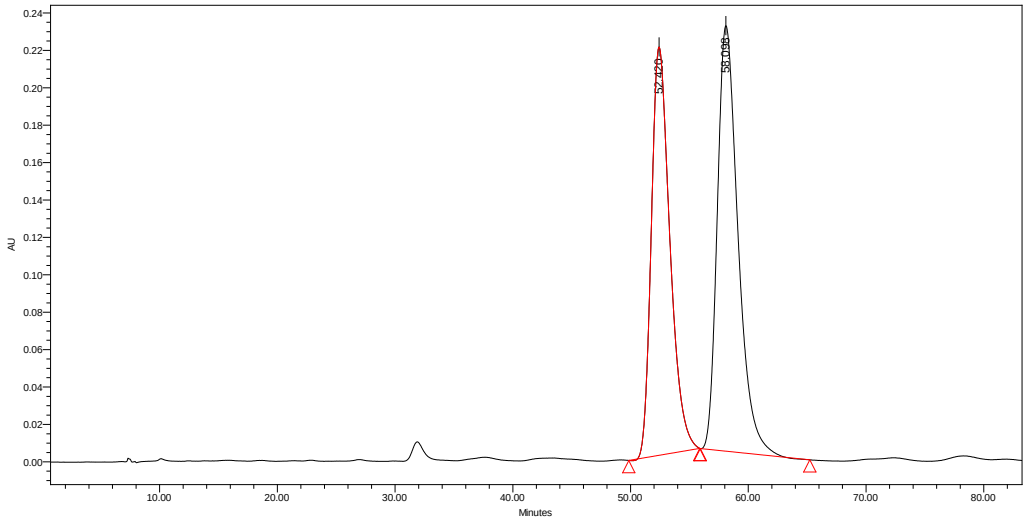
Enantio-enriched sample (-)-**2m**:



	Retention Time	Area	% Area	Height	Int Type
1	35.122	203109	5.01	2564	Bb
2	37.886	3847460	94.99	41307	bb

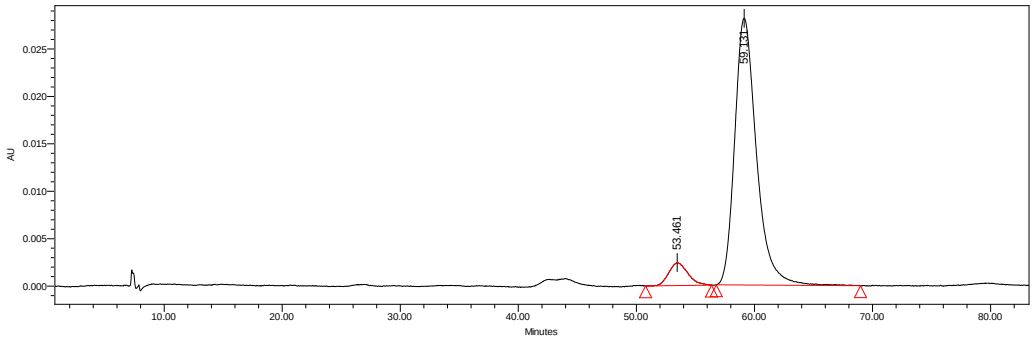
(-)-2n: 86% *ee* determined by HPLC analysis: Chiralpak 1A column (hexane/iPrOH = 30/70), 0.7 mL/min, t-major = 53.5 min, and t-minor = 59.1 min. $[\alpha]_D^{25}$ = -10.5 (c 1.00, CH_2Cl_2).

Raceimic Sample **2n**:

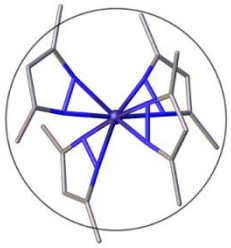


	Retention Time	Area	% Area	Height
1	52.420	23965838	46.26	218332
2	58.098	27841338	53.74	227529

Enantio-enriched sample (-)-**2n**:



	Retention Time	Area	% Area	Height
1	53.461	269950	6.96	2427
2	59.131	3606931	93.04	28104



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Structural report on **2n** (CCDC977964)

MAY 7, 2013

Crystallographic Experimental Section

Data Collection

A colorless crystal with approximate dimensions 0.4 x 0.2 x 0.1 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 5 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 9956 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 57938 data were harvested by collecting 5 sets of frames with 0.5º scans in ω and φ with exposure times of 30 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [1]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups *C*2, *Cm*, and *C*2/*m*. The *E*-statistics strongly suggested the non-centrosymmetric space group *C*2 that yielded chemically reasonable and computationally stable results of refinement [2-4].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares

cycles and difference Fourier maps. All non-disordered non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The asymmetric unit contains two symmetry independent molecules with the same composition, connectivity, and absolute configuration, C8(S), C14(R). The two molecules differ in the orientation of the bicyclic fragment. In the Br1A molecule six atoms in the bicyclic unit are disordered over two positions with the major component contribution of 64.8(2)%. The disordered atoms were refined isotropically with constraints and geometrical restraints. Additionally, all phenyl rings were refined with an idealized geometry.

Whereas the absolute structure was unambiguously established by anomalous dispersion effects the statistical indicators point to the presence of the opposite diastereomer in the amount of 4.3(9)%.

There were three partially occupied solvate molecules disordered over two-fold axes in the asymmetric unit. A significant amount of time was invested in identifying and refining the disordered molecules. Bond length restraints were applied to model the molecules but the resulting isotropic displacement coefficients suggested the molecules were mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON [5] was used to correct the diffraction data for diffuse scattering effects and to identify the solvent molecules. PLATON calculated the upper limit of volume that can be occupied by the solvent to be 1436 $Å^3$, or 25.7% of the unit cell volume. The program calculated 365 electrons in the unit cell for the diffuse species. Six solvents were used in the synthesis/crystallization and it is hard to match the number of electrons to a specific solvent. Compositional disorder between two solvent molecules of different nature at each solvent site is plausible. Please note that all derived results in the following tables are based on the known contents. No data are given for the diffusely scattering species.

The final least-squares refinement of 519 parameters against 13840 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0499 and 0.1259, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{24}H_{25}BrN_2O_4S$ (M =517.43): monoclinic, space group C2 (no. 5), a = 9.512(4) Å, b = 19.054(7) Å, c = 30.838(14) Å, β = 93.810(8)°, V = 5577(4) Å^3, Z = 8, T = 100.0 K, μ(MoKα) = 1.577 mm^{-1}, *Dcalc* = 1.233 g/mm^3, 57938 reflections measured ($2.648 \leq 2\Theta \leq 56.68$), 13840 unique ($R_{int}$ = 0.0399) which were used in all calculations. The final R_1 was 0.0499 ($I > 2\sigma(I)$) and wR_2 was 0.1259 (all data).

References

[1] Bruker-AXS. (2007-2013) APEX2 (Ver. 2013.2-0), SADABS (2012-1), and SAINT+ (Ver. 8.30C) Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.

[2] Sheldrick, G. M. (2008) SHELXL. *Acta Cryst.* **A64**, 112-122.

[3] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. "OLEX2: a complete structure solution, refinement and analysis program". *J. Appl. Cryst.* (2009) **42**, *339-341*.

[4] Guzei, I.A. (2013). Internal laboratory computer programs Gn.

[5] A.L. Spek (1990) *Acta Cryst.* A46, C34.

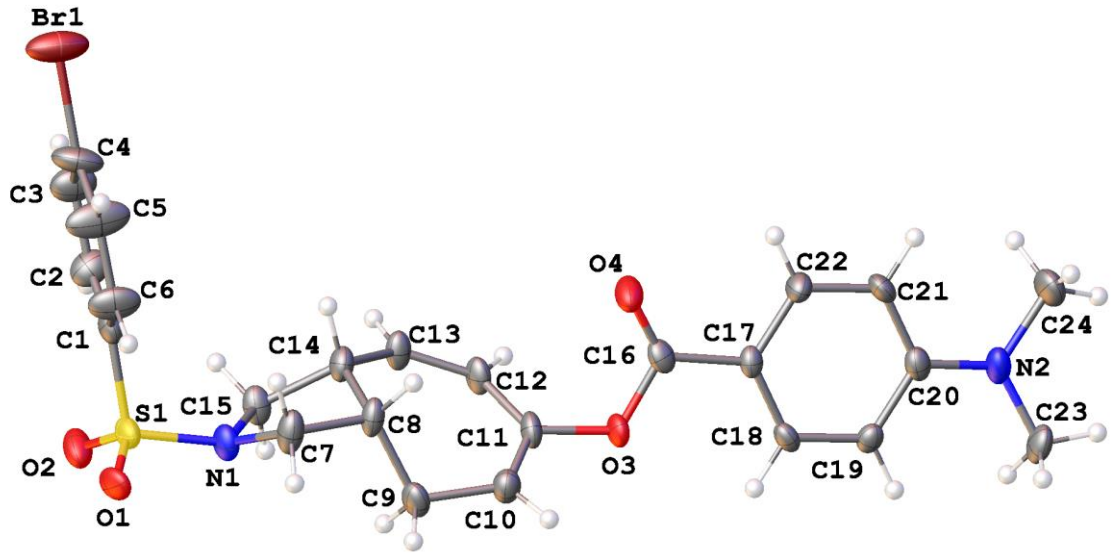


Figure S1. A molecular drawing of the Br1 molecule of **2n** shown with 50% probability ellipsoids.

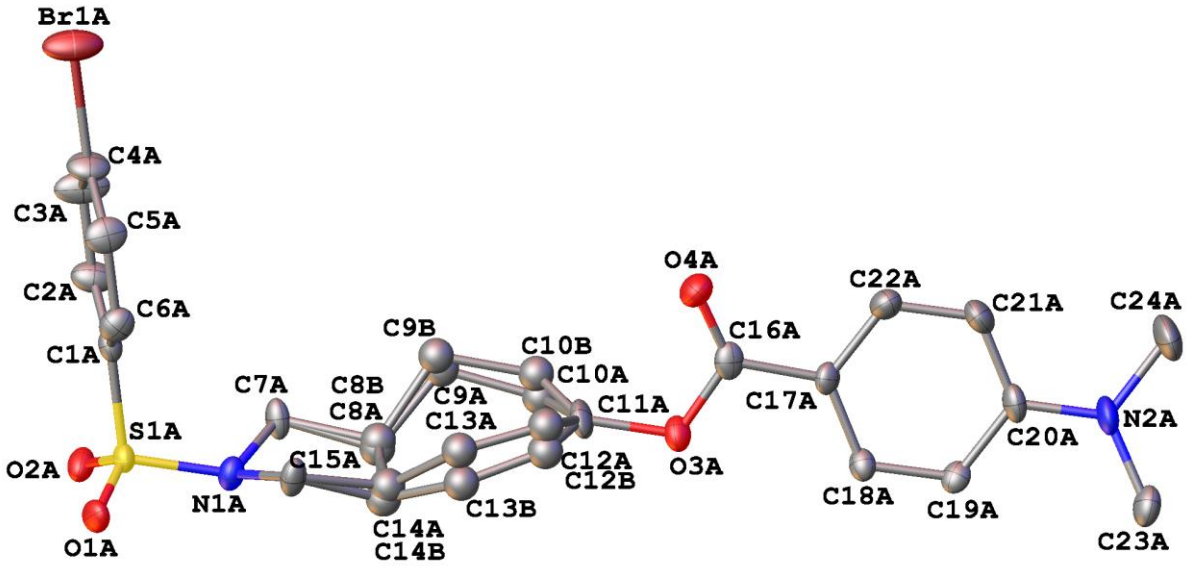


Figure S2. A molecular drawing of the Br1A molecule of **2n** shown with 50% probability ellipsoids. All H atoms are omitted, but all disordered atoms are shown.

Table 1 Crystal data and structure refinement for **2n**

Identification code	**2n**
Empirical formula	$C_{24}H_{25}BrN_2O_4S$
Formula weight	517.43
Temperature/K	100.0
Crystal system	monoclinic
Space group	C2
a/Å	9.512(4)
b/Å	19.054(7)
c/Å	30.838(14)
α/°	90
β/°	93.810(8)
γ/°	90
Volume/Å^3	5577(4)
Z	8
ρ_{calc}mg/mm^3	1.233
m/mm^{-1}	1.577
F(000)	2128.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
2Θ range for data collection	2.648 to 56.68°
Index ranges	$-12 \le h \le 12$, $-25 \le k \le 25$, $-41 \le l \le 41$
Reflections collected	57938
Independent reflections	13840[R(int) = 0.0399]
Data/restraints/parameters	13840/80/519
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0499, wR_2 = 0.1229
Final R indexes [all data]	R_1 = 0.0570, wR_2 = 0.1259
Largest diff. peak/hole / e Å^{-3}	0.72/-0.45
Flack parameter	0.043(9)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2n**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	2305.8(7)	8491.7(5)	4762.2(2)	58.9(2)

S1	3417.2(14)	7871.1(6)	6793.5(4)	27.7(3)
O3	3427(4)	3659.3(16)	6928.6(11)	25.5(7)
N1	3511(4)	7034(2)	6867.2(15)	27.6(9)
C7	4736(5)	6665(2)	6695(2)	35.3(12)
C8	4274(4)	5897(2)	6689.8(16)	26.6(9)
C9	4550(5)	5531(2)	7127.4(17)	29.7(11)
C10	4492(5)	4747(2)	7086.6(17)	29.1(10)
C11	3382(5)	4399(2)	6903.5(16)	25.7(10)
C12	2033(5)	4682(2)	6734.2(17)	26.9(10)
C13	1750(5)	5338(2)	6601.4(18)	27.3(10)
C14	2687(5)	5957(2)	6557.5(16)	26.5(10)
C15	2202(5)	6596(2)	6812.1(18)	28.5(10)
O1	4784(4)	8155.2(19)	6923.4(12)	35.3(9)
O2	2205(5)	8115(2)	6994.3(13)	39.6(9)
O4	3247(5)	3602(2)	6198.7(12)	37.7(9)
N2	2992(5)	359(2)	6732.2(16)	32.1(10)
C1	3140(3)	8029.3(19)	6238.0(8)	26.3(10)
C2	1769(3)	8031(2)	6051.2(10)	35.2(12)
C3	1520(3)	8175(2)	5610.8(11)	42.6(14)
C4	2641(4)	8316(3)	5357.3(8)	46.8(16)
C5	4012(3)	8314(3)	5544.1(11)	59(2)
C6	4261(3)	8170(2)	5984.5(11)	43.4(15)
C16	3318(5)	3306(3)	6542.8(16)	24.4(9)
C17	3311(3)	2529.9(10)	6602.4(9)	21.0(9)
C18	3498(3)	2216.8(13)	7009.3(7)	21.7(9)
C19	3425(3)	1491.1(14)	7047.8(7)	22.1(9)
C20	3166(4)	1078.4(10)	6679.4(9)	25.5(10)
C21	2980(4)	1391.5(14)	6272.5(8)	28.7(10)
C22	3052(4)	2117.3(14)	6234.0(7)	27.1(10)
C23	3372(6)	23(3)	7136.6(19)	33.6(12)
C24	2692(7)	-91(3)	6351(2)	42.3(14)
Br1A	7844.4(5)	813.3(4)	10149.5(2)	44.79(18)
S1A	5851.9(12)	1200.8(5)	8142.0(4)	19.8(2)
O3A	5933(3)	5473.7(16)	8204.3(11)	24.6(7)
N1A	5718(4)	2031.5(19)	8054.1(13)	22.6(8)
C7A	4670(4)	2429(2)	8288.4(17)	23.6(9)
C8B	4928(9)	3192(3)	8180(3)	29.2(6)

C9B	4944(11)	3653(4)	8578(3)	29.2(6)
C10B	4910(9)	4423(4)	8482(3)	29.2(6)
C11A	5951(5)	4736(2)	8283.8(17)	27.2(10)
C12B	7246(8)	4411(4)	8161(4)	29.2(6)
C13B	7364(8)	3755(4)	8021(4)	29.2(6)
C14B	6297(8)	3184(3)	7931(3)	29.2(6)
C15A	7000(5)	2471(2)	8056.9(17)	24.6(10)
O1A	6957(4)	943.5(17)	7889.7(11)	27.9(7)
O2A	4466(4)	911.3(18)	8085.7(10)	26.8(7)
O4A	6717(4)	5616.3(19)	8900.3(12)	34.0(8)
N2A	6182(5)	8786(2)	8253.0(15)	31.9(10)
C1A	6403(3)	1098.0(17)	8688.3(7)	19.0(9)
C2A	5416(2)	1004(2)	8995.9(9)	29.4(11)
C3A	5857(3)	921(2)	9431.7(8)	37.1(13)
C4A	7286(3)	932(2)	9559.8(7)	30.1(11)
C5A	8273(2)	1026(2)	9252.3(9)	28.9(11)
C6A	7832(2)	1108.9(18)	8816.5(8)	26.3(10)
C8A	4899(13)	3186(5)	8144(5)	29.2(6)
C9A	4662(18)	3700(6)	8509(5)	29.2(6)
C10A	4717(12)	4453(6)	8369(6)	29.2(6)
C12A	7332(11)	4416(6)	8284(6)	29.2(6)
C13A	7473(13)	3742(5)	8178(8)	29.2(6)
C14A	6423(12)	3214(5)	7995(5)	29.2(6)
C16A	6339(4)	5871(3)	8554.3(15)	23.0(9)
C17A	6226(3)	6628.9(10)	8458.5(9)	19.4(8)
C18A	5997(3)	6892.7(12)	8039.5(8)	20.1(9)
C19A	5958(3)	7613.6(13)	7970.8(7)	20.2(9)
C20A	6147(3)	8070.8(10)	8321.0(9)	25.1(10)
C21A	6376(4)	7807.1(14)	8740.0(8)	31.8(11)
C22A	6415(4)	7086.1(15)	8808.8(7)	27.5(10)
C23A	6158(6)	9076(3)	7818.3(18)	30.8(11)
C24A	6083(9)	9265(3)	8616(2)	53.4(18)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **2n**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**

Br1	38.3(3)	109.4(7)	28.1(3)	5.0(4)	-4.7(2)	-3.2(4)
S1	41.3(7)	14.6(5)	27.0(6)	-1.7(5)	0.4(5)	-3.2(5)
O3	32.7(18)	11.6(15)	32.0(18)	-2.4(13)	-0.1(14)	-2.3(12)
N1	27(2)	16.2(19)	39(2)	-2.6(17)	0.2(17)	-4.3(16)
C7	26(2)	20(2)	59(4)	2(2)	-3(2)	0(2)
C8	20.4(19)	15(2)	44(3)	2(2)	2.2(18)	1.5(17)
C9	29(2)	20(2)	40(3)	-7(2)	-6(2)	-2.5(18)
C10	29(2)	22(2)	36(3)	-1(2)	-3(2)	2.6(19)
C11	31(2)	12(2)	35(3)	-1.8(19)	8(2)	0.7(18)
C12	24(2)	15(2)	42(3)	-3(2)	1(2)	-4.6(17)
C13	18(2)	18(2)	46(3)	-1(2)	1.2(19)	1.2(17)
C14	30(2)	16(2)	34(2)	2.8(19)	3.5(19)	1.6(18)
C15	21(2)	22(2)	44(3)	-4(2)	6(2)	-1.4(18)
O1	50(2)	18.9(17)	35(2)	-5.2(15)	-9.7(16)	-11.7(16)
O2	64(3)	24.1(18)	33(2)	-1.6(15)	15.1(18)	6.7(18)
O4	63(3)	22.6(18)	28.0(19)	0.9(15)	9.8(17)	7.4(18)
N2	32(2)	17(2)	46(3)	-4.2(18)	-9.0(19)	1.6(16)
C1	33(2)	15(2)	31(3)	-5.0(18)	1(2)	-0.7(18)
C2	30(2)	39(3)	36(3)	9(2)	4(2)	-3(2)
C3	27(2)	61(4)	39(3)	2(3)	-5(2)	1(3)
C4	47(3)	70(5)	22(3)	-10(3)	-5(2)	-10(3)
C5	21(2)	117(7)	39(3)	12(4)	2(2)	1(3)
C6	21(2)	73(4)	35(3)	4(3)	-6(2)	-8(3)
C16	20(2)	22(2)	31(2)	-6.8(19)	5.5(17)	0.6(17)
C17	18.9(19)	15(2)	29(2)	-1.5(18)	3.0(17)	1.0(16)
C18	19.6(19)	19(2)	26(2)	-8.6(18)	-1.4(17)	-0.9(16)
C19	19(2)	19(2)	27(2)	2.3(18)	-4.6(17)	-0.4(17)
C20	22(2)	20(2)	35(3)	-4.5(18)	-0.4(18)	1.9(16)
C21	38(3)	22(2)	26(2)	-10.5(19)	-4.6(19)	2(2)
C22	39(3)	19(2)	23(2)	2.1(19)	1.8(19)	3(2)
C23	37(3)	16(2)	46(3)	7(2)	-5(2)	-1(2)
C24	56(4)	23(3)	46(3)	-10(2)	-10(3)	-4(2)
Br1A	24.7(2)	87.1(5)	21.8(2)	2.2(3)	-4.23(17)	-2.6(3)
S1A	27.0(5)	11.3(5)	20.8(5)	-0.7(4)	0.5(4)	0.7(4)
O3A	27.0(16)	16.6(16)	29.7(18)	-1.1(13)	-3.5(13)	-1.9(12)
N1A	24.2(18)	16.3(18)	28(2)	2.7(15)	5.1(15)	-0.1(15)
C7A	16.7(19)	14(2)	40(3)	-2.8(19)	2.8(18)	1.1(16)

C11A	31(2)	13(2)	36(3)	-4.6(19)	-7(2)	-3.7(18)
C15A	23(2)	16(2)	36(3)	3.5(19)	11.1(19)	-1.1(17)
O1A	41.8(18)	16.4(16)	26.2(16)	-1.3(13)	8.9(14)	8.6(14)
O2A	34.9(17)	17.6(16)	26.6(16)	3.6(14)	-7.9(13)	-4.2(14)
O4A	50(2)	25.4(19)	25.9(18)	5.0(14)	0.9(16)	0.7(16)
N2A	48(3)	11.6(18)	36(2)	-4.4(17)	-2(2)	1.7(17)
C1A	18.5(19)	14(2)	25(2)	-3.1(16)	0.5(16)	-0.8(15)
C2A	20(2)	46(3)	23(2)	-3(2)	-1.2(17)	-1.4(19)
C3A	13.8(19)	73(4)	25(2)	3(3)	2.4(16)	-1(2)
C4A	25(2)	44(3)	20(2)	-2(2)	-7.9(17)	-2(2)
C5A	13.4(18)	42(3)	31(2)	3(2)	0.8(17)	-3.6(18)
C6A	21(2)	29(3)	29(2)	3.2(19)	5.7(18)	0.3(18)
C16A	14.7(17)	21(2)	34(2)	0(2)	5.0(16)	-2.6(18)
C17A	18.1(19)	15(2)	25(2)	1.5(17)	2.4(16)	-3.9(16)
C18A	18.2(19)	17(2)	25(2)	-0.9(17)	-2.4(16)	1.8(16)
C19A	15.7(18)	21(2)	24(2)	3.8(17)	-3.0(16)	0.6(16)
C20A	26(2)	14(2)	37(3)	-4.3(19)	3.5(19)	2.0(17)
C21A	46(3)	22(2)	27(3)	-8(2)	3(2)	-4(2)
C22A	37(3)	24(2)	22(2)	2.6(19)	5.6(19)	2(2)
C23A	34(3)	18(2)	40(3)	5(2)	-1(2)	3(2)
C24A	90(6)	20(3)	50(4)	-12(3)	0(4)	3(3)

Table 4 Bond Lengths for **2n**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	C4	1.872(3)	O3A	C11A	1.427(5)
S1	N1	1.613(4)	O3A	C16A	1.354(6)
S1	O1	1.440(4)	N1A	C7A	1.477(5)
S1	O2	1.423(4)	N1A	C15A	1.479(5)
S1	C1	1.742(3)	C7A	C8B	1.516(8)
O3	C11	1.412(5)	C7A	C8A	1.530(10)
O3	C16	1.365(6)	C8B	C9B	1.507(8)
N1	C7	1.488(6)	C8B	C14B	1.556(8)
N1	C15	1.499(6)	C9B	C10B	1.497(8)
C7	C8	1.528(6)	C10B	C11A	1.339(8)
C8	C9	1.526(6)	C11A	C12B	1.451(8)
C8	C14	1.541(6)	C11A	C10A	1.334(10)

C9	C10	1.498(6)	C11A	C12A	1.447(10)
C10	C11	1.341(6)	C12B	C13B	1.329(8)
C11	C12	1.456(6)	C13B	C14B	1.501(8)
C12	C13	1.338(6)	C14B	C15A	1.552(8)
C13	C14	1.489(6)	C15A	C14A	1.525(10)
C14	C15	1.536(6)	O4A	C16A	1.205(6)
O4	C16	1.200(6)	N2A	C20A	1.379(5)
N2	C20	1.392(5)	N2A	C23A	1.449(7)
N2	C23	1.426(7)	N2A	C24A	1.452(7)
N2	C24	1.469(7)	C1A	C2A	1.3900
C1	C2	1.3900	C1A	C6A	1.3900
C1	C6	1.3900	C2A	C3A	1.3900
C2	C3	1.3900	C3A	C4A	1.3900
C3	C4	1.3900	C4A	C5A	1.3900
C4	C5	1.3900	C5A	C6A	1.3900
C5	C6	1.3900	C8A	C9A	1.518(11)
C16	C17	1.491(5)	C8A	C14A	1.550(10)
C17	C18	1.3900	C9A	C10A	1.501(11)
C17	C22	1.3900	C12A	C13A	1.335(10)
C18	C19	1.3900	C13A	C14A	1.501(10)
C19	C20	1.3900	C16A	C17A	1.477(5)
C20	C21	1.3900	C17A	C18A	1.3900
C21	C22	1.3900	C17A	C22A	1.3900
Br1A	C4A	1.874(2)	C18A	C19A	1.3900
S1A	N1A	1.609(4)	C19A	C20A	1.3900
S1A	O1A	1.435(3)	C20A	C21A	1.3900
S1A	O2A	1.429(3)	C21A	C22A	1.3900
S1A	C1A	1.742(2)			

Table 5 Bond Angles for **2n**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	S1	C1	108.2(2)	C7A	N1A	C15A	106.8(3)
O1	S1	N1	107.0(2)	C15A	N1A	S1A	120.0(3)
O1	S1	C1	106.5(2)	N1A	C7A	C8B	105.1(4)
O2	S1	N1	107.5(2)	N1A	C7A	C8A	103.2(5)
O2	S1	O1	119.9(3)	C7A	C8B	C14B	104.6(5)

O2	S1	C1	107.3(2)	C9B	C8B	C7A	111.9(6)
C16	O3	C11	116.4(4)	C9B	C8B	C14B	116.4(7)
C7	N1	S1	117.0(3)	C10B	C9B	C8B	114.3(6)
C7	N1	C15	111.2(4)	C11A	C10B	C9B	121.3(7)
C15	N1	S1	119.8(3)	O3A	C11A	C12B	112.1(5)
N1	C7	C8	103.0(4)	O3A	C11A	C12A	114.6(6)
C7	C8	C14	102.0(3)	C10B	C11A	O3A	121.1(5)
C9	C8	C7	113.3(4)	C10B	C11A	C12B	126.6(6)
C9	C8	C14	112.1(4)	C10A	C11A	O3A	115.5(6)
C10	C9	C8	112.2(4)	C10A	C11A	C12A	129.8(8)
C11	C10	C9	123.5(4)	C13B	C12B	C11A	125.2(7)
O3	C11	C12	114.4(4)	C12B	C13B	C14B	132.2(7)
C10	C11	O3	116.8(4)	C13B	C14B	C8B	118.6(6)
C10	C11	C12	128.2(4)	C13B	C14B	C15A	108.3(5)
C13	C12	C11	127.6(4)	C15A	C14B	C8B	104.3(5)
C12	C13	C14	131.2(4)	N1A	C15A	C14B	98.8(4)
C13	C14	C8	119.9(4)	N1A	C15A	C14A	103.6(5)
C13	C14	C15	112.3(4)	C20A	N2A	C23A	121.2(4)
C15	C14	C8	104.2(4)	C20A	N2A	C24A	120.1(5)
N1	C15	C14	102.9(3)	C23A	N2A	C24A	118.3(4)
C20	N2	C23	121.3(4)	C2A	C1A	S1A	120.07(16)
C20	N2	C24	120.0(4)	C2A	C1A	C6A	120.0
C23	N2	C24	117.6(4)	C6A	C1A	S1A	119.93(16)
C2	C1	S1	118.98(19)	C3A	C2A	C1A	120.0
C2	C1	C6	120.0	C2A	C3A	C4A	120.0
C6	C1	S1	120.99(19)	C3A	C4A	Br1A	118.88(15)
C1	C2	C3	120.0	C5A	C4A	Br1A	121.12(15)
C4	C3	C2	120.0	C5A	C4A	C3A	120.0
C3	C4	Br1	119.93(19)	C4A	C5A	C6A	120.0
C3	C4	C5	120.0	C5A	C6A	C1A	120.0
C5	C4	Br1	120.06(19)	C7A	C8A	C14A	105.7(7)
C6	C5	C4	120.0	C9A	C8A	C7A	111.2(9)
C5	C6	C1	120.0	C9A	C8A	C14A	112.6(10)
O3	C16	C17	112.5(4)	C10A	C9A	C8A	113.2(10)
O4	C16	O3	122.4(4)	C11A	C10A	C9A	119.4(10)
O4	C16	C17	125.1(4)	C13A	C12A	C11A	120.7(10)
C18	C17	C16	122.4(3)	C12A	C13A	C14A	131.5(10)

C18	C17	C22	120.0		C15A	C14A	C8A	105.5(7)	
C22	C17	C16	117.6(3)		C13A	C14A	C15A	110.5(8)	
C17	C18	C19	120.0		C13A	C14A	C8A	121.6(10)	
C20	C19	C18	120.0		O3A	C16A	C17A	112.0(4)	
C19	C20	N2	118.5(3)		O4A	C16A	O3A	122.2(5)	
C21	C20	N2	121.3(3)		O4A	C16A	C17A	125.8(4)	
C21	C20	C19	120.0		C18A	C17A	C16A	123.0(3)	
C20	C21	C22	120.0		C18A	C17A	C22A	120.0	
C21	C22	C17	120.0		C22A	C17A	C16A	117.0(3)	
N1A	S1A	C1A	106.79(19)		C17A	C18A	C19A	120.0	
O1A	S1A	N1A	107.3(2)		C18A	C19A	C20A	120.0	
O1A	S1A	C1A	107.56(18)		N2A	C20A	C19A	120.3(3)	
O2A	S1A	N1A	107.3(2)		N2A	C20A	C21A	119.6(3)	
O2A	S1A	O1A	120.4(2)		C21A	C20A	C19A	120.0	
O2A	S1A	C1A	106.84(17)		C22A	C21A	C20A	120.0	
C16A	O3A	C11A	114.5(4)		C21A	C22A	C17A	120.0	
C7A	N1A	S1A	118.0(3)						

Table 6 Torsion Angles for **2n**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
Br1	C4	C5	C6	-178.8(3)	C7A	N1A	C15A	C14B	-45.4(5)
S1	N1	C7	C8	-163.1(3)	C7A	N1A	C15A	C14A	-38.2(7)
S1	N1	C15	C14	136.8(4)	C7A	C8B	C9B	C10B	-168.6(6)
S1	C1	C2	C3	178.3(3)	C7A	C8B	C14B	C13B	-140.1(7)
S1	C1	C6	C5	-178.3(3)	C7A	C8B	C14B	C15A	-19.6(9)
O3	C11	C12	C13	-167.0(5)	C7A	C8A	C9A	C10A	-173.7(10)
O3	C16	C17	C18	-4.2(5)	C7A	C8A	C14A	C15A	0.5(14)
O3	C16	C17	C22	173.2(3)	C7A	C8A	C14A	C13A	-126.3(12)
N1	S1	C1	C2	86.6(3)	C8B	C7A	C8A	C9A	-28(8)
N1	S1	C1	C6	-95.1(3)	C8B	C7A	C8A	C14A	94(9)
N1	C7	C8	C9	-84.0(5)	C8B	C9B	C10B	C11A	-62.5(10)
N1	C7	C8	C14	36.7(5)	C8B	C14B	C15A	N1A	38.8(7)
C7	N1	C15	C14	-4.8(6)	C8B	C14B	C15A	C14A	-86(4)
C7	C8	C9	C10	-163.3(4)	C9B	C8B	C14B	C13B	-16.2(11)
C7	C8	C14	C13	-167.2(5)	C9B	C8B	C14B	C15A	104.4(8)
C7	C8	C14	C15	-40.6(5)	C9B	C10B	C11A	O3A	-178.2(6)

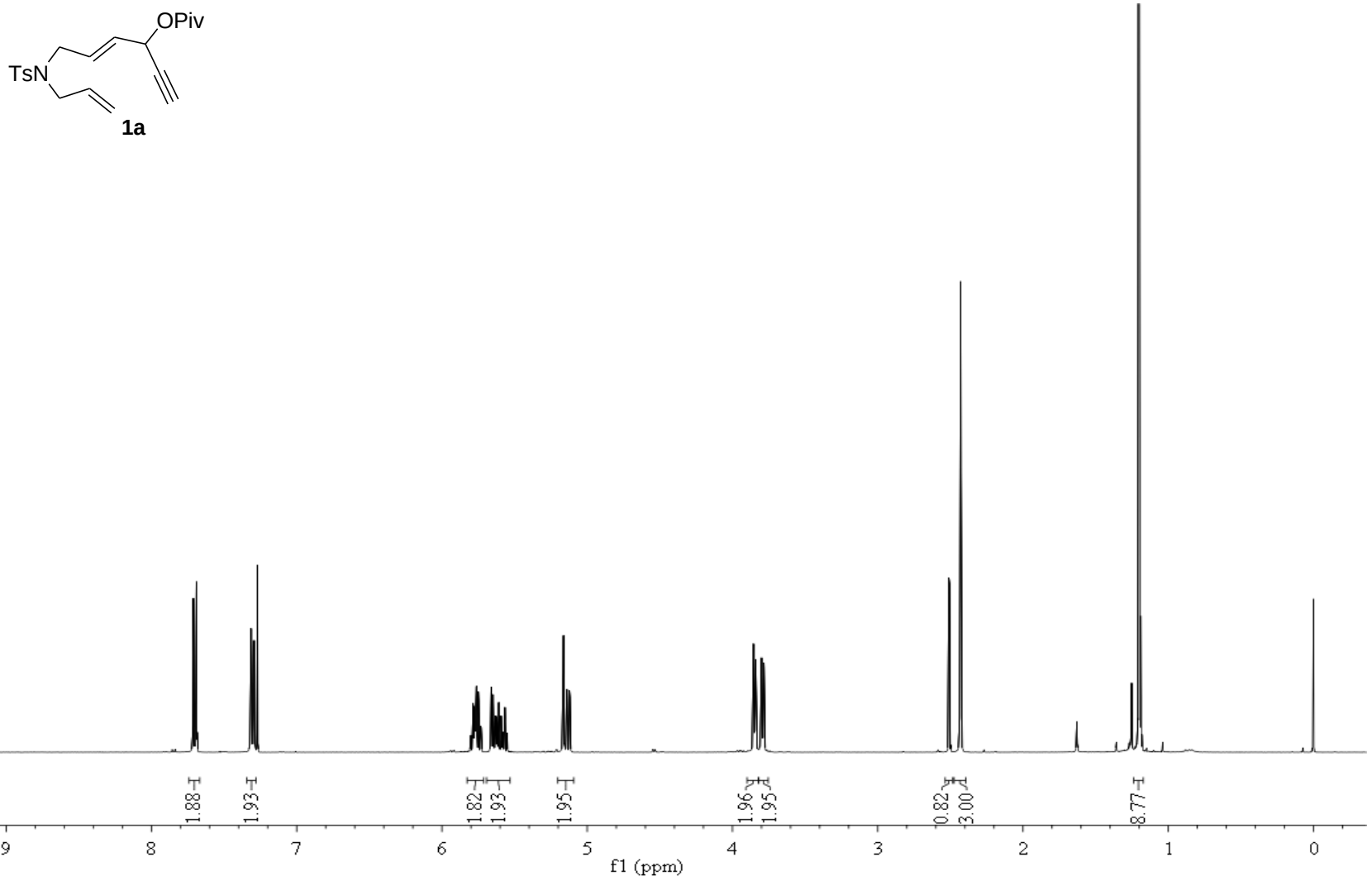
C8	C9	C10	C11	-55.3(7)	C9B	C10B	C11A	C12B	-3.9(11)
C8	C14	C15	N1	27.9(5)	C9B	C10B	C11A	C10A	107(3)
C9	C8	C14	C13	-45.7(6)	C9B	C10B	C11A	C12A	-20.9(11)
C9	C8	C14	C15	80.9(5)	C10B	C11A	C12B	C13B	35.5(12)
C9	C10	C11	O3	-173.8(5)	C10B	C11A	C10A	C9A	-59(2)
C9	C10	C11	C12	-3.4(9)	C10B	C11A	C12A	C13A	48.7(17)
C10	C11	C12	C13	22.5(9)	C11A	O3A	C16A	O4A	1.7(6)
C11	O3	C16	O4	3.1(6)	C11A	O3A	C16A	C17A	-176.9(3)
C11	O3	C16	C17	-177.4(3)	C11A	C12B	C13B	C14B	2.8(15)
C11	C12	C13	C14	4.2(10)	C11A	C12A	C13A	C14A	8(2)
C12	C13	C14	C8	-1.9(9)	C12B	C11A	C10A	C9A	23.0(18)
C12	C13	C14	C15	-124.6(6)	C12B	C11A	C12A	C13A	-69(2)
C13	C14	C15	N1	159.2(4)	C12B	C13B	C14B	C8B	-26.4(14)
C14	C8	C9	C10	81.9(5)	C12B	C13B	C14B	C15A	-144.9(10)
C15	N1	C7	C8	-20.4(6)	C13B	C14B	C15A	N1A	166.0(6)
O1	S1	N1	C7	-48.0(4)	C13B	C14B	C15A	C14A	41(4)
O1	S1	N1	C15	172.6(4)	C14B	C8B	C9B	C10B	71.3(9)
O1	S1	C1	C2	-158.7(3)	C14B	C15A	C14A	C8A	79(4)
O1	S1	C1	C6	19.6(3)	C14B	C15A	C14A	C13A	-148(5)
O2	S1	N1	C7	-178.0(4)	C15A	N1A	C7A	C8B	34.4(6)
O2	S1	N1	C15	42.6(5)	C15A	N1A	C7A	C8A	38.3(8)
O2	S1	C1	C2	-29.1(3)	O1A	S1A	N1A	C7A	-178.2(3)
O2	S1	C1	C6	149.2(3)	O1A	S1A	N1A	C15A	-44.9(4)
O4	C16	C17	C18	175.3(4)	O1A	S1A	C1A	C2A	-151.8(2)
O4	C16	C17	C22	-7.3(6)	O1A	S1A	C1A	C6A	28.1(3)
N2	C20	C21	C22	175.0(4)	O2A	S1A	N1A	C7A	51.1(4)
C1	S1	N1	C7	66.4(4)	O2A	S1A	N1A	C15A	-175.6(3)
C1	S1	N1	C15	-73.0(4)	O2A	S1A	C1A	C2A	-21.3(3)
C1	C2	C3	C4	0.0	O2A	S1A	C1A	C6A	158.6(2)
C2	C1	C6	C5	0.0	O4A	C16A	C17A	C18A	169.6(4)
C2	C3	C4	Br1	178.8(3)	O4A	C16A	C17A	C22A	-7.8(5)
C2	C3	C4	C5	0.0	N2A	C20A	C21A	C22A	-176.7(4)
C3	C4	C5	C6	0.0	C1A	S1A	N1A	C7A	-63.1(4)
C4	C5	C6	C1	0.0	C1A	S1A	N1A	C15A	70.2(4)
C6	C1	C2	C3	0.0	C1A	C2A	C3A	C4A	0.0
C16	O3	C11	C10	-122.0(5)	C2A	C1A	C6A	C5A	0.0
C16	O3	C11	C12	66.4(5)	C2A	C3A	C4A	Br1A	-179.7(3)

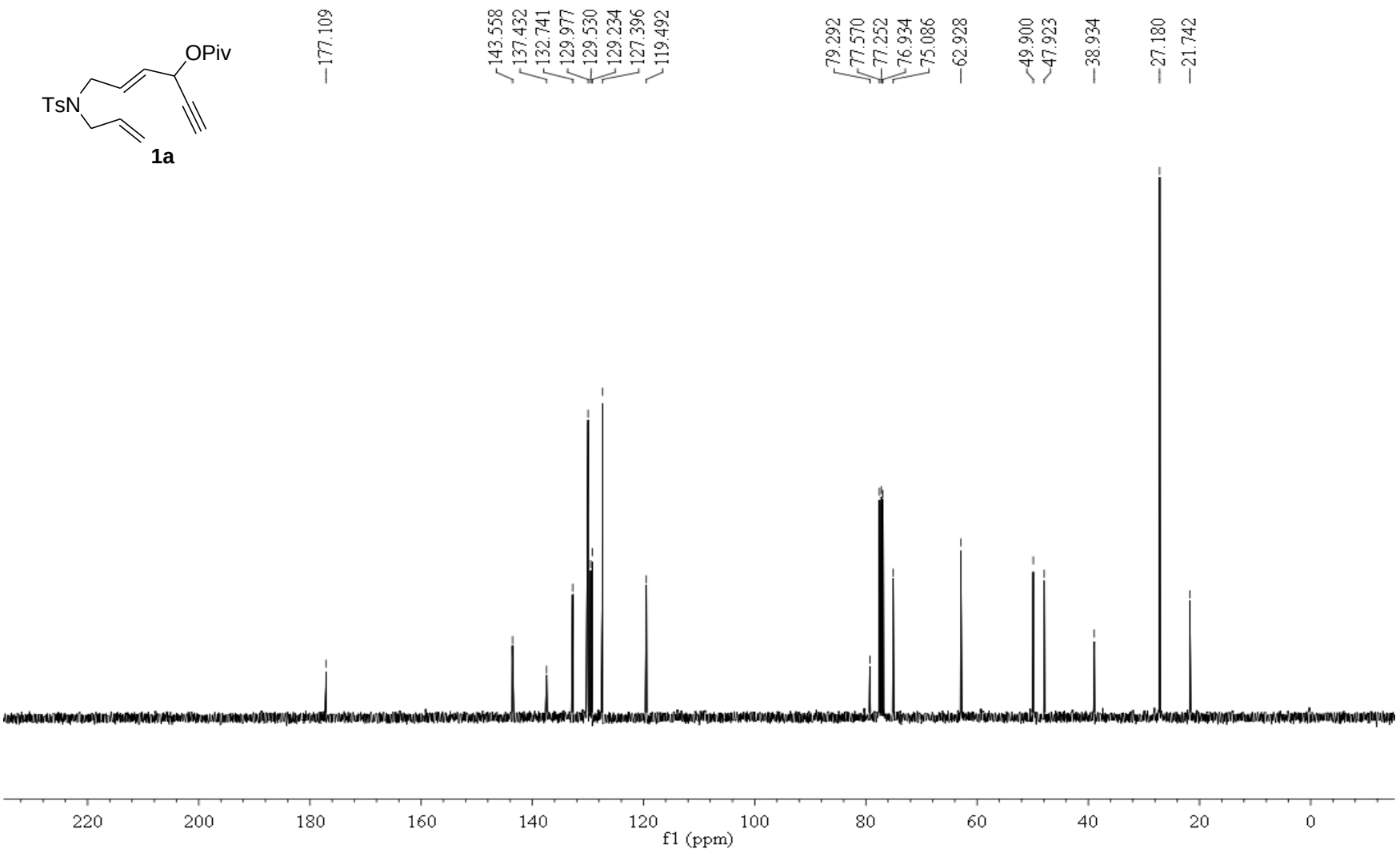
C16	C17	C18	C19	177.4(3)	C2A	C3A	C4A	C5A	0.0
C16	C17	C22	C21	-177.5(3)	C3A	C4A	C5A	C6A	0.0
C17	C18	C19	C20	0.0	C4A	C5A	C6A	C1A	0.0
C18	C17	C22	C21	0.0	C6A	C1A	C2A	C3A	0.0
C18	C19	C20	N2	-175.1(4)	C8A	C7A	C8B	C9B	162(9)
C18	C19	C20	C21	0.0	C8A	C7A	C8B	C14B	-72(8)
C19	C20	C21	C22	0.0	C8A	C9A	C10A	C11A	-71.4(16)
C20	C21	C22	C17	0.0	C9A	C8A	C14A	C15A	122.1(12)
C22	C17	C18	C19	0.0	C9A	C8A	C14A	C13A	-4.7(17)
C23	N2	C20	C19	-13.8(6)	C10A	C11A	C12B	C13B	14.8(15)
C23	N2	C20	C21	171.2(4)	C10A	C11A	C12A	C13A	32(2)
C24	N2	C20	C19	178.9(4)	C12A	C11A	C12B	C13B	108(3)
C24	N2	C20	C21	3.8(6)	C12A	C11A	C10A	C9A	3.0(18)
Br1A	C4A	C5A	C6A	179.7(3)	C12A	C13A	C14A	C15A	-163.1(16)
S1A	N1A	C7A	C8B	173.2(5)	C12A	C13A	C14A	C8A	-39(2)
S1A	N1A	C7A	C8A	177.1(7)	C14A	C8A	C9A	C10A	67.9(14)
S1A	N1A	C15A	C14B	176.7(4)	C16A	O3A	C11A	C10B	79.0(7)
S1A	N1A	C15A	C14A	-176.0(7)	C16A	O3A	C11A	C12B	-96.1(6)
S1A	C1A	C2A	C3A	179.9(2)	C16A	O3A	C11A	C10A	96.8(10)
S1A	C1A	C6A	C5A	-179.9(2)	C16A	O3A	C11A	C12A	-79.7(10)
O3A	C11A	C12B	C13B	-149.8(7)	C16A	C17A	C18A	C19A	-177.4(3)
O3A	C11A	C10A	C9A	-172.8(9)	C16A	C17A	C22A	C21A	177.5(3)
O3A	C11A	C12A	C13A	-152.6(12)	C17A	C18A	C19A	C20A	0.0
O3A	C16A	C17A	C18A	-11.7(4)	C18A	C17A	C22A	C21A	0.0
O3A	C16A	C17A	C22A	170.8(3)	C18A	C19A	C20A	N2A	176.7(4)
N1A	S1A	C1A	C2A	93.3(2)	C18A	C19A	C20A	C21A	0.0
N1A	S1A	C1A	C6A	-86.8(2)	C19A	C20A	C21A	C22A	0.0
N1A	C7A	C8B	C9B	-134.6(6)	C20A	C21A	C22A	C17A	0.0
N1A	C7A	C8B	C14B	-7.7(8)	C22A	C17A	C18A	C19A	0.0
N1A	C7A	C8A	C9A	-145.5(10)	C23A	N2A	C20A	C19A	-6.0(6)
N1A	C7A	C8A	C14A	-22.9(12)	C23A	N2A	C20A	C21A	170.7(4)
N1A	C15A	C14A	C8A	22.1(12)	C24A	N2A	C20A	C19A	167.1(5)
N1A	C15A	C14A	C13A	155.4(10)	C24A	N2A	C20A	C21A	-16.2(7)

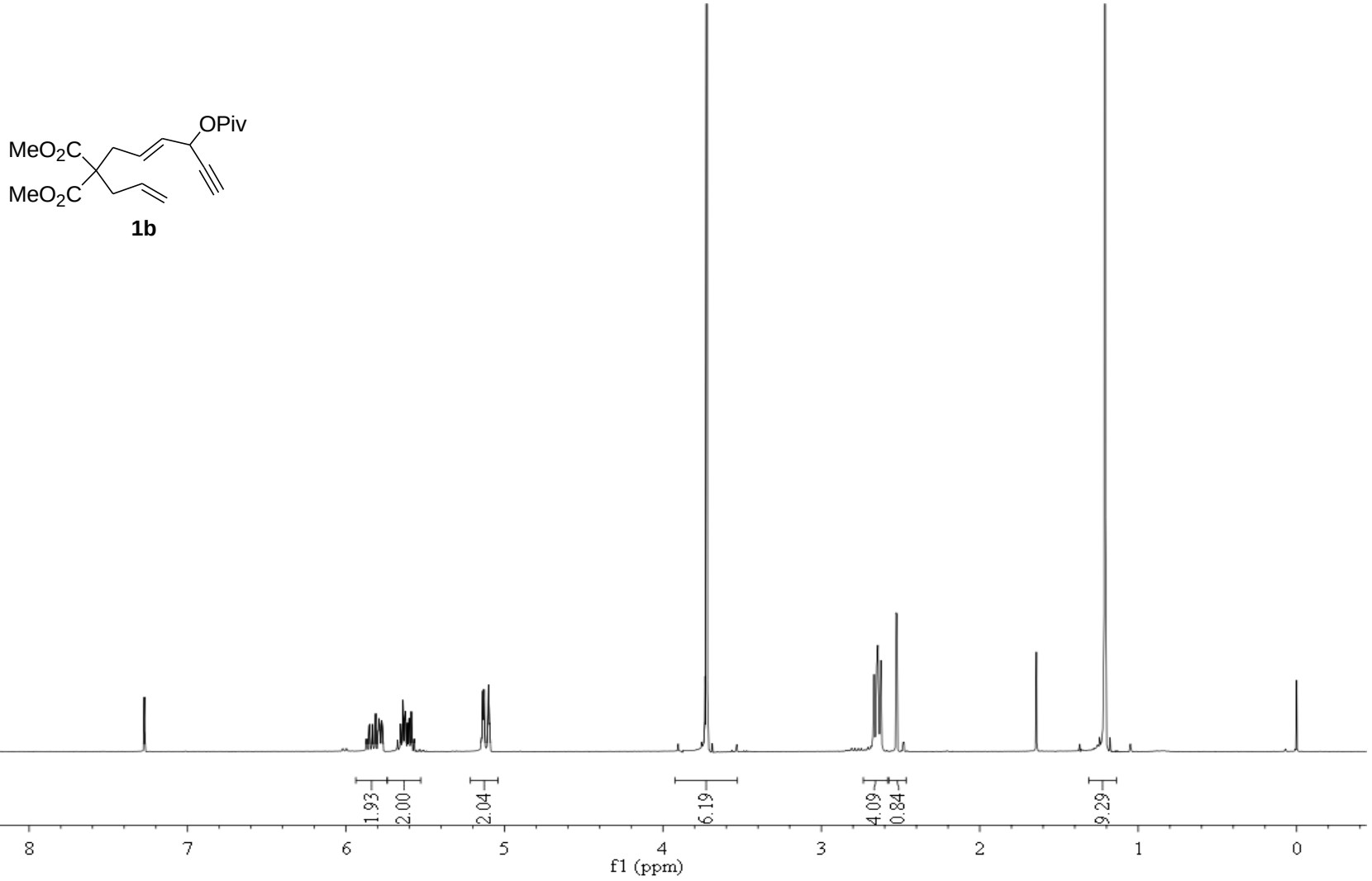
Table 7 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2n**.

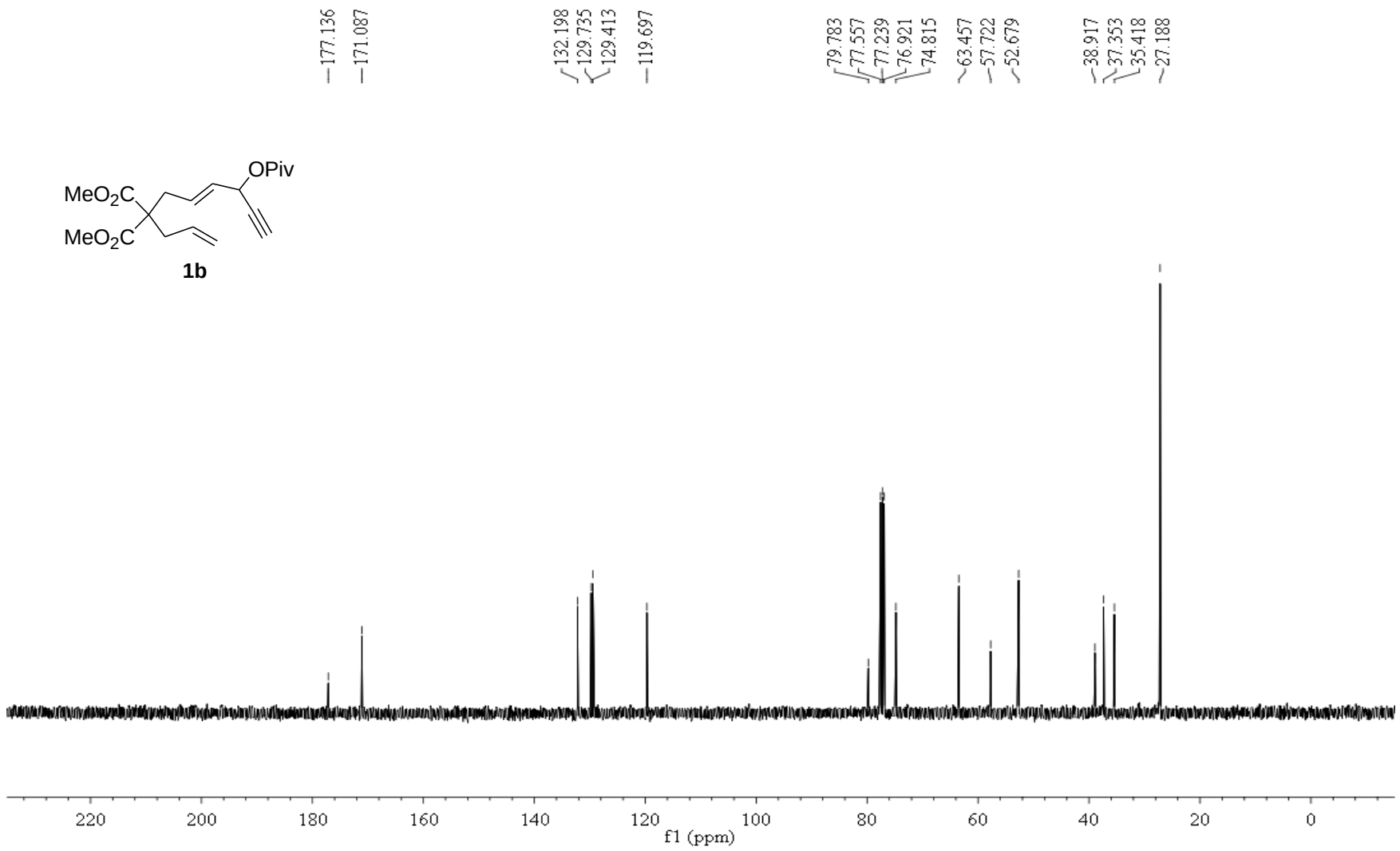
Atom	*x*	*y*	*z*	U(eq)
H7A	5599	6734	6888	42
H7B	4912	6831	6400	42
H8	4757	5637	6461	32
H9A	5491	5670	7256	36
H9B	3840	5687	7327	36
H10	5286	4484	7196	35
H12	1264	4363	6716	32
H13	784	5425	6521	33
H14	2607	6092	6243	32
H15E	1436	6851	6646	34
H15F	1872	6454	7097	34
H2	1003	7935	6225	42
H3	583	8176	5483	51
H5	4778	8410	5371	70
H6	5198	8169	6112	52
H18	3675	2499	7261	26
H19	3553	1277	7326	26
H21	2803	1110	6021	34
H22	2925	2331	5956	32
H23D	4360	125	7224	50
H23E	3245	-485	7105	50
H23F	2771	199	7359	50
H24D	1939	120	6161	63
H24E	2392	-556	6445	63
H24F	3544	-139	6191	63
H7AC	4808	2348	8606	28
H7AD	3700	2287	8189	28
H7AA	4848	2379	8607	28
H7AB	3700	2269	8204	28
H8B	4138	3352	7974	35
H9BA	4120	3533	8744	35
H9BB	5803	3547	8766	35
H10B	4134	4695	8564	35
H12B	8076	4690	8181	35
H13B	8300	3623	7968	35
H14B	6026	3179	7612	30(20)

H15C	7649	2312	7839	29
H15D	7507	2487	8348	29
H15A	7589	2339	7817	29
H15B	7569	2426	8336	29
H2A	4439	996	8908	35
H3A	5182	856	9642	44
H5A	9249	1033	9340	35
H6A	8506	1173	8606	32
H8A	4224	3295	7890	35
H9AA	3731	3605	8622	35
H9AB	5389	3620	8749	35
H10A	3880	4726	8342	35
H12A	8146	4689	8361	35
H13A	8404	3565	8226	35
H14A	6332	3297	7675	35
H18A	5867	6580	7800	24
H19A	5801	7794	7684	24
H21A	6506	8120	8979	38
H22A	6572	6906	9095	33
H23A	6836	8824	7650	46
H23B	6412	9574	7835	46
H23C	5211	9026	7676	46
H24A	5316	9116	8792	80
H24B	5892	9740	8505	80
H24C	6973	9263	8795	80

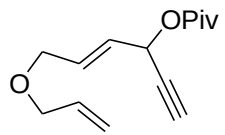

OPiv
TsN
1a
1.88
1.93
1.82
1.93
1.95
1.96
1.95
0.82
3.00
8.77
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


OPiv
TsN
1a
177.109
143.558
137.432
132.741
129.977
129.530
129.234
127.396
119.492
79.292
77.570
77.252
76.934
75.086
62.928
49.900
47.923
38.934
27.180
21.742
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

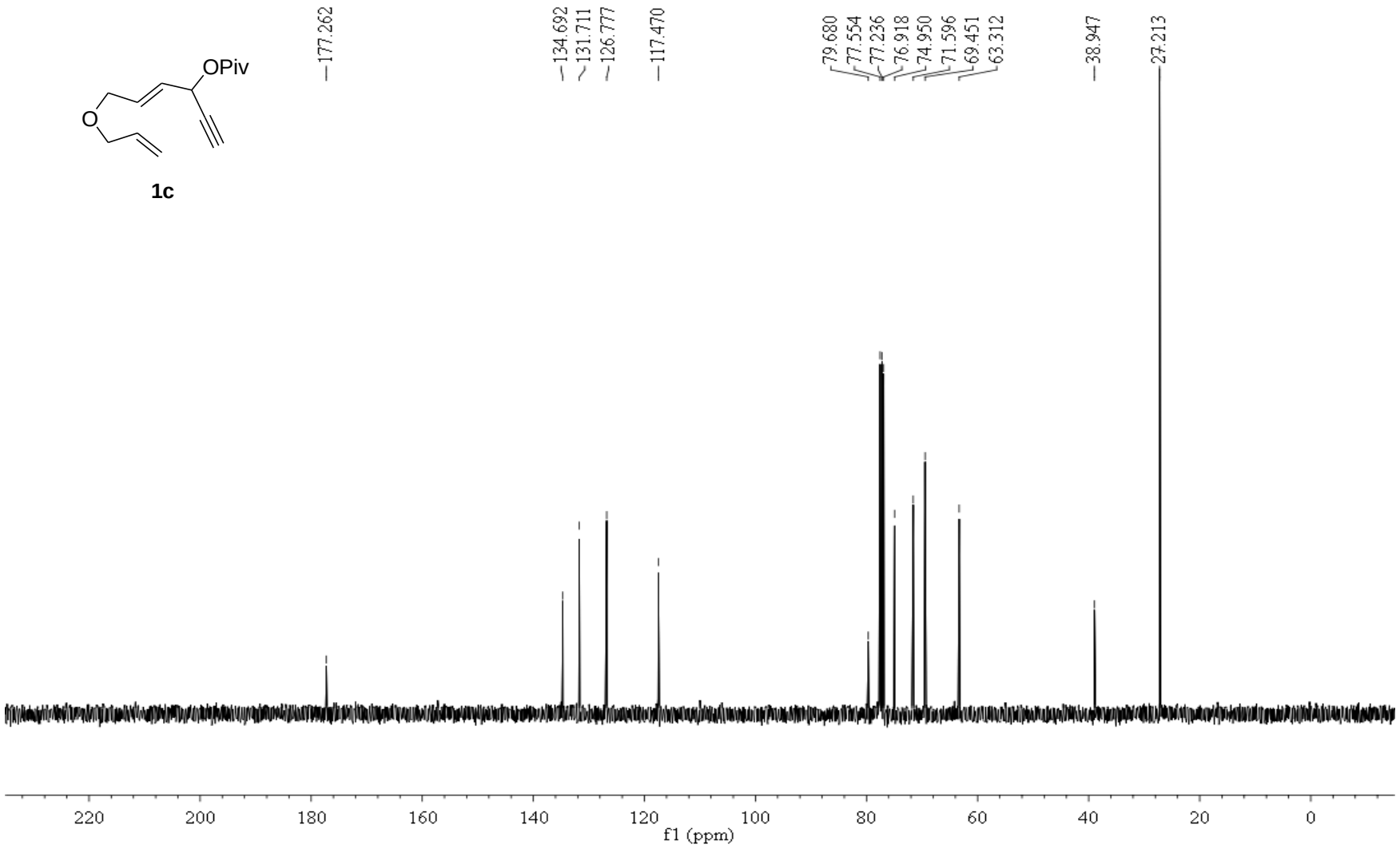

OPiv
MeO2C
MeO2C
1b
1.93
2.00
2.04
6.19
4.09
0.84
9.29
8
7
6
5
4
3
2
1
0
f1 (ppm)

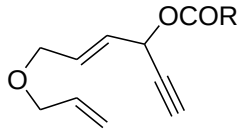

177.136
171.087
132.198
129.735
129.413
119.697
79.783
77.557
77.239
76.921
74.815
63.457
57.722
52.679
38.917
37.353
35.418
27.188
OPiv
MeO2C
MeO2C
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1b

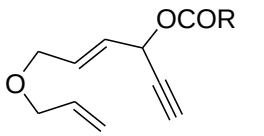


1c

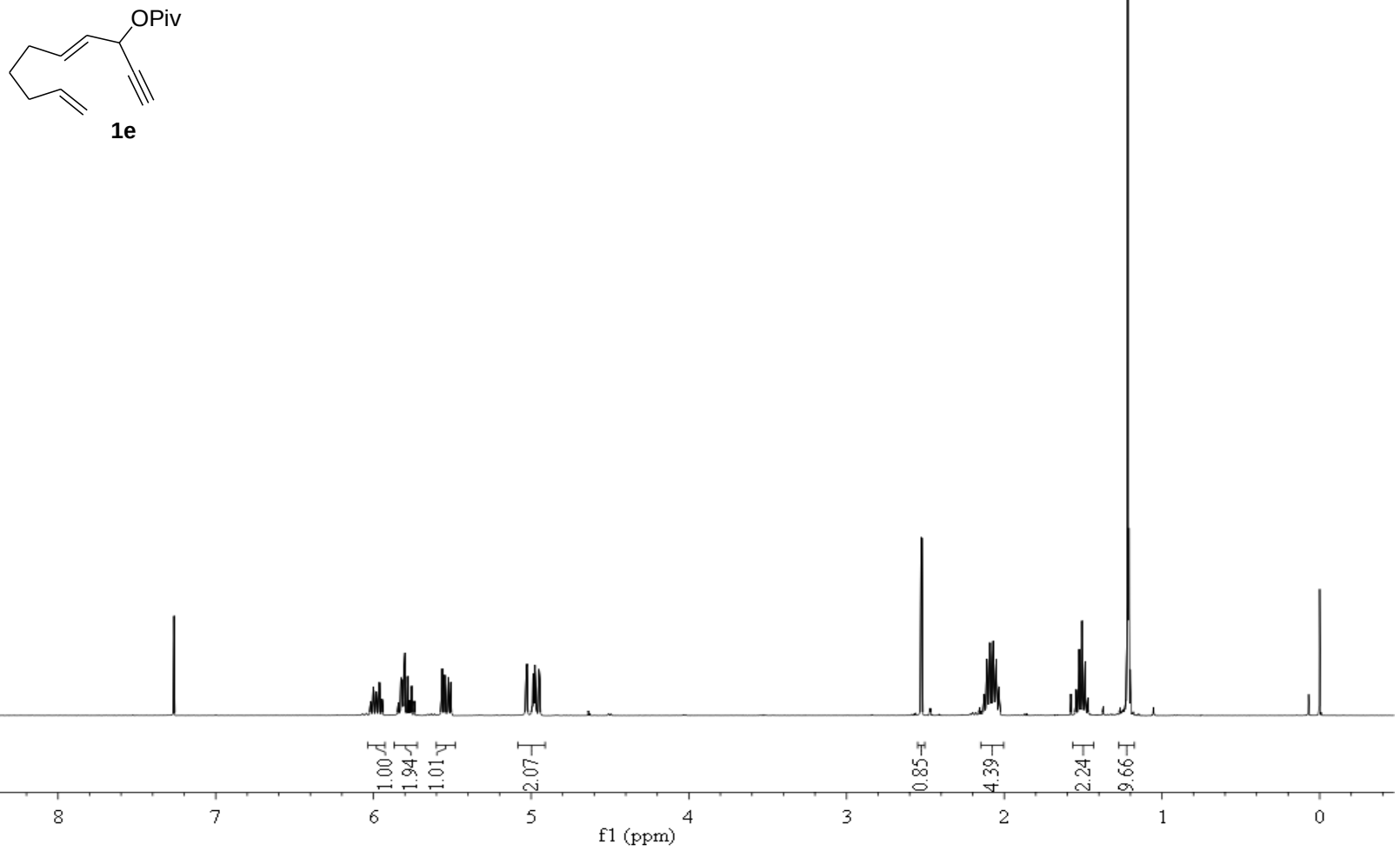

OPiv
O
1c
177.262
134.692
131.711
126.777
117.470
79.680
77.554
77.236
76.918
74.950
71.596
69.451
63.312
38.947
27.213
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

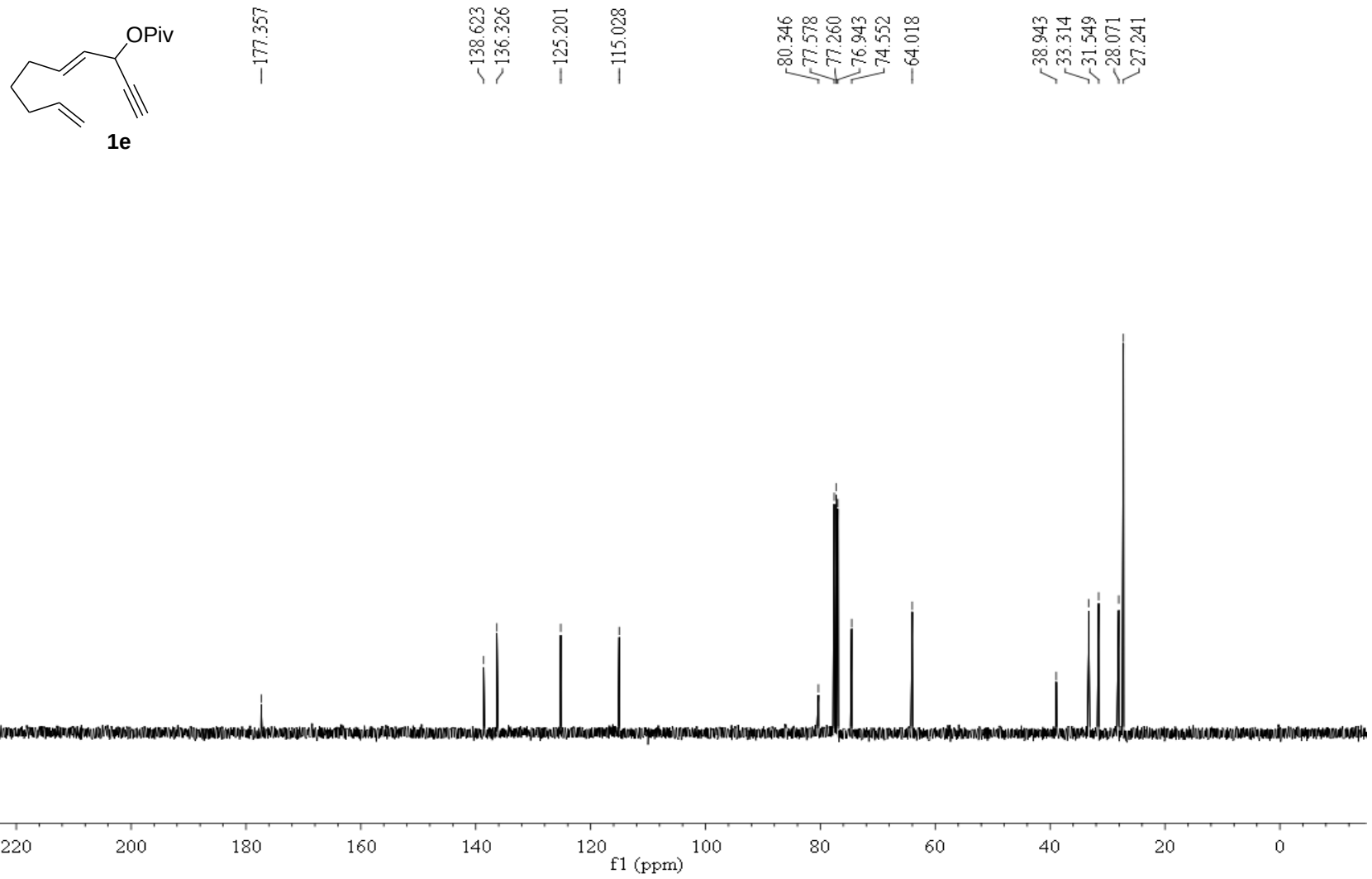


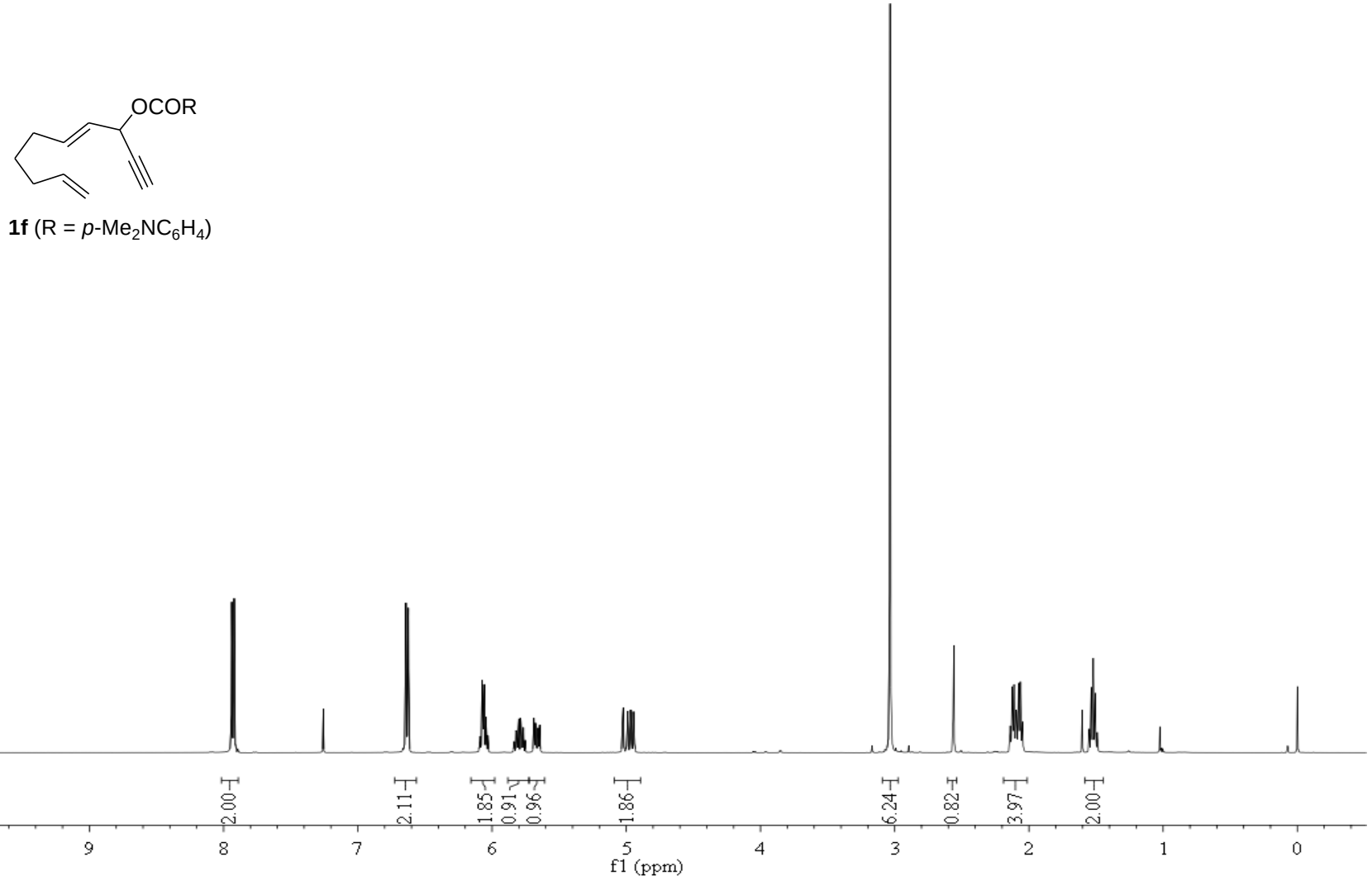
1d (R = *p*-$Me_2NC_6H_4$)



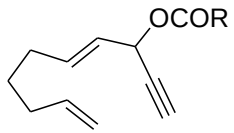
1d (R = *p*-$Me_2NC_6H_4$)


OPiv
1e
1.00
1.94
1.01
2.07
0.85
4.39
2.24
9.66
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

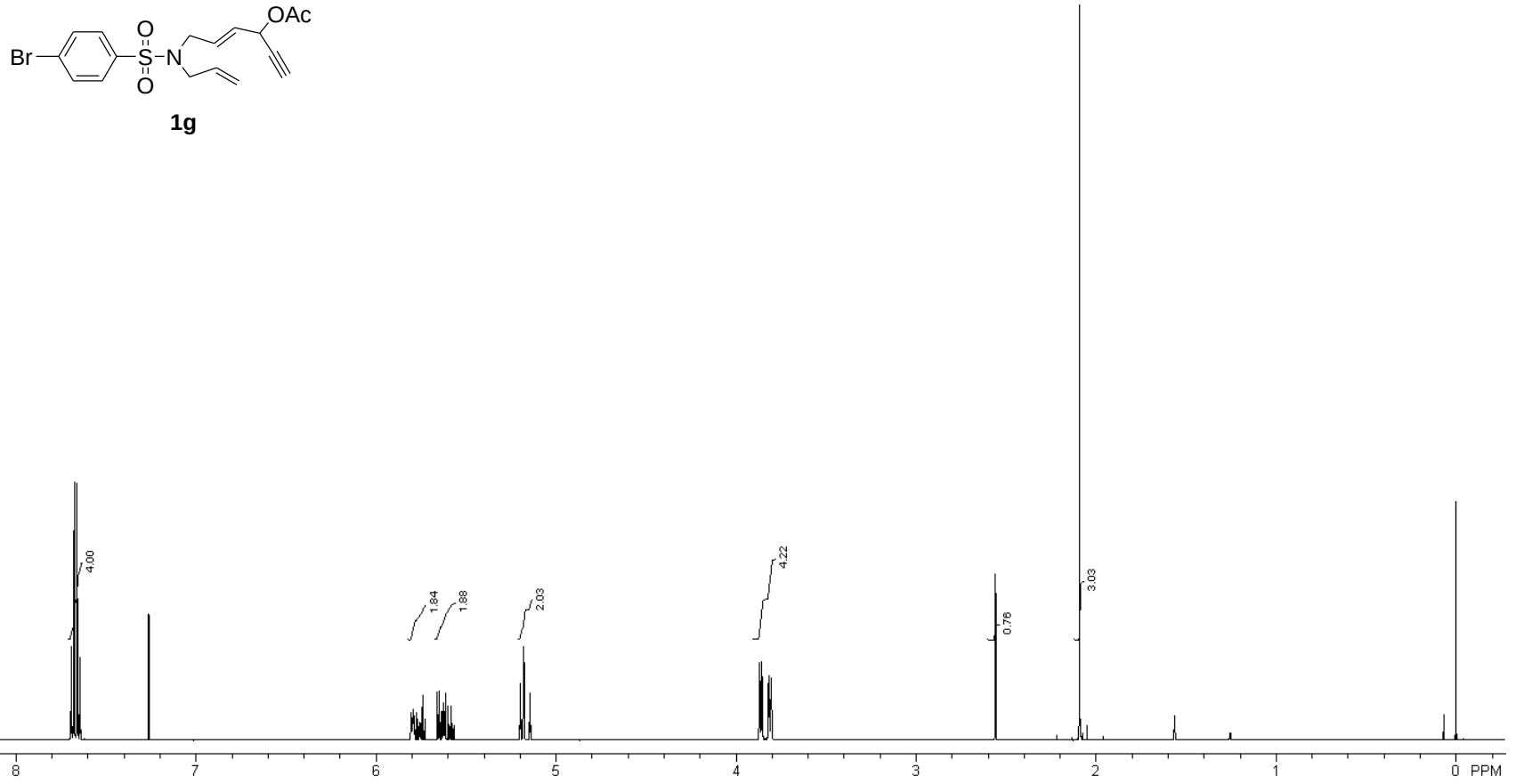

OPiv
1e
177.357
138.623
136.326
125.201
115.028
80.346
77.578
77.260
76.943
74.552
64.018
38.943
33.314
31.549
28.071
27.241
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



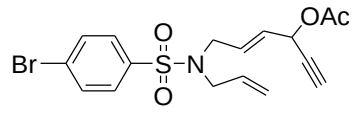
1f (R = *p*-$Me_2NC_6H_4$)



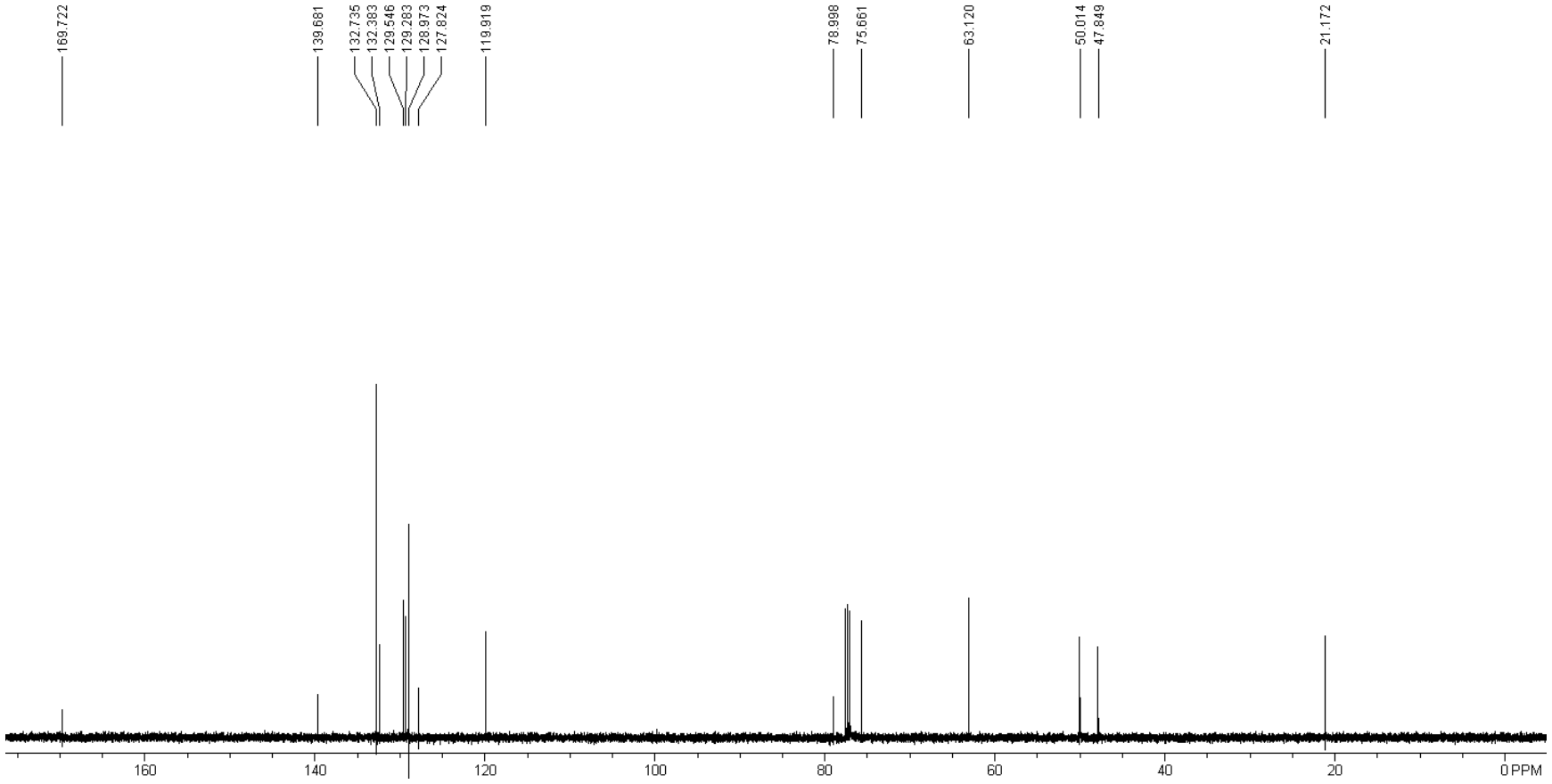
1f (R = *p*-$Me_2NC_6H_4$)

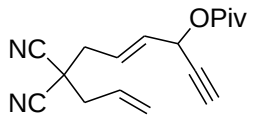


1g

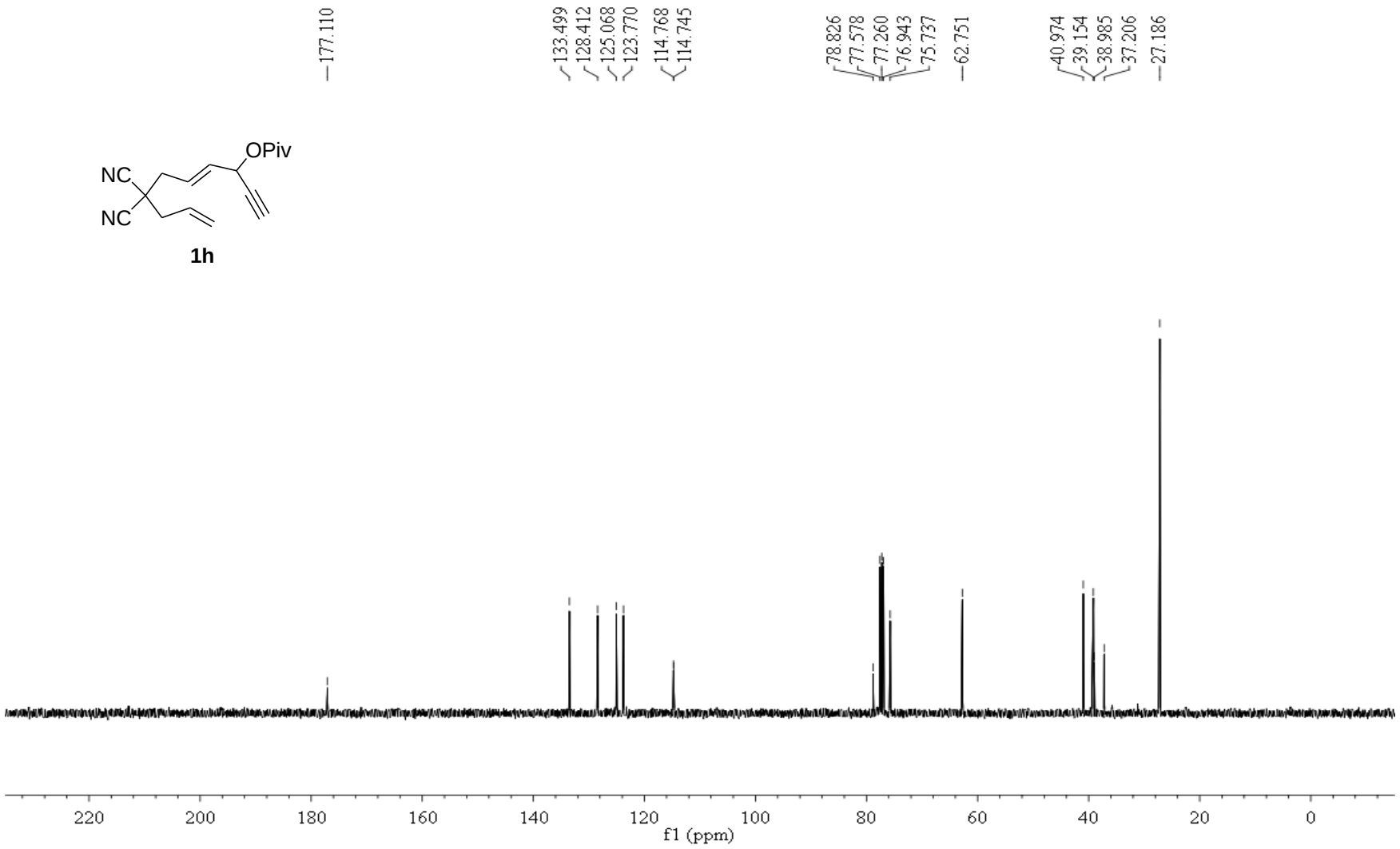

Br
O
S
N
O
OAc

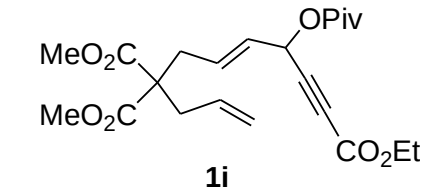
1g


169.722
139.681
132.735
132.383
129.546
129.283
128.973
127.824
119.919
78.998
75.661
63.120
50.014
47.849
21.172
160
140
120
100
80
60
40
20
0 PPM

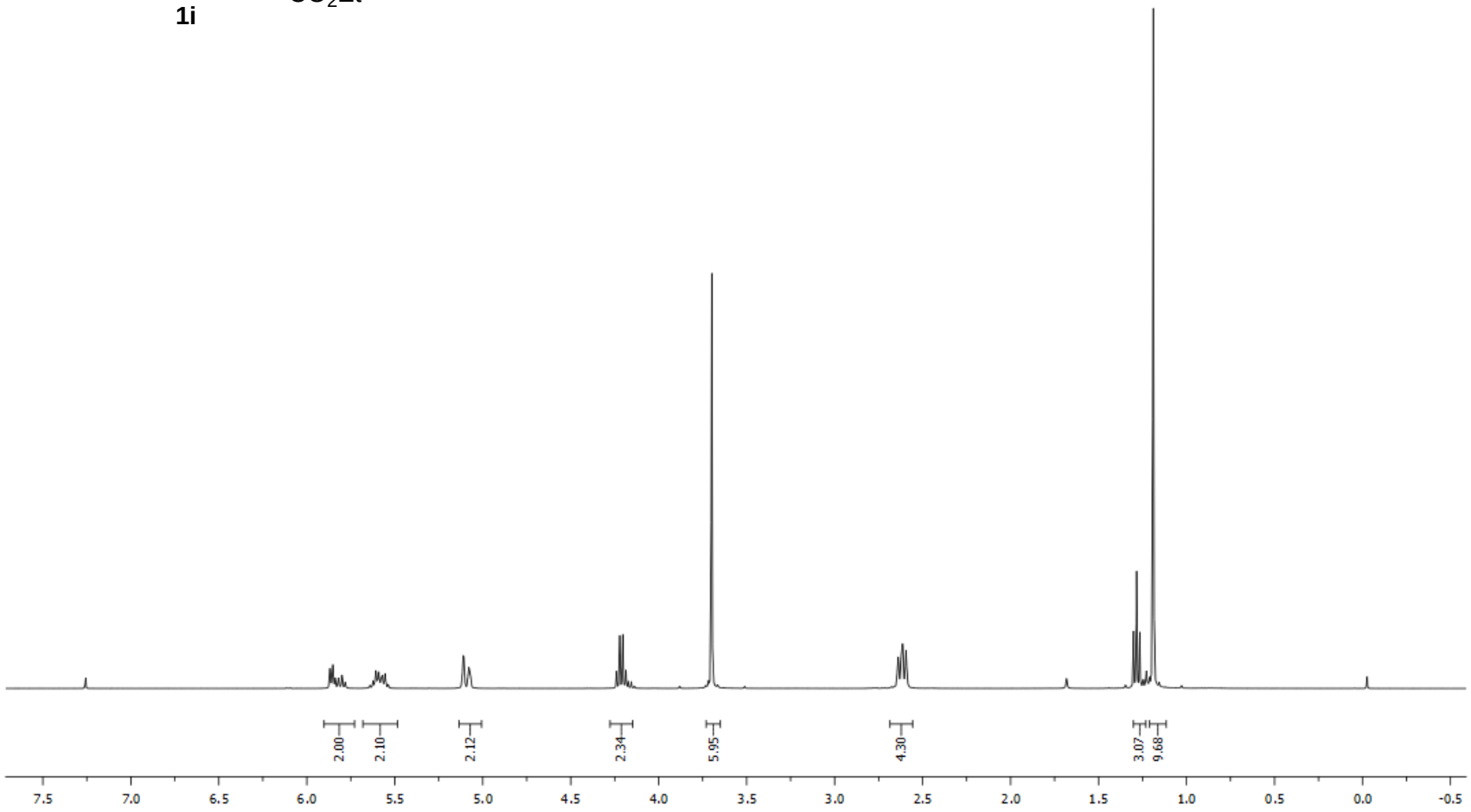


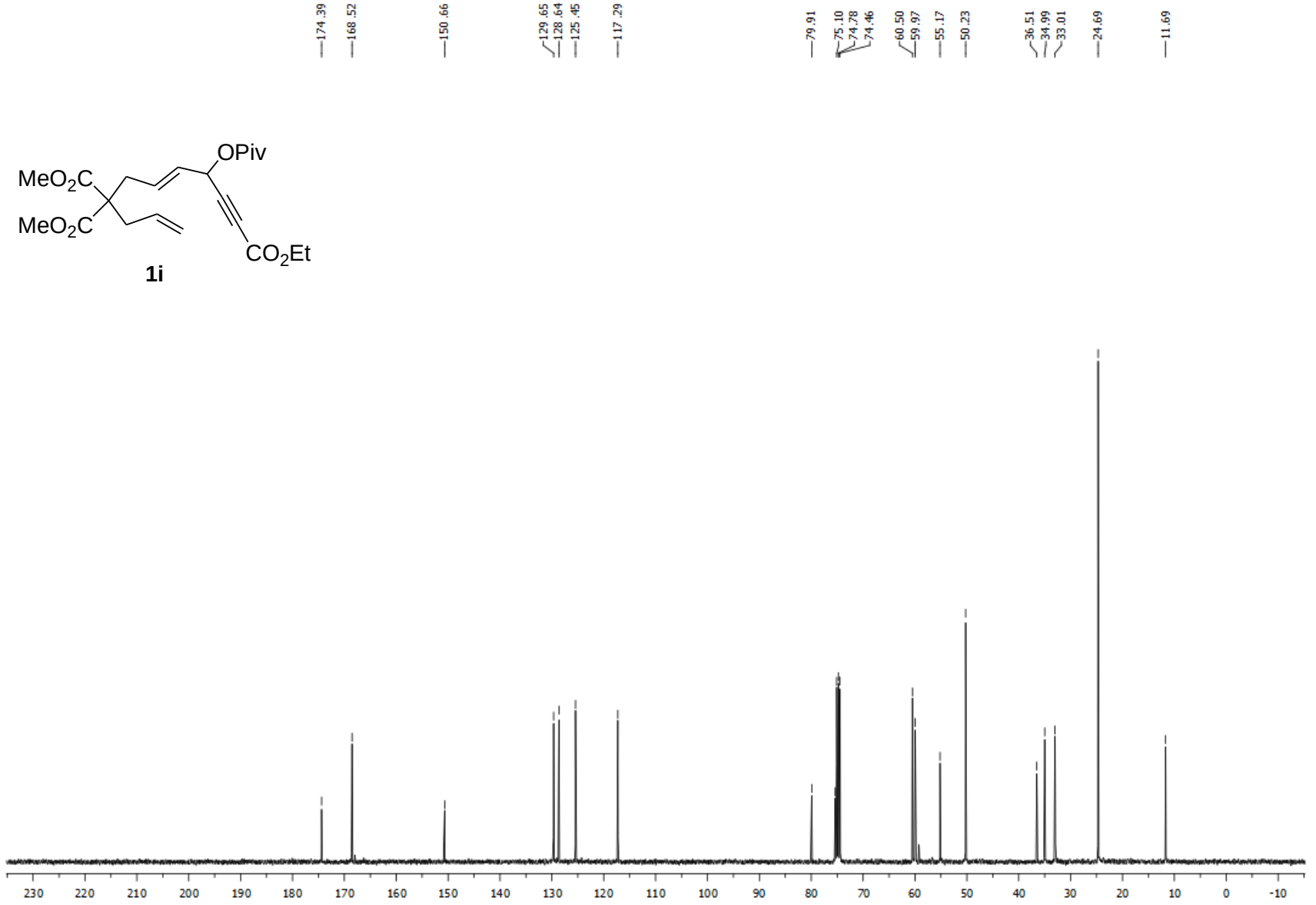
1h

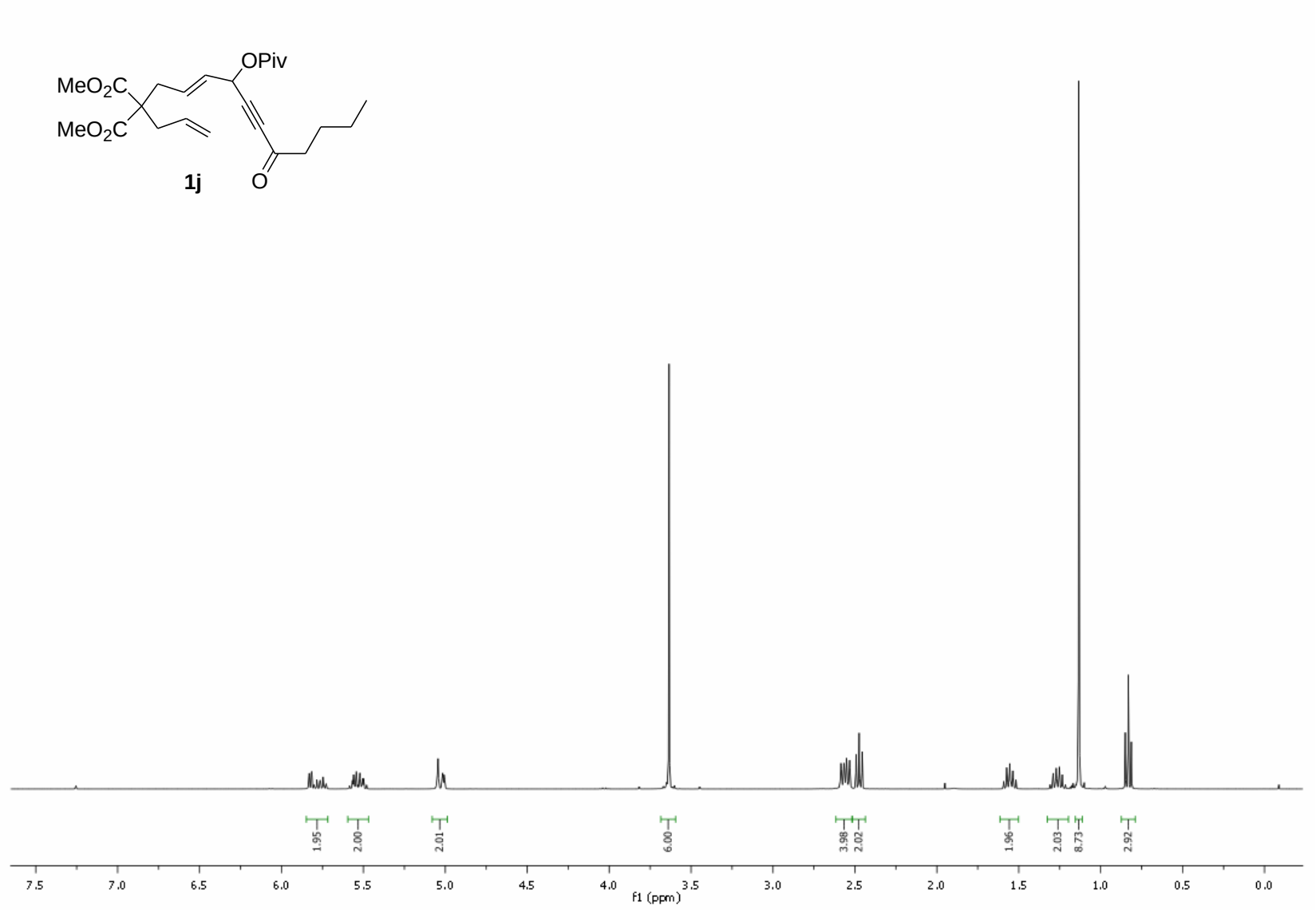

177.110
133.499
128.412
125.068
123.770
114.768
114.745
78.826
77.578
77.260
76.943
75.737
62.751
40.974
39.154
38.985
37.206
27.186
OPiv
NC
NC
1h
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

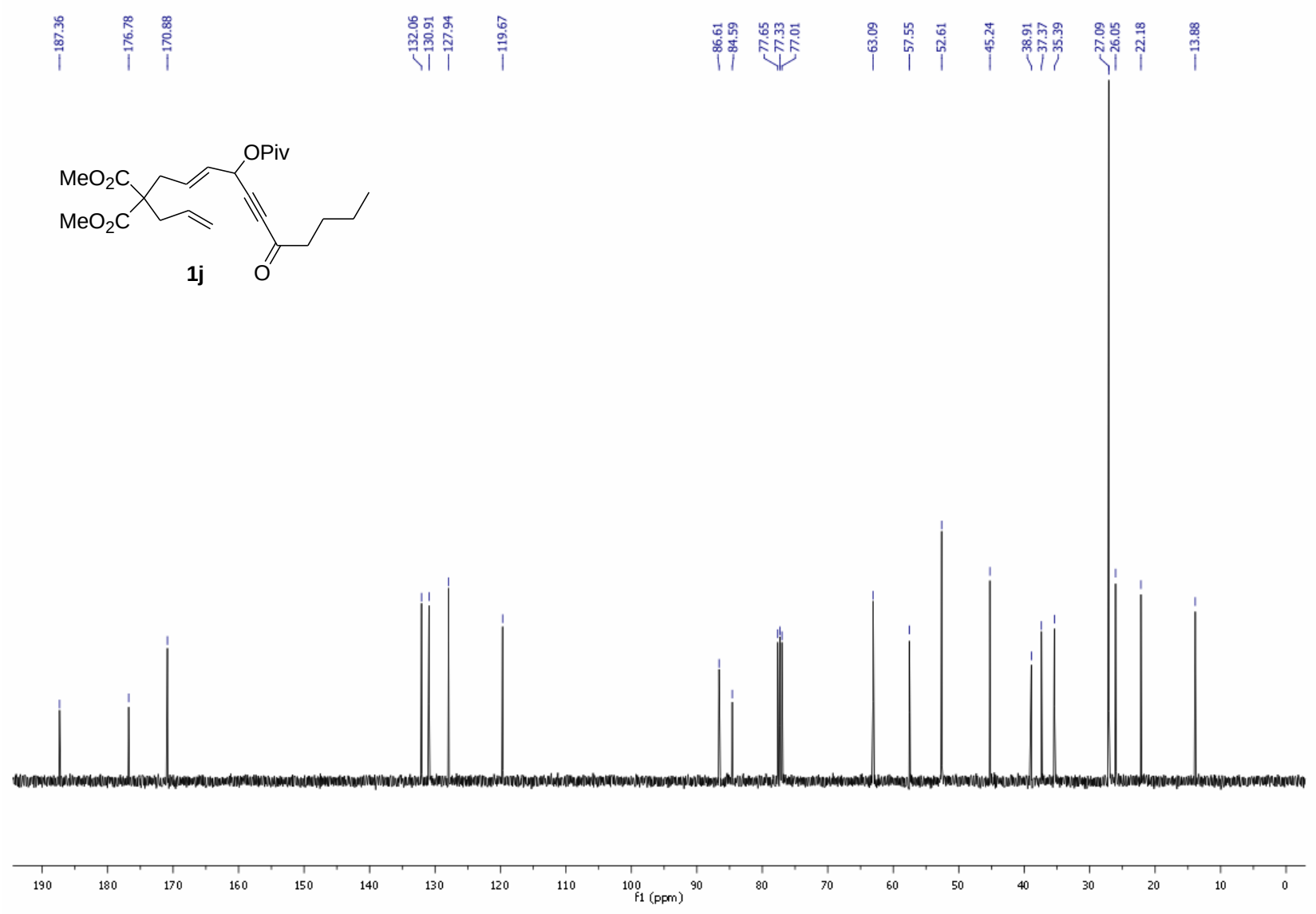

OPiv
MeO2C
MeO2C
CO2Et

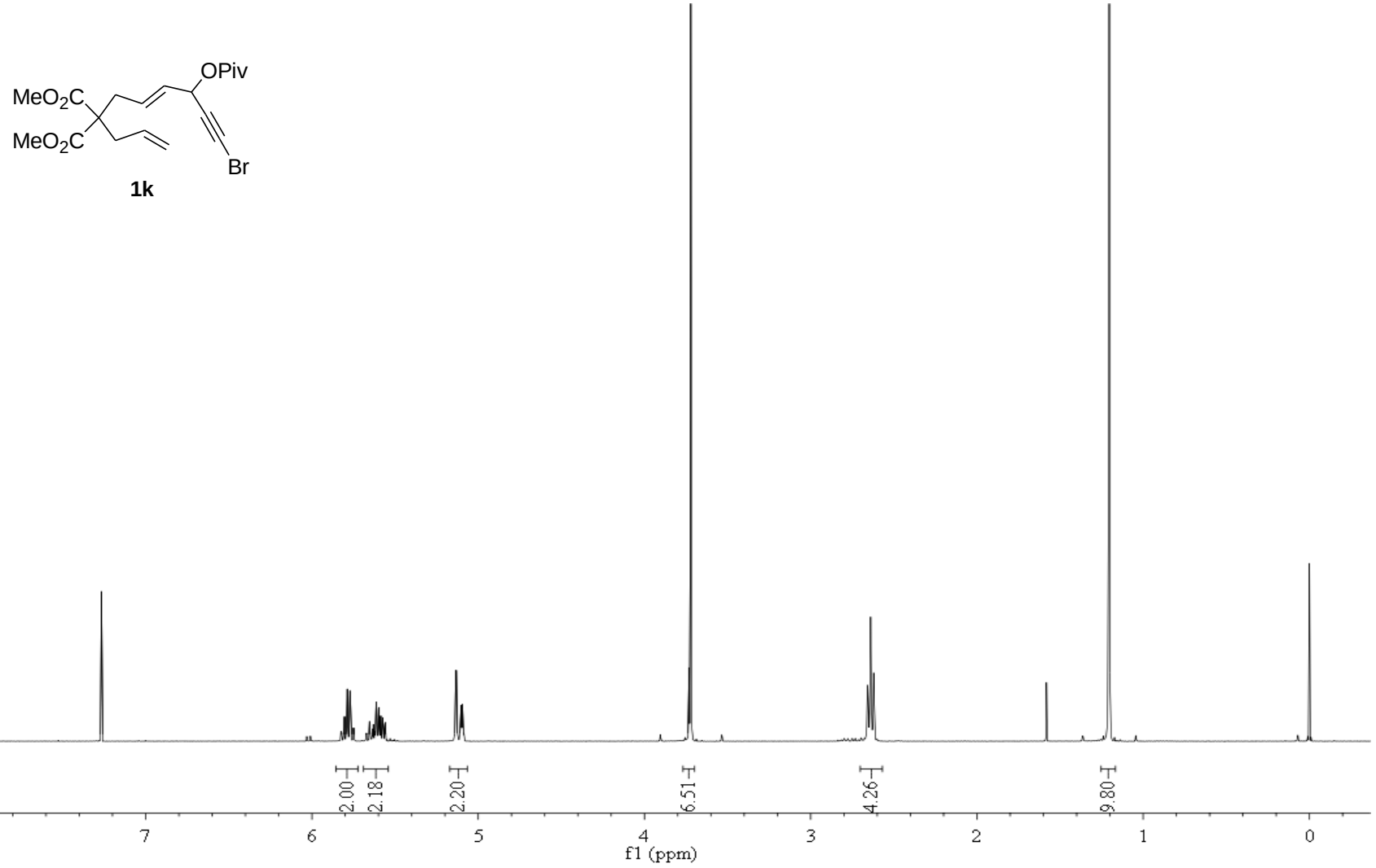
1i


2.00
2.10
2.12
2.34
5.95
4.30
3.07
9.68
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

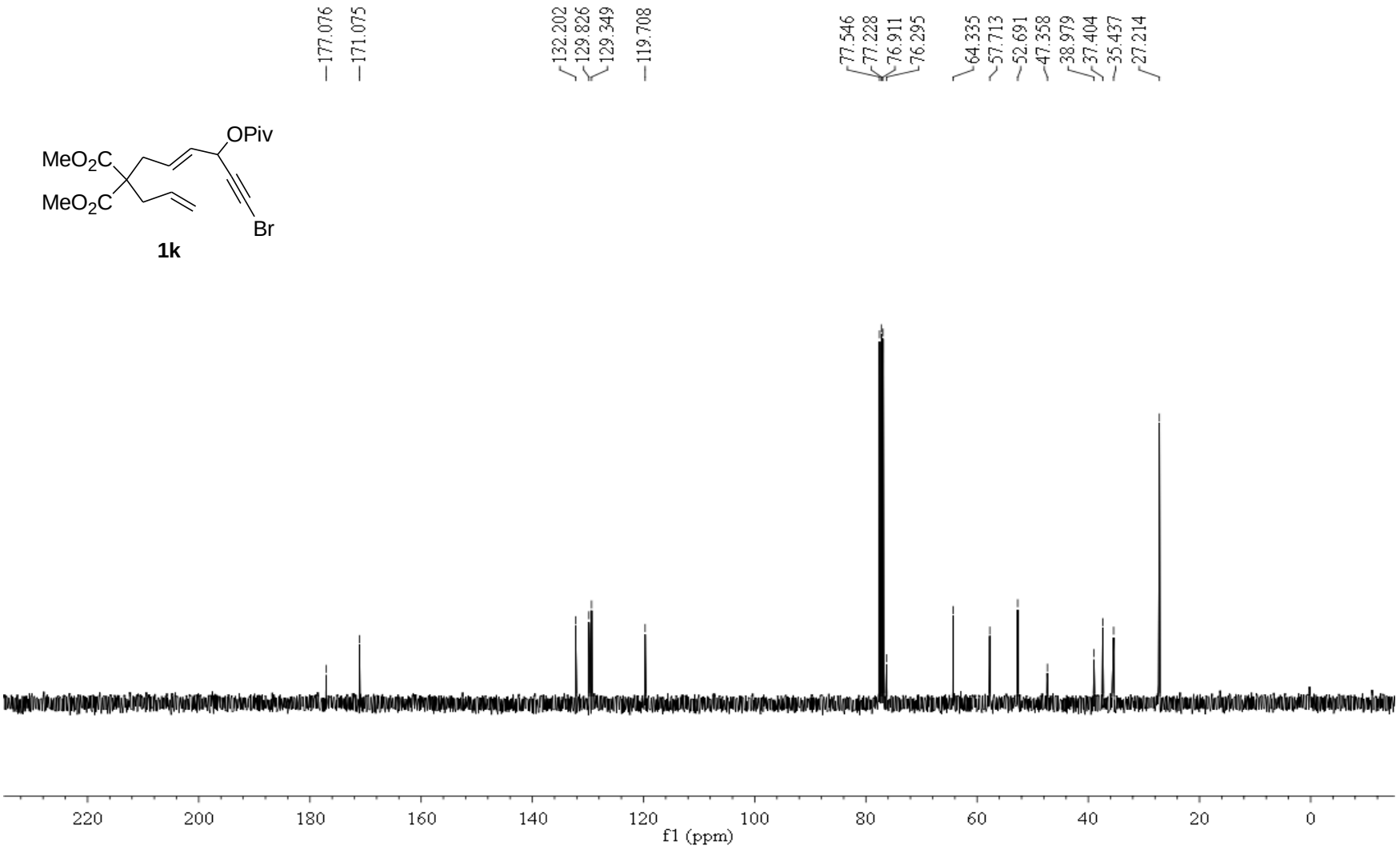

174.39
168.52
150.66
129.65
128.64
125.45
117.29
79.91
75.10
74.78
74.46
60.50
59.97
55.17
50.23
36.51
34.99
33.01
24.69
11.69
OPiv
MeO2C
MeO2C
CO2Et
1i
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

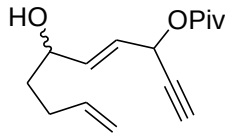

OPiv
MeO2C
MeO2C
O
1j
1.95
2.00
2.01
6.00
3.98
2.02
1.96
2.03
8.73
2.92
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


187.36
176.78
170.88
132.06
130.91
127.94
119.67
86.61
84.59
77.65
77.33
77.01
63.09
57.55
52.61
45.24
38.91
37.37
35.39
27.09
26.05
22.18
13.88
OPiv
MeO2C
MeO2C
O
1j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

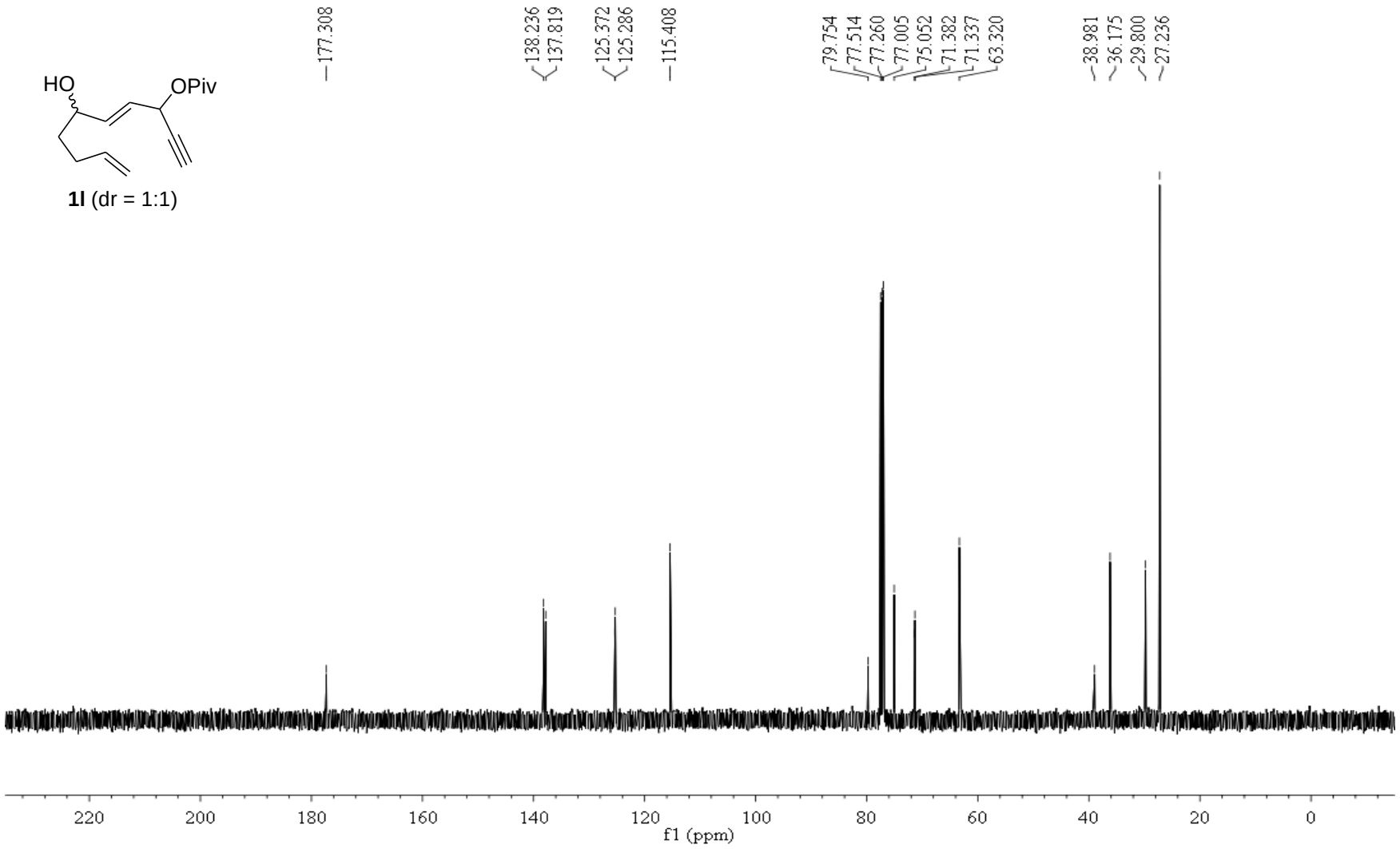


1k

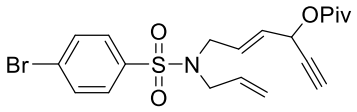

177.076
171.075
132.202
129.826
129.349
119.708
77.546
77.228
76.911
76.295
64.335
57.713
52.691
47.358
38.979
37.404
35.437
27.214
OPiv
MeO2C
MeO2C
Br
1k
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



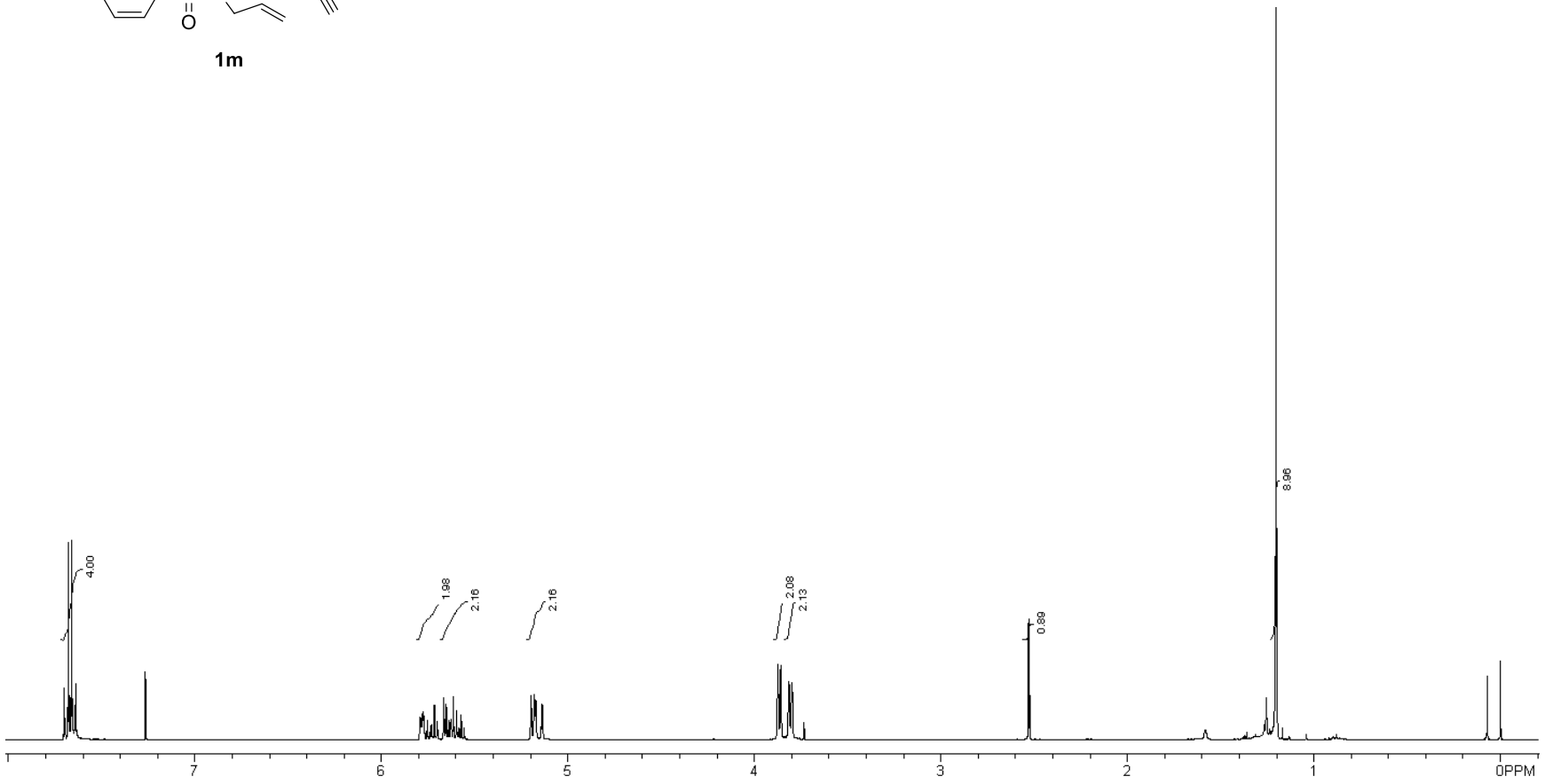
1l (dr = 1:1)

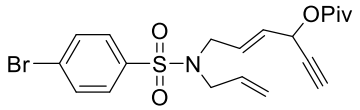

HO
OPiv
177.308
138.236
137.819
125.372
125.286
115.408
79.754
77.514
77.260
77.005
75.052
71.382
71.337
63.320
38.981
36.175
29.800
27.236
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1l (dr = 1:1)

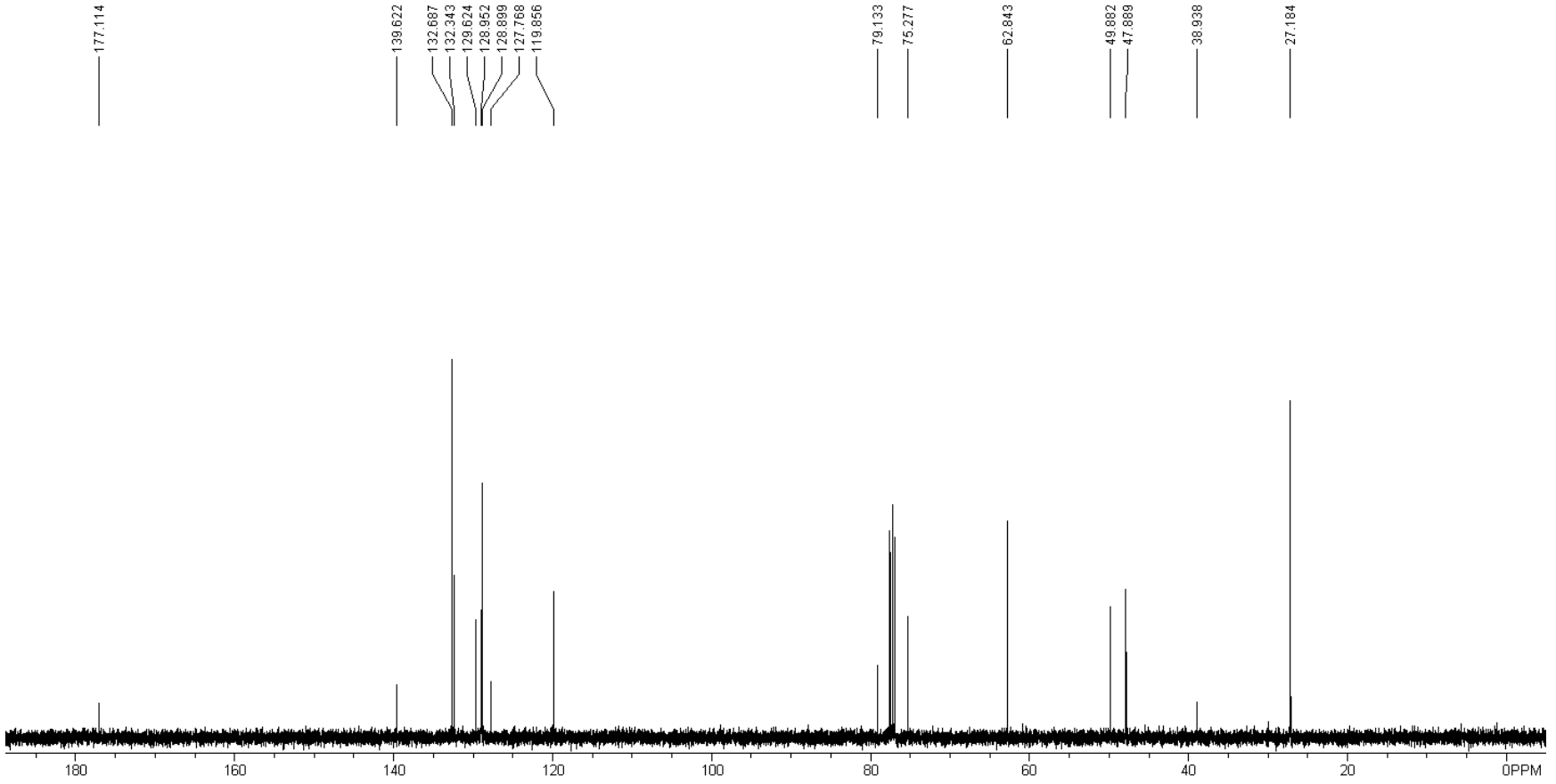


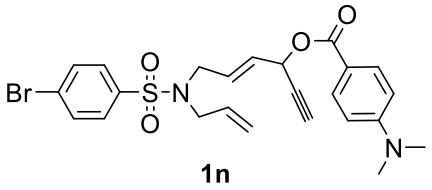
1m



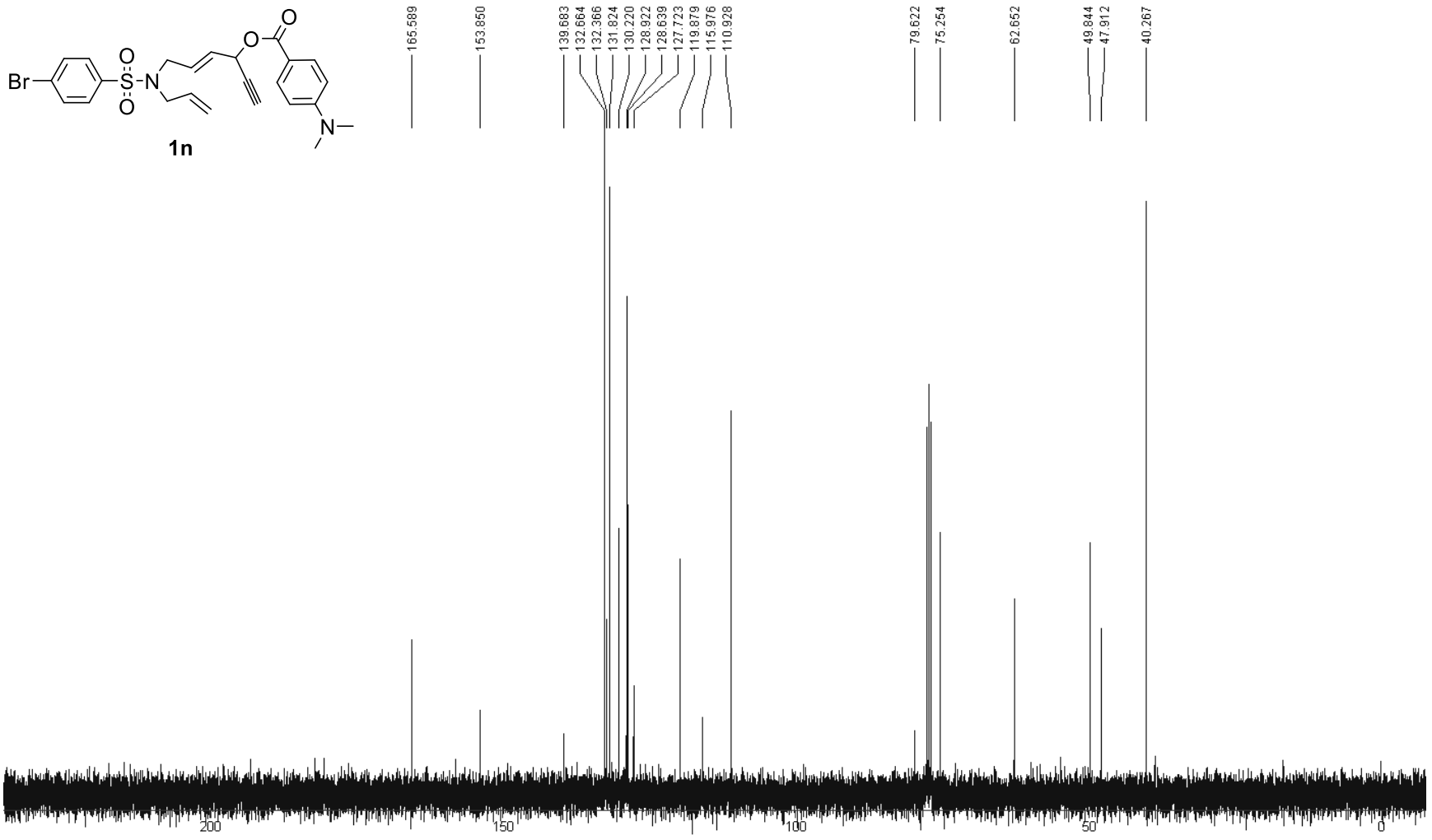

OPiv
Br
O
S
N
O

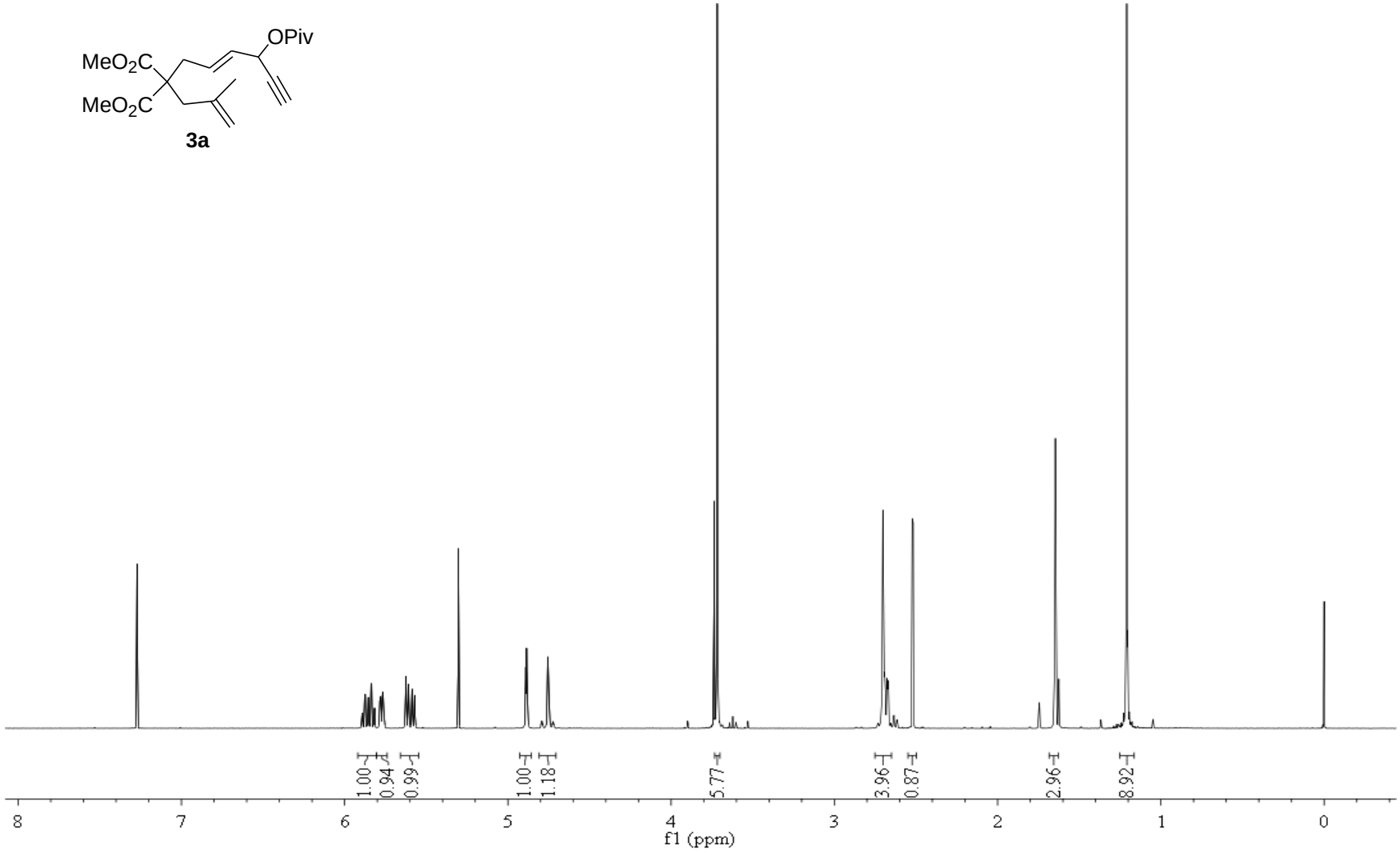
1m

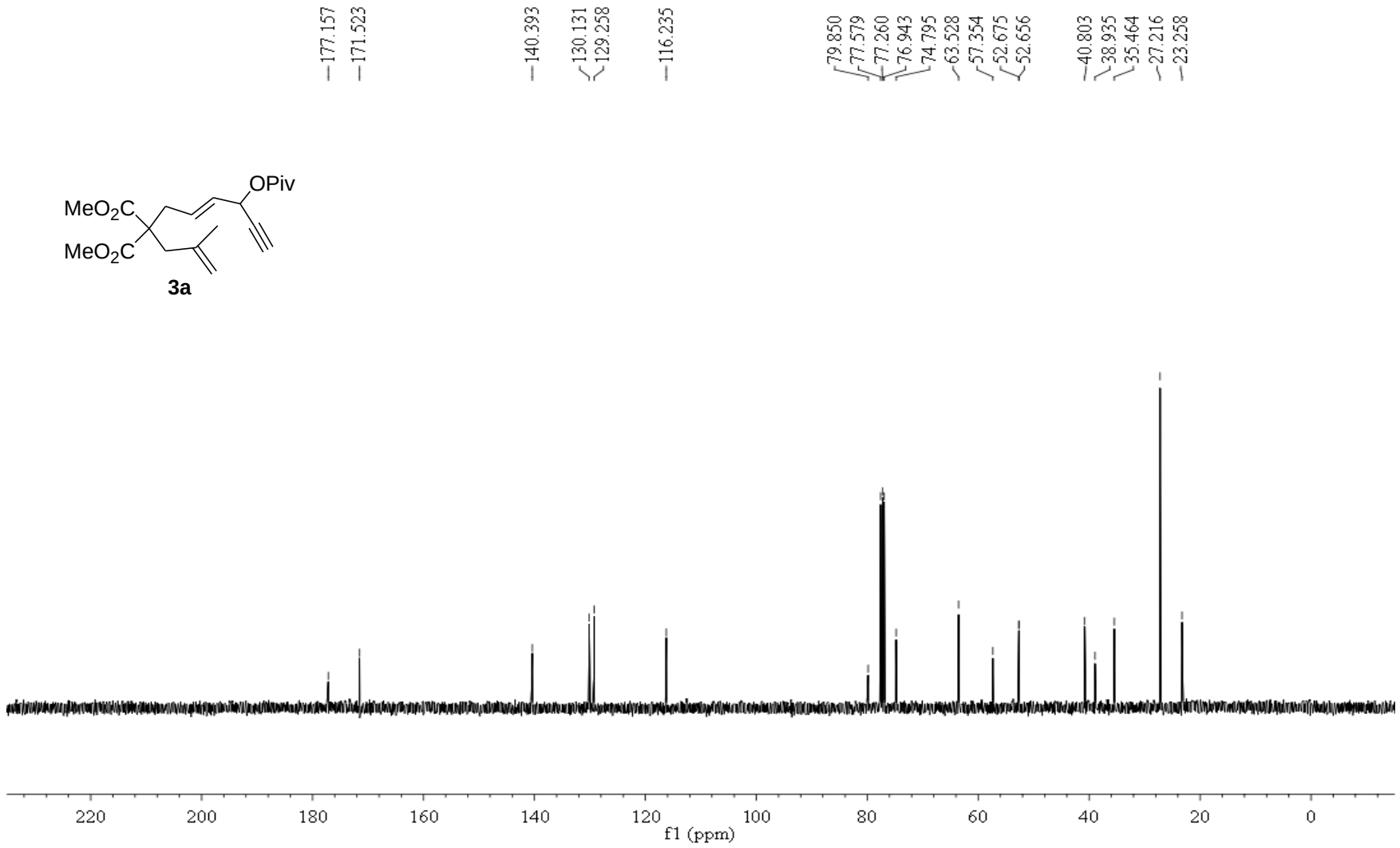

177.114
139.622
132.687
132.343
129.624
128.952
128.899
127.768
119.856
79.133
75.277
62.843
49.882
47.889
38.938
27.184
180
160
140
120
100
80
60
40
20
0PPM

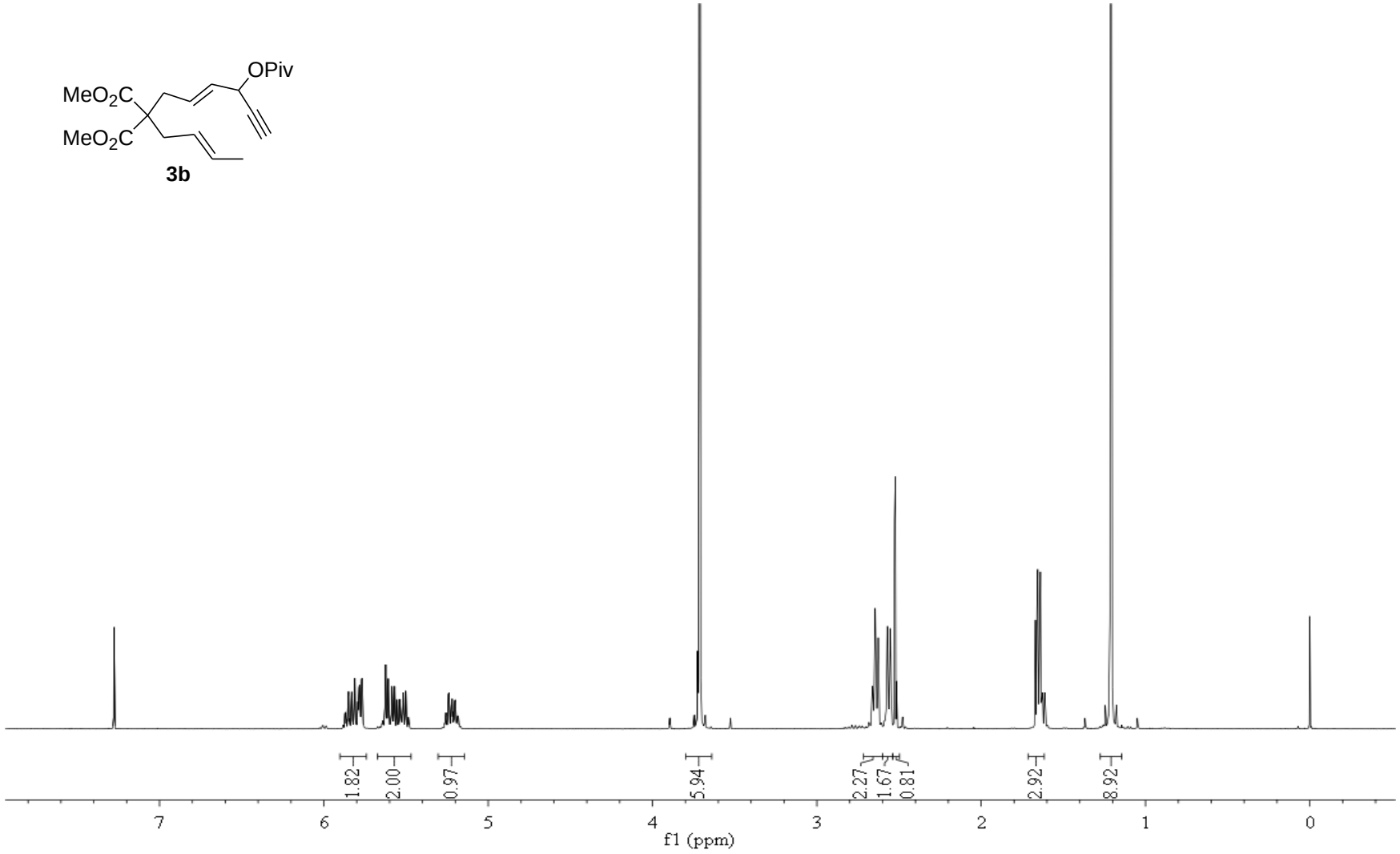


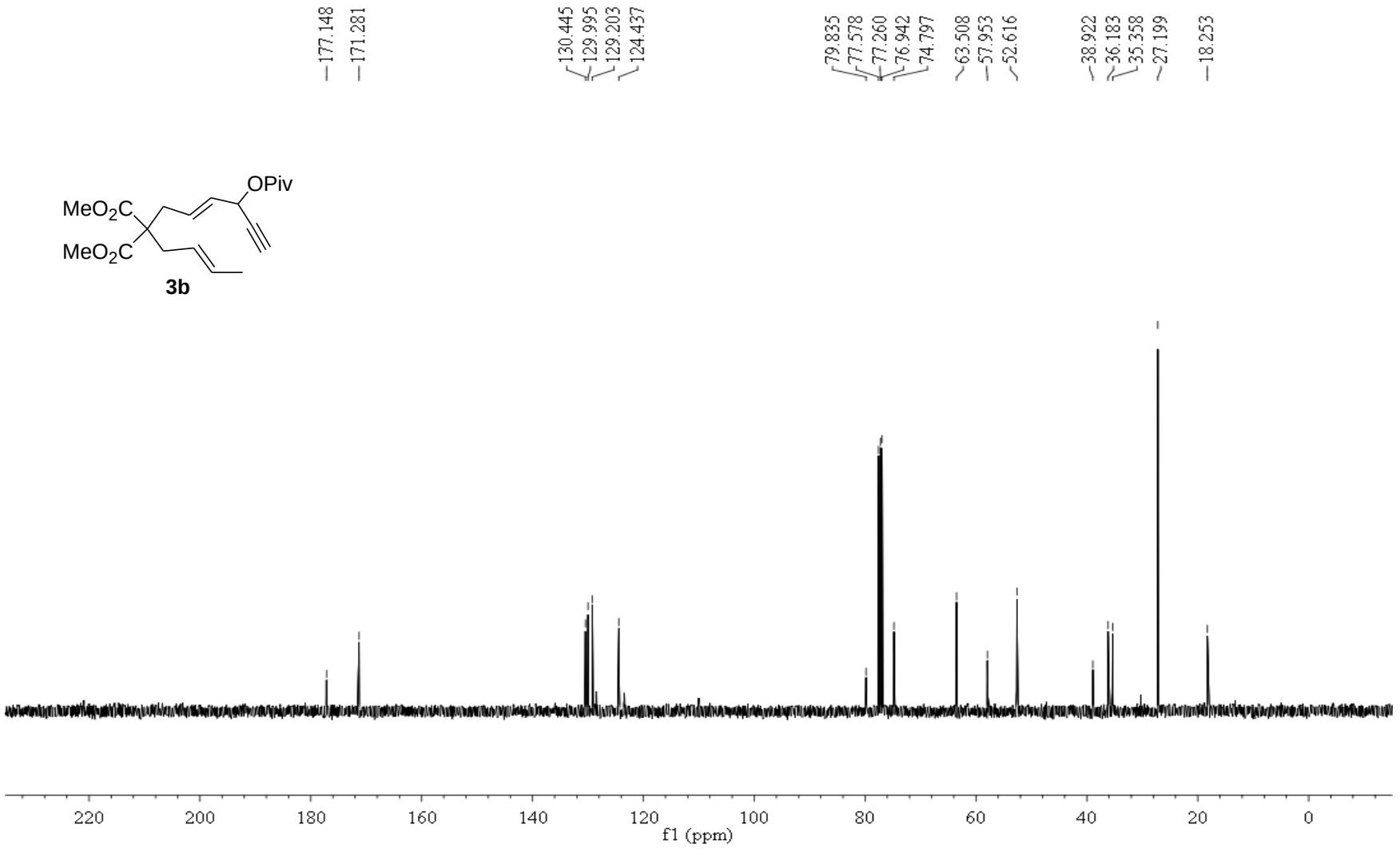
1n

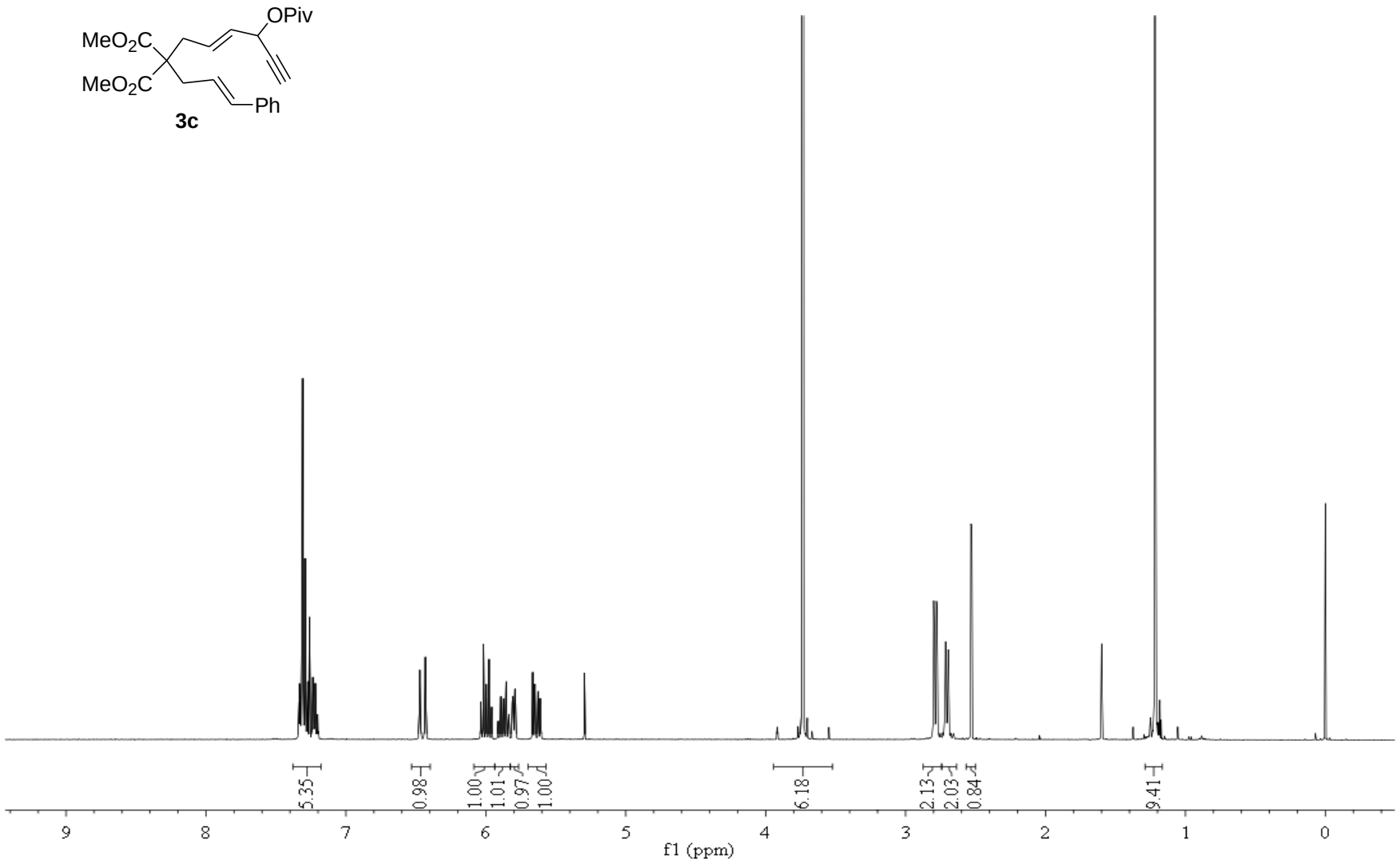

Br
O
S
N
O
O
O
N
1n
165.589
153.850
139.683
132.664
132.366
131.824
130.220
128.922
128.639
127.723
119.879
115.976
110.928
79.622
75.254
62.652
49.844
47.912
40.267
200
150
100
50
0

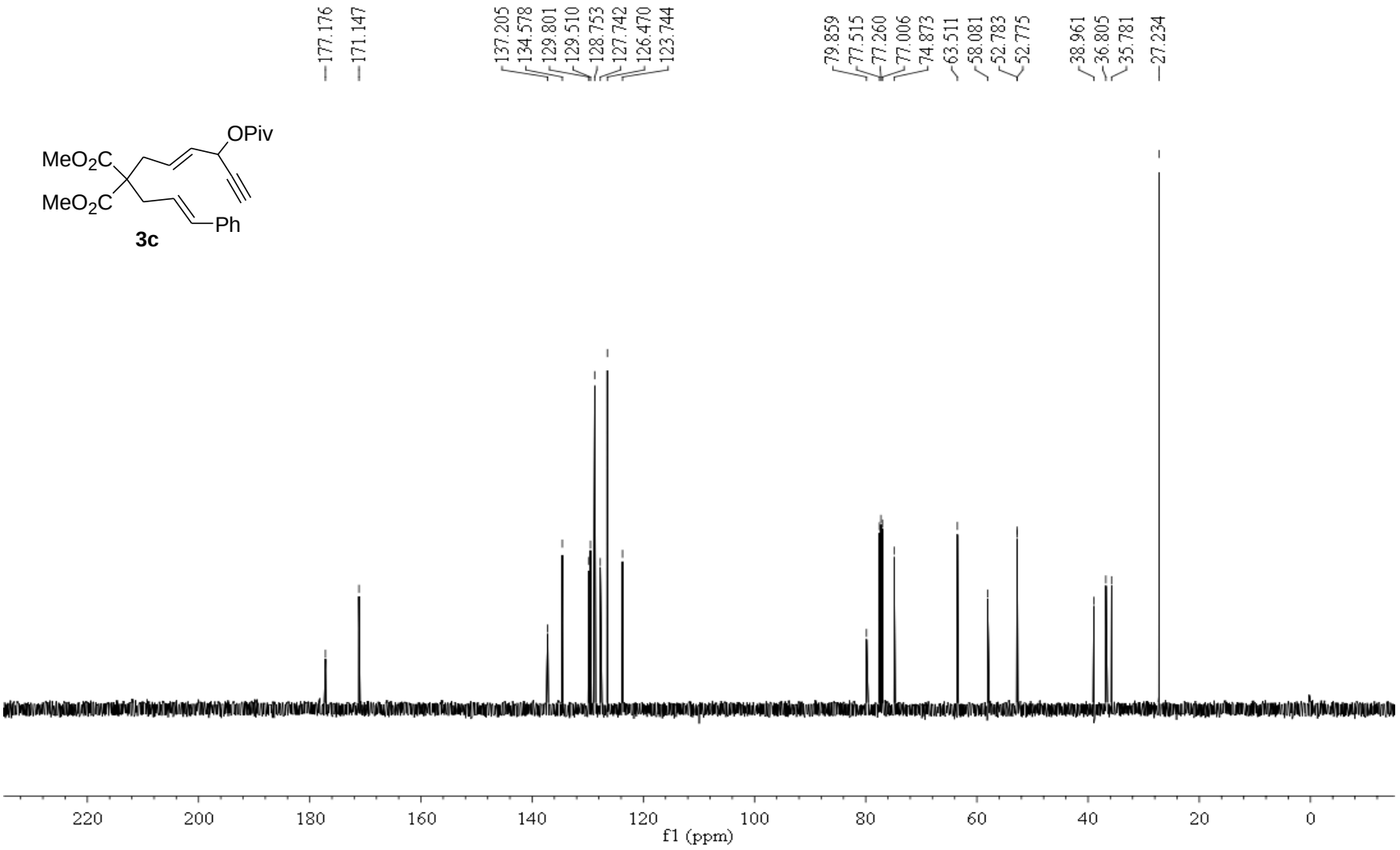

MeO2C
MeO2C
OPiv
3a
1.00
0.94
0.99
1.00
1.18
5.77
3.96
0.87
2.96
8.92
8
7
6
5
4
3
2
1
0
f1 (ppm)

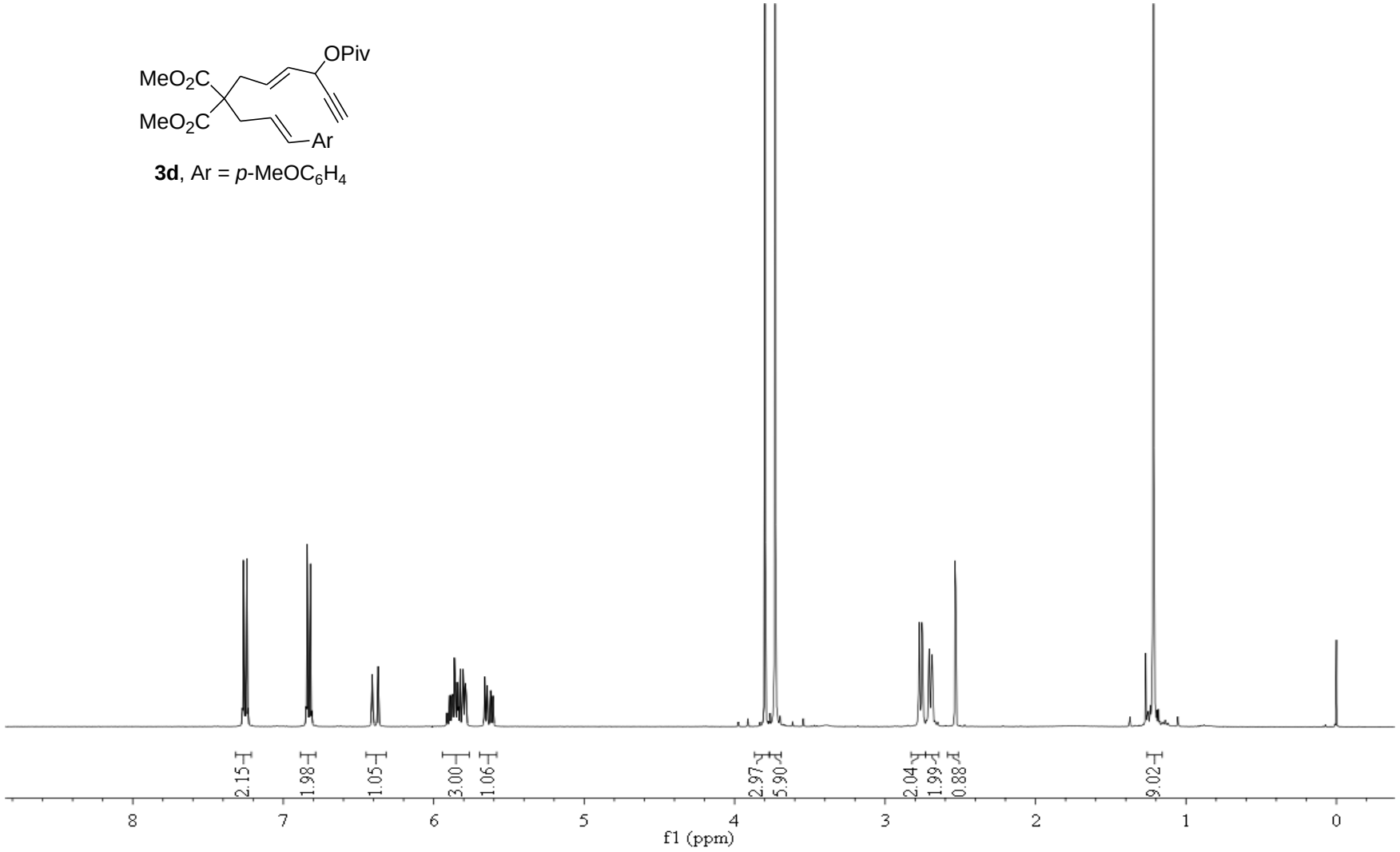

177.157
171.523
140.393
130.131
129.258
116.235
79.850
77.579
77.260
76.943
74.795
63.528
57.354
52.675
52.656
40.803
38.935
35.464
27.216
23.258
OPiv
MeO2C
MeO2C
3a
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


OPiv
MeO2C
MeO2C
3b
1.82
2.00
0.97
5.94
2.27
1.67
0.81
2.92
8.92
7
6
5
4
3
2
1
0
f1 (ppm)

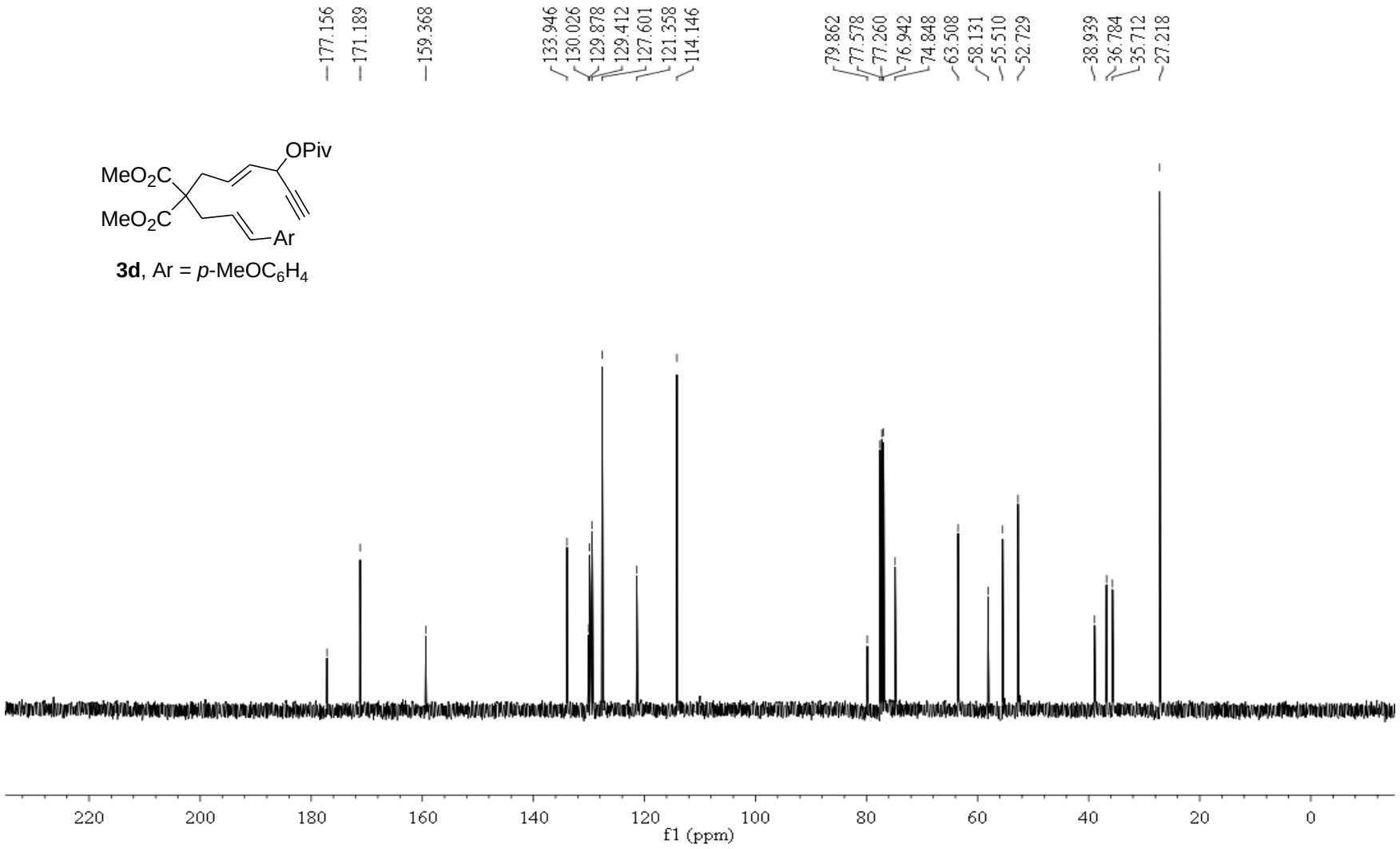

177.148
171.281
130.445
129.995
129.203
124.437
79.835
77.578
77.260
76.942
74.797
63.508
57.953
52.616
38.922
36.183
35.358
27.199
18.253
OPiv
MeO2C
MeO2C
3b
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


MeO2C
MeO2C
OPiv
Ph
3c
5.35
0.98
1.00
1.01
0.97
1.00
6.18
2.13
2.03
0.84
9.41
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

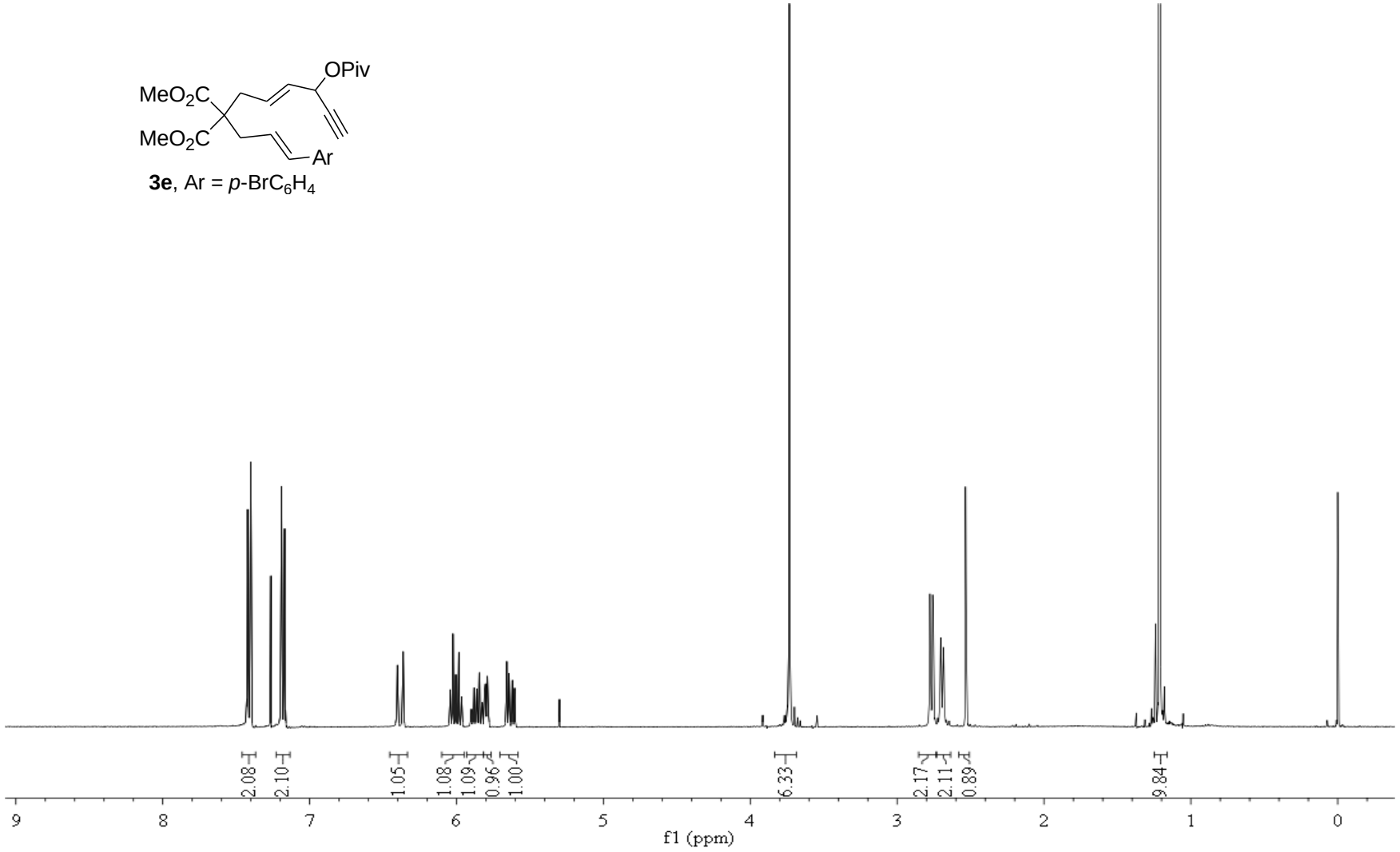

177.176
171.147
137.205
134.578
129.801
129.510
128.753
127.742
126.470
123.744
79.859
77.515
77.260
77.006
74.873
63.511
58.081
52.783
52.775
38.961
36.805
35.781
27.234
OPiv
MeO2C
MeO2C
Ph
3c
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

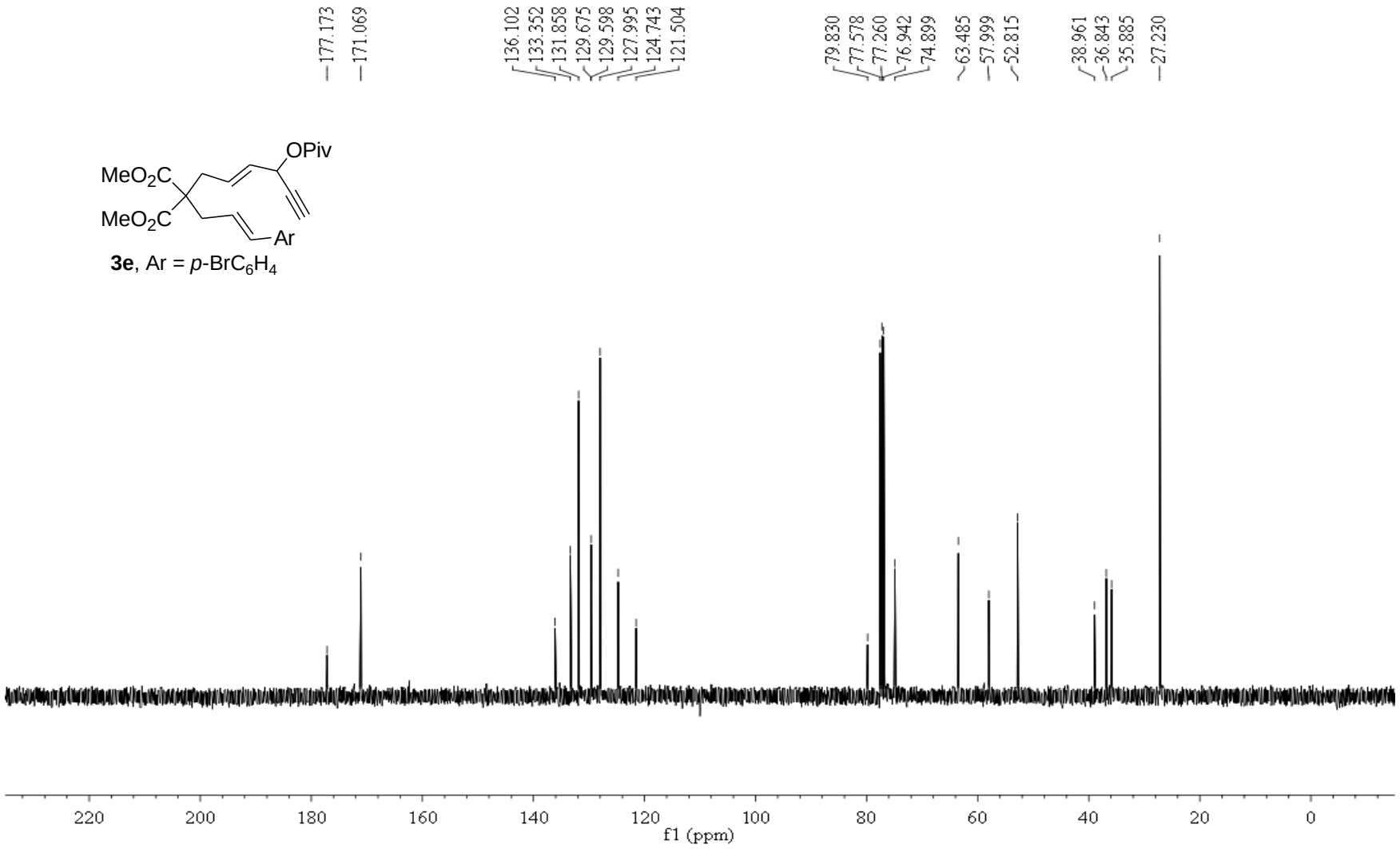


3d, Ar = *p*-$MeOC_6H_4$

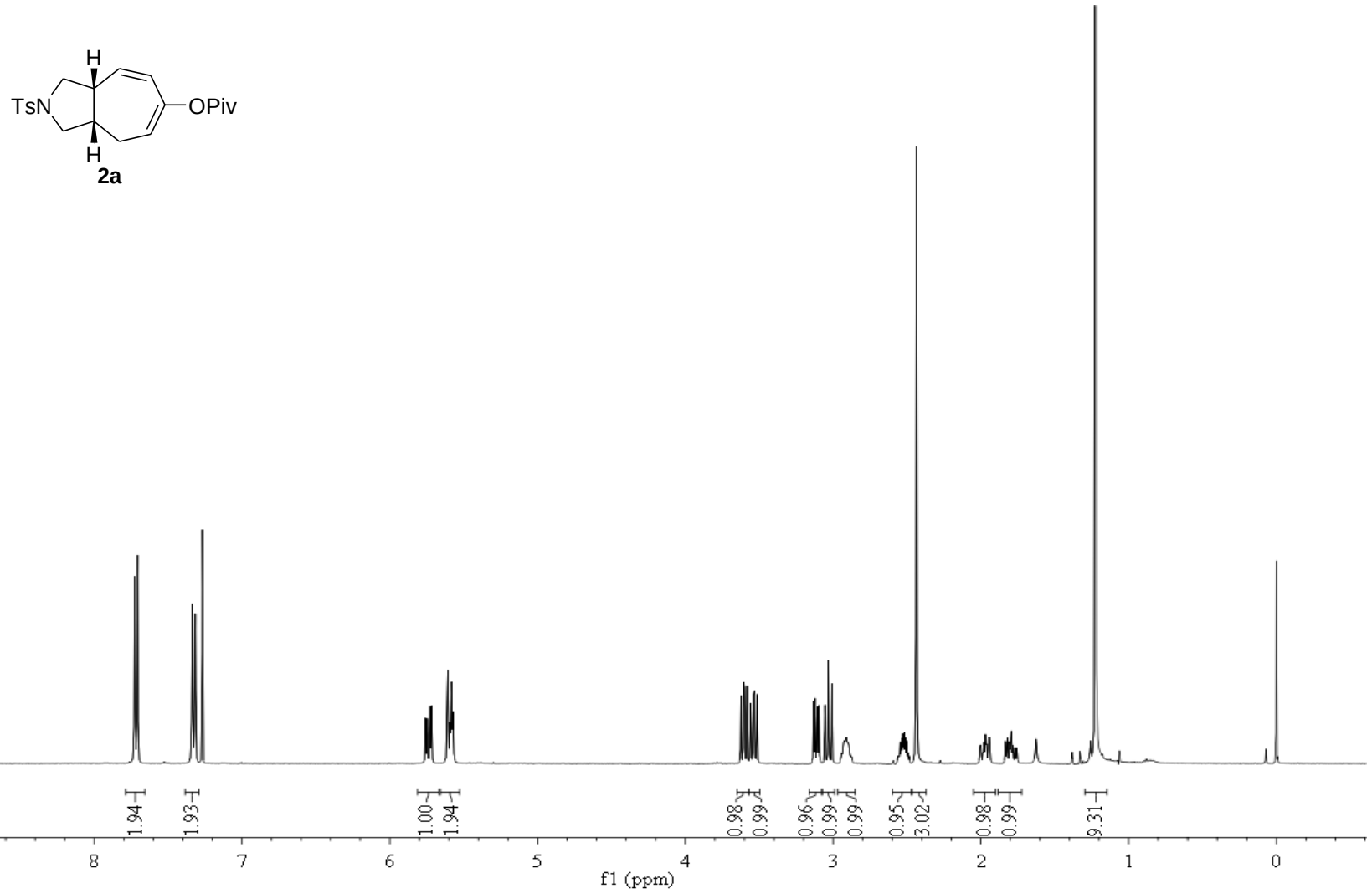


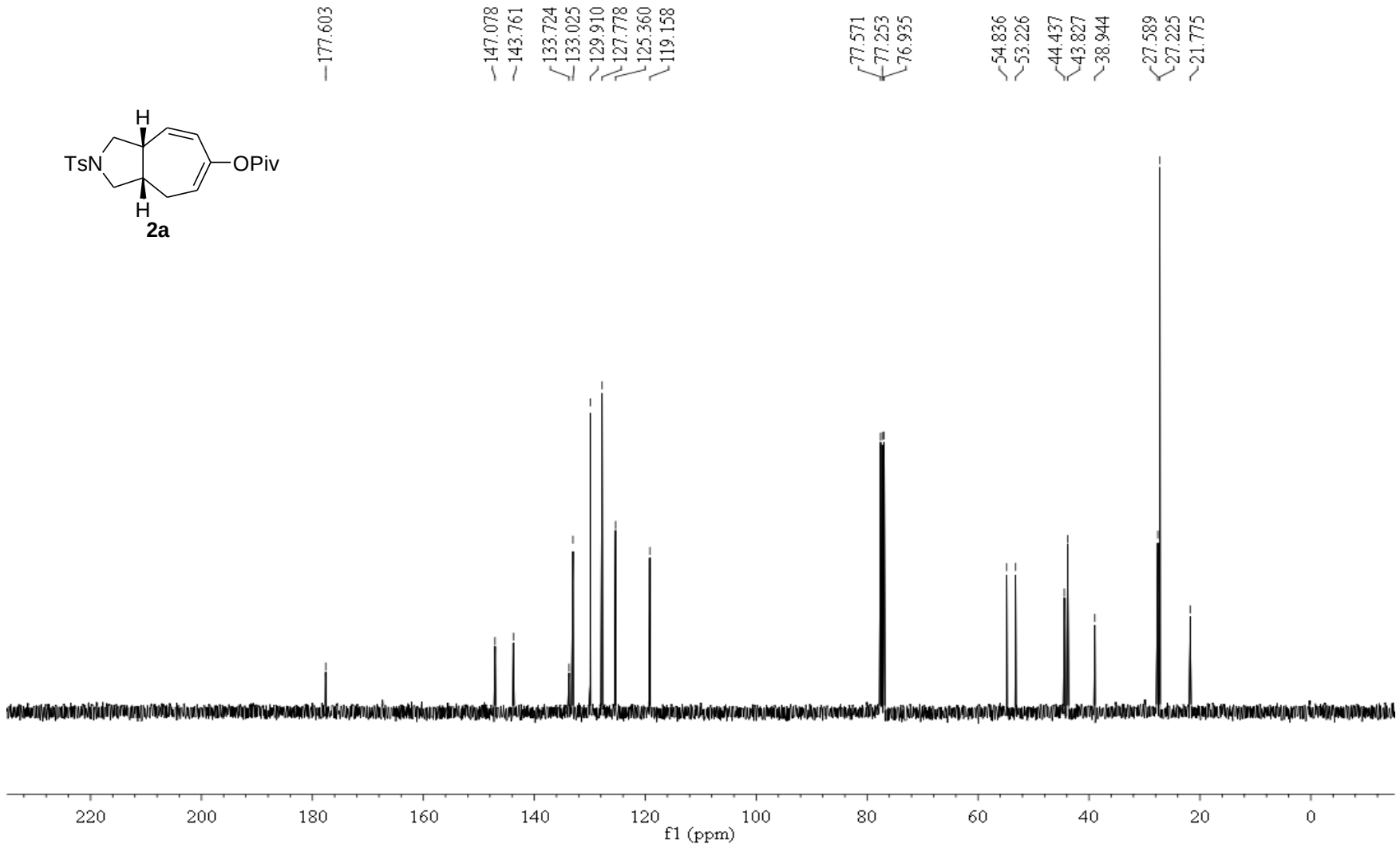
3d, Ar = *p*-$MeOC_6H_4$

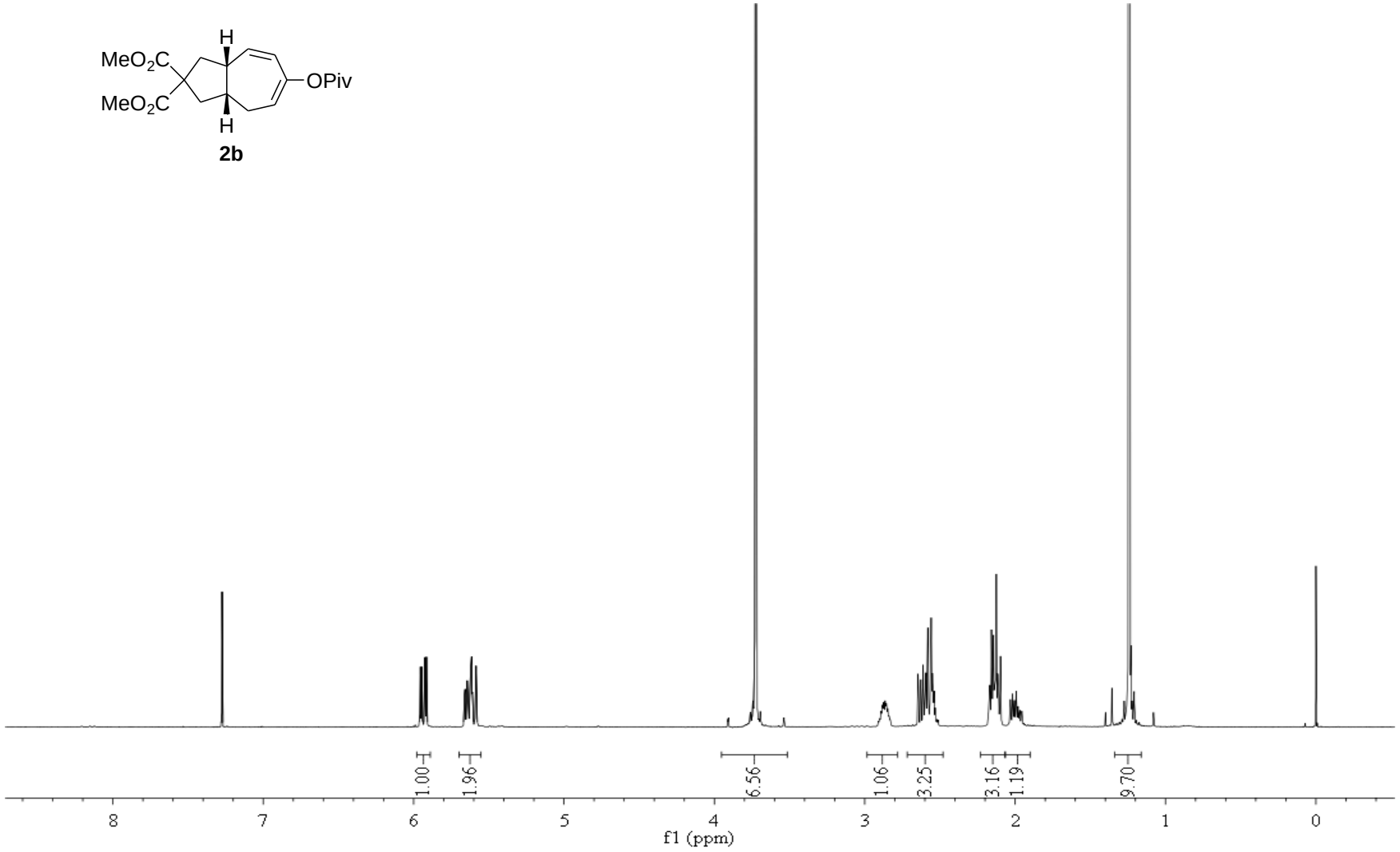

OPiv
MeO2C
MeO2C
Ar
3e, Ar = p-BrC6H4
2.08
2.10
1.05
1.08
1.09
0.96
1.00
6.33
2.17
2.11
0.89
9.84
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

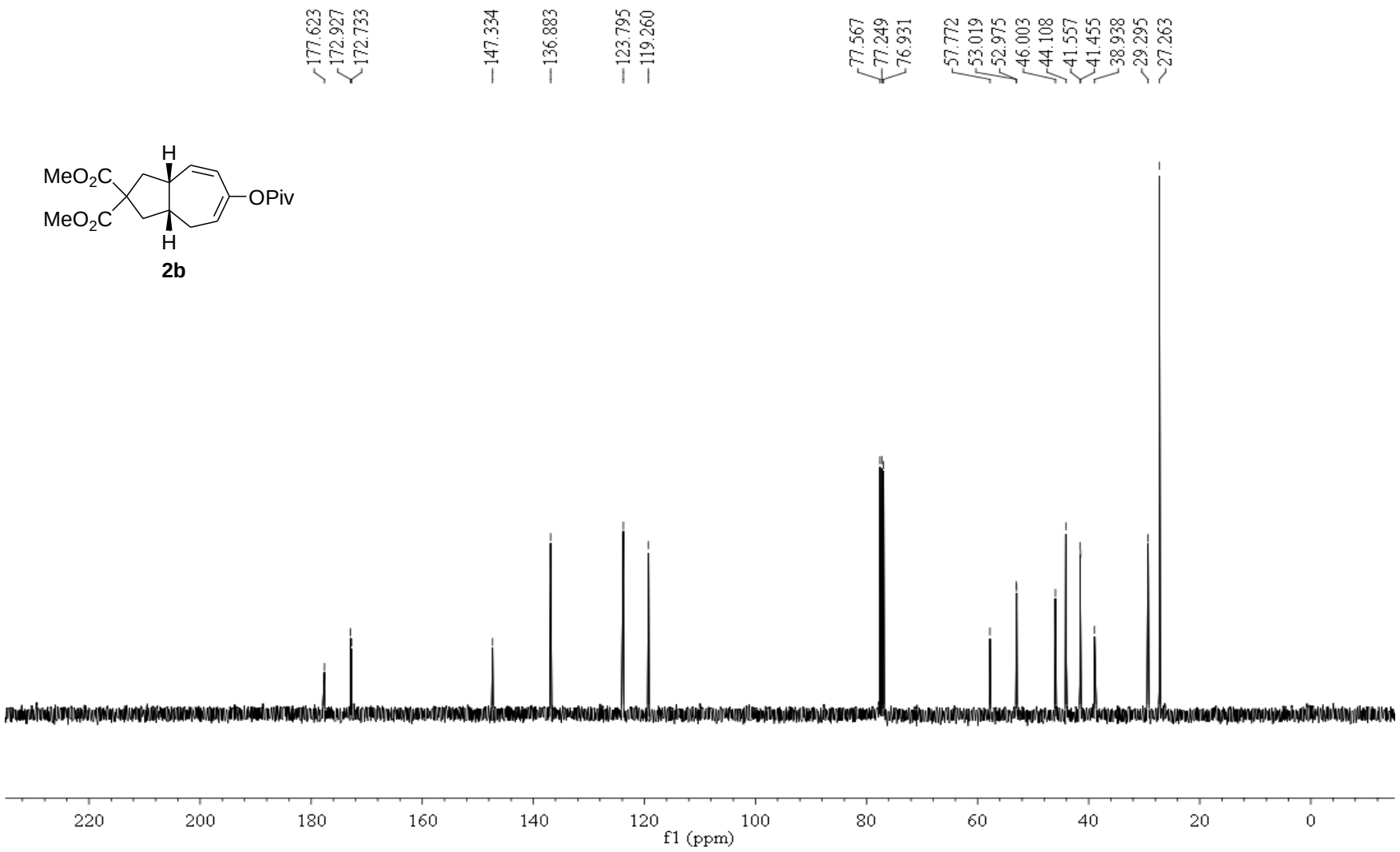


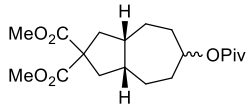
3e, Ar = *p*-BrC_6H_4


H
TsN
OPiv
H
2a
1.94
1.93
1.00
1.94
0.98
0.99
0.96
0.99
0.99
0.95
3.02
0.98
0.99
9.31
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


177.603
147.078
143.761
133.724
133.025
129.910
127.778
125.360
119.158
77.571
77.253
76.935
54.836
53.226
44.437
43.827
38.944
27.589
27.225
21.775
TsN
OPiv
H
H
2a
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

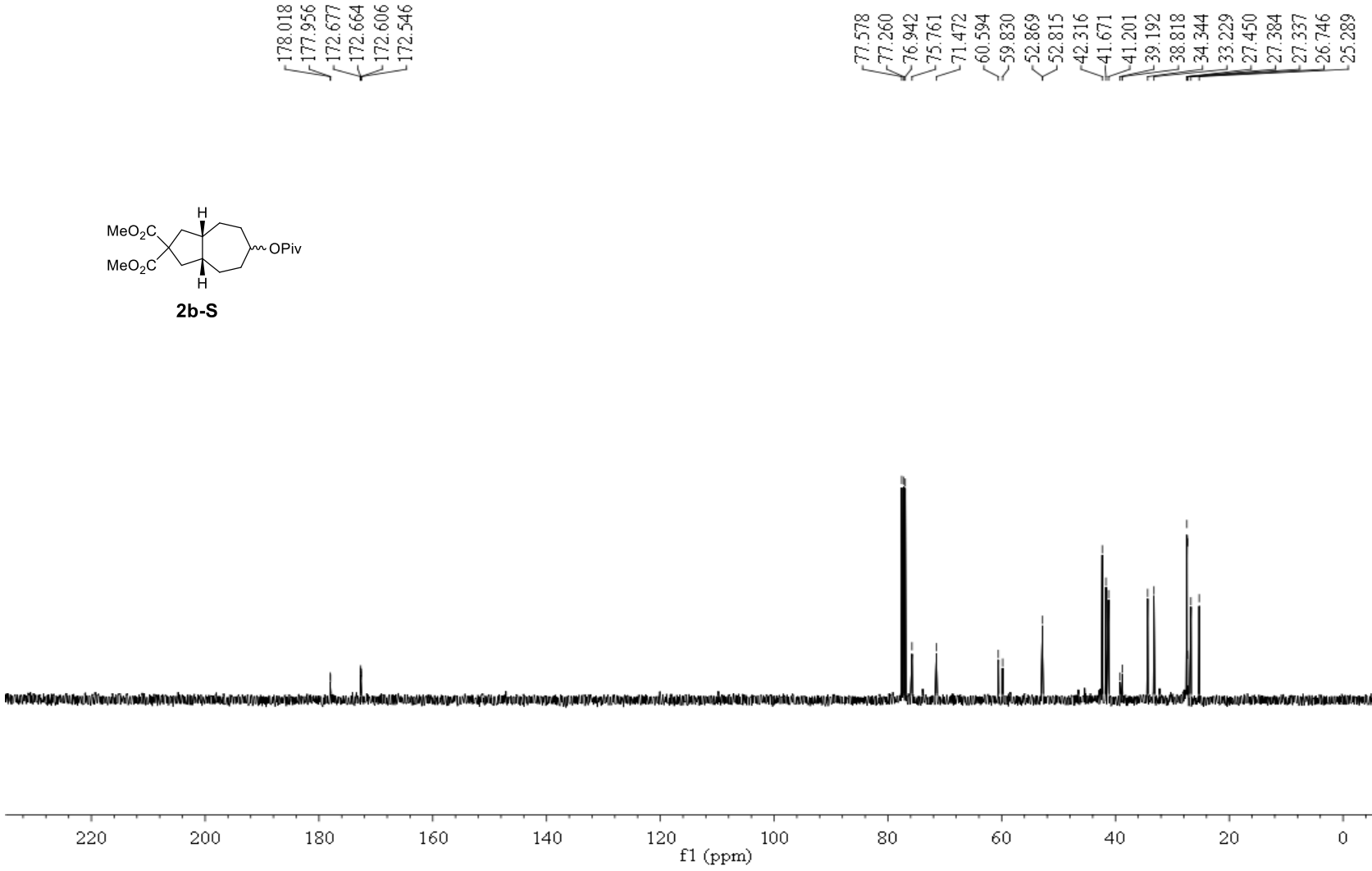

MeO2C
MeO2C
H
H
OPiv
2b
1.00
1.96
6.56
1.06
3.25
3.16
1.19
9.70
8
7
6
5
4
3
2
1
0
f1 (ppm)

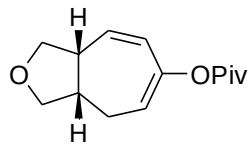

177.623
172.927
172.733
147.334
136.883
123.795
119.260
77.567
77.249
76.931
57.772
53.019
52.975
46.003
44.108
41.557
41.455
38.938
29.295
27.263
MeO2C
MeO2C
H
H
OPiv
2b
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


H
MeO2C
MeO2C
OPiv
H

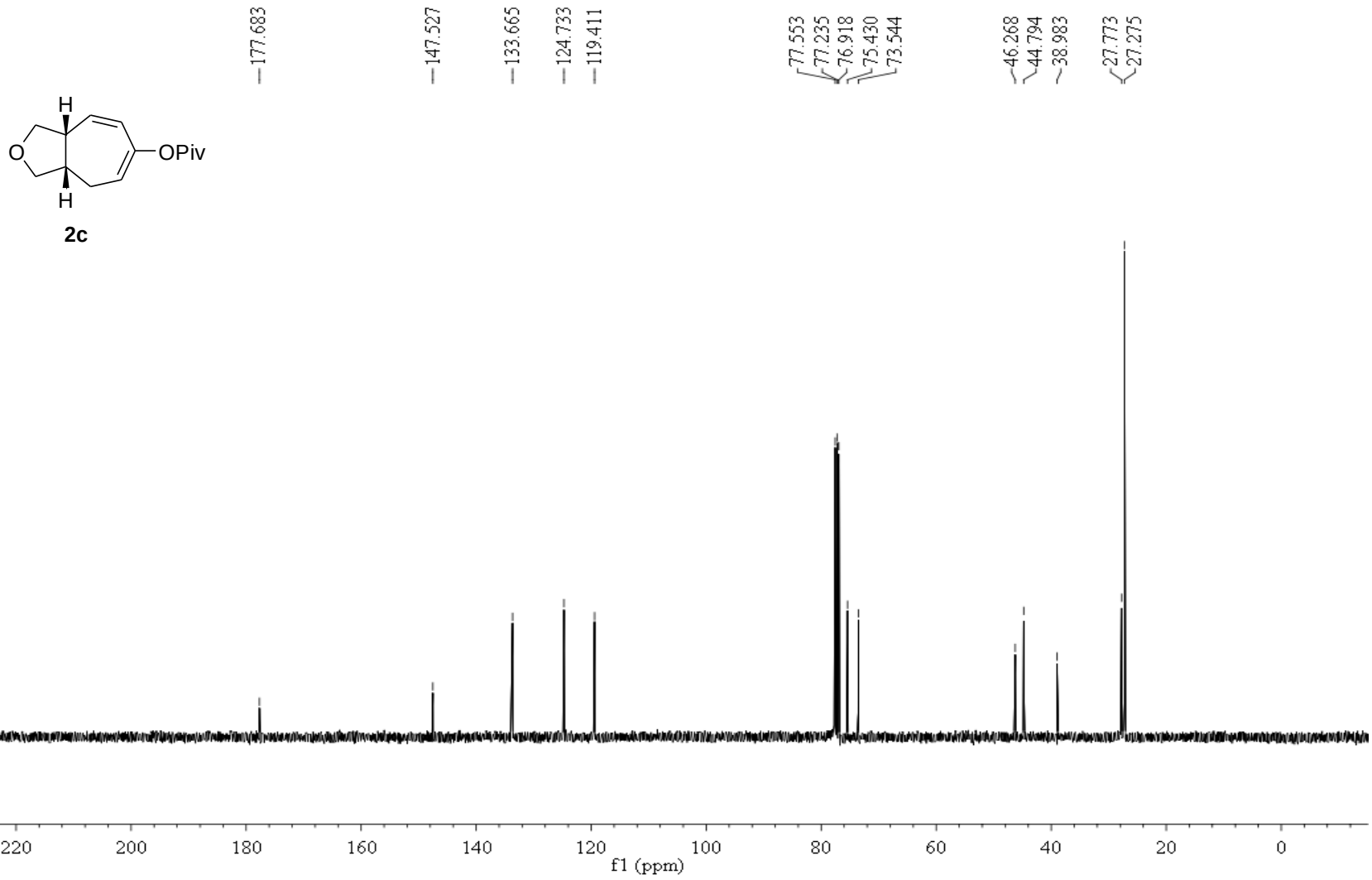
2b-S

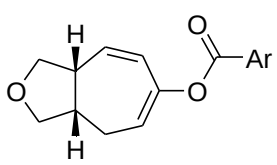
0.48
0.45
2.76
2.88
2.00
1.86
1.87
5.00
1.93
2.34
4.21
4.00
8
7
6
5
4
3
2
1
0
f1 (ppm)


178.018
177.956
172.677
172.664
172.606
172.546
77.578
77.260
76.942
75.761
71.472
60.594
59.830
52.869
52.815
42.316
41.671
41.201
39.192
38.818
34.344
33.229
27.450
27.384
27.337
26.746
25.289
MeO2C
MeO2C
H
H
OPiv
2b-S
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



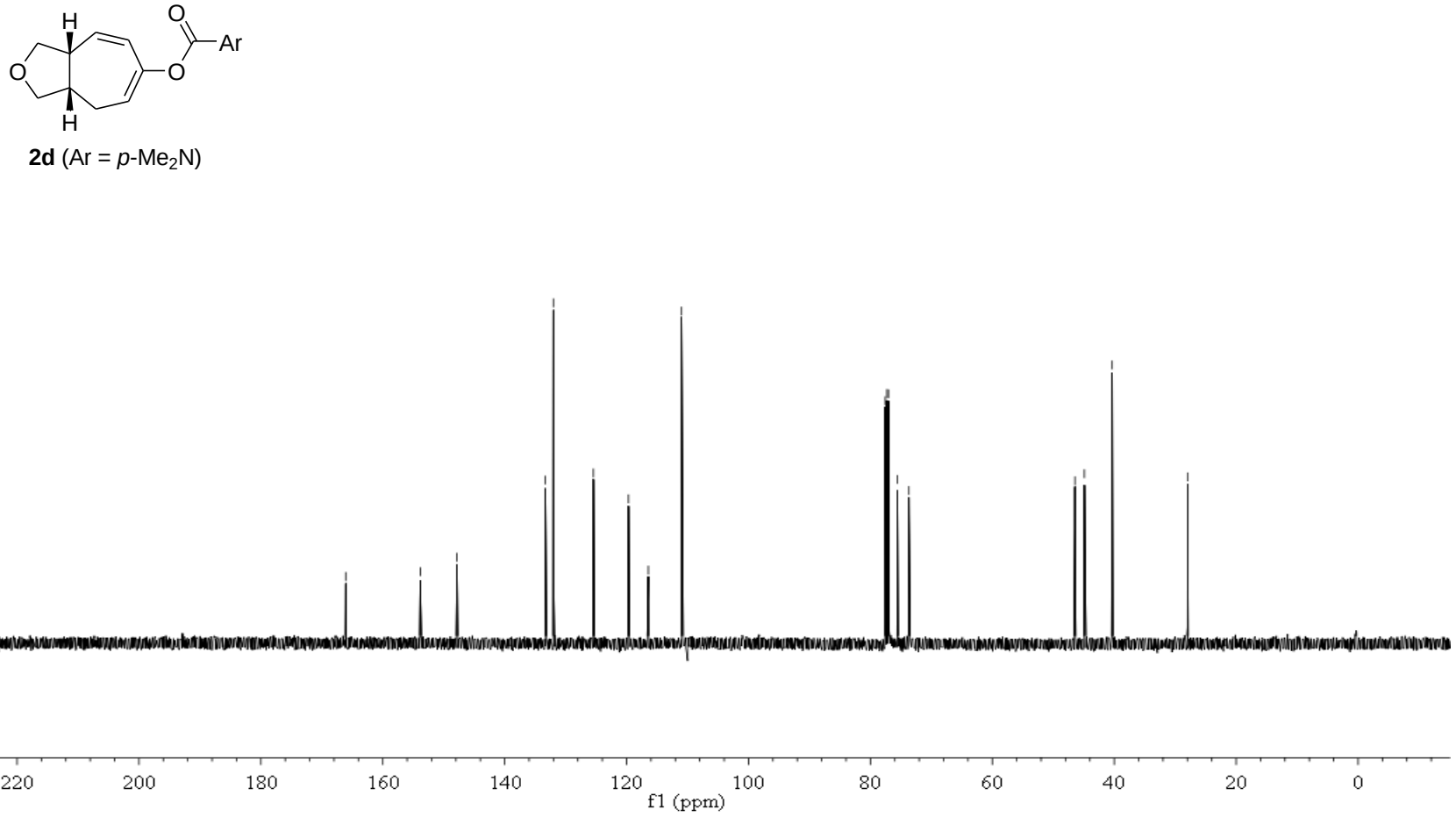
2c


177.683
147.527
133.665
124.733
119.411
77.553
77.235
76.918
75.430
73.544
46.268
44.794
38.983
27.773
27.275
H
O
OPiv
H
2c
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

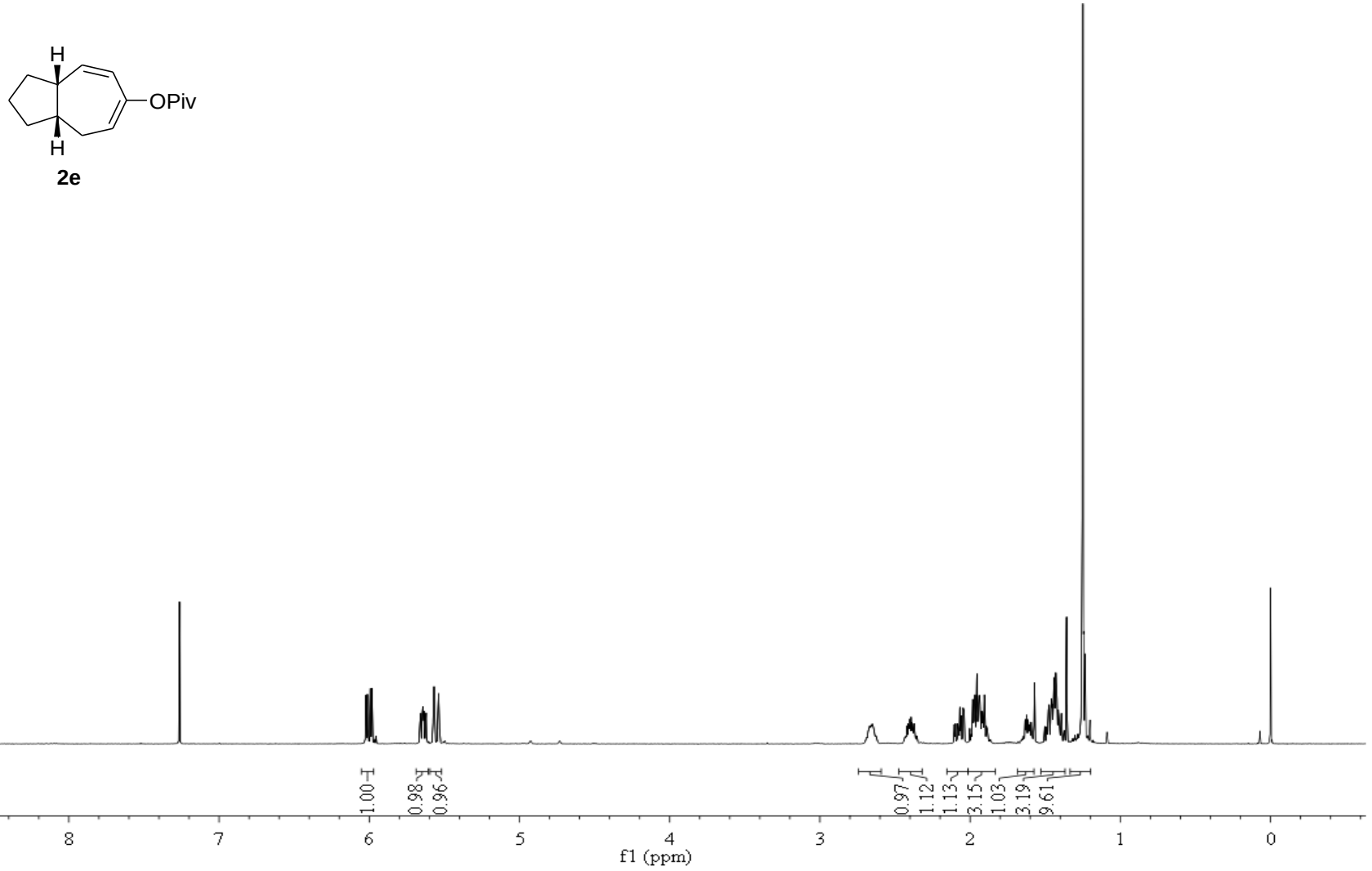

H
O
Ar
O
O
H

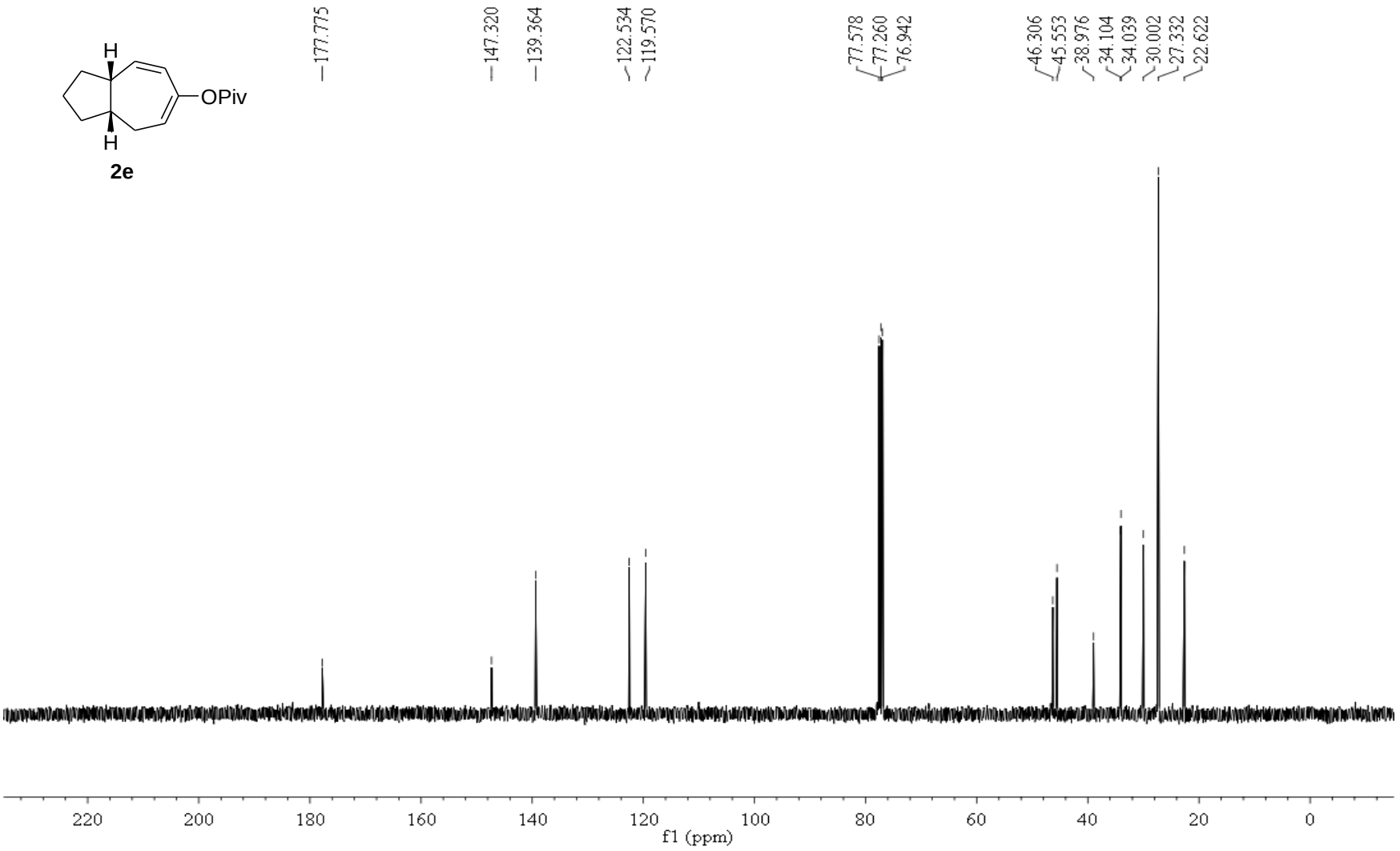
2d (Ar = *p*-Me_2N)

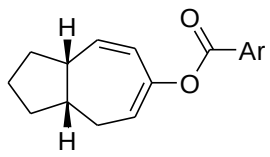
1.88
2.00
0.99
1.85
1.95
0.98
0.96
6.72
0.94
1.92
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


166.074
153.847
147.822
133.324
132.013
125.448
119.690
116.433
110.985
77.560
77.305
77.051
75.558
73.691
46.438
44.896
40.332
27.979
H
O
O
Ar
O
H
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

2d (Ar = *p*-Me_2N)

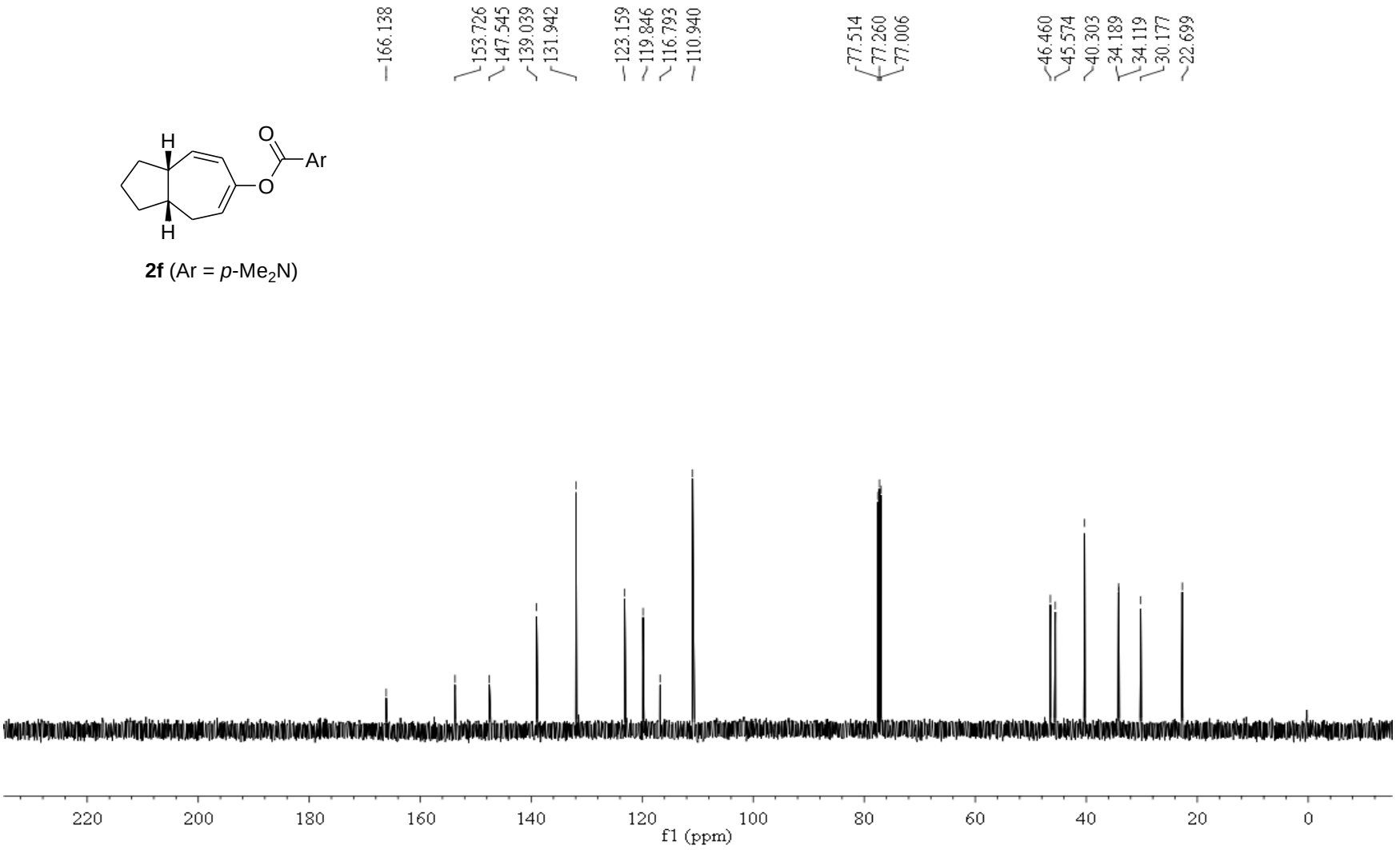

H
OPiv
H
2e
1.00
0.98
0.96
0.97
1.12
1.13
3.15
1.03
3.19
9.61
8
7
6
5
4
3
2
1
0
f1 (ppm)


H
OPiv
H
2e
177.775
147.320
139.364
122.534
119.570
77.578
77.260
76.942
46.306
45.553
38.976
34.104
34.039
30.002
27.332
22.622
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

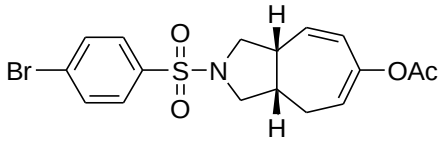

H
O
Ar
O
H

2f (Ar = *p*-Me_2N)

2.00
2.17
1.02
1.92
6.34
0.96
1.05
1.09
3.11
1.03
3.10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

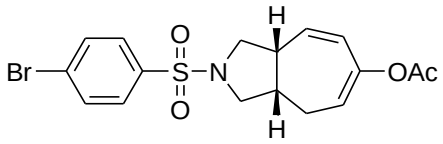

166.138
153.726
147.545
139.039
131.942
123.159
119.846
116.793
110.940
77.514
77.260
77.006
46.460
45.574
40.303
34.189
34.119
30.177
22.699
H
O
Ar
O
H
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

2f (Ar = *p*-Me_2N)

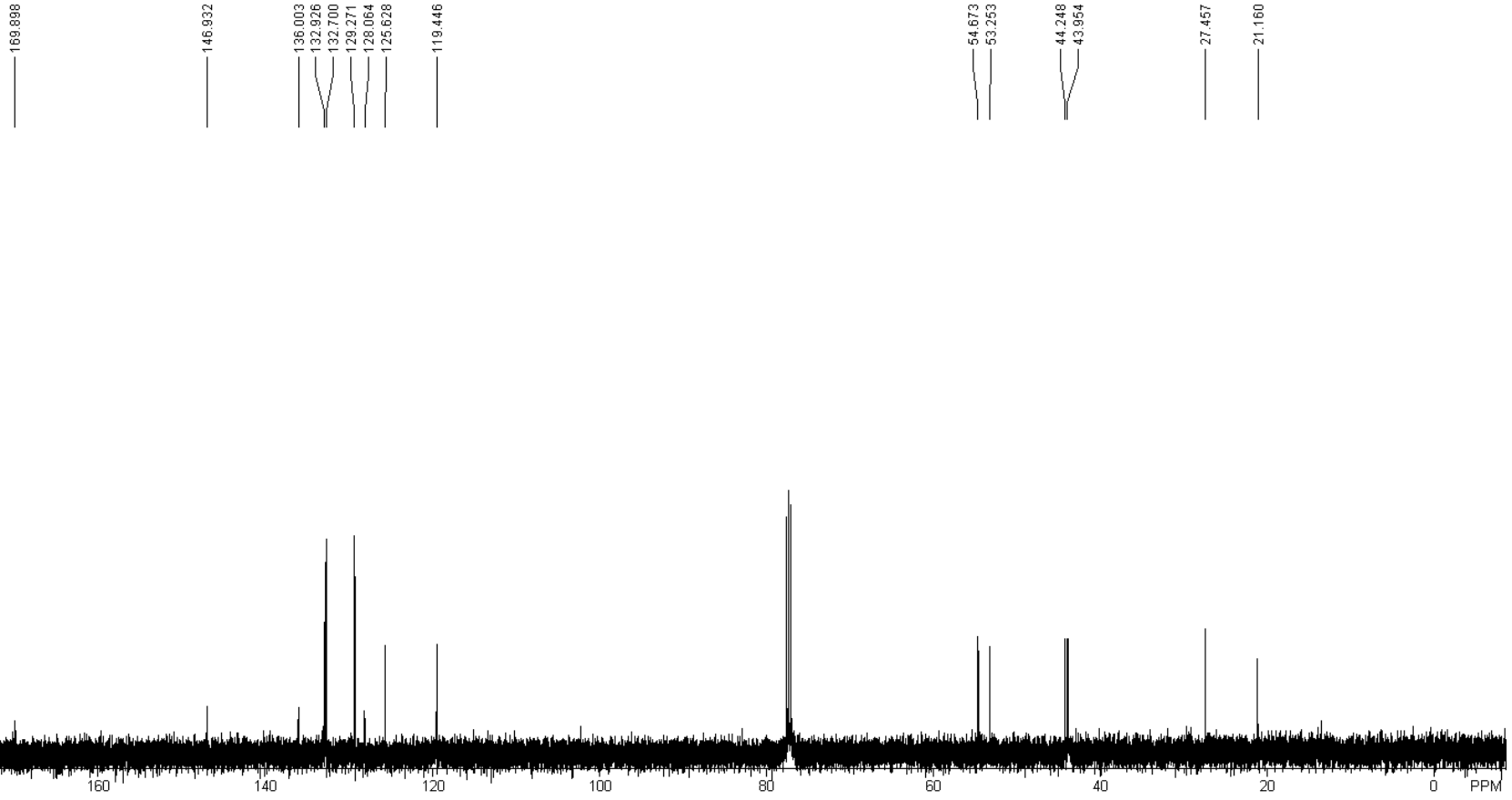

Br
O
S
O
N
H
H
OAc

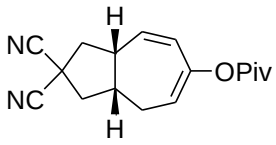
2g

4.00
1.10
2.03
2.29
1.19
1.11
1.10
1.12
3.04
1.04
1.03
8
7
6
5
4
3
2
1
0 PPM

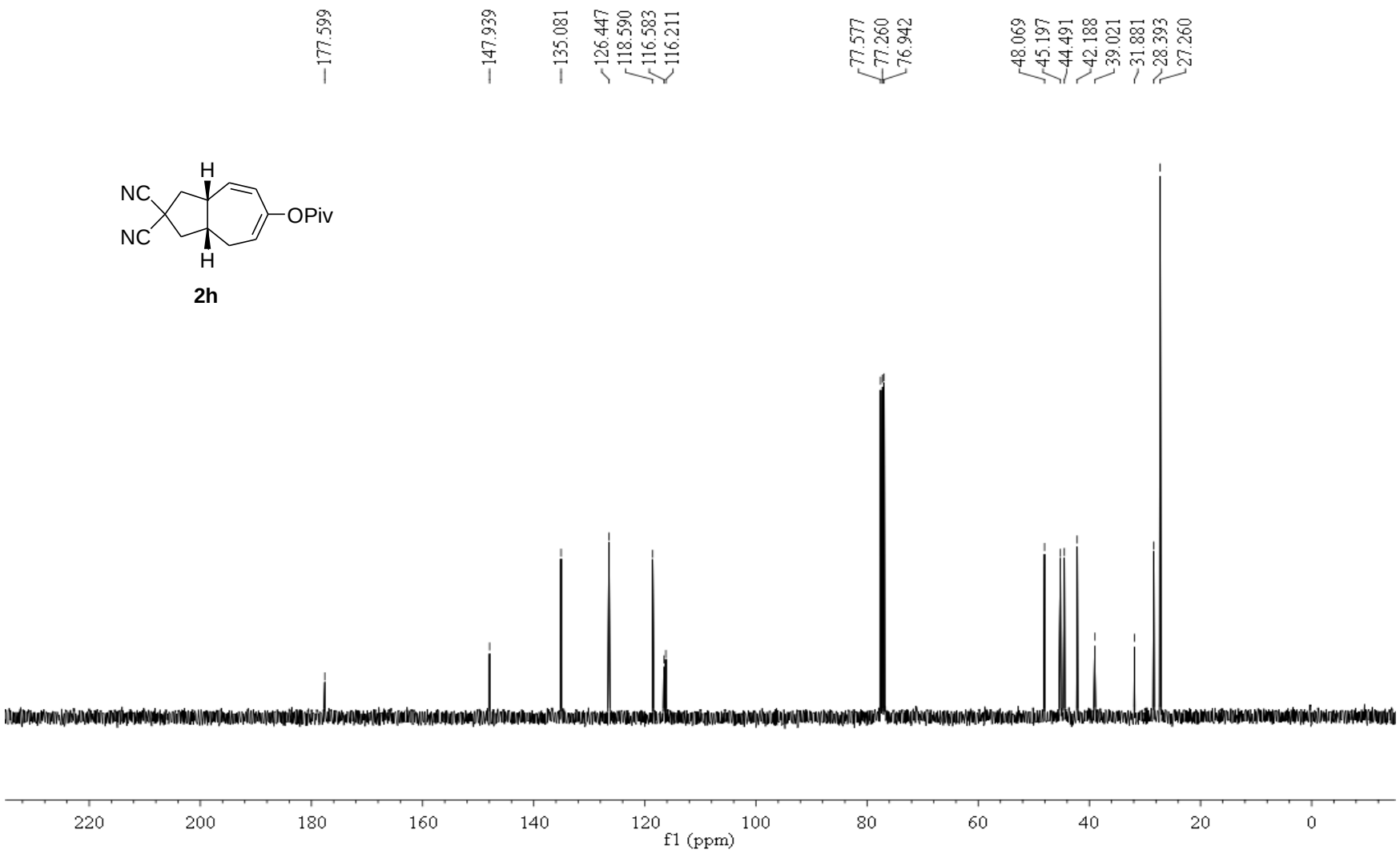

Br
O
S
O
N
H
H
OAc

2g

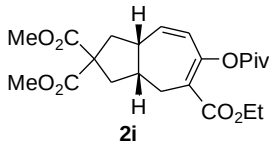

169.898
146.932
136.003
132.926
132.700
129.271
128.064
125.628
119.446
54.673
53.253
44.248
43.954
27.457
21.160
160
140
120
100
80
60
40
20
0
PPM



2h

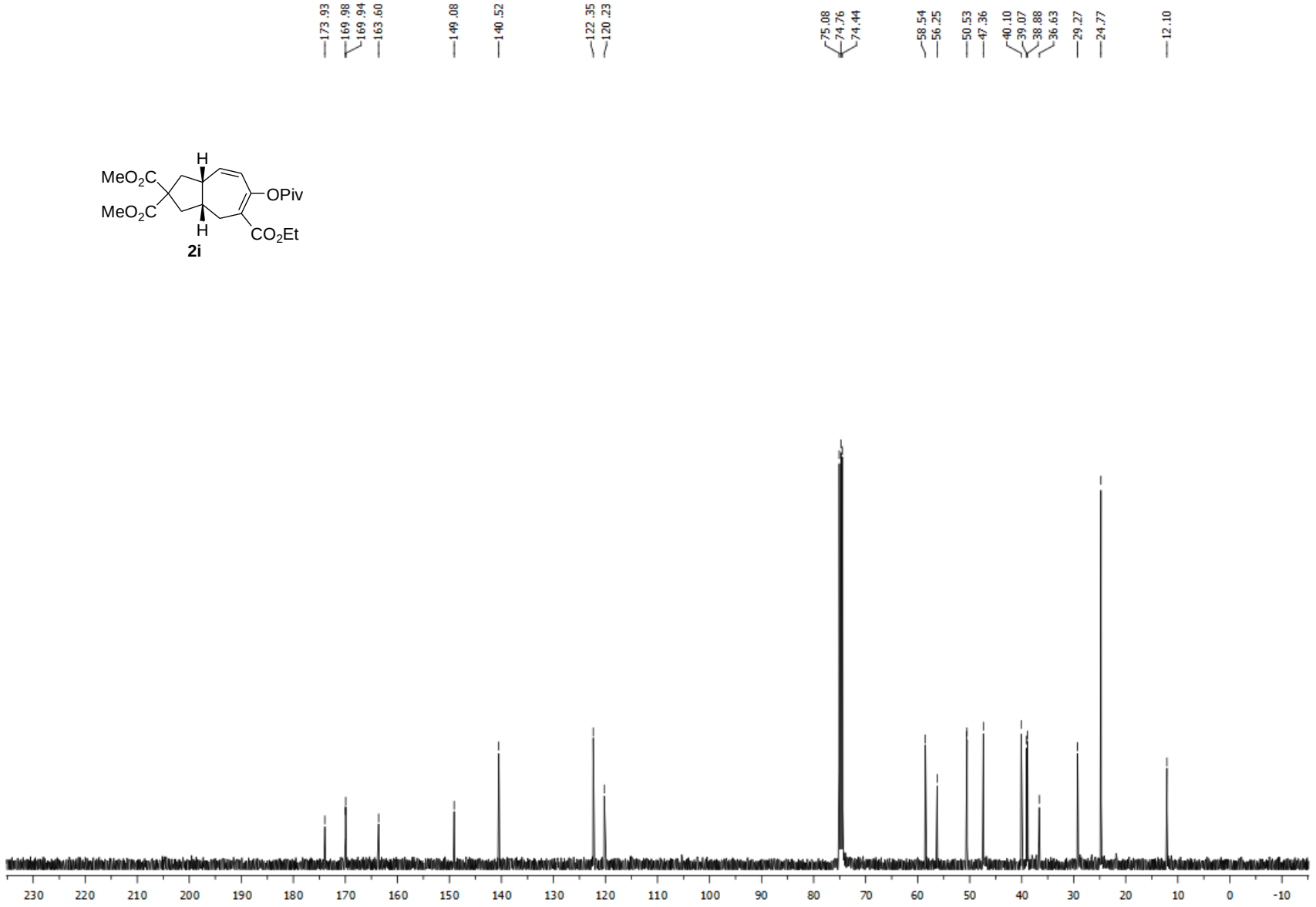

177.599
147.939
135.081
126.447
118.590
116.583
116.211
77.577
77.260
76.942
48.069
45.197
44.491
42.188
39.021
31.881
28.393
27.260
NC
NC
H
H
OPiv
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

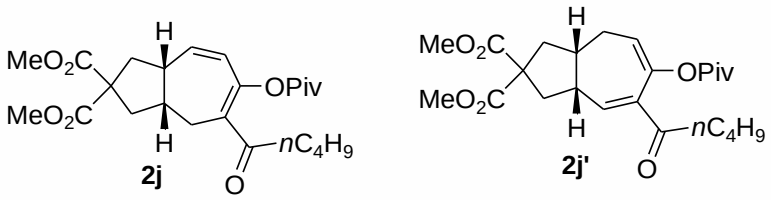
2h


H
MeO2C
OPiv
MeO2C
CO2Et
H

2i

1.00
1.01
1.98
5.34
1.02
1.81
1.64
0.94
1.85
10.85
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

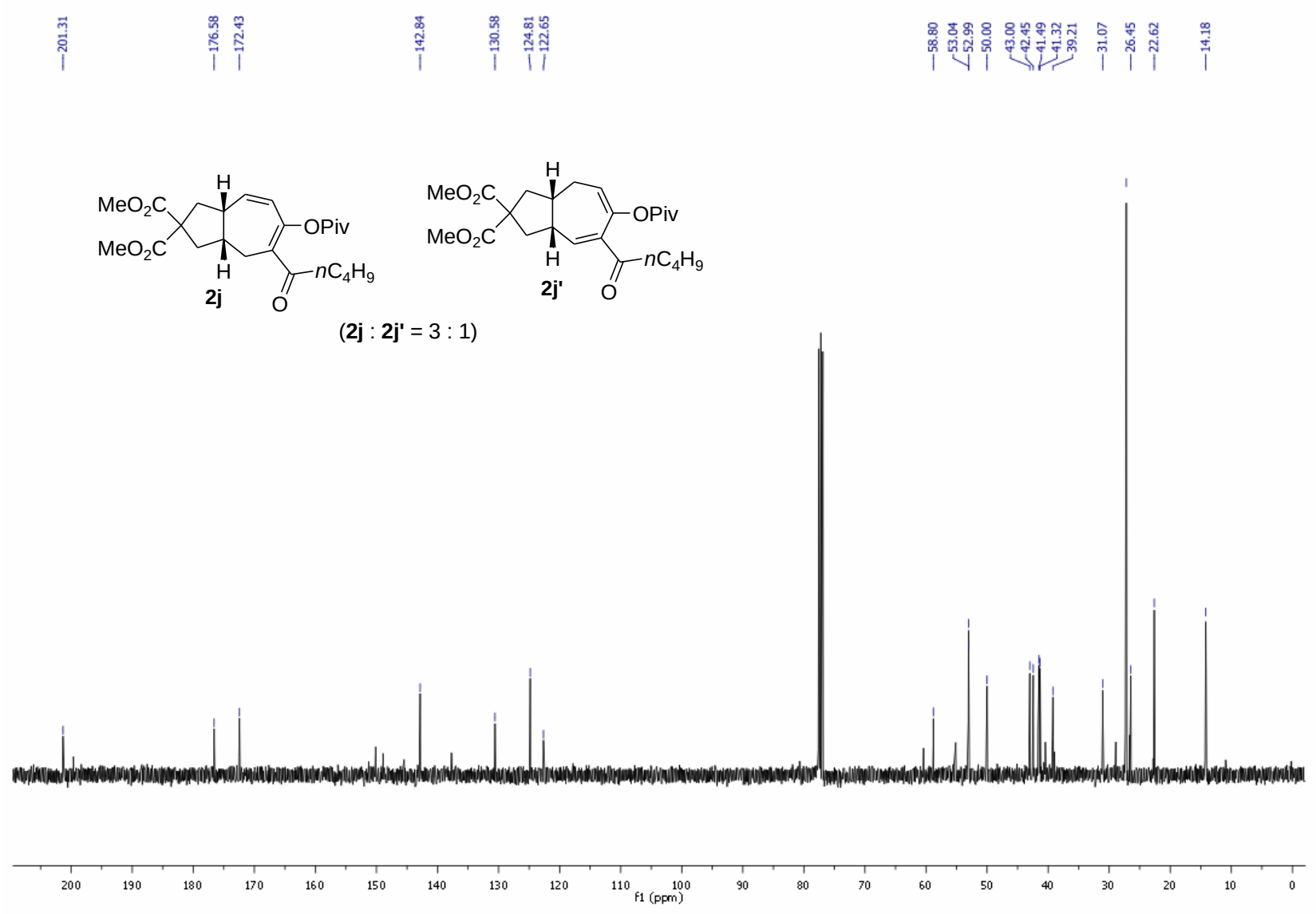

173.93
169.98
169.94
163.60
149.08
140.52
122.35
120.23
75.08
74.76
74.44
58.54
56.25
50.53
47.36
40.10
39.07
38.88
36.63
29.27
24.77
12.10
MeO2C
MeO2C
H
H
OPiv
CO2Et
2i
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

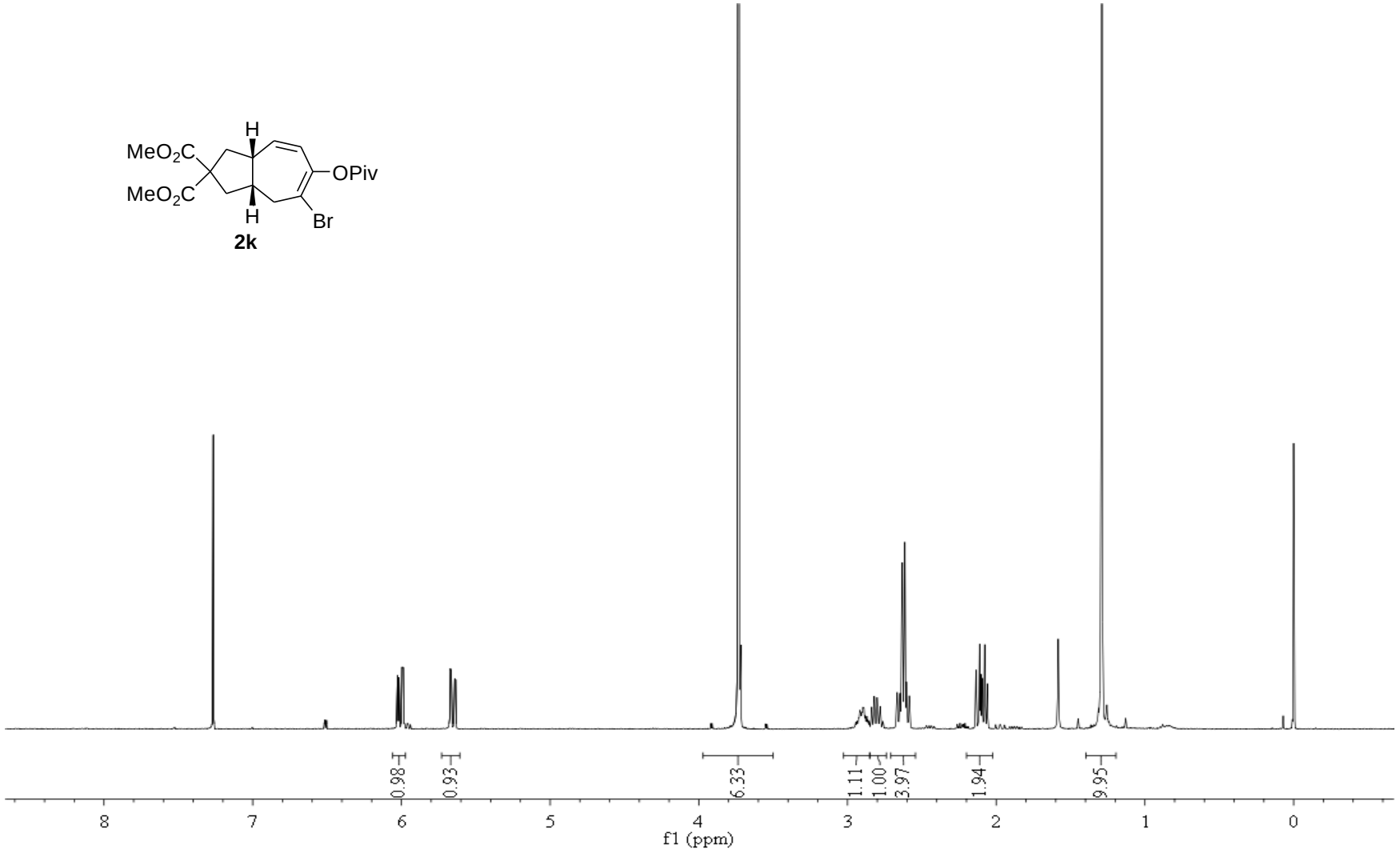

MeO2C
MeO2C
H
OPiv
nC4H9
O
H
2j

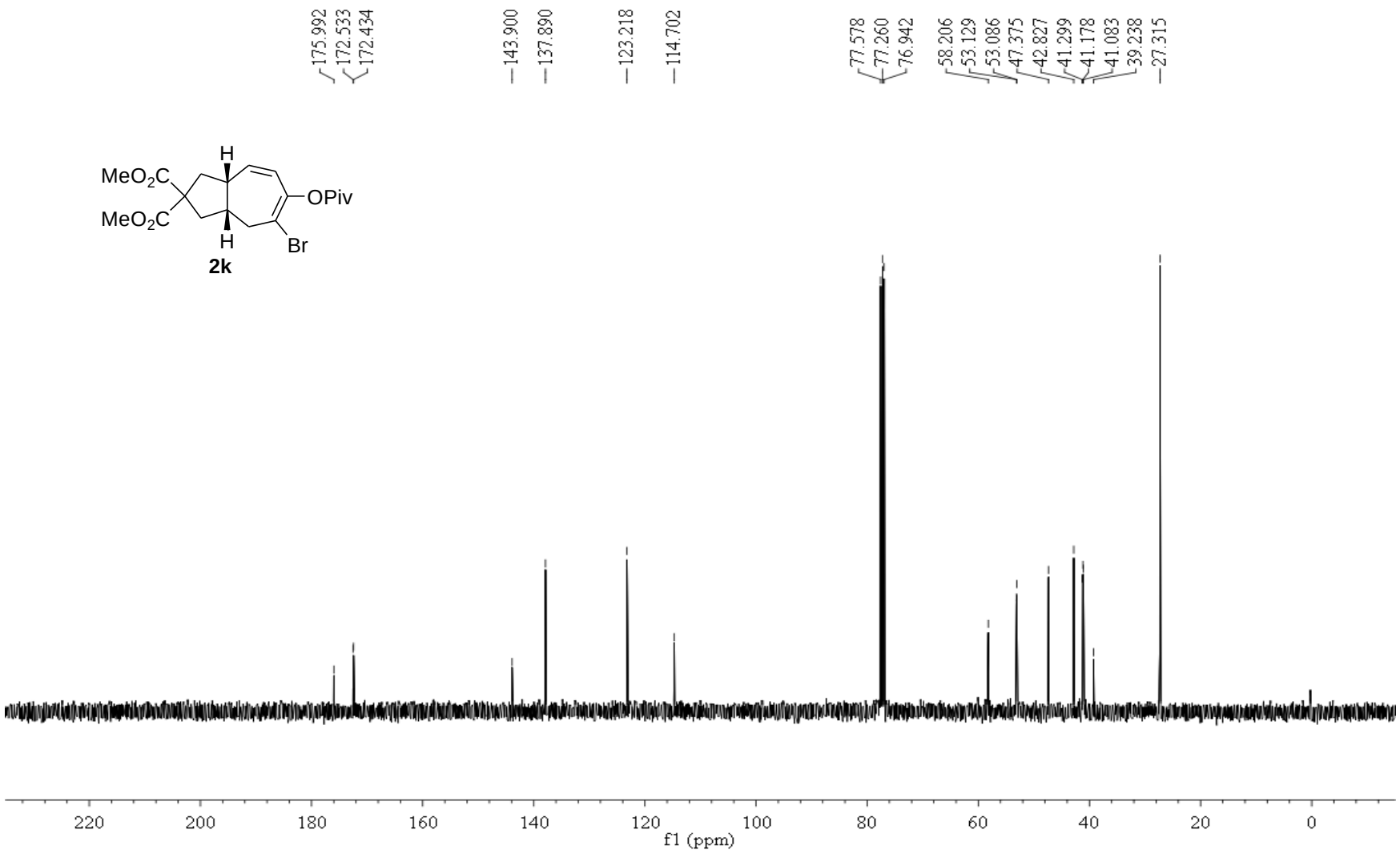
MeO2C
MeO2C
H
OPiv
nC4H9
O
H
2j'

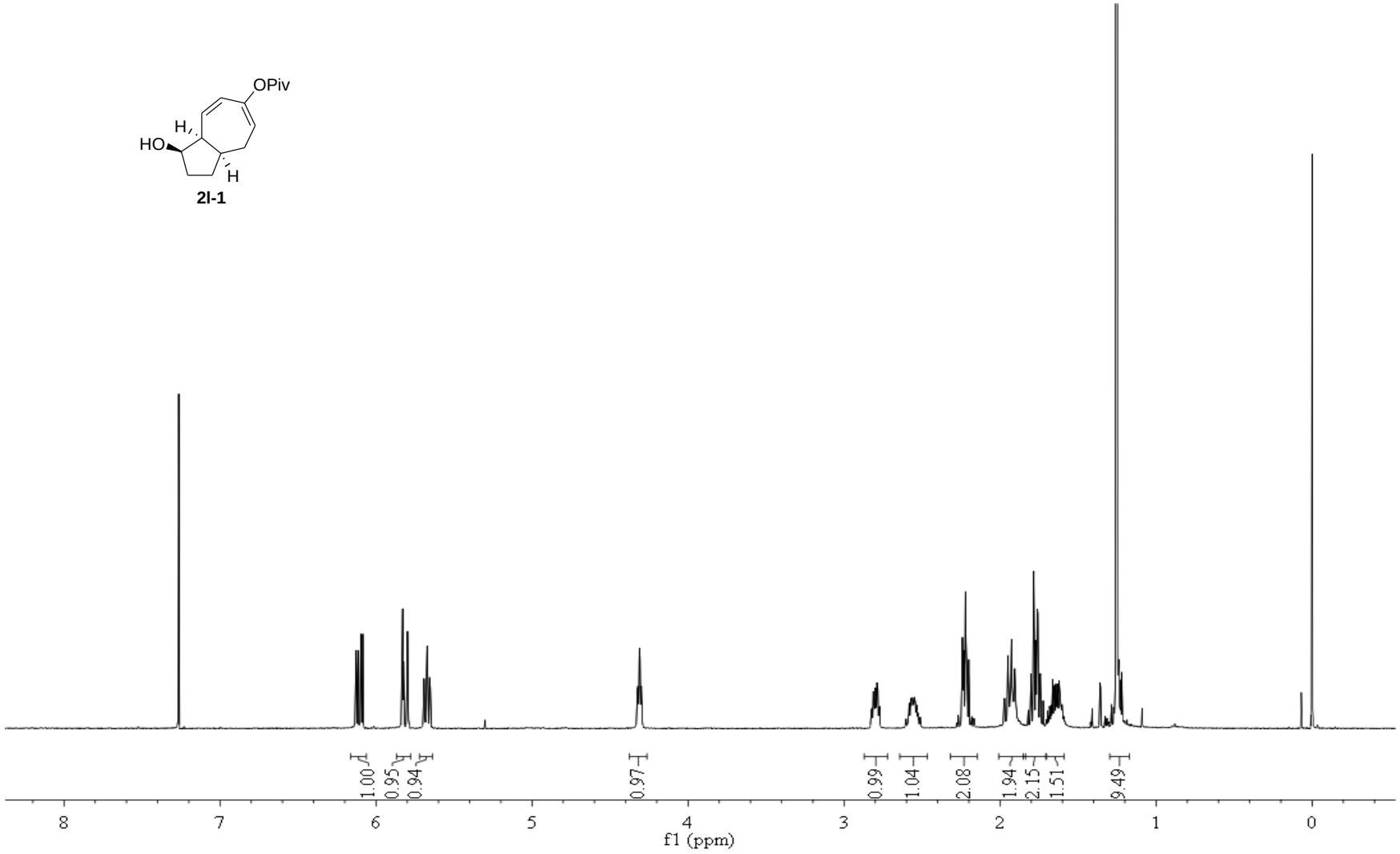
(**2j** : **2j'** = 3 : 1)

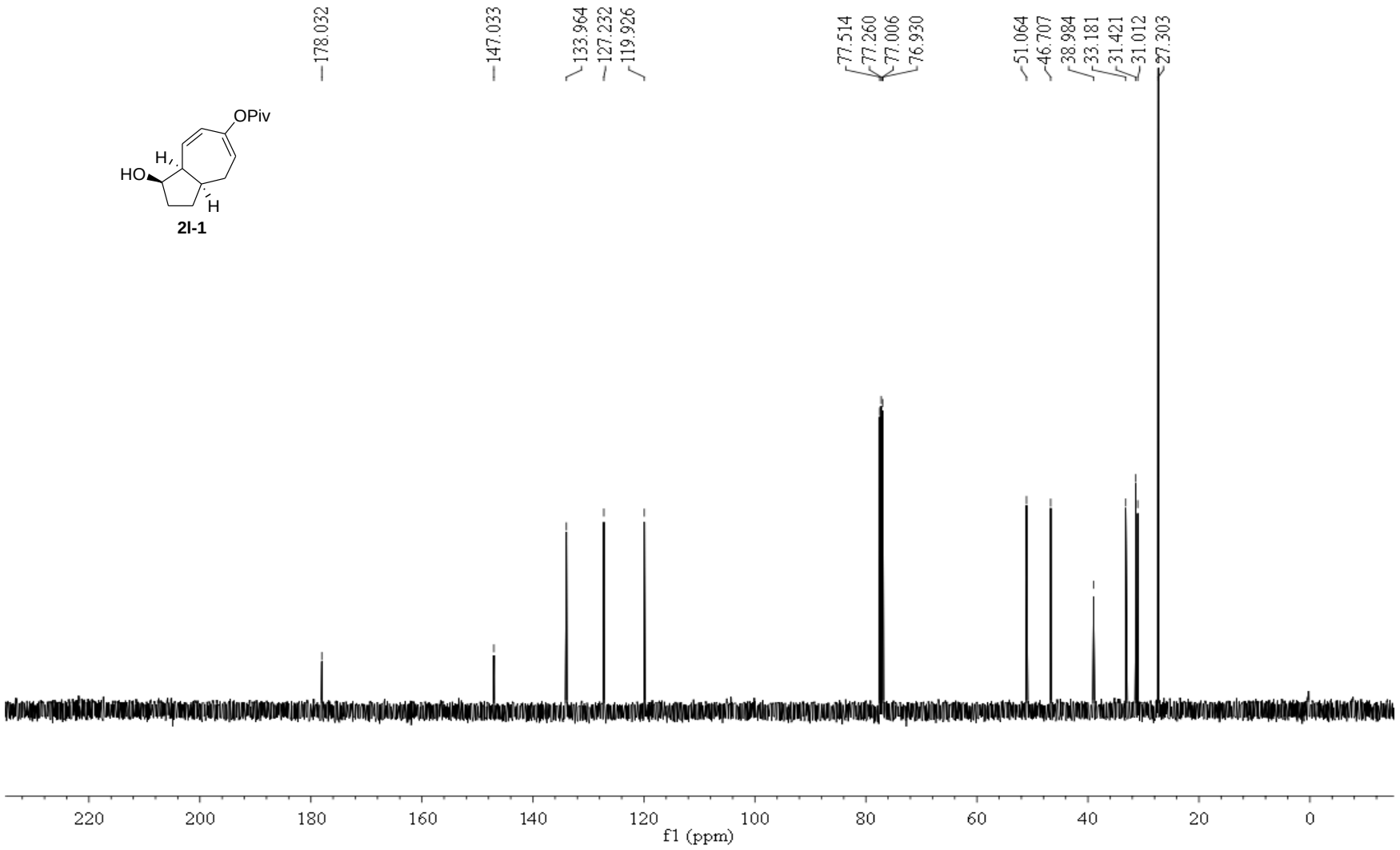
0.24
1.03
0.26
1.00
8.00
0.26
1.23
7.30
0.89
1.15
1.12
1.33
3.39
13.51
4.37
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

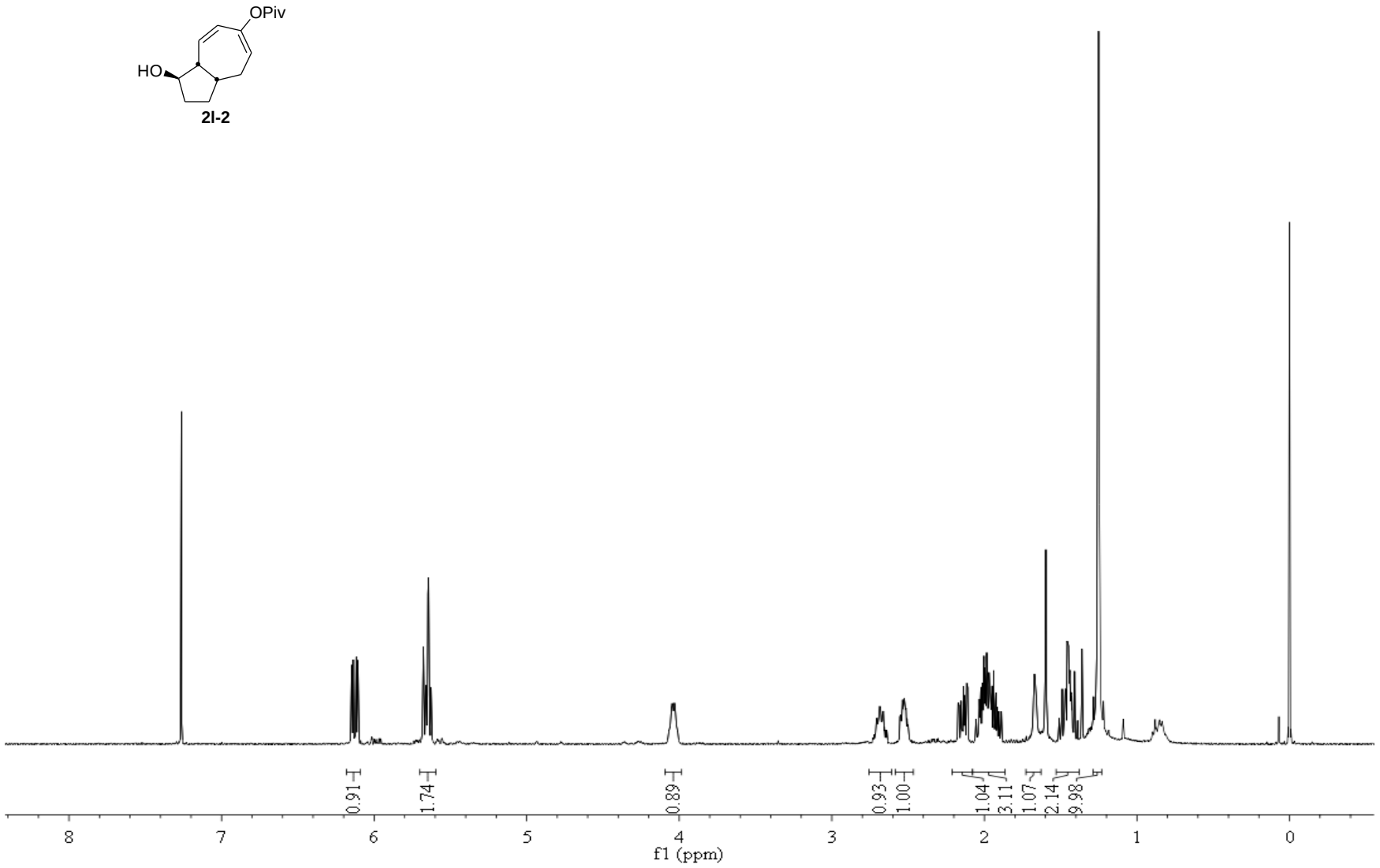

201.31
176.58
172.43
142.84
130.58
124.81
122.65
58.80
53.04
52.99
50.00
43.00
42.45
41.49
41.32
39.21
31.07
26.45
22.62
14.18
MeO2C
MeO2C
H
OPiv
nC4H9
O
2j
2j'
(2j : 2j' = 3 : 1)
f1 (ppm)

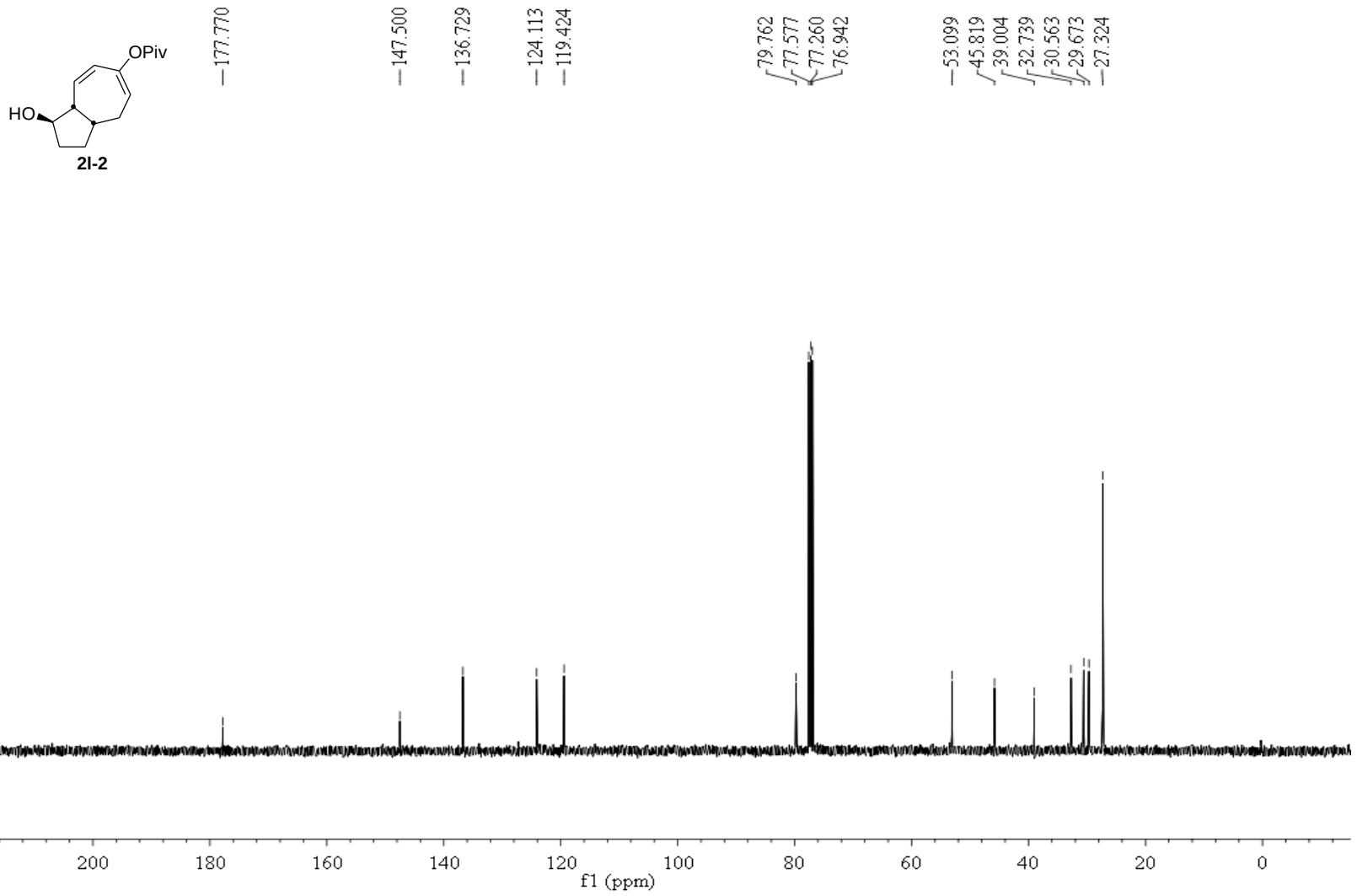

MeO2C
MeO2C
H
H
OPiv
Br
2k
0.98
0.93
6.33
1.11
1.00
3.97
1.94
9.95
8
7
6
5
4
3
2
1
0
f1 (ppm)

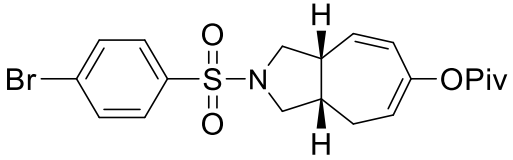

175.992
172.533
172.434
143.900
137.890
123.218
114.702
77.578
77.260
76.942
58.206
53.129
53.086
47.375
42.827
41.299
41.178
41.083
39.238
27.315
MeO2C
MeO2C
H
H
OPiv
Br
2k
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


OPiv
H
HO
H
2l-1
1.00
0.95
0.94
0.97
0.99
1.04
2.08
1.94
2.15
1.51
9.49
8
7
6
5
4
3
2
1
0
f1 (ppm)


178.032
147.033
133.964
127.232
119.926
77.514
77.260
77.006
76.930
51.064
46.707
38.984
33.181
31.421
31.012
27.303
OPiv
H
HO
H
2l-1
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

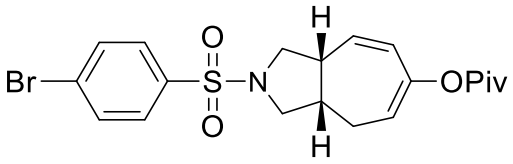

OPiv
HO
2l-2
0.91
1.74
0.89
0.93
1.00
1.04
3.11
1.07
2.14
9.98
8
7
6
5
4
3
2
1
0
f1 (ppm)


OPiv
HO
2l-2
177.770
147.500
136.729
124.113
119.424
79.762
77.577
77.260
76.942
53.099
45.819
39.004
32.739
30.563
29.673
27.324
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

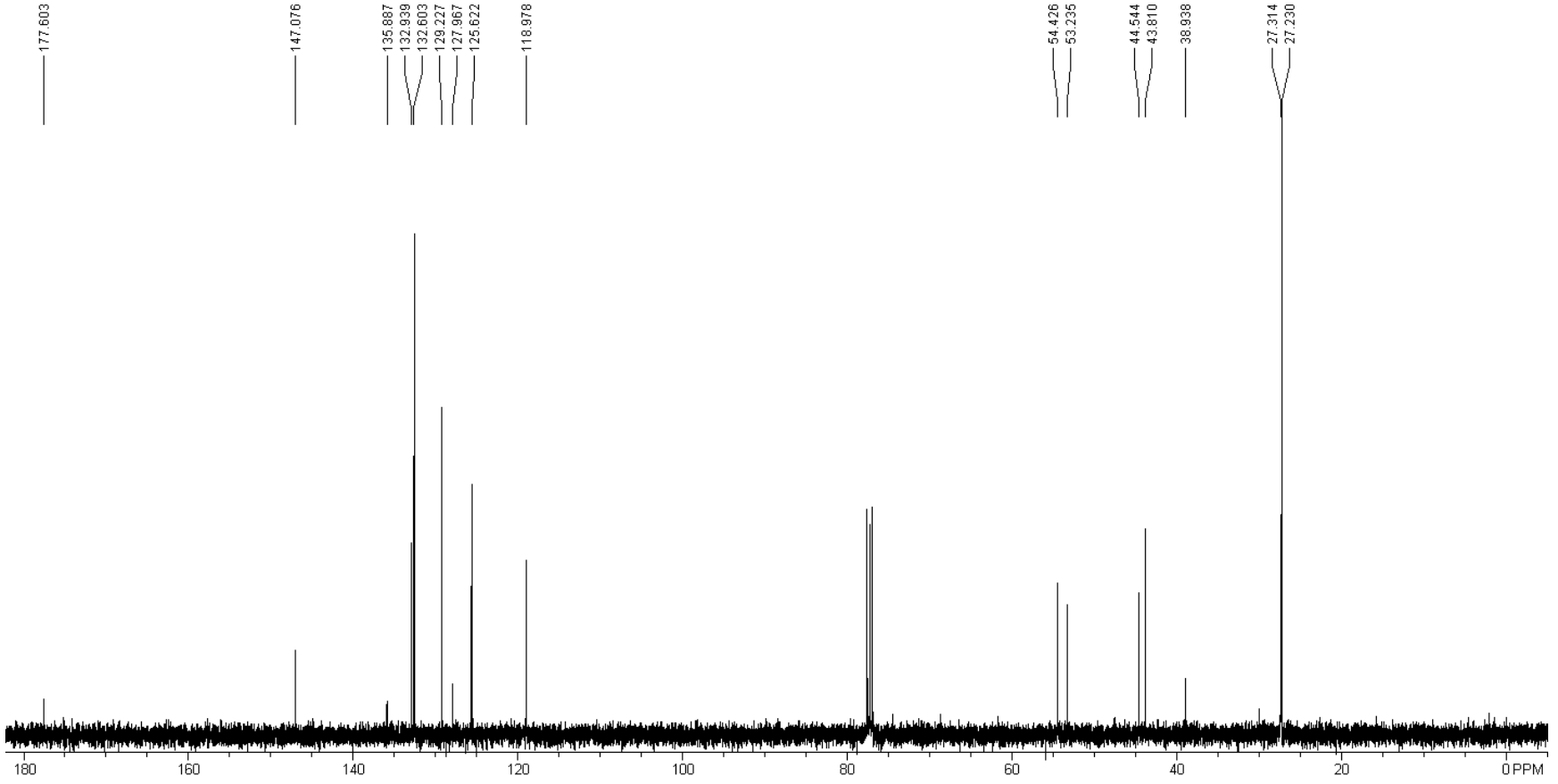

Br
O
S
O
N
H
H
OPiv

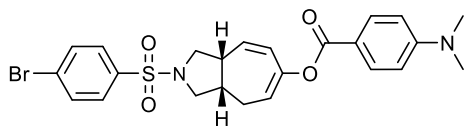
2m

4.00
1.08
2.05
2.18
1.11
1.13
1.12
1.10
1.19
1.16
8.72
8
7
6
5
4
3
2
1
0
PPM

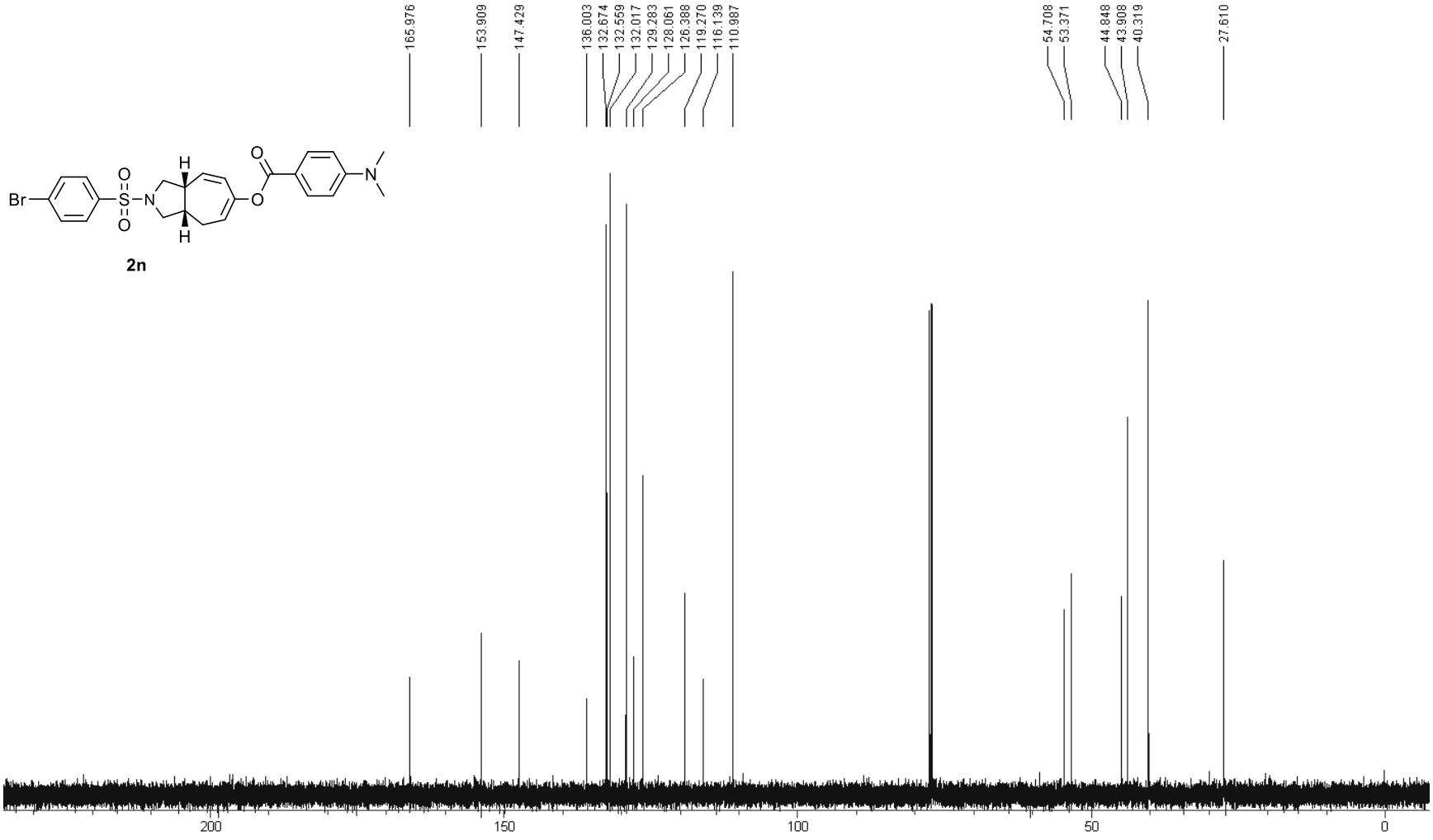

Br
O
S
O
N
H
H
OPiv

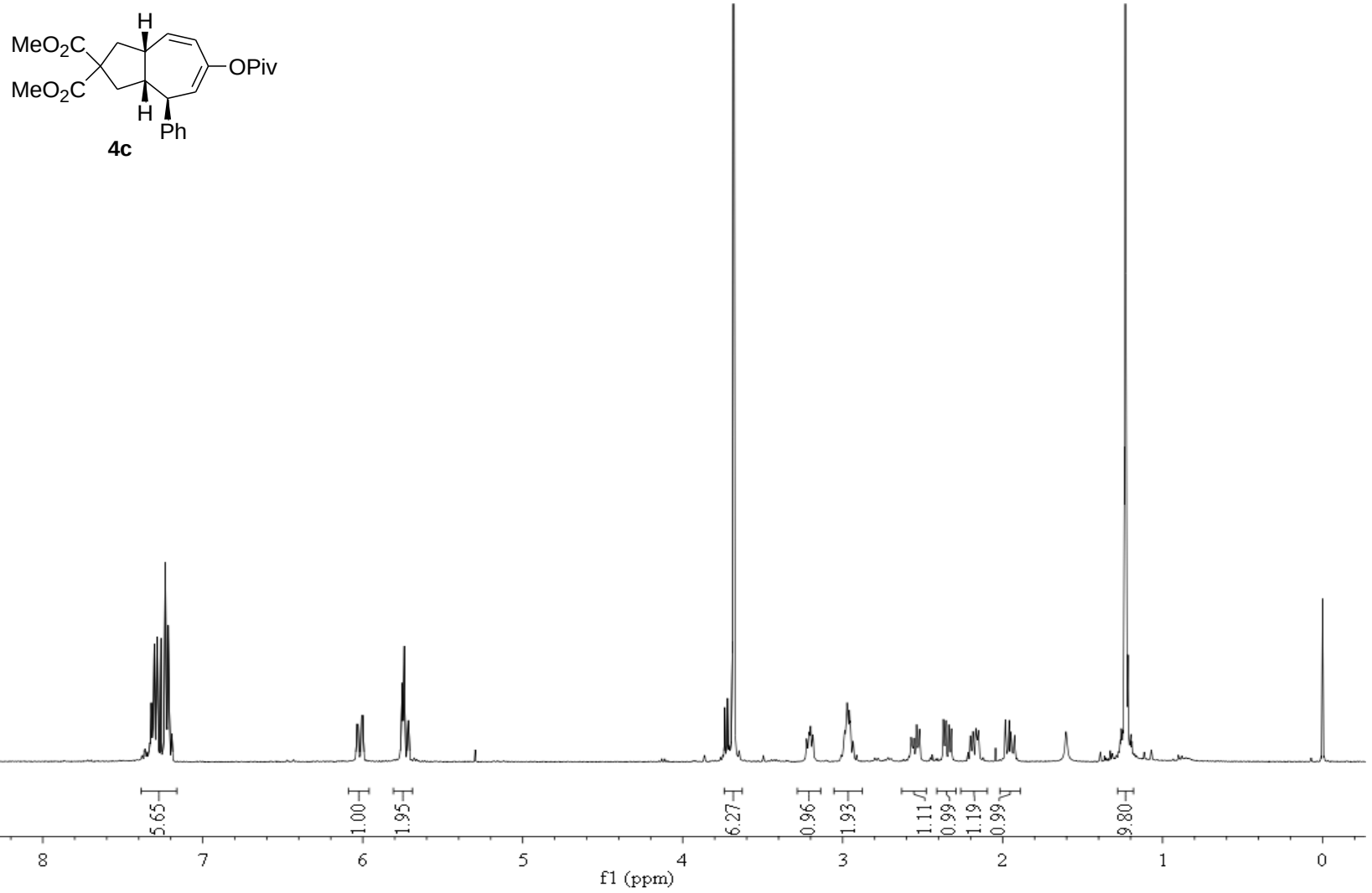
2m

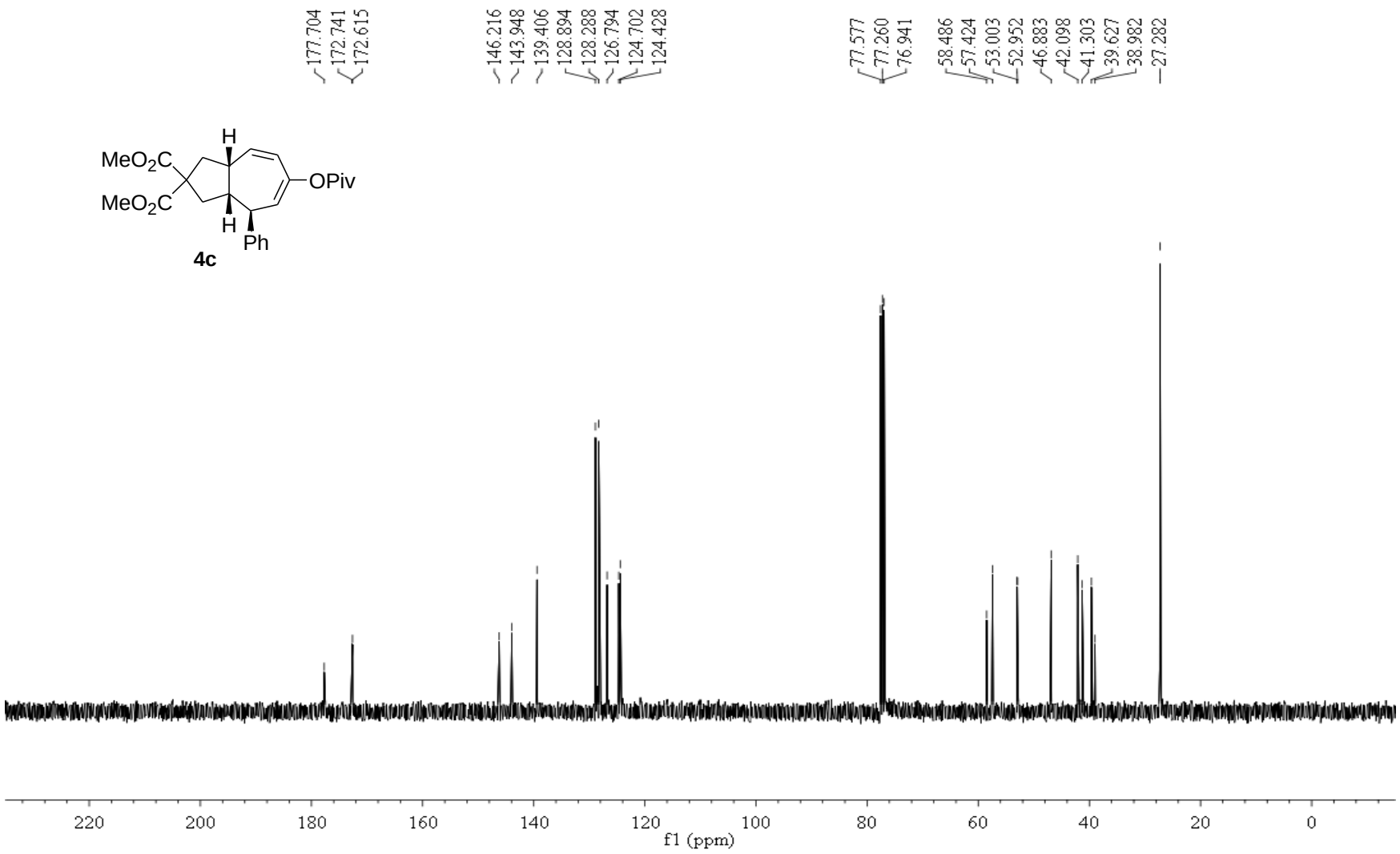

177.603
147.076
135.887
132.939
132.603
129.227
127.967
125.622
118.978
54.426
53.235
44.544
43.810
38.938
27.314
27.230
180
160
140
120
100
80
60
40
20
0 PPM

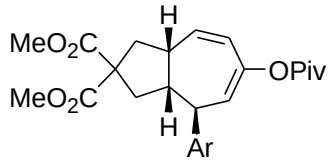


2n

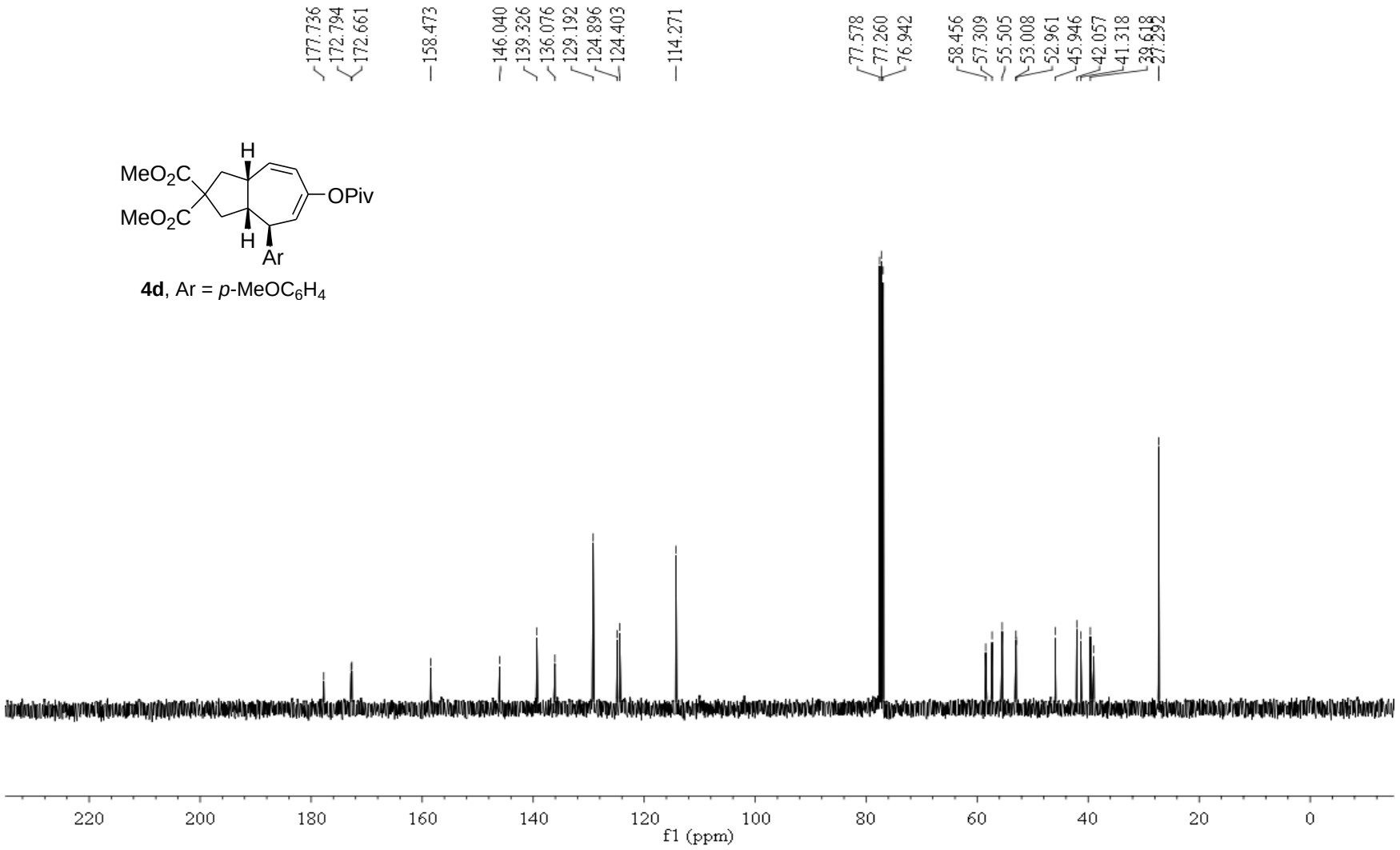

165.976
153.909
147.429
136.003
132.674
132.559
132.017
129.283
128.061
126.388
119.270
116.139
110.987
54.708
53.371
44.848
43.908
40.319
27.610
Br
O
S
O
N
H
H
O
O
N
2n
200
150
100
50
0


MeO2C
MeO2C
H
H
Ph
OPiv
4c
5.65
1.00
1.95
6.27
0.96
1.93
1.11
0.99
1.19
0.99
9.80
8
7
6
5
4
3
2
1
0
f1 (ppm)

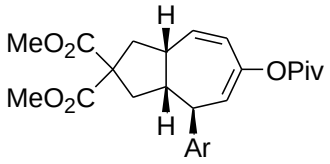

177.704
172.741
172.615
146.216
143.948
139.406
128.894
128.288
126.794
124.702
124.428
77.577
77.260
76.941
58.486
57.424
53.003
52.952
46.883
42.098
41.303
39.627
38.982
27.282
MeO2C
MeO2C
H
H
Ph
OPiv
4c
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



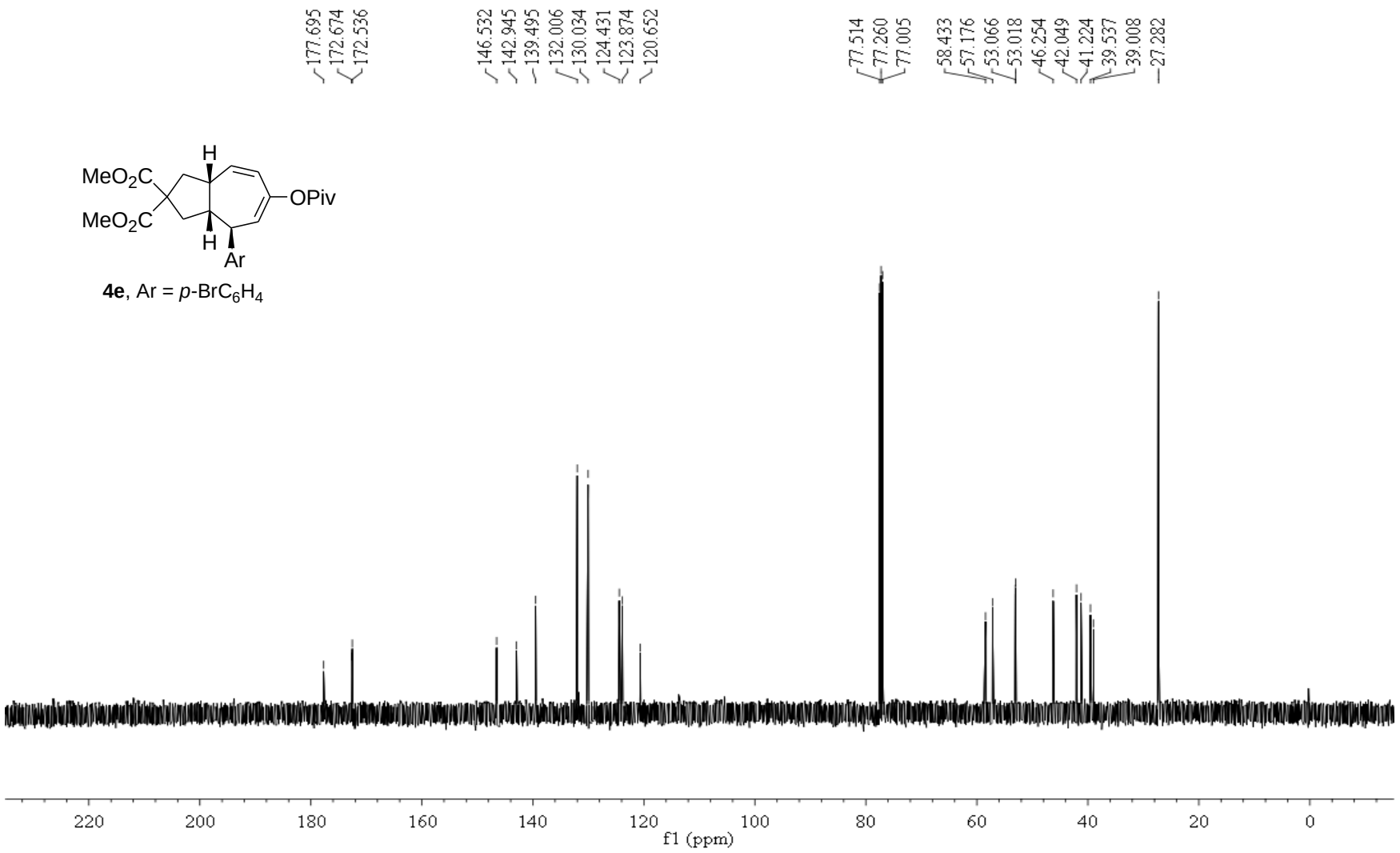
4d, Ar = *p*-$MeOC_6H_4$



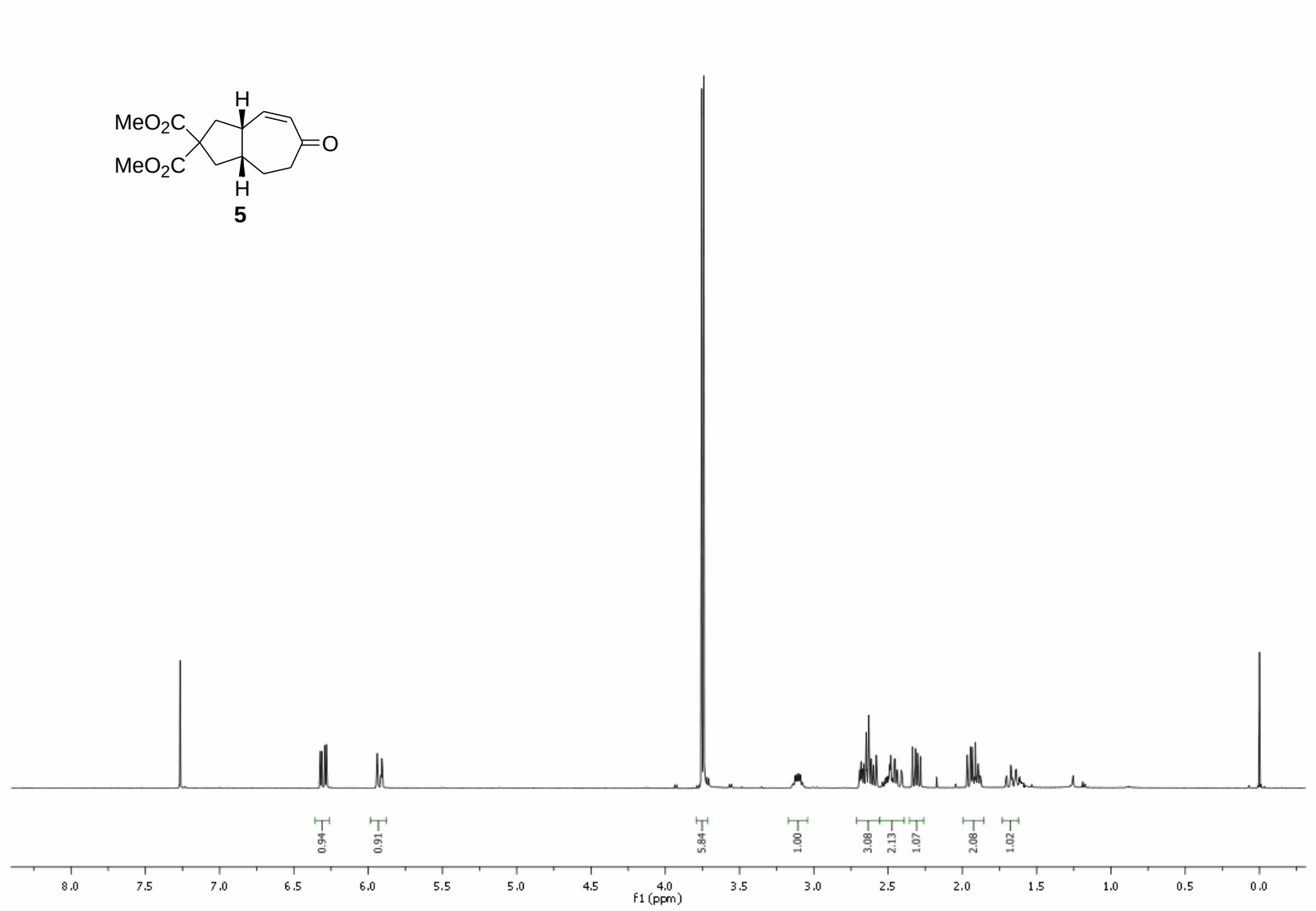
4d, Ar = *p*-$MeOC_6H_4$

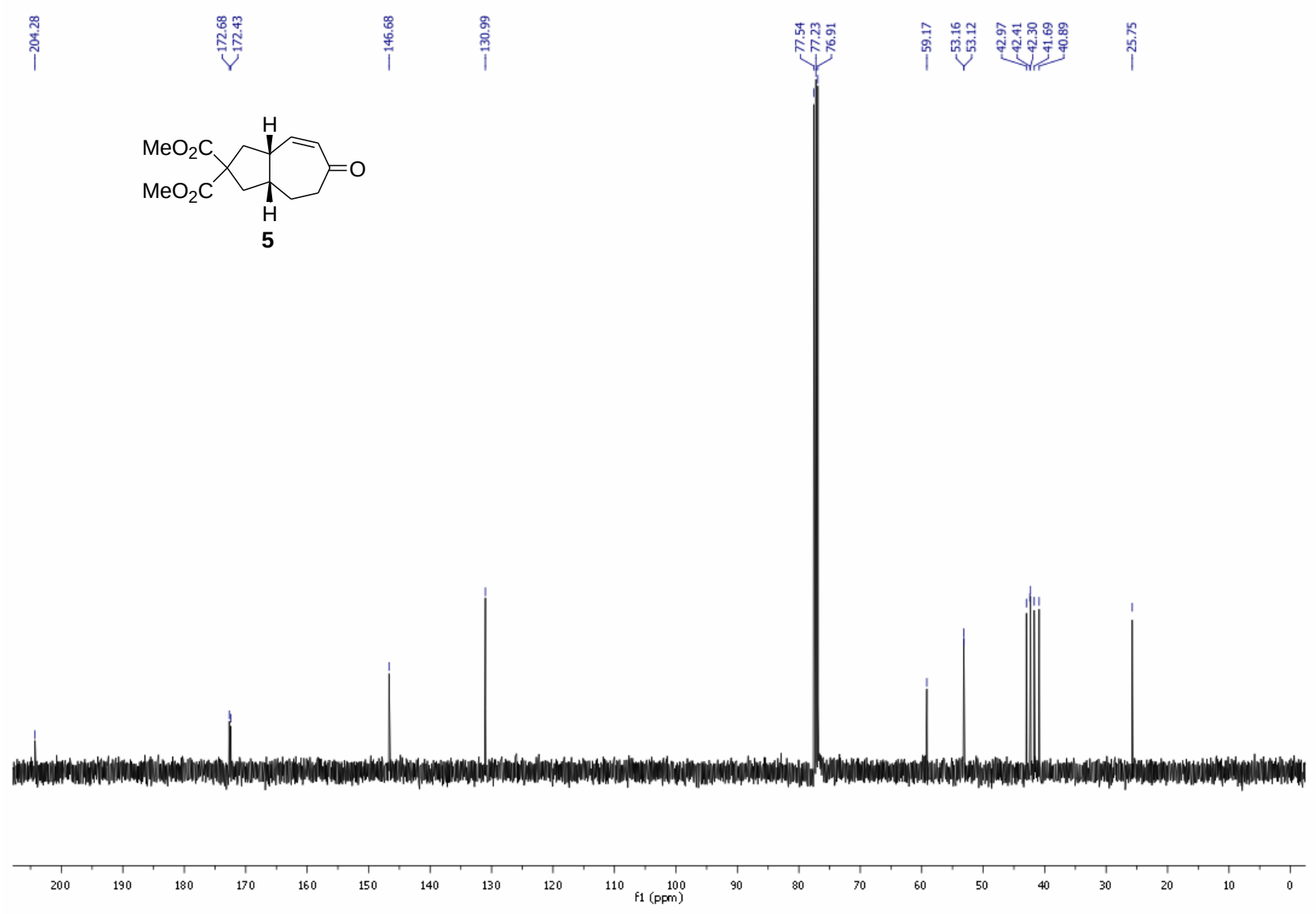


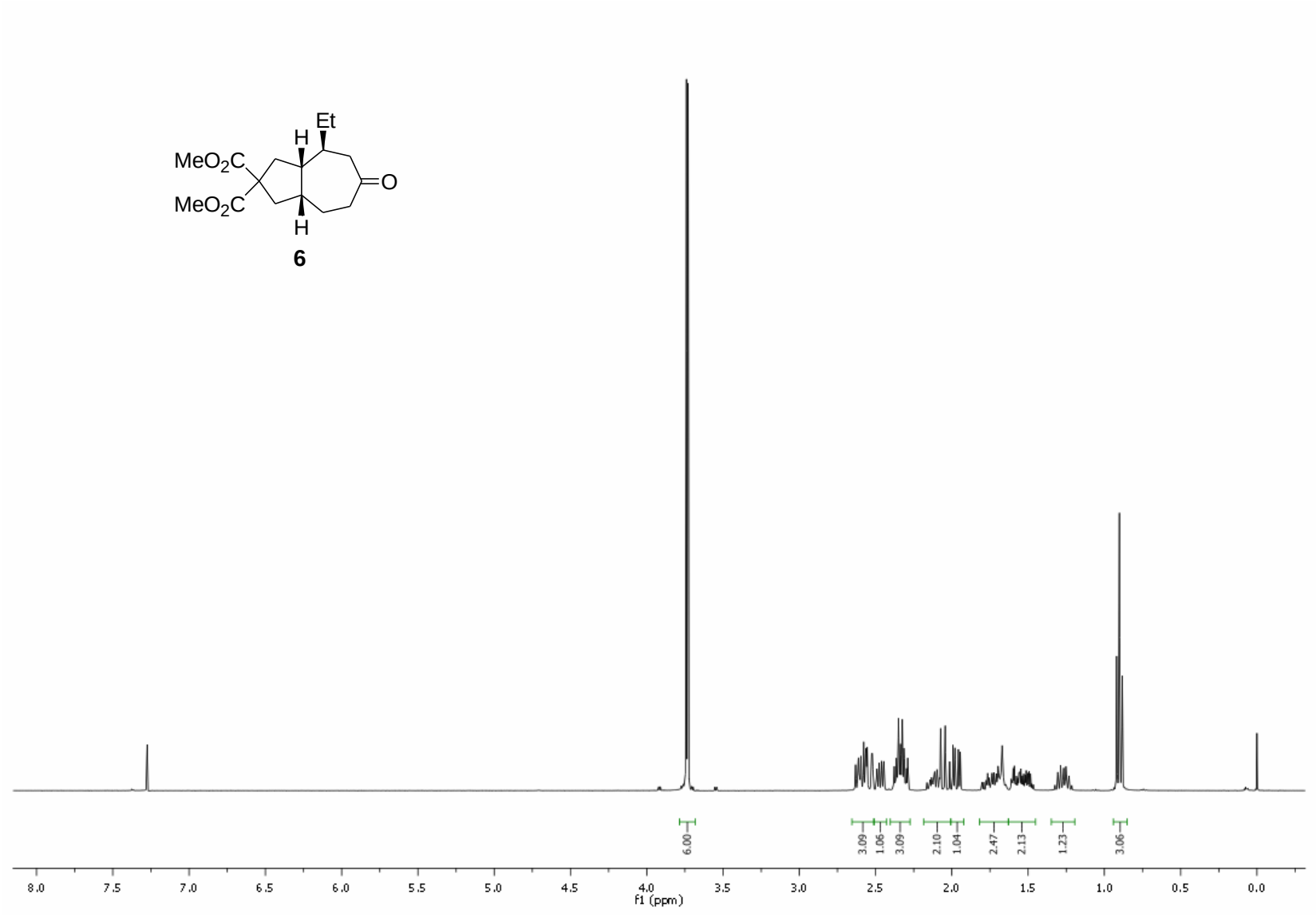
4e, Ar = *p*-BrC_6H_4

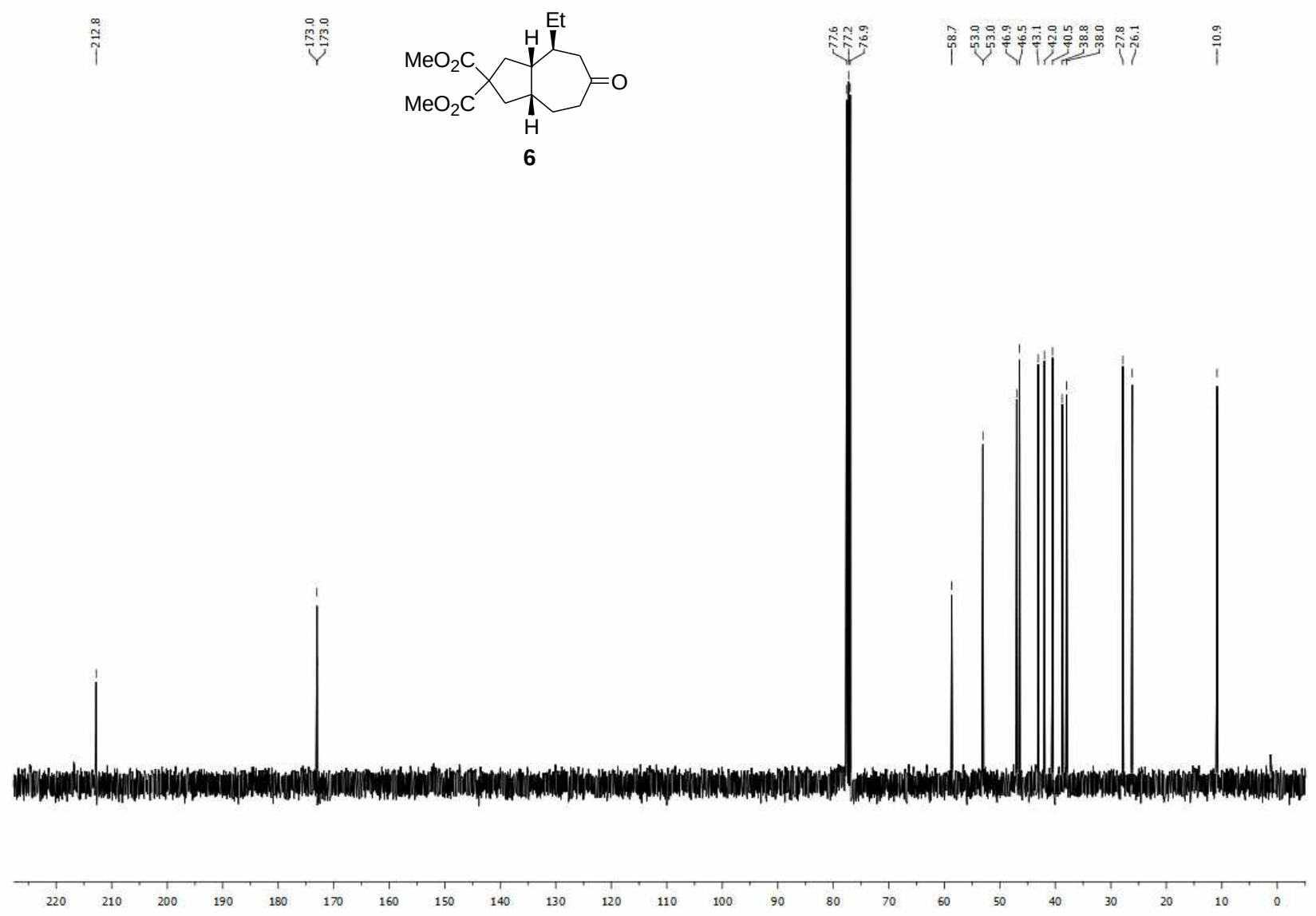


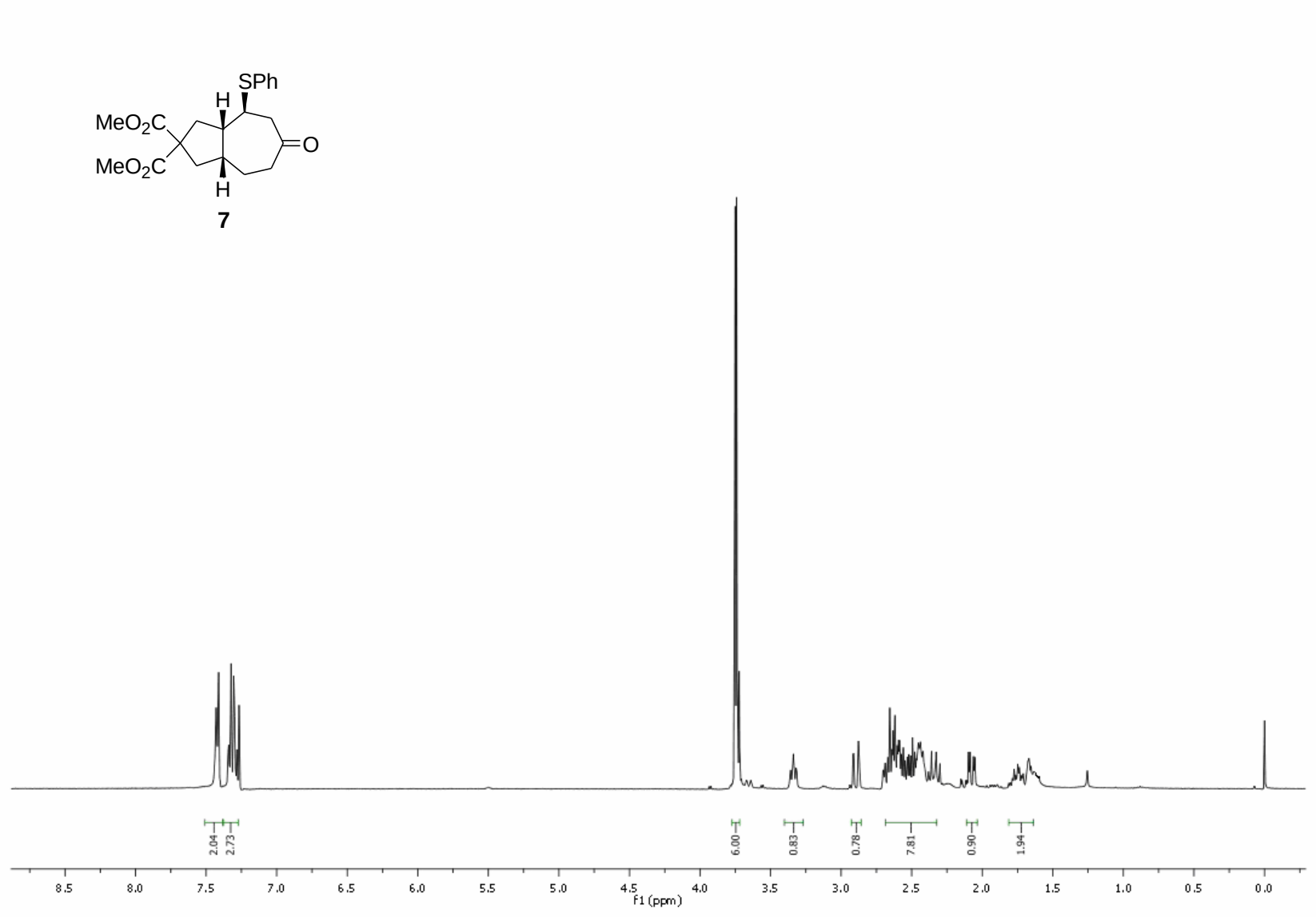
4e, Ar = *p*-BrC_6H_4

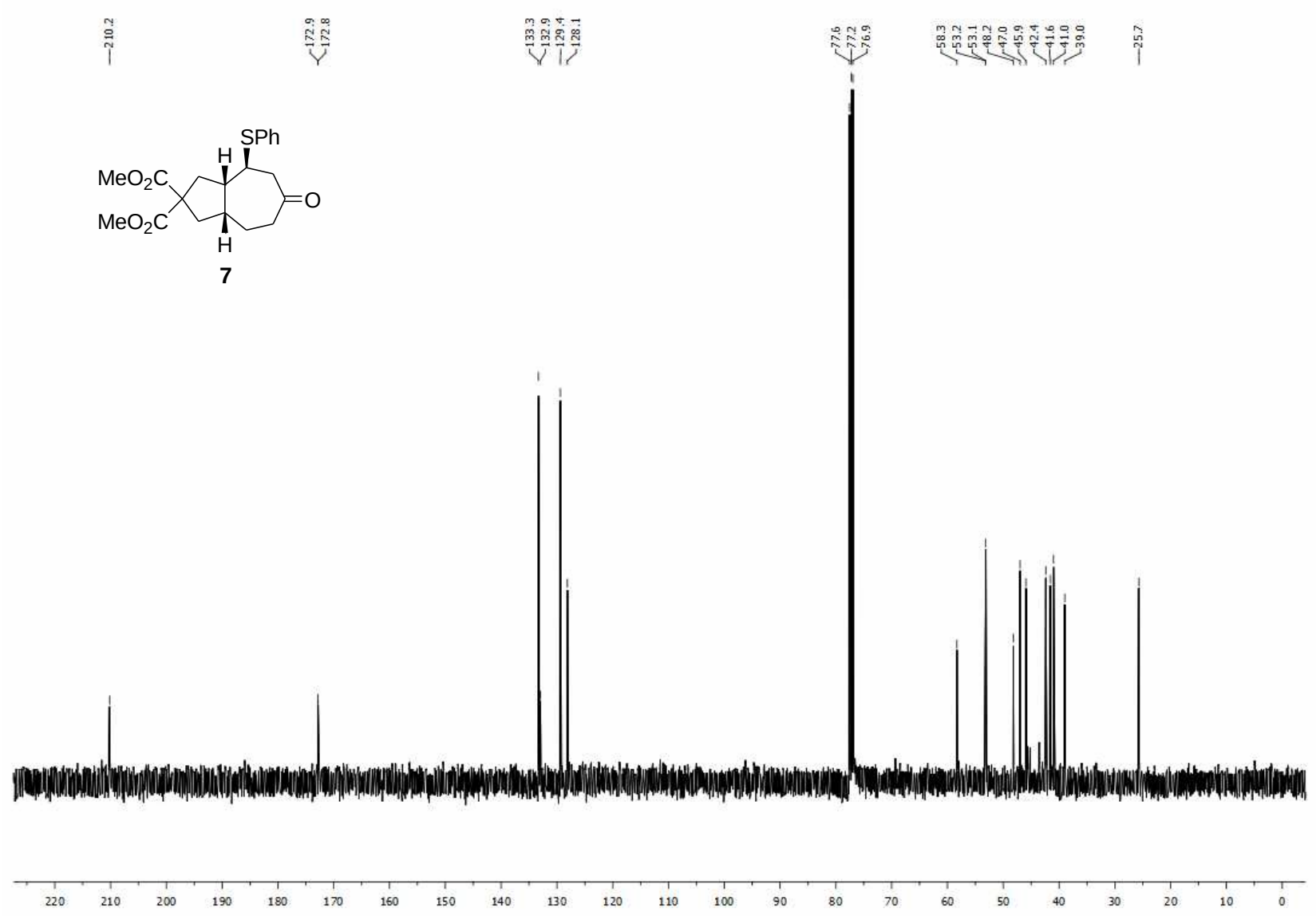

MeO2C
MeO2C
H
H
O
5
0.94
0.91
5.84
1.00
3.08
2.13
1.07
2.08
1.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


204.28
172.68
172.43
146.68
130.99
77.54
77.23
76.91
59.17
53.16
53.12
42.97
42.41
42.30
41.69
40.89
25.75
MeO2C
MeO2C
H
H
O
5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Et
H
MeO2C
MeO2C
O
H
6
6.00
3.09
1.06
3.09
2.10
1.04
2.47
2.13
1.23
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


212.8
173.0
173.0
77.6
77.2
76.9
58.7
53.0
53.0
46.9
46.5
43.1
42.0
40.5
38.8
38.0
27.8
26.1
10.9
Et
H
MeO2C
MeO2C
O
H
6
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


SPh
H
MeO2C
MeO2C
O
H
7
2.04
2.73
6.00
0.83
0.78
7.81
0.90
1.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


210.2
172.9
172.8
133.3
132.9
129.4
128.1
77.6
77.2
76.9
58.3
53.2
53.1
48.2
47.0
45.9
42.4
41.6
41.0
39.0
25.7
SPh
H
MeO2C
MeO2C
O
H
7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0