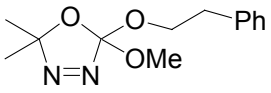
Supporting Information

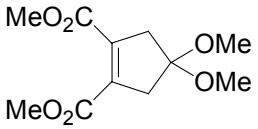
Compound characterization

2-Methoxy-2-phenylethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline **15b**



To a solution of phenethyl alcohol (240 μL, 2.00 mmol) in dry CH_2Cl_2 (5 mL) was added under nitrogen 2-acetoxy-2-methoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (452 mg, 2.40 mmol) and camphorsulfonic acid (23 mg, 0.1 mmol). After 1h of heating to reflux, the solvent was removed under vacuum and the crude product was purified by flash chromatography eluting with CH_2Cl_2/ether 95:5 to give 415 mg (83%) of **15b** as a colorless oil . ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (s, 3H), 1.53 (s, 3H) 2.94 (t, 2H, J = 7.1 Hz), 3.41 (s, 3H), 3.84-4.03 (m, 2H), 7.24 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.0 (q), 36.0 (t), 51.8 (q), 65.4 (t), 119.1 (s), 126.4 (d), 128.4 (d), 129.0 (d), 138.2 (s).

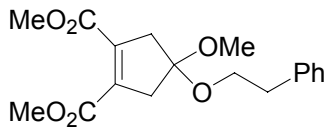
4,4-Dimethoxy-cyclopent-1-ene-1,2-dicarboxylic acid dimethyl ester **18a**



To the solution of dimethyl 1,3-butadiene-2,3-dicarboxylate[1] (0.5 mmol, 85 mg) in dry chlorobenzene (3 mL) was added 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline **15a** (3 eq. 240 mg) and the solution was refluxed under argon for 5 h. After concentrating under vacuum the crude was purified by flash chromatography using CH_2Cl_2/ether 95:5 to give 81.1 mg of **18a** as a colorless oil (67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.88 (s, 4H), 3.21 (s, 6H), 3.75 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.8 (t), 49.3 (q), 52.1 (q), 108.8 (s), 136.3 (s), 165.1 (s); IR (neat, cm^{-1}): 2956, 2836, 1727, 1651; LRMS (m/z (relative intensity)): 244, 212, 153; HRMS calcd for $C_{11}H_{16}O_6$: 244.0947, found : 244.0951.

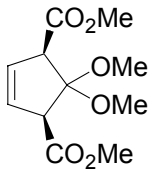
[1] David P. G. Hamon, Paul R. Spurr. *Synthesis*, **1981**, 873-874.

4-Methoxy-4-phenylethoxy-cyclopent-1-ene-1,2-dicarboxylic acid dimethyl ester **18b**



To a solution of dimethyl 1,3-butadiene-2,3-dicarboxylate (85 mg, 0.5 mmol) in dry chlorobenzene (3 mL) was added 2-methoxy-2-phenylethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline **15b** (313 mg, 1.13 mmol) and the solution was refluxed under argon for 3.5 h. After concentrating under vacuum the product was purified by flash chromatography using CH_2Cl_2/ether 95:5 to give 101.4 mg (60%) of **18b** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.86 (m, 2H), 2.88 (s, 4H), 3.10 (s, 3H), 3.63 (t, 2H, J = 7.1 Hz), 3.77 (s, 3H), 7.25 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.3 (t), 43.1 (t), 49.2 (q), 52.1 (q), 63.0 (t), 108.6 (s), 126.2 (d), 128.3 (d), 129.0 (d), 136.3 (s), 138.9 (s), 165.1 (s); IR (neat, cm^{-1}): 3025, 2952, 1719, 1651; LRMS (m/z (relative intensity)): 334, 303, 213, 181; HRMS calcd for $C_{18}H_{22}O_6$: 334.1416, found : 334.1411.

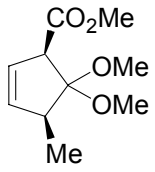
2,2-Dimethoxycyclopent-4-ene-1,3-dicarboxylic acid dimethyl ester **20a**



To the solution of (*E*,*E*)-hexa-2,4-dienedioic acid dimethyl ester (85 mg, 0.5 mmol) in dry chlorobenzene (2 mL) was added over 3h a solution of 2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline **15a** (400 mg, 2.5 mmol) in chlorobenzene (3 mL). At the end of the addition the solution was heated to reflux for 30 min. After concentrating under vacuum, the crude was purified by flash chromatography using CH_2Cl_2/ether 95:5 to give 47 mg (38%) of **20a** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.28 (s, 3H), 3.39 (s, 3H),

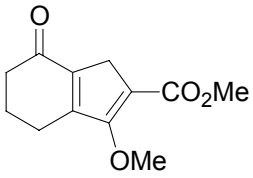
3.67 (m, 2H), 3.70 (s, 6H), 5.88 (s, 2H); LRMS (m/z (relative intensity)): 244, 212, 185, 169; HRMS calcd for $C_{11}H_{16}O_6$: 244.0947, found: 244.0941.

2,2-Dimethoxy-3-methylcyclopent-4-ene-1-carboxylic acid, methyl ester **20b**



The reaction was performed as per cyclopentene **20a** starting with methyl 2,4-hexadienoate (126 mg, 1.0 mmol) The crude was purified by flash chromatography using CH_2Cl_2/ether 95:5 to give 55 mg (28%) of **20b** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (d, 3H, *J* = 7.7 Hz), 2.74-2.80 (m, 1H), 3.30 (s, 3H), 3.63-3.69 (m, 1H), 3.70 (s, 3H), 5.58 (m, 1H), 5.97 (m, 1H).

2-Carboxy-1-methoxy-4-oxo-4,6-dihydro-3*H*-indene, methyl ester (**22**).

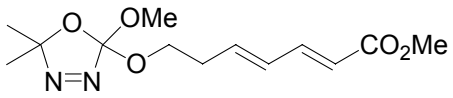


To a solution of methyl 3-(1-oxo-2-cyclohexen-2-yl)acrylate (**21**) (90 mg, 0.5 mmol) in dry toluene (3 mL) under argon was added the 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline **15a** (160 mg, 1.0 mmol). After 6 h of heating to reflux the crude product was concentrated under vacuum and purified by flash chromatography using CH_2Cl_2/ether 95:5 to give 32 mg (30%) of **22** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.09 (qi, 2H, *J* = 6.6 Hz), 2.48 (m, 4H), 3.43 (m, 2H), 3.75 (s, 3H), 4.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1 (t), 23.4 (t), 35.7 (t), 38.1 (t), 51.4 (q), 61.6 (q),

112.3 (s), 130.5 (s), 139.8 (s), 158.8 (s), 162.4 (s), 195.3 (s); LRMS (m/z (relative intensity)): 222, 190, 163, 135; HRMS calcd for $C_{12}H_{14}O_4$: 222.0892, found: 222.0898.

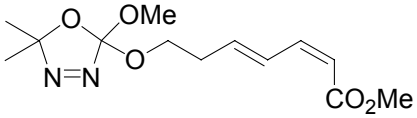
Compounds **23a-c** : see after compound **34**.

(*EE*)-Oxadiazoline **24a**.



The reaction was performed according to the preparation of **24b** starting from **23a** (5.6 mmol). The product was purified by flash chromatography by using CH_2Cl_2/ether 98:2 to give 1.39 g of **24a** as a colorless oil (86 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (s, 3H), 1.54 (s, 3H), 2.49 (q, 2H, *J* = 6.6 Hz), 3.42 (s, 3H), 3.73 (s, 3H), 3.73-3.89 (m, 2H), 5.80 (d, 1H, *J* = 15.4 Hz), 6.09 (m, 1H), 6.23 (dd, 1H, *J* = 15.1, 10.4 Hz), 7.25 (dd, 1H, *J* = 15.4, 10.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.9 (q), 24.1 (q), 33.0 (t), 51.4 (q), 51.8 (q), 63.3 (t), 119.1 (s), 119.7 (d), 130.2 (d), 136.8 (s), 139.4 (d), 144.5 (d), 167.3 (s); IR (neat, cm^{-1}): 1713, 1643, 1615; LRMS (C.I. NH_3, m/z): 302, 253, 232; HRMS calcd for $C_{13}H_{24}N_3O_5$ (MNH_4^+): 302.1716, found: 302.1710.

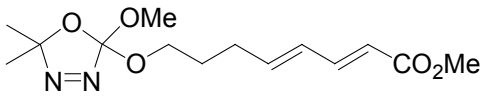
(2*Z*-4*E*)-Oxadiazoline **24a**



The reaction was performed according to the preparation of **24b** starting from the corresponding alcohol (434 mg, 2.7 mmol) to give *ZE*-**24a** (571 mg, 74 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 3H), 1.54 (s, 3H), 2.53 (q, 2H, *J* = 6.6 Hz), 3.43 (s, 3H), 3.71 (s, 3H), 3.74-3.91 (m, 2H), 5.59 (d, 1H, *J* = 11.5 Hz), 6.05 (dt, 1H, *J* = 15.4, 7.7 Hz), 6.53 (t, 1H, *J* = 11.5 Hz), 7.41 (dd, 1H, *J* = 15.4, 11.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.9 (q), 24.1 (q), 33.1 (d), 51.1 (q), 51.9 (q), 63.6 (t), 116.0 (d), 119.2 (s), 128.8 (d), 140.4 (d), 144.8 (d), 166.7 (s); IR (neat, cm^{-1}): 2994, 2952, 2900, 1719, 1644, 1605;

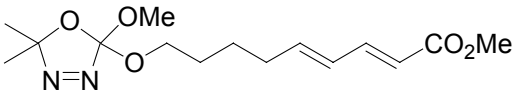
LRMS (m/z (relative intensity)): 302, 285, 232, 215; HRMS calcd for $C_{13}H_{24}N_3O_5$ (MNH_4^+): 302.1716, found: 302.1721.

(*EE*)-Oxadiazoline **24b**



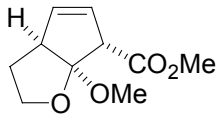
To a solution of alcohol **23b** (340 mg, 2.0 mmol) in dry CH_2Cl_2 (5 mL) was added under nitrogen the 2-acetoxy-2-methoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline **15c** (753 mg, 4.0 mmol) and a catalytic amount of camphorsulfonic acid (23 mg, 0.1 mmol). After 45 min of heating to reflux, the solvent was removed under vacuum and the crude product dissolved in a mixture of dry THF/MeOH (5:10 mL) under nitrogen. To this solution was added sodium methoxide (1.08 g, 20.0 mmol) to remove the excess of oxadiazoline and its acyclic isomer. After stirring 30 min at r.t., 70 mL of ether was added and the reaction was hydrolyzed with a solution of 20% citric acid. The aqueous layer was then extracted with diethyl ether and the combined organic layers were washed with $NaHCO_3$, then dried over Na_2SO_4. After concentrating under vacuum, the crude product was purified by flash chromatography using hexanes/ether 50:50 as solvent to give the corresponding oxadiazoline **24b** as a colorless oil (534 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (s, 3H), 1.55 (s, 3H), 1.78 (qi, 2H, *J* = 7.1 Hz), 2.27 (q, 2H, *J* = 7.1 Hz), 3.44 (s, 3H), 3.65-3.80 (m, 2H), 3.74 (s, 3H), 5.80 (d, 1H, *J* = 15.4 Hz), 6.16 (m, 2H), 7.24 (dd, 1H, *J* = 13.2, 10.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.9 (q), 24.1 (q), 28.5 (t), 29.3 (t), 51.4 (q), 51.8 (q), 63.7 (t), 119.0 (s), 119.1 (d), 129.0 (d), 143.1 (d), 144.9 (d), 167.5 (s); IR (neat, cm^{-1}): 2990, 2947, 2843, 1718, 1642, 1614; LRMS (m/z (relative intensity)): 267, 212, 197; HRMS calcd for $C_{13}H_{19}N_2O_4$ (M-OCH_3): 267.1345, found: 267.1349.

(*EE*)-Oxadiazoline **24c**



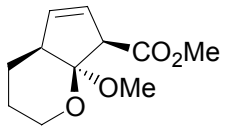
The reaction was performed according to the preparation of **24b** starting from **23c** (553 mg, 3.0 mmol). The product was purified by flash chromatography by using hexanes/ether 60:40 to give 920 mg of **24c** (98 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48-1.55 (m, 2H), 1.53 (s, 3H), 1.54 (s, 3H), 1.63 (m, 2H), 2.20 (q, 2H, *J* = 6.8 Hz), 3.44 (s, 3H), 3.65 (m, 1H), 3.73 (s, 3H), 3.76 (m, 1H), 5.79 (d, 1H, *J* = 15.4 Hz), 6.12 (m, 2H), 7.25 (dd, 1H, *J* = 15.9, 9.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.9 (q), 24.1 (q), 25.0 (t), 28.8 (t), 32.4 (t), 51.3 (q), 51.7 (q), 64.3 (t), 118.9 (d), 128.6 (d), 137.0 (s), 139.6 (s), 144.0 (d), 145.1 (d), 167.6 (s); IR (neat, cm^{-1}): 1717, 1645, 1613; LRMS (m/z (relative intensity)): 312, 281, 272, 253; HRMS calcd for $C_{15}H_{24}N_2O_5$: 312.1685, found: 312.1696.

Cycloadduct (±)-**26a**

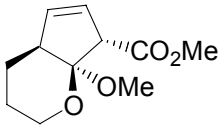


The reaction was performed according to the preparation of **25b**/**26b** starting from from **24a** (568 mg, 2.0 mmol). The crude adduct was purified by flash chromatography by using CH_2Cl_2/ether 95:5 to give **26a** (340 mg, 86 %) as the major product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.80 (m, 1H), 2.14 (m, H), 3.29 (s, 3H), 3.39 (m, 1H), 3.70 (s, 3H), 3.76 (m, 1H), 3.84 (q, 1H, *J* = 8.3 Hz), 4.05 (dt, 1H, *J* = 8.3, 4.4 Hz), 5.63 (m, 1H), 5.79 (m, H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.9 (t), 50.8 (q), 51.9 (q), 52.1 (d), 58.9 (d), 68.2 (t), 118.2 (q), 127.7 (d), 136.3 (d), 171.1 (s); IR (neat, cm^{-1}): 3057, 2950, 2888, 1738, 1614; LRMS (m/z (relative intensity)): 198, 183, 139; HRMS calcd for $C_{10}H_{14}O_4$: 198.0892, found: 198.0897.

Cycloadducts (±)-**25b** and (±)-**26b**



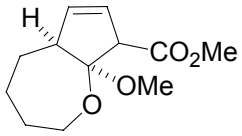
25b



26b

Oxadiazoline **24b** (298 mg, 1.0 mmol) in clean glassware was dissolved in dry toluene (10 mL) under argon and refluxed overnight. After evaporationg the solvent the crude product was purified by flash chromatography using CH_2Cl_2/ether 98:2 as solvent to give 184 mg of **25b** and **26b** (60%) as well as 25% of carbonate as a colorless oils. The isomers **25b** and **26b** were separated using preparative TLC to obtain pure samples. **25b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42-1.58 (m, 2H), 1.76 (m ,2H), 2.62 (m, 1H), 3.43 (s, 3H), 3.62 (m, 2H), 3.70 (s, 3H), 3.71 (m, 1H), 5.71 (m, 1H), 5.76 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5 (t), 22.6 (t), 48.8 (d), 50.3 (q), 51.9 (q), 58.8 (d), 59.8 (t), 108.6 (s), 127.1 (d), 135.2 (d), 171.6 (s); IR (neat, cm^{-1}): 1740, 1643; LRMS (m/z (relative intensity)): 212, 197, 180, 165, 152; HRMS calcd for $C_{11}H_{16}O_4$: 212.1048, found: 212.1054. **26b:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39 (m, 1H), 1.51 (m, 1H), 1.80 (m, 2H), 3.06 (m, 1H), 3.32 (s, 3H), 3.60 (m, 3H), 3.70 (s, 3H), 5.80 (m, 1H), 5.84 (m, H); LRMS (m/z (relative intensity)): 212, 197, 180, 165, 152; HRMS calcd for $C_{11}H_{16}O_4$: 212.1048, found: 212.1053

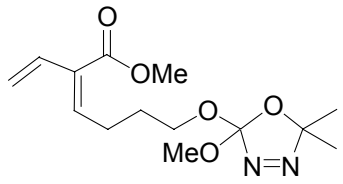
Cycloadduct (±)-**25c** or (±)-**26c**



The reaction was performed according to the preparation of **25b**/**26b** from **24c** (468 mg, 1.5 mmol). The product was inseparable from the corresponding carbonate (339 mg, 70 % product, 30% carbonate by NMR) and the crude was used for the next step (see

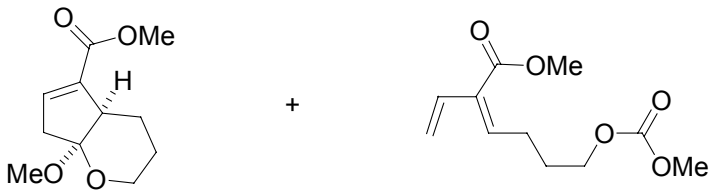
reduction of **25c** or **26c**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30-1.86 (m, 6H), 2.62 (m, 1H), 3.29 (s, 3H), 3.63-3.79 (m, 3H), 3.71 (s, 3H), 5.51 (m, H), 5.93 (m, 1H); LRMS (m/z (relative intensity)): 226, 211, 194, 184; HRMS calcd for $C_{12}H_{18}O_4$: 226.1205, found: 226.1210.

Diene **27**



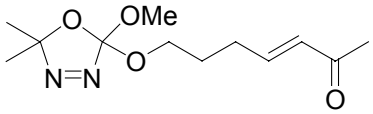
The crude product **37b** (98 mg, 0.58 mmole) and oxadiazoline **15c** (239 mg, 1.3 mmole) were dissolved in methylene chloride (2.3 mL) and 10-camphorsulfonic acid (15 mg, 0.065 mmol) was added. The reaction mixture was heated to reflux and stirred for 1h. The solvent was removed under vacuum and THF (2 mL), MeOH (2 mL) and sodium methoxyde (40 mg, 0.74 mmol) were added successively. The reaction mixture was stirred at room temperature for 30 min and then quenched with saturated NH_4Cl. The reaction mixture was extracted three times with diethyl ether. The organic layers were combined, washed once with brine, dried over anhydrous magnesium sulfate and concentrated under vacuum to give a yellow oil. The crude product was purified by flash chromatography on a silica gel column eluting with ethyl acetate / hexanes (10% → 20%) to give **27** as a colorless oil (88 mg, 51 %). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 6.32 (dd, 1H, *J* = 17,6, 11.0 Hz), 5.96 (t, 1H, *J* = 7.7 Hz), 5.25 (d, 1H, *J* = 17.6 Hz), 5.10 (d, 1H, *J* = 11.0 Hz), 3.80-3.62 (m, 2H), 3.79 (s, 3H), 3.44 (s, 3H) 2.42-2.34 (m, 2H), 1.81-1.72 (m, 2H), 1.54 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.6 (s), 138.9 (d), 137.0 (s), 134.5 (d), 133.7 (s), 119.0 (s), 115.1 (t), 64.0 (t), 51.9 (q), 51.6 (q), 29.0 (t), 26.3 (t), 24.1 (q), 24.0 (q). IR (neat, cm^{-1}) 3068, 1726, 1584, 1469. LRMS (*m/z*, relative intensity) 316 (MNH_4^+, 10), 246 (100), 229 (97), 213 (75). HRMS calcd for $C_{14}H_{26}O_5N_3$ (MNH_4^+) : 316.1872, found : 316.1881.

Adduct (±)-**28**



Diene **27** (80.0 mg, 0.27 mmol) was dissolved in toluene (5 mL). The reaction mixture was heated to reflux and stirred for 12h. The solvent was removed under vacuum to give a yellow oil. The crude product was purified by flash chromatography on a silica gel column eluting with ethyl acetate / hexanes (10%) to give 54 mg of **28** and a carbonate, both as colorless oils in 80% and 16%, respectively. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79-6.76 (m, 1H), 3.74 (s, 3H), 3.70 (m, 2H), 3.29 (s, 3H), 2.60-2.56 (m, 2H), 2.10-1.77 (m, 2H), 1.69-1.43 (m, 2H). ^{13}C NMR (75MHz, toluene-d_8) : δ 165.2 (s), 141.6 (d), 137.3 (s), 108.3 (s), 60.7 (t), 51.3 (q), 50.2 (q), 48.2 (d), 42.5 (t), 22.1 (t), 21.8 (t). IR (neat, cm^{-1}) 3054, 1717, 1249. LRMS (*m/z*, relative intensity) 212 (M^+, 75), 180 (100), 152 (88), 121 (83). HRMS calcd for $C_{11}H_{16}O_4$: 212.1048, found : 212.1052.

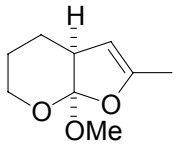
Enone **29**



Under argon, 7-hydroxy-3-hepten-2-one (0.559 g, 4.36 mmol), was dissolved in anhydrous dichloromethane (25 mL). Then, oxadiazoline **15c** (1.749 g, 9.30 mmol) and camphorsulfonic acid (50 mg, 0.218 mmol) were added to the solution. The reaction mixture was heated to reflux and stirred for 30 min. Then, it was cooled down to r.t. The solvent was removed by evaporation under reduced pressure to give a yellowish oil. The crude product was purified by flash chromatography on a silica gel column eluting with 2.5% diethyl ether/ hexanes to 4% diethyl ether / hexanes to give **29** as a colorless oil (378.0 mg , 34% for 2 steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.75 (dt, 1H, *J* = 15.9 Hz,

6.6 Hz), 6.03 (d, 1H, , J = 15.9 Hz), 3.77-3.70 (m, 1H), 3.67-3.59 (m, 1H), 3.38 (s, 3H), 2.27 (q, 2H, , J = 6.6.Hz), 2.18 (s, 3H), 1.74 (quintet, 2H, J = 6.6 Hz), 1.49(s, 3H), 1.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.3 (s), 146.9 (d), 136.9 (s), 131.6 (d), 119.0 (s), 63.7 (t), 51.8 (q), 28.8 (t), 27.9 (t), 26.8 (q), 24.1 (q), 23.9 (q). IR (neat, cm^{-1}) 1675, 1255, 1144. LRMS (*m/z*, relative intensity): 228 ((M^+-N_2), 1), 225 ((M^+-OMe), 3), 170 (5), 142 (26), 127 (48), 110 (93), 84 (100). HRMS calcd for $C_{11}H_{17}N_2O_3$ (M^+-OMe): 225.1239, found: 225.1245.

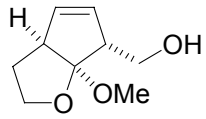
Adduct (±)-**30**



In a dry 50 mL r.b.-flask (pre-washed with 1N HCl, distilled H_2O, and acetone) under an argon atmosphere, was placed 7-(2-methoxy-5,5-dimethyl-2,5-dihydro-[1,3,4]oxadiazol-2-yloxy)-hept-3-en-2-one (386 mg, 1.51 mmol) in anhydrous toluene (15 mL). The solution was heated to reflux and stirred overnight. Then, it was cooled to r.t. The toluene was evaporated under reduced pressure and the crude product was purified by flash chromatography on a silica gel column eluting with NEt_3 / EtOAc / Hexane (1:20:79) to give the ortho ester **30** as a colorless oil (212 mg, 82%).^{1}H NMR (300 MHz, C_6D_6): δ 4.35 (s, 1H), 3.68-3.51 (m, 2H), 3.49 (s, 3H), 2.86 (m, 1H), 1.64 (s, 3H), 1.62-1.52 (m, 1H), 1.47 -1.34 (m, 1H), 1.31-1.12 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6 (s), 121.5 (s), 100.3 (d), 61.8 (t), 49.2 (d), 44.3 (q), 23.7 (t), 19.3 (t), 13.8 (q). IR (neat, cm^{-1}) 3093, 2947, 2875, 2739, 1675, 1438, 1255. LRMS (*m/z*, relative intensity): 170 ($M^{+\cdot}$, 77), 139 ((M-OMe)$^+$, 36), 110 (100), 94 (67), 82 (53). HRMS calcd for $C_9H_{14}O_3$: 170.0943, found: 170.0947.

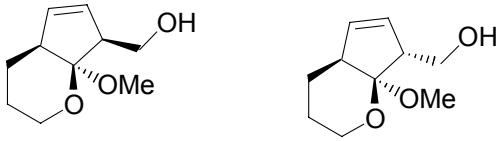
Proof of structures of **25b**, **26a**, and **26b**.

Reduction of adduct **26a**.



The reaction was performed according to the reduction of **25b**/**26b** starting from **26a** (340 mg, 1.72 mmol) to give the alcohol (296 mg, 100 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79 (m, 1H), 2.11 (m, 1H), 2.56 (bs, 1H), 2.97 (m, 1H), 3.27 (m, 1H), 3.34 (s, 3H), 3.51 (dd, 1H, *J* = 11.5, 7.1 Hz), 3.57 (dd, 1H, *J* = 11.5, 3.8 Hz), 3.80 (m, 1H), 4.13 (dt, 1H, *J* = 7.1, 2.2 Hz), 5.58 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.6, 50.5, 51.1, 56.4, 62.7, 68.2, 118.9, 130.6, 133.0; IR (neat, cm^{-1}): 3436, 3051, 2946, 2876; HRMS calcd for $C_9H_{14}O_3$: 170.0943, found: 170.0947.

Reduction of adducts **25b** and **26b**.

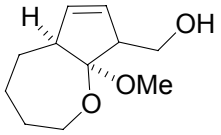


Major *Minor*

The crude reaction of carbene cyclization (2.0 mmol) in dry ether (10 mL) was added dropwise to a solution of $LiAlH_4$ (100 mg, 2.5 mmol) in ether (10 mL). After 2h of heating to reflux under argon, the reaction was hydrolysed at 0 °C by the dropwise addition of water (36 μL). After 10 min, diethyl ether (5 mL) was added at r.t. followed by the addition of 15% NaOH (70 μL) and water (70 μL). The slurry was well stirred at r.t. for 30 min then filtered over celite and washed with AcOEt. After concentrating under vacuum the crude was purified by flash chromatography using CH_2Cl_2/ether 90:10 then

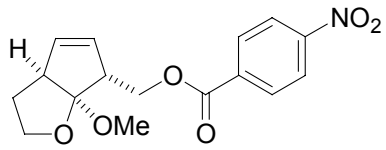
80:20 to give 167 mg of the major isomer and 51 mg of the minor isomer, both as colorless oils in a combined yield of 59 %. *Major:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35-1.52 (m, 2H), 1.78 (m, 2H), 2.54 (m, 1H), 2.94 (bs, 1H), 3.01 (m ,1H), 3.33 (s, 3H), 3.63 (m, H), 3.69 (m, 2H), 3.85 (m, 1H), 5.59 (m, 1H), 5.68 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6 (t), 23.2 (t), 49.6 (q), 54.1 (d), 58.9 (d), 63.1 (t), 109.4 (s), 129.6 (d), 133.8 (d). *Minor*: ^{1}H NMR ($CDCl_3$ ppm): 1.40 (m, 1H), 1.55-1.80 (m, 3H), 2.75 (m, 2H), 3.37 (s, 3H), 3.58-3.72 (m, 4H), 5.72 (d, 1H), 5.88 (m, H). ^{13}C NMR (75 MHz, C_6D_6): δ 20.9 (t), 22.1 (t), 45.0 (q), 50.3 (d), 54.7 (d), 60.6 (t), 61.5 (t), 107.0 (s), 132.4 (d), 134.1 (d).

Reduction of adducts **25c** or **26c**.



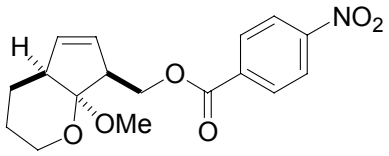
The reaction was performed according to the reduction of **25b**/**26b** starting from **25c** or **26c** (one or the other since its stereochemistry is not defined) (340 mg, 1.72 mmol). Purification by flash chromatography gave the product as a colorless oil (91 mg, 46 %). The product was unstable under lightly acidic condition (silica or $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21-1.42 (m, 2H), 1.68 (m, 3H), 1.86 (m, 1H), 2.57 (m ,1H), 2.96 (m, 1H), 3.19 (m, 1H), 3.25 (s, 3H), 3.54 (m, 2H), 3.66-3.89 (m, 2H), 5.39 (m, 1H), 5.72 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.1 (t), 30.9 (t), 33.2 (t), 48.1 (q), 52.0 (d), 58.8 (d), 63.8 (t), 64.4 (t), 113.6 (s), 126.9 (d), 135.8 (d); IR (neat, cm^{-1}): 3464, 3047, 2926; LRMS (m/z (relative intensity)): 198, 167, 126; HRMS calcd for $C_{11}H_{18}O_3$: 198.1256, found: 198.1252.

p-nitrobenzoate of the alcohol derived from **26a**



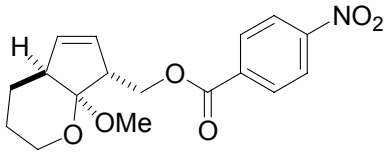
The alcohol obtained from the reduction of **26a** (0.223 g, 1.31 mmol) was dissolved in anhydrous THF (17 mL) and the solution was cooled to 0°C. Then, triphenylphosphine (0.415 g, 1.58 mmol) followed by *p*-nitrobenzoic acid (0.293 g, 1.75 mmol) were added and the reaction mixture was stirred at 0 °C for 5 minutes. Then, diethyl azodicarboxylate (0.25 mL, 1.59 mmol) was added and the reaction mixture was stirred while warming to r.t. over a period of 50 min. The reaction mixture was then quenched with a solution of saturated $NaHCO_3$ / Na_2CO_3 (50:50). Diethyl ether was added and the phases were separated. The aqueous phase was extracted three times with diethyl ether and the combined organic layers were washed once with brine, dried over Anhydrous magnesium sulfate and concentrated under vacuum to give a yellowish solid. The crude product was purified by flash chromatography on a silica gel column eluting with hexane and diethyl ether (4:1) to give ester as a white solid (0.377 g, 93%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.28 (d, 2H, *J* = 8.8 Hz), 8.18 (d, 2H, *J* = 11.0 Hz), 5.74 (m, 1H), 5.66 (m, 1H), 4.53 (dd, 1H, *J* = 11.0 and 5.5 Hz), 4.30 (dd, 1H, *J* = 11.5 and 6.3 Hz), 4.07 (td, 1H, *J* = 8.5 and 4.0 Hz), 3.85 (q, 1H, *J* = 8.1 Hz), 3.32 (s, 3H), 3.27 (m, 2H), 2.23-2.03 (m, 1H), 1.85-1.76 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5 (s), 150.4 (s), 135.8 (s), 134.1 (d), 130.6 (d), 130.4 (d), 123.5 (d), 117.2 (s), 61.8 (t), 65.1 (t), 52.0 (d), 51.8 (d), 50.8 (q), 29.2 (t). IR (neat, cm^{-1}) 3116, 3034, 3010, 2966, 2892, 2833, 1723, 1529, 1455, 1350, 1287, 1210, 1121. LRMS (*m/z*, relative intensity): 319 (M^+,27), 169 (2), 153 (100), 121 (16), 104 (25), 93 (33), 84 (22). HRMS calcdd for $C_{16}H_{17}NO_6$: 319.1056, found: 319.1059.

p-nitrobenzoate of the alcohol derived from **25b**



The alcohol obtained from the reduction of **25b** (137 mg, 0.75 mmol) was dissolved in anhydrous THF (10 mL) and the solution was cooled to 0°C. Then, triphenylphosphine (237 mg, 0.90 mmol) followed by *p*-nitrobenzoic acid (167 mg, 1.0 mmol) were added and the reaction mixture was stirred at 0 °C for 5 minutes. Then, diethyl azodicarboxylate (110 μL, 0.90 mmol) was added and the reaction mixture was stirred while warming to r.t. over a period of 50 min. The reaction mixture was then quenched with a solution of saturated $NaHCO_3$ / Na_2CO_3 (50:50). Diethyl ether was added and the phases were separated. The aqueous phase was extracted three times with diethyl ether and the combined organic layers were washed once with brine, dried over Anhydrous magnesium sulfate and concentrated under vacuum to give a yellowish solid. The crude product was purified by flash chromatography on a silica gel column eluting with hexane and diethyl ether (4:1) to give the ester as a white solid (163 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (ABq, 4H), 5.71 (m, 2H), 4.75 (dd, 1H, *J* = 11.0 and 5.5 Hz), 4.28 (dd, 1H, *J* = 11.0 and 8.3 Hz), 3.62-3.57 (dd, 2H, *J* = 8.3 and 4.4 Hz), 3.38 (s, 3H), 3.22 (m, 1H), 2.67 (m, 1H), 1.83-1.43 (m, 4H).

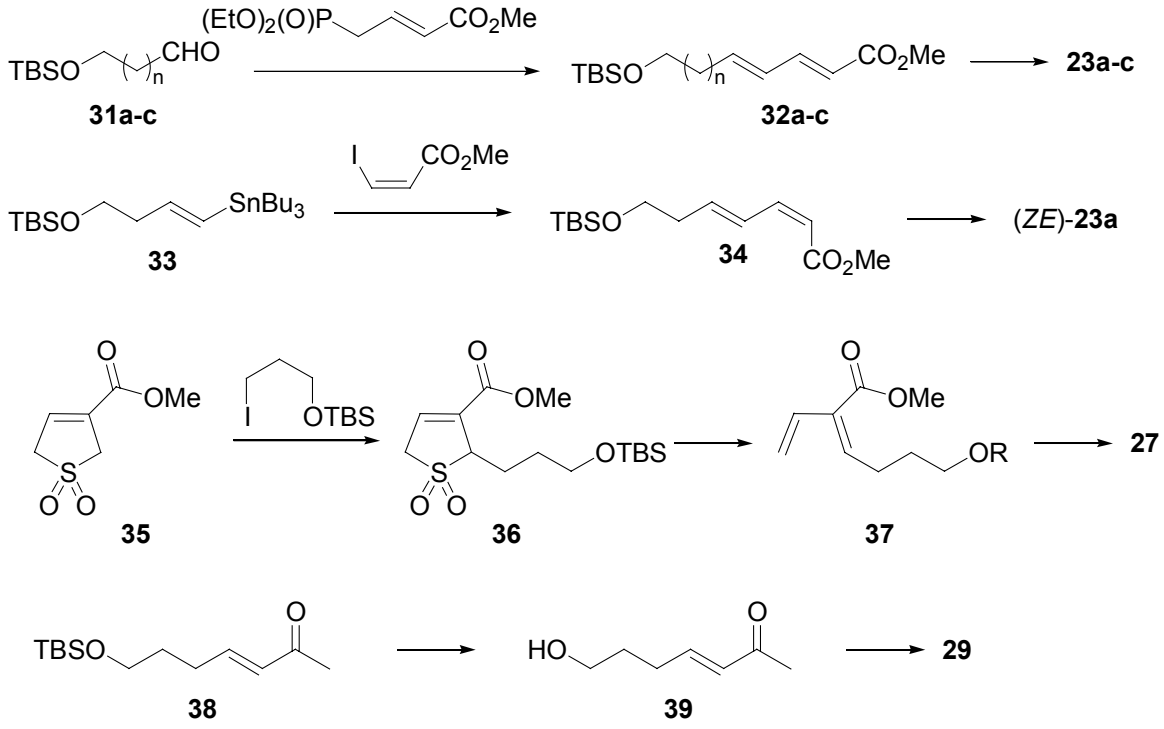
p-nitrobenzoate of the alcohol derived from **26b**



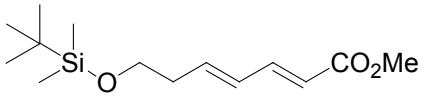
The alcohol obtained from the reduction of **26b** (60 mg, 0.33 mmol) was dissolved in anhydrous THF (5 mL) and the solution was cooled to 0°C. Then, triphenylphosphine

(105 mg, 0.4 mmol) followed by *p*-nitrobenzoic acid (84 mg, 0.50 mmol) were added and the reaction mixture was stirred at 0 °C for 5 minutes. Then, diethyl azodicarboxylate (50 μL, 0.40 mmol) was added and the reaction mixture was stirred while warming to r.t. over a period of 50 min. The reaction mixture was then quenched with a solution of saturated $NaHCO_3$ / Na_2CO_3 (50:50). Diethyl ether was added and the phases were separated. The aqueous phase was extracted three times with diethyl ether and the combined organic layers were washed once with brine, dried over Anhydrous magnesium sulfate and concentrated under vacuum to give a yellowish solid. The crude product was purified by flash chromatography on a silica gel column eluting with hexane and diethyl ether (4:1) to give the ester as a white solid (70 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (ABq, 4H), 5.92 (m, 1H), 5.71 (d, 1H, J = 6.1 Hz), 4.50 (dd, 1H, J = 11.0 and 5.0 Hz), 4.23 (dd, 1H, J = 11.5 and 7.1 Hz), 3.62-3.57 (m, 2H), 3.35 (s, 3H), 3.00 (m, 1H), 2.82 (m, 1H), 1.84-1.80 (m, 2H), 1.69-1.58 (m, 1H), 1.43-1.38 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5 (s), 150.5 (s), 135.4 (s), 135.4 (d), 130.9 (d), 130.6 (d), 123.5 (d), 106.6 (s), 64.3 (t), 61.0 (t), 51.2 (d), 50.8 (q), 44.7 (d), 21.8 (t), 20.7 (t). IR (neat, cm^{-1}) 3116, 3034, 3010, 1723, 1529, 1455.

Syntheses of dienes **23a-c** and **27** and enone **29** and compound characterization for that sequence

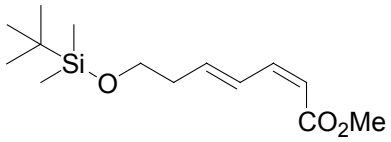


E-E-7-(*tert*-Butyl-dimethyl-silanyloxy)-hepta-2,4-dienoic acid methyl ester **32a**



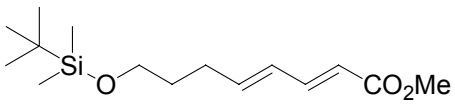
The reaction was performed according to the preparation of **32b**, starting from aldehyde **31a** (2.82 g, 15 mmol) to give the diene **32a** (2.13 g, 47 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.04 (s, 6H), 0.88 (s, 9H), 2.38 (q, 2H, *J* = 6.6 Hz), 3.69 (t, 2H, *J* = 6.6 Hz), 3.74 (s, 3H), 5.80 (d, 1H, *J* = 15.4 Hz), 6.19 (m, 2H), 7.26 (dd, 1H, *J* = 13.2, 10.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ -5.4 (q), 18.2 (s), 25.8 (q), 36.4 (t), 51.3 (q), 62.0 (t), 119.2 (d), 126.9 (d), 140.9 (d), 144.9 (d), 167.5 (s); IR (neat, cm^{-1}): 2953, 2855, 1719, 1644, 1617; LRMS (m/z (relative intensity)): 255, 239, 213; HRMS calcd for $C_{10}H_{17}O_3Si_1$ (M-C_4H_9): 213.0947, found : 213.0951.

Z-E-7-(*tert*-Butyl-dimethyl-silanyloxy)-hepta-2,4-dienoic acid methyl ester **32a**



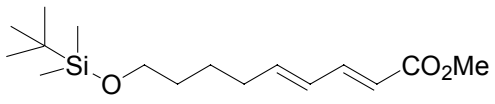
To a solution of the vinyltin **33** (950 mg, 2.0 mmol) in dry DMF (10 mL) under argon were added methyl *Z*-3-iodoacrylate (424 mg, 2.0 mmol) and 2 mol% bis(benzonitrile)-dichloropalladium-(II) (15 mg, 0.04 mmol). After stirring 6h at r.t., an aqueous solution of 10% citric acid (20 mL) and diethyl ether (50 mL) were added and the mixture stirred for 5 min. Then the organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were washed with water, brine and dried for 20 min over anhydrous magnesium sulfate plus two large spatula full of activated charcoal. After filtering and concentrating under vacuum the crude product was purified by flash chromatography using hexanes/ether 95:5 then 90:10 to afford the product **34** as a colorless oil (525 mg, 52 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.05 (s, 6H), 0.89 (s, 9H), 2.43 (q, 2H, *J* = 6.6 Hz), 3.70 (t, 2H, *J* = 6.6 Hz), 3.72 (s, 3H), 5.59 (d, 1H, *J* = 11.6 Hz), 6.09 (dt, 1H, *J* = 15.4, 7.7 Hz), 6.55 (t, 1H, *J* = 11.5 Hz), 7.39 (dd, 1H, *J* = 16.5, 12.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ -5.4 (q), 18.2 (s), 25.8 (q), 36.5 (t), 50.9 (q), 62.2 (t), 15.5 (d), 128.4 (d), 141.8 (d), 145.1 (d), 166.7 (s); IR (neat, cm^{-1}): 2958, 2932, 2858, 1719, 1642, 1603; LRMS (m/z (relative intensity)): 239, 213, 181; HRMS calcd for $C_{10}H_{17}O_3Si_1$: 213.0947, found: 213.0955.

E-E-8-(*tert*-Butyl-dimethyl-silanyloxy)-octa-2,4-dienoic acid methyl ester **32b**



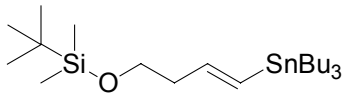
A mixture of methyl 4-bromocrotonate (4.48 g, 25 mmol) and triethyl phosphite (6 mL, 35 mmol) was refluxed neat for 1.5 h. The reaction was put under an argon flow to remove the bromoethane formed. The mixture was kept overnight under vacuum to remove the excess of triethyl phosphite and the resulting oil was used crude. The crude crotyl phosphate (3.48 g, 14 mmol) in dry THF (70 mL) was cooled at -78 °C before the dropwise addition of LiHMDS [1M/THF] (14 mL, 14 mmol). After 30 min at -78 °C a solution of aldehyde **31b** (2.0 g, 10 mmol) in THF (15 mL) was added. After 2h of stirring at r.t., the reaction was hydrolysed with an aqueous solution of 20% citric acid (30 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with a solution of 20% citric acid, saturated $NaHCO_3$, and dried over anhydrous magnesium sulfate. After concentrating under vacuum the crude product was purified by flash chromatography on silica using hexanes/ether 80:20 as solvent to give compound **32b** as a colorless oil (1.96 g, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.04 (s, 6H), 0.89 (s, 9H), 1.64 (qi, 2H, *J* = 7.7 Hz), 2.23 (q, 2H, *J* = 7.7 Hz), 3.61 (t, 2H, *J* = 6.6 Hz), 3.73 (s, 3H), 5.78 (d, 1H, *J* = 15.4 Hz), 6.15 (m, H), 7.25 (dd, 1H, *J* = 15.4, 9.9 Hz).

E-E-9-(*tert*-Butyl-dimethyl-silanyloxy)-nona-2,4-dienoic acid methyl ester **32c**



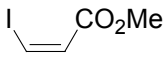
The reaction was performed according to the preparation of **32b**, starting from aldehyde **31c** (3.25 g, 15 mmol) to give **32c** as a colorless oil (1.57 g, 39 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.04 (s, 6H), 0.89 (s, 9H), 1.50 (m, 4H), 2.18 (q, 2H, *J* = 6.6 Hz), 3.61 (t, 2H, *J* = 6.1 Hz), 3.73 (s, 3H), 5.90 (d, 1H, *J* = 15.4 Hz), 6.14 (m, 2H), 7.26 (dd, 1H, *J* = 15.4, 9.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ -5.4 (q), 18.3 (s), 25.0 (q), 25.9 (t), 32.2 (t), 32.7 (t), 51.3 (q), 62.8 (t), 118.7 (d), 128.4 (d), 144.5 (d), 145.2 (d), 167.6 (s); IR (neat, cm^{-1}): 1721, 1642, 1615; LRMS (m/z (relative intensity)): 267, 241, 209; HRMS calcd for $C_{16}H_{30}O_3Si_1$: 298.1964, found : 298.1969.

E-(*tert*-Butyl-dimethyl-silanyloxy)-4-tributylstannanyl-but-3-ene **33**



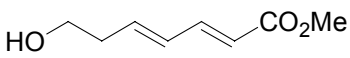
To a solution of (*t*-butyl-dimethylsilanyloxy)-but-3-yne (1.84 g, 10.0 mmol) in toluene (20 mL), was added tributyltin hydride (2.75 mL, 10.02 mmol) and a catalytic amount of AIBN (*c.a.* 5 mg) under argon. The mixture was refluxed for 2.5 h. After concentrating under vacuum the crude product was purified by flash chromatography on silica using hexanes/CH_2Cl_2 90:10 to give 1.78 g (37 %) of the trans vinyl stannane **33** as the major product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.05 (s, 6H), 0.89 (m, 15H), 0.90 (s, 9H), 1.31 (m, 6H), 1.48 (m, 6H), 2.35 (m, 2H), 3.67 (t, 2H, *J* = 6.6 Hz), 5.96 (m, 2H).

Z-Methyl-3-iodoacrylate **34**



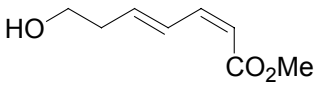
To a solution of methyl propiolate (1.78 mL, 20 mmol), in acetic acid (10 mL) was added sodium iodide (6 g, 40 mmol) and the mixture was heated at 70 °C overnight. Ether was then added followed by the addition of 1N NaOH (50 mL). The aqueous layer was separated then extracted with ether. The combined organic layers were washed with Na_2CO_3, $NaHCO_3$, dried over anhydrous magnesium sulfate and concentrated under vacuum to give the vinyl iodide (4.56 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.78 (s, 3H), 6.90 (d, 1H, *J* = 9.4 Hz), 7.47 (d, 1H, *J* = 8.8 Hz).

E-*E*-7-Hydroxy-hepta-2,4-dienoic acid methyl ester **23a**



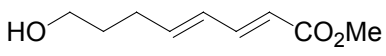
The reaction was performed according to the preparation of **23b**, starting from **32a** (1.57 g, 5.8 mmol). In this case the crude was purified by flash chromatography using CH_2Cl_2/ether 60:40 (847 mg, 96 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (qi, 2H, *J* = 6.6 Hz), 3.73 (t, 2H, *J* = 6.6 Hz), 3.73 (s, 3H), 5.81 (d, 1H, *J* = 15.4 Hz), 6.13 (m, 1H), 6.25 (m, 1H), 7.25 (dd, 1H, *J* = 14.9, 11.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.1 (t), 51.5 (q), 61.3 (t), 119.5 (d), 130.4 (d), 140.3 (d), 144.8 (d), 167.7 (s); IR (neat, cm^{-1}): 3406, 3022, 2951, 1706, 1641, 1617; LRMS (m/z (relative intensity)): 156, 126, 111; HRMS calcd for $C_8H_{12}O_3$: 156.0786, found : 156.0790.

<u>*Z*-*E*-7-Hydroxy-hepta-2,4-dienoic acid methyl ester (*ZE*)-**23a**</u>



The reaction was performed according to the preparation of **23b**, starting from **34** (541 mg, 2 mmol). The crude was filtered through silica using CH_2Cl_2/ether 60:40 to give *ZE*-**23a** (312 mg, 100 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (q, 2H, *J* = 6.1 Hz), 3.72 (s, 3H), 3.75 (t, H, *J* = 6.6 Hz), 5.62 (d, 1H, *J* = 11.6 Hz), 6.08 (dt, 1H, *J* = 15.4, 7.1 Hz), 6.57 (t, 1H, *J* = 11.0 Hz), 7.45 (dd, 1H, *J* = 15.4, 11.0 Hz); IR (neat, cm^{-1}): 3370, 2945, 2916, 1713, 1640, 1600; LRMS (m/z (relative intensity)): 156, 126, 111; HRMS calcd for $C_8H_{12}O_3$: 156.0786, found: 156.0789.

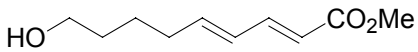
<u>*E*-*E*-8-Hydroxy-octa-2,4-dienoic acid methyl ester **23b**.</u>



The silyl ether **32b** (569 mg, 2.0 mmol) in a mixture of AcOH/THF/H_2O/ : 3/1/1 (30/10/10 mL) was stirred for ~4h at r.t. when TLC showed no more starting material a saturated solution of Na_2CO_3 was added carefully followed by a mixture of ether/AcOEt :

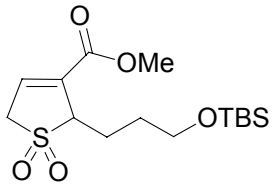
(75/25 mL). The aqueous layer was then separated and extracted with ether (2x30 mL). The combined organic layers were washed with a saturated solution of Na_2CO_3 and dried over $NaHCO_3$. After concentrating under vacuum the crude (340 mg) was used in the next step. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.66 (qi, 2H, *J* = 7.7 Hz), 2.23 (q, 2H, *J* = 6.6 Hz), 2.31 (bs, 1H), 3.60 (m, 2H), 3.70 (s, 3H), 5.75 (d, 1H, *J* = 15.4 Hz), 6.12 (m, 2H), 7.21 (dd, 1H, *J* = 15.4, 9.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.2 (t), 31.5 (t), 51.4 (q), 61.8 (t), 118.9 (d), 128.6 (d), 143.8 (d), 145.1 (d), 167.8 (s); IR (neat, cm^{-1}): 3423, 2945, 2867, 1717, 1641, 1636; LRMS (m/z (relative intensity)): 170, 111, 93; HRMS calcd for $C_9H_{14}O_3$: 170.0943, found : 170.0948.

E-E-9-Hydroxy-nona-2,4-dienoic acid methyl ester **23c**



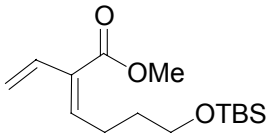
The reaction was performed according to the preparation of **23b**, starting from **32c** (2.12 g, 7.1 mmol) to give 920 mg of crude material that was used as is in the next step. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (m, 4H), 2.20 (q, 2H, *J* = 6.6 Hz), 3.65 (t, 2H, *J* = 6.0 Hz), 3.73 (s, 3H), 5.78 (d, 1H, *J* = 15.4 Hz), 6.15 (m, 2H), 7.25 (dd, 1H, *J* = 15.4, 9.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.6 (t), 32.0 (t), 32.6 (t), 51.4 (q), 62.3 (t), 118.8 (d), 128.5 (d), 144.3 (d), 145.2 (d), 167.7 (s); IR (neat, cm^{-1}): 3407, 3026, 2934, 2865, 1715, 1646, 1619; LRMS (m/z (relative intensity)): 184, 152, 113; HRMS calcd for $C_{10}H_{16}O_3$: 184.1099, found : 184.1096.

Sulfolene **36**



Methyl 3-sulfolene-3-carboxylate (97.8 mg, 0.56 mmol) was dissolved in THF (5.5 mL) and HMPA (202.8 µl, 1.17 mmol). The solution was cooled to –78 °C and a 2.0M solution of *n*-BuLi in hexanes (466.4 µl, 1.17mmol) was added dropwise. The reaction mixture was stirred at –78 °C for 30 min and 3-*tert*-butylsilyoxy-1-iodopropane (249.2 mg, 0.83 mmole) was added dropwise at –78 °C over 10 min. The reaction mixture was stirred over a period of 1h at –78 °C and then quenched with saturated NH_4Cl. The reaction mixture was stirred while warming to room temperature and diethyl ether was added. The phases were separated and the aqueous phase was extracted three times with diethyl ether. The organic layers were combined, washed once with brine, dried over anhydrous magnesium sulfate and concentrated under vacuum to give a brown oil. The crude product was purified by flash chromatography on a silica gel column eluting with ethyl acetate (10% → 50%) / hexanes to give **36** as a colorless oil (160 mg, 83 %).^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.03 (t, 1H, *J* = 3.8 Hz), 3.90-3.89 (m, 3H), 3.82 (s, 3H), 3.64 (t, 2H, *J* = 6.1 Hz), 2.04-1.97 (m, 2H), 1.76-1.66 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6 (s), 134.5 (s), 133.0 (d), 64.3 (d), 62.2 (t), 56.1 (t), 52.3 (q), 29.1 (t), 25.8 (q), 18.2 (s), -5.4 (q). IR (neat, cm^{-1}) 3083, 1722, 1474. LRMS (*m/z*, relative intensity) 291(M^+- C_4H_9, 5), 227 (100), 119 (38). HRMS calcd for $C_{11}H_{19}O_5SSi$ (M^+- C_4H_9): 291.0722, found : 291.0725.

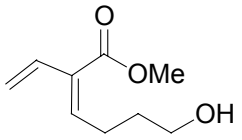
Diene **37a**



Sulfolene **36** (151 mg, 0.43 mmol) was dissolved in toluene (4.3 mL) and the reaction mixture was heated to reflux and stirred for 5h. The solution was cooled to room temperature and the solvent was removed under vacuum to give a yellow oil. The crude product was purified by flash chromatography on a silica gel column eluting with ethyl acetate (10%) / hexanes to give **37a** as a colorless oil (102 mg, 83 %). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 6.33 (dd, 1H, *J* = 17.6, 11.0 Hz, 5.99 (t, 1H, *J* = 7.7 Hz), 5.25 (d, 1H, *J* = 17.6 Hz), 5.09 (d, 1H, *J* = 11.0 Hz), 3.80 (s, 3H), 3.63 (t, 2H, *J* = 6.0 Hz), 2.39-2.31

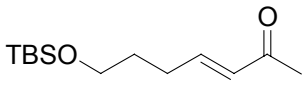
(m, 2H), 1.70-1.62 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8 (s), 139.8 (d), 134.7 (d), 133.3 (s), 114.7 (t), 62.5 (t), 51.5 (q), 32.3 (t), 26.4 (t), 25.9 (q), 18.3 (s), -5.4 (q). IR (neat, cm^{-1}) 3081, 1725, 1629, 1465. LRMS (*m/z*, relative intensity) 269 (M^+- CH_3, 5), 253 (M^+- OCH_3, 10), 227 (100), 195 (10). HRMS calcd for $C_{14}H_{25}SiO_3$ (M^+- CH_3) : 269.1573, found : 269.1567.

Diene **37b**



Diene **37a** (185 mg, 0.65 mmol) was dissolved in THF (3 mL), water (1 mL) and acetic acid (1 mL) and the reaction mixture was stirred at room temperature for 6h. The solvent was removed under vacuum and diethyl ether was added. The reaction mixture was then quenched with saturated sodium carbonate. The phases were separated and the organic phase was washed twice with saturated sodium carbonate. The organic layer was dried over anhydrous magnesium sulfate and concentrated under vacuum to give **37b** as a colorless oil (108 mg, 97 %). The crude product was used directely in the next step.

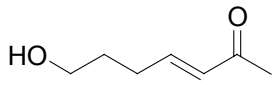
7-(tert-Butyldimethylsilyloxy)-3-hepten-2-one **38**



To a cold suspension of NaH (60% dispersion in mineral oil, 1.47 g, 36.7 mmol) in anhydrous THF (200 mL) was added diethyl(2-oxopropyl)phosphonate (7.3 mL, 36.5 mmol) at 0°C, under an argon atmosphere. The homogenous solution was stirred 1 h at 0 °C and a solution of 4-(*t*-butyl-dimethylsilyloxy)butyraldehyde (6.74 g, 33.3 mmol) in anhydrous THF (20 mL) was added dropwise via canula. The reaction was stirred 45 min at 0 °C and the mixture was allowed warm to r.t. Then, 70 mL of diethyl ether were

added and the reaction mixture was quenched with H_2O (134 mL) and 2 drops of concentrated HCl. The phases were separated and the aqueous phase was extracted three times with diethyl ether (~75 mL each). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate and concentrated under vacuum to give a yellowish oil (2.2461 g, 124%). The crude product was purified by flash chromatography on a silica gel column eluting with EtOAc/ hexane (1:9) to give the enone **38** as a colorless oil (6.6016 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 6.80 (dt, 1H, *J* = 15.9 Hz, 6.9 Hz), 6.05 (d, 1H, *J* = 15.9 Hz), 3.61 (t, 2H, *J* = 6.0 Hz), 2.28 (m, 2H), 2.21 (s, 3H), 1.65 (quintet, 2H, *J* = 6.9 Hz), 0.85 (s, 9H), 0.02 (s, 6H). IR (neat, cm^{-1}) 2954, 2930, 2857, 1677, 1629, 1472, 1389, 1253, 1102, 837. LRMS (*m/z*, relative intensity): 227 ($(M-CH_3)^+$, 1), 185 ($(M-C_4H_9)^+$, 76), 141 (31), 75 (100). HRMS calcdd for $C_9H_{17}O_2Si$ ($M-C_4H_9$): 185.0998, found: 185.1002.

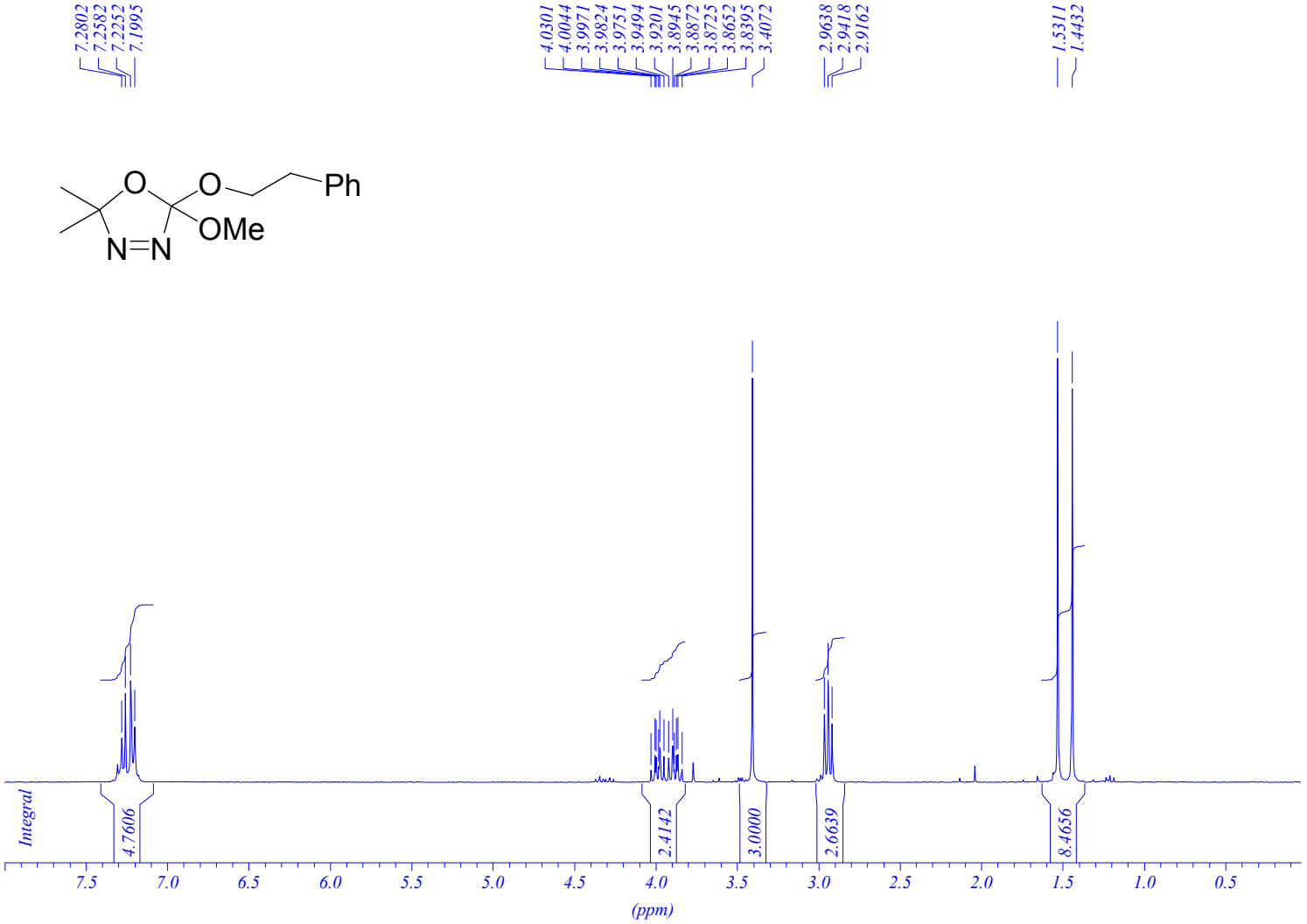
7-Hydroxy-3-hepten-2-one **39**



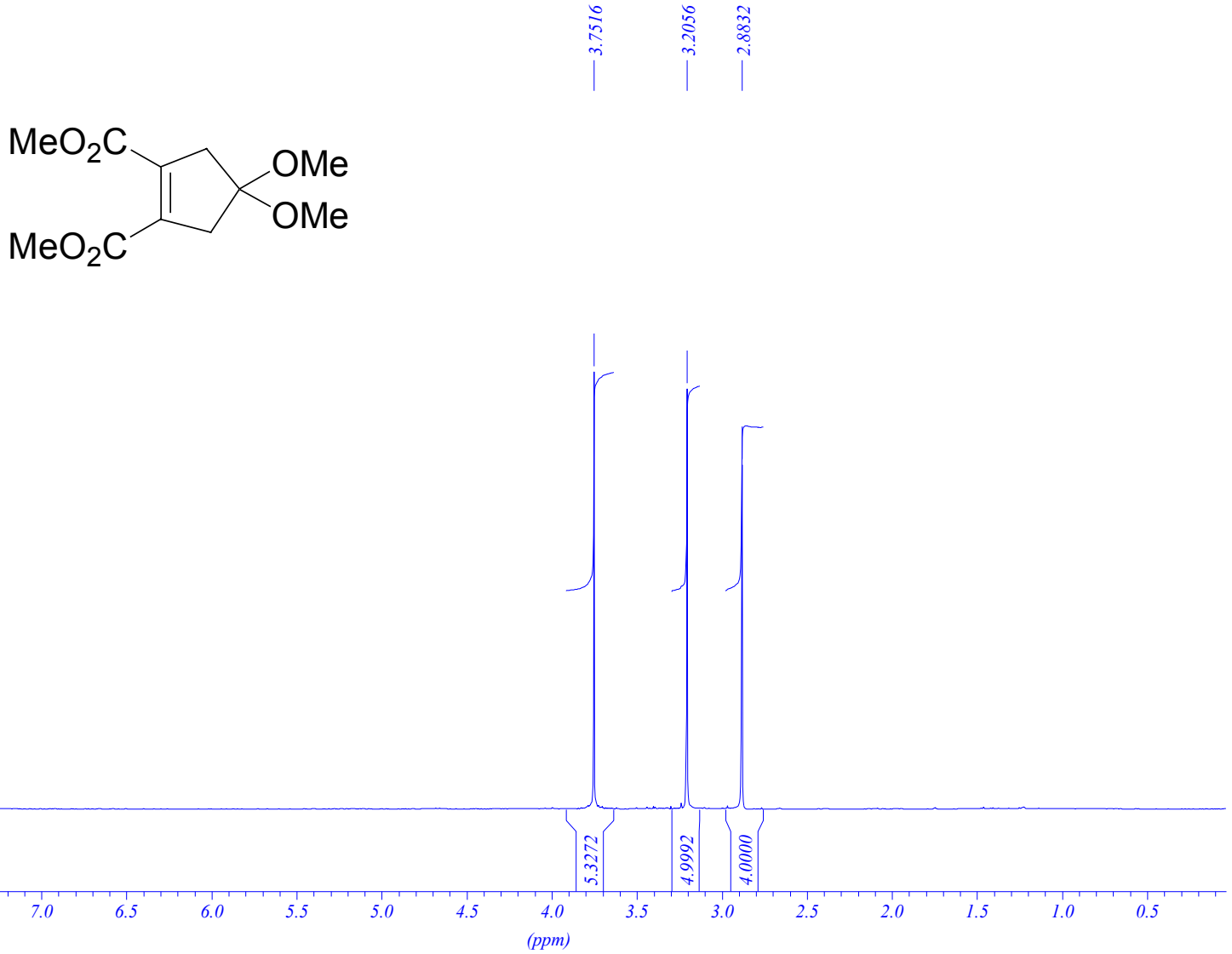
Enone **38** (1.05 g, 4.36 mmol) was dissolved in 32 mL of a THF/H_2O/AcOH solution (1:1:2) and the solution was stirred 3.5 h at room temperature. The reaction was stopped when it was almost complete as with time, there was formation of a cyclized product. Diethyl ether (~200 mL) and a saturated Na_2CO_3 aqueous solution were added. The phases were separated, the organic layer was washed twice with saturated Na_2CO_3 and once with saturated $NaHCO_3$ aqueous solution. The combined organic layers were dried over anhydrous magnesium sulfate and concentrated under vacuum to give the alcool as a yellowish oil (711 mg, >100%). The crude product was used in the next transformation without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 6.81 (dt, 1H, *J* = 15.6 and 6.9 Hz), 6.43 (d, 1H, *J* = 15.9 Hz), 3.65 (t, 2H, *J* = 6.3 Hz), 2.31 (m, 2H), 2.22 (s, 3H), 1.71 (quintet, 2H, *J* = 6.6 Hz).

^{1}H NMR spectra

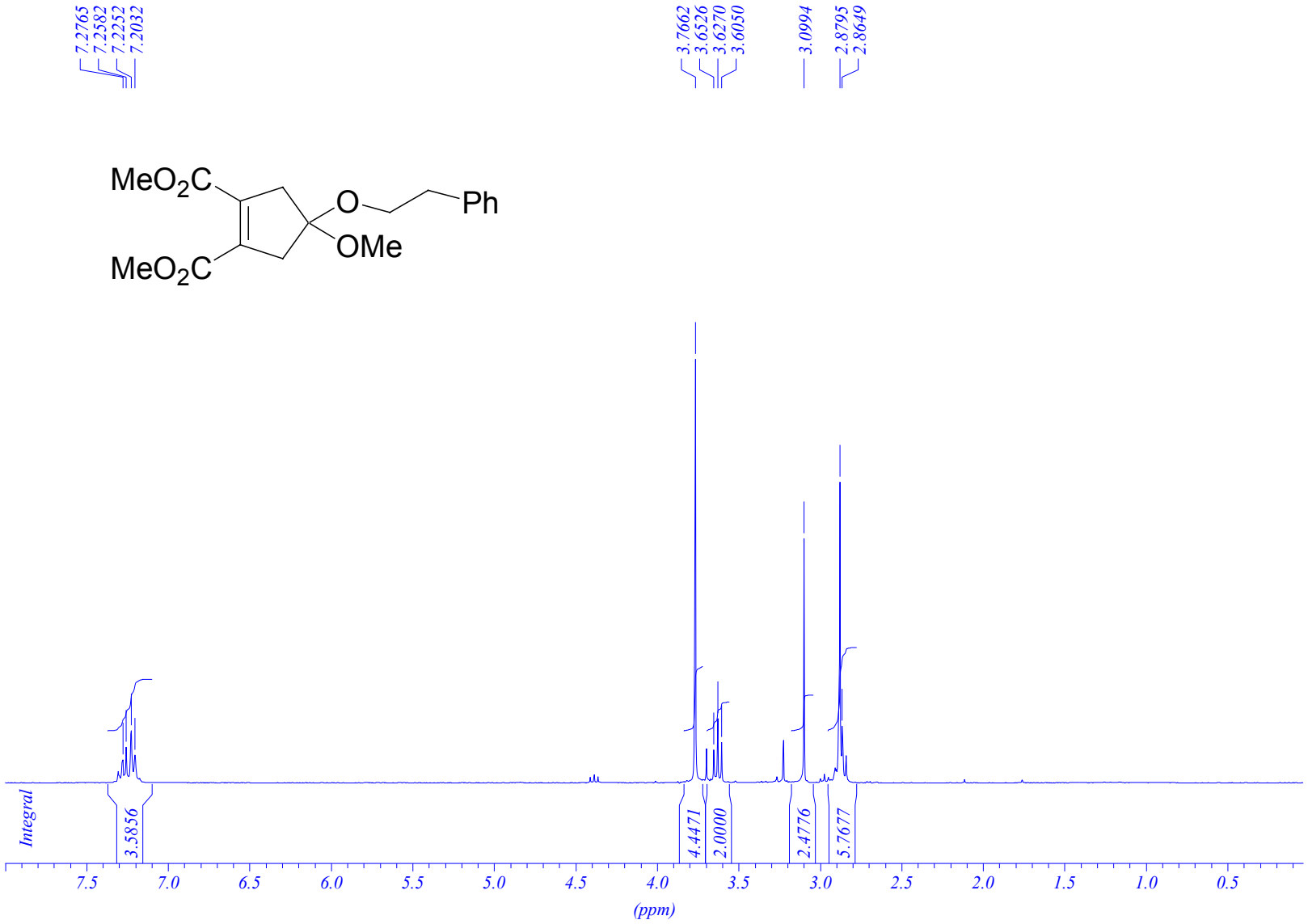
^{1}H NMR of **15b**



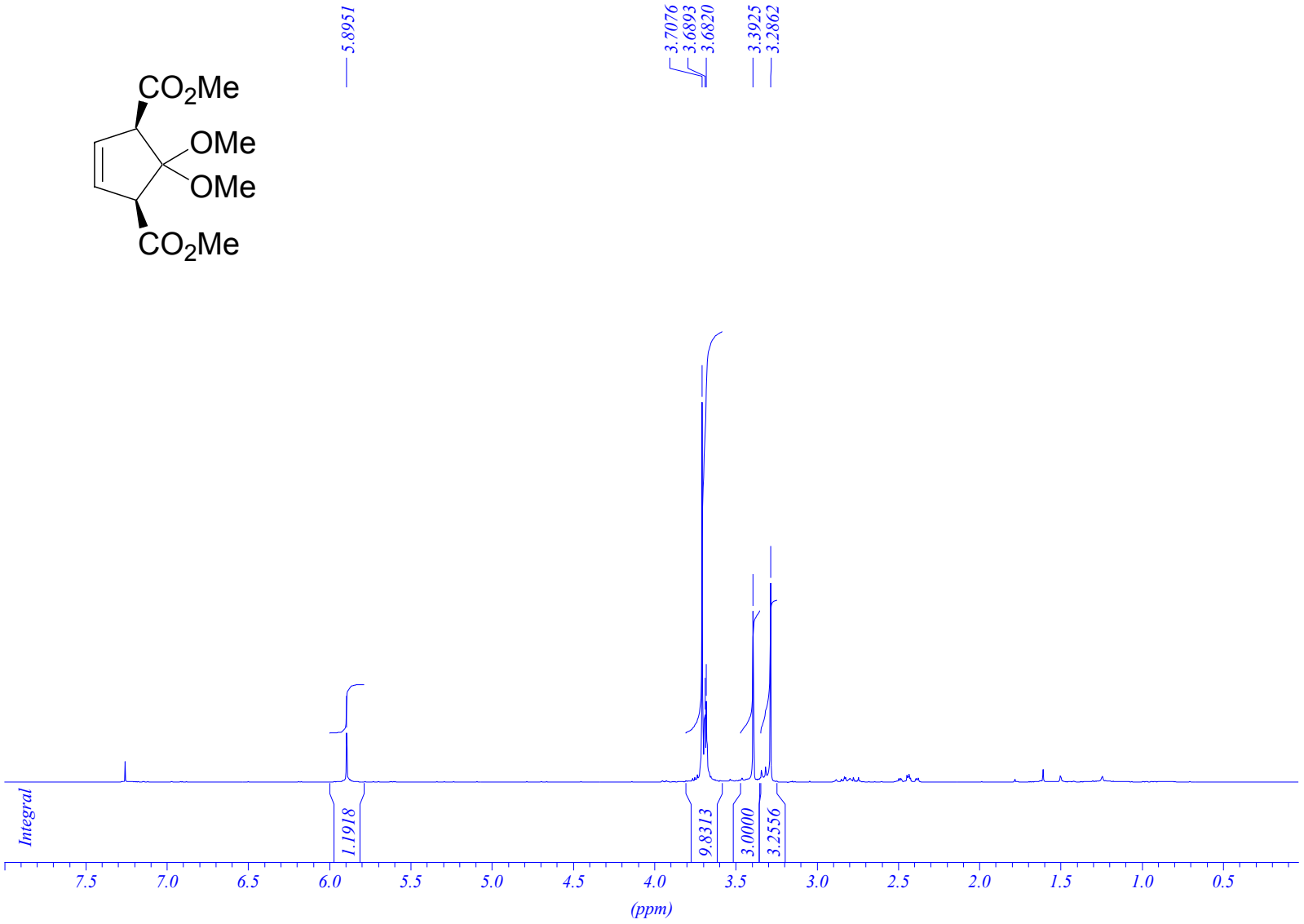
^{1}H NMR of **18a**.


3.7516
3.2056
2.8832
MeO2C
OMe
OMe
MeO2C
Integral
5.3272
4.9992
4.0000
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
(ppm)

^{1}H NMR of **18b**


7.2765
7.2582
7.2252
7.2032
3.7662
3.6526
3.6270
3.6050
3.0994
2.8795
2.8649
MeO2C
MeO2C
O
Ph
OMe
Integral
3.5856
4.4471
2.0000
2.4776
5.7677
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
(ppm)

^{1}H NMR of **20a**


CO2Me
OMe
OMe
CO2Me
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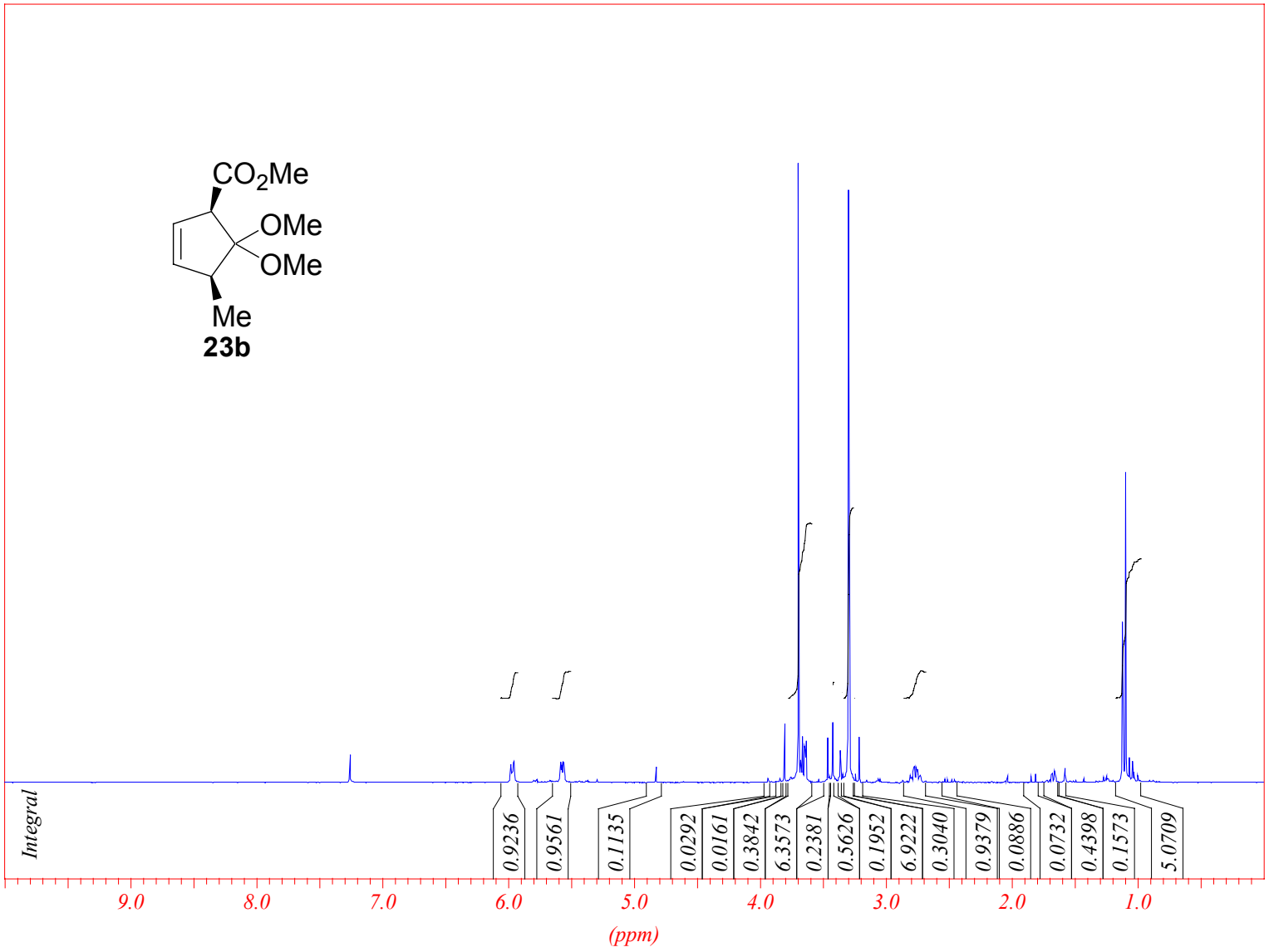
3.7076
3.6893
3.6820
3.3925
3.2862
Integral
1.1918
9.8313
3.0000
3.2556
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

^{1}H NMR of **20b**


CO2Me
OMe
OMe
Me
23b
Integral
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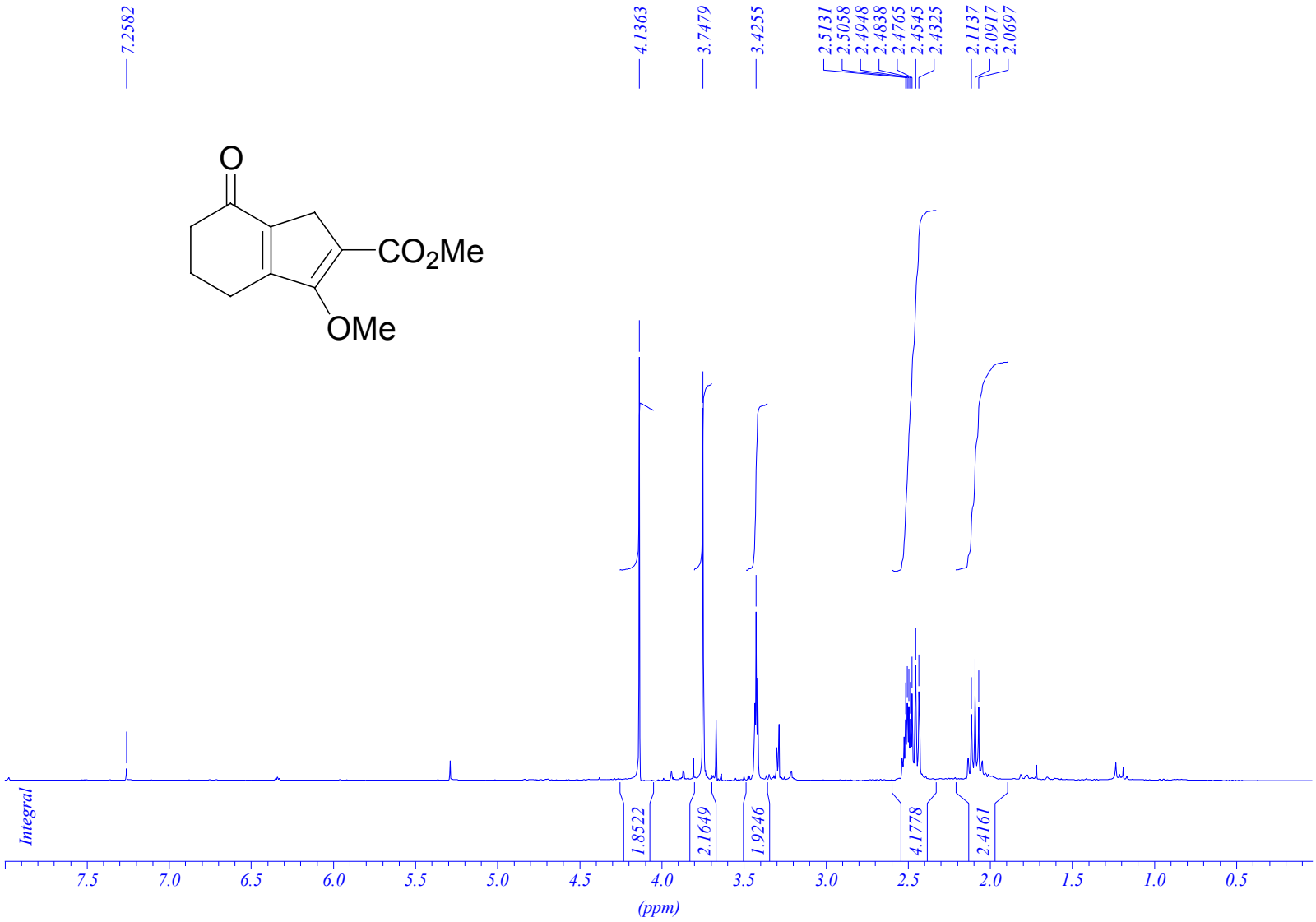
0.9561
0.1135
0.0292
0.0161
0.3842
6.3573
0.2381
0.5626
0.1952
6.9222
0.3040
0.9379
0.0886
0.0732
0.4398
0.1573
5.0709
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

^{1}H NMR of **22**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3.7479
3.4255
2.5131
2.5058
2.4948
2.4838
2.4765
2.4545
2.4325
2.1137
2.0917
2.0697
O
CO2Me
OMe
Integral
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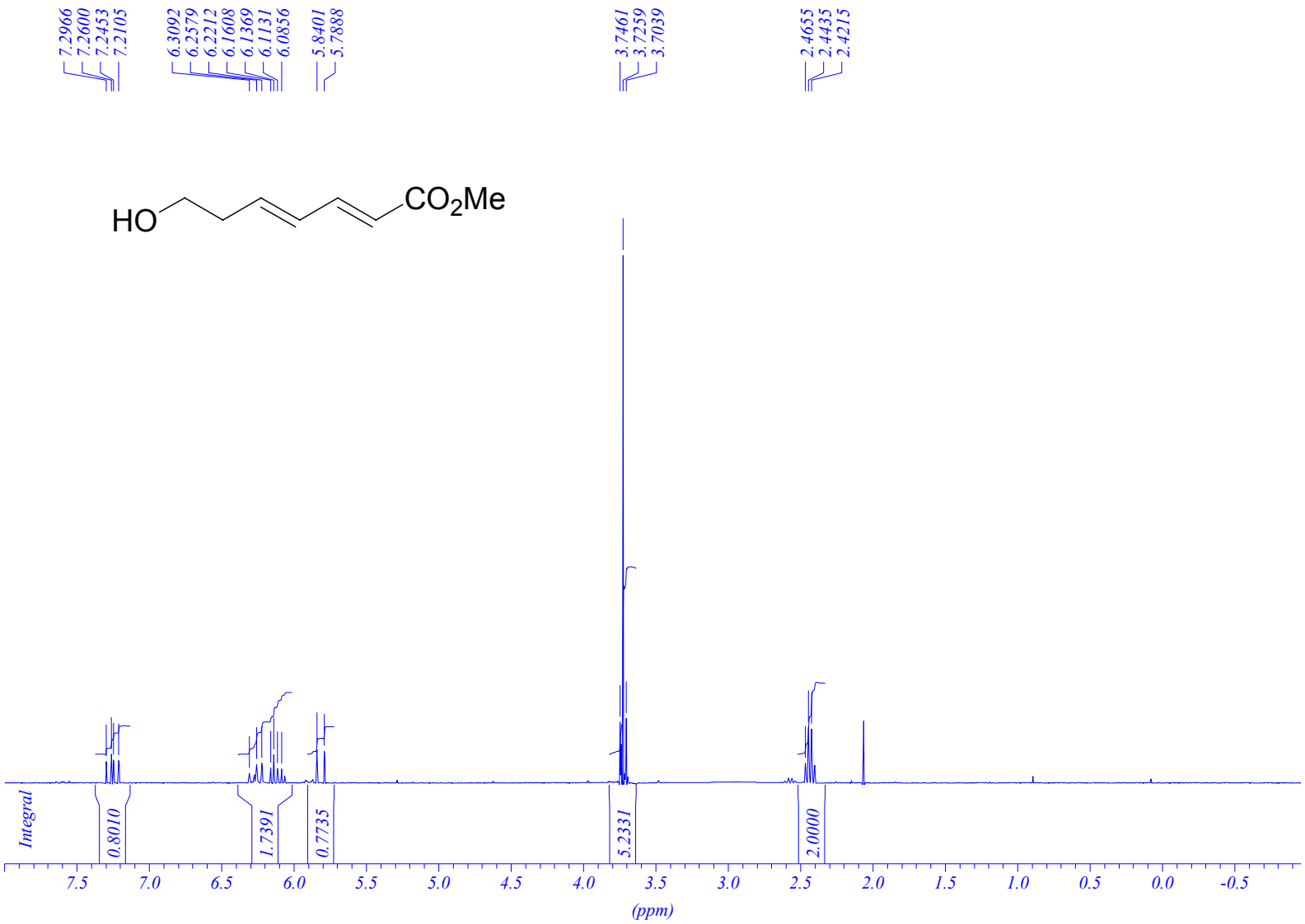
2.1649
1.9246
4.1778
2.4161
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

^{1}H NMR of **23a**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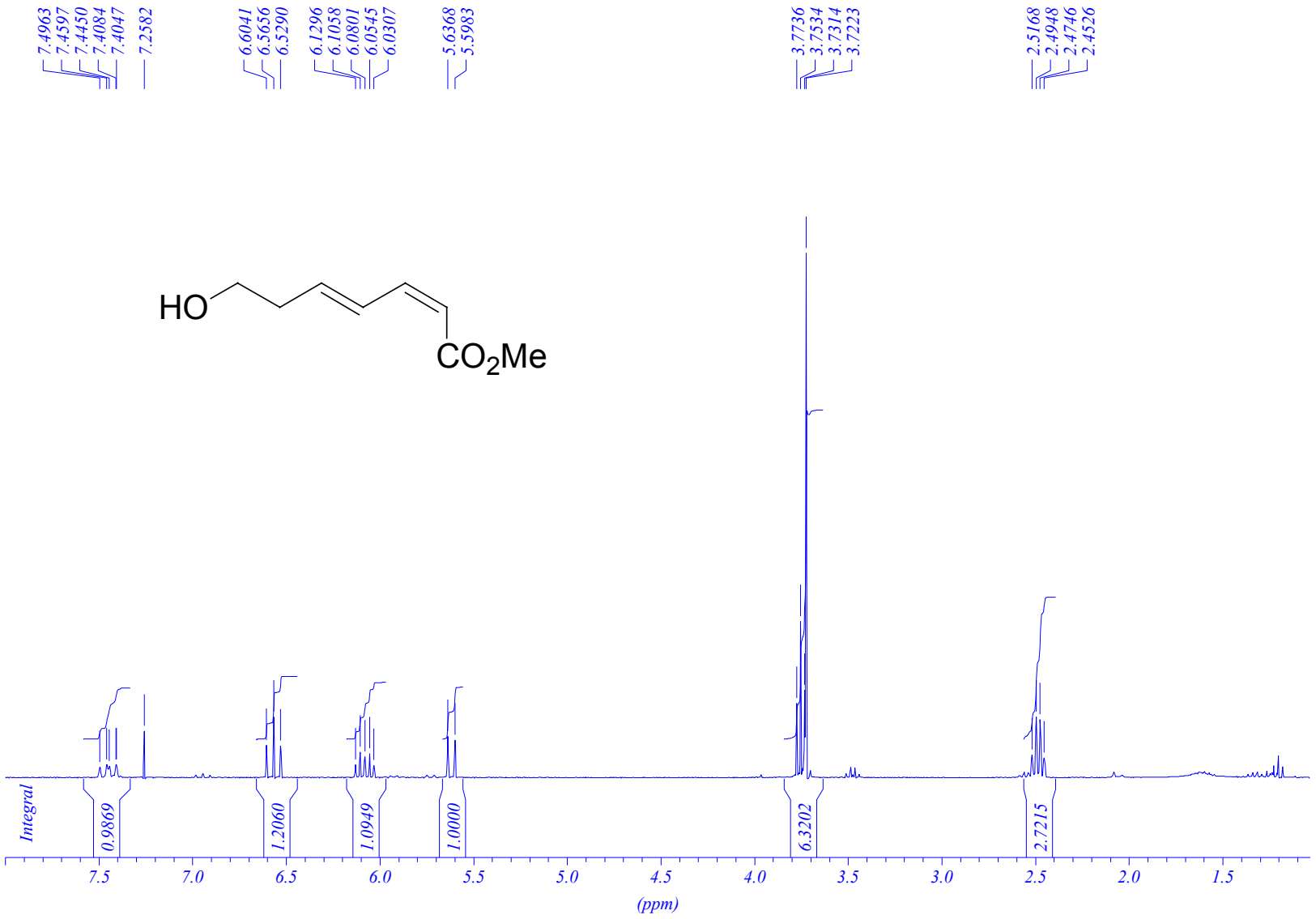
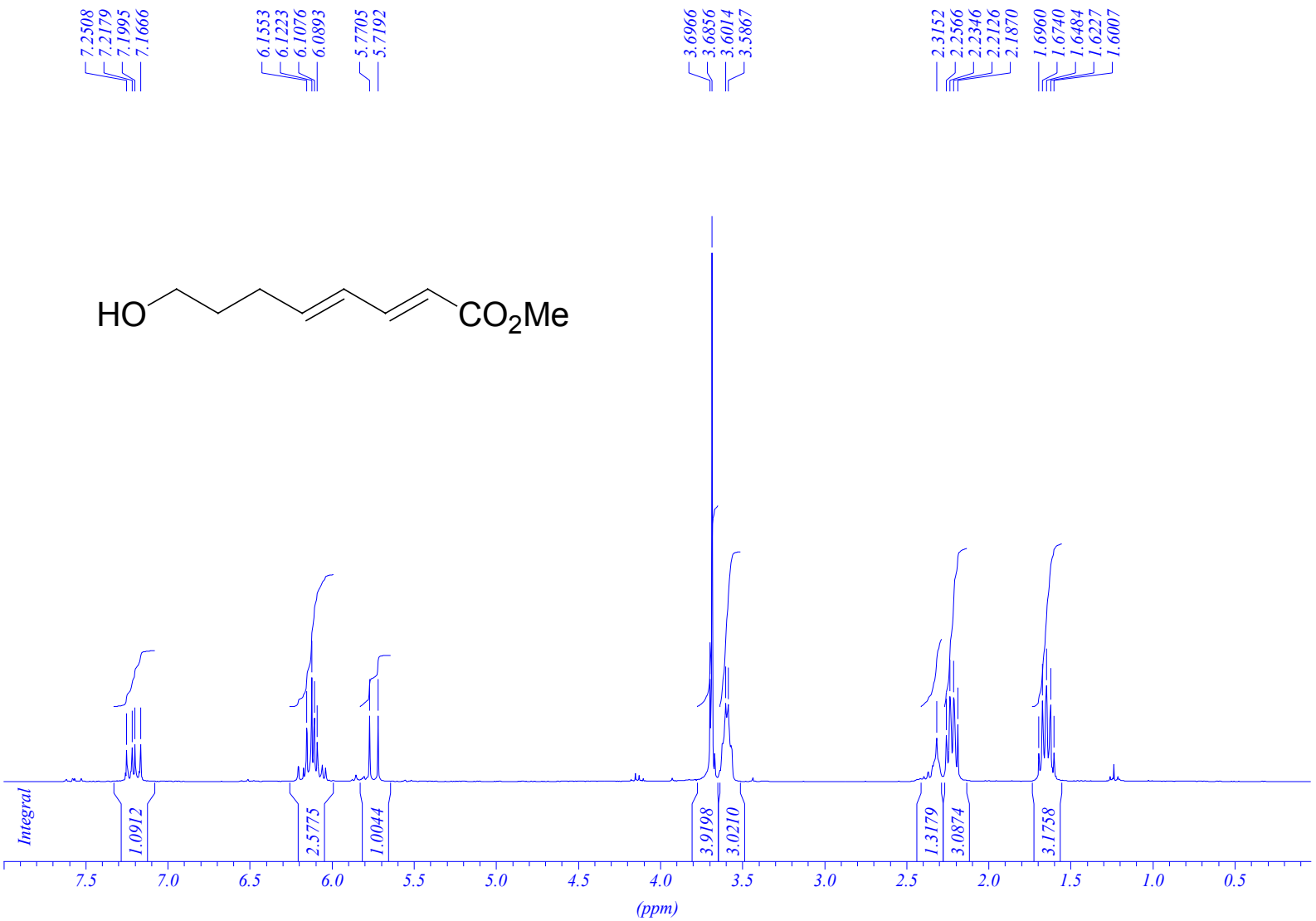
7.2600
7.2453
7.2105
6.3092
6.2579
6.2212
6.1608
6.1369
6.1131
6.0856
5.8401
5.7888
3.7461
3.7259
3.7039
2.4655
2.4435
2.4215
HO
CO2Me
Integral
0.8010
1.7391
0.7735
5.2331
2.0000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
(ppm)

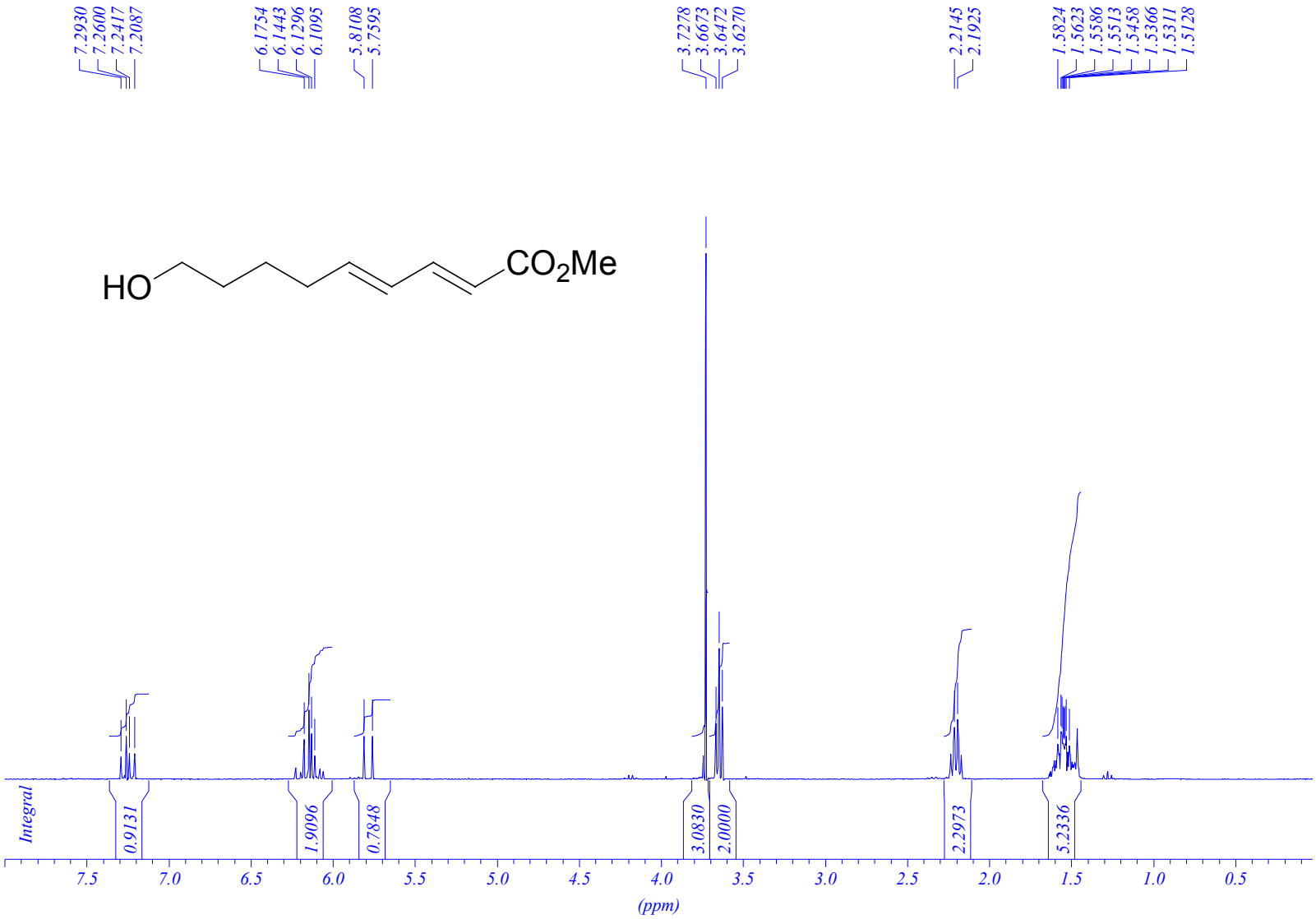
^{1}H NMR of *ZE*-**23a**



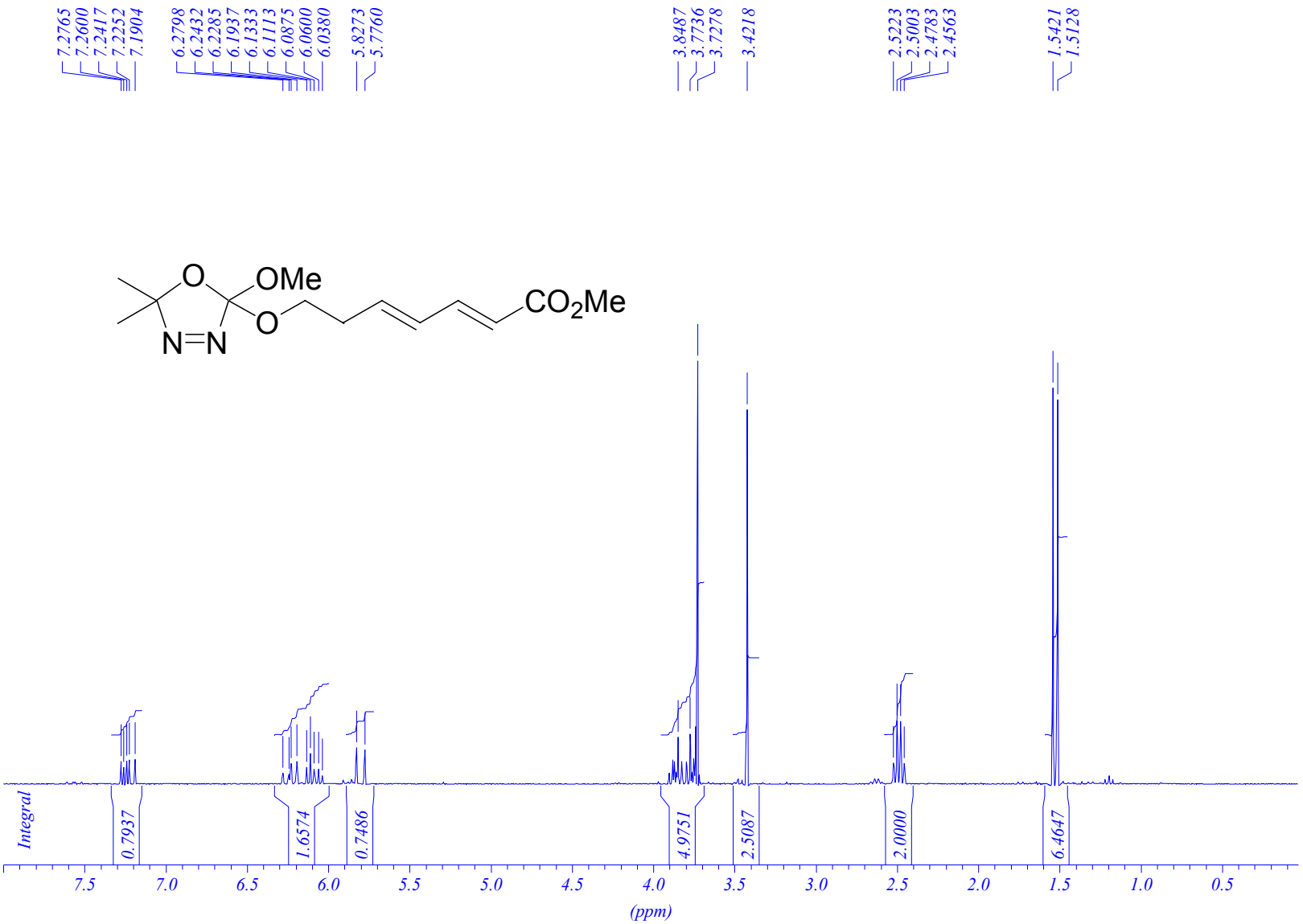
^{1}H NMR of **23b**


7.2508
7.2179
7.1995
7.1666
6.1553
6.1223
6.1076
6.0893
5.7705
5.7192
3.6966
3.6856
3.6014
3.5867
2.3152
2.2566
2.2346
2.2126
2.1870
1.6960
1.6740
1.6484
1.6227
1.6007
HO
CO2Me
Integral
1.0912
2.5775
1.0044
3.9198
3.0210
1.3179
3.0874
3.1758
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
(ppm)

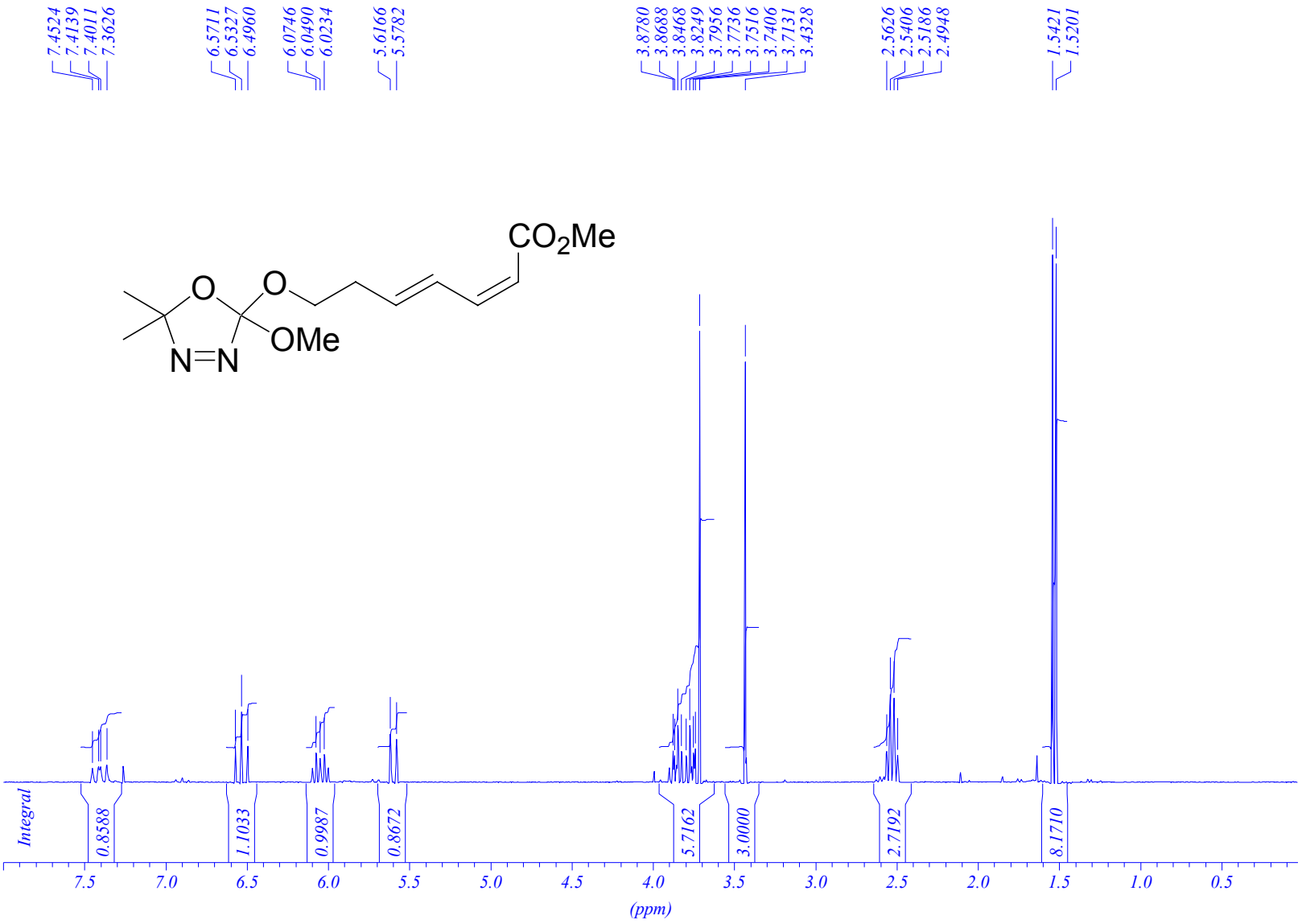
^{1}H NMR of **23c**


7.2930
7.2600
7.2417
7.2087
6.1754
6.1443
6.1296
6.1095
5.8108
5.7595
3.7278
3.6673
3.6472
3.6270
2.2145
2.1925
1.5824
1.5623
1.5586
1.5513
1.5458
1.5366
1.5311
1.5128
HO
CO2Me
Integral
0.9131
1.9096
0.7848
3.0830
2.0000
2.2973
5.2336
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
(ppm)

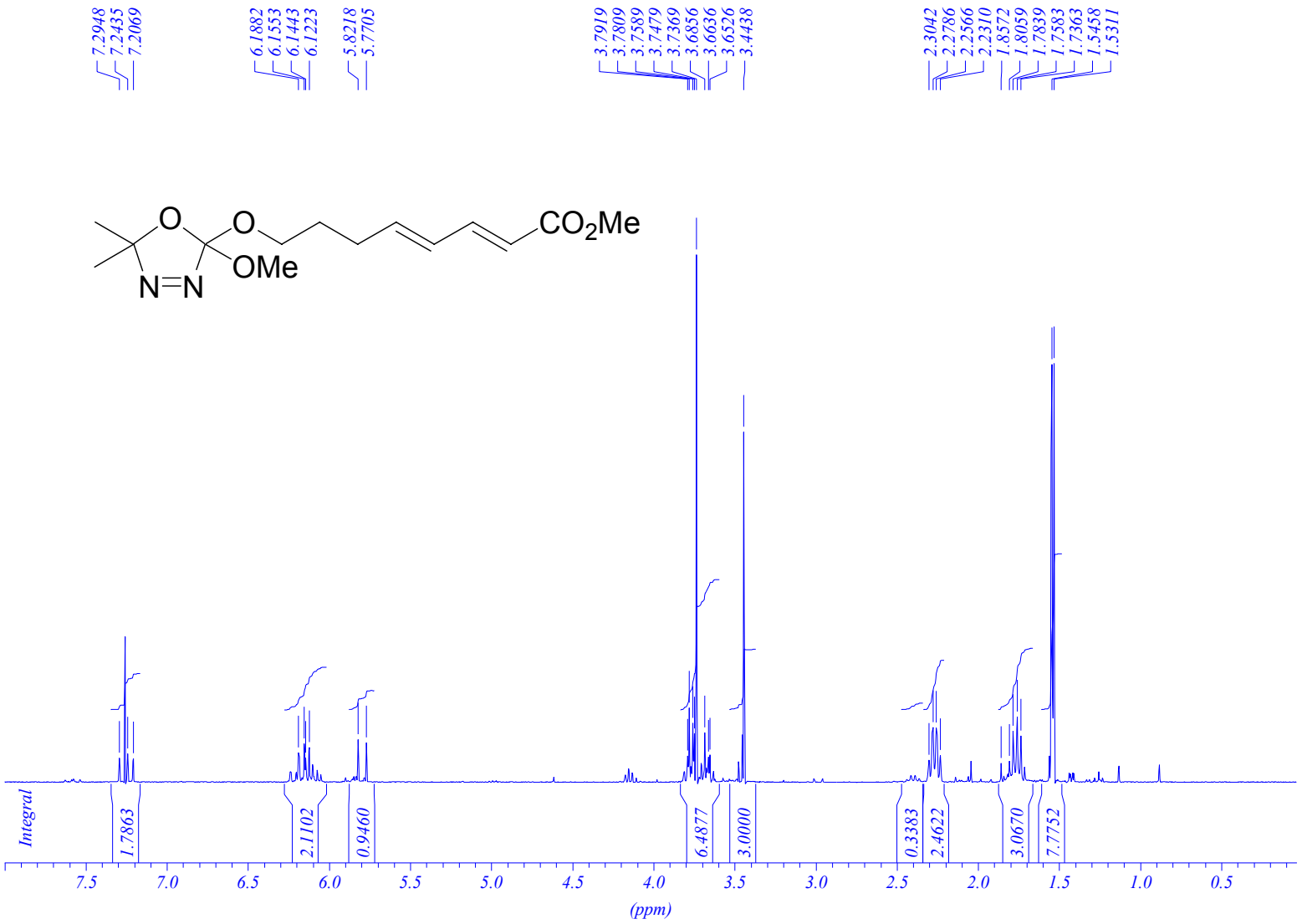
^{1}H NMR of **24a**


7.2765
7.2600
7.2417
7.2252
7.1904
6.2798
6.2432
6.2285
6.1937
6.1333
6.1113
6.0875
6.0600
6.0380
5.8273
5.7760
3.8487
3.7736
3.7278
3.4218
2.5223
2.5003
2.4783
2.4563
1.5421
1.5128
O
OMe
O
N=N
CO2Me
Integral
0.7937
1.6574
0.7486
4.9751
2.5087
2.0000
6.4647
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
(ppm)

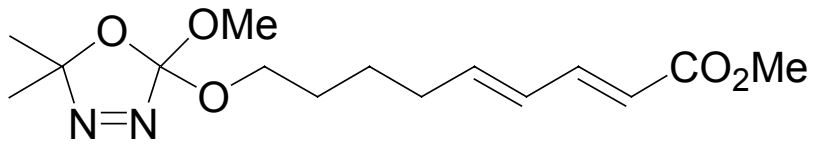
^{1}H NMR of *EZ*-**24a**

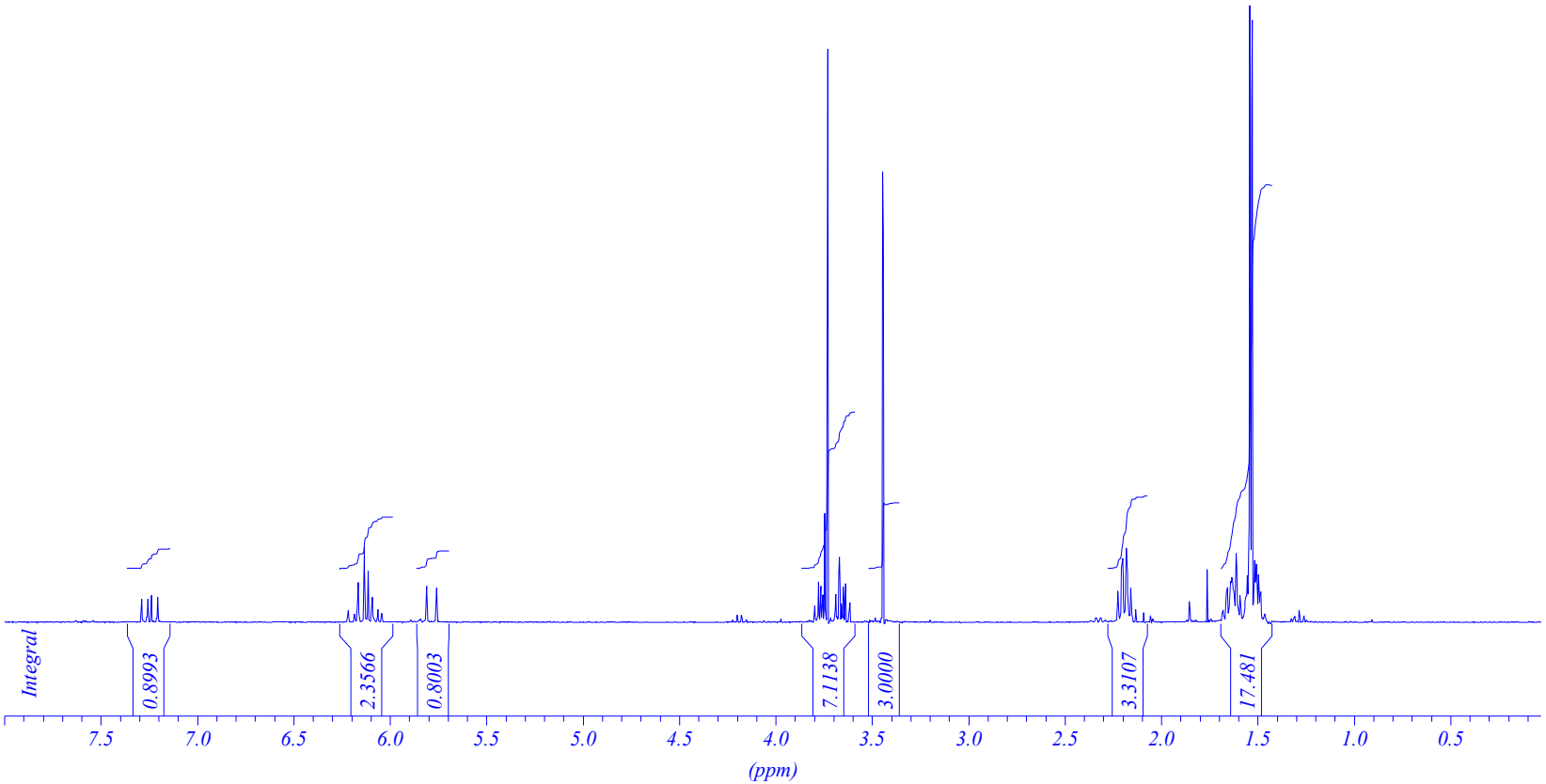


^{1}H NMR of **24b**

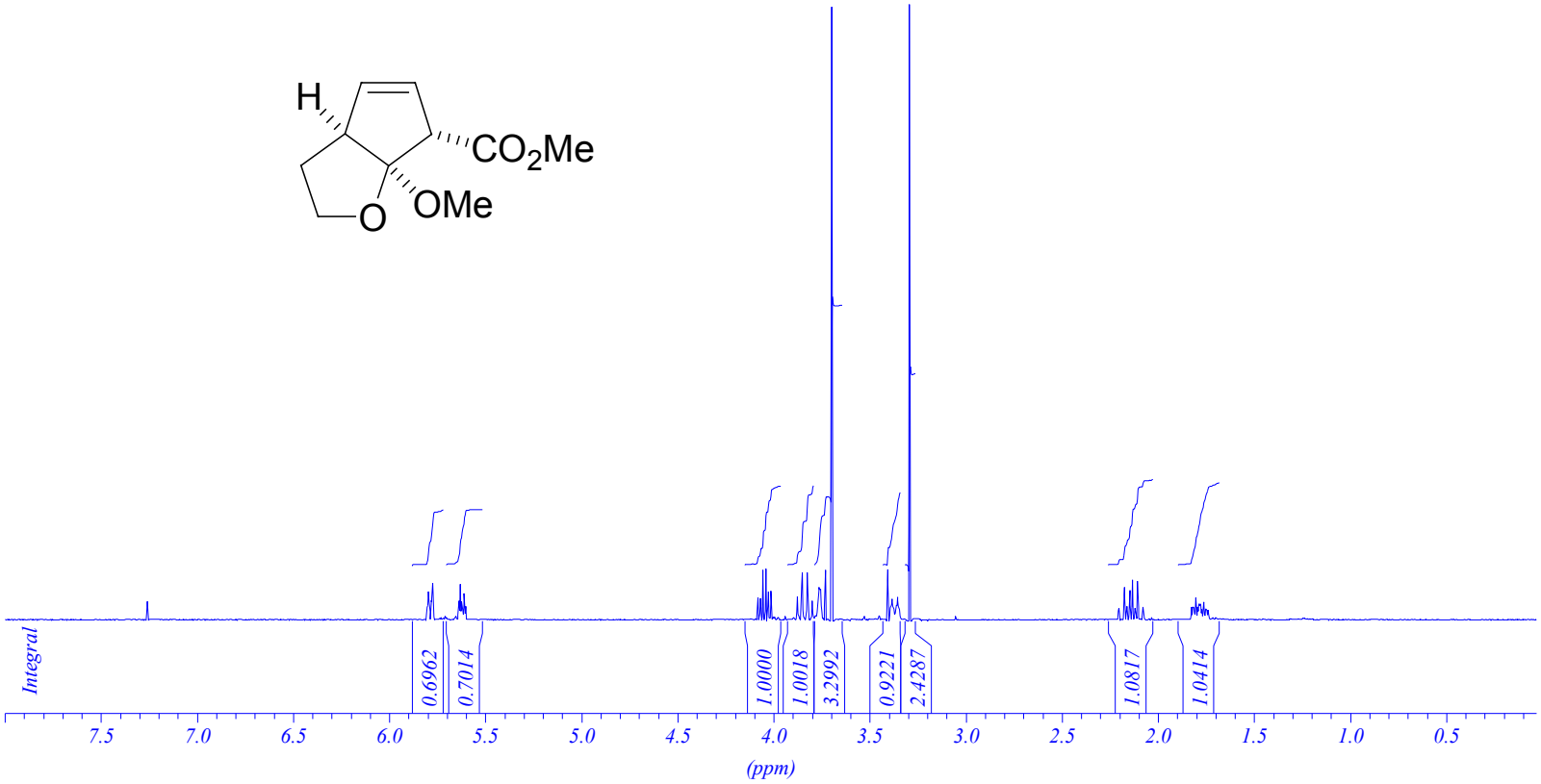

7.2948
7.2435
7.2069
6.1882
6.1553
6.1443
6.1223
5.8218
5.7705
3.7919
3.7809
3.7589
3.7479
3.7369
3.6856
3.6636
3.6526
3.4438
2.3042
2.2786
2.2566
2.2310
1.8572
1.8059
1.7839
1.7583
1.7363
1.5458
1.5311
O
O
OMe
N=N
CO2Me
Integral
1.7863
2.1102
0.9460
6.4877
3.0000
0.3383
2.4622
3.0670
7.7752
7.5
7.0
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
(ppm)

^{1}H NMR of **24c**

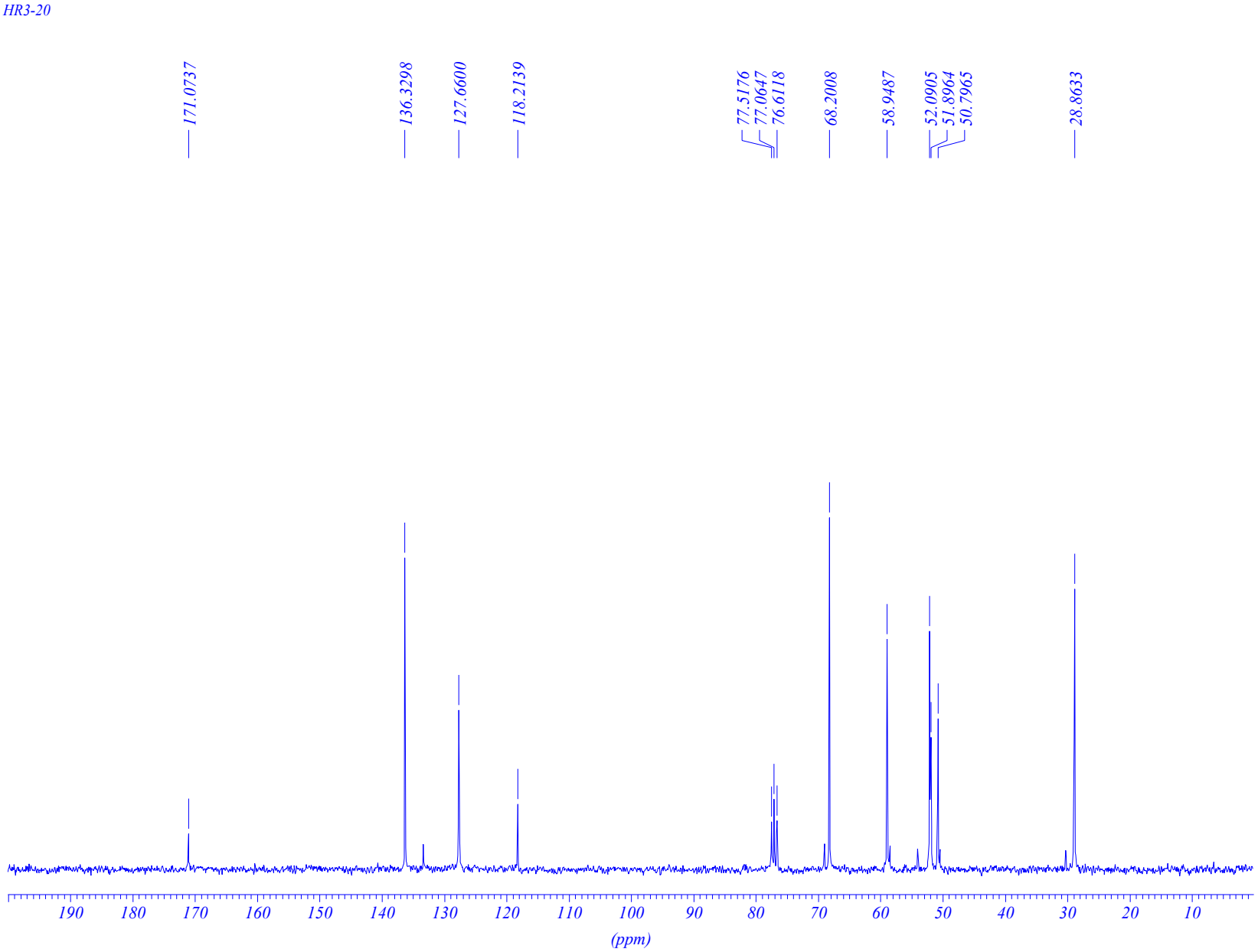

O
OMe
O
N=N
CO2Me


Integral
0.8993
2.3566
0.8003
7.1138
3.0000
3.3107
17.481
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
(ppm)

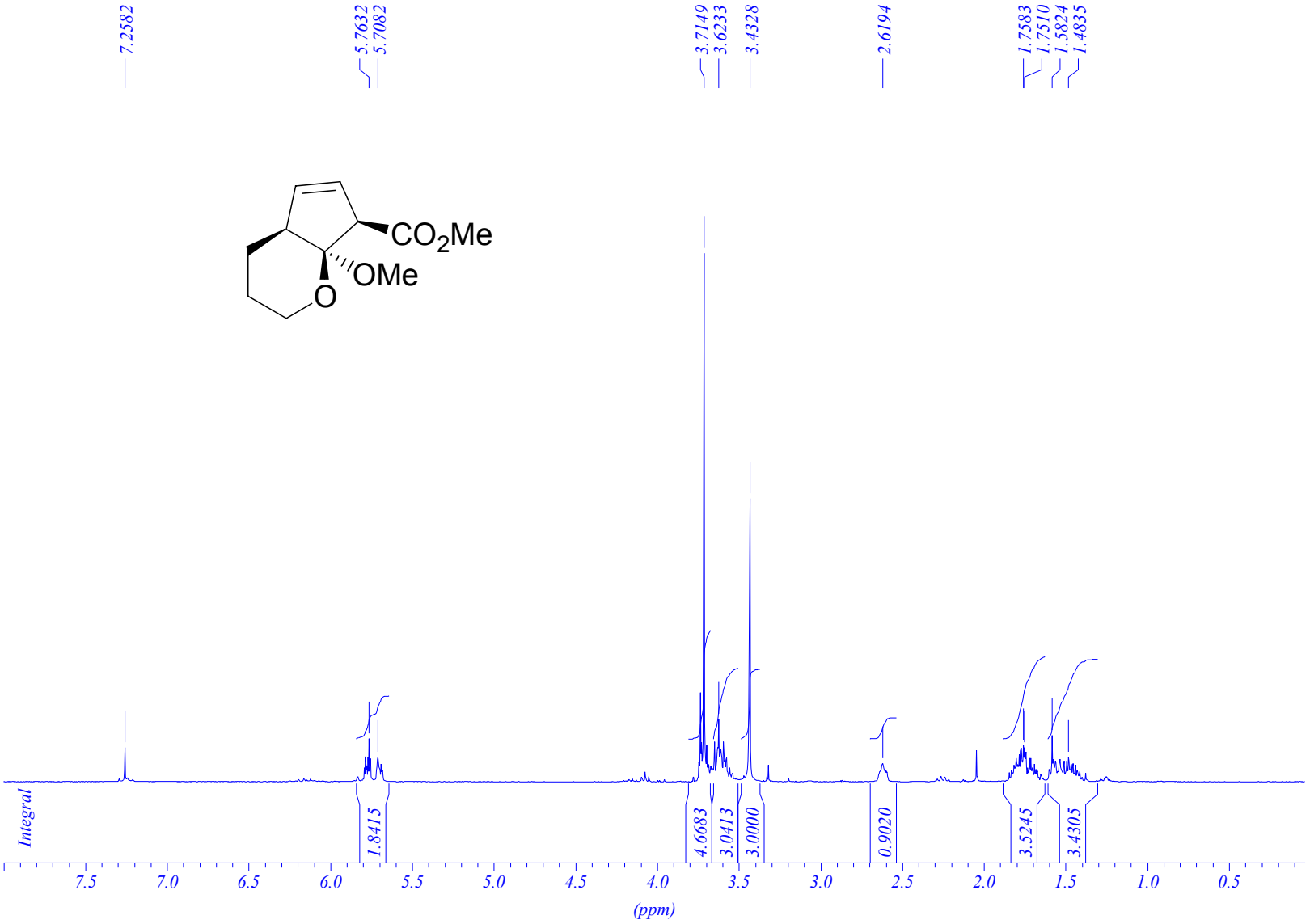
^{1}H NMR of **26a**


H
CO2Me
OMe
O
Integral
0.6962
0.7014
1.0000
1.0018
3.2992
0.9221
2.4287
1.0817
1.0414
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
(ppm)

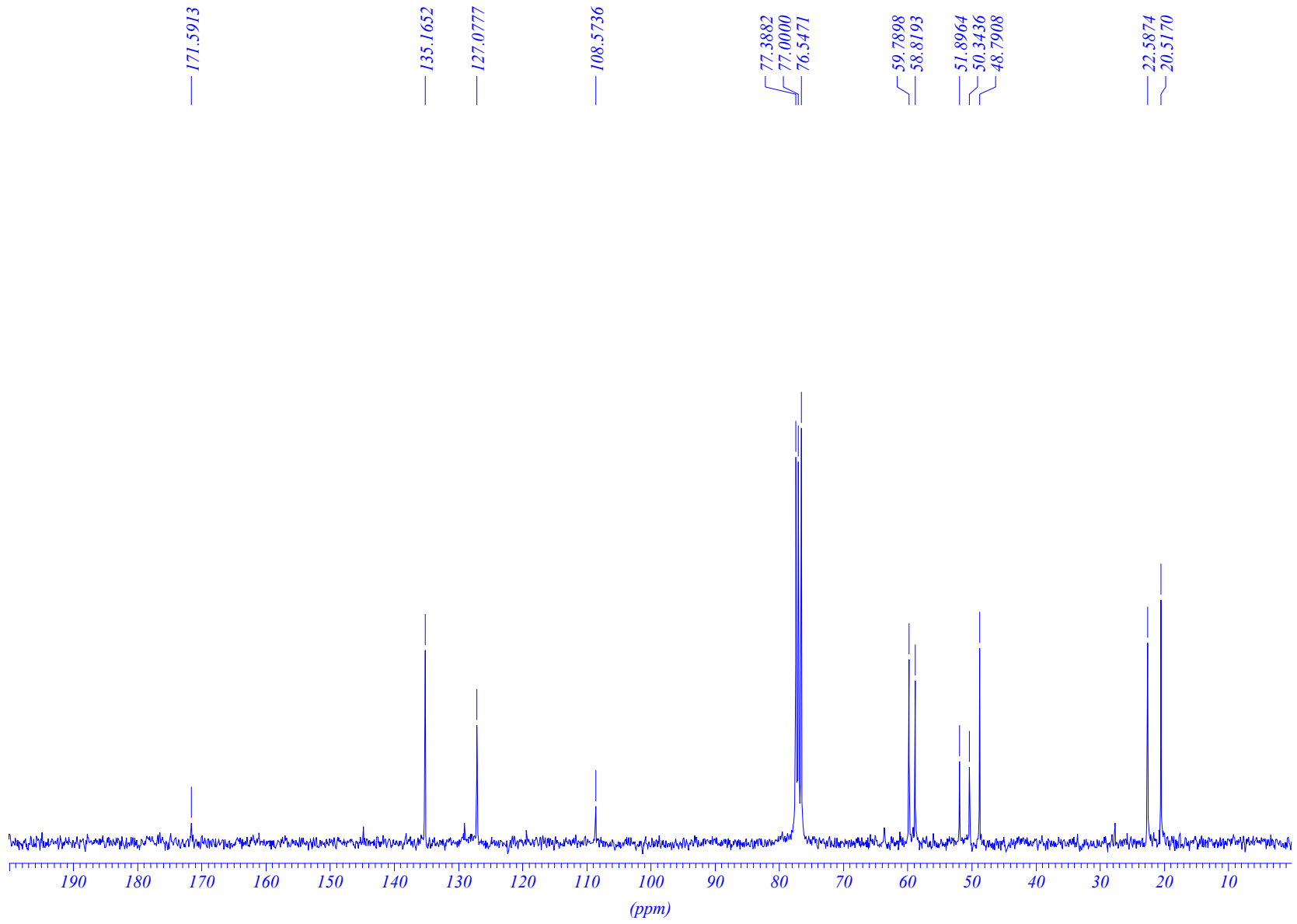
^{13}C NMR of **26a**



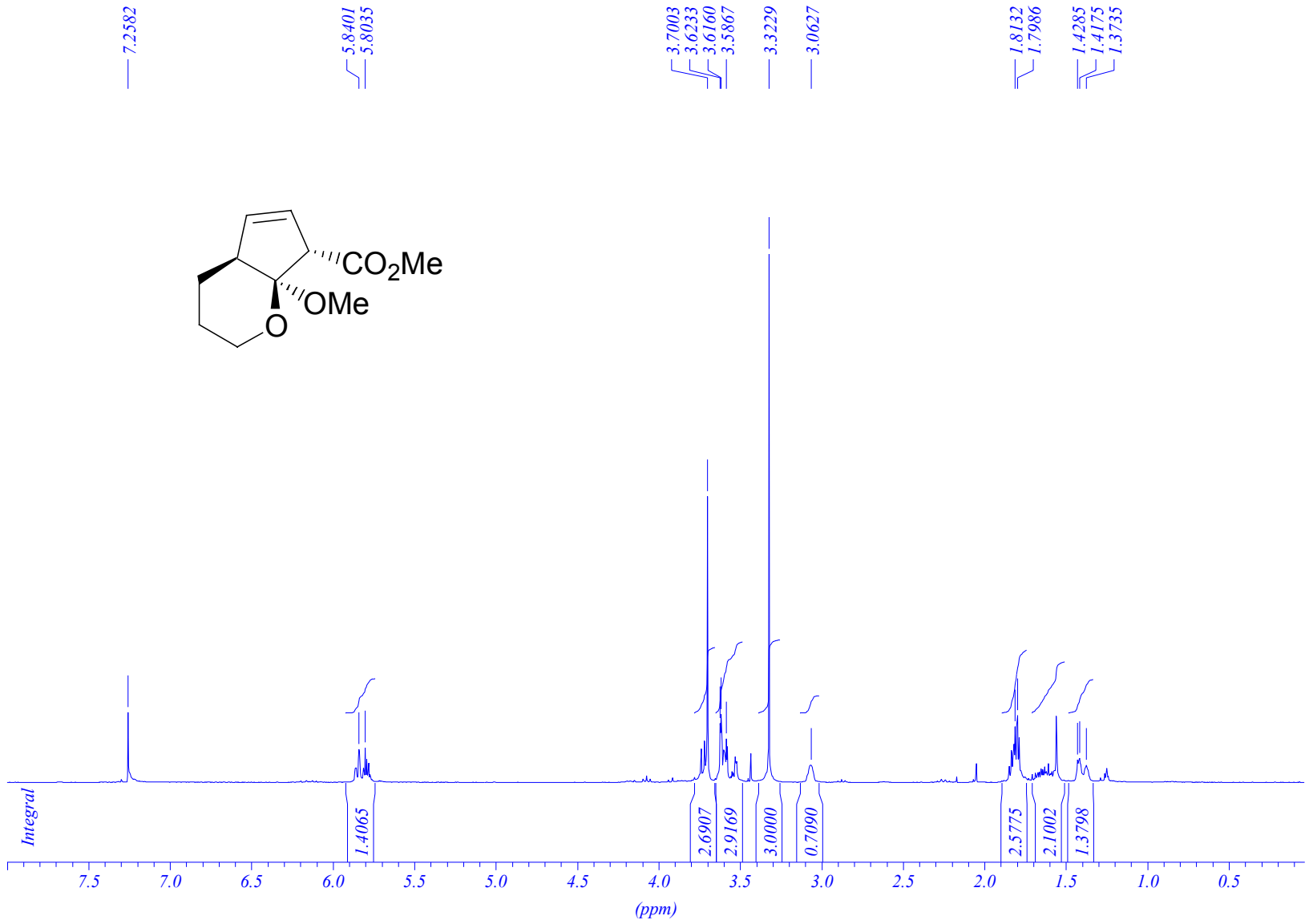
^{1}H NMR of **25b**


7.2582
5.7632
5.7082
3.7149
3.6233
3.4328
2.6194
1.7583
1.7510
1.5824
1.4835
CO2Me
OMe
O
Integral
1.8415
4.6683
3.0413
3.0000
0.9020
3.5245
3.4305
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
(ppm)

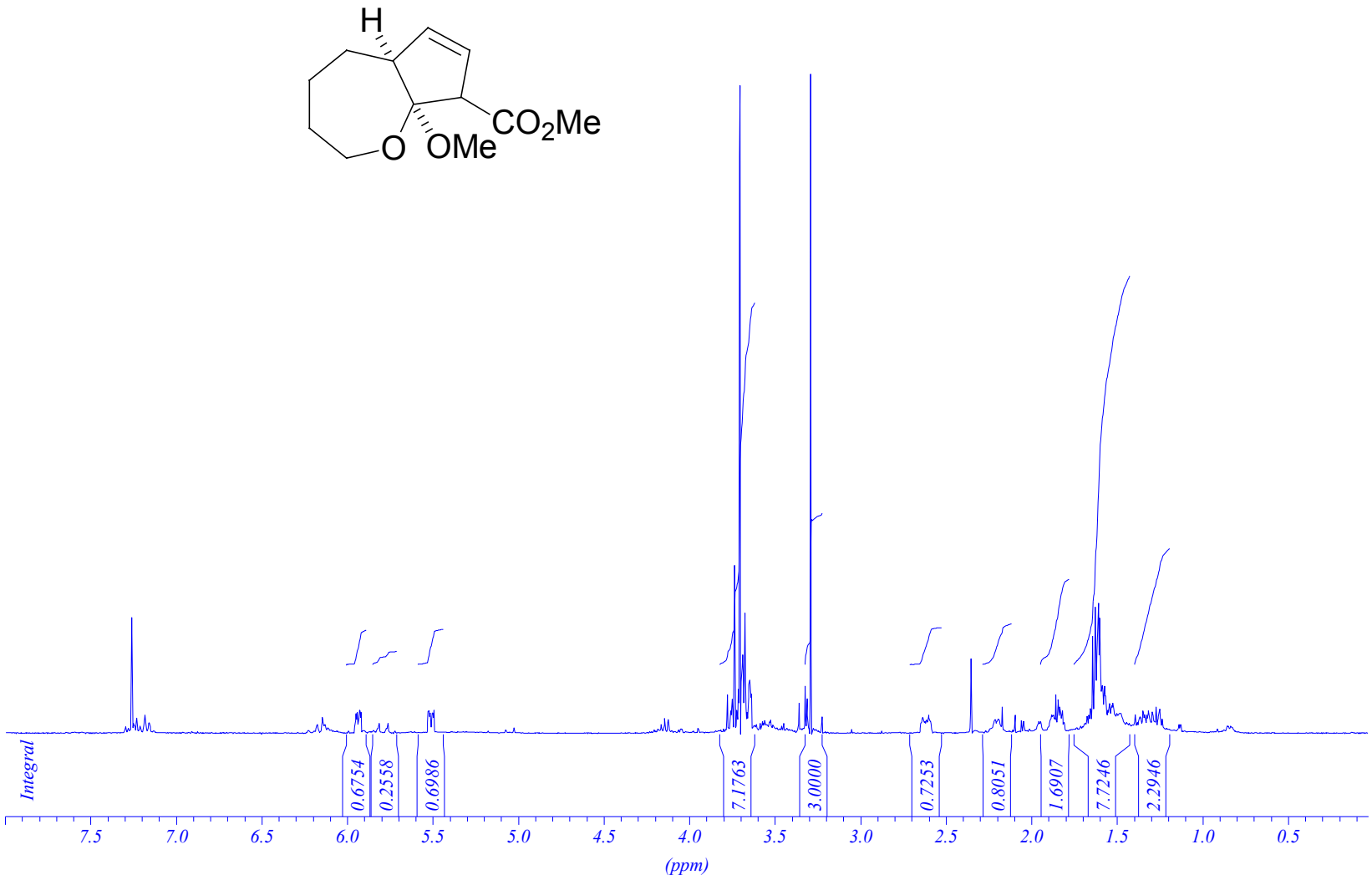
^{13}C NMR of **25b**



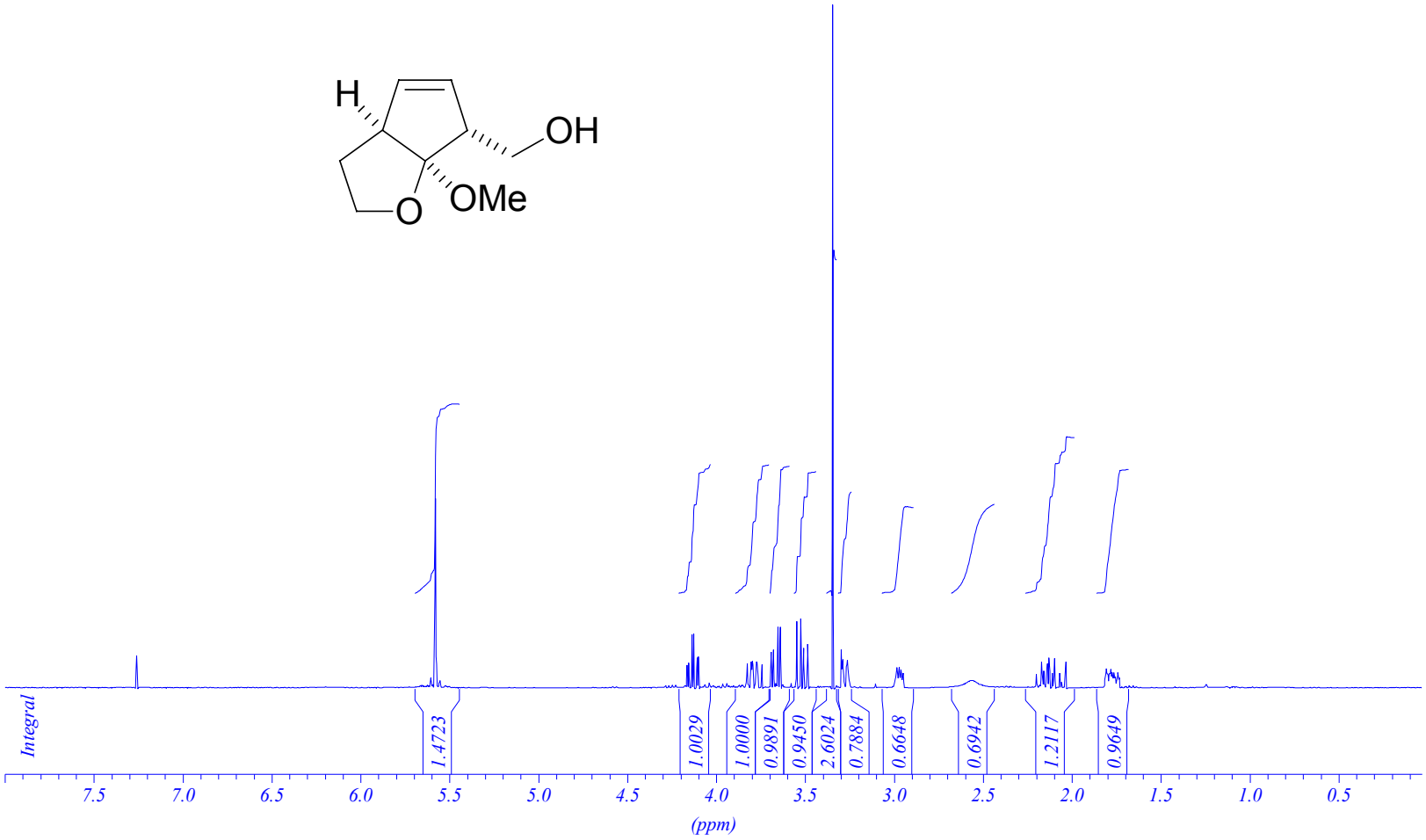
^{1}H NMR of **26b**


7.2582
5.8401
5.8035
3.7003
3.6233
3.6160
3.5867
3.3229
3.0627
1.8132
1.7986
1.4285
1.4175
1.3735
CO2Me
OMe
O
Integral
1.4065
2.6907
2.9169
3.0000
0.7090
2.5775
2.1002
1.3798
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
(ppm)

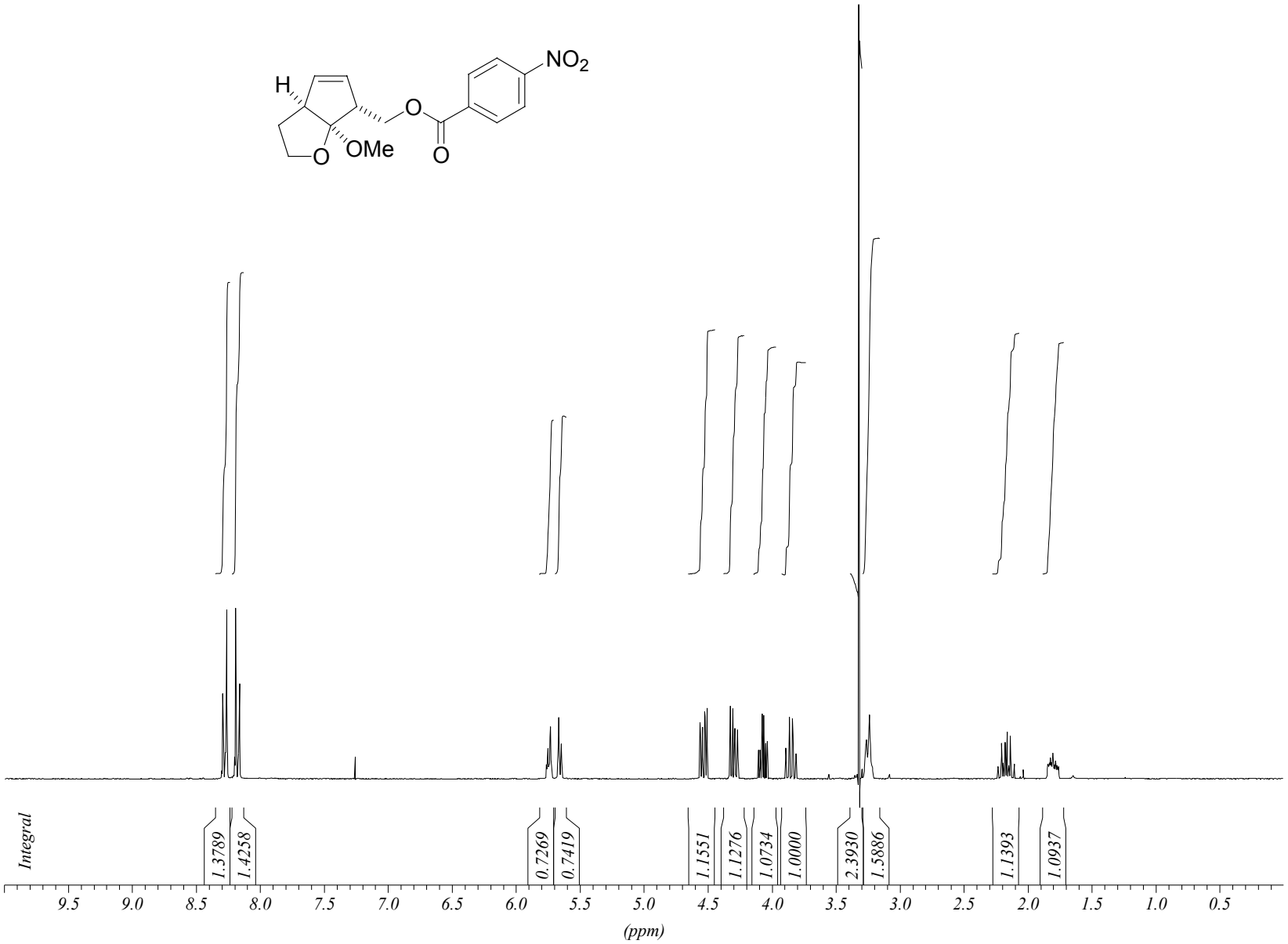
^{1}H NMR of **25c** or **26c**



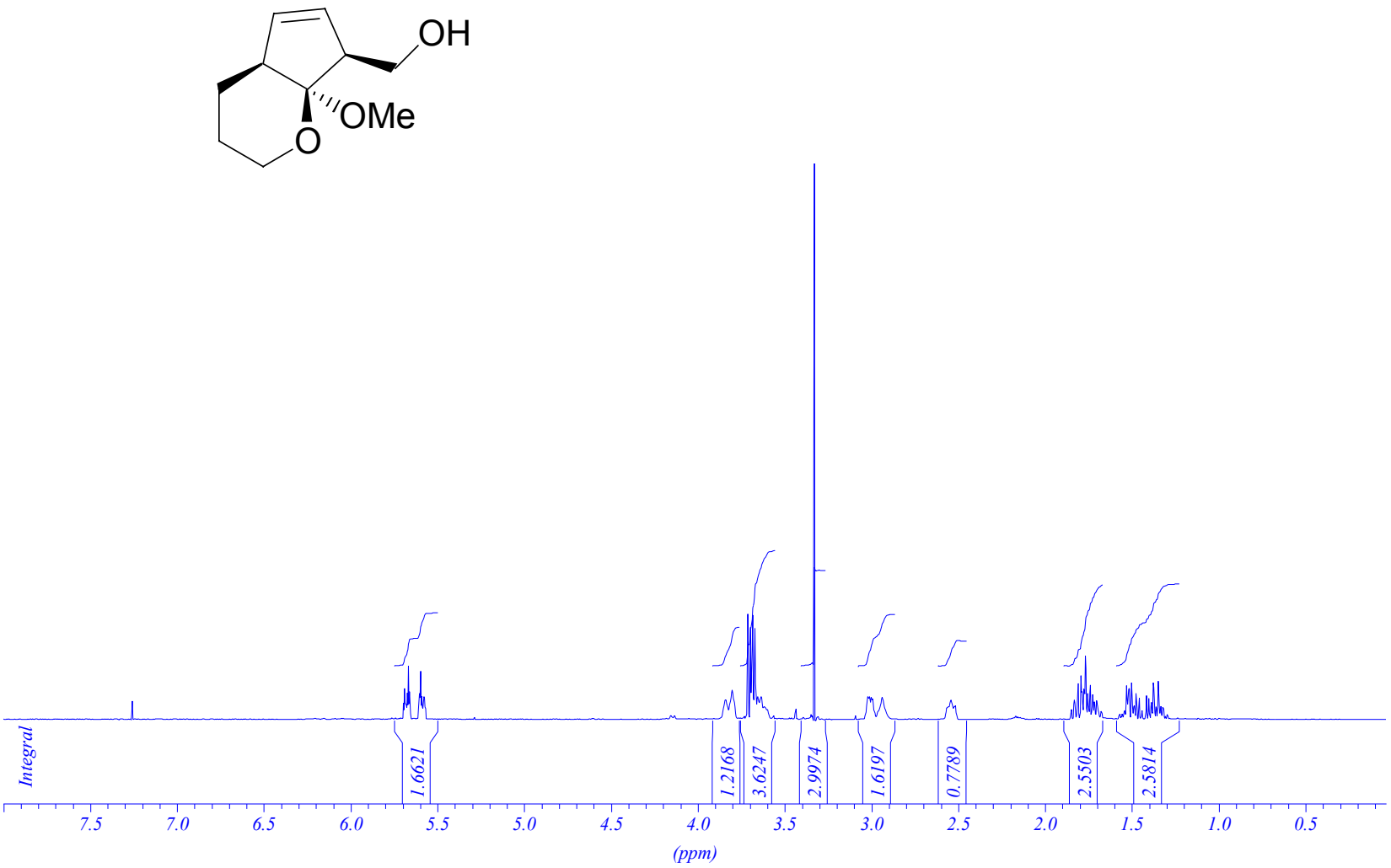
^{1}H NMR of reduction product from **26a**



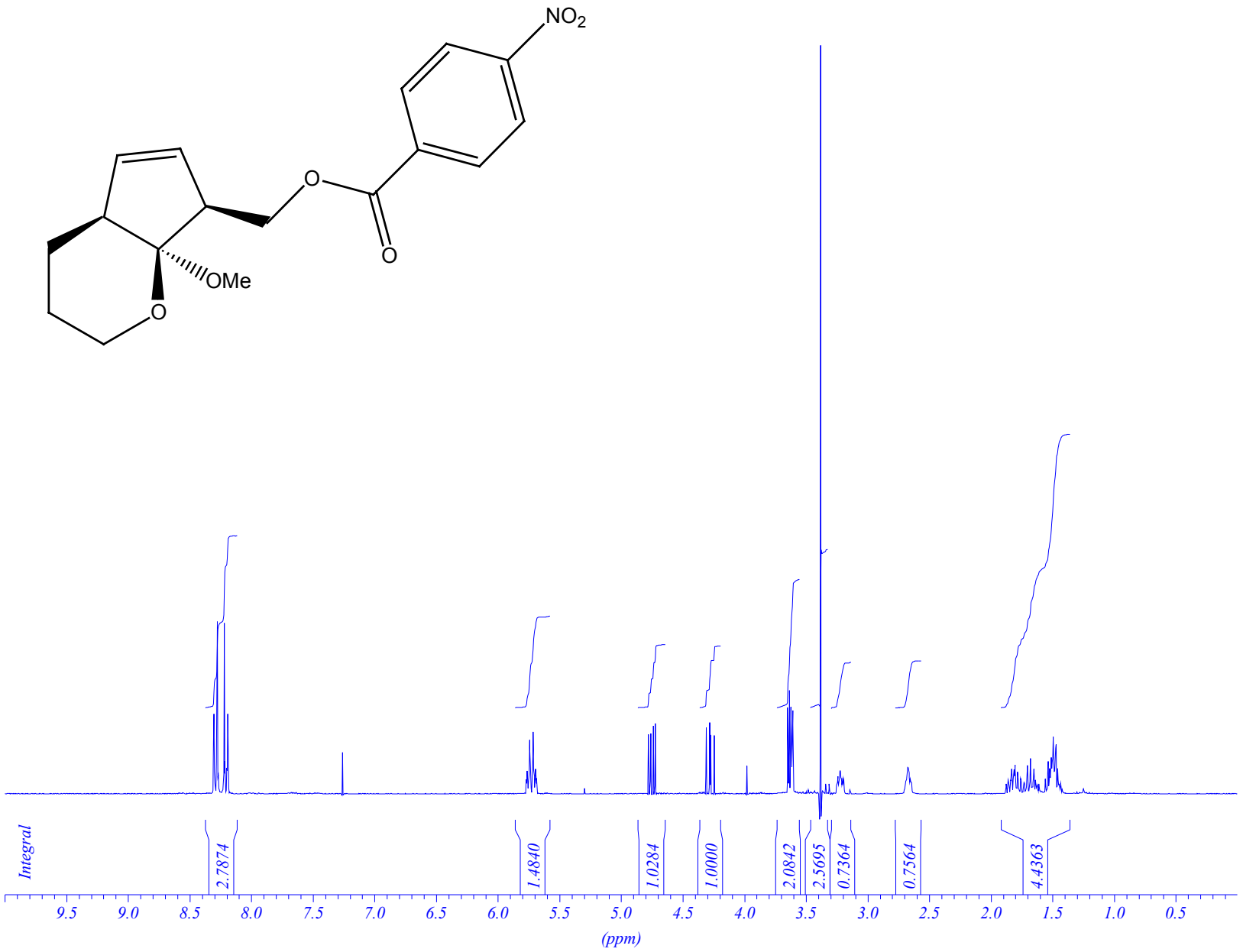
^{1}H NMR of *p*-nitrobenzoate from the reduction of **26a**



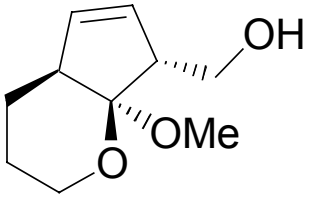
^{1}H NMR of reduction of adduct **25b**

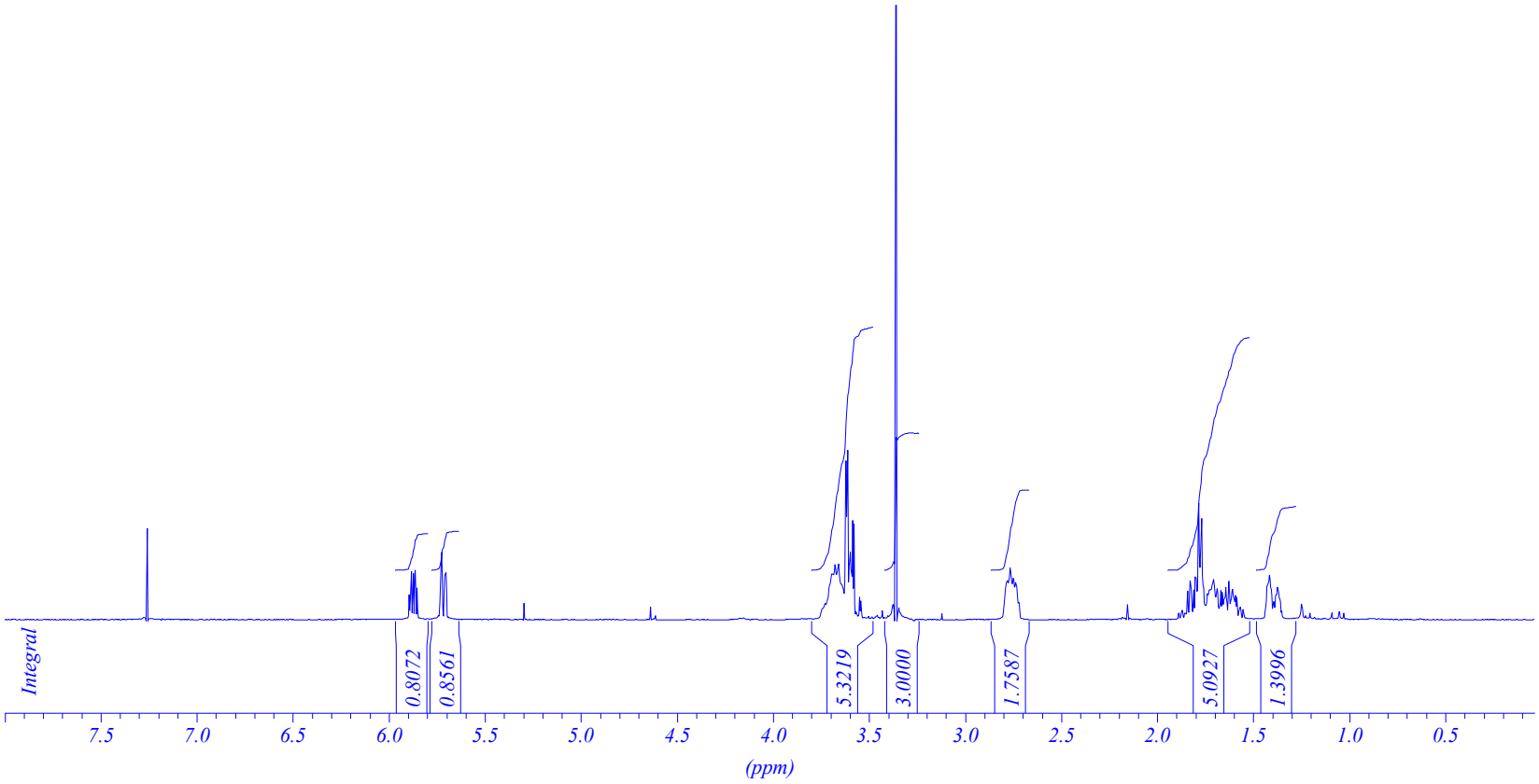


^{1}H NMR of *p*-nitrobenzoate from the reduction of **25b**

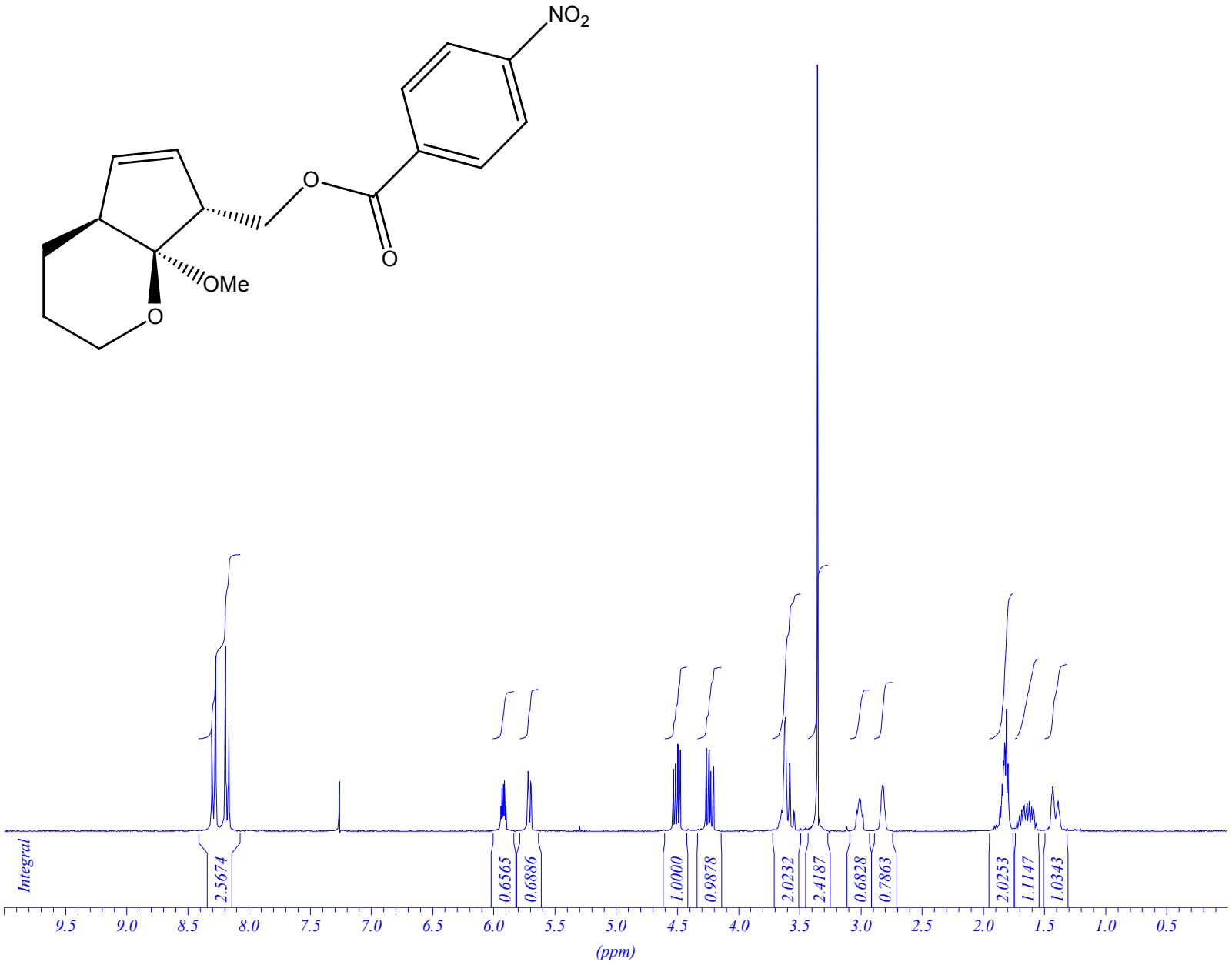


^{1}H NMR of reduction of adduct **26b**

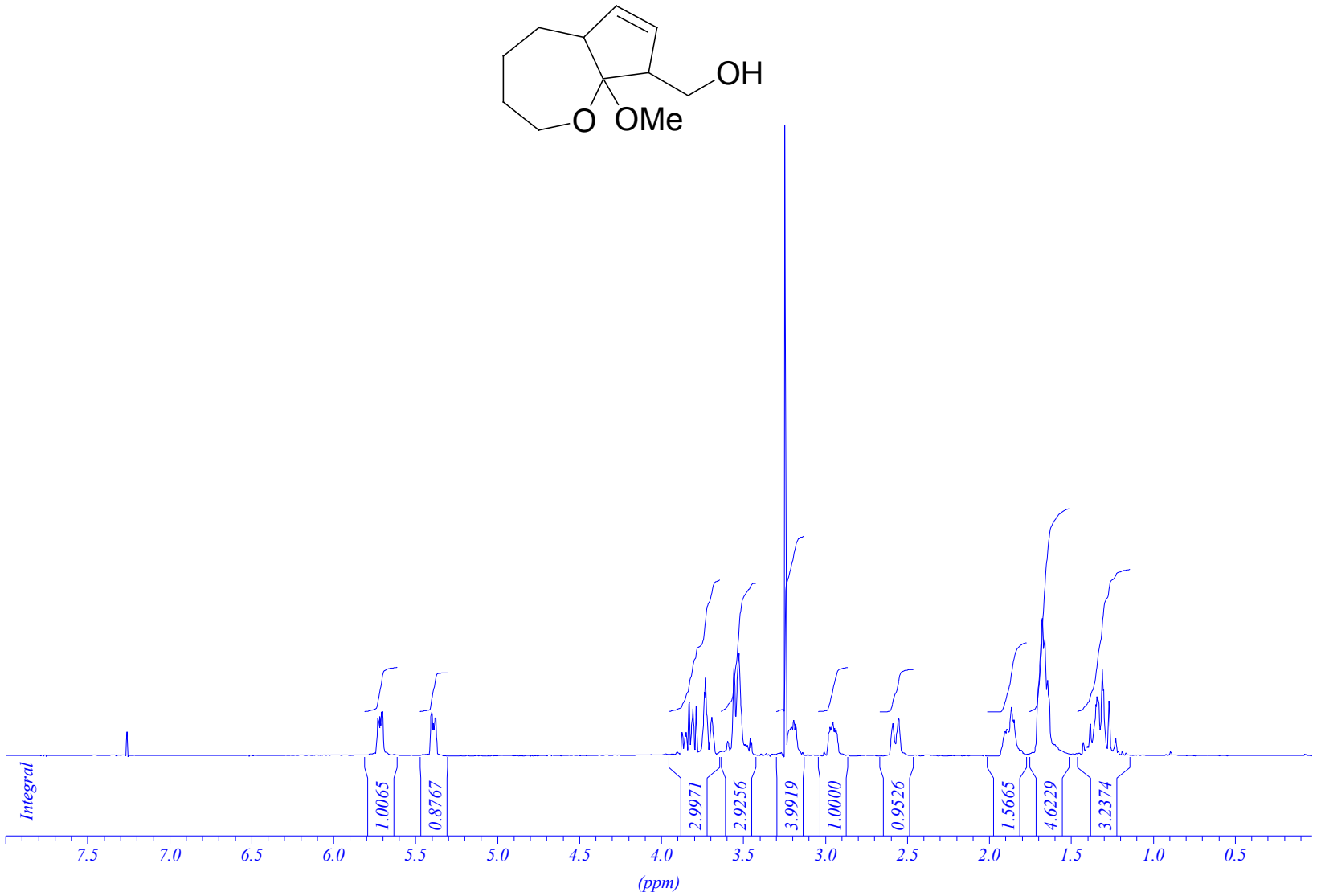




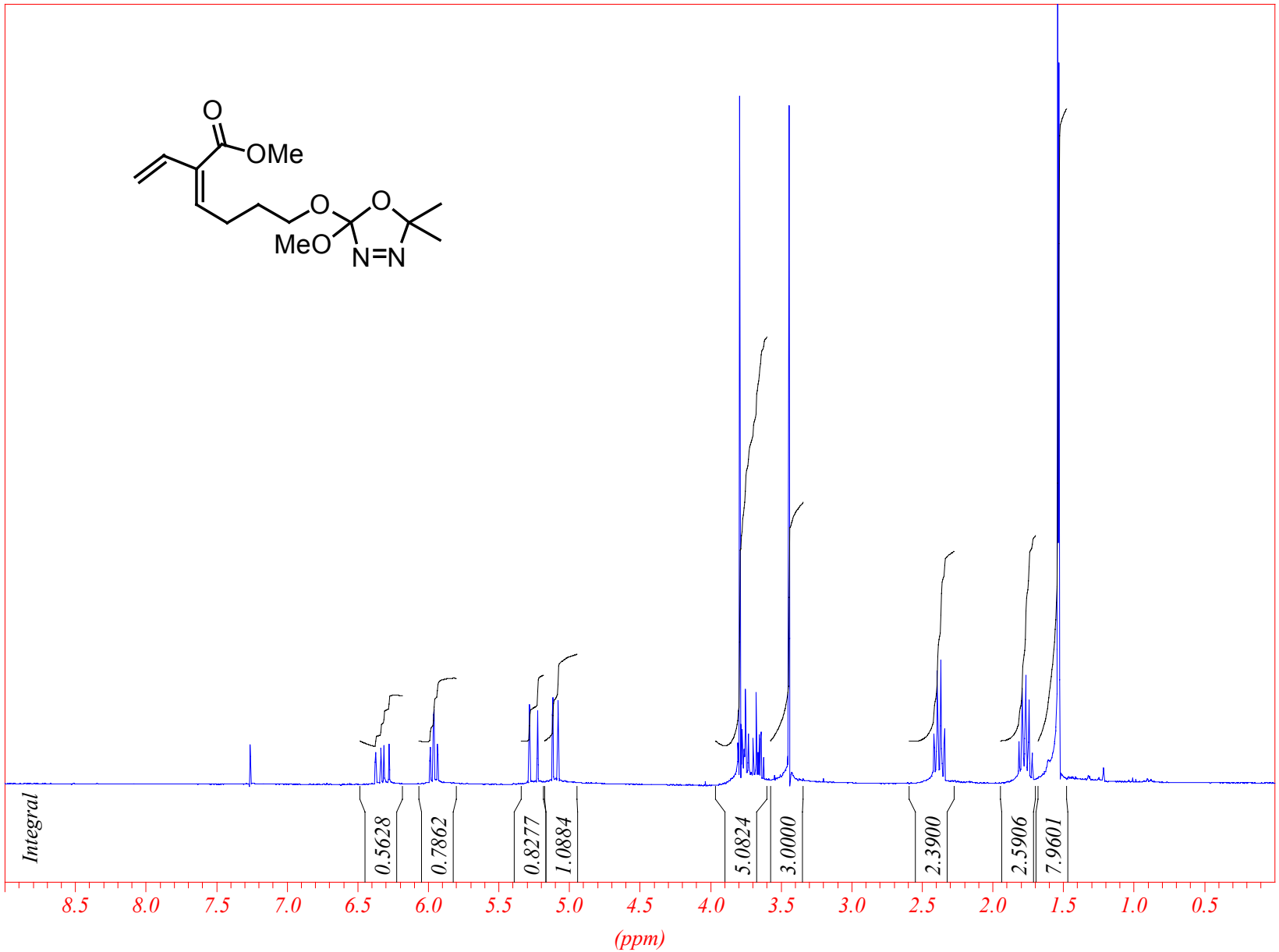
^{1}H NMR of *p*-nitrobenzoate from the reduction of **26b**



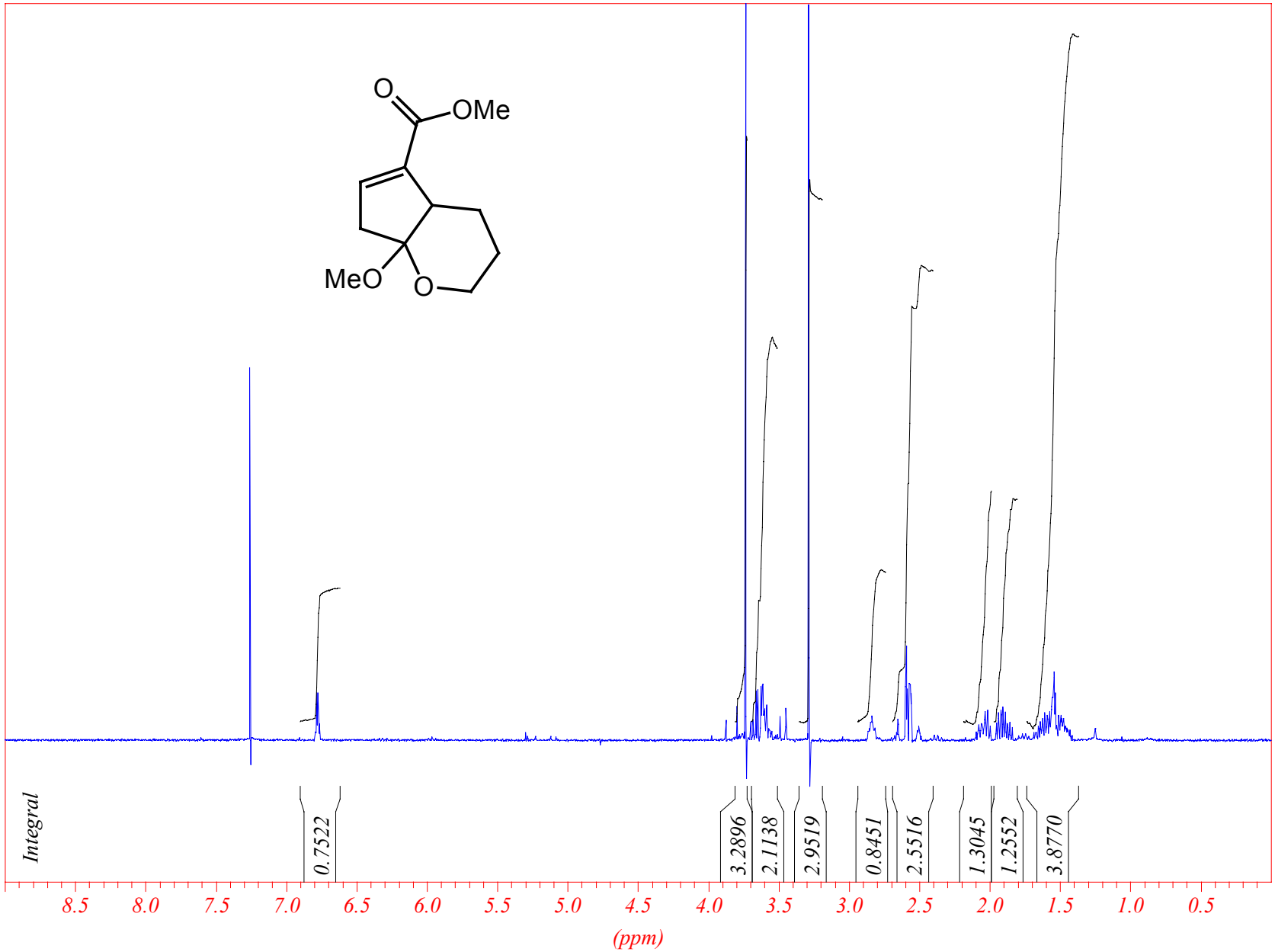
^{1}H NMR of reduction of adduct **25c** or **26c**



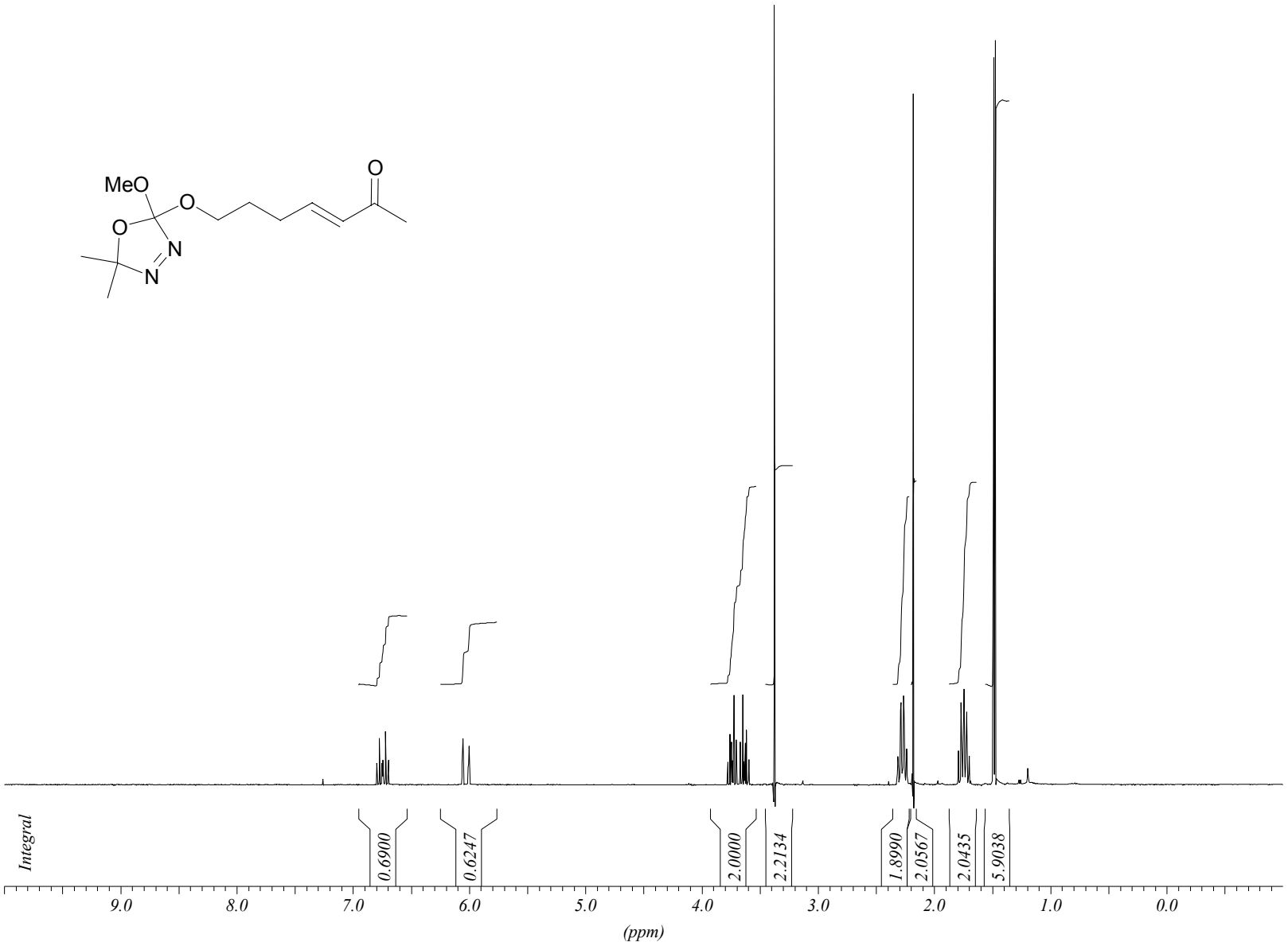
^{1}H NMR of oxadiazoline **27**



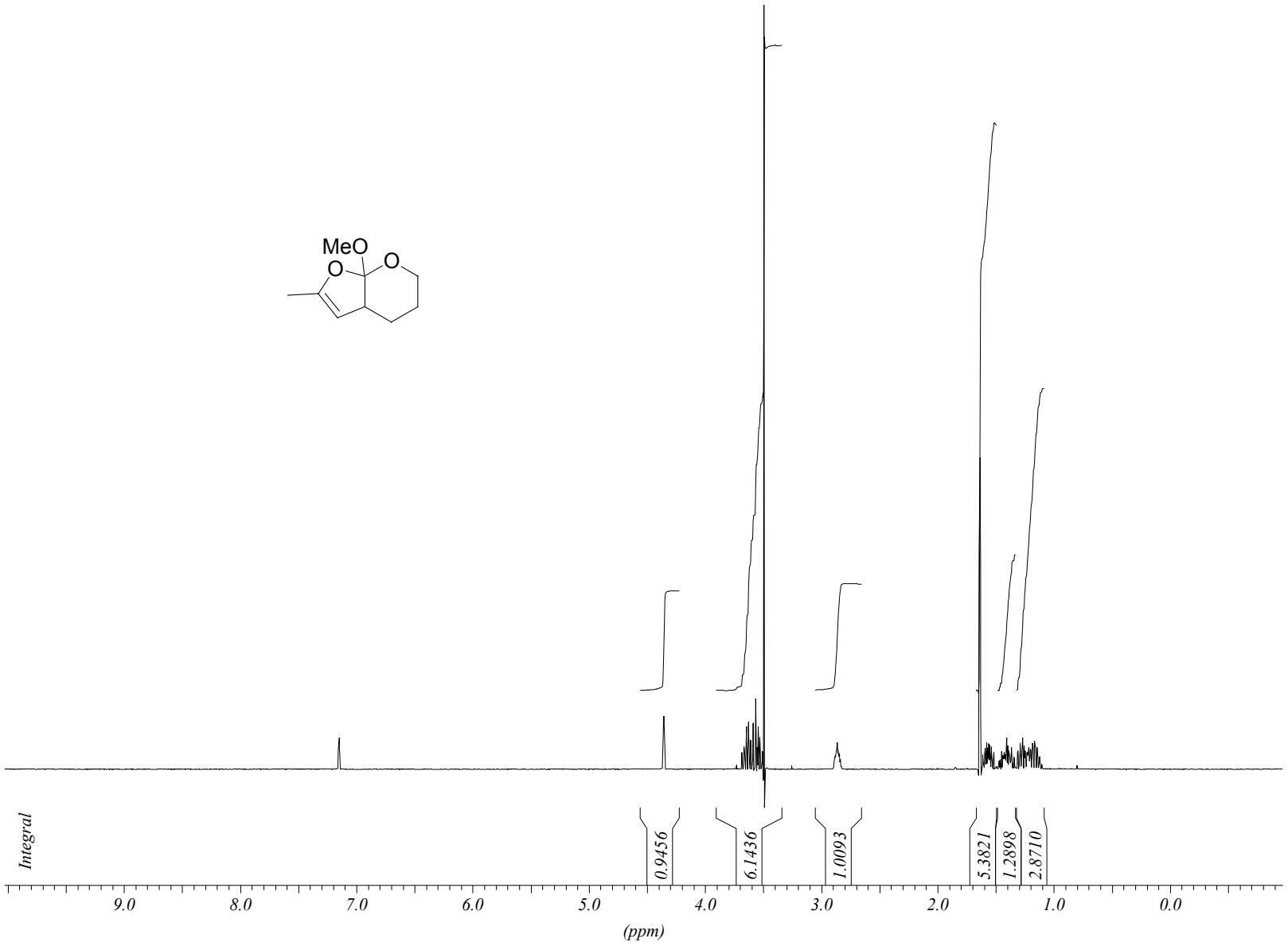
^{1}H NMR of adduct **28**



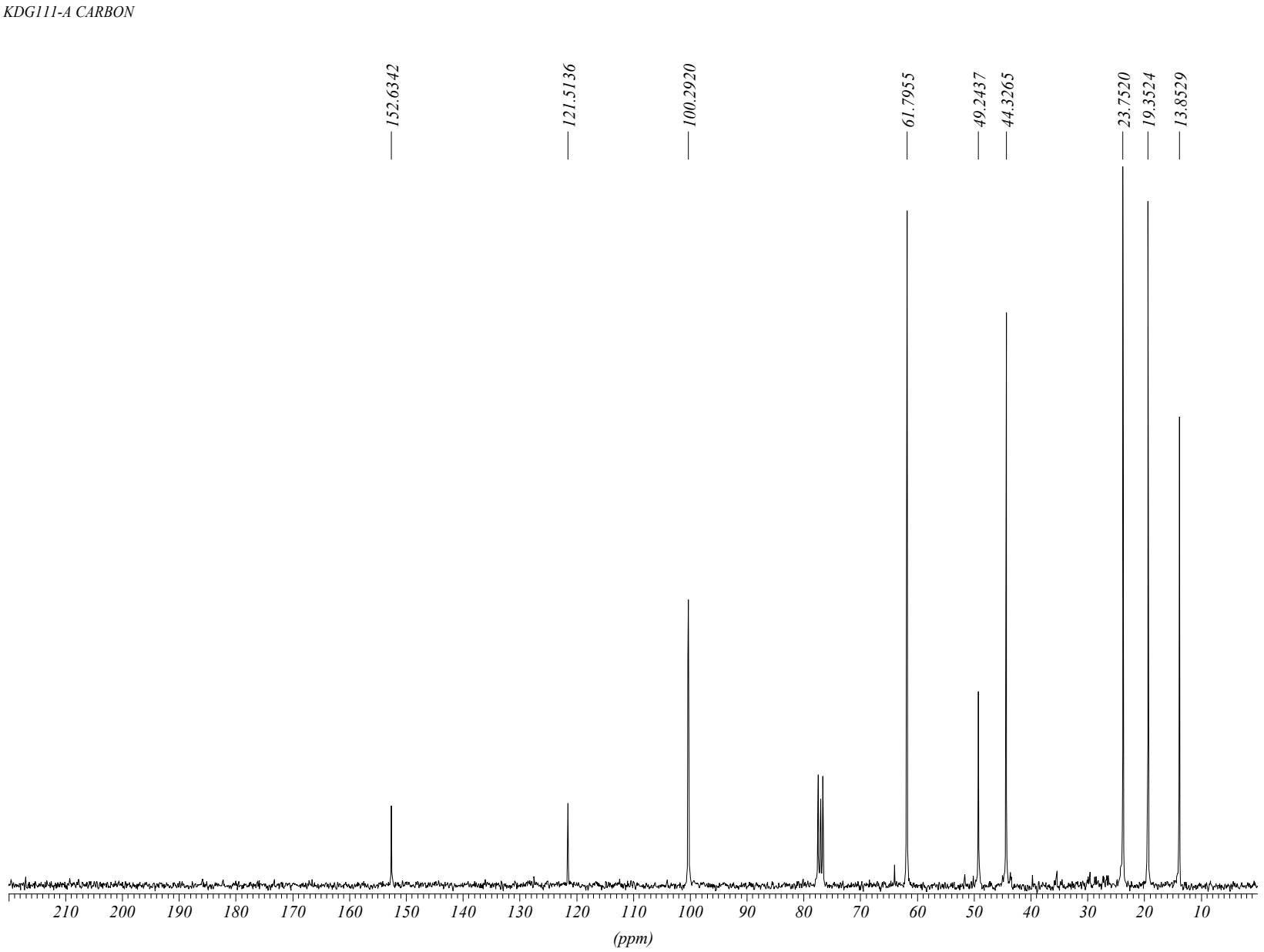
^{1}H NMR of oxadiazoline **29**



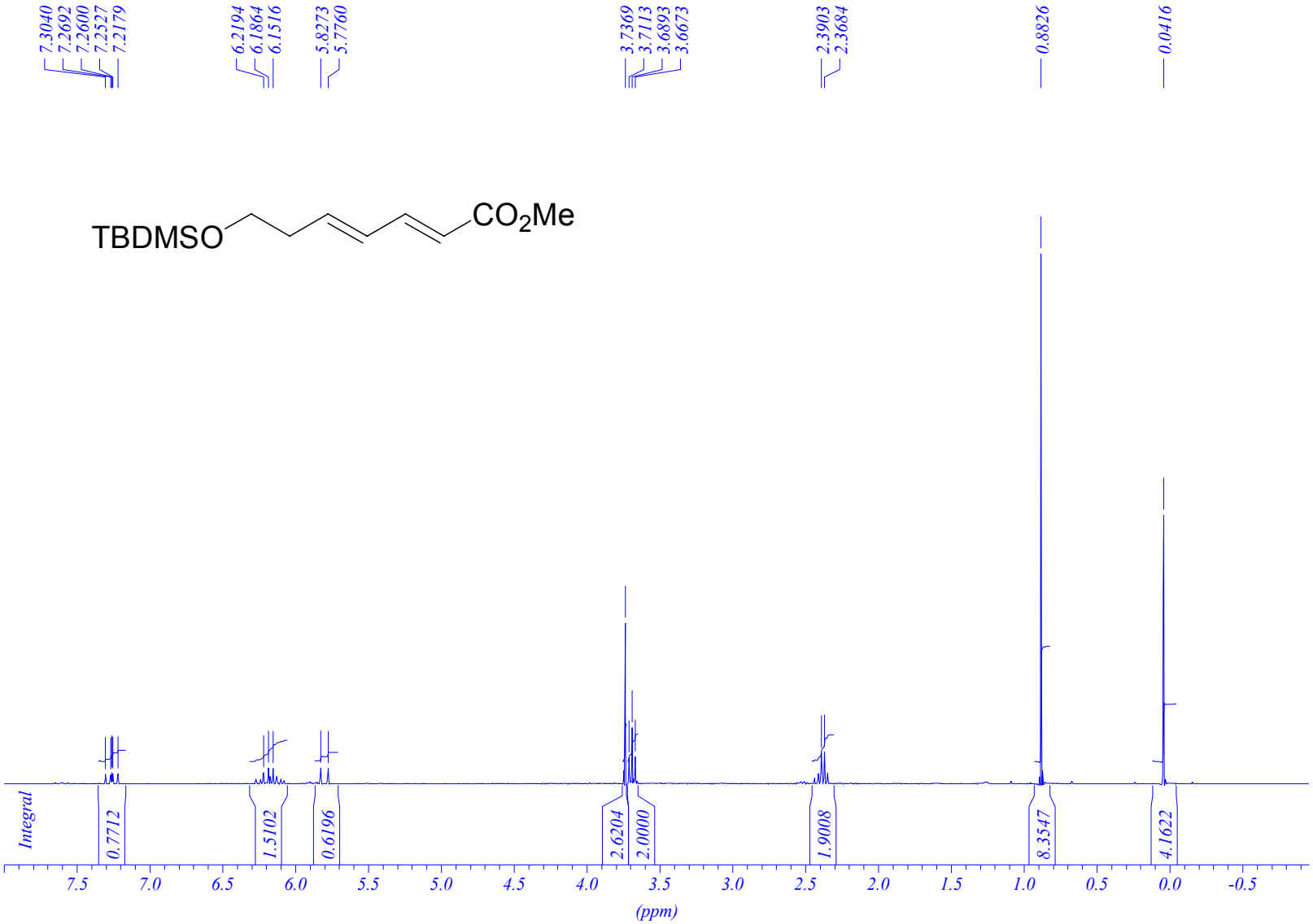
^{1}H NMR of adduct **30**



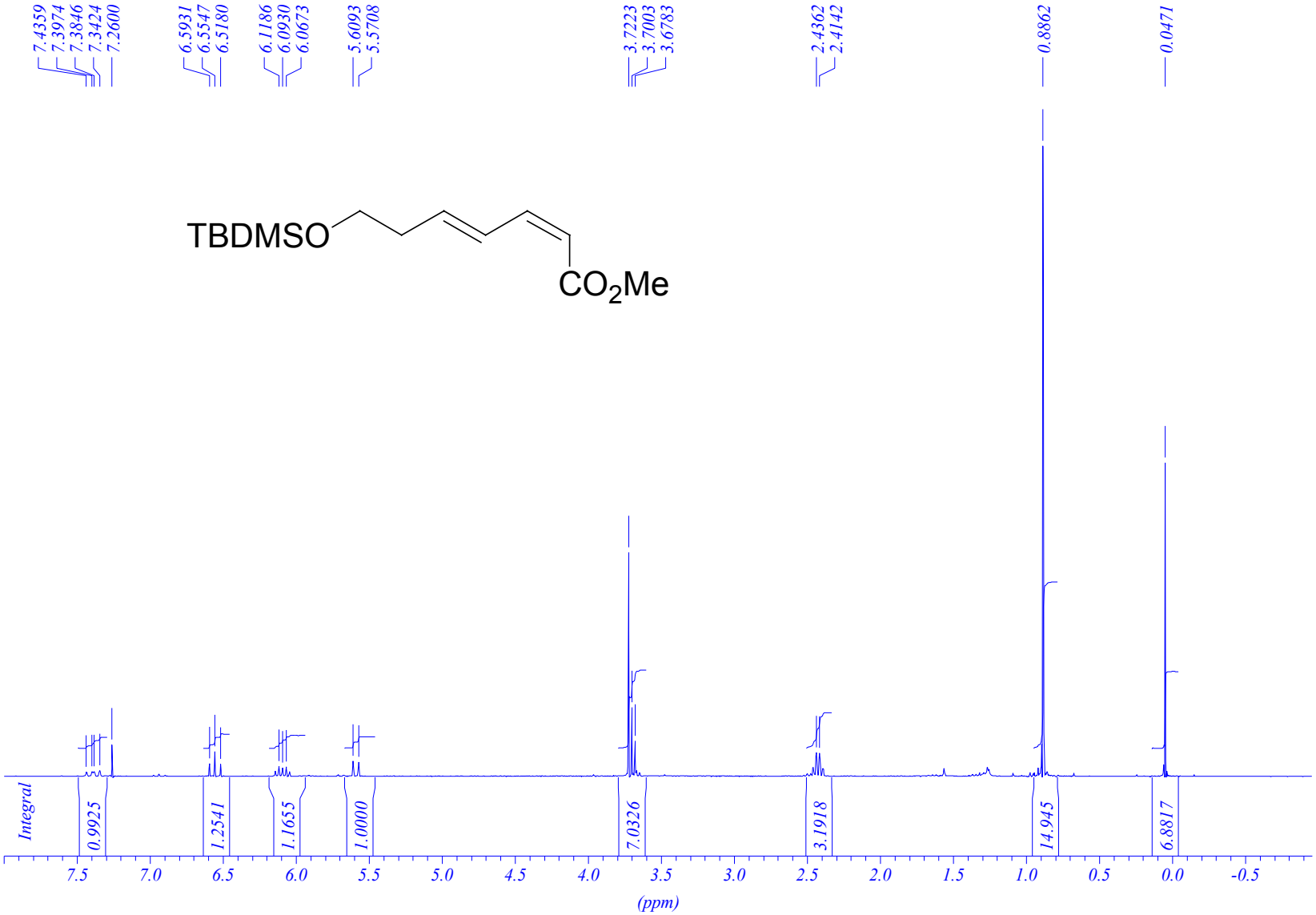
^{13}C NMR of adduct **30**



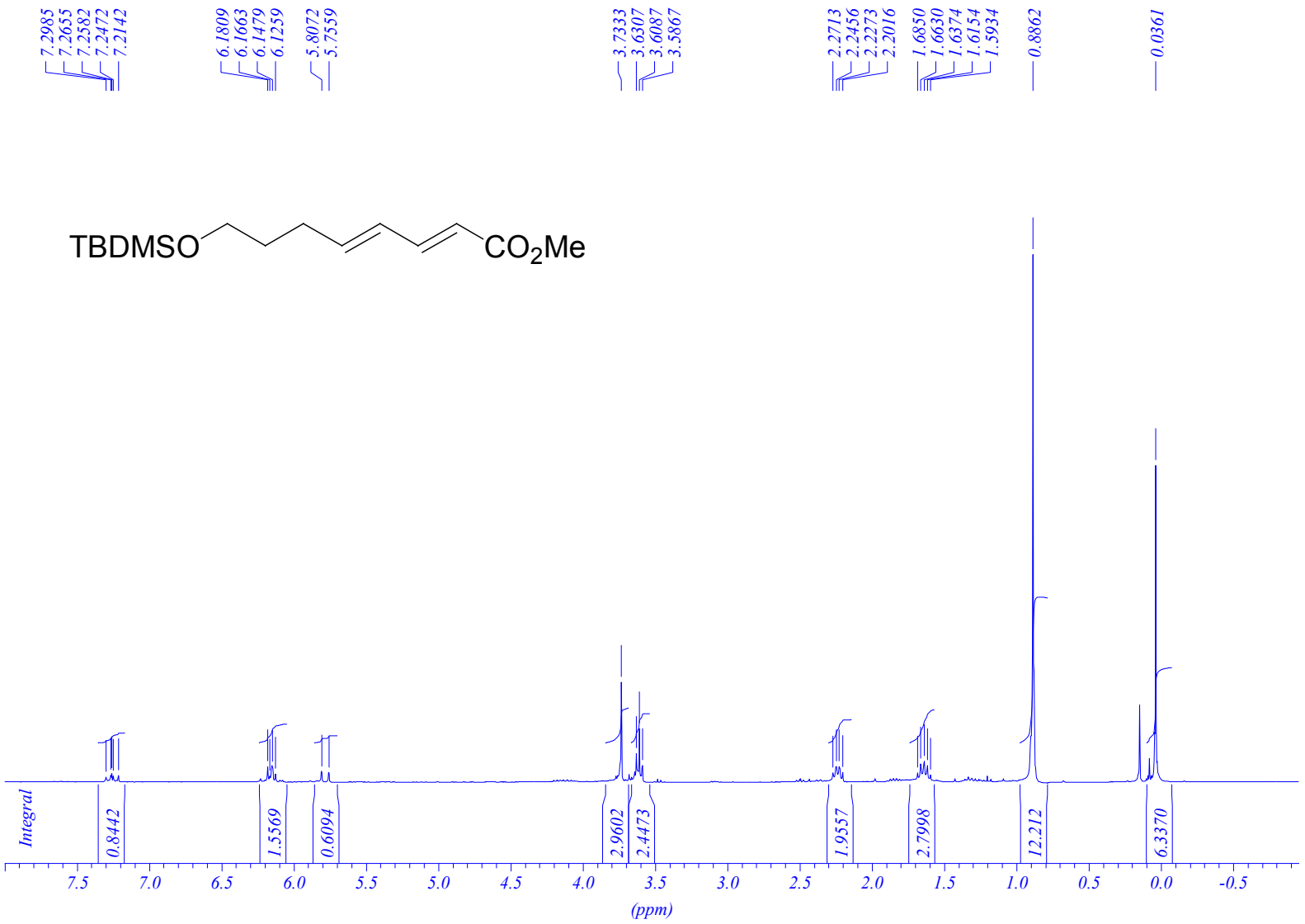
^{1}H NMR of diene **32a**



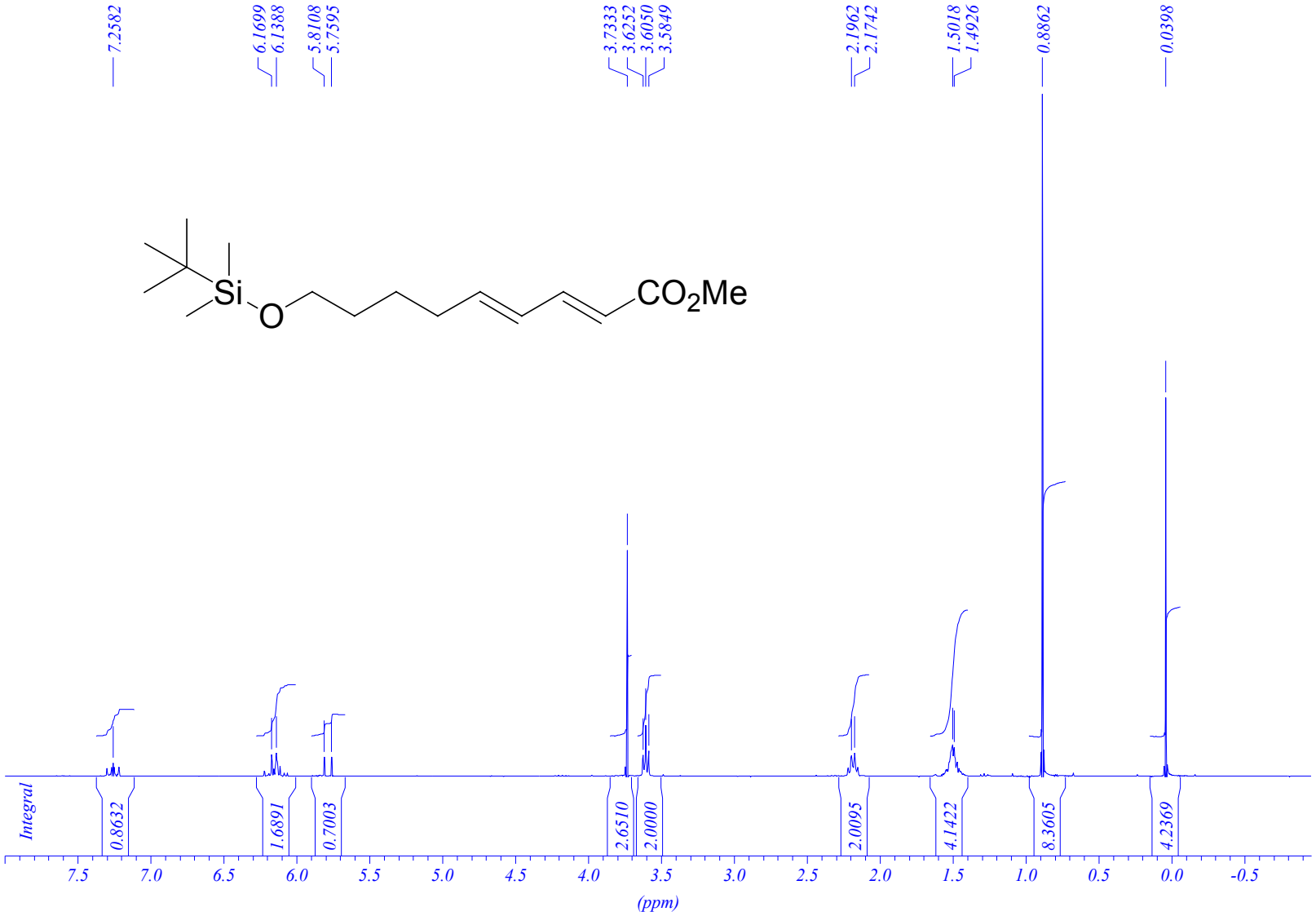
^{1}H NMR of diene *EZ*-**32a**



^{1}H NMR of diene **32b**

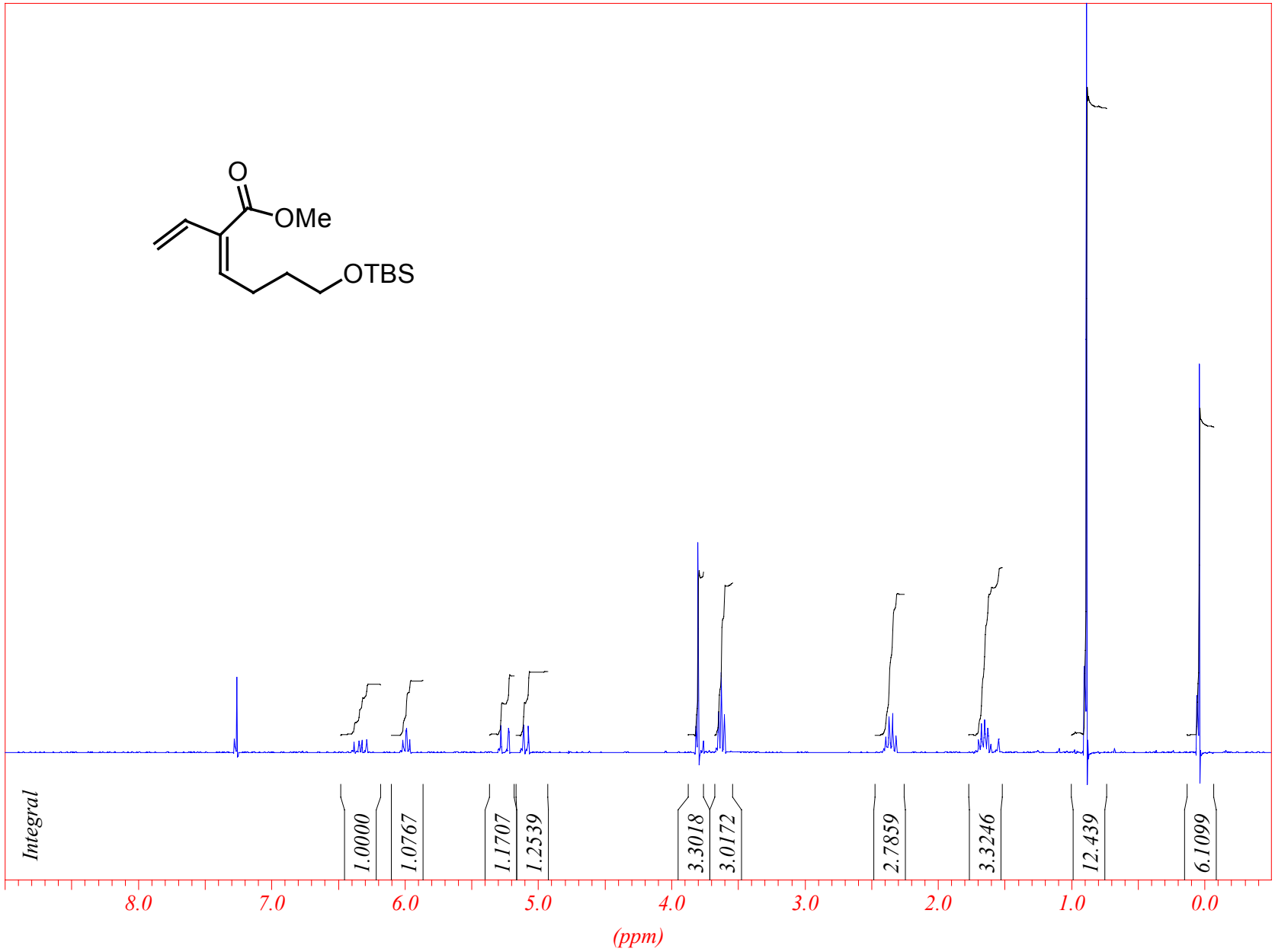


^{1}H NMR of diene **32c**

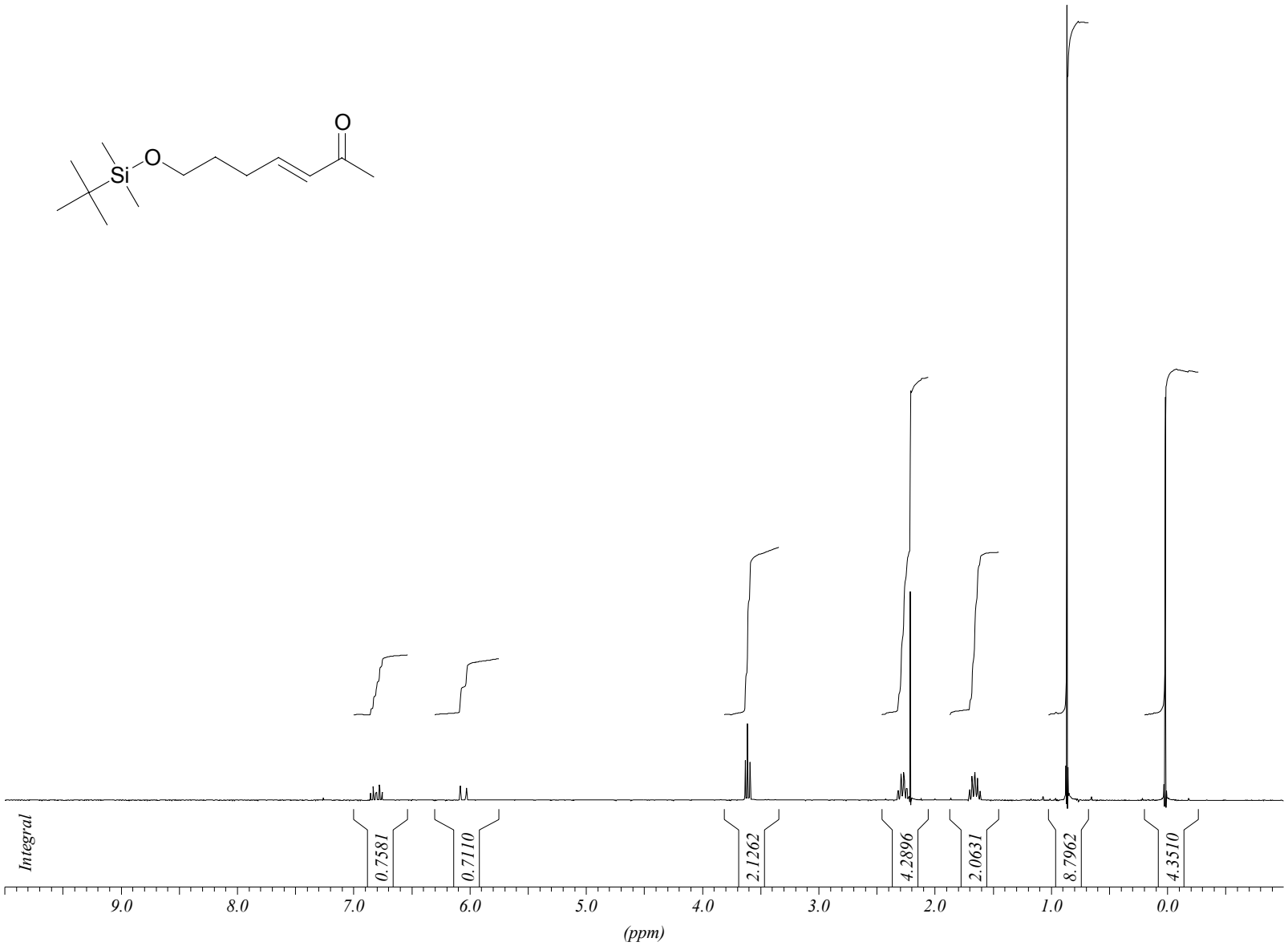


^{1}H NMR of sulfolene **36**

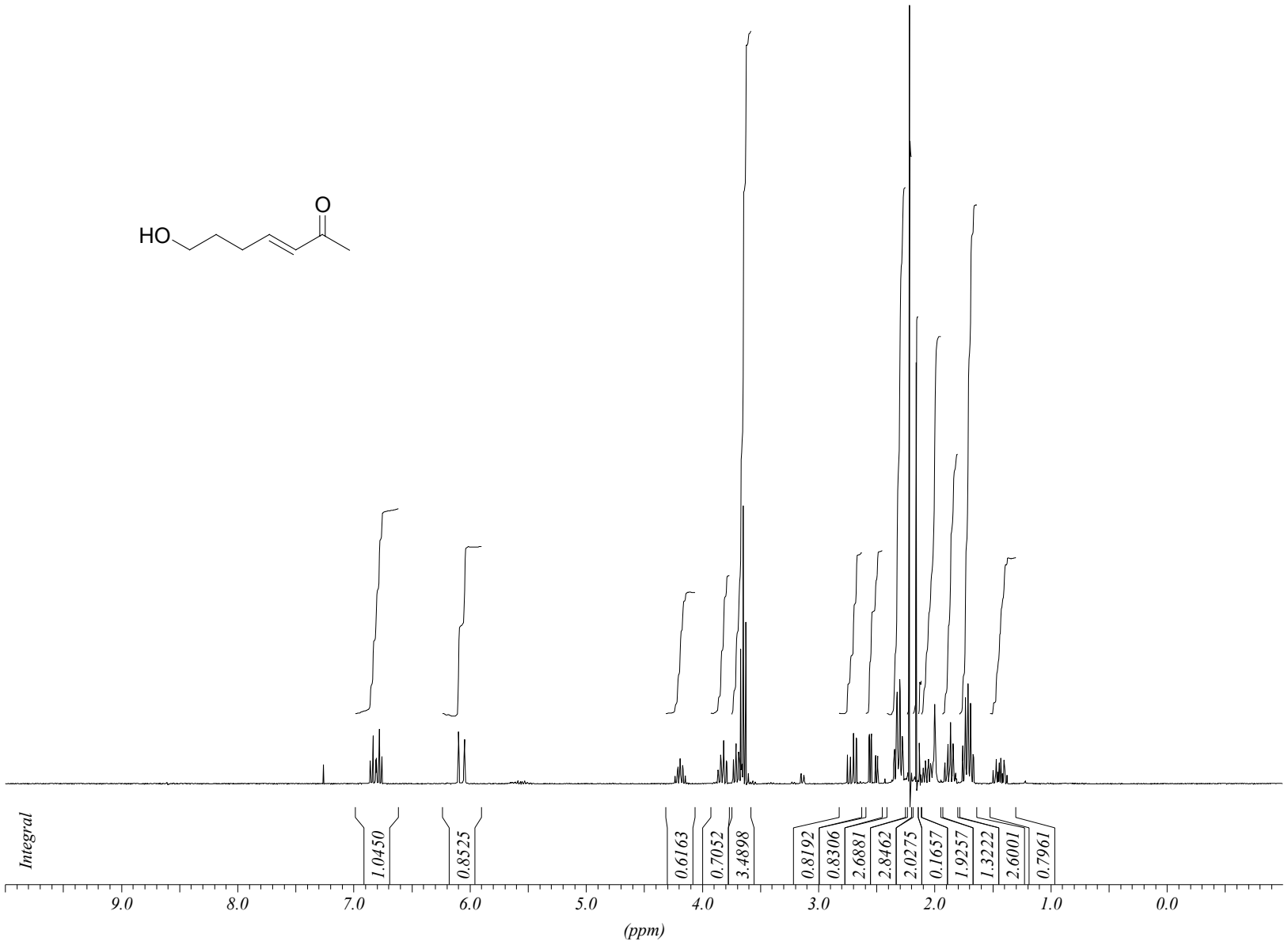
^{1}H NMR of diene **37a**



^{1}H NMR of enone **38**

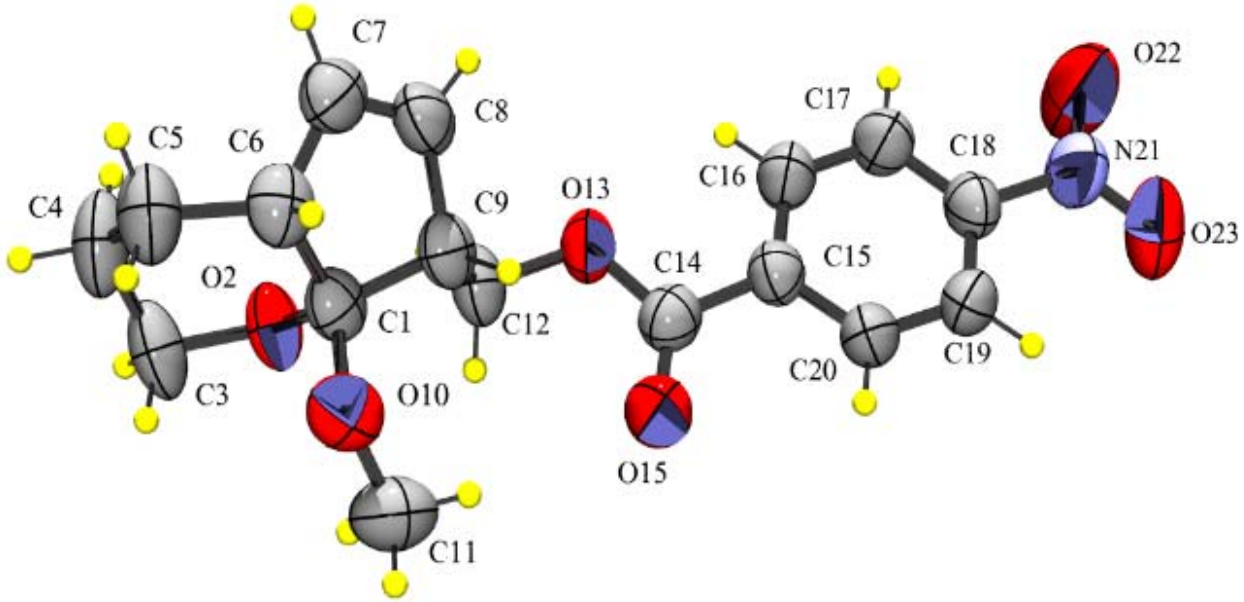


^{1}H NMR of enone **39**

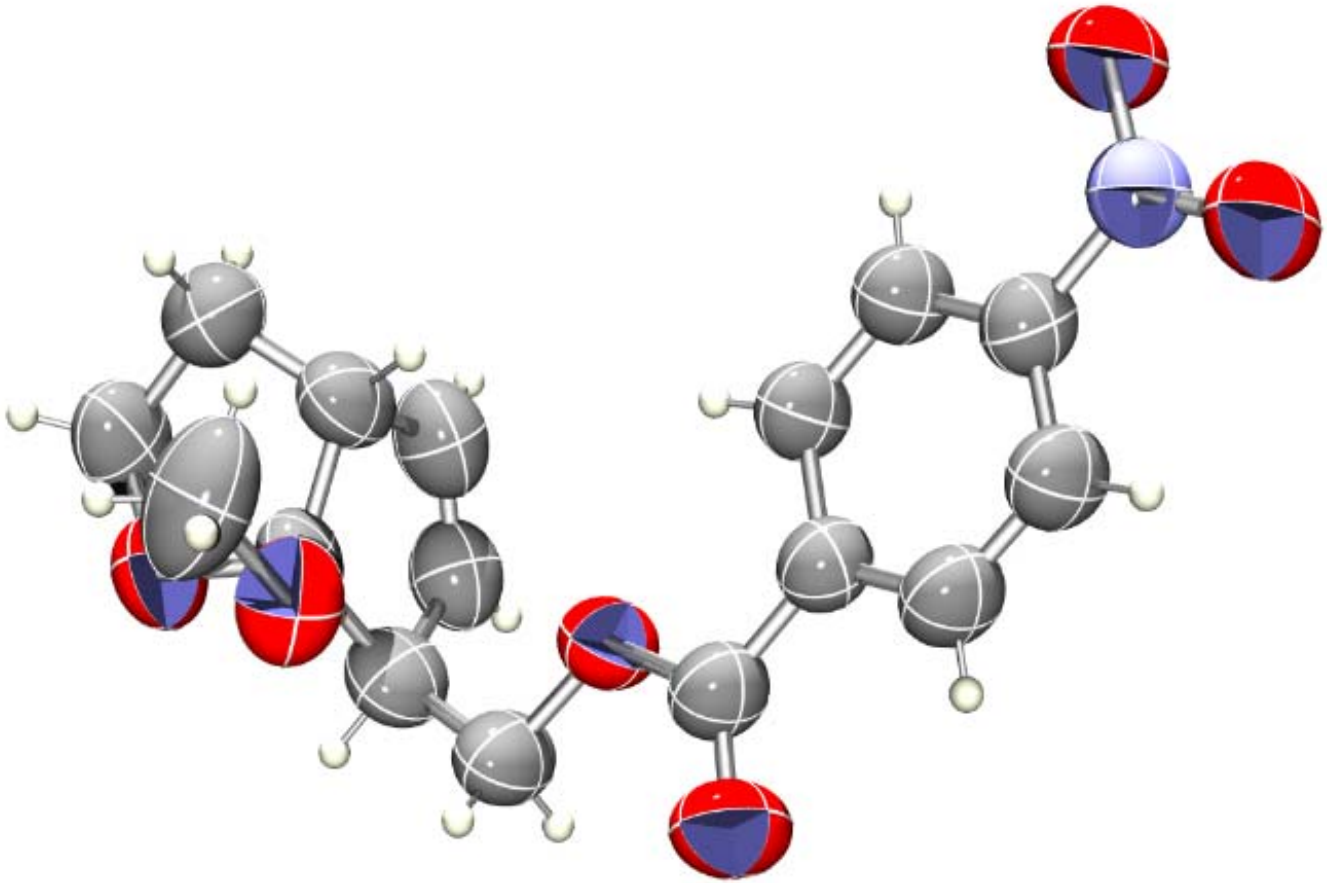


ORTEP diagrams

ORTEP of benzoate ester **25b**



ORTEP of benzoate ester **26a**



ORTEP of benzoate ester **26b**