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Supporting Information Binder, Kirsch

Iterative approach to polyketide-type structures: stereoselective synthesis of 1,3-polyols utilizing the catalytic asymmetric Overman esterification

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Supporting Information

Representative experimental procedures, and copies of ^{1}H and ^{13}C NMR of **2**, **3**, **5-11**, **14**, and **15**. Copies of HPLC traces used to determine enantiopurity for **2** and **14**.

General experimental details: All commercially available chemicals were used without further purification. (+)-COP-OAc and (−)-COP-OAc were purchased from Aldrich and purified by column chromatography on silica (100% CH_2Cl_2) prior to usage. All reactions were performed under argon. CH_2Cl_2 was dried according to published procedures.[1]

^{1}H NMR spectra were obtained on 500 MHz FT-NMR, 360 MHz FT-NMR and 250 MHz FT-NMR spectrometers. ^{13}C NMR spectra were recorded at 90.6 MHz. Chemical shifts are reported in ppm relative to solvent signal. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets); quin (quintet). Flash chromatography was performed with E. Merck silica gel (43−60 μm). The eluent used is reported in parentheses (P = pentane). Thin-layer chromatography (TLC) was performed on precoated glass-backed plates (Merck Kieselgel 60 F_{254}), and components were visualized by observation under UV light or by treating the plates with $KMnO_4/H_2SO_4$ followed by heating. HPLC determination of enantiopurity was carried out on a Dionex using a Chiralcel® OJ-H column (250 mm x 4.6 mm). All HPLC analyses used to determine enantiomeric purity were calibrated with samples of the racemate.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

Synthesis of (*R*)-5-Phenylpent-1-en-3-yl benzoate (2).

(*Z*)-Ethyl 5-phenylpent-2-enoate

To a solution of ethyl (diphenylphosphono)acetate (4.23 g, 13.2 mmol) in dry THF (53 mL) was added NaH (687 mg, 17.2 mmol; 60 % in oil) at 0 °C under argon. The resulting mixture was stirred for 20 min at 0 °C, and then it was cooled to −78°C. 3-Phenylpropanal (1.95 g, 14.5 mmol) was added dropwise. The stirred mixture was allowed to warm up to −10°C over 3 h. The reaction was then quenched by addition of saturated aqueous NH_4Cl (100 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. ^{1}H NMR of the crude mixture indicated a *Z*/*E* ratio of 85:15. Purification of the residue by flash chromatography on silica (P/EtOAc = 99/01) gave the title compound (2.30 mg, 11.2 mmol, 85%) as a single diastereoisomer. R_f = 0.44 (P/EtOAc = 95/5); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.2 Hz, 3 H), 2.77 (t, *J* = 7.6 Hz, 2 H), 2.99 (qd, *J* = 7.7 Hz, *J* = 1.6 Hz, 2 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 5.78 (dt, *J* = 11.4 Hz, *J* = 1.7 Hz, 1 H), 6.24 (dt, *J* = 11.4 Hz, *J* = 7.5 Hz, 1H), 7.15─7.24 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 14.4, 30.6, 35.2, 60.0, 120.5, 126.2, 128.5, 128.6, 141.3, 149.0, 166.5. The analytical data are identical to those reported elsewhere.[2]

(*Z*)-5-Phenylpent-2-en-1-ol

To a solution of (*Z*)-ethyl 5-phenylpent-2-enoate (7.95 mmol, 1.62 mg) in CH_2Cl_2 (57 mL) at −78°C was added DIBAL-H (23.9 mL, 23.9 mmol; 1M in CH_2Cl_2). The resulting solution was stirred for 1 h at −78°C, before H_2O was added (8 mL). The mixture was allowed to warm to room temperature, aqueous potassium sodium tartrate (300 mL, 10% aq. solution), glycerine (0.2 mL/mmol) and Et_2O (300 mL) were added, and stirring was continued for 2 h (, until both layers were clear and readily separated). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 90/10) gave the title compound (1.03 g, 6.38 mmol, 80%) as a colourless liquid. R_f = 0.33 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.78 (t, *J* = 5.2 Hz, 1 H), 2.41 (q, *J* = 7.3 Hz, 2 H), 2.69 (t, *J* = 7.4 Hz, 2 H), 4.01 (t, *J* = 5.1 Hz, 2 H), 5.52─5.66 (m, 2 H), 7.16─7.22 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR

[2] J. Bach, C. Blachere, S. D. Bull, S. G. Davies, R. L. Nicholson, P. D. Price, H. J. Sanganee, A. D. Smith, *Org. Biomol. Chem.* **2003**, *1*, 2001.

(90.6 MHz, $CDCl_3$): δ = 29.4, 35.8, 58.6, 126.2, 128.5, 128.8, 129.5, 131.8, 141.7. The analytical data are identical to those reported elsewhere.[3]

General procedure for the conversion of (*Z*)-2-allylic alcohols into (*Z*)-2-enyl-trichloroacetimidates (Method A)

(*Z*)-5-Phenylpent-2-enyl 2,2,2-trichloroacetimidate (1)

To a solution of (*Z*)-5-phenylpent-2-en-1-ol (1.07 g, 6.60 mmol) in dry CH_2Cl_2 (29 mL) was added trichloroacetonitrile (0.66 mL, 6.60 mmol) and DBU (90.4 mg, 0.60 mmol) at 0 °C. The resulting pale brown solution was warmed to room temperature. After stirred for 2 h at room temperature (until TLC analysis indicated complete conversion), the mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 98/02) gave the title compound as a colourless liquid (1.91 g, 6.23 mmol, 94 %). R_f = 0.41 (P/EtOAc = 95/5); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.45─2.53 (m, 2 H), 2.72 (t, *J* = 7.8 Hz, 2 H), 4.78 (d, *J* = 6.1 Hz, 2 H), 5.64─5.81 (m, 2 H), 7.15─7.23 (m, 3 H), 7.26─7.34 (m, 2 H), 8.28 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 29.7, 35.7, 65.2, 123.6, 126.2, 128.5, 128.6, 135.1, 141.5, 162.8 (*C*Cl_3 is missing). The analytical data are identical to those reported elsewhere.[4]

General procedure for the enantioselective allylic esterification catalyzed by COP-OAc (Method B)

(*R*)-5-Phenylpent-1-en-3-yl benzoate (2)

(+)-COP-OAc (1 mol %, 0.12 mmol , 178 mg) was added in one portion to a solution of **1** (11.7 mmol, 3.59 g) and benzoic acid (35.1 mmol, 4.29 g) in dry CH_2Cl_2 (9 mL). The orange solution was protected from light and maintained at room temperature. After 24 h (until ^{1}H NMR analysis of the crude mixture indicated complete conversion), the solution was concentrated under reduced pressure. The residue was purified by flash chromatography on silica to afford **2** as a pale yellow oil (2.89 g, 10.85 mmol, 93%). R_f = 0.41 (P/EtOAc = 95/5); $[\alpha]^{23}_D$ = –8.6 (*c* = 0.93 $CDCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.01─2.24 (m, 2 H), 2.68─2.83 (m, 2 H), 5.25 (dt, *J* = 10.5 Hz, *J* = 1.1 Hz, 1 H), 5.36 (dt, *J* = 17.3 Hz, *J* = 1.3 Hz, 1 H), 5.50─5.58 (m, 1 H), 5.94 (ddd, *J* = 17.3 Hz, *J* = 10.7 Hz, *J* = 6.1 Hz, 1 H), 7.15─7.22

[3] D. C. Martyn, D. A. Hoult, A. D. Abell, *Aust. J. Chem.* **2001**, *54*, 391.
[4] L. E. Overman, C. E. Owen, M. M. Pavan, *Org. Lett.* **2003**, *5*, 1809.

(m, 3 H), 7.26─7.32 (m, 2 H), 7.42─7.49 (m, 2 H), 7.57 (tt, *J* = 7.3 Hz, *J* = 1.4 Hz, 1 H), 8.04─8.09 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 31.6, 36.1, 74.9, 117.1, 126.1, 128.5, 128.5, 128.6, 129.8, 130.7, 133.1, 136.4, 141.5, 166.0; LRMS (EI): 266 (1%) [M^+], 144 (100%), 129 (81%), 105 (78%), 91 (48%); HRMS 266.1306 [266.1307 calcd for $C_{18}H_{18}O_2$ (M^+)].

HPLC analysis indicated an enantiomeric excess of 92% [Daicel OJ-H column; flow: 1.0 mL/min; pentanes/*i*-PrOH, 95:5; 210 nm; major enantiomer, t_R = 11.30 min; minor enantiomer, t_R = 11.97 min].

The absolute configuration was assigned according to the literature data.[5]

General procedure for the chain extension cycle $\mathbf{1^{OH}}$-3$\boldsymbol{R^{OH}}$ (Method C)

Synthesis of (*R*)-6-Phenethyl-5,6-dihydropyran-2-one (3)

(*R*)-5-Phenylpent-1-en-3-yl but-3-enoate

To a solution of **2** (4.19 mmol, 1.12 g) in dry CH_2Cl_2 (42 mL) at −78°C under argon was added DIBAL-H (12.6 mL, 12.6 mmol; 1M in CH_2Cl_2). The resulting solution was stirred for 2 h at −78°C, before H_2O was added (5 mL). The mixture was allowed to warm to room temperature, aqueous potassium sodium tartrate (200 mL, 10% aq. solution), glycerine (0.2 mL/mmol) and Et_2O (200 mL) were added, and stirring was continued for 2 h (, until both layers were clear and readily separated). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to give (*R*)-5-phenylpent-1-en-3-ol as a colourless liquid, which was directly used in the next step without further purification. R_f = 0.42 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.57 (s, 1 H), 1.80─1.94 (m, 2 H), 2.65─2.81 (m, 2 H), 4.10─4.17 (m, 1 H), 5.15 (d, *J* = 10.5 Hz, 1 H), 5.26 (d, *J* = 17.3 Hz, 1 H), 5.92 (ddd, *J* = 17.3 Hz, *J* = 10.5 Hz, *J* = 6.1 Hz, 1 H), 7.15─7.24 (m, 3 H), 7.26─7.33 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 31.8, 38.7, 72.6, 115.0, 126.0, 128.5, 128.6, 141.2, 142.0.

To a solution of crude (*R*)-5-phenylpent-1-en-3-ol in dry CH_2Cl_2 (42 mL) was added DCC (1.04 mg, 5.03 mmol), vinyl acetic acid (0.43 mL, 5.03 mmol) and DMAP (77 mg, 0.63 mmol) at room temperature. The resulting mixture was stirred for 16 h at room temperature before it was filtered and quenched with water (50 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were

[5] S. F. Kirsch, L. E. Overman, *J. Am. Chem. Soc.* **2005**, *127*, 2866.

washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 99/1) gave (*R*)-5-phenylpent-1-en-3-yl but-3-enoate as a colourless liquid (847 mg, 3.68 mmol, 88%). $[\alpha]^{23}_D = -10.0$ (*c* = 0.34 $CDCl_3$) R_f = 0.92 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.86─2.08 (m, 2 H), 2.57─2.72 (m, 2 H), 3.10 (dt, *J* = 6.8 Hz, *J* = 1.4 Hz, 2 H), 5.13─5.37 (m, 5 H), 5.76─6.01 (m, 2 H), 7.16─7.22 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 31.5, 35.9, 39.5, 74.6, 117.2, 118.7, 126.1, 128.5, 128.6, 130.4, 136.3, 141.4, 170.9. HRMS 230.1300 [230.1307 calcd for $C_{15}H_{18}O_2$ (M^+)].

(*R*)-6-Phenethyl-5,6-dihydropyran-2-one (3)

To a solution of (*R*)-5-phenylpent-1-en-3-yl but-3-enoate (836 mg, 3.63 mmol) in degassed CH_2Cl_2 (400 mL) was added Grubbs II catalyst (28 mg, 0.03 mmol). The reaction mixture was refluxed for 15 h. After disappearance of the starting material, the reaction mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 90/10) gave a colourless oil (647 mg, 3.2 mmol, 88%), which contained (*R*)-6-phenethyl-3*H*-pyran-2(6*H*)-one as the major product (90% pure by ^{1}H NMR analysis). The minor product was (*R*)-6-Phenethyl-5,6-dihydropyran-2-one (**3**). This mixture was subjected to the subsequent isomerization reaction. Analytical data for (*R*)-6-phenethyl-3*H*-pyran-2(6*H*)-one: R_f = 0.28 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.97─2.10 (m, 2 H), 2.71─2.89 (m, 2 H), 3.04─3.11 (m, 2 H), 4.94─5.02 (m, 1 H), 5.80─5.91 (m, 2 H), 7.15─7.23 (m, 3 H), 7.26─7.33 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 30.1, 30.8, 37.5, 78.8, 122.0, 126.3, 126.6, 128.7, 128.7, 140.9, 169.1.

To a solution of crude (*R*)-6-phenethyl-3*H*-pyran-2(6*H*)-one (647 mg, 3.2 mmol) in dry CH_2Cl_2 (16 mL) was added DBU (49 mg, 0.32 mmol) at room temperature. The resulting mixture was stirred for 16 h before it was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 70/30) gave **3** as a colourless liquid (602 mg, 2.98 mmol, 93%). R_f = 0.25 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.86─2.02 (m, 1 H), 2.04─2.23 (m, 1 H), 2.28─2.39 (m, 2 H), 2.70─2.96 (m, 2 H), 4.35─4.48 (m, 1 H), 6.03 (dt, *J* = 9.8 Hz, *J* = 1.8 Hz, 1 H), 6.81─6.91 (m, 1 H), 7.15─7.24 (m, 3 H), 7.26─7.34 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 29.6, 31.1, 36.6, 77.0, 121.6, 126.3, 128.6, 128.7, 141.0, 145.0, 164.6. HRMS 202.0981 [202.0994 calcd for $C_{13}H_{14}O_2$ (M^+)].

Synthesis of (*R,Z*)-5-(Triethylsilyloxy)-7-phenylhept-2-enyl 2,2,2-trichloroacetimidate (4)

(*R,Z*)-5-(Triethylsilyloxy)-7-phenylhept-2-en-1-ol

To a solution of **3** (876 mg, 4.3 mmol) in MeOH (500 mL) was added $CeCl_3$*7 H_2O (4.6 g, 12.4 mmol) at room temperature. The mixture was cooled to 0 °C. Then, $NaBH_4$ (470 mg, 12.4 mmol) was added in three portions. The reaction mixture was stirred at 0 °C for 6 h, then, the mixture was concentrated under reduced pressure. The residue was diluted with H_2O (200 mL) and EtOAc (200 mL), and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine, dried ($NaSO_4$), and concentrated under reduced pressure. The crude product was directly used in the next step without further purification.

To a solution of crude (*R,Z*)-7-phenylhept-2-ene-1,5-diol in CH_2Cl_2 (21 mL) were added 2,6-lutidine (1.2 mL, 9.9 mmol) and TESOTf (2.1 mL, 9.05 mmol) at 0 °C. The resulting mixture was stirred for 1 h at 0 °C before H_2O (20 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine, dried ($NaSO_4$), and concentrated under reduced pressure. The crude product was directly used in the next step without further purification.

The crude product was dissolved in MeOH (83 mL), and K_2CO_3 (5.1 mg, 37.1 mmol) was added at 0°C. The mixture was stirred for additional 3 h at 0 °C. After addition of H_2O (100 mL) and Et_2O (100 mL), the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine, dried ($NaSO_4$), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 90/10) gave (*R,Z*)-5-(triethylsilyloxy)-7-phenylhept-2-en-1-ol as a colourless liquid (1.1 g, 3.39 mmol, 79%). R_f = 0.48 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.62 (q, *J* = 7.8 Hz, 6 H), 0.98 (t, *J* = 7.8 Hz, 9 H), 1.66─1.73 (m, 1 H), 1.74─1.87 (m, 2 H), 2.24─2.43 (m, 2 H), 2.57─2.75 (m, 2 H), 3.78 (virt. quin, *J* = 5.8 Hz, 1 H), 4.09─4.23 (m, 2 H), 5.55─5.66 (m, 1 H), 5.74─5.83 (m, 1 H), 7.15─7.21 (m, 3 H), 7.26─7.31 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.19, 7.05, 31.8, 35.2, 39.0, 58.6, 71.5, 125.9, 128.5, 128.5, 129.2, 130.9, 142.4.

(*R,Z*)-5-(Triethylsilyloxy)-7-phenylhept-2-enyl 2,2,2-trichloroacetimidate (4)

Following the general procedure (**Method A**), **4** was obtained as a colourless oil (94%) after flash chromatography on silica (P/EtOAc = 99/1). R_f = 0.49 (P/EtOAc = 95/5); ^{1}H NMR (360

MHz, $CDCl_3$): δ = 0.62 (q, *J* = 7.9 Hz, 6 H), 0.97 (t, *J* = 7.9 Hz, 9 H), 1.69─1.85 (m, 2 H), 2.38 (t, *J* = 5.9 Hz, 2 H), 2.55─2.66 (m, 1 H), 2.67─2.77 (m, 1 H), 3.82 (virt. quin, *J* = 5.8 Hz, 1 H), 4.80─4.91 (m, 2 H), 5.72─5.85 (m, 2 H), 7.14─7.21 (m, 3 H), 7.23─7.31 (m, 2 H), 8.29 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.3, 7.1, 32.0, 35.7, 39.0, 65.4, 71.6, 124.7, 125.9, 128.5, 128.5, 132.2, 142.5, 162.8 (*C*Cl_3 is missing).

Synthesis of (3*R*,5*R*)-5-(Triethylsilyloxy)-7-phenylhept-1-en-3-yl benzoate (5)

Following the general procedure (**Method B**, (+)-COP-OAc), **5** was obtained as a crude product, which was a 94:6 mixture of the diastereoisomers. The diastereoisomers were separated by flash chromatography on silica (P/EtOAc = 98/2) to provide **5** in 95%. R_f = 0.49 (P/EtOAc = 95/5); $[\alpha]^{23}_D$ = +7.2 (*c* = 0.85 $CDCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.63 (q, *J* = 7.9 Hz, 6 H), 0.98 (t, *J* = 7.9 Hz, 9 H), 1.74─1.86 (m, 1 H), 1.87─1.98 (m, 2 H), 2.05─2.14 (m, 1 H), 2.59─2.77 (m, 2 H), 3.89 (virt. quin, *J* = 5.5 Hz, 1 H), 5.22 (dt, *J* = 10.5 Hz, *J* = 1.1 Hz, 1 H), 5.34 (dt, *J* = 17.3 Hz, *J* = 1.1 Hz, 1 H), 5.59−5.67 (m, 1 H), 5.91 (ddd, *J* = 17.0 Hz, *J* = 10.7 Hz, *J* = 6.4 Hz, 1 H), 7.11─7.18 (m, 3 H), 7.20─7.25 (m, 2 H), 7.40─7.48 (m, 2 H), 7.57 (tt, *J* = 7.4 Hz, *J* = 1.3 Hz, 1 H), 8.01─8.08 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.4, 7.1, 31.6, 38.9, 42.1, 68.8, 72.8, 117.0, 125.9, 128.5, 128.5, 128.5, 129.7, 130.6, 133.0, 139.7, 142.4, 165.8. LRMS (EI): 395 (1%) [M^+-Et], 341 (3%), 249 (5%), 207 (100%), 171 (32%).

Synthesis of (3*S*,5*R*)-5-(Triethylsilyloxy)-7-phenylhept-1-en-3-yl benzoate (6)

Following the general procedure (**Method B**, (−)-COP-OAc), **6** was obtained as a crude product, which was a 97:3 mixture of the diastereoisomers. The diastereoisomers were separated by flash chromatography on silica (P/EtOAc = 98/2) to provide **6** in 94%. R_f = 0.49 (P/EtOAc = 95/5); $[\alpha]^{23}_D$ = –13.3 (*c* = 0.92 $CDCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.49 (q, *J* = 8.0 Hz, 6 H), 0.91 (t, *J* = 8.0 Hz, 9 H), 1.80─1.91 (m, 3 H), 2.07 (ddd, *J* = 14.1 Hz, *J* = 9.5 Hz, *J* = 4.1 Hz, 1 H), 2.59─2.77 (m, 2 H), 3.87─3.96 (m, 1 H), 5.20 (dt, *J* = 10.5 Hz, *J* = 1.1 Hz, 1 H), 5.32 (dt, *J* = 17.2 Hz, *J* = 1.1 Hz, 1 H), 5.54─5.62 (m, 1 H), 5.93 (ddd, *J* = 17.2 Hz, *J* = 10.5 Hz, *J* = 6.1 Hz, 1 H), 7.14─7.21 (m, 3 H), 7.23─7.30 (m, 2 H), 7.41─7.48 (m, 2 H), 7.57 (tt, *J* = 7.4 Hz, *J* = 1.3 Hz, 1 H), 8.01─8.06 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.3, 7.1, 31.4, 39.8, 42.0, 68.4, 72.9, 116.5, 125.9, 128.5, 128.5, 128.5, 129.7, 130.7, 133.0, 137.0, 142.3, 165.9. LRMS (EI): 395 (1%) [M^+-Et], 341 (3%), 249 (4%), 207 (100%), 171 (33%).

Synthesis of triol derivatives 7, 8, 9, and 10

(3*R*,5*S*,7*R*)-5,7-Bis(triethylsilyloxy)-9-phenylnon-1-en-3-yl benzoate (7)

Following the general procedure (**Method C**, (+)-COP-OAc), **7** was obtained from **5** as a pure diastereoisomer (32%) after flash chromatography on silica (P/EtOAc = 98/2). R_f = 0.56 (P/EtOAc = 95/5); $[\alpha]^{23}_D$ = –7.6 (*c* = 0.58 $CDCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.59 (q, *J* = 7.9 Hz, 6 H), 0.60 (q, *J* = 7.9 Hz, 6 H), 0.95 (t, *J* = 7.9 Hz, 9 H), 0.97 (t, *J* = 7.9 Hz, 9 H), 1.58─1.82 (m, 4 H), 1.86─1.95 (m, 1 H), 1.98─2.07 (m, 1 H), 2.51─2.69 (m, 2 H), 3.86─3.96 (m, 2 H), 5.20 (d, *J* = 10.5 Hz, 1 H), 5.34 (d, *J* = 17.3 Hz, 1 H), 5.62─5.70 (m, 1 H), 5.90 (ddd, J = 17.3 Hz, J = 10.5 Hz, J = 6.1 Hz, 1 H), 7.03─7.08 (m, 2 H), 7.11─7.24 (m, 3 H), 7.39─7.45 (m, 2 H), 7.55 (tt, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H), 8.01─8.06 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.3, 5.4, 7.1, 7.1, 31.4, 39.1, 42.6, 44.8, 66.8, 69.1, 72.5, 116.8, 125.7, 128.4, 128.4, 128.5, 129.7, 130.5, 133.0, 136.7, 142.7, 165.6.

(3*S*,5*S*,7*R*)-5,7-Bis(triethylsilyloxy)-9-phenylnon-1-en-3-yl benzoate (8)

Following the general procedure (**Method C**, (−)-COP-OAc), **8** was obtained from **5** as a pure diastereoisomer (25%) after flash chromatography on silica (P/EtOAc = 98/2). R_f = 0.56 (P/EtOAc = 95/5); $[\alpha]^{23}_D$ = +30.5 (*c* = 0.20 $CDCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.52─0.65 (m, 12 H), 0.87─0.99 (m, 18 H), 1.64─1.87 (m, 5 H), 2.03─2.13 (m, 1 H), 2.57─2.73 (m, 2 H), 3.82─3.91 (m, 1 H), 3.94─4.03 (m, 1 H), 5.18 (dt, *J* = 10.5 Hz, *J* = 1.1 Hz, 1 H), 5.31 (dt, *J* = 17.3 Hz, *J* = 1.1 Hz, 1 H), 5.57─5.65 (m, 1 H), 5.90 (ddd, J = 17.3 Hz, J = 10.5 Hz, J = 6.1 Hz, 1 H), 7.14─7.21 (m, 3 H), 7.25─7.31 (m, 2 H), 7.38─7.44 (m, 2 H), 7.55 (tt, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H), 8.02─8.06 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.3, 5.4, 7.1, 7.1, 31.6, 39.6, 42.6, 45.8, 66.5, 69.1, 72.7, 116.5, 125.9, 128.4, 128.5, 128.5, 129.7, 130.8, 132.9, 137.1, 142.5, 165.9.

(3*R*,5*R*,7*R*)-5,7-Bis(triethylsilyloxy)-9-phenylnon-1-en-3-yl benzoate (9)

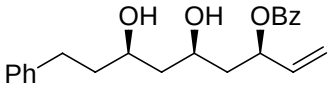
Following the general procedure (**Method C**, (+)-COP-OAc), **9** was obtained from **6** as a pure diastereoisomer (21%) after flash chromatography on silica (P/EtOAc = 98/2). $[\alpha]^{23}_D$ = –14.8 (*c* = 0.63 $CDCl_3$) R_f = 0.56 (P/EtOAc = 95/5); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.59 (q, *J* = 8.0 Hz, 6 H), 0.62 (q, *J* = 7.8 Hz, 6 H), 0.91 (t, *J* = 7.8 Hz, 9 H), 0.97 (t, *J* = 8.0 Hz, 9 H), 1.69─1.88 (m, 5 H), 1.96─2.06 (m, 1 H), 2.60─2.77 (m, 2 H), 3.80─3.89 (m, 1 H), 3.90─3.99 (m, 1 H), 5.19 (d, *J* = 10.7 Hz, 1 H), 5.32 (d, *J* = 17.3 Hz, 1 H), 5.54─5.64 (m, 1 H), 5.92 (ddd, J = 17.3 Hz, J = 10.5 Hz, J = 6.1 Hz, 1 H), 7.13─7.21 (m, 3 H), 7.24─7.30 (m, 2 H),

7.34─7.43 (m, 2 H), 7.55 (t, *J* = 7.5 Hz, 1 H), 8.01─8.06 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.4, 5.5, 7.1, 7.1, 31.5, 39.4, 42.7, 46.2, 66.9, 69.6, 72.7, 116.5, 125.9, 128.5, 128.5, 128.5, 129.6, 130.7, 133.0, 137.0, 142.5, 165.8.

(3*S*,5*R*,7*R*)-5,7-Bis(triethylsilyloxy)-9-phenylnon-1-en-3-yl benzoate (10)

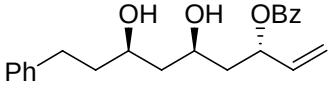
Following the general procedure (**Method C**, (−)-COP-OAc), **10** was obtained from **6** as a pure diastereoisomer (21%) after flash chromatography on silica (P/EtOAc = 98/2). R_f = 0.56 (P/EtOAc = 95/5); $[\alpha]^{23}_D$ = +32.4 (*c* = 0.93 $CDCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.56 (q, *J* = 7.8 Hz, 6 H), 0.64 (q, *J* = 7.8 Hz, 6 H), 0.91 (t, *J* = 7.8 Hz, 9 H), 0.98 (t, *J* = 7.8 Hz, 9 H), 1.65─1.94 (m, 5 H), 2.00─2.10 (m, 1 H), 2.54─2.70 (m, 2 H), 3.80─3.89 (m, 1 H), 3.94─4.03 (m, 1 H), 5.22 (d, *J* = 10.5 Hz, 1 H), 5.35 (d, *J* = 17.3 Hz, 1 H), 5.59─5.68 (m, 1 H), 5.90 (ddd, J = 17.3 Hz, J = 10.5 Hz, J = 6.4 Hz, 1 H), 7.10─7.21 (m, 3 H), 7.24─7.32 (m, 2 H), 7.34─7.48 (m, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 8.03─8.10 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.5, 5.6, 7.1, 7.2, 31.6, 40.0, 42.9, 45.7, 67.2, 69.7, 72.7, 117.1, 125.8, 128.4, 128.5 (*one* C_{Ar} is missing), 129.8, 130.7, 133.0, 136.7, 142.6, 165.6.

For compounds **7**, **8**, **9**, and **10**, HRMS data were only obtained from the corresponding diols after cleavage of the silylether:



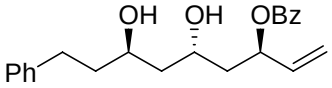
from **7**

LRMS (EI): 354 (2%) [M^+], 336 (3%), 232 (6%), 214 (18%), 160 (23%), 123 (28%), 105 (100%), 91 (73%); HRMS 354.1832 [354.1831 calcd for $C_{22}H_{26}O_4$ (M^+)].



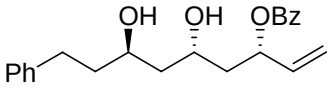
from **8**

LRMS (EI): 354 (3%) [M^+], 336 (3%), 232 (8%), 214 (19%), 160 (24%), 123 (30%), 105 (100%), 91 (68%); HRMS 354.1825 [354.1831 calcd for $C_{22}H_{26}O_4$ (M^+)].



from **9**

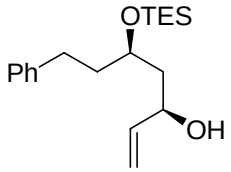
LRMS (EI): 354 (2%) [M^+], 336 (3%), 232 (7%), 214 (23%), 160 (28%), 123 (29%), 105 (100%), 91 (59%); HRMS 354.1827 [354.1831 calcd for $C_{22}H_{26}O_4$ (M^+)].



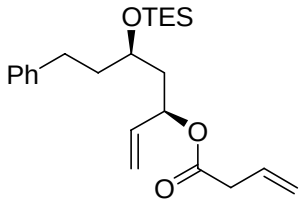
from **10**

LRMS (EI): 354 (1%) [M^+], 336 (4%), 232 (6%), 214 (20%), 160 (27%), 123 (29%), 105 (100%), 91 (70%); HRMS 354.1828 [354.1831 calcd for $C_{22}H_{26}O_4$ (M^+)].

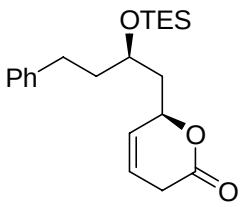
NMR data for key intermediates towards the synthesis of triol derivatives 7, 8, 9, and 10



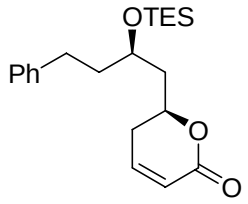
^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.65 (q, J = 7.9 Hz, 6 H), 0.98 (t, J = 7.9 Hz, 9 H), 1.66─1.77 (m, 2 H), 1.80─1.95 (m, 2 H), 2.56─2.73 (m, 2 H), 3.17 (d, J = 2.0 Hz, 1 H), 3.99─4.08 (m, 1 H), 4.26─4.34 (m, 1 H), 5.10 (dt, J = 10.5 Hz, J = 1.5 Hz, 1 H), 5.28 (dt, J = 17.2 Hz, J = 1.5 Hz, 1 H), 5.88 (ddd, J = 17.2 Hz, J = 10.5 Hz, J = 5.7 Hz, 1 H), 7.14─7.22 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.3, 7.0, 31.3, 39.9, 43.2, 72.1, 72.4, 114.3, 126.0, 128.4, 128.6, 141.0, 142.2.



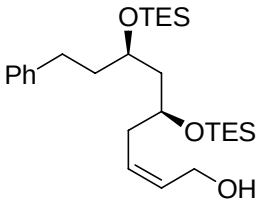
^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.61 (q, J = 7.9 Hz, 6 H), 0.98 (t, J = 7.9 Hz, 9 H), 1.67─2.00 (m, 4 H), 2.56─2.76 (m, 2 H), 3.06 (dt, J = 7.0 Hz, J = 1.4 Hz, 2 H), 3.74─3.82 (m, 1 H), 5.11─5.20 (m, 3 H), 5.25 (dt, J = 17.3 Hz, J = 1.1 Hz, 1 H), 5.34─5.42 (m, 1 H), 5.72─5.97 (m, 2 H), 7.14─7.21 (m, 3 H), 7.24─7.31 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.3, 7.1, 31.6, 38.9, 39.6, 42.0, 68.7, 72.5, 117.1, 118.7, 125.9, 128.5, 128.5, 130.4, 136.5, 142.4, 170.7.



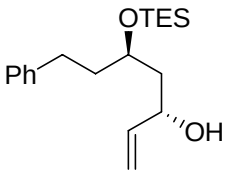
^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.61 (q, J = 7.8 Hz, 6 H), 0.97 (t, J = 7.8 Hz, 9 H), 1.75─1.97 (m, 3 H), 2.04 (ddd, J = 13.9 Hz, J = 7.7 Hz, J = 5.9 Hz, 1 H), 2.59─2.74 (m, 2 H), 2.99─3.14 (m, 2 H), 4.00 (virt. quin, J = 5.9 Hz, 1 H), 5.05─5.13 (m, 1 H), 5.81─5.91 (m, 2 H), 7.14─7.21 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.2, 7.1, 30.1, 31.7, 38.9, 43.2, 68.4, 77.1 121.6, 126.0, 127.1, 128.5, 128.6, 142.2, 169.1.



^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.61 (q, J = 7.8 Hz, 6 H), 0.97 (t, J = 7.8 Hz, 9 H), 1.73─1.95 (m, 3 H), 2.10 (ddd, J = 13.9 Hz, J = 7.3 Hz, J = 5.5 Hz, 1 H), 2.27─2.43 (m, 2 H), 2.60─2.75 (m, 2 H), 4.00 (virt. quin, J = 5.8 Hz, 1 H), 4.54─4.63 (m, 1 H), 6.03 (dt, J = 9.8 Hz, J = 1.7 Hz, 1 H), 6.84─6.90 (m, 1 H), 7.15─7.22 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.2, 7.1, 30.0, 31.8, 38.7, 42.2, 68.3, 75.4, 121.7, 126.0, 128.5, 128.6, 142.2, 145.1, 164.5.

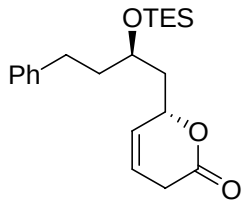


^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.61 (q, J = 7.9 Hz, 12 H), 0.96 (t, J = 7.9 Hz, 9 H), 0.98 (t, J = 7.9 Hz, 9 H), 1.58─1.86 (m, 5 H), 2.25─2.31 (m, 2 H), 2.57─2.72 (m, 2 H), 3.78─3.91 (m, 2 H), 4.08─4.20 (m, 2 H), 5.52─5.62 (m, 1 H), 5.75─5.84 (m, 1 H), 7.14─7.22 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.1, 5.3, 7.0, 7.1, 31.6, 35.3, 39.7, 44.7, 58.5, 69.1, 69.3, 125.9, 128.5, 128.5, 129.2, 131.1, 142.6.

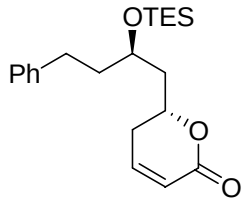


^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.63 (q, J = 7.9 Hz, 6 H), 0.98 (t, J = 7.9 Hz, 9 H), 1.70─1.75 (m, 2 H), 1.87─1.96 (m, 2 H), 2.60─2.67 (m, 2 H), 3.13 (d, J = 3.0 Hz, 1 H), 4.02─4.11 (m, 1 H), 4.40─4.48 (m, 1 H), 5.09 (dt, J = 10.5 Hz, J = 1.5 Hz, 1 H), 5.26 (dt, J = 17.0 Hz, J = 1.5 Hz, 1 H), 5.88 (ddd, J = 17.0 Hz, J = 10.5 Hz, J = 5.5 Hz, 1 H), 7.15─7.22

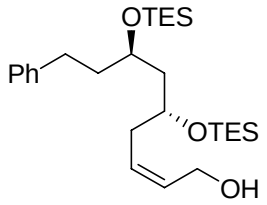
(m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.1, 7.0, 32.1, 38.6, 42.1, 69.9, 70.7, 114.1, 126.0, 128.4, 128.6, 141.4, 142.1.



^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.66 (q, J = 7.9 Hz, 6 H), 0.98 (t, J = 7.9 Hz, 9 H), 1.77─1.88 (m, 4 H), 2.57─2.72 (m, 2 H), 3.05─3.09 (m, 2 H), 4.11─4.19 (m, 1 H), 5.10─5.17 (m, 1 H), 5.81─5.88 (m, 2 H), 7.14─7.22 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.2, 7.1, 30.2, 31.2, 40.2, 43.5, 67.8, 67.9 121.5, 126.0, 127.6, 128.4, 128.6, 142.2, 168.9



^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.63 (q, J = 7.9 Hz, 6 H), 0.96 (t, J = 7.8 Hz, 9 H), 1.66─1.75 (m, 1 H), 1.77─1.86 (m, 2 H), 1.92─2.01 (m, 1 H), 2.30─2.38 (m, 2 H), 2.57─2.72 (m, 2 H), 4.11─4.20 (m, 1 H), 4.59─4.68 (m, 1 H), 6.04 (dt, J = 9.8 Hz, J = 1.8 Hz, 1 H), 6.86─6.93 (m, 1 H), 7.14─7.22 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.2, 7.1, 30.2, 31.2, 40.3, 42.4, 67.6, 74.9, 121.7, 126.0, 128.4, 128.6, 142.3, 145.3, 164.3.



^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.61 (q, J = 7.9 Hz, 6 H), 0.62 (q, J = 7.9 Hz, 6 H), 0.92─1.01 (m, 18 H), 1.65─1.85 (m, 5 H), 2.21─2.35 (m, 2 H), 2.53─2.78 (m, 2 H), 3.77─3.86 (m, 2 H), 4.08─4.20 (m, 2 H), 5.55─5.65 (m, 1 H), 5.74─5.83 (m, 1 H), 7.14─7.21 (m, 3 H), 7.26─7.32 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.3, 5.5, 7.1, 7.1, 31.6, 35.8, 39.8, 45.2, 58.6, 69.8, 69.9, 125.9, 128.5, 128.5, 129.1, 131.0, 142.5.

Synthesis of Solistatin

3-(2-Methylnaphthalen-1-yl)propanal (13)

To a solution of 1-bromo-2-methylnaphtalene (**12**) (2 g, 9.1 mmol) in degassed NEt_3 (90 mL) were added ethyl acrylate (0.98 mL, 9.1 mmol), $Pd(OAc)_2$ (203 mg, 0.90 mmol), and PPh_3 (356 mg, 1.36 mmol). The resulting mixture was stirred for 16 h at 100 °C before it was quenched with saturated aqueous NH_4Cl (200 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 95/5) gave (*E)*-ethyl 3-(2-methylnaphthalen-1-yl)acrylate as a colourless liquid (1.86 g, 7.73 mmol, 86%). R_f = 0.10 (P/EtOAc = 99/1); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.39 (t, *J* = 7.2 Hz, 3 H), 2.52 (s, 3 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 6.24 (d, *J* = 16.4 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 7.41─7.52 (m, 2 H), 7.74 (d, *J* = 8.4 Hz, 1 H), 7.78─7.85 (m, 1 H), 8.04 (d, *J* = 8.2 Hz, 1 H), 8.20 (d, *J* = 16.4 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 14.5, 21.1, 60.8, 124.8, 125.3, 125.8, 126.7, 128.4, 128.7, 129.0, 131.0, 131.6, 132.3, 134.2, 142.7, 166.8.

To a solution of (*E)*-ethyl 3-(2-methylnaphthalen-1-yl)acrylate (2.25 g, 9.38 mmol) in EtOH (95 mL) was added Pd/C (2 g, 50% in water, 0.47 mmol). The mixture was stirred under a H_2 atmosphere for 20 h at room temperature before it was filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 95/05) gave ethyl 3-(2-methylnaphthalen-1-yl)propanoate as a colourless liquid (2.08 g, 8.56 mmol, 91%). R_f = 0.43 (P/EtOAc = 95/5); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.2 Hz, 3 H), 2.53 (s, 3 H), 2.57─2.64 (m, 2 H), 3.39─3.47 (m, 2 H), 4.20 (q, *J* = 7.1 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 1 H), 7.39─7.46 (m, 1 H), 7.48─7.56 (m, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.82 (d, *J* = 8.2 Hz, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 14.4, 20.2, 24.2, 34.5, 60.7, 123.3, 124.8, 126.3, 126.8, 128.8, 129.3, 132.0, 132.7, 133.4, 133.7, 173.3.

To a solution of ethyl 3-(2-methylnaphthalen-1-yl)propanoate (2.86 mmol, 694 mg) in CH_2Cl_2 (30 mL) at −78°C was added DIBAL-H (3.1 mL, 3.15 mmol; 1 M in CH_2Cl_2). The resulting solution was stirred for 2 h at −78°C, before H_2O was added (2 mL). The mixture was allowed to warm to room temperature, aqueous potassium sodium tartrate (200 mL, 10% aq. solution), glycerine (0.2 mL/mmol) and Et_2O (200 mL) were added, and stirring was continued for 2 h (until both layers were clear and readily separated). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic

layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 95/05) gave **13** (383 mg, 1.93 mmol, 67%) as a colourless liquid. R_f = 0.31 (P/EtOAc = 95/5); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.51 (s, 3 H), 2.74─2.81 (m, 2 H), 3.37─3.45 (m, 2 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 7.40─7.47 (m, 1 H), 7.48─7.56 (m, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 7.7 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 9.92, (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.2, 20.9, 44.0, 123.1, 124.8, 126.4, 126.8, 128.9, 129.3, 131.9, 132.8, 133.2, 133.4, 201.6. HRMS 198.1051 [198.1045 calcd for $C_{14}H_{14}O$ (M^+)].

(*R*)-5-(2-methylnaphthalen-1-yl)pent-1-en-3-yl benzoate (14)

To a solution of methyl (diphenylphosphono)acetate (2.04 g, 6.67 mmol) in dry THF (24 mL) was added NaH (315 mg, 7.9 mmol; 60 % in oil)at 0 °C under argon. The resulting mixture was stirred for 20 min at 0 °C, and then it was cooled to −78°C. Aldehyd **13** (1.20 g, 6.06 mmol) was added dropwise. The stirred mixture was allowed to warm up to −10°C over 3 h. The reaction was then quenched by addition of saturated aqueous NH_4Cl (50 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 96/04) gave (*Z*)-methyl 5-(2-methylnaphthalen-1-yl)pent-2-enoate (1.23 g, 4.85 mmol, 80%) as a single diastereoisomer (d.r. > 95:5). R_f = 0.5 (P/EtOAc = 95/5); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.55 (s, 3 H), 2.96─3.05 (m, 2 H), 3.19─3.27 (m, 2 H), 3.72 (s, 3 H), 5.85 (dt, *J* = 11.6 Hz, *J* = 1.4 Hz, 1 H), 6.39 (dt, *J* = 11.6 Hz, *J* = 7.7 Hz, 1 H), 7.32 (d, *J* = 8.2 Hz, 1 H), 7.39─7.46 (m, 1 H), 7.49─7.55 (m, 1 H), 7.66 (d, *J* = 8.2 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 8.11 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.3, 27.8, 29.4, 51.2, 120.1, 123.7, 124.7, 126.1, 126.5, 128.7, 129.3, 132.3, 132.7, 133.4, 134.4, 149.0, 166.8.

To a solution of (*Z*)-methyl 5-(2-methylnaphthalen-1-yl)pent-2-enoate (4.76 mmol, 1.21 g) in THF (50 mL) at −78°C was added DIBAL-H (14.3 mL, 14.3 mmol; 1M in CH_2Cl_2). The resulting solution was stirred for 4 h at −78°C, before H_2O was added (2 mL). The mixture was allowed to warm to room temperature, aqueous potassium sodium tartrate (200 mL, 10% aq. solution), glycerine (0.2 mL/mmol) and Et_2O (200 mL) were added, and stirring was continued for 2 h (until both layers were clear and readily separated). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 75/25) gave (*Z*)-5-

(2-methylnaphthalen-1-yl)pent-2-en-1-ol (1.03 g, 4.55 mmol, 96%) as a colourless oil. R_f = 0.2 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.93 (s, 1 H), 2.45 (q, *J* = 8.0 Hz, 2 H), 2.51 (s, 3 H), 3.14─3.20 (m, 2 H), 4.01 (d, *J* = 6.6 Hz, 2 H), 5.57─5.67 (m, 1 H), 5.58─5.79 (m, 1 H), 7.31 (d, *J* = 8.2 Hz, 1 H), 7.39─7.45 (m, 1 H), 7.47─7.54 (m, 1 H), 7.64 (d, *J* = 8.2 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 8.02 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.5, 28.0, 28.4, 58.5, 123.6, 124.7, 126.1, 126.5, 128.8, 129.3, 129.5, 131.9, 132.1, 132.7, 133.3, 134.7. HRMS 226.1355 [226.1358 calcd for $C_{16}H_{18}O$ (M^+)].

Following the general procedure (**Method A**), (*Z*)-5-(2-methylnaphthalen-1-yl)pent-2-enyl 2,2,2-trichloroacetimidate was obtained as a colourless oil (87%) after flash chromatography on silica (P/EtOAc = 98/2). R_f = 0.44 (P/EtOAc = 95/5); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.46─2.59 (m, 2 H), 2.53 (s, 3 H), 3.15─3.24 (m, 2 H), 4.82 (d, *J* = 6.8 Hz, 2 H), 5.70─5.79 (m, 1 H), 5.86─5.96 (m, 1 H), 7.31 (d, *J* = 8.4 Hz, 1 H), 7.39─7.46 (m, 1 H), 7.47─7.55 (m, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 8.05 (d, *J* = 8.6 Hz, 1 H), 8.30 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.4, 28.2, 28.5, 65.0, 123.5, 123.6, 124.7, 126.1, 126.5, 128.8, 129.3, 132.2, 132.8, 133.2, 134.6, 135.4, 162.7.

Following the general procedure (**Method B**, (+)-COP-OAc), **14** was obtained after flash chromatography on silica (P/EtOAc = 98/2) in 92%. R_f = 0.35 (P/EtOAc = 95/5); $[\alpha]^{23}_D$ = +9.3 (*c* = 0.55 $CDCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.02─2.14 (m, 2 H), 2.51 (s, 3 H), 3.14─3.29 (m, 2 H), 5.32 (dt, *J* = 10.5 Hz, *J* = 1.1 Hz, 1 H), 5.45 (dt, *J* = 17.1 Hz, *J* = 1.1 Hz, 1 H), 5.69─5.76 (m, 1 H), 6.04 (ddd, *J* = 17.1 Hz, *J* = 10.7 Hz, *J* = 6.1 Hz, 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.38─7.44 (m, 1 H), 7.45─7.53 (m, 3 H), 7.57─7.66 (m, 2 H), 7.78─7.83 (m, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 8.11─8.18 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.2, 24.3, 34.5, 75.5, 117.3, 123.4, 124.7, 126.2, 126.5, 128.6, 128.8, 129.4, 129.8, 130.6, 132.1, 132.8, 133.0, 133.2, 134.6, 136.3, 166.1; HRMS 330.1620 [330.1620 calcd for $C_{23}H_{22}O_2$ (M^+)].

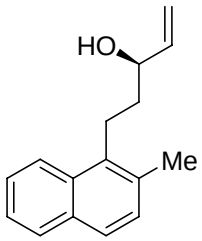
HPLC analysis indicated an enantiomeric excess of 94% [Daicel OJ-H column; flow: 1.0 mL/min; pentanes/*i*-PrOH, 80:20; 254 nm; minor enantiomer, t_R = 8.21 min; major enantiomer, t_R = 10.89 min].

(3*R*,5*R*)-5-(Triethylsilyloxy)-7-(2-methylnaphthalen-1-yl)hept-1-en-3-yl benzoate (15)

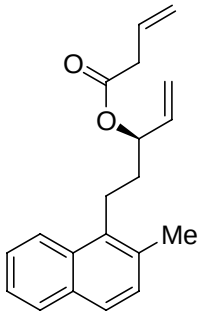
Following the general procedure (**Method C**, (+)-COP-OAc), **15** was obtained in 40 % yield from **14** in a diastereomeric ratio of 94:6 according to ^{1}H NMR of the crude mixture after flash chromatography on silica (P/EtOAc = 99/1). R_f = 0.33 (P/EtOAc = 95/5); $[\alpha]^{23}_D$ = +2.6

(*c* = 0.72 $CDCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.70 (q, *J* = 8.0 Hz, 6 H), 1.03 (t, *J* = 8.0 Hz, 9 H), 1.71─1.84 (m, 1 H), 1.87─2.07 (m, 2 H), 2.11─2.22 (m, 1 H), 2.48 (s, 3 H), 3.04 (td, *J* = 12.8 Hz, *J* = 4.8 Hz, 1 H), 3.21 (td, *J* = 12.8 Hz, *J* = 4.8 Hz, 1 H), 3.97─4.09 (m, 1 H), 5.23 (d, *J* = 10.5 Hz, 1 H), 5.36 (d, *J* = 17.2 Hz, 1 H), 5.61─5.69 (m, 1 H), 5.94 (ddd, *J* = 17.2 Hz, *J* = 10.5 Hz, *J* = 6.1 Hz, 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.36─7.47 (m, 4 H), 7.54─7.64 (m, 2 H), 7.74─7.81 (m, 1 H), 8.01─8.09 (m, 3 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.4, 7.2, 20.1, 24.6, 37.0, 42.4, 69.6, 72.8, 117.0, 123.7, 124.6, 126.0, 126.2, 128.5, 128.7, 129.3, 129.7, 130.5, 132.2, 132.7, 132.9, 133.1, 135.5, 136.7, 165.8; LRMS (EI): 488 (9%) [M^+], 235 (18%), 207 (85%), 181 (79%), 155 (100%), 105 (42%); HRMS 488.2747 [488.2747 calcd for $C_{31}H_{40}O_3S_i$ (M^+)].

NMR data for key intermediates towards the synthesis 15

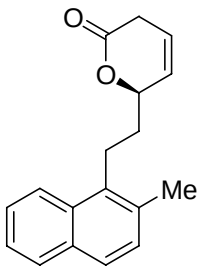


^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.65 (s, 1 H), 1.80─1.91 (m, 2 H), 2.52 (s, 3 H), 3.08─3.18 (m, 1 H), 3.19─3.29 (m, 1 H), 4.27−4.35 (m, 1 H), 5.20 (d, *J* = 10.5 Hz, 1 H), 5.33 (d, *J* = 17.2 Hz, 1 H), 6.00 (ddd, *J* = 17.2 Hz, *J* = 10.5 Hz, *J* = 6.1 Hz, 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.38─7.44 (m, 1 H), 7.46─7.53 (m, 1 H), 7.64 (d, *J* = 8.4 Hz, 1 H), 7.81 (d, *J* = 8.2 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.2, 24.4, 37.0, 73.3, 115.1, 123.7, 124.6, 126.1, 126.3, 128.7, 129.4, 132.2, 132.7, 133.1, 135.2, 141.1.

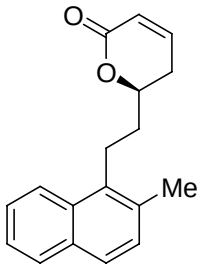


^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.87─2.03 (m, 2 H), 2.49 (s, 3 H), 3.03─3.16 (m, 2 H), 3.20 (d, *J* = 7.0 Hz, 2 H), 5.19─5.31 (m, 3 H), 5.37 (d, *J* = 17.3 Hz, 1 H), 5.44−5.52 (m, 1 H), 5.87─6.08 (m, 2 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 7.38─7.45 (m, 1 H), 7.47─7.53 (m, 1 H), 7.64 (d, *J* = 8.4 Hz, 1 H), 7.81 (d, *J* = 7.7 Hz, 1 H), 7.98 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (90.6 MHz,

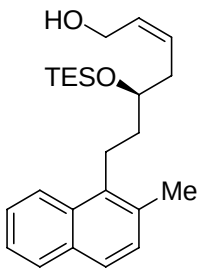
$CDCl_3$): δ = 20.1, 24.2, 34.3, 39.7, 75.2, 117.3, 118.9, 123.4, 124.7, 126.2, 126.5, 128.8, 129.3, 130.4, 132.1, 132.7, 133.0, 134.6, 136.2, 171.0.



^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.93─2.22 (m, 2 H), 2.52 (s, 3 H), 3.10─3.16 (m, 2 H), 3.16─3.25 (m, 1 H), 3.24─3.36 (m, 1 H), 5.09─5.16 (m, 1 H), 5.86─5.97 (m, 2 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.38─7.45 (m, 1 H), 7.47─7.54 (m, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.81 (d, *J* = 8.2 Hz, 1 H), 8.01 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.2, 23.4, 30.1, 35.8, 79.5, 122.3, 123.4, 124.8, 126.3, 126.5, 126.6, 128.8, 129.4, 132.1, 132.7, 133.3, 134.1, 169.0.



^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.90─2.01 (m, 1 H), 2.06─2.18 (m, 1 H), 2.30─2.45 (m, 2 H), 2.53 (s, 3 H), 3.17─3.27 (m, 1 H), 3.35─3.45 (m, 1 H), 4.56─4.59 (m, 1 H), 6.04─6.10 (m, 1 H), 6.89 (ddd, *J* = 9.8 Hz, *J* = 5.6 Hz, *J* = 2.7 Hz, 1 H) 7.31 (d, *J* = 8.4 Hz, 1 H), 7.39─7.45 (m, 1 H), 7.47─7.54 (m, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.3, 24.0, 29.7, 35.2, 77.7, 121.7, 123.5, 124.8, 126.3, 126.6, 128.8, 129.4, 132.1, 132.7, 133.3, 134.2, 145.1, 164.5.



^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.68 (q, *J* = 7.9 Hz, 6 H), 1.02 (t, *J* = 7.9 Hz, 9 H), 1.63 (s, 1 H), 1.69─1.85 (m, 2 H), 2.35─2.56 (m, 2 H), 2.49 (s, 3 H), 2.99─3.10 (m, 1 H), 3.12─3.22

(m, 1 H), 3.95 (virt. quin, *J* = 5.8 Hz, 1 H), 4.12─4.27 (m, 2 H), 5.61─5.70 (m, 1 H), 5.74─5.84 (m, 1 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 7.37─7.44 (m, 1 H), 7.45─7.51 (m, 1 H), 7.62 (d, *J* = 8.2 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 8.02 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.2, 7.1, 20.2, 24.6, 35.4, 37.1, 58.7, 72.2, 123.6, 124.6, 126.0, 126.2, 128.7, 129.1, 129.3, 131.0, 132.2, 132.7, 132.8, 135.5.

Completion of the solistatin synthesis

To a solution of **15** (0.19 mmol, 95 mg) in CH_2Cl_2 (1.9 mL) at −78°C was added DIBAL-H (0.44 mL, 0.49 mmol; 1.1 M in cyclohexane). The resulting solution was stirred for 3 h at −78°C before H_2O was added (0.5 mL). The mixture was allowed to warm to room temperature, aqueous potassium sodium tartrate (50 mL, 10% aq. solution), glycerine (0.2 mL/mmol) and Et_2O (50 mL) were added, and stirring was continued for 2 h (, until both layers were clear and readily separated). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 90/10) gave (3*R*,5*R*)-5-(triethylsilyloxy)-7-(2-methylnaphthalen-1-yl)hept-1-en-3-ol as a yellow oil, which was directly subjected to TES protection to give the corresponding triethylsilyl ether (69 mg, 0.14 mmol) in 72% yield. R_f = 0.75 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.68 (q, *J* = 7.9 Hz, 6 H), 1.00 (t, *J* = 7.9 Hz, 9 H), 1.78─1.97 (m, 4 H), 2.50 (s, 3 H), 3.08 (t, *J* = 8.5 Hz, 2 H), 4.10─4.22 (m, 1 H), 4.31─4.40 (m, 1 H), 5.14 (d, *J* = 10.5 Hz, 1 H), 5.31 (d, *J* = 17.3 Hz, 1 H), 5.94 (ddd, *J* = 17.3 Hz, *J* = 10.5 Hz, *J* = 5.9 Hz, 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.38─7.44 (m, 1 H), 7.46─7.52 (m, 1 H), 7.63 (d, *J* = 8.2 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 8.01 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.3, 7.1, 20.2, 24.4, 37.9, 43.6, 72.0, 72.5, 114.4, 123.5, 124.7, 126.0, 126.3, 128.8, 129.4, 132.1, 132.8, 132.8, 135.3, 141.1.

To a solution of 1-[(3*R*,5*R*)-3,5-bis(triethylsilyloxy)hept-6-enyl]-2-methylnaphthalene (69 mg, 0.14 mmol) in dry THF (1.4 mL) was added a solution of 9-BBN in THF (0.8 mL, 0.41 mmol; 0.5 M) at 0°C. The mixture was stirred for 19 h at room temperature, and then the mixture was cooled to 0 °C. Aqueous NaOH (0.09 mL, 3 M) and H_2O_2 (0.09 mL, 35% in water) were added subsequently, and stirring was then continued for 2 h at room temperature. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 90/10) gave (3*S*,5*R*)-3,5-bis(triethylsilyloxy)-7-(2-methylnaphthalen-1-yl)heptan-1-ol as a

colourless oil (57 mg, 0.11 mmol, 79%). R_f = 0.65 (P/EtOAc = 80/20); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.61─0.72 (m, 12 H), 0.97─1.06 (m, 18 H), 1.60─2.01 (m, 7 H), 2.51 (s, 3 H), 2.99─3.23 (m, 2 H), 3.69─3.81 (m, 1 H), 3.82─4.03 (m, 2 H), 4.03─4.18 (m, 1 H) 7.30 (d, *J* = 8.4 Hz, 1 H), 7.37─7.53 (m, 2 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.77─7.84 (m, 1 H), 8.04 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.2, 5.4, 7.0, 7.1, 20.1, 24.3, 37.7, 38.4, 44.6, 60.4, 69.5, 69.7, 123.6, 124.6, 126.0, 126.2, 128.7, 129.4, 132.1, 132.7, 132.8, 135.5.

To a solution of (3*S*,5*R*)-3,5-bis(triethylsilyloxy)-7-(2-methylnaphthalen-1-yl)heptan-1-ol (23 mg, 0.04 mmol) in DMSO (0.44 mL) was added IBX (24.4 mg, 0.09 mmol). The mixture was stirred for 1 h at room temperature before CH_2Cl_2 (10 mL) was added. Stirring was continued until a precipitation occurred (30 min). The mixture was filtered, and the filtrate was washed with aqueous saturated $NaHCO_3$ (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 95/05) gave (3*R*,5*R*)-3,5-bis(triethylsilyloxy)-7-(2-methylnaphthalen-1-yl)heptanal as a colourless liquid (14.7 mg, 0.03 mmol, 66%). R_f = 0.93 (P/EtOAc = 80/20); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.58─0.72 (m, 12 H), 0.95─1.05 (m, 18 H), 1.63─1.97 (m, 4 H), 2.51─2.60 (m, 4 H), 2.66 (ddd, *J* = 16.0 Hz, *J* = 5.2 Hz, *J* = 1.8 Hz, 1 H), 3.01─3.11 (m, 1 H), 3.12─3.23 (m, 1 H), 4.01 (virt. quin, *J* = 6.0 Hz, 1 H), 4.35 (virt. quin, *J* = 6.0 Hz. 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.38─7.44 (m, 1 H), 7.45─7.51 (m, 1 H), 7.63 (d, *J* = 8.2 Hz, 1 H), 7.78─7.83 (m, 1 H), 8.05 (d, *J* = 8.6 Hz, 1 H), 9.83 (t, *J* = 2.3 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 5.2, 5.4, 7.0, 7.2, 20.2, 24.3, 37.2, 45.6, 51.5, 65.7, 69.5, 123.7, 124.6, 126.0, 126.2, 128.8, 129.4, 132.2, 132.8, 132.8, 135.5, 201.9.

To a solution of (3*R*,5*R*)-3,5-bis(triethylsilyloxy)-7-(2-methylnaphthalen-1-yl)heptanal (14.7 mg, 0.03 mmol) and 2-methyl-2-butene (0.15 mL) in *t*BuOH (0.6 mL) were subsequently added aqueous $NaClO_2$ (19.4 mg in 0.3 mL water) and aqueous NaH_2PO_4 (33.4 mg in 0.3 mL water). The mixture was stirred at room temperature for 16 h. The organic products were extracted with EtOAc (3 x 5 mL). The organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in EtOH (0.5 mL), and *p*-TsOH (2 mg) was added to this solution. The mixture was stirred for 1h at 50°C before it was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica (P/EtOAc = 30/70) gave solistatin (**11**) as a colourless solid (6.9 mg, 0.024 mmol, 85%). R_f = 0.13 (P/EtOAc = 40/60); $[\alpha]^{20}_D$ = +32.5 (*c* = 0.80 EtOH); natural product:[6] $[\alpha]^{20}_D$ = +32.0 (*c* = 0.251, EtOH). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.81─2.07 (m, 4 H), 2.52 (s, 3 H),

[6] D. Sorensen, T. O. Larsen, C. Christophersen, P. H. Nielsen, U. Anthoni, *Phytochemistry* **1999**, *51*, 1027.

2.67 (ddd, *J* = 17.7 Hz, *J* = 3.9 Hz, *J* = 1.6 Hz, 1 H), 2.80 (dd, *J* = 17.7 Hz, *J* = 5.2 Hz, 1 H), 3.14─3.24 (m, 1 H), 3.36─3.46 (m, 1 H), 4.40─4.46 (m, 1 H), 4.81─4.89 (m, 1 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 7.38─7.45 (m, 1 H), 7.47─7.54 (m, 1 H), 7.64 (d, *J* = 8.4 Hz, 1 H), 7.81 (d, *J* = 7.7 Hz, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.1, 24.0, 35.6, 36.1, 38.7, 62.9, 75.4, 123.3, 124.6, 126.1, 126.4, 128.6, 129.2, 131.9, 132.6, 133.1, 134.2, 170.1; LRMS (EI): 284 (68%) [M^+], 179 (44%), 155 (100%), 59 (41%); HRMS 284.1413 [284.1412 calcd for $C_{18}H_{20}O_3$ (M^+)].

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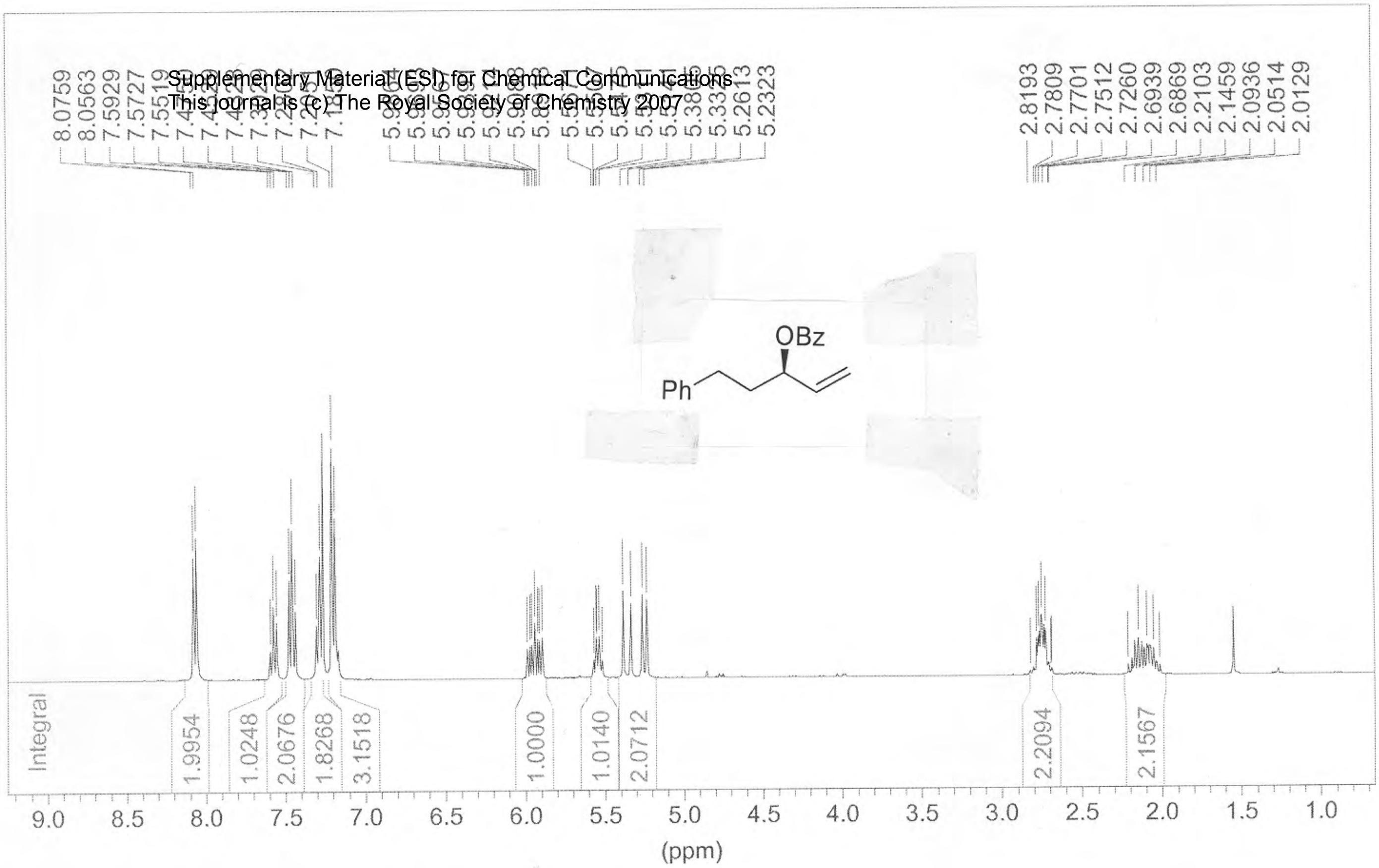

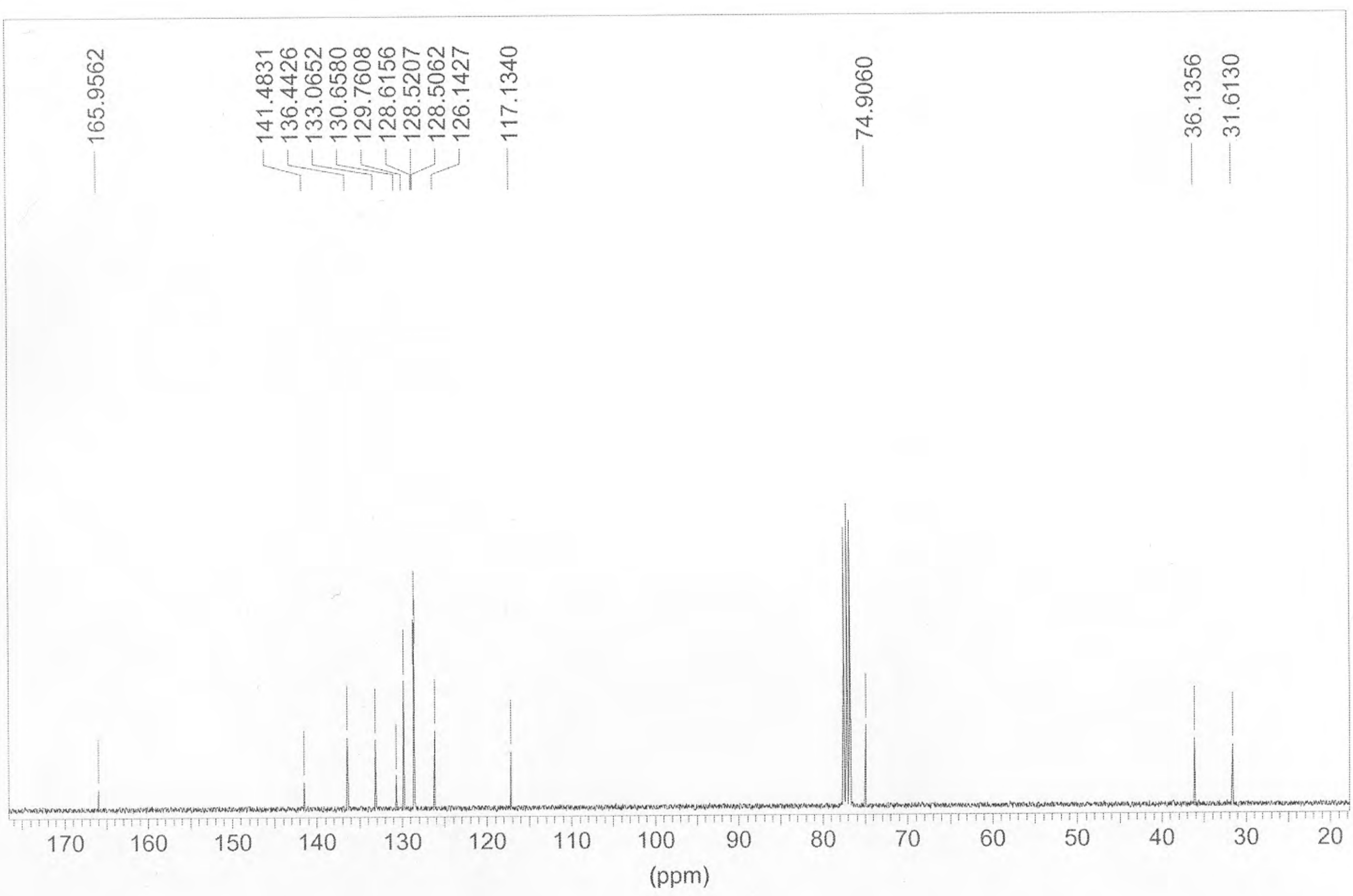

281 JB-5-59

Daicel Chiralcel OJ-H 250 x 4.6

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Sample Type:	**unknown**	*Wavelength:*	**210**
Control Program:	**SäuleB_NP_ISO_95_5_1_30**	*Bandwidth:*	**1**
Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
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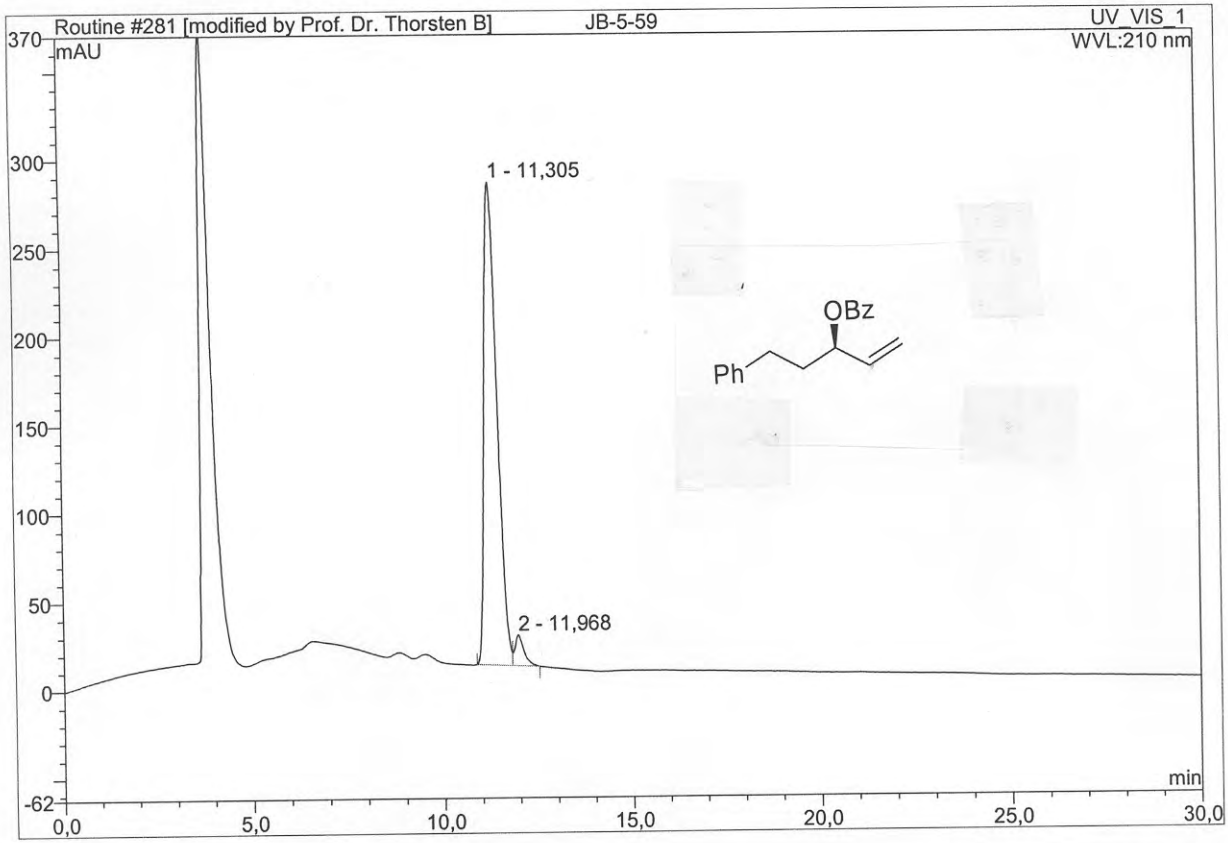
Run Time (min):	**30,00**	*Sample Amount:*	**1,0000**



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Total:			290,953	113,229	100,00	0,000	

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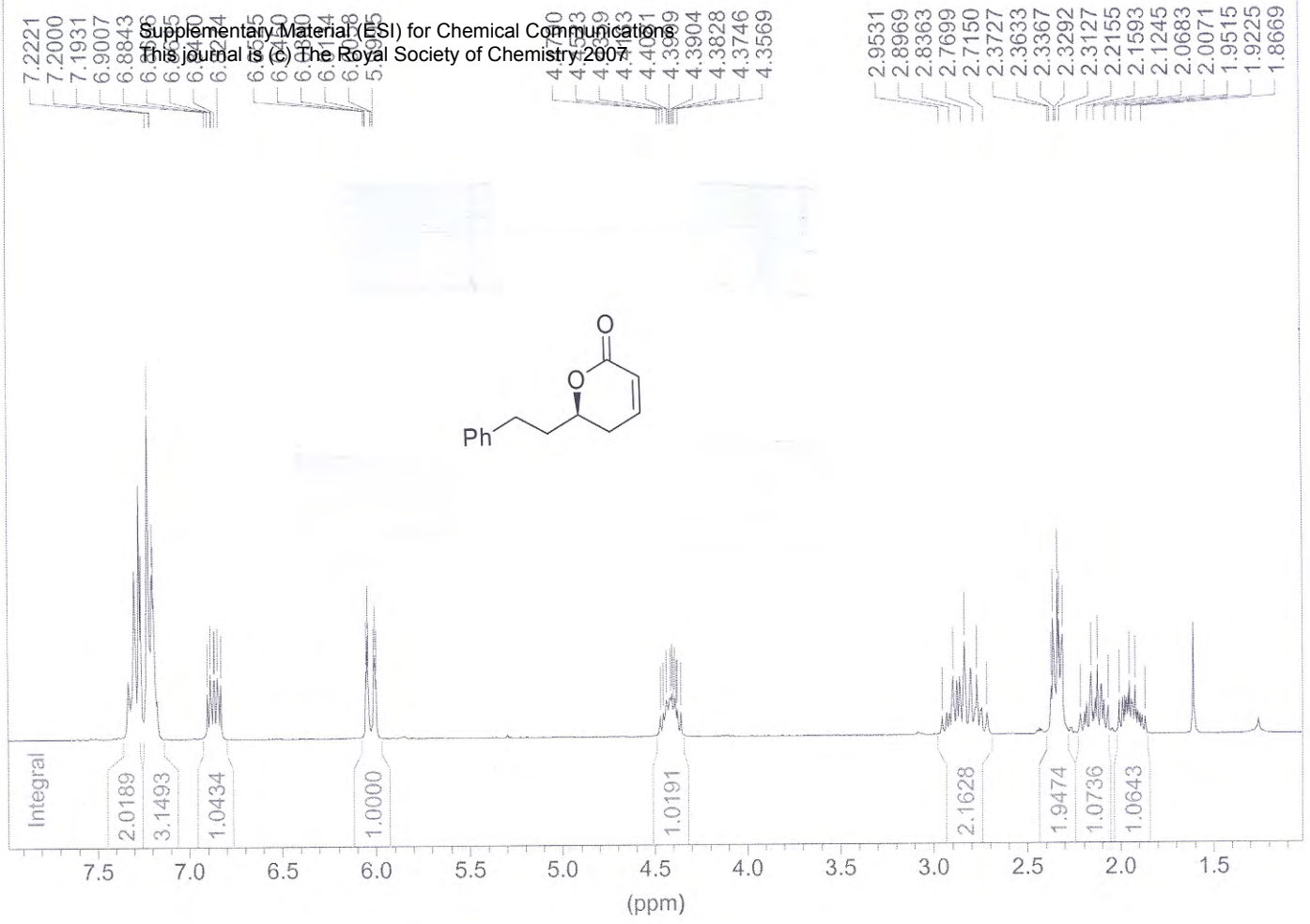

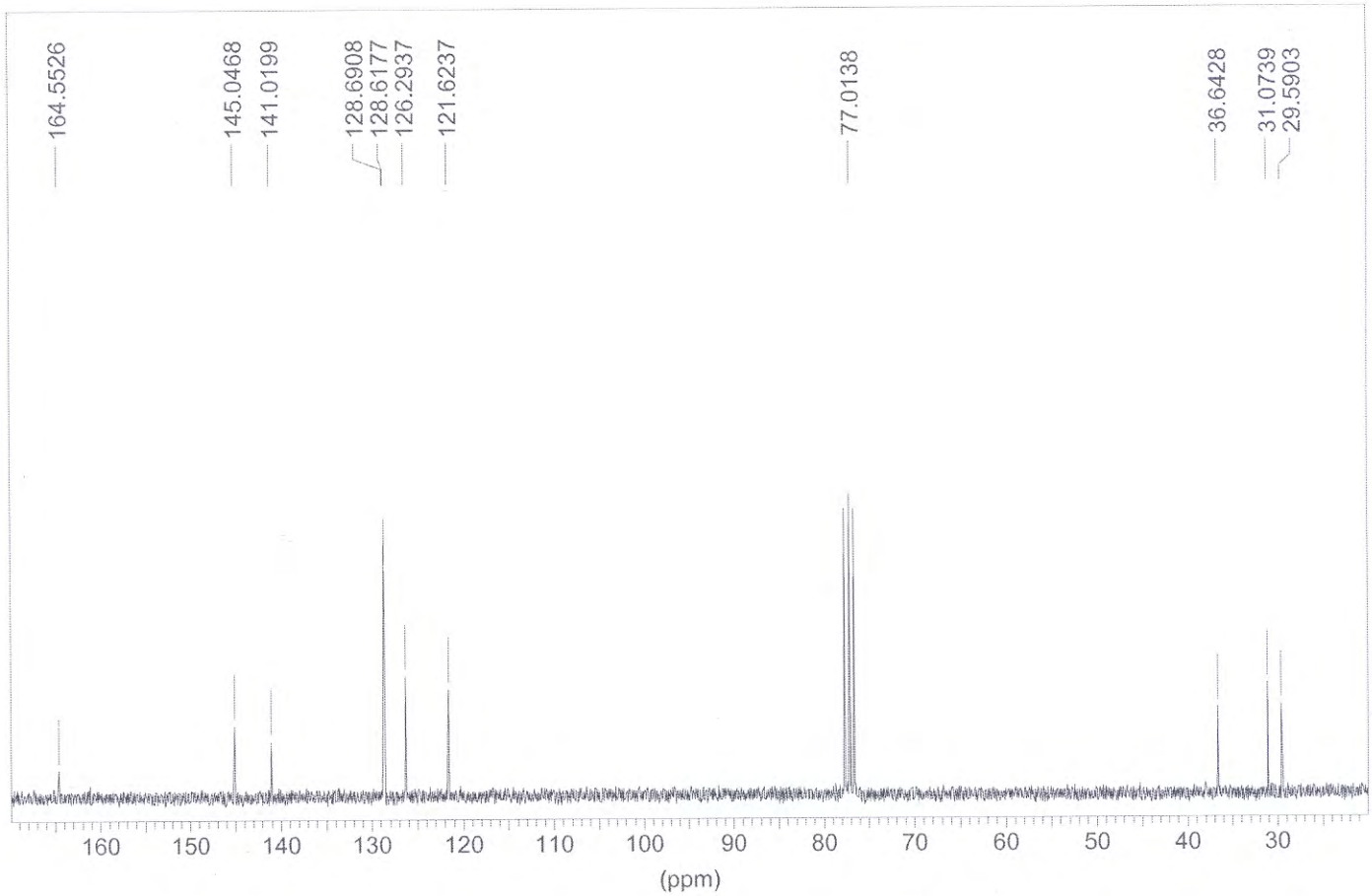

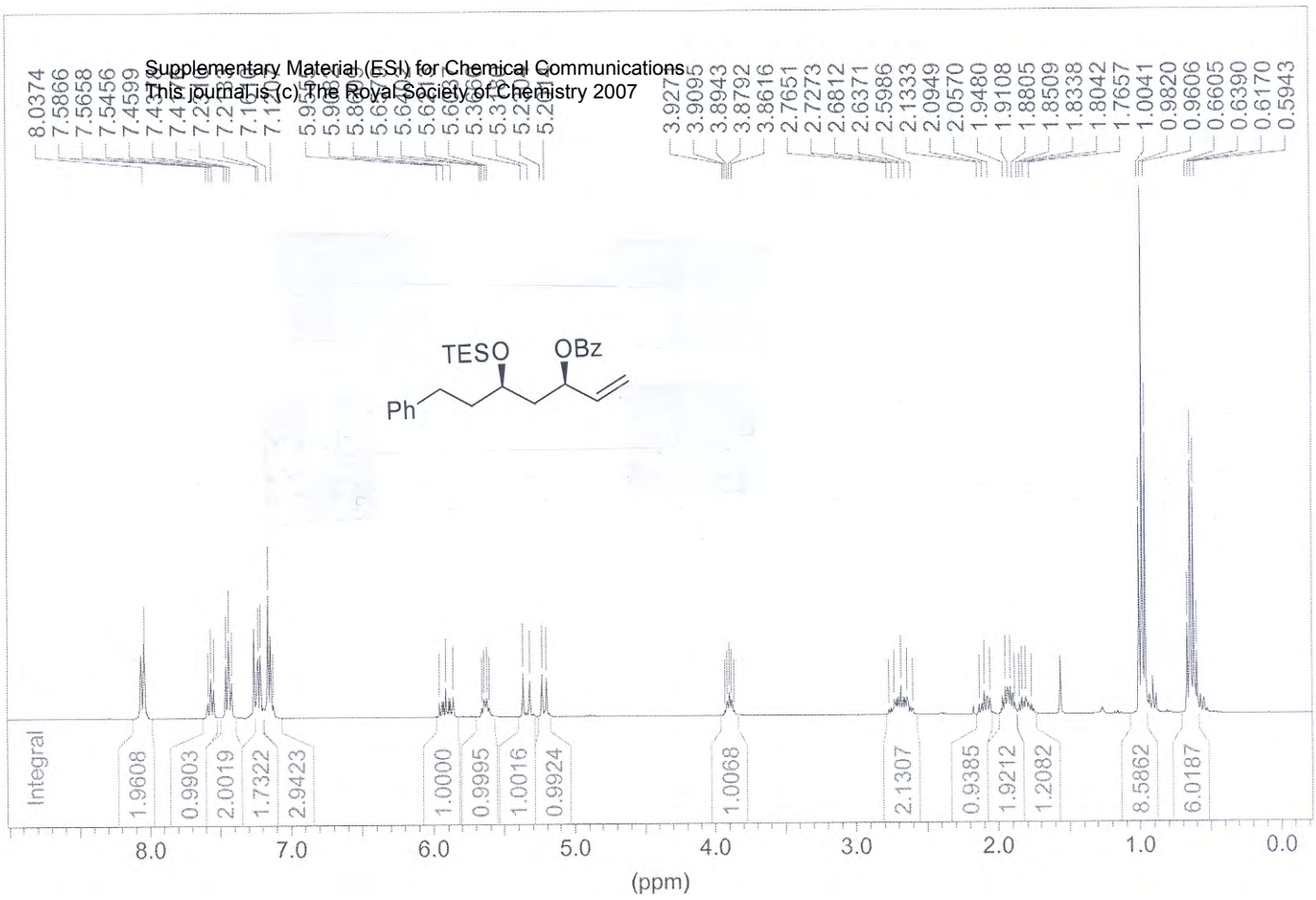
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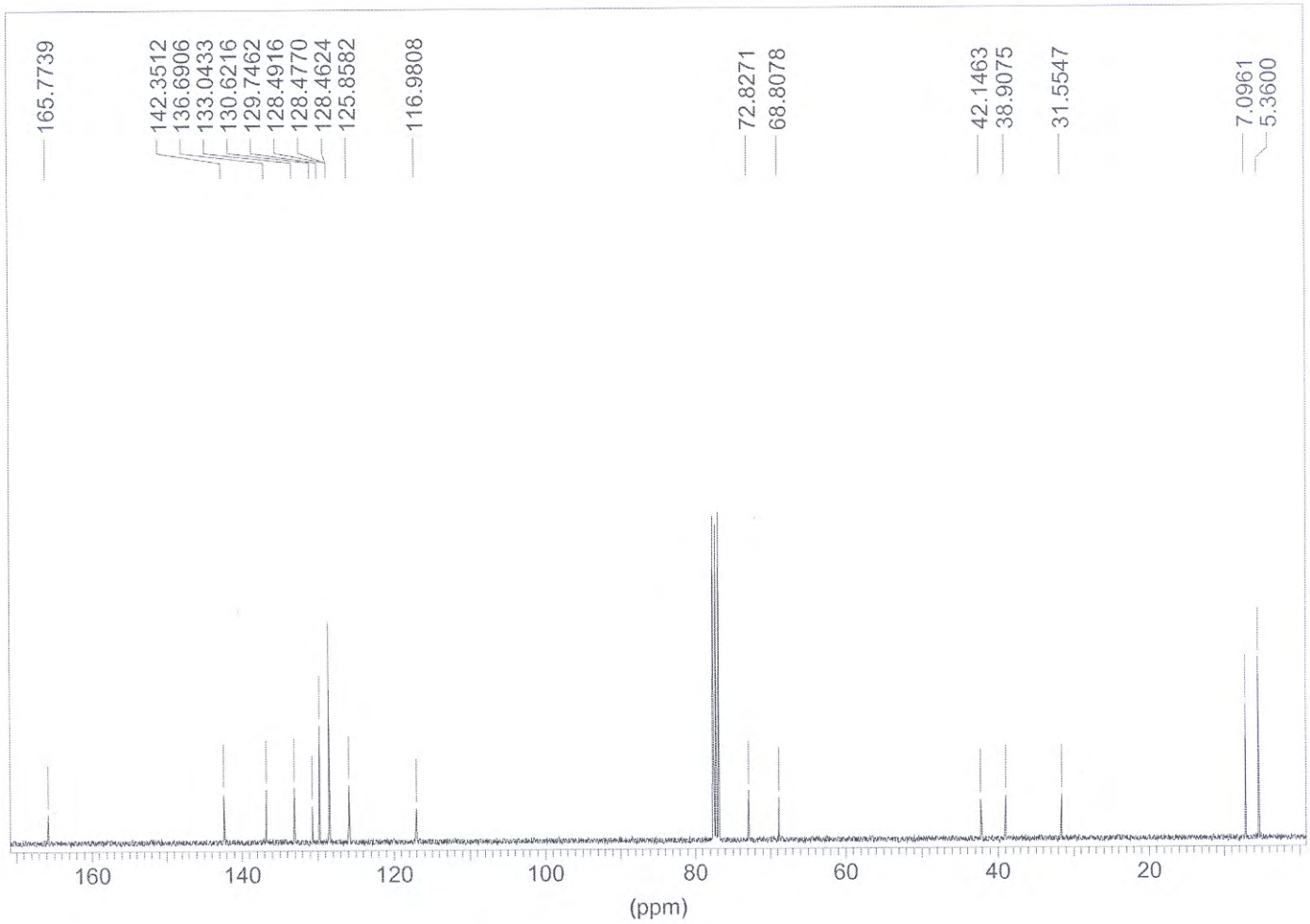
(ppm)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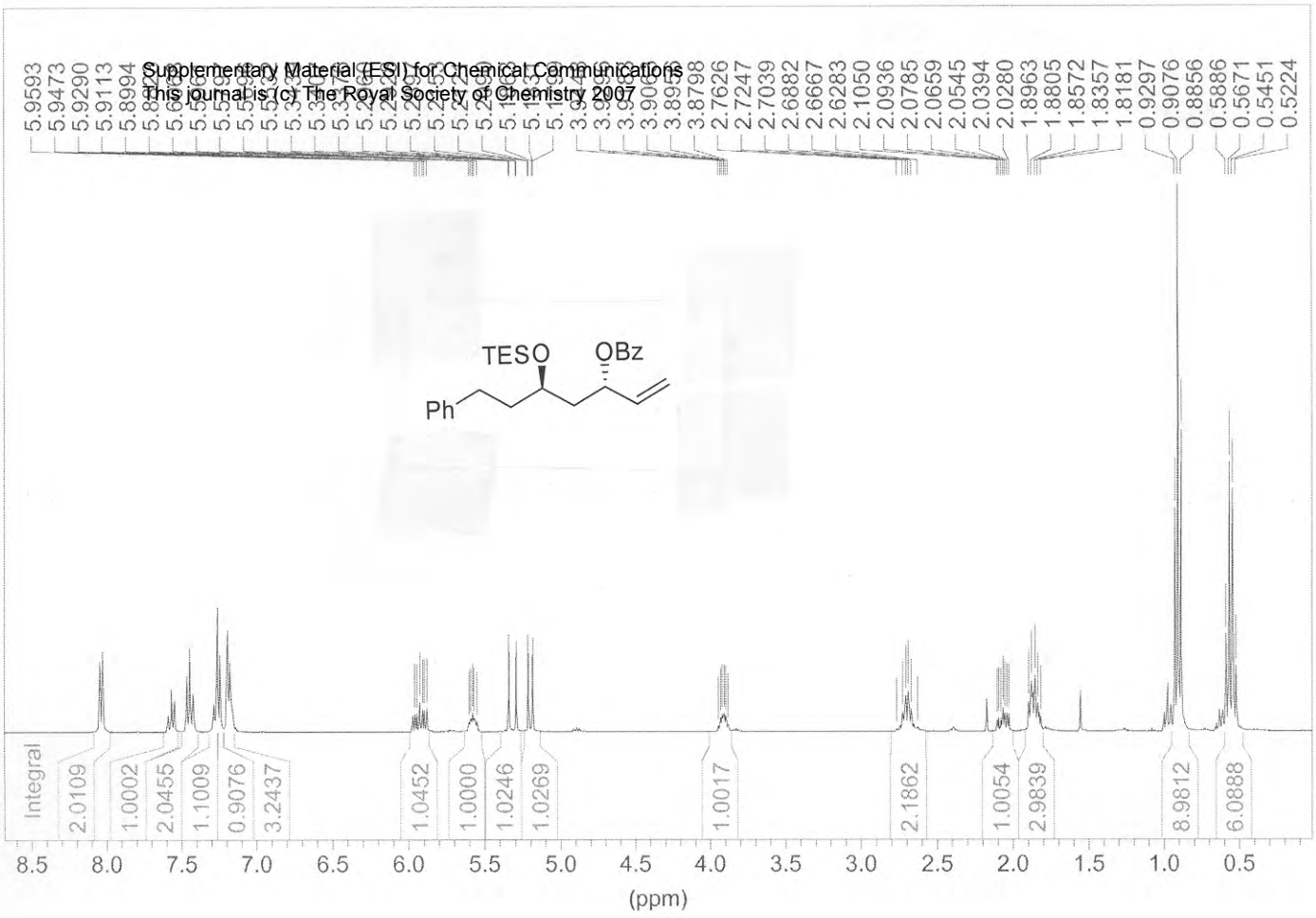
5.3600
(ppm)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OBz
Ph
Integral
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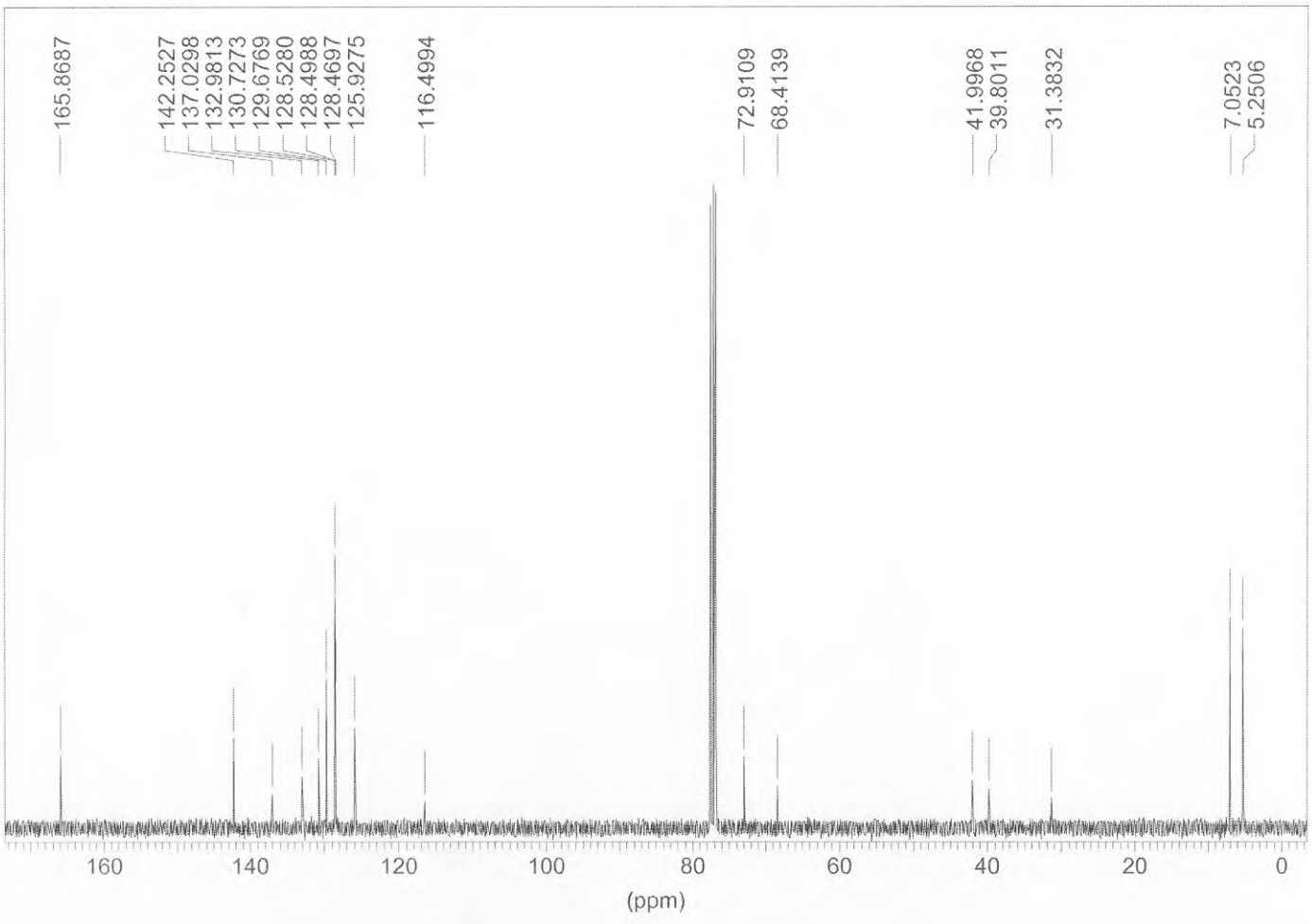
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(ppm)

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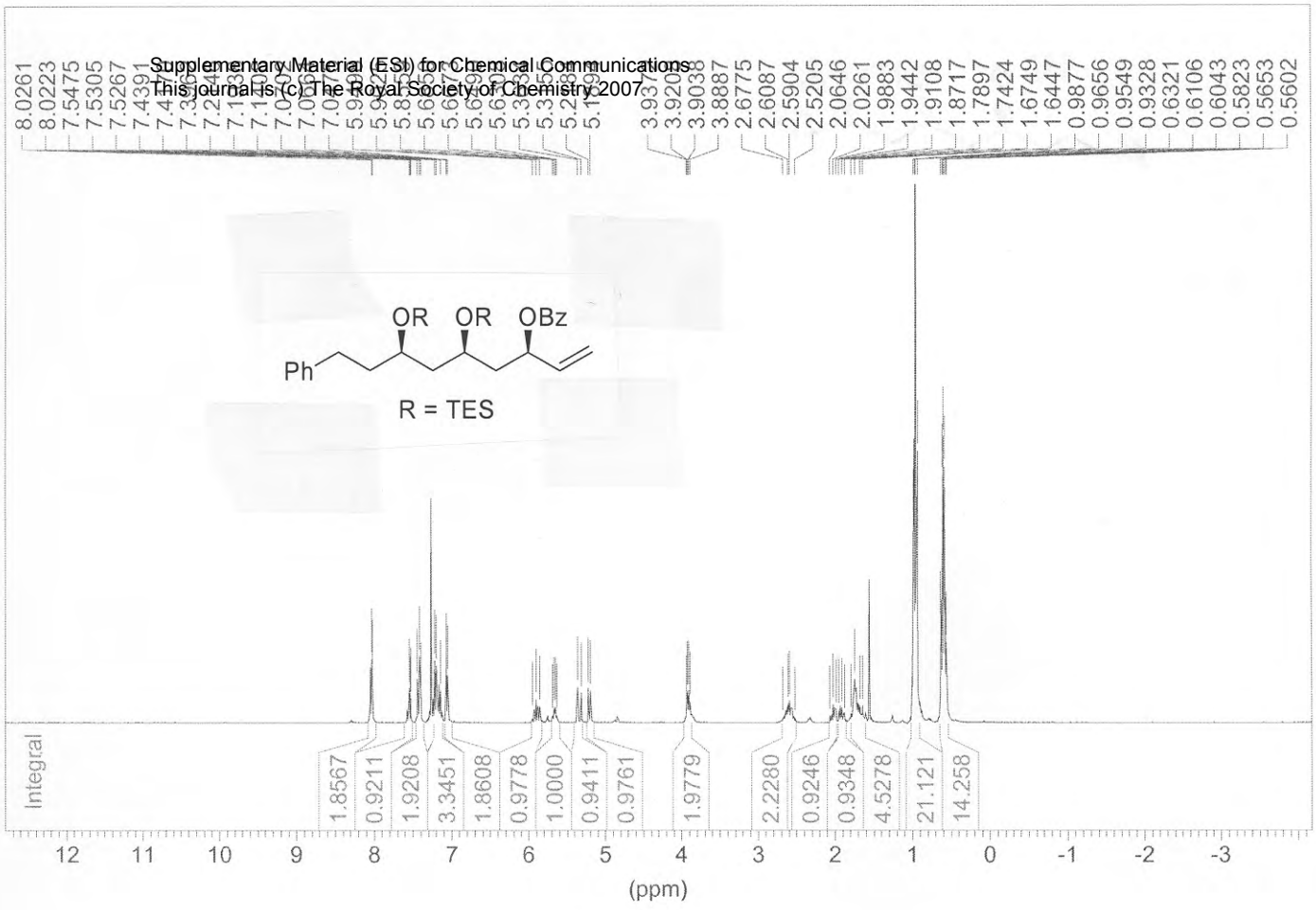

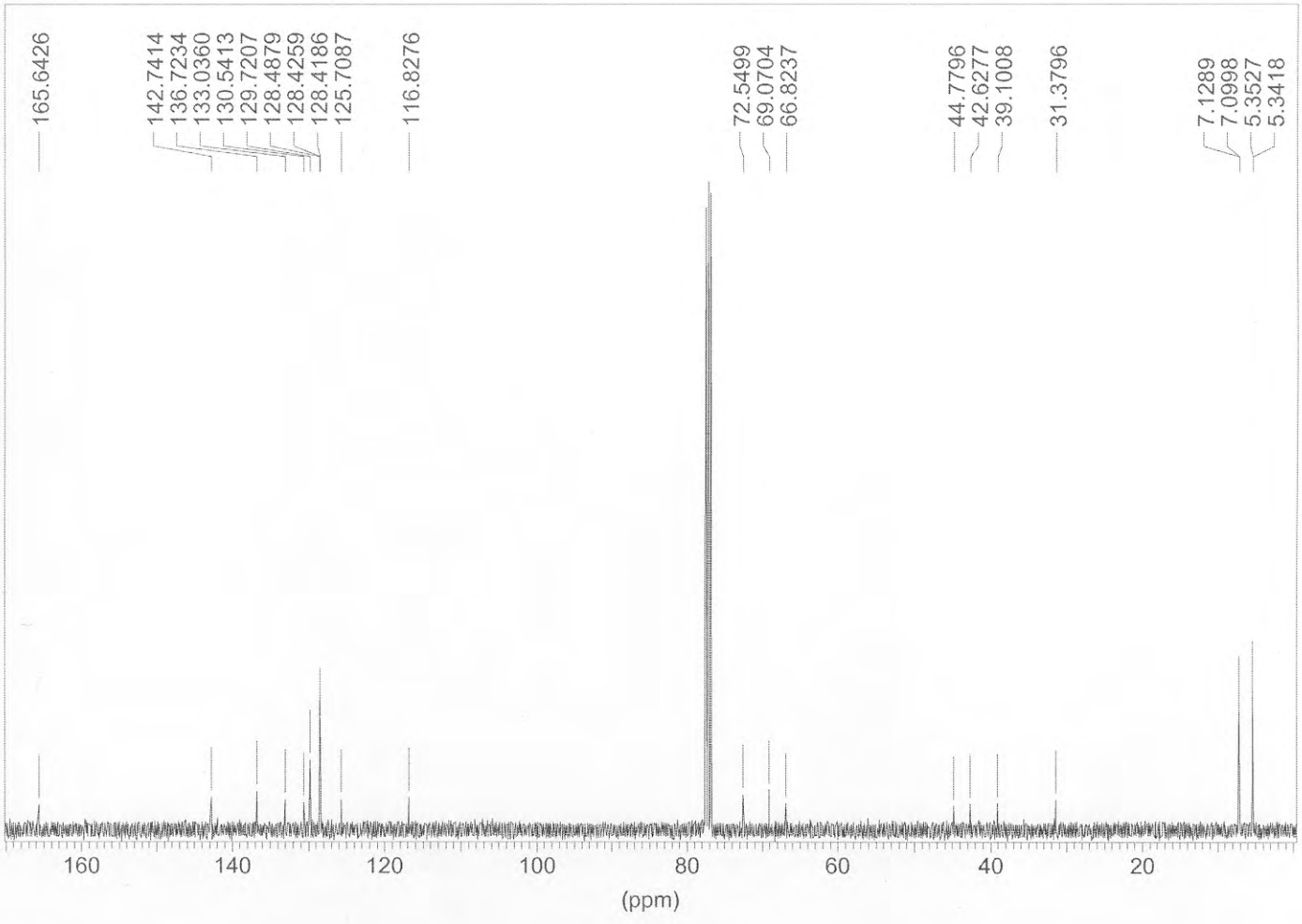

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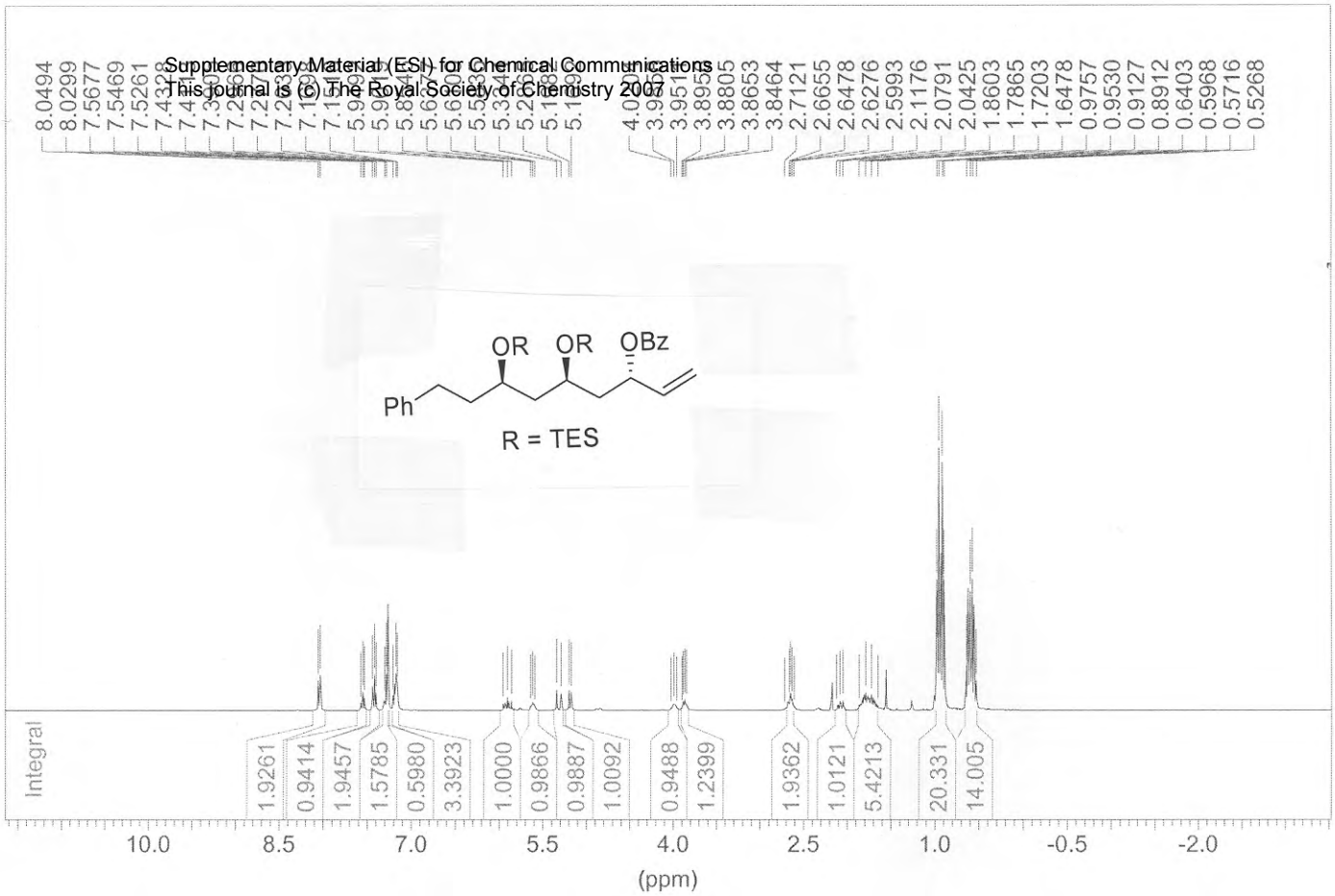

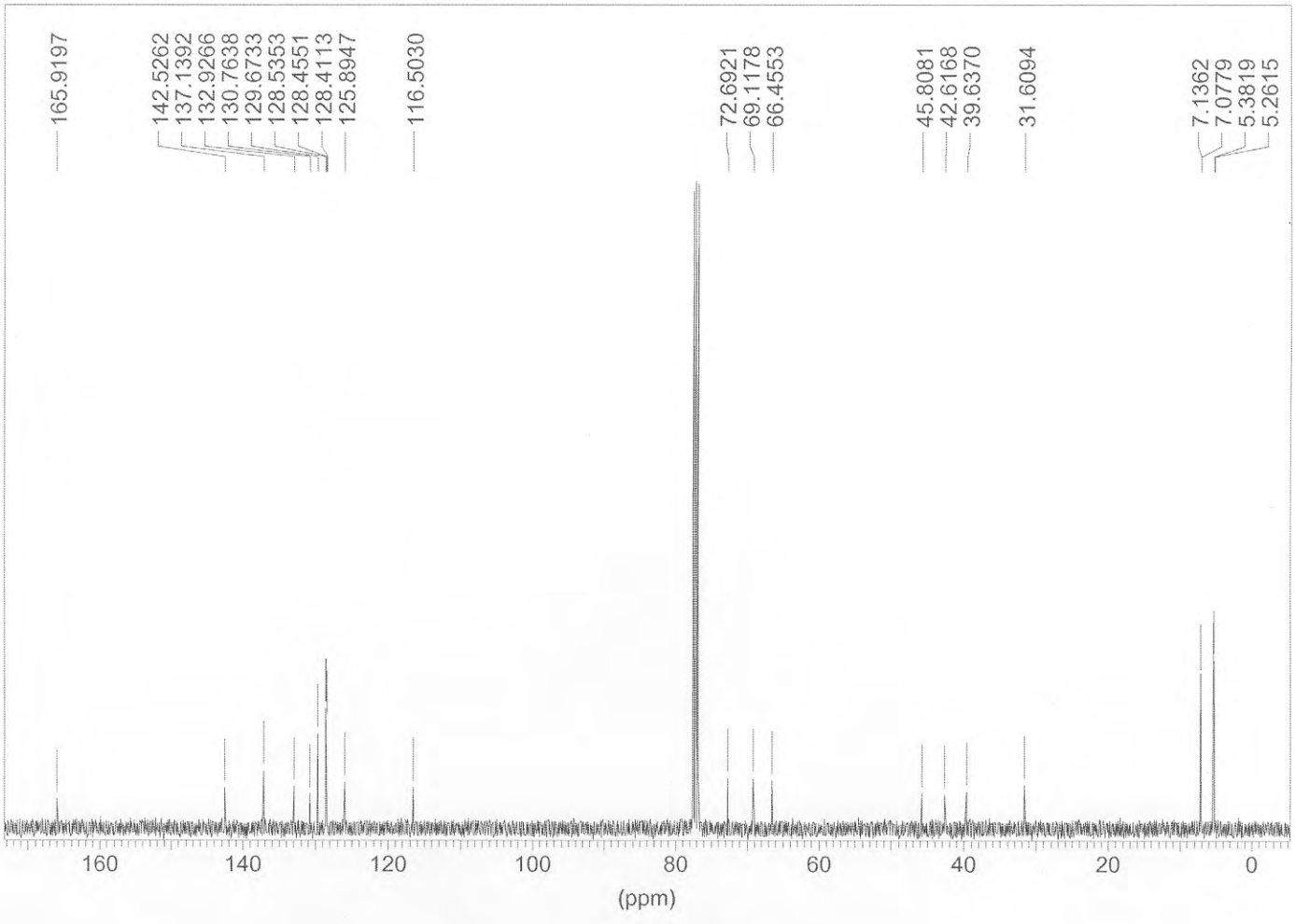

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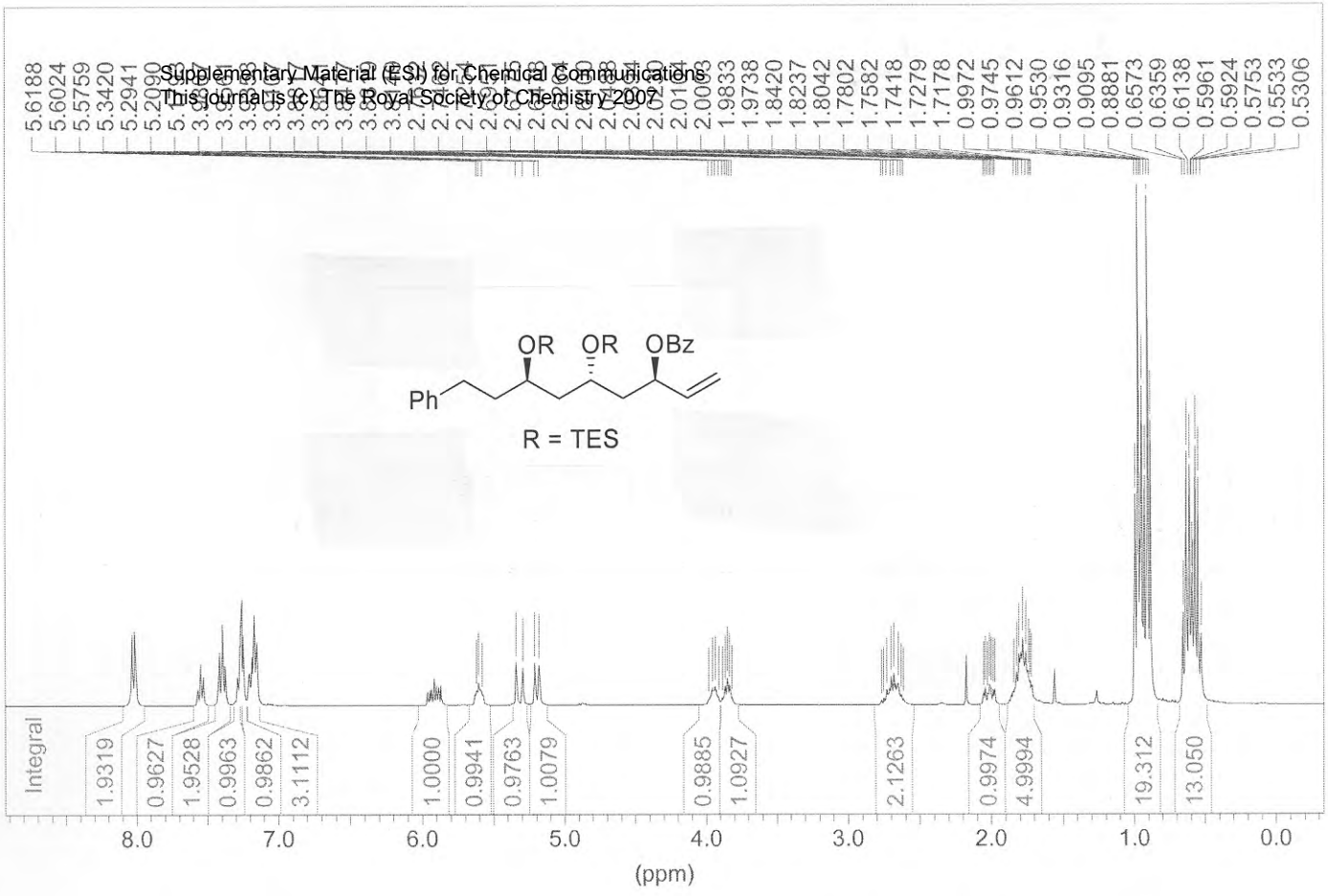

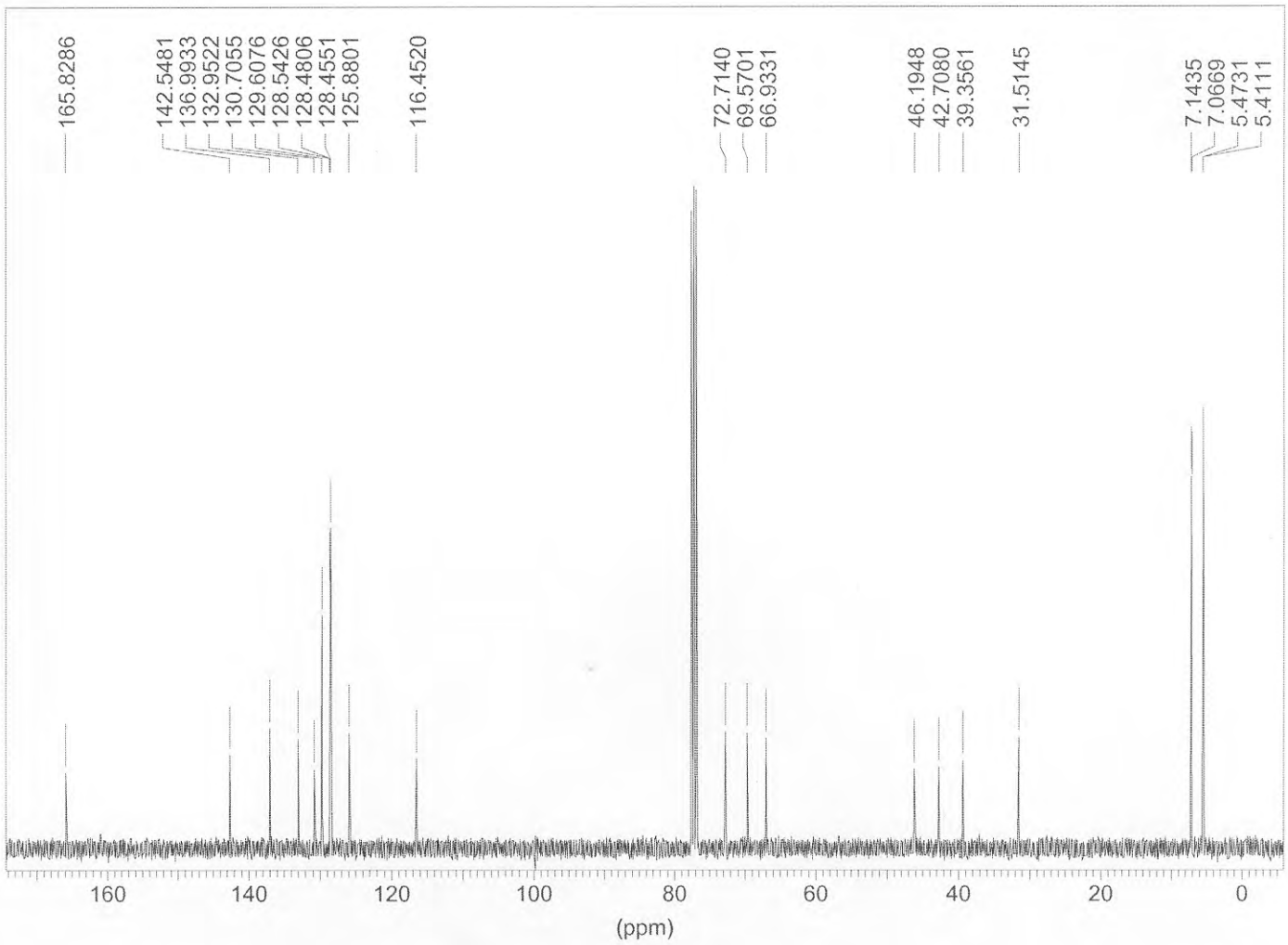

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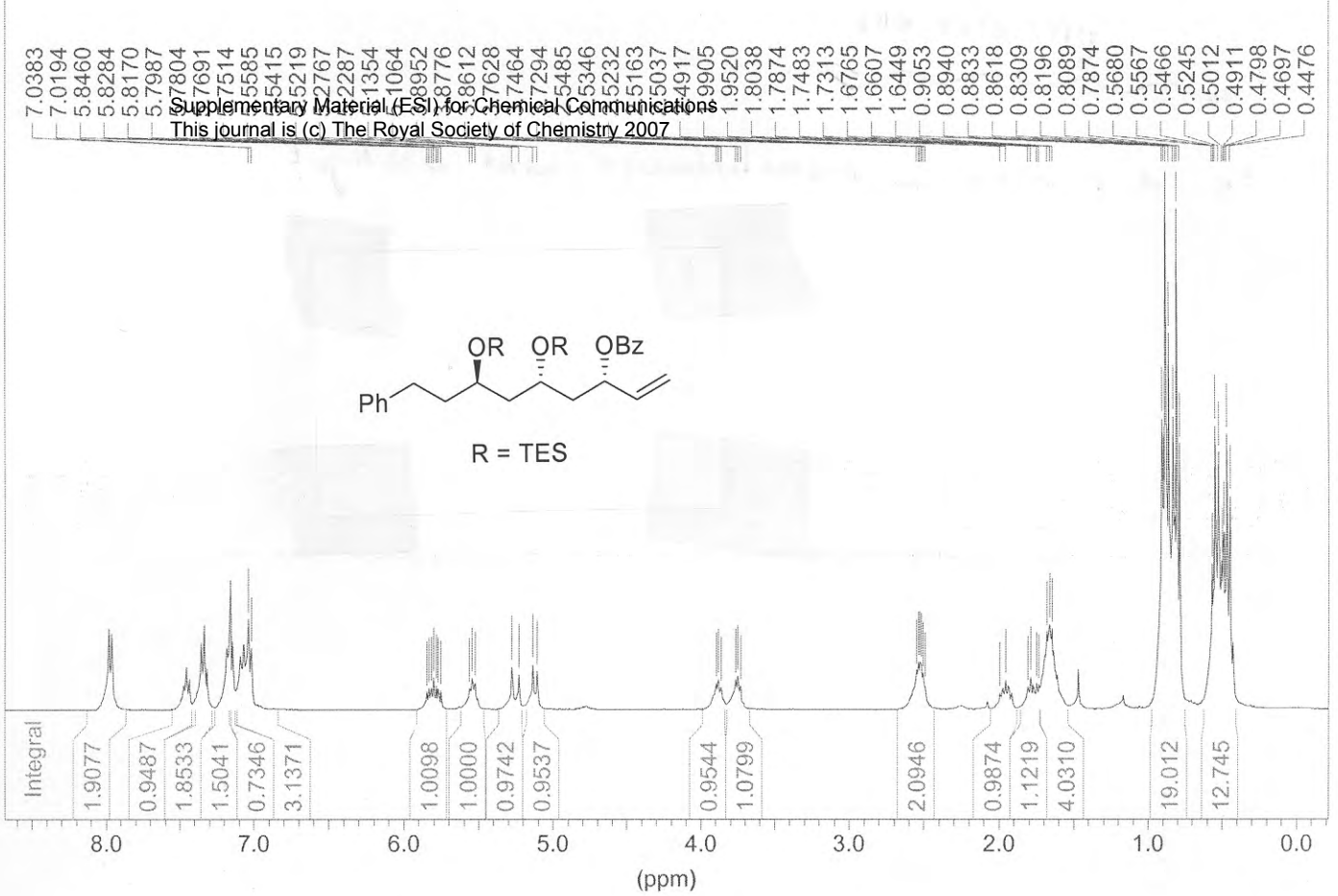

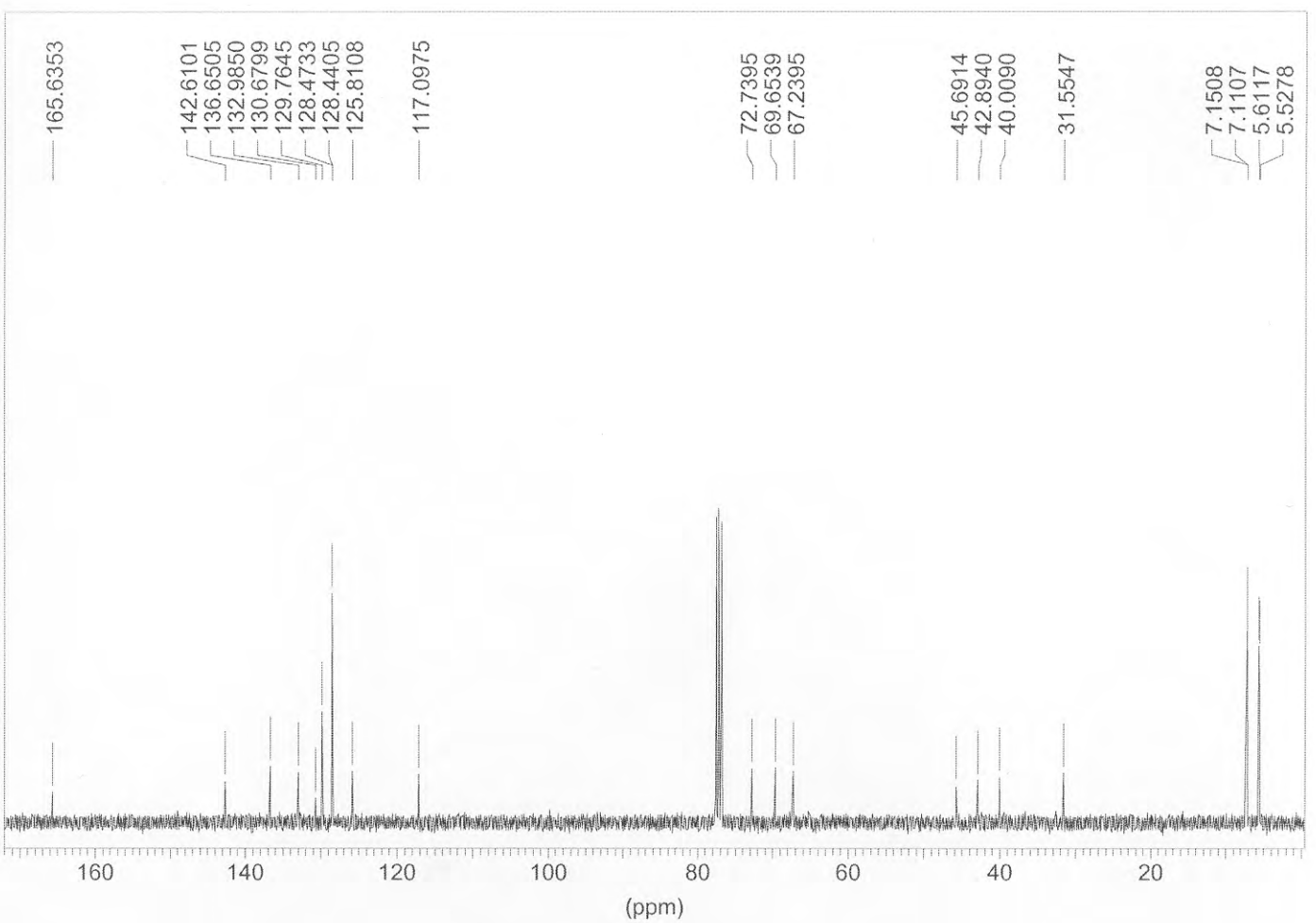

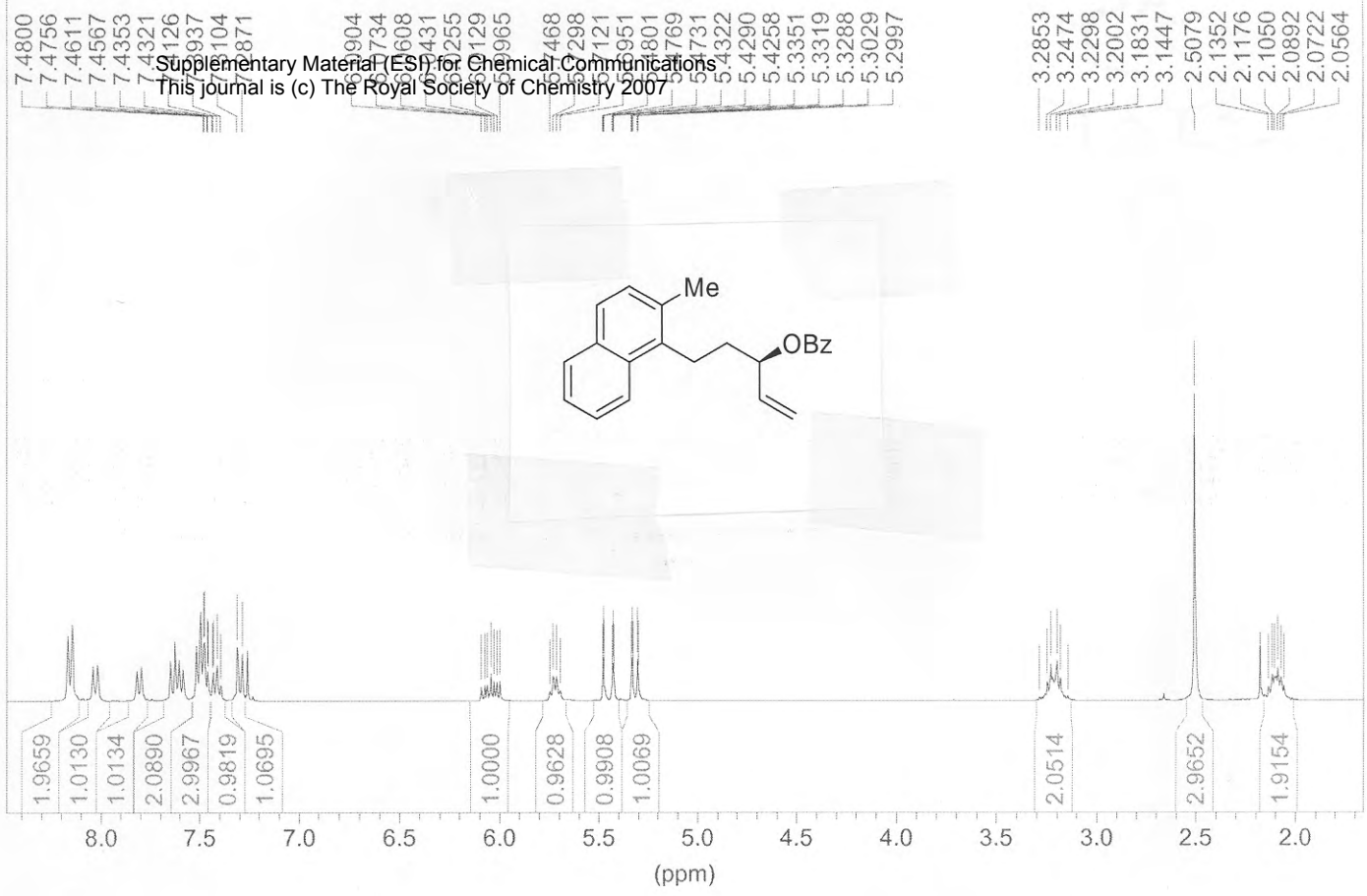
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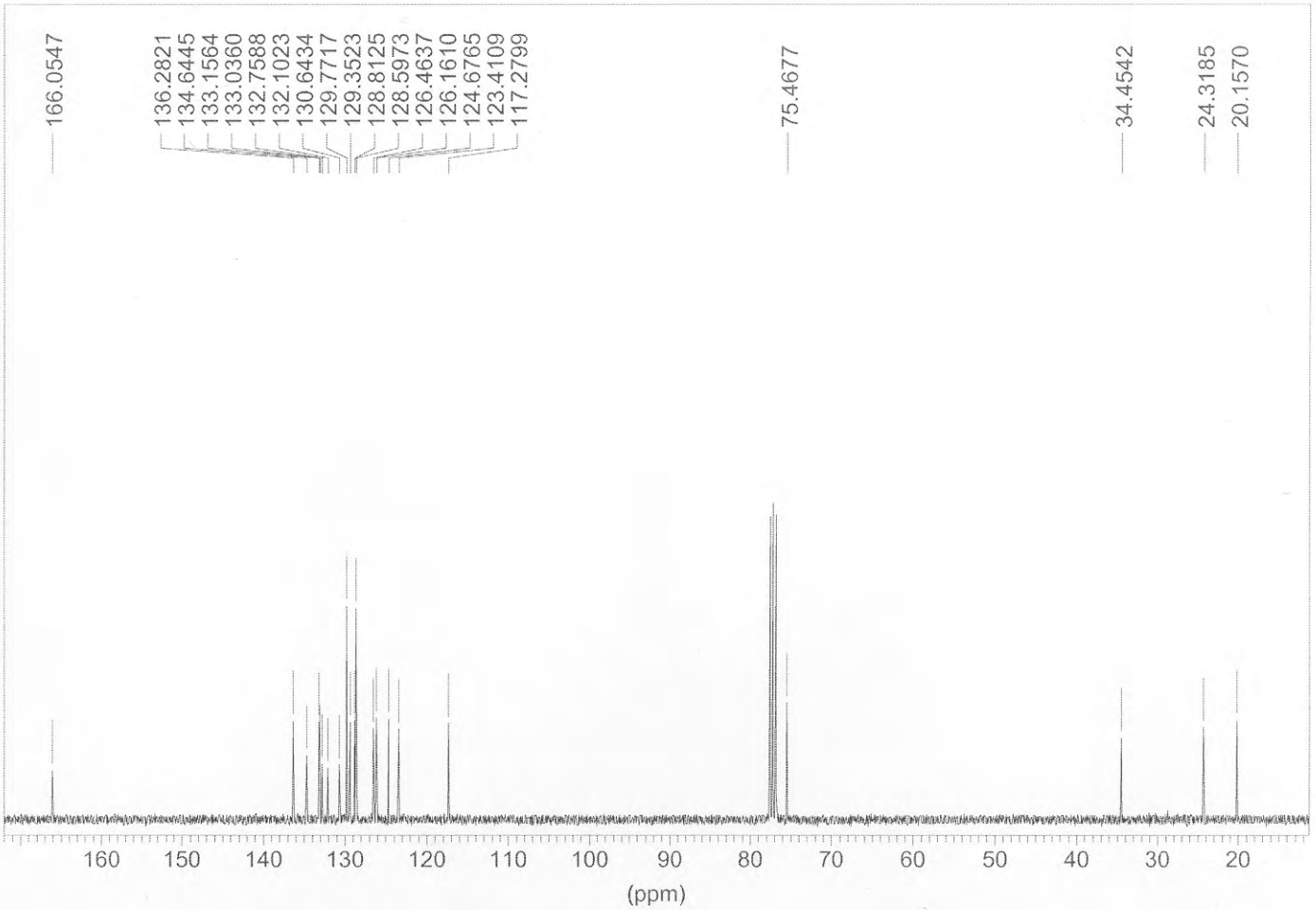
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140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

203 JB7-49-EE

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Daicel Chiralcel OD-H 250x4.6

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Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
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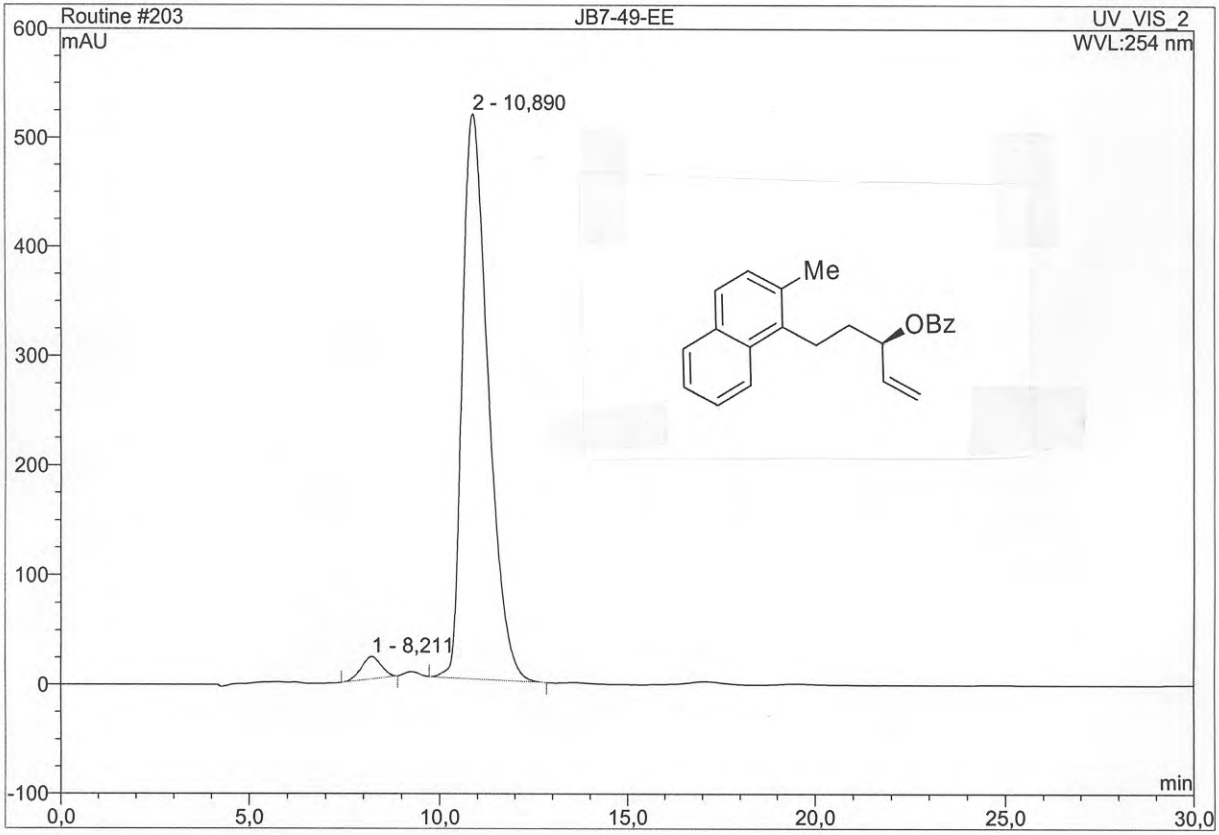
Run Time (min):	**30,00**	*Sample Amount:*	**1,0000**



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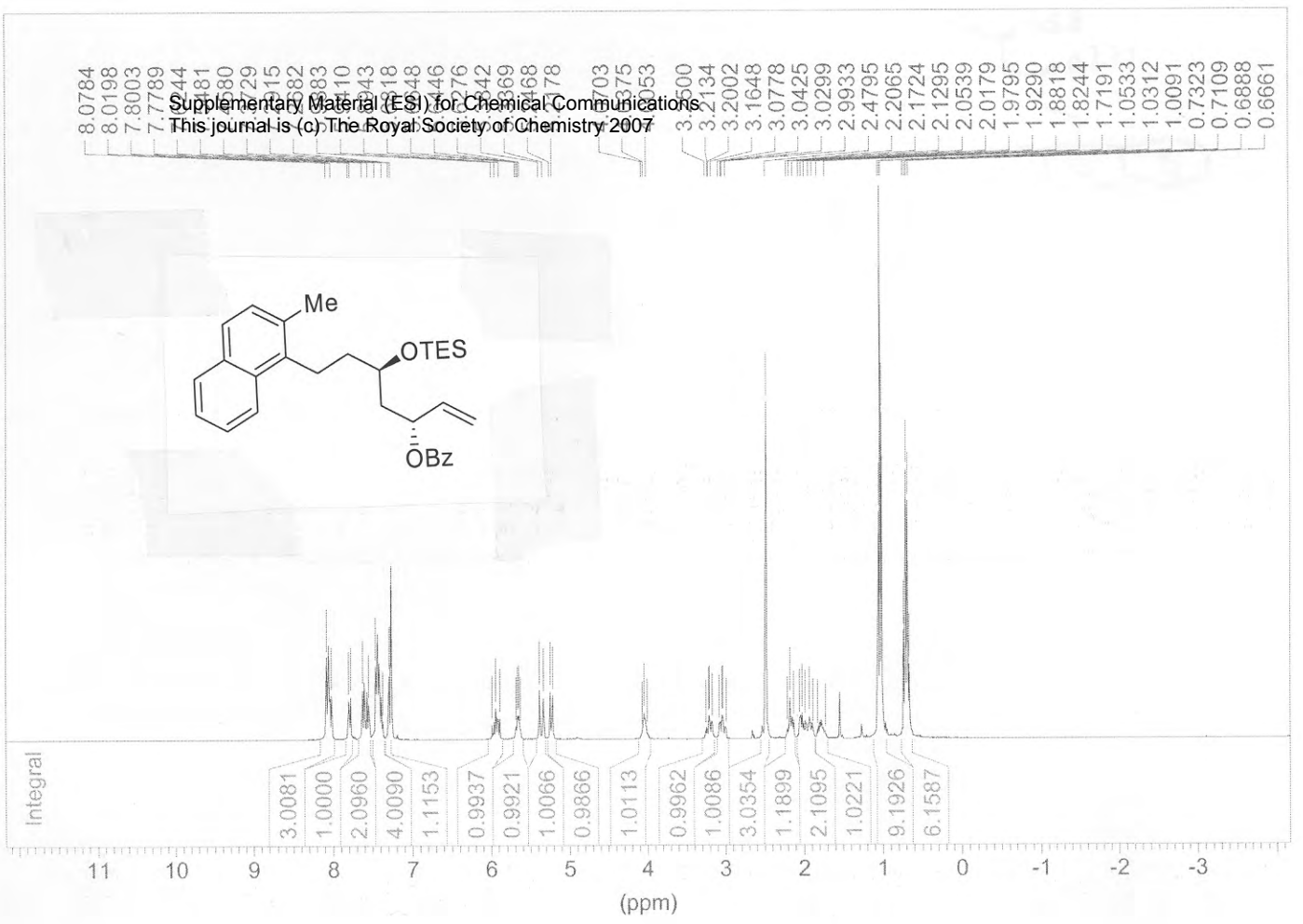
Total:			537,117	422,723	100,00	0,000	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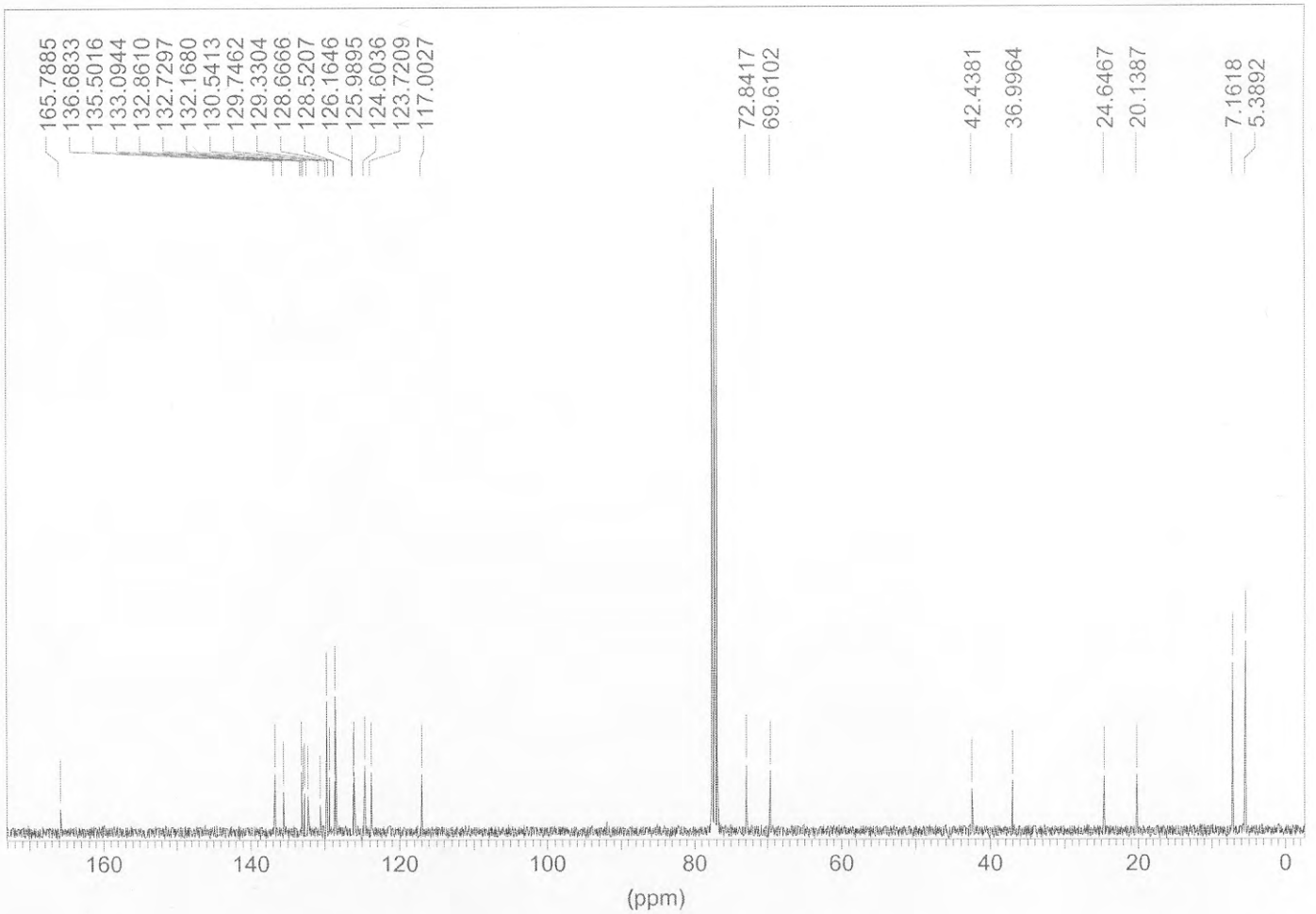
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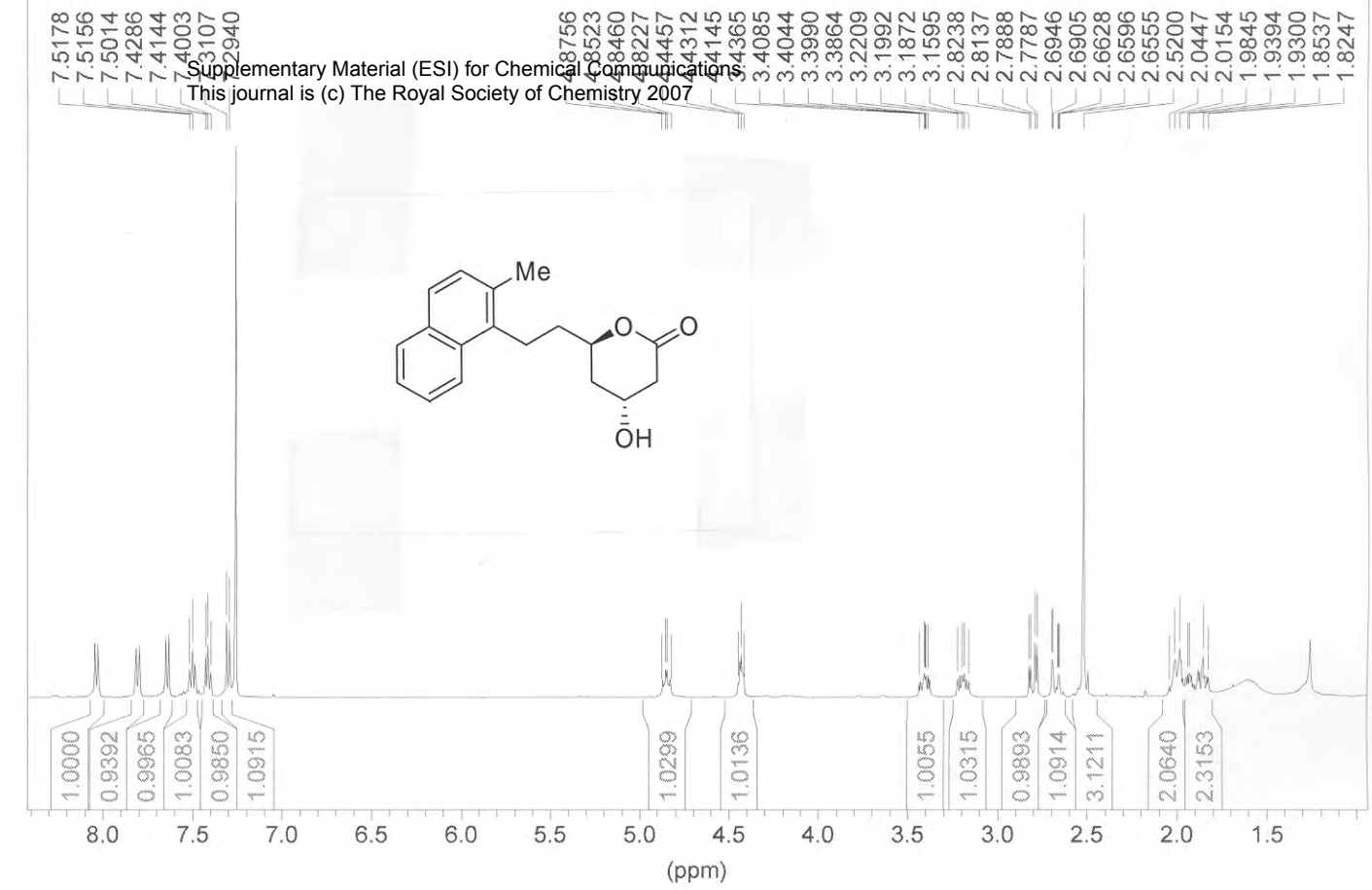
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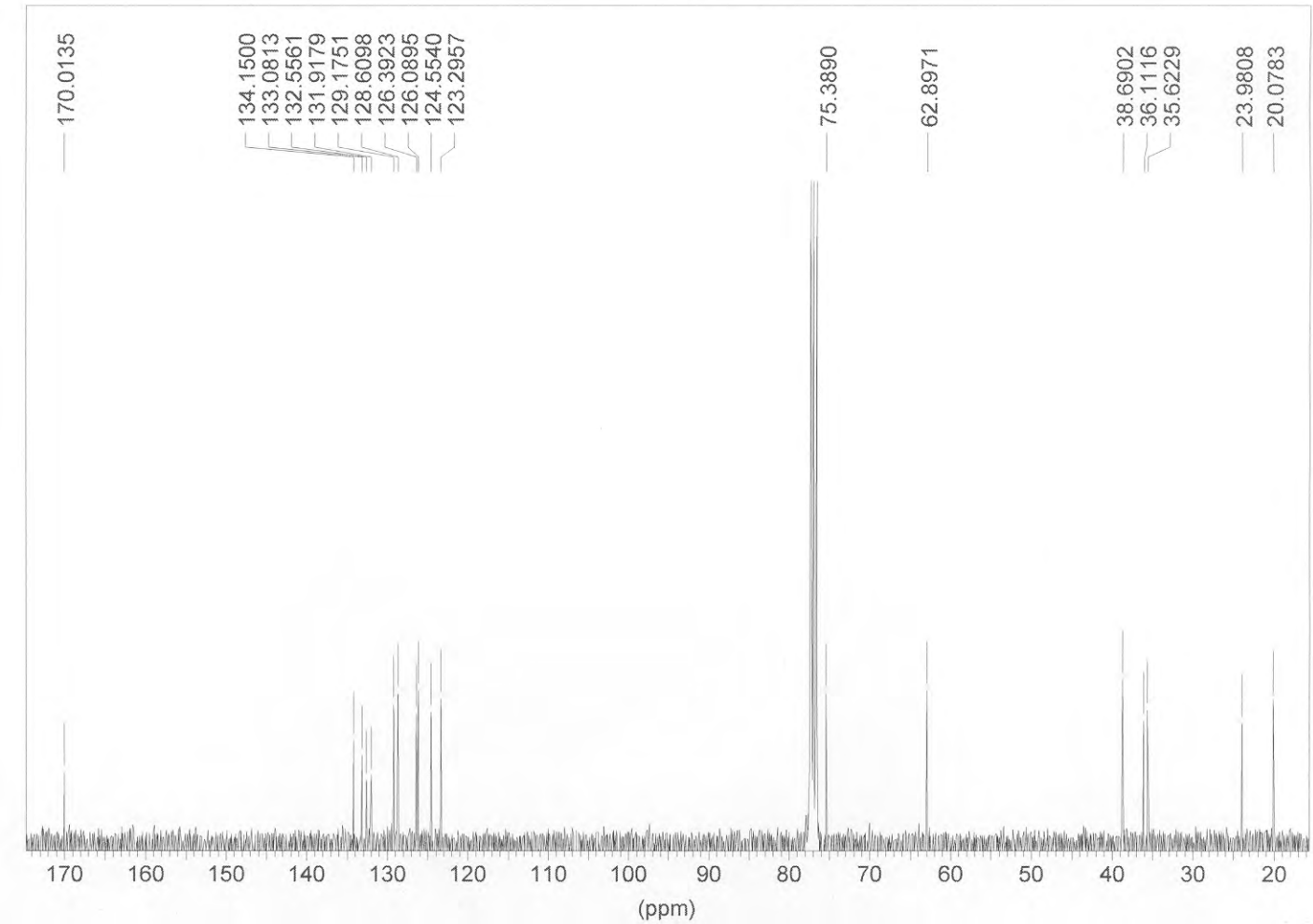
(ppm)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