Electronic Supplementary Material (ESI) for ChemComm.

Asymmetric Synthesis of Rauhut–Currier-type esters via Mukaiyama-Michael Reaction to Acylphosphonates under Bifunctional Catalysis

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1. General methods and starting materials

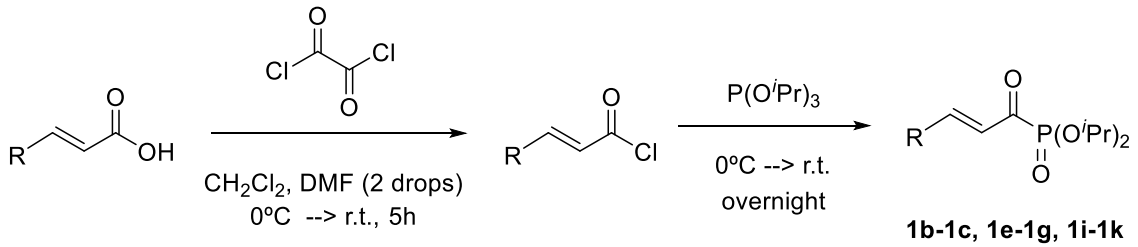
All solvents were dried using activated 4Å molecular sieves and stored under nitrogen. 4Å molecular sieves, 1.6-2.5 mm of particle size, were activated by microwave (700W) (3 x 60 sec) and subsequent cycles of vacuum/nitrogen. Catalyst **3a** and **3b** were acquired from commercial sources and catalysts **3c**, **3d**, **3e** and **3f** were synthesized following a procedure described in the literature.[1] For thin layer chromatography (TLC) silica gel plates with fluorescence indicator 254 nm were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of potassium permanganate in water followed by heating. Flash column chromatography was performed using Geduran® Silica Gel 60 (0.040-0.063 nm) or Iatrobeads 6RS-8060 silica gel and compressed air. Cyclohexane and ethyl acetate for flash chromatography were acquired from commercial sources and were used without previous purification. Optical rotation was recorded in cells with 10 cm path length; the specific solvents and concentrations (in g/100 mL) are indicated. NMR spectra were acquired on a *Bruker Avance 300 MHz spectrometer*, running at 300, 75, 282 and 122 MHz for ^{1}H, ^{13}C, ^{19}F and ^{31}P respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.2 ppm for ^{13}C NMR respectively). ^{13}C, ^{19}F and ^{31}P spectra were acquired on a broad band decoupled mode. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), bs (broad singlet). Electrospray ionization has been used for measuring the exact mass (indicated for each case): MS (ESI) (Electrospray ionization mass spectroscopy) was acquired with an *Agilent Technologies 6120 Quadrupole LC/MS*. In this technique, *MassWorks software ver. 4.0.0.0 (Cerno Bioscience*) was used for the formula identification. *MassWorks* is a MS calibration software which calibrates for isotope profile as well as for mass accuracy, allowing highly accurate comparisons between calibrated and theoretical spectra.[2]

Enantiomeric excesses were determined in a Supercritical Fluid Chromatography (SFC) with chiral columns. The chromatograms were acquired with an *Agilent Technologies 1260 Infinity* with a *SFC module* and a UV-vis detector. The chiral columns used were: Chiralpak IA, IB-3, IC, ID-3, IG-3 (see in each case).

[1] C. Cassani, R. Martín-Rapún, E. Arceo, F. Bravo and P. Melchiorre, *Nature Protocols* 2013, **8**, 325–344.
[2] a) Y. Wang and M. Gu, *Anal. Chem.* 2010, **82**, 7055-7062; b) Y. Wang, Methods for Operating MS Instrument Systems, United States Patent No. 6,983,213, **2006**; c) N. Ochiaia, K. Sasamoto, K. MacNamara *Journal of Chromatography A*, 2012, **1270**, 296-304; d) H.-P. Ho, R.-Y. Lee, C.-Y. Chen, S.-R. Wang, Z.-G. Li and M.-R. Lee, *Rapid Commun. Mass Spectrom.* 2011, **25**, 25-32.

2. Synthesis and characterization data of acylphosphonates 1.

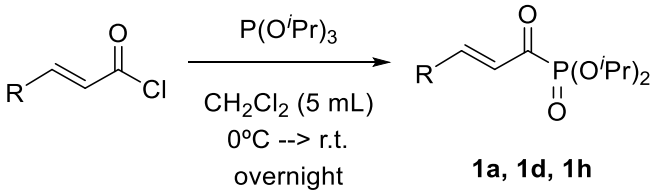
2.1. General procedure A: Synthesis of acylphosphonates 1.



1b-1c, 1e-1g, 1i-1k

It was prepared following a modified procedure described in the literature:[3] A round bottom flask previously oven-dried was charged with a magnetic stirrer and the corresponding α,β-unsaturated carboxylic acid (12 mmol, 1.2 equiv.) under nitrogen atmosphere. Then, CH_2Cl_2 (5 mL) was added and the reaction mixture was cooled to 0°C. Oxalylchloride (1.0 mL, 12 mmol, 1.2 equiv.) was added dropwise, followed by the addition of two drops of DMF, and the reaction mixture was stirred for 5 hours at room temperature. Then, the reaction mixture was cooled again to 0°C and triisopropylphosphite (2.5 mL, 10 mmol, 1.0 eq.) was added dropwise. Finally, the reaction mixture was stirred overnight at room temperature. The solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography using Iatrobeads silica gel and the eluent indicated in each case.

2.2. General procedure B: Synthesis of acylphosphonates 1.

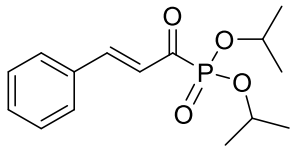


1a, 1d, 1h

A round bottom flask previously oven-dried was charged with a magnetic stirrer and the corresponding α,β-unsaturated acyl chloride (12 mmol, 1.2 eq.) under nitrogen atmosphere. Then, CH_2Cl_2 (5 mL) was added and the reaction mixture was cooled to 0°C. Triisopropylphosphite (2.5 mL, 10 mmol, 1.0 eq.) was added dropwise and the reaction mixture was stirred overnight at room temperature. The solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography using Iatrobeads silica gel and the eluent indicated in each case.

[3] C.F. Weise, V. H. Lauridsen, R. S. Rambo, E. H. Iversen, M.-L. Olsen and K. A. Jørgensen, *J. Org. Chem.* 2014, **79**, 3537−3546.

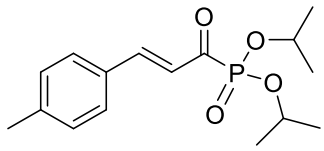
(*E*)-Diisopropyl cinnamoylphosphonate (1a)[3]



Following general procedure B, cinnamoyl chloride (2.00 g, 12 mmol, 1.2 eq.) and triisopropylphosphite, gave **1a** as a yellow oil (80% yield). Eluent: cyclohexane: ethyl acetate from 3:1 to 1:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 8.09 (d, *J* = 16.3 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.49 – 7.39 (m, 3H), 7.12 (dd, *J* = 16.3, 10.8 Hz, 1H), 4.89 – 4.74 (m, 2H), 1.39 (d, *J* = 6.2 Hz, 12H) ppm.

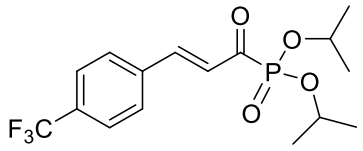
Diisopropyl (*E*)-(3-(p-tolyl)acryloyl)phosphonate (1b)[3]



Following general procedure A, (*E*)-3-(*p*-tolyl)acrylic acid (1.95 g, 12 mmol, 1.2 eq.), oxalylchloride and triisopropylphosphite, gave **1b** as a yellow oil (51% yield). Eluent: cyclohexane: ethyl acetate from 3:1 to 1:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 8.07 (d, *J* = 16.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.09 (dd, *J* = 16.1, 10.9 Hz, 1H), 4.90 – 4.73 (m, 2H), 2.40 (s, 3H), 1.39 (d, *J* = 6.2 Hz, 12H) ppm.

Diisopropyl (*E*)-(3-(4-(trifluoromethyl)phenyl)acryloyl)phosphonate (1c)



Following general procedure A, (*E*)-3-(4-(trifluoromethyl)phenyl)acrylic acid (2.59 g, 12 mmol, 1.2 eq.), oxalylchloride and triisopropylphosphite, gave **1c** as a yellow oil (23% yield). Eluent: cyclohexane: ethyl acetate from 9:1 to 1:1.

^{1}H-NMR: δ 8.07 (d, *J* = 16.3 Hz, 1H), 7.79 – 7.63 (m, 4H), 7.13 (dd, *J* = 16.3, 10.3 Hz, 1H), 4.89 – 4.73 (m, 2H), 1.38 (d, *J* = 6.2 Hz, 12H) ppm.

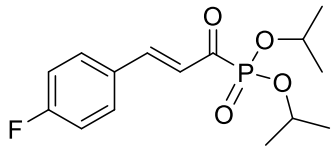
^{13}C-NMR: δ 199.6 (d, *J* = 179.8 Hz), 145.8, 137.6, 132.9 (q, *J* = 32.7 Hz), 129.1 (s, 2C), 127.0 (d, *J* = 65.6 Hz), 126.1 (q, *J* = 3.8 Hz, 2C), 123.8 (q, *J* = 272.0 Hz), 73.3 (d, *J* = 7.3 Hz, 2C), 24.2 (d, *J* = 3.8 Hz, 2C), 24.0 (d, *J* = 4.7 Hz, 2C) ppm.

^{31}P-NMR: δ -3.66 ppm.

^{19}F-NMR: δ -63.0 ppm.

HRMS (ESI^{+}): calculated for $C_{16}H_{21}O_4PF_3$ $[M+H]^+$: 365.1124; found: 365.1154.

Diisopropyl (*E*)-(3-(4-fluorophenyl)acryloyl)phosphonate (1d)



Following general procedure B, (*E*)-3-(4-fluorophenyl)acryloyl chloride (2.21 g, 12 mmol, 1.2 eq.) and triisopropylphosphite, gave **1d** as a yellow oil (34% yield). Eluent: cyclohexane: ethyl acetate from 9:1 to 1:1.

^{1}H-NMR: δ 8.04 (d, *J* = 16.3 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.15 – 7.06 (m, 2H), 7.03 (dd, *J* = 16.3, 10.9 Hz, 1H), 4.89 – 4.71 (m, 2H), 1.38 (d, *J* = 6.2 Hz, 12H) ppm.

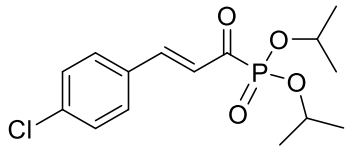
^{13}C-NMR: δ 199.3 (d, *J* = 178.2 Hz), 164.8 (d, *J* = 253.7 Hz), 146.7 (d, *J* = 2.3 Hz), 131.2 (d, *J* = 8.8 Hz, 2C), 130.6 (dd, *J* = 3.4, 1.8 Hz), 124.7 (dd, *J* = 66.0, 2.4 Hz), 116.5 (d, *J* = 22.2 Hz, 2C), 73.2 (d, *J* = 7.2 Hz, 2C), 24.2 (d, *J* = 3.9 Hz, 2C), 24.1 (d, *J* = 4.7 Hz, 2C) ppm.

^{31}P-NMR: δ -3.27 ppm.

^{19}F-NMR: δ -107.2 ppm.

HRMS (ESI^{+}): calculated for $C_{15}H_{21}O_4PF$ $[M+H]^+$: 315.1156; found: 315.1200.

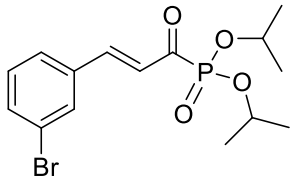
Diisopropyl (*E*)-(3-(4-chlorophenyl)acryloyl)phosphonate (1e)[3]



Following general procedure A, (*E*)-3-(4-chlorophenyl)acrylic acid (2.19 g, 12 mmol, 1.2 eq.), oxalylchloride and triisopropylphosphite, gave **1e** as a yellow oil (20% yield). Eluent: cyclohexane: ethyl acetate from 9:1 to 1:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 8.03 (d, *J* = 16.3 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.07 (dd, *J* = 16.3, 10.5 Hz, 1H), 4.88 – 4.72 (m, 2H), 1.39 (d, *J* = 6.2 Hz, 12H) ppm.

Diisopropyl (*E*)-(3-(3-bromophenyl)acryloyl)phosphonate (1f)



Following general procedure A, (*E*)-3-(3-bromophenyl)acrylic acid (2.72 g, 12 mmol, 1.2 eq.), oxalylchloride and triisopropylphosphite, gave **1f** as a yellow oil (34% yield). Eluent: cyclohexane: ethyl acetate from 3:1 to 1:1.

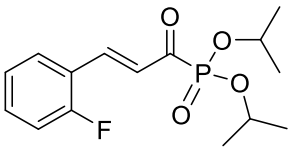
^{1}H-NMR: δ 7.99 (d, *J* = 16.3 Hz, 1H), 7.76 (s, 1H), 7.61 – 7.48 (m, 2H), 7.33 – 7.24 (m, 1H), 7.08 (dd, *J* = 16.2, 10.3 Hz, 1H), 4.89 – 4.73 (m, 2H), 1.39 (d, *J* = 6.2 Hz, 12H) ppm.

^{13}C-NMR: δ 199.3 (d, *J* = 179.1 Hz), 145.9 (d, *J* = 2.2 Hz), 136.2 (d, *J* = 1.8 Hz), 134.2, 131.5, 130.5, 127.5, 126.0 (d, *J* = 65.7 Hz), 123.2, 73.1 (d, *J* = 7.2 Hz), 24.1 (d, *J* = 3.9 Hz, 2C), 23.9 (d, *J* = 4.7 Hz, 2C).

^{31}P-NMR: δ -3.52 ppm.

HRMS (ESI$^+$): calculated for $C_{15}H_{20}O_4PBrNa$ $[M+Na]^+$: 397.0175; found: 397.0222.

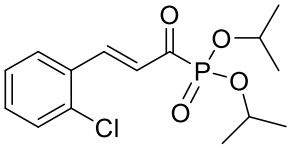
Diisopropyl (*E*)-(3-(2-fluorophenyl)acryloyl)phosphonate (1g)[3]



Following general procedure A, (*E*)-3-(2-fluorophenyl)acrylic acid (1.99 g, 12 mmol, 1.2 eq.), oxalylchloride and triisopropylphosphite, gave **1g** as a yellow oil (30% yield). Eluent: cyclohexane: ethyl acetate from 9:1 to 1:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 8.19 (d, *J* = 16.4 Hz, 1H), 7.62 (td, *J* = 7.5, 1.8 Hz, 1H), 7.47 – 7.35 (m, 1H), 7.25 – 7.06 (m, 3H), 4.90 – 4.74 (m, 2H), 1.39 (d, *J* = 6.2 Hz, 12H).

Diisopropyl (*E*)-(3-(2-chlorophenyl)acryloyl)phosphonate (1h)



Following general procedure B, (*E*)-3-(2-chlorophenyl)acryloyl chloride (2.41 g, 12 mmol, 1.2 eq.) and triisopropylphosphite, gave **1h** as a yellow oil (24% yield). Eluent: cyclohexane:acetate from 3:1 to 1:1.

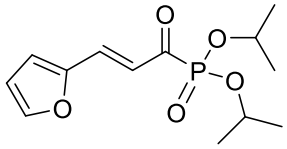
^{1}H-NMR: δ 8.52 (d, *J* = 16.3 Hz, 1H), 7.70 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.47 – 7.27 (m, 3H), 7.05 (dd, *J* = 16.3, 11.2 Hz, 1H), 4.91 – 4.77 (m, 2H), 1.40 (d, *J* = 6.2 Hz, 12H) ppm.

^{13}C-NMR: δ 199.6 (d, *J* = 179.5 Hz), 143.8 (d, *J* = 2.1 Hz), 136.4, 132.6 (d, *J* = 1.9 Hz), 132.3, 130.6, 127.9, 127.4, 127.1 (d, *J* = 66.0 Hz) 73.2 (d, *J* = 7.2 Hz, 2C), 24.3 (d, *J* = 3.8 Hz, 2C), 24.1 (d, *J* = 4.9 Hz, 2C) ppm.

^{31}P-NMR: δ – 3.16 ppm.

HRMS (ESI$^+$): calculated for $C_{15}H_{21}O_4PCl$ $[M+H]^+$: 331.0861; found: 331.0840.

Diisopropyl (E)-(3-(furan-2-yl)acryloyl)phosphonate (1i)



Following general procedure A, (*E*)-3-(furan-2-yl)acrylic acid (1.66 g, 12 mmol, 1.2 eq.), oxalylchloride and triisopropylphosphite, gave **1i** as an orange oil (43% yield). Eluent: cyclohexane: ethyl acetate from 9:1 to 1:1.

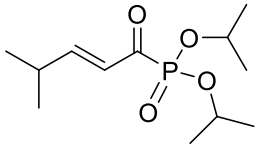
^{1}H-NMR: δ 7.87 (d, *J* = 15.9 Hz, 1H), 7.62 – 7.49 (m, 1H), 6.96 (dd, *J* = 15.9, 11.8 Hz, 1H), 6.83 (d, *J* = 3.5 Hz, 1H), 6.53 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.88 – 4.69 (m, 2H), 1.38 (d, *J* = 2.7 Hz, 6H), 1.36 (d, *J* = 2.7 Hz, 6H) ppm.

^{13}C-NMR: δ 198.9 (d, *J* = 178.0 Hz), 151.1 (d, *J* = 1.5 Hz), 146.4, 133.6 (d, *J* = 2.4 Hz), 122.7 (d, *J* = 66.9 Hz), 118.7, 113.3, 73.0 (d, *J* = 7.2 Hz, 2C), 24.2 (d, *J* = 3.9 Hz, 2C), 24.1 (d, *J* = 4.7 Hz, 2C) ppm.

^{31}P-NMR: δ – 3.24 ppm.

HRMS (ESI^{+}): calculated para $C_{13}H_{20}O_5P$ $[M+H]^+$: 287.1043; found: 287.1001.

Diisopropyl (*E*)-(4-methylpent-2-enoyl)phosphonate (1j)



Following general procedure A, (*E*)-4-methylpent-2-enoic acid (1.4 mL, 1.37 g, 12 mmol, 1.2 eq.), oxalylchloride and triisopropylphosphite, gave **1j** as a yellow oil (33% yield). Eluent: cyclohexane: ethyl acetate from 9:1 to 1:1.

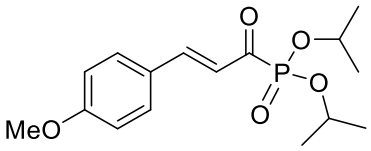
^{1}H-NMR: δ 7.39 (dd, *J* = 16.0, 6.6 Hz, 1H), 6.38 (ddd, *J* = 16.0, 12.9, 1.5 Hz, 1H), 4.82 – 4.67 (m, 2H), 2.64 – 2.44 (m, 1H), 1.34 (d, *J* = 6.1 Hz, 12H), 1.09 (d, *J* = 6.7 Hz, 6H) ppm.

^{13}C-NMR: δ 199.8 (d, *J* = 174.8 Hz), 160.5, 126.8 (d, *J* = 64.9 Hz), 72.9 (d, *J* = 7.3 Hz, 2C), 32.0, 24.2 (d, *J* = 3.7 Hz, 2C), 23.9 (d, *J* = 4.8 Hz, 2C), 21.0 (2C).

^{31}P-NMR: δ – 3.09 ppm.

HRMS (ESI^{+}): calculated for $C_{12}H_{24}O_4P$ $[M+H]^+$: 263.1407; found: 263.1429.

Diisopropyl (*E*)-(3-(4-methoxyphenyl)acryloyl)phosphonate (1k)



Following general procedure A, (*E*)-3-(4-methoxyphenyl)acrylic acid chloride (2.14 g, 12 mmol, 1.2 eq.), oxalylchloride and triisopropylphosphite, gave **1k** as a yellow oil (34% yield). Eluent: cyclohexane: ethyl acetate from 3:1 to 1:1.

^{1}H-NMR: δ 8.06 (d, *J* = 16.1 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.02 (dd, *J* = 16.1, 11.0 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.89 – 4.71 (m, 2H), 3.86 (s, 3H), 1.39 (d, *J* = 1.9 Hz, 6H), 1.37 (d, *J* = 1.8 Hz, 6H) ppm.

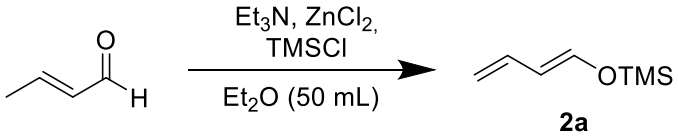
^{13}C-NMR: δ 198.9 (d, *J* = 176.3 Hz), 162.8, 148.0 (d, *J* = 2.7 Hz), 131.2 (2C), 127.1 (d, *J* = 1.8 Hz), 122.9 (d, *J* = 66.3 Hz), 114.8 (2C), 72.9 (d, *J* = 7.2 Hz, 2C), 55.7, 24.3 (d, *J* = 3.8 Hz, 2C), 24.1 (d, *J* = 4.7 Hz, 2C) ppm.

^{31}P-NMR: δ -2.74 ppm.

HRMS (ESI^{+}): calculated for $C_{16}H_{24}O_5P$ $[M+H]^+$: 327.1356; found: 327.1346.

3. Synthesis and characterization data of silyl dienol ethers 2.

(*E*)-(Buta-1,3-dien-1-yloxy)trimethylsilane (2a)[4]

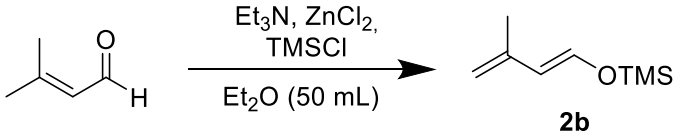


2a

It was prepared following a modified procedure described in the literature: To a two-neck round bottom flask charged with a condenser previously oven-dried was added a magnetic stirrer and anhydrous powder zinc chloride (204 mg, 1.5 mmol, 0.03 eq.) under nitrogen atmosphere. Then, Et_3N (10.1 mL, 73 mmol, 1.5 eq.) was added and the mixture was stirred at room temperature for 1h. A solution of crotonaldehyde (4.1 mL, 50 mmol, 1.0 eq.) in anhydrous diethylether (50 mL) was added under nitrogen atmosphere. Then, TMSCl (12.7 mL, 100 mmol, 2.0 eq.) was added dropwise and the reaction mixture was refluxed for 48h. The solvent was evaporated under reduced pressure and pentane was added. The mixture was filtered through Iatrobeads silica gel and the filtrate was concentrated under reduced pressure. Purification by Kugelrohr distillation (b.p. 40-45°C, 25 mmHg) gave **2a** as colorless liquid (82% yield). The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 6.54 (d, *J* = 11.9 Hz, 1H), 6.22 (dt, *J* = 16.9, 10.6 Hz, 1H), 5.72 (t, *J* = 11.4 Hz, 1H), 5.03 – 4.95 (m, 2H), 4.86 – 4.80 (m, 1H), 0.21 (s, 9H) ppm.

(*E*)-Trimethyl((3-methylbuta-1,3-dien-1-yl)oxy)silane (2b)



2b

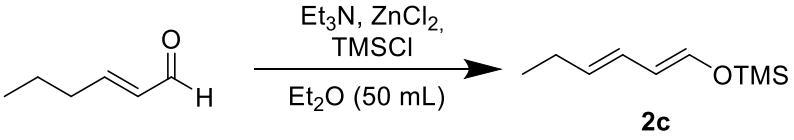
It was prepared following a modified procedure described in the literature: To a two-neck round bottom flask charged with a condenser previously oven-dried was added a magnetic stirrer and anhydrous powder zinc chloride (204 mg, 1.5 mmol, 0.03 eq.) under nitrogen atmosphere. Then, Et_3N (10.1 mL, 73 mmol, 1.5 eq.) was added and the mixture was stirred at room temperature for 1h. A solution of 3-methylbut-2-enal (4.8 mL, 50 mmol, 1.0 eq.) in anhydrous diethylether (50 mL) was added under nitrogen atmosphere. Then, TMSCl (12.7 mL, 100 mmol, 2.0 eq.) was added dropwise and the reaction mixture was refluxed for 72h. The solvent was evaporated under reduced pressure and pentane was added. The mixture was filtered through Iatrobeads silica gel and the filtrate was concentrated under reduced pressure.

[4] V. Laina-Martín, J. Humbrías-Martín, J. A. Fernández-Salas and J. Alemán, *Chem. Commun.* 2018, **54**, 2781-2784.

Purification by Kugelrohr distillation (b.p. 75-80°C, 25 mmHg) gave **2b** as colorless liquid (71% yield). The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 6.50 (d, *J* = 12.2 Hz, 1H), 5.82 (d, *J* = 12.2 Hz, 1H), 4.80 – 4.65 (m, 2H), 1.82 – 1.79 (m, 3H), 0.21 (s, 9H) ppm.

[(Hexa-1,3-dien-1-yl)oxy]trimethylsilane (2c)



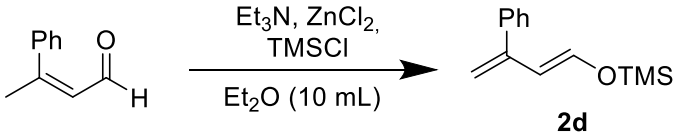
2c

It was prepared following a modified procedure described in the literature: To a two-neck round bottom flask charged with a condenser previously oven-dried was added a magnetic stirrer and anhydrous powder zinc chloride (204 mg, 1.5 mmol, 0.03 eq.) under nitrogen atmosphere. Then, Et_3N (10.1 mL, 73 mmol, 1.5 eq.) was added and the mixture was stirred at room temperature for 1h. A solution of (*E*)-hex-2-enal (5.8 mL, 50 mmol, 1.0 eq.) in anhydrous diethylether (50 mL) was added under nitrogen atmosphere. Then, TMSCl (12.7 mL, 100 mmol, 2.0 eq.) was added dropwise and the reaction mixture was refluxed for 72h. The solvent was evaporated under reduced pressure and pentane was added. The mixture was filtered through Iatrobeads silica gel and the filtrate was concentrated under reduced pressure. Purification by Kugelrohr distillation (b.p. 90-100°C, 25 mmHg) gave **2c** as colorless liquid (69% yield, 60:40 mixture of isomers).

^{1}H-NMR: δ 6.51 (d, *J* = 11.4 Hz, 1H, *major*), 6.45 (d, *J* = 11.9 Hz, 1H, *minor*), 6.00 – 5.62 (m, 4H), 5.57 – 5.44 (m, 1H, *minor*), 5.21 (dt, *J* = 10.4, 7.5 Hz, 1H, *major*), 2.21 – 1.99 (m, 4H), 0.98 (td, *J* = 7.5, 3.1 Hz, 6H), 0.21 (s, 9H, *major*), 0.20 (s, 9H, *minor*) ppm.

^{13}C-NMR: δ 144.0 (*major*), 142.3 (*minor*), 131.5 (*minor*), 129.5 (*major*), 125.0 (*minor*), 123.7 (*major*), 114.1 (*minor*), 109.8 (*major*), 26.0 (*minor*), 21.2 (*major*), 14.5 (*major*), 14.0 (*minor*), -0.3 (6C) ppm.

Trimethyl((3-phenylbuta-1,3-dien-1-yl)oxy)silane (2d)

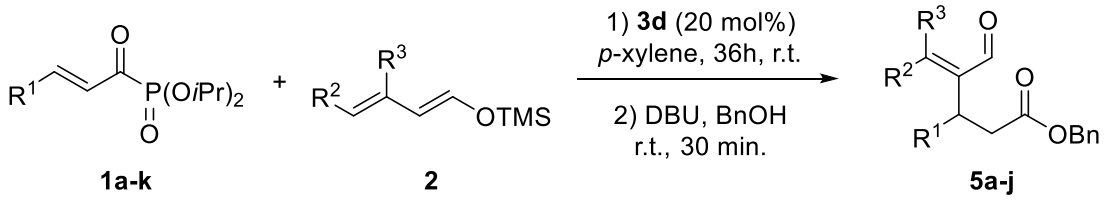


2d

It was prepared following a modified procedure described in the literature: To a two-neck round bottom flask charged with a condenser previously oven-dried was added a magnetic stirrer and anhydrous powder zinc chloride (20 mg, 0.14 mmol, 0.03 eq.) under nitrogen atmosphere. Then, Et_3N (1.0 mL, 7.2 mmol, 1.5 eq.) was added and the mixture was stirred at room temperature for 1h. A solution of 3-phenylbut-2-enal (700 mg, 4.8 mmol, 1.0 eq.) in anhydrous diethylether (10 mL) was added under nitrogen atmosphere. Then, TMSCl (1.2 mL, 9.6 mmol, 2.0 eq.) was added dropwise and the reaction mixture was refluxed for 72h. The solvent was evaporated under reduced pressure and pentane was added. The mixture was filtered through Iatrobeads silica gel and the filtrate was concentrated under reduced pressure to give **2d** as a colorless liquid (65% yield, 55:45 *Z:E*).

^{1}H-NMR: δ 7.42 – 7.23 (m, 10H), 6.45 (d, *J* = 12.0 Hz, 1H, *E*), 6.43 – 6.41 (d, *J* = 6.5 Hz, 1H, *Z*), 5.95 (d, *J* = 12.0, 1H, *E*), 5.75 (d, *J* = 2.0 Hz, 1H, *Z*), 5.40 (dt, *J* = 2.0, 0.8 Hz, 1H, *Z*), 5.17 (dt, *J* = 6.5, 0.8 Hz, 1H, *Z*), 5.07 (d, *J* = 1.9 Hz, 1H, *E*), 4.91 (d, *J* = 1.9 Hz, 1H, *E*), 0.19 (s, 9H, *E*), 0.18 (s, 9H, *Z*) ppm.

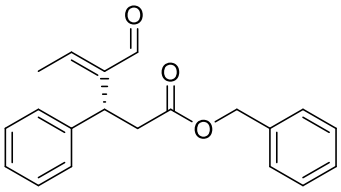
4. General procedure C: Asymmetric Synthesis of Rauhut–Currier type esters 5 and lactones 4.



1a-k **2** **5a-j**

Catalyst **3d** (12.6 mg, 0.02 mmol, 0.2 equiv.) and the corresponding acylphosphonate **1** (0.1 mmol, 1.0 eq.) were dissolved in anhydrous *p*-xylene (0.6 mL) in an oven-dried vial. Then, the silyl dienol ether **2** (0.4 mmol, 4.0 equiv.) was added. The reaction was stirred for 36h. Benzyl alcohol (50 µl, 0.5 mmol, 5.0 equiv.) and DBU (23 µl, 0.11 mmol, 1.1 equiv.) were sequentially added. After 30 min, the mixture was concentrated *in vacuo.* Finally, the crude mixture was purified by flash column chromatography using silica gel and eluting with the solvent indicated in each case.

Benzyl (*R*,*E*)-4-formyl-3-phenylhex-4-enoate (5a)



Following general procedure C, diisopropyl cinnamoylphosphonate **1a** (29.6 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5a** as a mixture of *E*:*Z* isomers 94:6 (57% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. **$[\alpha]^{20}_D$** = +22.5 (*c* 0.45, $CHCl_3$).

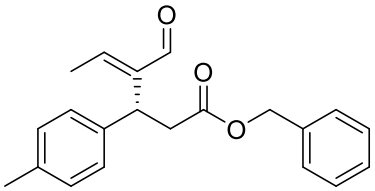
^{1}H-NMR: δ 9.29 (d, *J* = 1.3 Hz, 1H), 7.37 – 7.15 (m, 10H), 6.58 (q, *J* = 7.1 Hz, 1H), 5.06 (s, 2H), 4.49 – 4.41 (m, 1H), 3.32 (dd, *J* = 16.0, 9.1 Hz, 1H), 3.14 (dd, *J* = 16.0, 6.6 Hz, 1H), 2.02 (d, *J* = 7.1 Hz, 3H) ppm.

^{13}C-NMR: δ 194.9, 172.3, 152.8, 144.9, 141.5, 136.1, 128.7 (2C), 128.6 (2C), 128.4 (2C), 128.4, 127.8 (2C), 126.8, 66.4, 38.5, 36.8, 15.3 ppm.

HRMS (ESI$^+$): calculated for $C_{20}H_{21}O_3$ $[M+H]^+$: 309.1485; found: 309.1520.

The enantiomeric excess was determined by SFC using a Chiralpak IG-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 5.87 min, τ_{minor} = 6.94 min (97% *ee*).

Benzyl (*R*,*E*)-4-formyl-3-(*p*-tolyl)hex-4-enoate (5b)



Following general procedure C, diisopropyl (*E*)-(3-(*p*-tolyl)acryloyl)phosphonate **1b** (31.0 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5b** as a mixture of *E*:*Z* isomers 93:7 (47% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. $[\alpha]^{20}_{D}$ = +47.2 (*c* 0.90, $CHCl_3$).

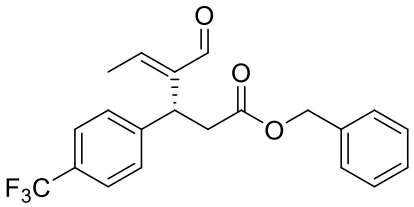
^{1}H-NMR: δ 9.29 (d, *J* = 1.5 Hz, 1H), 7.37 – 7.21 (m, 5H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.63 – 6.48 (m, 1H), 5.06 (s, 2H), 4.51 – 4.30 (m, 1H), 3.30 (dd, *J* = 16.0, 9.1 Hz, 1H), 3.13 (dd, *J* = 16.0, 9.1 Hz, 1H), 2.29 (s, 3H), 2.03 (d, *J* = 7.1 Hz, 3H) ppm.

^{13}C-NMR: δ 194.9, 172.4, 152.7, 145.0, 138.5, 136.4, 136.1, 129.3 (2C), 128.6 (2C), 128.4 (2C), 128.3, 127.7 (2C), 66.4, 38.1, 36.9, 21.1, 15.3 ppm.

HRMS (ESI$^+$): calculated for $C_{21}H_{26}O_3N$ $[M+NH_4]^+$: 340.1907; found: 340.1889.

The enantiomeric excess was determined by SFC using a Chiralpak IA column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 3.0 mL/min], τ_{major} = 3.46 min, τ_{minor} = 3.75 min (96% *ee*).

Benzyl (R,*E*)-4-formyl-3-(4-(trifluoromethyl)phenyl)hex-4-enoate (5c)



Following general procedure C, diisopropyl (*E*)-(3-(4-(trifluoromethyl)phenyl)acryloyl)phosphonate **1c** (36.4 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5c** (42% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. $[\alpha]^{20}_{D}$ = +44.9 (*c* 0.93, $CHCl_3$).

^{1}H-NMR: δ 9.29 (d, *J* = 1.4 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.35–7.26 (m, 5H), 6.65 (q, *J* = 7.1 Hz, 1H), 5.07 (s, 2H), 4.50 (t, *J* = 7.8 Hz, 1H), 3.27 (dd, *J* = 14.1, 6.2 Hz, 1H), 3.20 (dd, *J* = 14.1, 5.3 Hz, 1H), 2.07 (d, *J* = 7.1 Hz, 3H) ppm.

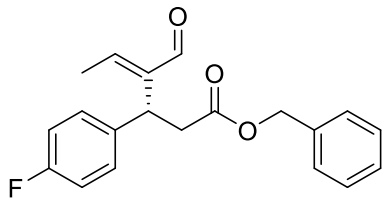
^{13}C-NMR: δ 194.5, 171.9, 153.2, 145.3, 144.2, 135.8, 129.1 (q, *J* =32.3 Hz), 128.7 (2C), 128.5 (3C), 128.2 (2C), 125.5 (q, *J* = 3.8 Hz, 2C), 124.1 (q, 272.8 Hz), 66.6, 38.3, 36.4, 15.4 ppm.

^{19}F-NMR: δ -62.5 ppm.

HRMS (ESI$^+$): calculated for $C_{21}H_{20}O_3F_3$ $[M+H]^+$: 377.1359; found: 377.1368.

The enantiomeric excess was determined by SFC using a Chiralpak ID-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 1.25 min, τ_{minor} = 1.44 min (96% *ee*).

Benzyl (*R*,*E*)-3-(4-fluorophenyl)-4-formylhex-4-enoate (5d)



Following general procedure C, diisopropyl (*E*)-(3-(4-fluorophenyl)acryloyl)phosphonate **1d** (31.4 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5d** (49% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 98:2 to 90:10. $[\alpha]^{20}_D$ = +37.7 (*c* 1.10, $CHCl_3$).

^{1}H-NMR: δ 9.28 (d, *J* = 1.6 Hz, 1H), 7.39 – 7.17 (m, 7H), 6.93 (t, *J* = 8.7 Hz, 1H), 6.60 (q, *J* = 7.1 Hz, 1H), 5.07 (s, 2H), 4.42 (t, *J* = 7.9 Hz, 1H), 3.26 (dd, *J* = 16.0, 8.7 Hz, 1H), 3.15 (dd, *J* = 16.0, 7.1 Hz, 1H), 2.04 (d, *J* = 7.1 Hz, 2H) ppm.

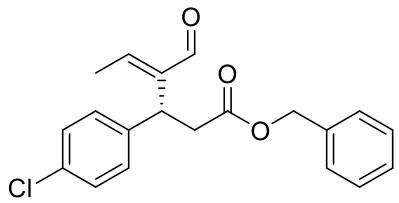
^{13}C-NMR: δ 194.8, 172.2, 161.7 (d, *J* = 245.0 Hz), 152.8, 144.7, 137.1 (d, *J* = 3.3 Hz), 136.0, 129.4 (d, *J* = 8.0 Hz, 2C), 128.7 (2C), 128.4 (2C), 128.4, 115.4 (d, *J* = 21.2 Hz, 2C), 66.5, 37.9, 36.9, 15.3 ppm.

^{19}F-NMR: δ -116.4 ppm.

HRMS (ESI$^+$): calculated for $C_{20}H_{20}O_3F$ $[M+H]^+$: 327.1391; found: 327.1350.

The enantiomeric excess was determined by SFC using a Chiralpak ID-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 1.66 min, τ_{minor} = 1.85 min (97% *ee*).

Benzyl (*R*,*E*)-3-(4-chlorophenyl)-4-formylhex-4-enoate (5e)



Following general procedure C, diisopropyl (*E*)-(3-(4-chlorophenyl)acryloyl)phosphonate **1e** (33.1 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5e** as a mixture of *E*:*Z* isomers 97:3 (46% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. $[\alpha]^{20}_D$ = +58.0 (*c* 1.03, $CHCl_3$).

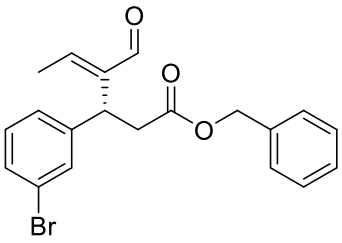
^{1}H-NMR: δ 9.28 (d, *J* = 1.5 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.29 – 7.23 (m, 2H), 7.21 (bs, 4H), 6.60 (q, *J* = 7.1 Hz, 1H), 5.06 (s, 2H), 4.45 – 4.37 (m, 1H), 3.24 (dd, *J* = 16.0, 8.5 Hz, 1H), 3.15 (dd, *J* = 16.0, 7.2 Hz, 1H), 2.04 (d, *J* = 7.1 Hz, 3H) ppm.

^{13}C-NMR: δ 194.7, 172.1, 153.0, 144.5, 139.9, 136.0, 132.6, 129.2 (2C), 128.7 (2C), 128.7 (2C), 128.5 (2C), 128.4, 66.5, 38.0, 36.7, 15.3 ppm.

HRMS (ESI^{+}): calculated for $C_{20}H_{20}O_3Cl$ $[M+H]^+$: 343.1095; found: 343.1112.

The enantiomeric excess was determined by SFC using a Chiralpak ID-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 2.09 min, τ_{minor} = 2.55 min (95% *ee*).

Benzyl (*R*,*E*)-3-(3-bromophenyl)-4-formylhex-4-enoate (5f)



Following general procedure C, diisopropyl (*E*)-(3-(3-bromophenyl)acryloyl)phosphonate **1f** (37.5 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5f** as a mixture of *E*:*Z* isomers 94:6 (43% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. **$[\alpha]^{20}_{D}$** = +40.7 (*c* 0.76, $CHCl_3$).

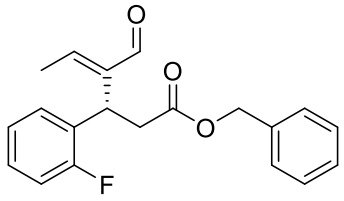
^{1}H-NMR: 9.29 (d, *J* = 1.5 Hz, 1H), 7.44 – 7.06 (m, 9H), 6.62 (q, *J* = 7.2 Hz, 1H), 5.07 (s, 2H), 4.42 (t, *J* = 7.9 Hz, 1H), 3.26 (dd, *J* = 16.1, 8.8 Hz, 1H), 3.14 (dd, *J* = 16.1, 6.9 Hz, 1H), 2.04 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C-NMR: δ 194.6, 172.0, 153.2, 144.3, 143.7, 136.0, 131.0, 130.2, 130.0, 128.7 (2C), 128.4 (3C), 126.4, 122.7, 66.6, 38.1, 36.6, 15.4 ppm.

HRMS (ESI^{+}): calculated for $C_{20}H_{20}O_3Br$ $[M+H]^+$: 387.0590; found: 387.0610.

The enantiomeric excess was determined by SFC using a Chiralpak ID-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 2.11 min, τ_{minor} = 2.32 min (96% *ee*).

Benzyl (*S*,*E*)-3-(2-fluorophenyl)-4-formylhex-4-enoate (5g)



Following general procedure C, diisopropyl (*E*)-(3-(2-fluorophenyl)acryloyl)phosphonate **1g** (31.4 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5g** (41% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. $[\alpha]^{20}_{D}$ = +74.0 (*c* 0.70, $CHCl_3$).

^{1}H-NMR: δ 9.26 (d, *J* = 1.6 Hz, 1H), 7.51 (td, *J* = 7.8, 1.9 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.22 – 7.12 (m, 1H), 7.07 (td, *J* = 7.6, 1.5 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.60 (q, *J* = 7.1 Hz, 1H), 5.08 (s, 2H), 4.76 – 4.69 (m, 1H), 3.35 (dd, *J* = 16.1, 9.3 Hz, 1H), 3.11 (dd, *J* = 16.1, 6.5 Hz, 1H), 2.08 (dd, *J* = 7.1, 1.1 Hz, 3H) ppm.

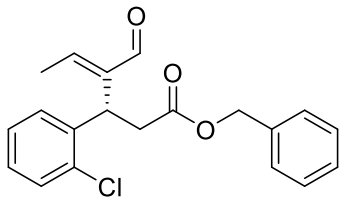
^{13}C-NMR: δ 194.8, 172.0, 153.9, 143.0, 136.0, 129.8 (d, *J* = 3.8 Hz), 128.6 (2C), 128.5, 128.4 (3C), 128.3, 127.8 (d, *J* = 13.9 Hz), 124.2 (d, *J* = 3.6 Hz), 115.2 (d, *J* = 22.7 Hz), 66.5, 35.9, 31.4 (d, *J* = 3.4 Hz), 15.2 (d, *J* = 3.6 Hz) ppm.

^{19}F-NMR: δ -116.7 ppm.

HRMS (ESI$^+$): calculated for $C_{20}H_{20}O_3F$ $[M+H]^+$: 327.1391; found: 327.1360.

The enantiomeric excess was determined by SFC using a Chiralpak ID-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 1.50 min, τ_{minor} = 1.78 min (94% *ee*).

Benzyl (*S*,*E*)-3-(2-chlorophenyl)-4-formylhex-4-enoate (5h)



Following general procedure C, diisopropyl (*E*)-(3-(2-chlorophenyl)acryloyl)phosphonate **1h** (33.1 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5h** (40% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 98:2 to 90:10. $[\alpha]^{20}_{D}$ = +31.9 (*c* 0.80, $CHCl_3$).

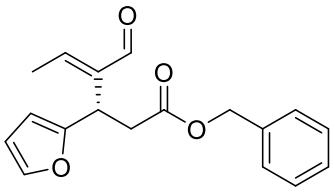
^{1}H-NMR: δ 9.29 (d, *J* = 1.6 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.36 – 7.26 (m, 6H), 7.24 – 7.09 (m, 2H), 6.63 (q, *J* = 7.2 Hz, 1H), 5.07 (s, 2H), 4.78 (t, *J* = 7.8 Hz, 1H), 3.33 (dd, *J* = 16.0, 9.5 Hz, 1H), 3.05 (dd, *J* = 16.0, 6.3 Hz, 1H), 2.05 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C-NMR: δ 195.1, 171.8, 154.5, 142.7, 138.3, 136.0, 133.7, 130.2, 129.7, 128.7 (2C), 128.4 (3C), 128.2, 127.0, 66.5, 36.8, 35.9, 15.9 ppm.

HRMS (ESI$^+$): calculated for $C_{20}H_{20}O_3Cl$ $[M+H]^+$: 343.1095; found: 343.1131.

The enantiomeric excess was determined by SFC using a Chiralpak IC column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 3.0 mL/min], τ_{major} = 3.87 min, τ_{minor} = 4.18 min (95% *ee*).

Benzyl (*S*,*E*)-4-formyl-3-(furan-2-yl)hex-4-enoate (5i)



Following general procedure C, benzyl (*E*)-4-formyl-3-(furan-2-yl)hex-4-enoate **1i** (29.8 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5i** as a mixture of *E*:*Z* isomers 94:6 (50% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 98:2 to 90:10. **$[\alpha]^{20}_D$** = +35.9 (*c* 1.21, $CHCl_3$).

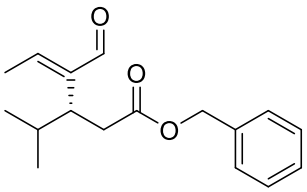
^{1}H-NMR: δ 9.32 (d, *J* = 1.2 Hz, 1H), 7.41 – 7.22 (m, 6H), 6.67 (q, *J* = 7.2 Hz, 1H), 6.26 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.04 (dt, *J* = 3.3, 1.1 Hz, 1H), 4.57 (t, *J* = 7.7 Hz, 1H), 3.24 – 3.03 (m, 2H), 2.01 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C-NMR: δ 193.9, 171.7, 154.3, 153.3, 142.4, 141.3, 136.0, 128.7 (2C), 128.5 (2C), 128.4, 110.5, 105.9, 66.6, 35.6, 32.2, 15.1 ppm.

HRMS (ESI$^+$): calculated for $C_{18}H_{19}O_4$ $[M+H]^+$: 299.1278; found: 299.1230.

The enantiomeric excess was determined by SFC using a Chiralpak ID-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 1.70 min, τ_{minor} = 1.90 min (96% *ee*).

Benzyl (*R*,*E*)-4-formyl-3-isopropylhex-4-enoate (5j)



Following general procedure C, diisopropyl (*E*)-(4-methylpent-2-enoyl)phosphonate **1j** (22.2 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **5j** (30% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 98:2 to 90:10. **$[\alpha]^{20}_D$** = +1.1 (*c* 0.76, $CHCl_3$).

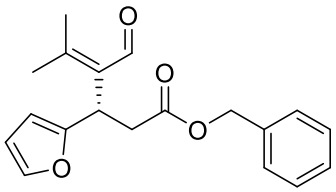
^{1}H-NMR: δ 9.25 (d, *J* = 1.8 Hz, 1H), 7.38 – 7.28 (m, 5H), 6.55 (q, *J* = 7.1 Hz, 1H), 5.05 (d, *J* = 12.2 Hz, 1H), 4.99 (d, *J* = 12.2 Hz, 1H), 2.94 – 2.64 (m, 3H), 2.15 – 1.99 (m, 1H), 1.90 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.72 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C-NMR: δ 195.4, 173.3, 153.6, 144.8, 136.2, 128.6 (2C), 128.5 (2C), 128.4, 66.2, 41.4, 35.8, 29.7, 21.4, 21.3, 15.4 ppm.

HRMS (ESI$^+$): calculated for $C_{17}H_{23}O_3$ $[M+H]^+$: 275.1642; found: 275.1656.

The enantiomeric excess was determined by SFC using a Chiralpak IC column [CO_2/MeOH 97:3, flow rate 2.0 mL/min], τ_{major} = 17.46 min (99% *ee*).

Benzyl (*S*)-4-formyl-3-(furan-2-yl)-5-methylhex-4-enoate (5k)



Following general procedure C, diisopropyl cinnamoylphosphonate **1a** (29.6 mg, 0.1 mmol) and silyl dienol ether **2b** (80 µL, 0.4 mmol) after 36h at room temperature, gave **5k** (40% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. **$[\alpha]^{20}_D$** = +28.7 (*c* 0.70, $CHCl_3$).

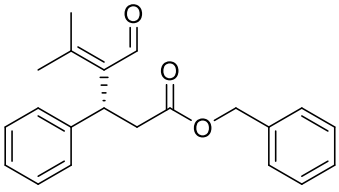
^{1}H-NMR: δ 10.05 (d, *J* = 1.2 Hz, 1H), 7.38 – 7.29 (m, 5H), 7.24 – 7.21 (m, 1H), 6.25 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.00 (dt, *J* = 3.3, 1.1 Hz, 1H), 5.10 (s, 2H), 4.62 (t, *J* = 7.6 Hz, 1H), 3.17 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.07 (dd, *J* = 16.0, 8.5 Hz, 1H), 2.17 (s, 3H), 2.03 (s, 3H) ppm.

^{13}C-NMR: δ 190.4, 172.0, 158.4, 155.5, 140.9, 136.1, 135.1, 128.7 (2C), 128.5 (2C), 128.4, 110.5, 105.4, 66.5, 36.2, 34.0, 23.8, 20.7 ppm.

HRMS (ESI$^+$): calculated for $C_{19}H_{21}O_4$ $[M+H]^+$: 313.1434; found: 313.1499.

The enantiomeric excess was determined by SFC using a Chiralpak ID-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 1.75 min, τ_{minor} = 1.88 min (96% *ee*).

Benzyl (*R*)-4-formyl-5-methyl-3-phenylhex-4-enoate (5l)



Following general procedure C, diisopropyl cinnamoylphosphonate **1a** (29.6 mg, 0.1 mmol) and silyl dienol ether **2b** (80 µL, 0.4 mmol) after 36h at room temperature, gave **5l** (41% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. **$[\alpha]^{20}_D$** = +34.4 (*c* 0.60, $CHCl_3$).

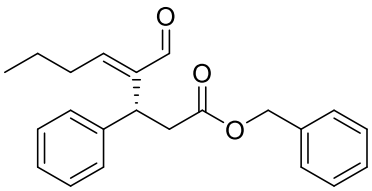
^{1}H-NMR: δ 10.08 (d, *J* = 1.4 Hz, 1H), 7.40 – 7.15 (m, 10H), 5.10 (s, 2H), 4.62 – 4.50 (m, 1H), 3.29 (dd, *J* = 15.7, 8.9 Hz, 1H), 3.17 (dd, *J* = 15.7, 6.7 Hz, 1H), 2.16 (s, 3H), 2.07 (s, 3H) ppm.

^{13}C-NMR: δ 191.2, 172.7, 157.5, 142.4, 137.6, 136.2, 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.3, 127.7 (2C), 126.4, 66.4, 39.8, 37.3, 24.1, 20.7 ppm.

HRMS (ESI$^+$): calculated for $C_{21}H_{26}O_3N$ $[M+NH_4]^+$: 340.1907; found: 340.1880.

The enantiomeric excess was determined by SFC using a Chiralpak IA column [CO_2/MeOH 95:5, flow rate 3.0 mL/min], τ_{major} = 6.27 min, τ_{minor} = 5.94 min (98% *ee*).

Benzyl (*R,E*)-4-formyl-3-phenyloct-4-enoate (5m)



Following general procedure C, diisopropyl cinnamoylphosphonate **1a** (29.6 mg, 0.1 mmol) and silyl dienol ether **2c** (127 µL, 0.4 mmol) after 36h at room temperature, gave **5m** (48% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. **$[\alpha]^{20}_D$** = +96.4 (*c* 0.91, $CHCl_3$).

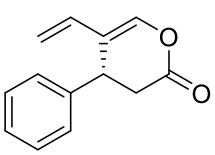
^{1}H-NMR: δ 9.31 (d, *J* = 1.5 Hz, 1H), 7.36 – 7.17 (m, 10H), 6.47 (t, *J* = 7.3 Hz, 1H), 5.07 (s, 2H), 4.46 (ddd, *J* = 8.8, 7.0, 1.4 Hz, 1H), 3.28 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.17 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.47 – 2.36 (m, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C-NMR: δ 195.0, 172.3, 158.2, 143.8, 141.6, 136.1, 128.7 (2C), 128.6 (2C), 128.4 (2C), 128.3, 127.8 (2C), 126.8, 66.4, 38.8, 37.0, 31.4, 22.0, 14.1 ppm.

HRMS (ESI$^+$): calculated for $C_{22}H_{25}O_3$ $[M+H]^+$: 337.1798; found: 337.1774.

The enantiomeric excess was determined by SFC using a Chiralpak IB-3 column [CO_2/MeOH 97:3, flow rate 2.0 mL/min], τ_{major} = 4.18 min, τ_{minor} = 3.74 min (92% *ee*).

(*R*)-4-Phenyl-5-vinyl-3,4-dihydro-2H-pyran-2-one (4a)



Following general procedure C without the addition of DBU and BnOH, (*E*)-diisopropyl cinnamoylphosphonate **1a** (29.6 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **4a** (35% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 98:2 to 90:10. **$[\alpha]^{20}_D$** = -84.9 (*c* 0.61, $CHCl_3$).

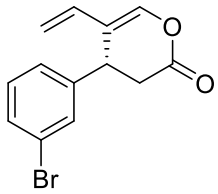
^{1}H-NMR: δ 7.38 – 7.14 (m, 5H), 6.90 (s, 1H), 6.30 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.09 (d, *J* = 17.4 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 3.98 (dd, *J* = 7.7, 1.9 Hz, 1H), 3.03 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.84 (dd, *J* = 15.9, 1.9 Hz, 1H) ppm.

^{13}C-NMR: δ 166.9, 142.1, 139.9, 131.1, 129.4 (2C), 127.8, 126.8 (2C), 120.9, 114.5, 37.2, 37.0 ppm.

HRMS (ESI^{+}): calculated for $C_{13}H_{13}O_2$ $[M+H]^+$: 200.0837; found: 200.0849.

The enantiomeric excess was determined by SFC using a Chiralpak IA column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 3.0 mL/min], τ_{major} = 4.73 min, τ_{minor} = 5.04 min (97% *ee*).

(*R*)-4-(3-Bromophenyl)-5-vinyl-3,4-dihydro-2H-pyran-2-one (4b)



Following general procedure C without the addition of DBU and BnOH, (*E*)-(3-(3-bromophenyl)acryloyl)phosphonate **1f** (37.5 mg, 0.1 mmol) and silyl dienol ether **2a** (72 µL, 0.4 mmol) after 36h at room temperature, gave **4b** (39% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate from 99:1 to 90:10. **$[\alpha]^{20}_{D}$** = -64.9 (*c* 0.62, $CHCl_3$).

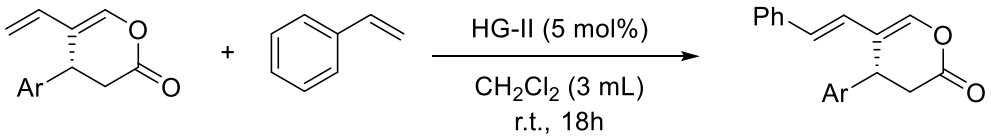
^{1}H-NMR: δ 7.40 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.32 (t, *J* = 1.9 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.15 – 7.09 (m, 1H), 6.91 (s, 1H), 6.30 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.08 (d, *J* = 10.9 Hz, 1H), 5.05 (d, *J* = 17.4 Hz, 1H), 3.95 (dd, *J* = 7.6, 1.9 Hz, 1H), 3.04 (dd, *J* = 15.9, 7.6 Hz, 1H), 2.83 (dd, *J* = 15.9, 1.9 Hz, 1H) ppm.

^{13}C-NMR: δ 166.4, 142.4, 142.1, 131.1, 131.0, 130.8, 130.1, 125.5, 123.5, 120.1, 114.8, 37.0, 36.6 ppm.

HRMS (ESI^{+}): calculated for $C_{13}H_{12}BrO_2$ $[M+H]^+$: 277.9942; found: 277.9956.

The enantiomeric excess was determined by SFC using a Chiralpak ID-3 column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 2.0 mL/min], τ_{major} = 1.28 min, τ_{minor} = 1.43 min (98% *ee*).

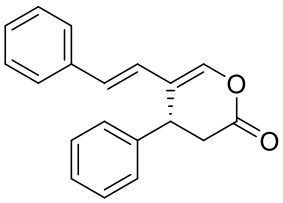
5. General procedure D: Synthesis of 6.



4 **6**

A vial previously oven-dried was charged with a magnetic stirrer, Hoveyda-Grubbs 2nd Generation Catalyst™ (1.0 mg, 0.0015 mmol, 0.05 equiv.) and **6** (0.03 mmol, 1.0 equiv.). Then, CH_2Cl_2 (3 mL) was added and the reaction was purged with nitrogen for 10 minutes. Styrene (11 µL, 0.09 mmol, 1.2 equiv.) was added and the reaction mixture was stirred for 18 hours at room temperature. Finally, the solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography.

(*R*,*E*)-4-phenyl-5-styryl-3,4-dihydro-2H-pyran-2-one (6a)[5]



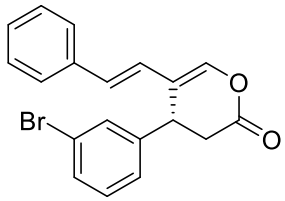
Following general procedure D, (*R*)-4-phenyl-5-vinyl-3,4-dihydro-2H-pyran-2-one **4a** (6.4 mg, 0.03 mmol) and styrene (11 µL, 0.09 mmol) after 18h at room temperature, gave **6a** (51% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate 9:1. The ^{1}H-NMR is in accordance with the literature.[5] **$[\alpha]^{20}_D$** = -16.1 (*c* 0.41, $CHCl_3$). For *S* enantiomer: [5] *Lit.* $[\alpha]^{20}_D$ = +310.0 (c 0.1, $CHCl_3$).

^{1}H-NMR: δ 7.39 – 7.16 (m, 10H), 7.03 (s, 1H), 6.72 (d, *J* = 16.2 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 4.13 (d, *J* = 6.6 Hz, 1H), 3.09 (dd, *J* = 15.4, 7.6 Hz, 1H), 2.90 (d, *J* = 15.9 Hz, 1H) ppm.

The enantiomeric excess was determined by SFC using a Chiralpak IA column [CO_2/MeOH from 95:5 to 60:40 in 8 min, flow rate 3.0 mL/min], τ_{major} = 4.55 min, τ_{minor} = 4.37 min (96% *ee*).

[5] S. Reddy-Yetra, T. Kaicharla, S. S. Kunte, R. G. Gonnade and A. T. Biju, *Org. Lett.* 2013, **15**, 5202-5205.

(*R,E*)-4-(3-bromophenyl)-5-styryl-3,4-dihydro-2H-pyran-2-one (6b)



Following general procedure D, (*R*)-4-(3-bromophenyl)-5-vinyl-3,4-dihydro-2H-pyran-2-one **4b** (8.4 mg, 0.03 mmol) and styrene (11 µL, 0.09 mmol) after 18h at room temperature, gave **6b** (54% yield) as a yellow oil. Eluent: cyclohexane: ethyl acetate 9:1. **$[\alpha]^{20}_{D}$** = -11.7 (*c* 1.03, $CHCl_3$).

^{1}H-NMR: δ 7.43-7.40 (m, 2H), 7.35-7.26 (m, 4H), 7.24-7.16 (m, 3H), 7.05 (s, 1H), 6.72 (d, *J* = 16.2 Hz, 1H), 6.36 (d, *J* = 16.2 Hz, 1H), 4.10 (d, *J* = 8.7 Hz, 1H), 3.09 (dd, *J* = 15.9, 7.6 Hz, 1H), 2.89 (dd, *J* = 15.9, 1.7 Hz, 1H).

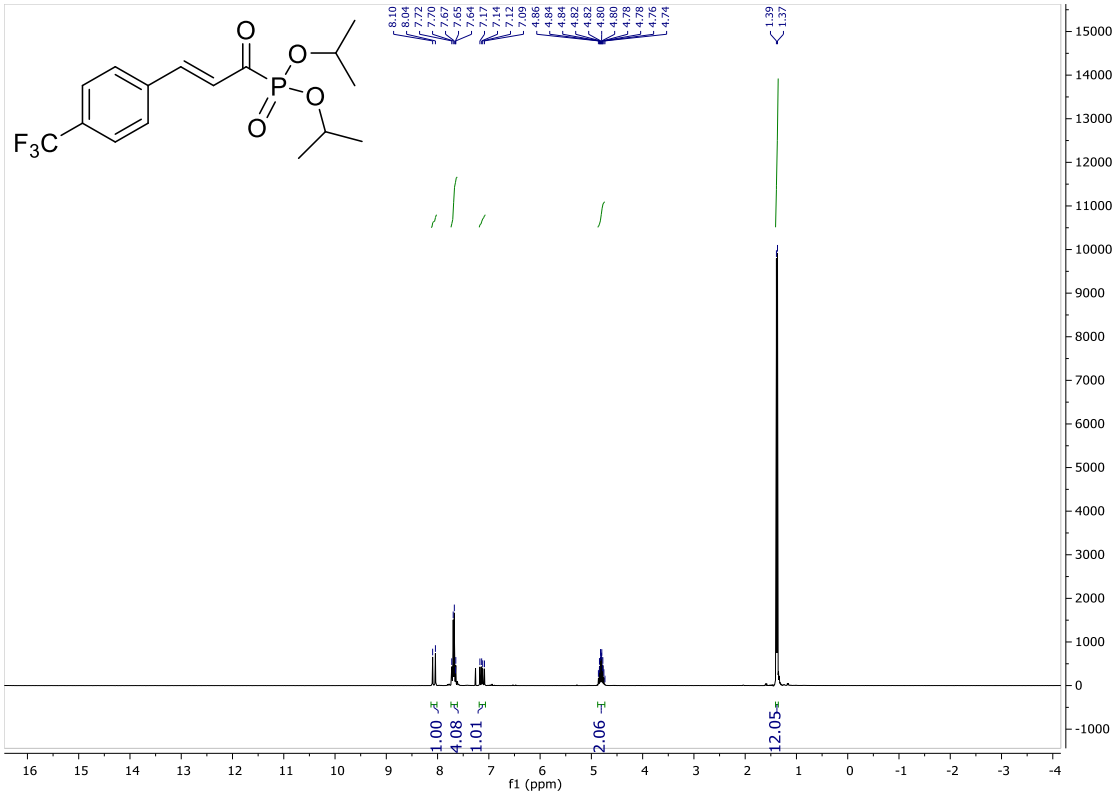
^{13}C-NMR: δ 166.3, 142.4, 141.9, 136.6, 131.2, 131.0, 130.1, 129.3, 128.8, 128.0, 126.4, 125.5, 123.5, 122.7, 120.2, 37.1, 37.1 ppm.

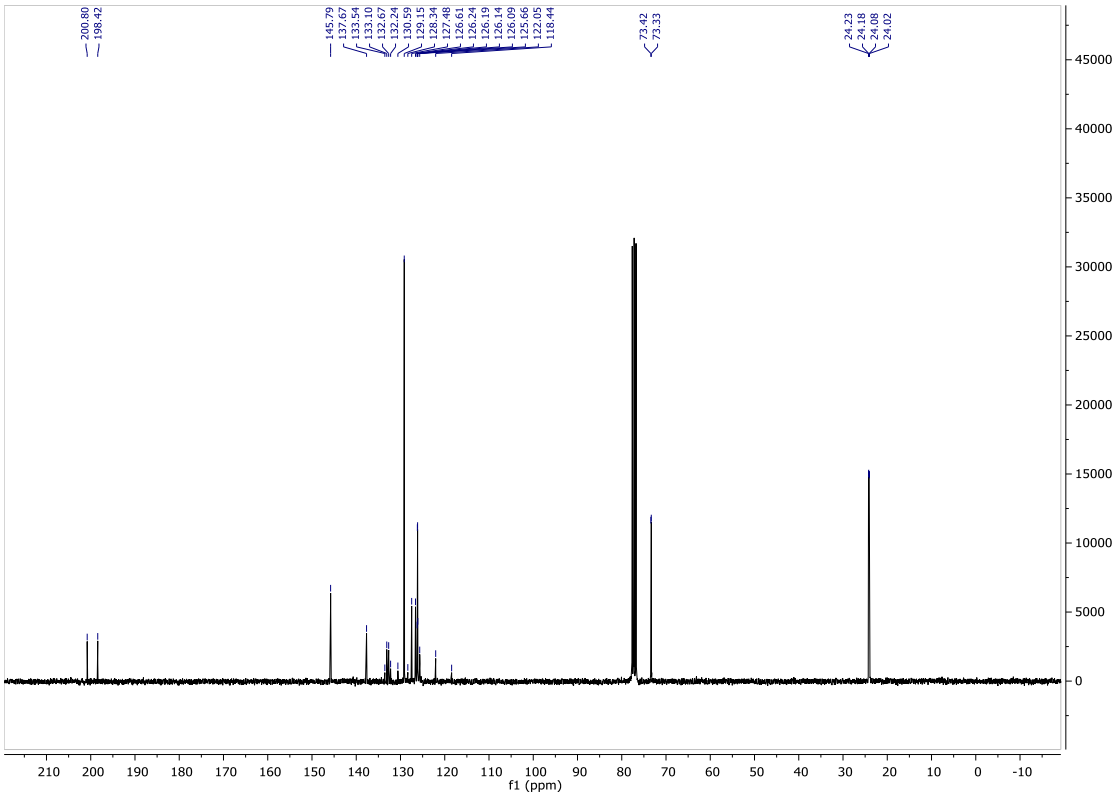
HRMS (ESI^{+}): calculated for $C_{19}H_{16}BrO_2$ $[M+H]^{+}$: 354.0255; found: 3540274.

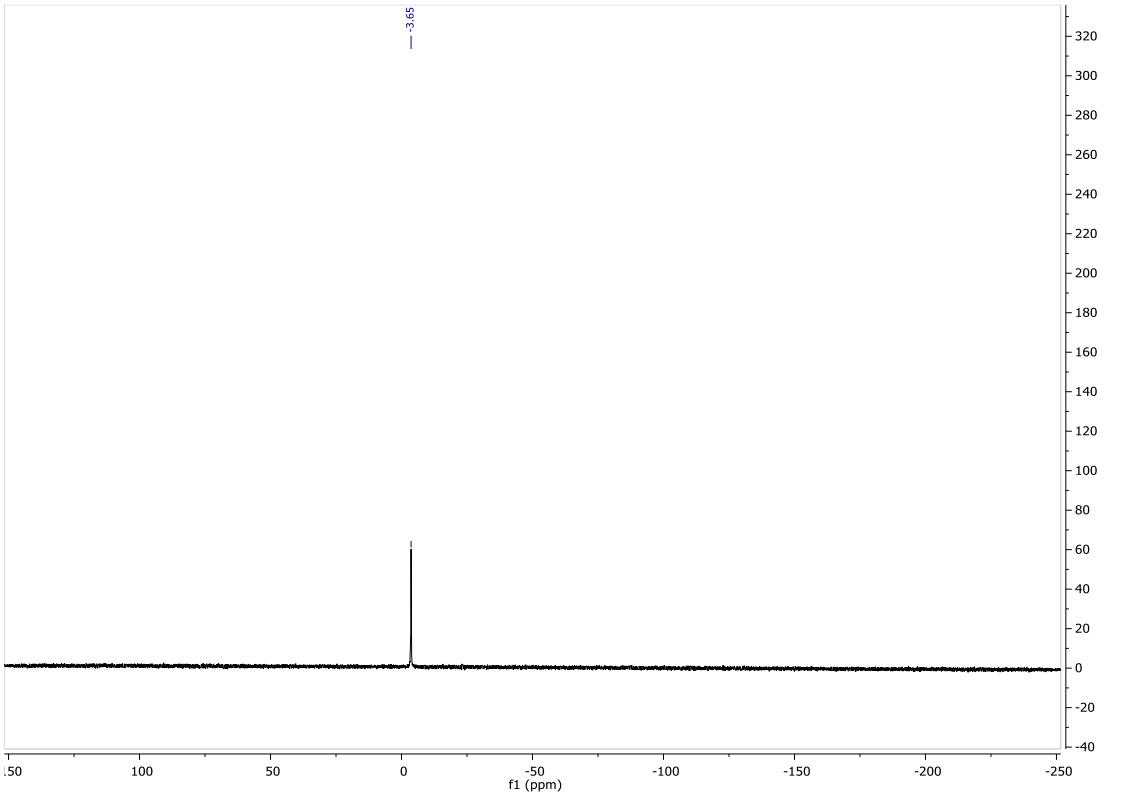
The enantiomeric excess was determined by SFC using a Chiralpak IA column [CO_2/MeOH 90:10, flow rate 3.0 mL/min], τ_{major} = 8.12 min, τ_{minor} = 7.47 min (97% *ee*).

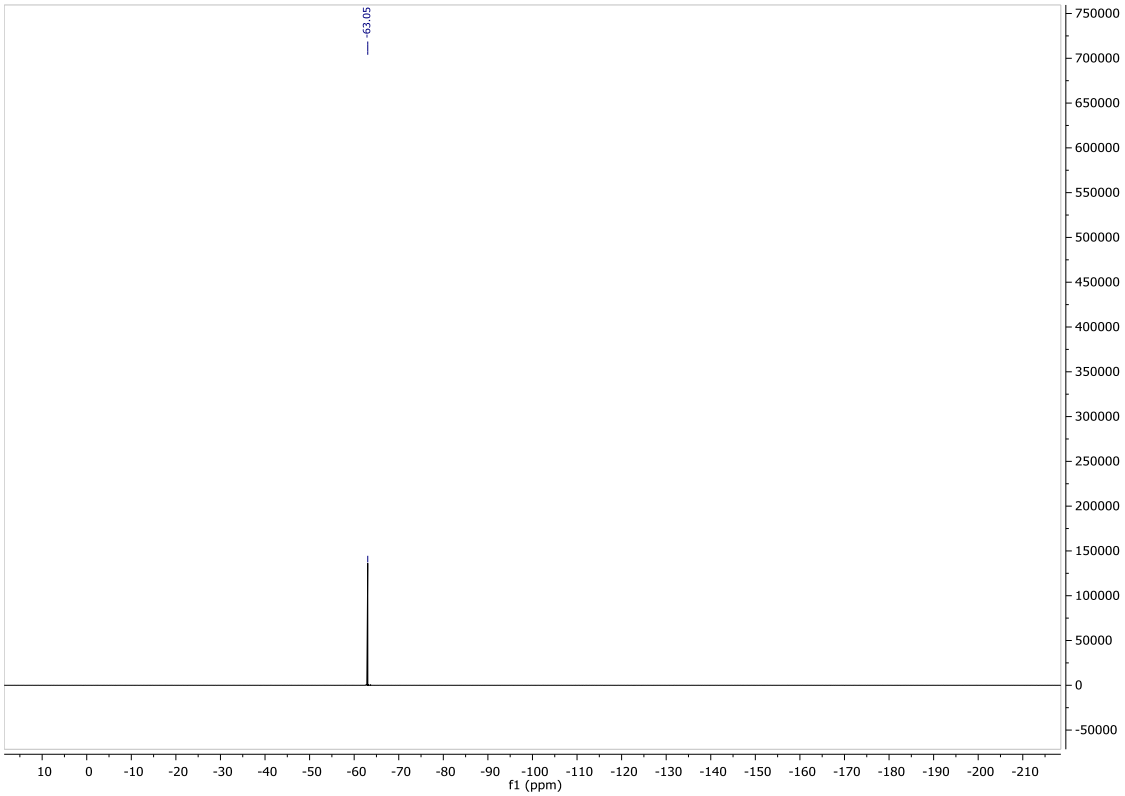
6. NMR Spectra and SFC chromatograms:

Diisopropyl (*E*)-(3-(4-(trifluoromethyl)phenyl)acryloyl)phosphonate (1c)

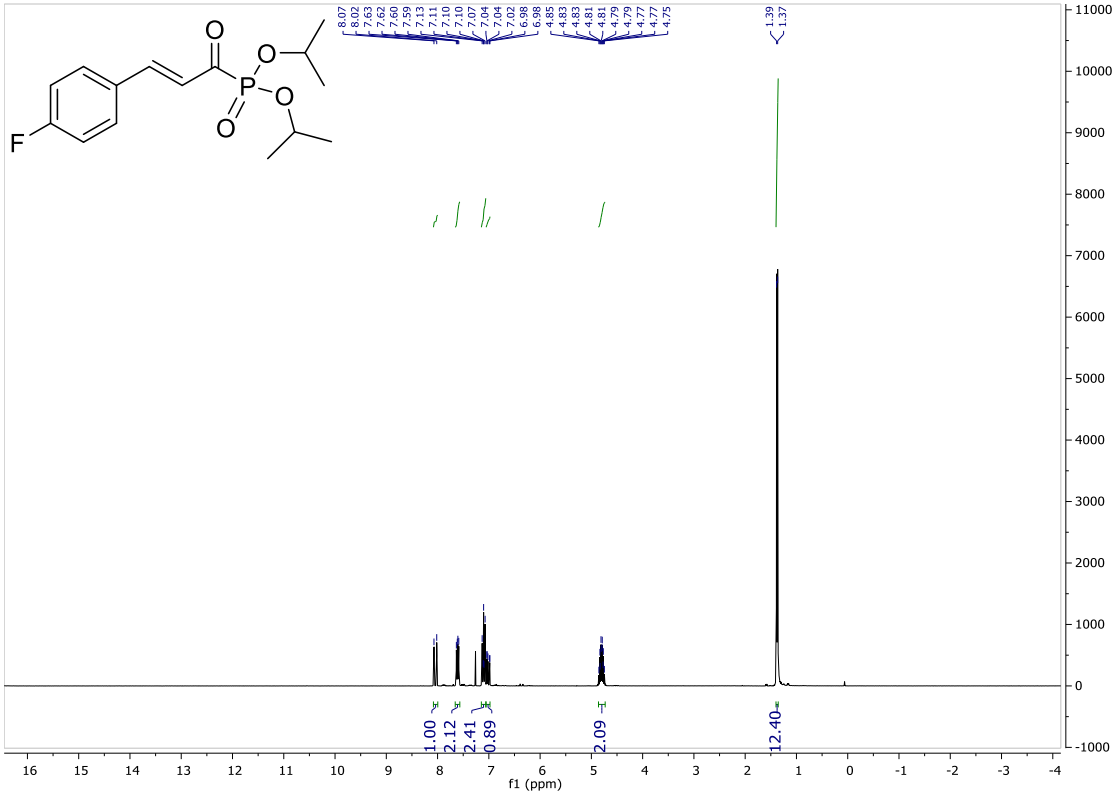


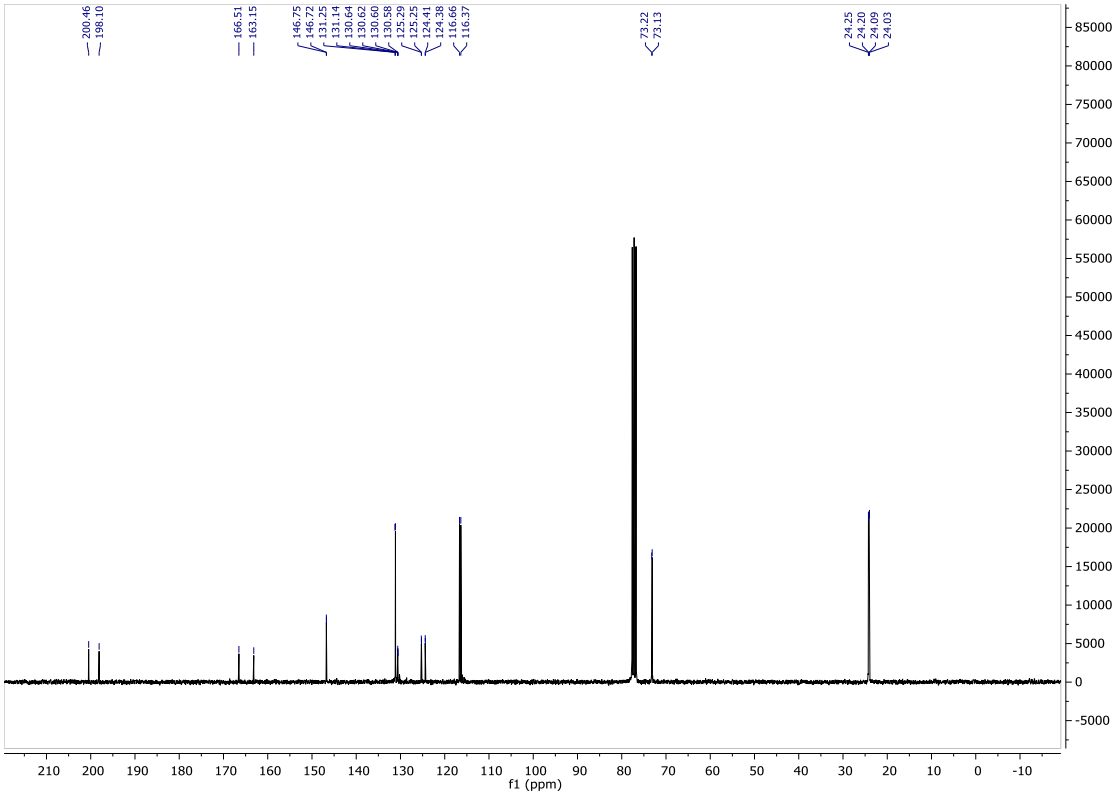


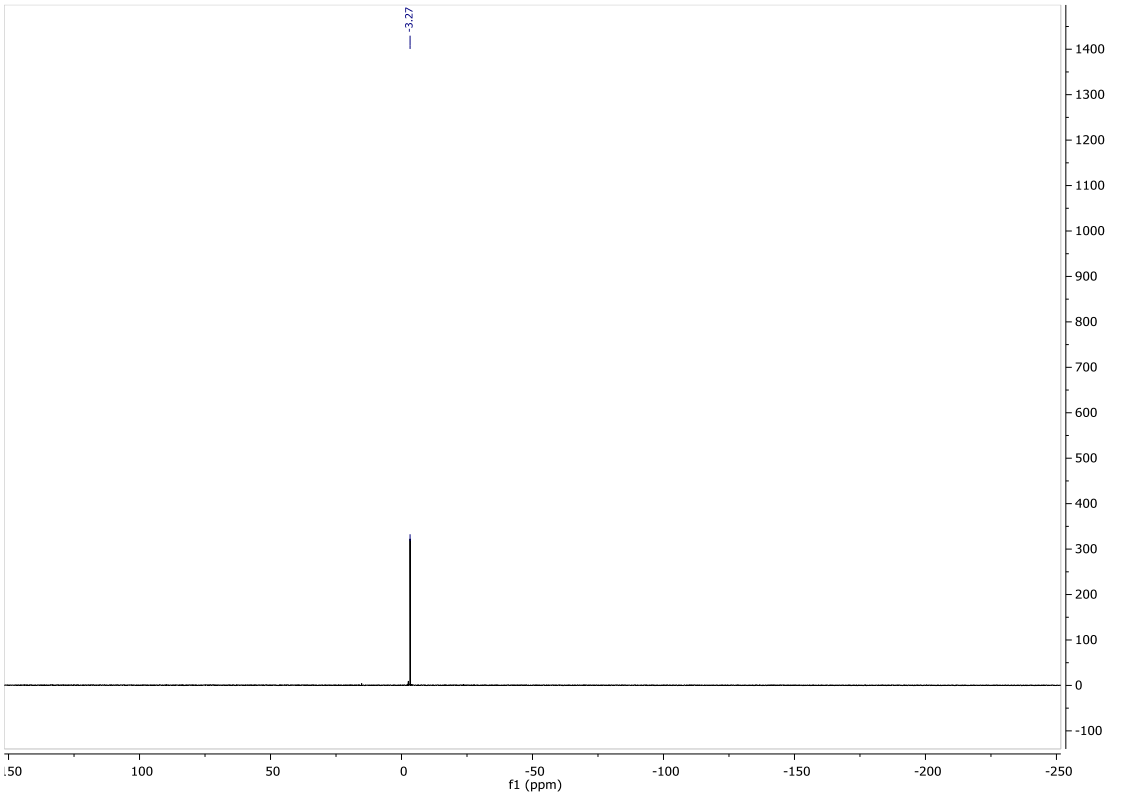

-3.65
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
50
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

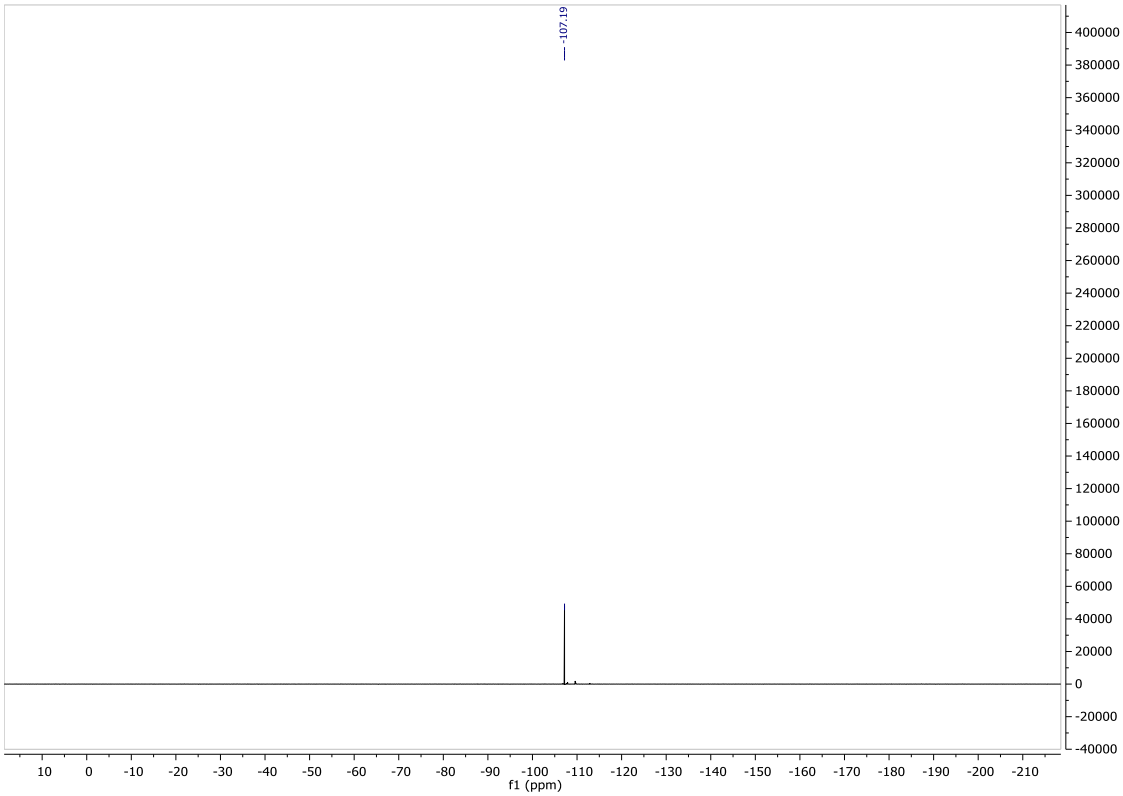

-63.05
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Diisopropyl (*E*)-(3-(4-fluorophenyl)acryloyl)phosphonate (1d)

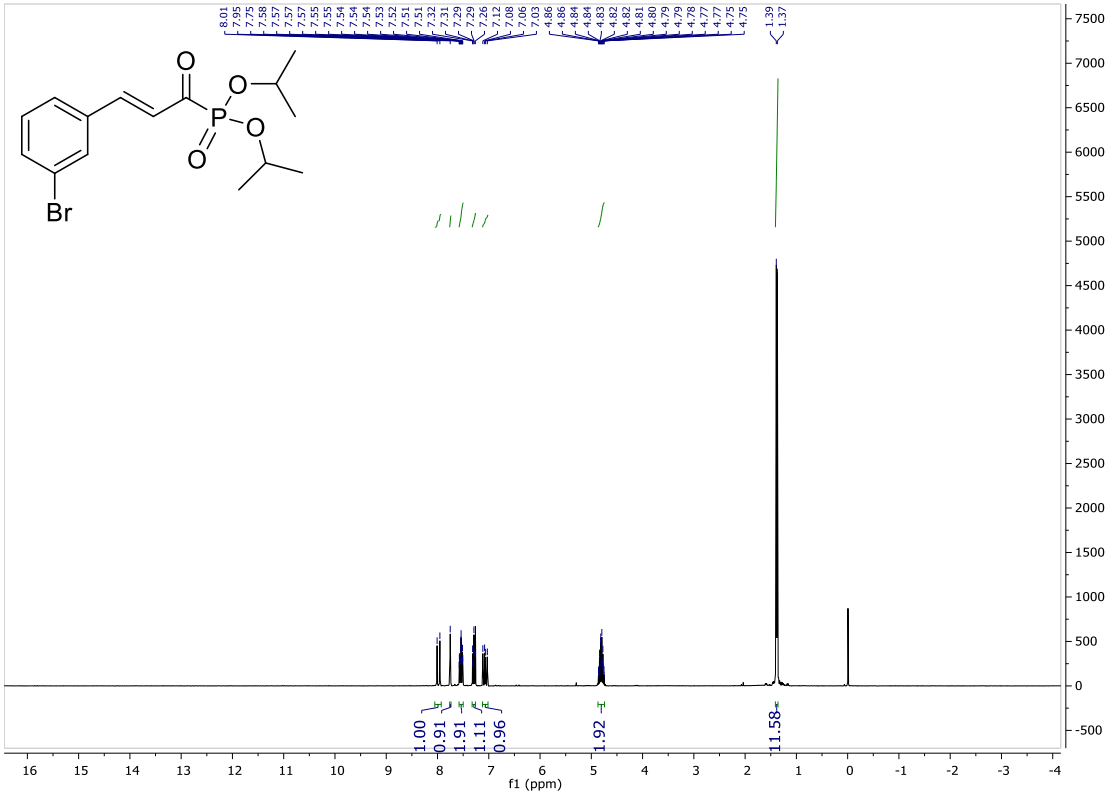


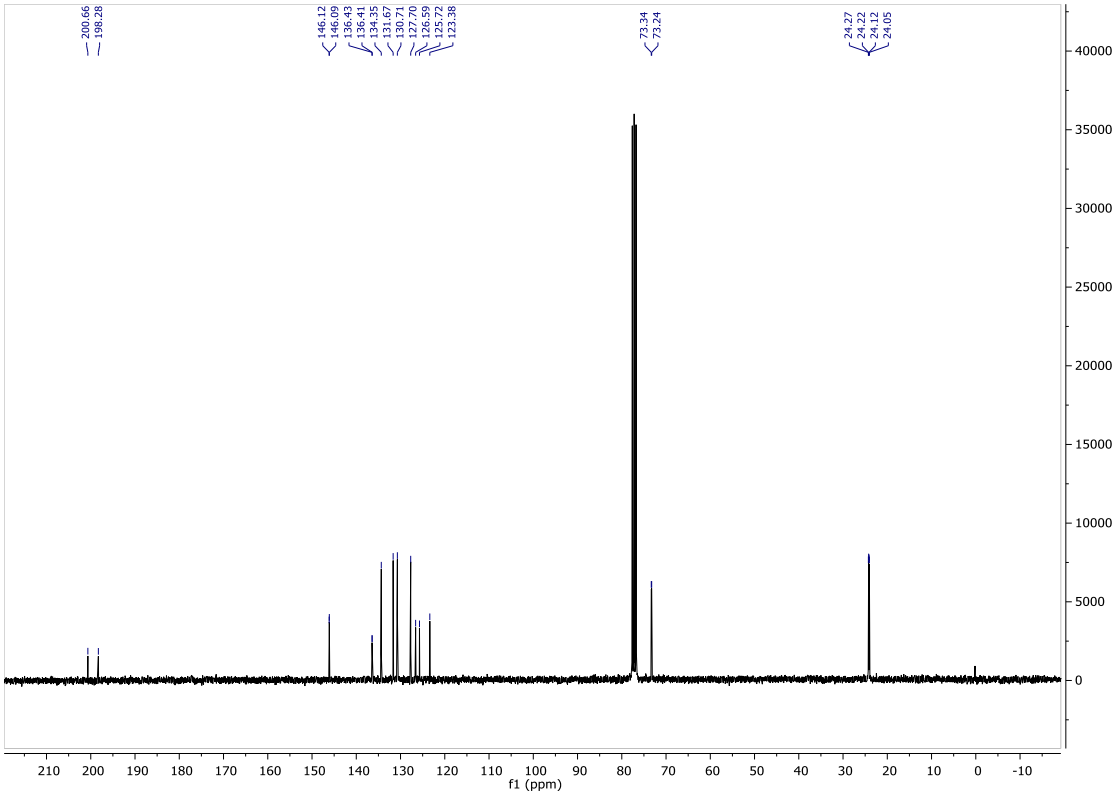


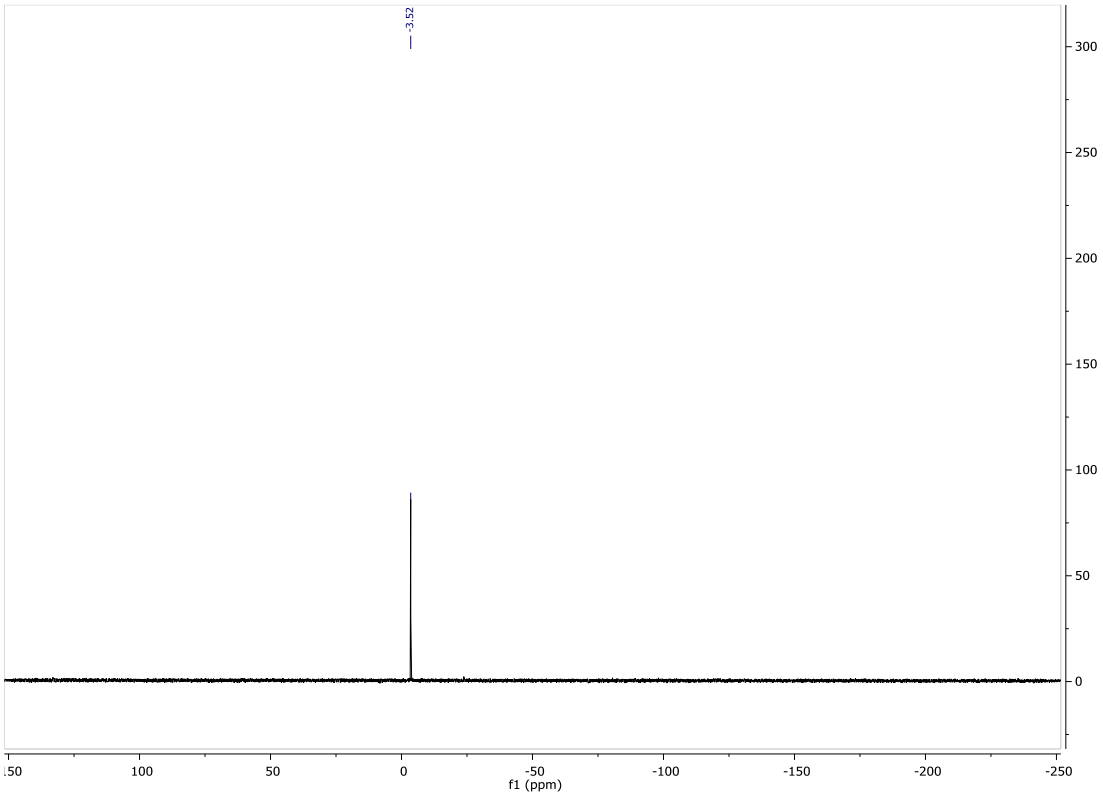

-3.27
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)


-107.19
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

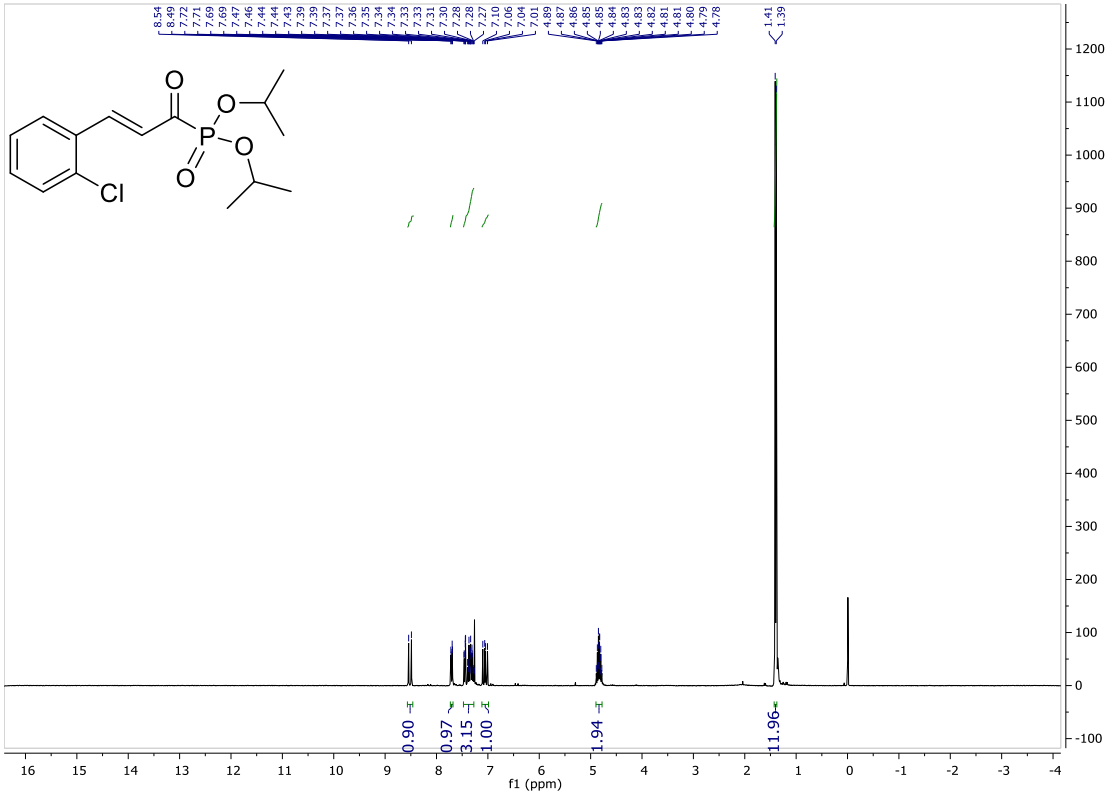
Diisopropyl (*E*)-(3-(3-bromophenyl)acryloyl)phosphonate (1f)

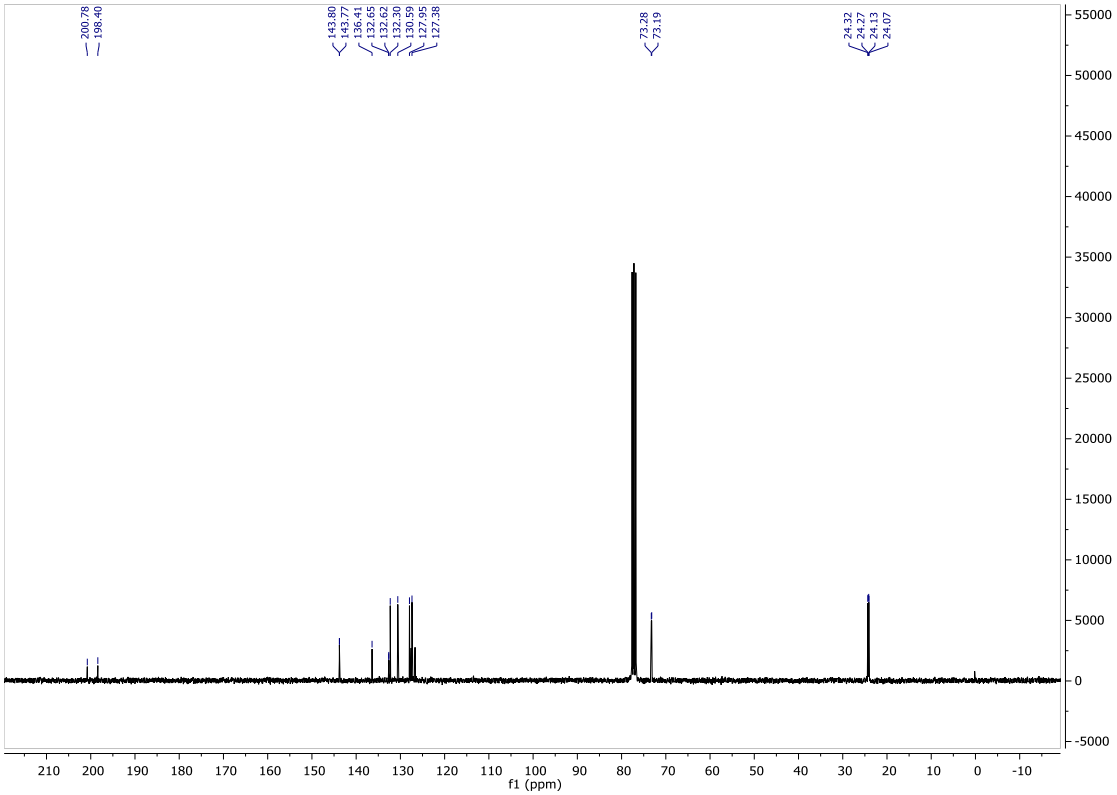


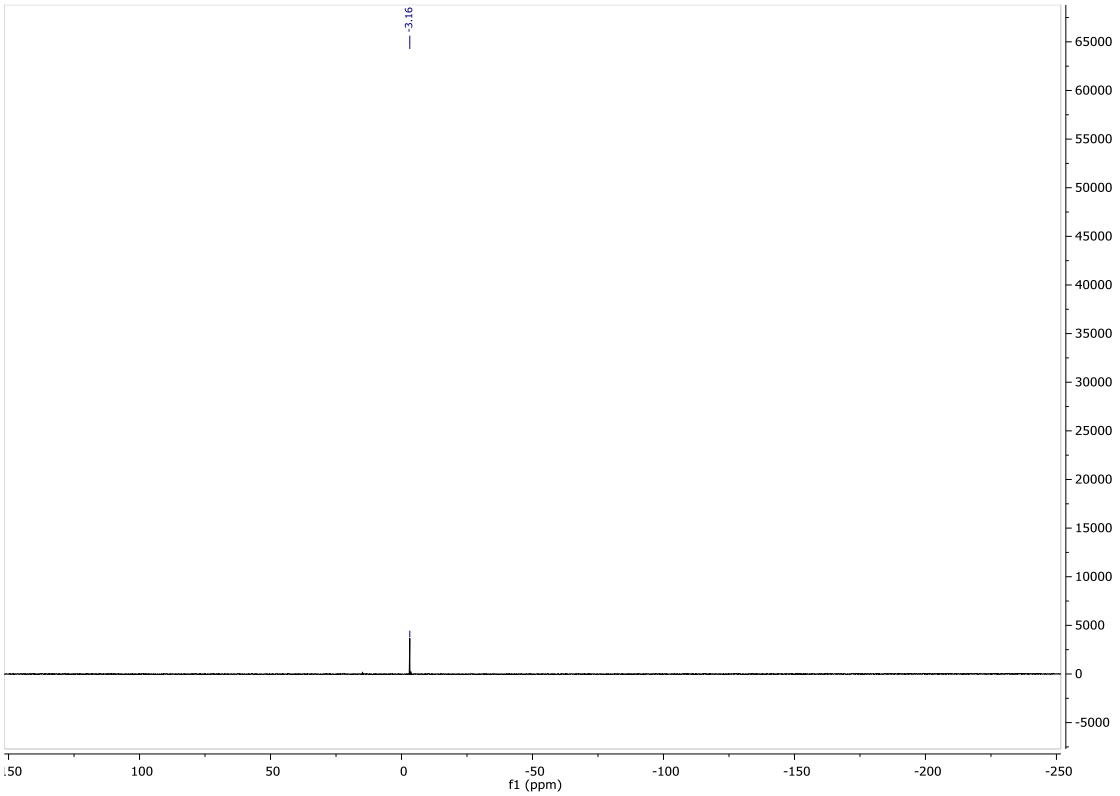



-3.52
300
250
200
150
100
50
0
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

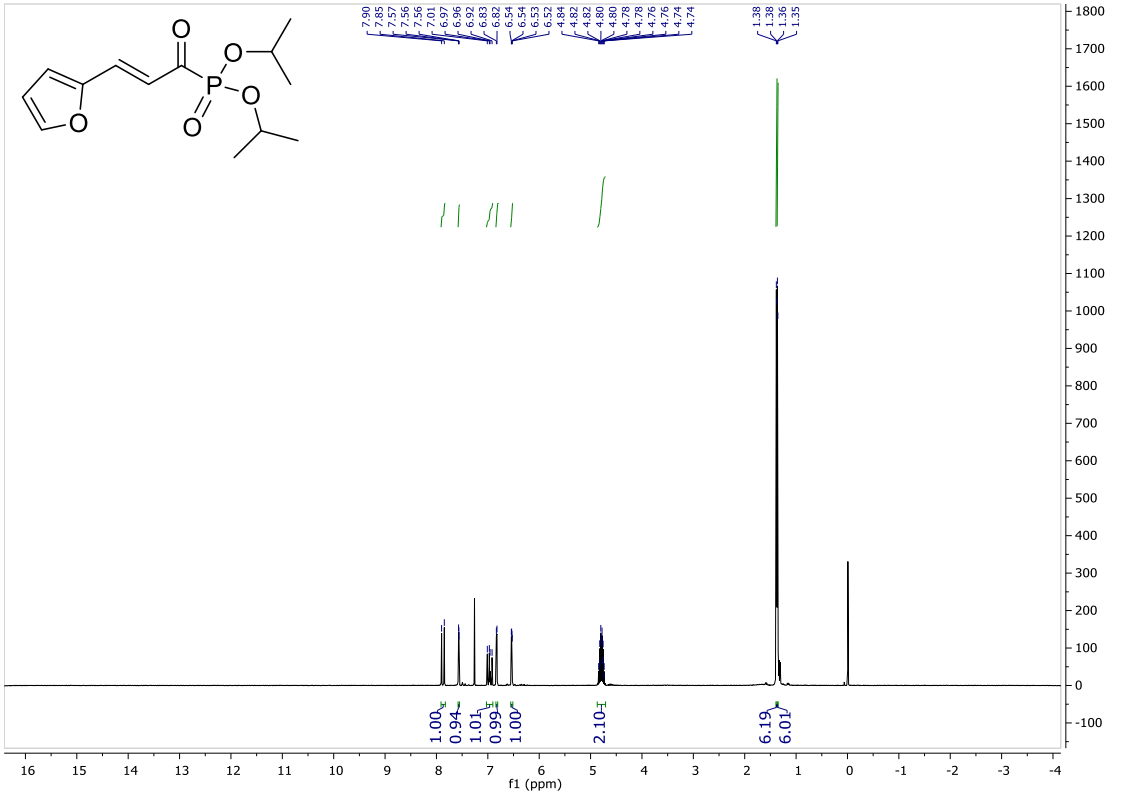
(E)-Diisopropil (3-(2-clorofenil)acriloil)fosfonato (1h)

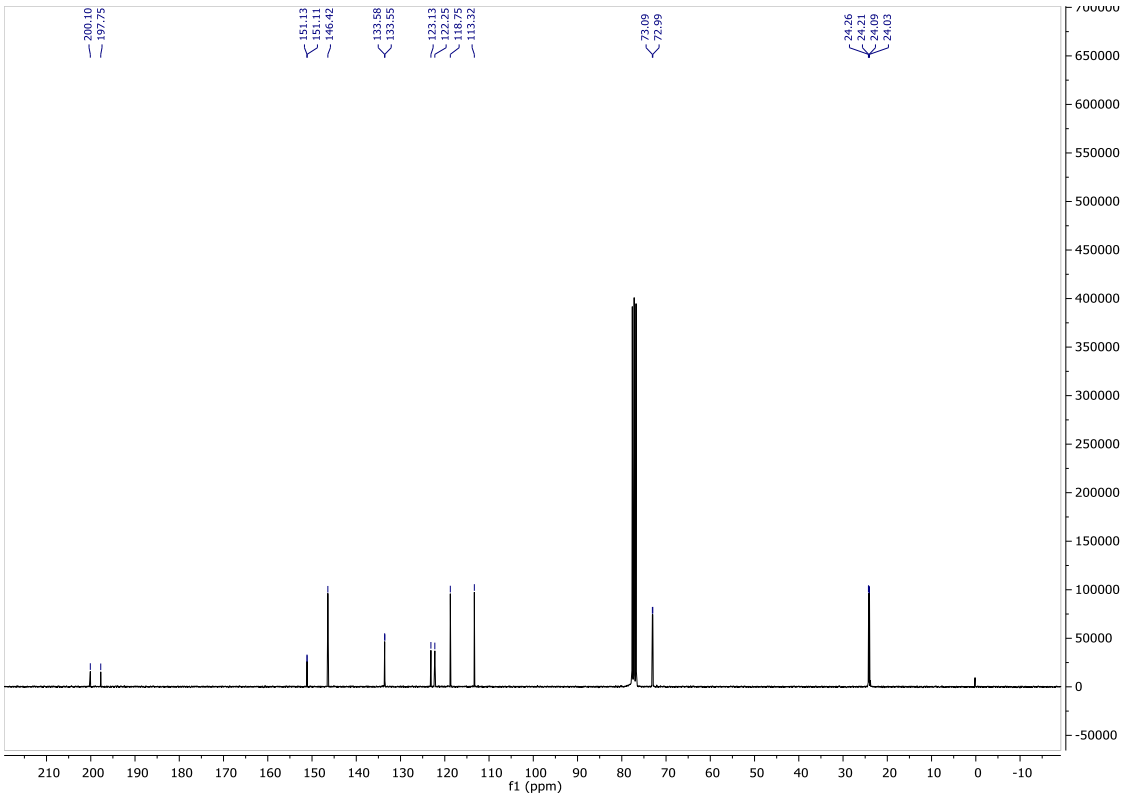


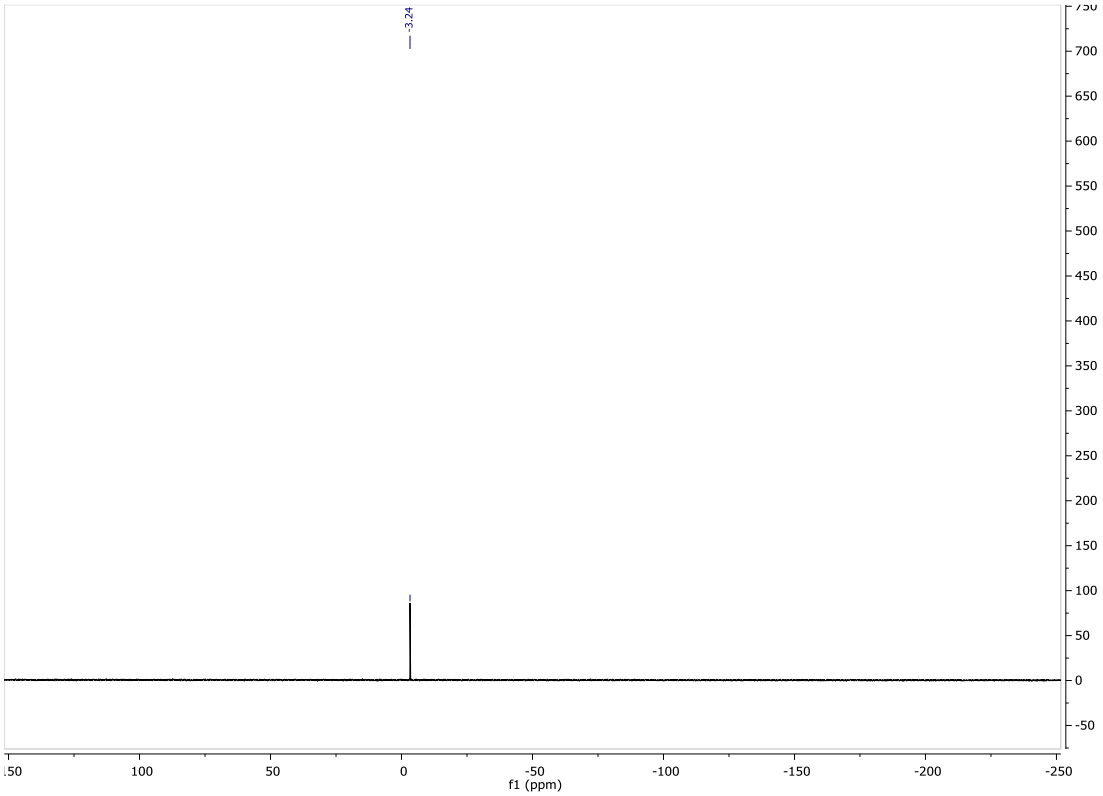



3.16
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

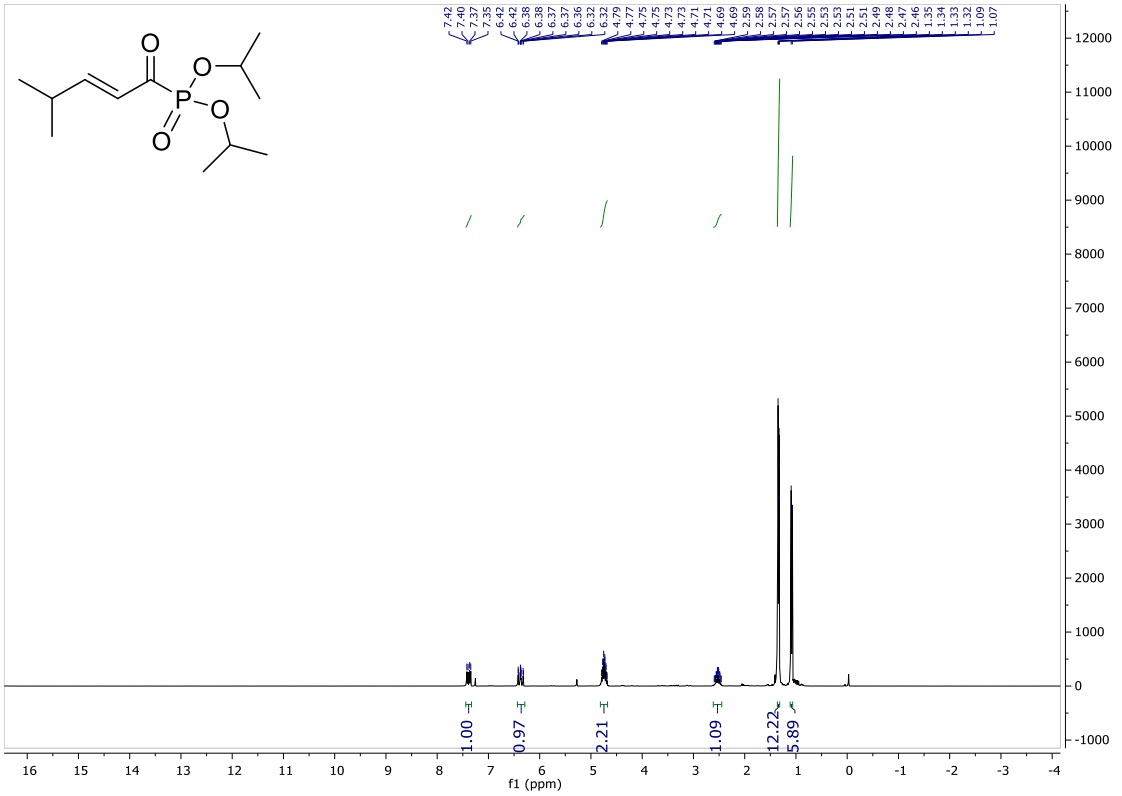
Diisopropyl (E)-(3-(furan-2-yl)acryloyl)phosphonate (1i)

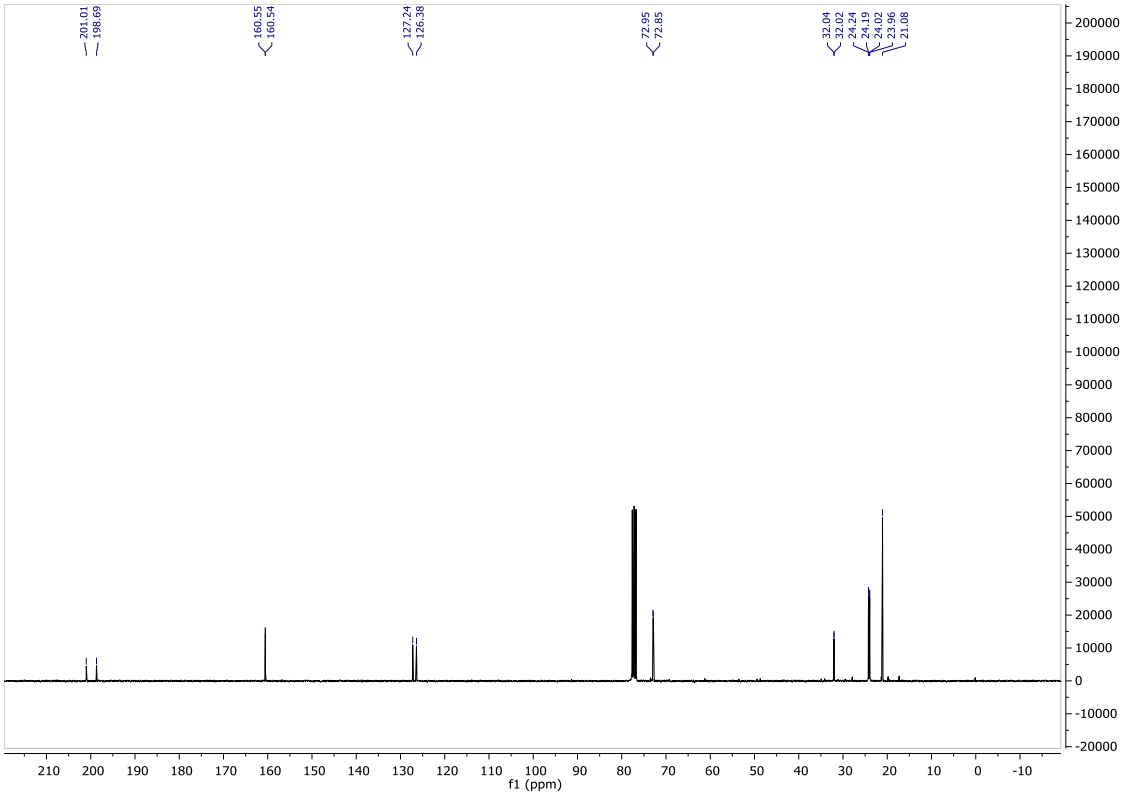


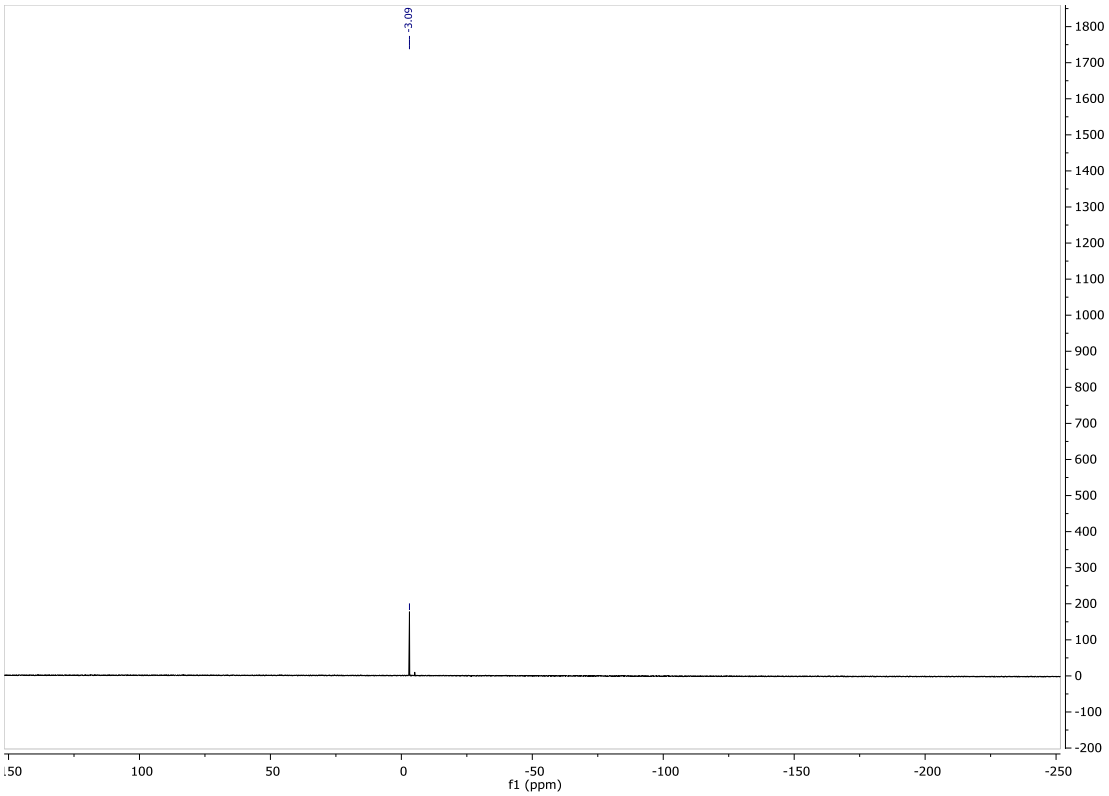



-3.24
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

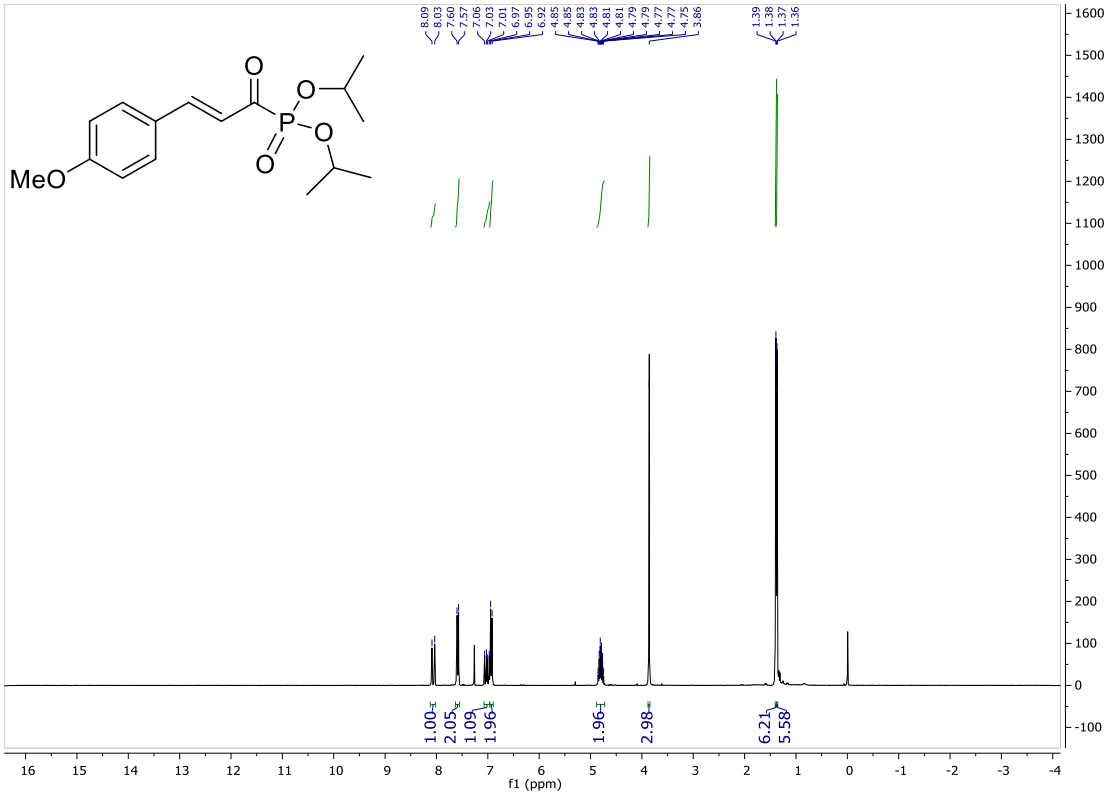
Diisopropyl (*E*)-(4-methylpent-2-enoyl)phosphonate (1j)

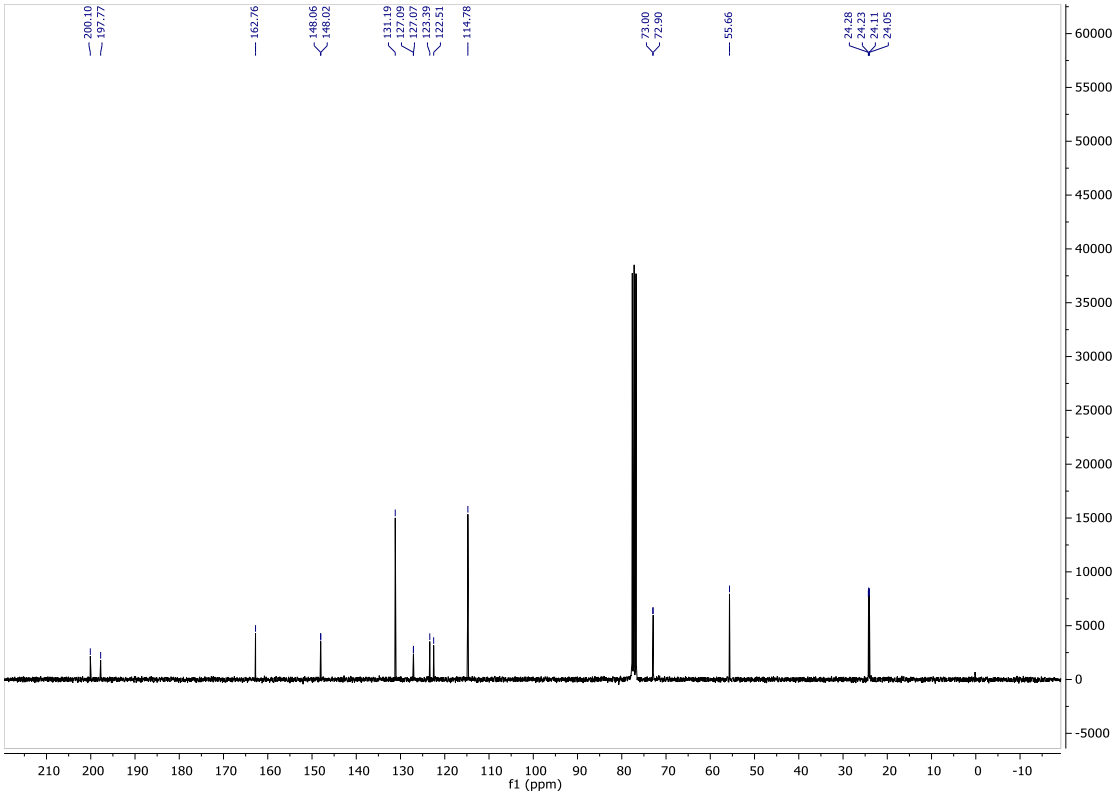


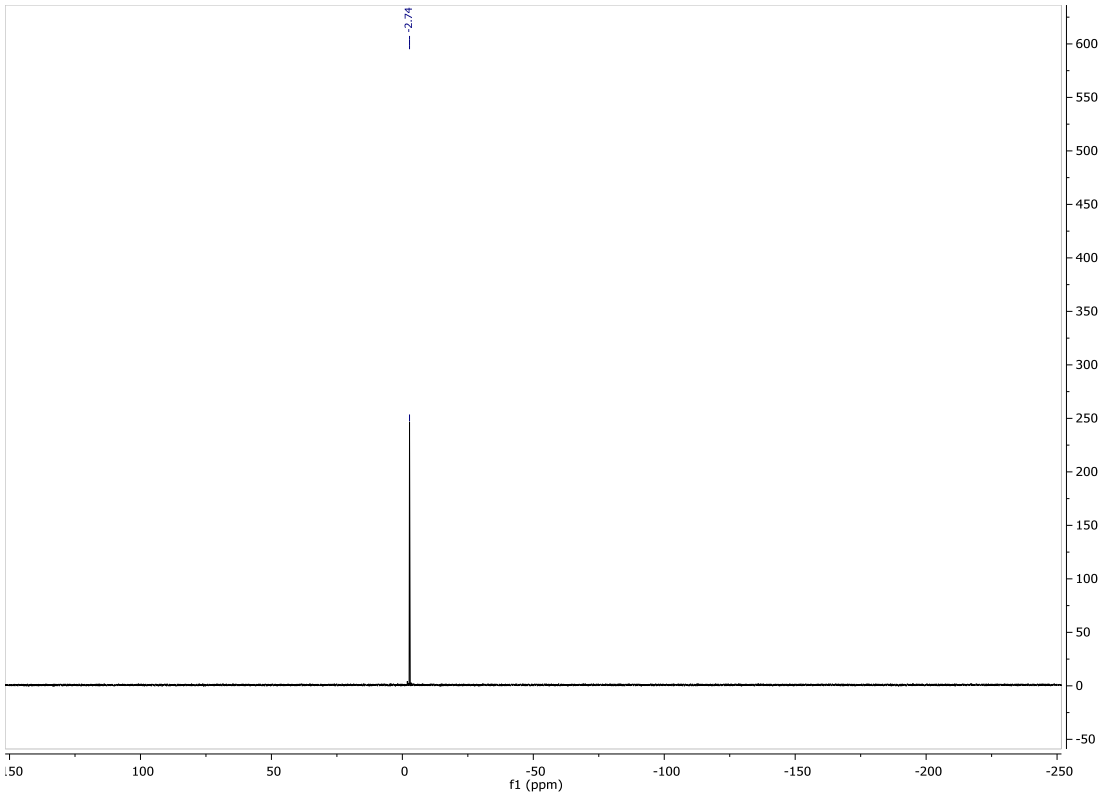



3.09
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

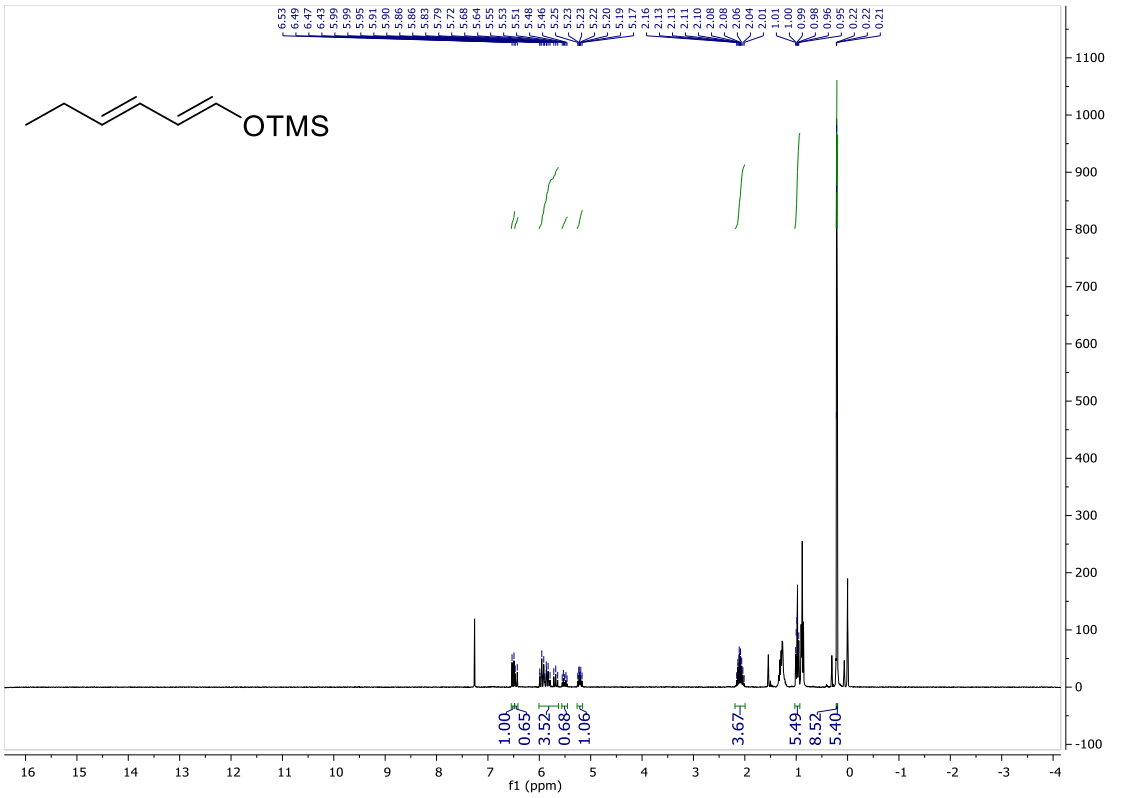
Diisopropyl (*E*)-(3-(4-methoxyphenyl)acryloyl)phosphonate (1k)

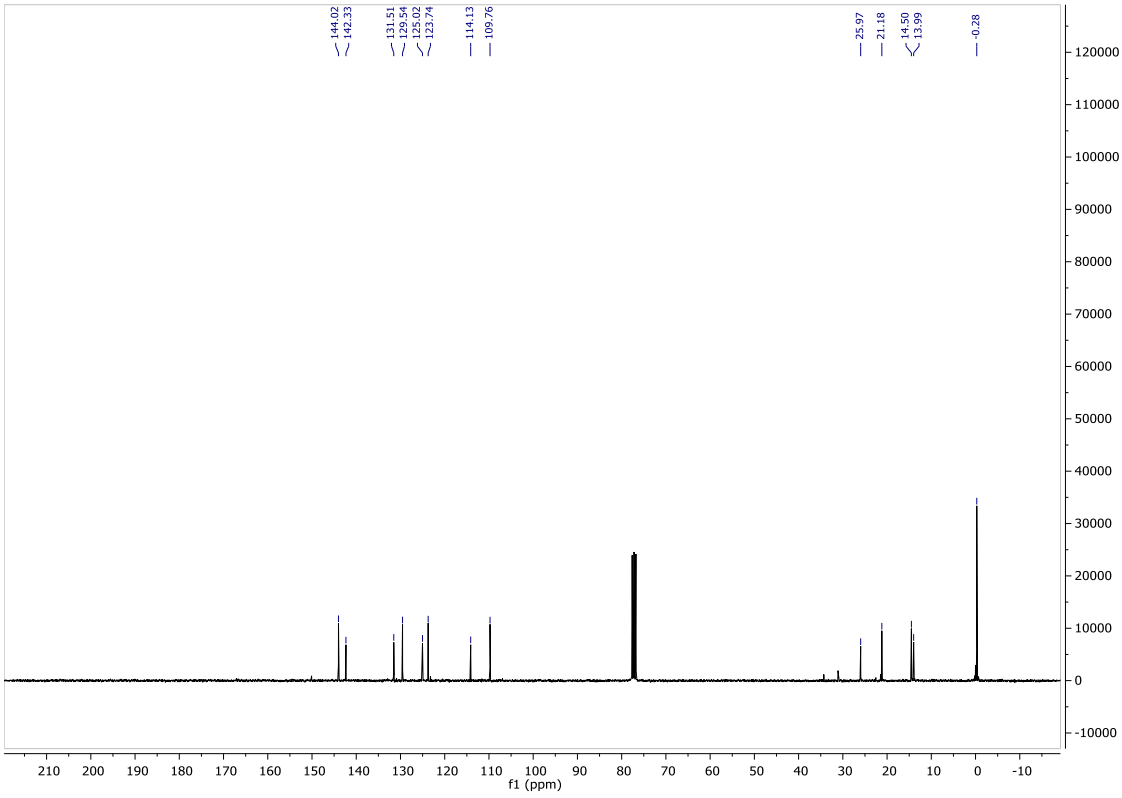




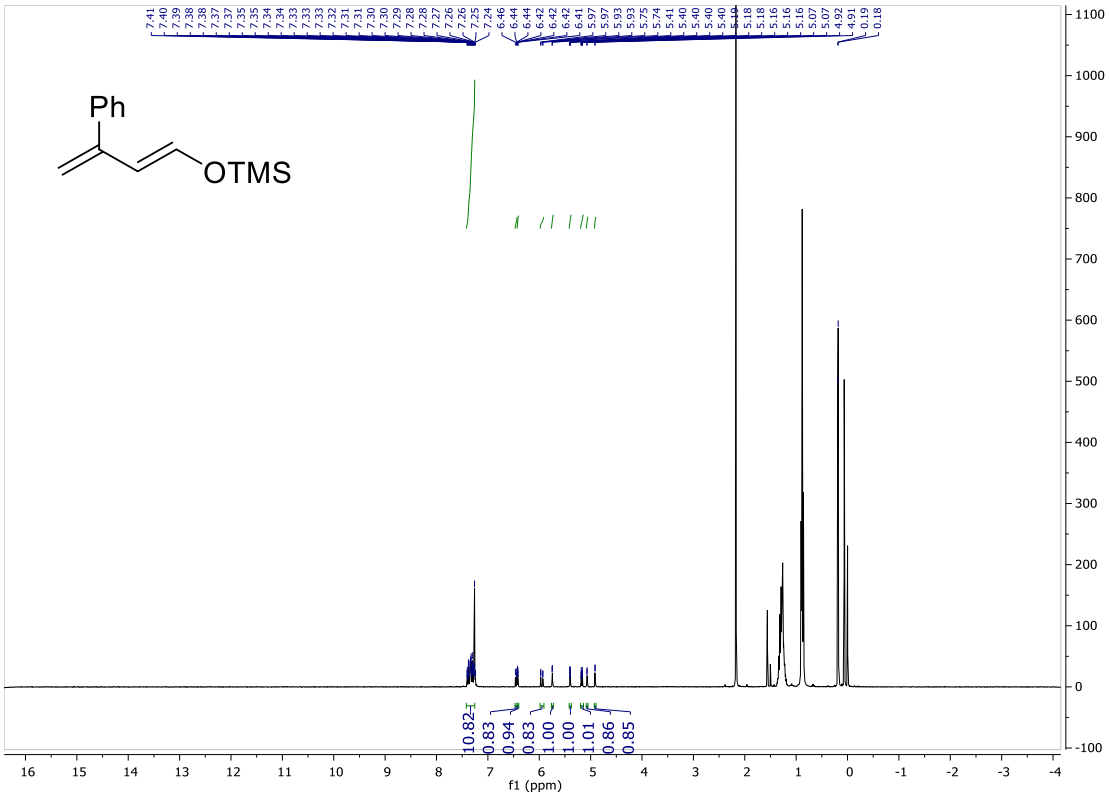

2.74
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

[(Hexa-1,3-dien-1-yl)oxy]trimethylsilane (2c)

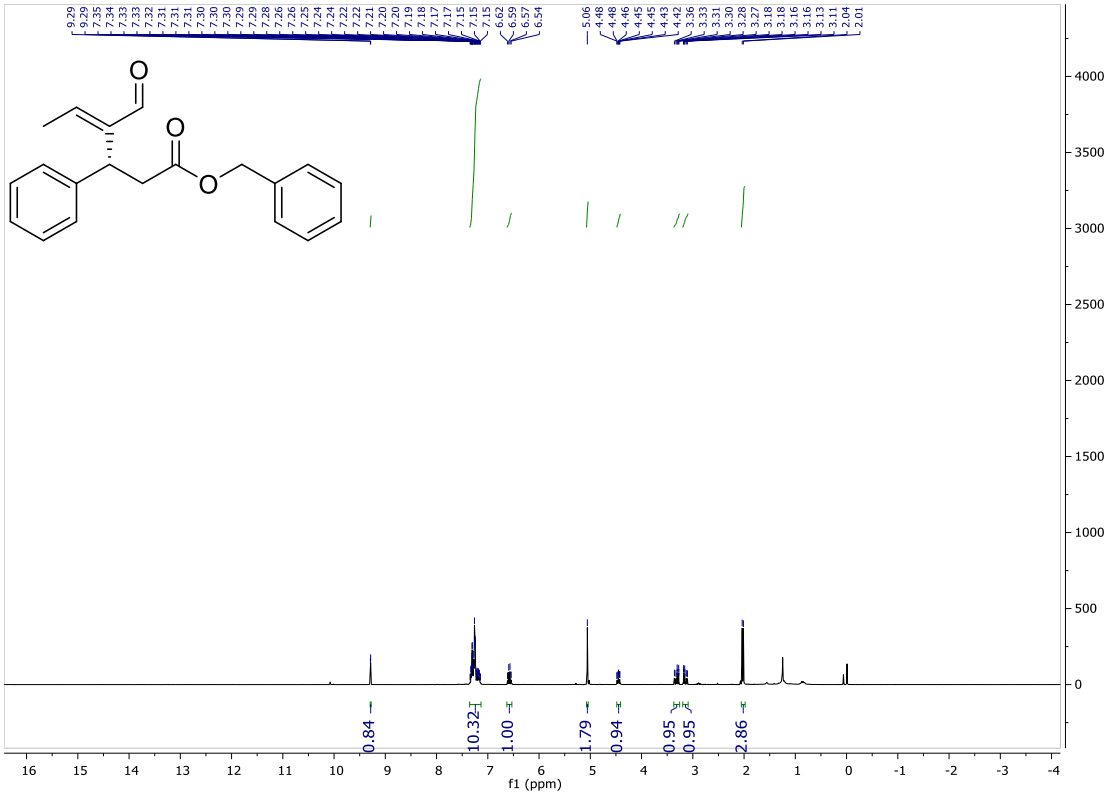


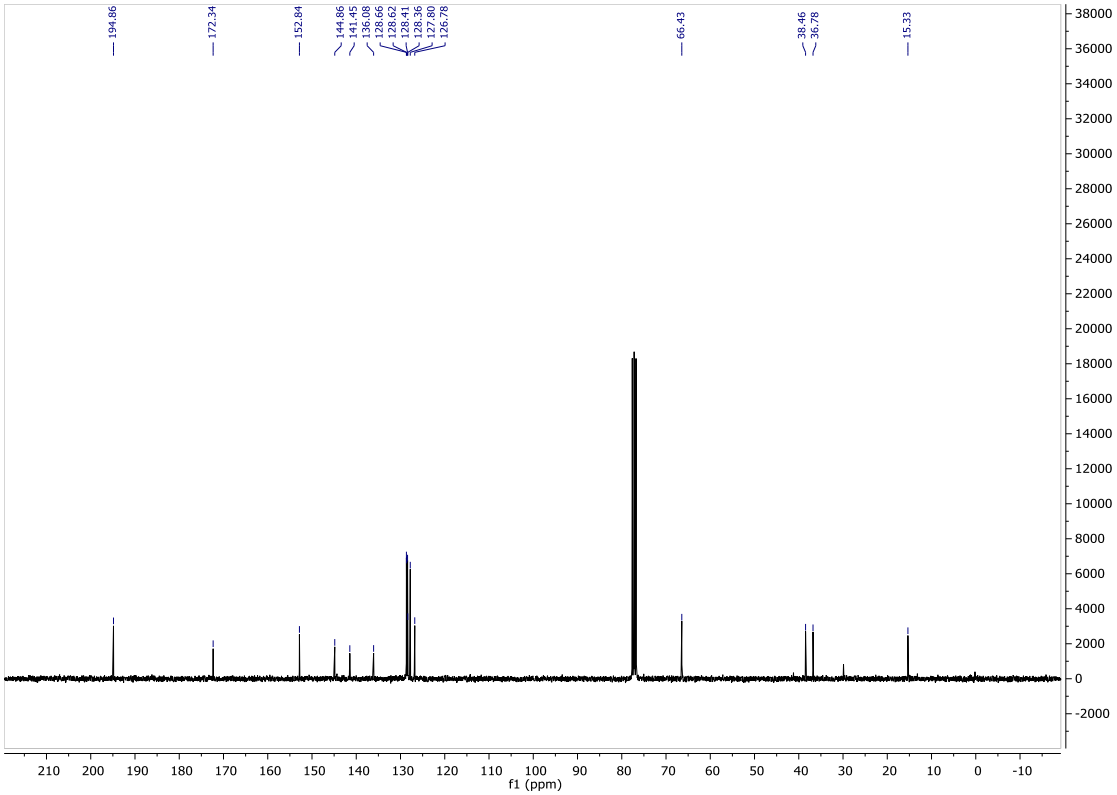


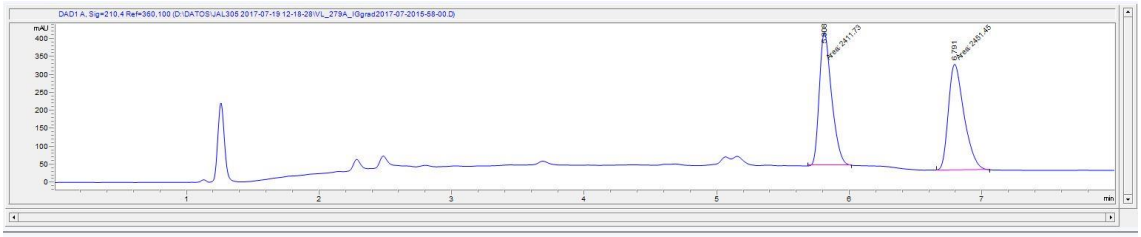
Trimethyl((3-phenylbuta-1,3-dien-1-yl)oxy)silane (2d)



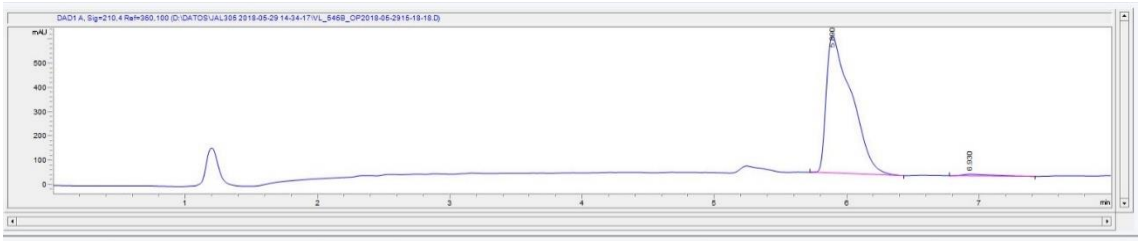
Benzyl (*R*,*E*)-4-formyl-3-phenylhex-4-enoate (5a)





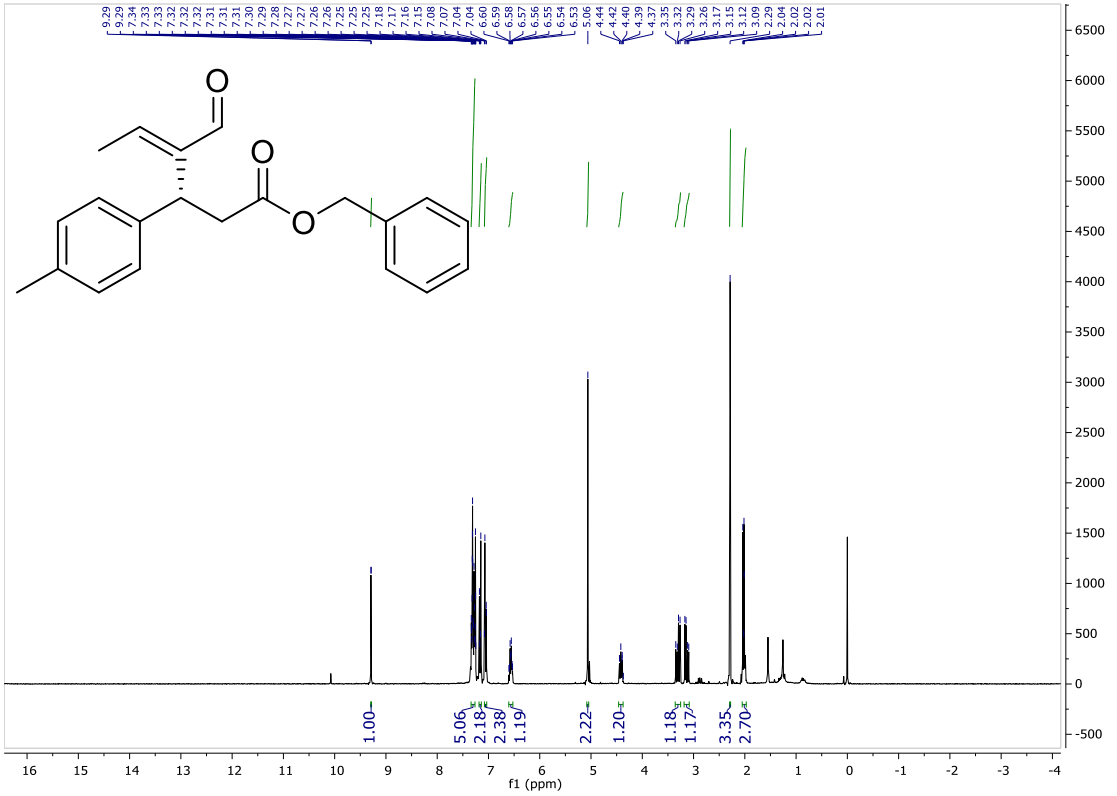


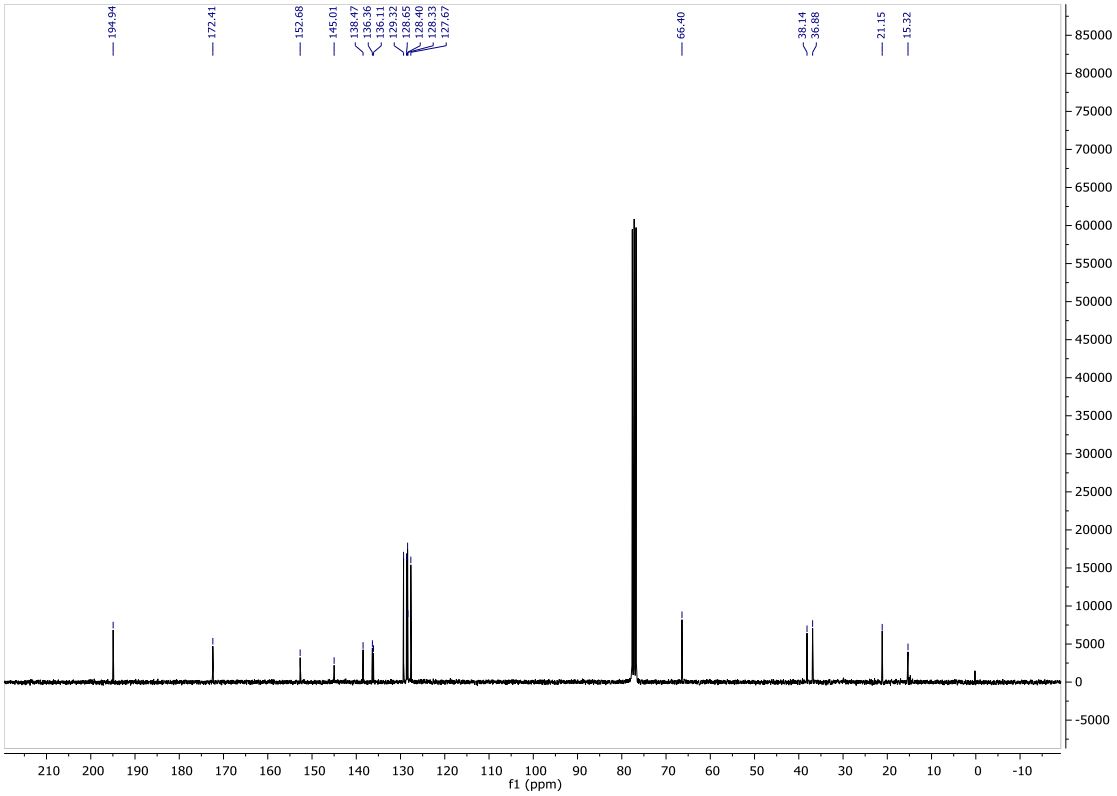
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.808	MM	2411.7	373.2	0.1077	49.592	0.668
2	6.791	MM	2451.5	296.4	0.1379	50.408	0.646

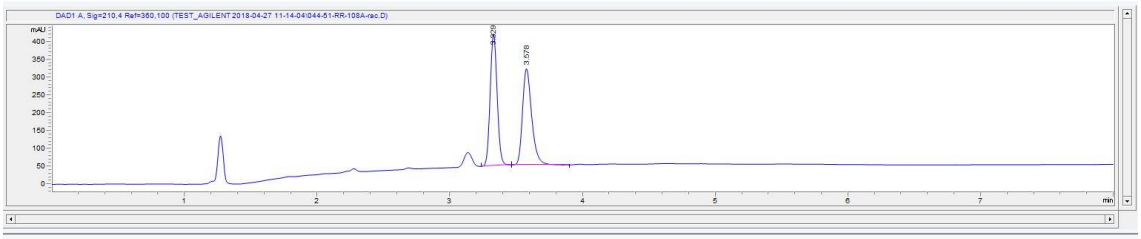


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.89	BB	7494.8	566	0.1805	98.519	0.305
2	6.93	BB	112.7	6.9	0.2297	1.481	0.316

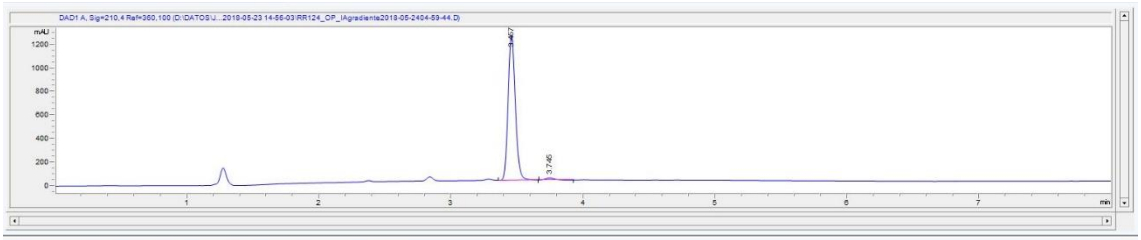
Benzyl (*R*,*E*)-4-formyl-3-(*p*-tolyl)hex-4-enoate (5b)





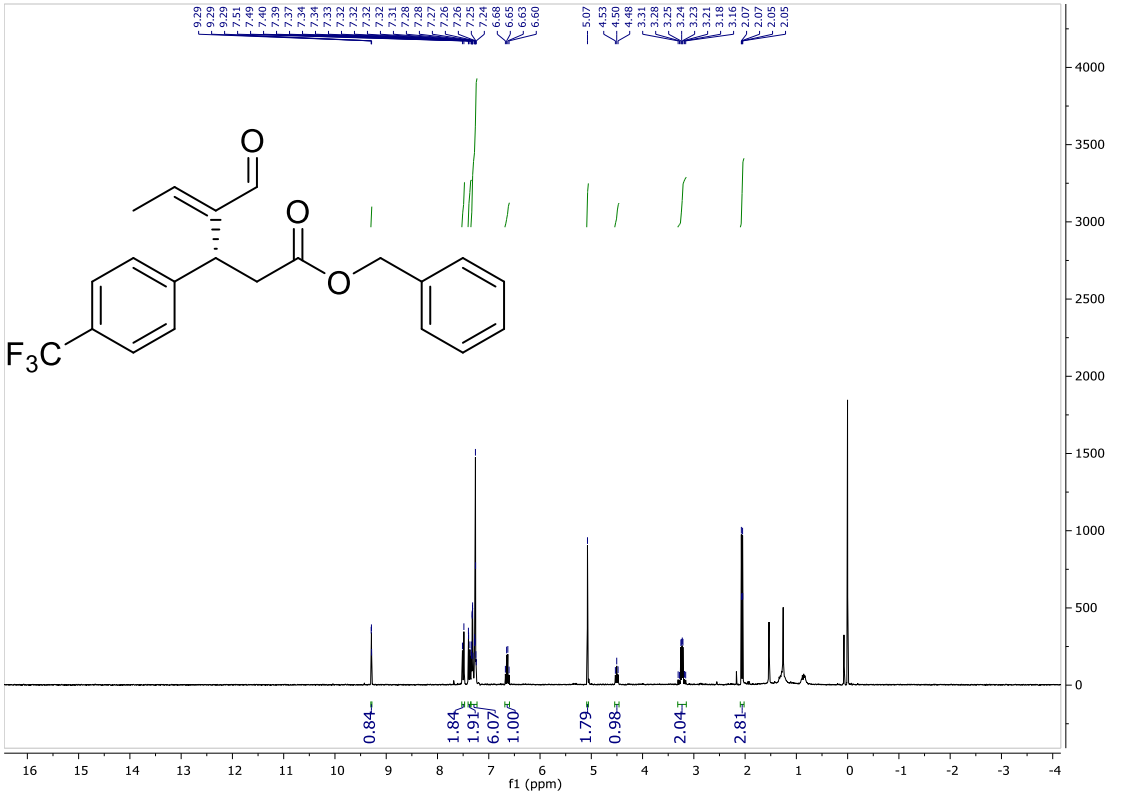


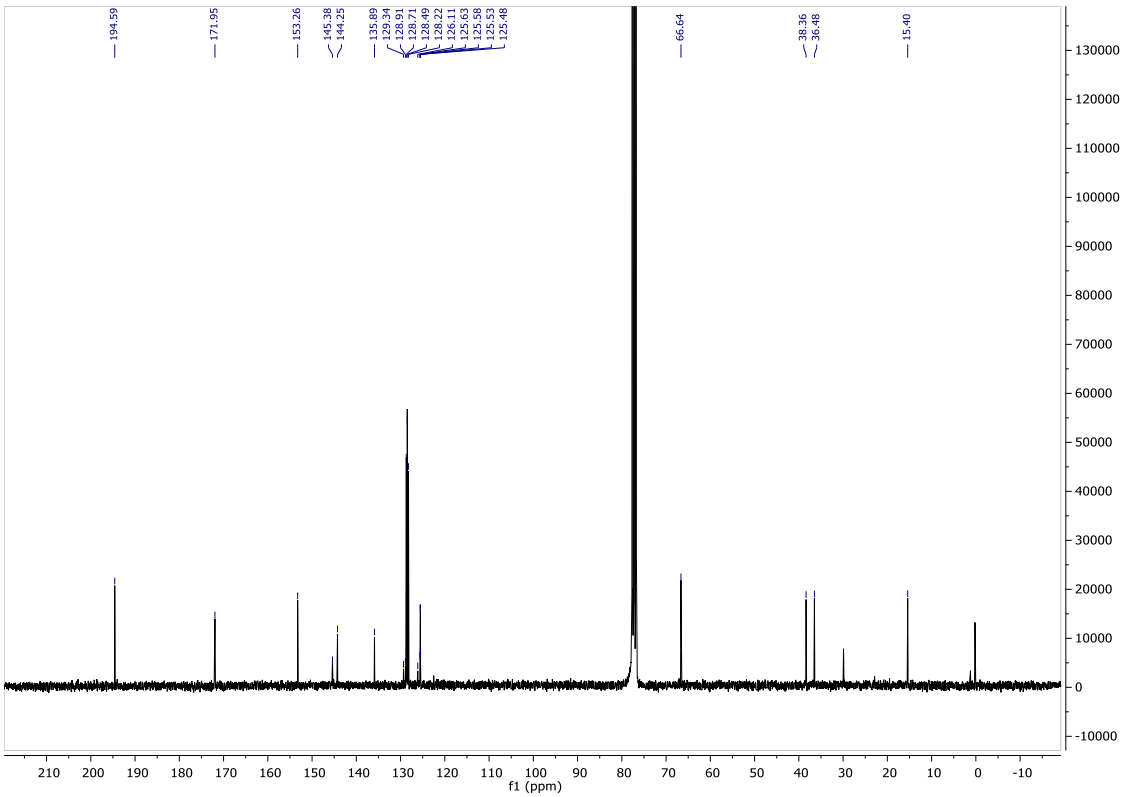
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.329	BB	1350.9	371	0.0565	50.856	0.909
2	3.578	BB	1305.4	271.1	0.0742	49.144	0.703

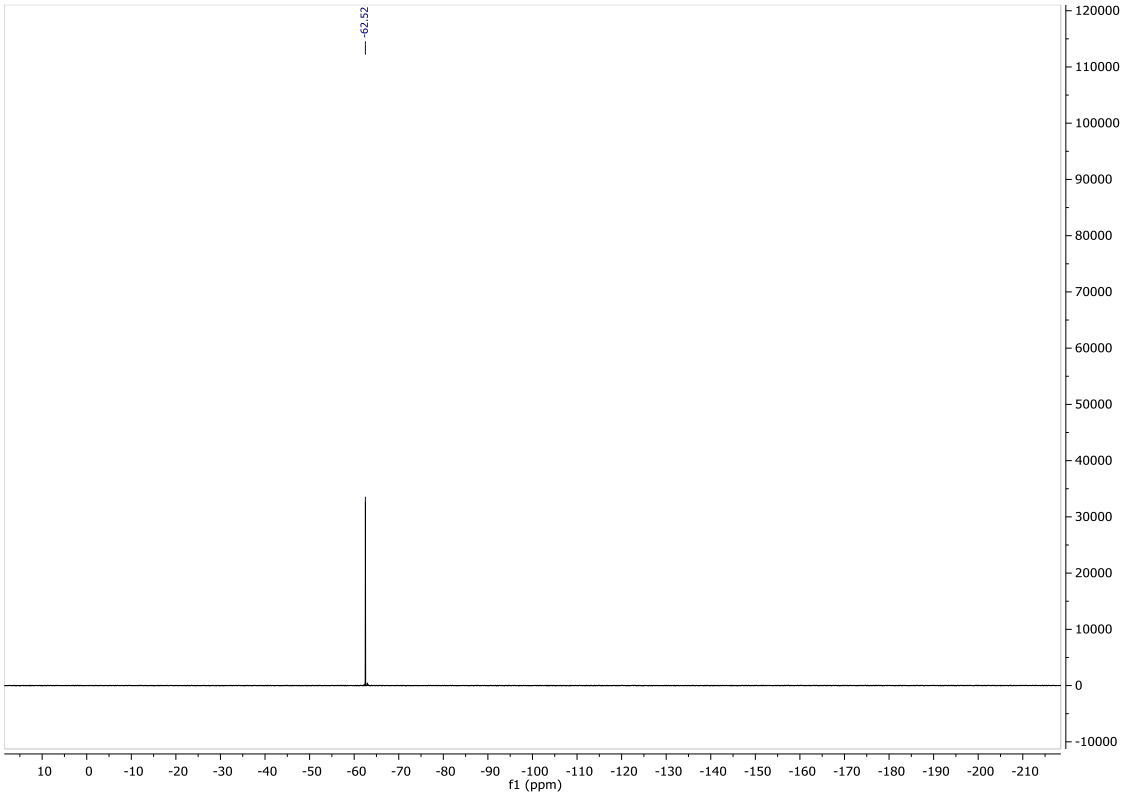


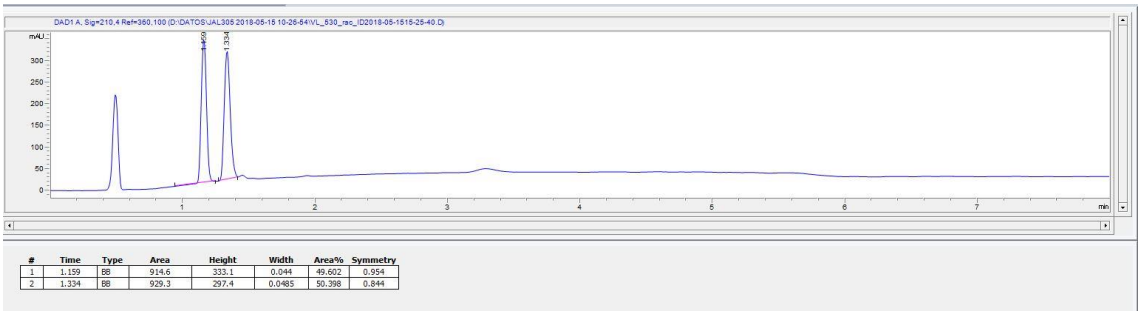
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.457	BB	4671.3	1232.5	0.0602	98.212	0.83
2	3.745	BB	85.1	18	0.073	1.788	0.768

Benzyl (R,*E*)-4-formyl-3-(4-(trifluoromethyl)phenyl)hex-4-enoate (5c)





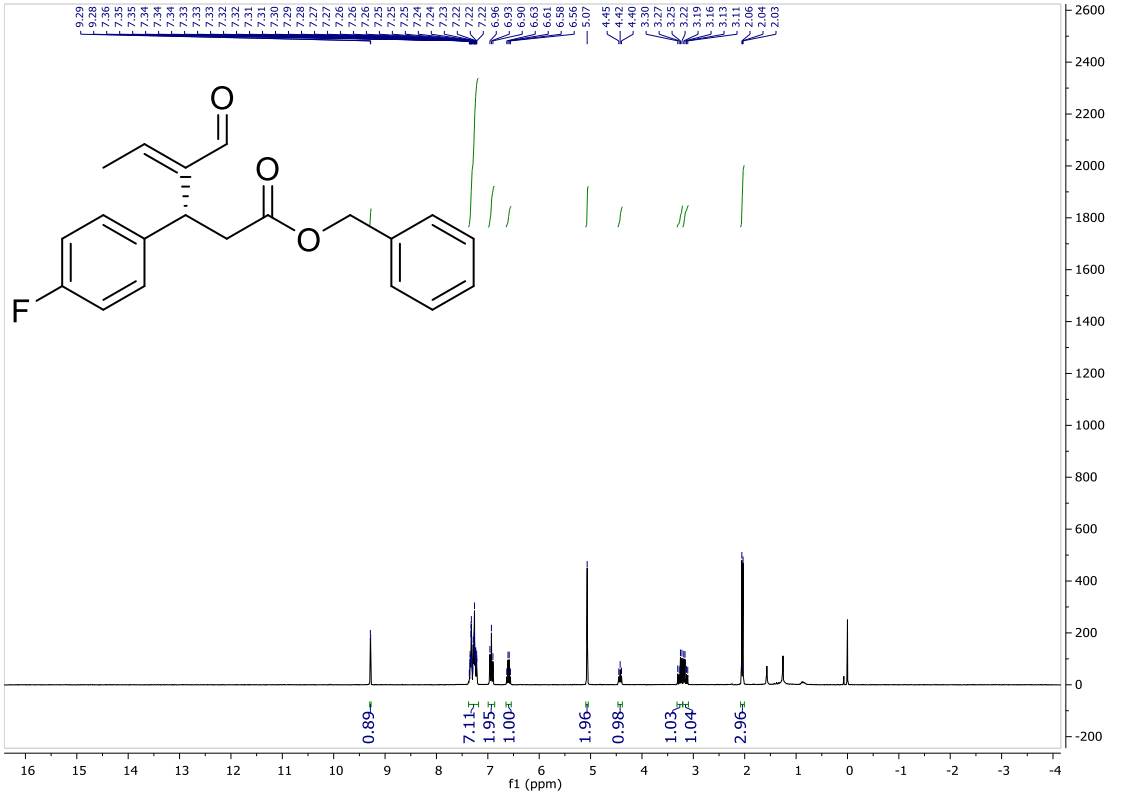


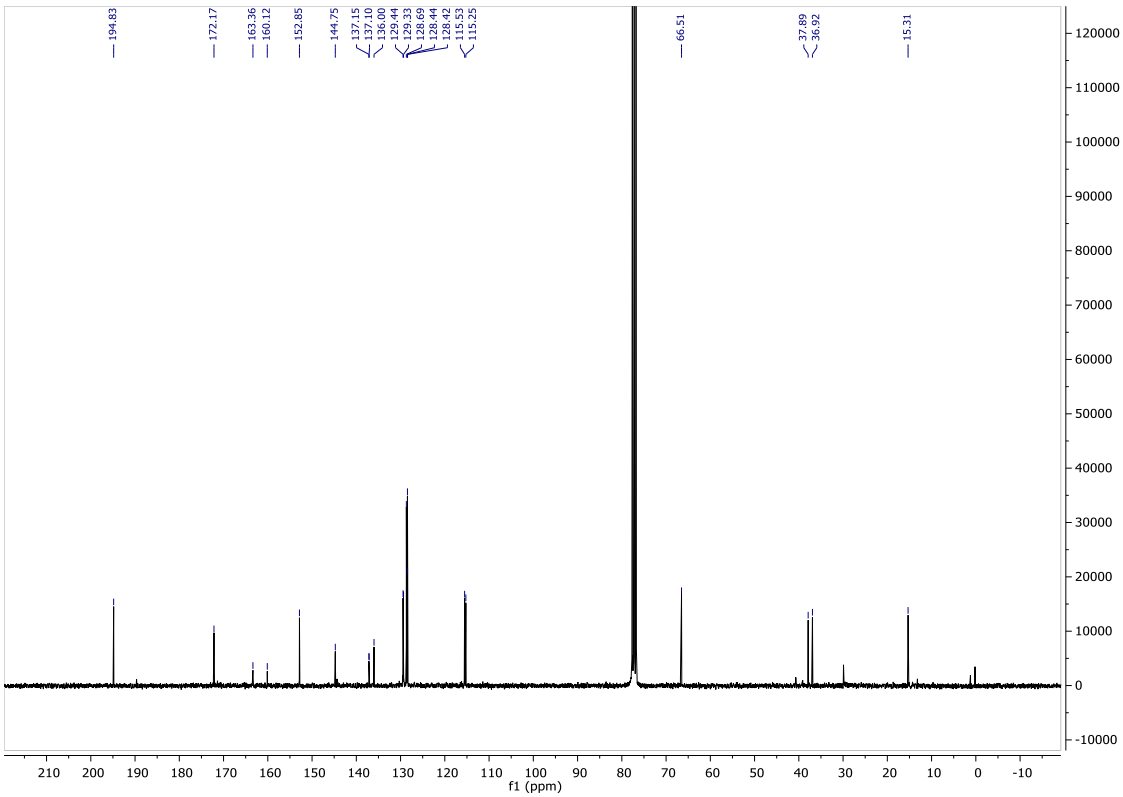


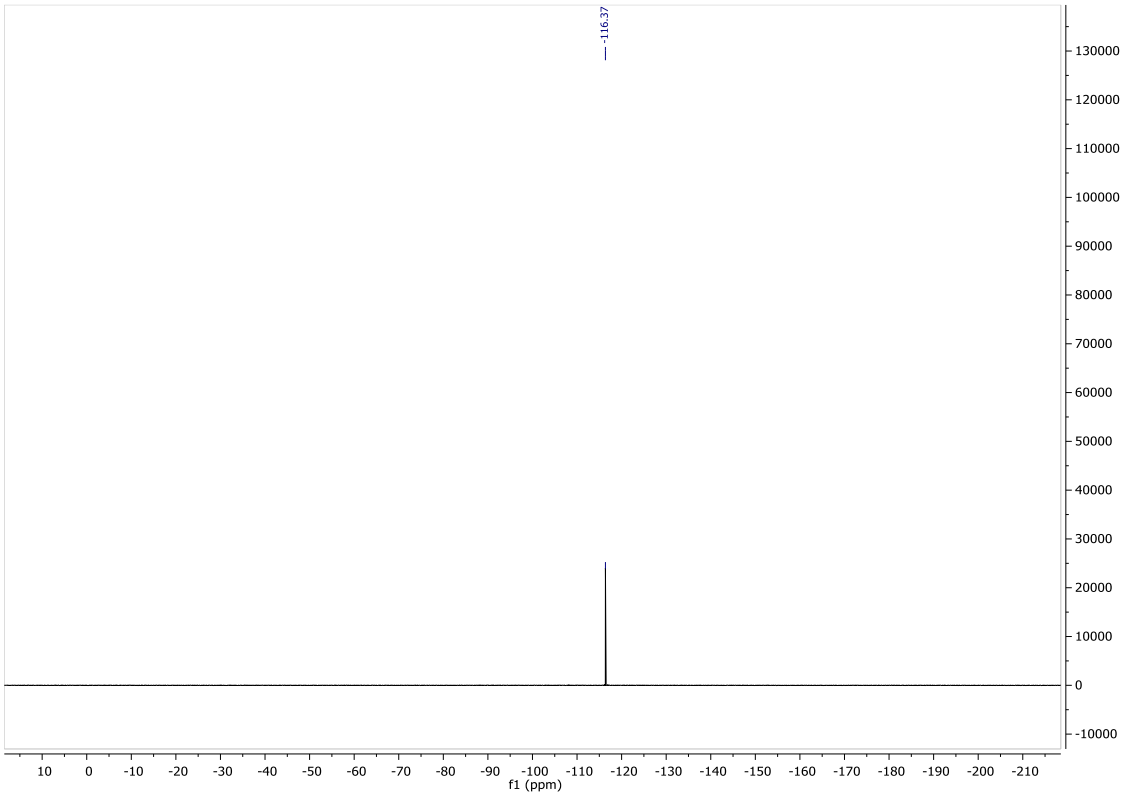
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.159	BB	914.6	333.1	0.044	49.602	0.954
2	1.334	BB	929.3	297.4	0.0485	50.398	0.844

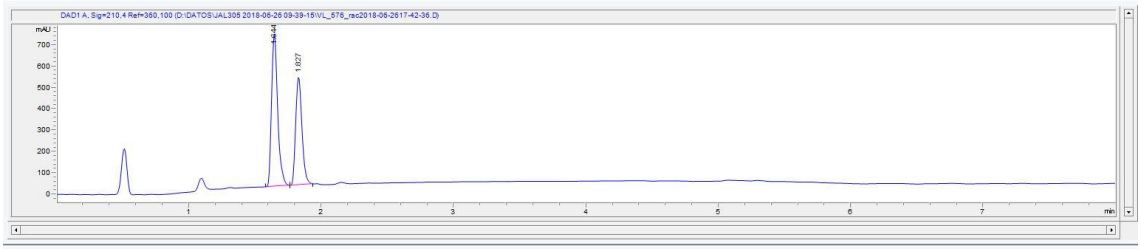
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.249	BB	3020.4	1084.2	0.0445	97.929	0.939
2	1.442	BB	63.9	19.5	0.0502	2.071	0.847

Benzyl (*R*,*E*)-3-(4-fluorophenyl)-4-formylhex-4-enoate (5d)

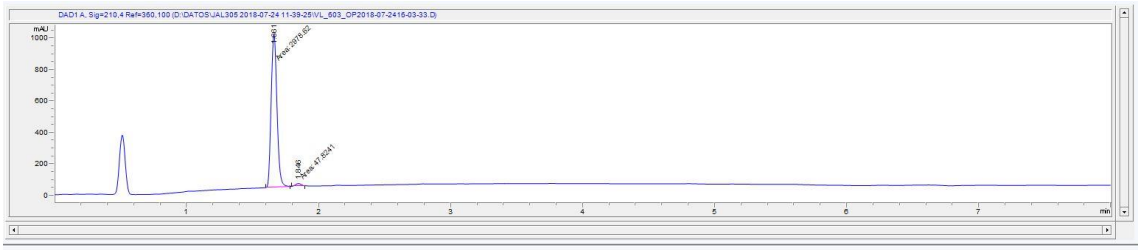






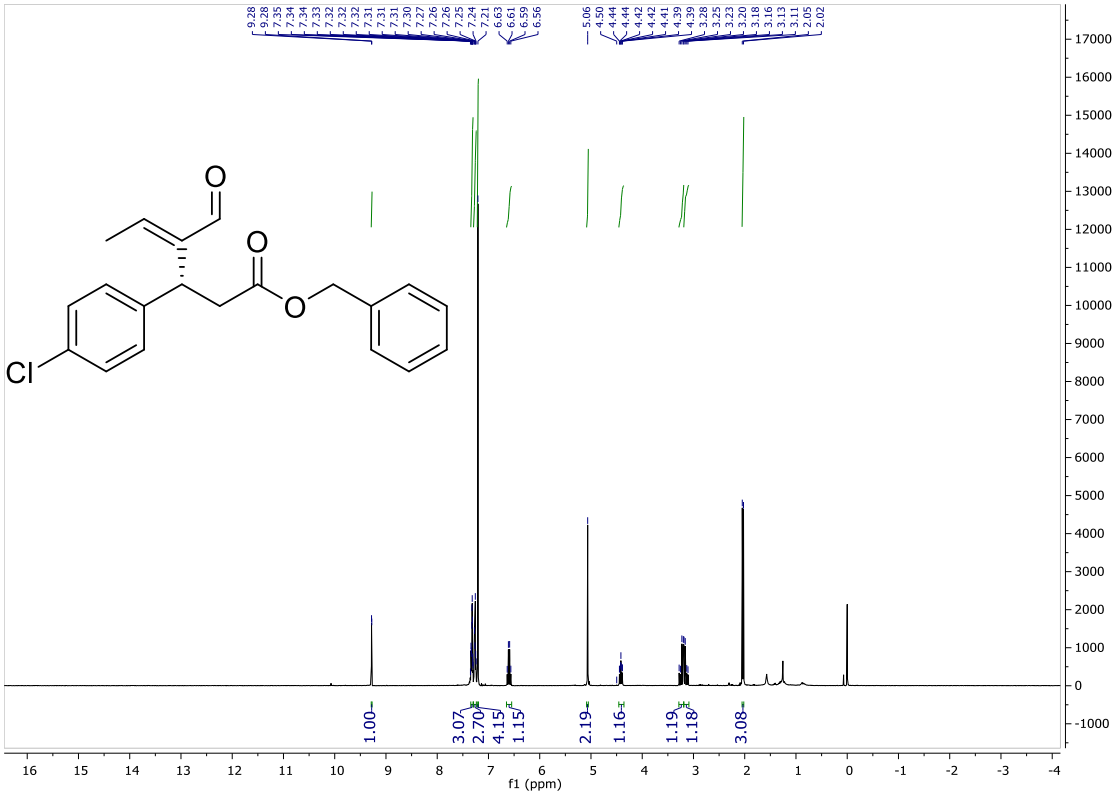


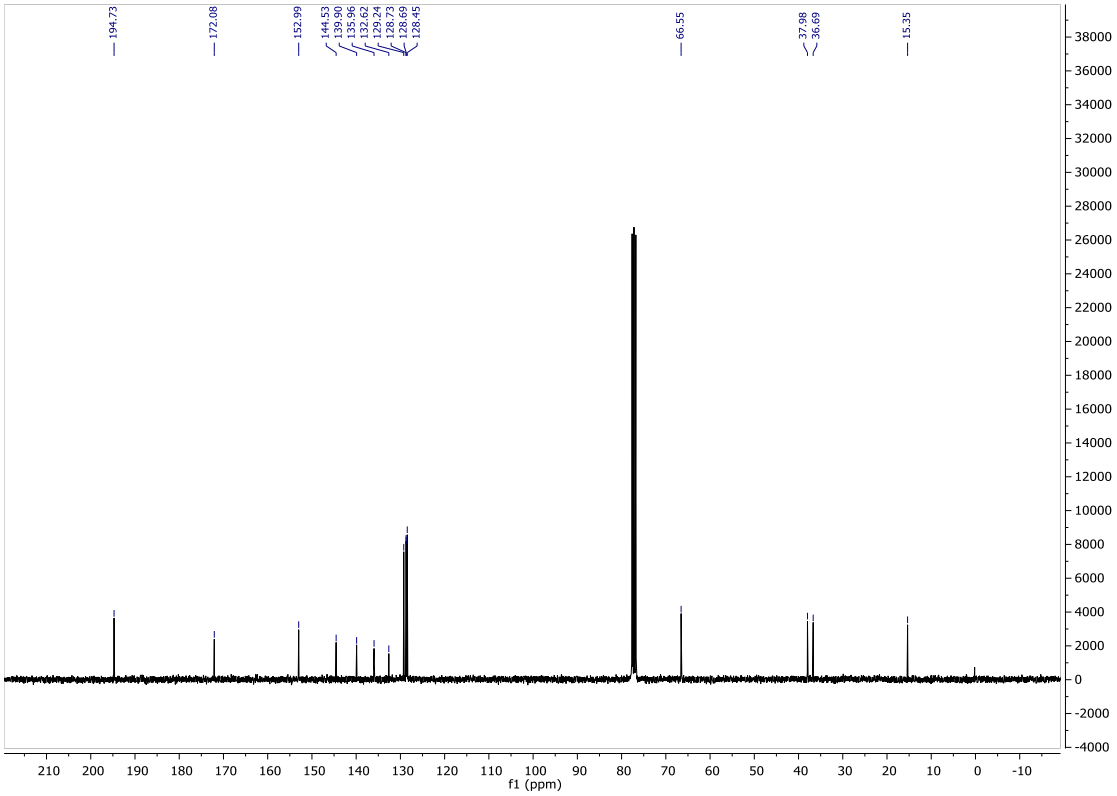
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.644	BB	2301.7	715.2	0.0495	57.917	0.766
2	1.827	BB	1672.4	507.3	0.0525	42.083	0.803

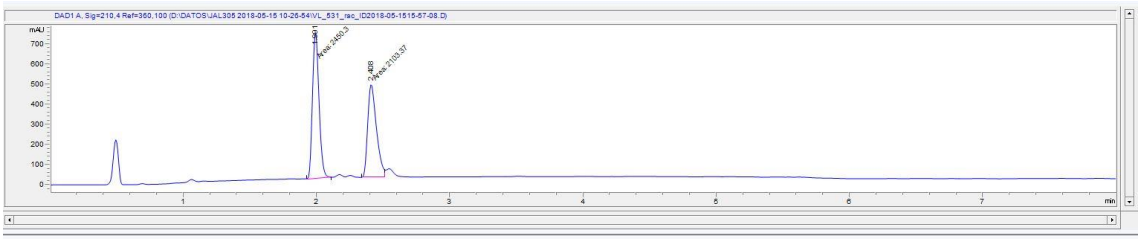


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.661	MM	2978.6	985.1	0.0504	98.420	0.887
2	1.846	MM	47.8	16.8	0.0475	1.580	1.052

Benzyl (*R*,*E*)-3-(4-chlorophenyl)-4-formylhex-4-enoate (5e)



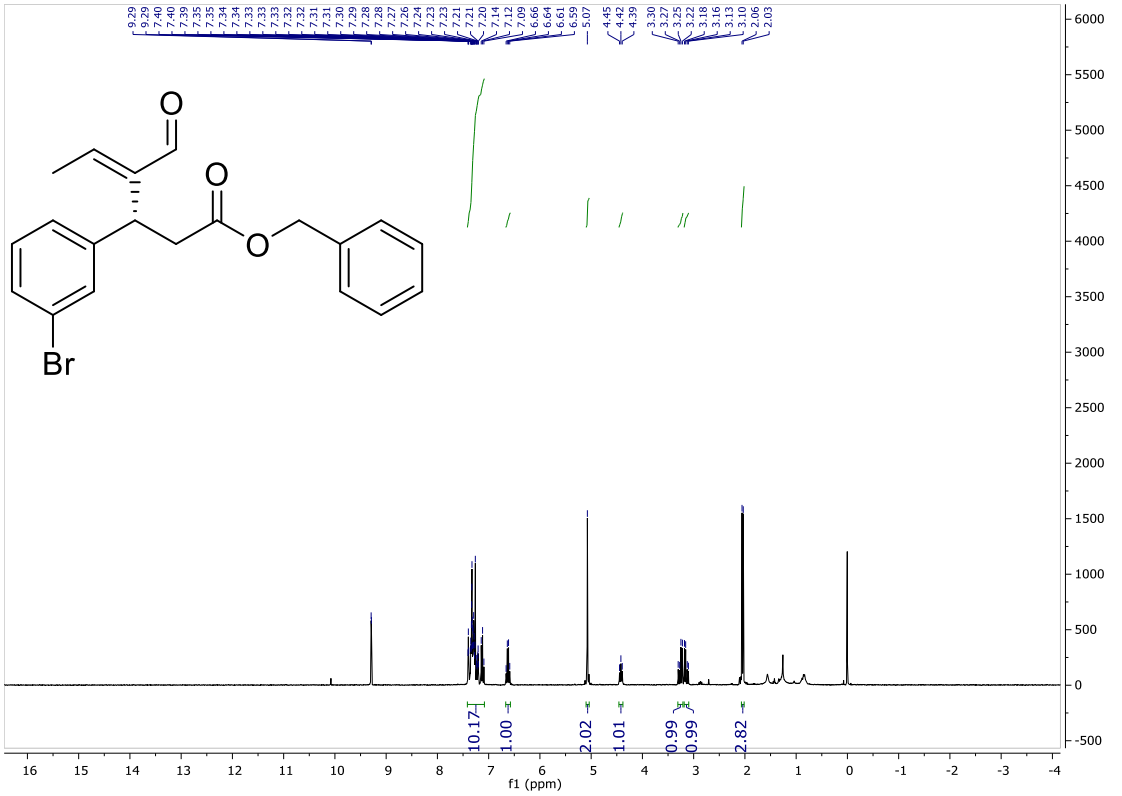


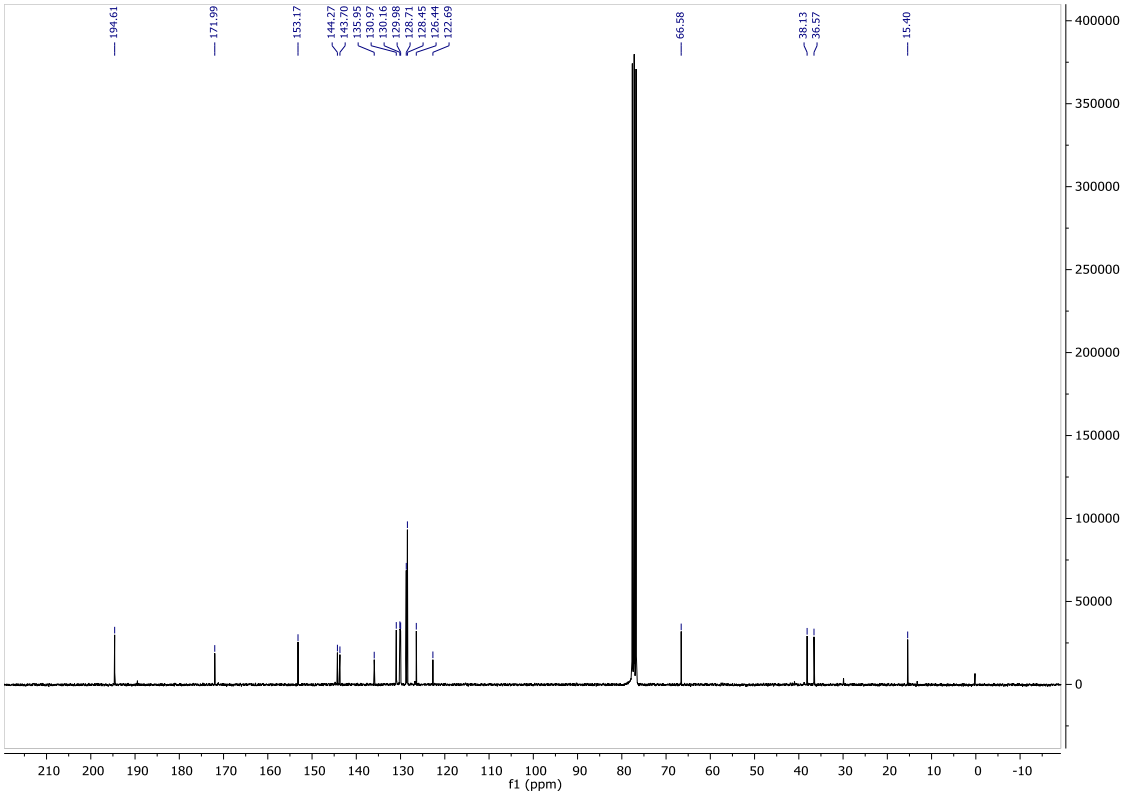


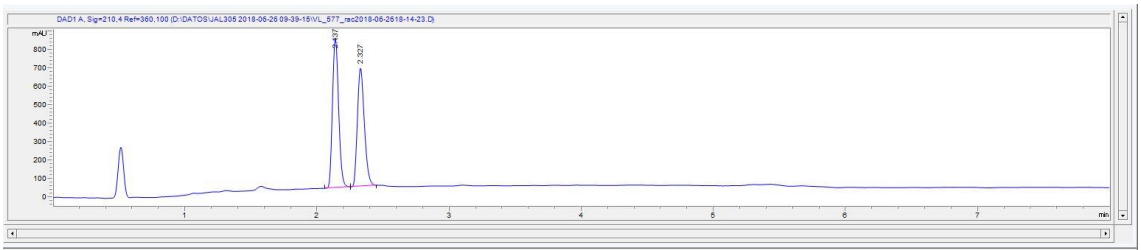
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.991	MM	2450.3	725.6	0.0563	53.809	0.835
2	2.408	MF	2103.4	460.4	0.0761	46.191	0.628

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.093	BB	4348.6	1238.7	0.055	97.488	0.756
2	2.555	BB	112.1	25.9	0.0665	2.512	0.674

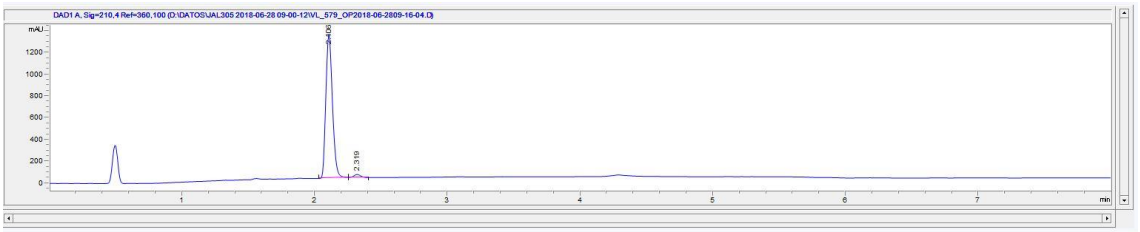
Benzyl (*R*,*E*)-3-(3-bromophenyl)-4-formylhex-4-enoate (5f)





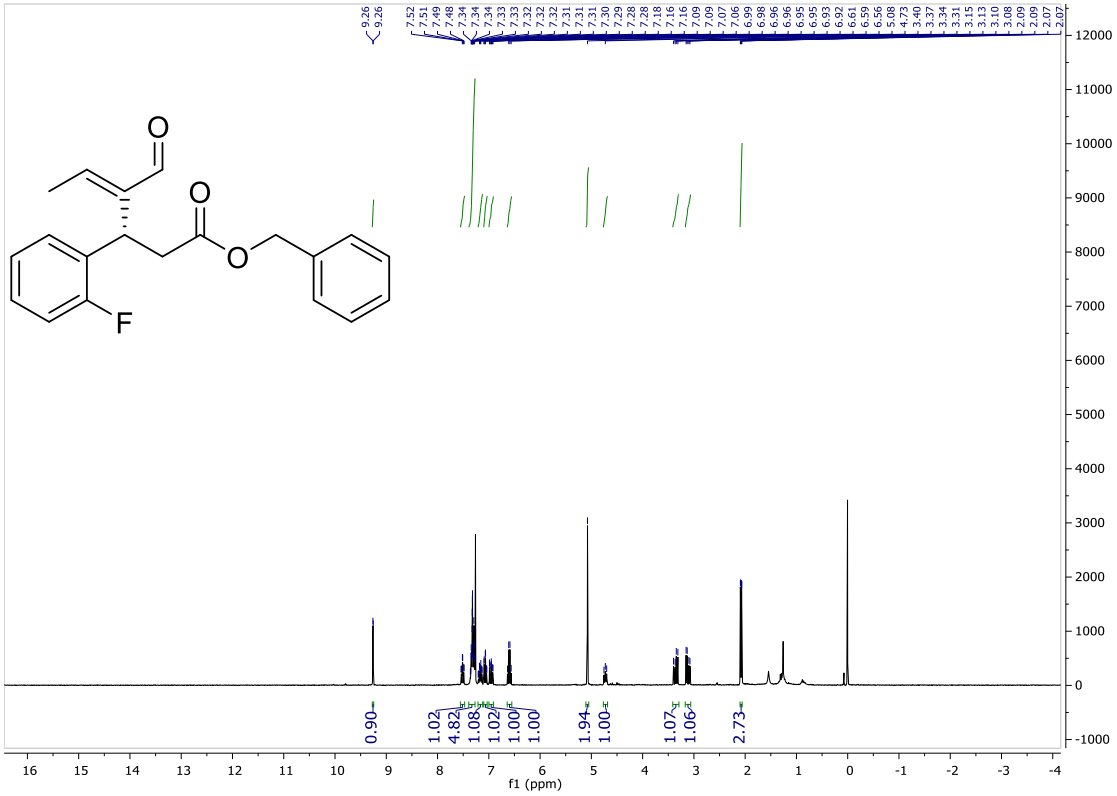


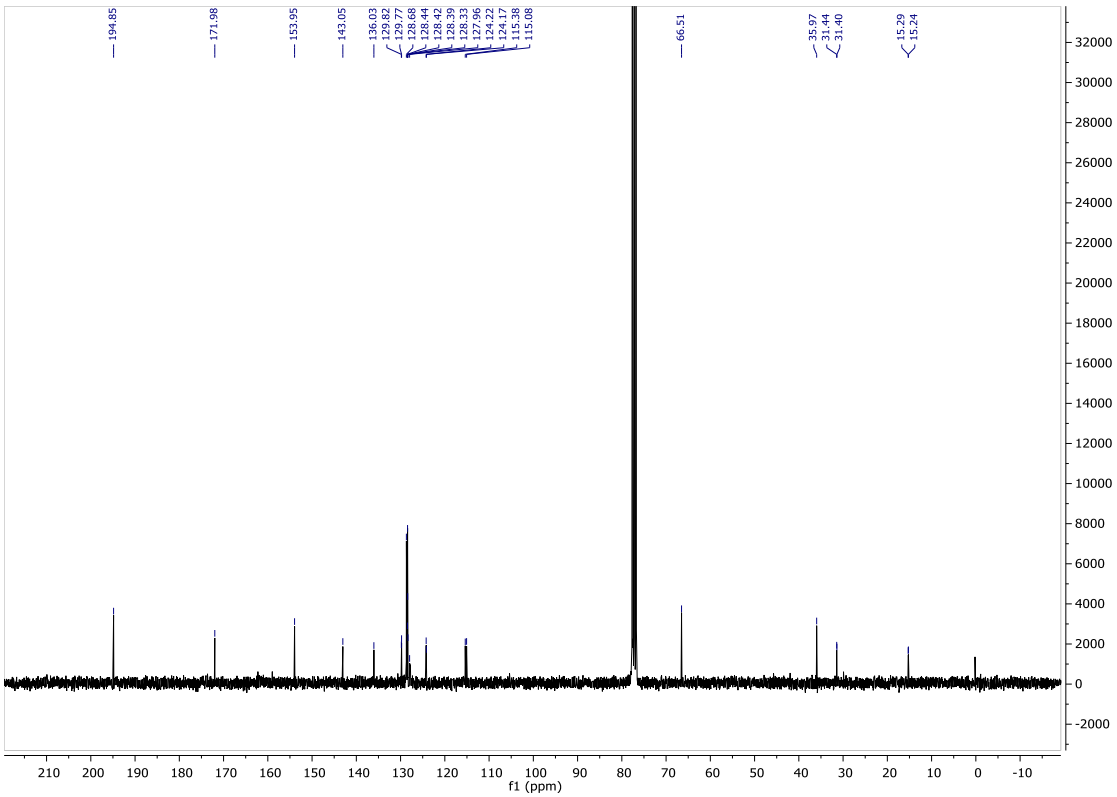
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.137	BB	2619.2	813.7	0.0496	52.666	0.849
2	2.327	BB	2354	644.8	0.0566	47.334	0.766

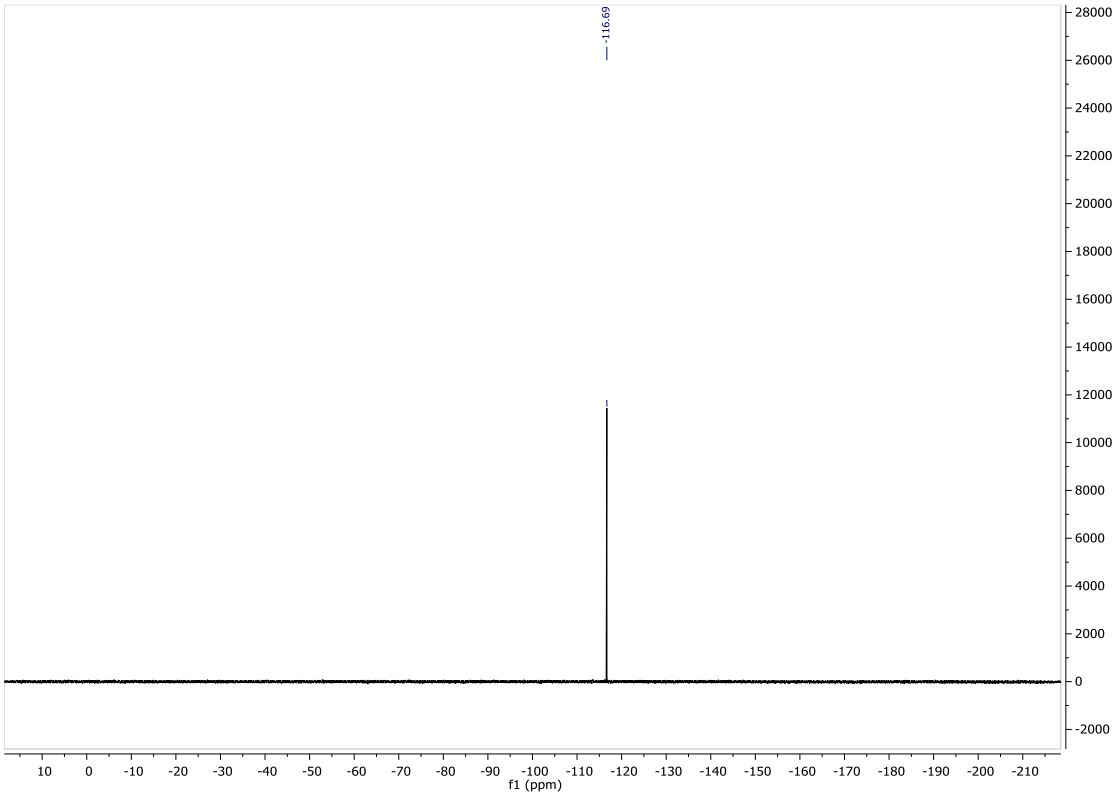


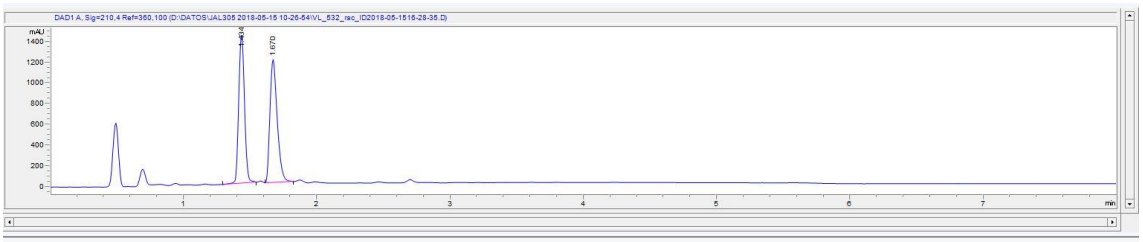
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.106	BB	4571.3	1333.8	0.054	97.908	0.79
2	2.319	BB	97.7	28.1	0.0545	2.092	0.836

Benzyl (*S*,*E*)-3-(2-fluorophenyl)-4-formylhex-4-enoate (5g)

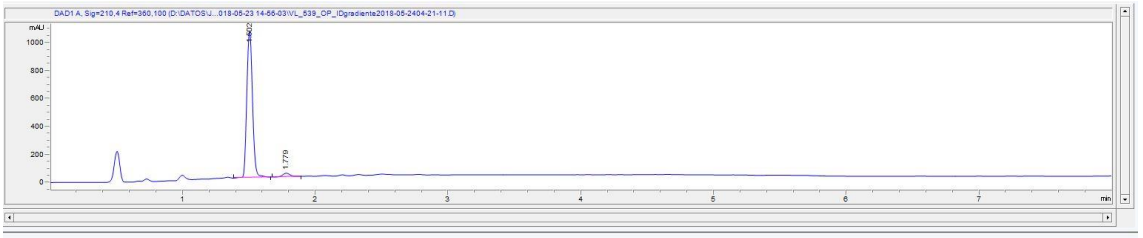






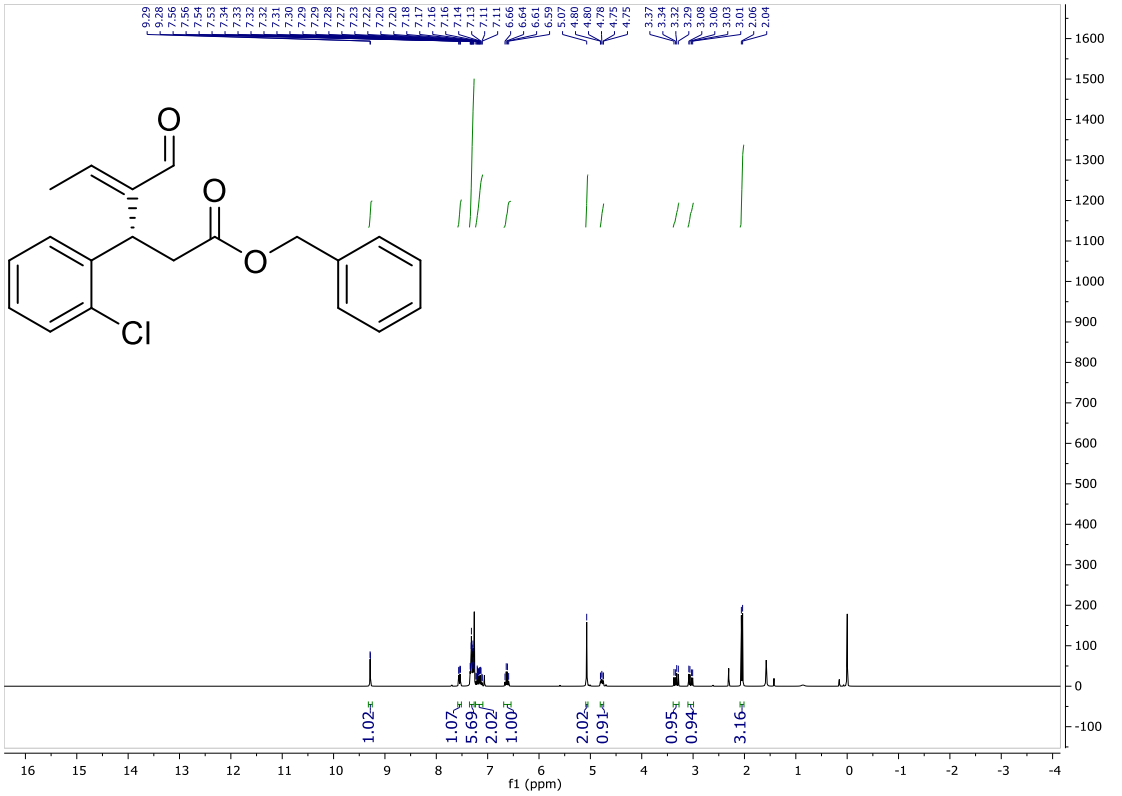


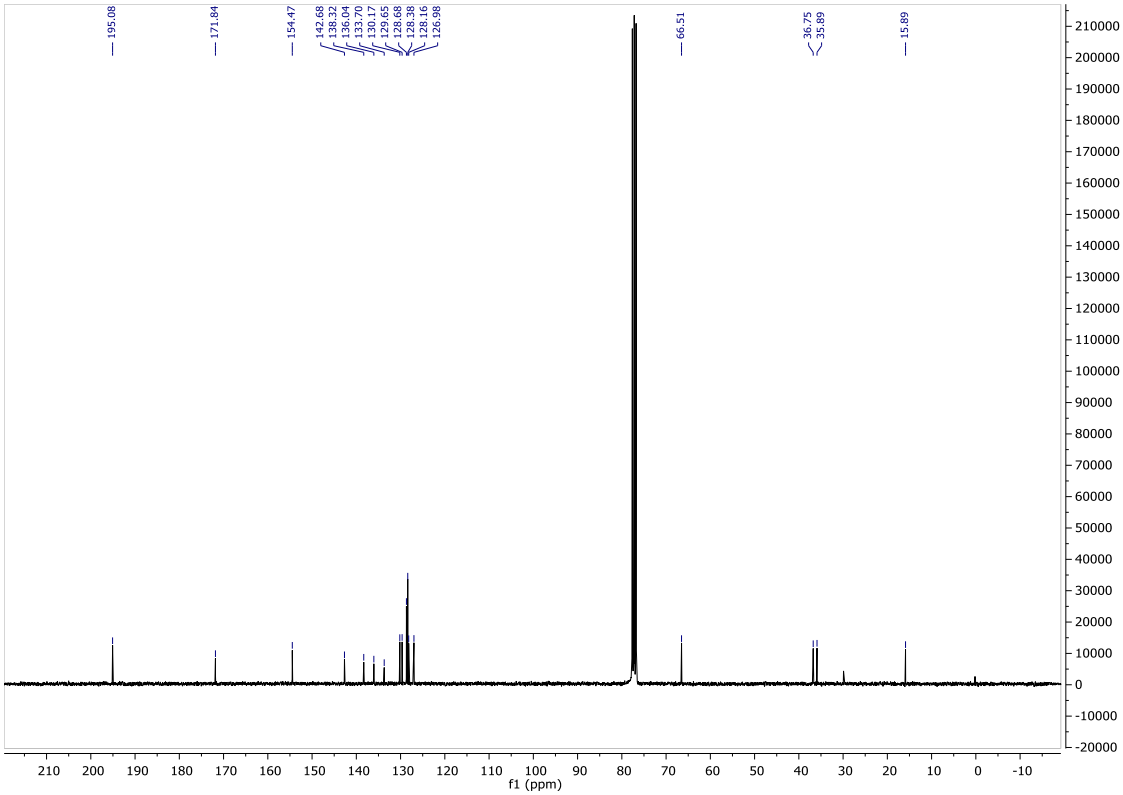
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.434	BB	4296.4	1434.4	0.0489	49.056	0.922
2	1.67	BB	4461.7	1181.8	0.058	50.944	0.686

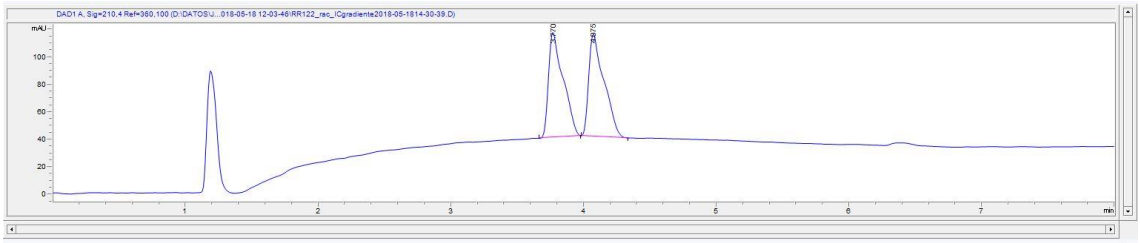


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.502	BB	3120.8	1054.8	0.0465	96.950	0.89
2	1.779	BB	98.2	25.7	0.0585	3.050	0.888

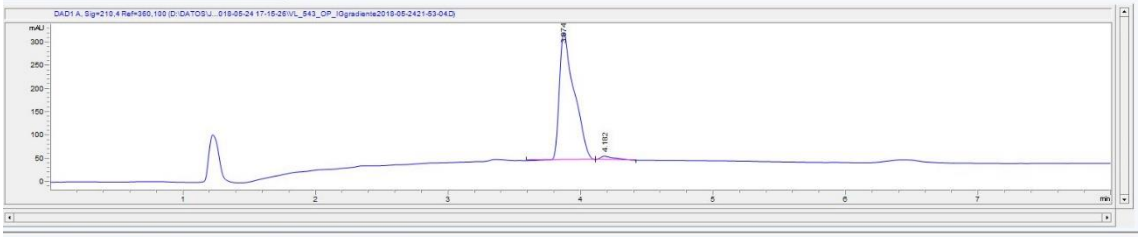
Benzyl (*S*,*E*)-3-(2-chlorophenyl)-4-formylhex-4-enoate (5h)





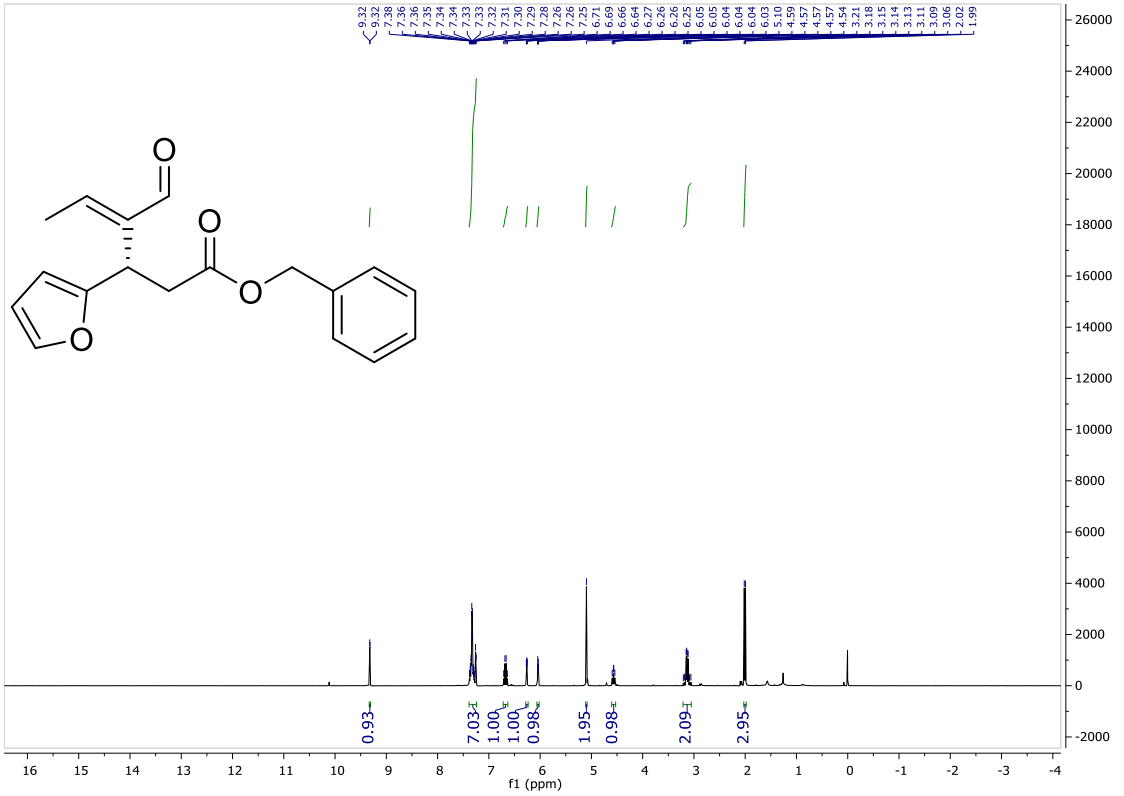


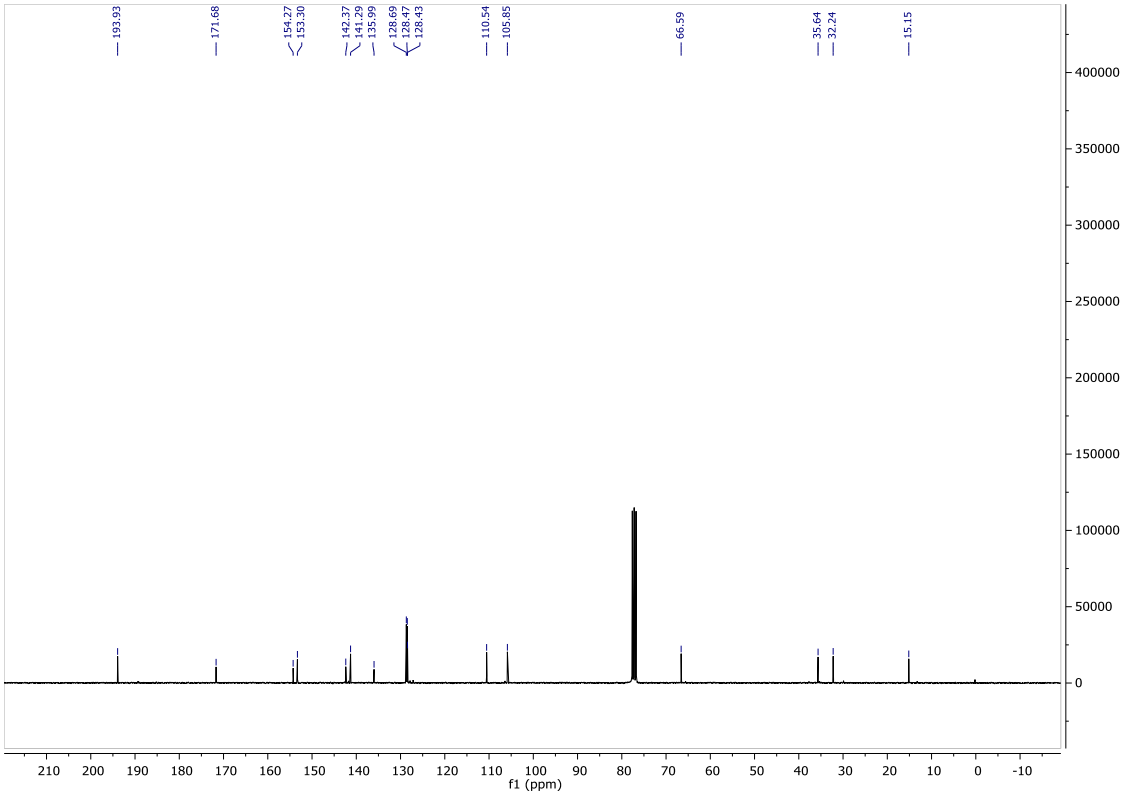
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.77	BB	587.2	76.6	0.1054	49.546	0.401
2	4.075	BB	598	74.7	0.1114	50.454	0.395

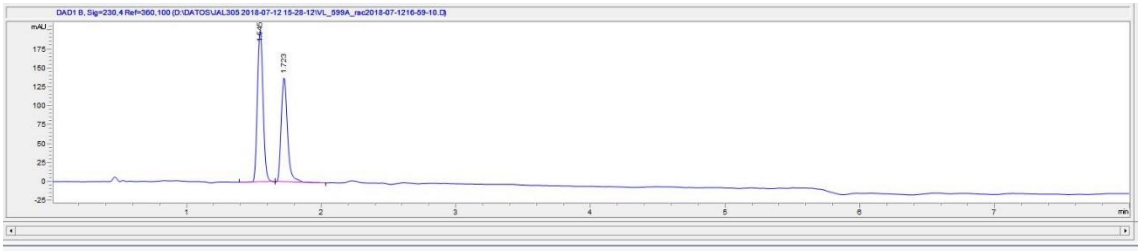


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3,874	BB	2139,4	276,1	0,1084	97,401	0,406
2	4,182	BB	57,1	7,4	0,1077	2,599	0,382

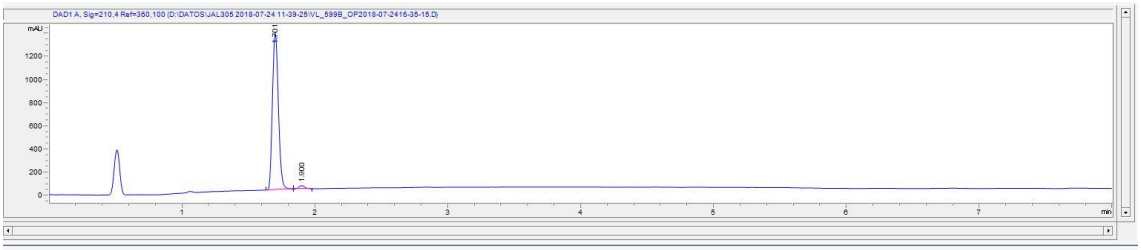
Benzyl (*S*,*E*)-4-formyl-3-(furan-2-yl)hex-4-enoate (5i)





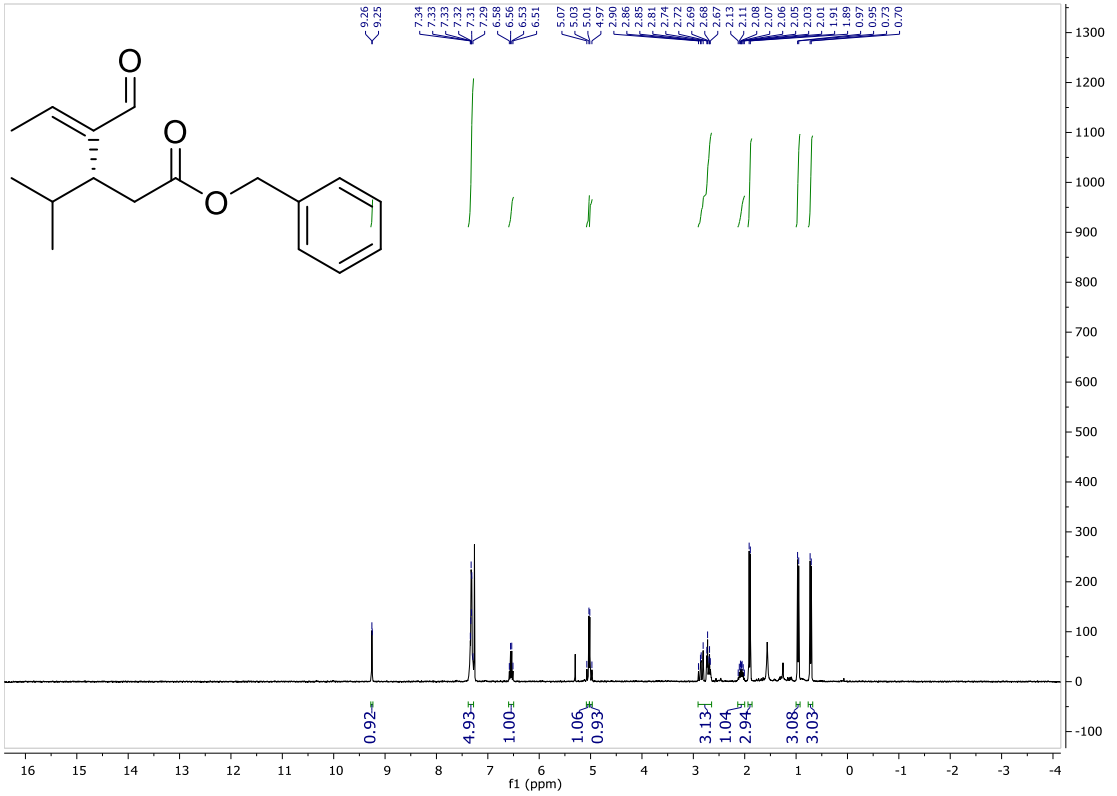


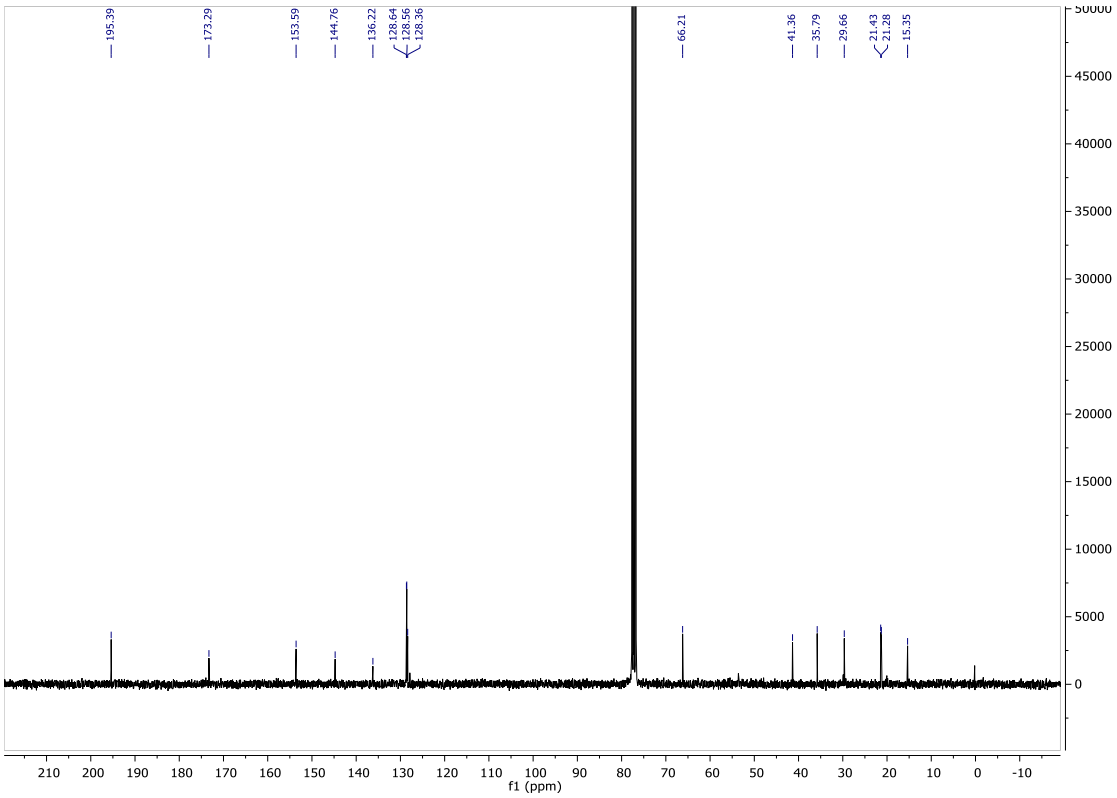
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.545	BB	585.7	199.9	0.0462	56.408	0.897
2	1.723	BB	452.6	138.6	0.0521	43.592	0.765

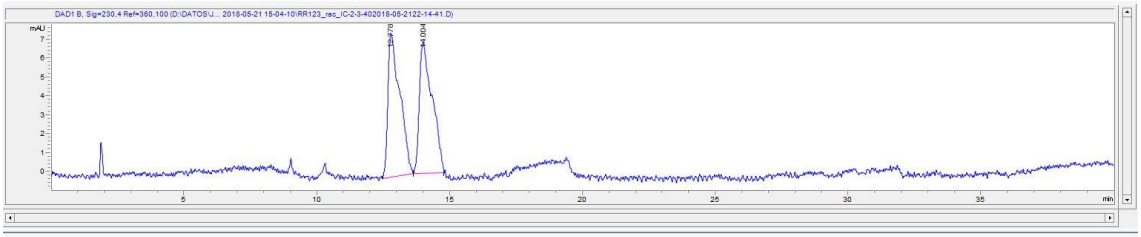


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.701	BB	4192	1356.1	0.0501	97.901	0.846
2	1.9	BB	89.9	28.8	0.0504	2.099	0.87

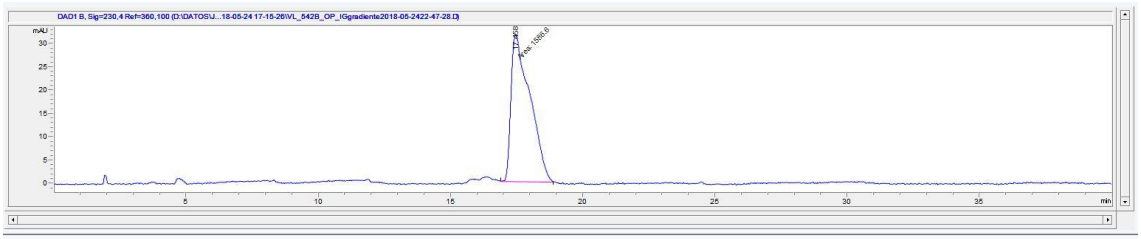
Benzyl (*R*,*E*)-4-formyl-3-isopropylhex-4-enoate (5j)





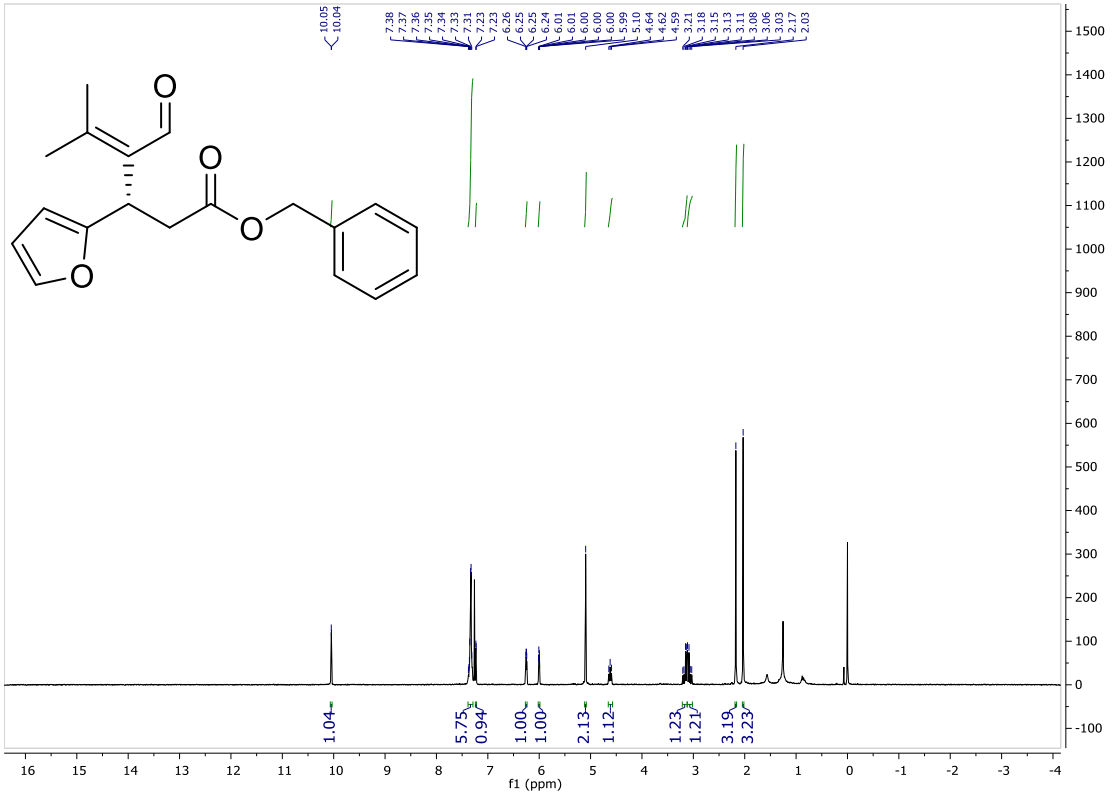


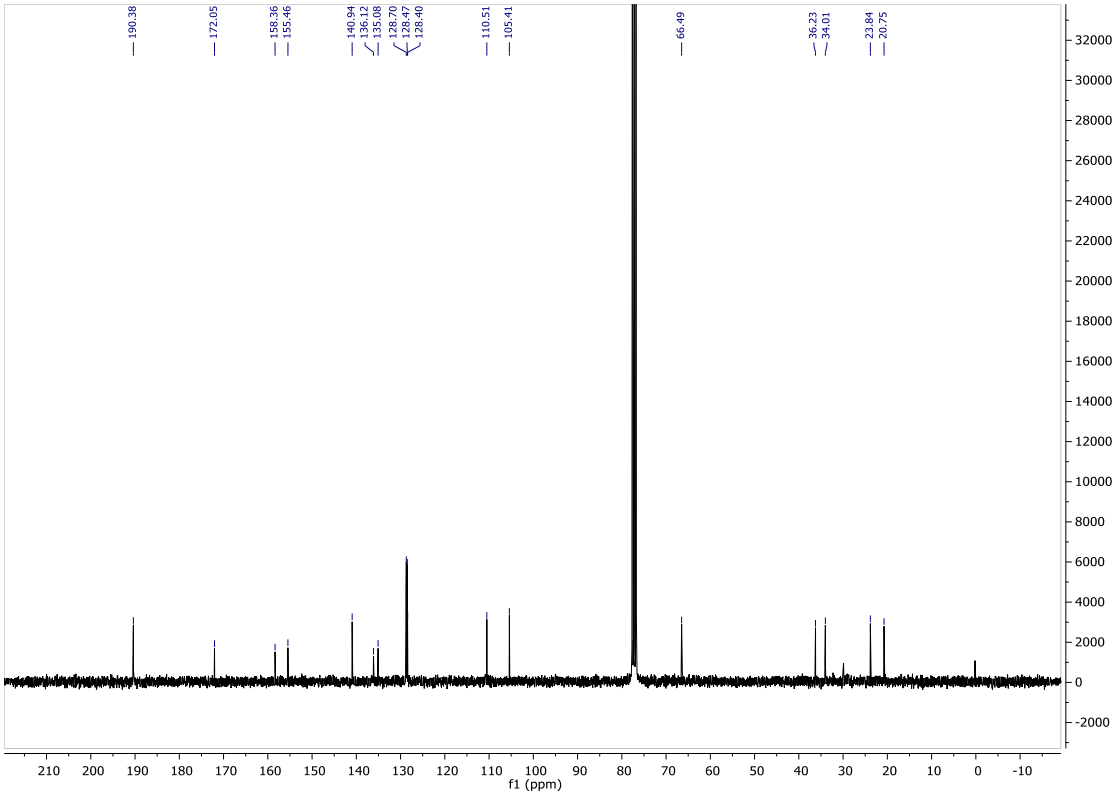
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.778	BB	240.3	7.7	0.3841	50.511	0.317
2	14.004	BB	235.5	7	0.4126	49.489	0.428

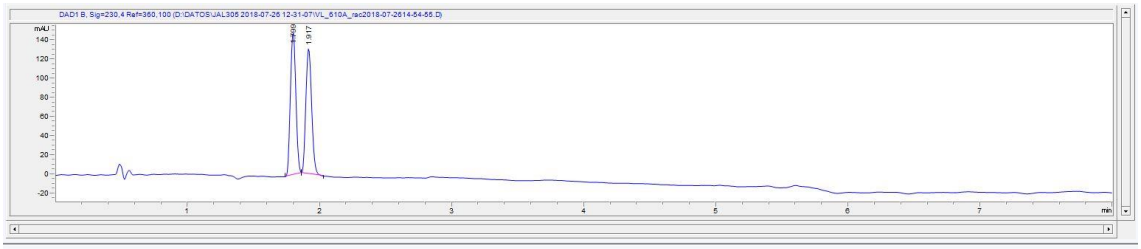


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.458	MM	1586.6	31.6	0.8362	100.000	0.324

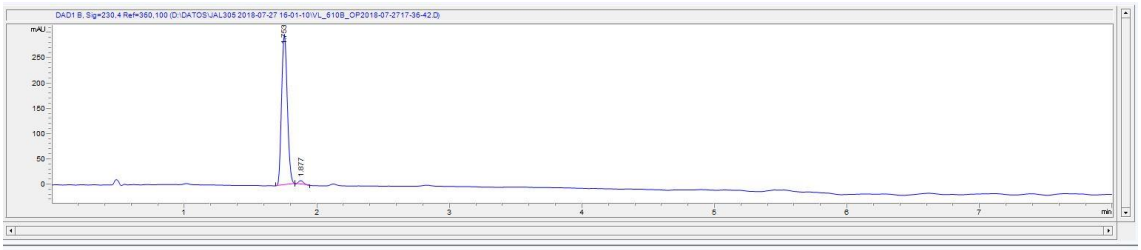
Benzyl (*S*)-4-formyl-3-(furan-2-yl)-5-methylhex-4-enoate (5k)





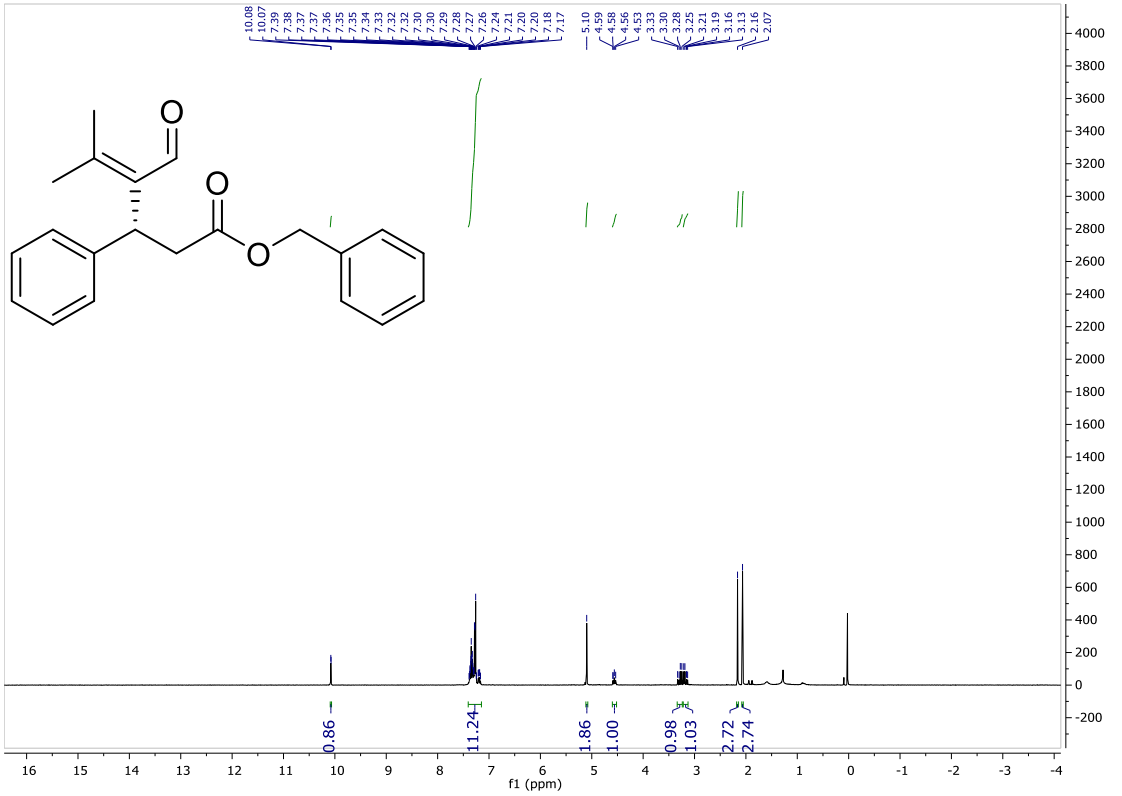


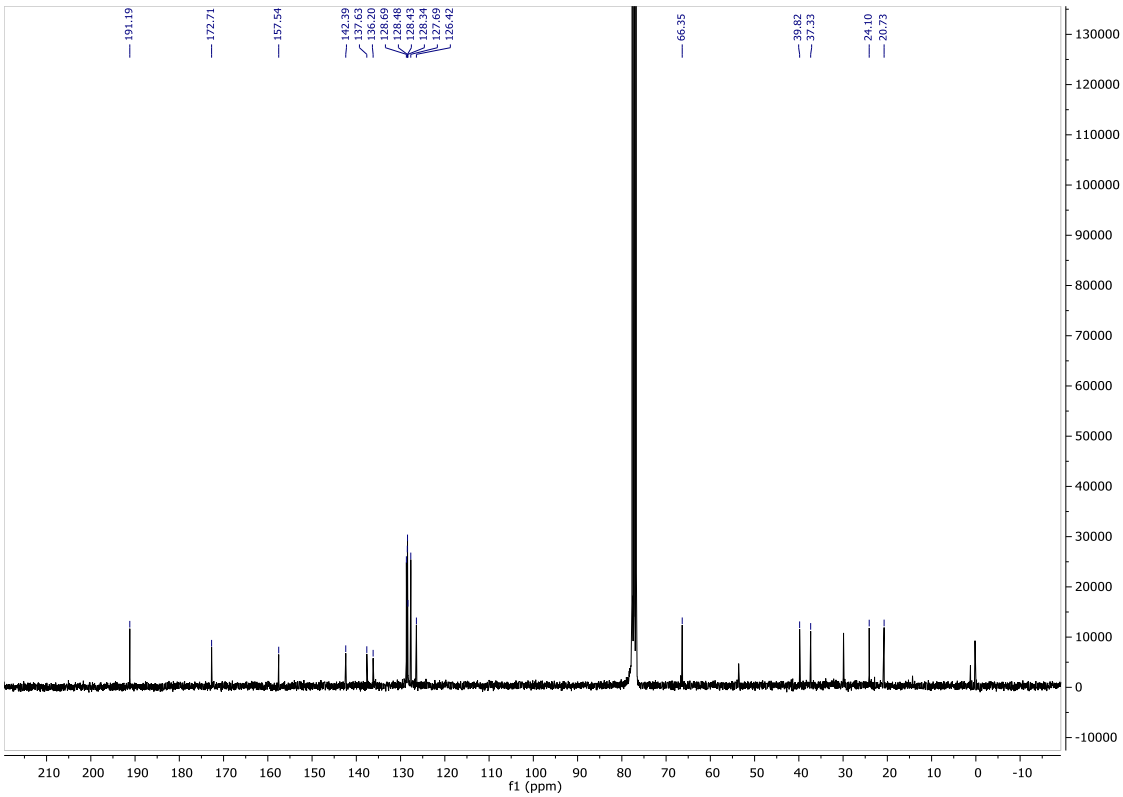
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.799	BB	428.4	149.6	0.0454	51.709	0.945
2	1.917	BB	400.1	131.2	0.0496	48.291	0.863

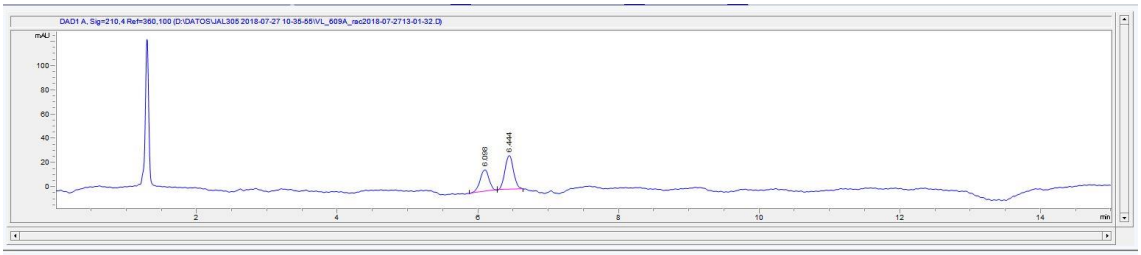


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.753	BB	898.4	299.5	0.047	97.748	0.894
2	1.877	BB	20.7	7.6	0.0439	2.252	0.776

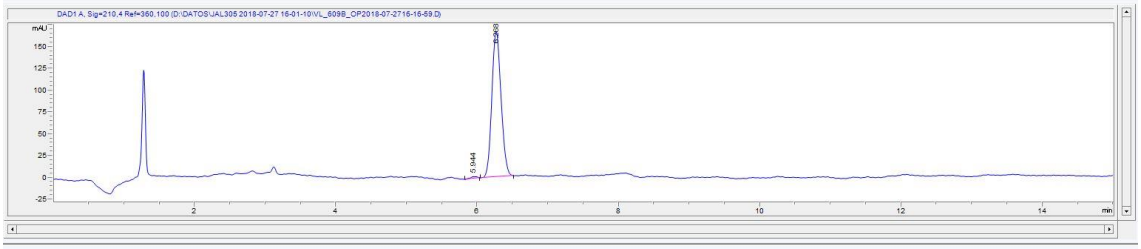
Benzyl (*R*)-4-formyl-5-methyl-3-phenylhex-4-enoate (5l)





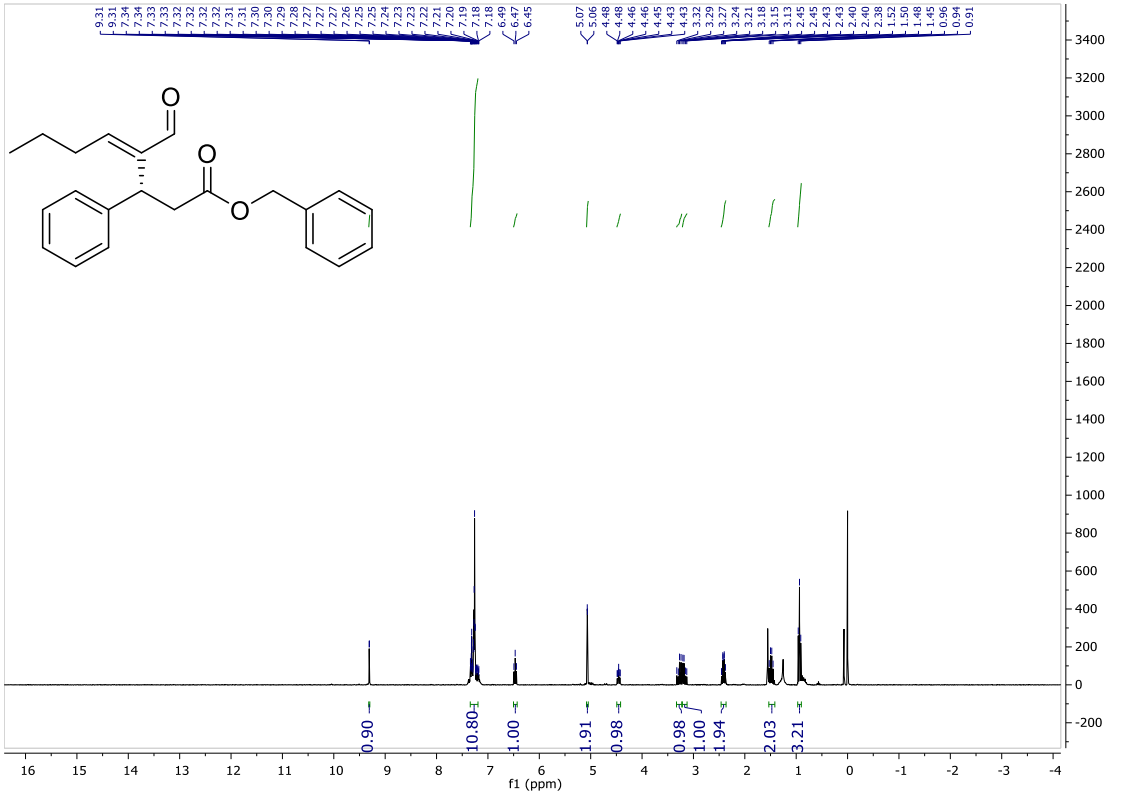


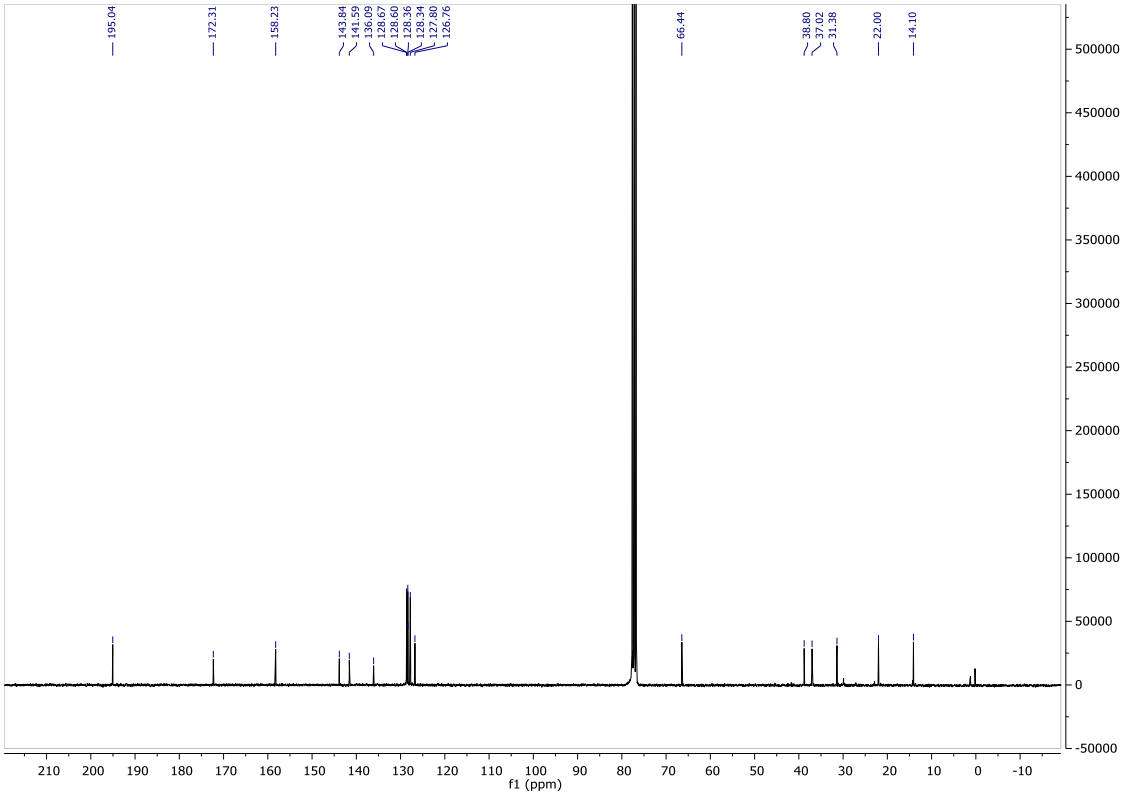
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.098	BB	161.4	17.9	0.1389	40.269	1.226
2	6.444	BB	239.4	28	0.1318	59.731	0.995

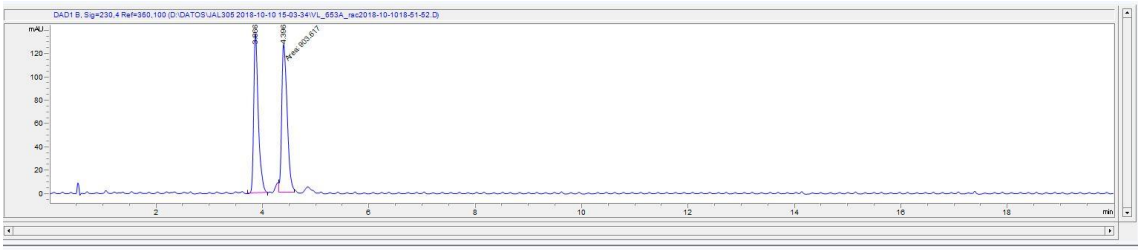


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.944	BB	15.6	2.3	0.0922	1.025	0.921
2	6.268	BB	1504.4	165.8	0.1399	98.975	0.87

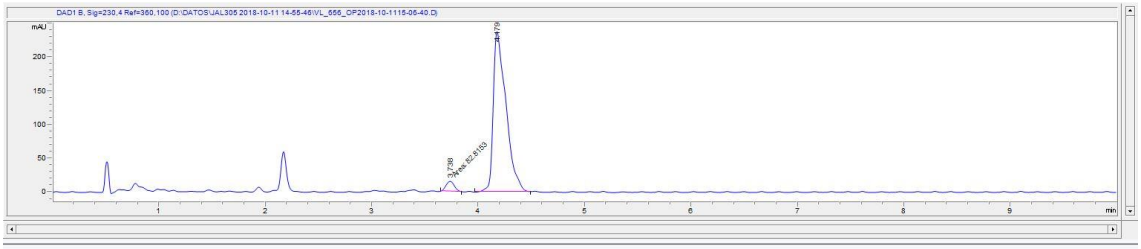
Benzyl (*R,E*)-4-formyl-3-phenyloct-4-enoate (5m)





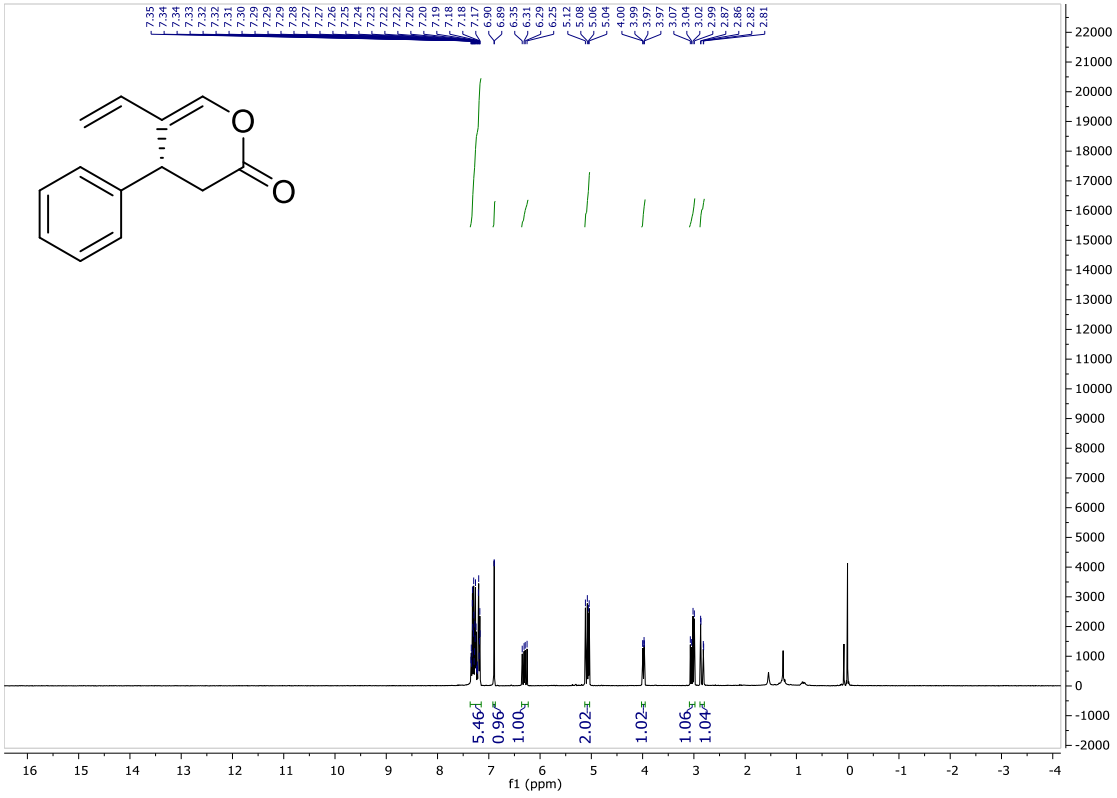


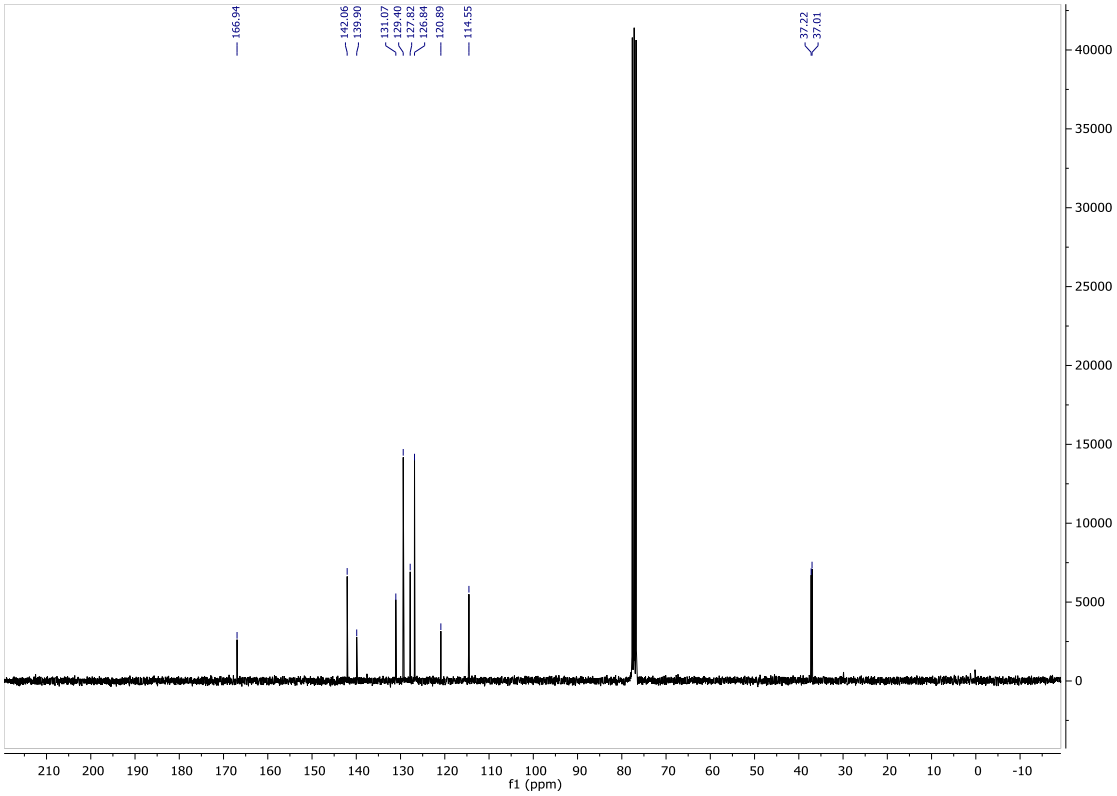
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.866	BB	819.1	137.2	0.0877	47.547	0.591
2	4.396	MM	903.6	127.8	0.1179	52.453	0.545

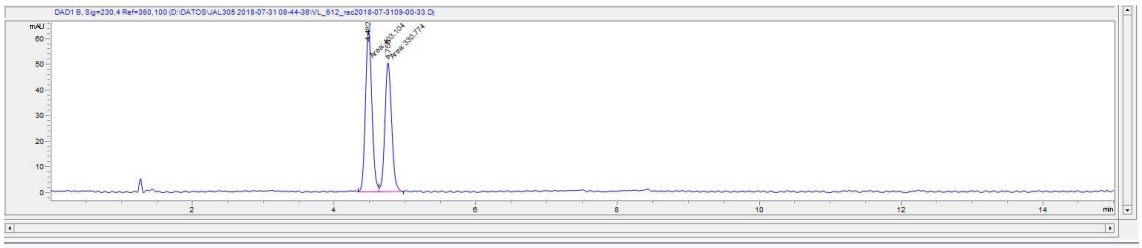


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.738	MM	82.8	15.2	0.091	4.017	1.021
2	4.179	BB	1978.6	238.1	0.1169	95.983	0.414

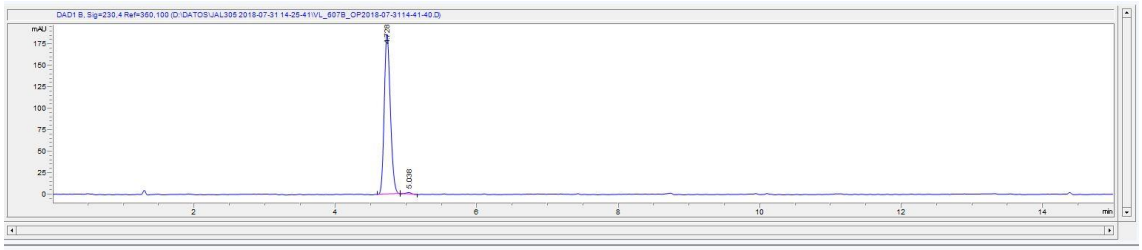
(*R*)-4-Phenyl-5-vinyl-3,4-dihydro-2H-pyran-2-one (4a)





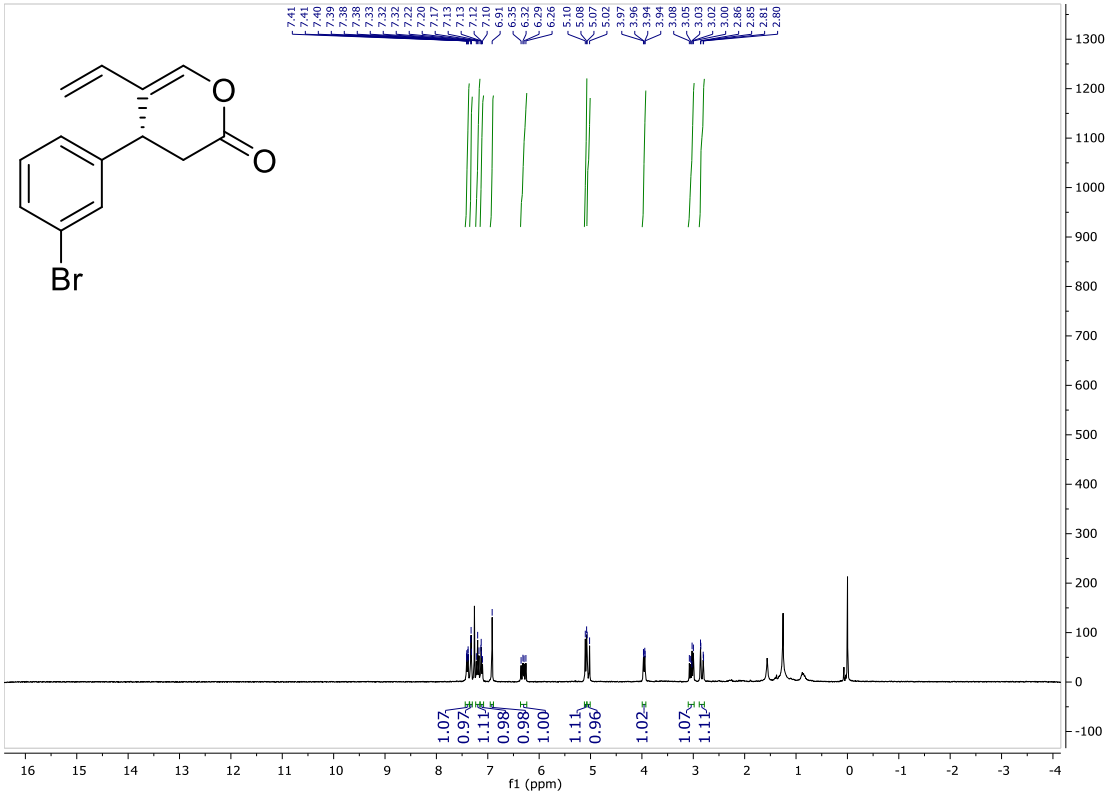


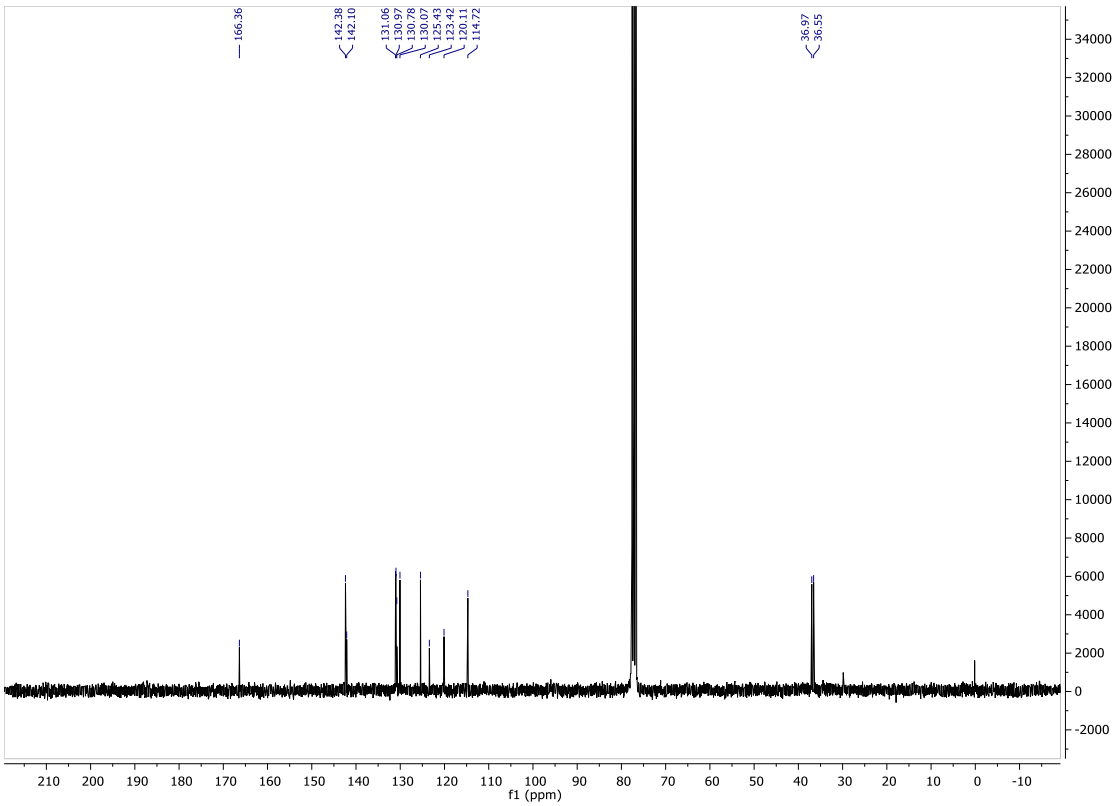
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.482	MF	403.1	63.2	0.1063	54.928	0.873
2	4.758	FM	330.8	50.3	0.1096	45.072	0.847

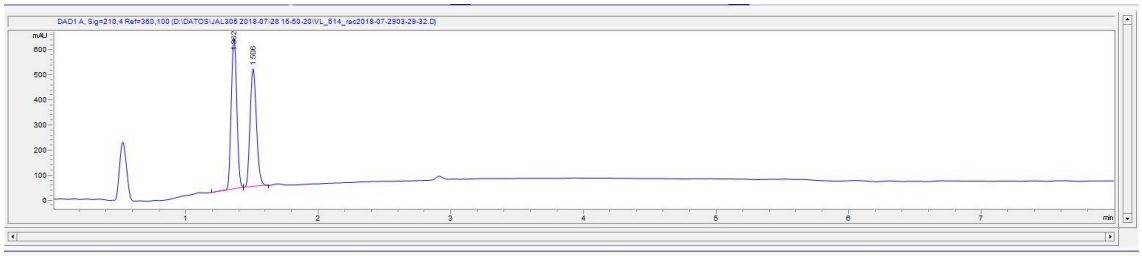


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.728	BB	1128.5	188	0.092	99.007	0.787
2	5.038	BB	11.3	2	0.0892	0.993	1.375

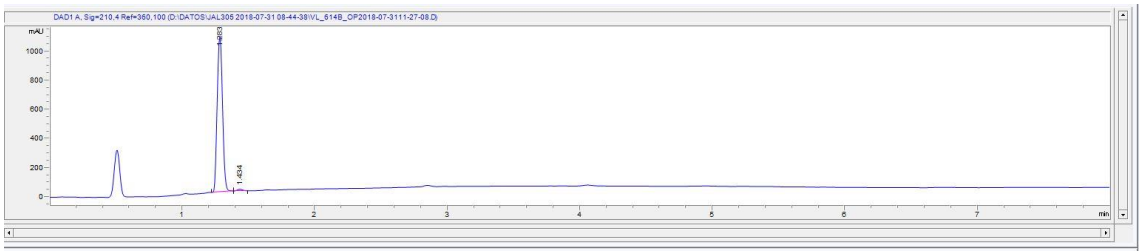
(*R*)-4-(3-Bromophenyl)-5-vinyl-3,4-dihydro-2H-pyran-2-one (4b)





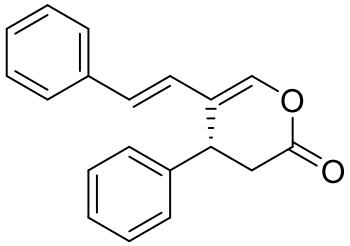


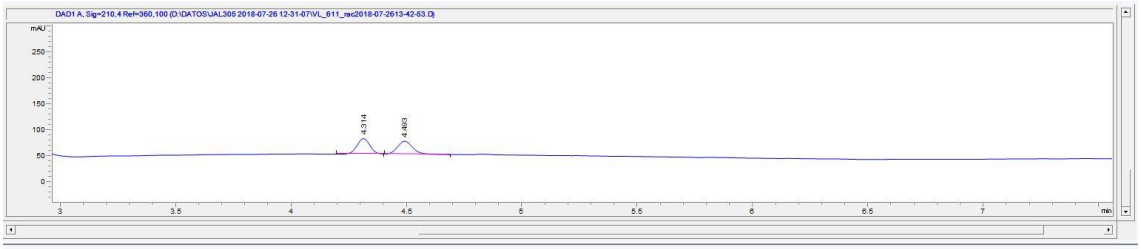
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.362	BB	1746.9	601.9	0.0459	52.676	0.951
2	1.506	BB	1569.4	469.8	0.053	47.324	0.842



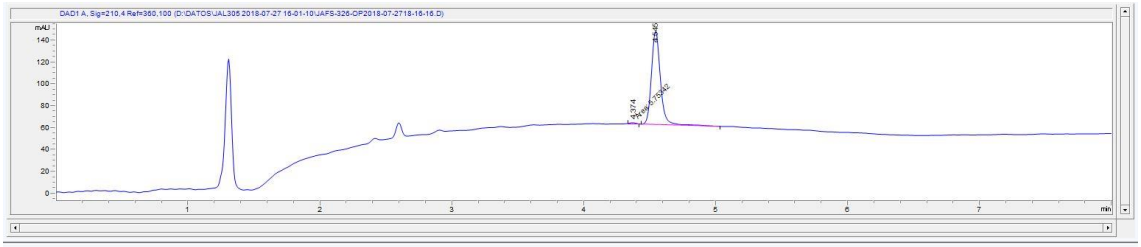
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.283	BB	2985.7	1074.1	0.0444	98.899	0.939
2	1.434	BB	33.2	11.9	0.0445	1.101	0.894

(*R*,*E*)-4-phenyl-5-styryl-3,4-dihydro-2H-pyran-2-one (6a)[5]



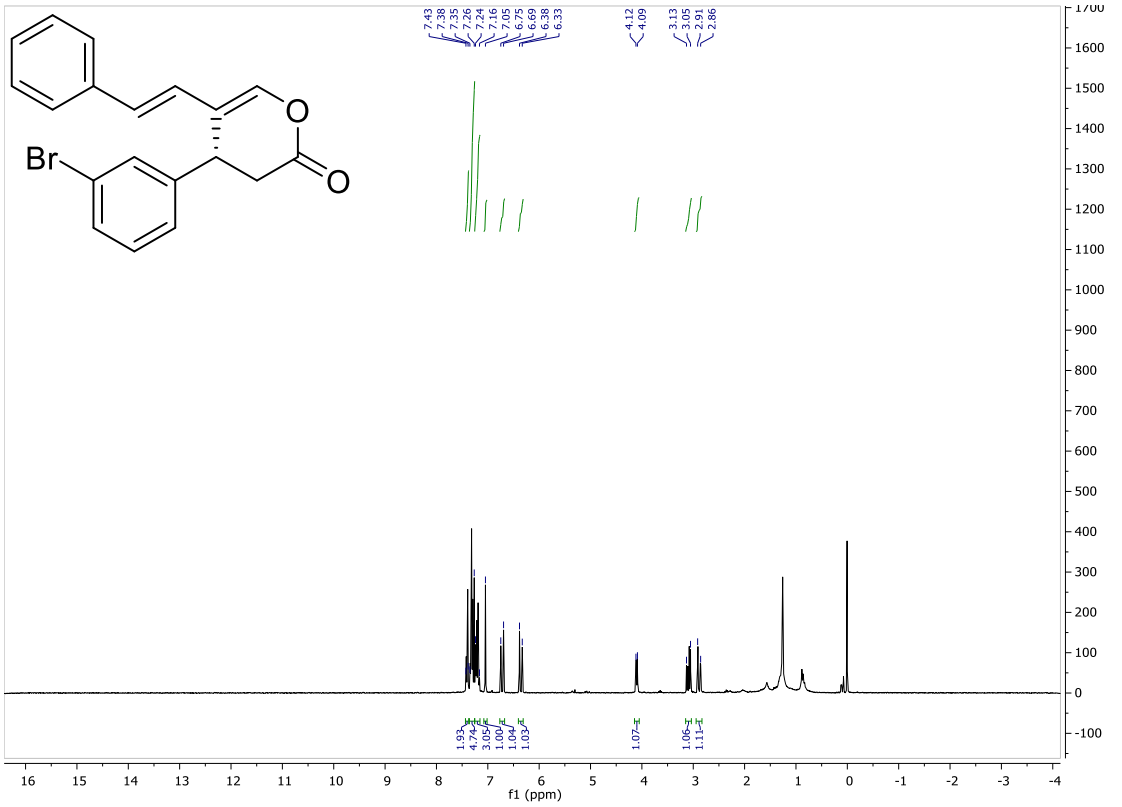


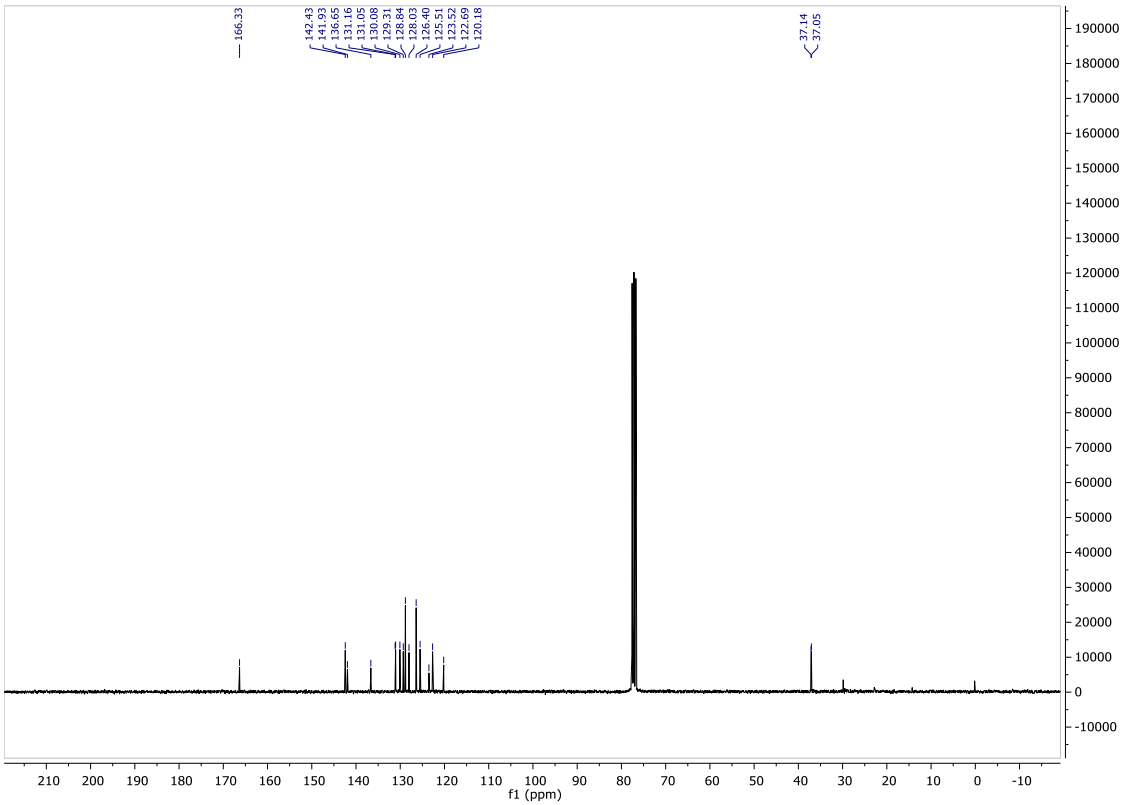
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.314	BB	116.9	30	0.0614	50.455	1.001
2	4.493	BB	114.8	25.2	0.071	49.545	0.845

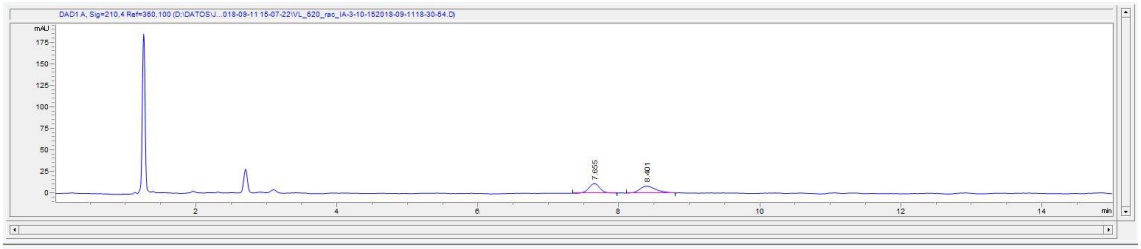


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.374	MM	5.8	1.5	0.0654	1.407	0.667
2	4.545	BB	403	85	0.0713	98.593	0.78

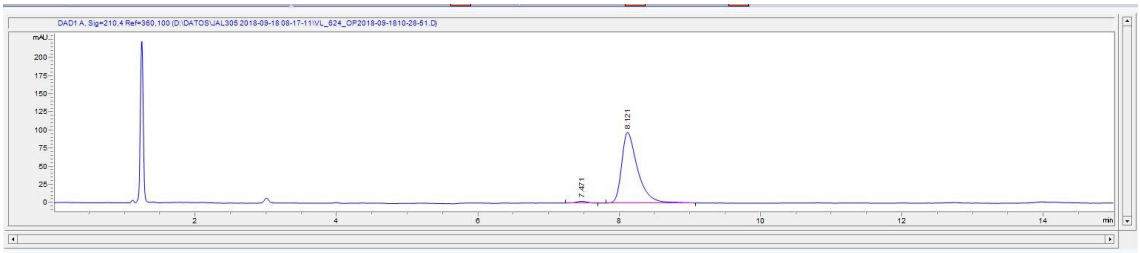
(*R,E*)-4-(3-bromophenyl)-5-styryl-3,4-dihydro-2H-pyran-2-one (6b)







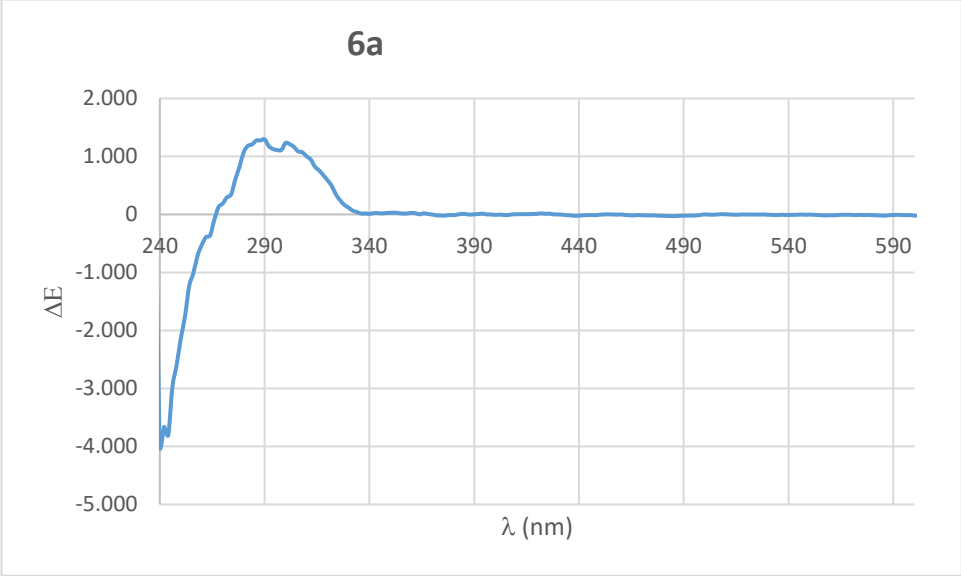
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.655	BB	122.8	11.2	0.1674	49.316	1.03
2	8.401	BB	126.2	8	0.2283	50.684	0.758



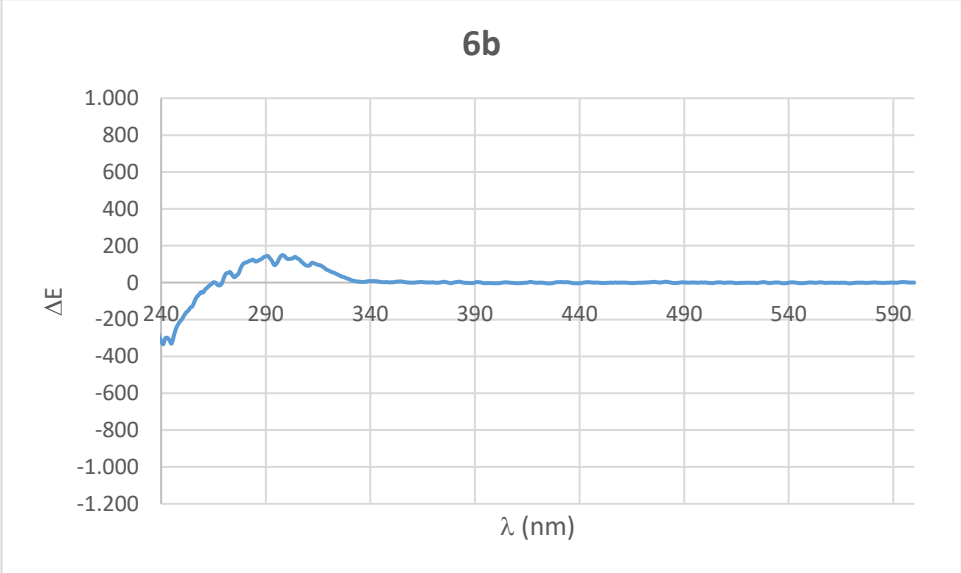
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.471	BB	25.5	2.4	0.1581	1.637	1.005
2	8.121	BB	1530.1	97.4	0.2333	98.363	0.554

7. Circular dichroism. Computational Details. DFT calculations.

Circular dichroism (CD) spectra were recorded at 25 ^{o}C on a Jasco J-815 CD-spectrometer including a Jasco Peltier ETCT-762 temperature controller. measurements were performed using quartz cuvettes (1cm)

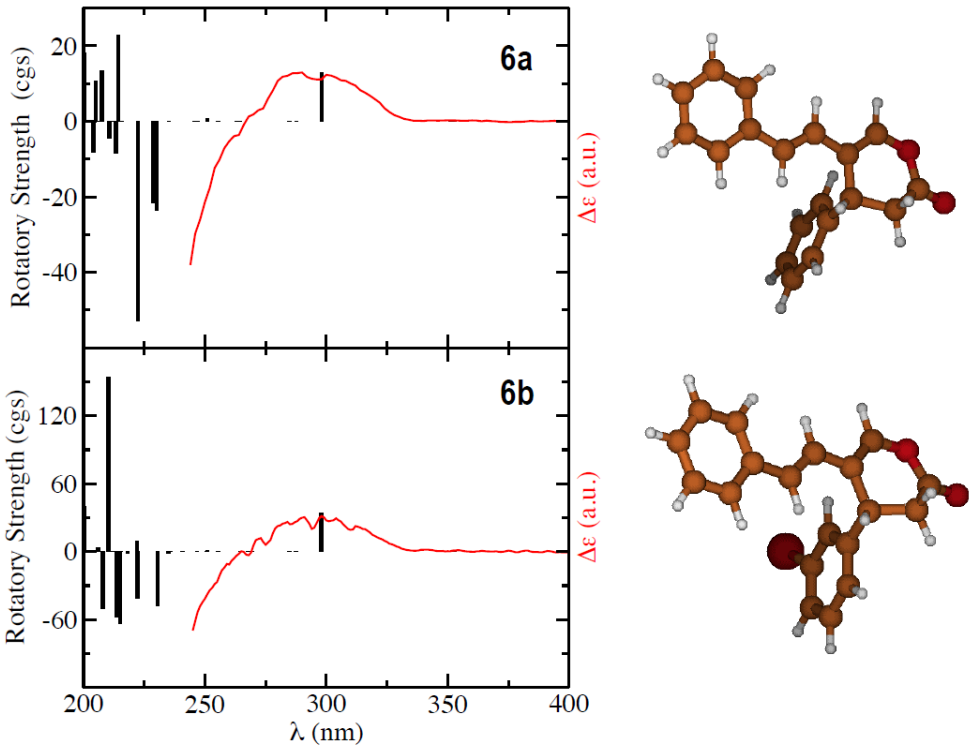


c = 5.23E-5 in CH_2Cl_2 spectroscopic grade



c = 7.53E-4 in CH_2Cl_2 spectroscopic grade

Quantum-chemical calculations were performed using the density functional theory (DFT). In particular, geometry optimization of all the structures was carried out using the B3LYP functional, which combines the Becke's three parameter non-local hybrid exchange potential[6] with the non-local correlation functional of Lee, Yang and Parr[7], in combination with the 6-311+G(d,p) basis set. Over the optimized geometries, simulations of the electronic circular dichroism ECD spectra were done with the long-range-corrected version of the B3LYP functional using the Coulomb-Attenuating Method CAM-B3LYP[8], in combination with the cc-pVTZ basis set. In all the calculations we included solvent effects by means of the integral equation formalism variant of the Polarizable Continuum Model (IEF-PCM)[9]. All simulations were carried out with the Gaussian09 program[10]. These methods have been shown to be appropriate for a correct description of electronic circular dichroism (ECD) spectroscopy (see e.g.[11]).



Experimental CD spectrum (full lines) and computed rotatory strength for **(*R*)-6a** and **(*R*)-6b**: vertical lines correspond to individual excitations.

[6] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

[7] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter. Mater. Phys.*, 1988, **37**, 785–789.

[8] T. Yanai, D. Tew, and N. Handy, *Chem. Phys. Lett.*,2004, **393**, 51-57

[9] a) S. Miertuš, E. Scrocco, and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117-129. b) S. Miertuš and J. Tomasi, *Chem. Phys.*, 1982. **65**, 239-245. c) J. L. Pascual-Ahuir, E. Silla, and I. Tuñón, *J. Comp. Chem.*, 1994, **15**, 1127-38.

[10] M.J. Frisch et al, Gaussian 09, Revision E.01, Gaussian, Inc.: Wallingford, CT, 2013.

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Optimized Structures

(coordinates in Anstroms)

(*R*)-6a

C	3.38521600	-1.81960100	-0.32850100
C	1.25993100	-2.29328300	0.66834600
C	0.58399500	-1.32638600	0.02554300
H	0.81041500	-3.02342100	1.32709700
O	2.63445300	-2.45886700	0.62451400
O	4.58320500	-1.90918800	-0.26261600
C	2.60452700	-1.11149800	-1.40347800
H	2.28541800	-1.88802200	-2.10941200
H	3.28037900	-0.44009900	-1.93063100
C	1.34999400	-0.37583500	-0.87298500
C	-0.85475000	-1.23028800	0.21435700
H	-1.27988800	-1.98464400	0.87105600
C	-1.66099900	-0.30097800	-0.33637200
H	-1.22262800	0.45813800	-0.97808900
C	-3.11151100	-0.17872100	-0.15864900
C	-3.77573500	0.90186800	-0.76632900
C	-3.88441700	-1.08843200	0.58802500
C	-5.15153900	1.07326400	-0.63281000
H	-3.20059700	1.61508200	-1.34777400
C	-5.25758100	-0.91755600	0.72103300
H	-3.41324200	-1.93859200	1.06709900
C	-5.90036900	0.16407500	0.11260000
H	-5.63751600	1.91647500	-1.11085400
H	-5.83188400	-1.63181000	1.30065200
H	-6.97140200	0.29288500	0.21878100
H	0.73580300	-0.15885700	-1.74988800
C	1.69776200	0.96274400	-0.22128300
C	1.78925000	2.10559600	-1.02556100
C	1.97340200	1.08383100	1.14421500
C	2.15115100	3.33674900	-0.48250600
H	1.57208900	2.03201600	-2.08671000
C	2.33655800	2.31508500	1.69111000
H	1.89429400	0.21821900	1.79214200
C	2.42746300	3.44523700	0.88056100
H	2.21216800	4.21037400	-1.12190100
H	2.54488800	2.38927500	2.75260200
H	2.70635000	4.40221300	1.30675100

(*R*)-6b

C	-1.41166700	3.73917300	-0.51198500
C	0.80982400	3.35788800	0.29701000
C	0.90669800	2.09283700	-0.14500400
H	1.61198200	3.90495600	0.77280000
O	-0.34440300	4.12198400	0.25936400
O	-2.43085400	4.37255700	-0.42810100
C	-1.16110500	2.57819800	-1.43701900
H	-0.62205000	2.98694700	-2.30021100
H	-2.12237000	2.20818000	-1.79005300
C	-0.30144100	1.45780600	-0.80331500
C	2.16337900	1.38017000	0.02203700
H	2.95546100	1.95572900	0.49334700
C	2.39694700	0.10280500	-0.33977900
H	1.59320700	-0.46743000	-0.79698800
C	3.64804100	-0.64421600	-0.17592700
C	3.68345800	-1.99273000	-0.57388300
C	4.82495100	-0.08622500	0.35866200
C	4.84083400	-2.75616600	-0.44171000
H	2.78845500	-2.44386200	-0.98987400
C	5.98019400	-0.84807100	0.49014400
H	4.84278200	0.95052500	0.67338100
C	5.99629400	-2.18755300	0.09177800
H	4.83927100	-3.79401700	-0.75558200
H	6.87468600	-0.39615800	0.90437400
H	6.89965300	-2.77745400	0.19609200
H	0.04411300	0.83702100	-1.63293900
C	-1.11999000	0.55997400	0.12551800
C	-1.82219300	-0.51593800	-0.43275600
C	-1.22805000	0.79635200	1.49843700
C	-2.61160300	-1.32028000	0.38010800
H	-1.74833700	-0.72262900	-1.49384500
C	-2.02513900	-0.02128200	2.29813400
H	-0.67964800	1.61216600	1.95398800
C	-2.72792000	-1.09096200	1.74729600
H	-2.09916500	0.17160400	3.36212400
H	-3.34422700	-1.72876100	2.36720200
Br	-3.56231000	-2.79611000	-0.40858300