

Enantioselective Metallo-Organocatalyzed Preparation of Cyclopentanes Bearing an All-Carbon Quaternary Stereocenter

Supporting Information

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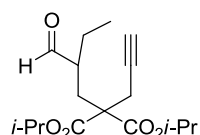
A. General information

Dioxane and cyclohexylamine were distilled on CaH₂. All manipulations were carried out under argon atmosphere. All signals were expressed as ppm (δ) and internally referenced to residual protio solvent signals. Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. High resolution mass spectra and X-ray diffraction analysis were performed at the University Pierre and Marie Curie (Paris). IR spectra were recorded on a JASCO FT/IR 6300. Melting points (m.p.) were determined on a Kofler block and were uncorrected. Enantiomeric excesses were determined by HPLC analyses with Waters alliance e2695 system using stationary phase column: Chiralpak IA, IB, IC or ID and UV detector at 215 nm. Optical rotations were measured on a Perkin-Elmer 241.

B. Description of new aldehyde substrates

Aldehyde substrates **1**, **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17** were already described in the literature.¹ New aldehyde substrates **19**, **21**, **23** and **25** were prepared according the same procedure.

diisopropyl 2-(2-formylbutyl)-2-(prop-2-ynyl)malonate (**19**) :



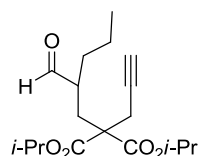
¹H NMR (300 MHz, CDCl₃) δ 9.50 (d, *J* = 3.1 Hz, 1H), 5.10 – 4.86 (m, 2H), 2.77 (d, *J* = 2.7 Hz, 2H), 2.52 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.10 – 2.00 (m, 2H), 1.74 – 1.47 (m, 2H), 1.28 – 1.16 (m, 12H), 0.92 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (CDCl₃, 75 MHz) δ 209.5, 169.3, 78.6, 71.8, 69.5, 69.4, 55.9, 49.0, 30.4, 23.8, 23.5, 21.4, 11.1.

HRMS calculated for C₁₇H₂₆O₅Na : 333.16725 ; found : 333.16665.

IR (neat, cm⁻¹) 2981, 1726, 1733, 1198, 1103.

diisopropyl 2-(2-formylpentyl)-2-(prop-2-ynyl)malonate (**21**) :



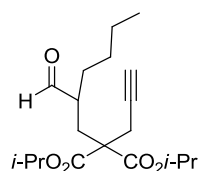
¹H NMR (300 MHz, CDCl₃) δ 9.52 (d, *J* = 3.2 Hz, 1H), 5.13 – 4.92 (m, 2H), 2.79 (d, *J* = 2.7 Hz, 2H), 2.54 (dd, *J* = 14.7, 9.0 Hz, 1H), 2.44 – 2.33 (m, 1H), 2.12 – 2.00 (m, 2H), 1.70 – 1.56 (m, 1H), 1.49 – 1.28 (m, 3H), 1.26 – 1.16 (m, 12H), 0.91 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (CDCl₃, 75 MHz) δ 201.4, 167.3 (2C), 76.6, 69.8, 67.5, 67.4, 53.9, 45.4, 30.9, 28.8, 24.8, 21.5, 19.4, 17.8, 12.0.

HRMS calculated for C₁₈H₂₈O₅Na : 347.18290 ; found : 347.18247.

IR (neat, cm⁻¹) 2978, 1725, 1197, 1102.

diisopropyl 2-(2-formylhexyl)-2-(prop-2-ynyl)malonate (**23**) :



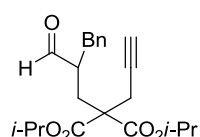
¹H NMR (300 MHz, CDCl₃) δ 9.50 (d, *J* = 3.3 Hz, 1H), 5.17 – 4.86 (m, 2H), 2.78 (d, *J* = 2.7 Hz, 2H), 2.53 (dd, *J* = 14.7, 9.0 Hz, 1H), 2.40 – 2.27 (m, 1H), 2.07 (dd, *J* = 14.7, 2.4 Hz, 1H), 2.02 (t, *J* = 2.7 Hz, 1H), 1.70 – 1.52 (m, 1H), 1.52 – 1.37 (m, 1H), 1.35 – 1.24 (m, 4H), 1.24 – 1.14 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (CDCl₃, 75 MHz) δ 203.5, 169.3, 78.6, 71.8, 69.5, 69.4, 55.9, 47.6, 30.8, 30.5, 28.7, 23.5, 22.6, 21.4, 13.8.

HRMS calculated for C₁₉H₃₀O₅Na : 361.19855 ; found : 361.19814.

IR (neat, cm⁻¹) 2933, 1725, 1197, 1102.

diisopropyl 2-(2-benzyl-3-oxopropyl)-2-(prop-2-ynyl)malonate (**25**) :



¹H NMR (300 MHz, CDCl₃) δ 9.51 (d, *J* = 2.7 Hz, 1H), 7.31 – 7.04 (m, 5H), 5.03 – 4.83 (m, 2H), 2.92 – 2.79 (m, 1H), 2.77 – 2.64 (m, 4H), 2.50 (dd, *J* = 14.8, 8.5 Hz, 1H), 2.07 (dd, *J* = 14.9, 2.2 Hz, 1H), 1.86 (t, *J* = 2.7 Hz, 1H), 1.36 (s, 1H), 1.19 – 1.06 (m, 12H).

¹ (a) B. Montaignac, M. R. Vitale, V. Michelet, V. Ratovelomanana-Vidal, *Org. Lett.*, 2010, **12**, 2582;
(b) B. Montaignac, M. R. Vitale, V. Ratovelomanana-Vidal, V. Michelet, *J. Org. Chem.*, 2010, **75**, 8322;
(c) B. Montaignac, M. R. Vitale, V. Ratovelomanana-Vidal, V. Michelet, *Eur. J. Org. Chem.*, **2011**, 3723

^{13}C NMR (CDCl_3 , 75 MHz) δ 203.1, 169.3, 169.2, 137.6, 129.2, 128.6, 126.6, 78.4, 71.8, 69.6, 69.5, 55.8, 49.1, 37.2, 30.7, 26.8, 23.5, 21.4.

HRMS calculated for $\text{C}_{22}\text{H}_{28}\text{O}_5\text{Na}$: 395.18290 ; found : 395.18284.

IR (neat, cm^{-1}) 3286, 2987, 1733, 1193, 1102.

mp 35-37°C.

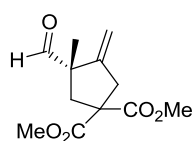
C. Enantioselective carbocyclization reactions

General procedure for the enantioselective carbocyclization reactions

In a sealed vial under argon atmosphere were successively introduced (*R*)-4-MeO-3,5-(*t*-Bu)₂-MeOBIPHEP (0.03 mmol, 0.15 eq.), copper(II) trifluoromethanesulfonate (0.012 mmol, 0.06 eq.) and 0.15 mL of dioxane. The resulting mixture was stirred for 15 minutes at room temperature before freshly purified formyl-alkyne (0.2 mmol, 1 eq.) in 0.1 mL of a freshly prepared 0.1 M solution of cyclohexylamine in dioxane (0.02 mmol, 0.1 eq.) was added. After introduction of additional 0.25 mL of dioxane, the reaction mixture was stirred at the specified temperature until GC or TLC analysis indicated complete conversion (see *vide infra*). The reaction mixture was then treated with 1 mL of an aqueous solution of AcOH (1/1 v/v) and then vigorously stirred for 15 min at room temperature before extraction of the aqueous layer with dichloromethane. The combined organic layers were dried over anhydrous sodium sulphate, filtered, concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to afford the pure carbocyclized aldehyde.

(*S*)-4,4-bis-(carbomethoxy)-1-methyl-2-methylene-cyclopentanecarbaldehyde (**2**) :

Carbocyclization reaction performed at 20°C for 29 hours.



^1H NMR (CDCl_3 , 300 MHz) δ 9.29 (s, 1H), 5.23 (t, $J = 2.1$ Hz, 1H), 4.95 (t, $J = 2.0$ Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.07-2.92 (m, 2H), 2.95 (d, $J = 14.4$ Hz, 1H), 2.27 (d, $J = 14.0$ Hz, 1H), 1.27 (s, 3H).

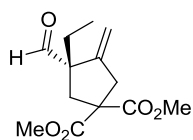
^{13}C NMR (CDCl_3 , 75 MHz) δ 199.6, 171.7, 171.5, 149.3, 110.7, 58.0, 56.7, 53.0, 52.9, 41.0, 40.3, 21.7.

The ^1H and ^{13}C NMR data obtained were in agreement with that reported in the literature.²

Enantiomeric ratio : 93.5/6.5, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 80/20, flow rate 1.0 mL/min, T = 20°C, 215 nm), $t_{\text{R}} = 8.88$ min (major), $t_{\text{R}} = 11.66$ min (minor). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_{\text{D}}^{20} = +101.0$ (c 1.01, CHCl_3).

(*S*)-dimethyl 3-ethyl-3-formyl-4-methylenecyclopentane-1,1-dicarboxylate (**4**) :

Carbocyclization reaction performed at 30°C for 14 days.



^1H NMR (300 MHz, C_6D_6) δ 9.04 (s, 1H), 4.97 (t, $J = 2.0$ Hz, 1H), 4.69 (t, $J = 2.2$ Hz, 1H), 3.39 (s, 3H), 3.30 (s, 3H), 3.20 – 3.07 (m, 2H), 2.67 (dt, $J = 16.4, 2.3$ Hz, 1H), 2.43 (d, $J = 14.2$ Hz, 1H), 1.59 – 1.21 (m, 2H), 0.58 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 199.0, 171.5, 171.3, 148.9, 110.0, 61.3, 57.9, 52.4, 52.2, 41.2, 36.7, 28.3, 8.6.

HRMS calculated for $\text{C}_{13}\text{H}_{18}\text{O}_5\text{Na}$: 277.10464 ; found : 277.10484.

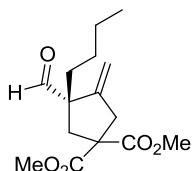
IR (neat, cm^{-1}) 2962, 1734, 1651, 1434, 1278, 1255, 1230, 1203, 1175, 1068, 900.

² J. T. Binder, B. Crone, T. T. Haug, H. Menz, S. F. Kirsch, *Org. Lett.*, 2008, **10**, 1025

Enantiomeric ratio : 86/14, determined by HPLC (Chiralpak-ID, hexane / *i*-PrOH = 70/30, flow rate 1.0 mL/min, T = 20°C, 215 nm), t_R = 5.83 min (major), t_R = 6.90 min (minor). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_D^{20}$ = +101.0 (*c* 1.01, CHCl₃).

(S)-dimethyl 3-butyl-3-formyl-4-methylenecyclopentane-1,1-dicarboxylate (6) :

Carbocyclization reaction performed at 30°C for 14 days.



¹H NMR (300 MHz, CDCl₃) δ 9.08 (s, 1H), 4.97 (d, *J* = 1.8 Hz, 1H), 4.72 (t, *J* = 2.1 Hz, 1H), 3.41 (s, 3H), 3.29 (s, 3H), 3.26 – 3.09 (m, 2H), 2.78 – 2.60 (m, 1H), 2.50 (d, *J* = 14.0 Hz, 1H), 1.51 (ddd, *J* = 13.7, 11.2, 4.9 Hz, 1H), 1.41 – 1.21 (m, 1H), 1.16 – 0.82 (m, 4H), 0.73 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 199.1, 171.7, 171.5, 149.3, 110.1, 61.1, 58.1, 52.6, 52.4, 41.3, 37.5, 35.7, 26.9, 23.3, 14.0.

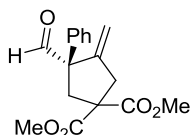
HRMS calculated for C₁₅H₂₂O₅Na : 305.13594 ; found : 305.13554.

IR (neat, cm⁻¹) 2956, 2933, 1861, 1735, 1650, 1434, 1258, 1255, 1203, 1068, 893.

Enantiomeric ratio : 88.5/11.5, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 95/5, flow rate 1.0 mL/min, T = 20°C, 215 nm), t_R = 19.23 min (major), t_R = 22.69 min (minor). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_D^{20}$ = +66.8 (*c* 0.97, CHCl₃).

(S)-dimethyl 3-formyl-4-methylene-3-phenylcyclopentane-1,1-dicarboxylate (8) :

Carbocyclization reaction performed at 30°C for 14 days.



¹H NMR (300 MHz, C₆D₆) δ 9.23 (d, *J* = 1.0 Hz, 1H), 7.24 – 6.82 (m, 5H), 5.19 (t, *J* = 2.1 Hz, 1H), 4.72 (t, *J* = 2.3 Hz, 1H), 3.65 (dd, *J* = 13.9, 1.0 Hz, 1H), 3.37 (d, *J* = 1.6 Hz, 3H), 3.19 – 3.08 (m, 4H), 2.92-2.85 (m, 1H), 2.71 (d, *J* = 13.9 Hz, 1H).

¹³C NMR (75 MHz, C₆D₆) δ 195.7, 171.2, 171.1, 147.0, 140.3, 129.2, 128.4, 128.0, 127.9, 127.7, 127.6, 114.2, 66.3, 58.3, 52.7, 52.3, 42.8, 41.7.

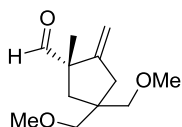
HRMS calculated for C₁₇H₁₈O₅Na : 325.10464 ; found : 325.10431.

IR (neat, cm⁻¹) 2958, 1737, 1646, 1435, 1260, 1206, 1069.

Enantiomeric ratio : 68/32, determined by HPLC (Chiralpak-IB, hexane / *i*-PrOH = 95/5, flow rate 0.5 mL/min, T = 20°C, 215 nm), t_R = 15.45 min (major), t_R = 16.72 min (minor). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_D^{20}$ = -20.8 (*c* 0.51, CHCl₃).

(S)-4,4-bis(methoxymethyl)-1-methyl-2-methylenecyclopentanecarbaldehyde (10) :

Carbocyclization reaction performed at 20°C for 6 days.



$^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 9.32 (s, 1H), 5.12 (t, $J = 2.0$ Hz, 1H), 4.88 (t, $J = 2.1$ Hz, 1H), 3.33 (s, 3H), 3.32 (s, 3H), 3.27-3.19 (m, 4H), 2.37 (dt, $J = 16.1$ Hz, $J = 1.5$ Hz, 1H), 2.30 (d, $J = 14.1$ Hz, 1H), 2.22 (dt, $J = 16.0$ Hz, $J = 2.3$ Hz, 1H), 1.47 (d, $J = 14.2$ Hz, 1H), 1.25 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 200.8, 152.5, 109.8, 76.0, 75.9, 59.2, 56.7, 45.9, 40.2, 38.8, 22.3.

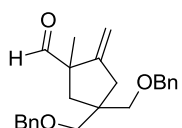
The ^1H and ^{13}C NMR data obtained were in agreement with that reported in the literature.²

Enantiomeric ratio : 70.5/29.5, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 99/1, flow rate 1.0 mL/min, T = 20°C, 215 nm), $t_{\text{R}} = 7.05$ min (major), $t_{\text{R}} = 7.83$ min (minor).

The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_{\text{D}}^{20} = -60.0$ (c 0.30, CHCl_3).

4,4-bis(benzyloxymethyl)-1-methyl-2-methylenecyclopentanecarbaldehyde (**12**) :

Carbocyclization reaction performed at 20°C for 40 hours.



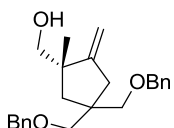
$^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 9.24 (s, 1H), 7.31-7.22 (m, 10H), 5.05 (t, $J = 1.9$ Hz, 1H), 4.80 (t, $J = 2.0$ Hz, 1H), 4.46 (s, 2H), 4.45 (s, 4H), 3.38-3.31 (m, 4H), 2.42-2.32 (m, 2H), 2.32 (d, $J = 14.2$ Hz, 1H), 1.48 (d, $J = 14.1$ Hz, 1H), 1.17 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 200.8, 152.6, 138.7, 128.4, 127.5, 109.8, 73.2, 73.5, 56.8, 46.3, 40.5, 39.0, 22.4.

The ^1H and ^{13}C NMR data obtained were in agreement with that reported in the literature.²

Enantiomeric ratio was determined after reduction of the aldehyde 12 into alcohol 12'.

(S)-(4,4-bis(benzyloxymethyl)-1-methyl-2-methylenecyclopentyl)methanol (**12'**) :



$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.47 – 7.14 (m, 10H), 4.95 (s, 1H), 4.77 (s, 1H), 4.51 (s, 2H), 4.50 (s, 2H), 3.43 (d, $J = 8.8$ Hz, 1H), 3.39 (d, $J = 8.8$ Hz, 1H), 3.37 – 3.27 (m, 4H), 2.47 – 2.30 (m, 2H), 1.75 (d, $J = 14.1$ Hz, 1H), 1.66 (bs, 1H), 1.51 (d, $J = 14.1$ Hz, 1H), 1.07 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 156.8, 138.7, 138.7, 128.3, 127.4, 127.3, 106.5, 74.4, 73.7, 73.2, 73.1, 70.3, 46.8, 45.0, 41.9, 40.6, 24.7.

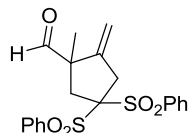
IR (neat, cm^{-1}) 3401, 2861, 1453, 1362, 1096, 1076, 1029, 885.

HRMS calculated for $\text{C}_{24}\text{H}_{30}\text{O}_3\text{Na}$: 389.20872 ; found : 389.20882.

Enantiomeric ratio : 71.5/28.5, determined by SFC (Chiralpak-AD-H, pressure 150 bar, flow rate 3.5 mL/min, MeOH 5%), $t_{\text{R}} = 5.14$ min (minor), $t_{\text{R}} = 5.73$ min (major). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_{\text{D}}^{20} = -6.7$ (c 0.36, CHCl_3).

1-methyl-2-methylene-4,4-bis(phenylsulfonyl)cyclopentanecarbaldehyde (**14**) :

Carbocyclization reaction performed at 20°C for 40 hours.



¹H NMR (CDCl₃, 300 MHz) δ 9.36 (s, 1H), 8.21 – 7.93 (m, 4H), 7.73 (m, 2H), 7.62 (m, 4H), 5.17 (s, 1H), 5.00 (t, *J* = 1.8 Hz, 1H), 3.40 (d, *J* = 16.1 Hz, 1H), 3.32 – 3.24 (m, 2H), 2.52 (d, *J* = 16.2 Hz, 1H), 1.33 (s, 3H).

¹³C NMR (CDCl₃, 75 MHz) δ 199.0, 147.8, 135.9, 135.8, 134.8, 131.5, 131.3, 128.8, 128.8, 110.2, 91.0, 57.4, 38.9, 37.3, 22.1.

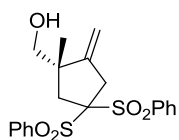
HRMS calculated for C₂₀H₂₀O₅NaS₂ : 427.06444 ; found : 427.06411.

IR (neat, cm⁻¹) 1725, 1642, 1447, 1327, 1309, 1143, 1077.

mp 132-134°C.

Enantiomeric ratio was determined after reduction of the aldehyde 14 into alcohol 14'.

(S)-(1-methyl-2-methylene-4,4-bis(phenylsulfonyl)cyclopentyl)methanol (14') :



¹H NMR (300 MHz, CDCl₃) δ 8.17 – 8.07 (m, 2H), 8.07 – 7.95 (m, 2H), 7.80 – 7.67 (m, 2H), 7.66 – 7.52 (m, 4H), 4.90 (s, 1H), 4.76 (t, *J* = 1.9 Hz, 1H), 3.61 – 3.35 (m, 3H), 3.24 (d, *J* = 17.7 Hz, 1H), 2.93 (d, *J* = 16.5 Hz, 1H), 2.49 (d, *J* = 16.5 Hz, 1H), 1.97 (s, 1H), 1.11 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 151.0, 136.2, 136.0, 134.7, 131.5, 131.4, 128.8, 128.7, 107.5, 90.9, 68.6, 48.6, 39.6, 39.5, 23.5.

HRMS calculated for C₂₀H₂₂O₅NaS₂ : 428.08009 ; found : 429.07987.

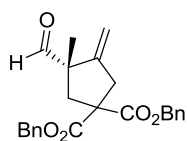
IR (neat, cm⁻¹) 3556, 1446, 1322, 1306, 1158, 1141, 1039, 993, 901.

mp 162-164°C

Enantiomeric ratio : 73.5/26.5, determined by HPLC (Chiralpak-IA, hexane / EtOH = 70/30, flow rate 1.0 mL/min, T = 20°C, 215 nm), *t_R* = 13.00 min (major), *t_R* = 16.48 min (minor). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_D^{20} = -12.9$ (*c* 0.35, CHCl₃).

(S)-dibenzyl 3-formyl-3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (16) :

Carbocyclization reaction performed at 20°C for 6 days.



¹H NMR (300 MHz, CDCl₃) δ 9.19 (s, 1H), 7.37 – 6.99 (m, 10H), 5.12 (t, *J* = 2.0 Hz, 1H), 5.03 (s, 4H), 4.85 (t, *J* = 2.2 Hz, 1H), 3.04 – 2.81 (m, 3H), 2.21 (d, *J* = 14.1 Hz, 1H), 1.15 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 199.6, 170.9, 170.8, 149.4, 135.3, 135.2, 128.5, 128.4, 128.3, 128.1, 110.8, 67.6, 67.5, 58.2, 56.7, 41.0, 40.2, 21.6.

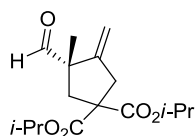
HRMS calculated for C₂₄H₂₄O₅Na : 415.15160 ; found : 415.15200.

IR (neat, cm⁻¹) 2962, 1730, 1654, 1455, 1261, 1227, 1172, 1060.

Enantiomeric ratio : 94/6, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 90/10, flow rate 1.0 mL/min, T = 20°C, 215 nm), *t_R* = 10.22 min (major), *t_R* = 11.66 min (minor). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_D^{20} = +75.8$ (*c* 1.00, CHCl₃).

(S)-diisopropyl 3-formyl-3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (18) :

Carbocyclization reaction performed at 20°C for 4 days.



¹H NMR (300 MHz, C₆D₆) δ 9.16 (s, 1H), 4.99 (m, 2H), 4.92 (t, *J* = 1.9 Hz, 1H), 4.66 (t, *J* = 2.2 Hz, 1H), 3.23 – 3.03 (m, 2H), 2.92 (d, *J* = 16.5 Hz, 1H), 2.35 (d, *J* = 14.0 Hz, 1H), 1.07 (d, *J* = 6.3 Hz, 3H), 1.04 – 0.90 (m, 12H).

¹³C NMR (75 MHz, C₆D₆) δ 198.9, 170.8, 170.6, 150.6, 110.0, 69.1, 68.9, 58.5, 57.0, 41.4, 40.6, 21.7, 21.5.

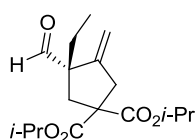
HRMS calculated for C₁₆H₂₄O₅Na : 319.15160 ; found : 319.15176.

IR (neat, cm⁻¹) 2983, 1727, 1650, 1261, 1106.

Enantiomeric ratio : 97/3, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 90/10, flow rate 1.0 mL/min, T = 20°C, 215 nm), *t_R* = 7.29 min (major), *t_R* = 8.79 min (minor). The absolute configuration of **18** was determined by X-Ray analysis of the chiral ester **18''** (see part D of this supporting information). [α]_D²⁰ = +70.9 (*c* 1.09, CHCl₃).

(S)-diisopropyl 3-ethyl-3-formyl-4-methylenecyclopentane-1,1-dicarboxylate (20) :

Carbocyclization reaction performed at 20°C for 14 days.



¹H NMR (300 MHz, CDCl₃) δ 9.26 (s, 1H), 5.23 (t, *J* = 1.9 Hz, 1H), 5.13 – 4.86 (m, 3H), 2.99 (d, *J* = 17.3 Hz, 1H), 2.86 (d, *J* = 14.2 Hz, 1H), 2.77 (dt, *J* = 16.4, 2.0 Hz, 1H), 2.32 (d, *J* = 14.2 Hz, 1H), 1.92 – 1.71 (m, 1H), 1.70 – 1.46 (m, 1H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.24 – 1.17 (m, 8H), 0.83 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 200.2, 170.9, 170.7, 148.8, 110.2, 69.2, 69.1, 61.2, 58.0, 41.1, 36.2, 28.4, 21.5, 8.9.

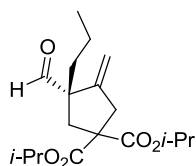
HRMS calculated for C₁₇H₂₆O₅Na : 333.16638 ; found : 333.16725.

IR (neat, cm⁻¹) 2937, 1725, 1654, 1239, 1098.

Enantiomeric ratio : 95/5, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 95/5, flow rate 1.0 mL/min, T = 20°C, 215 nm), *t_R* = 10.04 min (major), *t_R* = 10.78 min (minor). The absolute configuration was assigned by analogy with compound **18**. [α]_D²⁰ = +93.3 (*c* 1.00, CHCl₃).

(S)-diisopropyl 3-formyl-4-methylene-3-propylcyclopentane-1,1-dicarboxylate (22) :

Carbocyclization reaction performed at 20°C for 14 days.



¹H NMR (300 MHz, CDCl₃) δ 9.20 (s, 1H), 5.29 – 5.09 (m, 1H), 5.08 – 4.79 (m, 3H), 3.08 – 2.60 (m, 3H), 2.27 (d, *J* = 14.1 Hz, 1H), 1.82 – 1.62 (m, 1H), 1.54 – 1.32 (m, 1H), 1.30 – 0.97 (m, 14H), 0.84 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 75 MHz) δ 200.0, 170.9, 170.6, 148.9, 110.1, 69.1, 69.0, 60.8, 58.0, 40.9, 38.0, 36.6, 21.4, 17.9, 13.8.

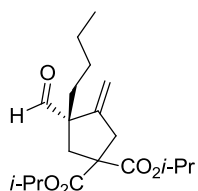
HRMS calculated for C₁₈H₂₈O₅Na : 347.18290 ; found : 347.18248.

IR (neat, cm⁻¹) 2978, 1725, 1645, 1260, 1106.

Enantiomeric ratio : 93/7, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 90/10, flow rate 1.0 mL/min, T = 20°C, 215 nm), t_R = 6.56 min (major), t_R = 7.48 min (minor). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_D^{20} = +67.1$ (*c* 0.50, CHCl₃).

(S)-diisopropyl 3-butyl-3-formyl-4-methylenecyclopentane-1,1-dicarboxylate (24) :

Carbocyclization reaction performed at 20°C for 14 days.



¹H NMR (300 MHz, CDCl₃) δ 9.27 (s, 1H), 5.21 (d, *J* = 12.8 Hz, 1H), 5.13 – 4.88 (m, 3H), 3.10 – 2.65 (m, 3H), 2.33 (d, *J* = 14.1 Hz, 1H), 1.89 – 1.68 (m, 1H), 1.66 – 1.43 (m, 1H), 1.37 – 1.05 (m, 16H), 0.88 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 200.1, 170.9, 170.7, 149.0, 110.1, 69.2, 69.1, 60.7, 58.0, 41.0, 36.7, 35.6, 26.7, 23.1, 21.5, 13.9.

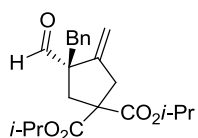
HRMS calculated for C₁₉H₃₀O₅Na : 361.19855 ; found : 361.19833.

IR (neat, cm⁻¹) 2983, 1725, 1650, 1260, 1106.

Enantiomeric ratio : 91/9, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 90/10, flow rate 1.0 mL/min, T = 20°C, 215 nm), t_R = 6.37 min (major), t_R = 6.99 min (minor). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_D^{20} = +15.5$ (*c* 0.50, CHCl₃).

(S)-diisopropyl 3-benzyl-3-formyl-4-methylenecyclopentane-1,1-dicarboxylate (26) :

Carbocyclization reaction performed at 20°C for 14 days.



¹H NMR (300 MHz, CDCl₃) δ 9.40 (s, 1H), 7.30 – 6.97 (m, *J* = 7.1 Hz, 5H), 5.32 – 5.17 (m, 1H), 5.08 – 4.82 (m, 3H), 3.13 (d, *J* = 13.9 Hz, 1H), 2.96 – 2.75 (m, 2H), 2.63 (d, *J* = 17.5 Hz, 2H), 2.36 (d, *J* = 14.4 Hz, 1H), 1.27 – 0.97 (m, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 199.5, 170.8, 170.6, 148.5, 136.7, 130.1, 128.4, 126.8, 111.1, 69.2, 69.2, 61.5, 58.2, 41.6, 41.4, 36.4, 21.5.

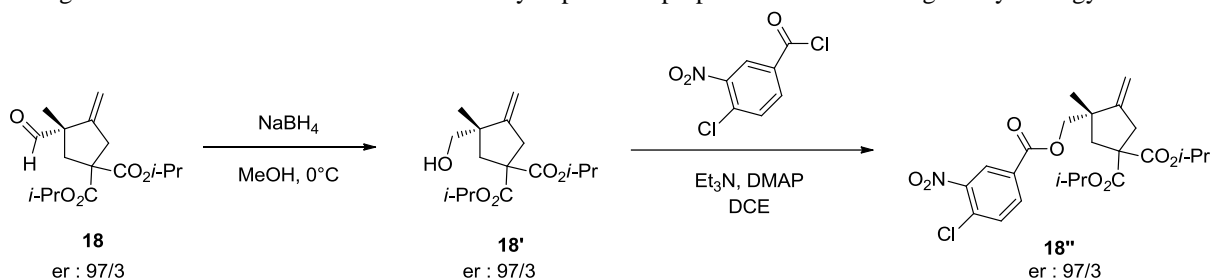
HRMS calculated for C₂₂H₂₈O₅Na : 395.18290 ; found : 395.18283.

IR (neat, cm⁻¹) 2978, 1728, 1671, 1197, 1102.

Enantiomeric ratio : 91/9, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 90/10, flow rate 1.0 mL/min, T = 20°C, 215 nm), t_R = 8.60 min (minor), t_R = 11.19 min (major). The absolute configuration was assigned by analogy with compound **18**. $[\alpha]_D^{20} = +9.5$ (*c* 0.50, CHCl₃).

D. X-Ray determination of the absolute configuration

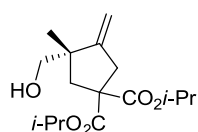
The determination of absolute configuration was established X-Ray diffraction studies of an enantiopur single crystal of benzoate **18''**, prepared in two steps from the chiral carbocyclized aldehyde **18**. The absolute configuration of all the other enantio-enriched cyclopentanes prepared herein was assigned by analogy to **18**.



Experimental procedure for the reduction of chiral aldehyde **18**

To a solution of chiral aldehyde **18** (250 mg, 0.84 mmol) in 3.0 mL of *iso*-propanol at 0°C was added sodium borohydride (33 mg, 0.84 mmol), and the resulting mixture was allowed to stir for 30 min between 0°C and 5°C. After completion of the reaction was evidenced by TLC, the reaction mixture was quenched with 5 mL of sat. NH₄Cl solution. The mixture was concentrated under reduced pressure followed by extraction with EtOAc (3 x 10 mL). The combined organic extract was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to afford the crude product which purified by flash column chromatography on silica gel (17 % EtOAc/cyclohexane) to give **18'** as a colorless oil (223 mg, 89% yield).

(*S*)-diisopropyl 3-(hydroxymethyl)-3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (**18'**) :



¹H NMR (300 MHz, CDCl₃) δ 5.14 – 4.90 (m, 3H), 4.81 (t, *J* = 2.1 Hz, 1H), 3.43 – 3.18 (m, 2H), 3.11 – 2.87 (m, 2H), 2.47 (d, *J* = 14.0 Hz, 1H), 2.15 (d, *J* = 14.0 Hz, 1H), 1.81 (s, 1H), 1.30 – 1.14 (m, 12H), 1.11 (s, 3H).

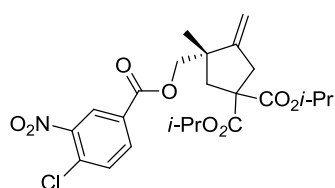
¹³C NMR (75 MHz, CDCl₃) δ 171.89, 171.48, 154.30, 106.89, 69.56, 69.20, 69.06, 57.75, 47.52, 43.01, 41.42, 24.23, 21.58.

IR (neat, cm⁻¹) 3477, 2979, 1725, 1653, 1467, 1373, 1256, 1185, 1102, 1053, 894.

Experimental procedure for esterification of chiral alcohol **18'**

To a room temperature solution of chiral alcohol **18'** (50 mg, 0.17 mmol) in 2.5 mL of 1,2-dichloroethane was added triethylamine (140 μL, 1.0 mmol) and 4-dimethylaminopyridine (20 mg, 0.17 mmol). To this mixture was added 4-chloro-3-nitrobenzoyl chloride (184 mg, 0.84 mmol) and the resulting mixture was allowed to stir at room temperature for 1 hour. After completion of the reaction was evidenced by TLC, the reaction mixture was quenched with saturated sodium bicarbonate solution and extracted with dichloromethane (3 x 5 mL). The combined organic extract was washed with 20 mL of saturated solution of NH₄Cl, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to afford the crude product which was purified by flash column chromatography on silica gel (12 % EtOAc/cyclohexane) to afford benzoate **18''** as a white solid (70 mg, 87% yield). Recrystallization in *n*-hexane allowed to obtain single crystals suitable for X-Ray analysis.

(*S*)-diisopropyl 3-((4-chloro-3-nitrobenzoyloxy)methyl)-3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (**18''**) :



¹H NMR (300 MHz, CDCl₃) δ 8.49 (s, 1H), 8.16 (d, *J* = 10.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 5.19 – 4.95 (m, 3H), 4.88 (d, *J* = 2.1 Hz, 1H), 4.30 – 4.04 (m, 2H), 3.22 – 2.93 (m, 2H), 2.58 (d, *J* = 14.1 Hz, 1H), 2.31 (d, *J* = 14.1 Hz, 1H), 1.34 – 1.13 (m, 16H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.9, 170.8, 163.3, 152.9, 147.7, 133.2, 131.9, 131.3, 129.8, 126.2, 107.5, 71.9, 69.0, 69.0, 57.5, 44.8, 43.1, 41.2, 24.5, 21.2.

IR (neat, cm^{-1}) 2980, 1720, 1602, 1543, 1367, 1278, 1242, 1107.

mp: 73-75°C (recrystallization from hexane)

Enantiomeric ratio: 97/3, determined by HPLC (Chiralpak-IC, hexane / *i*-PrOH = 95/5, flow rate 1.0 mL/min, T = 20°C, 215 nm), t_{R} = 16.92 min (major), t_{R} = 18.74 min (minor). $[\alpha]_{\text{D}}^{20} = +10.7$ (c 1.00, CHCl_3).

Recrystallization of benzoate **18''** in *n*-hexane allowed to obtain a single crystal suitable for X-ray diffraction analysis which allowed to determine that the absolute configuration of **18''** is (*S*), and therefore, that cyclopentane carbaldehyde **18** is also (*S*). Notably, after X-ray analysis, the enantiopure single crystal was confirmed to be the major enantiomer of **18''** by chiral HPLC.

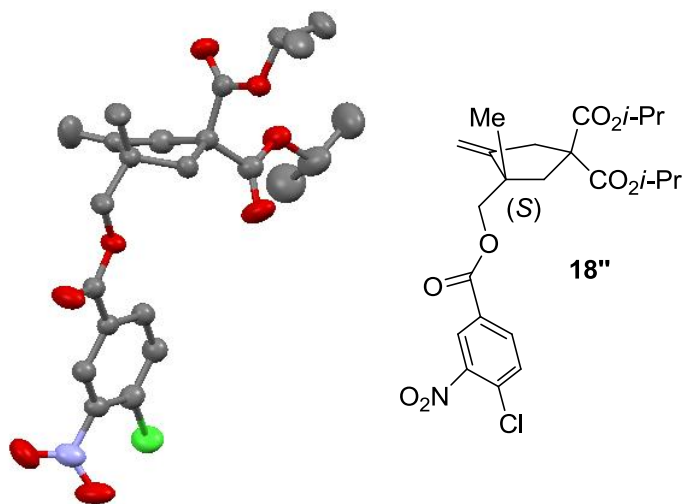


Table 1. Crystal data and structure refinement for compound **18''**

Empirical formula	C ₂₃ H ₂₈ Cl N O ₈	
Formula weight	481.91	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 2	
Unit cell dimensions	$a = 35.5028(9)$ Å	$\alpha = 90^\circ$.
	$b = 7.2712(2)$ Å	$\beta = 90^\circ$.
	$c = 9.7552(3)$ Å	$\gamma = 90^\circ$.
Volume	$2518.28(12)$ Å ³	
Z	4	
Density (calculated)	1.271 Mg/m ³	

Absorption coefficient	1.736 mm ⁻¹
F(000)	1016
Crystal size	0.37 x 0.27 x 0.24 mm ³
Theta range for data collection	4.70 to 66.61°.
Index ranges	-41<=h<=42, -8<=k<=8, -11<=l<=11
Reflections collected	19460
Independent reflections	4418 [R(int) = 0.0193]
Completeness to theta = 66.61°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.753 and 0.639
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4418 / 0 / 304
Goodness-of-fit on F ²	1.074
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0969
R indices (all data)	R1 = 0.0350, wR2 = 0.0973
Absolute structure parameter	0.009(14)
Largest diff. peak and hole	0.512 and -0.253 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for cp91_0ma. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4077(1)	2149(2)	1154(2)	40(1)
C(2)	3876(1)	3660(3)	1949(2)	45(1)
C(3)	3635(1)	2840(3)	3044(2)	49(1)
C(4)	3590(1)	784(2)	2661(2)	39(1)
C(5)	3958(1)	350(2)	1868(2)	39(1)
C(6)	3962(1)	2161(3)	-361(2)	56(1)
C(7)	3907(1)	5419(3)	1711(3)	74(1)
C(8)	4503(1)	2367(3)	1215(2)	43(1)
C(9)	4974(1)	2527(3)	2921(2)	39(1)
C(10)	5046(1)	2550(2)	4429(2)	36(1)
C(11)	5409(1)	2948(2)	4870(2)	39(1)
C(12)	5485(1)	2962(2)	6254(2)	40(1)
C(13)	5207(1)	2601(3)	7217(2)	44(1)
C(14)	4843(1)	2239(3)	6764(2)	48(1)

C(15)	4764(1)	2196(3)	5381(2)	43(1)
C(16)	3559(1)	-334(3)	3970(2)	46(1)
C(17)	3144(1)	-1146(5)	5770(2)	76(1)
C(18)	3232(1)	426(6)	6816(3)	104(1)
C(19)	2736(1)	-1592(6)	5868(3)	103(1)
C(20)	3242(1)	465(2)	1773(2)	41(1)
C(21)	2909(1)	-1896(3)	555(2)	55(1)
C(22)	3048(1)	-3457(4)	-314(3)	77(1)
C(23)	2599(1)	-2437(4)	1517(3)	76(1)
N(1)	5869(1)	3425(3)	6690(2)	53(1)
O(1)	4609(1)	2414(2)	2649(1)	44(1)
O(2)	5217(1)	2598(3)	2067(1)	62(1)
O(3)	6020(1)	2437(3)	7537(2)	78(1)
O(4)	6014(1)	4763(3)	6167(2)	79(1)
O(5)	3822(1)	-966(3)	4570(2)	70(1)
O(6)	3206(1)	-392(2)	4415(2)	57(1)
O(7)	3013(1)	1617(2)	1473(2)	60(1)
O(8)	3232(1)	-1282(2)	1365(1)	46(1)
Cl(1)	5288(1)	2668(1)	8960(1)	60(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for 18''.

C(1)-C(8)	1.522(2)
C(1)-C(2)	1.523(3)
C(1)-C(6)	1.533(2)
C(1)-C(5)	1.542(2)
C(2)-C(7)	1.304(3)
C(2)-C(3)	1.493(3)
C(3)-C(4)	1.549(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(16)	1.518(3)
C(4)-C(20)	1.526(2)
C(4)-C(5)	1.550(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800

C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9500
C(7)-H(7B)	0.9500
C(8)-O(1)	1.448(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-O(2)	1.200(2)
C(9)-O(1)	1.326(2)
C(9)-C(10)	1.493(2)
C(10)-C(15)	1.389(2)
C(10)-C(11)	1.389(2)
C(11)-C(12)	1.377(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.387(3)
C(12)-N(1)	1.469(2)
C(13)-C(14)	1.391(3)
C(13)-Cl(1)	1.7252(17)
C(14)-C(15)	1.378(3)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-O(5)	1.193(2)
C(16)-O(6)	1.328(2)
C(17)-O(6)	1.447(3)
C(17)-C(19)	1.485(4)
C(17)-C(18)	1.564(5)
C(17)-H(17)	1.0000
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-O(7)	1.203(2)
C(20)-O(8)	1.332(2)
C(21)-O(8)	1.463(2)
C(21)-C(23)	1.500(3)
C(21)-C(22)	1.500(4)
C(21)-H(21)	1.0000

C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
N(1)-O(4)	1.212(3)
N(1)-O(3)	1.219(3)

C(8)-C(1)-C(2)	111.74(15)
C(8)-C(1)-C(6)	107.57(15)
C(2)-C(1)-C(6)	111.23(16)
C(8)-C(1)-C(5)	110.14(14)
C(2)-C(1)-C(5)	104.66(14)
C(6)-C(1)-C(5)	111.55(15)
C(7)-C(2)-C(3)	124.5(2)
C(7)-C(2)-C(1)	125.3(2)
C(3)-C(2)-C(1)	110.16(15)
C(2)-C(3)-C(4)	105.81(15)
C(2)-C(3)-H(3A)	110.6
C(4)-C(3)-H(3A)	110.6
C(2)-C(3)-H(3B)	110.6
C(4)-C(3)-H(3B)	110.6
H(3A)-C(3)-H(3B)	108.7
C(16)-C(4)-C(20)	109.81(14)
C(16)-C(4)-C(3)	108.73(16)
C(20)-C(4)-C(3)	111.59(14)
C(16)-C(4)-C(5)	111.71(14)
C(20)-C(4)-C(5)	111.60(15)
C(3)-C(4)-C(5)	103.23(14)
C(1)-C(5)-C(4)	106.53(14)
C(1)-C(5)-H(5A)	110.4
C(4)-C(5)-H(5A)	110.4
C(1)-C(5)-H(5B)	110.4
C(4)-C(5)-H(5B)	110.4
H(5A)-C(5)-H(5B)	108.6
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5

H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	120.0
C(2)-C(7)-H(7B)	120.0
H(7A)-C(7)-H(7B)	120.0
O(1)-C(8)-C(1)	107.32(13)
O(1)-C(8)-H(8A)	110.2
C(1)-C(8)-H(8A)	110.2
O(1)-C(8)-H(8B)	110.2
C(1)-C(8)-H(8B)	110.2
H(8A)-C(8)-H(8B)	108.5
O(2)-C(9)-O(1)	124.46(15)
O(2)-C(9)-C(10)	124.12(15)
O(1)-C(9)-C(10)	111.42(14)
C(15)-C(10)-C(11)	119.98(15)
C(15)-C(10)-C(9)	122.25(15)
C(11)-C(10)-C(9)	117.77(15)
C(12)-C(11)-C(10)	119.11(16)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	121.55(16)
C(11)-C(12)-N(1)	117.85(16)
C(13)-C(12)-N(1)	120.58(16)
C(12)-C(13)-C(14)	118.80(16)
C(12)-C(13)-Cl(1)	122.89(14)
C(14)-C(13)-Cl(1)	118.26(14)
C(15)-C(14)-C(13)	120.26(16)
C(15)-C(14)-H(14)	119.9
C(13)-C(14)-H(14)	119.9
C(14)-C(15)-C(10)	120.27(16)
C(14)-C(15)-H(15)	119.9
C(10)-C(15)-H(15)	119.9
O(5)-C(16)-O(6)	124.40(18)
O(5)-C(16)-C(4)	124.36(18)
O(6)-C(16)-C(4)	111.04(15)
O(6)-C(17)-C(19)	106.9(2)

O(6)-C(17)-C(18)	106.8(2)
C(19)-C(17)-C(18)	108.2(3)
O(6)-C(17)-H(17)	111.6
C(19)-C(17)-H(17)	111.6
C(18)-C(17)-H(17)	111.6
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(7)-C(20)-O(8)	125.05(17)
O(7)-C(20)-C(4)	125.38(17)
O(8)-C(20)-C(4)	109.56(14)
O(8)-C(21)-C(23)	108.52(18)
O(8)-C(21)-C(22)	106.17(18)
C(23)-C(21)-C(22)	113.4(2)
O(8)-C(21)-H(21)	109.6
C(23)-C(21)-H(21)	109.6
C(22)-C(21)-H(21)	109.6
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

O(4)-N(1)-O(3)	124.9(2)
O(4)-N(1)-C(12)	117.06(18)
O(3)-N(1)-C(12)	118.01(19)
C(9)-O(1)-C(8)	116.61(13)
C(16)-O(6)-C(17)	117.08(16)
C(20)-O(8)-C(21)	118.20(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cp91_0ma. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	38(1)	41(1)	42(1)	5(1)	-6(1)	-4(1)
C(2)	38(1)	39(1)	59(1)	-1(1)	-14(1)	-2(1)
C(3)	50(1)	44(1)	51(1)	-9(1)	-5(1)	6(1)
C(4)	35(1)	40(1)	42(1)	2(1)	0(1)	3(1)
C(5)	35(1)	37(1)	45(1)	0(1)	1(1)	0(1)
C(6)	54(1)	67(1)	47(1)	9(1)	-14(1)	-10(1)
C(7)	68(1)	42(1)	112(2)	5(1)	10(2)	2(1)
C(8)	40(1)	53(1)	37(1)	7(1)	-4(1)	-6(1)
C(9)	35(1)	41(1)	41(1)	2(1)	-1(1)	1(1)
C(10)	36(1)	35(1)	37(1)	1(1)	-1(1)	4(1)
C(11)	37(1)	42(1)	38(1)	-3(1)	2(1)	2(1)
C(12)	38(1)	43(1)	38(1)	-5(1)	-3(1)	5(1)
C(13)	50(1)	46(1)	35(1)	-4(1)	2(1)	7(1)
C(14)	44(1)	58(1)	41(1)	3(1)	7(1)	2(1)
C(15)	37(1)	45(1)	46(1)	2(1)	1(1)	1(1)
C(16)	43(1)	52(1)	42(1)	2(1)	2(1)	7(1)
C(17)	64(1)	113(2)	51(1)	26(1)	16(1)	14(1)
C(18)	111(3)	133(3)	68(2)	-7(2)	20(2)	1(2)
C(19)	92(2)	141(3)	76(2)	31(2)	11(2)	-30(2)
C(20)	37(1)	43(1)	44(1)	9(1)	1(1)	1(1)
C(21)	51(1)	63(1)	51(1)	10(1)	-18(1)	-13(1)
C(22)	87(2)	76(2)	69(2)	-9(1)	-24(1)	-16(1)
C(23)	58(1)	93(2)	77(2)	15(2)	-10(1)	-27(1)
N(1)	45(1)	76(1)	40(1)	-14(1)	-4(1)	3(1)

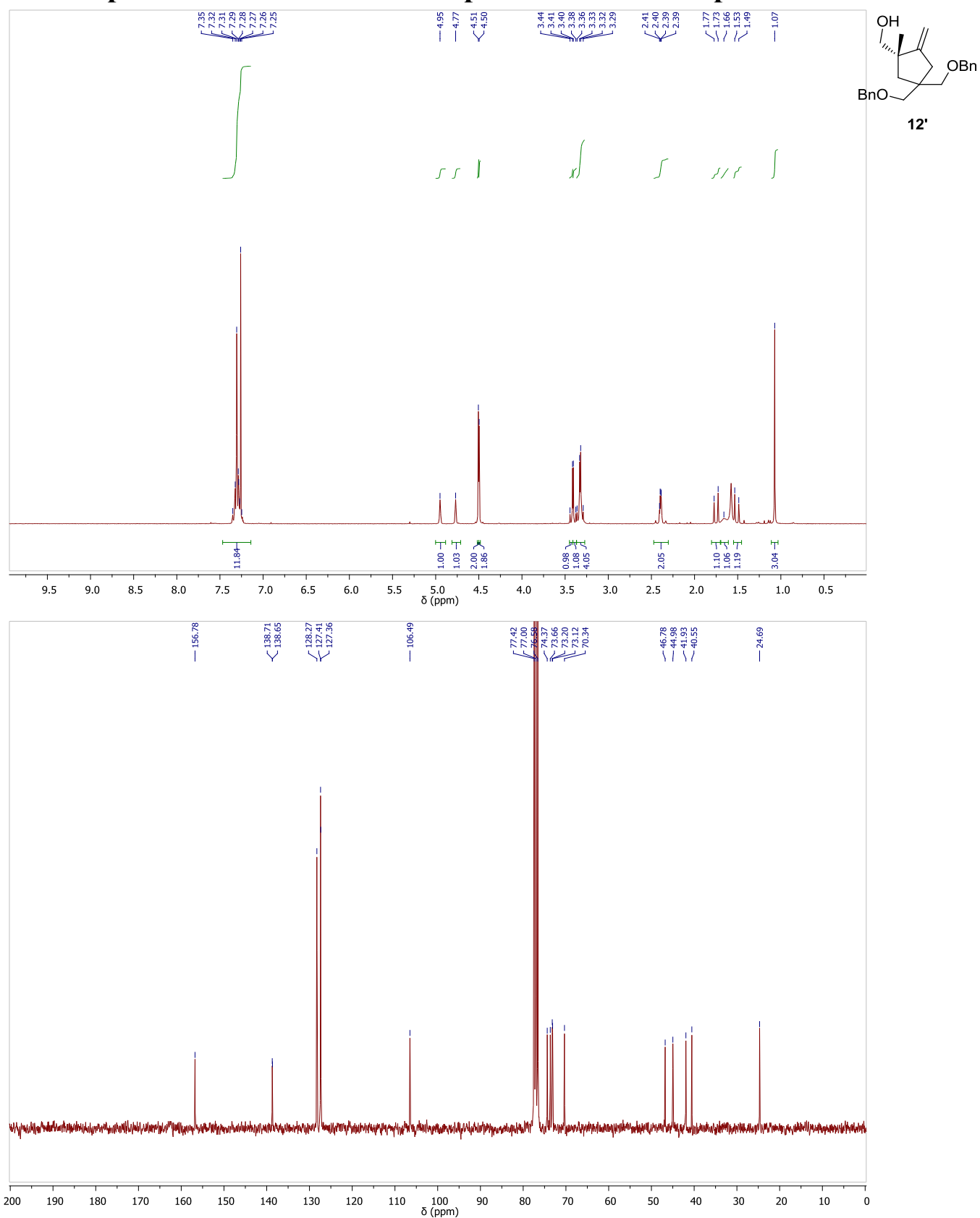
O(1)	34(1)	60(1)	37(1)	3(1)	-4(1)	-4(1)
O(2)	38(1)	111(1)	38(1)	0(1)	0(1)	-5(1)
O(3)	51(1)	138(2)	45(1)	4(1)	-11(1)	16(1)
O(4)	60(1)	88(1)	89(1)	-6(1)	-10(1)	-27(1)
O(5)	54(1)	101(1)	56(1)	28(1)	2(1)	24(1)
O(6)	45(1)	80(1)	45(1)	16(1)	6(1)	7(1)
O(7)	48(1)	55(1)	78(1)	10(1)	-16(1)	11(1)
O(8)	42(1)	44(1)	53(1)	4(1)	-13(1)	-4(1)
Cl(1)	62(1)	86(1)	33(1)	-6(1)	2(1)	3(1)

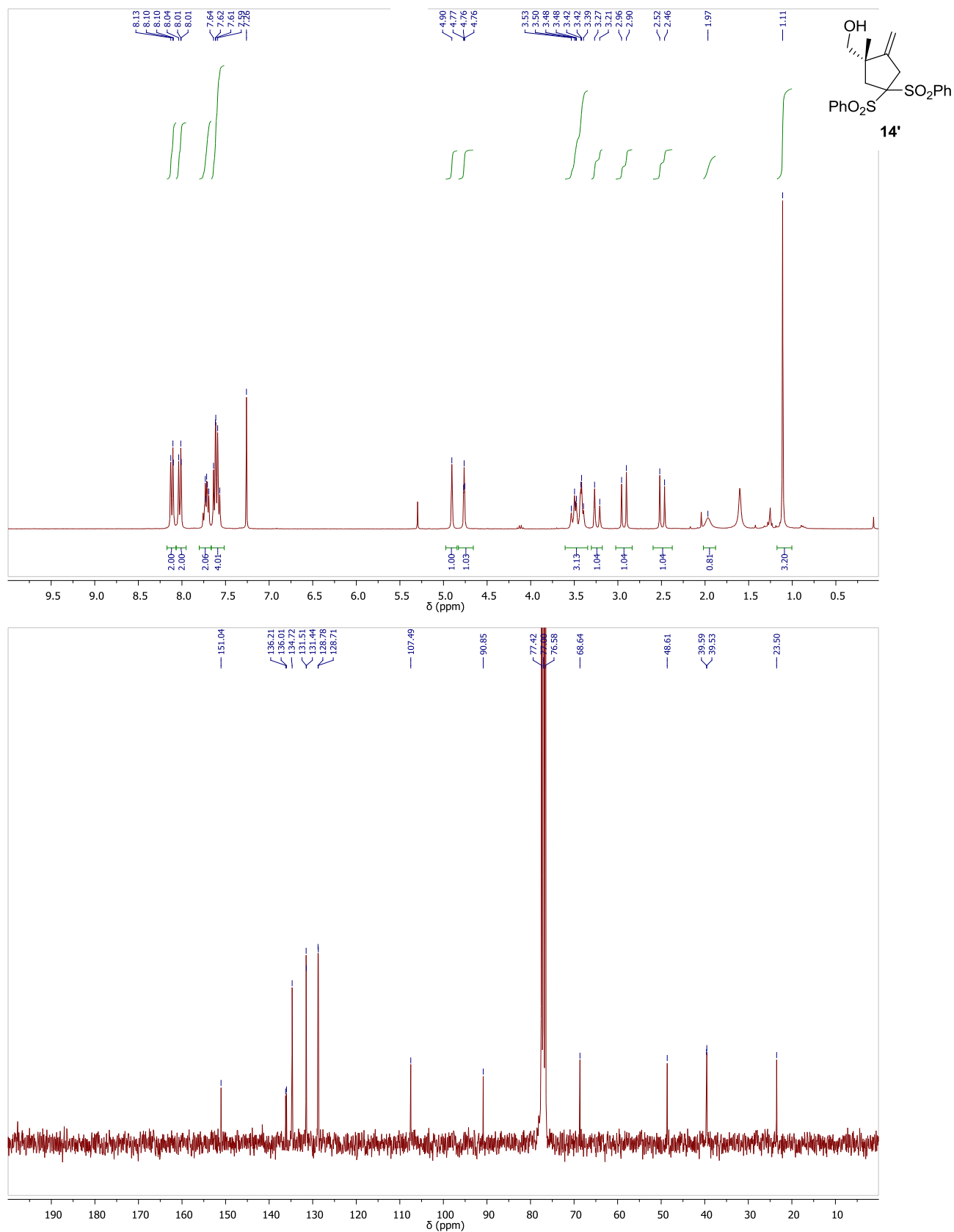
Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cp91_0ma.

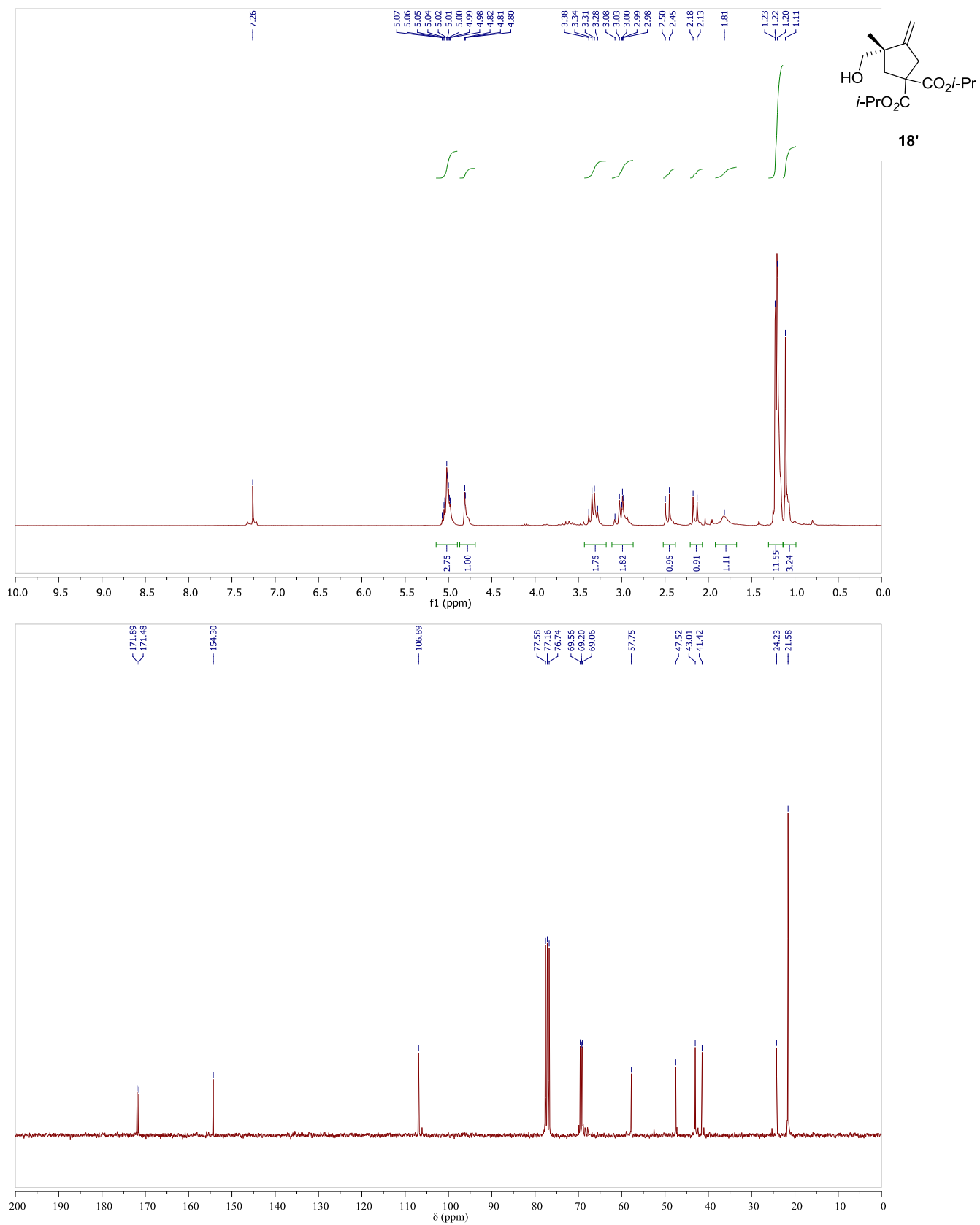
	x	y	z	U(eq)
H(3A)	3387	3457	3075	58
H(3B)	3757	2967	3951	58
H(5A)	4156	-68	2508	47
H(5B)	3913	-630	1182	47
H(6A)	4027	3352	-768	84
H(6B)	3690	1958	-436	84
H(6C)	4096	1180	-848	84
H(7A)	3770	6274	2254	89
H(7B)	4065	5846	995	89
H(8A)	4628	1322	749	52
H(8B)	4581	3520	755	52
H(11)	5602	3207	4225	47
H(14)	4648	2021	7410	57
H(15)	4516	1922	5078	51
H(17)	3304	-2253	5938	91
H(18A)	3497	779	6739	156
H(18B)	3181	-8	7749	156
H(18C)	3072	1493	6617	156
H(19A)	2588	-494	5654	155
H(19B)	2678	-2005	6800	155
H(19C)	2675	-2571	5215	155
H(21)	2821	-870	-49	66

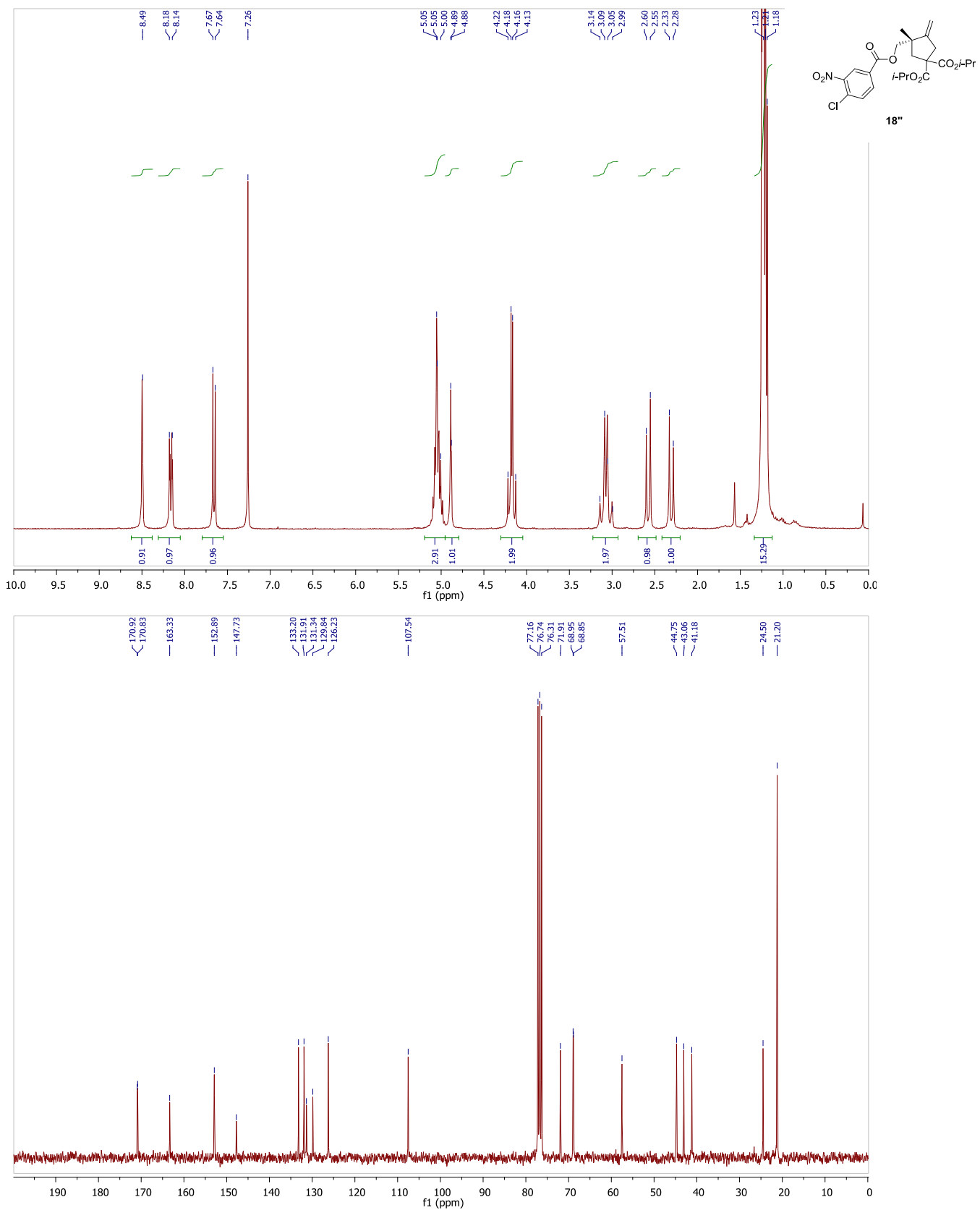
H(22A)	3270	-3061	-832	116
H(22B)	2849	-3834	-952	116
H(22C)	3116	-4498	276	116
H(23A)	2681	-3481	2077	114
H(23B)	2376	-2788	988	114
H(23C)	2537	-1396	2114	114

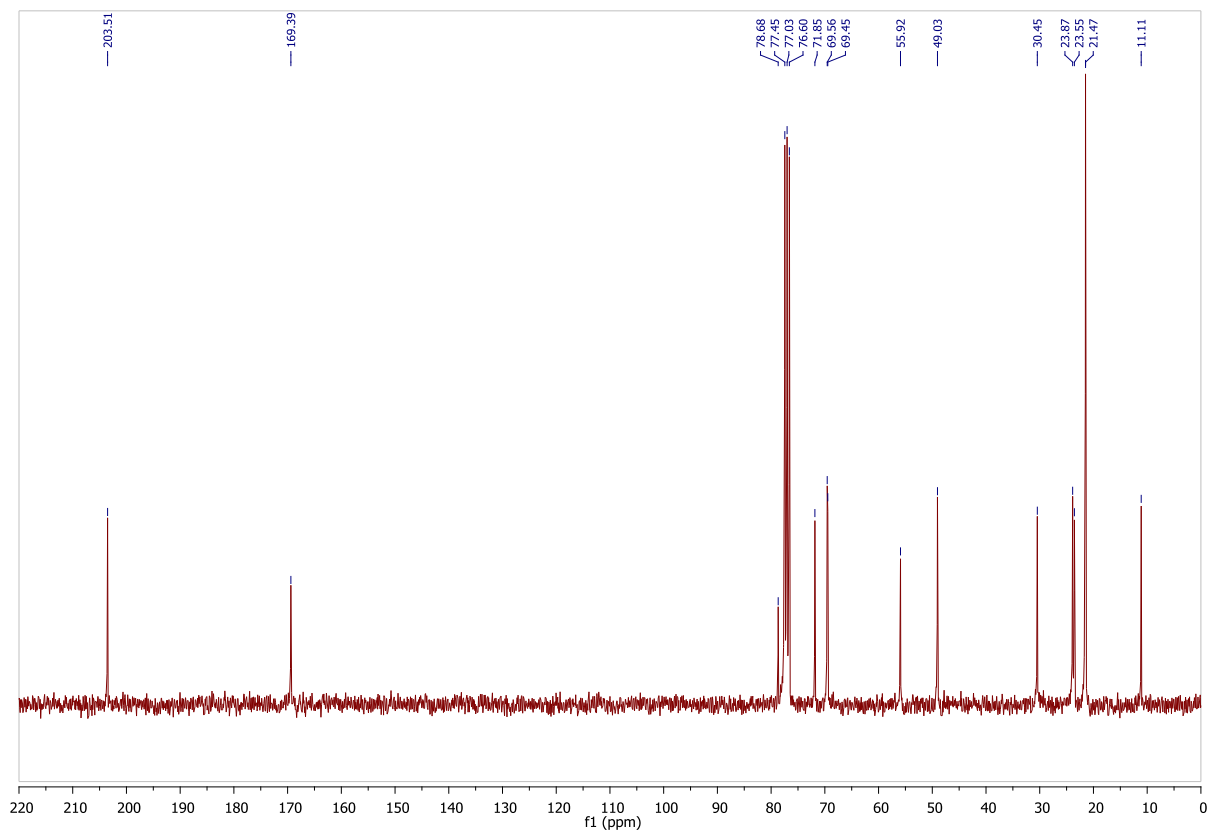
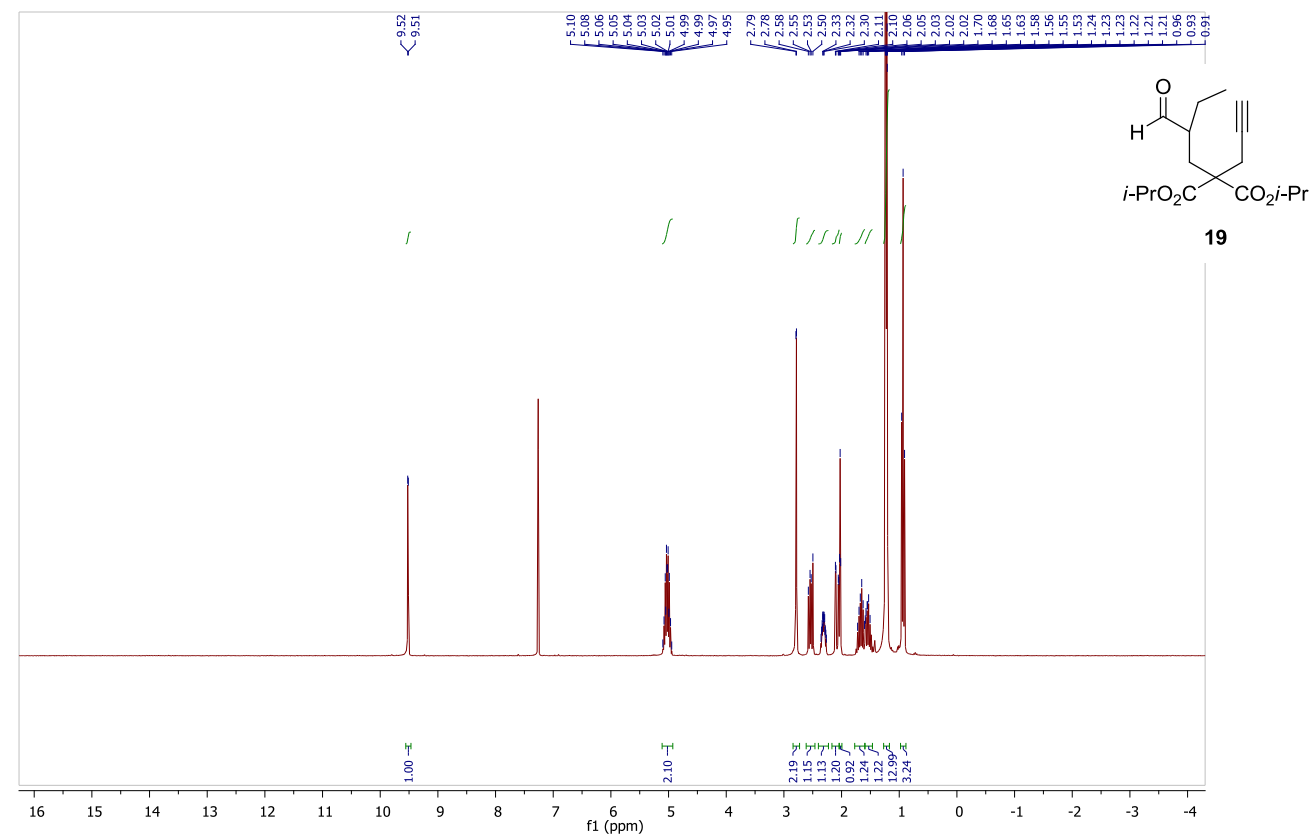
E. Copies of ^1H and ^{13}C NMR Spectra of new Compounds

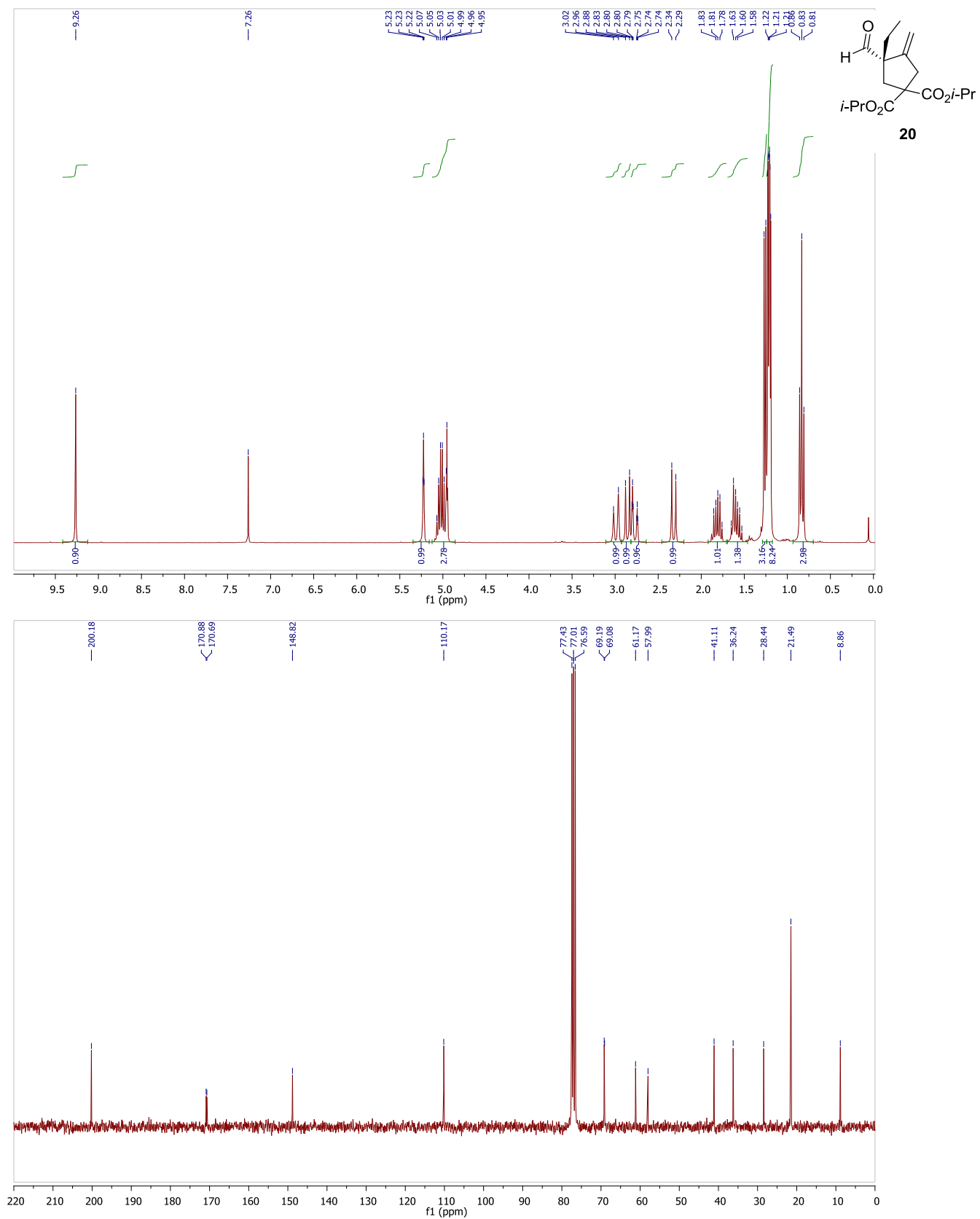


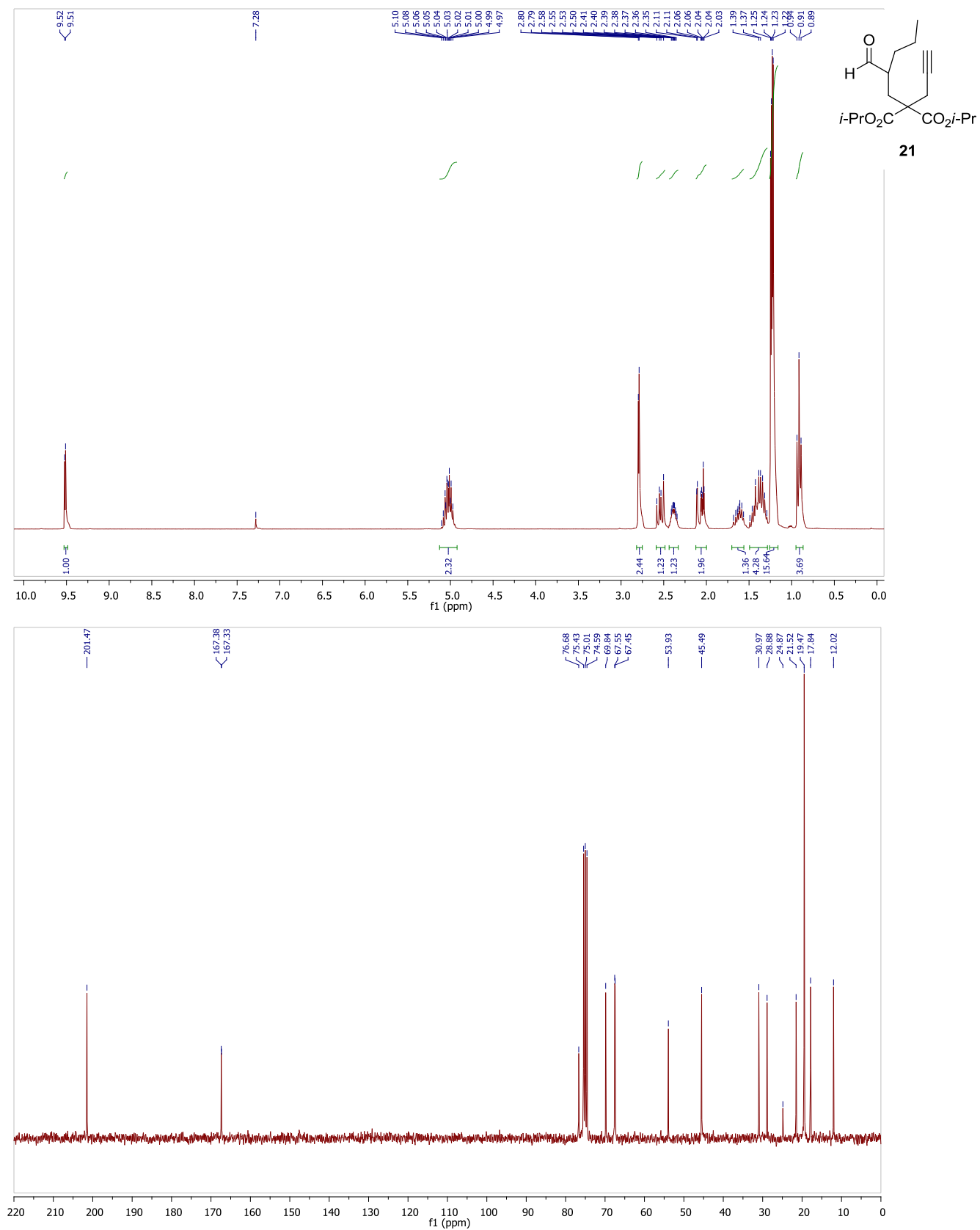


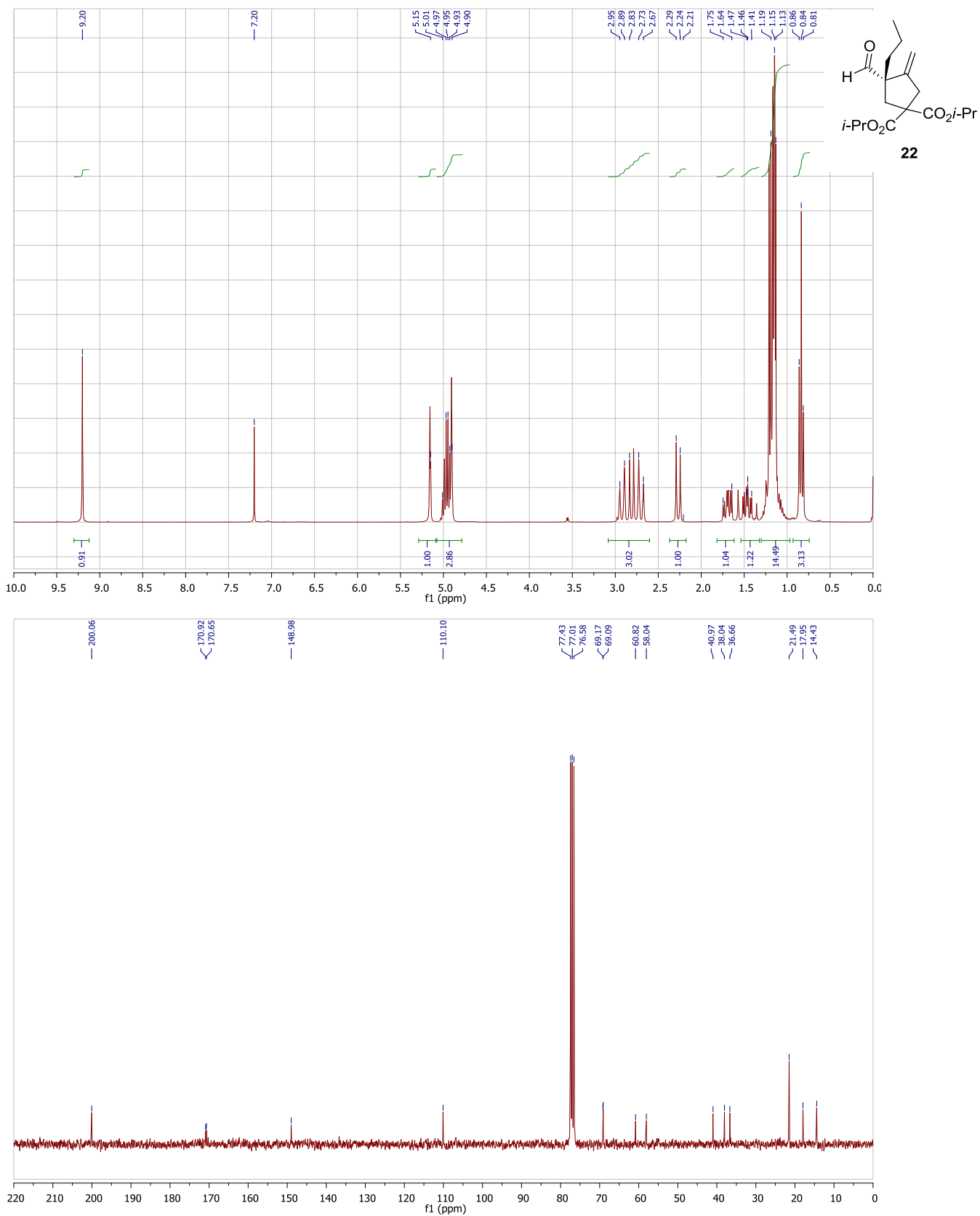


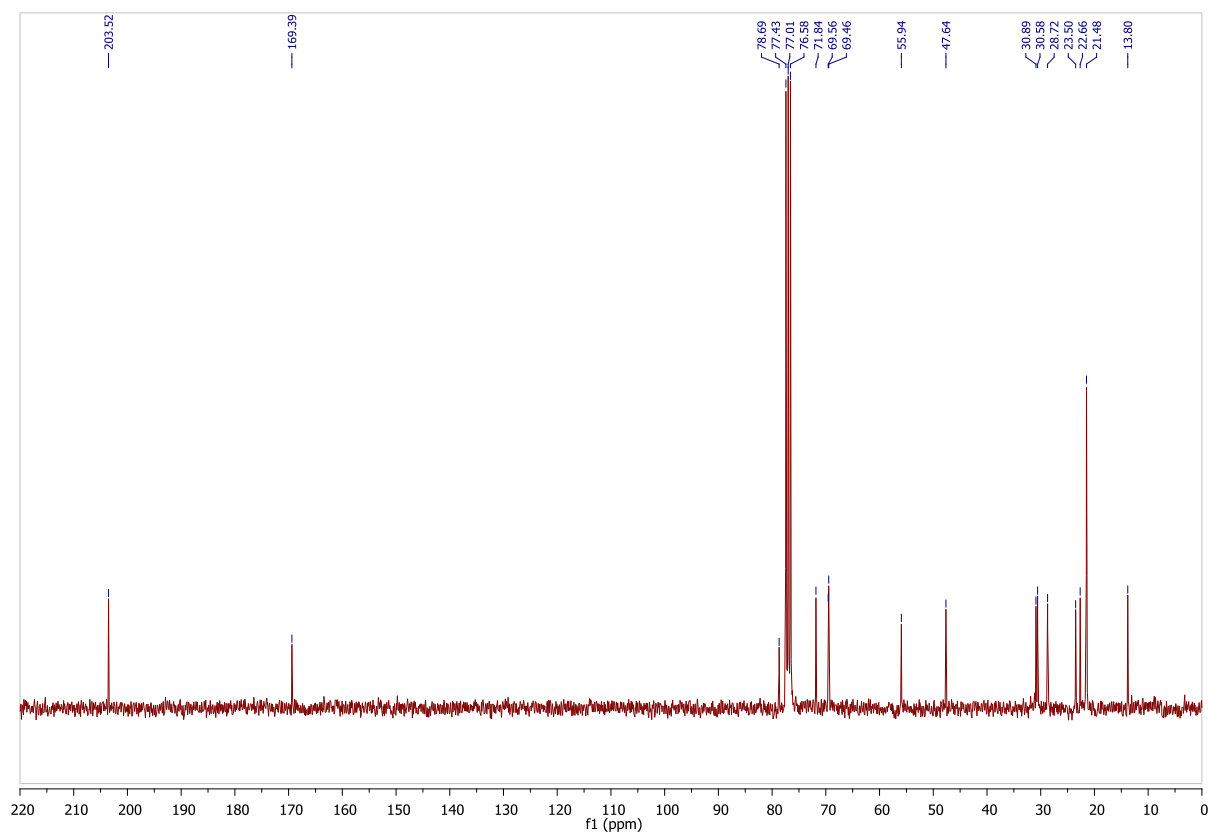
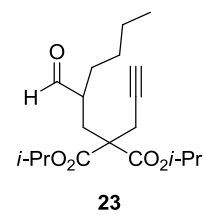
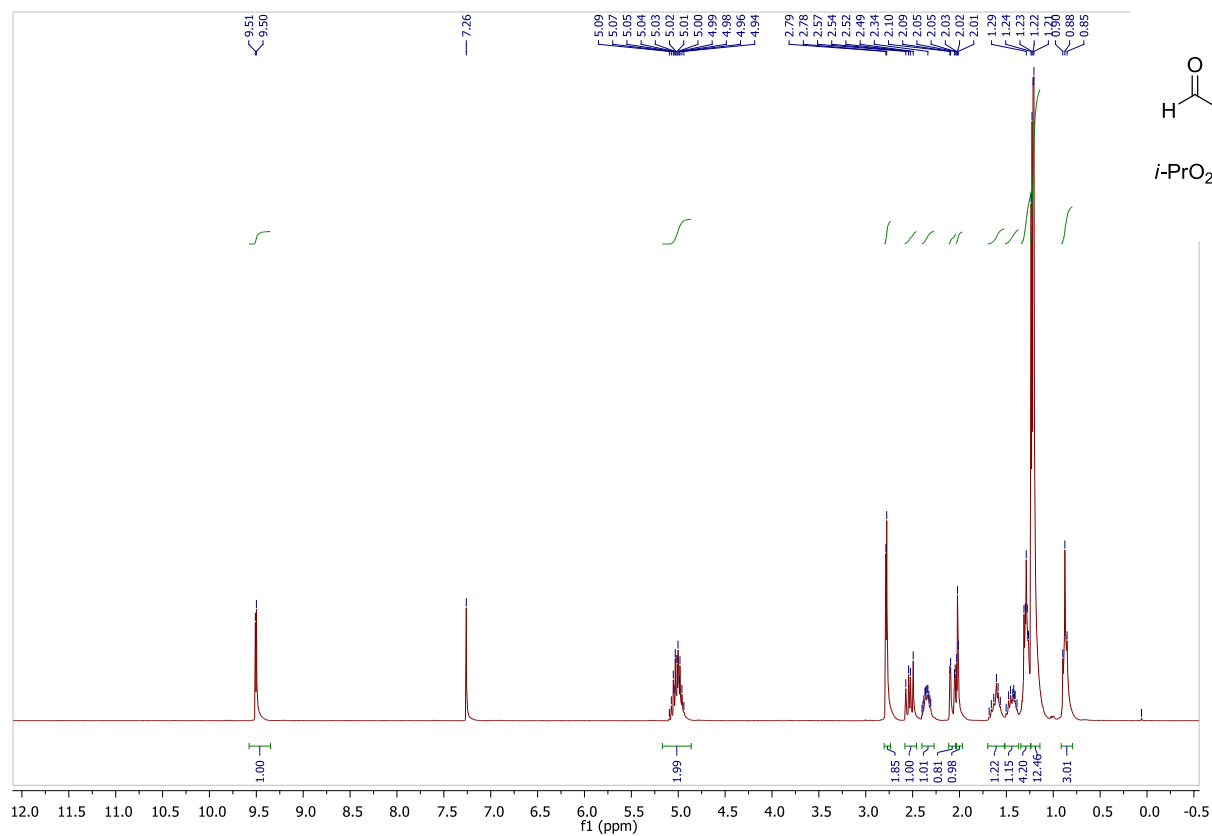


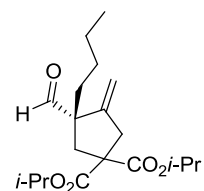
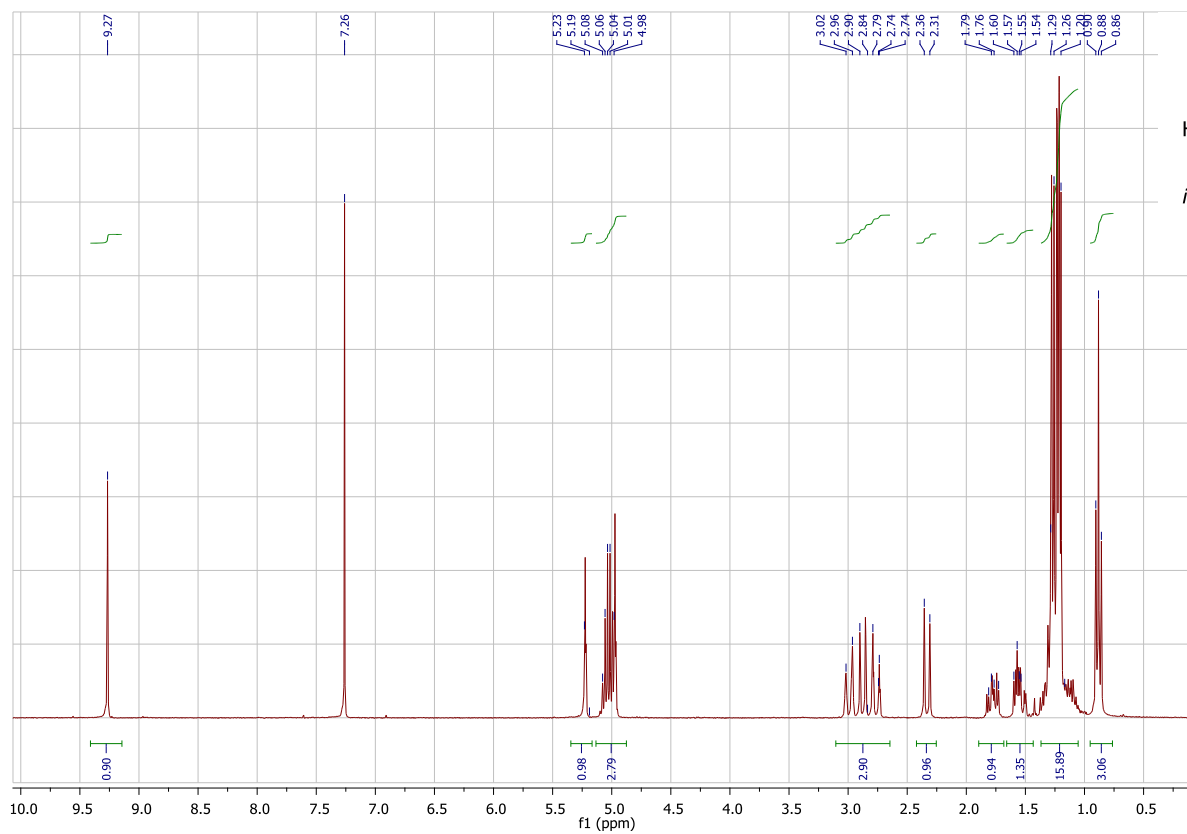




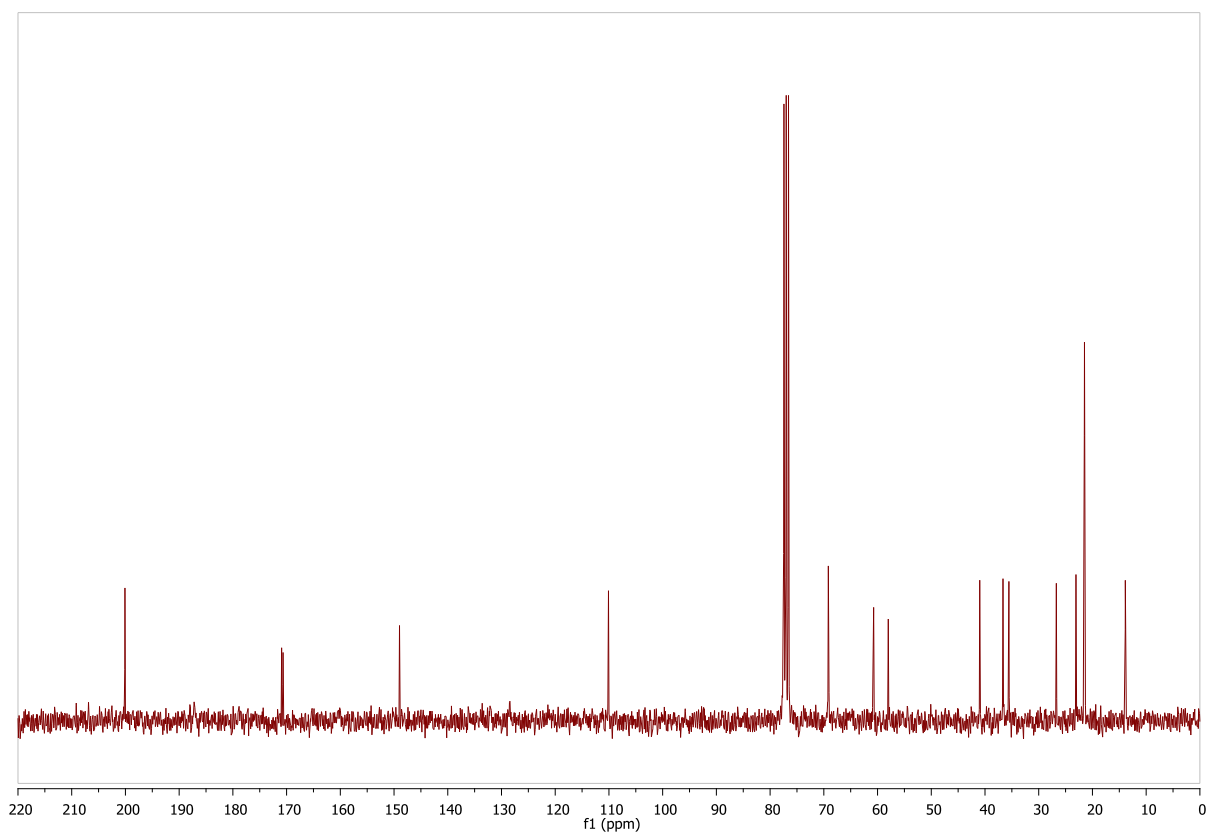


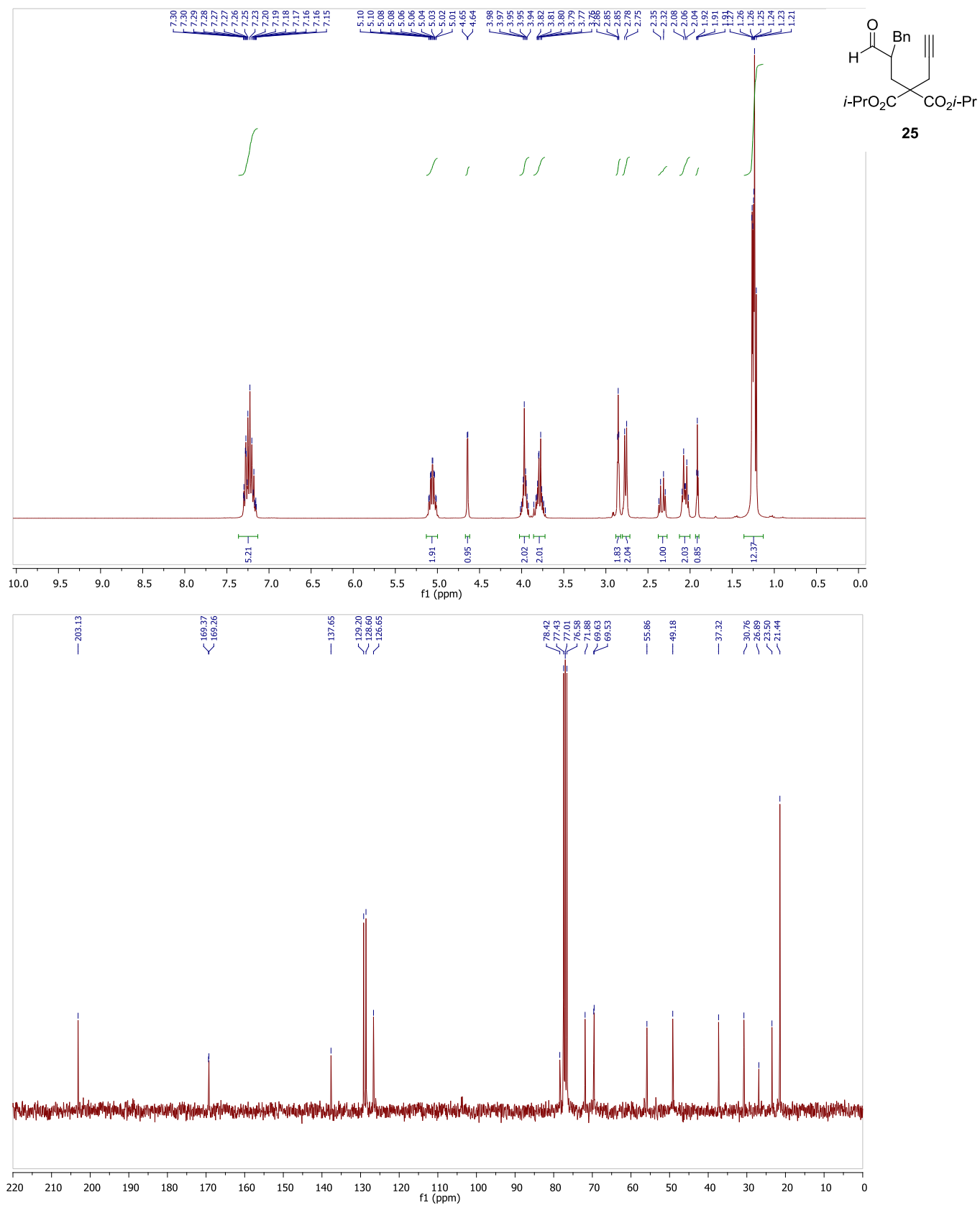


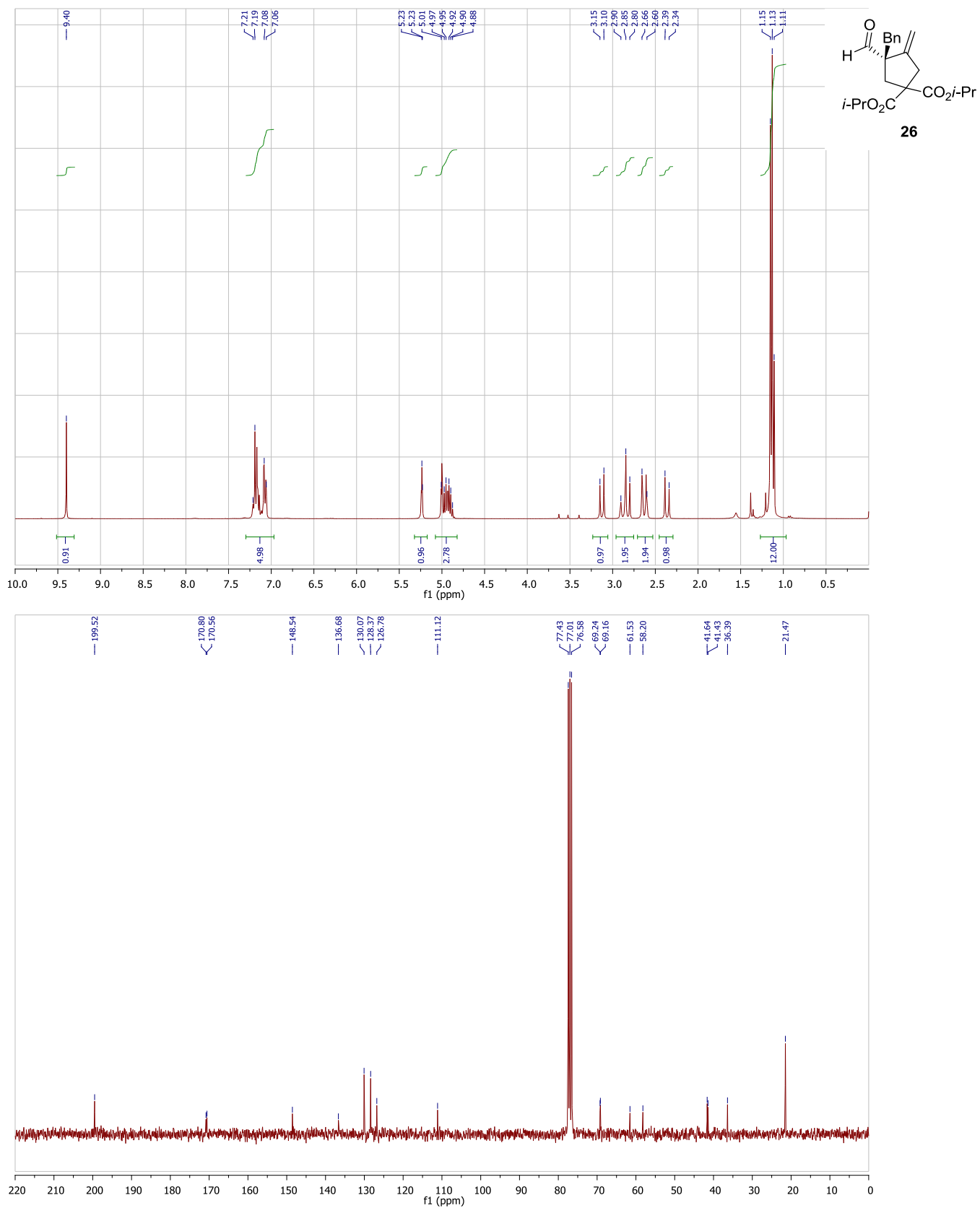




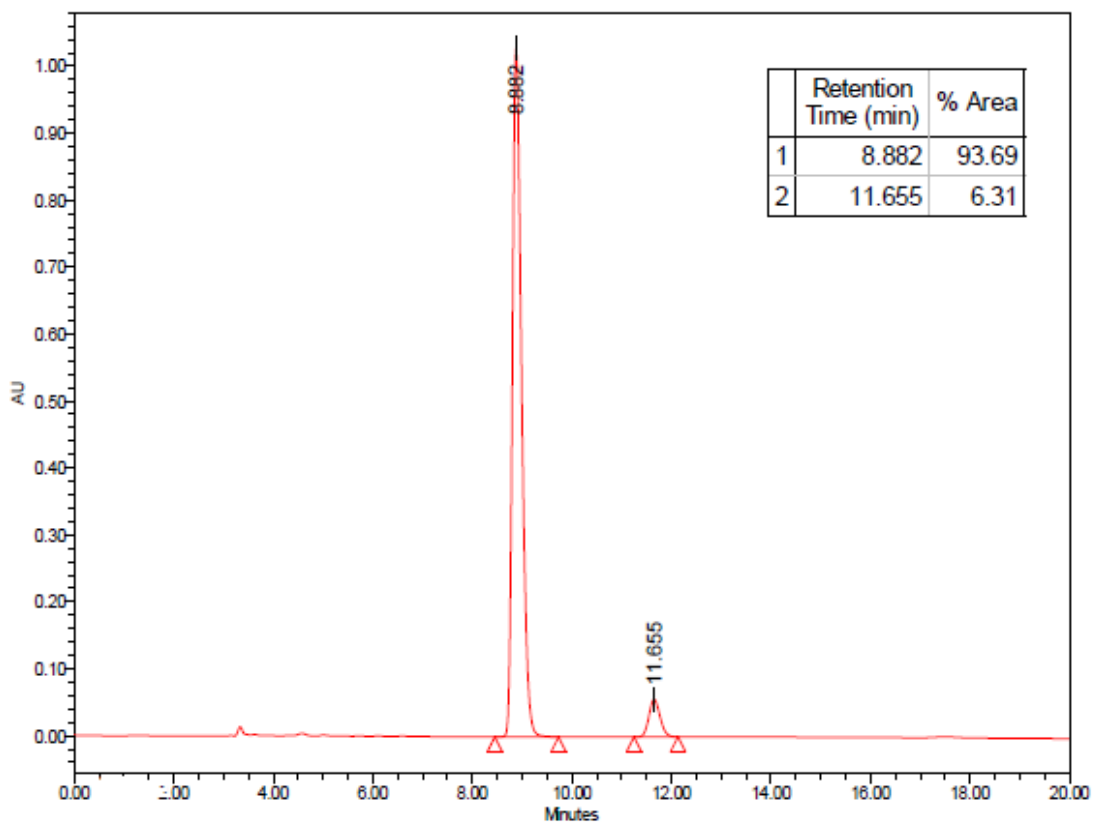
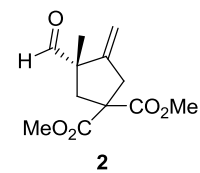
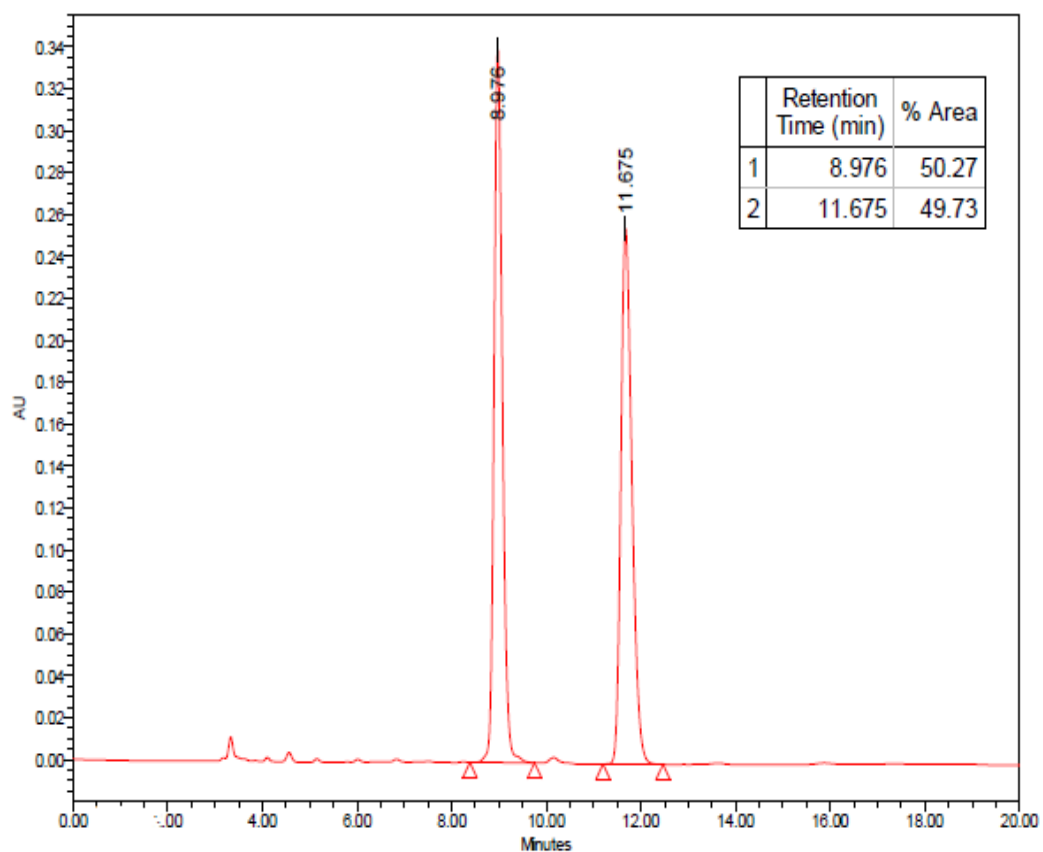
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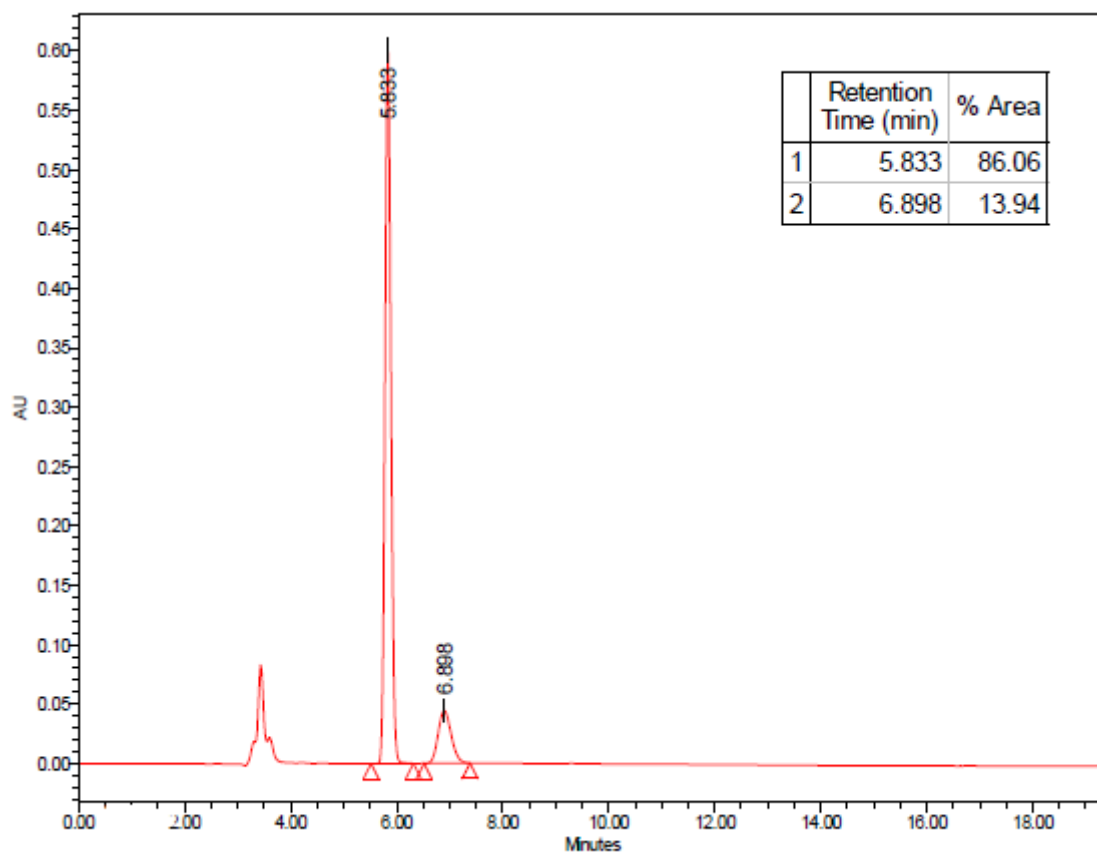
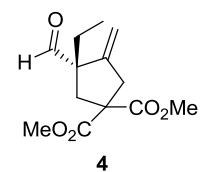
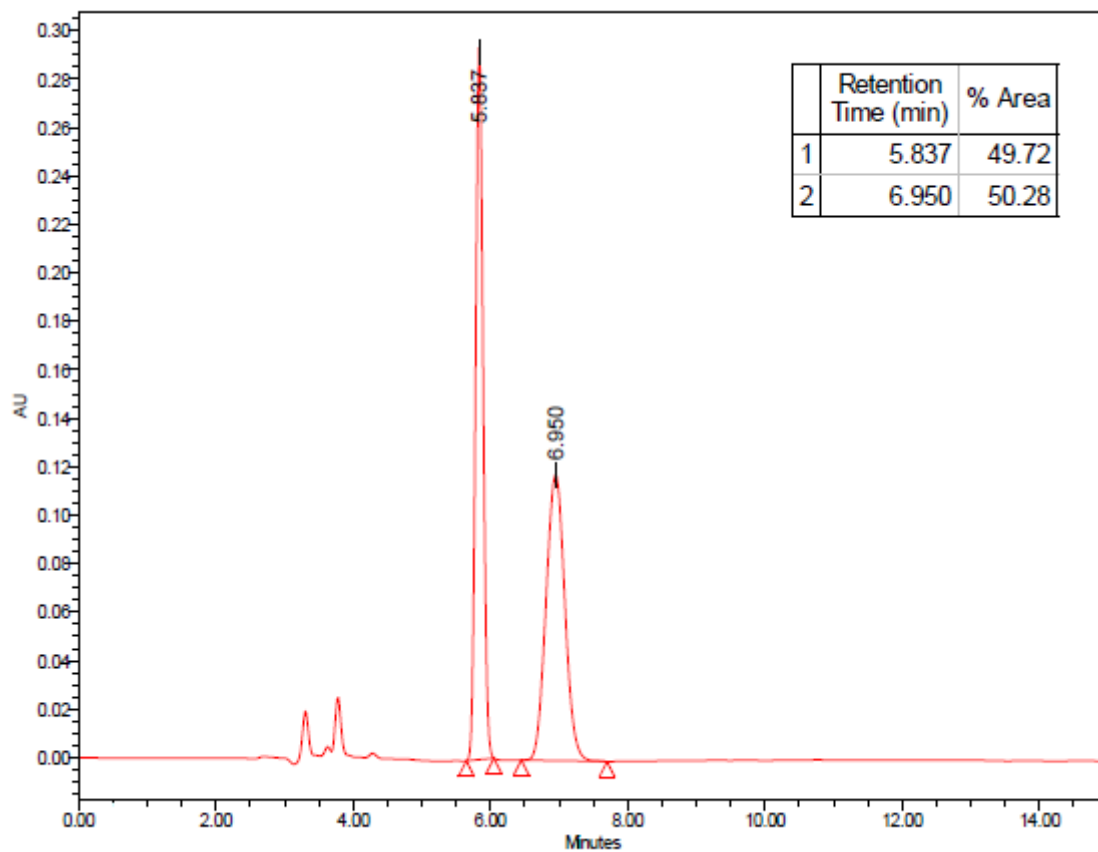


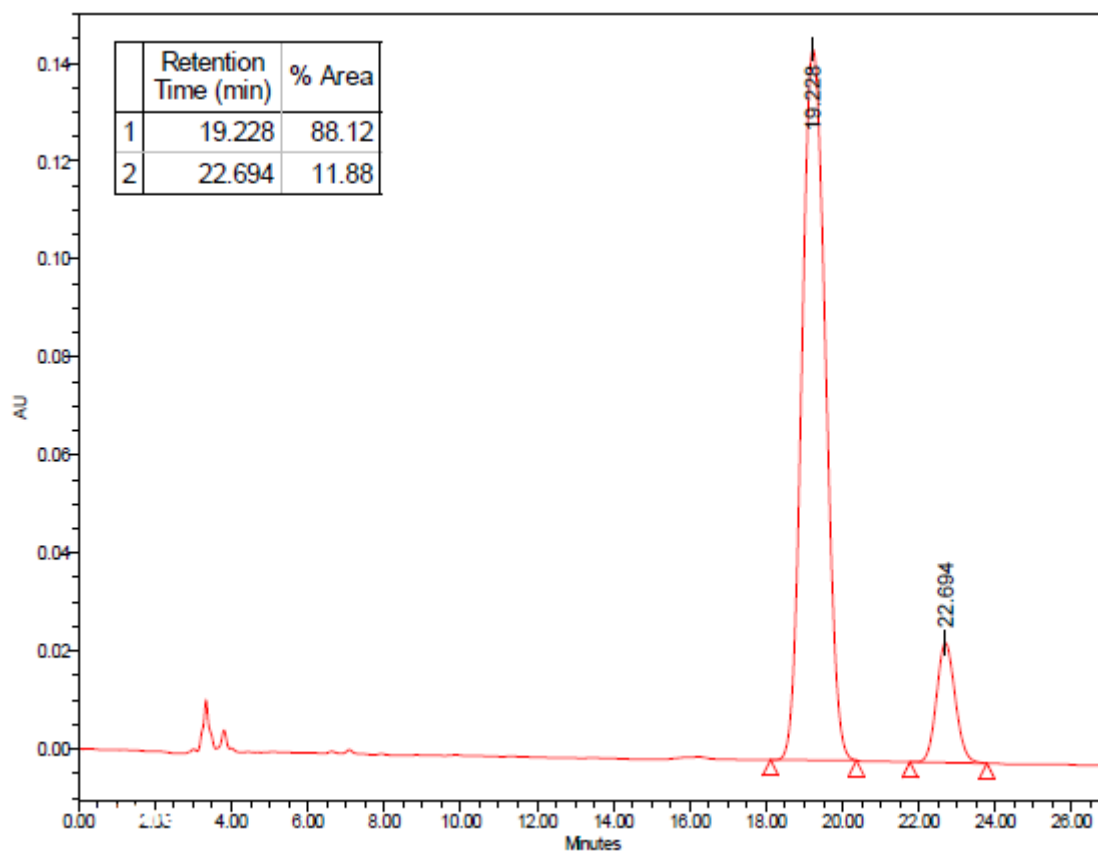
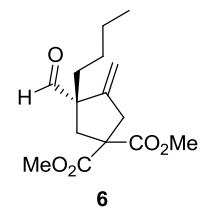
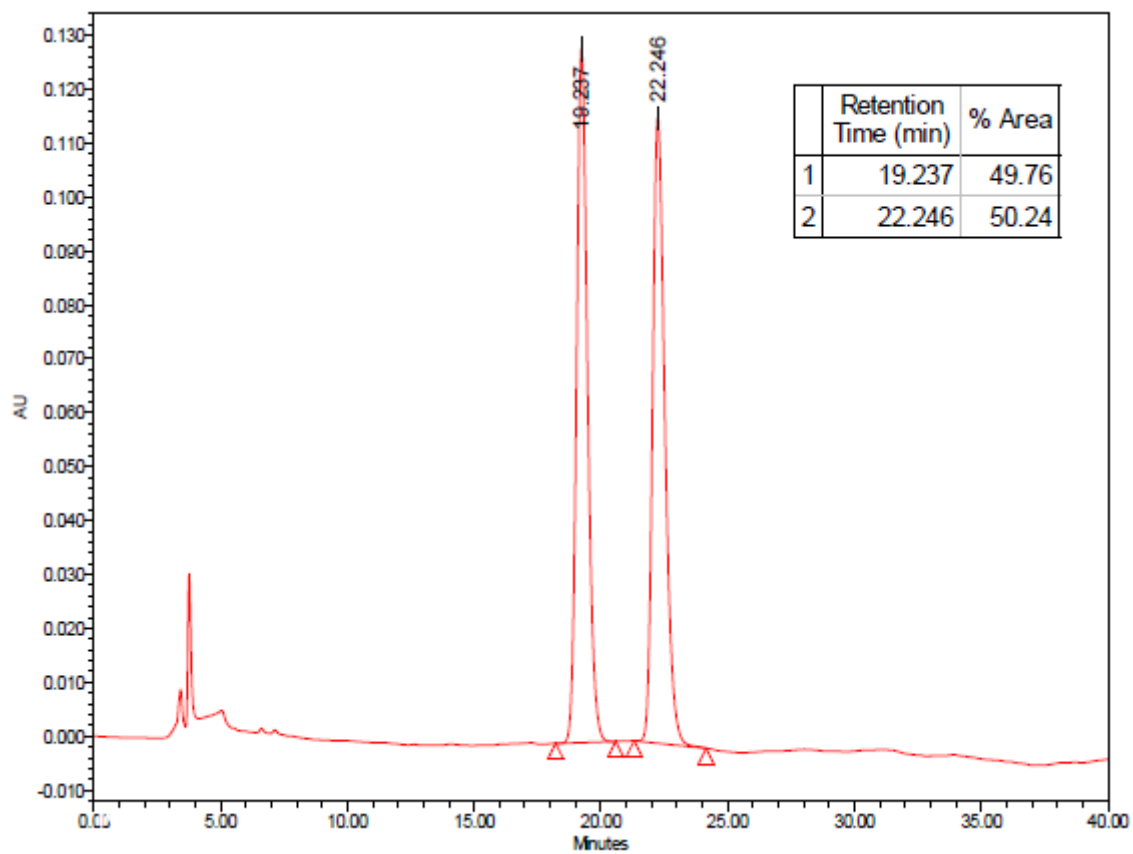


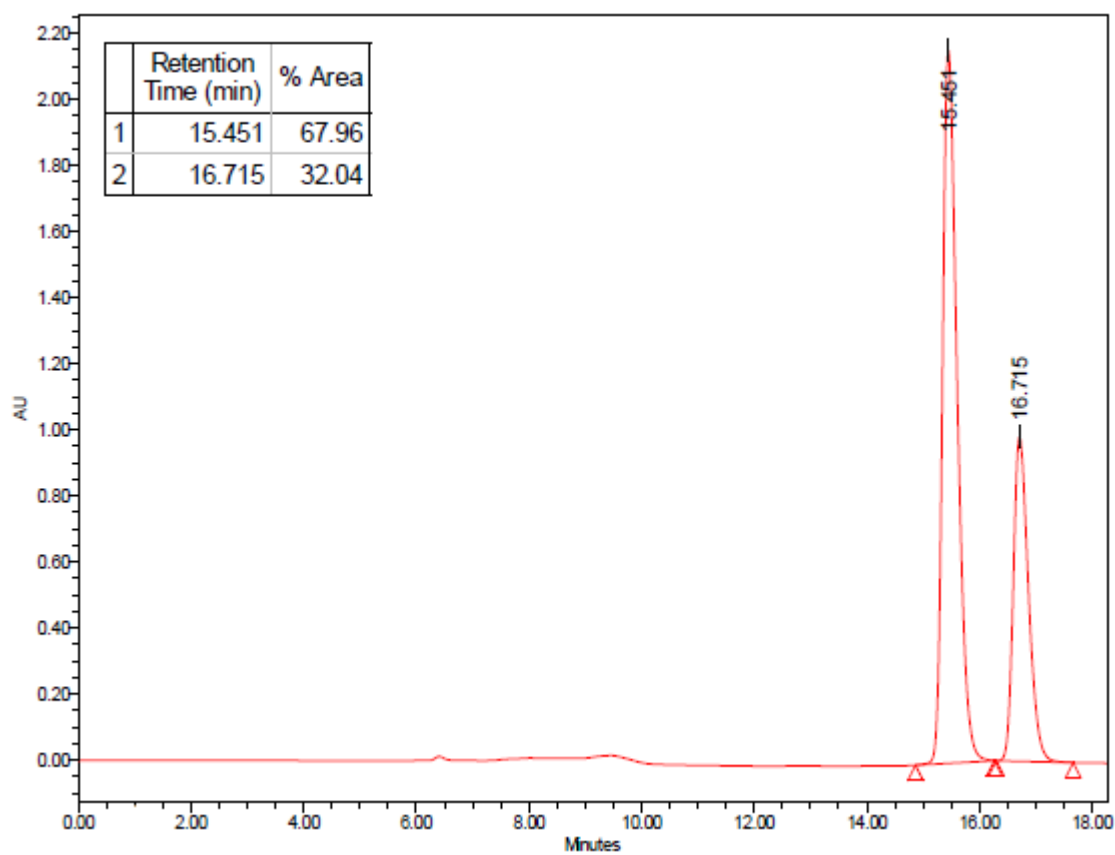
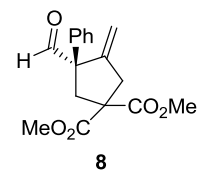
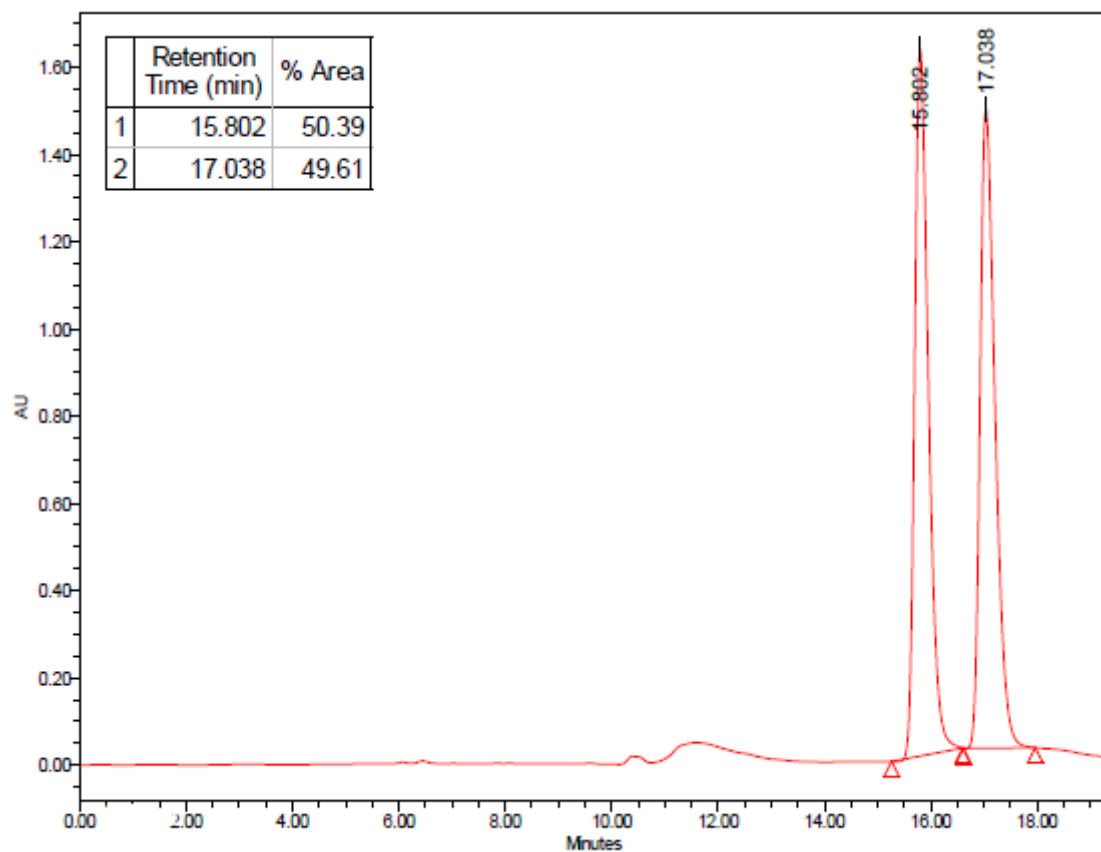


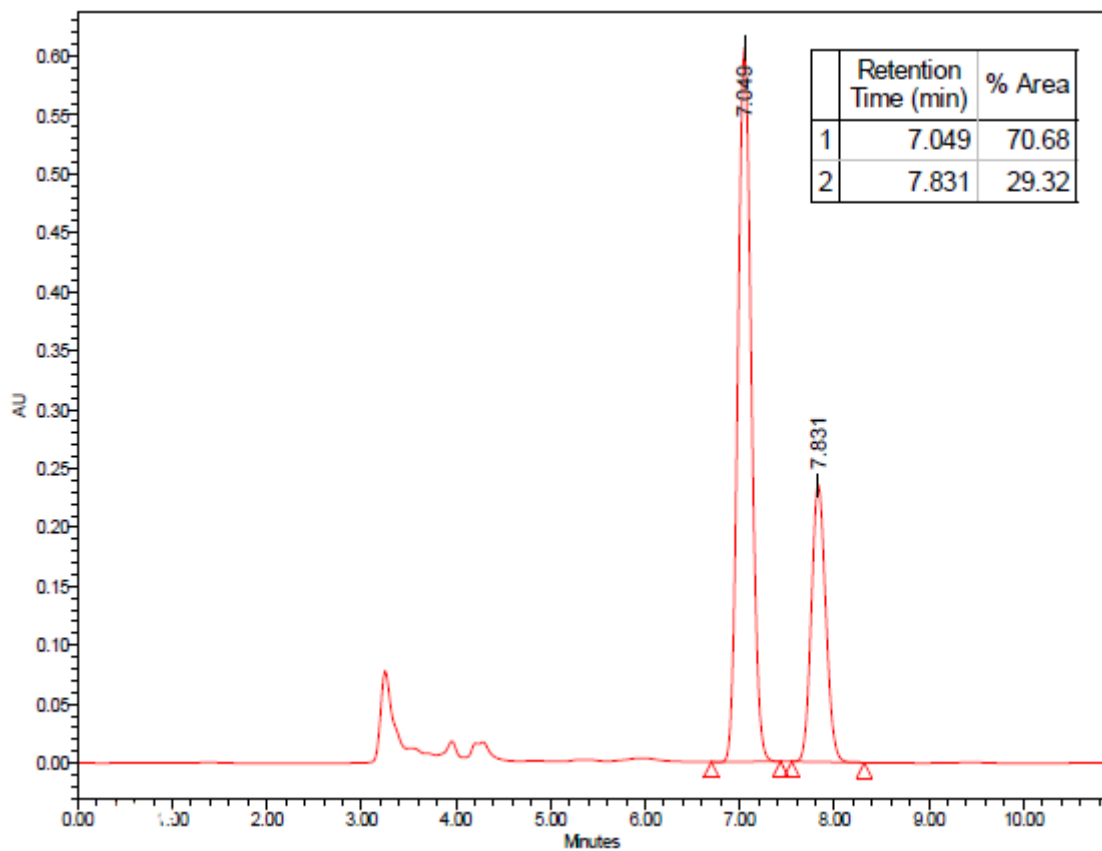
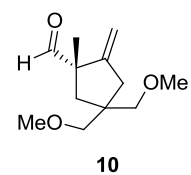
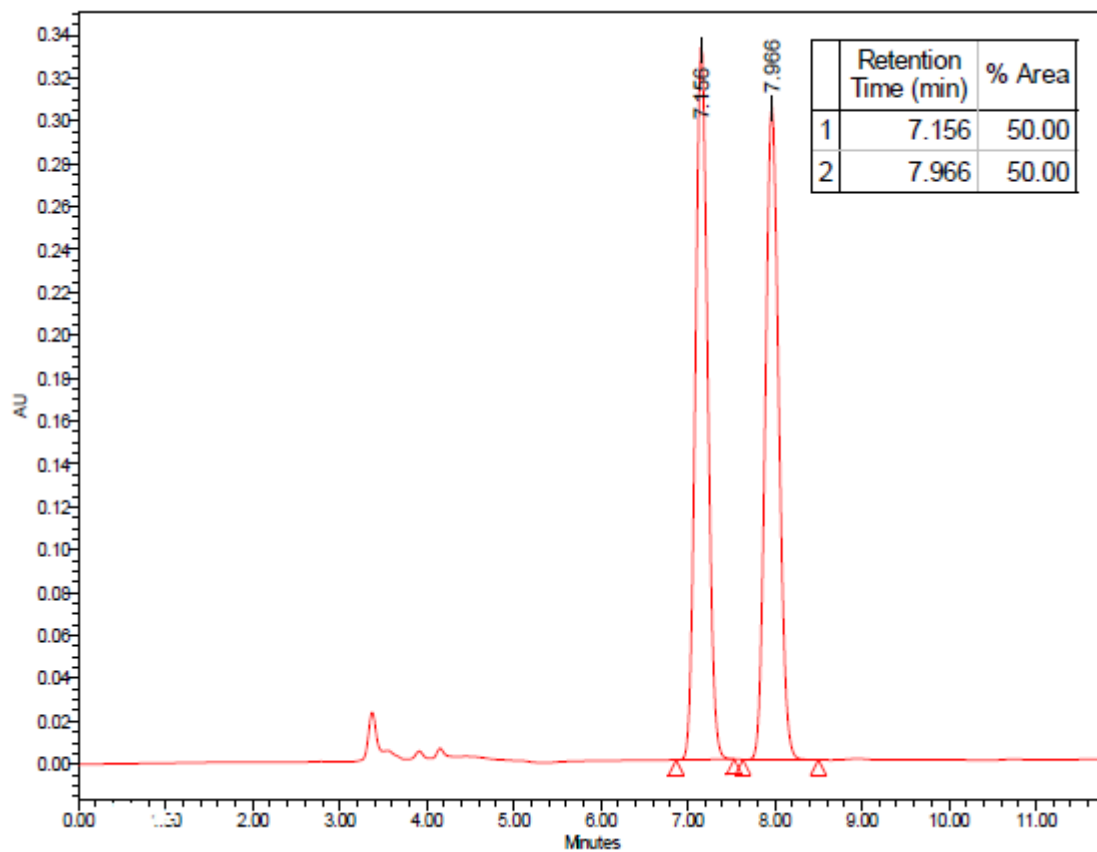
F. Copies of HPLC Spectra

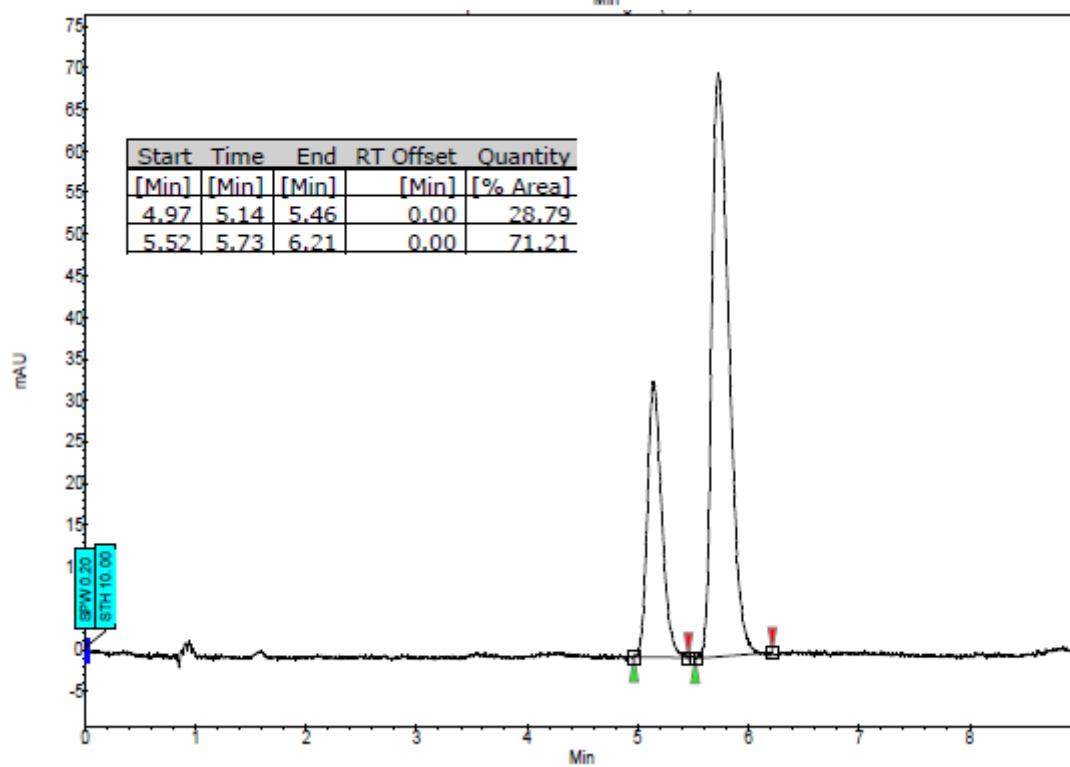
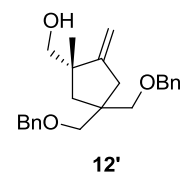
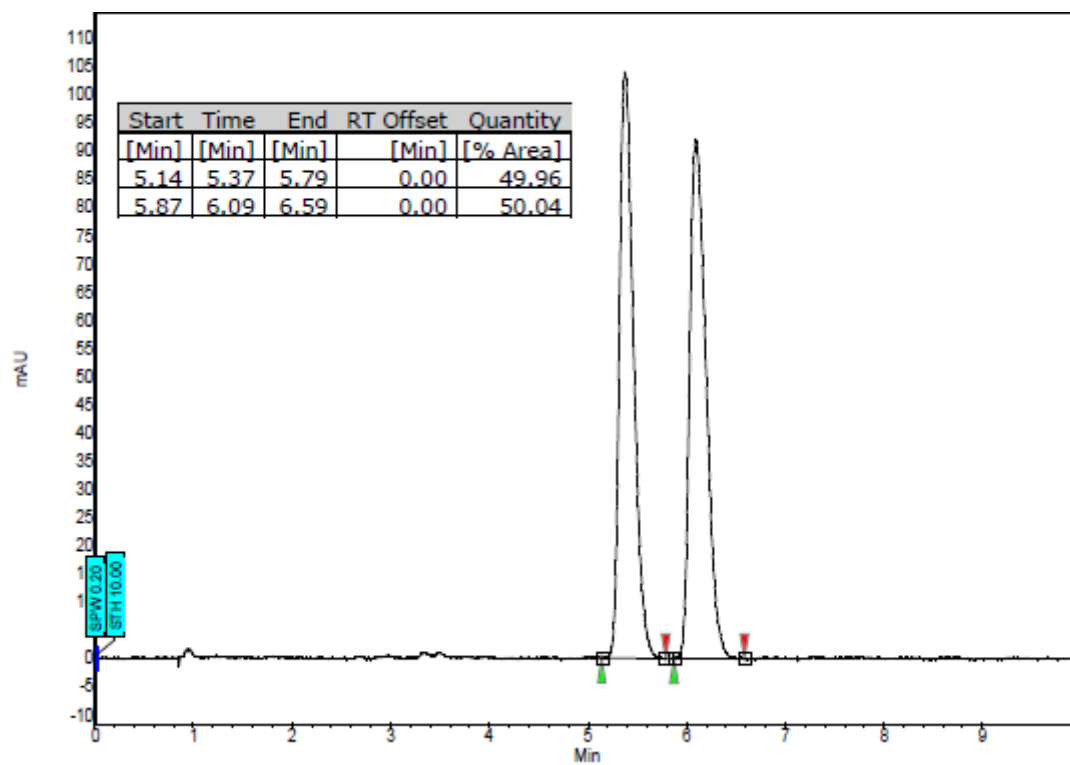


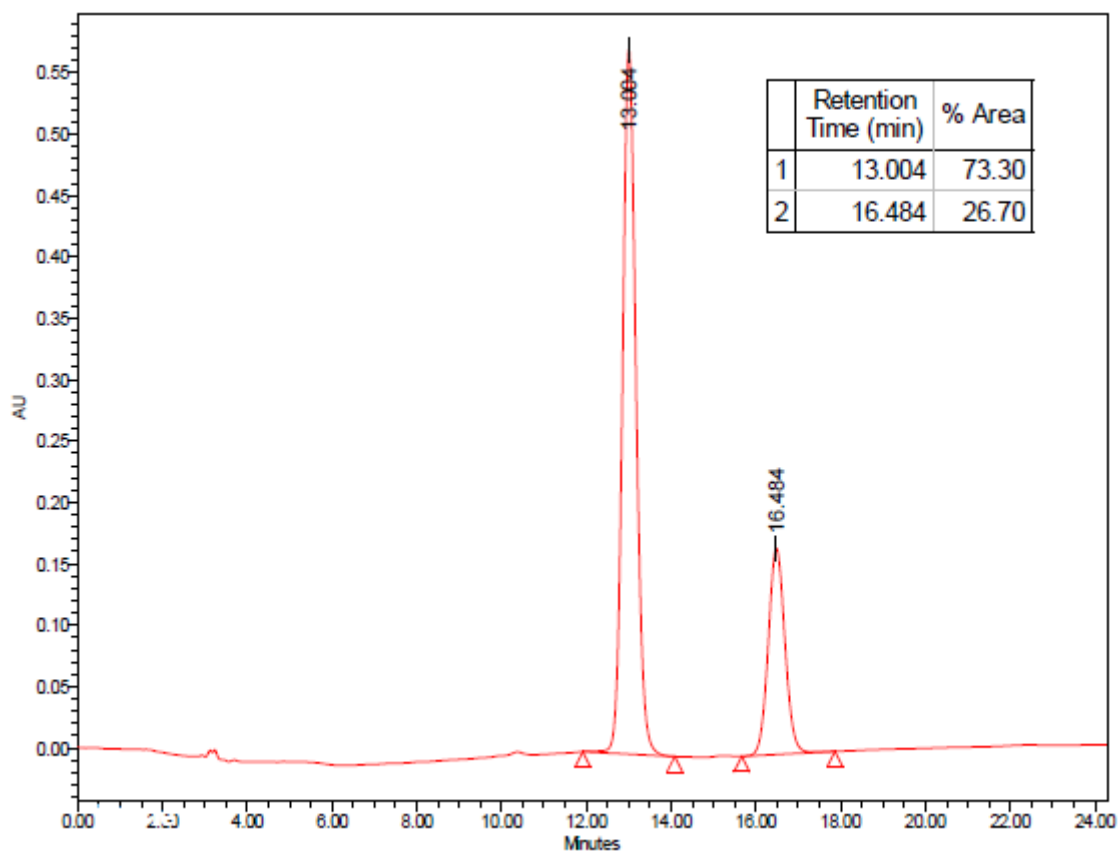
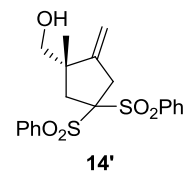
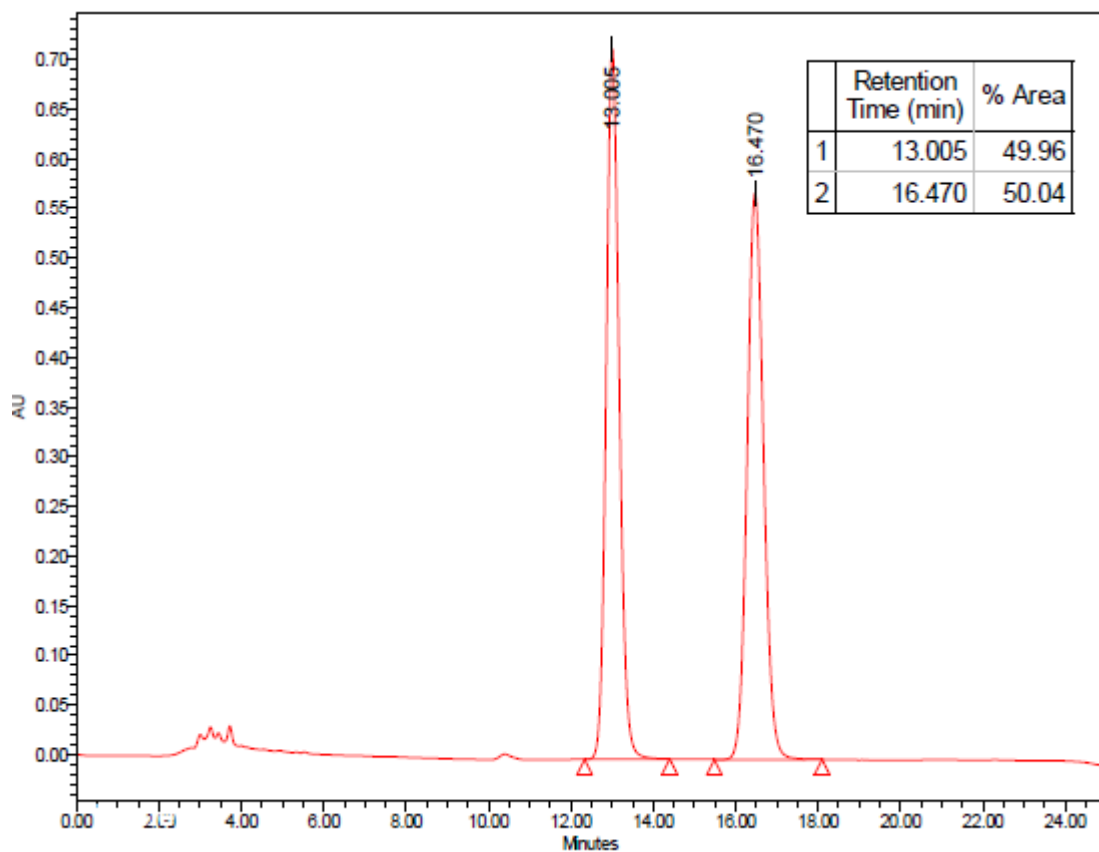


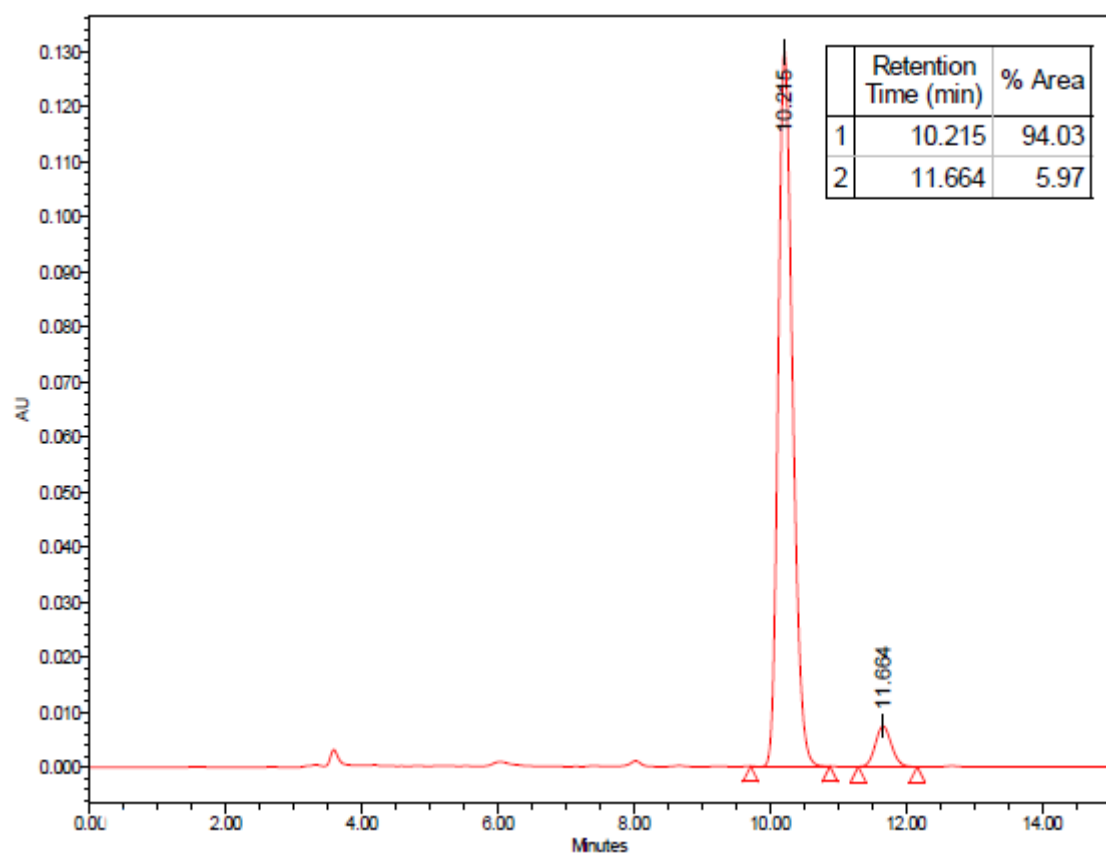
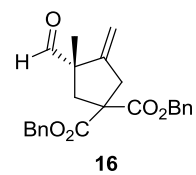
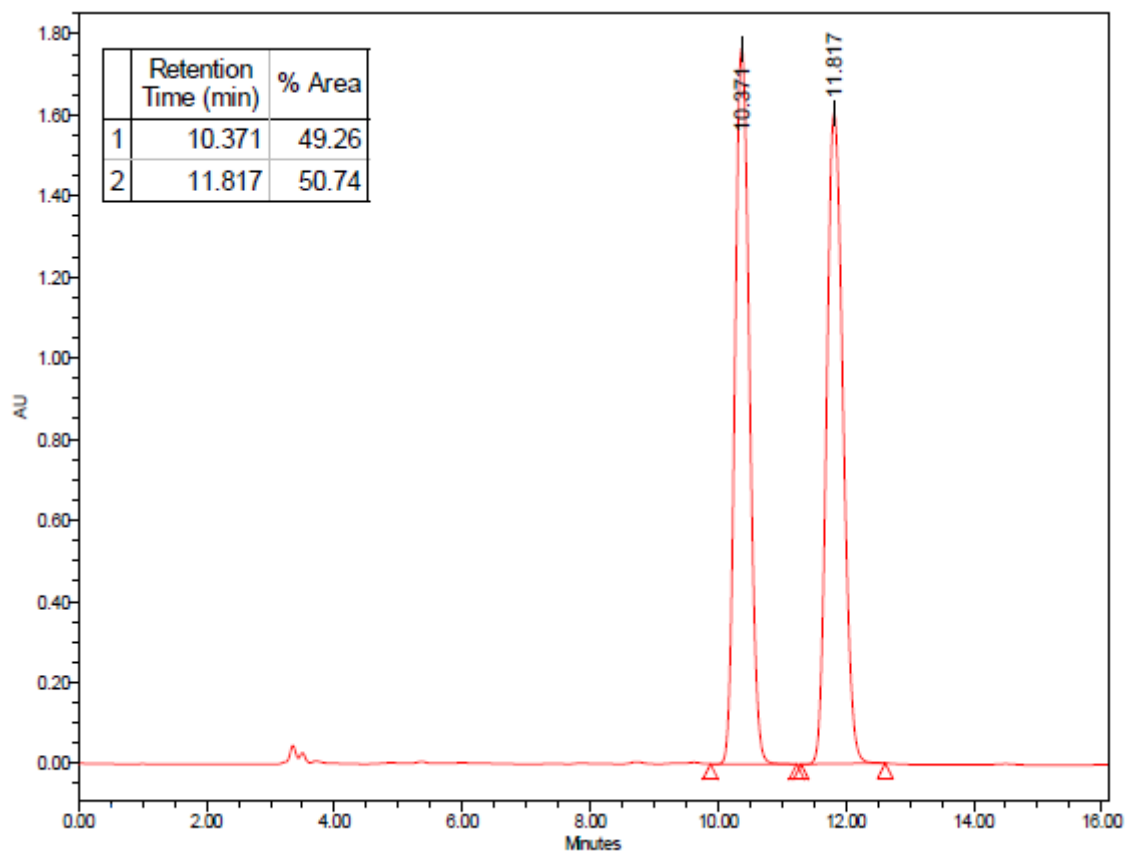


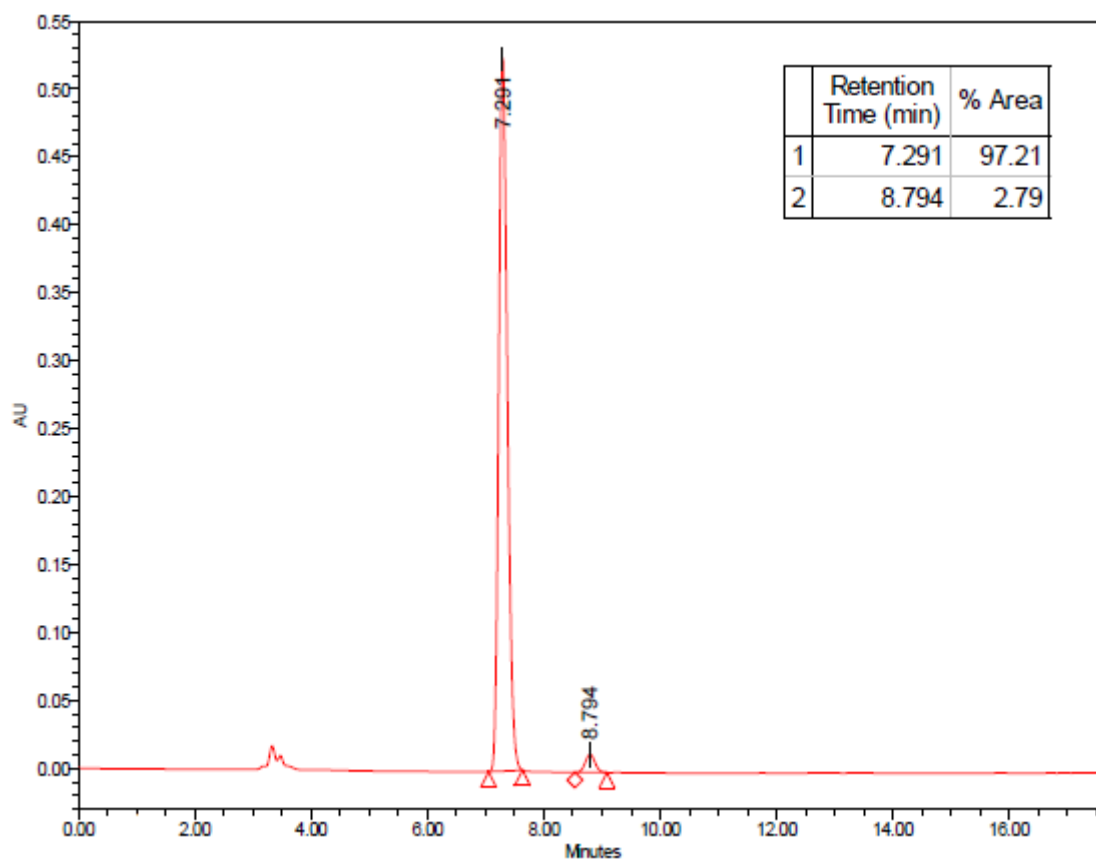
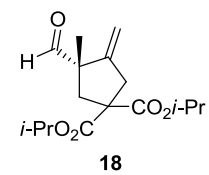
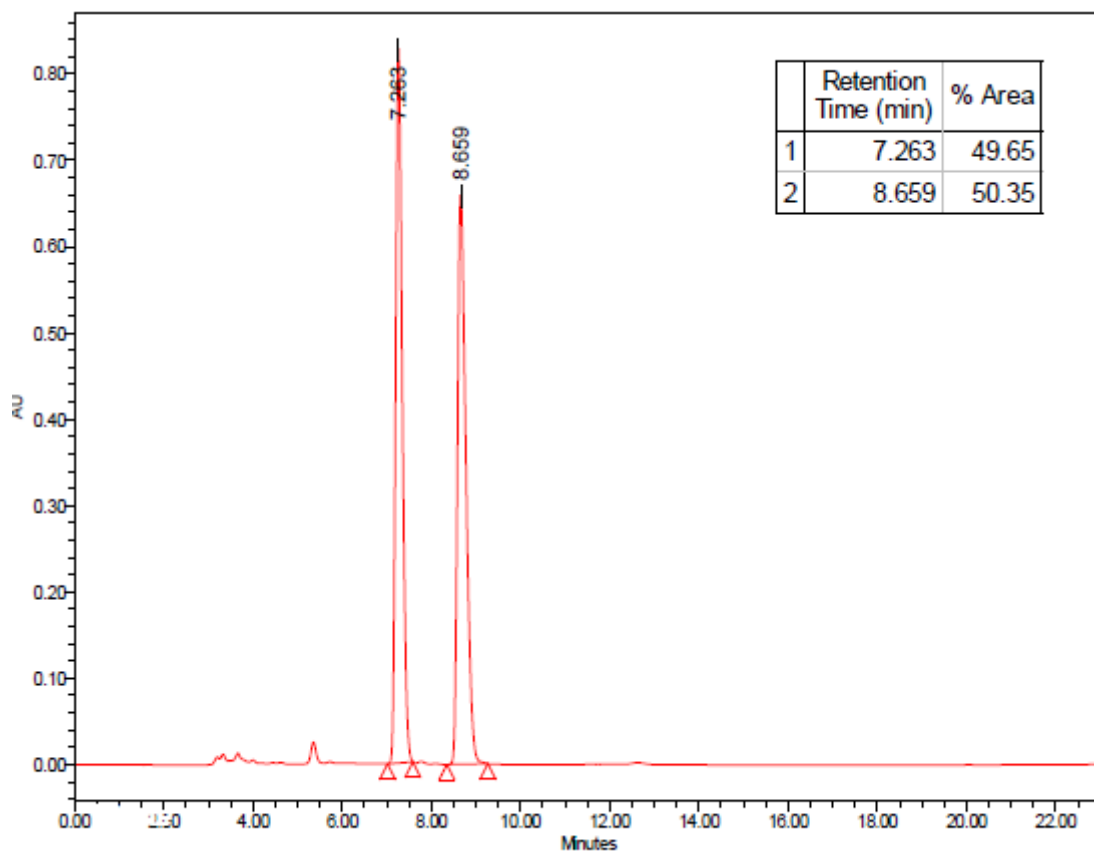


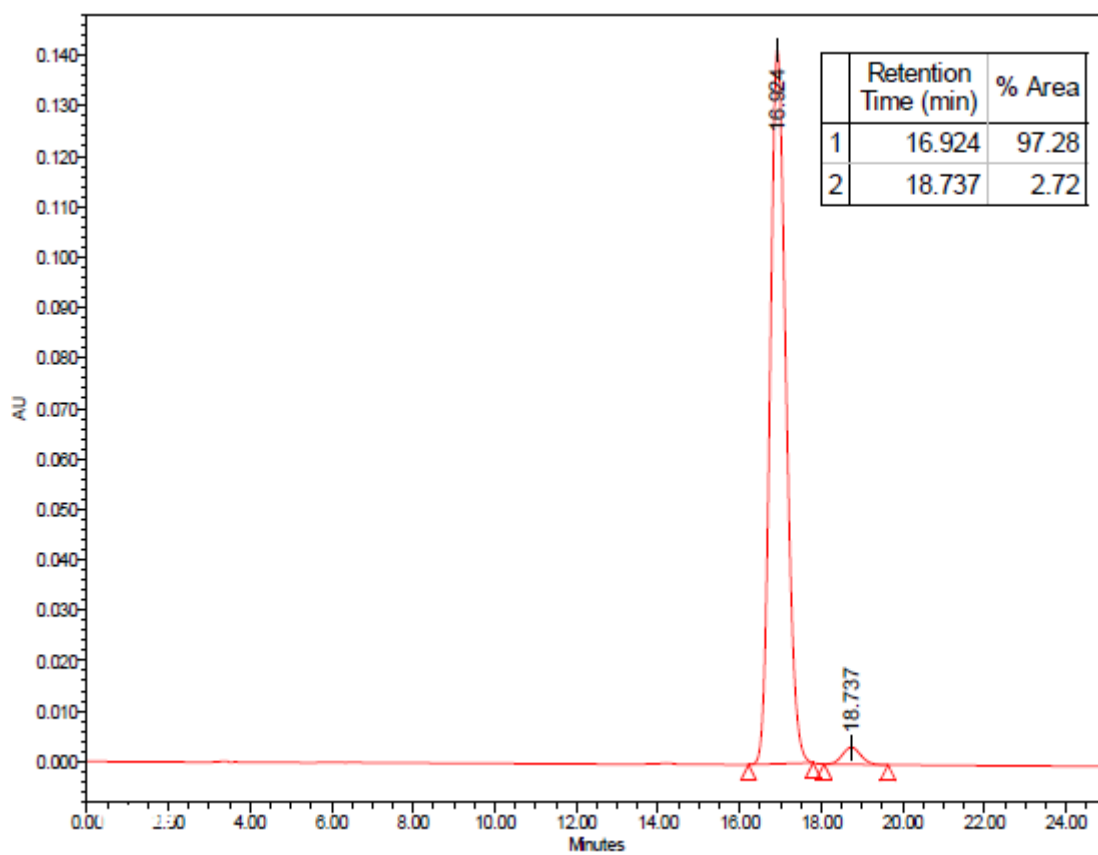
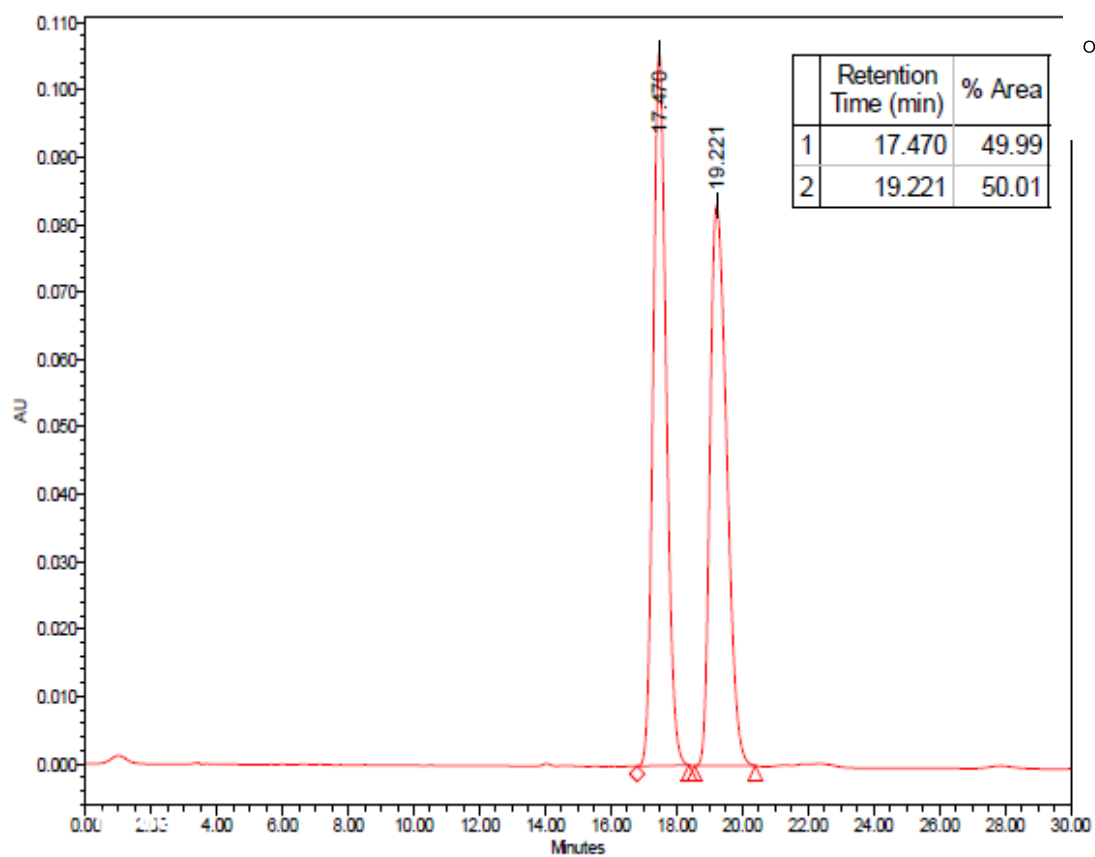
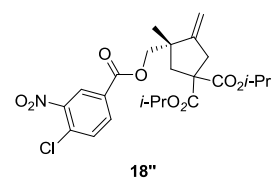












HPLC of the enantiopur single crystal used for X-Ray analysis confirmed that the enantiomer which crystallized is the major enantiomer.

