Supporting Information

Asymmetric Hydrogenation of Exocyclic γ,δ-Unsaturated β-Ketoesters to Functionalized Chiral Allylic Alcohols via Dynamic Kinetic Resolution

Huai-Yu Bin,[a] Li Cheng,[a] Xiong Wu,[a] Chang-Liang Zhu,[a] Xiao-Hui Yang,*[ab] Jian-Hua Xie,*[a] Qi-Lin Zhou[a]

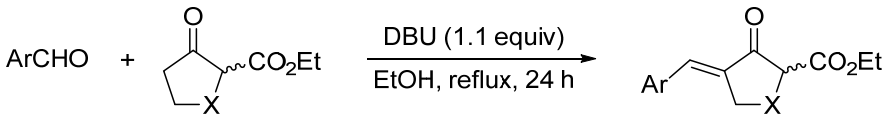
[a] State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China; [b] Advanced Research Institute of Multidisciplinary Science, and School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China

Contents

General: All reactions and manipulations which are sensitive to moisture or air were performed under inert atmosphere of nitrogen. All chemicals were purchased from *J & K*, Acros and Aldrich, and were used as received. The chiral Ru-catalyst (R_a,*S*,*S*)-**3**, Ir-catalysts (*R*)-**4**-**6** and (*S*)-**6b** were available in our lab or were purchased from Zhejiang Jiuzhou Pharmaceutical Co., Ltd. Hydrogen gas (99.999%) was purchased from Boc Gas Inc., Tianjin. Chemical reagents such as *n*BuLi, KO*t*Bu and Pd/C were purchased from Aldrich, Alfa Aesar, and Strem chemical companies. Petroleum ether refers to the fraction boiling in the 60–90 °C range. Anhydrous THF was distilled from sodium benzophenone ketyl. Anhydrous *n*PrOH, *i*PrOH, CH_2Cl_2, NEt_3, DMF and HMPA were freshly distilled from calcium hydride. MeOH and EtOH were distilled from magnesium. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λmax = 254 nm). Flash chromatography was performed using Silica gel (200−300 mesh) purchased from Qingdao Haiyang Chemical Co., China. Melting points were measured on a RY-I apparatus and uncorrected. NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR). Chemical shifts were reported in ppm relative to internal TMS for ^{1}H NMR data, deuterated solvent for ^{13}C NMR data, respectively. Data are presented in the following space: chemical shift, multiplicity, coupling constant in hertz (Hz), and signal area integration in natural numbers. Optical rotations were determined using a Perkin Elmer 341 polarimeter. High resolution mass spectrum (HRMS) were recorded on Varian 7.0T FTMS using an electrospray (ESI) ionization source. HPLC analyses were performed using Hewlett Packard Model HP1100 instruments using Chiral column (AD-H, AD-3, IC-3, OD-H, OD-3, OJ-H, AS-H, AS-3) with hexane and 2-propanol as eluent with, Wavelength = 254, 220 or 210 nm.

(A) Preparation of Exocyclic γ,δ-Unsaturated β-Ketoesters

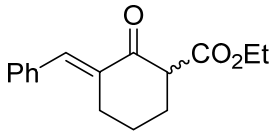
Method I:[1]



(1.1 equiv) *rac*-**7a-c, 7e-t**, **7w, 7z, 11b, 11d**

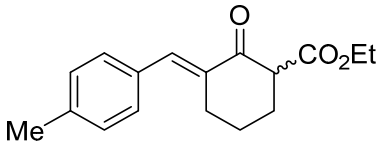
General procedure: To a solution of aromatic aldehyde (30.0 mmol) in EtOH (100 mL) were added ethyl 2-oxocyclohexane-1-carboxylate (or ethyl 2-oxocyclopentane-1-carboxylate) (33.0 mmol) and DBU (5.0 g, 33.0 mmol, 5.0 mL) in a 250 mL, three-necked, round-bottomed flask with a condenser tube under argon atmosphere. The reaction mixture was reflux for 24 h to complete the reaction in an oil bath. The reaction mixture was cool to 0 °C with ice-water bath, quenched with saturated aqueous NH_4Cl (100 mL), and extracted with ethyl acetate (100 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by a column chromatography on a silica gel with petroleum ether/ethyl acetate (50:1 to 10:1 v/v) as an eluent to give the target products (*rac*-**7a-c**, **7e-t**, **7w**, **7z**, **11b**, **11d**).

Ethyl (*E*)-3-benzylidene-2-oxocyclohexane-1-carboxylate (7a)



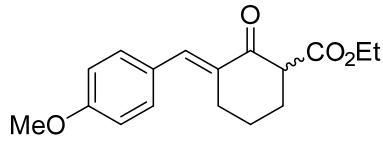
White solid, 5.0 g, 64% yield. R_f = 0.60 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 42−43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.46 (s, 1H), 7.35 (s, 1H), 7.39–7.32 (m, 4H), 7.29–7.23 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.71–2.64 (m, 2H), 2.40 (t, *J* = 6.0 Hz, 2H), 1.70−1.62 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 164.9, 136.7, 131.6, 129.6, 129.5, 128.1, 127.4, 100.3, 60.5, 27.0, 23.1, 22.5, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{18}O_3$+H^+: 259.1334 $[M+H]^+$; found: 2259.1330.

Ethyl (*E*)-3-(4-methylbenzylidene)-2-oxocyclohexane-1-carboxylate (7b)



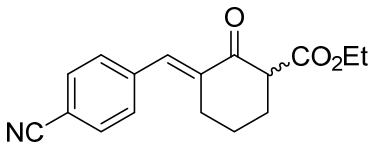
Pale yellow solid, 4.6 g, 56% yield. R_f = 0.62 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 98−99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.46 (s, 1H), 7.40 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.72–2.63 (m, 2H), 2.40 (t, *J* = 6.1 Hz, 2H), 2.36 (s, 3H), 1.67 (q, *J* = 6.2 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 165.2, 137.4, 133.8, 130.8, 129.7, 129.5, 128.9, 99.0, 60.5, 27.1, 23.1, 22.5, 21.3, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{20}O_3$+H^+: 273.1491 $[M+H]^+$; Found: 273.1489.

Ethyl (*E*)-3-(4-methoxybenzylidene)-2-oxocyclohexane-1-carboxylate (7c)



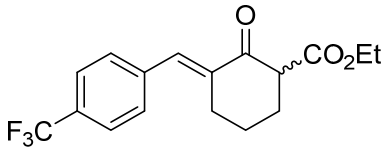
Pale yellow solid, 5.0 g, 58% yield. R_f = 0.57 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 98−99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.48 (s, 1H), 7.38 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.73–2.64 (m, 2H), 2.40 (t, *J* = 6.1 Hz, 2H), 1.71−1.62 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 165.3, 158.0, 131.2, 129.7, 129.3, 129.2, 113.7, 60.5, 55.3, 27.1, 23.1, 22.5, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{20}O_4$+H^+: 289.1440 $[M+H]^+$; Found: 289.1435.

Ethyl (*E*)-3-(4-cyanobenzylidene)-2-oxocyclohexane-1-carboxylate (7e)



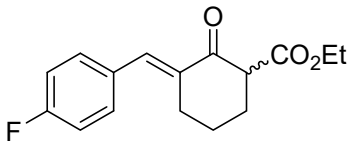
White solid, 5.4 g, 63% yield. R_f = 0.33 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 141−142 °C. ^{1}NMR (400 MHz, $CDCl_3$): δ = 11.32 (br s, 1H), 7.71 (s, 1H), 7.60 (d, *J* = 8.0, 1H), 7.35–7.27 (m, 2H), 7.20–7.14 (m, 1H), 4.30 (d, *J* = 7.1 Hz, 2H), 2.47–2.40 (m, 2H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.88−1.77 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.2, 167.5, 139.3, 136.1, 133.8, 132.7, 130.0, 129.6, 127.2, 123.9, 61.0, 33.4, 26.8, 23.8, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}NO_3$+H^+: 284.1284 $[M+H]^+$; found: 284.1284.

Ethyl (*E*)-2-oxo-3-(4-(trifluoromethyl)benzylidene)cyclohexane-1-carboxylate (7f)



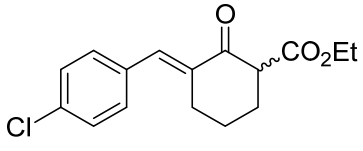
White solid, 7.0 g, 71% yield. R_f = 0.59 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 98−99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.43 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.51–7.33 (m, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.75−2.58 (m, 2H), 2.42 (t, *J* = 6.1 Hz, 2H), 1.77−1.63 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ =173.0, 164.1, 140.3, 133.6, 129.7, 129.1 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 127.8, 125.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.1 (q, $^1J_{C\text{-}F}$= 272.0 Hz), 101.2, 60.7, 27.0, 23.1, 22.4, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}F_3O_3$+H^+: 327.1204 $[M+H]^+$; found: 327.1204.

Ethyl (*E*)-3-(4-fluorobenzylidene)-2-oxocyclohexane-1-carboxylate (7g)



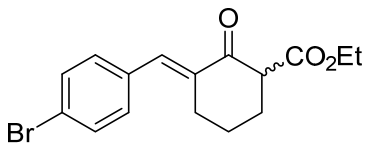
White solid, 5.0 g, 60% yield. R_f = 0.60 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 57−58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.45 (s, 1H), 7.37 (s, 1H), 7.33 (dd, *J* = 8.6, 5.6 Hz, 1H), 7.05 (t, *J* = 8.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 1H), 2.69–2.58 (m, 1H), 2.41 (t, *J* = 6.1 Hz, 1H), 1.73−1.63 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 164.8, 162.0 (d, $^1J_{C\text{-}F}$ = 248.0 Hz), 132.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 131.4, 131.4 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 128.3, 115.2 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 100.3, 60.6, 26.9, 23.1, 22.4, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{17}FO_3$+H^+: 277.1240 $[M+H]^+$; found: 277.1234.

Ethyl (*E*)-3-(4-chlorobenzylidene)-2-oxocyclohexane-1-carboxylate (7h)



White solid, 5.4 g, 62% yield. R_f = 0.61 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 118−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.43 (s, 1H), 7.40–7.20 (m, 5H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.69−2.54 (m, 2H), 2.41 (t, *J* = 6.1 Hz, 2H), 1.75−1.62 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 164.5, 135.1, 133.2, 132.1, 130.9, 128.4, 128.1, 100.6, 60.6, 27.0, 23.0, 22.4, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{17}ClO_3$+H^+: 293.0944 $[M+H]^+$; Found: 293.0941.

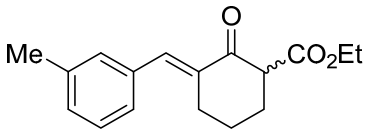
Ethyl (*E*)-3-(4-bromobenzylidene)-2-oxocyclohexane-1-carboxylate (7i)



White solid, 6.0 g, 59% yield. R_f = 0.60 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 126−127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.42 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.33 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.66–2.59 (m, 2H), 2.40 (t, *J* = 6.1 Hz, 2H), 1.72−1.63 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.5, 135.6, 132.3, 131.3, 131.2, 128.2, 121.4, 60.7, 26.0, 23.1, 22.4, 14.3. HRMS (ESI): *m*/*z* calcd for

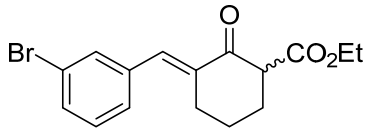
$C_{16}H_{17}BrO_3$+H^+: 337.0439 $[M+H]^+$; found: 337.0433.

Ethyl (*E*)-3-(3-methylbenzylidene)-2-oxocyclohexane-1-carboxylate (7j)



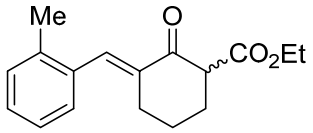
White solid, 4.3 g, 53% yield. R_f = 0.62 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 93−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.45 (s, 1H), 7.41 (s, 1H), 7.30–7.21 (m, 1H), 7.20−7.12 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 3H), 2.78−2.60 (m, 2H), 2.47–2.27 (m, 5H), 1.73–1.62 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 165.2, 137.9, 136.8, 131.6, 130.6, 129.8, 128.4, 128.2, 126.9, 100.3, 60.7, 27.2, 23.3, 22.7, 21.6, 14.5. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{20}O_3$+H^+: 273.1491 $[M+H]^+$; found: 273.1487.

Ethyl (*E*)-3-(3-bromobenzylidene)-2-oxocyclohexane-1-carboxylate (7k)



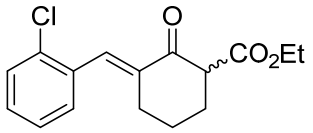
White solid, 5.5 g, 54% yield. R_f = 0.60 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 63−64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.41 (s, 1H), 7.49 (s, 1H), 7.42−7.37 (m, 2H), 7.33 (s, 1H), 7.29–7.19 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 3H), 2.68−2.60 (m, 2H), 2.41 (t, *J* = 6.1 Hz, 2H), 1.73−1.63 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 164.3, 138.8, 132.9, 132.2, 130.3, 129.7, 128.2, 127.8, 122.3, 100.9, 60.7, 26.9, 23.1, 22.4, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{17}BrO_3$+H^+: 337.0439 $[M+H]^+$; Found: 337.0433.

Ethyl (*E*)-3-(2-methylbenzylidene)-2-oxocyclohexane-1-carboxylate (7l)



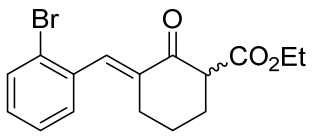
White solid, 3.8 g, 47% yield. R_f = 0.63 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 47−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.43 (s, 1H), 7.45 (s, 1H), 7.22–7.15 (m, 4H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.53−2.46 (m, 2H), 2.40 (t, *J* = 6.1 Hz, 2H), 2.30 (s, 3H), 1.68−1.60 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 164.9, 137.1, 135.9, 131.9, 129.9, 129.1, 128.7, 127.5, 125.3, 100.1, 60.5, 26.9, 23.3, 22.6, 20.0, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{20}O_3$+H^+: 273.1491 $[M+H]^+$; found: 273.1482.

Ethyl (*E*)-3-(2-chlorobenzylidene)-2-oxocyclohexane-1-carboxylate (7m)



White solid, 4.3 g, 49% yield. R_f = 0.61 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 40−41 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.39 (s, 1H), 7.49 (s, 1H), 7.44−7.38 (m, 1H), 7.32−7.28 (m, 1H), 7.27–7.18 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.57−2.37 (m, 2H), 2.41 (t, *J* = 6.1 Hz, 2H), 1.72−1.63 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 164.3, 135.1, 134.4, 133.2, 130.6, 129.5, 128.6, 126.5, 126.1, 100.8, 60.6, 26.9, 23.2, 22.4, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{17}ClO_3$+H^+: 293.0944 $[M+H]^+$; found: 293.0939.

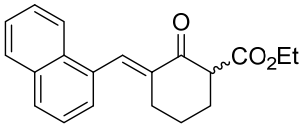
Ethyl (*E*)-3-(2-bromobenzylidene)-2-oxocyclohexane-1-carboxylate (7n)



White solid, 5.3 g, 52% yield. R_f = 0.60 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 45−46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.39 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.43 (s, 1H), 7.32–7.24 (m, 2H), 7.17–7.10 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.54−2.47 (m, 2H), 2.41 (t, *J* = 6.1 Hz, 2H), 1.72−1.63 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9, 164.2, 136.9, 132.9,

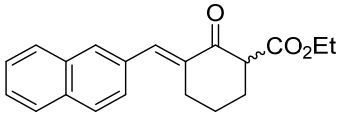
132.6, 130.6, 128.8, 128.8, 126.7, 100.7, 60.6, 29.6, 26.8, 23.2, 22.4, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{17}BrO_3+H^+$: 337.0439 $[M+H]^+$; found: 337.0435.

Ethyl (*E*)-3-(naphthalen-1-ylmethylene)-2-oxocyclohexane-1-carboxylate (7o)



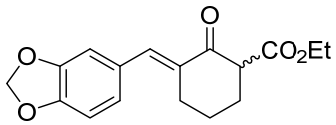
Pale yellow oil, 4.4 g, 48% yield. R_f = 0.56 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.49 (s, 1H), 8.03–7.97 (m, 1H), 7.92 (s, 1H), 7.88–7.83 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.53–7.43 (m, 3H), 7.36 (d, *J* = 7.1 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.55−2.46 (m, 2H), 2.42 (t, *J* = 6.1 Hz, 2H), 1.67−1.58 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 164.7, 133.9, 133.5, 133.3, 131.9, 128.4, 127.9, 127.6, 126.7, 126.1, 125.9, 125.0, 124.9, 100.3, 60.6, 27.1, 23.3, 22.6, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}O_3+H^+$: 309.1491 $[M+H]^+$; found: 309.1485.

Ethyl (*E*)-3-(naphthalen-2-ylmethylene)-2-oxocyclohexane-1-carboxylate (7p)



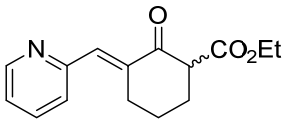
White solid, 4.7 g, 51% yield. R_f = 0.55 (petroleum ether/ethyl acetate = 1:1 v/v). M.p. 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.50 (s, 1H), 7.87–7.78 (m, 4H), 7.58 (s, 1H), 7.53–7.43 (m, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.85–2.74 (m, 2H), 2.44 (t, *J* = 6.1 Hz, 2H), 1.75−1.66 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 164.9, 134.2, 133.1, 132.5, 131.9, 129.5, 128.9, 128.1, 127.6, 127.6, 127.6, 126.2, 126.2, 100.4, 60.6, 27.2, 23.1, 22.5, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}O_3+H^+$: 309.1491 $[M+H]^+$; found: 309.1488.

Ethyl (*E*)-3-(benzo[d][1,3]dioxol-5-ylmethylene)-2-oxocyclohexane-1-carboxylate (7q)



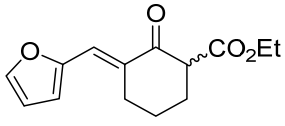
White solid, 4.2 g, 46% yield. R_f = 0.43 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 74−75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.46 (s, 1H), 7.33 (s, 1H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 1H), 5.97 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.70–2.62 (m, 2H), 2.40 (t, *J* = 6.1 Hz, 2H), 1.72−1.63 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 165.1, 147.5, 146.0, 130.8, 130.3, 129.3, 124.3, 109.6, 108.1, 101.1, 99.9, 60.5, 27.1, 23.0, 22.4, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{18}O_5+H^+$: 303.1232 $[M+H]^+$; found: 303.1225.

Ethyl (*E*)-2-oxo-3-(pyridin-2-ylmethylene)cyclohexane-1-carboxylate (7r)



White solid, 4.1 g, 53% yield. R_f = 0.26 (petroleum ether/ethyl acetate = 5:2 v/v). M.p. 66−67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.40 (s, 1H), 8.70–8.61 (m, 1H), 7.71–7.62 (m, 1H), 7.42–7.29 (m, 2H), 7.17–7.09 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.09–3.00 (m, 2H), 2.42 (t, *J* = 6.1 Hz, 2H), 1.76–1.66 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 164.6, 156.1, 149.2, 136.0, 135.5, 127.4, 125.9, 121.6, 101.6, 60.6, 26.9, 23.1, 22.3, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{15}NO_3+H^+$: 260.1287 $[M+H]^+$; Found: 260.1284.

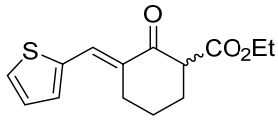
Ethyl (*E*)-3-(furan-2-ylmethylene)-2-oxocyclohexane-1-carboxylate (7s)



White solid, 5.3 g, 71% yield. R_f = 0.53 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 93−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.39 (s, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.18 (d, *J* = 1.9 Hz, 1H), 6.52–6.44 (m, 2H), 4.25

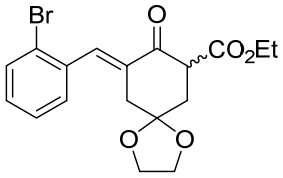
(q, J = 7.1 Hz, 2H), 2.56−2.50 (m, 2H), 2.40 (t, J = 6.1 Hz, 2H), 1.71−1.64 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.8, 143.1, 128.7, 116.7, 113.0, 111.8, 100.3, 60.5, 27.0, 22.9, 21.9, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}O_4$+H^+: 249.1127 $[M+H]^+$; found: 249.1123.

Ethyl (*E*)-2-oxo-3-(thiophen-2-ylmethylene)cyclohexane-1-carboxylate (7t)



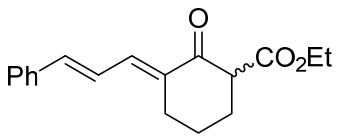
White solid, 5.8 g, 73% yield. R_f = 0.53 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 87−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.46 (d, J = 1.9 Hz, 1H), 7.60 (d, J = 2.1 Hz, 1H), 7.39 (d, J = 5.0 Hz, 1H), 7.20 (d, J = 3.6 Hz, 1H), 7.08 (dd, J = 5.1, 3.7 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.77−2.68 (m, 2H), 2.41 (t, J = 6.1 Hz, 2H), 1.81−1.72 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9, 164.9, 140.0, 130.4, 128.5, 127.6, 127.2, 122.5, 100.2, 60.5, 27.2, 22.8, 21.9, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}O_3S$+H^+: 265.0898 $[M+H]^+$; found: 265.0895.

Ethyl (*E*)-9-(2-bromobenzylidene)-8-oxo-1,4-dioxaspiro[4.5]decane-7-carboxylate (7w)



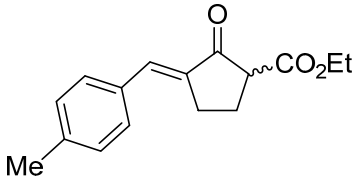
White solid, 7.2 g, 61% yield. R_f = 0.40 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 125−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.34−7.28 (m, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.19–7.13 (m, 1H), 4.26 (q, J = 7.1 Hz, 3H), 4.00–3.86 (m, 4H), 2.71 (s, 2H), 2.66 (s, 2H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 163.7, 136.5, 132.8, 131.7, 130.6, 130.4, 129.1, 126.9, 124.7, 106.9, 97.9, 64.6, 60.8, 36.1, 33.5, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{19}BrO_5$+H^+: 395.0494 $[M+H]^+$; found: 395.0490.

Ethyl (*E*)-2-oxo-3-((*E*)-3-phenylallylidene)cyclohexane-1-carboxylate (7z)



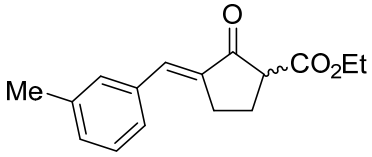
Pale yellow solid, 3.7 g, 43% yield. R_f = 0.68 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 81−82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.33 (s, 1H), 7.46 (d, J = 7.4 Hz, 2H), 7.36−7.30 (m, 2H), 7.27−7.23 (m, 1H), 7.18–7.04 (m, 2H), 6.86−6.74 (m, 1H), 4.25 (q, J = 7.2 Hz, 2H), 2.66–2.53 (m, 2H), 2.40 (t, J = 6.1 Hz, 2H), 1.79−1.68 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9, 164.7, 137.2, 136.8, 130.9, 129.2, 128.7, 128.1, 126.8, 124.1, 100.1, 60.5, 25.7, 23.2, 22.1, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{20}O_3$+H^+: 285.1491 $[M+H]^+$; found: 285.1485.

Ethyl (*E*)-3-(4-methylbenzylidene)-2-oxocyclopentane-1-carboxylate (11b)



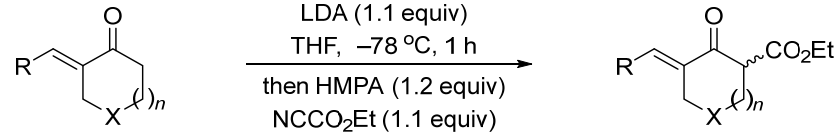
Pale yellow solid, 4.6 g, 59% yield. R_f = 0.60 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 82−83 °C. Enol/keto = 1.18:1 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.27 (s), 7.48–7.40 (m), 7.36 (d, J = 8.1 Hz), 7.23 (d, J = 7.9 Hz), 7.18 (d, J = 8.0 Hz), 4.35−4.15 (m), 3.48 (s), 3.40 (t, J = 8.6 Hz), 3.18–3.06 (m), 2.96–2.82 (m), 2.71–2.61 (m), 2.46–2.25 (m), 1.40−1.26 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.9, 169.8, 169.8, 169.5, 140.2, 137.3, 137.0, 134.7, 133.7, 133.4, 132.1, 130.6, 129.4, 129.1, 128.9, 123.8, 105.5, 61.3, 56.0, 54.1, 50.2, 27.5, 26.1, 24.9, 24.1, 21.3, 21.1, 14.2, 14.0. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{18}O_3$+H^+: 259.1334 $[M+H]^+$; found: 259.1332.

Ethyl (*E*)-3-(3-methylbenzylidene)-2-oxocyclopentane-1-carboxylate (11d)



White solid, 4.7 g, 61% yield. R_f = 0.61 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 93−94 °C. Enol/keto = 2.4:1 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.26 (s), 7.49−7.42 (m), 7.38–7.30 (m), 7.30−7.23 (m), 7.21 (d, *J* = 7.2 Hz), 7.13–7.03 (m), 6.92−6.84 (m), 4.40–4.14 (m), 3.41 (t, *J* = 8.7), 3.22−3.06 (m), 2.96–2.82 (m), 2.70–2.60 (m), 2.44−2.26 (m), 1.37−1.27 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.8, 169.9, 169.7, 169.5, 138.4, 138.0, 136.7, 135.0, 134.8, 134.36, 131.4, 130.6, 129.9, 128.6, 128.4, 128.3, 127.7, 126.2, 124.1, 105.9, 61.4, 60.1, 54.2, 27.7, 26.3, 25.1, 24.3, 21.4, 21.4, 14.4, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{18}O_3$+H^+: 259.1334 $[M+H]^+$; found: 259.1330.

Method II:

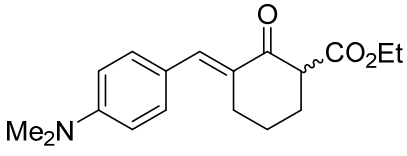


n = 1, 2;
R = aryl, alkyl, CO_2Et;
X = CH_2, NBoc, O, *etc.*

rac-**7d**, **7u**, **7v**, **7x**, **7y**, **7ak-ap**, **9a-i**

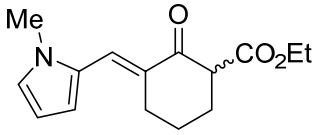
General procedure: To a solution of *i*Pr_2NH (2.4 g, 3.4 mL, 24.2 mmol) in THF (40 mL) was added *n*BuLi (2.5 M in hexane, 8.8 mL, 22.0 mmol) at −10 °C in a 250 mL, three-necked, round-bottomed flask with a thermometer under argon atmosphere. The mixture was stirred at −10 °C for 30 min and then a solution of exocyclic α,β-unsaturated ketones (20.0 mmol), which were prepared according to our previous or literature method,[2] in THF (20 mL) was added over 15 min at −78 °C. After the reaction mixture was stirred at −78 °C for another 1 h, HMPA (4.3 g, 4.2 mL, 24.0 mmol) was added at −78 °C, and the solution of ethyl cyanoacetate (2.2 g, 2.2 ml, 22.0 mmol) in THF (5 mL) was subsequently added over 15 min at the same temperature. The reaction mixture was allowed to warm up to 0 °C over 6 h, then quenched with saturated aqueous NH_4Cl (80 mL). The mixture was extracted with ethyl acetate (80 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by a column chromatography on a silica gel with petroleum ether/ethyl acetate (10:1 to 5:2 v/v) as an eluent to give target product (*rac*-**7d**, **7u**, **7v**, **7x**, **7y**, **7ak-ap**, **9a-i**).

Ethyl (*E*)-3-(4-(dimethylamino)benzylidene)-2-oxocyclohexane-1-carboxylate (7d)



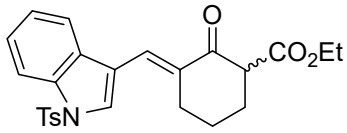
Yellow solid, 3.9 g, 65% yield. R_f = 0.42 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 92−93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.53 (s, 1H), 7.36 (s, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.98 (s, 6H), 2.75–2.67 (m, 2H), 2.39 (t, *J* = 6.1 Hz, 2H), 1.72−1.63 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 166.0, 149.7, 131.3, 130.0, 127.5, 124.7, 111.7, 98.7, 60.3, 40.2, 27.3, 23.0, 22.5, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{23}NO_3$+H^+: 302.1756 $[M+H]^+$; found: 302.1754.

Ethyl (*E*)-3-((1-methyl-1H-pyrrol-2-yl)methylene)-2-oxocyclohexane-1-carboxylate (7u)



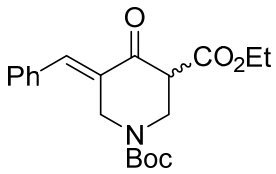
Pale yellow solid, 3.6 g, 68% yield. R_f = 0.46 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.51 (s, 1H), 7.29 (s, 1H), 6.73 (d, *J* = 3.0 Hz, 1H), 6.43 (d, *J* = 3.1 Hz, 1H), 6.25 – 6.15 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 2.71−2.63 (m, 2H), 2.41 (t, *J* = 6.1 Hz, 2H), 1.76−1.67 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 165.6, 130.1, 126.9, 124.6, 117.0, 112.6, 108.5, 99.0, 60.4, 34.3, 27.3, 22.8, 22.1, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{19}NO_3$+H^+: 262.1443 $[M+H]^+$; found: 262.1436.

Ethyl (*E*)-2-oxo-3-((1-tosyl-1H-indol-3-yl)methylene)cyclohexane-1-carboxylate (7v)



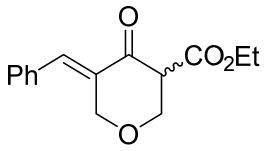
Pale yellow solid, 5.7 g, 63% yield. R_f = 0.25 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 163−164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.45 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.71–7.66 (m, 1H), 7.65 (s, 1H), 7.48 (s, 1H), 7.38−7.32 (m, 1H), 7.31–7.26 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.77−2.63 (m, 2H), 2.45 (t, *J* = 6.1 Hz, 2H), 2.33 (s, 3H), 182−1.70 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 164.4, 145.2, 134.9, 134.4, 132.1, 129.9, 126.8, 125.2, 124.8, 123.5, 119.7, 118.7, 118.0, 113.5, 100.4, 60.6, 28.0, 22.8, 22.0, 21.6, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{25}NO_5S$+H^+: 452.1532 $[M+H]^+$; found: 452.1526.

1-(Tert-butyl) 3-ethyl (*E*)-5-benzylidene-4-oxopiperidine-1,3-dicarboxylate (7x)



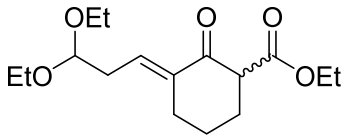
White solid, 5.2 g, 72% yield. R_f = 0.35 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 102−103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.18 (s, 1H), 7.44 (s, 1H), 7.41–7.28 (m, 5H), 4.48 (s, 2H), 4.37–4.10 (m, 4H), 1.59−1.15 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1, 163.4, 154.4, 135.4, 130.3, 129.4, 128.4, 128.1, 97.9, 80.2, 60.8, 43.1, 40.8, 28.1, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{25}NO_5$+Na^+: 382.1630 $[M+Na]^+$; found: 382.1621.

Ethyl (*E*)-5-benzylidene-4-oxotetrahydro-2H-pyran-3-carboxylate (7y)



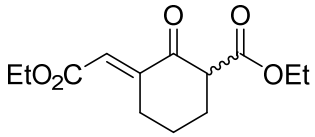
White solid, 4.9 g, 63% yield. R_f = 0.55 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.98 (s, 1H), 7.44–7.35 (m, 3H), 7.35–7.31 (m, 1H), 7.23 (d, *J* = 72 Hz, 2H), 4.68 (s, 2H), 4.44 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.5, 162.4, 135.3, 129.6, 129.2, 128.5, 128.3, 127.9, 98.7, 66.1, 63.7, 60.7, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{16}O_4$+H^+: 261.1127 $[M+H]^+$; found: 261.1124.

Ethyl (*E*)-3-(3,3-diethoxypropylidene)-2-oxocyclohexane-1-carboxylate (7ak)



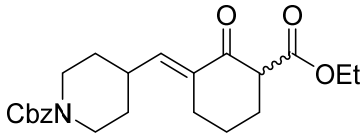
Pale yellow oil, 4.8 g, 80% yield. R_f = 0.47 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.29 (s, 1H), 6.45 (t, *J* = 7.4 Hz, 1H), 4.58 (t, *J* = 5.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.74–3.61 (m, 2H), 3.57–3.47 (m, 2H), 2.57 (t, *J* = 6.6 Hz, 2H), 2.42−2.28 (m, 4H), 1.70−1.62 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 164.7, 131.9, 126.3, 102.1, 98.8, 61.6, 60.4, 33.2, 25.6, 23.0, 22.0, 15.3, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{26}O_5$+H^+: 299.1858 $[M+H]^+$; found: 299.1854.

Ethyl (*E*)-3-(2-ethoxy-2-oxoethylidene)-2-oxocyclohexane-1-carboxylate (7al)



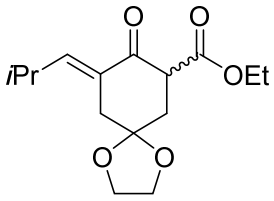
White solid, 3.5 g, 68% yield. R_f = 0.43 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 46−47 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.08 (s, 1H), 6.58 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.02−2.91 (m, 2H), 2.37 (t, *J* = 6.1 Hz, 2H), 1.72−1.64 (m, 2H), 1.31 (t, *J* = 6.0 Hz, 3H), 1.28 (t, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.5, 166.6, 162.3, 147.0, 117.4, 104.6, 61.0, 60.1, 26.5, 22.9, 21.7, 14.2, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{19}O_5$+H^+: 255.1232 $[M+H]^+$; found: 255.1230.

Benzyl (*E*)-4-((3-(ethoxycarbonyl)-2-oxocyclohexylidene)methyl)piperidine-1-carboxylate (7am)



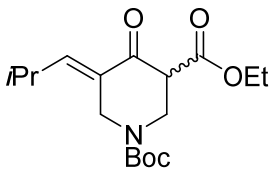
Colourless oil, 6.3 g, 79% yield. R_f = 0.36 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.33 (s, 1H), 7.51–7.20 (m, 5H), 6.25 (d, *J* = 9.4 Hz, 1H), 5.13 (s, 2H), 4.30−4.13 (m, 4H), 2.96−2.76 (m, 2H), 2.54−2.44 (m, 1H), 2.43–2.31 (m,4H), 1.73−1.58 (m, 4H), 1.44–1.34 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 164.5, 155.2, 136.8, 134.6, 129.7, 128.4, 127.9, 127.7, 99.1, 66.9, 60.4, 43.6, 35.0, 31.1, 25.4, 23.0, 22.1, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{23}H_{29}NO_5$+Na^+: 422.1943 $[M+Na]^+$; found: 422.1939.

Ethyl (*E*)-9-(2-methylpropylidene)-8-oxo-1,4-dioxaspiro[4.5]decane-7-carboxylate (7an)



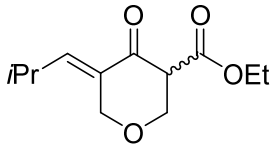
White solid, 4.6 g, 82% yield. R_f = 0.42 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 54−56 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.35 (s, 1H), 6.44 (d, *J* = 9.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.07−3.98 (m, 4H), 2.65–2.54 (m, 5H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.6, 164.6, 142.2, 126.0, 107.1, 95.7, 64.6, 60.6, 34.7, 33.2, 27.3, 22.3, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{22}O_5$+H^+: 283.1545 $[M+H]^+$; found: 283.1540.

1-(Tert-butyl) 3-ethyl (*E*)-5-(2-methylpropylidene)-4-oxopiperidine-1,3-dicarboxylate (7ao)



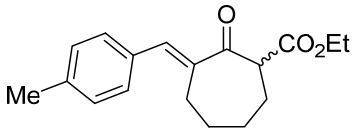
Colourless oil, 5.0 g, 77% yield. R_f = 0.44 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.05 (s, 1H), 6.27 (d, *J* = 10.6 Hz, 1H), 4.41–3.98 (m, 6H), 2.80−2.50 (m, 1H), 1.46 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.2, 163.5, 154.3, 139.4, 124.3, 96.6, 80.1, 60.6, 42.2, 40.7, 28.3, 27.5, 22.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{27}NO_5$+Na^+: 348.1787 $[M+Na]^+$; found: 348.1783.

Ethyl (*E*)-5-(2-methylpropylidene)-4-oxotetrahydro-2*H*-pyran-3-carboxylate (7ap)



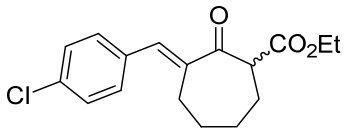
Colourless oil, 2.7 g, 60% yield. R_f = 0.46 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.85 (s, 1H), 6.24 (d, *J* = 10.1 Hz, 1H), 4.41 (s, 2H), 4.37 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.59−2.45 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 162.6, 138.5, 124.7, 97.3, 65.2, 63.7, 60.5, 27.1, 22.4, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{18}O_4$+H^+: 227.1283 $[M+H]^+$; found: 227.1281.

Ethyl (*E*)-3-(4-methylbenzylidene)-2-oxocycloheptane-1-carboxylate (9a)



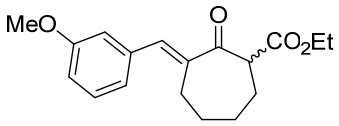
Colourless oil, 5.8 g, 67% yield. R_f = 0.46 (petroleum ether/ethyl acetate = 5:1 v/v). Enol/keto = 2:3 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.04 (s), 7.55 (s), 7.41–7.30 (m), 7.30–7.22 (m), 4.33−4.15 (m), 3.89−3.75 (m), 2.96 (dd, *J* = 14.8, 7.5 Hz), 2.64–2.43 (m), 2.41−2.28 (m), 2.25−2.12 (m), 2.09–1.96 (m), 1.95−1.83 (m), 1.82–1.62 (m), 1.58−1.45 (m), 1.40−1.22 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.1, 173.8, 170.9 (d), 139.9, 137.6, 136.1, 135.0, 134.4, 134.01, 133.3, 131.9, 130.6, 130.5, 128.7, 128.5, 101.6, 61.1, 60.8, 57.8, 29.3, 29.2, 28.1, 27.6, 27.0, 26.1, 25.7, 22.8, 14.3, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{22}O_3$+H$^+$: 287.1647 [M+H]$^+$; found: 287.1649.

Ethyl (*E*)-3-(4-chlorobenzylidene)-2-oxocycloheptane-1-carboxylate (9b)



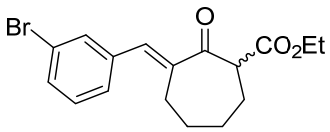
White solid, 5.7 g, 62% yield. R_f = 0.48 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 44−45 °C. Enol/keto = 1:6.1 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.06 (s), 7.61 (s), 7.34–7.11 (m), 4.35–4.15 (m), 3.84 (dd, *J* = 10.8, 2.1 Hz), 3.05 (dd, *J* = 15.0, 6.8 Hz), 2.66−2.56 (m), 2.52–2.45 (m), 2.43–2.27 (m), 2.25–2.13 (m), 2.09–1.95 (m), 1.93−1.82 (m), 1.81–1.60 (m), 1.58–1.45 (m), 1.37−1.23 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.4, 173.8, 171.6, 171.2, 138.6, 138.5, 137.6, 137.5, 136.1, 133.6, 133.2, 132.7, 129.5, 129.3, 129.2, 129.0, 101.0, 61.0, 60.6, 57.8, 29.3, 29.3, 28.1, 27.7, 27.0, 26.1, 25.7, 22.8, 21.3, 21.2, 14.3, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}ClO_3$+H$^+$: 307.1101 [M+H]$^+$; found: 307.1101.

Ethyl (*E*)-3-(3-methoxybenzylidene)-2-oxocycloheptane-1-carboxylate (9c)



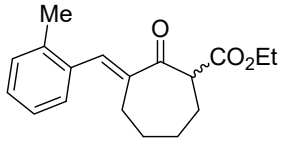
Colourless oil, 5.4 g, 59% yield. R_f = 0.36 (petroleum ether/ethyl acetate = 5:1 v/v). Enol/keto = 1:10 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (s), 7.37−7.20 (m), 7.04–6.76 (m), 4.38−4.13 (m), 3.94–3.68 (m), 3.15−2.95 (m), 2.65−2.55 (m), 2.49−2.44 (m), 2.42−2.29 (m), 2.25–2.14 (m), 2.12−1.97 (m), 1.96–1.82 (m), 1.82–1.61 (m), 1.59−1.44 (m), 1.37−1.20 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.3, 173.8, 171.3, 171.0, 159.5, 159.4, 139.6, 137.9, 137.4, 137.2, 137.0, 133.1, 129.4, 129.2, 121.7, 114.8, 114.6, 114.0, 113.2, 101.4, 61.0, 60.7, 57.8 (d), 55.2, 29.4, 29.2, 28.1, 27.7, 27.1, 26.3, 25.7, 22.9, 14.3, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{22}O_4$+H$^+$: 303.1596 [M+H]$^+$; found: 303.1596.

Ethyl (*E*)-3-(3-bromobenzylidene)-2-oxocycloheptane-1-carboxylate (9d)



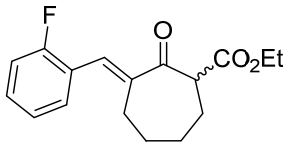
Colourless oil, 7.1 g, 67% yield. R_f = 0.45 (petroleum ether/ethyl acetate = 5:1 v/v). Enol/keto = 2:3 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.03 (s), 7.52 (s), 7.48–7.37 (m), 7.33–7.19 (m), 4.35−4.17 (m), 3.84 (dd, *J* = 10.7, 2.2 Hz), 2.95 (dd, *J* = 15.1, 6.9 Hz), 2.60−2.53 (m), 2.52–2.46 (m), 2.39–2.30 (m), 2.24–2.14 (m), 2.07–1.95 (m), 1.94−1.82 (m), 1.81–1.61 (m, 1H), 1.57–1.43 (m), 1.34 (t, *J* = 7.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.9, 173.6, 170.8, 170.6, 140.5, 138.6, 138.2, 137.7, 135.6, 131.9, 131.9, 131.6, 131.2, 130.3, 129.9, 129.7, 127.8, 127.7, 122.4, 122.3, 101.7, 61.0, 60.7, 57.78, 29.2, 29.01, 28.1, 27.5, 26.9, 26.1, 25.6, 22.7, 14.2, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}BrO_3$+H$^+$: 351.0596 [M+H]$^+$; found: 351.0600.

Ethyl (*E*)-3-(2-methylbenzylidene)-2-oxocycloheptane-1-carboxylate (9e)



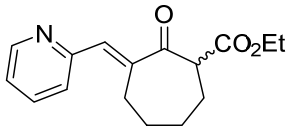
White solid, 5.5 g, 64% yield. R_f = 0.45 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 57−58 °C. Enol/keto = 2:3 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.04 (s), 7.77−7.70 (m), 7.40−7.34 (m), 7.30–7.16 (m), 7.14−7.08 (m), 4.35–4.18 (m), 3.91−3.79 (m), 2.89–2.78 (m), 2.57−2.48 (m), 2.47−2.38 (m), 2.36–2.16 (m), 2.07–1.81 (m), 1.78–1.58 (m), 1.52–1.39 (m), 1.37–1.23 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.9, 173.6, 170.8, 170.6, 140.5, 138.6, 138.2, 137.7, 135.6, 131.9, 131.9, 131.6, 131.2, 130.3, 129.9, 129.7, 127.8, 127.7, 122.4, 122.3, 101.7, 61.0, 60.7, 57.8, 29.2, 29.1, 28.1, 27.5, 26.9, 26.1, 25.6, 22.7, 14.2, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{22}O_3$+H^+: 287.1647 $[M+H]^+$; found: 287.1647.

Ethyl (*E*)-3-(2-fluorobenzylidene)-2-oxocycloheptane-1-carboxylate (9f)



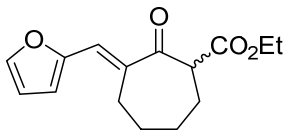
Colourless oil, 5.1 g, 58% yield. R_f = 0.42 (petroleum ether/ethyl acetate = 5:1 v/v). Enol/keto = 1:10 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.03 (s), 7.62 (s), 7.47–7.29 (m), 7.29–7.22 (m), 7.21–7.02 (m), 6.34 (d, *J* = 6.4 Hz), 4.34–4.13 (m), 3.84 (dd, *J* = 10.8, 2.1 Hz), 3.49–3.40 (m), 2.97−2.78 (m), 2.56–2.44 (m), 2.41–2.26 (m), 2.25−2.14 (m), 2.10–1.82 (m), 1.78−1.59 (m), 1.58–1.42 (m), 1.40–1.22 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.6, 170.9, 160.4 (d, $^1J_{C\text{-}F}$ = 249.3 Hz), 141.21, 130.7 (d, $^4J_{C\text{-}F}$ = 2.0 Hz), 130.3 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 130.2 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 123.9 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 123.6 (d, $^2J_{C\text{-}F}$ = 15.0 Hz), 115.8 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 61.0, 57.8, 29.2, 29.0, 28.1, 27.5, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}FO_3$+H^+: 291.1396 $[M+H]^+$; found: 291.1399.

Ethyl (*E*)-2-oxo-3-(pyridin-2-ylmethylene)cycloheptane-1-carboxylate (9g)



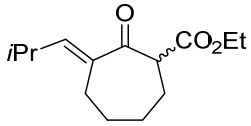
White solid, 6.0 g, 73% yield. R_f = 0.26 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 77−78 °C. Enol/keto = 1:5.7 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.00 (s), 8.73−8.58 (m), 7.75−7.61 (m), 7.44 (s), 7.37−7.31 (m), 7.24−7.17 (m), 7.16−7.10 (m), 4.33–4.17 (m), 3.97–3.82 (m), 2.97 (t, *J* = 6.3 Hz), 2.53–2.39 (m), 2.25–2.14 (m), 2.10–1.95 (m), 1.94–1.75 (m), 1.73–1.60 (m), 1.59–1.47 (m), 1.34 (t, *J* = 7.2 Hz), 1.29 (t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.3, 173.7, 171.3, 171.1, 156.0, 155.0, 149.5, 149.3, 143.2, 141.4, 136.2, 136.0, 134.1, 130.9, 126.7, 125.5, 122.6, 121.7, 102.1, 61.0, 60.7, 57.7, 29.3, 29.1, 28.3, 27.9, 26.7, 25.6, 25.5, 23.0, 14.3, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{19}NO_3$+H^+: 274.1443 $[M+H]^+$; found: 274.1444.

Ethyl (*E*)-3-(furan-2-ylmethylene)-2-oxocycloheptane-1-carboxylate (9h)



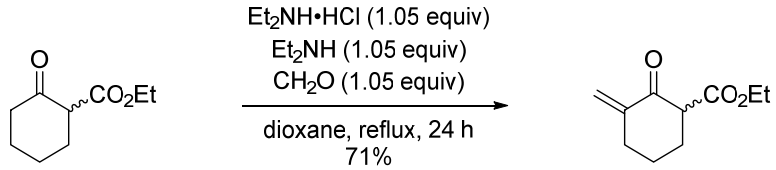
White solid, 5.4 g, 69% yield. R_f = 0.42 (petroleum ether/ethyl acetate = 5:1 v/v). M.p. 83−84 °C. Enol/keto =1:3.4 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.93 (s), 7.53 (d, *J* = 2.0 Hz), 7.47 (d, *J* = 1.9 Hz), 7.28 (s), 7.03 (s), 6.65 (d, *J* = 3.4 Hz), 6.49 (dd, *J* = 3.5, 1.9 Hz), 6.46 (dd, *J* = 3.5, 1.8 Hz), 4.32−4.15 (m), 3.84 (dd, *J* = 10.7, 2.1 Hz), 3.47 (dd, *J* = 14.9, 7.0 Hz), 2.79–2.72 (m), 2.49–2.37 (m), 2.21–2.10 (m), 2.09−1.97 (m), 1.89–1.75 (m), 1.73–1.61 (m), 1.56–1.46 (m), 1.36−1.27 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.3, 173.7, 171.2, 171.0, 152.6, 151.7, 144.4, 143.0, 135.7, 134.4, 123.5, 120.1, 116.7, 112.6, 112.1, 111.7, 101.1, 60.9, 60.6, 57.5, 29.4, 29.0, 28.0, 27.95, 27.4, 25.4, 24.5, 22.6, 14.3, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{18}O_4$+H^+: 263.1283 $[M+H]^+$; found: 263.1284.

Ethyl (*E*)-3-(2-methylpropylidene)-2-oxocycloheptane-1-carboxylate (9i)



Colourless oil, 4.6 g, 65% yield. R_f = 0.63 (petroleum ether/ethyl acetate = 5:1 v/v). Enol/keto = 1:10 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.92 (s), 6.54 (d, *J* = 9.9 Hz), 6.07 (d, *J* = 9.8 Hz), 4.32–4.09 (m), 3.72 (dd, *J* = 10.8, 1.7 Hz), 2.72 (dd, *J* = 14.9, 6.7 Hz), 2.67−2.56 (m), 2.42−2.35 (m), 2.21–2.07 (m), 2.03–1.91 (m), 1.85−1.72 (m), 1.67–1.54 (m), 1.38−1.25 (m), 1.03 (d, *J* = 4.7 Hz), 1.02 (d, *J* = 4.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.2, 173.7, 172.2, 171.2, 147.9, 142.2, 136.7, 133.0, 99.7, 60.8, 60.4, 57.7, 29.5, 29.4, 27.8, 27.3, 26.9, 26.5, 26.2, 26.0, 25.3, 22.7, 22.6, 22.2, 22.0, 14.2, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{22}O_3$+H^+: 239.1647 $[M+H]^+$; found: 239.1648.

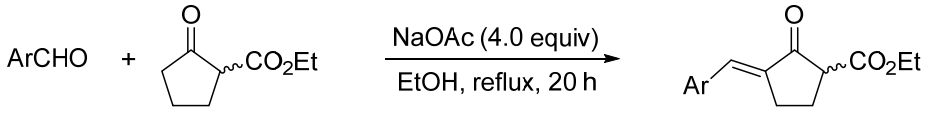
Method III:[3]



rac-**7ab**

To a solution of ethyl 2-oxocyclohexane-1-carboxylate (8.5 g, 50.0 mmol) in dioxane (80 mL) was sequentially added $Et_2NH·HCl$ (5.8 g, 52.5 mmol), Et_2NH (3.8 g, 52.5 mmol, 5.4 mL) and 37% formaldehyde solution (aq. 4.3 g, 52.5 mmol, 4.0 mL) in a 250 mL, three-necked, round-bottomed flask with a condenser tube at room temperature, and the reaction mixture was allowed to reflux in an oil bath for 24 h. The reaction was quenched by addition of a saturated solution of NH_4Cl (80 mL), and the mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with brine (100 mL), and dried with Na_2SO_4. The solvent was removed in vacuum, and the residue was purified by a column chromatography on a silica gel with petroleum ether/ethyl acetate (100:1 to 50:1 v/v) as an eluent to give target product *rac*-**7ab** (6.5 g, 71% yield) as a colourless oil. R_f = 0.61 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.12 (s, 1H), 5.84 (s, 1H), 5.20 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.48−2.41 (m, 2H), 2.39 (t, *J* = 6.1 Hz, 2H), 1.76−1.65 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9, 163.8, 138.6, 115.4, 100.1, 60.5, 31.2, 23.4, 22.5, 14.2. (the spectra are in accordance with those of the compound reported in the literature).

Method IV:[1]



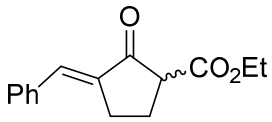
(1.1 equiv)

rac-**11a**, **11c**, **11e-g**

General procedure: To a 250 mL flame-dried three-neck flask was added NaOAc (9.8 g, 120.0 mmol, dehydrated under high temperature and reduced pressure), anhydrous ethanol (100 mL), aromatic aldehyde (30.0 mmol) and ethyl 2-oxocyclopentanecarboxylate (5.2 g, 33.0 mmol, 4.9 mL) under argon atmosphere. The reaction mixture was allowed to reflux in an oil bath for 20 h. The reaction mixture was acidified with 2 M HCl once the reaction mixture was allowed to cool to 0 °C. The mixture was extracted with ethyl acetate (100 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by a

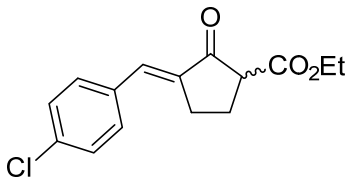
column chromatography on a silica gel with petroleum ether/ethyl acetate (50:1 to 20:1 v/v) as an eluent to give target product (*rac*-**11a, 11c**, **11e-g**).

Ethyl (*E*)-3-benzylidene-2-oxocyclopentane-1-carboxylate (11a)



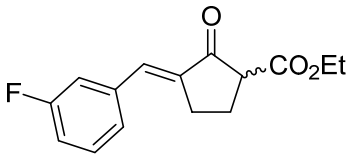
White solid, 5.6 g, 76% yield. R_f = 0.57 (petroleum ether/ethyl acetate = 5:1 v/v). M. p. 88−93 °C. Enol/keto = 2.5:1 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.27 (s), 7.53 (d, *J* = 7.7 Hz), 7.49–7.33 (m), 7.30–7.22 (m), 6.91 (s,), 4.40−4.13 (m), 3.41 (t, *J* = 8.7 Hz), 3.19−3.08 (m), 2.98–2.83 (m), 2.74–2.59 (m), 2.46–2.24 (m), 1.42−1.26 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.6, 169.7, 169.5, 169.3, 138.1, 136.5, 134.9, 134.4, 134.3, 130.5, 129.5, 128.9, 128.5, 128.3, 127.2, 123.8, 105.9, 61.2, 60.0, 54.0, 27.4, 26.1, 25.0, 24.1, 14.2, 14.0. HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_3$+H^+: 245.1178 $[M+H]^+$; found: 245.1174.

Ethyl (*E*)-3-(4-chlorobenzylidene)-2-oxocyclopentane-1-carboxylate (11c)



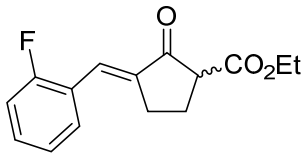
White solid, 7.1 g, 85% yield. R_f = 0.59 (petroleum ether/ethyl acetate = 5:1 v/v). M. p. 117−118 °C. Enol/keto = 12.5:1 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.24 (s, 1H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.84 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.87−2.80 (m, 2H), 2.70–2.58 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9, 169.1, 138.9, 135.2, 133.1, 130.2, 128.7, 122.7, 106.5, 60.3, 26.2, 25.2, 14.4. HRMS (ESI): *m/z* calcd for $C_{15}H_{15}ClO_3$+H^+ $[M+H]^+$: 279.0788; found: 279.0783.

Ethyl (*E*)-3-(3-fluorobenzylidene)-2-oxocyclopentane-1-carboxylate (11e)



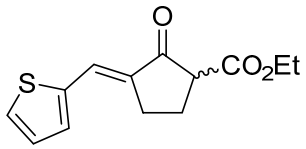
White solid, 6.5 g, 83% yield. R_f = 0.58 (petroleum ether/ethyl acetate = 5:1 v/v). M. p. 100−101 °C. Enol/keto = 3.3:1 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.23 (s), 7.45–7.27 (m), 7.25–7.12 (m), 7.11−7.04 (m), 7.00−6.91 (m), 6.85 (s), 4.49–4.07 (m), 3.42 (t, *J* = 8.6 Hz), 3.20−3.07 (m), 2.98–2.79 (m), 2.74–2.55 (m), 2.48–2.26 (m), 1.45−1.22 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 169.1, 160.6 (d, $^1J_{C\text{-}F}$ = 250.7 Hz), 140.1, 128.9 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 128.9, 124.7 (d, $^2J_{C\text{-}F}$ = 11.9 Hz), 123.8 (d, $^4J_{C\text{-}F}$ = 3.7 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 115.4 (d, $^3J_{C\text{-}F}$ = 6.2 Hz), 106.7, 60.3, 26.2, 25.1, 14.3. HRMS (ESI): *m/z* calcd for $C_{15}H_{15}FO_3$+H^+: 263.1083 $[M+H]^+$; found: 263.1082.

Ethyl (*E*)-3-(2-fluorobenzylidene)-2-oxocyclopentane-1-carboxylate (11f)



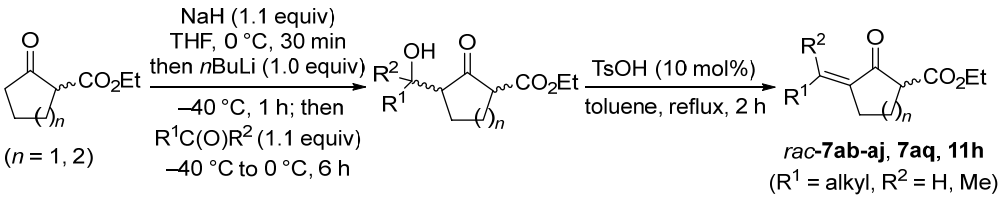
Pale yellow solid, 6.6 g, 84% yield. R_f = 0.59 (petroleum ether/ethyl acetate = 5:1 v/v). M. p. 83−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.20 (s, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.26–7.19 (m, 1H), 7.17–7.01 (m, 3H), 4.28 (q, *J* = 7.1 Hz, 3H), 2.98−2.79 (m, 2H), 2.71–2.58 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 169.1, 160.6 (d, $^1J_{C\text{-}F}$ = 250.7 Hz), 140.1, 128.9 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 128.9, 124.7 (d, $^2J_{C\text{-}F}$ = 11.9 Hz), 123.8 (d, $^4J_{C\text{-}F}$ = 3.7 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 115.4 (d, $^3J_{C\text{-}F}$ = 6.2 Hz), 106.7, 60.3, 26.2, 25.1, 14.3. HRMS (ESI): *m/z* calcd for $C_{15}H_{15}FO_3$+H^+: 263.1083 $[M+H]^+$; found: 263.1080.

Ethyl (*E*)-2-oxo-3-(thiophen-2-ylmethylene)cyclopentane-1-carboxylate (11g)



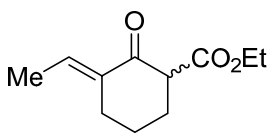
White solid, 6.2 g, 82% yield. R_f = 0.51 (petroleum ether/ethyl acetate = 5:1 v/v). M. p. 88−89 ºC. Enol/keto = 1:3.3 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.21 (s, 2H), 7.68−7.64 (m), 7.57 (d, *J* = 5.1 Hz), 7.38 (d, *J* = 4.7 Hz), 7.17−7.09 (m), 7.10–7.05 (m), 4.38−4.16 (m), 3.43 (t, *J* = 8.6 Hz,), 3.14–3.00 (m,), 2.87–2.80 (m,), 2.80–2.73 (m), 2.71–2.63 (m), 2.50–2.29 (m,), 1.40−1.25 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.2, 169.7 (d), 168.9, 141.1, 139.5, 136.3, 133.3, 132.1, 130.8, 128.5, 128.1, 127.5, 127.2, 126.9, 117.1, 106.6, 61.4, 60.1, 54.5, 27.4, 26.1, 25.1, 23.9, 14.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}O_3S$+H^+: 251.0742 $[M+H]^+$; found: 251.0736.

Method V:



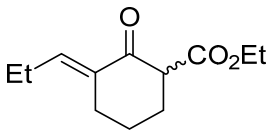
General procedure: To a solution of NaH (0.8 g, 33.0 mmol) in THF (80 mL) was added ethyl 2-oxocyclohexane-1-carboxylate (or ethyl 2-oxocyclopentane-1-carboxylate) (30.0 mmol) dropwise over 15 min in a 250 mL, three-necked, round-bottomed flask with a thermometer at 0 °C under argon atmosphere. After stirred at 0 °C for 30 min, a solution of *n*BuLi (2.5 M in hexane, 12.0 mL, 30.0 mmol) was added dropwise to the mixture over 15 min at –40 °C. The reaction mixture was allowed to warm up to –20 °C for 1 h. a solution of aliphatic aldehydes (or acetone) (33.0 mmol) in THF (10 mL) was added dropwise to the mixture over 15 min at –40 °C. The reaction mixture was allowed to warm up to 0 °C over a period of 6 h. Saturated aqueous NH_4Cl (100 mL) was added into the reaction mixture at 0 °C. The mixture was extracted with ethyl acetate (100 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by a column chromatography on a silica gel with petroleum ether / ethyl acetate (10:1 to 5:1) as an eluent to give the corresponding alcohol. To a solution of alcohol in toluene (100 ml) was then added *p*-toluenesulfonic acid (10 mol%). The reaction mixture was refluxed in an oil bath for 2 h and the water formed was removed by using a Dean-Stark apparatus. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (80 mL) at 0 ºC. The mixture was extracted with ethyl acetate (80 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by a column chromatography on a silica gel with petroleum ether/ethyl acetate (50:1 to 20:1 v/v) as an eluent to give target product (*rac*-**7ab-aj**, **7aq**, **11h**).

Ethyl (*E*)-3-ethylidene-2-oxocyclohexane-1-carboxylate (7ab)



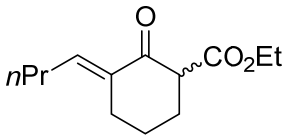
Colourless oil, 2.4 g, 41% yield (2 steps). R_f = 0.52 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.32 (s, 1H), 6.54 (q, *J* = 7.1 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.37−2.30 (m, 4H), 1.77 (d, *J* = 7.2 Hz, 3H), 1.70−1.63 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 165.1, 130.8, 126.7, 98.2, 60.3, 25.0, 23.0, 22.1, 14.3, 13.6. HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}O_3$+H^+: 197.1178 $[M+H]^+$; found: 197.1176.

Ethyl (*E*)-3-propylidene-2-oxocyclohexane-1-carboxylate (7ac)



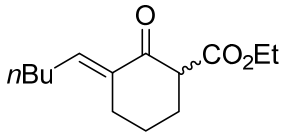
Colourless oil, 2.7 g, 43% yield (2 steps). R_f = 0.56 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.34 (s, 1H), 6.28 (d, *J* = 9.7, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.70−2.57 (m, 1H), 2.42–2.28 (m, 4H), 1.71−1.63 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.6 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$): δ =173.1, 165.2, 139.2, 127.9, 98.6, 60.4, 27.2, 25.2, 23.1, 22.4, 22.2, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{18}O_3$+H^+: 211.1334 $[M+H]^+$; found: 211.1330.

Ethyl (*E*)-3-butylidene-2-oxocyclohexane-1-carboxylate (7ad)



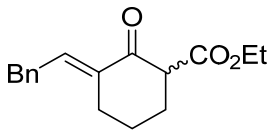
Colourless oil, 3.2 g, 47% yield (2 steps). R_f = 0.63 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.34 (s, 1H), 6.46 (t, *J* = 7.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.40−2.31 (m, 4H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.70−1.62 (m, 2H), 1.52−1.42 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 165.1, 132.4, 130.1, 98.4, 60.3, 30.1, 25.4, 23.1, 22.2, 22.2, 14.3, 13.9. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{20}O_3$+H^+: 225.1491 $[M+H]^+$; found: 225.1483.

Ethyl (*E*)-2-oxo-3-pentylidenecyclohexane-1-carboxylate (7ae)



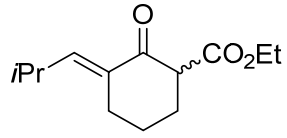
Colourless oil, 3.5 g, 49% yield (2 steps). R_f = 0.63 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.33 (s, 1H), 6.46 (t, *J* = 7.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.42−2.28 (m, 4H), 2.21−2.10 (m, 2H), 1.71−1.62 (m, 2H), 1.47–1.38 (m, 2H), 1.38−1.25 (m, 5H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 165.1, 132.6, 129.9, 98.3, 60.3, 31.2, 27.7, 25.3, 23.1, 22.5, 22.2, 14.3, 13.9. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{22}O_3$+H^+: 239.1647 $[M+H]^+$; found: 239.1645.

Ethyl (*E*)-2-oxo-3-(2-phenylethylidene)cyclohexane-1-carboxylate (7af)



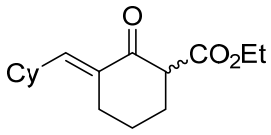
Colourless liquid, 4.1 g, 50% yield (2 steps). R_f = 0.58 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.30 (s, 1H), 7.33−7.25 (m, 2H), 7.24−7.15 (m, 3H), 6.64 (t, *J* = 7.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.52 (d, *J* = 7.8 Hz, 2H), 2.47 (t, *J* = 6.3 Hz, 2H), 2.37 (t, *J* = 6.1 Hz, 2H), 1.75−1.66 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 164.7, 139.8, 130.7, 130.1, 128.5, 128.4, 126.1, 98.9, 60.4, 34.1, 25.4, 23.0, 22.1, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{20}O_3$+H^+: 273.1491 $[M+H]^+$; found: 273.1479.

Ethyl (*E*)-3-(2-methylpropylidene)-2-oxocyclohexane-1-carboxylate (7ag)



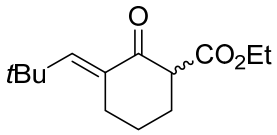
Colourless oil, 3.3 g, 49% yield (2 steps). R_f = 0.61 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.35 (s, 1H), 6.28 (d, *J* = 9.6 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.70−2.58 (m, 1H), 2.42–2.31 (m, 4H), 1.70−1.62 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 165.2, 139.1, 127.9, 98.4, 60.3, 27.1, 25.2, 23.0, 22.3, 22.2, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{20}O_3$+H^+: 225.1491 $[M+H]^+$; found: 225.1486.

Ethyl (*E*)-3-(cyclohexylmethylene)-2-oxocyclohexane-1-carboxylate (7ah)



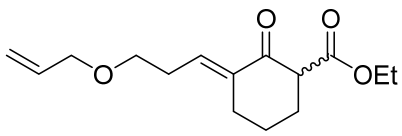
Colourless oil, 3.5 g, 44% yield (2 steps). R_f = 0.65 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.35 (s, 1H), 6.29 (d, *J* = 9.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.44–2.25 (m, 5H), 1.77−1.70 (m, 2H), 1.68−1.60 (m, 5H), 1.35–1.09 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 165.3, 137.7, 128.3, 98.5, 60.3, 37.0, 32.4, 25.9, 25.76, 25.4, 23.1, 22.3, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{24}O_3$+H^+: 265.1804 $[M+H]^+$; found: 265.1799.

Ethyl (*E*)-3-(2,2-dimethylpropylidene)-2-oxocyclohexane-1-carboxylate (7ai)



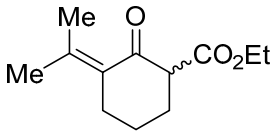
Colourless oil, 2.6 g, 36% yield (2 steps). R_f = 0.64 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ =12.47 (s, 1H), 6.53 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.56–2.48 (m, 2H), 2.33 (t, *J* = 6.1 Hz, 2H), 1.71–1.62 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 165.8, 141.8, 129.5, 98.4, 60.4, 32.6, 30.5, 26.4, 22.9, 22.2, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{22}O_3$+H^+: 239.1647 $[M+H]^+$; found: 239.1642.

(+)-Ethyl (*E*)-3-(3-(allyloxy)propylidene)-2-oxocyclohexane-1-carboxylate (7aj)



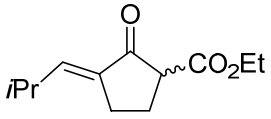
Pale yellow oil, 3.3 g, 41% yield (2 steps). R_f = 0.62 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.30 (s, 1H), 6.44 (t, *J* = 7.2 Hz, 1H), 6.03−5.81 (m, 1H), 5.27 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.18 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.99 (d, *J* = 5.7 Hz, 2H), 3.52 (t, *J* = 7.0 Hz, 2H), 2.47 (q, *J* = 7.1 Hz, 2H), 2.40–2.29 (m, 4H), 1.71–1.64 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 164.7, 134.7, 131.6, 128.0, 116.9, 98.7, 71.9, 69.1, 60.4, 28.8, 25.4, 23.0, 22.0, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{22}O_4$+H^+: 267.1596 $[M+H]^+$; found: 267.1592.

Ethyl 2-oxo-3-(propan-2-ylidene)cyclohexane-1-carboxylate (7aq)



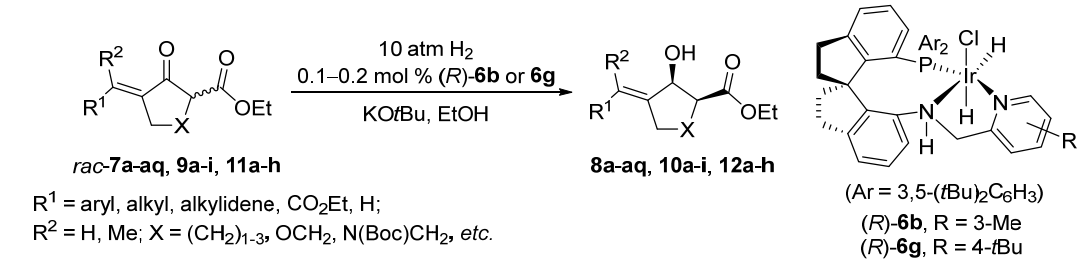
Colourless oil, 3.9 g, 62% yield (2 steps). R_f = 0.59 (petroleum ether/ethyl acetate = 5:1 v/v). Enol/keto = 10:1 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.89 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.30 (t, *J* = 6.3 Hz, 2H), 2.18 (s, 3H), 1.83 (s, 3H), 1.68−1.61 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.6, 169.1, 139.6, 124.8, 98.3, 60.2, 28.4, 23.9, 23.9, 23.3, 22.7, 14.3. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{18}O_3$+H^+: 211.1334 $[M+H]^+$; found: 211.1319.

Ethyl (*E*)-3-(2-methylpropylidene)-2-oxocyclopentane-1-carboxylate (11h)



Colourless oil, 1.8 g, 29% yield (2 steps). R_f = 0.57 (petroleum ether/ethyl acetate = 5:1 v/v). Enol/keto = 3.2:1 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.15 (s), 6.48 (dt, *J* = 9.8, 2.7 Hz), 5.82 (d, *J* = 9.7 Hz), 4.32–4.16 (m), 3.32 (t, *J* = 8.7 Hz), 2.82−2.71 (m), 2.60−2.40 (m), 2.36–2.18 (m), 1.35−1.27 (m), 1.08−0.97 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.3, 170.1, 169.7, 169., 145.2, 135.6, 133.7, 133.2, 104.9, 61.3, 59.9, 54.9, 29.3, 28.8, 24.7, 24.2, 23.9, 23.0, 22.2, 21.6, 21.5, 14.3, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{18}O_3$+H^+: 211.1334 $[M+H]^+$; found: 211.1332.

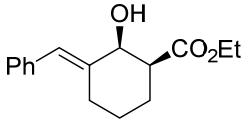
(B) Asymmetric Hydrogenation of Exocyclic γ,δ-Unsaturated β-Ketoesters



General procedure I (S/C = 1000): To a 40 mL hydrogenation vessel in an autoclave (50 mL) were added exocyclic γ,δ-unsaturated β-ketoesters **7a-al**, **7an**, **7aq**, **9a-i** or **11a-h** (1.0 mmol), a solution of iridium catalyst Ir-(*R*)-**6b** or **6g** in EtOH (0.001 mmol/mL, 1.0 mL, 0.001 mmol, 0.1 mol%), a solution of KO*t*Bu in EtOH (0.01 mmol/mL, 1.0 mL, 0.01 mmol, 1.0 mol%), and EtOH (2.0 mL) under argon atmosphere. The autoclave was purged with hydrogen by pressurizing to 5 atm and releasing the pressure. This procedure was repeated three times and then pressurized to 10 atm of H_2. The reaction mixture was stirred at room temperature (25–30 °C) until no obvious hydrogen pressure drop was observed. After releasing the hydrogen pressure, the reaction mixture was then quenched with saturated NH_4Cl (5 mL) and extracted with ethyl acetate (5 mL × 3). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silical gel with petroleum ether/ethyl acetate as an eluent to afford the chiral alcohols **8a-al**, **8an**, **8aq**, **10a-i**, **11a-h**.

General procedure II (S/C = 500): To a 40 mL hydrogenation vessel in an autoclave (50 mL) were added exocyclic γ,δ-unsaturated β-ketoesters **7am**, **7ao**, **7ap** (1.0 mmol), a solution of iridium catalyst Ir-(*R*)-**6b** in EtOH (0.002 mmol/mL, 1.0 mL, 0.002 mmol, 0.2 mol%), a solution of KO*t*Bu in EtOH (0.02 mmol/mL, 1.0 mL, 0.02 mmol, 2.0 mol%), and EtOH (2.0 mL) under argon atmosphere. The autoclave was purged with hydrogen by pressurizing to 5 atm and releasing the pressure. This procedure was repeated three times and then pressurized to 10 atm of H_2. The reaction mixture was stirred at room temperature (25–30 °C) until no obvious hydrogen pressure drop was observed. After releasing the hydrogen pressure, the reaction mixture was then quenched with saturated NH_4Cl (5 mL) and extracted with ethyl acetate (5 mL × 3). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silical gel with petroleum ether/ethyl acetate as an eluent to afford the chiral alcohols **8am**, **8ao**, **8ap**.

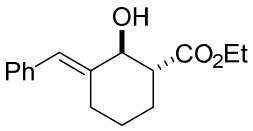
(+)-*cis*-Ethyl 3-((*E*)-benzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-*cis*-8a)



Colourless oil, 250 mg, 96% yield, 99% ee. R_f = 0.53 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +78.5 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 2H), 7.25–7.18 (m, 2H), 6.54 (s, 1H), 4.56 (d, *J* = 2.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.26 (s, 1H), 2.69–2.57 (m, 2H), 2.45–2.34 (m, 1H), 2.19–2.05 (m, 1H), 1.91–1.71 (m, 2H), 1.44–1.34 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.0, 141.0, 137.0, 128.9, 128.1, 126.6, 125.5, 74.1, 60.8, 48.6, 25.7, 24.2, 23.5, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{20}O_3$+Na^+: 283.1305 $[M+Na]^+$; Found: 283.1302. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0

mL/min; 254 nm UV detector; t_R = 18.38 min (minor); t_R = 11.61 min (major).

The *trans*-product of the asymmetric hydrogenation of **7a** is (+)-*trans*-ethyl 3-((*E*)-benzylidene)-2-hydroxycyclohexane-1-carboxylate (**(+)-*trans*-8a**).

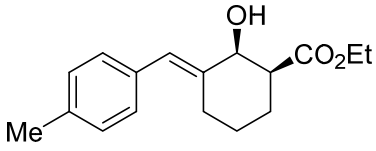


Colourless oil, 46.9 mg, 18% yield, 87% ee. R_f = 0.53 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +8.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.29 (m, 2H), 7.24–7.18 (m, 3H), 6.72 (s, 1H), 4.42 (d, *J* = 10.1 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.01–2.91 (m, 2H), 2.49–2.40 (m, 1H), 2.16−2.09 (m, 1H), 1.88−1.78 (m, 2H), 1.71−1.62 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 141.0, 137.8, 128.9, 128.1, 126.3, 120.9, 73.1, 60.8, 52.8, 28.2, 27.9, 26.2, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{20}O_3$+Na^+: 283.1305 $[M+Na]^+$; Found: 283.1301. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 9.19 min (minor); t_R = 11.10 min (major).

Asymmetric Hydrogenation of *rac*-7a at S/C = 50000.

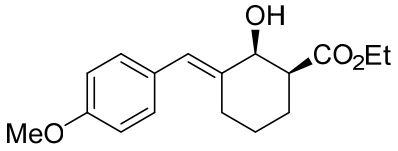
To a 200 mL hydrogenation vessel in an autoclave (250 mL) were added *rac*-**7a** (5.0 g, 20.0 mmol), a solution of iridium catalyst Ir-(*R*)-**6b** in EtOH (0.0002 mmol/mL, 2.0 mL, 0.0004 mmol, 0.0002 mol%), a solution of KO*t*Bu in EtOH (0.02 mmol/mL, 2.0 mL, 0.04 mmol, 0.02 mol%), and EtOH (46.0 mL) under argon atmosphere. The autoclave was purged with hydrogen by pressurizing to 10 atm and releasing the pressure. This procedure was repeated three times and then pressurized to 50 atm of H_2. The reaction mixture was stirred at room temperature (25–30 °C) for 24 h. After releasing the hydrogen pressure, the reaction mixture was then quenched with saturated NH_4Cl (50 mL) and extracted with ethyl acetate (50 mL × 3). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silical gel with petroleum ether/ethyl acetate (10:1 to 5:1 v/v) as an eluent to afford the chiral alcohol (+)-**8a** as a colourless oil in 98% yield (5.1 g, 19.6 mmol, >99% conversion) with 99% ee.

(+)-Ethyl 2-hydroxy-3-((*E*)-4-methylbenzylidene)cyclohexane-1-carboxylate ((+)-8b)



Colourless oil, 258 mg, 94% yield, 98% ee. R_f = 0.55 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +54.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17−7.07 (m, 4H), 6.49 (s, 1H), 4.54 (d, *J* = 2.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.23 (s, 1H), 2.67–2.59 (m, 2H), 2.42–2.36 (m, 1H), 2.33 (s, 3H), 2.17–2.04 (m, 1H), 1.89–1.77 (m, 2H), 1.45–1.33(m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 140.4, 136.3, 134.0, 128.8 (4C), 125.4, 74.2, 60.7, 48.6, 25.7, 24.1, 23.4, 21.1, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{22}O_3$+Na^+: 297.1467 $[M+Na]^+$; Found: 297.1461. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 16.15 min (minor); t_R = 12.04 min (major).

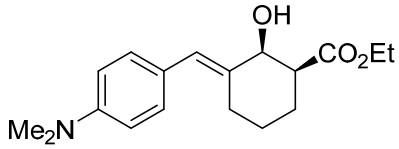
(+)-Ethyl 2-hydroxy-3-((*E*)-4-methoxybenzylidene)cyclohexane-1-carboxylate ((+)-8c)



Colourless oil, 285 mg, 98% yield, 99% ee. R_f = 0.49 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +56.6 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.46 (s, 1H), 4.54 (d, *J* = 2.7 Hz, 1H), 4.19 (q, *J* =

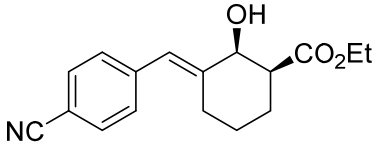
7.2 Hz, 2H), 3.79 (s, 3H), 3.24 (s, 1H), 2.66–2.57 (m, 2H), 2.42–2.31 (m, 1H), 2.17–2.01 (m, 1H), 1.90–1.75 (m, 2H), 1.45–1.35 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 158.2, 139.7, 130.0, 129.4, 125.0, 113.5, 74.2, 60.6, 55.1, 48.5, 25.6, 24.0, 23.3, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{22}O_4$+Na^+: 313.1411 $[M+Na]^+$; Found: 313.1408. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 28.60 min (minor); t_R = 18.61 min (major).

(+)-Ethyl 3-((*E*)-4-(dimethylamino)benzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8d)



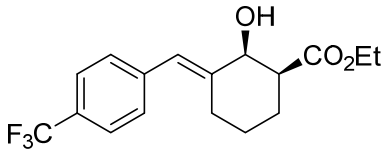
Colourless oil, 291 mg, 96% yield, 99% ee. R_f = 0.42 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ +33.9 (*c* 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 7.13 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 6.44 (s, 1H), 4.54 (d, J = 2.6 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.08 (s, 1H), 2.95 (s, 6H), 2.75–2.67 (m, 1H), 2.66–2.57 (m, 1H), 2.42–2.31 (m, 1H), 2.17–2.03 (m, 1H), 1.89–1.79 (m, 2H), 1.43–1.33 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.1, 149.2, 138.1, 129.9, 125.8, 125.1, 112.0, 74.5, 60.7, 48.6, 40.5, 25.7, 24.1, 23.3, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{25}NO_3$+H^+: 304.1913 $[M+H]^+$; found: 304.1911. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 83:17; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 20.02 min (minor); t_R = 15.87 min (major).

(+)-Ethyl 3-((*E*)-4-cyanobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8e)



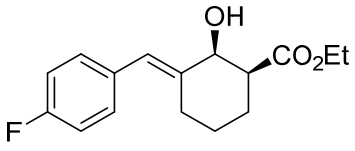
Colourless oil, 257 mg, 90% yield, 98% ee. R_f = 0.31 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ +81.4 (*c* 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 6.54 (s, 1H), 4.55 (d, J = 2.6 Hz, 1H), 4.21 (q, J = 6.2, 5.3 Hz, 2H), 3.44 (s, 1H), 2.75−2.62 (m, 1H), 2.51−2.37 (m, 2H), 2.21–2.04 (m, 1H), 1.93–1.76 (m, 2H), 1.49–1.37 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.7, 144.2, 141.9, 132.0, 129.5, 123.6, 118.9, 110.1, 73.8, 60.9, 48.4, 25.5, 24.6, 23.6, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}NO_3$+Na^+: 308.1263 $[M+Na]^+$; found: 308.1255. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 80:20; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 14.69 min (minor); t_R = 19.57 min (major).

(+)-Ethyl 2-hydroxy-3-((*E*)-4-(trifluoromethyl)benzylidene)cyclohexane-1-carboxylate ((+)-8f)



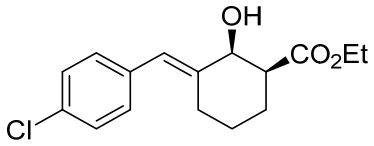
White soild, 318 mg, 97% yield, 96% ee. R_f = 0.52 (petroleum ether/ethyl acetate = 5:2 v/v). M.p. 58−59 °C. $[\alpha]_D^{25}$ = +62.0 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.55 (s, 1H), 4.57 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.47 (s, 1H), 2.76−2.63 (m, 1H), 2.57–2.36 (m, 2H), 2.21−2.05 (m, 1H), 1.95−1.77 (m, 2H), 1.48−1.35 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ =174.7, 143.2, 140.7, 129.1, 128.5 (q, $^2J_{C\text{-}F}$ = 33.3 Hz), 125.0 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 271.9 Hz), 123.9, 73.8, 60.8, 48.5, 25.5, 24.4, 23.5, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}F_3O_3$+Na^+: 351.1184 $[M+Na]^+$; found: 351.1173. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 9.41 min (minor); t_R = 8.24 min (major).

(+)-Ethyl 3-((*E*)-4-fluorobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8g)



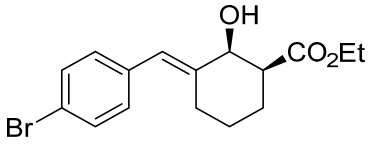
Colourless oil, 270 mg, 97% yield, 97% ee. R_f = 0.53 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +74.5 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.09 (m, 2H), 7.04–6.90 (m, 2H), 6.47 (s, 1H), 4.52 (d, *J* = 2.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 1H), 3.34 (s, 1H), 2.66−2.56 (m, 1H), 2.55−2.43 (m, 1H), 2.41–2.29 (m, 1H), 2.17–2.01 (m, 1H), 1.88–1.75 (m, 2H), 1.42−1.30 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 161.5 (d, $^1J_{C\text{-}F}$ = 245.9 Hz), 141.1, 132.9 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 130.4 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 124.2, 114.9 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 73.9, 60.7, 48.5, 25.6, 24.1, 23.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{19}FO_3$+Na^+: 301.1216 $[M+Na]^+$; found: 301.1211. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 93:7; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 19.18 min (minor); t_R = 13.42 min (major).

(+)-Ethyl 3-((*E*)-4-chlorobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8h)



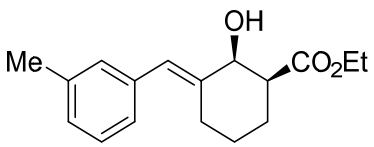
Colourless oil, 283 mg, 96% yield, 95% ee. R_f = 0.54 (petroleum ether/ethyl acetate = 1:1 v/v). $[\alpha]_D^{25}$ = +58.4 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.47 (s, 1H), 4.54 (d, *J* = 2.6 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.40 (s, 1H), 2.68−2.62 (m, 1H), 2.59–2.45 (m, 1H), 2.42–2.33 (m, 1H), 2.17–2.02 (m, 1H), 1.89–1.76 (m, 2H), 1.45–1.35 (m, 1H), 1.28 (s, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 141.8, 135.6, 132.3, 130.2, 128.3, 124.2, 73.9, 60.8, 48.4, 25.6, 24.2, 23.5, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{19}ClO_3$+Na^+: 317.0915 $[M+Na]^+$; Found: 317.0913. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 14.30 min (minor); t_R = 12.54 min (major).

(+)-Ethyl 3-((*E*)-4-bromobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8i)



Colourless oil, 326 mg, 96% yield, 97% ee. R_f = 0.54 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +69.8 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.45 (s, 1H), 4.53 (d, *J* = 2.5 Hz, 1H), 4.20 (q, *J* = 6.6 Hz, 2H), 3.37 (s, 1H), 2.70–2.61 (m, 1H), 2.57–2.48 (m, 1H), 2.44–2.33 (m, 1H), 2.18–2.05 (m, 1H), 1.91−1.74 (m, 2H), 1.45–1.33 (m, 1H), 1.29 (t, *J* = 6.7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 141.8, 135.8, 131.2, 130.5, 124.2, 120.4, 73.9, 60.7, 48.4, 25.5, 24.2, 23.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{19}BrO_3$+Na^+: 361.0410 $[M+Na]^+$; Found: 361.0408. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 14.39 min (minor); t_R = 12.61 min (major).

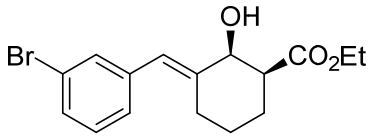
(+)-Ethyl 2-hydroxy-3-((*E*)-3-methylbenzylidene)cyclohexane-1-carboxylate ((+)-8j)



Colourless oil, 261 mg, 95% yield, 97% ee. R_f = 0.56 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +63.5 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (t, *J* = 7.8 Hz, 1H), 7.12−6.97 (m, 3H), 6.51 (s, 1H), 4.55 (d, *J* = 2.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.22 (s, 1H), 2.71–2.58 (m, 2H), 2.42–2.36 (m, 1H), 2.34 (s, 3H), 2.17–2.05 (m, 1H), 1.88–1.79 (m,

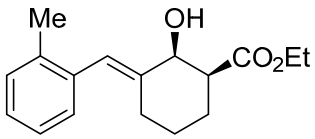
2H), 1.44–1.34 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.0, 140.8, 137.7, 136.9, 129.6, 128.0, 127.4, 125.9, 125.6, 74.2, 60.8, 48.6, 25.7, 24.2, 23.4, 21.4, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{22}O_3$+Na^+: 297.1467 $[M+Na]^+$; Found: 297.1465. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 80:20; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 12.71 min (minor); t_R = 14.63 min (major).

(+)-Ethyl 3-((*E*)-3-bromobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8k)



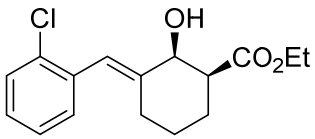
Colourless oil, 329 mg, 97% yield, 97% ee. R_f = 0.54 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +66.5 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 2H), 7.17 (t, J = 8.1 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 6.46 (s, 1H), 4.53 (d, J = 2.6 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.45 (br s, 1H), 2.69–2.58 (m, 1H), 2.58−2.48 (m, 1H), 2.45–2.35 (m, 1H), 2.17–2.04 (m, 1H), 1.90–1.75 (m, 2H), 1.45–1.33 (m, 1H), 1.28 (s, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 142.4, 139.1, 131.7, 129.6, 129.6, 127.5, 123.9, 122.2, 73.8, 60.8, 48.4, 25.6, 24.3, 23.5, 14.12. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{19}BrO_3$+Na^+: 361.0410 $[M+Na]^+$; Found: 361.0407. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 94:6; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 28.88 min (minor); t_R = 17.55 min (major).

(+)-Ethyl 2-hydroxy-3-((*E*)-2-methylbenzylidene)cyclohexane-1-carboxylate ((+)-8l)



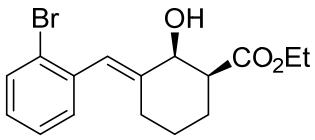
White soild, 255 mg, 93% yield, 97% ee. R_f = 0.57 (petroleum ether/ethyl acetate = 1:1 v/v). M.p. 50–51 °C. $[\alpha]_D^{25}$ = +63.5 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.05 (m, 4H), 6.49 (s, 1H), 4.59 (d, J = 2.9 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.38 (br s, 1H), 2.71−2.63 (m, 1H), 2.36–2.28 (m, 2H), 2.23 (s, 3H), 2.17–2.06 (m, 1H), 1.87−1.72 (m, 2H), 1.41−1.31 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 140.9, 136.4, 136.0, 129.6, 129.1, 126.8, 125.2, 124.2, 73.8, 60.6, 48.6, 25.6, 24.4, 23.5, 19.8, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{22}O_3$+Na^+: 297.1467 $[M+Na]^+$; Found: 297.1459. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 15.09 min (minor); t_R = 9.71 min (major).

(+)-Ethyl 3-((*E*)-2-chlorobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8m)



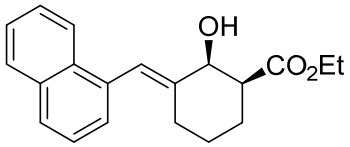
Colourless oil, 289 mg, 98% yield, 98% ee. R_f = 0.53 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +48.0 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 7.4 Hz, 1H), 7.26–7.14 (m, 3H), 6.54 (s, 1H), 4.62 (d, J = 2.9 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.36 (s, 1H), 2.77−2.58 (m, 1H), 2.40−2.32 (m, 2H), 2.19–2.02 (m, 1H), 1.88−1.73 (m, 2H), 1.47−1.34 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.7, 142.5, 135.3, 133.8, 130.7, 129.2, 128.1, 126.2, 122.5, 73.7, 60.7, 48.5, 25.5, 24.6, 23.5, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{19}ClO_3$+Na^+: 317.0920 $[M+Na]^+$; found: 317.0917. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 19.16 min (minor); t_R = 16.60 min (major).

(+)-Ethyl 3-((*E*)-2-bromobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8n)



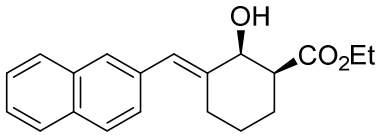
Colourless oil, 322 mg, 95% yield, 97% ee. R_f = 0.54 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +41.3 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.49 (s, 1H), 4.62 (d, *J* = 2.6 Hz, 1H), 4.21 (q, *J* = 6.9 Hz, 2H), 3.37 (s, 1H), 2.75−2.64 (m, 1H), 2.38–2.28 (m, 2H), 2.17−2.04 (m, 1H), 1.87−1.74 (m, 2H), 1.45–1.33 (m, 1H), 1.30 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 142.1, 137.1, 132.4, 130.8, 128.3, 126.8, 124.8, 124.2, 73.6, 60.8, 48.5, 25.5, 24.6, 23.5, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{19}BrO_3$+Na^+: 361.0410 $[M+Na]^+$; Found: 361.0405. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 14.48 min (minor); t_R = 12.04 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-(naphthalen-1-ylmethylene)cyclohexane-1-carboxylate ((+)-8o)



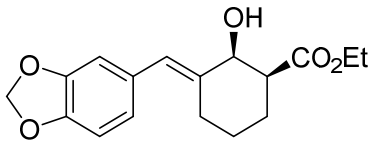
White solid, 292 mg, 94% yield, 98% ee. R_f = 0.32 (petroleum ether/ethyl acetate = 1:1 v/v). M.p. 83–84 °C. $[\alpha]_D^{25}$ = +42.1 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.91 (m, 1H), 7.88–7.82 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.52–7.40 (m, 3H), 7.28 (d, *J* = 7.0 Hz, 1H), 6.94 (s, 1H), 4.72 (d, *J* = 2.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.44 (s, 1H), 2.82−2.73 (m, 1H), 2.39–2.25 (m, 2H), 2.19–2.08 (m, 1H), 1.91–1.80 (m, 1H), 1.77−1.67 (m, 1H), 1.42−1.34 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.0, 142.7, 134.2, 133.5, 132.1, 128.3, 127.3, 126.5, 125.8, 125.8, 125.2, 125.1, 123.2, 73.9, 60.8, 48.8, 25.7, 25.1, 23.9, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{22}O_3$+Na^+: 333.1467 $[M+Na]^+$; found: 333.1457. HPLC conditions: Chiralcel AS-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 10.37 min (minor); t_R = 15.36 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-(naphthalen-2-ylmethylene)cyclohexane-1-carboxylate ((+)-8p)



White soild, 298 mg, 96% yield, 92% *ee*. R_f = 0.33 (petroleum ether/ethyl acetate = 1:1 v/v). M.p. 62−63 °C. $[\alpha]_D^{25}$ = +79.0 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.75 (m, 3H), 7.66 (s, 1H), 7.49–7.41 (m, 2H), 7.35 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.69 (s, 1H), 4.61 (d, *J* = 2.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.30 (s, 1H), 2.75−2.62 (m, 2H), 2.52−2.41 (m, 1H), 2.21−2.07 (m, 1H), 1.91–1.79 (m, 1H), 1.48−1.34 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.0, 141.4, 134.5, 133.2, 132.1, 127.8, 127.6 (2C), 127.5, 127.3, 126.0, 125.7, 125.5, 74.1, 60.8, 48.6, 25.7, 24.4, 23.5, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{22}O_3$+Na^+: 333.1467 $[M+Na]^+$; found: 333.1463. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 20.52 min (minor); t_R = 14.91 min (major).

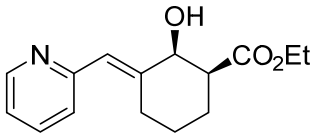
(+)-Ethyl (*E*)-3-(benzo[d][1,3]dioxol-5-ylmethylene)-2-hydroxycyclohexane-1-carboxylate ((+)-8q)



Colourless oil, 295 mg, 97% yield, 98% ee. R_f = 0.46 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +61.2 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 7.9 Hz, 1H), 6.75–6.64 (m, 2H), 6.43 (s, 1H), 5.99−5.88 (m, 2H), 4.52 (d, *J* = 2.8 Hz, 1H),

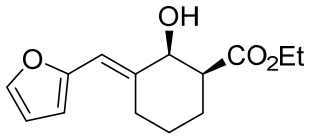
4.20 (q, J = 7.1 Hz, 2H), 3.33−3.17 (m, 1H), 2.68−2.53 (m, 2H), 2.43−2.30 (m, 1H), 2.16–2.03 (m, 1H), 1.91–1.76 (m, 2H), 1.43–1.32 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 147.3, 146.4, 140.2, 130.9, 125.1, 122.4, 109.2, 108.0, 100.9, 74.1, 60.7, 48.5, 25.6, 24.1, 23.3, 14.1. HRMS (ESI): m/z calcd for $C_{17}H_{20}O_5$+Na^+: 327.1208 $[M+Na]^+$; found: 327.1207. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 20.35 min (minor); t_R = 25.07 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-(pyridin-2-ylmethylene)cyclohexane-1-carboxylate ((+)-8r)



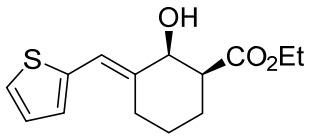
White soild, 248 mg, 95% yield, >99% ee. R_f = 0.21 (petroleum ether/ethyl acetate = 1:1 v/v). M.p. 54–55 °C. $[\alpha]_D^{25}$ = +104.4 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 4.7 Hz, 1H), 7.67–7.57 (m, 1H), 7.19 (d, J = 6.4 Hz, 1H), 7.15–7.06 (m, 1H), 6.53 (s, 1H), 4.62–4.54 (m, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.42 (br s, 1H), 3.10–2.98 (m, 1H), 2.72−2.65 (m, 1H), 2.62–2.51 (m, 1H), 2.19–2.03 (m, 1H), 1.87–1.80 (m, 2H), 1.48–1.34 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.3, 156.1, 149.0, 145.6, 136.0, 124.3, 124.3, 124.2, 121.2, 74.0, 60.5, 25.4, 24.2, 23.1, 14.1. HRMS (ESI): m/z calcd for $C_{15}H_{19}NO_3$+H^+: 262.1443 $[M+H]^+$; Found: 262.1440. HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 97:3; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 35.04 min (major).

(+)-Ethyl (*E*)-3-(furan-2-ylmethylene)-2-hydroxycyclohexane-1-carboxylate ((+)-8s)



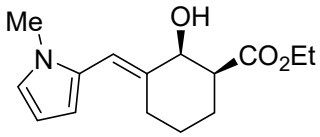
Colourless oil, 238 mg, 95% yield, 99% ee. R_f = 0.46 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +96.3 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40−7.32 (m, 1H), 6.41–6.32 (m, 1H), 6.30– 6.17 (m, 2H), 4.49 (d, J = 3.2 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.26 (s, 1H), 3.03−2.89 (m, 1H), 2.67–2.58 (m, 1H), 2.58−2.48 (m, 1H), 2.16–2.04 (m, 1H), 1.90–1.79 (m, 2H), 1.48−1.37 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.7, 152.3, 141.4, 139.5, 113.7, 110.9, 109.7, 73.9, 60.7, 48.5, 25.3, 24.9, 23.4, 14.1. HRMS (ESI): m/z calcd for $C_{14}H_{18}O_4$+Na^+: 273.1103 $[M+Na]^+$; found: 273.1093. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 10.36 min (minor); t_R = 12.67 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-(thiophen-2-ylmethylene)cyclohexane-1-carboxylate ((+)-8t)



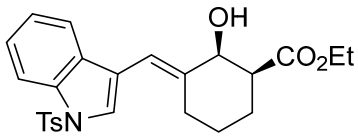
Colourless oil, 256 mg, 96% yield, 99% ee. R_f = 0.47 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +103.7 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 4.8 Hz, 1H), 7.02–6.94 (m, 2H), 6.60 (s, 1H), 4.54 (d, J = 2.8 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.20 (s, 1H), 2.92–2.82 (m, 1H), 2.68–2.58 (m, 1H), 2.55–2.46 (m, 1H), 2.17–2.04 (m, 1H), 1.93−1.81 (m, 2H), 1.48−1.37 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 139.8, 139.5, 127.9, 126.7, 125.0, 118.4, 74.2, 60.8, 48.6, 25.3, 25.1, 23.4, 14.2. HRMS (ESI): m/z calcd for $C_{14}H_{18}O_3S$+Na^+: 289.0874 $[M+Na]^+$; found: 289.0870. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 11.72 min (minor); t_R = 14.59 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-((1-methyl-1*H*-pyrrol-2-yl)methylene)cyclohexane-1-carboxylate ((+)-8u)



Colourless oil, 250 mg, 95% yield, >99% ee. R_f = 0.43 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +61.3 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.65−6.55 (m, 1H), 6.25 (s, 1H), 6.18–6.14 (m, 1H), 6.14−6.09 (m, 1H), 4.53 (d, *J* = 2.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 3H), 3.20 (s, 1H), 2.80−2.72 (m, 1H), 2.66−2.59 (m, 1H), 2.48−2.38 (m, 1H), 2.18–2.04 (m, 1H), 1.89–1.77 (m, 2H), 1.46–1.34 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 139.6, 129.1, 122.2, 114.3, 109.2, 107.3, 74.2, 60.7, 48.6, 34.1, 25.3, 24.7, 23.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{21}NO_3$+H^+: 264.1600 $[M+H]^+$; found: 264.1595. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 14.90 min (major).

(1*S*,2*S*)-(+)-Ethyl (*E*)-2-hydroxy-3-((1-tosyl-1H-indol-3-yl)methylene)cyclohexane-1-carboxylate ((1*S*,2*S*)-8v)



White soild, 417 mg, 92% yield, >99% ee. R_f = 0.51 (petroleum ether/ethyl acetate = 1:1 v/v). M.p. 119−120 °C. $[\alpha]_D^{25}$ = +39.4 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.52–7.44 (m, 2H), 7.35−7.29 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.43 (s, 1H), 4.61 (d, *J* = 2.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.37 (s, 1H), 2.71−2.64 (m, 1H), 2.62–2.54 (m, 1H), 2.51−2.42 (m, 1H), 2.32 (s, 3H), 2.20−2.08 (m, 1H), 1.91−1.80 (m, 2H), 1.45–1.33 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 144.9, 143.1, 135.0, 134.6, 130.9, 129.8, 126.7, 124.8, 123.7, 123.2, 119.7, 118.5, 114.4, 113.6, 73.9, 60.8, 48.4, 25.5, 23.5, 21.5, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{27}NO_5S$+Na^+: 476.1508 $[M+Na]^+$; found: 476.1501. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 35.35 min (major).

The product **8v** (10 mg) was dissolved in the mixture solvent of CH_2Cl_2 (0.5 mL) and *n*-hexane (1.5 mL). After slowly evaporation of solvents at ambient temperature, the fine crystals which were suitable for the X-ray diffraction analyses were obtained. The intensity data were collected on an a Rigaku 007HF Saturn724 diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The absolute configuration of **8v** was determined as (1*S*,2*S*). The crystal structure (OPTEP representation, 50% thermal probability ellpsoids) and the data were outlined below (**Table S1**).

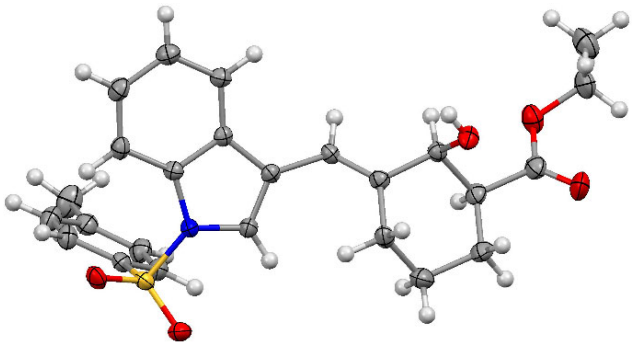
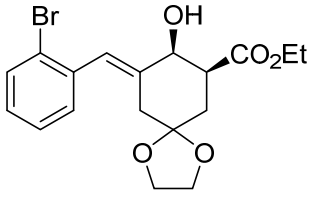


Table S1. Crystal data and structure refinement for **8v** (**CCDC** Number: 1936853)

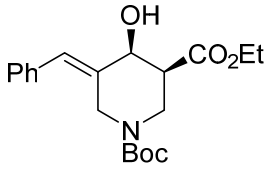
Empirical formula	$C_{25}H_{27}NO_5S$
Formula weight	453.55
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.954(2) A α = 90 deg. b = 14.826(3) A β = 94.53(3) deg. c = 15.404(3) A γ = 90 deg.
Volume	2266.4(8) $Å^3$
Z, Calculated density	4, 1.329 Mg/m^3
Absorption coefficient	0.180 mm^{-1}
F(000)	960
Crystal size	0.200 x 0.180 x 0.120 mm
Theta range for data collection	1.909 to 27.909 deg.
Limiting indices	-13⩽h⩽12, -19⩽k⩽19, -20⩽l⩽20
Reflections collected / unique	24519 / 10608 [R(int) = 0.0460]
Completeness to theta = 67.684	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.8206
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10608 / 1 / 583
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R_1 = 0.0465, wR_2 = 0.1097
R indices (all data)	R_1 = 0.0568, wR_2 = 0.1169
Absolute structure parameter	-0.02(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.273 and -0.330 $e.A^{-3}$

(+)-Ethyl 9-((*E*)-2-bromobenzylidene)-8-hydroxy-1,4-dioxaspiro[4.5]decane-7-carboxylate ((+)-8w)



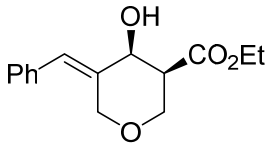
White solid, 381 mg, 96% yield. 99% ee. R_f = 0.41 (petroleum ether/ethyl acetate = 1:1 v/v). M.p. 72–73 °C. $[\alpha]_D^{25}$ = +55.5 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30–7.23 (m, 2H), 7.16−7.07 (m, 1H), 6.62 (s, 1H), 4.70 (d, *J* = 2.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.01–3.89 (m, 3H), 3.88−3.80 (m, 1H), 2.96 (s, 1H), 2.91 (d, *J* = 12.7 Hz, 1H), 2.61 (d, *J* = 14.1 Hz, 1H), 2.55 (d, *J* = 14.1 Hz, 1H), 2.35 (t, *J* = 13.1 Hz, 1H), 1.95 (d, *J* = 13.1 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.0, 138.3, 136.6, 132.5, 131.0, 128.6, 127.8, 126.8, 124.3, 108.5, 72.67, 64.6, 64.4, 61.0, 45.4, 33.8, 32.0, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{21}BrO_5$+Na^+: 419.0470 $[M+Na]^+$; found: 419.0464. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 20.91 min (minor); t_R = 18.57 min (major).

(+)-1-(*tert*-Butyl) 3-ethyl 5-((*E*)-benzylidene)-4-hydroxypiperidine-1,3-dicarboxylate ((+)-8x)



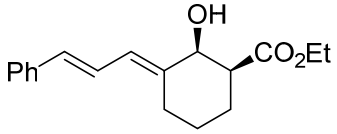
Colourless oil, 350 mg, 97% yield, 98% ee. R_f = 0.32 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +46.4 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.31 (m, 2H), 7.30−7.22 (m, 4H), 6.63 (s, 1H), 4.75 (d, *J* = 14.5 Hz, 1H), 4.71–4.64 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.19–4.07 (m, 1H), 3.88 (d, *J* = 15.4 Hz, 1H), 3.55 (br s, 1H), 3.22–3.03 (m, 1H), 2.90–2.77 (m, 1H), 1.45−1.08 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 154.3, 135.7, 135.3, 128.8, 128.3, 127.7, 127.3, 79.9, 72.3, 61.1, 47.3, 41.4, 40.3, 28.0, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{27}NO_5$+H^+: 362.1967 $[M+H]^+$; found: 362.1959. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 8.95 min (minor); t_R = 10.56 min (major).

(+)-Ethyl 5-((*E*)-benzylidene)-4-hydroxytetrahydro-2H-pyran-3-carboxylate ((+)-8y)



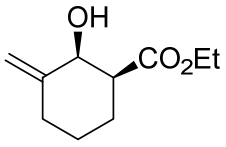
White solid, 244 mg, 93% yield, 97% ee. R_f = 0.47 (petroleum ether/ethyl acetate = 5:2 v/v). M.p. 58–59 °C. $[\alpha]_D^{25}$ +7.2 (*c* 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37−7.29 (m, 2H), 7.28–7.21 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.68 (s, 1H), 4.72−4.64 (m, 1H), 4.41 (s, 1H), 4.27–4.11 (m, 3H), 3.92 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.43 (d, *J* = 4.6 Hz, 1H), 3.07–2.91 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.8, 136.3, 135.5, 128.8, 128.2, 127.5, 127.2, 71.1, 64.3, 64.0, 60.9, 48.2, 14.0. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{18}O_4$+Na^+: 285.1103 $[M+Na]^+$; found: 285.1093. HPLC conditions: Chiralcel AS-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 21.57 min (minor); t_R = 14.61 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-((*E*)-3-phenylallylidene)cyclohexane-1-carboxylate ((+)-8z)



Colourless oil, 272 mg, 95% yield, 99% ee. R_f = 0.40 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +175.4 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.4 Hz, 2H), 7.34−7.28 (m, 2H), 7.25–7.18 (m, 1H), 7.01 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.57 (d, *J* = 15.5 Hz, 1H), 6.22 (d, *J* = 11.0 Hz, 1H), 4.49 (d, *J* = 2.7 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.17 (s, 1H), 2.67−2.53 (m, 2H), 2.47−2.37 (m, 1H), 2.16–2.04 (m, 1H), 1.92−1.80 (m, 2H), 1.45–1.33 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 141.2, 137.4, 133.1, 128.6, 127.5, 126.3, 125.2, 123.9, 73.8, 60.7, 48.5, 25.6, 24.5, 23.5, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{22}O_3$+Na^+: 309.1467 $[M+Na]^+$; found: 309.1467. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 10.83 min (minor); t_R = 12.59 min (major).

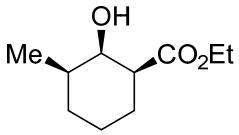
(+)-Ethyl 2-hydroxy-3-methylenecyclohexane-1-carboxylate ((+)-8aa)



Colourless liquid, 99 mg, 54% yield, 94% ee. R_f = 0.15 (petroleum ether/ethyl acetate = 5:1 v/v). $[\alpha]_D^{25}$ = +41.6 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.95 (s, 1H), 4.83 (s, 1H), 4.46 (d, *J* = 3.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.24 (s, 1H), 2.61−2.53 (m, 1H), 2.47−2.37 (m, 1H), 2.15−2.00 (m, 2H), 1.83−1.73 (m, 2H), 1.46−1.35 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 147.9, 110.1, 72.2, 60.7, 48.2, 30.2, 25.9, 23.6, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{10}H_{16}O_3$+Na^+: 207.0997 $[M+Na]^+$; found: 207.0993. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID);

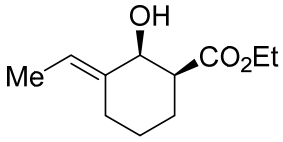
n-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 13.52 min (minor); t_R = 14.46 min (major).

The by-product of the asymmetric hydrogenation of **8aa** is *cis,cis*-ethyl 2-hydroxy-3-methylcyclohexane-1-carboxylate.



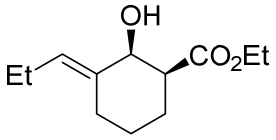
Colourless liquid, 76 mg, 41% yield, 1.2% ee. R_f = 0.23 (petroleum ether/ethyl acetate = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.16 (q, *J* = 7.2 Hz, 2H), 4.03 (s, 1H), 2.92 (s, 1H), 2.55–2.23 (m, 1H), 1.83−1.67 (m, 3H), 1.55−1.30 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.8, 69.9, 60.4, 47.8, 36.2, 27.0, 25.1, 22.3, 18.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{16}O_3$+Na^+: 209.1154 $[M+Na]^+$; found: 209.1150. HPLC conditions: Chiralcel AC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 25.43 min (minor); t_R = 10.37 min (major).

(+)-Ethyl (*E*)-3-ethylidene-2-hydroxycyclohexane-1-carboxylate ((+)-8ab)



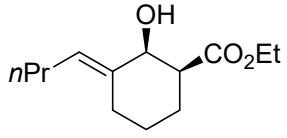
Colourless oil, 186 mg, 94% yield, 95% ee. R_f = 0.58 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +94.0 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.51 (q, *J* = 6.6 Hz, 1H), 4.39 (d, *J* = 2.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.03 (s, 1H), 2.53−2.48 (m, 1H), 2.42−2.32 (m, 1H), 2.21−2.10 (m, 1H), 2.09–1.97 (m, 1H), 1.87–1.77 (m, 1H), 1.65−1.57 (d, *J* = 6.8 Hz, 1H), 1.34−1.21 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.1, 138.6, 120.2, 73.9, 60.5, 48.4, 25.5, 23.3, 22.8, 14.1, 12.5. HRMS (ESI): *m*/*z* calcd for $C_{11}H_{18}O_3$+Na^+: 221.1154 $[M+Na]^+$; found: 221.1149. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 11.69 min (minor); t_R = 13.44 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-propylidenecyclohexane-1-carboxylate ((+)-8ac)



Colourless oil, 204 mg, 96% yield, >99% ee. R_f = 0.60 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +57.6 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43 (t, *J* = 7.0 Hz, 1H), 4.37 (d, *J* = 2.6 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.04 (s, 1H), 2.54–2.45 (m, 1H), 2.37–2.30 (m, 1H), 2.21–2.12 (m, 1H), 2.08–1.99 (m, 3H), 1.87–1.78 (m, 2H), 1.33−1.21 (m, 4H), 0.96 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.1, 137.4, 127.8, 74.0, 60.5, 48.5, 25.8, 23.4, 23.2, 20.2, 14.3, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{20}O_3$+Na^+: 235.1310 $[M+Na]^+$; found: 235.1306. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 10.19 min (major).

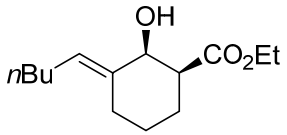
(+)-Ethyl (*E*)-3-butylidene-2-hydroxycyclohexane-1-carboxylate ((+)-8ad)



Colourless oil, 220 mg, 97% yield, 99% ee. R_f = 0.61 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +72.3 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43 (t, *J* = 7.2 Hz, 1H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.04 (s, 1H), 2.57−2.42 (m, 1H), 2.39−2.28 (m, 1H), 2.22−2.12 (m, 1H), 2.10–1.95 (m, 3H), 1.86−1.76 (m, 2H), 1.44−1.30 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.1, 138.1, 126.0, 74.1, 60.5, 48.6, 28.9, 25.7, 23.4, 23.3, 22.7, 14.10, 13.7. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{22}O_3$+Na^+: 249.1467 $[M+Na]^+$; found: 249.1464.

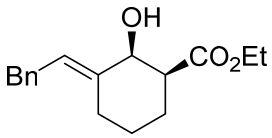
HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 10.73 min (minor); t_R = 11.22 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-pentylidenecyclohexane-1-carboxylate ((+)-8ae)



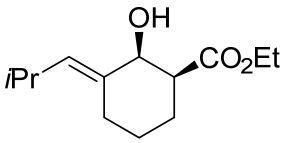
Colourless oil, 236 mg, 98% yield, 99% ee. R_f = 0.51 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +66.8 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43 (t, *J* = 7.4 Hz, 1H), 4.39 (d, *J* = 2.7 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.01 (s, 1H), 2.54–2.46 (m, 1H), 2.38−2.31 (m, 1H), 2.22−2.13 (m, 1H), 2.09–1.97 (m, 3H), 1.88−1.77 (m, 2H), 1.38–1.24 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 137.9, 126.0, 74.0, 60.4, 48.5, 31.7, 26.4, 25.6, 23.3, 23.2, 22.1, 14.0, 13.8. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{24}O_3$+Na^+: 263.1623 $[M+Na]^+$; found: 263.1622. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 11.44 min (minor); t_R = 12.45 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-(2-phenylethylidene)cyclohexane-1-carboxylate ((+)-8af)



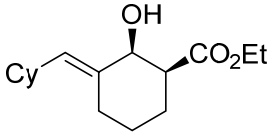
Colourless oil, 263 mg, 96% yield, 99% ee. R_f = 0.54 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +40.2 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.23 (m, 2H), 7.22–7.10 (m, 3H), 5.61 (t, *J* = 7.1 Hz, 1H), 4.42 (d, *J* = 2.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.46−3.31 (m, 2H), 3.13 (s, 1H), 2.57−2.50 (m, 1H), 2.50−2.42 (m, 1H), 2.34–2.24 (m, 1H), 2.14–2.01 (m, 1H), 1.90–1.79 (m, 2H), 1.40–1.29 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.0, 140.7, 139.0, 128.4, 128.3, 125.9, 124.2, 73.9, 60.6, 48.5, 33.1, 25.7, 23.5, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{22}O_3$+Na^+: 297.1467 $[M+Na]^+$; found: 297.1461. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 21.59 min (minor); t_R = 16.90 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-(2-methylpropylidene)cyclohexane-1-carboxylate ((+)-8ag)



Colourless oil, 215 mg, 95% yield, >99% ee. R_f = 0.61 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +68.5 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (d, *J* = 8.3 Hz, 1H), 4.35 (d, *J* = 2.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.03 (s, 1H), 2.60–2.47 (m, 2H), 2.37–2.30 (m, 1H), 2.24–2.14 (m, 1H), 2.09–1.98 (m, 1H), 1.89–1.74 (m, 2H), 1.34–1.23 (m, 4H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.1, 135.8, 133.6, 74.0, 60.5, 48.6, 26.1, 25.9, 23.5, 23.5, 23.4, 23.0, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{22}O_3$+Na^+: 249.1467 $[M+Na]^+$; found: 249.1465. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 11.55 min (major).

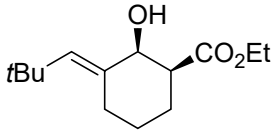
(+)-Ethyl (*E*)-3-(cyclohexylmethylene)-2-hydroxycyclohexane-1-carboxylate ((+)-8ah)



White solid, 256 mg, 96% yield, 98% ee. R_f = 0.67 (petroleum ether/ethyl acetate = 5:2 v/v). M.p. 49−50 °C. $[\alpha]_D^{25}$ = +65.3 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (d, *J* = 8.8 Hz, 1H), 4.34 (d, *J* = 2.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.99 (s, 1H), 2.56–2.42 (m, 1H), 2.37−2.29 (m, 1H), 2.26–2.13 (m, 2H), 2.10–1.96 (m, 1H), 1.87−1.76 (m, 2H), 1.74–1.60 (m, 4H), 1.58–1.50 (m, 1H), 1.34–1.13 (m, 7H), 1.11−0.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.1, 136.4, 132.2, 74.1, 60.6, 48.7,

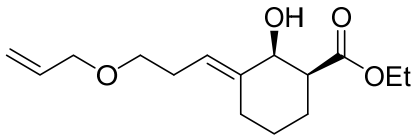
35.9, 33.6, 33.1, 26.1, 26.0, 25.9, 25.9, 23.7, 23.5, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{26}O_3$+Na^+: 289.1780 $[M+Na]^+$; found: 289.1778. HPLC conditions: Chiralcel AS-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 6.18 min (minor); t_R = 8.33 min (major).

(+)-Ethyl (*E*)-3-(2,2-dimethylpropylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8ai)



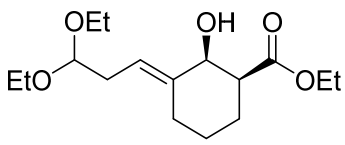
Colourless liquid, 233 mg, 97% yield, 98% ee. R_f = 0.65 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +68.4 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.48 (s, 1H), 4.29 (d, *J* = 2.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.98 (s, 1H), 2.64−2.56 (m, 1H), 2.54−2.47 (m, 1H), 2.28−2.18 (m, 1H), 2.07–1.95 (m, 1H), 1.87−1.76 (m, 2H), 1.37–1.30 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.2, 137.7, 136.5, 75.2, 60.6, 48.8, 31.8, 31.2, 25.7, 24.1, 23.1, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{24}O_3$+Na^+: 263.1623 $[M+Na]^+$; found: 263.1619. HPLC conditions: Chiralcel AS-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 5.52 min (minor); t_R = 86.58 min (major).

(+)-Ethyl (*E*)-3-(3-(allyloxy)propylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8aj)



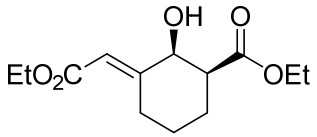
Colourless oil, 255 mg, 95% yield. >99% ee. R_f = 0.45 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +40.0 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.00–5.81 (m, 1H), 5.47 (t, *J* = 7.1 Hz, 1H), 5.28 (d, *J* = 15.7 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.41 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.98 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.48−3.41 (m, 2H), 3.05 (s, 1H), 2.55−2.48 (m, 1H), 2.40−2.31 (m, 3H), 2.26−1.99 (m, 1H), 2.1−1.98 (m, 1H), 1.89−1.79 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.0, 140.1, 134.8, 121.7, 116.8, 73.8, 71.7, 69.7, 60.6, 48.4, 27.6, 25.7, 23.4, 23.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{24}O_4$+Na^+: 291.1572 $[M+Na]^+$; Found: 291.1569. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 25.42 min (major).

(+)-Ethyl (*E*)-3-(3,3-diethoxypropylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8ak)



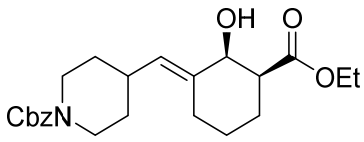
Colourless oil, 273 mg, 91% yield. 97% ee. R_f = 0.34 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +39.0 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.42–5.29 (m, 1H), 4.40 (t, *J* = 5.8 Hz, 1H), 4.36 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.64–3.50 (m, 2H), 3.48–3.36 (m, 2H), 3.00 (s, 1H), 2.43 (dt, *J* = 12.2 Hz, 1H), 2.37–2.23 (m, 3H), 2.22−2.10 (m, 1H), 2.04–1.89 (m, 1H), 1.85−1.75 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 140.4, 120.1, 102.3, 73.8, 61.2, 61.1, 60.5, 48.4, 31.8, 25.6, 23.5, 23.26, 15.2, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{28}O_5$+Na^+: 323.1834 $[M+Na]^+$; Found: 323.1827. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 21.51 min (major); t_R = 23.97 min (minor).

(+)-Ethyl (*E*)-3-(2-ethoxy-2-oxoethylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8al)



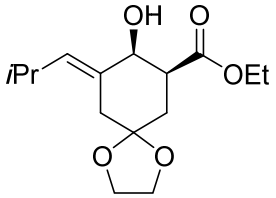
Colourless oil, 246 mg, 96% yield. 86% ee. R_f = 0.48 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +68.2 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.90 (s, 1H), 4.37 (d, *J* = 4.1 Hz, 1H), 4.20−4.13 (m, 4H), 3.56 (s, 1H), 3.05–2.96 (m, 1H), 2.90–2.81 (m, 1H), 2.75−2.68 (m, 1H), 2.19–2.08 (m, 1H), 1.84–1.73 (m, 2H), 1.56–1.44 (m, 1H), 1.32−1.23 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.1, 166.4, 159.2, 114.8, 73.2, 60.8, 59.8, 48.4, 25.2, 25.0, 24.0, 14.1, 14.0. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{20}O_5$+Na^+: 279.1208 $[M+Na]^+$; Found: 279.1203. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 12.88 min (major); t_R = 11.89 min (minor).

(+)-Benzyl 4-((*E*)-(3-(ethoxycarbonyl)-2-hydroxycyclohexylidene)methyl)piperidine-1-carboxylate ((+)-8am)



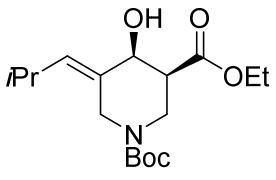
Colourless oil, 377 mg, 94% yield. 96% ee. R_f = 0.29 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +32.4 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 5H), 5.24 (d, *J* = 8.8 Hz, 1H), 5.12 (s, 2H), 4.35 (d, *J* = 2.7 Hz, 1H), 4.24−4.06 (m, 4H), 3.17 (s, 1H), 2.95–2.68 (m, 2H), 2.50 (dt, *J* = 11.9, 3.4 Hz, 1H), 2.45–2.18 (m, 3H), 2.11–1.97 (m, 1H), 1.87−1.76 (m, 2H), 1.65−1.48 (m, 2H), 1.35−1.21 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.0, 155.2, 138.1, 136.8, 129.4, 128.4, 127.8, 127.7, 73.7, 66.9, 60.6, 48.5, 43.7, 43.7, 34.0, 32.1, 31.8, 25.9, 23.8, 23.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{23}H_{31}NO_5$+H^+: 402.228 $[M+H]^+$; found: 402.225. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 31.94 min (major); t_R = 27.06 min (minor).

(+)-Ethyl (*E*)-8-hydroxy-9-(2-methylpropylidene)-1,4-dioxaspiro[4.5]decane-7-carboxylate ((+)-8an)



White solid, 276 mg, 97% yield, 96% ee. R_f = 0.44 (petroleum ether/ethyl acetate = 5:2 v/v). M.p. 42–43 °C. $[\alpha]_D^{25}$ = +14.0 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.38 (d, *J* = 9.0 Hz, 1H), 4.40 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.05–3.89 (m, 4H), 2.86 (s, 1H), 2.78−2.68 (m, 1H), 2.58–2.42 (m, 3H), 2.28 (t, *J* = 13.2 Hz, 1H), 1.93–1.84 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.1, 136.6, 132.4, 108.3, 73.0, 64.5, 64.3, 60.7, 45.4, 33.2, 31.8, 26.2, 23.0, 22.7, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{24}O_5$+Na^+: 307.1521 $[M+Na]^+$; Found: 307.1518. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 16.06 min (major); t_R = 19.20 min (minor).

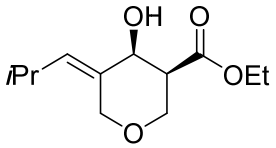
(+)-1-(*tert*-Butyl) 3-ethyl (*E*)-4-hydroxy-5-(2-methylpropylidene)piperidine-1,3-dicarboxylate ((+)-8ao)



Colourless oil, 311 mg, 95% yield. 94% ee. R_f = 0.36 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +7.6 (*c* = 1.0 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.30 (d, *J* = 9.7 Hz, 1H), 4.64–4.38 (m, 2H), 4.28−3.91 (m, 3H), 3.60 (d, *J* = 14.3 Hz, 1H), 3.53−3.25 (m, 1H), 2.96 (s, 1H), 2.69–2.49 (m, 2H), 1.44 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101

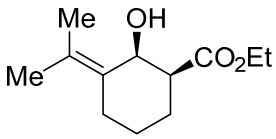
MHz, $CDCl_3$): δ = 172.3, 154.3, 135.9, 130.7, 79.9, 72.2, 60.9, 47.5, 40.9, 40.4, 28.3, 26.5, 23.2, 22.9, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{29}NO_5$+H^+: 328.2124 $[M+H]^+$; found: 328.2120. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 99:1; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 25.83 min (major); t_R = 13.42 min (minor).

(+)-Ethyl (*E*)-4-hydroxy-5-(2-methylpropylidene)tetrahydro-2H-pyran-3-carboxylate ((+)-8ap)



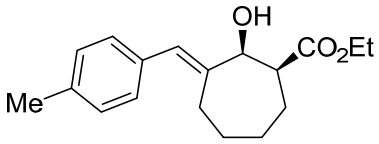
Colourless oil, 215 mg, 94% yield. >99% *ee*. R_f = 0.43 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +37.6 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.39 (d, *J* = 9.5 Hz, 1H), 4.49 (d, *J* = 2.9 Hz, 1H), 4.29–4.15 (m, 4H), 4.09 (dd, *J* = 11.3, 9.6 Hz, 1H), 3.91 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.06 (s, 1H), 2.91−2.83 (m, 1H), 2.62−2.51 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.98 (d, *J* = 5.4 Hz, 3H), 0.96 (d, *J* = 5.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0, 135.7, 131.5, 71.1, 64.3, 63.4, 60.9, 48.3, 26.2, 23.1, 23.0, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{20}O_4$+Na^+: 251.1259 $[M+Na]^+$; Found: 251.1255. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 15.71 min (major).

(+)-Ethyl 2-hydroxy-3-(propan-2-ylidene)cyclohexane-1-carboxylate ((+)-8aq)



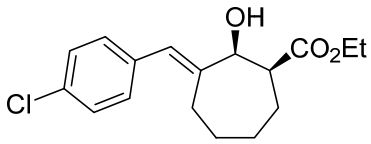
Colourless oil, 208 mg, 98% yield, 99% ee. R_f = 0.60 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +86.1 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.05 (s, 1H), 4.18 (q, *J* = 6.8 Hz, 2H), 2.94 (s, 1H), 2.52–2.42 (m, 1H), 2.39–2.27 (m, 1H), 2.21–2.08 (m, 1H), 2.06–1.93 (m, 1H), 1.89–1.78 (m, 2H), 1.76 (s, 3H), 1.69 (s, 3H),1.29 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.7, 130.7, 126.5, 66.3, 60.6, 48.0, 25.9, 24.0, 22.9, 20.3, 19.8, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{20}O_3$+Na^+: 235.1310 $[M+Na]^+$; found: 235.1308. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 9.69 min (minor); t_R = 13.76 min (major).

(+)-Ethyl 2-hydroxy-3-((*E*)-4-methylbenzylidene)cycloheptane-1-carboxylate ((+)-10a)



Colourless oil, 274 mg, 95% yield, 98% ee. R_f = 0.52 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +107.5 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20−7.05 (m, 4H), 6.54 (s, 1H), 4.76 (d, *J* = 2.9 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.17 (s, 1H), 2.73–2.55 (m, 2H), 2.53–2.41 (m, 1H), 2.34 (s, 3H), 2.00–1.70 (m, 5H), 1.42–1.32 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.0, 141.9, 136.2, 134.5, 128.8, 128.7, 127.8, 77.0, 60.8, 51.5, 26.6, 26.2, 26.1, 26.0, 21.1, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{24}O_3$+H^+: 289.1804 $[M+H]^+$; found: 289.1805. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 10.67 min (minor); t_R = 9.52 min (major).

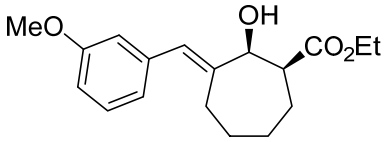
(+)-Ethyl 3-((*E*)-4-chlorobenzylidene)-2-hydroxycycloheptane-1-carboxylate ((+)-10b)



Colourless oil, 296 mg, 96% yield, 99% ee. R_f = 0.45 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +89.6 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.52 (s, 1H), 4.76 (d, *J* = 3.2 Hz, 1H), 4.20 (q, *J* = 7.1

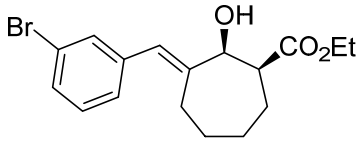
Hz, 2H), 3.26 (s, 1H), 2.68−2.55 (m, 2H), 2.46–2.35 (m, 1H), 2.00–1.71 (m, 5H), 1.40–1.32 (m, 1H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.9, 143.5, 135.8, 132.2, 130.0, 128.2, 126.6, 76.7, 60.8, 51.3, 26.6, 26.2, 26.1, 25.9, 14.1. HRMS (ESI): m/z calcd for $C_{17}H_{21}ClO_3$+Na^+: 331.1077 $[M+Na]^+$; found: 331.1075. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 13.17 min (minor); t_R = 12.34 min (major).

(+)-Ethyl 2-hydroxy-3-((*E*)-3-methoxybenzylidene)cycloheptane-1-carboxylate ((+)-10c)



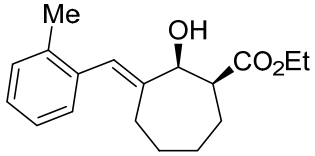
Colourless oil, 289 mg, 95% yield, >99% ee. R_f = 0.47 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +109.6 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.20 (m, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.81–6.73 (m, 2H), 6.56 (s, 1H), 4.77 (d, J = 1.7 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 3.18 (s, 1H), 2.68–2.59 (m, 2H), 2.52−2.42 (m, 1H), 2.00–1.73 (m, 5H), 1.42−1.34 (m, 1H), 1.30 (t, J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.0, 159.3, 143.0, 138.9, 129.0, 127.8, 121.3, 114.4, 112.0, 76.9, 60.8, 55.1, 51.5, 26.6, 26.3, 26.1, 26.0, 14.2. HRMS (ESI): m/z calcd for $C_{18}H_{24}O_4$+Na^+: 327.1572 $[M+Na]^+$; found: 327.1572. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 9.06 min (major).

(+)-Ethyl 3-((*E*)-3-bromobenzylidene)-2-hydroxycycloheptane-1-carboxylate ((+)-10d)



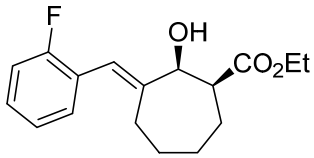
Colourless oil, 325 mg, 92% yield, 98% ee. R_f = 0.48 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +84.2 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.33 (m, 2H), 7.23–7.12 (m, 2H), 6.51 (s, 1H), 4.76 (d, J = 3.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.27 (s, 1H), 2.67−2.57 (m, 2H), 2.46−2.36 (s, 1H), 1.98–1.83 (m, 3H), 1.82–1.71 (m, 2H), 1.40–1.32 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.9, 144.2, 139.5, 131.6, 129.6, 129.5, 127.3, 126.3, 122.1, 76.6, 60.8, 51.3, 26.6, 26.2, 26.1, 25.9, 14.1. HRMS (ESI): m/z calcd for $C_{17}H_{21}BrO_3$+Na^+: 375.0572 $[M+Na]^+$; found: 375.0561. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 9.11 min (minor); t_R = 10.45 min (major).

(+)-Ethyl 2-hydroxy-3-((*E*)-2-methylbenzylidene)cycloheptane-1-carboxylate ((+)-10e)



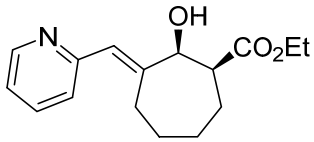
Colourless oil, 271 mg, 94% yield, 98% ee. R_f = 0.53 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +86.8 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.06 (m, 4H), 6.54 (s, 1H), 4.8d (d, J = 2.1 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.67−2.59 (m, 1H), 2.51−2.41 (m, 1H), 2.33–2.25 (m, 1H), 2.23 (s, 3H), 1.97−1.80 (m, 3H), 1.76−1.60 (m, 2H), 1.40−1.33 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.2, 142.7, 136.8, 136.3, 129.7, 129.0, 127.0, 126.8, 125.3, 76.6, 60.8, 51.8, 26.8, 26.5, 26.1, 26.0, 20.0, 14.2. HRMS (ESI): m/z calcd for $C_{18}H_{24}O_3$+Na^+: 311.1623 $[M+Na]^+$; found: 311.1617. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 96:4; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 10.84 min (minor); t_R = 11.33 min (major).

(+)-Ethyl 3-((*E*)-2-fluorobenzylidene)-2-hydroxycycloheptane-1-carboxylate ((+)-10f)



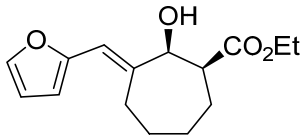
Colourless oil, 281 mg, 96% yield, 98% ee. R_f = 0.53 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +92.3 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.16 (m, 2H), 7.11–6.98 (m, 2H), 6.54 (s, 1H), 4.84 (d, *J* = 2.8 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 1H), 3.34 (s, 1H), 2.69–2.61 (m, 1H), 2.61−2.52 (m, 1H), 2.41−2.30 (m, 1H), 1.98−1.68 (m, 5H), 1.41–1.32 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.7, 160.0 (d, $^1J_{C\text{-}F}$ = 246.7 Hz), 145.1, 130.4 (d, $^3J_{C\text{-}F}$ = 3.5 Hz), 128.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 125.0 (d, $^2J_{C\text{-}F}$ = 14.8 Hz), 123.4 (d, $^3J_{C\text{-}F}$ = 3.6 Hz), 120.2 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 76.4, 60.7, 51.3, 26.5, 26.4, 26.2, 14.0. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{21}FO_3$+Na^+: 315.1372 $[M+Na]^+$; found: 315.1373. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 7.62 min (minor); t_R = 9.10 min (major).

(+)-Ethyl (*E*)-2-hydroxy-3-(pyridin-2-ylmethylene)cycloheptane-1-carboxylate ((+)-10g)



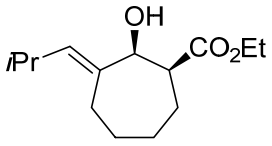
Colourless oil, 256 mg, 93% yield, 98% ee. R_f = 0.26 (petroleum ether/ethyl acetate = 1:1 v/v). $[\alpha]_D^{25}$ = +78.6 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66–8.54 (m, 1H), 7.69−7.58 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.13−7.05 (m, 1H), 6.63 (s, 1H), 4.83 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.56 (br s, 1H), 2.94–2.84 (m, 1H), 2.80–2.64 (m, 2H), 1.97–1.79 (m, 5H), 1.42−1.32 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.3, 156.4, 149.0, 147.6, 135.9, 126.5, 123.9, 121.0, 76.7, 60.6, 51.4, 26.7, 26.2, 25.9, 25.5, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{21}NO_3$+H^+: 276.1600 $[M+H]^+$; found: 276.1600. HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 95:5; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 22.52 min (minor); t_R = 14.45 min (major).

(+)-Ethyl (*E*)-3-(furan-2-ylmethylene)-2-hydroxycycloheptane-1-carboxylate ((+)-10h)



Pale yellow oil, 251 mg, 95% yield, 99% ee. R_f = 0.50 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +47.6 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 2.0 Hz, 1H), 6.45−6.34 (m, 2H), 6.29 (d, *J* = 3.4 Hz, 1H), 4.73 (d, *J* = 3.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.14 (s, 1H), 2.83−2.71 (m, 1H), 2.66−2.59 (m, 1H), 2.58−2.49 (m, 1H), 1.97−1.79 (m, 5H), 1.40–1.31 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.6, 152.6, 141.4, 141.1, 116.1, 111.2, 109.2, 76.4, 60.8, 51.4, 27.7, 27.3, 25.7, 25.4, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{20}O_4$+Na^+: 287.1259 $[M+Na]^+$; found: 287.1259. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 9.92 min (minor); t_R = 12.39 min (major).

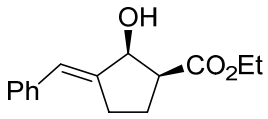
(+)-Ethyl (*E*)-2-hydroxy-3-(2-methylpropylidene)cycloheptane-1-carboxylate ((+)-10i)



Colourless oil, 216 mg, 90% yield, >99% ee. R_f = 0.54 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +46.4 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.28 (d, *J* = 9.4 Hz, 1H), 4.55 (d, *J* = 2.8 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.97 (s, 1H), 2.58–2.38 (m, 3H), 2.28−2.18 (m, 1H), 1.90–1.78 (m, 3H), 1.73–1.64 (m, 2H), 1.35–1.21 (m, 5H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.1, 136.9, 136.0, 76.5, 60.6, 51.9, 29.7, 26.8, 26.5, 25.8, 25.5, 24.7, 23.0, 22.9,

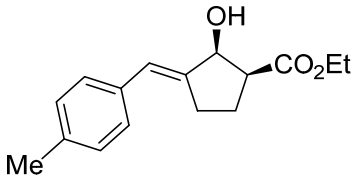
14.2. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{24}O_3$+Na^+: 263.1623 $[M+Na]^+$; found: 263.1624. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 98:2; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 12.21 min (major).

(+)-Ethyl 3-((*E*)-benzylidene)-2-hydroxycyclopentane-1-carboxylate ((+)-12a)



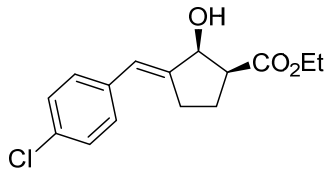
White solid, 239 mg, 97% yield, M.p. 44–45 °C. 92% ee. R_f = 0.41 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +7.6 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 4H), 7.25–7.19 (m, 1H), 6.64 (s, 1H), 4.76−4.68 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.13–3.06 (m, 1H), 2.93–2.81 (m, 2H), 2.65–2.51 (m, 1H), 2.36–2.20 (m, 1H), 2.16–2.04 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.8, 144.4, 137.3, 128.5, 128.3, 126.8, 125.4, 77.4, 60.7, 48.2, 28.1, 26.0, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{18}O_3$+Na^+: 269.1149 $[M+Na]^+$; Found: 269.1147. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 14.49 min (minor); t_R = 15.22 min (major).

(+)-Ethyl 2-hydroxy-3-((*E*)-4-methylbenzylidene)cyclopentane-1-carboxylate ((+)-12b)



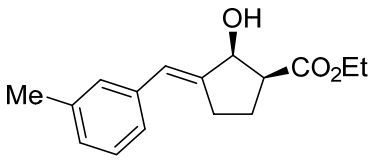
White solid, 247 mg, 95% yield. 93% ee. R_f = 0.35 (petroleum ether/ethyl acetate = 5:2 v/v). M.p. 40–41 °C. $[\alpha]_D^{25}$ = +3.1 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.61 (s, 1H), 4.76−4.68 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.07 (br s, 1H), 2.92−2.82 (m, 2H), 2.62−2.52 (m, 1H), 2.34 (s, 3H), 2.32–2.23 (m, 1H), 2.14–2.03 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.8, 143.3, 136.6, 134.5, 129.0, 128.5, 125.4, 77.5, 60.7, 48.3, 28.2, 26.1, 21.2, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{20}O_3$+Na^+: 283.1310 $[M+Na]^+$; found: 283.1307. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 94:6; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 15.63 min (minor); t_R = 19.86 min (major).

(+)-Ethyl 3-((*E*)-4-chlorobenzylidene)-2-hydroxycyclopentane-1-carboxylate ((+)-12c)



Pale yellow solid, 270 mg, 96% yield. 89% ee. R_f = 0.40 (petroleum ether/ethyl acetate = 5:2 v/v). M.p. 44–45 °C. $[\alpha]_D^{25}$ = +8.7 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.22 (m, 4H), 6.58 (s, 1H), 4.74−4.67 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.19 (s, 1H), 2.95–2.76 (m, 2H), 2.61−2.48 (m, 1H), 2.34−2.22 (m, 1H), 2.13–2.04 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.7, 145.0, 135.8, 132.4, 129.7, 128.4, 124.1, 77.2, 60.8, 48.1, 28.1, 25.9, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{17}ClO_3$+Na^+: 303.0764 $[M+Na]^+$; found: 303.0760. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 12.05 min (minor); t_R = 13.47 min (major).

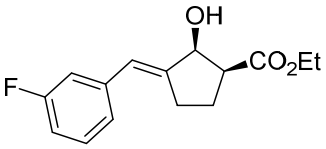
(+)-Ethyl 2-hydroxy-3-((*E*)-3-methylbenzylidene)cyclopentane-1-carboxylate ((+)-12d)



White solid, 250 mg, 96% yield. 93% ee. R_f = 0.45 (petroleum ether/ethyl acetate = 5:2 v/v). M. p. 59−60 °C. $[\alpha]_D^{25}$ = +8.4 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.20 (m, 1H), 7.16 (d, *J* = 5.5 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 4.78−4.62

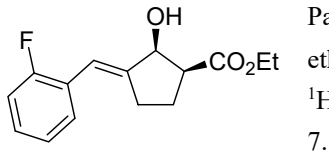
(m, 1H), 4.19 (q, J = 6.8 Hz, 2H), 3.17–2.99 (m, 1H), 2.97–2.76 (m, 2H), 2.64–2.47 (m, 1H), 2.34 (s, 3H), 2.31–2.21 (m, 1H), 2.13–2.01 (m, 1H),1.28 (t, J = 7.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.7, 144.2, 137.7, 137.2, 129.3, 128.1, 127.6, 125.5, 125.4, 77.4, 60.7, 48.2, 28.1, 25.9, 21.4, 14.1. HRMS (ESI): m/z calcd for $C_{16}H_{20}O_3$+Na^+: 283.1310 $[M+Na]^+$; found: 283.1305. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 60.84 min (minor); t_R = 25.67 min (major).

(+)-Ethyl 3-((*E*)-3-fluorobenzylidene)-2-hydroxycyclopentane-1-carboxylate ((+)-12e)



White solid, 259 mg, 98% yield. 92% ee. R_f = 0.34 (petroleum ether/ethyl acetate = 5:2 v/v). M. p. 59−60 °C. $[\alpha]_D^{25}$ = +19.6 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36−7.24 (m, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 10.4 Hz, 1H), 6.97–6.87 (m, 1H), 6.60 (s, 1H), 4.75−4.68 (m, 1H), 4.20 (q, J = 7.2 Hz, 5H), 3.22 (br s, 1H), 2.93–2.80 (m, 2H), 2.63−2.52 (m, 1H), 2.33−2.22 (m, 1H), 2.14–2.02 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.4, 162.6 (d, $^1J_{C\text{-}F}$ = 244.3 Hz), 145.8, 139.4 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.5 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 124.2 (d, $^4J_{C\text{-}F}$ = 2.7 Hz), 123.9 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 114.7 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 113.4 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 77.1, 60.6, 48.0, 27.9, 25.6, 14.0. HRMS (ESI): m/z calcd for $C_{15}H_{17}FO_3$+Na^+: 287.1059 $[M+Na]^+$; found: 287.1056. HPLC conditions: Chiralcel OD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 7.83 min (minor); t_R = 9.39 min (major).

(1*S*,2*S*)-(+)-Ethyl 3-((*E*)-2-fluorobenzylidene)-2-hydroxycyclopentane-1-carboxylate ((1*S*,2*S*)-12f)



Pale yellow solid, 254 mg, 96% yield. 92% ee. R_f = 0.40 (petroleum ether/ethyl acetate = 5:2 v/v). M. p. 66−67 °C. $[\alpha]_D^{25}$ = +2.4 (c = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.35 (m, 1H), 7.24–7.17 (m, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.04 (dd, J = 10.6, 8.1 Hz, 1H), 6.81 (s, 1H), 4.78−4.70 (m, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.07 (s, 1H), 2.95−2.87 (m, 1H), 2.86−2.73 (m, 1H), 2.59–2.43 (m, 1H), 2.33–2.20 (m, 1H), 2.14−2.00 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.7, 160.2 (d, $^1J_{C\text{-}F}$ = 248.7 Hz), 146.6, 129.1 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 128.4 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 125.1 (d, $^2J_{C\text{-}F}$ = 12.9 Hz), 123.6 (d, $^4J_{C\text{-}F}$ = 3.8 Hz), 117.1 (d, $^3J_{C\text{-}F}$ = 5.4 Hz), 115.3 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 77.2, 60.8, 48.2, 27.8, 25.8, 14.2. HRMS (ESI): m/z calcd for $C_{15}H_{17}FO_3$+Na^+: 287.1059 $[M+Na]^+$; found: 287.1057. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 11.13 min (minor); t_R = 10.02 min (major).

The product **12f** (10 mg) was dissolved in the mixture solvent of diethyl ether (0.5 mL) and *n*-hexane (1.5 mL). After slowly evaporation of solvents at ambient temperature, the fine crystals which were suitable for the X-ray diffraction analyses were obtained. The intensity data were collected on an a Rigaku 002 Saturn 994 diffractometer using graphite-monochromated Cu Kα (λ = 1.54184 Å) radiation. The absolute configuration of **12f** was determined as (1*S*,2*S*). The crystal structure (OPTEP representation, 30% thermal probability ellpsoids) and the data were outlined below (**Table S2**).

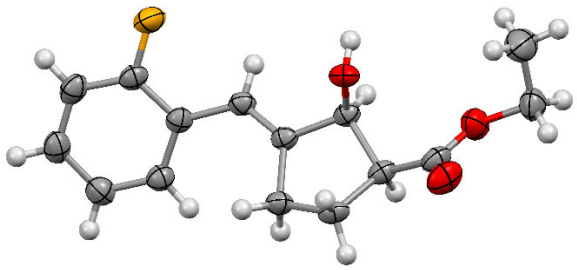
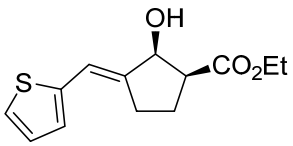


Table S2. Crystal data and structure refinement for **12f** (CCDC Number: 2054732)

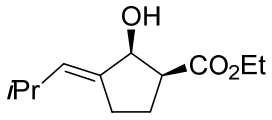
Empirical formula	$C_{15}H_{17}FO_3$
Formula weight	264.28
Temperature	291.15 K
Crystal system, space group	orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 8.22580(10) A α = 90 deg. b = 11.19040(10) A β = 90 deg. c = 14.72280(10) A γ = 90 deg.
Volume	1355.23(2) $Å^3$
Z, Calculated density	4, 1.295 Mg/m^3
Absorption coefficient	0.817 mm^{-1}
F(000)	560
Crystal size	0.220 x 0.180 x 0.160 mm
Radiation	Cu Kα (λ = 1.54184)
Theta range for data collection	9.928 to 158.81 deg.
Index ranges	-9⩽h⩽12, -19⩽k⩽19, -20⩽l⩽20
Reflections collected	10637
Independent reflections	2751 [R_{int} = 0.0249, R_{sigma} = 0.0165]
Data/restraints/parameters	2751/28/195
Goodness-of-fit on F^2	1.064
Final R indices [I⩾2σ(I)]	R_1 = 0.0340, wR_2 = 0.0912
R indices (all data)	R_1 = 0.0355, wR_2 = 0.0924
Largest diff. peak and hole	0.21 and -0.15 e.A^{-3}
Flack parameter	0.04(5)

(+)-Ethyl (*E*)-2-hydroxy-3-(thiophen-2-ylmethylene)cyclopentane-1-carboxylate ((+)-12g)



White solid, 242 mg, 96% yield. 89% ee. R_f = 0.36 (petroleum ether/ethyl acetate = 5:2 v/v). M. p. 32−33 °C. $[\alpha]_D^{25}$ = +7.0 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35−7.26 (m, 1H), 7.10−6.98 (m, 2H), 6.87 (s, 1H), 4.82–4.67 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.08 (s, 1H), 2.95−2.87 (m, 1H), 2.85−2.73 (m, 1H), 2.60−2.46 (m, 1H), 2.39–2.25 (m, 1H), 2.18 – 2.05 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.7, 142.3, 141.3, 127.0, 126.8, 125.5, 118.7, 76.8, 60.8, 48.7, 28.5, 25.9, 25.9, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}O_3S$+Na^+: 275.0718 $[M+Na]^+$; found: 275.0715. HPLC conditions: Chiralcel AD-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 11.85 min (minor); t_R = 14.18 min (major).

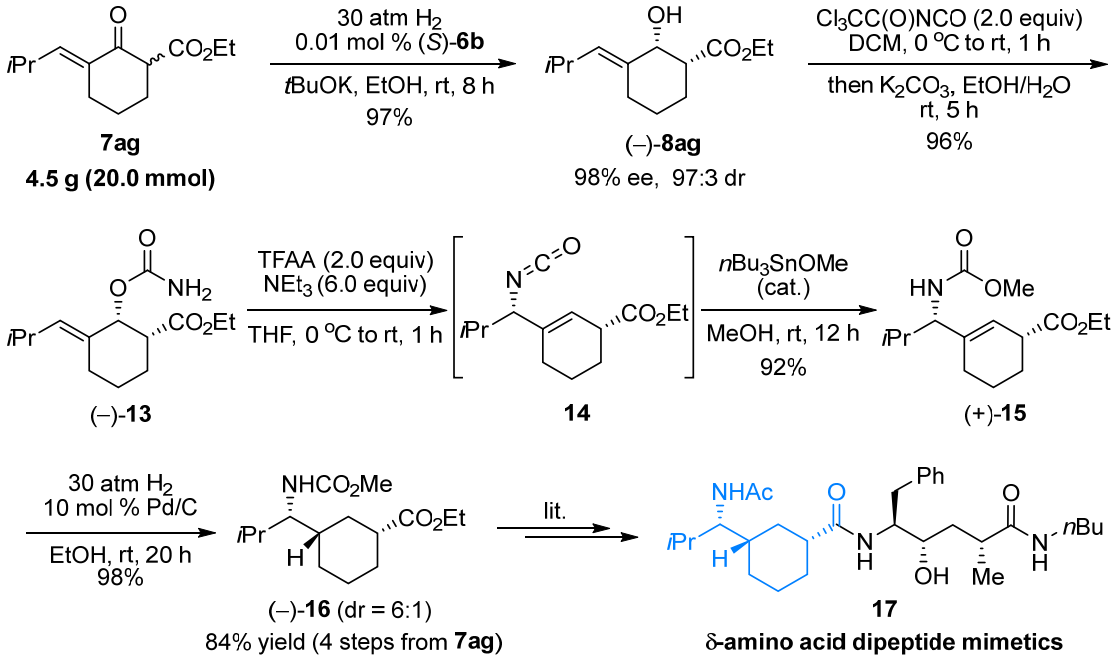
(+)-Ethyl (*E*)-2-hydroxy-3-(2-methylpropylidene)cyclopentane-1-carboxylate ((+)-12h)



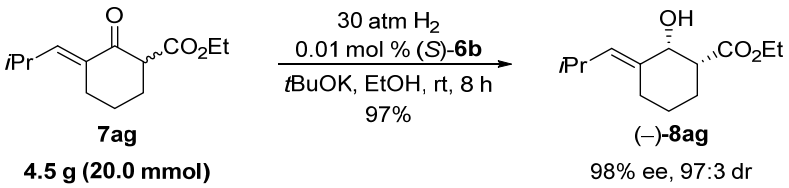
Colourless oil, 206 mg, 97% yield. 87% ee. R_f = 0.55 (petroleum ether/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +5.2 (*c* = 1.0 $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.46 (d, *J* = 9.3 Hz, 1H), 4.59−4.42 (m, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.85−2.70 (m, 2H), 2.58–2.48 (m, 1H), 2.44–2.32 (m, 1H), 2.28–2.11 (m, 2H), 2.04−1.99 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 4H), 1.02−0.92 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.9, 140.2, 133.8, 75.7, 60.6, 49.1, 28.6, 25.6, 25.4, 22.5, 22.4, 14.2. HRMS (ESI): *m/z* calcd for $C_{12}H_{20}O_3+H^+$: 213.1491 $[M+H]^+$; found: 213.1489. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 13.35 min (minor); t_R = 9.58 min (major).

(C) Enantioselective Synthesis of Carbocyclic δ-Amino Acid Ester (−)-16

The route for the enantioselective synthesis of the δ-amino acids ester (−)-**16** is outlined below.



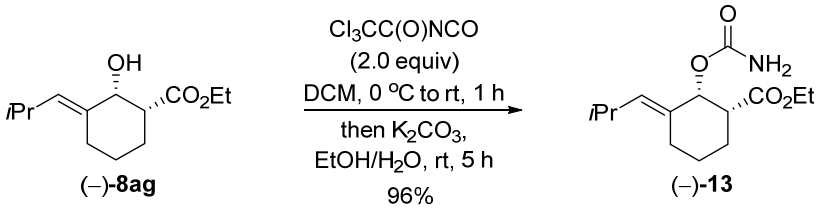
Asymmetric hydrogenation of 7ag on a gram-scale.



To a 200 mL hydrogenation vessel in an autoclave (250 mL) was added **7ag** (4.5 g, 20.0 mmol), a solution of iridium catalyst (*S*)-**6b** in EtOH (2.0 mg, 0.001 mmol/mL, 2.0 mL, 0.002 mmol, 0.001 mol%), a solution of KO*t*Bu in EtOH (2.2 mg, 0.01 mmol/mL, 2.0 mL, 0.02 mmol, 0.01 mol%), and EtOH (36 mL) under argon atmosphere. The autoclave was purged with hydrogen by pressurizing to 10 atm and releasing the pressure. This procedure was repeated three times and then pressurized to 30 atm of H_2. The reaction mixture was stirred at room temperature (25–30 °C) for 8 h. After releasing the hydrogen

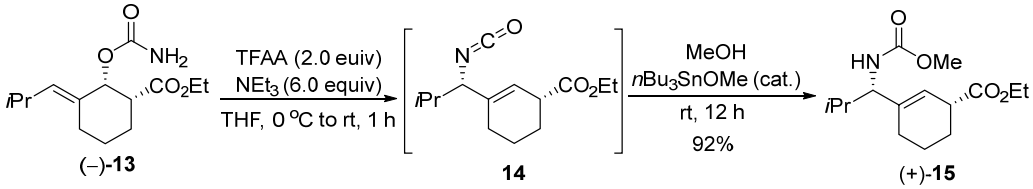
pressure, the reaction mixture was then quenched with saturated NH_4Cl (40 mL) and extracted with ethyl acetate (40 mL × 3). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silical gel with petroleum ether/ethyl acetate (10:1 to 5:1 v/v) as an eluent to afford the chiral alcohol (−)-**8ag** (4.4 g, 19.4 mmol, 98% ee) as colourless oil in 97% yield (R_f = 0.61, petroleum ether/ethyl acetate= 5:2 v/v) with 98% ee. $[\alpha]_D^{25}$ = –67.8 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (d, *J* = 9.0 Hz, 1H), 4.35 (d, *J* = 2.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.00 (s, 1H), 2.60–2.46 (m, 2H), 2.37–2.30 (m, 1H), 2.23−2.13 (m, 1H), 2.09–1.97 (m, 1H), 1.87−1.77 (m, 2H), 1.36−1.21 (m, 4H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.2, 135.9, 133.7, 74.1, 60.6, 48.6, 26.1, 26.0, 23.6, 23.5, 23.4, 23.0, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{22}O_3$+Na^+: 249.1467 $[M+Na]^+$; found: 249.1463. HPLC conditions: Chiralcel IC-3 column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 90:10; temp, rt; flow rate = 1.0 mL/min; 210 nm UV detector; t_R = 10.13 min (minor); t_R = 13.25 min (major).

Synthesis of enecarbamate (−)-**13.**[4]



To a solution of (−)-**8ag** (2.5 g, 11.0 mmol) in CH_2Cl_2 (60 ml) was added trichloroacetyl isocyanate (4.1 g, 22.0 mmol, 2.6 mL) over 10 min in a 250 mL, three-necked, round-bottomed flask with a thermometer at 0 °C under argon atmosphere. The reaction mixture was allowed to warm up to ambient temperature naturally during 1 h, then CH_2Cl_2 was evaporated. The resulting residue was dissolved in a mixture of EtOH/H_2O (100 mL, 1:1 v/v), and K_2CO_3 (9.2 g, 66.0 mmol) was added in one portion. After 5 h, EtOH was removed and the aqueous residue was extracted with CH_2Cl_2 (60 mL × 3). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silical gel with petroleum ether/ethyl acetate (5:1 v/v) as an eluent to afford (−)-**13** (2.8 g, 10.6 mmol) as white solid in 96% yield (R_f = 0.49, petroleum ether/ethyl acetate = 1:1 v/v). M.p. 123–124 °C. $[\alpha]_D^{25}$ = –98.2 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.48 (d, *J* = 2.9 Hz, 1H), 5.42 (d, *J* = 9.0 Hz, 1H), 4.81 (s, 2H), 4.28–3.93 (m, 2H), 2.65−2.47 (m, 2H), 2.47−2.33 (m, 1H), 2.03–1.82 (m, 4H), 1.36−1.17 (m, 4H), 1.02−0.83 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 155.9, 136.4, 132.5, 76.7, 60.5, 47.8, 26.2, 25.4, 23.9, 23.2, 23.0, 22.7, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{23}NO_4$+Na^+: 292.1525 $[M+Na]^+$; found: 292.1522.

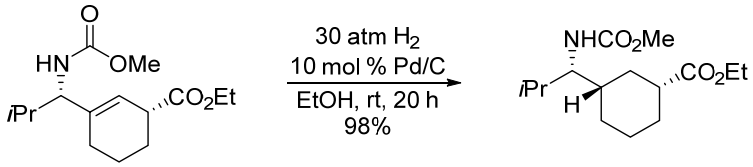
Synthesis of compound (+)-15.[5]



To a solution of (−)-**13** (862 mg, 3.2 mmol) and Et_3N (1.9 g, 19.2 mmol, 2.7 mL) in dry THF (20 mL)

cooled to 0 °C was added TFAA (1.3 g, 6.4 mmol, 0.9 mL) in a 100 mL, three-necked, round-bottomed flask with a thermometer, and the resulting mixture was warmed to room temperature naturally. After 1 h, dry MeOH (5 mL) and *n*Bu_3SnOMe (103 mg, 0.3 mmol, 92 μL) were added, and the reaction mixture was stirred overnight. After the removal of the solvents, the residue was purified by flash column chromatography on silical gel with petroleum ether/ethyl acetate (5:1 v/v) as an eluent to afford (+)-**15** (834 mg, 2.9 mmol) as white solid in 92% yield (R_f = 0.37, petroleum ether/ethyl acetate = 5:2 v/v). M.p. 73–74 °C. $[\alpha]_D^{25}$ = +1.0 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.61 (s, 1H), 4.77 (d, *J* = 9.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.94–3.77 (m, 1H), 3.67 (s, 3H), 3.15–3.06 (m, 1H), 1.99–1.69 (m, 6H), 1.64−1.52 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.5, 156.7, 139.4, 119.5, 61.5, 60.5, 52.1, 41.4, 29.8, 26.0, 25.2, 21.2, 20.1, 17.0, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{25}NO_4$+Na^+: 306.1681 $[M+Na]^+$; Found: 306.1676.

Synthesis of carbocyclic δ-amino acid ester (−)-16.

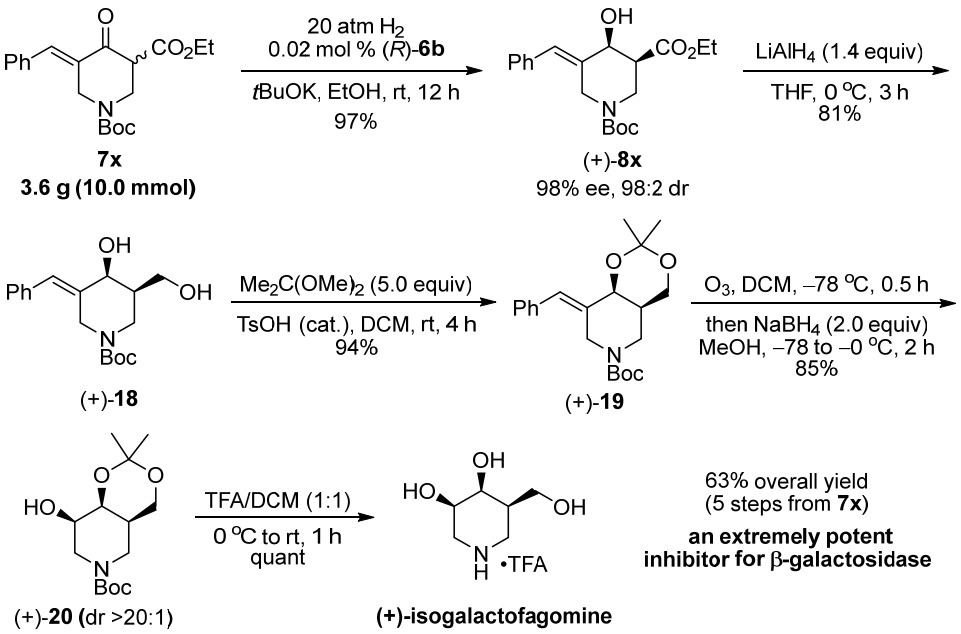


(+)-**15** (–)-**16** (dr = 6:1)

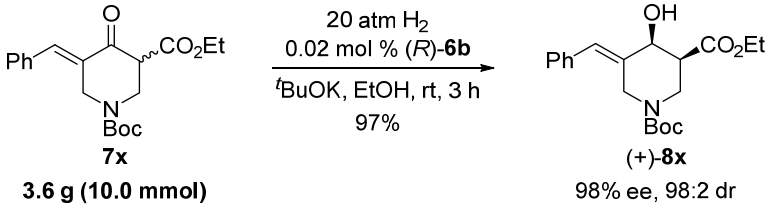
To a 40 mL hydrogenation vessel in an autoclave (50 mL) was added a solution of (+)-**15** (142 mg, 0.5 mmol) in MeOH (6 mL) and 10% Pd/C (53 mg, 0.05 mmol). The autoclave was purged with hydrogen by pressurizing to 10 atm and releasing the pressure. This procedure was repeated three times and then pressurized to 30 atm of H_2. The reaction mixture was stirred at room temperature for 20 h. After releasing the hydrogen pressure, the catalyst was removed by filtration through a pad of Celite, which was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by a column chromatography on a silica gel with petroleum ether/ethyl acetate (20:1 to 10:1 v/v) as an eluent to give (−)-**16** (140 mg, 0.49 mmol) as colourless oil (R_f = 0.39, petroleum ether/ethyl acetate = 5:2 v/v) in 99% yield. dr = 6:1 (determined by ^{1}H NMR). $[\alpha]_D^{25}$ = −12.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.45 (d, *J* = 10.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 3.38−3.22 (m, 1H), 2.34−2.22 (m, 1H), 2.00–1.80 (m, 4H), 1.79–1.69 (m, 2H), 1.52−1.39 (m, 1H), 1.37–1.16 (m, 6H), 0.99–0.87 (m, 4H), 0.84 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.7, 157.4, 60.6, 60.2, 52.0, 43.4, 39.1, 32.6, 28.9, 28.7, 27.2, 25.1, 20.1, 17.1, 14.2. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{27}NO_4$+H^+: 286.2018 $[M+H]^+$; Found: 286.2018.

(D) Enantioselective Synthesis of (+)-Isogalactofagomine

The route for enantioselective synthesis of (+)-isogalactofagomine is outlined below.

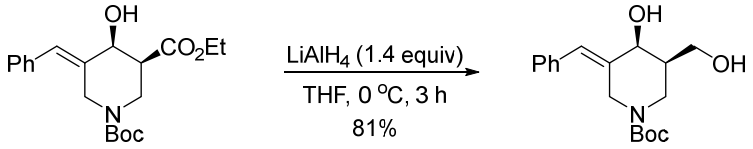


Asymmetric hydrogenation of 7x on a gram-scale.



To a 200 mL hydrogenation vessel in an autoclave (250 mL) was added **7x** (3.6 g, 10.0 mmol), a solution of iridium catalyst (*R*)-**6b** in EtOH (2.0 mg, 0.0025 mmol/mL, 2.0 mL, 0.002 mmol, 0.002 mol%), a solution of KO*t*Bu in EtOH (2.3 mg, 0.025 mmol/mL, 2.0 mL, 0.02 mmol, 0.02 mol%), and EtOH (36 mL) under argon atmosphere. The autoclave was purged with hydrogen by pressurizing to 10 atm and releasing the pressure. This procedure was repeated three times and then pressurized to 20 atm of H_2. The reaction mixture was stirred at room temperature (25–30 °C) for 4 h. After releasing the hydrogen pressure, the reaction mixture was then quenched with saturated NH_4Cl (40 mL) and extracted with ethyl acetate (40 mL × 3). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silical gel with ether petroleum/ethyl acetate (6:1 v/v) as an eluent to afford the chiral alcohols (+)-**8x** (3.5 g, 9.8 mmol, 98% ee) as colourless oil in 97% yield (R_f = 0.32, ether petroleum/ethyl acetate = 5:2 v/v). $[\alpha]_D^{25}$ = +46.4 (*c* = 1.0 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45−7.31 (m, 3H), 7.30−7.16 (m, 3H), 6.62 (s, 1H), 4.76 (d, *J* = 14.5 Hz, 1H), 4.69 (d, *J* = 2.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.88 (d, *J* = 14.5 Hz, 1H), 3.57 (s, 1H), 2.90−2.74 (m, 1H), 1.57−1.18 (m, 13H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0, 154.3, 135.7, 135.3, 128.7, 128.2, 127.6, 127.2, 79.9, 72.3, 61.0, 47.3, 41.4, 40.2, 28.0, 14.0. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{27}NO_5$+H^+: 362.1967 $[M+H]^+$; found: 362.1959. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 92:8; temp, rt; flow rate = 1.0 mL/min; 254 nm UV detector; t_R = 8.95 min (minor); t_R = 10.56 min (major).

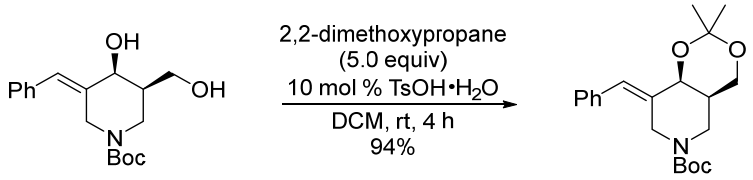
Synthesis of compound (+)-18.



(+)-**8x** (+)-**18**

To a solution of (+)-**8x** (1.4 g, 4.0 mmol) in THF (20 ml) was added $LiAlH_4$ (1.0 M in THF, 5.6 mmol, 5.6 mL) in a 100 mL, three-necked, round-bottomed flask with a thermometer over 10 min at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 3 h. The solution was quenched with saturated aqueous potassium sodium tartrate (20 mL) at 0 °C. The mixture was extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by a column chromatography on a silica gel with ether petroleum/ethyl acetate (2:1 to 1:1 v/v) as an eluent to give (+)-**18** (1.0 g, 3.2 mmol) as colourless oil (R_f = 0.35, ether petroleum/ethyl acetate = 3:1 v/v) in 81% yield. $[\alpha]_D^{25}$ = +2.8 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37−7.29 (m, 2H), 7.28−7.17 (m, 3H), 6.61 (s, 1H), 4.54 (s, 1H), 4.25 (m, 2H), 3.88–3.41 (m, 6H), 2.11 (br s, 1H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.2, 136.4, 136.2, 128.8, 128.2, 127.0, 125.6, 80.0, 74.3, 61.7, 43.5, 42.8, 42.0, 28.0. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{25}NO_4$+Na^+: 342.1681 $[M+Na]^+$; found: 342.1675.

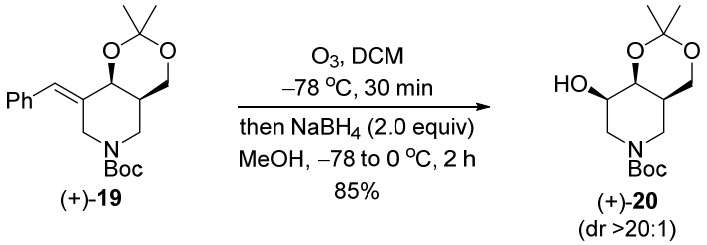
Synthesis of compound (+)-19.



(+)-**18** (+)-**19**

To a solution of (+)-**18** (639 mg, 2.0 mmol) and $TsOH·H_2O$ (38 mg, 0.2 mmol) in dry CH_2Cl_2 (10 mL) was added 2,2-dimethoxypropane (1.0 g, 10.0 mmol, 1.2 mL) dropwise over 5 min in a 25 mL Schlenk tube. The reaction mixture was stirred at room temperature for 4 h. The solution was quenched with saturated aqueous $NaHCO_3$ (10 mL) at 0 °C. The mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by a column chromatography on a silica gel with ether petroleum/ethyl acetate (10:1 to 5:1 v/v) as an eluent to give (+)-**19** (676 mg, 1.9 mmol) as white solid (R_f = 0.69, ether petroleum/ethyl acetate = 3:1 v/v) in 94% yield. M. p. 49−50 °C. $[\alpha]_D^{25}$ = +28.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36−7.31 (m, 2H), 7.30–7.20 (m, 3H), 6.59 (s, 1H), 5.04−4.87 (m, 1H), 4.55 (d, *J* = 2.6 Hz, 1H), 4.21−4.12 (m, 1H), 4.03−3.92 (m, 1H), 3.67−3.49 (m, 3H), 1.78–1.69 (br s, 1H), 1.56 (s, 3H), 1.47 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.6, 135.7, 134.6, 128.9, 128.3, 128.1, 127.2, 98.7, 79.4, 73.2, 62.0, 41.4, 35.7, 29.6, 28.3, 28.0, 18.9. HRMS (ESI): *m*/*z* calcd for $C_{21}H_{29}NO_4$+Na^+: 382.1994 $[M+Na]^+$; found: 382.1990.

Synthesis of compound (+)-20.



To a 25 mL Schlenk tube was added a solution of (+)-**19** (360 mg, 1.0 mmol) in dry CH_2Cl_2 (8 mL), and the mixture was cooled to −78 °C while ozone was passed through the solution via a gas dispersion tube until the solution became blue in color (in 20–30 seconds). The reaction mixture was stirred at −78 °C for 30 min, and then argon was passed through the solution at −78 °C for 15 min. Then MeOH (2 mL) and $NaBH_4$ (76 mg, 2.0 mmol) were added, and the reaction mixture was allowed to warm up to 0 °C over a period of 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by a column chromatography on a silica gel with ether petroleum/ethyl acetate (5:2 to 1:1 v/v) as an eluent to give (+)-**20** (244 mg, 0.85 mmol) as white solid in 85% yield (R_f = 0.45, ether petroleum/ethyl acetate = 1:1 v/v). M. p. 60−61 °C. $[\alpha]_D^{25}$ = +4.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27 (s, 1H), 4.18–3.72 (m, 3H), 3.70–3.44 (m, 2H), 3.22 (br s, 1H), 2.82 (br s, 1H), 2.40 (br s, 1H), 1.49 (s, 3H), 1.46 (s, 9H), 1.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.9, 99.2, 79.9, 67.9, 67.3, 61.7, 45.0, 40.2, 33.6, 29.5, 28.4, 18.8. HRMS (ESI): *m*/*z* calcd for $C_{14}H_{25}NO_5$+Na^+: 310.1630 $[M+Na]^+$; found: 310.1627.

Synthesis of (+)-isogalactofagomine.

To a solution of (+)-**20** (86 mg, 0.3 mmol) in CH_2Cl_2 (3 mL) was added TFA (3 mL) in a 25 mL Schlenk tube at 0 °C. The reaction mixture was allowed to warm up to room temperature over 1 h, and then concentrated in vacuo to provide (+)-isogalactofagomine (74 mg, quant, pale yellow oil) as a TFA salt (R_f = 0.29, MeOH/NH_4OH (25%) = 1:5 v/v). $[\alpha]_D^{25}$ = +2.6 (*c* = 1.0, H_2O) [lit.[6] $[\alpha]_D^{22}$ = +2.5 (c = 1.0, H_2O)]. ^{1}H NMR (400 MHz, D_2O): δ = 4.15 (br s, 1H), 4.02−3.92 (ddd, *J* = 11.5, 5.0, 2.7 Hz, 1H), 3.74 (dd, *J* = 11.3, 6.6 Hz, 1H), 3.63 (dd, *J* = 11.3, 7.3 Hz, 1H), 3.36−3.22 (m, 2H), 3.09 (t, *J* = 11.8 Hz, 1H), 2.95 (t, *J* = 12.7 Hz, 1H), 2.20−2.07 (m, 1H). ^{13}C NMR (101 MHz, D_2O): δ = 68.7, 68.5, 62.7, 44.8, 42.4, 41.9. HRMS (ESI): *m*/*z* calcd for $C_6H_{13}NO_3$+H^+: 148.0974 $[M+H]^+$; found: 148.0970. The characterization data were consistent with those reported. [6]

(E) Computational Studies.

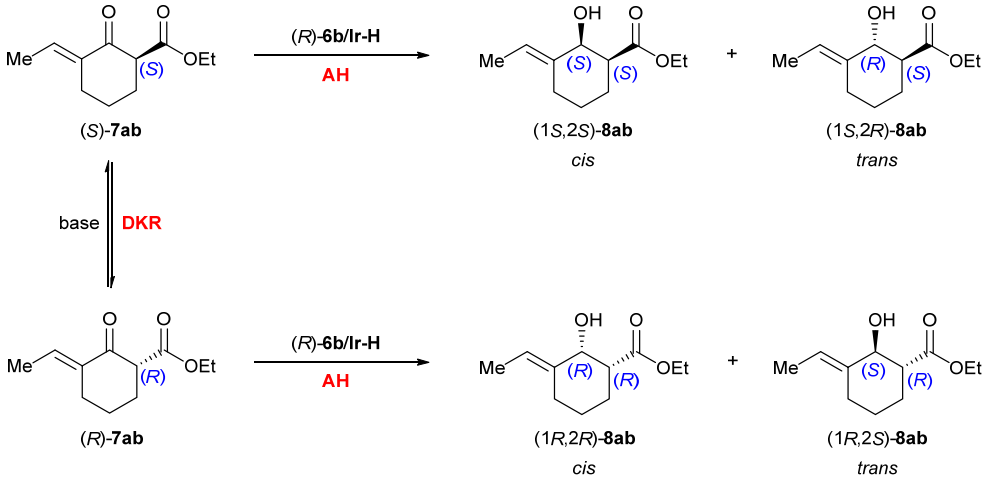
1. Density functional theory (DFT) Details.

All DFT calculations have been carried out using the Gaussian 16-RevA.03 quantum program package.[7]

The B3LYP[8] functional with Def2-SVP[9] basis set has been selected for geometry optimizations and calculation of Gibbs energy corrections at 298 K, including the GD3BJ[10] dispersion correction scheme developed by Grimme[11]. Final energies were retrieved from single-point calculations at the B3LYP/Def2-TZVPP[12] level, including the GD3BJ dispersion correction scheme developed by Grimme. Intrinsic reaction coordinate (IRC)[13] calculations were done to confirm that the transition states proposed connected the appropriate reactants and products. All structures have been optimized considering solvent effects using the SMD[14] Model for MeOH. All energetics reported throughout the text are in kcal/mol. Transition states were optimized starting from the X-ray crystal structure of the Ir-catalyst (*R*)-**6b**[15]. The independent gradient model (IGM) analysis[16] was performed by Multiwfn program (Version 3.8)[17] to visualize the non-covalent interactions (NCIs). Graphical structures were visualized with CYLview (Version 1.0b)[18] and VMD (Version 1.9.3)[19].

2. DFT Structures

The proposed mechanism for the iridium catalyzed asymmetric hydrogenation (AH) of exocyclic γ,δ-unsaturated β-ketoesters was shown in **Scheme S1**. Owing to the effective chiral recognition of the catalyst, i.e., the iridium-hydride (Ir-H) generated *in situ* from Ir-complex (*R*)-**6b**, one enantiomer of the racemic exocyclic γ,δ-unsaturated β-ketoester [e.g., (*S*)-**7ab**] would undergo a preferential reduction by the Ir-H species, thus leading to a faster hydrogenation than the other under the reaction conditions. Meanwhile, the residual enantioenriched exocyclic γ,δ-unsaturated β-ketoester undergoes rapid racemization by base-catalyzed enol-keto tautomerization, eventually generating two contiguous chiral centers by asymmetric hydrogenation via a dynamic kinetic resolution (DKR) process.



Scheme S1 Asymmetric hydrogenation of exocyclic γ,δ-unsaturated β-ketoesters via dynamic kinetic resolution.

Both diastereo- and enantioselectivity were rationalized by DFT calculations on the stereo-determining hydride/proton transfer step, assuming a Noyori bifunctional mechanism in which the keto carbonyl of the substrate forms a hydrogen bond to the N−H group of the ligand, via a six-membered cyclic transition state.[20] For the (*R*)-**6b** catalyzed asymmetric hydrogenation, the chiral Ir-H intermediate can be generated in situ from the reaction mixture. Since Ir-H may act as an effective reductant for the *Si*- or *Re*-attack on either of the exocyclic γ,δ-unsaturated β-ketoesters [(*S*)-**7ab** and (*R*)-**7ab**], four initial guessed structures of transition states need to be considered for the stereochemistry of the hydride/proton transfer step (**Figure S1**).

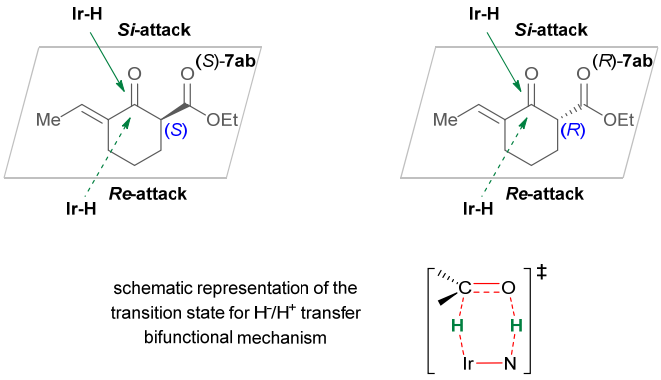


Figure S1 *Si*- or *Re*-attack of the Ir-H species onto the ketocarbonyl of (*S*)- or (*R*)-exocyclic γ,δ-unsaturated β-ketoester **7ab**.

According to the bifunctional mechanism depicted in **Figure S1**, different spatial arrangements can exist for the reaction of Ir-H and the exocyclic γ,δ-unsaturated β-ketoester [two conformers each for (*S*)-**7ab** or (*R*)-**7ab**, *Re*- or *Si*-attack] for the H^-/H^+ transfer step. Although this can in principle lead to a number of distinct initially guessed transition state (**TS**) structures, some of them can safely be excluded due to the severe steric clashes between the substrate and the catalyst. For the reaction of Ir-H with **7ab**, four **TS** structures [**TS-*SS***, **TS-*SR***, **TS-*RR***, and **TS-*RS***] were found to be energetically viable, which would lead to stereoisomeric products (1*S*,2*S*)-, (1*S*,2*R*)-, (1*R*,2*R*)-, and (1*R*,2*S*)-**8ab**, respectively. These identified **TS** structures were and collectively shown in **Figure S2**. Remarkably, a comparison of the relative heights in free energy barriers for these **TS**s indicated that the hydride/proton transfer step was dominated by the reactivity of Ir-H.

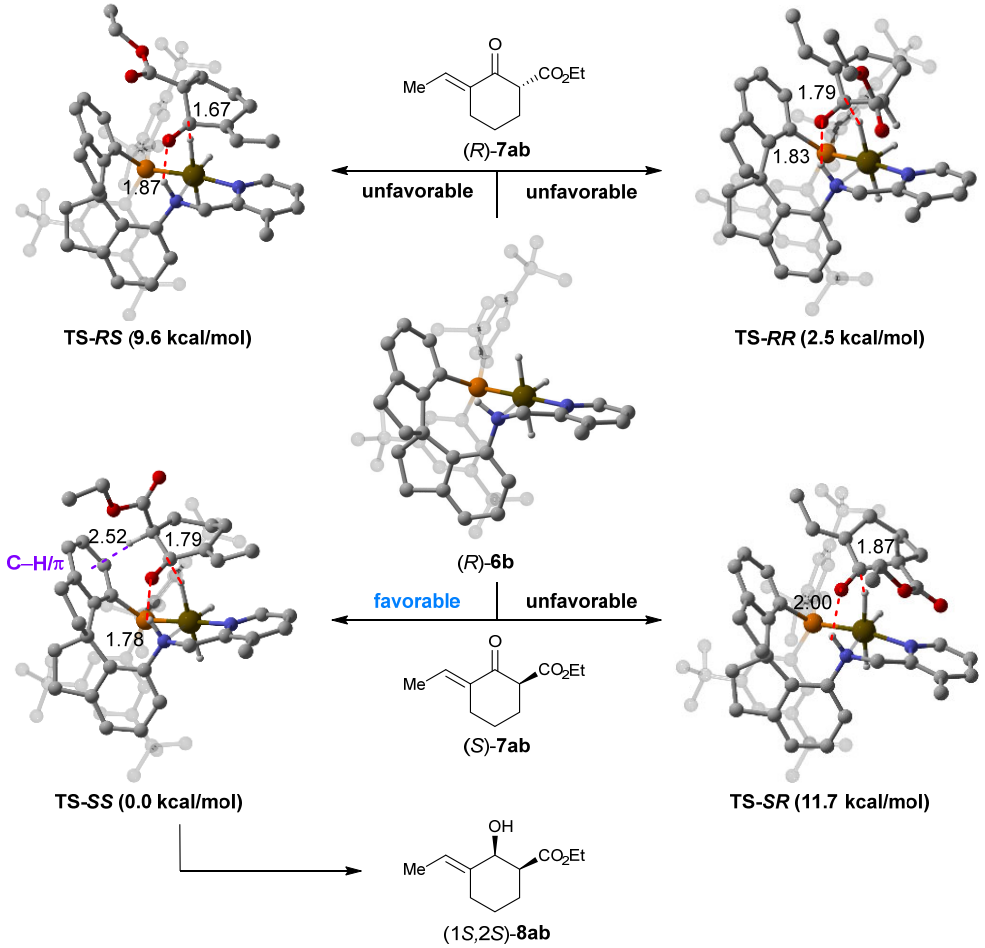


Figure S2 The transition state structures for the H^-/H^+ transfer to the exocyclic γ,δ-unsaturated β-ketoester **7ab**

For this multiple transition states reaction, the Boltzmann analysis of the four competing TS structures were summarized in **Table S3**. A calculation of the ee and dr values, based on the Boltzmann distribution for each TS structure, indicated that **TS-*SS*** is the most important single TS, leading to formation of (1*S*,2*S*)-**8ab** as the major product with a calculated >99:1 dr (*cis*/*trans*) and 97.3% ee, which are in agreement with the experimental results (>99:1 *cis*/*trans*, 95.0% ee).

Table S3 DFT-calculated Boltzmann distribution of the TS structures for (*R*)-**6b** catalyzed hydride/proton transfer to **7ab**[a]

Transition States	Free energy in solution (a.u.)	relative G (kcal/mol)	Boltzmann weights
TS-*SS*	-3232.65148186	0.0000000	0.98656559
TS-*SR*	-3232.63281451	11.71376212	0.00000000
TS-*RR*	-3232.64742785	2.543891275	0.01343432
TS-*RS*	-3232.63615853	9.61538958	0.00000009
		Total	1.0000000
		dr (*cis*/*trans*)[b]	>99:1
		ee (%)[c]	97.3

[a] DFT-calculated transition states for the stereoselectivity-determining hydride/proton transfer to **7ab**. [b] Diastereomeric ratio (dr) = *cis*/*trans* = [**TS-*SS*** + **TS-*RR***]/[**TS-*SR*** + **TS-*RS***]. [c] Enantiomeric excess (%) of the (1*S*,2*S*)-**8ab** = [**TS-*SS*** − **TS-*RR***]/[**TS-*SS*** + **TS-*RR***].

3. Rationalization of the diastereo- and enantioselectivities

From these calculation results, it is clear that stereochemical outcomes of the reaction are dominated by the distinct reactivity of Ir-H towards (*S*)- and (*R*)-**7ab**, as a result of effective chiral discrimination in the assembly of the TS structures. To rationalize the diastereo- and enantioselectivities of the reaction, a comparative study was performed on **TS-*SS***, **TS-*SR***, **TS-*RR*** and **TS-*RS***, based on the analysis of NCIs with IGM method in each of these TS structures. IGM analysis in these TS structures were studied using the Multiwfn program, and were visualized by VMD program. Only intermolecular NCIs between Ir-H and **7ab** were displayed graphically as colored isosurfaces, with color codes indicating qualitatively the nature and strength of NCIs (strongly attractive, blue; weak, green; strongly repulsive, red).

The most favorable transition state leading to the (1*S*,2*S*)-**8ab**, **TS-*SS***, features a very strong Ir-H···C interaction in the region of the forming C−H bond, a N–H···O H-bond between the ligand and **7ab**, a significant C−H/π interactions between α-C−H bond of ester group and the ligand benzene ring (2.52 Å), as well as several sites of less prominent van der Waals interactions between the C(sp^3)−H atoms of the exocyclic γ,δ-unsaturated β-ketoester **7ab** and the ligand (**Figure S3**). These attractive interactions work together to stabilize the TS structure.

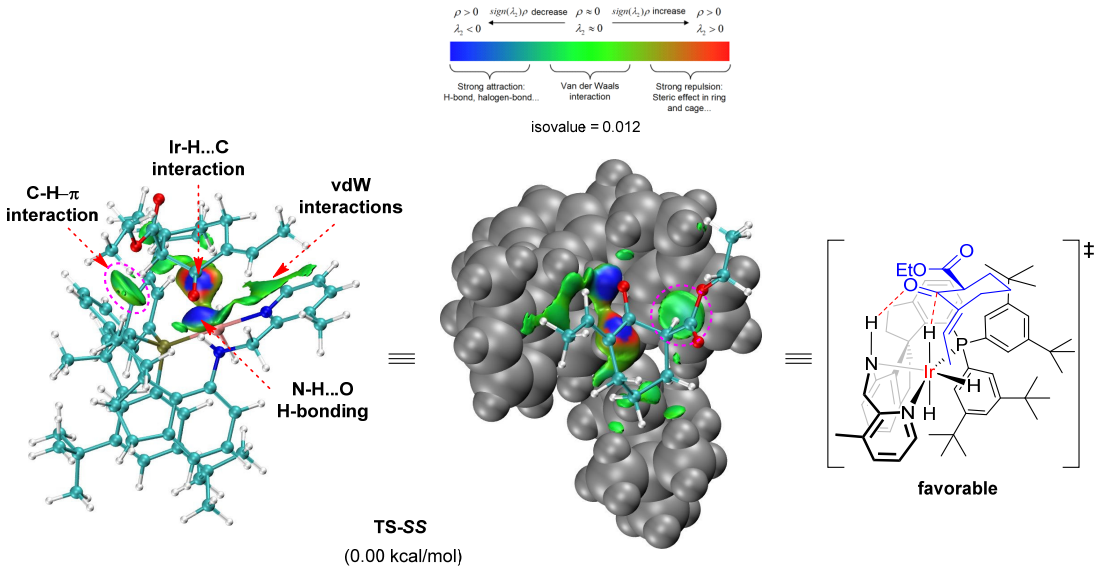


Figure S3 Intermolecular NCIs in **TS-*SS*** as visualized by VMD

IGM analysis of **TS-*SR***, the transition state leading to the (1*S*,2*R*)-**8ab**, also revealed the presence of very strong Ir-H···C interaction and a N–H···O H-bond, along with several sites of relatively weak van der Waals interactions in regions between substrate (*S*)-**7ab** and the Ir-H catalyst (**Figure S4**). The most striking difference from that of **TS-*SS***, is that no attractive C−H/π interactions between α-C−H bond of ester group and the ligand benzene ring of the substrate **7ab** can be found in **TS-*SS***.

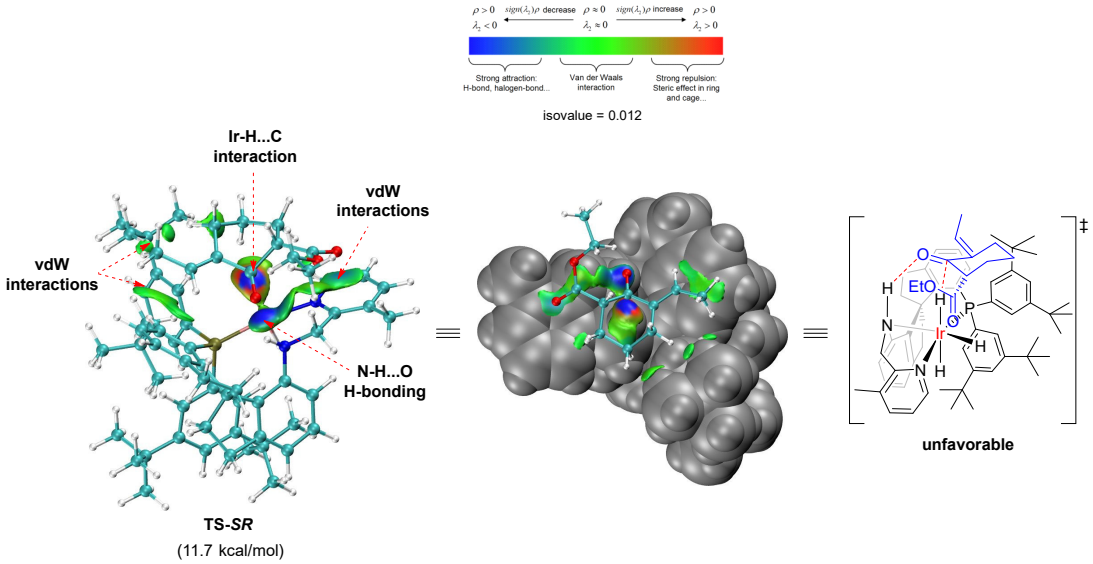


Figure S4 Intermolecular NCIs in **TS-*SR*** as visualized by VMD

IGM analysis of **TS-*RR***, the transition state leading to the (1*R*,2*R*)-**8ab**, also revealed the presence of very strong Ir-H···C interaction and a N–H···O H-bond, along with several sites of relatively weak van der Waals interactions in regions between substrate (*R*)-**7ab** and the Ir-H catalyst (**Figure S5**). The most striking difference from that of **TS-*SS***, is that no attractive C−H/π interactions between α-C−H bond of ester group and the ligand benzene ring of the substrate **7ab** can be found in **TS-*SS***.

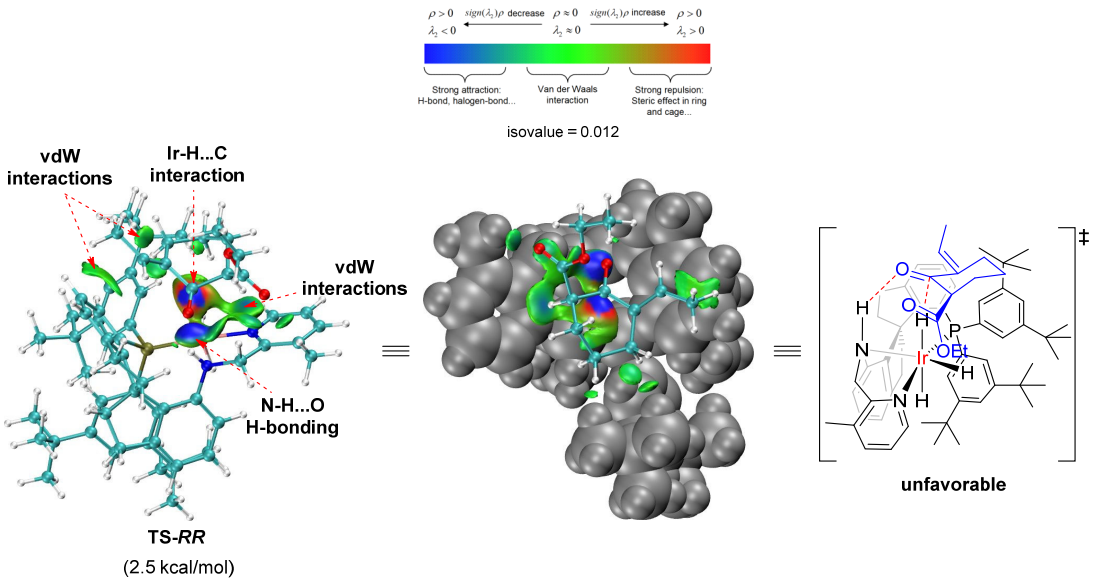


Figure S5 Intermolecular NCIs in **TS-*RR*** as visualized by VMD

IGM analysis of **TS-*RS***, the transition state leading to the (1*R*,2*S*)-**8ab**, also revealed the presence of very strong Ir-H···C interaction and a N–H···O H-bond, along with several sites of relatively weak van der Waals interactions in regions between substrate (*R*)-**7ab** and the Ir-H catalyst (**Figure S6**). The most striking difference from that of **TS-*SS***, is that no attractive C−H/π interactions between α-C−H bond of ester group and the ligand benzene ring of the substrate **7ab** can be found in **TS-*SS***.

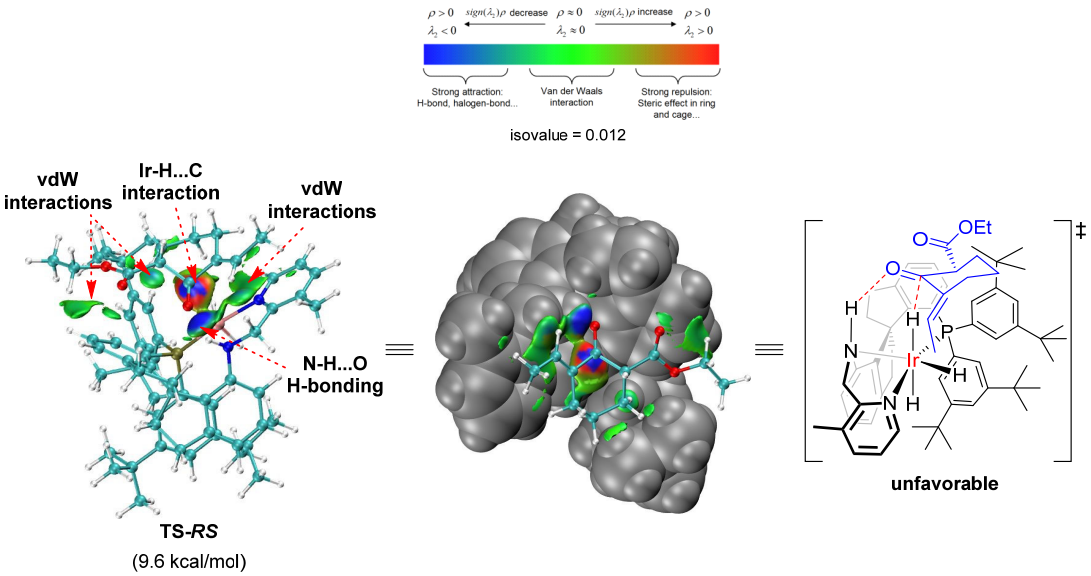


Figure S6 Intermolecular NCIs in **TS-*RS*** as visualized by VMD

4. Energy summary

Table S4. Energy summary[a]

TS	Opt freq b3lyp-GD3BJ/def2svp		SP b3lyp-GD3BJ/def2tzvpp scrf (SMD-MeOH)		
	H_{corr}	G_{corr}	E(b3lyp)	Enthalpy (total)	Gibbs (total)
TS-*SS*	1.40049900	1.22322300	-3233.87470486	-3232.47420586	-3232.65148186
TS-*SR*	1.40036500	1.22383800	-3233.85665251	-3232.45628751	-3232.63281451
TS-*RR*	1.40069200	1.22289100	-3233.87031885	-3232.46962685	-3232.64742785
TS-*RS*	1.39984800	1.22302900	-3233.85918753	-3232.45933953	-3232.63615853

[a] H_{corr} = Thermal correction to Enthalpy; G_{corr} = Thermal correction to Gibbs Free Energy; Gibbs (total) = E(b3lyp) + G_{corr}; Enthalpy (total) = E(b3lyp) + H_{corr}

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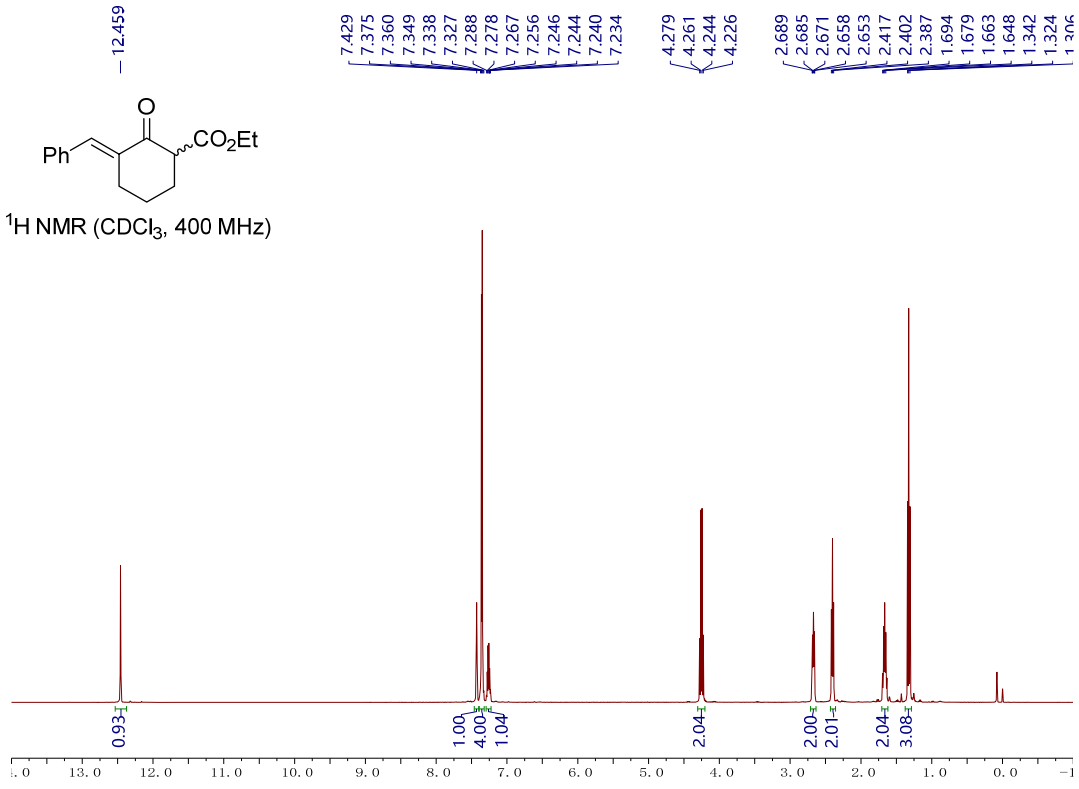
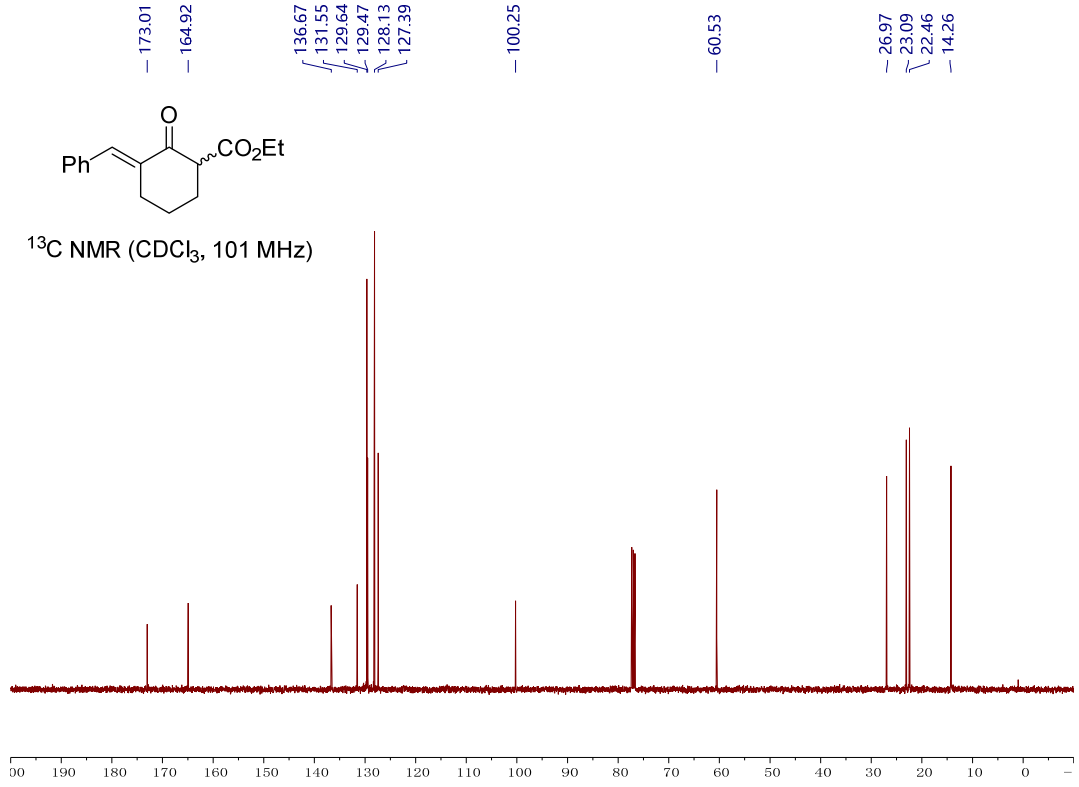
(F) NMR Spectra for New Compounds

Ethyl (*E*)-3-benzylidene-2-oxocyclohexane-1-carboxylate (7a)





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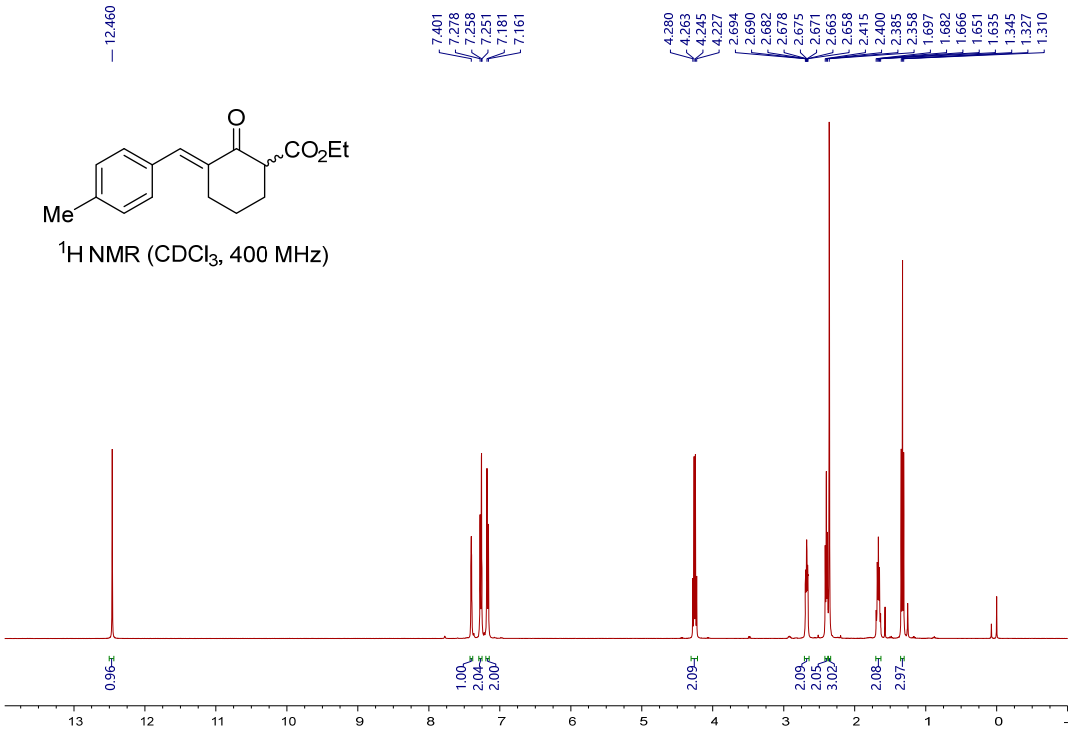

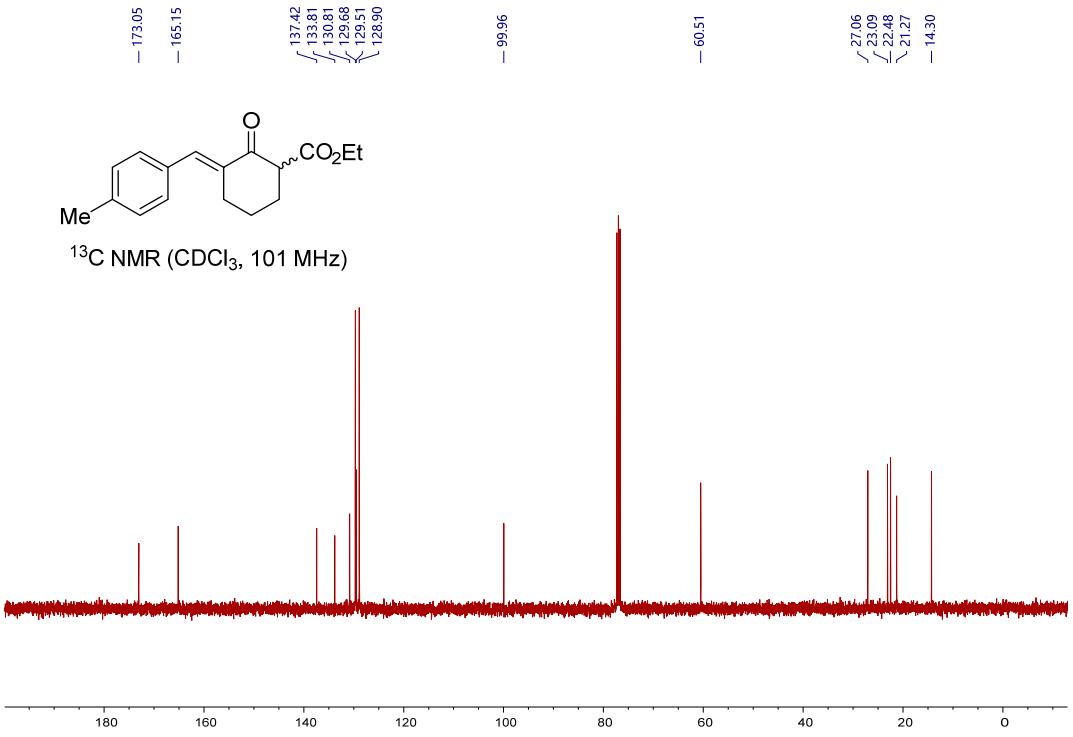

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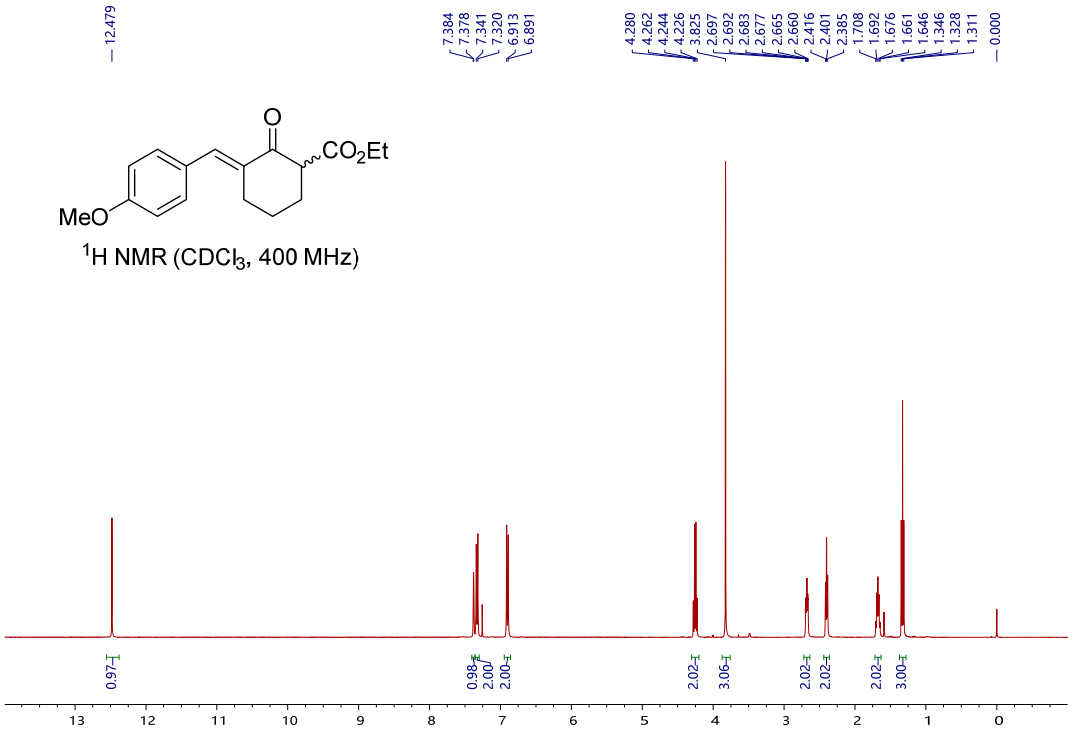

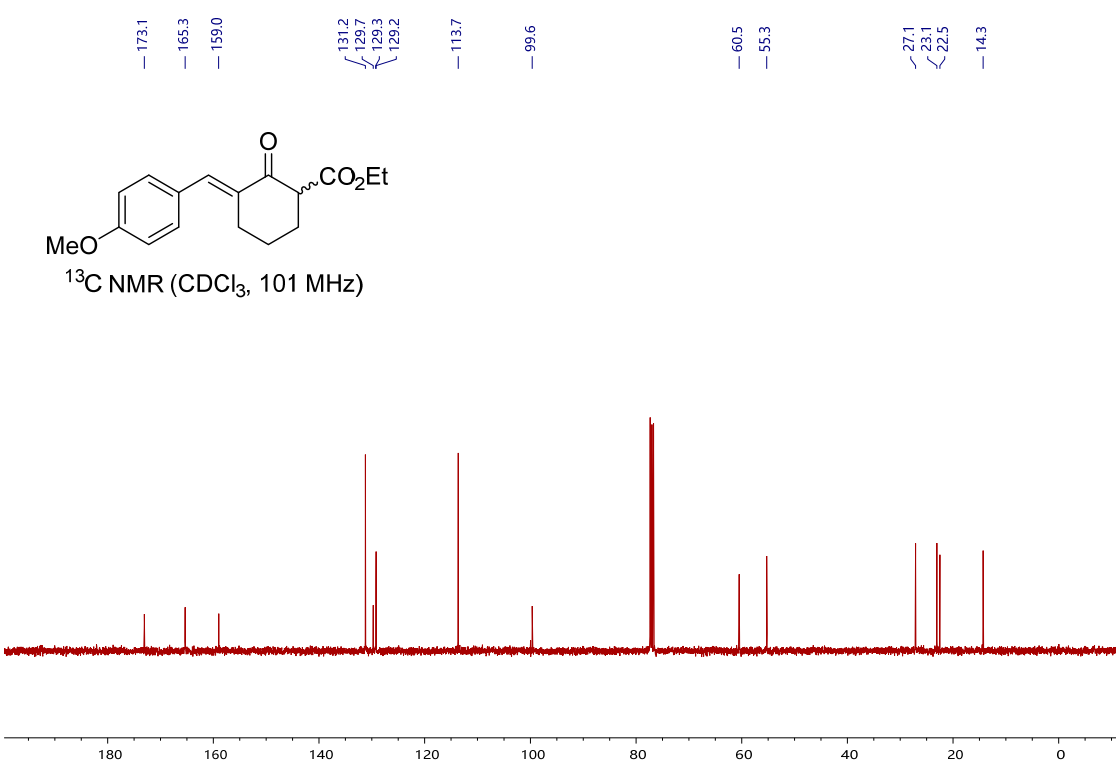

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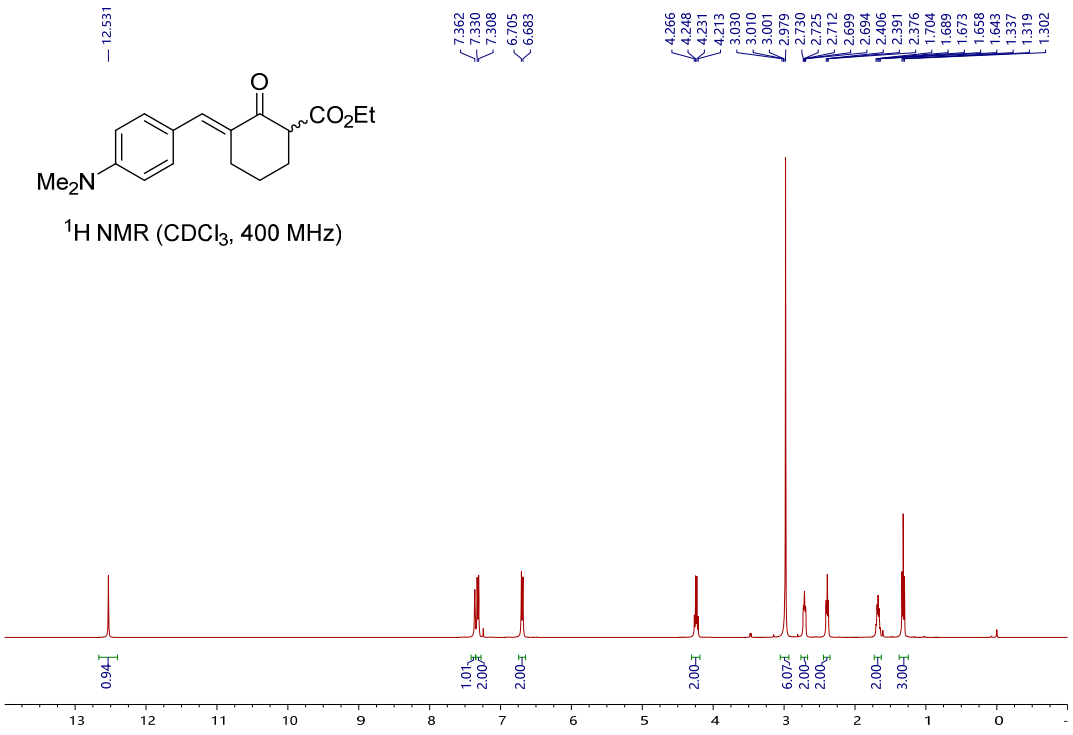

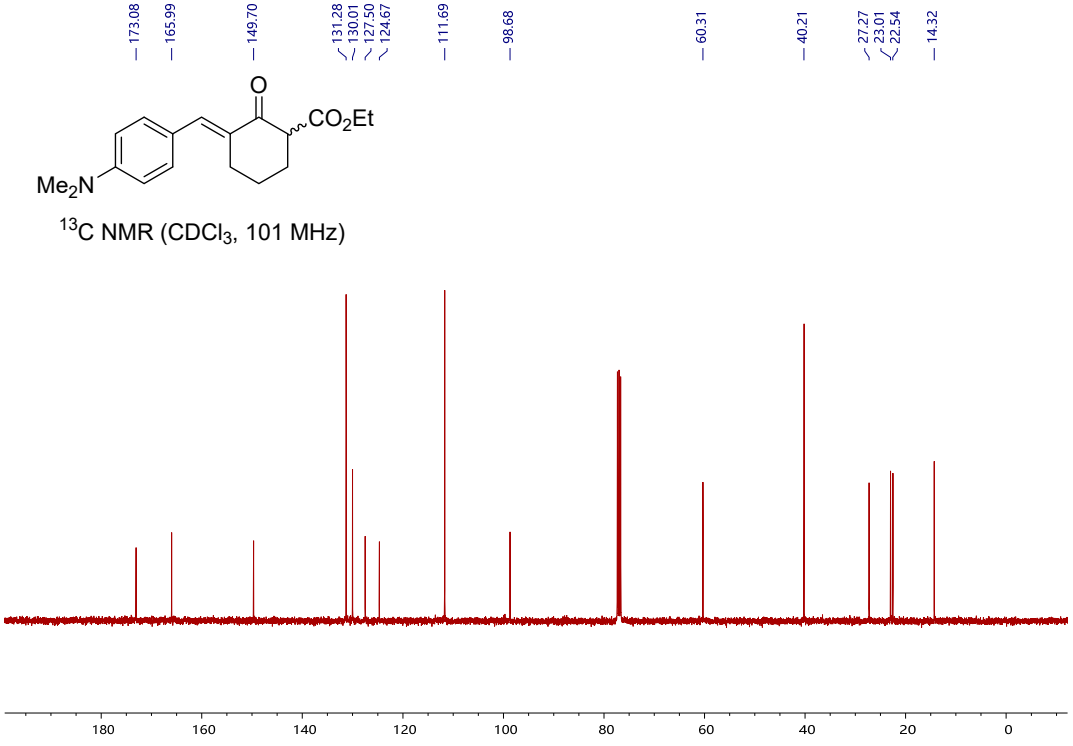

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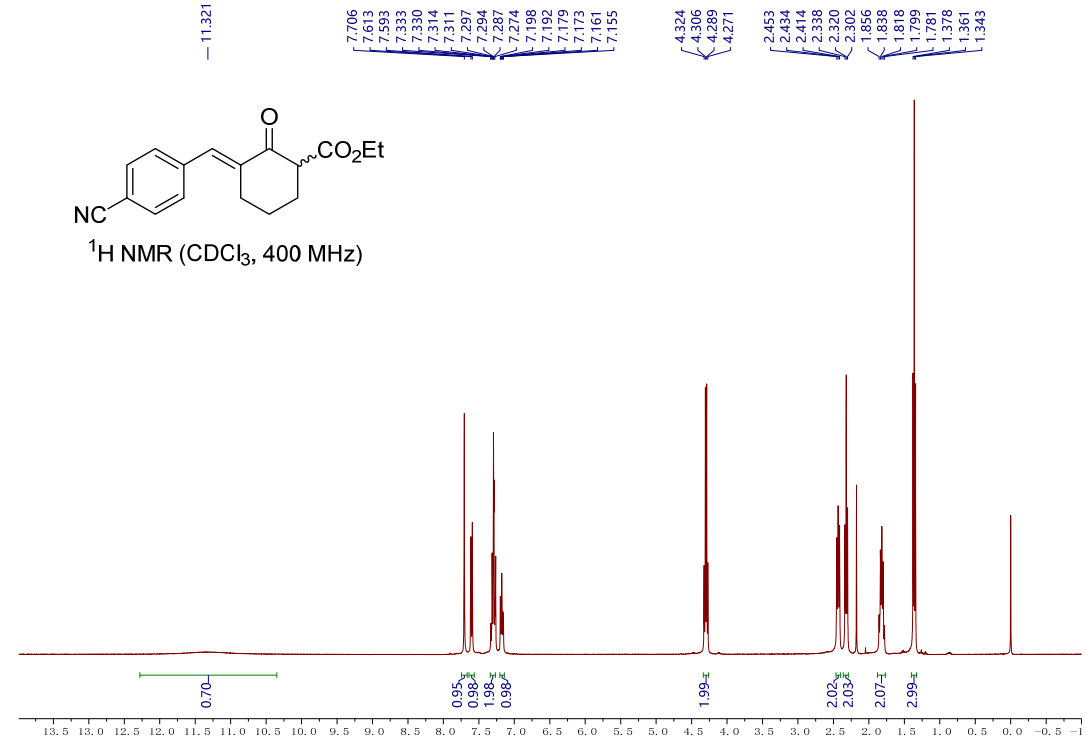

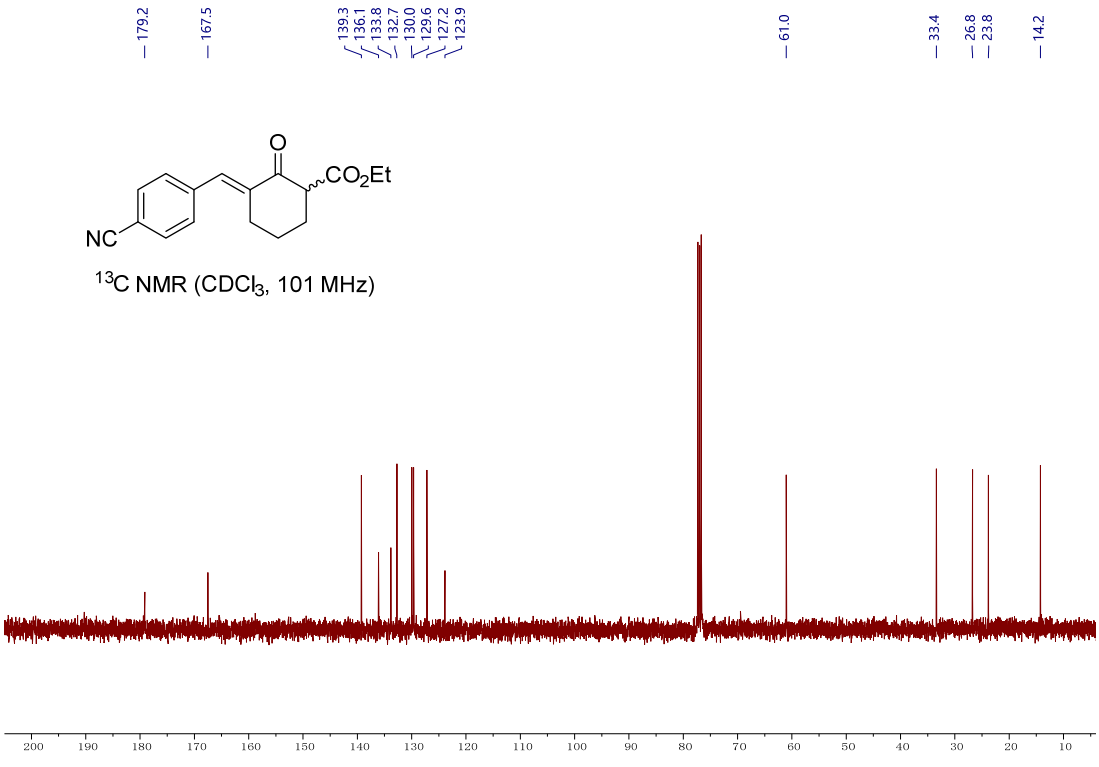

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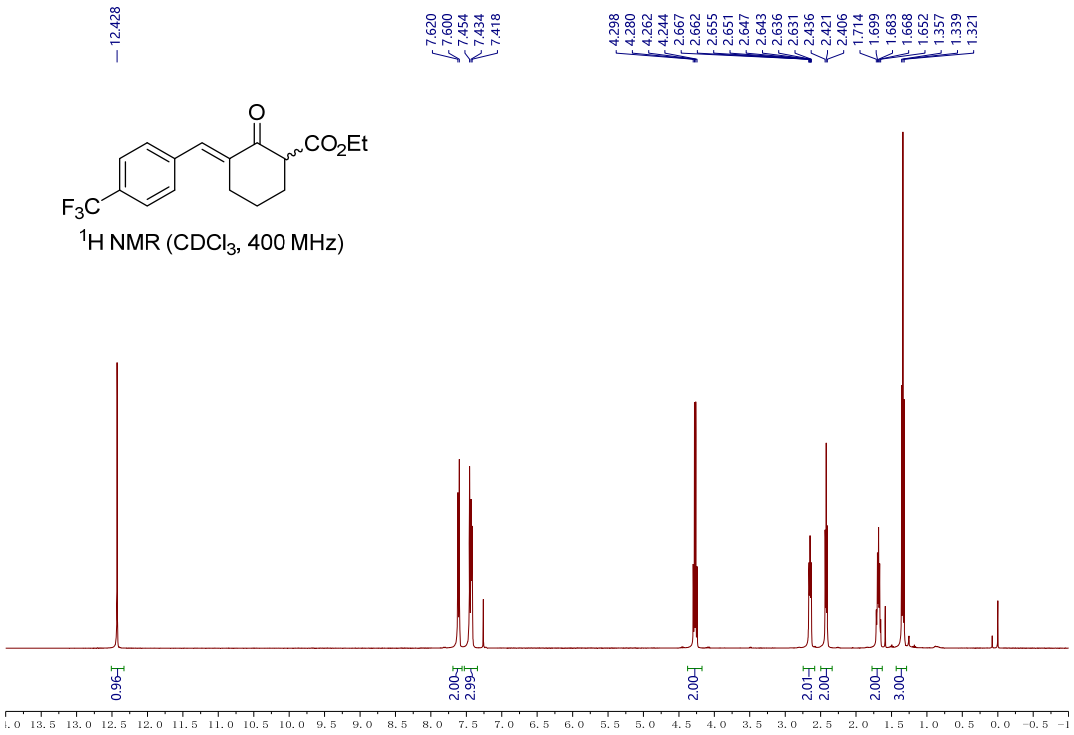

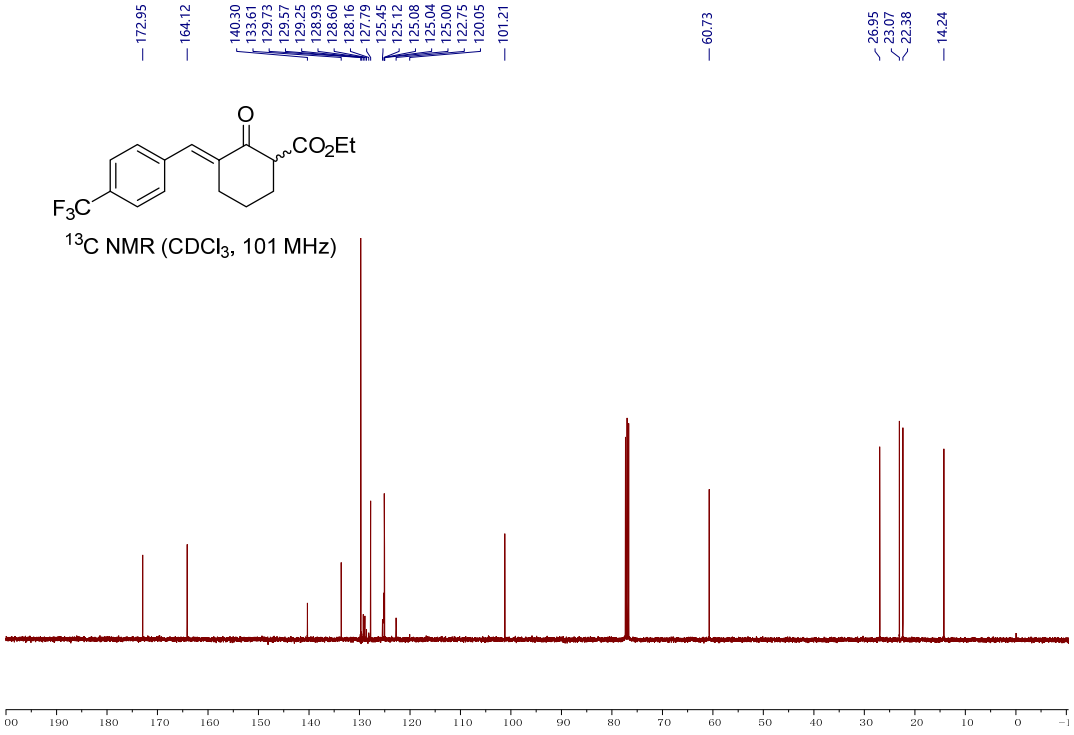

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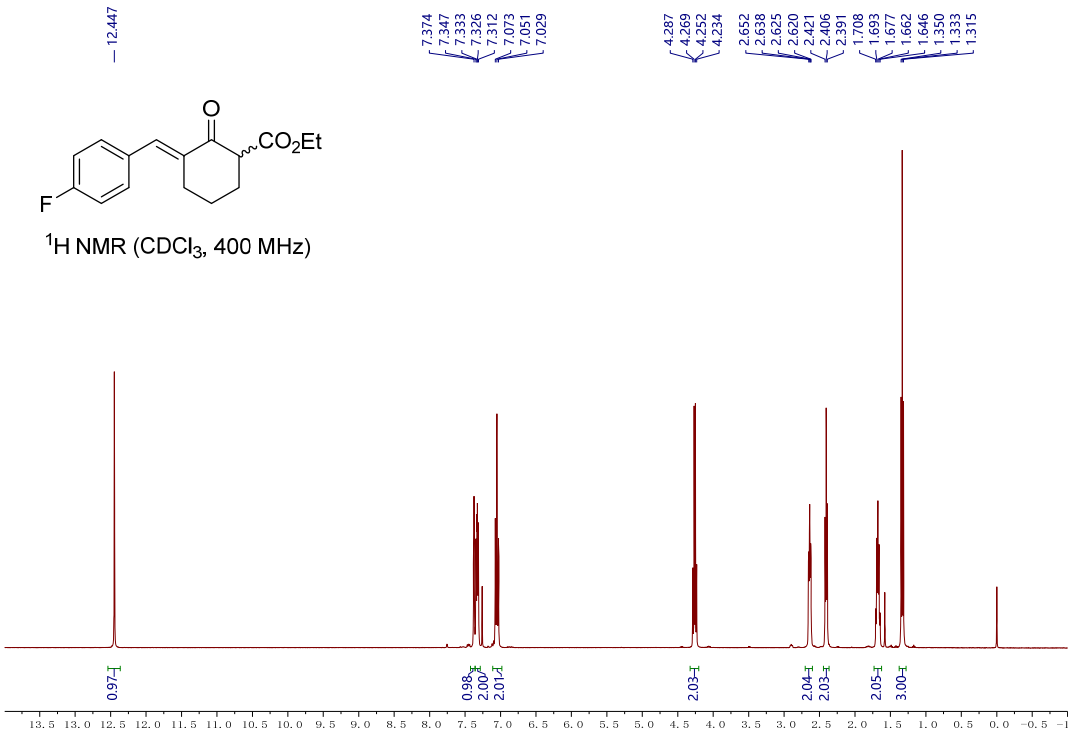

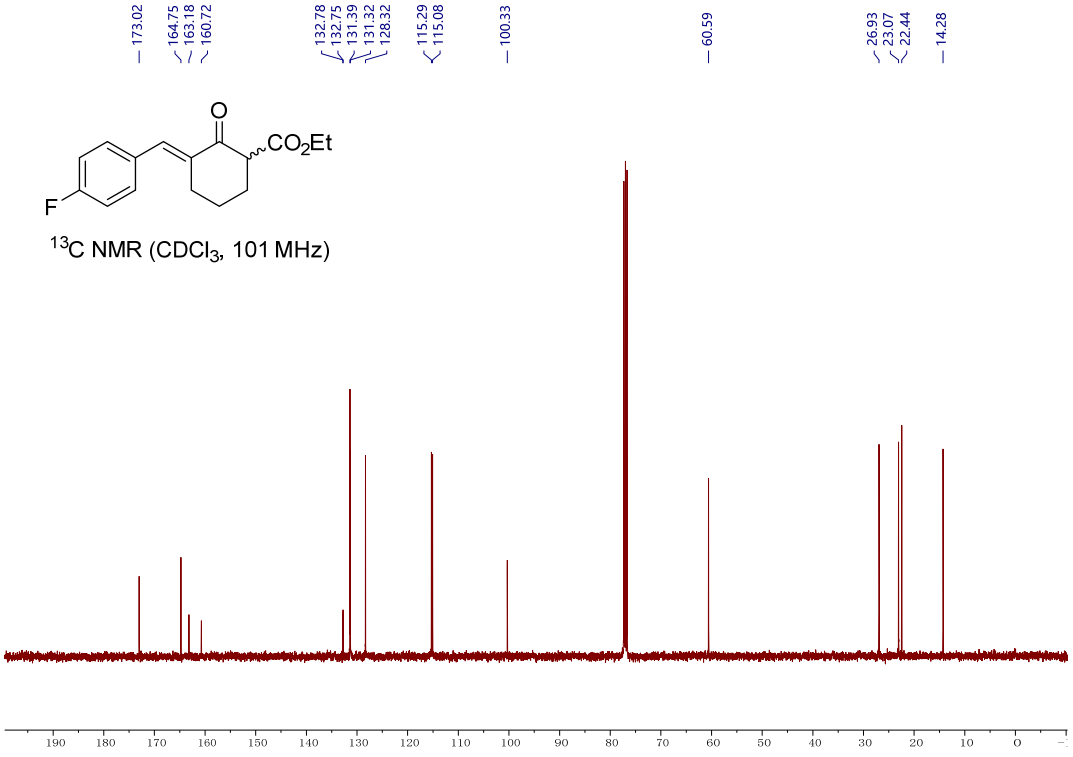

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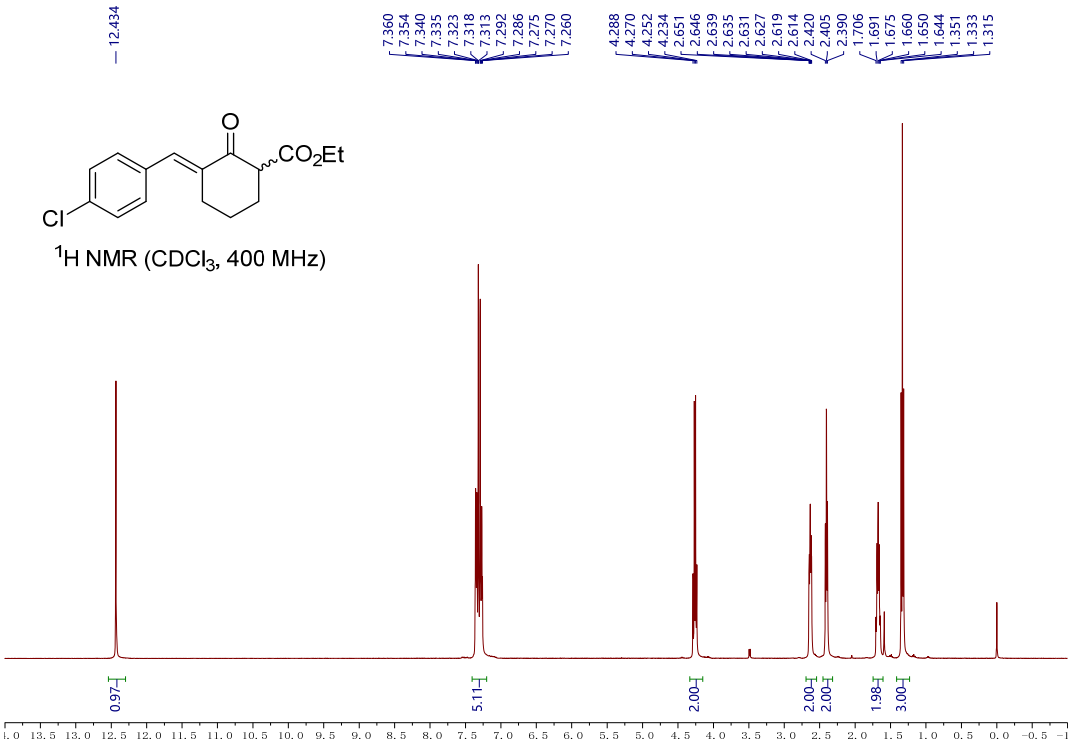

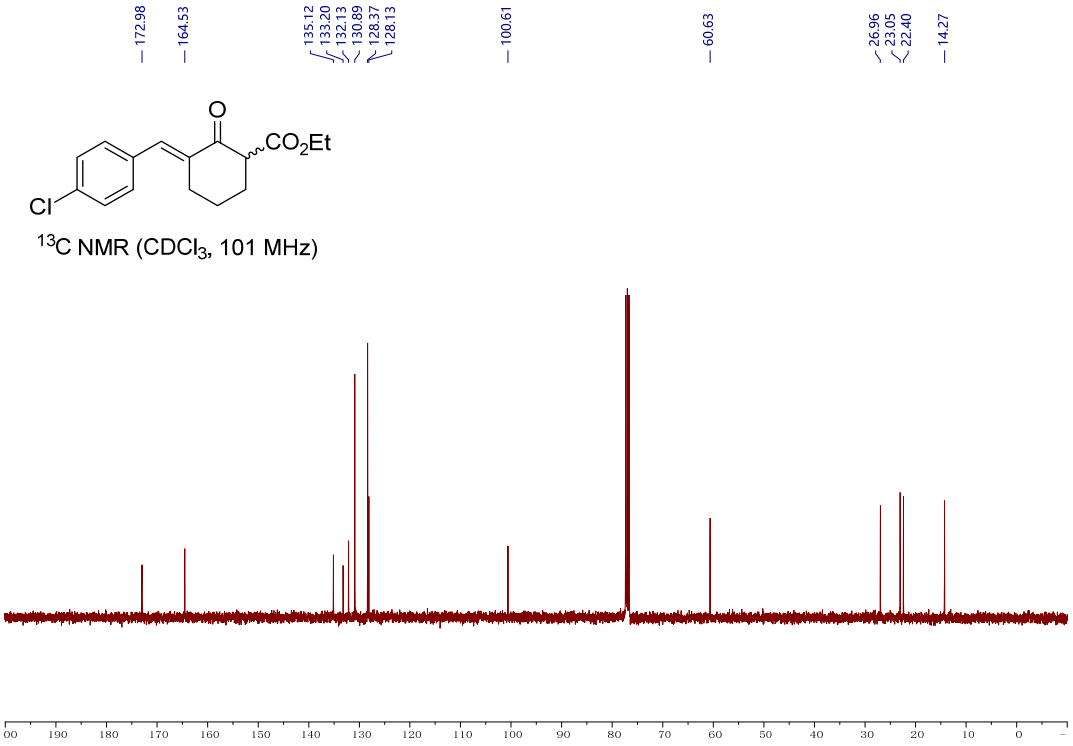

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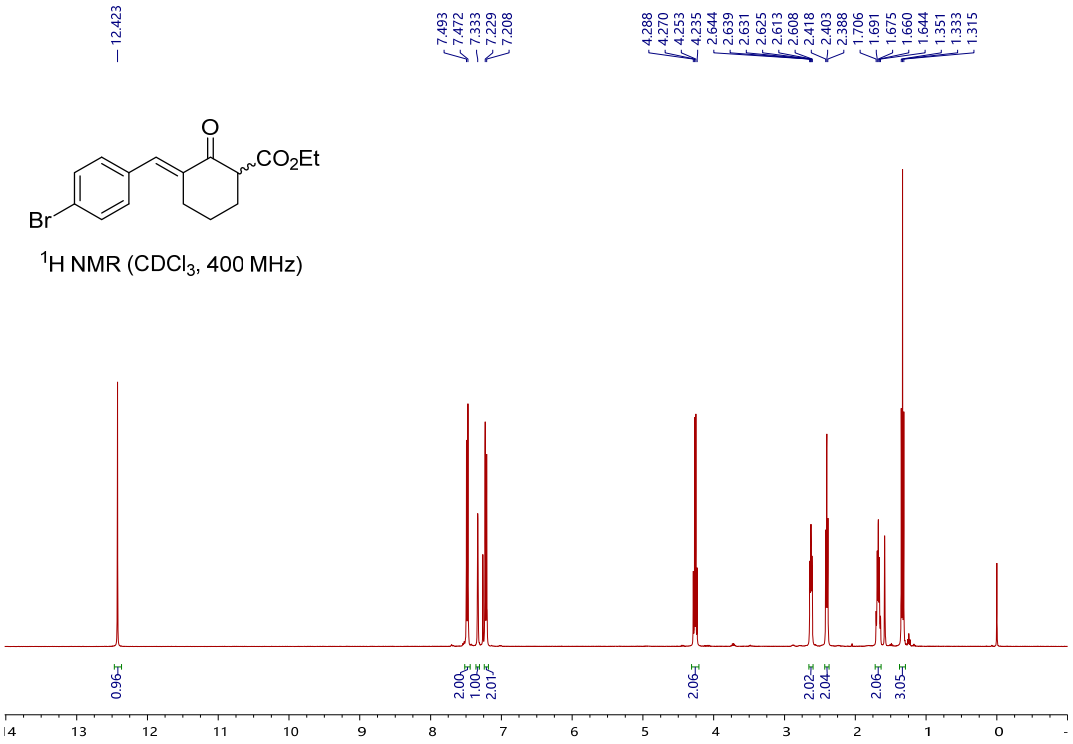

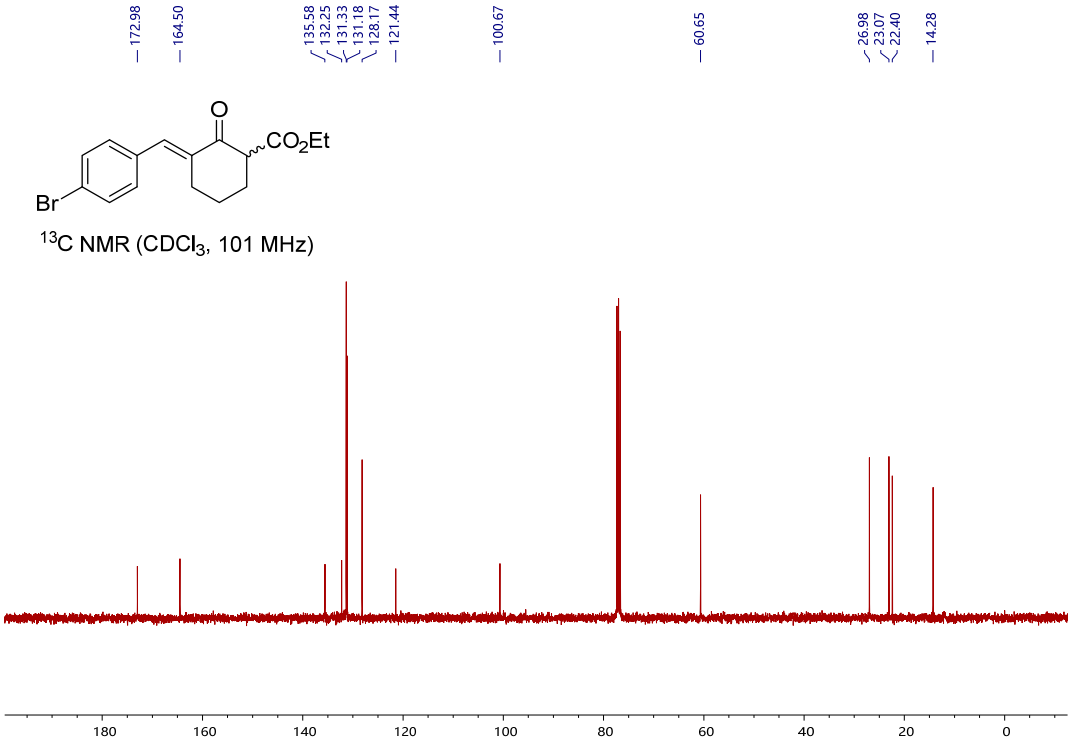

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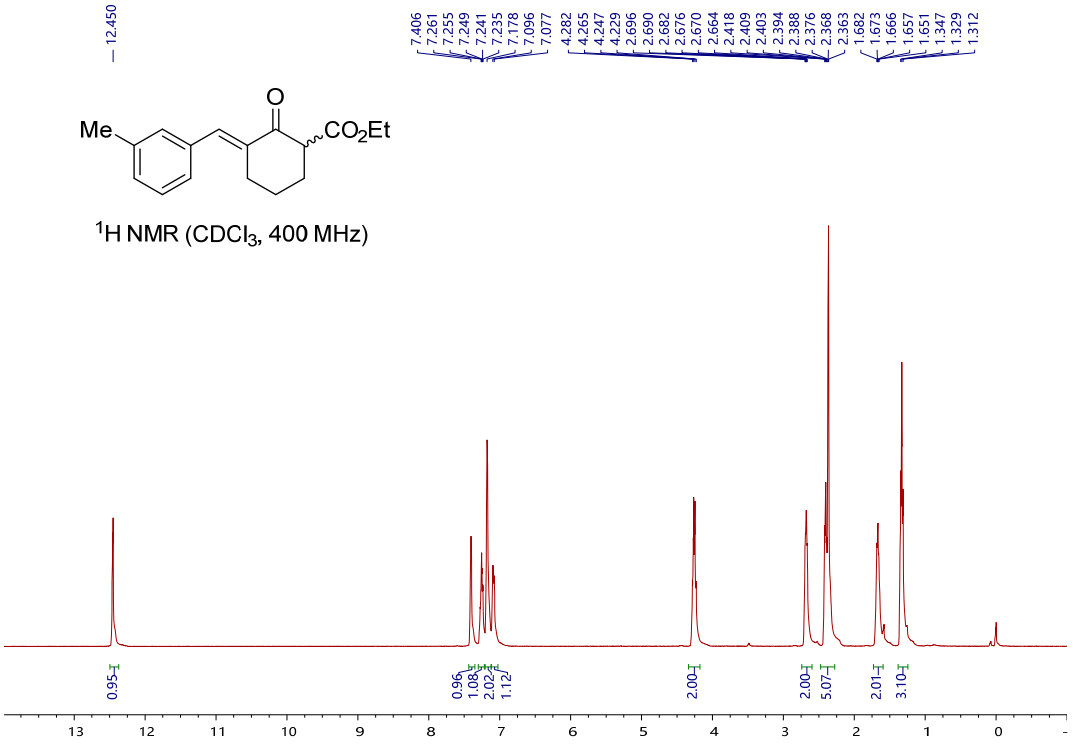

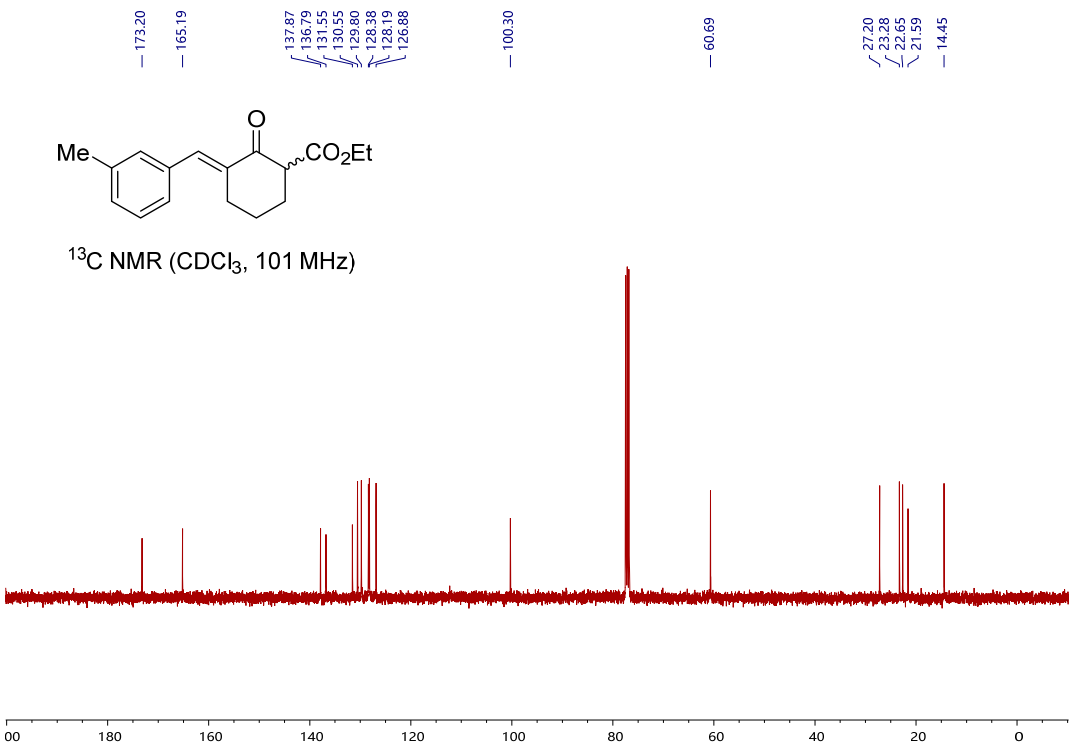

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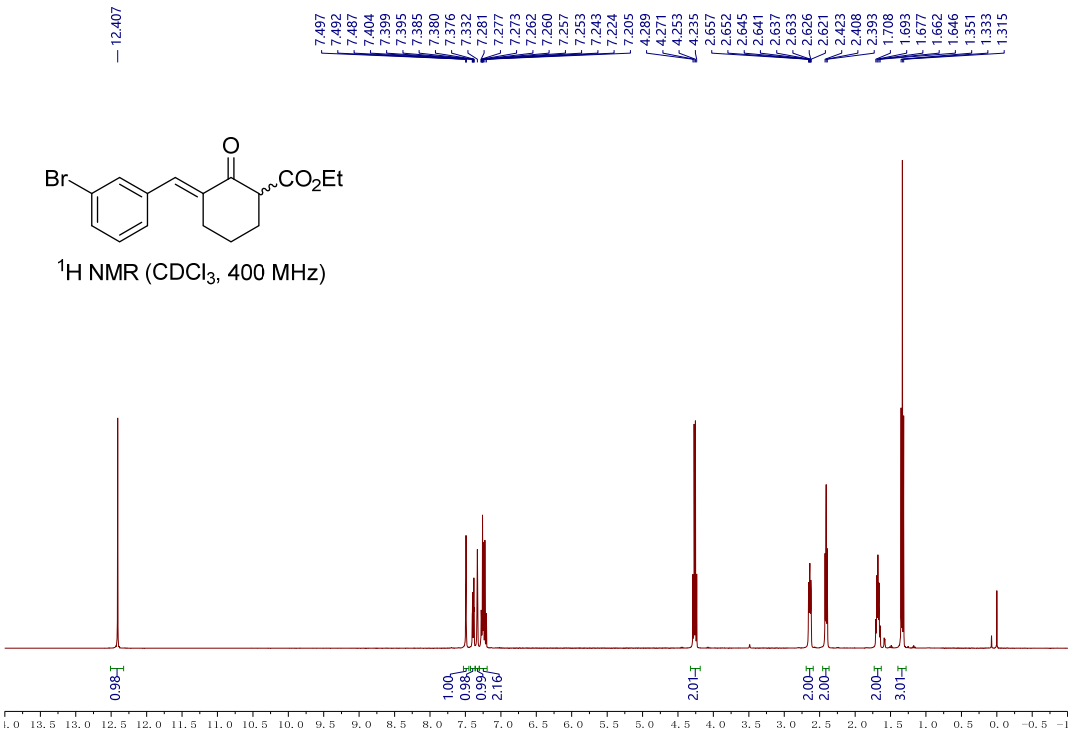

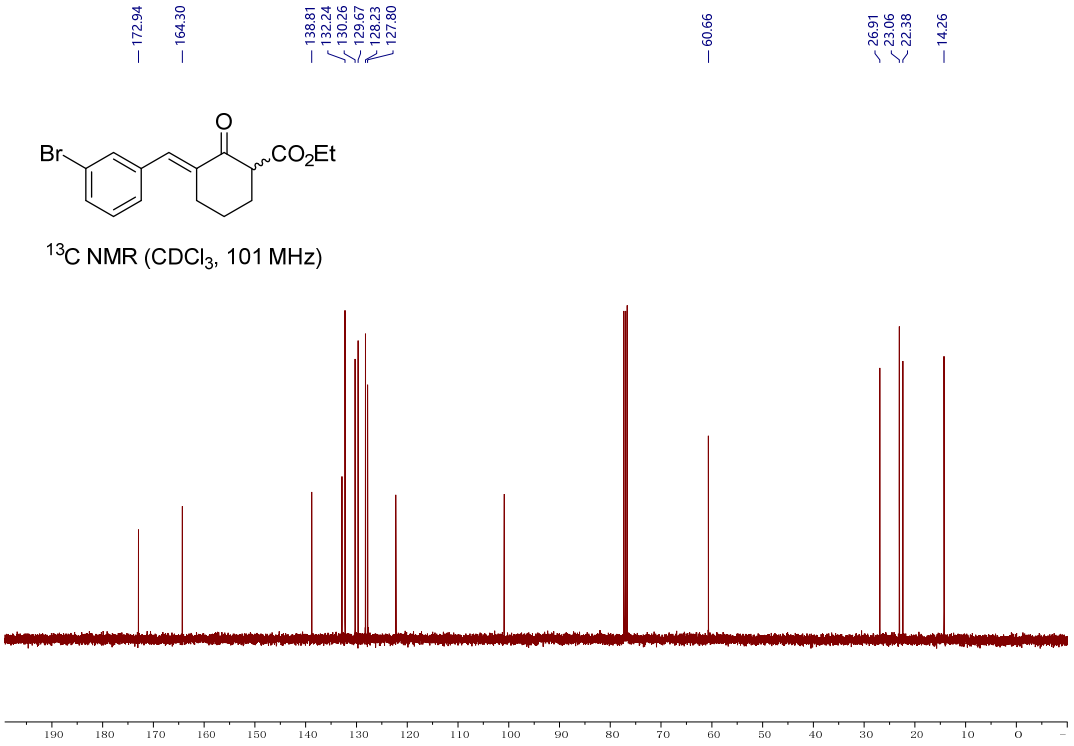

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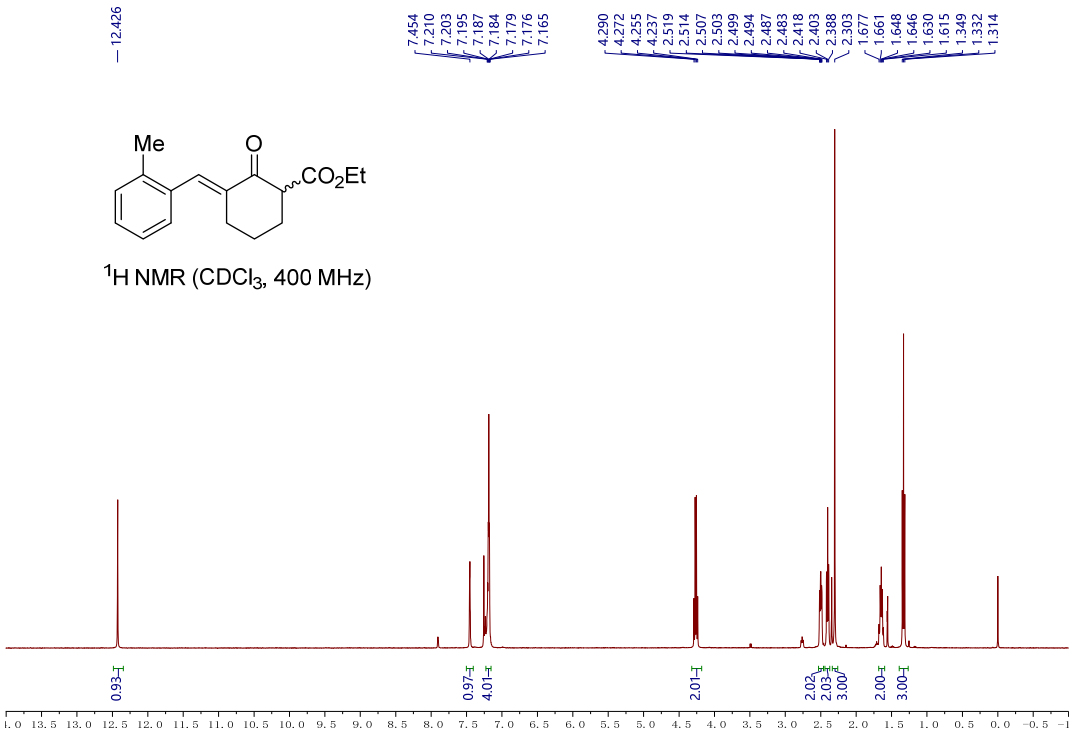

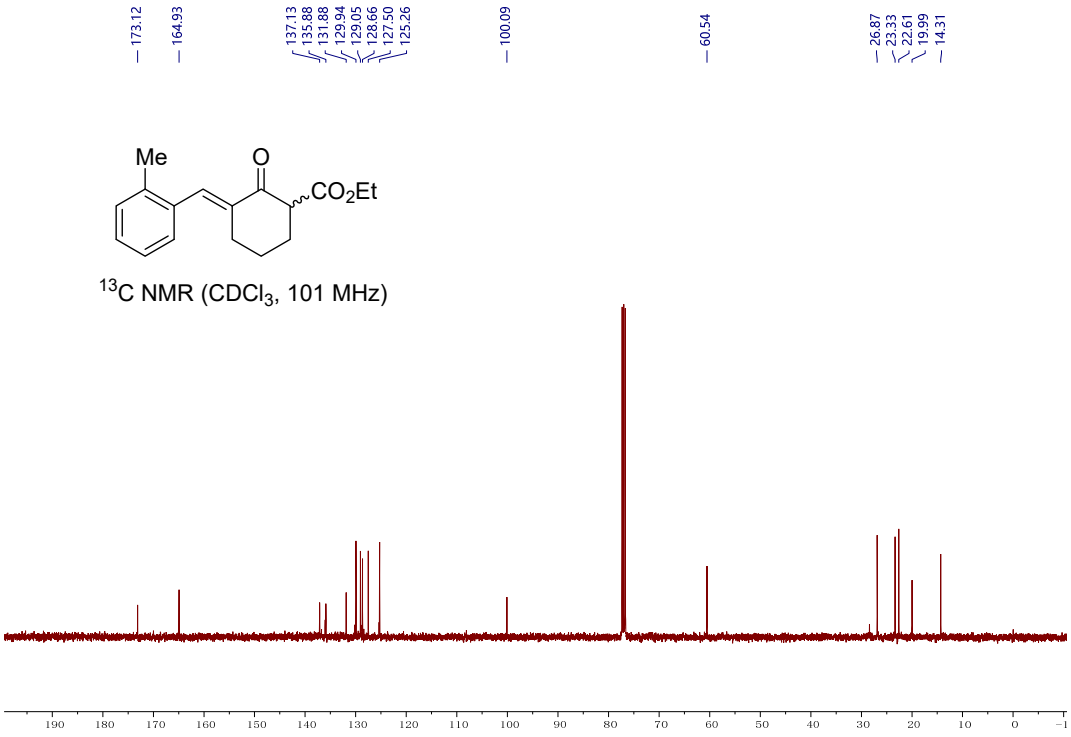

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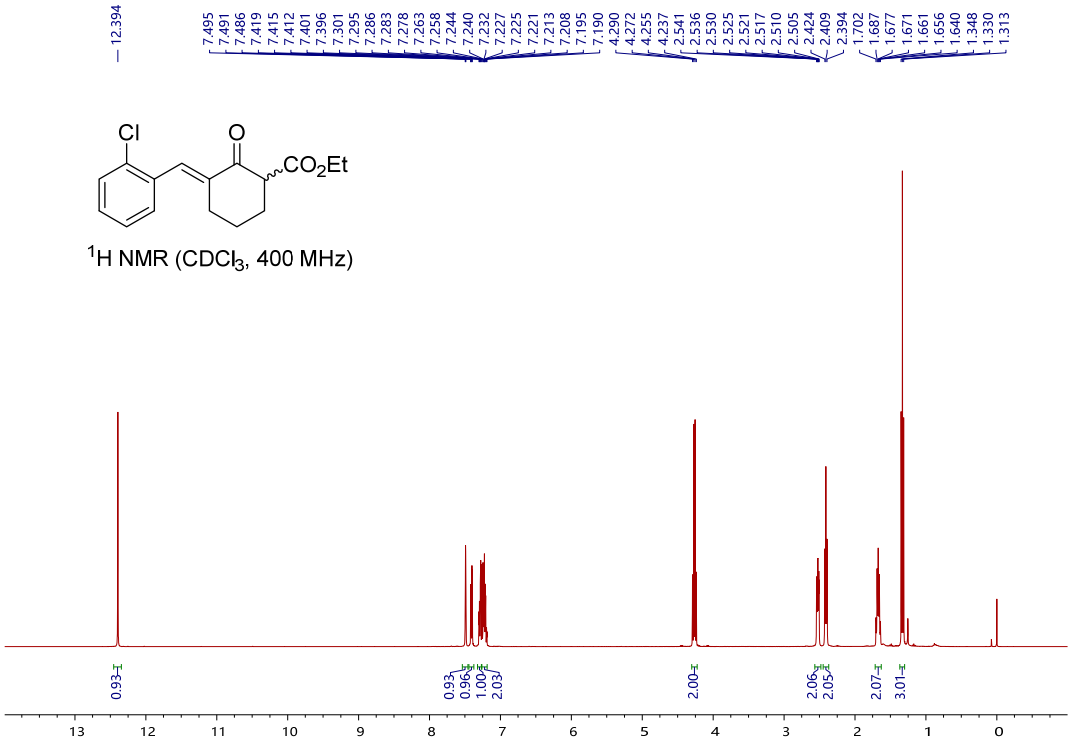

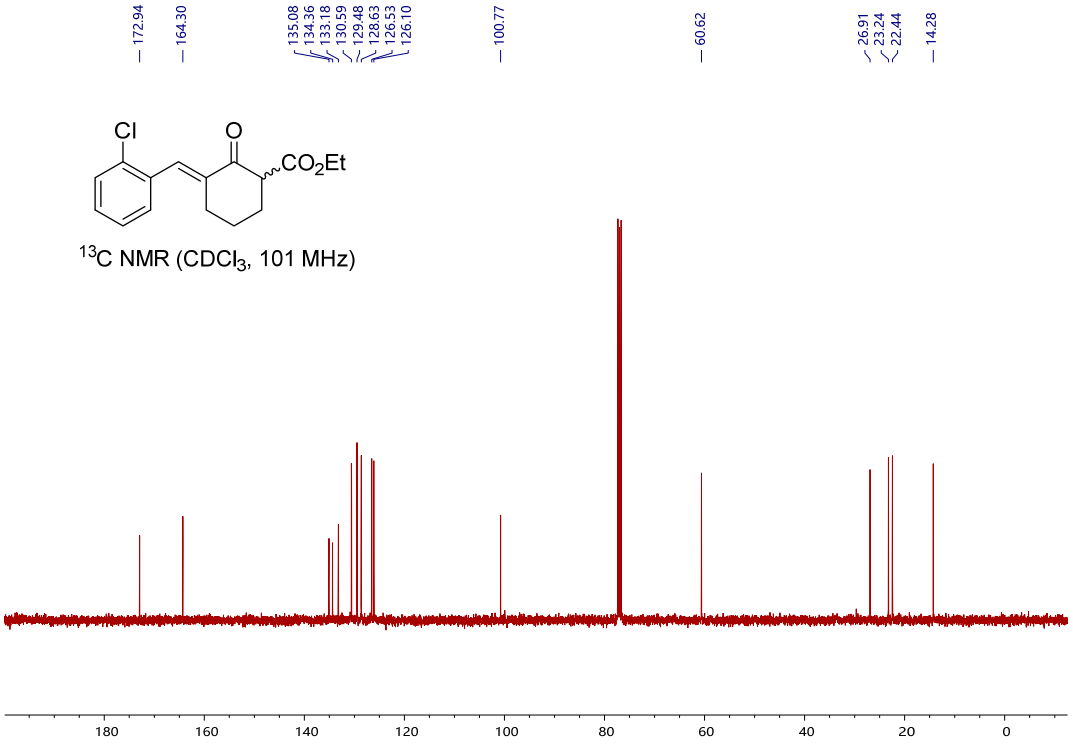

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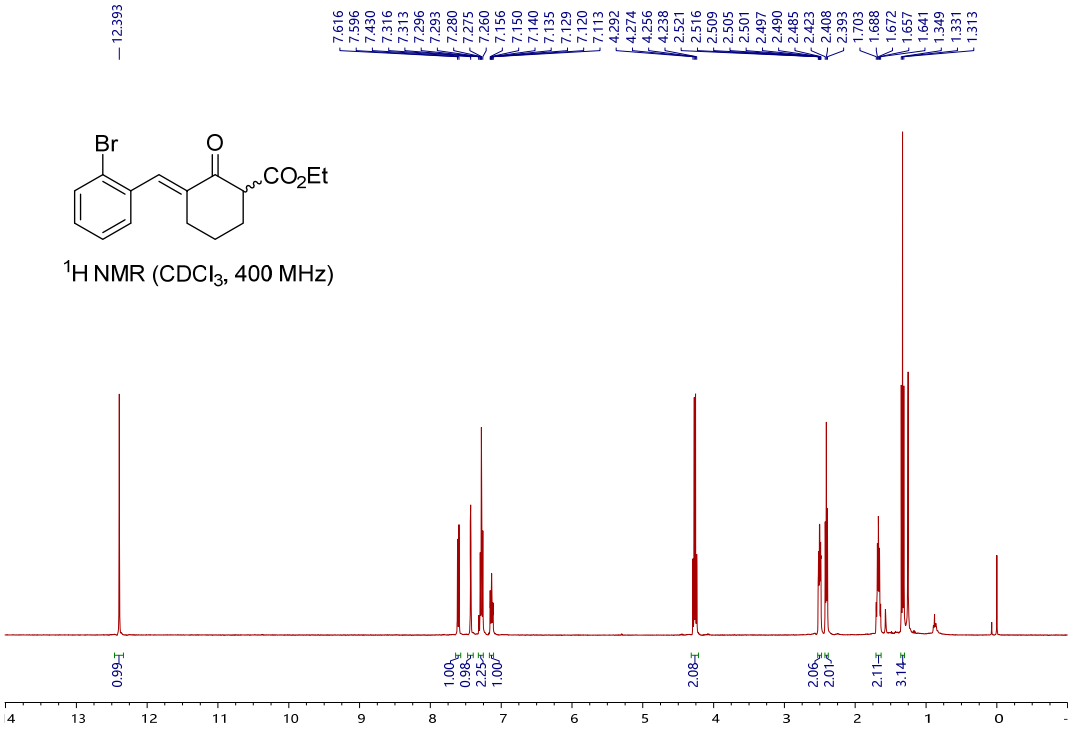

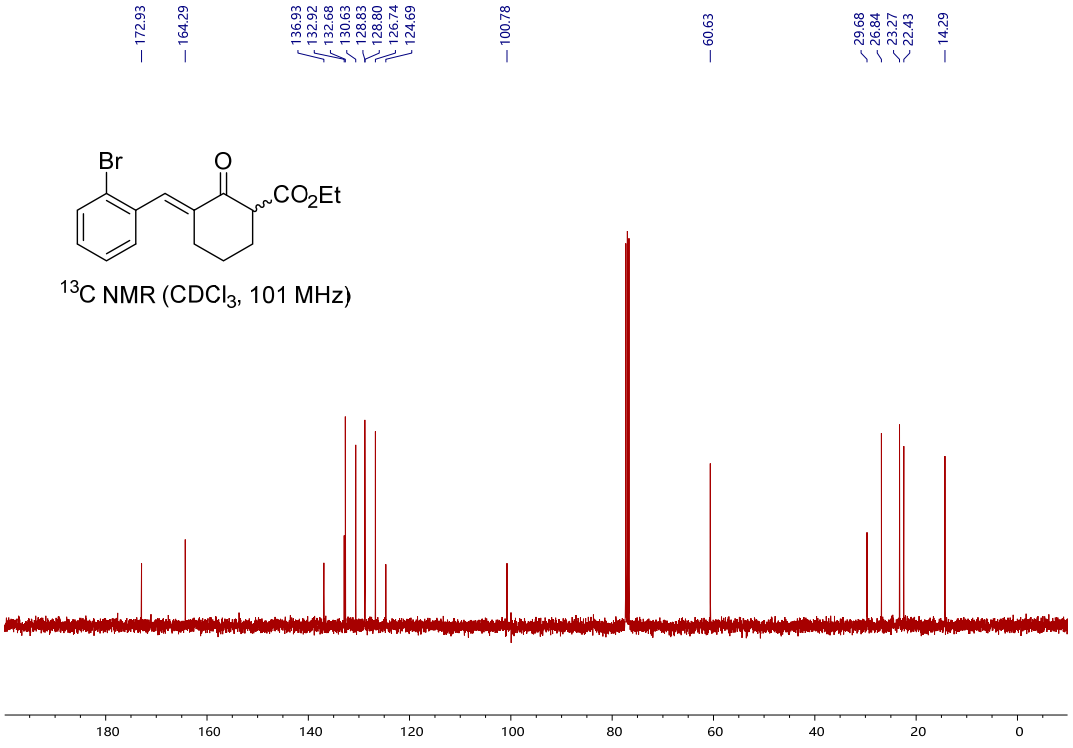

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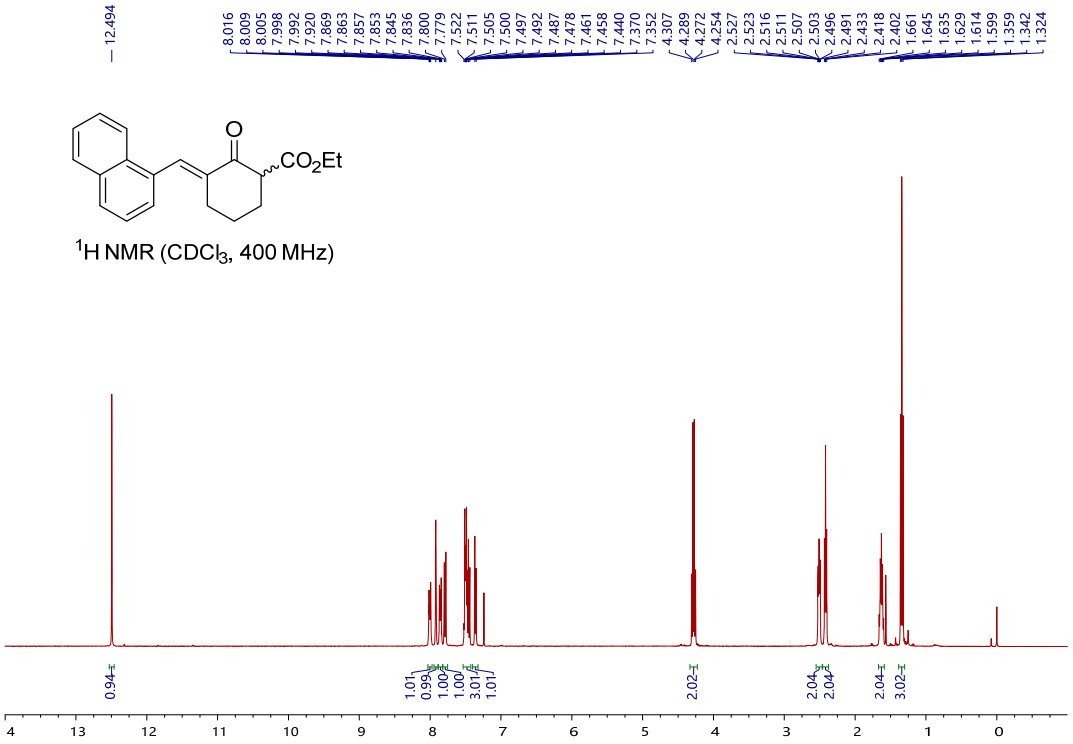
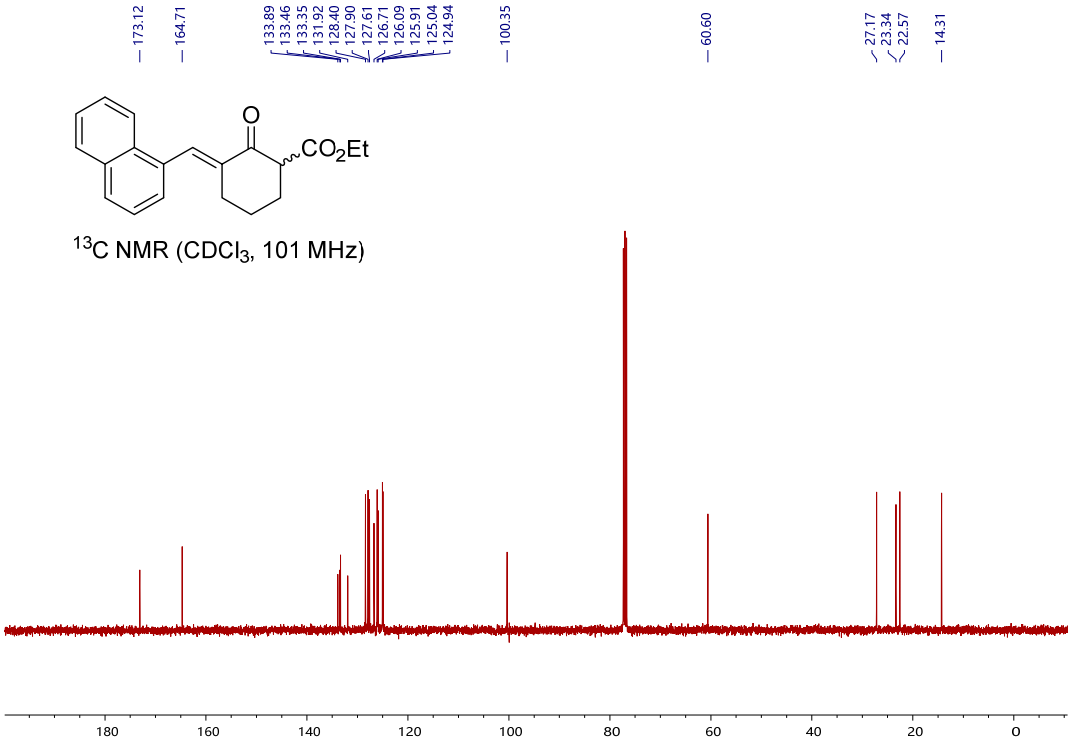
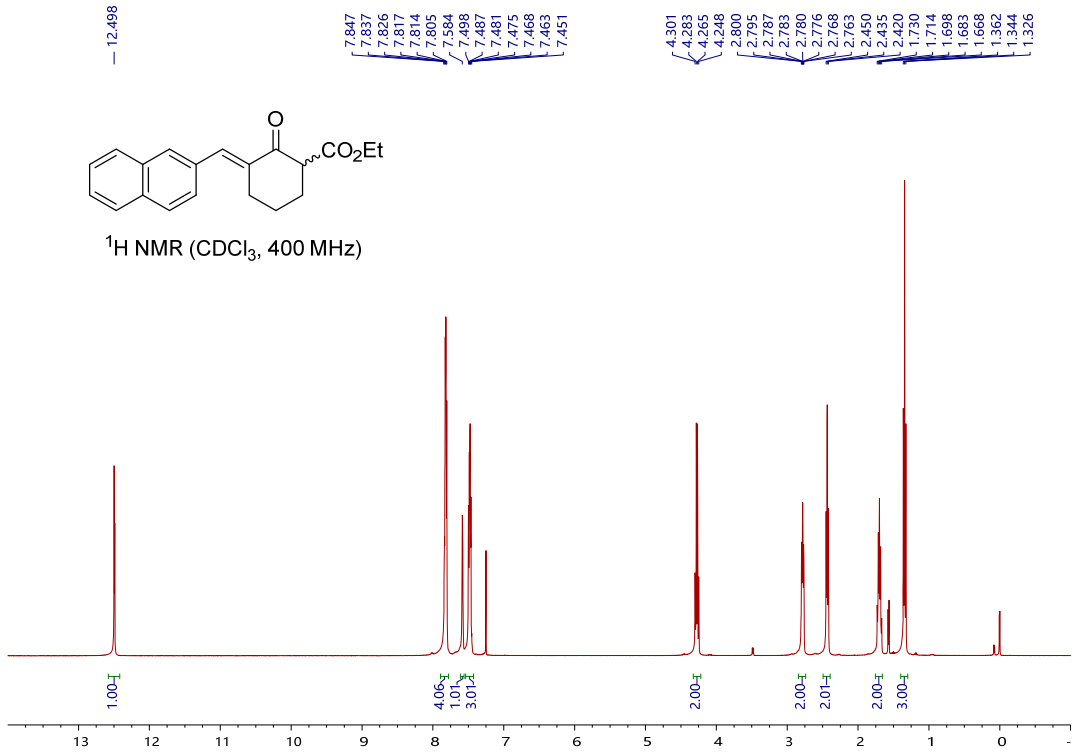
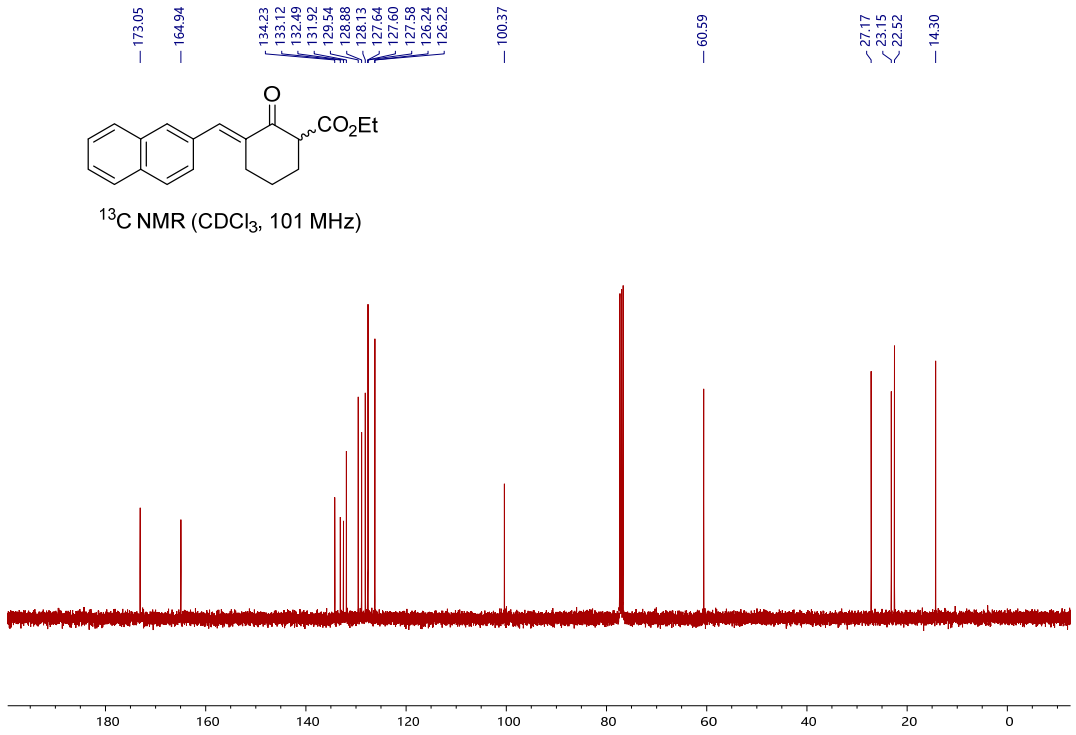


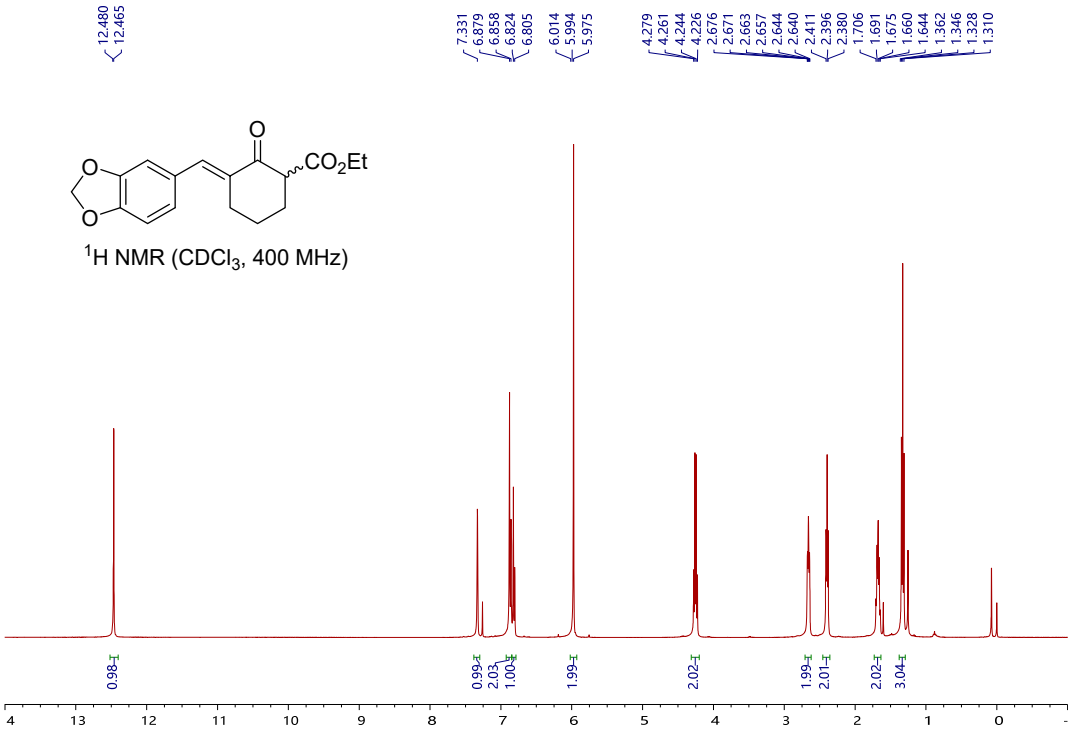


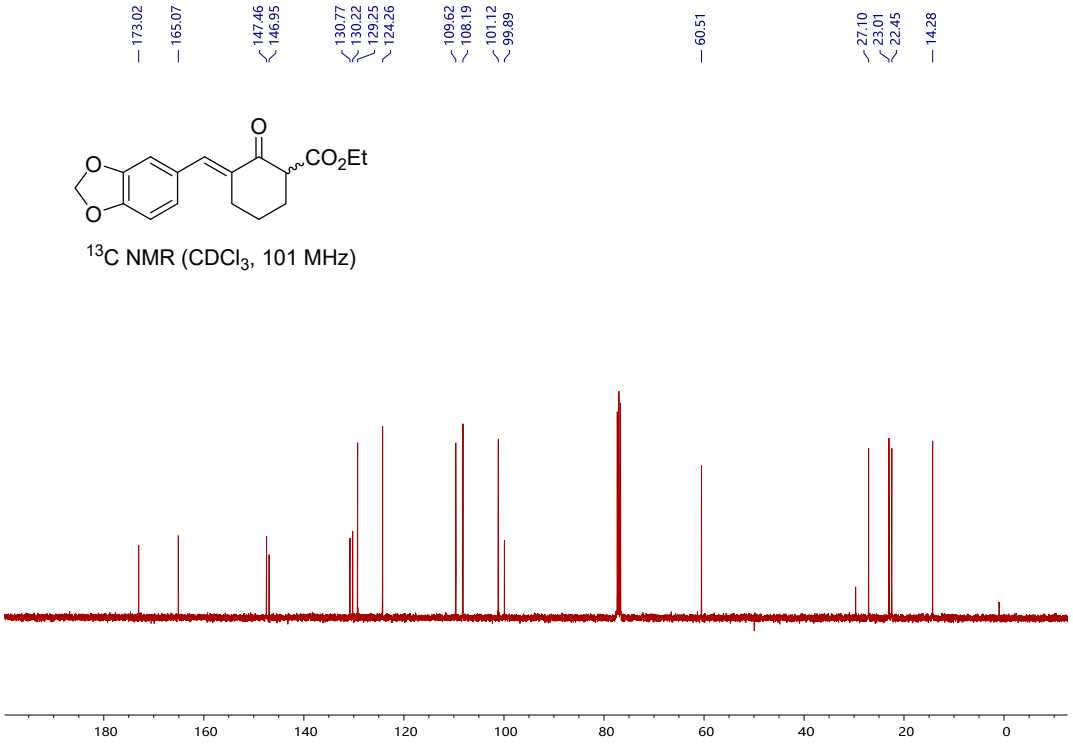
Ethyl (*E*)-3-(naphthalen-2-ylmethylene)-2-oxocyclohexane-1-carboxylate (7p)



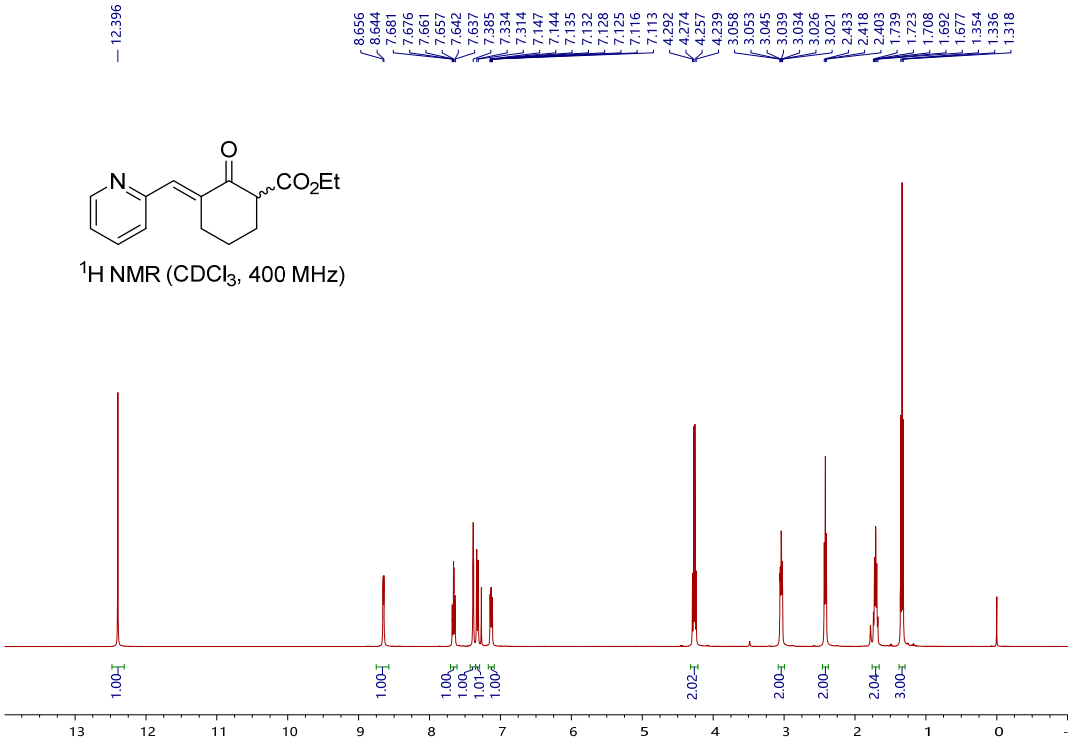


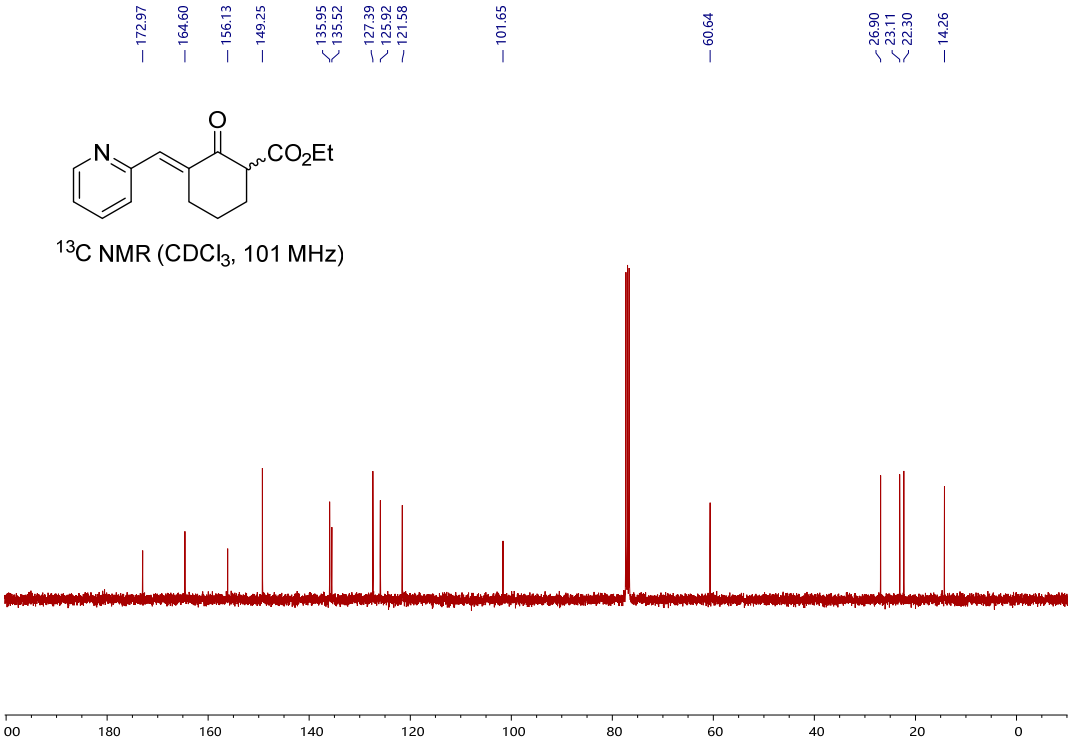
Ethyl (*E*)-3-(benzo[d][1,3]dioxol-5-ylmethylene)-2-oxocyclohexane-1-carboxylate (7q)



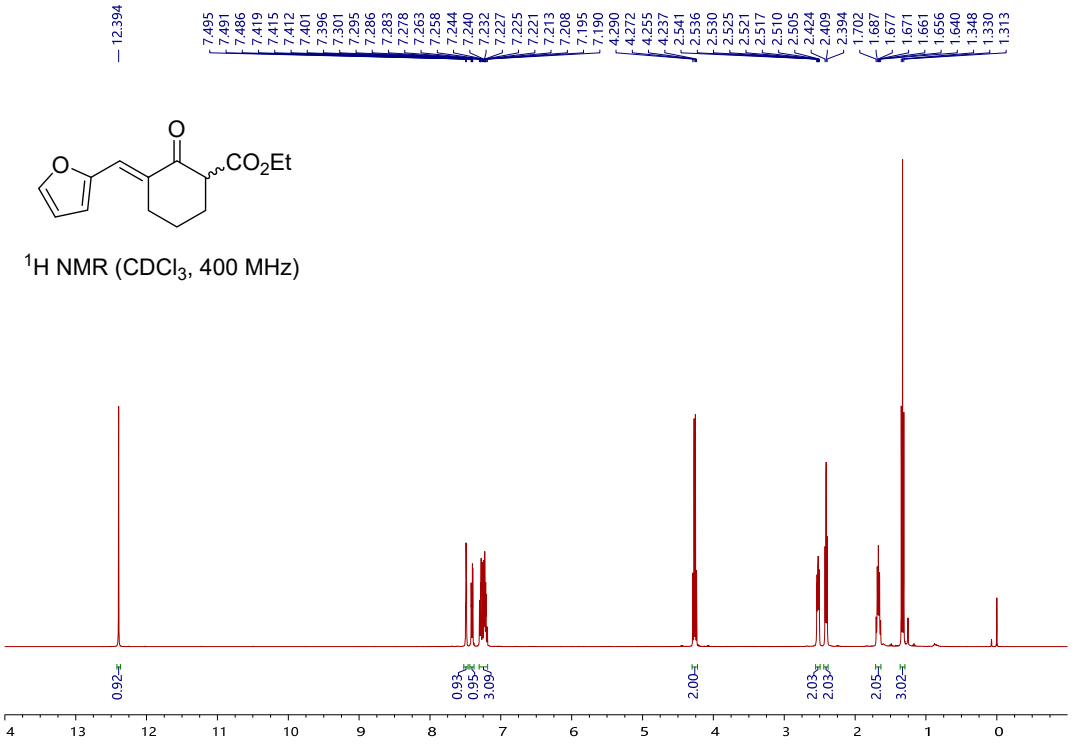


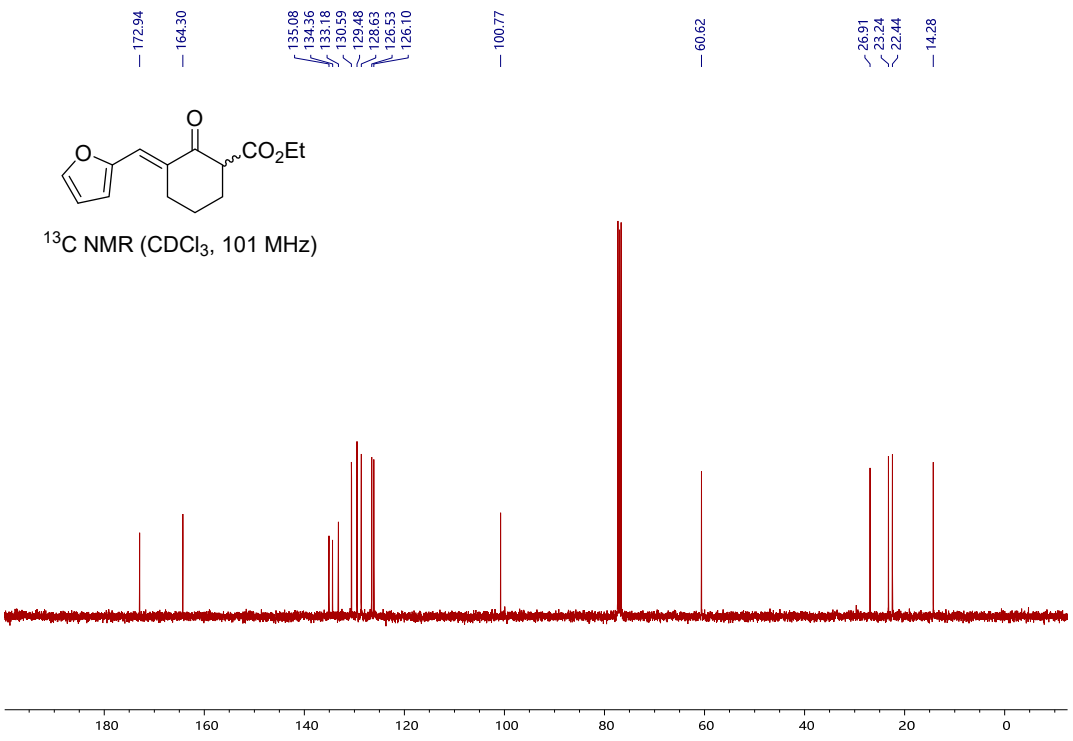
Ethyl (*E*)-2-oxo-3-(pyridin-2-ylmethylene)cyclohexane-1-carboxylate (7r)



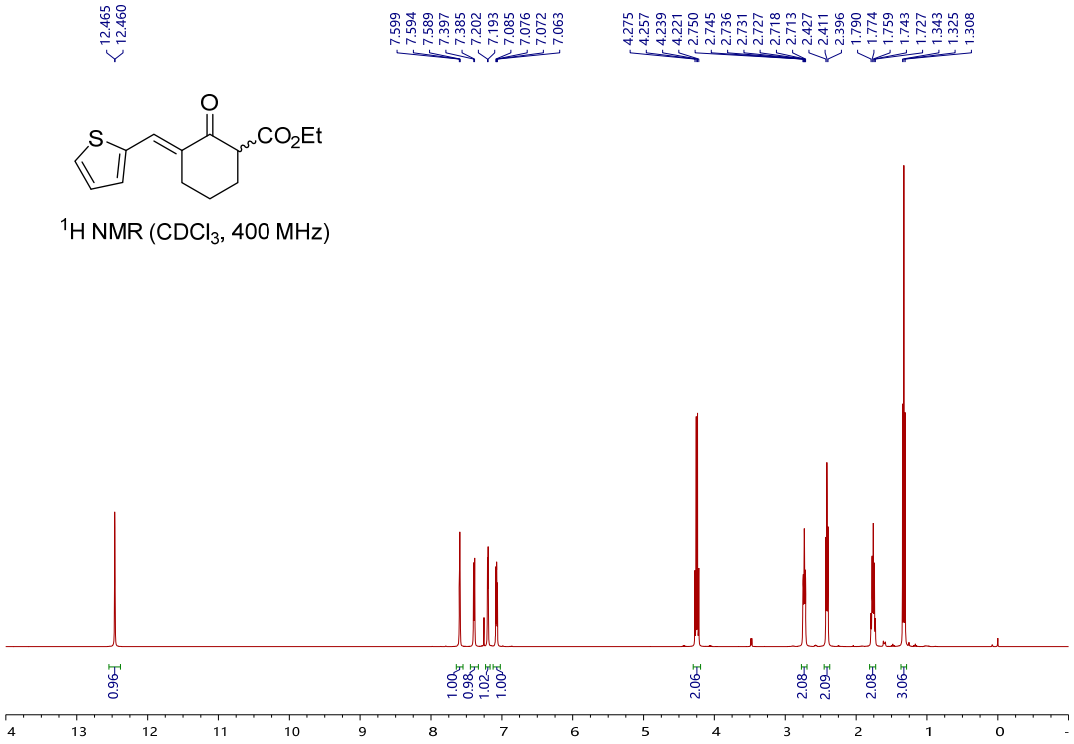


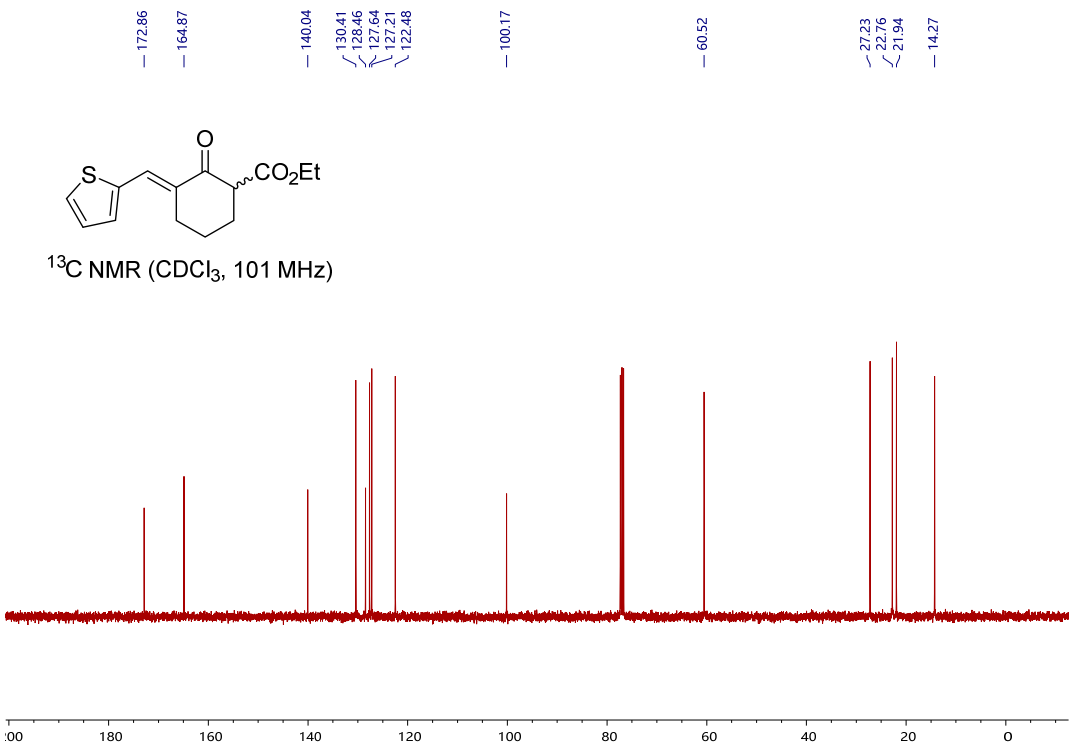
Ethyl (*E*)-3-(furan-2-ylmethylene)-2-oxocyclohexane-1-carboxylate (7s)



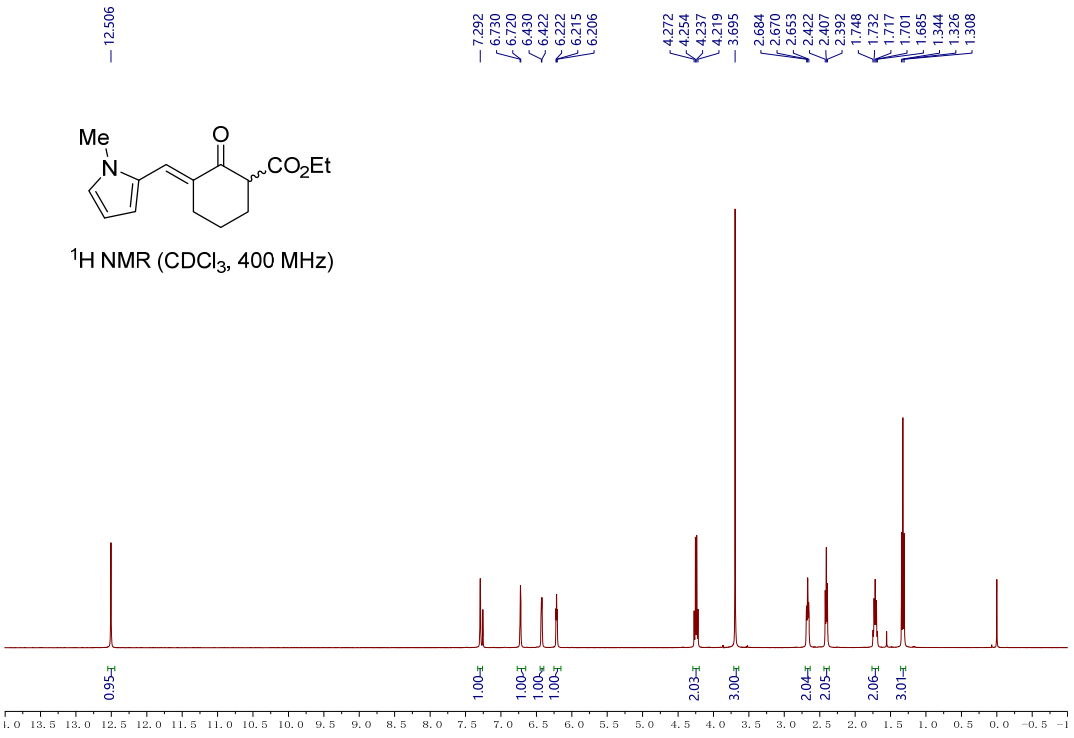


Ethyl (*E*)-2-oxo-3-(thiophen-2-ylmethylene)cyclohexane-1-carboxylate (7t)

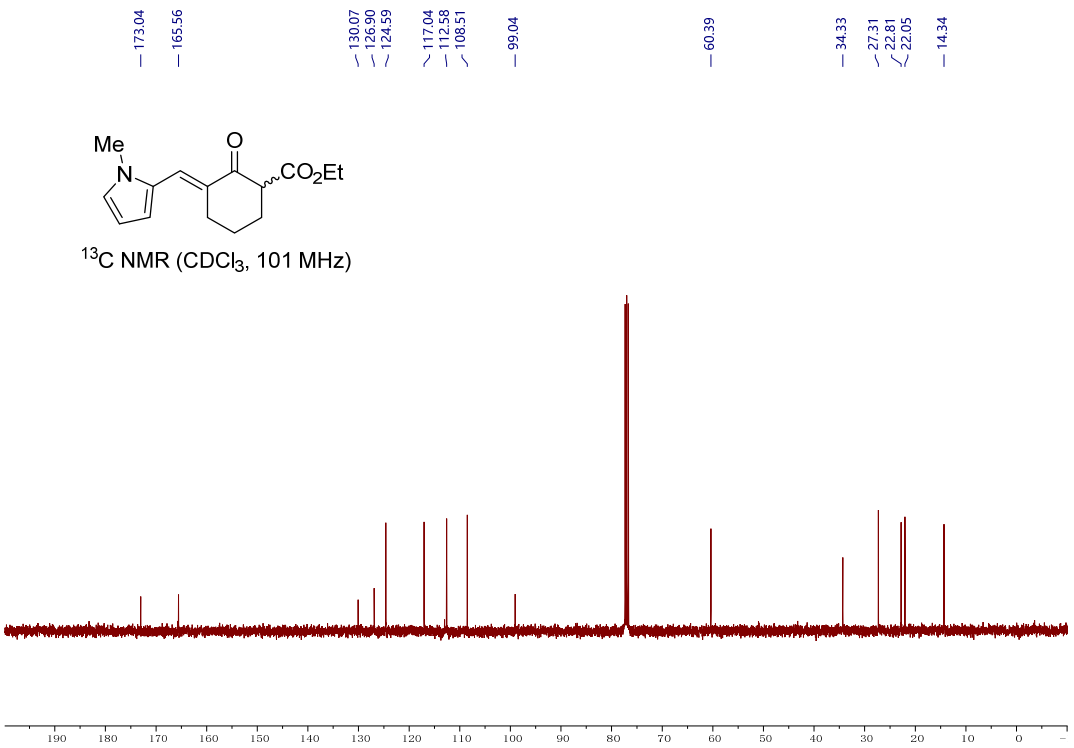




Ethyl (*E*)-3-((1-methyl-1H-pyrrol-2-yl)methylene)-2-oxocyclohexane-1-carboxylate (7u)

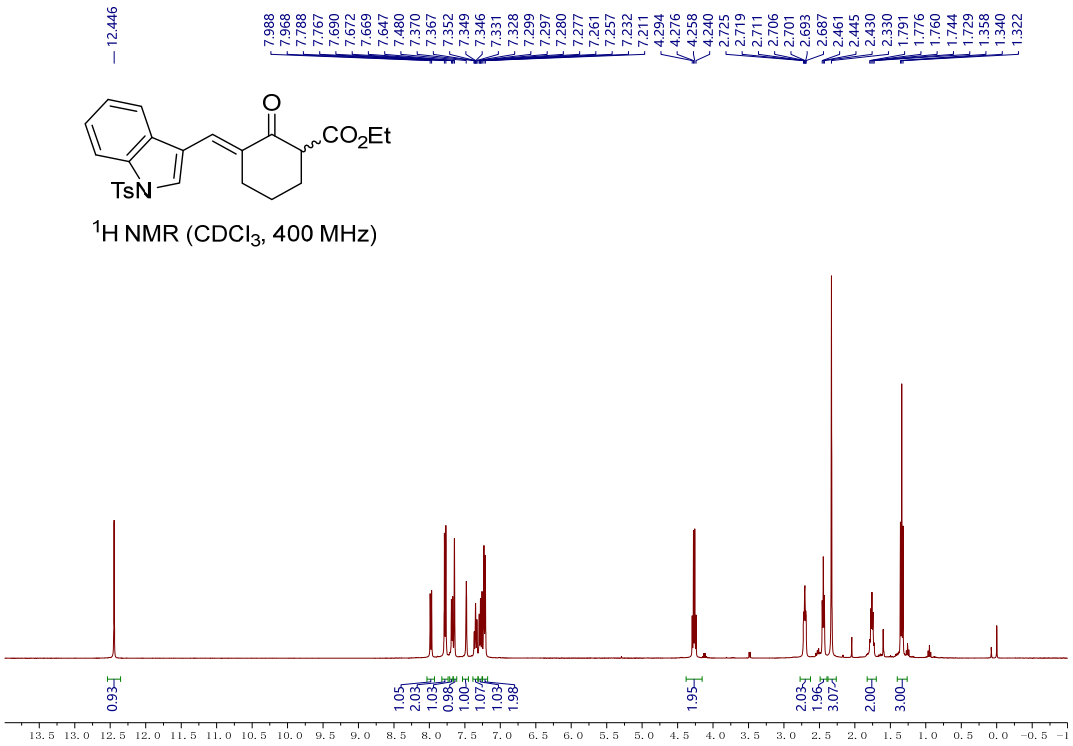


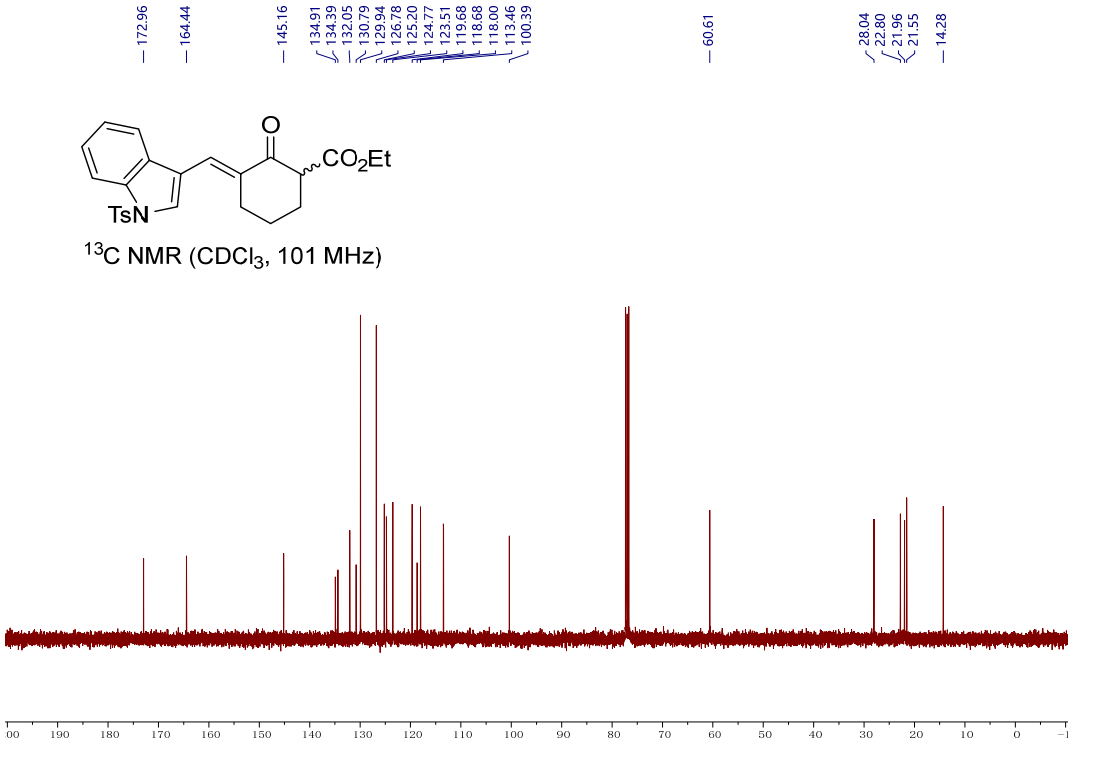
^{1}H NMR ($CDCl_3$, 400 MHz)



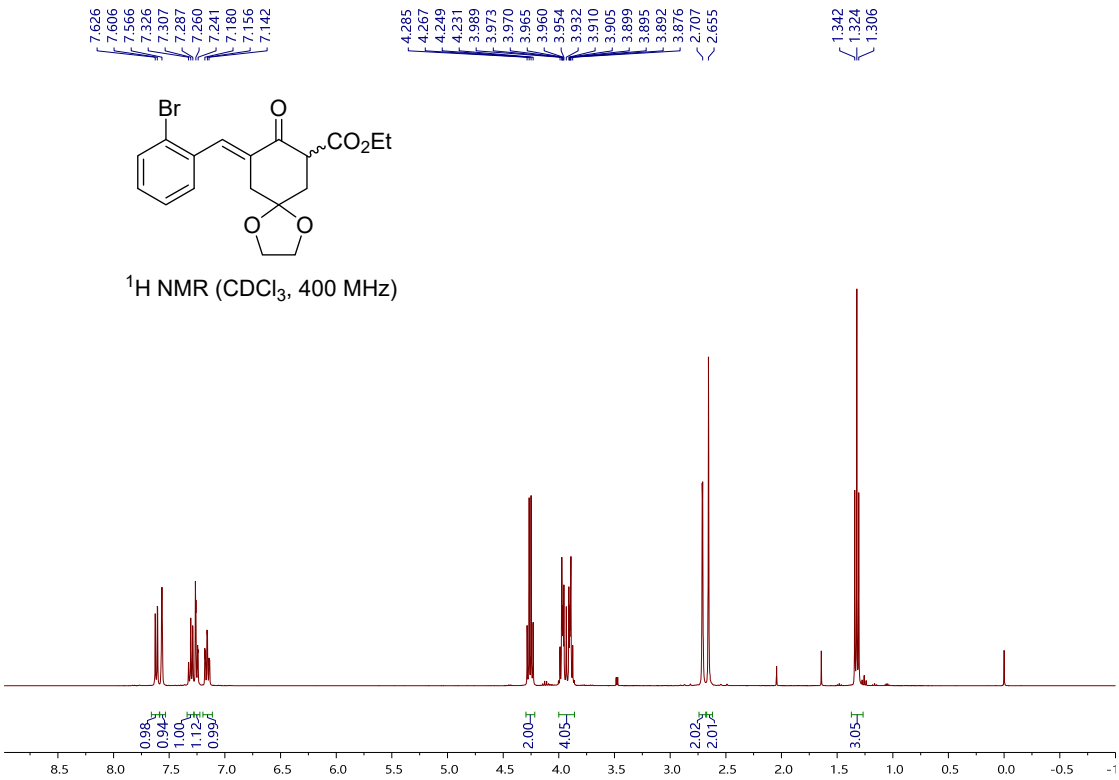
^{13}C NMR ($CDCl_3$, 101 MHz)

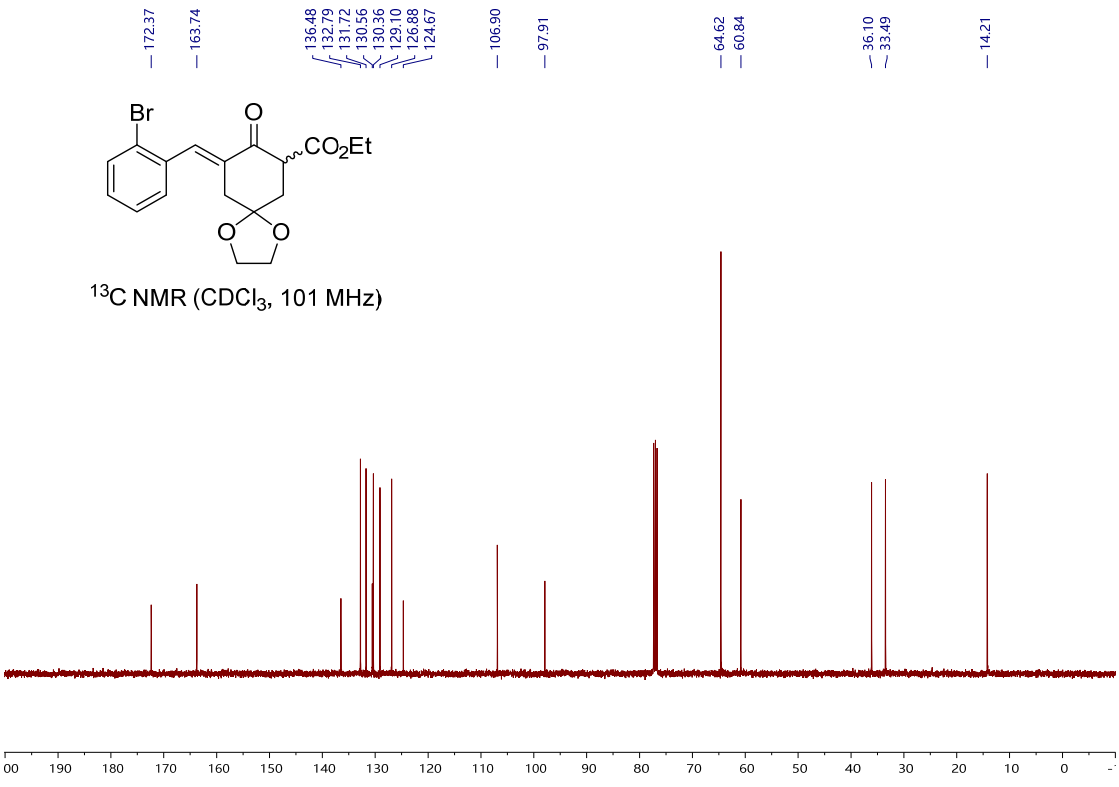
Ethyl (*E*)-2-oxo-3-((1-tosyl-1H-indol-3-yl)methylene)cyclohexane-1-carboxylate (7v)



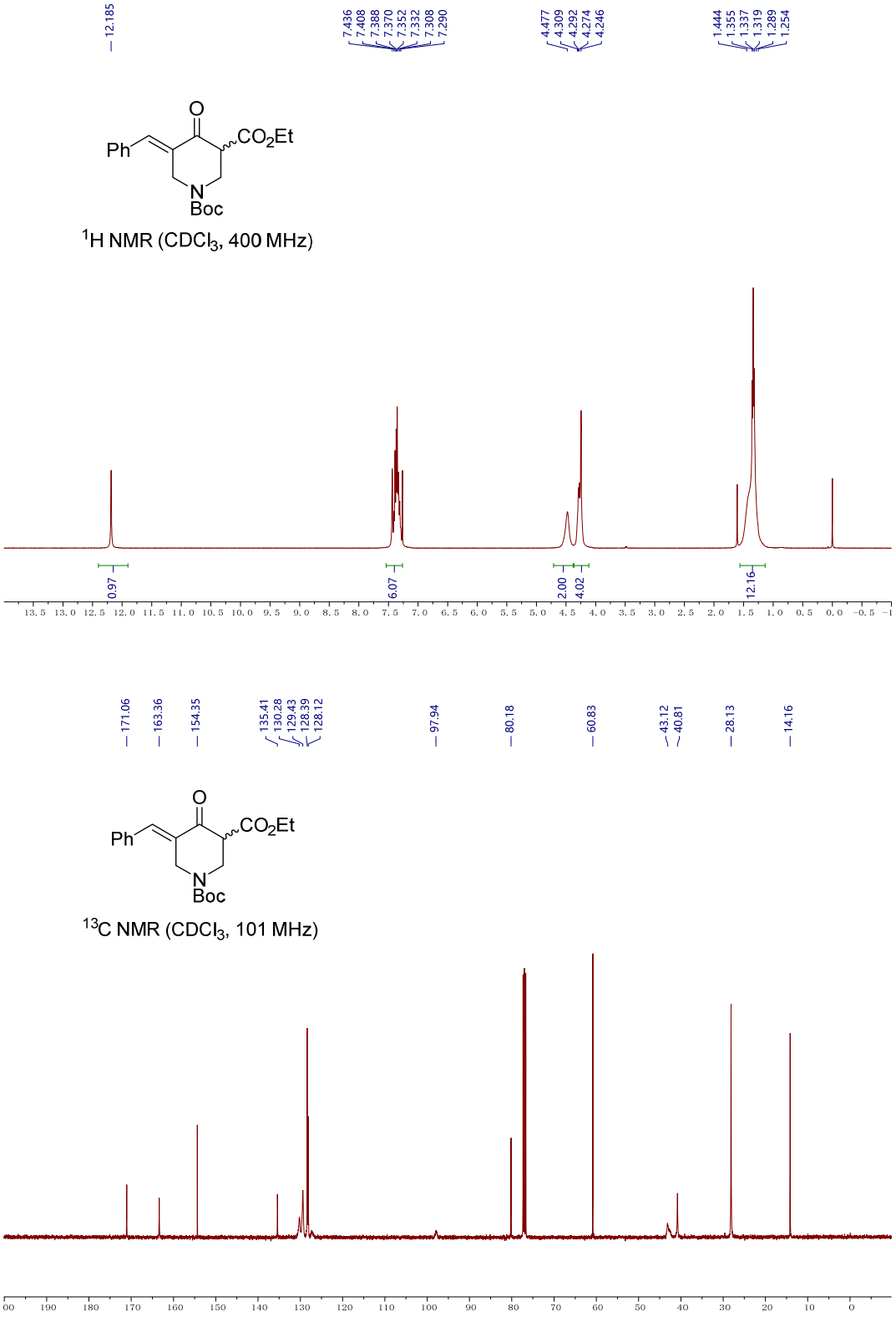


Ethyl (*E*)-9-(2-bromobenzylidene)-8-oxo-1,4-dioxaspiro[4.5]decane-7-carboxylate (7w)

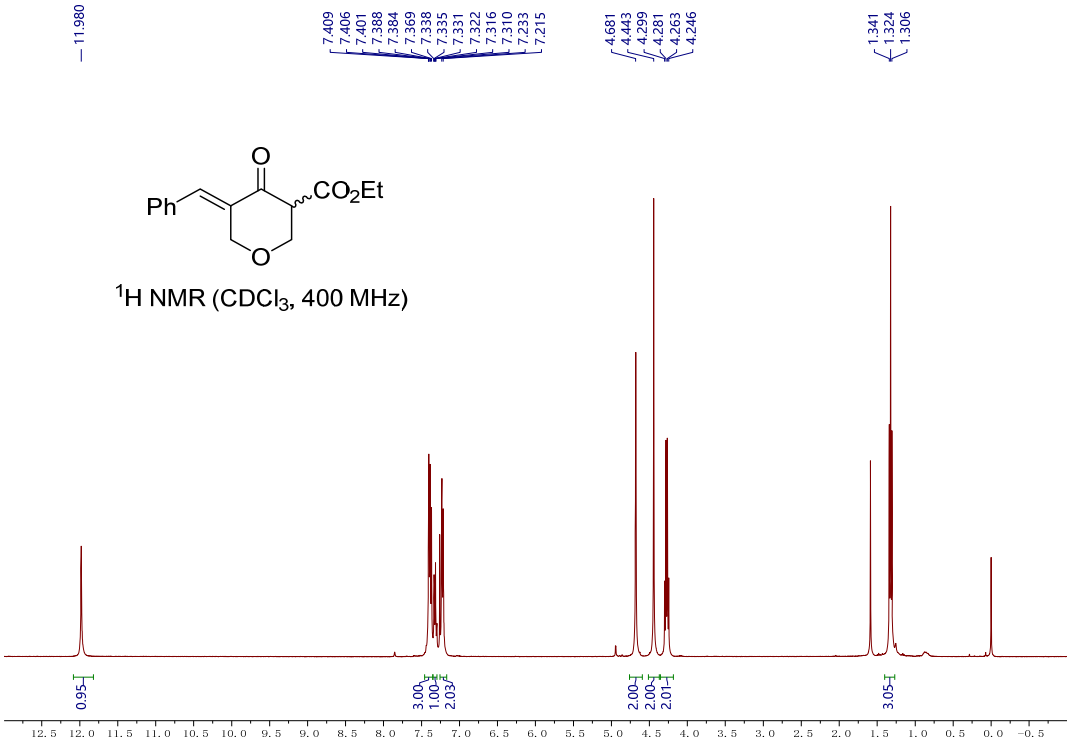


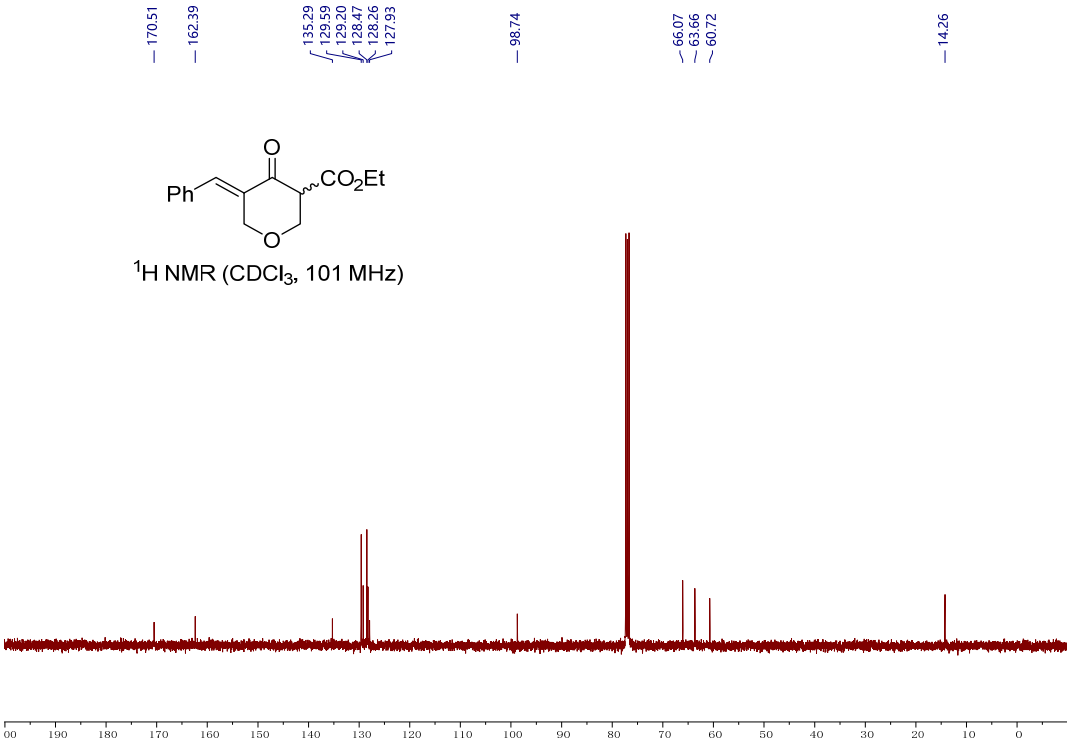


1-(*tert*-Butyl) 3-ethyl (E)-5-benzylidene-4-oxopiperidine-1,3-dicarboxylate (7x)

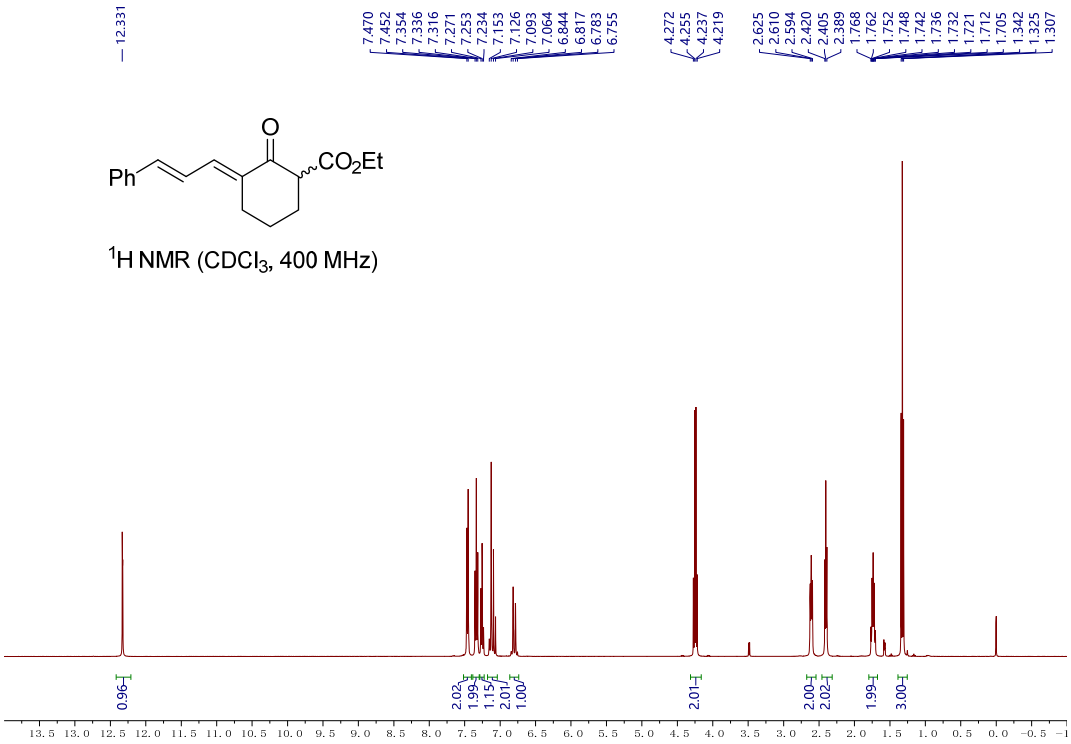


Ethyl (*E*)-5-benzylidene-4-oxotetrahydro-2H-pyran-3-carboxylate (7y)

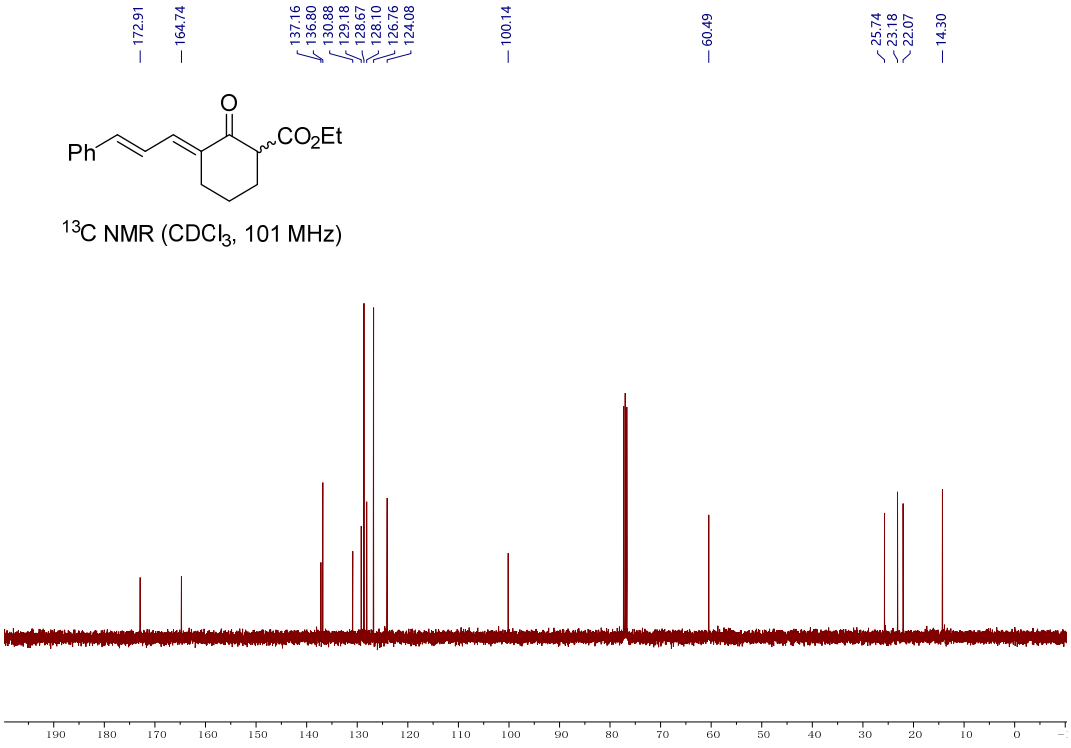




Ethyl (*E*)-2-oxo-3-((*E*)-3-phenylallylidene)cyclohexane-1-carboxylate (7z)

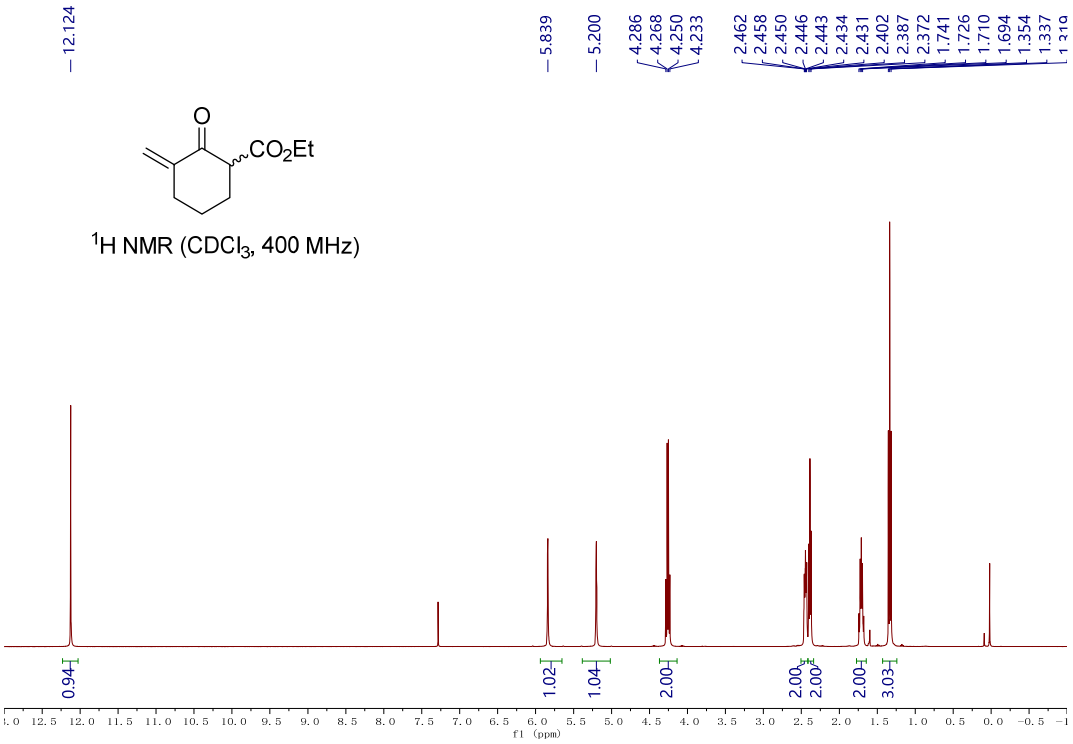


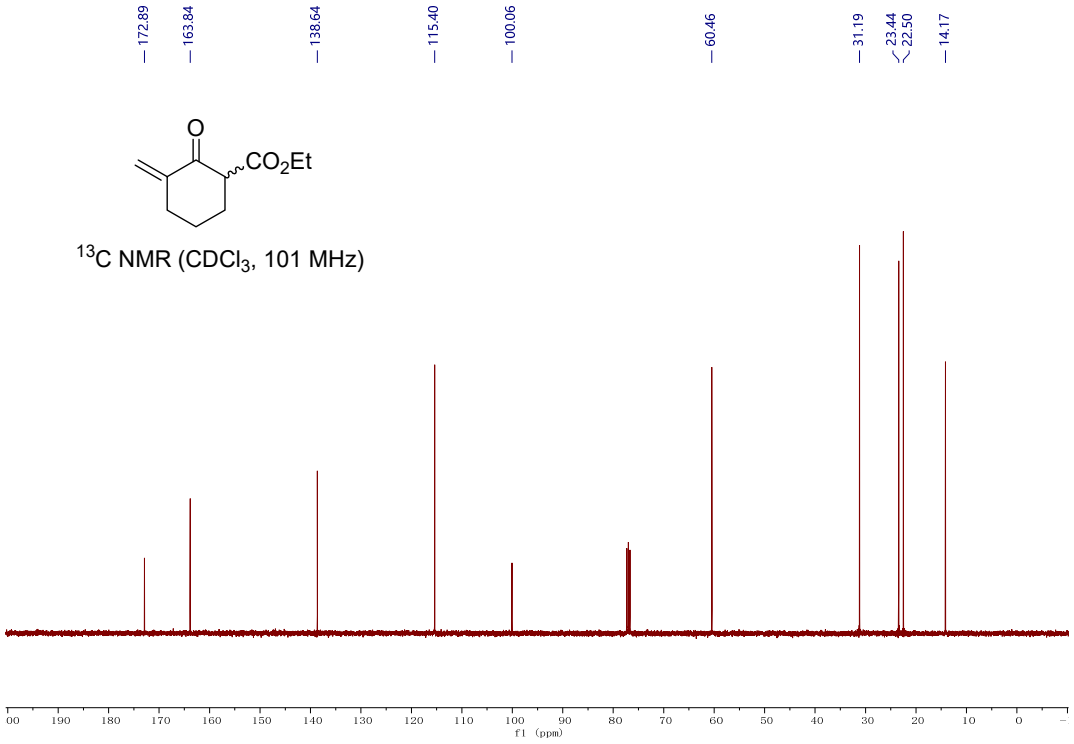
^{1}H NMR ($CDCl_3$, 400 MHz)



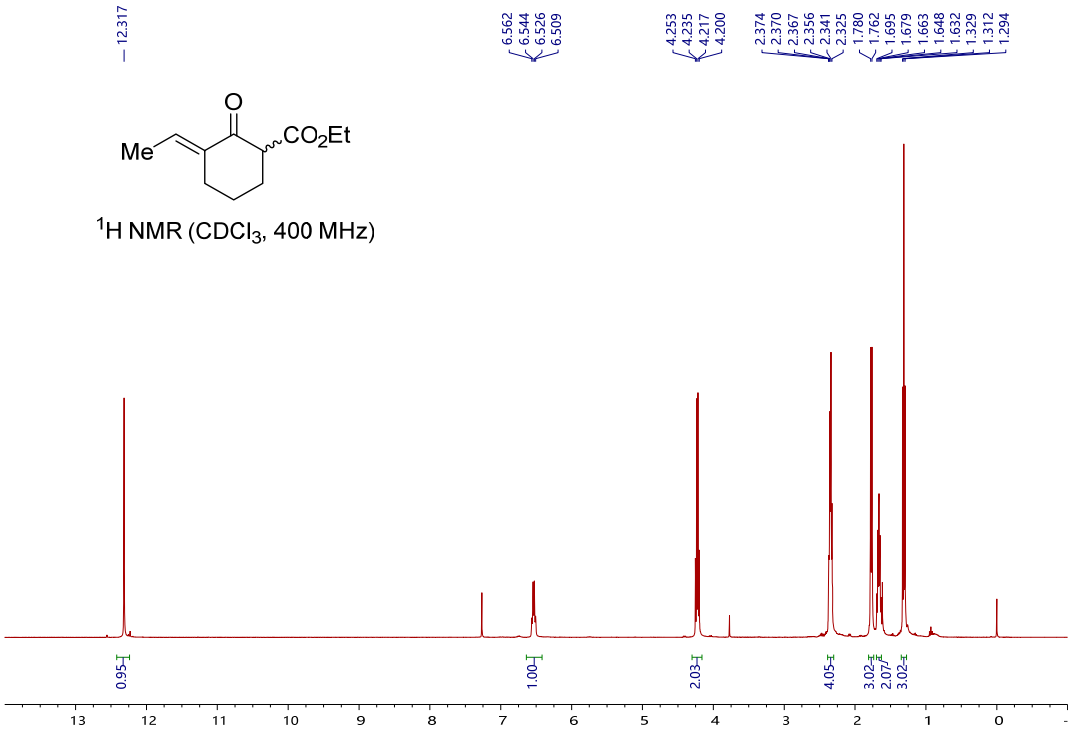
^{13}C NMR ($CDCl_3$, 101 MHz)

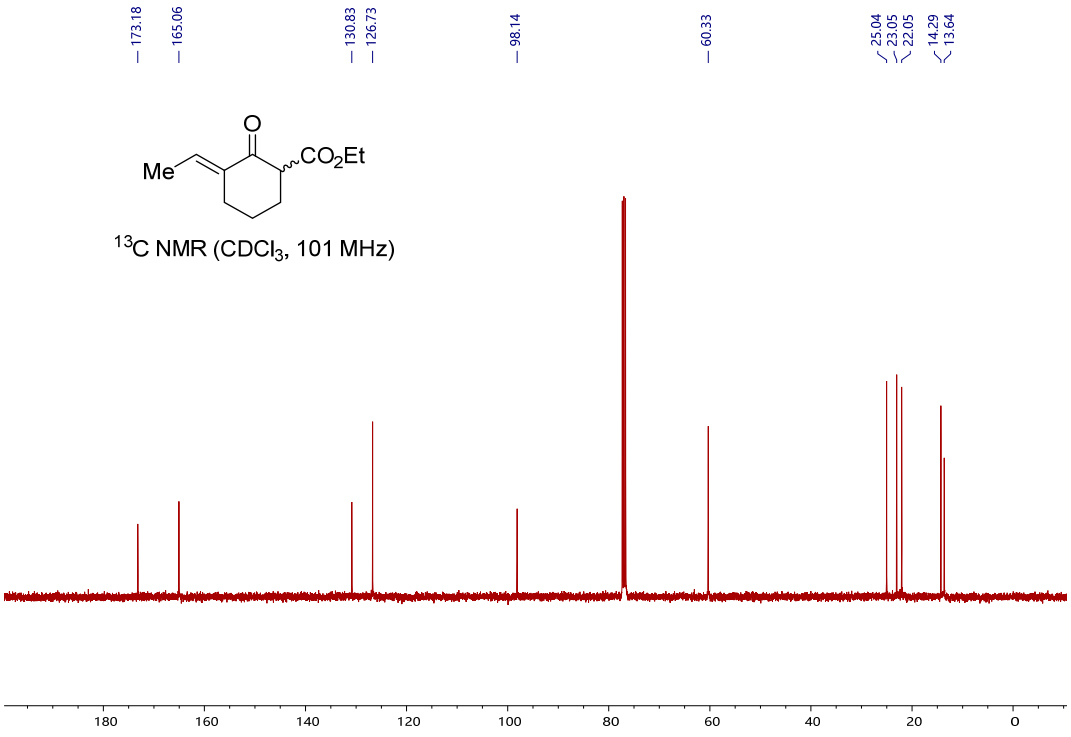
Ethyl 3-methylene-2-oxocyclohexane-1-carboxylate (7aa)



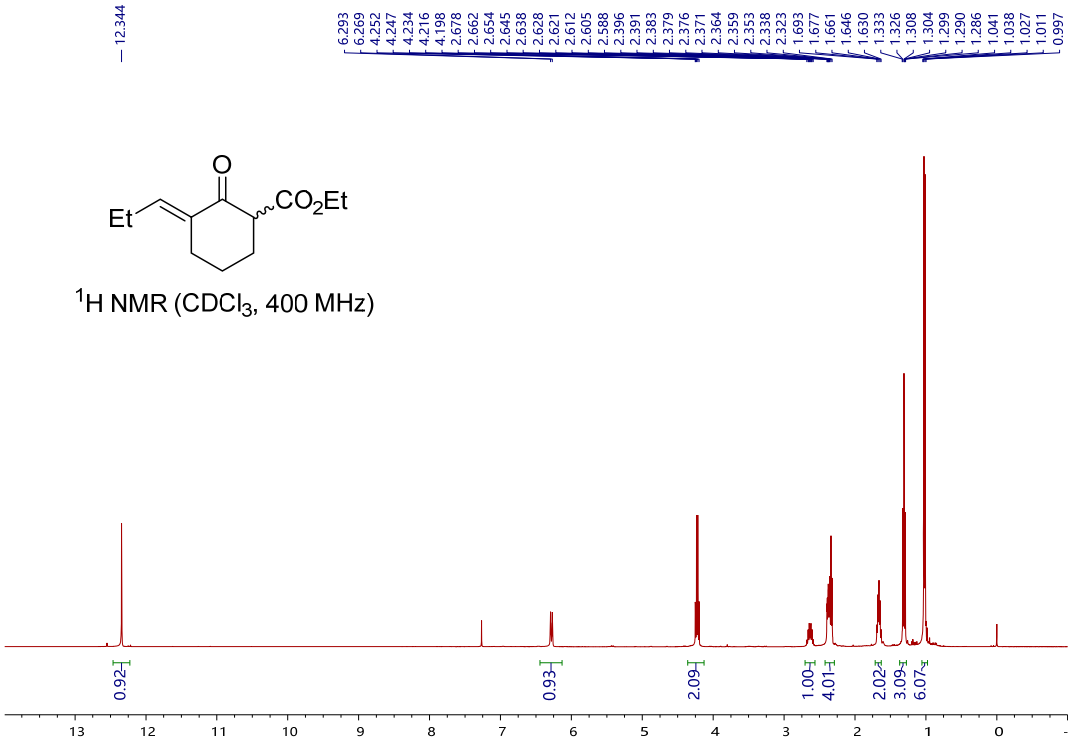


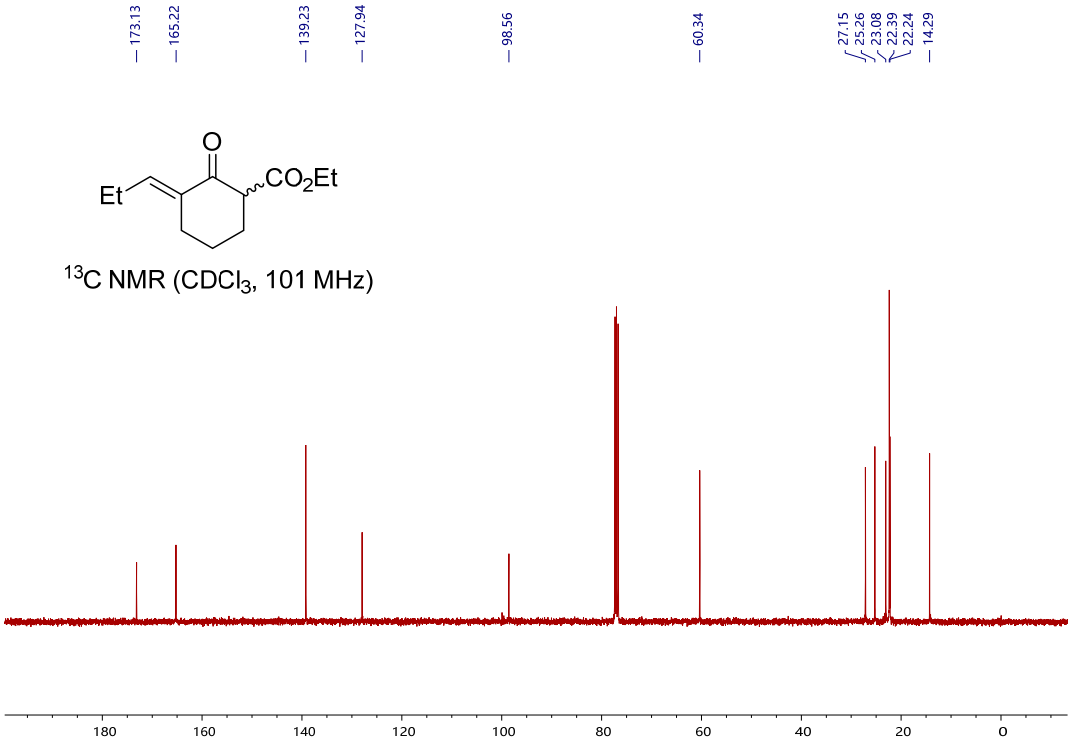
Ethyl (*E*)-3-ethylidene-2-oxocyclohexane-1-carboxylate (7ab)



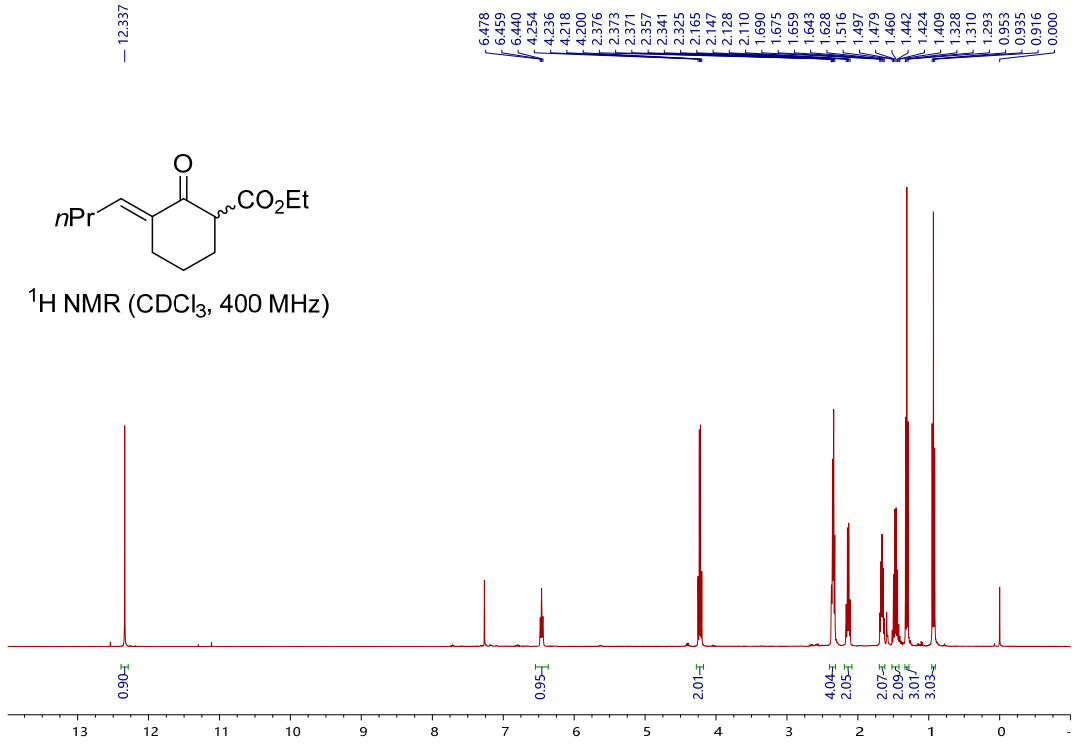


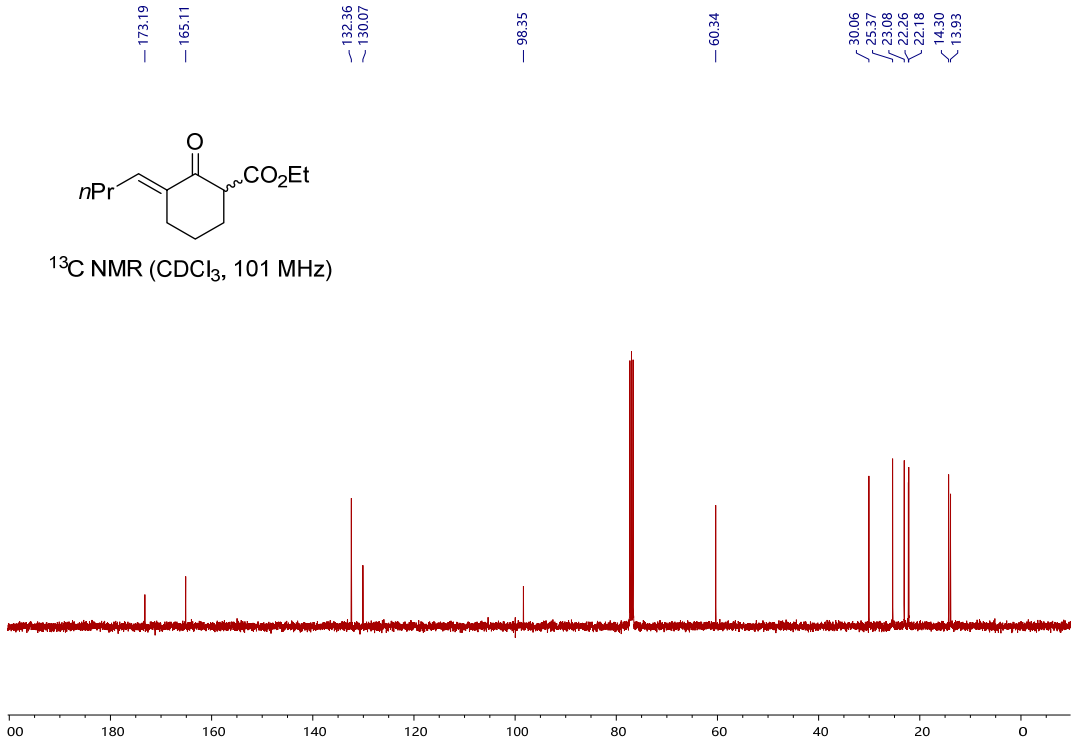
Ethyl (*E*)-3-propylidene-2-oxocyclohexane-1-carboxylate (7ac)



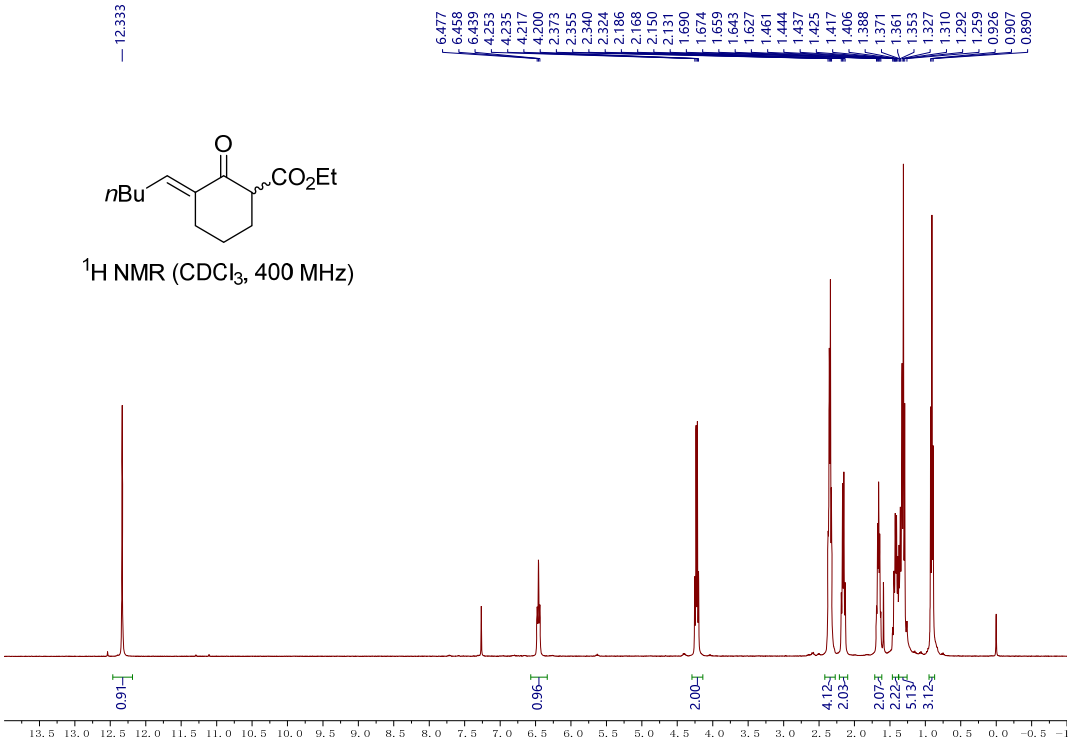


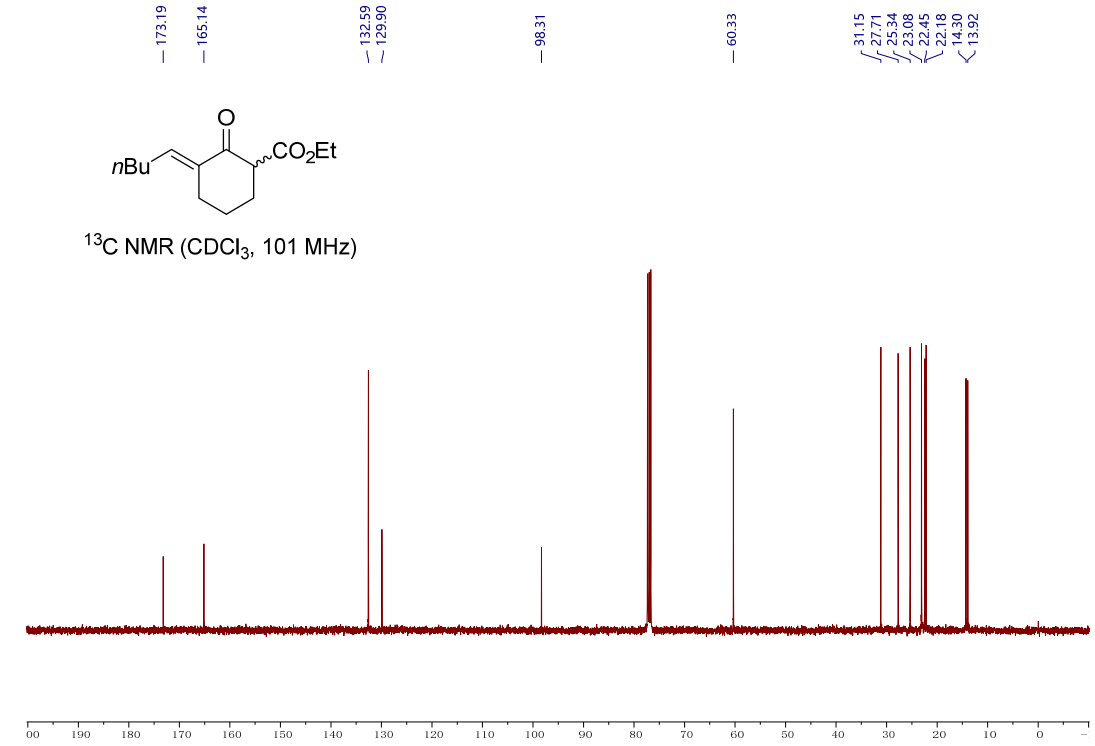
Ethyl (*E*)-3-butylidene-2-oxocyclohexane-1-carboxylate (7ad)



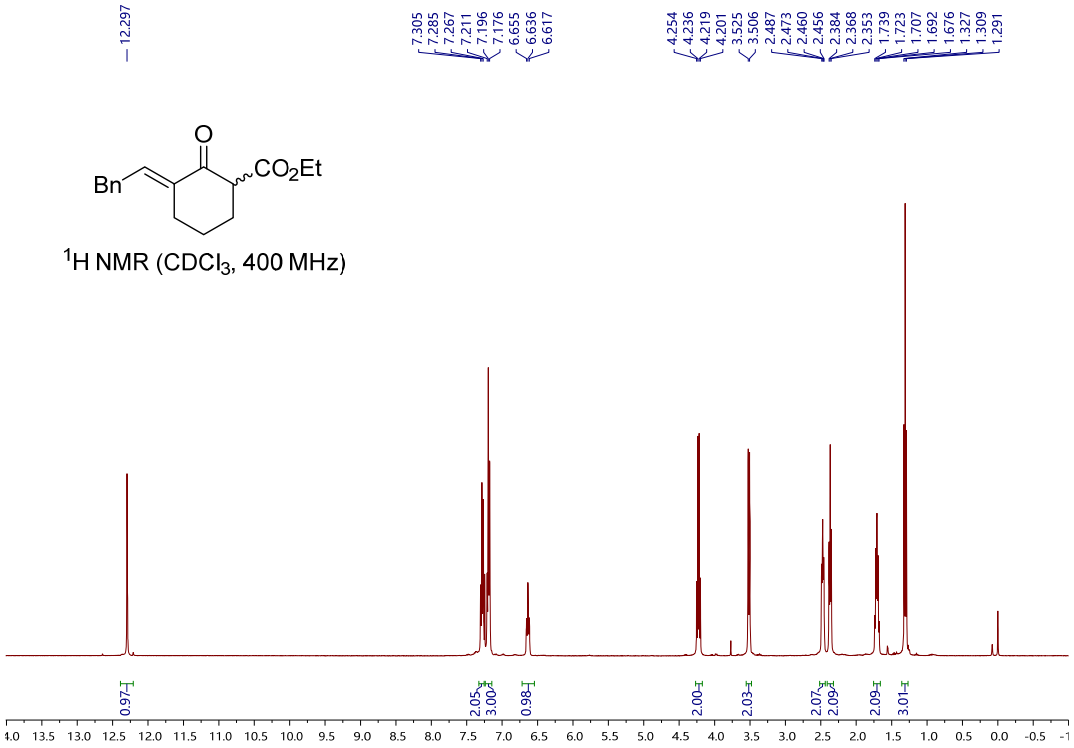


Ethyl (*E*)-2-oxo-3-pentylidenecyclohexane-1-carboxylate (7ae)

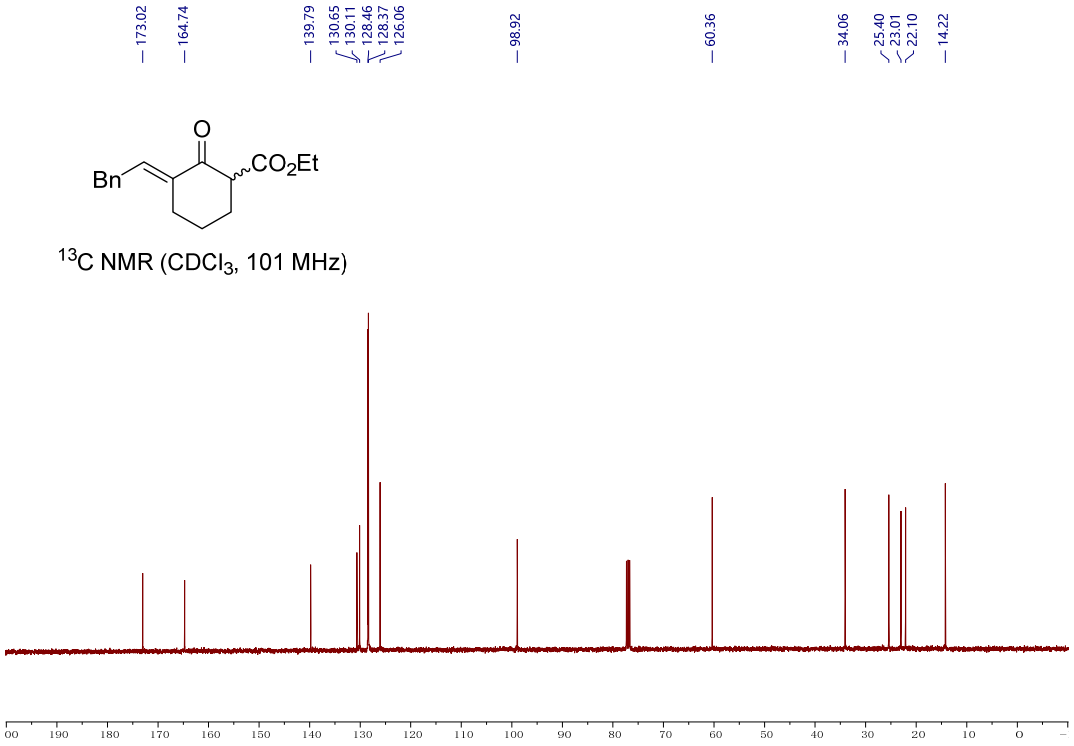




Ethyl (*E*)-2-oxo-3-(2-phenylethylidene)cyclohexane-1-carboxylate (7af)

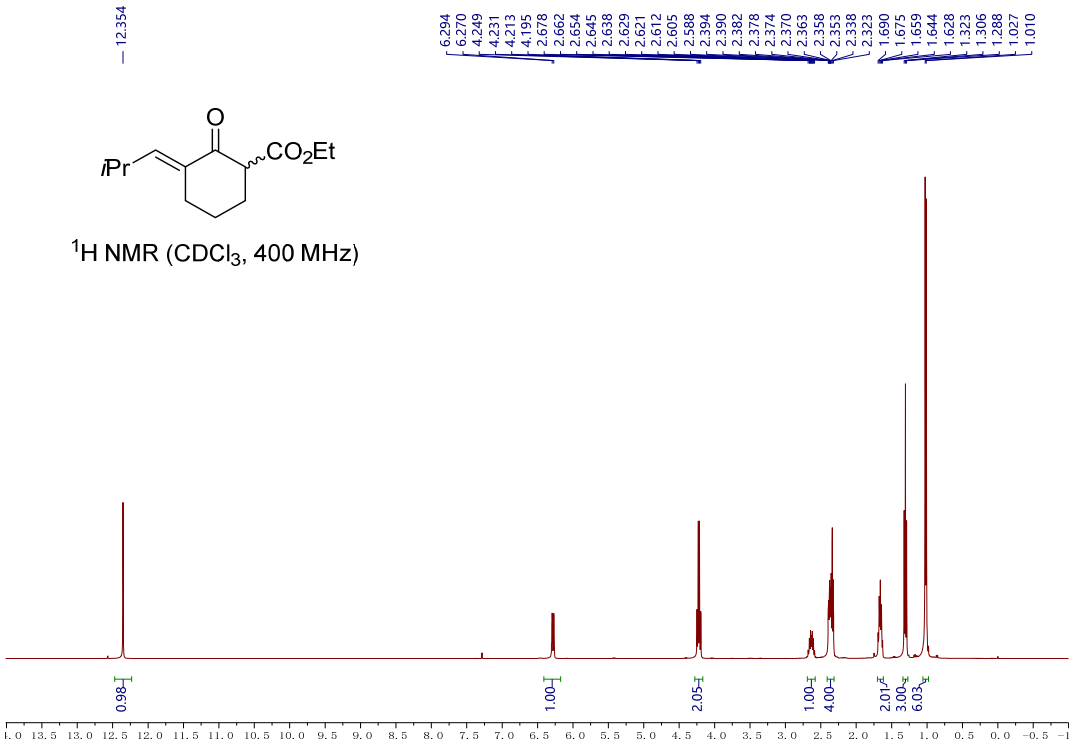


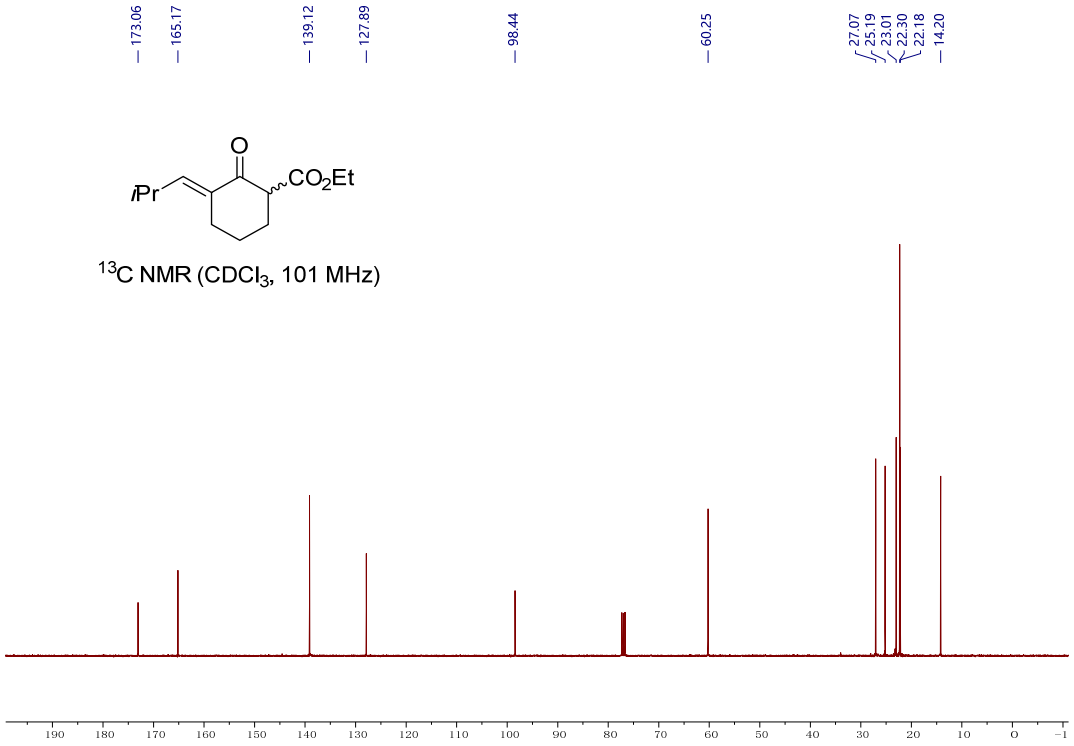
^{1}H NMR ($CDCl_3$, 400 MHz)



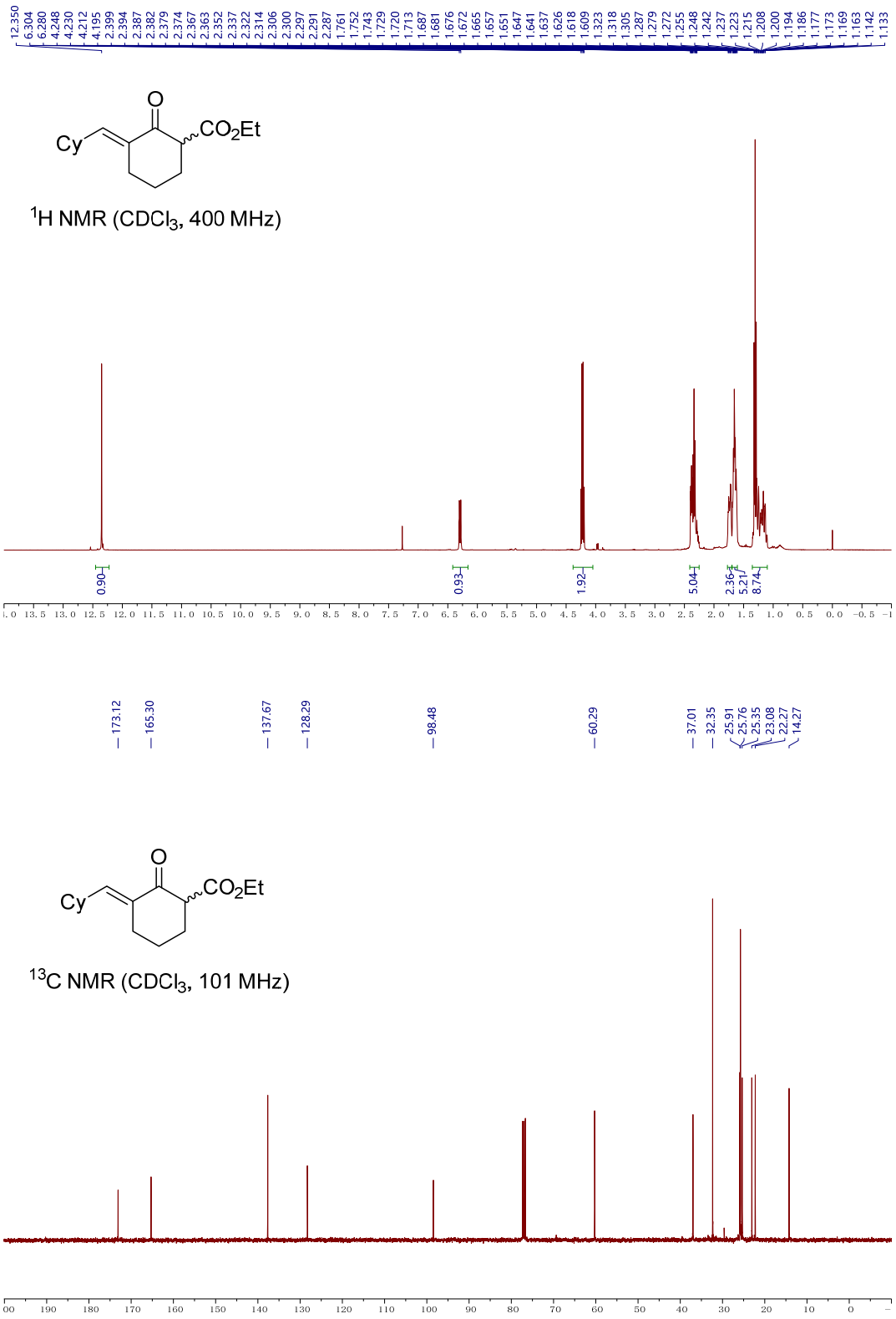
^{13}C NMR ($CDCl_3$, 101 MHz)

Ethyl (*E*)-3-(2-methylpropylidene)-2-oxocyclohexane-1-carboxylate (7ag)

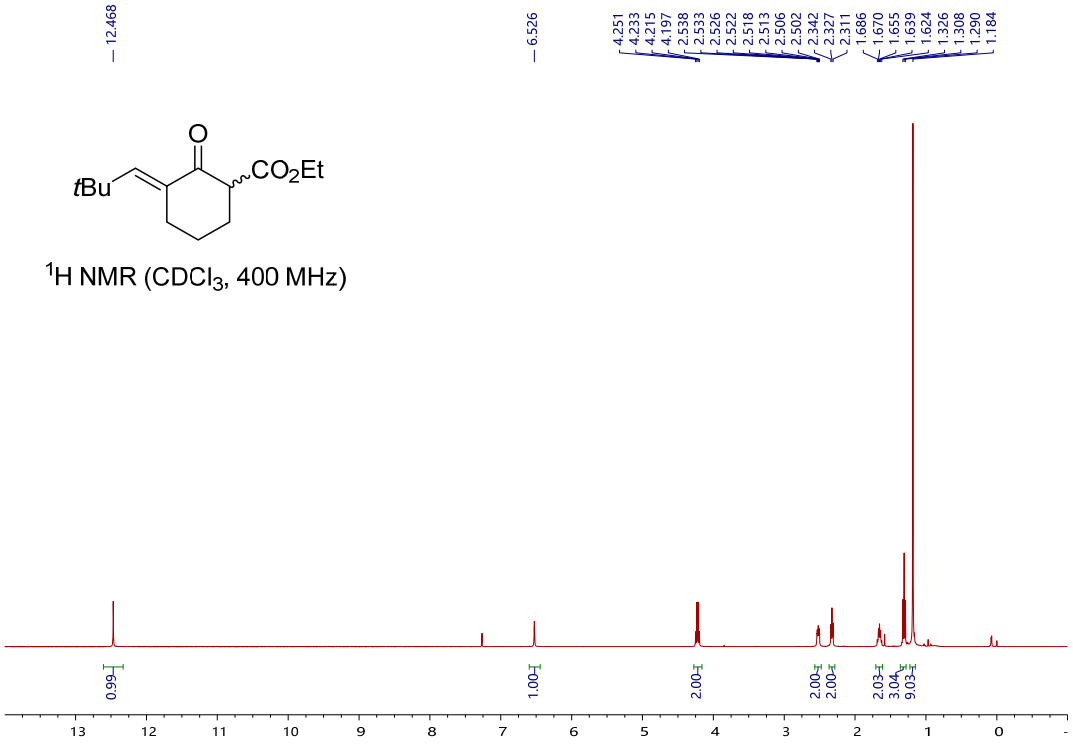


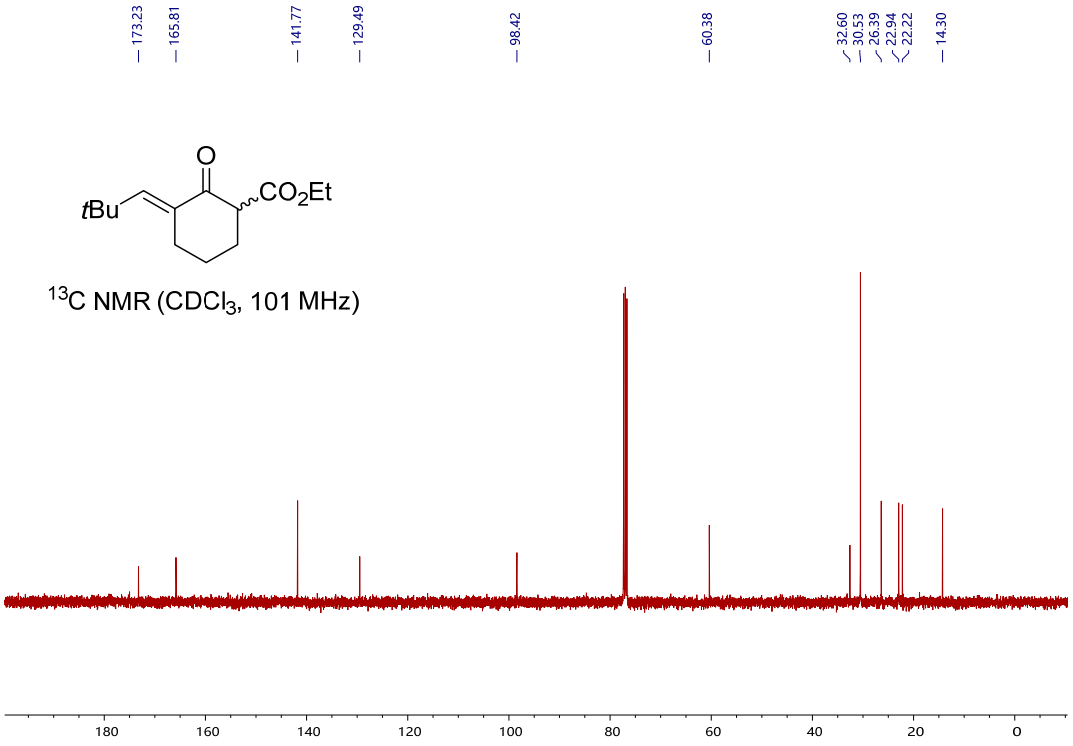


Ethyl (*E*)-3-(cyclohexylmethylene)-2-oxocyclohexane-1-carboxylate (7ah)

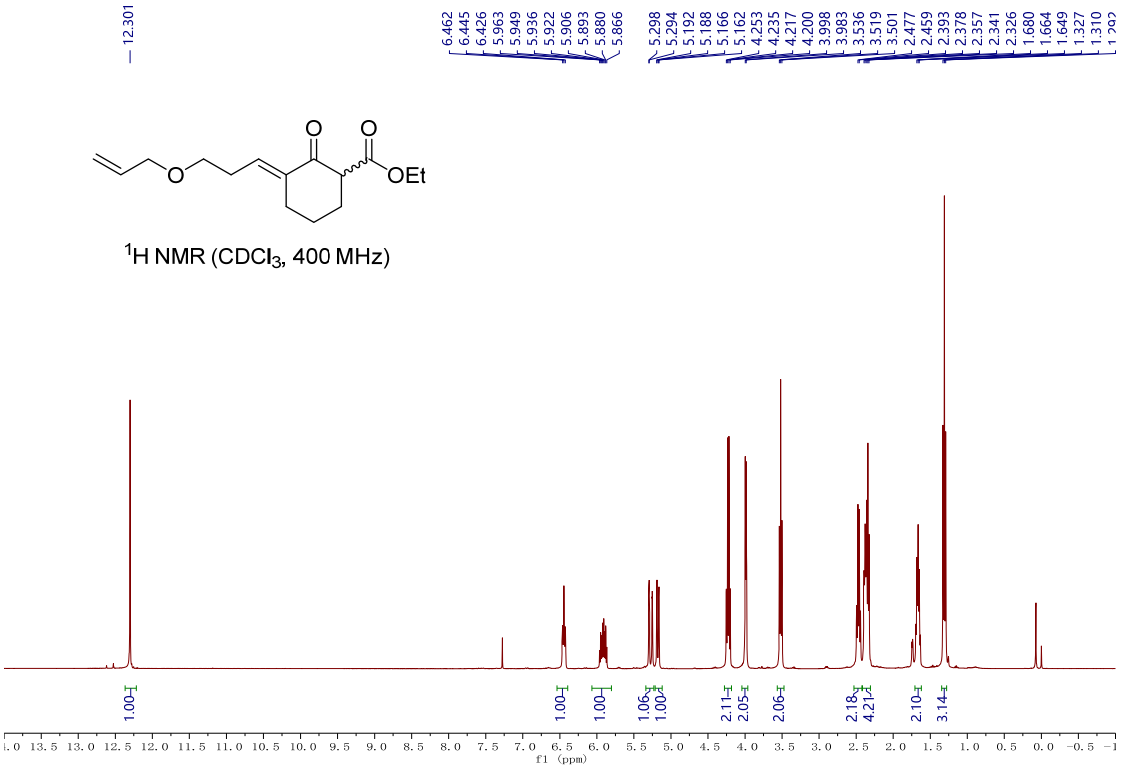


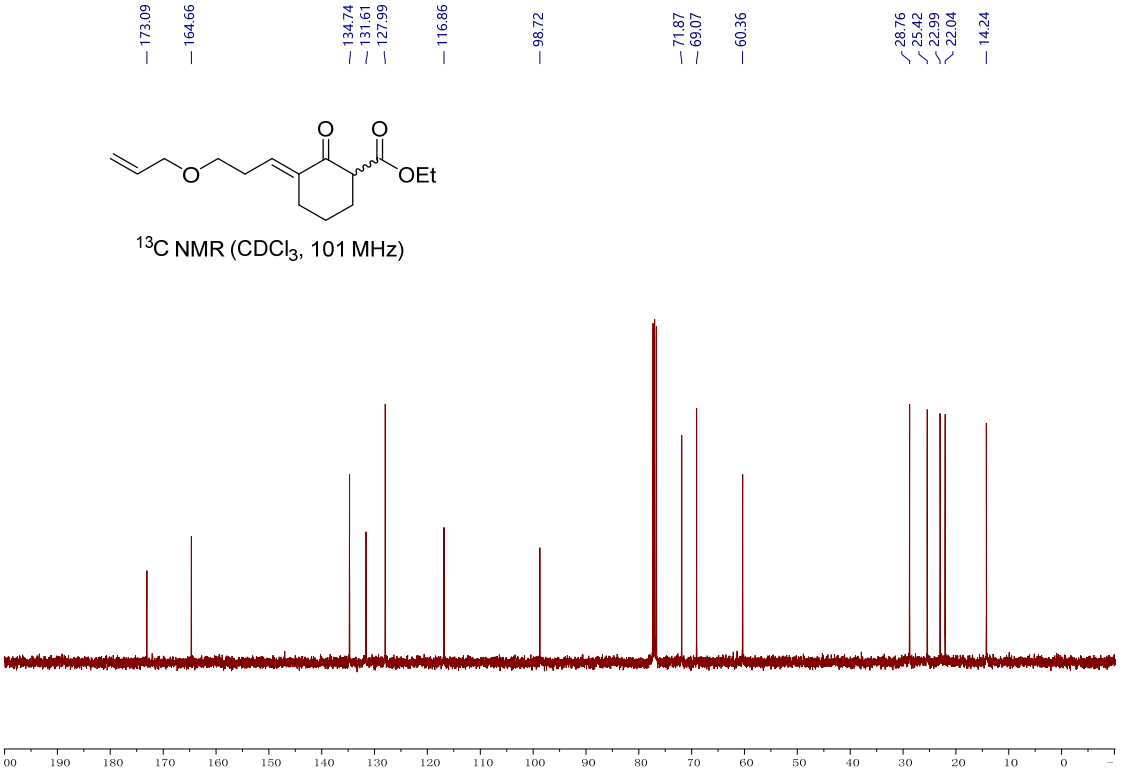
Ethyl (*E*)-3-(2,2-dimethylpropylidene)-2-oxocyclohexane-1-carboxylate (7ai)



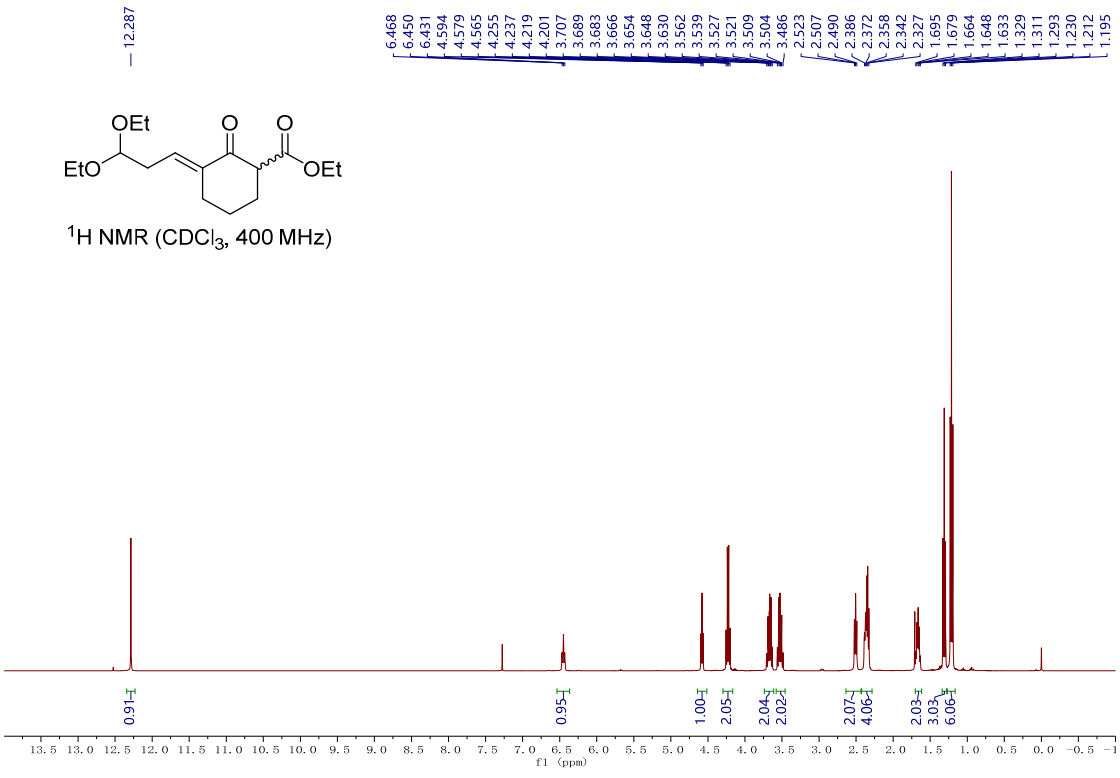


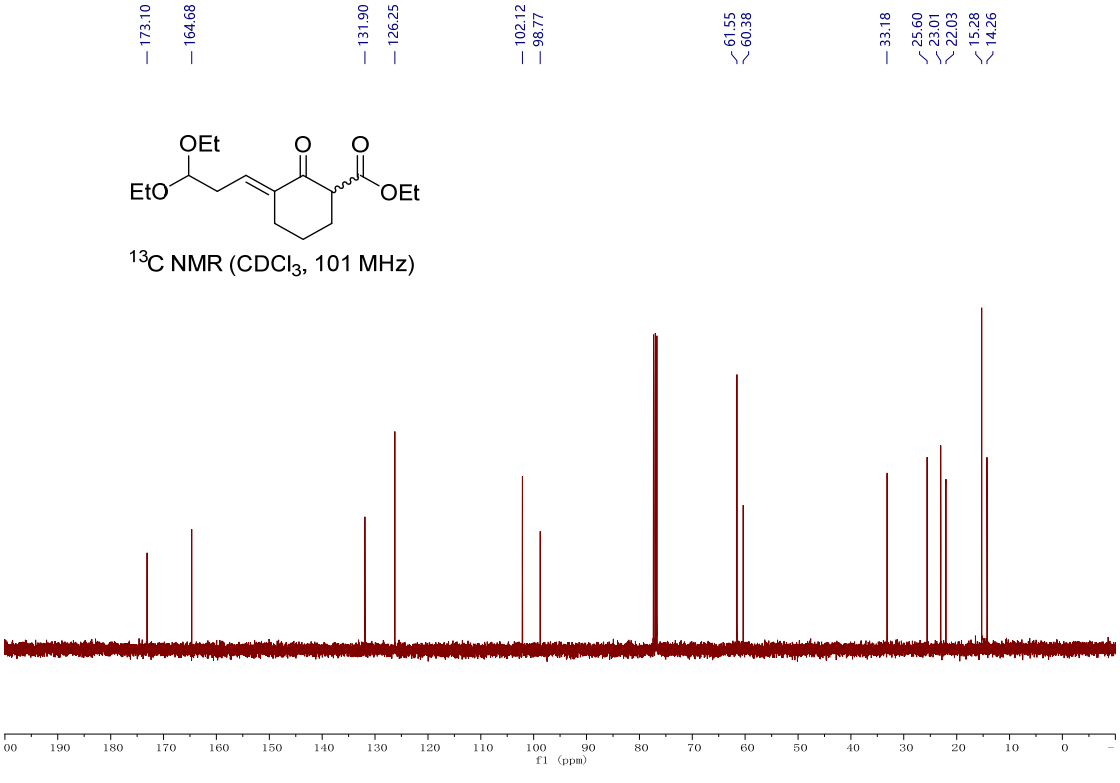
(+)-Ethyl (*E*)-3-(3-(allyloxy)propylidene)-2-oxocyclohexane-1-carboxylate (7aj)



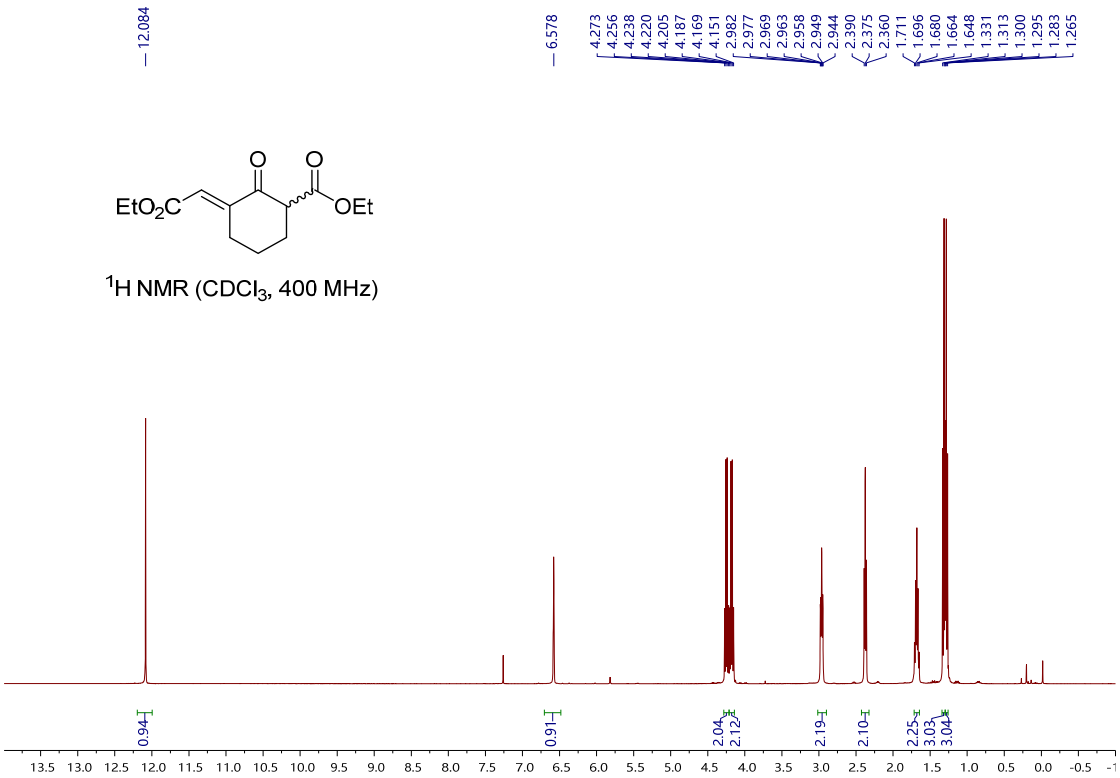


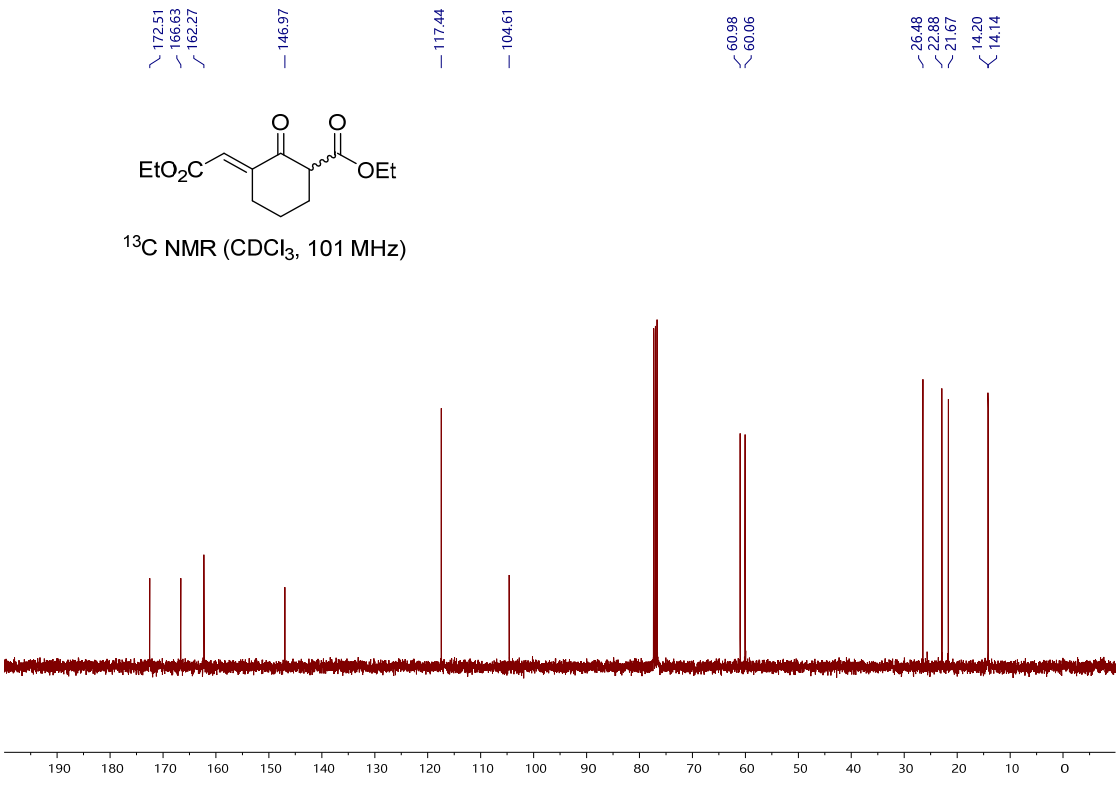
Ethyl (*E*)-3-(3,3-diethoxypropylidene)-2-oxocyclohexane-1-carboxylate (7ak)



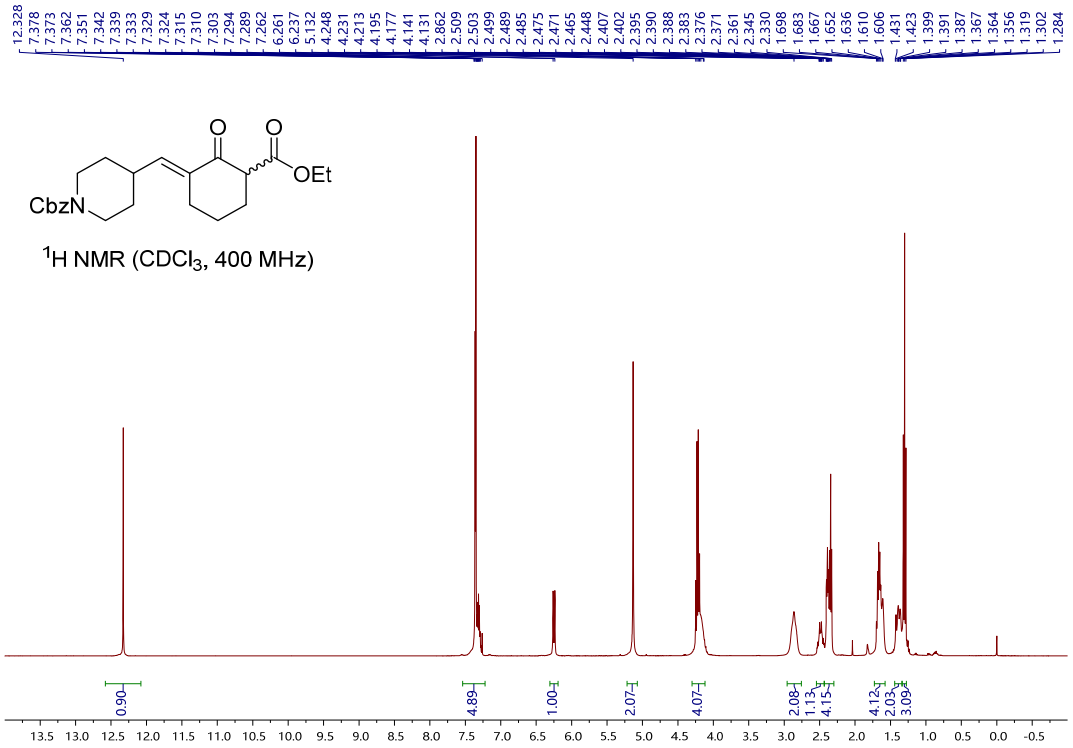


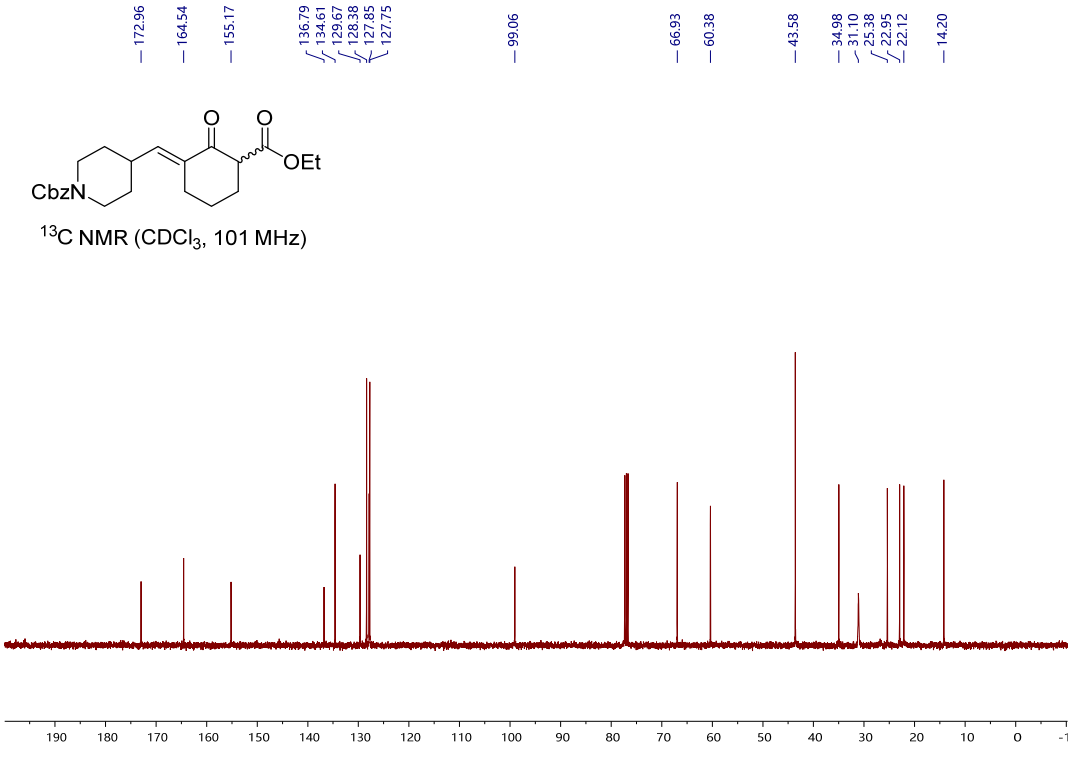
Ethyl (*E*)-3-(2-ethoxy-2-oxoethylidene)-2-oxocyclohexane-1-carboxylate (7al)



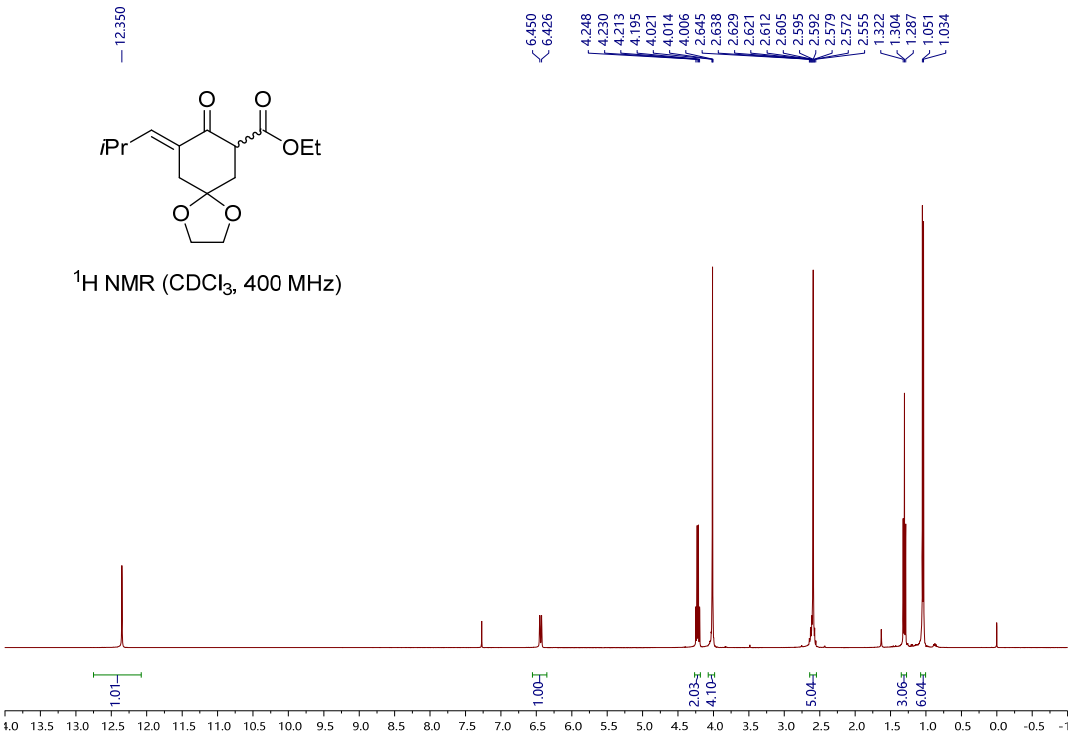


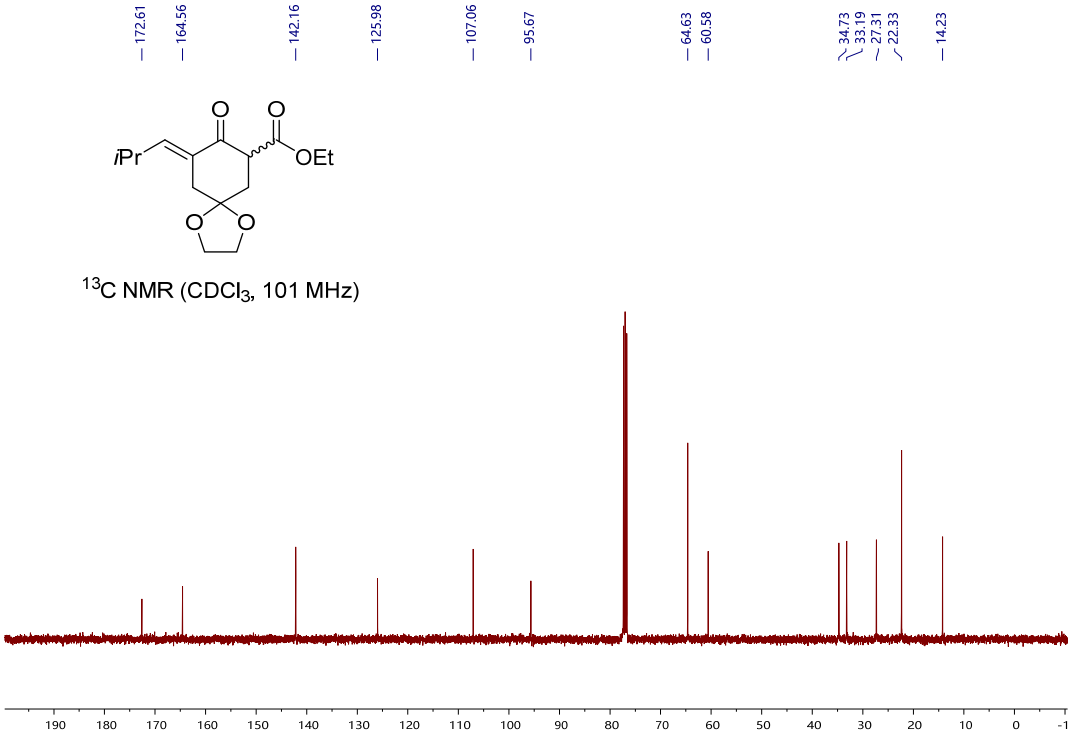
Benzyl (*E*)-4-((3-(ethoxycarbonyl)-2-oxocyclohexylidene)methyl)piperidine-1-carboxylate (7am)



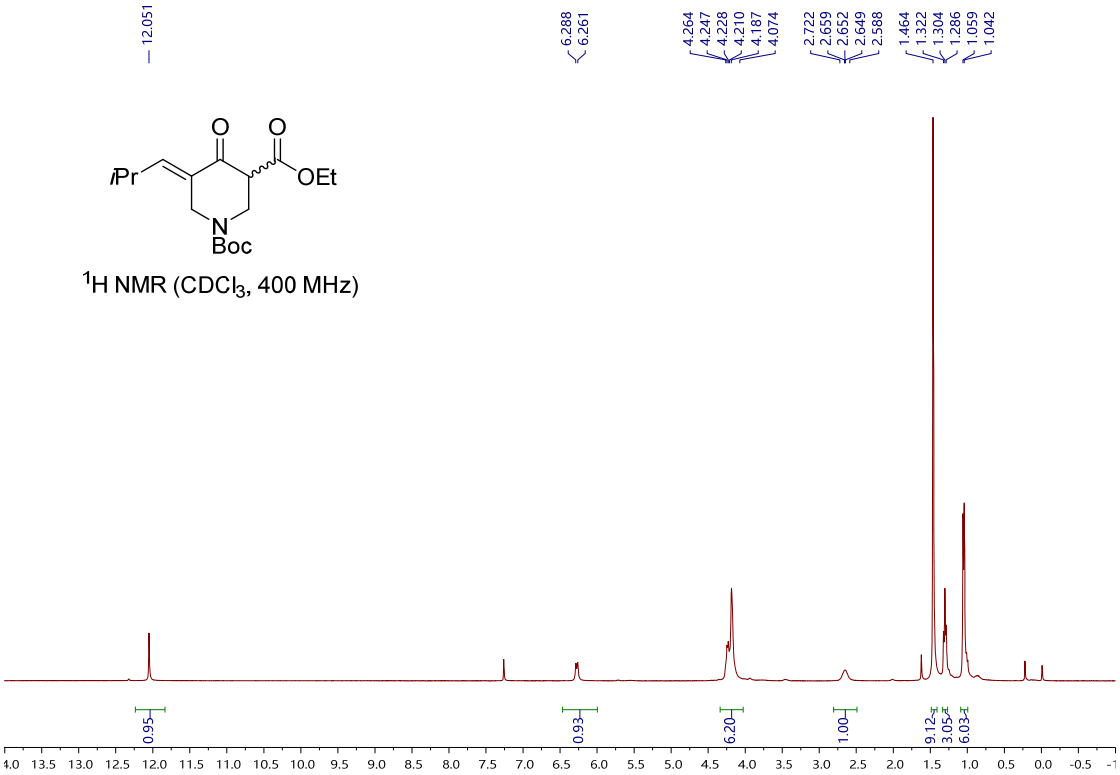


Ethyl (*E*)-9-(2-methylpropylidene)-8-oxo-1,4-dioxaspiro[4.5]decane-7-carboxylate (7an)

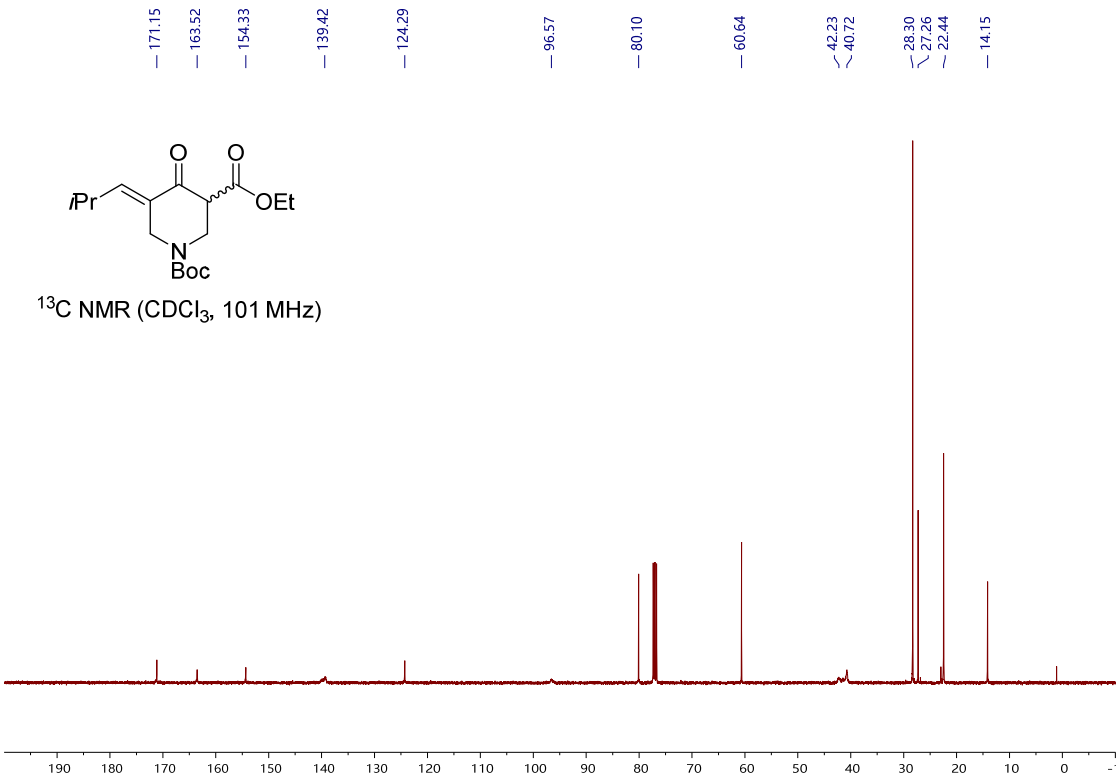




1-(*tert*-Butyl) 3-ethyl (*E*)-5-(2-methylpropylidene)-4-oxopiperidine-1,3-dicarboxylate (7ao)

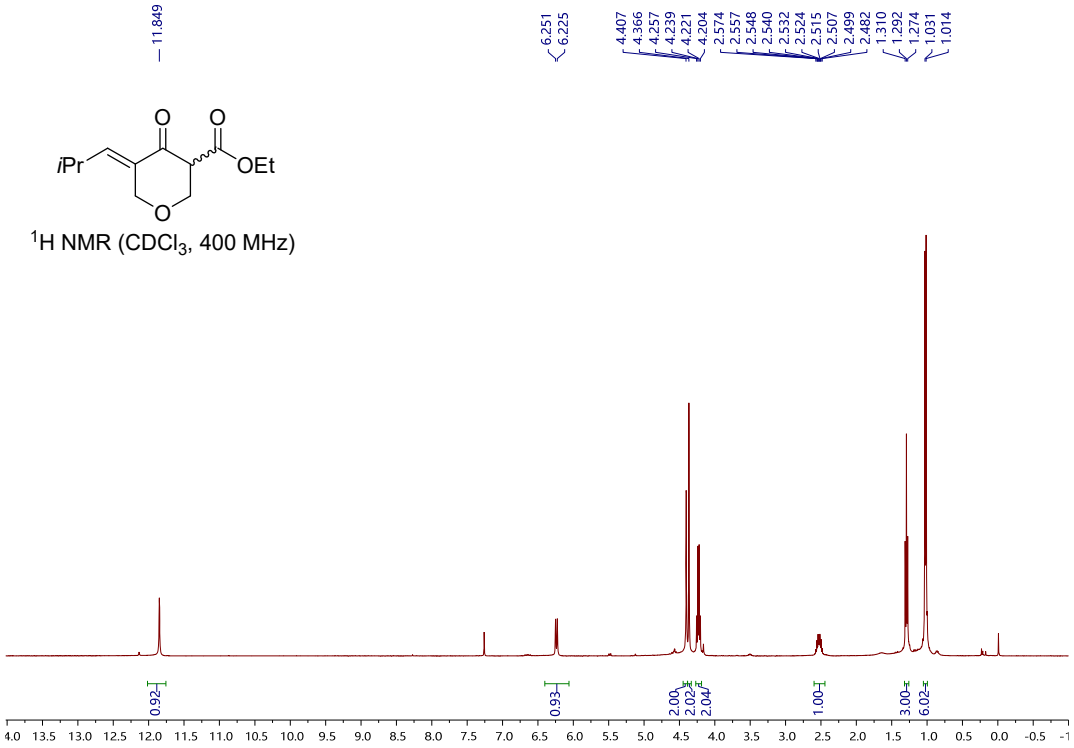


^{1}H NMR ($CDCl_3$, 400 MHz)

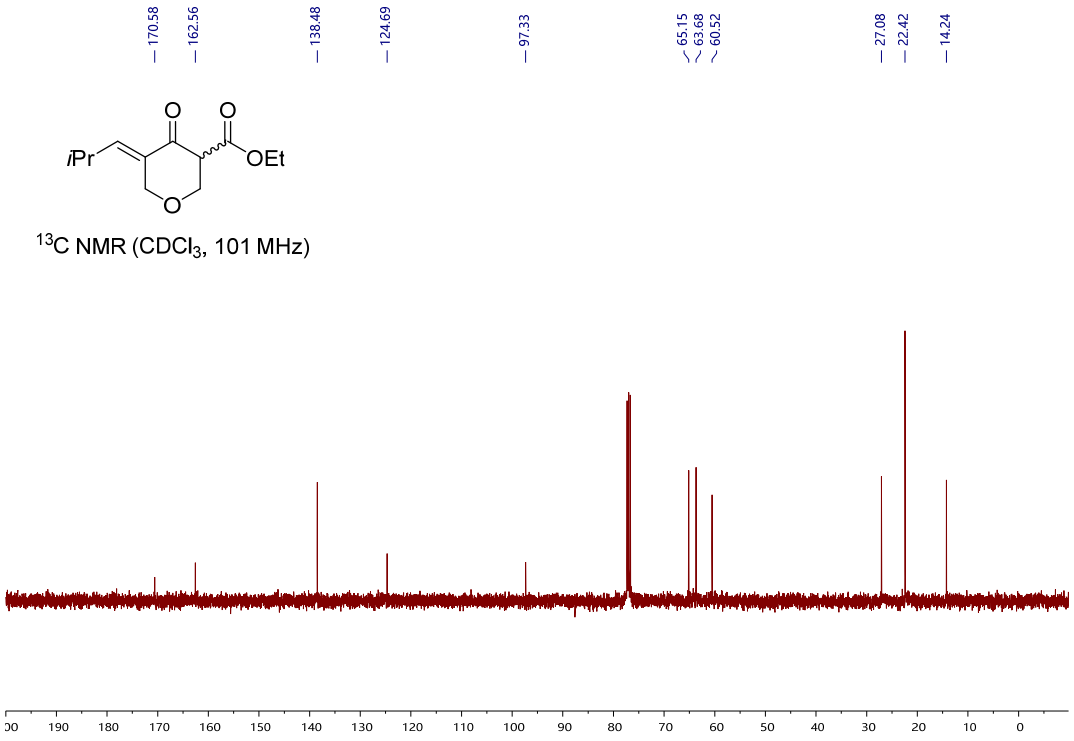


^{13}C NMR ($CDCl_3$, 101 MHz)

Ethyl (*E*)-5-(2-methylpropylidene)-4-oxotetrahydro-2H-pyran-3-carboxylate (7ap)

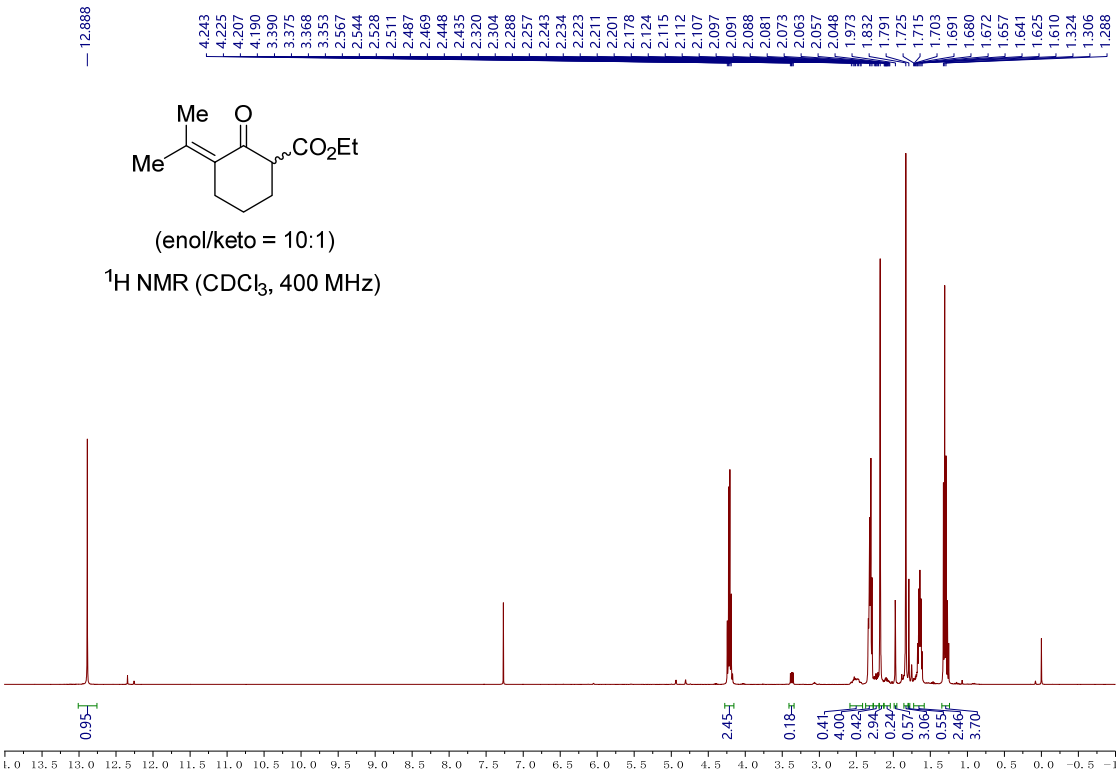


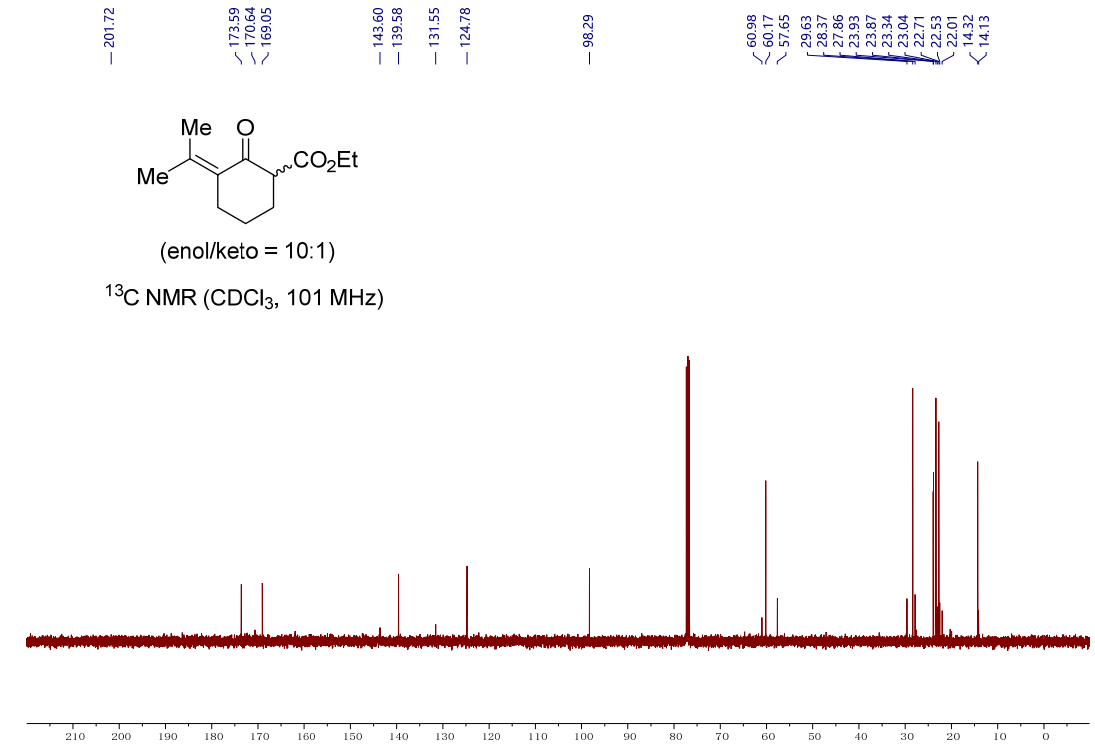
^{1}H NMR ($CDCl_3$, 400 MHz)



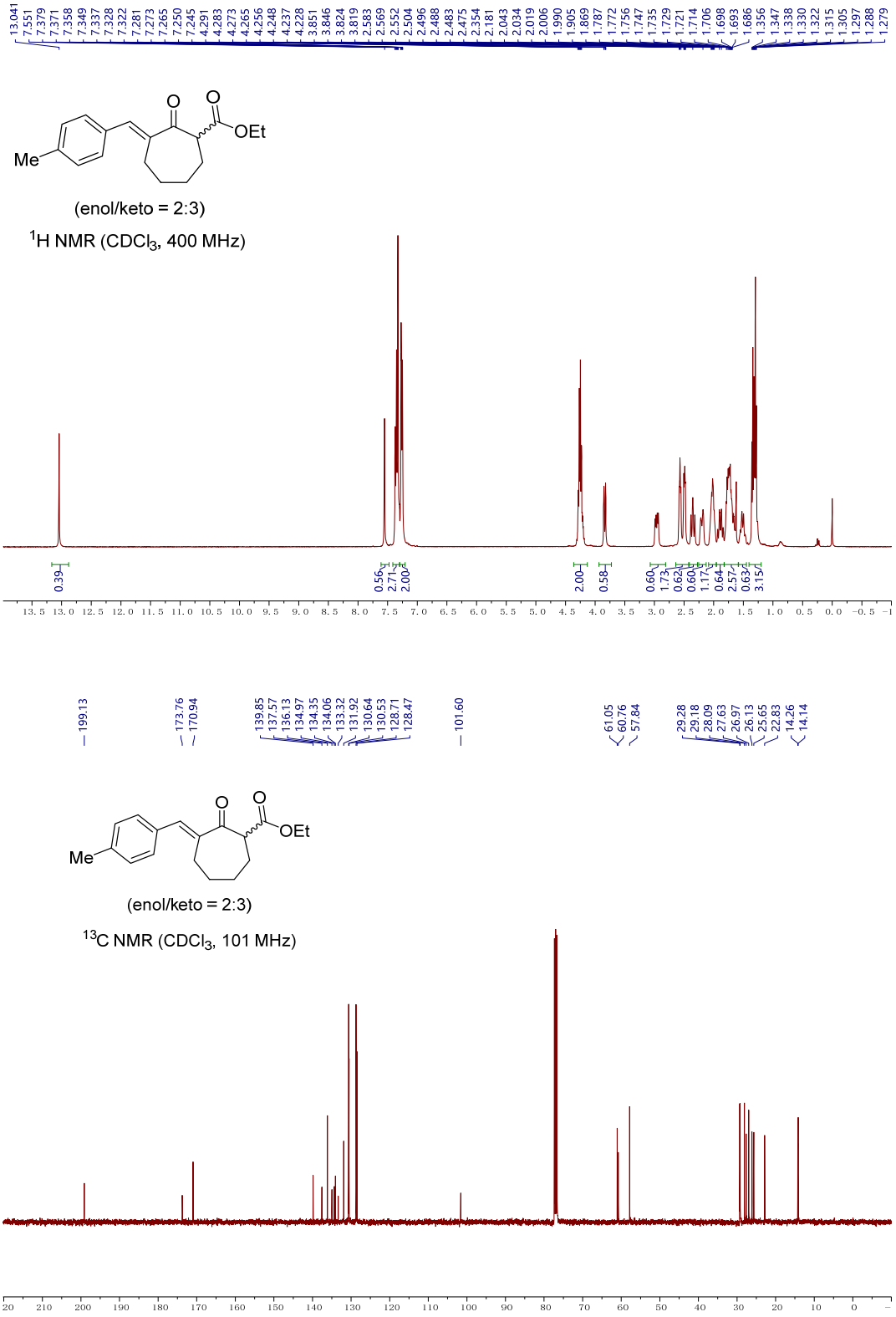
^{13}C NMR ($CDCl_3$, 101 MHz)

Ethyl 2-oxo-3-(propan-2-ylidene)cyclohexane-1-carboxylate (7aq)

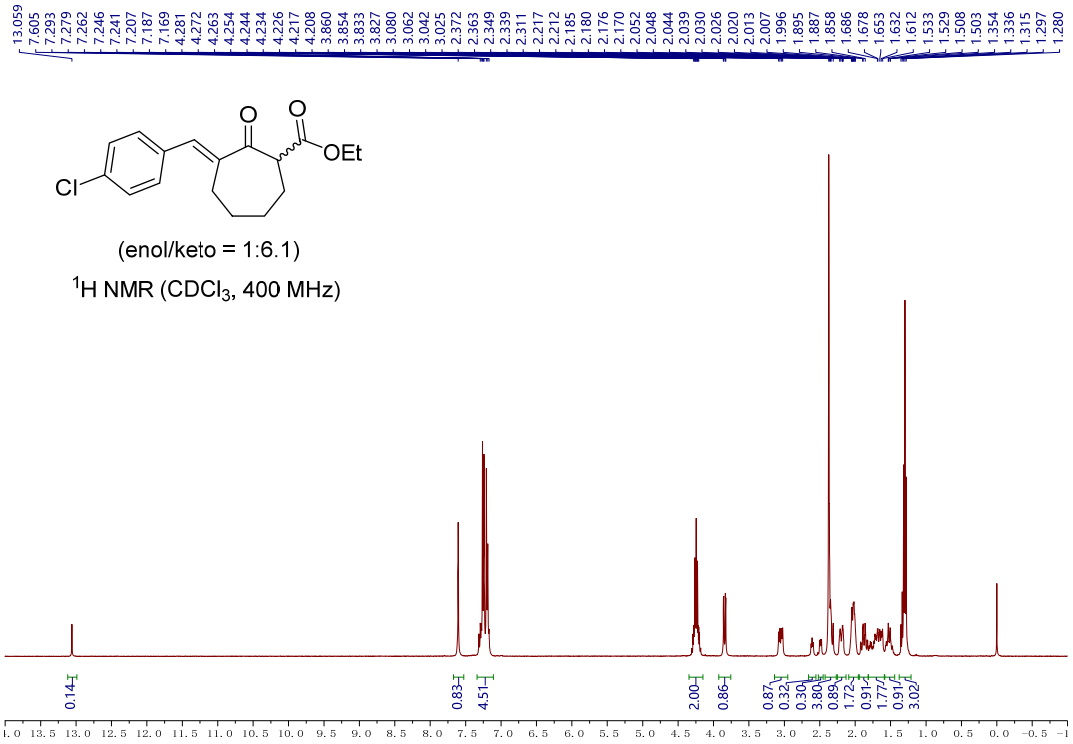


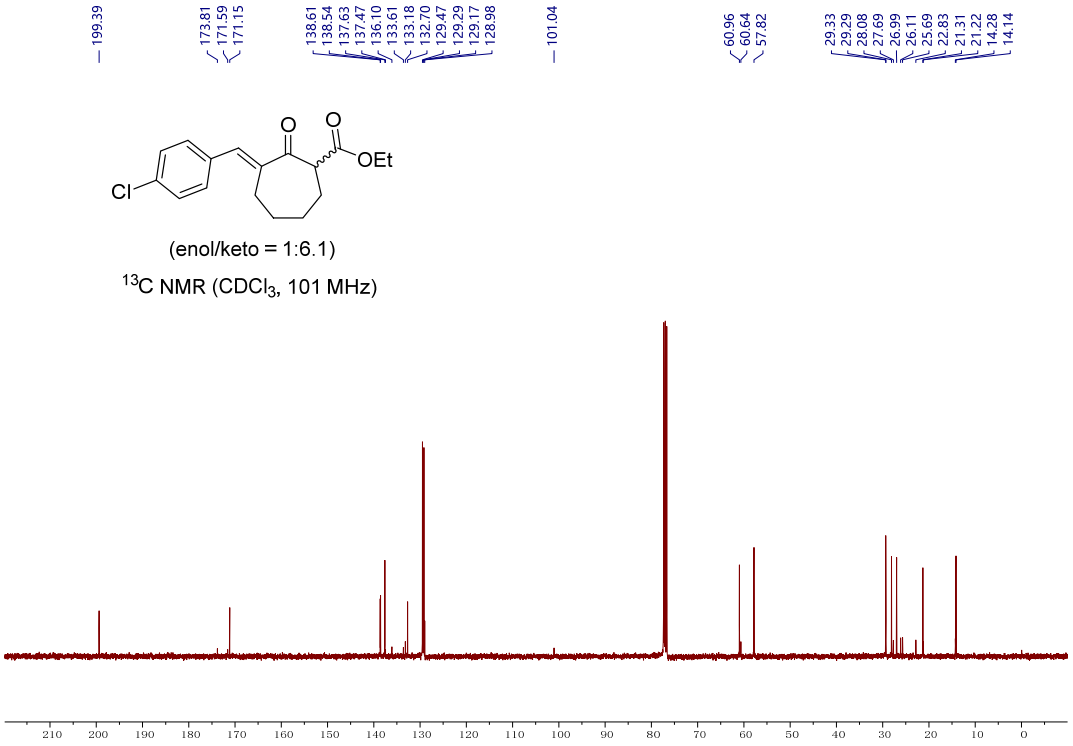


Ethyl (*E*)-3-(4-methylbenzylidene)-2-oxocycloheptane-1-carboxylate (9a)

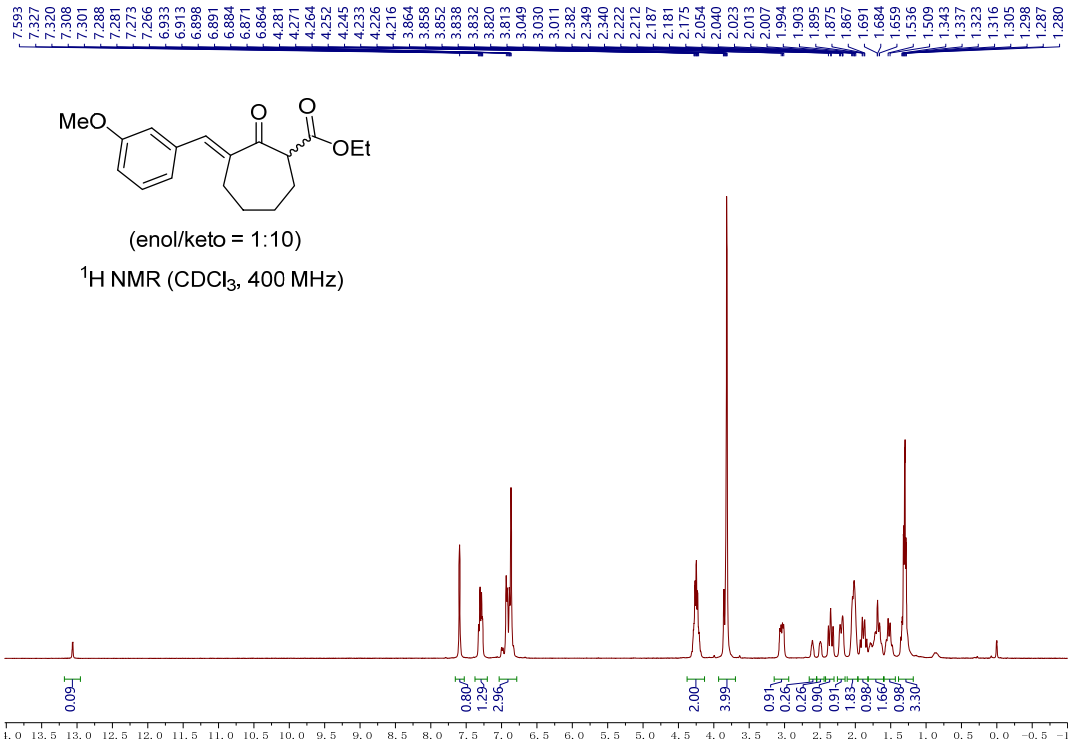


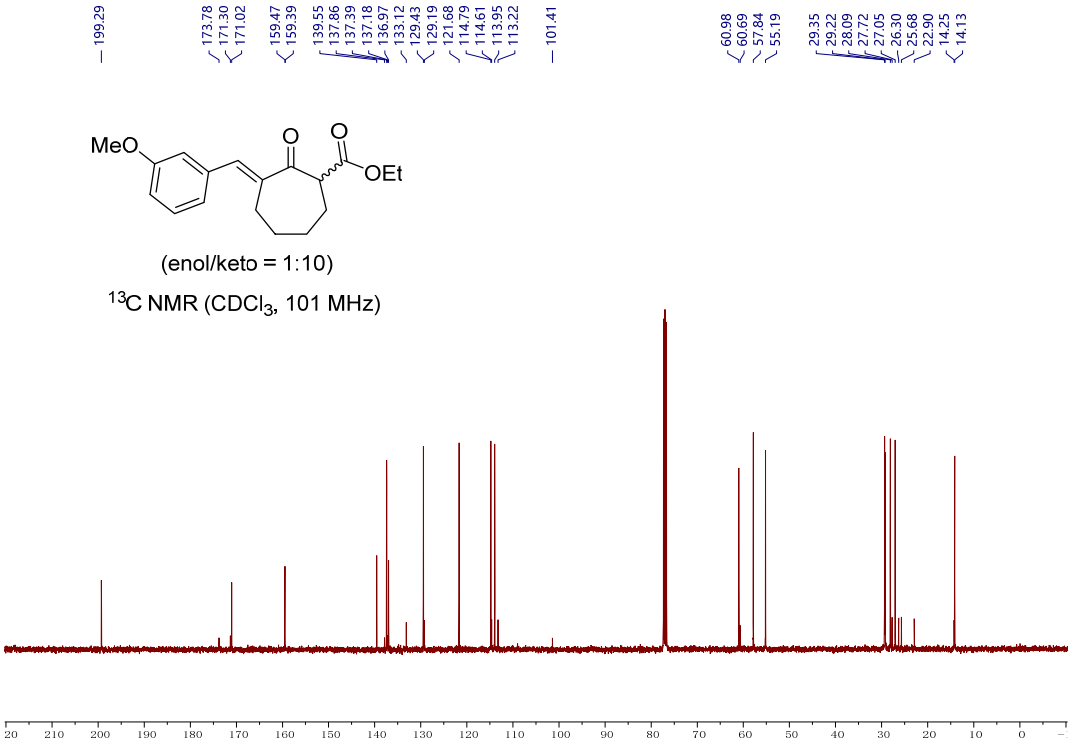
Ethyl (*E*)-3-(4-chlorobenzylidene)-2-oxocycloheptane-1-carboxylate (9b)



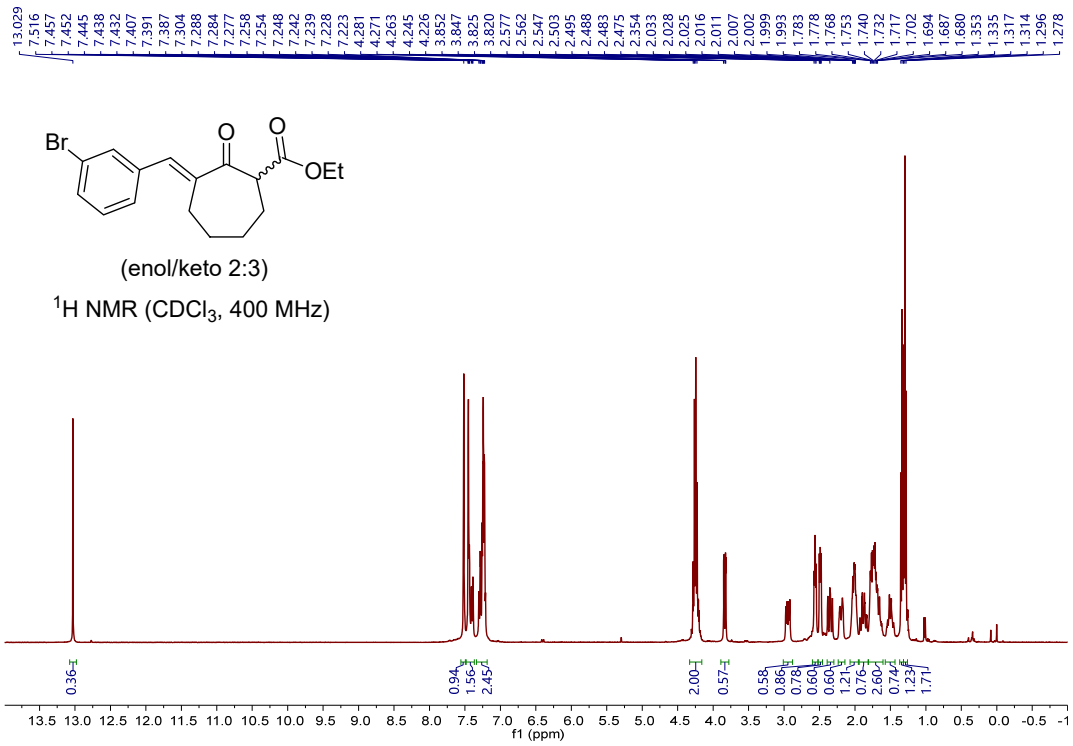


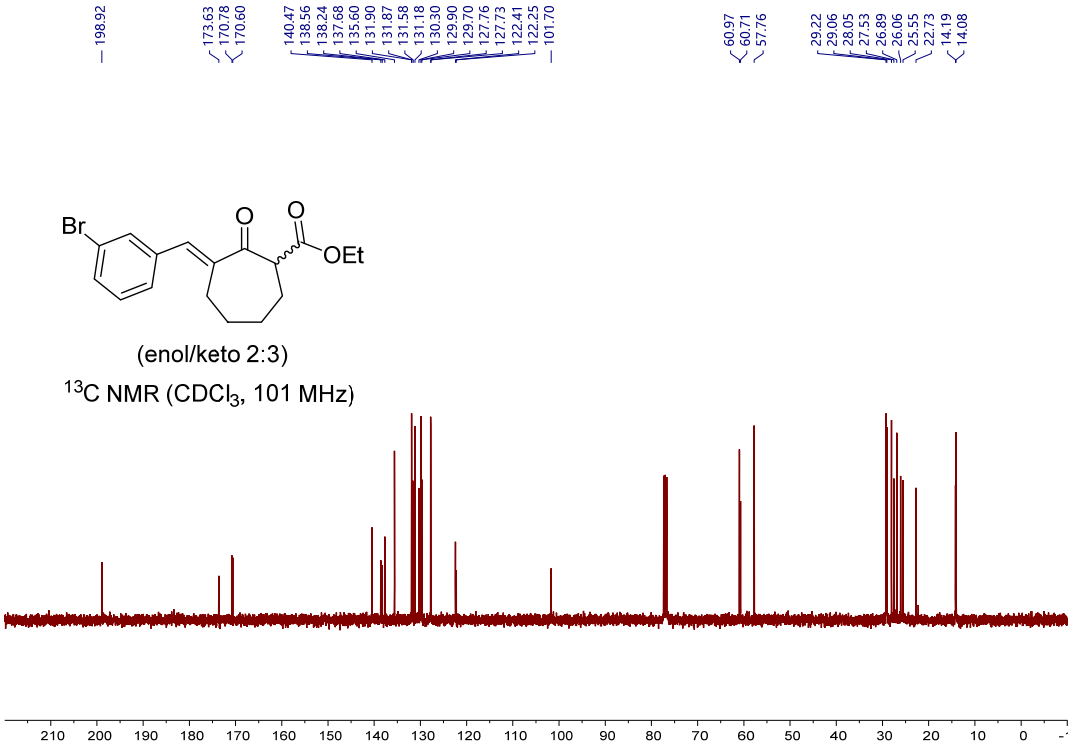
Ethyl (*E*)-3-(3-methoxybenzylidene)-2-oxocycloheptane-1-carboxylate (9c)



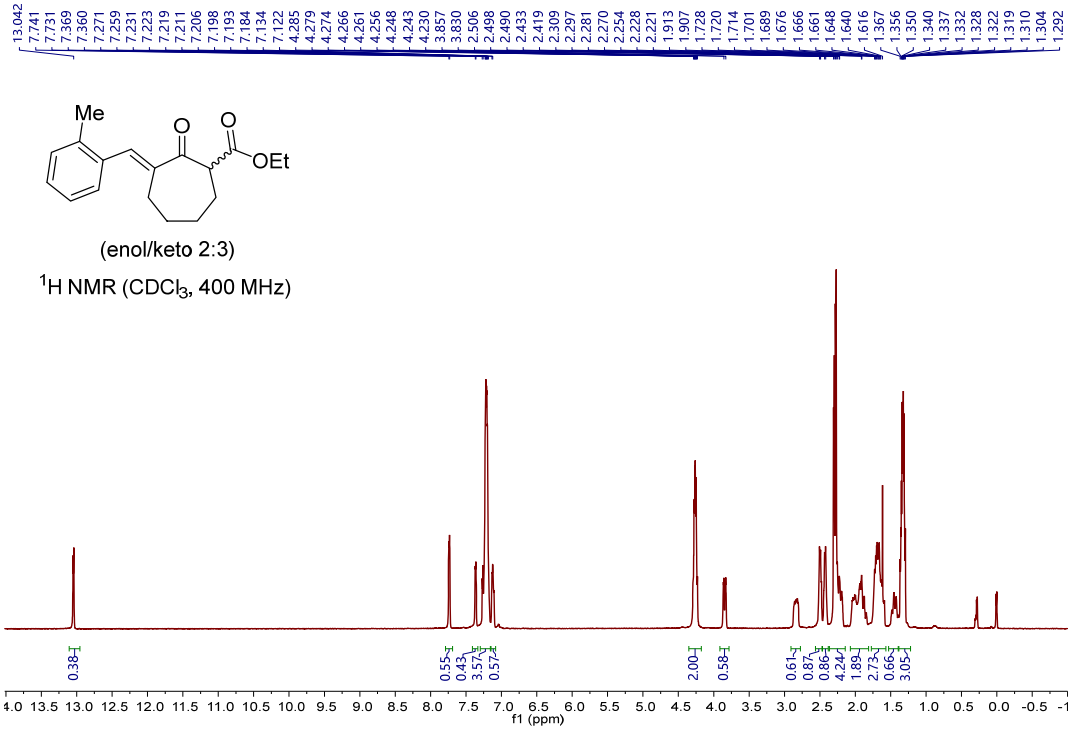


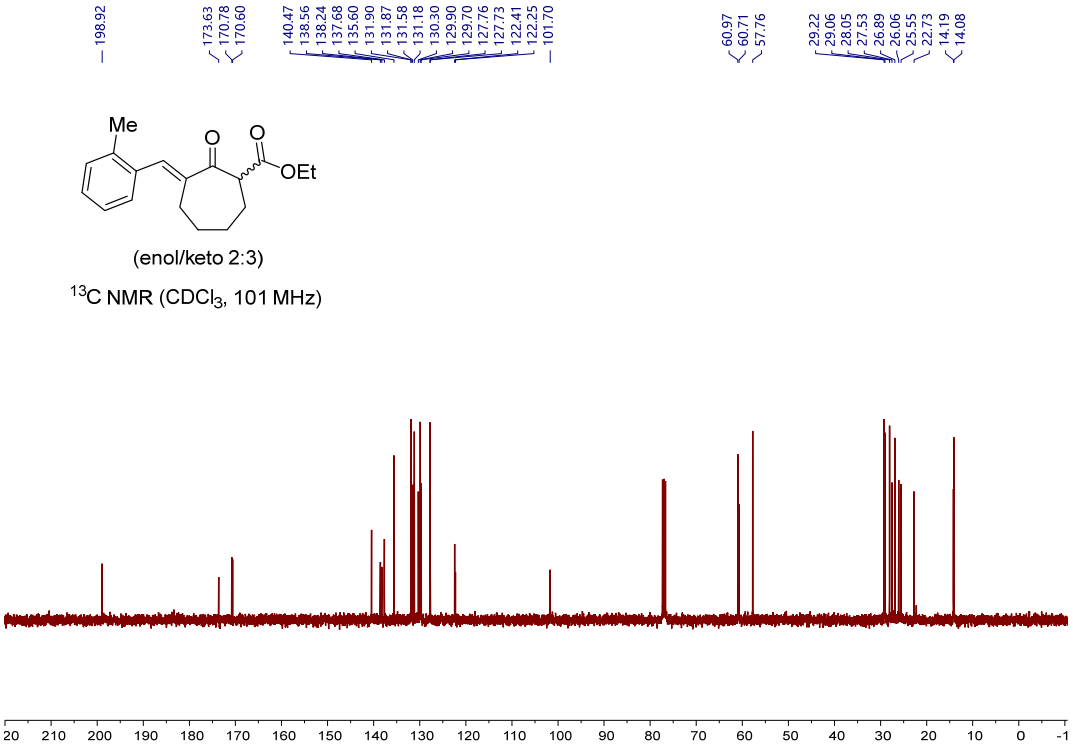
Ethyl (*E*)-3-(3-bromobenzylidene)-2-oxocycloheptane-1-carboxylate (9d)



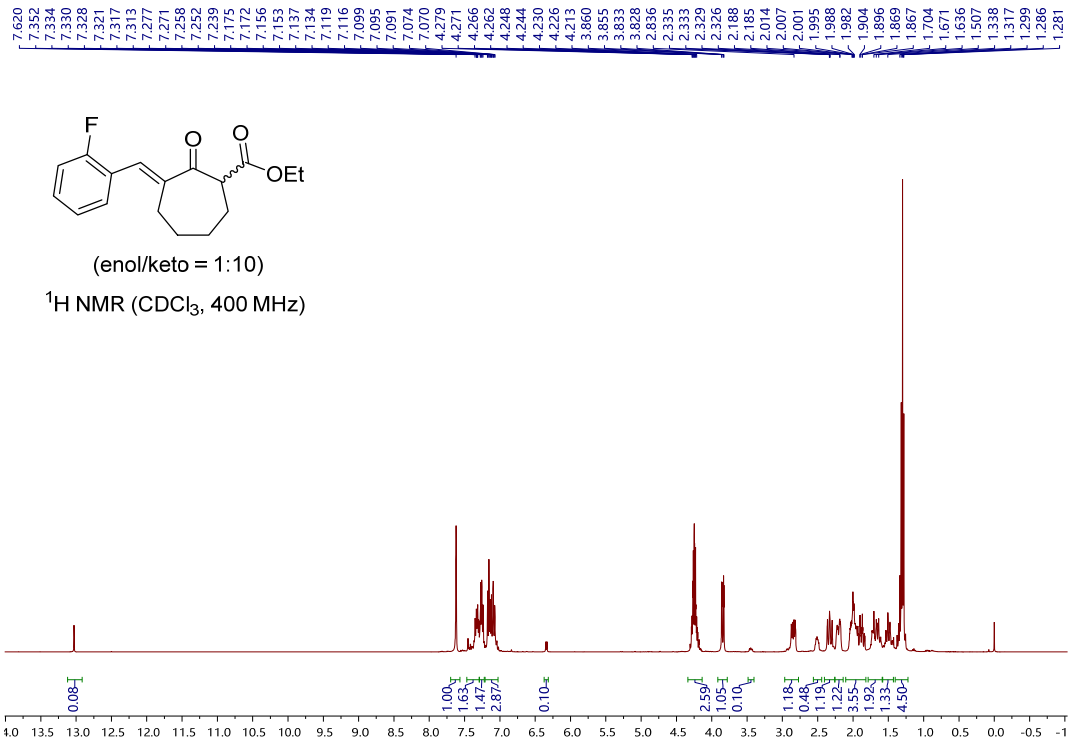


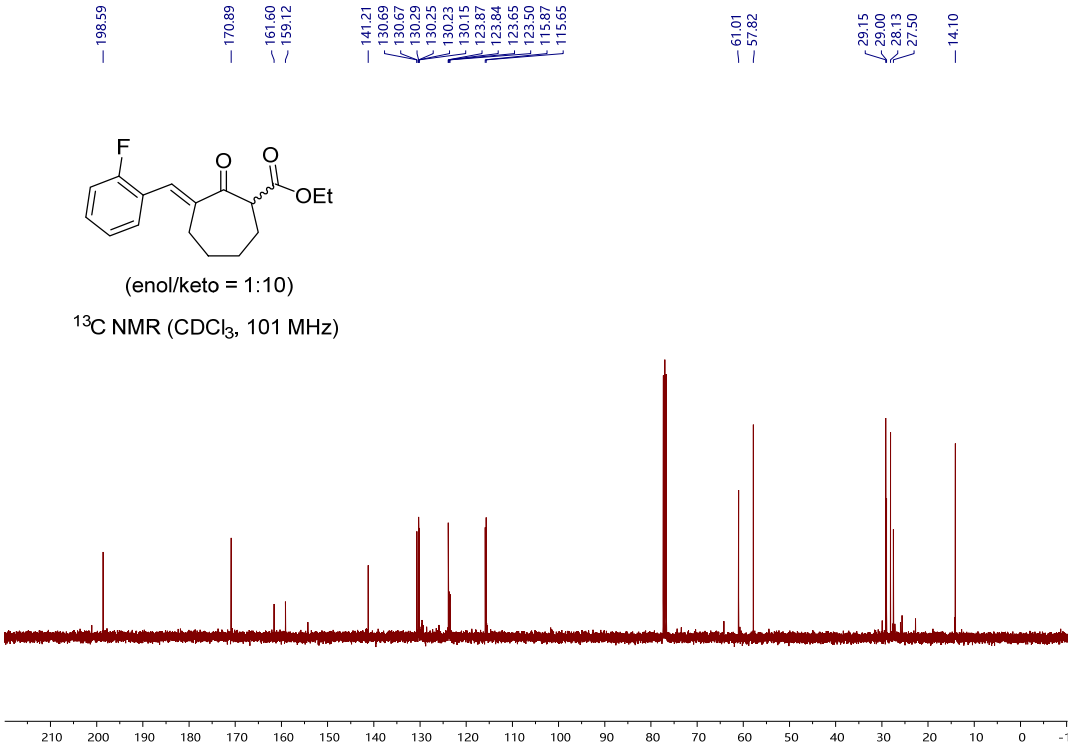
Ethyl (*E*)-3-(2-methylbenzylidene)-2-oxocycloheptane-1-carboxylate (9e)



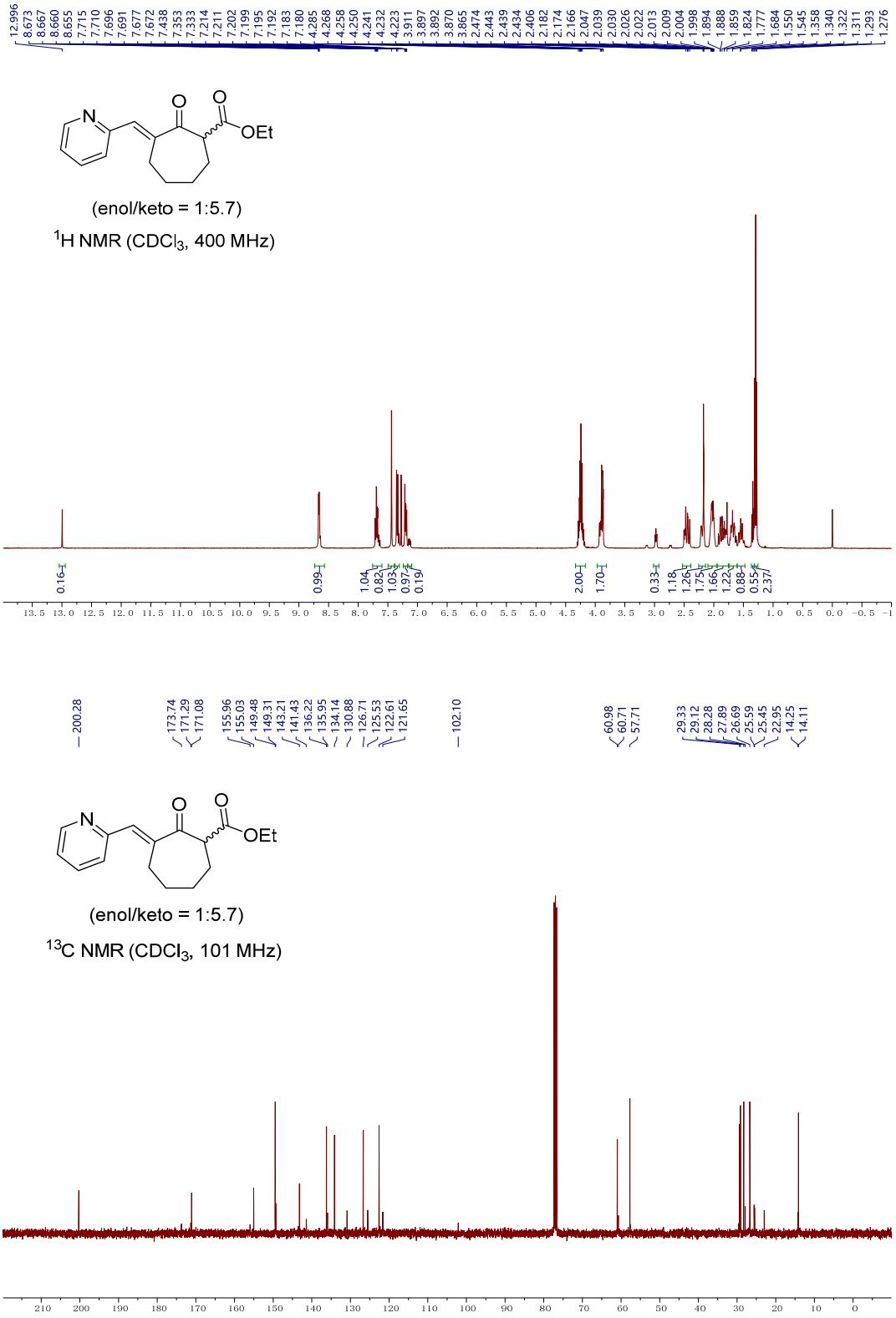


Ethyl (*E*)-3-(2-fluorobenzylidene)-2-oxocycloheptane-1-carboxylate (9f)

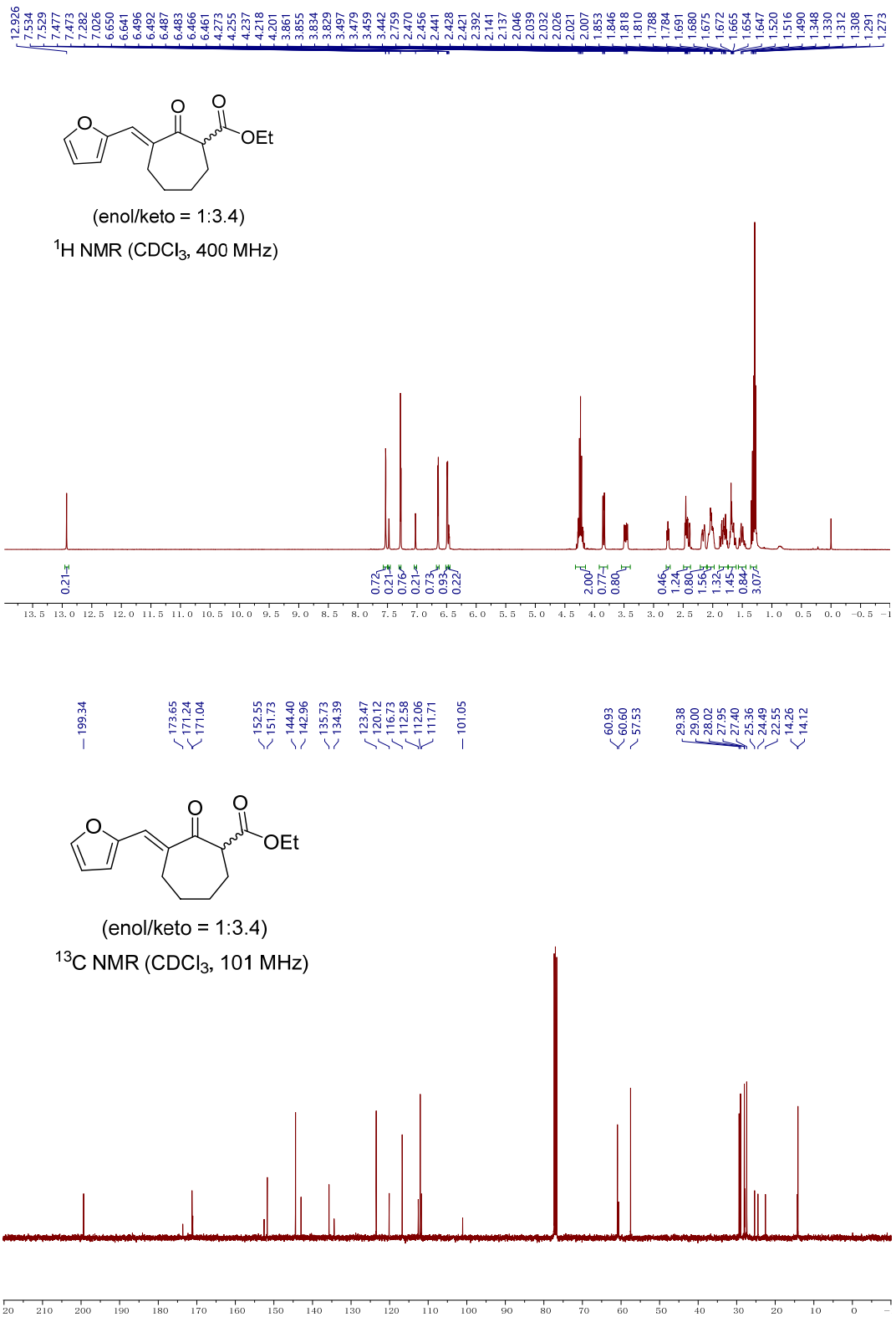




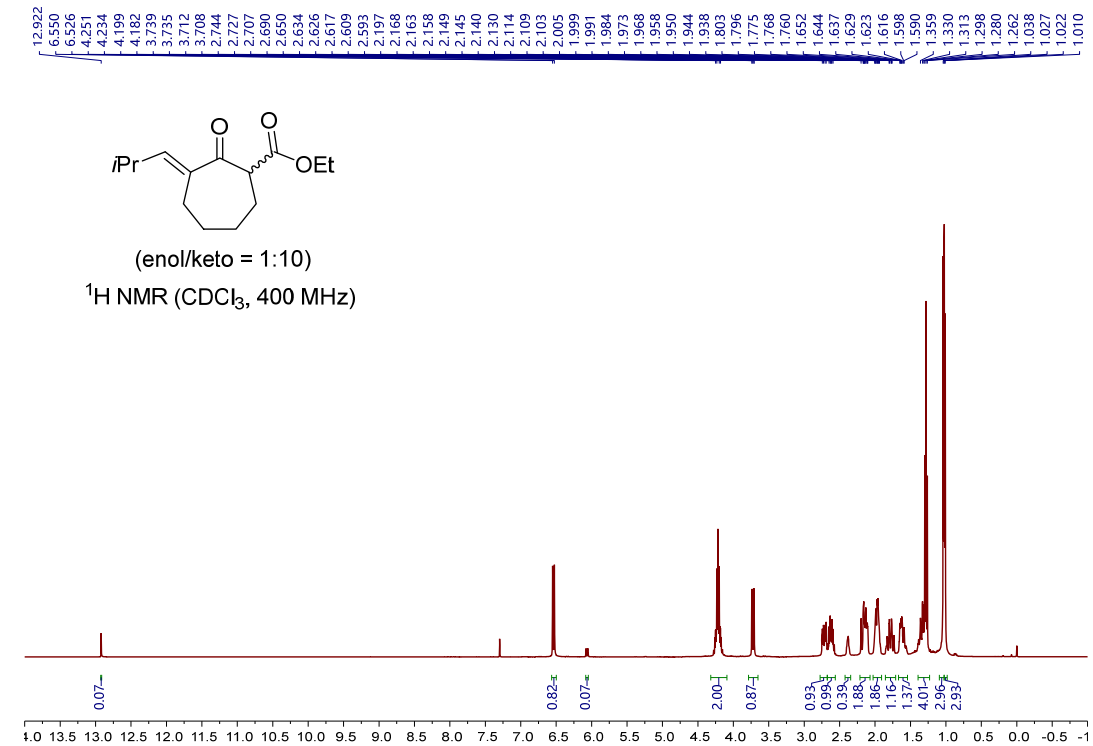
Ethyl (*E*)-2-oxo-3-(pyridin-2-ylmethylene)cycloheptane-1-carboxylate (9g)

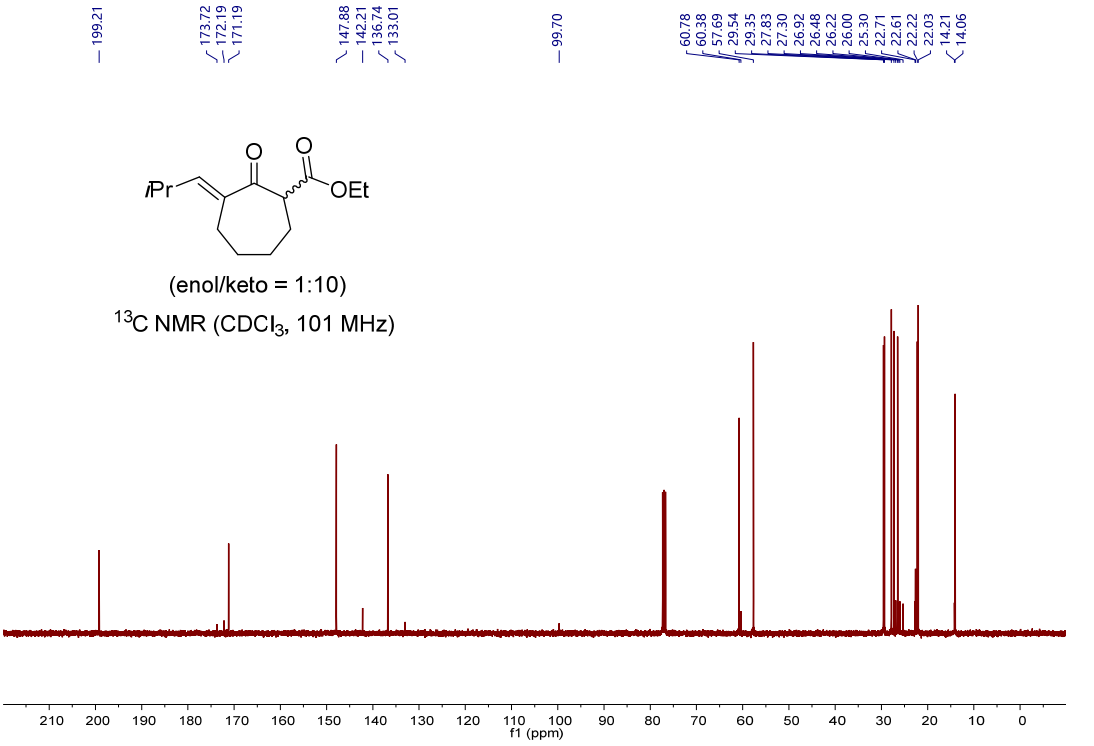


Ethyl (*E*)-3-(furan-2-ylmethylene)-2-oxocycloheptane-1-carboxylate (9h)

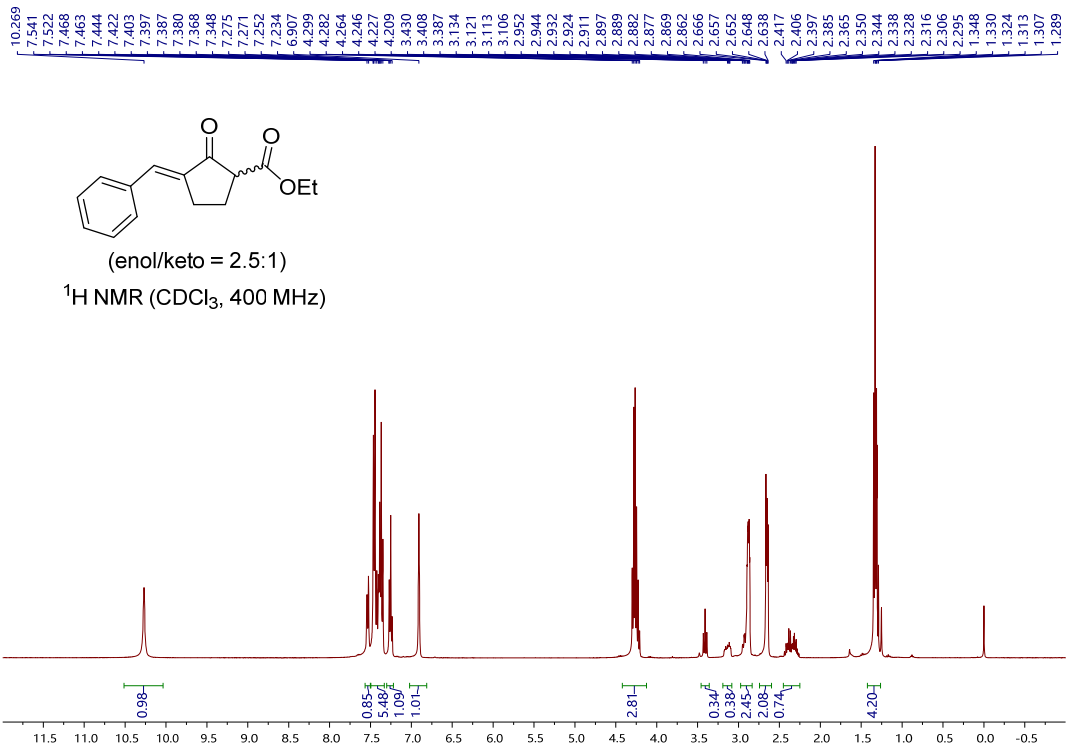


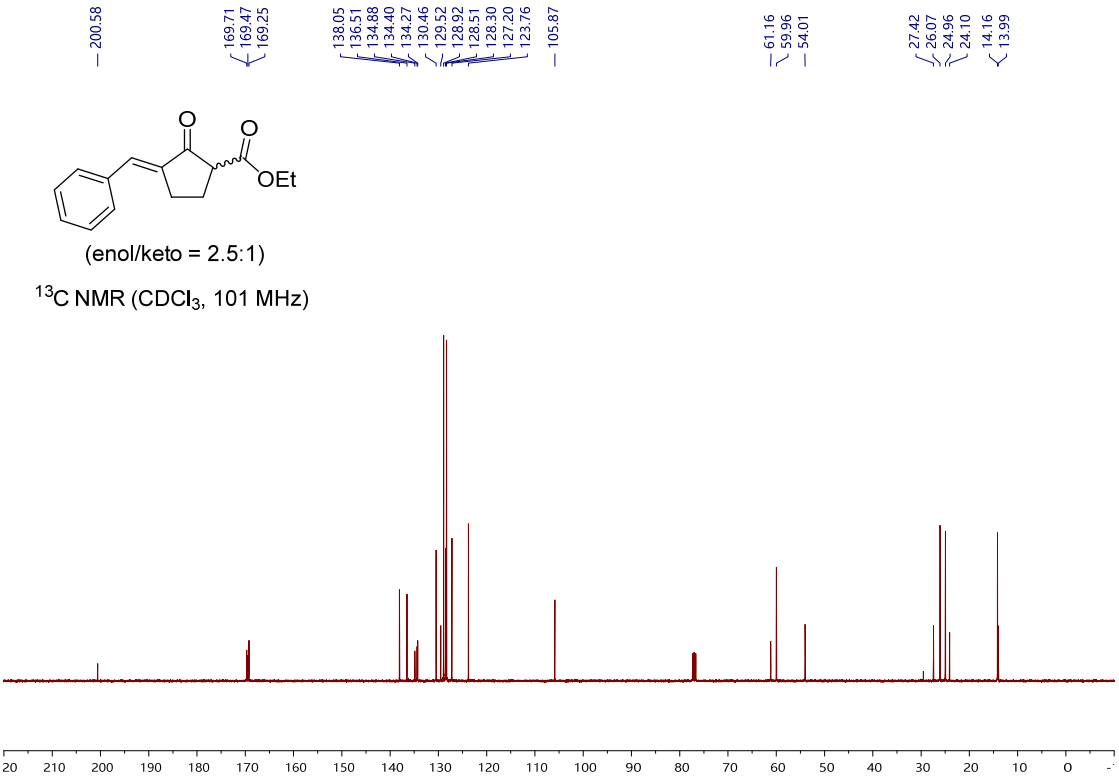
Ethyl (*E*)-3-(2-methylpropylidene)-2-oxocycloheptane-1-carboxylate (9i)



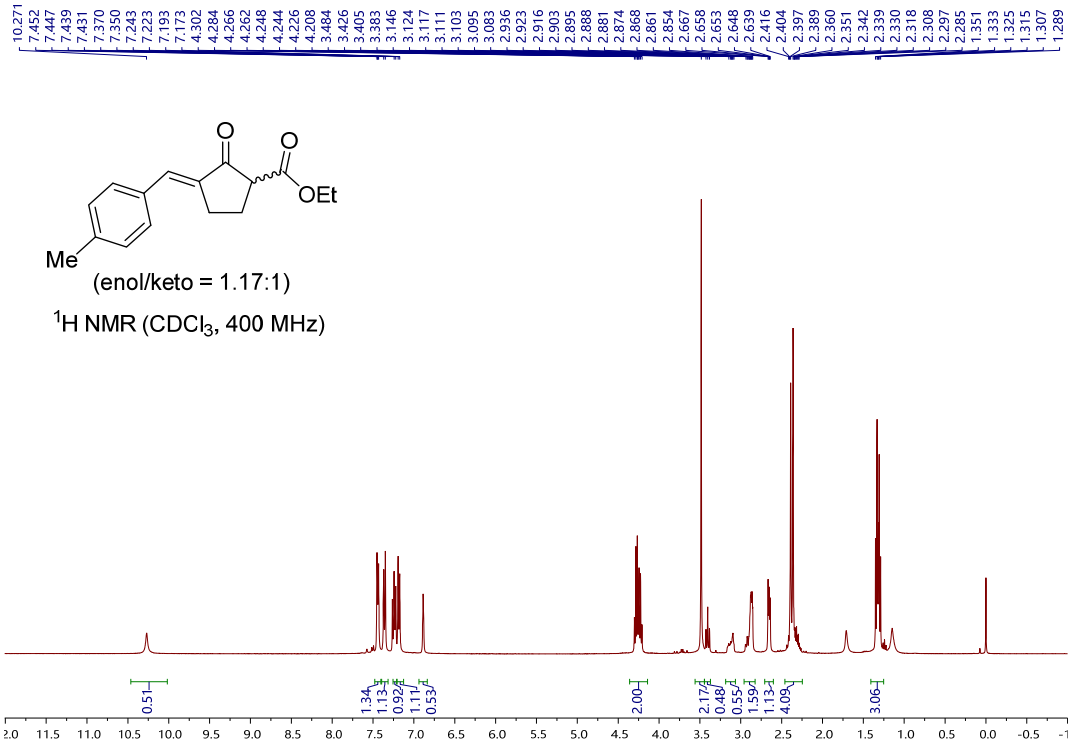


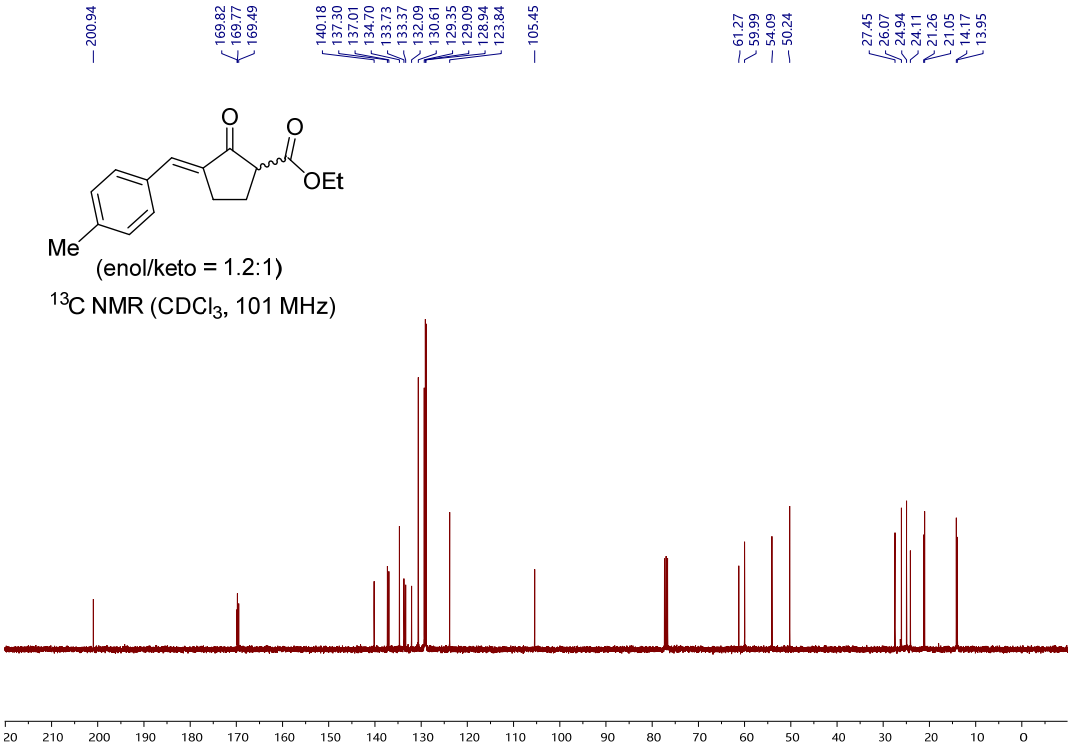
Ethyl (*E*)-3-benzylidene-2-oxocyclopentane-1-carboxylate (11a)



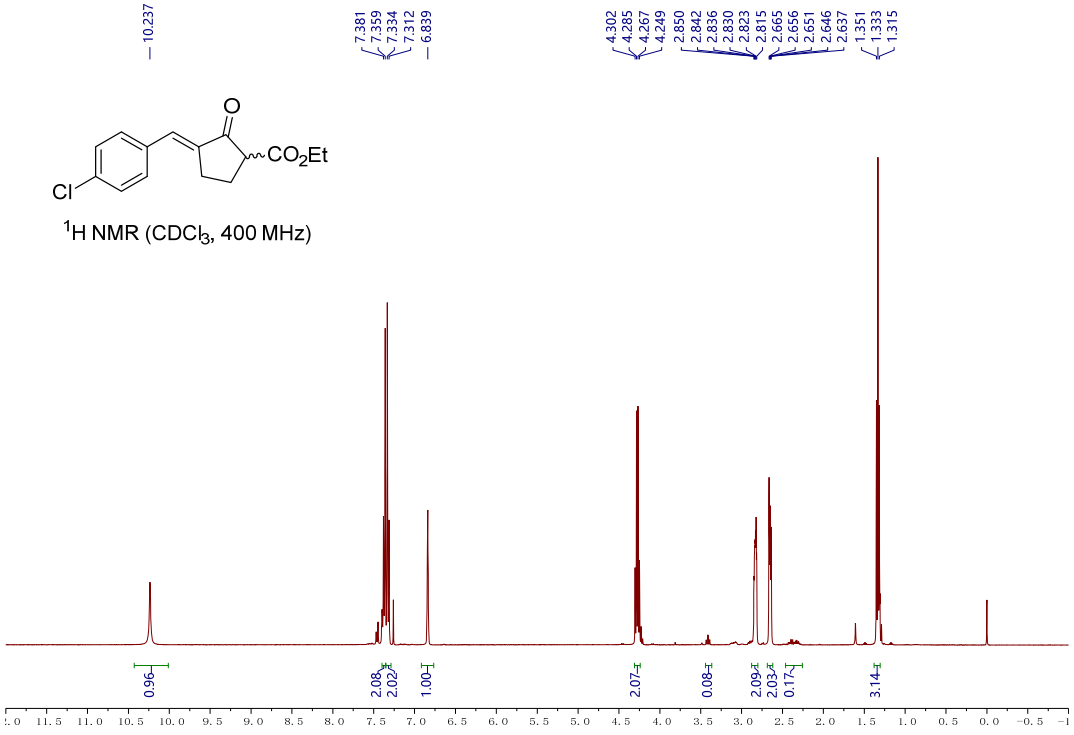


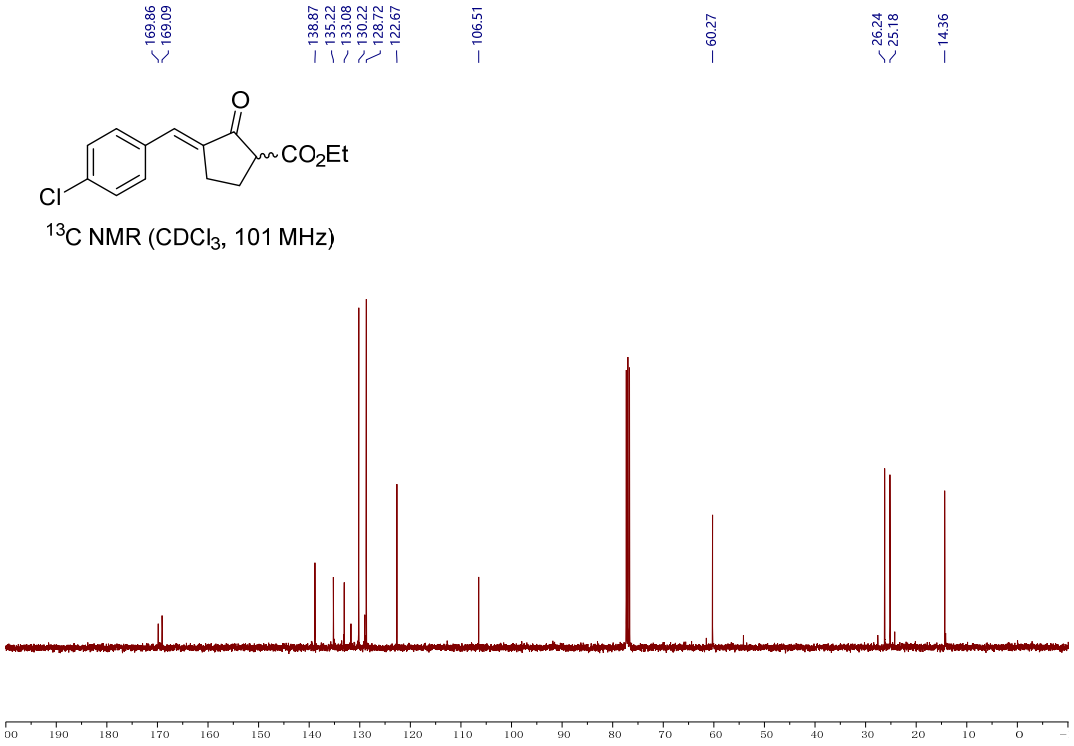
Ethyl (*E*)-3-(4-methylbenzylidene)-2-oxocyclopentane-1-carboxylate (11b)



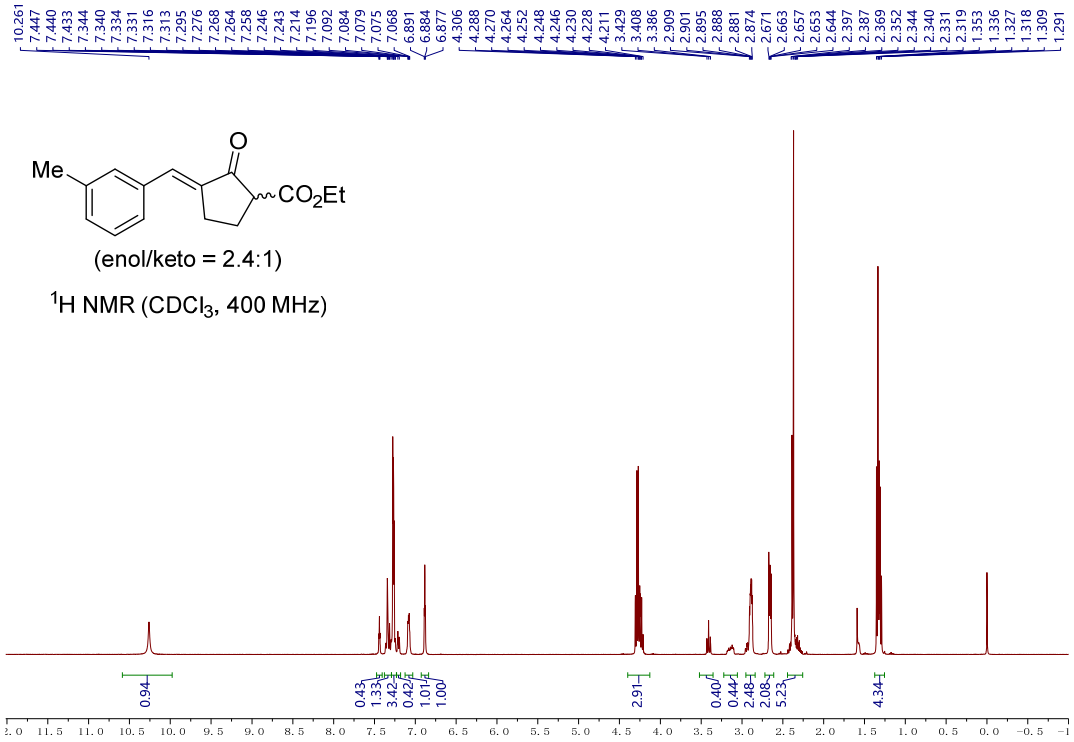


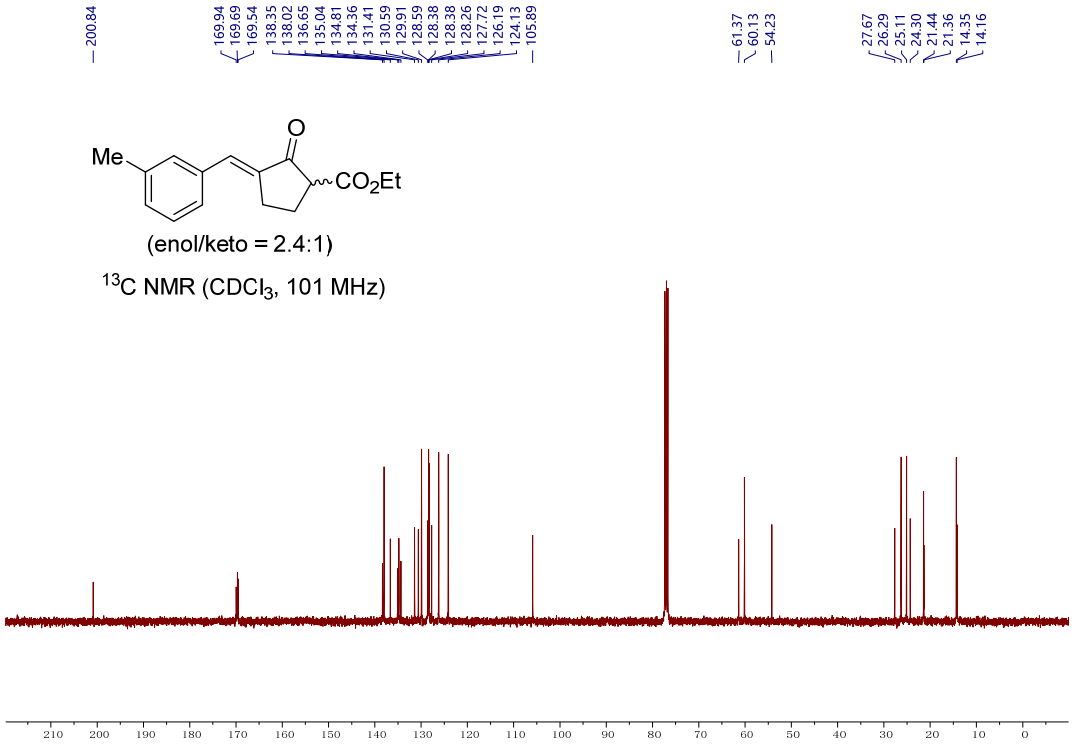
Ethyl (*E*)-3-(4-chlorobenzylidene)-2-oxocyclopentane-1-carboxylate (11c)



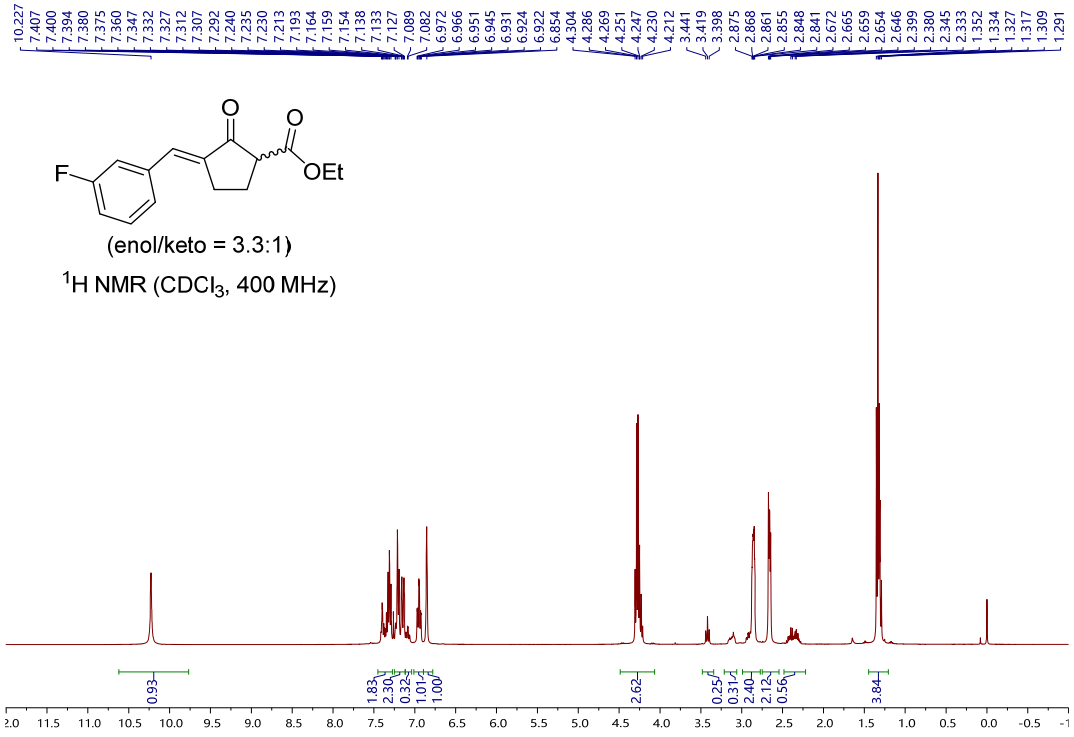


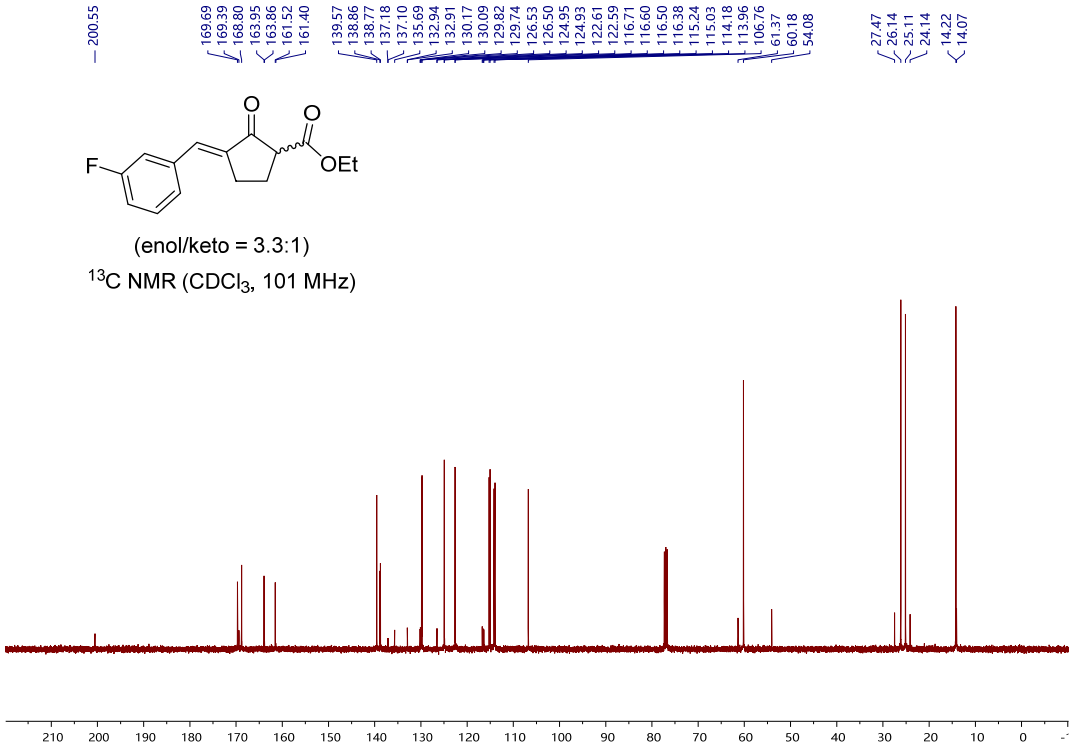
Ethyl (*E*)-3-(3-methylbenzylidene)-2-oxocyclopentane-1-carboxylate (11d)



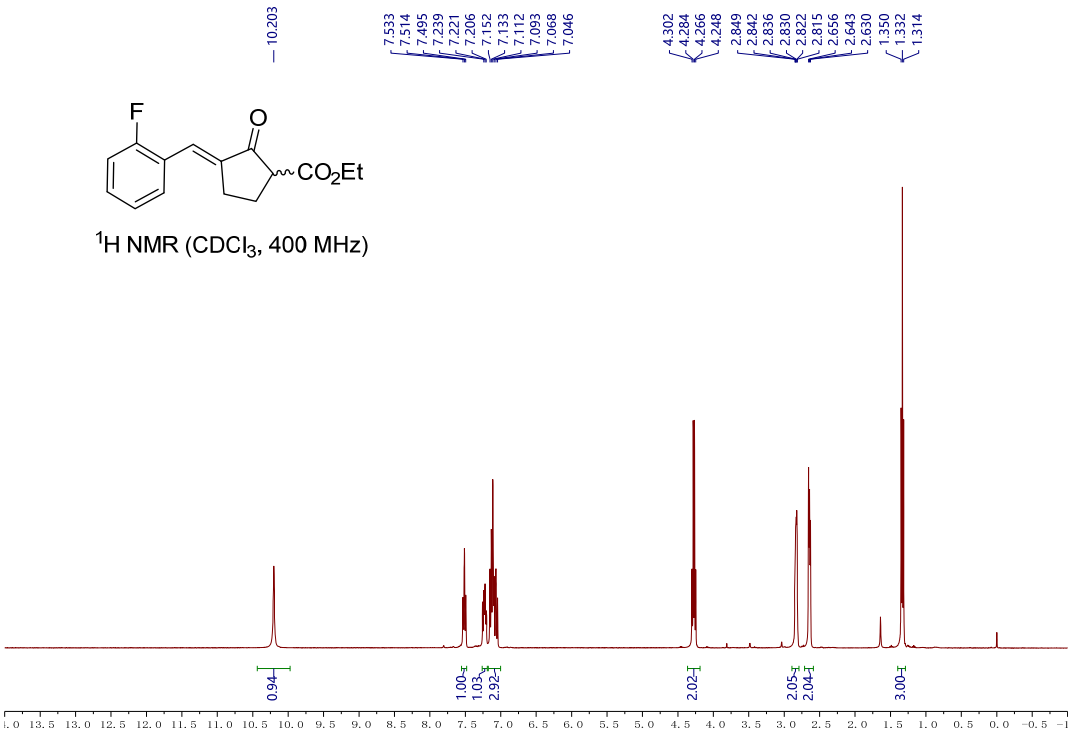


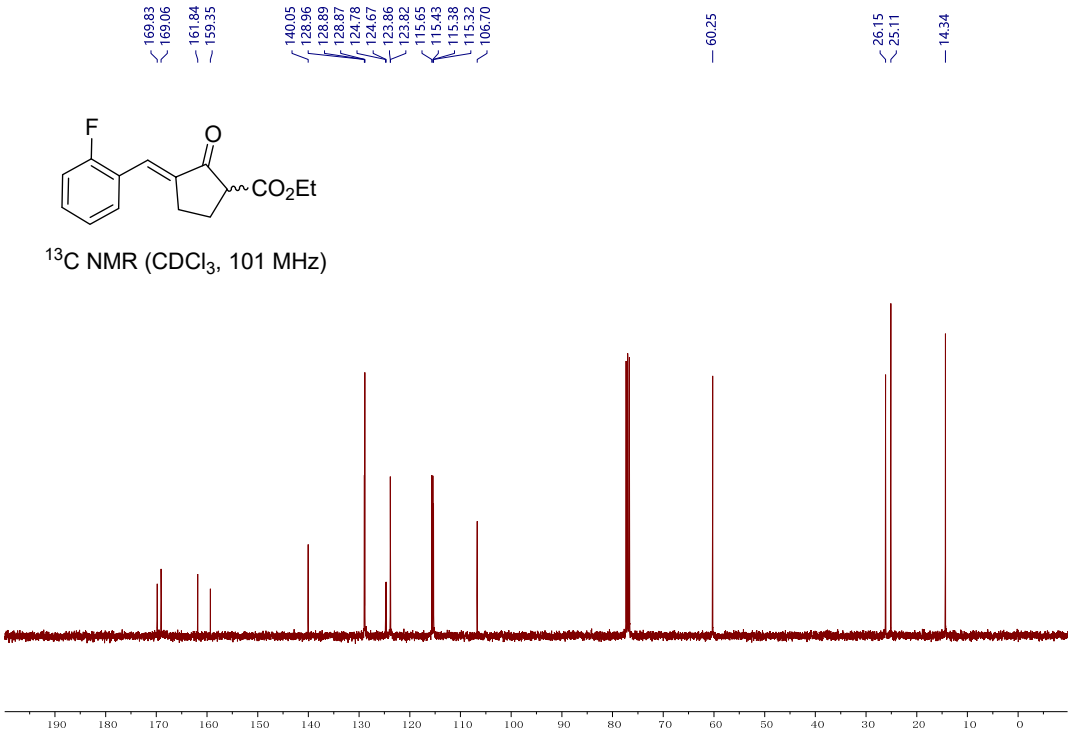
Ethyl (*E*)-3-(3-fluorobenzylidene)-2-oxocyclopentane-1-carboxylate (11e)



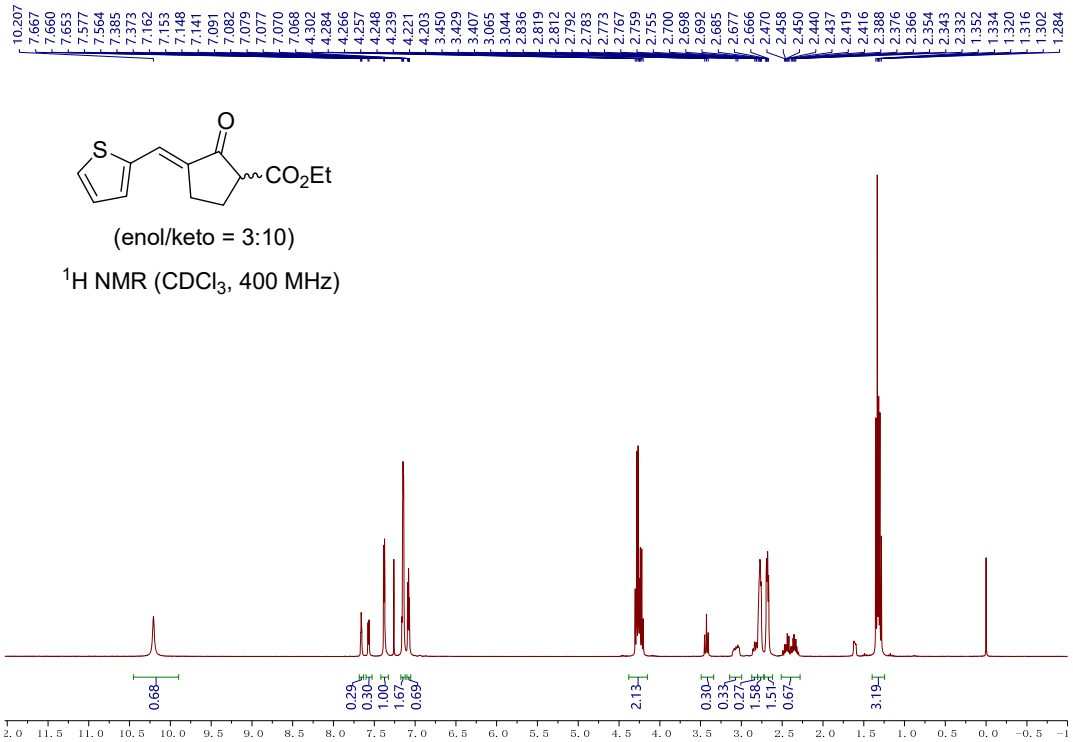


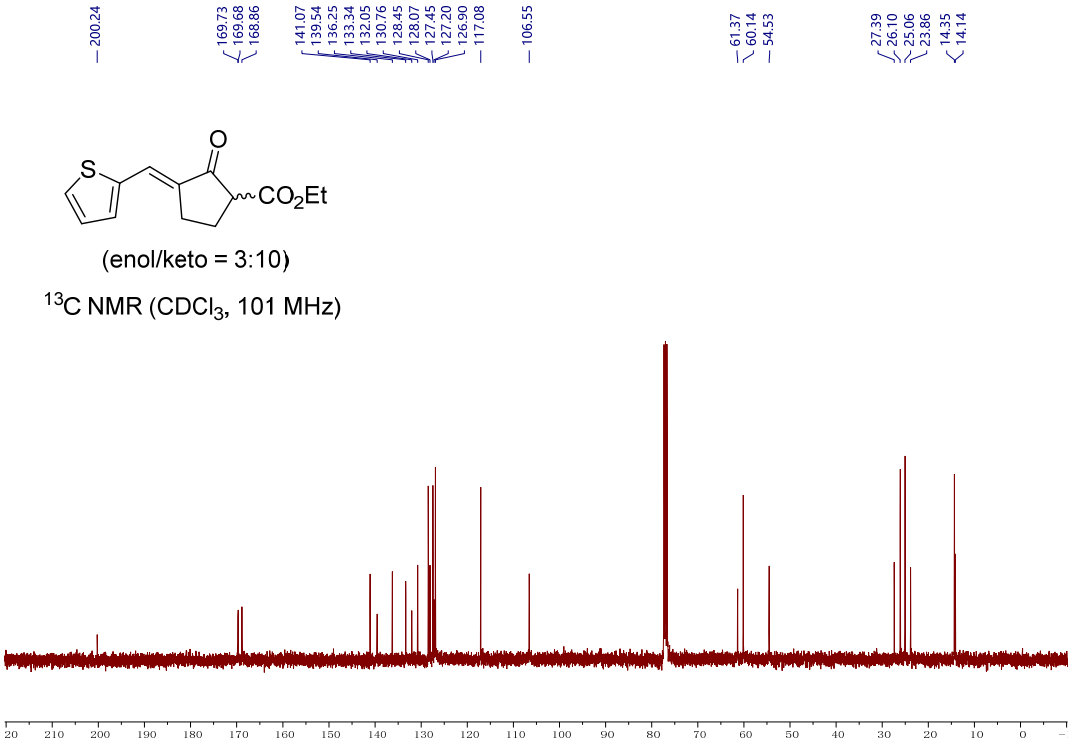
Ethyl (*E*)-3-(2-fluorobenzylidene)-2-oxocyclopentane-1-carboxylate (11f)



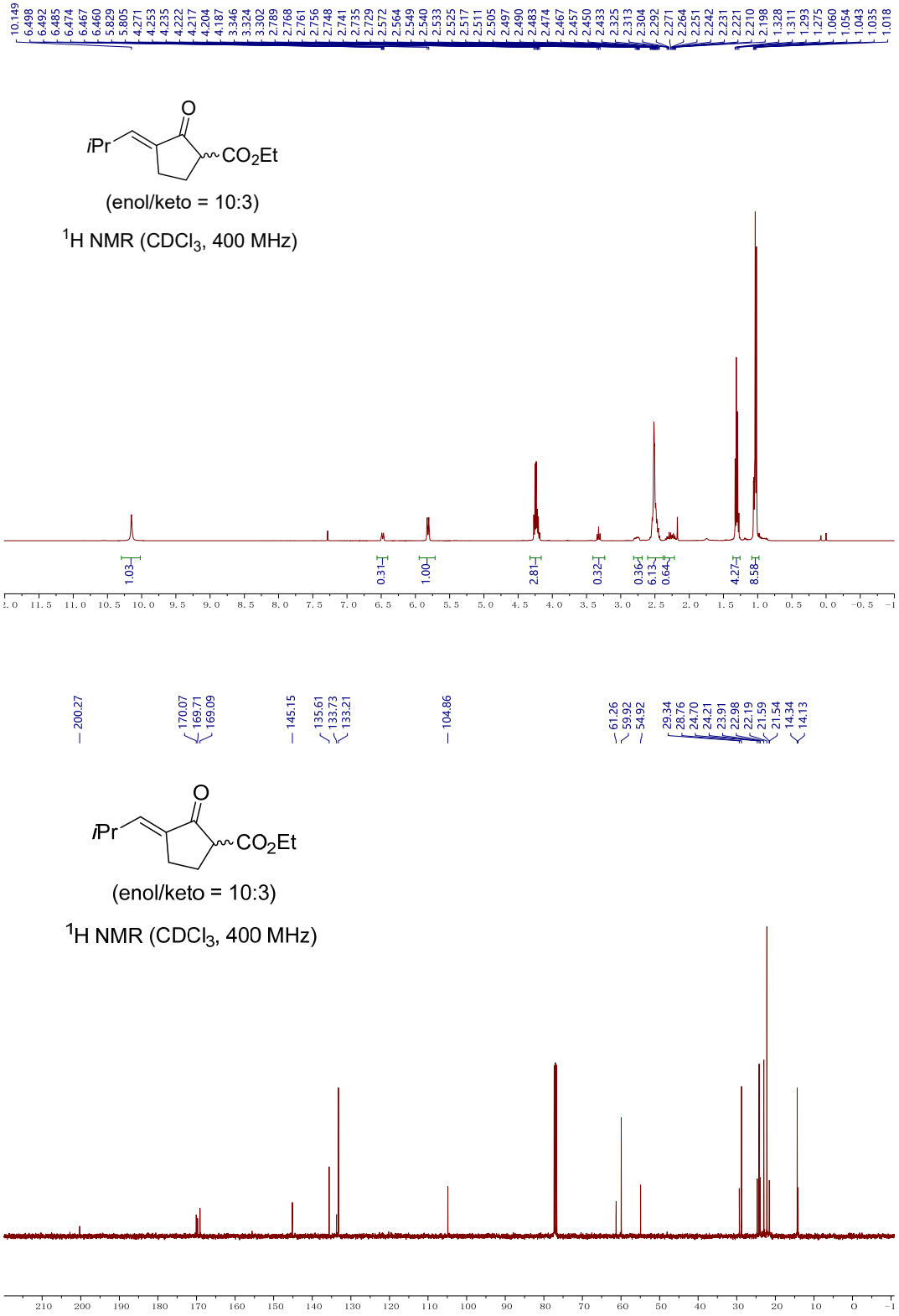


Ethyl (*E*)-2-oxo-3-(thiophen-2-ylmethylene)cyclopentane-1-carboxylate (11g)

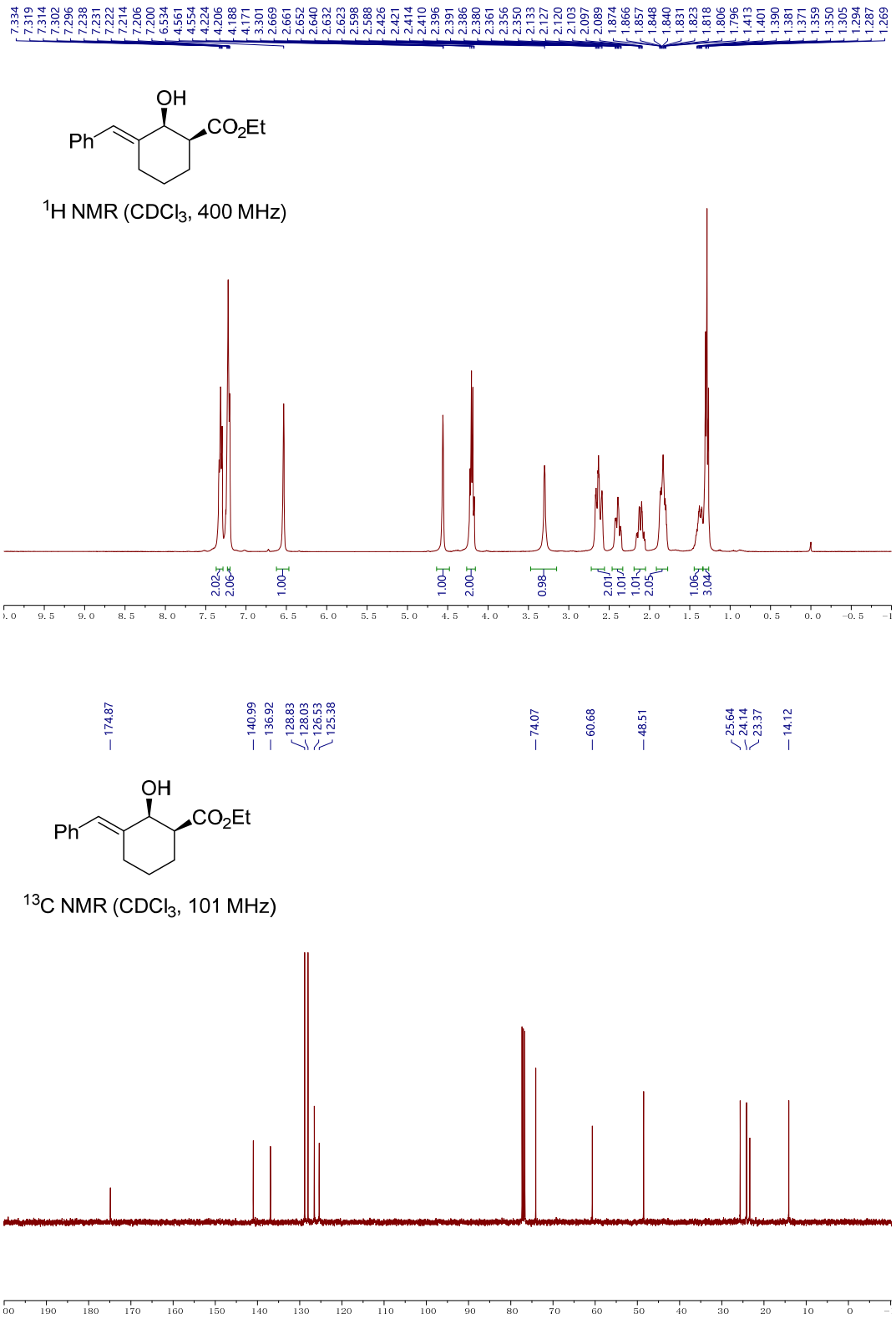




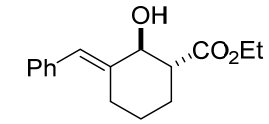
Ethyl (*E*)-3-(2-methylpropylidene)-2-oxocyclopentane-1-carboxylate (11h)



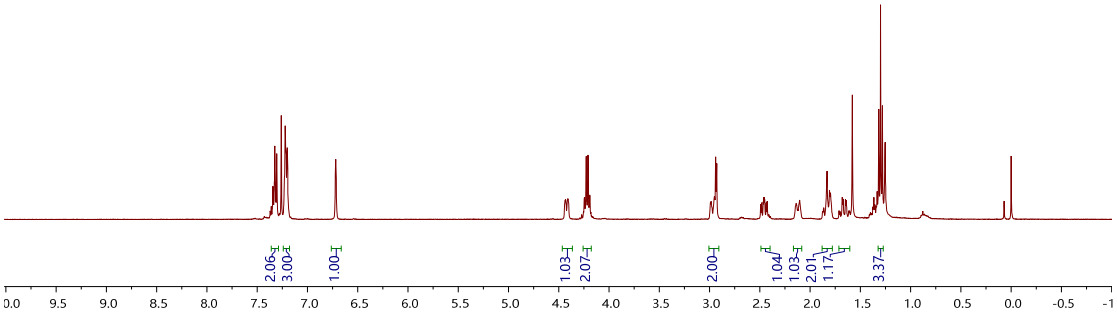
(+)-*cis*-Ethyl 3-((*E*)-benzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-*cis*-8a)

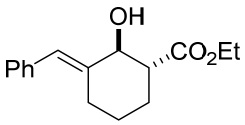


(+)-*trans*-Ethyl 3-((*E*)-benzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-*trans*-8a)



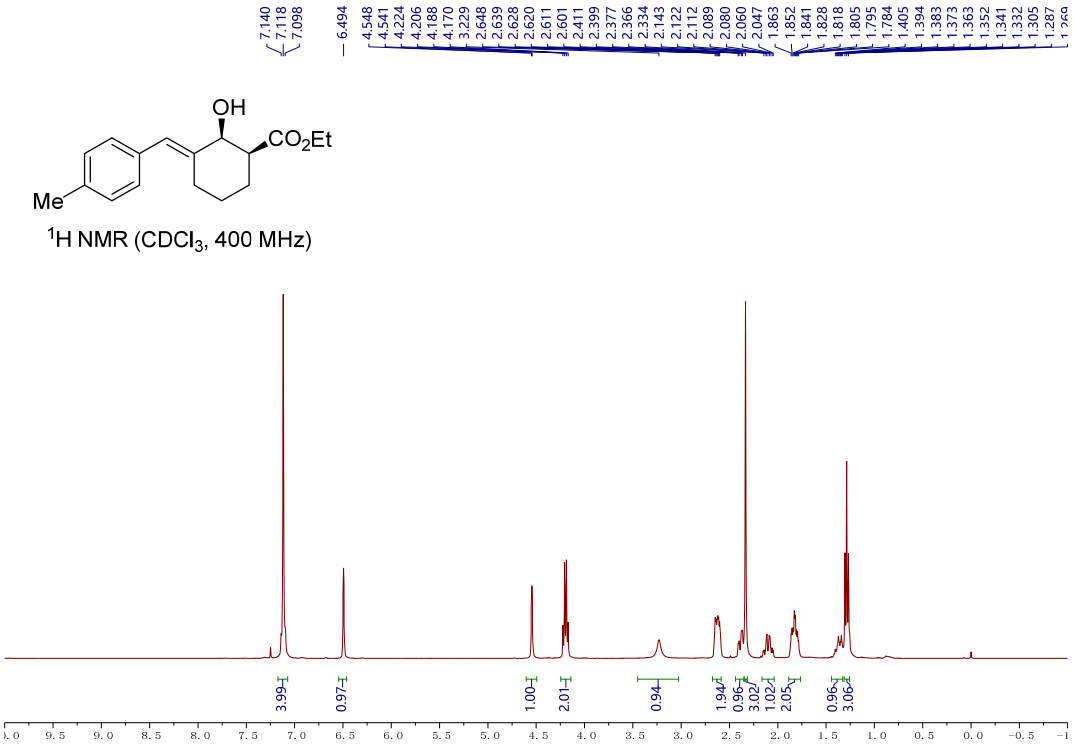
^{1}H NMR ($CDCl_3$, 400 MHz)

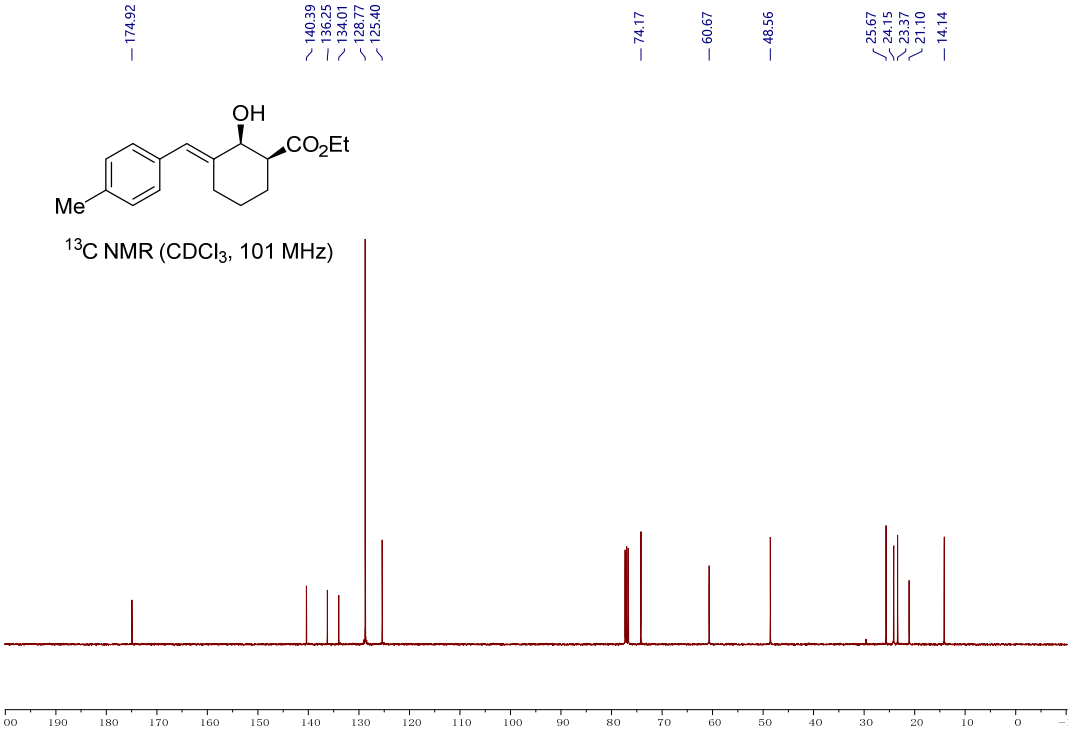




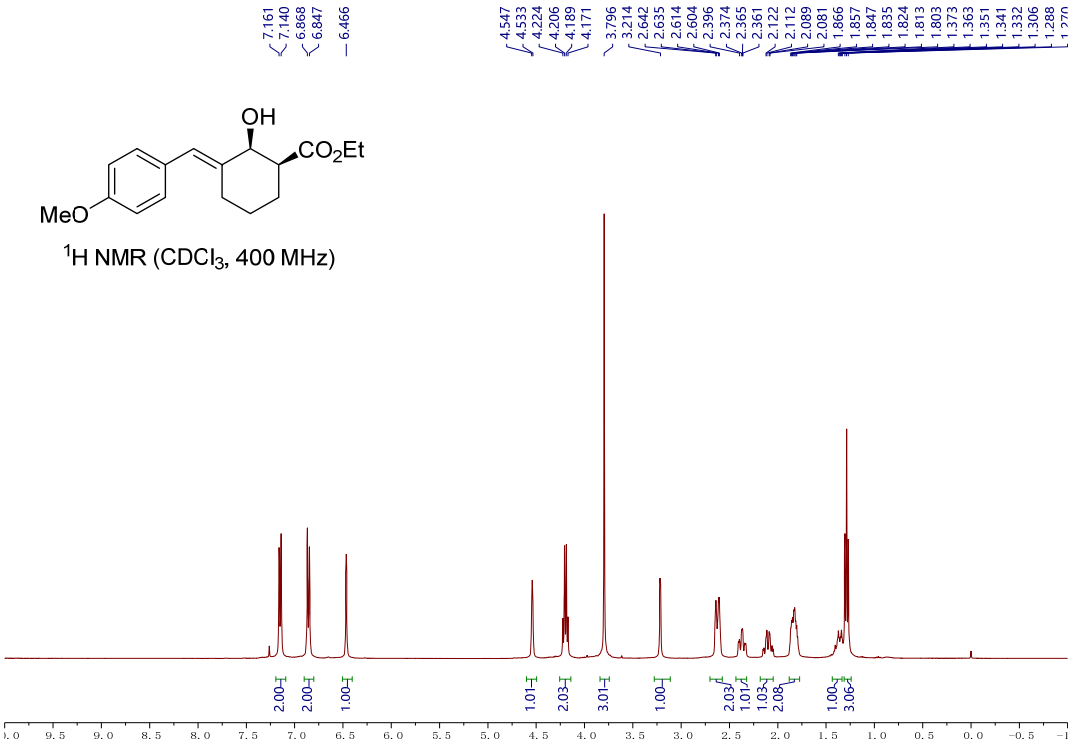
^{13}C NMR ($CDCl_3$, 101 MHz)

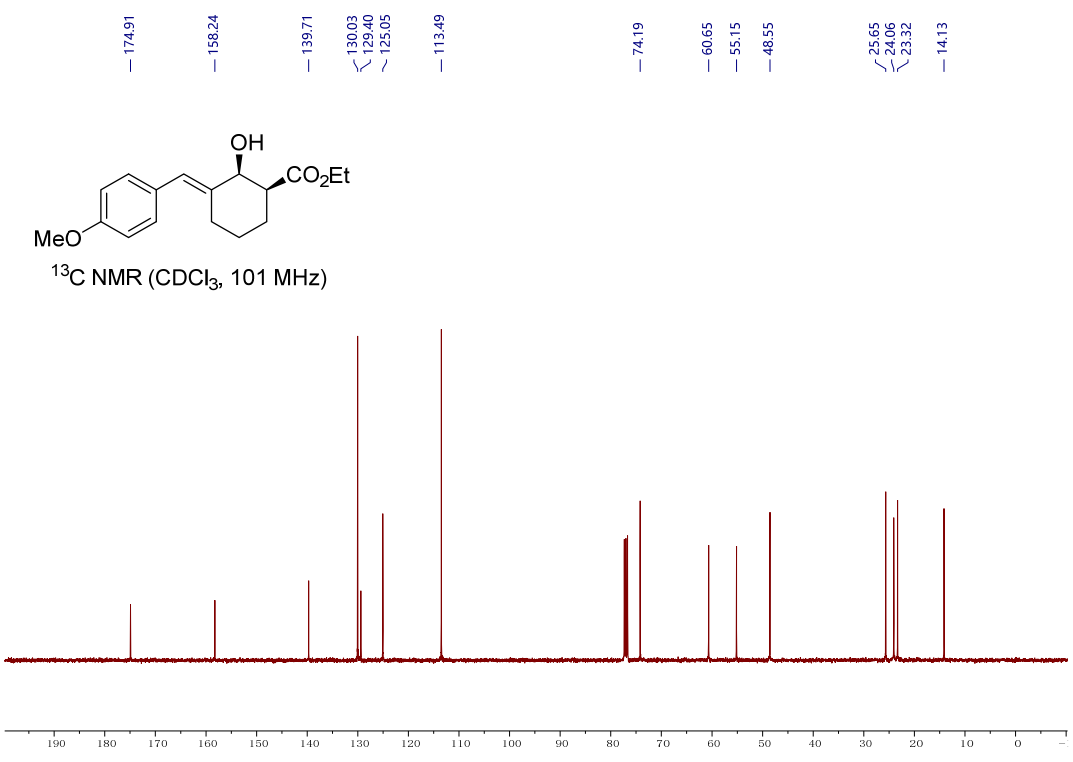
(+)-Ethyl 2-hydroxy-3-((*E*)-4-methylbenzylidene)cyclohexane-1-carboxylate ((+)-8b)



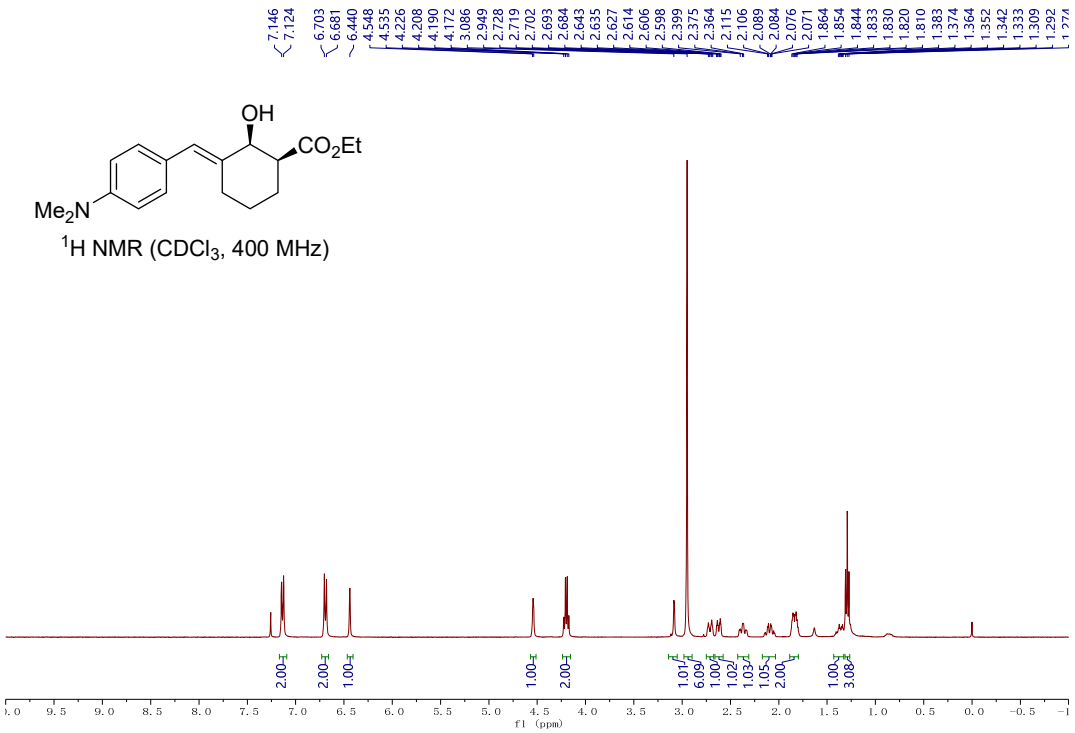


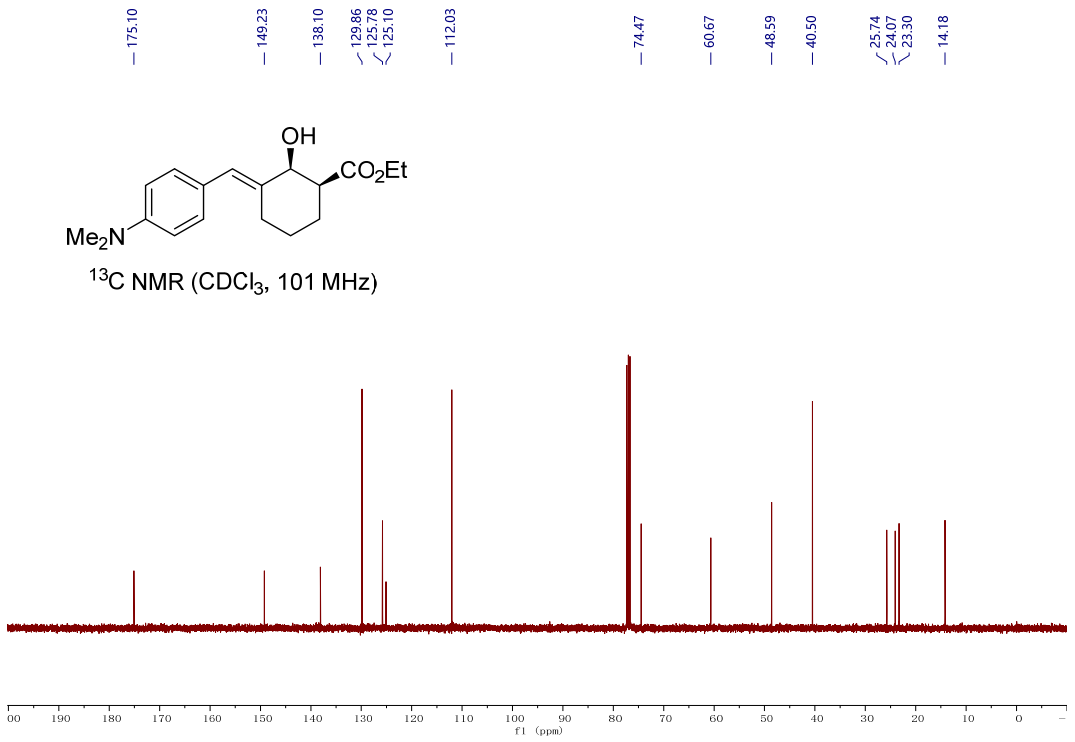
(+)-Ethyl 2-hydroxy-3-((*E*)-4-methoxybenzylidene)cyclohexane-1-carboxylate ((+)-8c)



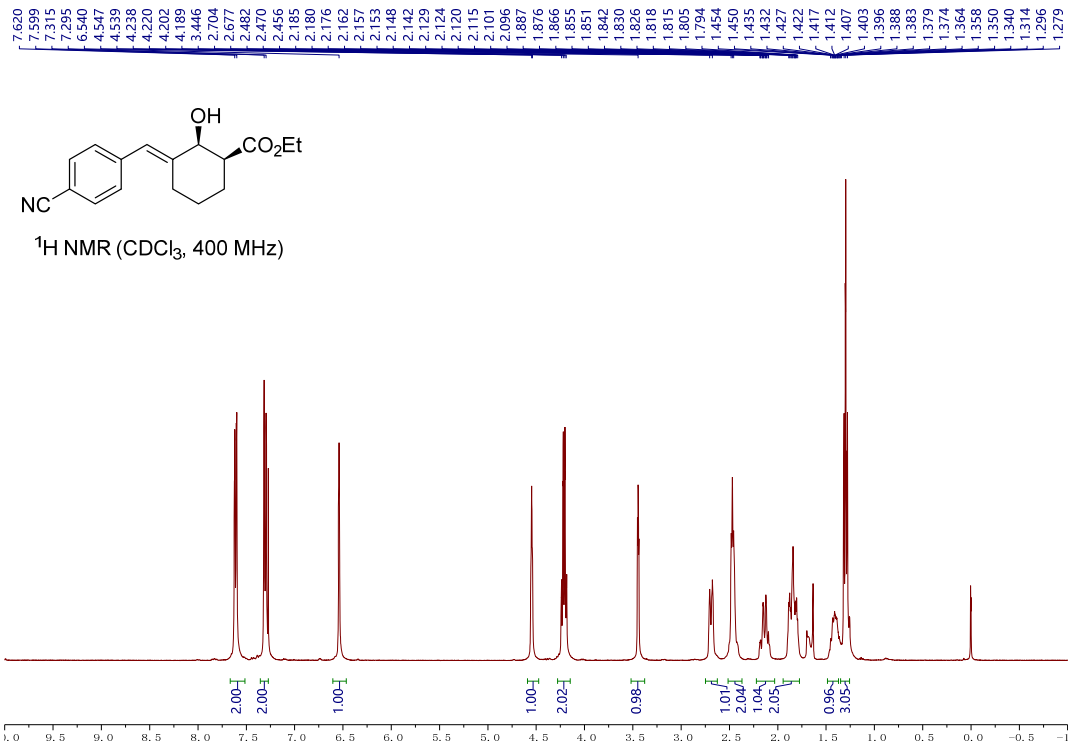


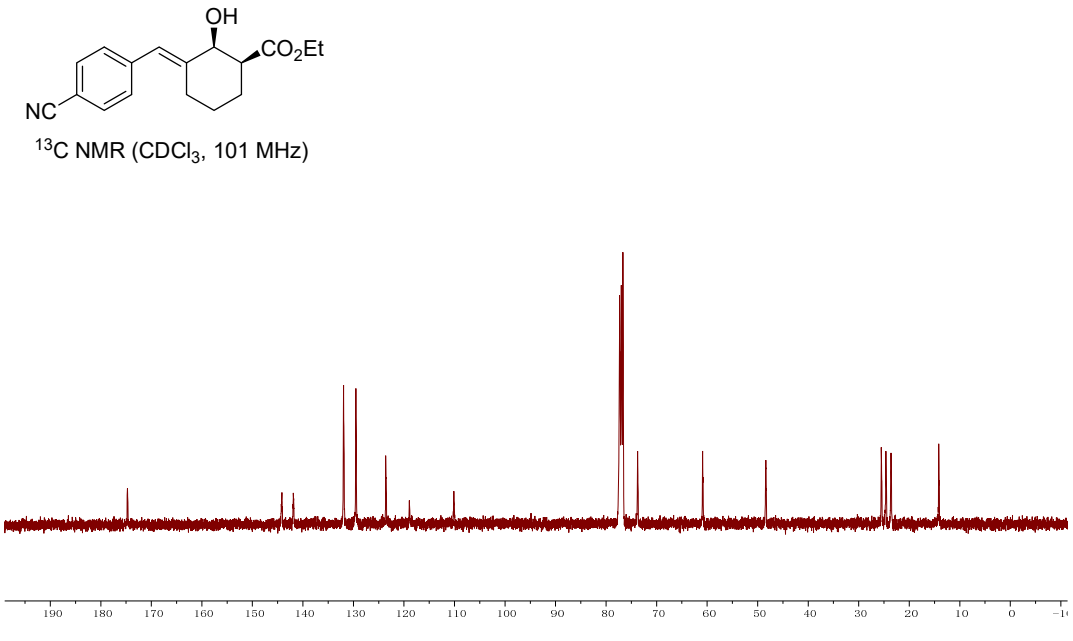
(+)-Ethyl 3-((*E*)-4-(dimethylamino)benzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8d)



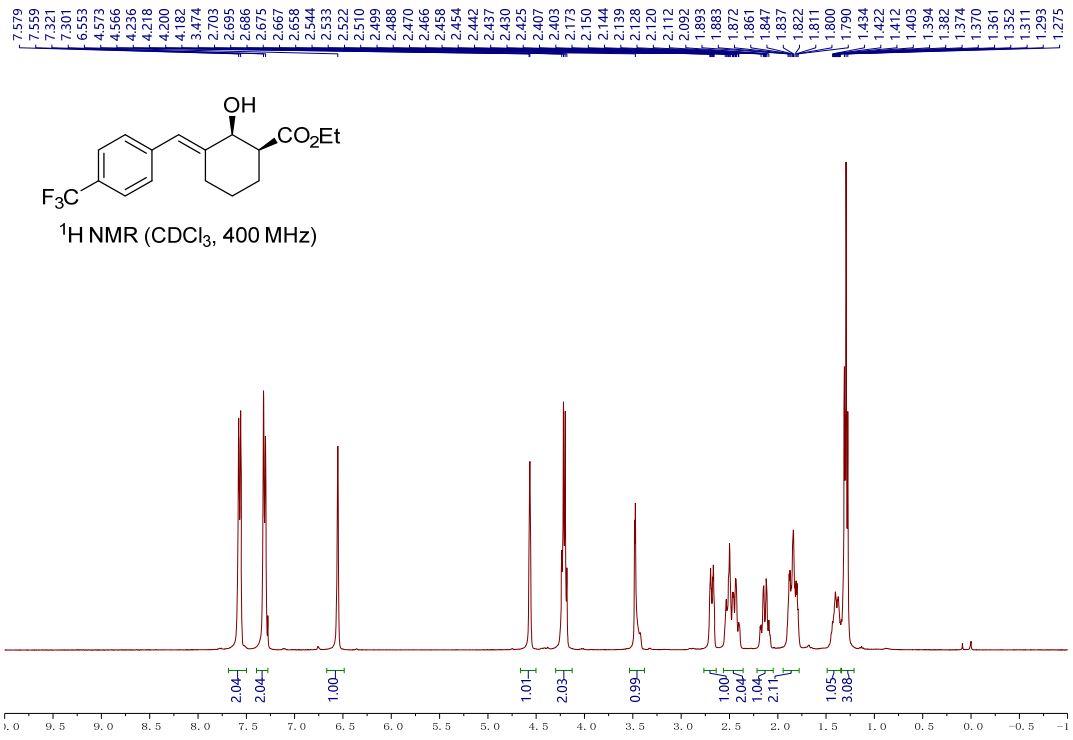


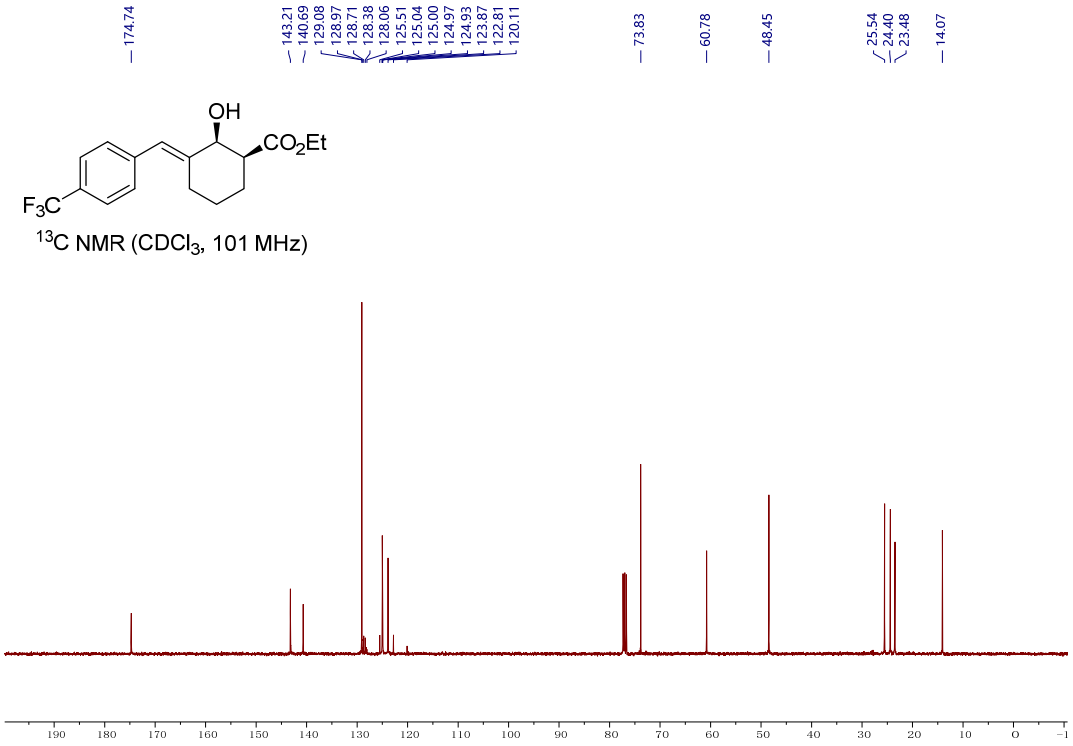
(+)-Ethyl 3-((*E*)-4-cyanobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8e)



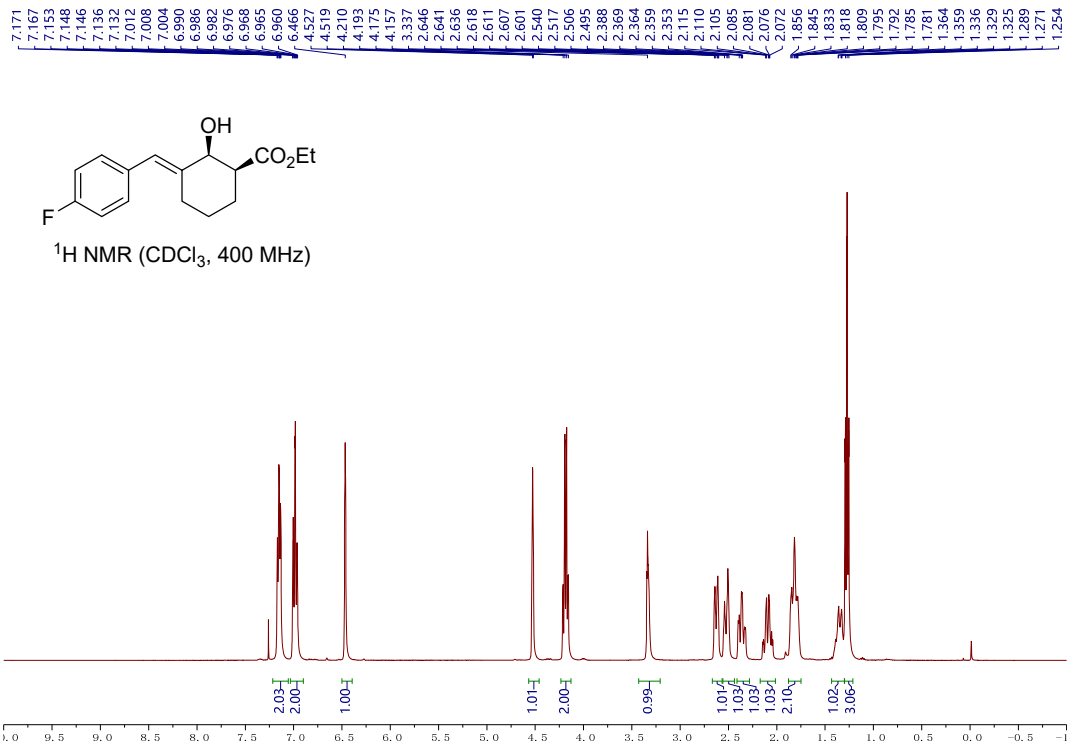


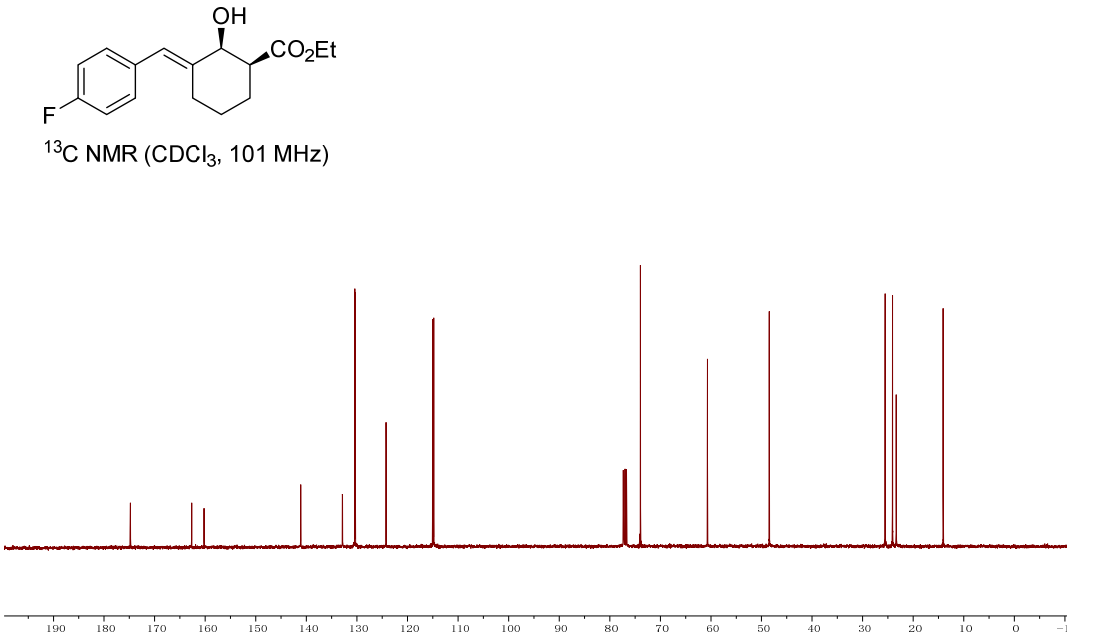
(+)-Ethyl 2-hydroxy-3-((*E*)-4-(trifluoromethyl)benzylidene)cyclohexane-1-carboxylate ((+)-8f)



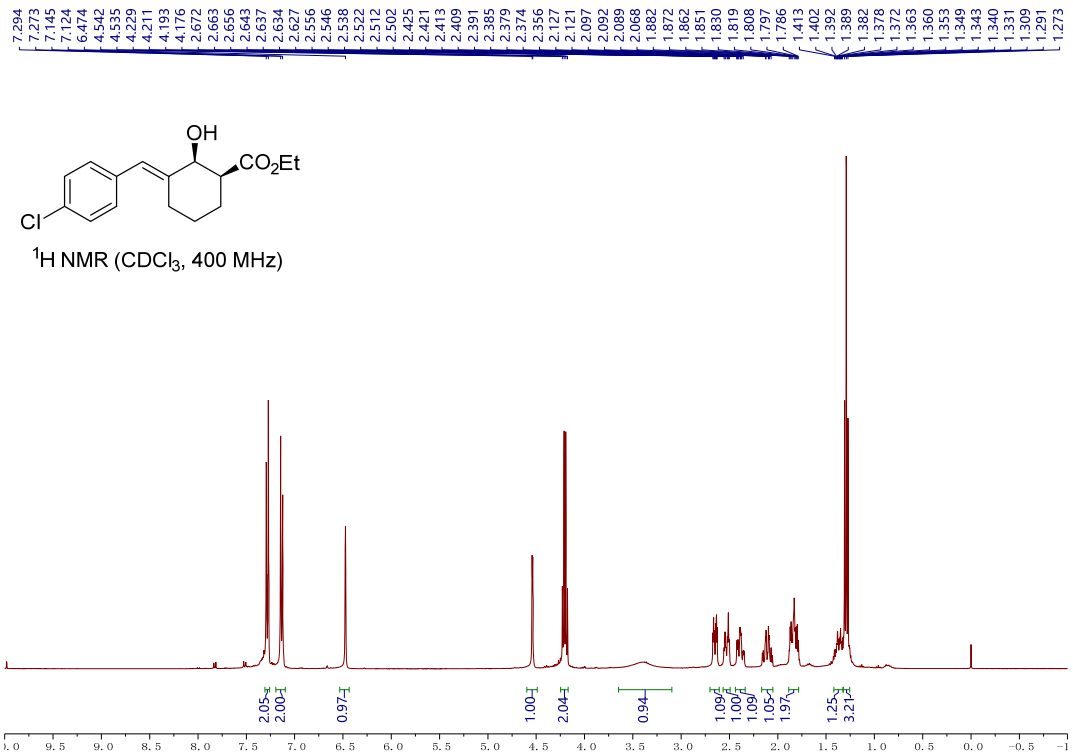


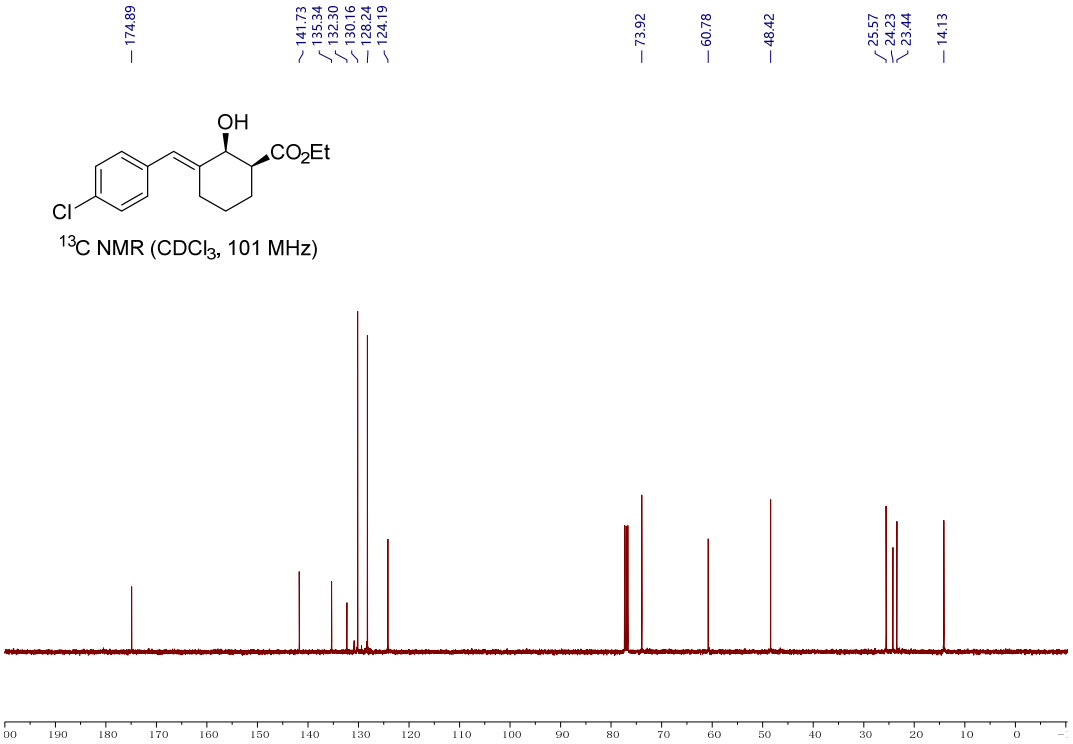
(+)-Ethyl 3-((*E*)-4-fluorobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8g)



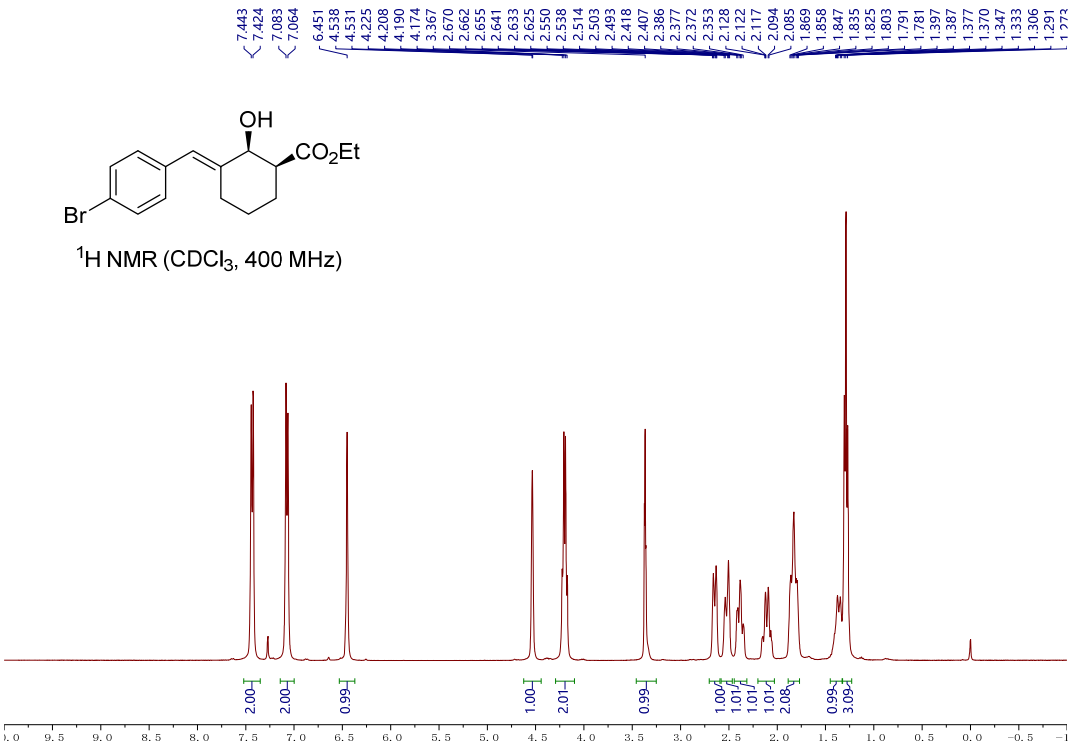


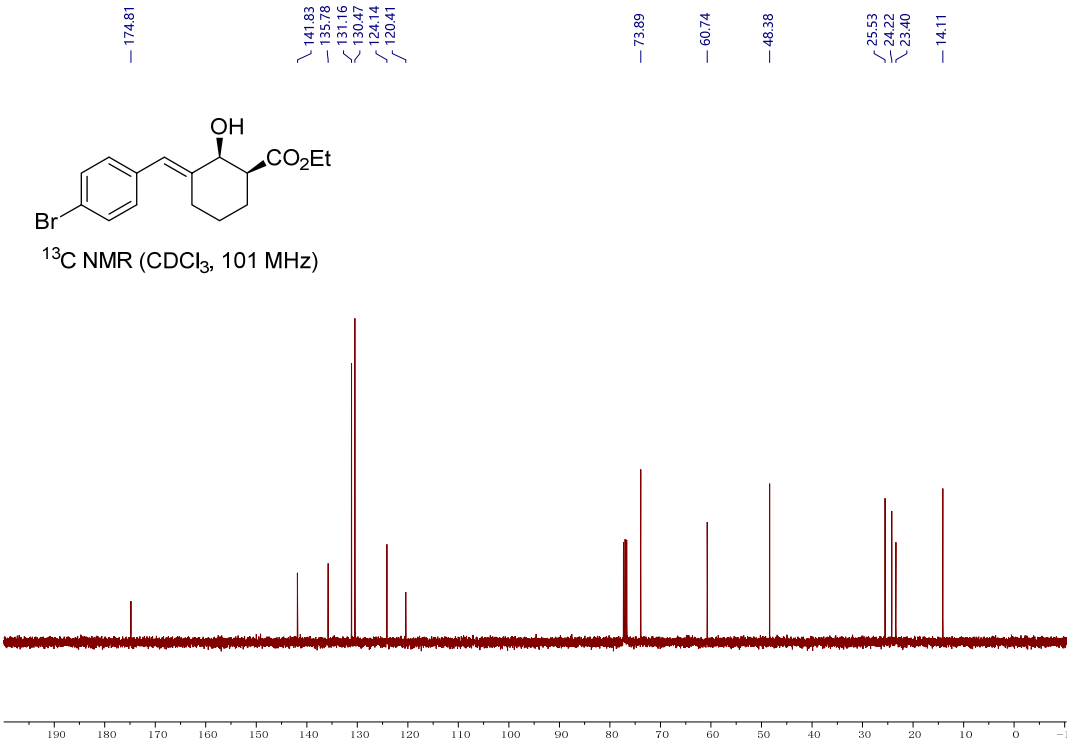
(+)-Ethyl 3-((*E*)-4-chlorobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8h)



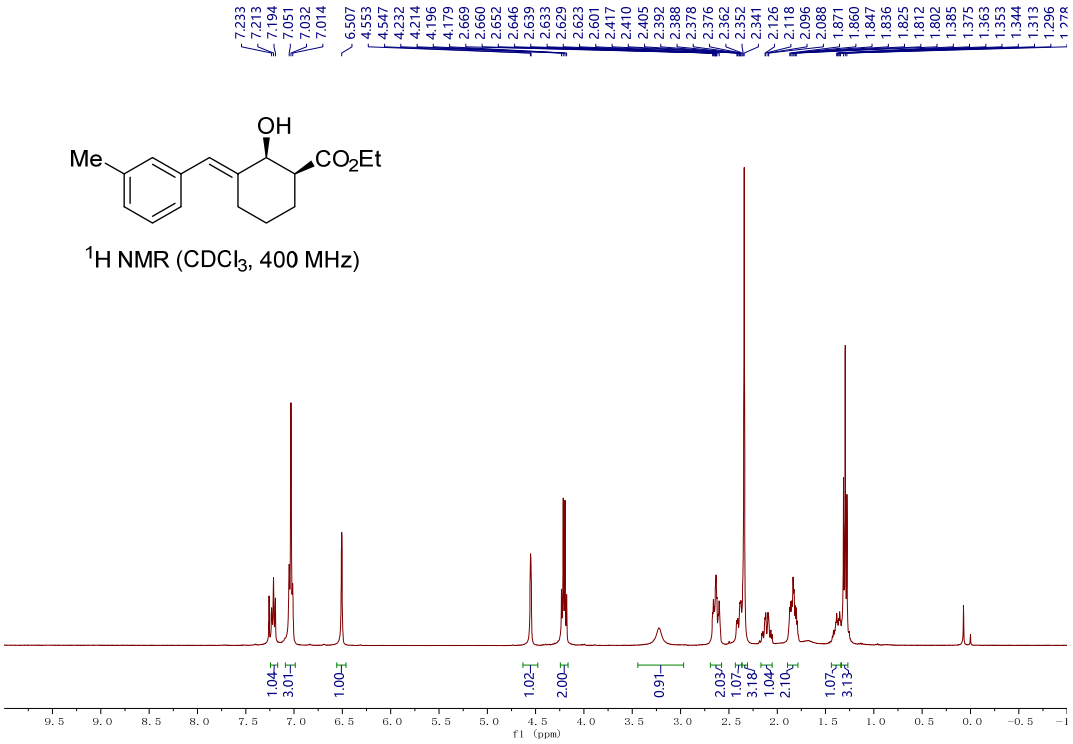


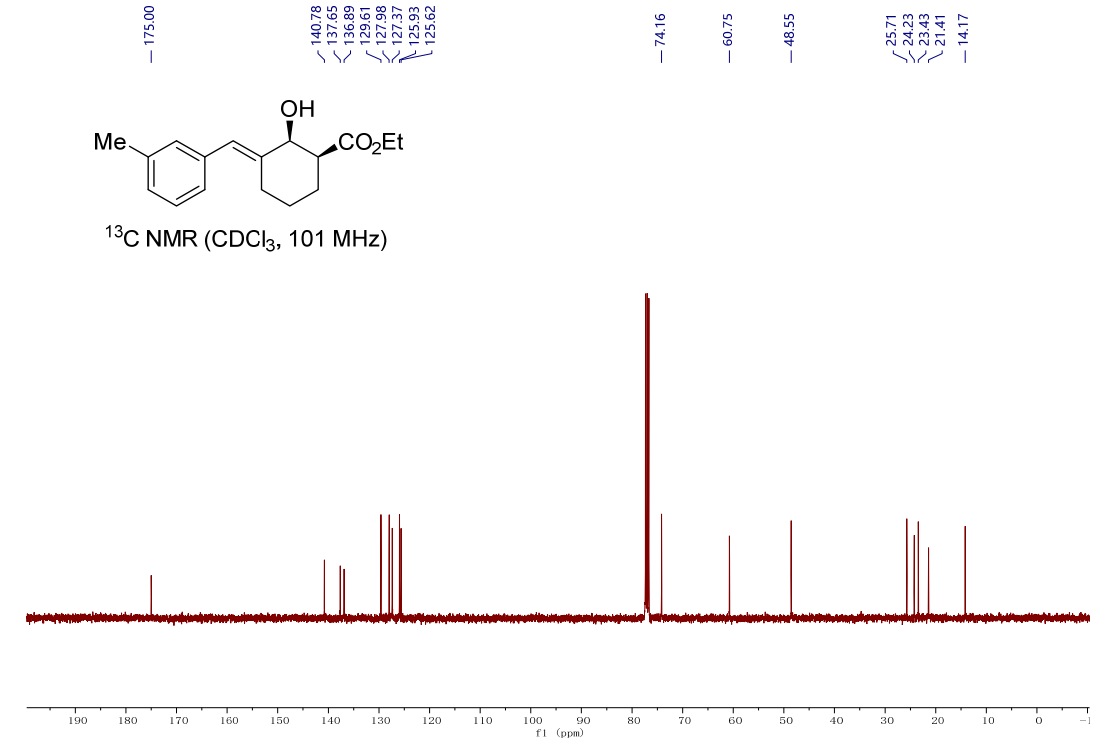
(+)-Ethyl 3-((*E*)-4-bromobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8i)



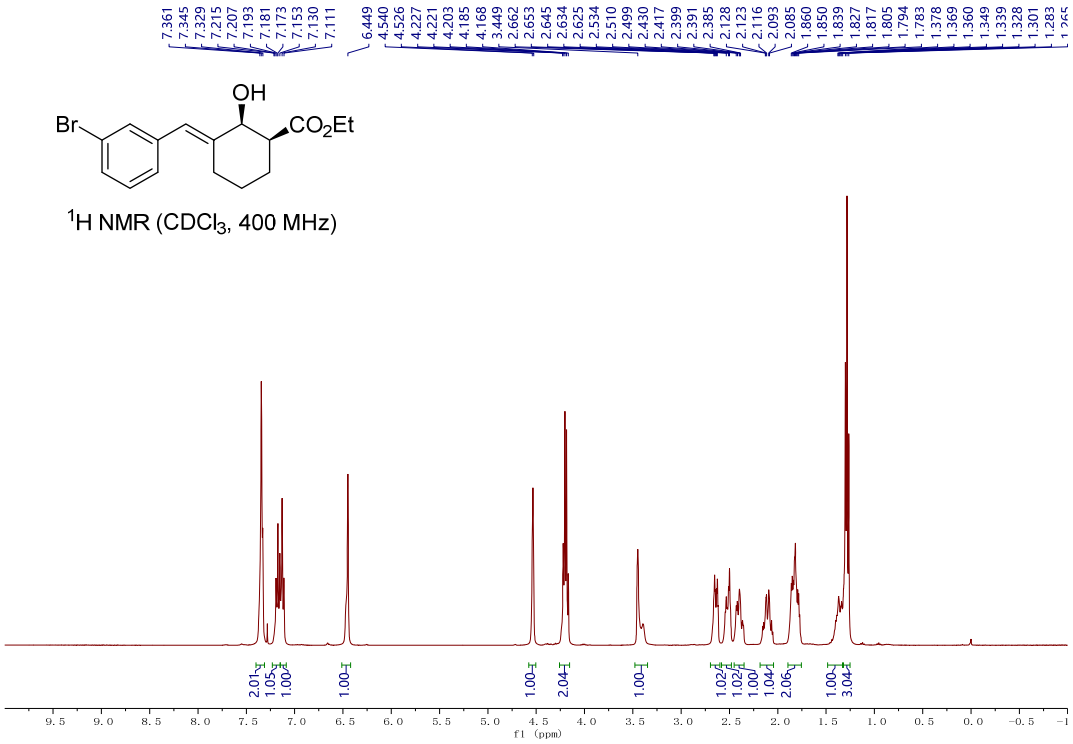


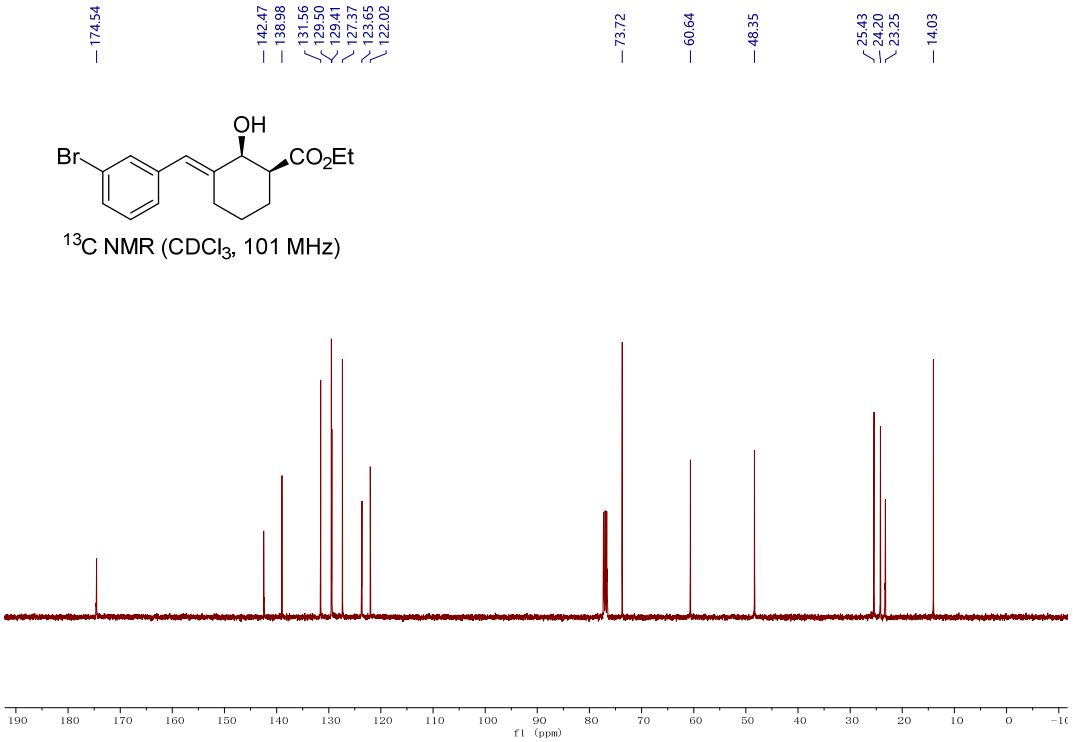
(+)-Ethyl 2-hydroxy-3-((*E*)-3-methylbenzylidene)cyclohexane-1-carboxylate ((+)-8j)



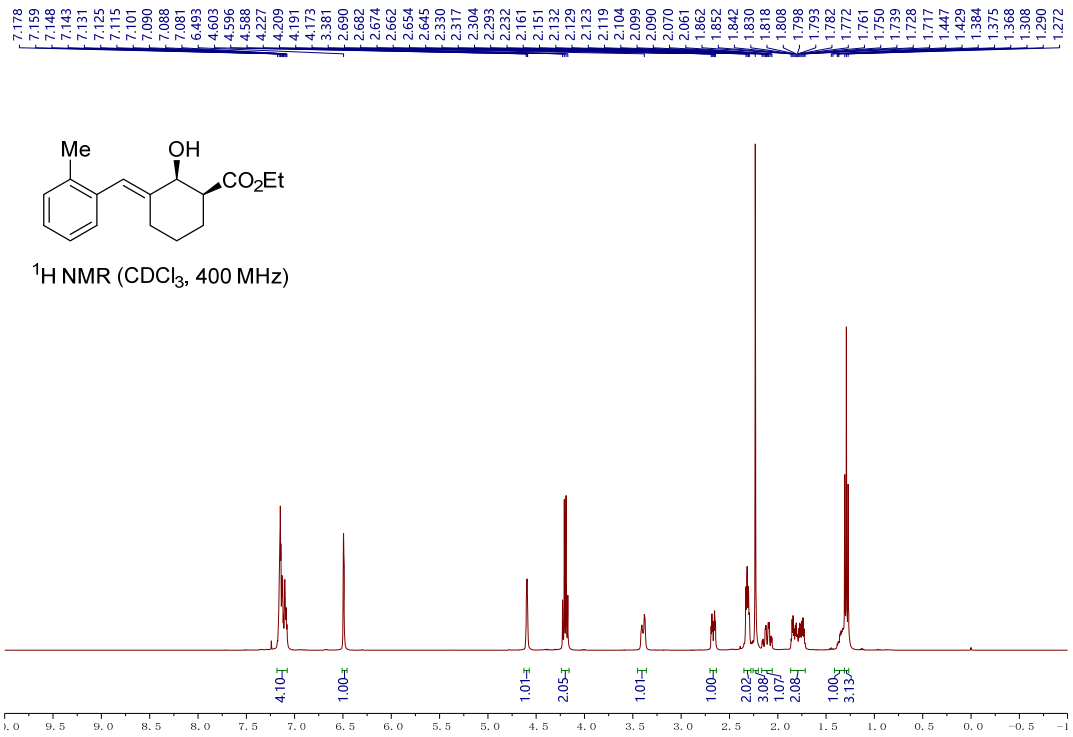


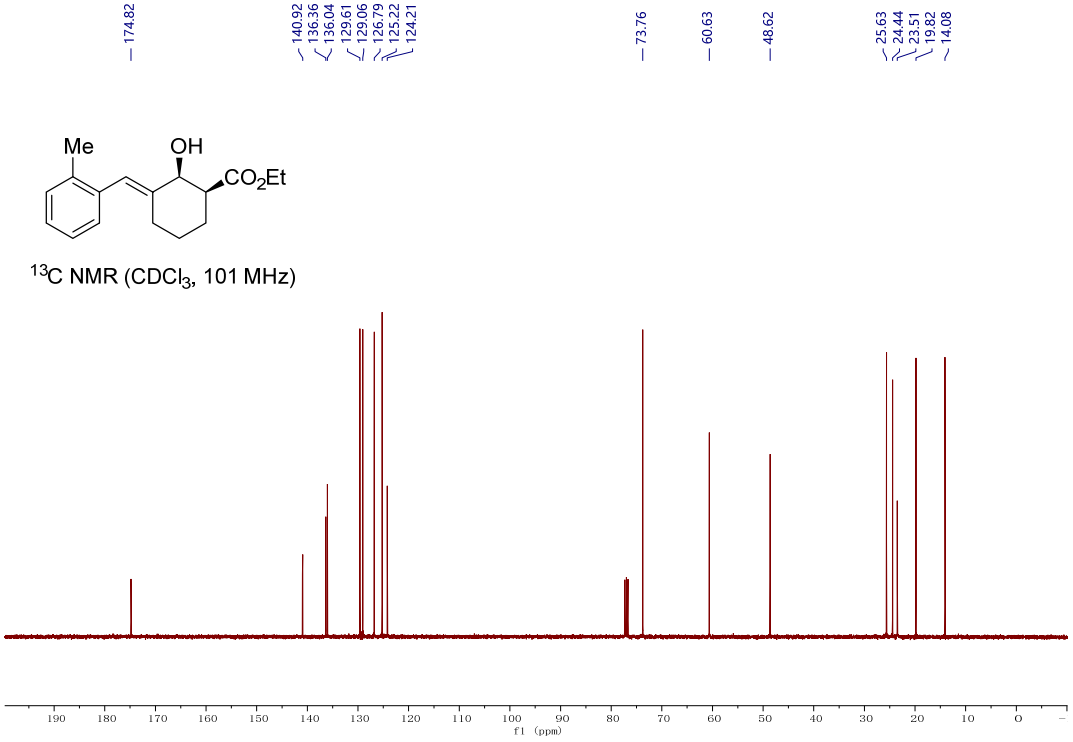
(+)-Ethyl 3-((*E*)-3-bromobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8k)



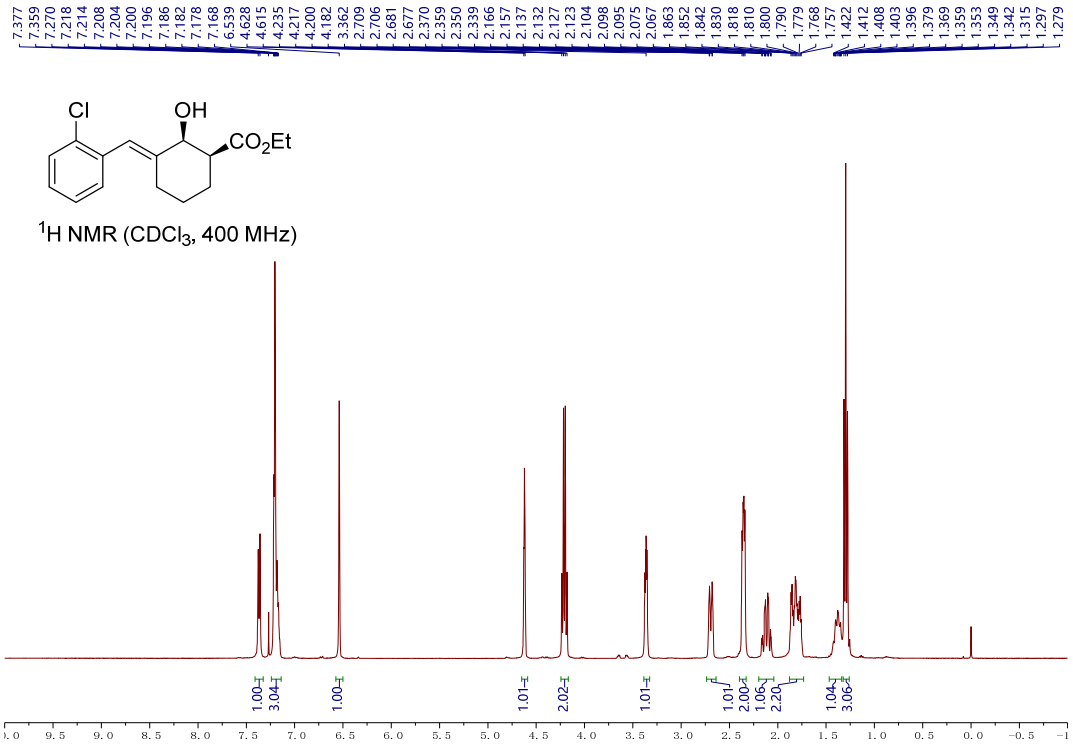


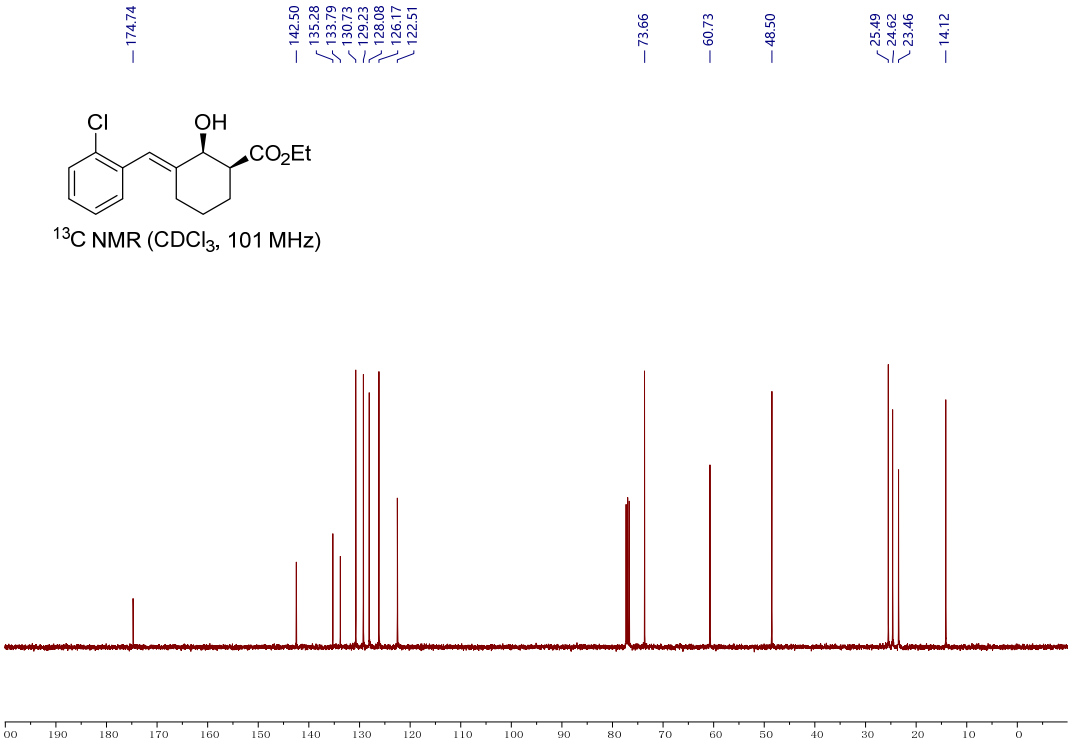
(+)-Ethyl 2-hydroxy-3-((*E*)-2-methylbenzylidene)cyclohexane-1-carboxylate ((+)-8l)



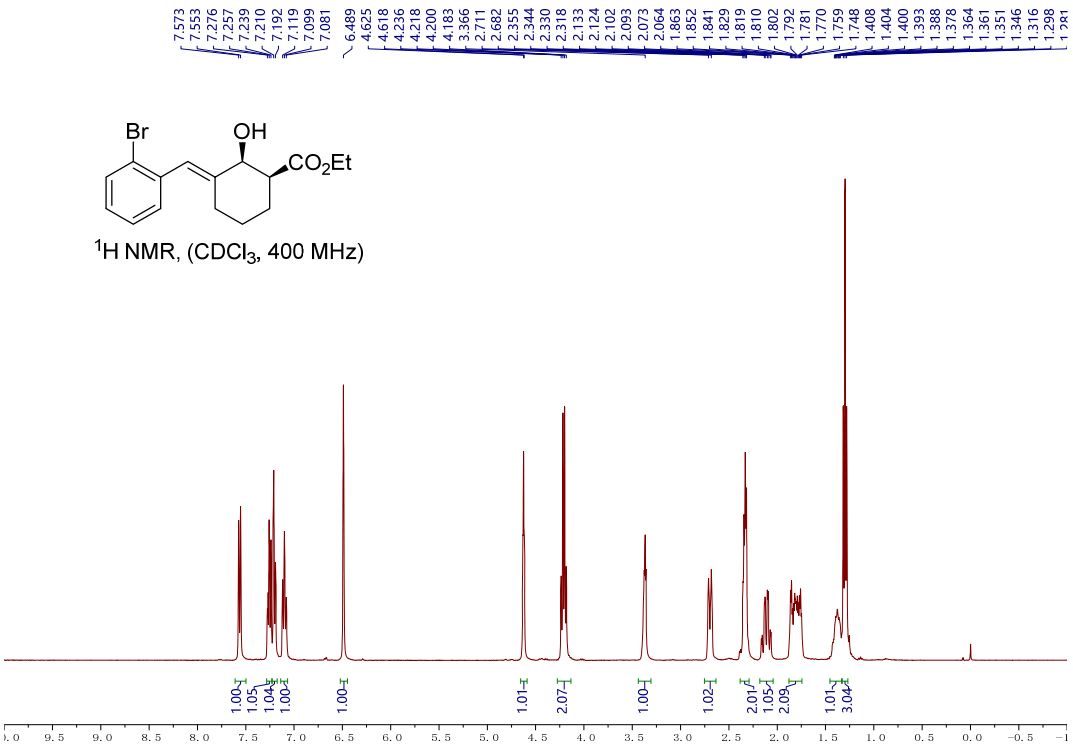


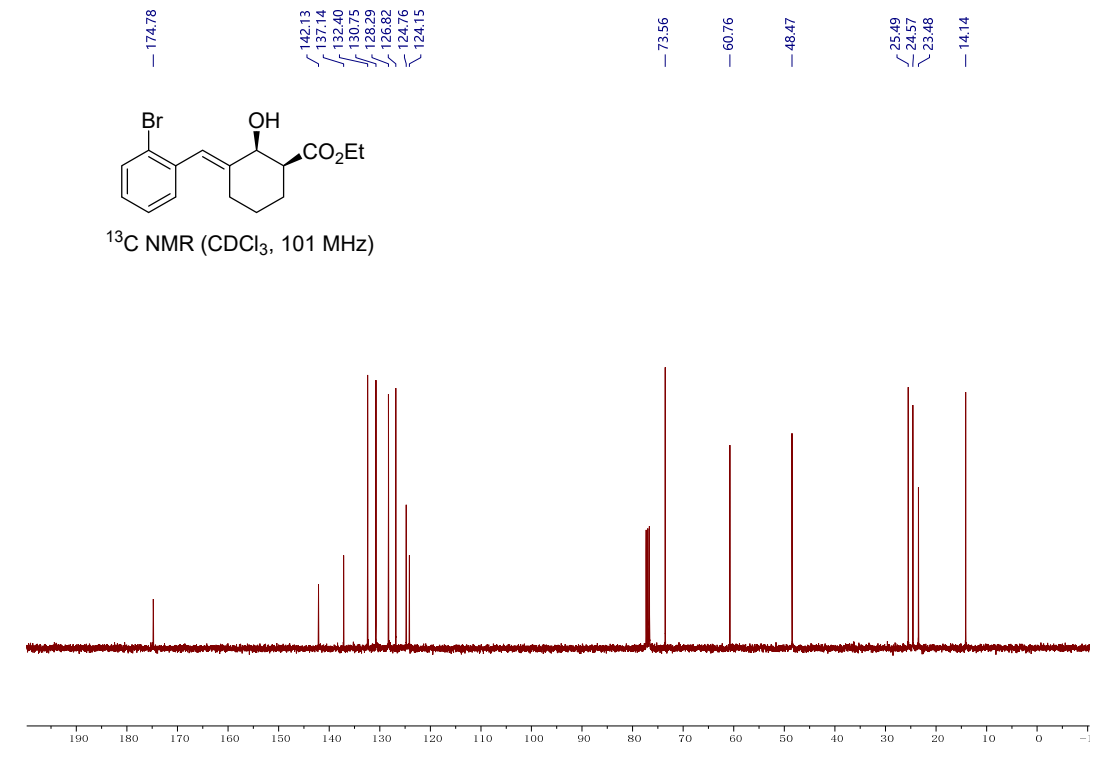
(+)-Ethyl 3-((*E*)-2-chlorobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8m)



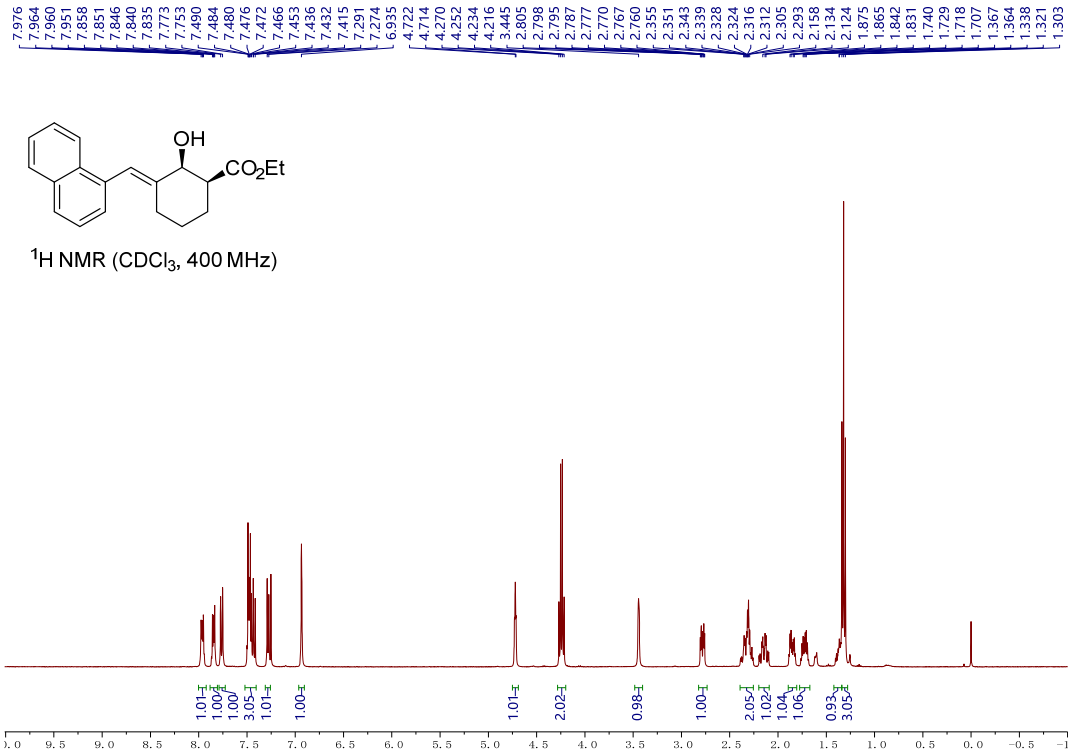


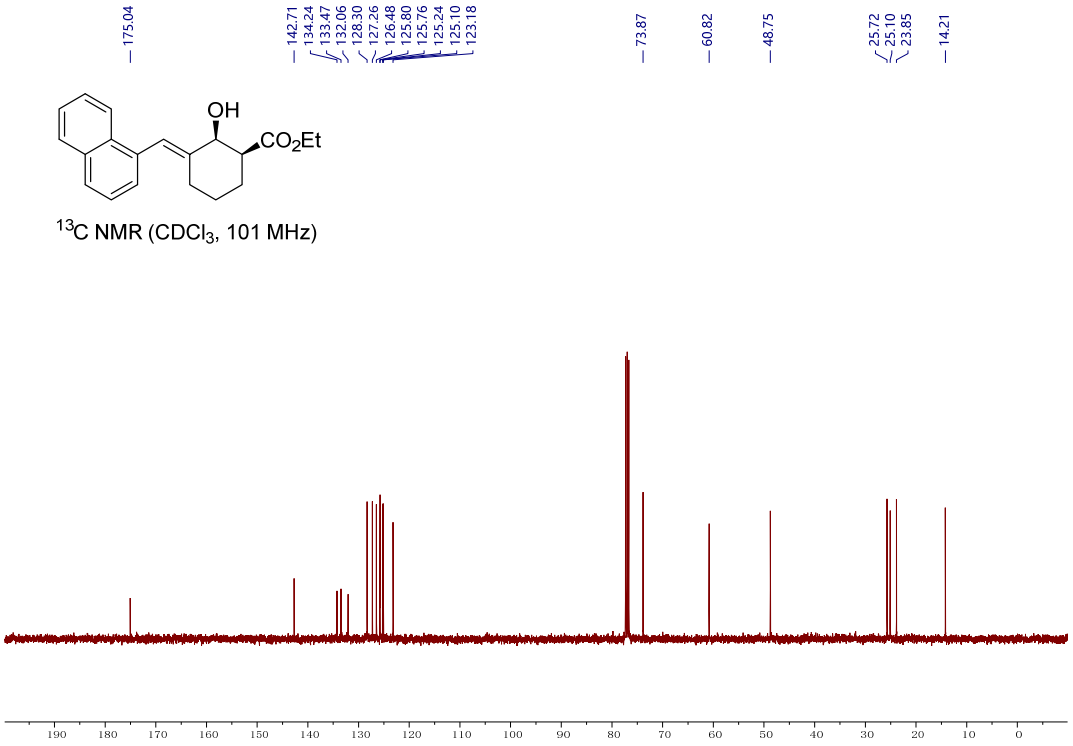
(+)-Ethyl 3-((*E*)-2-bromobenzylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8n)



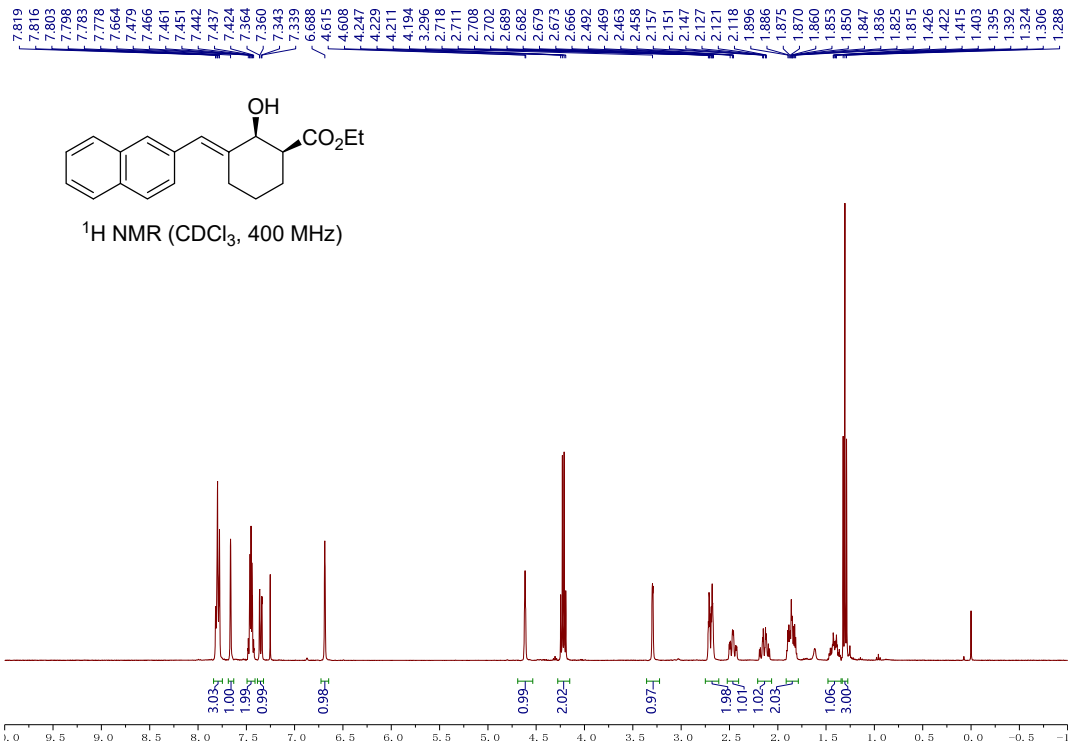


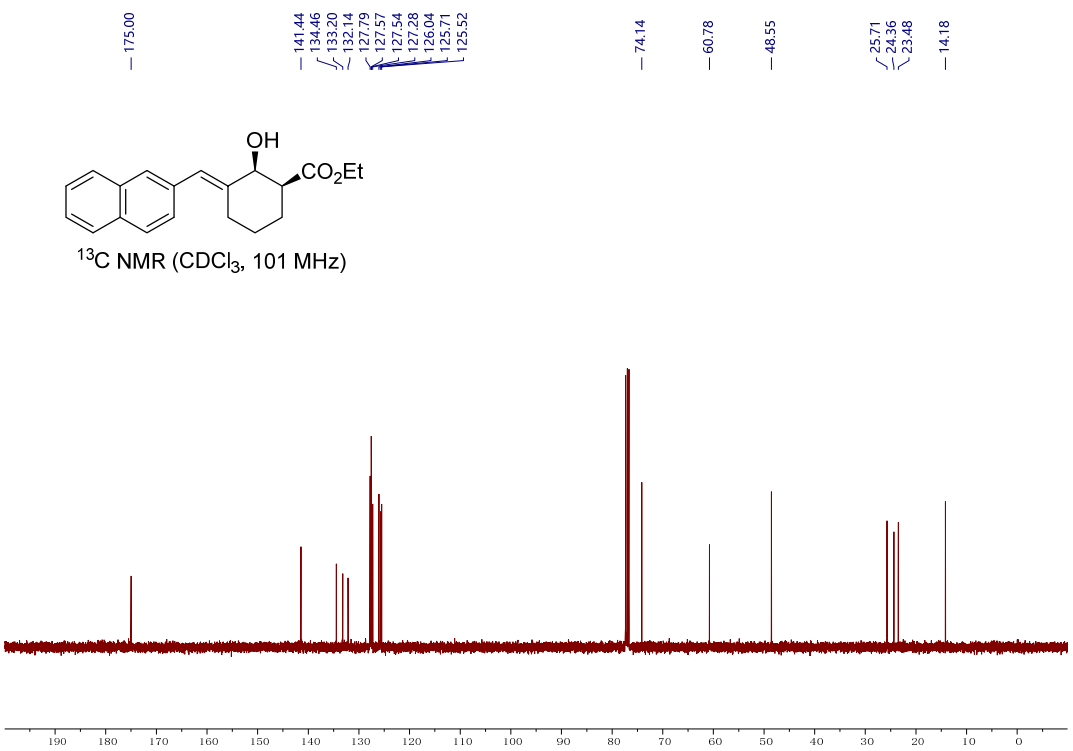
(+)-Ethyl (*E*)-2-hydroxy-3-(naphthalen-1-ylmethylene)cyclohexane-1-carboxylate ((+)-8o)



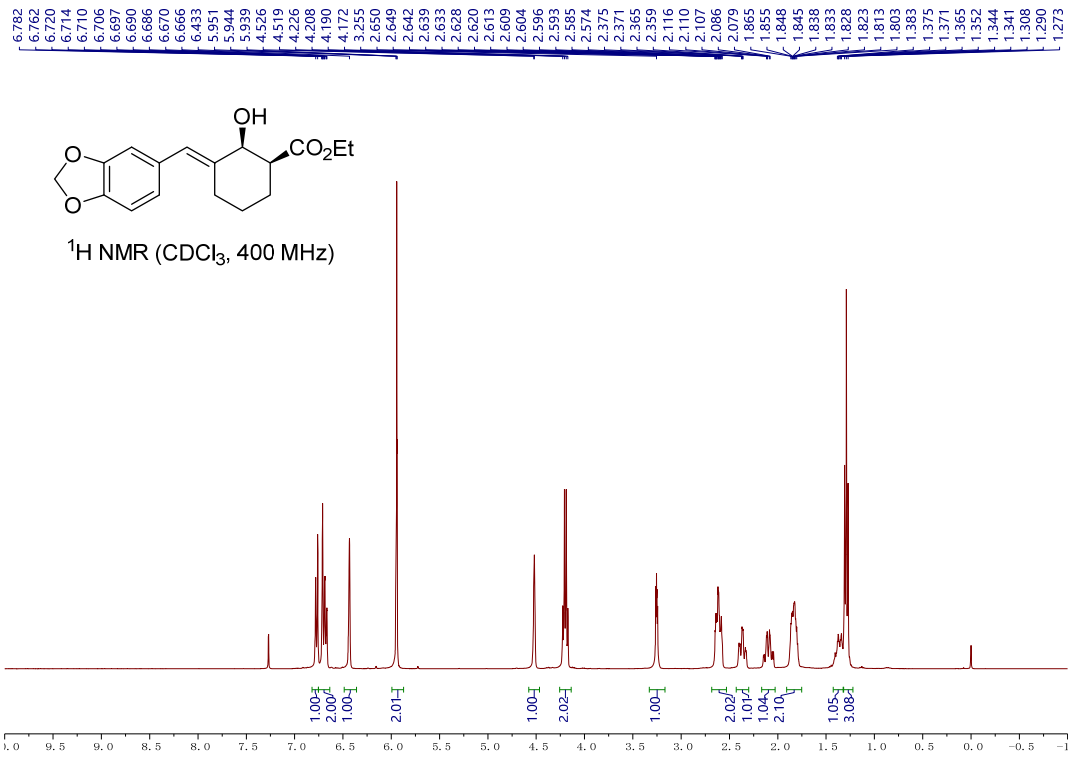


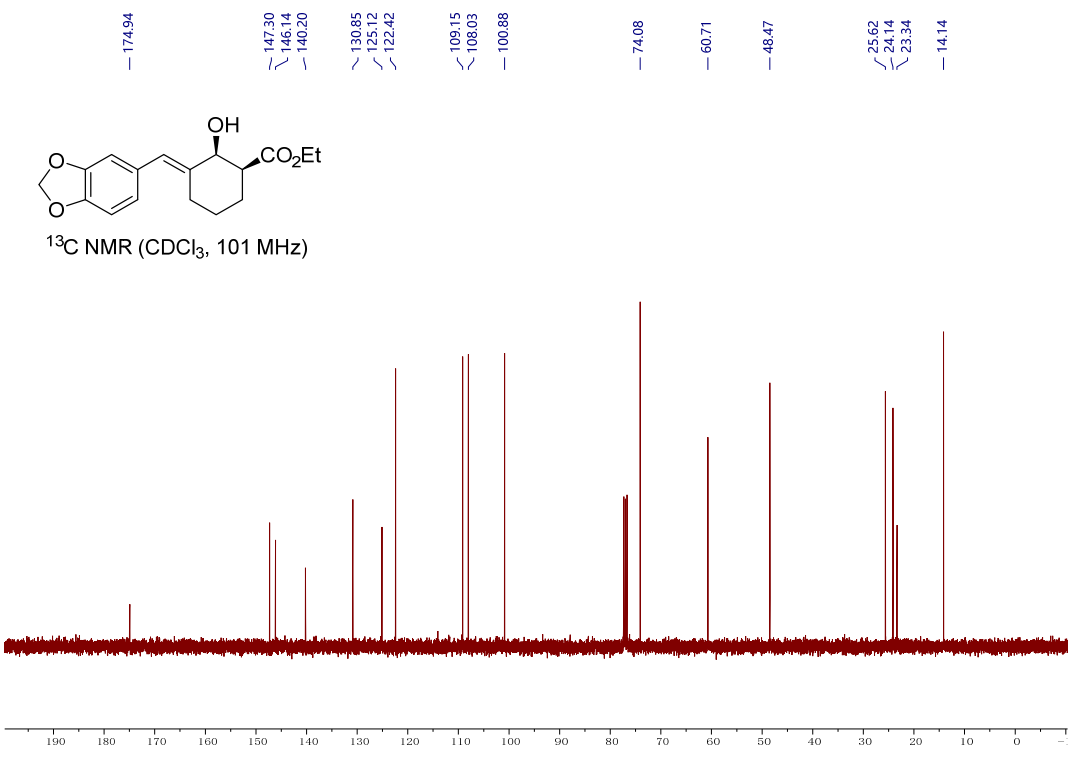
(+)-Ethyl (*E*)-2-hydroxy-3-(naphthalen-2-ylmethylene)cyclohexane-1-carboxylate ((+)-8p)



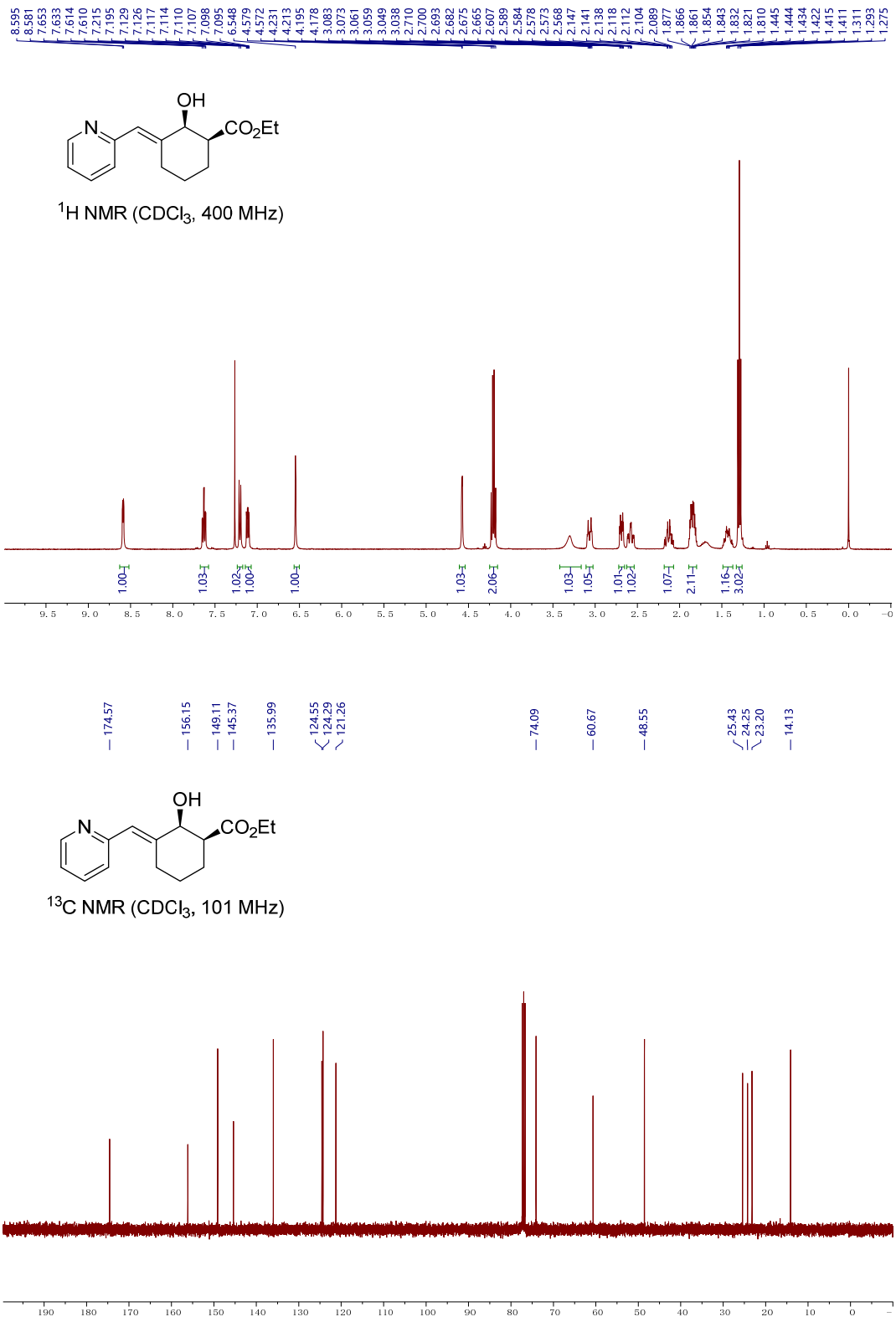


(+)-Ethyl (*E*)-3-(benzo[d][1,3]dioxol-5-ylmethylene)-2-hydroxycyclohexane-1-carboxylate ((+)-8q)

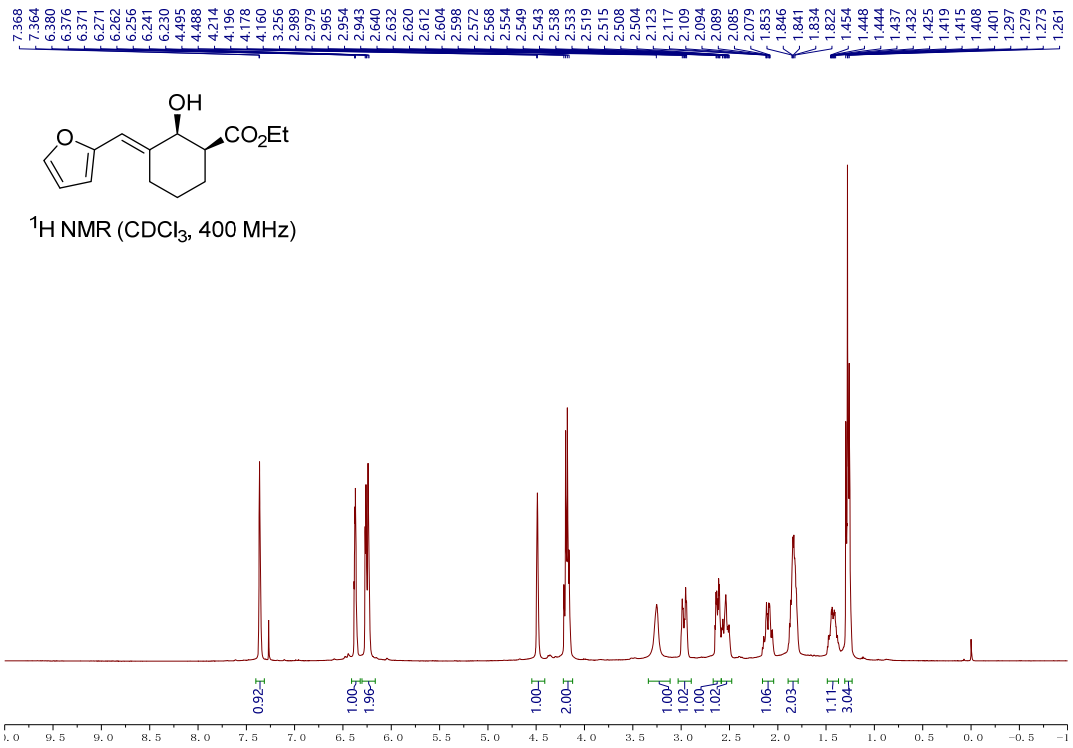


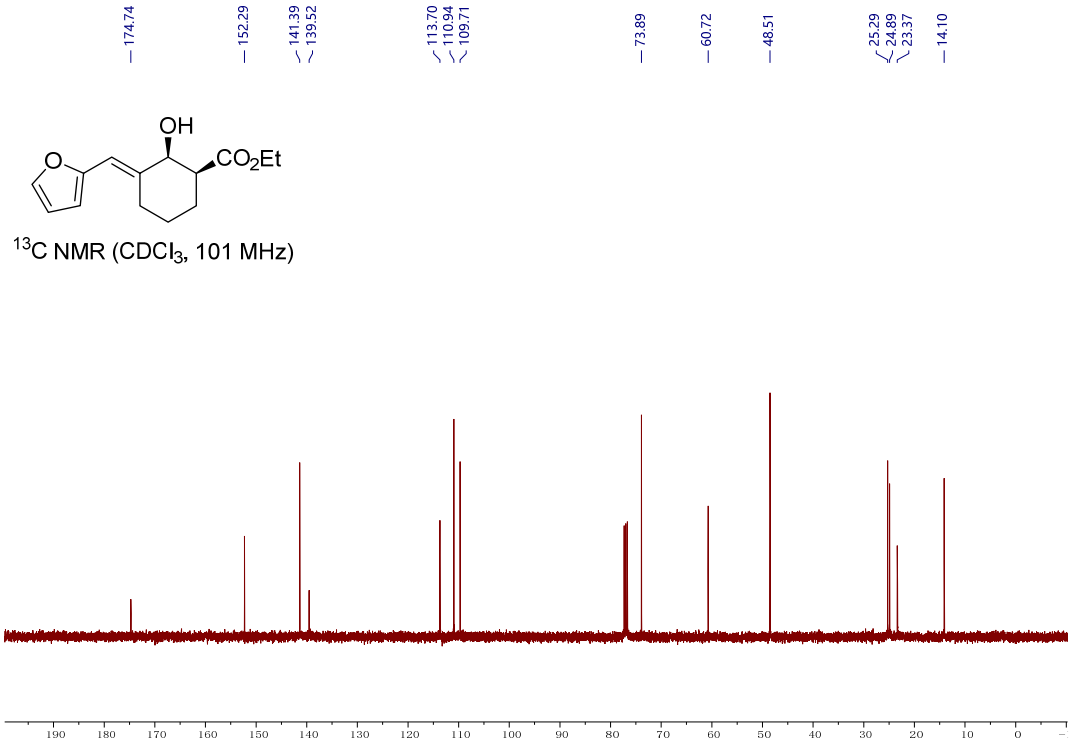


(+)-Ethyl (*E*)-2-hydroxy-3-(pyridin-2-ylmethylene)cyclohexane-1-carboxylate ((+)-8r)

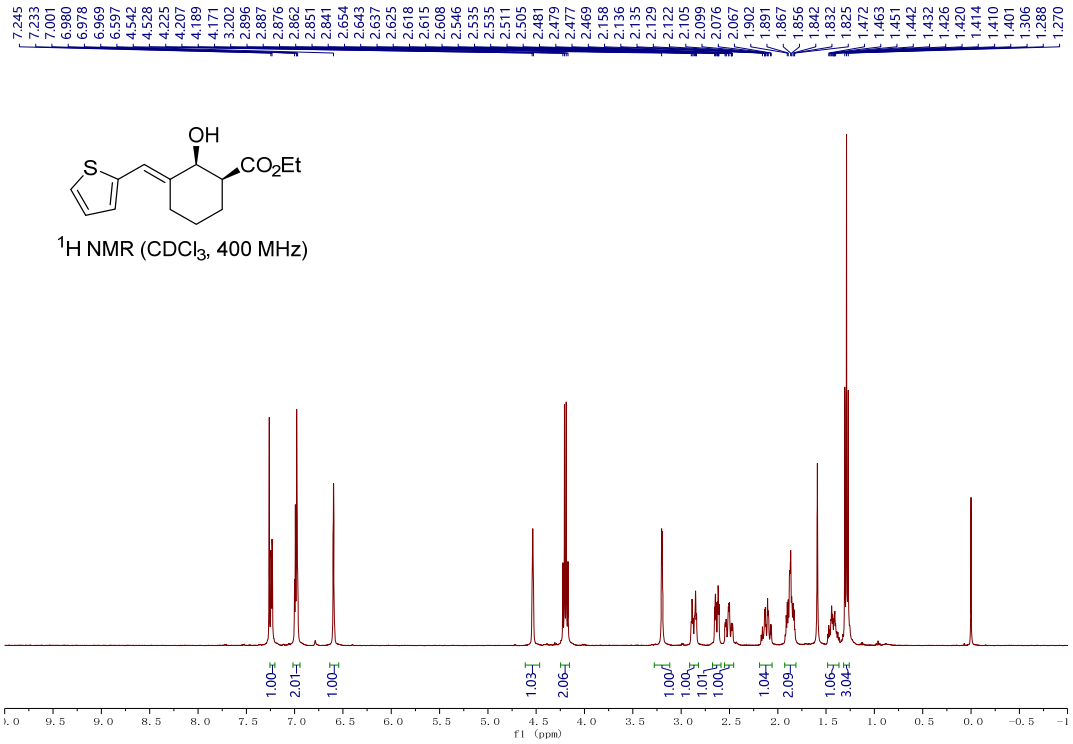


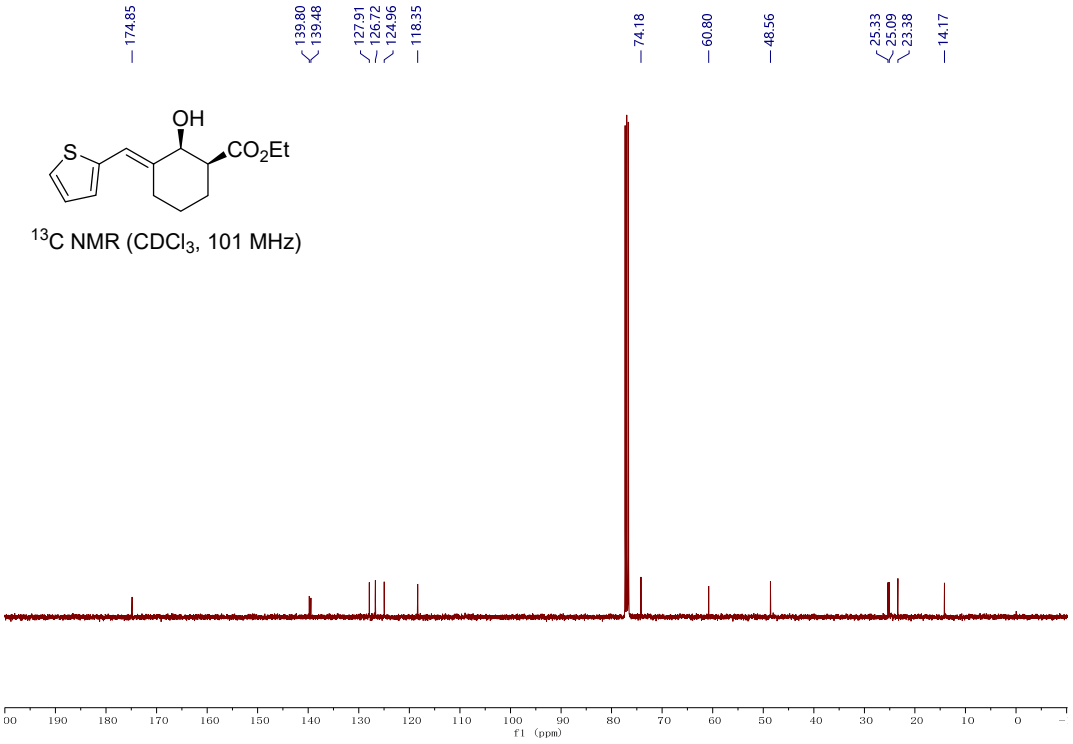
(+)-Ethyl (*E*)-3-(furan-2-ylmethylene)-2-hydroxycyclohexane-1-carboxylate ((+)-8s)



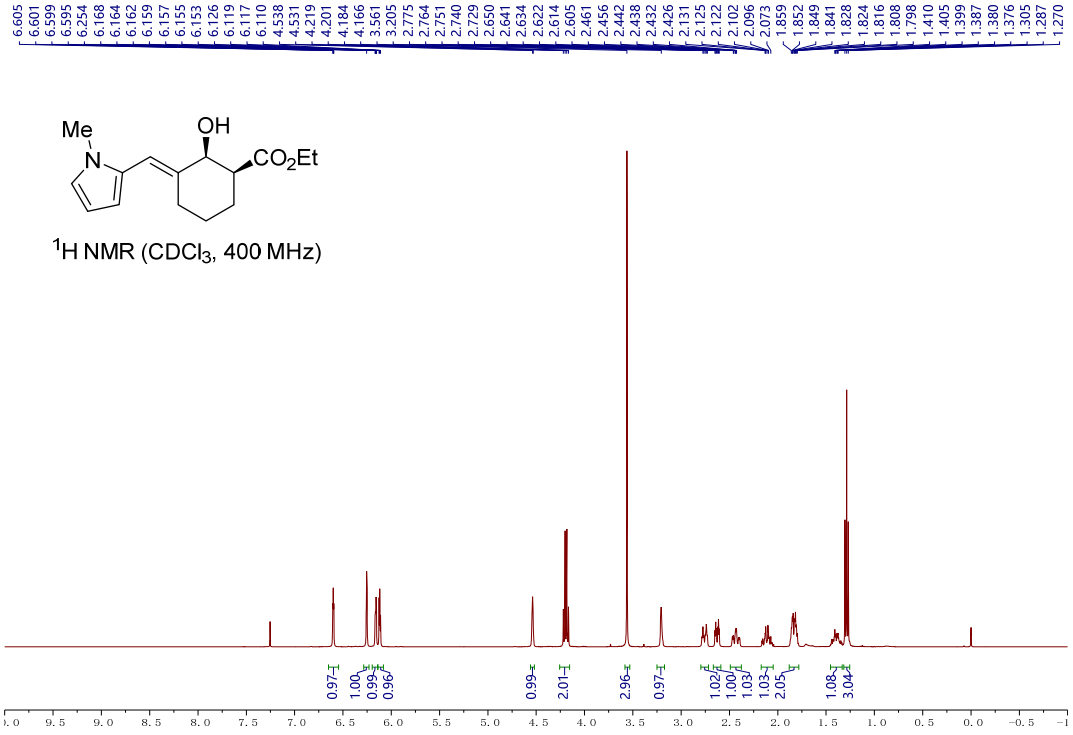


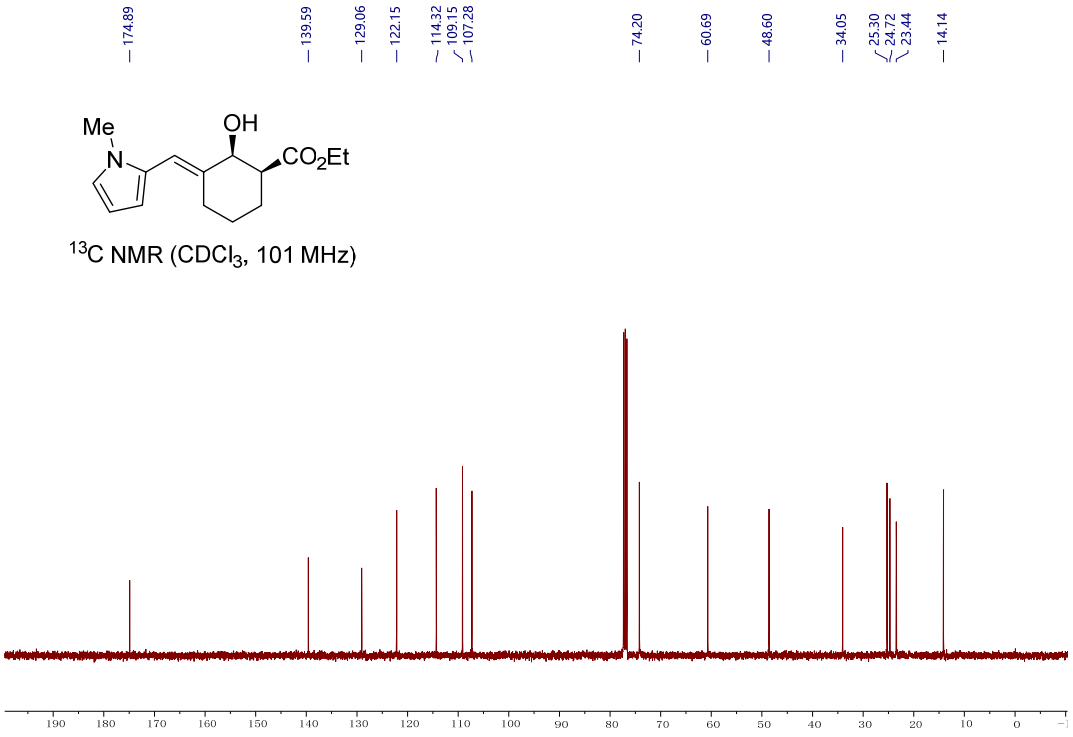
(+)-Ethyl (*E*)-2-hydroxy-3-(thiophen-2-ylmethylene)cyclohexane-1-carboxylate ((+)-8t)



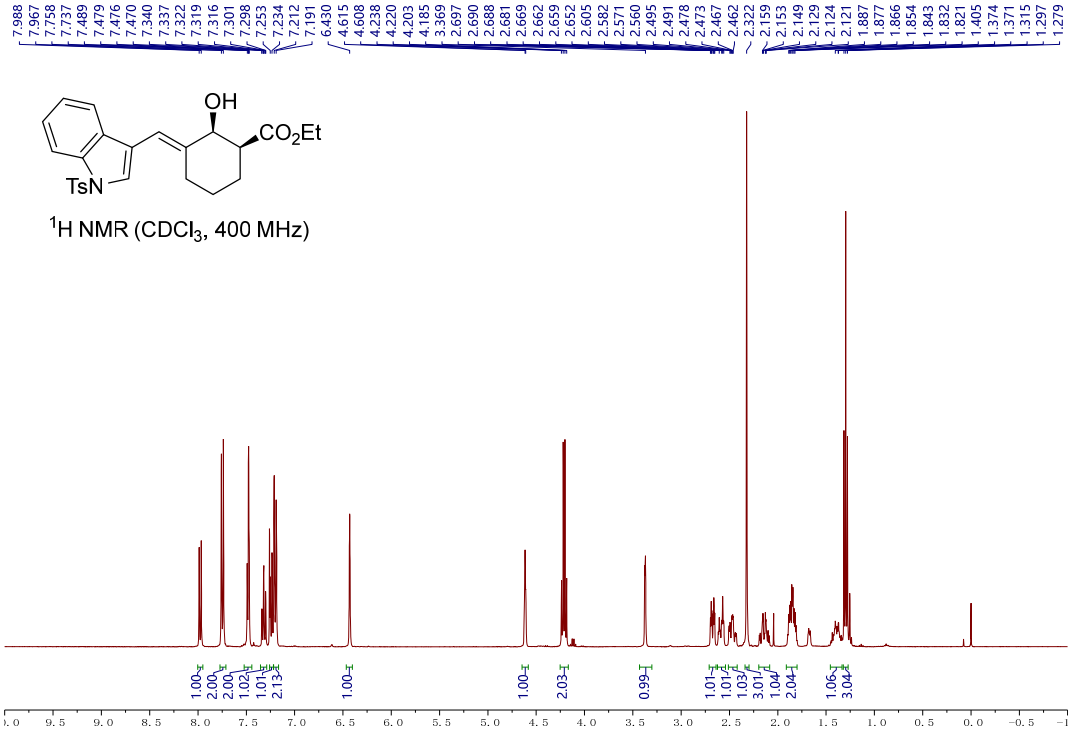


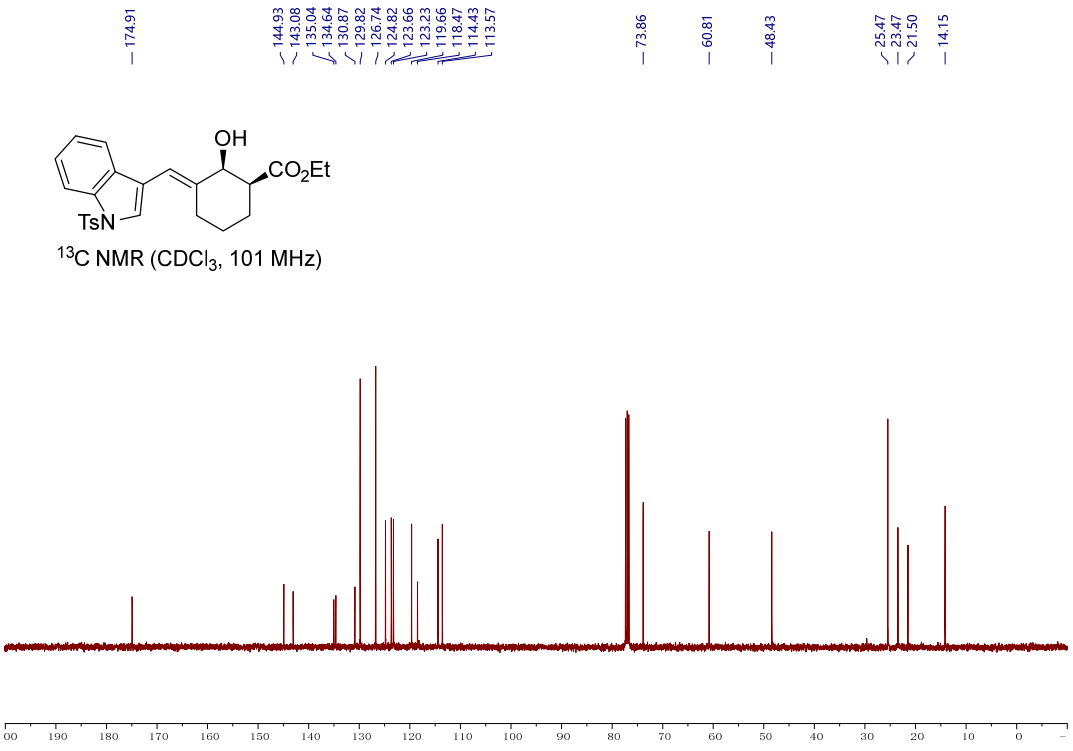
(+)-Ethyl (*E*)-2-hydroxy-3-((1-methyl-1H-pyrrol-2-yl)methylene)cyclohexane-1-carboxylate ((+)-8u)



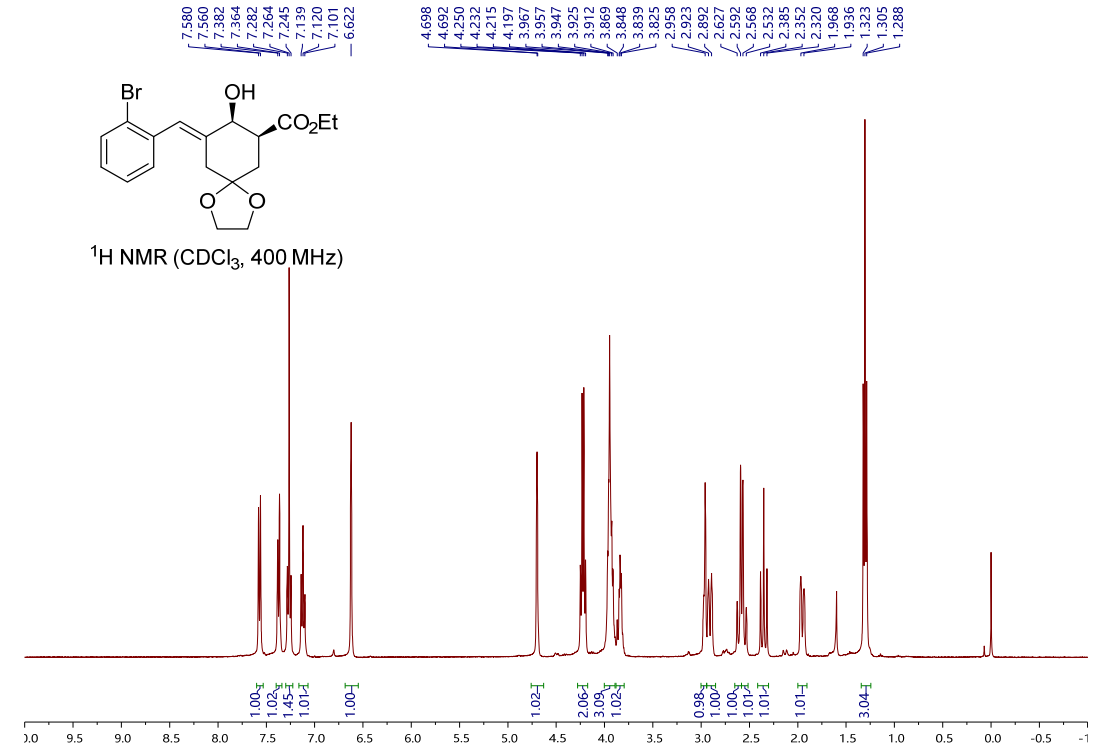


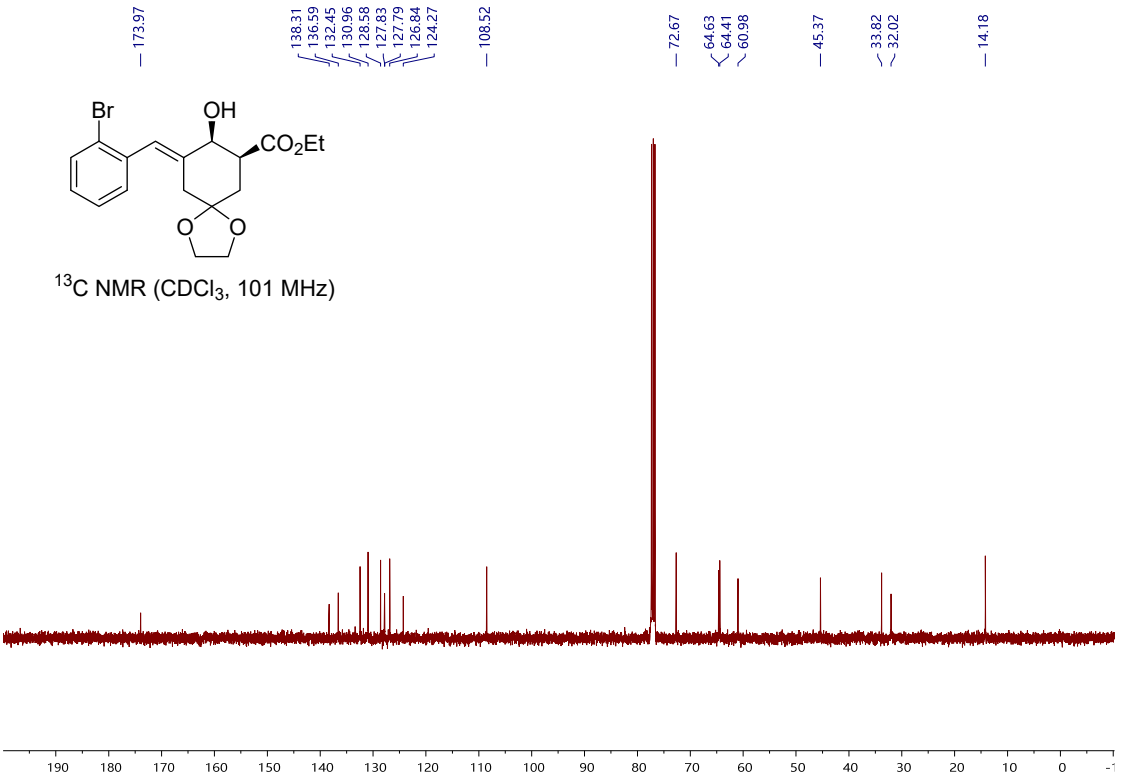
Ethyl (1*S*,2*S*,*E*)-2-hydroxy-3-((1-tosyl-1H-indol-3-yl)methylene)cyclohexane-1-carboxylate ((1*S*,2*S*)-8v)



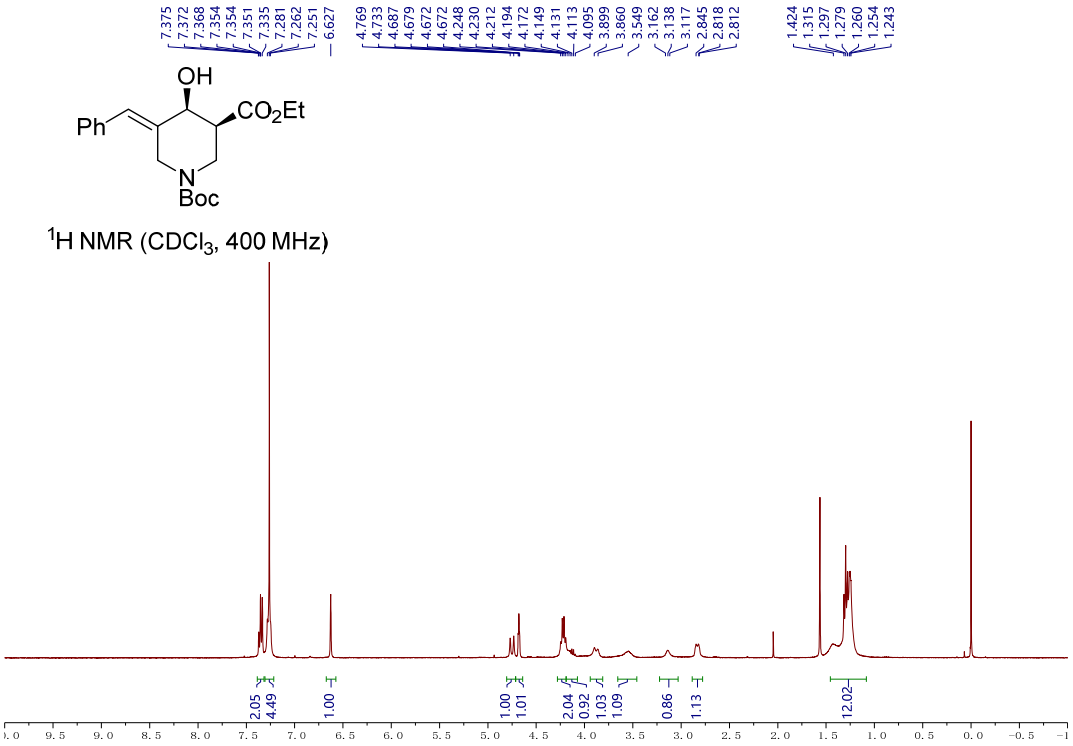


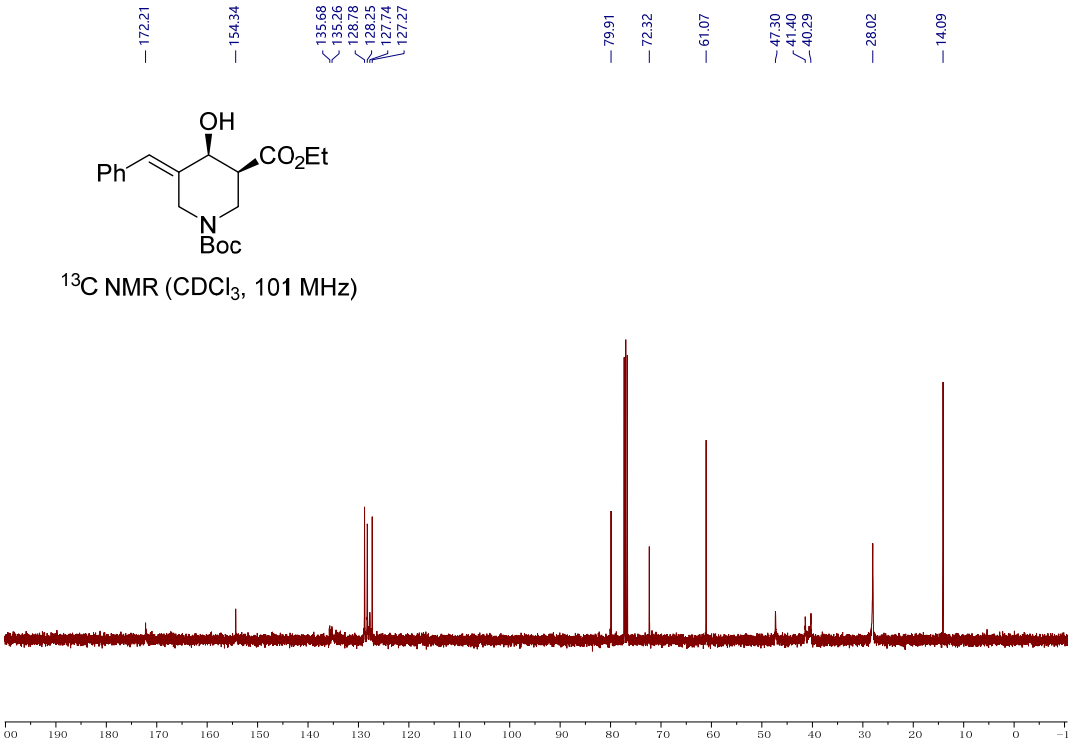
(+)-Ethyl 9-((*E*)-2-bromobenzylidene)-8-hydroxy-1,4-dioxaspiro[4.5]decane-7-carboxylate ((+)-8w)



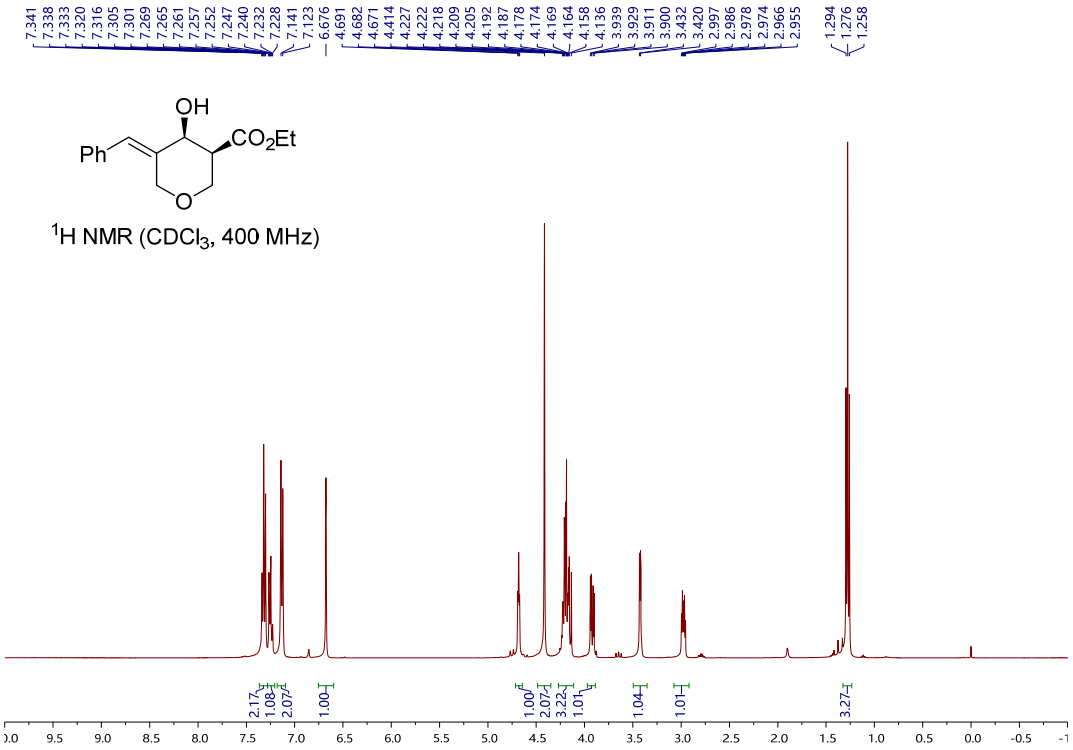


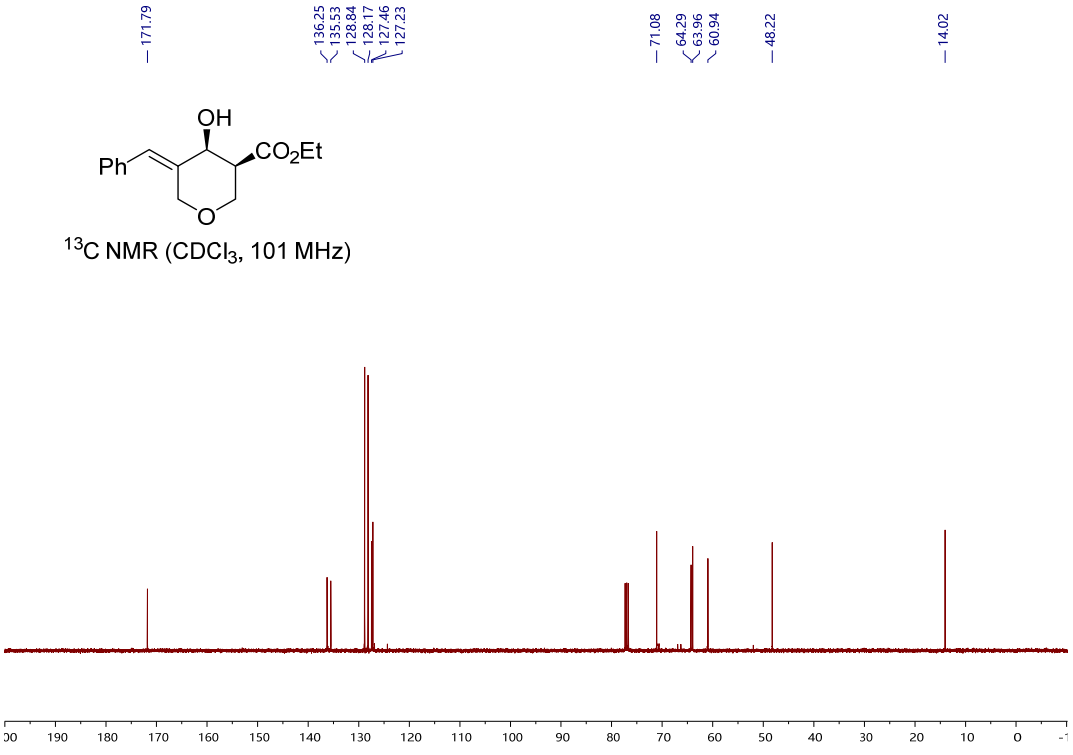
(+)-1-(*tert*-Butyl) 3-ethyl 5-((*E*)-benzylidene)-4-hydroxypiperidine-1,3-dicarboxylate ((+)-8x)



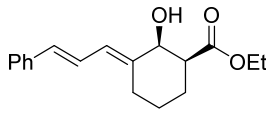


(+)-Ethyl 5-((*E*)-benzylidene)-4-hydroxytetrahydro-2H-pyran-3-carboxylate ((+)-8y)

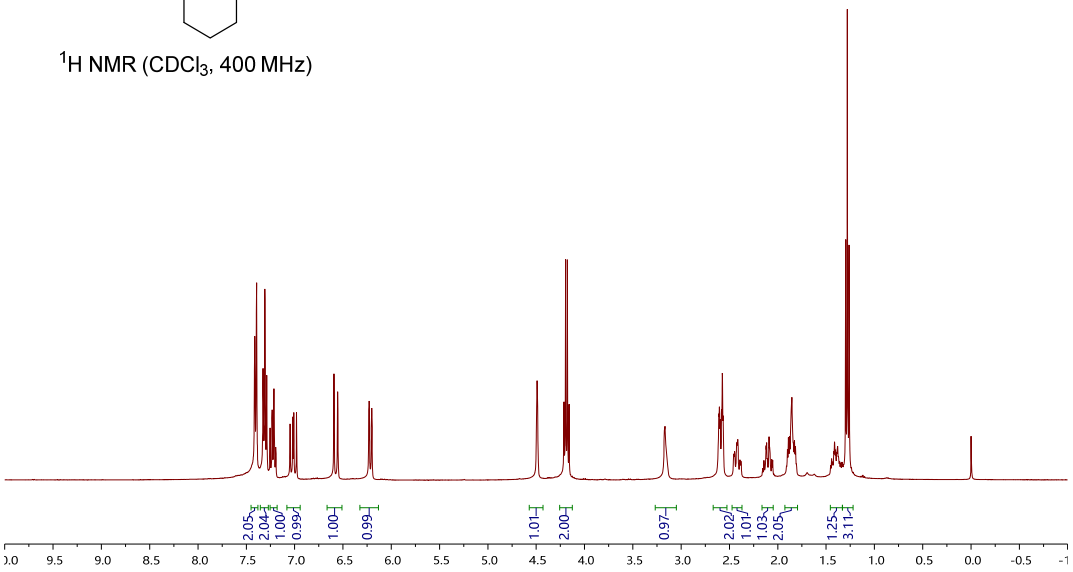


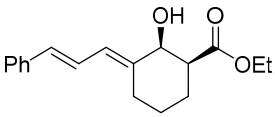


(+)-Ethyl (*E*)-2-hydroxy-3-((*E*)-3-phenylallylidene)cyclohexane-1-carboxylate ((+)-8z)

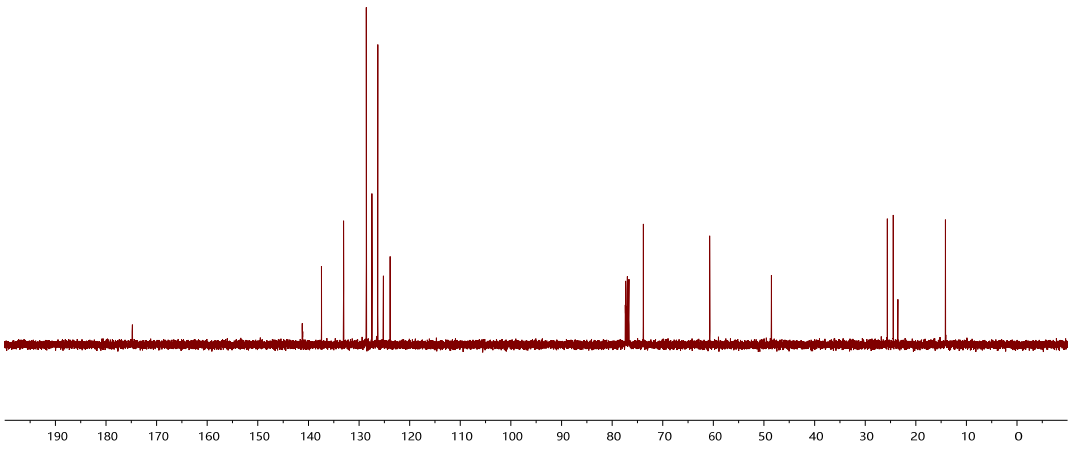


^{1}H NMR ($CDCl_3$, 400 MHz)

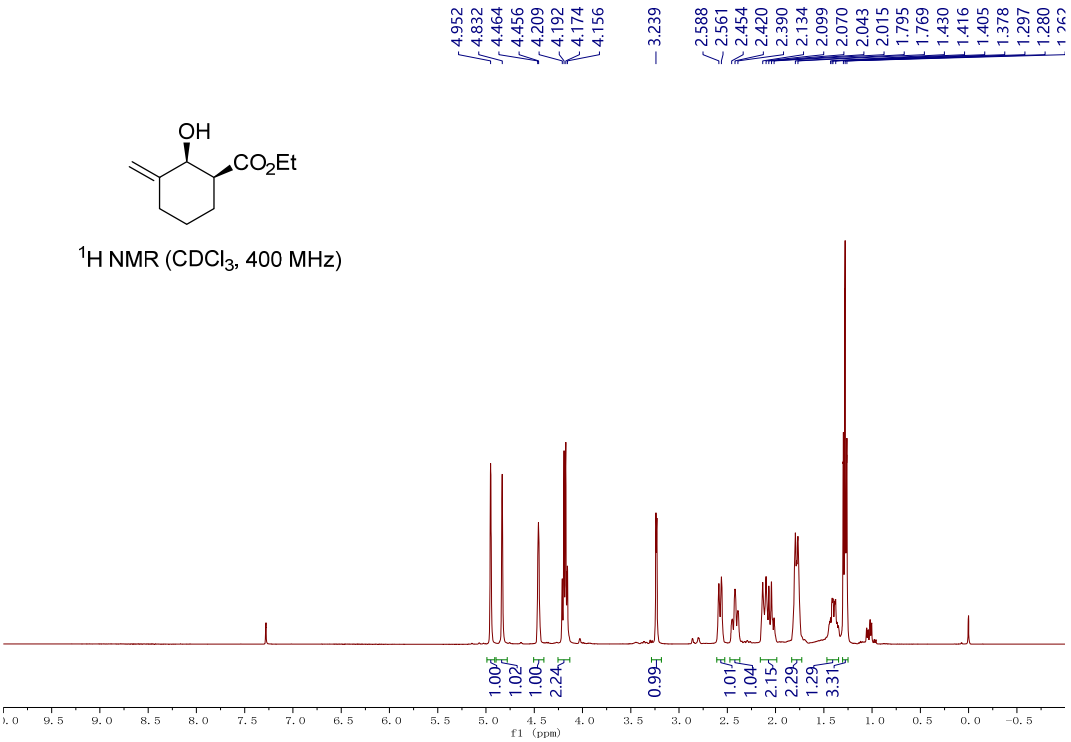


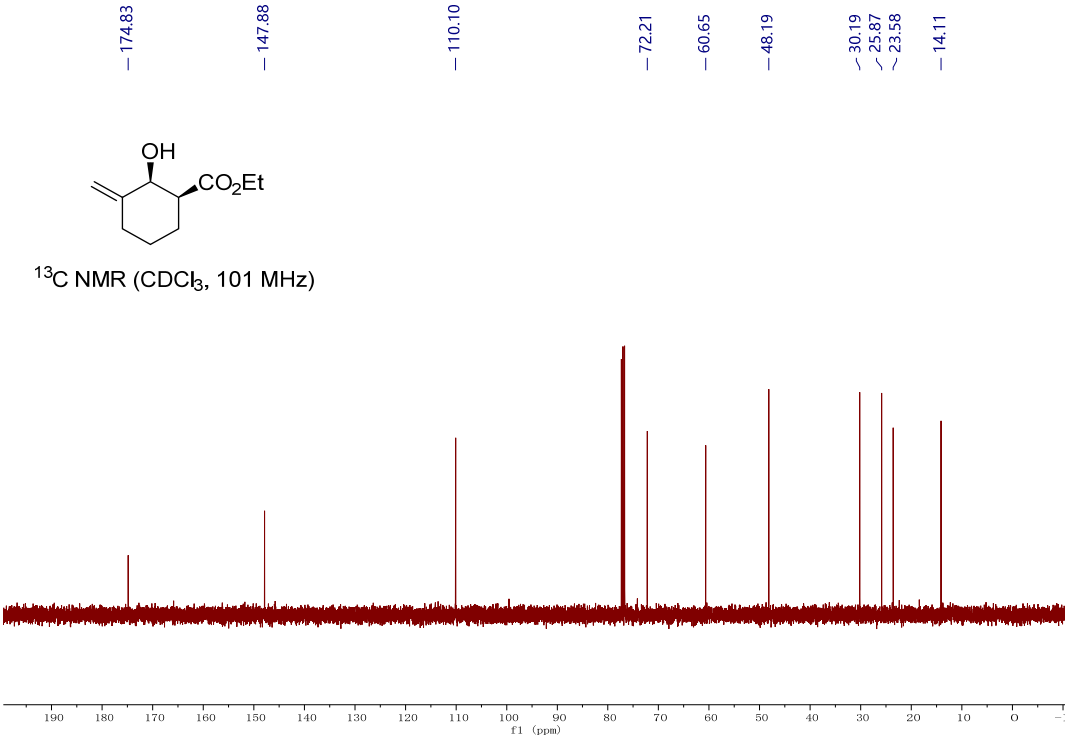


^{13}C NMR ($CDCl_3$, 101 MHz)

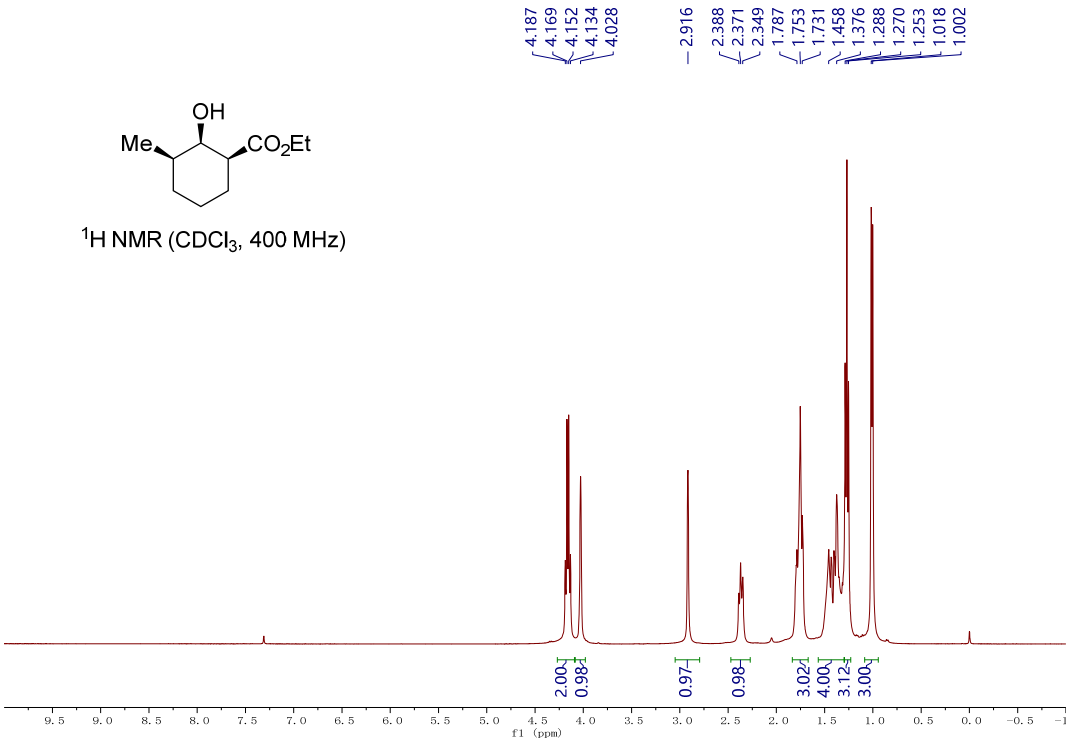


(+)-Ethyl 2-hydroxy-3-methylenecyclohexane-1-carboxylate ((+)-8aa)

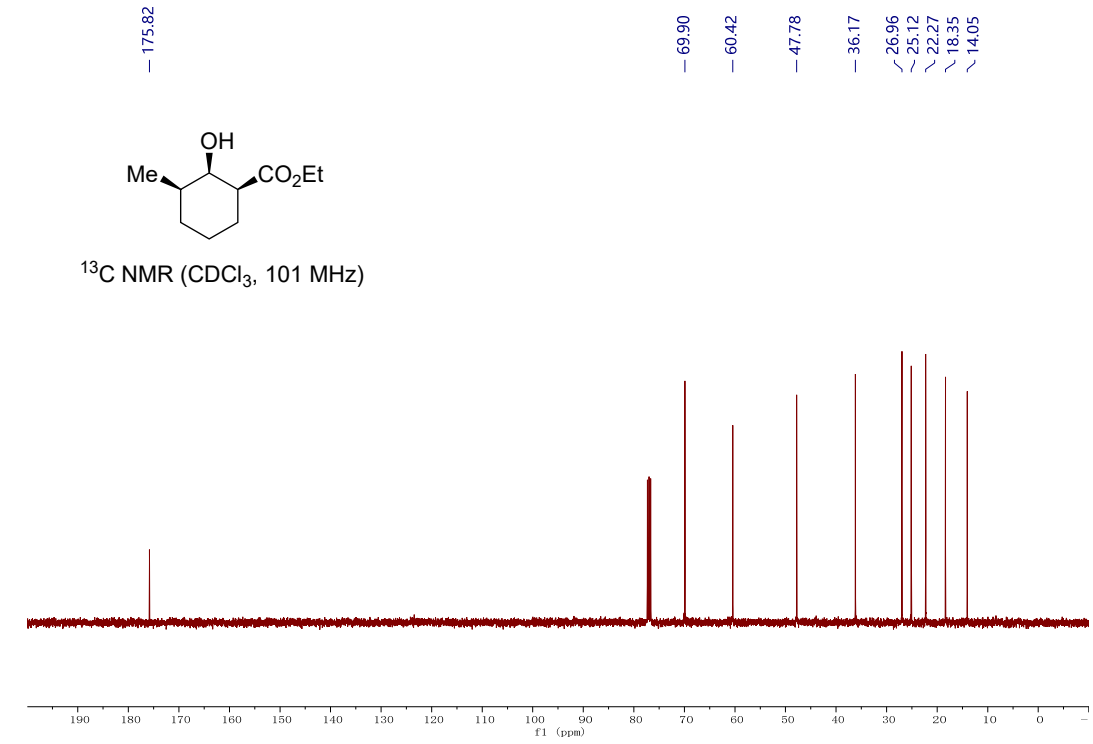




(*cis*,*cis*)-Ethyl 2-hydroxy-3-methylcyclohexane-1-carboxylate

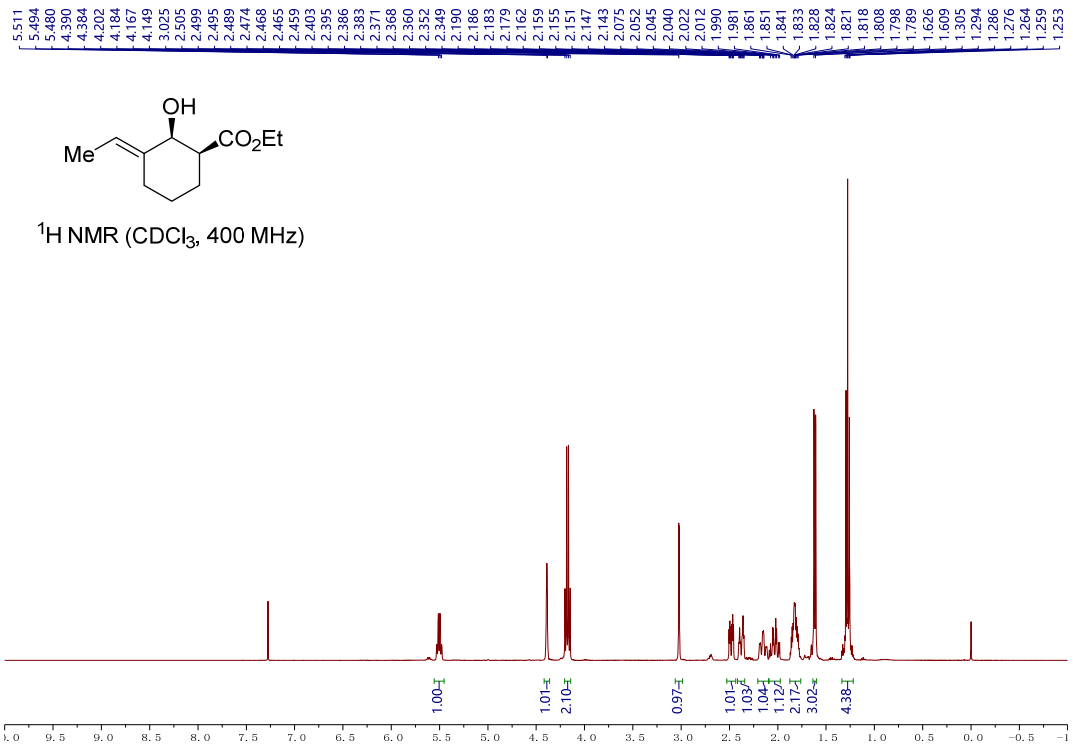


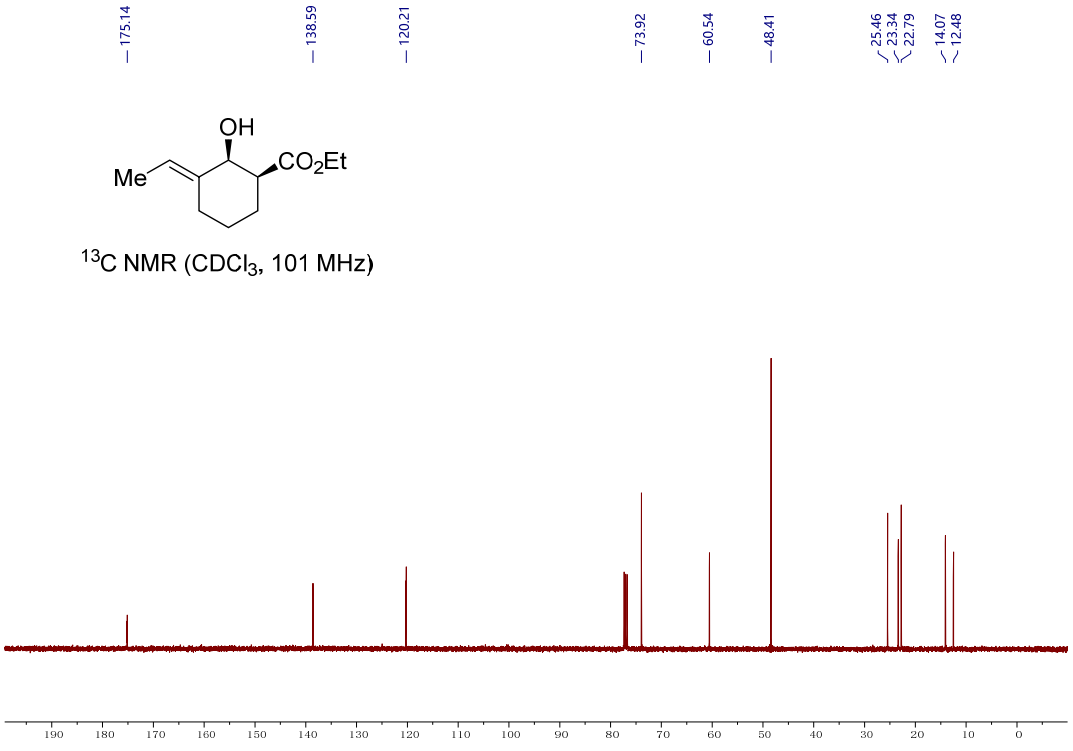
^{1}H NMR ($CDCl_3$, 400 MHz)



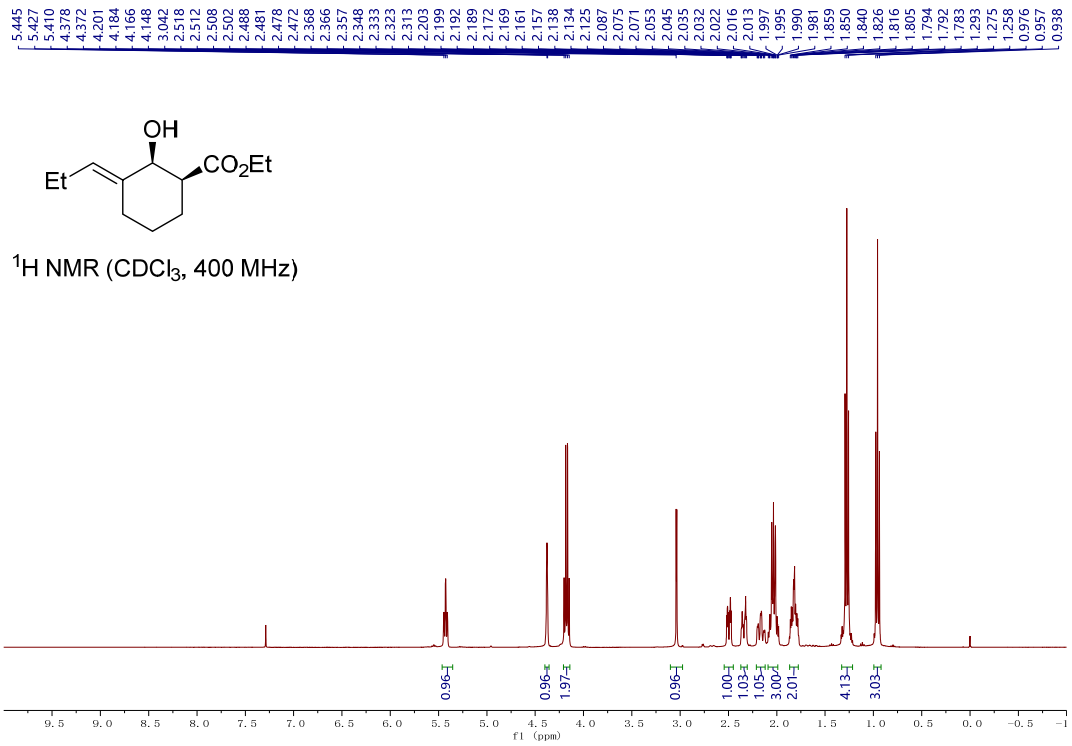
^{13}C NMR ($CDCl_3$, 101 MHz)

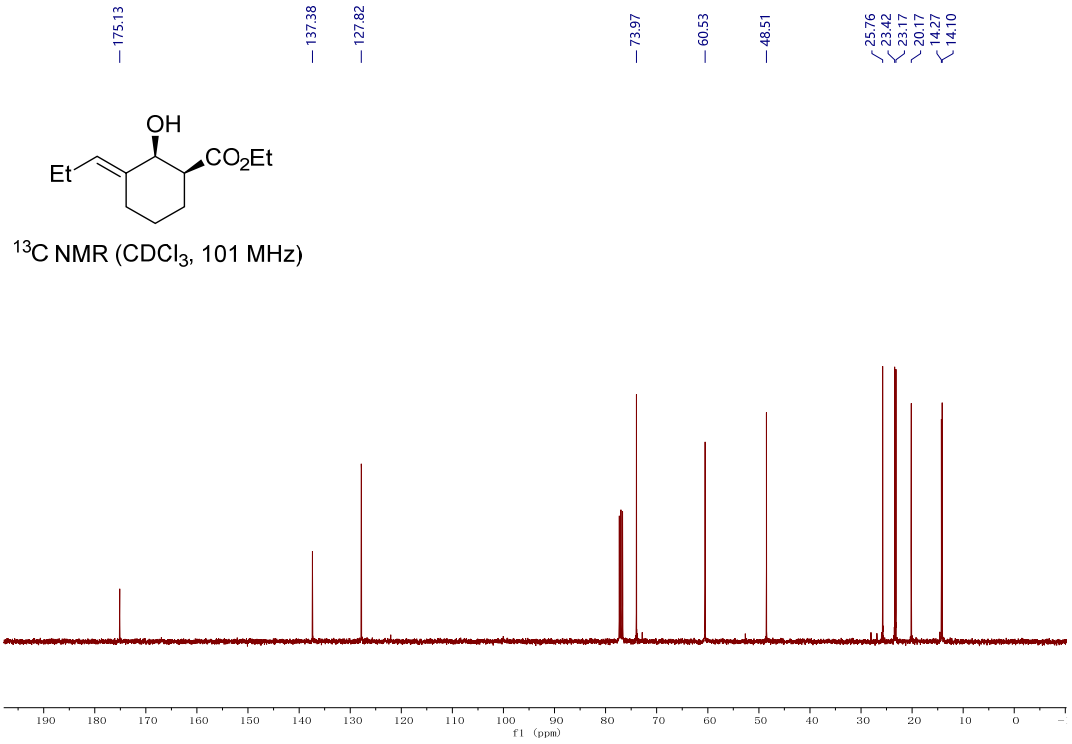
(+)-Ethyl (*E*)-3-ethylidene-2-hydroxycyclohexane-1-carboxylate ((+)-8ab)



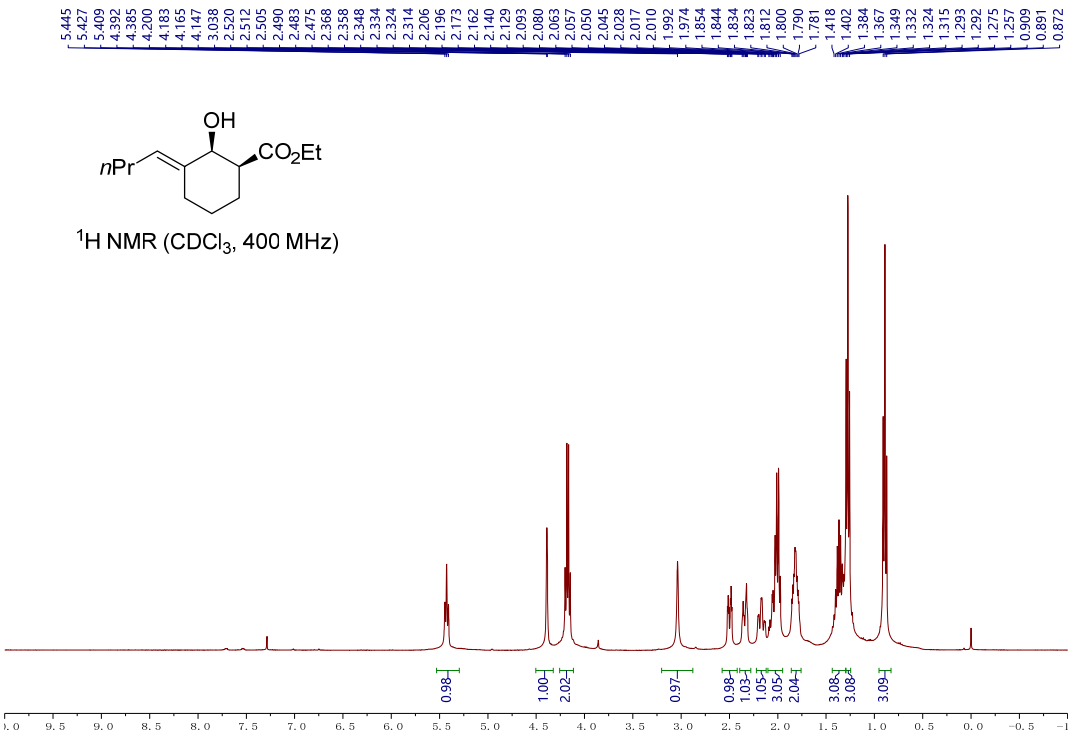


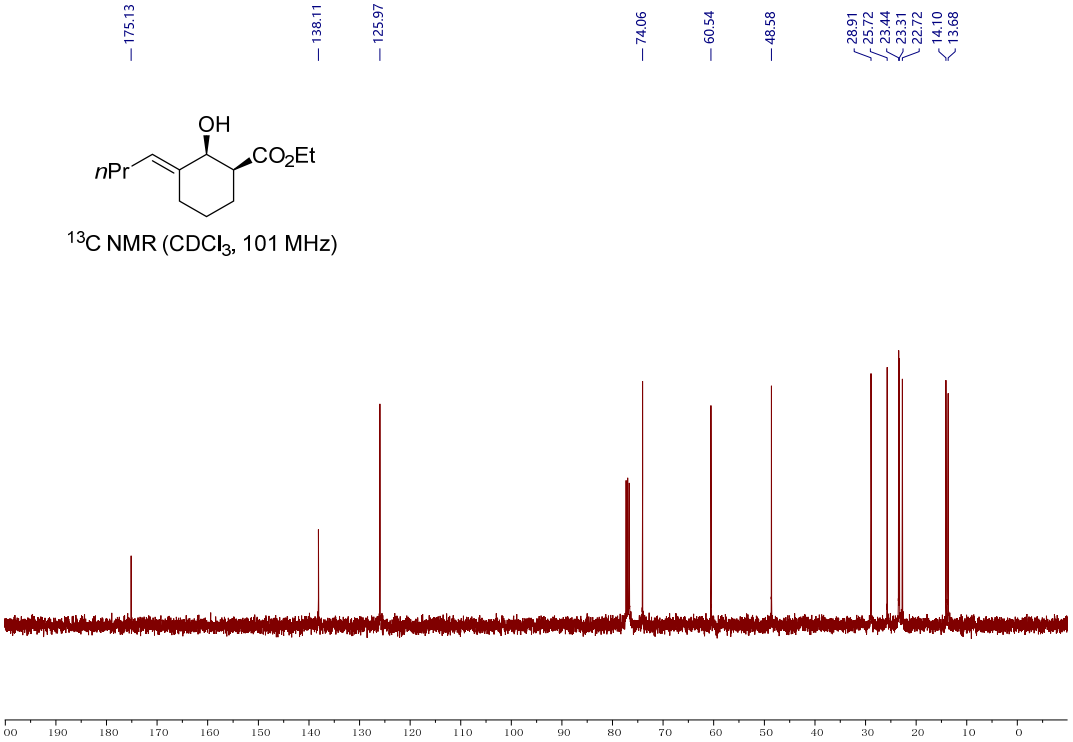
(+)-Ethyl (*E*)-2-hydroxy-3-propylidenecyclohexane-1-carboxylate ((+)-8ac)



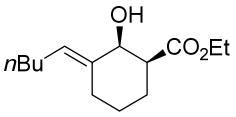


(+)-Ethyl (*E*)-3-butylidene-2-hydroxycyclohexane-1-carboxylate ((+)-8ad)

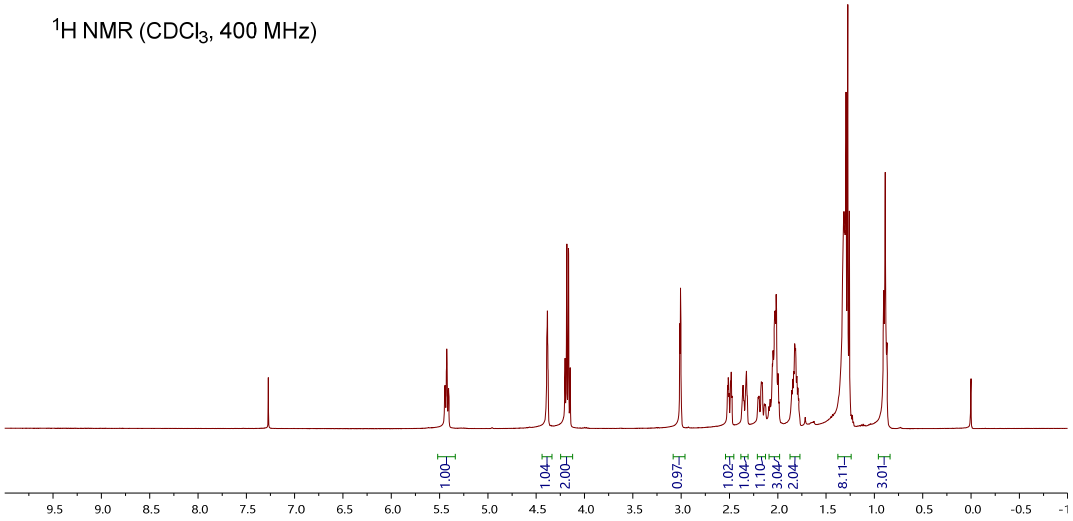


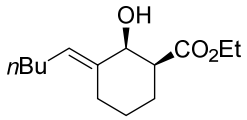


(+)-Ethyl (*E*)-2-hydroxy-3-pentylidenecyclohexane-1-carboxylate ((+)-8ae)

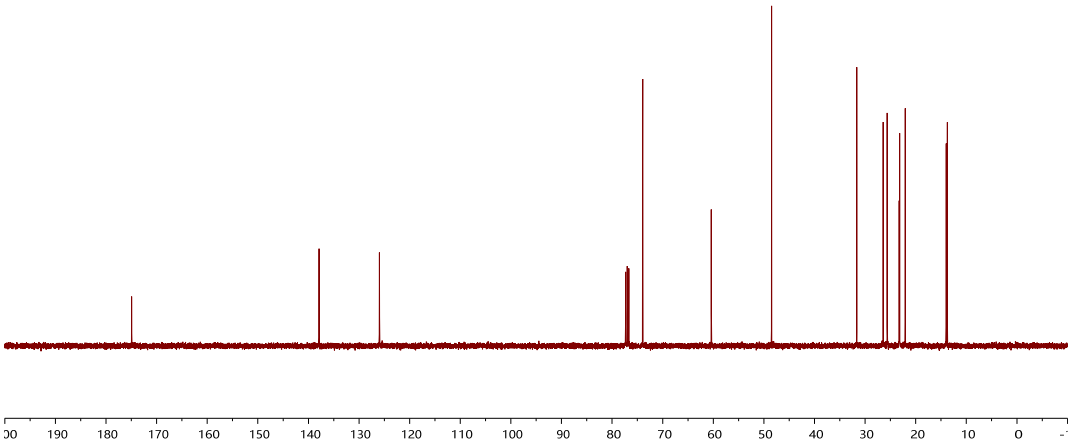


^{1}H NMR ($CDCl_3$, 400 MHz)

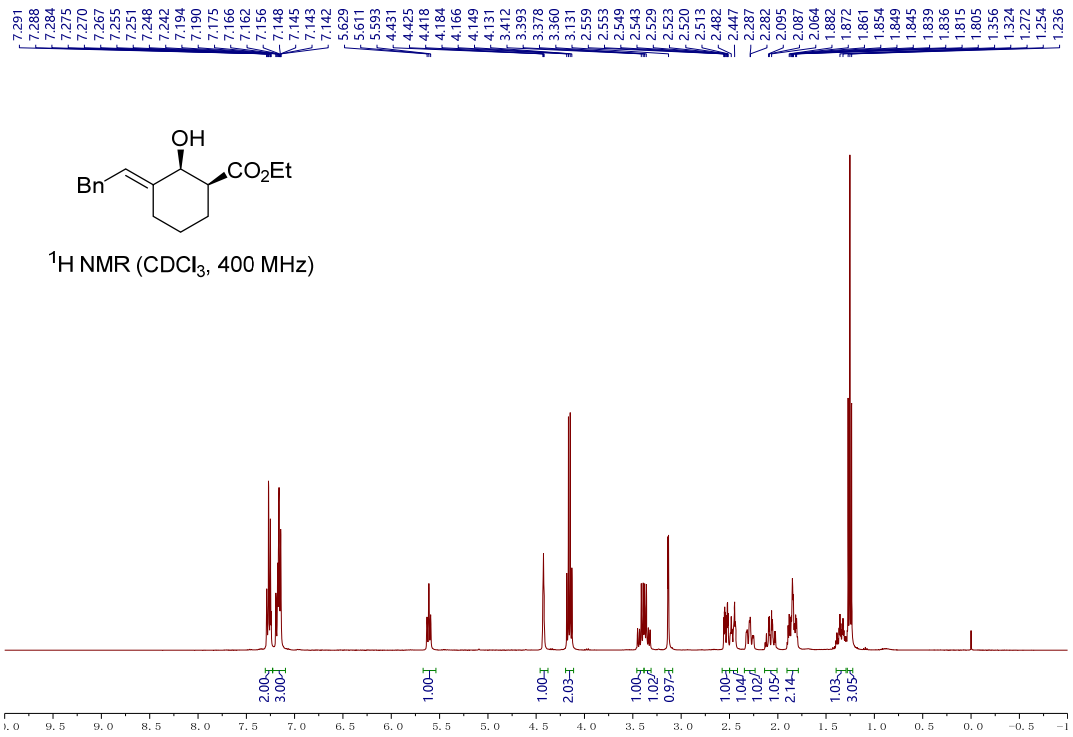


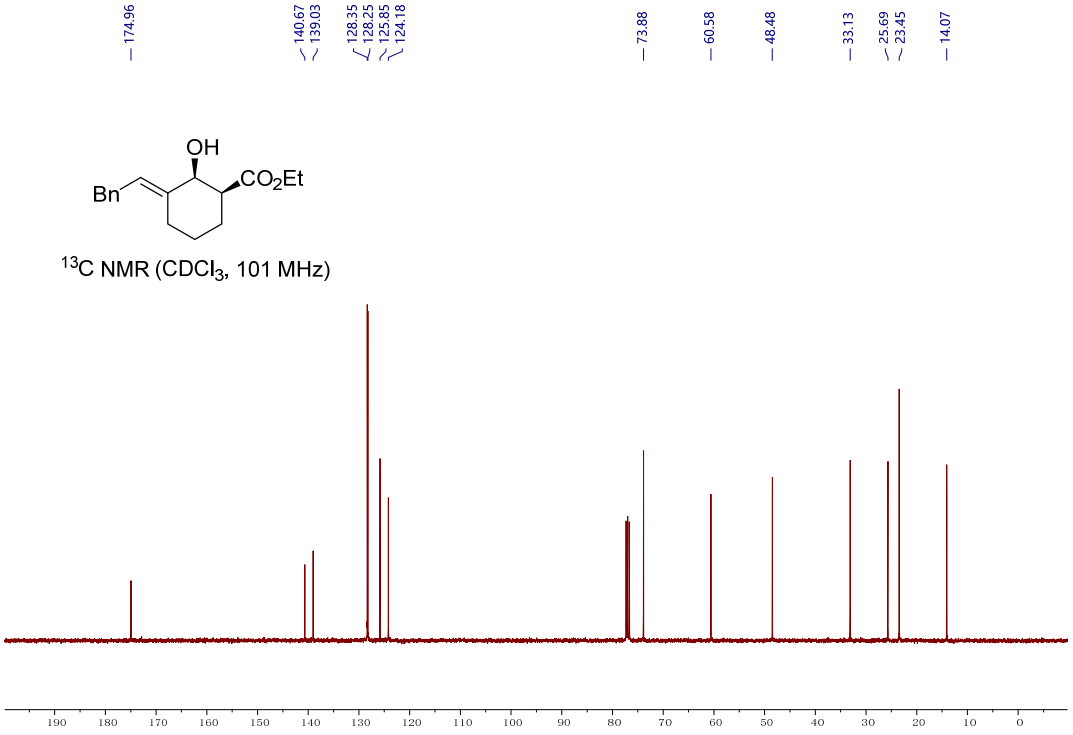


^{13}C NMR ($CDCl_3$, 101 MHz)

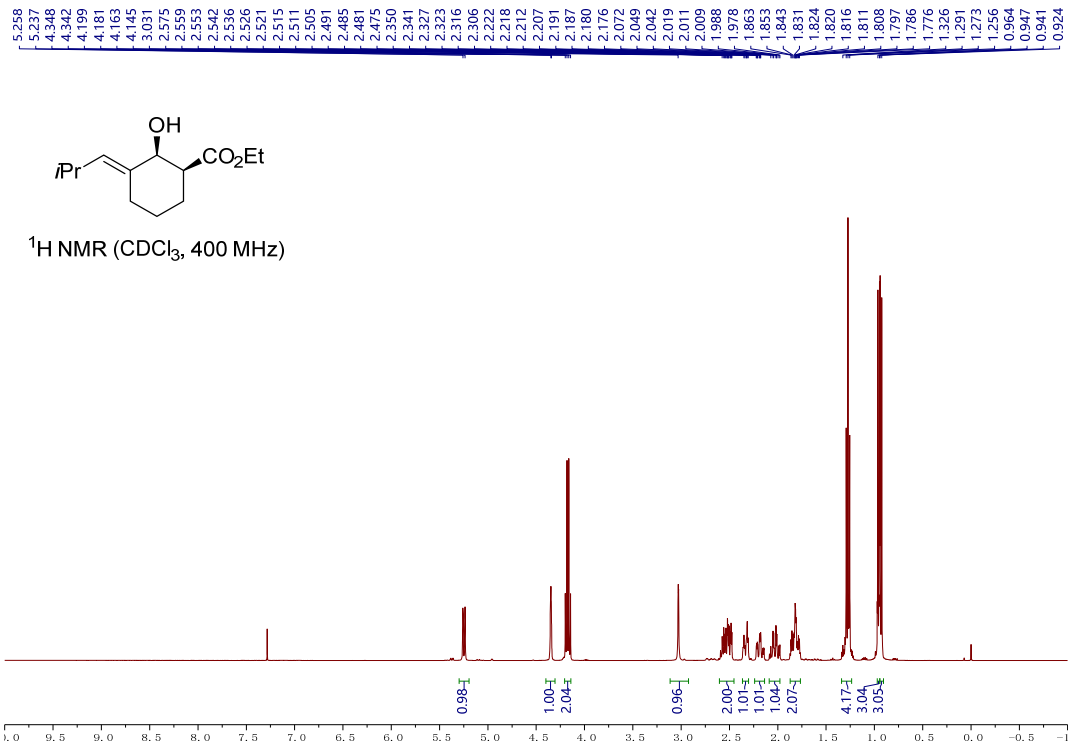


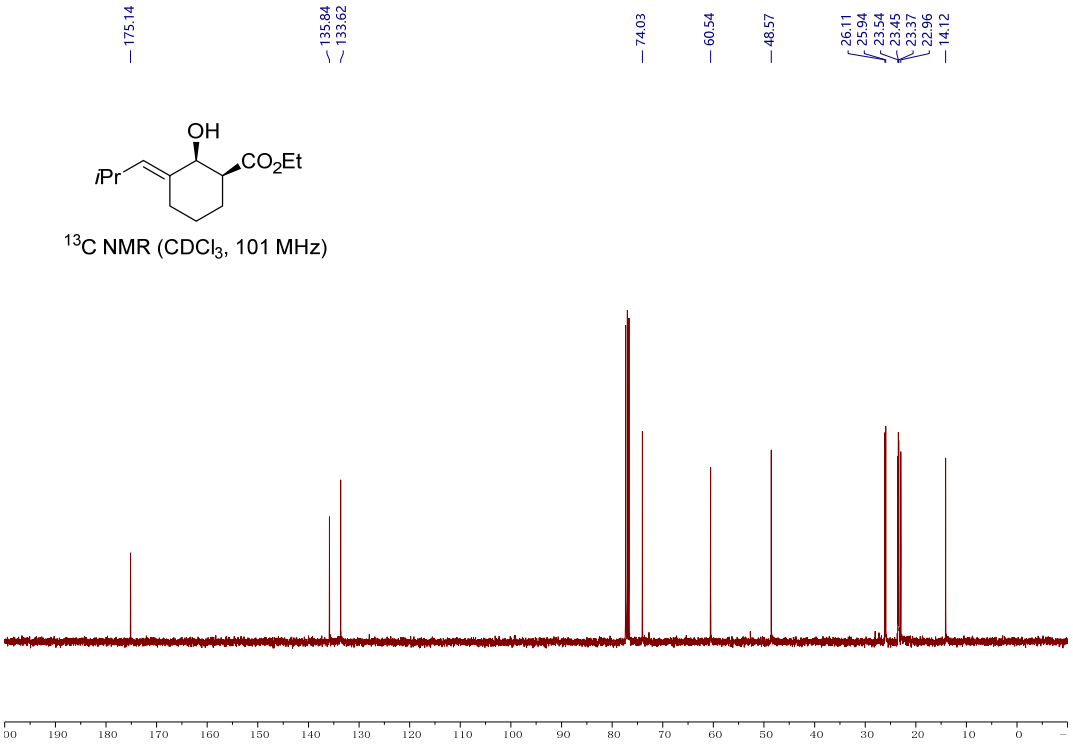
(+)-Ethyl (*E*)-2-hydroxy-3-(2-phenylethylidene)cyclohexane-1-carboxylate ((+)-8af)



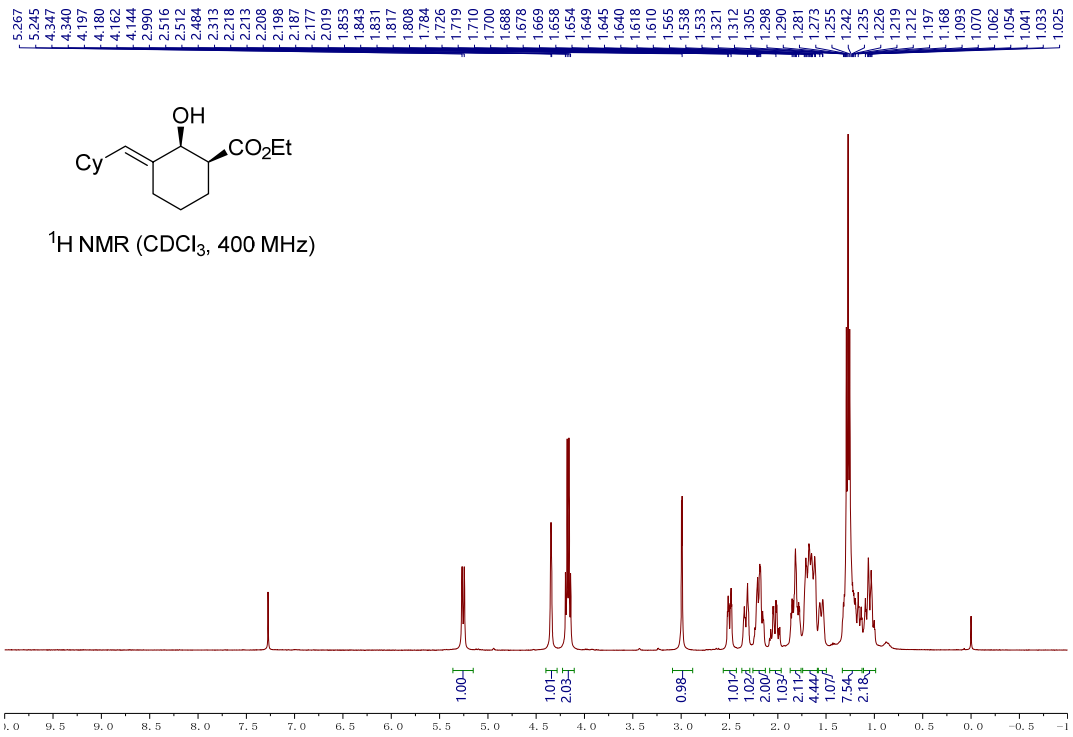


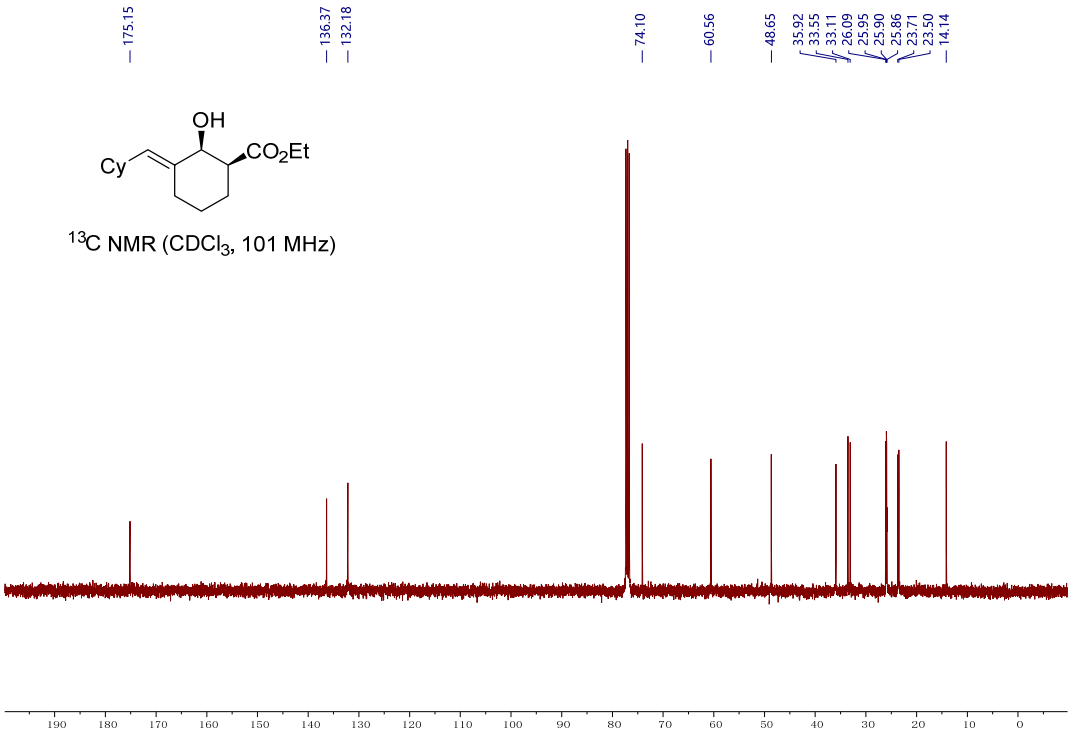
(+)-Ethyl (*E*)-2-hydroxy-3-(2-methylpropylidene)cyclohexane-1-carboxylate ((+)-8ag)



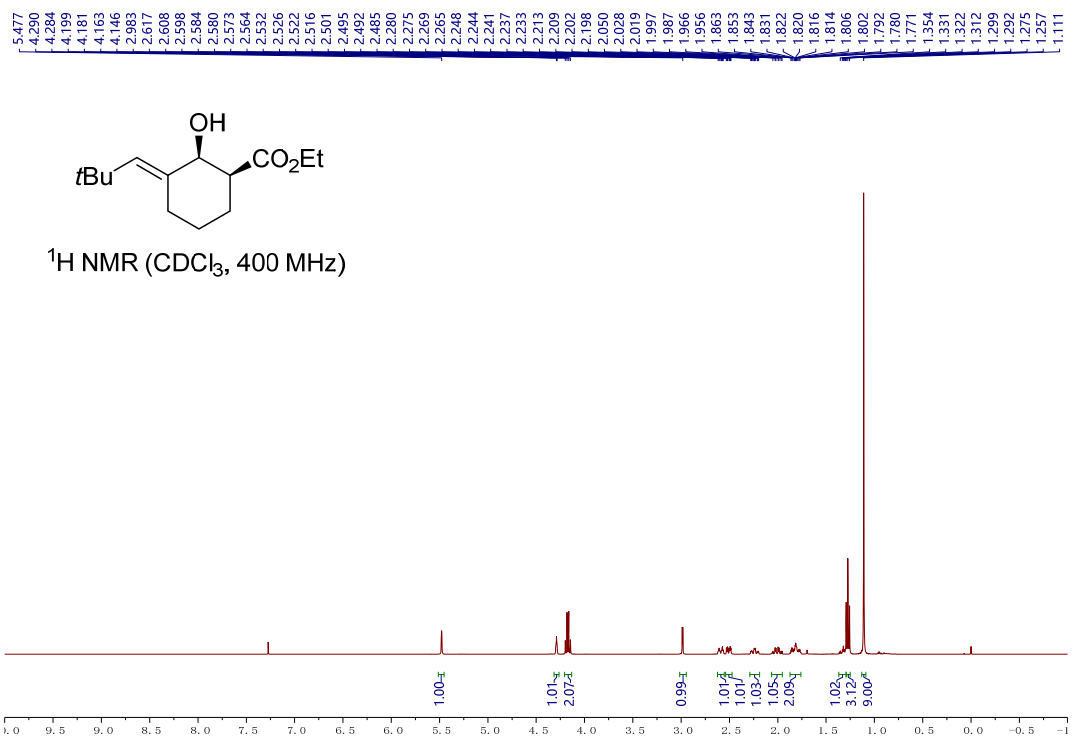


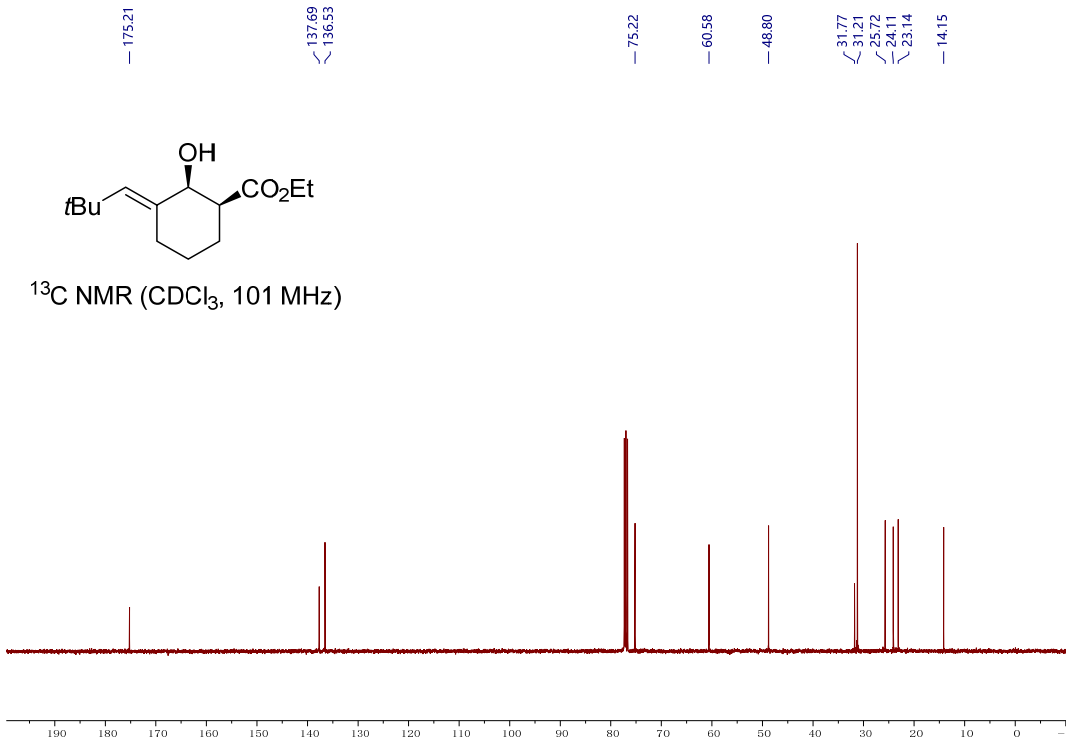
(+)-Ethyl (*E*)-3-(cyclohexylmethylene)-2-hydroxycyclohexane-1-carboxylate ((+)-8ah)



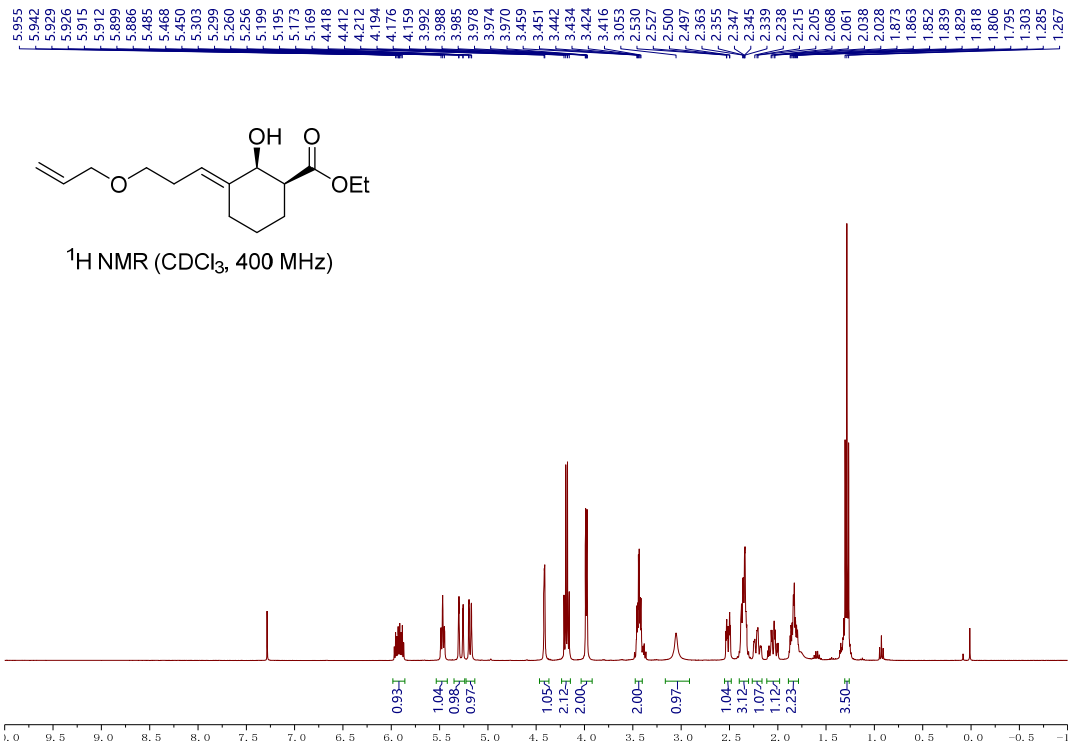


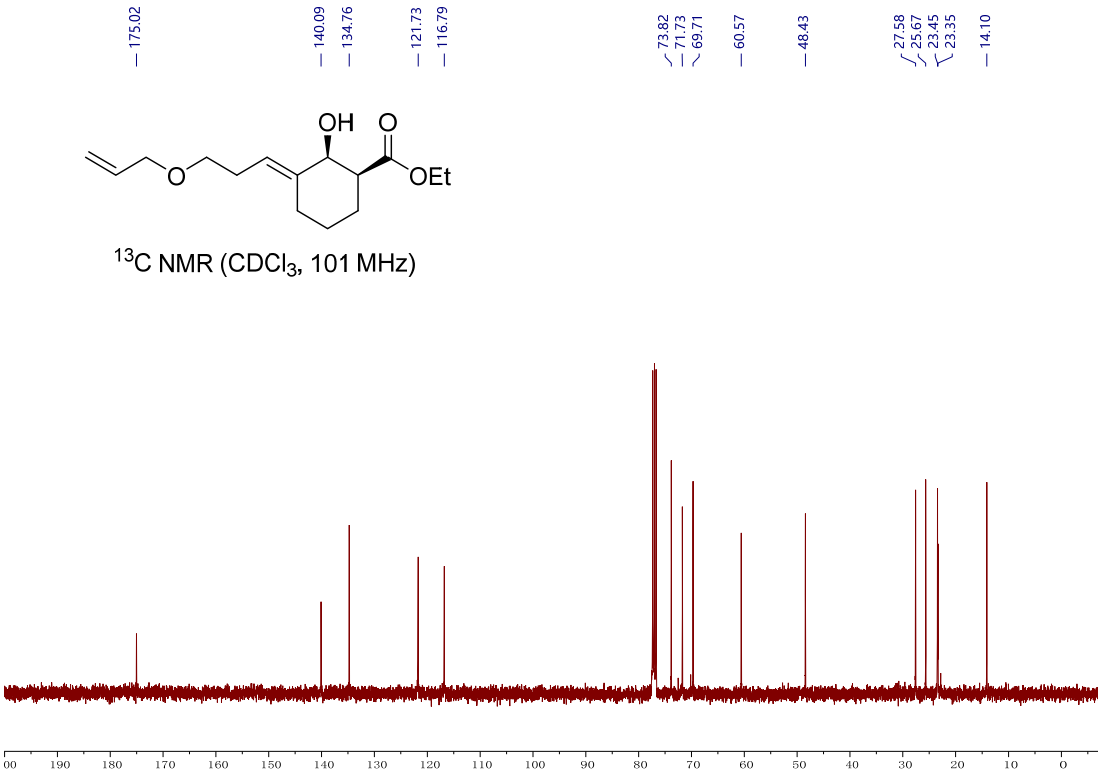
(+)-Ethyl (*E*)-3-(2,2-dimethylpropylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8ai)



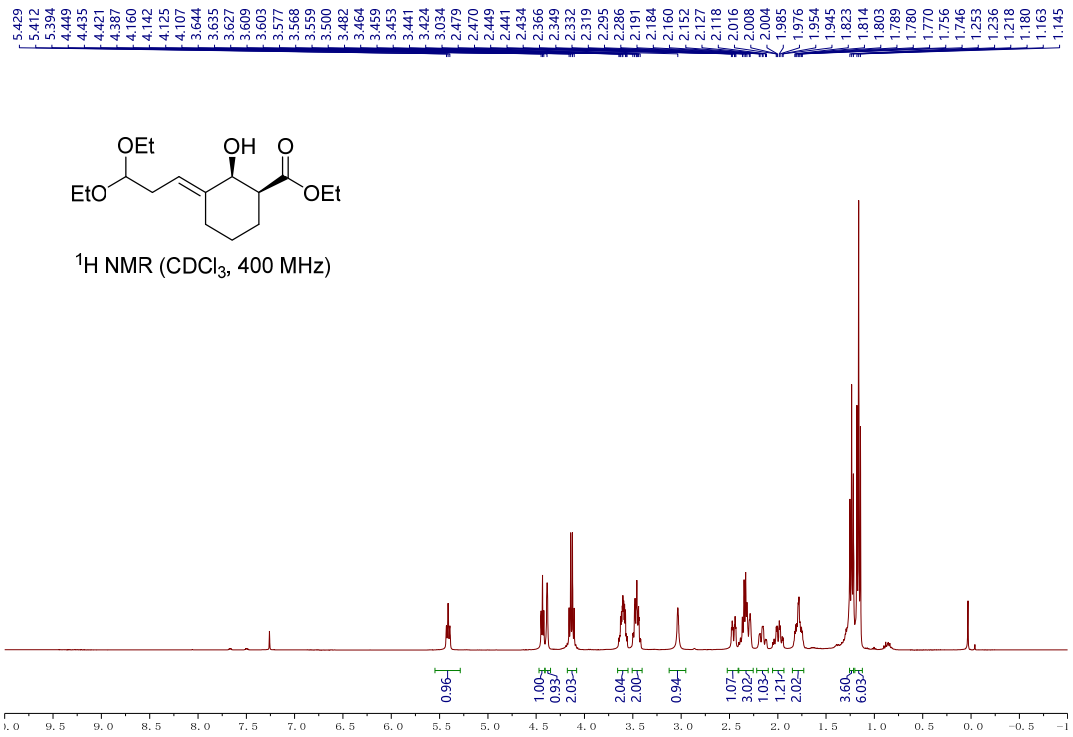


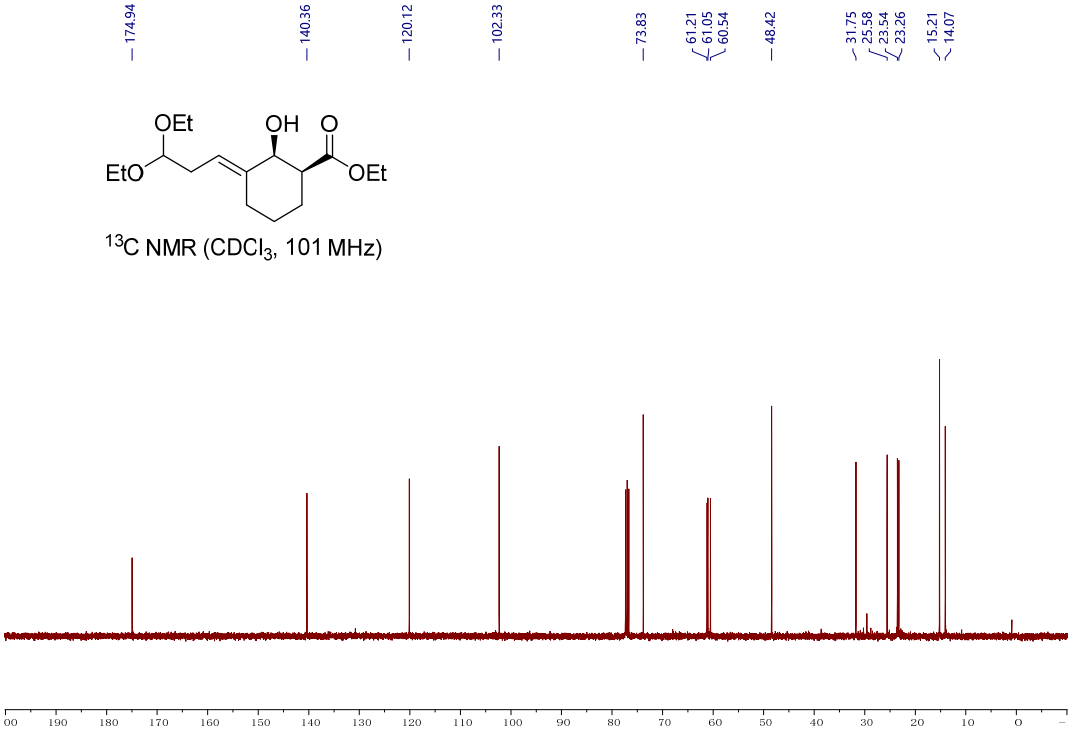
(+)-Ethyl (*E*)-3-(3-(allyloxy)propylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8aj)



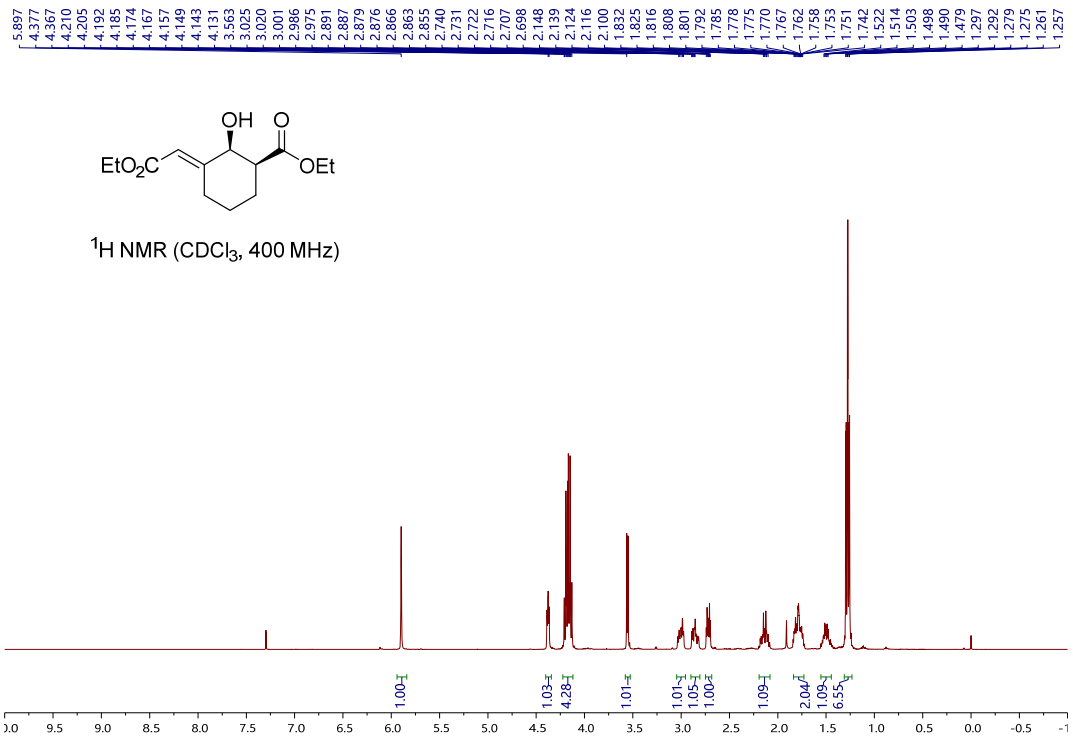


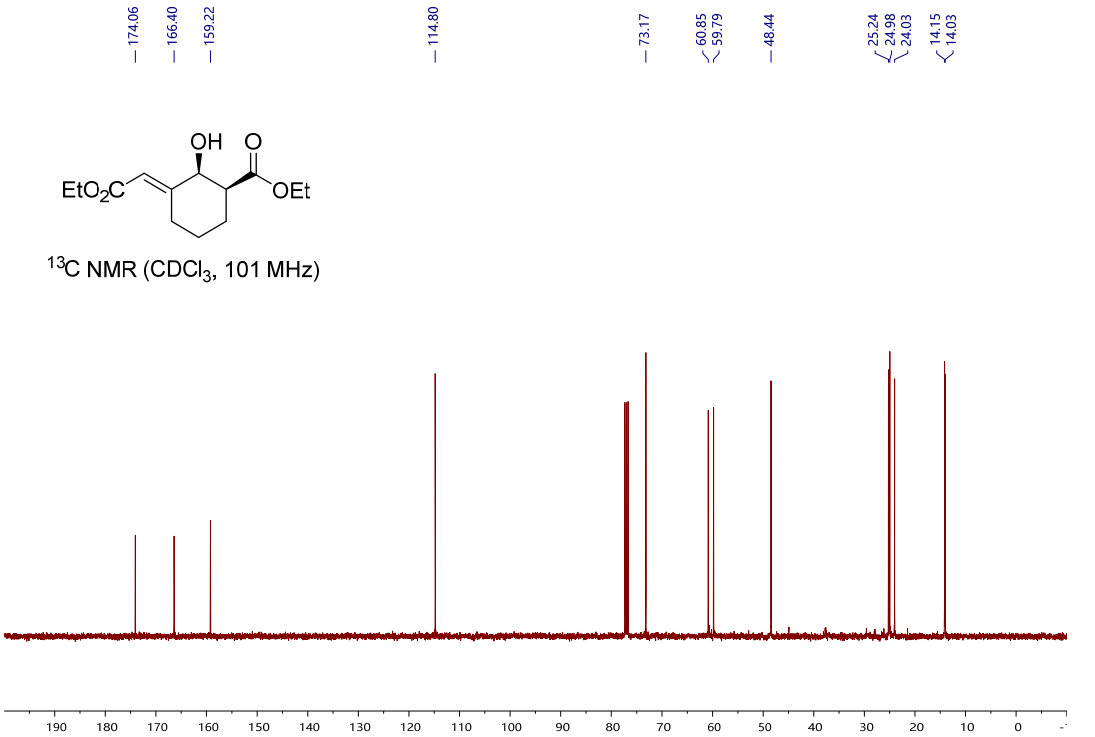
Ethyl (*E*)-3-(3,3-diethoxypropylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8ak)



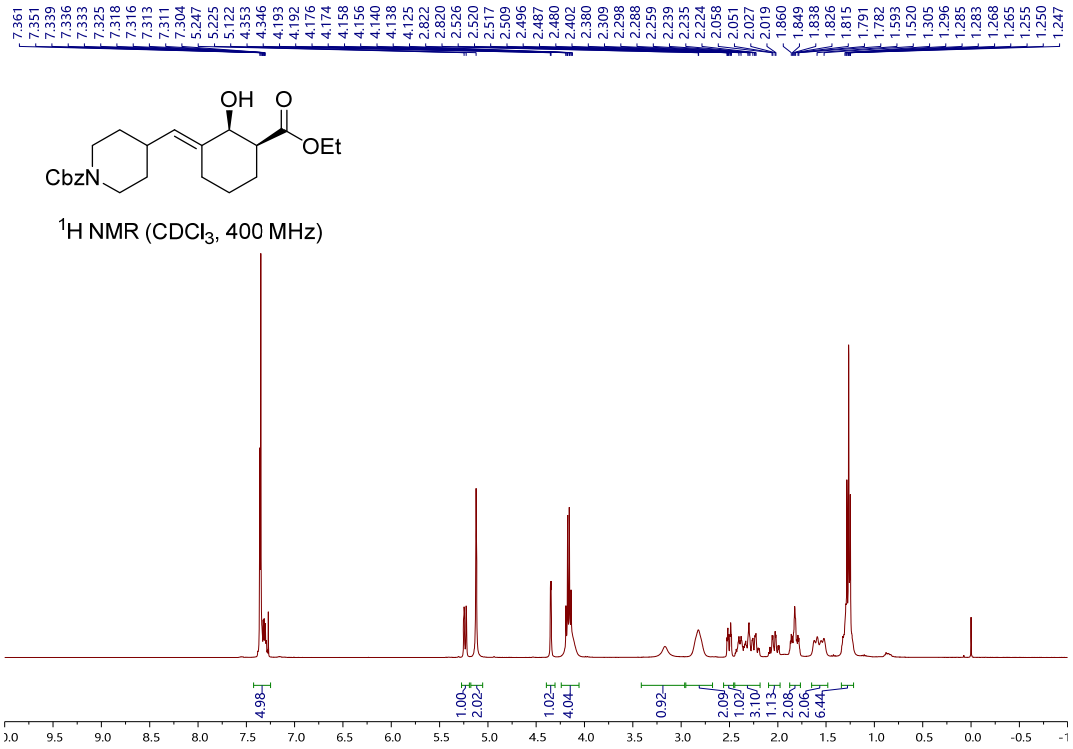


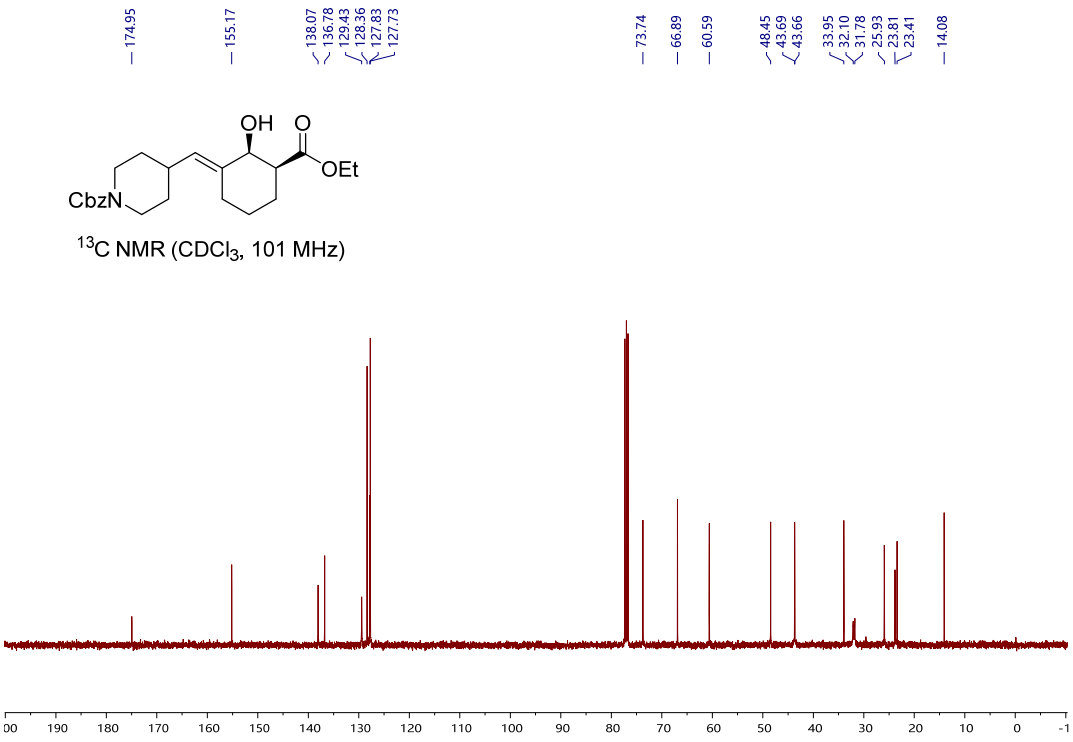
Ethyl (*E*)-3-(2-ethoxy-2-oxoethylidene)-2-hydroxycyclohexane-1-carboxylate ((+)-8al)



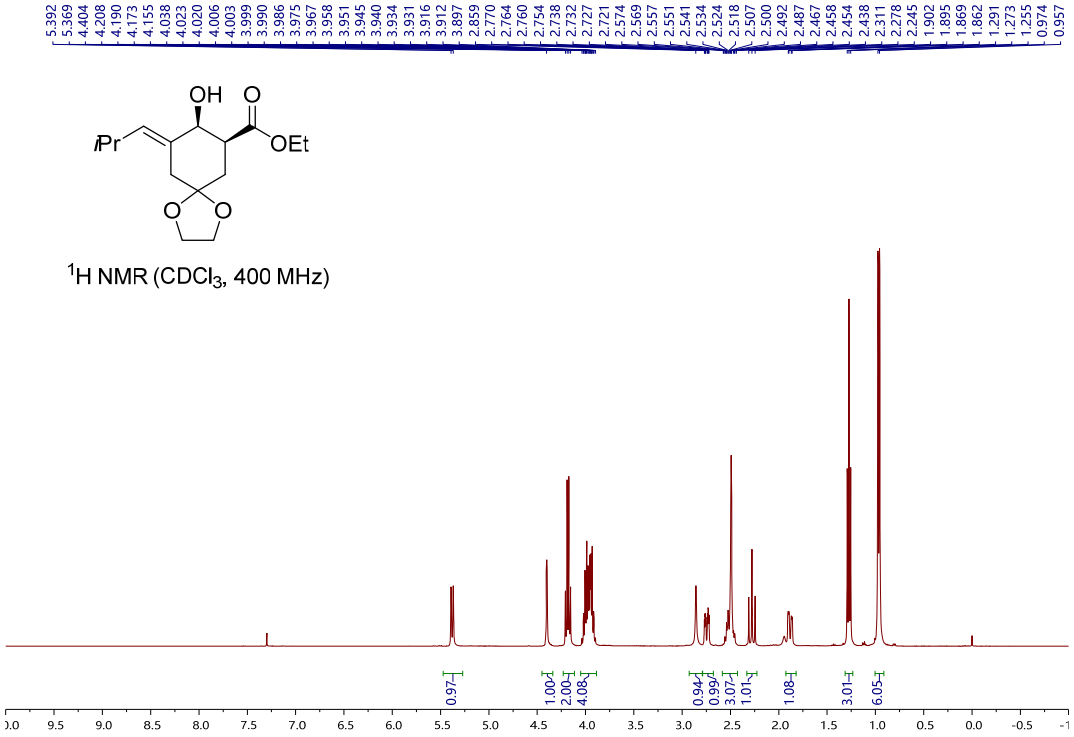


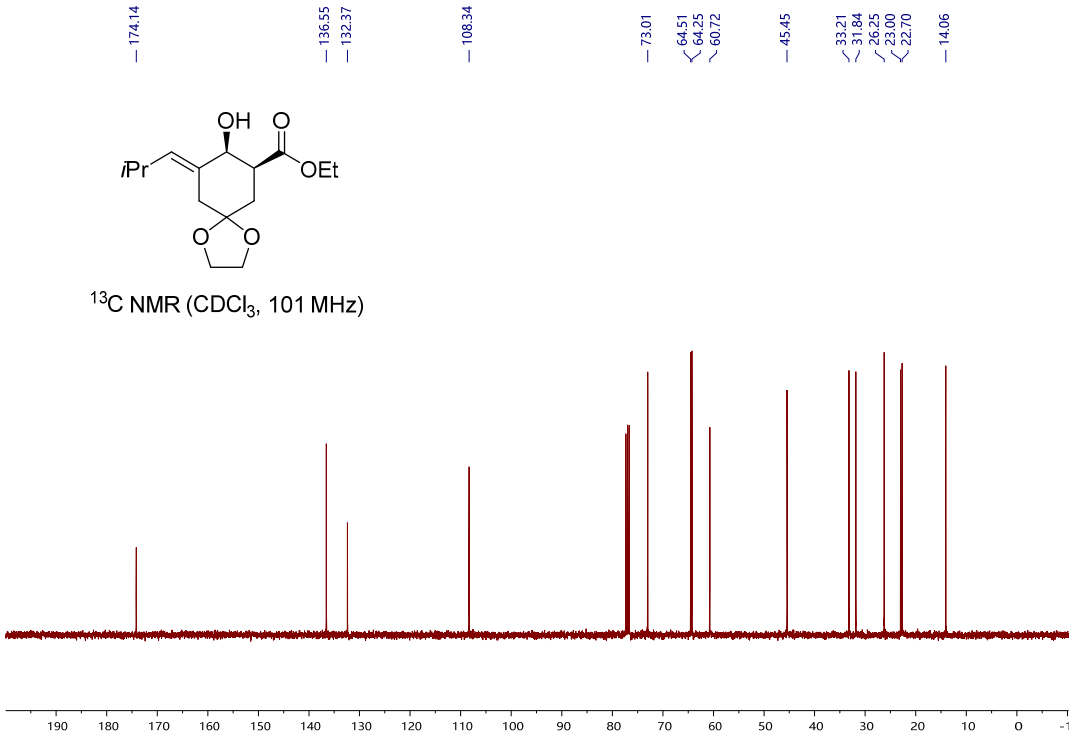
(+)-Benzyl 4-((*E*)-((2S,3S)-3-(ethoxycarbonyl)-2-hydroxycyclohexylidene)methyl)piperidine-1-carboxylate ((+)-8am)



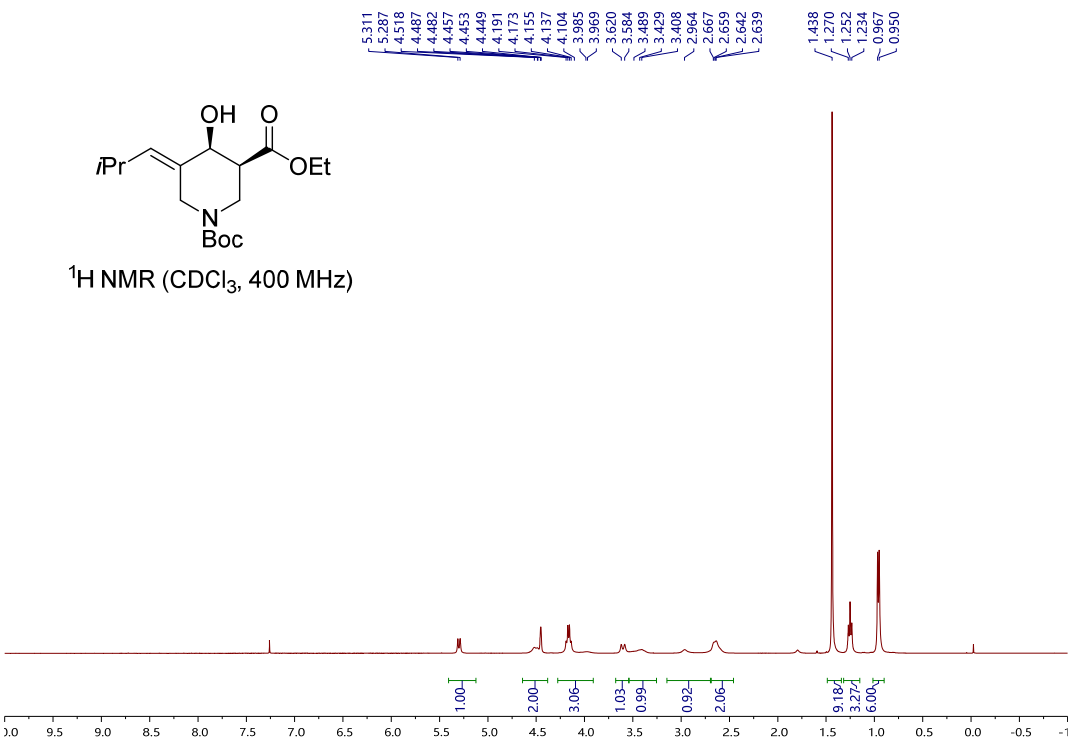


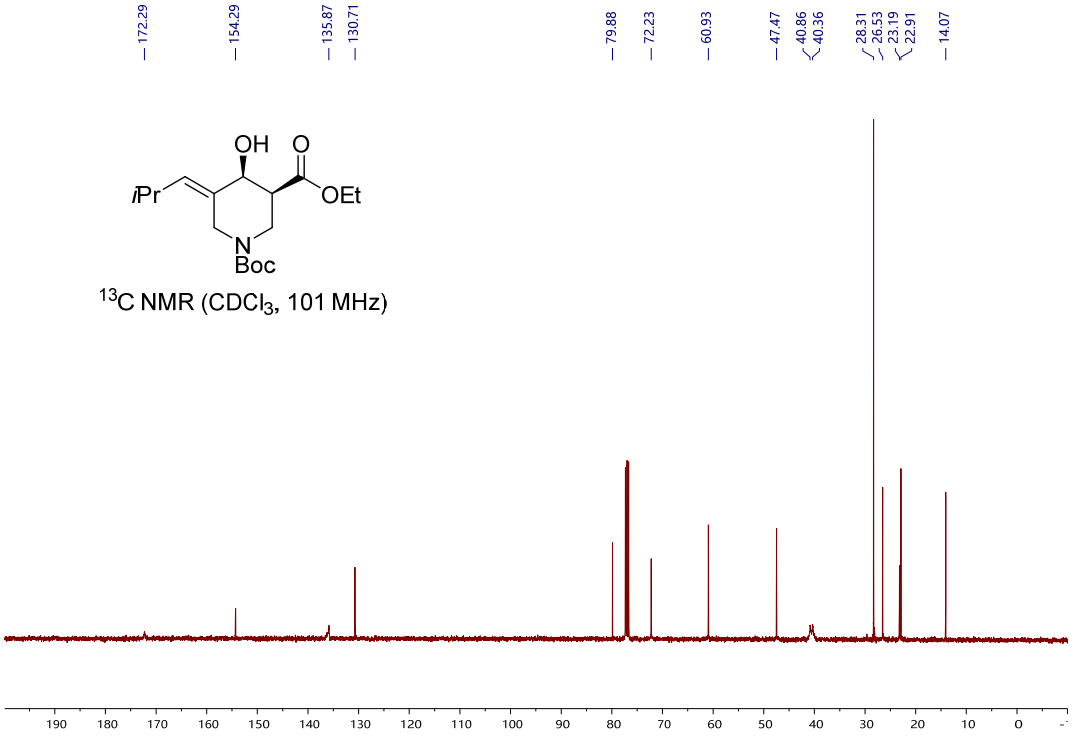
(+)-Ethyl (*E*)-8-hydroxy-9-(2-methylpropylidene)-1,4-dioxaspiro[4.5]decane-7-carboxylate ((+)-8an)



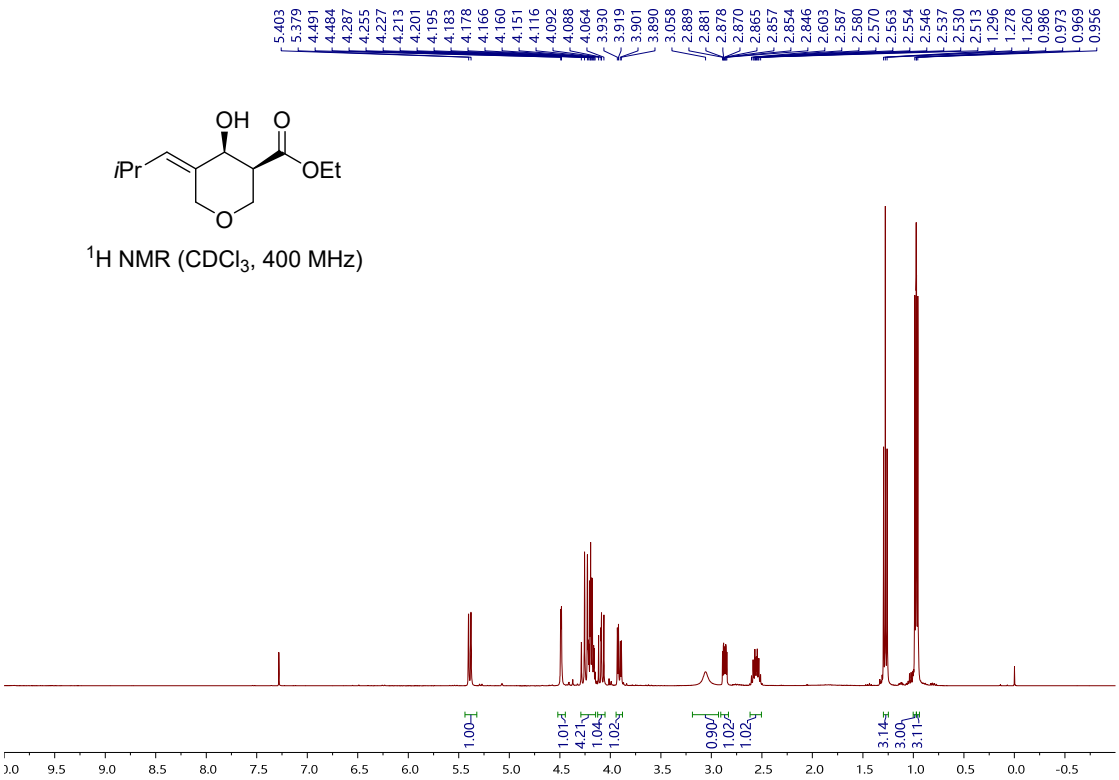


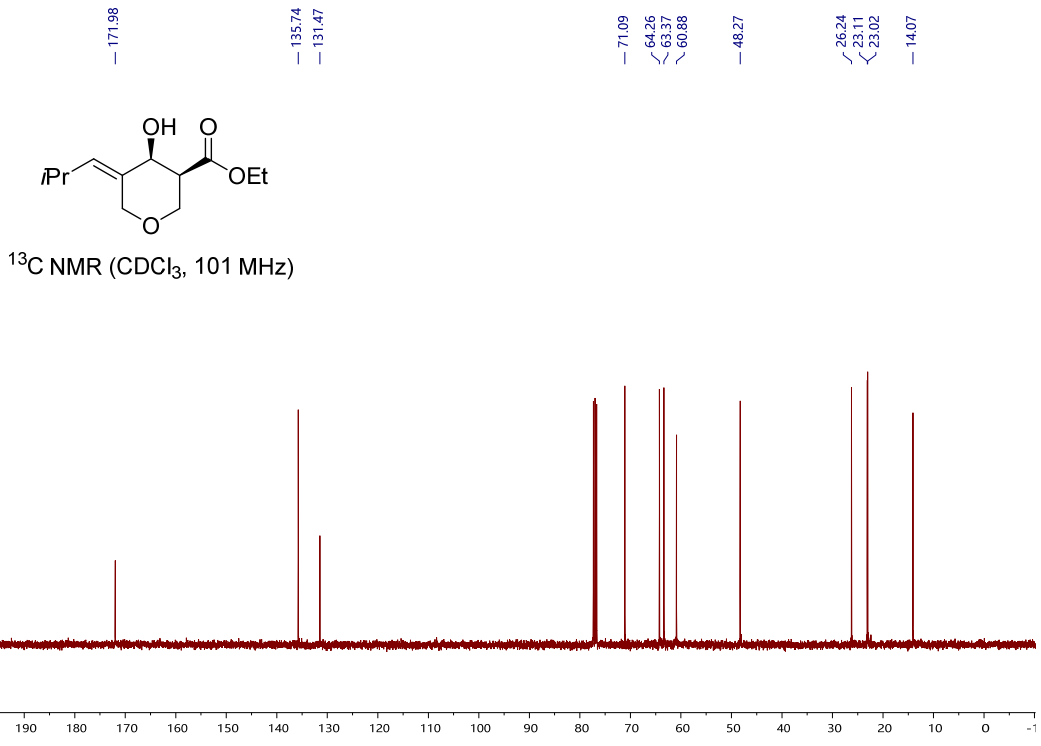
(+)-1-(*tert*-Butyl) 3-ethyl (*E*)-4-hydroxy-5-(2-methylpropylidene)piperidine-1,3-dicarboxylate ((+)-8ao)



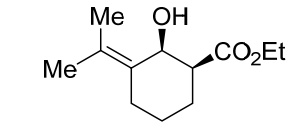


(+)-Ethyl (*E*)-4-hydroxy-5-(2-methylpropylidene)tetrahydro-2H-pyran-3-carboxylate ((+)-8ap)

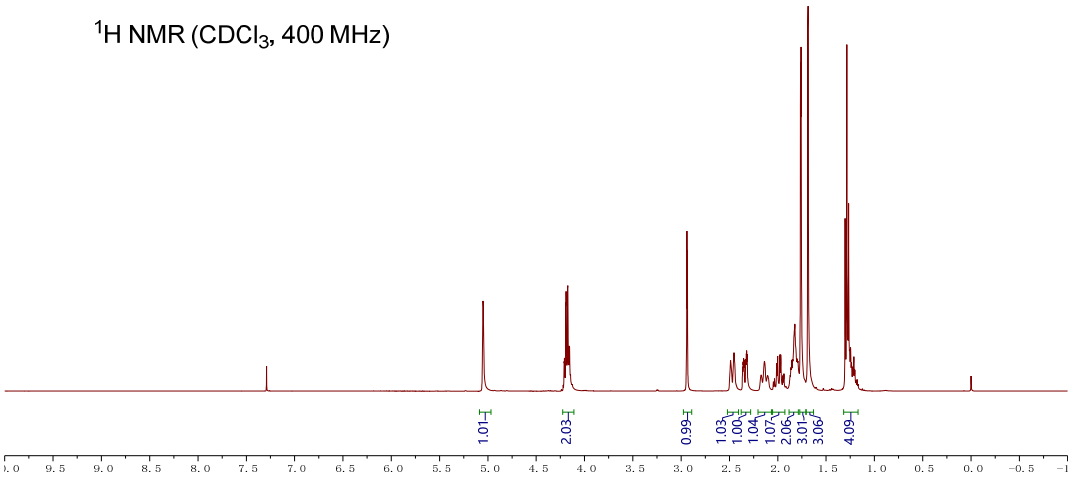


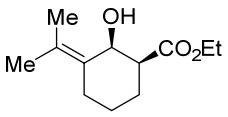


(+)-Ethyl 2-hydroxy-3-(propan-2-ylidene)cyclohexane-1-carboxylate ((+)-8aq)

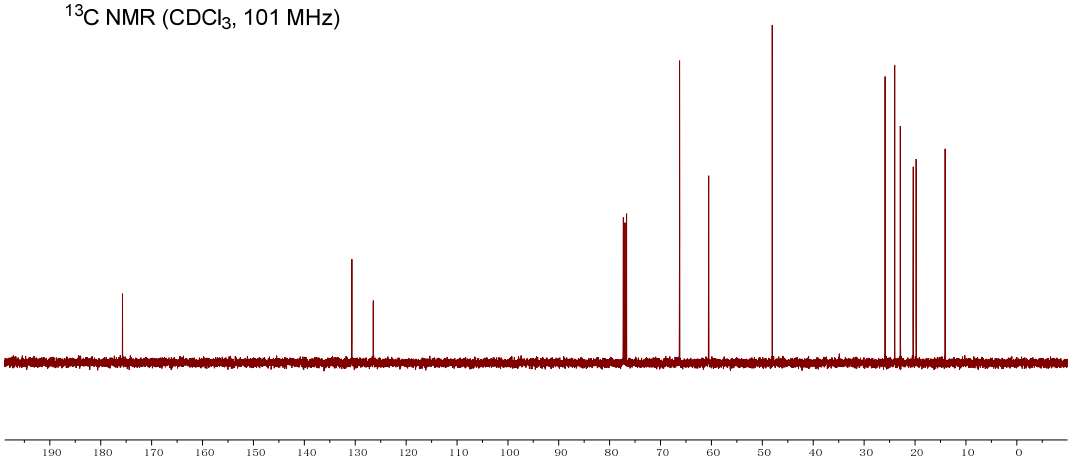


^{1}H NMR ($CDCl_3$, 400 MHz)

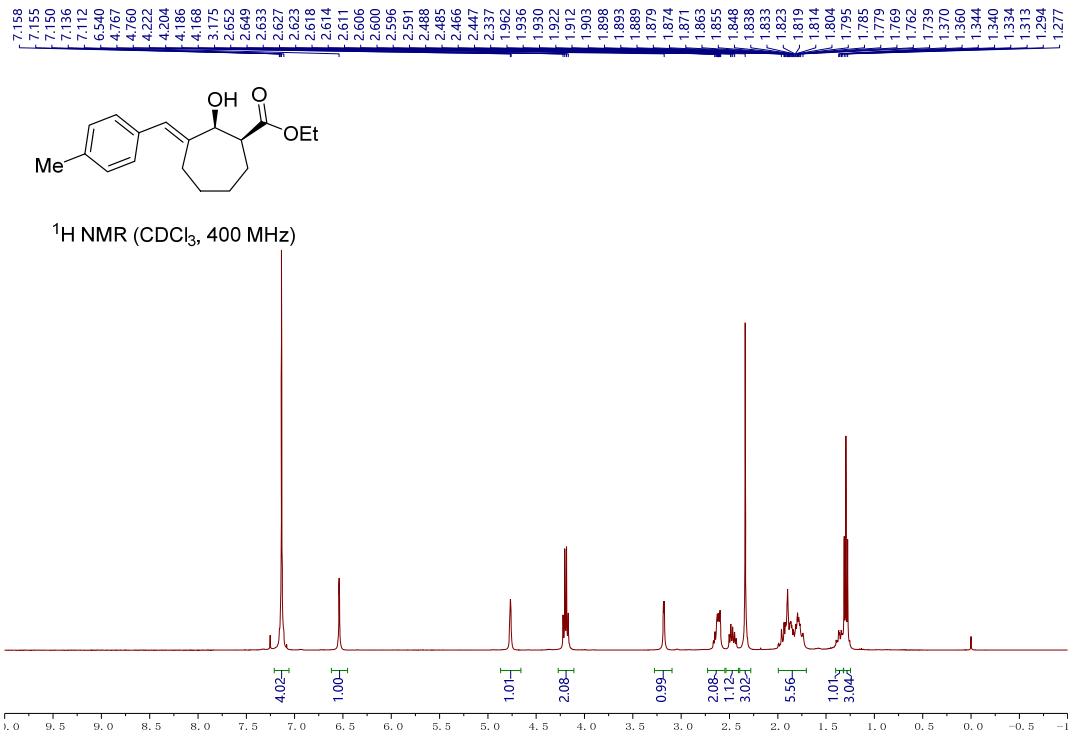


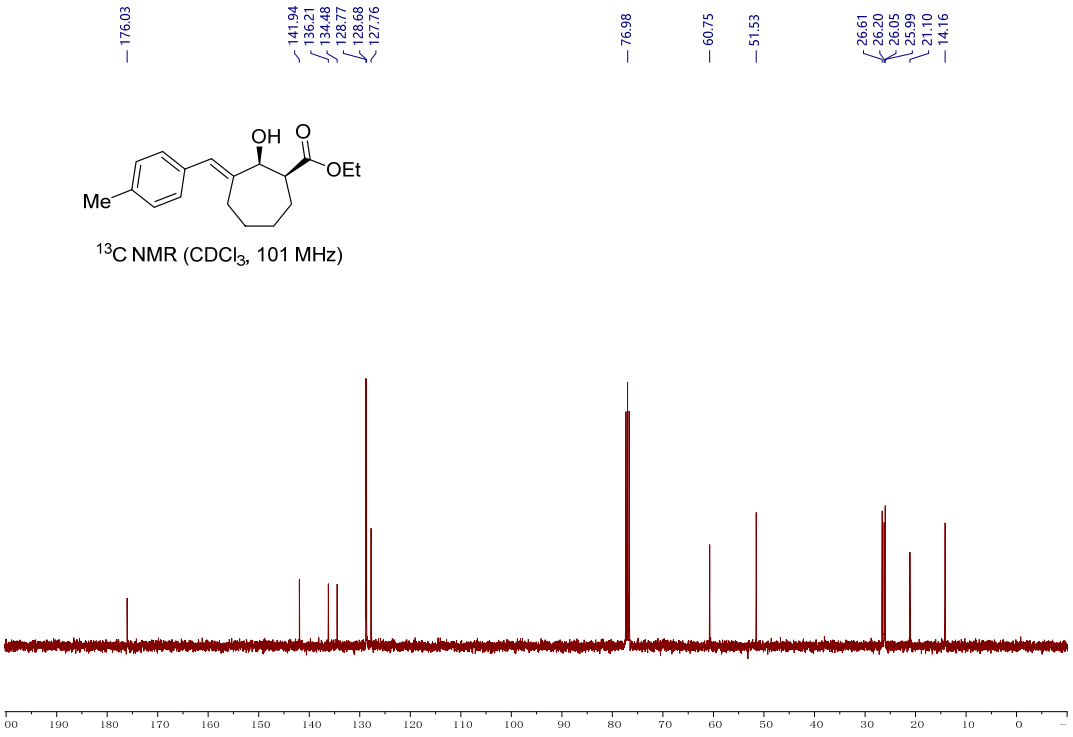


^{13}C NMR ($CDCl_3$, 101 MHz)

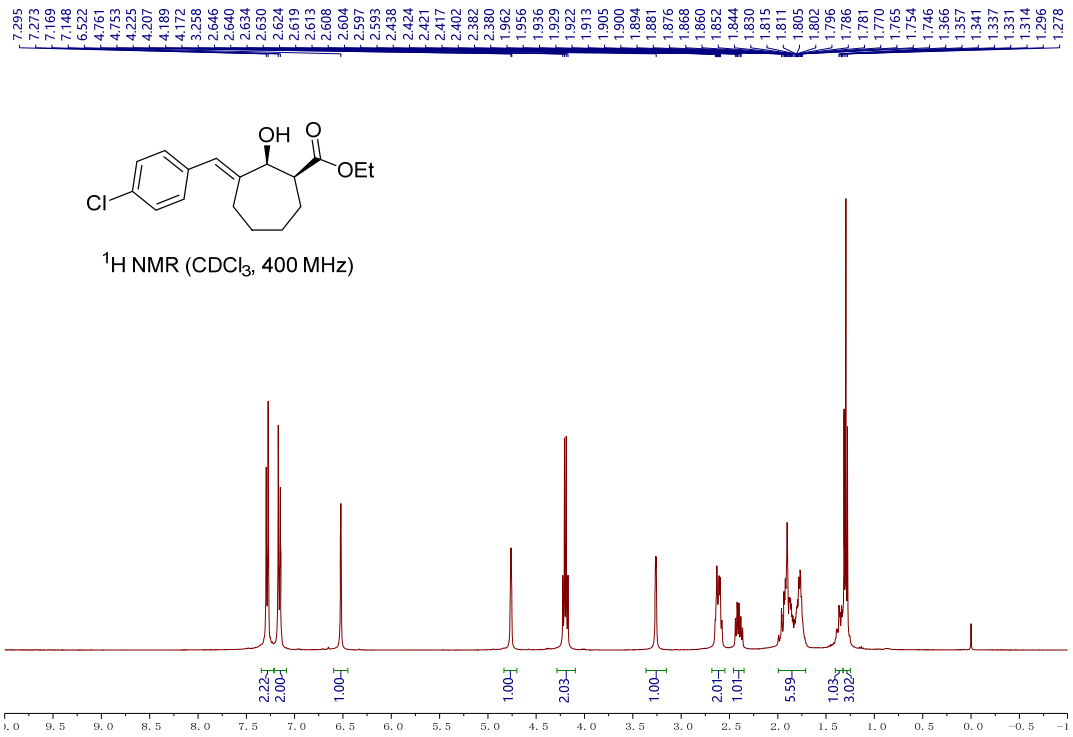


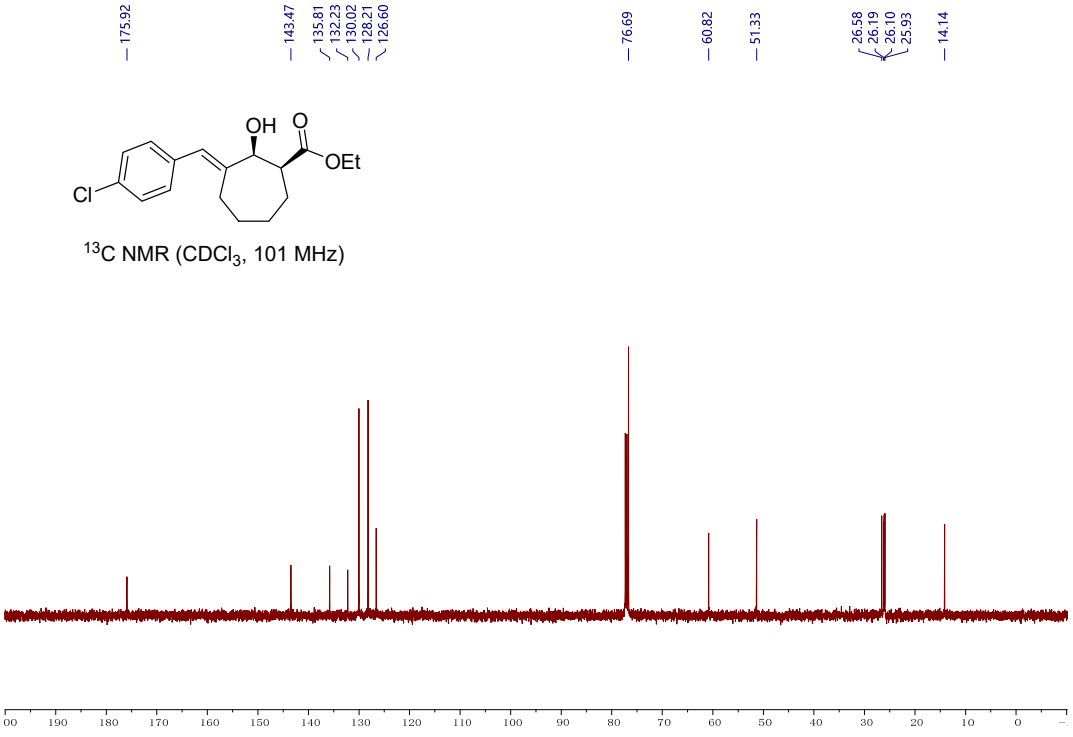
(+)-Ethyl 2-hydroxy-3-((*E*)-4-methylbenzylidene)cycloheptane-1-carboxylate ((+)-10a)



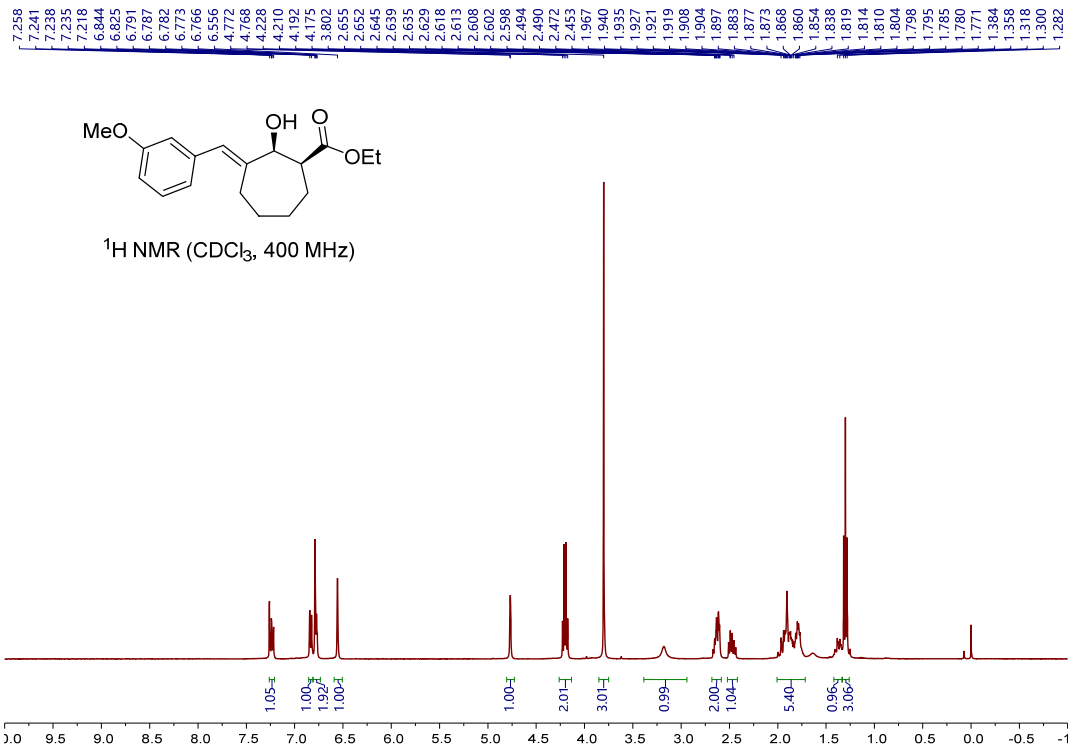


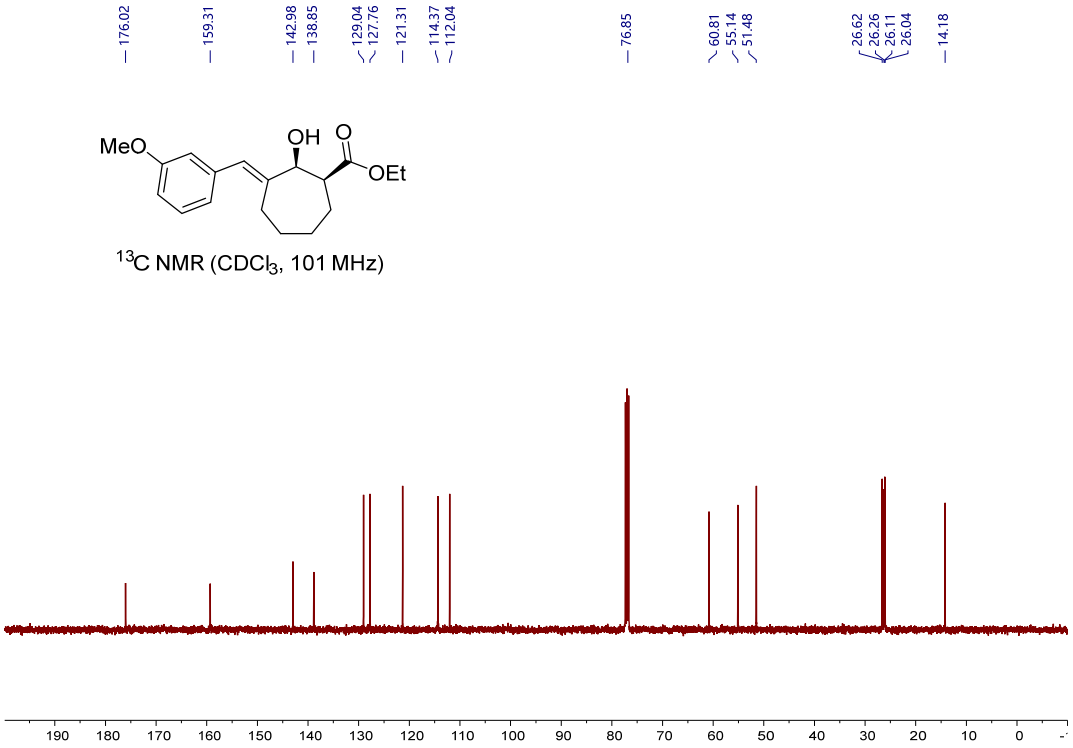
(+)-Ethyl 3-((*E*)-4-chlorobenzylidene)-2-hydroxycycloheptane-1-carboxylate ((+)-10b)



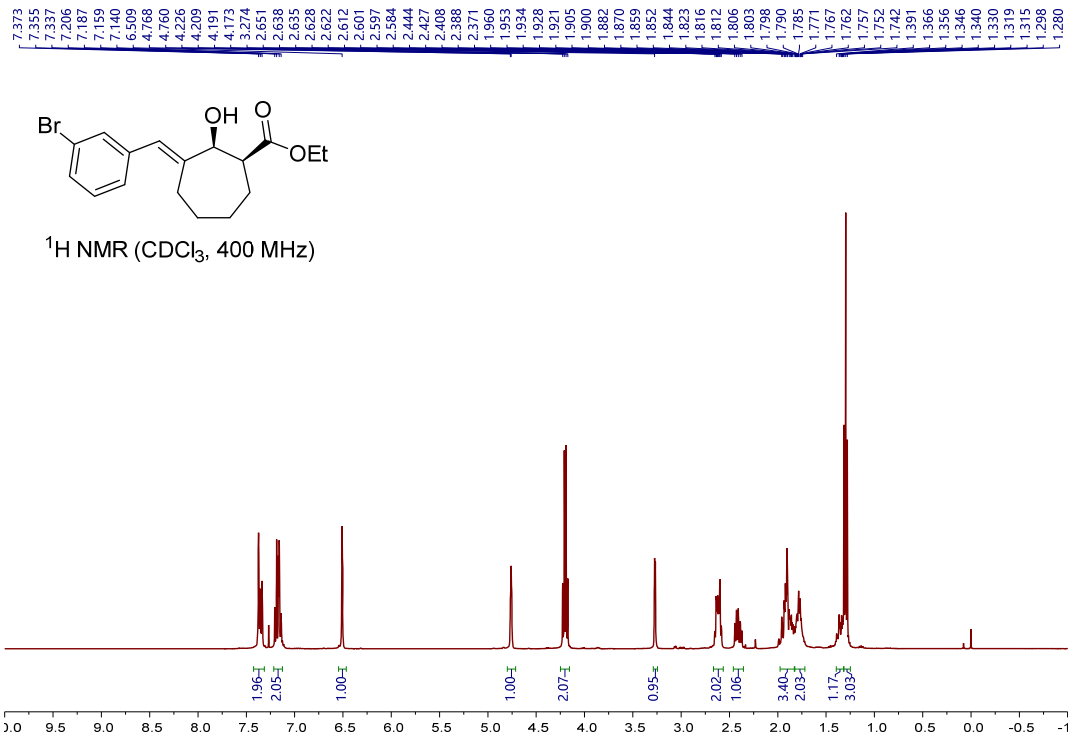


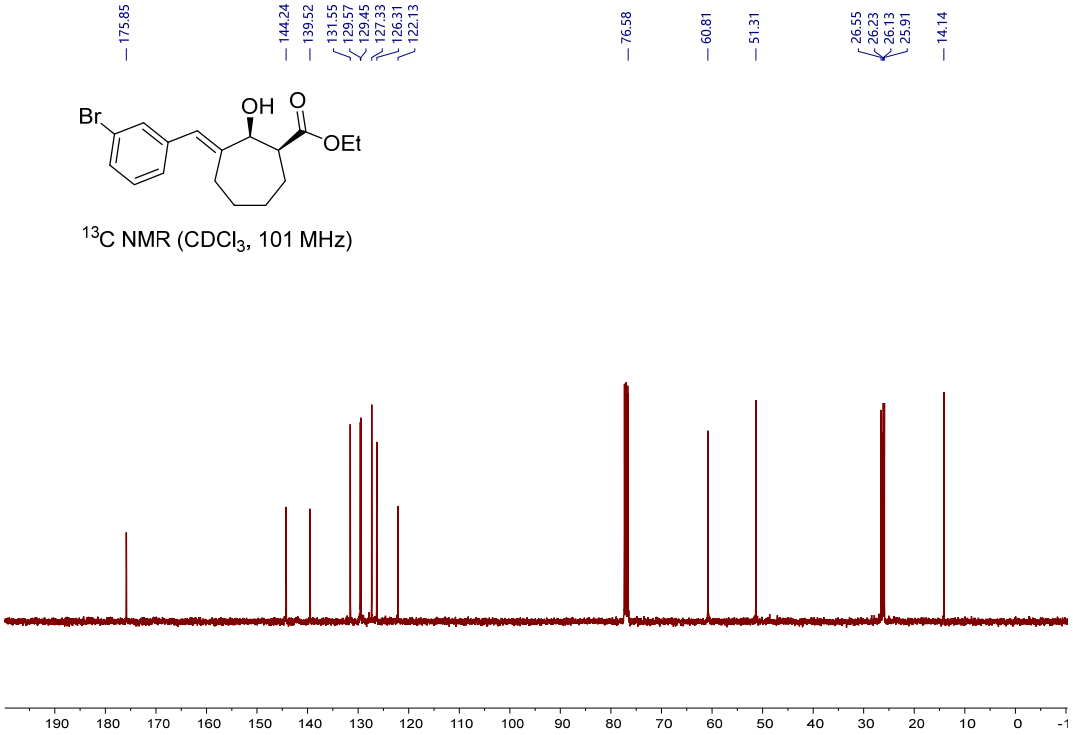
(+)-Ethyl 2-hydroxy-3-((*E*)-3-methoxybenzylidene)cycloheptane-1-carboxylate ((+)-10c)



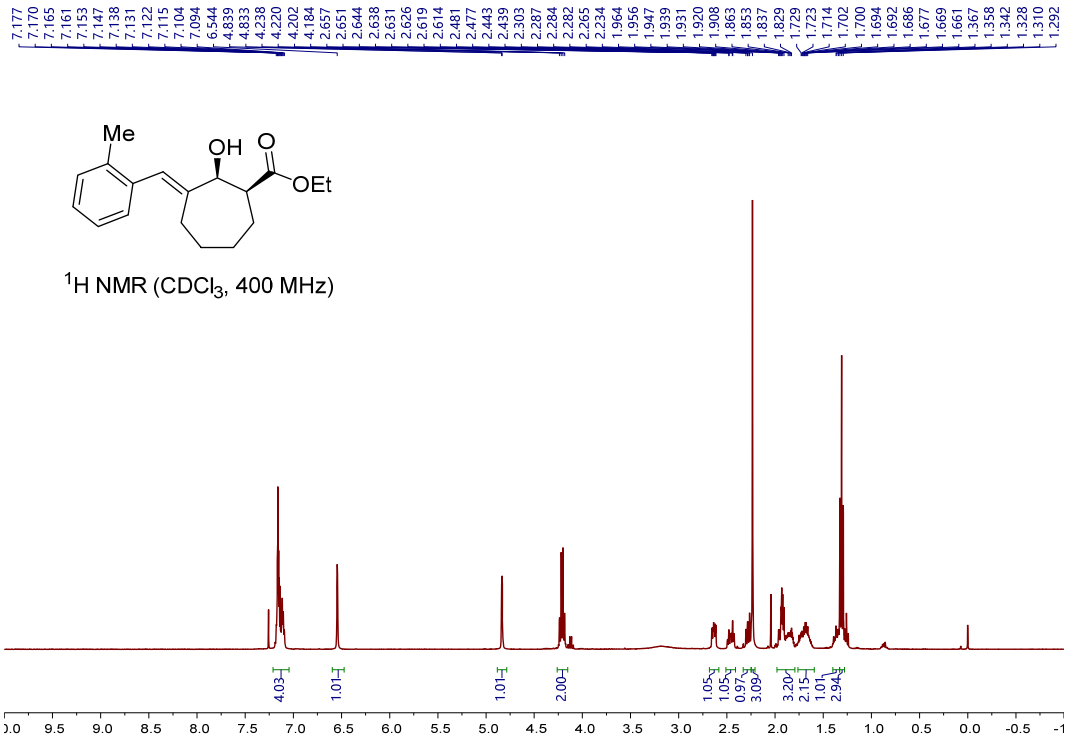


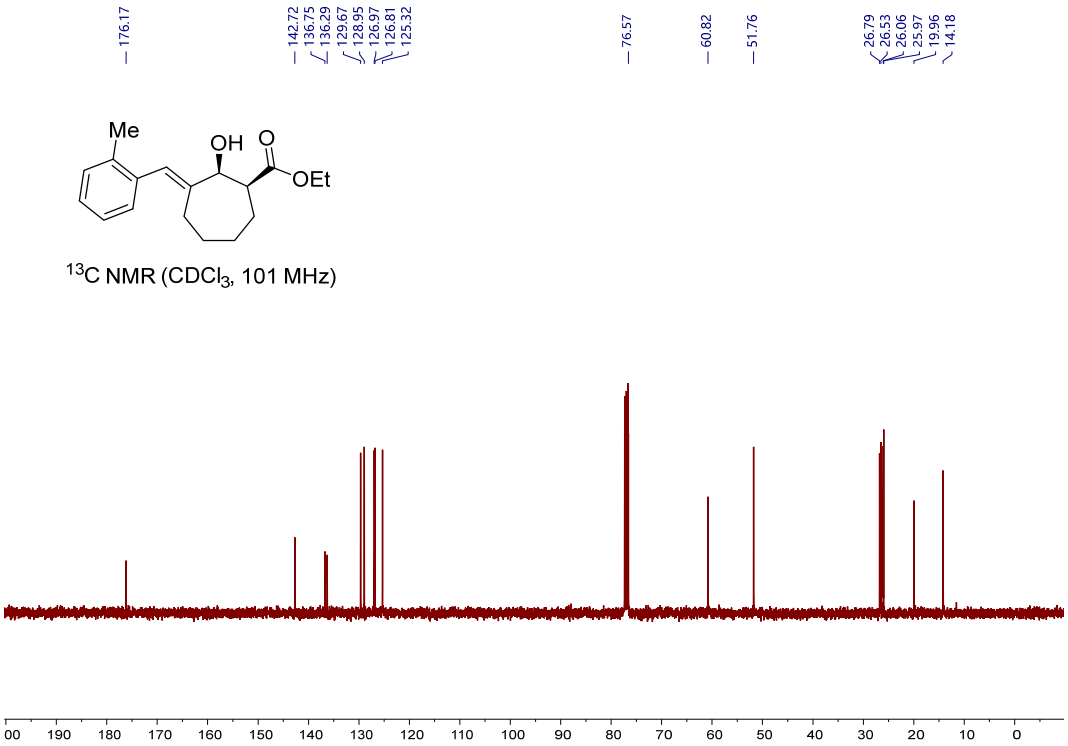
(+)-Ethyl 3-((*E*)-3-bromobenzylidene)-2-hydroxycycloheptane-1-carboxylate ((+)-10d)



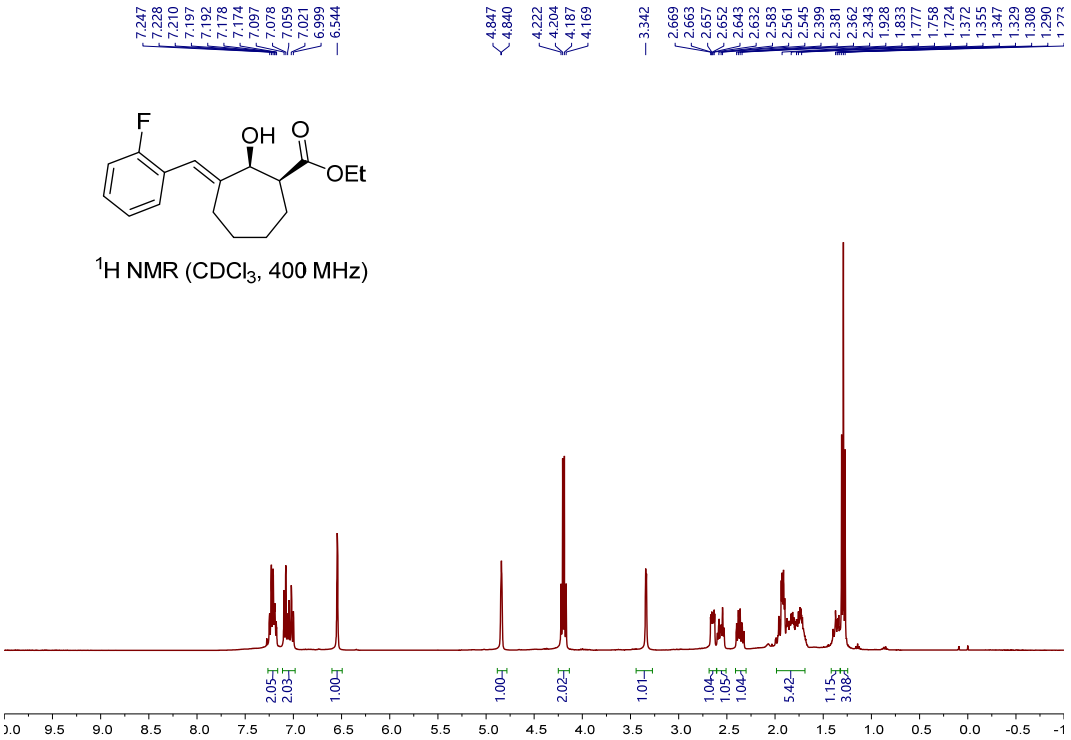


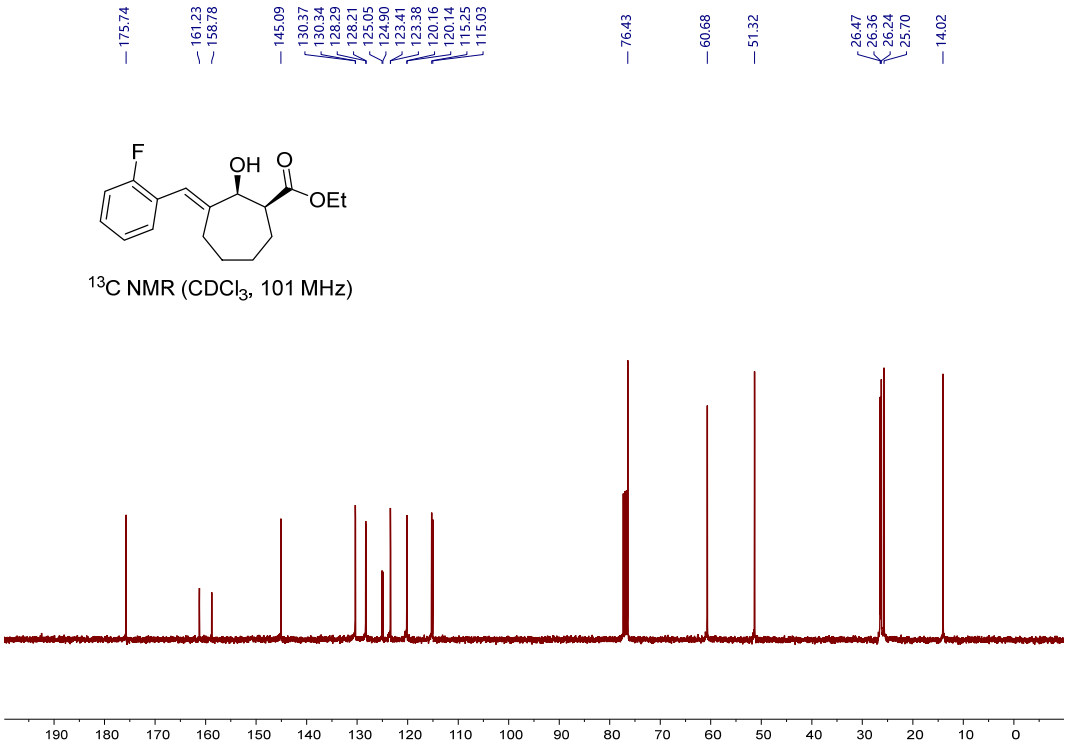
(+)-Ethyl 2-hydroxy-3-((*E*)-2-methylbenzylidene)cycloheptane-1-carboxylate ((+)-10e)



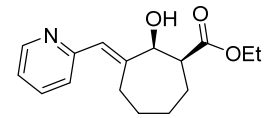


(+)-Ethyl 3-((*E*)-2-fluorobenzylidene)-2-hydroxycycloheptane-1-carboxylate ((+)-10f)

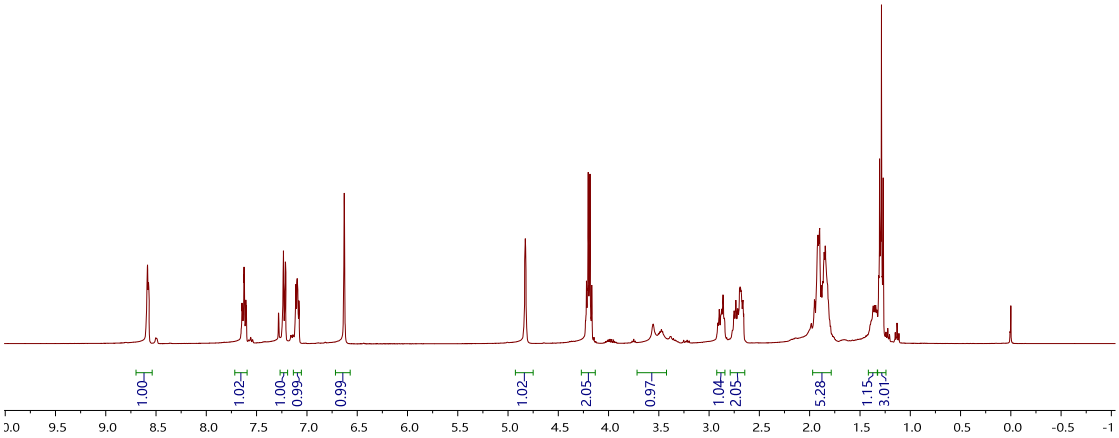


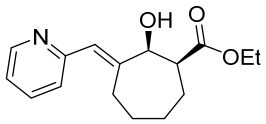


(+)-Ethyl (*E*)-2-hydroxy-3-(pyridin-2-ylmethylene)cycloheptane-1-carboxylate ((+)-10g)

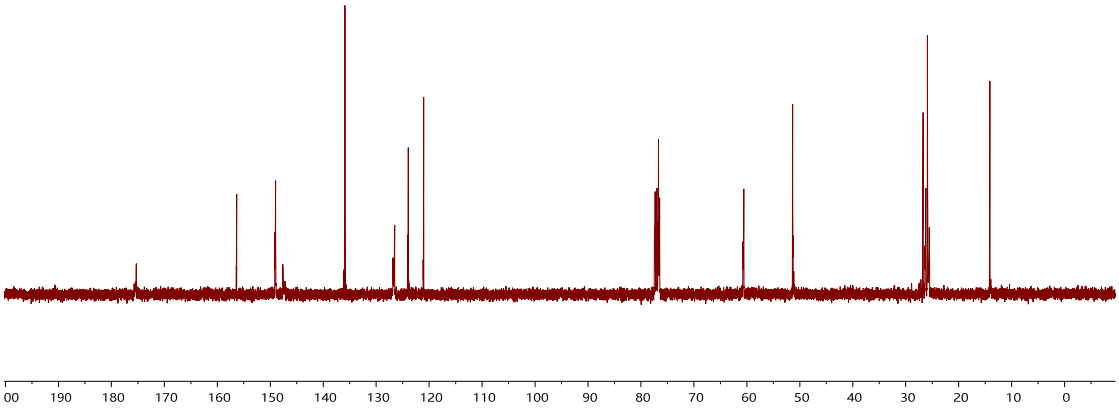


^{13}C NMR ($CDCl_3$, 101 MHz)

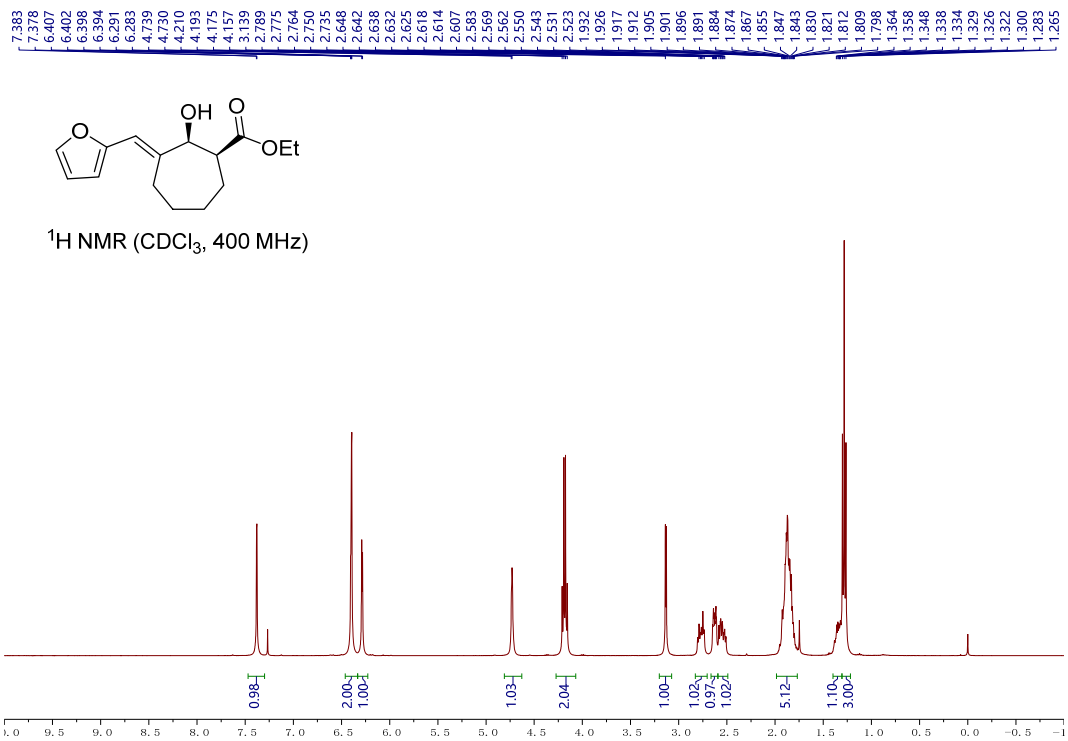


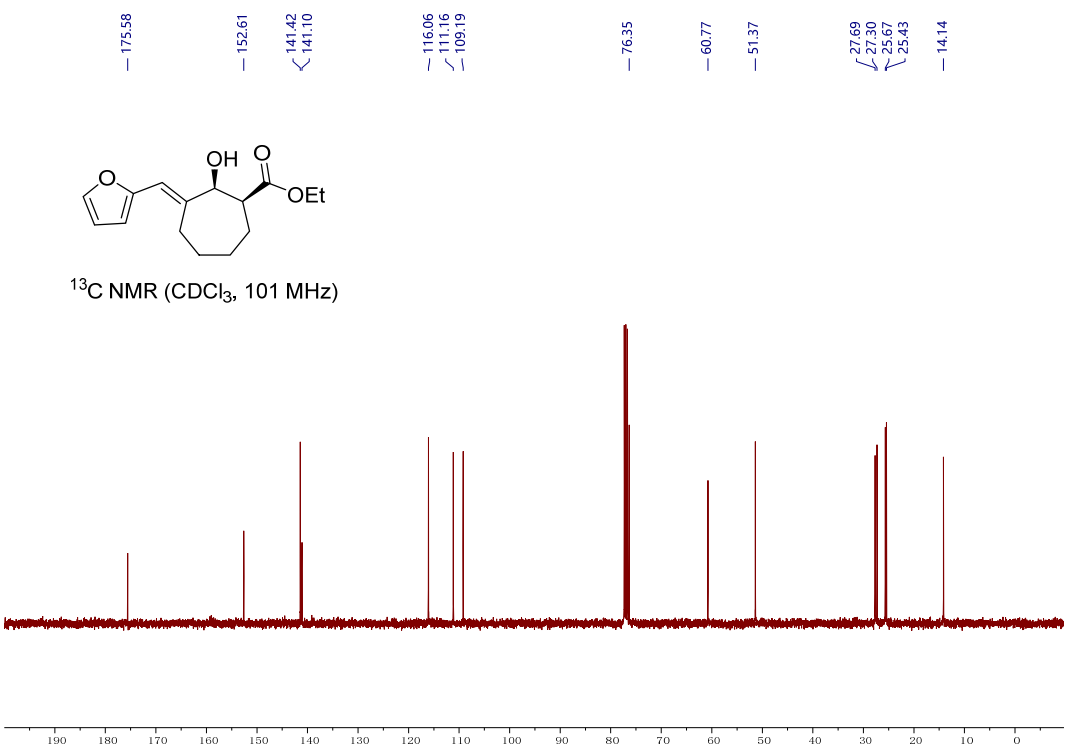


^{13}C NMR ($CDCl_3$, 101 MHz)

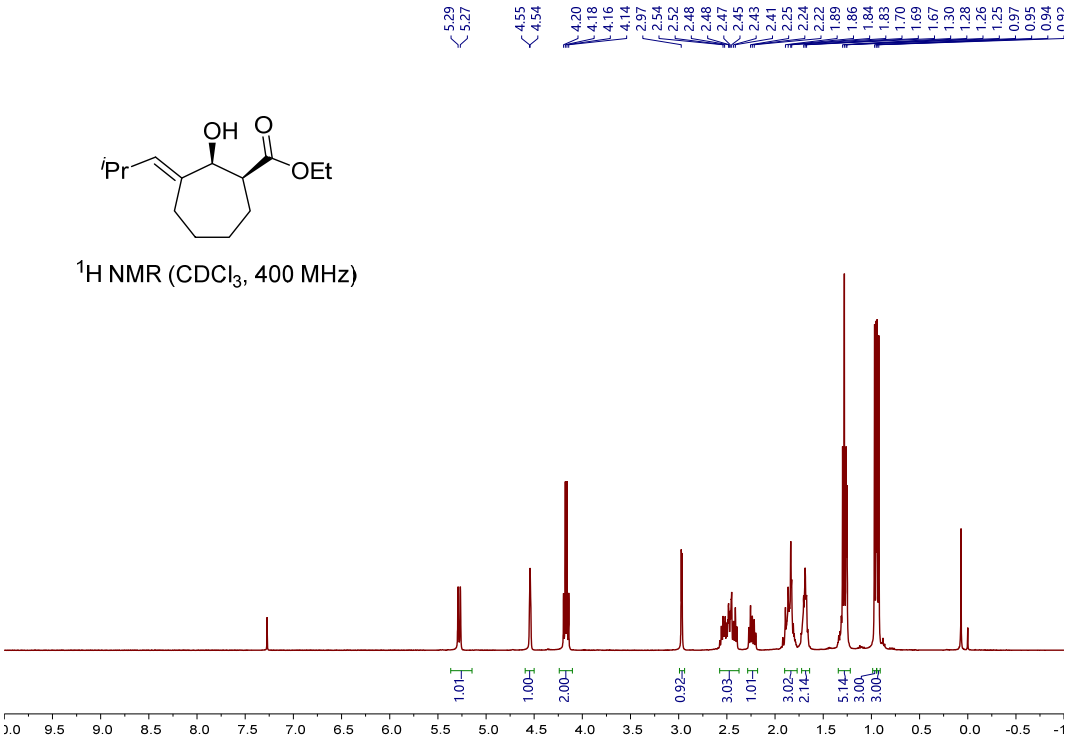


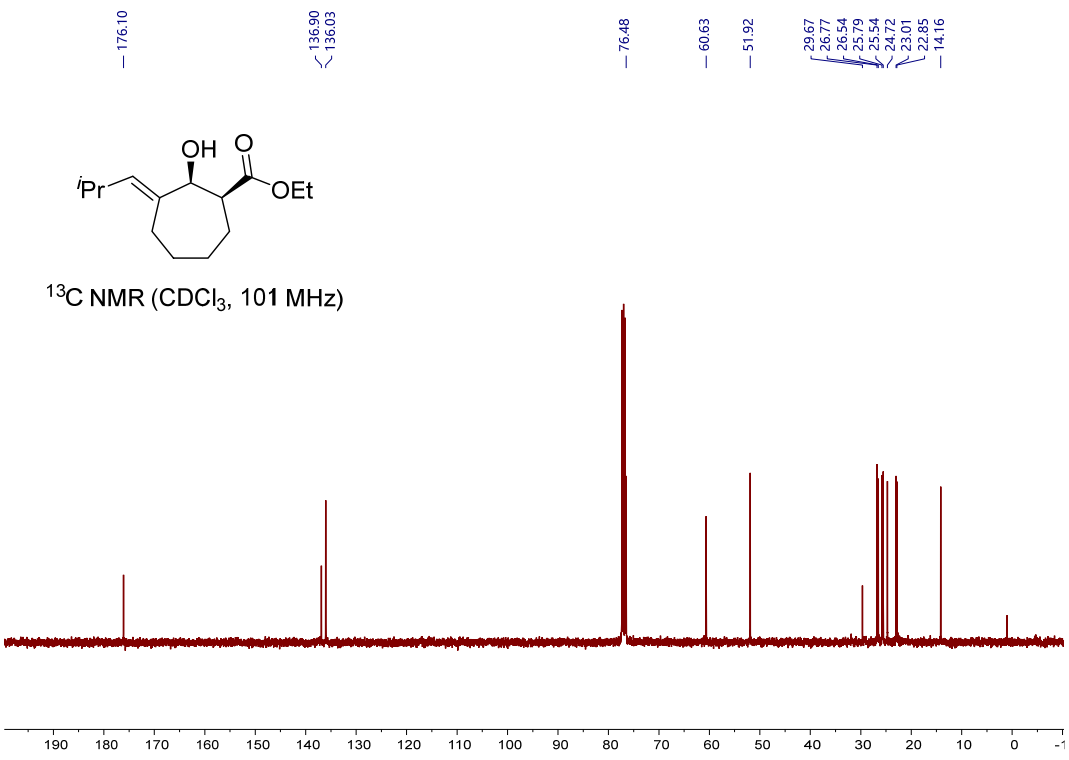
(+)-Ethyl (*E*)-3-(furan-2-ylmethylene)-2-hydroxycycloheptane-1-carboxylate ((+)-10h)



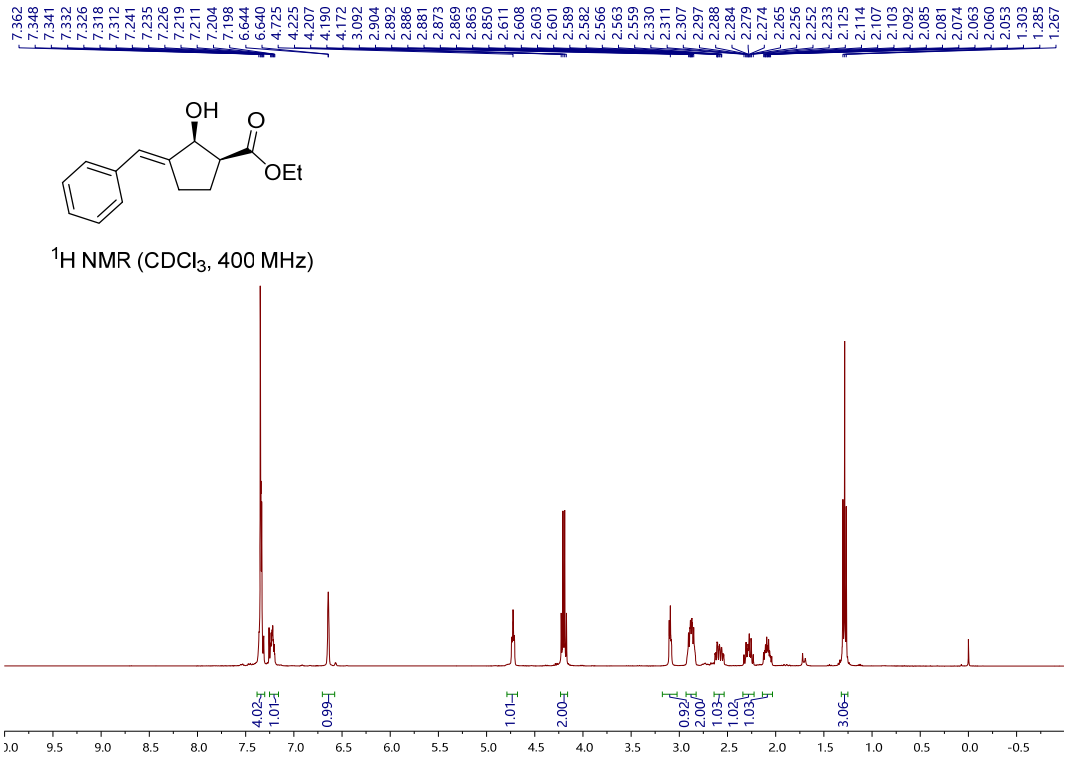


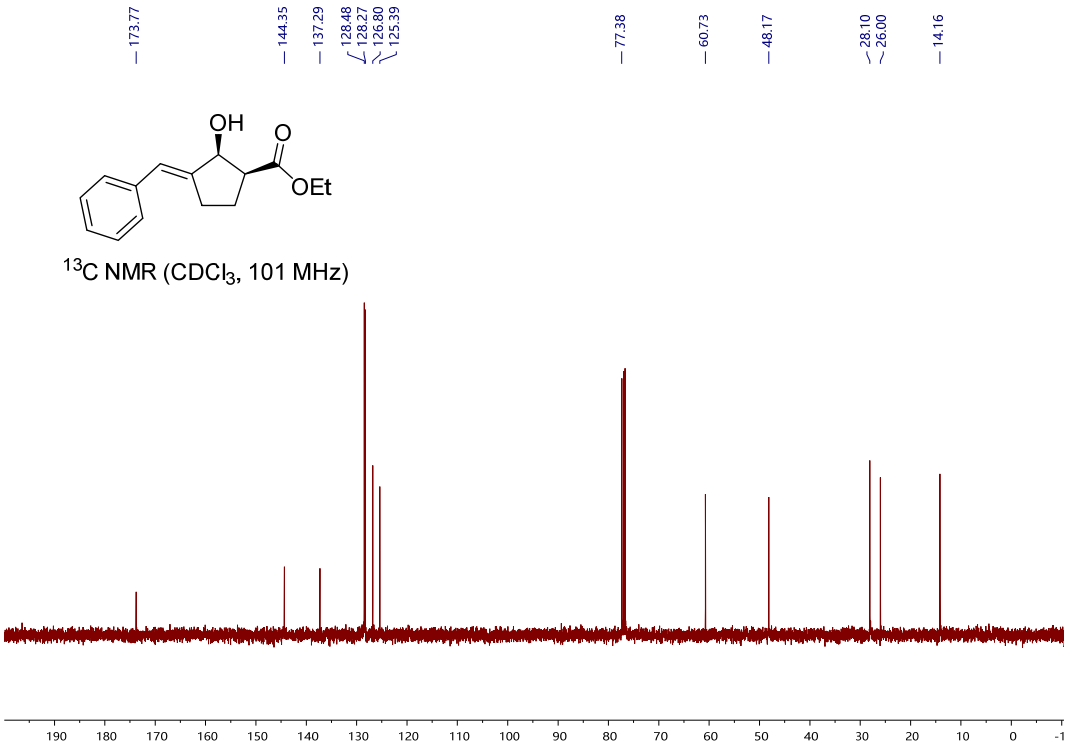
(+)-Ethyl (*E*)-2-hydroxy-3-(2-methylpropylidene)cycloheptane-1-carboxylate ((+)-10i)



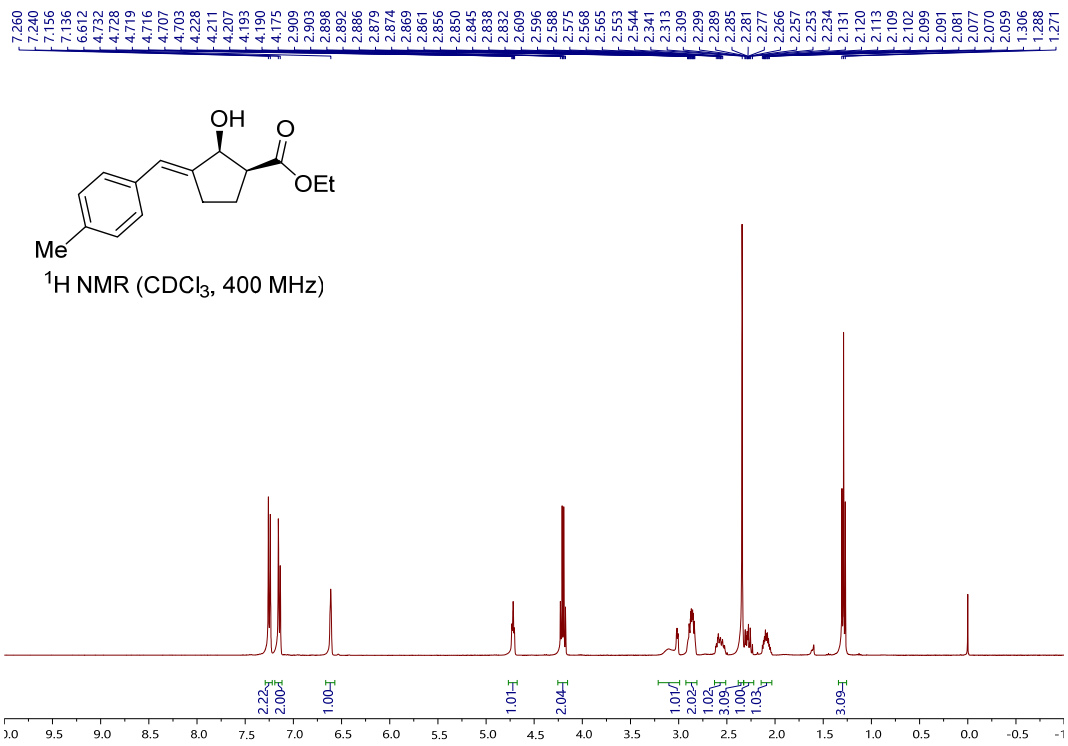


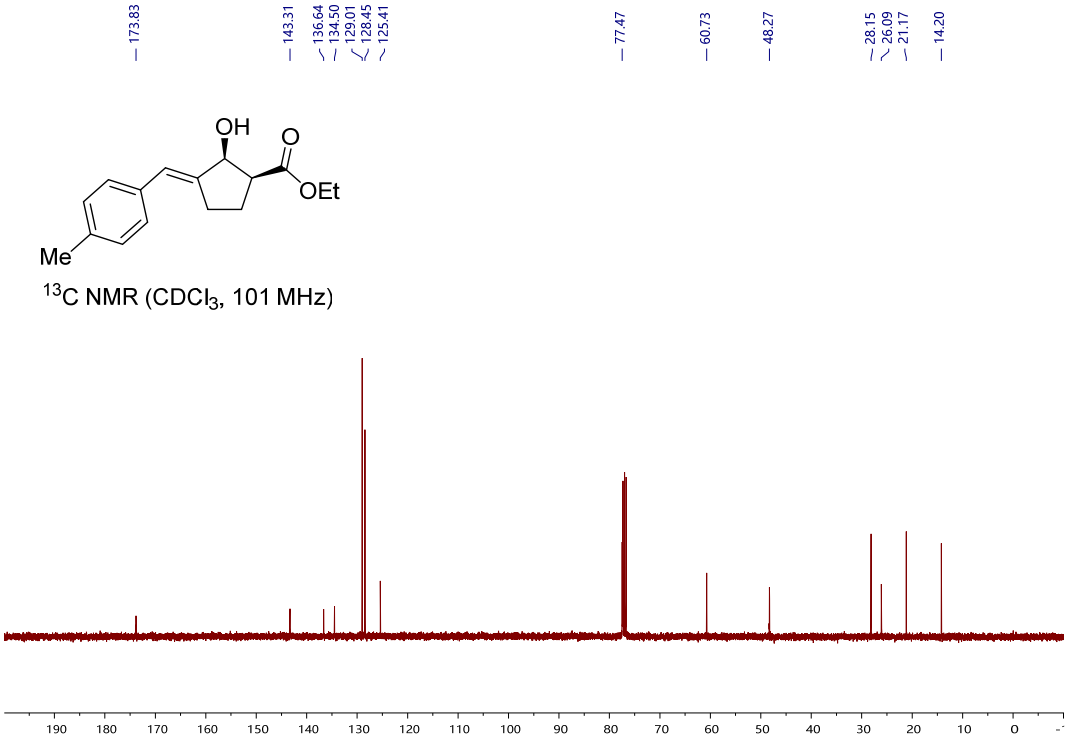
(+)-Ethyl 3-((*E*)-benzylidene)-2-hydroxycyclopentane-1-carboxylate ((+)-12a)



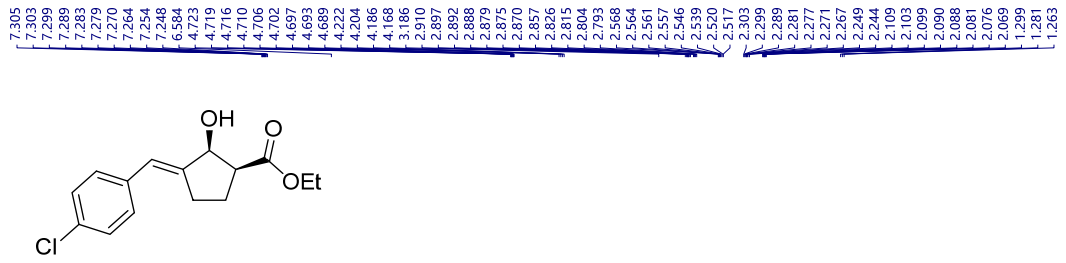


(+)-Ethyl 2-hydroxy-3-((*E*)-4-methylbenzylidene)cyclopentane-1-carboxylate ((+)-12b)

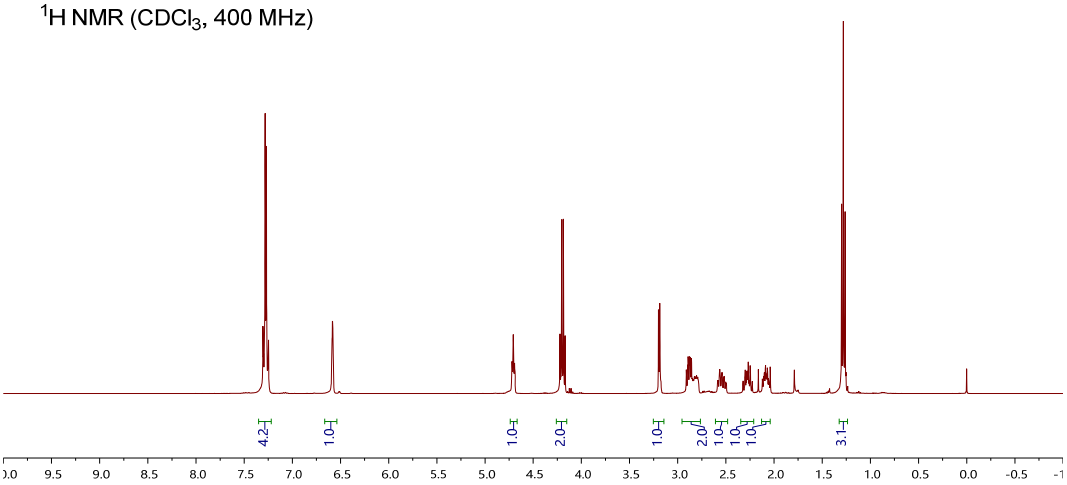


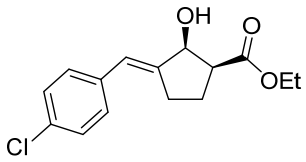


(+)-Ethyl 3-((*E*)-4-chlorobenzylidene)-2-hydroxycyclopentane-1-carboxylate ((+)-12c)

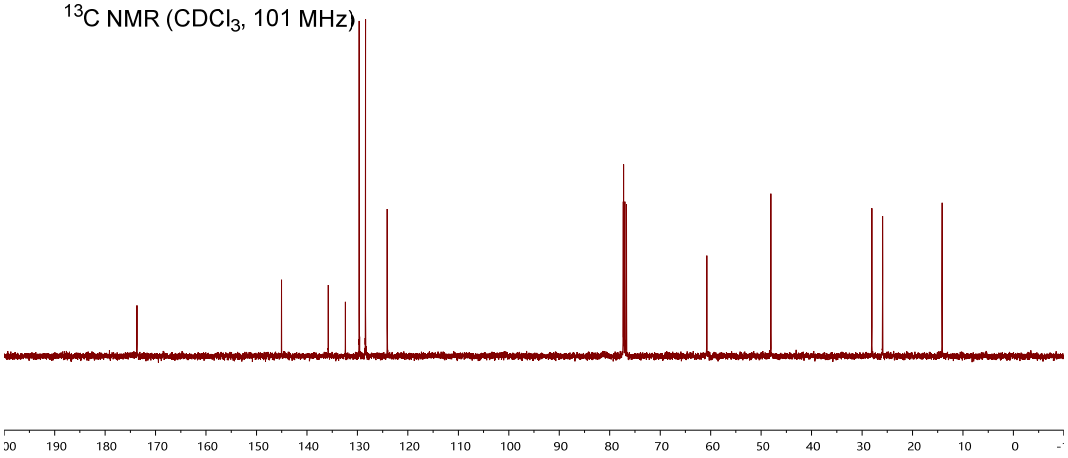


^{1}H NMR ($CDCl_3$, 400 MHz)

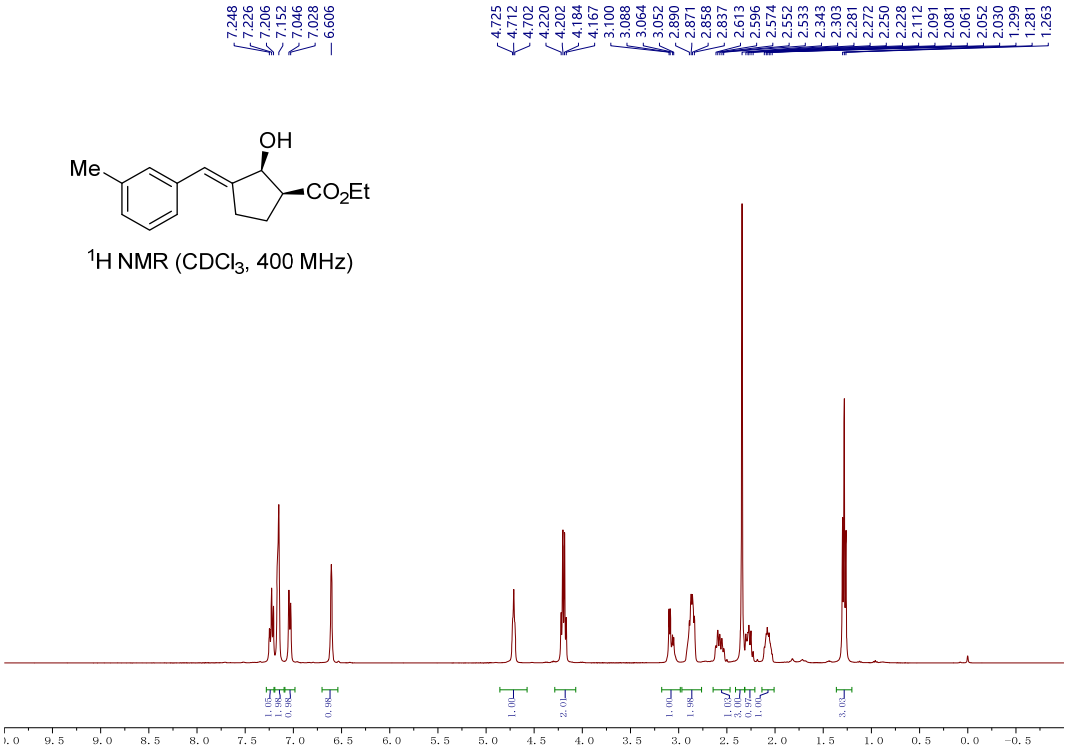


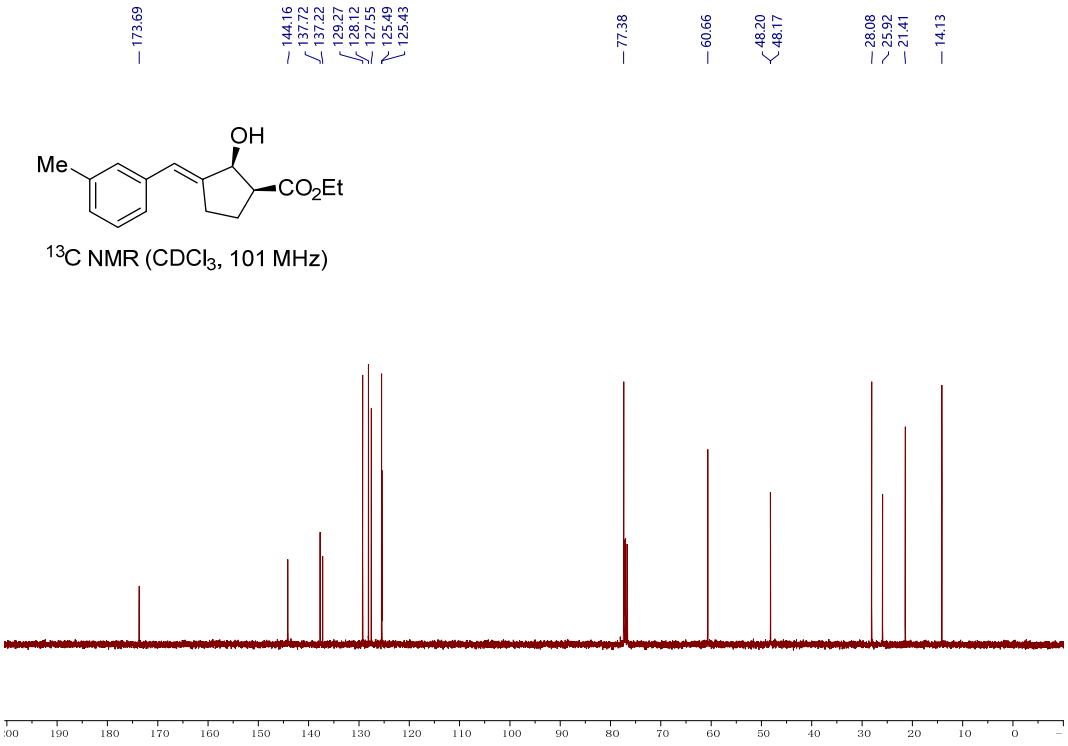


^{13}C NMR ($CDCl_3$, 101 MHz)

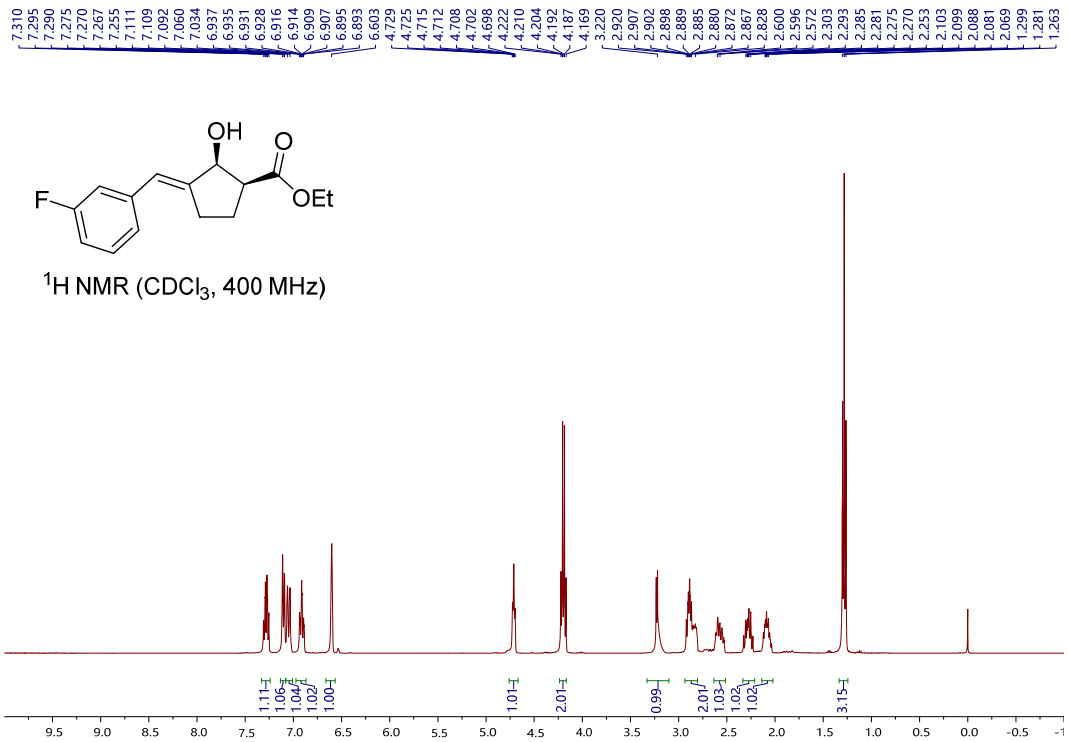


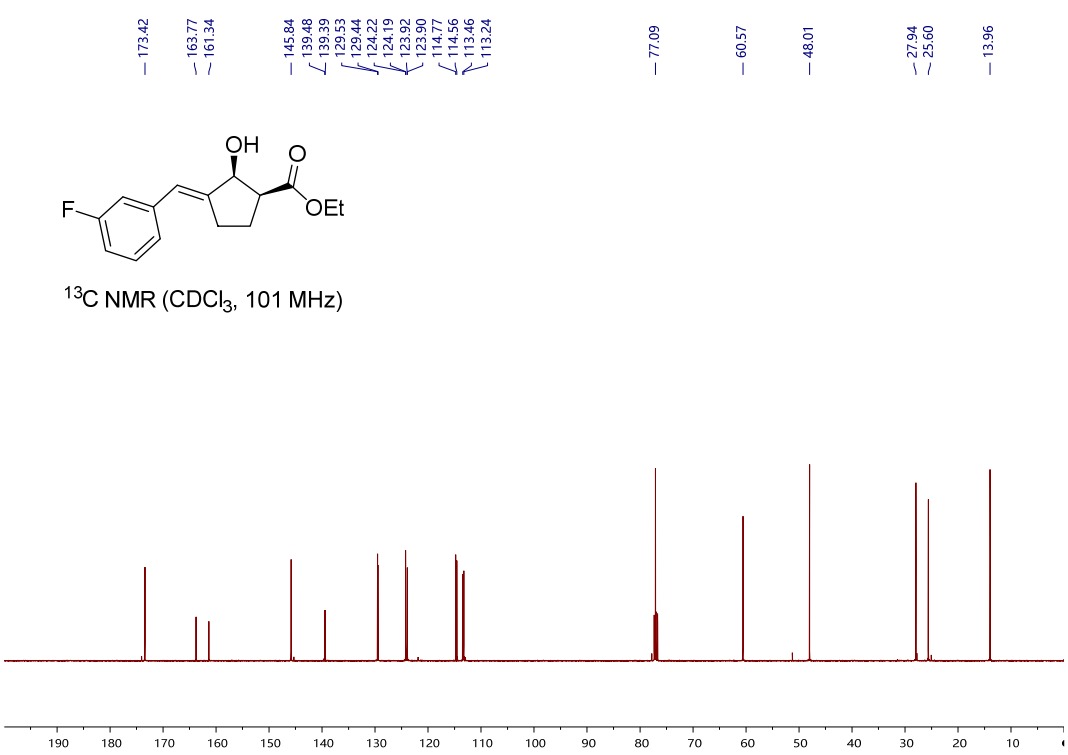
(+)-Ethyl 2-hydroxy-3-((*E*)-3-methylbenzylidene)cyclopentane-1-carboxylate ((+)-12d)



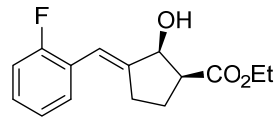


(+)-Ethyl 3-((*E*)-3-fluorobenzylidene)-2-hydroxycyclopentane-1-carboxylate ((+)-12e)

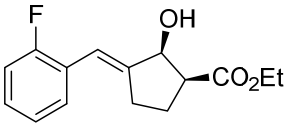




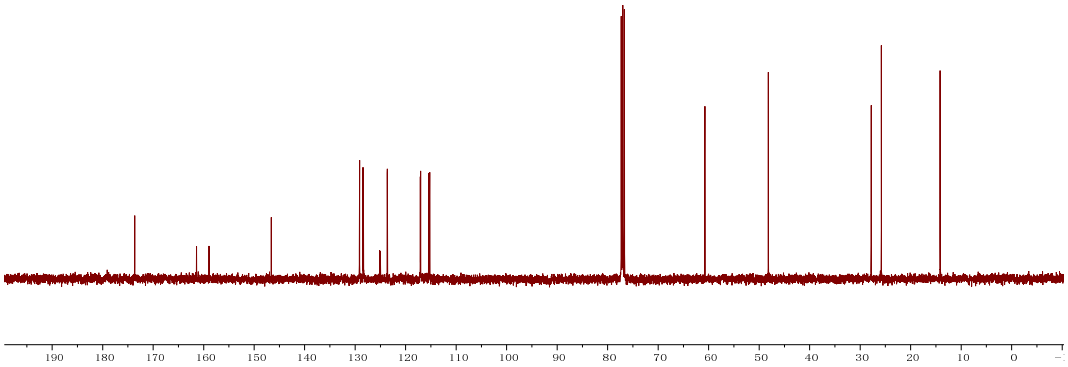
Ethyl (1*S*,2*S*)-3-((*E*)-2-fluorobenzylidene)-2-hydroxycyclopentane-1-carboxylate ((1*S*,2*S*)-12f)



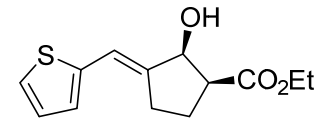
^{1}H NMR ($CDCl_3$, 400 MHz)



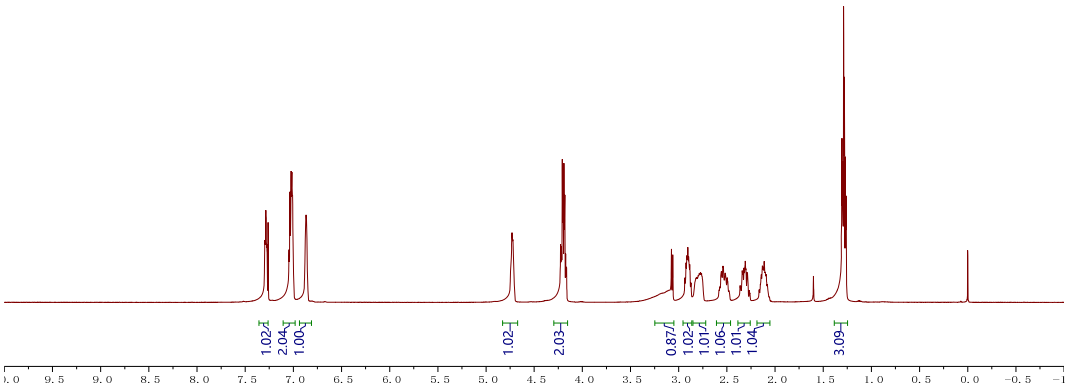
^{13}C NMR ($CDCl_3$, 101 MHz)

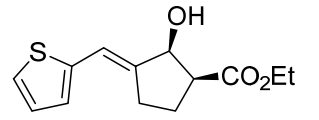


(+)-Ethyl (*E*)-2-hydroxy-3-(thiophen-2-ylmethylene)cyclopentane-1-carboxylate ((+)-12g)

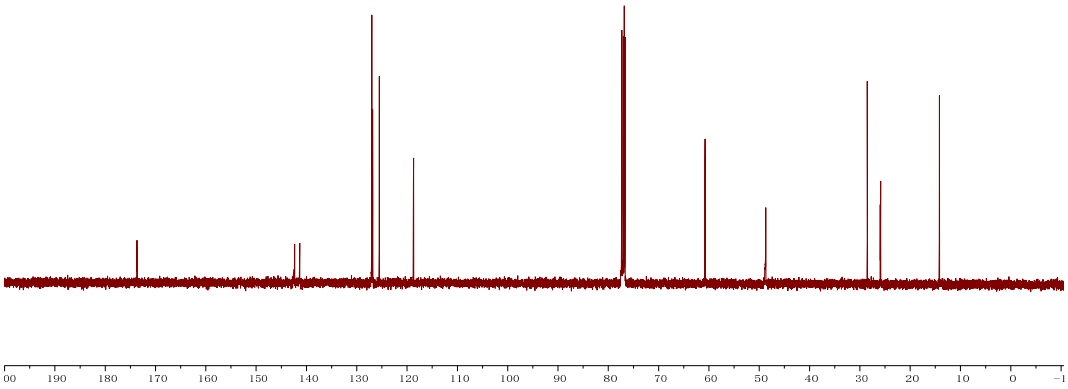


^{1}H NMR ($CDCl_3$, 400 MHz)

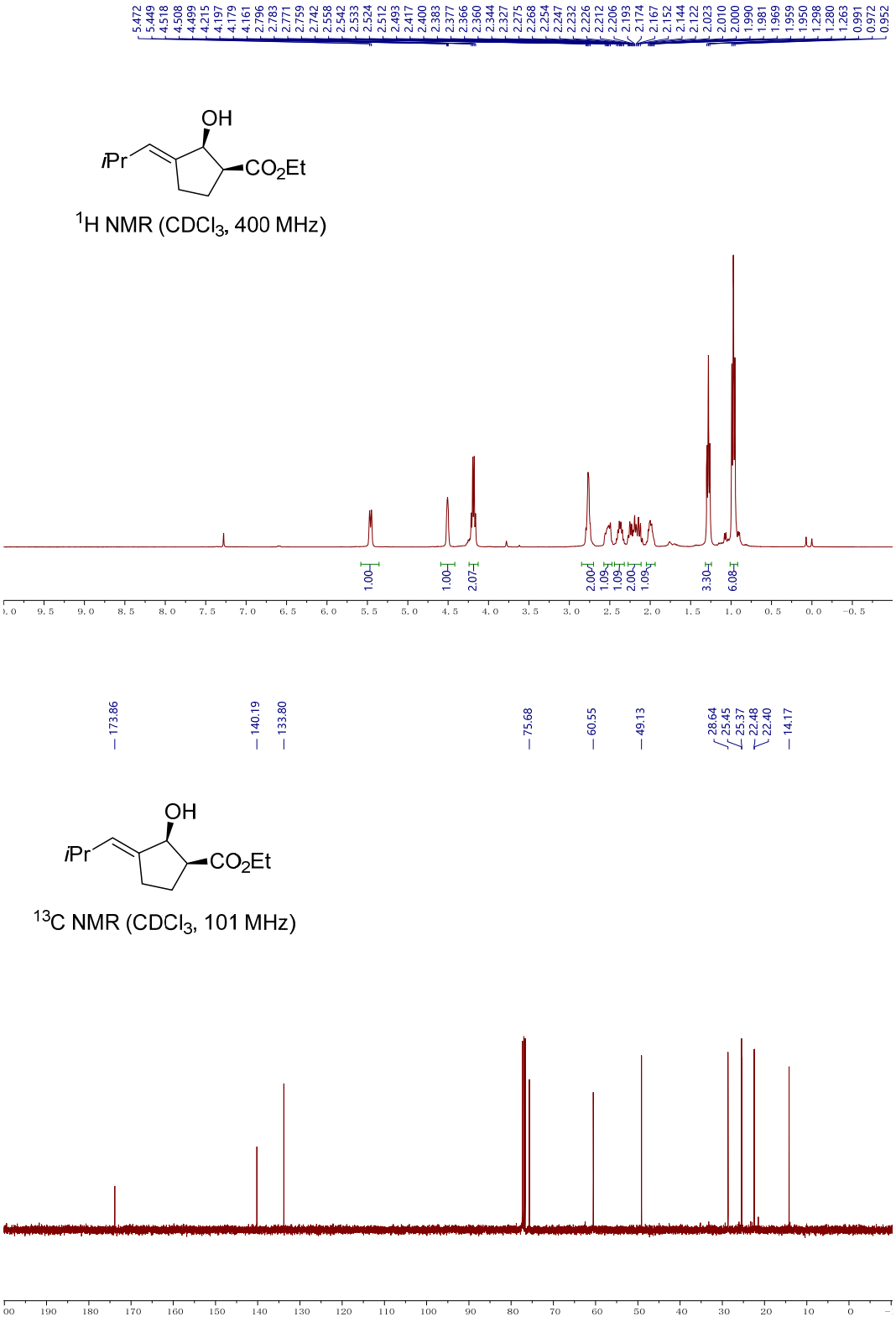




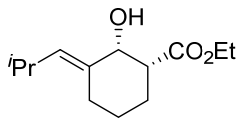
^{13}C NMR ($CDCl_3$, 101 MHz)



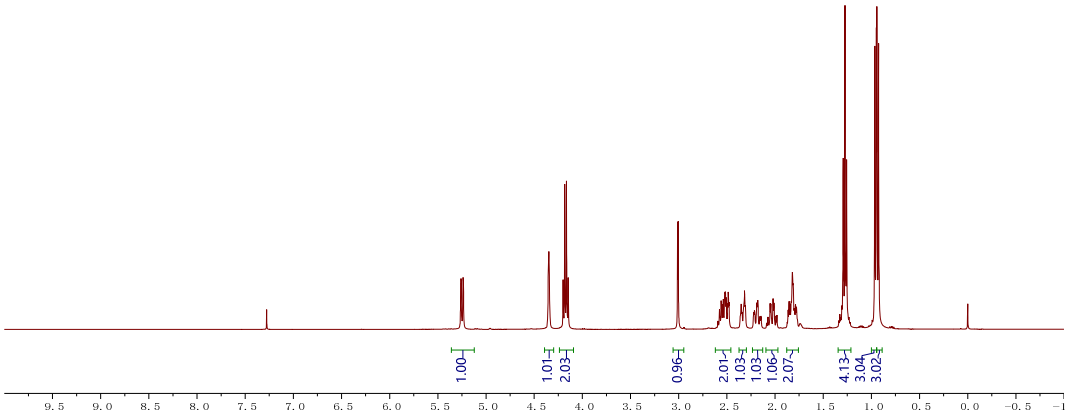
(+)-Ethyl (*E*)-2-hydroxy-3-(2-methylpropylidene)cyclopentane-1-carboxylate ((+)-12h)

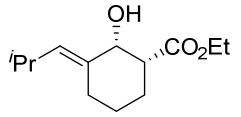


Compound (−)-8ag

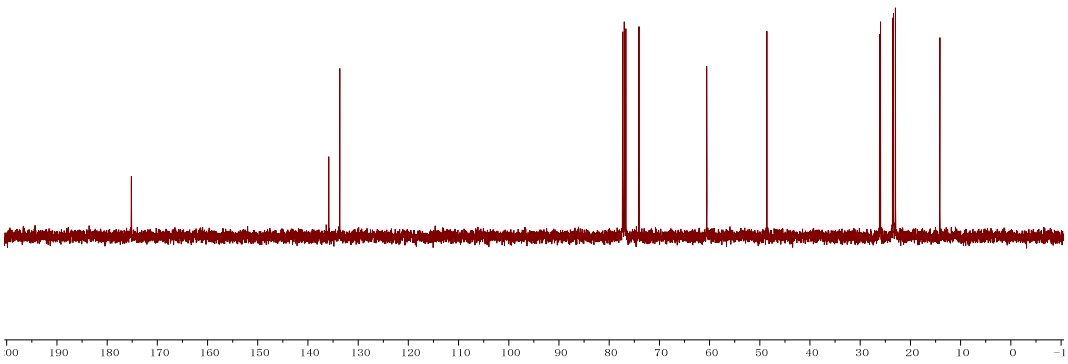


^{1}H NMR ($CDCl_3$, 400 MHz)

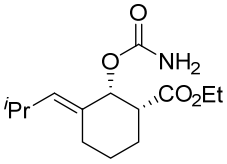




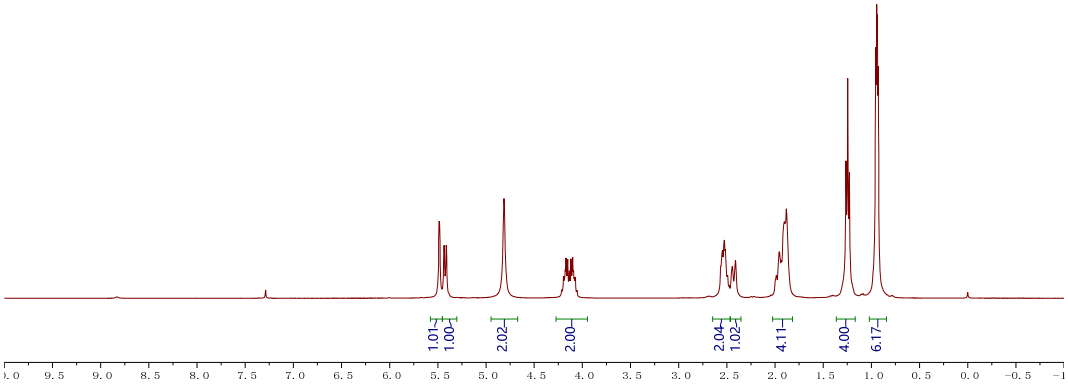
^{13}C NMR ($CDCl_3$, 101 MHz)

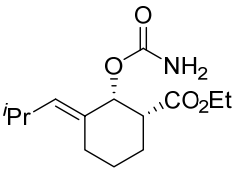


Compound (−)-13

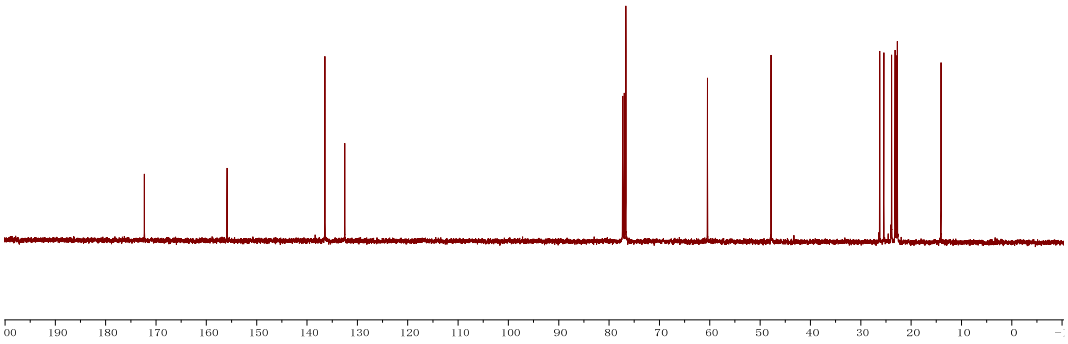


^{1}H NMR ($CDCl_3$, 400 MHz)

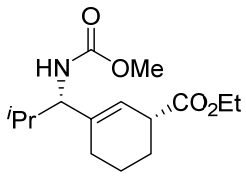




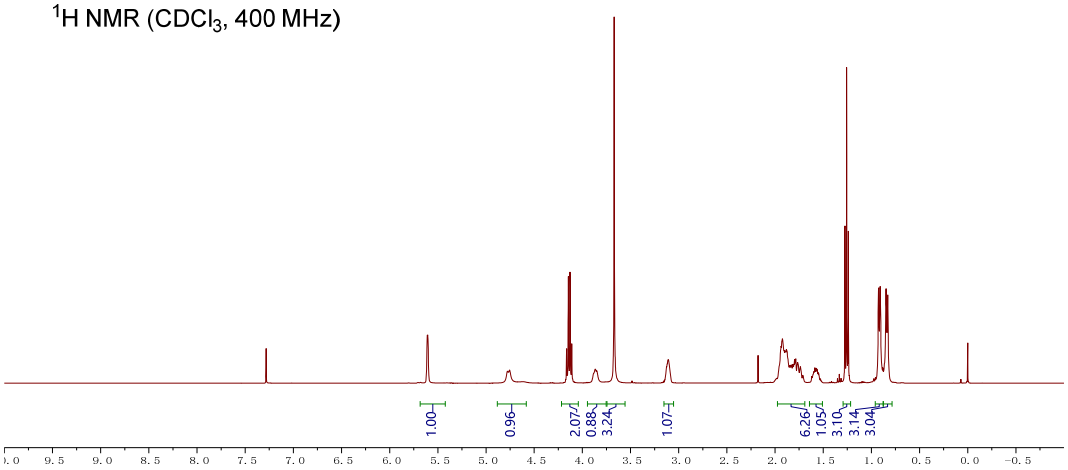
^{13}C NMR ($CDCl_3$, 101 MHz)

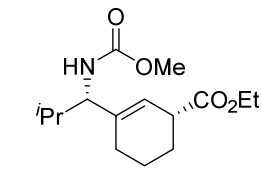


Compound (+)-15

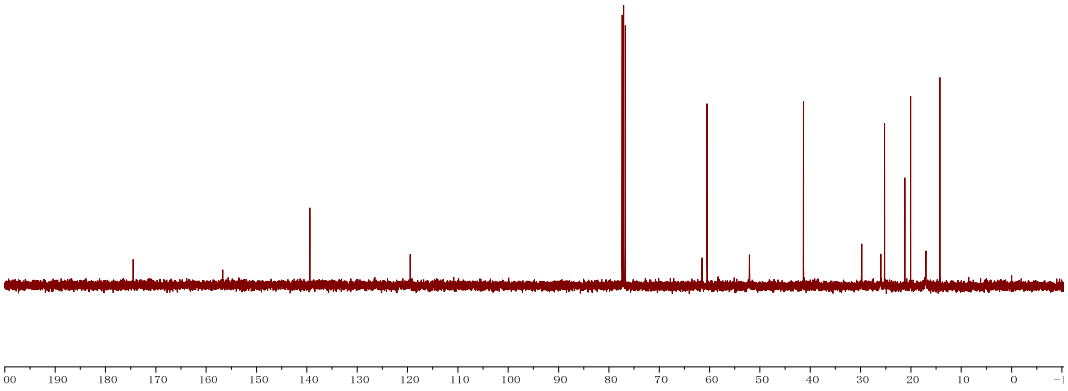


^{1}H NMR ($CDCl_3$, 400 MHz)





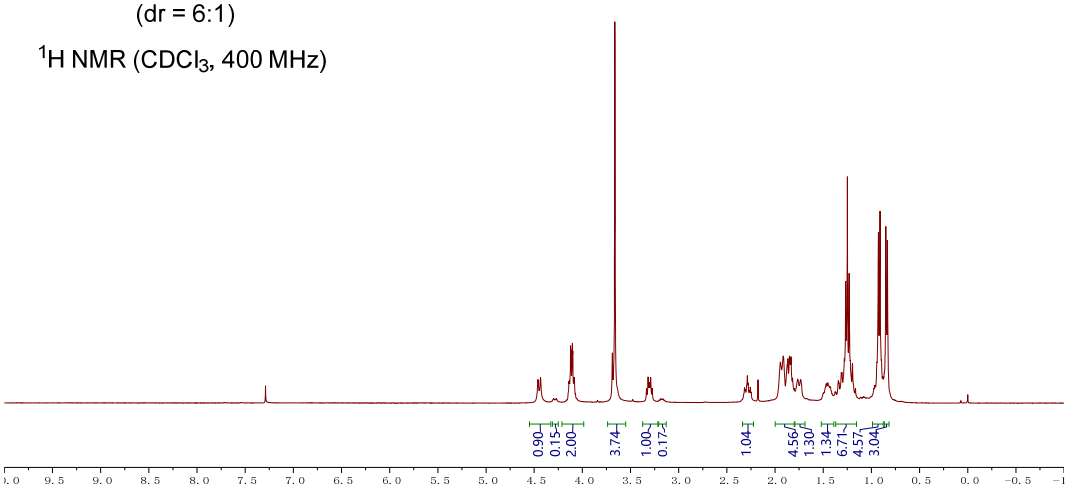
^{13}C NMR ($CDCl_3$, 101 MHz)

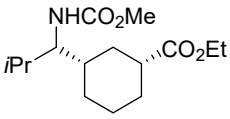


Compound (−)-16

(dr = 6:1)

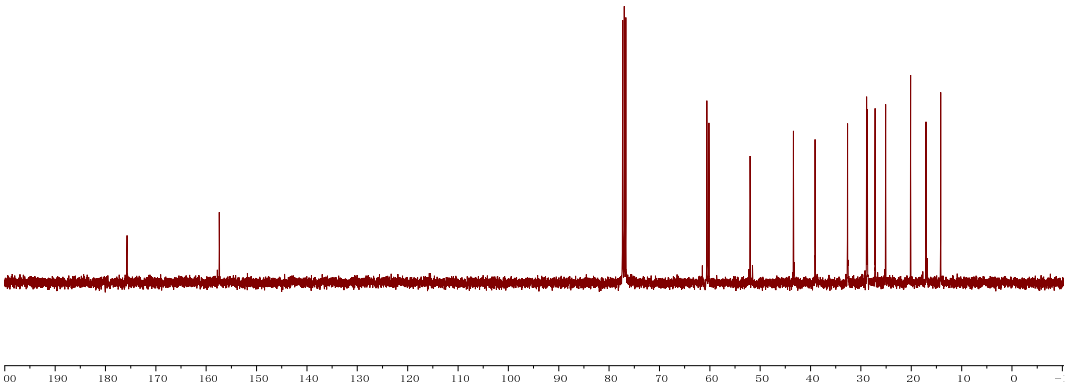
^{1}H NMR ($CDCl_3$, 400 MHz)



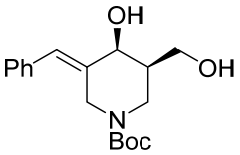


(dr = 6:1)

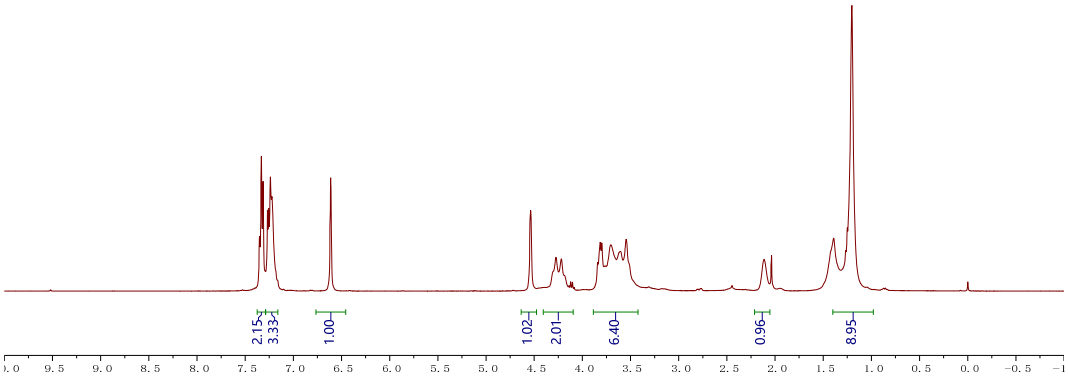
^{13}C NMR ($CDCl_3$, 101 MHz)

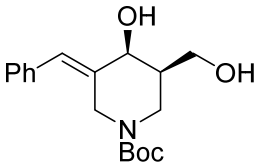


Compound (+)-18

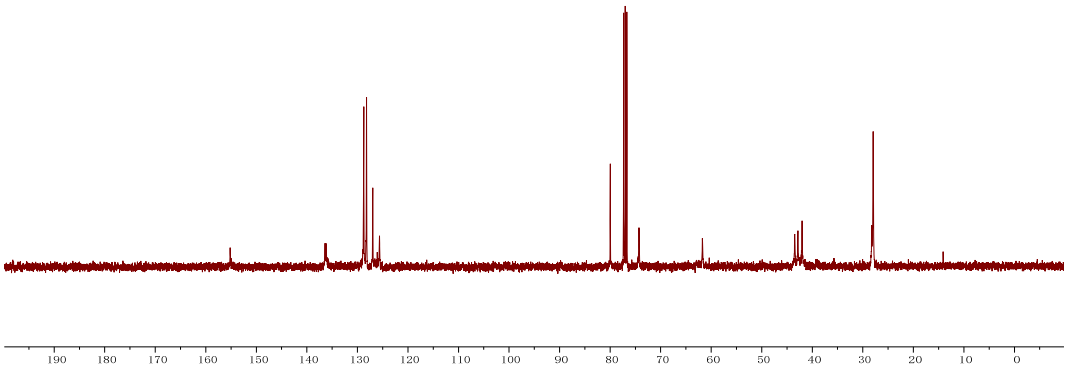


^{1}H NMR ($CDCl_3$, 400 MHz)

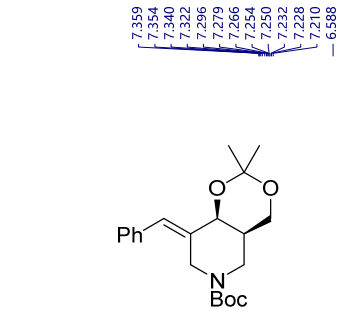




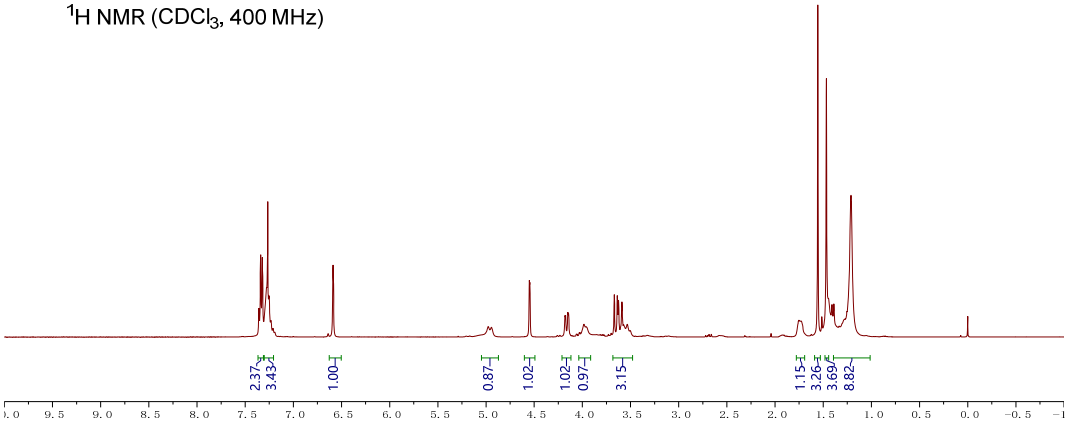
^{13}C NMR ($CDCl_3$, 101 MHz)

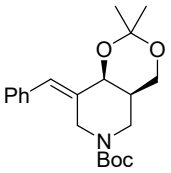


Compound (+)-19

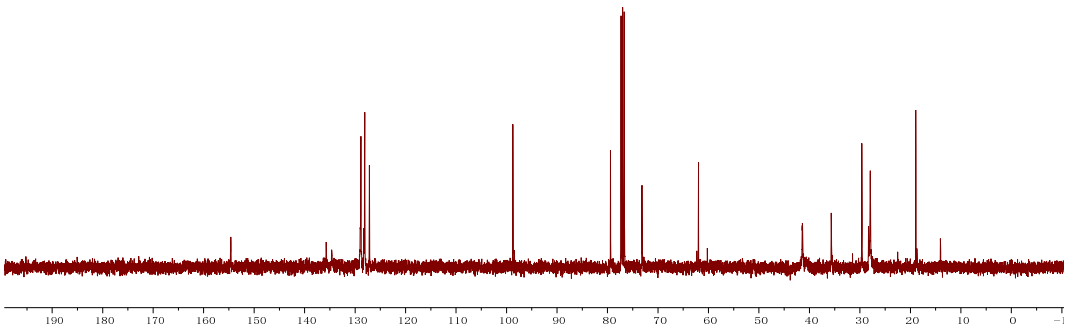


^{1}H NMR ($CDCl_3$, 400 MHz)

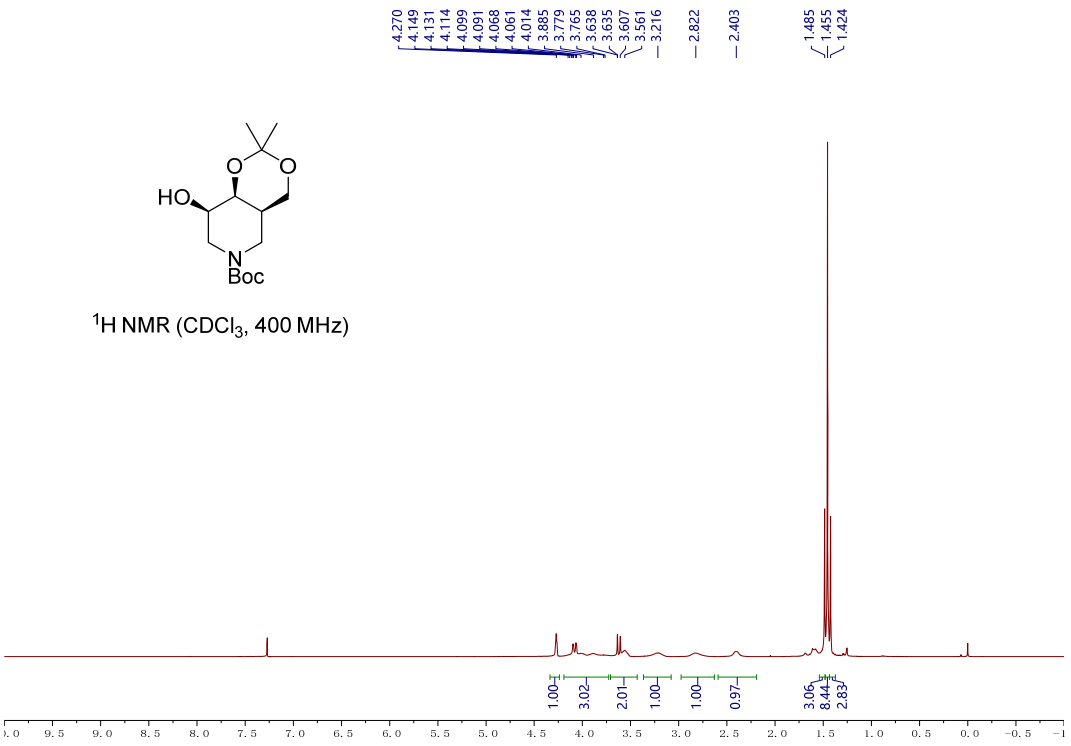




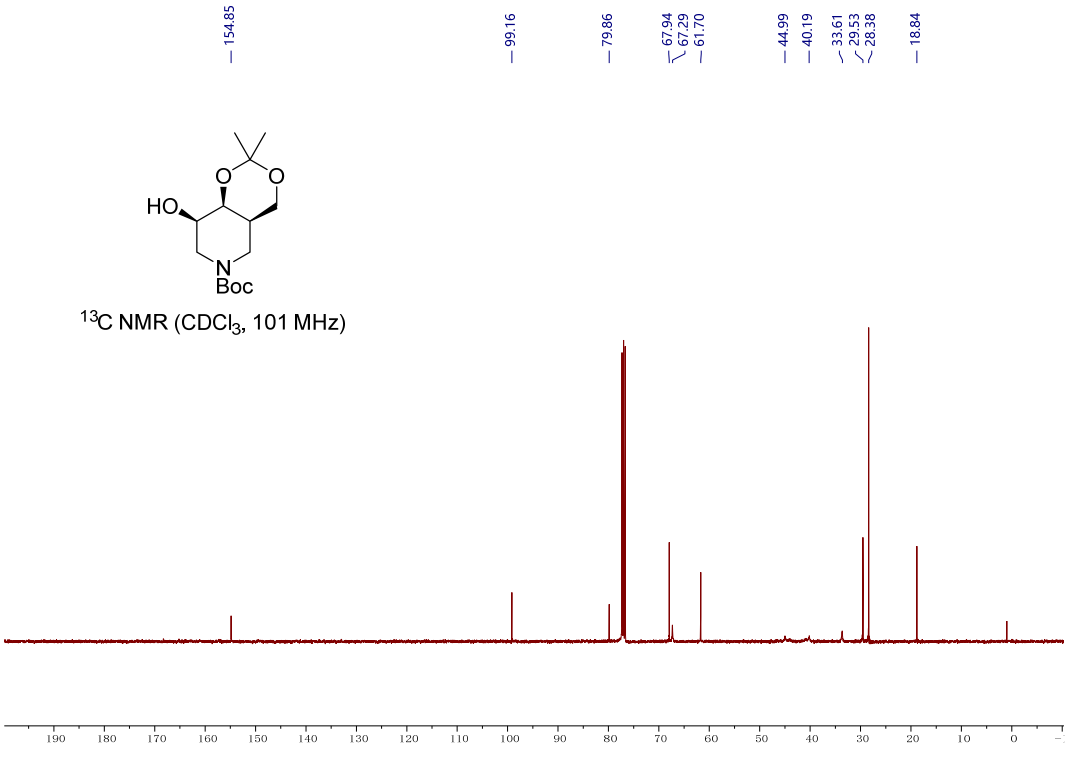
^{13}C NMR ($CDCl_3$, 101 MHz)



Compound (+)-20

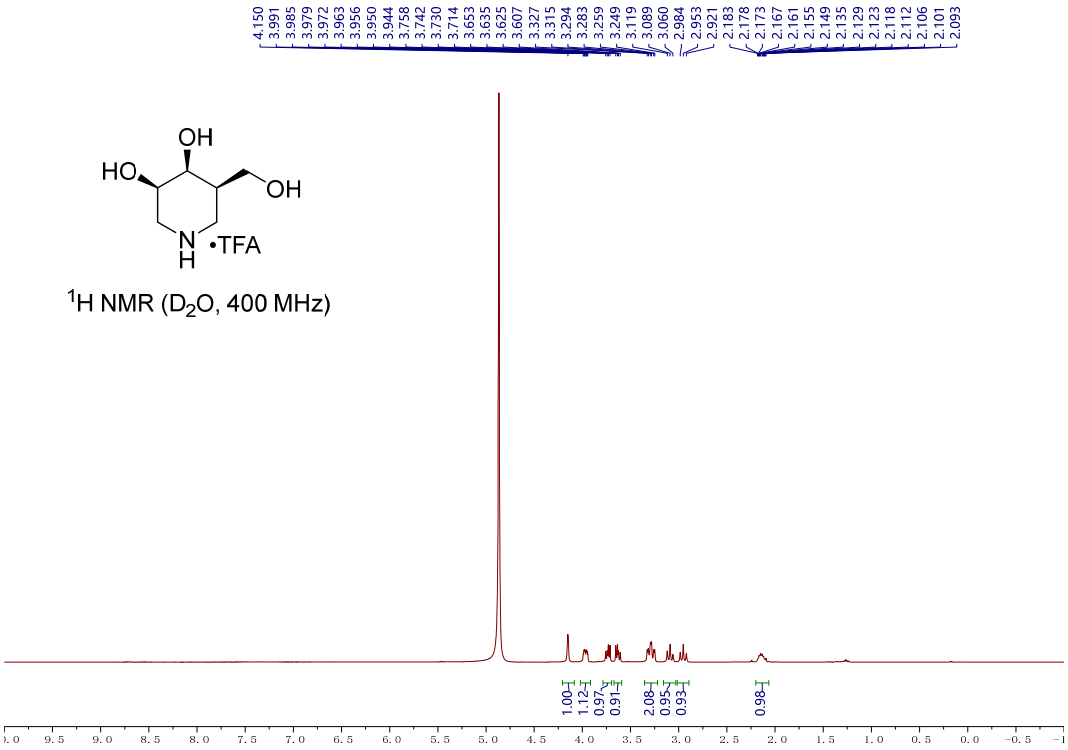


^{1}H NMR ($CDCl_3$, 400 MHz)

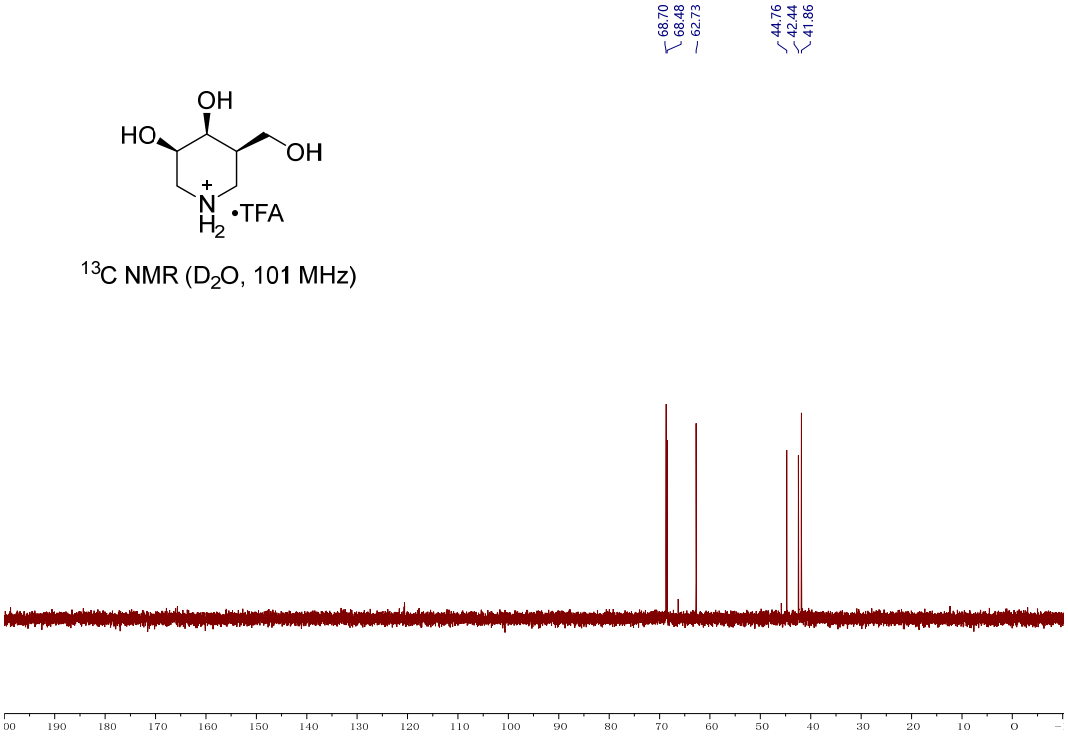


^{13}C NMR ($CDCl_3$, 101 MHz)

(+)-isogalactofagomine



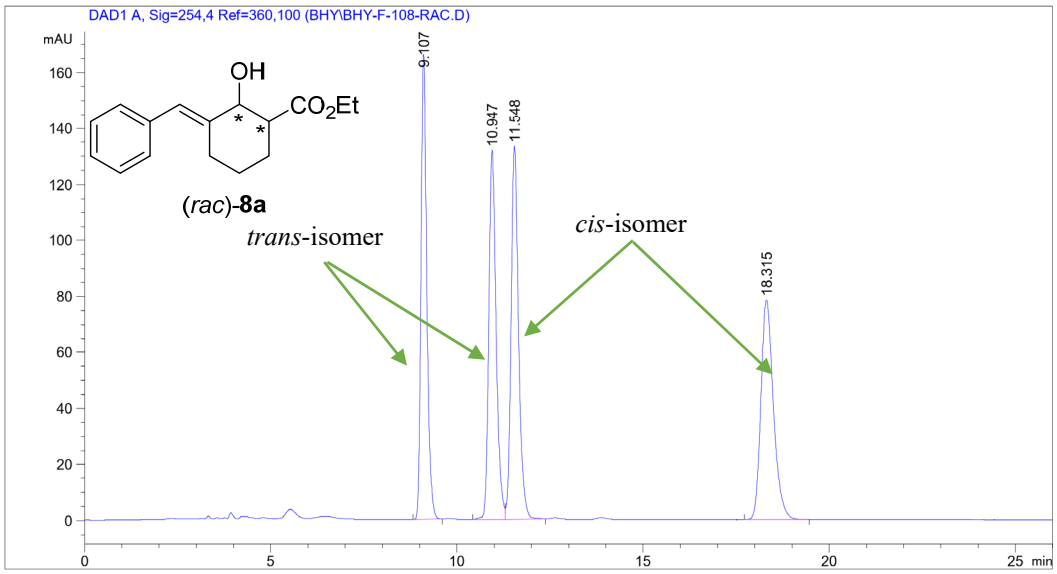
^{1}H NMR (D_2O, 400 MHz)



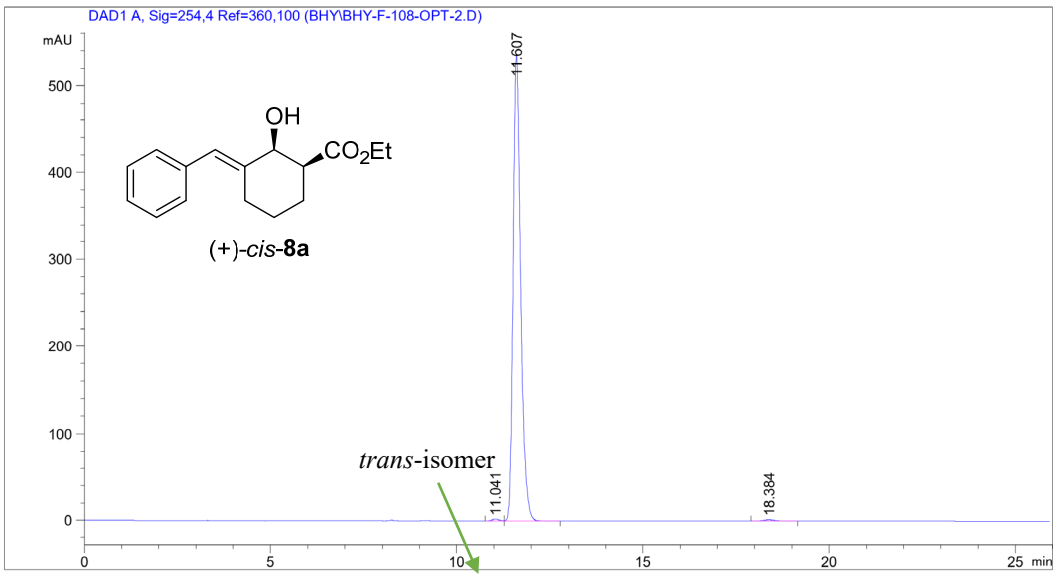
^{13}C NMR (D_2O, 101 MHz)

(G) HPLC Charts for Products

For compound (+)-*cis*-8a

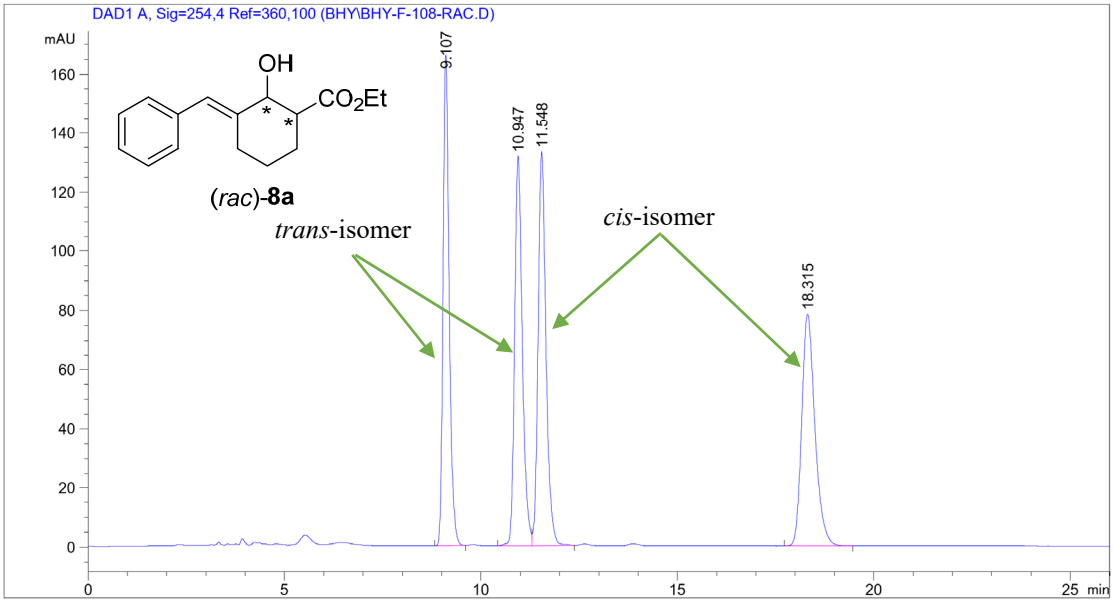


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.107	BB	0.1644	1797.42651	165.89624	24.7033
2	10.947	BV	0.2074	1799.05896	131.67825	24.7258
3	11.548	VB	0.2105	1852.35132	132.97411	25.4582
4	18.315	BB	0.3558	1827.21606	78.41668	25.1127

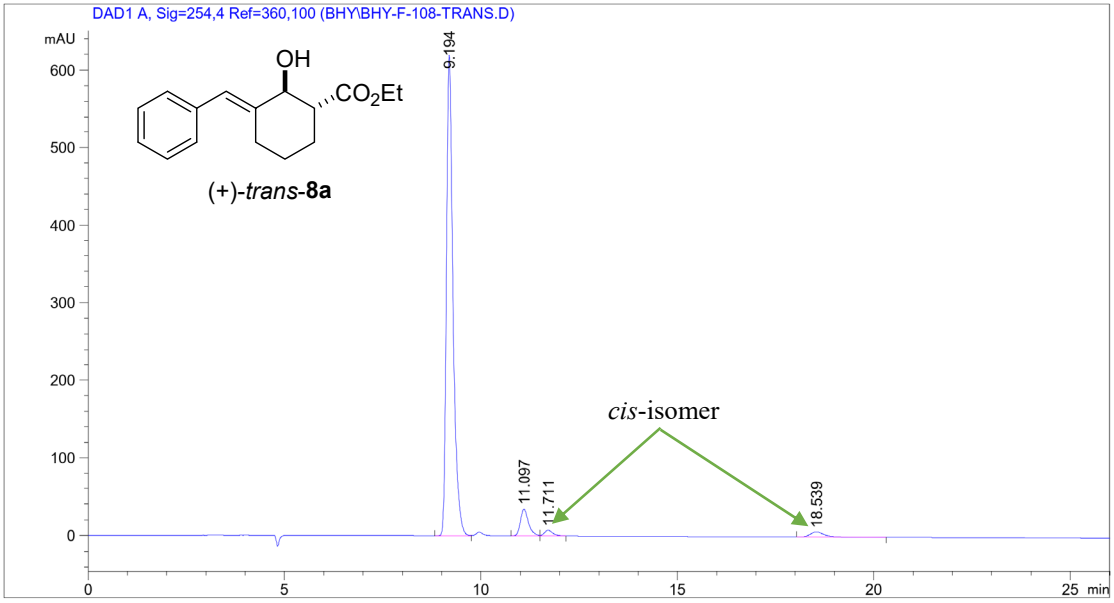


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.041	BV	0.2047	26.51124	1.97442	0.3478
2	11.607	VB	0.2147	7559.20215	535.58044	99.1765
3	18.384	BB	0.3570	36.25856	1.56099	0.4757

For compound (+)-*trans*-8a

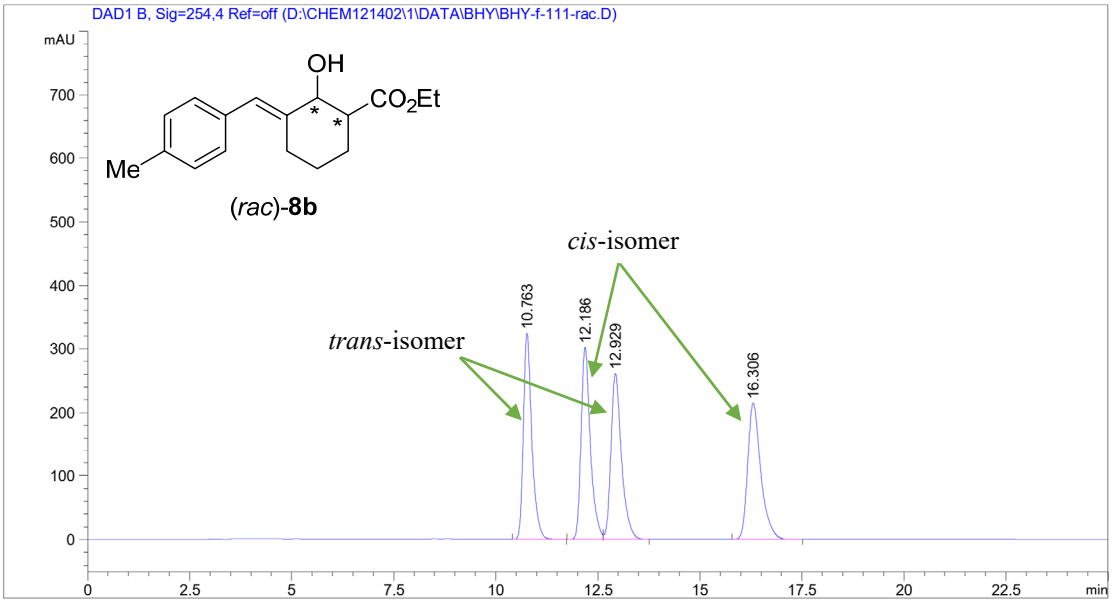


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.107	BB	0.1644	1797.42651	165.89624	24.7033
2	10.947	BV	0.2074	1799.05896	131.67825	24.7258
3	11.548	VB	0.2105	1852.35132	132.97411	25.4582
4	18.315	BB	0.3558	1827.21606	78.41668	25.1127

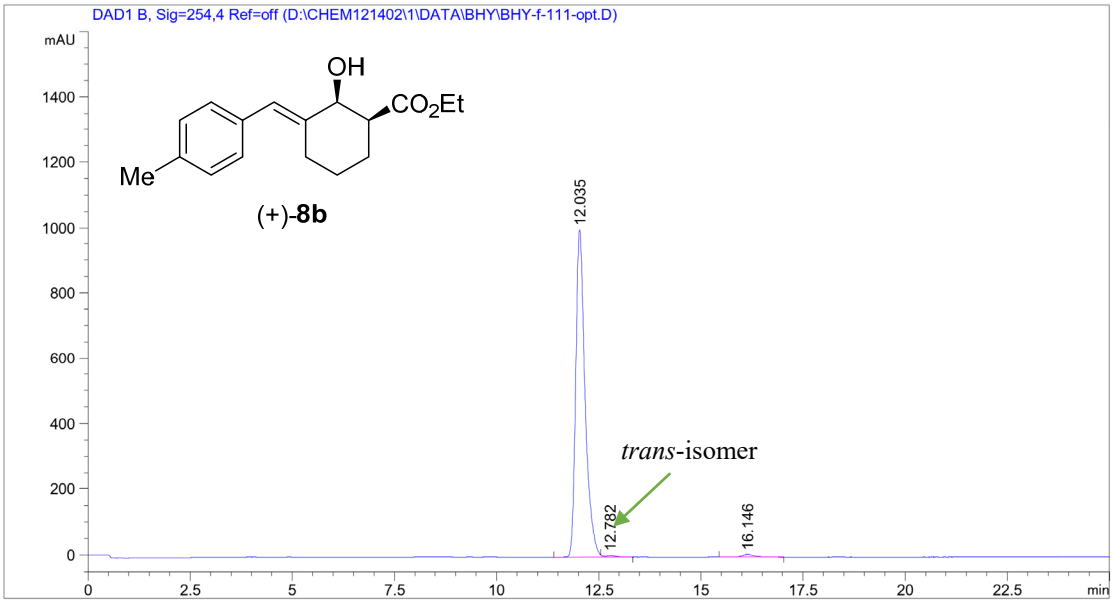


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.194	BV	0.1758	7206.50537	619.15076	90.4360
2	11.097	BV	0.2170	490.36520	34.24862	6.1537
3	11.711	VB	0.2219	109.09803	7.40272	1.3691
4	18.539	BB	0.3701	162.65210	6.58693	2.0412

For compound (+)-8b

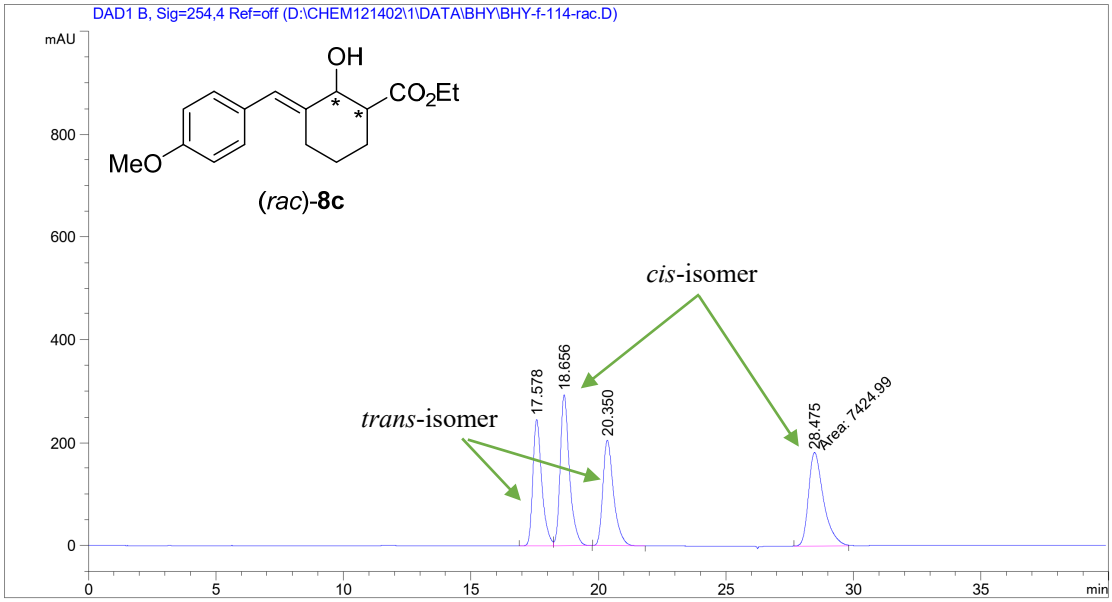


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.763	BB	0.2159	4658.08545	323.61978	24.7174
2	12.186	BV	0.2379	4756.52002	301.73047	25.2397
3	12.929	VB	0.2687	4663.55713	260.63864	24.7464
4	16.306	BB	0.3352	4767.21631	214.60905	25.2965

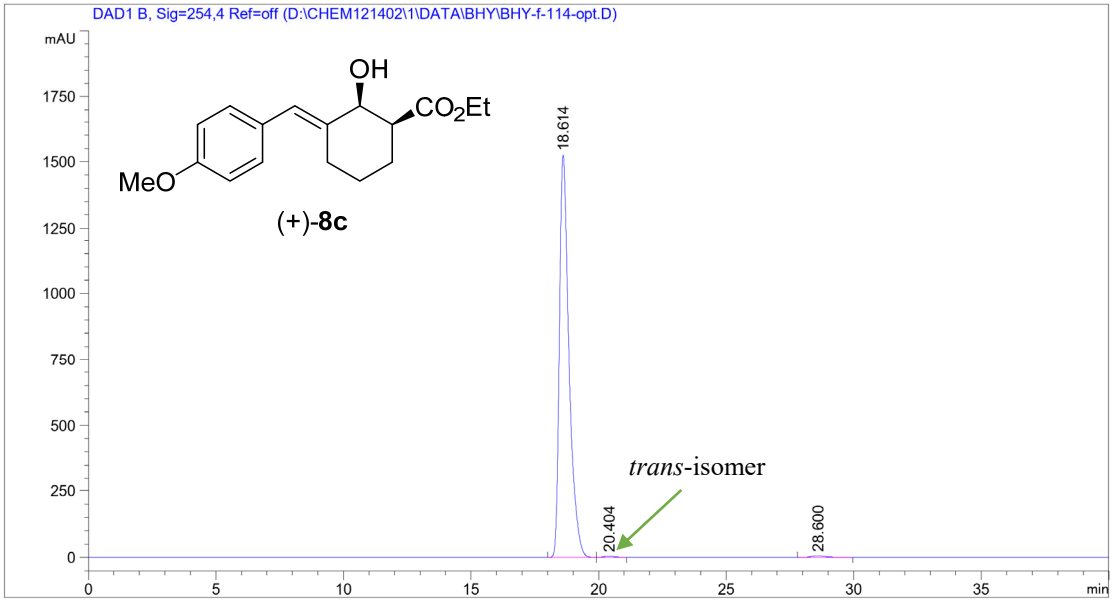


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.035	BV R	0.2389	1.58628e4	1000.70447	98.4280
2	12.782	VB E	0.2478	86.17661	5.13579	0.5347
3	16.146	BB	0.3284	167.16289	7.54824	1.0372

For compound (+)-8c

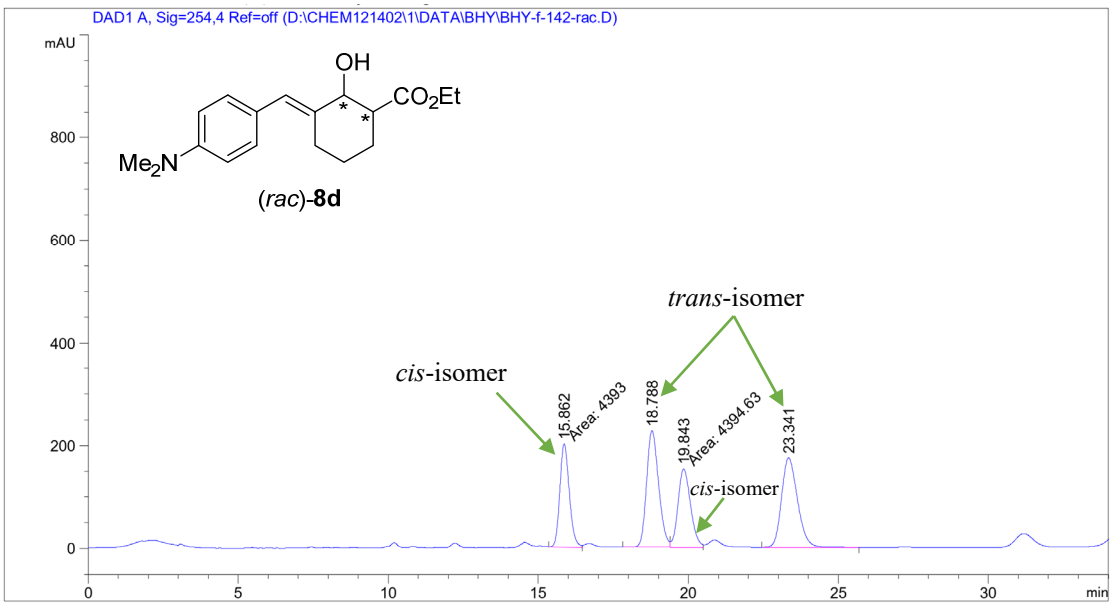


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.578	BV	0.3678	5983.69287	245.94641	22.3397
2	18.656	VB	0.3804	7397.00586	293.15726	27.6162
3	20.350	BB	0.4368	5979.37744	205.91537	22.3235
4	28.475	MM	0.6849	7424.99023	180.69176	27.7206

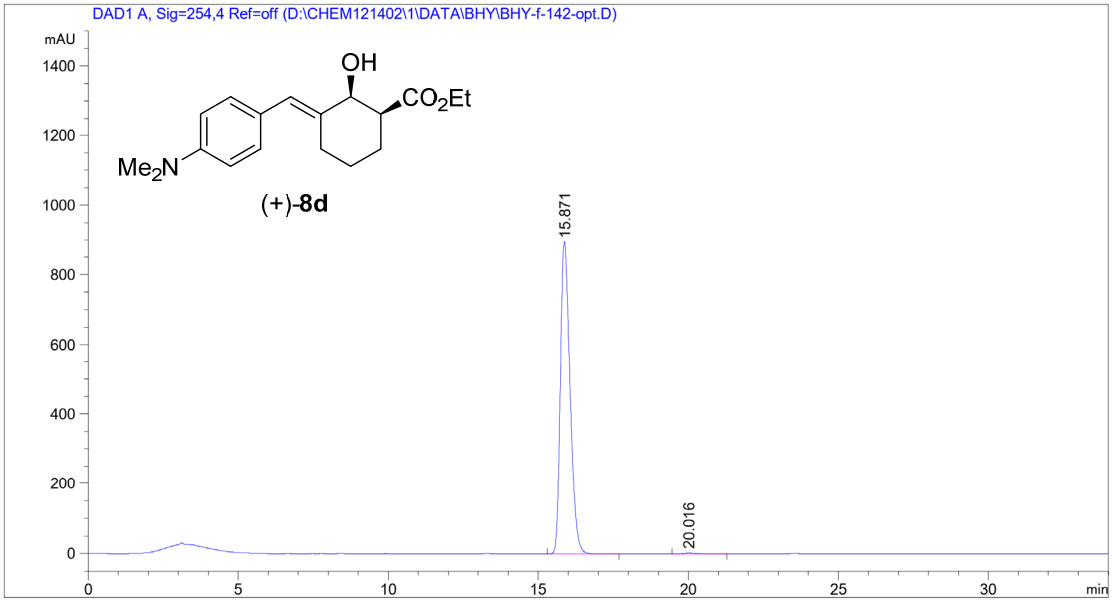


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.614	BB	0.3948	3.98461e4	1524.92590	99.1428
2	20.404	BB	0.4085	114.39816	4.21725	0.2846
3	28.600	BB	0.5858	230.11456	5.69062	0.5726

For compound (+)-8d

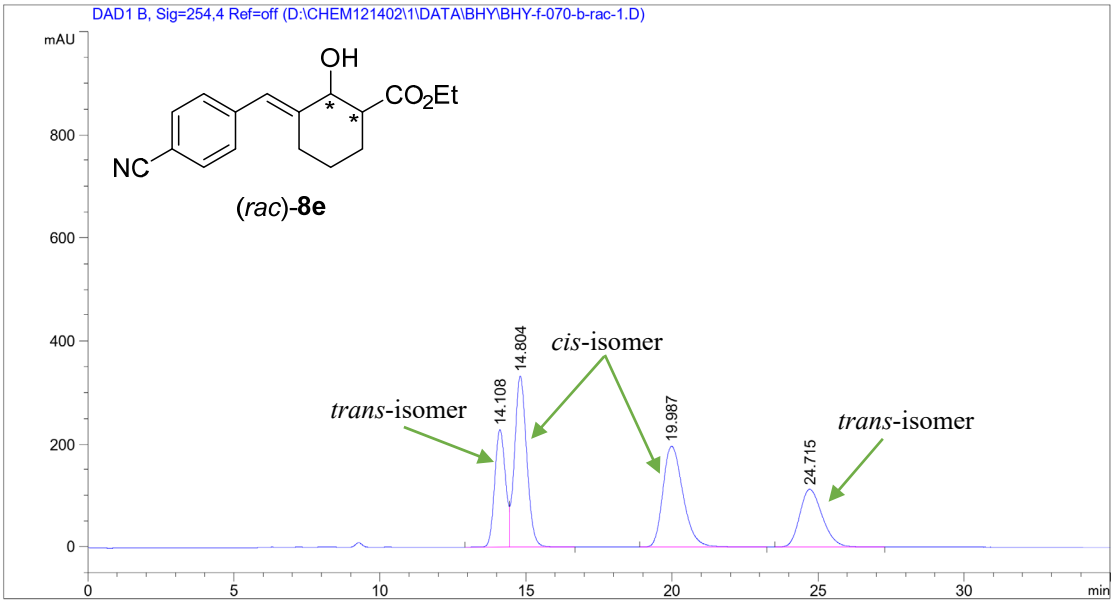


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.862	MM	0.3649	4393.00244	200.65739	20.4707
2	18.788	BV	0.4308	6307.72461	226.53874	29.3931
3	19.843	MM	0.4786	4394.63037	153.04070	20.4783
4	23.341	BB	0.5647	6364.54443	174.01308	29.6578



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.871	BB	0.3444	1.99712e4	894.67688	99.6034
2	20.016	BB	0.4159	79.52099	2.49469	0.3966

For compound (+)-8e



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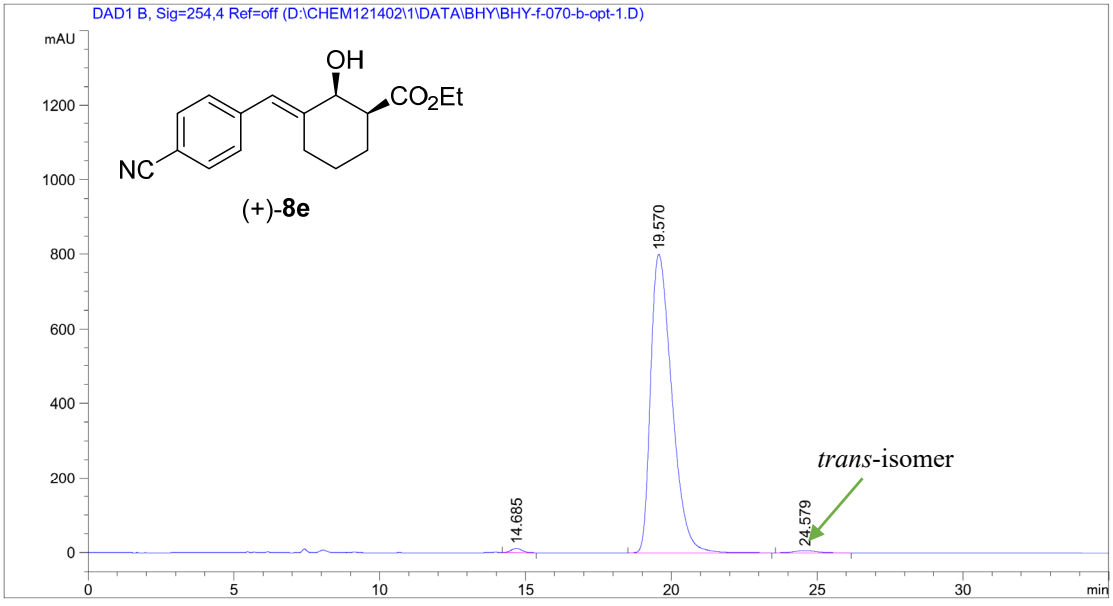
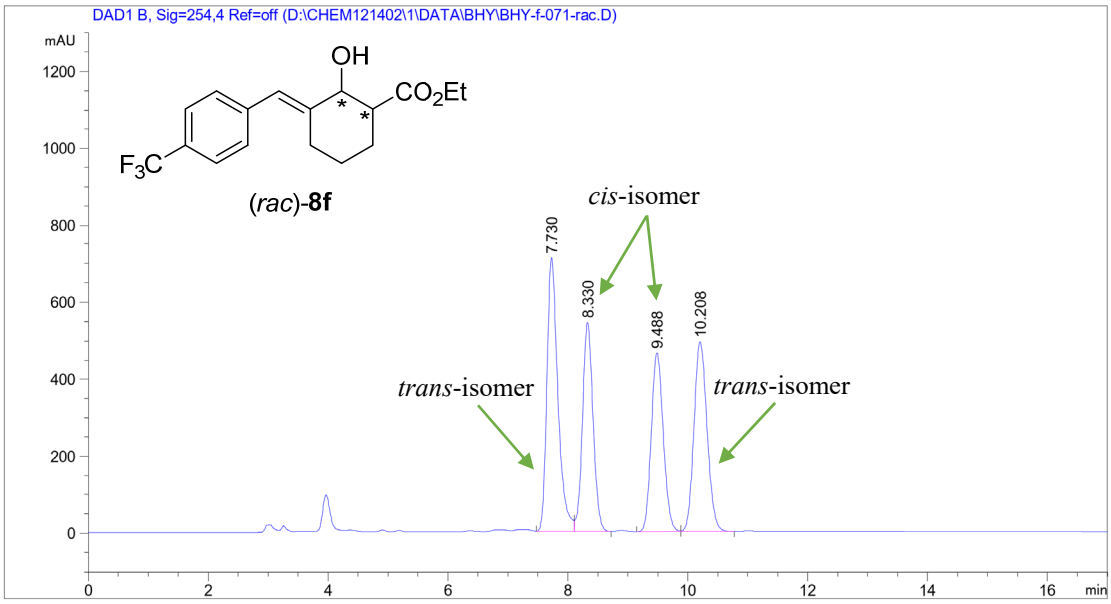
1	14.108	BV	0.3980	5867.46436	229.73602	18.9363
2	14.804	VB	0.4487	9665.31055	332.95621	31.1932
3	19.987	BB	0.7357	9424.14648	197.86966	30.4149
4	24.715	BB	0.8272	6028.41504	112.14260	19.4557

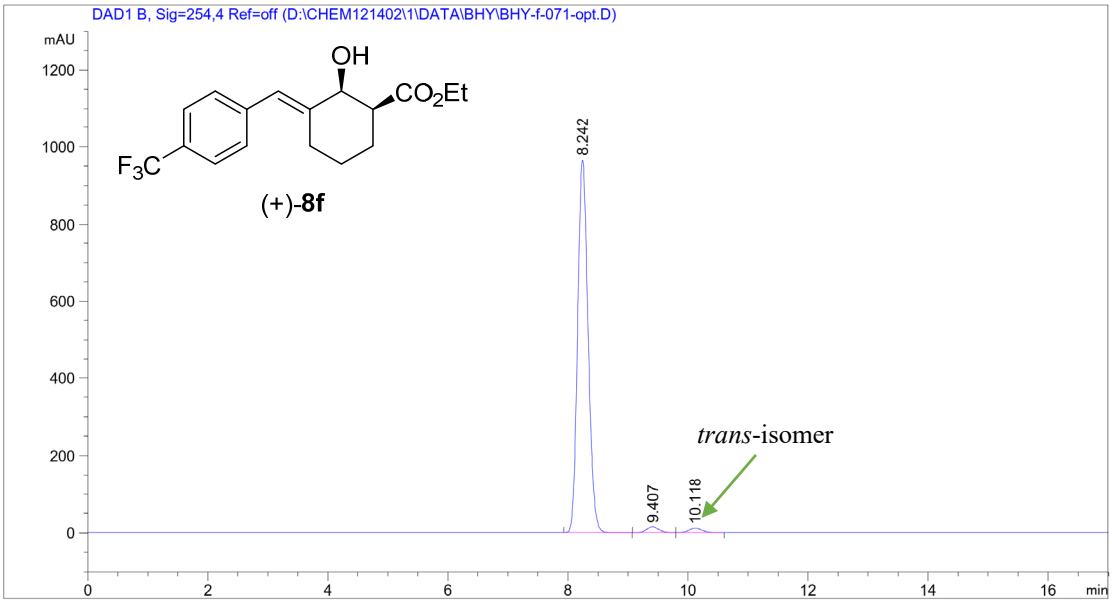


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.685	BB	0.4022	288.36212	11.13337	0.7031
2	19.570	BB	0.7835	4.04044e4	799.64417	98.5193
3	24.579	BB	0.6473	318.90155	6.18765	0.7776

For compound (+)-8f

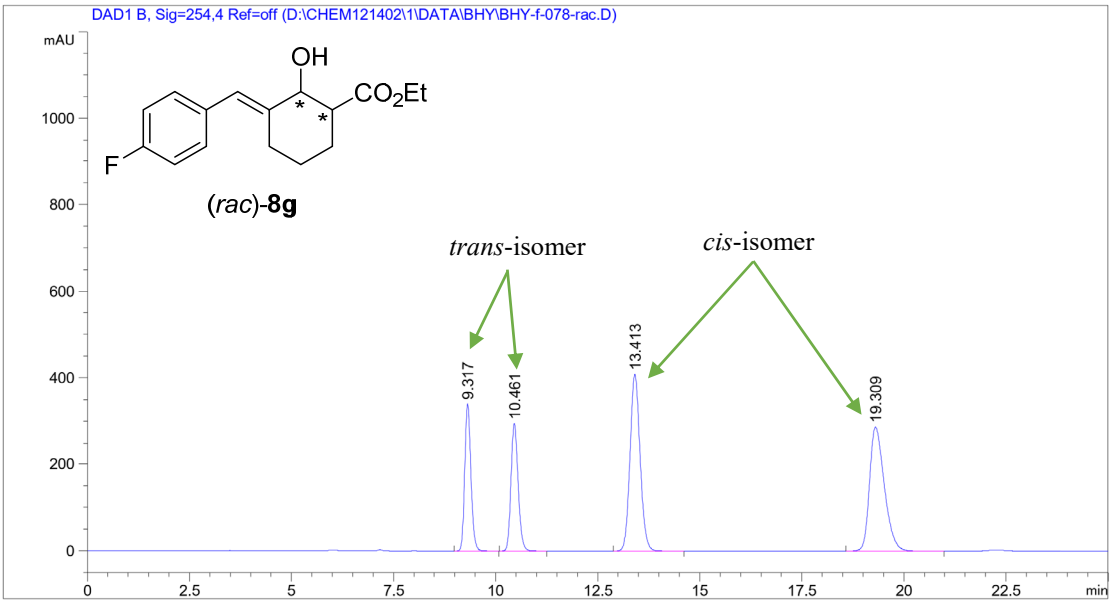


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.730	BV	0.1907	9045.74219	709.54840	30.4712
2	8.330	VB	0.1890	6662.22559	543.67438	22.4421
3	9.488	BV	0.2162	6479.25049	466.15579	21.8258
4	10.208	VB	0.2349	7499.01025	494.68222	25.2609

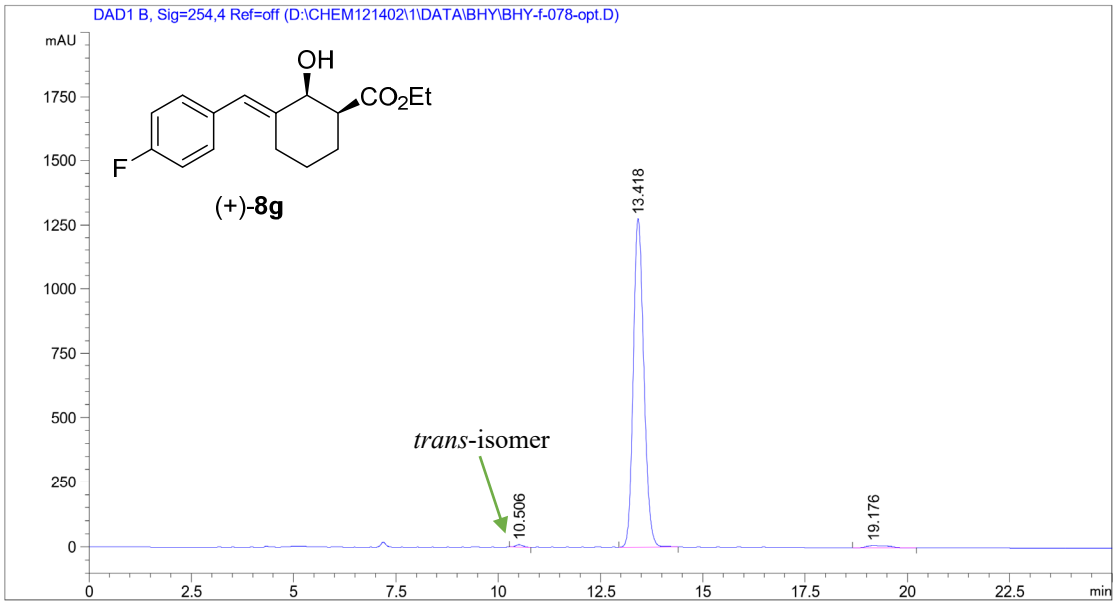


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.242	BB	0.1884	1.16094e4	965.01428	96.9354
2	9.407	BB	0.2158	201.14343	14.50659	1.6795
3	10.118	BB	0.2335	165.88058	11.02433	1.3851

For compound (+)-8g

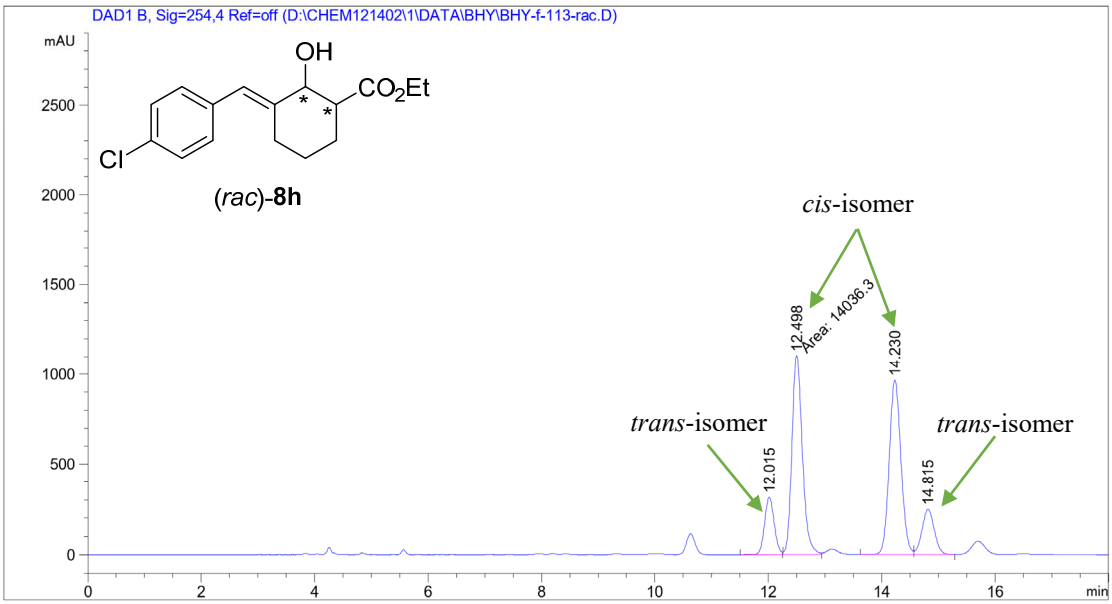


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.317	BB	0.1603	3572.77173	340.73895	16.7189
2	10.461	BB	0.1872	3576.22314	295.56680	16.7351
3	13.413	BB	0.2646	7020.05615	408.29947	32.8506
4	19.309	BB	0.3821	7200.59277	287.63055	33.6954

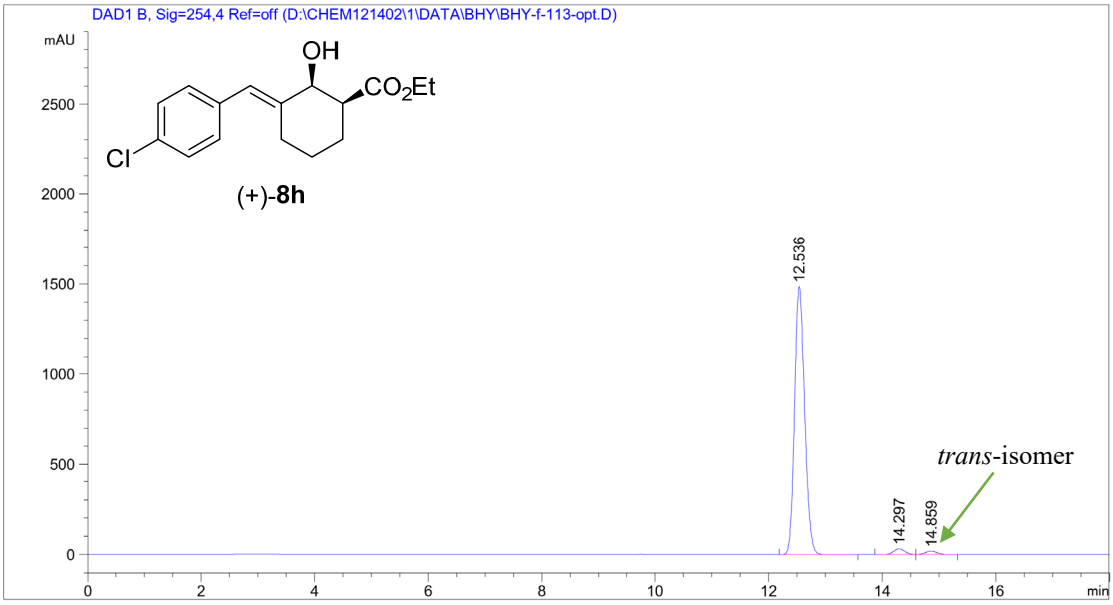


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.506	BB	0.1854	107.83539	9.15523	0.4634
2	13.418	BB	0.2770	2.28299e4	1274.63232	98.1007
3	19.176	BB	0.5116	334.17072	8.86820	1.4359

For compound (+)-8h

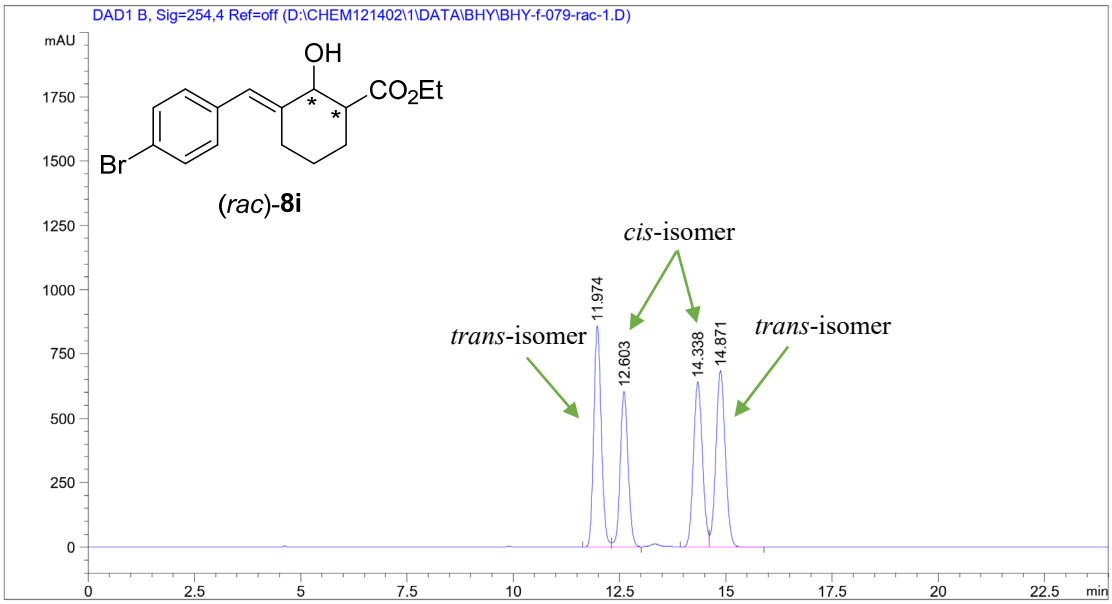


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.015	BV	0.1834	3688.07544	313.19598	10.4602
2	12.498	MM	0.2117	1.40363e4	1105.28345	39.8102
3	14.230	BV	0.2210	1.38321e4	966.17822	39.2308
4	14.815	VB	0.2332	3701.70483	246.55862	10.4988

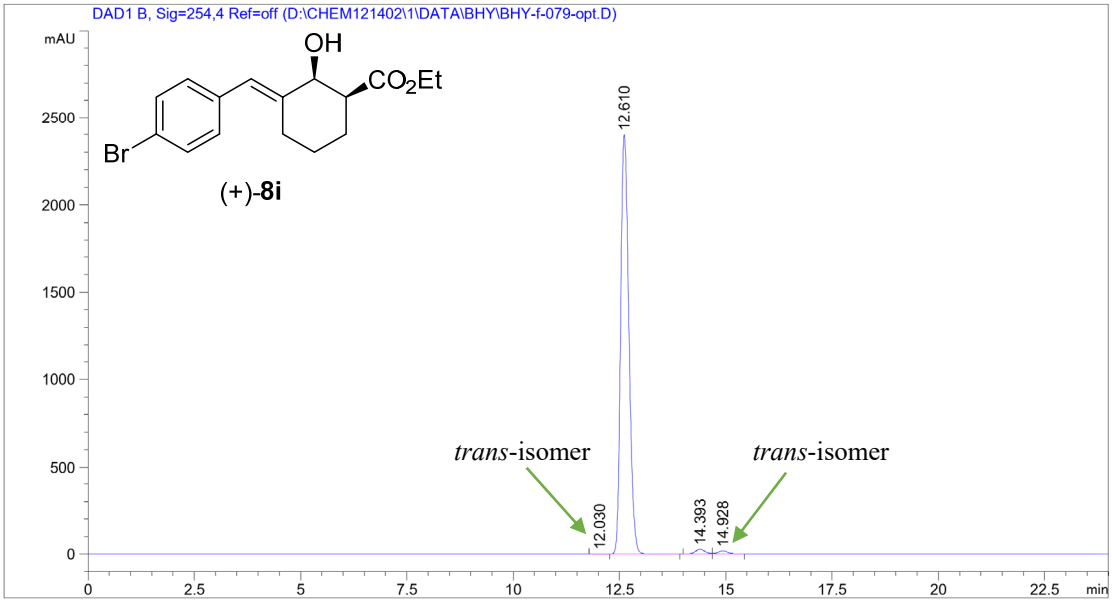


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.536	BB	0.1899	1.83237e4	1485.32373	96.1405
2	14.297	BV	0.2194	451.06305	32.21370	2.3666
3	14.859	VB	0.2297	284.53763	19.33331	1.4929

For compound (+)-8i

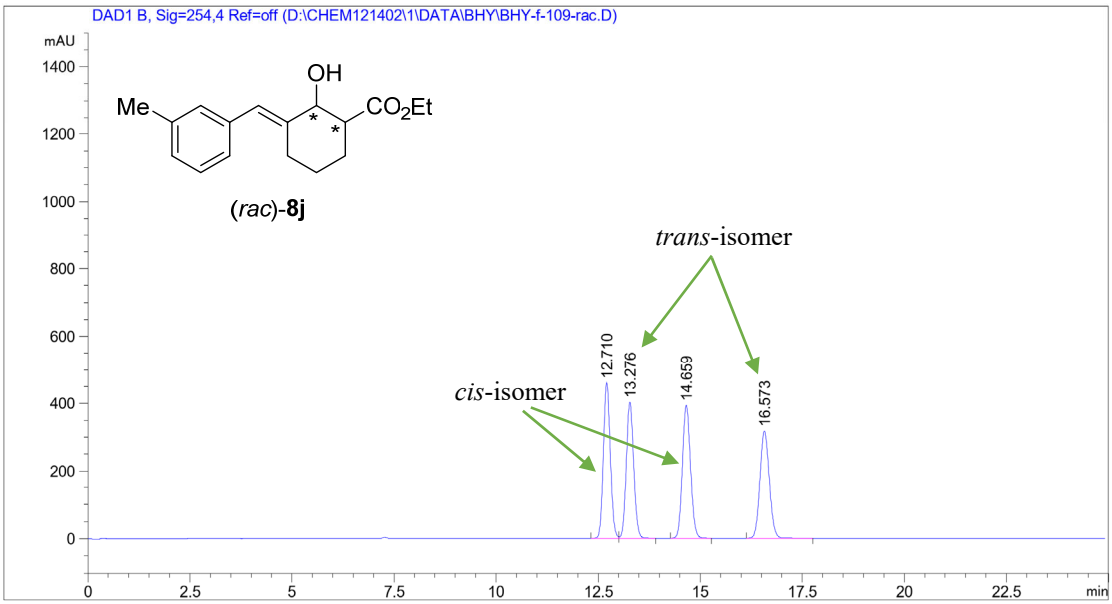


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.974	BV	0.1917	1.05453e4	856.17389	27.4915
2	12.603	VB	0.2007	7782.90430	602.69299	20.2900
3	14.338	BV	0.2310	9486.67090	639.92639	24.7317
4	14.871	VB	0.2378	1.05435e4	684.10663	27.4868

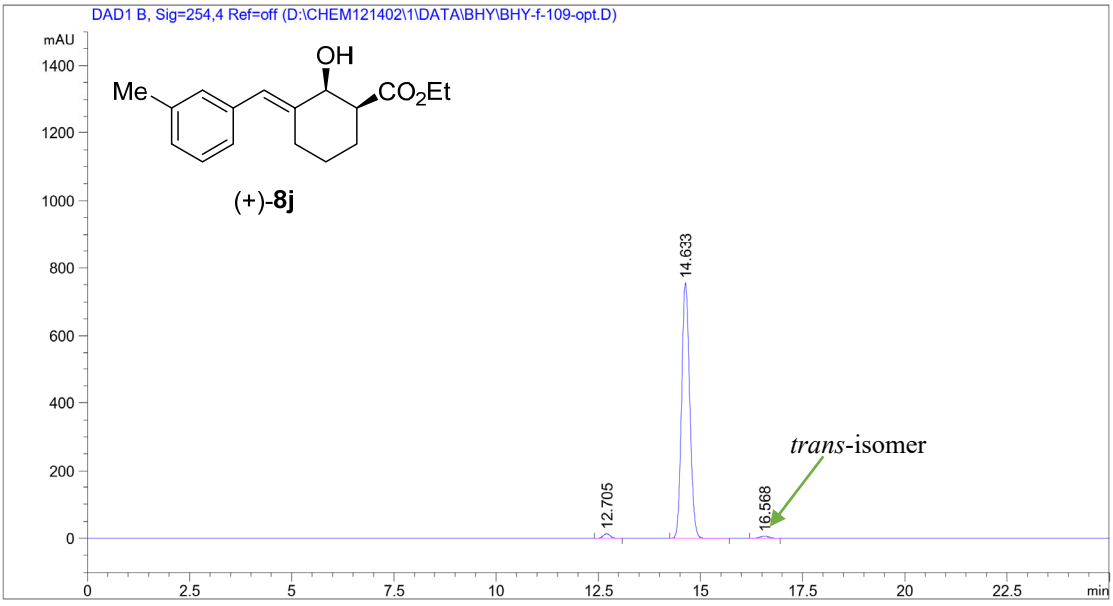


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.030	BV E	0.1905	13.64008	1.10135	0.0416
2	12.610	VB R	0.2083	3.21375e4	2399.37402	97.9147
3	14.393	BV	0.2399	408.38046	26.48299	1.2442
4	14.928	VB	0.2361	262.42056	17.19471	0.7995

For compound (+)-8j

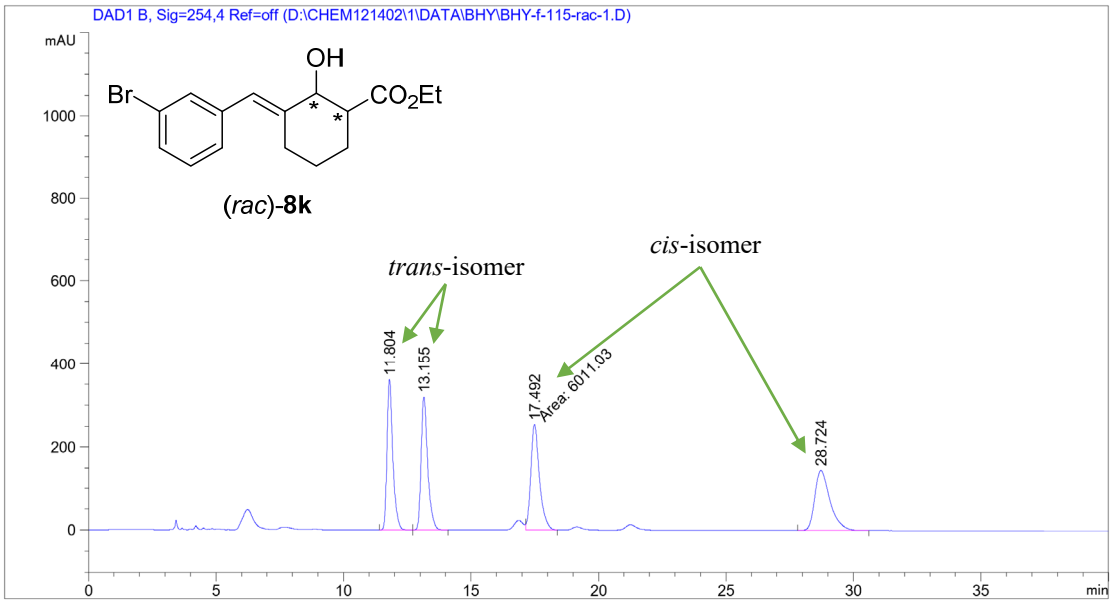


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.710	BV	0.1832	5398.17773	459.17838	25.8865
2	13.276	VB	0.1935	5018.88965	402.34531	24.0677
3	14.659	BB	0.2147	5410.83447	392.74646	25.9472
4	16.573	BB	0.2470	5025.34814	316.88458	24.0986

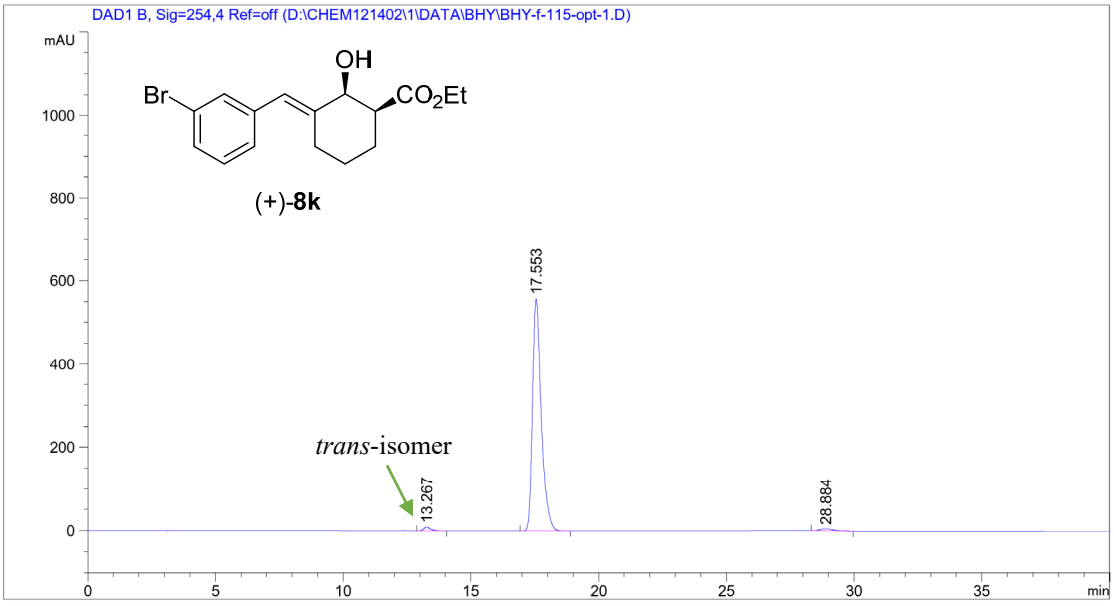


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.705	BB	0.1831	159.57303	13.57885	1.4938
2	14.633	BB	0.2148	1.04252e4	756.59967	97.5956
3	16.568	BB	0.2408	97.26112	6.20643	0.9105

For compound (+)-8k

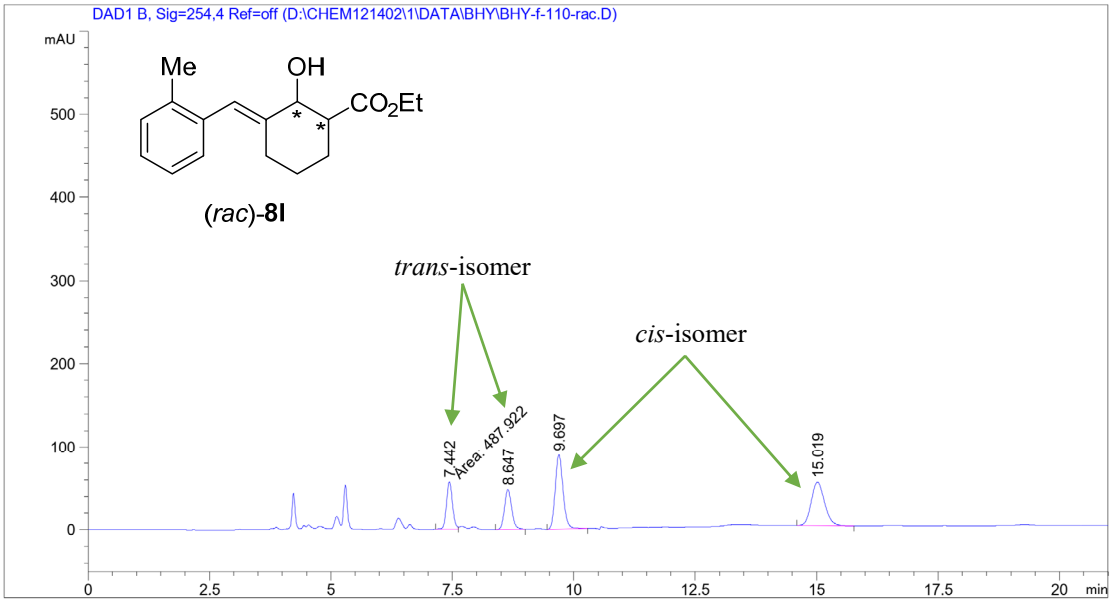


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.804	BB	0.2388	5726.71338	361.48666	24.4279
2	13.155	BB	0.2691	5727.30957	319.51968	24.4304
3	17.492	MM	0.3941	6011.02539	254.20740	25.6407
4	28.724	BB	0.6143	5978.27686	145.80811	25.5010

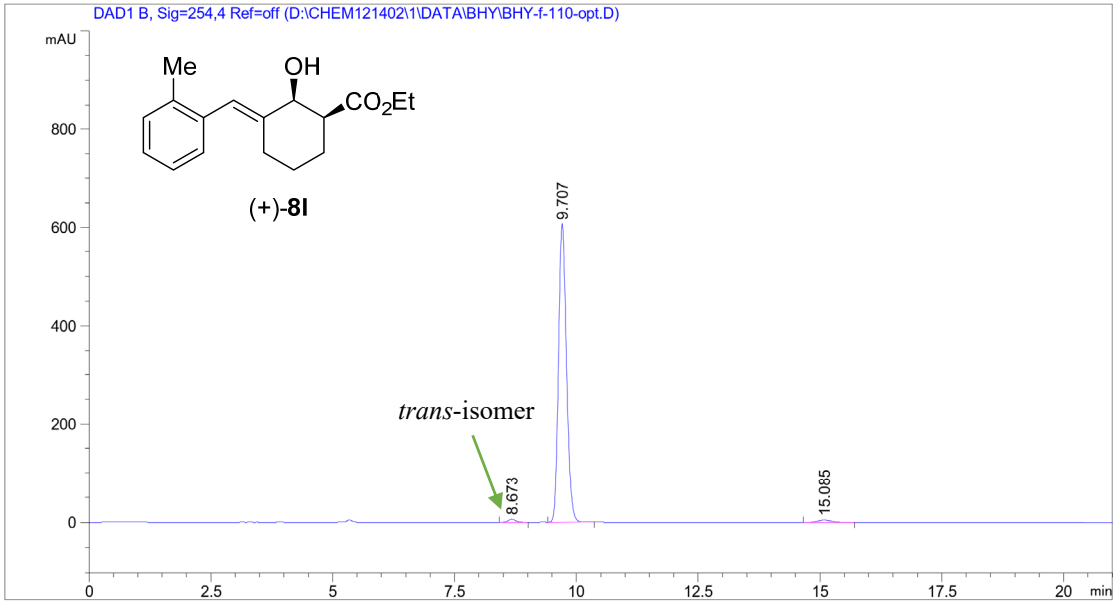


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.267	BB	0.2658	152.94151	8.58510	1.1309
2	17.553	BB	0.3568	1.32042e4	556.58740	97.6360
3	28.884	BB	0.5172	166.76025	4.73132	1.2331

For compound (+)-8l

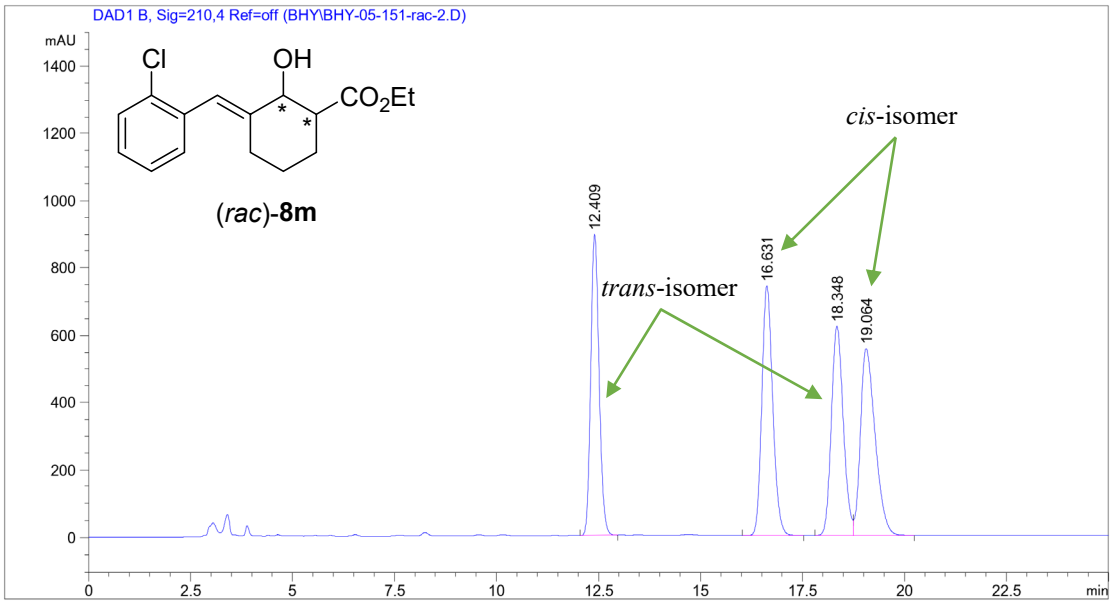


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.442	MM	0.1424	487.92184	57.11426	16.3910
2	8.647	BB	0.1605	493.65759	47.79517	16.5837
3	9.697	BB	0.1728	1004.61847	89.58767	33.7486
4	15.019	BB	0.2930	990.57043	52.30403	33.2767

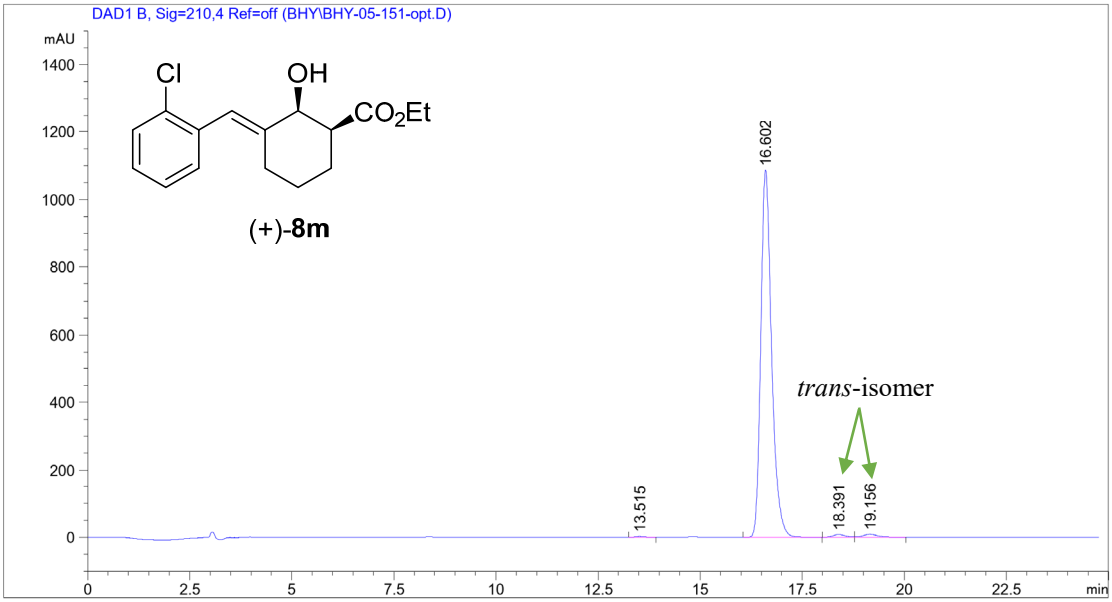


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.673	BB	0.1582	60.86807	5.90888	0.8642
2	9.707	BB	0.1764	6895.58838	607.72424	97.9079
3	15.085	BB	0.2890	86.47909	4.52362	1.2279

For compound (+)-8m

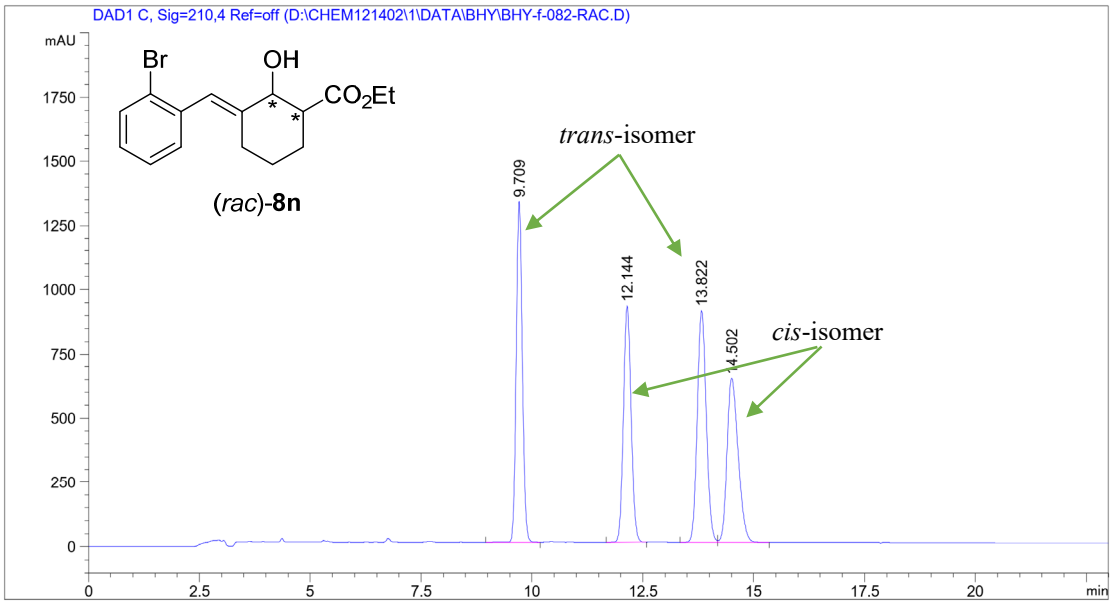


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.409	BB	0.2190	1.26501e4	894.38086	23.9745
2	16.631	BB	0.2860	1.37010e4	739.94861	25.9662
3	18.348	BV	0.3146	1.25912e4	620.80792	23.8630
4	19.064	VB	0.3825	1.38224e4	555.18066	26.1963

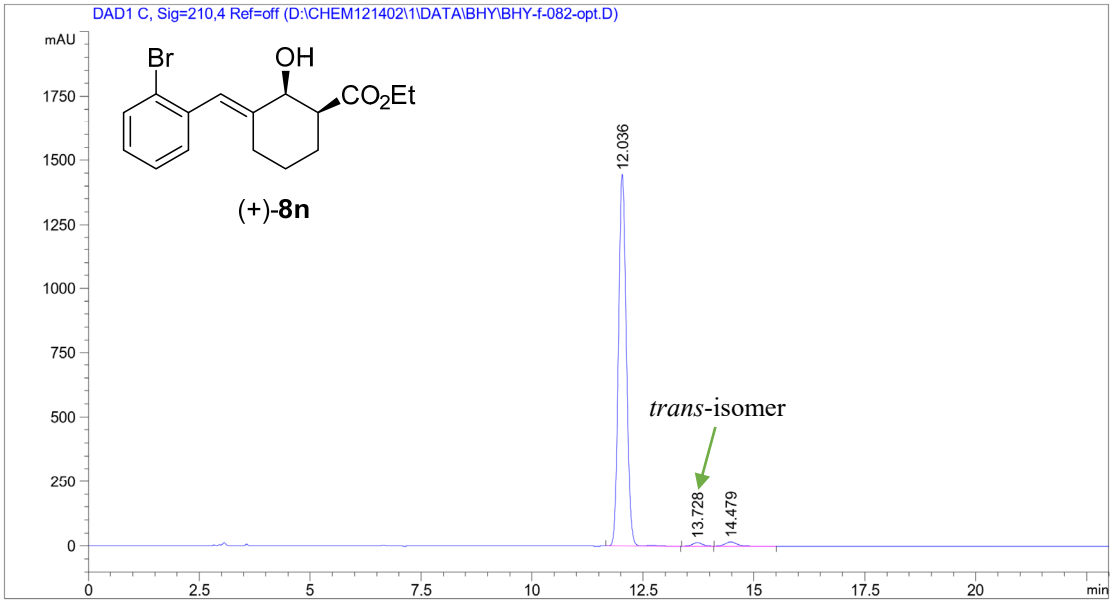


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.515	BB	0.2239	32.37782	2.22374	0.1587
2	16.602	BB	0.2806	1.99930e4	1086.69910	97.9716
3	18.391	BV	0.3048	163.15028	8.24692	0.7995
4	19.156	VB	0.3640	218.41270	9.10069	1.0703

For compound (+)-8n

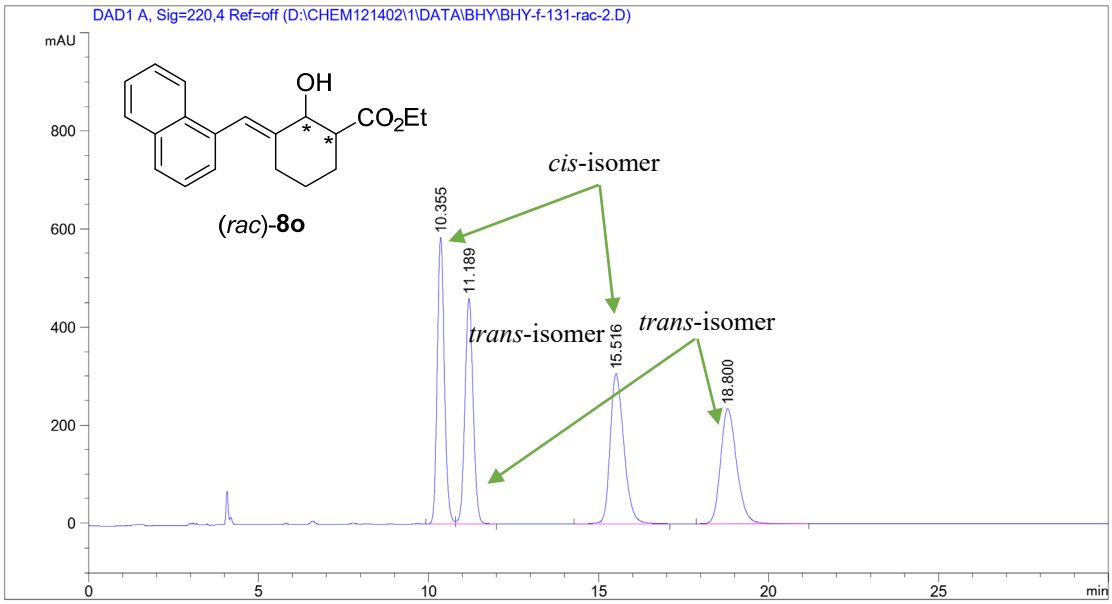


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.709	VB R	0.1473	1.26663e4	1325.70032	26.6463
2	12.144	BB	0.1867	1.10815e4	918.63031	23.3122
3	13.822	BV	0.2184	1.27054e4	901.74182	26.7285
4	14.502	VB	0.2688	1.10819e4	637.58325	23.3130

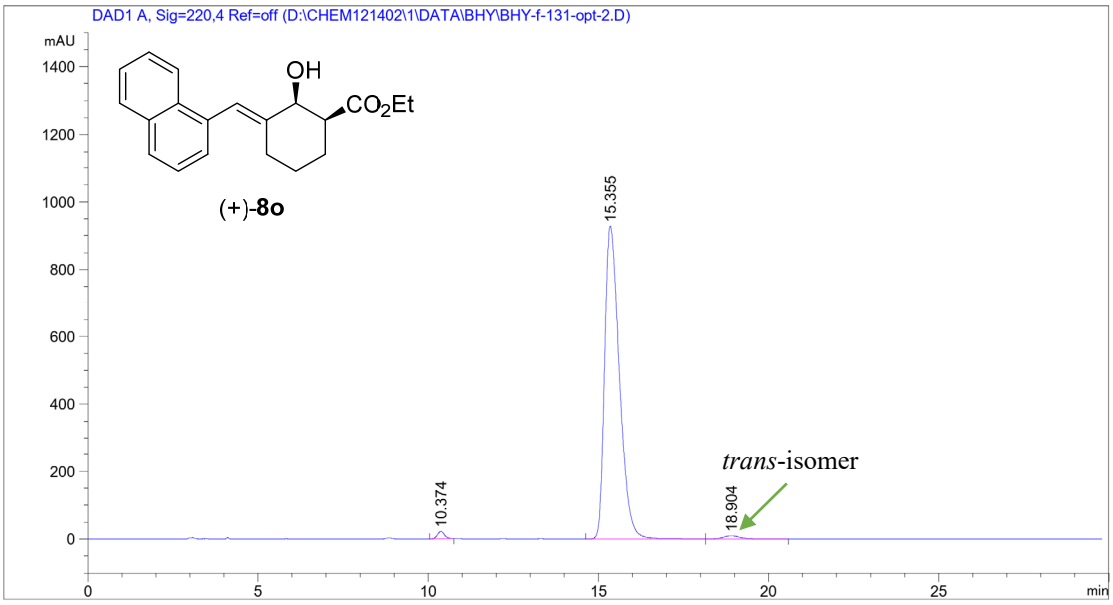


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.036	BV R	0.1905	1.77038e4	1445.24292	97.4166
2	13.728	BB	0.2190	191.32814	13.52810	1.0528
3	14.479	BB	0.2675	278.16992	16.10215	1.5306

For compound (+)-8o

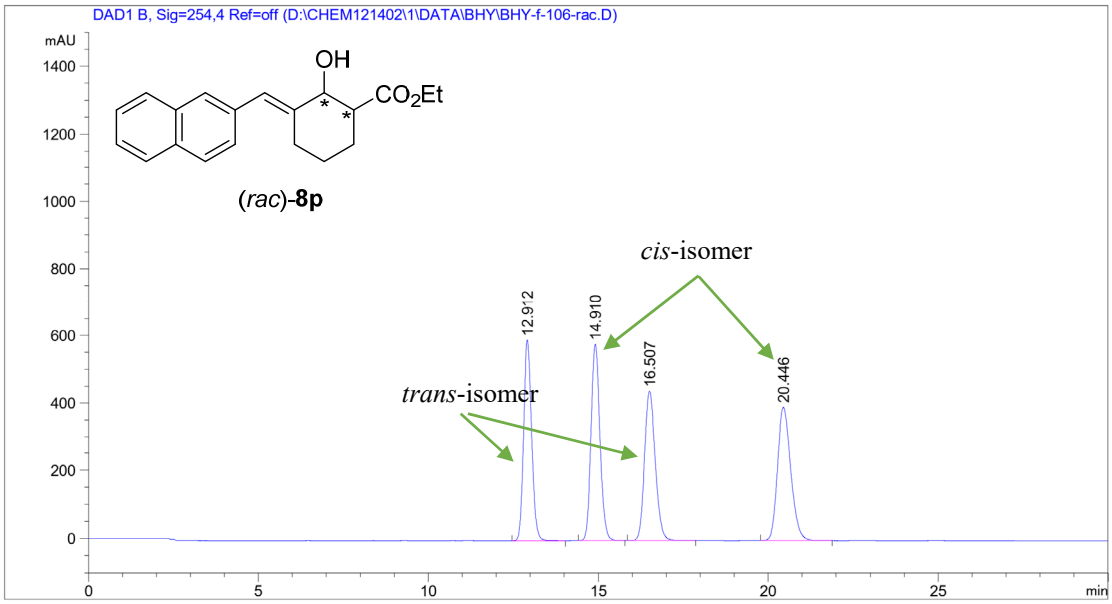


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.355	BV	0.2259	8525.68066	585.59021	26.1876
2	11.189	VB	0.2621	7733.97461	460.17957	23.7557
3	15.516	BB	0.4313	8590.19629	306.21603	26.3857
4	18.800	BB	0.5055	7706.37646	234.45883	23.6710

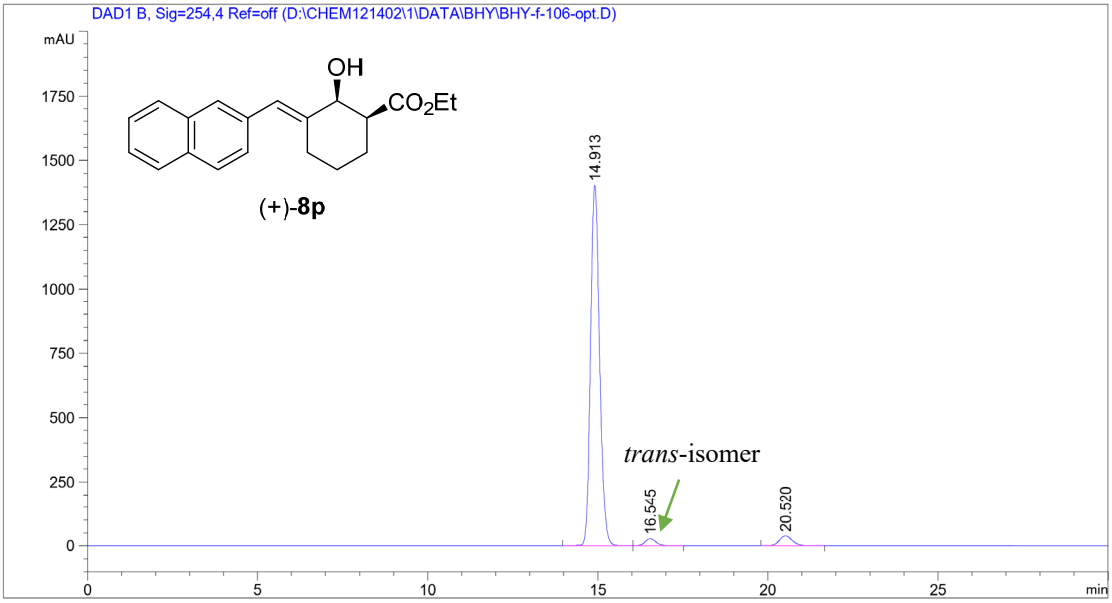


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.374	BB	0.2226	310.85187	21.50903	1.0858
2	15.355	BB	0.4660	2.80056e4	928.28369	97.8252
3	18.904	BB	0.4894	311.75031	9.43752	1.0890

For compound (+)-8p

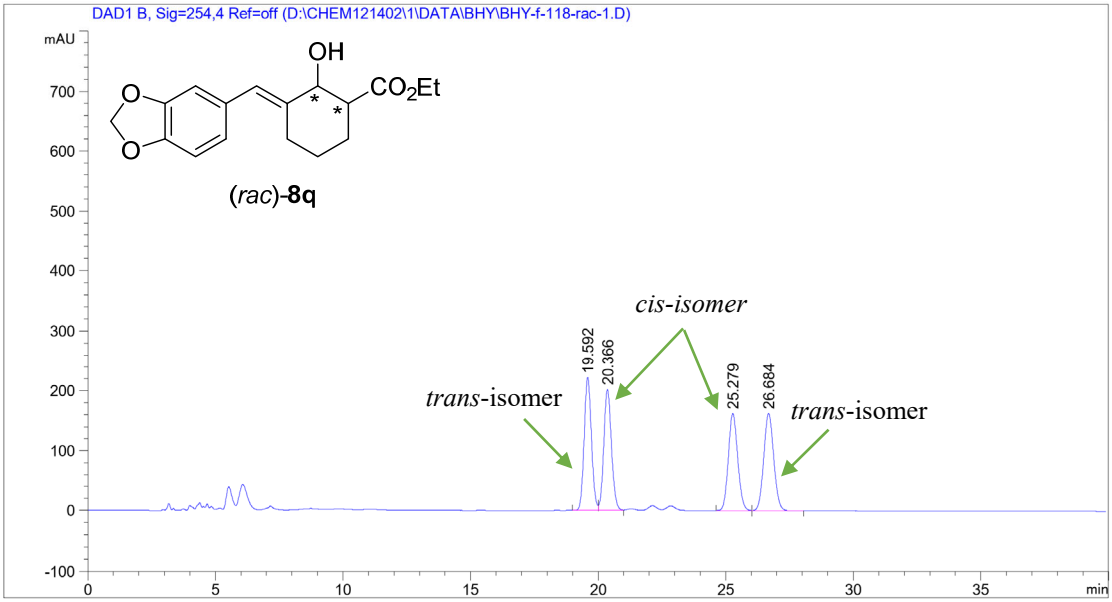


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.912	BB	0.2518	9641.79883	592.64398	23.8733
2	14.910	BB	0.2820	1.05348e4	579.79071	26.0845
3	16.507	BB	0.3385	9632.91406	441.62509	23.8513
4	20.446	BB	0.4155	1.05778e4	393.67126	26.1909

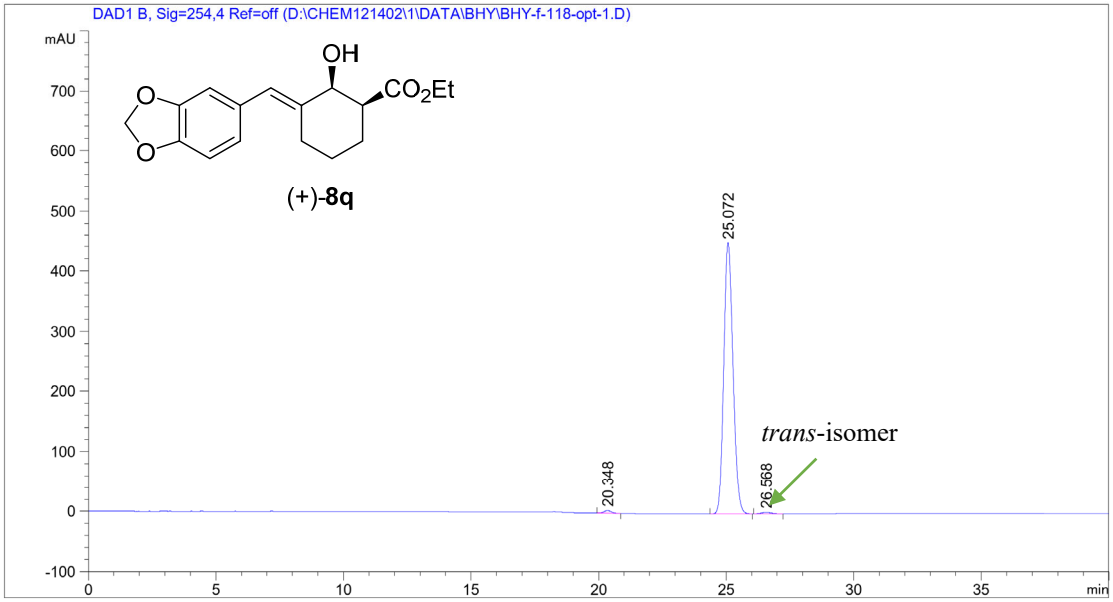


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.913	BB	0.2851	2.58824e4	1404.03076	94.0779
2	16.545	BB	0.3373	607.11633	27.74102	2.2068
3	20.520	BB	0.4099	1022.16034	38.23585	3.7154

For compound (+)-8q

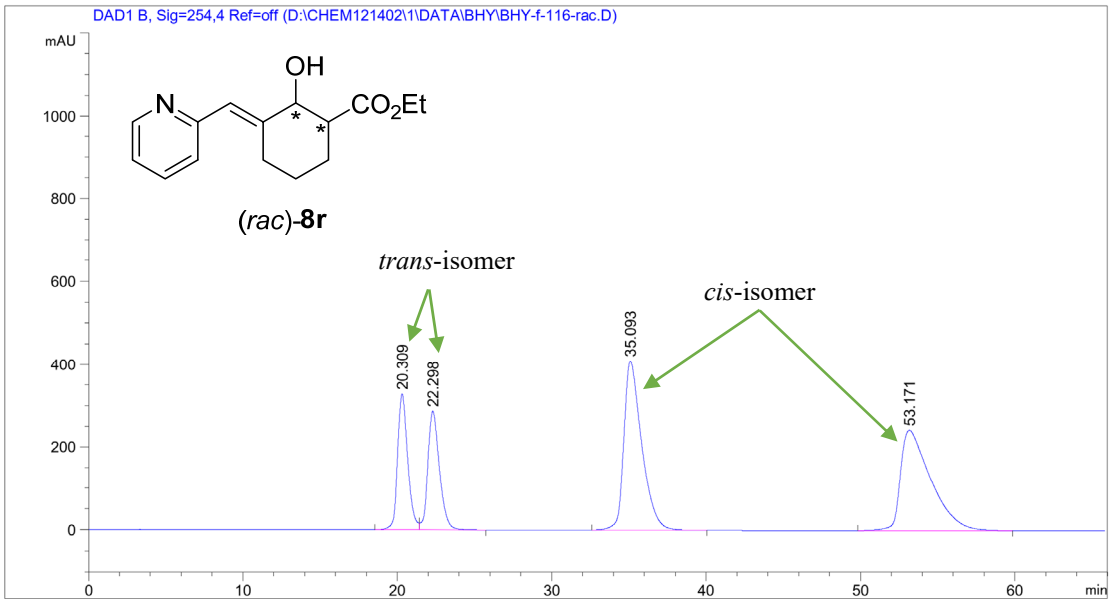


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.592	BV	0.3071	4396.28955	221.96567	25.6851
2	20.366	VB	0.3227	4194.76758	201.68262	24.5077
3	25.279	BB	0.3950	4125.54492	162.06537	24.1033
4	26.684	BB	0.4221	4399.49316	162.37959	25.7038

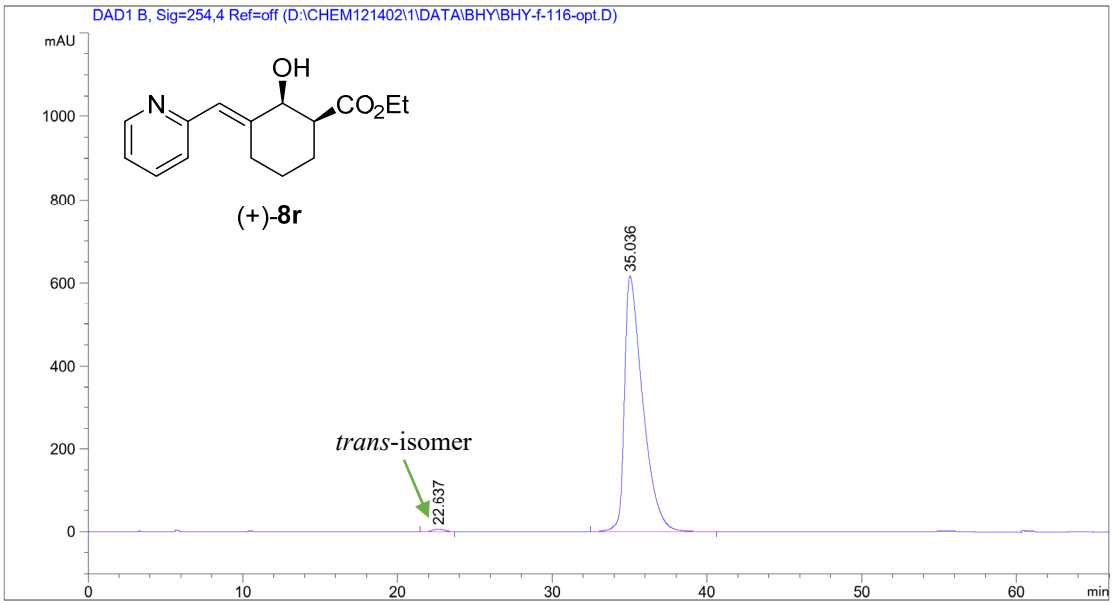


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.348	BB	0.3067	90.57007	4.54173	0.7890
2	25.072	BB	0.3892	1.13300e4	450.79468	98.6999
3	26.568	BB	0.3418	58.67062	2.26811	0.5111

For compound (+)-8r

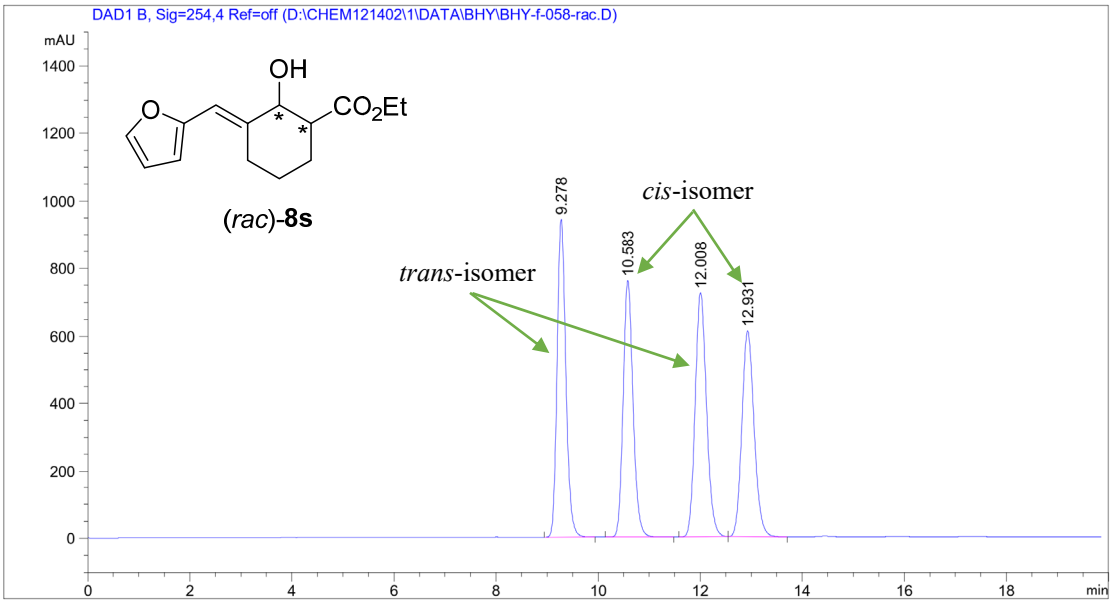


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.309	BV	0.7102	1.50225e4	328.10217	15.6916
2	22.298	VB	0.8092	1.50226e4	286.75363	15.6916
3	35.093	BB	1.1768	3.28318e4	408.88602	34.2940
4	53.171	BB	1.9114	3.28593e4	242.10742	34.3228

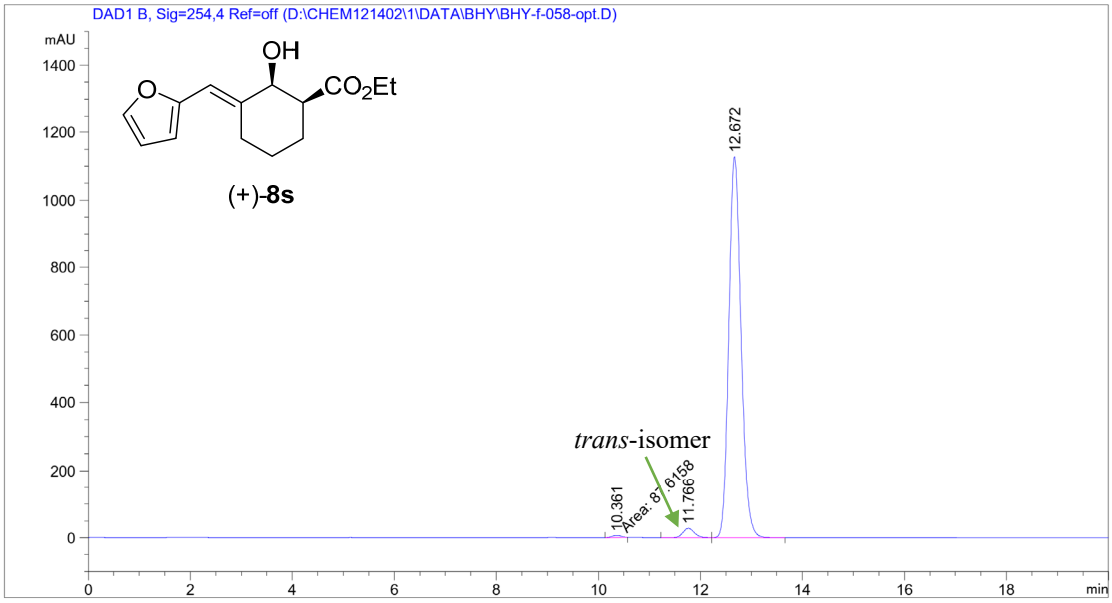


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.637	BB	0.6977	311.14331	5.99270	0.6105
2	35.036	BB	1.1806	5.06571e4	616.50824	99.3895

For compound (+)-8s

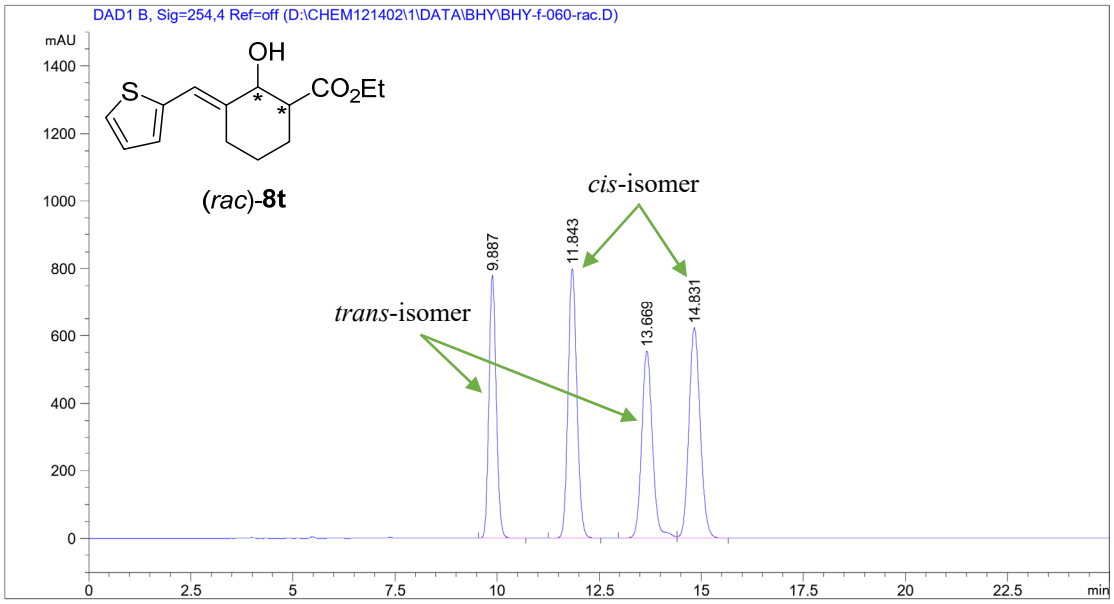


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.278	BB	0.1826	1.12172e4	943.92767	26.1687
2	10.583	BB	0.2070	1.02332e4	760.22748	23.8732
3	12.008	BB	0.2385	1.12152e4	724.78534	26.1640
4	12.931	BB	0.2583	1.01993e4	612.26910	23.7940

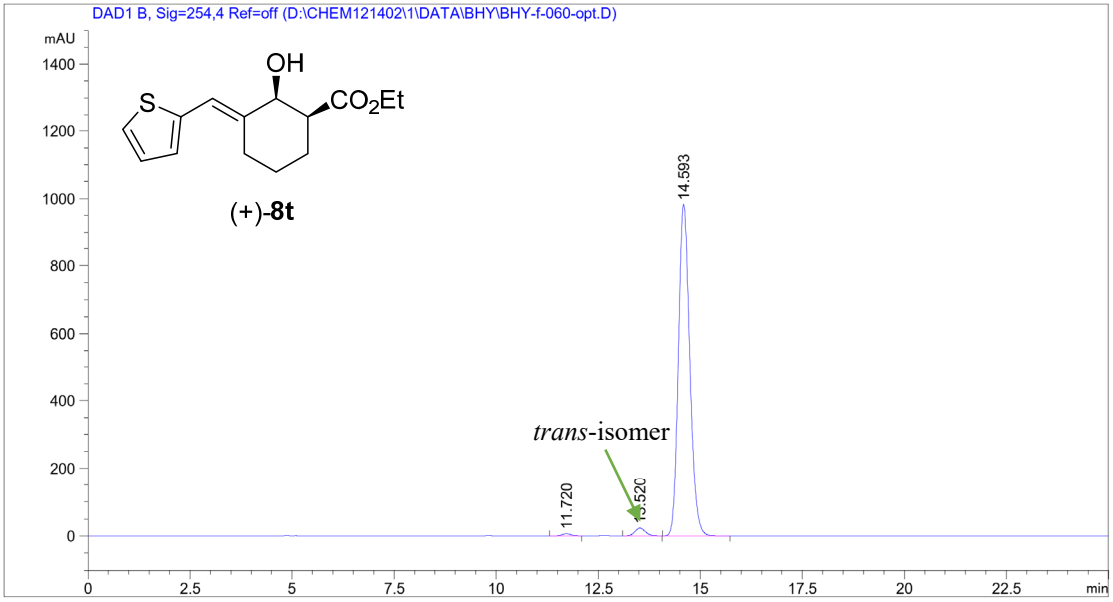


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.361	MM	0.2082	87.61578	7.01376	0.4525
2	11.766	BV	0.2354	432.91913	28.15737	2.2360
3	12.672	VB	0.2589	1.88408e4	1128.00464	97.3115

For compound (+)-8t

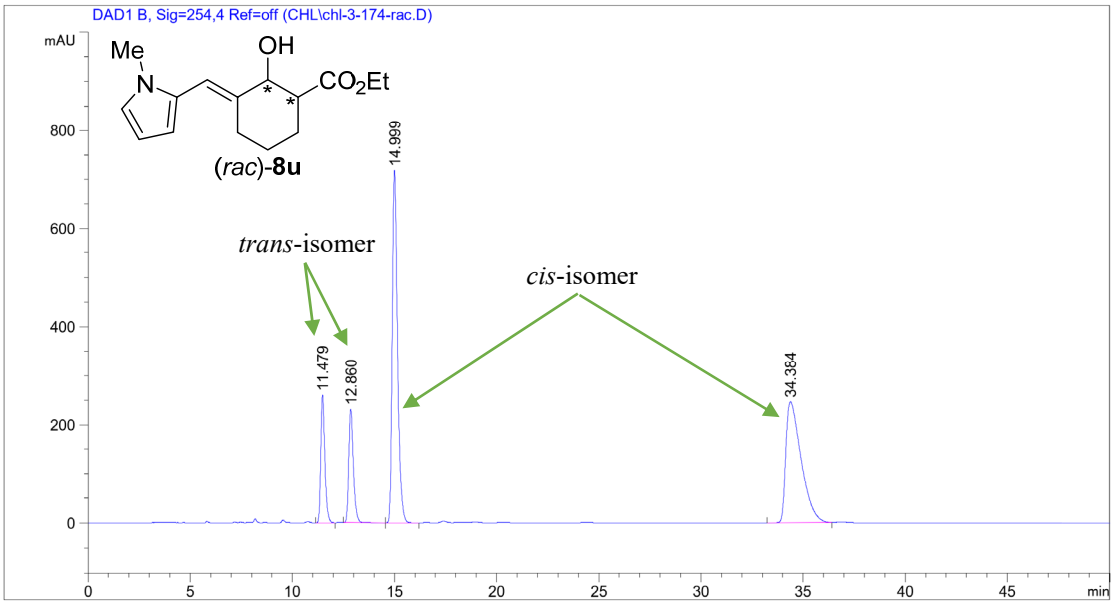


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.887	BB	0.1899	9624.28223	780.09210	22.0337
2	11.843	BB	0.2324	1.19476e4	799.01990	27.3528
3	13.669	BV	0.2820	1.01519e4	553.51996	23.2418
4	14.831	VB	0.2981	1.19559e4	622.35278	27.3717

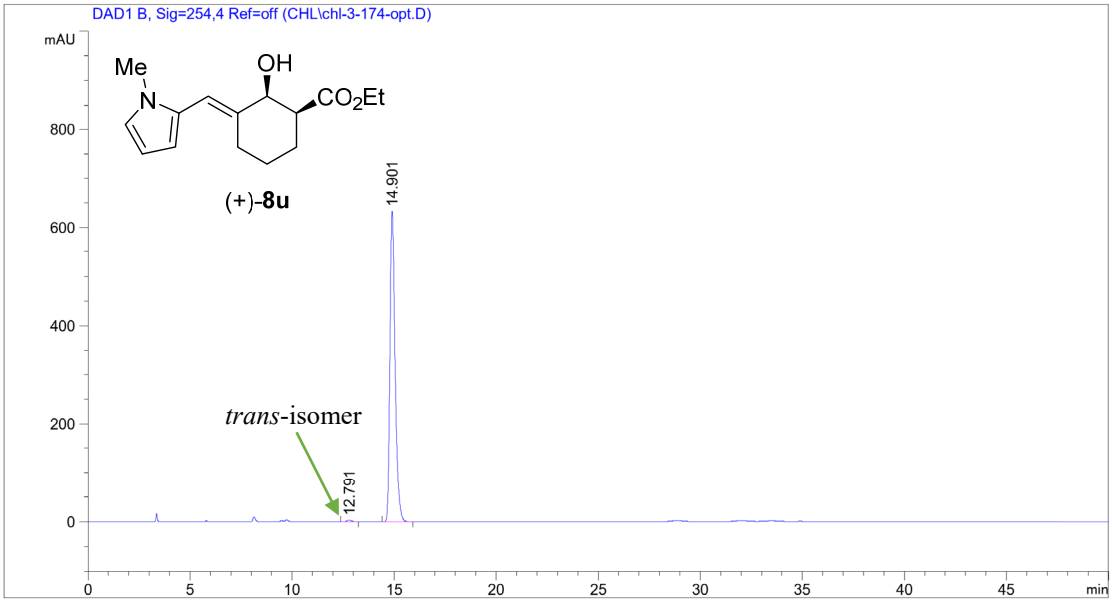


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.720	BB	0.2290	91.18582	6.22191	0.4685
2	13.520	BB	0.2714	398.03027	22.60775	2.0450
3	14.593	BB	0.2992	1.89746e4	983.05237	97.4865

For compound (+)-8u

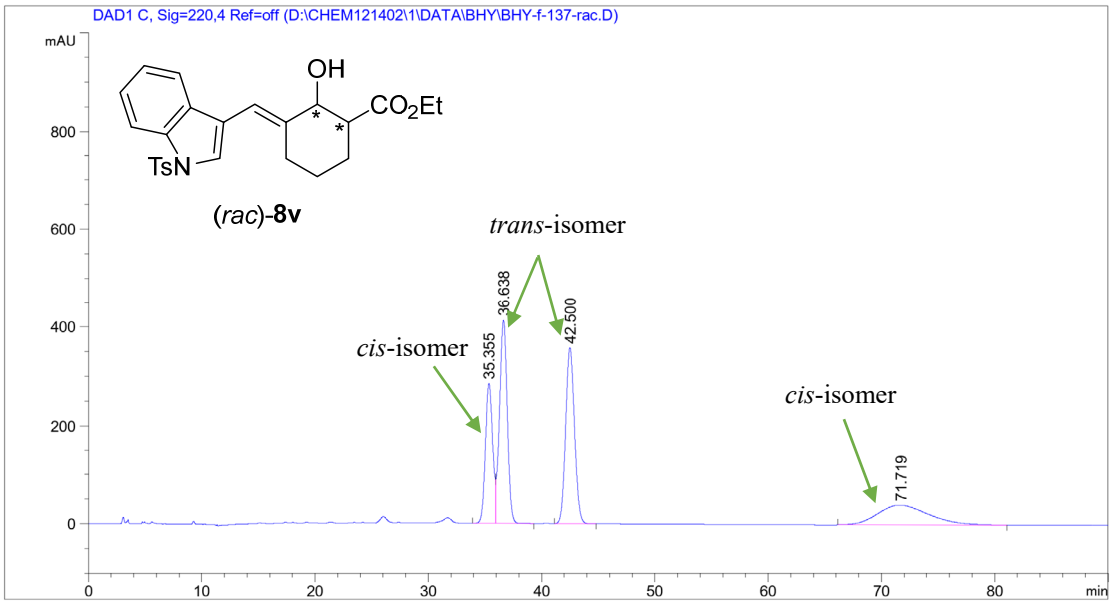


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.479	BB	0.2088	3583.17358	260.02039	10.9227
2	12.860	BB	0.2389	3624.54541	231.16721	11.0488
3	14.999	BB	0.2724	1.28323e4	718.40497	39.1168
4	34.384	BB	0.7885	1.27650e4	246.36507	38.9117

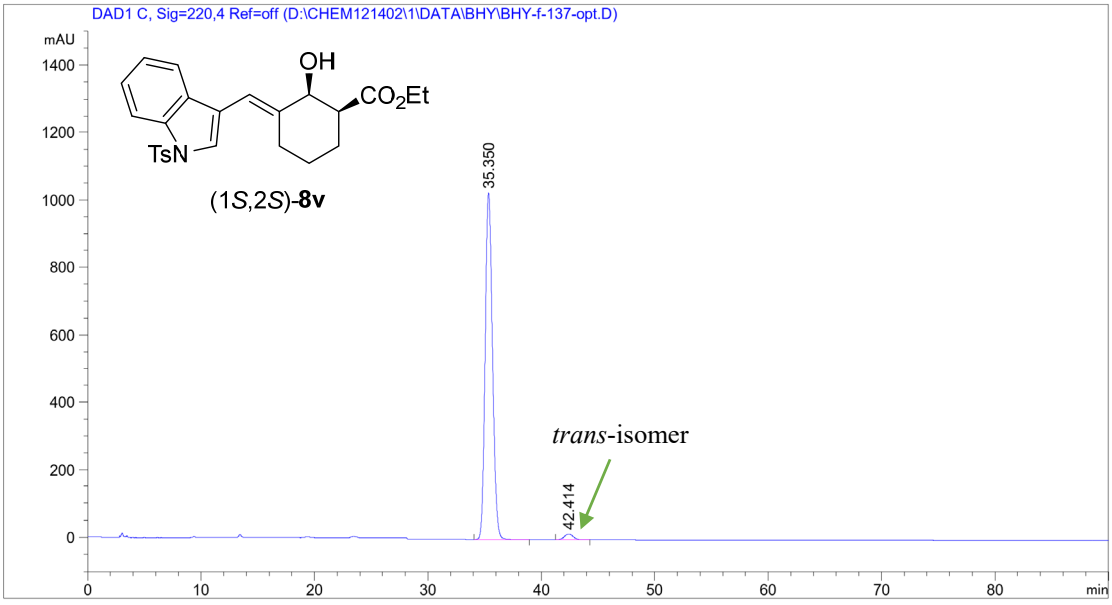


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.791	BB	0.2339	52.39444	3.43636	0.4667
2	14.901	BB	0.2697	1.11743e4	633.87640	99.5333

For compound (1*S*,2*S*)-8v

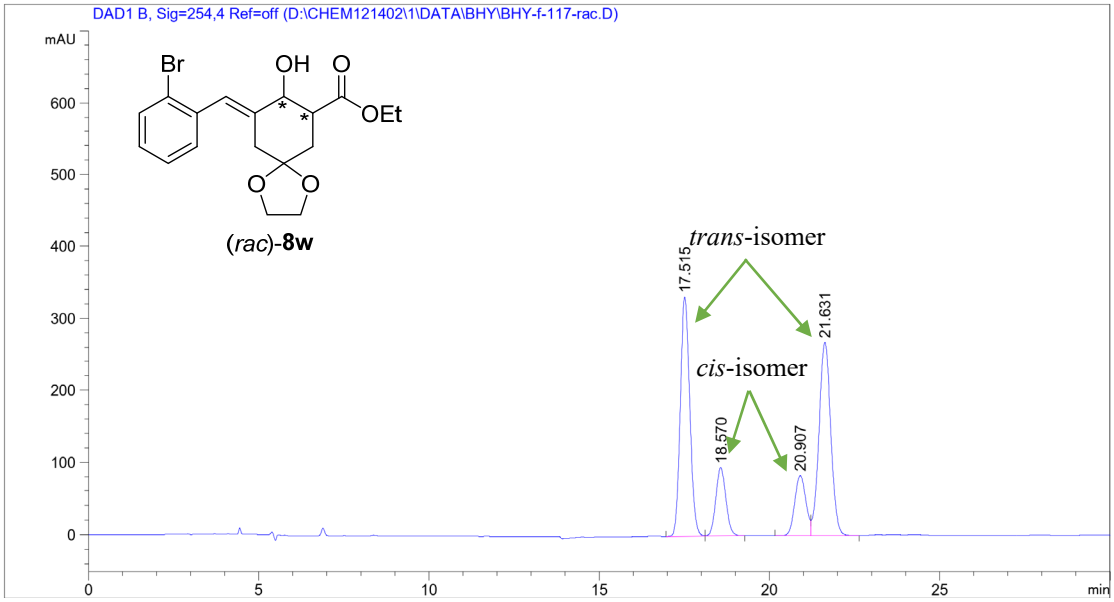


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.355	BV	0.6901	1.26992e4	284.88574	19.7315
2	36.638	VB	0.7372	1.97108e4	412.68100	30.6259
3	42.500	BB	0.8459	1.94390e4	357.74686	30.2036
4	71.719	BB	3.6723	1.25109e4	39.87623	19.4390

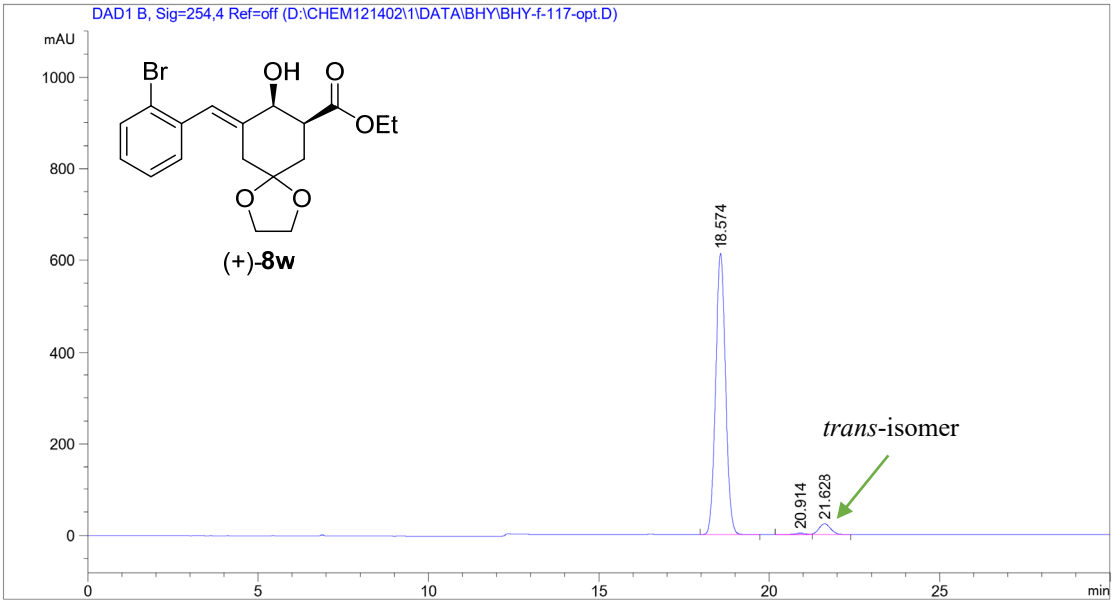


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.350	BB	0.6956	4.59508e4	1027.75195	98.0408
2	42.414	BB	0.8029	918.25830	17.25447	1.9592

For compound (+)-8w

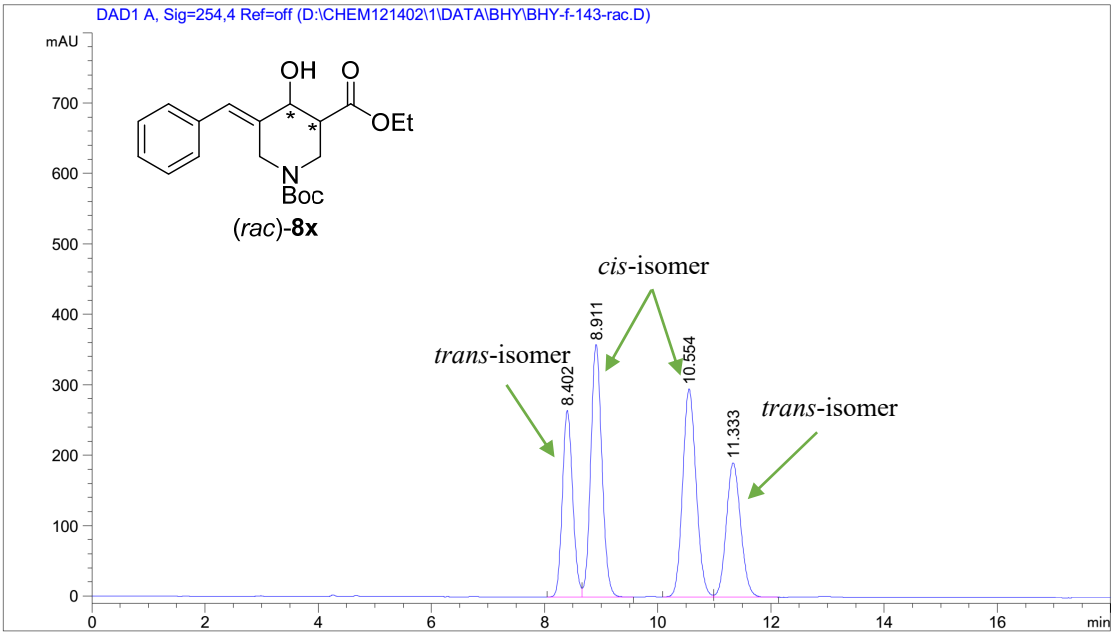


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.515	BV	0.2986	6387.08252	331.70230	38.3873
2	18.570	VB	0.3162	1936.06165	94.82726	11.6360
3	20.907	BV	0.3515	1881.11646	83.27859	11.3058
4	21.631	VB	0.3717	6434.28125	268.40546	38.6709

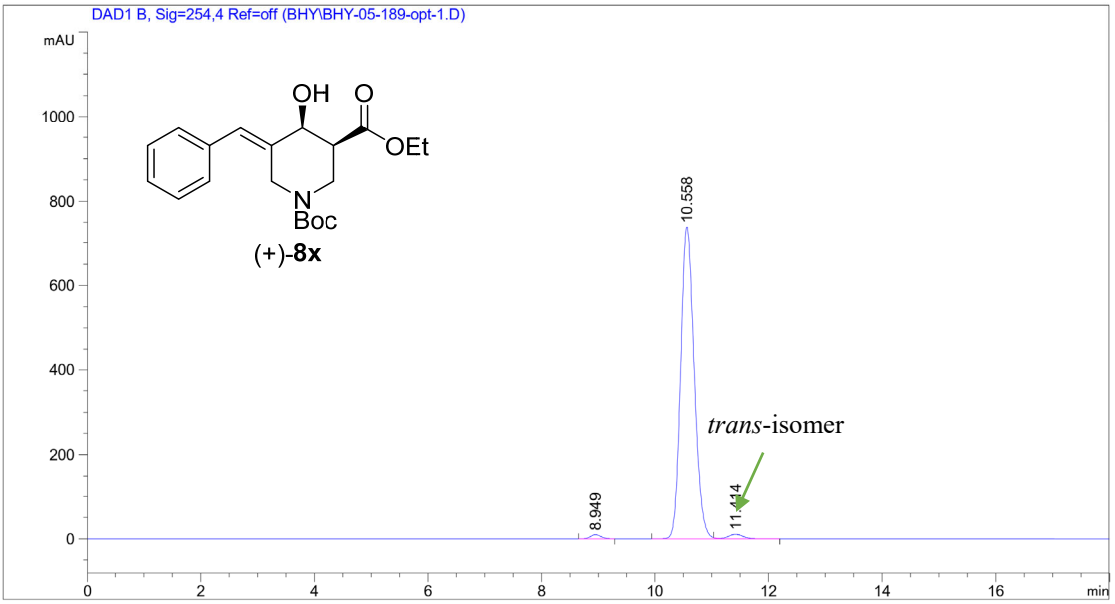


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.574	BB	0.3140	1.23799e4	612.04474	95.1616
2	20.914	BV E	0.3359	62.61126	2.85396	0.4813
3	21.628	VB R	0.3739	566.83020	23.45486	4.3571

For compound (+)-8x

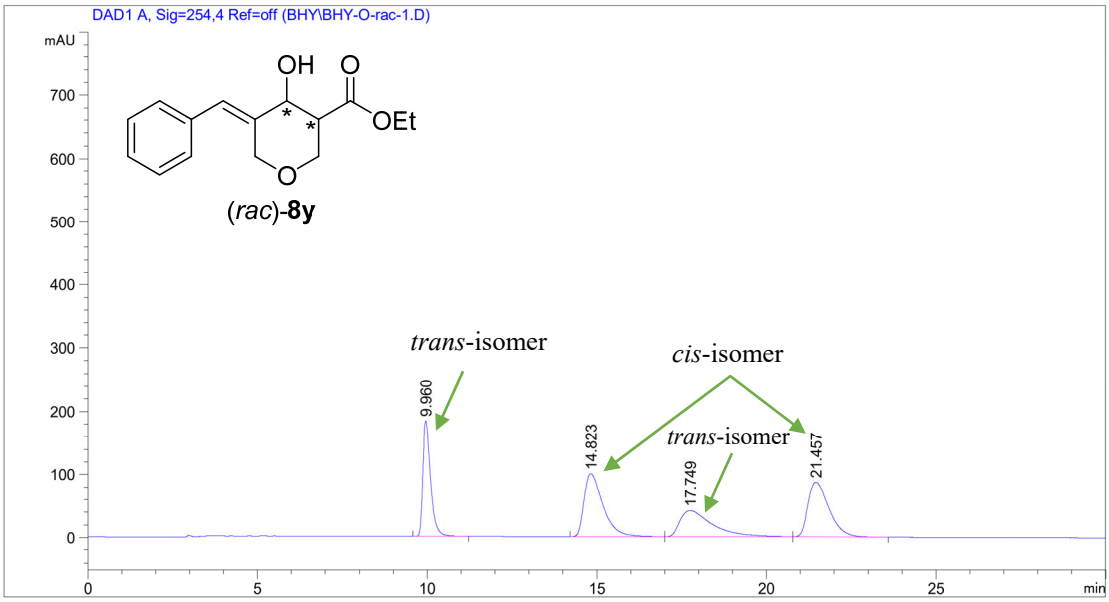


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.402	BV	0.1984	5120.24072	402.61105	20.8088
2	8.911	VB	0.2119	7139.65967	520.80475	29.0157
3	10.554	BV	0.2601	7167.03271	430.80774	29.1270
4	11.333	VB	0.2748	5179.23682	292.12299	21.0485

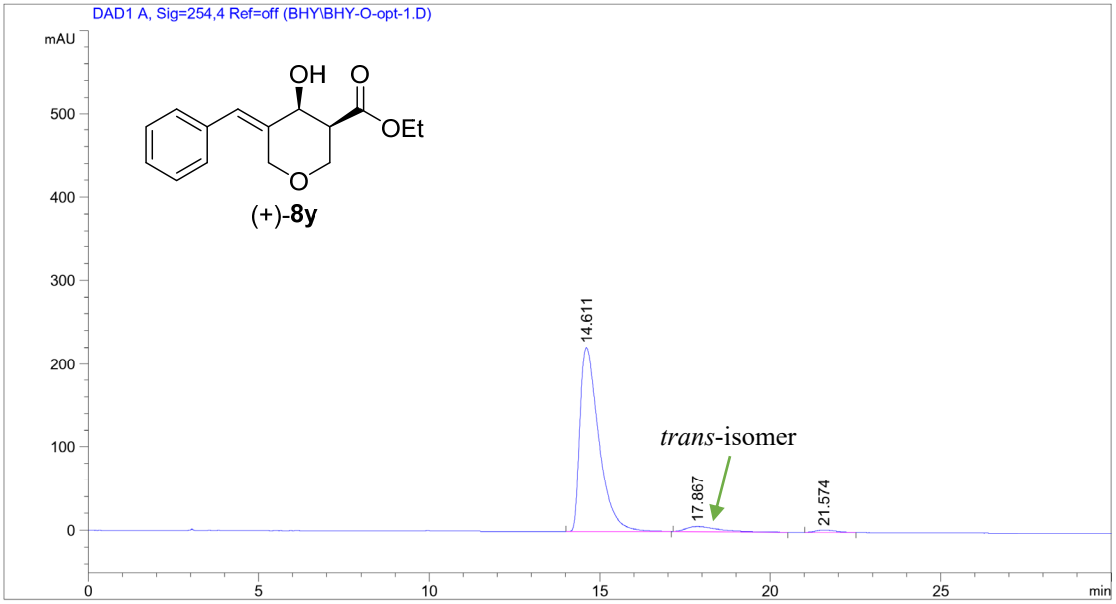


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.949	BB	0.2026	131.31857	10.04220	1.0426
2	10.558	BV R	0.2574	1.22609e4	739.54810	97.3472
3	11.414	VB E	0.2820	202.79996	11.05463	1.6102

For compound (+)-8y

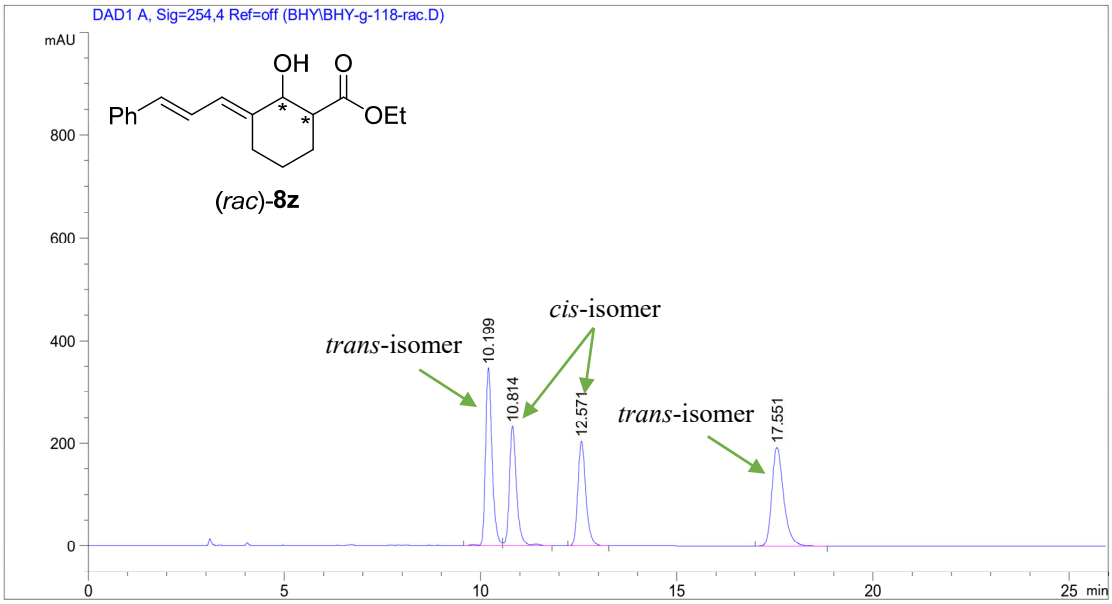


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.960	BB	0.2378	2882.91919	182.95895	21.9326
2	14.823	BB	0.5880	3847.96021	99.76550	29.2744
3	17.749	BB	0.9303	2704.42285	41.06936	20.5747
4	21.457	BB	0.6412	3709.13770	86.67689	28.2183

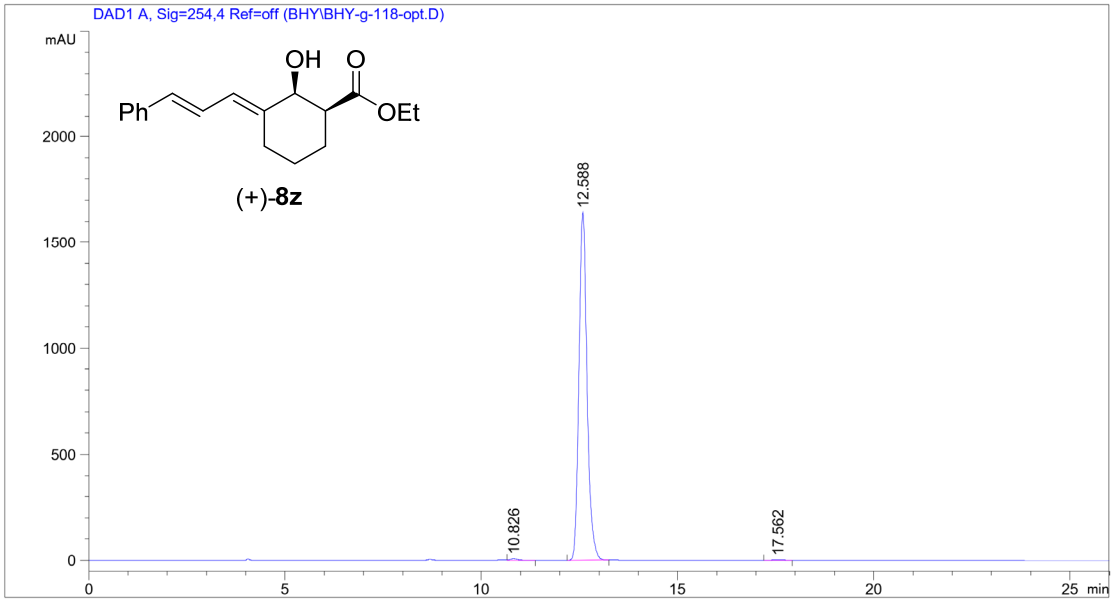


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.611	BB	0.5911	8561.44238	221.44174	94.4139
2	17.867	BB	0.7603	391.68158	6.05821	4.3194
3	21.574	BB	0.4544	114.86387	2.98873	1.2667

For compound (+)-8z

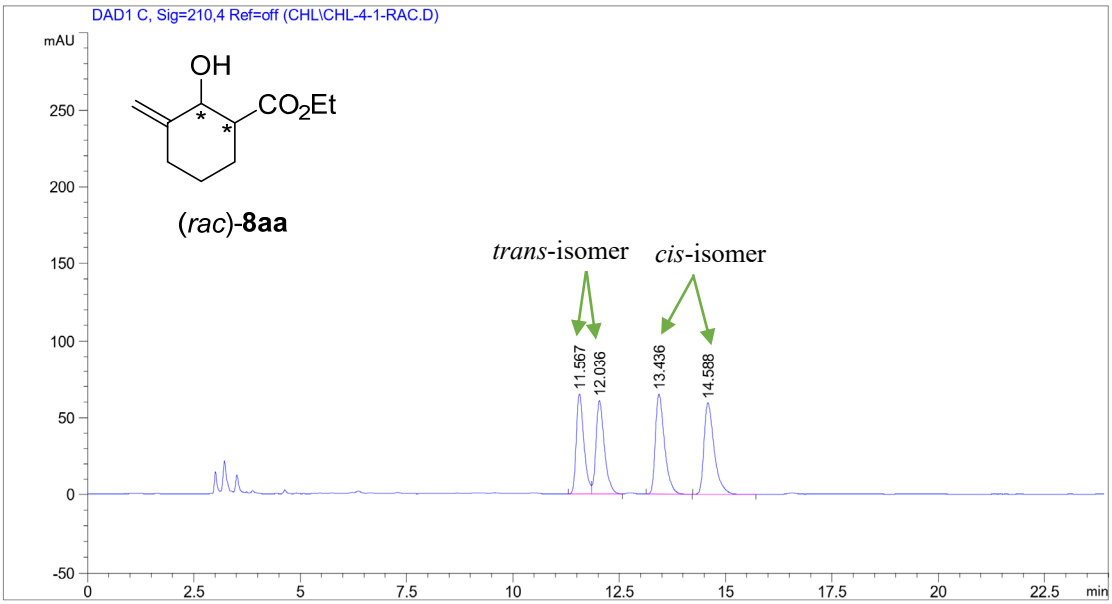


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.199	VV R	0.1759	4010.11401	347.33017	28.9426
2	10.814	VV R	0.1885	2959.50903	232.29977	21.3600
3	12.571	BB	0.2153	2884.34277	203.51955	20.8175
4	17.551	BB	0.3166	4001.42432	192.42418	28.8799

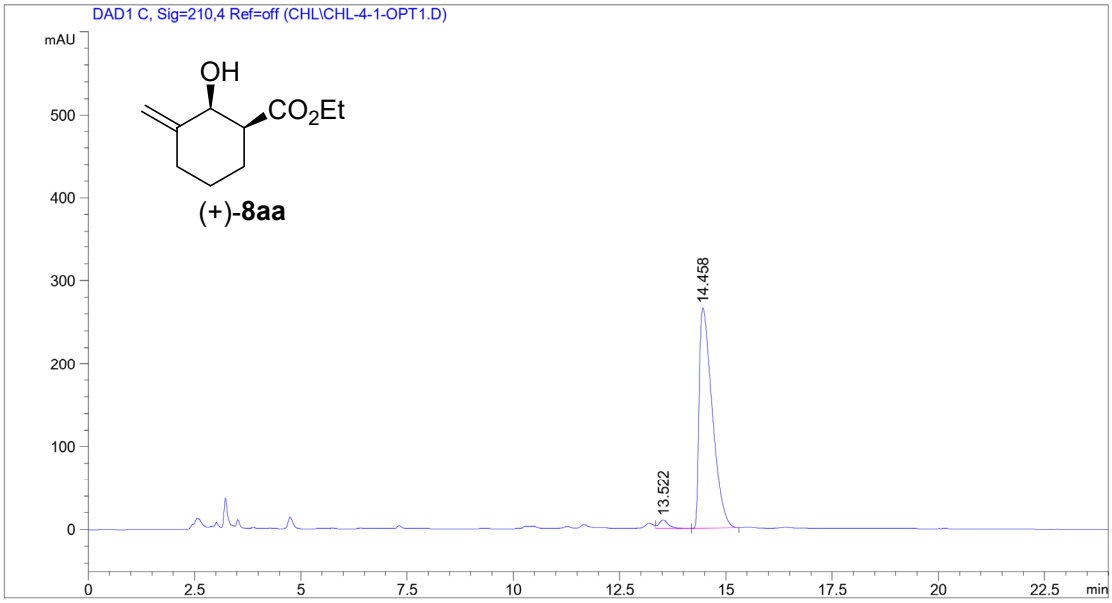


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.826	VB	0.1885	95.38097	7.59658	0.4020
2	12.588	BB	0.2196	2.35967e4	1642.48535	99.4602
3	17.562	BB	0.2713	32.68964	1.83992	0.1378

For compound (+)-8aa

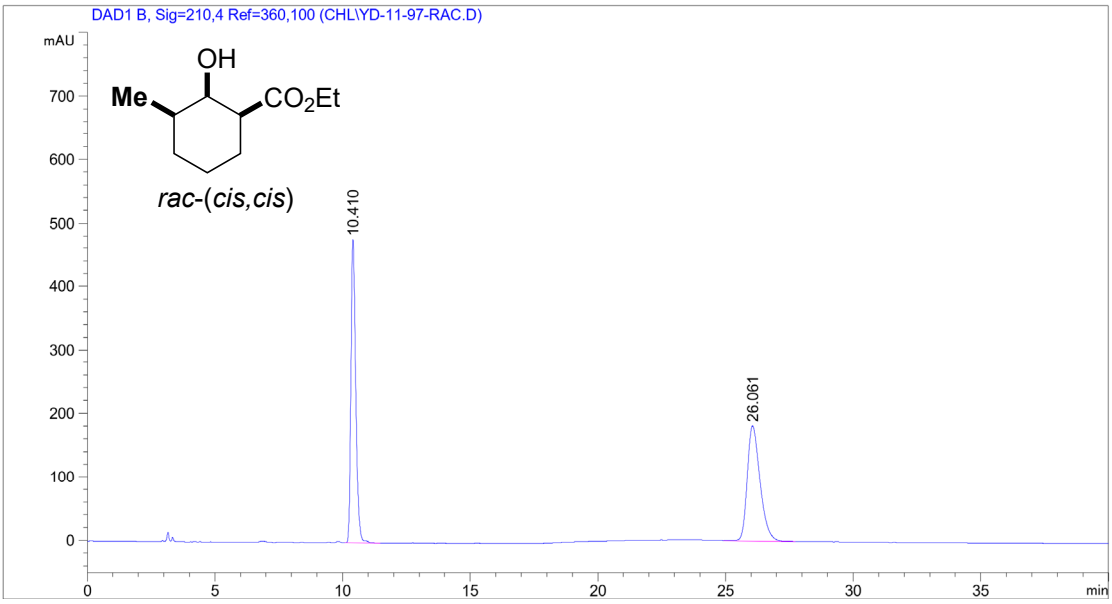


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.567	BV	0.1901	816.40454	65.20199	22.4636
2	12.036	VB	0.2092	840.94659	60.84756	23.1389
3	13.436	BB	0.2273	978.51630	65.12363	26.9242
4	14.588	BB	0.2534	998.46906	59.62774	27.4732

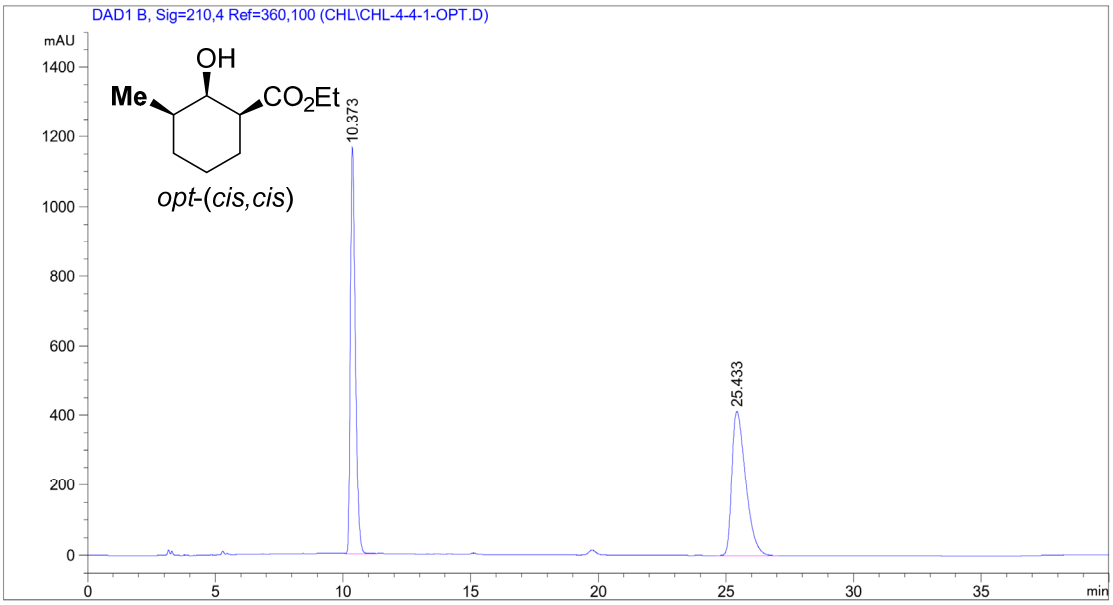


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.522	VB	0.2264	159.27521	10.29933	2.7212
2	14.458	BB	0.3299	5693.78369	265.78506	97.2788

For (*cis,cis*)-ethyl 2-hydroxy-3-methylcyclohexane-1-carboxylate

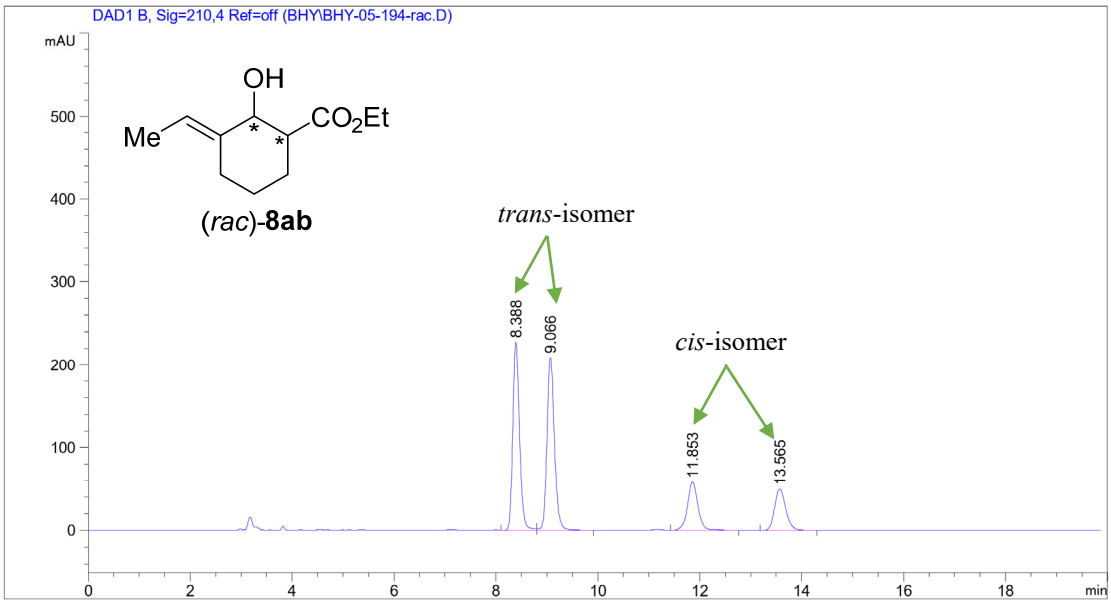


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.410	VB	0.2049	6256.85059	477.56158	49.8512
2	26.061	BB	0.5330	6294.19727	181.32877	50.1488

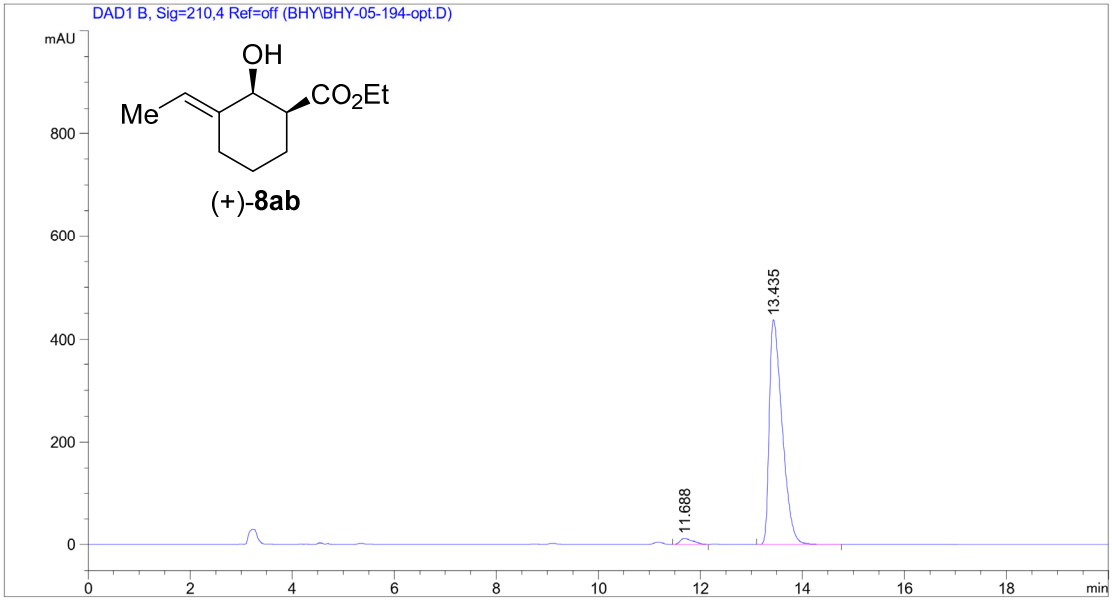


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.373	VV	0.2103	1.57773e4	1162.57288	50.5914
2	25.433	BB	0.5768	1.54084e4	411.56027	49.4086

For compound (+)-8ab

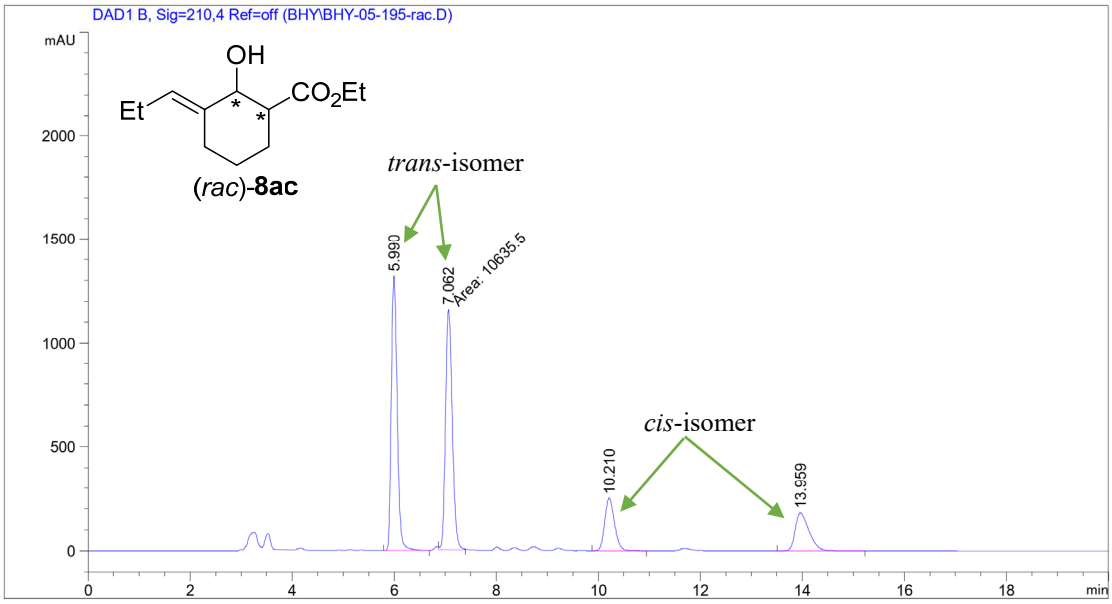


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.388	BV	0.1412	2088.74097	227.42029	36.0874
2	9.066	VB	0.1543	2119.22607	209.01027	36.6141
3	11.853	BB	0.2170	829.31140	57.92685	14.3281
4	13.565	BB	0.2329	750.72076	49.52088	12.9703

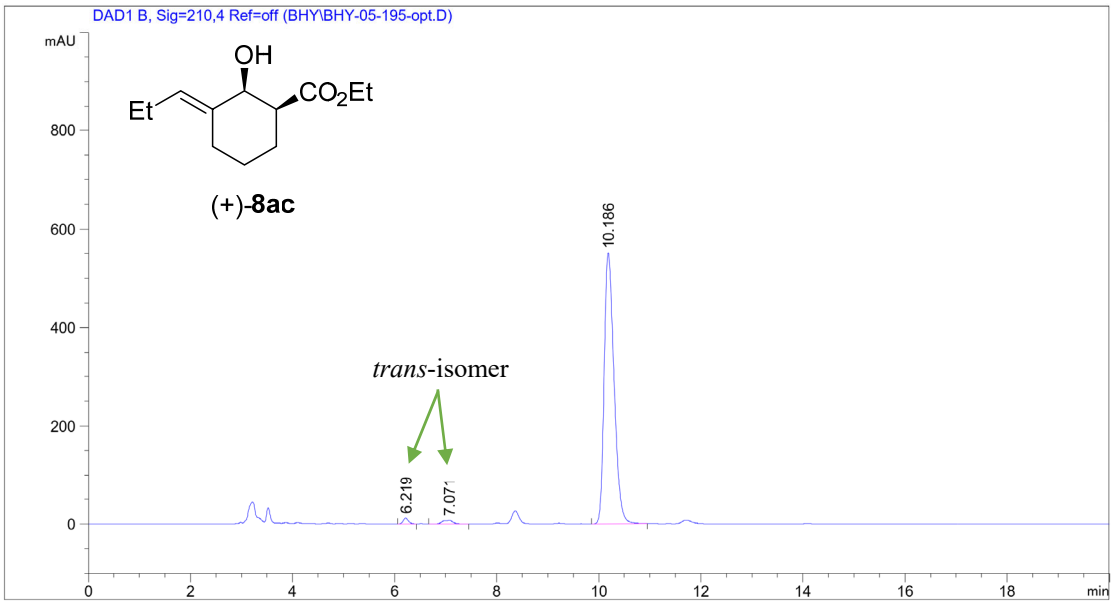


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.688	BB	0.2438	200.37968	11.81922	2.5483
2	13.435	BB	0.2665	7662.98291	437.24719	97.4517

For compound (+)-8ac

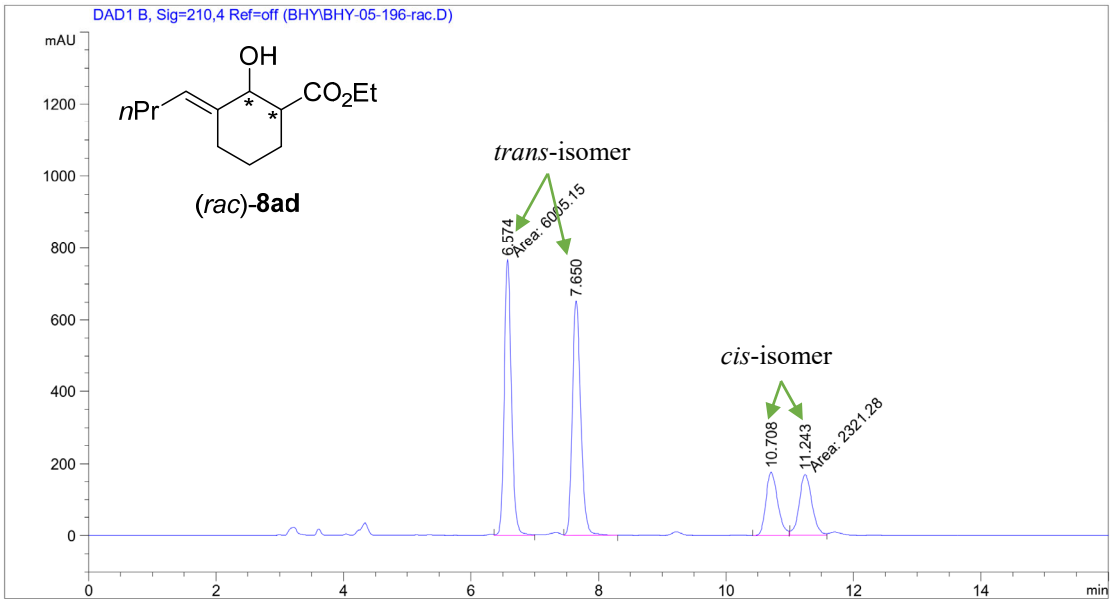


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.990	BV	0.1260	1.06435e4	1320.56409	38.0467
2	7.062	MM	0.1533	1.06355e4	1156.38550	38.0182
3	10.210	BB	0.2055	3335.16992	250.16077	11.9221
4	13.959	BB	0.2877	3360.62842	180.09370	12.0131

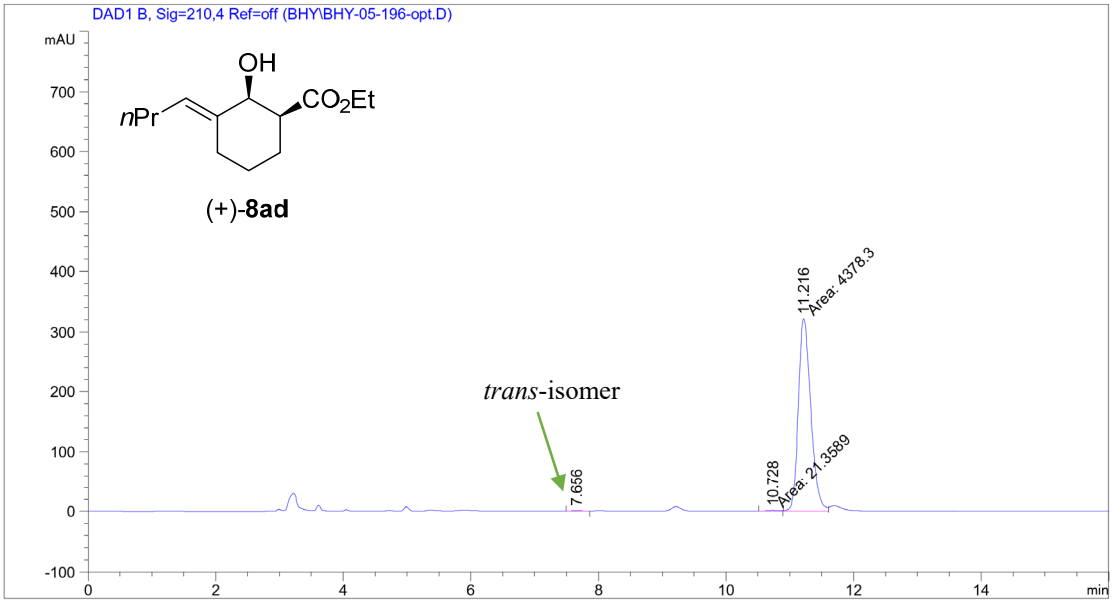


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.219	BB	0.1099	81.84636	11.65987	1.0788
2	7.071	BB	0.1891	101.38461	7.25148	1.3364
3	10.186	BB	0.2088	7403.23975	550.93030	97.5848

For compound (+)-8ad

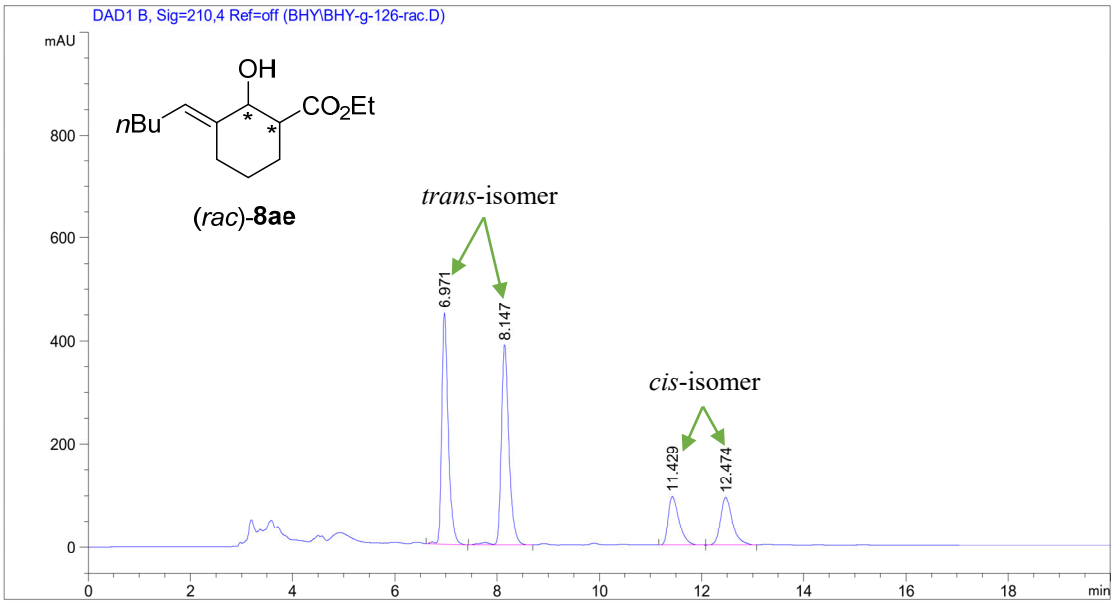


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.574	MM	0.1306	6005.15137	766.29791	36.2188
2	7.650	VB	0.1431	5988.13086	652.35559	36.1161
3	10.708	BV	0.1973	2265.66309	177.04327	13.6648
4	11.243	MM	0.2279	2321.28149	169.72208	14.0003

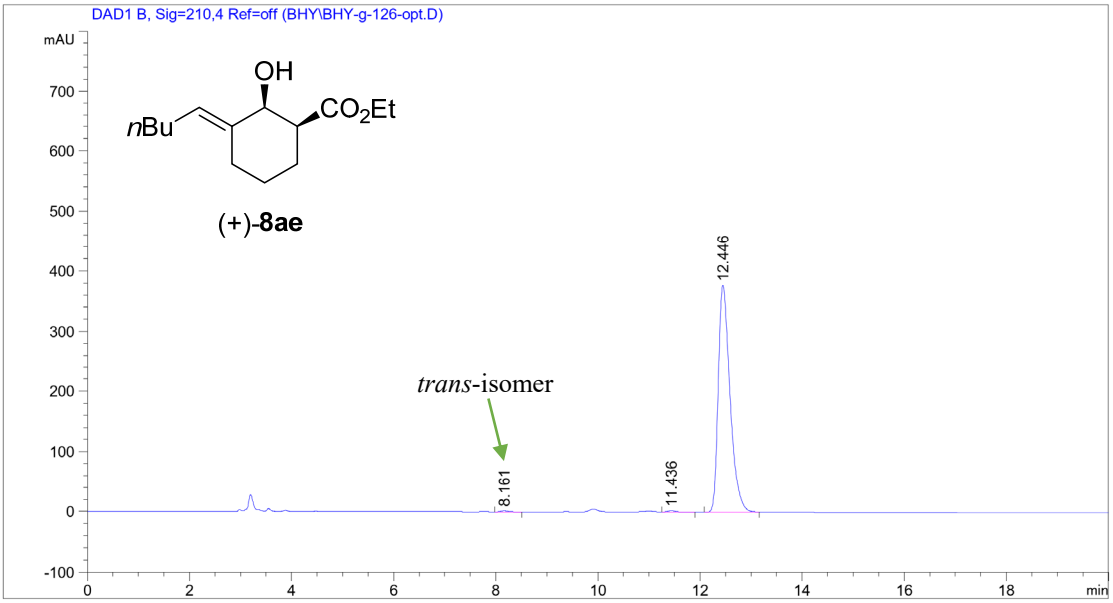


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.656	BB	0.1348	10.04896	1.16313	0.2279
2	10.728	MM	0.2396	21.35891	1.48572	0.4844
3	11.216	MM	0.2267	4378.30176	321.91272	99.2878

For compound (+)-8ae

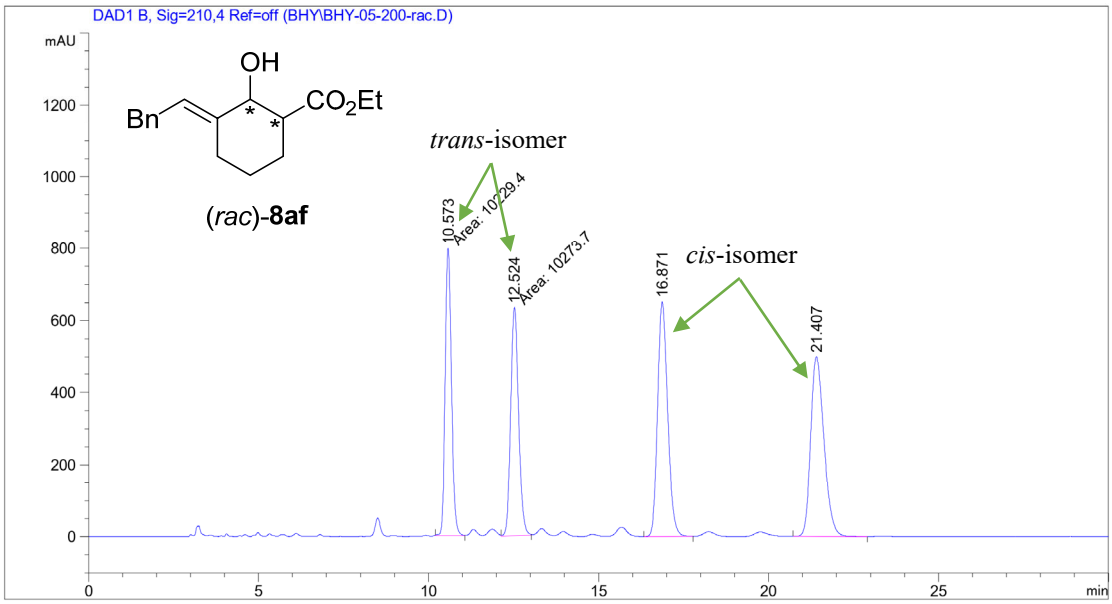


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.971	VB R	0.1301	3959.96436	449.70551	36.6062
2	8.147	VB R	0.1530	4013.62280	387.73581	37.1023
3	11.429	BB	0.2196	1368.15393	94.08977	12.6473
4	12.474	BB	0.2403	1475.98792	92.41047	13.6442

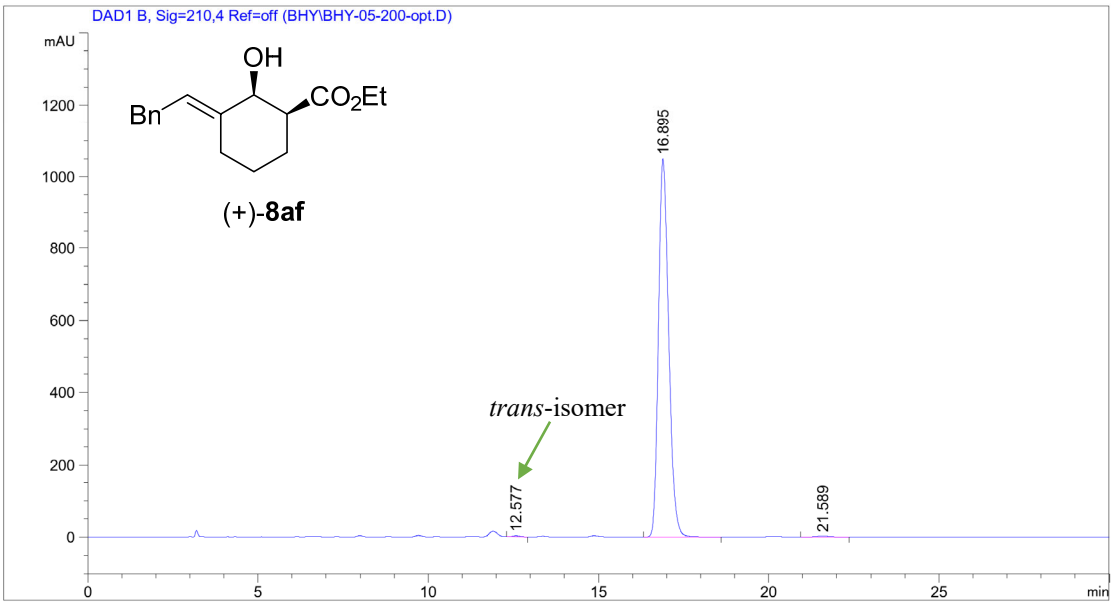


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.161	BB	0.1505	18.89267	1.89184	0.3103
2	11.436	VB	0.1587	27.43983	2.52721	0.4507
3	12.446	BB	0.2449	6042.22607	377.19983	99.2390

For compound (+)-8af

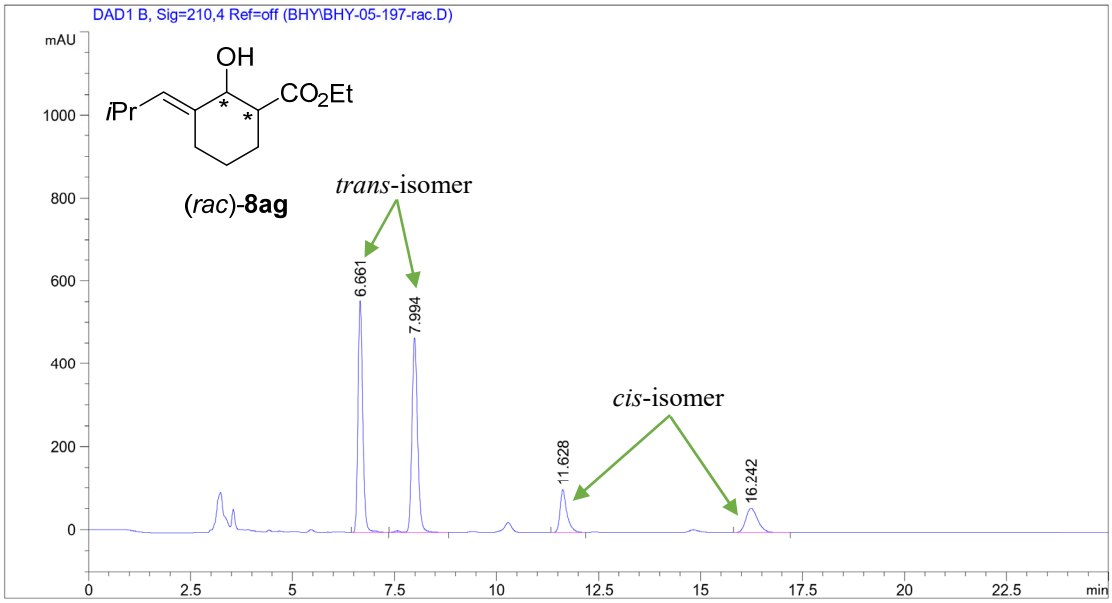


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.573	MM	0.2137	1.02294e4	797.72046	21.5460
2	12.524	MM	0.2702	1.02737e4	633.75824	21.6393
3	16.871	BB	0.3203	1.34277e4	651.90759	28.2825
4	21.407	BB	0.4182	1.35462e4	499.76904	28.5322

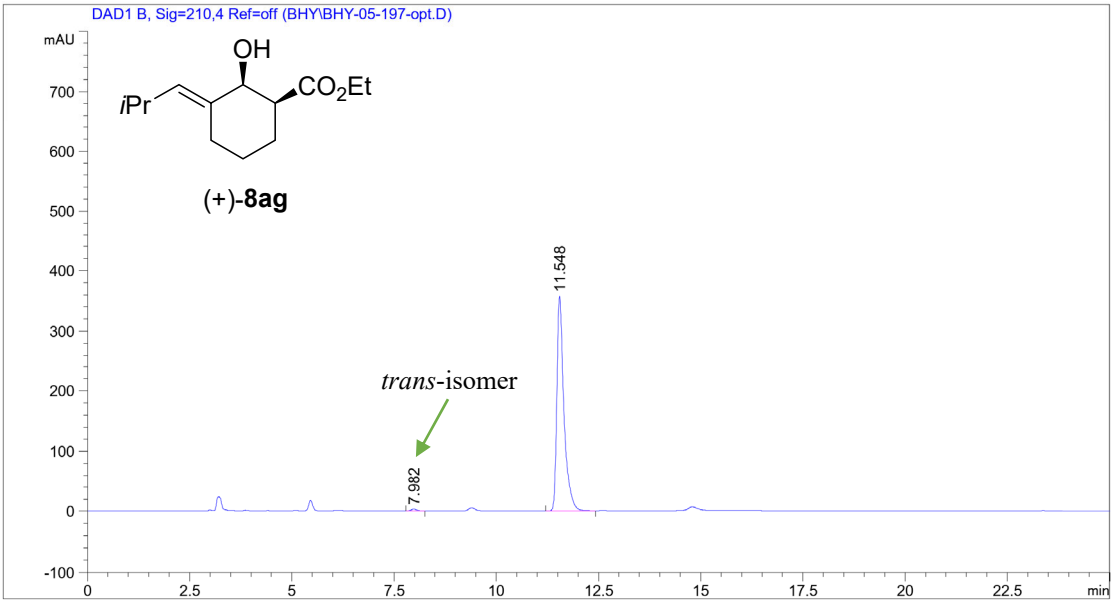


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.577	BB	0.2320	43.54992	2.91937	0.1973
2	16.895	BB	0.3262	2.19554e4	1049.03723	99.4655
3	21.589	BB	0.3828	74.42360	2.65656	0.3372

For compound (+)-8ag

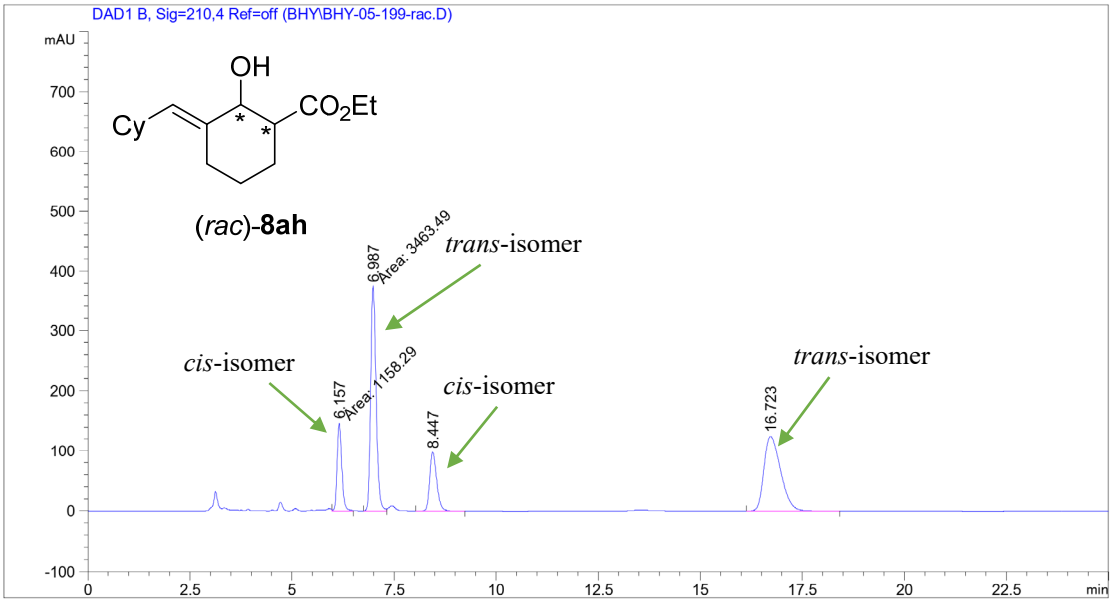


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.661	BB	0.1236	4481.40479	558.30042	39.5630
2	7.994	VB R	0.1474	4514.94775	469.06653	39.8592
3	11.628	BB	0.1663	1174.27039	101.98779	10.3668
4	16.242	BB	0.3102	1156.62561	57.62910	10.2110

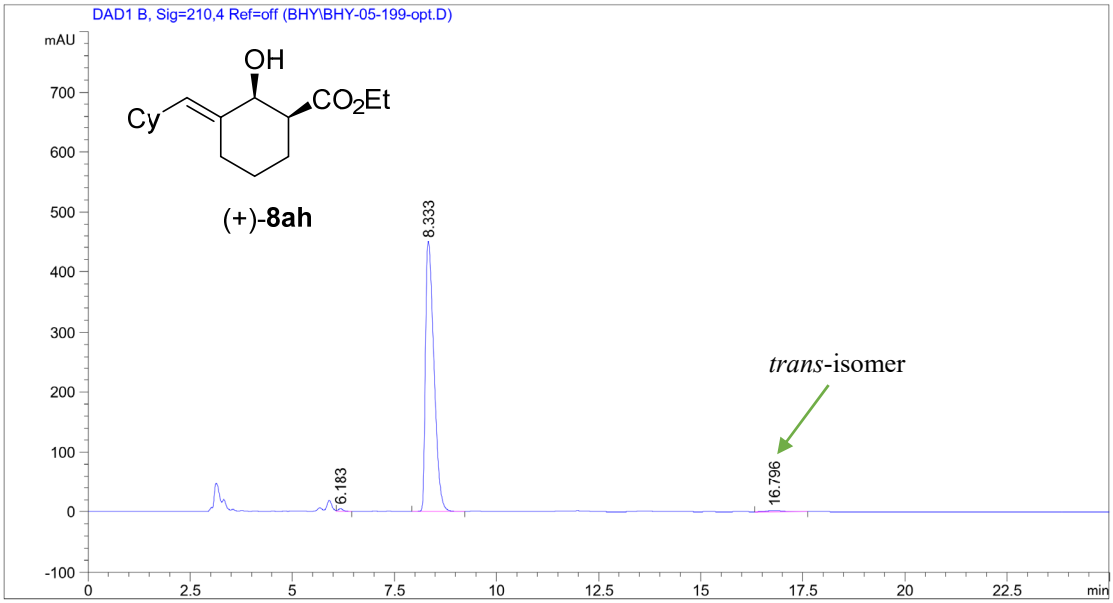


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.982	BB	0.1416	29.06971	3.15080	0.6701
2	11.548	BB	0.1788	4308.78125	357.10538	99.3299

For compound (+)-8ah

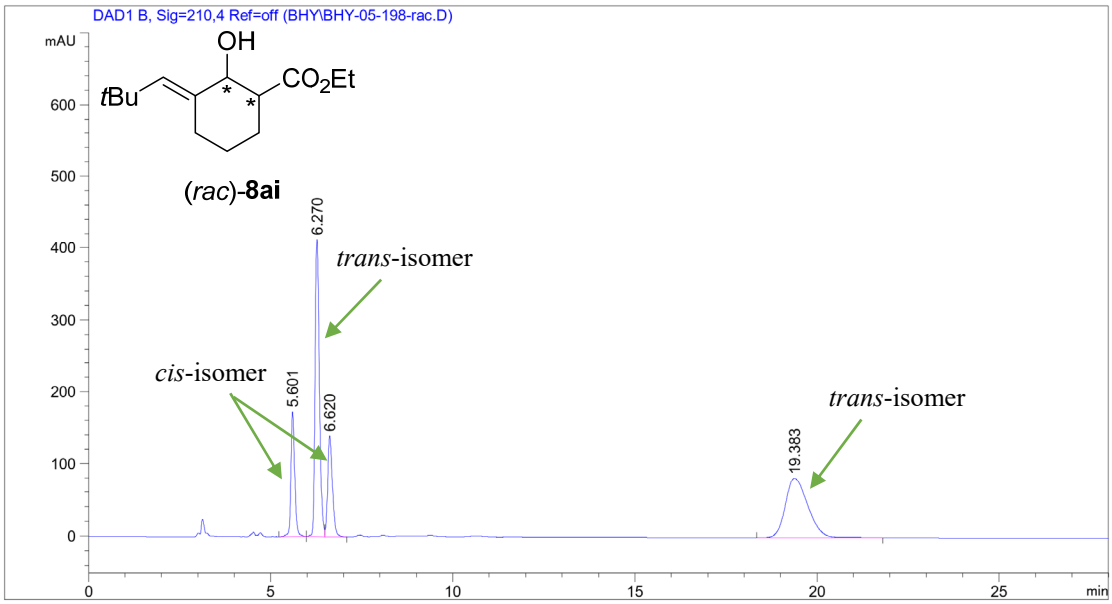


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.157	MM	0.1318	1158.28772	146.48009	12.4493
2	6.987	MM	0.1539	3463.48950	375.07623	37.2255
3	8.447	BB	0.1839	1172.50391	97.80279	12.6020
4	16.723	BB	0.4400	3509.79224	124.84492	37.7232

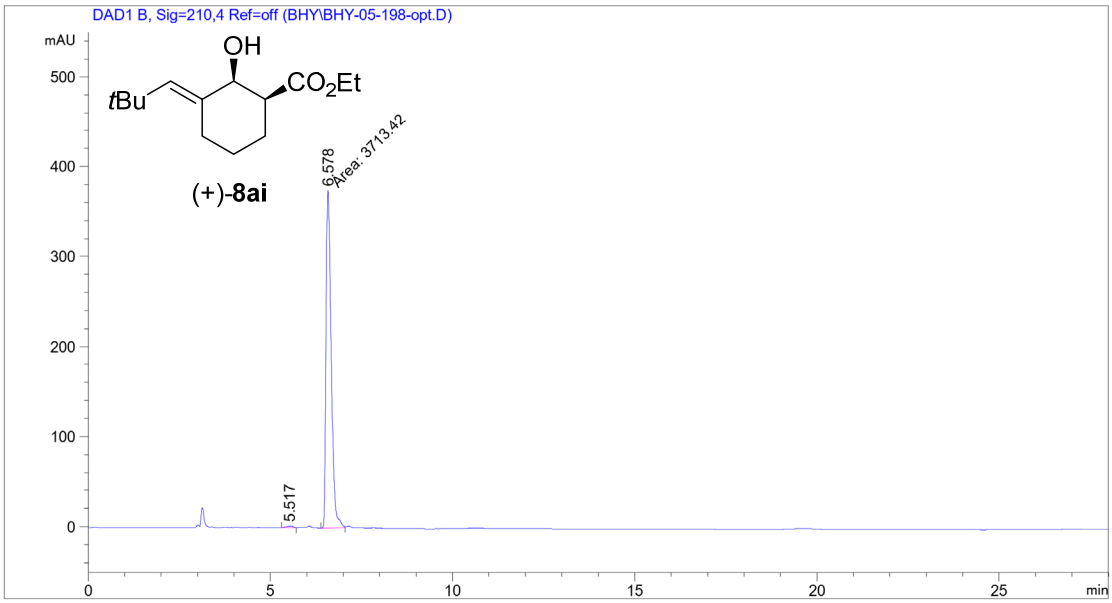


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.183	VB	0.1307	40.79198	4.63470	0.6162
2	8.333	BB	0.2290	6520.25537	450.03940	98.4890
3	16.796	BB	0.3755	59.23974	2.23270	0.8948

For compound (+)-8ai

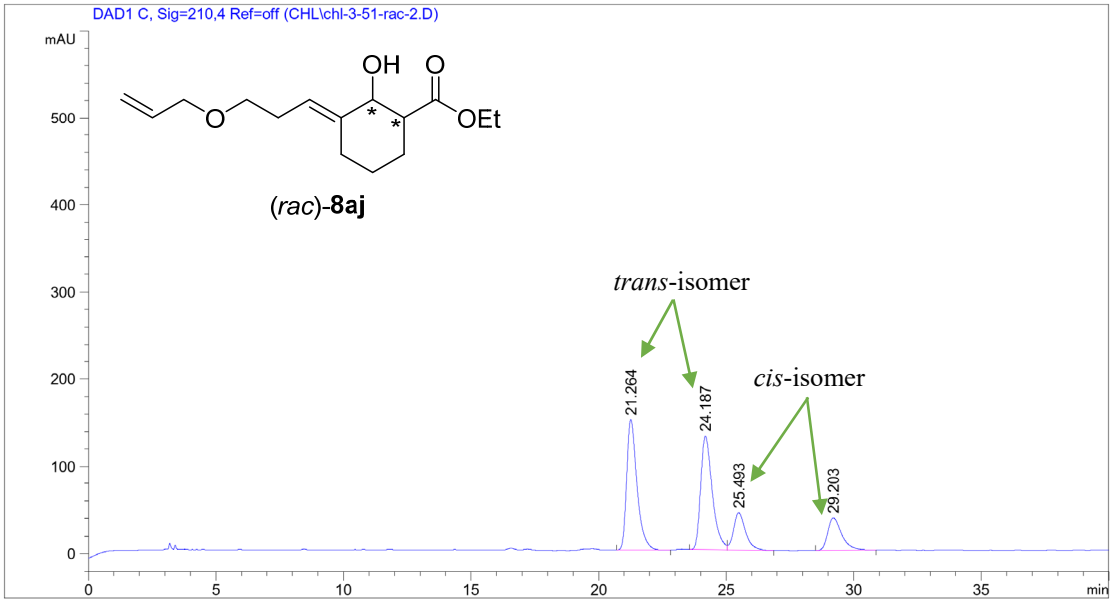


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.601	BB	0.1105	1255.14319	173.34535	13.3672
2	6.270	BV	0.1254	3377.80957	413.16370	35.9735
3	6.620	VB	0.1391	1261.09570	139.97054	13.4306
4	19.383	BB	0.6507	3495.67871	82.10207	37.2288

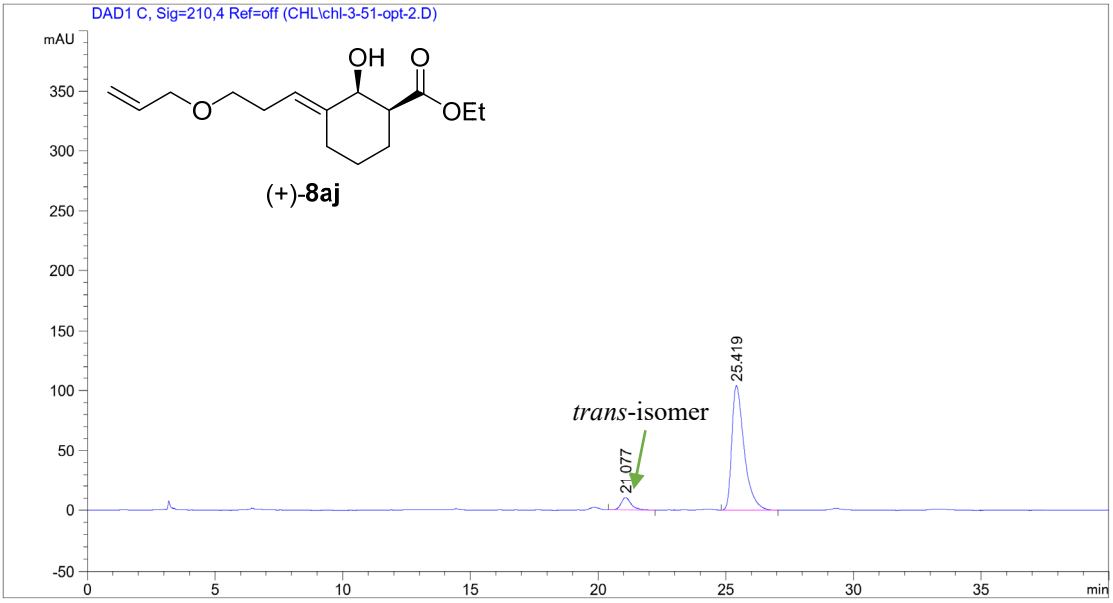


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.517	BV	0.1809	23.90779	1.73373	0.6397
2	6.578	MF	0.1650	3713.42261	375.03815	99.3603

For compound (+)-8aj

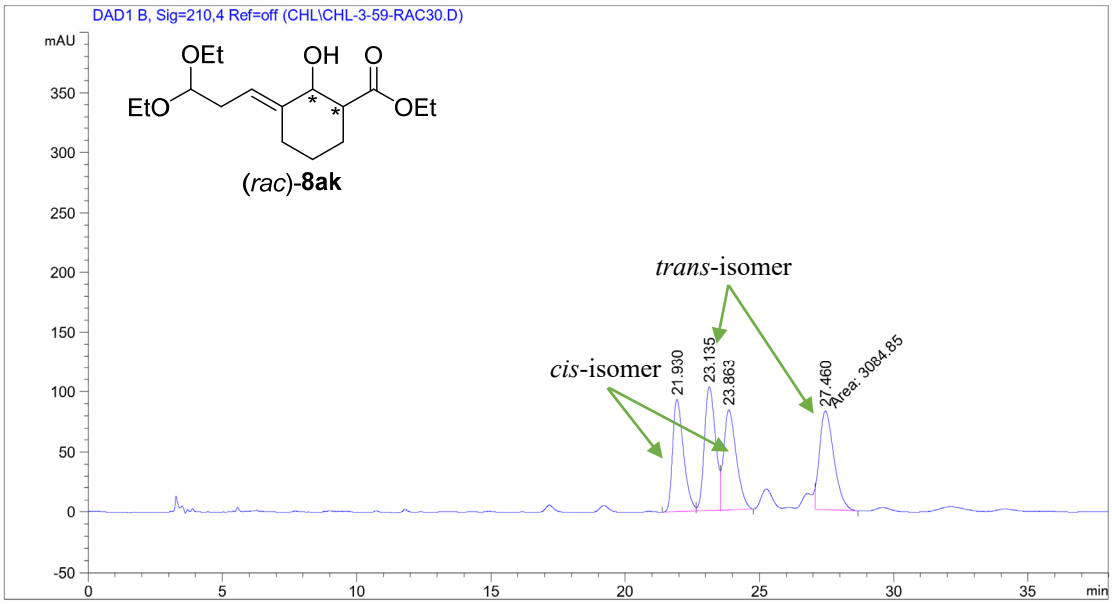


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.264	BB	0.4249	4188.25977	149.45776	37.6584
2	24.187	BV	0.4817	4129.91699	130.33606	37.1338
3	25.493	VB	0.4982	1398.26404	42.46426	12.5724
4	29.203	BB	0.5656	1405.28333	36.95968	12.6355

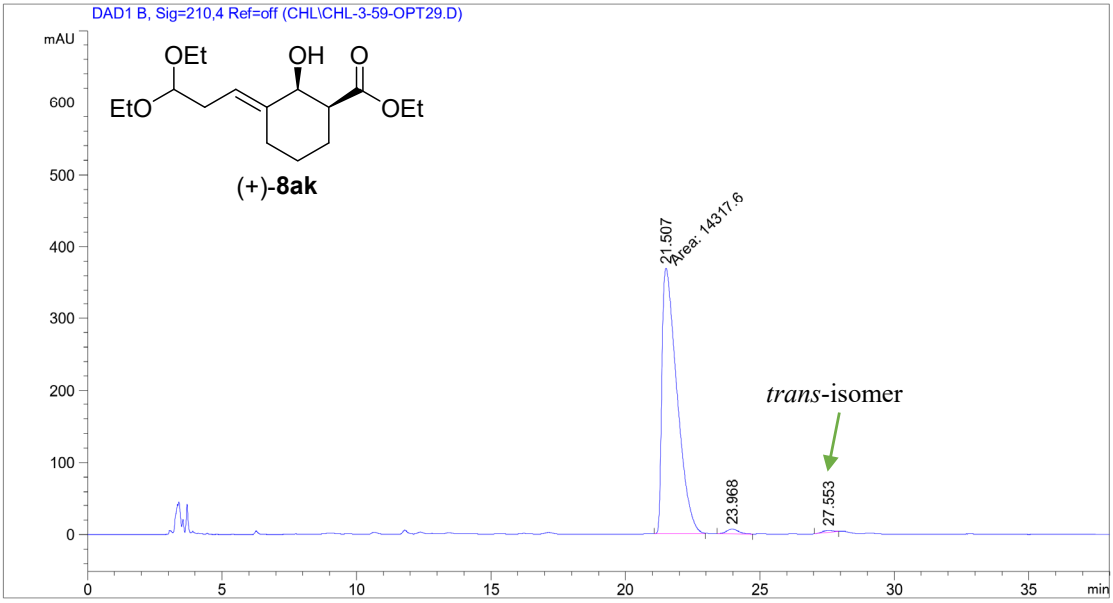


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.077	BB	0.4112	272.65741	10.02712	7.2326
2	25.419	BB	0.5074	3497.17676	103.72208	92.7674

For compound (+)-8ak

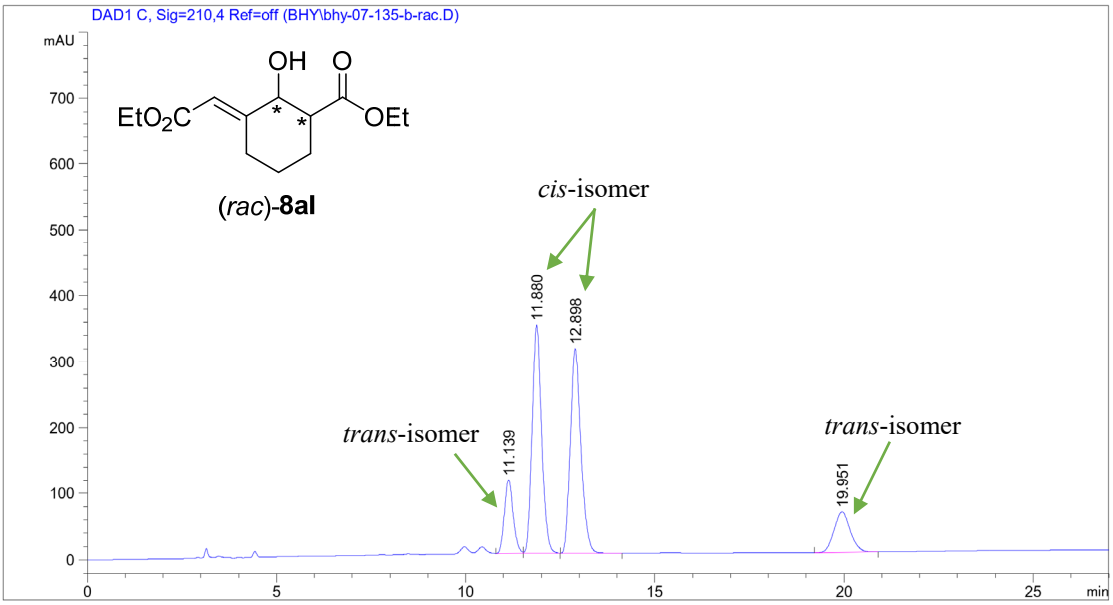


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.930	BV	0.4363	2640.94653	93.28783	23.0740
2	23.135	VV	0.4499	2982.46216	102.96295	26.0579
3	23.863	VB	0.4974	2737.26660	83.28714	23.9156
4	27.460	FM	0.6251	3084.85498	82.24385	26.9525

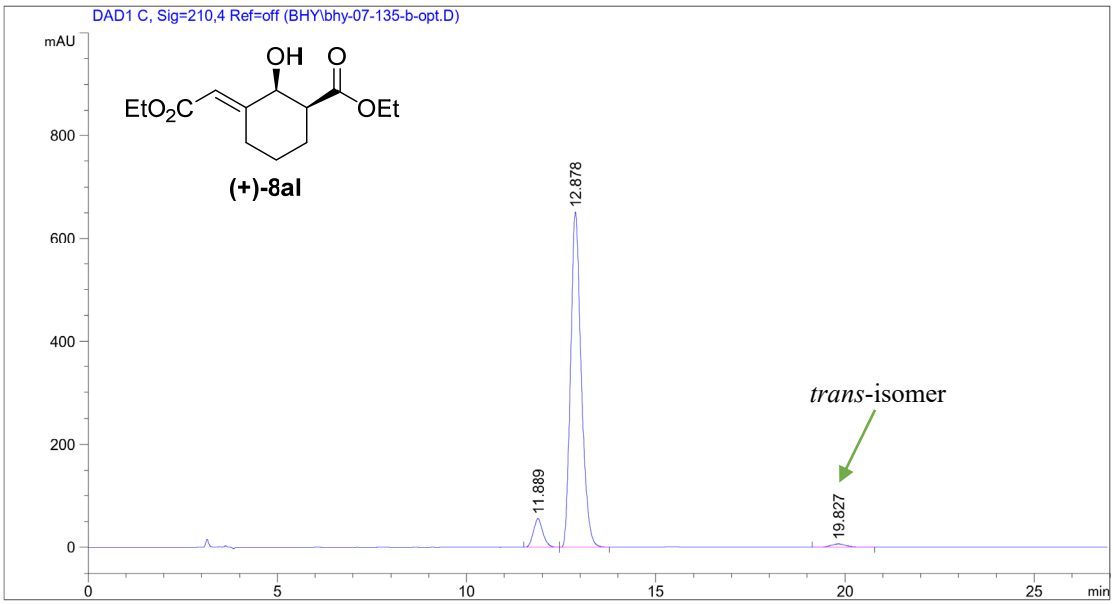


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.507	MF	0.6457	1.43176e4	369.55042	98.1412
2	23.968	BB	0.4535	195.92056	6.53996	1.3430
3	27.553	BB	0.4145	75.25644	2.79163	0.5159

For compound (+)-8al

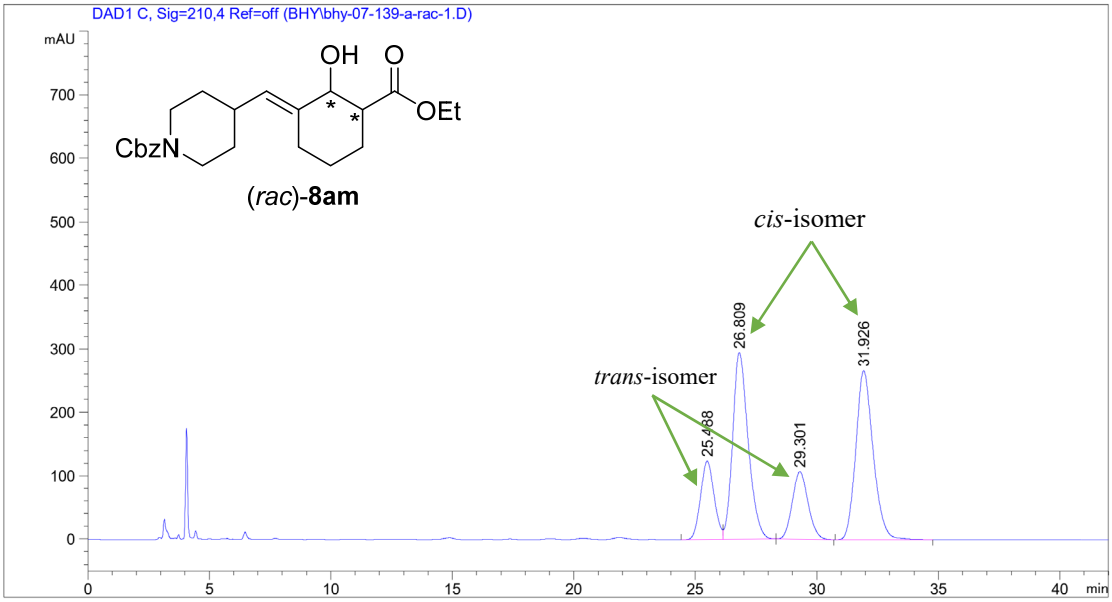


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.139	BV	0.2427	1782.76758	111.38406	11.3900
2	11.880	VB	0.2630	6023.15381	346.20486	38.4815
3	12.898	BB	0.2867	6029.63184	310.28391	38.5229
4	19.951	BB	0.4563	1816.53162	60.83800	11.6057

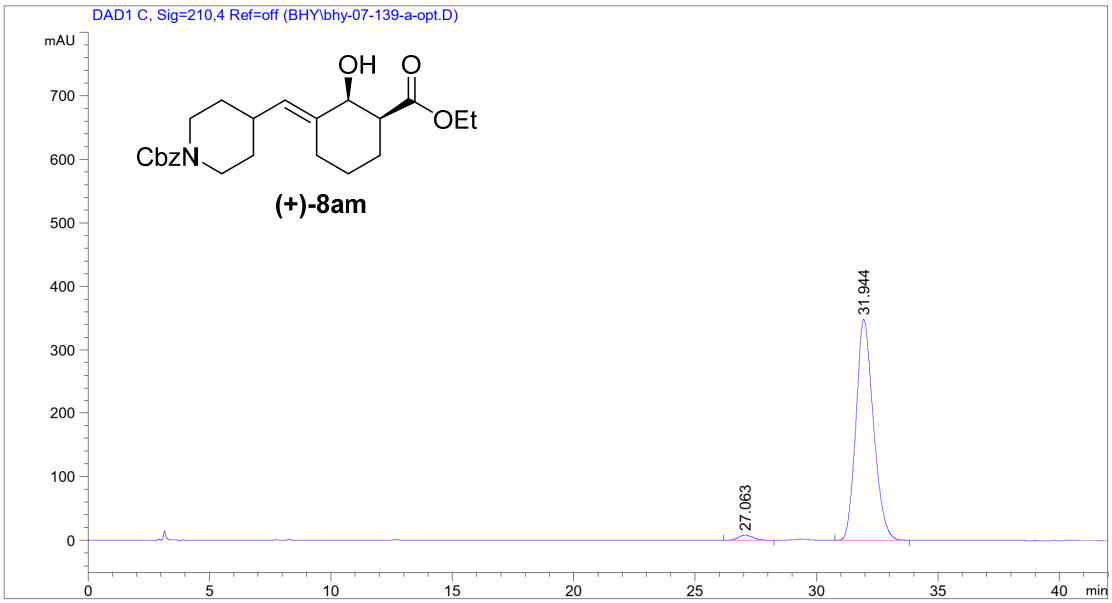


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.889	BB	0.2642	960.01318	55.38147	6.9327
2	12.878	BB	0.2873	1.27017e4	651.89374	91.7248
3	19.827	BB	0.4363	185.89673	6.22718	1.3425

For compound (+)-8am

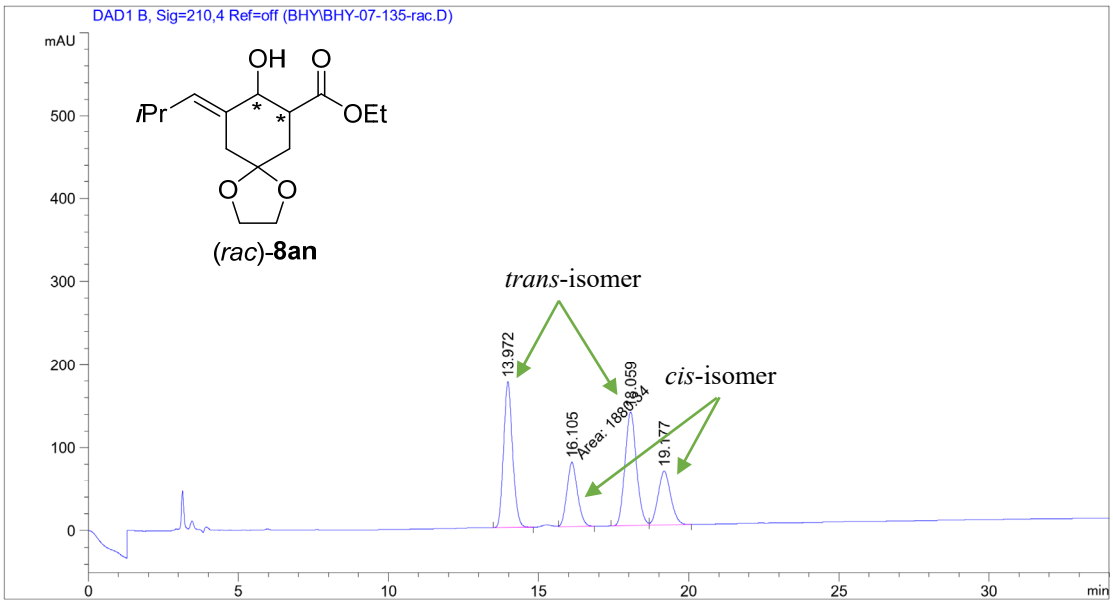


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.488	BV	0.5929	4835.48389	124.56743	13.4120
2	26.809	VB	0.6663	1.31068e4	295.01416	36.3538
3	29.301	BB	0.6863	4843.24365	107.78024	13.4335
4	31.926	BB	0.7457	1.32679e4	266.12042	36.8007

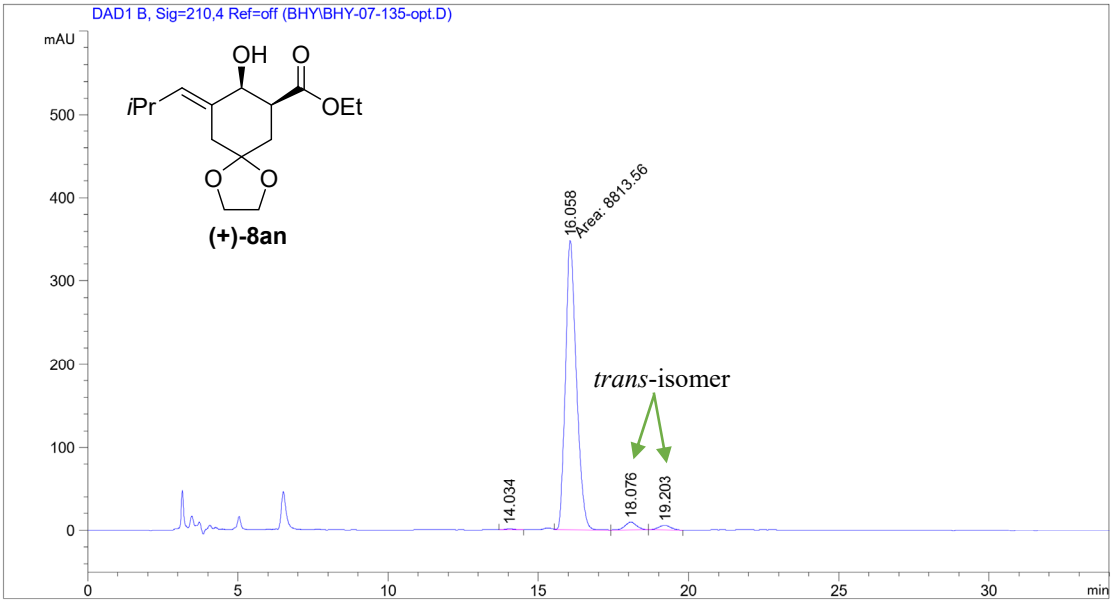


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.063	BB	0.5982	335.78473	7.99210	1.9000
2	31.944	BB	0.7456	1.73370e4	347.74994	98.1000

For compound (+)-8an

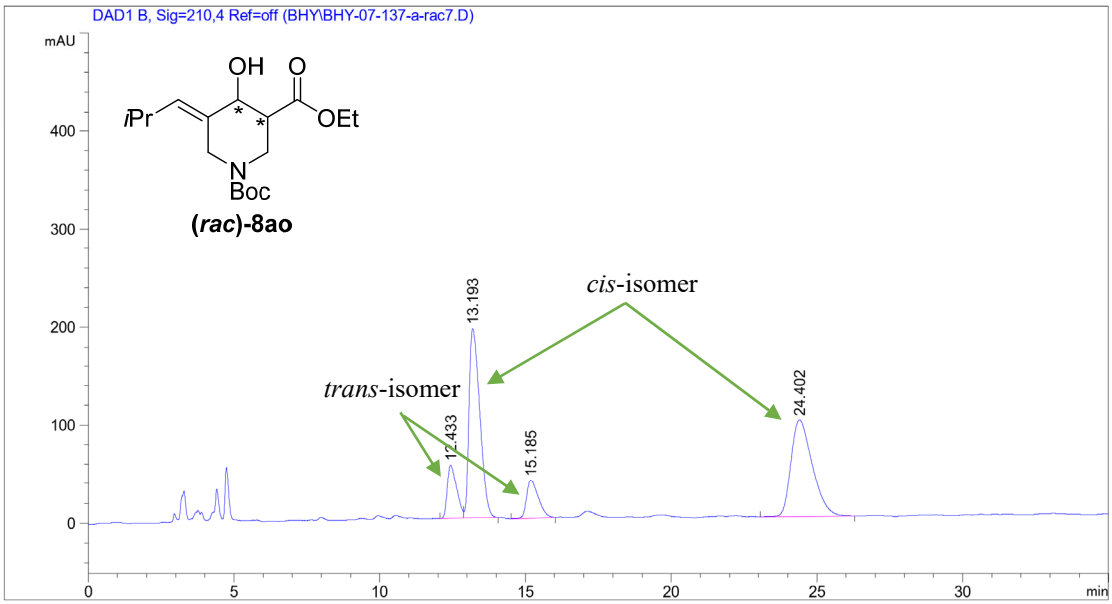


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.972	BB	0.3144	3641.88550	175.27980	32.9170
2	16.105	FM	0.4026	1880.34399	77.84354	16.9954
3	18.059	BV	0.4086	3651.90527	137.15486	33.0076
4	19.177	VB	0.4340	1889.70251	65.62367	17.0800

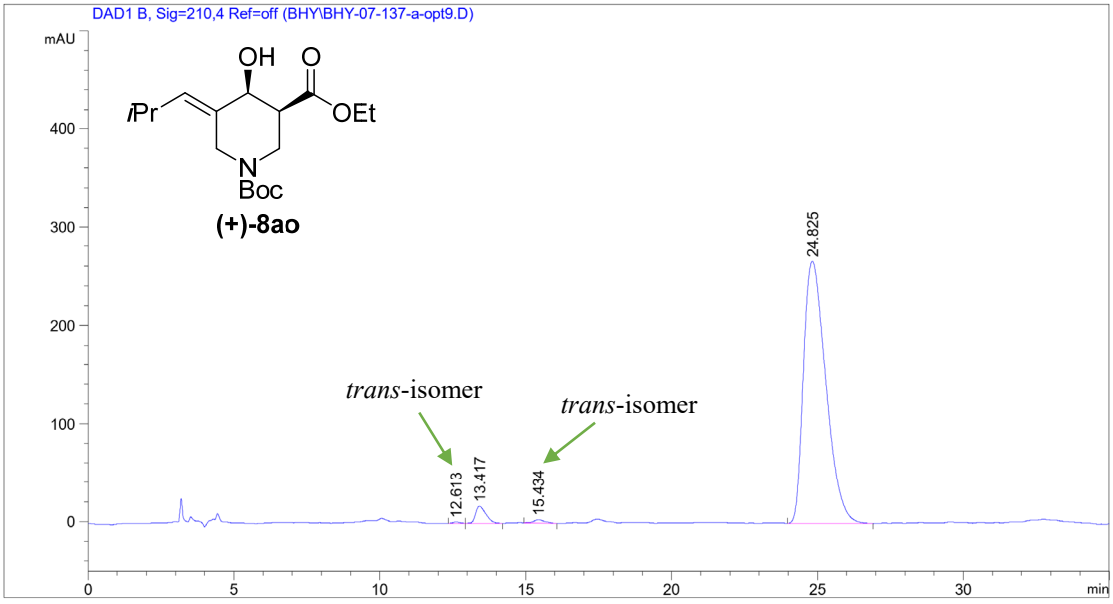


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.034	BB	0.2954	26.12832	1.31729	0.2831
2	16.058	FM	0.4217	8813.56055	348.29379	95.5026
3	18.076	BB	0.3945	238.12634	9.18417	2.5803
4	19.203	BB	0.4067	150.79079	5.48585	1.6339

For compound (+)-8ao

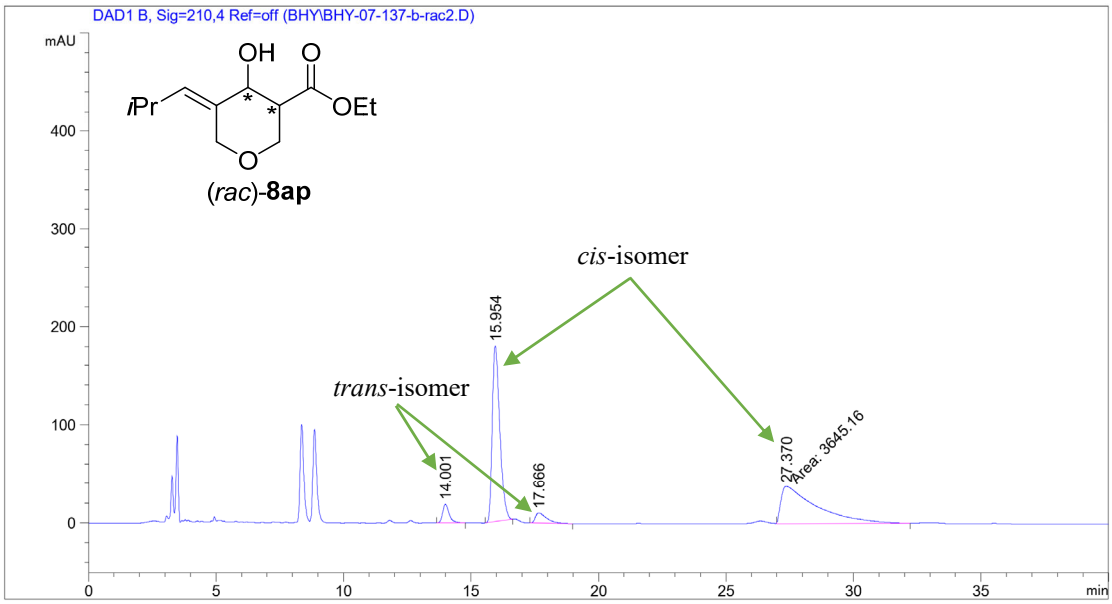


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.433	BV	0.3437	1207.47839	54.25001	9.8383
2	13.193	VB	0.4092	4966.42480	193.63818	40.4656
3	15.185	BB	0.4278	1060.24561	38.43367	8.6387
4	24.402	BB	0.7658	5039.04883	98.67349	41.0573

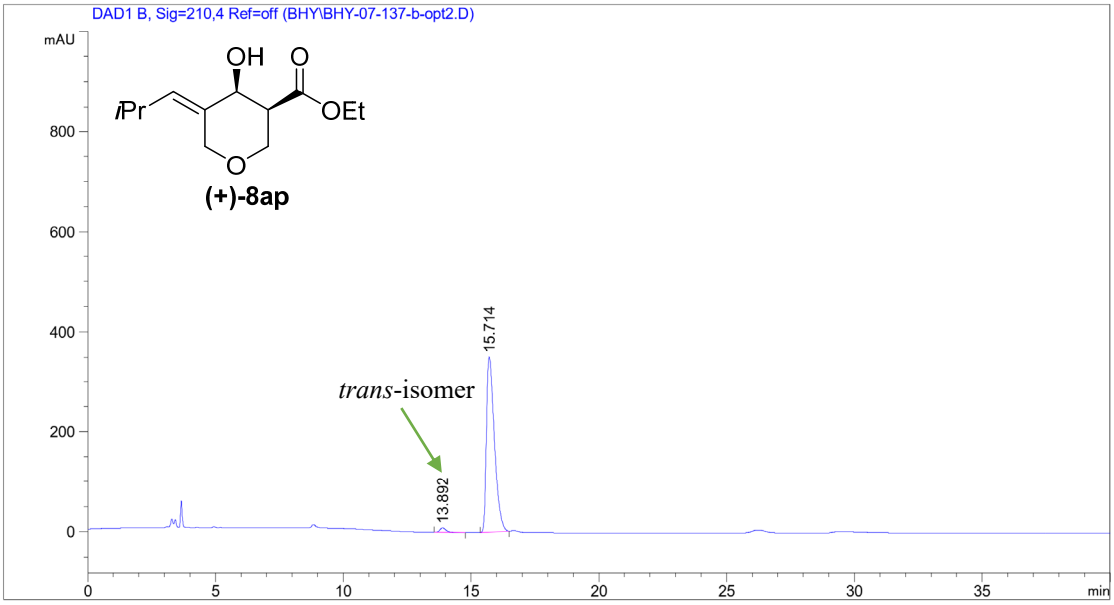


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.613	BB	0.2475	19.07212	1.19950	0.1289
2	13.417	BB	0.3658	423.01797	17.51550	2.8600
3	15.434	BB	0.3756	90.69881	3.48526	0.6132
4	24.825	BB	0.8279	1.42582e4	266.63245	96.3979

For compound (+)-8ap

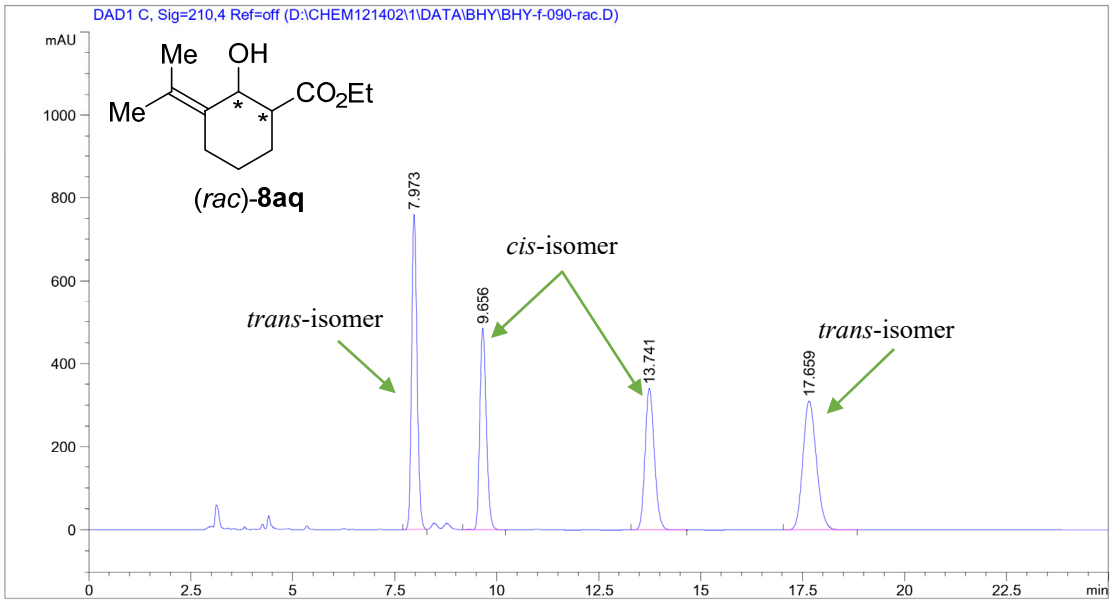


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.001	BB	0.2676	334.10071	18.78005	4.1916
2	15.954	BB	0.3150	3673.47290	179.29735	46.0872
3	17.666	BB	0.4522	317.97095	10.29796	3.9892
4	27.370	FM	1.6062	3645.16089	37.82485	45.7320

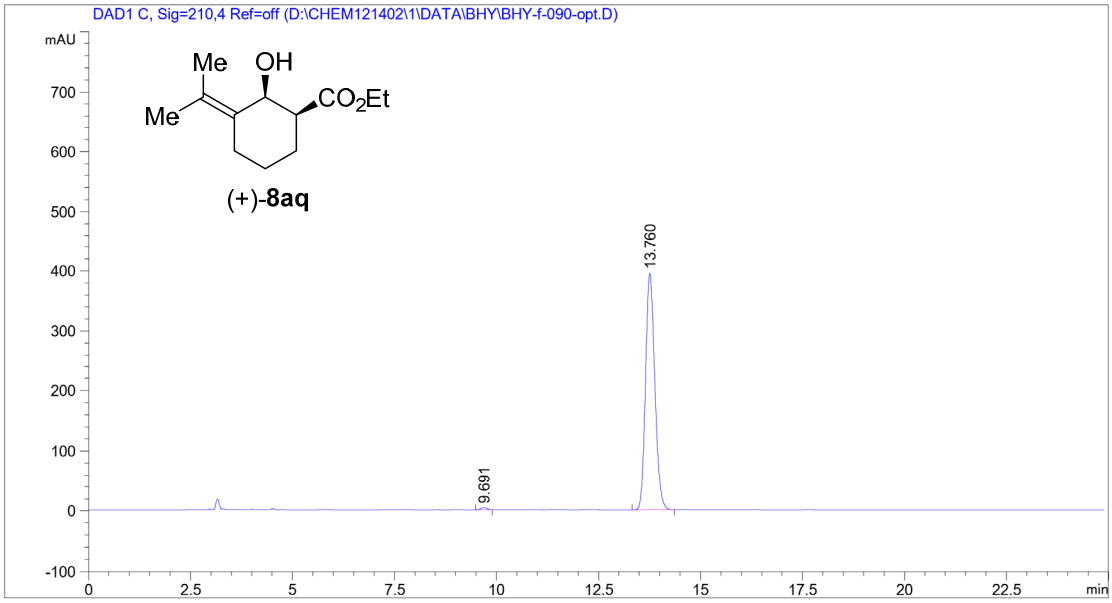


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.892	BB	0.2544	148.00224	8.88006	1.9113
2	15.714	BB	0.3324	7595.67529	351.15857	98.0887

For compound (+)-8aq

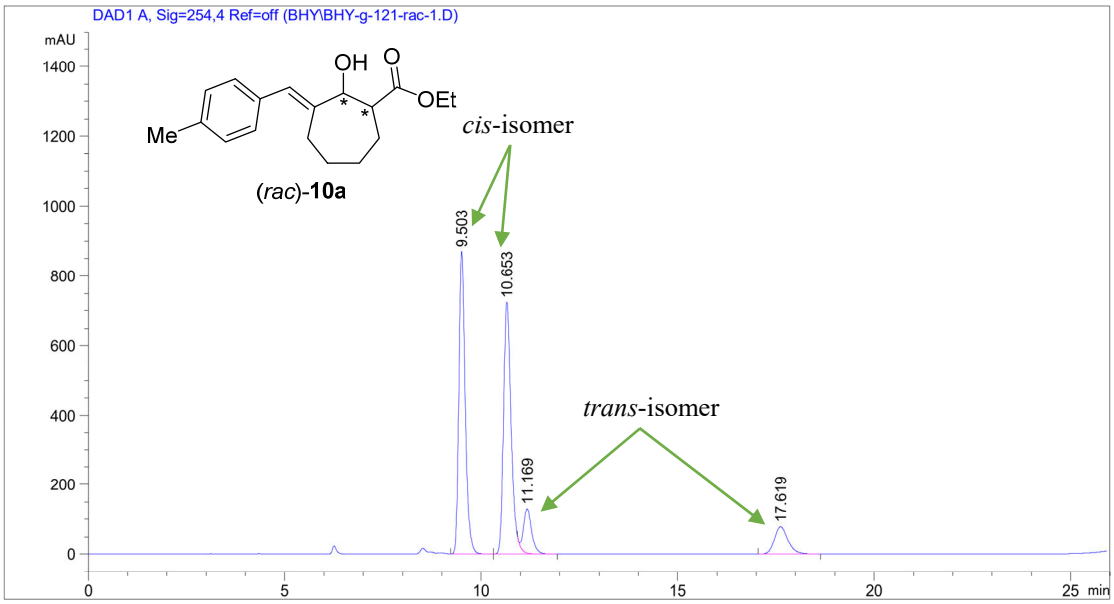


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.973	BB	0.1439	7032.94678	760.25964	28.1652
2	9.656	VB R	0.1713	5389.58936	485.24304	21.5840
3	13.741	BB	0.2447	5393.21875	340.59729	21.5985
4	17.659	BB	0.3566	7154.54785	310.77859	28.6522

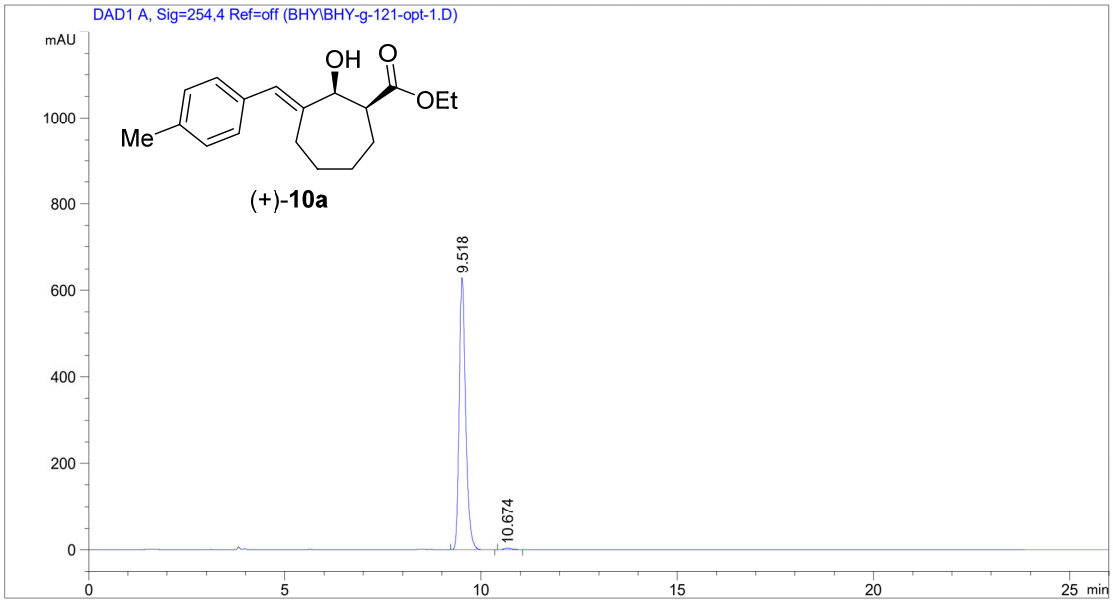


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.691	BB	0.1608	36.95268	3.62858	0.5876
2	13.760	BB	0.2470	6252.23145	394.38052	99.4124

For compound (+)-10a

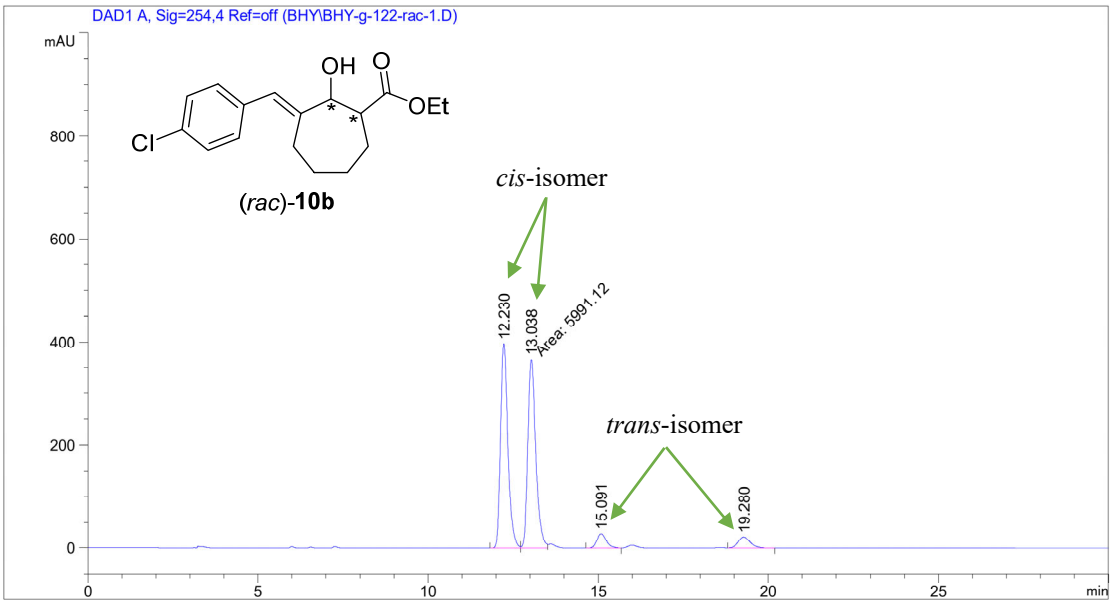


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.503	BB	0.1711	9772.98535	869.62811	41.9543
2	10.653	BV R	0.2062	9832.68457	725.30560	42.2106
3	11.169	VB E	0.2159	1821.69250	128.08986	7.8203
4	17.619	BB	0.3652	1866.98914	78.58557	8.0148

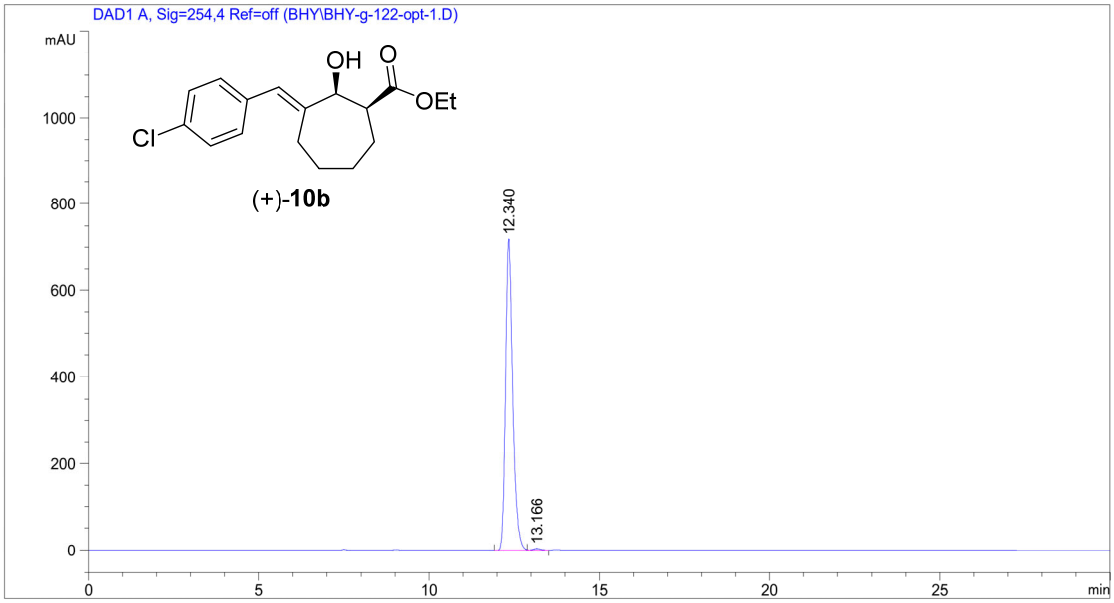


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.518	BB	0.1741	7227.69678	629.03687	99.3702
2	10.674	BB	0.2063	45.80545	3.33317	0.6298

For compound (+)-10b

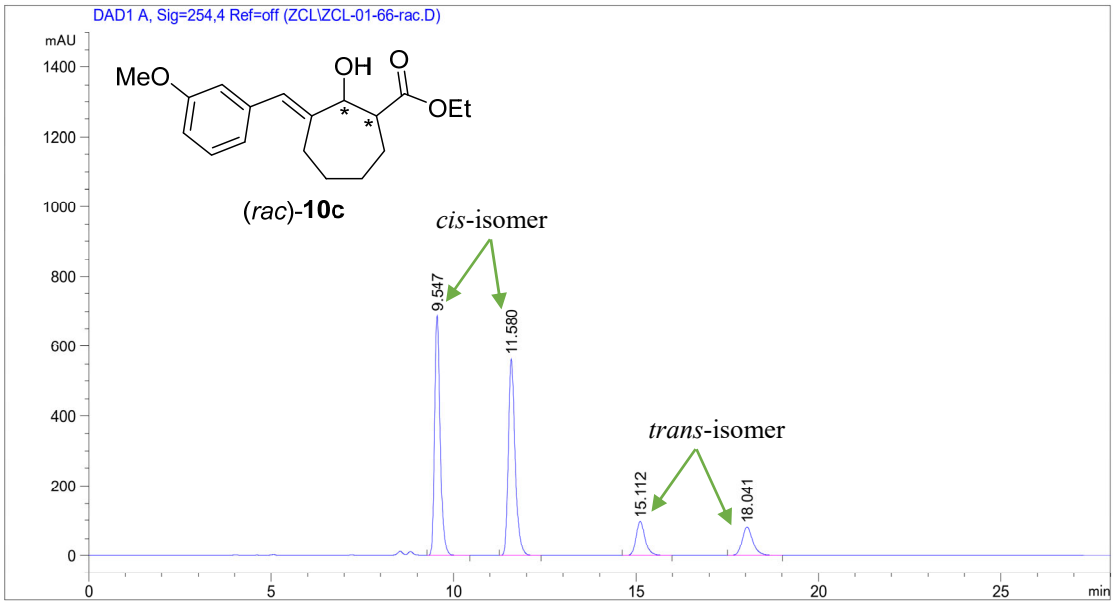


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.230	BV	0.2292	5978.49316	398.12463	45.7491
2	13.038	MF	0.2723	5991.11816	366.70767	45.8457
3	15.091	BB	0.2933	553.43091	28.91636	4.2350
4	19.280	BB	0.3790	544.96747	22.15607	4.1702

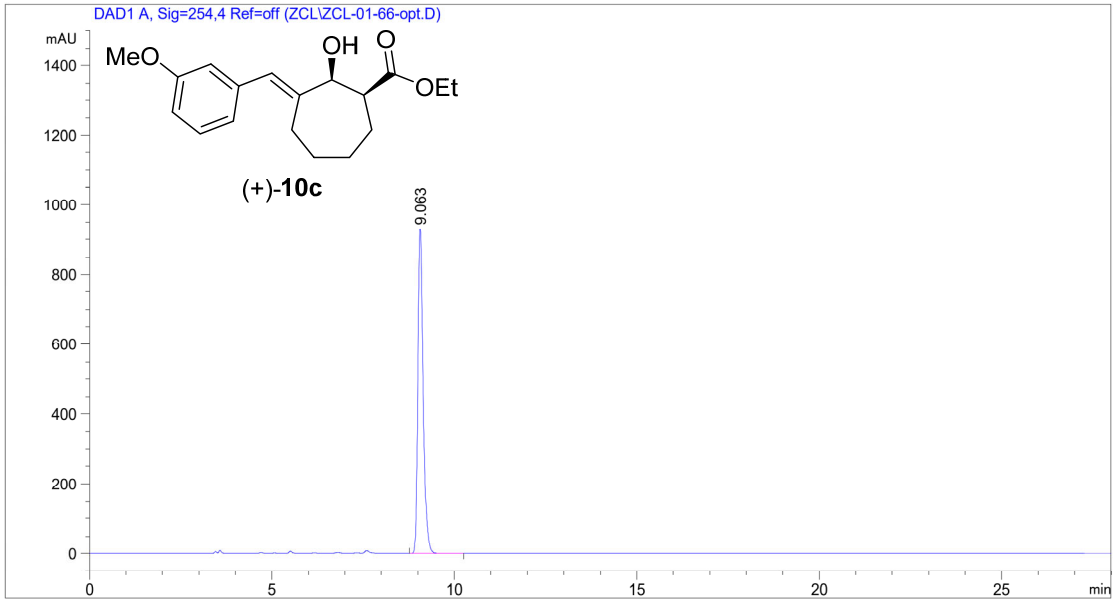


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.340	BV R	0.2229	1.05326e4	719.03937	99.4705
2	13.166	VB E	0.2243	56.06481	3.79637	0.5295

For compound (+)-10c

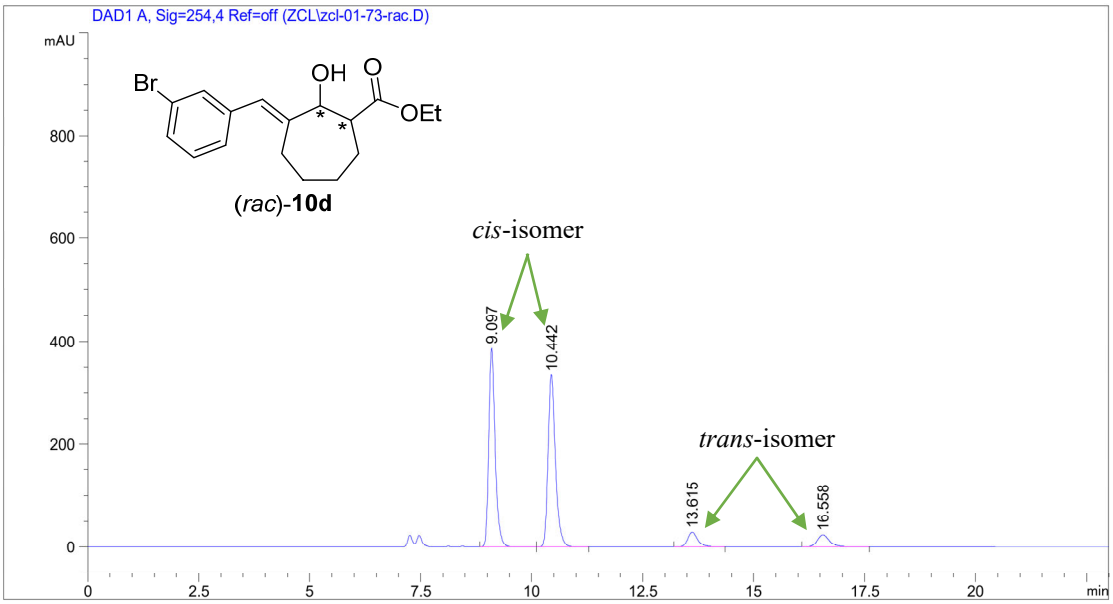


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.547	BB	0.1610	7275.47168	690.11829	40.6700
2	11.580	BB	0.1969	7271.54834	562.26544	40.6481
3	15.112	BB	0.2644	1671.16943	96.31079	9.3419
4	18.041	BB	0.3164	1670.84497	80.42332	9.3401

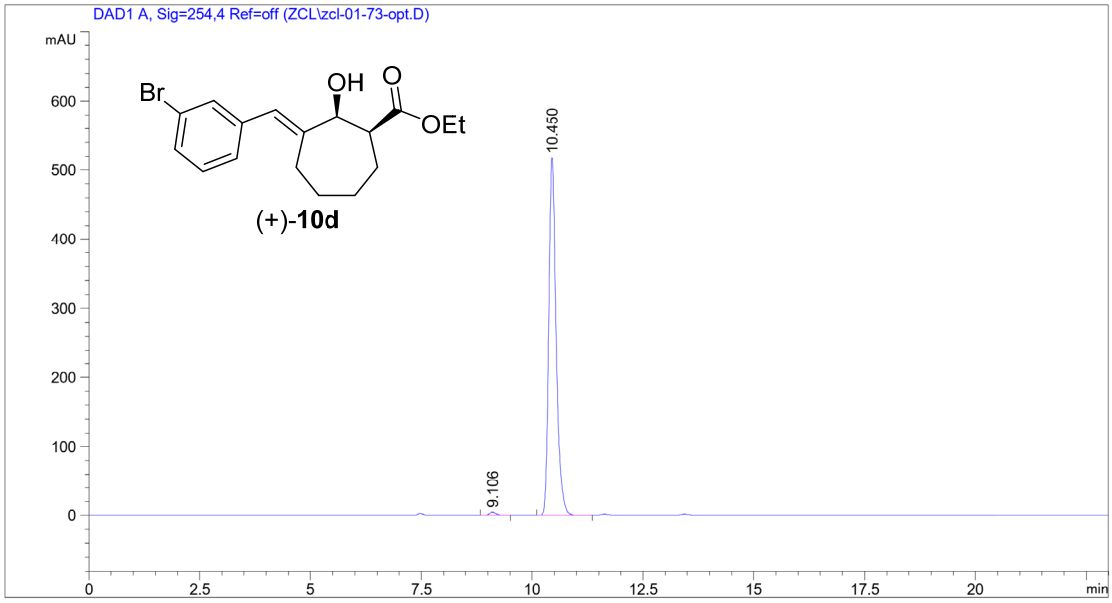


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.063	BB	0.1535	9366.28223	930.33936	100.0000

For compound (+)-10d

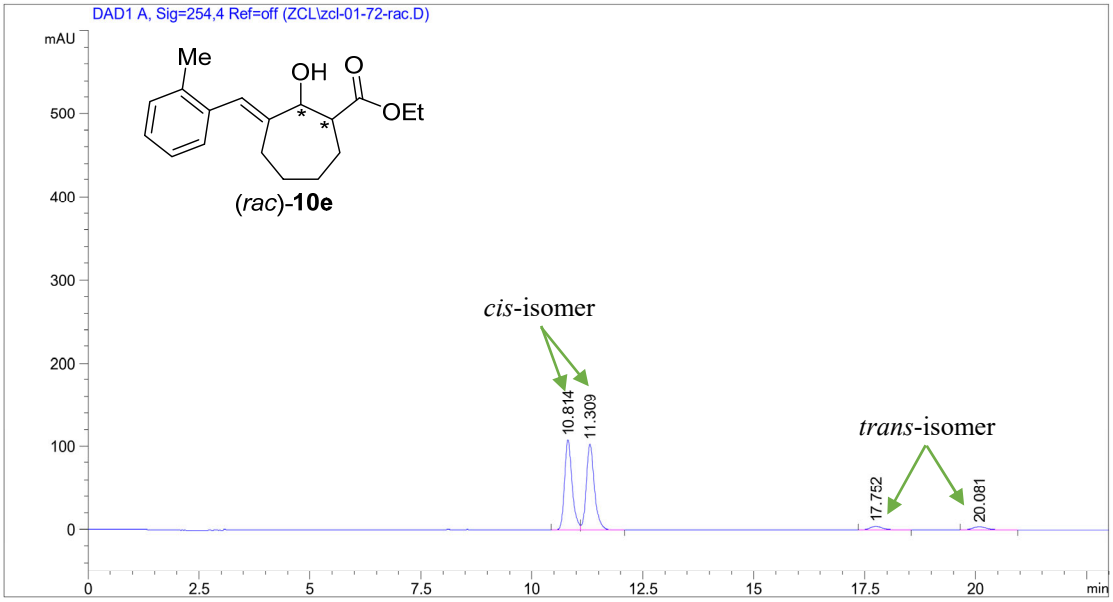


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.097	BB	0.1525	3858.42310	386.39081	44.7596
2	10.442	BB	0.1749	3858.64478	333.73032	44.7621
3	13.615	BB	0.2369	452.26440	29.16910	5.2465
4	16.558	BB	0.2885	451.00116	23.86644	5.2318

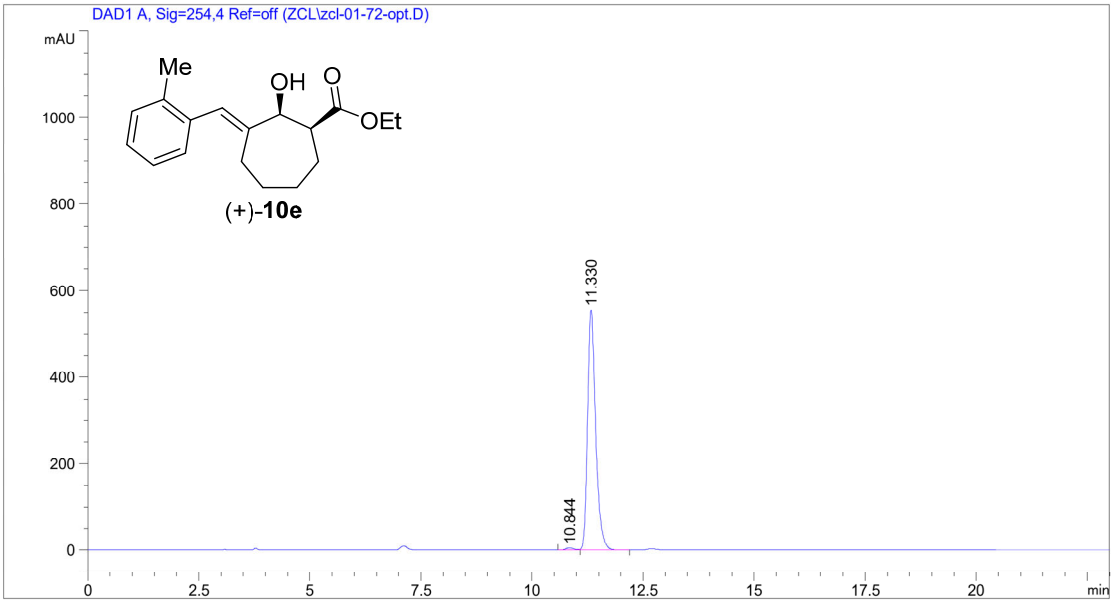


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.106	BB	0.1500	45.42704	4.56920	0.7536
2	10.450	BB	0.1769	5982.45801	517.56171	99.2464

For compound (+)-10e

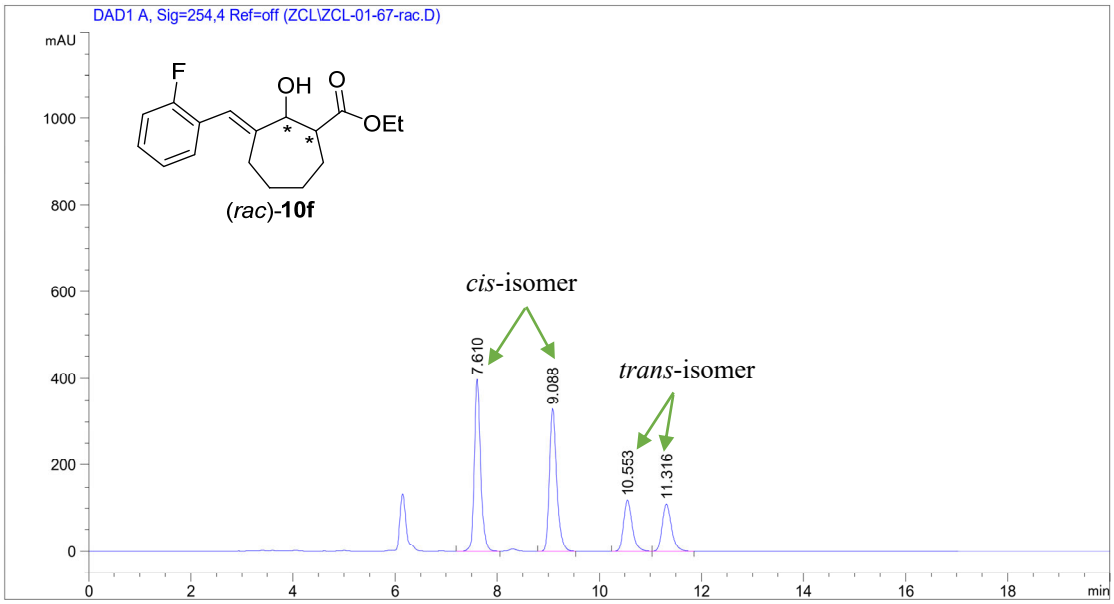


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.814	BV	0.1807	1283.95288	108.02396	46.7429
2	11.309	VB	0.1916	1305.31995	103.14165	47.5208
3	17.752	BB	0.2969	78.92590	3.98856	2.8733
4	20.081	BB	0.3420	78.64236	3.50203	2.8630

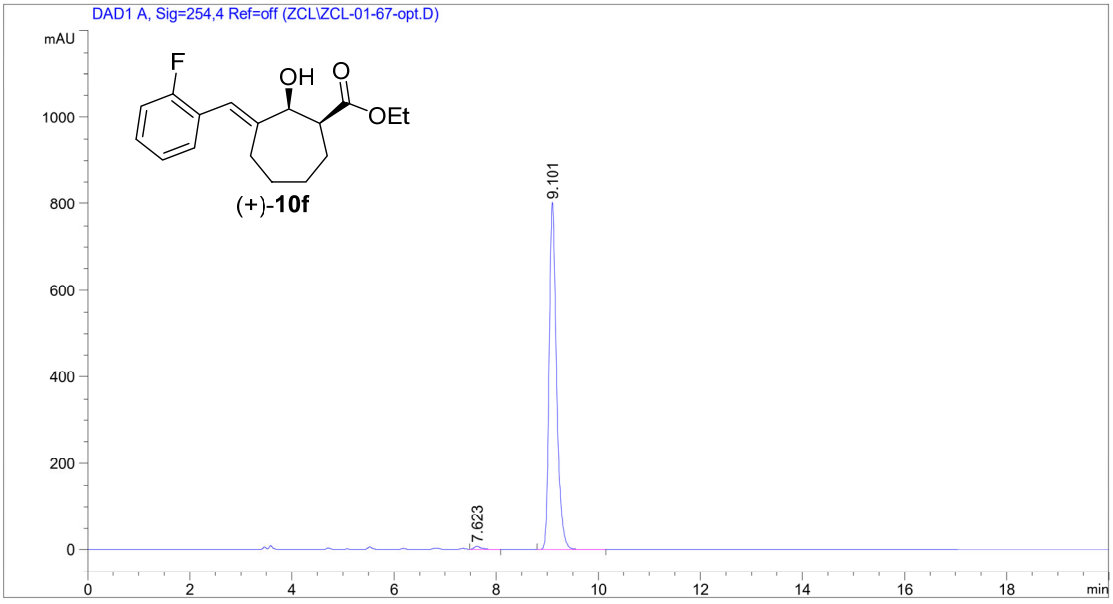


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.844	BV E	0.1770	52.25447	4.58384	0.7358
2	11.330	VB R	0.1921	7049.37988	555.33612	99.2642

For compound (+)-10f

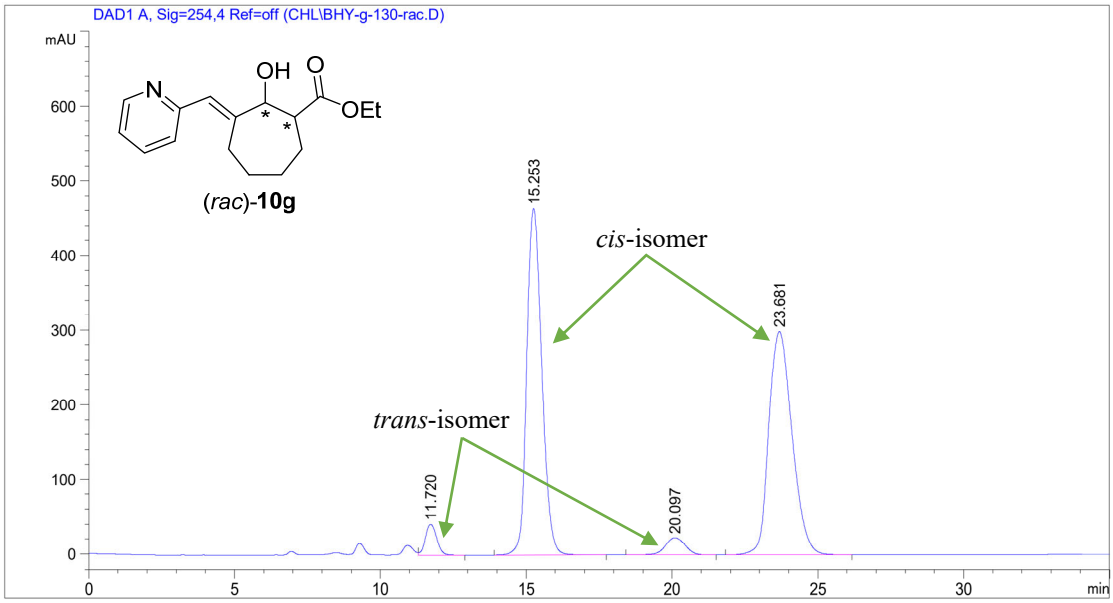


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.610	BB	0.1293	3388.09888	398.13919	35.9796
2	9.088	BB	0.1500	3270.15283	328.85623	34.7271
3	10.553	BB	0.1791	1381.16077	117.54485	14.6671
4	11.316	BB	0.1934	1377.31677	108.99957	14.6263

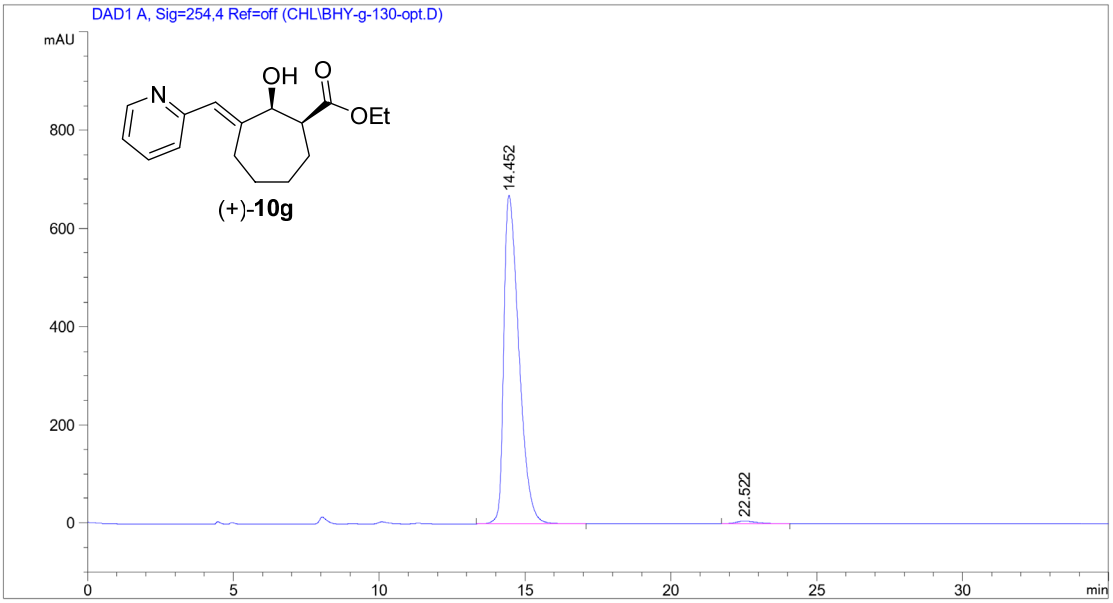


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.623	VB	0.1377	65.83412	6.99909	0.8083
2	9.101	BB	0.1516	8078.94678	801.54016	99.1917

For compound (+)-10g

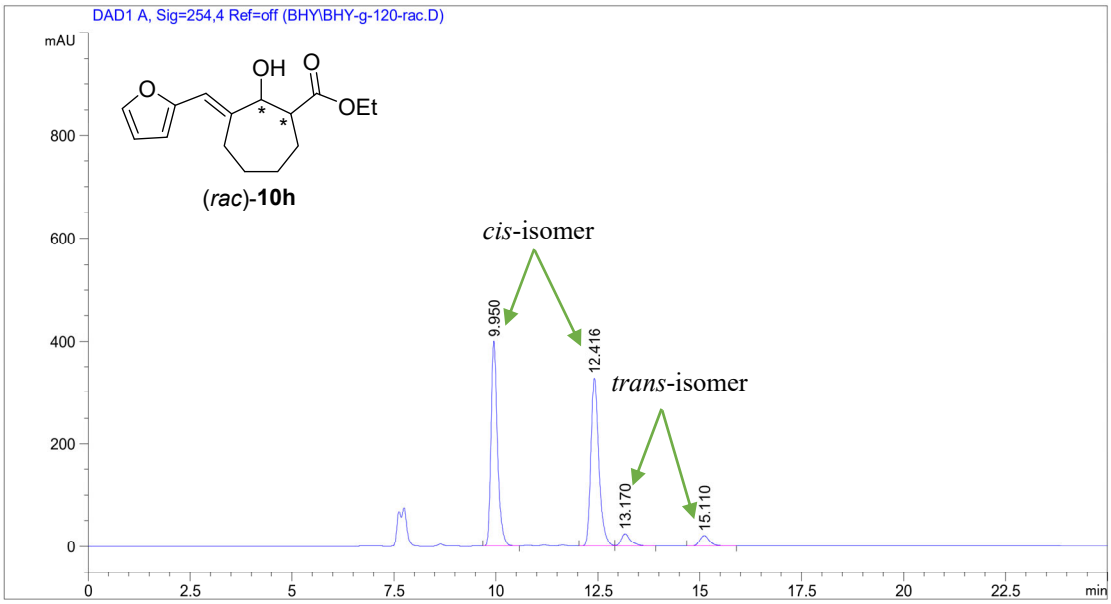


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.720	VB	0.4225	1101.94739	41.14275	3.1117
2	15.253	BB	0.5623	1.66305e4	463.82404	46.9619
3	20.097	BB	0.7460	1083.39404	22.73335	3.0593
4	23.681	BB	0.8767	1.65969e4	299.42075	46.8670

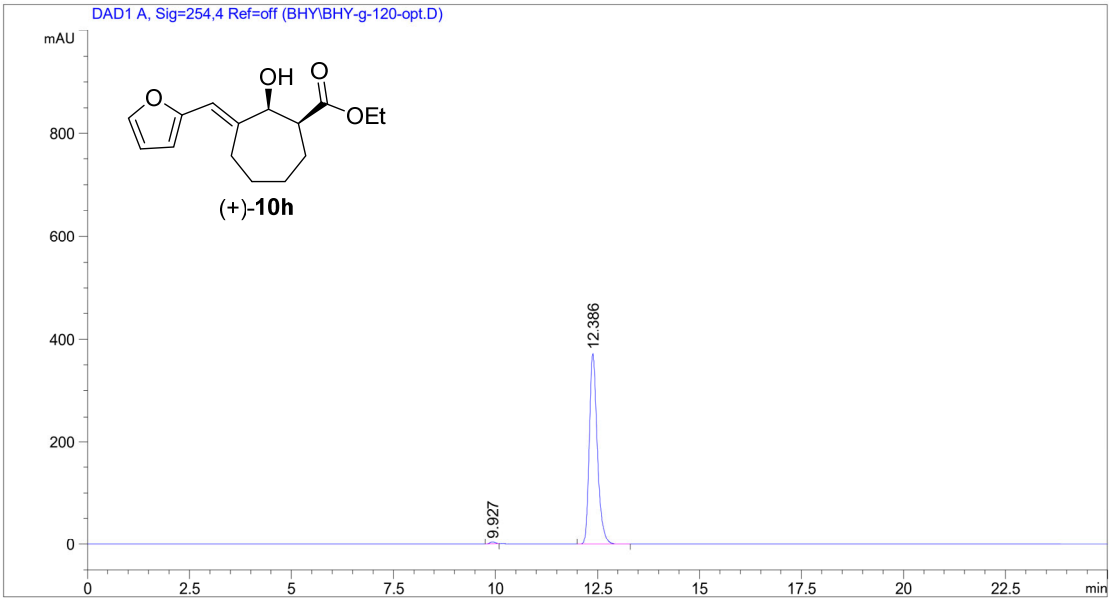


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.452	BB	0.5589	2.40401e4	669.48071	99.0066
2	22.522	BB	0.6368	241.20044	5.10902	0.9934

For compound (+)-10h

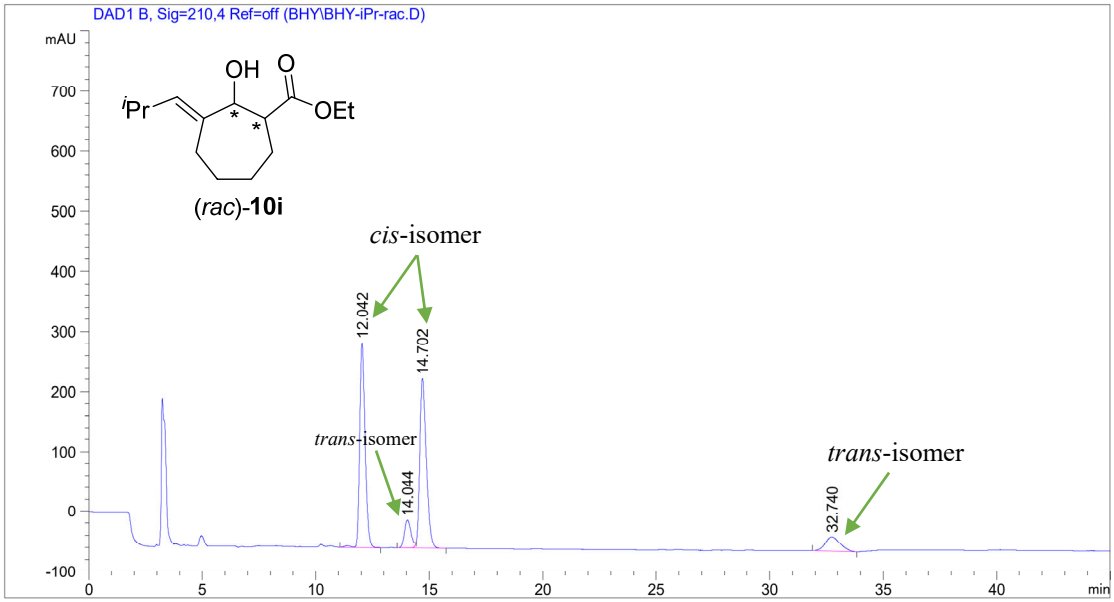


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.950	BB	0.1680	4387.79395	399.80316	45.8049
2	12.416	BV	0.2071	4461.32568	327.12396	46.5726
3	13.170	VB	0.2405	386.09729	23.64948	4.0305
4	15.110	BB	0.2582	344.08435	20.25668	3.5920

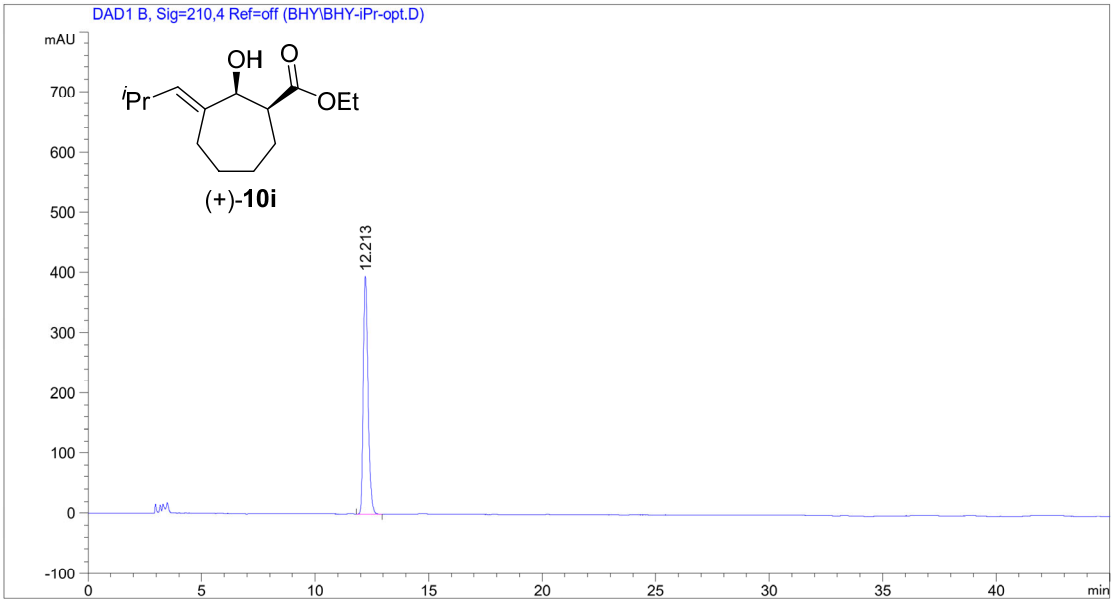


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.927	BB	0.1396	28.97747	3.32631	0.5678
2	12.386	BB	0.2069	5074.91113	372.67474	99.4322

For compound (+)-10i

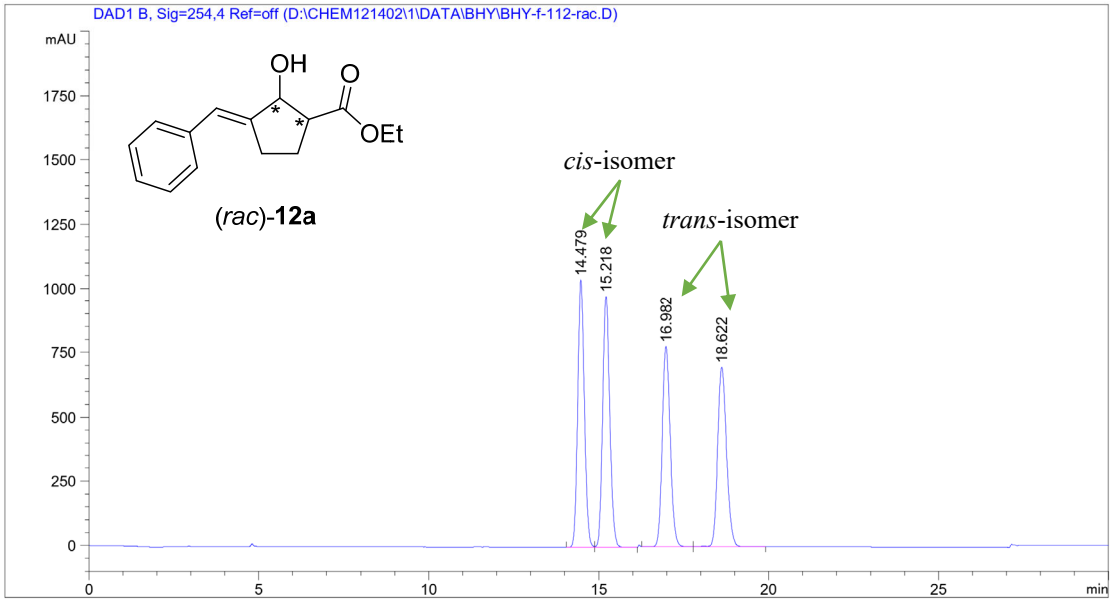


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.042	VB R	0.2534	5654.61670	341.84619	42.2585
2	14.044	BV E	0.3145	926.63690	45.71442	6.9250
3	14.702	VB R	0.3087	5685.34912	282.62888	42.4882
4	32.740	BB	0.6247	1114.40088	24.13250	8.3282

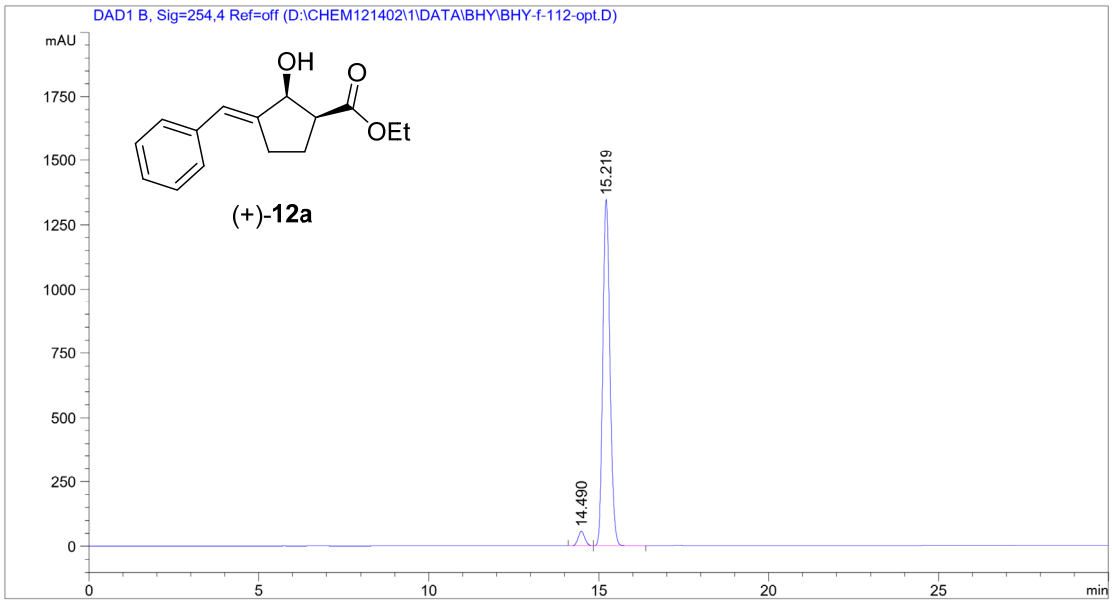


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.213	BB	0.2234	5746.91846	395.88965	100.0000

For compound (+)-12a

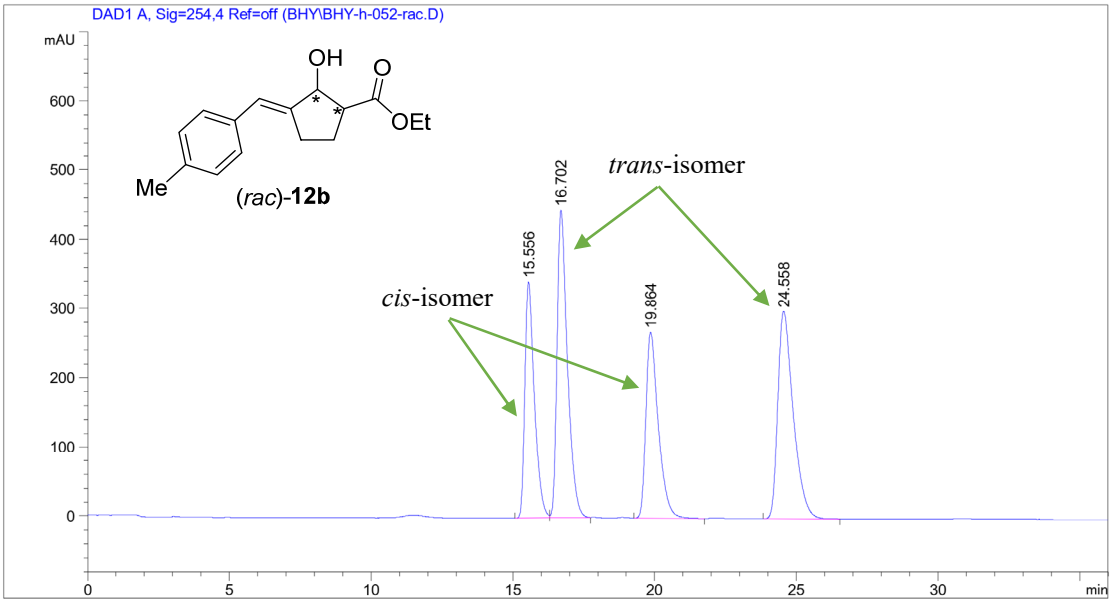


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.479	BV	0.2112	1.41847e4	1039.37915	26.3420
2	15.218	VB	0.2262	1.42355e4	975.59717	26.4363
3	16.982	BB	0.2547	1.27168e4	777.95953	23.6160
4	18.622	VB R	0.2799	1.27112e4	698.74585	23.6056

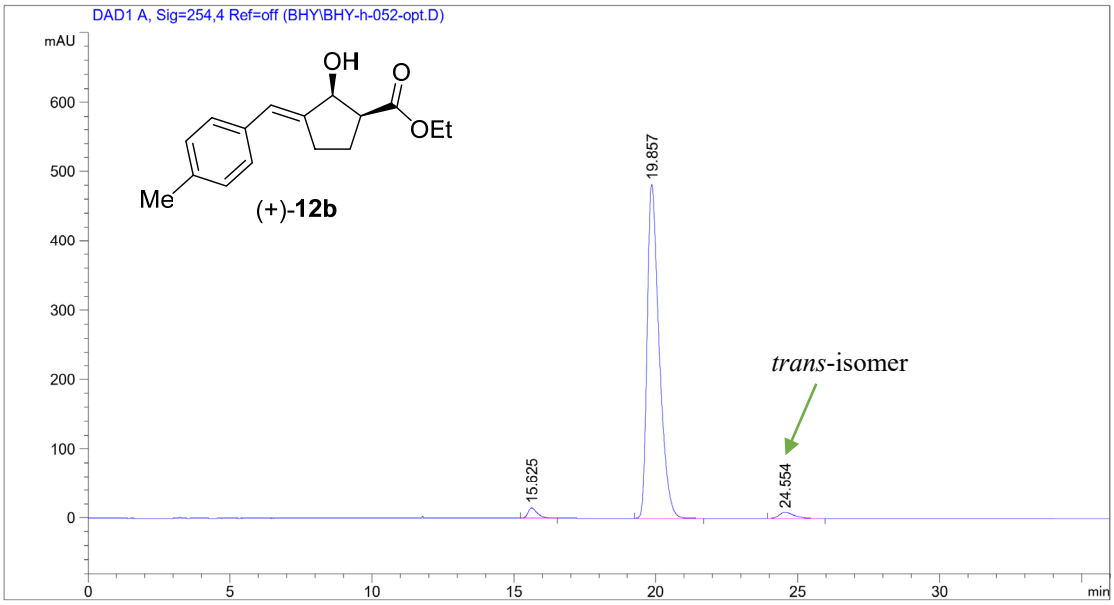


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.490	BV	0.2098	771.18927	57.02386	3.7808
2	15.219	VB	0.2262	1.96262e4	1344.97998	96.2192

For compound (+)-12b

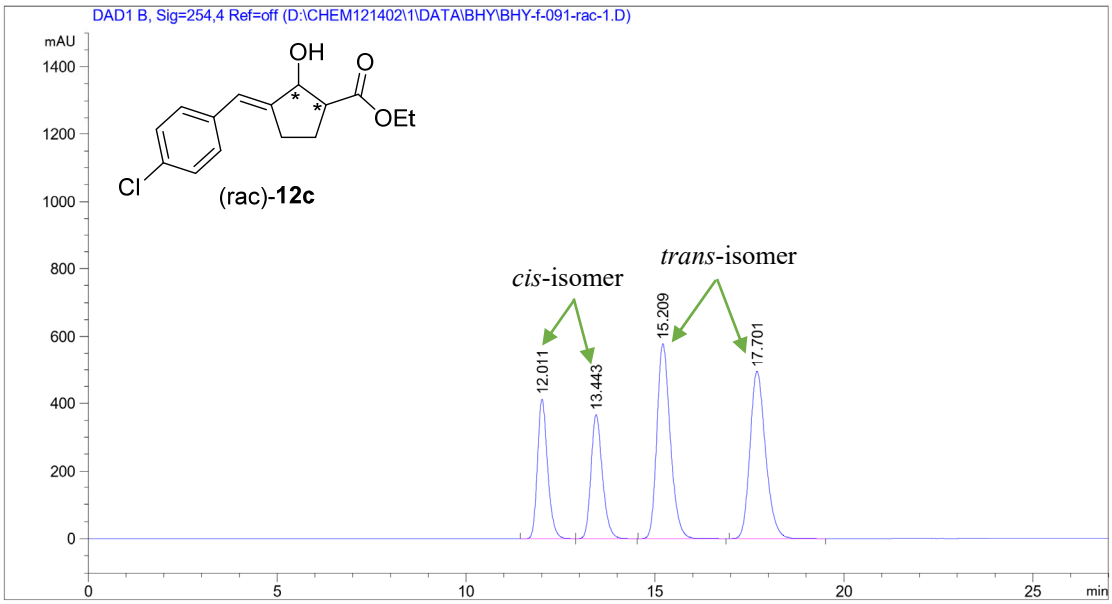


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.556	BV	0.3436	7963.17773	342.01938	20.5441
2	16.702	VB	0.3780	1.12741e4	444.31110	29.0860
3	19.864	BB	0.4536	8189.07617	268.63876	21.1269
4	24.558	BB	0.5654	1.13350e4	299.60165	29.2430

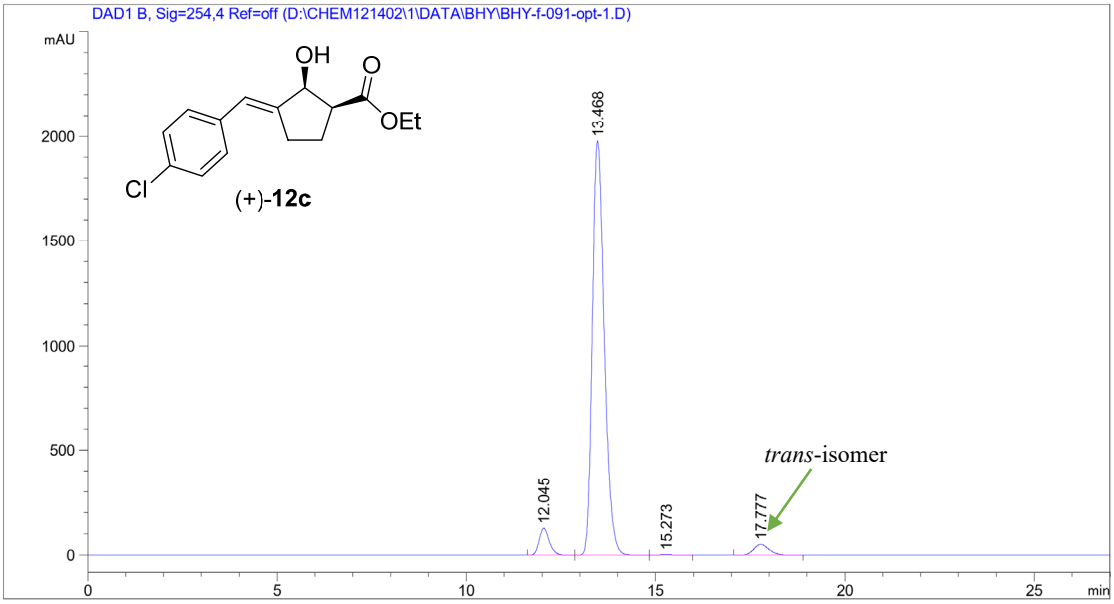


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.625	BB	0.3293	330.79895	14.76842	2.2305
2	19.857	BB	0.4392	1.41823e4	482.13892	95.6296
3	24.554	BB	0.5147	317.34354	8.80044	2.1398

For compound (+)-12c

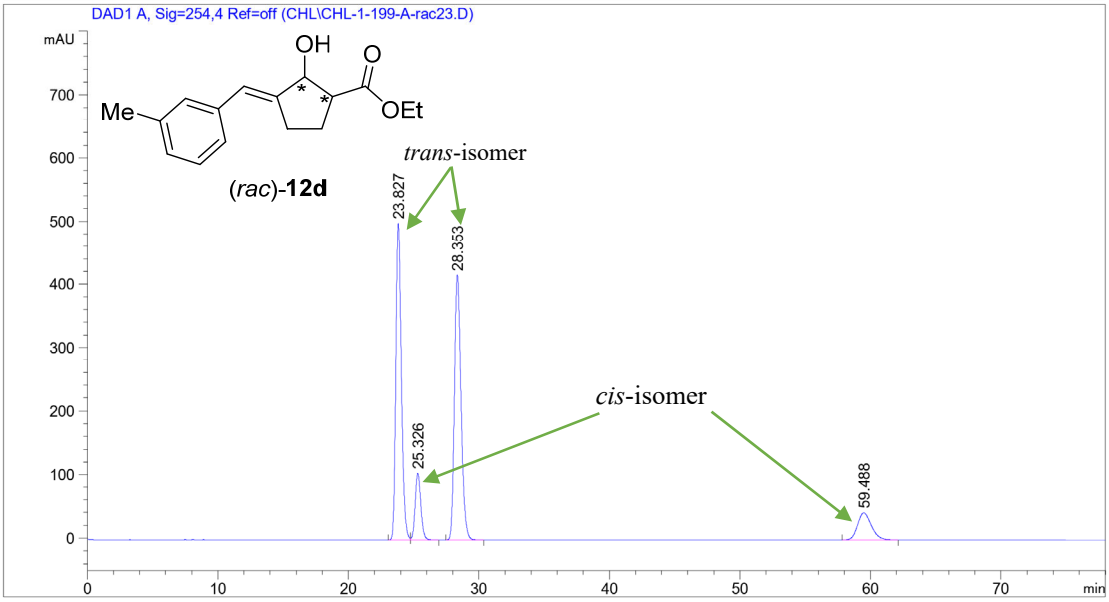


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.011	BB	0.2818	7648.06885	413.45151	17.5528
2	13.443	BB	0.3173	7654.17480	366.96295	17.5668
3	15.209	BB	0.3751	1.41425e4	578.82806	32.4578
4	17.701	BB	0.4389	1.41272e4	495.10403	32.4227

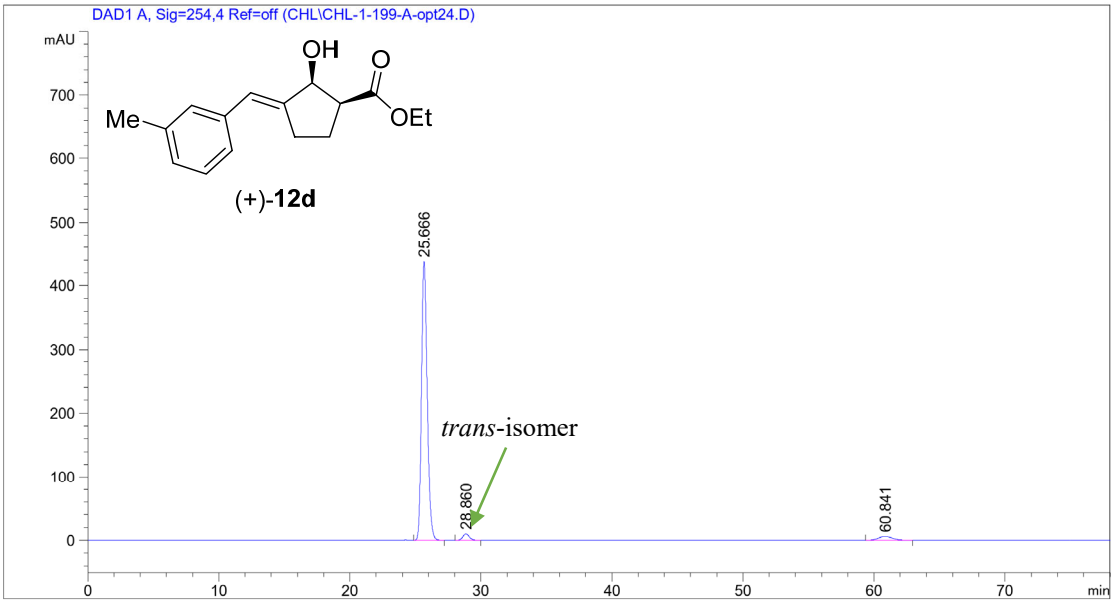


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.045	BB	0.2822	2373.26392	128.09634	5.0313
2	13.468	BB	0.3372	4.32679e4	1977.85266	91.7280
3	15.273	BB	0.3478	69.07902	2.90059	0.1464
4	17.777	BB	0.4352	1459.52222	51.41938	3.0942

For compound (+)-12d

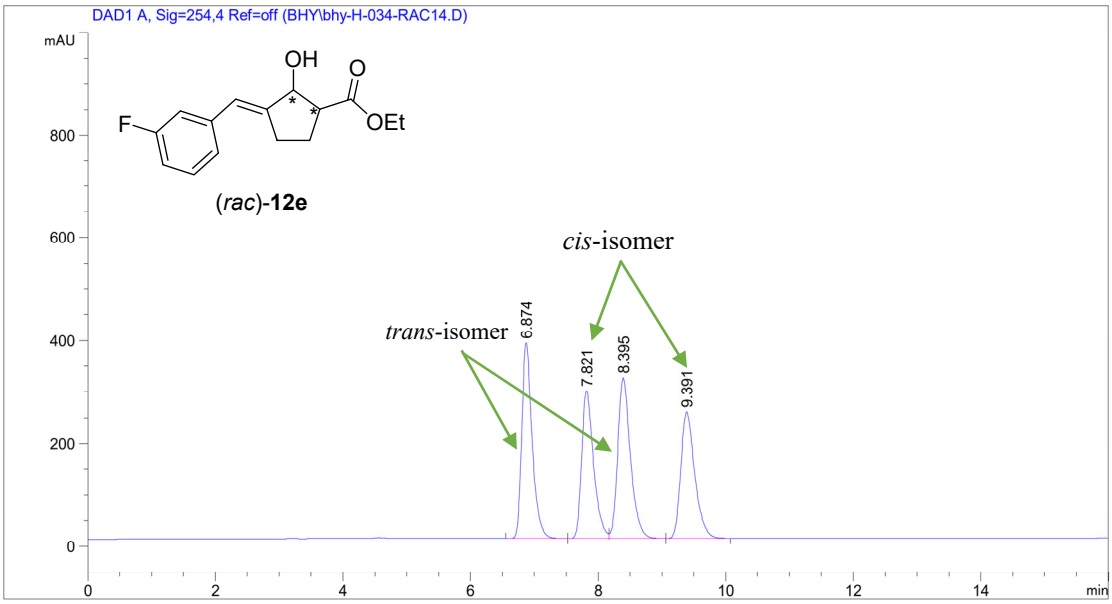


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.827	BV	0.4526	1.46725e4	499.68506	41.1820
2	25.326	VB	0.4603	3148.99097	105.48721	8.8385
3	28.353	BB	0.5428	1.46876e4	417.15201	41.2244
4	59.488	BB	1.0823	3119.29346	42.20421	8.7551

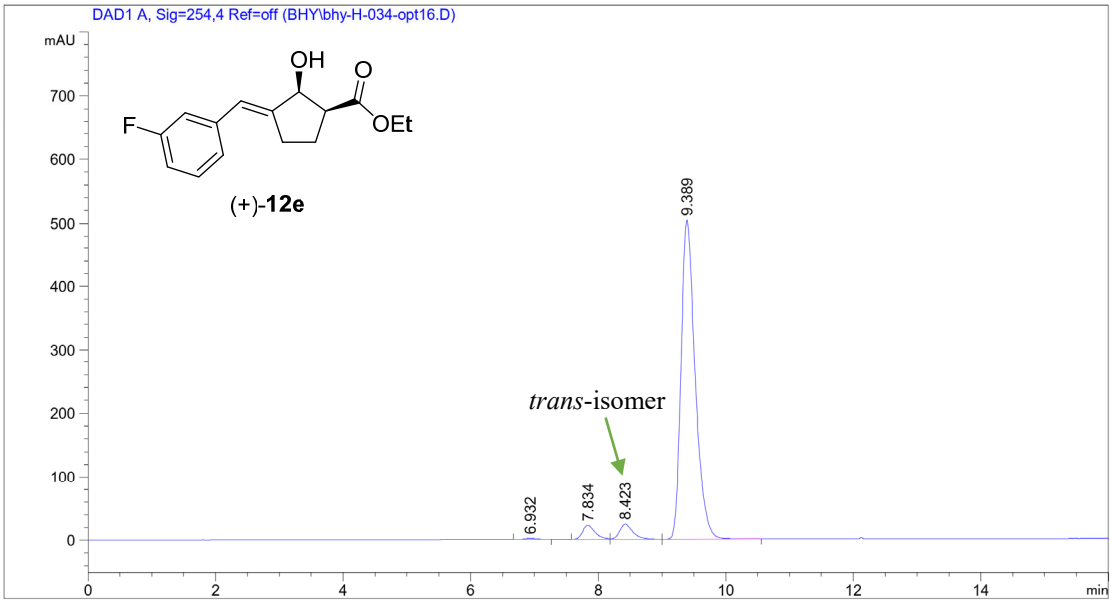


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.666	BB	0.4693	1.33157e4	437.26038	94.1669
2	28.860	BB	0.5354	356.01138	10.09548	2.5177
3	60.841	BB	0.8875	468.82141	6.26149	3.3154

For compound (+)-12e

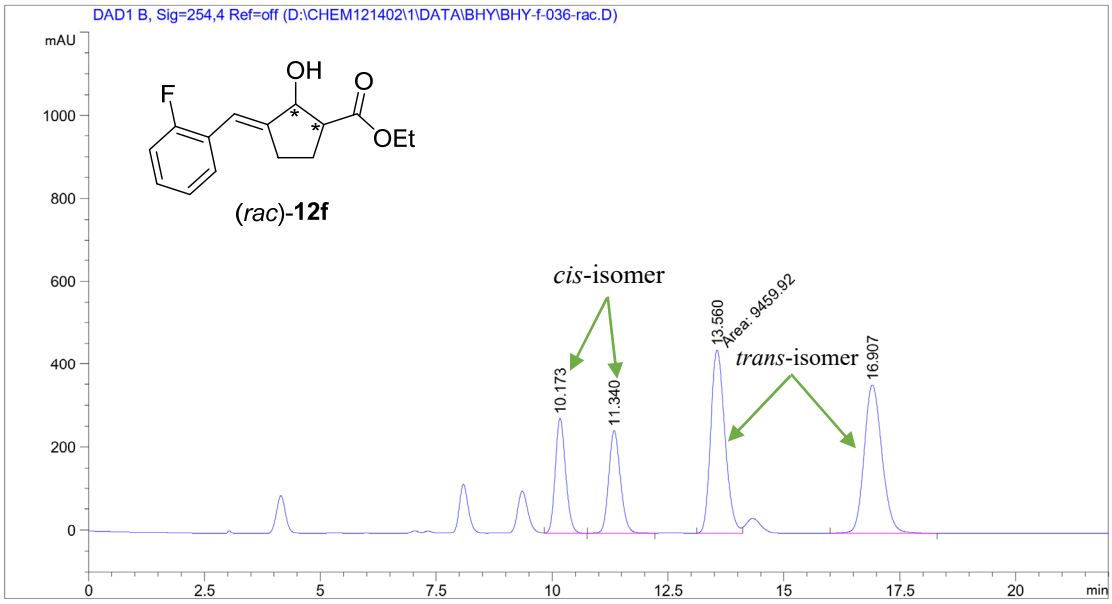


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.874	BB	0.1715	4282.63867	379.85229	26.7021
2	7.821	BV	0.1948	3707.69458	286.77072	23.1173
3	8.395	VB	0.2095	4318.44922	311.99359	26.9254
4	9.391	BB	0.2312	3729.80957	245.59418	23.2552

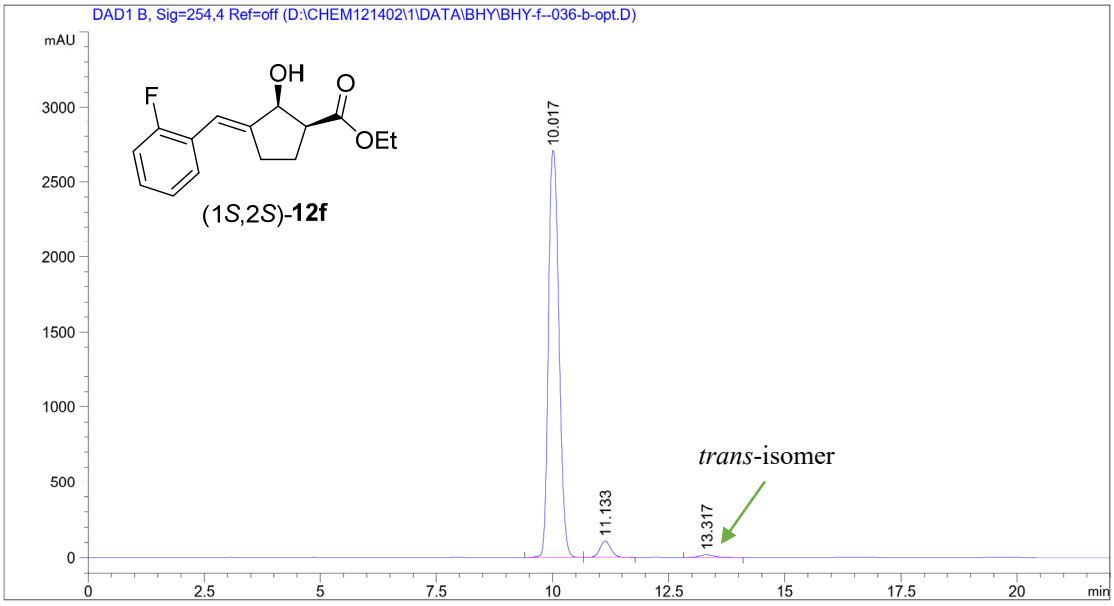


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.932	BB	0.2111	20.73678	1.35067	0.2477
2	7.834	BV	0.1992	294.97824	22.17453	3.5234
3	8.423	VB	0.2127	335.43887	23.75508	4.0067
4	9.389	BB	0.2307	7720.83789	504.00952	92.2222

For compound (1*S*,2*S*)-12f

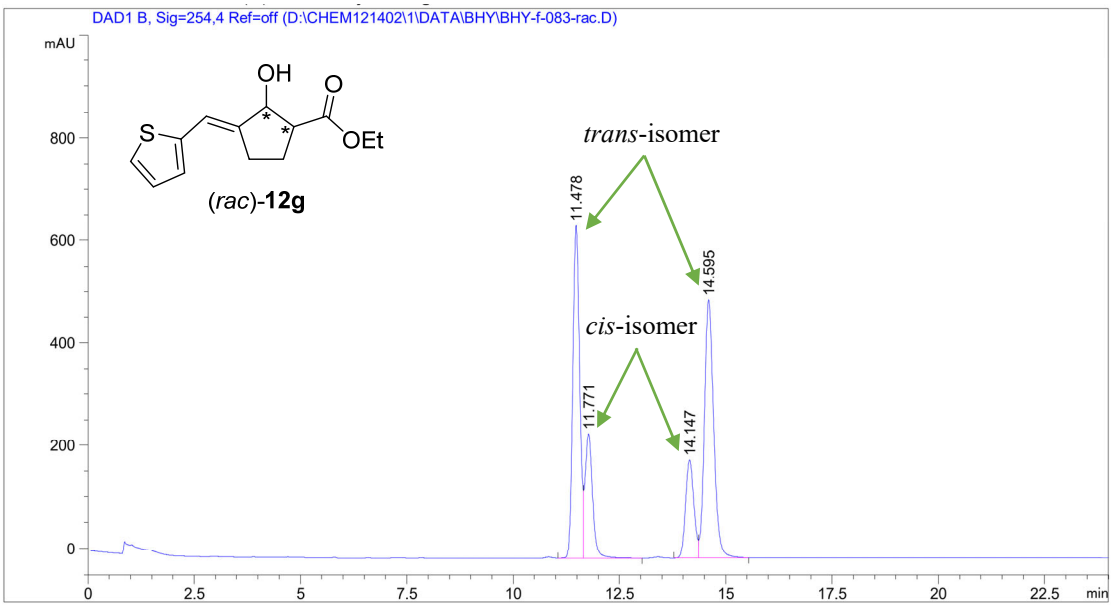


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.173	VB	0.2387	4279.45166	276.24265	15.5009
2	11.340	BB	0.2698	4317.56982	247.19951	15.6390
3	13.560	MM	0.3570	9459.91797	441.67776	34.2655
4	16.907	BB	0.4149	9550.74805	356.15527	34.5945

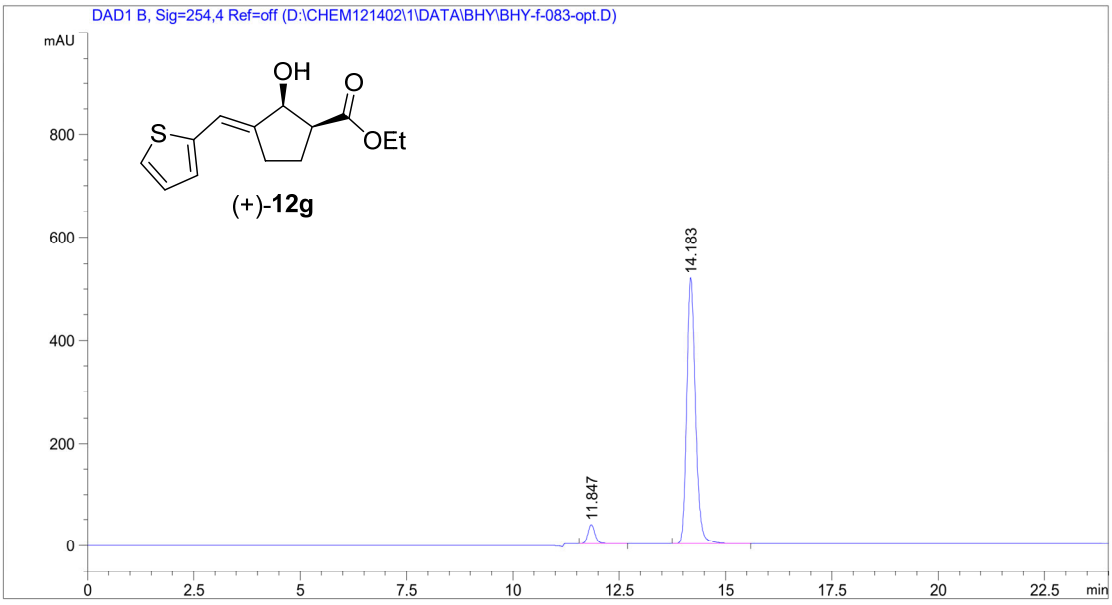


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.017	BB	0.2497	4.26136e4	2707.00000	95.2927
2	11.133	BB	0.2550	1764.95898	107.83104	3.9468
3	13.317	BB	0.3053	340.09198	17.15217	0.7605

For compound (+)-12g

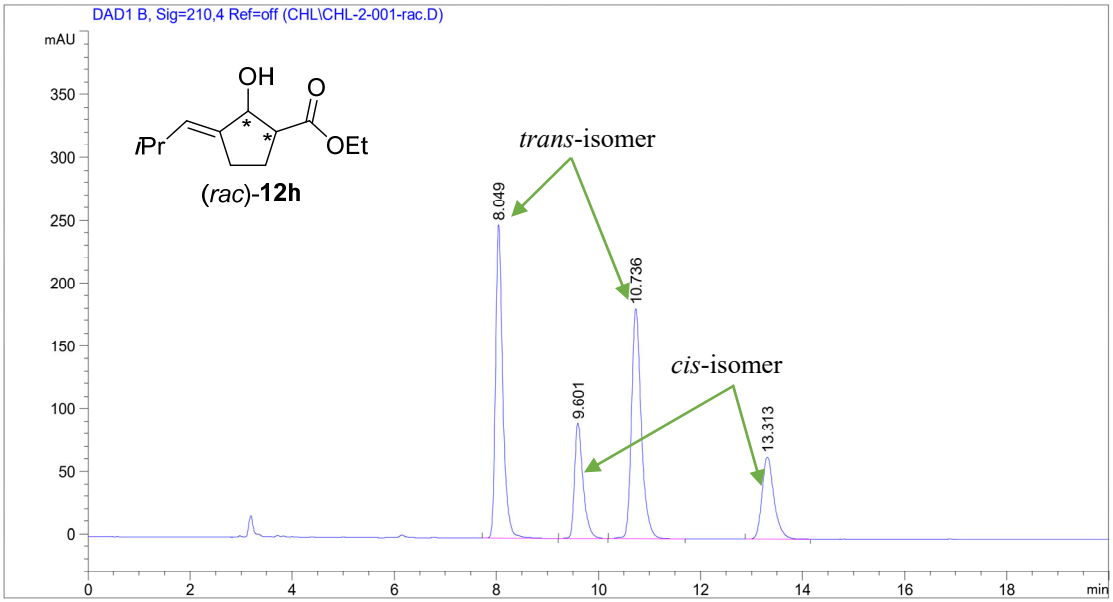


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.478	BV	0.1731	7274.67920	647.13495	35.7785
2	11.771	VB	0.1811	2914.10986	240.99153	14.3322
3	14.147	BV	0.2106	2573.05249	189.31419	12.6548
4	14.595	VB	0.2301	7570.71436	501.62393	37.2344

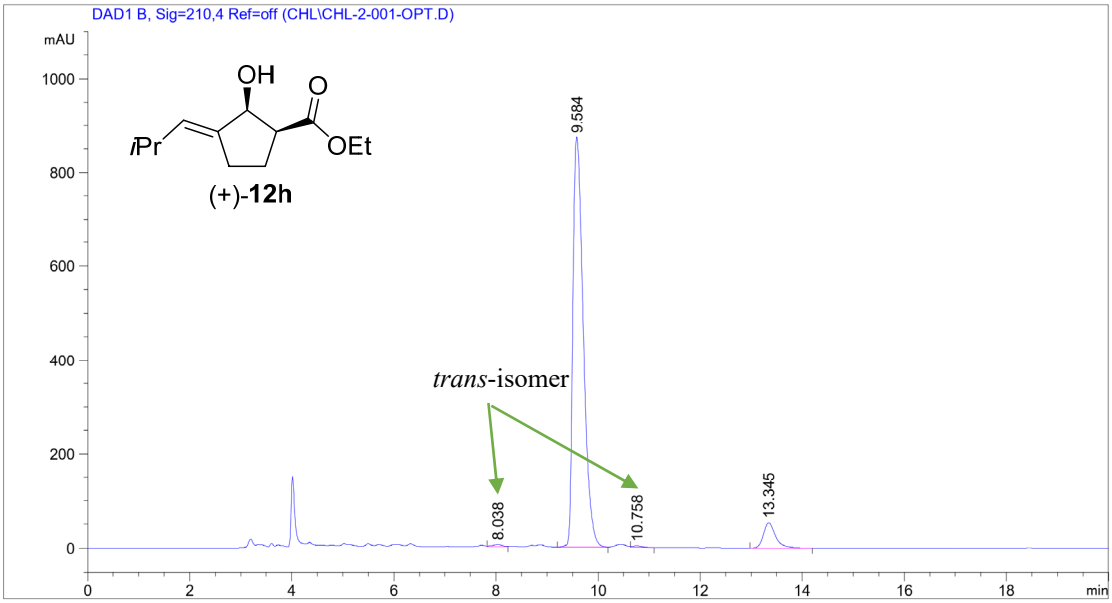


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.847	BB	0.1772	414.29309	36.28078	5.3164
2	14.183	BB	0.2202	7378.49023	518.00116	94.6836

For compound (+)-12h

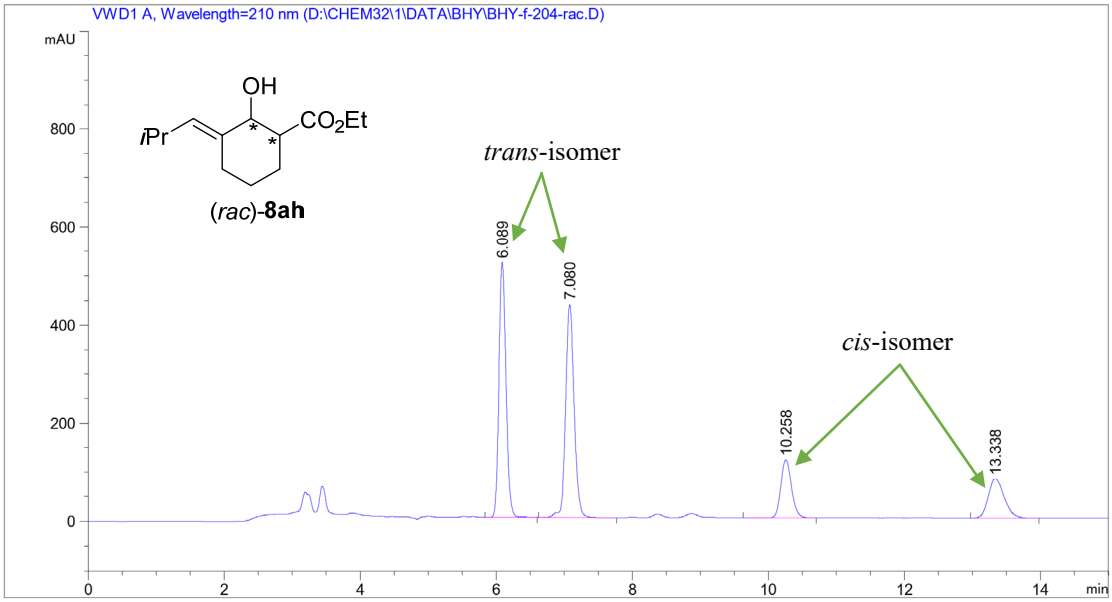


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.049	BB	0.1463	2446.20752	249.77707	35.0088
2	9.601	BB	0.1719	1055.10144	91.93131	15.1001
3	10.736	BB	0.2009	2428.84229	182.90088	34.7603
4	13.313	BB	0.2435	1057.24731	65.77809	15.1308

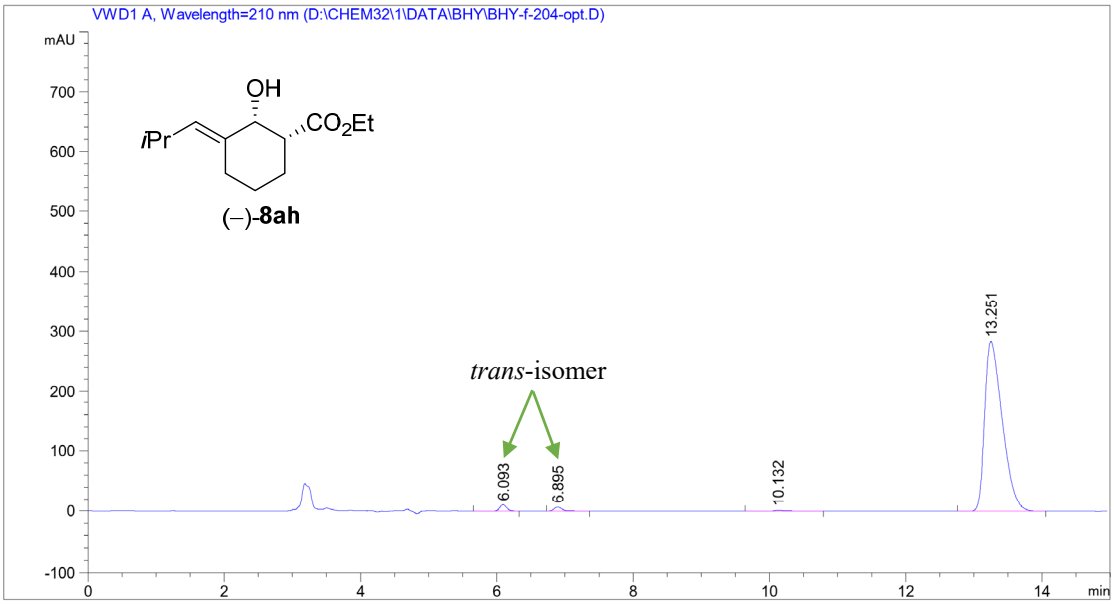


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.038	VV	0.1862	67.34023	5.09533	0.5048
2	9.584	BB	0.2251	1.23587e4	873.14685	92.6485
3	10.758	VB	0.1992	47.21932	3.55009	0.3540
4	13.345	BB	0.2465	866.09106	53.04769	6.4927

For compound (−)-8ah



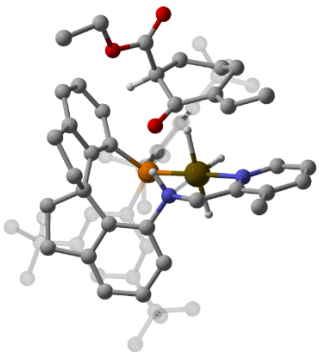
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.089	BV R	0.1110	3744.45264	519.93439	36.9402
2	7.080	VB R	0.1346	3793.97998	435.65695	37.4288
3	10.258	BB	0.1691	1297.22729	119.09271	12.7975
4	13.338	BB	0.2506	1300.87378	80.05941	12.8335



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.093	VB R	0.1130	79.64333	10.67502	1.5131
2	6.895	BB	0.1289	58.92641	6.88333	1.1195
3	10.132	BB	0.2257	32.45448	1.90572	0.6166
4	13.251	BB	0.2752	5092.41406	284.02182	96.7507

(H) The Cartesian coordinates (Å) and energies at 298 K for the optimized structures

TS-*SS*



0 1

Ir	0.86295900	-0.11532500	-1.28005800
P	-0.85099400	0.34043000	0.12828700
C	0.09502100	-2.19039500	2.41402200
C	1.36408300	-2.69712500	3.15397400
C	1.55893600	-1.70237800	4.31121000
C	0.88477600	-0.44728300	3.80996500
C	0.22971500	-0.66127200	2.58055500
C	-0.34165600	0.43979900	1.90204200
C	-0.35783200	1.68583700	2.56240200
C	0.18729600	1.84782600	3.83553600
C	0.84952600	0.78662600	4.44988100
C	-1.19042400	-2.57588900	3.23307900
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C	-1.15506000	-3.89986700	1.25585800
C	-0.13673100	-2.93919100	1.10367200
C	0.57598500	-2.90207700	-0.10467600
C	0.18482900	-3.75548100	-1.15297700
C	-0.84399900	-4.67854600	-0.98850700
C	-1.51758000	-4.76839700	0.23109100
N	1.65183500	-1.99781400	-0.31552600
C	2.79860600	-2.50979800	-1.08560400
C	3.03926600	-1.82731000	-2.40561800
C	4.04870700	-2.29544300	-3.27085100
C	4.27181300	-1.58431900	-4.45162700
C	3.51738700	-0.44405500	-4.73662900
C	2.55692500	-0.03420500	-3.82398700
N	2.33000000	-0.71276900	-2.68215100
C	-1.69064400	1.94768100	-0.24187400
C	-3.07042200	2.02946300	-0.47029500
C	-3.67547500	3.23995500	-0.82687000
C	-2.86423000	4.38211200	-0.92054900
C	-1.47984100	4.33448500	-0.70881200

C	-0.90739000	3.09543100	-0.39023000
C	-5.19181600	3.33257200	-1.06635600
C	-5.84689500	3.93289700	0.19602900
C	-5.81058400	1.94938800	-1.33712400
C	-5.49808500	4.23305600	-2.27930300
C	-0.57697000	5.57326600	-0.81780000
C	0.05746300	5.85081200	0.56180400
C	-1.35415800	6.82455100	-1.25355700
C	0.53445000	5.30651300	-1.85450200
C	-2.30957800	-0.78094500	0.17124100
C	-2.65038700	-1.53951000	-0.95363100
C	-3.87212600	-2.21630600	-1.01087700
C	-4.72980200	-2.13369200	0.10066800
C	-4.41931600	-1.38088000	1.23994700
C	-3.19115100	-0.70201100	1.25326300
C	-4.32854400	-2.97925100	-2.26411900
C	-3.24956100	-2.98010600	-3.35798100
C	-4.66230200	-4.44053400	-1.90256900
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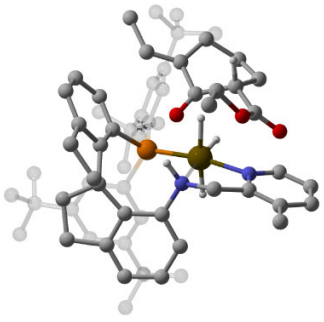
TS-*SR*



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C	-0.85541800	1.71426200	2.59484000
C	-0.57000200	1.94684900	3.94013000
C	0.15990000	1.00705100	4.66848200
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C	0.23388700	-2.83035500	1.30720800
C	1.06665600	-2.71589800	0.18404100
C	0.92767100	-3.65245800	-0.86048600
C	0.03372700	-4.71429600	-0.77176500
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N	2.02190200	-1.67315200	0.03429800
C	3.27750000	-2.06310100	-0.62902000
C	3.41838000	-1.59631100	-2.05430500
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C	3.69229900	-0.57109700	-4.59006200
C	2.75232900	-0.07988100	-3.69674000
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H	3.41299000	-3.15222900	-0.57418400
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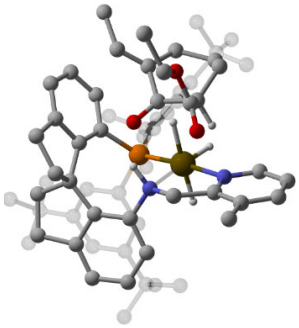

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C	4.45204500	-1.33297900	-4.34194700
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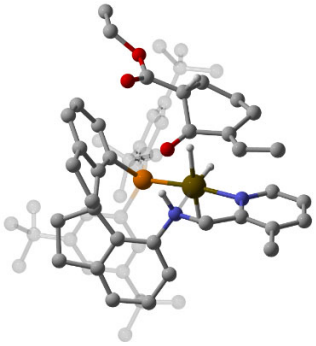
TS-*RS*



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