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Supporting Information

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Lewis Acid Activated Synthesis of Highly Substituted Cyclopentanes by the N-Heterocyclic-Carbene-Catalyzed Addition of Homoenolate Equivalents to Unsaturated Ketoesters**

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Supporting Information

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General Information

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring. THF, toluene, and DMF were purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] Isopropanol (IPA) was distilled from CaH_2. Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain or potassium permangenate stain followed by heating. Infrared spectra were recorded on a Brucker Tensor 37 FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker Avance 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on a Brucker Avance 500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.1 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer.

Trans-cinnamaldehyde, 3-(4-Methoxy-phenyl)-propenal, and (E)-3-(2-methoxyphenyl)acrylaldehyde were used from commercial sources (Sigma Aldrich, Acros Chemical Company respectively). Other enals prepared according to Cacchi.[3]

E-γ-aryl-α-oxobutenoic esters were prepared according to Dujardin[4], Chen[5], Srivastava[6], and Meijer.[7]

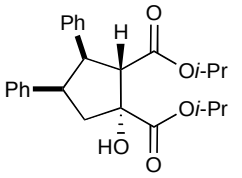
General Procedure for the Synthesis of Cyclopentanols

A oven dried screw-capped vial equipped with a magnetic stirbar was charged with azolium precatalyst **E** (0.2 equiv) and *E*-γ-aryl-α-oxobutenoic ester (3.0 equiv). The vial was capped with a septum cap, removed from the drybox and put under positive N_2 pressure. Into the vial were then successively added cinnamaldehyde (32.2 mg, 0.244 mmol), THF (0.50 M), $Ti(O\textit{i}Pr)_4$ (5.0 equiv.), *i*-PrOH (6.0 equiv) and finally DBU (0.4 equiv) by a syringe. The reaction mixture was stirred at room temperature under static nitrogen. Upon consumption of the aldehyde and transesterification (all reactions were

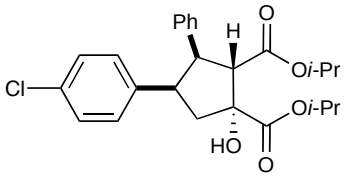
[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518.
[2] D. D. Perrin, W. L. Armarego, *Purification of Laboratory Chemicals;* 3rd Ed., Pergamon Press, Oxford. 1988.
[3] G. Battistuzzi, S. Cacchi, G. Fabrizi, *Org. Lett.* **2003**, *5*, 777-780.
[4] G. Dujardin, S. Leconte, A. Benard, E. Brown, *Synlett* **2001**, 147–149.
[5] Y-C. Wu, L. Liu, H-J. Li, D. Wang, Y-J. Chen, *J. Org. Chem.*, **2006**, *71*, 6592-6595.
[6] B. K. Srivastava,* A. Joharapurkar, S. Raval, J. Z. Patel, R. Soni, P. Raval, A. Gite, A. Goswami, N. Sadhwani, N. Gandhi, H. Patel, B. Mishra, M. Solanki, B. Pandey, M. R. Jain, and P. R. Patel, *J. Med. Chem.* **2007,** *50,* 5951–5966.
[7] L. H. P. Meijer, J. C. G. Van Niel, U. K. Pandit, *Tetrahedron* **1984**, *40,* 5185–5195.

completed within 48 hours) the reaction mixture was filtered through a short plug of SiO_2 and washed with EtOAc. The solution was concentrated under reduced pressure and purified by flash chromatography with EtOAc/hexanes to afford the corresponding cyclopentanol.

The corresponding racemic compounds were prepared by employing the same protocol but with achiral azolium precatalyst **A** (20 mol%) and no *i*-PrOH.

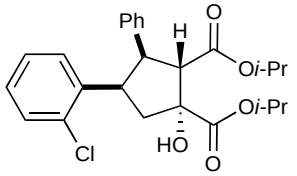


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3,4-diphenylcyclopentane-1,2-dicarboxylate (3): Prepared according to the general procedure using *trans*-cinnamaldehyde (31 μL, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 78 mg (78% yield) of **3** (20:1 dr) as a yellowish oil. Analytical data for **3**: IR (film) 3502, 3058, 3030, 2981, 2920, 2851, 1737, 1679, 1604, 1498, 1455, 1375, 1321, 1263, 1241, 1182, 1107, 1067, 911, 742, 699 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.06-6.97 (m, 6H), 6.97-6.90 (m, 4H), 5.26 (sept, *J* = 6.3 Hz, 1H), 4.97 (sept, *J* = 6.2 Hz, 1H), 4.26 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.05 (ddd, *J* = 9.8, 7.3, 7.3 Hz, 1H), 3.99 (s, 1H), 3.85 (d, *J* = 9.2 Hz, 1H), 2.80 (dd, *J* = 13.4, 10.1 Hz, 1H), 2.36 (dd, *J* = 13.5, 7.2 Hz, 1H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.43 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.8, 170.2, 140.9, 140.7, 128.7(2C), 128.5(2C), 127.8(2C), 127.7(2C), 126.1, 126.0, 81.5, 70.7, 68.5, 59.0, 50.1, 47.9, 44.3, 22.0(2C), 21.9(2C); LRMS (ESI): Mass calcd for $C_{25}H_{31}O_5$ $[M+H]^+$, 411. Found $[M+H]^+$, 411. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OD-H, 5% *i*-PrOH/Hexanes, 0.50 mL/min, 210 nm), Rt (major) = 13.2 min, Rt (minor) = 18.7 min; ee = 95%.

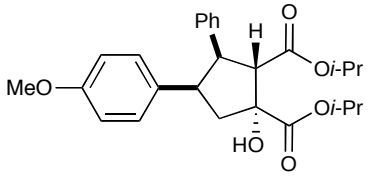


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 4-(4-chlorophenyl)-1-hydroxy-3-phenylcyclopentane-1,2-dicarboxylate (4): Prepared according to the general procedure using *trans*-cinnamaldehyde (31 μL, 0.244 mmol) and (*E*)-methyl 4-(4-chlorophenyl)-2-oxobut-3-enoate (164 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 75 mg (69% yield) of **4** (20:1 dr) as a white solid. Analytical data for **4**: IR (film) 3518, 3069, 3030, 2981, 2921, 2851, 1737, 1699, 1664, 1603, 1494, 1454, 1375, 1283, 1248, 1182, 1107, 1014, 911, 830, 738, 700 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.08-6.99 (m, 5H), 6.91-6.90 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.25 (sept, *J* = 6.3 Hz, 1H), 4.96 (sept, *J* = 6.3 Hz, 1H), 4.24 (dd, *J* = 9.3, 9.3 Hz, 1H), 4.01 (ddd, *J* = 9.9, 7.2, 7.2 Hz, 1H), 3.97 (s, 1H), 3.82 (d, *J* = 9.0 Hz, 1H), 2.72 (dd, *J* = 13.4, 10.3 Hz,

1H), 2.33 (dd, *J* = 13.4, 7.1 Hz, 1H), 1.44 (d, *J* = 6.3 Hz, 3H), 1.42 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.6, 170.0, 140.5, 139.4, 131.8, 129.8(2C), 128.7(2C), 128.0(2C), 127.8(2C), 126.4, 81.3, 70.9, 68.6, 59.1, 49.9, 47.4, 44.3, 22.0, 21.9(2C), 21.8; LRMS (ESI): Mass calcd for $C_{25}H_{30}O_5Cl$ $[M+H]^+$, 445. Found $[M+H]^+$, 445. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 1.0 mL/min, 210 nm), Rt (major) = 16.0 min, Rt (minor) = 12.8 min; ee = 97%.

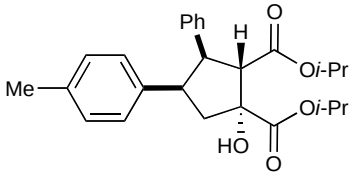


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 4-(2-chlorophenyl)-1-hydroxy-3-phenylcyclopentane-1,2-dicarboxylate (5): Prepared according to general procedure using cinnamaldehyde (15.4 μL, 0.12 mmol) and (*E*)-methyl 4-(2-chlorophenyl)-2-oxobut-3-enoate (82 mg, 0.37 mmol) and purified by flash chromatography using 5% EtOAc/hexanes to 15% EtOAc/hexanes to afford 39 mg (72% yield) of **5** (13:1 dr) as a yellowish oil. Analytical data for **5**: IR (film) 3499, 2981, 2937, 1737, 1375, 1244, 1196, 1182, 1107, 1055, 911, 754, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 1.3, 7.5 Hz, 1H), 7.05-6.91 (m, 8H), 5.25 (sept, *J* = 6.3 Hz, 1H), 4.99 (sept, *J* = 6.3 Hz, 1H), 4.53-4.45 (m, 2H), 3.94 (s, 1H), 3.82 (d, *J* = 6.9 Hz, 1H), 2.86-2.77 (m, 1H), 2.23-2.17 (m, 1H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.41 (d, *J* = 6.2 Hz, 3H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 169.9, 141.2, 138.1, 134.7, 129.0, 128.5(2C), 128.0, 127.6(2C), 127.3, 126.1, 125.8, 81.0, 70.6, 68.5, 60.5, 47.3, 44.7, 43.0, 21.9, 21.8(2C), 21.7; LRMS (ESI): Mass calcd for $C_{25}H_{29}NaClO_5$ $[M+Na]^+$, 467. Found $[M+Na]^+$, 467; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OD-H, 3% *i*-PrOH/Hexanes, 0.5 mL/min, 210 nm), Rt (major) = 12.7 min, Rt (minor) = 18.1 min; ee = 95%.

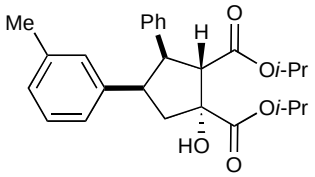


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-4-(4-methoxyphenyl)-3-phenylcyclopentane-1,2-dicarboxylate (6): Prepared according to the general procedure using *trans*-cinnamaldehyde (31 μL, 0.244 mmol) and (*E*)-methyl 4-(4-methoxyphenyl)-2-oxobut-3-enoate (164 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 88 mg (82% yield) of **4** (20:1 dr) as a orange oil. Analytical data for **4**: IR (film) 3502, 3062, 3031, 2981, 2932, 2852, 1735, 1612, 1584, 1514, 1455, 1375, 1250, 1180, 1107, 1038, 971, 910, 830, 738, 701 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.06-6.99 (m, 3H), 6.92-6.90 (m, 2H), 6.84 (m, 2H), 6.59-6.58 (m, 2H), 5.25 (sept, *J* = 6.3 Hz, 1H), 4.96 (sept, *J* = 6.3 Hz, 1H), 4.20 (dd, *J* = 9.4, 9.4 Hz, 1H), 4.01-

3.96 (m, 2H), 3.83 (d, *J* = 9.2 Hz, 1H), 3.68 (s, 3H), 2.73 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.33 (dd, *J* = 13.5, 7.2 Hz, 1H), 1.44 (d, *J* = 6.3 Hz, 3H), 1.43 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.8, 170.3, 157.8, 140.8, 133.0, 129.4(2C), 128.8(2C), 127.9(2C), 126.1, 113.1(2C), 81.4, 70.7, 68.5, 58.9, 55.2, 50.1, 47.2, 44.6, 22.0(2C), 21.9(2C); LRMS (ESI): Mass calcd for $C_{26}H_{33}O_6$ $[M+H]^+$, 441. Found $[M+H]^+$, 441. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 0.75 mL/min, 210 nm), Rt (major) = 27.0 min, Rt (minor) = 22.1 min; ee = 96%.

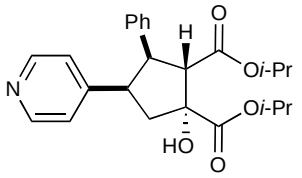


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-phenyl-4-*p*-tolylcyclopentane-1,2-dicarboxylate (7): Prepared according to general procedure using cinnamaldehyde (29.7 μL, 0.236 mmol) and (*E*)-methyl 2-oxo-4-*p*-tolylbut-3-enoate (145 mg, 0.708 mmol) and purified by flash chromatography using 7.5% EtOAc/hexanes to 20% EtOAc/hexanes to afford 82 mg (82% yield) of **7** (20:1 dr) as a yellowish oil. Analytical data for **7**: IR (film) 3498, 2980, 2935, 1737, 1375, 1241, 1226, 1181, 1108, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07-6.97 (m, 3H), 6.93-6.89 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 5.24 (sept, *J* = 6.3 Hz, 1H), 4.95 (sept, *J* = 6.3 Hz, 1H), 4.22 (d, *J* = 9.4, 9.4 Hz, 1H), 4.00 (ddd, *J* = 7.8, 9.7, 9.7 Hz, 1H), 3.97 (s, 1H), 3.83 (d, *J* = 9.2 Hz, 1H), 2.76 (dd, *J* = 10.1, 13.3 Hz, 1H), 2.34 (dd, *J* = 7.2, 13.5 Hz, 1H), 2.18 (s, 3H), 1.44 (d, *J* = 6.3 Hz, 3H), 1.42 (d, *J* = 6.2 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 170.2, 140.8, 137.7, 135.4, 128.7(2C), 128.33(2C), 128.31(2C), 127.7(2C), 126.0, 81.3, 70.6, 68.4, 58.9, 50.0, 47.5, 44.4, 21.9, 21.8(3C), 21.0; LRMS (ESI): Mass calcd for $C_{26}H_{32}NaO_5$ $[M+Na]^+$, 447. Found $[M+Na]^+$, 447; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OD-H, 3% *i*-PrOH/Hexanes, 0.5 mL/min, 210 nm), Rt (major) = 11.7 min, Rt (minor) = 13.9 min; ee = 97%.

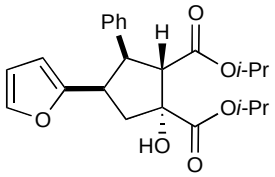


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-phenyl-4-*m*-tolylcyclopentane-1,2-dicarboxylate (8): Prepared according to general procedure using cinnamaldehyde (29.7 μL, 0.236 mmol) and (*E*)-methyl 2-oxo-4-*m*-tolylbut-3-enoate (145 mg, 0.708 mmol) and purified by flash chromatography using 7.5% EtOAc/hexanes to 20% EtOAc/hexanes to afford 68 mg (68% yield) of **8** (20:1 dr) as a yellowish oil. Analytical data for **8**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06-6.96 (m, 3H), 6.94-6.88 (m, 3H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.73-6.70 (m, 2H), 5.25 (sept, *J* = 6.3 Hz, 1H), 4.96 (sept, *J* = 6.3 Hz, 1H), 4.23 (dd, *J* =

9.6, 9.6 Hz, 1H), 3.99 (ddd, *J* = 7.6, 9.7, 9.7 Hz, 1H), 3.98 (s, 1H), 3.84 (d, *J* = 9.3 Hz, 1H), 2.77 (dd, *J* = 9.9, 13.4 Hz, 1H), 2.34 (dd, *J* = 7.2, 13.5 Hz, 1H), 2.15 (s, 3H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.43 (d, *J* = 6.2 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 170.1, 140.7, 140.6, 137.0, 129.3, 128.6(2C), 127.5(2C), 127.4, 126.6, 126.0, 125.4, 81.4, 70.6, 68.4, 58.7, 50.0, 47.7, 44.2, 21.9, 21.7(3C), 21.3; IR (film) 3501, 2981, 2937, 1736, 1375, 1235, 1182, 1107, 701 cm^{-1}; LRMS (ESI): Mass calcd for $C_{26}H_{32}NaO_5$ $[M+Na]^+$, 447. Found $[M+Na]^+$: 447; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OD-H, 5% *i*-PrOH/Hexanes, 0.5 mL/min, 210 nm), Rt (major) = 11.5 min, Rt (minor) = 15.7 min; ee = 97%.

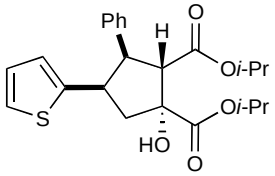


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-phenyl-4-(pyridin-4-yl)cyclopentane-1,2-dicarboxylate (9): Prepared according to general procedure using cinnamaldehyde (12.6 μL, 0.10 mmol) and (*E*)-methyl 2-oxo-4-(pyridin-4-yl)but-3-enoate (57 mg, 0.30 mmol) and purified by flash chromatography using 30% EtOAc/hexanes to 70% EtOAc/hexanes to afford 21 mg (51% yield) of **9** (12:1 dr) as a yellowish oil. Analytical data for **9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s broad, 2H), 7.08-6.99 (m, 3H), 6.93-6.90 (m, 2H), 6.88-6.82 (m, 2H), 5.26 (sept, *J* = 6.3 Hz, 1H), 4.97 (sept, *J* = 6.3 Hz, 1H), 4.31 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.01 (ddd, *J* = 7.1, 10.0 Hz, 1H), 3.98 (s, 1H), 3.81 (d, *J* = 9.0 Hz, 1H), 2.76 (dd, *J* = 10.3, 13.3 Hz, 1H), 2.35 (dd, *J* = 7.0, 13.4 Hz, 1H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.43 (d, *J* = 6.2 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.11 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 169.6, 150.0, 149.0(2C), 139.9, 128.4(2C), 128.0(2C), 126.5(2C), 123.7, 81.2, 70.9, 68.6, 59.1, 49.5, 47.1, 43.3, 21.9, 21.73, 21.71, 21.70; IR (film) 3495, 2981, 2930, 1738, 1375, 1231, 1182, 1108, 702 cm^{-1}; LRMS (ESI): Mass calcd for $C_{24}H_{30}O_5$ $[M+H]^+$, 412. Found $[M+H]^+$, 412; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 12% *i*-PrOH/Hexanes, 1 mL/min, 210 nm), Rt (major) = 25.6 min, Rt (minor) = 14.4 min; ee = 97%.

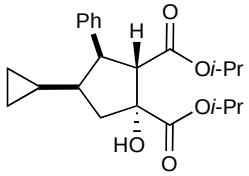


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 4-(furan-2-yl)-1-hydroxy-3-phenylcyclopentane-1,2-dicarboxylate (10): Prepared according to general procedure using cinnamaldehyde (30.2 μL, 0.24 mmol) and (*E*)-methyl 4-(furan-2-yl)-2-oxobut-3-enoate (135 mg, 0.72 mmol) and purified by flash chromatography using 7.5% EtOAc/hexanes to 30% EtOAc/hexanes to afford 77 mg (77% yield) of **10** (20:1 dr) as a yellowish oil. Analytical data for **10**: IR (film) 3495, 2982, 1735, 1375, 1233, 1182, 1107, 737, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14-7.08 (m, 3H), 7.06-7.04 (m, 1H), 7.02-6.98 (m, 2H), 6.07 (dd,

J = 1.9, 2.9 Hz, 1H), 5.89 (d, *J* = 3.1 Hz, 1H), 5.21 (sept, *J* = 6.3 Hz, 1H), 4.92 (sept, *J* = 6.3 Hz, 1H), 4.14 (dd, *J* = 10.2, 10.2 Hz, 1H), 4.02 (s, 1H), 3.96 (dd, *J* = 8.5, 17.6 Hz, 1H), 3.80 (d, *J* = 10.9 Hz, 1H), 2.72 (dd, *J* = 8.4, 13.8 Hz, 1H), 2.38 (dd, *J* = 8.1, 13.8 Hz, 1H), 1.41 (d, *J* = 6.3 Hz, 3H), 1.40 (d, *J* = 6.2 Hz, 3H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.04 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 170.1, 155.1, 141.1, 139.7(2C), 128.2(2C), 127.7, 126.3, 109.8, 106.6, 81.2, 70.4, 68.3, 57.9, 49.6, 43.0, 41.4, 21.8, 21.7, 21.6(2C); LRMS (ESI): Mass calcd for $C_{23}H_{28}O_6Na$ $[M+Na]^+$, 423. Found $[M+Na]^+$, 423; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OD-H, 5% *i*-PrOH/Hexanes, 0.5 mL/min, 210 nm), Rt (major) = 11.8 min, Rt (minor) = 14.8 min; ee = 97%.

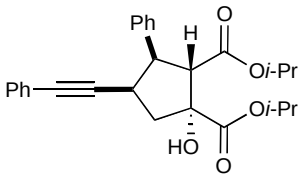


(1*R*,2*S*,3*S*,4*R*)-diisopropyl 1-hydroxy-3-phenyl-4-(thiophen-2-yl)cyclopentane-1,2-dicarboxylate (11): Prepared according to general procedure using cinnamaldehyde (31.5 μL, 0.25 mmol) and (*E*)-methyl 2-oxo-4-(thiophen-2-yl)but-3-enoate (141 mg, 0.75 mmol) and purified by flash chromatography using 7.5% EtOAc/hexanes to 20% EtOAc/hexanes to afford 85 mg (85% yield) of **11** (20:1 dr) as a yellowish oil. Analytical data for **11**: IR (film) 3501, 2981, 2936, 1738, 1375, 1233, 1182, 1107, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14-7.05 (m, 3H), 7.02-6.98 (m, 2H), 6.95-6.93 (m, 1H), 6.72 (dd, *J* = 3.7, 4.9 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 5.24 (sept, *J* = 6.3 Hz, 1H), 4.95 (sept, *J* = 6.2 Hz, 1H), 4.25-4.15 (m, 2H), 3.98 (s, 1H), 3.86 (d, *J* = 6.9 Hz, 1H), 2.77-2.71 (m, 1H), 2.51-2.46 (m, 1H), 1.44 (d, *J* = 6.5 Hz, 3H), 1.43 (d, *J* = 6.4 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 169.9, 144.9, 140.1, 128.6(2C), 127.8(2C), 126.4, 126.2(2C), 124.9, 123.7, 81.1, 70.7, 68.5, 58.4, 50.2, 46.3, 43.3, 21.9, 21.8(2C), 21.7; LRMS (ESI): Mass calcd for $C_{23}H_{29}O_5S$ $[M+H]^+$, 417. Found $[M+H]^+$, 417; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ, 10% *i*-PrOH/Hexanes, 1 mL/min, 210 nm), Rt (major) = 5.3 min, Rt (minor) = 7.6 min; ee = 97%.

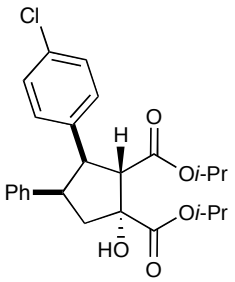


(1*R*,2*S*,3*R*,4*S*)-diisopropyl 4-cyclopropyl-1-hydroxy-3-phenylcyclopentane-1,2-dicarboxylate (12): Prepared according to general procedure using cinnamaldehyde (12.6 μL, 0.10 mmol) and (*E*)-methyl 4-cyclopropyl-2-oxobut-3-enoate (46 mg, 0.30 mmol) and purified by flash chromatography using 5% EtOAc/hexanes to 20% EtOAc/hexanes to afford 23 mg (61% yield) of **12** (20:1 dr) as a yellowish oil. Analytical data for **12**: IR (film) 3505, 2981, 2936, 1738, 1375, 1230, 1181, 1108, 750, 702 cm^{-1}; ^{1}H

NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 4H), 7.24-7.18 (m, 1H), 5.18 (sept, *J* = 6.2 Hz, 1H), 4.93 (sept, *J* = 6.2 Hz, 1H), 3.95 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.80 (s, 1H), 3.76 (d, *J* = 9.1 Hz, 1H), 2.20 (dd, *J* = 10.5, 13.0 Hz, 1H), 2.10 (dd, *J* = 6.8, 13.2 Hz, 1H), 1.92 (dddd, *J* = 7.1, 9.8, 9.8, 9.8 Hz, 1H), 1.38 (d, *J* = 6.0 Hz, 3H), 1.37 (d, *J* = 5.7 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.2 Hz, 3H), 0.30-0.16 (m, 2H), 0.04- -0.03 (m, 2H), -0.11- -0.17 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 170.3, 142.0, 128.8(2C), 127.9(2C), 126.1, 81.3, 70.2, 68.2, 59.4, 48.0(2C), 45.1, 21.8, 21.73, 21.70, 21.66, 12.8, 4.6, 3.8, ; LRMS (ESI): Mass calcd for $C_{22}H_{31}O_5$ $[M+H]^+$, 375. Found $[M+H]^+$, 375; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 0.5 mL/min, 210 nm), Rt (major) = 18.8 min, Rt (minor) = 15.7 min; ee = 99%.

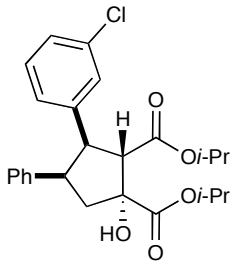


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-phenyl-4-(phenylethynyl)cyclopentane-1,2-dicarboxylate (13): Prepared according to general procedure using cinnamaldehyde (12.6 μL, 0.10 mmol) and (*E*)-methyl 2-oxo-6-phenylhex-3-en-5-ynoate (64 mg, 0.30 mmol) and purified by flash chromatography using 5% EtOAc/hexanes to 15% EtOAc/hexanes to afford 27 mg (62% yield) of **13** (20:1 dr) as a yellowish oil. Analytical data for **13**: IR (film) 3496, 2981, 2935, 1734, 1375, 1233, 1181, 757, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.33 (m, 4H), 7.29-7.26 (m, 1H), 7.22-7.16 (m, 3H), 7.05-7.01 (m, 2H), 5.18 (sept, *J* = 6.3 Hz, 1H), 4.94 (sept, *J* = 6.3 Hz, 1H), 4.09 (dd, *J* = 9.9, 9.9 Hz, 1H), 3.90 (s, 1H), 3.78 (d, *J* = 10.4 Hz, 1H), 3.75 (ddd, *J* = 7.9, 8.6, 8.6 Hz, 1H), 2.56 (dd, *J* = 8.7, 13.4 Hz, 1H), 2.42 (dd, *J* = 7.6, 13.4 Hz, 1H), 1.35 (d, *J* = 6.3 Hz, 3H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 169.6, 140.5, 131.2(2C), 128.8(2C), 128.0(2C), 127.9(2C), 127.6, 126.8, 123.4, 90.3, 85.0, 81.1, 70.5, 68.5, 58.7, 48.5, 46.2, 35.0, 21.74, 21.71, 21.66, 21.63; LRMS (ESI): Mass calcd for $C_{27}H_{30}NaO_5$ $[M+Na]^+$, 457. Found $[M+Na]^+$, 457.4; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 0.5 mL/min, 210 nm), Rt (major) = 23.9 min, Rt (minor) = 18.3 min; ee = 94%.

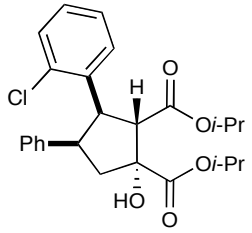


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 3-(4-chlorophenyl)-1-hydroxy-4-phenylcyclopentane-1,2-dicarboxylate (14): Prepared according to the general procedure using *(E)*-3-(4-Chloro-phenyl)-propenal (40.6 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate

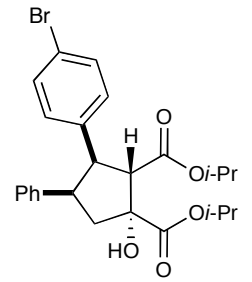
(139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 81 mg (74% yield) of **14** (20:1 dr) as a yellow oil. Analytical data for **14**: IR (film) 3488, 3068, 3030, 2983, 2938, 1734, 1699, 1664, 1623, 1602, 1494, 1454, 1366, 1266, 1229, 1182, 1106, 1014, 910, 827, 739, 702, 640 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.06 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.26 (sep, *J* = 6.3 Hz, 1H), 4.96 (sep, *J* = 6.2 Hz, 1H), 4.23 (dd, *J* = 9.7, 9.7 Hz, 1H), 4.01 (ap q, *J* = 8.7 Hz, 1H), 3.97 (s, 1H), 3.77 (d, *J* = 9.8 Hz, 1H), 2.77 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.40 (dd, *J* = 13.7, 7.5 Hz, 1H), 1.44 (d, *J* = 6.7 Hz, 3H), 1.45 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.6, 169.9, 140.8, 139.1, 131.9, 130.0(2C), 128.5(2C), 128.0(2C), 127.9(2C), 126.3, 81.4, 70.9, 68.7, 58.8, 49.6, 47.6, 44.4, 22.0, 21.9(2C), 21.8; LRMS (ESI): Mass calcd for $C_{25}H_{30}O_5Cl$ $[M+H]^+$, 445. Found $[M+H]^+$, 445. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 0.75 mL/min, 210 nm), Rt (major) = 20.3 min, Rt (minor) = 12.0 min; ee = 97%.



(1*R*,2*S*,3*R*,4*R*)-diisopropyl 3-(3-chlorophenyl)-1-hydroxy-4-phenylcyclopentane-1,2-dicarboxylate (15): Prepared according to the general procedure using *(E)*-3-(3-Chlorophenyl)-propenal (40.6 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 80 mg (73% yield) of **15** (20:1 dr) as a clear oil. Analytical data for **15**: IR (film) 3500, 3066, 3029, 2981, 2938, 2877, 1736, 1598, 1573, 1496, 1467, 1454, 1434, 1375, 1318, 1239, 1194, 1106, 1035, 912, 828, 786, 747, 700 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.06 (m, 3H), 6.96-6.93 (m, 5H), 6.73 (d, *J* = 7.4 Hz, 1H), 5.26 (sep, *J* = 6.3 Hz, 1H), 4.97 (sep, *J* = 6.2 Hz, 1H), 4.22 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.02 (ddd, *J* = 9.8, 7.5, 7.5 Hz, 1H), 3.97 (s, 1H), 3.79 (d, *J* = 9.3 Hz, 1H), 2.77 (dd, *J* = 13.5, 9.8 Hz, 1H), 2.37 (dd, *J* = 13.6, 7.3 Hz, 1H), 1.46 (d, *J* = 6.4 Hz, 3H), 1.45 (d, *J* = 6.4 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.6, 169.9, 142.8, 140.5, 133.6, 129.0, 128.6(2C), 128.4(2C), 127.9, 127.2, 126.4, 126.3, 81.4, 71.0, 68.7, 58.6, 49.9, 47.9, 44.2, 22.0, 21.88(2C), 21.86; LRMS (ESI): Mass calcd for $C_{25}H_{30}O_5Cl$ $[M+H]^+$, 445. Found $[M+H]^+$, 445. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 1.0 mL/min, 210 nm), Rt (major)= 12.7 min, Rt (minor) = 10.2 min; ee = 97%.

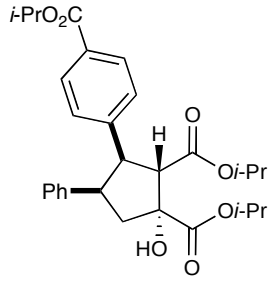


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 3-(2-chlorophenyl)-1-hydroxy-4-phenylcyclopentane-1,2-dicarboxylate (16): Prepared according to the general procedure using *(E)*-3-(2-Chlorophenyl)-propenal (40.6 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 81 mg (74% yield) of **16** (10:1 dr) as a light yellow solid. Analytical data for **16**: IR (film) 3502, 3063, 3029, 2981, 2936, 2876, 1738, 1603, 1496, 1477, 1455, 1444, 1375, 1321, 1238, 1183, 1106, 1034, 970, 910, 828, 786, 749, 727, 702 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.17 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.03 (m, 4H), 7.01-6.96 (m, 1H), 6.91 (td, *J* = 7.6, 1.6 Hz, 1H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 1H), 5.26 (sep, *J* = 6.3 Hz, 1H), 4.94 (sep, *J* = 6.2 Hz, 1H), 4.73 (dd, *J* = 11.6, 10.0 Hz, 1H), 4.16 (ap q, *J* = 8.5 Hz, 1H), 4.00 (s, 1H), 3.89 (d, *J* = 11.9 Hz, 1H), 2.77 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.53 (dd, *J* = 14.3, 8.5 Hz, 1H), 1.46 (d, *J* = 6.1 Hz, 3H), 1.45 (d, *J* = 6.2 Hz, 3H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.6, 169.9, 141.8, 137.6, 134.7, 129.2, 128.3(2C), 128.1, 127.7(2C), 127.3, 126.2, 125.9, 81.5, 70.8, 68.6, 56.7, 47.0, 45.2, 45.1, 21.2, 21.9, 21.83, 21.77; LRMS (ESI): Mass calcd for $C_{25}H_{30}O_5Cl$ $[M+H]^+$, 445. Found $[M+H]^+$, 445. Enantiomeric ratio was measured by chiral phase HPLC (Regis-Pirkle Welk-01, 3% *i*-PrOH/Hexanes, 0.50 mL/min, 210 nm), Rt (major) = 45.3 min, Rt (minor) 41.2 min; ee = 98%.

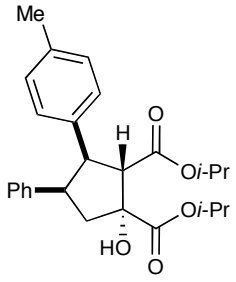


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 3-(4-bromophenyl)-1-hydroxy-4-phenylcyclopentane-1,2-dicarboxylate (17): Prepared according to the general procedure using *(E)*-3-(4-bromophenyl)-propenal (51.5 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 81 mg (74% yield) of **17** (20:1 dr) as a yellow oil. Analytical data for **17**: IR (film) 3502, 3062, 3029, 2981, 2936, 2873, 1786, 1733, 1603, 1491, 1454, 1386, 1237, 1183, 1107, 1010, 910, 825, 777, 749, 700 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.16-7.13 (m, 2H), 7.10-7.02 (m, 3H), 6.95-6.93 (m, 2H), 6.77-6.74 (m, 2H), 5.25 (sep, *J* = 6.3 Hz, 1H), 4.95 (sep, *J* = 6.3 Hz, 1H), 4.21 (dd, *J* = 9.7, 9.7 Hz, 1H), 4.00 (ddd, *J* = 9.6, 7.4, 7.4 Hz, 1H), 3.96 (s, 1H), 3.75 (d, *J* = 9.8 Hz, 1H), 2.76 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.39 (dd, *J* = 13.7, 7.5 Hz, 1H), 1.44 (d, *J* = 6.3 Hz, 3H), 1.43 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.6, 169.9, 140.7, 139.7,

130.8(2C), 130.4(2C), 128.5(2C), 128.0(2C), 126.4, 120.0, 81.4, 70.9, 68.7, 58.8, 49.7, 47.6, 44.4, 22.0, 21.9(2C), 21.8; LRMS (ESI): Mass calcd for $C_{25}H_{30}O_5Br$ $[M+H]^+$, 489. Found $[M+H]^+$, 489. Enantiomeric ratio was measured by chiral phase HPLC (Regis-Pirkle Welk-01, 30% *i*-PrOH/Hexanes, 0.50 mL/min, 210 nm), Rt (major) = 19.5 min, Rt (minor) = 4.6 min; ee = 96%.

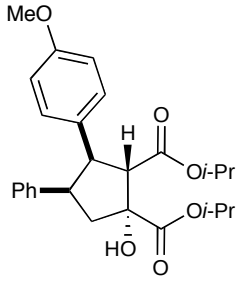


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-(4-(isopropoxycarbonyl)phenyl)-4-phenylcyclopentane-1,2-dicarboxylate (18): Prepared according to the general procedure (except 6.0 eq of Ti(O*i*-Pr)$_4$ was used and the reaction mixture was stirred for 96 hrs to facilitate complete transesterification of all 3 esters) using *(E)*-methyl 4-(3-oxoprop-1-enyl)benzoate (46.4 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 74 mg (61% yield) of **18** (18:1 dr) as a yellow oil. Analytical data for **18**: IR (film) 3499, 3062, 3030, 2981, 2937, 2876, 1738, 1714, 1611, 1497, 1467, 1454, 1374, 1277, 1242, 1181, 1104, 913, 829, 747, 701 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.71-7.69 (m, 2H), 7.07-7.00 (m, 3H), 6.97-6.94 (m, 4H), 5.25 (sep, *J* = 6.3 Hz, 1H), 5.16 (sep, *J* = 6.3 Hz, 1H), 4.95 (sep, *J* = 6.3 Hz, 1H), 4.31 (dd, *J* = 9.7, 9.7 Hz, 1H), 4.06 (ddd, *J* = 9.4, 7.6, 7.6 Hz, 1H), 3.96 (s, 1H), 3.83 (d, *J* = 9.7 Hz, 1H), 2.79 (dd, *J* = 13.6, 9.5 Hz, 1H), 2.40 (dd, *J* = 13.6, 7.4 Hz, 1H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.43 (d, *J* = 6.2 Hz, 3H), 1.31 (d, *J* = 6.3 Hz, 6H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.6, 169.8, 166.2, 146.1, 140.6, 129.1(2C), 128.7, 128.6(2C), 128.4(2C), 128.0(2C), 126.4, 81.5, 70.9, 68.7, 68.3, 58.9, 50.1, 47.7, 44.5, 22.1(2C), 22.0, 21.9(2C), 21.8; LRMS (ESI): Mass calcd for $C_{29}H_{37}O_7$ $[M+H]^+$, 497. Found $[M+H]^+$, 497. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OD-H, 5% *i*-PrOH/Hexanes, 0.50 mL/min, 210 nm), Rt (major) = 18.7 min, Rt (minor) = 23.5 min; ee = 91%.

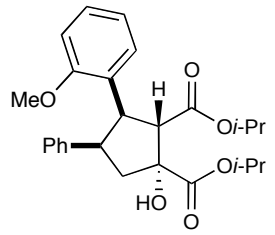


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-4-phenyl-3-*p*-tolylcyclopentane-1,2-dicarboxylate (19): Prepared according to the general procedure using (*E*)-3-*p*-

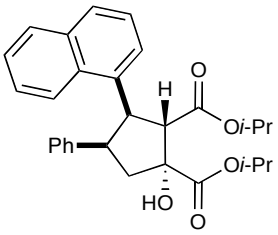
tolylacrylaldehyde (35.7 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 66 mg (63% yield) of **19** (20:1 dr) as a white solid. Analytical data for **19**: IR (film) 3505, 3058, 3028, 2981, 2937, 2876, 1734, 1603, 1515, 1497, 1454, 1375, 1323, 1241, 1183, 1107, 1035, 971, 911, 820, 750, 700, 641 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.07-6.99 (m, 3H), 6.95 (d, *J* = 7.1 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 5.25 (sep, *J* = 6.3 Hz, 1H), 4.96 (sep, *J* = 6.3 Hz, 1H), 4.22 (dd, *J* = 9.4, 9.4 Hz, 1H), 4.02 (ddd, *J* = 9.7, 7.3, 7.3 Hz, 1H), 3.97 (s, 1H), 3.81 (d, *J* = 9.1 Hz, 1H), 2.79 (dd, *J* = 13.4, 10.1 Hz, 1H), 2.35 (dd, *J* = 13.4, 7.1 Hz, 1H), 2.17 (s, 3H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.42 (d, *J* = 6.2 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.9, 170.2, 141.1, 137.7, 135.5, 128.61(2C), 128.56(2C), 128.5(2C), 127.7(2C), 126.0, 81.4, 70.7, 68.5, 59.3, 49.7, 47.8, 44.3, 22.0, 21.89(2C), 21.86, 21.1; LRMS (ESI): Mass calcd for $C_{26}H_{33}O_5$ $[M+H]^+$, 425. Found $[M+H]^+$, 425. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OD-H, 5% *i*-PrOH/Hexanes, 0.50 mL/min, 210 nm), Rt (major) = 12.9 min, Rt (minor) = 16.9 min; ee = 97%.



(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-(4-methoxyphenyl)-4-phenylcyclopentane-1,2-dicarboxylate (20): Prepared according to the general procedure using (*E*)-3-(4-methoxyphenyl)acrylaldehyde (39.6 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 60 mg (56% yield) of **20** (17:1 dr) as a yellow oil. Analytical data for **20**: IR (film) 3498, 3271, 3062, 3029, 2980, 2934, 2854, 1785, 1729, 1676, 1612, 1514, 1454, 1386, 1250, 1181, 1108, 1036, 971, 910, 829, 749, 702 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.04 (m, 3H), 6.94 (d, *J* = 7.1 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 5.24 (sep, *J* = 6.2 Hz, 1H), 4.96 (sep, *J* = 6.2 Hz, 1H), 4.20 (dd, *J* = 9.5, 9.5 Hz, 1H), 3.99 (m, 2H), 3.77 (d, *J* = 9.4 Hz, 1H), 3.68 (s, 3H), 2.77 (dd, *J* = 13.4, 9.9 Hz, 1H), 2.35 (dd, *J* = 13.5, 7.2 Hz, 1H), 1.44 (d, *J* = 6.3 Hz, 3H), 1.42 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.8, 170.3, 157.9, 141.1, 132.8, 129.7(2C), 128.6(2C), 127.8(2C), 126.1, 113.2(2C), 81.4, 70.7, 68.5, 59.1, 55.2, 49.5, 47.8, 44.3, 22.0, 21.89(2C), 21.86; LRMS (ESI): Mass calcd for $C_{26}H_{33}O_6$ $[M+H]^+$, 441. Found $[M+H]^+$, 441. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 0.75 mL/min, 210 nm), Rt (major) = 28.2 min, Rt (minor) = 16.7 min; ee = 96%.

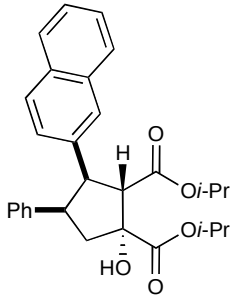


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-(2-methoxyphenyl)-4-phenylcyclopentane-1,2-dicarboxylate (21): Prepared according to the general procedure using (*E*)-3-(2-methoxyphenyl)acrylaldehyde (39.6 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 66 mg (62% yield) of **21** (5:1 dr) as a yellow oil. Analytical data for **21**: IR (film) 3484, 3068, 3030, 2981, 2935, 1784, 1665, 1602, 1495, 1466, 1454, 1387, 1366, 1293, 1266, 1108, 1032, 911, 830, 747, 701, 648 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.10-6.93 (m, 7H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 5.23 (sep, *J* = 6.2 Hz, 1H), 4.97 (sep, *J* = 6.3 Hz, 1H), 4.56-4.50 (m, 1H), 4.12 (ap q, *J* = 8.9 Hz, 1H), 4.00-3.89 (m, 2H), 3.63 (s, 3H), 2.81-2.75 (m, 1H), 2.36 (dd, *J* = 13.0, 7.3 Hz, 1H), 1.42 (d, *J* = 6.3 Hz, 6H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.9, 170.7, 157.0, 141.7, 128.8, 128.3(2C), 127.4, 127.2(2C), 125.7, 119.8, 109.7(2C), 81.8, 70.4, 68.4, 56.4, 54.7, 45.9, 44.6(2C), 22.0, 21.91, 21.90(2C); LRMS (ESI): Mass calcd for $C_{26}H_{33}O_6$ $[M+H]^+$, 441. Found $[M+H]^+$, 441. Enantiomeric ratio was measured by chiral phase HPLC (Regis-Pirkle Welk-01, 5% *i*-PrOH/Hexanes, 1.5 mL/min, 210 nm), Rt (major) = 25.8 min, Rt (minor) = 16.4 min; ee = 97%.

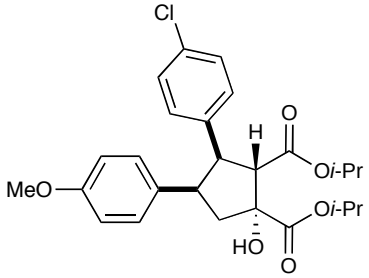


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-(naphthalen-1-yl)-4-phenylcyclopentane-1,2-dicarboxylate (22): Prepared according to the general procedure using (*E*)-3-(naphthalen-1-yl)acrylaldehyde (44.5 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 87 mg (78% yield) of **22** (12:1 dr) as a clear foam. Analytical data for **22**: IR (film) 3493, 3030, 2981, 2936, 2874, 1732, 1600, 1512, 1496, 1455, 1374, 1312, 1258, 1236, 1179, 1107, 911, 830, 777, 746, 700 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 8.26 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.54-7.49 (m, 2H), 7.42 (ddd, *J* = 8.1, 6.8, 1.0 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.83-6.81 (m, 3H), 6.79-6.77 (m, 2H), 5.28 (sep, *J* = 6.3 Hz, 1H), 5.10 (dd, *J* = 11.6, 9.7 Hz, 1H), 4.93 (sep, *J* = 6.2 Hz, 1H), 4.21 (ddd, *J* = 9.2, 7.1, 7.1 Hz, 1H), 4.10 (s, 1H), 4.08 (d, *J* = 11.8 Hz, 1H), 2.85 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.62 (dd, *J* = 14.4, 8.5 Hz, 1H), 1.49 (d, *J* = 6.2 Hz, 3H), 1.47 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.7, 170.2, 141.9, 135.7, 133.6, 132.4,

128.6, 128.2(2C), 127.4(2C), 126.8, 126.0, 125.8, 125.3, 124.6, 124.0, 123.9, 81.6, 70.8, 68.6, 56.8, 46.7, 45.8, 45.7, 22.03, 21.96, 21.9, 21.8; LRMS (ESI): Mass calcd for $C_{29}H_{33}O_5$ $[M+H]^+$, 461. Found $[M+H]^+$, 461. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 1.0 mL/min, 210 nm), Rt (major) = 24.4 min, Rt (minor) = 18.4 min; ee = 97%.

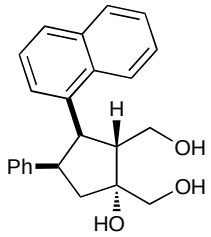


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 1-hydroxy-3-(naphthalen-1-yl)-4-phenylcyclopentane-1,2-dicarboxylate (23): Prepared according to the general procedure using *(E)*-3-(naphthalen-1-yl)acrylaldehyde (44.5 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 86 mg (77% yield) of **23** (16:1 dr) as a yellow oil. Analytical data for **23**: IR (film) 3504, 3058, 3028, 2980, 2936, 2877, 1734, 1602, 1508, 1454, 1375, 1242, 1221, 1182, 1107, 1035, 911, 747, 699 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.65 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.48-7.46 (m, 2H), 7.39-7.33 (m, 2H), 6.98-6.97 (m, 4H), 6.96-6.91 (m, 2H), 5.29 (sep, *J* = 6.3 Hz, 1H), 4.96 (sep, *J* = 6.3 Hz, 1H), 4.44 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.14 (ddd, *J* = 9.8, 7.2, 7.2 Hz, 1H), 4.04 (s, 1H), 3.95 (d, *J* = 9.3 Hz, 1H), 2.88 (dd, *J* = 13.5, 9.9 Hz, 1H), 2.43 (dd, *J* = 13.5, 7.2 Hz, 1H), 1.49 (d, *J* = 6.3 Hz, 3H), 1.46 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.8, 170.2, 140.8, 138.4, 133.2, 132.0, 128.5(2C), 127.8(2C), 127.7, 127.5, 127.3, 127.25, 127.21, 126.1, 125.7, 125.3, 81.5, 70.8, 68.6, 59.1, 50.2, 47.8, 44.5, 22.0, 21.9, 21.87, 21.86; LRMS (ESI): Mass calcd for $C_{29}H_{33}O_5$ $[M+H]^+$, 461. Found $[M+H]^+$, 461. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel AD-H, 5% *i*-PrOH/Hexanes, 1.0 mL/min, 210 nm), Rt (major) = 18.5 min, Rt (minor) = 14.6 min; ee = 96%.

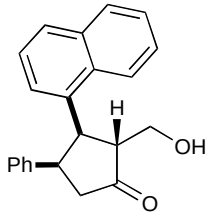


(1*R*,2*S*,3*R*,4*R*)-diisopropyl 3-(4-chlorophenyl)-1-hydroxy-4-(4-methoxyphenyl) cyclopentane-1,2-dicarboxylate (24): Prepared according to the general procedure using *(E)*-3-(4-Chloro-phenyl)-propenal (40.6 mg, 0.244 mmol) and (*E*)-methyl 2-oxo-4-

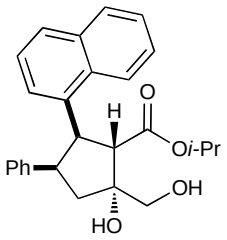
phenylbut-3-enoate (139 mg, 0.732 mmol) and purified by flash chromatography using 9% EtOAc/hexanes to afford 91 mg (78% yield) of **24** (20:1 dr) as an orange oil. Analytical data for **24**: IR (film) 3500, 3061, 3032, 2981, 2936, 2837, 1735, 1612, 1514, 1494, 1466, 1454, 1375, 1251, 1180, 1107, 1037, 1015, 971, 910, 830, 746, 704 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.03-7.00 (m, 2H), 6.86-6.80 (m, 4H), 6.63-6.60 (m, 2H), 5.24 (sep, *J* = 6.3 Hz, 1H), 4.95 (sep, *J* = 6.3 Hz, 1H), 4.17 (dd, *J* = 9.7, 9.7 Hz, 1H), 3.97-3.91 (m, 2H), 3.74 (d, *J* = 9.8 Hz, 1H), 3.71 (s, 3H), 2.71 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.37 (dd, *J* = 13.7, 7.5 Hz, 1H), 1.44 (d, *J* = 6.7 Hz, 3H), 1.42 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.7, 170.0, 157.9, 139.3, 132.8, 131.8, 130.0(2C), 129.4(2C), 127.9(2C), 113.3(2C), 81.3, 70.8, 68.6, 58.7, 55.3, 49.7, 46.9, 44.7, 22.0, 21.9(2C), 21.8; LRMS (ESI): Mass calcd for $C_{26}H_{32}O_6Cl$ $[M+H]^+$, 475. Found $[M+H]^+$, 475. Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OD-H, 5% *i*-PrOH/Hexanes, 0.50 mL/min, 210 nm), Rt (major) = 22.7 min, Rt (minor) = 17.3 min; ee = 97%.



(1*R*,2*R*,3*R*,4*R*)-1-hydroxy-3,4-diphenylcyclopentane-1,2-diyl)dimethanol (25): Into a flame-dried 50 mL round bottom flask equipped with a magnetic stirbar was weighed bis-ester **22** (>20:1 dr), (430 mg, 0.935 mmol). The flask was purged with N_2 and THF (19 mL, 0.05M) was added under positive N_2 pressure. The mixture was cooled at 0 °C and $LiAlH_4$ (355 mg, 9.35 mmol) was added in small portions. The reaction mixture was stirred at 0 °C for 30 min and at 25 °C for 16h. The mixture was then slowly quenched with the addition of water until gas evolution ceased. The mixture was transferred into an extraction funnel containing 100 mL of 1M HCl solution. The aqueous phase was extracted with EtOAc (3x), and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography using 80% EtOAc/hexanes to 100% EtOAc to afford 245 mg (75% yield) of **25** as a white solid. Analytical data for **25**: IR (film) 3324 (broad), 3060, 3029, 2939, 2907, 1736 (weak), 1455, 1263, 1030, 778, 701 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.73-7.70 (m, 1H), 7.54-7.47 (m, 2H), 7.42 (ddd, *J* = 1.0, 6.8, 8.0 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.82-6.78 (m, 3H), 6.64-6.60 (m, 2H), 4.43 (dd, *J* = 9.8, 12.5 Hz, 1H), 4.12 (s broad, 1H), 4.05 (ddd, *J* = 6.8, 9.3 Hz, 1H), 4.00 (d, *J* = 11.3 Hz, 1H), 3.84 (d, *J* = 11.2 Hz, 1H), 3.77 (ddd, *J* = 9.3, 10.9, 10.9 Hz, 1H), 3.73 (dd, *J* = 3.2, 10.9 Hz, 1H), 3.33 (d, *J* = 1.0 Hz, 1H), 2.75 (ddd, *J* = 3.2, 8.9, 12.3 Hz, 1H), 2.48 (dd, *J* = 8.9, 14.8 Hz, 1H), 2.44 (s broad, 1H), 2.25 (d, *J* = 6.7, 15.2 Hz, 1H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 142.5, 135.6, 133.4, 132.5, 128.6, 128.1(2C), 127.2(2C), 126.5, 125.7, 125.6, 125.2, 124.7, 124.0, 123.6, 80.7, 68.5, 60.3, 52.9, 45.6, 45.4, 44.0; LRMS (ESI): Mass calcd for $C_{23}H_{24}O_3Na$ $[M+Na]^+$, 371. Found $[M+H]^+$, 371.



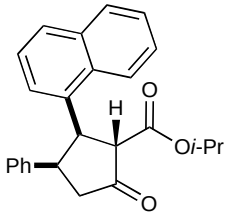
(2*R*,3*R*,4*R*)-2-(hydroxymethyl)-3-(naphthalen-1-yl)-4-phenylcyclopentanone (26): Into a flame-dried 10 mL round bottom flask equipped with a magnetic stirbar was weighed triol **25** (90 mg, 0.258 mmol). The flask was purged with N_2 and CH_2Cl_2 (4 mL) was added under positive N_2 pressure. $NaIO_4$ adsorbed onto silica gel (520 mg of a 1 mmol $NaIO_4$/g SiO_2, 4 equiv.)[8] was added to the solution and stirring was maintained at 25 °C until TLC analysis indicated complete conversion of the triol (5-16h). The mixture was then filtered over a short plug of SiO_2, washed with EtOAc and concentrated under reduced pressure. The crude mixture was purified by flash chromatography using 20% EtOAc/hexanes to 40% EtOAc/hexanes to afford 57 mg (69% yield) of **26** as a colorless gum. Analytical data for **26**: IR (film) 3447 (broad), 3060, 3031, 2930, 2881, 1736, 779, 733, 700 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 8.30 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.64 (ddd, *J* = 1.3, 6.9, 8.4 Hz, 1H), 7.55 (ddd, *J* = 0.9, 6.8, 7.9 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 7.05-7.00 (m, 1H), 6.97-6.92 (m, 2H), 6.52 (d, *J* = 7.2 Hz, 1H), 6.43-6.39 (m, 2H), 4.58 (dd, *J* = 6.7, 13.3 Hz, 1H), 4.13 (dt, *J* = 2.9, 6.6 Hz, 1H), 3.96 (ddd, *J* = 3.8, 7.7, 11.4 Hz, 1H), 3.70-3.65 (m, 1H), 3.11 (ddd, *J* = 4.2, 5.6, 13.2 Hz, 1H), 3.03-3.00 (m, 2H), 2.49-2.42 (m, 1H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 220.6, 139.8, 133.8, 133.3, 132.1, 129.2, 127.7(2C), 127.5(2C), 127.4, 126.5, 126.4, 125.6, 124.9, 123.3, 122.7, 60.2, 50.6, 45.1, 44.3, 43.4; LRMS (ESI): Mass calcd for $C_{22}H_{21}O_2$ $[M+H]^+$, 317. Found $[M+H]^+$, 317.



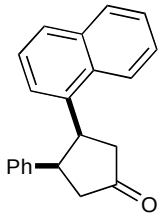
(1*S*,2*R*,4*R*,5*R*)-isopropyl 2-hydroxy-2-(hydroxymethyl)-5-(naphthalen-1-yl)-4-phenylcyclopentanecarboxylate (27): Into an oven-dried vial equipped with a magnetic stirbar was weighed bis-ester **22** (>20:1 dr), (50 mg, 0.11 mmol). The vial was purged with N_2 and THF (1.2 mL) and MeOH (0.6 mL) were added under positive N_2 pressure. The solution was cooled to 0 °C and $NaBH_4$ (62 mg, 1.62 mmol) was added in one portion. The mixture was stirred at 0 °C for 1hr before an additional 5 equiv. of $NaBH_4$ (21 mg, 0.54 mmol) was added. The mixture was stirred an additional 30 min at 0 °C, after which time TLC analysis indicated complete conversion of the bis-ester. The reaction mixture was slowly quenched with 1M HCl, and the aqueous phase was extracted with EtOAc (3x). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. ^1H NMR analysis of the crude indicated

8) Zhong, Y.-L.; Shing, T. K. M. *J. Org. Chem.* **1997**, *62*, 2622-2624.

regioselective reduction (>20:1) and a 4:1 ratio (diol **27**:triol **25**). The crude mixture was purified by flash chromatography using 30% EtOAc/hexanes to 50% EtOAc/hexanes to afford 31 mg (71% yield) of **27** as a colorless gum. Analytical data for **27**: IR (film) 3437 (broad), 3060, 3029, 2937, 2874, 1703, 1384, 1106, 699 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 8.21 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.54 (ddd, *J* = 1.3, 6.8, 8.4 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.43 (ddd, *J* = 1.0, 6.8, 7.9 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.84-6.79 (m, 3H), 6.66-6.63 (m, 2H), 5.04 (dd, *J* = 9.6, 12.6 Hz, 1H), 4.92 (sep, *J* = 6.3 Hz, 1H), 4.51 (d, *J* = 1.0 Hz, 1H), 4.19 (ddd, *J* = 6.3, 9.2 Hz, 1H), 3.93 (dd, *J* = 6.2, 11.3 Hz, 1H), 3.89 (dd, *J* = 6.3, 11.3 Hz, 1H), 3.58 (d, *J* = 12.6 Hz, 1H), 2.58 (dd, *J* = 8.9, 14.7 Hz, 1H), 2.39 (t, *J* = 6.3 Hz, 1H), 2.29 (ddd, *J* = 0.9, 6.3, 14.8 Hz, 1H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.97 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.5, 142.1, 134.4, 133.3, 132.2, 128.5, 128.0(2C), 127.3(2C), 126.8, 125.8, 125.7, 125.2, 124.4(2C), 123.7, 81.9, 68.9, 68.8, 53.0, 48.3, 46.1, 43.3, 21.5(2C); LRMS (ESI): Mass calcd for $C_{26}H_{29}O_4$ $[M+H]^+$, 405. Found $[M+H]^+$, 405.

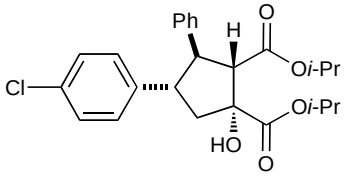


(2*R*,3*R*)-isopropyl 2-(naphthalen-1-yl)-5-oxo-3-phenylcyclopentanecarboxylate (30): β-ketoester **30** was prepared from diol **27** (14.6 mg, 0.036 mmol) by the same procedure described for compound **26**. The crude reaction mixture was purified by flash chromatography using 5% EtOAc/hexanes to 7.5% EtOAc/hexanes to afford 13.5 mg (74% yield) of **30** as a colorless gum and 12:1 (keto:enol). ^1H NMR (500 MHz; $CDCl_3$): ***keto:*** δ 8.30 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.67-7.60 (m, 2H), 7.56-7.52 (m, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.04-7.00 (m, 1H), 6.96-6.91 (m, 2H), 6.57 (d, *J* = 7.2 Hz, 1H), 6.42-6.39 (m, 2H), 5.06 (dd, *J* = 6.6, 12.9 Hz, 1H), 4.97 (sep, *J* = 6.2 Hz, 1H), 4.21 (ddd, *J* = 1.1, 6.5, 7.9 Hz, 1H), 3.95 (d, *J* = 12.8 Hz, 1H), 3.15 (dd, *J* = 8.2, 19.0 Hz, 1H), 3.02 (td, *J* = 0.9, 19.0 Hz, 1H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.11 (d, *J* = 6.3 Hz, 3H); ***enol (key signals):*** 11.00 (s broad, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.30-7.27 (m, 1H), 7.19 (ddd, *J* = 1.3, 6.9, 8.2 Hz, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 6.75-6.69 (m, 3H), 6.68-6.65 (m, 2H), 5.23 (d, *J* = 8.7 Hz, 1H), 3.06 (ddd, *J* = 1.2, 10.9, 17.8 Hz, 1H), 2.91 (dd, *J* = 8.6, 17.7 Hz, 1H), 1.05 (d, *J* = 6.2 Hz, 3H).



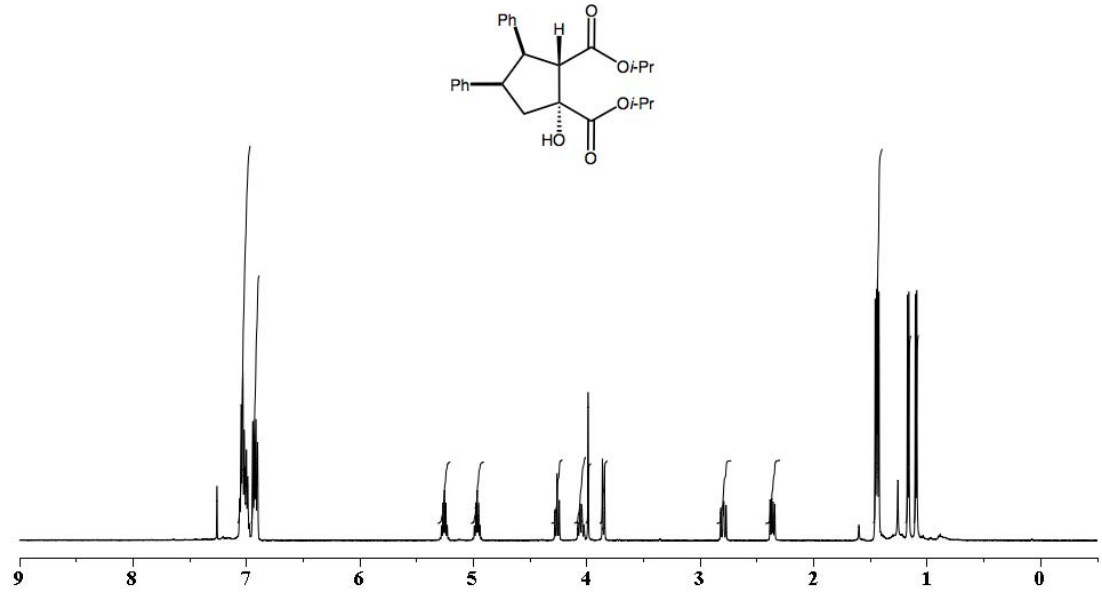
(3*S*,4*R*)-3-(naphthalen-1-yl)-4-phenylcyclopentanone (28): Into a tube equipped with a magnetic stirbar was weighed β-ketoester **30** (19 mg, 0.051 mmol). The tube was purged

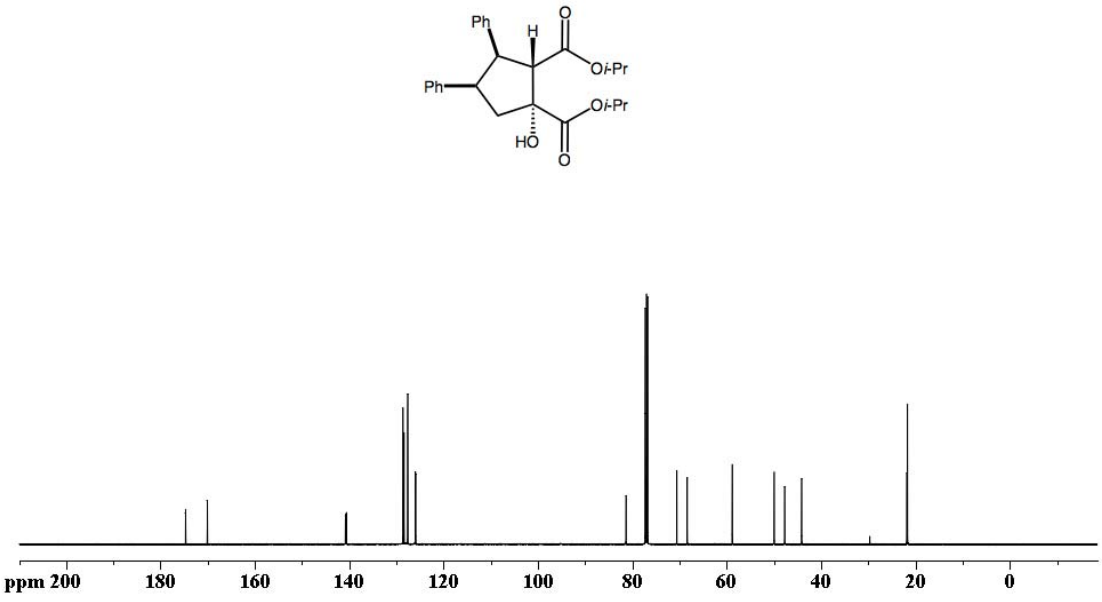
with N_2 and DMSO (1.0 mL) and H_2O (0.25 mL) were added under positive N_2 pressure. The solution was heated to 130 °C for 3 hours, after which time TLC analysis indicated complete conversion. The mixture was transferred into an extraction funnel containing brine. The aqueous phase was extracted with EtOAc (3x) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography using 5% EtOAc/hexanes to 10% EtOAc/hexanes to afford 14 mg (96% yield) of **28** as a colorless gum. Analytical data for **27**: IR (film) 3059, 3048, 2959, 2850, 1740, 1261, 798, 702 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 8.12-8.08 (m, 1H), 7.86-7.82 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.52-7.45 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.00-6.96 (m, 1H), 6.93-6.88 (m, 2H), 6.71 (d, *J* = 7.2 Hz, 1H), 6.47-6.44 (m, 2H), 4.71 (ddd, *J* = 7.0, 7.0, 10.6 Hz, 1H), 4.16 (ddd, *J* = 6.4, 6.4, 6.4 Hz, 1H), 2.97 (dd, *J* = 10.6, 18.3 Hz, 1H), 2.92 (d, *J* = 1.8 Hz, 1H), 2.91 (s, 1H), 2.65 (dd, *J* = 7.3, 18.3 Hz, 1H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 218.3, 139.4, 134.8, 133.6, 132.0, 128.9, 127.62(2C), 127.56(2C), 127.3, 126.5, 126.0, 125.4, 124.8, 123.5, 123.0, 45.7, 44.8, 42.5, 41.6; LRMS (EI): Mass calcd for $C_{21}H_{18}O$ $[M]^+$, 286. Found $[M]^+$, 286.

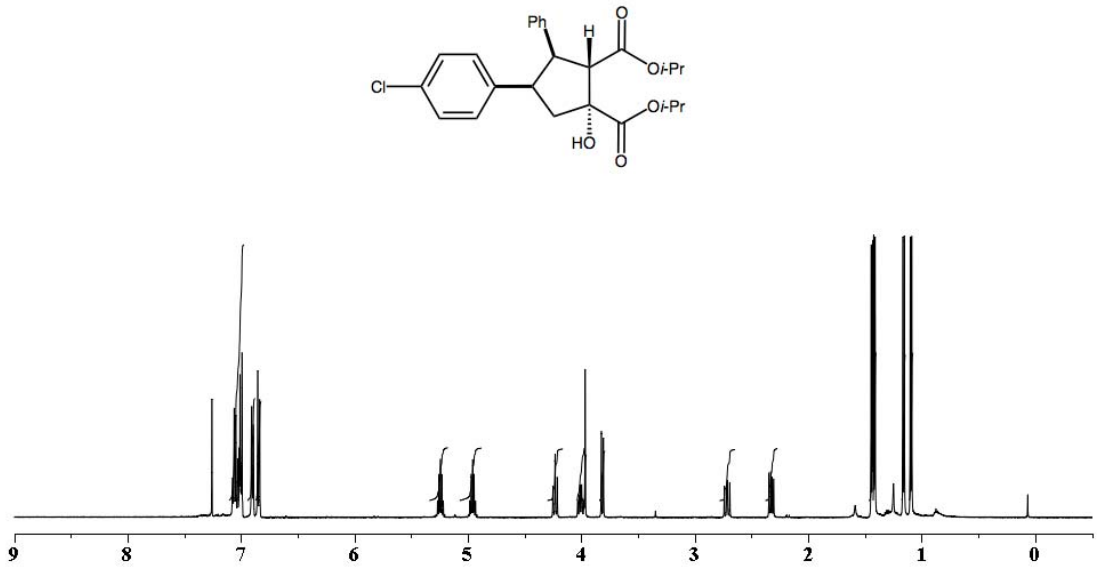


(1*R*,2*S*,3*R*,4*S*)-diisopropyl 4-(4-chlorophenyl)-1-hydroxy-3-phenylcyclopentane-1,2-dicarboxylate (29): A screw-capped vial equipped with a magnetic stirbar was charged with azolium precatalyst **E** (42 mg, 0.098 mmol, 0.2 equiv.) and *E*-methyl 4-(4-chlorophenyl)-2-oxobut-3-enoate (330 mg, 1.47 mmol, 3.0 equiv.). The vial was capped with a septum cap, removed from the drybox and put under positive N_2 pressure. Into the vial were then successively added cinnamaldehyde (61.5 μL, 0.489 mmol, 1.0 equiv.), THF (1.0 mL, 0.50 M), $Ti(OiPr)_4$ (297 μL, 0.978 mmol, 2.0 equiv.) and finally DBU (29 μL, 0.195 mmol, 0.4 equiv.) via a syringe. Upon consumption of the aldehyde (24 hours), 3 equiv. of $Ti(OiPr)_4$ (350 μL) were added and stirring was maintained for an additional 48 hours to allow for complete transesterification. The reaction mixture was filtered through a short plug of SiO_2 and washed with EtOAc. The solution was concentrated under reduced pressure and analysis of the ^1H NMR of the crude indicated 9:1 dr (**4**:**29**). The crude reaction mixture was purified by flash chromatography using 93% EtOAc/hexanes to afford a 1:10 mixture (**4**:**29**) of diastereoisomers. This mixture was further purified by flash chromatography using 5% Et_2O/hexanes to 20% Et_2O/hexanes affording 5.8 mg of **29** as a white solid. An X-ray of a crystal was obtained for compound **29** (see below) after recrystallization from hexanes. Analytical data for **29**: ^1H NMR (500 MHz; $CDCl_3$): δ 7.25-7.20 (m, 2H), 7.19-7.15 (m, 3H), 7.15-7.11 (m, 4H), 5.20 (sep, *J* = 6.3 Hz, 1H), 4.90 (sep, *J* = 6.1 Hz, 1H), 4.09 (s, 1H), 3.71 (dd, *J* = 11.7, 11.7 Hz, 1H), 3.52 (d, *J* = 12.4 Hz, 1H), 3.34 (ddd, *J* = 8.2, 10.6, 10.6 Hz, 1H), 2.87 (dd, *J* = 10.5, 14.4 Hz, 1H), 2.15 (dd, *J* = 7.5, 14.5 Hz, 1H), 1.38 (d, *J* = 6.4 Hz, 3H), 1.37 (d, *J* = 6.2 Hz, 3H), 1.11 (d, *J* = 6.2 Hz, 3H), 1.03 (d, *J* = 6.1 Hz, 3H).

Selected NMR Spectra



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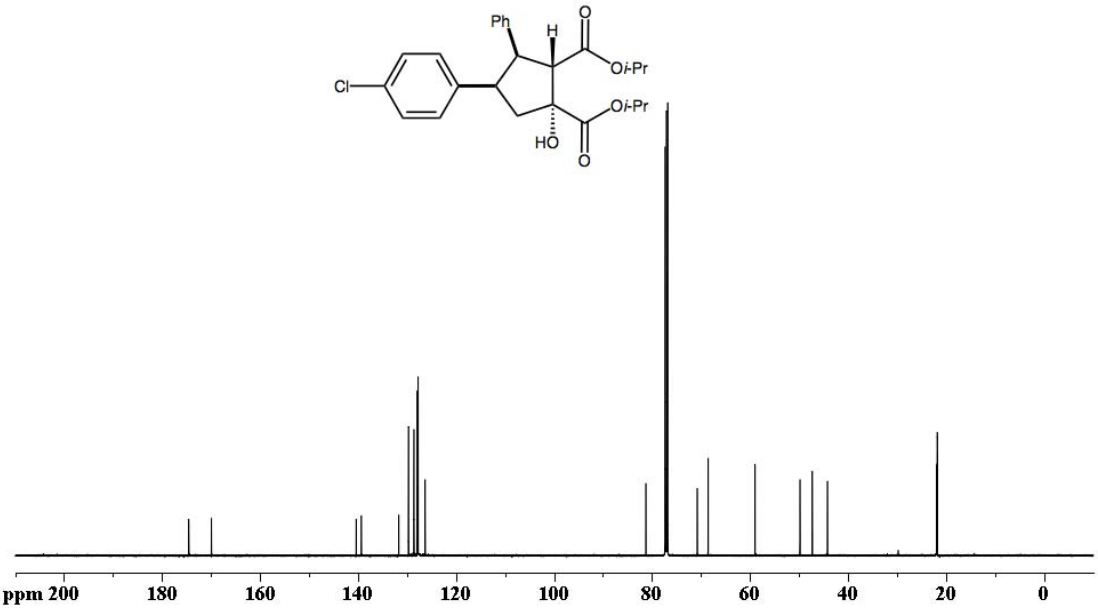
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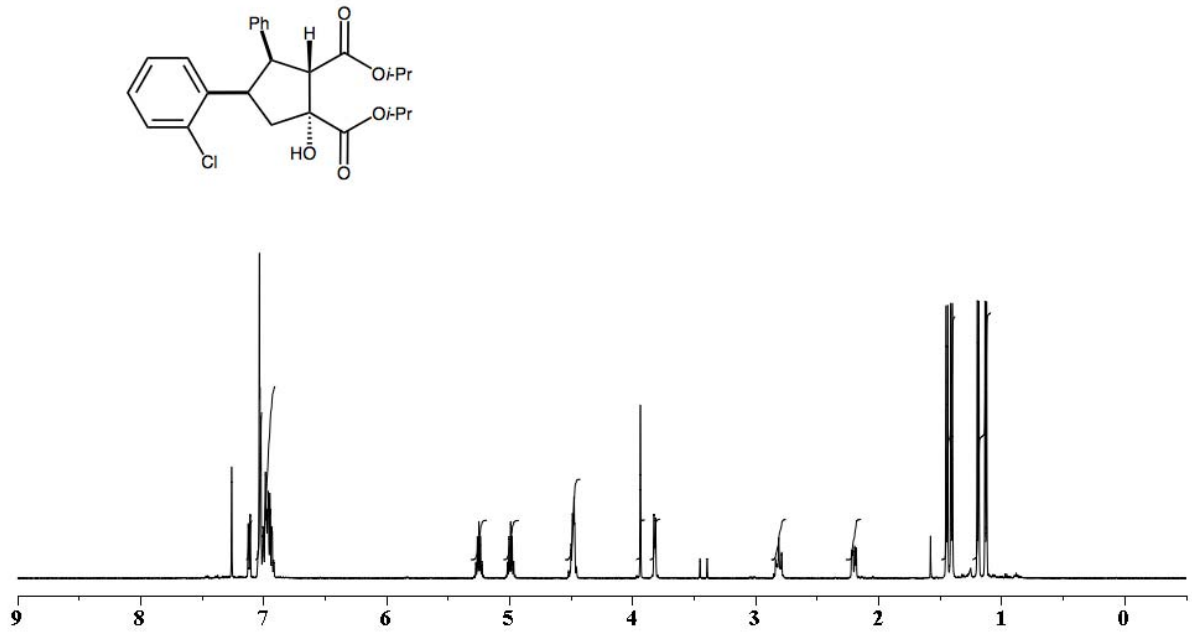
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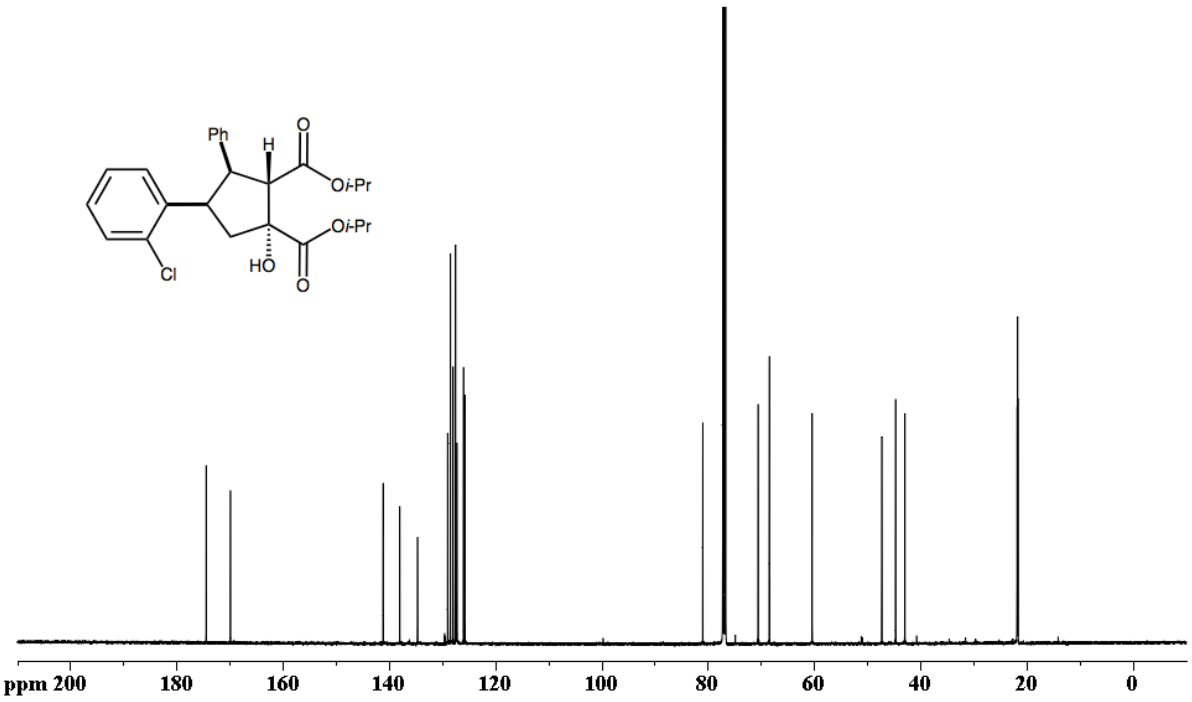
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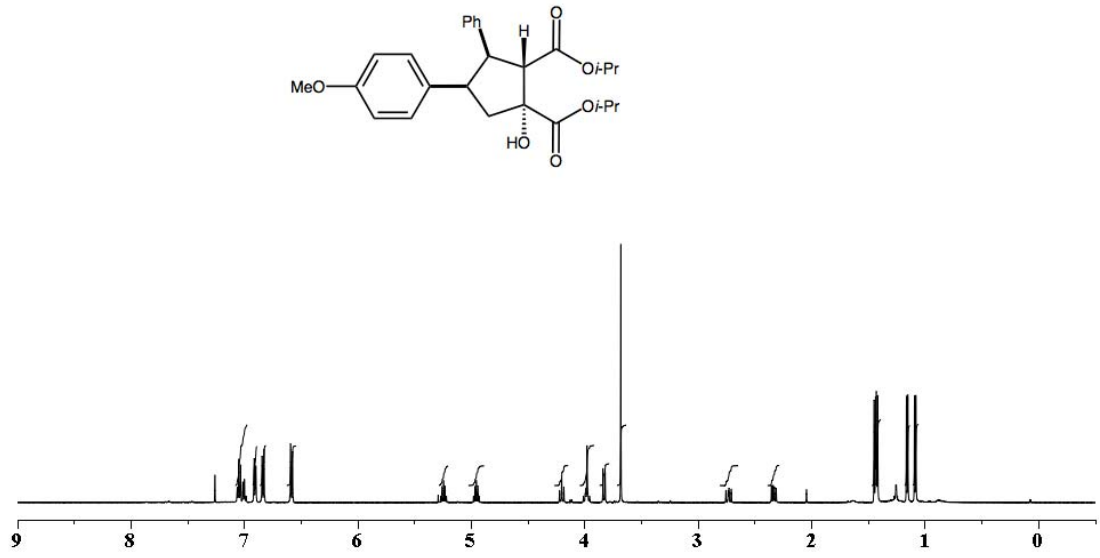
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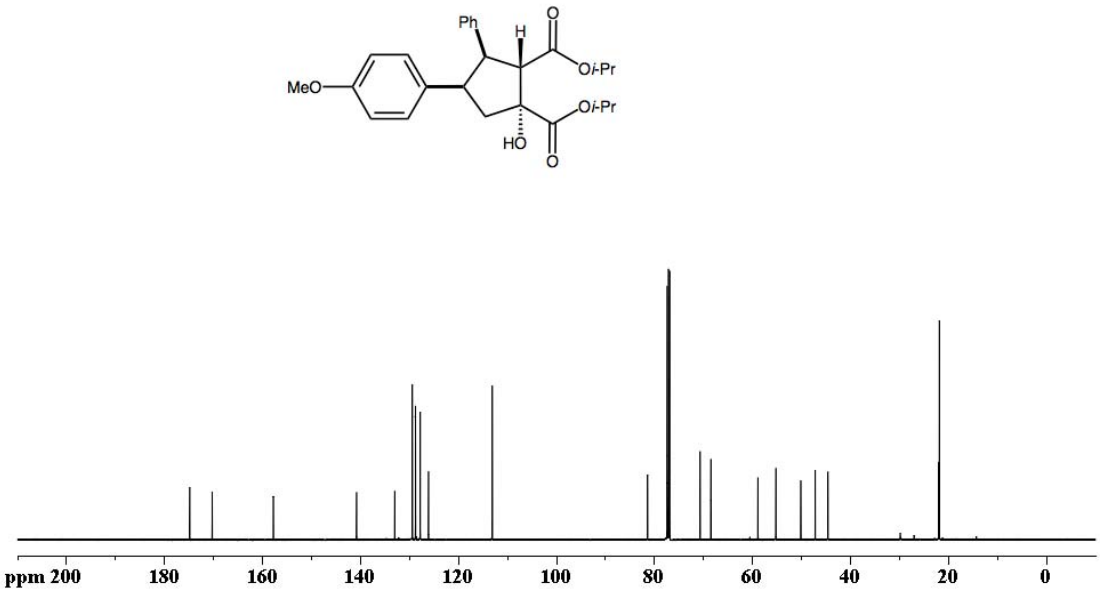
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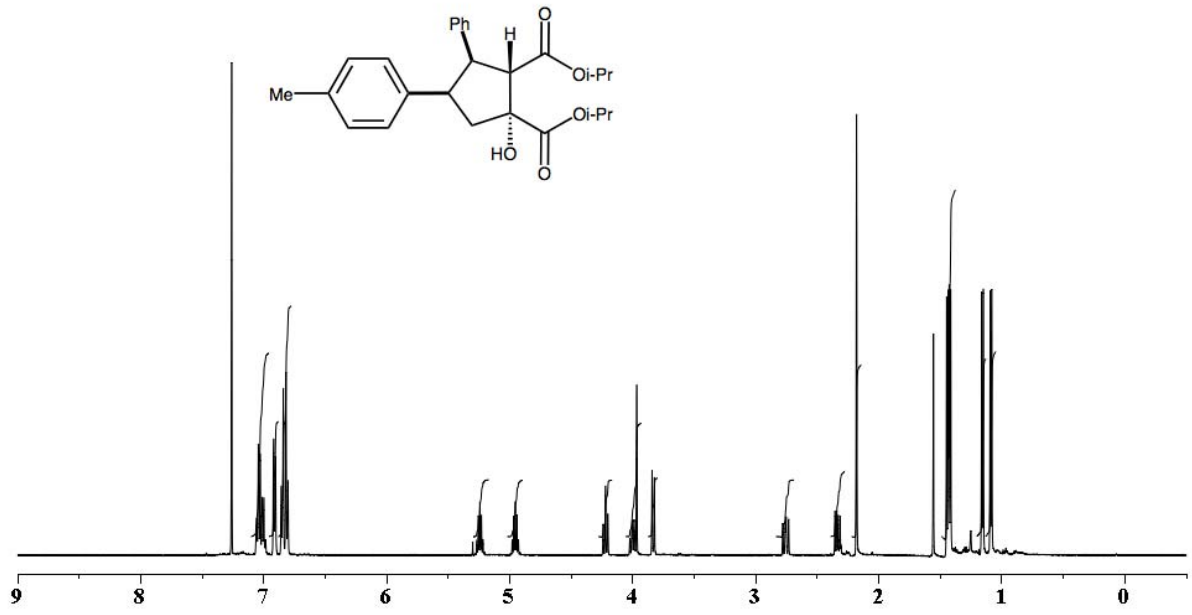
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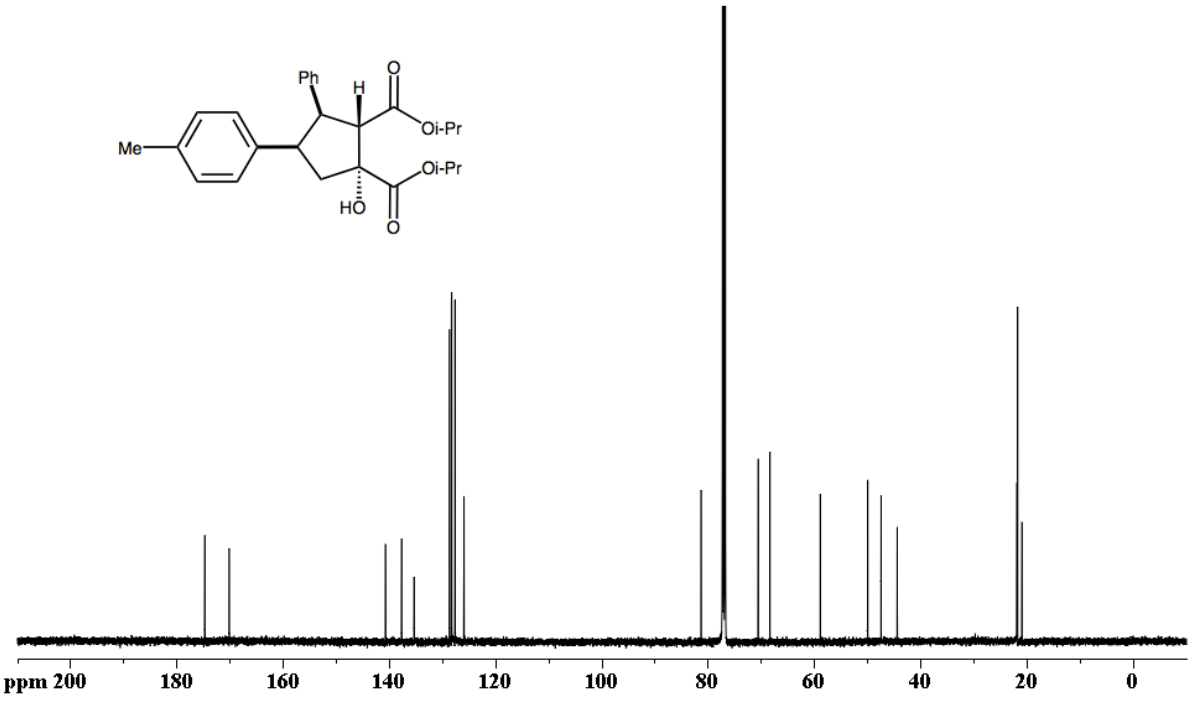
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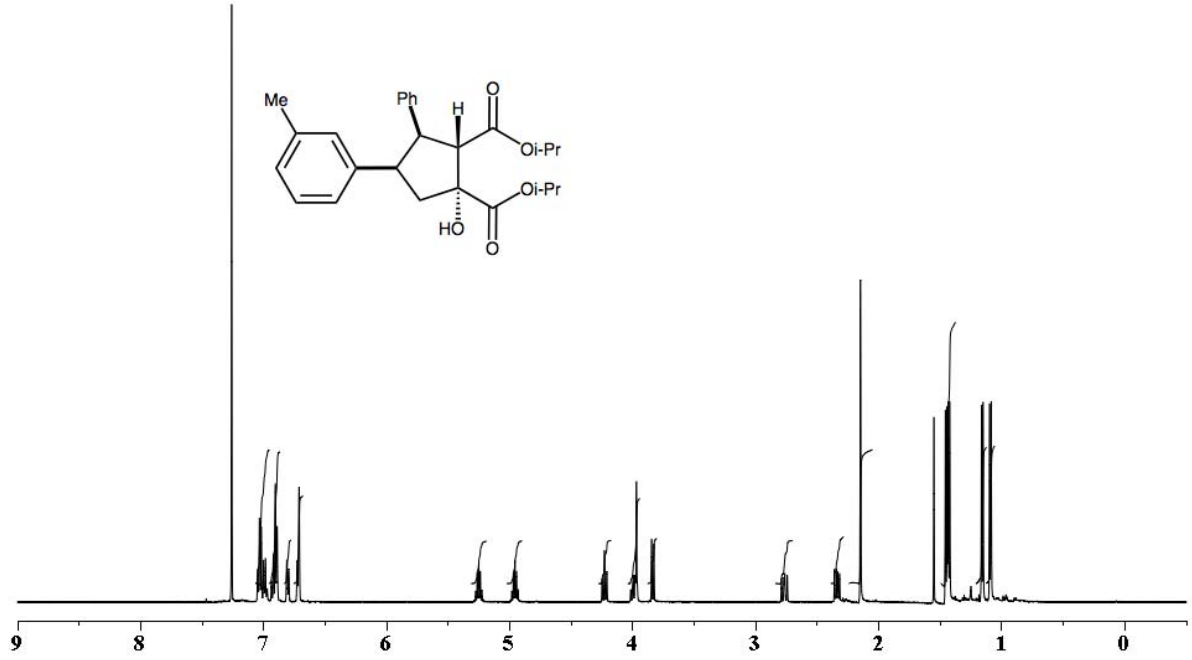
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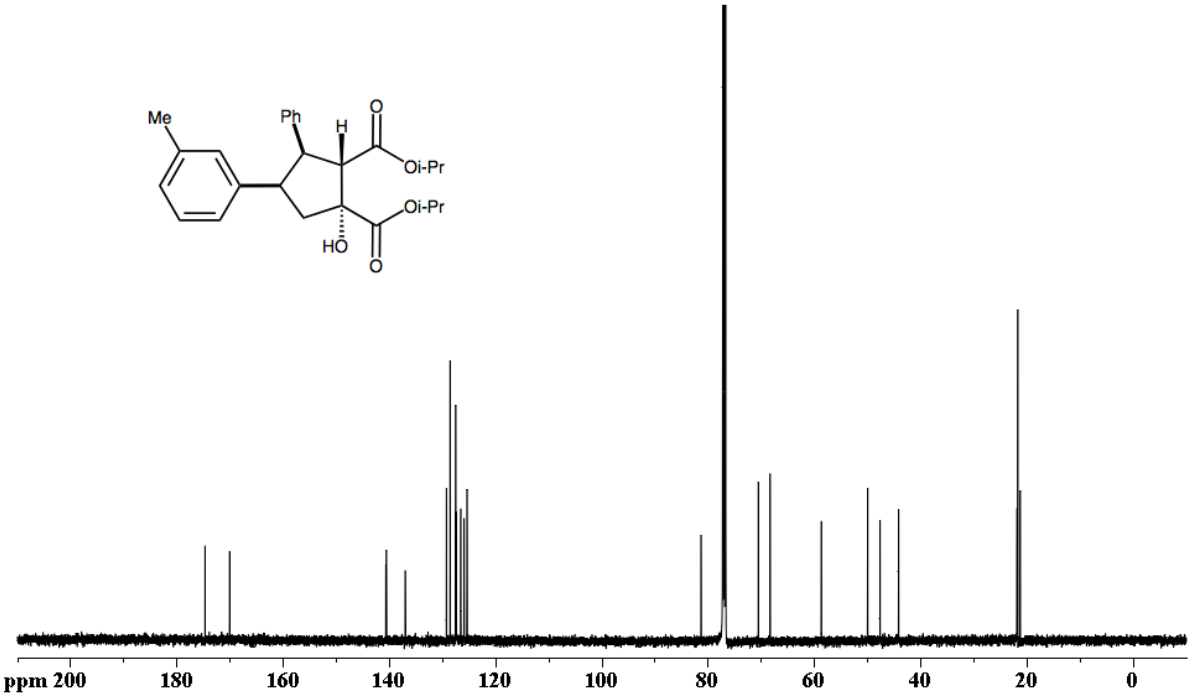
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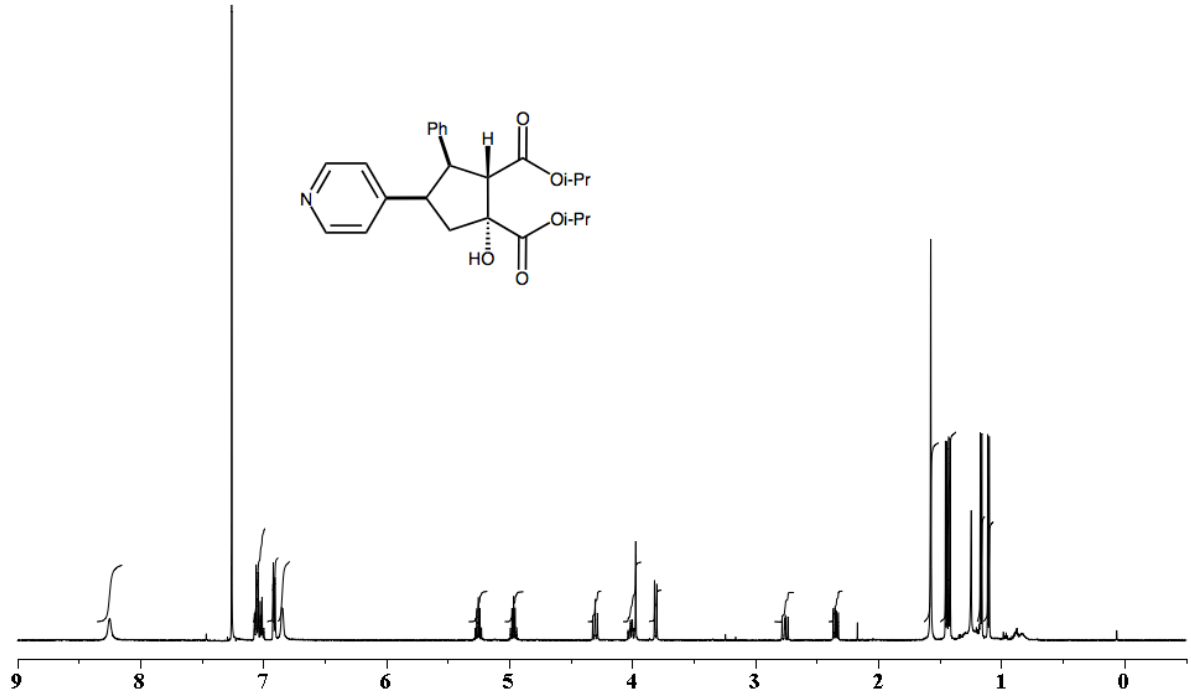
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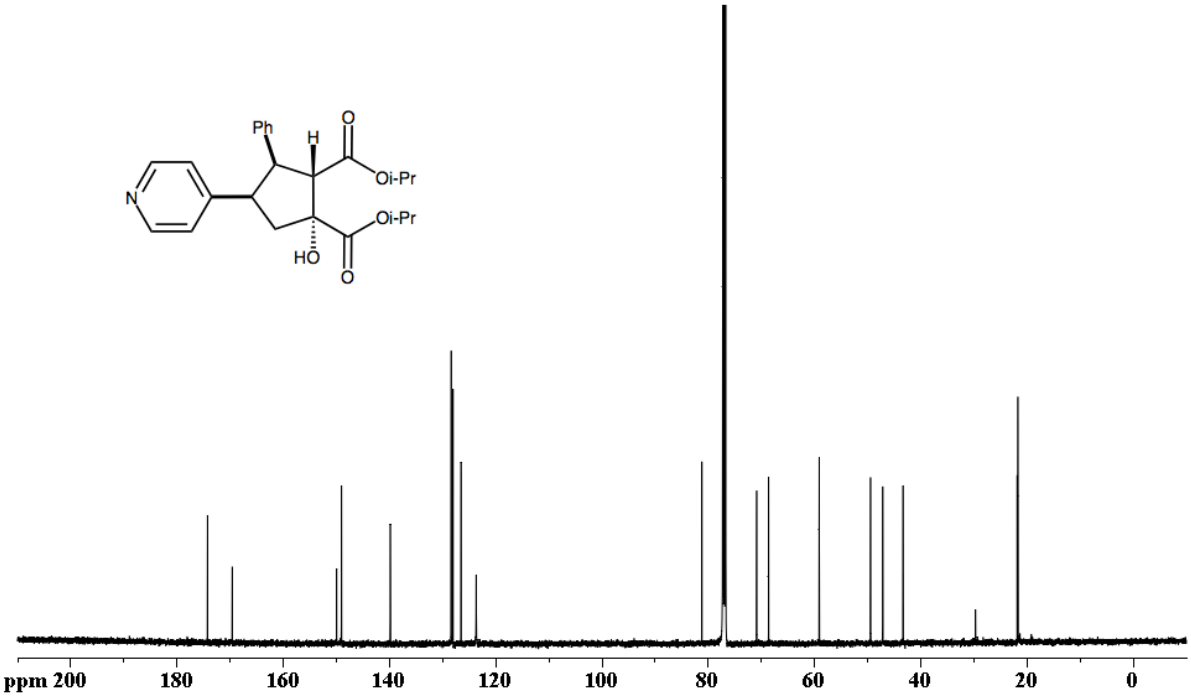
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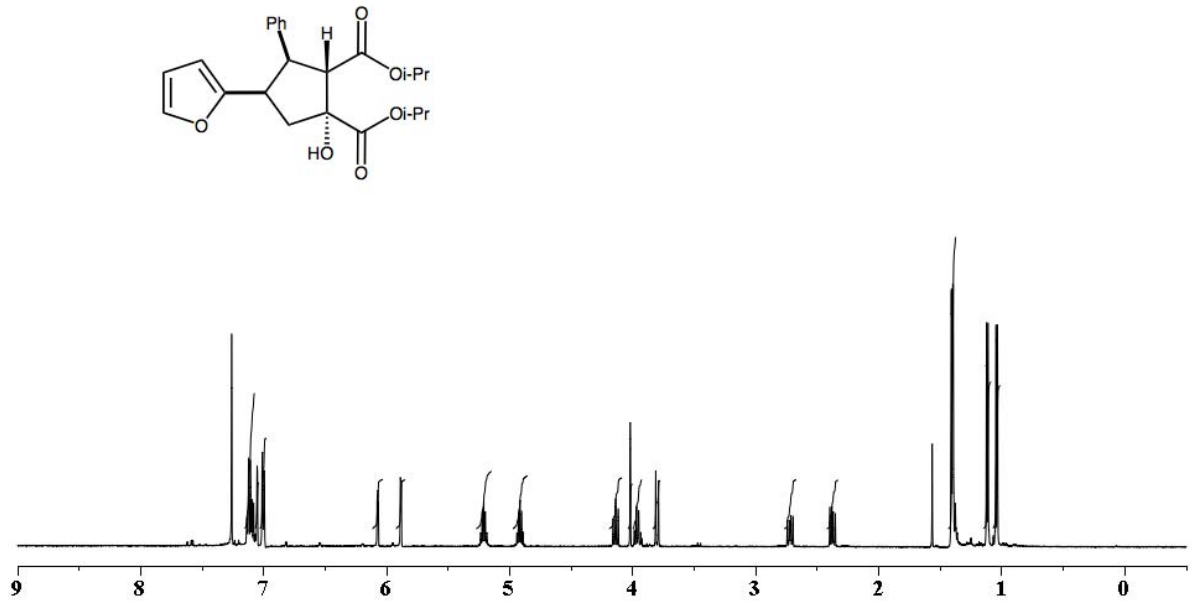
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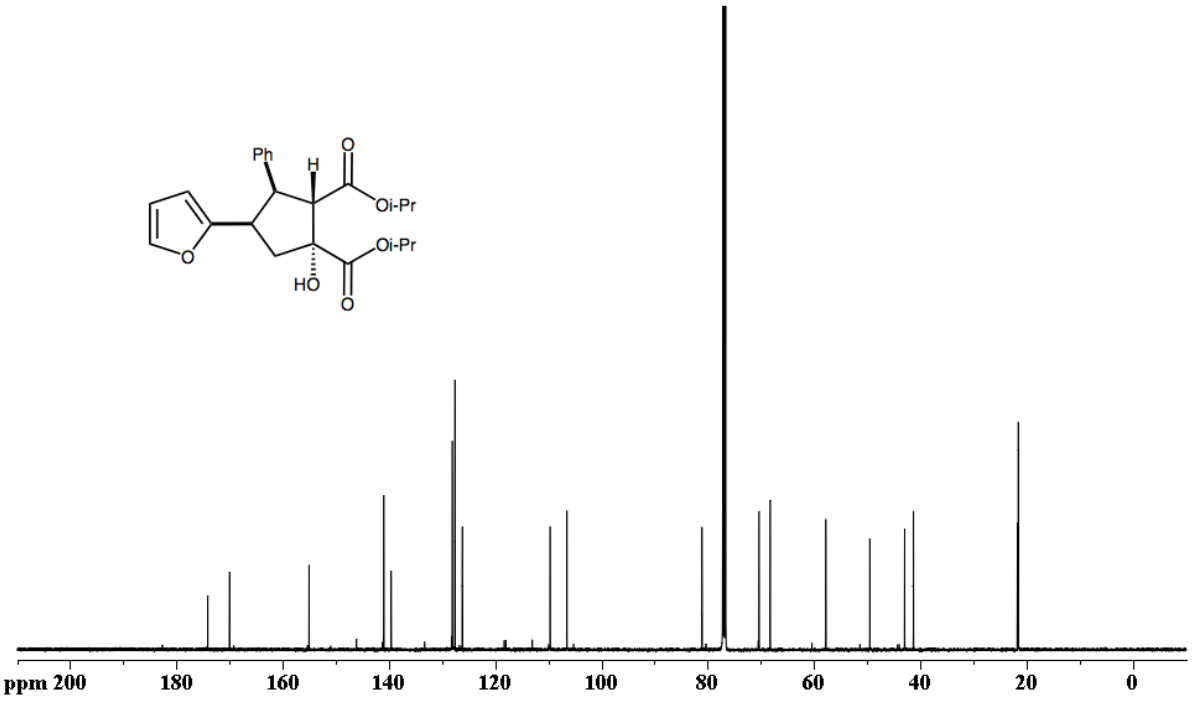
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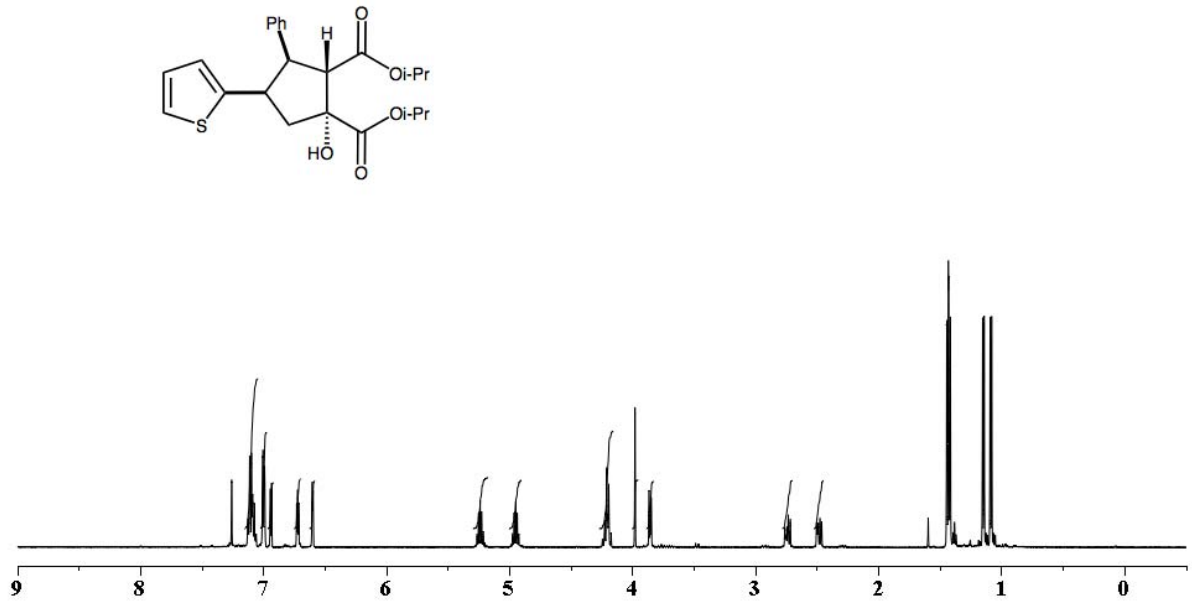
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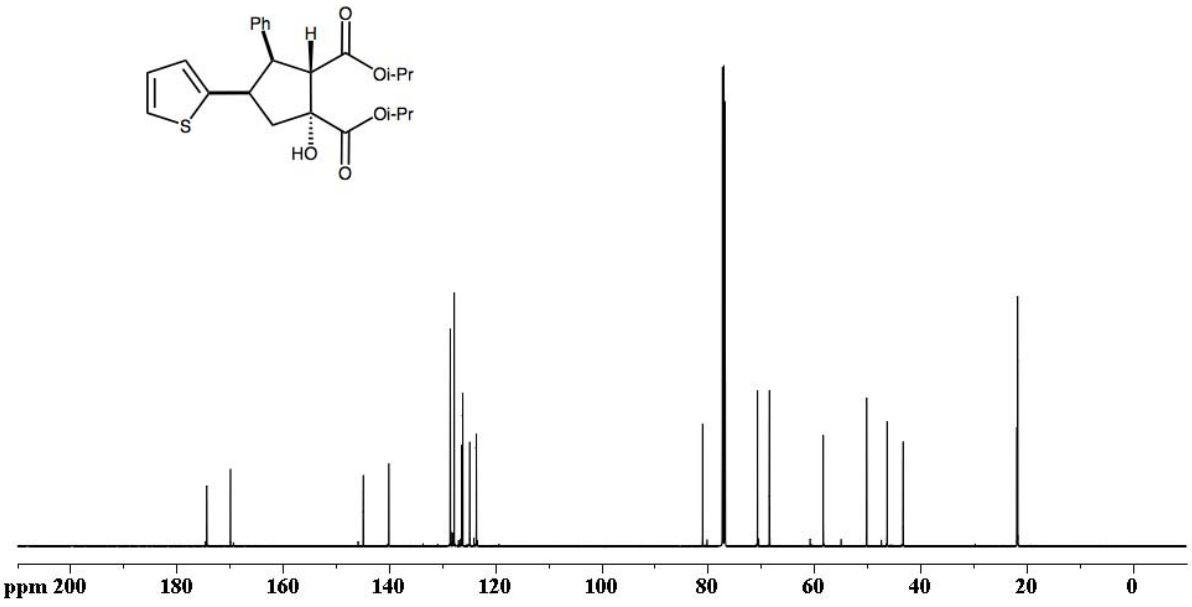
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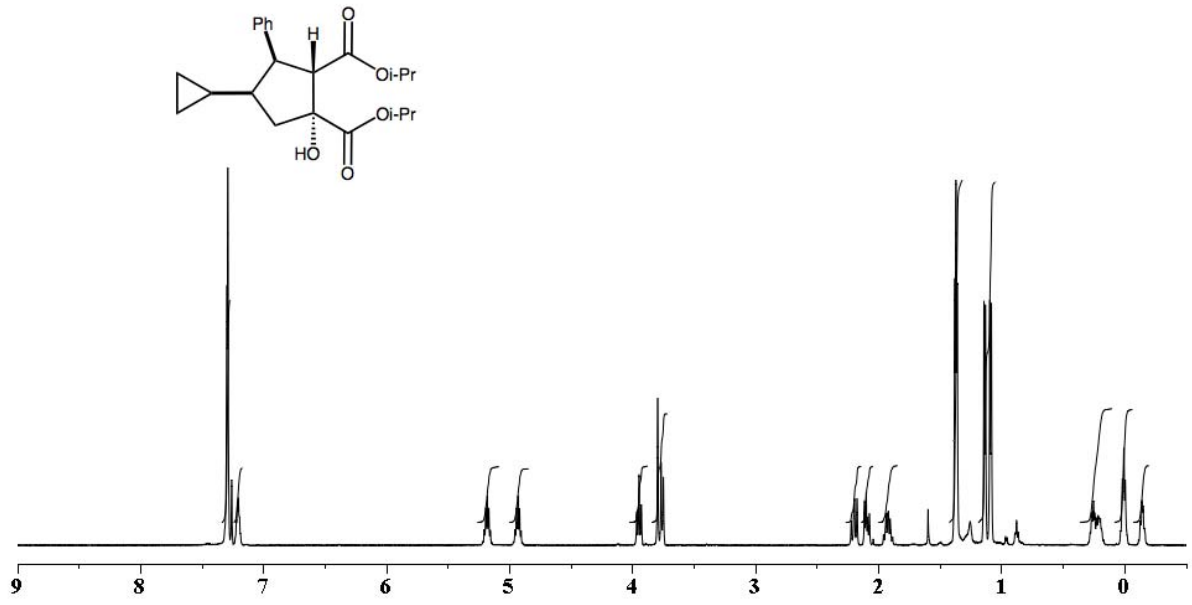
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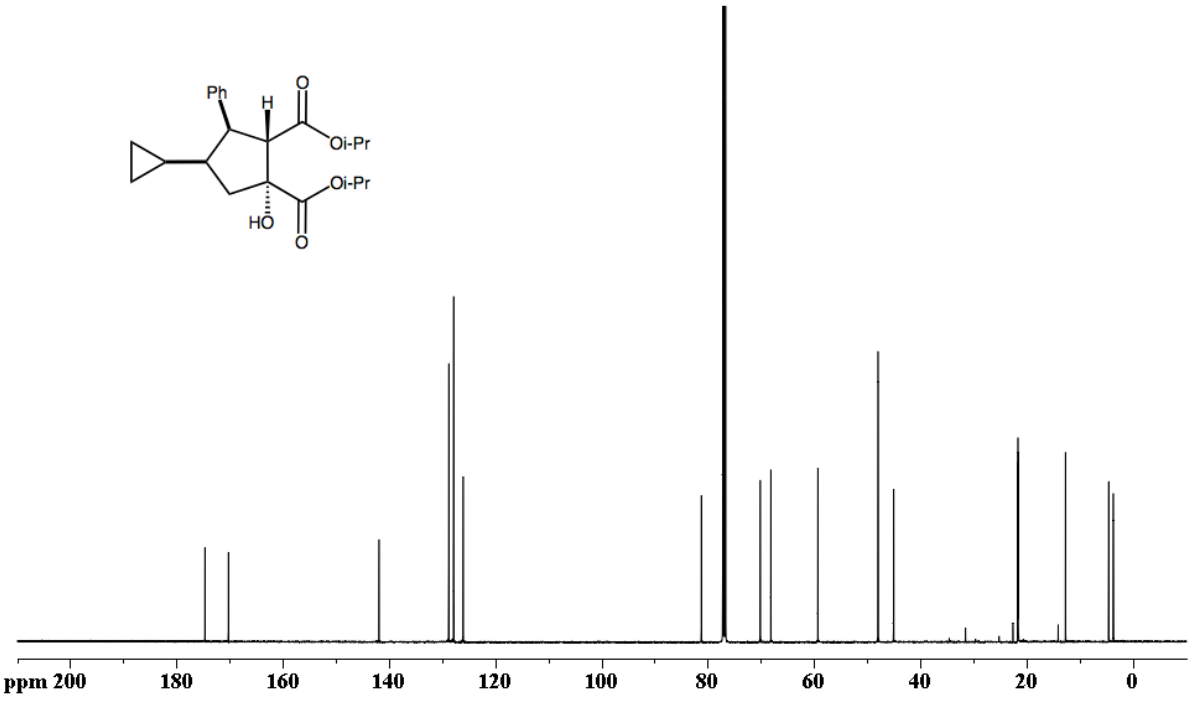
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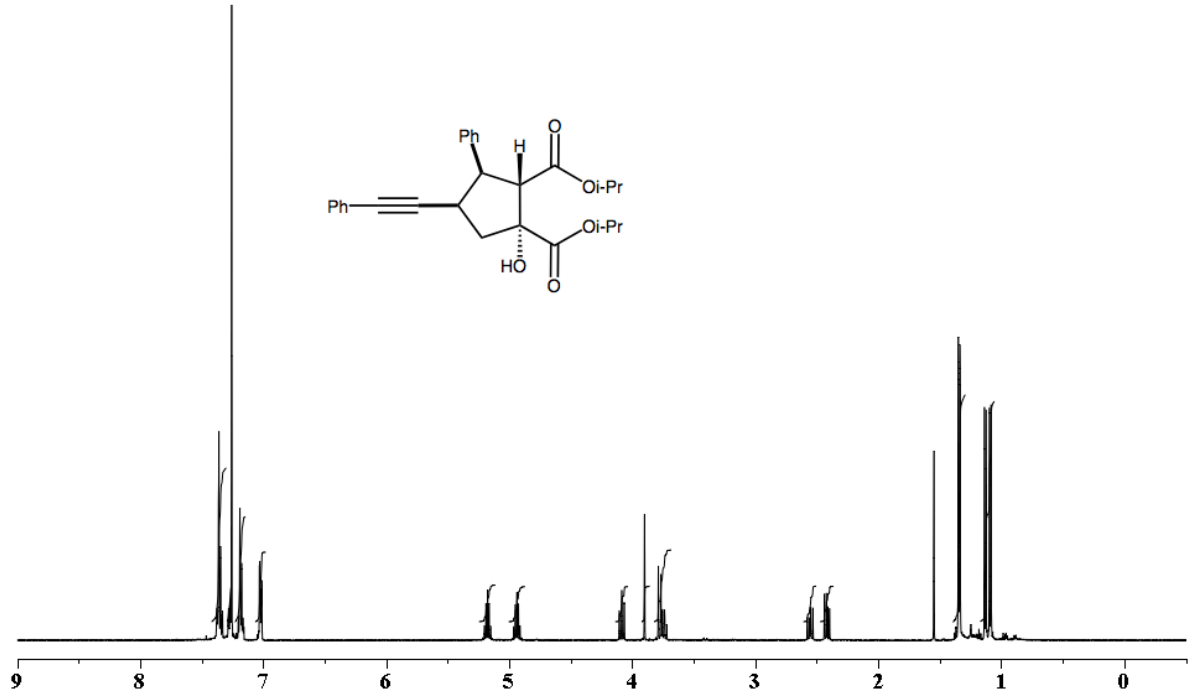
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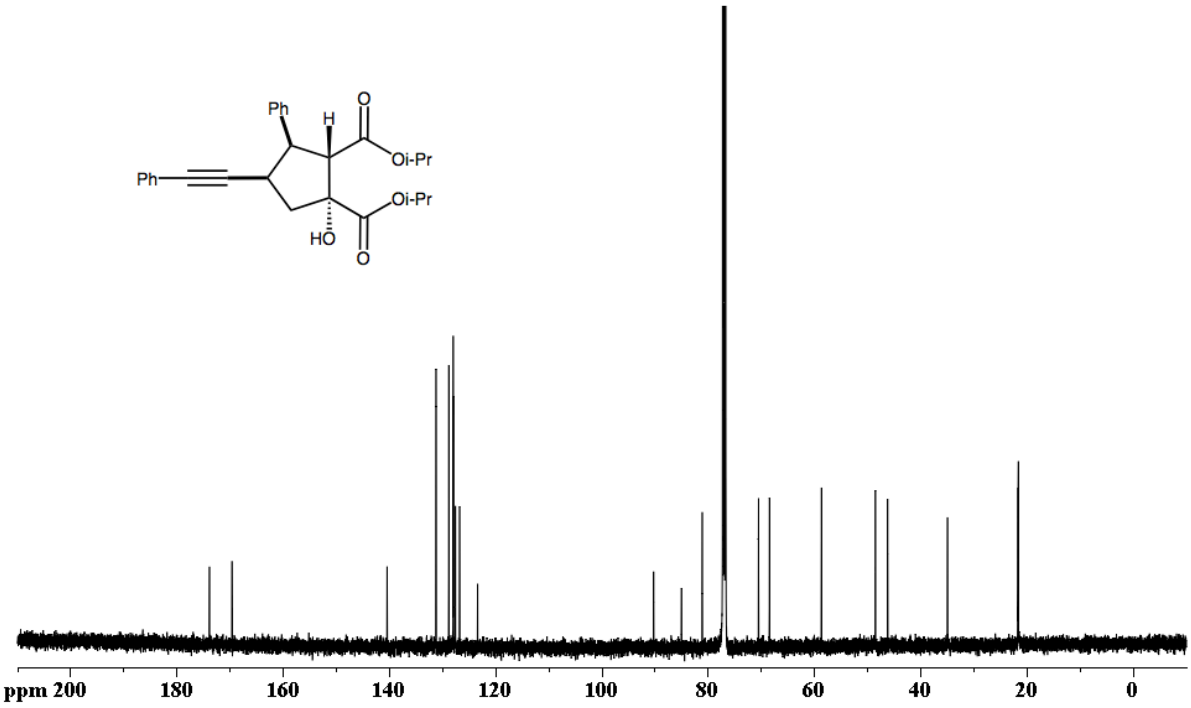
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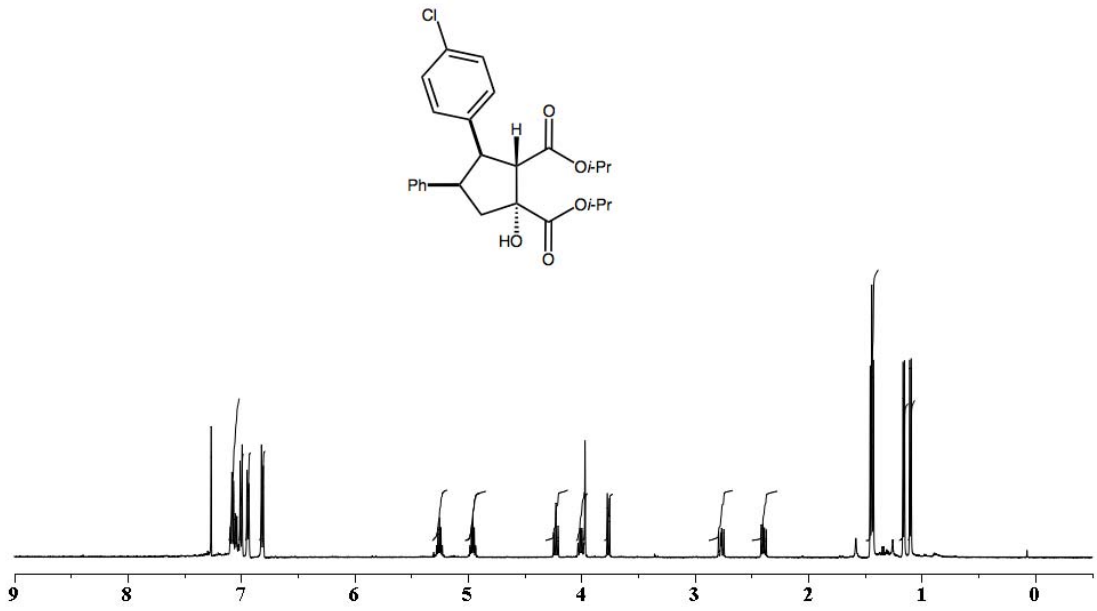
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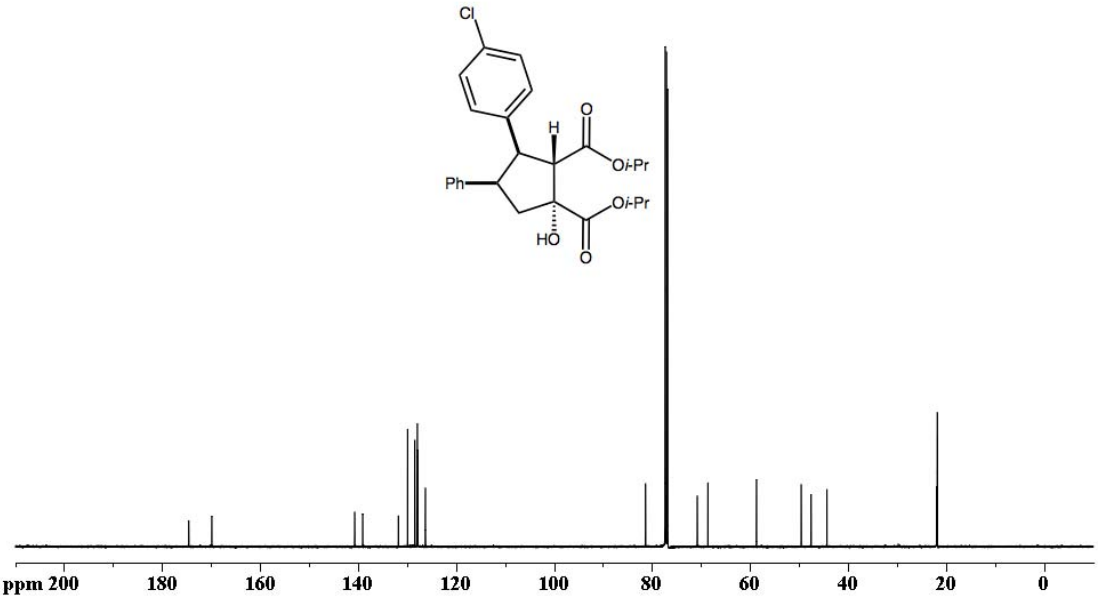
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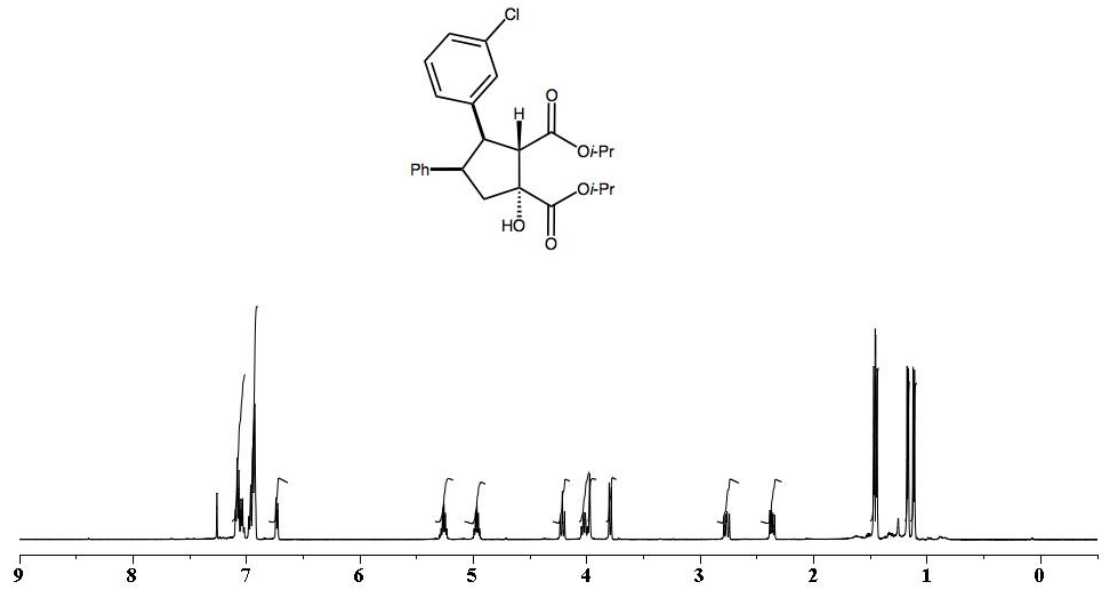
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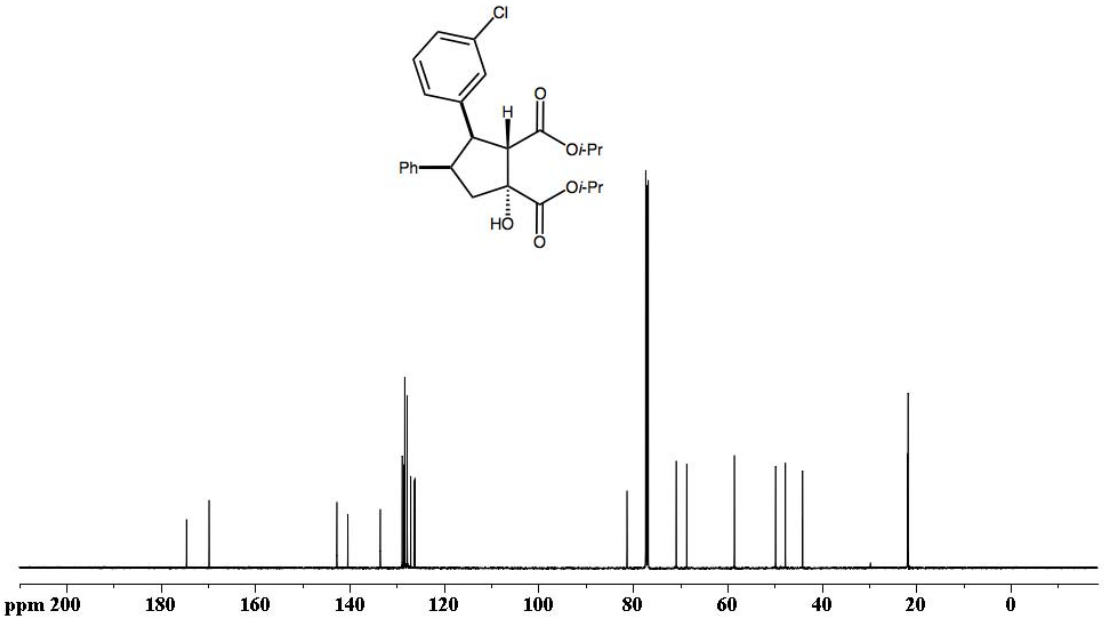
Cl
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O
Oi-Pr
Ph
Oi-Pr
HO
O
ppm 200
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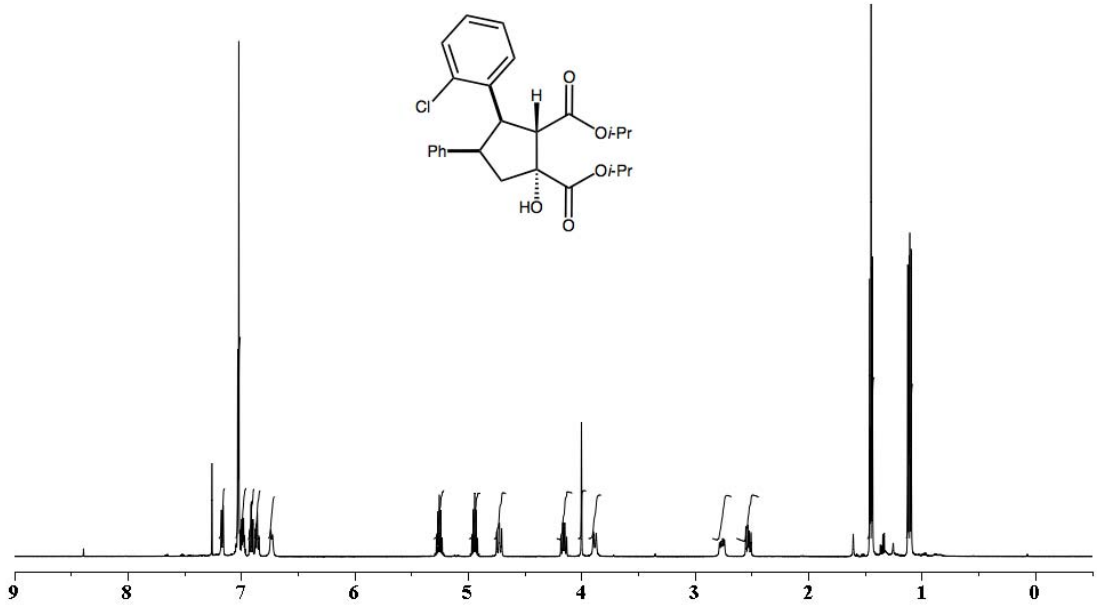
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O
Oi-Pr
Ph
Oi-Pr
HO
O
9
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7
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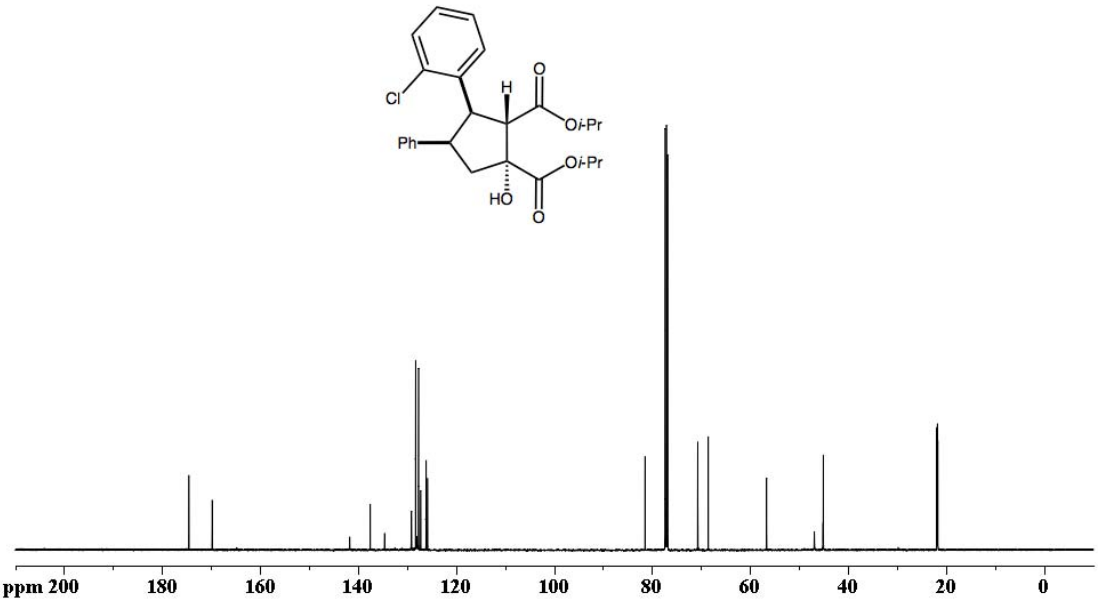
Cl
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O
Oi-Pr
Ph
Oi-Pr
HO
O
ppm 200
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140
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20
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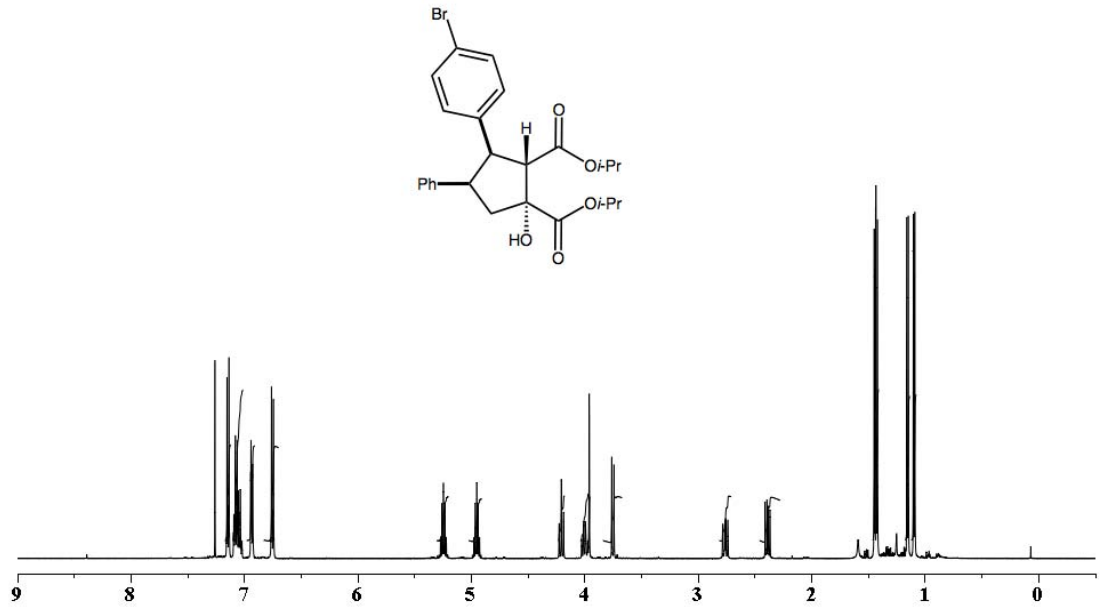
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Oi-Pr
Ph
Oi-Pr
HO
O
9
8
7
6
5
4
3
2
1
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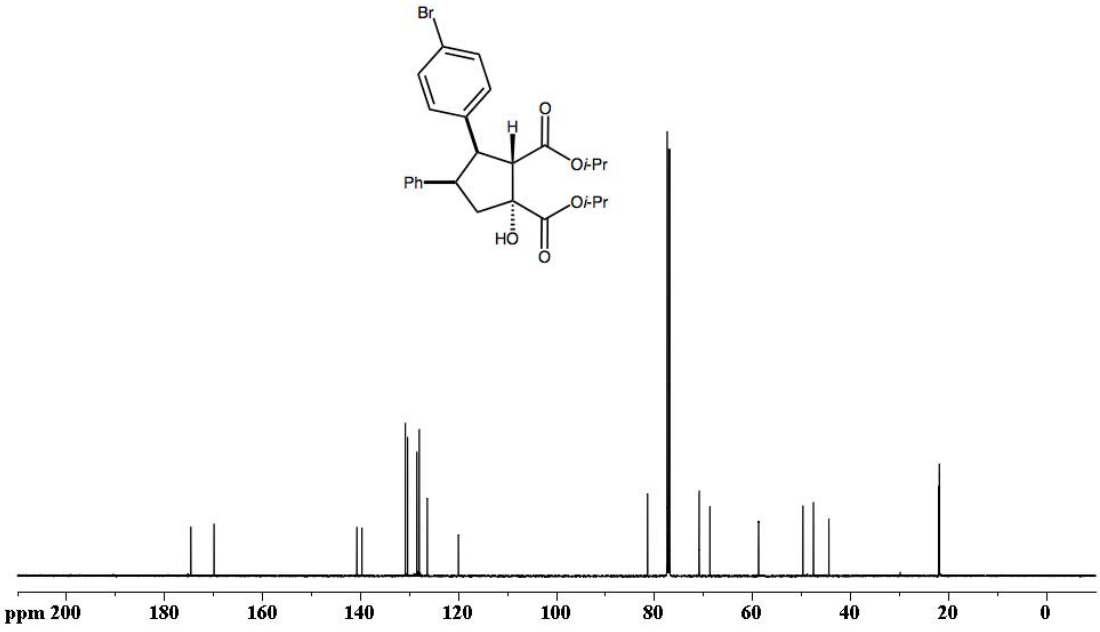
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Oi-Pr
Ph
Oi-Pr
HO
O
ppm 200
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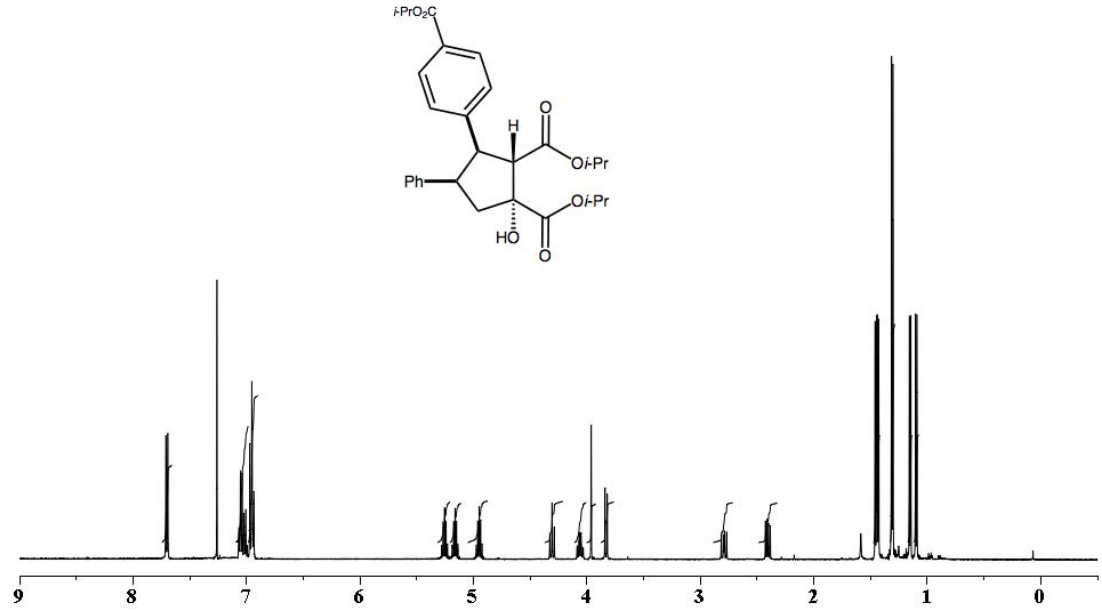
i-PrO2C
H
O
Oi-Pr
Ph
Oi-Pr
HO
O
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8
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4
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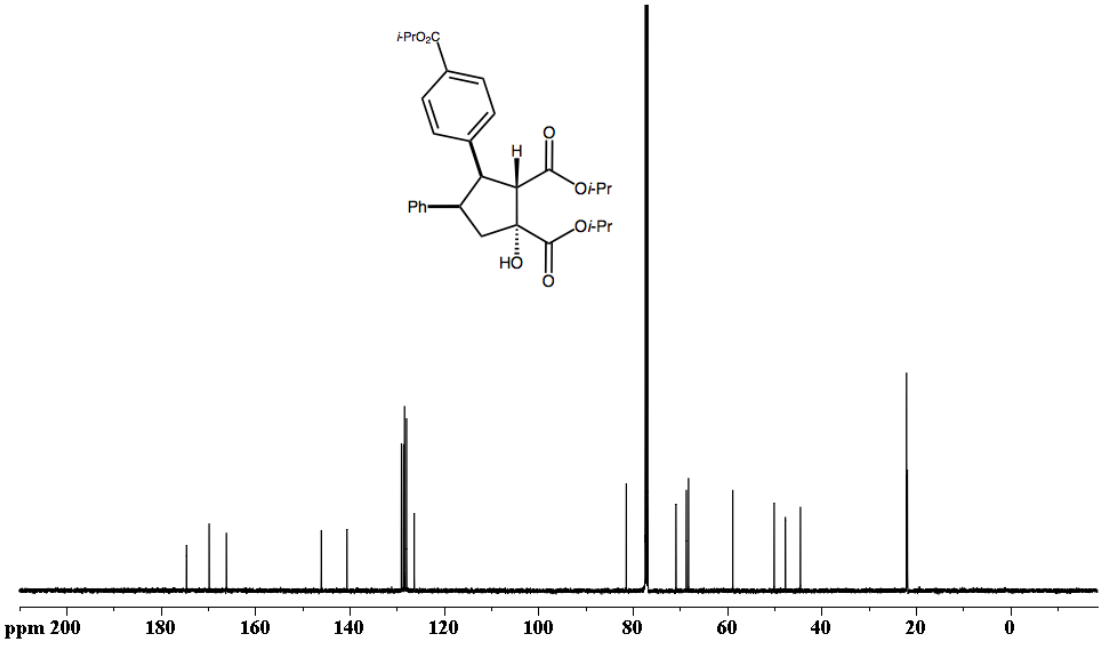
2
1
0


i-PrO2C
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Oi-Pr
Ph
Oi-Pr
HO
O
ppm 200
180
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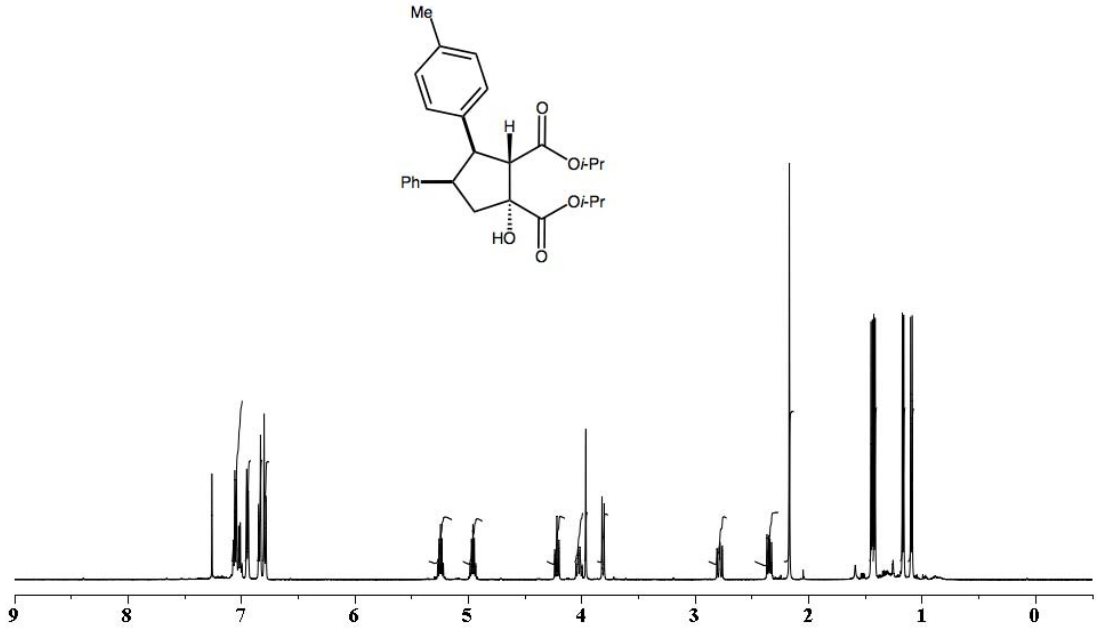
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Ph
O*i*-Pr
HO
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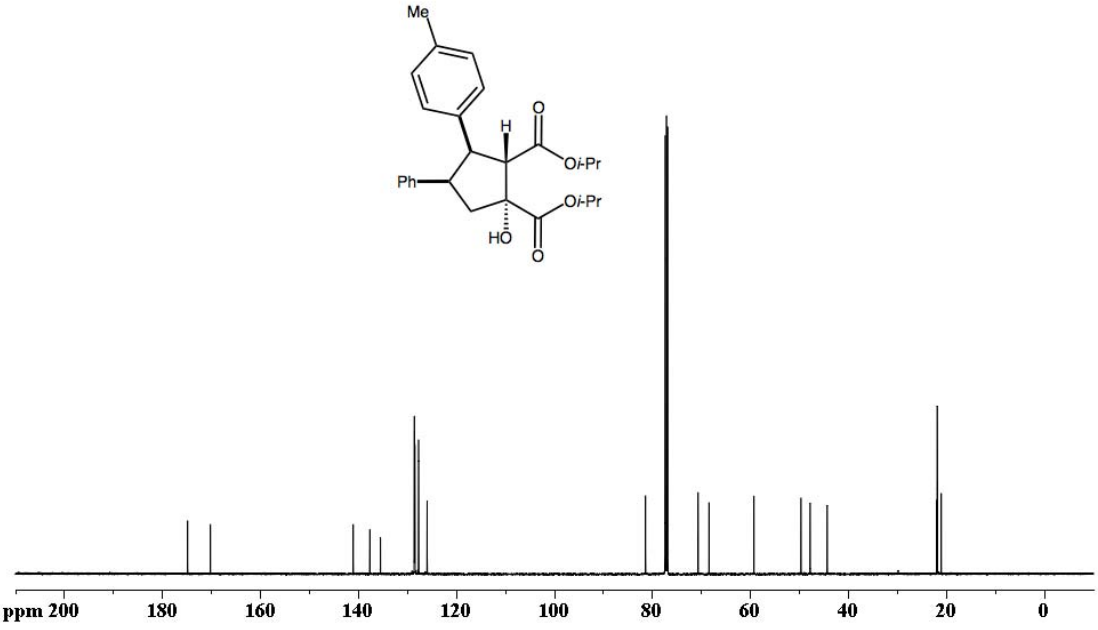
Me
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O
O*i*-Pr
Ph
O*i*-Pr
HO
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ppm 200
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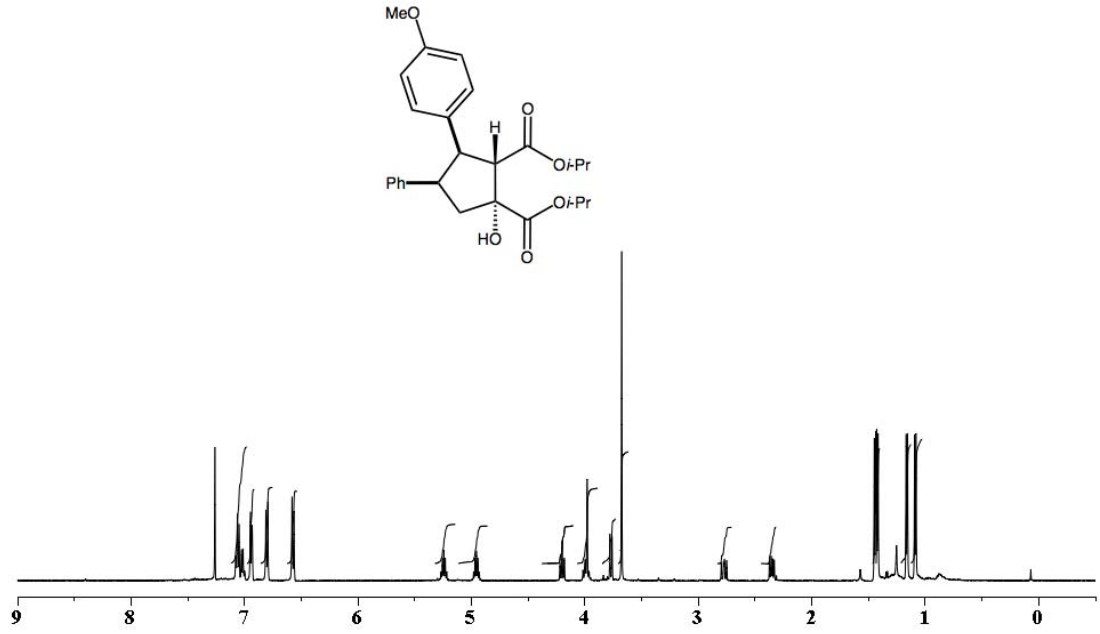
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Ph
Oi-Pr
HO
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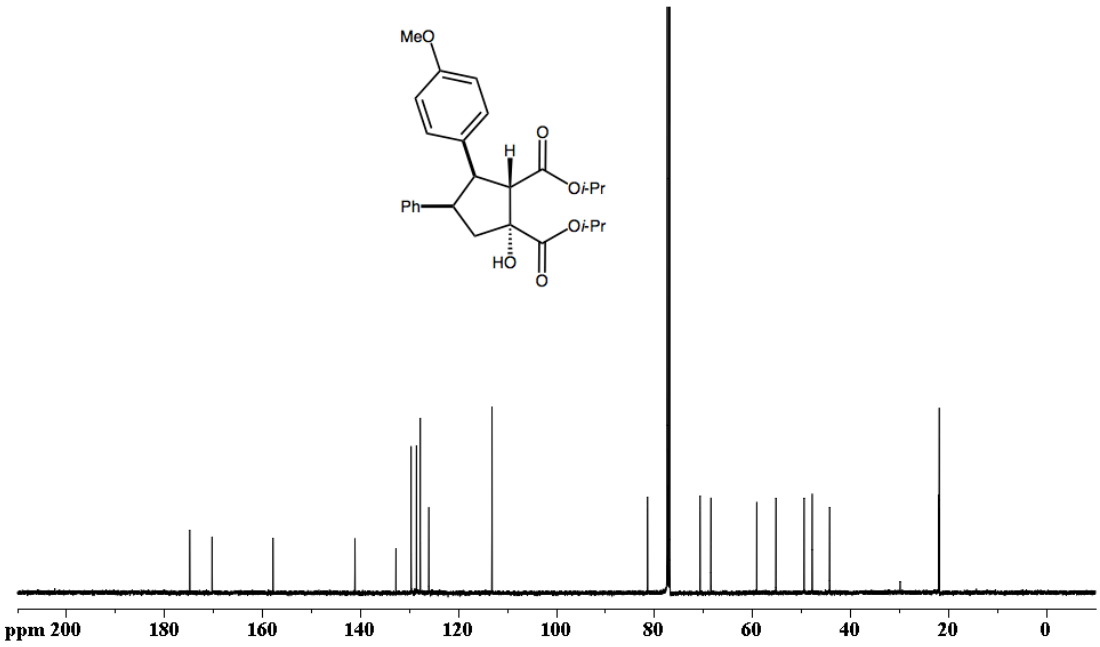
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Oi-Pr
Ph
Oi-Pr
HO
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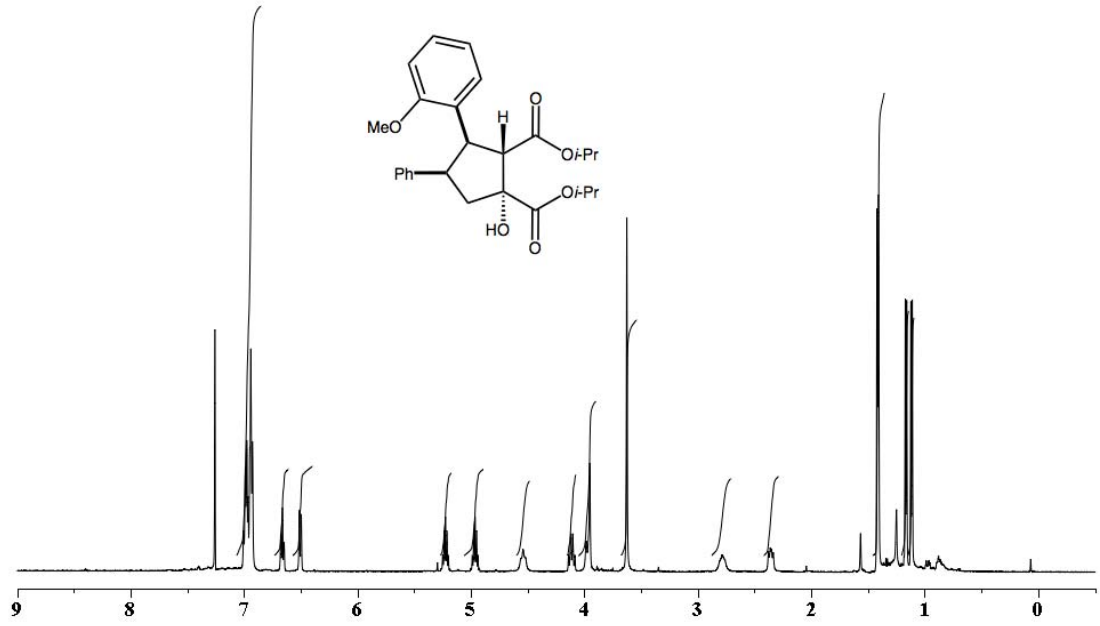
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Oi-Pr
Ph
Oi-Pr
HO
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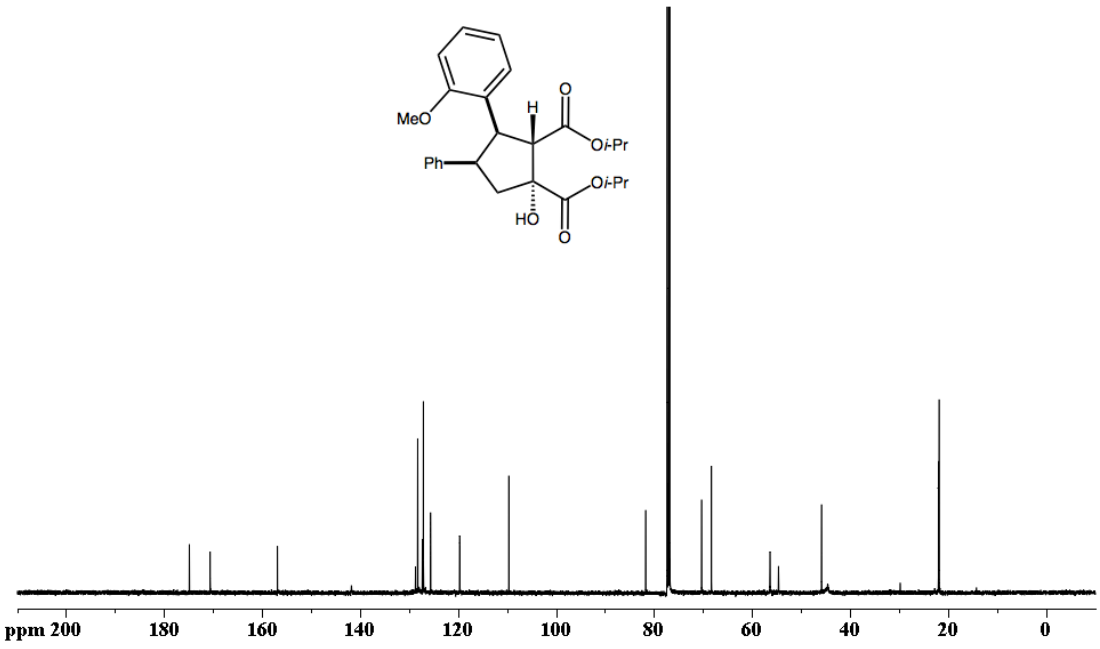
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Oi-Pr
Ph
Oi-Pr
HO
O
ppm 200
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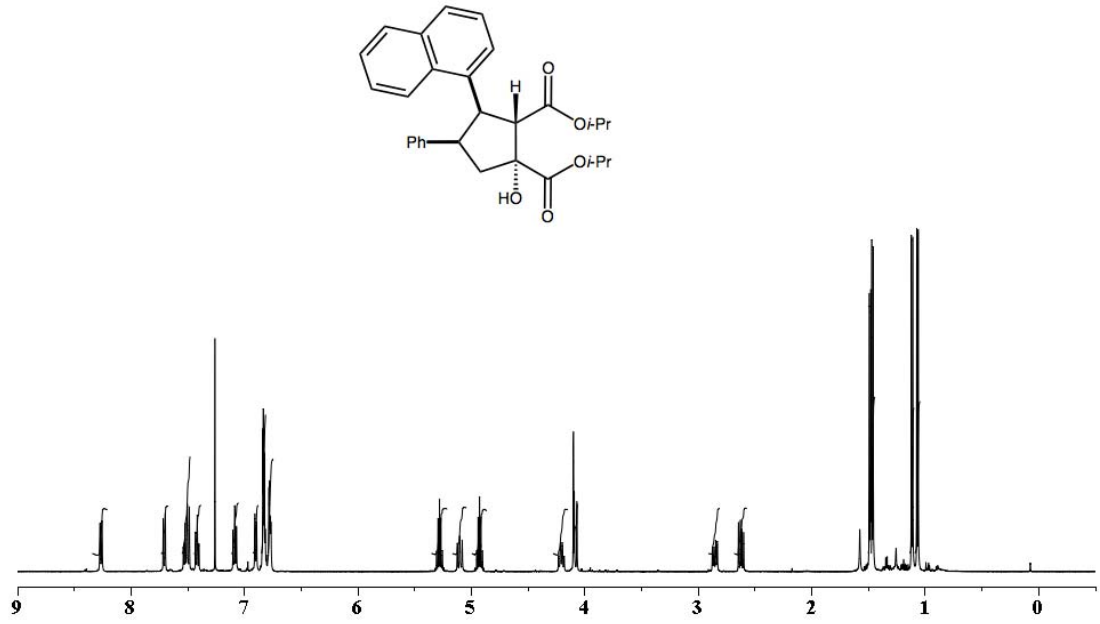
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O
Oi-Pr
Ph
Oi-Pr
HO
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2
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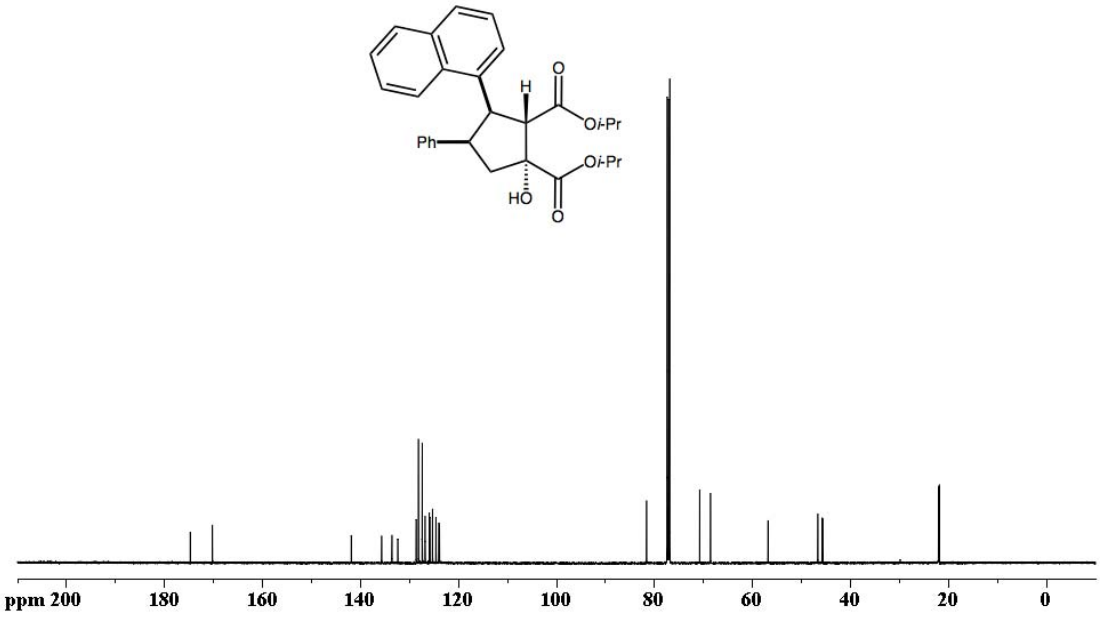
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Oi-Pr
Ph
Oi-Pr
HO
O
ppm 200
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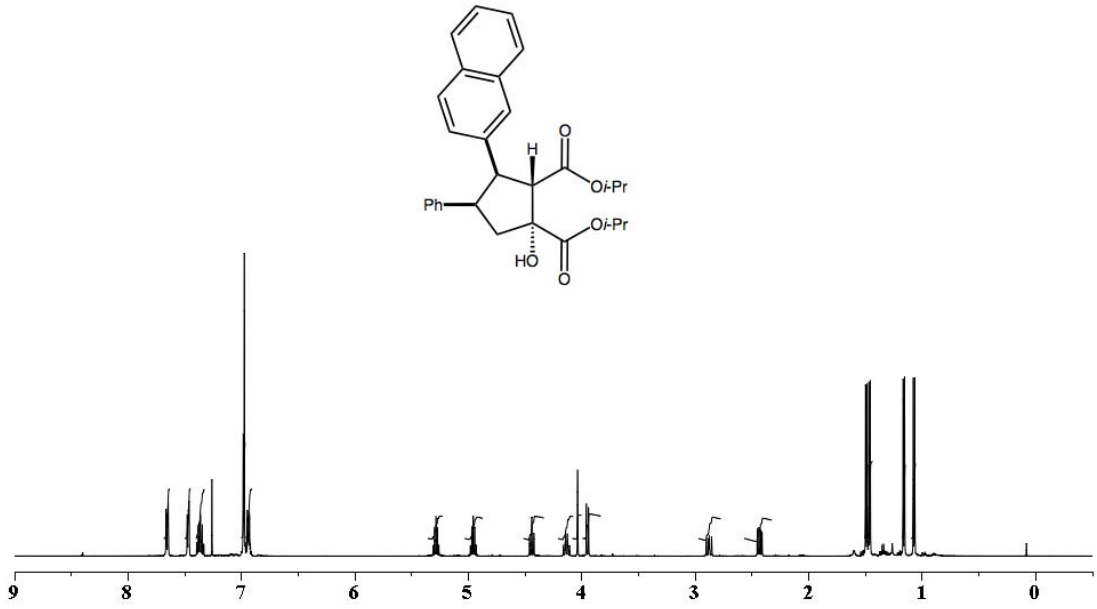
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Oi-Pr
Ph
Oi-Pr
HO
O
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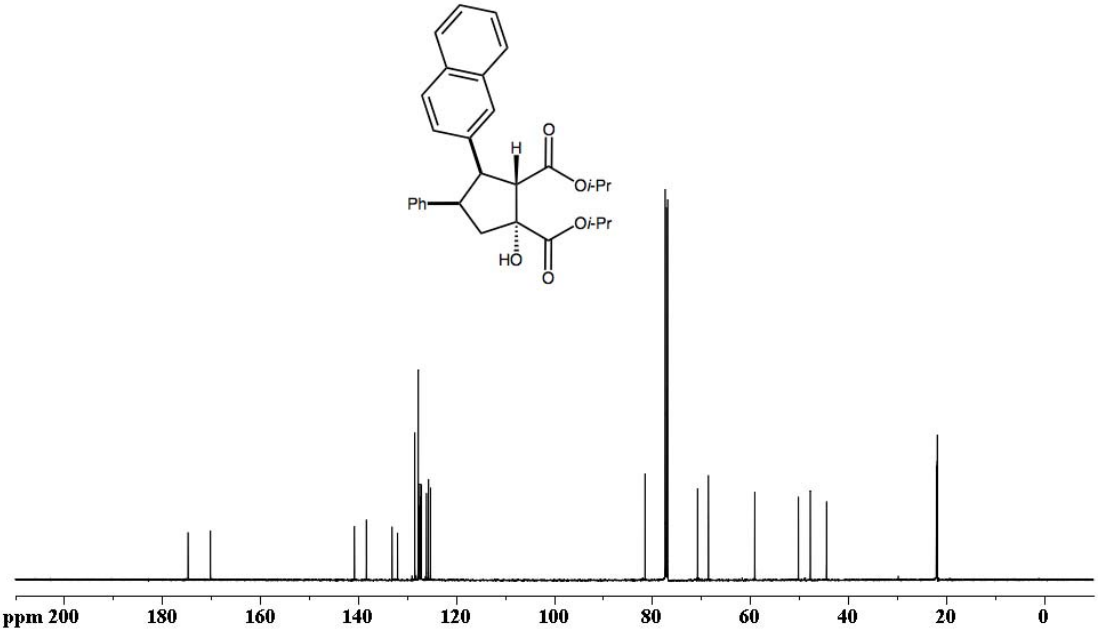
0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O
Oi-Pr
Ph
Oi-Pr
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100
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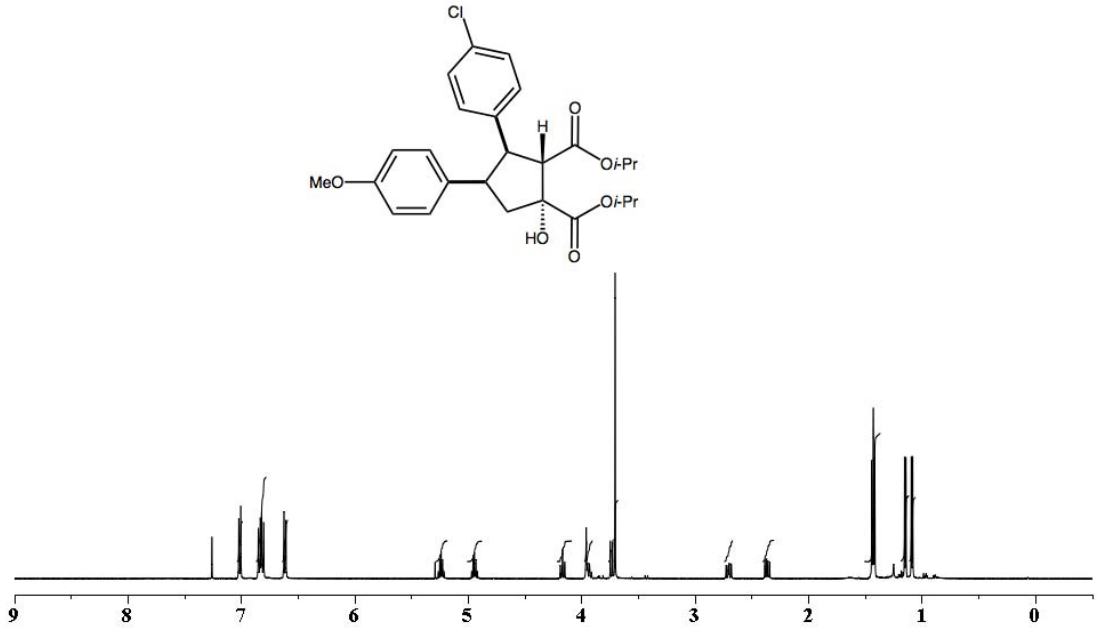
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MeO
Oi-Pr
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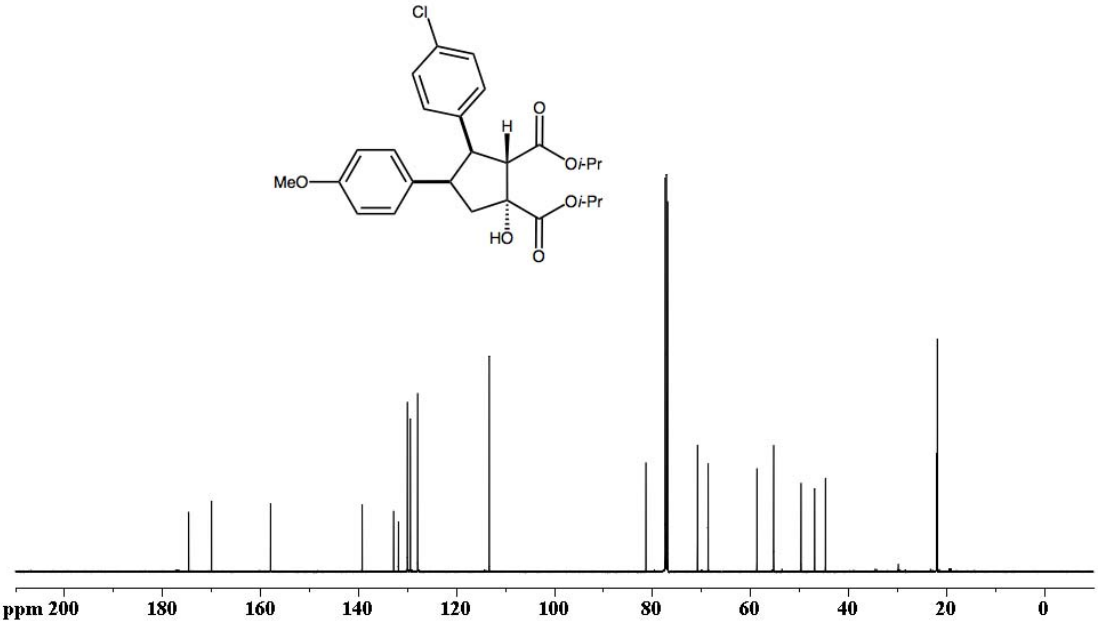
0


Cl
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O
Oi-Pr
MeO
Oi-Pr
HO
O
ppm 200
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140
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100
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20
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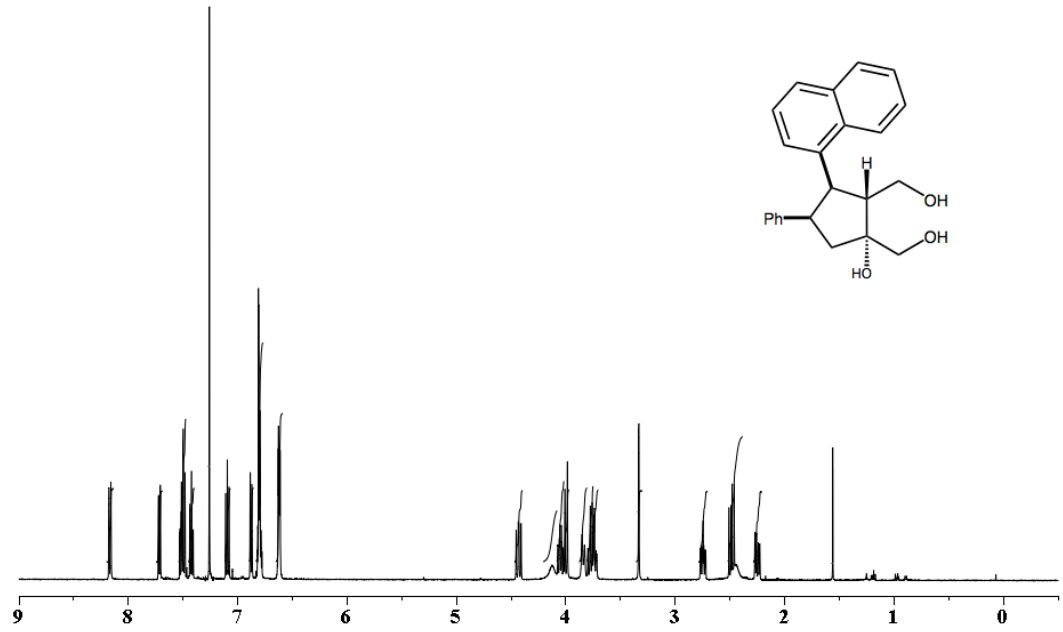
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Ph
OH
HO
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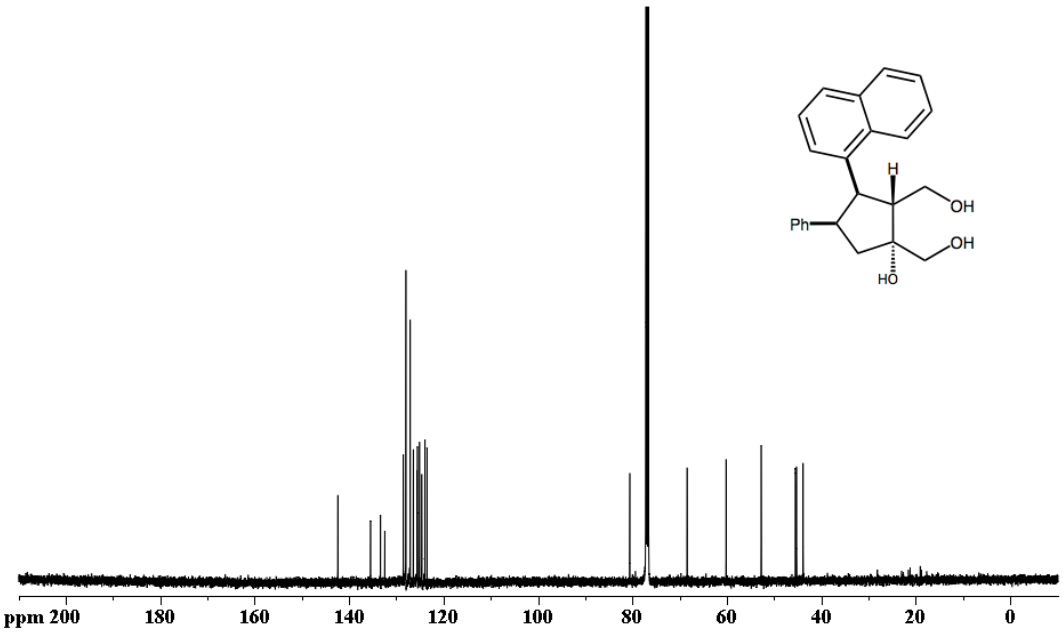
1
0


H
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Ph
OH
HO
ppm 200
180
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140
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60
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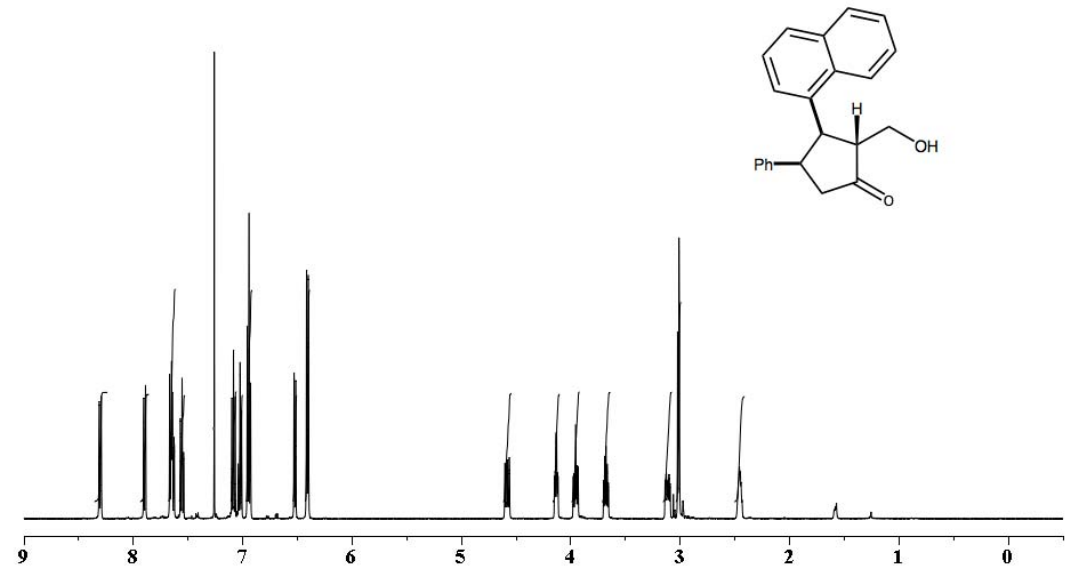
H
OH
Ph
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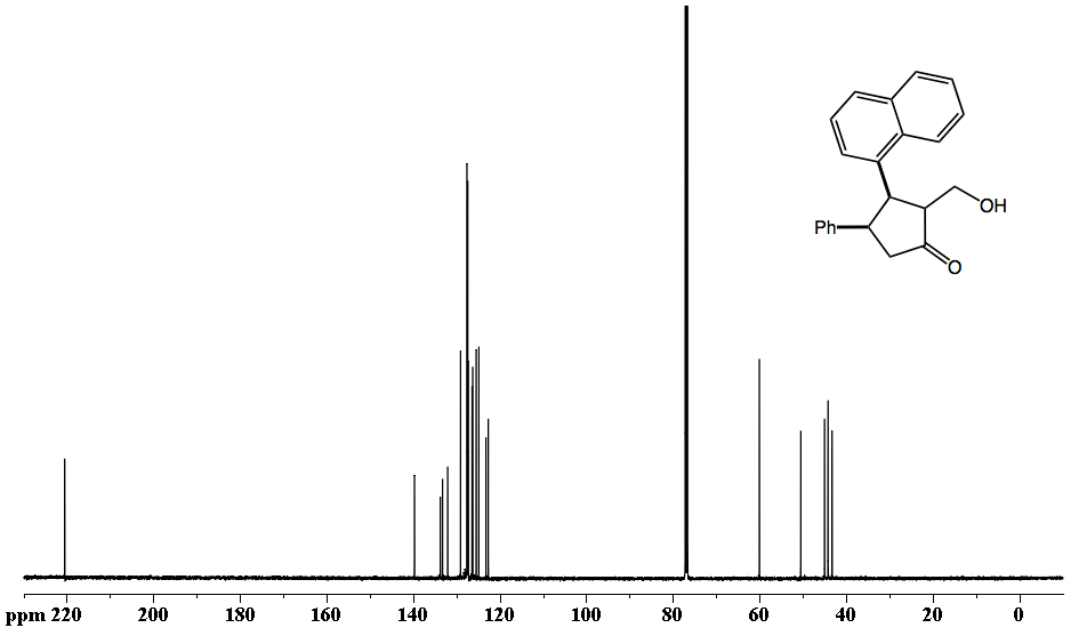
1
0


OH
Ph
O
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200
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100
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20
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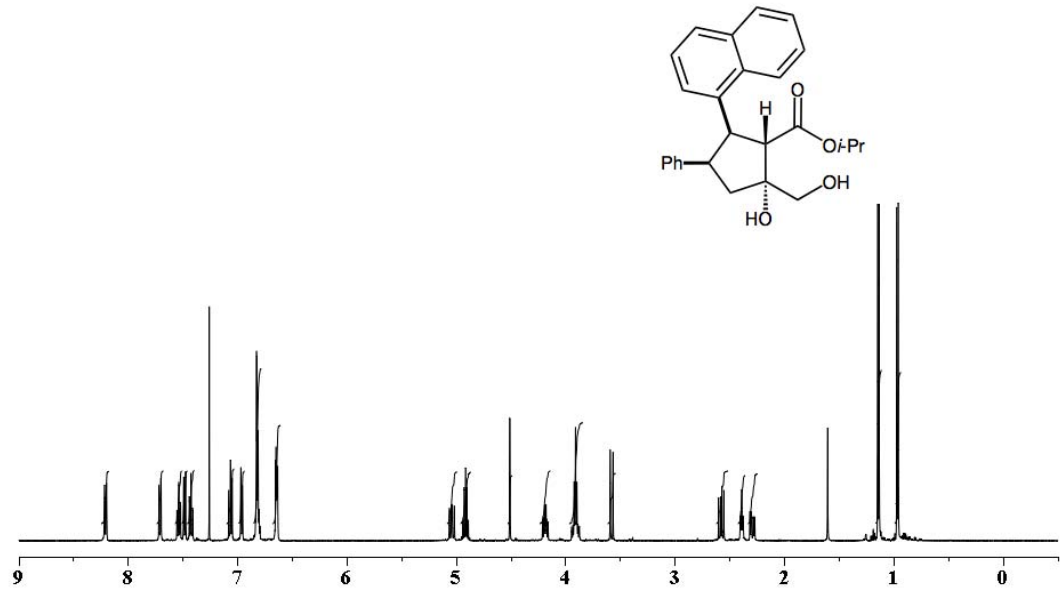
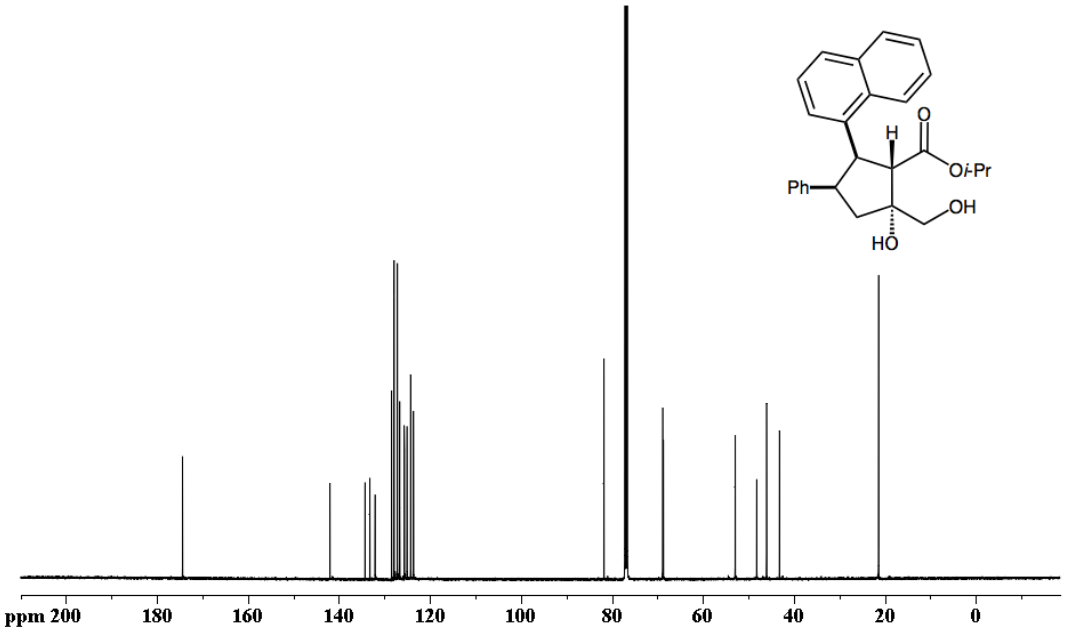

O
H
Oi-Pr
Ph
OH
HO
9
8
7
6
5
4
3
2
1
0


O
H
Oi-Pr
Ph
OH
HO
ppm 200
180
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140
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100
80
60
40
20
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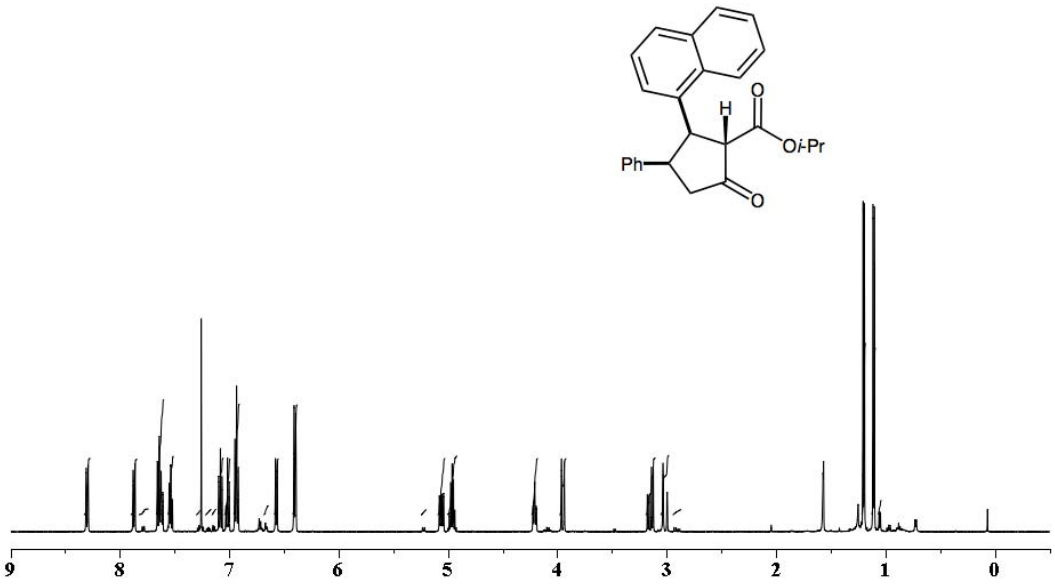
H
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O*i*-Pr
Ph
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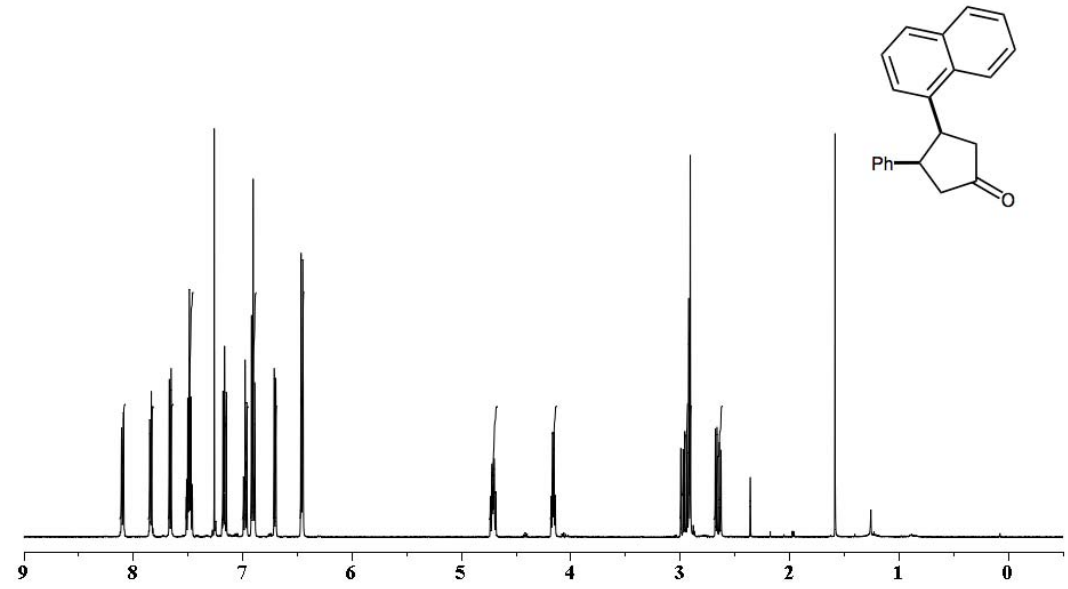
Ph
O
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3
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1
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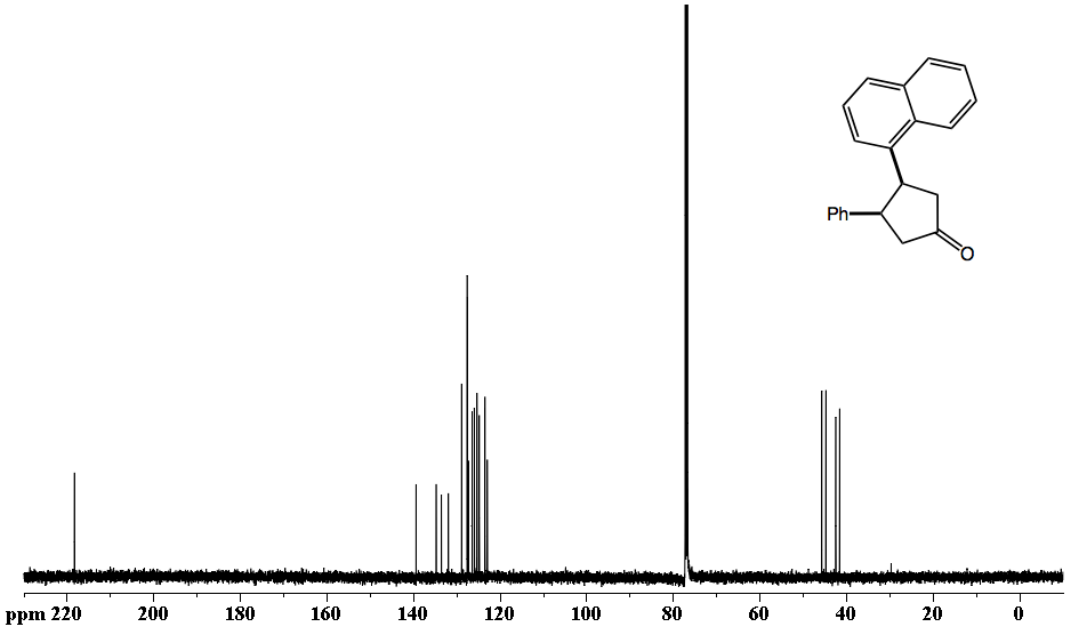
Ph
O
ppm 220
200
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160
140
120
100
80
60
40
20
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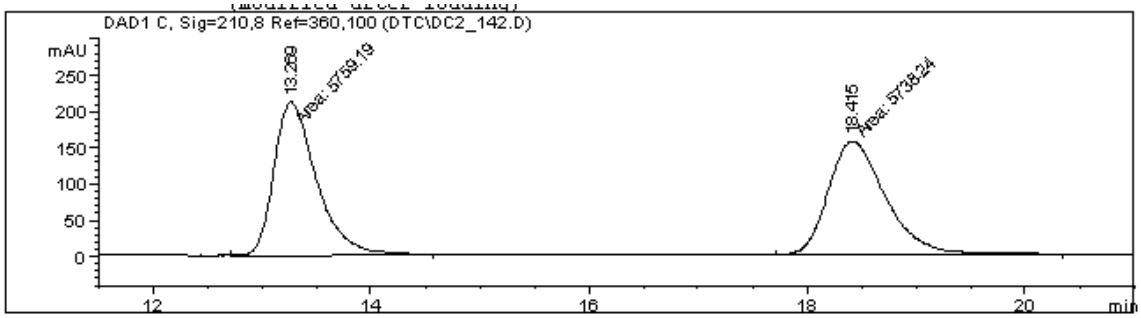
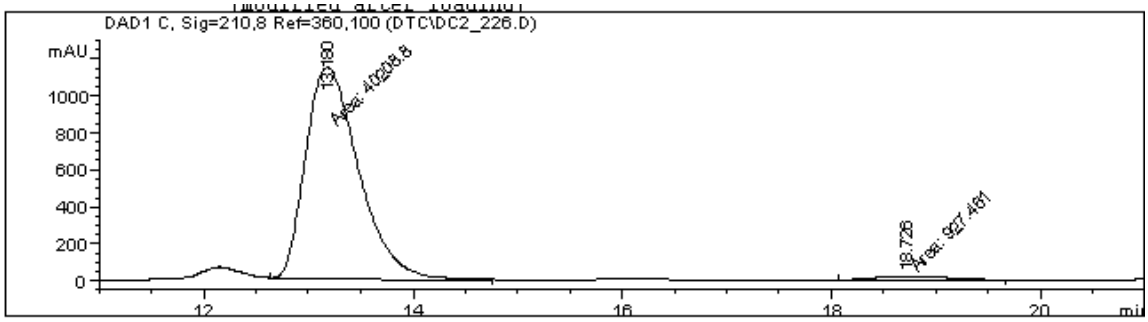
HPLC Traces of Racemic and Enantioenriched Compounds

Racemic 3



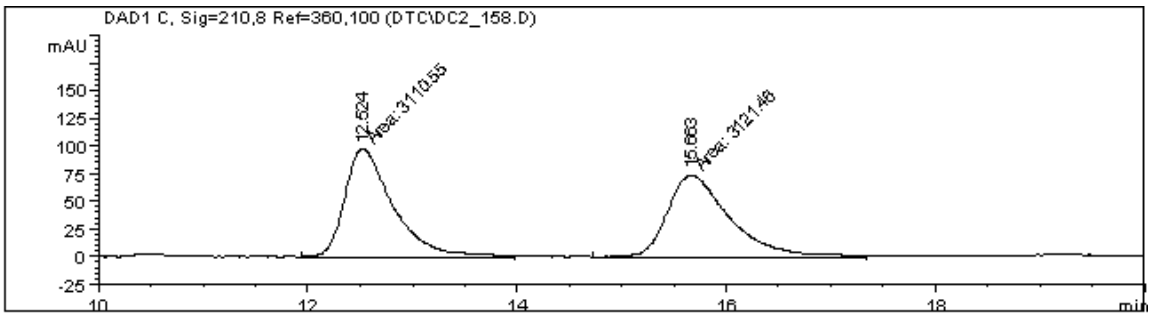

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.269 MM    0.4531 5759.18896  211.84776  50.0911
   2  18.415 MM    0.6111 5738.24023  156.50308  49.9089

Totals :                  1.14974e4   368.35085
```

Enatioenriched 3



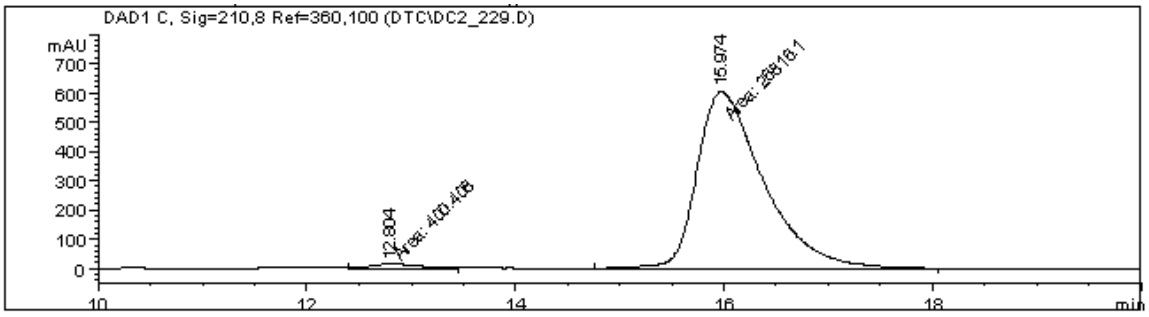

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.180 MM    0.5858 4.02088e4  1143.91345  97.7454
   2  18.726 MM    0.7381  927.46082   20.94258   2.2546

Totals :                  4.11362e4  1164.85604
```

Racemic 4



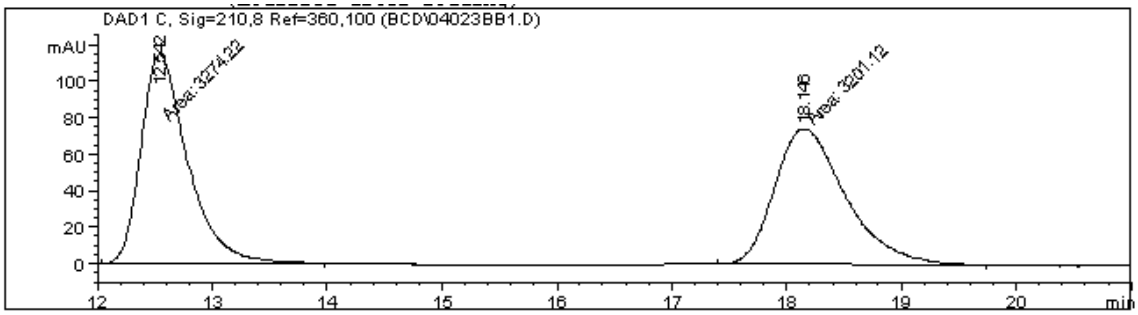

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.524 MM    0.5313 3110.54614   97.58183  49.9124
   2  15.663 MM    0.6944 3121.45898   74.92123  50.0876

Totals :                  6232.00513  172.50305
```

Enatioenriched 4



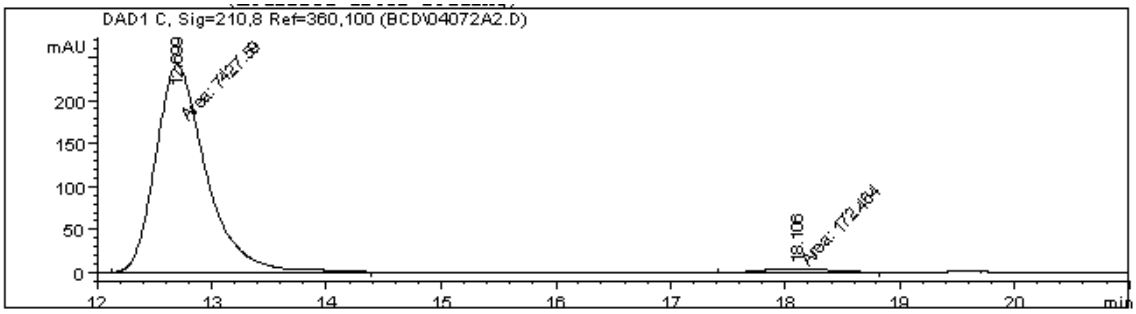

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.804 MM    0.5229  400.40820   12.76304   1.4712
   2  15.974 MM    0.7397 2.68161e4   604.21637  98.5288

Totals :                  2.72165e4   616.97941
```

Racemic 5



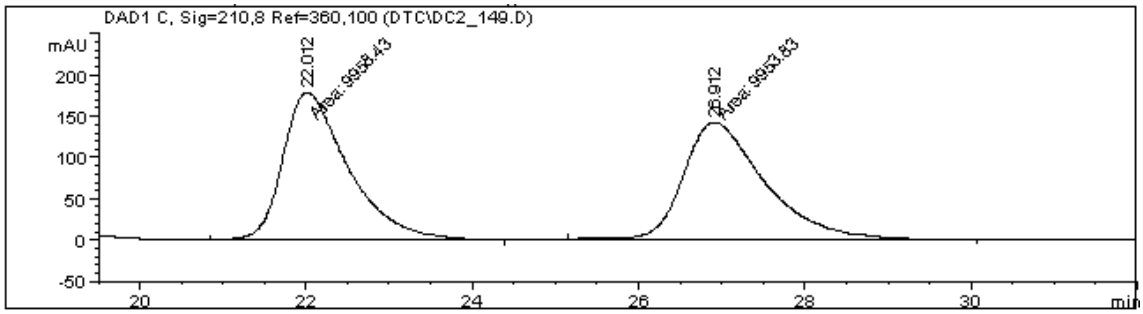

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.542 MM    0.4760 3274.21533  114.65311  50.5644
   2  18.146 MM    0.7178 3201.12476   74.32366  49.4356

Totals :                  6475.34009  188.97677
```

Enantioenriched 5



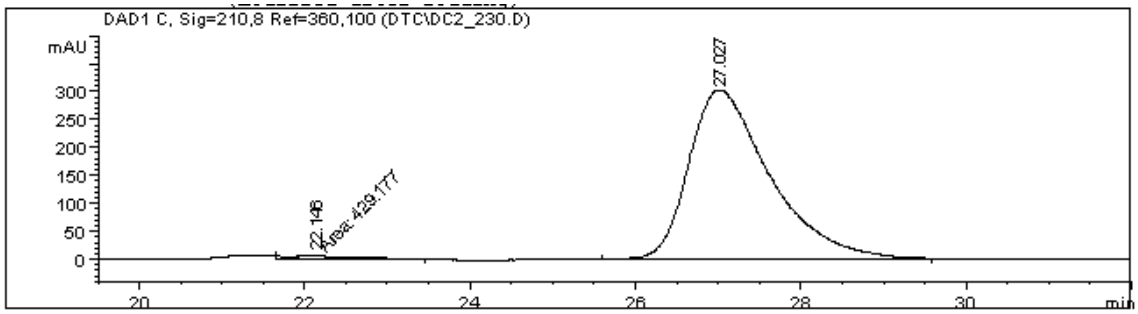

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.699 MM    0.5127 7427.59375  241.47023  97.7308
   2  18.106 MM    0.6762  172.46419    4.25109   2.2692

Totals :                  7600.05794  245.72132
```

Racemic 6



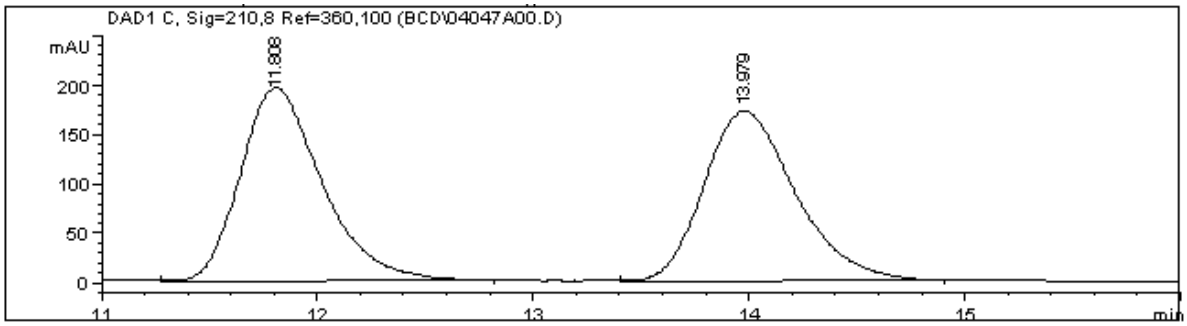

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.012 MM    0.9231 9958.43164  179.80490  50.0116
   2  26.912 MM    1.1619 9953.83008  142.78087  49.9884

Totals :                  1.99123e4   322.58577
```

Enatioenriched 6



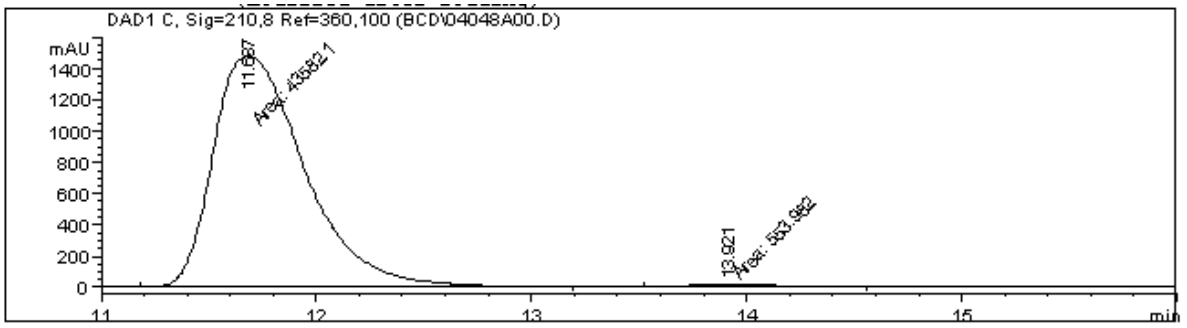

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.146 MM    1.0649  429.17670    6.71727   2.0309
   2  27.027 VB    0.8261 2.07031e4   302.64142  97.9691

Totals :                  2.11322e4   309.35869
```

Racemic 7



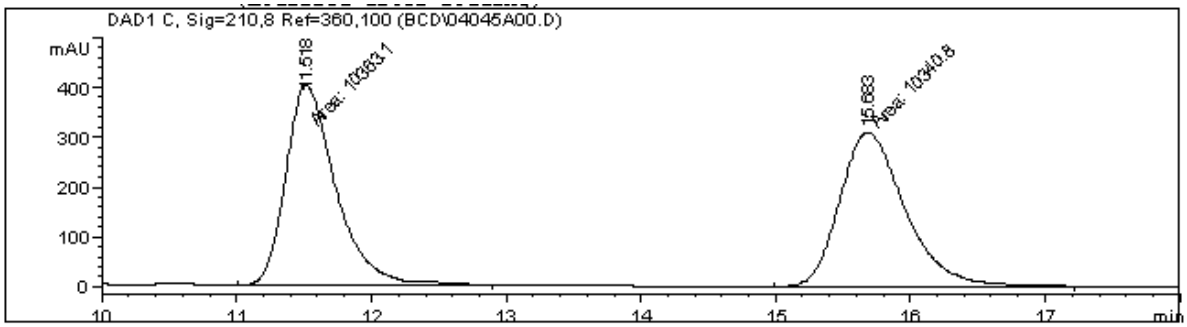

```
=====================================================================
                       Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.808 VB    0.3993 5186.56104  195.62614  50.4879
   2  13.979 BB    0.4529 5086.31543  172.05933  49.5121

Totals :                  1.02729e4   367.68547
```

Enantioenriched 7



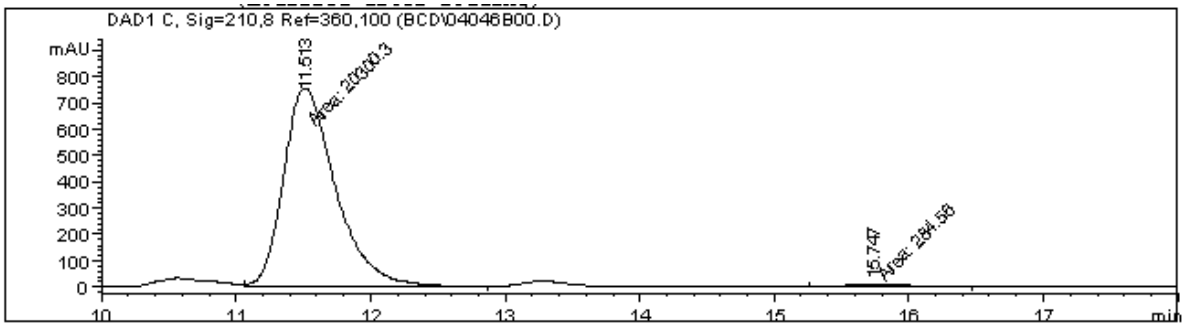

```
=====================================================================
                       Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.687 MM    0.4910 4.3582le4  1479.45947  98.7448
   2  13.921 MM    0.4726  553.98181   19.53677   1.2552

Totals :                  4.41360e4  1498.99624
```

Racemic 8



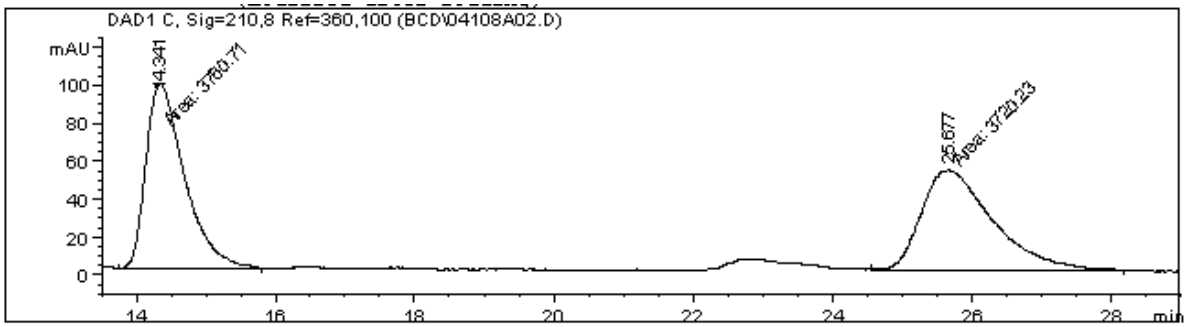

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.518 MM    0.4312 1.03631e4   400.52957  50.0538
   2  15.683 MM    0.5581 1.03408e4   308.79007  49.9462

Totals :                  2.07039e4   709.31964
```

Enantioenriched 8



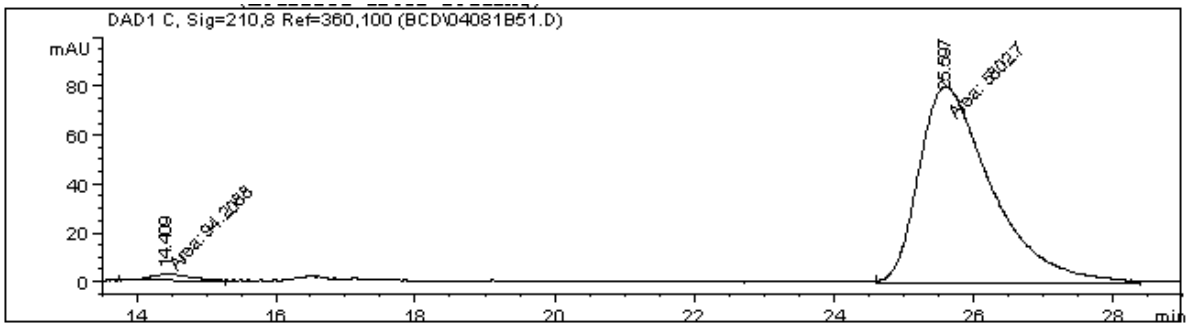

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.513 MM    0.4481 2.03003e4   755.02045  98.6176
   2  15.747 MM    0.5348  284.56036    8.86790   1.3824

Totals :                  2.05849e4   763.88835
```

Racemic 9



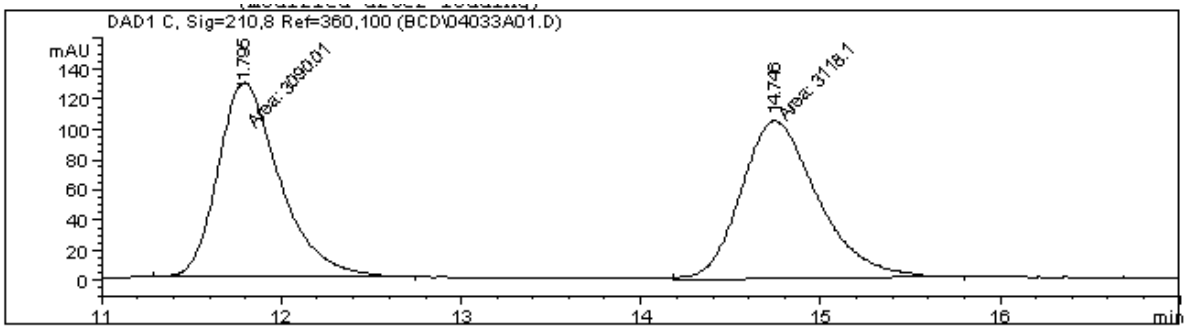

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.341 MM    0.6440 3760.70752   97.33033  50.2705
   2  25.677 MM    1.1746 3720.23462   52.78723  49.7295

Totals :                  7480.94214  150.11756
```

Enantioenriched 9



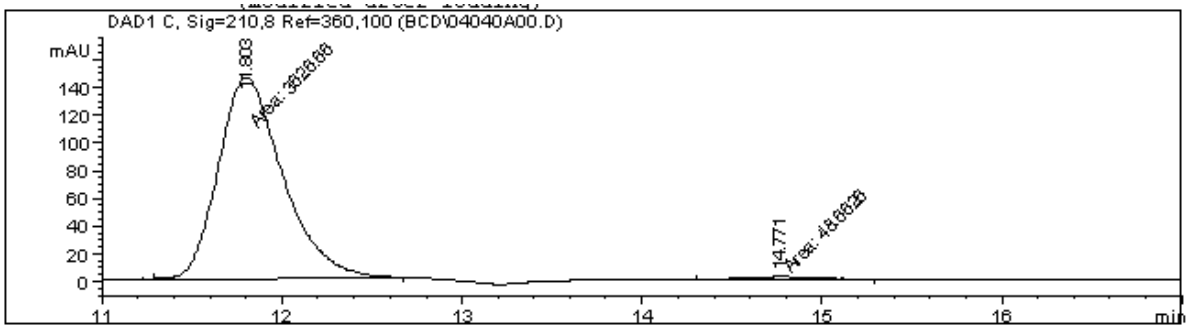

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.409 MM    0.6392   94.20879    2.45639   1.5976
   2  25.597 MM    1.2072 5802.69629   80.11526  98.4024

Totals :                  5896.90508   82.57165
```

Racemic 10



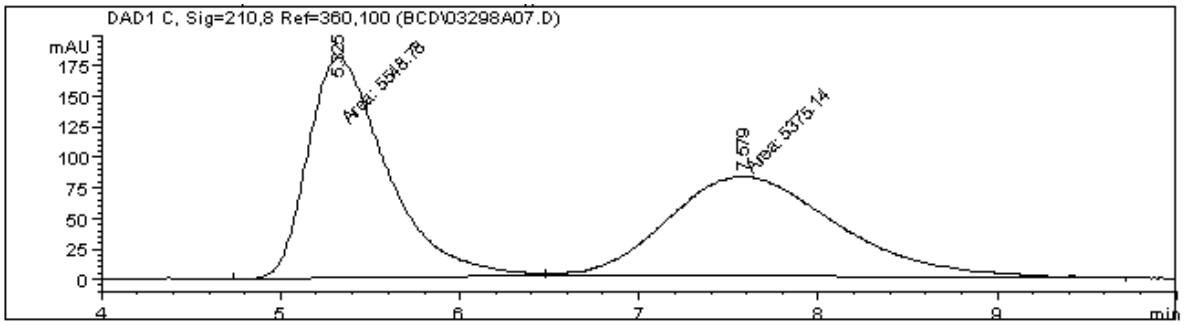

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.795 MM    0.4001 3090.01025  128.71451  49.7737
   2  14.746 MM    0.4982 3118.10400  104.30837  50.2263

Totals :                  6208.11426  233.02288
```

Enantioenriched 10



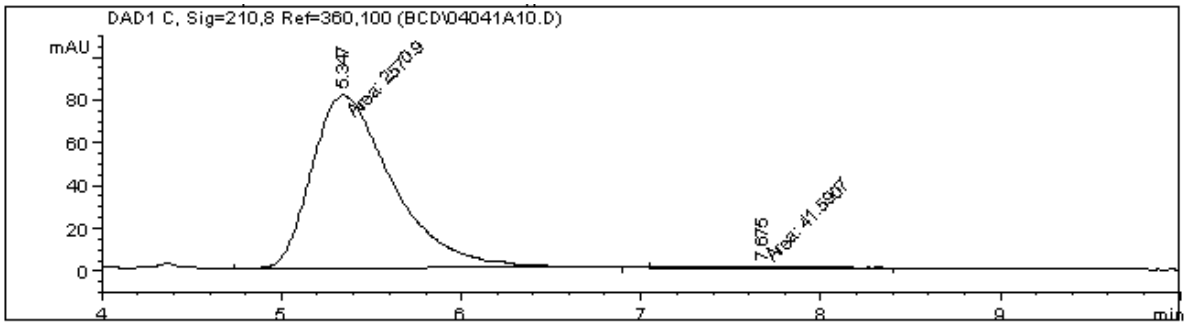

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.803 MM    0.4166 3626.66235  145.08121  98.6760
   2  14.771 MM    0.4320   48.66262    1.87721   1.3240

Totals :                  3675.32497  146.95842
```

Racemic 11



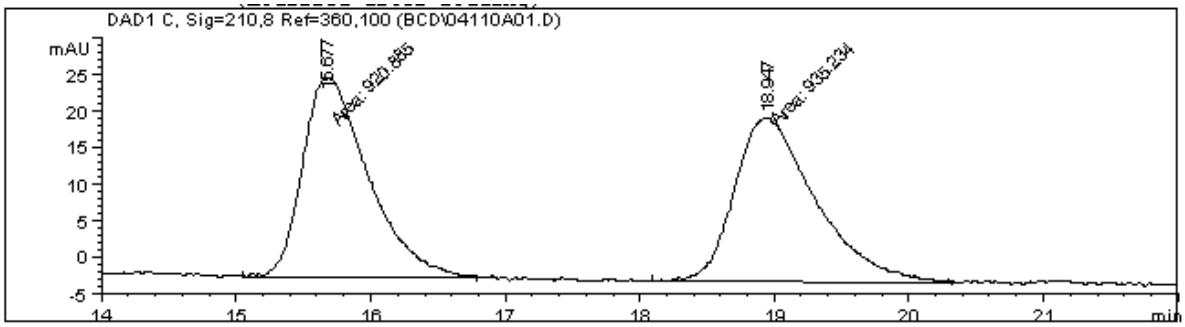

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.325 MM    0.5141 5548.77686  179.90102  50.7947
   2   7.579 MM    1.0957 5375.14258   81.76292  49.2053

Totals :                  1.09239e4   261.66394
```

Enantioenriched 11



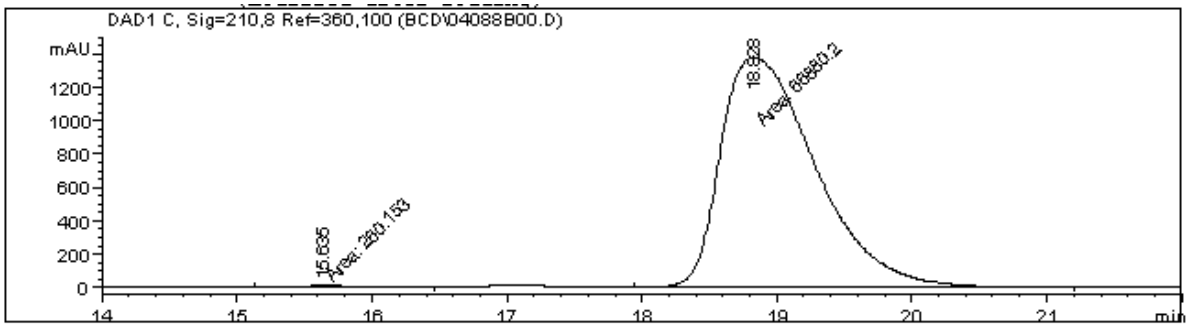

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.347 MM    0.5287 2570.90283   81.04272  98.4080
   2   7.675 MM    0.5765   41.59067    1.20242   1.5920

Totals :                  2612.49350   82.24513
```

Racemic 12



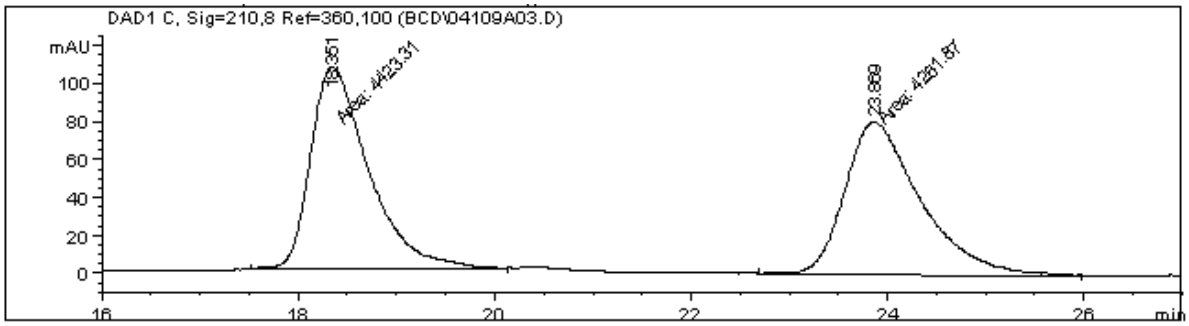

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.677 MM    0.5643  920.88477   27.20081  49.6135
   2  18.947 MM    0.6941  935.23383   22.45778  50.3865

Totals :                  1856.11859   49.65860
```

Enantioenriched 12



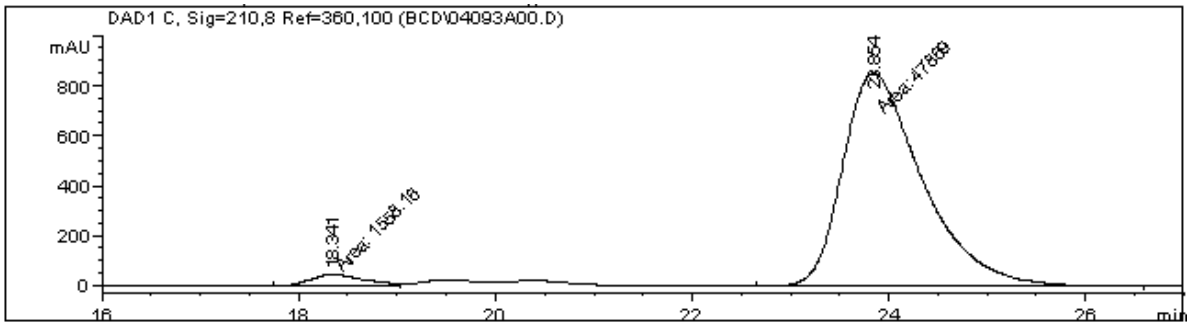

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.635 MM    0.5241  260.15283    8.27343   0.3875
   2  18.828 MM    0.8088 6.68802e4  1378.17578  99.6125

Totals :                  6.71404e4  1386.44921
```

Racemic 13



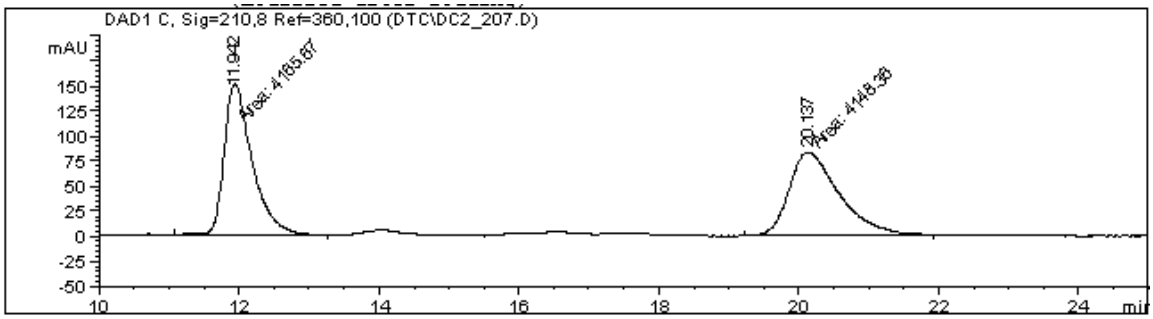

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.351 MM    0.6920 4423.31494  106.52859  50.9294
   2  23.869 MM    0.8878 4261.86865   80.00665  49.0706

Totals :                  8685.18359  186.53524
```

Enantioenriched 13



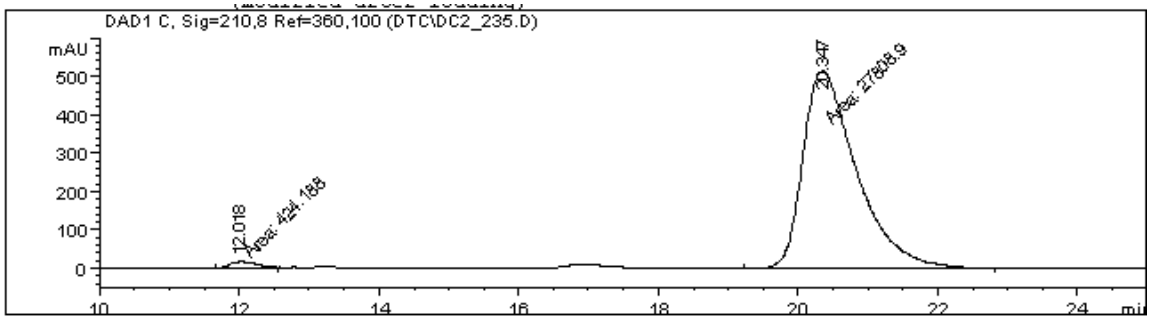

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.341 MM    0.6215 1558.15771   41.78444   3.1524
   2  23.854 MM    0.9369 4.78690e4   851.51935  96.8476

Totals :                  4.94272e4   893.30378
```

Racemic 14



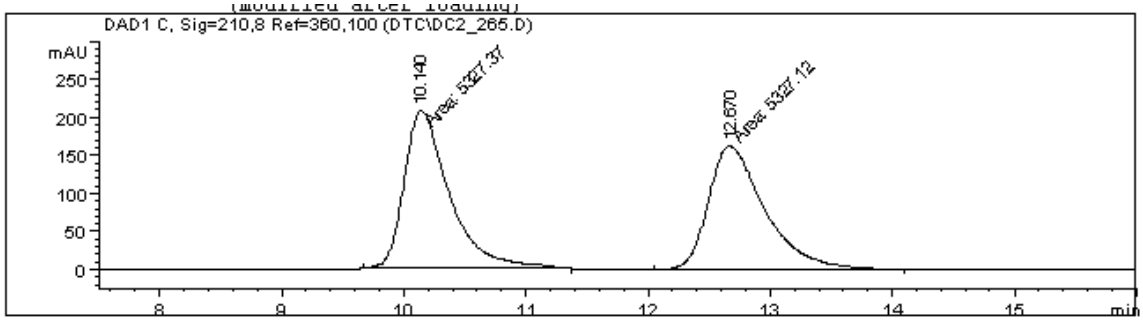

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.942 MM    0.4602 4165.66943  150.87856  50.1041
   2  20.137 MM    0.8329 4148.36035   83.00745  49.8959

Totals :                  8314.02979  233.88600
```

Enantioenriched 14



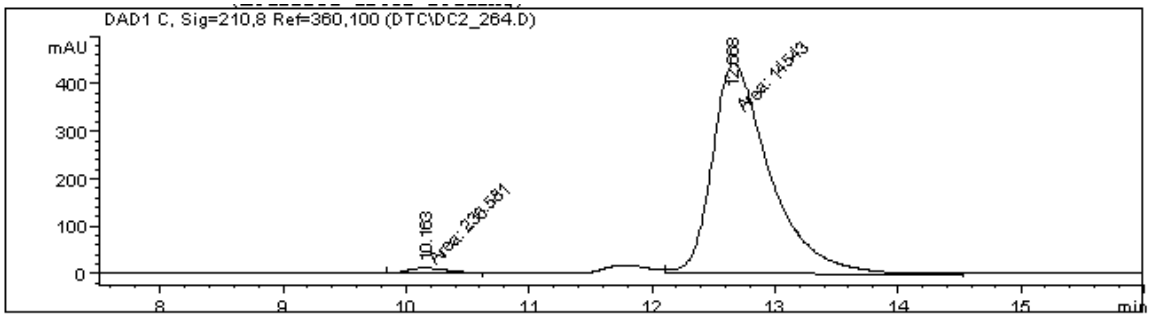

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.018 MM    0.4210  424.18753   16.79468   1.5024
   2  20.347 MM    0.8968 2.78089e4   516.81549  98.4976

Totals :                  2.82331e4   533.61017
```

Racemic 15



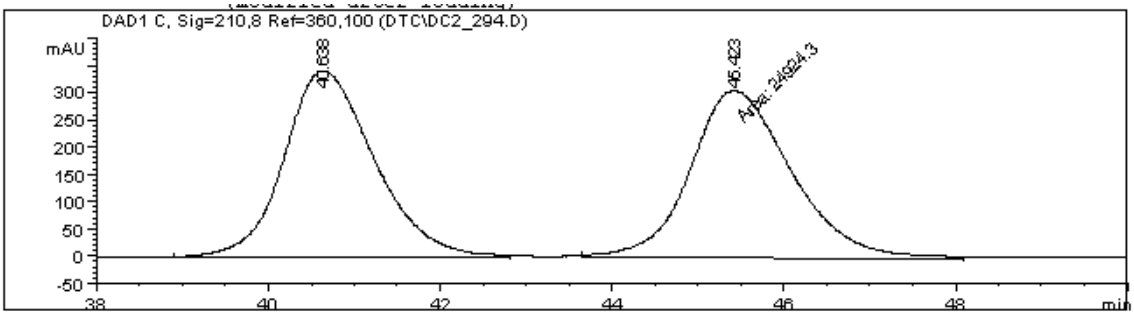

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.140 MM    0.4286 5327.37012  207.18054  50.0012
   2  12.670 MM    0.5420 5327.12061  163.80513  49.9988

Totals :                  1.06545e4   370.98567
```

Enantioenriched 15



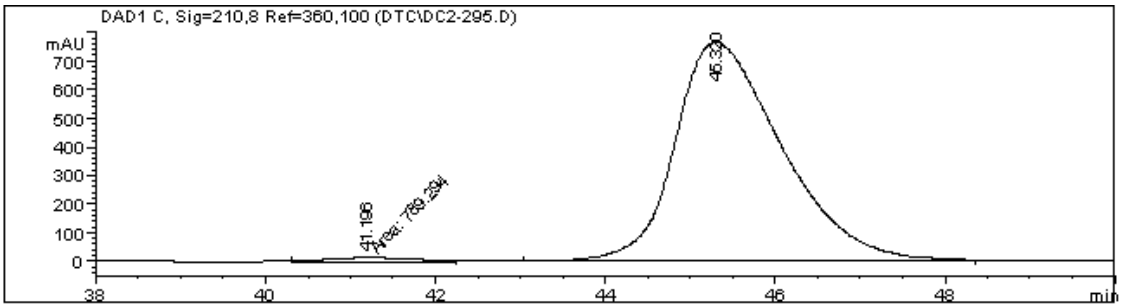

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.163 MM    0.4001  236.58078    9.85502   1.6007
   2  12.668 MM    0.5476 1.45430e4   442.65964  98.3993

Totals :                  1.47796e4   452.51466
```

Racemic 16



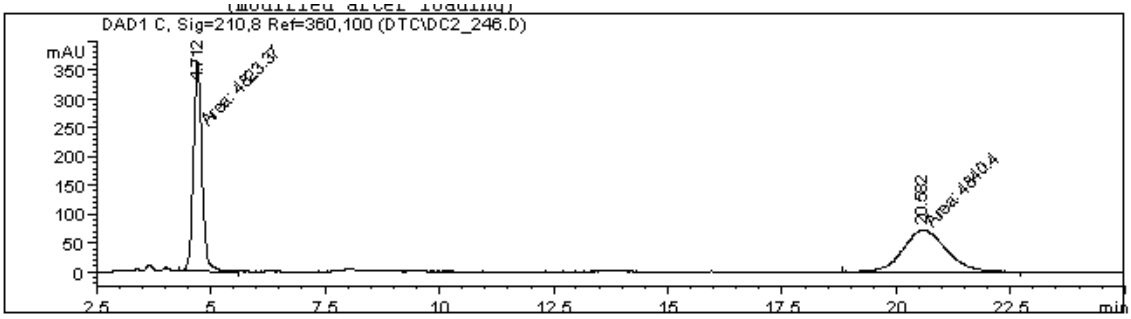

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  40.638 BB    0.8969 2.48786e4   341.12720  49.9541
   2  45.423 MM    1.3571 2.49243e4   306.09680  50.0459

Totals :                  4.98030e4   647.22400
```

Enantioenriched 16



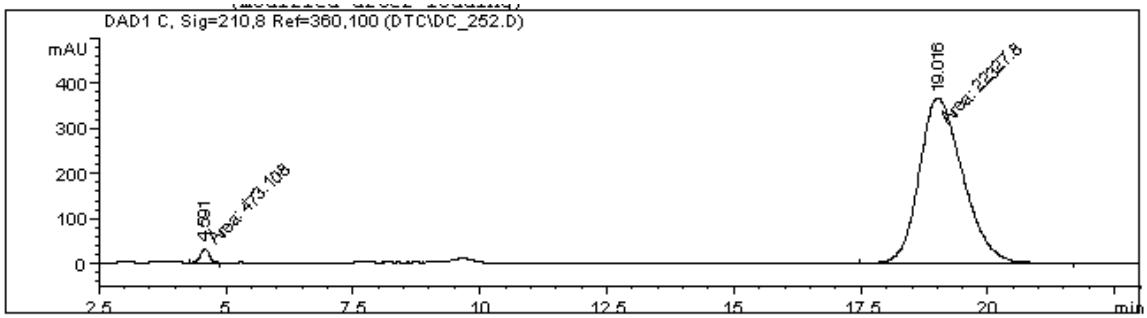

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  41.196 MM    1.1268  789.29370   11.67497   1.1737
   2  45.320 VB    1.0323 6.64607e4   764.43768  98.8263

Totals :                  6.72500e4   776.11266
```

Racemic 17



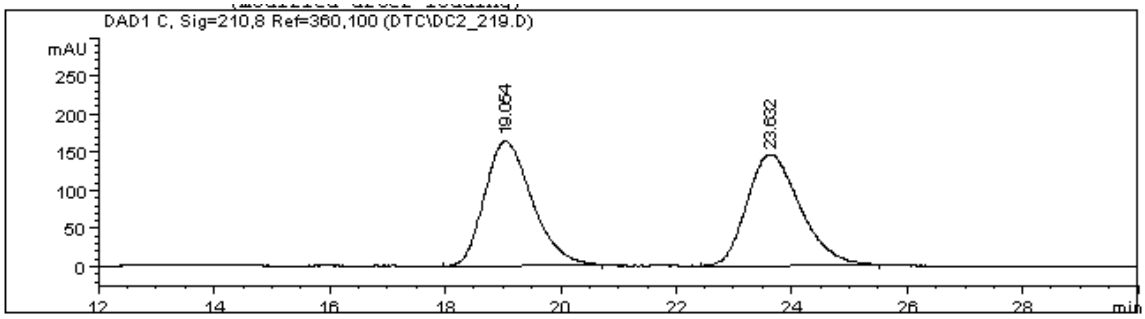

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.712 MM    0.2206 4823.36768  364.35986  49.9119
   2  20.582 MM    1.1157 4840.39795   72.30647  50.0881

Totals :                  9663.76563  436.66634
```

Enantioenriched 17



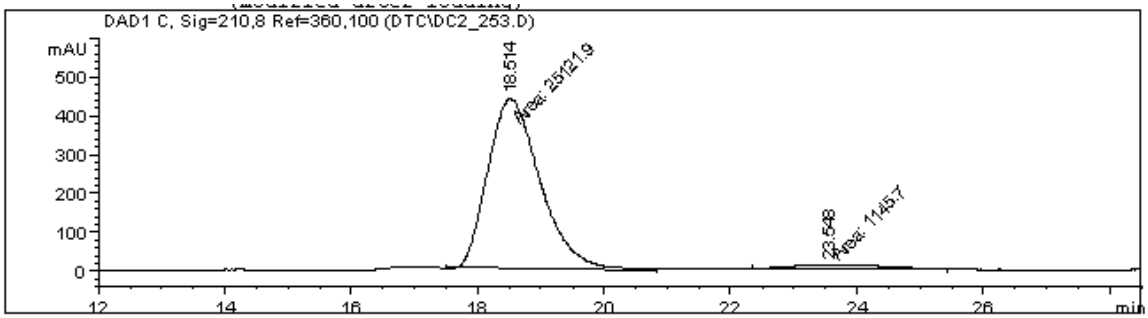

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.591 MM    0.2267  473.10818   34.77486   2.0750
   2  19.016 MM    1.0096 2.23278e4   368.59753  97.9250

Totals :                  2.28009e4   403.37240
```

Racemic 18



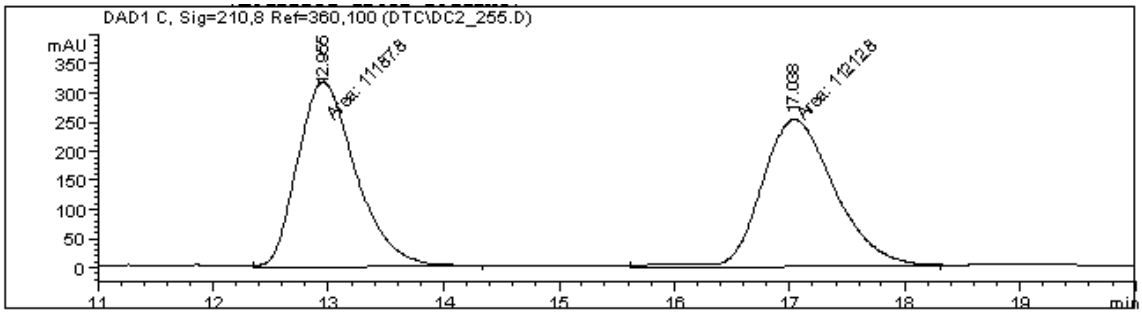

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.054 VB    0.7431 9324.69629  163.56812  50.0357
   2  23.632 VB    0.7600 9311.39551  145.61209  49.9643

Totals :                  1.8636le4   309.18021
```

Enantioenriched 18



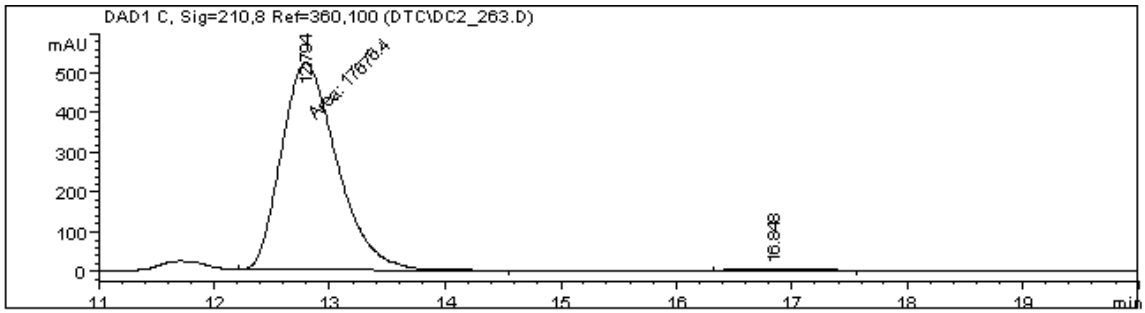

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.514 MM    0.9574 2.51219e4   437.34329  95.6384
   2  23.548 MM    1.6736 1145.69629   11.40958   4.3616
```

Racemic 19



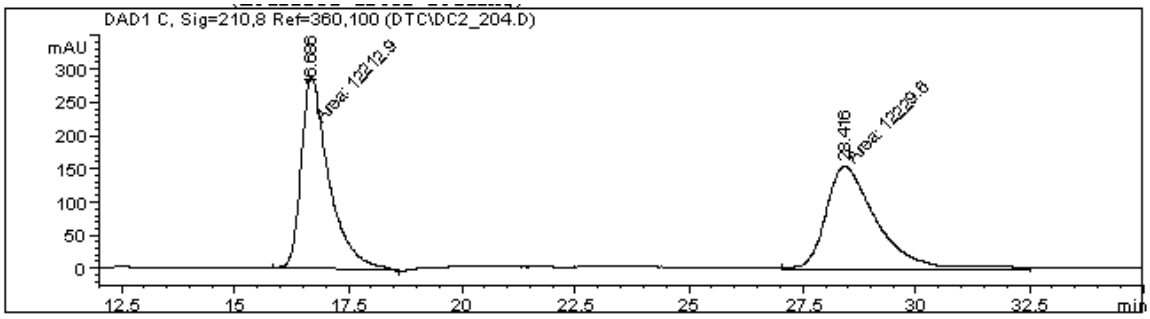

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.955 MM    0.5848 1.11878e4   318.82336  49.9442
   2  17.038 MM    0.7372 1.12128e4   253.50572  50.0558

Totals :                  2.24006e4   572.32909
```

Enantioenriched 19



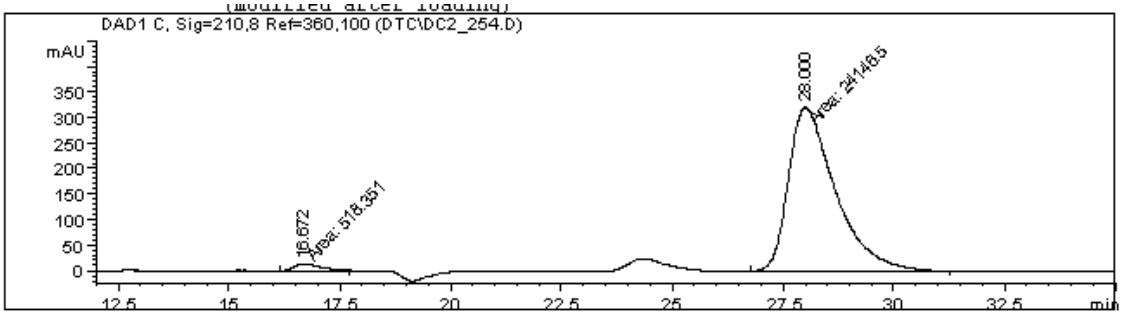

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.794 MM    0.5631 1.76764e4   523.14374  98.5410
   2  16.848 VV    0.4749  261.71262    6.53989   1.4590

Totals :                  1.79382e4   529.68363
```

Racemic 20



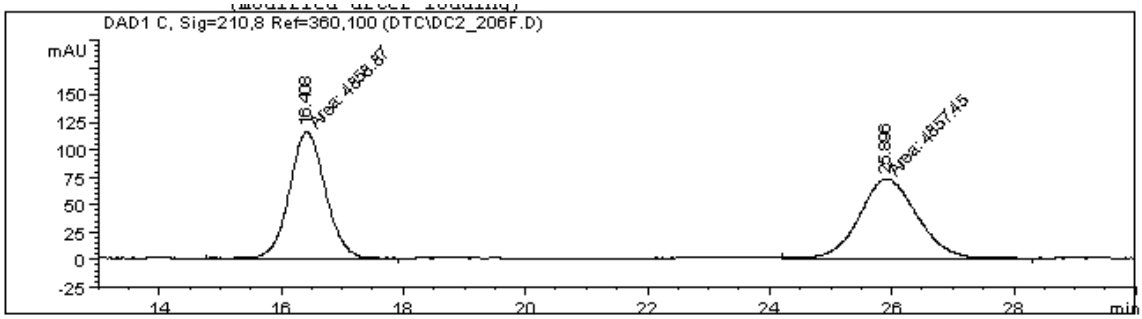

```
==================================================================================
                              Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.686 MM    0.7058 1.22129e4   288.40906  49.9659
   2  28.416 MM    1.3164 1.22296e4   154.84006  50.0341

Totals :                  2.44424e4   443.24911
```

Enantioenriched 20



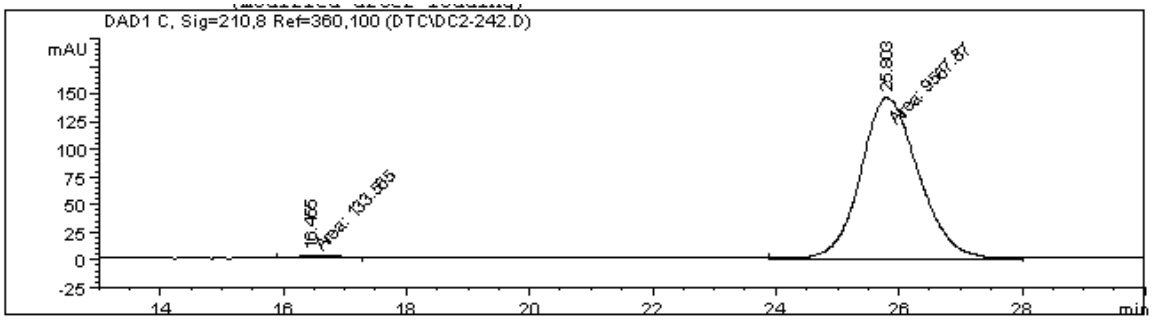

```
==================================================================================
                              Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.672 MM    0.6819  518.35059   12.66867   2.1016
   2  28.000 MM    1.2475 2.41465e4   322.60889  97.8984

Totals :                  2.46649e4   335.27755
```

Racemic 21



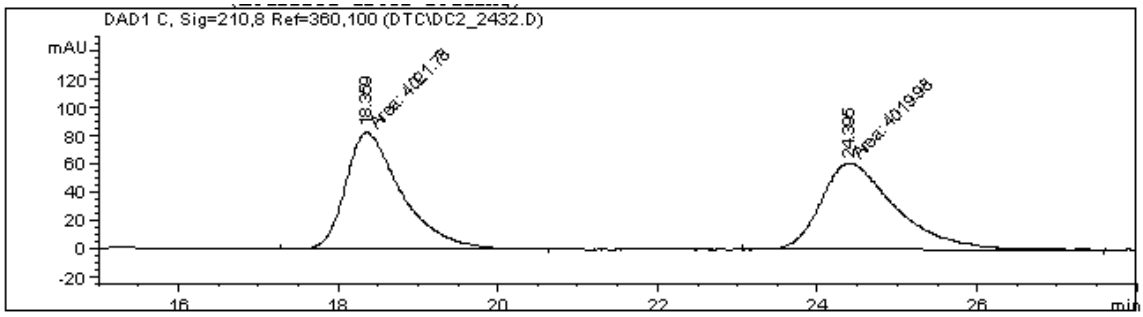

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.408 MM    0.6987 4858.87061  115.90540  50.0073
   2  25.896 MM    1.1123 4857.45020   72.78550  49.9927

Totals :                  9716.32080  188.69090
```

Enantioenriched 21



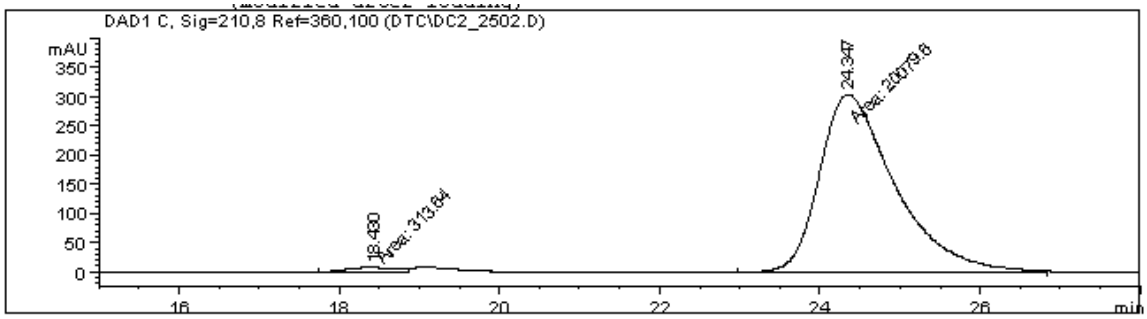

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.455 MM    0.7143  133.56480    3.11629   1.3768
   2  25.803 MM    1.0957 9567.86523  145.54152  98.6232

Totals :                  9701.43004  148.65781
```

Racemic 22



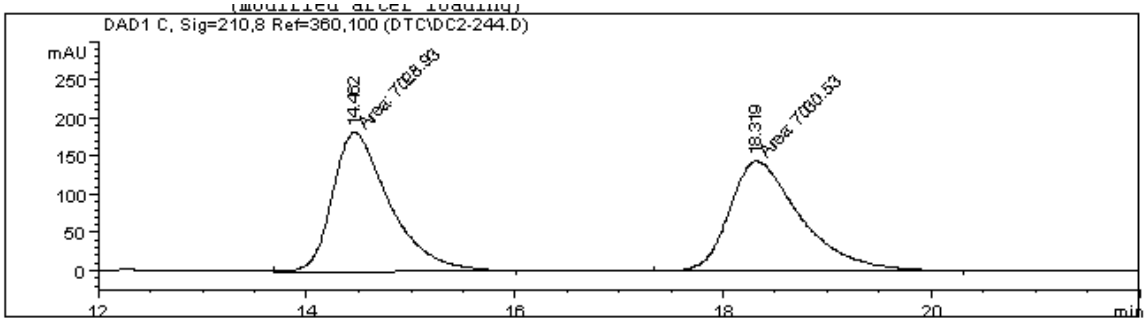

```
==================================================================================
                              Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.359 MM    0.8126 4021.78052   82.48543  50.0112
   2  24.395 MM    1.0936 4019.97705   61.26331  49.9888

Totals :                  8041.75757  143.74874
```

Enantioenriched 22



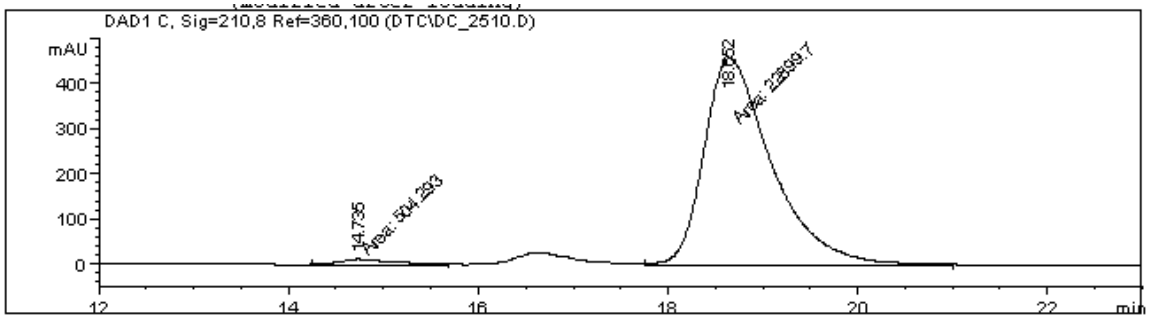

```
==================================================================================
                              Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.430 MM    0.7665  313.64005    6.81946   1.5380
   2  24.347 MM    1.0983 2.00796e4   304.70801  98.4620

Totals :                  2.03932e4   311.52747
```

Racemic 23



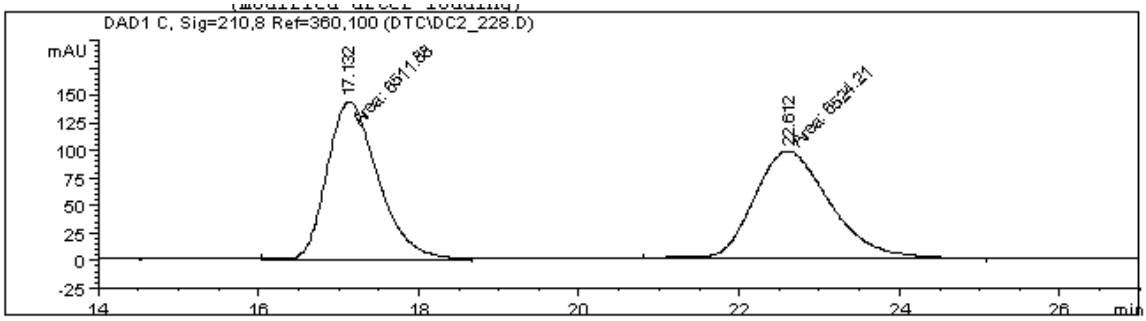

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.462 MM    0.6419 7028.93018  182.49583  49.9943
   2  18.319 MM    0.8103 7030.52881  144.60455  50.0057

Totals :                  1.40595e4   327.10039
```

Enantioenriched 23



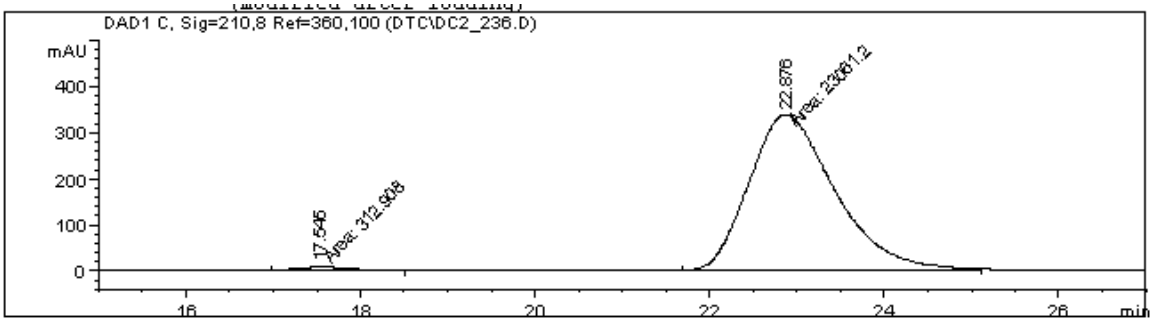

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.735 MM    0.6665  504.29297   12.60953   2.1547
   2  18.652 MM    0.8314 2.28997e4   459.04889  97.8453

Totals :                  2.34040e4   471.65842
```

Racemic 24




```
==================================================================================
                              Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.132 MM    0.7522 6511.87793  144.28413  49.9527
   2  22.612 MM    1.1124 6524.20947   97.74577  50.0473

Totals :                  1.30361e4   242.02991
```

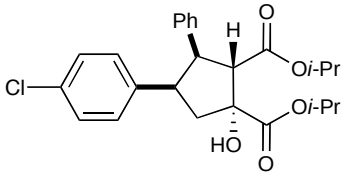
Enantioenriched 24




```
==================================================================================
                              Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.545 MM    0.7349  312.90839    7.09670   1.3387
   2  22.876 MM    1.1402 2.30612e4   337.08762  98.6613

Totals :                  2.33741e4   344.18432
```

Determination of Absolute Stereochemistry of 4

The absolute stereochemistry of **4** was determined by the X-ray diffraction. Pure material was obtained by recrystallization from hexanes.

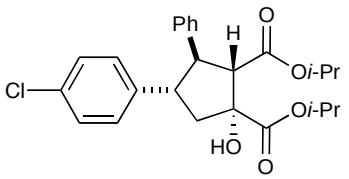


X-ray crystal structure of (1*R*,2*S*,3*R*,4*R*)-diisopropyl 4-(4-chlorophenyl)-1-hydroxy-3-phenylcyclopentane-1,2-dicarboxylate**:**

X-ray diffraction was performed at –120 ºC and raw frame data were processed using SAINT. Molecular structure was solved using direct methods and refined by F2 by full-matrix least-squares techniques. The GOF = 0.80 for 285 variables refined to R1 = 0.04 for 3272 reflections with I>2α(I). There was no absorption correction. The flack parameter was –0.11. Further information is contained in the CCDC file 793381.

Determination of Relative Stereochemistry of the Minor Diastereomer (29)

The relative stereochemistry of **29** (the minor diastereomer from the reaction) was determined by the X-ray diffraction. Pure material was obtained by recrystallization from hexanes.



X-ray crystal structure of Diisopropyl 4-(4-chlorophenyl)-1-hydroxy-3-phenylcyclopentane-1,2-dicarboxylate**:**

X-ray diffraction was performed at –120 ºC and raw frame data were processed using SAINT. Molecular structure was solved using direct methods and refined by F2 by full-matrix least-squares techniques. The GOF = 1.03 for 285 variables refined to R1 = 0.04 for 2679 reflections with I>2α(I). There was no absorption correction. The flack parameter was 0.0. Further information is contained in the CCDC file 793382.