Supporting Information

Enantioselective Stetter Reactions Catalyzed by Bis(amino)cyclopropenylidenes (BACs): Important Role for Water as an Additive

*Mehran Rezazadeh Khalkhali, Myron M. D. Wilde and Michel Gravel**

Department of Chemistry, University of Saskatchewan, 110 Science Place Saskatoon Canada S7N 5C9

Email: michel.gravel@usask.ca

Table of Contents

Experimental procedures

General methods

Anhydrous $CHCl_3$, CH_2Cl_2, Et_2O, toluene, and THF were dried using a Braun Solvent Purification System and stored under nitrogen over 4 Å molecular sieves. DMF was dried via distillation over CaH_2. Unless otherwise noted, all reactions were performed under an inert atmosphere of argon. Preparative thin layer chromatography (TLC) was carried out on glass plates (20×20 cm) pre–coated (0.25 mm) with silica gel 60 F254. Materials were detected by visualization under an ultraviolet lamp (254 nm) and/or by treating a 1 cm vertical strip removed from the plate with a solution of phosphomolybdic acid (5%) containing a trace of ceric sulfate in sulfuric (aq.) acid (5% v/v), or with basic $KMnO_4$ [$KMnO_4$ (1.5 g), K_2CO_3 (10 g), 10% aq. NaOH (1.25 mL), in H_2O (200 mL)], followed by charring with a heat gun. Analytical TLC was carried out on glass plates (4×3 cm) pre–coated (0.25 mm) with silica gel 60 F_{254} and was visualized in the same manner as described for preparative TLC. Flash column chromatography was performed according to Still et al.[1] with Merck silica gel 60 (0.040– 0.063 mm). All mixed solvents eluents are reported as v/v solutions. Unless otherwise noted, all reported compounds were homogenous by thin layer chromatography (TLC) and by ^{1}H NMR spectroscopy. Concentration refers to removal of volatiles with a rotary evaporator under vacuum supplied by vacuum pump (ca. 30 Torr). Evacuation at ca. 0.5 Torr with a vacuum pump generally followed rotary evaporation.

Spectral Data

High resolution mass spectra (HRMS) and low-resolution mass spectra (LRMS) were obtained on a VG 70E double focusing high resolution spectrometer; only partial data are reported. Electron impact (EI) ionization was accomplished at 70 eV, chemical ionization (CI) at 50 eV with ammonia as the reagent gas. Alternatively, HRMS was obtained on a LC–MS/MS time–of–flight high resolution spectrometer with electrospray ionization (ESI) from acetonitrile solution. Infrared spectra were recorded on a Fourier transform interferometer using a diffuse reflectance cell (DRIFT); only diagnostic peaks and/or intense peaks are reported. Unless otherwise noted, all experiments used DRIFT. Unless otherwise noted, NMR spectra were measured in $CDCl_3$ solution at 500 MHz or 600 MHz for ^{1}H and 125 or 150 MHz for ^{13}C. Signals due to the solvent (^{13}C NMR) or residual protonated solvent (^{1}H NMR) served as the internal standard: $CDCl_3$ (7.26 δH, 77.16 δC); C_6D_6 (7.16 δH, 128.39 δC); CD_3OD (3.31 δH, 49.00 δC). The ^{1}H NMR chemical shifts and coupling constants were determined assuming first–order behavior. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), m (multiplet), br (broad), app (apparent); the list of coupling constants (J) corresponds to the order of the multiplicity assignment. Coupling constants are reported to the nearest 0.1 Hz. The ^{13}C NMR assignments were made based on chemical shift. Specific rotations ($[\alpha]_D$) are the average of five determinations at ambient temperature using a 1 mL, 10 dm cell; the units are 10^{-1} deg. cm^2 g $^{-1}$ and the concentrations (*c*) are reported in g/100 mL. The values reported are rounded to reflect the

[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.

accuracy of the measured concentrations (the major source of error). HPLC analyses were carried out using an Agilent Technologies 1200 series liquid chromatograph.

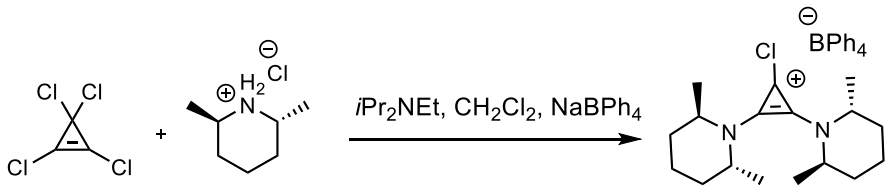
Materials

All commercially available aldehydes were purified by bulb–to–bulb distillation prior to use. Cs_2CO_3 was dried overnight at 250 °C under high vacuum. Unless otherwise noted, all other reagents were purchased and used without further purification.

Synthesis of Catalysts

2,3-Bis((2*R*,6*R*)-2,6-dimethylpiperidin-1-yl)cycloprop-2-en-1-ylium tetraphenyborate (2)

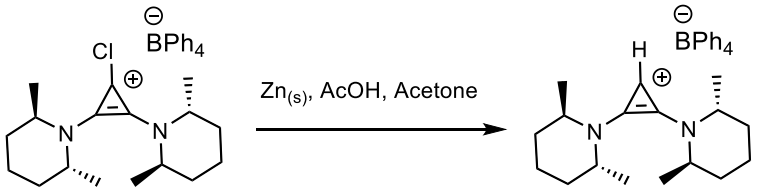
Boc protected amine was prepared analogous to the method described by Aggarwal.[2] To a solution of Boc amine (4.5 g, 20.9 mmol) in Et_2O (60 ml) was added HCl (22 ml, 2.0 M in Et_2O) at room temperature. The resulting precipitate that formed after 24 h was filtered and found to be the pure desired amine HCl salt. To the filtrate was added CH_2Cl_2 (10 ml) followed by HCl (15 ml, 2.0 M in Et_2O) and the mixture was stirred for another 24 h. The additional precipitate that was formed was filtered and the both precipitates were combined to give (2*R*,6*R*)-2,6-dimethylpiperidin-1-ium chloride as a white solid (2.53 g, 81%). The ^{1}H NMR spectrum matched the one previously reported.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.60-9.40, (br s, 2H), 3.60-3.50 (br s, 2H), 2.00-1.90 (m, 2H), 1.80-1.60 (m, 4H), 1.47 (d, *J* = 6.8 Hz, 6H).



To a solution of amine salt (100 mg, 0.67 mmol, 2.1 equiv.) in CH_2Cl_2 (6.4 ml) was added $NaBPh_4$ (109 mg, 0.32 mmol, 1.0 equiv.) and tetrachlorocyclopropene (39 µL, 0.32 mmol, 1.0 equiv.) under inert atmosphere. Then, *i*Pr_2NEt (277 µL, 1.6 mmol, 5.0 equiv.) was added to the reaction mixture dropwise at room temperature. The reaction mixture was stirred for 2 h and transferred to a separatory funnel and washed with HCl 1N (aq.) and water respectively. The organic phase was separated and dried over Na_2SO_4. The crude product was purified using crystallization with $CHCl_3$: Et_2O and 158 mg (79%) of (2*R*,2'*R*,6*R*,6'*R*)-1,1'-(3-chlorocycloprop-1-ene-1,2-diyl)bis(2,6-dimethylpiperidinium) tetraphenylborate as a white solid was obtained. **^{1}H NMR** (500 MHz,

[2] M. F. A. Adamo, V. K. Aggarwal, M. A. Sage, *Synth. Commun.* **1999**, *29*, 1747-1756.

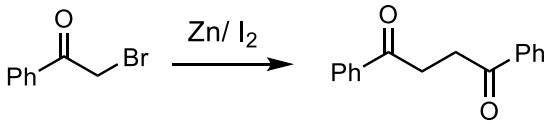
$CDCl_3$) δ 7.36 (s, 8H), 7.01 (dd, *J* = 7.3, 7.3 Hz, 8H), 6.78 (t, *J* = 7.2 Hz, 4H), 3.95-3.85 (br s, 2H), 3.50-3.40 (m, 2H), 1.78 (d, *J* = 13.7 Hz, 2H), 1.75-1.40 (m, 8H), 1.34 (d, *J* = 6.3 Hz, 6H), 1.33-1.25 (m, 2H),1.23 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.0, 164.6, 164.2, 163.9, 136.4, 134.2, 125.6, 121.8, 92.3, 54.8, 52.6, 34.1, 30.3, 20.6, 18.2, 17.6; **FTIR** (KBr thin film) ν_{max} (cm^{-1}): 3249, 3055, 3035, 2982, 2942, 1907, 1587, 1480, 1456, 1440, 1429, 1410, 1387, 1363, 1332, 1316, 1139, 1084, 732, 704, 612; **HRMS (**ESI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{28}N_2{}^{35}Cl$ 295.1941; found: 295.1967.



Chloro-bis(amino)cyclopropenium salt (2.0 mg, 3.3 mmol, 1.0 equiv.) was placed in a round bottom flask with a stir bar under argon. It was dissolved in acetone (3.3 ml) and AcOH (16.5 ml) was added. To the mixture was added zinc dust (1.2 g, 18 mmol, 5.6 equiv.) and it was stirred for 18 h. The mixture was passed through Celite with CH_2Cl_2 and the solvent was removed *in vacuo*. The mixture was filtered, and the mother liquor was washed with a solution of sodium tetraphenylborate (283 mg, 0.82 mmol, 0.25 equiv.) in water to convert the acetate salt of the product remaining into tetraphenylborate salt. The organic phase was separated and washed with water and dried over Na_2SO_4 and then the solvent was removed *in vacuo*. The crude product was triturated with EtOAc and Et_2O which yielded more of the 2,3-Bis((2*R*,6*R*)-2,6-dimethylpiperidin-1-yl)cycloprop-2-en-1-ylium tetraphenylborate as a white solid (1.4 g total, 73%). **m.p.** (°C): 176 (decomposed); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (s, 8H), 7.01 (dd app t, *J* = 7.4 Hz, 8H), 6.84 (t, *J* = 7.2 Hz, 4H), 4.20 (s, 1H), 3.80-3.70 (br s, 2H), 3.50-3.40 (m, 2H), 1.75-140 (m, 10H), 1.31 (d, *J* = 6.5 Hz, 8H), 1.05 (d, *J* = 5.6 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.7, 165.3, 164.9, 164.5, 136.5, 133.6, 126.1, 122.0, 98.9, 58.1, 53.0, 34.3, 30.6, 20.4, 18.5, 17.6; **FTIR** (KBr thin film) ν_{max} (cm^{-1}): 3102, 3053, 2982, 2495, 1869, 1653, 1576, 1479, 1457, 1437, 1329, 1363, 1114, 1085, 909, 732, 704; **HRMS (**ESI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{29}N_2$ 261.2331; found: 261.2329.

$[\alpha]_D^{21}$ = -104 (*c* = 0.9745, CH_2Cl_2)

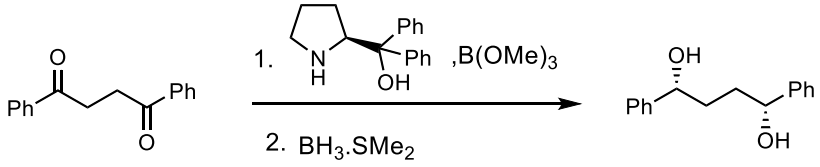
2,3-bis((2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl)cycloprop-2-en-1-ylium tetraphenylborate (3)



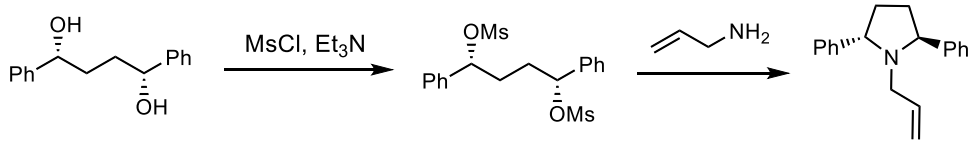
1,4-Diphenylbutane-1,4-dione was prepared according to the previously described protocol by Ceylan.[3] Elemental zinc dust (2.0 g, 30.6 mmol, 1.0 equiv.) followed by solid I_2 (200 mg, 0.79

[3] M. Ceylan, M. B. Gürdere, Y. Budak, C. Kazaz, H. Seçen, *Synthesis* **2004**, *11,* 1750-1754.

mmol, 0.03 equiv.) were added to a vigorously stirring solution of 2-bromo-1-phenylethan-1-one (6.0 g, 30 mmol, 1.0 equiv.) in dried THF (60 ml) under argon at 66 °C. The mixture was refluxed for 16 h and then cooled down to room temperature. The resulting mixture was filtered, and water (100 ml) was added to the filtrate. The aqueous phase was washed with $CHCl_3$ (3×100 ml). The organic phase was separated and dried by Na_2SO_4. The solvent was removed *in vacuo* and the crude product was crystallized using $CHCl_3$: Hexanes to give 1,4-diphenylbutane-1,4-dione as a pale-yellow powder (1.14 g, 32%). The ^{1}H NMR spectrum matched the one previously reported. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.0, 1.0 Hz, 8H), 7.59 (tt, *J* = 5.6, 1.8 Hz, 2H), 7.47 (dd app t, *J* = 13.7 Hz, 4H), 3.47 (s, 4H).



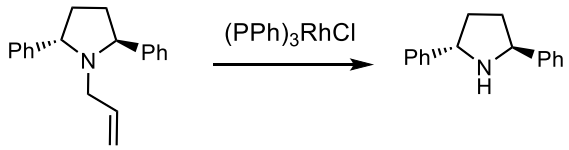
(1*R*,4*R*)-1,4-Diphenylbutane-1,4-diol was prepared in an analogous manner to the method described by Lindsley.[4] (*S*)-diphenyl(pyrrolidin-2-yl)methanol (223 mg, 0.9 mmol, 0.2 equiv.) was put in a round bottom flask equipped with a magnet stir bar. THF (5.6 ml) was added to it. Then, $B(OMe)_3$ (130 µl, 1.2 mmol, 0.2 equiv.) was added to the mixture and it was stirred for 1 h. Then, $BH_3.SMe_2$ (1.0 ml, 11 mmol, 2.1 equiv.) was added followed by adding 1,4-diphenylbutane-1,4-dione (1.2 g, 5.2 mmol, 1.0 equiv.) in THF (11 ml) over an hour. It was stirred for another hour and was quenched with HCl (8.5 ml, 2 N). The aqueous phase was extracted with Et_2O (3×11 ml) and subsequently, the merged organic layers were washed with water and brine and dried with Na_2SO_4. The solvent was removed *in vacuo*. The crude product was purified using flash column chromatography (35% EtOAc in petroleum ether) and white crystals (1.1 g, 94%) were obtained. The ^{1}H NMR spectrum matched the one previously reported. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.32 (m, 8H), 7.29-7.25 (m, 2H), 4.76-4.70 (m, 2H), 2.46 (br s, 2H), 1.97-1.91 (m, 2H), 1.86-1.86 (m, 2H).



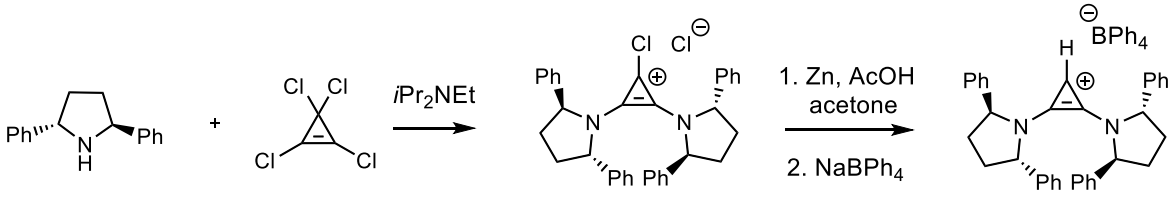
(2*S*,5*S*)-1-Allyl-2,5-diphenylpyrrolidine was prepared according to the procedure described by described by Steel.[5] To a solution of methanesulfonylchloride (840 µl, 11 mmol, 2.5 equiv.) in CH_2Cl_2 (42 ml) was added a solution of (1*R*,4*R*)-1,4-diphenylbutane-1,4-diol (1.0 g, 4.4 mmol, 1.0 equiv.) and Et_3N (1.8 ml, 13 mmol, 3.0 equiv.) in CH_2Cl_2 (42 ml) at 0 °C under argon. The reaction was quenched using aqueous NH_4Cl (sat.) after stirring for 2 h at 0 °C. The mixture warmed up to room temperature and the solvent was removed *in vacuo* up to about 35 ml followed by adding EtOAc (170 ml). The organic layer was washed with a mixture of (1:2:1) water: brine:

[4] T. J. Senter, M. C. O'Reilly, K. M. Chong, G. A. Sulikowski, C. W. Lindsley, *Tetrahedron Lett.* **2015**, *56*, 1276-1279.
[5] D. J. Aldous, W. M. Dutton, P. G. Steel, *Tetrahedron : Asymmetry* **2000**, *11*, 2455-2462.

aqueous $NaHCO_3$ (sat.) (4×40 ml). The organic phase was concentrated up to 15 ml *in vacuo*. The crude product was put in a round bottom flask equipped with a stir bar and put under argon to be used directly for the next step. Allylamine (60 ml, 690 mmol, 158 equiv.) was added portion wise under argon at 0 °C. The mixture was stirred at 0 °C overnight. The excess of allylamine was removed *in vacuo* and to the crude product was added Et_2O (150 ml). It was washed with aqueous $NaHCO_3$ (sat.) (50 ml) and brine (50 ml) and dried over Na_2SO_4. The organic phase was concentrated, and the crude product was purified with flash column chromatography (3% Et_2O in petroleum ether) to give the product (920 mg, 80%) as a colorless oil. The ^{1}H NMR spectrum matched the one previously reported. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.34 (m, 8H), 7.29-7.25 (m, 2H), 5.70-5.62 (m, 1H), 4.96-4.91 (m, 2H), 4.36-4.34 (m, 2H), 3.02-2.98 (m, 1H), 2.73 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.57-2.51 (m, 2H), 1.95-1.90 (m, 2H);



(2*S*,5*S*)-2,5-Diphenylpyrrolidine was prepared analogous to the method described by Steel.[5] $(PPh)_3RhCl$ (6 mg, 0.06 mmol, 5 mol %) and (2*S*,5*S*)-1-allyl-2,5-diphenylpyrrolidine (340 g, 1.3 mmol, 1.0 equiv.) were placed inside a Schlenk tube equipped with a magnet stir bar under tight Schlenk conditions. To that, a mixture of (water: acetonitrile 16: 84) (3.5 ml) was added under argon. The mixture was degassed for 20 min using argon flow. A condenser was installed, and the mixture was heated up to 90 °C (oil bath) and stirred for 5 h. After cooling to room temperature, the mixture was transferred to a separatory funnel and was added Et_2O (5.0 ml). The organic layer was washed with brine (2×5.0 ml). The aqueous phase was back extracted with Et_2O (5.0 ml) and the organic layers were combined and dried over Na_2SO_4. The filtrate was concentrated *in vacuo* and purified by flash column chromatography (33% EtOAc in petroleum ether) to give the product as a pale-yellow solid (310 mg, 69%). The ^{1}H NMR spectrum matched the one previously reported. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.4 Hz, 4H), 7.35 (dd app t, *J* = 7.4, 4H), 7.26 (t, *J* = 7.2 Hz, 2H), 4.57 (dd app t, *J* = 6.8, 2H), 2.45-2.38 (m, 2H), 2.23 (br s, 1H), 1.96-1.91 (m, 2H).

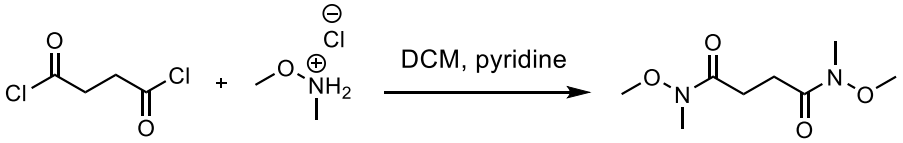


To a solution of tetrachlorocyclopropene (91 µL, 0.74 mmol, 1.0 equiv.) in dried CH_2Cl_2 (14 ml) was added a solution of (2*S*,5*S*)-2,5-diphenylpyrrolidine (326 mg, 1.5 mmol, 2.0 equiv.) and *i*Pr_2NEt (258 µL, 1.5 mmol, 2.0 equiv.) in CH_2Cl_2 (4.0 ml) under argon at -78 °C. The reaction mixture was brought to room temperature and stirred for 6 h before the solvent was removed *in vacuo*. To the crude product was added zinc dust (27 mg, 4.1 mmol, 5.6 equiv.) and was charged with argon. The mixture was dissolved in acetone (1.4 ml) and then to this mixture AcOH (7.2 ml)

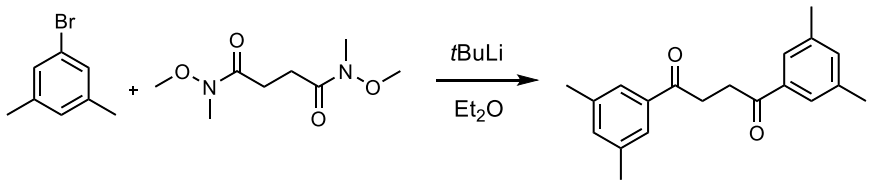
was added and stirred overnight. To the crude product was added a solution of $NaBPh_4$ (1.3 g, 3.7 mmol, 5 equiv.) in water (30 ml) and extracted with dichloromethane (30 ml). The organic phase was washed with water (3×30 ml) to remove AcOH entirely and dried over Na_2SO_4.The solvent was removed *in vacuo*, and to the crude product was added $CHCl_3$ (6.0 ml). The *i*$Pr_2NEt.HBPh_4$ salt was precipitated and filtered. The filtrate was concentrated. To the residue was added MeOH and cooled down to 0 °C for an hour. The product crystallized and was washed with cold MeOH several times to give the pure 2,3-bis((2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl)cycloprop-2-en-1-ylium tetraphenyborate as a pale-yellow powder (463 mg, 78%). **m.p.** (°C): 190-192; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54-7.47 (m, 6H), 7.28-7.30 (m, 14H), 6.88-6.85 (m, 12H), 6.80 (t, *J* = 7.0 Hz, 4H), 6.72 (dd, *J* = 7.2, 1.4 Hz, 4H), 4.59 (dd app t, *J* = 6.3 Hz, 2H), 4.29 (s, 1H), 3.63 (dd app t, *J* = 6.1 Hz, 6H), 2.25-2.12 (m, 4H), 1.69-1.60 (m, 4H) ; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.8-163.5 (q, $^1J_{C\text{-}B}$ = 49 Hz) , 139.4, 137.8, 136.3, 134.6, 129.3, 129.26, 128.8, 128.78, 126.0, 125.7, 125.60-125.57 (d, $^2J_{C\text{-}B}$ = 2.9 Hz), 121.5, 103.4, 67.6, 65.1, 34.7, 33.4; **FTIR** (KBr thin film) ν_{max} (cm^{-1}): 2982, 1892, 1580, 1494, 1452, 1427, 1355, 1304, 1288, 1182, 1142, 1076, 1030; **HRMS (**ESI-TOF) m/z: $[M]^+$ calcd for $C_{35}H_{33}N_2$ 481.2644; found: 481.2651.

$[\alpha]_D^{21}$ = -144 (*c* = 1.0, CH_2Cl_2)

2,3-Bis((2*S*,5*S*)-2,5-bis(3,5-dimethylphenyl)pyrrolidin-1-yl)cycloprop-2-en-1-ylium tetraphenylborate (4)

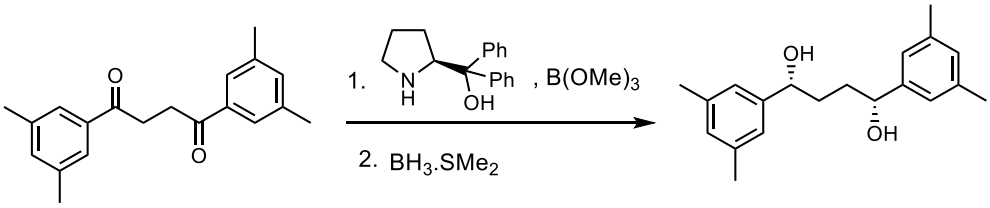


N^1,N^4-Dimethoxy-N^1,N^4-dimethylsuccinamide was made according to the method previously reported by Jagadish.[6] To a solution of N,O-dimethylhydroxylammonium chloride (24.5 g, 0.25 mol, 2.2 equiv.) in CH_2Cl_2 (228 ml) was added succinyl chloride (13 ml, 0.11 mol, 1.0 equiv.) followed by pyridine (40 ml, 0.50 mol, 4.4 equiv.) drop wise. The mixture was stirred for 16 h and quenched with aqueous HCl (2 M) and extracted with $CHCl_3$. Et_2O was added to the $CHCl_3$ to the point where the solution became milky. The crude product was put into ice and crystals formed after 30 min and filtered. The pure product was obtained as a light brown crystal (18.5 g, 80%). The ^{1}H NMR spectrum matched the one previously reported. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.72 (s, 6H), 3.17 (s, 6H), 2.76 (s, 4H).



[6] B. Jagadish, G. L. Brickert-Albrecht, G. S. Nichol, E. A. Mash, N. Raghunand, *Tetrahedron Lett.* **2011**, *52*, 2058-2061.

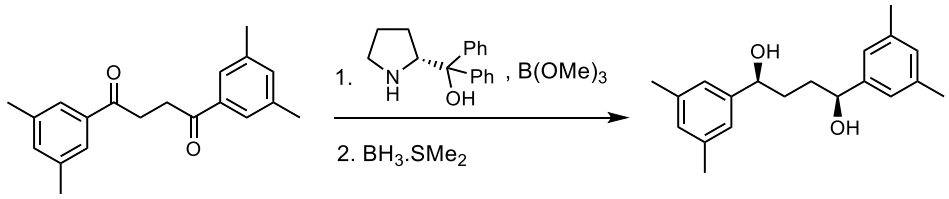
1,4-Bis(3,5-dimethylphenyl)butane-1,4-dione was prepared in an analogous manner to the method described by Hayashi.[7] To a solution of 1-bromo-3,5-dimethylbenzene (16.3 ml, 120 mmol, 2.4 equiv.) in dried Et_2O (119 ml) was added a solution of *t*BuLi in pentane (1.7 M) (150 ml, 255 mmol, 2.4 equiv.) drop wise at -78 °C under argon. The mixture was stirred for 30 min and then was warmed to room temperature and was kept stirring for another 20 min and was cooled down to 0 °C. To the mixture was added a solution of N^1,N^4-dimethoxy-N^1,N^4-dimethylsuccinamide (10.1 g, 49.5 mmol, 1.0 equiv.) in dried THF (102 ml) under argon slowly and was stirred for another hour and quenched with aqueous NH_4Cl (sat.). The mixture was extracted with $CHCl_3$ and the organic layer was washed with brine and dried with Na_2SO_4. The mixture was concentrated, and to it $CHCl_3$ (10 ml) was added. Et_2O (40 ml) was added to the mixture and it was kept in fridge overnight. Pale-yellow crystals formed and filtered (9.4 g, 65%). The crystals were washed with Et_2O and the ^{1}H NMR spectrum matched the one previously reported. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (s, 4H), 7.21 (s, 2H), 3.42 (s, 4H), 2.38 (s, 12H).



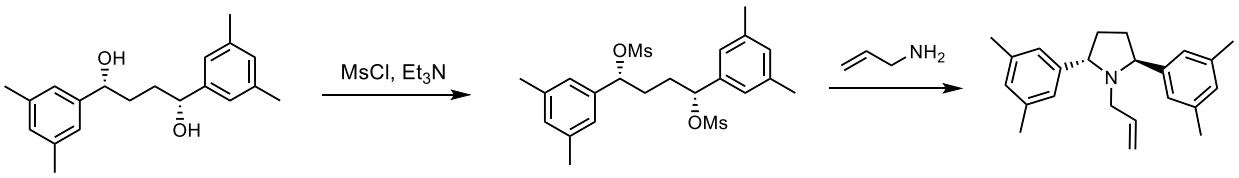
(1R,4R)-1,4-bis(3,5-dimethylphenyl)butane-1,4-diol was prepared in an analogous manner to the method described by Hayashi.[7] (*S*)-diphenyl(pyrrolidin-2-yl)methanol (0.13 g, 0.5 mmol, 0.2 equiv.) was put in a round bottom flask equipped with a magnet stir bar. THF (2.3 ml) and was added to it. Then, $B(OMe)_3$ (80 µl, 0.65 mmol, 0.3 equiv.) was added and it was kept stirring for 1 h. $BH_3.SMe_2$ (580 µl, 6.0 mmol, 2.8 equiv.) was added followed by adding 1,4-diphenylbutane-1,4-dione (640 mg, 2.2 mmol, 1.0 equiv.) in THF (5.0 ml) over an h. It was stirred for 1 h and was quenched with HCl (4.0 ml, 2 N). The aqueous phase was extracted with Et_2O (3.0×4.6 ml) and subsequently, the merged organic layers was washed with water and brine and dried with Na_2SO_4. The solvent was removed *in vacuo*. The crude product was purified using flash column chromatography (35% EtOAc in petroleum ether) and white crystals (590 mg, 92%) were obtained. The ^{1}H NMR spectrum matched the one previously reported.[7] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.95 (s, 4H), 6.90 (s, 2H), 4.62 (s, 2H), 2.66 (br s, 2H), 2.31 (s, 12H), 1.94-1.89 (m, 2H), 1.87-1.77 (m, 2H). HPLC (compared to the other enantiomer sample). HPLC: Chiralpak IA 2.1×150 mm column, 10% isopropanol in Hexanes, 0.2 ml/min Major peak at 7.17 min Minor peak at 6.14 min. (*ee*: 99%).

The opposite enantiomer of the diol was prepared as described above using (*R*)-diphenyl(pyrrolidin-2-yl)methanol. It is not clear that why the enantioselectivity is lower, but it has been observed that this reaction is sensitive to the reaction conditions.[8] The purpose of preparing two enantiomers of this diol was to identify each enantiomer in HPLC chromatogram which this lower *ee* serves the purpose well.

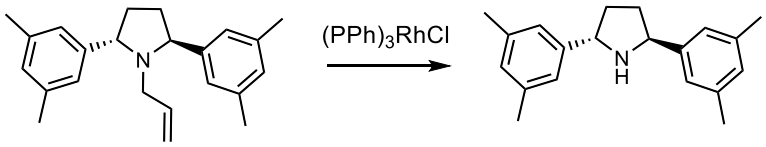
[7] R. Shintani, T. Ito, M. Nagamoto, H. Otomo, T. Hayashi, *Chem. Commun.* **2012**, *48*, 9936-9938.
[8] E. J. Corey, R. K. Bakshi, S. Shibata, *J. Am. Chem. Soc.* **1987**, *109*, 5551-5553.



Major peak at 6.13 min Minor peak at 7.03 min. (*ee*: 82%).

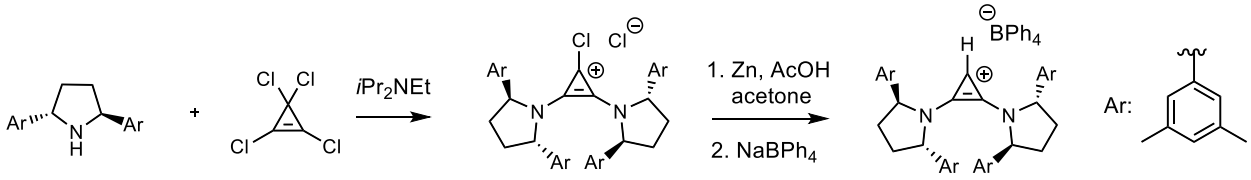


(2*S*,5*S*)-1-Allyl-2,5-bis(3,5-dimethylphenyl)pyrrolidine was prepared according to the procedure described by described by Steel.[5] To a solution of methanesolfunylchloride (380 µl, 4.9 mmol, 2.5 equiv.) in CH_2Cl_2 (19 ml) was added a solution of (1*R*,4*R*)-1,4-diphenylbutane-1,4-diol (0.58 g, 2.0 mmol, 1.0 equiv.) and Et_3N (820 µl, 5.9 mmol, 3.0 equiv.) in CH_2Cl_2 (19 ml) at 0 °C under argon. The reaction mixture was quenched using aqueous NH_4Cl (sat.) after stirring for 2 h at 0 °C. The mixture warmed up to room temperature and the solvent was removed *in vacuo* up to about 16 ml followed by adding EtOAc (78 ml). The organic layer was washed with a mixture of (1:2:1) water: brine: aqueous $NaHCO_3$ (sat.) (4×19 ml). The organic phase was concentrated up to 7.0 ml *in vacuo*. The crude product was put in a round bottom flask equipped with a stir bar and put under argon to be used directly for the next step. Allylamine (20 ml, 267 mmol, 60 equiv.) was added portion wise under argon at 0 °C to the mixture. Then, it was stirred at 0 °C overnight. The excess of allylamine was removed *in vacuo* and to the crude product was added Et_2O (68 ml). It was washed with aqueous $NaHCO_3$ (sat.) (23 ml) and brine (10 ml) and dried over Na_2SO_4. The organic phase was concentrated, and the crude product was purified with flash column chromatography (3% Et_2O in petroleum ether) to give the product as a pale-yellow oil (320 mg, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.94 (s, 4H), 6.89 (s, 2H), 5.72-5.64 (m, 1H), 4.97-4.90 (m, 2H), 4.25 (dd app t, *J* = 4.4, 5.6 Hz, 2H), 2.98 (ddd, *J* = 14.6, 4.3, 2.2 Hz, 1H), 2.71 (dd, *J* = 14.6, 7.4 Hz, 1H), 2.52-2.46 (m, 2H), 2.33 (s, 12H), 1.92-1.87 (m, 2H).



(2*S*,5*S*)-2,5-Bis(3,5-dimethylphenyl)pyrrolidine was prepared according to the procedure described by described by Steel.[5] $(PPh)_3RhCl$ (9.6 mg, 0.01 mmol, 1 mol %) and (2*S*,5*S*)-1-allyl-2,5-diphenylpyrrolidine (322 mg, 1.0 mmol, 1.0 equiv.) were placed inside a Schlenk tube equipped with a magnet stir bar under tight Schlenk conditions. To a mixture of (water: acetonitrile

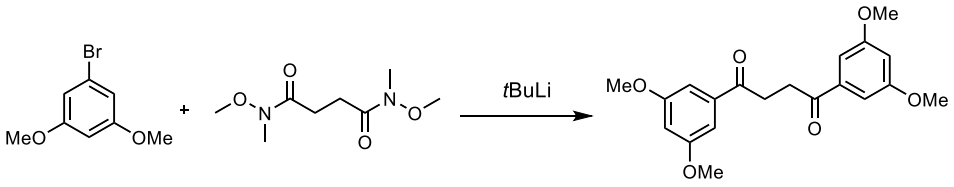
16: 84) (3.0 ml) was added under argon. The mixture was degassed for 20 min using argon flow. A condenser was installed, and the mixture was heated up to 90 °C (oil bath) and stirred for 24 h. After cooling to room temperature, the mixture was transferred to a separatory funnel and was added Et_2O (4.5 ml). The organic layer was washed with brine (2×4.5 ml). The aqueous phase was back extracted with Et_2O (4.5 ml) and the organic layers were combined and dried over Na_2SO_4. The solvent was concentrated and purified by flash column chromatography (9% EtOAc in hexanes) to give the product as a colorless oil (0.19 g, 69%). The ^{1}H NMR spectrum matched the one previously reported.[7] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.02 (s, 4H), 6.88 (s, 2H), 4.48 (dd app t, *J* = 7.2, 6.6 Hz, 2H), 2.38-4.33 (m, 2H), 2.32 (s, 12H), 2.07 (br, s, 1H), 1.93-1.85 (m, 2H).



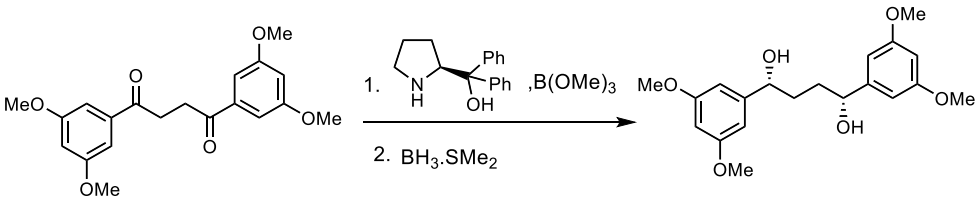
To a solution of tetrachlorocyclopropene (42 µL, 0.34 mmol, 1.0 equiv.) in dried CH_2Cl_2 (6.5 ml) was added a solution of (2*S*,5*S*)-2,5-diphenylpyrrolidine (0.19 g, 0.69 mmol, 2.0 equiv.) and *i*Pr_2NEt (120 µL, 0.69 mmol, 2.0 equiv.) in CH_2Cl_2 (1.9 ml) under argon at -78 °C. The reaction mixture was brought to room temperature and stirred for 6 h before the solvent was removed *in vacuo*. To the mixture was added zinc dust (150 g, 1.9 mmol, 5.6 equiv.) with no further purification and was charged with argon. To the reaction mixture, acetone (0.8 ml) followed by AcOH (3.4 ml) were added and the mixture was stirred overnight. To the crude product was added a solution of $NaBPh_4$ (47 mg, 1.4 mmol, 4.0 equiv.) in water (15 ml) and extracted with CH_2Cl_2 (15 ml). The organic phase was washed with water (3×15 ml) to remove AcOH entirely and dried over Na_2SO_4. The solvent was removed *in vacuo*, and to the crude product was added $CHCl_3$ (5.0 ml). The *i*Pr_2NEt salt was precipitated and filtered. The filtrate was concentrated *in vacuo*. To the crude product was added MeOH and cooled down to 0 °C for an hour. The product crystallized and filtered following by washing with cold MeOH to give the pure 2,3-bis((2*S*,5*S*)-2,5-bis(3,5-dimethylphenyl)pyrrolidin-1-yl)cycloprop-2-en-1-ylium tetraphenylborate as a pale-yellow powder (242 mg, 77%). **m.p.** (°C): 186-189; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (s, 8H), 7.01 (s, 2H), 6.92 (s, 2H), 6.89 (dd app t, *J* = 17.5, 14.6 Hz, 8H), 6.78 (t, *J* = 7.1 Hz, 4H), 6.42 (s, 4H), 6.37 (s, 4H), 4.52-4.51 (m, 2H), 4.40-4.38 (m, 1H), 3.58 (dd app t, *J* = 6.5, 5.5 Hz, 2H), 2.45 (s, 12H), 2.25 (s, 12H), 2.22-2.15 (m, 4H), 1.70-1.60 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.8-163.6 (q, $^1J_{C\text{-}B}$ = 50 Hz), 139.7, 138.9, 138.7, 136.2, 133.9, 130.6, 130.0, 125.6, 123.9, 121.3, 102.2, 67.9, 65.0, 33.8, 33.4, 21.6, 21.4; **FTIR** (KBr thin film) ν_{max} (cm^{-1}): 3102, 3054, 1893, 1609, 1546, 1479, 1425, 1339, 1182, 1033, 847, 733, 701, 608; **HRMS (**ESI-TOF) m/z: $[M]^+$ calcd for $C_{43}H_{49}N_2$ 593.3896; found: 593.3920.

$[\alpha]_D^{21}$ = -118 (*c* = 1.0, CH_2Cl_2)

2,3-Bis((2*S*,5*S*)-2,5-bis(3,5-dimethoxyphenyl)pyrrolidin-1-yl)cycloprop-2-en-1-ylium tetraphenyborate (5)



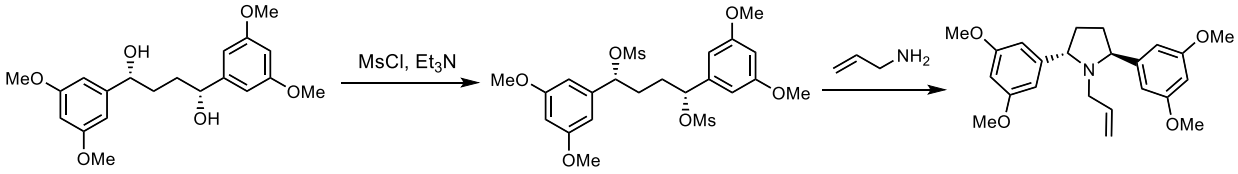
1,4-Bis(3,5-dimethoxyphenyl)butane-1,4-dione was prepared in an analogous manner to the method described by Hayashi.[7] To a solution of 1-bromo-3,5-dimethoxybenzene (16.3 ml, 120 mmol, 2.4 equiv.) in THF (12 ml) was added a solution of *t*BuLi in pentane (14.9 ml, 1.65 M, 5 equiv.) drop wise at -78 °C under argon. The mixture was stirred for 30 min and then was warmed to room temperature and was kept stirring for another 20 min and then, was cooled down to 0 °C. To the mixture was added a solution of N^1,N^4-dimethoxy-N^1,N^4-dimethylsuccinamide (1.0 g, 4.9 mmol, 1.0 equiv.) in dried THF (8.5 ml) under argon slowly and was stirred for another hour and quenched with aqueous NH_4Cl (sat.). The mixture was extracted with $CHCl_3$ and the organic layer was washed with brine and dried with Na_2SO_4. The crude product was concentrated and was dissolved in EtOAc (13.5 ml). Hexanes (3.5 ml) was added and the mixture was kept stirring at -20 °C for 12 h. Crystals formed and were filtered and washed with cold hexanes (780 g, 44 %). **m.p.** (°C): 181.0; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 2.0 Hz, 4H), 6.66 (s, 2H), 3.84 (s, 12H), 3.40 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.3, 160.9, 138.7, 105.9, 105.5, 55.6, 32.8; **FTIR** (thin film in $CHCl_3$) ν_{max} (cm^{-1}): 1684, 1592, 1458, 1426, 1347, 1316, 1209, 1166, 1073, 1060, 1021, 878, 686, 554; **HRMS (**FD-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{22}O_6$ 358.1416; found: 358.1420.



(1*R*,4*R*)-1,4-Bis(3,5-dimethoxyphenyl)butane-1,4-diol was prepared in an analogous manner to the method described by Steel.[5*] (*S*)-diphenyl(pyrrolidin-2-yl)methanol (120 mg, 0.48 mmol, 0.2 equiv.) was put in a round bottom flask equipped with a magnet stir bar. THF (3.0 ml) was added to it and stirred. Then, $B(OMe)_3$ (70 µl, 0.63 mmol, 0.3 equiv.) was added and it was kept stirring for 1 h. Next, $BH_3.SMe_2$ (560 ml, 5.9 mmol, 2.8 equiv.) was added followed by adding 1,4-diphenylbutane-1,4-dione (750 mg, 2.1 mmol, 1.0 equiv.) in THF (5.0 ml) over 1 h. It was stirred for another hour and was quenched with HCl (4.0 ml, 2 N). The aqueous phase was extracted with Et_2O (3×5 ml) and subsequently, the merged organic layers was washed with water and brine and dried with Na_2SO_4. The solvent was removed *in vacuo*. The crude product was purified using flash column chromatography (50% EtOAc in petroleum ether) and white crystals (506 mg, 67%) were obtained. **m.p.** (°C): 85.2-86.1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.47 (s, 4H), 6.34 (s, 2H), 4.60 (s, 2H), 3.76 (s, 12H), 3.05-3.03 (m, 2H), 1.88-1.85 (m, 2H), 1.80-1.78 (m, 2H); **^{13}C NMR** (150 MHz,

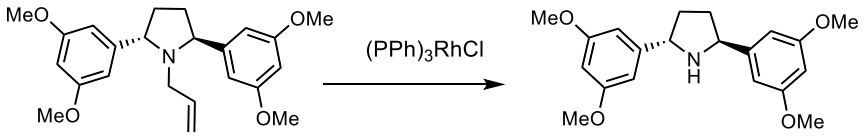
$CDCl_3$) δ 160.8, 147.3, 103.7, 99.4, 74.2, 55.3, 35.8; **FTIR** (thin film in dichloromethane) ν_{max} (cm^{-1}): 3397, 2999, 2940, 2838, 1597, 1464, 1429, 1348, 1295, 1204, 1154, 1063, 924, 834; **HRMS (**FD-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{26}O_6$ 362.1729; found: 362.1734.

$[\alpha]_D^{21}$ = +53 (c = 1.0, CH_2Cl_2)



(2*S*,5*S*)-1-Allyl-2,5-bis(3,5-dimethoxyphenyl)pyrrolidine was prepared according to the procedure described by described by Steel.[5] To a solution of methanesolfunylchloride (59 µl, 0.76 mmol, 2.5 equiv.) in CH_2Cl_2 (3.0 ml) was added a solution of (1*R*,4*R*)-1,4-diphenylbutane-1,4-diol (110 mg, 0.304 mmol, 1.0 equiv.) and Et_3N (0.128 ml, 0.91 mmol, 3.0 equiv.) in CH_2Cl_2 (3.0 ml) at 0 °C under argon. The reaction mixture was quenched using aqueous NH_4Cl (sat.) after stirring for 2 h at 0 °C. The mixture warmed up to room temperature and the solvent was removed *in vacuo* up to about 11 ml followed by adding EtOAc (12 ml). The organic layer was washed with a mixture of (1: 2: 1) water: brine: aqueous $NaHCO_3$ (sat.) (4×10 ml). The organic phase was concentrated up to 1 ml *in vacuo*. The crude product was put in a round bottom flask equipped with a stir bar and put under argon to be used directly for the next step. Allylamine (3.7 ml, 49.44 mmol, 163 equiv.) was added portion wise under argon at 0 °C. The mixture was stirred at 0 °C overnight. The excess of allylamine was removed *in vacuo* and to the crude product was added Et_2O (3.0 ml). It was washed with aqueous $NaHCO_3$ (sat.) (4.0 ml) and brine (4.0 ml) and dried over Na_2SO_4. The organic phase was concentrated, and the crude product was purified with flash column chromatography (15% Et_2O in petroleum ether) to give the product (76 mg, 65%) as a pale-yellow oil. **m.p.** (°C): 153.6; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.51 (d, , *J*=2.3 Hz, 4H), 6.37 (t, *J*=2.2 Hz, 2H), 5.76-5.69 (m, 1H), 5.03-4.98 (m, 2H), 4.29-4.28 (m, 2H), 3.81 (s, 12H), 3.07-3.02 (m, 1H), 2.83 (dd, *J* = 14.9, 7.3 Hz, 1H), 2.52-2.45 (m, 2H), 1.92-1.84 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.7, 147.0, 137.1, 115.5, 105.8, 98.6, 65.7, 55.3, 49.8, 32.9; **FTIR** (thin film in dichloromethane) ν_{max} (cm^{-1}): 3077, 2998, 2956, 2836, 1596, 1463, 1428, 1346, 1311, 1292, 1205, 1154, 1063, 923; **HRMS (**FD-TOF) m/z: $[M]^+$ calcd for $C_{23}H_{29}O_4N$ 383.2097; found: 383.2094.

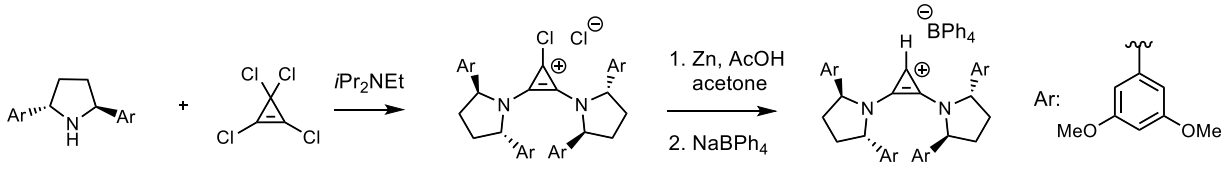
$[\alpha]_D^{21}$ = -208 (*c* = 1.3, CH_2Cl_2)



(2*S*,5*S*)-2,5-Bis(3,5-dimethoxyphenyl)pyrrolidine was prepared analogous to the method described by Steel.[5] $(PPh)_3RhCl$ (1.6 mg, 0.0017 mmol, 1.0 mol %) and (2*S*,5*S*)-1-allyl-2,5-diphenylpyrrolidine (66 mg, 0.17 mmol, 1.0 equiv.) were placed inside a Schlenk tube equipped with a magnet stir bar under tight Schlenk conditions. To a mixture of (water: acetonitrile 16: 84)

(0.6 ml) was added to it under argon. The mixture was degassed for 20 min using argon flow. A condenser was installed, and the mixture was heated up (oil bath) to 90 °C and refluxed for 24 h. After cooling to room temperature, the mixture was transferred to a separatory funnel and was added Et_2O (0.7 ml). The organic layer was washed with brine (2×0.7 ml). The aqueous phase was back extracted with Et_2O (0.7 ml) and the organic layers were combined and dried over Na_2SO_4. The filtrate was concentrated *in vacuo* and purified by flash column chromatography (33% EtOAc in petroleum ether) to give the product as an orange oil (35 mg, 60%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.57 (d, *J* = 2.0 Hz, 4H), 6.35 (s, 2H), 4.48 (dd app t, *J* = 6.5 Hz, 2H), 3.80 (s, 12H), 2.23-2.33 (m, 2H), 2.08 (br s, 1H), 1.89-1.82 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.19, 148.7, 104.3, 98.6, 62.3, 55.3, 35.2; **FTIR** (thin film in CH_2Cl_2) ν_{max} (cm^{-1}): 3372, 2957, 2836, 2102, 1596, 1457, 1428, 11351, 1295, 1204, 1152, 1061, 926, 835; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{25}O_4N$ 343.1784; found: 343.1792.

$[\alpha]_D^{21}$ = -118 (c=1.0, CH_2Cl_2)

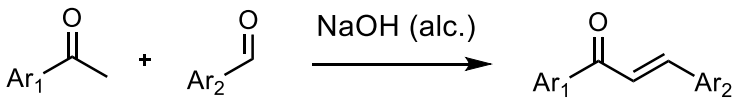


To a solution of tetrachlorocyclopropene (55 µL, 0.45 mmol, 1.0 equiv.) in dried CH_2Cl_2 (8.5 ml) was added a solution of (2*S*,5*S*)-2,5-diphenylpyrrolidine (307 mg, 0.90 mmol, 2.0 equiv.) and *i*Pr_2NEt (160 µL, 0.90 mmol, 2.0 equiv.) in CH_2Cl_2 (2.5 ml) under argon at -78 °C. The reaction mixture was brought to room temperature and stirred for 6 h before the solvent was removed *in vacuo*. To the crude product was added zinc dust (164 mg, 2.5 mmol, 5.6 equiv.) and was charged with argon. To the mixture was added acetone (1.0 ml) followed by AcOH (4.5 ml) and the reaction mixture was stirred overnight. To the reaction mixture was added a solution of $NaBPh_4$ (612 mg, 1.8 mmol, 4.0 equiv.) in water (20 ml) and extracted with CH_2Cl_2 (20 ml). The organic phase was washed with water (20 ml) to remove AcOH entirely and dried over Na_2SO_4.The solvent was removed *in vacuo*, and to the crude product was added $CHCl_3$ (6.5 ml). The *i*Pr_2Net.$HBPh_4$ salt was precipitated and filtered. The filtrate was concentrated. To the crude product was added MeOH and it was cooled down to 0 °C for 1 h. The product crystallized and filtered following by washing with cold MeOH to give the pure 2,3-bis((2*S*,5*S*)-2,5-bis(3,5-dimethylphenyl)pyrrolidin-1-yl)cycloprop-2-en-1-ylium tetraphenylborate as a pale-yellow powder (276 mg, 59%). **m.p.** (°C): 179-181; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (s, 8H), 6.89 (dd app t, *J* = 7.4 Hz, 8H), 6.78 (t, *J* = 7.1 Hz, 4H), 6.49 (t, *J* = 2.0, 2H), 6.36 (t, *J* = 2.0 Hz, 2H), 5.96 (d, *J* = 2.1 Hz, 4H), 5.94 (d, *J* = 2.0 Hz, 4H), 4.40 (dd app t, *J* = 5.8 Hz, 2H), 4.14 (s, 1H), 3.84 (s, 12H), 3.67 (s, 12H), 2.21-2.16 (m, 4H), 1.70-1.64 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.6-163.6 (q, $^1J_{C\text{-}B}$ = 49 Hz) , 161.5, 161.4, 141.9, 140.4, 136.2, 134.2, 125.7-125.6 (d, $^2J_{C\text{-}B}$ = 2.7 Hz), 121.4, 104.6, 103.9, 103.2, 98.03, 99.0, 67.6, 65.0, 55.5, 55.4, 34.4, 33.1; **FTIR** (thin film in CH_2Cl_2) ν_{max} (cm^{-1}): 3462, 2999, 2838, 1893, 1653, 1597, 1546, 1457, 1429, 1351, 1205, 1158, 1065, 927; **HRMS (**ESI-TOF) m/z: $[M]^+$ Calcd for $C_{43}H_{49}N_2O_8$ 721.3489; found: 721.3454.

$[\alpha]_D^{21}$ = -88 (*c* = 1.0, CH_2Cl_2)

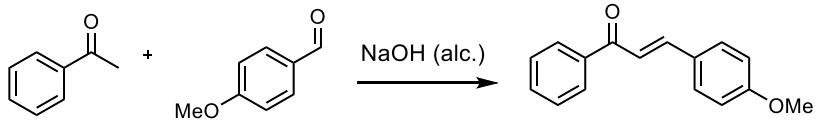
Synthesis of enones

General methods



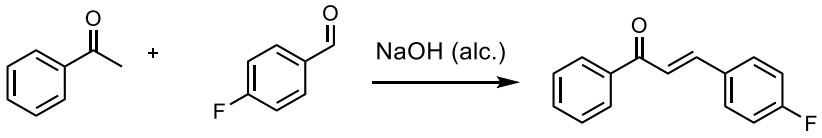
The chalcone derivatives were prepared using the previously described procedure by Siva.[9] To solution of acetophenone derivative (1.0 equiv.) and aromatic aldehyde (1.0 equiv.) in EtOH (2.5 M) was added a solution of NaOH (1 M, 0.75 equiv.) in EtOH at 0 °C drop wise. The mixture was stirred at room temperature for 15 min (in some cases more time is required) until crystals formed. The mixture was cooled down to 0 °C and the solid was filtered and washed with cold EtOH. In some cases, recrystallization in EtOH was carried out for more purification.

(E)-3-(4-Methoxyphenyl)-1-phenylprop-2-en-1-one



To a solution of acetophenone (410 µl, 2.5 mmol, 1.0 equiv.) and 4-methoxy benzaldehyde (304 µl, 2.5 mmol, 1.0 equiv.) in EtOH (1.0 ml) was added a solution of NaOH (1.5 ml, 1.5 mmol, 0.75 equiv.) in EtOH at 0 °C drop wise. The mixture was stirred at room temperature for 2 h until crystals formed. The mixture was cooled down to 0 °C and the solid was filtered and washed with cold EtOH. The product was obtained as yellow crystals (315 mg, 53%). The ^{1}H NMR spectrum matched the one previously reported.[9] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 15.5 Hz, 1H), 7.61-7.56 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 15.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.86 (s , 3H).

(E)-3-(4-Fluorophenyl)-1-phenylprop-2-en-1-one

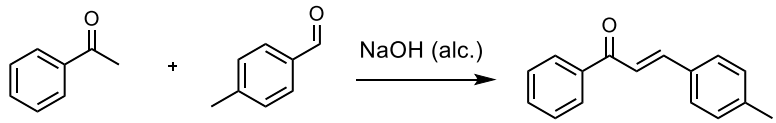


To a solution of acetophenone (410 µl, 2.5 mmol, 1.0 equiv.) and 4-fluoro benzaldehyde (270 µl, 2.5 mmol, 1.0 equiv.) in EtOH (1.0 ml) was added a solution of NaOH (2.5 ml, 2.5 mmol, 1.0

[9] J. Sivamani, V. Ashokkumar, V. Sadhasivam, K. Duraimurugan, A. Siva, *RSC Adv.* **2014**, *4*, 60293-60299.

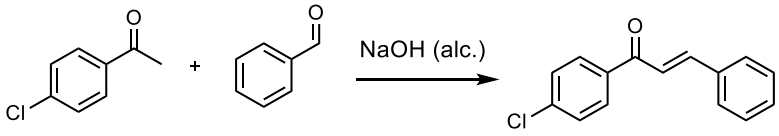
equiv.) in EtOH at 0 °C drop wise. The mixture was stirred at room temperature for 1 h until crystals formed. The mixture was cooled down to 0 °C and the solid was filtered and washed with cold EtOH. The product was obtained as yellow crystals (100 mg, 18%). The ^{1}H NMR spectrum matched the one previously reported.[9] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 15.5 Hz, 1H), 7.66-7.63 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 16.0 Hz, 2H), 7.12 (t, *J* = 8.5 Hz, 2H).

(E)-1-Phenyl-3-(p-tolyl)prop-2-en-1-one



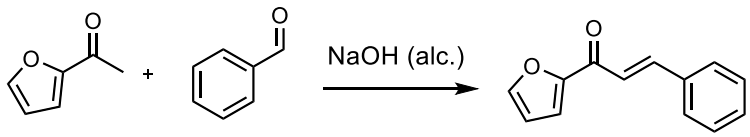
To a solution of acetophenone (41 µl, 2.5 mmol, 1.0 equiv.) and 4-methylbenzaldehyde (295 µl, 2.5 mmol, 1.0 equiv.) in EtOH (1.0 ml) was added a solution of NaOH (2.5 ml, 2.5 mmol, 1.0 equiv.) in EtOH at 0 °C drop wise. The mixture was stirred at room temperature for 30 min until crystals formed. The mixture was cooled down to 0 °C and the solid was filtered and washed with cold EtOH. The product was obtained as yellow crystals (322 mg, 58%). The ^{1}H NMR spectrum matched the one previously reported.[9] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.80 (d, *J* = 15.5 Hz, 1H), 7.58-7.48 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H).

(E)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-one



To a solution of 1-(4-chlorophenyl)ethan-1-one (324 µl, 2.5 mmol, 1.0 equiv.) and benzaldehyde (255 µl, 2.5 mmol, 1.0 equiv.) in EtOH (1.0 ml) was added a solution of NaOH (2.5 ml, 2.5 mmol, 1.0 equiv.) in EtOH at 0 °C dropwise. The mixture was stirred at room temperature for 15 min until crystals formed. The mixture was cooled down to 0 °C and the solid was filtered and washed with cold EtOH. The product was obtained as yellow crystals (225 mg, 93%). The ^{1}H NMR spectrum matched the one previously reported.[9] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 15.6 Hz, 1H), 7.64 (s, 2H), 7.49-7.43 (m, 6H).

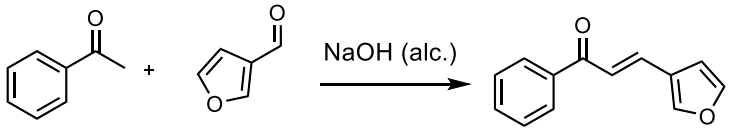
(E)-1-(Furan-2-yl)-3-phenylprop-2-en-1-one



To a solution of 1-(furan-2-yl)ethan-1-one (550 µl, 5.0 mmol, 1.0 equiv.) and benzaldehyde (530 µl, 5.0 mmol, 1.0 equiv.) in EtOH (1.0 ml) was added a solution of NaOH (1.8 ml, 5.0 mmol, 1.0

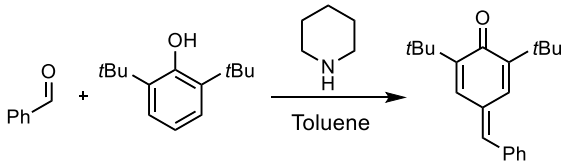
equiv.) in EtOH at 0 °C drop wise. The mixture was stirred at room temperature for 1 h until crystals formed. The mixture was cooled down to 0 °C and the solid was filtered and washed with cold EtOH. The product was obtained as a white solid (844 mg, 85%). The ^{1}H NMR spectrum matched the one previously reported.[9] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 15.8 Hz, 1H), 7.66-7.65 (m, 3H), 7.46 (d, *J* = 15.8 Hz, 1H), 7.43-7.41 (m, 3H), 7.34 (dd, *J* = 3.5, 0.4 Hz, 1H), 6.60 (dd, *J* = 3.6, 1.6 Hz, 1H).

(E)-3-(Furan-3-yl)-1-phenylprop-2-en-1-one



It was prepared in an analogous manner to the method described by Armstrong.[10] To a solution of fine powder KOH (561 mg, 10 mmol, 2.0 equiv.) in MeOH (12 ml) and water (2.5 ml) was added acetophenone (583 µl, 5.0 mmol, 1.0 equiv.) and stirred at room temperature for 10 min, then, 3-furaldehyde (430 µl, 5.0 mmol, 1.0 equiv.) was added dropwise. The mixture was stirred for 2 h. The reaction progress was monitored by TLC over the reaction course. After completion, the reaction mixture was added water (17 ml) and subsequently, NH_4Cl (aq.). The mixture was extracted with Et_2O (3×20 ml) and the merged organic phase was washed with brine (10 ml) and dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude product was subjected to crystallization using EtOH. The mixture was stirred at room temperature for 1 h until crystals formed. The mixture was cooled down to 0 °C and the solid was filtered and washed with cold EtOH. The product was obtained as a brown solid (512 mg, 52%). The ^{1}H NMR spectrum matched the one previously reported.[10] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.75-7.71 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52-7.48 (m, 3H), 7.23 (s, 1H merged with solvent), 6.72 (s, 1H).

4-Benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one



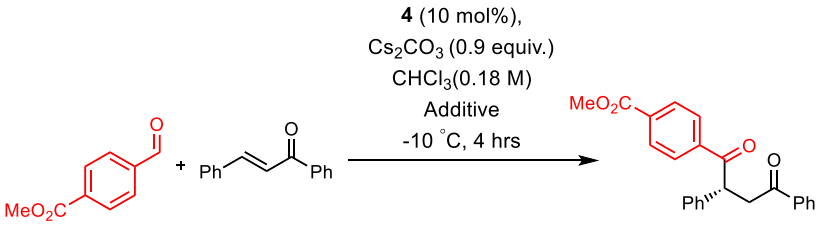
It was prepared analogous to the previously described procedure by Anand.[11] In a Dean-Stark equipment, to a solution of benzaldehyde (990 µl, 9.7 mmol, 1.0 equiv.) and 2,6-di-tert-butylphenol (2.0 g, 9.7 mmol, 1.0 equiv.) in dried toluene (13 ml) was added piperidine (1.9 ml, 19 mmol, 2.0 equiv.) over 1 h under argon and at reflux conditions. The mixture was refluxed

[10] A. Armstrong, C. A. Baxter, S. G. Lamont, A. R. Pape, R. Wincewicz, *Org. Lett.* **2007**, *9*, 351-353.
[11] V. Reddy, R. V. Anand, *Org. Lett.* **2015**, *17*, 3390-3393.

further for 12 h. The mixture was cooled down to 100 °C and to that, acetic anhydride was added (1.84 ml, 19.4 mmol, 2.0 equiv.). The reaction was kept stirring at this temperature for 30 min and then, cooled to room temperature and poured into ice-water (10 ml). The mixture was extracted with CH_2Cl_2 (1×15 ml). The organic layers were merged and dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified using flash column chromatography (2% EtOAc in hexanes) to give orange solid and the ^{1}H NMR spectrum matched the one previously reported. (902 mg, 32%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.3 Hz, 1H), 7.46-7.45 (m, 4H), 7.41-7.39 (m, 1H), 7.19 (s, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 1.34 (s, 9H), 1.30 (s, 9H).

Optimization of enantioselective Stetter reactions

Additive effect



An oven-dried Schlenk tube was charged with pre-dried Cs_2CO_3 (20 mg, 0.06 mmol, 0.8 equiv.) and 4Å M.S. (20 mg) under argon. They were dried further using heat gun for 5 min. *Trans*-chalcone (15 mg, 0.072 mmol, 1 equiv.) and methyl 4-formylbenzoate (14 mg, 0.085 mmo, 1.2 equiv.) were put in the reaction vessel with a magnetic stir bar. The atmosphere in the tube was evacuated under vacuum and replaced with argon three times. Then, CH_3Cl (0.18 M) was added. The mixture was cooled down to -10 °C using salt and ice bath. **4** (10 mol %) was added to the tube and it was sealed and stirred at the same temperature for 5h. A wide range of results was obtained. Eventually, water was found to be the reason for this variability. The amount of water as well as more additives were tested, and the results are shown in Table **1**.

Table 1. Additive optimization

entry	**additive (equiv.)**	**yield (%)**	***ee* (%)**
1	H_2O (0.8)	30	94
2	H_2O (0.4)	38	93
3	H_2O (0.2)	80	90
4	MeOH (0.6)	85	62
5	EtOH (0.3)	90	80
6	*i*PrOH (0.5)	82	50
7	*n*BuOH (0.5)	86	88
8	BHT (0.5)	90	88
9	*n*Pr (0.4)	82	50

Temperature effect

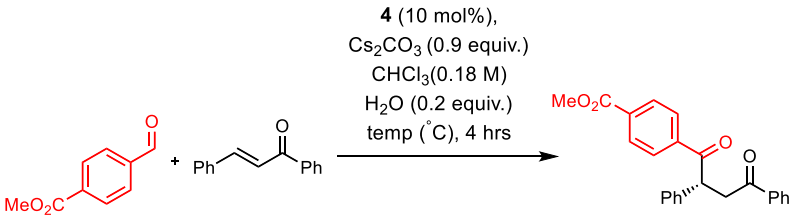


Table 2. Temperature optimization

entry	temperature (°C)	yield (%)	*ee* (%)
1	-25	19	96
2	-10	33	94
3	-5	36	94
4	0	91	91
5	rt	78	87

Concentration effect

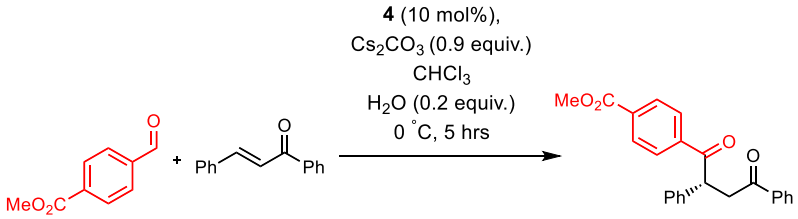


Table 3. Concentration optimization

entry	concentration (M)	yield (%)	*ee* (%)
1	0.36	54	90
2	0.09	31	93

Solvent effect

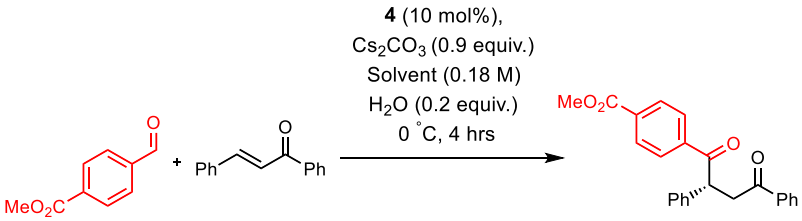


Table 4. Solvent optimization

entry	solvent (M)	yield (%)	*ee* (%)

1	CH_2Cl_2	83	85
2	THF	83	77
3	acetonitrile	8	75
4	1,4-dioxane	86	60
5	toluene	0	0
6	DMF	57	0

Base effect

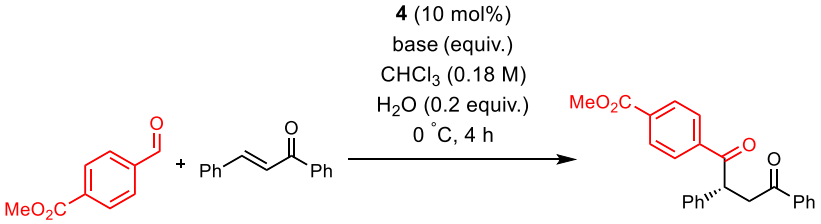


Table 5. Base optimization

entry	**base (equiv.)**	**yield (%)**	***ee* (%)**
1	CS_2CO_3 (1.5)	90	87
2	CS_2CO_3 (0.7)	95	89
3	CS_2CO_3 (0.5)	96	90
4	CS_2CO_3 (0.3)	92	91o
5	CS_2CO_3 (0.15)	69	92
6	Rb_2CO_3 (1)	59	91
7	DBU	87	55
8	K_2CO_3	0	0

Time effect

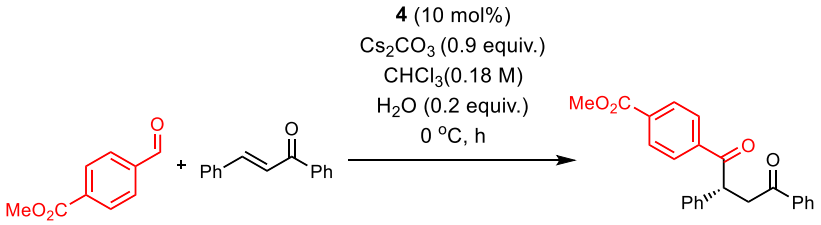


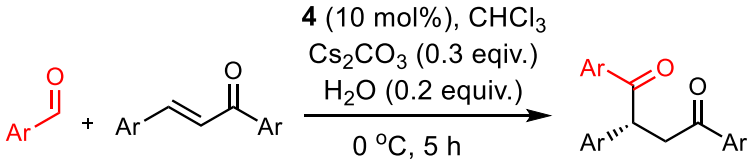
Table 6. Time optimization

entry	**time (h)**	**yield (%)**	***ee* (%)**
1	0.75	60	91
2	2	84	90

3	5	92	92
4	24	93	88

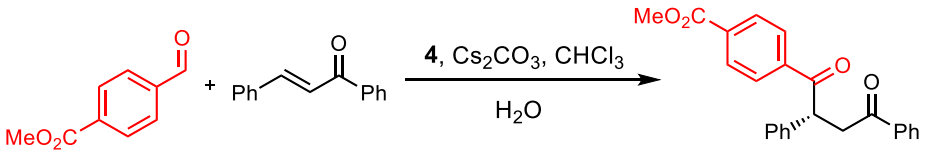
Stetter reactions

General method



An oven-dried Schlenk tube was applied full Schlenk conditions and charged with pre-dried Cs_2CO_3 (0.3 equiv.) under argon. The base was dried further using heat gun for 5 min. Chalcone (1.0 equiv.) and solid aldehydes (1.2 equiv.) were put in the reaction vessel with a magnet stir bar. The tube was undergone deaeration cycles for three times. Then, CH_3Cl (0.16 M) was added under argon. Subsequently, all the liquid components including liquid aldehydes (1.2 equiv.) and water (0.2 equiv.) were added. The mixture was cooled down to 0 °C using ice bath. **4** (10 mol %) was added to the reaction mixture under argon the tube was sealed and stirred at the same temperature for 5 h. The reaction mixture was passed through a silica plug immediately after the reaction vessel was opened and washed with CH_2Cl_2. The solvent was removed *in vacuo* and to the crude product was added dimethyl terephthalate, EtOAc or trichloroethylene as an internal standard. The conversion was measured using ^{1}H NMR. The crude product was purified with flash column chromatography and the yield was calculated based on the weight of pure isolated product. The *ee* (%) was determined by HPLC using a chiral stationary phase.

Methyl (*R*)-4-(4-oxo-2,4-diphenylbutanoyl)benzoate (6)

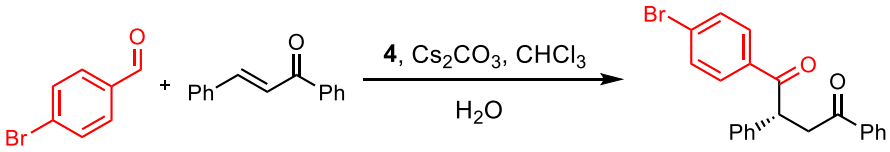


A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (16 mg, 0.49 mmol, 0.3 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, chalcone (34 mg, 0.164 mmol, 1.0 equiv.) and methyl 4-formylbenzoate (32 mg, 0.20 mmol, 1.2 equiv.) were added. CH_3Cl (1.0 ml) and water (0.6 µL, 0.03 mmol, 0.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (15 mg, 0.016 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (8.0 mg, 0.041 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 92% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (15% EtOAc in hexanes) to afford **6** (60

mg, 90%) as a white solid. The ^{1}H NMR spectrum matched the one previously reported.[12] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 4H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, app t, *J* = 7.6 Hz, 2H), 7.35-7.30 (m, 4H), 7.24 (t, *J* = 7.0 Hz, 1H), 5.30 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.23 (dd, *J* = 18.1, 10 Hz, 1H), 3.91 (s, 3H), 3.34 (dd, *J* = 3.4, 10 Hz, 1H). HPLC analysis: Chiralpak IC 2.1×150mm column, 15% *i*PrOH in hexanes, 30 deg, 0.2 mL/min Major 14.0 min, minor 9.6 min, (91% *ee*).

$[\alpha]_D^{21}$ = -469 (*c*=1.0, CH_2Cl_2)

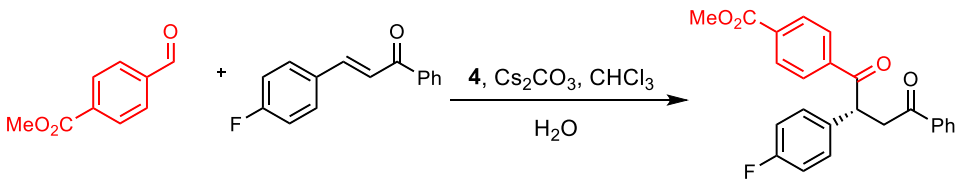
(*R*)-1-(4-Bromophenyl)-2,4-diphenylbutane-1,4-dione (7)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (16 mg, 0.49 mmol, 0.3 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, chalcone (34 mg, 0.16 mmol, 1.0 equiv.) and 4-bromobenzaldehyde (36 mg, 0.20 mmol, 1.2 equiv.) were added. CH_3Cl (1.0 ml) and water (0.6 µL, 0.033 mmol, 0.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (15 mg, 0.016 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (8.0 mg, 0.041 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 53% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (3% EtOAc in toluene) to afford **7** (26 mg, 40%) as a yellow powder. The ^{1}H NMR spectrum matched the one previously reported.[13] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.58-7.53 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.33-7.30 (m, 4H), 7.26-7.25 (m, 1H), 5.24 (dd, *J* = 10.1, 3.0 Hz, 1H), 4.20 (dd, *J* = 18.0, 10 Hz, 1H), 3.30 (dd, *J* = 18.0, 0.8 Hz, 1H). HPLC analysis: Chiralpak IA 2.1×150mm column, 10% *i*PrOH in hexanes, 30 deg, 0.2 mL/min Major 11.1 min, minor 9.7 min. (82% *ee*).

$[\alpha]_D^{21}$ = -241 (*c* = 2.0, CH_2Cl_2)

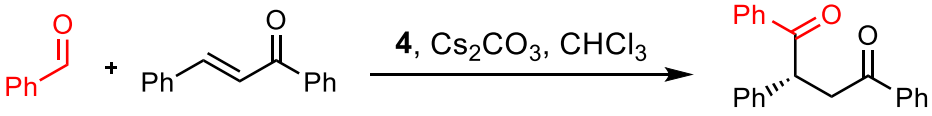
Methyl (*R*)-4-(2-(4-fluorophenyl)-4-oxo-4-phenylbutanoyl)benzoate (8)



[12] M. M. D. Wilde, M. Gravel, *Angew. Chem. Int. Ed.* **2013**, *52*, 12651-12654.
[13] D. Enders, J. Han, A. Henseler, *Chem. Commun.* **2008**, 3989-3991.

A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (27 mg, 0.082 mmol, 0.5 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (37 mg, 0.16 mmol, 1.0 equiv.) and methyl 4-formylbenzoate (34 mg, 0.20 mmol, 1.2 equiv.) were added. CH_3Cl (1.0 ml) and water (0.6 µL, 0.03 mmol, 0.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that **4** was added (15 mg, 0.016 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (8.0 mg, 0.041 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 92% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (10% EtOAc in hexanes) to afford **8** (58 mg, 91%) as a pale-yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09-8.04 (m, 4H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (dd app t, *J* = 7.8, 2H), 7.32 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.00 (dd app t, *J* = 8.6 Hz, 2H), 5.30 (dd, *J* = 10.0, 3.7 Hz, 1H), 4.18 (dd, *J* = 18.0, 10 Hz, 1H), 3.92 (s, 3H), 3.33 (dd, *J* = 18.0, 3.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.6, 197.8, 166.2, 162.2 (d, *J* = 246 Hz, chemical shifts for two peaks: 163.1, 161.2), 139.7, 136.2, 133.7, 133.6, 133.6, 133.5, 129.9, 129.8, 128.7 (d, *J* = 10 Hz, chemical shifts for two peaks: 128.8, 128.7), 128.2, 116.3 (d, *J* = 21 Hz, chemical shifts for two peaks: 116.4, 116.2), 52.4, 48.2, 43.8; **FTIR** (thin film in dichloromethane) ν_{max} (cm^{-1}): 3433, 1725, 1681, 1600, 1507, 1442, 1404, 1282, 1229, 1200, 1161, 998, 954, 840; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{24}H_{19}O_4F$ 390.1267; found: 390.1272. HPLC analysis: Chiralpak IB 2.1×150 mm column, 50% *i*PrOH in hexanes, 0.2 ml/min Major peak at 7.8 min, minor 9.8 min. (76% *ee*). $[\alpha]_D^{21}$ = -519 (*c* = 1.4, CH_2Cl_2)

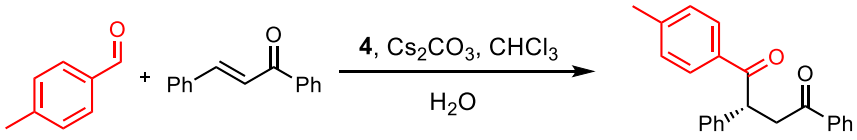
(*R*)-1,2,4-Triphenylbutane-1,4-dione (9)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (44 mg, 0.13 mmol, 0.9 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-chalcone (32 mg, 0.15 mmol, 1.0 equiv.) was added. CH_3Cl (950 µl) and freshly distilled benzaldehyde (22 µL, 0.18 mmol, 1.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (14 mg, 0.015 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (7.3 mg, 0.038 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 93% conversion was observed according to ^{1}H NMR. The crude product was purified further using flash column chromatography (18% EtOAc in hexanes) to afford **9** (42 mg, 88%) as a white solid. The ^{1}H NMR spectrum matched the one previously reported.[12] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.46 (dd app t, *J* = 7.9 Hz, 2H), 7.41 (dd app t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.32 (dd app t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 5.33 (dd, *J* = 10.3, 3.4 Hz, 1H), 4.24 (dd, *J* = 18.1, 10 Hz, 1H), 3.33 (dd, *J* = 18.0, 3.4 Hz, 1H). HPLC analysis: Chiralpak IC 2.1×150mm column, 10% *i*PrOH in hexanes, 30 deg, 0.2 mL/min Major 6.0 min, minor 7.5 min (81% *ee*).

$[\alpha]_D^{21}$ = -211 (*c* = 1.1, CH_2Cl_2)

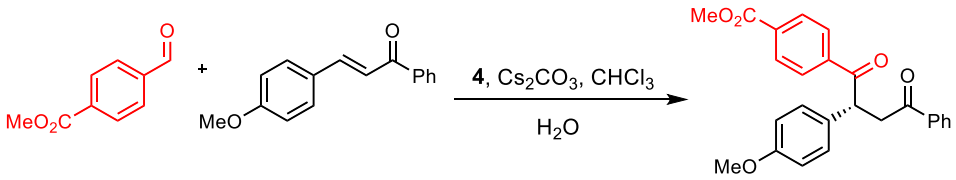
(*R*)-2,4-Diphenyl-1-(p-tolyl)butane-1,4-dione (10)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (48 mg, 0.15 mmol, 0.9 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-chalcone (34 mg, 0.164 mmol, 1 equiv.) was added. CH_3Cl (1.0 ml) and freshly distilled 4-methylbenzaldehyde (24 µL, 0.18 mmol, 1.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (15 mg, 0.016 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (8.0 mg, 0.041 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 94% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (15% EtOAc in hexanes) to afford **10** (49 mg, 91%) as a white solid. The ^{1}H NMR spectrum matched the one previously reported.[12] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (dd app t, *J* = 7.8 Hz, 2H), 7.38-7.36 (m, 2H), 7.30 (dd app t, *J* = 7.5 Hz, 2H), 7.24-7.19 (m, 3H), 5.33 (dd, *J* = 9.8, *J* = 3.0 Hz, 1H), 4.21 (dd, *J* = 18.0, 10 Hz, 1H), 3.30 (dd, *J* = 18.0, 3.0 Hz, 1H), 2.36 (s, 3H). HPLC analysis: Chiralpak IC 2.1×150mm column, 10% *i*PrOH in hexanes, 30 deg, 0.3 mL/min Major 4.7 min, minor 5.9 min, (79% *ee*).

$[\alpha]_D^{21}$ = -211 (*c* = 1.1, CH_2Cl_2)

Methyl (*R*)-4-(2-(4-methoxyphenyl)-4-oxo-4-phenylbutanoyl)benzoate (11)

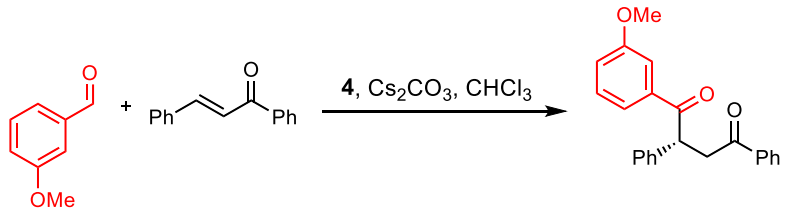


A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (27 mg, 0.082 mmol, 0.5 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (39 mg, 0.16 mmol, 1.0 equiv.) and methyl 4-formylbenzoate (32 mg, 0.20 mmol, 1.2 equiv.) were added. CH_3Cl (1.0 ml) and water (0.6 µL, 0.03 mmol, 0.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (15 mg, 0.016 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (8 mg, 0.041 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 32% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (16% EtOAc in hexanes) to afford **11** (19 mg, 30%) as a yellow oil. **^{1}H**

NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 4H), 8.00 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (dd app t, *J* = 7.4 Hz, 2H), 7.28 (s, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.28 (dd, *J* = 10.1, 3.5 Hz, 1H), 4.21 (dd, *J* = 18.1, 10 Hz, 1H), 3.94 (s, 3H), 3.78 (s, 3H), 3.34 (dd, *J* = 18.0, 3.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.8, 198.1, 166.3, 159.0, 140.0, 136.4, 133.5, 133.4, 129.7, 129.3, 129.1, 128.8, 128.6, 128.2, 114.7, 55.2, 52.4, 48.3, 43.9; **FTIR** (thin film in dichloromethane) ν_{max} (cm^{-1}): 3433, 1724, 1680, 1609, 1597, 1581, 1511, 1448, 1436, 1406, 1281, 1251, 1201, 1180, 1109, 1001; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{25}H_{22}O_5$ 402.1467; found: 402.1462. HPLC analysis: Chiralpak IB 2.1×150 mm column, 50% *i*PrOH in hexanes, 0.2 ml/min Major peak at 9.1 min, minor 11.4 min. (92% *ee*).

$[\alpha]_D^{21}$ = -290 (*c* = 0.8, CH_2Cl_2)

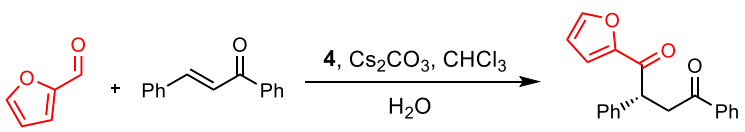
(*R*)-1-(3-Methoxyphenyl)-2,4-diphenylbutane-1,4-dione (12)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (44 mg, 0.13 mmol, 0.9 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-chalcone (32 mg, 0.15 mmol, 1.0 equiv.) was added. CH_3Cl (950 µl) and freshly distilled 3-methoxybenzaldehyde (22 µL, 0.18 mmol, 1.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (14 mg, 0.015 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (7.3 mg, 0.038 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 72% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (18% EtOAc in hexanes) to afford **12** (36 mg, 70%) as a pale-yellow solid. The ^{1}H NMR spectrum matched the one previously reported.[12] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.57-7.54 (m, 2H), 7.45 (dd app t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.33-7.29 (m, 3H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.04 (dd, *J* = 2.6, 0.5 Hz, 1H), 5.30 (dd, *J* = 10.1, 3.7 Hz, 1H), 4.21 (dd, *J* = 17.9, 10 Hz, 1H), 3.81 (s, 3H), 3.31 (dd, *J* = 17.9, 3.7 Hz, 1H). HPLC analysis: Chiralpak IA 2.1×150mm column, 10% *i*PrOH in hexanes, 30 deg, 0.13 mL/min Major 15.2 min, minor 14.3 min (88% *ee*).

$[\alpha]_D^{21}$ = -230 (*c* = 1.0, CH_2Cl_2)

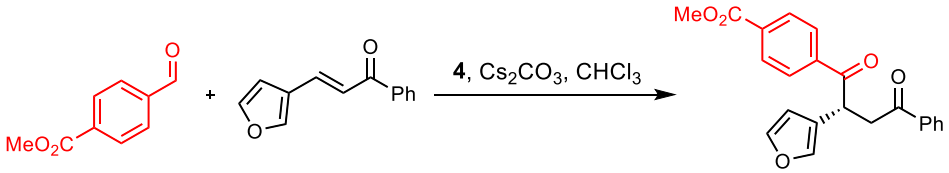
(*R*)-1-(Furan-2-yl)-2,4-diphenylbutane-1,4-dione (13)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (16 mg, 0.049 mmol, 0.3 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-chalcone (34 mg, 0.16 mmol, 1.0 equiv.) was added. Dried CH_3Cl (1.0 ml) and freshly distilled furan-2-carbaldehyde (16 µL, 0.20 mmol, 1.2 equiv.) and distilled water (0.6 µL, 0.03 mmol, 0.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (15 mg, 0.016 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (8.0 mg, 0.041 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 89% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (15% EtOAc in hexanes) to afford **13** (43 mg, 86%) as a white solid. The ^{1}H NMR spectrum matched the one previously reported.[12] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.55 (dd app t, *J* = 7.5 Hz, 2H), 7.46-7.40 (m, 4H), 7.32 (dd app t, *J* = 7.6 Hz, 2H), 7.25-7.24 (m, 2H), 6.48 (dd, *J* = 3.4, 1.6 Hz, 1H), 5.12 (dd, *J* = 10.2, 3.8 Hz, 1H), 4.18 (dd, *J* = 18.0, 10 Hz, 1H), 3.33 (dd, *J* = 18.0, 3.8 Hz, 1H). HPLC: Chiralpak IC 2.1×150 mm column, 15% *i*PrOH in hexanes, 0.3 ml/min. Major peak at 5.7 min, minor 10.2 min, (90% *ee*).

$[\alpha]_D^{21}$ = -240 (*c* = 0.9, CH_2Cl_2)

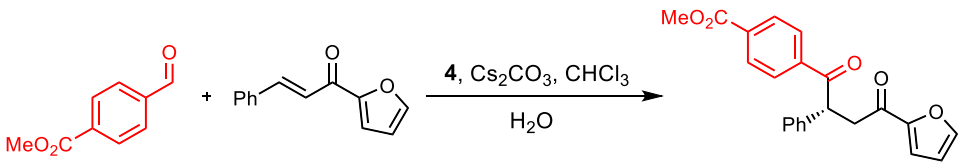
Methyl (*R*)-4-(2-(furan-3-yl)-4-oxo-4-phenylbutanoyl)benzoate (14)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (51 mg, 0.16 mmol, 0.9 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-3-(furan-3-yl)-1-phenylprop-2-en-1-one (35 mg, 0.18 mmol, 1.0 equiv.) and methyl 4-formylbenzoate (35 mg, 0.21 mmol, 1.2 equiv.) were added. CH_3Cl (1.1 ml) was transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (16 mg, 0.018 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. EtOAc (9 mg, 0.088 mmol, 0.5 equiv.) was added to the crude product as the internal standard. 99% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (20% EtOAc in hexanes) to afford **14** (57 mg, 87%) as a yellow solid. **m.p.** (°C): 147–151; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12-8.08 (m, 4H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.46 (dd app t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 5.2 Hz, 2H), 6.35 (s, 1H), 5.23 (dd, *J* = 9.9, 3.8 Hz, 1H), 4.12 (dd, *J* = 18.1, 9.9 Hz, 1H), 3.94 (s, 3H), 3.37 (dd, *J* = 18.2, 3.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.6, 197.9, 166.2, 143.7, 140.1, 139.7, 136.2, 133.8, 133.4, 129.8, 128.7, 128.6, 128.2, 122.1, 109.9, 52.4, 42.8, 39.3; **FTIR** (KBr thin film) ν_{max} (cm^{-1}): 1725, 1682, 1447, 1279, 1223, 1183, 1109, 877, 745, 704, 692, 663, 600; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{22}H_{18}O_5$ 362.1154; found: 362.1158. HPLC analysis: Chiralpak IC 2.1×150mm column, 35% *i*PrOH in hexanes, 30 deg, 0.3 mL/min Major 5.2 min, minor 4.3 min (65% *ee*).

$[\alpha]_D^{21}$ = -133 (*c* = 1.0, CH_2Cl_2)

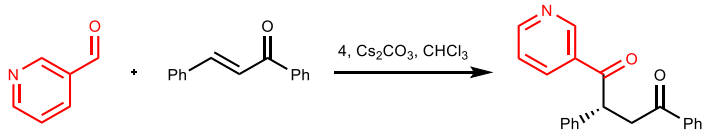
Methyl (*R*)-4-(4-(furan-2-yl)-4-oxo-2-phenylbutanoyl)benzoate (15)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (24 mg, 0.08 mmol, 0.5 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-1-(furan-2-yl)-3-phenylprop-2-en-1-one (30 mg, 0.15 mmol, 1.0 equiv.) and methyl 4-formylbenzoate (30 mg, 0.18 mmol, 1.2 equiv.) were added. CH_3Cl (830 µl) and water (0.54 µL, 0.03 mmol, 0.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (14 mg, 0.015 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Dimethyl terephthalate (7.3 mg, 0.041 mmol, 0.25 equiv.) was added to the crude product as an internal standard. 81% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (20% EtOAc in hexanes) to afford **15** (44 mg, 81%) as a white solid. **m.p.** (°C): 99-101; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05-8.02 (m, 4H), 7.57 (d, *J* = 0.9 Hz, 1H), 7.32-7.29 (m, 4H), 7.24-7.20 (m, 2H), 6.52 (dd, *J* = 3.5, 1.6 Hz, 1H), 5.27 (dd, *J* = 10.0, 4.1, 1H), 4.05 (dd, *J* = 17.9, 10 Hz, 1H), 3.90 (s, 3H), 3.20 (dd, *J* = 17.8, 4.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.4, 187.0, 166.2, 152.3, 146.5, 139.8, 137.8, 133.6, 129.7, 129.3, 128.8, 128.2, 127.6, 117.4, 112.3, 52.4, 48.8, 43.2; **FTIR** (thin film in CH_2Cl_2) ν_{max} (cm^{-1}): 3423, 1724, 1675, 1570, 1495, 1469, 1436, 1396, 1282, 1235, 1182, 1109, 1033, 1018, 948; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{22}H_{18}O_5$ 362.1154; found: 362.1151. HPLC: Chiralpak IC 2.1×150 mm column, 35% *i*PrOH in hexanes, 0.3 ml/min Major peak at 14.7 min, minor 7.0 min, (86% *ee*).

$[\alpha]_D^{21}$ = -150 (*c* = 1.0, CH_2Cl_2)

(R)-2,4-diphenyl-1-(pyridin-3-yl)butane-1,4-dione(16)

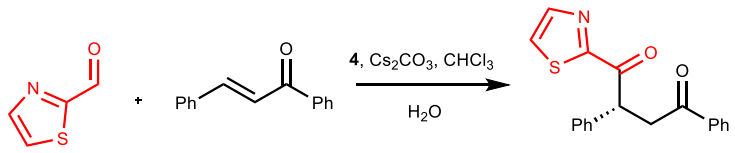


A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (46 mg, 0.14 mmol, 0.7 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, *trans*-Chalcone (42 mg, 0.2 mmol, 1.0 equiv.) was added. CH_3Cl (1.13 ml) and Pyridine-2-carboxaldehyde (23 µL, 0.24 mmol, 1.2 equiv.) was transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (18 mg, 0.04 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a plug of cotton and was concentrated. Trichloroethene (18

µL, 0.2 mmol, 1 equiv.) was added to the crude product as an internal standard. More than 99% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (33% EtOAc in hexanes) to afford **16** (33 mg, 52%) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.71 (d, *J* = 3.75 Hz, 1H), 8.27 (ddd app. td, *J* = 8.0, 2.0 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 8.0, 2H), 7.38-7.33 (m, 5H), 7.28-7.24 (m, 1H), 5.26 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.24 (dd, *J* = 18.1, 10.4 Hz, 1H), 3.35 (dd, *J* = 18.2, 3.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.9, 197.9, 153.1, 150.3, 137.6, 136.3, 136.2, 133.4, 132.8, 131.9, 129.9, 129.4, 128.7, 128.3, 128.3, 128.2, 127.9, 127.8, 123.6, 49.2, 43.8; **FTIR** (thin film in CH_2Cl_2) ν_{max} (cm^{-1}): 3029, 1679, 1598, 1581, 1388, 1234, 1204, 1149, 1061, 992, 876, 689, 566; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{21}H_{17}NO_2$ 315.1259; found: 315.1254. HPLC: Chiralpak IA 2.1×150 mm column, 35% *i*PrOH in hexanes, 0.2 ml/min Major peak at 7.4 min, minor 6.6 min, (75% *ee*).

$[\alpha]_D^{21}$ = -139 (c=1.0, CH_2Cl_2)

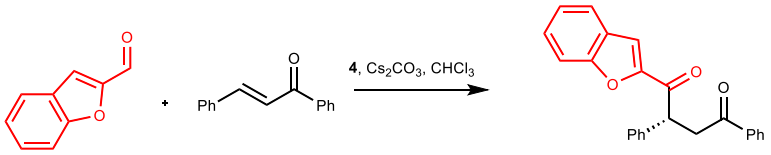
(R)-2,4-diphenyl-1-(thiazol-2-yl)butane-1,4-dione(17)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (46 mg, 0.14 mmol, 0.7 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, *trans*-Chalcone (42 mg, 0.2 mmol, 1.0 equiv.) was added. CH_3Cl (1.13 ml) and 2-thiazolecarboxaldehyde (21 µL, 0.24 mmol, 1.2 equiv.) and water (0.36 µL, 0.02 mmol, 0.1 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (18 mg, 0.04 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a plug of cotton and was concentrated. Trichloroethene (18 µL, 0.2 mmol, 1 equiv.) was added to the crude product as an internal standard. More than 99% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (25% EtOAc in hexanes) to afford **17** (61 mg, 95%) as an orange solid. **m.p.** (°C): 125-128; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 3.3 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 3.0 Hz, 1H), 7.56 (t, *J* = 13.7 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 15.5, 2H), 7.33 (dd, app. t, *J* = 15.5, 2H), 7.25 (t, *J* = 7.4, 1H), 5.71 (dd, *J* = 12.0, 3.4 Hz, 1H), 4.23 (dd, *J* = 20.2, 11.1 Hz, 1H), 3.49 (dd, *J* = 18.2, 3.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.7, 192.3, 166.4, 145.0, 137.3, 136.2, 133.4, 129.6, 129.0, 128.8, 128.6, 128.5, 128.3, 128.2, 127.7, 127.6, 126.3, 48.0, 43.4; **FTIR** (thin film in CH_2Cl_2) ν_{max} (cm^{-1}): 3028, 1681, 1597, 1584, 1335, 1234, 1203, 1076, 1025, 997, 951, 747, 668; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_{15}NO_2S$ 321.0823; found: 321.0819. HPLC: Chiralpak IA 2.1×150 mm column, 20% *i*PrOH in hexanes, 0.2 ml/min Major peak at 7.3 min, minor 5.9 min, (49% *ee*).

$[\alpha]_D^{21}$ = -106 (c=1.0, CH_2Cl_2)

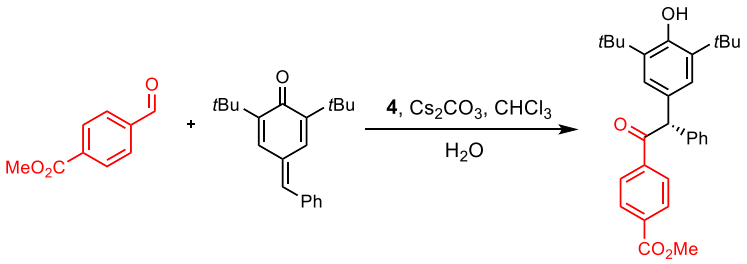
(R)-1-(benzofuran-2-yl)-2,4-diphenylbutane-1,4-dione (18)



A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (32 mg, 0.01 mmol, 0.5 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, *trans*-Chalcone (42 mg, 0.2 mmol, 1.0 equiv.) was added. CH_3Cl (1.3 ml) and 2-Benzofurancarboxaldehyde (29 µL, 0.24 mmol, 1.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (18 mg, 0.02 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a plug of silica and was concentrated. Trichloroethene (36 µL, 0.2 mmol, 1 equiv.) was added to the crude product as an internal standard. More than 99% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (10% EtOAc in hexanes) to afford **18** (63 mg, 89%) as an orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.59-7.55 (m, 3H), 7.47-7.42 (m, 5H), 7.34 (dd app. t, *J* = 7.34 Hz, 2H), 7.29-7.24 (m, 2H), 5.27 (dd, *J* = 14.0, 6.6 Hz, 1H), 4.24 (dd, *J* = 18.1, 10.3 Hz, 1H), 3.40 (dd, *J* = 18.2, 3.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.8, 189.7, 155.7, 152.1, 137.9, 136.3, 133.4, 129.2, 128.6, 128.4, 128.2, 128.2, 127.6, 127.2, 123.8, 123.3, 114.0, 112.5, 49.1, 43.0; **FTIR** (thin film in CH_2Cl_2) ν_{max} (cm^{-1}): 3062, 2923, 2362, 1689, 1611, 1555, 1493, 1448, 1398, 1332, 1243, 1202, 1156, 1002, 907, 886, 752, 689; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{24}H_{18}O_3$ 354.1256; found: 354.1263. HPLC: Chiralpak IC 2.1×150 mm column, 20% *i*PrOH in hexanes, 0.4 ml/min Major peak at 4.2 min, minor 6.1 min, (70% *ee*).

$[\alpha]_D^{21}$ = -431 (c=1.1, CH_2Cl_2)

Methyl 4-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylacetyl)benzoate (19)



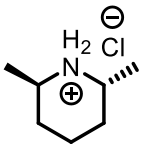
A dried Schlenk tube was charged with pre-dried Cs_2CO_3 (24 mg, 0.075 mmol, 0.5 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (44 mg, 0.15 mmol, 1.0 equiv.) and 4-formylbenzoate (30 mg, 0.18 mmol, 1.2 equiv.) were added. CH_3Cl (830 µl) and water (0.54 µL, 0.03 mmol, 0.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (14 mg, 0.015 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. The crude product was purified using flash column chromatography (5% EtOAc in hexanes) to afford **19** (43 mg, 86%) as a yellow solid. **m.p.** (°C): 186–188; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10-8.05 (m, 4H), 7.37-7.26 (m, 5H), 7.08 (s, 2H),

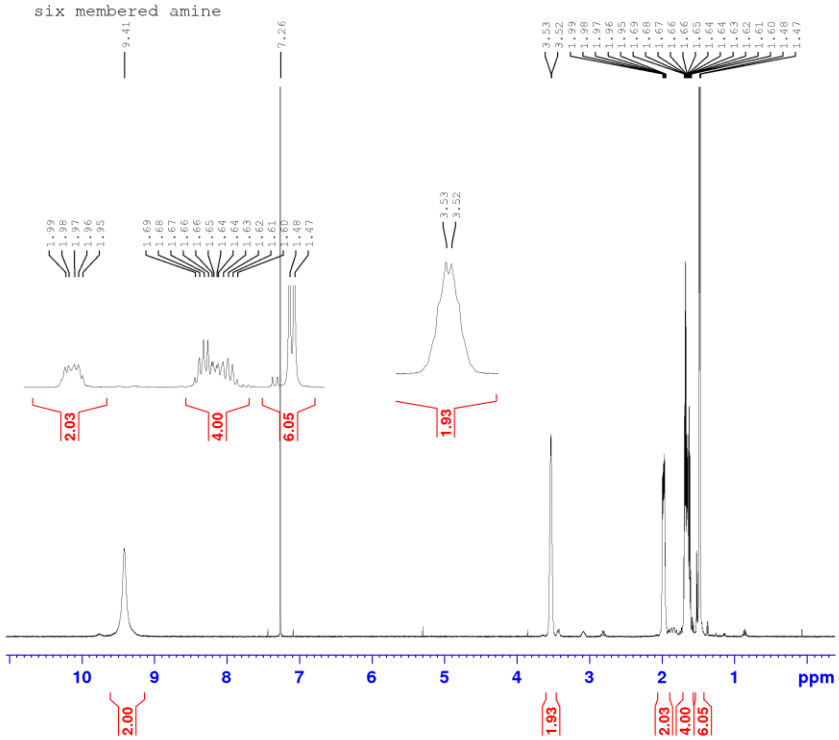
5.96 (s, 1H), 5.18 (s, 1H), 3.95 (s, 3H), 1.41 (s, 18H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.4, 166.2, 153.0, 140.5, 139.2, 136.0, 133.5, 129.8, 129.1, 128.9, 128.8, 128.7, 127.1, 125.8, 59.8, 52.4, 34.4, 30.3; **FTIR** (thin film in dichloromethane) ν_{max} (cm^{-1}): 3442, 2955, 1725, 1688, 1436, 1404, 1362, 1280, 1236, 1202, 1108, 875, 812; **HRMS (**FD-TOF) m/z: $[M]^+$ Calcd for $C_{30}H_{34}O_4$ 458.2457; found: 458.2465. **HPLC**: Chiralpak IC 2.1×150 mm column, 15% *i*PrOH in hexanes, 0.2 ml/min Major peak at 13.4 min, minor 11.4 min. (76% *ee*).
$[\alpha]_D^{21}$ = -4 (*c* = 1.0, CH_2Cl_2).

(*R*)-1-(Furan-2-yl)-2,4-diphenylbutane-1,4-dione (1 mmol scale)

A dried Schlenk flask was charged with pre-dried Cs_2CO_3 (98 mg, 0.3 mmol, 0.3 equiv.) under argon. The base was dried further using heat gun for 5 min and subsequently, (E)-chalcone (209 mg, 1 mmol, 1.0 equiv.) was added. Dried CH_3Cl (6.5 ml) and freshly distilled furan-2-carbaldehyde (100 µL, 1.2 mmol, 1.2 equiv.) and distilled water (3.6 µL, 0.2 mmol, 0.2 equiv.) were transferred to the tube. The mixture was cooled down to 0 °C and to that, **4** was added (91 mg, 0.1 mmol, 10 mol %) and the tube was sealed and stirred for 5 h at 0 °C. The mixture was passed through a silica plug and was concentrated. Trichloroethylene (180 µL, 1 mmol, 1 equiv.) was added to the crude product as an internal standard. 99% conversion was observed according to ^{1}H NMR. The crude product was purified using flash column chromatography (15% EtOAc in hexanes) to afford **13** (252 mg, 83%) as a white solid. The ^{1}H NMR spectrum matched the one previously reported. (89% *ee*).

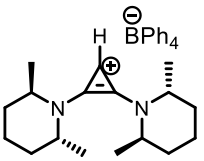
^{1}H NMR spectrum for (2*R*,6*R*)-2,6-dimethylpiperidin-1-ium chloride



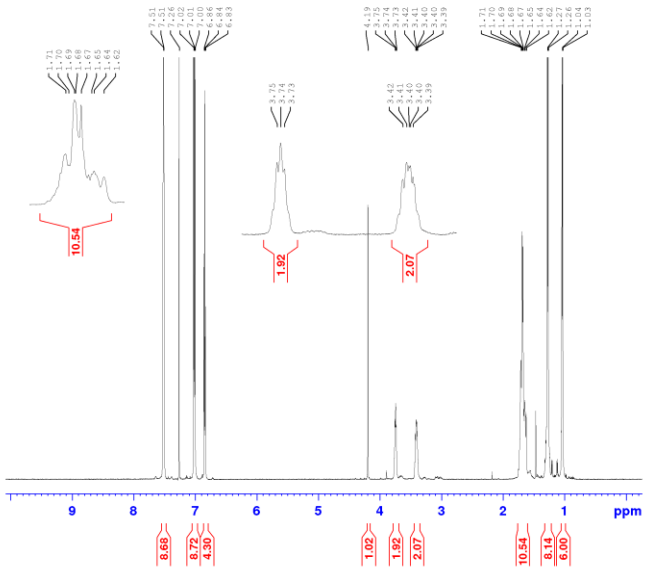



```
Current Data Parameters
NAME      six membered amine
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_              20190225
Time                 14.14 h
INSTRUM                spect
PROBHD    Z847801_0323 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                8417.509 Hz
FIDRES             0.256882 Hz
AQ                 3.8928385 sec
RG                    195.93
DW                   59.400 usec
DE                    6.50 usec
TE                   298.0 K
D1                1.10000002 sec
TD0                       1
SFO1           600.1736010 MHz
NUC1                     1H
P1                    12.50 usec
PLW1           15.00000000 W

F2 - Processing parameters
SI                    65536
SF             600.1700137 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

^{1}H NMR and ^{13}C NMR spectra for compound 2

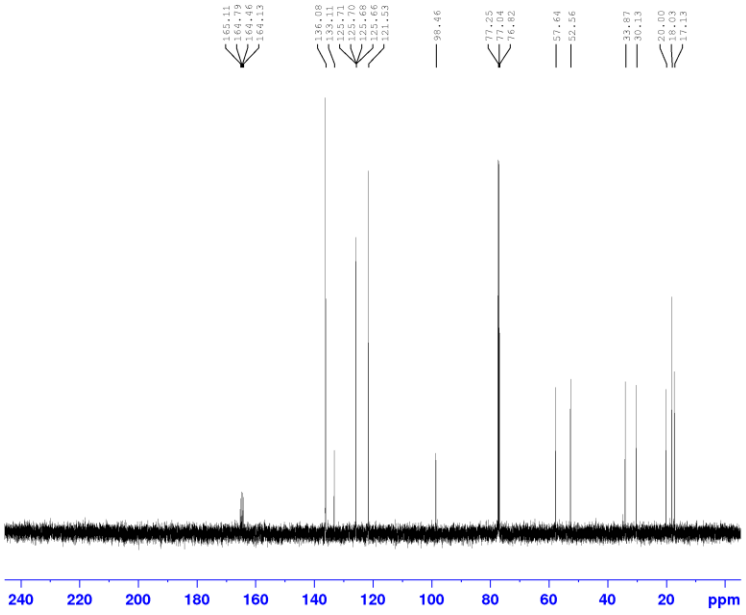


six membered



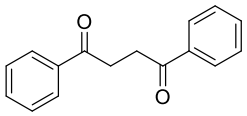

```
Current Data Parameters
NAME        six membered
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180917
Time               15.49 h
INSTRUM             spect
PROBHD    Z847801_0323 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8417.509 Hz
FIDRES          0.256882 Hz
AQ              3.8928385 sec
RG                 195.93
DW                59.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.10000002 sec
TD0                    1
SFO1          600.1736010 MHz
NUC1                  1H
P1                12.50 usec
PLW1          15.00000000 W

F2 - Processing parameters
SI                 65536
SF          600.1700139 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

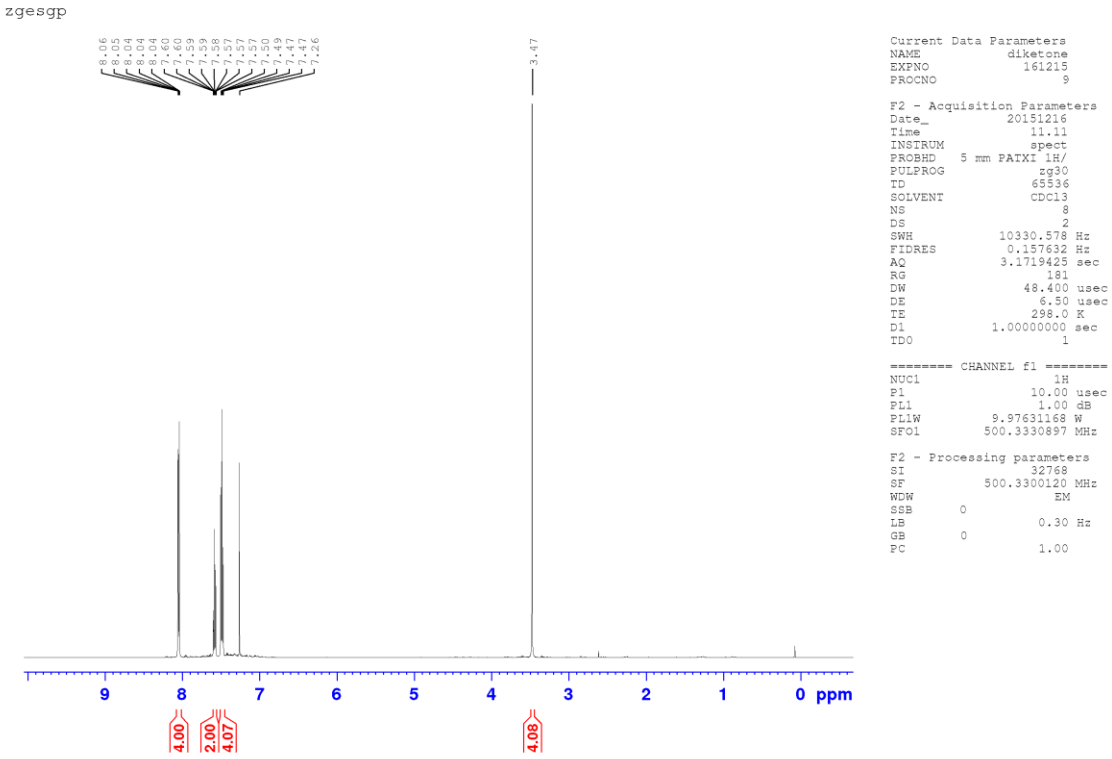
six membered




```
Current Data Parameters
NAME        six membered
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180917
Time               16.07 h
INSTRUM             spect
PROBHD    Z847801_0323 (
PULPROG             udeft
TD                 65536
SOLVENT            CDCl3
NS                   100
DS                     4
SWH            37878.789 Hz
FIDRES          1.155969 Hz
AQ              0.8650752 sec
RG                 195.93
DW                13.200 usec
DE                 6.50 usec
TE                298.0 K
D1             3.20000005 sec
D12            0.00002000 sec
D20          200.00000000 sec
TD0                    1
SFO1          150.9309761 MHz
NUC1                  13C
P1                10.50 usec
P13             2000.00 usec
P26              500.00 usec
PLW1          40.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5           6.73799992 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8   0 Hz
SPW8           6.73799992 W
SFO2          600.1724007 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             70.00 usec
PLW2          15.00000000 W
PLW12          0.47832000 W

F2 - Processing parameters
SI                 65536
SF          150.9128665 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

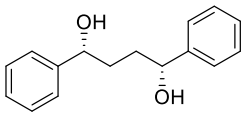
^{1}H NMR spectrum for 1,4-diphenylbutane-1,4-dione

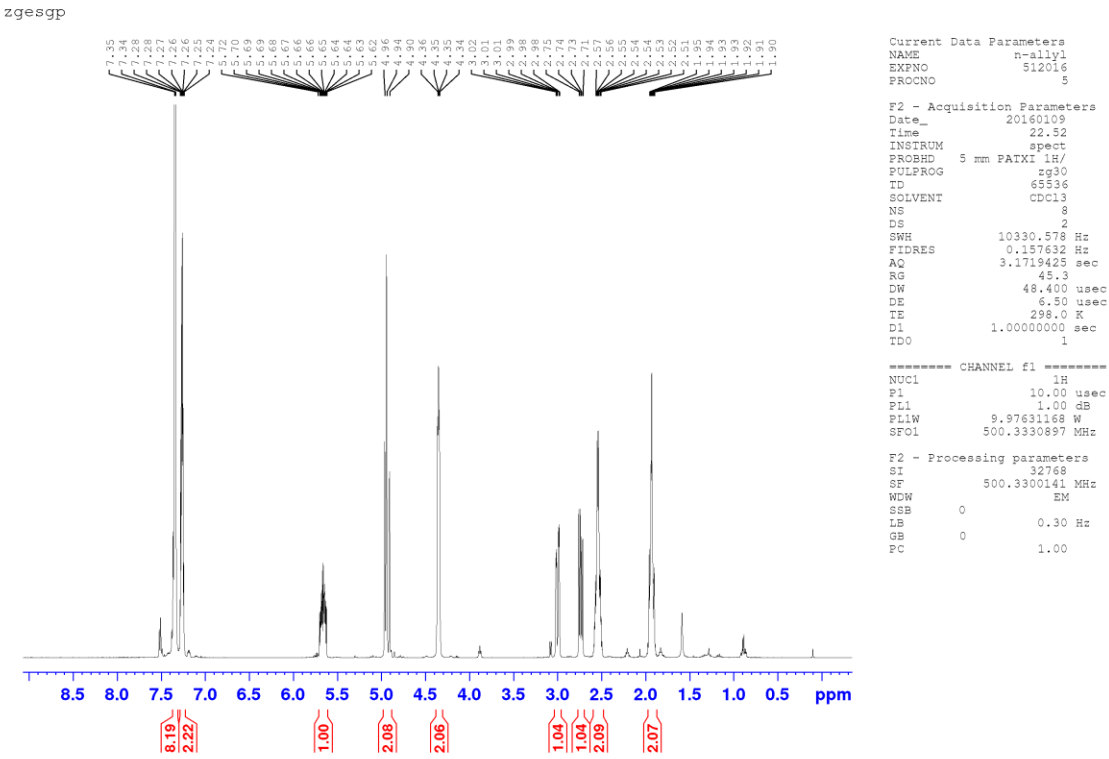




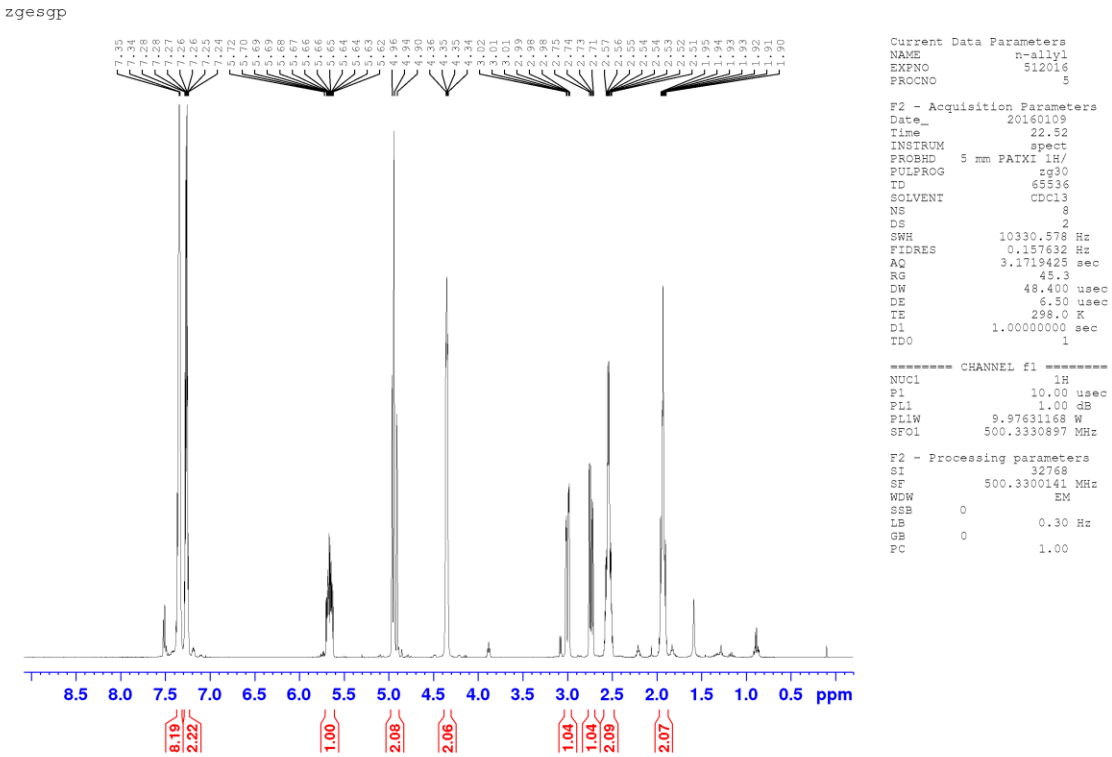

```
Current Data Parameters
NAME                  diketone
EXPNO                   161215
PROCNO                       9

F2 - Acquisition Parameters
Date_               20151216
Time                    11.11
INSTRUM                 spect
PROBHD    5 mm PATXI 1H/
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                10330.578 Hz
FIDRES              0.157632 Hz
AQ                  3.1719425 sec
RG                       181
DW                    48.400 usec
DE                     6.50 usec
TE                    298.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.00 usec
PL1                     1.00 dB
PL1W               9.97631168 W
SFO1             500.3330897 MHz

F2 - Processing parameters
SI                       32768
SF                500.3300120 MHz
WDW                         EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

^{1}H NMR spectrum for (1*R*,4*R*)-1,4-diphenylbutane-1,4-diol

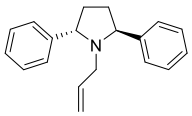




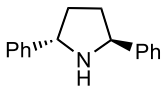
[1]Hspectrum for (2*S*,5*S*)-1-allyl-2,5-diphenylpyrrolidine

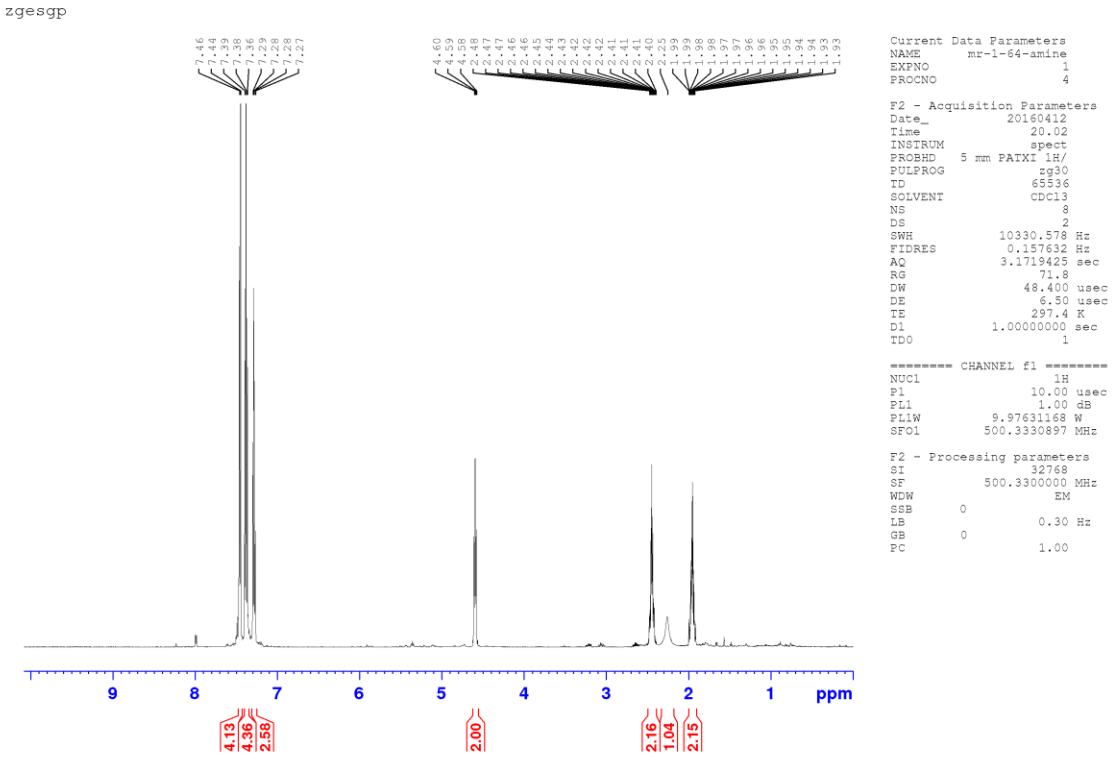



```
Current Data Parameters
NAME                  n-allyl
EXPNO                  512016
PROCNO                      5

F2 - Acquisition Parameters
Date_                20160109
Time                    22.52
INSTRUM                 spect
PROBHD    5 mm PATXI 1H/
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719425 sec
RG                      45.3
DW                    48.400 usec
DE                     6.50 usec
TE                    298.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.00 usec
PL1                     1.00 dB
PL1W              9.97631168 W
SFO1            500.3330897 MHz

F2 - Processing parameters
SI                       32768
SF                500.3300141 MHz
WDW                         EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

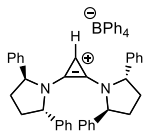


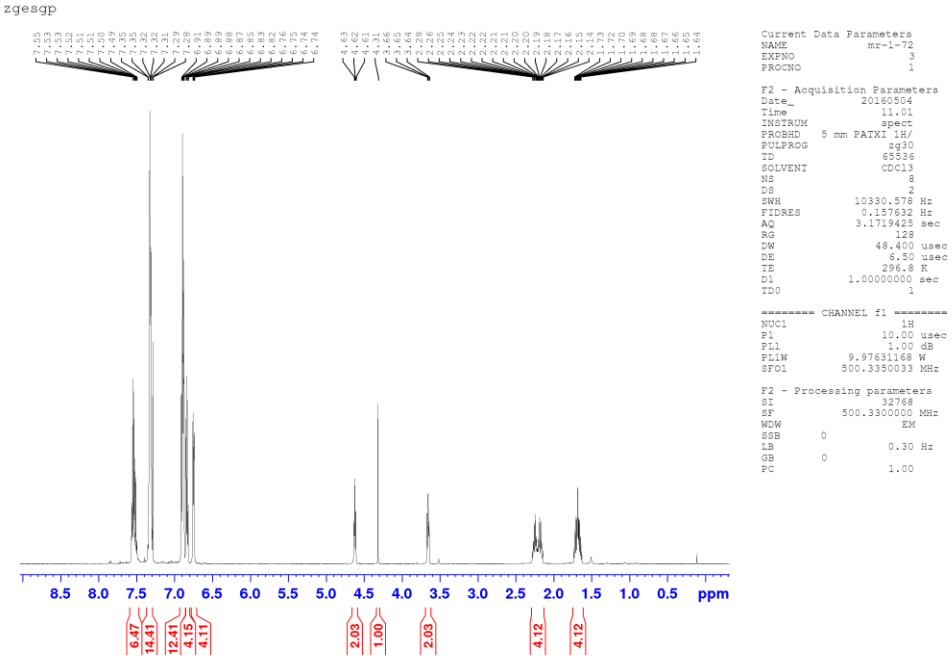
^{1}H NMR spectrum for (2*S*,5*S*)-2,5-diphenylpyrrolidine



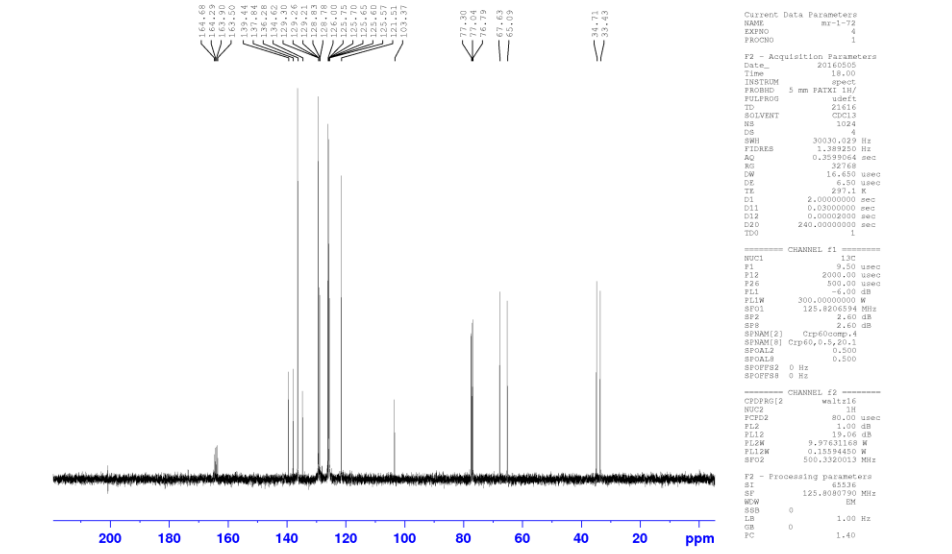


^{1}H NMR and ^{13}C NMR spectra for compound 3



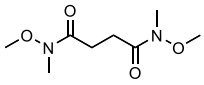


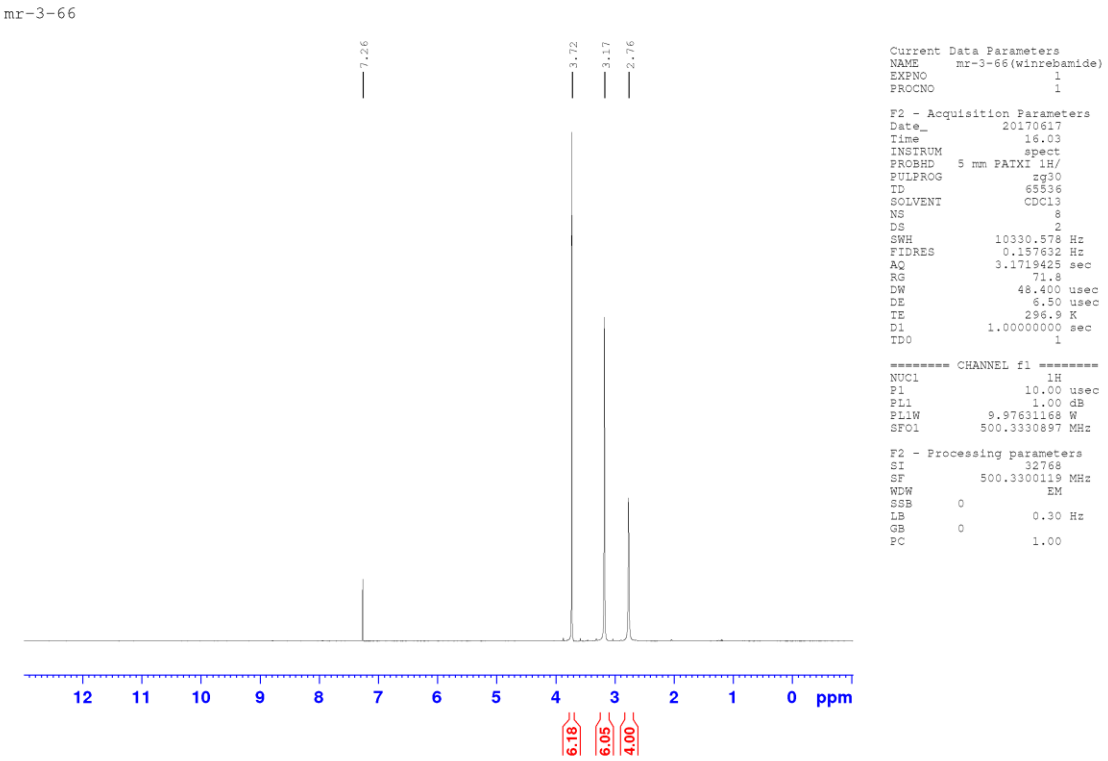

```
Current Data Parameters
NAME                  mr-1-72
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_               20160504
Time                   11.01
INSTRUM                spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719425 sec
RG                      128
DW                   48.400 usec
DE                    6.50 usec
TE                   296.8 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.00 usec
PL1                   1.00 dB
PL1W            9.97631168 W
SFO1          500.3350033 MHz

F2 - Processing parameters
SI                    32768
SF              500.3300000 MHz
WDW                      EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```




```
Current Data Parameters
NAME                  mr-1-72
EXPNO                       4
PROCNO                      1

F2 - Acquisition Parameters
Date_               20160505
Time                   18.00
INSTRUM                spect
PROBHD   5 mm PATXI 1H/
PULPROG             udeft
TD                    21616
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               30030.029 Hz
FIDRES             1.389250 Hz
AQ                 0.3599064 sec
RG                    32768
DW                   16.650 usec
DE                    6.50 usec
TE                   297.1 K
D1              2.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D20           240.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
P12                2000.00 usec
P26                 500.00 usec
PL1                  -6.00 dB
PL1W          300.00000000 W
SFO1          125.8206594 MHz
SP2                   2.60 dB
SP8                   2.60 dB
SPNAM[2]    Crp60comp.4
SPNAM[8] Crp60,0.5,20.1
SPOAL2                0.500
SPOAL8                0.500
SPOFFS2  0 Hz
SPOFFS8  0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   1.00 dB
PL12                 19.06 dB
PL2W           9.97631168 W
PL12W          0.13894450 W
SFO2          500.3320013 MHz

F2 - Processing parameters
SI                    65536
SF              125.8080790 MHz
WDW                      EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```

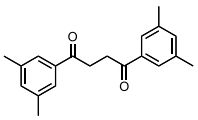
^{1}H NMR spectrum for N^{1},N^{4}-dimethoxy-N^{1},N^{4}-dimethylsuccinamide

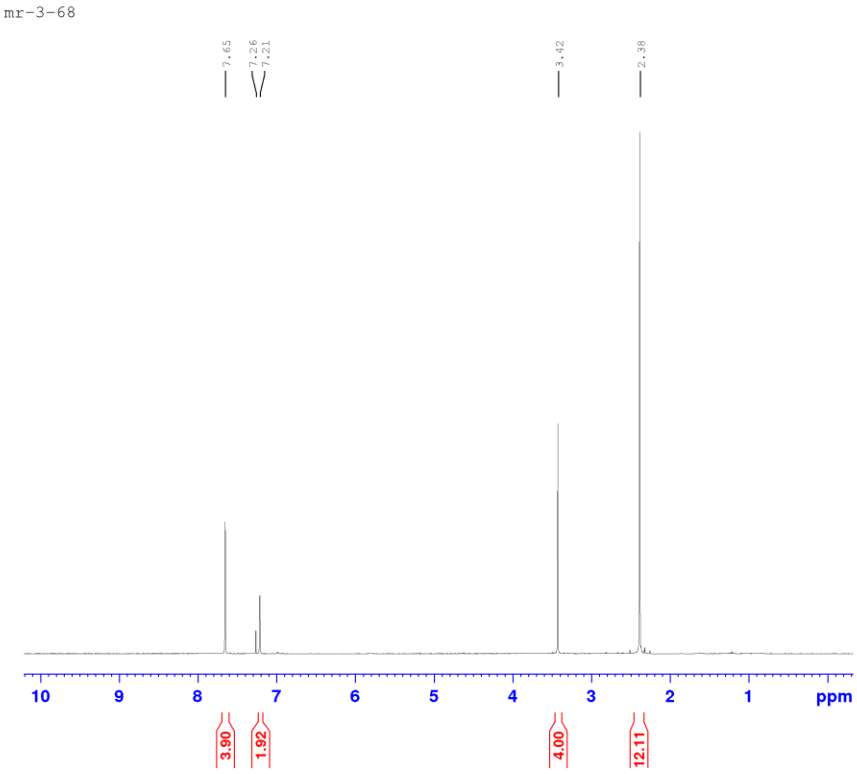





```
Current Data Parameters
NAME      mr-3-66(winrebamide)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170617
Time              16.03
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                 71.8
DW               48.400 usec
DE                6.50 usec
TE               296.9 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.00 usec
PL1                1.00 dB
PL1W         9.97631168 W
SFO1        500.3330897 MHz

F2 - Processing parameters
SI                32768
SF           500.3300119 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

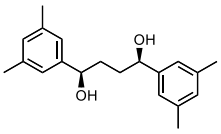
^{1}H NMR spectrum for 1,4-bis(3,5-dimethylphenyl)butane-1,4-dione

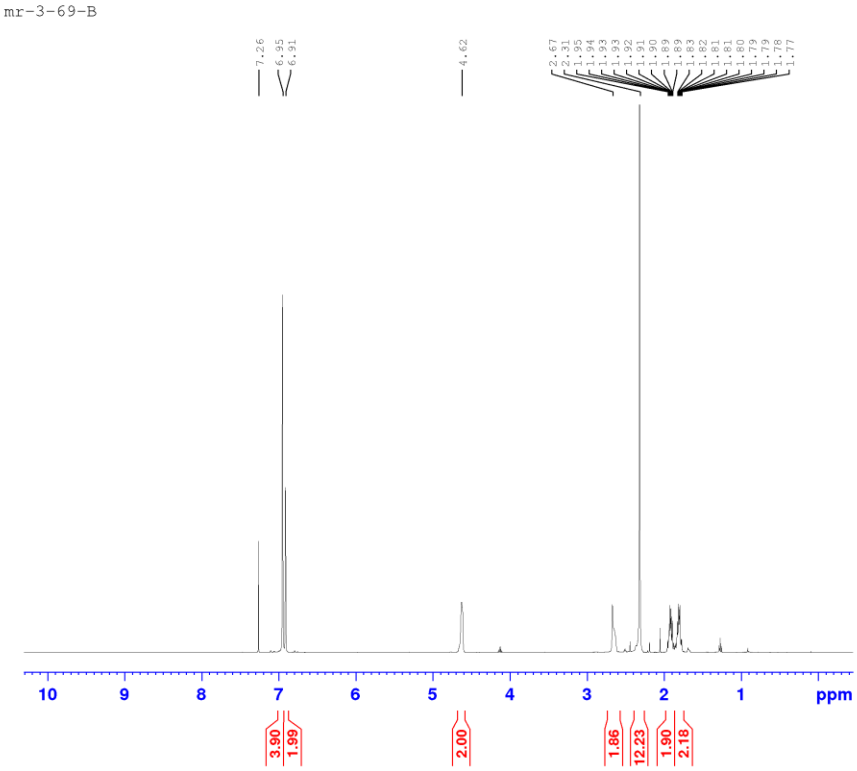





```
Current Data Parameters
NAME      mr-3-68(diketone)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170620
Time                 11.15
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719425 sec
RG                   71.8
DW                48.400 usec
DE                 6.50 usec
TE                297.0 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 1.00 dB
PL1W          9.97631168 W
SFO1        500.3330897 MHz

F2 - Processing parameters
SI                  32768
SF            500.3300112 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

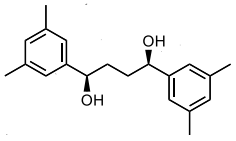
^{1}H NMR spectrum for (1*R*,4*R*)-1,4-bis(3,5-dimethylphenyl)butane-1,4-diol



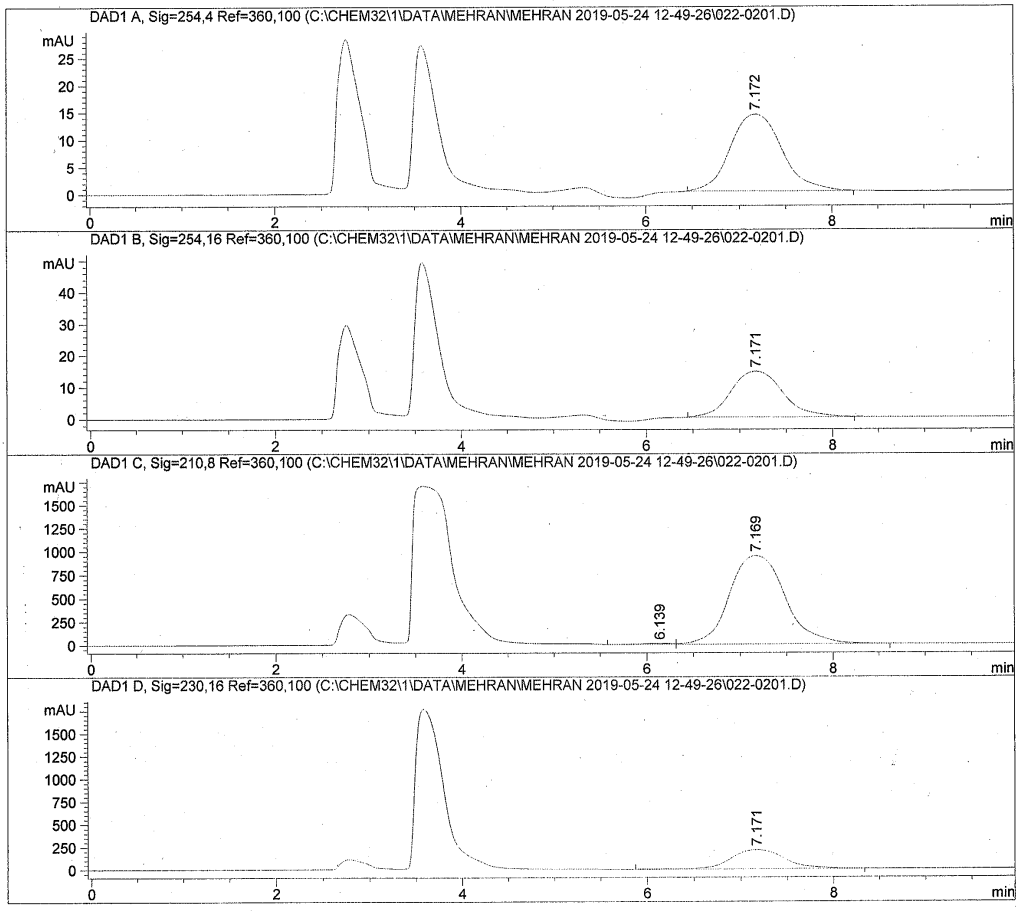



```
Current Data Parameters
NAME          mr-3-69(diol)
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170626
Time                 18.53
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719425 sec
RG                   35.9
DW                48.400 usec
DE                 6.50 usec
TE                296.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 1.00 dB
PLIW          9.97631168 W
SFO1         500.3330897 MHz

F2 - Processing parameters
SI                  32768
SF           500.3300112 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

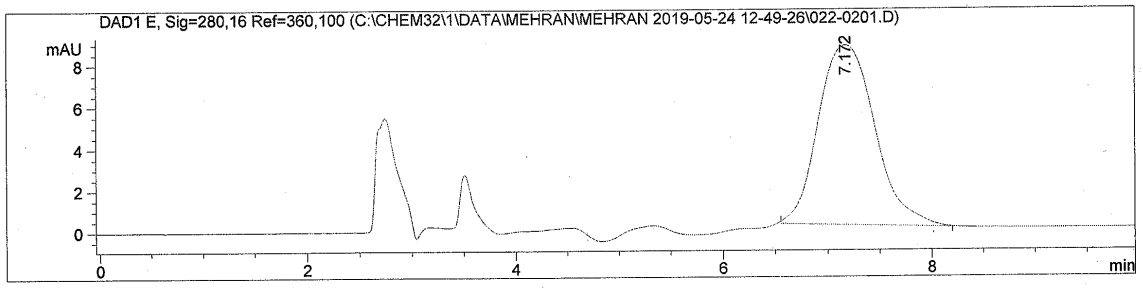
HPLC chromatogram for (1*R*,4*R*)-1,4-bis(3,5-dimethylphenyl)butane-1,4-diol




```
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\022-0201.D
Sample Name: mr-3-69

==========================================================================
Acq. Operator   : MEHRAN                          Seq. Line :   2
Acq. Instrument : Instrument 1                    Location : Vial 22
Injection Date  : 05-24-2019 1:01:43 PM                Inj :   1
                                                 Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\MEHRAN.M
Last changed    : 05-24-2019 12:49:24 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\022-0201.D\DA.M (
                  MEHRAN.M)
Last changed    : 05-24-2019 1:52:27 PM by MEHRAN
Method Info     : IC, 15% Isopropanol in hexanes  0.2 ml/min, 1 ul injection, 30 oC
```



Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\022-0201.D
Sample Name: mr-3-69



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.172	BB	0.6105	542.83990	14.05909	100.0000
Totals :				542.83990	14.05909	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.171	BB	0.6104	551.17596	14.27632	100.0000
Totals :				551.17596	14.27632	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.139	BV	0.3369	232.26187	9.64797	0.5886
2	7.169	VB	0.6611	3.92311e4	943.44958	99.4114
Totals :				3.94634e4	953.09755	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\022-0201.D
Sample Name: mr-3-69

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

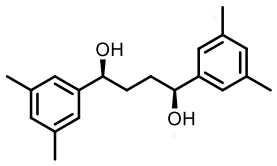
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.171	BB	0.6365	8444.18359	210.28835	100.0000
Totals :				8444.18359	210.28835	

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.172	BB	0.5950	324.89767	8.59558	100.0000
Totals :				324.89767	8.59558	

*** End of Report ***

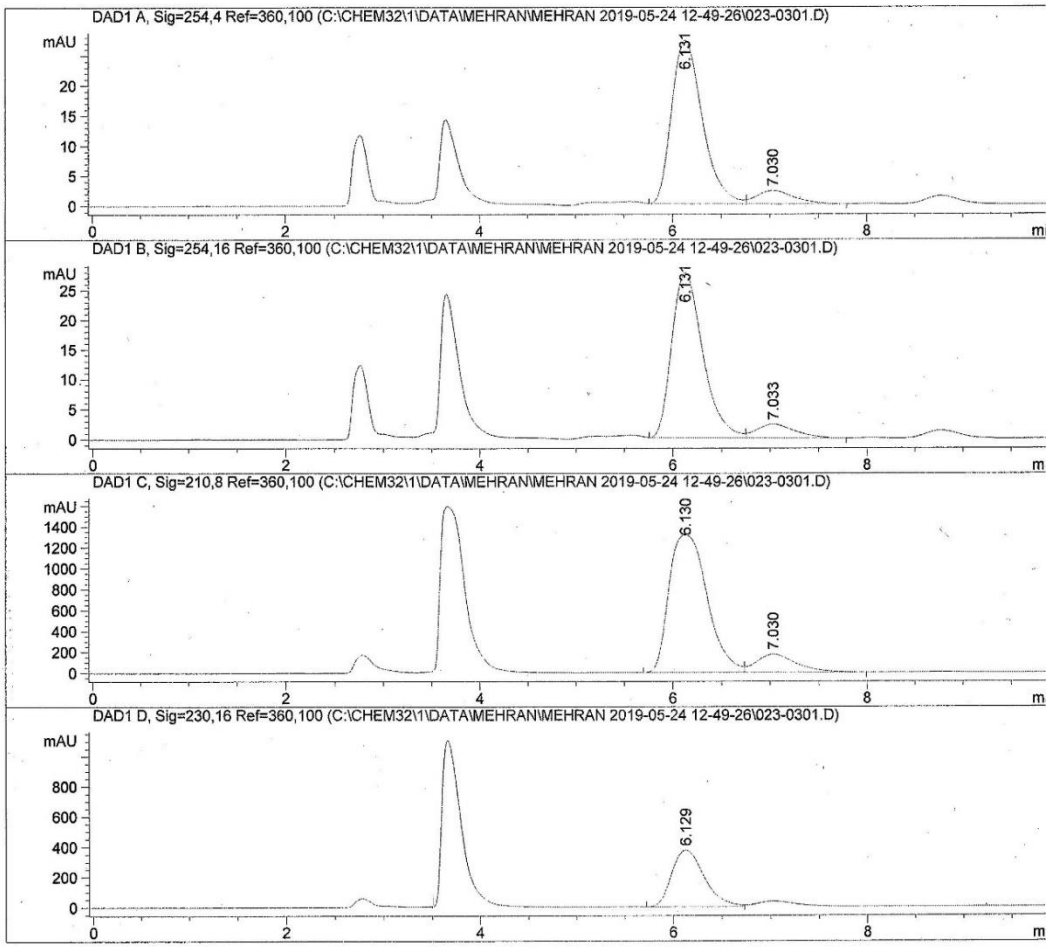
HPLC chromatogram for (1*S*,4*S*)-1,4-bis(3,5-dimethylphenyl)butane-1,4-diol



Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\023-0301.D
Sample Name: mr-4-81

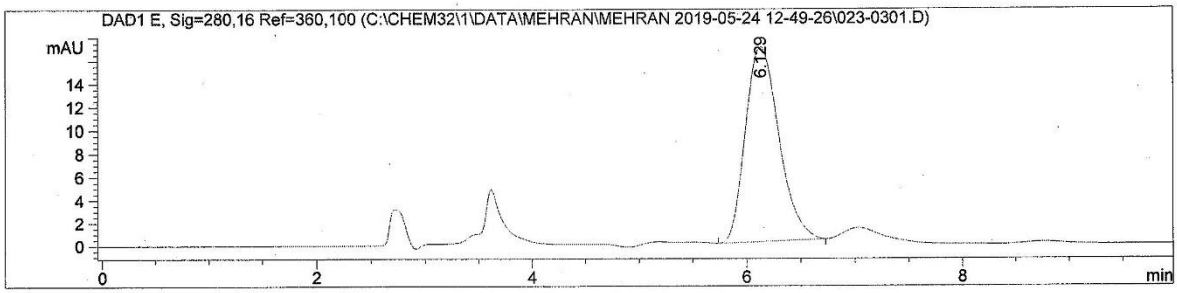
Acq. Operator	: MEHRAN	Seq. Line	: 3
Acq. Instrument	: Instrument 1	Location	: Vial 23
Injection Date	: 05-24-2019 1:12:59 PM	Inj	: 1
		Inj Volume	: 5 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 2 µl

Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\MEHRAN.M
Last changed : 05-24-2019 12:49:24 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\023-0301.D\DA.M (MEHRAN.M)
Last changed : 05-24-2019 12:49:24 PM by MEHRAN
Method Info : IC, 15% Isopropanol in hexanes 0.2 ml/min, 1 ul injection, 30 oC



Instrument 1 05-24-2019 1:57:45 PM MEHRAN Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\023-0301.D
Sample Name: mr-4-81



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.131	BB	0.3437	599.66309	27.14610	90.9261
2	7.030	BB	0.3845	59.84284	2.24872	9.0739
Totals :				659.50593	29.39482	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.131	BB	0.3435	608.35522	27.56430	90.9085
2	7.033	BB	0.3914	60.83986	2.27971	9.0915
Totals :				669.19508	29.84401	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.130	BV	0.4367	3.59362e4	1315.54602	87.9990
2	7.030	VB	0.4175	4900.83496	174.58629	12.0010
Totals :				4.08370e4	1490.13231	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2019-05-24 12-49-26\023-0301.D
Sample Name: mr-4-81

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

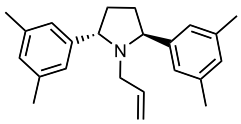
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.129	BV	0.3678	8733.14160	374.90289	100.0000
Totals :				8733.14160	374.90289	

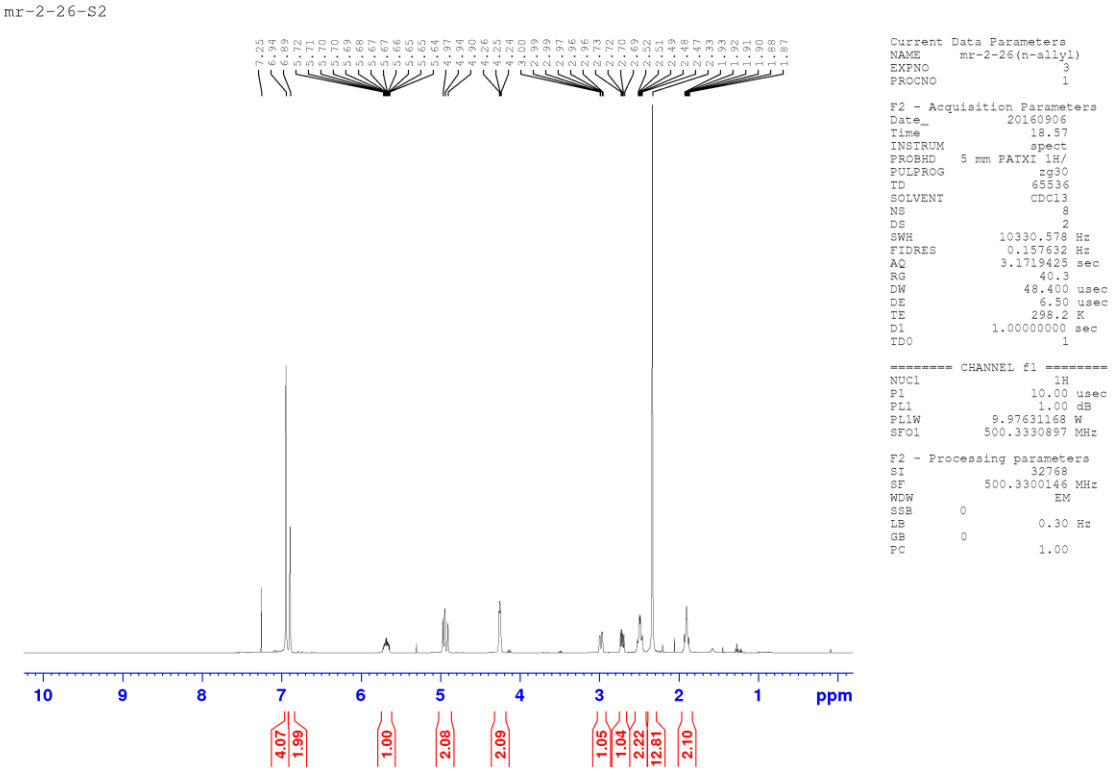
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.129	BB	0.3382	364.69043	16.86869	100.0000
Totals :				364.69043	16.86869	

*** End of Report ***

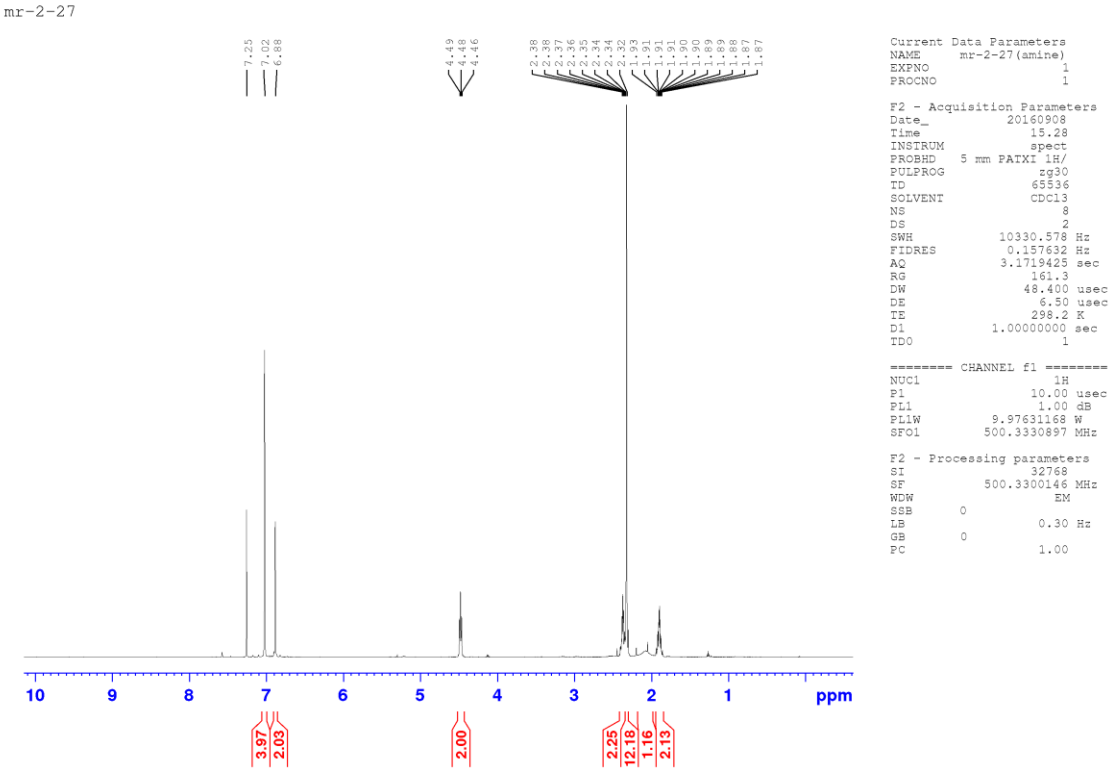
^{1}H NMR spectrum for (2*S*,5*S*)-1-allyl-2,5-bis(3,5-dimethylphenyl)pyrrolidine

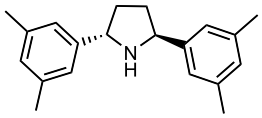




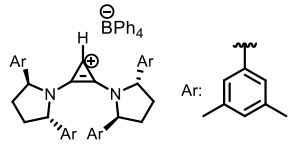

```
Current Data Parameters
NAME      mr-2-26(n-allyl)
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_              20160906
Time                 18.57
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719425 sec
RG                   40.3
DW                48.400 usec
DE                 6.50 usec
TE                298.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 1.00 dB
PL1W          9.97631168 W
SFO1         500.3330897 MHz

F2 - Processing parameters
SI                  32768
SF           500.3300146 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

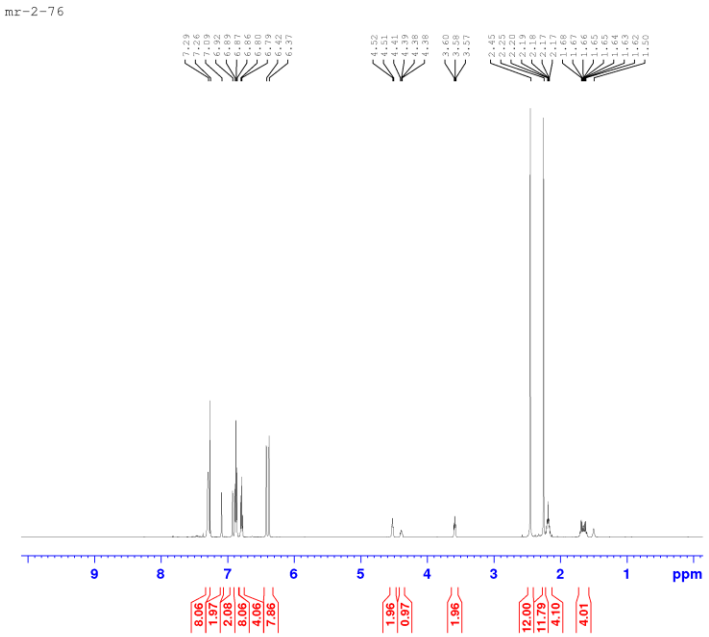
^{1}H NMR spectrum for (2*S*,5*S*)-2,5-bis(3,5-dimethylphenyl)pyrrolidine



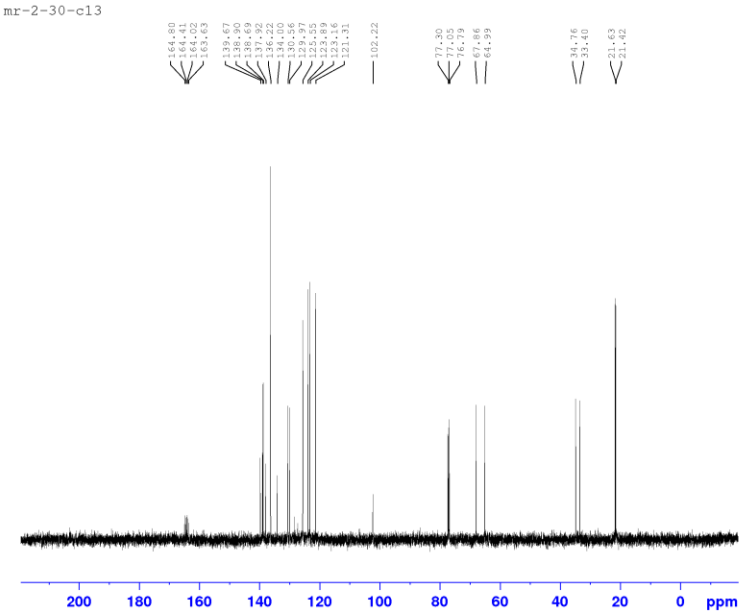


^{1}H NMR and ^{13}C NMR spectra for compound 4



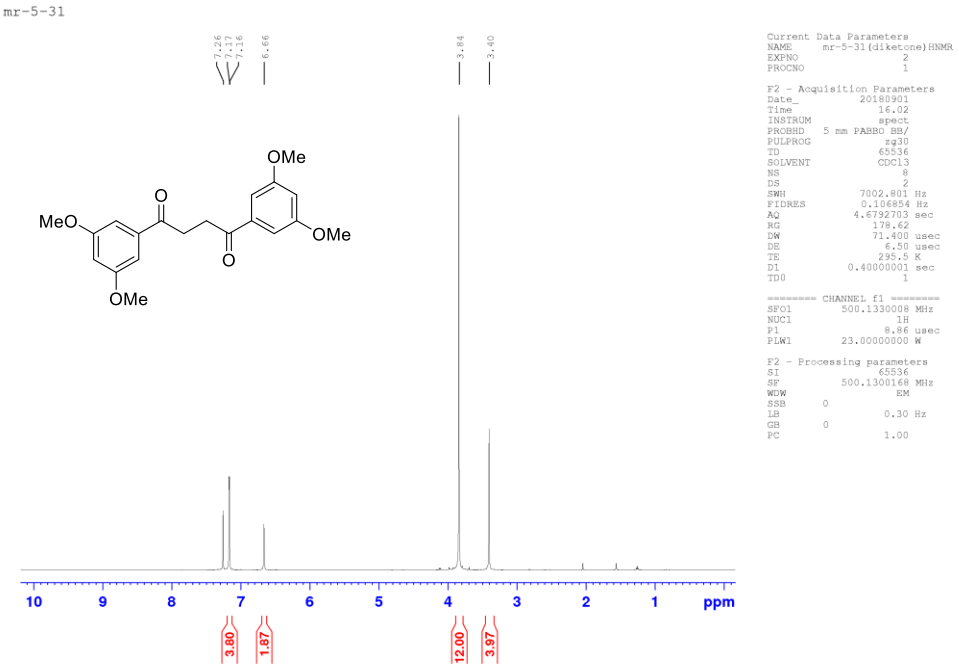


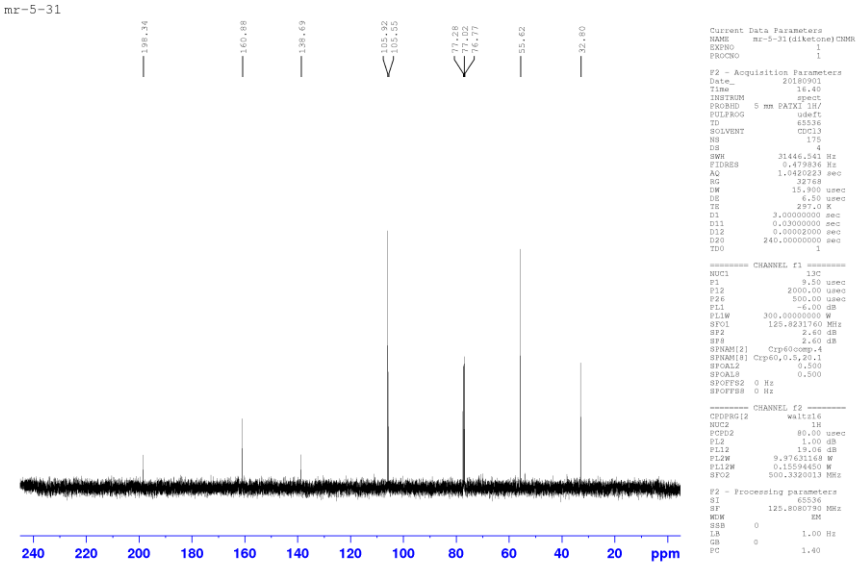

```
Current Data Parameters
NAME      mr-2-76(catalyst)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_           20161108
Time               14.57
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            10330.578 Hz
FIDRES             0.157632 Hz
AQ             3.1719425 sec
RG                   128
DW                48.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 1.00 dB
PL1W          9.97631168 W
SFO1          500.3330897 MHz

F2 - Processing parameters
SI                 32768
SF            500.3300121 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



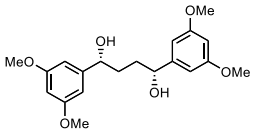

```
Current Data Parameters
NAME      mr-2-30(catalyst)
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_           20160914
Time               10.30
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG             udeft
TD                 21616
SOLVENT            CDCl3
NS                   400
DS                     4
SWH            30030.029 Hz
FIDRES             1.389250 Hz
AQ             0.3599064 sec
RG                 32768
DW                16.650 usec
DE                 6.50 usec
TE                297.8 K
D1             2.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
D20          240.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 9.50 usec
P12             2000.00 usec
P26              500.00 usec
PL1               -6.00 dB
PL1W       300.00000000 W
SFO1        125.8206594 MHz
SP2                2.60 dB
SP8                2.60 dB
SPNAM[2]    Crp60comp.4
SPNAM[8] Crp60,0.5,20.1
SPOAL2               0.500
SPOAL8               0.500
SPOFFS2  0 Hz
SPOFFS8  0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                1.00 dB
PL12              19.06 dB
PL2W          9.97631168 W
PL12W         0.15594450 W
SFO2          500.3320013 MHz

F2 - Processing parameters
SI                 65536
SF            125.8080790 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

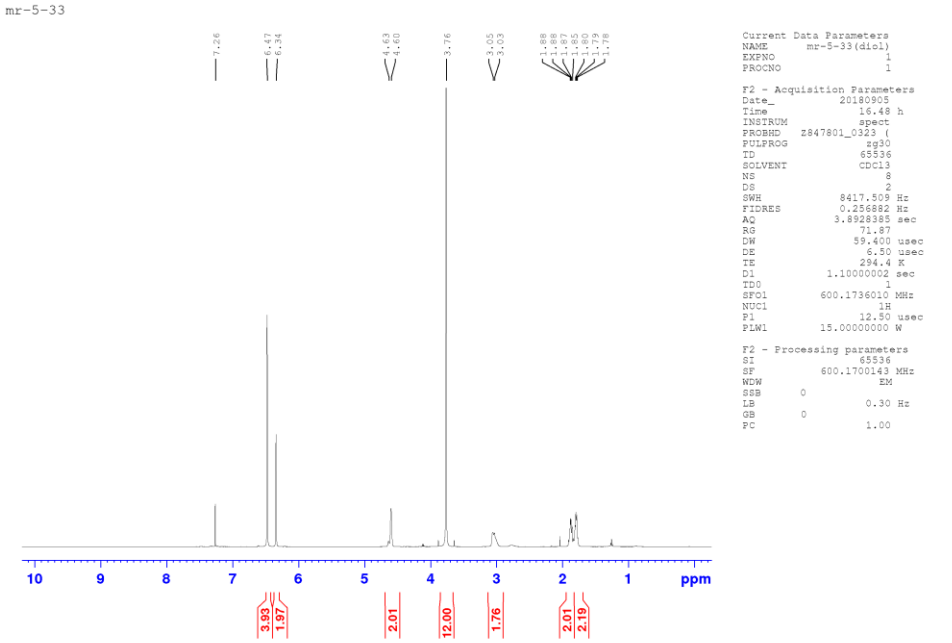
^{1}H NMR and ^{13}C NMR spectra for 1,4-bis(3,5-dimethoxyphenyl)butane-1,4-dione

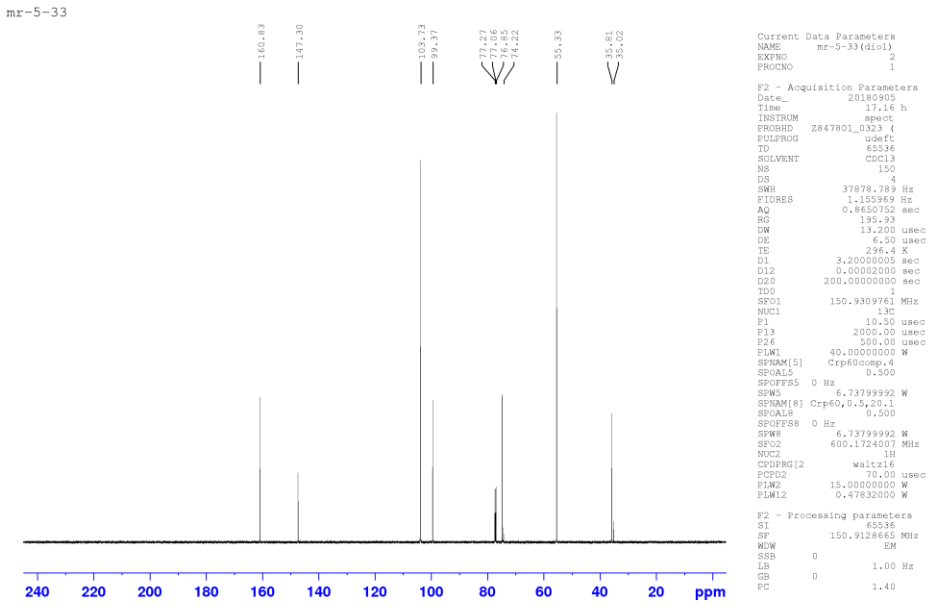




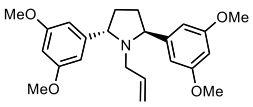
^{1}H NMR and ^{13}C NMR spectra for (1*R*,4*R*)-1,4-bis(3,5-dimethoxyphenyl)butane-1,4-diol



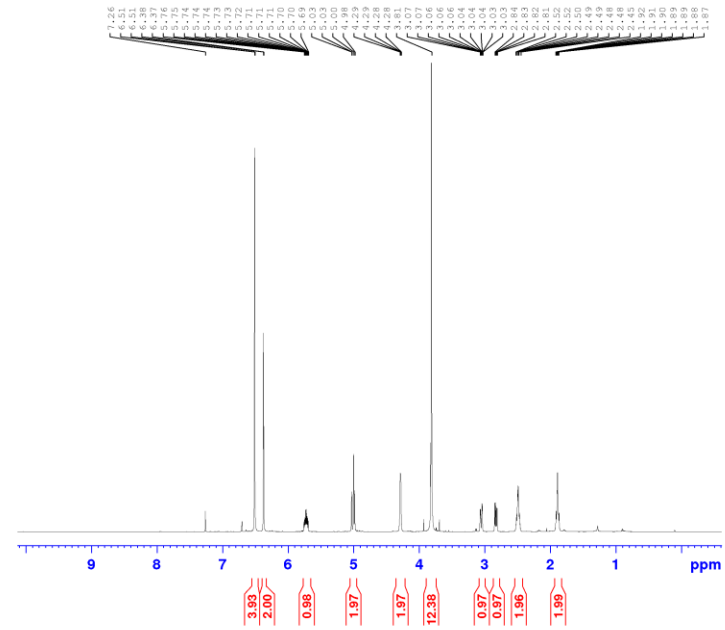




^{1}H NMR and ^{13}C NMR spectra for (2*S*,5*S*)-1-allyl-2,5-bis(3,5-dimethoxyphenyl)pyrrolidine

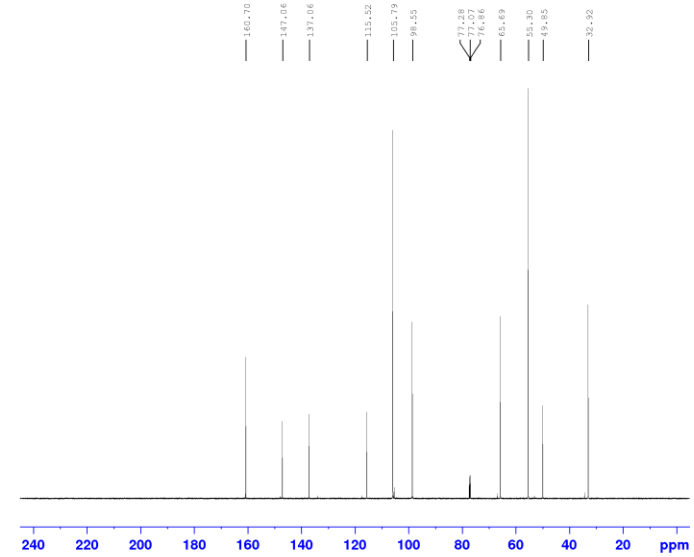


mr-5-36



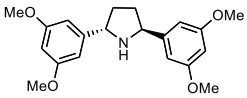

```
Current Data Parameters
NAME      mr-5-36(n-allyl)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20180911
Time              15.25 h
INSTRUM             spect
PROBHD    Z847801_0323 (
PULPROG             zg30
TD                 65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             8417.509 Hz
FIDRES          0.256882 Hz
AQ              3.8928385 sec
RG                 31.65
DW                59.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.10000002 sec
TD0                     1
SFO1         600.1736010 MHz
NUC1                   1H
P1                12.50 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1700132 MHz
WDW                    EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

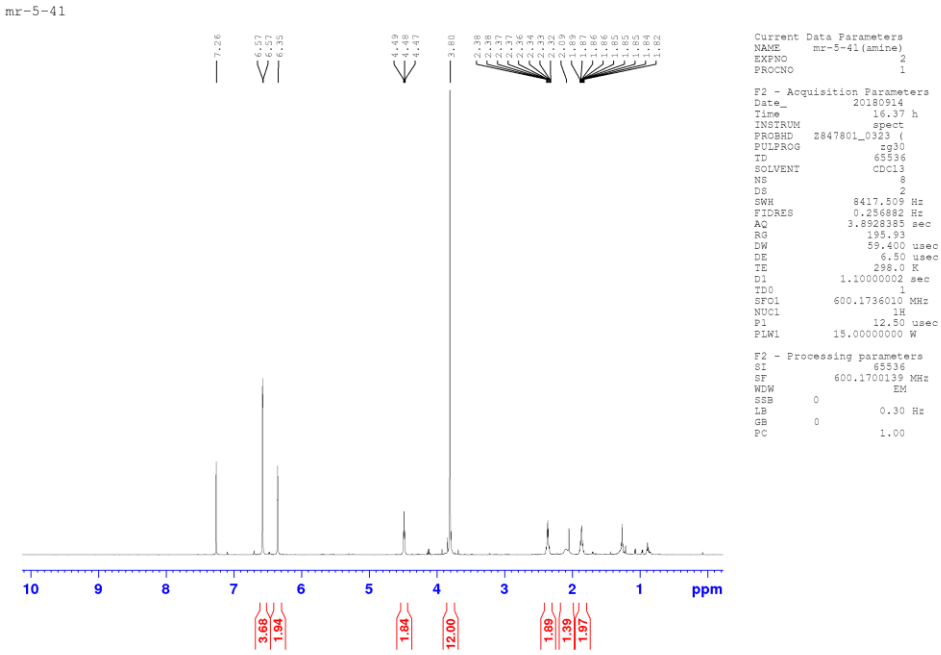
mr-5-36

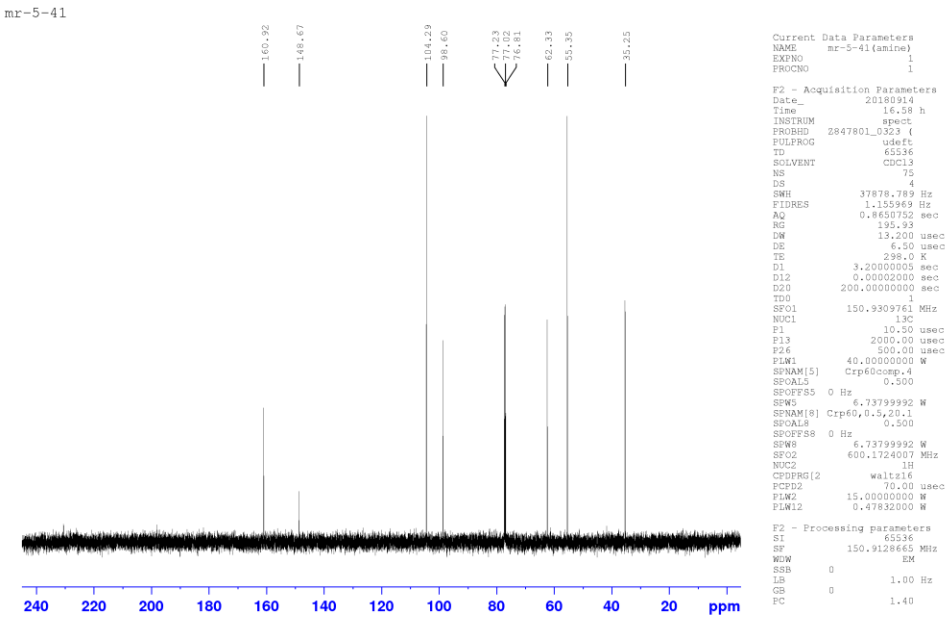



```
Current Data Parameters
NAME      mr-5-36(n-allyl)
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20180911
Time              15.48 h
INSTRUM             spect
PROBHD    Z847801_0323 (
PULPROG             udeft
TD                 65536
SOLVENT             CDCl3
NS                   100
DS                     4
SWH            37878.789 Hz
FIDRES          1.155969 Hz
AQ              0.8650752 sec
RG                 195.93
DW                13.200 usec
DE                 6.50 usec
TE                298.0 K
D1             3.20000005 sec
D12            0.00002000 sec
D20          200.00000000 sec
TD0                     1
SFO1         150.9309761 MHz
NUC1                   13C
P1                10.50 usec
P13             2000.00 usec
P26              500.00 usec
PLW1         40.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          6.73799992 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          6.73799992 W
SFO2         600.1724087 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               70.00 usec
PLW2         15.00000000 W
PLW12         0.47832000 W

F2 - Processing parameters
SI                  65536
SF           150.9128665 MHz
WDW                    EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

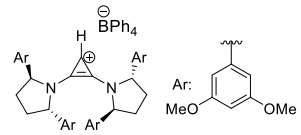
^{1}H NMR and ^{13}C NMR spectra for (2*S*,5*S*)-2,5-bis(3,5-dimethoxyphenyl)pyrrolidine



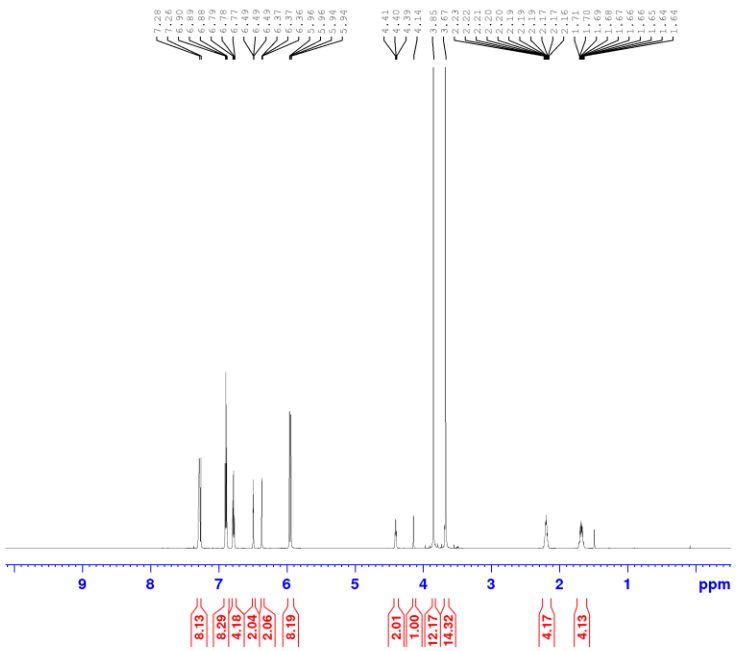




^{1}H NMR and ^{13}C NMR spectra for compound 5

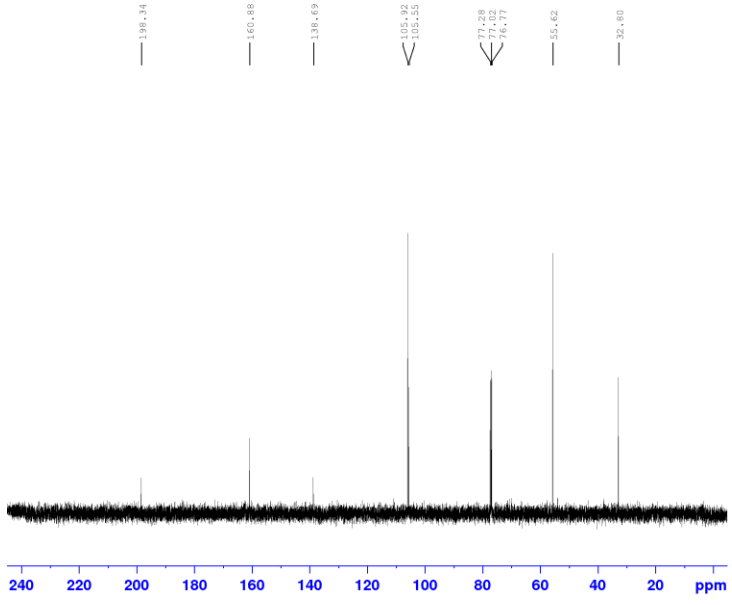


mr-2-78



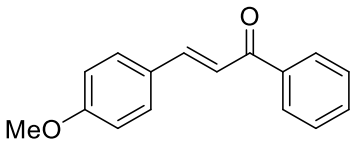

```
Current Data Parameters
NAME      mr-2-78(catalyst)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_           20180917
Time              16.11 h
INSTRUM             spect
PROBHD   Z847801_0323 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8417.509 Hz
FIDRES          0.256882 Hz
AQ              3.8928385 sec
RG                 175.84
DW                59.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.10000002 sec
TD0                    1
SFO1          600.1736010 MHz
NUC1                  1H
P1                 12.50 usec
PLW1          15.00000000 W

F2 - Processing parameters
SI                 65536
SF            600.1700139 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

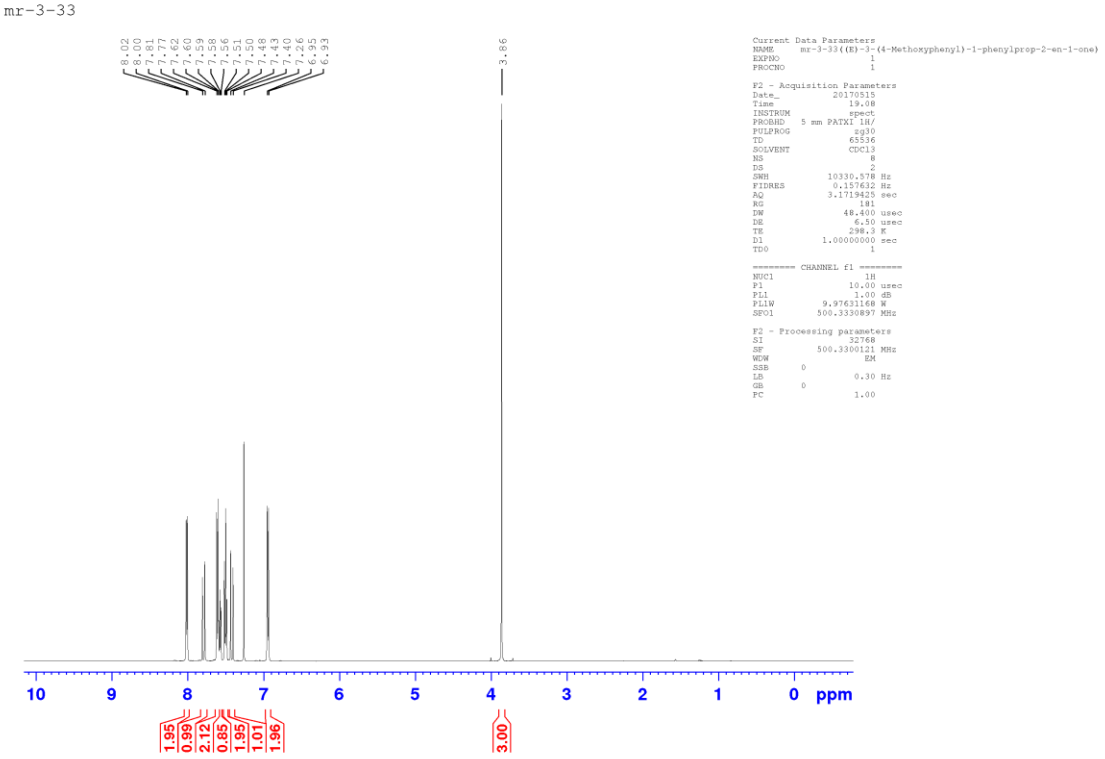
mr-5-31



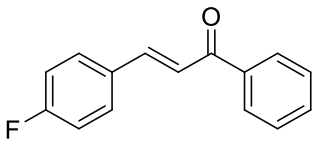

```
Current Data Parameters
NAME      mr-5-31(diketone)CNMR
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_           20180901
Time              16.40
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG             udeft
TD                 65536
SOLVENT            CDCl3
NS                   175
DS                     4
SWH            31446.541 Hz
FIDRES          0.479836 Hz
AQ              1.0420223 sec
RG                 32768
DW                15.900 usec
DE                 6.50 usec
TE                297.0 K
D1             3.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
D20          240.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.50 usec
P12              2000.00 usec
P26               500.00 usec
PL1                -6.00 dB
PL1W        300.00000000 W
SFO1         125.8231760 MHz
SP2                2.60 dB
SP8                2.60 dB
SPNAM[2]    Crp60comp.4
SPNAM[8] Crp60,0.5,20.1
SPOAL2              0.500
SPOAL8              0.500
SPOFFS2  0 Hz
SPOFFS8  0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                1.00 dB
PL12              19.06 dB
PL12W         9.97631168 W
PL13W         0.15594450 W
SFO2         500.3320013 MHz

F2 - Processing parameters
SI                 65536
SF            125.8080790 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

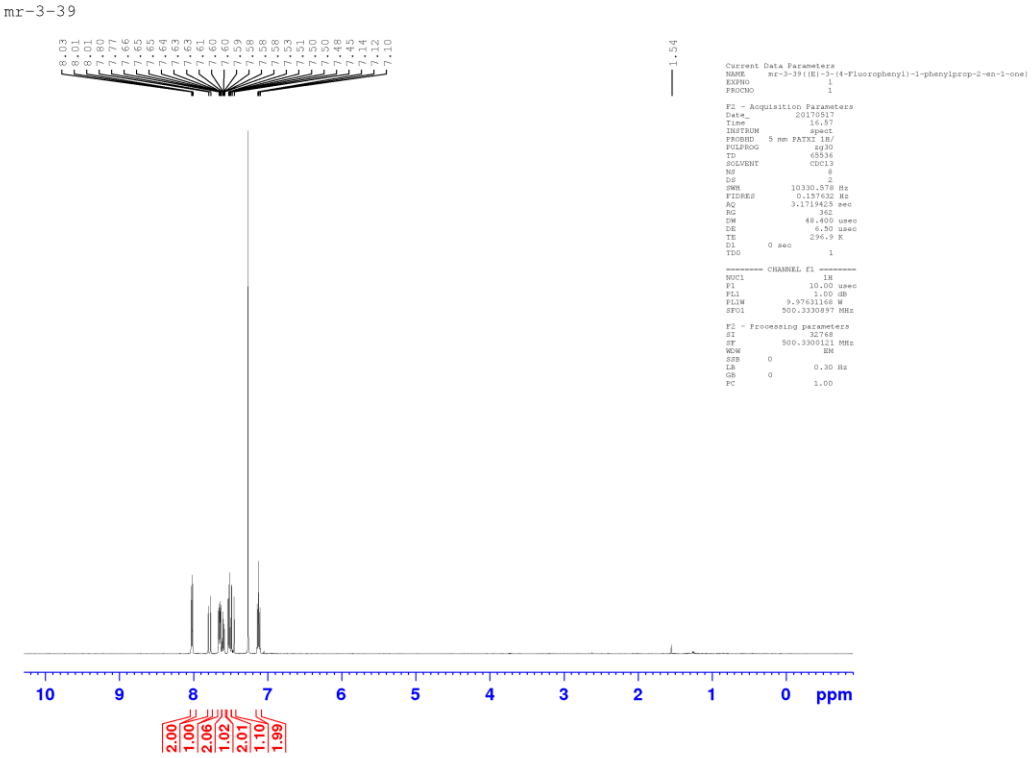
^{1}H NMR spectrum (E)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one



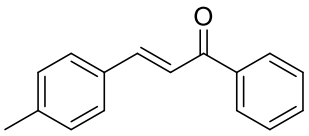


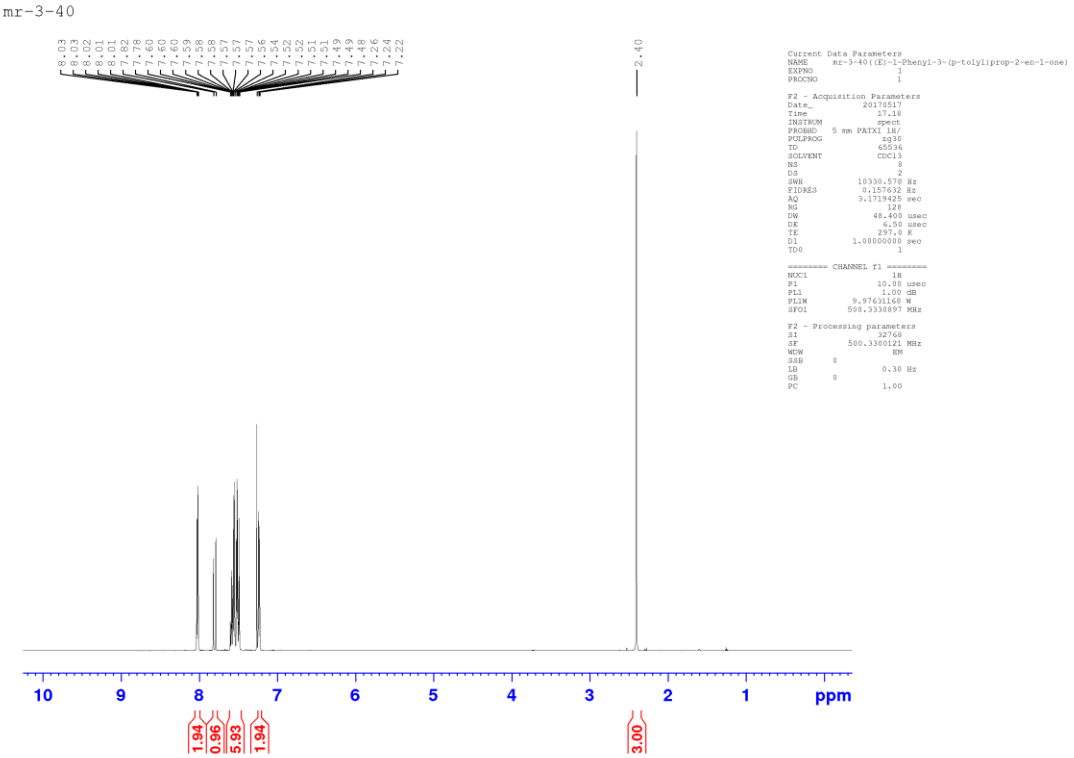
^{1}H NMR spectrum (E)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one





^{1}H NMR spectrum for (E)-1-phenyl-3-(p-tolyl)prop-2-en-1-one





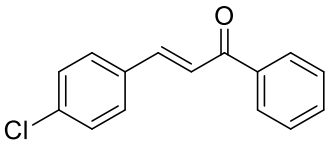
Current Data Parameters
NAME mr-3-40((E)-1-Phenyl-3-(p-tolyl)prop-2-en-1-one)
EXPNO 1
PROCNO 1

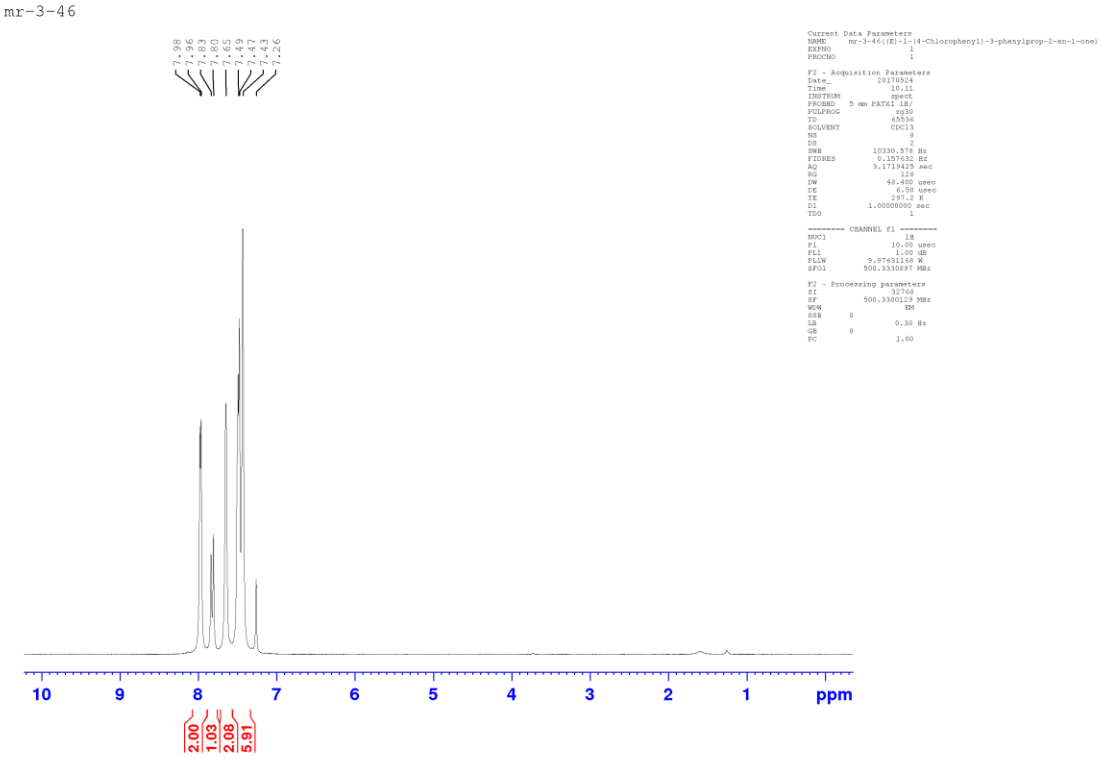
F2 - Acquisition Parameters
Date_ 20178517
Time 17.18
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 128
DW 48.400 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 1.00 dB
PL1W 9.97631168 W
SFO1 500.3338897 MHz

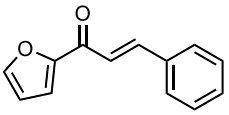
F2 - Processing parameters
SI 32768
SF 500.3300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

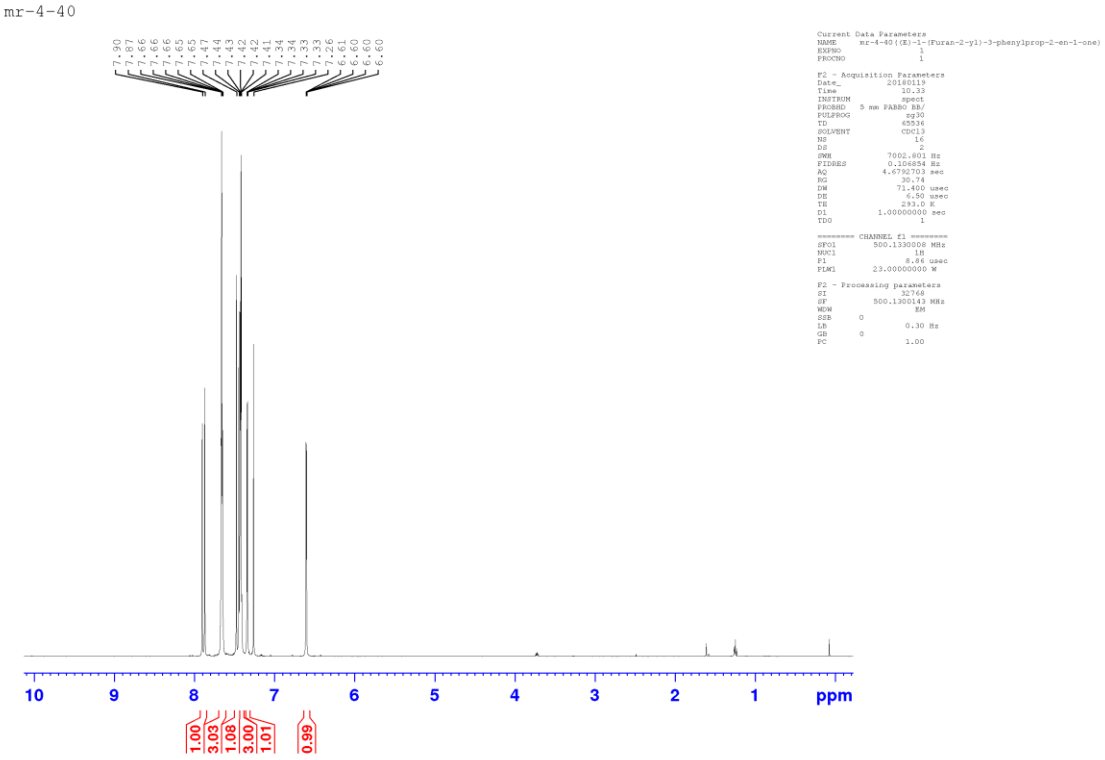
^{1}H NMR spectrum for (E)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one





^{1}H NMR spectrum for (E)-1-(furan-2-yl)-3-phenylprop-2-en-1-one





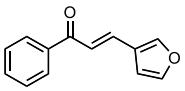
Current Data Parameters
NAME mr-4-40((E)-1-(Furan-2-yl)-3-phenylprop-2-en-1-one)
EXPNO 1
PROCNO 1

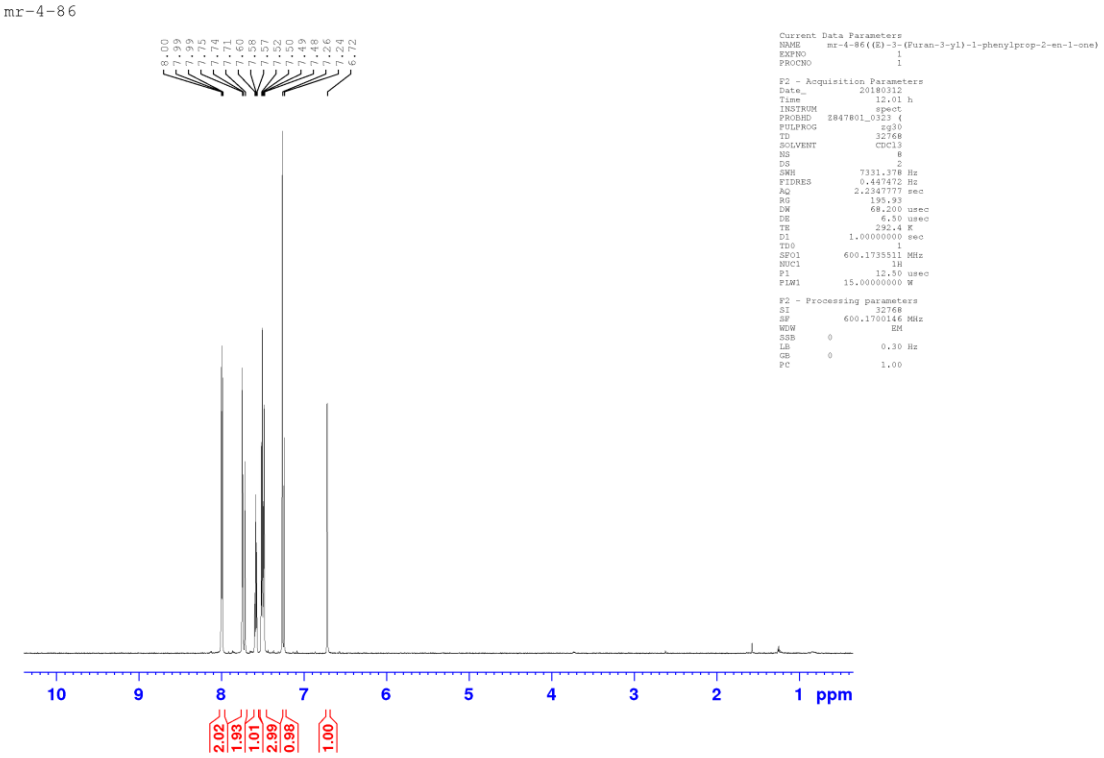
F2 - Acquisition Parameters
Date_ 20180119
Time 10.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 7002.801 Hz
FIDRES 0.106854 Hz
AQ 4.6792703 sec
RG 30.74
DW 71.400 usec
DE 6.50 usec
TE 293.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330008 MHz
NUC1 1H
P1 8.86 usec
PLW1 23.00000000 W

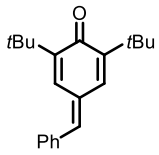
F2 - Processing parameters
SI 32768
SF 500.1300143 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

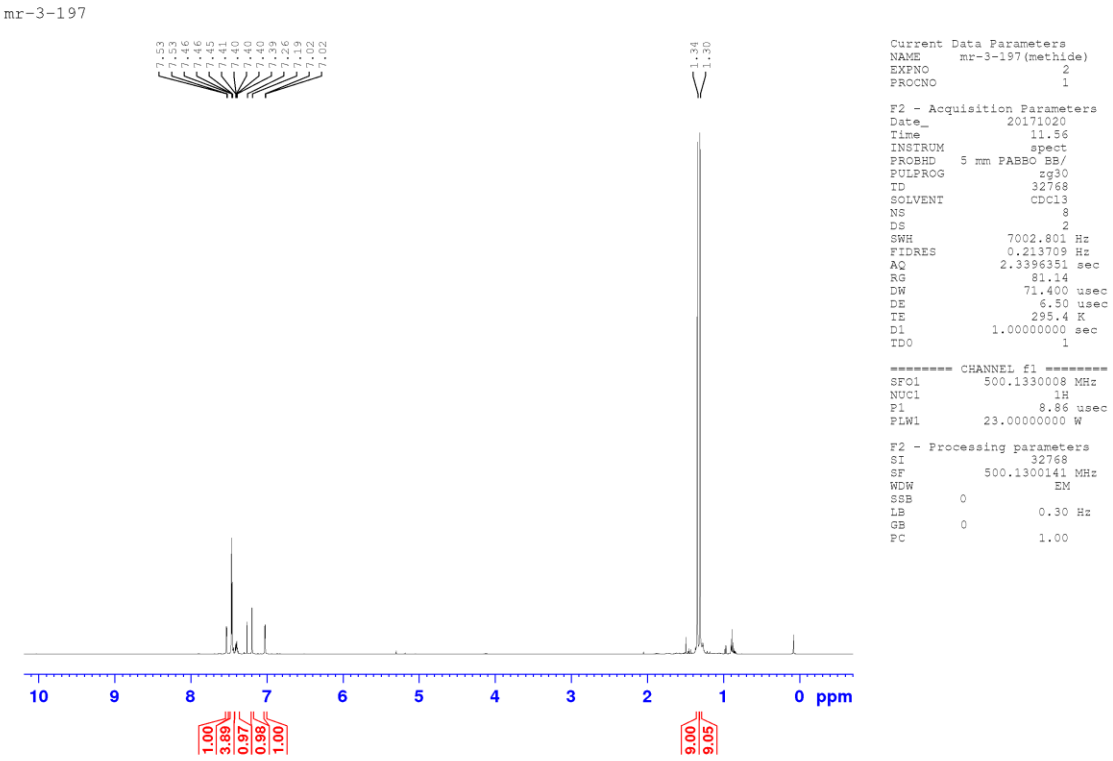
^{1}H NMR for (E)-3-(furan-3-yl)-1-phenylprop-2-en-1-one





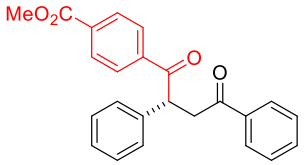
^{1}H NMR for 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one



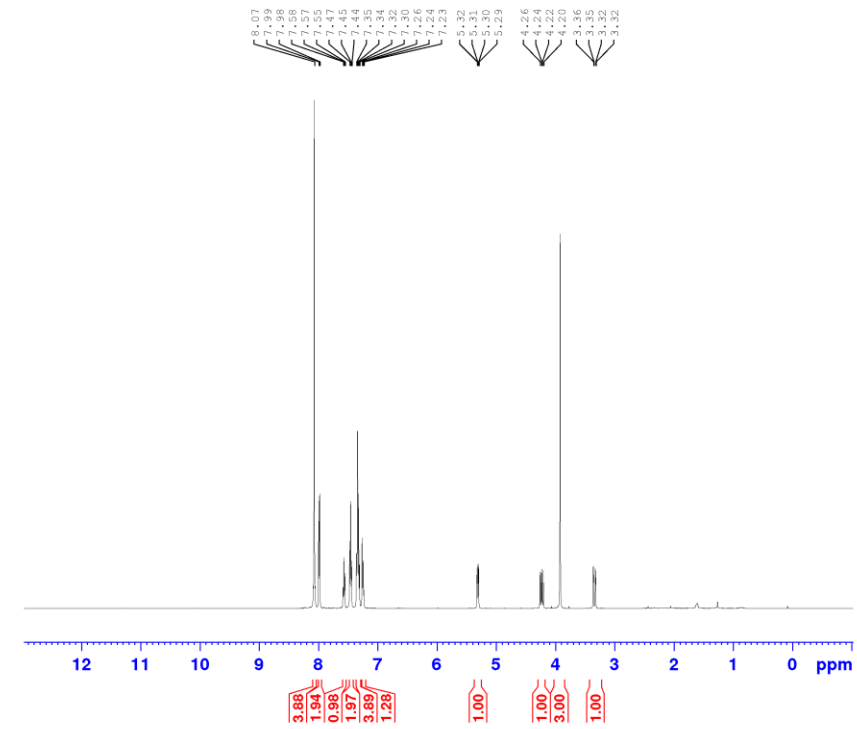



```
Current Data Parameters
NAME      mr-3-197(methide)
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20171020
Time              11.56
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           7002.801 Hz
FIDRES        0.213709 Hz
AQ            2.3396351 sec
RG               81.14
DW              71.400 usec
DE               6.50 usec
TE              295.4 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.1330008 MHz
NUC1               1H
P1                8.86 usec
PLW1       23.00000000 W

F2 - Processing parameters
SI               32768
SF          500.1300141 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```

^{1}H NMR for compound 6



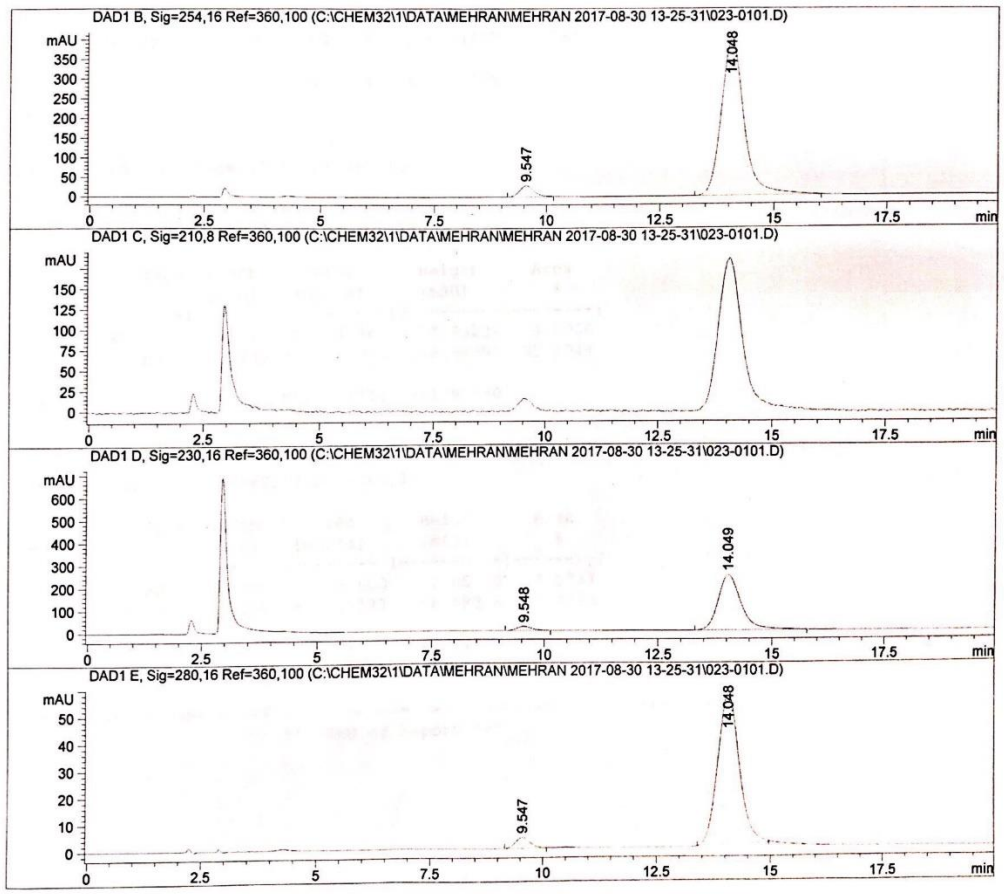
mr-3-164




```
Current Data Parameters
NAME                  mr-3-164
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20170831
Time                     17.03
INSTRUM                  spect
PROBHD    5 mm PATXI 1H/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                           8
DS                           2
SWH                10330.578 Hz
FIDRES              0.157632 Hz
AQ                  3.1719425 sec
RG                        71.8
DW                      48.400 usec
DE                       6.50 usec
TE                      295.8 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                      10.00 usec
PL1                      1.00 dB
PL1W               9.97631168 W
SFO1             500.3330897 MHz

F2 - Processing parameters
SI                       32768
SF                 500.3300093 MHz
WDW                         EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```

HPLC chromatogram for compound 6

```
Acq. Operator   : MEHRAN                          Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 23
Injection Date  : 08-30-2017 1:26:33 PM               Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2017-08-30 13-25-31\MEHRAN.M
Last changed    : 08-30-2017 1:25:29 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2017-08-30 13-25-31\023-0101.D\DA.M (
                  MEHRAN.M)
Last changed    : 08-30-2017 1:52:32 PM by DYLAN
Method Info     : IC, 15% Isopropanol, in hexane. 0.2ml/min, 1.0 ul injection, 30 oC.
```



Area Percent Report

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

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.547	BB	0.3442	639.42065	28.44693	4.4144
2	14.048	BB	0.5270	1.38455e4	398.84467	95.5856
Totals :				1.44849e4	427.29159	

Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.548	BB	0.3312	401.45941	17.93232	4.5056
2	14.049	BB	0.5269	8508.71973	243.98398	95.4944
Totals :				8910.17914	261.91630	

Signal 4: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.547	BB	0.3347	89.27600	4.05783	4.5787
2	14.048	BB	0.5056	1860.53577	56.58328	95.4213
Totals :				1949.81177	60.64111	

*** End of Report ***

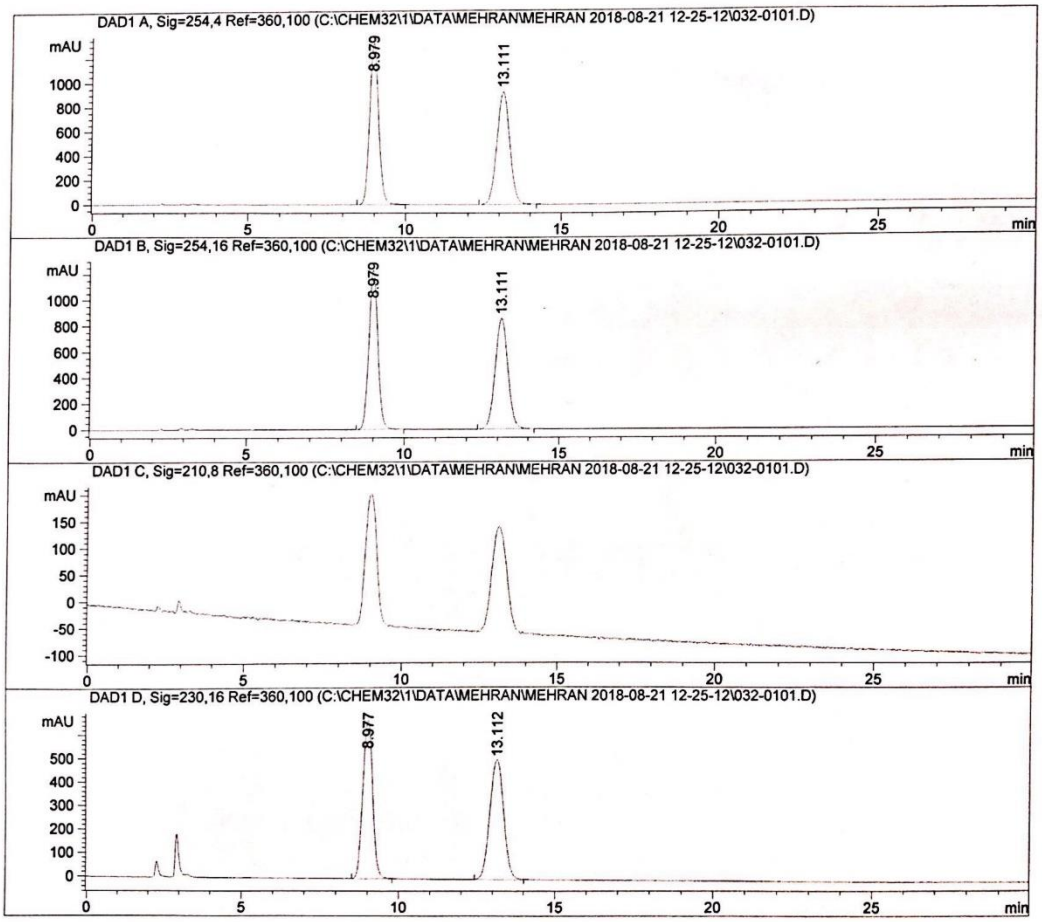
Instrument 1 08-30-2017 1:52:49 PM DYLAN

HPLC chromatogram for racemic of compound 6

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-21 12-25-12\032-0101.D
Sample Name: mr-2-176

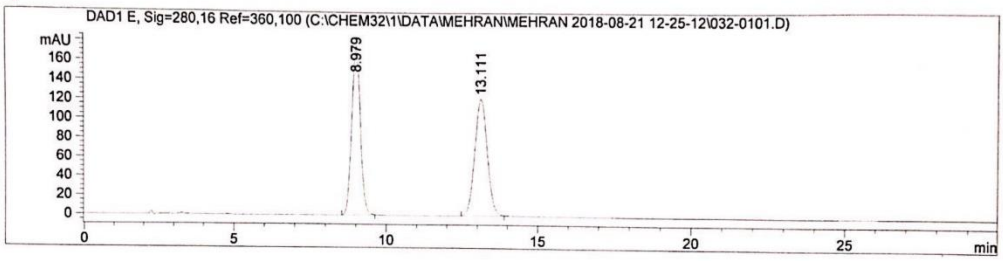
Acq. Operator	: MEHRAN	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 32
Injection Date	: 08-21-2018 12:26:16 PM	Inj	: 1
		Inj Volume	: 5 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 1 µl

Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-21 12-25-12\MEHRAN.M
Last changed : 08-21-2018 12:25:10 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-21 12-25-12\032-0101.D\DA.M (MEHRAN.M)
Last changed : 09-25-2018 1:16:57 PM by MEHRAN
Method Info : IC, 15% Isopropanol in hexanes 0.2 ml/min, 1 ul injection, 30 oC



Instrument 1 09-25-2018 1:23:47 PM MEHRAN Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-21 12-25-12\032-0101.D
Sample Name: mr-2-176



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.979	BB	0.3086	2.62527e4	1316.83704	49.8930
2	13.111	BB	0.4479	2.63653e4	915.68005	50.1070
Totals :				5.26180e4	2232.51709	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.979	BB	0.3085	2.46732e4	1237.91309	49.8947
2	13.111	BB	0.4479	2.47773e4	860.67566	50.1053
Totals :				4.94506e4	2098.58875	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.977	VB	0.3478	1.46753e4	669.39789	48.3713
2	13.112	VV	0.4892	1.56635e4	505.87491	51.6287
Totals :				3.03388e4	1175.27280	

Instrument 1 09-25-2018 1:23:47 PM MEHRAN

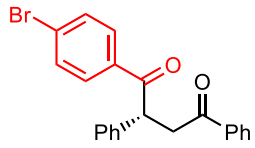
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-21 12-25-12\032-0101.D
Sample Name: mr-2-176

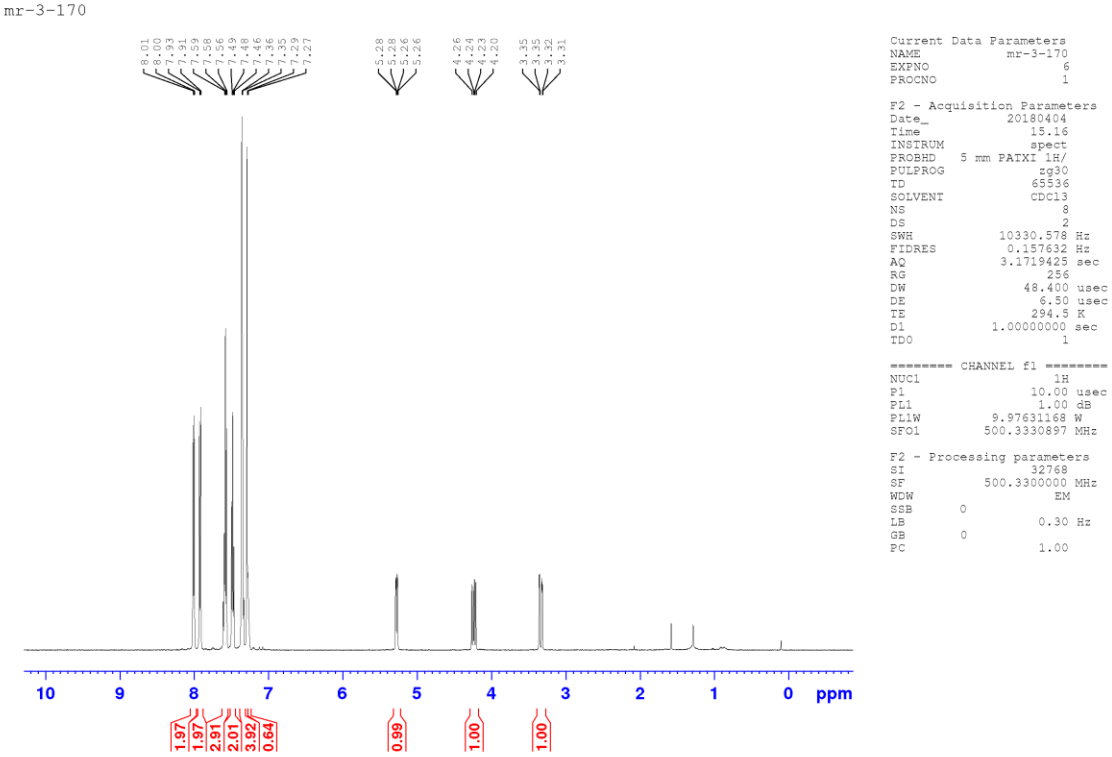
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.979	BB	0.3068	3500.82495	176.97174	49.9371
2	13.111	BB	0.4465	3509.64185	122.42441	50.0629
Totals :				7010.46680	299.39615	

*** End of Report ***

^{1}H NMR for compound 7



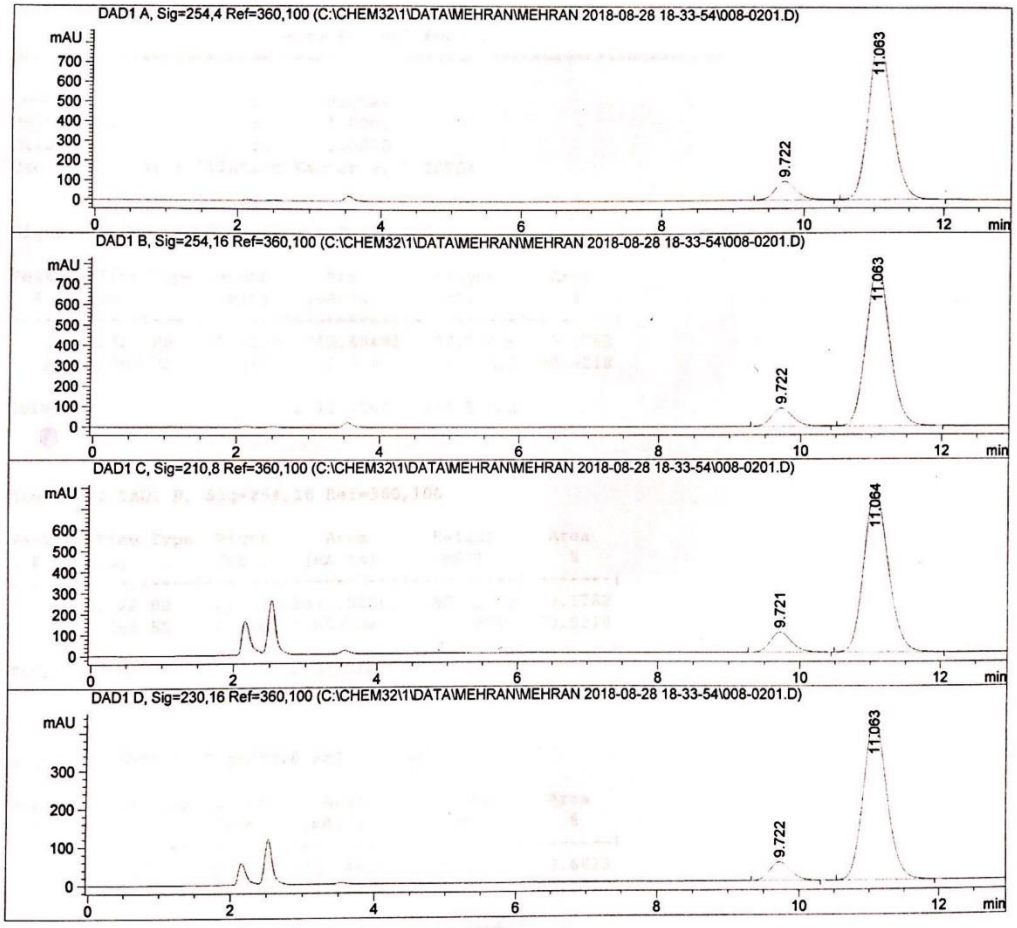



```
Current Data Parameters
NAME                  mr-3-170
EXPNO                        6
PROCNO                       1

F2 - Acquisition Parameters
Date_               20180404
Time                   15.16
INSTRUM                spect
PROBHD    5 mm PATXI 1H/
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                           8
DS                           2
SWH                10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719425 sec
RG                         256
DW                    48.400 usec
DE                     6.50 usec
TE                     294.5 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                      10.00 usec
PL1                      1.00 dB
PL1W               9.97631168 W
SFO1             500.3330897 MHz

F2 - Processing parameters
SI                       32768
SF               500.3300000 MHz
WDW                         EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

HPLC chromatogram for compound 7

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\008-0201.D
Sample Name: mr-5-30

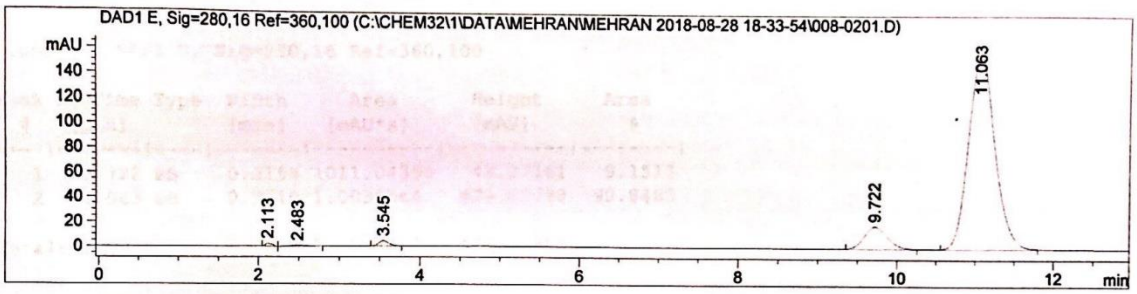
```
Acq. Operator   : MEHRAN                          Seq. Line :   2
Acq. Instrument : Instrument 1                     Location : Vial 8
Injection Date  : 08-28-2018 6:49:08 PM                Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\MEHRAN.M
Last changed    : 08-28-2018 6:33:53 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\008-0201.D\DA.M (
                  MEHRAN.M)
Last changed    : 08-28-2018 6:33:53 PM by MEHRAN
Method Info     : IA, 10% Isopropanol in hexanes  0.2 ml/min, 1 ul injection, 30 oC
```



Instrument 1 09-26-2018 10:26:58 AM MEHRAN

Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\008-0201.D
Sample Name: mr-5-30



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.722	BB	0.3173	1943.65491	93.97488	9.1782
2	11.063	BB	0.3608	1.92331e4	822.60333	90.8218
Totals :				2.11768e4	916.57822	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.722	BB	0.3173	1872.58887	90.55508	9.1782
2	11.063	BB	0.3608	1.85300e4	792.48285	90.8218
Totals :				2.04026e4	883.03793	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.721	BB	0.3194	2002.44153	96.76131	9.6623
2	11.064	BB	0.3765	1.87219e4	773.15808	90.3377
Totals :				2.07244e4	869.91939	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\008-0201.D
Sample Name: mr-5-30

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.722	BB	0.3154	1011.04395	49.27161	9.1517
2	11.063	BB	0.3610	1.00366e4	428.89798	90.8483
Totals :				1.10476e4	478.16959	

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

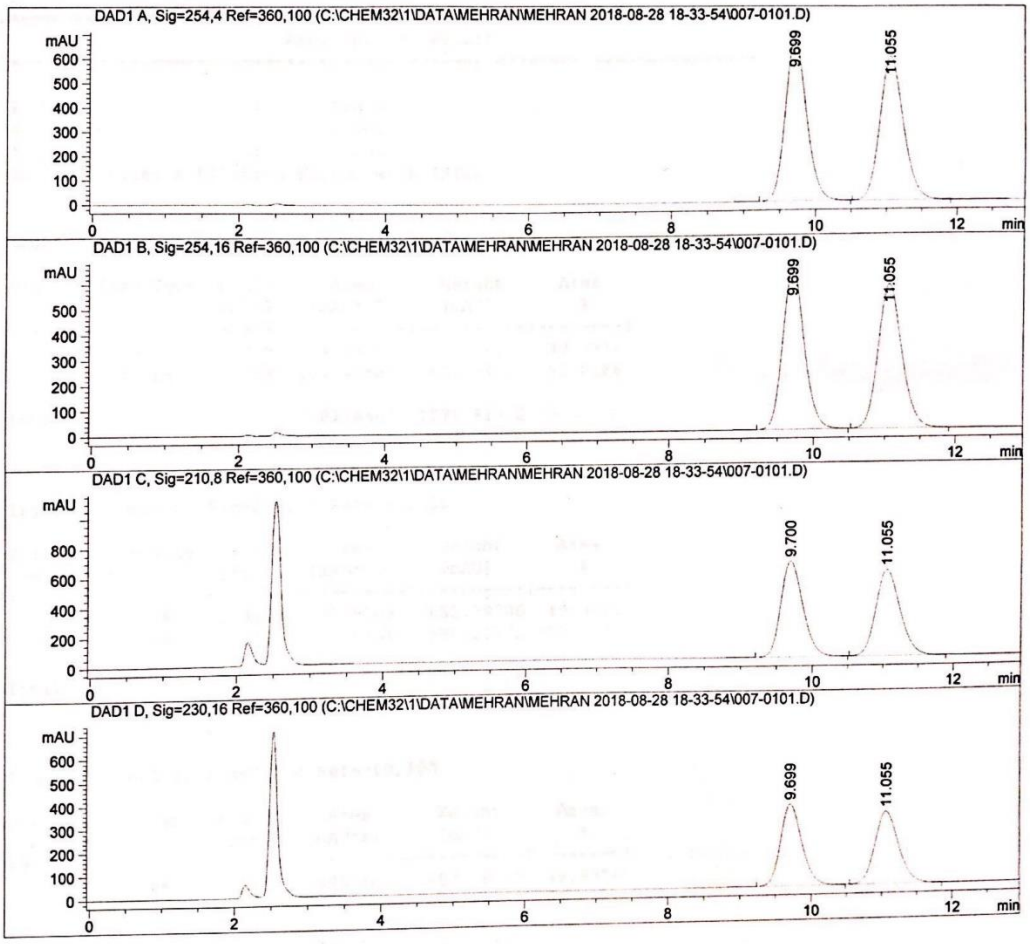
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.113	BV	0.0794	14.36686	2.48555	0.3438
2	2.483	VB	0.2118	16.07137	1.00910	0.3846
3	3.545	BB	0.1323	35.50468	4.12788	0.8497
4	9.722	BB	0.3148	377.12296	18.42580	9.0255
5	11.063	BB	0.3609	3735.33423	159.70837	89.3963
Totals :				4178.40010	185.75670	

*** End of Report ***

HPLC chromatogram for racemic of compound 7

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\007-0101.D
Sample Name: mr-4-202

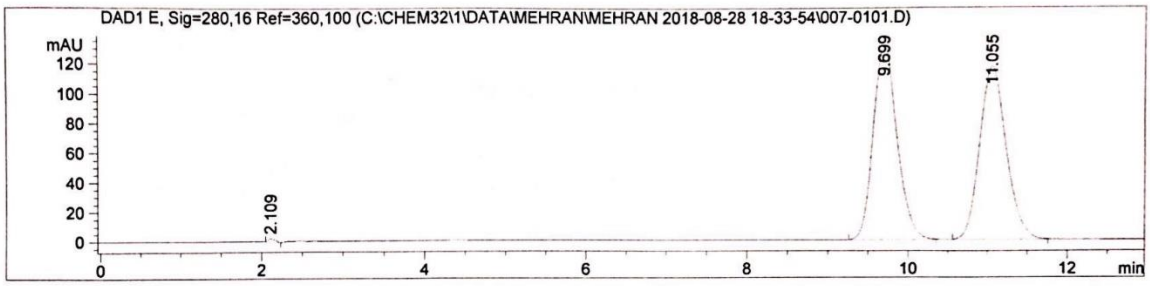
```
==========================================================================
Acq. Operator   : MEHRAN                          Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 7
Injection Date  : 08-28-2018 6:35:13 PM               Inj :   1
                                                 Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\MEHRAN.M
Last changed    : 08-28-2018 6:33:53 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\007-0101.D\DA.M (
                  MEHRAN.M)
Last changed    : 08-28-2018 6:33:53 PM by MEHRAN
Method Info     : IA, 10% Isopropanol in hexanes  0.2 ml/min, 1 ul injection, 30 oC
```



Instrument 1 09-26-2018 10:26:07 AM MEHRAN

Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\007-0101.D
Sample Name: mr-4-202



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.699	BB	0.3185	1.40831e4	677.56647	49.9814
2	11.055	BB	0.3590	1.40935e4	602.24725	50.0186
Totals :				2.81766e4	1279.81372	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.699	BB	0.3185	1.35691e4	652.79706	49.9816
2	11.055	BB	0.3590	1.35791e4	580.21722	50.0184
Totals :				2.71482e4	1233.01428	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.700	BB	0.3295	1.39698e4	653.16248	49.9356
2	11.055	BB	0.3728	1.40059e4	585.99237	50.0644
Totals :				2.79757e4	1239.15485	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 18-33-54\007-0101.D
Sample Name: mr-4-202

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

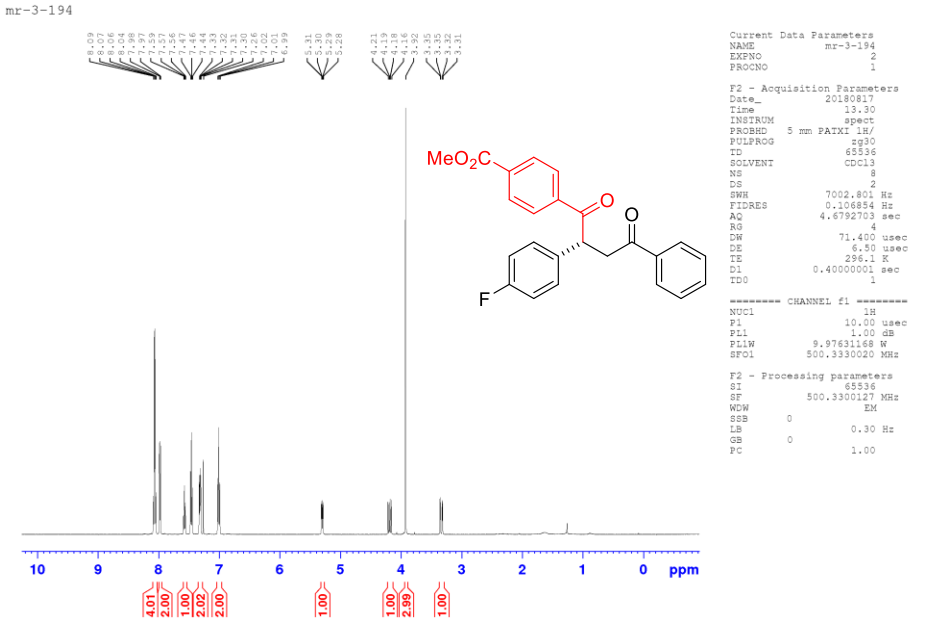
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.699	BB	0.3192	7375.62646	353.87714	50.0364
2	11.055	BB	0.3592	7364.90723	314.45432	49.9636
Totals :				1.47405e4	668.33145	

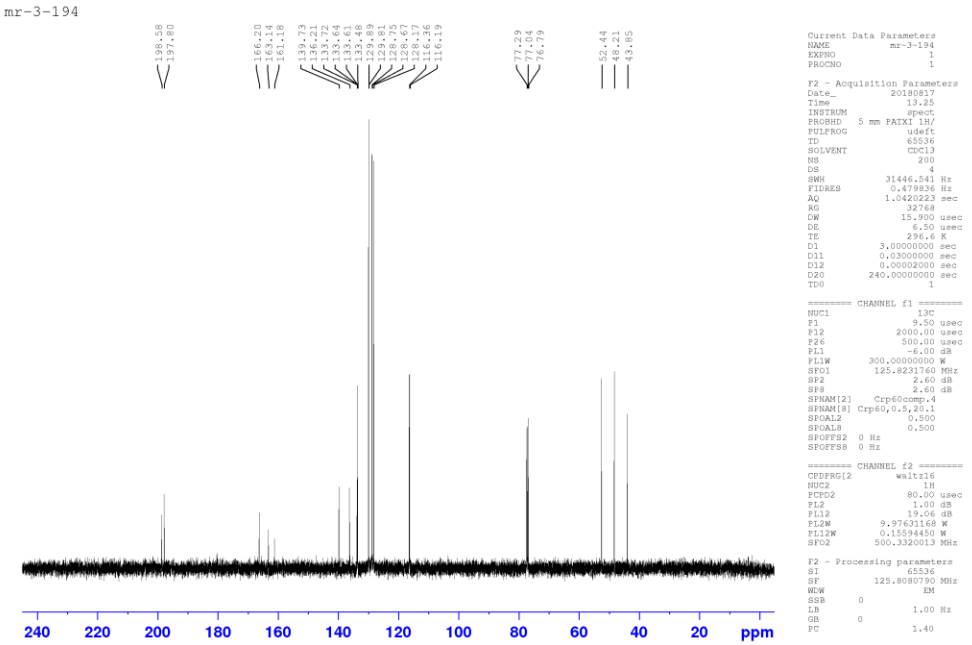
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.109	BV	0.0786	14.19637	2.48592	0.2586
2	9.699	BB	0.3185	2739.15186	131.79910	49.8877
3	11.055	BB	0.3587	2737.28931	117.11939	49.8538
Totals :				5490.63754	251.40441	

*** End of Report ***

^{1}H NMR and ^{13}C NMR for compound 8

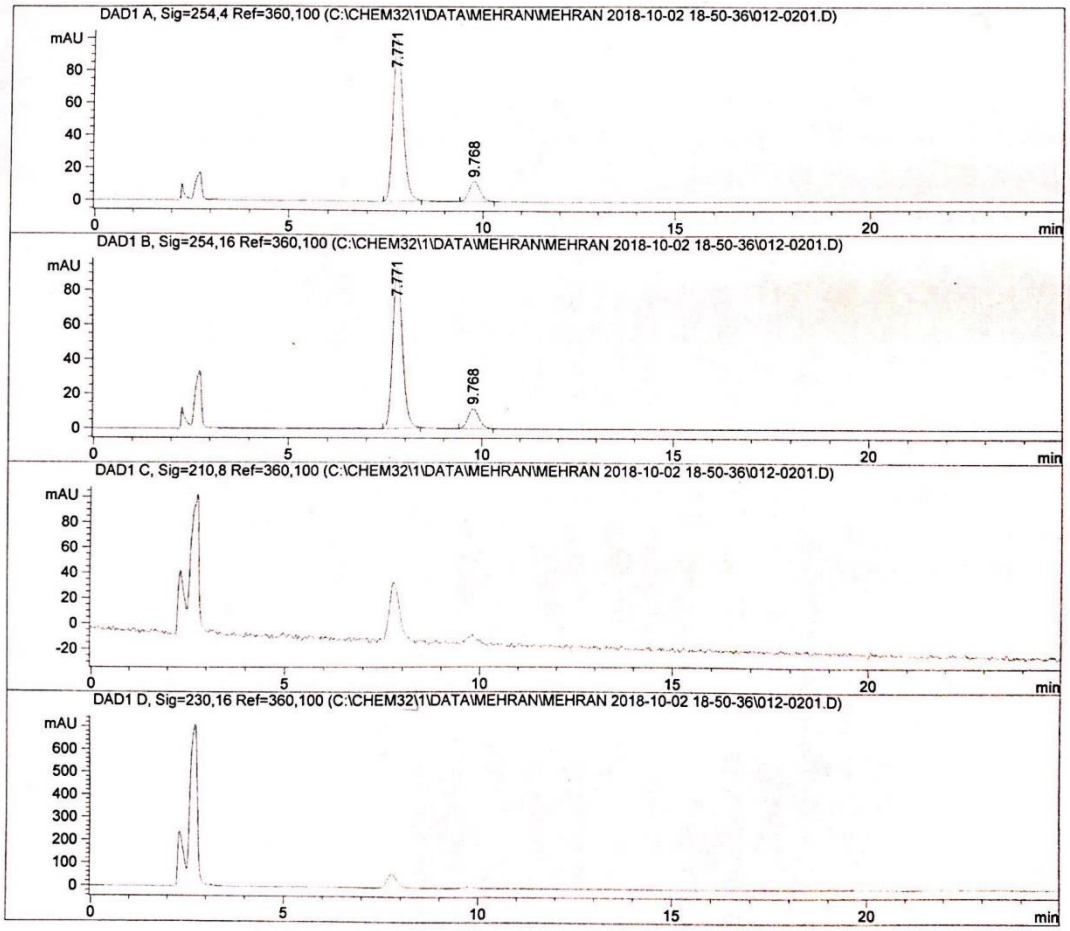




HPLC chromatogram for compound 8

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\012-0201.D
Sample Name: mr-3-194

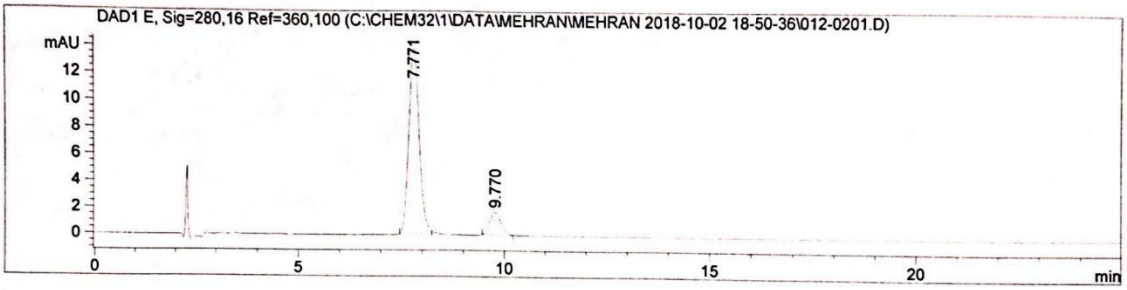
```
==========================================================================
Acq. Operator   : MEHRAN                          Seq. Line :   2
Acq. Instrument : Instrument 1                    Location : Vial 12
Injection Date  : 10-02-2018 7:17:46 PM                Inj :   1
                                                 Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\MEHRAN.M
Last changed    : 10-02-2018 6:50:35 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\012-0201.D\DA.M (
                  MEHRAN.M)
Last changed    : 02-28-2019 11:58:11 AM by Hemkalyan
Method Info     : IB, 50% Isopropanol in hexanes  0.2 ml/min, 1 ul injection, 30 oC
```



Instrument 1 02-28-2019 11:58:32 AM Hemkalyan

Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\012-0201.D
Sample Name: mr-3-194



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.771	BB	0.2724	1756.78088	99.31010	87.7575
2	9.768	BB	0.3076	245.07735	12.34726	12.2425
Totals :				2001.85823	111.65735	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.771	BB	0.2724	1654.69238	93.53693	87.7708
2	9.768	BB	0.3095	230.55011	11.62031	12.2292
Totals :				1885.24249	105.15723	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\012-0201.D
Sample Name: mr-3-194

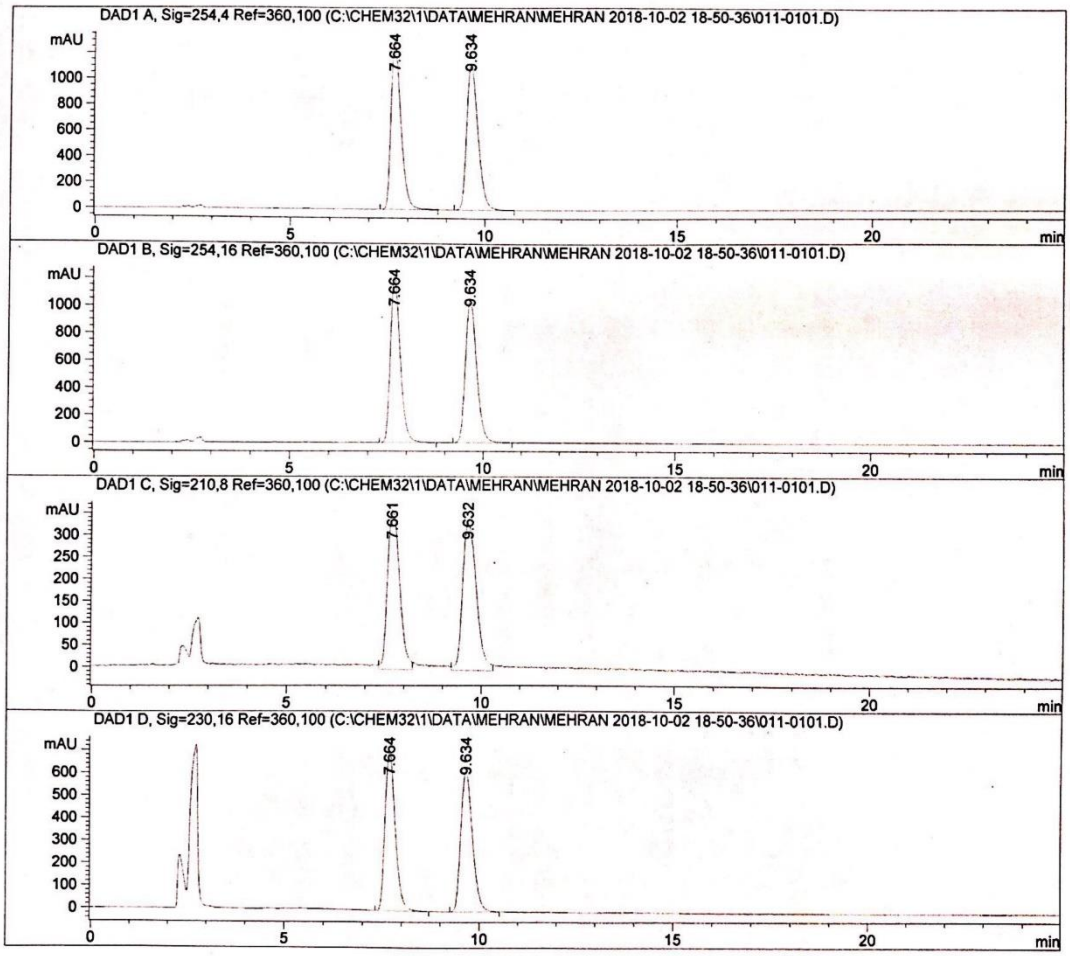
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.771	BB	0.2699	243.30424	13.92460	88.1842
2	9.770	BB	0.2897	32.60033	1.70041	11.8158
Totals :				275.90457	15.62501	

*** End of Report ***

HPLC chromatogram for racemic of compound 8

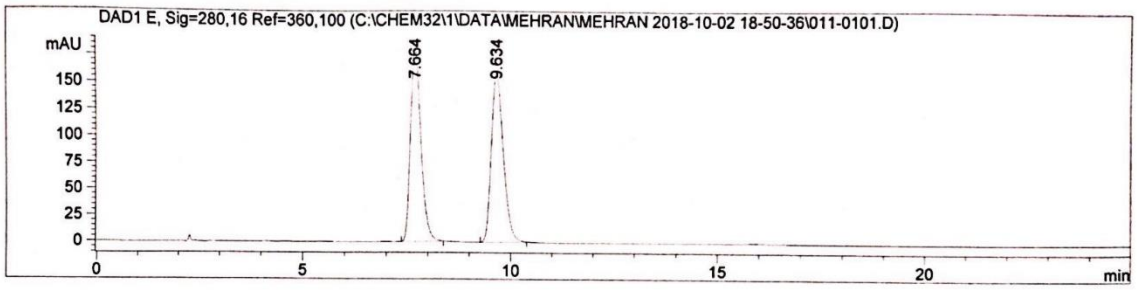
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\011-0101.D
Sample Name: mr-5-48

Acq. Operator : MEHRAN Seq. Line : 1
Acq. Instrument : Instrument 1 Location : Vial 11
Injection Date : 10-02-2018 6:51:36 PM Inj : 1
Inj Volume : 5 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 1 µl
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\MEHRAN.M
Last changed : 10-02-2018 6:50:35 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\011-0101.D\DA.M (MEHRAN.M)
Last changed : 02-28-2019 11:57:01 AM by Hemkalyan
Method Info : IB, 50% Isopropanol in hexanes 0.2 ml/min, 1 ul injection, 30 oC



Instrument 1 02-28-2019 11:57:32 AM Hemkalyan Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\011-0101.D
Sample Name: mr-5-48



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.664	BB	0.2729	2.29238e4	1292.81677	49.9967
2	9.634	BB	0.3141	2.29268e4	1123.55212	50.0033
Totals :				4.58506e4	2416.36890	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.664	BB	0.2728	2.15938e4	1218.37109	50.0008
2	9.634	BB	0.3140	2.15931e4	1058.64587	49.9992
Totals :				4.31870e4	2277.01697	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.661	VV	0.3017	7960.03223	363.19885	48.5498
2	9.632	VV	0.3404	8435.56738	336.54111	51.4502
Totals :				1.63956e4	699.73996	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\011-0101.D
Sample Name: mr-5-48

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

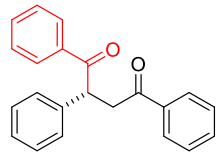
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.664	BB	0.2835	1.28845e4	704.06842	49.8185
2	9.634	BB	0.3266	1.29784e4	618.92700	50.1815
Totals :				2.58630e4	1322.99542	

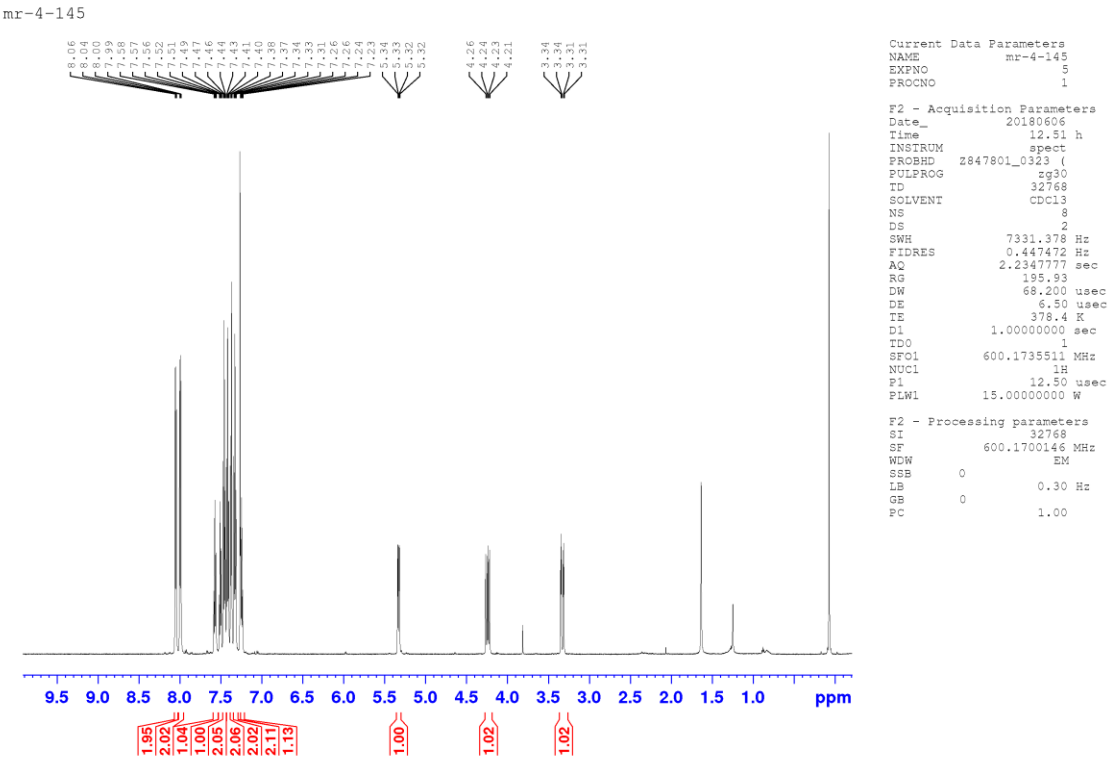
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.664	BB	0.2688	3198.46729	182.18298	49.9156
2	9.634	BB	0.3125	3209.28857	158.29874	50.0844
Totals :				6407.75586	340.48172	

*** End of Report ***

^{1}H NMR for compound 9

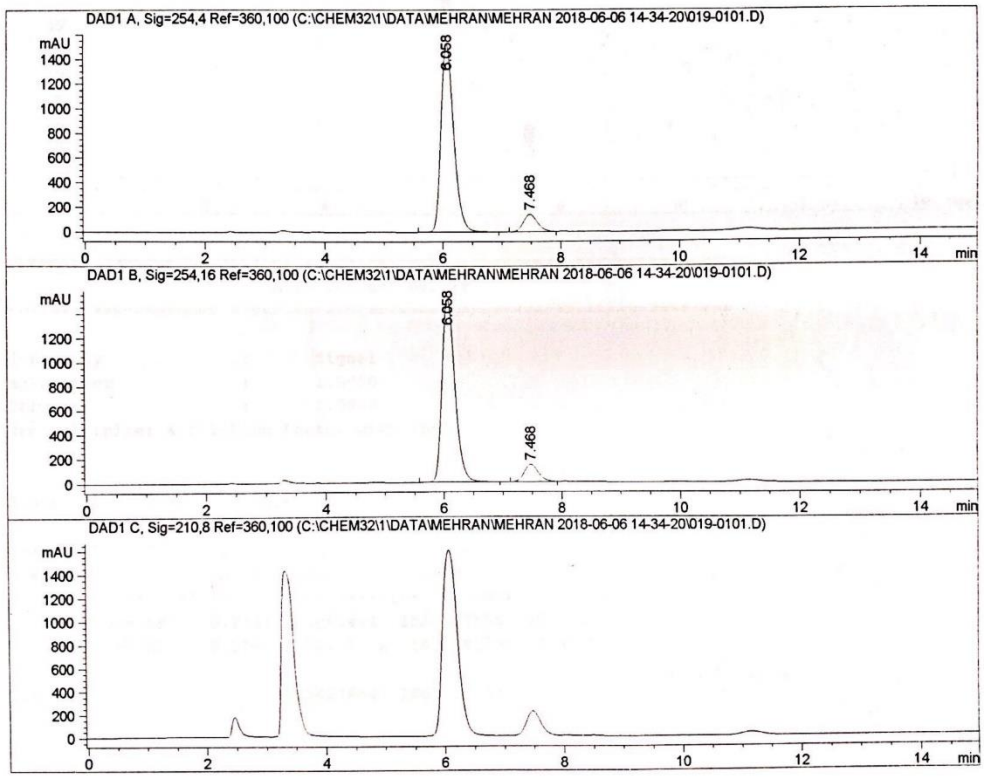




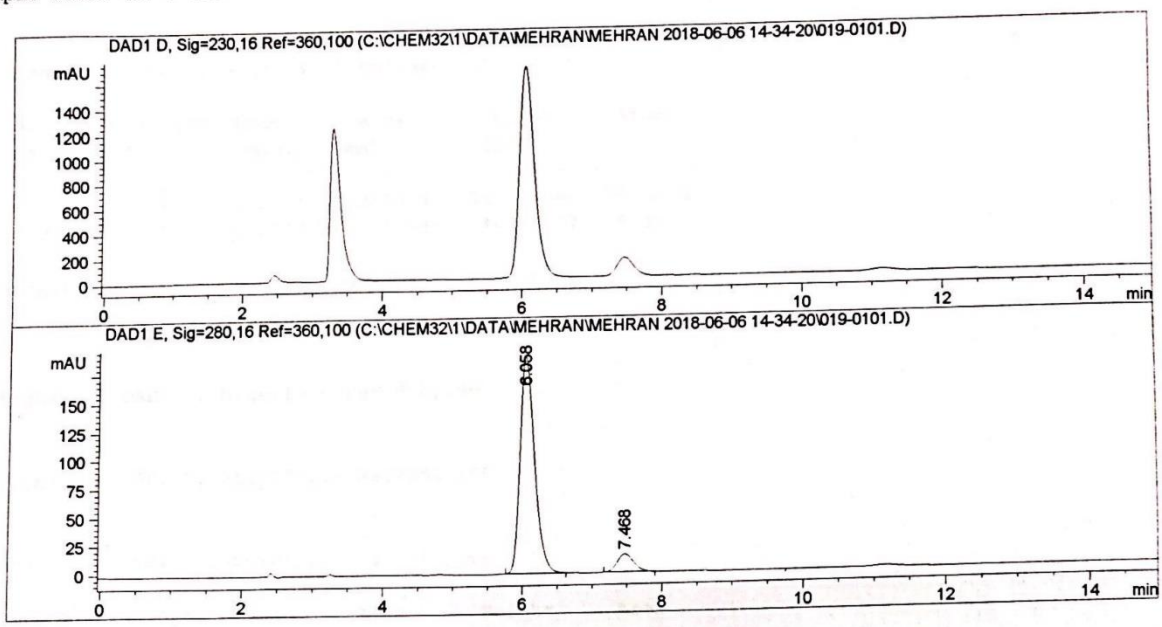
HPLC chromatogram for compound 9

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-06-06 14-34-20\019-0101.D
Sample Name: mr-4-149

```
======================================================================
Acq. Operator   : Naveen                        Seq. Line :   1
Acq. Instrument : Instrument 1                   Location : Vial 19
Injection Date  : 06-06-2018 2:35:20 PM               Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-06-06 14-34-20\MEHRAN.M
Last changed    : 06-06-2018 2:03:21 PM by Naveen
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-06-06 14-34-20\019-0101.D\DA.M (
                  MEHRAN.M)
Last changed    : 06-06-2018 3:27:19 PM by Naveen
Method Info     : IC, 10% Isopropanol in hexane  0.2ml/min, 1 ul injection, 30 oC
```



Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-06-06 14-34-20\019-0101.D
Sample Name: mr-4-149



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.058	BB	0.2344	2.30414e4	1523.67554	90.6645
2	7.468	BV	0.2565	2372.51172	142.28189	9.3355
Totals :				2.54139e4	1665.95743	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-06-06 14-34-20\019-0101.D
Sample Name: mr-4-149

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.058	BB	0.2394	2.32519e4	1511.69543	90.6418
2	7.468	BV	0.2564	2400.61938	144.07387	9.3582
Totals :				2.56526e4	1655.76930	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

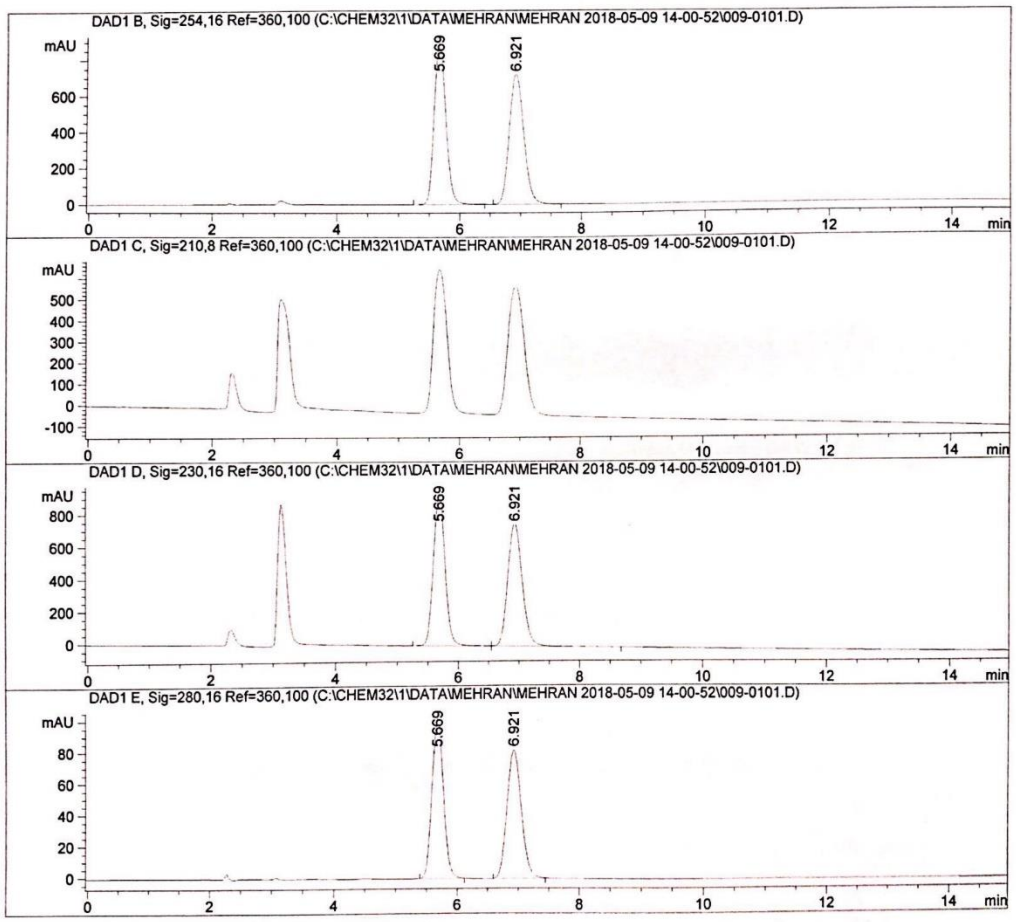
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.058	BB	0.2229	2749.74072	189.97871	91.3187
2	7.468	BB	0.2535	261.40839	15.92212	8.6813
Totals :				3011.14911	205.90084	

*** End of Report ***

HPLC chromatogram for racemic of compound 9

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-05-09 14-00-52\009-0101.D
Sample Name: mr-4-135

Acq. Operator	: MEHRAN	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 9
Injection Date	: 05-09-2018 2:01:54 PM	Inj	: 1
		Inj Volume	: 5 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 1 µl
Acq. Method	: C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-05-09 14-00-52\MEHRAN.M		
Last changed	: 05-09-2018 2:00:50 PM by MEHRAN		
Analysis Method	: C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-05-09 14-00-52\009-0101.D\DA.M (MEHRAN.M)		
Last changed	: 09-26-2018 11:06:55 AM by MEHRAN		
Method Info	: IC, 10% Isopropanol in hexane 0.2ml/min, 1 ul injection, 30 oC		



Instrument 1 09-26-2018 11:07:19 AM MEHRAN

Page 1 of 2

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-05-09 14-00-52\009-0101.D
Sample Name: mr-4-135

Area Percent Report

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

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.669	BB	0.2071	1.17906e4	887.09833	49.8844
2	6.921	BB	0.2593	1.18453e4	714.80200	50.1156
Totals :				2.36359e4	1601.90033	

Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

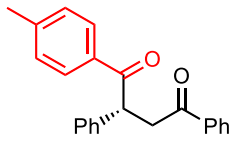
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.669	BV	0.2071	1.26550e4	952.15546	49.7721
2	6.921	VB	0.2603	1.27709e4	766.96820	50.2279
Totals :				2.54259e4	1719.12366	

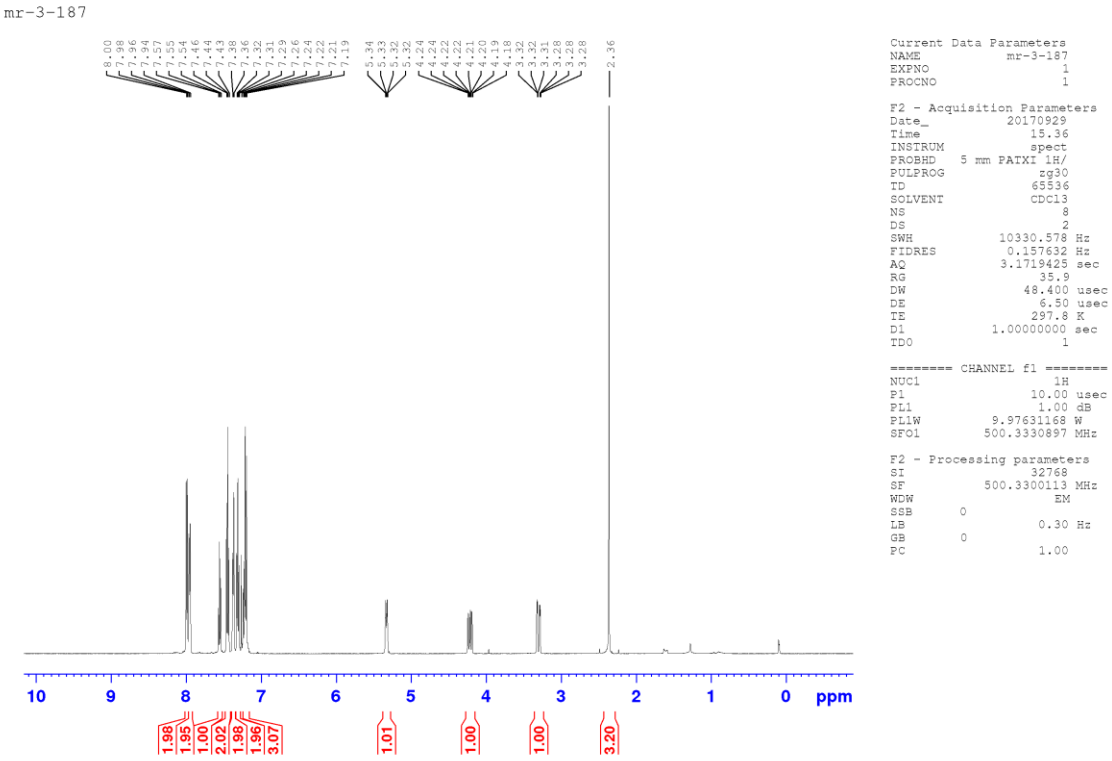
Signal 4: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.669	BB	0.2044	1330.63770	101.88956	49.9376
2	6.921	BB	0.2554	1333.96436	81.33164	50.0624
Totals :				2664.60205	183.22121	

*** End of Report ***

^{1}H NMR for compound 10

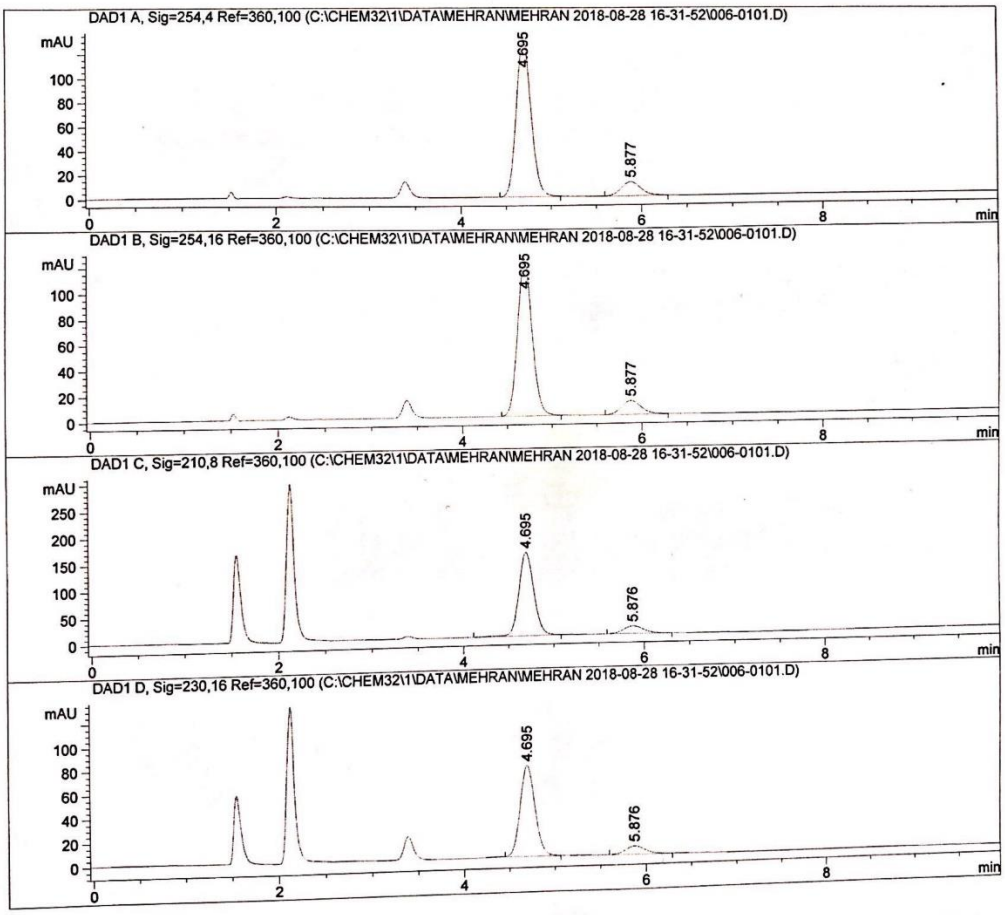




HPLC chromatogram for compound 10

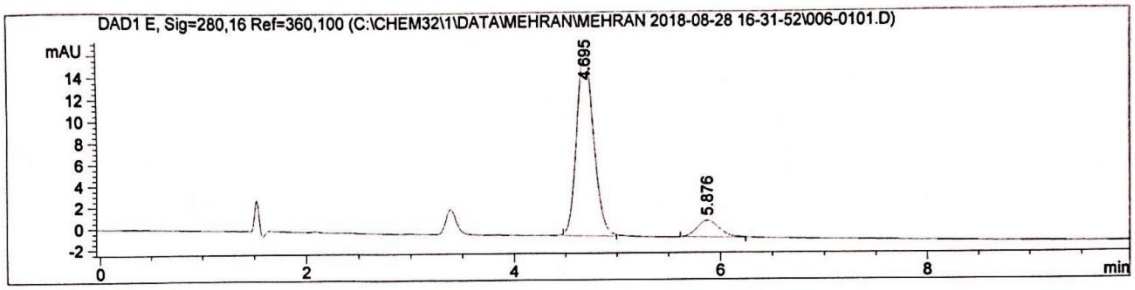
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\006-0101.D
Sample Name: mr-3-175

```
==========================================================================
Acq. Operator    : MEHRAN                          Seq. Line :   1
Acq. Instrument : Instrument 1                      Location : Vial 6
Injection Date  : 08-28-2018 4:32:52 PM                Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\MEHRAN.M
Last changed    : 08-28-2018 4:31:51 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\006-0101.D\DA.M (
                  MEHRAN.M)
Last changed    : 08-28-2018 4:31:51 PM by MEHRAN
Method Info     : IC, 10% Isopropanol in hexanes  0.3 ml/min, 1 ul injection, 30 oC
```



Instrument 1 09-26-2018 10:44:35 AM MEHRAN

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\006-0101.D
Sample Name: mr-3-175



Area Percent Report

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.695	BB	0.1772	1487.73743	130.28329	89.3577
2	5.877	BB	0.2351	177.18527	11.67295	10.6423
Totals :				1664.92270	141.95625	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.695	BB	0.1772	1407.91943	123.30837	89.3514
2	5.877	BB	0.2351	167.79147	11.05382	10.6486
Totals :				1575.71091	134.36220	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.695	BB	0.1790	1841.57227	159.16896	89.1703
2	5.876	BB	0.2322	223.65907	14.64199	10.8297
Totals :				2065.23134	173.81095	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\006-0101.D
Sample Name: mr-3-175

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.695	BB	0.1764	869.36053	76.60010	88.9918
2	5.876	BB	0.2352	107.53956	7.00321	11.0082
Totals :				976.90009	83.60330	

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

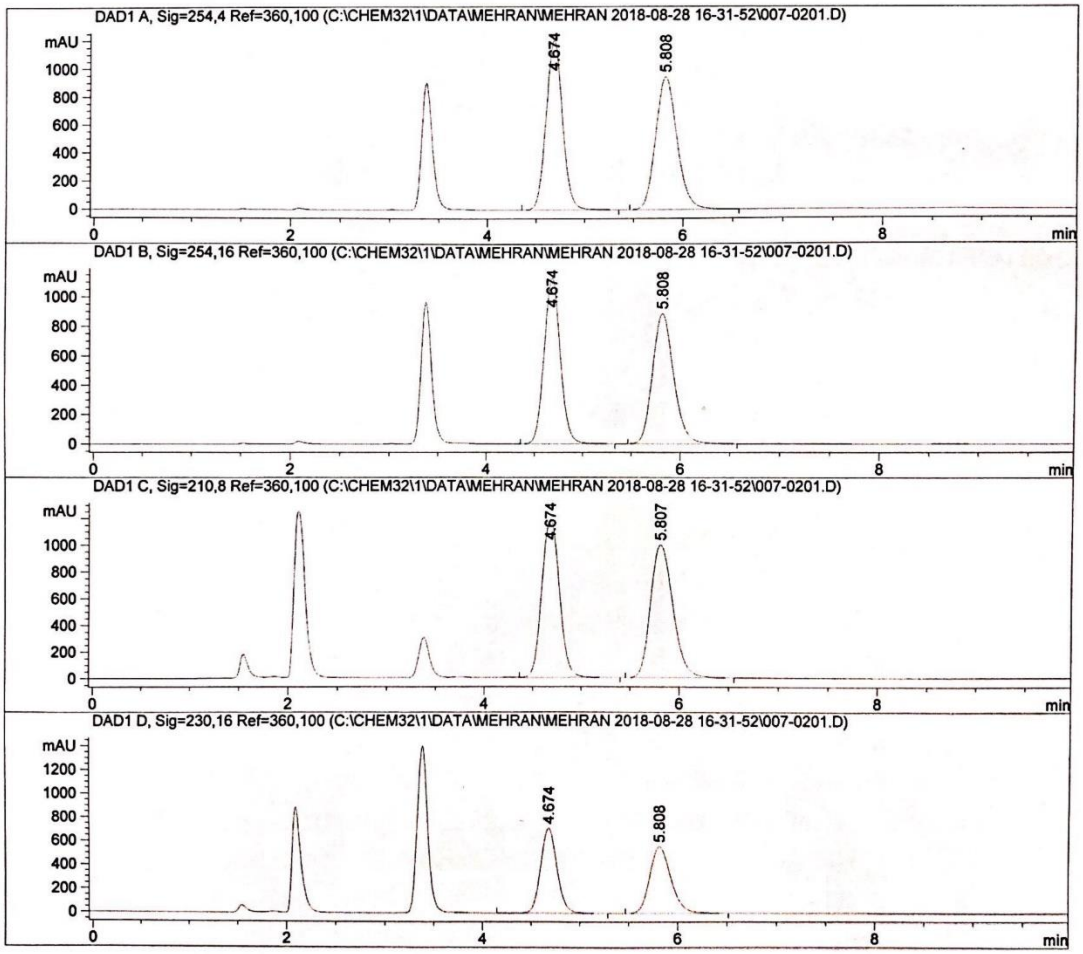
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.695	BB	0.1765	196.22400	17.28266	89.5471
2	5.876	BB	0.2278	22.90540	1.53779	10.4529
Totals :				219.12940	18.82046	

*** End of Report ***

HPLC chromatogram for racemic of compound 10

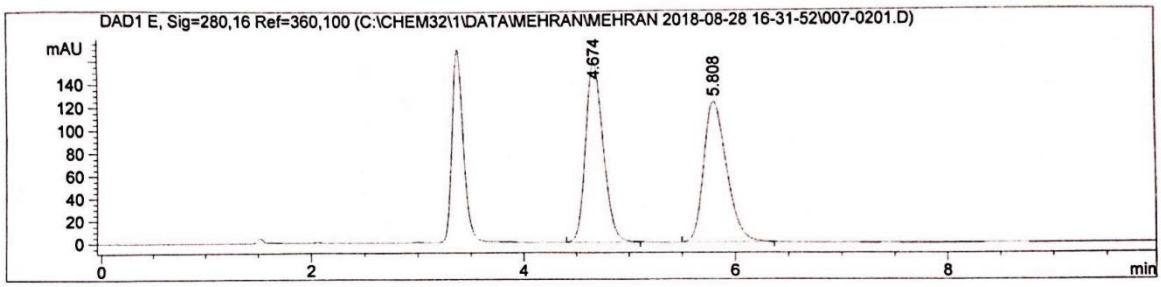
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\007-0201.D
Sample Name: mr-5-29

Acq. Operator : MEHRAN Seq. Line : 2
Acq. Instrument : Instrument 1 Location : Vial 7
Injection Date : 08-28-2018 4:44:06 PM Inj : 1
Inj Volume : 5 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 1 µl
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\MEHRAN.M
Last changed : 08-28-2018 4:31:51 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\007-0201.D\DA.M (MEHRAN.M)
Last changed : 09-26-2018 10:43:16 AM by MEHRAN
Method Info : IC, 10% Isopropanol in hexanes 0.3 ml/min, 1 ul injection, 30 oC



Instrument 1 09-26-2018 10:43:35 AM MEHRAN Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\007-0201.D
Sample Name: mr-5-29



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.674	VB	0.1826	1.40278e4	1197.80774	49.8959
2	5.808	BB	0.2308	1.40863e4	940.36469	50.1041
Totals :				2.81141e4	2138.17242	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.674	VB	0.1826	1.33013e4	1135.94653	49.8938
2	5.808	BB	0.2308	1.33579e4	891.44971	50.1062
Totals :				2.66592e4	2027.39624	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.674	VB	0.2004	1.51040e4	1187.09717	48.9341
2	5.807	BB	0.2489	1.57621e4	994.50830	51.0659
Totals :				3.08661e4	2181.60547	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-28 16-31-52\007-0201.D
Sample Name: mr-5-29

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

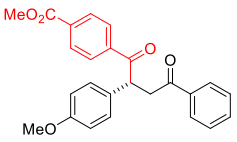
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.674	BB	0.1810	8340.74707	710.47150	49.9866
2	5.808	BB	0.2309	8345.20703	556.78754	50.0134
Totals :				1.66860e4	1267.25903	

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

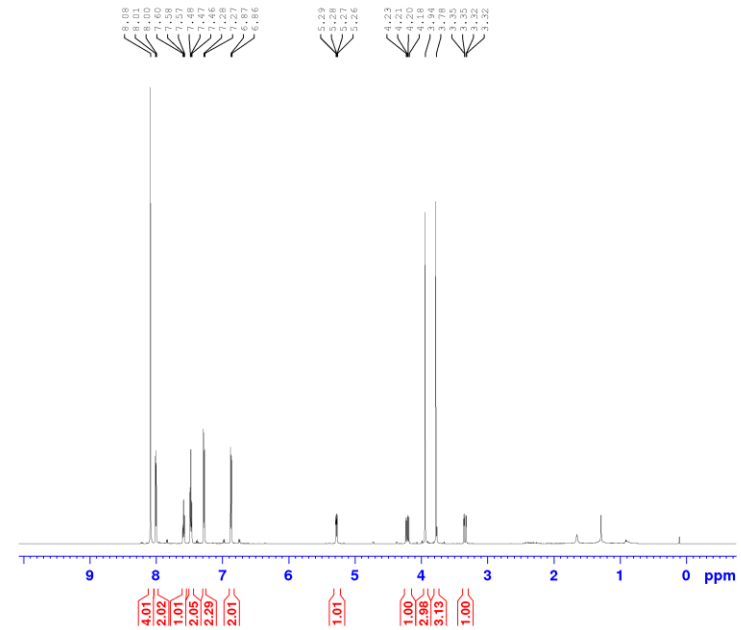
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.674	BB	0.1801	1850.82202	158.65958	49.9009
2	5.808	BB	0.2306	1858.17029	124.18262	50.0991
Totals :				3708.99231	282.84219	

*** End of Report ***

^{1}H NMR and ^{13}C NMR for compound 11

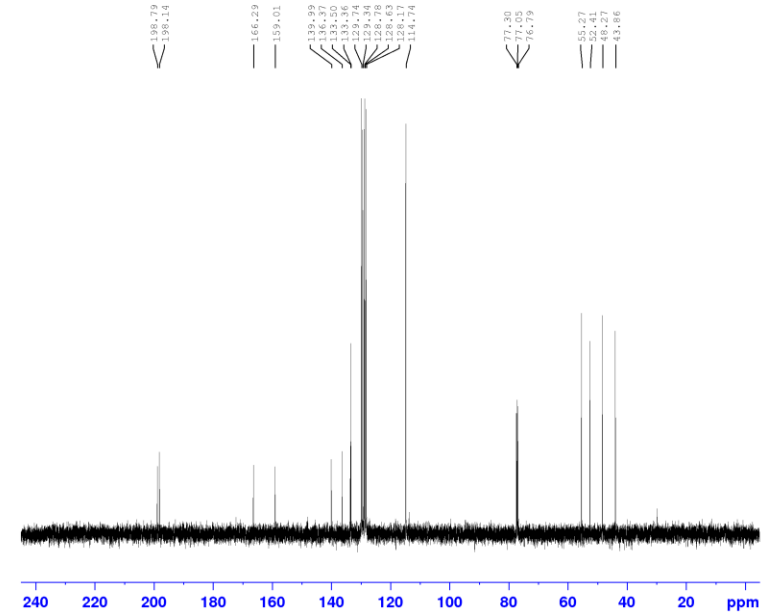


mr-3-193




```
Current Data Parameters
NAME                  mr-3-193 H
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20180819
Time                      13.44 h
INSTRUM                   spect
PROBHD     Z847801_0323 (
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                           8
DS                           2
SWH                   8417.509 Hz
FIDRES                0.256882 Hz
AQ                    3.8928385 sec
RG                        141.9
DW                       59.400 usec
DE                        6.50 usec
TE                       298.0 K
D1                    1.10000002 sec
TD0                           1
SFO1                600.1736010 MHz
NUC1                         1H
P1                       12.50 usec
PLW1                15.00000000 W

F2 - Processing parameters
SI                           65536
SF                  600.1700000 MHz
WDW                             EM
SSB                  0
LB                        0.30 Hz
GB                   0
PC                        1.00
```

mr-3-193

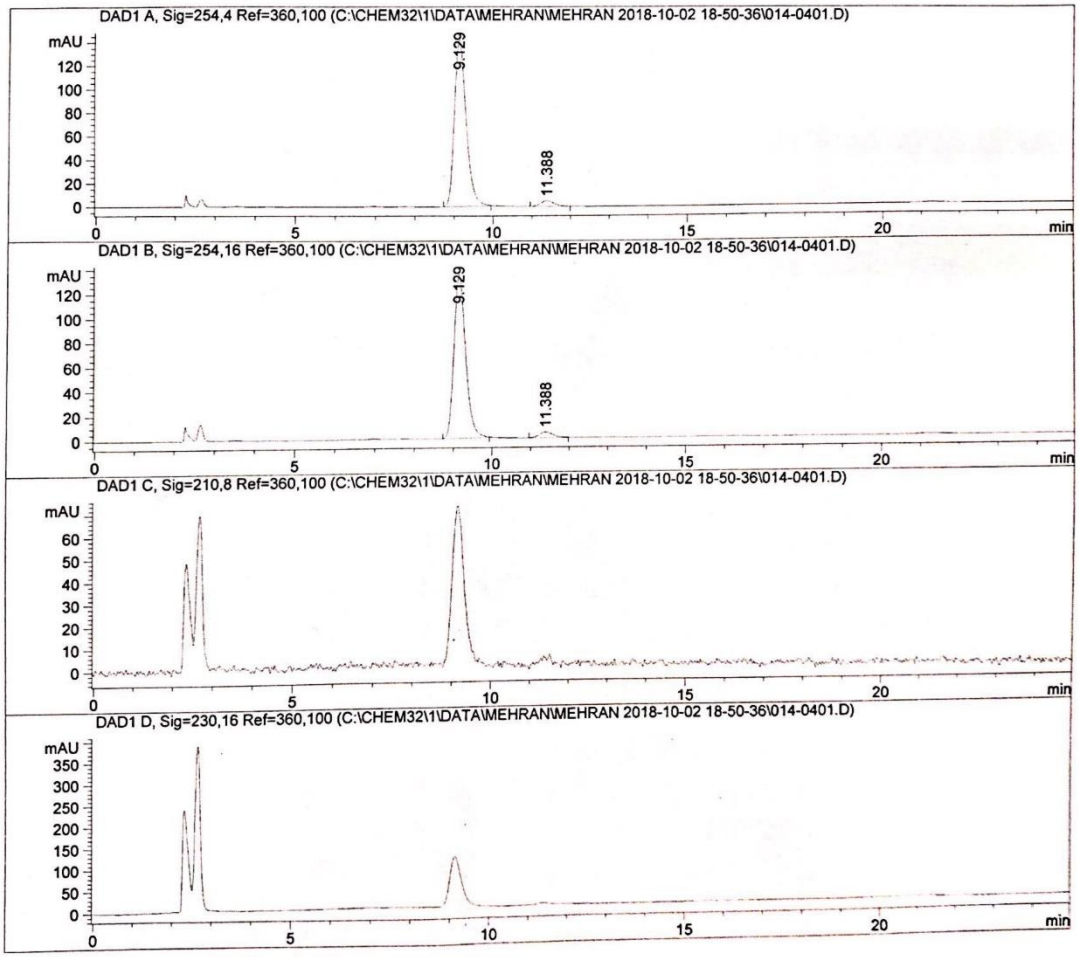



```
Current Data Parameters
NAME                     mr-3-193
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                   20180817
Time                       12.58
INSTRUM                    spect
PROBHD   5 mm PATXI 1H/
PULPROG                    udeft
TD                         65536
SOLVENT                    CDCl3
NS                           250
DS                             4
SWH                  31446.541 Hz
FIDRES                0.479836 Hz
AQ                    1.0420223 sec
RG                         32768
DW                        15.900 usec
DE                         6.50 usec
TE                        296.7 K
D1                    3.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec
D20                 240.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                          9.50 usec
P12                      2000.00 usec
P26                       500.00 usec
PL1                       -6.00 dB
PL1W            300.000000000 W
SFO1             125.8231760 MHz
SP2                        2.60 dB
SP8                        2.60 dB
SFNAM[2]     Crp60comp.4
SFNAM[8] Crp60,0.5,20.1
SPOAL2                     0.500
SPOAL8                     0.500
SPOFFS2  0 Hz
SPOFFS8  0 Hz

======== CHANNEL f2 ========
CPDPRG[2            waltz16
NUC2                         1H
PCPD2                    80.00 usec
PL2                        1.00 dB
PL12                      19.06 dB
PL2W             9.97631168 W
PL12W            0.15594450 W
SFO2             500.3320013 MHz

F2 - Processing parameters
SI                           65536
SF                   125.8080790 MHz
WDW                             EM
SSB                  0
LB                        1.00 Hz
GB                   0
PC                        1.40
```

HPLC chromatogram for compound 11

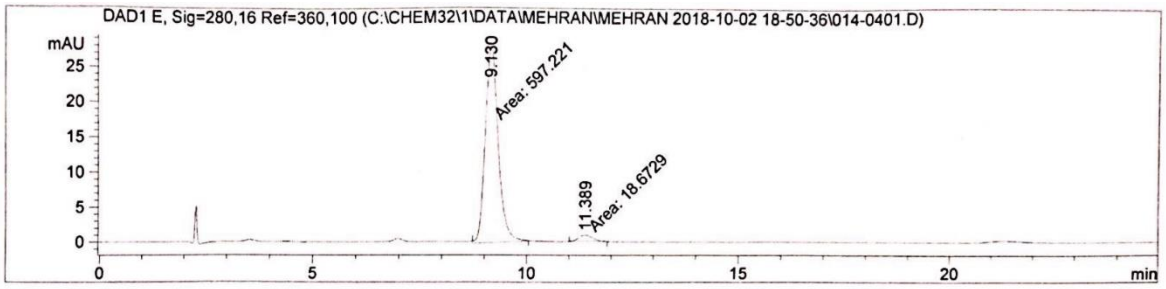
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\014-0401.D
Sample Name: mr-3-193

```
==========================================================================
Acq. Operator   : MEHRAN                          Seq. Line :   4
Acq. Instrument : Instrument 1                    Location : Vial 14
Injection Date  : 10-02-2018 8:10:13 PM               Inj :   1
                                                 Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\MEHRAN.M
Last changed    : 10-02-2018 6:50:35 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\014-0401.D\DA.M (
                  MEHRAN.M)
Last changed    : 02-28-2019 12:00:01 PM by Hemkalyan
Method Info     : IB, 50% Isopropanol in hexanes  0.2 ml/min, 1 ul injection, 30 oC
```



Instrument 1 02-28-2019 12:00:39 PM Hemkalyan

Page 1 of 3




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

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.129 BB    0.3200 2958.65771  141.45621  96.1843
   2  11.388 BB    0.3648  117.37246    4.87625   3.8157

Totals :                  3076.03017  146.33245


Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.129 BB    0.3199 2839.48267  135.84123  96.1811
   2  11.388 BB    0.3669  112.74178    4.68289   3.8189

Totals :                  2952.22445  140.52412


Signal 3: DAD1 C, Sig=210,8 Ref=360,100


Signal 4: DAD1 D, Sig=230,16 Ref=360,100


Signal 5: DAD1 E, Sig=280,16 Ref=360,100
```

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\014-0401.D
Sample Name: mr-3-193

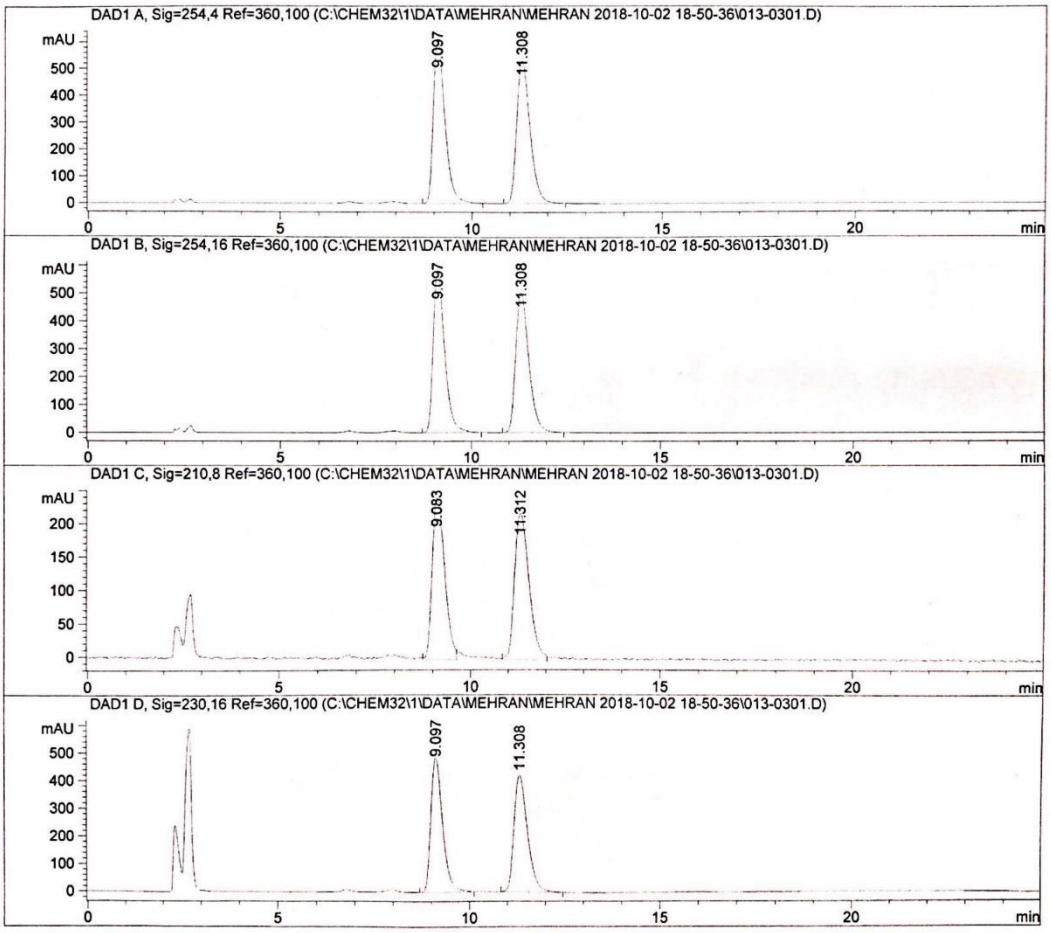
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.130	MM	0.3537	597.22058	28.13994	96.9682
2	11.389	MM	0.3560	18.67290	8.74171e-1	3.0318
Totals :				615.89348	29.01411	

*** End of Report ***

HPLC chromatogram for racemic of compound 11

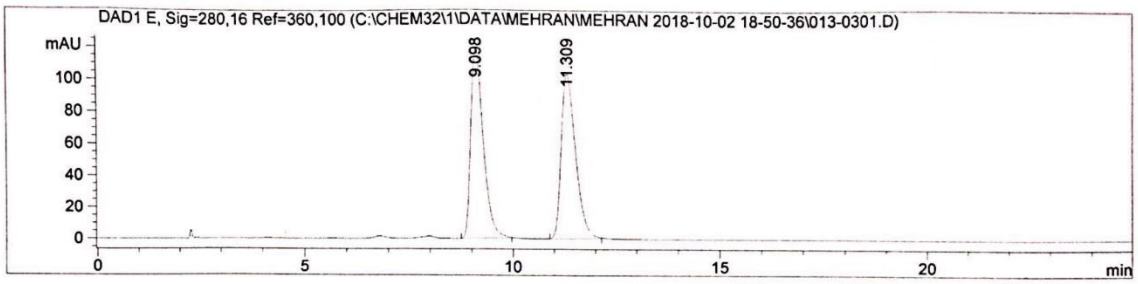
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\013-0301.D
Sample Name: mr-5-49

```
==========================================================================
Acq. Operator   : MEHRAN                          Seq. Line :   3
Acq. Instrument : Instrument 1                    Location : Vial 13
Injection Date  : 10-02-2018 7:43:58 PM               Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\MEHRAN.M
Last changed    : 10-02-2018 6:50:35 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\013-0301.D\DA.M (
                  MEHRAN.M)
Last changed    : 02-28-2019 11:59:06 AM by Hemkalyan
Method Info     : IB, 50% Isopropanol in hexanes  0.2 ml/min, 1 ul injection, 30 oC
```



Instrument 1 02-28-2019 11:59:33 AM Hemkalyan Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\013-0301.D
Sample Name: mr-5-49



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.097	BB	0.3232	1.29049e4	609.08429	50.1708
2	11.308	BB	0.3743	1.28171e4	526.04205	49.8292
Totals :				2.57220e4	1135.12634	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.097	BB	0.3230	1.23983e4	585.61292	50.1669
2	11.308	BB	0.3741	1.23158e4	505.68427	49.8331
Totals :				2.47140e4	1091.29718	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.083	VV	0.3153	5662.28809	243.53091	48.7500
2	11.312	VV	0.3400	5952.65234	221.15103	51.2500
Totals :				1.16149e4	464.68195	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-10-02 18-50-36\013-0301.D
Sample Name: mr-5-49

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

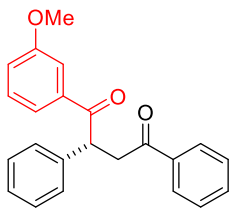
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.097	BB	0.3229	1.02980e4	482.75662	49.7147
2	11.308	BB	0.3766	1.04162e4	421.09448	50.2853
Totals :				2.07142e4	903.85110	

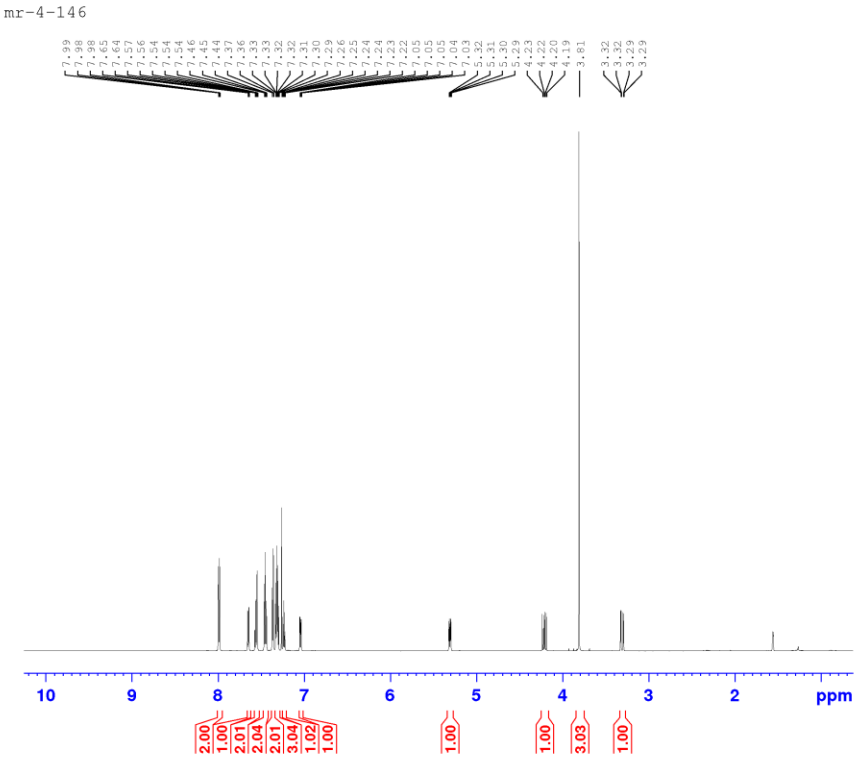
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.098	BB	0.3214	2526.13892	120.11795	50.1480
2	11.309	BB	0.3725	2511.23169	103.72657	49.8520
Totals :				5037.37061	223.84452	

*** End of Report ***

^{1}H NMR for compound 12



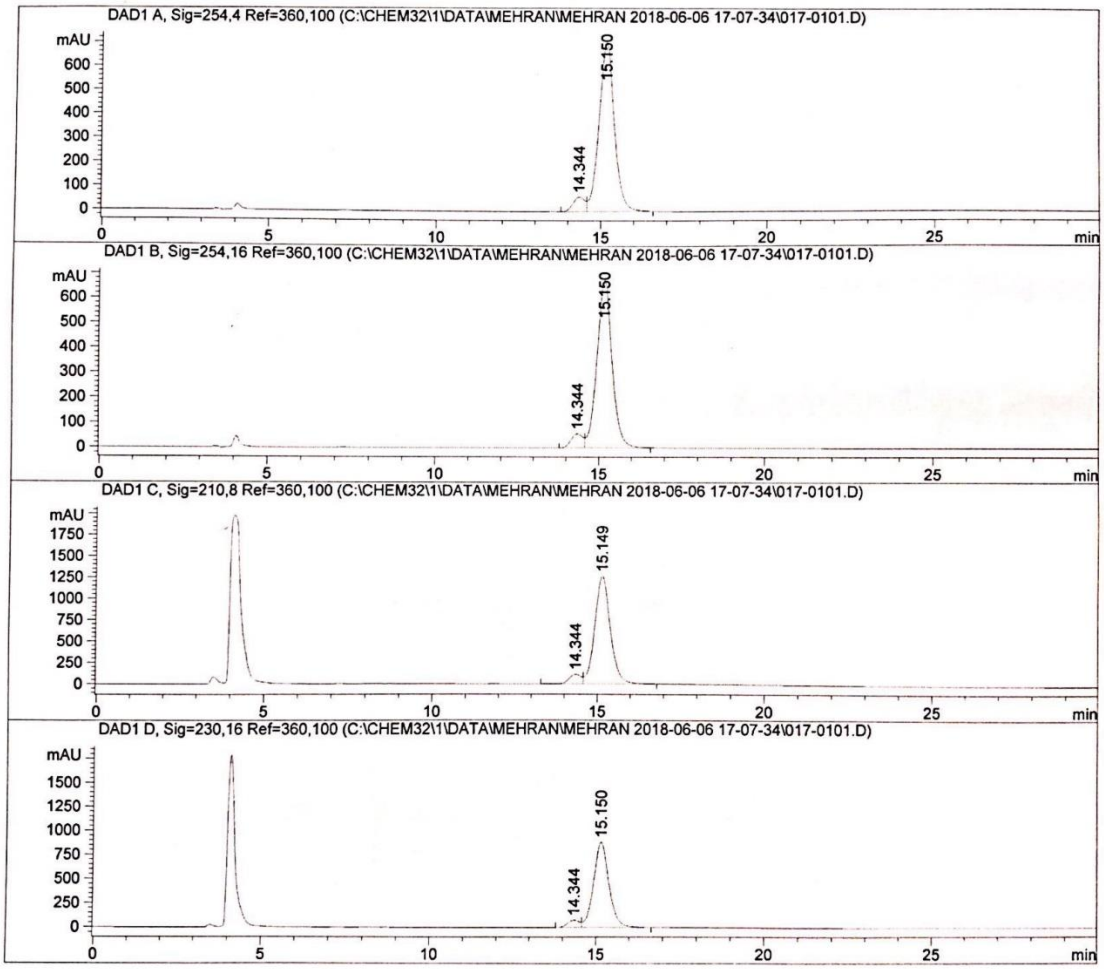



```
Current Data Parameters
NAME                  mr-4-146
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_               20180605
Time                   14.41 h
INSTRUM                spect
PROBHD    Z847801_0323 (
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                           8
DS                           2
SWH                 7331.378 Hz
FIDRES              0.447472 Hz
AQ                  2.2347777 sec
RG                     195.93
DW                     68.200 usec
DE                      6.50 usec
TE                     300.2 K
D1                 10.00000000 sec
TD0                          1
SFO1               600.1735511 MHz
NUC1                        1H
P1                     12.50 usec
PLW1               15.00000000 W

F2 - Processing parameters
SI                       32768
SF                 600.1700146 MHz
WDW                         EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

HPLC chromatogram for compound 12

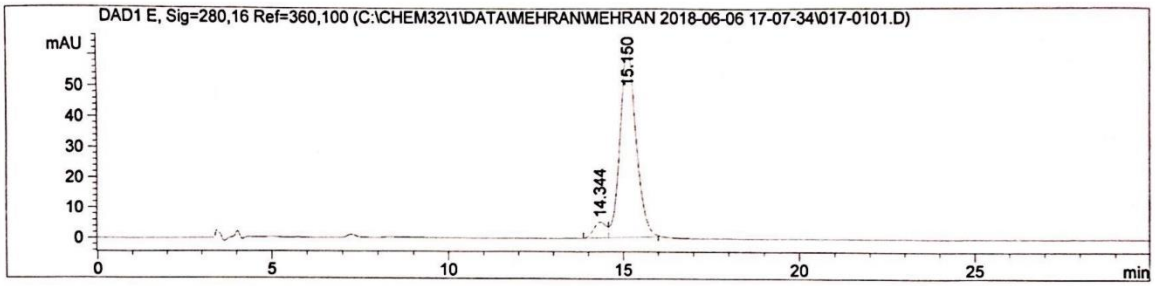
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-06-06 17-07-34\017-0101.D
Sample Name: mr-4-146

```
==================================================================
Acq. Operator   : Mehran                          Seq. Line :   1
Acq. Instrument : Instrument 1                     Location : Vial 17
Injection Date  : 06-06-2018 5:08:33 PM                Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-06-06 17-07-34\MEHRAN.M
Last changed    : 06-06-2018 5:09:43 PM by Mehran
                  (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-06-06 17-07-34\017-0101.D\DA.M (
                  MEHRAN.M)
Last changed    : 09-26-2018 12:11:18 PM by MEHRAN
Method Info     : IA, 10% Isopropanol in hexane  0.13ml/min, 1 ul injection, 30 oC
```



Instrument 1 09-26-2018 12:11:32 PM MEHRAN Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-06-06 17-07-34\017-0101.D
Sample Name: mr-4-146



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.344	BV	0.3846	1484.54077	59.59650	6.1756
2	15.150	VB	0.4808	2.25542e4	702.07813	93.8244
Totals :				2.40387e4	761.67463	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.344	BV	0.3846	1431.86450	57.48893	6.1570
2	15.150	VB	0.4801	2.18240e4	680.51300	93.8430
Totals :				2.32558e4	738.00193	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.344	BV	0.3877	2835.87793	111.87664	6.4125
2	15.149	VB	0.4918	4.13885e4	1264.58362	93.5875
Totals :				4.42243e4	1376.46026	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-06-06 17-07-34\017-0101.D
Sample Name: mr-4-146

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.344	BV	0.3848	1847.48413	74.13074	6.1434
2	15.150	VB	0.4797	2.82250e4	881.19055	93.8566
Totals :				3.00724e4	955.32129	

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

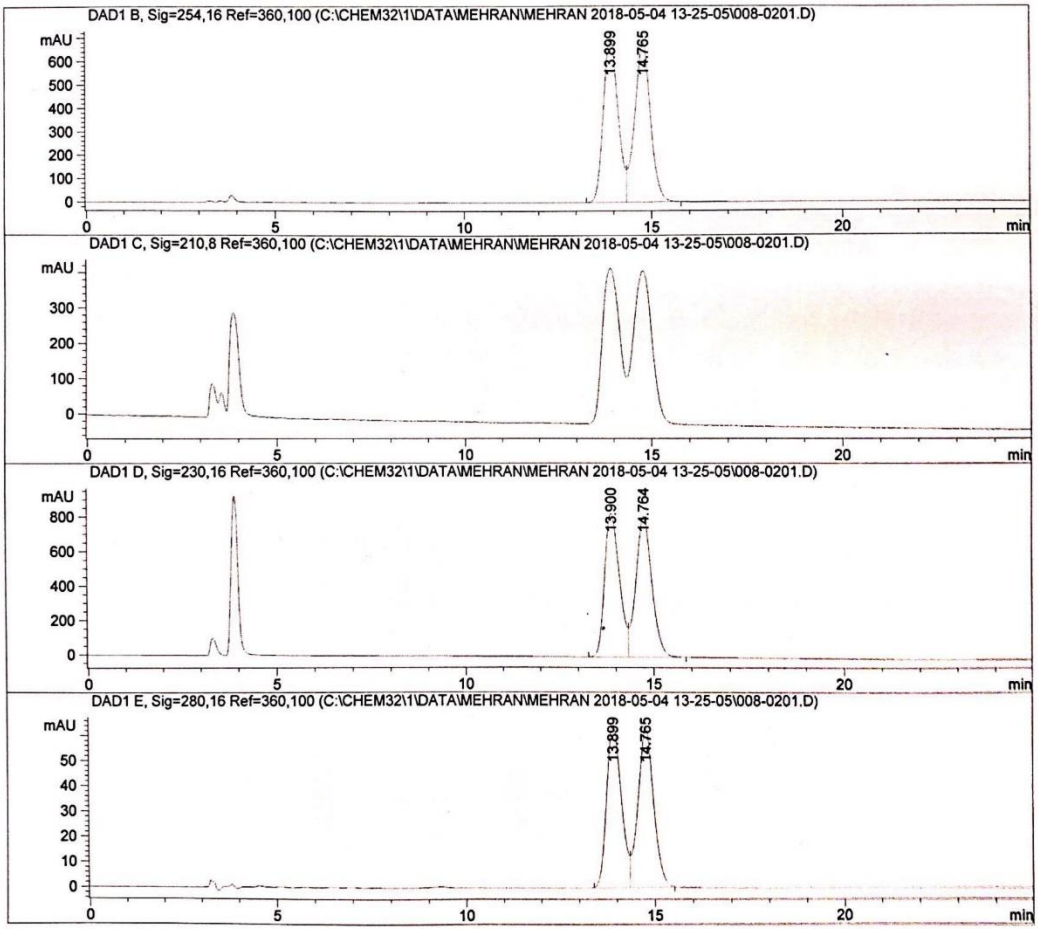
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.344	BV	0.3791	126.79607	5.15292	6.0369
2	15.150	VB	0.4744	1973.55444	62.49875	93.9631
Totals :				2100.35051	67.65167	

*** End of Report ***

HPLC chromatogram for racemic of compound 12

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-05-04 13-25-05\008-0201.D
Sample Name: mr-4-132

```
======================================================================
Acq. Operator   : MEHRAN                        Seq. Line :   2
Acq. Instrument : Instrument 1                   Location : Vial 8
Injection Date  : 05-04-2018 1:52:25 PM             Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-05-04 13-25-05\MEHRAN.M
Last changed    : 05-04-2018 1:25:03 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-05-04 13-25-05\008-0201.D\DA.M (
                  MEHRAN.M)
Last changed    : 09-26-2018 12:00:31 PM by MEHRAN
Method Info     : IA, 10% Isopropanol in hexane  0.13ml/min, 1 ul injection, 30 oC
```



Instrument 1 09-26-2018 12:01:14 PM MEHRAN Page 1 of 2

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-05-04 13-25-05\008-0201.D
Sample Name: mr-4-132

==========

Area Percent Report

==========

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

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.899	BV	0.4178	1.87833e4	693.81665	48.9989
2	14.765	VB	0.4342	1.95508e4	678.38104	51.0011
Totals :				3.83340e4	1372.19769	

Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.900	BV	0.4264	2.28561e4	832.17236	48.9503
2	14.764	VB	0.4473	2.38363e4	814.91333	51.0497
Totals :				4.66924e4	1647.08569	

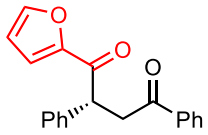
Signal 4: DAD1 E, Sig=280,16 Ref=360,100

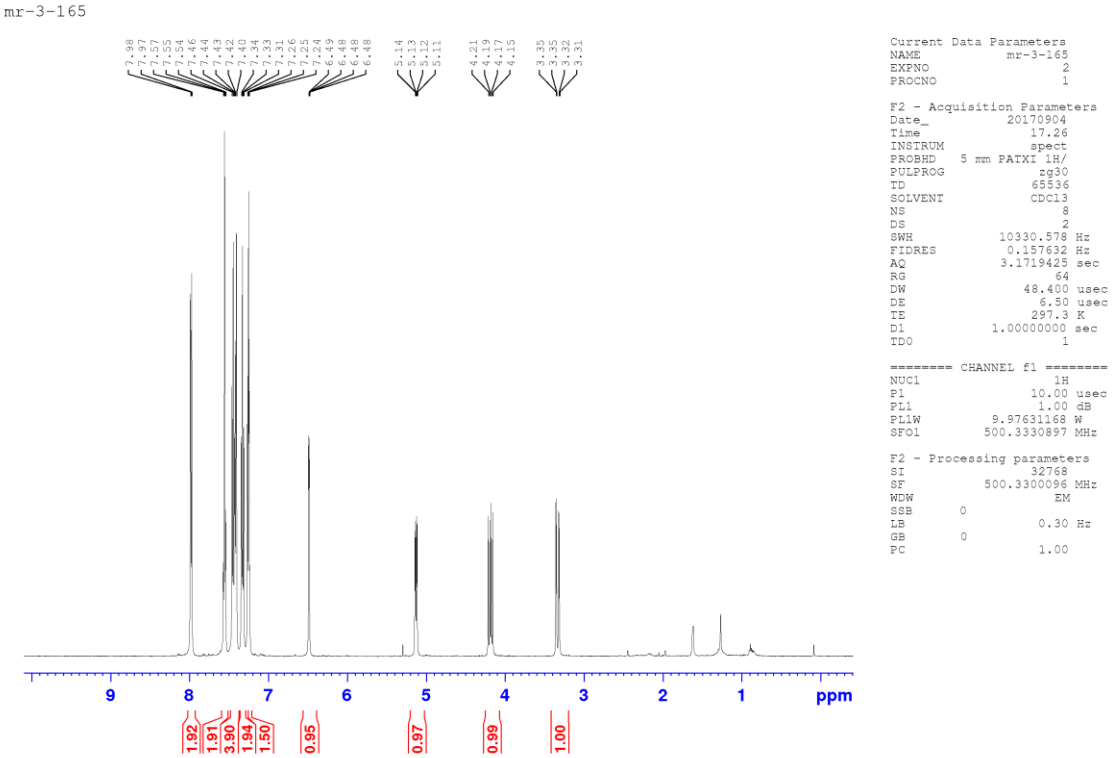
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.899	BV	0.4170	1729.51245	64.05817	49.0811
2	14.765	VB	0.4344	1794.26904	62.60539	50.9189
Totals :				3523.78149	126.66356	

==========

*** End of Report ***

^{1}H NMR for compound 13





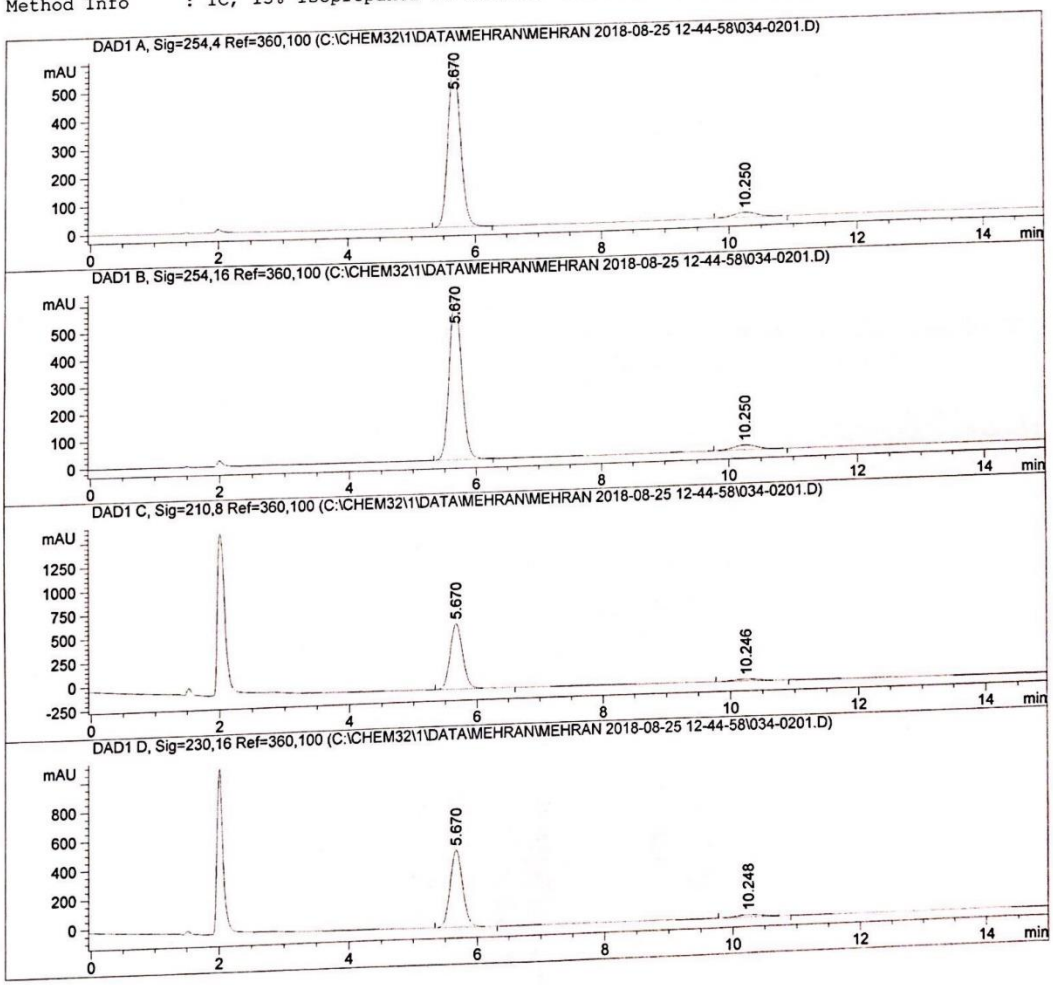

```
Current Data Parameters
NAME                  mr-3-165
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20170904
Time                     17.26
INSTRUM                  spect
PROBHD    5 mm PATXI 1H/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                           8
DS                           2
SWH                10330.578 Hz
FIDRES              0.157632 Hz
AQ                  3.1719425 sec
RG                          64
DW                     48.400 usec
DE                      6.50 usec
TE                     297.3 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                      10.00 usec
PL1                      1.00 dB
PL1W               9.97631168 W
SFO1             500.3330897 MHz

F2 - Processing parameters
SI                       32768
SF                 500.3300096 MHz
WDW                         EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```

HPLC chromatogram for compound 13

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\034-0201.D
Sample Name: mr-3-165

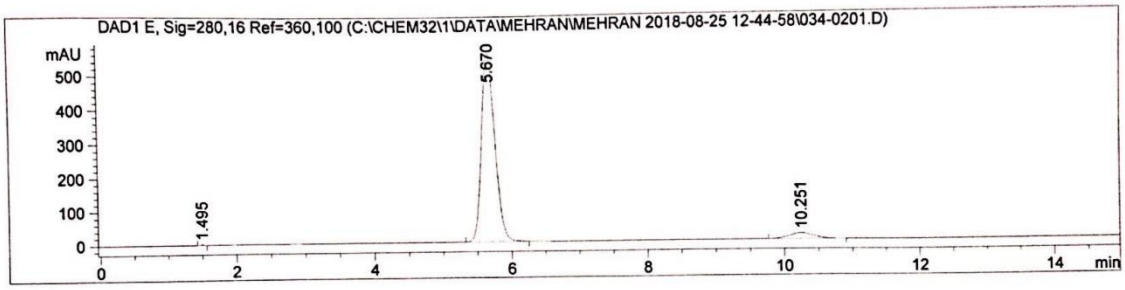
Acq. Operator : MEHRAN
Acq. Instrument : Instrument 1
Injection Date : 08-25-2018 1:02:09 PM
Seq. Line : 2
Location : Vial 34
Inj : 1
Inj Volume : 5 µl
Actual Inj Volume : 1 µl

Different Inj Volume from Sequence !
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\MEHRAN.M
Last changed : 08-25-2018 12:44:56 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\034-0201.D\DA.M (MEHRAN.M)
Last changed : 09-25-2018 1:08:28 PM by MEHRAN
Method Info : IC, 15% Isopropanol in hexanes 0.3 ml/min, 1 ul injection, 30 oC



Instrument 1 09-25-2018 1:08:43 PM MEHRAN

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\034-0201.D
Sample Name: mr-3-165



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.670	BB	0.2105	7920.42969	582.94159	94.8193
2	10.250	BB	0.3858	432.75278	17.30243	5.1807
Totals :				8353.18246	600.24402	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.670	BB	0.2105	8388.29980	617.40057	94.8166
2	10.250	BB	0.3880	458.56589	18.32467	5.1834
Totals :				8846.86569	635.72524	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.670	BB	0.2145	9494.99414	690.17657	94.6438
2	10.246	BB	0.3833	537.34863	21.37097	5.3562
Totals :				1.00323e4	711.54754	

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\034-0201.D
Sample Name: mr-3-165

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.670	BB	0.2105	7056.80908	519.46533	94.8176
2	10.248	BB	0.3875	385.69812	15.43796	5.1824
Totals :				7442.50720	534.90329	

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

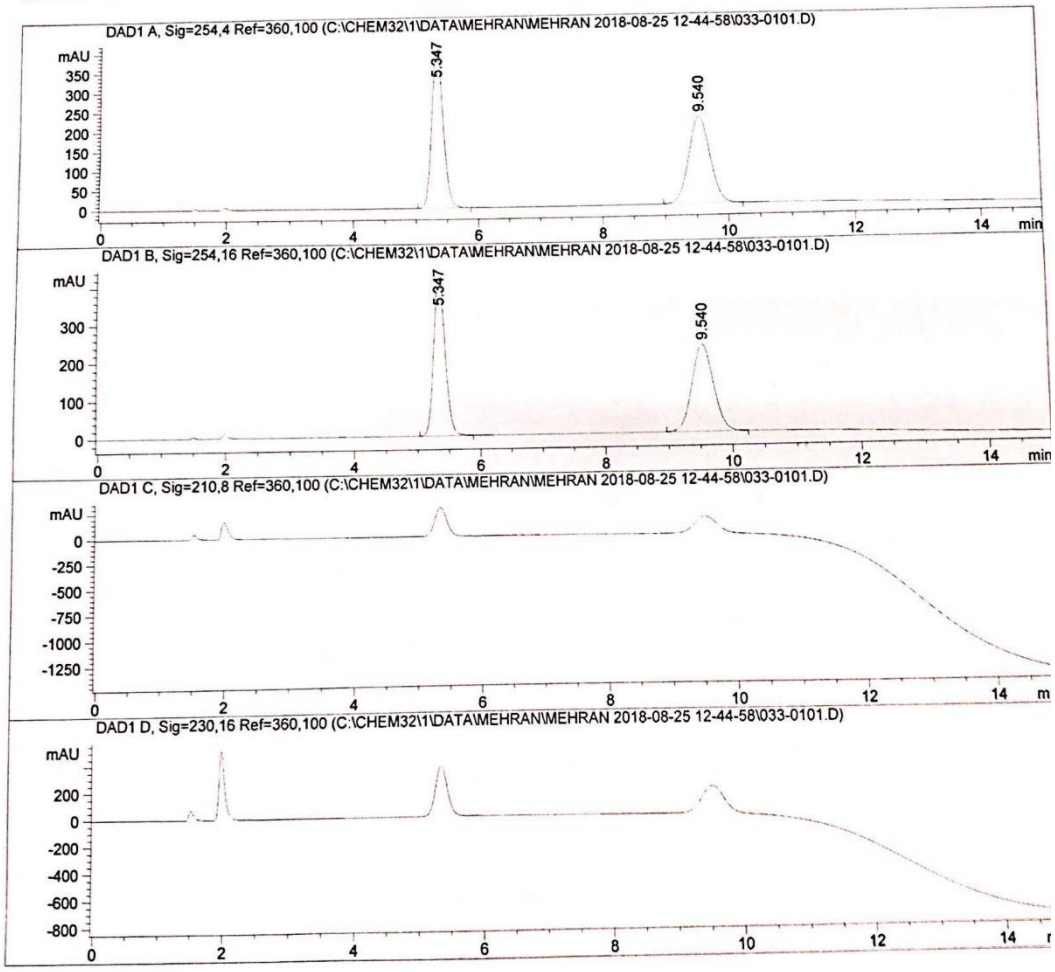
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.495	BV	0.0566	7.12647	2.04830	0.0880
2	5.670	BB	0.2109	7673.75049	563.57587	94.7273
3	10.251	BB	0.3870	420.01266	16.83641	5.1848
Totals :				8100.88962	582.46057	

*** End of Report ***

HPLC chromatogram for racemic of compound 13

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\033-0101.D
Sample Name: mr-4-205

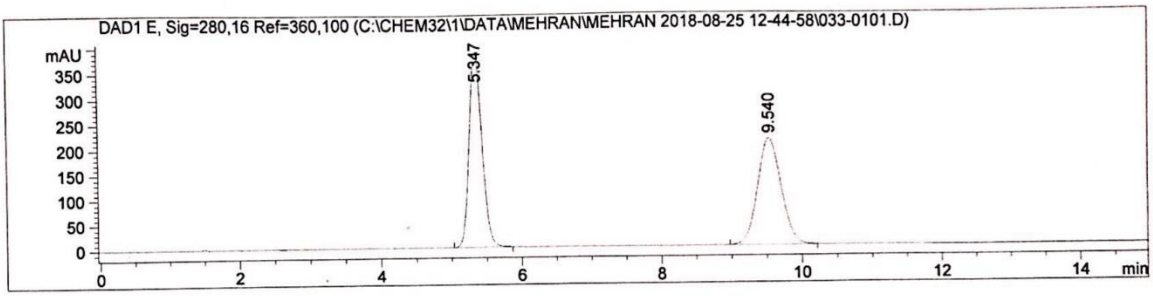
Acq. Operator	: MEHRAN	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 33
Injection Date	: 08-25-2018 12:46:18 PM	Inj	: 1
		Inj Volume	: 5 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 1 µl
Acq. Method	: C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\MEHRAN.M		
Last changed	: 08-25-2018 12:44:56 PM by MEHRAN		
Analysis Method	: C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\033-0101.D\DA.M (MEHRAN.M)		
Last changed	: 09-25-2018 1:07:23 PM by MEHRAN		
Method Info	: IC, 15% Isopropanol in hexanes 0.3 ml/min, 1 ul injection, 30 oC		



strument 1 09-25-2018 1:07:48 PM MEHRAN

Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\033-0101.D
Sample Name: mr-4-205



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.347	BB	0.1961	5097.45557	401.42773	49.9598
2	9.540	BB	0.3616	5105.65283	219.33453	50.0402
Totals :				1.02031e4	620.76227	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.347	BB	0.1961	5400.17285	425.26550	49.9392
2	9.540	BB	0.3618	5413.31445	232.39946	50.0608
Totals :				1.08135e4	657.66496	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

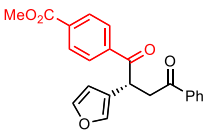
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-25 12-44-58\033-0101.D
Sample Name: mr-4-205

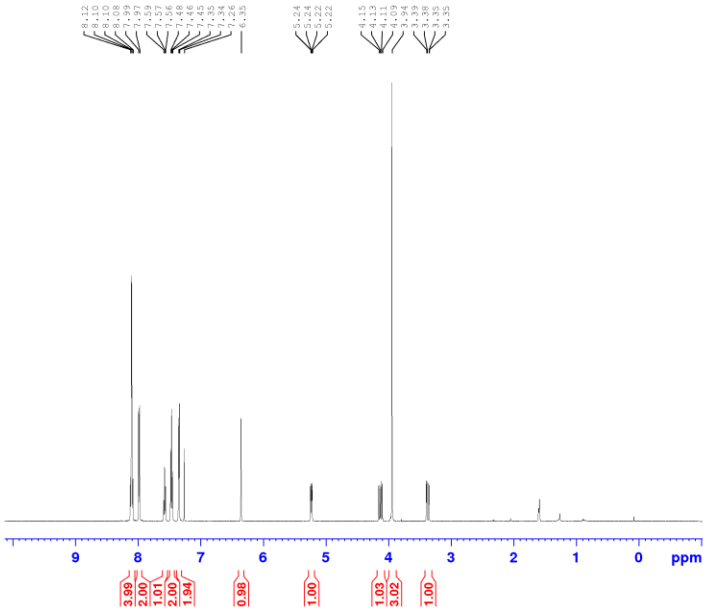
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.347	BB	0.1963	4952.77100	389.56061	49.9499
2	9.540	BB	0.3616	4962.69678	213.17010	50.0501
Totals :				9915.46777	602.73071	

*** End of Report ***

^{1}H NMR and ^{13}C NMR for compound 14

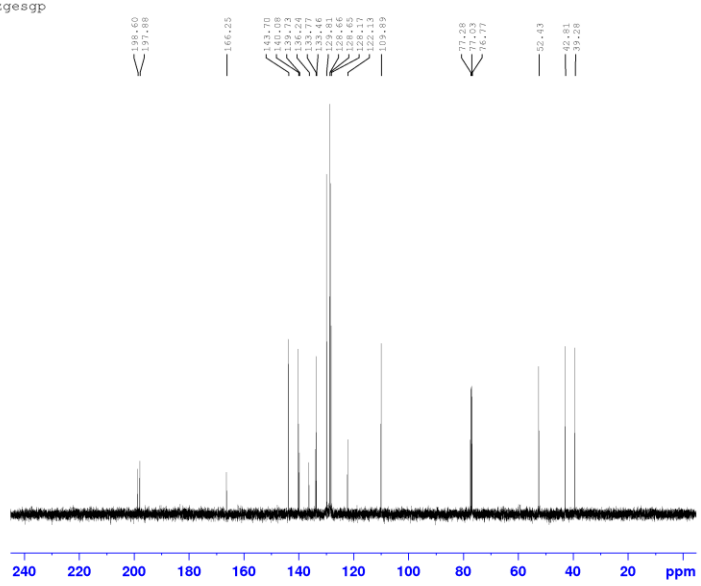


mr-4-150




```
Current Data Parameters
NAME                  mr-4-150
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_               20180608
Time                   11.36
INSTRUM                spect
PROBHD    5 mm PATXI 1H/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                7002.801 Hz
FIDRES            0.106854 Hz
AQ                4.6792703 sec
RG                       4
DW                  71.400 usec
DE                   6.50 usec
TE                  297.6 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                      10.00 usec
PL1                      1.00 dB
PLW1              9.97631168 W
SFO1            500.3330020 MHz

F2 - Processing parameters
SI                       65536
SF              500.3300122 MHz
WDW                         EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```

zgesgp

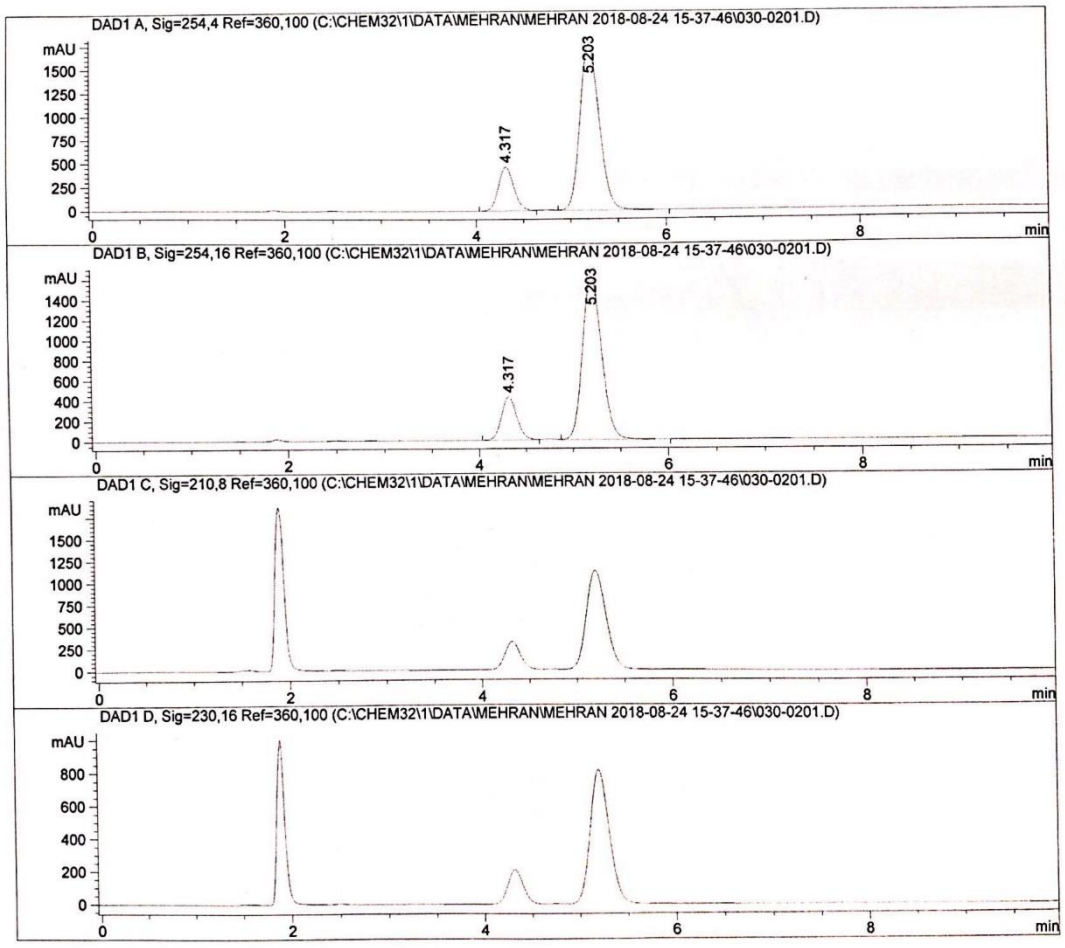



```
Current Data Parameters
NAME                  mr-4-150
EXPNO                        3
PROCNO                       1

F2 - Acquisition Parameters
Date_               20180608
Time                   11.20
INSTRUM                spect
PROBHD    5 mm PATXI 1H/
PULPROG                udeft
TD                    65536
SOLVENT               CDCl3
NS                      300
DS                        4
SWH               31446.541 Hz
FIDRES            0.479836 Hz
AQ                1.0420223 sec
RG                    32768
DW                  15.900 usec
DE                   6.50 usec
TE                  298.3 K
D1                3.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
D20             240.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       9.50 usec
P12                   2000.00 usec
P26                    500.00 usec
PL1                     -6.00 dB
PLW1            300.00000000 W
SFO1            125.8231760 MHz
SF2                      2.60 dB
SF8                      2.60 dB
SFNAM[2]     Crp60comp.4
SFNAM[8]  Crp60,0.5,20.1
SPOAL2                   0.500
SPOAL8                   0.500
SPOFFS2   0 Hz
SPOFFS8   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                       1H
PCPD2                 80.00 usec
PL2                     1.00 dB
PL12                   19.06 dB
PL2W              9.97631168 W
PL12W             0.15594450 W
SFO2            500.3320013 MHz

F2 - Processing parameters
SI                       65536
SF              125.8080791 MHz
WDW                         EM
SSB          0
LB                       1.00 Hz
GB           0
PC                       1.00
```

HPLC chromatogram for compound 14

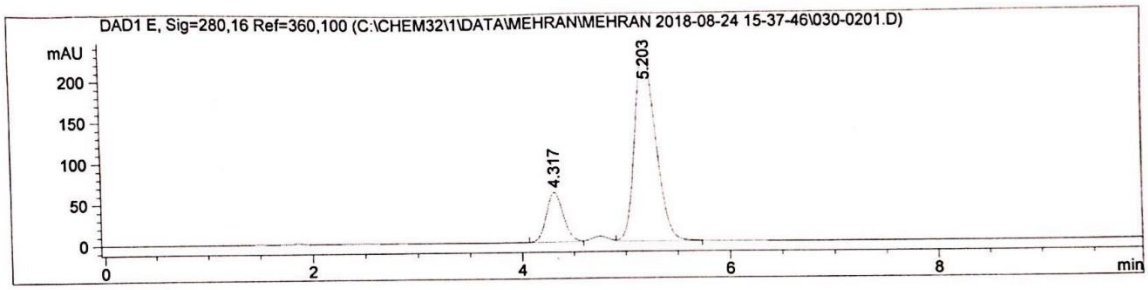
Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\030-0201.D
Sample Name: mr-4-150

Acq. Operator : MEHRAN
Acq. Instrument : Instrument 1
Injection Date : 08-24-2018 3:50:03 PM
Seq. Line : 2
Location : Vial 30
Inj : 1
Inj Volume : 5 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 1 µl
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\MEHRAN.M
Last changed : 08-24-2018 3:37:44 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\030-0201.D\DA.M (MEHRAN.M)
Last changed : 09-25-2018 1:12:08 PM by MEHRAN
Method Info : IC, 35% Isopropanol in hexanes 0.3 ml/min, 1 ul injection, 30 oC



Instrument 1 09-25-2018 1:12:23 PM MEHRAN Page 1 of 3

Data File: C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\030-0201.D
Sample Name: mr-4-150



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.317	BV	0.1773	5263.49658	460.71036	17.6618
2	5.203	VB	0.2206	2.45380e4	1739.22229	82.3382
Totals :				2.98015e4	2199.93265	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.317	BV	0.1773	4926.72314	431.27863	17.6459
2	5.203	VB	0.2204	2.29931e4	1631.96265	82.3541
Totals :				2.79199e4	2063.24127	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\030-0201.D
Sample Name: mr-4-150

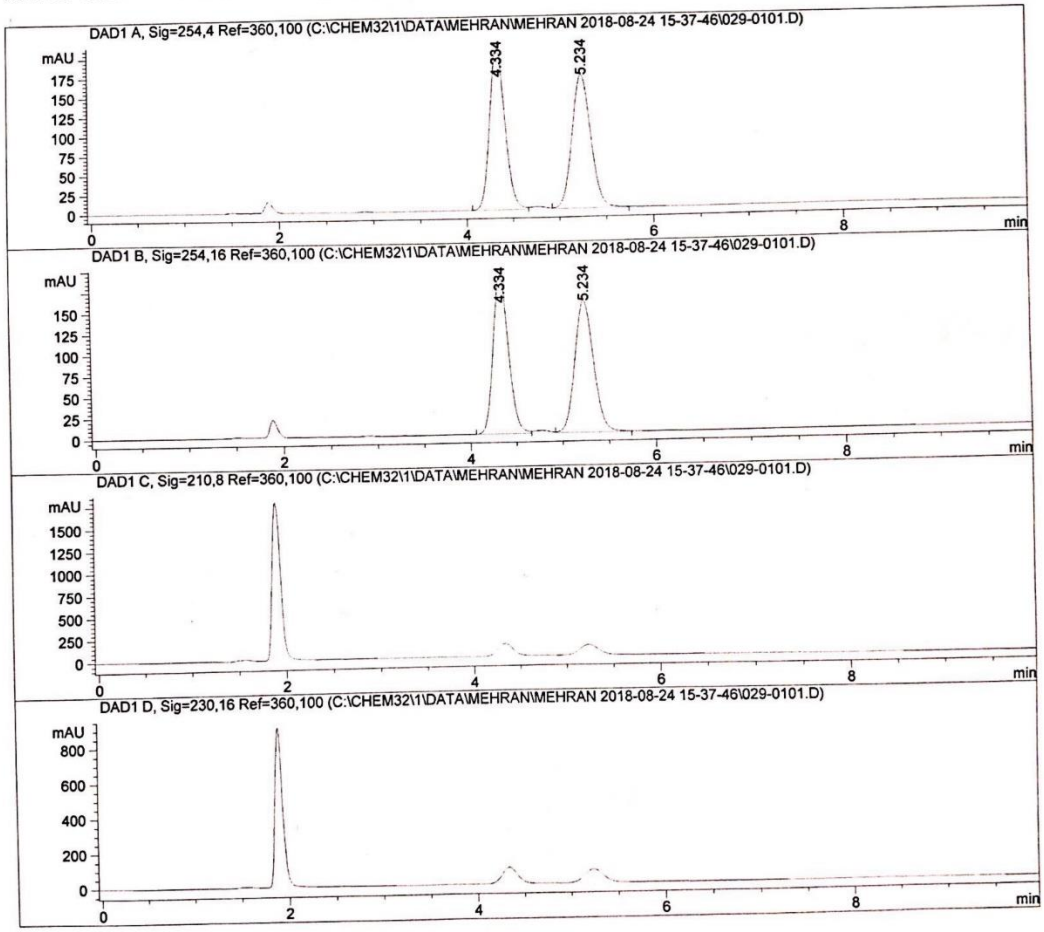
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.317	BV	0.1770	693.66779	60.85649	17.5052
2	5.203	VB	0.2183	3268.96655	234.99359	82.4948
Totals :				3962.63434	295.85008	

*** End of Report ***

HPLC chromatogram for racemic of compound 14

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\029-0101.D
Sample Name: mr-4-203

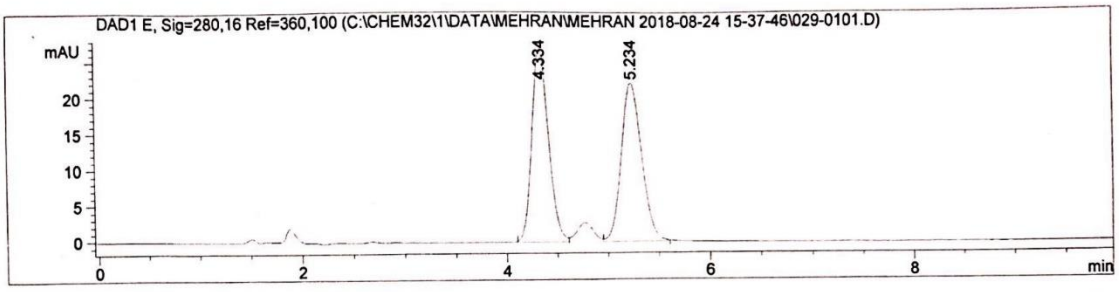
Acq. Operator	: MEHRAN	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 29
Injection Date	: 08-24-2018 3:39:08 PM	Inj	: 1
		Inj Volume	: 5 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 1 µl
Acq. Method	: C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\MEHRAN.M		
Last changed	: 08-24-2018 3:37:44 PM by MEHRAN		
Analysis Method	: C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\029-0101.D\DA.M (MEHRAN.M)		
Last changed	: 08-24-2018 3:37:44 PM by MEHRAN		
Method Info	: IC, 35% Isopropanol in hexanes 0.3 ml/min, 1 ul injection, 30 oC		



Instrument 1 09-25-2018 1:11:30 PM MEHRAN

Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\029-0101.D
Sample Name: mr-4-203



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.334	BV	0.1784	2353.76001	204.37337	49.9063
2	5.234	VB	0.2171	2362.59961	169.02751	50.0937

Totals : 4716.35962 373.40088

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.334	BV	0.1783	2203.00000	191.31328	49.9023
2	5.234	VB	0.2171	2211.62256	158.22250	50.0977

Totals : 4414.62256 349.53578

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

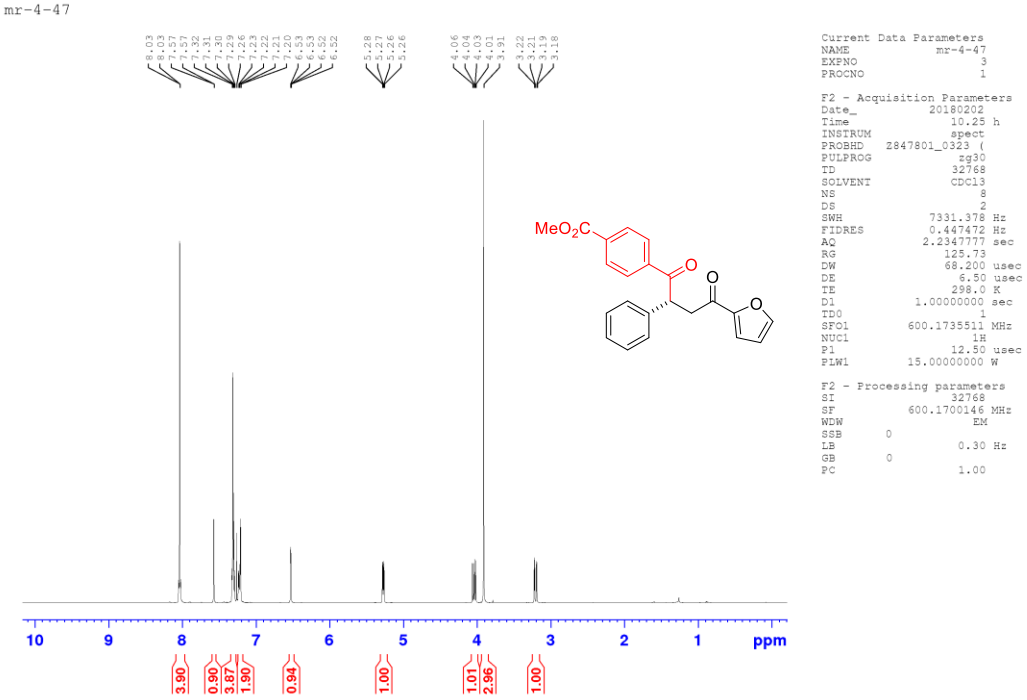
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 15-37-46\029-0101.D
Sample Name: mr-4-203

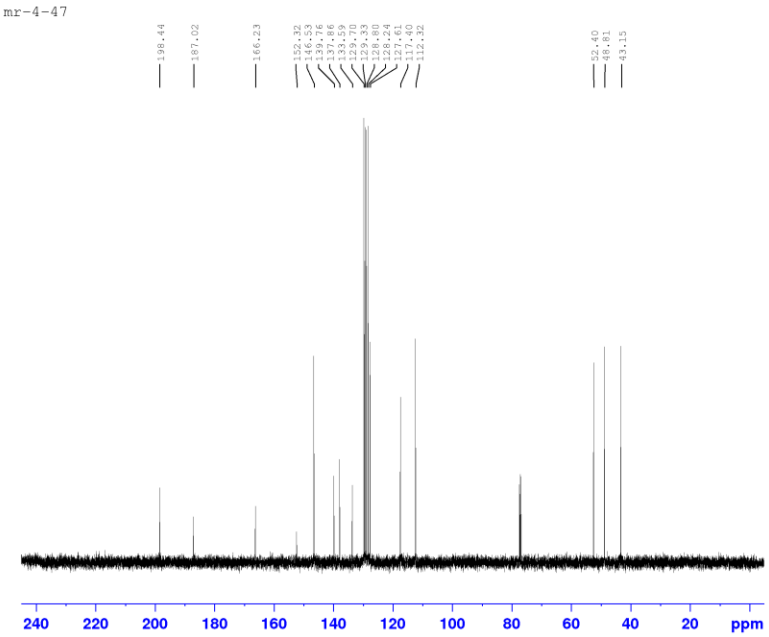
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.334	BV	0.1780	310.41705	27.02706	49.9611
2	5.234	VB	0.2164	310.90009	22.33193	50.0389
Totals :				621.31714	49.35899	

*** End of Report ***

^{1}H NMR and ^{13}C NMR for compound 15




```
Current Data Parameters
NAME                  mr-4-47
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180202
Time                   10.25 h
INSTRUM                spect
PROBHD    Z847801_0323 (
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                7331.378 Hz
FIDRES             0.447472 Hz
AQ                 2.2347777 sec
RG                    125.73
DW                    68.200 usec
DE                     6.50 usec
TE                   298.0 K
D1                 1.00000000 sec
TD0                       1
SFO1             600.1735511 MHz
NUC1                      1H
P1                     12.50 usec
PLW1            15.00000000 W

F2 - Processing parameters
SI                    32768
SF               600.1700146 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

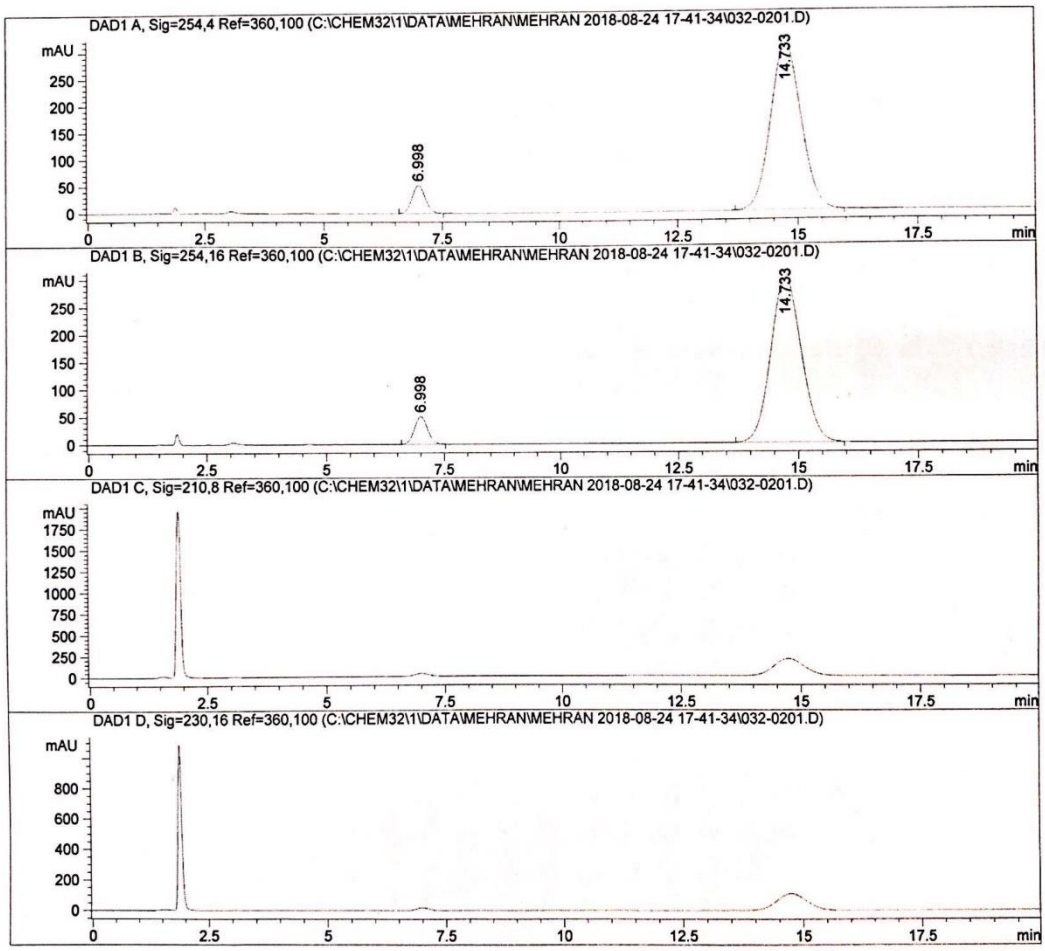



```
Current Data Parameters
NAME                  mr-4-47 c
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180817
Time                   12.22
INSTRUM                spect
PROBHD   5 mm PATXI 1H/
PULPROG                udeft
TD                    65536
SOLVENT               CDCl3
NS                      100
DS                        4
SWH               31446.541 Hz
FIDRES             0.479836 Hz
AQ                 1.0420223 sec
RG                    32768
DW                    15.900 usec
DE                     6.50 usec
TE                   296.9 K
D1                 3.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec
D20              240.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                      9.50 usec
P12                  2000.00 usec
P26                   500.00 usec
PL1                    -6.00 dB
PL1W          300.00000000 W
SFO1           125.8231760 MHz
SP2                    2.60 dB
SP8                    2.60 dB
SPNAM[2]     Crp60comp.4
SPNAM[8]  Crp60,0.5,20.1
SPOAL2                0.500
SPOAL8                0.500
SPOFFS2    0 Hz
SPOFFS8    0 Hz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    1.00 dB
PL12                  19.06 dB
PL2W           9.97631168 W
PL12W          0.15594450 W
SFO2           500.3320013 MHz

F2 - Processing parameters
SI                    65536
SF               125.8080790 MHz
WDW                      EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

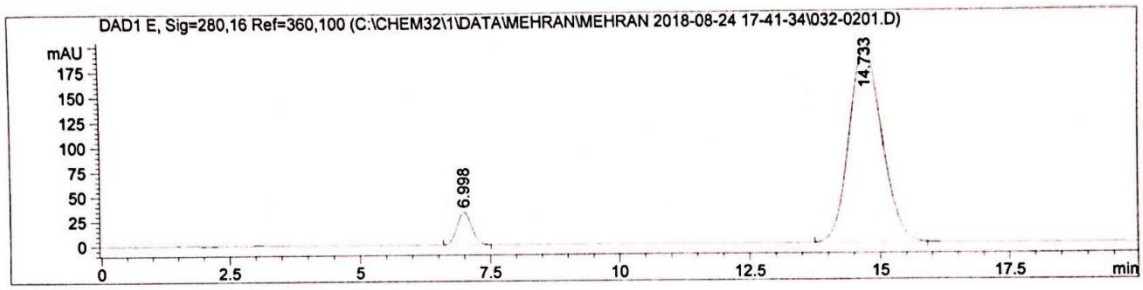
HPLC chromatogram for compound 15

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\032-0201.D
Sample Name: mr-4-47

```
==========================================================================
Acq. Operator   : MEHRAN                          Seq. Line :   2
Acq. Instrument : Instrument 1                    Location : Vial 32
Injection Date  : 08-24-2018 6:03:47 PM               Inj :   1
                                                 Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\MEHRAN.M
Last changed    : 08-24-2018 5:41:32 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\032-0201.D\DA.M (
                  MEHRAN.M)
Last changed    : 09-25-2018 1:04:22 PM by MEHRAN
Method Info     : IC, 35% Isopropanol in hexanes  0.3 ml/min, 1 ul injection, 30 oC
```



Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\032-0201.D
Sample Name: mr-4-47



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.998	BB	0.3049	1022.09381	52.10192	6.9766
2	14.733	BB	0.6918	1.36283e4	308.24319	93.0234
Totals :				1.46504e4	360.34511	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.998	BB	0.3049	995.50690	50.73539	6.9775
2	14.733	BB	0.6918	1.32720e4	300.18582	93.0225
Totals :				1.42675e4	350.92121	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\032-0201.D
Sample Name: mr-4-47

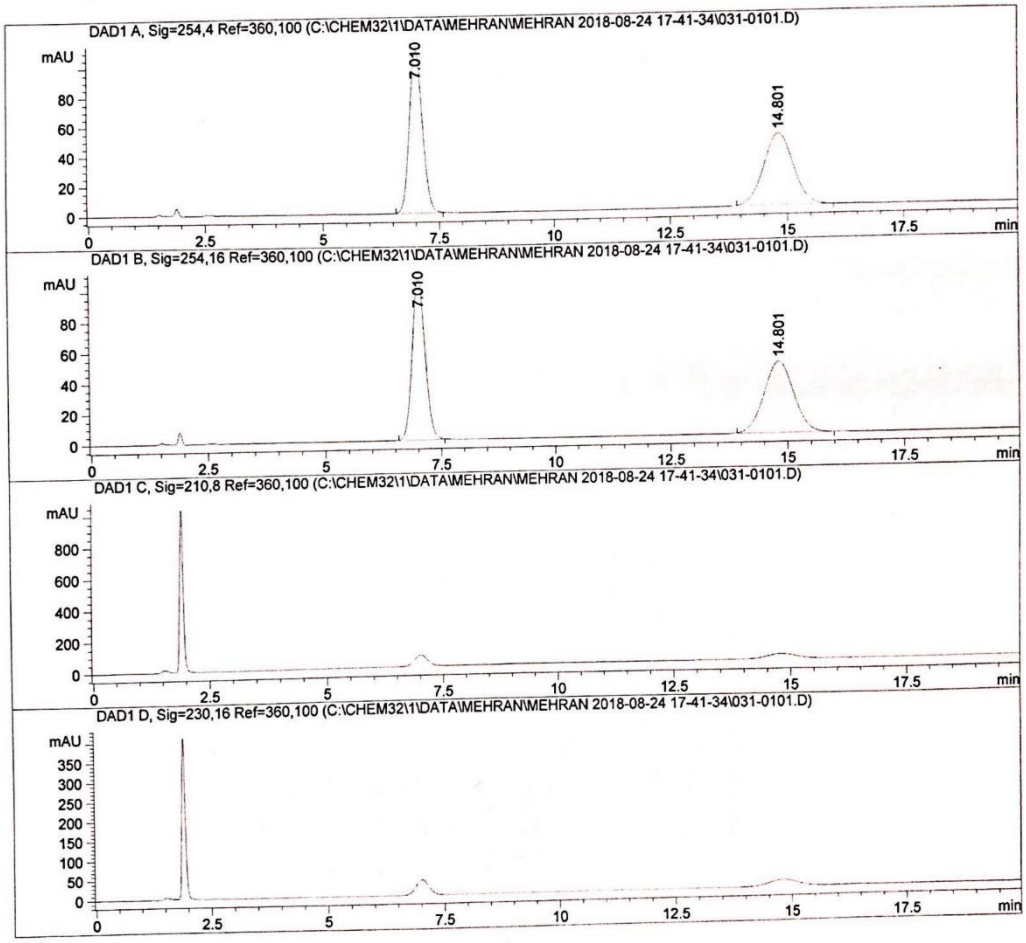
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.998	BB	0.3048	646.16058	32.94838	6.9941
2	14.733	BB	0.6896	8592.53223	194.44255	93.0059
Totals :				9238.69281	227.39093	

*** End of Report ***

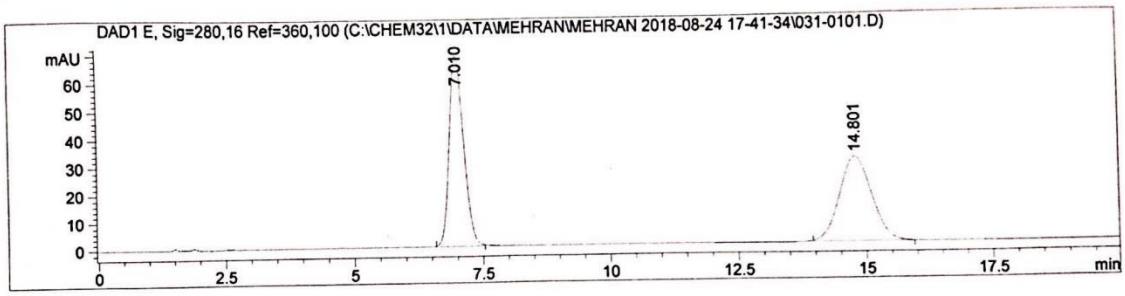
HPLC chromatogram for racemic of compound 15

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\031-0101.D
Sample Name: mr-4-204

```
==========================================================================
Acq. Operator   : MEHRAN                          Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 31
Injection Date  : 08-24-2018 5:42:33 PM              Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\MEHRAN.M
Last changed    : 08-24-2018 5:41:32 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\031-0101.D\DA.M (
                  MEHRAN.M)
Last changed    : 08-24-2018 5:41:32 PM by MEHRAN
Method Info     : IC, 35% Isopropanol in hexanes  0.3 ml/min, 1 ul injection, 30 oC
```



Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\031-0101.D
Sample Name: mr-4-204



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.010	BB	0.3042	2137.78076	109.29403	50.0502
2	14.801	BB	0.6897	2133.49365	48.45315	49.9498
Totals :				4271.27441	157.74718	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

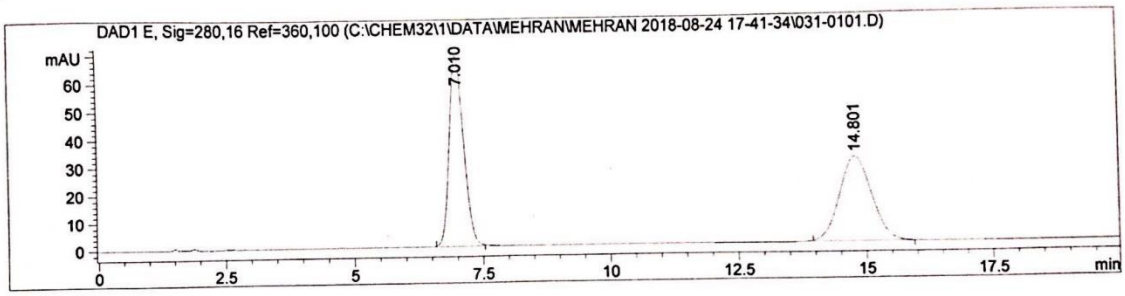
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.010	BB	0.3042	2081.19141	106.42201	50.0406
2	14.801	BB	0.6918	2077.81836	47.17977	49.9594
Totals :				4159.00977	153.60178	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-24 17-41-34\031-0101.D
Sample Name: mr-4-204



Area Percent Report

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.010	BB	0.3042	2137.78076	109.29403	50.0502
2	14.801	BB	0.6897	2133.49365	48.45315	49.9498
Totals :				4271.27441	157.74718	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

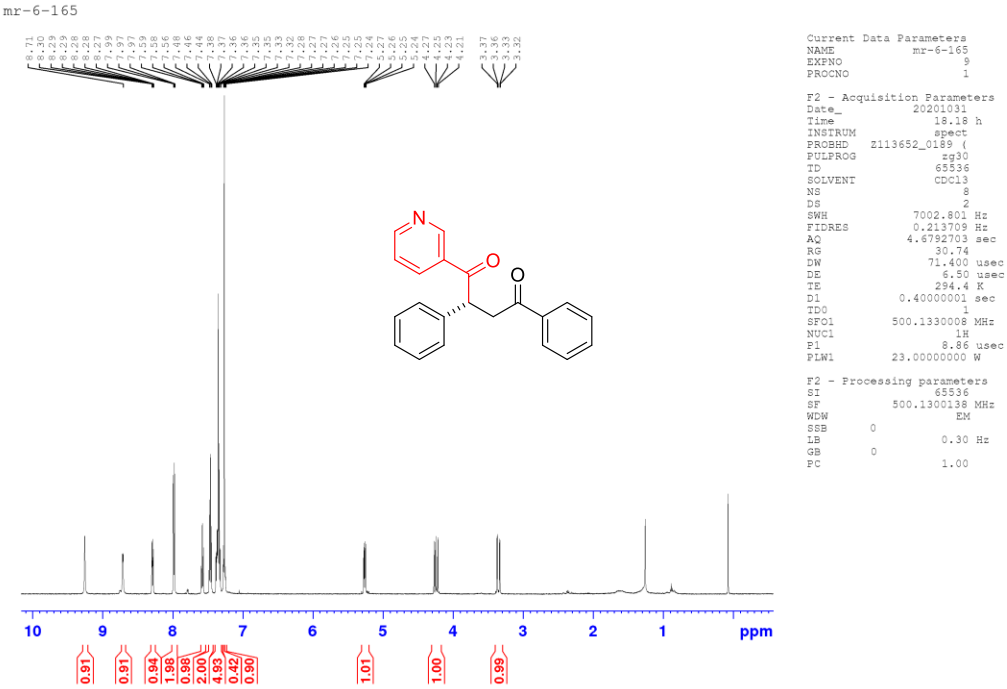
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.010	BB	0.3042	2081.19141	106.42201	50.0406
2	14.801	BB	0.6918	2077.81836	47.17977	49.9594
Totals :				4159.00977	153.60178	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

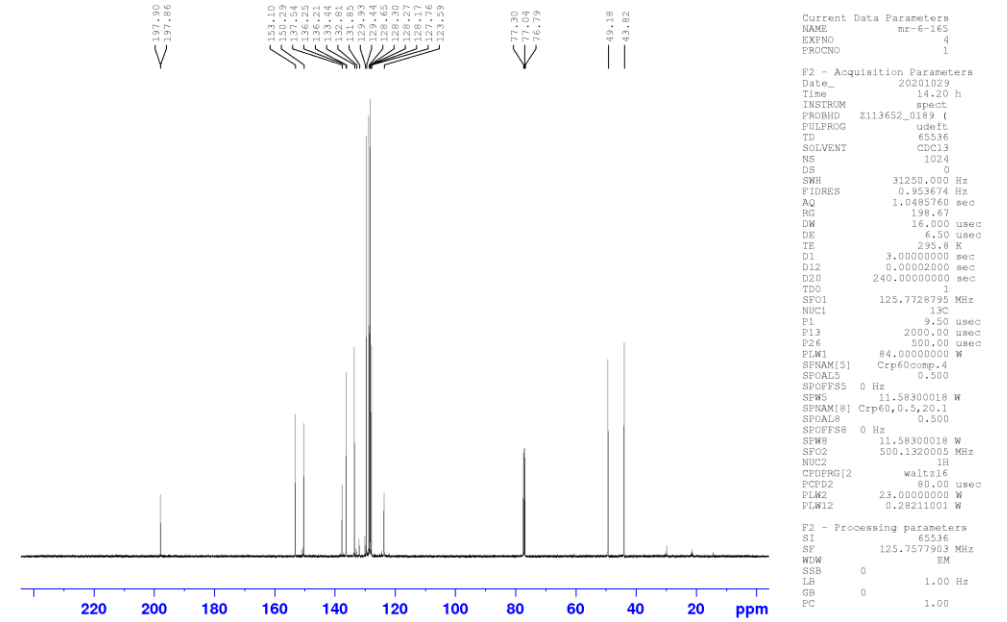
Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

^{1}H NMR and ^{13}C NMR for compound 16




```
Current Data Parameters
NAME                  mr-6-165
EXPNO                        9
PROCNO                       1

F2 - Acquisition Parameters
Date_               20201031
Time                   18.18 h
INSTRUM                spect
PROBHD    Z113652_0189 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                7002.801 Hz
FIDRES             0.213709 Hz
AQ                 4.6792703 sec
RG                      30.74
DW                     71.400 usec
DE                      6.50 usec
TE                     294.4 K
D1                0.40000001 sec
TD0                       1
SFO1             500.1330008 MHz
NUC1                      1H
P1                      8.86 usec
PLW1            23.00000000 W

F2 - Processing parameters
SI                    65536
SF               500.1300138 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```




```
Current Data Parameters
NAME                  mr-6-165
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_               20201029
Time                   14.20 h
INSTRUM                spect
PROBHD    Z113652_0189 (
PULPROG                udeft
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        0
SWH               31250.000 Hz
FIDRES             0.953674 Hz
AQ                 1.0485760 sec
RG                    198.67
DW                    16.000 usec
DE                      6.50 usec
TE                     295.8 K
D1                3.00000000 sec
D12               0.00002000 sec
D20             240.00000000 sec
TD0                       1
SFO1             125.7728795 MHz
NUC1                     13C
P1                      9.50 usec
P13                  2000.00 usec
P26                   500.00 usec
PLW1             84.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5                0.500
SPOFFS5   0 Hz
SPW5             11.58300018 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8                0.500
SPOFFS8   0 Hz
SPW8             11.58300018 W
SFO2             500.1320005 MHz
NUC2                      1H
CPDPRG[2            waltz16
PCPD2                80.00 usec
PLW2            23.00000000 W
PLW12            0.28211001 W

F2 - Processing parameters
SI                    65536
SF               125.7577903 MHz
WDW                      EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.00
```

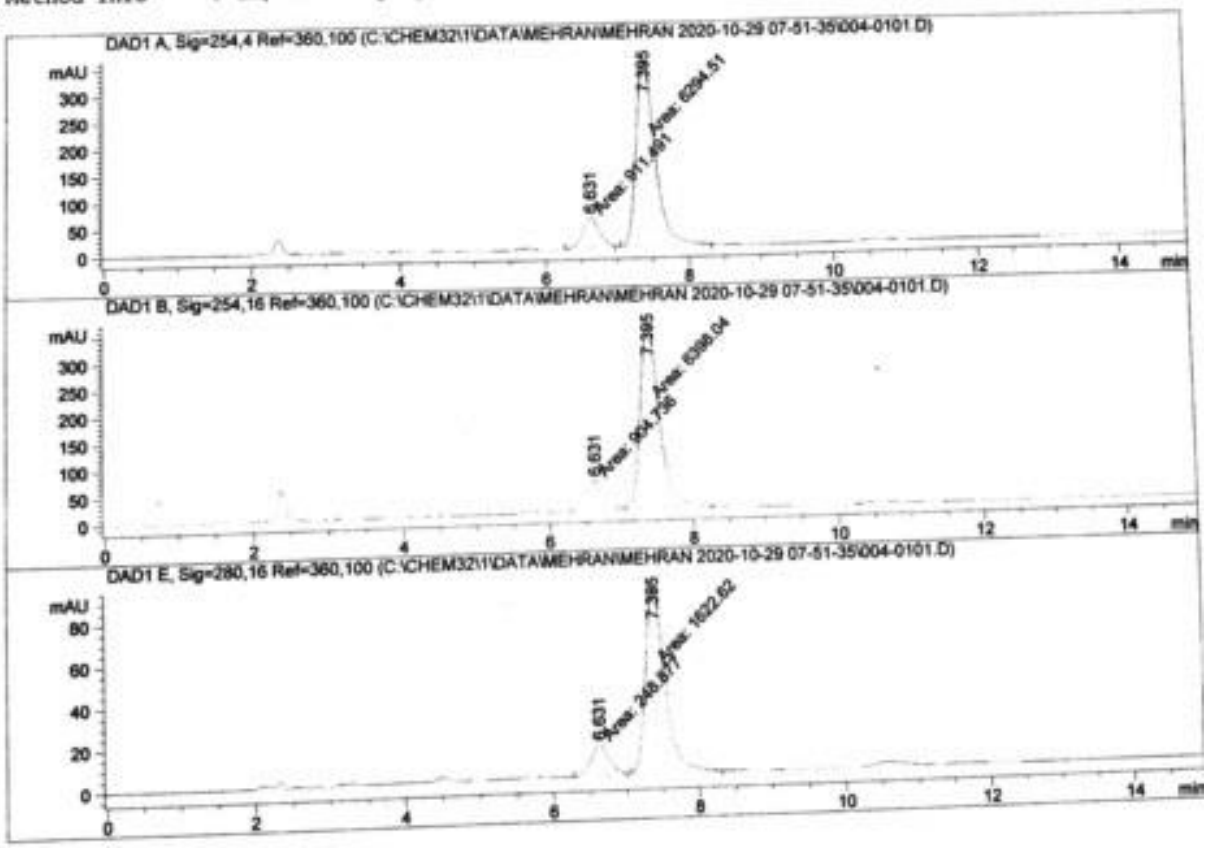
HPLC chromatogram for compound 16

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-10-29 07-51-35\004-0101.D
Sample Name: mr-6-165

Acq. Operator : MEHRAN
Acq. Instrument : Instrument 1
Injection Date : 10-29-2020 7:52:40 AM

Seq. Line : 1
Location : Vial 4
Inj : 1
Inj Volume : 1 µl

Different Inj Volume from Sequence ! Actual Inj Volume : 3 µl
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2020-10-29 07-51-35\MEHRAN.M
Last changed : 10-29-2020 7:51:33 AM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-10-29 07-51-35\004-0101.D\DA.M (MEHRAN.M)
Last changed : 10-29-2020 8:08:15 AM by MEHRAN
Method Info : IA, 35% Isopropanol in hexanes, 0.2 ml/min, 3 ul injection, 30 oC



Area Percent Report

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

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-10-29 07-51-35\004-0101.D
Sample Name: mr-6-165

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.631	MM	0.2761	911.49060	55.02177	12.6490
2	7.395	MM	0.3030	6294.51172	346.17627	87.3510
Totals :				7206.00232	401.19804	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.631	MM	0.2709	904.73639	55.66335	12.3889
2	7.395	MM	0.3012	6398.04053	354.00775	87.6111
Totals :				7302.77692	409.67110	

Signal 3: DAD1 E, Sig=280,16 Ref=360,100

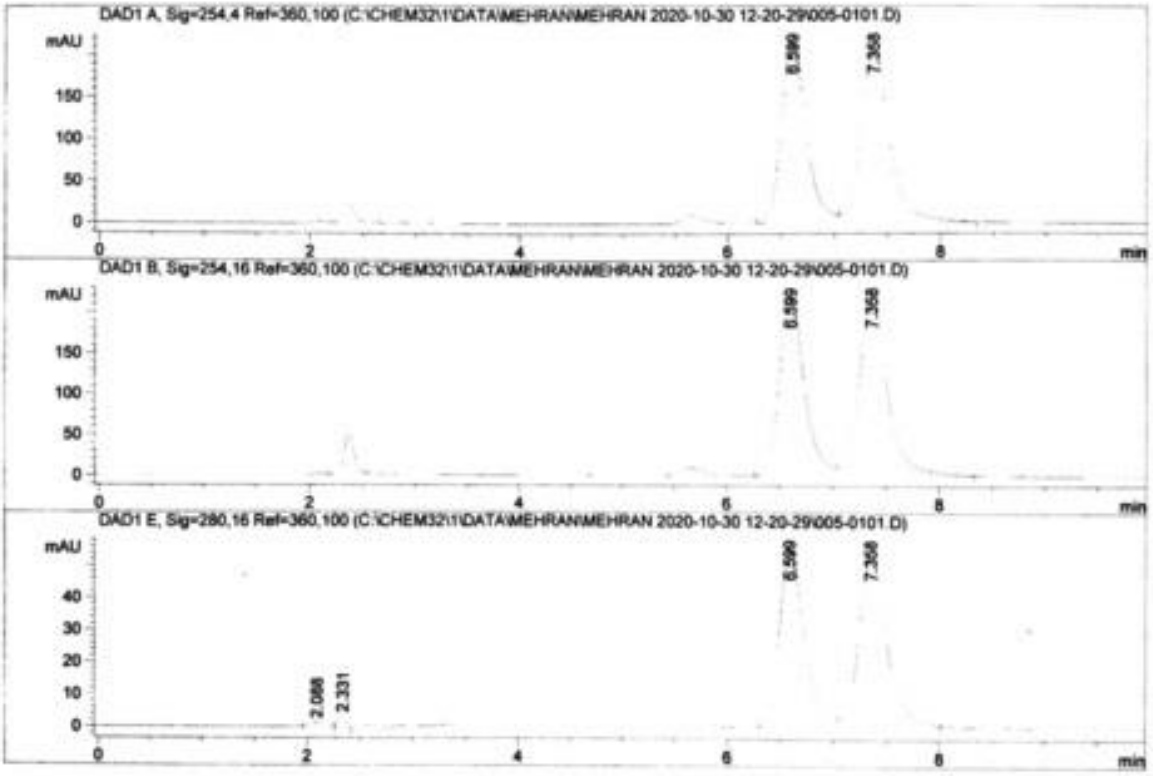
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.631	MM	0.2878	248.87727	14.41341	13.2983
2	7.395	MM	0.3021	1622.61926	89.53198	86.7017
Totals :				1871.49654	103.94539	

*** End of Report ***

HPLC chromatogram for racemic of compound 16

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-10-30 12-20-29\005-0101.D
Sample Name: mr-7-151

Acq. Operator : MEHRAN Seq. Line : 1
Acq. Instrument : Instrument 1 Location : Vial 5
Injection Date : 10-30-2020 12:21:41 PM Inj : 1
Inj Volume : 5 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 2 µl
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2020-10-30 12-20-29\MEHRAN.M
Last changed : 10-30-2020 12:19:29 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-10-30 12-20-29\005-0101.D\DA.M (MEHRAN.M)
Last changed : 10-30-2020 12:32:02 PM by MEHRAN
Method Info : IA, 35% Isopropanol in hexanes, 0.2 ml/min, 3 ul injection, 30 oC



Area Percent Report

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

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-10-30 12-20-29\005-0101.D
Sample Name: mr-7-151

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.599	BV	0.2472	3488.45557	215.16478	47.4941
2	7.358	VB	0.2792	3856.57910	207.14568	52.5059
Totals :				7345.03467	422.31046	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

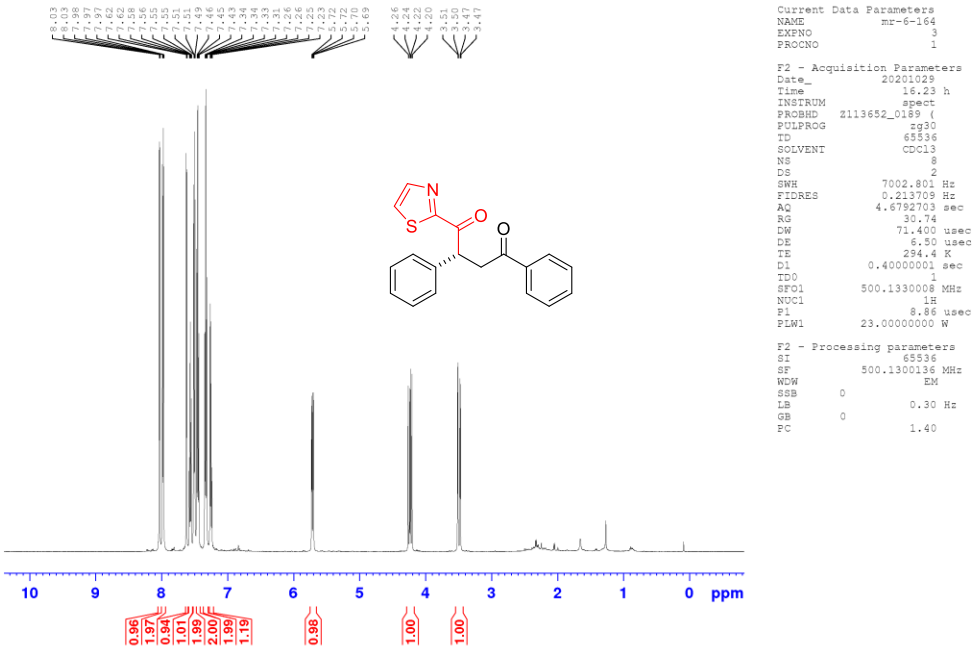
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.599	BV	0.2470	3567.58862	220.18150	47.5343
2	7.358	VB	0.2790	3937.70264	211.73361	52.4657
Totals :				7505.29126	431.91512	

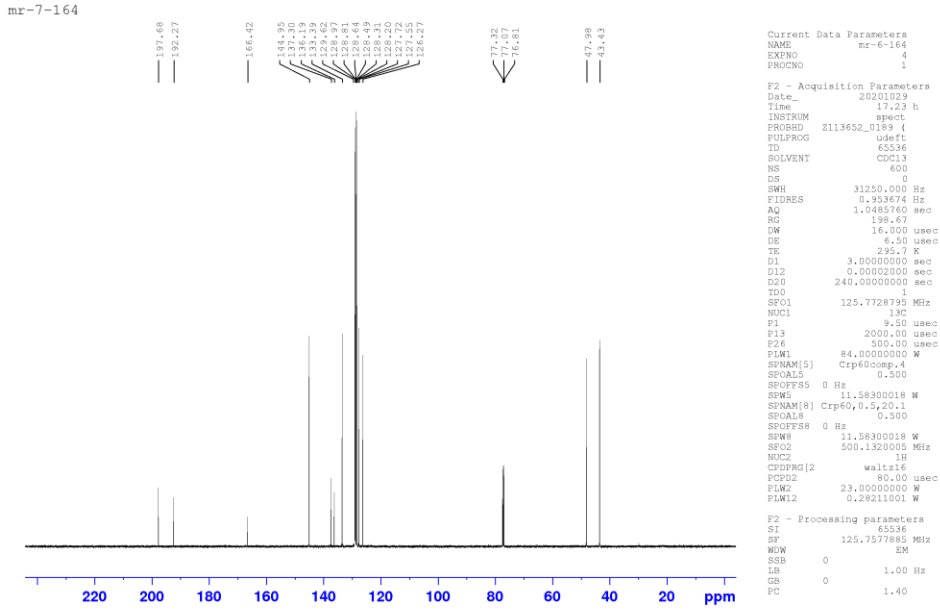
Signal 3: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.088	BV	0.1522	14.44772	1.33561	0.7667
2	2.331	VV	0.0693	14.96217	3.40278	0.7940
3	6.599	BV	0.2460	888.83698	55.15345	47.1705
4	7.358	VB	0.2738	966.06195	53.20580	51.2688
Totals :				1884.30881	113.09764	

*** End of Report ***

^{1}H NMR and ^{13}C NMR for compound 17

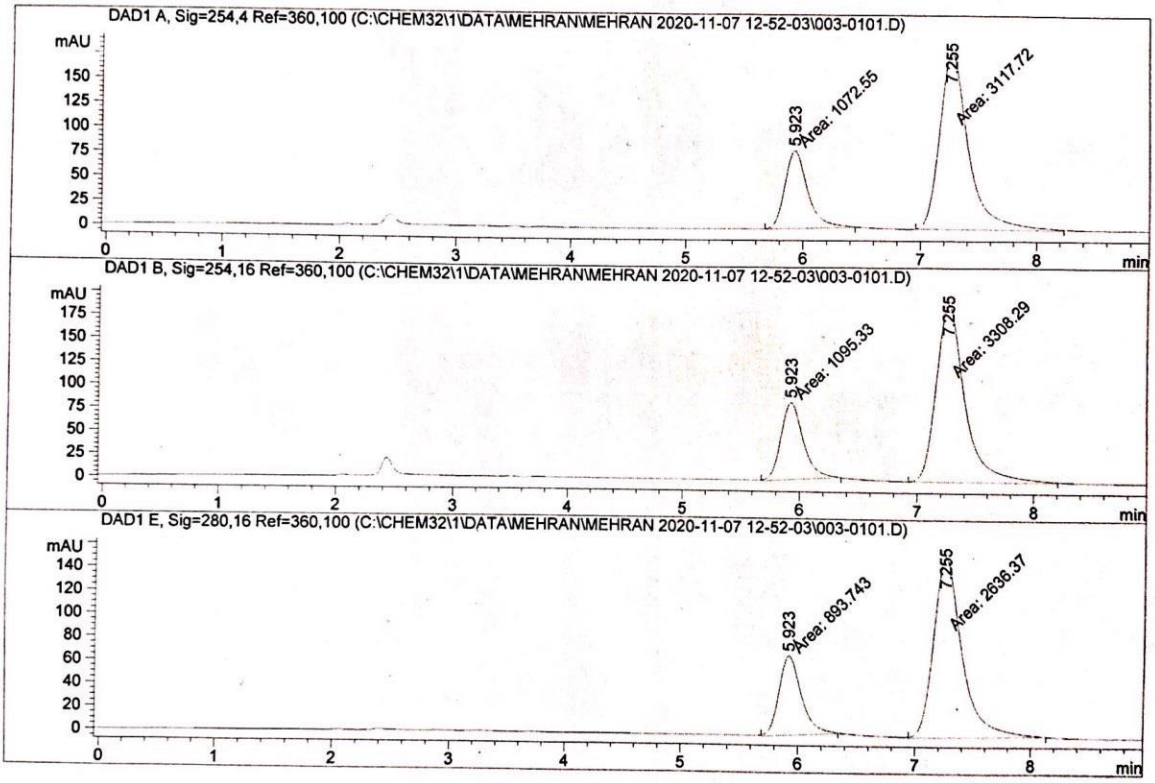




HPLC chromatogram for compound 17

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-07 12-52-03\003-0101.D
Sample Name: mr-6-164

Acq. Operator : MEHRAN
Acq. Instrument : Instrument 1
Injection Date : 11-07-2020 12:53:04 PM
Seq. Line : 1
Location : Vial 3
Inj : 1
Inj Volume : 1 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 0.5 µl
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2020-11-07 12-52-03\MEHRAN.M
Last changed : 11-07-2020 12:52:01 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-07 12-52-03\003-0101.D\DA.M (MEHRAN.M)
Last changed : 11-07-2020 1:03:28 PM by MEHRAN
Method Info : IA, 20% Isopropanol in hexanes, 0.2 ml/min, 1 ul injection, 30 oC



Area Percent Report

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

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-07 12-52-03\003-0101.D
Sample Name: mr-6-164

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.923	MM	0.2249	1072.54736	79.49503	25.5962
2	7.255	MM	0.2866	3117.72021	181.33620	74.4038
Totals :				4190.26758	260.83123	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.923	MM	0.2184	1095.33350	83.57187	24.8735
2	7.255	MM	0.2870	3308.28760	192.13058	75.1265
Totals :				4403.62109	275.70245	

Signal 3: DAD1 E, Sig=280,16 Ref=360,100

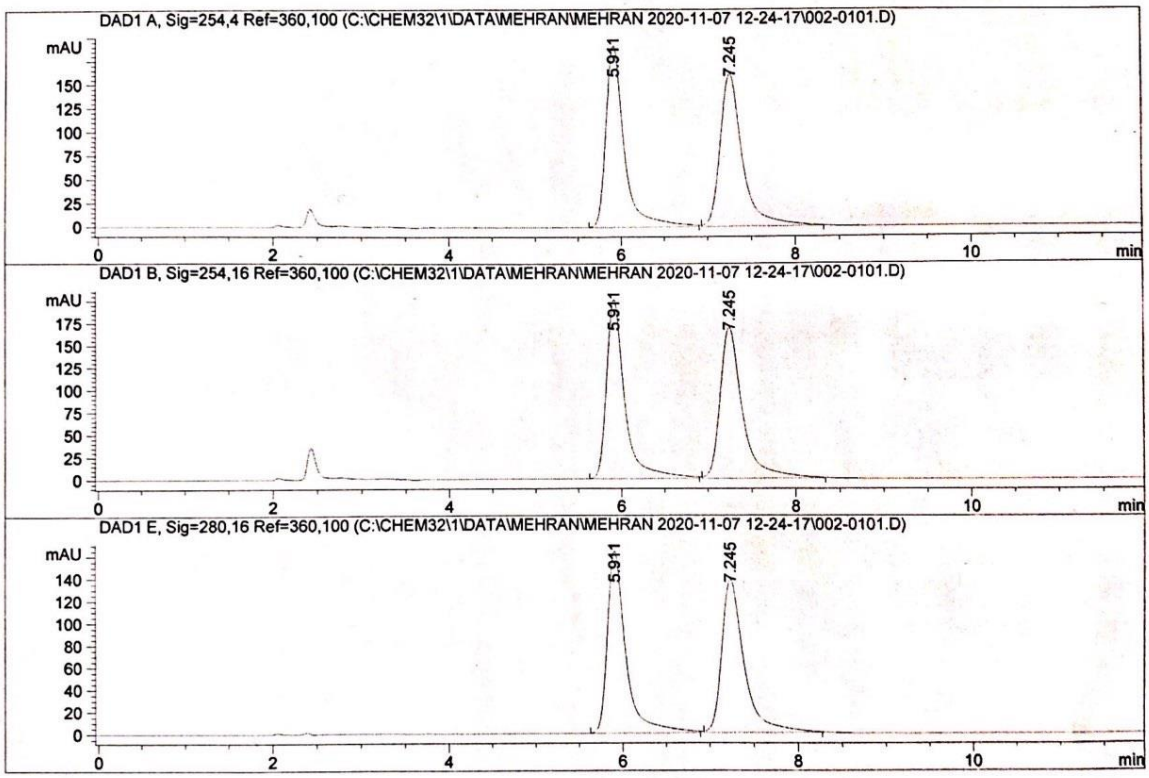
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.923	MM	0.2203	893.74323	67.61564	25.3177
2	7.255	MM	0.2828	2636.36890	155.39818	74.6823
Totals :				3530.11212	223.01382	

*** End of Report ***

HPLC chromatogram for racemic of compound 17

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-07 12-24-17\002-0101.D
Sample Name: mr-7-152

Acq. Operator	: MEHRAN	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 2
Injection Date	: 11-07-2020 12:25:18 PM	Inj	: 1
		Inj Volume	: 1 µl
Acq. Method	: C:\Chem32\1\DATA\MEHRAN\MEHRAN 2020-11-07 12-24-17\MEHRAN.M		
Last changed	: 11-07-2020 12:24:16 PM by MEHRAN		
Analysis Method	: C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-07 12-24-17\002-0101.D\DA.M (MEHRAN.M)		
Last changed	: 11-07-2020 12:24:16 PM by MEHRAN		
Method Info	: IA, 20% Isopropanol in hexanes, 0.2 ml/min, 1 ul injection, 30 oC		



Area Percent Report

Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

Use Multiplier & Dilution Factor with ISTDs

Page 1 of 2

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-07 12-24-17\002-0101.D
Sample Name: mr-7-152

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.911	BB	0.2212	2836.15210	191.00049	49.9749
2	7.245	BB	0.2640	2838.99756	160.75795	50.0251
Totals :				5675.14966	351.75844	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

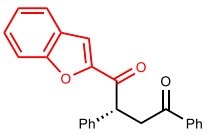
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.911	BB	0.2211	2997.87646	201.99878	49.9530
2	7.245	BB	0.2641	3003.51270	169.98917	50.0470
Totals :				6001.38916	371.98795	

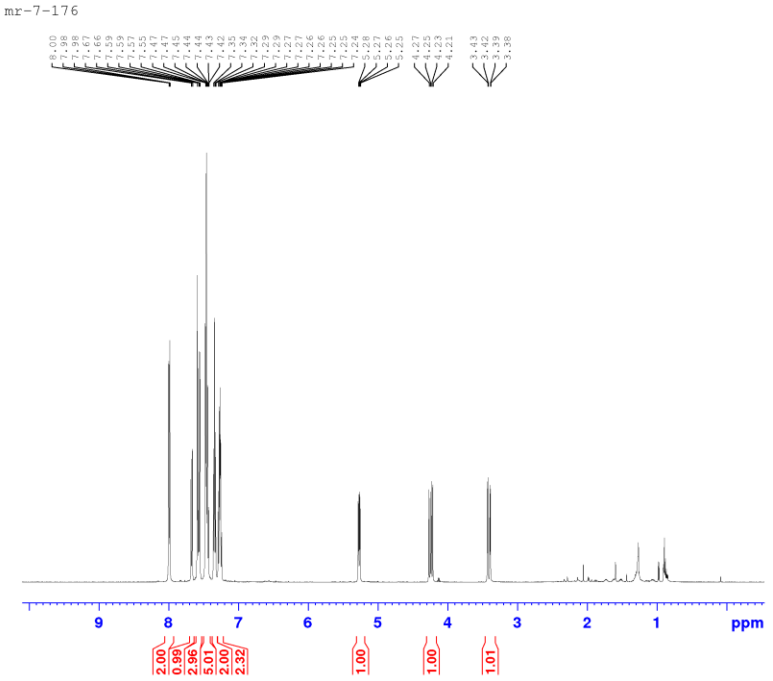
Signal 3: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.911	BB	0.2205	2416.65186	163.40746	50.0717
2	7.245	BB	0.2627	2409.73389	137.31396	49.9283
Totals :				4826.38574	300.72142	

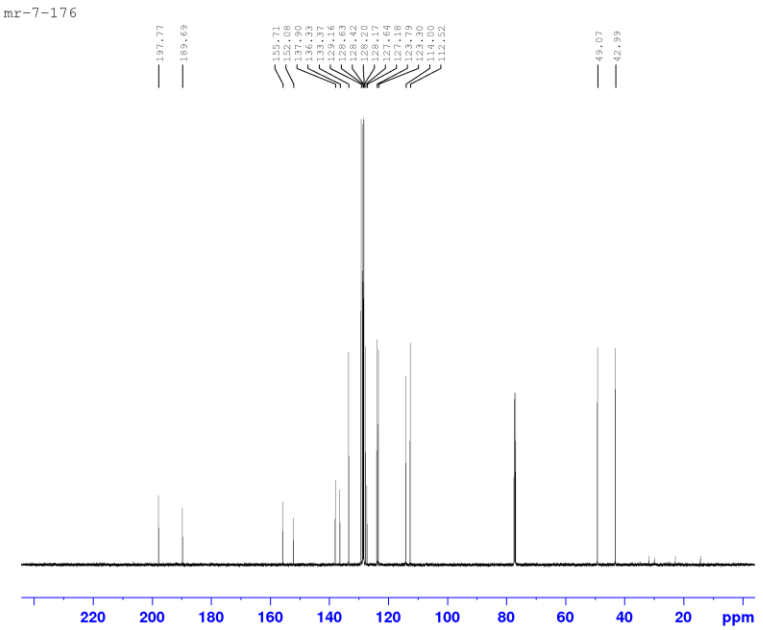
*** End of Report ***

^{1}H NMR and ^{13}C NMR for compound 18






```
Current Data Parameters
NAME                  mr-7-176
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20201112
Time                   12.55 h
INSTRUM                spect
PROBHD    Z113652_0189 (
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                           8
DS                           2
SWH                 7002.801 Hz
FIDRES              0.213709 Hz
AQ                  4.6792703 sec
RG                     30.74
DW                     71.400 usec
DE                      6.50 usec
TE                     294.3 K
D1                  0.40000001 sec
TD0                          1
SFO1             500.1330008 MHz
NUC1                        1H
P1                      8.86 usec
PLW1            23.00000000 W

F2 - Processing parameters
SI                     65536
SF               500.1300138 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```



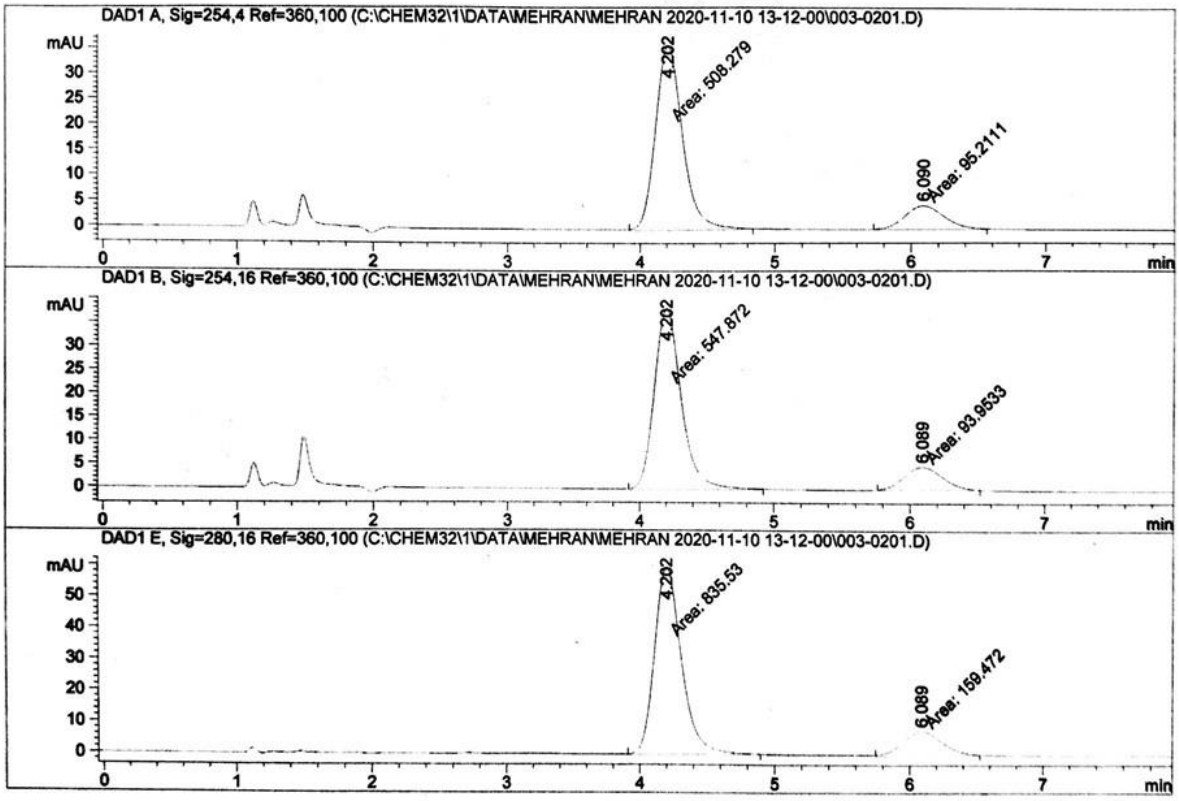

```
Current Data Parameters
NAME                  mr-7-176
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_               20201112
Time                   14.28 h
INSTRUM                spect
PROBHD    Z113652_0189 (
PULPROG                 udeft
TD                     65536
SOLVENT                CDCl3
NS                       984
DS                         0
SWH                31250.000 Hz
FIDRES              0.953674 Hz
AQ                  1.0485760 sec
RG                     198.67
DW                     16.000 usec
DE                      6.50 usec
TE                     295.8 K
D1                  3.00000000 sec
D12                 0.00002000 sec
D20               240.00000000 sec
TD0                          1
SFO1             125.7728795 MHz
NUC1                       13C
P1                      9.50 usec
P13                  2000.00 usec
P26                   500.00 usec
PLW1             84.00000000 W
SPNAM[5]      Crp60comp.4
SPOAL5                 0.500
SPOFFS5   0 Hz
SPW5             11.58300018 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8                 0.500
SPOFFS8   0 Hz
SPW8             11.58300018 W
SFO2             500.1320005 MHz
NUC2                        1H
CPDPRG[2              waltz16
PCPD2                  80.00 usec
PLW2            23.00000000 W
PLW12            0.28211001 W

F2 - Processing parameters
SI                     65536
SF               125.7577885 MHz
WDW                       EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

HPLC chromatogram for compound 18

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-10 13-12-00\003-0201.D
Sample Name: mr-6-176

Acq. Operator	: MEHRAN	Seq. Line	: 2
Acq. Instrument	: Instrument 1	Location	: Vial 3
Injection Date	: 11-10-2020 1:22:16 PM	Inj	: 1
		Inj Volume	: 5 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 1 µl

Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2020-11-10 13-12-00\MEHRAN.M
Last changed : 11-10-2020 1:11:59 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-10 13-12-00\003-0201.D\DA.M (MEHRAN.M)
Last changed : 11-10-2020 1:43:12 PM by MEHRAN
Method Info : IC, 20% Isopropanol in hexanes, 0.4 ml/min, 1 ul injection, 30 oC



Area Percent Report

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

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-10 13-12-00\003-0201.D
Sample Name: mr-6-176

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.202	MM	0.2339	508.27945	36.21480	84.2233
2	6.090	MM	0.3401	95.21106	4.66524	15.7767
Totals :				603.49051	40.88004	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.202	MM	0.2348	547.87213	38.88736	85.3615
2	6.089	MM	0.3225	93.95333	4.85472	14.6385
Totals :				641.82546	43.74208	

Signal 3: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.202	MM	0.2333	835.52979	59.68930	83.9727
2	6.089	MM	0.3414	159.47180	7.78414	16.0273
Totals :				995.00159	67.47344	

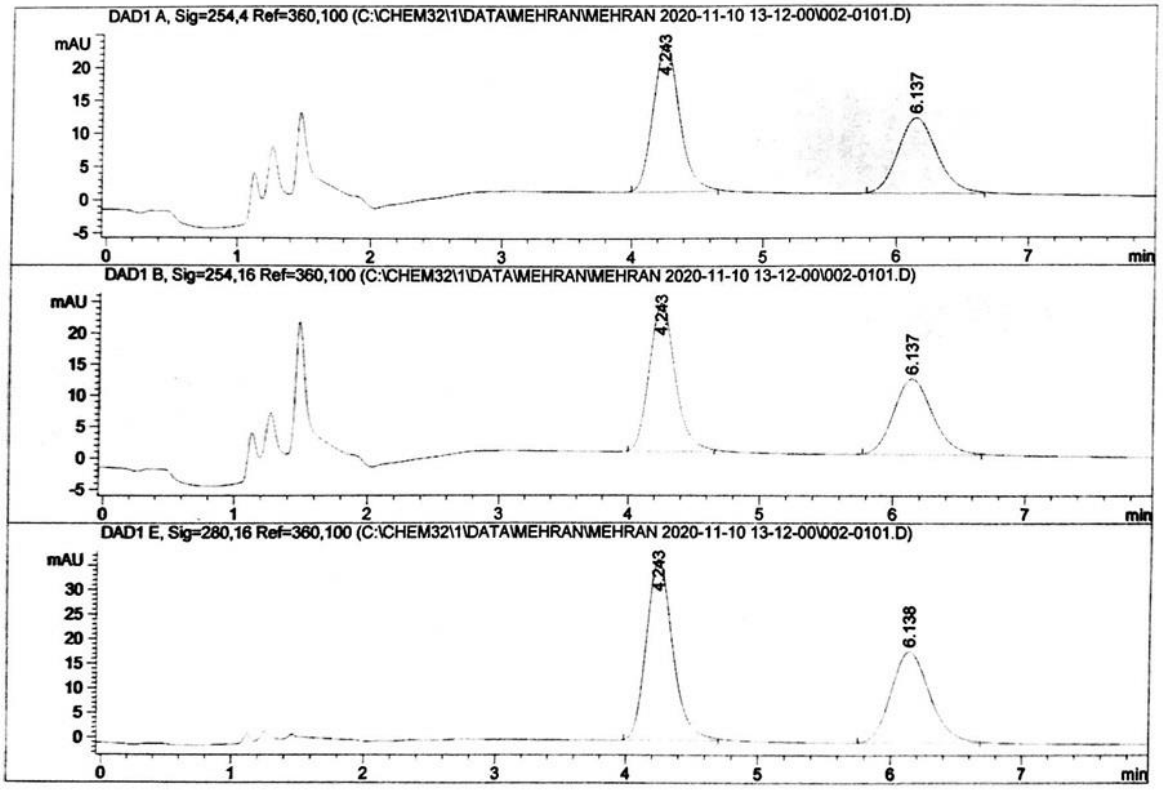
*** End of Report ***

HPLC chromatogram for racemic of compound 18

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-10 13-12-00\002-0101.D
Sample Name: mr-6-175

Acq. Operator	: MEHRAN	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 2
Injection Date	: 11-10-2020 1:13:03 PM	Inj	: 1
		Inj Volume	: 5 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 1 µl

Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2020-11-10 13-12-00\MEHRAN.M
Last changed : 11-10-2020 1:11:59 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-10 13-12-00\002-0101.D\DA.M (MEHRAN.M)
Last changed : 11-10-2020 1:42:43 PM by MEHRAN
Method Info : IC, 20% Isopropanol in hexanes, 0.4 ml/min, 1 ul injection, 30 oC



Area Percent Report

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

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-11-10 13-12-00\002-0101.D
Sample Name: mr-6-175

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.243	BB	0.2123	309.75854	22.26927	57.4207
2	6.137	BB	0.3126	229.69621	11.22942	42.5793
Totals :				539.45476	33.49868	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

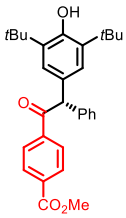
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.243	BB	0.2122	332.33102	23.90490	57.3862
2	6.137	BB	0.3147	246.78250	12.06362	42.6138
Totals :				579.11353	35.96851	

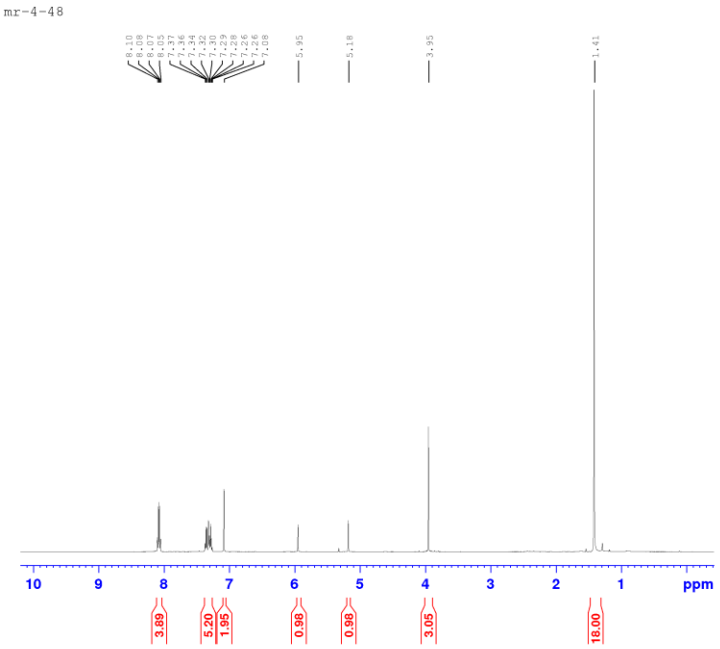
Signal 3: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.243	BB	0.2129	511.75836	36.65051	57.4278
2	6.138	BB	0.3174	379.37436	18.49077	42.5722
Totals :				891.13272	55.14128	

*** End of Report ***

^{1}H NMR and ^{13}C NMR for compound 19



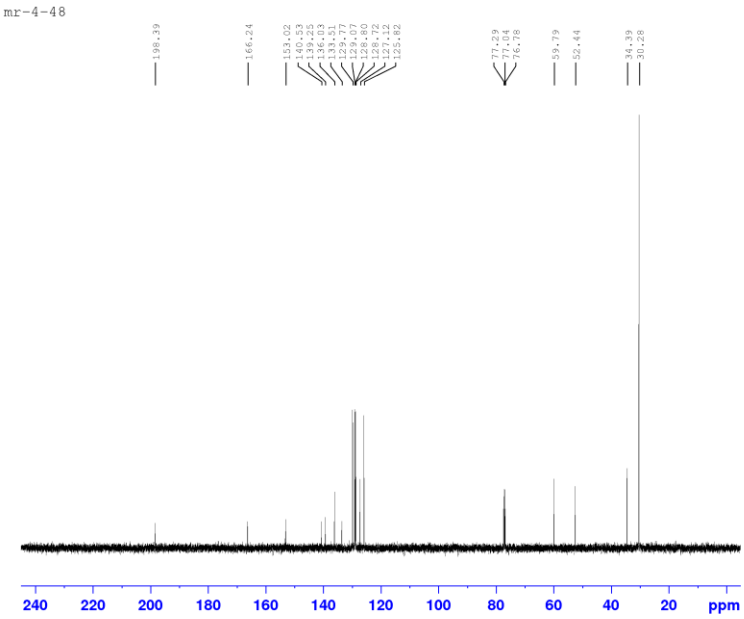


Current Data Parameters
NAME mr-4-48
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180817
Time 11.42
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 7002.801 Hz
FIDRES 0.106854 Hz
AQ 4.6792703 sec
RG 64
DW 71.400 usec
DE 6.50 usec
TE 296.7 K
D1 0.40000001 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 1.00 dB
PL1W 9.97631168 W
SFO1 500.3330020 MHz

F2 - Processing parameters
SI 65536
SF 500.3300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME mr-4-48
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180817
Time 12.02
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG udeft
TD 65536
SOLVENT CDCl3
NS 100
DS 4
SWH 31446.541 Hz
FIDRES 0.479836 Hz
AQ 1.0420223 sec
RG 32768
DW 15.900 usec
DE 6.50 usec
TE 297.1 K
D1 3.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D20 240.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
P12 2000.00 usec
P26 500.00 usec
PL1 -6.00 dB
PL1W 300.00000000 W
SFO1 125.8231760 MHz
SF2 2.60 dB
SF8 2.60 dB
SPNAM[2] Crp60comp.4
SPNAM[8] Crp60,0.5,20.1
SPOAL2 0.500
SPOAL8 0.500
SPOFFS2 0 Hz
SPOFFS8 0 Hz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 19.06 dB
PL2W 9.97631168 W
PL12W 0.15594450 W
SFO2 500.3320013 MHz

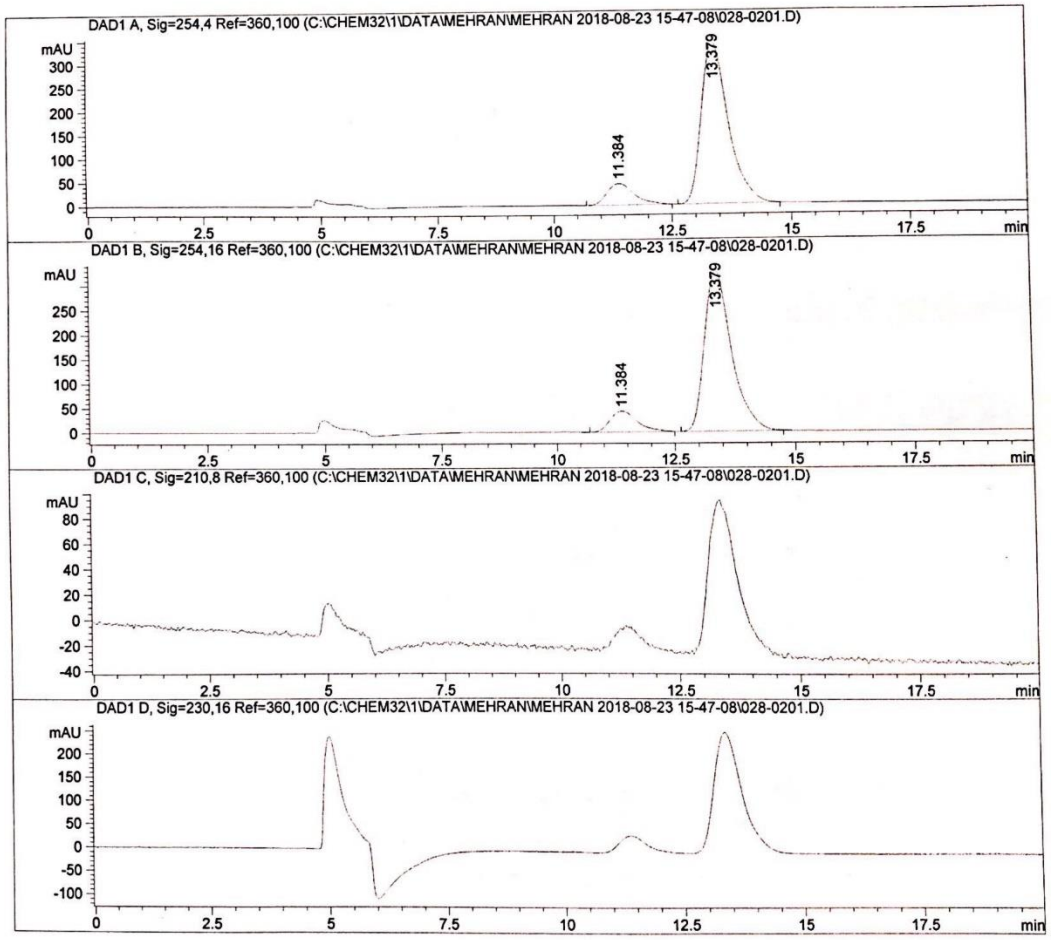
F2 - Processing parameters
SI 65536
SF 125.8080790 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

HPLC chromatogram for compound 19

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\028-0201.D
Sample Name: mr-4-48

Acq. Operator	: MEHRAN	Seq. Line	: 2
Acq. Instrument	: Instrument 1	Location	: Vial 28
Injection Date	: 08-23-2018 4:09:21 PM	Inj	: 1
		Inj Volume	: 5 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 1 µl

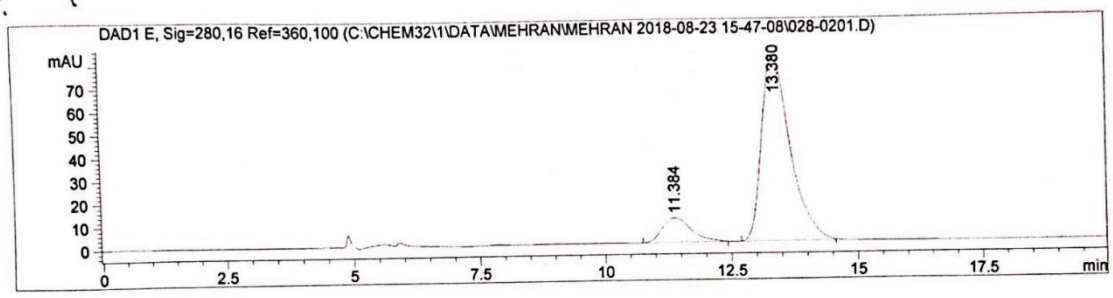
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\MEHRAN.M
Last changed : 08-23-2018 3:47:02 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\028-0201.D\DA.M (MEHRAN.M)
Last changed : 09-25-2018 1:15:30 PM by MEHRAN
Method Info : IC, 15% Isopropanol in hexanes 0.2 ml/min, 1 ul injection, 30 oC



Instrument 1 09-25-2018 1:15:44 PM MEHRAN

Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\028-0201.D
Sample Name: mr-4-48



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.384	BB	0.6242	1777.49451	44.48188	11.8332
2	13.379	BB	0.6032	1.32438e4	337.95276	88.1668
Totals :				1.50213e4	382.43464	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.384	BB	0.6239	1708.01562	42.77423	11.8198
2	13.379	BB	0.6033	1.27425e4	325.12265	88.1802
Totals :				1.44505e4	367.89688	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\028-0201.D
Sample Name: mr-4-48

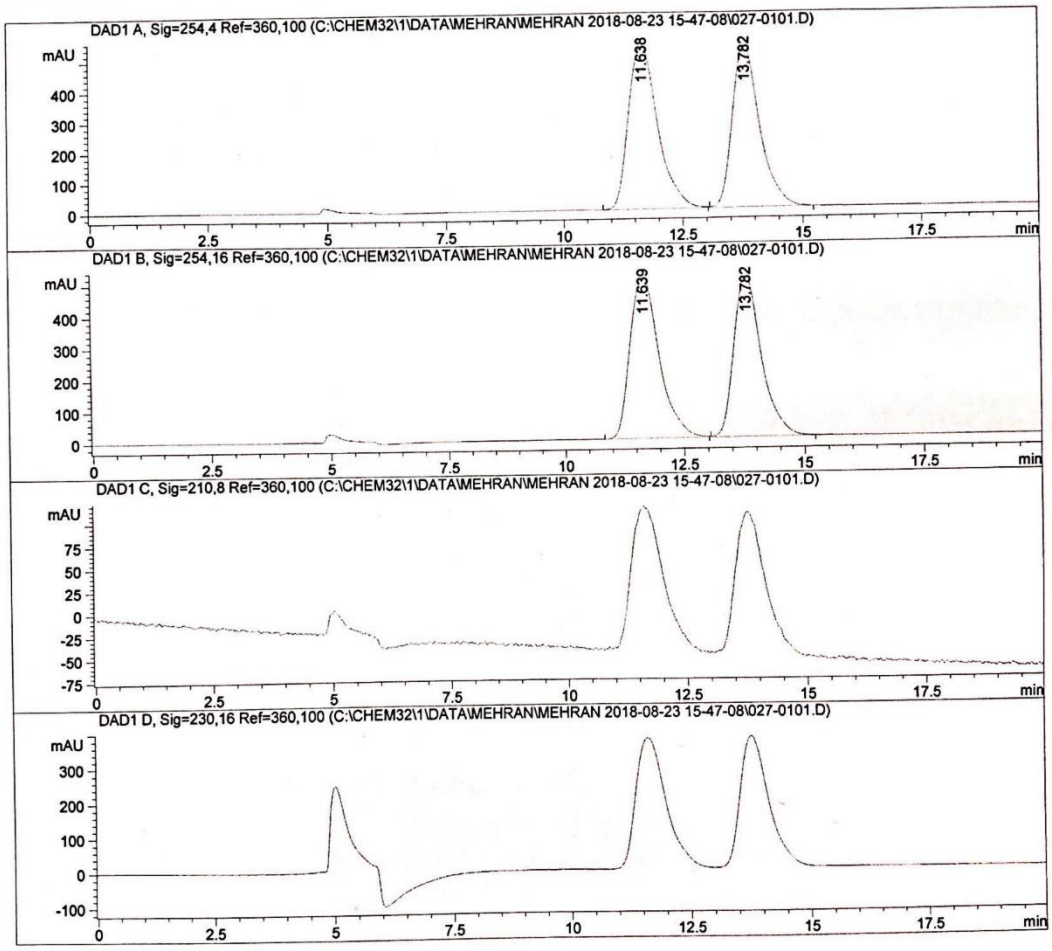
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.384	BB	0.6210	434.72266	10.90644	11.8742
2	13.380	BB	0.6025	3226.33984	82.46169	88.1258
Totals :				3661.06250	93.36813	

*** End of Report ***

HPLC chromatogram for racemic of compound 19

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\027-0101.D
Sample Name: mr-4-201

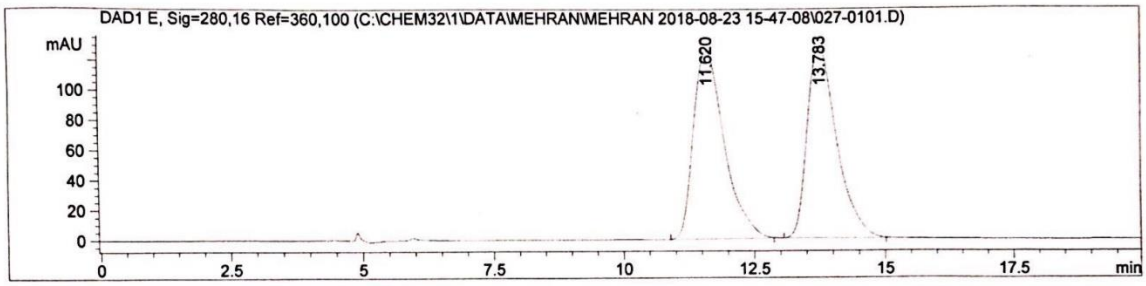
Acq. Operator : MEHRAN
Acq. Instrument : Instrument 1
Injection Date : 08-23-2018 3:48:08 PM
Seq. Line : 1
Location : Vial 27
Inj : 1
Inj Volume : 5 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 1 µl
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\MEHRAN.M
Last changed : 08-23-2018 3:47:02 PM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\027-0101.D\DA.M (MEHRAN.M)
Last changed : 09-25-2018 1:14:21 PM by MEHRAN
Method Info : IC, 15% Isopropanol in hexanes 0.2 ml/min, 1 ul injection, 30 oC



Instrument 1 09-25-2018 1:14:55 PM MEHRAN

Page 1 of 3

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\027-0101.D
Sample Name: mr-4-201



==========

Area Percent Report

==========

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

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.638	BB	0.6701	2.27639e4	533.18353	52.0269
2	13.782	BB	0.6061	2.09902e4	532.28735	47.9731
Totals :				4.37540e4	1065.47089	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.639	BB	0.6702	2.18983e4	512.84760	52.0335
2	13.782	BB	0.6061	2.01867e4	511.89642	47.9665
Totals :				4.20850e4	1024.74402	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

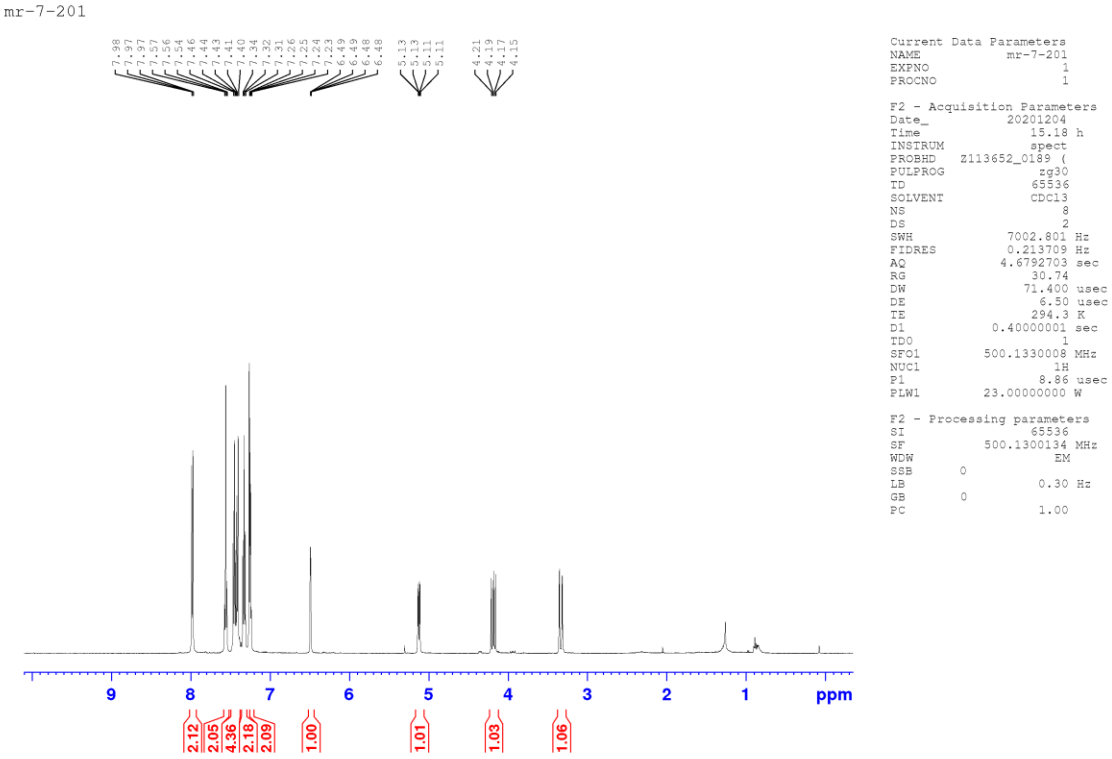
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2018-08-23 15-47-08\027-0101.D
Sample Name: mr-4-201

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.620	BB	0.6449	5237.86279	126.53807	50.7748
2	13.783	BB	0.6042	5078.00439	129.30806	49.2252
Totals :				1.03159e4	255.84613	

*** End of Report ***

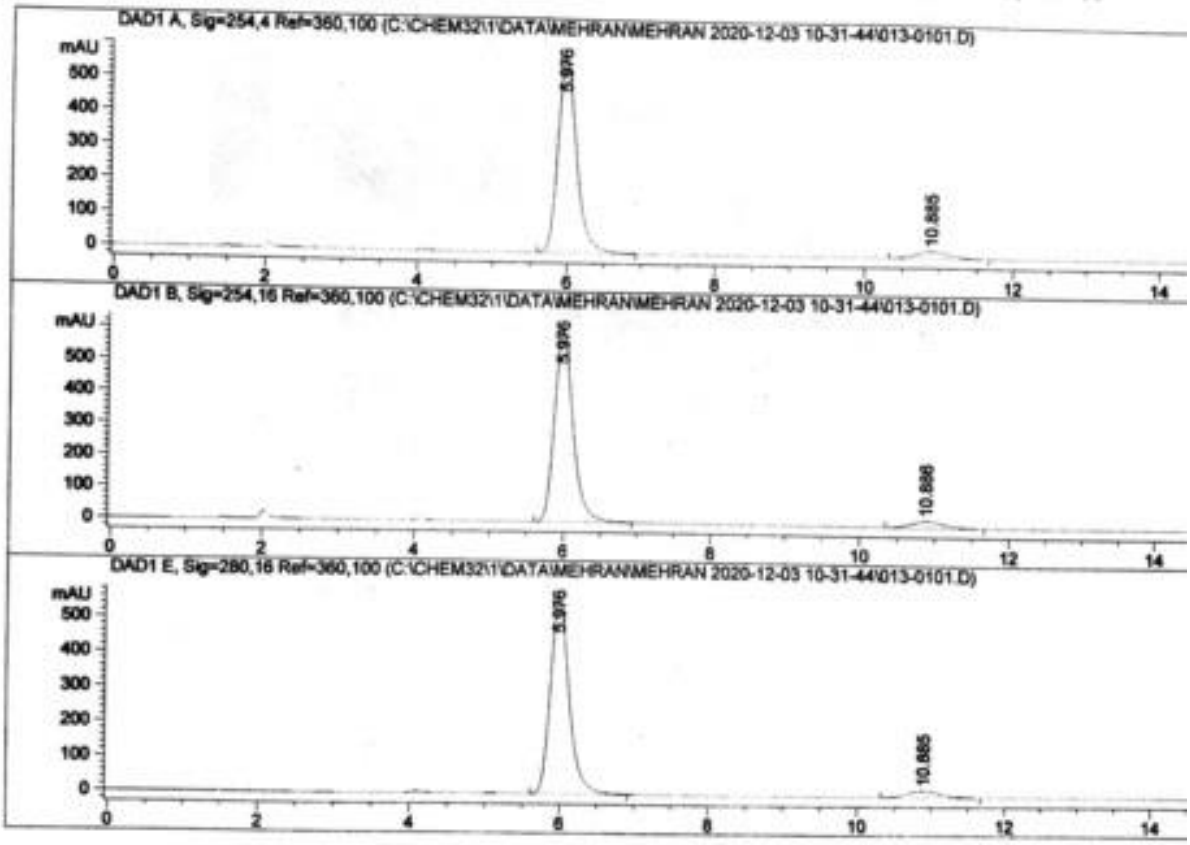
^{1}H NMR for compound 13 (1 mmol scale)



HPLC chromatogram for compound 13 (1 mmol scale)

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-12-03 10-31-44\013-0101.D
Sample Name: mr-7-201

Acq. Operator : MEHRAN
Acq. Instrument : Instrument 1
Injection Date : 12-03-2020 10:32:44 AM
Seq. Line : 1
Location : Vial 13
Inj : 1
Inj Volume : 5 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 1 µl
Acq. Method : C:\Chem32\1\DATA\MEHRAN\MEHRAN 2020-12-03 10-31-44\MEHRAN.M
Last changed : 12-03-2020 10:31:43 AM by MEHRAN
Analysis Method : C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-12-03 10-31-44\013-0101.D\DA.M (MEHRAN.M)
Last changed : 12-03-2020 10:55:08 AM by MEHRAN
Method Info : IC, 15% Isopropanol in hexanes, 0.3 ml/min, 1 ul injection, 30 oC



Area Percent Report

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

Data File C:\CHEM32\1\DATA\MEHRAN\MEHRAN 2020-12-03 10-31-44\013-0101.D
Sample Name: mr-7-201

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.976	BB	0.2685	1.00890e4	575.46118	94.3589
2	10.885	BB	0.4591	603.15106	20.27194	5.6411
Totals :				1.06922e4	595.73312	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.976	BB	0.2685	1.06958e4	610.06500	94.3557
2	10.886	BB	0.4592	639.81134	21.50003	5.6443
Totals :				1.13356e4	631.56504	

Signal 3: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.976	BB	0.2690	9815.70898	558.56873	94.3366
2	10.885	BB	0.4633	589.27222	19.79602	5.6634
Totals :				1.04050e4	578.36475	

*** End of Report ***