Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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69451 Weinheim, Germany

Highly Enantioselective Catalytic Conjugate Addition of *N*-Heterocycles to α,β-Unsaturated Ketones and Imides

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General Methods. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar and used as received. Solvents were purified and dried using standard methods: toluene were distilled from sodium; THF was distilled from sodium/ benzophenone ketyl. Reactions were performed without using inert atmosphere techniques. Flash chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM 500 spectrometer at 23˚C. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual proton in the NMR solvent ($CDCl_3$: δ 7.24). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.0). Abbreviations used in NMR data: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Infrared (IR) spectra were obtained using a Mattson Galaxy Series FTIR 3000 spectrometer referenced to polystyrene standard. Optical rotations were measured using 2 mL cell with a 1dm path lengh on a Jasco DIP 370 digital polarimeter. The mass spectroscopic data were obtained at the Harvard University mass spectrometry facility. Chiral HPLC analysis was performed on either a Hewlett-Packard 1050 or a Shimadzu VP-series instrument.

General procedure for the conjugate addition of purine to enones.

3a: Aluminum complex **1** (29 mg, 0.025 mmol, 5 mol%), purine (72 mg, 0.6 mmol, 1.2 equiv) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension the ketone **2a** (64.6 mg, 0.5 mmol, 65% purity) was added. The reaction mixture was stirred at room temperature for 48 h, and then purified by flash column chromatography on silica (eluent: 5% methanol in ethyl acetate). The product **3a** was obtained in 78% yield (80 mg) and 90% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = -27 (c = 1.65 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.0 (s, 1H; ArH), 8.8 (s, 1H; ArH), 8.1 (s, 1H; ArH), 5.1 (m, 1H, CH), 3.4 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.0 (dd, ^3J = 6 Hz, ^2J = 18 Hz, 1H; CH_2), 2.0 (s, 3H; CH_3), 1.6 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.8, 151.9, 150.9, 148.5, 134.7, 48.3, 47.9, 30.1, 19.8. IR: ν = 2968, 1714, 1590, 1408, 1205, 646 cm^{-1}. MS (CI): *m/z* (%): 205 (100) $[M+H]^+$.

Analytical data, products **3b-3e**:

3b: 3-hepten-2-one (56 mg, 0.5 mmol) was used. The product **3b** was isolated in 80% yield (93 mg) and 95% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = -5 (c = 0.04 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.1 (s, 1H; ArH), 8.9 (s, 1H; ArH), 8.1 (s, 1H; ArH), 4.9 (m, 1H, CH), 3.5 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.1 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (m, 1H, CH_2), 2.0 (s, 3H; CH_3), 1.8 (m, 1H, CH_2), 1.2 (m, 1H, CH_2), 1.0 (m, 1H, CH_2), 0.8 (t, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.5, 154.5, 153.5, 151.1, 148.5, 137.2, 55.4, 49.3, 37.8, 32.7, 21.9, 15.8. IR: ν = 2977, 1716, 1594, 1409 cm^{-1}. MS (CI): *m/z* (%): 233 (40) $[M+H]^+$.

3c: 3-octen-2-one (63 mg, 0.5 mmol) was used. The product **3c** was isolated in 76% yield (93 mg) and 93% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 5 % ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = -3 (c = 0.85 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.0 (s, 1H; ArH), 8.9 (s, 1H; ArH), 8.1 (s, 1H; ArH), 4.9 (m, 1H, CH), 3.5 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.0 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (m, 1H, CH_2), 2.0 (s, 3H; CH_3), 1.8 (m, 1H, CH_2), 1.2 (m, 2H, CH_2), 1.1 (m, 1H,

CH_2), 0.8 (m, 1H, CH_2), 0.7 (t, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.5, 154.5, 153.5, 151.1, 148.5, 137.2, 55.6, 49.3, 35.4, 32.6, 30.8, 24.4, 16.2. IR: ν = 2958, 2931 1717, 1594, 1407, 1199, 648 cm^{-1}. MS (CI): *m/z* (%): 247 (80) $[M+H]^+$.

3d: 5-methyl-3-hexen-2-one (56 mg, 0.5 mmol) was used. The product **3d** was isolated in 86% yield (100 mg) and 91% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 9% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = -3 (c = 0.65 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=9.1 (s, 1H; ArH), 8.9 (s, 1H; ArH), 8.1 (s, 1H; ArH), 4.6 (m, 1H, CH), 3.6 (dd, ^3J = 10 Hz, ^2J = 18 Hz, 1H; CH_2), 3.1 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 2.5 (m, 1H, CH), 2.0 (s, 3H; CH_3), 1.0 (d, ^3J = 7 Hz, 3H, CH_2), 0.7 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.7, 154.5, 153.6, 151.2, 148.8, 137.1, 61.6, 46.7, 33.7, 32.7, 22.4, 21.9. IR: ν = 2967, 1719, 1593, 1406, 1201 cm^{-1}. MS (CI): *m/z* (%): 233 (50) $[M+H]^+$.

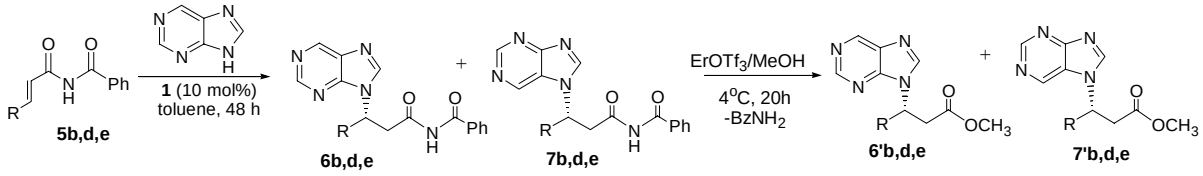
3e: 6-benzyloxy-3-hexen-2-one (102 mg, 0.5 mmol) was used. The product **3b** was isolated in 74% yield (120 mg) and 93% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 5% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = 44 (c = 1.00 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=9.0 (s, 1H; ArH), 8.8 (s, 1H; ArH), 8.0 (s, 1H; ArH), 7.2 (m, 5H; ArH), 5.1 (m, 1H, CH), 4.3 (d, ^2J = 12 Hz, 1H; O-CH_2), 4.2 (d, ^2J = 12 Hz, 1H; O-CH_2), 3.6 (dd, ^3J = 9 Hz, ^2J = 18 Hz, 1H; CH_2), 3.3 (dd, ^3J = 4 Hz, ^2J = 9 Hz, 1H; CH_2), 2.9 (m, 2H; CH_2), 2.5 (m, 1H, CH_2), 2.1 (m, 1H, CH_2), 2.0 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.8, 151.7, 151.0, 148.4, 146.8, 137.5, 134.8, 128.4, 127.8, 127.7, 73.1, 65.7, 50.4, 46.1, 32.8, 30.1. IR: ν = 2980, 1716, 1595, 1408, 1274, 1098, 715 cm^{-1}. MS (CI): *m/z* (%): 325 (100) $[M+H]^+$.

Reaction of purine with imides **6a-e**.

6a: Aluminum complex **1** (58 mg, 0.05 mmol, 10 mol%), purine (72 mg, 0.6 mmol, 1.2 equiv) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension the imide **5a** (95 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 48 h, and then purified by flash column chromatography on silica (eluent: 5% methanol in ethyl acetate). The product **6a** was obtained in 74% yield (115

mg) and 95% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 12% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 17 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.1 (s, 1H; ArH), 9.0 (s, 1H; ArH), 8.3 (s, 1H; ArH), 7.8 (m, 2H; ArH), 7.5 (m, 1H; ArH), 7.4 (m, 2H; ArH), 5.1 (m, 1H, CH), 3.0 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.9 (dd, ^{3}J = 6 Hz, ^{2}J = 17 Hz, 1H; CH_2), 1.7 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=172.3, 171.8, 163.5, 155.8, 149.1, 142.8, 135.8, 134.4, 131.1, 129.8, 126.8, 57.7, 52.9, 43.3, 23.2. IR: ν = 2908, 1715, 1690, 1500, 1248, 1204, 712 cm^{-1}. MS (CI): *m/z* (%): 310 (100) $[M]^{+}$.

General procedure for **6b, 6d, 6e** (these compounds were converted, in the mixture with their regioisomers **7**, to the corresponding methyl esters **6'** and **7'** for a facile separation (Scheme 1)).



Scheme 1

6'b. a) Preparation of mixture of **6b** and **7b**: Aluminum complex **1** (58 mg, 0.05 mmol, 10 mol%), purine (72 mg, 0.6 mmol, 1.2 equiv) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension the imide **5b** (109 mg, 0.5 mmol) was added. The reaction mixture was stirred for 48 h at 65˚C and then filtered through a silica plug, resulting in a crude mixture of products **6b** and **7b** in ratio 3:1.

b) Methanolysis: The crude mixture of **6b** and **7b** was dissolved in methanol (2 ml, excess) and cooled to 4˚C. Erbium trifluoromethanesulfonate (15 mg, 0.025 mmol) was added and the solution stirred at 4˚C for 20 hours. After removal of the solvent *in vacuo*, the major product (**6b**) was isolated by chromatography on silica (eluent: 5% methanol in ethyl acetate) in 69% yield (86 mg) and 95% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 12% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -18 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.1 (s, 1H; ArH), 9.0 (s, 1H; ArH), 8.1 (s, 1H; ArH), 4.9 (m, 1H, CH), 3.6 (s, 3H, CH_3), 3.3 (dd, ^{3}J = 9 Hz, ^{2}J = 17 Hz, 1H; CH_2), 2.9 (dd, ^{3}J = 5 Hz, ^{2}J = 17 Hz, 1H; CH_2), 2.3 (m, 1H, CH_2), 1.9 (m, 1H, CH_2),

1.2 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.9 (t, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=170.6, 152.2, 151.1, 148.6, 145.2, 134.6, 105.4, 53.6, 51.9, 38.3, 35.3, 19.3, 13.3. IR: ν = 2960, 1737, 1595, 1409, 1303, 1202, 648 cm^{-1}. MS (CI): *m/z* (%): 249 (100) $[M]^+$.

6c. Aluminum complex **1** (58 mg, 0.05 mmol, 10 mol%), purine (72 mg, 0.6 mmol, 1.2 equiv) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension the imide **5c** (109 mg, 0.5 mmol) was added. The reaction mixture was stirred at 65˚C for 48 h, and then purified by flash column chromatography on silica (eluent: 5% methanol in ethyl acetate). The product **6c** was obtained in 64% yield (108 mg) and 98% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 12% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = 27 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.4 (s, 1H; N-H), 8.9 (s, 1H; ArH), 8.8 (s, 1H; ArH), 8.1 (s, 1H; ArH), 7.7 (m, 2H; ArH), 7.5 (m, 1H; ArH), 7.4 (m, 2H; ArH), 4.8 (m, 1H, CH), 4.0 (dd, ^3J = 9 Hz, ^2J = 18 Hz, 1H; CH_2), 3.6 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 2.6 (m, 1H, CH); 1.1 (d, ^3J = 7 Hz, 3H; CH_3), 0.7 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.7, 168.6, 154.7, 153.9, 150.8, 148.5, 136.6, 135.9, 134.8, 131.4, 130.3, 61.3, 41.9, 34.1, 22.3, 21.9.IR: ν = 2967, 1714, 1688, 1598, 1251, 718 cm^{-1}. MS (CI): *m/z* (%): 338 (100) $[M]^+$.

6'd. Imide **5d** (133 mg, 0.5 mmol) was used. Product **6'd** was isolated, after methanolysis and chromatography on silica (eluent: 5% methanol in ethyl acetate) in 63% yield (94 mg) and 96% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 7% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = 94 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.1 (s, 1H; ArH), 8.9 (s, 1H; ArH), 7.8 (s, 1H; ArH), 7.1 (m, 3H; ArH), 6.9 (m, 2H; ArH), 5.1 (m, 1H, CH), 3.5 (s, 3H; CH_3), 3.5 (dd, ^3J = 9 Hz, ^2J = 14 Hz, 1H; CH_2), 3.4 (dd, ^3J = 10 Hz, ^2J = 14 Hz, 1H; CH_2), 3.3 (dd, ^3J = 6 Hz, ^2J = 14 Hz, 1H; CH_2), 3.0 (dd, ^3J = 4 Hz, ^2J = 14 Hz, 1H; CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ=168.3, 149.8, 148.9, 146.3, 143.3, 134.0, 132.4, 126.5, 126.4, 125.0, 53.7, 49.7, 37.2, 35.0. IR: ν = 3390, 1734, 1594, 1409, 1203, 703 cm^{-1}. MS (CI): *m/z* (%): 297 (100) $[M]^+$.

6'e. Imide **5e** (159 mg, 0.5 mmol) was used. Product **6'e** was isolated, after methanolysis and chromatography on silica (eluent: 5% methanol in ethyl acetate) in 65% yield (113 mg) and 96% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -10 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.0 (s, 1H; ArH), 8.9 (s, 1H; ArH), 8.1 (s, 1H; ArH), 5.1 (m, 1H, CH), 4.0 (dd, ^{3}J = 6 Hz, ^{2}J = 11 Hz, 1H; CH_2), 3.9 (dd, ^{3}J = 4 Hz, ^{2}J = 11 Hz, 1H; CH_2), 3.5 (s, 3H; CH_3), 3.2 (dd, ^{3}J = 8 Hz, ^{2}J = 15 Hz, 1H; CH_2), 3.0 (dd, ^{3}J = 4 Hz, ^{2}J = 15 Hz, 1H; CH_2), 0.71 (s, 9H; $C(CH_3)_3$), -0.1 (s, 3H; CH_3), -0.2 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=167.7, 150.9, 145.2, 138.1, 62.2, 53.4, 50.0, 33.15, 23.3, 15.8. IR: ν = 3390, 3191, 1645, 1578, 1406, 1203, 1117, 838 cm^{-1}. MS (CI): *m/z* (%): 351 (100) $[M+H]^{+}$.

General procedure for the conjugate addition of Boc-adenine to enones.

8a: Aluminum complex **1** (58 mg, 0.05 mmol, 10 mol%), Boc-adenine (141 mg, 0.6 mmol, 1.2 equiv), *tert*-butanol (22 mg, 0.3 mmol, 0.6 equiv) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension 3-hepten-2one (56 mg, 0.5 mmol) was added. The reaction mixture was stirred 4˚C for 48 h, and then purified by flash column chromatography on silica (eluent: 5% methanol in ethyl acetate). The product **8a** was obtained in 67% yield (116 mg) and 95% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 5% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -9 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.7 (s, 1H; ArH), 8.1 (s, 1H; N-H), 7.9 (s, 1H; ArH), 4.9 (m, 1H, CH), 3.5 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.1 (dd, ^{3}J = 5 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.2 (m, 1H, CH_2), 2.0 (s, 3H; CH_3), 1.8 (m, 1H, CH_2), 1.5 (s, 9H; $C(CH_3)_3$), 0.9 (t, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=203.0, 150.0, 148.4, 147.6, 147.4, 140.9, 120.0, 50.9, 44.5, 33.1, 28.0, 25.8, 17.1, 11.0. IR: ν = 2964, 1748, 1718, 1610, 1464, 1233, 1147 cm^{-1}. MS (CI): *m/z* (%): 348 (40) $[M+H]^{+}$.

8b. 5-methyl-3-hexen-2-one (56 mg, 0.5 mmol) was used. The product **8b** was isolated in 60% yield (104 mg) and 98% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 5% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -26 (c = 1.00 in

chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.6 (s, 1H; ArH), 8.1 (s, 1H; N-H), 8.0 (s, 1H; ArH), 4.5 (m, 1H, CH), 3.6 (dd, ^{3}J = 10 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.0 (dd, ^{3}J = 3 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.5 (m, 1H, CH), 2.0 (s, 3H; CH_3), 1.5 (s, 9H; $C(CH_3)_3$), 1.0 (d, ^{3}J = 7 Hz, 3H, CH_2), 0.7 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=203.1, 150.0, 148.5, 147.6, 147.4, 141.3, 119.8, 79.8, 58.0, 57.2, 42.0, 28.9, 27.9, 25.8, 17.6, 17.2, 11.9. IR: ν = 2975, 1749, 1718, 1610, 1465, 1233, 1148 cm^{-1}. MS (CI): *m/z* (%):348 (20) $[M+H]^+$.

8c. 6-benzyloxy-3-hexen-2-one (102 mg, 0.5 mmol) was used. The product **8c** was isolated in 61% yield (134 mg) and 99% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 42 (c = 0.90 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.7 (s, 1H; ArH), 8.0 (s, 1H; N-H), 7.9 (s, 1H; ArH), 7.3 (m, 3H; ArH), 7.2 (m, 2H; ArH), 5.1 (m, 1H, CH), 4.4 (d, ^{2}J = 12 Hz, 1H; O-CH_2), 4.2 (d, ^{2}J = 12 Hz, 1H; O-CH_2), 3.6 (dd, ^{3}J = 9 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.4 (dd, ^{3}J = 5 Hz, ^{2}J = 10 Hz, 1H; CH_2), 3.0 (dd, ^{3}J = 5 Hz, ^{2}J = 10 Hz, 1H; CH_2), 2.9 (dd, ^{3}J = 4 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.5 (m, 1H, CH_2), 2.1 (m, 1H, CH_2), 2.0 (s, 3H; CH_3), 1.5 (s, 9H; $C(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.8, 153.0, 149.9, 147.8, 147.5, 146.5, 146.4, 141.6, 135.5, 126.2, 125.5, 119.9, 79.9, 70.9, 63.5, 48.4, 43.9, 30.7, 27.9, 25.8. IR: ν = 2976, 2929, 1750, 1717, 1610, 1502, 1232, 1147 cm^{-1}. MS (CI): *m/z* (%): 440 (10) $[M+H]^+$, 340 (100) $[M\text{-Boc}]^+$.

General procedure for the conjugate addition of 6-benzyloxy-purine to enones.

9a: Aluminum complex **1** (58 mg, 0.05 mmol, 10 mol%), 6-benzyloxy-purine (135 mg, 0.6 mmol, 1.2 equiv) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension 3-hepten-2one (56 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 48 h, and then purified by flash column chromatography on silica (eluent: 5% methanol in ethyl acetate). The product **9a** was obtained in 93% yield (157 mg) and 97% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 6% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -12 (c = 0.90 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.5 (s, 1H; ArH), 7.9 (s, 1H; ArH), 7.5 (m, 2H; ArH), 7.3 (m, 3H; ArH), 5.6 (s, 1H, CH_2), 4.9 (m, 1H, CH), 3.4 (dd, ^{3}J = 8 Hz, ^{2}J

= 18 Hz, 1H; CH_2), 3.0 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (m, 1H, CH_2), 2.1 (s, 3H; CH_3), 1.8 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 1.0 (m, 1H, CH_2), 0.8 (t, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.5, 163.0, 154.4, 153.9, 145.2, 138.7, 130.8, 124.6, 70.7, 55.4, 49.6, 38.1, 32.7, 21.8,15.8. IR: ν = 2960, 1717, 1598, 1572, 1341, 1315, 1220 cm^{-1}. MS (CI): *m/z* (%): 339 (100) $[M]^+$.

9b. 5-methyl-3-hexen-2-one (56 mg, 0.5 mmol) was used. The product **9b** was isolated in 89% yield (150 mg) and 96% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = -23 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.5 (s, 1H; ArH), 7.9 (s, 1H; ArH), 7.5 (m, 2H; ArH), 7.3 (m, 3H; ArH), 5.6 (s, 1H, CH_2), 4.6 (m, 1H, CH), 3.6 (dd, ^3J = 10 Hz, ^2J = 18 Hz, 1H; CH_2), 3.0 (dd, ^3J = 3 Hz, ^2J = 18 Hz, 1H; CH_2), 2.5 (m, 1H, CH), 2.0 (s, 3H; CH_3), 1.0 (d, ^3J = 7 Hz, 3H, CH_2), 0.7 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.9, 158.3, 149.7, 149.2, 140.9, 133.9, 126.1, 126.0, 125.8, 119.7, 66.0, 56.8, 42.2, 29.2, 27.3, 17.6, 17.1. IR: ν = 2965, 1717, 1598, 1571, 1469, 1341, 1316, 1215 cm^{-1}. MS (CI): *m/z* (%): 339 (100) $[M+H]^+$.

9c. 6-benzyloxy-3-hexen-2-one (102 mg, 0.5 mmol) was used. The product **9c** was isolated in 75% yield (161 mg) and 95% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 12% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = 16 (c = 0.45 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.4 (s, 1H; ArH), 7.8 (s, 1H; ArH), 7.5 (m, 2H; ArH), 7.2 (m, 8H; ArH), 5.6 (s, 1H, CH_2), 5.1 (m, 1H, CH), 4.3 (d, ^2J = 12 Hz, 1H; O-CH_2), 4.2 (d, ^2J = 12 Hz, 1H; O-CH_2), 3.6 (dd, ^3J = 9 Hz, ^2J = 18 Hz, 1H; CH_2), 3.4 (dd, ^3J = 5 Hz, ^2J = 10 Hz, 1H; CH_2), 2.9 (m, 2H; CH_2), 2.4 (m, 1H, CH_2), 2.1 (m, 1H, CH_2), 2.0 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.4, 163.0, 154.3, 153.8, 146.1, 140.2, 138.7, 130.9, 130.5, 130.2, 124.775.6, 70.8, 68.3, 52.9, 48.9, 35.6, 32.7. IR: ν = 2970, 2929, 1715, 1598, 1572, 1453, 1342, 1315, 1218, 746 cm^{-1}. MS (CI): *m/z* (%): 431 (100) $[M+H]^+$.

General procedure for the conjugate addition of 6-chloro-purine and 6-methylmercapto-purine to enones.

10a: Aluminum complex **1** (29 mg, 0.025 mmol, 5 mol%), 6-benzyloxy-purine (135 mg, 0.6 mmol, 1.2 equiv) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension 3-hepten-2one (56 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 48 h, and then purified by flash column chromatography on silica (eluent: 5% methanol in ethyl acetate). The product **10a** was obtained in 95% yield (127 mg) and 91% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 6% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -8 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.7 (s, 1H; ArH), 8.1 (s, 1H; ArH), 4.9 (m, 1H, CH), 3.5 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.1 (dd, ^{3}J = 4 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.2 (m, 1H, CH_2), 2.1 (s, 3H; CH_3), 1.8 (m, 1H, CH_2), 1.2 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.8 (t, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.5, 149.1, 148.8, 143.7, 129.9, 51.1, 44.4, 33.0, 27.9, 17.1, 11.0. IR: ν = 2961, 1716, 1592, 1557, 1336, 1195, 1144, 936 cm^{-1}. MS (CI): *m/z* (%): 267 (50) $[M]^{+}$.

10b. 5-methyl-3-hexen-2-one (56 mg, 0.5 mmol) was used. The product **10b** was isolated in 85% yield (113 mg) and 93.5% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 6% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -16 (c = 0.75 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.7 (s, 1H; ArH), 8.1 (s, 1H; ArH), 4.6 (m, 1H, CH), 3.6 (dd, ^{3}J = 10 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.0 (dd, ^{3}J = 3 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.5 (m, 1H, CH), 2.0 (s, 3H; CH_3), 1.0 (d, ^{3}J = 7 Hz, 3H, CH_2), 0.7 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.7, 149.1, 148.9, 144.0, 129.8, 57.3, 41.9, 29.0, 27.9, 17.5, 17.1 IR: ν = 2967, 1718, 1592, 1557, 1394, 1336, 1195, 939 cm^{-1}. MS (CI): *m/z* (%): 267 (100) $[M]^{+}$.

10c. 6-benzyloxy-3-hexen-2-one (102 mg, 0.5 mmol) was used. The product **10c** was isolated in 82% yield (147 mg) and 96% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 12% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 25 (c = 0.50 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.6 (s, 1H; ArH), 8.1 (s, 1H; ArH), 7.3 (m, 3H; ArH), 7.2 (m, 2H; ArH), 5.2 (m, 1H, CH), 4.4 (d, ^{2}J = 8 Hz, 1H; O-CH_2), 4.3 (d, ^{2}J = 8 Hz, 1H; O-CH_2), 3.6 (dd, ^{3}J = 9 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.4 (dd, ^{3}J = 3 Hz, ^{2}J = 10 Hz, 1H; CH_2), 3.0 (m, 2H, CH_2), 2.5 (m, 1H, CH_2), 2.2 (m, 1H, CH_2), 2.0 (s, 3H;

CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.2, 153.9, 153.7, 153.5, 149.2, 140.0, 134.8, 130.9, 130.4, 130.2, 75.7, 68.2, 53.5, 48.6, 35.4, 32.6. IR: ν = 2925, 2862, 1716, 1592, 1558, 1336, 1194, 1142, 938 cm^{-1}. MS (CI): *m/z* (%): 359 (100) $[M]^+$.

11a. 3-hepten-2one (56 mg, 0.5 mmol) and 6-methylmercapto-purine (100 mg, 1.2 equiv) were used. The product **11a** was isolated in 91% yield (127 mg) and 97% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 6% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = -14 (c = 1.00 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=8.6 (s, 1H; ArH), 7.9 (s, 1H; ArH), 4.8 (m, 1H, CH), 3.4 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.0 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (m, 1H, CH_2), 2.0 (s, 3H; CH_3), 1.7 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.9 (m, 1H, CH_2), 0.8 (t, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.7, 159.3, 149.1, 145.6, 140.9, 129.8, 50.6, 44.7, 33.2, 28.0, 17.1, 11.0, 9.4. IR: ν = 2960, 2931, 1716, 1568, 1332, 1199, 946 cm^{-1}. MS (CI): *m/z* (%): 279 (90) $[M+H]^+$.

11b. 5-methyl-3-hexen-2-one (56 mg, 0.5 mmol) and 6-methylmercapto-purine (100 mg, 1.2 equiv) were used. The product **11b** was isolated in 88% yield (122 mg) and 98% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 6% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = -27 (c = 1.1 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=8.6 (s, 1H; ArH), 8.0 (s, 1H; ArH), 4.6 (m, 1H, CH), 3.6 (dd, ^3J = 10 Hz, ^2J = 18 Hz, 1H; CH_2), 3.0 (dd, ^3J = 3 Hz, ^2J = 18 Hz, 1H; CH_2), 2.7 (s, 3H; S-CH_3), 2.5 (m, 1H, CH), 2.0 (s, 3H; CH_3), 1.0 (d, ^3J = 7 Hz, 3H, CH_2), 0.7 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.9, 159.4, 149.1, 145.7, 141.3, 129.6, 56.8, 42.1, 29.1, 27.9, 17.6, 17.1, 9.4. IR: ν = 2966, 1718, 1567, 1332, 1199, 939 cm^{-1}. MS (CI): *m/z* (%): 279 (100) $[M+H]^+$.

11c. 6-benzyloxy-3-hexen-2-one (102 mg, 0.5 mmol) and 6-methylmercapto-purine (100 mg, 1.2 equiv) were used. The product **11c** was isolated in 79% yield (146 mg) and 96% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 12% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = 22 (c = 0.50 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=8.6 (s, 1H; ArH), 7.9 (s, 1H; ArH), 7.3 (m, 5H; ArH), 5.1 (m, 1H,

CH), 4.4 (d, ^{2}J = 6 Hz, 1H; O-CH_2), 4.3 (d, ^{2}J = 6 Hz, 1H; O-CH_2), 3.6 (dd, ^{3}J = 9 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.4 (dd, ^{3}J = 3 Hz, ^{2}J = 10 Hz, 1H; CH_2), 3.0 (m, 2H, CH_2), 2.7 (s, 3H; S-CH_3), 2.5 (m, 1H, CH_2), 2.2 (m, 1H, CH_2), 2.0 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.6, 159.3, 148.9, 145.6, 141.8, 135.5, 129.9, 126.2, 125.5, 125.4, 70.9, 63.5, 48.2, 44.1, 30.8, 27.9, 9.4. IR: ν = 2929, 1714, 1568, 1332, 1273, 939, 715 cm^{-1}. MS (CI): *m/z* (%): 371 (100) $[M+H]^{+}$.

Representative procedure for the conjugate addition of 6-benzyloxy-purine, 6-chloro-purine and 6-methylmercapto-purine to imides.

12a. Aluminum complex **1** (58 mg, 0.05 mmol, 10 mol%), 6-benzyloxy-purine (135 mg, 0.6 mmol, 1.2 equiv) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension (3-methyl-acryloyl)-benzamide (95 mg, 0.5 mmol) was added. The reaction mixture was stirred at 55˚C for 48 h, and then purified by flash column chromatography on silica (eluent: 5% methanol in ethyl acetate). The product **12a** was obtained in 81% yield (168 mg) and 91% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 12% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 8 (c = 0.40 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.8 (bs, 1H; N-H), 8.5 (s, 1H; ArH), 8.0 (s, 1H; ArH), 7.8 (m, 2H; ArH), 7.6 (m, 1H; ArH), 7.5 (m, 4H; ArH), 7.3 (m, 3H, ArH), 5.6 (m, 2H, O-CH_2), 5.2 (m, 1H, CH), 4.0 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.6 (dd, ^{3}J = 5 Hz, ^{2}J = 18 Hz, 1H; CH_2), 1.8 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=172.3, 165.5, 160.4, 151.9, 151.5, 141.6, 136.2, 133.4, 132.2, 128.9, 128.3, 128.2, 128.0, 127.6, 122.0, 68.2, 48.4, 43.1, 20.4. IR: ν = 2929, 1714, 1689, 1600, 1471, 1319, 1243, 1218, 1010, 710 cm^{-1}. MS (CI): *m/z* (%): 416 (100) $[M]^{+}$.

12b. [3-(t-butyl-dimethyl-silyloxymethyl)-acryloyl]-benzamide (159 mg, 0.5 mmol) was used. The product **12b** was isolated in 77% yield (209 mg) and 95% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 18 (c = 0.90 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.9 (bs, 1H;

N-H), 8.5 (s, 1H; ArH), 8.1 (s, 1H; ArH), 7.8 (m, 2H; ArH), 7.6 (m, 1H; ArH), 7.5 (m, 4H; ArH), 7.3 (m, 3H, ArH), 5.6 (m, 2H, O-CH_2), 5.2 (m, 1H, CH), 4.2 (dd, ^3J = 6 Hz, ^2J = 10 Hz, 1H; CH_2), 4.0 (dd, ^3J = 4 Hz, ^2J = 10 Hz, 1H; CH_2), 3.9 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.7 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 0.8 (s, 9H; $C(CH_3)_3$), -0.07 (s, 3H; CH_3), -0.11 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.8, 168.0, 162.2, 154.5, 154.0, 145.2, 136.2, 135.9, 135.0, 131.5, 130.9, 130.7, 130.5, 130.1, 70.7, 66.2, 56.2, 40.7, 28.2, 20.5, -3.2, -3.1. IR: ν = 2953, 2930, 1714, 1689, 1600, 1574, 1470, 1251, 836 cm^{-1}. MS (CI): *m/z* (%): 546 (100) $[M+H]^+$.

13a. Al-salen catalyst **1** (29 mg, 0.025 mmol, 5mol%), 6-chloro-purine (93 mg, 1.2 equiv) and (3-methyl-acryloyl)-benzamide (95 mg, 0.5 mmol) were used. Reaction time: 18 hours. The product **13a** was isolated in 92% yield (158 mg) and 97% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 5% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = 27 (c = 0.60 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.7 (s, 1H; ArH), 8.6 (bs, 1H; N-H), 8.2 (s, 1H; ArH), 7.8 (bd, 2H; ^3J = 7 Hz; ArH), 7.6 (t, 1H; ^3J = 7 Hz; ArH), 7.5 (t, 2H; ^3J = 7 Hz; ArH), 5.3 (m, 1H, CH), 4.0 (dd, ^3J = 9 Hz, ^2J = 18 Hz, 1H; CH_2), 3.6 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 1.8 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.7, 168.0, 154.0, 153.5, 147.5, 136.1, 134.5, 131.6, 130.1, 51.6, 45.4, 22.7. IR: ν = 3281, 2982, 1715, 1689, 1593, 1487, 1337, 1243, 1213, 710 cm^{-1}. MS (CI): *m/z* (%): 344 (50) $[M]^+$.

13b. Al-salen catalyst **1** (29 mg, 0.025 mmol, 5mol%), 6-chloro-purine (93 mg, 1.2 equiv) and [3-(t-butyl-dimethyl-silyloxymethyl)-acryloyl]-benzamide (159 mg, 0.5 mmol) were used. Reaction time: 24 hours. The product **13b** was isolated in 93% yield (220 mg) and 97% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D$ = 23 (c = 0.80 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.7 (bs, 1H; N-H), 8.6 (s, 1H; ArH), 8.3 (s, 1H; ArH), 7.8 (bd, 2H; ^3J = 7 Hz; ArH), 7.6 (t, 1H; ^3J = 7 Hz; ArH), 7.5 (t, 2H; ^3J = 7 Hz; ArH), 5.3 (m, 1H, CH), 4.2 (dd, ^3J = 6 Hz, ^2J = 10 Hz, 1H; CH_2), 4.0 (m, 2H; CH_2), 3.7 (dd, ^3J = 5 Hz, ^2J = 10 Hz, 1H; CH_2), 0.8 (s, 9H; $C(CH_3)_3$), -0.04 (s, 3H; CH_3), -0.05 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.7, 168.0, 154.0, 153.4, 148.4, 136.1, 134.6, 134.2, 131.6,

130.1, 66.0, 56.7, 40.5, 28.1, 20.5, -3.2, -3.3. IR: ν = 2954, 2931, 1715, 1689, 1593, 1471, 1254, 836, 710 cm^{-1}. MS (CI): *m/z* (%): 474 (100) $[M+H]^+$.

14a. Al-salen catalyst **1** (29 mg, 0.025 mmol, 5mol%), 6-methylmercapto-purine (100 mg, 1.2 equiv) and (3-methyl-acryloyl)-benzamide (95 mg, 0.5 mmol) were used. Reaction time: 48 hours. The product **14a** was isolated in 90% yield (160 mg) and 95.5% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 12% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D = 33$ (c = 1.00 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=8.7 (bs, 1H; N-H), 8.6 (s, 1H; ArH), 8.0 (s, 1H; ArH), 7.8 (bd, 2H; ^3J = 7 Hz; ArH), 7.6 (t, 1H; ^3J = 7 Hz; ArH), 7.5 (t, 2H; ^3J = 7 Hz; ArH), 5.4 (m, 1H, CH), 4.0 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.6 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 2.7 (s, 3H; S-CH_3), 1.8 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.8, 168.0, 164.0, 154, 150.5, 144.5, 136.0, 134.7, 134.4, 131.5, 130.1, 51.0, 45.6, 22.9, 14.2. IR: ν = 3271, 2963, 1714, 1687, 1567, 1482, 1242, 1208, 710 cm^{-1}. MS (CI): *m/z* (%): 356 (60) $[M]^+$.

14b. Al-salen catalyst **1** (29 mg, 0.025 mmol, 5mol%), 6-methylmercapto-purine (100 mg, 1.2 equiv) and [3-(t-butyl-dimethyl-silyloxymethyl)-acryloyl]-benzamide (159 mg, 0.5 mmol) were used. Reaction time: 48 hours. The product **14b** was isolated, after chromatography on silica (eluent: ethyl acetate/methylene chloride 1:1) in 79% yield (191 mg) and 96.5% enantiomeric excess, as determined by chiral HPLC (Chiralpack AD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D = 10$ (c = 0.50 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=8.7 (s, 1H; ArH), 8.6 (bs, 1H; N-H), 8.1 (s, 1H; ArH), 7.8 (m, 2H; ArH), 7.6 (t, 1H; ^3J = 7 Hz; ArH), 7.5 (t, 2H; ^3J = 7 Hz; ArH), 5.2 (m, 1H, CH), 4.2 (dd, ^3J = 6 Hz, ^2J = 10 Hz, 1H; CH_2), 4.0 (dd, ^3J = 4 Hz, ^2J = 10 Hz, 1H; CH_2), 3.9 (dd, ^3J = 8 Hz, ^2J = 19 Hz, 1H; CH_2), 3.7 (dd, ^3J = 6 Hz, ^2J = 19 Hz, 1H; CH_2), 2.7 (s, 3H; S-CH_3), 0.8 (s, 9H; $C(CH_3)_3$), -0.06 (s, 3H; CH_3), -0.10 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.7, 168.0, 163.9, 154.0, 150.6, 145.6, 136.0, 134.7, 134.0, 131.5, 130.1, 66.2, 56.1, 40.6, 28.2, 20.5, 14.2, -3.2, -3.3. IR: ν = 2952, 2929, 1715, 1688, 1568, 1471, 1253, 836, 710 cm^{-1}. MS (CI): *m/z* (%): 486 (100) $[M+H]^+$.

General procedure for the conjugate addition of benzotriazole to enones.

Addition to 3-penten-2-one. Formation of products **15a** and **16a**: Aluminum complex **1** (29 mg, 0.025 mmol, 5 mol%), benzotriazole (60 mg, 0.5 mmol) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension 3-penten-2-one (65 mg, 0.5 mmol, 65% purity) was added. The reaction mixture was stirred at room temperature for 2 h, resulting in a mixture of regioisomers **15a** and **16a**. The products were separated by flash column chromatography on silica (eluent: 33% ethyl acetate in hexanes).

Analytical data for **15a**: Yield: 72% (73 mg); ee: 90.5% (Chiral HPLC: Chiralpack OD, 5% ethanol/hexanes, 1.0 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -15 (c = 0.65 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.9 (d, ^{3}J = 9 Hz, 1H; ArH), 7.5 (d, ^{3}J = 8 Hz, 1H; ArH), 7.4 (t, ^{3}J = 8 Hz, 1H; ArH), 7.2 (t, ^{3}J = 8 Hz, 1H; ArH), 5.3 (m, 1H, CH), 3.5 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.0 (dd, ^{3}J = 6 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.0 (s, 3H; CH_3), 1.6 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.7, 143.6, 130.3, 124.9, 121.6, 117.5, 107.4, 47.9, 46.8, 28.1, 27.4, 18.9. IR: ν = 2924, 1717, 1454, 1370, 1164, 748 cm^{-1}. MS (CI): *m/z* (%): 204 (100) $[M+H]^{+}$.

Analytical data for **16a**: Yield: 23% (23 mg); ee: 94% (Chiral HPLC: Chiralpack OD, 3% *iso*-propanol/hexanes, 1.0 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -18 (c = 0.9 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.8 (dd, ^{4}J = 3 Hz, ^{3}J = 7 Hz, 2H; ArH), 7.3 (dd, ^{4}J = 3 Hz, ^{3}J = 6 Hz, 2H; ArH), 5.5 (m, 1H, CH), 3.5 (dd, ^{3}J = 7 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.0 (dd, ^{3}J = 6 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.2 (s, 3H; CH_3), 1.7 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=203.7, 141.7, 123.9, 115.8, 56.1, 46.9, 28.0, 19.1. IR: ν = 2924, 1720, 1365, 1322, 1277, 1170, 748 cm^{-1}. MS (CI): *m/z* (%): 204 (20) $[M+H]^{+}$.

15b, 16b. 3-hepten-2-one (56 mg, 0.5 mmol) was used. The products **15b** and **16b** were separated by chromatography on silica (eluent: 33% ethyl acetate in hexanes).

Analytical data for **15b**: Yield: 75% (87 mg); ee: 94% (Chiral HPLC: Chiralpack OD, 5% ethanol/hexanes, 1.0 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 4 (c = 0.50 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.0 (d, ^{3}J = 8 Hz, 1H; ArH), 7.7 (d, ^{3}J = 8 Hz, 1H; ArH), 7.5 (t, ^{3}J = 8 Hz, 1H; ArH), 7.4 (t, ^{3}J = 8 Hz, 1H; ArH), 5.3 (m, 1H, CH), 3.6 (dd, ^{3}J = 8 Hz, ^{2}J = 18

Hz, 1H; CH_2), 3.1 (dd, ^3J = 6 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (m, 1H, CH_2), 2.1 (s, 3H; CH_3), 1.9 (m, 1H, CH_2), 1.2 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.9 (t, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.7, 148.1, 136.1, 129.7, 126.4, 122.3, 112.3, 56.8, 50.7, 40.0, 32.9, 21.7, 16.0. IR: ν = 2962, 2933, 1719, 1453, 1369, 1161, 748 cm^{-1}. MS (CI): *m/z* (%): 232 (100) $[M]^+$.

Analytical data for **16b**: Yield: 22% (26 mg); ee: 98% (Chiral HPLC: Chiralpack OD, 3% *iso*-propanol/hexanes, 1.0 ml/min, 254 nm), $[\alpha]^{20}_D$ = -9 (c = 0.5 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.9 (dd, ^4J = 3 Hz, ^3J = 7 Hz, 2H; ArH), 7.4 (dd, ^4J = 3 Hz, ^3J = 7 Hz, 2H; ArH), 5.4 (m, 1H, CH), 3.5 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.1 (dd, ^3J = 6 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (s, 3H; CH_3), 2.1 (m, 1H, CH_2), 1.9 (m, 1H, CH_2), 1.3 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.9 (t, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.2, 146.5, 128.6, 120.6, 65.1, 50.6, 40.2, 32.8, 21.5, 16.0. IR: ν = 2960, 2930, 1721, 1362, 1323, 1274, 1166, 747 cm^{-1}. MS (CI): *m/z* (%): 232 (100) $[M]^+$.

15c, 16c. 5-methyl-3-hexen-2-one (56 mg, 0.5 mmol) was used. The products **15c** and **16c** were separated by chromatography on silica (eluent: 33% ethyl acetate in hexanes).

Analytical data for **15c**: Yield: 67% (78 mg); ee: 98% (Chiral HPLC: Chiralpack OD, 5% ethanol/hexanes, 1.0 ml/min, 254 nm), $[\alpha]^{20}_D$ = 27 (c = 0.90 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.0 (d, ^3J = 8 Hz, 1H; ArH), 7.7 (d, ^3J = 8 Hz, 1H; ArH), 7.4 (t, ^3J = 8 Hz, 1H; ArH), 7.3 (t, ^3J = 8 Hz, 1H; ArH), 5.0 (m, 1H, CH), 3.7 (dd, ^3J = 10 Hz, ^2J = 18 Hz, 1H; CH_2), 3.0 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 2.3 (m, 1H, CH), 2.0 (s, 3H; CH_3), 1.0 (d, ^3J = 7 Hz, 3H, CH_2), 0.7 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.7, 154.5, 153.6, 151.2, 148.8, 137.1, 61.6, 46.7, 33.7, 32.7, 22.4, 21.9. IR: ν = 2966, 1718, 1493, 1408, 1199, 748 cm^{-1}. MS (CI): *m/z* (%): 232 (100) $[M]^+$.

Analytical data for **16c**: Yield: 23% (27 mg); ee: 98% (Chiral HPLC: Chiralpack OD, 3% *iso*-propanol/hexanes, 1.0 ml/min, 254 nm), $[\alpha]^{20}_D$ = -19 (c = 0.5 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.8 (dd, ^4J = 3 Hz, ^3J = 6 Hz, 2H; ArH), 7.3 (dd, ^4J = 3 Hz, ^3J = 7 Hz, 2H; ArH), 5.2 (m, 1H, CH), 3.6 (dd, ^3J = 10 Hz, ^2J = 18 Hz, 1H; CH_2), 2.9 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 2.4 (m, 1H, CH), 2.1 (s, 3H; CH_3), 0.9 (d, ^3J = 7 Hz, 3H, CH_2), 0.8 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.7, 141.5, 123.8,

115.8, 65.5, 51.1, 42.1, 31.4, 28.0, 16.5. IR: ν = 2967, 1721, 1363, 1276, 1168, 749 cm^{-1}. MS (CI): *m/z* (%): 232 (50) $[M]^+$.

15d, 16d. 6-benzyloxy-3-hexen-2-one (102 mg, 0.5 mmol) was used. The products **15d** and **16d** were separated by chromatography on silica (eluent: 33% ethyl acetate in hexanes).

Analytical data for **15d**: Yield: 65% (105 mg); ee: 93% (Chiral HPLC: Chiralpack OD, 5% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D = 63$ (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.9 (d, ^3J = 8 Hz, 1H; ArH), 7.6 (d, ^3J = 8 Hz, 1H; ArH), 7.4 (t, ^3J = 8 Hz, 1H; ArH), 7.3 (t, ^3J = 8 Hz, 1H; ArH), 7.2 (m, 3H; ArH), 7.1 (m, 2H; ArH), 5.5 (m, 1H; CH), 4.3 (d, ^2J = 8 Hz, 2H; O-CH_2), 4.2 (d, ^2J = 8 Hz, 2H; O-CH_2), 3.5 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.3 (m, 1H, CH_2), 3.0 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 2.8 (m, 1H, CH_2), 2.3 (m, 1H, CH_2), 2.2 (m, 1H, CH_2), 2.1 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.8, 145.1, 137.8, 133.8, 128.3, 127.6, 127.2, 123.9, 119.5, 110.2, 73.0, 65.7, 51.1, 48.1, 35.4, 30.2. IR: ν = 2925, 1718, 1453, 1274, 1109, 747, 715 cm^{-1}. MS (CI): *m/z* (%): 324 (100) $[M+H]^+$.

Analytical data for **16d**: Yield: 26% (42 mg); ee: 95% (Chiral HPLC: Chiralpack OD, 3% *iso*-propanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D = 15$ (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.8 (dd, ^4J = 2 Hz, ^3J = 5 Hz, 2H; ArH), 7.3 (dd, ^4J = 2 Hz, ^3J = 5 Hz, 2H; ArH), 7.2 (m, 5H; ArH), 5.6 (m, 1H; CH), 4.4 (d, ^2J = 8 Hz, 2H; O-CH_2), 4.3 (d, ^2J = 8 Hz, 2H; O-CH_2), 3.4 (dd, ^3J = 8 Hz, ^2J = 17 Hz, 1H; CH_2), 3.3 (m, 1H, CH_2), 3.2 (m, 1H, CH_2), 3.0 (dd, ^3J = 5 Hz, ^2J = 17 Hz, 1H; CH_2), 2.3 (m, 1H, CH_2), 2.2 (m, 1H, CH_2), 2.1 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=205.1, 144.9, 138.6, 128.2, 127.6, 127.5, 126.1, 118.1, 74.2, 66.0, 60.9, 47.9, 35.5, 30.2. IR: ν = 2925, 1720, 1363, 1274, 1099, 749, 699 cm^{-1}. MS (CI): *m/z* (%): 324 (40) $[M+H]^+$.

15e, 16e. 4-phenyl-3-buten-2-one (73 mg, 0.5 mmol) was used. Reaction time: 48 h. The products **15e** and **16e** were separated by chromatography on silica (eluent: 33% ethyl acetate in hexanes).

Analytical data for **15e**: Yield: 53% (70 mg); ee: 88% (Chiral HPLC: Chiralpack OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D = 25$ (c = 1.00 in chloroform). ^{1}H NMR

(500 MHz, $CDCl_3$): δ=8.0 (d, ^3J = 8 Hz, 1H; ArH), 7.4 (m, 2H; ArH), 7.3 (m, 6H; ArH), 6.3 (dd, ^3J = 5 Hz, ^2J = 9 Hz, 1H; CH), 4.3 (dd, ^3J = 9 Hz, ^2J = 18 Hz, 1H; CH_2), 3.3 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=206.9, 148.8, 141.3, 135.5, 131.5, 131.0, 129.8, 129.0, 126.5, 122.3, 112.4, 60.8, 51.2, 32.9. IR: ν = 2929, 1718, 1454, 1367, 1160, 747, 700 cm^{-1}. MS (CI): *m/z* (%): 266 (100) $[M+H]^+$.

Analytical data for **16e**: Yield: 21% (28 mg); ee: % (Chiral HPLC: Chiralpack OD, 3% *iso*-propanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]\ ^{20}_D$ = 38 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.8 (dd, ^4J = 2 Hz, ^3J = 5 Hz, 2H; ArH), 7.5 (dd, ^4J = 2 Hz, ^3J = 5 Hz, 2H; ArH), 7.3 (m, 5H; ArH), 6.5 (dd, ^3J = 5 Hz, ^2J = 9 Hz, 1H; CH), 4.1 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.3 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=206.9, 148.7, 141.3, 135.5, 131.5, 131.0, 129.8, 129.0, 126.5, 122.3, 112.4, 60.8, 51.2, 32.9. IR: ν = 2923, 1720, 1454, 1363, 1321, 1270, 1162, 747, 699 cm^{-1}. MS (CI): *m/z* (%): 266 (30) $[M+H]^+$.

15f. 4-(4-bromophenyl)-3-buten-2-one (112.5 mg, 0.5 mmol) was used. Reaction time: 48 h. The product **15f** was isolated, after column chromatography (eluent: 6:4 of hexanes/ethyl acetate) in 60% yield (103 mg) and 70% enantiomeric excess, as determined by chiral HPLC (Chiralpack OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm). **15f** was re-crystallized from ether/methanol solution to give enantioenriched compound in 46% yield (84 mg) and 98% ee.

Analytical data for **15f**: $[\alpha]\ ^{20}_D$ = -12 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.0 (d, ^3J = 8 Hz, 1H; ArH), 7.4 (m, 2H; ArH), 7.3 (m, 3H; ArH), 7.1 (m, 2H; ArH), 6.3 (dd, ^3J = 5 Hz, ^2J = 9 Hz, 1H; CH), 4.2 (dd, ^3J = 9 Hz, ^2J = 18 Hz, 1H; CH_2), 3.3 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 2.2 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.0, 146.2, 137.8, 132.8, 132.2, 128.2, 127.5, 124.1, 122.5, 119.9, 109.6, 57.6, 48.6, 30.3. IR: ν = 2936, 1718, 1489, 1360, 1162, 1010, 747 cm^{-1}. MS (CI): *m/z* (%): 344 (40) $[M]^+$.

General procedure for the conjugate addition of benzotriazole to imides.

Addition to (3-propyl-acryloyl)-benzamide. Formation of products **17a** and **18a**: Aluminum complex **1** (29 mg, 0.025 mmol, 5 mol%), benzotriazole (60 mg, 0.5 mmol) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension (3-propyl-acryloyl)-benzamide (109 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, resulting in a mixture of regioisomers **17a** and **18a**. The products were separated by two successive chromatographic columns on silica (eluent: 17% ethyl acetate in methylene chloride).

Analytical data for **17a**: Yield: 69% (116 mg); ee: 99% (Chiral HPLC: Chiralpack OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D} = 31$ (c = 1.10 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.9 (s, 1H; N-H), 7.6 (m, 1H; ArH), 7.5 (m, 2H; ArH), 7.4 (m, 4H; ArH), 7.3 (dd, ^{4}J = 3 Hz, ^{3}J = 7 Hz, 2H; ArH), 5.5 (m, 1H, CH), 4.0 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.7 (dd, ^{3}J = 4 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.2 (m, 1H, CH_2), 2.0 (m, 1H, CH_2), 1.2 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.9 (t, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.1, 168.1, 146.5, 135.8, 134.9, 131.5, 130.2, 128.6, 120.6, 65.3, 45.3, 40.3, 21.5, 16.0. IR: ν = 3278, 2918, 1706, 1672, 1462, 1247, 746, 714 cm^{-1}. MS (CI): *m/z* (%): 337 (30) $[M]^{+}$.

Analytical data for **18a**: Yield: 27% (45 mg); ee: 98% (Chiral HPLC: Chiralpack OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D} = 28$ (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.6 (s, 1H; N-H), 8.0 (d, ^{3}J = 8 Hz, 1H; ArH), 7.8 (m, 2H; CH), 7.6 (m, 1H; CH), 7.5 (m, 1H; CH), 7.4 (m, 3H; CH), 7.3 (t, ^{3}J = 8 Hz, 1H; ArH), 5.4 (m, 1H, CH), 4.1 (dd, ^{3}J = 9 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.7 (dd, ^{3}J = 6 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.3 (m, 1H, CH_2), 2.2 (m, 1H, CH_2), 1.2 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.9 (t, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.1, 168.6, 148.1, 136.0, 134.7, 131.4, 130.2, 129.6, 128.6, 126.3, 122.3, 120.6, 57.4, 45.4, 39.8, 21.7, 16.0. IR: ν = 2961, 2927, 1715, 1689, 1483, 1259, 1091, 1025, 800, 747, 709 cm^{-1}. MS (CI): *m/z* (%): 337 (100) $[M]^{+}$.

17b, 18b. (3-*iso*-propyl-acryloyl)-benzamide (109 mg, 0.5 mmol) was used. The products **17b** and **18b** were separated by two successive chromatographic columns on silica (eluent: 17% ethyl acetate in methylene chloride).

Analytical data for **17b**: Yield: 65% (110 mg); ee: 99.5% (Chiral HPLC: Chiralpack OD, 5% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D} = 19$ (c = 0.65 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.2 (s, 1H; N-H), 7.8 (m, 4H; ArH), 7.6 (m, 1H; ArH), 7.5 (m, 2H; ArH), 7.3 (dd, ^{4}J = 2 Hz, ^{3}J = 7 Hz, 2H; ArH), 5.3 (m, 1H, CH), 4.2 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.0 (dd, ^{3}J = 3 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.5 (m, 1H, CH), 1.0 (d, ^{3}J = 7 Hz, 3H, CH_2), 0.8 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.8, 168.3, 146.3, 135.7, 134.8, 131.4, 130.3, 128.5, 120.6, 70.6, 42.1, 36.4, 21.4. IR: ν = 3288, 2967, 1708, 1685, 1467, 1373, 1245, 708 cm^{-1}. MS (CI): *m/z* (%): 337 (40) $[M]^{+}$.

Analytical data for **18b**: Yield: 23% (39 mg); ee: 99.5% (Chiral HPLC: Chiralpack OD, 5% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D} = 15$ (c = 0.90 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.3 (bs, 1H; N-H), 8.0 (d, ^{3}J = 8 Hz, 1H; ArH), 7.7 (m, 2H; CH), 7.6 (m, 1H; CH), 7.5 (m, 1H; CH), 7.4 (m, 3H; CH), 7.3 (m, 1H; ArH), 5.1 (m, 1H, CH), 4.2 (dd, ^{3}J = 10 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.7 (dd, ^{3}J = 4 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.5 (m, 1H, CH), 1.1 (d, ^{3}J = 7 Hz, 3H, CH_2), 0.8 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.3, 168.1, 148.0, 146.3, 136.5, 135.8, 131.4, 130.2, 129.6, 126.2, 122.3, 112.5, 63.0, 42.6, 35.9, 22.1, 21.6. IR: ν = 2964, 2926, 1712, 1689, 1482, 1246, 1165, 711 cm^{-1}. MS (CI): *m/z* (%): 337 (100) $[M]^{+}$.

17c, 18c. (3-benzyl-acryloyl)-benzamide (133 mg, 0.5 mmol) was used. The products **17c** and **18c** were separated by two successive chromatographic columns on silica (eluent: 17% ethyl acetate in methylene chloride).

Analytical data for **17c**: Yield: 67% (129 mg); ee: 96% (Chiral HPLC: Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D} = 26$ (c = 0.80 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.9 (s, 1H; N-H), 7.8 (m, 4H; ArH), 7.6 (m, 1H; ArH), 7.5 (m, 2H; ArH), 7.3 (dd, ^{4}J = 4 Hz, ^{3}J = 7 Hz, 2H; ArH), 7.2 (m, 3H; ArH), 7.1 (m, 2H; ArH), 5.7 (m, 1H, CH), 4.1 (dd, ^{3}J = 9 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.6 (dd, ^{3}J = 4 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.5 (dd, ^{3}J = 7 Hz, ^{2}J = 14 Hz, 1H; CH_2), 3.3 (dd, ^{3}J = 5 Hz, ^{2}J = 14 Hz, 1H; CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.3, 168.2, 146.5, 138.9, 135.8, 134.9, 131.7, 131.5, 131.2, 130.3, 129.6, 128.7, 120.7, 66.7, 44.5, 44.3. IR: ν = 2964, 1713, 1687, 1469, 1243, 749, 707 cm^{-1}. MS (CI): *m/z* (%): 385 (50) $[M]^{+}$.

Analytical data for **18c**: Yield: 28% (54 mg); ee: 96% (Chiral HPLC: Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 19 (c = 0.95 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.9 (s, 1H; N-H), 7.9 (d, ^{3}J = 7 Hz, 1H; ArH), 7.5 (m, 1H; CH), 7.4 (m, 2H; CH), 7.3 (m, 3H; CH), 7.1 (m, 3H; CH), 6.9 (m, 2H; ArH), 5.5 (m, 1H, CH), 4.2 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.7 (dd, ^{3}J = 3 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.4 (m, 2H; CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.3, 166.7, 145.2, 136.6, 133.5, 133.2, 128.9, 128.5, 127.7, 126.9, 123.6, 119.5, 109.5, 56.6, 42.2, 41.7. IR: ν = 2972, 1719, 1689, 1509, 1480, 1247, 745, 703 cm^{-1}. MS (CI): *m/z* (%): 385 (100) $[M]^{+}$.

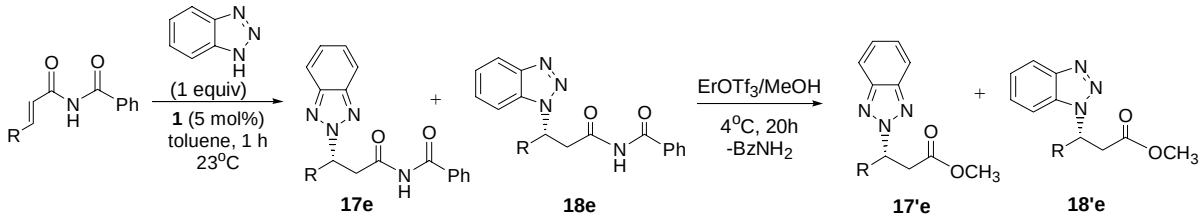
17d, 18d. (3-benzyloxymethyl-acryloyl)-benzamide (147 mg, 0.5 mmol) was used. The products **17d** and **18d** were separated by two successive chromatographic columns on silica (eluent: 17% ethyl acetate in methylene chloride).

Analytical data for **17d**: Yield: 64% (132 mg); ee: 99% (Chiral HPLC: Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 29 (c = 0.75 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.2 (s, 1H; N-H), 7.8 (m, 4H; ArH), 7.6 (m, 1H; ArH), 7.5 (m, 2H; ArH), 7.3 (dd, ^{4}J = 4 Hz, ^{3}J = 8 Hz, 2H; ArH), 7.2 (m, 3H; ArH), 7.1 (m, 2H; ArH), 5.7 (m, 1H, CH), 4.5 (d, ^{2}J = 12 Hz, 1H; CH_2), 4.4 (d, ^{2}J = 12 Hz, 1H; CH_2), 4.2 (dd, ^{3}J = 9 Hz, ^{2}J = 18 Hz, 1H; CH_2), 4.0 (m, 1H; CH_2), 3.9 (m, 1H; CH_2), 3.8 (dd, ^{3}J = 5 Hz, ^{2}J = 18 Hz, 1H; CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.2, 168.1, 146.6, 139.9, 135.8, 134.8, 131.4, 130.8, 130.3, 130.2, 130.1, 128.7, 120.7, 75.7, 74.1, 64.6, 42.0. IR: ν = 3280, 2974, 1711, 1680, 1467, 1243, 746, 709 cm^{-1}. MS (CI): *m/z* (%): 413 (100) $[M]^{+}$.

Analytical data for **18d**: Yield: 33% (68 mg); ee: 98% (Chiral HPLC: Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 12 (c = 0.80 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.7 (s, 1H; N-H), 7.7 (m, 2H; ArH), 7.6 (m, 1H; CH), 7.5 (m, 1H; CH), 7.4 (m, 3H; CH), 7.3 (m, 1H; CH), 7.2 (m, 3H; ArH), 7.0 (m, 2H; ArH), 5.7 (m, 1H, CH), 4.5 (d, ^{2}J = 12 Hz, 1H; CH_2), 4.4 (d, ^{2}J = 12 Hz, 1H; CH_2), 4.1 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 4.0 (m, 1H; CH_2), 3.9 (m, 1H; CH_2), 3.8 (dd, ^{3}J = 5 Hz, ^{2}J = 18 Hz, 1H; CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.6, 167.9, 148.3, 139.9, 136.2, 135.8, 134.8, 131.5, 130.8, 130.3, 130.1, 129.7, 126.4, 122.2, 112.9, 175.2, 168.1, 146.6, 139.9,

135.8, 134.8, 131.4, 130.8, 130.3, 130.2, 130.1, 128.7, 120.7, 75.9, 74.2, 57.3, 42.0. IR: ν = 3283, 2925, 1715, 1689, 1476, 1243, 1102, 747, 7089 cm^{-1}. MS (CI): *m/z* (%): 413 (80) $[M]^+$.

17e, 18e. (these compounds were converted to the corresponding methyl esters **17'e** and **18'e** for a facile separation (Scheme 2)).



Scheme 2

a) Preparation of mixture of **17e** and **18e**: Aluminum complex **1** (29 mg, 0.025 mmol, 5 mol%), benzotriazole (60 mg, 0.5 mmol) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension (3-phenyl-acryloyl)-benzamide (127 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and then filtered through a silica plug, resulting in a mixture of regioisomers **17e** and **18e**.

b) Methanolysis: The crude mixture of **17e** and **18e** was dissolved in methanol (2 ml, excess) and cooled to 4˚C. Erbium trifluoromethanesulfonate (15 mg, 0.025 mmol) was added and the solution stirred at 4˚C for 20 hours. After removal of the solvent *in vacuo*, the products **17'e** and **18'e** were separated by chromatography on silica (eluent: 30% ethyl acetate in hexanes).

Analytical data for **17'e**: Yield: 55% (78 mg); ee: 99% (Chiral HPLC: Chiralpack OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_D = 22$ (c = 0.50 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.8 (dd, ^4J = 4 Hz, ^3J = 8 Hz, 2H; ArH), 7.3 (m, 7H; ArH), 6.5 (dd, ^3J = 5 Hz, ^2J = 8 Hz, 1H; CH), 4.0 (dd, ^3J = 9 Hz, ^2J = 18 Hz, 1H; CH_2), 3.6 (s, 3H; CH_3), 3.3 (dd, ^3J = 6 Hz, ^2J = 18 Hz, 1H; CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ=172.6, 146.7, 140.5, 131.4, 131.2, 129.3, 128.8, 120.8, 69.0, 54.5, 42.4. IR: ν = 2953, 1741, 1324, 1264, 1169, 749, 704 cm^{-1}. MS (CI): *m/z* (%): 285 (100) $[M+H]^+$.

Analytical data for **18'e**: Yield: 41% (58 mg); ee: 95% (Chiral HPLC: Chiralpack OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D} = 66$ (c = 0.85 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.0 (d, ^{3}J = 8 Hz, 1H; ArH), 7.4 (m, 2H; ArH), 7.3 (m, 6H; ArH), 6.3 (dd, ^{3}J = 6 Hz, ^{2}J = 9 Hz, 1H; CH), 4.0 (dd, ^{3}J = 10 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.6 (s, 3H; CH_3), 3.4 (dd, ^{3}J = 6 Hz, ^{2}J = 18 Hz, 1H; CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ=173.0, 140.6, 135.2, 131.6, 131.2, 129.8, 129.2, 126.5, 122.4, 112.3, 61.9, 54.6, 42.6. IR: ν = 2952, 1739, 1453, 1266, 1201, 1174, 747, 704 cm^{-1}. MS (CI): *m/z* (%): 285 (40) $[M+H]^{+}$.

General procedure for the conjugate addition of 5-methyl-tetrazole to enones and imides. Addition to 3-hepten-2-one. Formation of products **19a** and **20a**: Aluminum complex **1** (29 mg, 0.025 mmol, 5 mol%), 5-methyl-tetrazole (42 mg, 0.5 mmol) and toluene (2.5 ml) were combined in a round-bottomed flask. The resulting suspension was cooled to 4˚C and 3-hepten-2-one (56 mg, 0.5 mmol) was added. The reaction mixture was stirred at 4˚C for 24 h, resulting in a mixture of regioisomers **19a** and **20a**. The products were separated by column chromatography on silica (eluent: 1:1 of ethyl acetate/hexanes).
Analytical data for **19a**: Yield: 42% (41 mg); ee: 94.5% (Chiral HPLC: Chiralcel OB, 4% *iso*-propanol/hexanes, 1.2 ml/min, 208 nm), $[\alpha]^{20}_{D}$ = -7 (c = 0.50 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=5.2 (m, 1H, CH), 3.3 (dd, ^{3}J = 8 Hz, ^{2}J = 20 Hz, 1H; CH_2), 2.9 (dd, ^{3}J = 6 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.5 (s, 3H; CH_3), 2.1 (s, 3H; CH_3), 1.9 (m, 1H, CH_2), 1.8 (m, 1H, CH_2), 1.2 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.8 (t, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.0, 162.4, 59.4, 47.0, 36.8, 30.1, 18.7, 13.2, 10.8. IR: ν = 2963, 2938, 1722, 1505, 1365, 1174, 1031 cm^{-1}. MS (CI): *m/z* (%): 197 (100) $[M+H]^{+}$.

Analytical data for **20a**: Yield: 40% (39 mg); ee: 94.5% (Chiral HPLC: Chiralcel AD, 10% ethanol/hexanes, 1.2 ml/min, 208 nm), $[\alpha]^{20}_{D}$ = -10 (c = 0.50 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=4.7 (m, 1H, CH), 3.4 (dd, ^{3}J = 10 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.9 (dd, ^{3}J = 5 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.6 (s, 3H; CH_3), 2.0 (s, 3H; CH_3), 1.9 (m, 1H, CH_2), 1.7 (m, 1H, CH_2), 1.21 (m, 1H, CH_2), 1.0 (m, 1H, CH_2), 0.8 (t, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.6, 152.2, 53.4, 47.9, 37.0, 30.0, 18.9, 13.3,

8.9. IR: ν = 2962, 2929, 1718, 1525, 1405, 1173 cm^{-1}. MS (CI): *m/z* (%): 197 (100) $[M+H]^+$.

19b, 20b. 5-methyl-3-hexen-2-one (56 mg, 0.5 mmol) was used. The products **19b** and **20b** were separated by chromatography on silica (eluent: 5% methylene chloride in ethyl acetate).

Analytical data for **19b**: Yield: 64% (63 mg); ee: 95% (Chiral HPLC: Chiralpack OD, 15% iso-propanol/hexanes, 1.2 ml/min, 208 nm), $[\alpha]^{20}_D$ = -32 (c = 0.75 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=5.1 (m, 1H, CH), 3.5 (dd, ^3J = 10 Hz, ^2J = 18 Hz, 1H; CH_2), 3.0 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 2.5 (s, 3H; CH_3), 2.2 (m, 1H, CH), 2.1 (s, 3H; CH_3), 0.9 (d, ^3J = 7 Hz, 3H, CH_2), 0.8 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.2, 164.7, 67.1, 45.9, 35.3, 32.7, 21.0, 20.8, 13.3. IR: ν = 2969, 1721, 1504, 1365, 1168 cm^{-1}. MS (CI): *m/z* (%): 197 (100) $[M+H]^+$.

Analytical data for **20b**: Yield: 27% (26 mg); ee: 96% (Chiral HPLC: Chiralpack AD, 10% ethanol/hexanes, 1.2 ml/min, 208 nm), $[\alpha]^{20}_D$ = 15 (c = 0.50 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=4.4 (m, 1H, CH), 3.5 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 2.9 (dd, ^3J = 2 Hz, ^2J = 18 Hz, 1H; CH_2), 2.6 (s, 3H; CH_3), 2.1 (m, 1H, CH), 2.0 (s, 3H; CH_3), 0.9 (d, ^3J = 7 Hz, 3H, CH_2), 0.7 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.9, 154.8, 59.0, 45.2, 32.8, 30.1, 19.2, 18.7, 9.0. IR: ν = 2969, 2923, 1720, 1525, 1405, 1385 cm^{-1}. MS (CI): *m/z* (%): 197 (100) $[M+H]^+$.

19c, 20c. 6-benzyloxy-3-hexen-2-one (102 mg, 0.5 mmol) was used. The products **19c** and **20c** were separated by chromatography on silica (eluent: 17% ethyl acetate in methylene chloride).

Analytical data for **19c**: Yield: 63% (91 mg); ee: 87.5% (Chiral HPLC: Chiralpack AD, 10% ethanol/hexanes, 1.2 ml/min, 205 nm), $[\alpha]^{20}_D$ = 9 (c = 1.00 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=7.2 (m, 5H; ArH), 5.4 (m, 1H; CH), 4.4 (d, ^2J = 12 Hz, 2H; O-CH_2), 4.3 (d, ^2J = 12 Hz, 2H; O-CH_2), 3.5 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.4 (m, 1H, CH_2), 3.2 (m, 2H, CH_2), 3.0 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 2.4 (s, 3H; CH_3), 2.1 (m, 2H, CH_2), 2.0 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=203.8, 162.5, 137.8,

128.3, 127.6, 73.0, 65.8, 57.3, 46.9, 34.8, 30.0, 10.8. IR: ν = 2928, 2866, 1721, 1504, 1362, 1101, 741, 700 cm^{-1}. MS (CI): *m/z* (%): 289 (100) $[M+H]^+$.

Analytical data for **20c**: Yield: 30% (43 mg); ee: 87% (Chiral HPLC: Chiralpack AD, 10% ethanol/hexanes, 1.2 ml/min, 205 nm), $[\alpha]\ ^{20}_D$ = 52 (c = 0.80 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=7.2 (m, 5H; ArH), 5.0 (m, 1H; CH), 4.3 (s, 2H; O-CH_2), 3.4 (m, 2H; CH_2), 2.8 (m, 2H, CH_2), 2.5 (s, 3H; CH_3), 2.1 (m, 2H, CH_2), 2.0 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.3, 152.9, 137.4, 128.4, 127.9, 127.7, 73.1, 65.0, 50.1, 47.9, 34.8, 29.9, 8.6. IR: ν = 2925, 2873, 1719, 1526, 1408, 1094, 701 cm^{-1}. MS (CI): *m/z* (%): 289 (100) $[M+H]^+$.

21a, 22a. (3-methyl-acryloyl)-benzamide (95 mg, 0.5 mmol) was used. The products **21a** and **22a** were separated by chromatography on silica (eluent: 1:1 of ethyl acetate/methylene chloride).

Analytical data for **21a**: Yield: 61% (84 mg); ee: 93% (Chiral HPLC: Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]\ ^{20}_D$ = 14 (c = 0.80 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=8.9 (bs, 1H; N-H), 7.8 (d, 2H; ^3J = 7 Hz; ArH), 7.6 (t, 1H; ^3J = 7 Hz; ArH), 7.5 (t, 2H; ^3J = 7 Hz; ArH), 5.5 (m, 1H, CH), 3.9 (dd, ^3J = 8 Hz, ^2J = 18 Hz, 1H; CH_2), 3.6 (dd, ^3J = 4 Hz, ^2J = 18 Hz, 1H; CH_2), 2.5 (s, 3H; CH_3), 1.8 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=167.2, 160.8, 157.9, 128.7, 127.5, 124.3, 122.9, 509, 38.6, 16.1, 6.1. IR: ν = 3296, 1710, 1691, 1504, 1467, 1241, 707 cm^{-1}. MS (CI): *m/z* (%): 274 (20) $[M]^+$.

Analytical data for **22a**: Yield: 35% (48 mg); ee: 92% (Chiral HPLC: Chiralpack OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]\ ^{20}_D$ = 18 (c = 0.25 in chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ=8.5 (bs, 1H; N-H), 7.8 (d, 2H; ^3J = 7 Hz; ArH), 7.6 (t, 1H; ^3J = 7 Hz; ArH), 7.5 (t, 2H; ^3J = 7 Hz; ArH), 5.1 (m, 1H, CH), 4.0 (dd, ^3J = 10 Hz, ^2J = 18 Hz, 1H; CH_2), 3.5 (dd, ^3J = 5 Hz, ^2J = 18 Hz, 1H; CH_2), 2.6 (s, 3H; CH_3), 1.6 (d, ^3J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=167.1, 160.5, 157.3, 128.6, 124.3, 122.8, 44.9, 39.1, 16.4, 4.1. IR: ν = 3256, 2925, 1716, 1690, 1507, 1247, 1195, 711 cm^{-1}. MS (CI): *m/z* (%): 274 (40) $[M]^+$.

21b, 22b. [3-(t-butyl-dimethyl-silyloxymethyl)-acryloyl]-benzamide (159 mg, 0.5 mmol) was used. The products **21b** and **22b** were separated by chromatography on silica (eluent: 17% of ethyl acetate in methylene chloride).

Analytical data for **21b**: Yield: 56% (113 mg); ee: 96% (Chiral HPLC: Chiralpack OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D} = 6$ (c = 0.45 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.9 (s, 1H; N-H), 7.8 (d, 2H; ^{3}J = 7 Hz; ArH), 7.6 (t, 1H; ^{3}J = 7 Hz; ArH), 7.5 (t, 2H; ^{3}J = 7 Hz; ArH), 5.5 (m, 1H, CH), 4.1 (m, 2H; CH_2), 4.0 (dd, ^{3}J = 9 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.7 (dd, ^{3}J = 5 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.5 (s, 3H; CH_3), 0.8 (s, 9H; $C(CH_3)_3$), -0.04 (s, 3H; CH_3), -0.07 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.7, 168.0, 154.0, 153.4, 148.4, 136.1, 134.6, 134.2, 131.6, 130.1, 66.0, 56.7, 40.5, 28.1, 20.5, -3.2, -3.3. IR: ν = 2930, 2858, 1717, 1684, 1466, 1243, 836, 779, 708 cm^{-1}. MS (CI): *m/z* (%): 404 (100) $[M+H]^{+}$.

Analytical data for **22b**: Yield: 35% (71 mg); ee: 94.5% (Chiral HPLC: Chiralpack OD, 5% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D} = 39$ (c = 0.60 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.6 (bs, 1H; N-H), 7.8 (d, 2H; ^{3}J = 7 Hz; ArH), 7.6 (t, 1H; ^{3}J = 7 Hz; ArH), 7.5 (t, 2H; ^{3}J = 7 Hz; ArH), 5.0 (m, 1H, CH), 4.0 (m, 3H; CH_2), 3.5 (dd, ^{3}J = 3 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.6 (s, 3H; CH_3), 0.8 (s, 9H; $C(CH_3)_3$), -0.04 (s, 3H; CH_3), -0.10 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=166.8, 160.7, 147.4, 128.8, 124.3, 122.8, 60.6, 51.1, 33.9, 20.8, 13.2, 4.2, -3.2, -3.3. IR: ν = 2954, 2931, 1716, 1691, 1471, 1254, 1117, 836, 780, 710 cm^{-1}. MS (CI): *m/z* (%): 404 (80) $[M+H]^{+}$.

General procedure for the conjugate addition of 5-phenyl-tetrazole to enones and imides.

23a: Aluminum complex **1** (29 mg, 0.025 mmol, 5 mol%), 5-phenyl-tetrazole (73 mg, 0.5 mmol) and toluene (2.5 ml) were combined in a round-bottomed flask. To the resulting suspension 3-hepten-2one (56 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 2 h, and then purified by flash column chromatography on silica (eluent: 6:4 of hexanes/ethyl acetate). The product **23a** was obtained in 94% yield (121 mg) and 99% enantiomeric excess, as determined by chiral

HPLC (Chiralcel OB, 7% *iso*-propanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -24 (c = 0.9 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=5.2 (m, 1H, CH), 3.3 (dd, ^{3}J = 8 Hz, ^{2}J = 20 Hz, 1H; CH_2), 2.9 (dd, ^{3}J = 6 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.5 (s, 3H; CH_3), 2.1 (s, 3H; CH_3), 1.9 (m, 1H, CH_2), 1.8 (m, 1H, CH_2), 1.2 (m, 1H, CH_2), 1.1 (m, 1H, CH_2), 0.8 (t, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=204.0, 162.4, 59.4, 47.0, 36.8, 30.1, 18.7, 13.2, 10.8. IR: ν = 2963, 2938, 1722, 1467, 1451, 1366, 734, 695 cm^{-1}. MS (CI): *m/z* (%): 259 (20) $[M+H]^{+}$.

23b. 5-methyl-3-hexen-2-one (56 mg, 0.5 mmol) was used. The product **23b** was obtained in 93% yield (120 mg) and 95.5% enantiomeric excess, as determined by chiral HPLC (Chiralcel AD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = -32 (c = 0.9 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.1 (m, 2H; ArH), 7.4 (m, 3H; ArH), 5.2 (m, 1H, CH), 3.6 (dd, ^{3}J = 10 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.0 (dd, ^{3}J = 3 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.3 (m, 1H, CH), 2.2 (s, 3H; CH_3), 1.0 (d, ^{3}J = 7 Hz, 3H, CH_2), 0.8 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=202.0, 162.2, 127.9, 126.5, 125.3, 124.5, 62.7, 41.2, 30.6, 28.0, 16.3, 16.1. IR: ν = 2969, 1722, 1467, 1450, 1366, 734, 695 cm^{-1}. MS (CI): *m/z* (%): 259 (30) $[M+H]^{+}$.

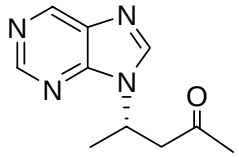
23c. 6-benzyloxy-3-hexen-2-one (102 mg, 0.5 mmol) was used. The product **23c** was obtained in 90% yield (158 mg) and 94% enantiomeric excess, as determined by chiral HPLC (Chiralcel AD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 9 (c = 0.6 in chloroform).

^{1}H NMR (500 MHz, $CDCl_3$): δ=8.1 (m, 2H; ArH), 7.4 (m, 3H; ArH), 7.2 (m, 5H; ArH), 5.6 (m, 1H; CH), 4.4 (d, ^{2}J = 12 Hz, 2H; O-CH_2), 4.3 (d, ^{2}J = 12 Hz, 2H; O-CH_2), 3.4 (m, 2H, CH_2), 3.2 (m, 1H, CH_2), 3.0 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 2.2 (m, 2H, CH_2), 2.1 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=201.6, 162.6, 135.6, 127.9, 126.5, 126.1, 125.4, 124.6, 70.9, 63.7, 55.5, 44.8, 32.6, 27.9. IR: ν = 2924, 1720, 1465, 1451, 1365, 1099, 734, 696 cm^{-1}. MS (CI): *m/z* (%): 351 (20) $[M+H]^{+}$.

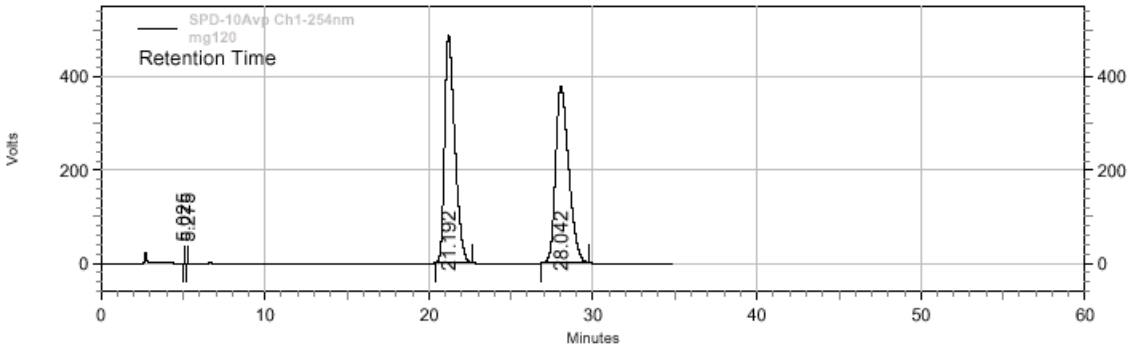
24a. (3-methyl-acryloyl)-benzamide (95 mg, 0.5 mmol) was used. The product **24a** was obtained in 93% yield (156 mg) and 95.5% enantiomeric excess, as determined by chiral

HPLC (Chiralcel OD, 10% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 10 (c = 1.00 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.0 (s, 1H; N-H), 8.1 (m, 2H; ArH), 7.8 (d, 2H; ^{3}J = 7 Hz; ArH), 7.6 (t, 1H; ^{3}J = 7 Hz; ArH), 7.4 (t, 2H; ^{3}J = 7 Hz; ArH), 7.3 (m, 3H; ArH), 5.5 (m, 1H, CH), 4.0 (dd, ^{3}J = 8 Hz, ^{2}J = 18 Hz, 1H; CH_2), 3.6 (dd, ^{3}J = 5 Hz, ^{2}J = 18 Hz, 1H; CH_2), 1.7 (d, ^{3}J = 7 Hz, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=170.1, 163.5, 162.6, 131.2, 129.9, 127.9, 126.8, 126.5, 125.5, 125.3, 124.6, 53.8, 41.0, 18.8. IR: ν = 3290, 1714, 1689, 1467, 1242, 709 cm^{-1}. MS (CI): *m/z* (%): 336 (20) $[M]^{+}$.

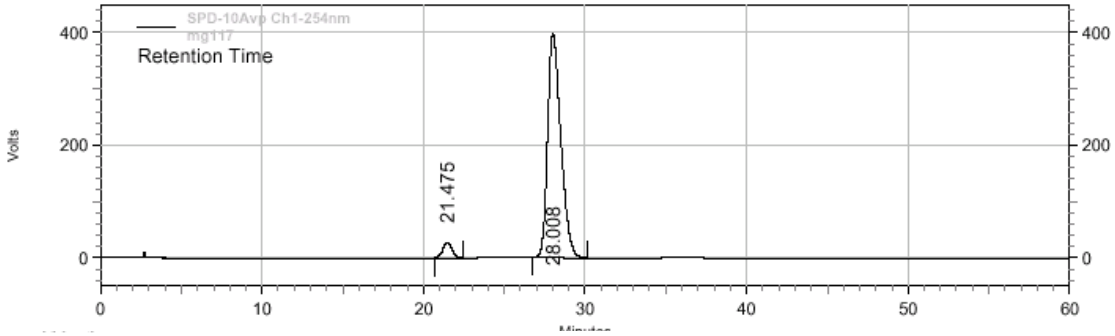
24b. [3-(t-butyl-dimethyl-silyloxymethyl)-acryloyl]-benzamide (159 mg, 0.5 mmol) was used. The product **24b** was obtained in 94% yield (218 mg) and 97% enantiomeric excess, as determined by chiral HPLC (Chiralcel OD, 8% ethanol/hexanes, 1.2 ml/min, 254 nm), $[\alpha]^{20}_{D}$ = 16 (c = 0.75 in chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.0 (s, 1H; N-H), 8.1 (m, 2H; ArH), 7.8 (m, 2H; ArH), 7.6 (t, 1H; ^{3}J = 7 Hz; ArH), 7.4 (t, 2H; ^{3}J = 7 Hz; ArH), 7.4 (m, 3H; ArH), 5.6 (m, 1H, CH), 4.1 (m, 3H; CH_2), 3.7 (dd, ^{3}J = 4 Hz, ^{2}J = 18 Hz, 1H; CH_2), 0.8 (s, 9H; $C(CH_3)_3$), -0.04 (s, 3H; CH_3), -0.06 (s, 3H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ=174.5, 168.7, 167.6, 131.4, 130.1, 128.9, 127.4, 126.9, 123.5, 123.1, 122.6, 67.1, 57.7, 42.4, 20.7, -3.2, -3.3. IR: ν = 2930, 2857, 1715, 1687, 1467, 1252, 1124, 836, 779, 709, 693 cm^{-1}. MS (CI): *m/z* (%): 464 (900) $[M+H]^{+}$.



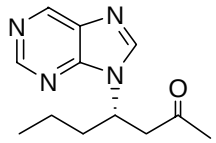
3a



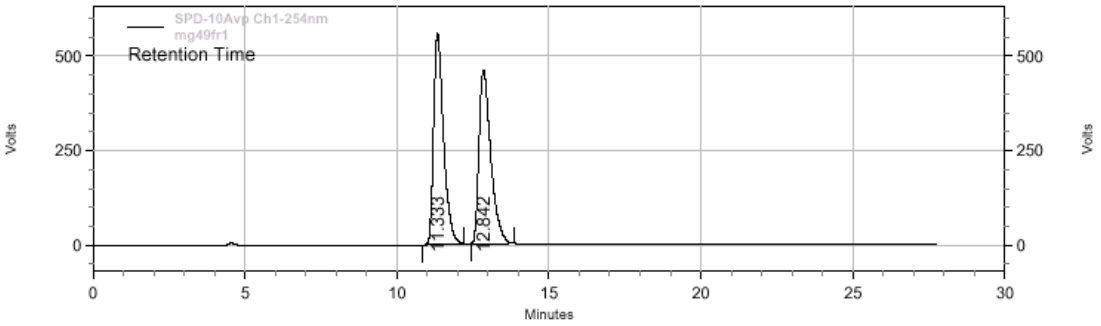
Retention Time	Area	Area %	Height	Height %
21.192	12168698	49.67	270435	55.58
28.042	12331618	50.33	216156	44.42
Totals	24500316	100.00	486591	100.00



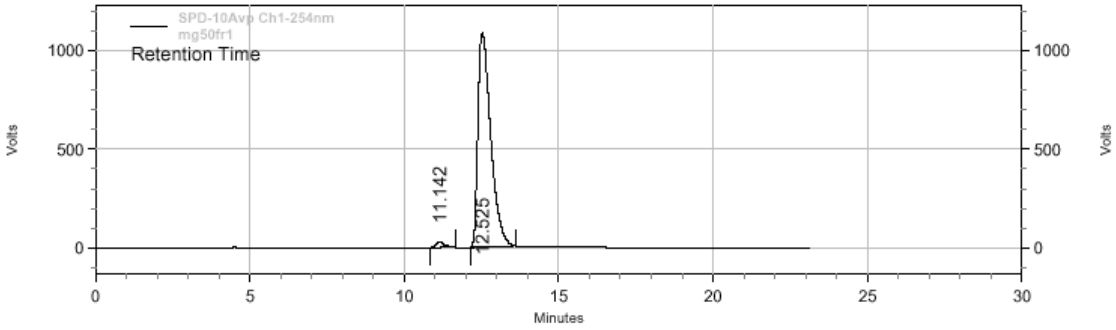
Retention Time	Area	Area %	Height	Height %
21.475	1074815	4.54	26790	6.31
28.008	22601089	95.46	397606	93.69
Totals	23675904	100.00	424396	100.00



3b

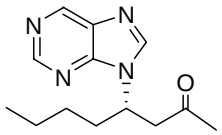


Retention Time	Area	Area %	Height	Height %
15.417	21025494	48.27	407467	55.49
19.700	22531350	51.73	326781	44.51
Totals	43556844	100.00	734248	100.00



SPD-10Avp
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.142	543341	1.70	26485	2.38
12.525	31395318	98.30	1087352	97.62
Totals	31938659	100.00	1113837	100.00



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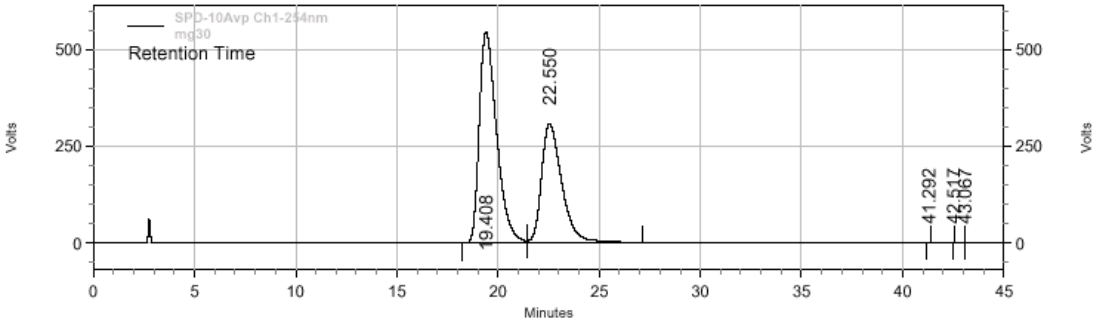
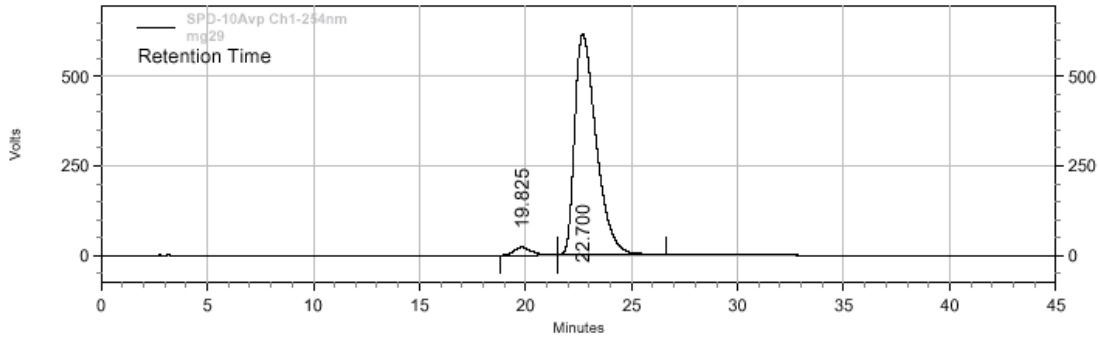
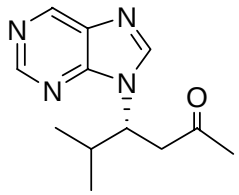


Retention Time	Area	Area %	Height	Height %
19.408	10002180	59.87	165158	63.58
22.550	6704518	40.13	94592	36.42
Totals	16706698	100.00	259750	100.00



Retention Time	Area	Area %	Height	Height %
19.825	1255514	2.80	21812	3.42
22.700	43545436	97.20	616533	96.58
Totals	44800950	100.00	638345	100.00



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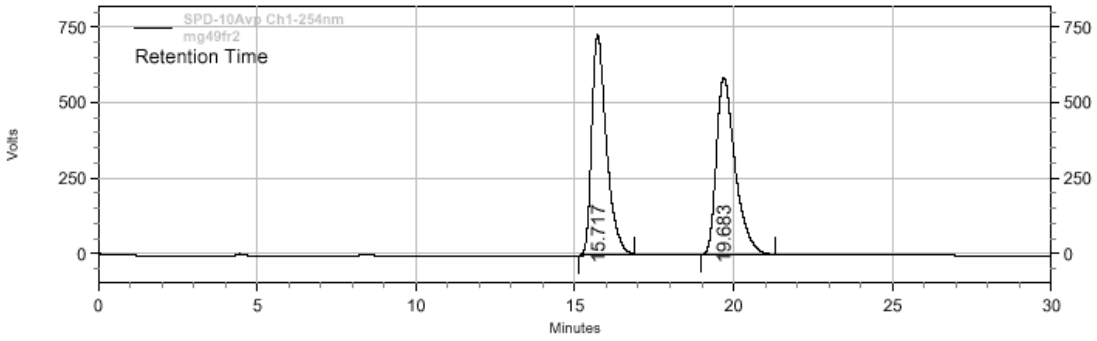
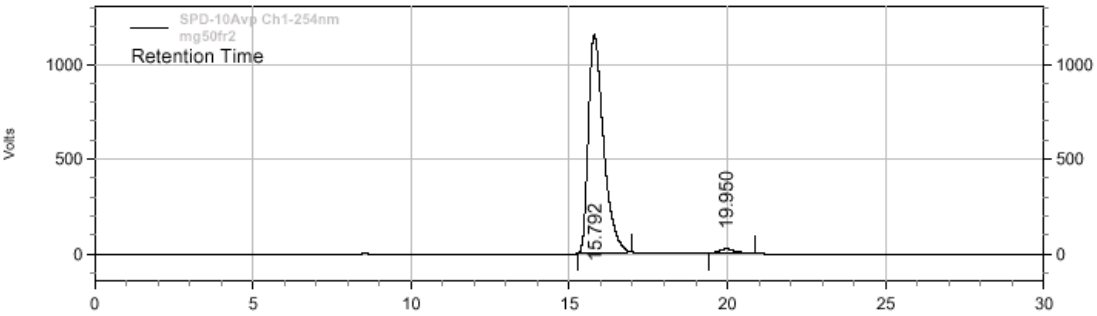
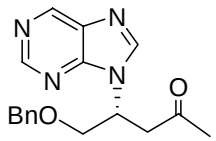


Retention Time	Area	Area %	Height	Height %
15.717	23465014	49.20	729522	55.34
19.683	24230496	50.80	588797	44.66
Totals	47695510	100.00	1318319	100.00



Retention Time	Area	Area %	Height	Height %
15.792	38209659	97.70	1152275	97.95
19.950	897563	2.30	24130	2.05
Totals	39107222	100.00	1176405	100.00



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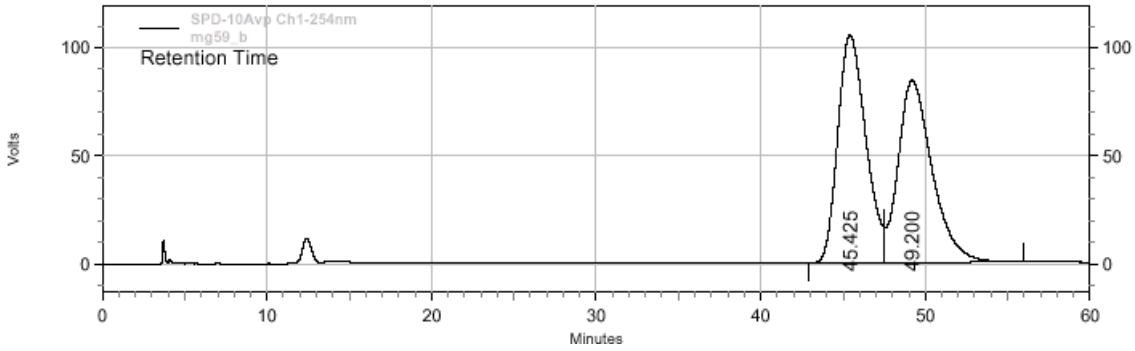
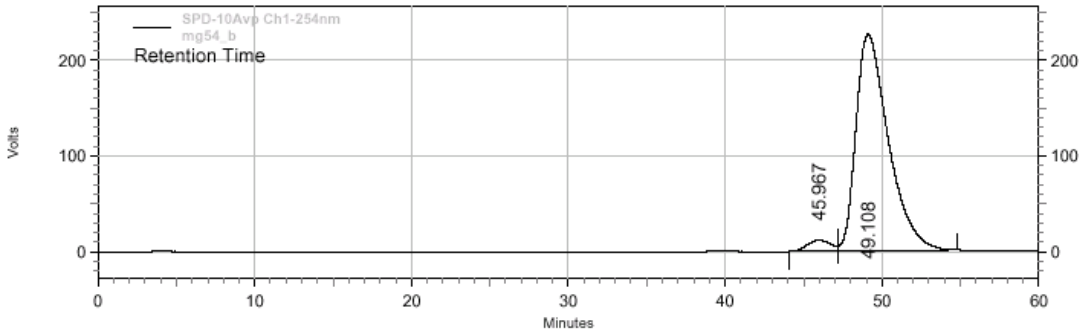
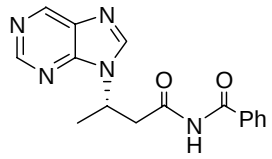


Retention Time	Area	Area %	Height	Height %
45.425	12501803	50.82	105368	55.50
49.200	12097963	49.18	84468	44.50
Totals	24599766	100.00	189836	100.00



Retention Time	Area	Area %	Height	Height %
45.967	1199163	3.56	11557	4.85
49.108	32506598	96.44	226530	95.15
Totals	33705761	100.00	238087	100.00



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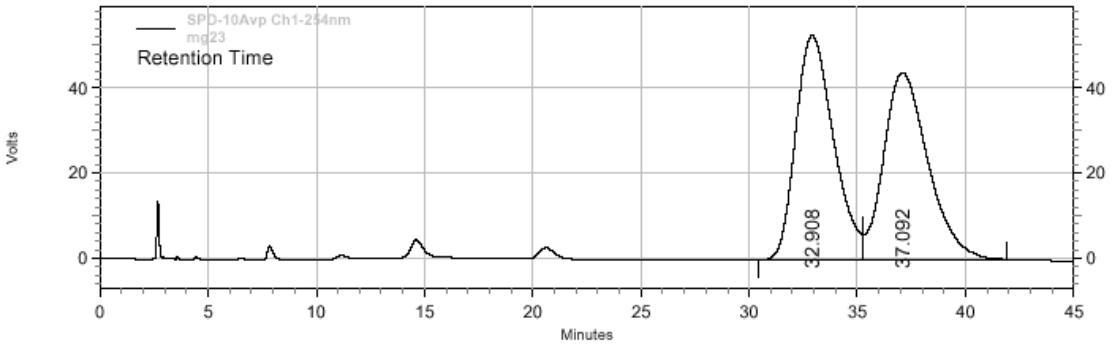
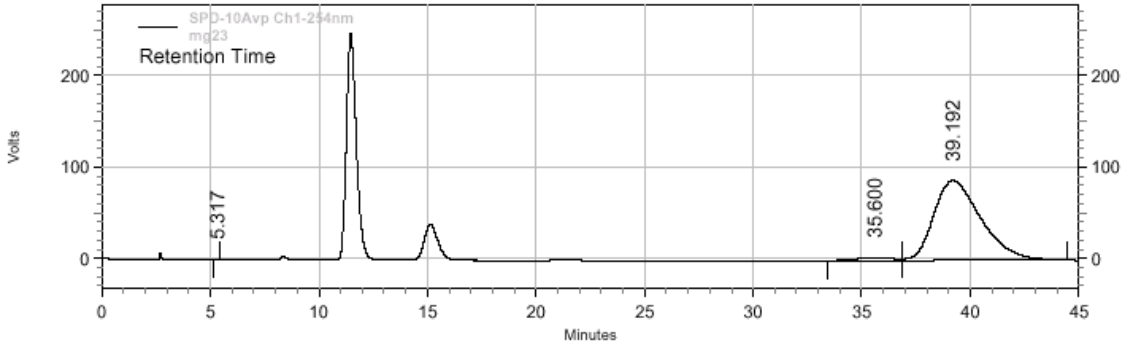
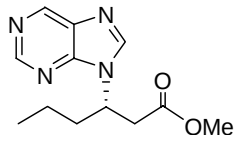


Retention Time	Area	Area %	Height	Height %
32.908	6399092	50.50	52668	54.50
37.092	6273260	49.50	43970	45.50
Totals	12672352	100.00	96638	100.00



Retention Time	Area	Area %	Height	Height %
5.317	1172	0.01	152	0.17
35.600	308046	2.28	2510	2.80
39.192	13173491	97.71	87085	97.03
Totals	13482709	100.00	89747	100.00



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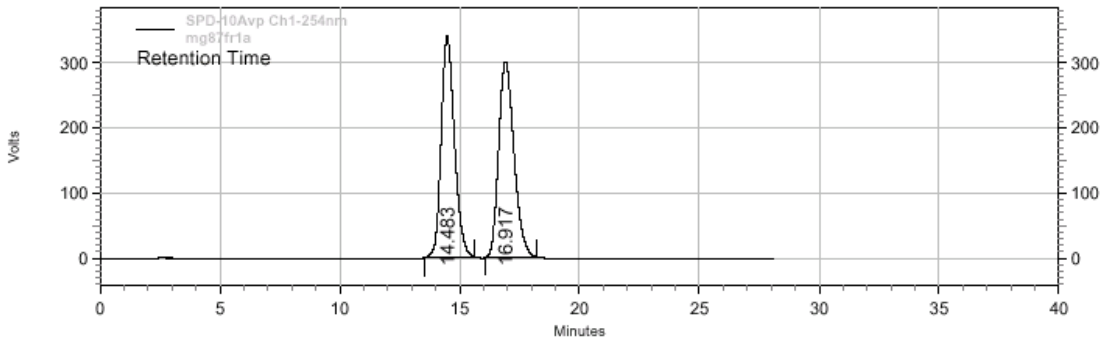
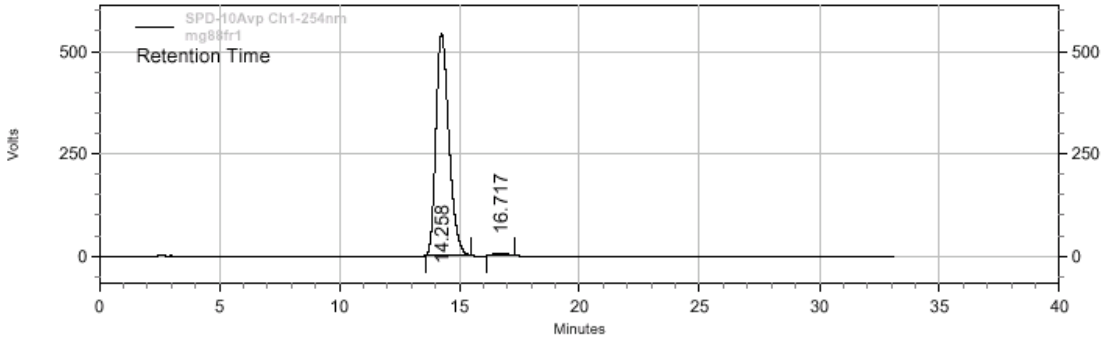
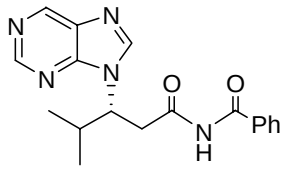


Retention Time	Area	Area %	Height	Height %
14.483	13088184	49.43	339979	53.05
16.917	13389308	50.57	300835	46.95
Totals	26477492	100.00	640814	100.00



Retention Time	Area	Area %	Height	Height %
14.258	20450365	98.85	542130	98.79
16.717	238663	1.15	6636	1.21
Totals	20689028	100.00	548766	100.00



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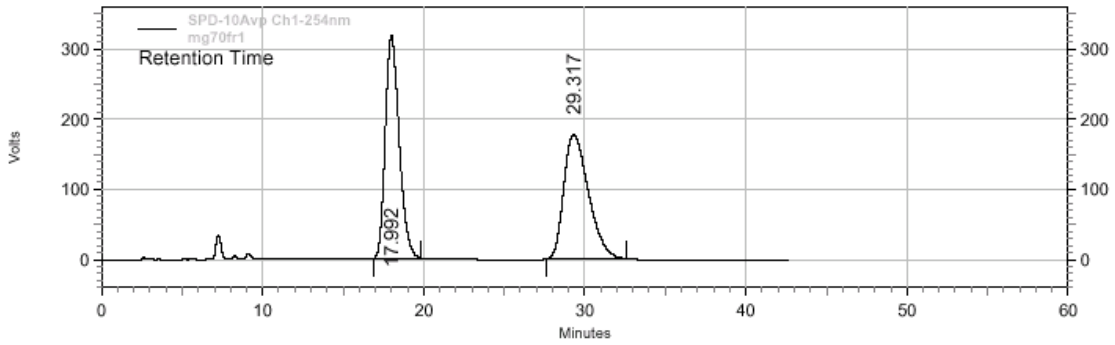
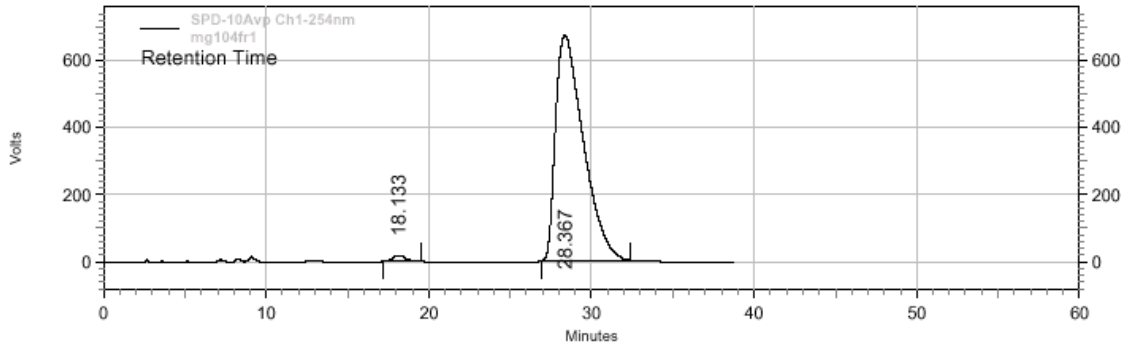
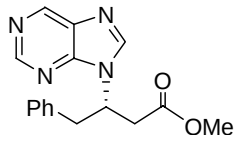


Retention Time	Area	Area %	Height	Height %
17.992	19077460	50.21	317288	64.07
29.317	18918205	49.79	177924	35.93
Totals	37995665	100.00	495212	100.00



Retention Time	Area	Area %	Height	Height %
18.133	1038042	1.28	18087	2.62
28.367	80094081	98.72	672612	97.38
Totals	81132123	100.00	690699	100.00



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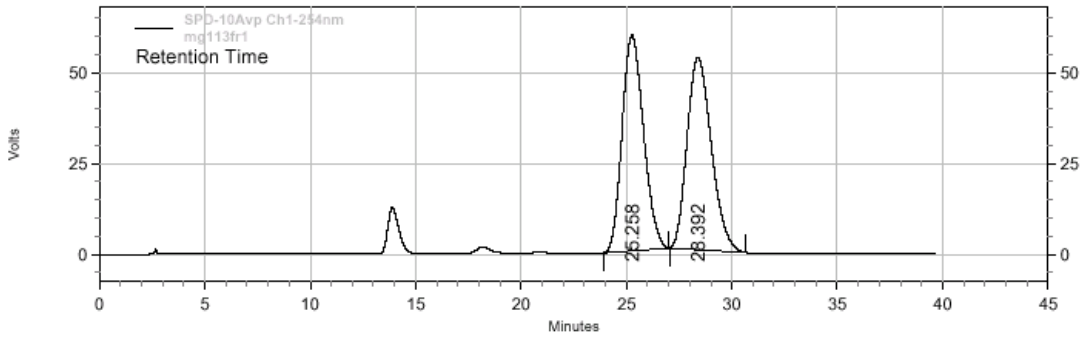
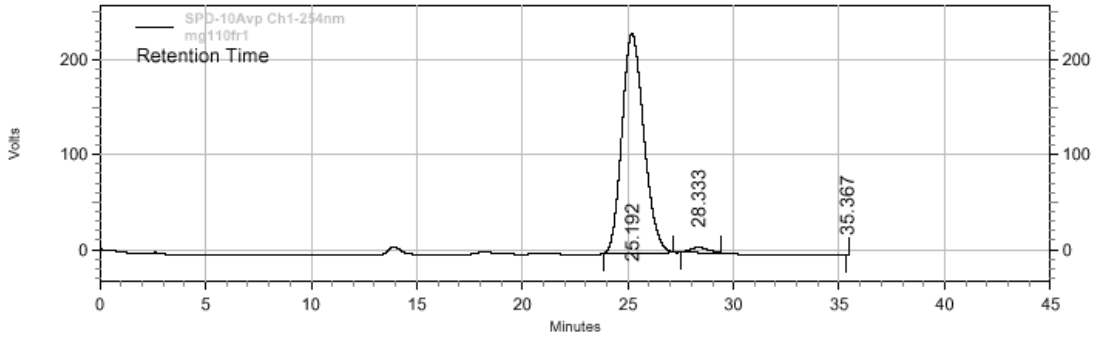
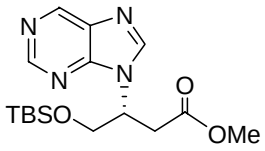


Retention Time	Area	Area %	Height	Height %
25.258	4209557	49.80	59366	52.87
28.392	4243133	50.20	52913	47.13
Totals	8452690	100.00	112279	100.00



Retention Time	Area	Area %	Height	Height %
25.192	16692037	98.13	231119	97.83
28.333	318403	1.87	5106	2.16
35.367	38	0.00	9	0.00
Totals	17010478	100.00	236234	100.00



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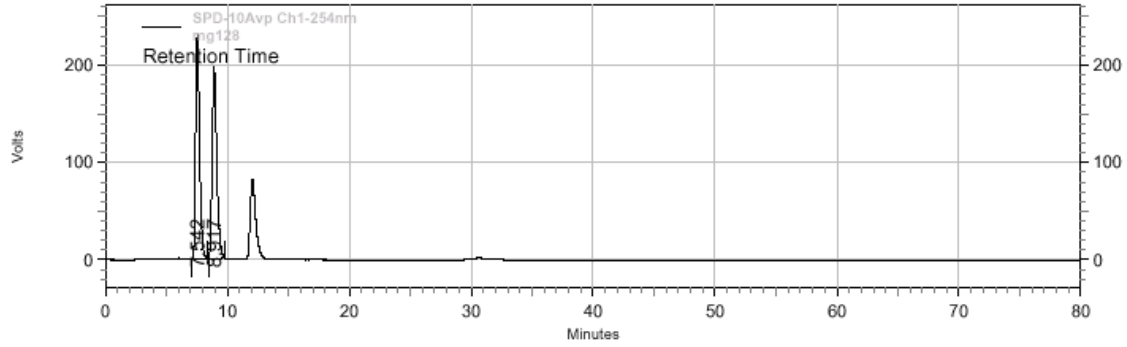
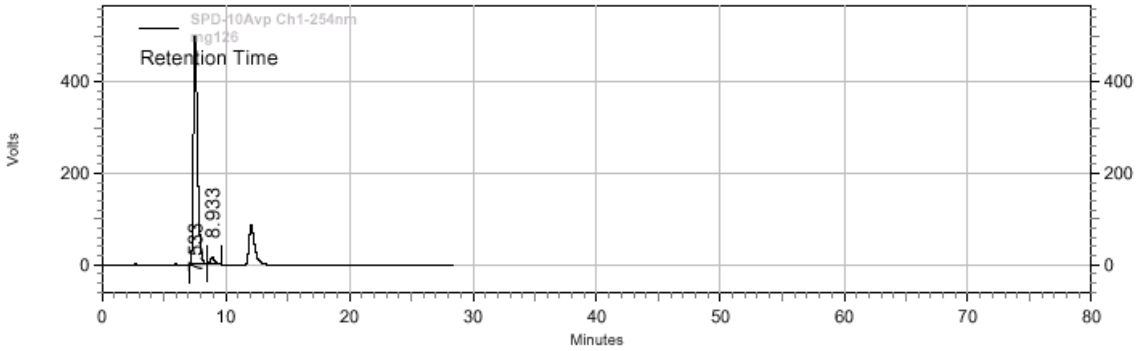
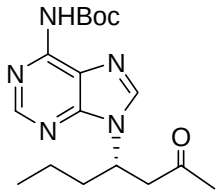


Retention Time	Area	Area %	Height	Height %
7.542	5123111	49.85	231776	54.13
8.917	5154960	50.15	196439	45.87
Totals	10278071	100.00	428215	100.00



Retention Time	Area	Area %	Height	Height %
7.533	11223948	97.09	501304	97.39
8.933	335842	2.91	13460	2.61
Totals	11559790	100.00	514764	100.00



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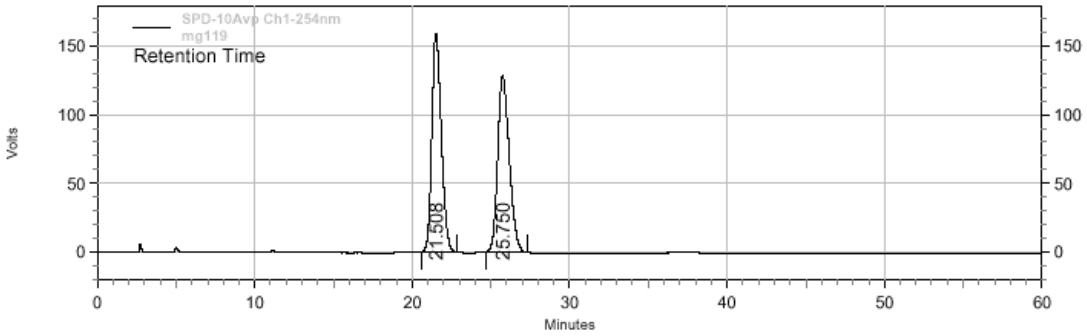
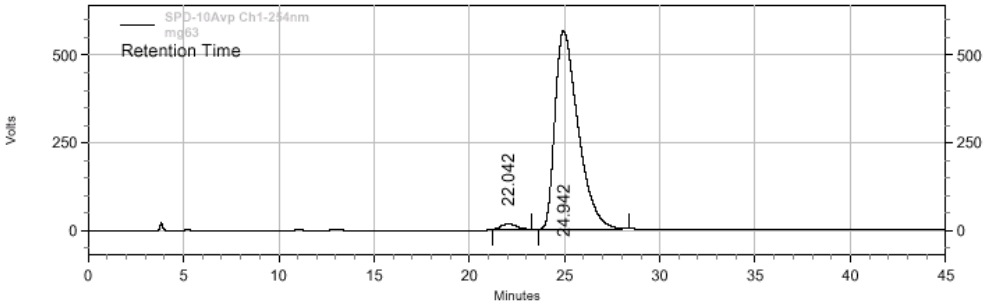
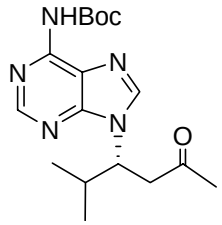


Retention Time	Area	Area %	Height	Height %
21.508	6667098	50.31	158836	55.21
25.750	6584439	49.69	128842	44.79
Totals	13251537	100.00	287678	100.00



Retention Time	Area	Area %	Height	Height %
22.042	890572	1.83	15191	2.62
24.942	47678067	98.17	565632	97.38
Totals	48568639	100.00	580823	100.00



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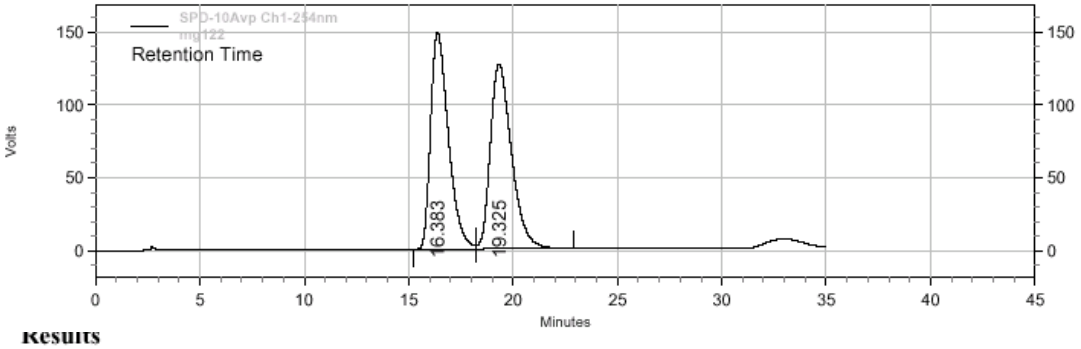
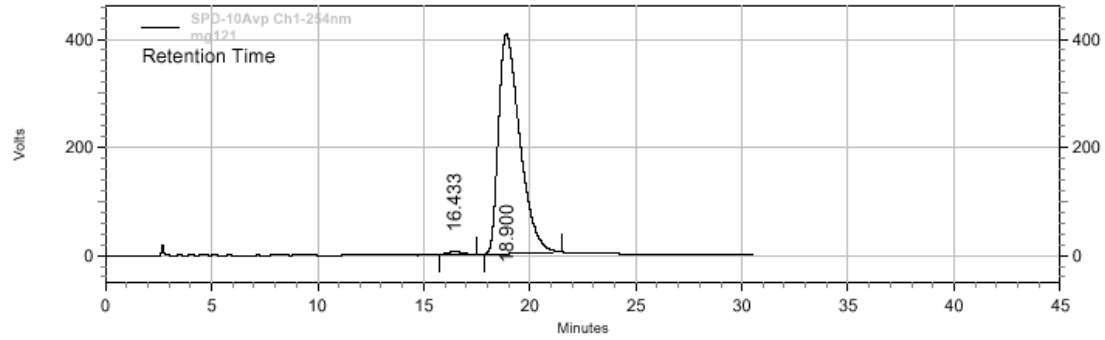
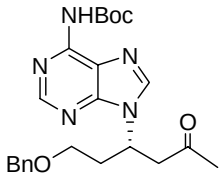


Results

Retention Time	Area	Area %	Height	Height %
16.383	8812223	49.65	148283	53.91
19.325	8936423	50.35	126763	46.09
Totals	17748646	100.00	275046	100.00



Retention Time	Area	Area %	Height	Height %
16.433	331134	1.15	6563	1.59
18.900	28467319	98.85	406474	98.41
Totals	28798453	100.00	413037	100.00



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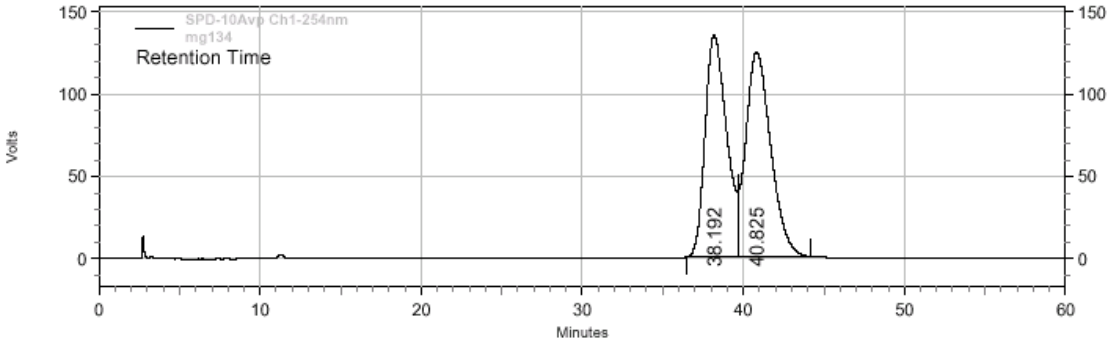
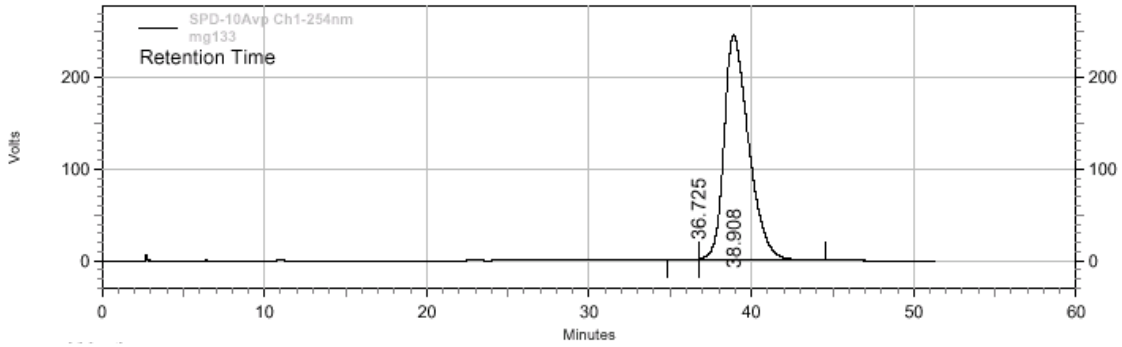
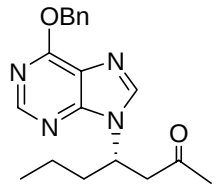


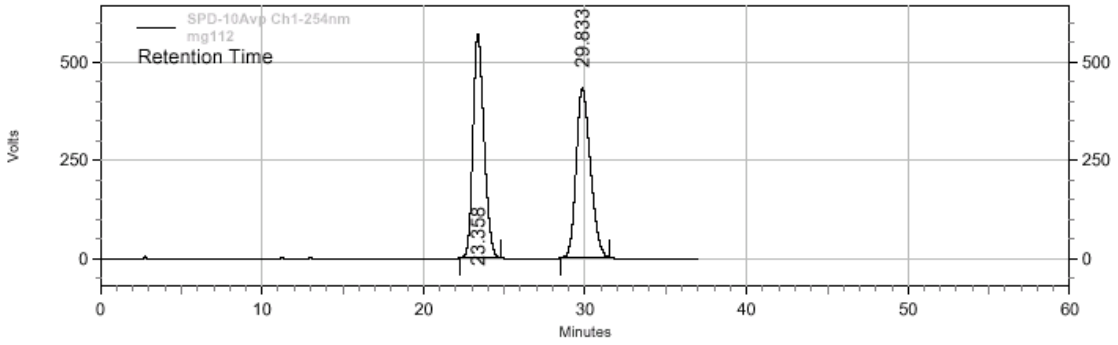
Retention Time	Area	Area %	Height	Height %
38.192	12494349	48.01	134714	51.93
40.825	13529604	51.99	124720	48.07
Totals	26023953	100.00	259434	100.00



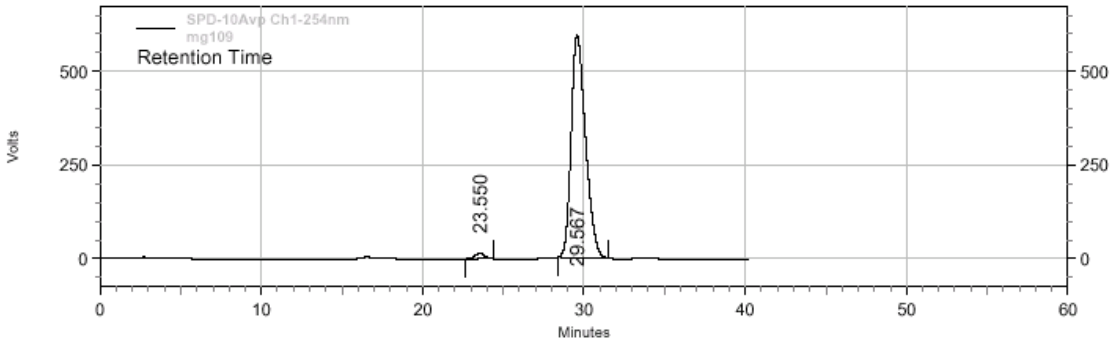
Retention Time	Area	Area %	Height	Height %
36.725	1215	0.00	874	0.35
38.908	25909702	100.00	245792	99.65
Totals	25910917	100.00	246666	100.00



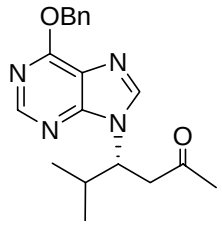
9a



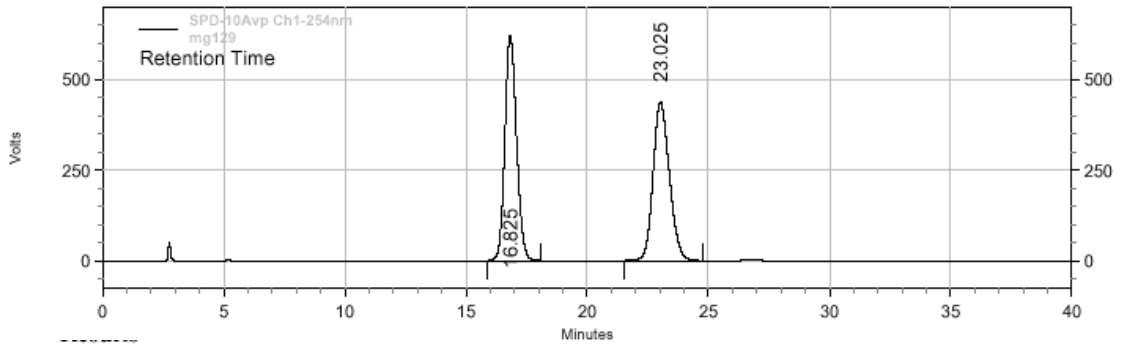
Retention Time	Area	Area %	Height	Height %
23.358	27214937	50.67	569092	56.83
29.833	26496009	49.33	432326	43.17
Totals	53710946	100.00	1001418	100.00



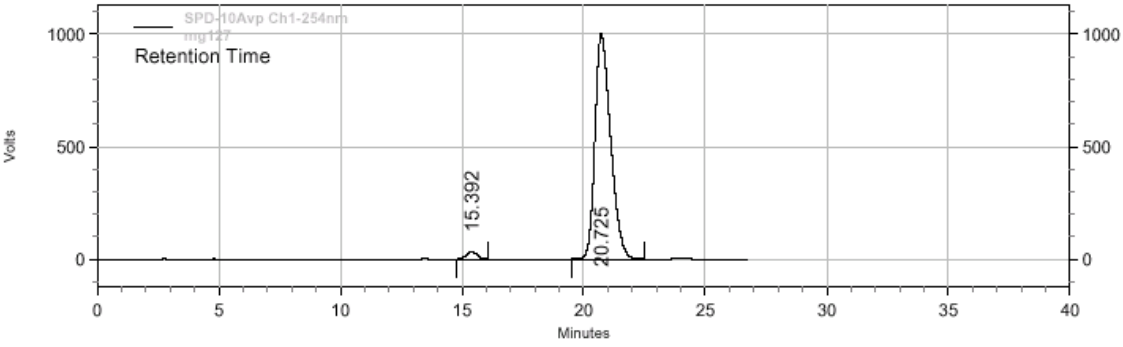
Retention Time	Area	Area %	Height	Height %
23.550	615384	1.65	13958	2.30
29.567	36779054	98.35	594052	97.70
Totals	37394438	100.00	608010	100.00



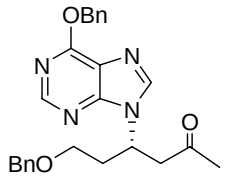
9b



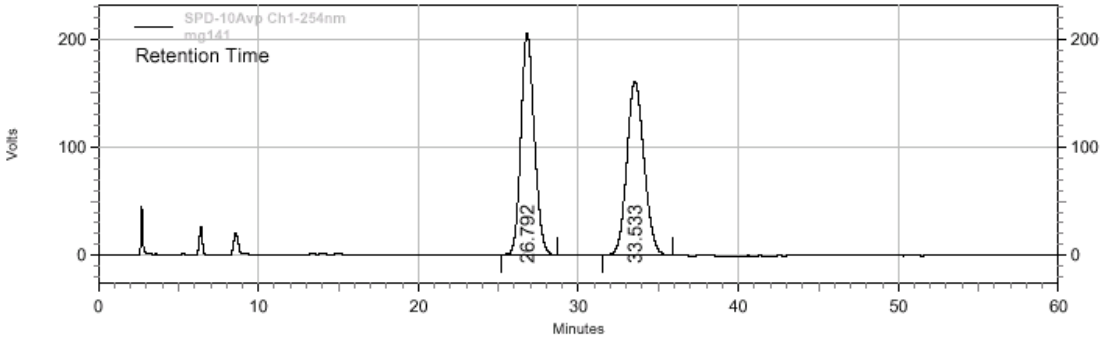
Retention Time	Area	Area %	Height	Height %
16.825	20785608	50.41	619699	58.63
23.025	20449335	49.59	437347	41.37
Totals	41234943	100.00	1057046	100.00



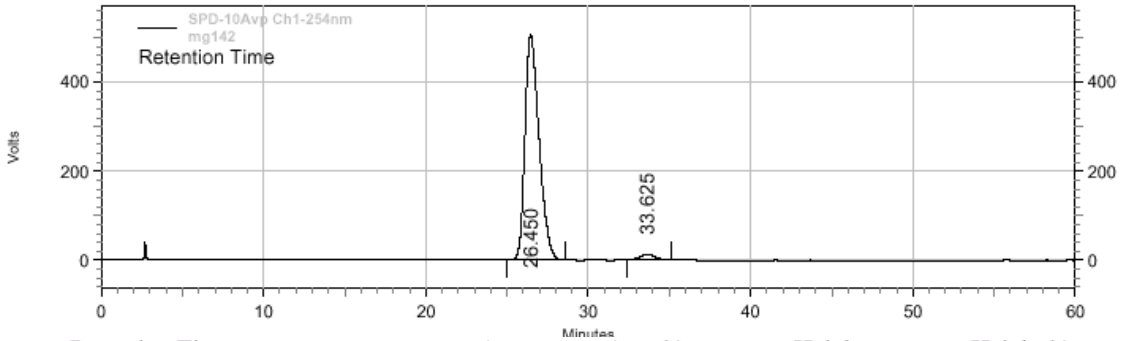
Retention Time	Area	Area %	Height	Height %
15.392	986709	2.16	32899	3.19
20.725	44644868	97.84	999814	96.81
Totals	45631577	100.00	1032713	100.00



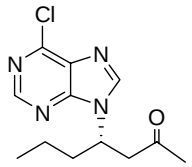
9c



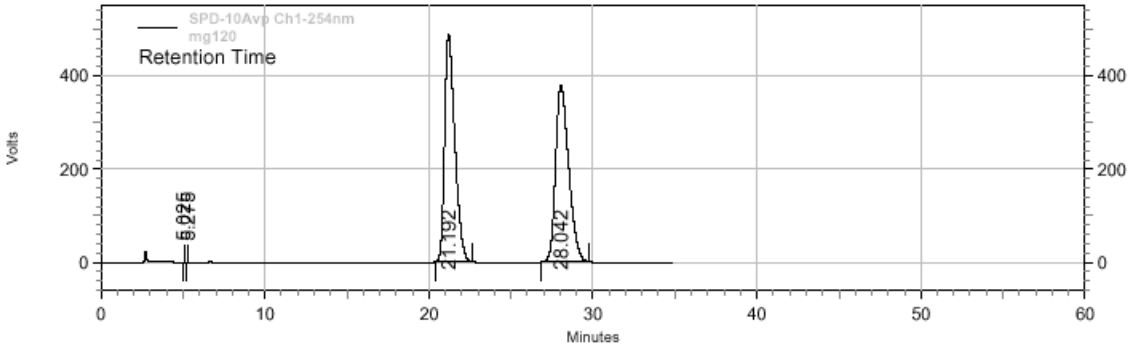
Retention Time	Area	Area %	Height	Height %
26.792	11920192	49.70	204874	56.01
33.533	12063471	50.30	160921	43.99
Totals	23983663	100.00	365795	100.00



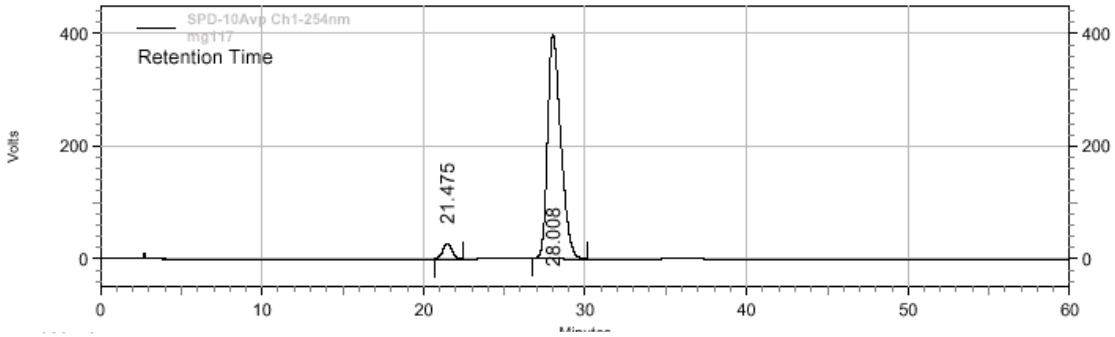
Retention Time	Area	Area %	Height	Height %
26.450	30662109	97.29	506549	97.65
33.625	855205	2.71	12188	2.35
Totals	31517314	100.00	518737	100.00



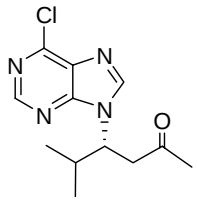
10a



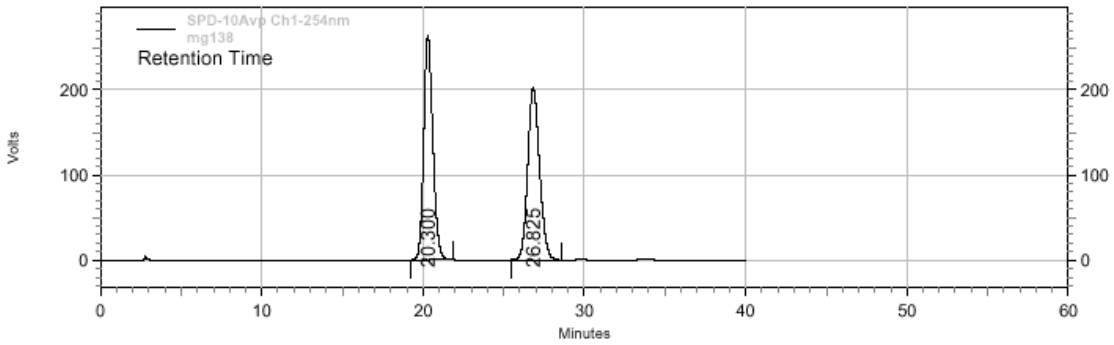
Retention Time	Area	Area %	Height	Height %
21.192	12168698	49.67	270435	55.58
28.042	12331618	50.33	216156	44.42
Totals	24500316	100.00	486591	100.00



Retention Time	Area	Area %	Height	Height %
21.475	1074815	4.54	26790	6.31
28.008	22601089	95.46	397606	93.69
Totals	23675904	100.00	424396	100.00

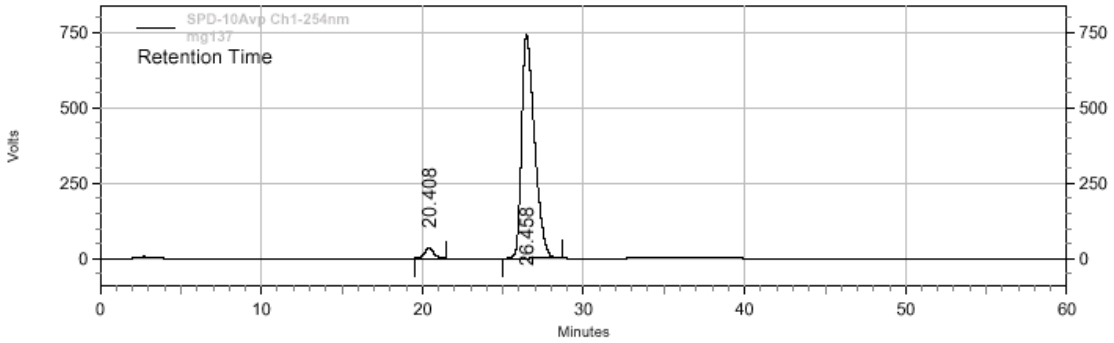


10b

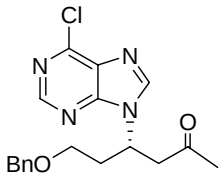


Results

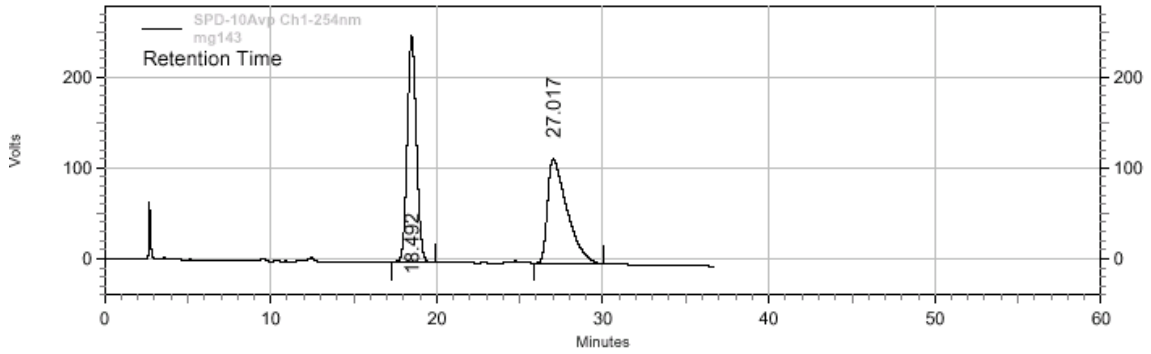
Retention Time	Area	Area %	Height	Height %
20.300	10325380	50.03	263276	56.56
26.825	10311881	49.97	202230	43.44
Totals	20637261	100.00	465506	100.00



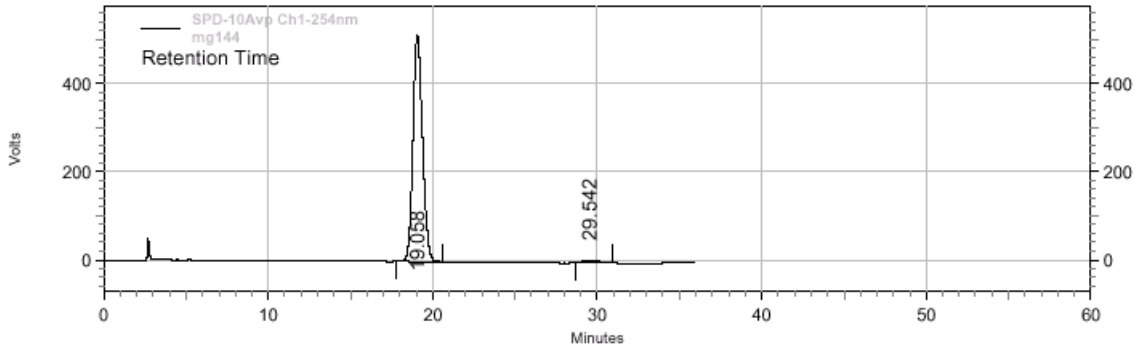
Retention Time	Area	Area %	Height	Height %
20.408	1319015	3.11	34549	4.45
26.458	41088453	96.89	742362	95.55
Totals	42407468	100.00	776911	100.00



10c

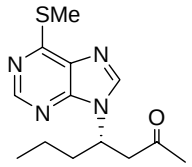


Retention Time	Area	Area %	Height	Height %
18.492	9515760	50.56	249374	68.53
27.017	9304898	49.44	114526	31.47
Totals	18820658	100.00	363900	100.00

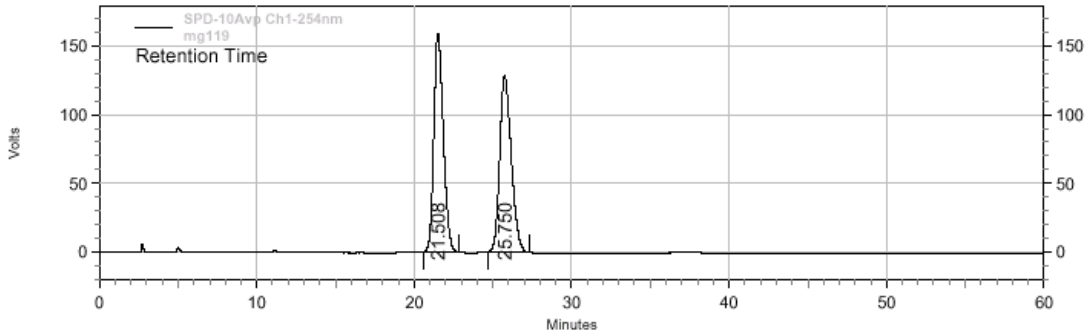


Results

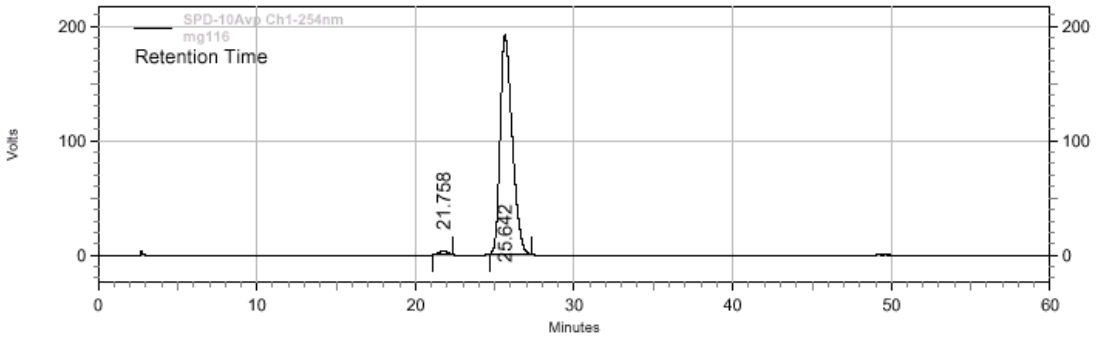
Retention Time	Area	Area %	Height	Height %
19.058	20637598	98.24	512841	98.93
29.542	369444	1.76	5535	1.07
Totals	21007042	100.00	518376	100.00



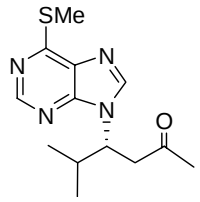
11a



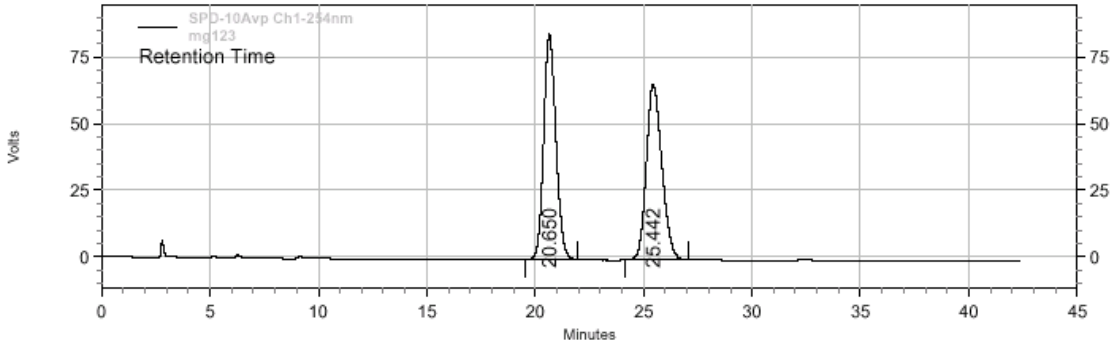
Retention Time	Area	Area %	Height	Height %
21.508	6667098	50.31	158836	55.21
25.750	6584439	49.69	128842	44.79
Totals	13251537	100.00	287678	100.00



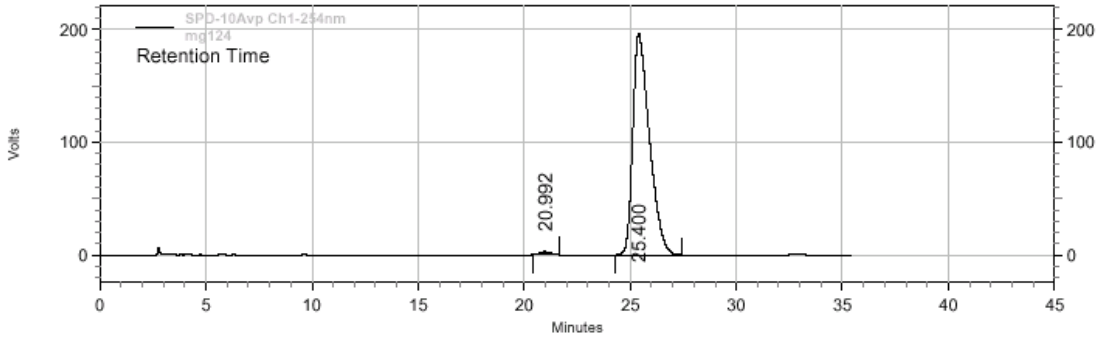
Retention Time	Area	Area %	Height	Height %
21.758	140575	1.37	3813	1.95
25.642	10117569	98.63	191837	98.05
Totals	10258144	100.00	195650	100.00



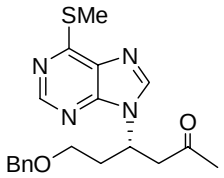
11b



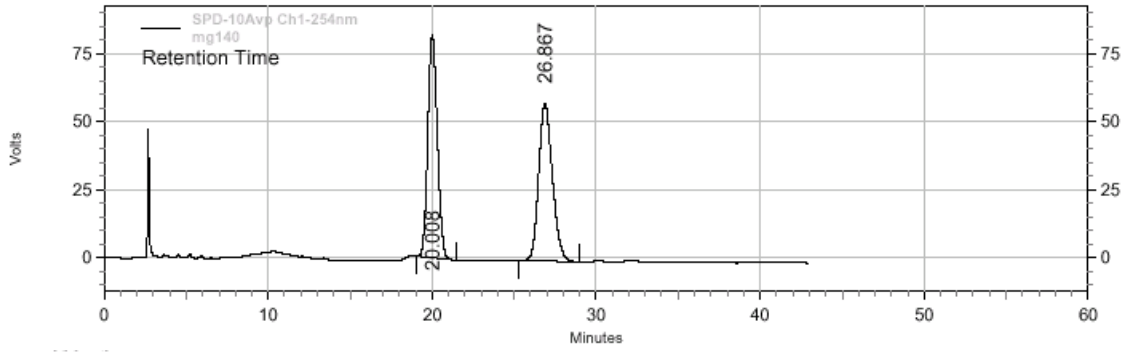
Retention Time	Area	Area %	Height	Height %
20.650	3326046	50.16	84845	56.19
25.442	3304195	49.84	66141	43.81
Totals	6630241	100.00	150986	100.00



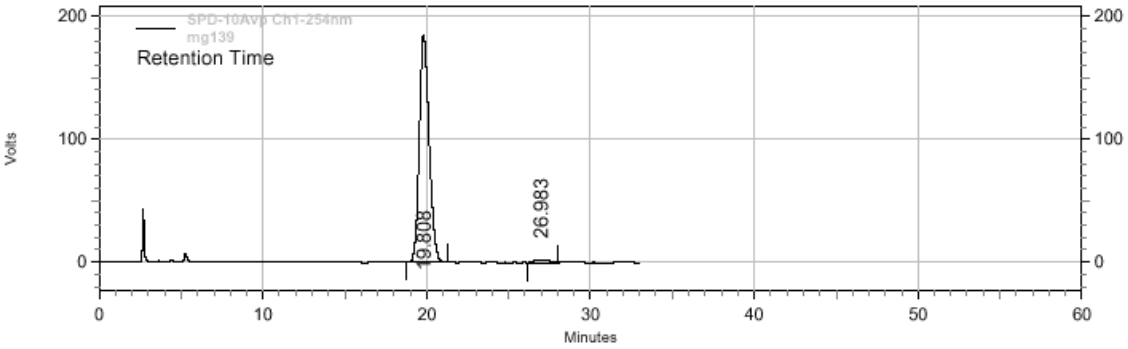
Retention Time	Area	Area %	Height	Height %
20.992	104173	0.96	2871	1.44
25.400	10706090	99.04	195889	98.56
Totals	10810263	100.00	198760	100.00



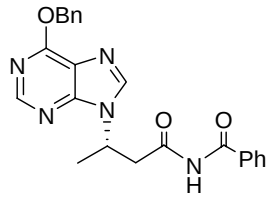
11c



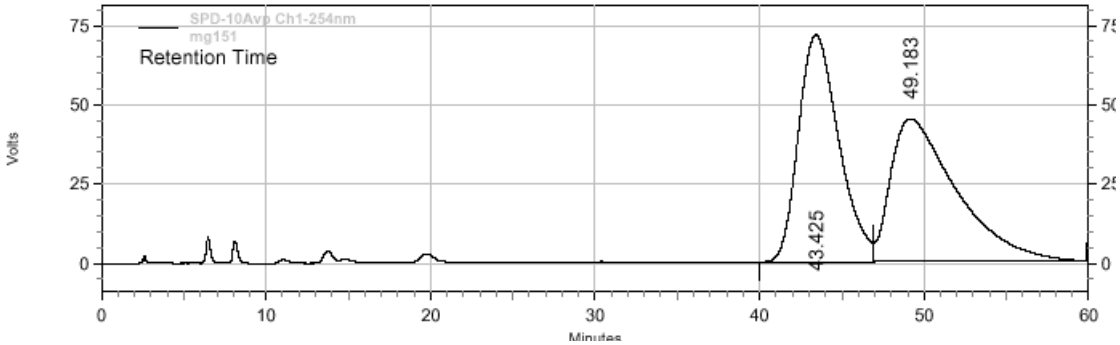
Retention Time	Area	Area %	Height	Height %
20.008	3302614	49.39	81903	58.55
26.867	3384247	50.61	57982	41.45
Totals	6686861	100.00	139885	100.00



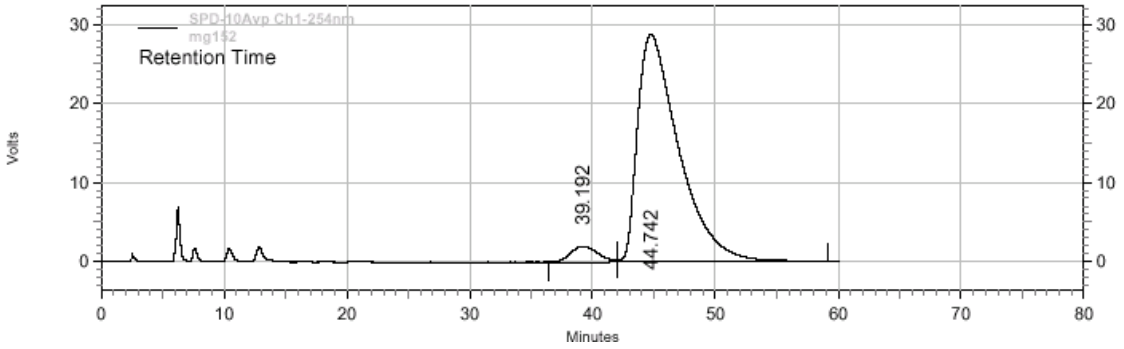
Retention Time	Area	Area %	Height	Height %
19.808	7711007	98.22	184565	98.60
26.983	139509	1.78	2622	1.40
Totals	7850516	100.00	187187	100.00



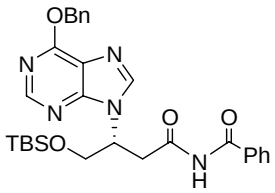
12a



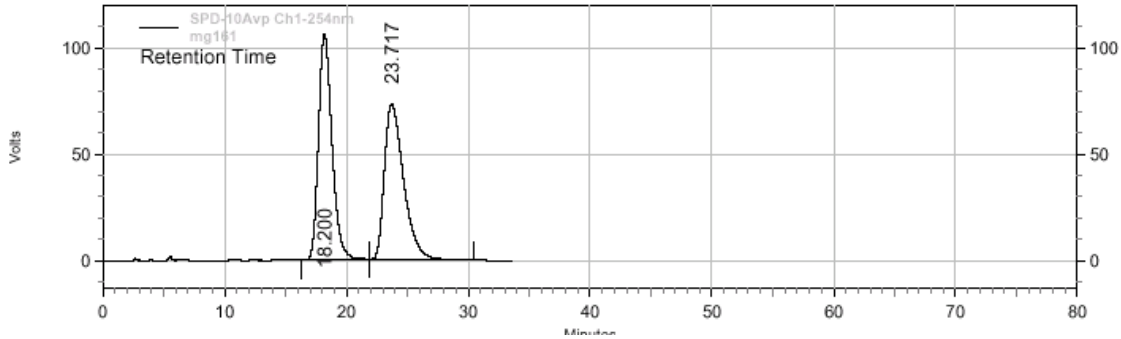
Retention Time	Area	Area %	Height	Height %
43.425	12221067	49.42	71684	61.42
49.183	12509396	50.58	45018	38.58
Totals	24730463	100.00	116702	100.00



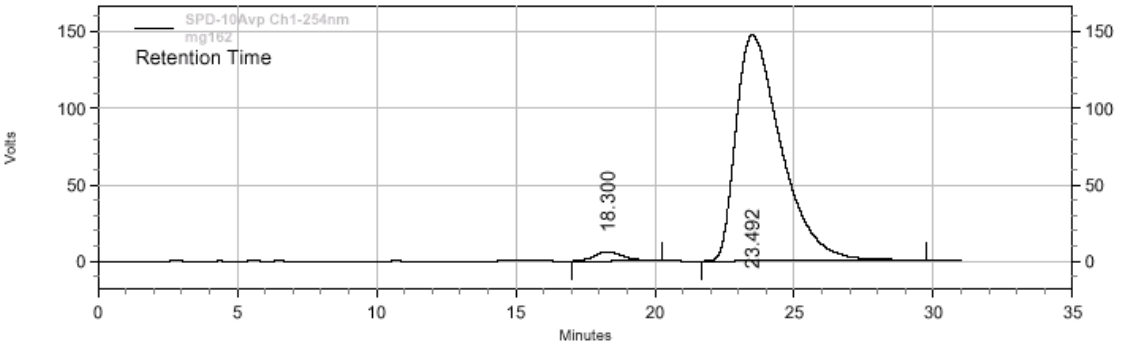
Retention Time	Area	Area %	Height	Height %
39.192	308576	4.38	1998	6.51
44.742	6731705	95.62	28713	93.49
Totals	7040281	100.00	30711	100.00



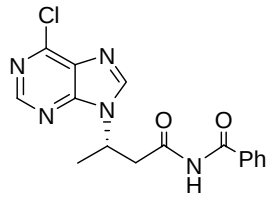
12b



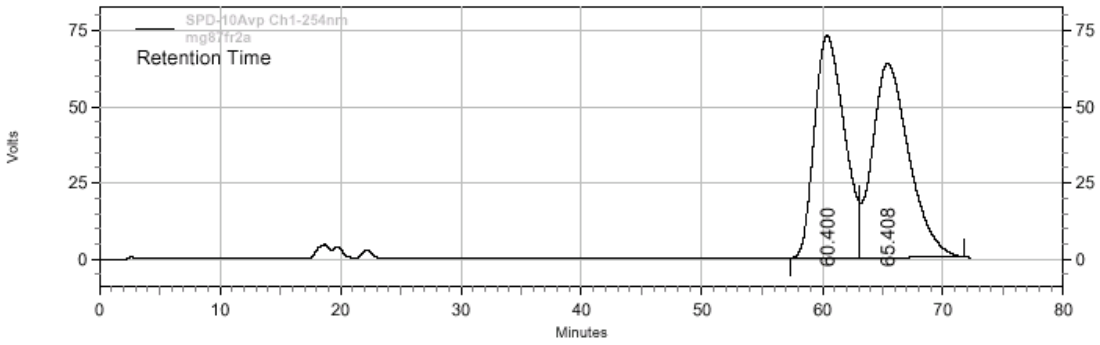
Retention Time	Area	Area %	Height	Height %
18.200	8177044	50.48	106126	59.16
23.717	8022531	49.52	73275	40.84
Totals	16199575	100.00	179401	100.00



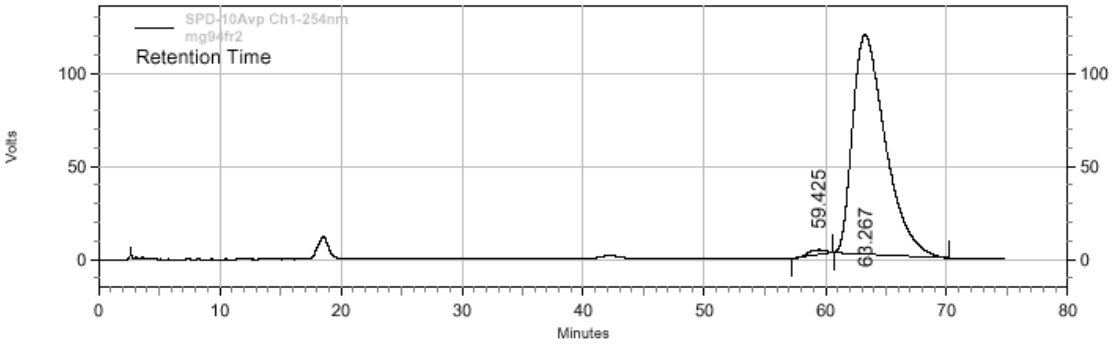
Retention Time	Area	Area %	Height	Height %
18.300	432006	2.52	5845	3.81
23.492	16702455	97.48	147618	96.19
Totals	17134461	100.00	153463	100.00



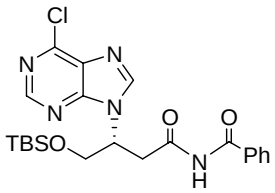
13a



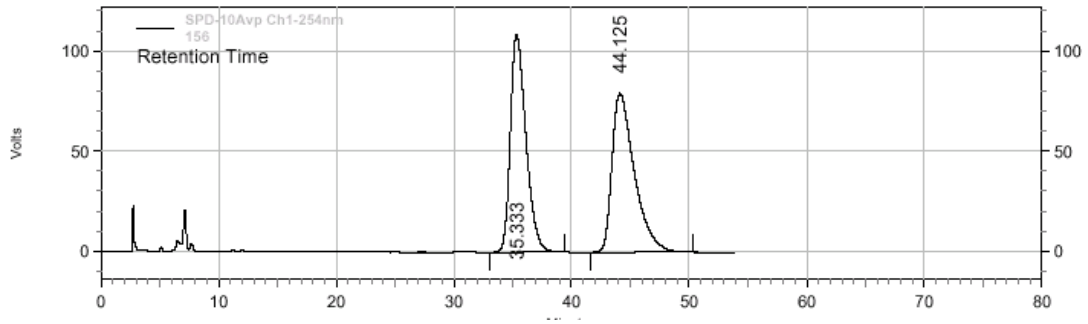
Retention Time	Area	Area %	Height	Height %
60.400	12589680	48.30	72916	53.38
65.408	13477732	51.70	63672	46.62
Totals	26067412	100.00	136588	100.00



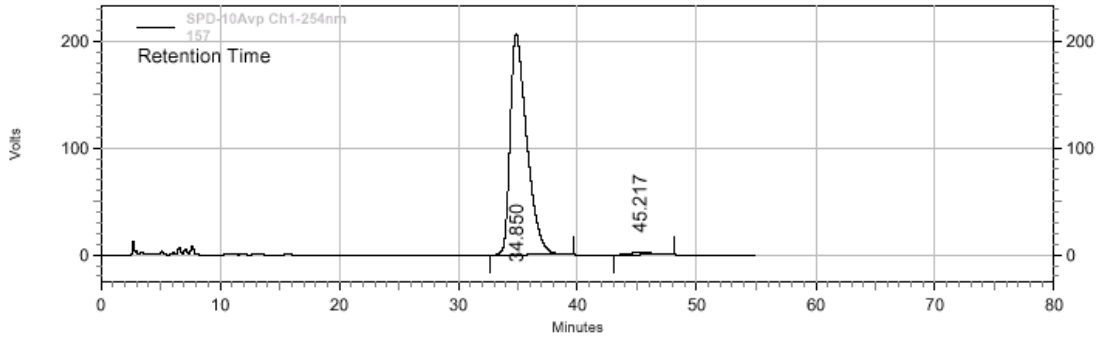
Retention Time	Area	Area %	Height	Height %
59.425	257663	1.15	2642	2.20
63.267	22178923	98.85	117683	97.80
Totals	22436586	100.00	120325	100.00



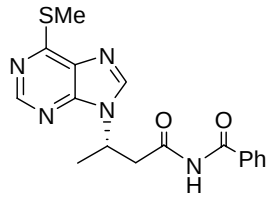
13b



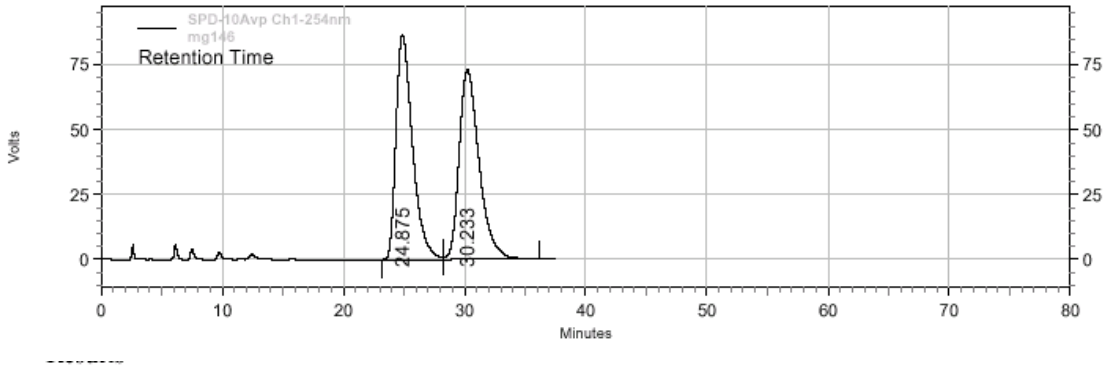
Retention Time	Area	Area %	Height	Height %
35.333	9989584	48.72	108430	57.76
44.125	10512931	51.28	79294	42.24
Totals	20502515	100.00	187724	100.00



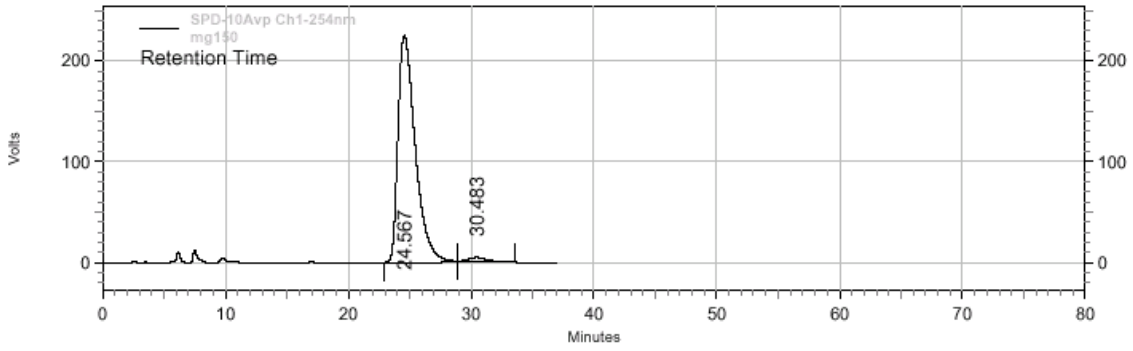
Retention Time	Area	Area %	Height	Height %
34.850	19971775	98.63	206471	98.98
45.217	276991	1.37	2127	1.02
Totals	20248766	100.00	208598	100.00



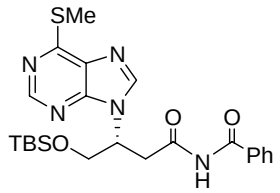
14a



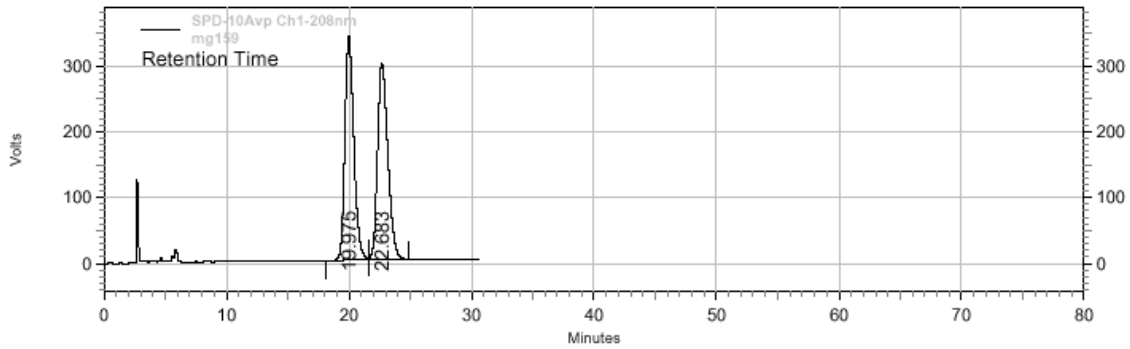
Retention Time	Area	Area %	Height	Height %
24.875	8230456	49.41	86637	54.22
30.233	8425499	50.59	73157	45.78
Totals	16655955	100.00	159794	100.00



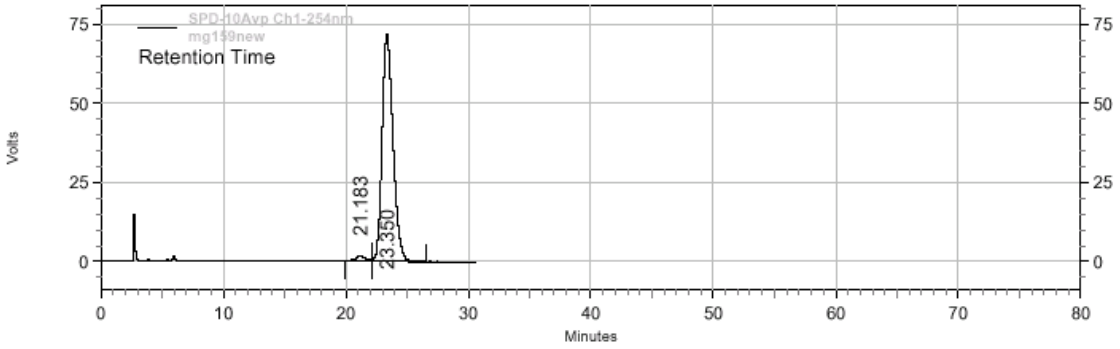
Retention Time	Area	Area %	Height	Height %
24.567	21965132	97.40	225216	97.89
30.483	587007	2.60	4846	2.11
Totals	22552139	100.00	230062	100.00



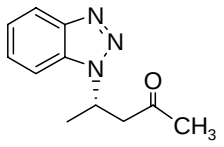
14b



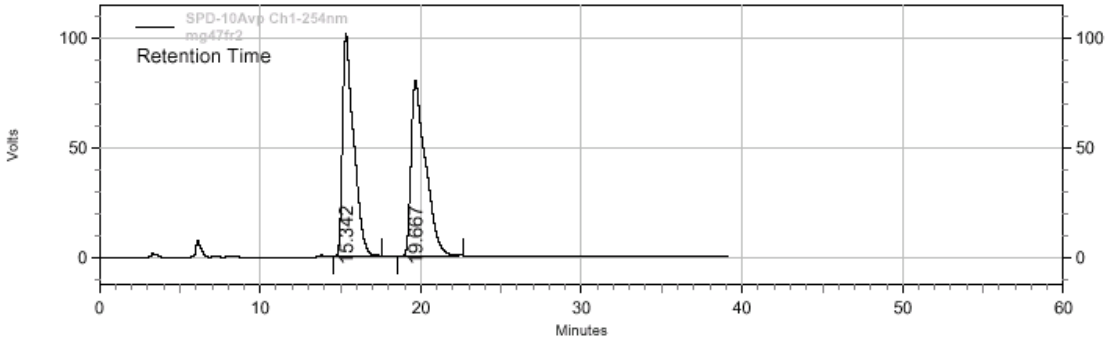
Retention Time	Area	Area %	Height	Height %
19.975	17193226	49.68	339351	53.28
22.683	17415718	50.32	297557	46.72
Totals	34608944	100.00	636908	100.00



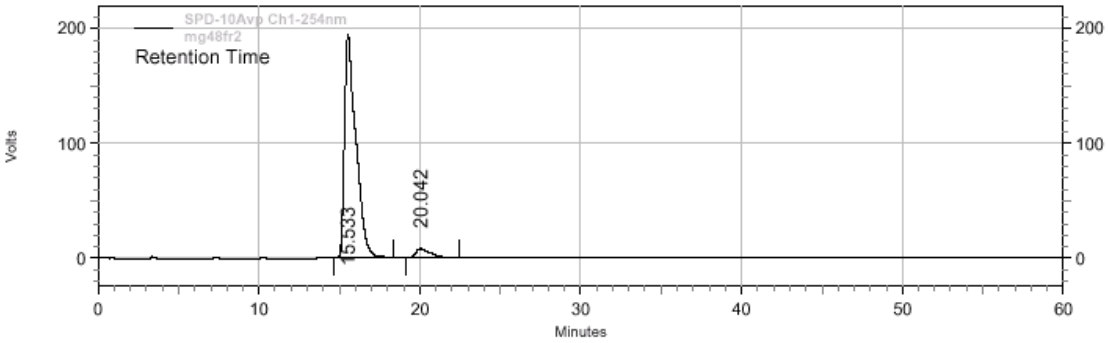
Retention Time	Area	Area %	Height	Height %
21.183	98169	2.16	1625	2.21
23.350	4457173	97.84	71836	97.79
Totals	4555342	100.00	73461	100.00



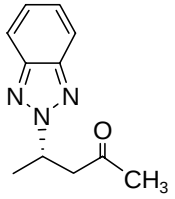
15a



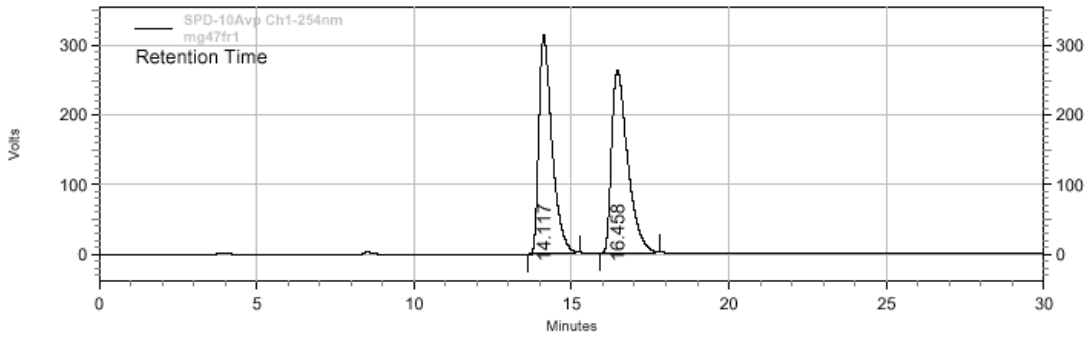
Retention Time	Area	Area %	Height	Height %
15.342	4884666	49.39	101341	55.85
19.667	5006066	50.61	80107	44.15
Totals	9890732	100.00	181448	100.00



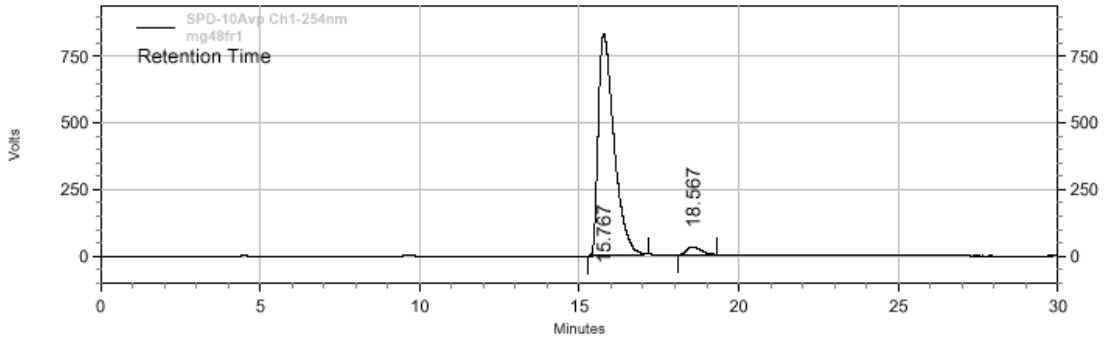
Retention Time	Area	Area %	Height	Height %
15.533	9607336	95.23	194092	96.13
20.042	481391	4.77	7805	3.87
Totals	10088727	100.00	201897	100.00



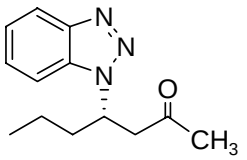
16a



Retention Time	Area	Area %	Height	Height %
14.117	9090828	49.51	313541	54.47
16.458	9271916	50.49	262105	45.53
Totals	18362744	100.00	575646	100.00



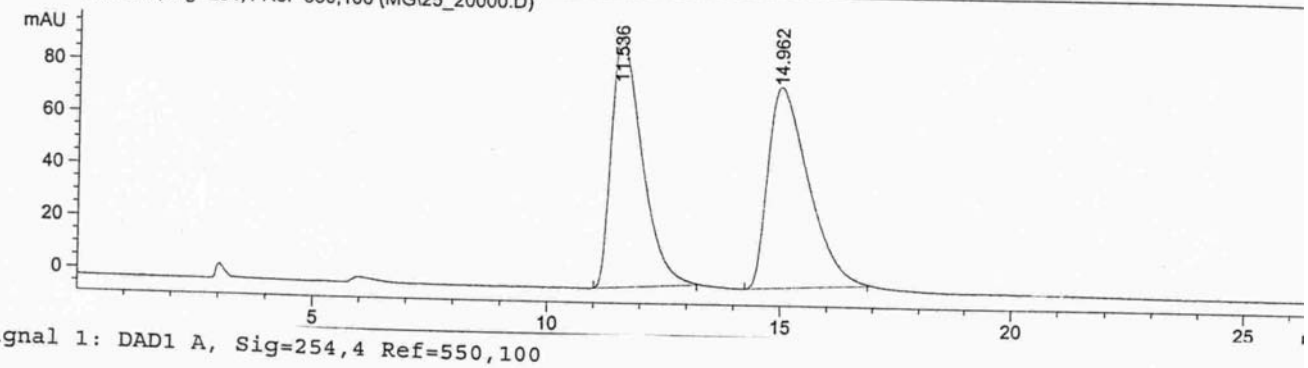
Retention Time	Area	Area %	Height	Height %
15.767	28461103	96.80	830556	96.64
18.567	940449	3.20	28893	3.36
Totals	29401552	100.00	859449	100.00



15b

(modified after loading)

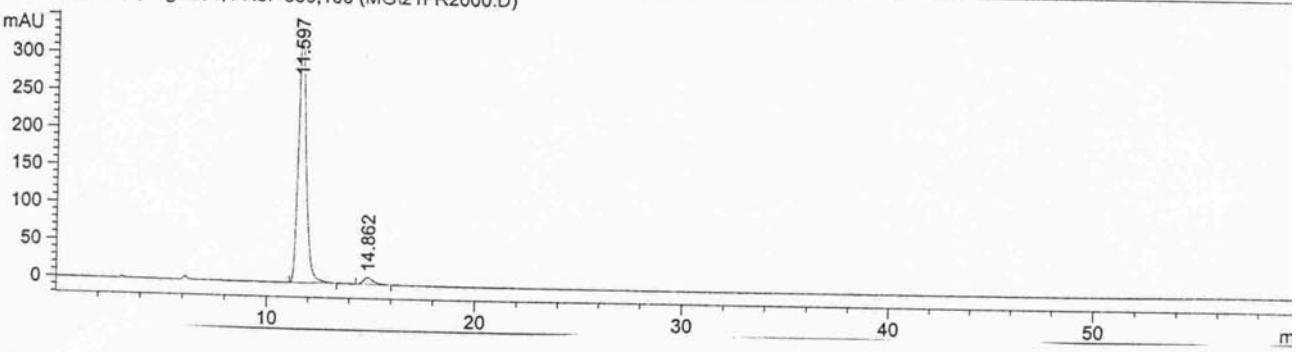
DAD1 A, Sig=254,4 Ref=550,100 (MG\25_20000.D)



Signal 1: DAD1 A, Sig=254,4 Ref=550,100

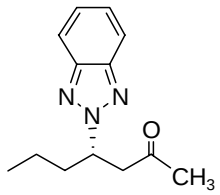
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.536	BB	0.6641	4405.47998	95.87392	48.6438
2	14.962	PB	0.8170	4651.12744	76.96938	51.3562
Totals :				9056.60742	172.84330	

DAD1 D, Sig=254,4 Ref=550,100 (MG\21FR2000.D)

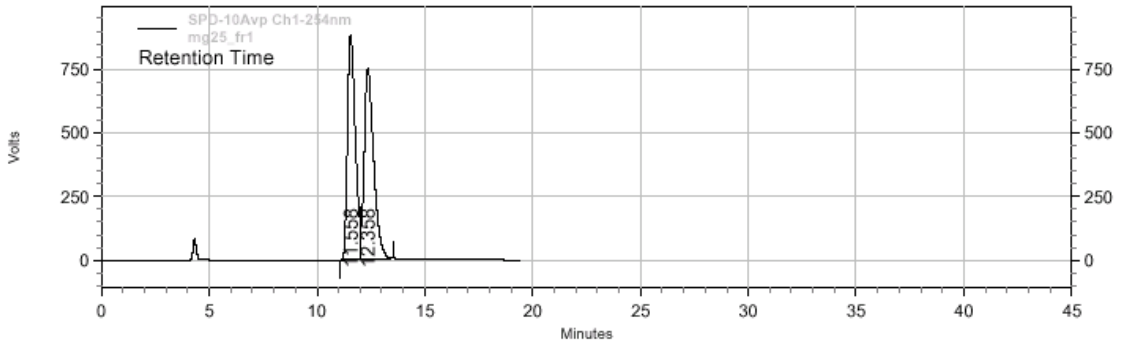


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.597	BB	0.3961	8899.55371	336.94302	96.7699
2	14.862	PB	0.4854	297.05658	9.08575	3.2301
Totals :				9196.61029	346.02877	

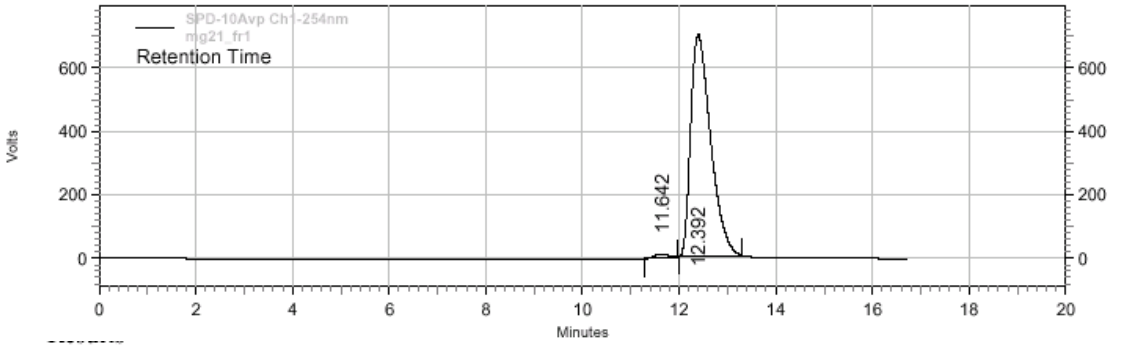
trument 1 11/8/03 2:02:47 PM MG



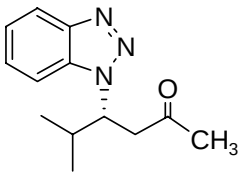
16b



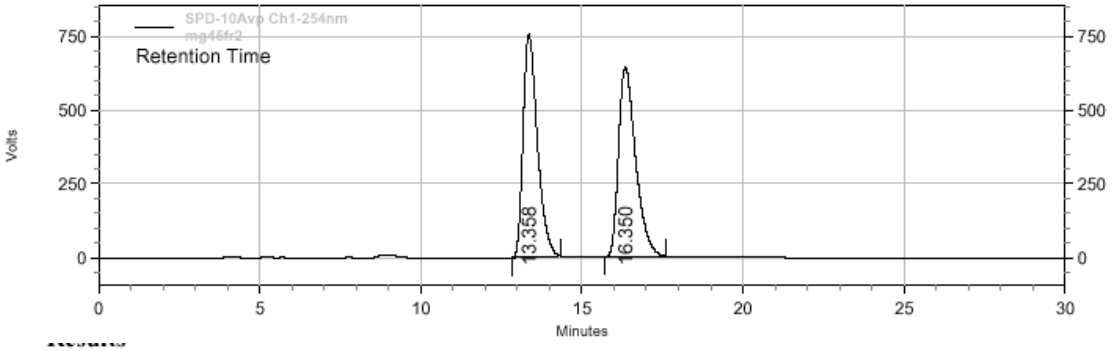
Retention Time	Area	Area %	Height	Height %
11.558	22503775	49.65	881503	54.03
12.358	22823882	50.35	750084	45.97
Totals	45327657	100.00	1631587	100.00



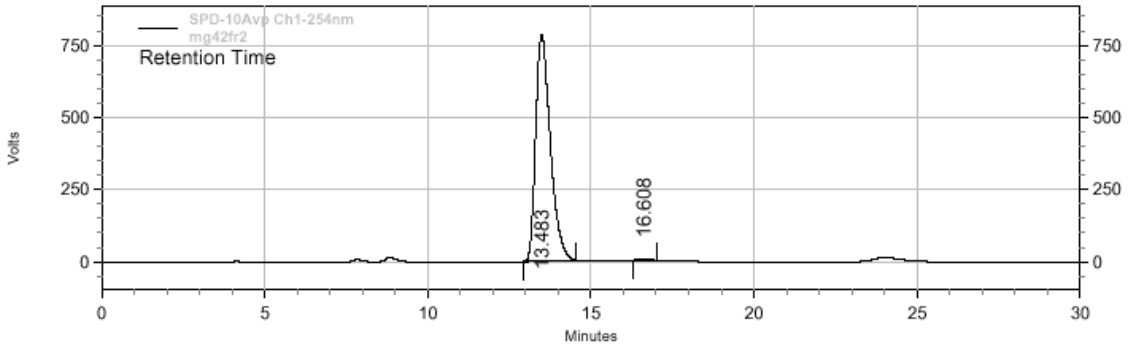
Retention Time	Area	Area %	Height	Height %
11.642	245116	1.21	12612	1.77
12.392	20048301	98.79	698511	98.23
Totals	20293417	100.00	711123	100.00



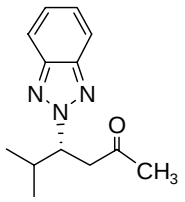
15c



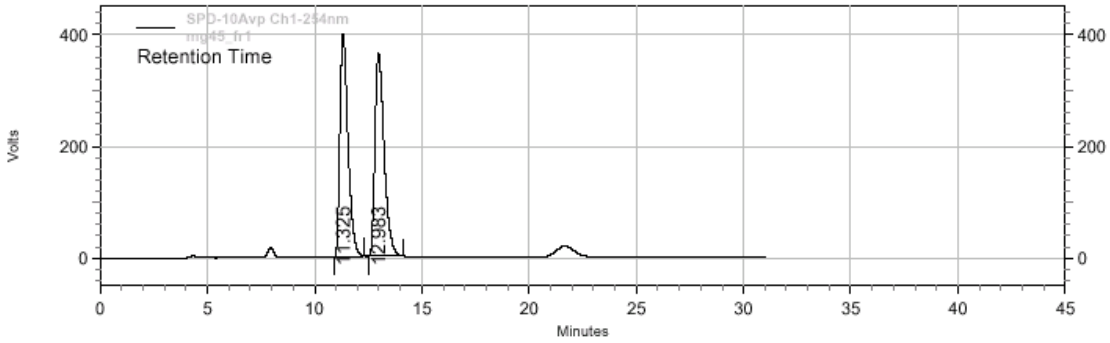
Retention Time	Area	Area %	Height	Height %
13.358	23146707	49.40	755602	54.06
16.350	23711597	50.60	642168	45.94
Totals	46858304	100.00	1397770	100.00



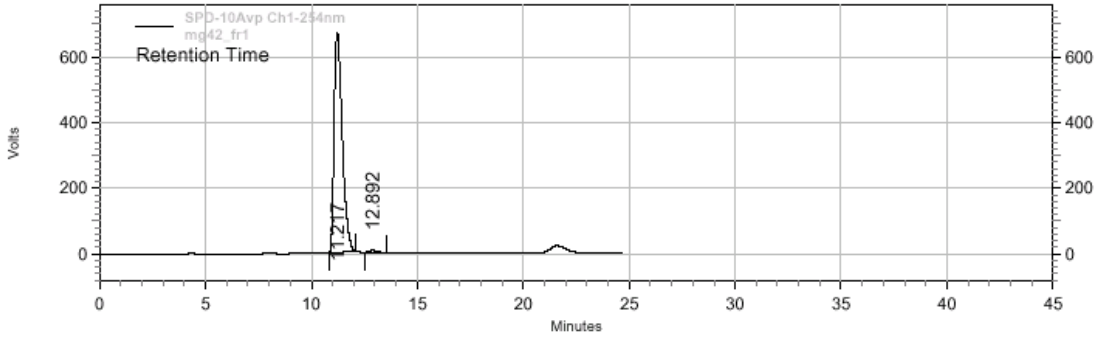
Retention Time	Area	Area %	Height	Height %
13.483	24426675	99.17	782401	99.00
16.608	203789	0.83	7891	1.00
Totals	24630464	100.00	790292	100.00



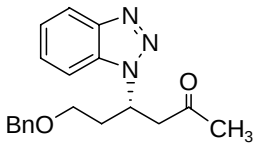
16c



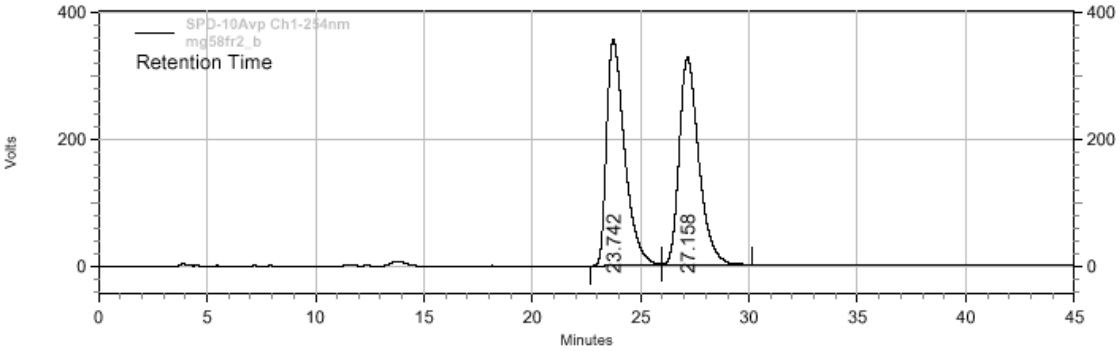
Retention Time	Area	Area %	Height	Height %
11.325	10567180	49.49	398740	52.36
12.983	10785477	50.51	362748	47.64
Totals	21352657	100.00	761488	100.00



Retention Time	Area	Area %	Height	Height %
11.217	17881230	99.07	668391	98.97
12.892	168329	0.93	6944	1.03
Totals	18049559	100.00	675335	100.00

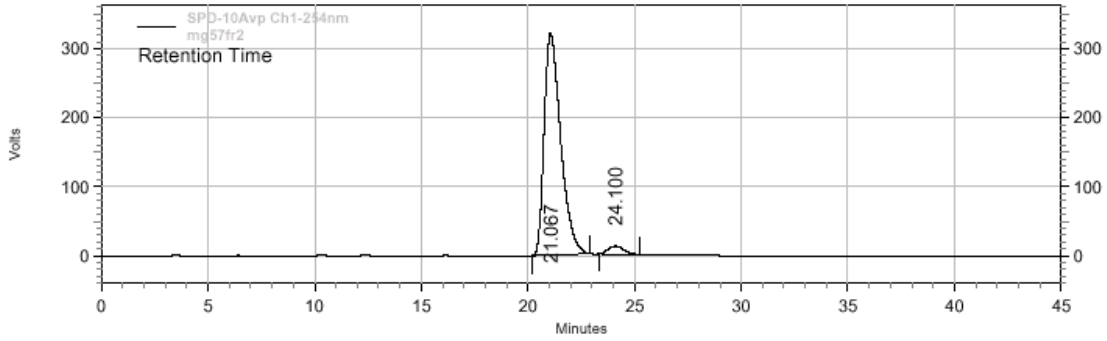


15d

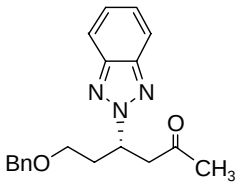


Results

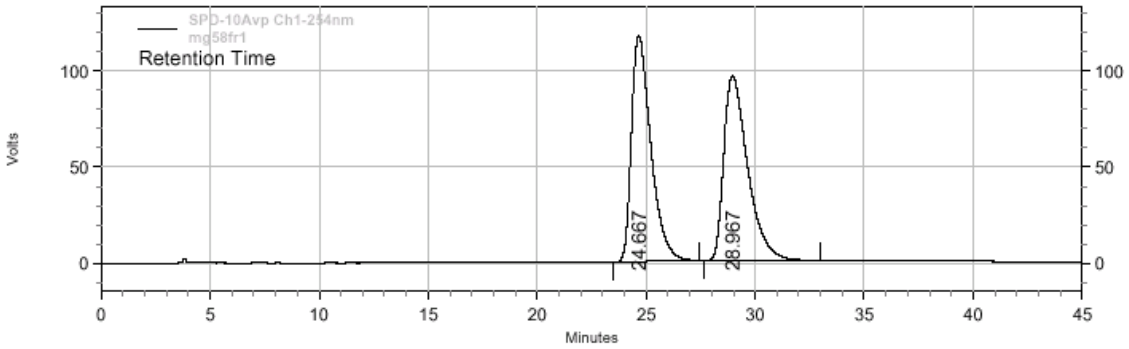
Retention Time	Area	Area %	Height	Height %
23.742	20586885	49.97	355845	52.05
27.158	20610948	50.03	327849	47.95
Totals	41197833	100.00	683694	100.00



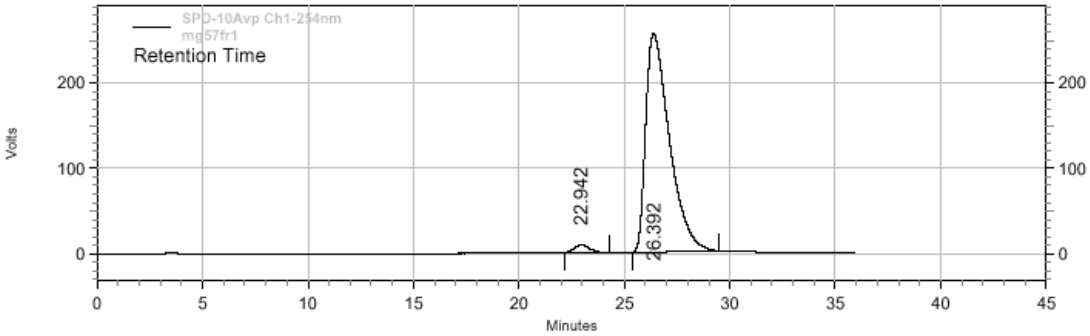
Retention Time	Area	Area %	Height	Height %
21.067	17300190	96.56	321084	96.46
24.100	616275	3.44	11781	3.54
Totals	17916465	100.00	332865	100.00



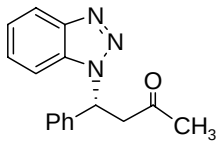
16d



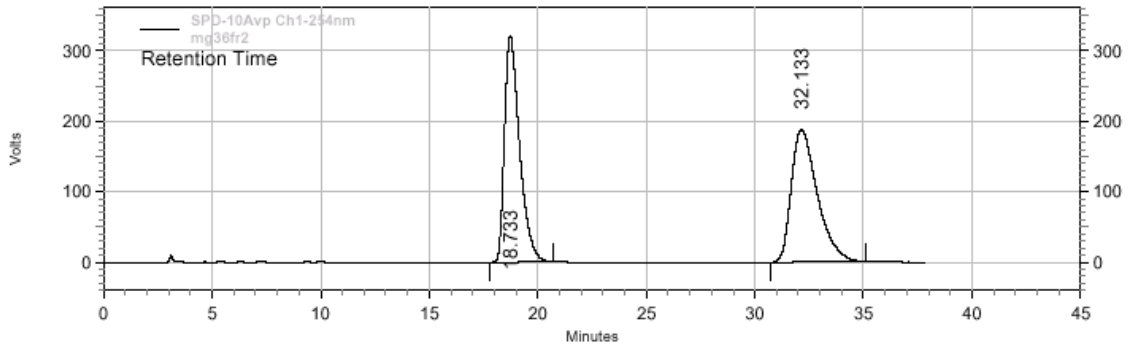
Retention Time	Area	Area %	Height	Height %
24.667	7241114	49.76	117517	55.04
28.967	7309657	50.24	96009	44.96
Totals	14550771	100.00	213526	100.00



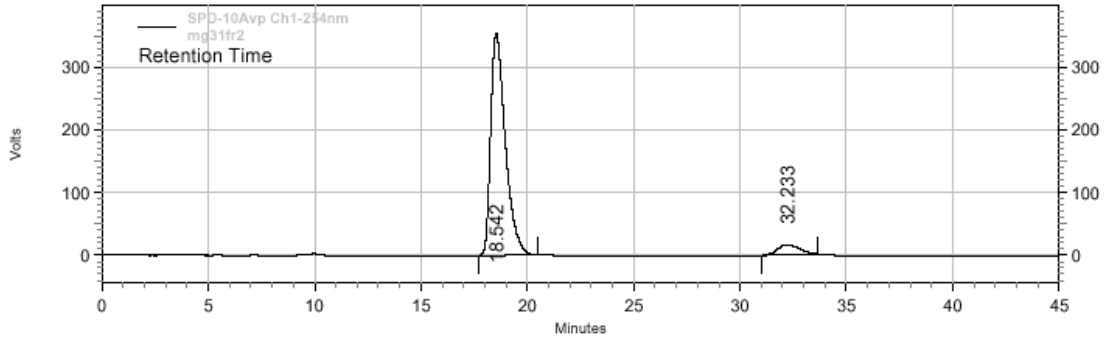
Retention Time	Area	Area %	Height	Height %
22.942	479934	2.33	8978	3.38
26.392	20097070	97.67	256354	96.62
Totals	20577004	100.00	265332	100.00



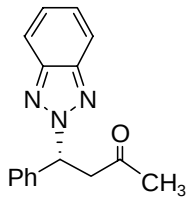
15e



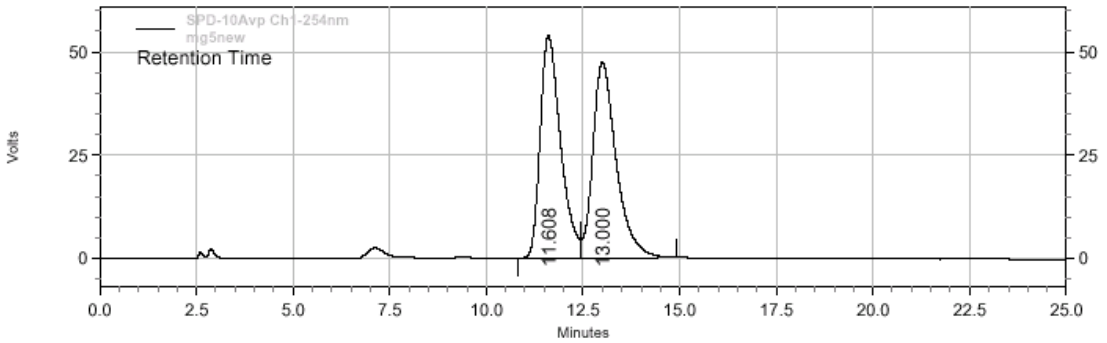
Retention Time	Area	Area %	Height	Height %
18.733	15521647	49.74	320650	63.01
32.133	15687032	50.26	188257	36.99
Totals	31208679	100.00	508907	100.00



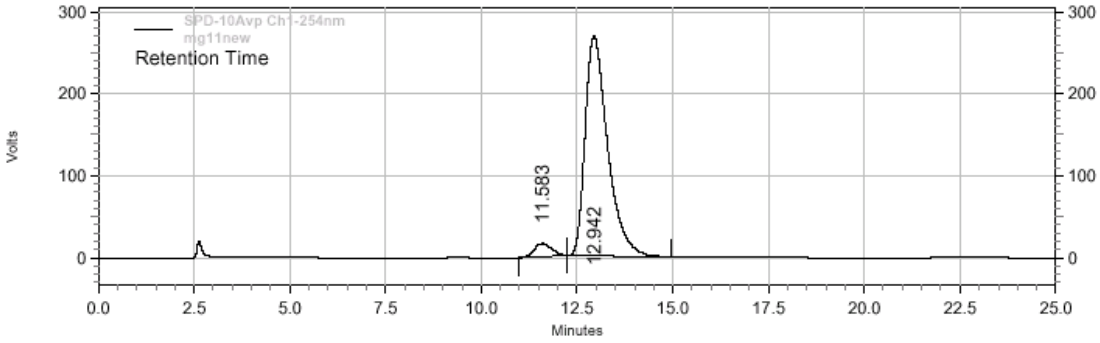
Retention Time	Area	Area %	Height	Height %
18.542	17003020	93.61	354543	95.60
32.233	1160318	6.39	16318	4.40
Totals	18163338	100.00	370861	100.00



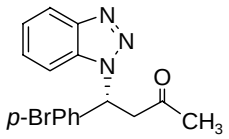
16e



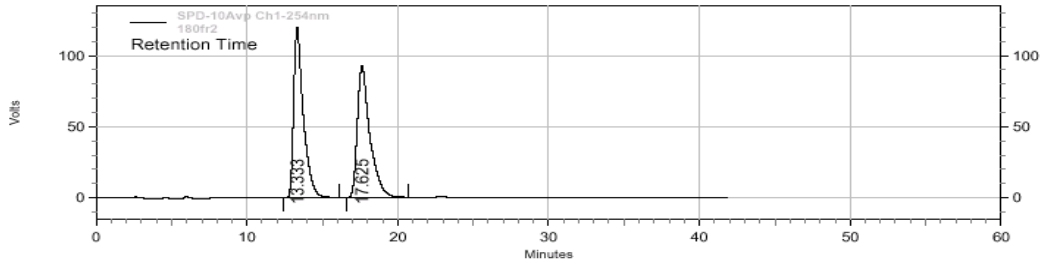
Retention Time	Area	Area %	Height	Height %
11.608	1969227	49.78	53755	53.15
13.000	1986997	50.22	47376	46.85
Totals	3956224	100.00	101131	100.00



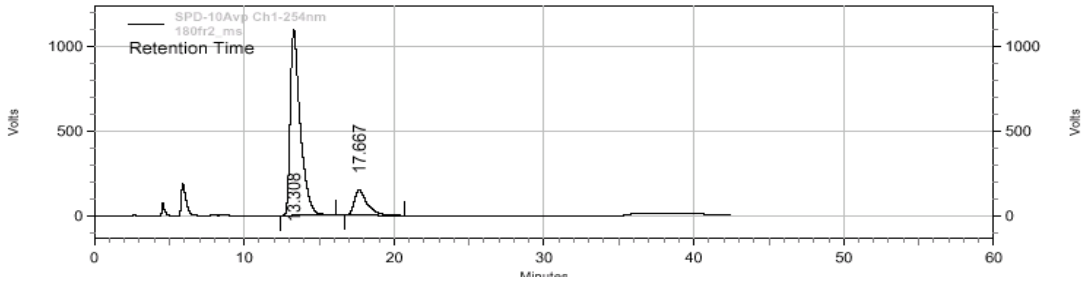
Retention Time	Area	Area %	Height	Height %
11.583	509881	4.45	15968	5.63
12.942	10942477	95.55	267590	94.37
Totals	11452358	100.00	283558	100.00



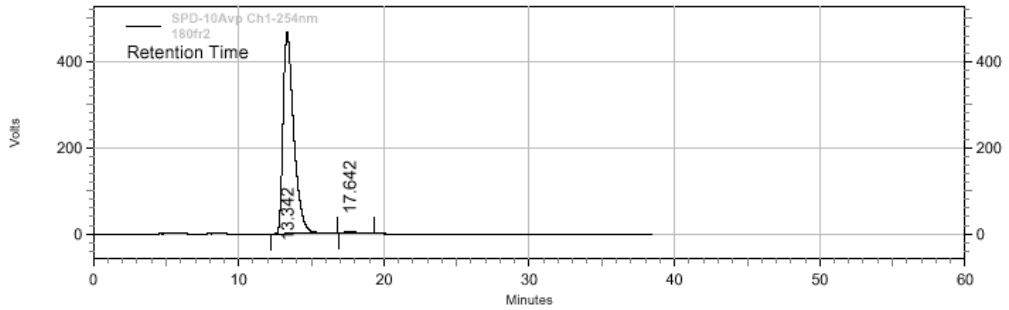
15f



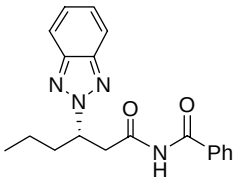
Retention Time	Area	Area %	Height	Height %
13.333	5333834	50.06	119543	56.46
17.625	5320928	49.94	92205	43.54
Totals	10654762	100.00	211748	100.00



Retention Time	Area	Area %	Height	Height %
13.308	50618607	85.30	1093211	88.06
17.667	8721125	14.70	148177	11.94
Totals	59339732	100.00	1241388	100.00

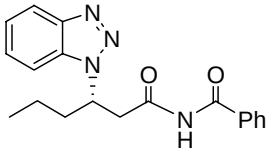


Retention Time	Area	Area %	Height	Height %
13.342	23872419	99.03	467167	99.15
17.642	234560	0.97	4026	0.85
Totals	24106979	100.00	471193	100.00



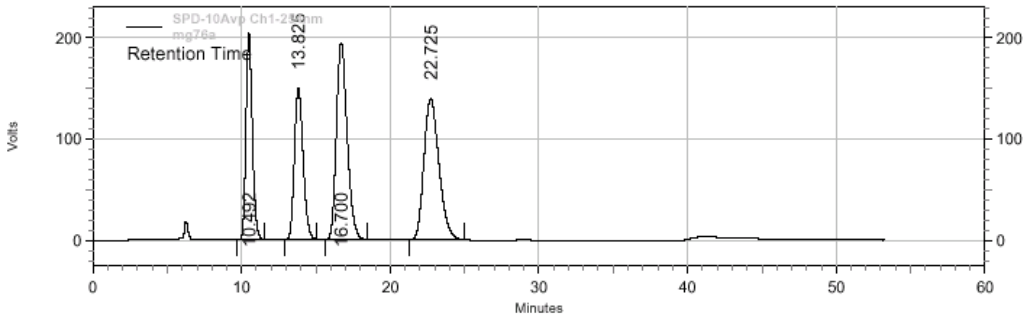
17a

(rt_{major} 10.5 min; rt_{minor} 14.0 min)

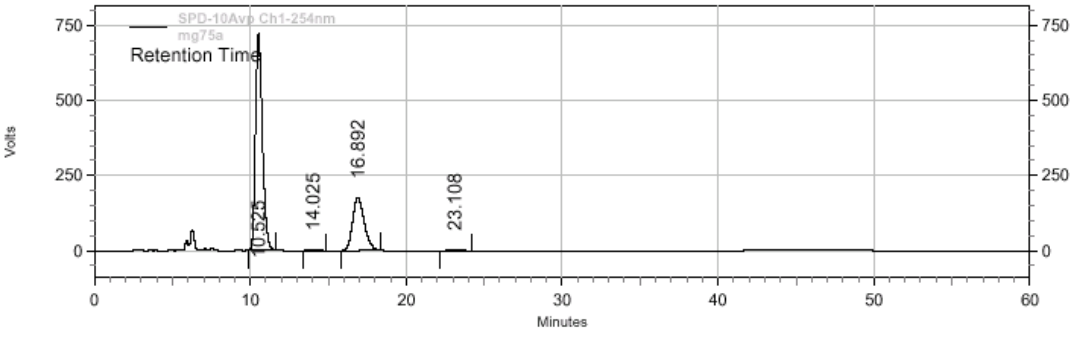


18a

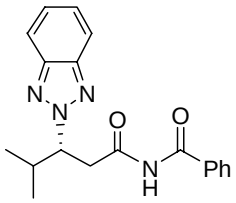
(rt_{major} 16.9 min; rt_{minor} 23.1 min)



Retention Time	Area	Area %	Height	Height %
10.492	6114466	19.23	203906	29.67
13.825	6059343	19.06	149547	21.76
16.700	9834917	30.93	194409	28.29
22.725	9789371	30.79	139284	20.27
Totals	31798097	100.00	687146	100.00

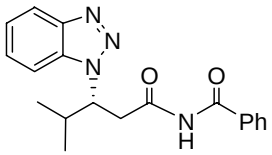


Retention Time	Area	Area %	Height	Height %
10.525	22518917	70.92	721864	80.15
14.025	81466	0.26	2045	0.23
16.892	9066545	28.55	175402	19.47
23.108	85884	0.27	1374	0.15
Totals	31752812	100.00	900685	100.00



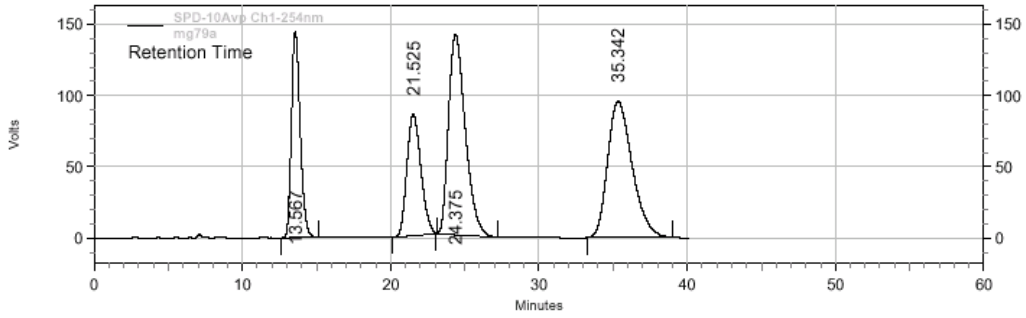
17b

(rt_{major} 13.3 min; rt_{minor} 21.6 min)

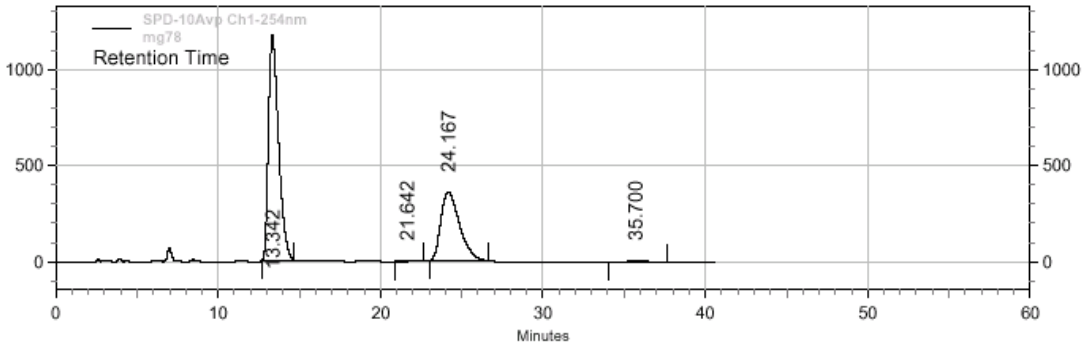


18b

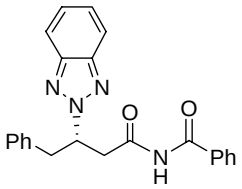
(rt_{major} 24.2 min; rt_{minor} 35.7 min)



Retention Time	Area	Area %	Height	Height %
13.567	5921898	17.62	144543	31.02
21.525	5600635	16.66	85175	18.28
24.375	11076176	32.95	140631	30.18
35.342	11017814	32.77	95626	20.52
Totals	33616523	100.00	465975	100.00

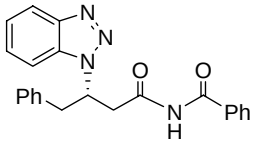


Retention Time	Area	Area %	Height	Height %
13.342	50366111	63.21	1170678	76.28
21.642	125859	0.16	2272	0.15
24.167	29048489	36.45	360442	23.48
35.700	144883	0.18	1389	0.09
Totals	79685342	100.00	1534781	100.00



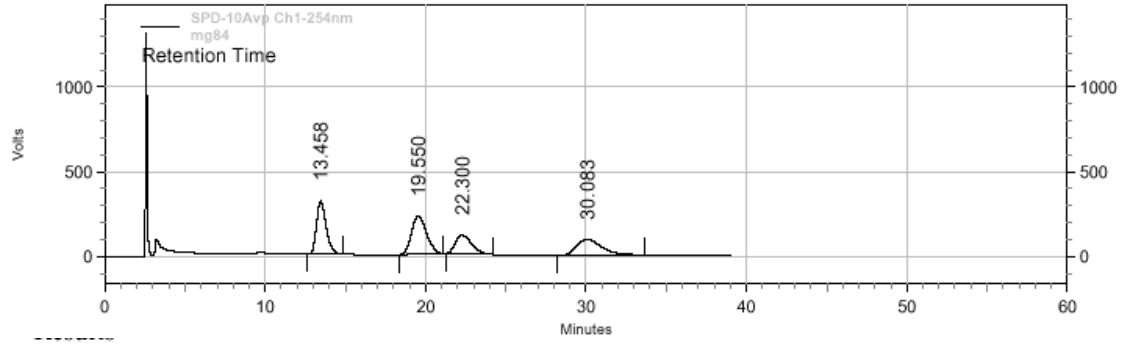
17c

(rt_{major} 13.4 min; rt_{minor} 19.3 min)

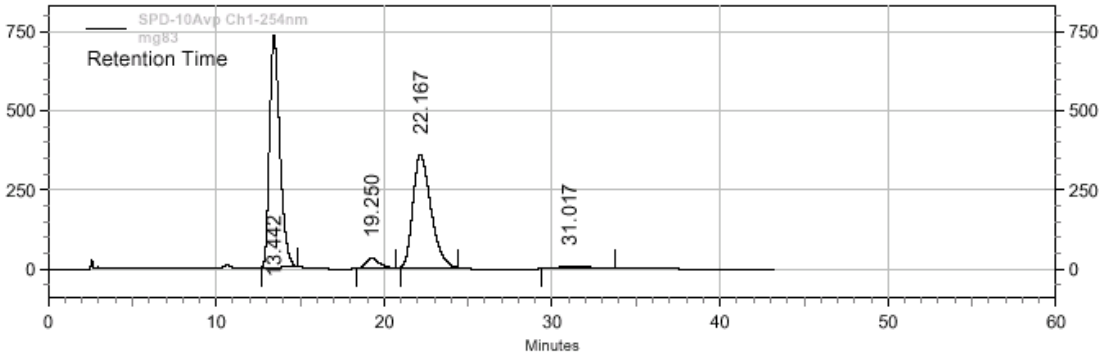


18c

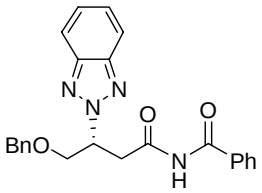
(rt_{major} 22.2 min; rt_{minor} 31.0 min)



Retention Time	Area	Area %	Height	Height %
13.458	12982458	28.33	313546	42.20
19.550	14791810	32.28	225407	30.34
22.300	7818208	17.06	110335	14.85
30.083	10237340	22.34	93706	12.61
Totals	45829816	100.00	742994	100.00

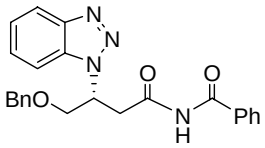


Retention Time	Area	Area %	Height	Height %
13.442	31200671	51.67	731377	64.90
19.250	1826871	3.03	32664	2.90
22.167	26568871	44.00	356437	31.63
31.017	791953	1.31	6375	0.57
Totals	60388366	100.00	1126853	100.00



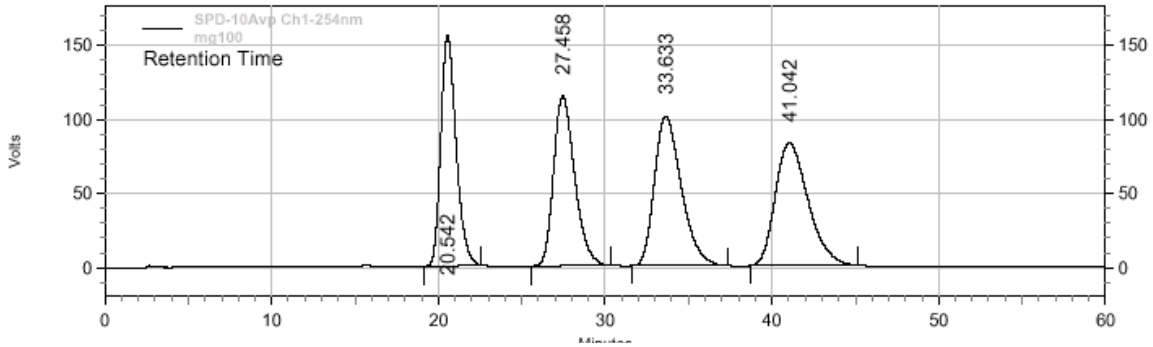
17d

(rt_{major} 20.5 min; rt_{minor} 27.6 min)

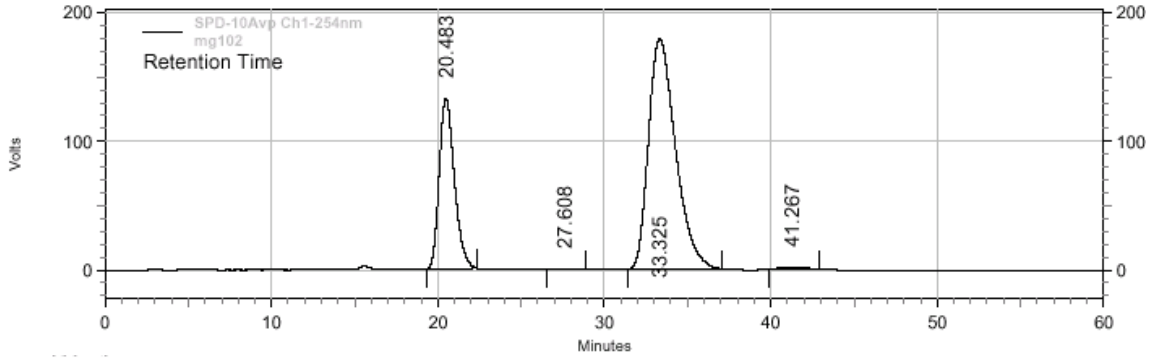


18d

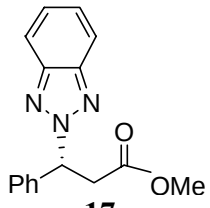
(rt_{major} 33.3 min; rt_{minor} 41.3 min)



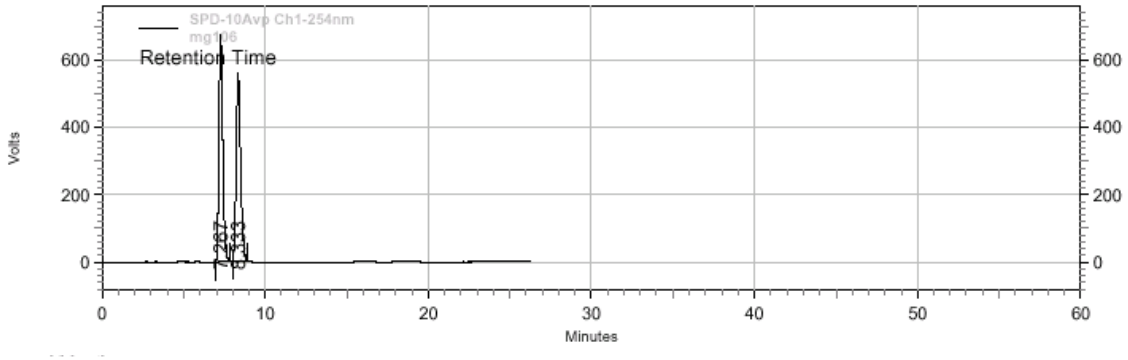
Retention Time	Area	Area %	Height	Height %
20.542	9919407	23.22	155239	34.23
27.458	10054527	23.54	114316	25.20
33.633	11369588	26.62	101016	22.27
41.042	11374163	26.63	83009	18.30
Totals	42717685	100.00	453580	100.00



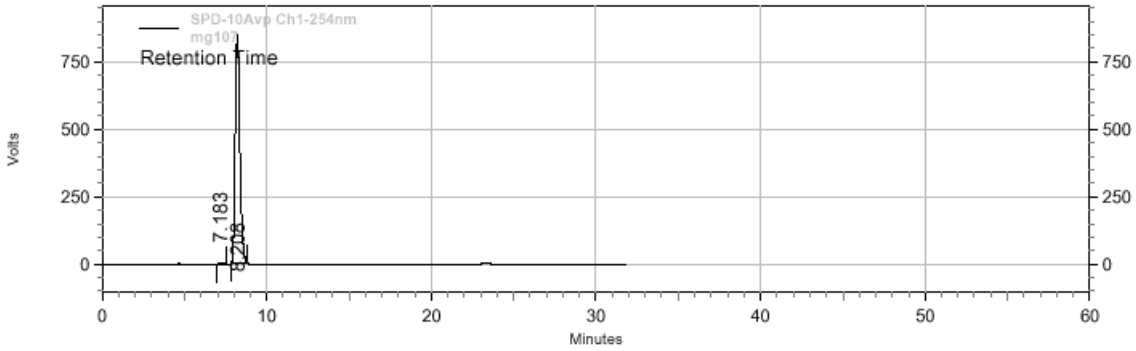
Retention Time	Area	Area %	Height	Height %
20.483	8354979	28.99	132447	42.22
27.608	42898	0.15	598	0.19
33.325	20248079	70.25	178882	57.03
41.267	175348	0.61	1744	0.56
Totals	28821304	100.00	313671	100.00



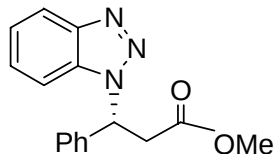
17e



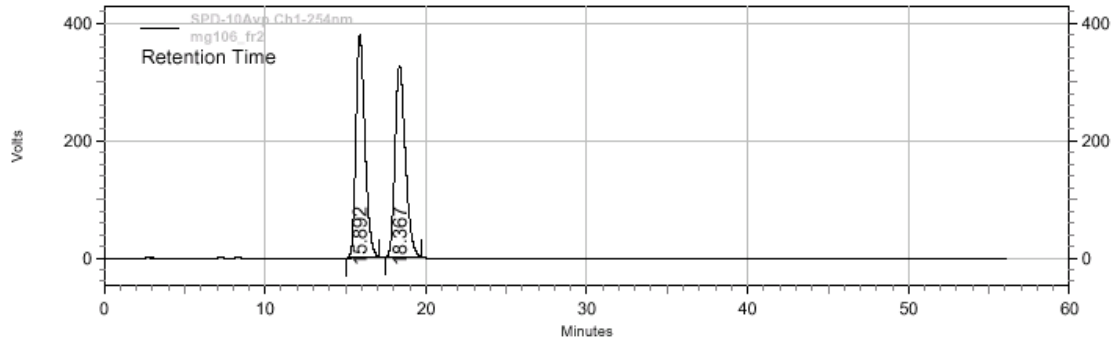
Retention Time	Area	Area %	Height	Height %
7.267	10696684	50.18	673117	54.64
8.333	10618599	49.82	558853	45.36
Totals	21315283	100.00	1231970	100.00



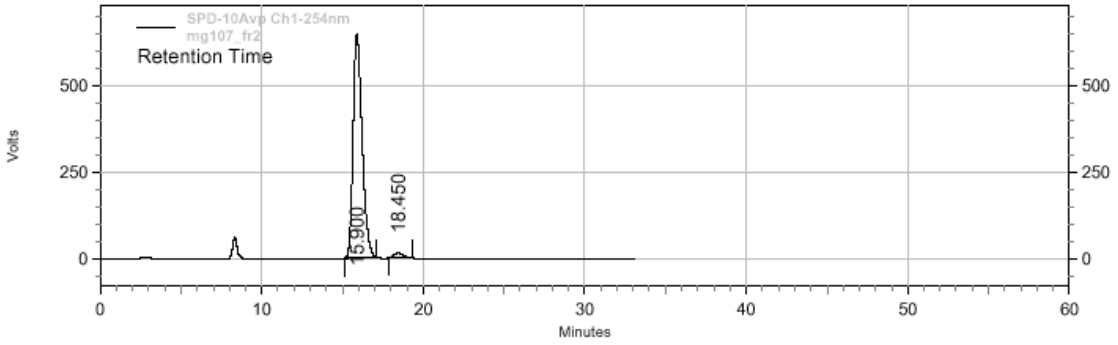
Retention Time	Area	Area %	Height	Height %
7.183	68428	0.41	4599	0.54
8.208	16489548	99.59	845911	99.46
Totals	16557976	100.00	850510	100.00



18e



Retention Time	Area	Area %	Height	Height %
15.892	14840442	50.29	379879	53.68
18.367	14670906	49.71	327769	46.32
Totals	29511348	100.00	707648	100.00



Results

Retention Time	Area	Area %	Height	Height %
15.900	25165924	97.78	646776	97.87
18.450	571957	2.22	14108	2.13
Totals	25737881	100.00	660884	100.00

Results

Retention Time	Area	Area %	Height	Height %
15.900	25165924	97.78	646776	97.87
18.450	571957	2.22	14108	2.13
Totals	25737881	100.00	660884	100.00