Supplementary Materials: Deep Eutectic Mixtures as Reaction Media for the Enantioselective Organocatalyzed α-Amination of 1,3-Dicarbonyl Compounds

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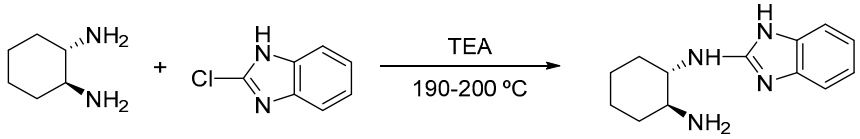
1. General

Unless otherwise noted, all commercial reagents and solvents were used without further purification. Reactions under argon atmosphere were carried out in oven-dried glassware sealed with a rubber septum using anhydrous solvents. Melting points were determined with a hot plate apparatus and are uncorrected. ^{1}H-NMR (300 or 400 MHz) and ^{13}C-NMR (75 or 101 MHz) spectra were obtained on a Bruker AC-300 or AC-400, using $CDCl_3$ as solvent and TMS (0.003%) as reference, unless otherwise stated. Chemical shifts (δ) are reported in ppm values relative to TMS and coupling constants (*J*) in Hz. Low-resolution mass spectra (MS) were recorded in the electron impact mode (EI, 70 eV, He as carrier phase) using an Agilent 5973 Network Mass Selective Detector spectrometer, being the samples introduced through a GC chromatograph Agilent 6890N equipped with a HP-5MS column [(5%-phenyl)-methylpolysiloxane; length 30 m; ID 0.25 mm; film 0.25 mm]. IR spectra were obtained using a JASCO FT/IR 4100 spectrophotometer equipped with an ATR component; wavenumbers are given in cm^{-1}. Analytical TLC was performed on Merck aluminium sheets with silica gel 60 F254. Analytical TLC was visualized with UV light at 254 nm Silica gel 60 (0.04-0.06 mm) was employed for flash chromatography whereas P/UV254 silica gel with $CaSO_4$ (28-32%) supported on glass plates was employed for preparative TLC. Chiral HPLC analyses were performed on an Agilent 1100 Series (Quat Pump G1311A, DAD G1315B detector and automatic injector) equipped with chiral columns using mixtures of

hexane/isopropanol as mobile phase, at 25 ºC.

2. Synthesis and spectroscopic data of chiral organocatalysts

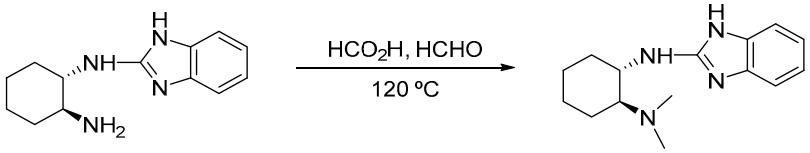
*(1S,2S)-N¹-(1H-benzo[d]imidazol-2-yl)cyclohexane-1,2-diamine (**5**)* [1].



Scheme S1. Synthesis of chiral organocatalyst **5**.

A mixture of 2-chloro-1*H*-benzo[*d*]imidazole (233 mg, 1.53 mmol, 1 equiv), (1*S*,2*S*)-cyclohexane-1,2-diamine (698 mg, 6.12 mmol, 4 equiv), and TEA (213 µL, 1.53 mmol, 1 equiv) was heated at 190-200 ºC during 16 h in a sealed pressure tube. Then, the reaction mixture was allowed to reach ~50 °C, and water (20 mL) was added. The obtained mixture was quickly extracted with CH_2Cl_2 (3 × 20 mL) before the temperature of the reaction reached rt in order to avoid solubility problems. The collected organic phases were dried over $MgSO_4$. After filtration, the organic solvents were evaporated under reduced pressure to give a crude mixture, which was purified by precipitation in CH_2Cl_2 to obtain **5** (229 mg, 65%) as a pale yellow solid: mp 235-240 °C (CH_2Cl_2); IR 2929, 2855, 1700, 1644, 1606, 1580, 1468, 1270, 1116, 1030; δ_H (300 MHz, CD_3OD) 1.19-1.49 (m, 4H, 2×CH_2), 1.74-1.77 (m, 2H, CH_2), 1.98-2.11 (m, 2H, CH_2), 2.50-2.58 (m, 1H, CH, C*H*NH_2), 3.34-3.40 (m, 1H, C*H*NH), 6.93-6.97 (m, 2H, ArH), 7.15-7.18 (m, 2H, ArH); *m/z* 230 [M^+, 10%], 160 (24), 134 (100), 133 (59), 97 (28).

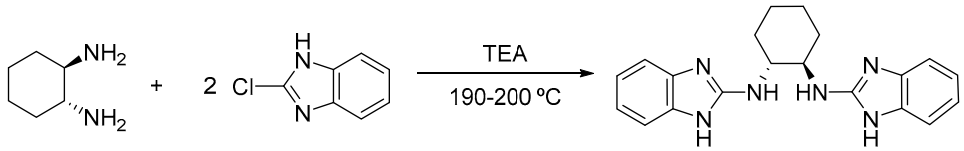
*(1S,2S)-N¹-(1H-benzo[d]imidazol-2-yl)-N²,N²-dimethylcyclohexane-1,2-diamine (**1**)* [1].



Scheme S2. Synthesis of chiral organocatalyst **1**.

A mixture of **5** (168 mg, 0.73 mmol, 1 equiv), 80% HCO_2H (3.5 mL), and a 36% aqueous solution of HCHO (127 µL, 1.61 mmol, 2.2 equiv) was stirred at 120 °C for 16 h. Then, the solvent was removed under reduced pressure. Saturated $NaHCO_3$ solution (15 mL) and 10% NaOH solution (until pH 8) were added in this order, and the resulting mixture was extracted with CH_2Cl_2 (3×15 mL). The organic phases were dried over $MgSO_4$. After filtration, the organic solvent was evaporated under reduced pressure to give a crude mixture, which was purified by precipitation in CH_3CN to afford pure **1** (87 mg, 46%) as a white solid; mp 248-250 °C (CH_3CN); IR 2923, 2856, 2818, 2775, 1700, 1633, 1576, 1499, 1461, 1375, 1265, 1064; δ_H (300 MHz, $CDCl_3$) 1.09-1.42 (m, 4H, 2×CH_2), 1.65-1.70 (m, 1H, CH), 1.82-1.87 (m, 2H, CH_2), 2.22 (s, 6H, CH_3), 2.33 (td, *J* = 10.9, 3.2 Hz, 1H, C*H*$CNMe_2$), 2.65-2.69 (m, 1H, CH), 3.44 (td, *J* = 10.4, 4.0 Hz, 1H, C*H*NH), 5.46 (br. s, 1H, NH), 6.91-6.96 (m, 2H, ArH), 7.14-7.20 (m, 2H, ArH); *m/z* 258 [M^+, 1.5%], 133 (30), 125 (100), 84 (20).

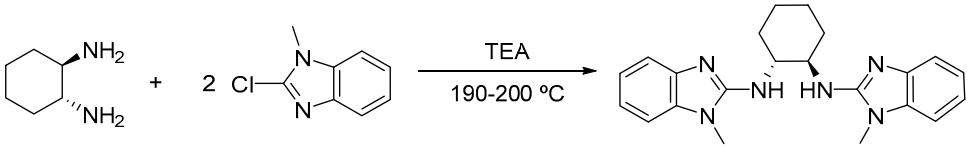
*(1R,2R)-N¹,N²-bis(1H-benzo[d]imidazol-2-yl)cyclohexane-1,2-diamine (**3**)* [2].



Scheme S3. Synthesis of chiral organocatalyst **3**.

2-chloro-1*H*-benzo[*d*]imidazole (2.064 g, 13.56 mmol) was added to (1*R*,2*R*)-cyclohexane-1,2-diamine (773.9 mg, 6.78 mmol) and the resulting mixture was stirred at 195-200 ºC for 20 h. After this time, the reaction mixture was allowed to reach 50 ºC and water (40 mL) was added. Then, the reaction was basified until pH 8 with a saturated aqueous solution of $NaHCO_3$ and the obtained mixture was extracted with CH_2Cl_2 (5×50 mL). The combined organic phases were dried over $MgSO_4$. After filtration, the organic solvent was evaporated under reduced pressure to give the corresponding crude product which was purified by flash chromatography (EtOAc/MeOH) to give pure **3** as a white solid (1.87 g, 40% yield); mp 193-196 ºC (Et_2O); IR 2944, 2916, 2847, 1630, 1603, 1580, 1461,1410, 1259, 1112, 1047; δ_H (300 MHz, CD_3OD,) 1.35-1.47 (m, 4H, 2×CH_2), 1.76 (br. s, 2H, CH_2), 2.18-2.23 (m, 2H, CH_2), 3.71-3.74 (m, 2H, 2×C*H*NH), 6.9-6.95 (m, 4H, ArH), 7.11-7.15 (m, 4H, ArH); *m/z* 346 [M^+, 33%], 214 (64), 213 (100), 212 (36), 184 (16), 173 (19), 172 (15), 170 (10), 160 (14), 159 (21), 158 (11), 146 (11), 145 (16), 134 (32), 133 (37), 132 (16).

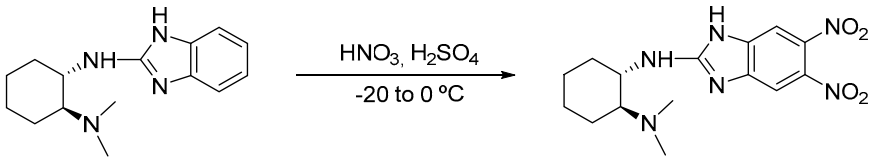
*(1R,2R)-N^1,N^2-bis(1-methyl-1H-benzo[d]imidazol-2-yl)cyclohexane-1,2-diamine (***6***)* [2].



Scheme S4. Synthesis of chiral organocatalyst **6**.

2-chloro-1-methyl-1*H*-benzo[d]imidazole (499.5 mg, 3 mmol) was added to (1*R*,2*R*)-cyclohexane-1,2-diamine (342 mg, 3 mmol) in triethylamine (0.42 mL, 3 mmol) and the resulting mixture was stirred under reflux at 195 ºC for 12 h. After this time, the reaction mixture was allowed to reach 50 ºC and water (40 mL) was added. Then, the reaction was basified until pH 8 with triethylamine and the obtained mixture was extracted with CH_2Cl_2 (2×40 mL). The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. After that, the crude was washed with Et_2O (10 mL) giving the corresponding pure product **6** as a white solid (448 mg, 80% yield); mp 123-124 ºC (EtOAc/Hexane); IR 3283, 2930, 1605, 1563, 1523, 1468, 1265, 1009, 728 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.38 (d, *J* = 7.8, 2H, ArH), 7.06 (dt, *J* = 7.7, 1.1, 2H, ArH), 7.97 (dt, *J* = 7.6, 1.0, 2H, ArH), 6.84 (d, *J* = 7.7, 2H, ArH), 5.49 (brs, 2H×NH), 4.04 (s, 2H, 2×CH), 3.15 (s, 6H, CH_3), 2.32 (d, *J* = 9.1, 2H, CH_2), 1.86 (s, 2H, CH_2), 1.50 (d, *J* = 7.5, 4H, CH_2); δ_C (101 MHz, $CDCl_3$) 155.2 (C=N), 141.7, 134.8 , 121.2, 119.4, 115.6, 107.1 (ArC), 58.8 (CHNH), 33.5 (CH_2), 28.1 (CH_3), 25.1 (CH_2); 374.2 (M^+, 24.5%), 228 (42), 227 (100), 226 (25), 187 (23), 186 (15), 174 (12), 173 (18), 160 (11), 159 (18), 148 (36), 147 (25), 146 (289, 132 (15), 131 (17).

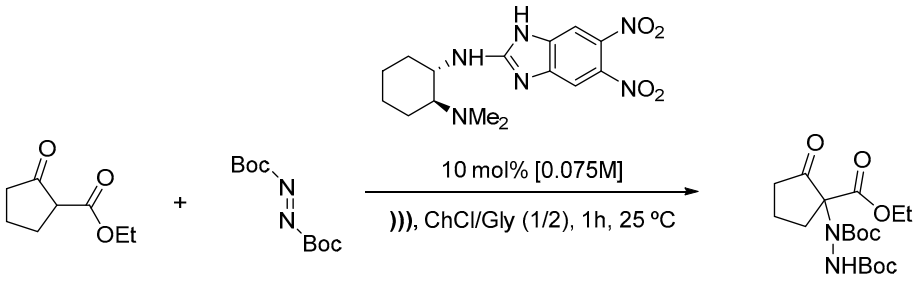
*(1S,2S)-N^1-(5,6-dinitro-1H-benzo[d]imidazol-2-yl)-N^2,N^2-dimethylcyclohexane-1,2-diamine (**2**)* [3].



Scheme S5. Synthesis of chiral organocatalyst **2**.

Catalyst **1** (50 mg, 0,2 mmol, 1 equiv.) was dissolved in concentrated H_2SO_4 (0.2 mL, 98%) and stirred vigorously for 5 minutes; after this time concentrated HNO_3 (0.4 mL, 65%) was carefully added to the mixture at -20 °C. Then, the reaction was stirred at room temperature during 16 hours. After this period, the mixture was treated with cold water and basified until pH 8 with a 25% aqueous solution of NH_3. Finally, the aqueous phase was extracted with AcOEt (3×20 mL). The collected organic phases were dried over anhydrous $MgSO_4$. After filtration, the organic solvent was removed under reduced pressure to give catalyst **2** without further purification as a red solid (74% yield, 52 mg, 0,15 mmol) ; mp 110-115 ºC (CH_2Cl_2, decompose); δ_H (300 MHz, $CDCl_3$) 1.19-1.49 (m, 4H, 2×CH_2), 1.63-1.98 (m, 4H, 2×CH_2), 2.37 (s, 6H, 2×Me), 2.51 (m, 1H, C*H*NMe_2), 3.66 (bs, 1H, C*H*NH),7.49 (s, 2H, ArH); δ_C (75 MHz, $CDCl_3$) 21.7, 24.4, 24.6, 33.2, 39.8, 53.8, 67.8, 108.3, 136.8, 142.0, 161.8; *m/z* 348 [M^+, <1%] 128 (10), 126 (11), 125 (100), 124 (25), 84 (64), 71 (24), 58 (20), 44 (10).

3. Typical experimental procedure for the amination reaction



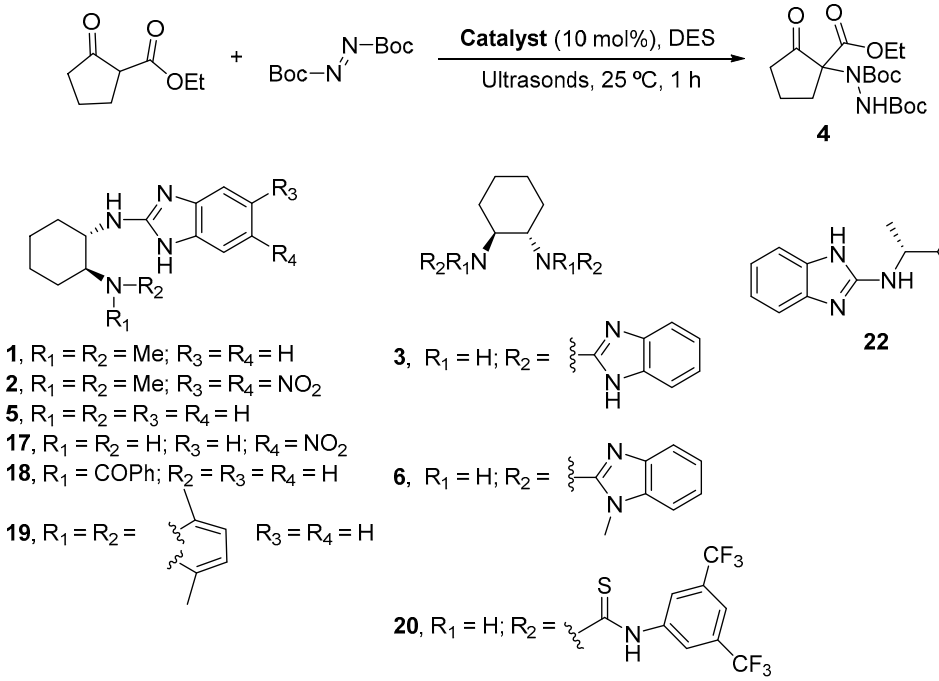
Catalyst **2** (5.22 mg, 0.015 mmol, 10 mol%) and ethyl 2-oxocyclopentane-1-carboxylate (23.4 mg, 0.15 mmol) were dissolved in a mixture of ChCl/Gly (1/2 molar ratio, 0.2 mL) and kept under stirring for 10 minutes at rt. Then, di-*tert*-butylazodicarboxylate (36.8 mg, 0.16 mmol) was added. The reaction was vigorously stirred under ultrasound irradiation for 1 hour. After this period, water (3 mL) was added to the mixture and the reaction product was extracted with EtOAc (3×5 mL). The collected organic phases were dried over anhydrous $MgSO_4$ and, after filtration, the solvent was evaporated under reduced pressure to give crude **4**. Purification by flash column chromatography on silica gel (hexane/EtOAc: 7/3) afforded pure **4** (45.1 mg, 78% yield). δ_H (300 MHz, $CDCl_3$) 1.28 (t, J = 7.1 Hz, 3H), 1.59 – 1.36 (m, 18H), 2.98 – 1.75 (m, 6H), 4.24 (m, 2H), 6.53 (br s, 1H) ppm). The enantiomeric excess of **4** was determined by chiral HPLC analysis (Chiralpack IA, hexane/EtOH: 96/04, 0.7 mL/min).

4. Recycling experiment

A mixture of catalyst **2** (5.22 mg, 0.015 mmol, 10 mol%) and ethyl 2-oxocyclopentane-1-carboxylate (23.4 mg, 0.15 mmol) in ChCl/Gly (1/2 molar ratio, 0.2 mL) was stirred for 10 minutes at rt. Then, di-*tert*-butylazodicarboxylate (36.8 mg, 0.16 mmol) was added. The reaction was vigorously stirred under ultrasound irradiation for 1 hour. After this period, the corresponding organic solvent was added (3 mL) and the mixture was stirred for 10 minutes at rt. The stirring was stopped to allow phase separation and the upper organic layer was

removed. This extractive procedure was repeated two more times and the combined organic extracts were washed with water (3×5 mL), dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Then, the next reaction cycle was performed with the obtained DES/**2** mixture, adding fresh ethyl 2-oxocyclopentane-1-carboxylate and di-*tert*-butylazodicarboxylate. This reaction mixture was subjected again to the above-described procedure and further reaction cycles were repeated using the recycled deep eutectic solvent phase.

5. Asymmetric α-amination of ethyl 2-oxocyclopentane-1-carboxylate with DBAB. Catalyst study.

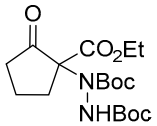


Entry	**Catalyst**	DES	Conversion (%)[1]	Ee (%)[2]
1	**1**	ChCl/Urea: 1/2	92	76
2	**1**	ChCl/Glycerol: 1/2	80	80
3	**2**	ChCl/Urea: 1/2	85	**84**
4	**2**	ChCl/Glycerol: 1/2	90	**82**
5	**5**	ChCl/Urea: 1/2	95	74
6	**5**	ChCl/Glycerol: 1/2	70	78
7	**3**	ChCl/Urea: 1/2	90	40
8	**3**	ChCl/Glycerol: 1/2	95	44
9	**6**	ChCl/Urea: 1/2	92	40
10	**6**	ChCl/Glycerol: 1/2	91	33
11	**17**	ChCl/Urea: 1/2	25	0
12	**17**	ChCl/Glycerol: 1/2	30	0
13	**18**	ChCl/Urea: 1/2	85	10
14	**18**	ChCl/Glycerol: 1/2	95	6
15	**19**	ChCl/Urea: 1/2	95	33
16	**19**	ChCl/Glycerol: 1/2	95	20
17	**20**	ChCl/Urea: 1/2	85	46
18	**20**	ChCl/Glycerol: 1/2	90	43
19	**21**	ChCl/Urea: 1/2	90	0

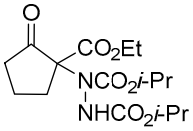
20	**21**	ChCl/Glycerol: 1/2	95	0
21	**22**	ChCl/Urea: 1/2	90	0
22	**22**	ChCl/Glycerol: 1/2	90	5

[1] Reaction conversion towards **4** determined by GC analysis. [2] Enantiomeric excess determined by chiral HPLC analysis.

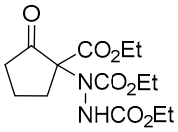
6. Physical and spectroscopic data for compounds 4, 7-16



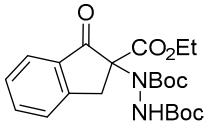
(*R*)-Di-*tert*-butyl 1-[1-(ethoxycarbonyl)-2-oxocyclopentyl]hydrazine-1,2-dicarboxylate (**4**) [4]: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.27 – 1.32 (t, *J* = 7.0 Hz, 3H), 1.45 – 1.47 (m, 18H), 1.95 – 2.64 (m, 6H), 4.25 (m, 2H), 6.28 – 6.56 (br s, 1H) ppm.



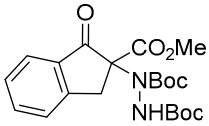
(*R*)-Diisopropyl 1-[1-(ethoxycarbonyl)-2-oxocyclopentyl]hydrazine-1,2-dicarboxylate (**7**) [5]: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.24 – 1.29 (m, 15H), 1.69 – 2.68 (m, 6H), 4.21 – 4.24 (m, 2H) 4.93 – 4.99 (m, 2H), 6.35 – 6.66 (br, 1H) ppm.



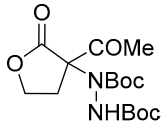
(*R*)-Diethyl 1-[1-(ethoxycarbonyl)-2-oxocyclopentyl]hydrazine-1,2-dicarboxylate (**8**) [5]: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.24 – 1.31 (m, 9H), 2.01 – 2.68 (m, 6H), 4.18 – 4.26 (m, 6H), 6.46 – 6.77 (br, 1H) ppm.



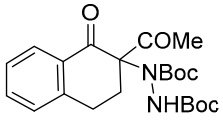
(*R*)-Di-*tert*-butyl 1-[2-(ethoxycarbonyl)-1-oxo-2,3-dihydro-1H-inden-2-yl]hydrazine-1,2-dicarboxylate (**10**) [6]: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.17 – 1.49 (m, 21H), 3.83 (d, *J* = 20.4 Hz, 1H), 4.25 (m, 3H), 6.37 – 6.74 (bs, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.78 (d, *J* = 9.9 Hz, 1H) ppm.



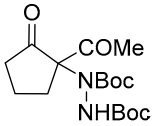
(*R*)-Di-*tert*-butyl 1-[2-(methoxycarbonyl)-1-oxo-2,3-dihydro-1H-inden-2-yl]hydrazine-1,2-dicarboxylate (**11**) [4]: Slightly yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.27 – 1.55 (m, 18H), 3.78 – 4.26 (m, 5H), 6.41 – 6.72 (m, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H) ppm.



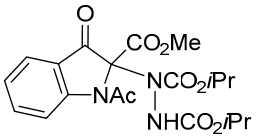
(*R*)-Di-*tert*-butyl 1-(3-acetyl-2-oxotetrahydrofuran-3-yl)hydrazine-1,2-dicarboxylate (**12**) [4]: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.47 (d, *J* = 2.0 Hz, 18H), 2.36 (m, 3H), 2.80 (bs, 1H), 3.2 (d, *J* = 43.5 Hz, 1H), 4.39 (bs, 2H) 6.57 (d, *J* = 159.6 Hz, 1H) ppm.



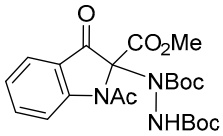
(*R*)-Di-tert-butyl 1-(2-acetyl-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazine-1,2-dicarboxylate (**13**) [4]: Brown oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.46 – 1.54 (m, 18H), 2.42 (m, 3H), 2.71 (br s, 2H), 2.92 – 3.04 (m, 2H), 6.21 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H) ppm.



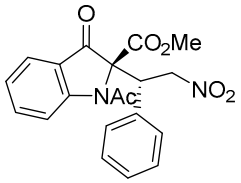
(*R*)-Di-*tert*-butyl 1-(1-acetyl-2-oxocyclopentyl)hydrazine-1,2-dicarboxylate (**14**) [4]: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.47 (d, *J* = 7.0 Hz, 18H), 1.56 – 2.09 (m, 3H), 2.20 – 2.51 (m, 5H), 2.51 – 2.84 (m, 1H), 6.24 – 6.48 (br s, 1H) ppm.



(*R*)-Diisopropyl 1-(1-acetyl-2-(methoxycarbonyl)-3-oxoindolin-2-yl)hydrazine-1,2-dicarboxylate (**15a**) [7]: Semi solid; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.10 – 1.42 (m, 12H), 2.51 (s, 1H) 2.61 (d, *J* = 5.3 Hz, 2H), 3.63 – 3.83 (m, 3H), 4.81 – 5.16 (m, 2H), 7.22 – 7.24 (m, 1H), 7.52 – 7.72 (m, 2H), 7.83 (d, *J* = 7.3 Hz, 1H) ppm.

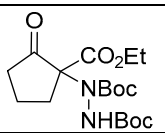


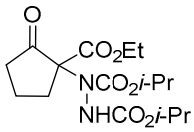
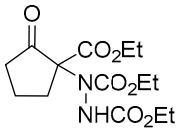
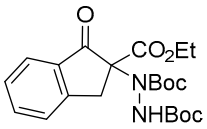
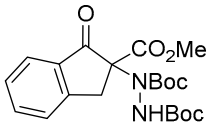
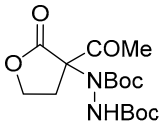
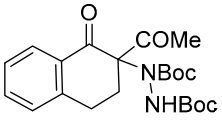
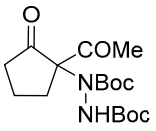
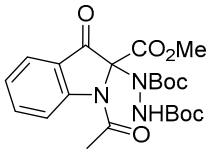
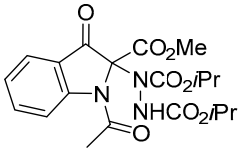
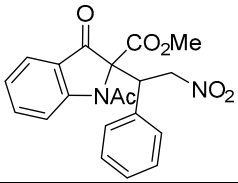
(*R*)-Di-*tert*-butyl1-(1-acetyl-2-(methoxycarbonyl)-3-oxoindolin-2-yl)hydrazine-1,2-dicarboxylate (**15b**) [7]: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H = 1.03 – 1.76 (m, 18H), 2.37 – 2.70 (m, 3H), 3.75 (d, *J* = 18.3 Hz, 3H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H) ppm.



(*S*)-Methyl 1-acetyl-2-((*S*)-2-nitro-1-phenylethyl)-3-oxoindoline-2-carboxylate (**16**) [8]: ^{1}H-NMR (300 MHz, $CDCl_3$): Colourless oil; δ_H = 2.30 (s, 3H), 3.73 (s, 3H), 5.06 (d, *J* = 10.9 Hz, 2H), 5.90 (m, 1H), 6.89 (d, *J* = 6.8 Hz, 2H) 6.95 − 7.10 (m, 4H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H).

7. Table S1. HPLC conditions and retention times for compounds

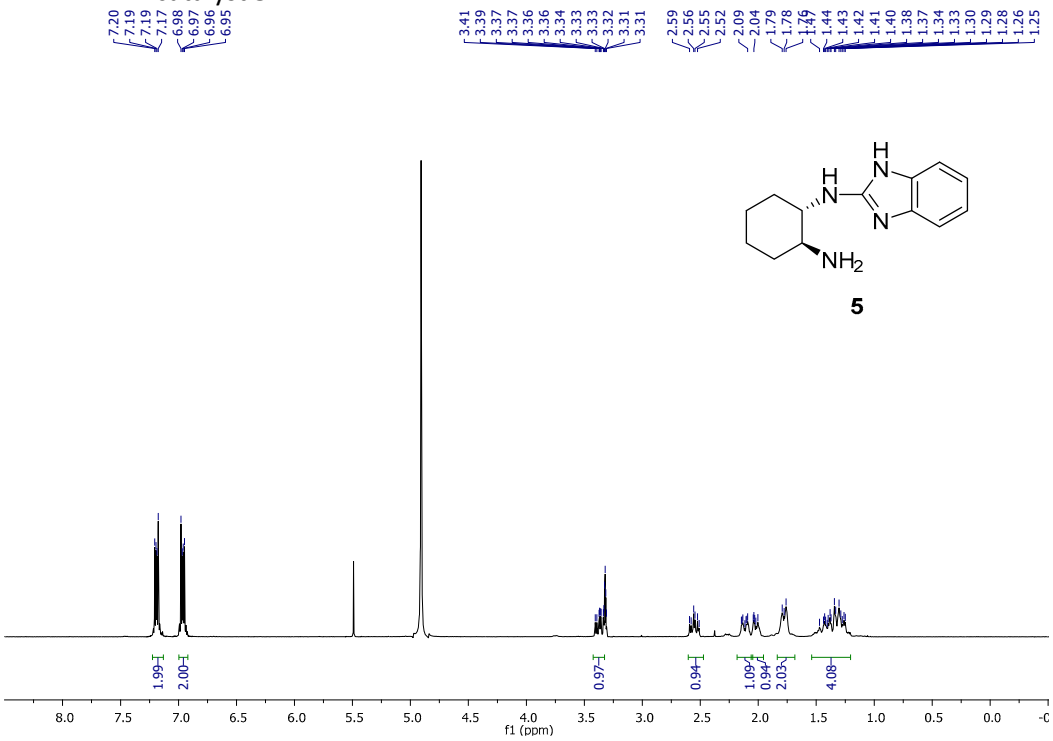
	Structure	Column λ (nm)	Eluent flow rate (mL/min)	t_R (min)
4		Chiralpak IA 230 nm	Hx/EtOH 96/04 1 mL/min	**10.3** (major enantiomer) 12.0

7		Chiralpak AD-H 210 nm	Hx/*i*-PrOH 90/10 1 mL/min	**19.2** (major enantiomer) 21.5
8		Chiralpak AD-H 230 nm	Hx/*i*-PrOH 95/5 1 mL/min	**6.9** (major enantiomer) 8.7
10		Chiralpak IA 240 nm	Hx/*i*-PrOH 90/10 1 mL/min	**11.4** (major enantiomer) 13.5
11		Chiralpak IA 240 nm	Hx/i-PrOH 90/10 1 mL/min	**15.9** (major enantiomer) 22.2
12		Chiralpak IA 254	Hx/EtOH 98/02 1 mL/min	**20.1** (major enantiomer) 25.5
13		Chiralpak IA 210 nm	Hx/i-PrOH 90/10 1 mL/min	22.9 **26.7** (major enantiomer)
14		Chiralpak IA 240 nm	Hx/EtOH 98/02 1 mL/min	**21.6** (major enantiomer) 36.5
15a		Chiralpak IA 240 nm	Hx/i-PrOH 90/10 1 mL/min	19.3 **24.6** (major enantiomer)
15b		Chiralpak IA 230 nm	Hx/i-PrOH 80/20 1 mL/min	12.5 **15.3** (major enantiomer)
16		Chiralpak OD-H 240 nm	Hx/i-PrOH 70/30 1 mL/min	**8.0** (major enantiomer) 10.0

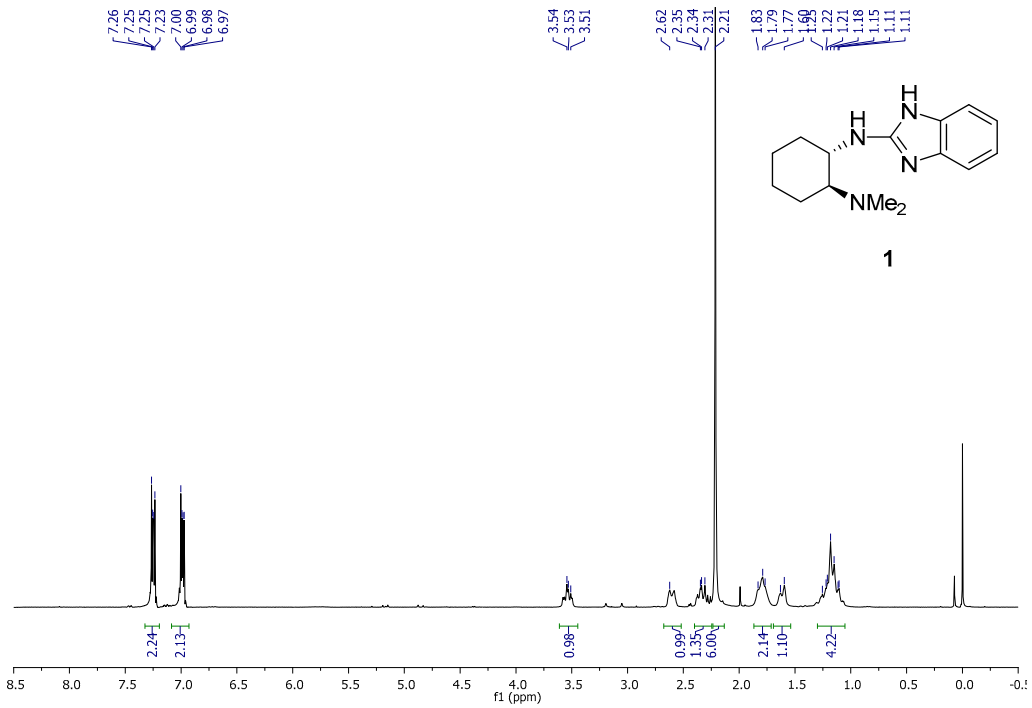
8. NMR spectra

Catalysts

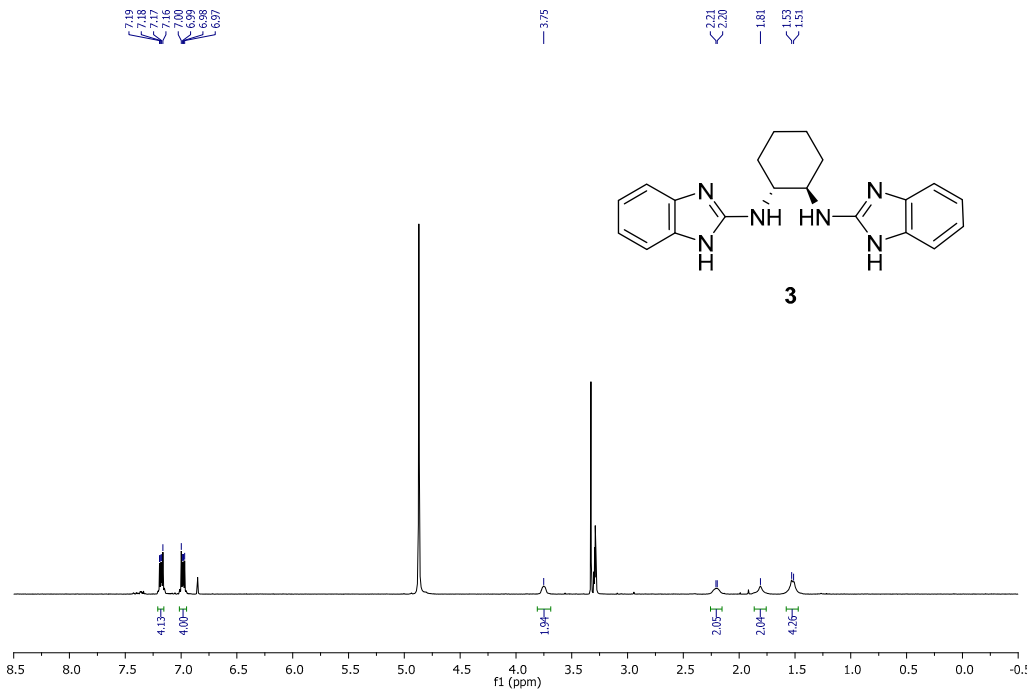
^{1}H-NMR catalyst **5**



^{1}H-NMR catalyst **1**

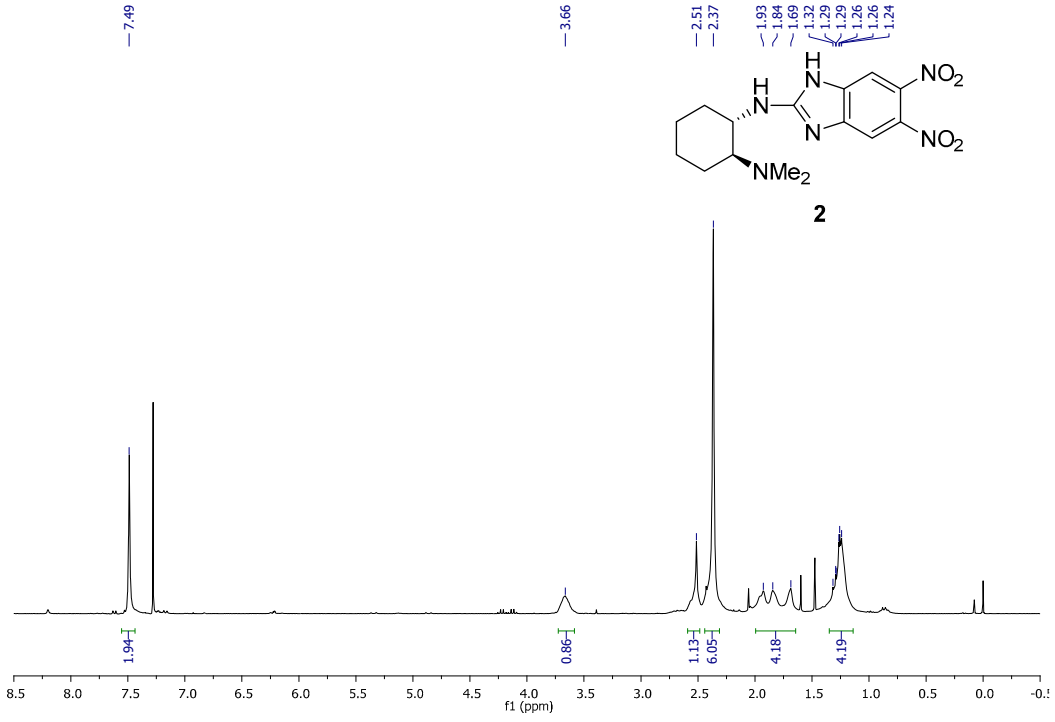


^{1}H-NMR catalyst **3**



3

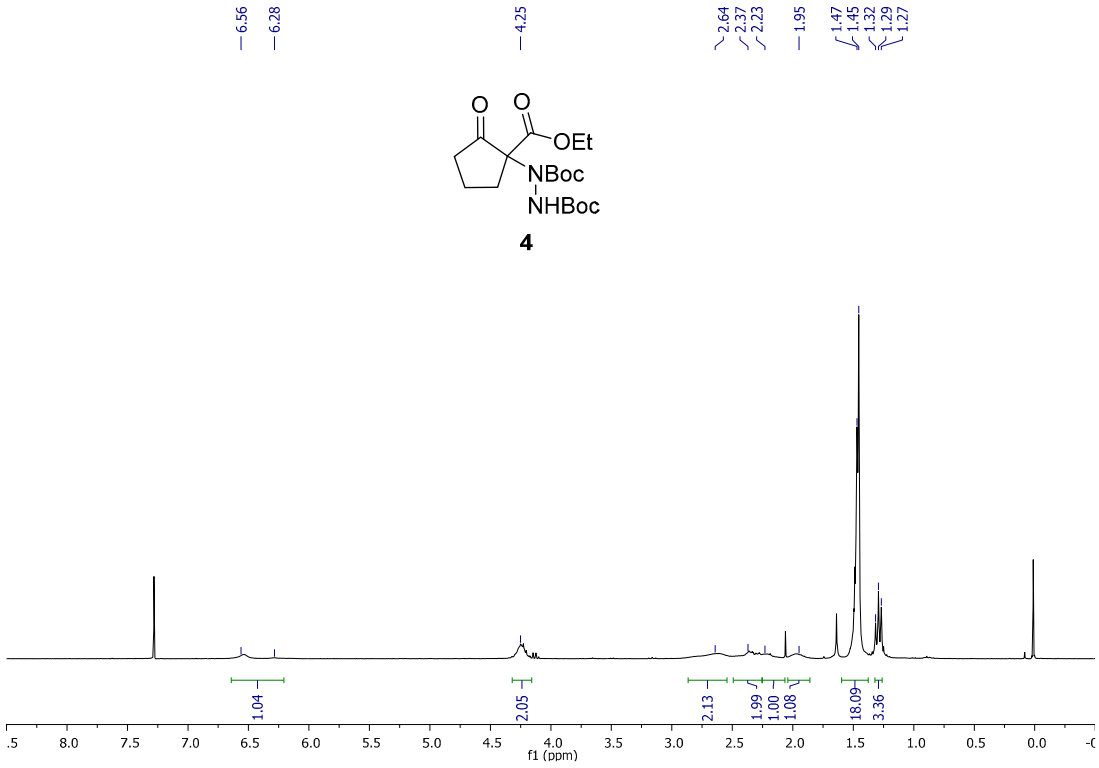
^{1}H-NMR catalyst **2**



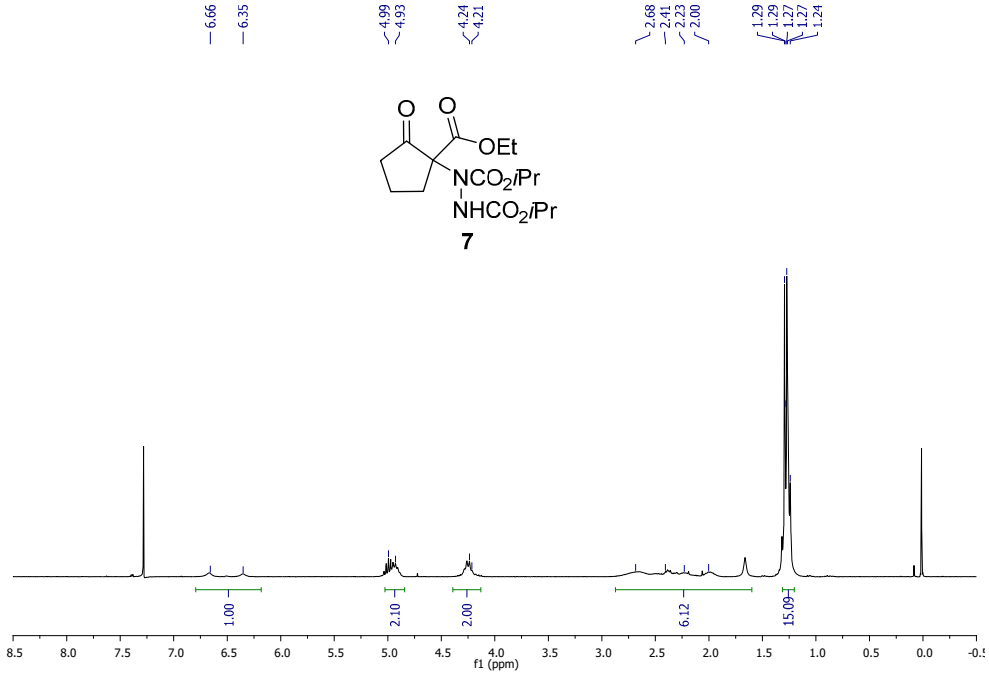
2

Products 4 - 16

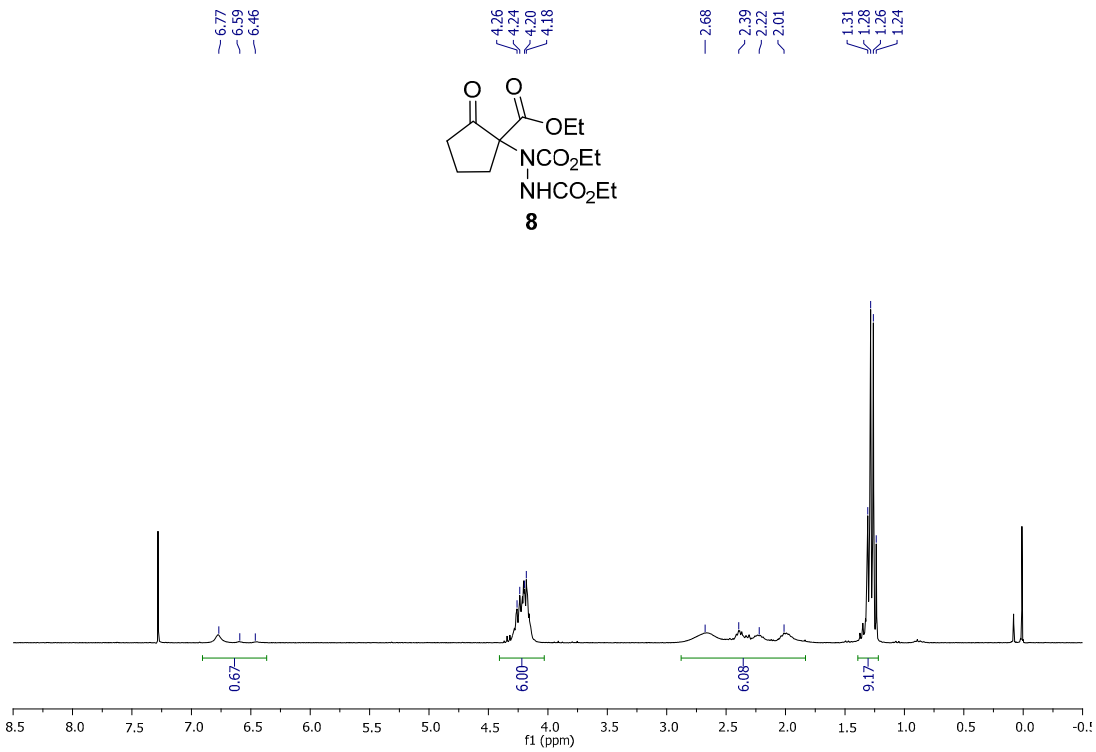
^{1}H-NMR product **4**



^{1}H-NMR product **7**

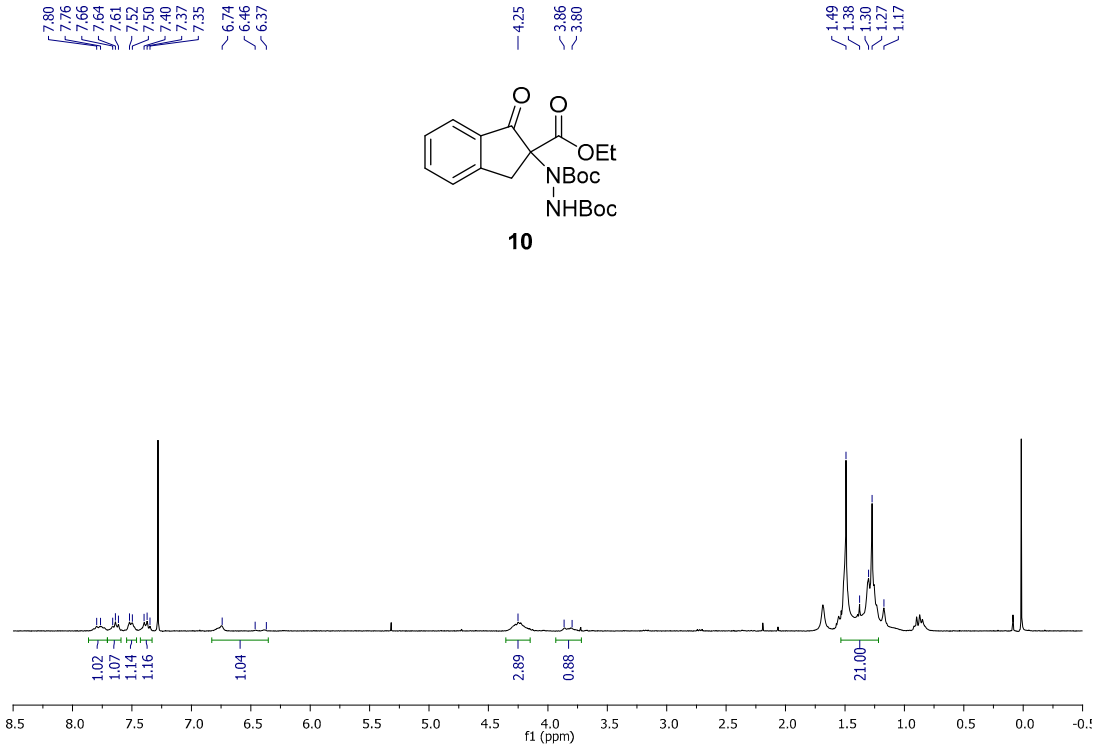


^{1}H-NMR product **7**



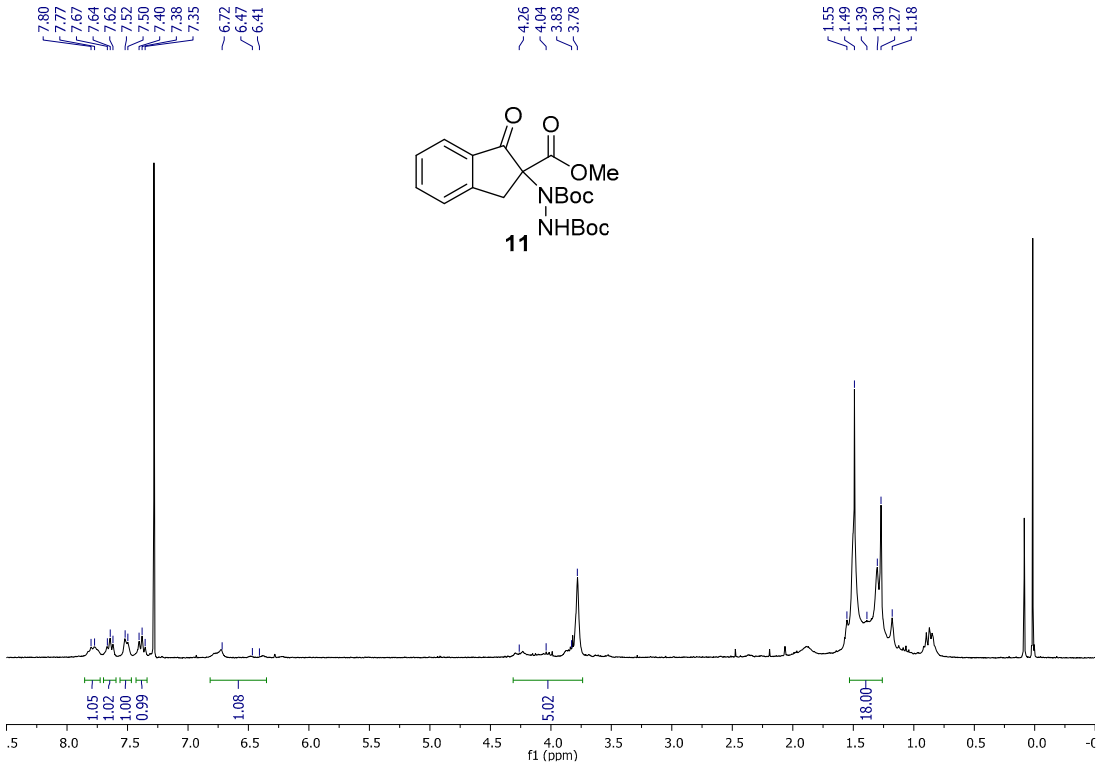
8

^{1}H-NMR product **10**

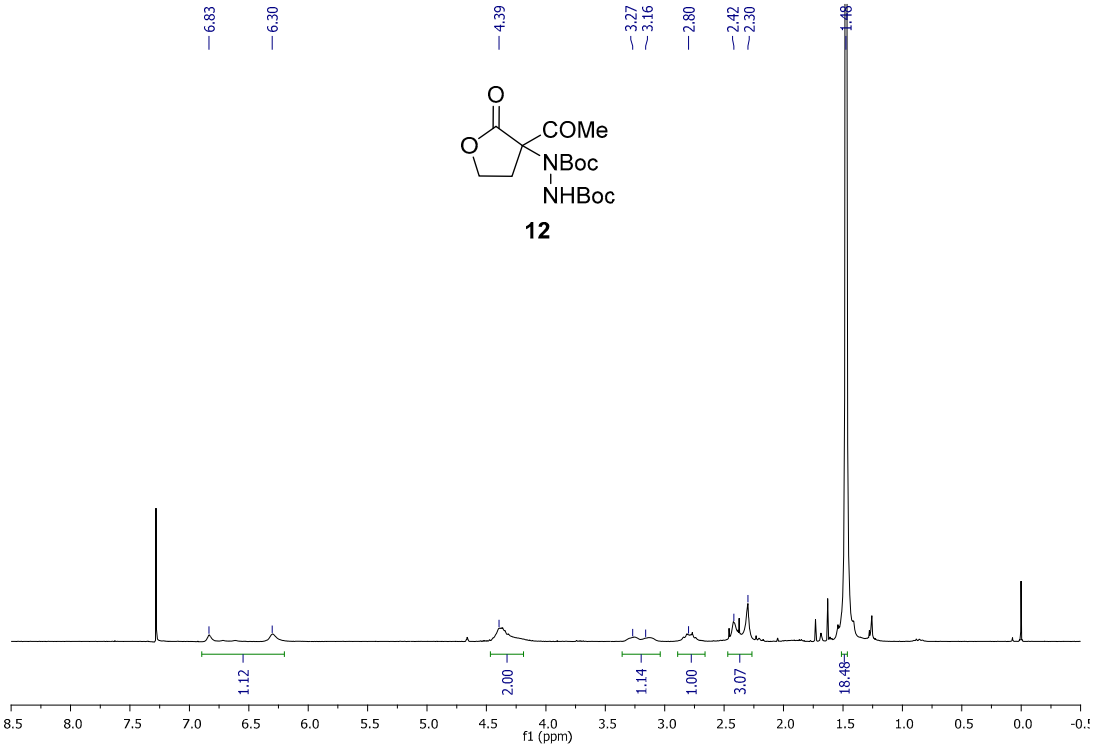


10

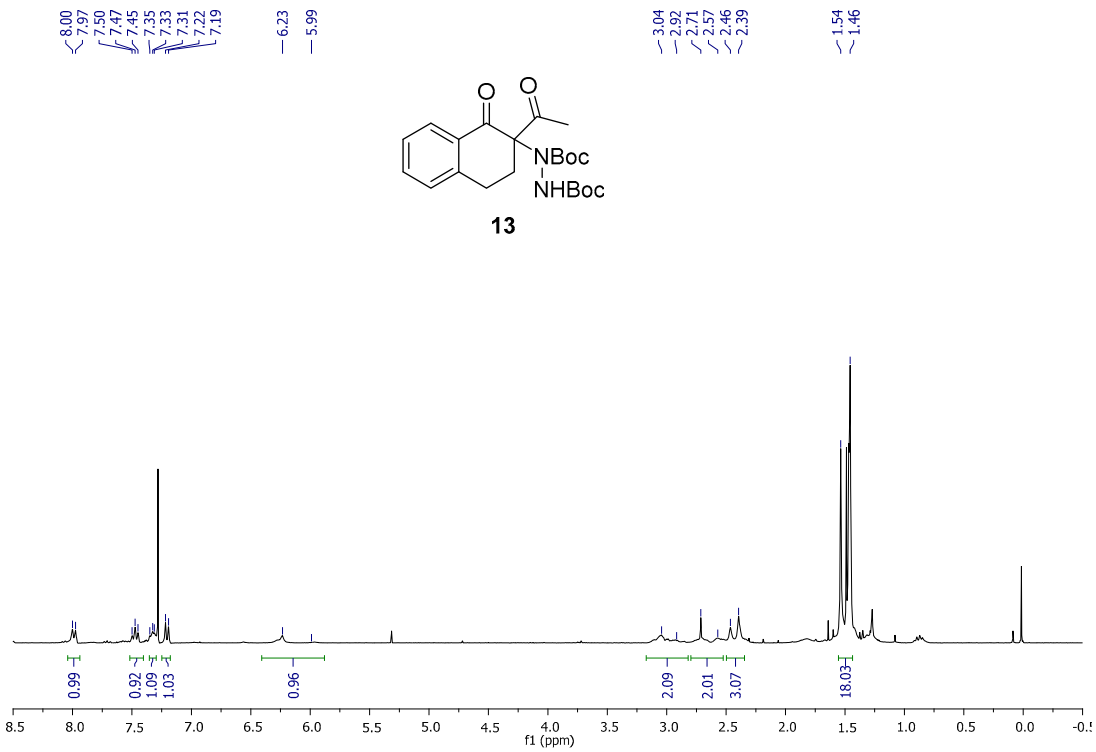
^{1}H-NMR product **11**



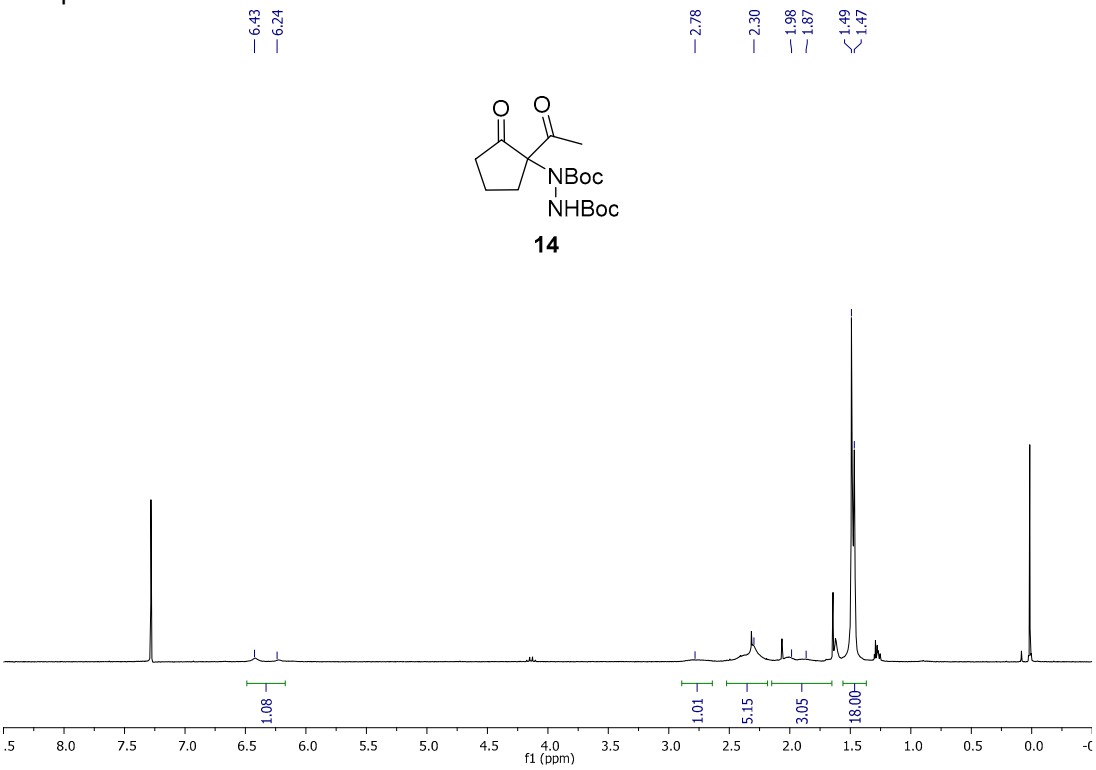
^{1}H-NMR product **12**



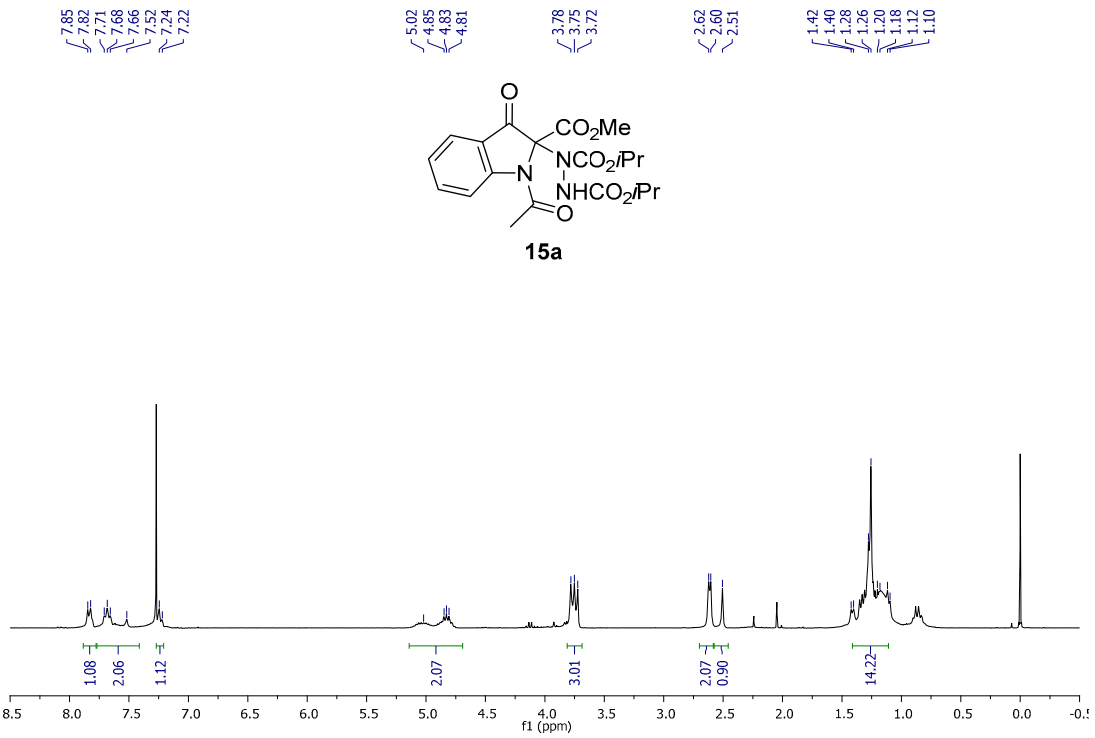
^{1}H-NMR product **13**



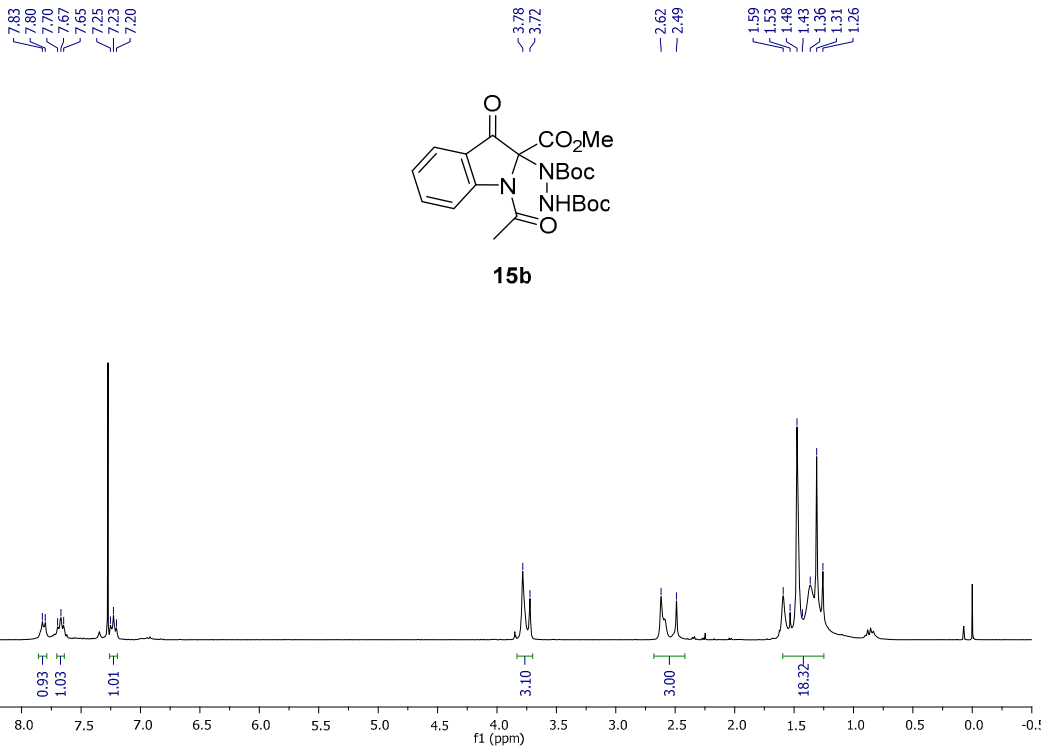
^{1}H-NMR product **14**



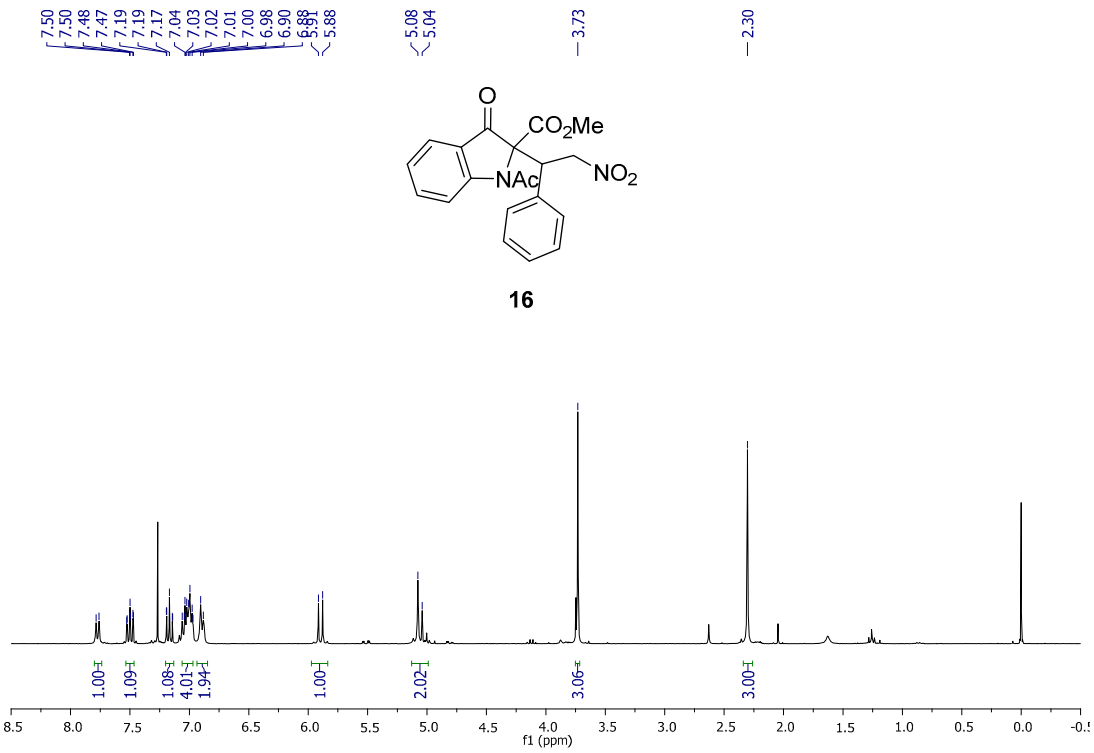
^{1}H-NMR product **15a**



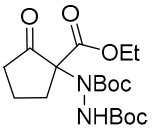
^{1}H-NMR product **15b**

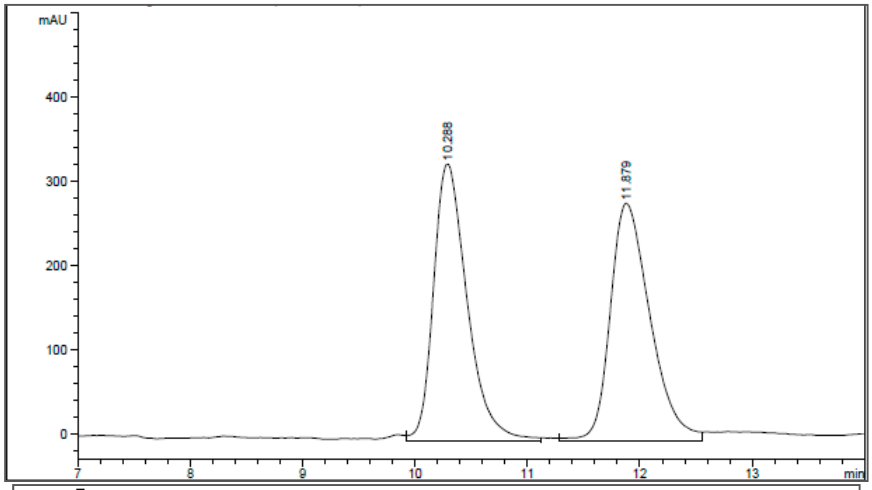


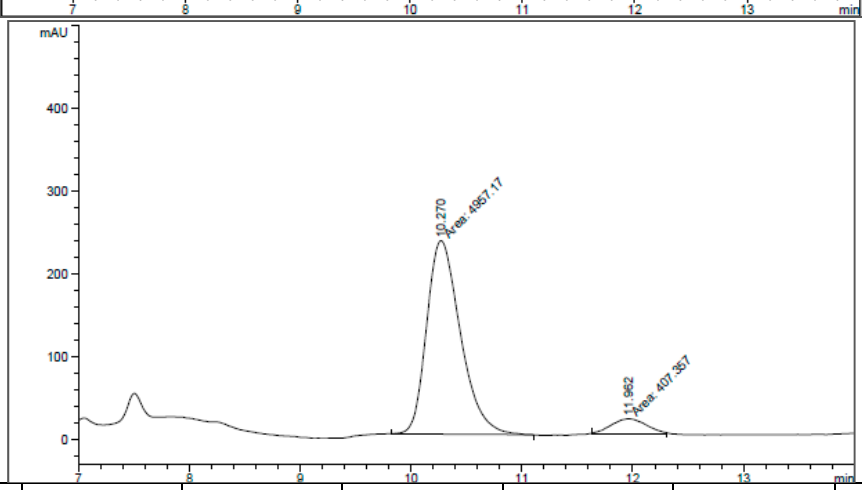
^{1}H-NMR product **16**



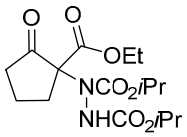
9. HPLC spectra for compounds 4, 7-16.



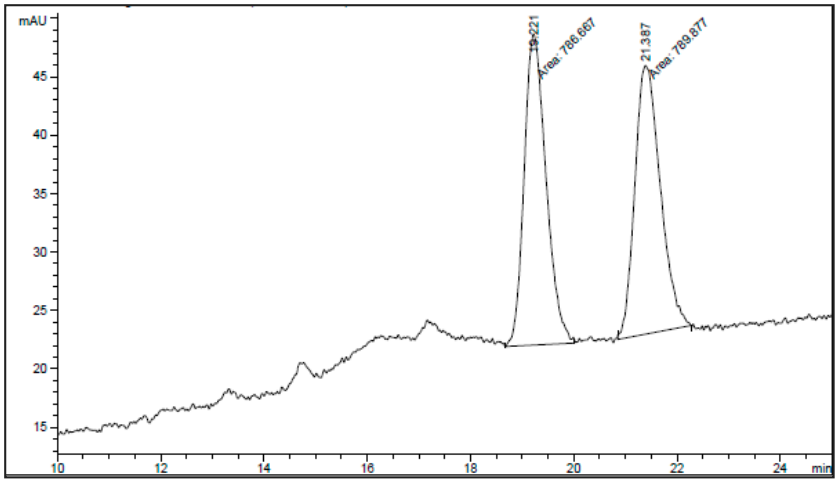


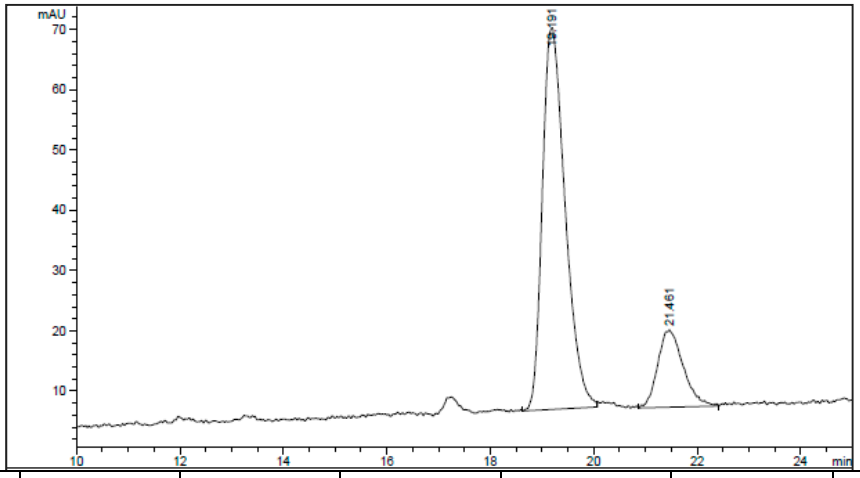


Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.27	MM	0.35	4957.16	233.95	92.40
2	11.96	MM	0.37	407.35	18.30	7.59

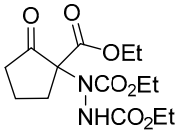


7

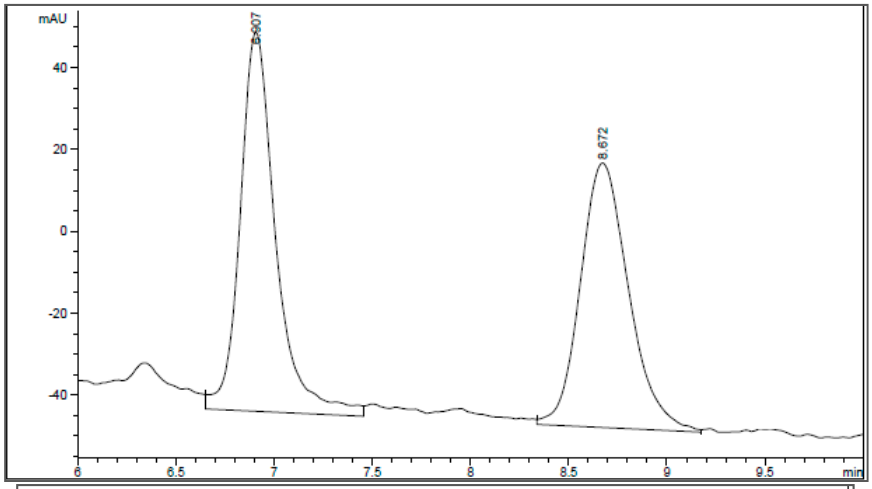


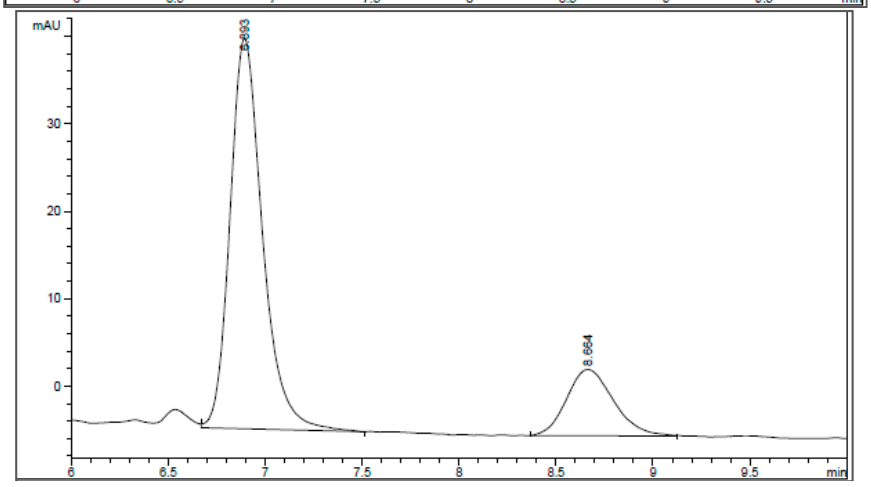


Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.19	VB	0.46	1943.16	63.38	81.4862
2	21.46	VV	0.41	441.48	12.84	18.5138

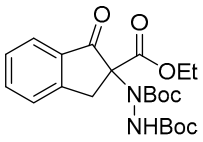


8





Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.89	VP	0.17	521.58	4.463.124	80.28
2	8.66	PB	0.24	128.09	759.861	19.71



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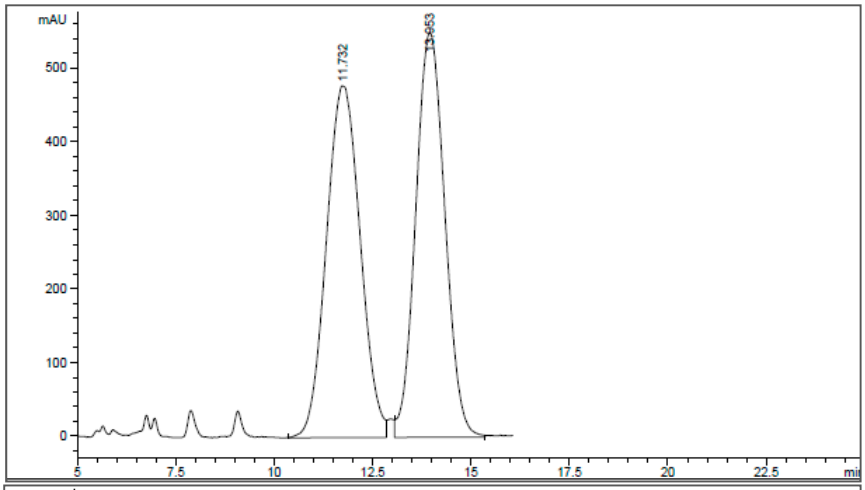
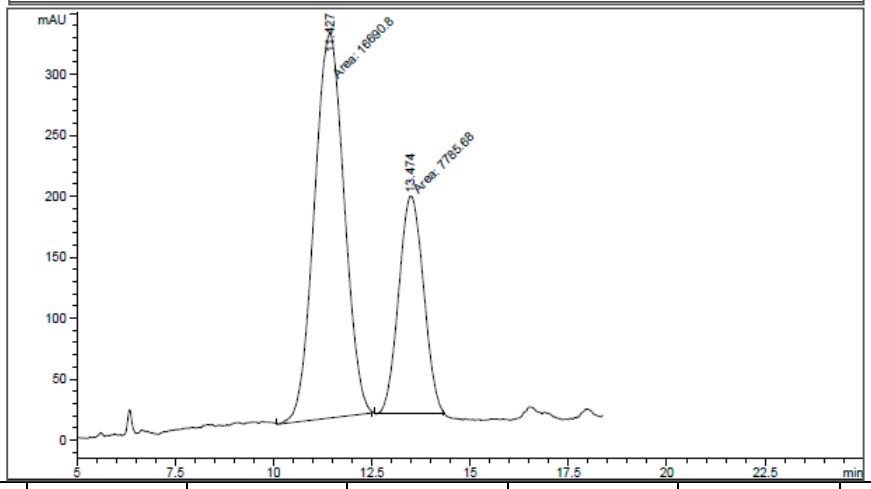
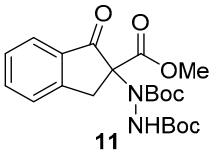
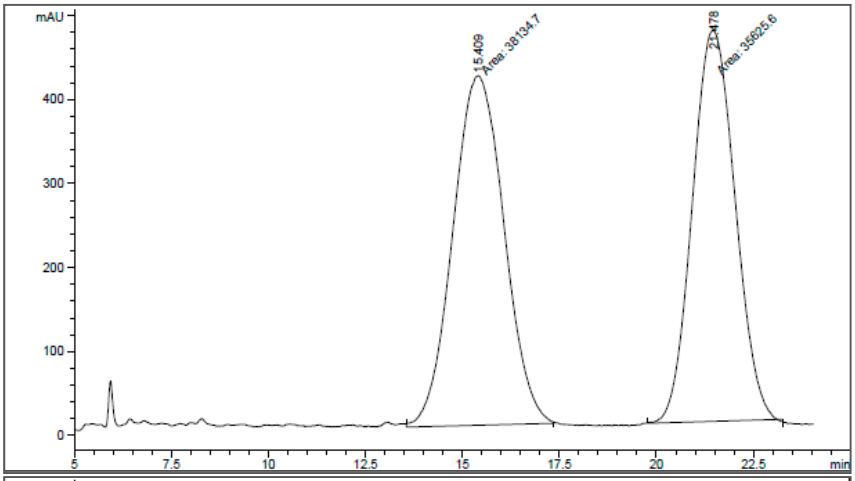


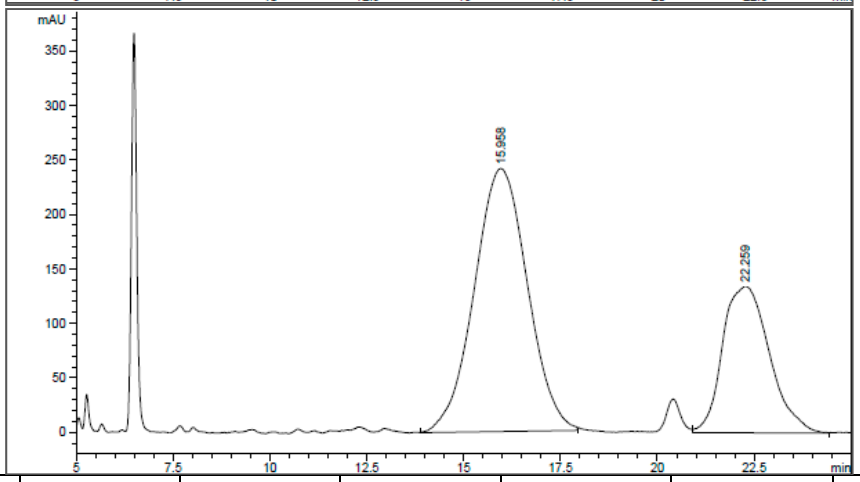


Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.4	MM	0.88	1.67e09	315.69	68.19
2	13.5	MM	0.72	7.78e09	178.05	31.80

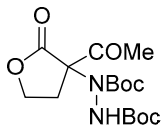


11

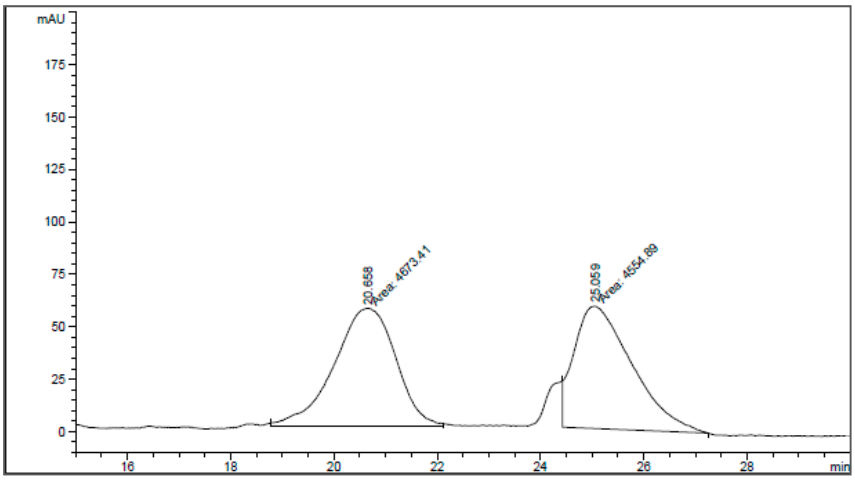


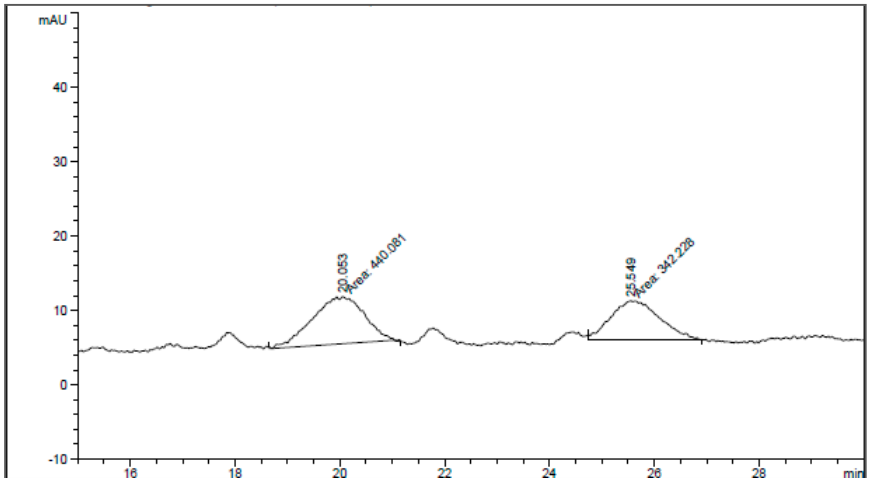


Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.9	VV	1.12	2.31e9	241.58	67.06
2	22.2	VV	0.99	1.13e9	134.51	32.93

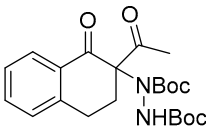


12

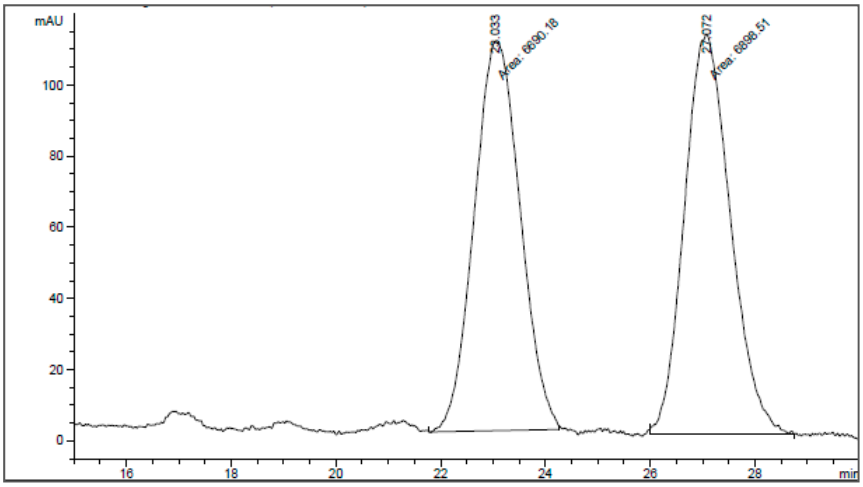


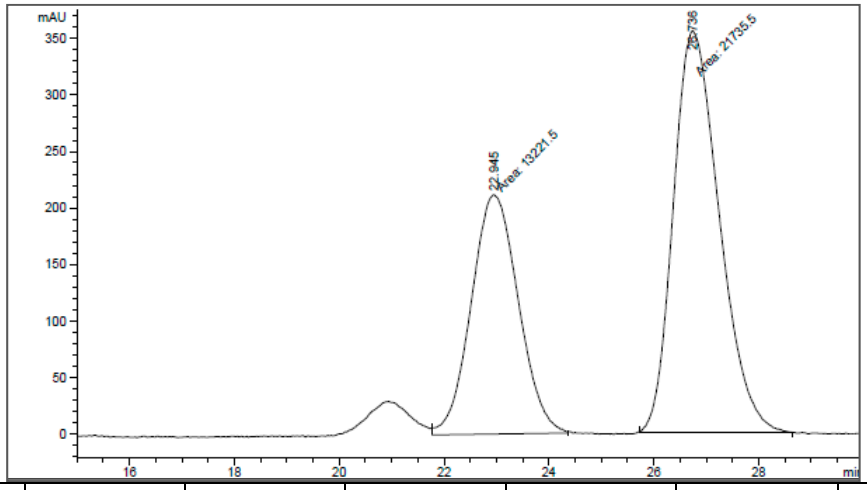


Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.1	MM	1.15	440.08	6.35	56.25
2	25.5	MM	1.08	342.22	5.27	43.74

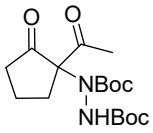


13

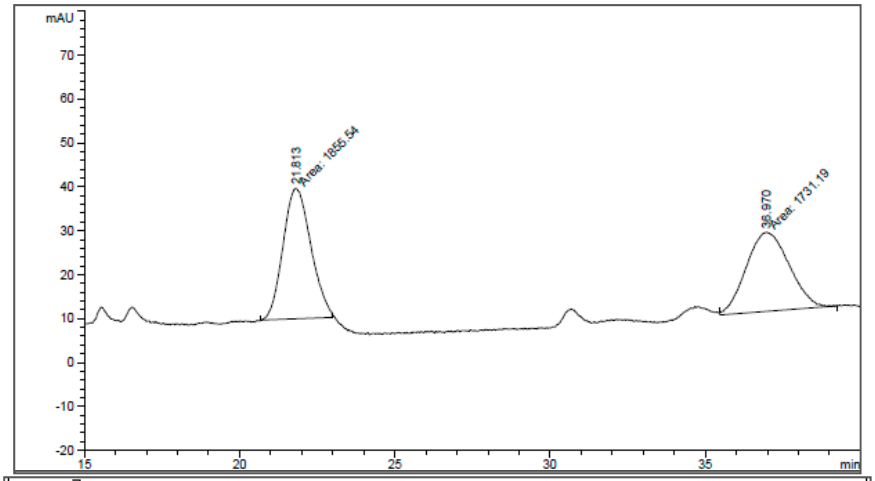


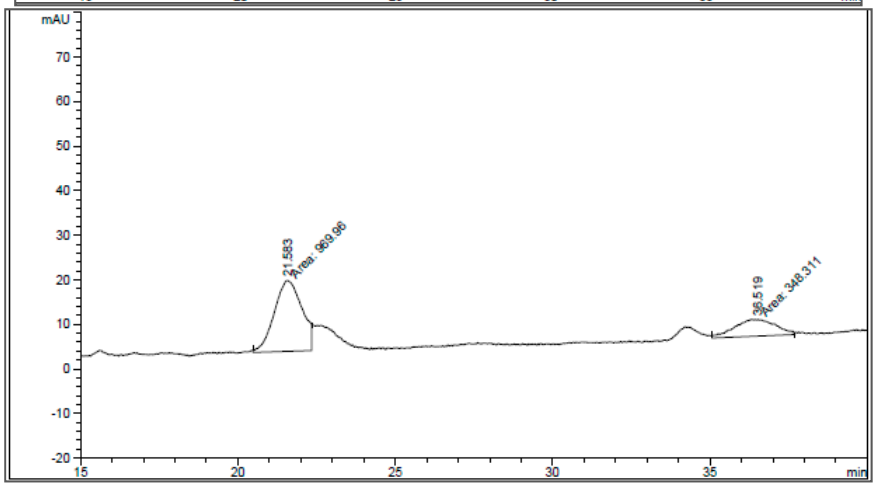


Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.9	MM	10.41	1.32e4	211.68	37.82
2	26.7	MM	10.18	2.17e4	355.73	62.17

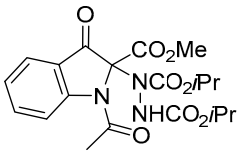


14

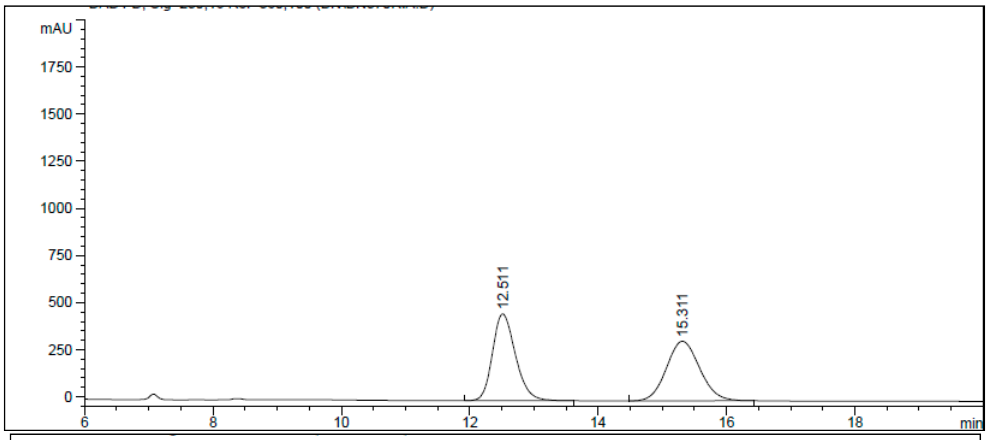


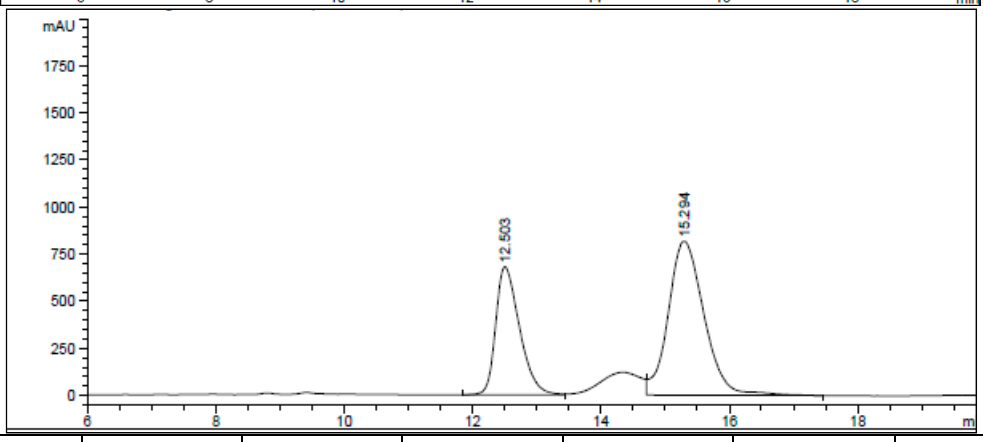


Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.6	MF	10.16	969.95	15.91	73.57
2	36.5	MM	15.34	348.31	37.83	26.42

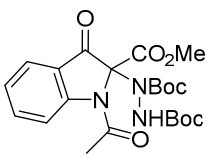


15a

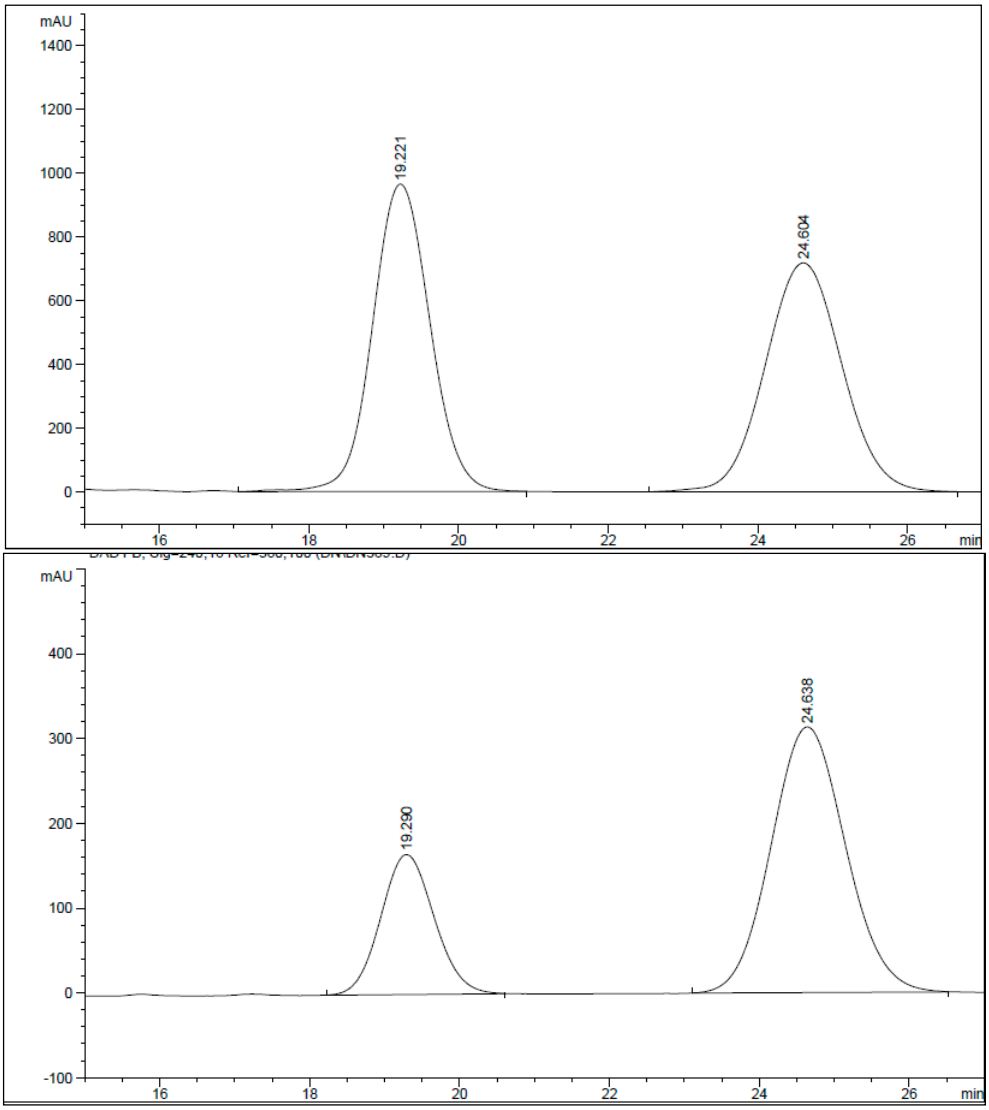




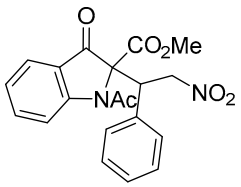
Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.5	BV	0.3919	1.76e4	680.35	35.67
2	15.3	VB	0.5954	3.17e4	816.97	64.33



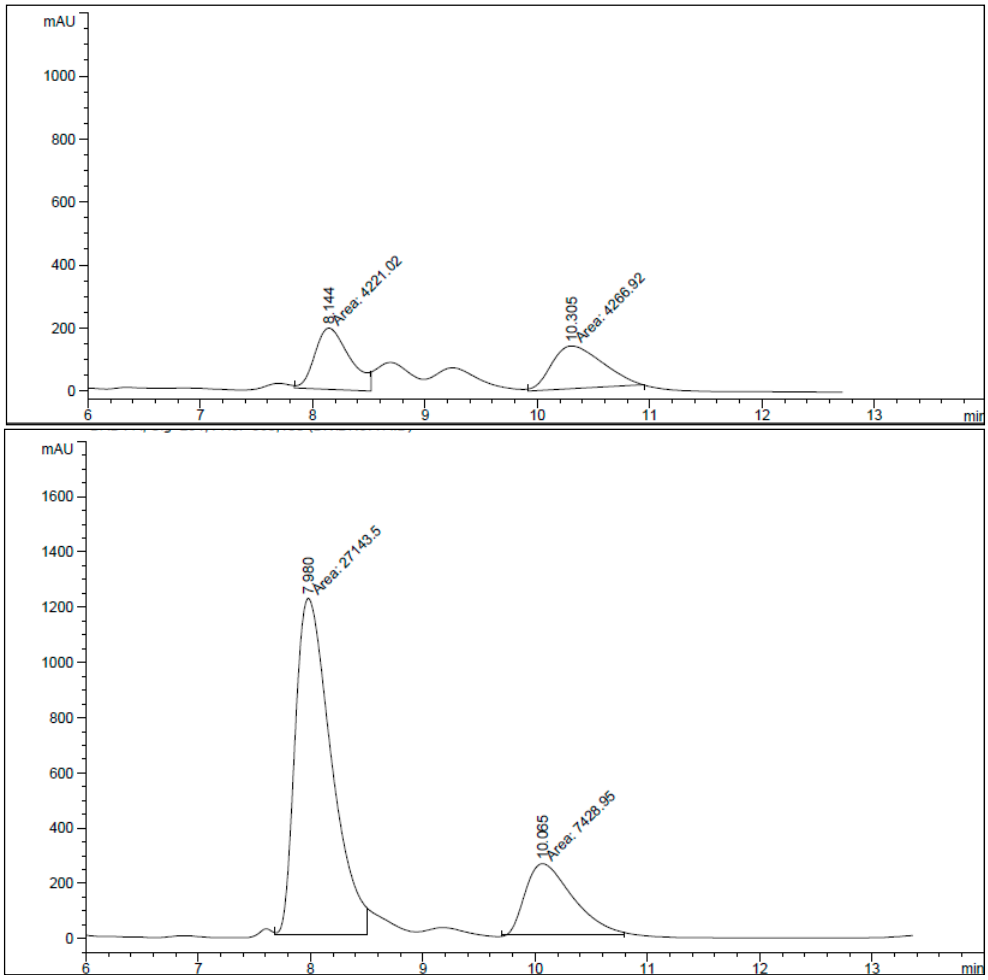
15b



Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.3	BB	0.7645	8193.16	165.22	27.41
2	24.6	BB	1.0616	2.16931e4	313.39	72.58



16



Peak	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.0	MM	0.3717	2.71435e4	1217.04	78.51
2	10.0	MM	0.4834	7428.95	256.12	21.48

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