Supporting Information

A recyclable hydrophobic anchor-tagged asymmetric amino thiourea catalyst

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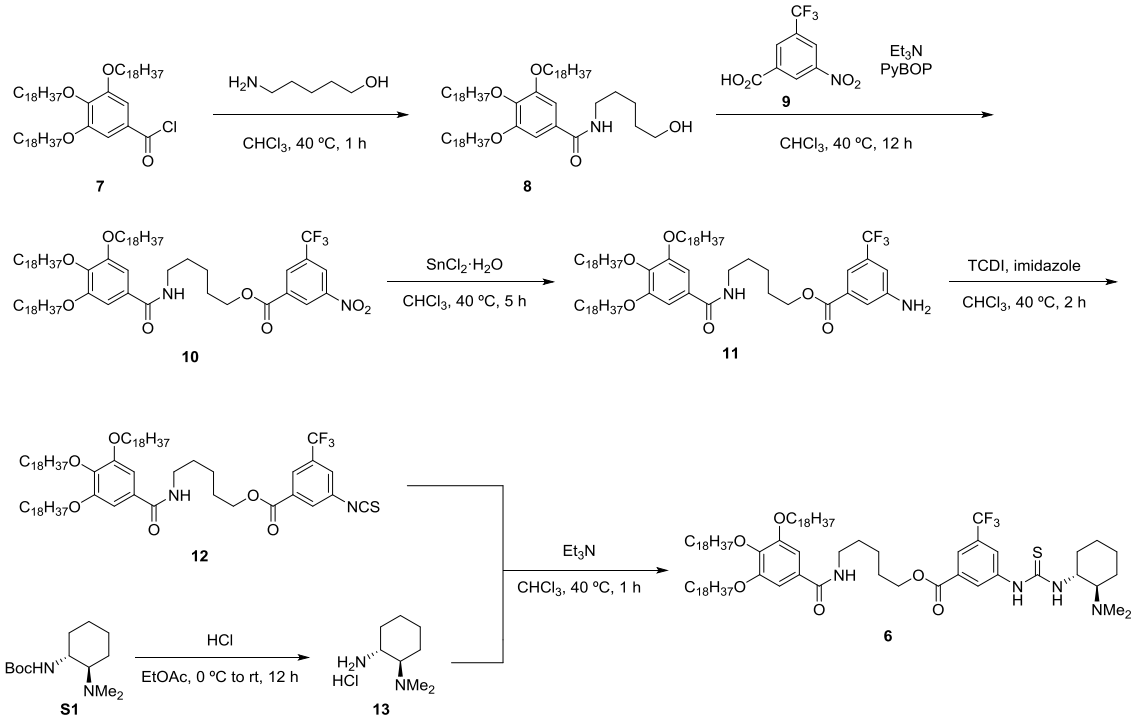
Contents

1. General methods

All reactions were carried out under a positive pressure of argon. Analytical TLC was performed on Merck TLC silica gel $60F_{254}$ silica gel plates. Visualization was accomplished with molybdenum phosphate, *p*-anisaldehyde, Hannessian's cocktail or ninhydrin. For column chromatography, silica gel (KANTO KAGAKU N-60) was employed. NMR spectra were recorded using a Bruker AV400N at 400 MHz frequency or JEOL JNM-AL300 for ^{1}H, and JEOL JNM-AL300 at 75 MHz frequency for ^{13}C in the stated solvents using tetramethylsilane as an internal standard. Chemical shifts were reported in parts per million (ppm) on the δ scale from an internal standard (NMR descriptions: s, singlet; d, doublet; t, triplet; q, quartet; hept, heptet; m, multiplet; br, broad). Coupling constants, *J*, are reported in Hertz. For chiral HPLC analysis, a Chiralpak IA (DAICEL, 4.6 × 250 mm) or a Chiralpak IC-3 (DAICEL, 4.6 × 250 mm) or a Chiralcel OD-H (DAICEL, 4.6 × 250 mm) were employed and eluting products were detected by UV at 254 nm. A solvent system consisting of HPLC grade of hexane and 2-propanol was used for HPLC analysis. Mass spectra were recorded on a Waters MICROMASS® LCT PREMIERTM (electrospray ionization-time-of-flight (ESI-TOF)). Optical rotations were measured using a JASCO P-2200 polarimeter (concentration in g dL^{-1}). IR was measured using a JEOL FT-IR 6200. Melting point was determined on YANAGIMOTO micro melting point apparatus. Elemental combustion analyses were performed using a J-SCIENCE LAB JM10. Measurement of absorbance at 250 nm was performed using a DU-650 spectrophotometer. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Ltd. (Japan), Aldrich Inc. (U.S.A.), Wako Pure Chemical Industries, Ltd. (Osaka, Japan), Nacalai Tesque Inc., Kanto Chemical Co., Inc. (Japan) commercial suppliers and were used as purchased.

2. Experimental procedures for synthesis of the catalysts

Synthesis of hydrophobic anchor-tagged thiourea organocatalyst **6**



N-(5-Hydroxypentyl)-3,4,5-tris(octadecyloxy)benzamide (**10**)

To a solution of **9**[1] (980 mg, 1.04 mmol) in $CHCl_3$ (19 mL) was added $H_2N(CH_2)_5OH$ (198 μL, 1.90 mmol) at 40 ºC and stirred at the same temperature for 1 h. After that, $CHCl_3$ was removed by evaporation. Then, CH_3CN was added and the white precipitate was washed with CH_3CN to yield **10** (1.06 g) as a white solid. 600 mg of thus obtained product was used for next step.

5-(3,4,5-Tris(octadecyloxy)benzamido)pentyl 3-nitro-5-(trifluoromethyl)benzoate (**12**)

To a solution of **10** (600 mg, *ca.* 0.59 mmol), **11** (479 mg, 0.889 mmol) and Et_3N (124 μL, 0.889 mmol) in $CHCl_3$ (12 mL) was added PyBOP (771 mg, 1.48 mmol) at 40 ºC and stirred at the same temperature for 12 h. After that, $CHCl_3$ was removed by evaporation. Then, CH_3CN was added and the white precipitate was washed with CH_3CN to yield **12** (725 mg) as a white solid. Thus obtained product was used for next step without further purifications.

5-(3,4,5-Tris(octadecyloxy)benzamido)pentyl 3-amino-5-(trifluoromethyl)benzoate (**13**)

To a solution of **12** (725 mg, *ca.* 0.59 mmol) in $CHCl_3$ (12 mL) was added $SnCl_2 \cdot H_2O$ (532 mg, 2.36 mmol) at 40 ºC and stirred at the same temperature for 24 h. After that, the reagents were removed by filtration through Celite® and $CHCl_3$ was removed by evaporation. Then, CH_3CN was added and the white precipitate was washed with CH_3CN to yield **13** (632 mg) as a white solid. 630 mg of thus obtained product was used for next step without further purifications.

5-(3,4,5-Tris(octadecyloxy)benzamido)pentyl 3-isothiocyanato-5-(trifluoromethyl)benzoate (**14**)

To a solution of **13** (630 mg, *ca.* 0.53 mmol) and imidazole (10.7 mg, 0.158 mmol) in $CHCl_3$ (11 mL) was added TCDI (374 mg, 2.10 mmol) at 30 ºC and stirred at 40 ºC for 2 h. After that, $CHCl_3$ was removed by evaporation. Then, CH_3CN was added and the white precipitate was washed with CH_3CN to yield **14** (652 mg) as a white solid. Thus obtained product was used for next step without further purifications.

(1*R*,2*R*)-N^1,N^1-Dimethylcyclohexane-1,2-diamine dihydrochloride (**15**)[2]

To a solution of **S1**[3] (507 mg, 2.09 mmol) in EtOAc (2.0 mL) was added HCl (4M in EtOAc, 6.0 mL, 24 mmol) at 0 ºC and stirred at room temperature for 20 h. After that, the volatiles were removed by evaporation to yield **15** (531 mg) as a white solid. Thus obtained product was used for next step without further purifications.

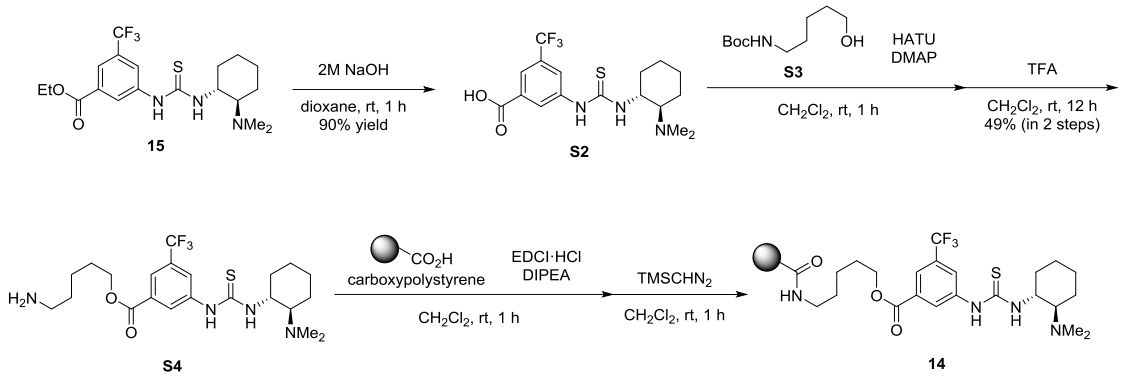
5-(3,4,5-Tris(octadecyloxy)benzamido)pentyl
3-(3-((1*R*,2*R*)-2-(dimethylamino)cyclohexyl)thioureido)-5-(trifluoromethyl)benzoate (**6**)

To a solution of **14** (652 mg, *ca.* 0.54 mmol) in $CHCl_3$ (11 mL) were added Et_3N (151 mL, 1.09 mmol) and **15** (234 mg, *ca.* 1.09 mmol) at 40 ºC and stirred at the same temperature for 1 h. After that, $CHCl_3$ was removed by evaporation. Then, CH_3CN was added and the white precipitate was washed with CH_3CN. The resulting crude solid was purified by silica gel column chromatography ($CHCl_3$/MeOH/Et_3N = 20/1/0.1) to afford **6** (610 mg, 0.441 mmol, 75% in 5 steps) as a white powder. $[\alpha]^{20}_D$ −7.6 (*c* = 1.02 in $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$); δ 0.88 (t, *J* = 6.8 Hz, 9H), 1.20–1.37 (m, 90H), 1.40–1.50 (m, 8H), 1.67–1.90 (m, 14H), 2.31 (s, 6H), 3.47 (dd, *J* = 14.4 and 6.2 Hz, 2H), 4.37 (t, *J* = 6.2 Hz, 2H), 6.13 (s, 1H),

(1) Wang, L.; Ishida, Y.; Maeda, R.; Tokita, M.; Horiuchi, S.; Hayakawa, T. *Langmuir*, 2014, **30**, 9797–9803.
(2) Yasukochi, T.; Imura, S.; Yoneda, Y.; Shimizu, H.; Yamasaki, T. *PCT Int. Appl.*, 2007, WO 2008072682.
(3) Amarasinghe, N. R.; Turner, P.; Todd, M. H. *Adv. Synth. Catal.*, 2012, **354**, 2954–2958.

6.95 (s, 1H), 7.97 (s, 1H), 8.04 (s, 1H), 8.12 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 23.8, 24.5, 24.7, 26.2, 28.4, 29.5, 29.6, 29.8, 29.9, 32.1, 40.1, 40.2, 65.6, 69.5, 73.6, 69.5, 73.6, 105.9, 121.7, 122.4, 125.3, 123.8, 127.2, 129.9, 131.4, 131.8, 132.0, 141.1, 153.2, 165.0, 167.7; IR (KBr) 1125, 1255, 1502, 1582, 1725, 2849, 2917, 3257 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{83}H_{145}F_3N_4O_6S$ $[M+H]^+$ 1384.0837, found 1384.0870.

Synthesis of resin-bound thiourea organocatalyst **8**



3-(3-((1*R*,2*R*)-2-(Dimethylamino)cyclohexyl)thioureido)-5-(trifluoromethyl)benzoic acid (**S2**)

To a solution of **15**[4] (82.0 mg, 0.197 mmol) in dioxane (2.0 mL) was added 2M $NaOH_{aq}$ (2.0 mL) at room temperature and stirred at the same temperature for 1 h. After that, the reaction mixture was evaporated in vacuo, acidified with 5% $KHSO_{4aq}$, extracted with EtOAc, washed with brine, dried over Na_2SO_4 and evaporated in vacuo to yield **S2** (70.0 mg, 90%) as a white powder. $[\alpha]^{20}_D$ +1.2 (*c* = 1.07 in $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$); δ 1.34–1.57 (m, 4H), 1.79–1.89 (m, 1H), 1.94–2.04 (m, 1H), 2.09–2.17 (m, 1H), 2.24–2.34 (m, 1H), 3.74 (m, 1H), 4.86 (m, 1H), 7.75 (s, 1H), 8.25 (s, 1H), 8.34 (s, 1H), 8.61 (d, *J* = 8.8 Hz, 1H), 9.24 (m, 2H); ^{13}C-NMR (100 MHz, DMSO-d_6); δ 22.8, 23.6, 23.7, 31.7, 52.4, 66.2, 120.1, 122.0, 125.4, 126.3, 129.0, 129.4, 132.4, 141.3, 165.9, 180.5; IR (KBr) 1341, 1543, 1607, 1707, 2866, 2944, 3303 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{22}F_3N_3O_2S$ [M+H] +390.1385, found 390.1453.

4-Aminobutyl 3-(3-((1*R*,2*R*)-2-(dimethylamino)cyclohexyl)thioureido)-5-(trifluoromethyl)benzoate (**S4**)

To a solution of **S2** (50.0 mg, 0.128 mmol) in CH_2Cl_2 (1.3 mL) were added HATU (59.3 mg, 0.156 mmol), **S3** (39.1 mg, 0.192 mmol) and DMAP (3.1 mg, 0.026 mmol) at room temperature and stirred at the same temperature for 1 h. After that, the reaction mixture was extracted with EtOAc, dried over Na_2SO_4 and evaporated in vacuo to yield the corresponding ester intermediate. This crude product was used for the next step without further purifications.

To a solution of above obtained ester in CH_2Cl_2 (2.1 mL) was added TFA (130 μL) at room temperature and stirred at the same temperature for 12 h. Then, TFA was removed by evaporation and the reaction mixture was purified by silica gel column chromatography ($CHCl_3$/MeOH = 50/1) to yield **S5** (30.4 mg, 49% in 2 steps) as a colorless oil. $[\alpha]^{20}_D$ +50.1 (*c* = 1.42 in MeOH); ^{1}H NMR (400 MHz, CD_3OD); δ 1.43–1.48 (m, 3H), 1.57–1.61 (m, 3H), 1.72–1.76 (m, 2H), 1.85–1.98 (m, 3H), 1.98 (br s, 1H), 2.17 (br s, 1H), 2.93 (s, 6H), 2.96 (m, 2H), 4.40 (t, *J* = 6.5 Hz, 2H), 7.99 (s, 1H), 8.31 (s, 1H), 8.43 (s, 1H); ^{13}C-NMR (100 MHz, CD_3OD); 24.0, 24.1, 25.1, 25.4, 28.2, 29.2, 33.2, 38.6, 40.6, 42.9, 54.3, 66.3, 69.0, 122.4, 123.2, 125.2, 128.5, 131.7, 132.1, 132.8, 142.4, 166.3, 183.5; IR (KBr) 1260, 1776, 2870, 2949, 3252, 3570 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{33}F_3N_4O_2S$ [M+Na] + 474.2276, found 474.2166.

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(4) Miyabe, H.; Tsuchida, S.; Yamauchi M.; Takemoto, Y. *Synthesis.*, 2006, 3295–3300.

Resin-bound thiourea (**14**)

To a suspension of carboxypolystyrene resine (10.0 mg, content = 1.6-3.0 mmol/g) in CH_2Cl_2 (0.63 mL) were added **S4** (30.0 mg, 0.0632 mmol), EDCI·HCl (6.1 mg, 0.032 mmol), DIPEA (5.5 μL, 0.032 mmol) at room temperature and stirred at the same temperature. After 2 h, the resulting precipitate was washed with CH_2Cl_2. To protect unreacted carboxylic acid of starting resin, capping of carboxyl group was performed as follows. The above obtained resin was suspended in CH_2Cl_2 (0.63 mL) and $TMSCHN_2$ (2.0 M hexane solution, 1.0 mL, 2.00 mmol) was added at room temperature. The mixture was stirred at the same temperature for 1 h. Then, the resulting precipitate was washed with CH_2Cl_2. Content of the thiourea moiety bound to the resin **14** was determined to be 0.69 mmol /g by quantification of the content of nitrogen atom by elemental analysis (N: 3.86%).

IR (KBr) 1603, 1724, 1787, 2852, 2926, 3298 cm^{-1}

3. Solubility of hydrophobic anchor-tagged catalyst in various solvents

Standard curve showing correlation between absorbance and concentration of **6** was prepared by measuring UV absorbance of the $CHCl_3$ solution of **6** in each concentration (Figure S1). Next, **6** was saturated in various solvents and each solution was stirred at each temperature for 3 days. After the insolubility of the suspension was filtered off, the absorbance of the filtrate at 250 nm was measured. Concentration of **6** in each solvent was estimated according to the standard curve (Table S1).

Figure S1. Standard curve.

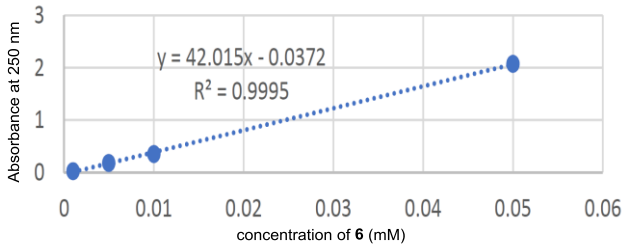
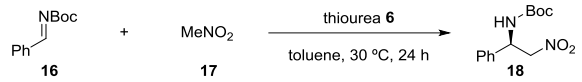


Table S1. Absorbence of the solution of **6** under each condition and concentration of 6 estimated by the standard curve.

solvent	4 °C abbsorbance at 250 nm	4 °C concentration of **6** (mM)	20 °C abbsorbance at 250 nm	20 °C concentration of **6** (mM)	30 °C abbsorbance at 250 nm	30 °C concentration of **6** (mM)
$CHCl_3$	3.36	141	3.73	156	4.20	177
CH_2Cl_2	0.153	6.39	0.180	7.53	0.737	30.9
toluene	0.0357	1.46	0.0417	1.71	0.941	39.5
THF	0.108	4.48	0.113	4.70	0.772	32.4
MeOH	N.D.	N.D.	N.D.	N.D.	0.00320	0.10
MeCN	N.D.	N.D.	N.D.	N.D.	0.00220	0.06

4. General procedure for Aza-Henry reaction using hydrophobic anchor-tagged catalyst

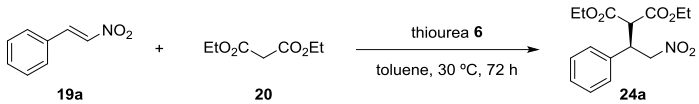


A solution of **16**[5] (20.6 mg, 0.100 mmol) and $MeNO_2$ (53.9 μL, 1.00 mmol) in $CHCl_3$ (1.0 mL) was added hydrophobic anchor-tagged catalyst **6** (13.8 mg, 10.0 μmol) and stirred at 30 ºC for 24 h. After that, $CHCl_3$ was removed by evaporation and MeCN was added to the residue. The precipitated catalyst was collected by filtration (13.7 mg, 99%). The filtrate was evaporated in vacuo and purified by silica gel column chromatography (Hexane/EtOAc = 10/1 to 4/1) to afford **18**[6] (20.5 mg, 77%) as a white solid.

tert-Butyl (*R*)-2-nitro-1-phenylethylcarbamate (**18**)

^{1}H NMR (400 MHz, $CDCl_3$); δ 1.46 (s, 9H), 4.68–4.72 (m, 1 H), 4.85 (br s, 1H), 5.29 (br s, 1H), 5.37 (br s, 1H), 7.25-7.38 (m, 5H); HPLC [Chiralpak IC-3, hexane/2-propanol = 85/15, 1.0 mL/min, λ = 254 nm, retention times: (major) 10.0 min, (minor) 15.6 min, 91% ee]; $[\alpha]^{20}_D$ −21.1 (*c* = 1.05 in $CHCl_3$).

5. Typical procedure for Michael reaction using hydrophobic anchor-tagged catalyst



A mixture of **19a** (14.9 mg, 0.100 mmol), catalyst **6** (41.5 mg, 0.0300 mmol) and **20** (30.2 μL, 0.199 mmol) in toluene (1.0 mL) was stirred at 30 °C for 72 h. Then, the reaction mixture was directly purified by silica gel column chromatography (Hexane/EtOAc = 10/1 to 4/1) to afford the desired product **24a**[7] (23.1 mg, 81%) as a colorless oil.

Diethyl (*S*)-2-(2-nitro-1-phenylethyl)malonate (**24a**)

^{1}H NMR (400 MHz, $CDCl_3$); δ 1.06 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 2.32 (d, *J* = 9.3 Hz, 1H), 4.01 (q, *J* = 7.3 Hz, 2H), 4.19–4.26 (m, 3H), 4.83–4.95 (m, 2H), 7.23–7.34 (m, 5H); HPLC [Chiralpak IA, hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (major) 14.6 min, (minor) 31.7 min, 89% ee]; $[\alpha]^{20}_D$ −7.4 (*c* = 0.76 in $CHCl_3$).

Ethyl (*S*)-2-carboethoxy-4-nitro-3-(4-chlorphenyl)butyrate (**24b**)[7]

A procedure similar to that described for the preparation of **24a** afforded **24b** in 80% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.09 (t, *J* = 9.3 Hz, 3H), 1.27 (t, *J* = 9.3 Hz, 3H), 3.78 (d, *J* = 12.2 Hz, 1H), 4.04 (q, *J* = 9.5 Hz, 2H), 4.18–4.25 (m, 3H), 4.83–4.92 (m, 2H), 7.19 (d, *J* = 11.0 Hz, 2H), 7.30 (d, *J* = 11.0 Hz, 2H); HPLC [Chiralcel OD-H, hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (major) 18.3 min, (minor) 15.7 min, 93% ee]; $[\alpha]^{20}_D$ −7.5 (*c* = 1.47 in $CHCl_3$)

(*R*)-3-(2-Nitro-1-phenylethyl)pentane-2,4-dione (**24c**)[8]

A procedure similar to that described for the preparation of **24a** afforded **24c** in 98% yield as a white solid. ^{1}H NMR (400

(5) Best, D.; Kujawa, S.; Lam, H. W. *J. Am. Chem. Soc*., 2012, **134**, 18193–18196.
(6) Xu, X.; Furukawa, T.; Okino, T.; Miyabe, H.; Takemoto, Y. *Chem. Eur. J*., 2005, **12**, 466–476.
(7) Okino, T.; Hoashi, Y.; Furukawa, T.; Xu, X.; Takemoto, Y. *J. Am. Chem. Soc*., 2005, **127**, 119–125.
(8) Jiménez, E. I.; Vallejo Narváez, W. E.; Román-Chavarría, C. A.; Vazquez-Chavez, J.; Rocha-Rinza, T. Hernández-Rodríguez, M. *J. Org. Chem.*, 2016, **81**, 7419–7431.

MHz, $CDCl_3$); δ 1.94 (s, 3H), 2.29 (s, 3H), 4.21–4.27 (m, 1H), 4.37 (d, *J* = 10.8 Hz, 1H), 4.59–4.68 (m, 2H), 7.17–7.19 (m, 2H), 7.29–7.35 (m, 3H); HPLC [Chiralpak IA, hexane/2-propanol = 95/5, 1.0 mL/min, λ = 210 nm, retention times: (major) 23.7 min, (minor) 17.5 min, 72% ee]; $[\alpha]^{20}_D$ −190.3 (*c* = 1.16 in $CHCl_3$)

(*R*)-3-(1-(4-Chlorophenyl)-2-nitroethyl)pentane-2,4-dione (**24d**)[8]

A procedure similar to that described for the preparation of **24a** afforded **24d** in 97% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.98 (s, 3H), 2.29 (s, 3H), 4.22–4.34 (m, 1H), 4.33 (d, *J* = 10.8 Hz, 1H), 4.60–4.62 (m, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H); HPLC [Chiralpak IA, hexane/2-propanol = 90/10, 1.0 mL/min, λ = 210 nm, retention times: (major) 17.4 min, (minor) 36.9 min, 89% ee]; $[\alpha]^{20}_D$ −176.0 (*c* = 1.07 in $CHCl_3$).

(*R*)-Ethyl 1-((*S*)-2-nitro-1-phenylethyl)-2-oxocyclopentane-1-carboxylate (**24e**)[9]

A procedure similar to that described for the preparation of **24a** afforded **24e** in 95% yield as a colorless oil (dr = 90 : 10). ^{1}H NMR (400 MHz, $CDCl_3$); Mixture of diastereomers δ1.28 (t, *J* = 7.3 Hz, 3H), 1.81−2.05 (m, 4H), 2.32−2.41 (m, 2H), 4.07 (dd, *J* = 7.3, 3.8 Hz, 1H), 4.19−4.24 (m, 2H), 4.8−5.04 (m, 1H), 5.15−5.31, (m, 1H), 7.24−7.33 (m, 5H); HPLC [Chiralcel OD-H, hexane/2-propanol = 93/7, 1.0 mL/min, λ = 210 nm, retention times: (major) 21.3 min, (minor) 15.2 min, 78% ee]; $[\alpha]^{20}_D$ −22.4 (*c* = 0.45 in $CHCl_3$).

(*R*) –Ethyl 1-((*S*)-1-(4-chlorophenyl)-2-nitroethyl)-2-oxocyclopentane-1-carboxylate (**24f**)[9]

A procedure similar to that described for the preparation of **24a** afforded **24f** in 88% yield as a colorless oil (dr = 90 : 10). ^{1}H NMR (400 MHz, $CDCl_3$) Mixture of diastereomers δ 1.24 (t, *J* = 5.8 Hz, 3H), 1.82−2.10 (m, 4H), 2.34−2.42 (m, 2H), 4.03 (dd, *J* = 8.8, 3.0 Hz, 1H), 4.19 (q, 4.0 Hz, 1H), 4.22 (q, 4.0 Hz, 1H), 4.97 (dd, *J* = 10.8, 9.1 Hz, 1H), 5.15 (dd, *J* = 11.1, 3.0 Hz, 1H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 2H); HPLC [Chiralcel IC-3, hexane/2-propanol = 95/5, 1.0 mL/min, λ = 210 nm, retention times: (major) 24.9 min, (minor) 19.6 min, 78% ee]; $[\alpha]^{20}_D$ −25.5 (*c* = 1.12 in $CHCl_3$).

(*S*)-2-Hydroxy-3-(2-nitro-1-phenylethyl)naphthalene-1,4-dione (**24g**)[10]

A procedure similar to that described for the preparation of **24a** afforded **24g** in 95% yield as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$); δ 5.15 (dd, *J* = 6.8, 13.3 Hz, 1H), 5.31 (dd, *J* = 6.8, 9.0 Hz, 1H), 5.48 (dd, *J* = 9.0, 13.3 Hz, 1H), 7.24−7.34 (m, 3H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.69 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.78 (dt, *J* = 1.3, 7.6 Hz, 1H), 8.07 (d, *J* = 6.5 Hz, 1H), 8.11 (d, *J* = 6.8 Hz, 1H). HPLC [Chiralcel IA hexane (0.1% TFA)/DCM/EtOH = 90/5/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 32.2 min, (minor) 41.7 min, 92% ee]; $[\alpha]^{20}_D$ +31.8 (*c* = 1.05 in $CHCl_3$).

(*S*)-2-(1-(4-Chlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (**24h**)[10]

A procedure similar to that described for the preparation of **24a** afforded **24h** in 90% yield as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6); δ 5.20 (t, *J* = 7.8, Hz, 1H), 5.33 (dd, *J* = 7.6, 13.8 Hz, 1H), 5.45 (dd, *J* = 8.3, 13.6 Hz, 1H), 7.36–7.43 (m, 4H), 7.78 (dt, *J* = 1.5, 7.6 Hz, 1H), 7.84 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H); HPLC [Chiralcel IA hexane (0.1% TFA)/DCM/EtOH = 90/5/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 32.8 min, (minor) 38.7 min, 93% ee]; $[\alpha]^{20}_D$ +15.5 (*c* =1.03 in CH_3COOH).

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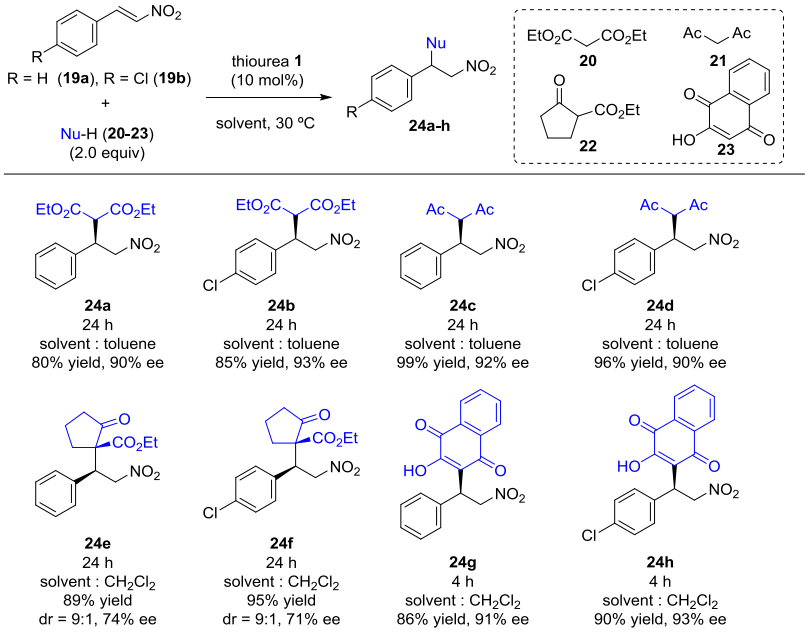
(9) Andrés, J. M.; Ceballos, M.; Maestro, A.; Sanz, I.; Pedrosa, R. *Beilstein J. Org. Chem.*, 2016, **12**, 628–635.
(10) Kasaplar, P.; Rodríguez-Escrich, C.; Pericàs, M. A. *Org. Lett.*, 2013, **15**, 3498–3501.

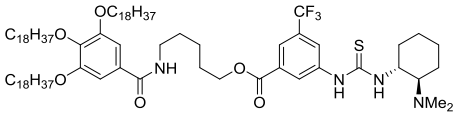
6. The parent thiourea-catalyzed Michael reaction

The results of the parent thiourea **1**-catalyzed Michael reaction of nitroolefins **19a**,**b** and carbon nucleophiles **20**-**23** are summarized in Table S2.

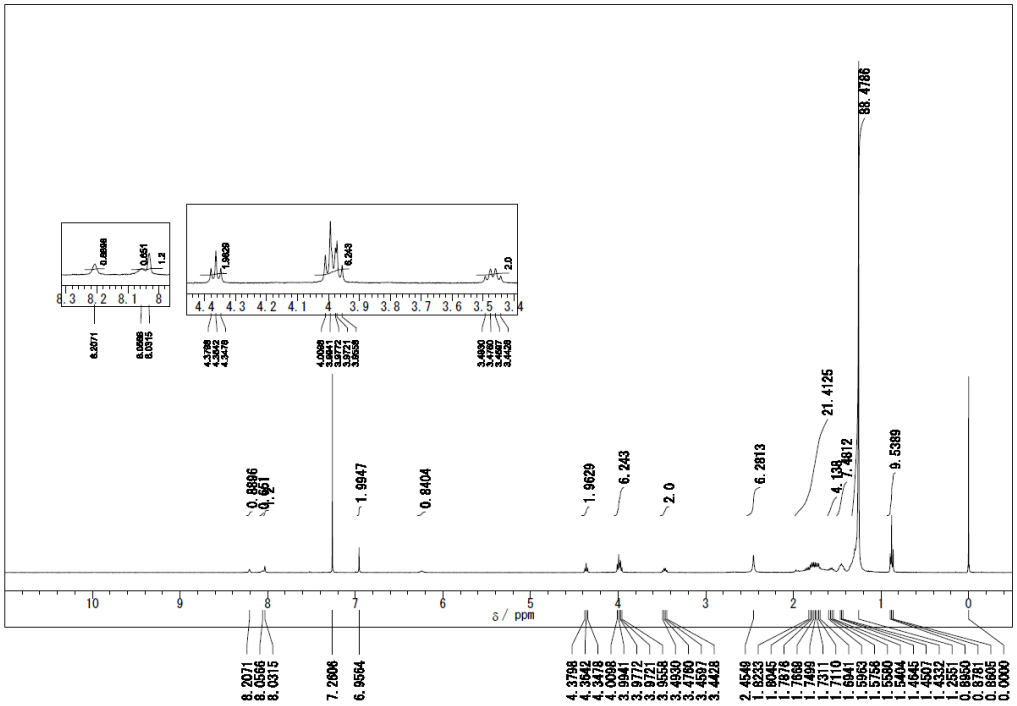
Table S2. The parent thiourea **1**-catalyzed Michael reaction of **19a**,**b** and **20**-**23**.

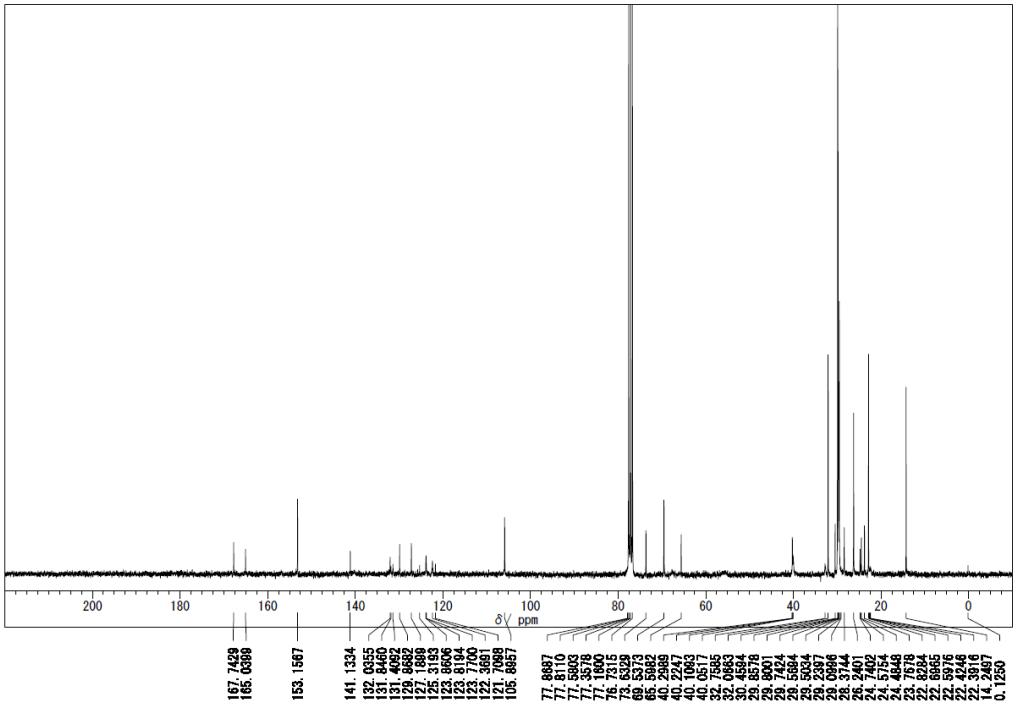


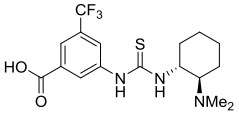
7. ^{1}H NMR and ^{13}C NMR spectra



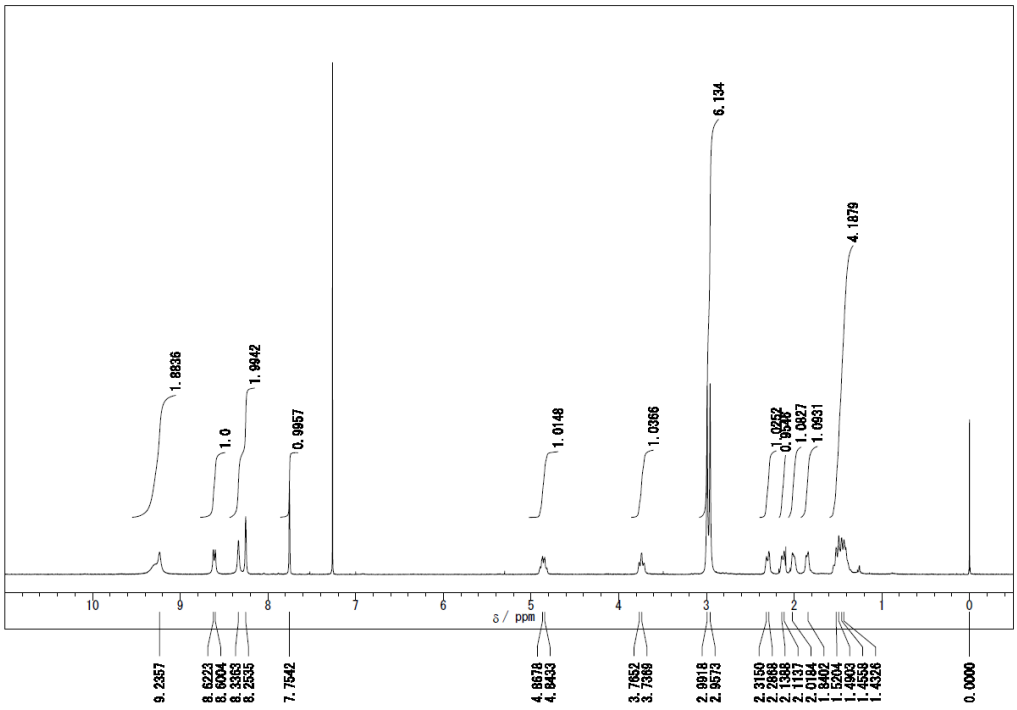
6

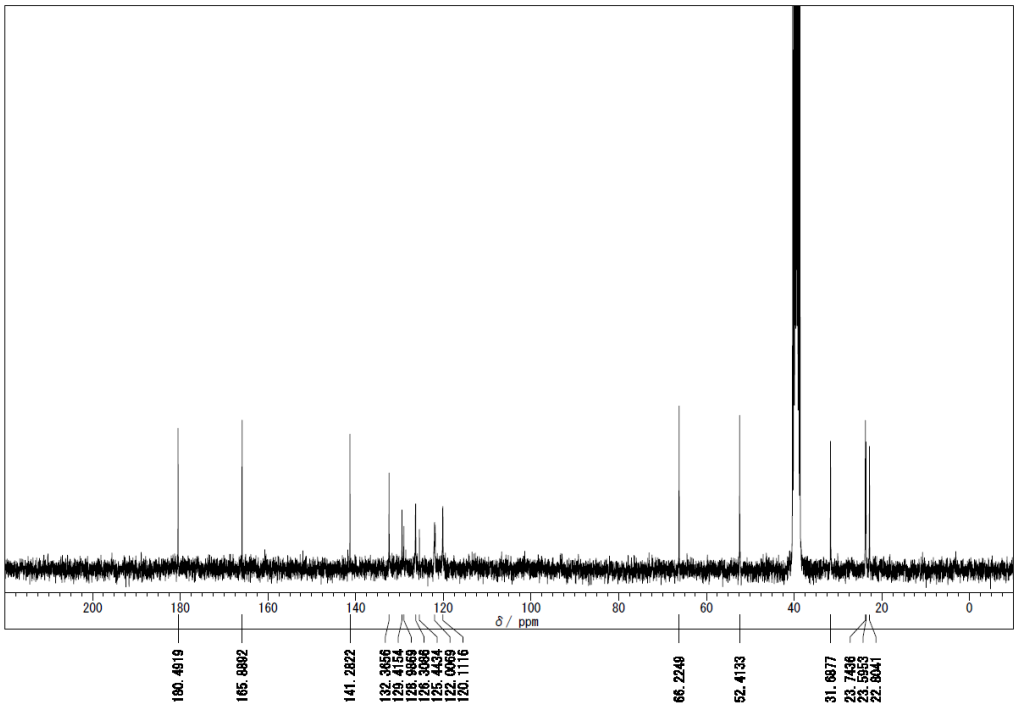


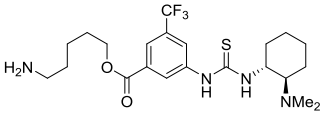



CF3
HO
O
S
N
H
N
H
NMe2

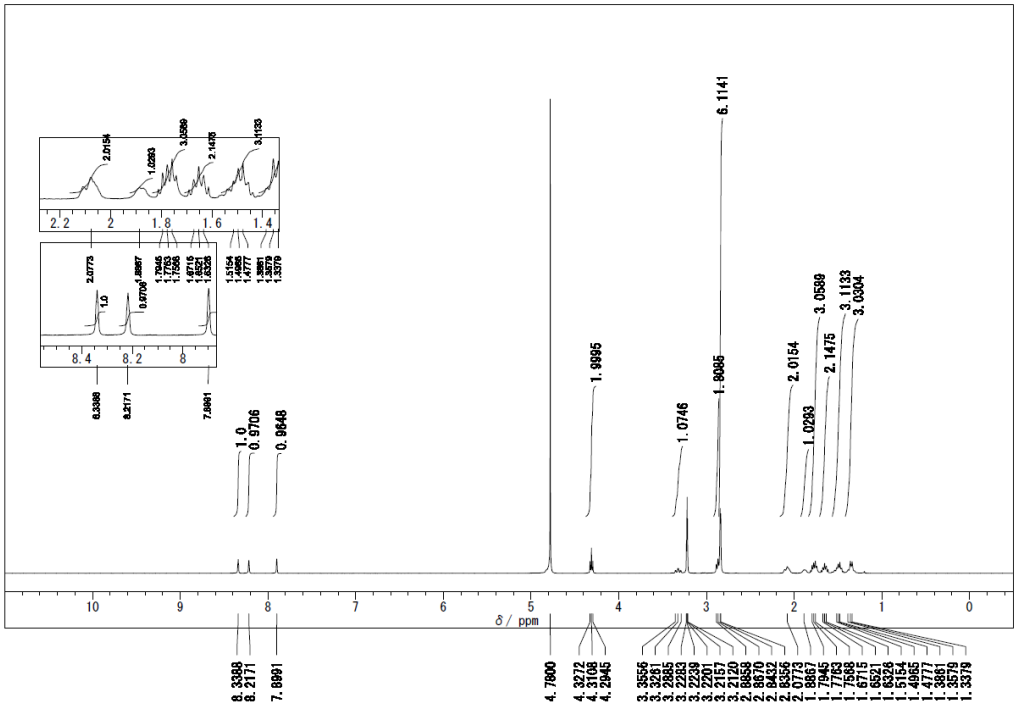
S2

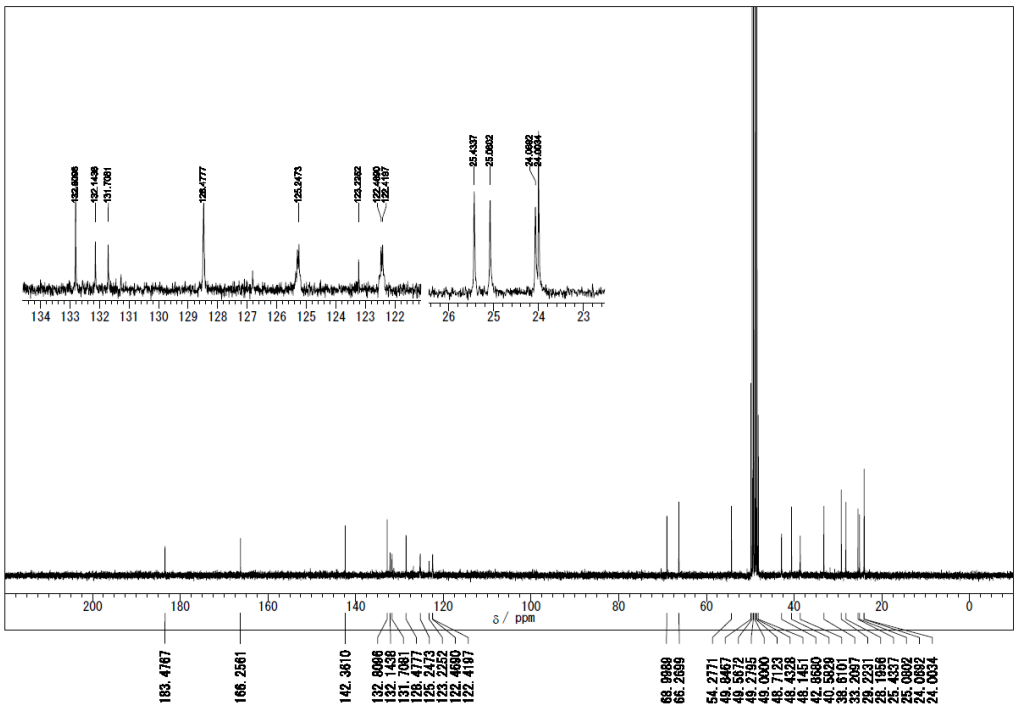

9.2357
8.6223
8.6004
8.3363
8.2535
7.7542
4.8678
4.8433
3.7652
3.7389
2.9918
2.9573
2.3150
2.2888
2.1388
2.1137
2.0184
2.0010
1.8402
1.5204
1.4963
1.4558
1.4326
0.0000
δ / ppm
10
9
8
7
6
5
4
3
2
1
0
1.8836
1.0
1.9942
0.9957
1.0148
1.0366
6.134
4.1879
1.0257
0.9548
1.0327
1.0931

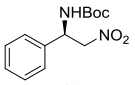

180.4919
165.8892
141.2822
132.3856
129.4154
128.9869
128.3066
125.4434
122.0069
120.1116
66.2249
52.4133
31.6877
23.7436
23.5953
22.8041
δ / ppm
200
180
160
140
120
100
80
60
40
20
0



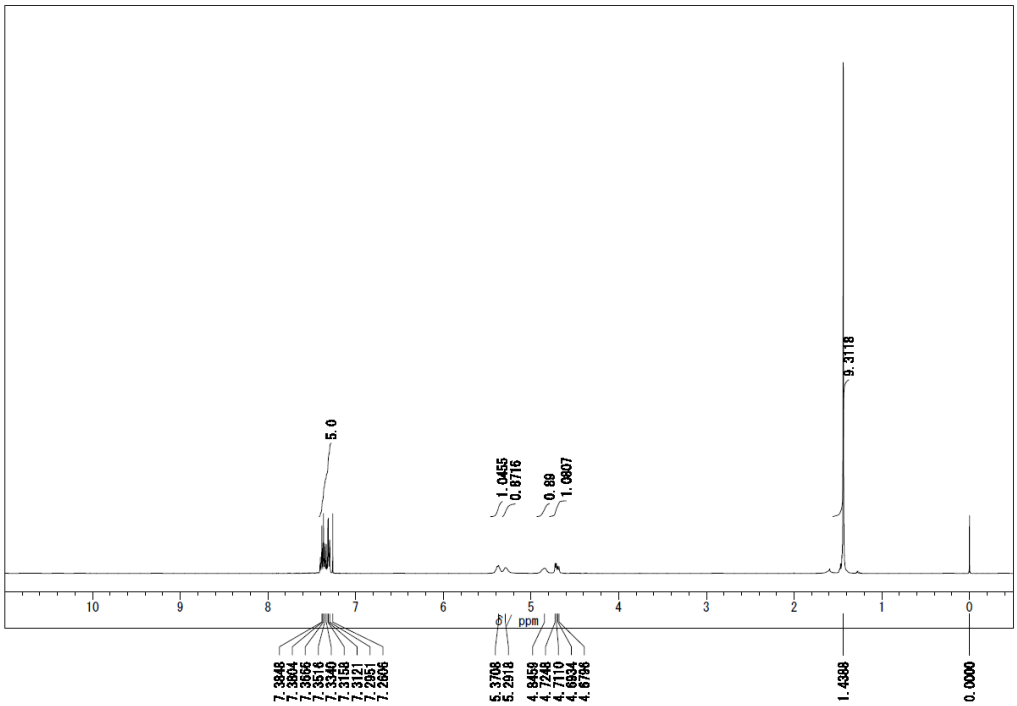
S4

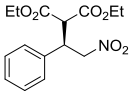




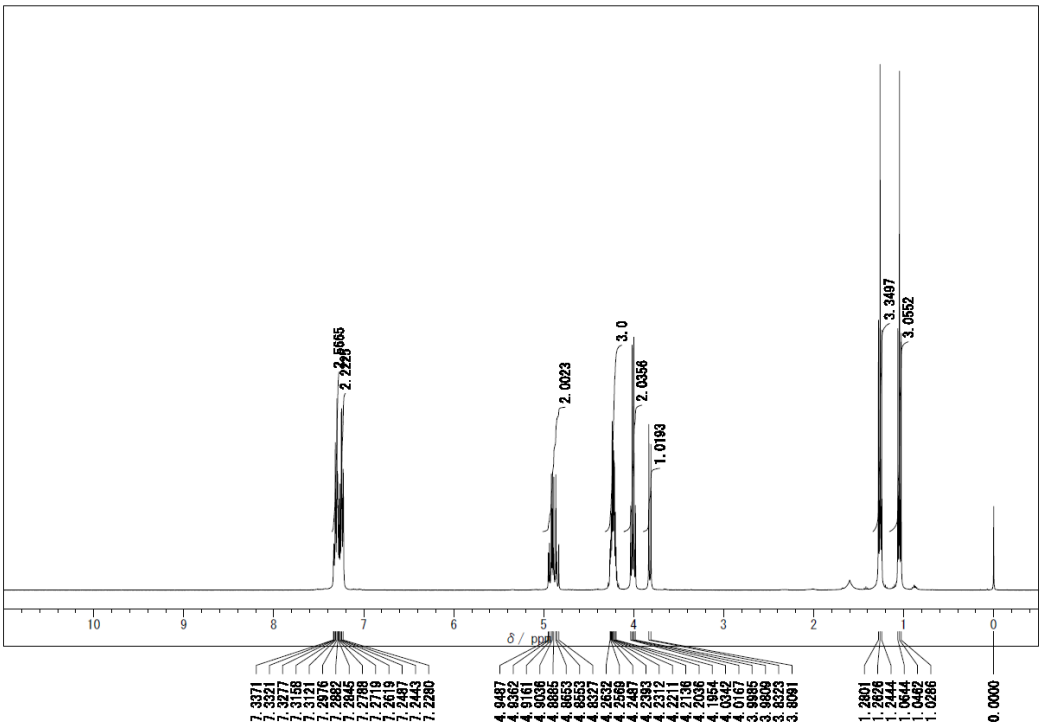

NHBoc
NO2

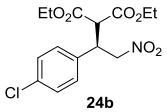
18


5.0
1.0455
0.8716
0.89
1.0807
9.3118
δ / ppm
7.3846
7.3804
7.3695
7.3516
7.3340
7.3158
7.3121
7.2951
7.2806
5.3708
5.2918
4.8459
4.7246
4.7110
4.6934
4.6798
1.4388
0.0000

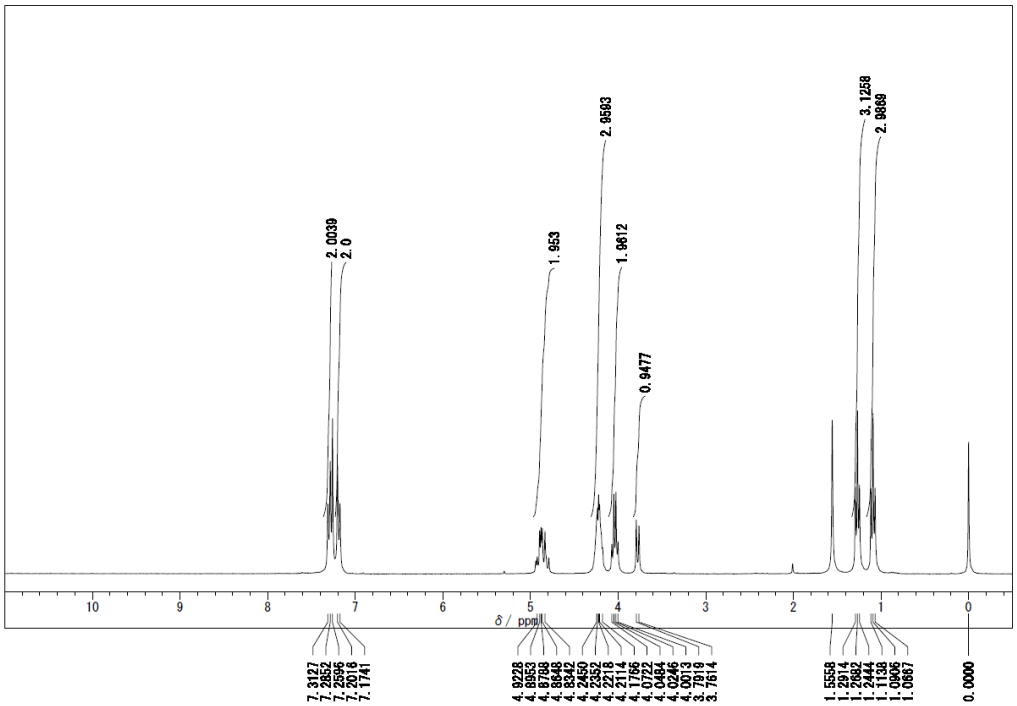

EtO2C
CO2Et
NO2

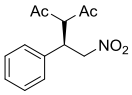
24a


2.2665
2.2228
2.0023
3.0
2.0356
1.0193
3.3497
3.0552
δ / ppm
7.3371
7.3321
7.3277
7.3158
7.3121
7.2976
7.2882
7.2845
7.2788
7.2719
7.2619
7.2497
7.2443
7.2280
4.9487
4.8362
4.8161
4.8038
4.8885
4.8653
4.8553
4.8327
4.2632
4.2569
4.2487
4.2393
4.2312
4.2211
4.2136
4.2036
4.1954
4.0342
4.0167
3.9865
3.9649
3.8323
3.8091
1.2801
1.2628
1.2444
1.0462
1.0286
0.0000

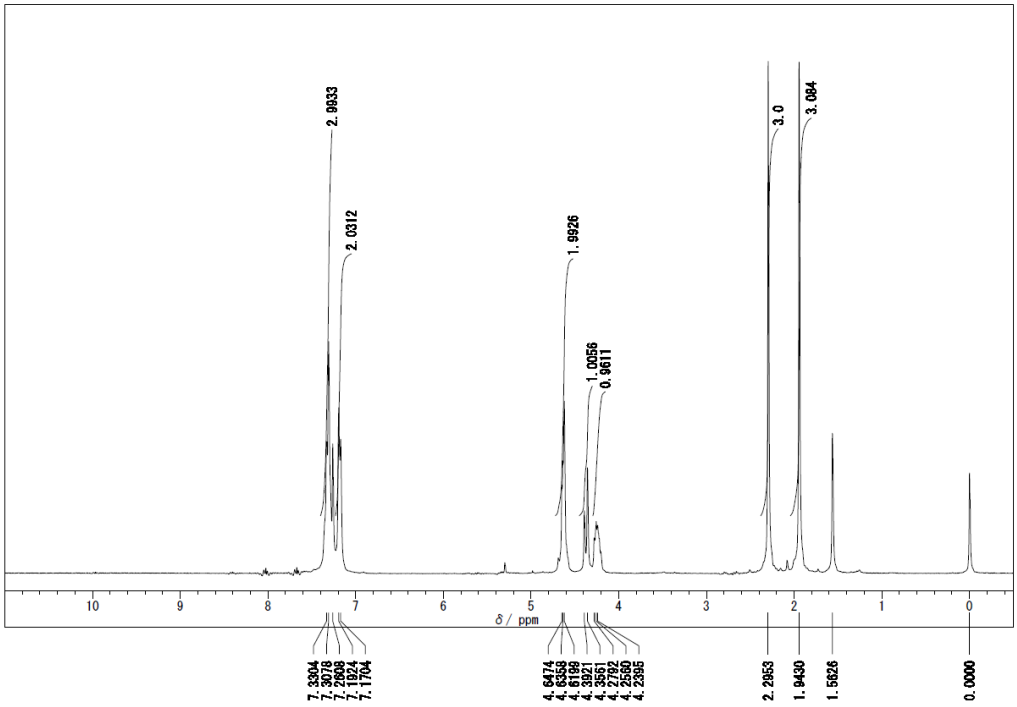


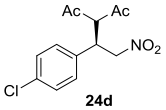
24b


2.0039
2.0
1.953
2.9563
1.9612
0.9477
3.1258
2.9889
δ / ppm
7.3127
7.2852
7.2596
7.2016
7.1741
4.9228
4.8953
4.8679
4.8348
4.8342
4.2450
4.2352
4.2218
4.2114
4.1766
4.0722
4.0484
4.0246
4.0013
3.7919
3.7514
1.5558
1.2914
1.2682
1.2444
1.1138
1.0906
1.0667
0.0000

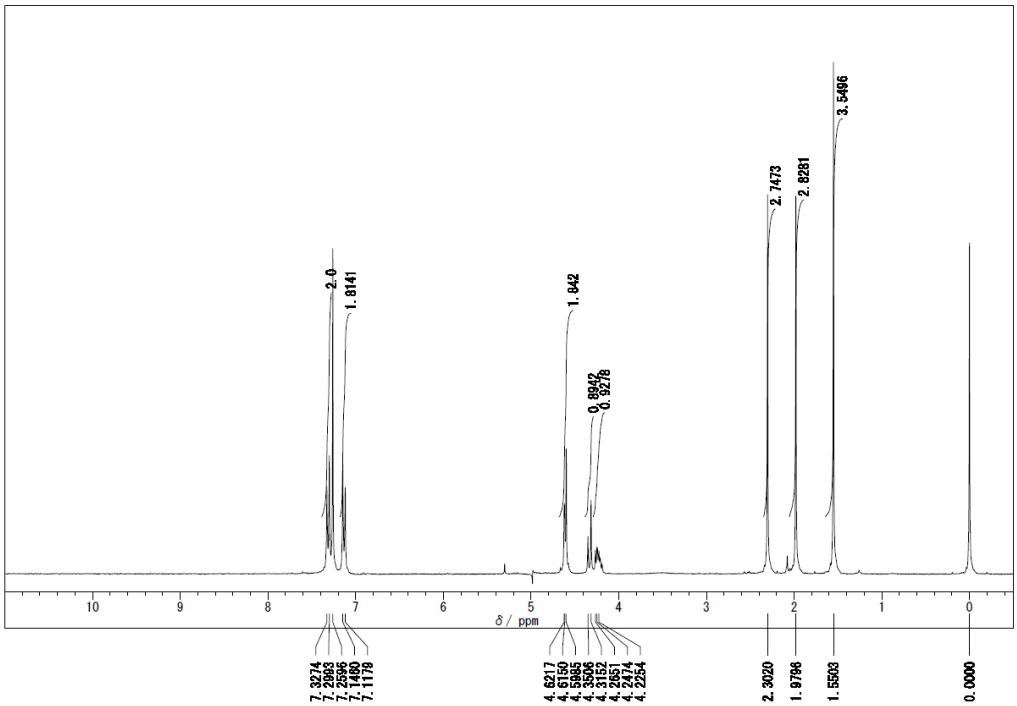


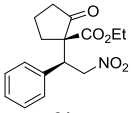
24c


2.9833
2.0312
1.9926
1.0056
0.9611
3.0
3.084
δ / ppm
7.3304
7.3078
7.2808
7.1924
7.1704
4.6474
4.6358
4.6199
4.3921
4.3561
4.2769
4.2580
4.2395
2.2953
1.9430
1.5626
0.0000

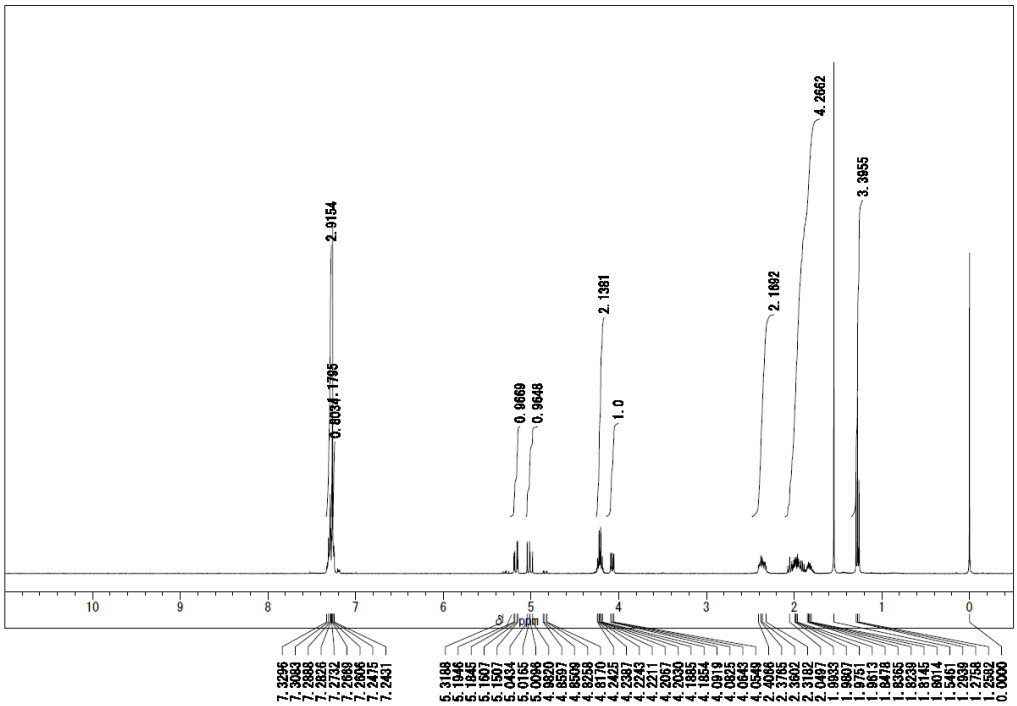

Ac
Ac
NO2
Cl

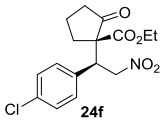
24d


2.0
1.8141
1.842
0.8942
0.9278
2.7473
2.8281
3.5496
δ / ppm
7.3274
7.2993
7.2596
7.1480
7.1178
4.6217
4.6150
4.5985
4.3506
4.3152
4.2951
4.2414
4.2254
2.3020
1.9796
1.5503
0.0000

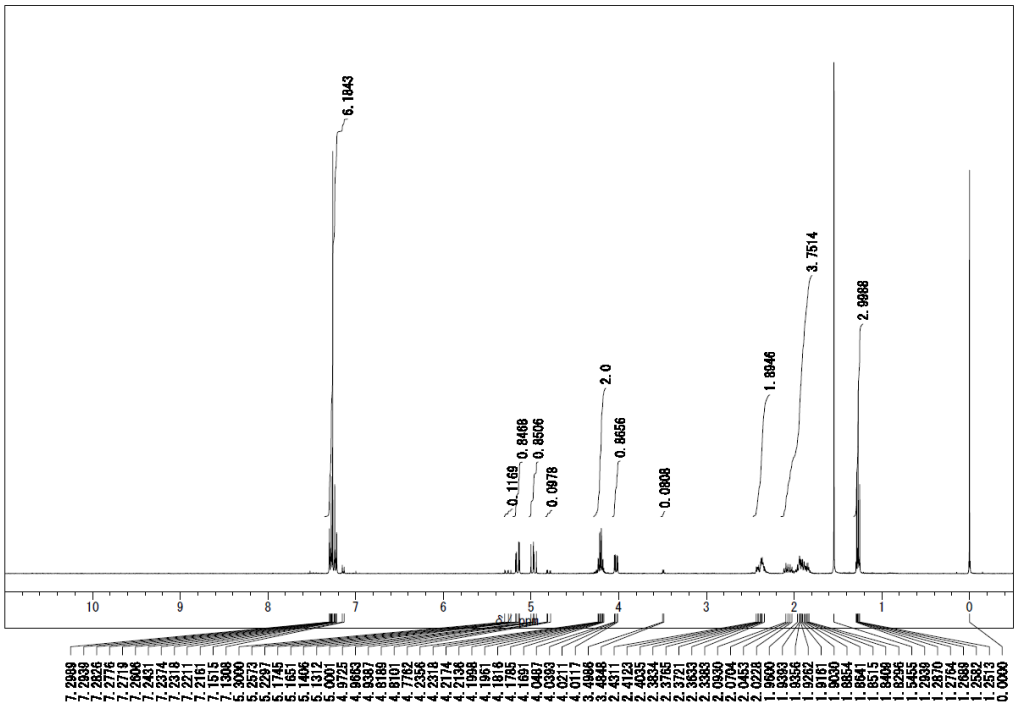

O
CO2Et
NO2

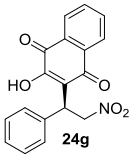
24e


2.9154
0.8034
1.1795
0.9669
0.9648
2.1381
1.0
2.1882
4.2662
3.3955
δ /ppm
7.3296
7.3083
7.2988
7.2826
7.2732
7.2596
7.2506
7.2475
7.2431
5.3198
5.1946
5.1845
5.1507
5.1507
5.0434
5.0155
5.0096
4.9820
4.8597
4.8509
4.8258
4.8170
4.7945
4.2397
4.2243
4.2211
4.2067
4.2030
4.1885
4.1854
4.0919
4.0625
4.0543
4.0549
4.0406
2.3775
2.3602
2.3192
2.0497
1.9833
1.9807
1.9751
1.9613
1.8478
1.8365
1.8239
1.8145
1.8014
1.5451
1.2951
1.2758
1.2592
0.0000

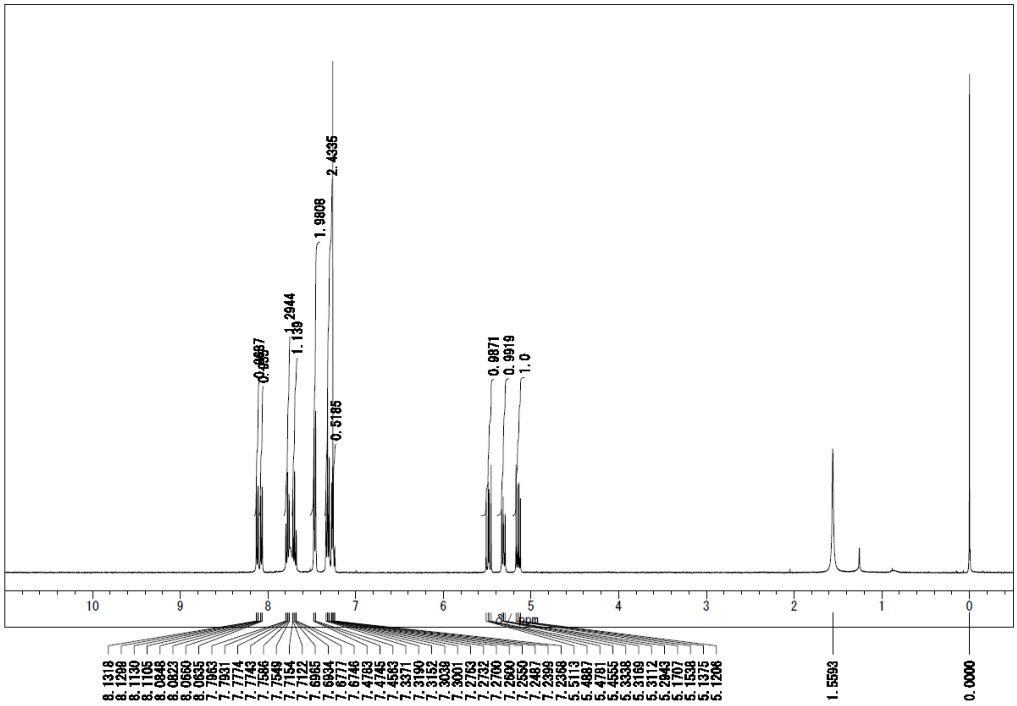


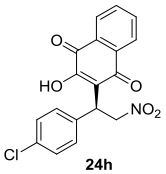
24f


6.1843
0.1169
0.8468
0.8506
0.0978
2.0
0.8656
0.0808
1.8946
3.7514
2.9988
ppm

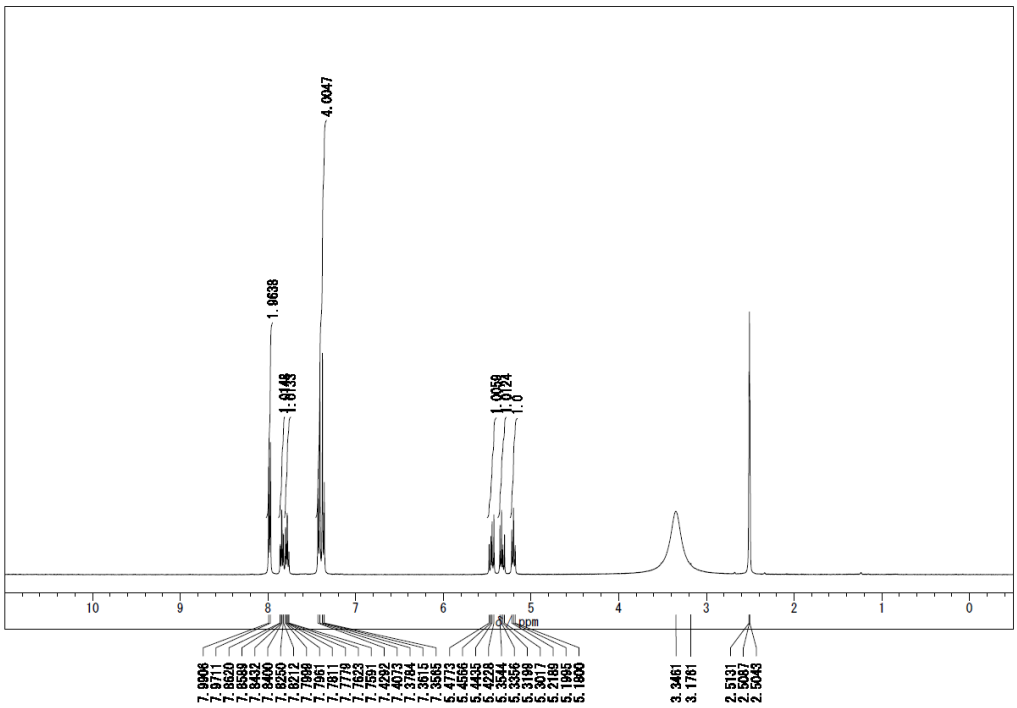


24g

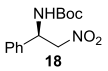

2.4335
1.9808
1.2944
1.139
0.9871
0.9919
1.0
0.5165
1.5593
0.0000
ppm

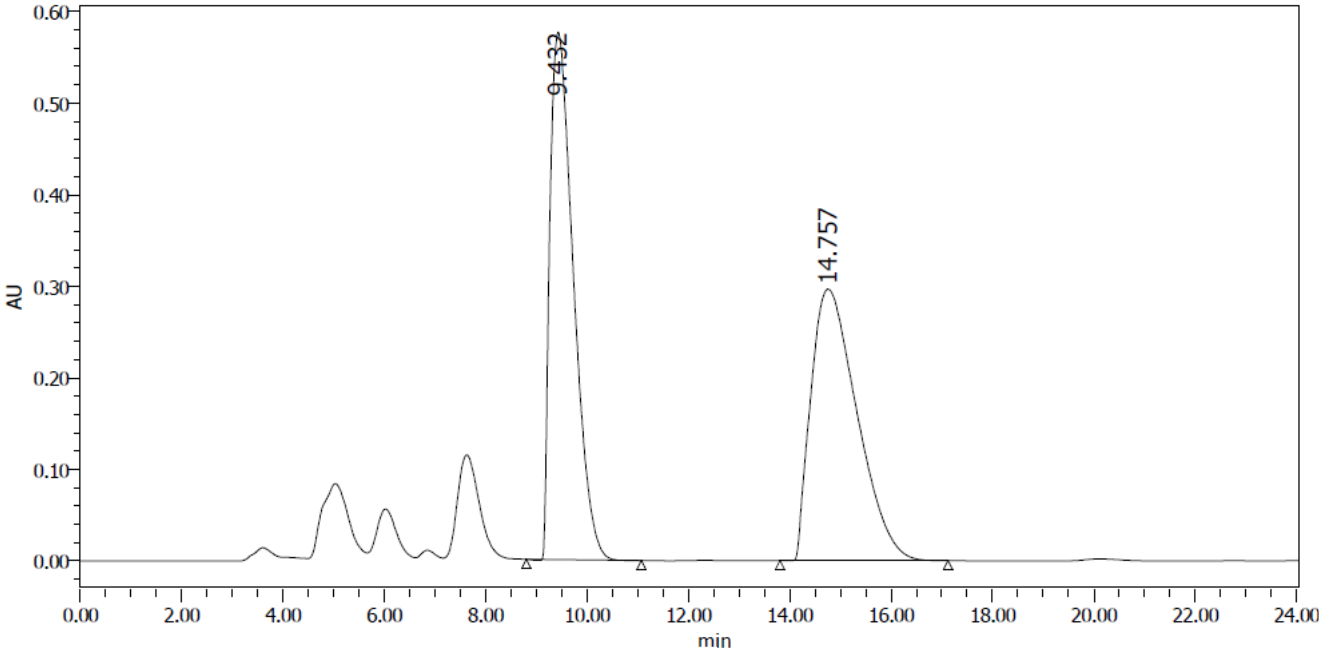

O
HO
O
NO2
Cl

24h

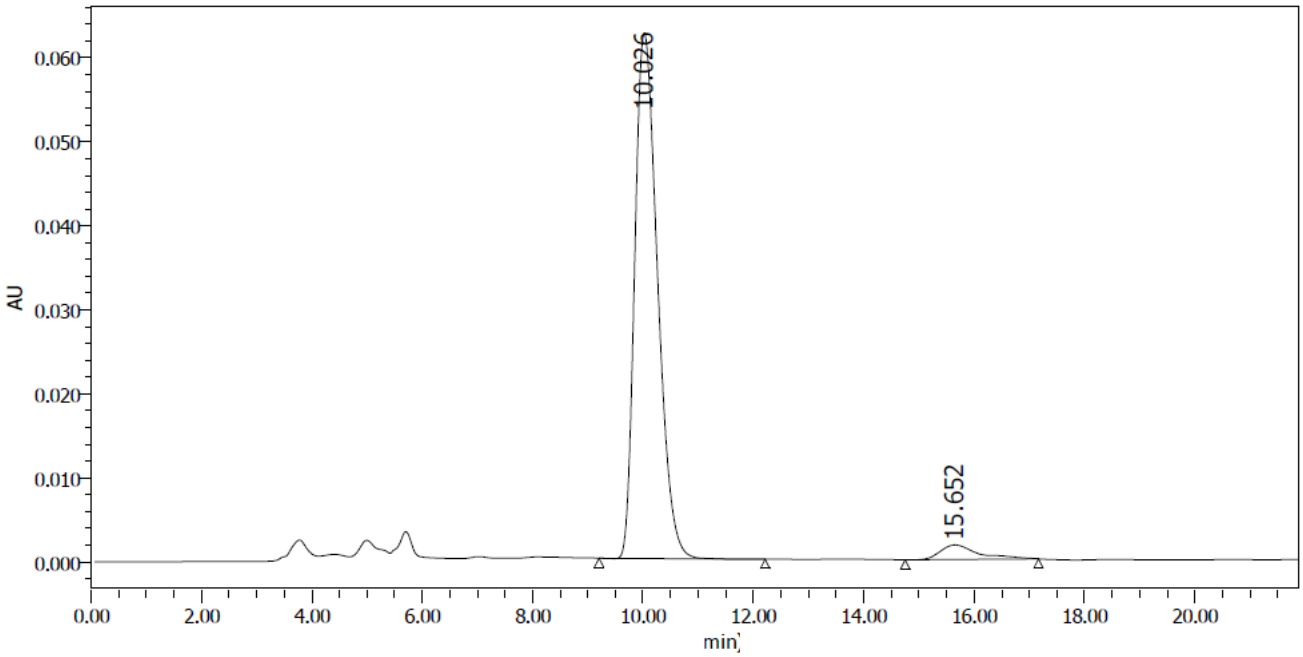

7.9906
7.9711
7.8620
7.8589
7.8432
7.8400
7.8250
7.8212
7.7986
7.7961
7.7811
7.7779
7.7623
7.7591
7.4292
7.4073
7.3784
7.3615
7.3565
5.4773
5.4566
5.4435
5.4228
5.4044
5.3356
5.3199
5.3017
5.2189
5.1995
5.1800
3.3461
3.1781
2.5131
2.5087
2.5043
1.9638
1.0058
1.0124
1.0
4.0047
10
9
8
7
6
5
4
3
2
1
0
ppm

8. Chiral HPLC charts

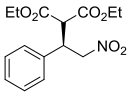




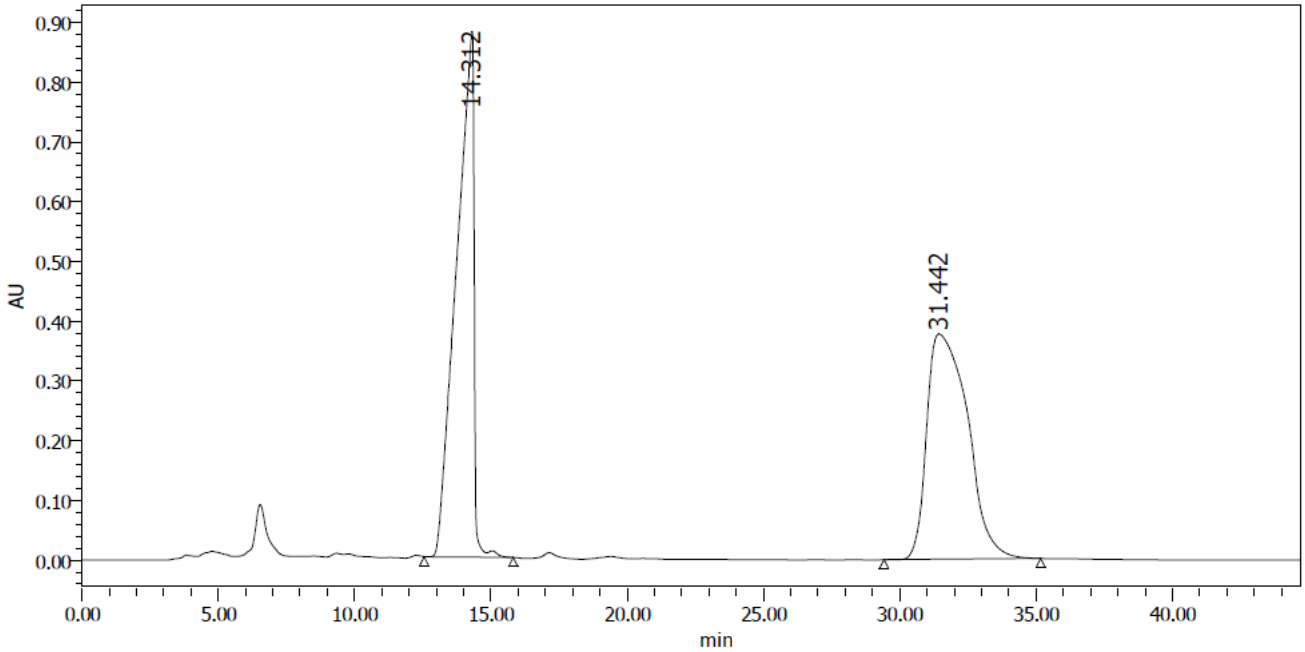
	retention time (min)	area (μV·sec)	%area
1	9.432	18549903	49.79
2	14.757	18706418	50.21



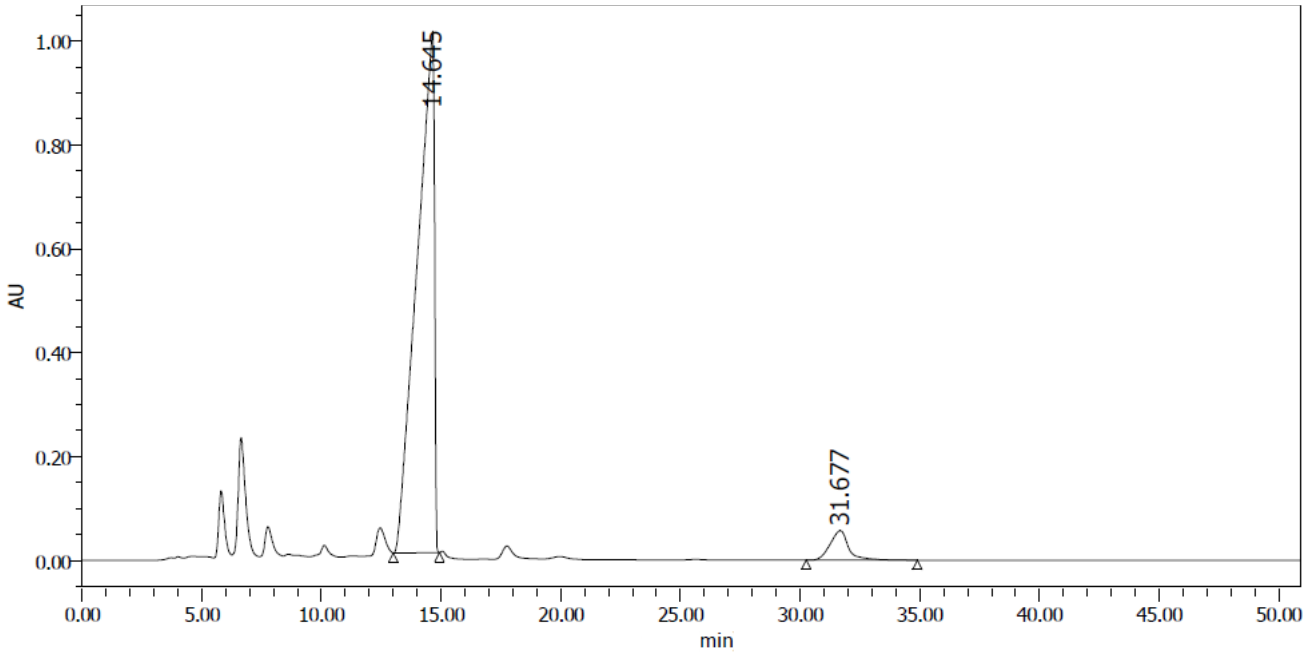
	retention time (min)	area (μV·sec)	%area
1	10.026	1791220	95.57
2	15.652	82932	4.43



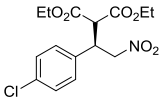
24a



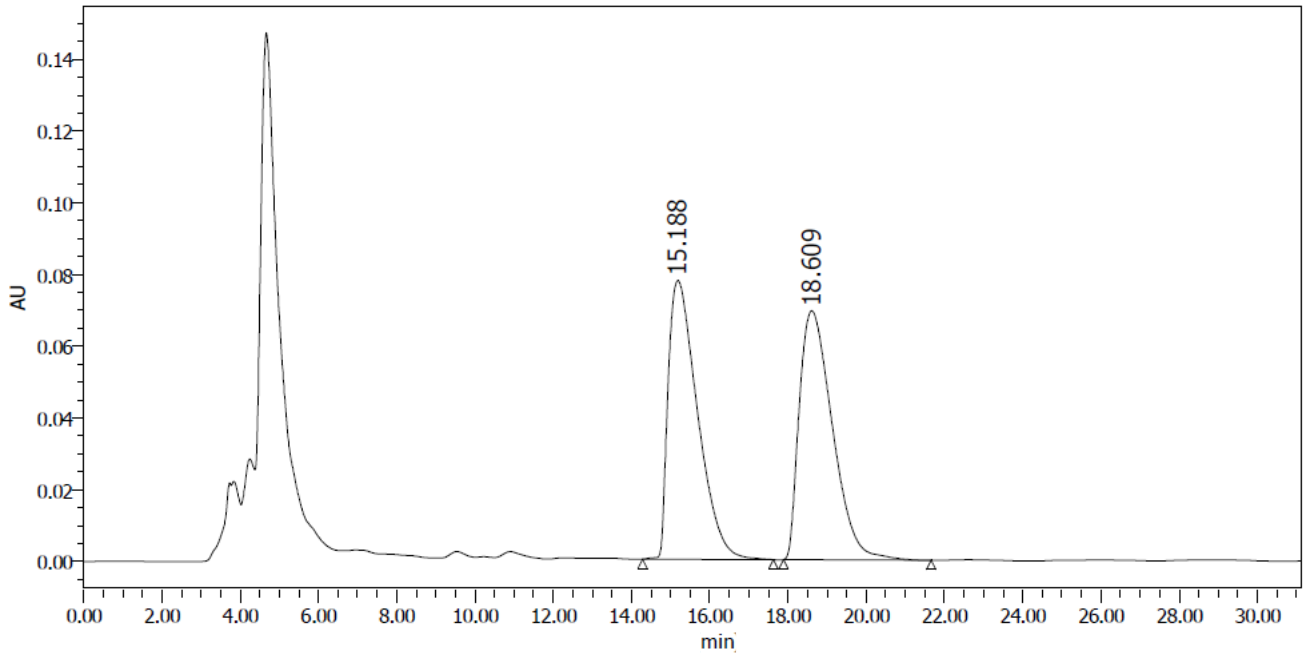
	retention time (min)	area (μV·sec)	%area
1	14.312	39320024	50.07
2	31.442	39212689	49.93



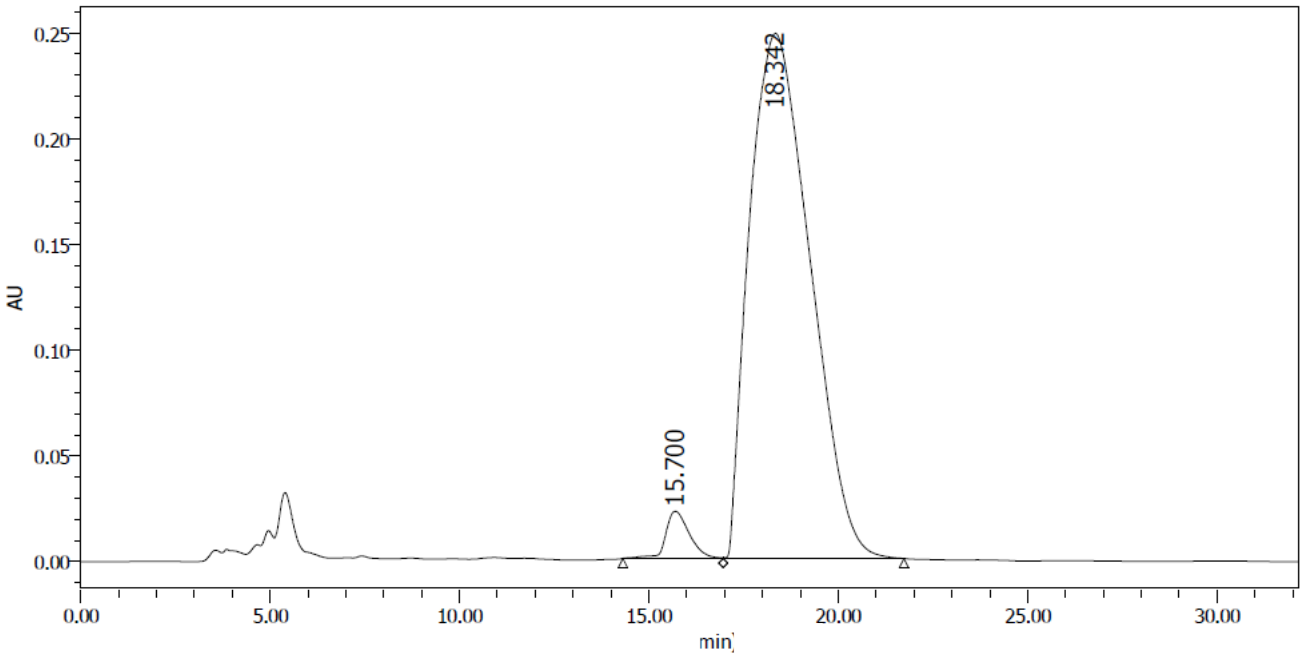
	retention time (min)	area (μV·sec)	%area
1	14.645	50196160	94.27
2	31.677	3051195	5.73



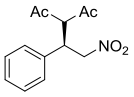
24b



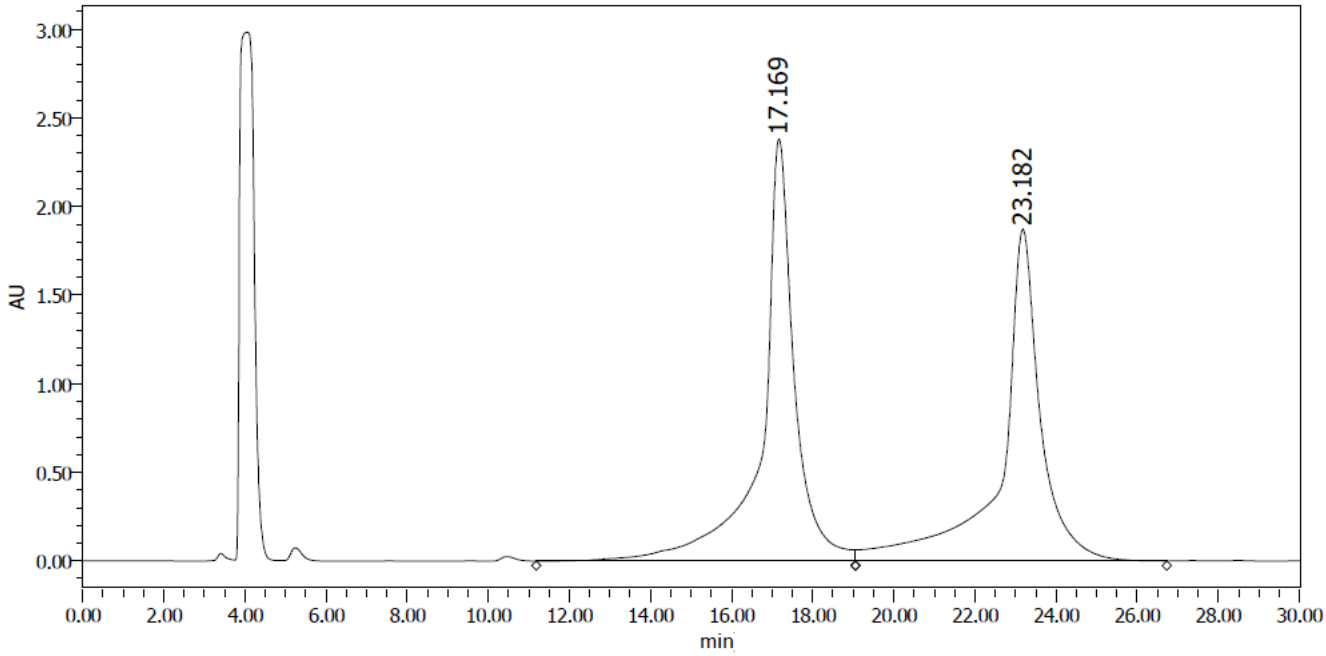
	retention time (min)	area (μV·sec)	%area
1	15.188	4045874	49.73
2	18.609	4090509	50.27



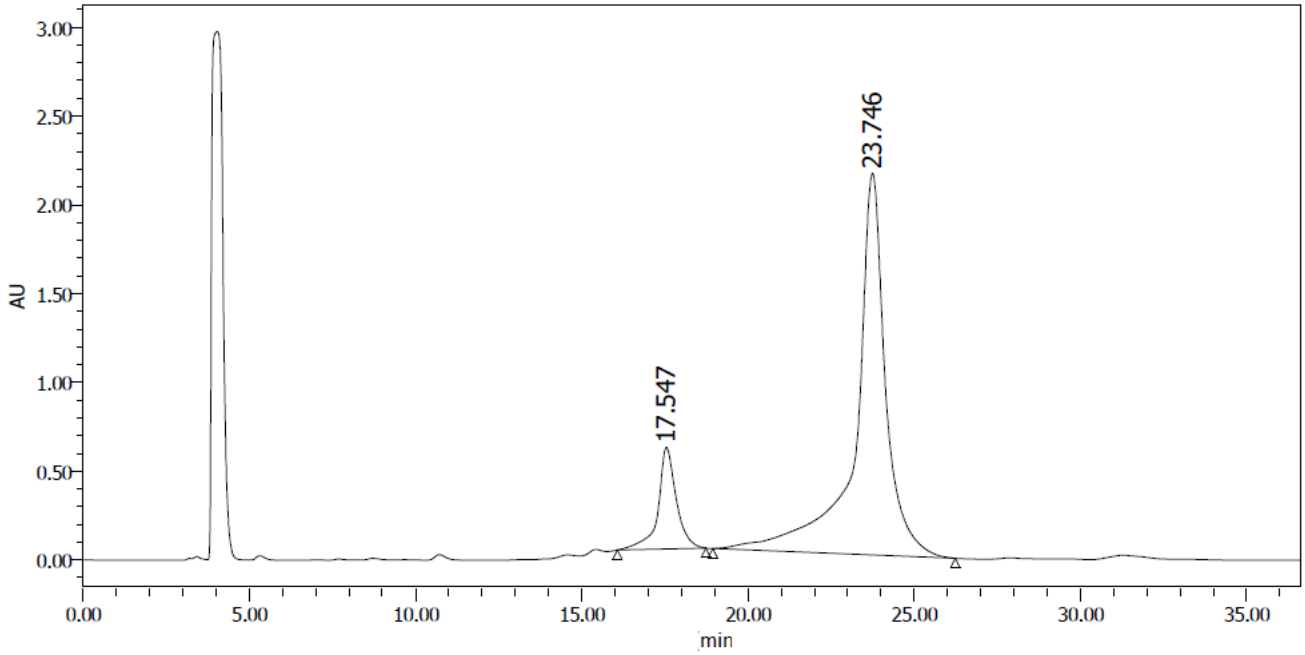
	retention time (min)	area (μV·sec)	%area
1	15.700	970233	3.40
2	18.342	27597869	96.60



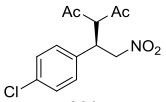
24c



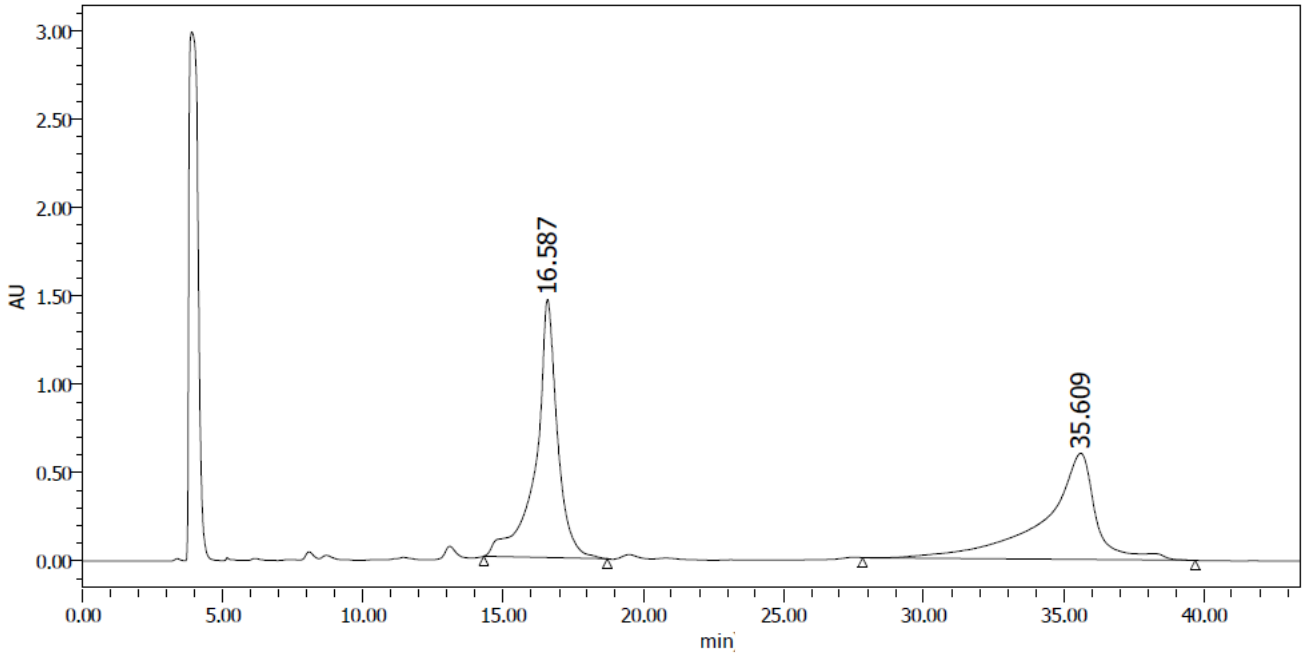
	retention time (min)	area (μV·sec)	%area
1	17.169	133549879	51.09
2	23.182	127852254	48.91



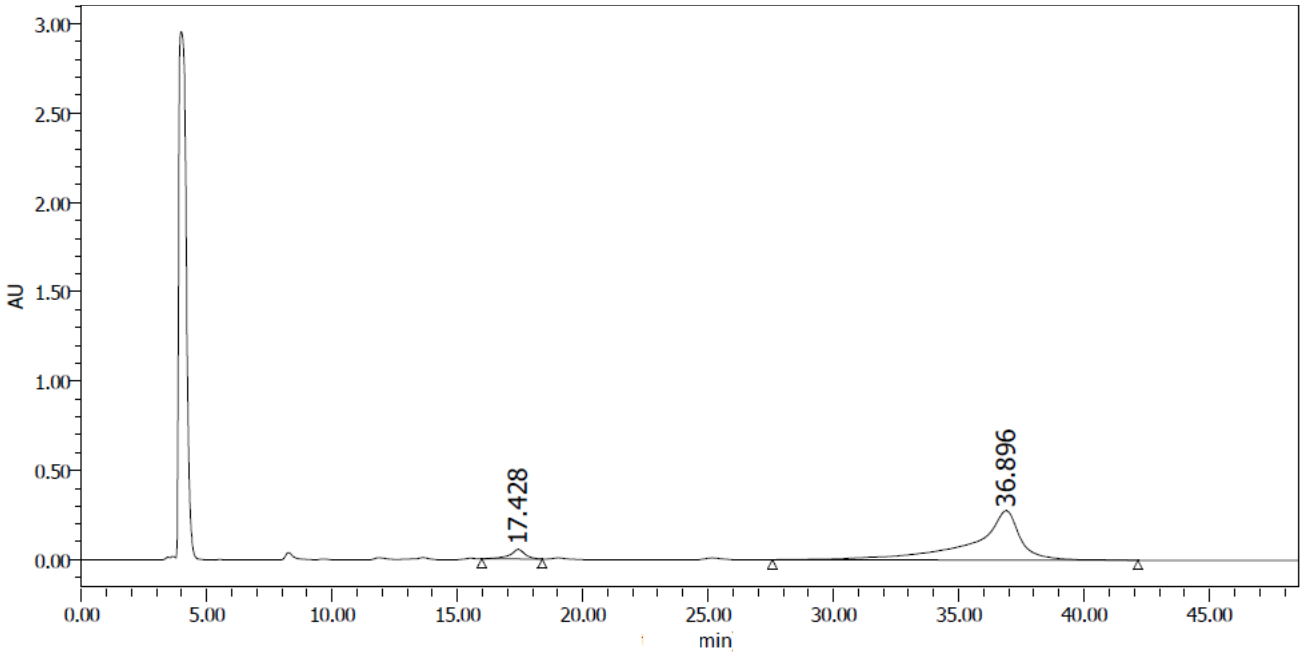
	retention time (min)	area (μV·sec)	%area
1	17.547	21837782	13.78
2	23.746	136665082	86.22



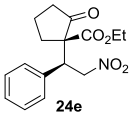
24d



	retention time (min)	area (μV·sec)	%area
1	16.587	78861172	50.63
2	35.609	76891263	49.37



	retention time (min)	area (μV·sec)	%area
1	17.428	2201827	5.75
2	36.896	36072372	94.25



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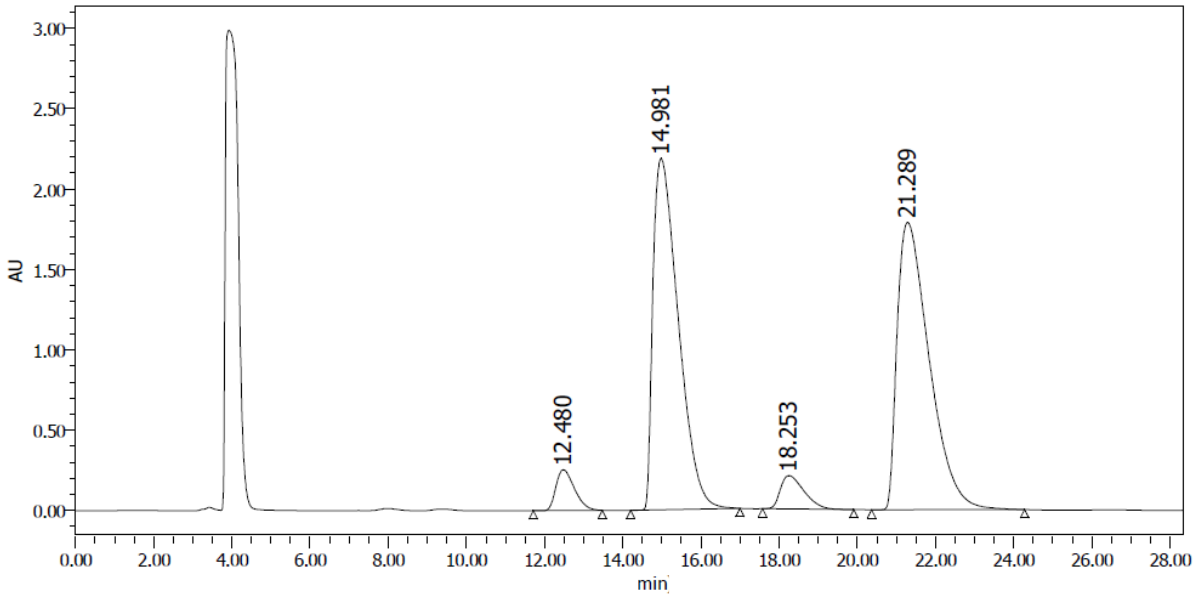
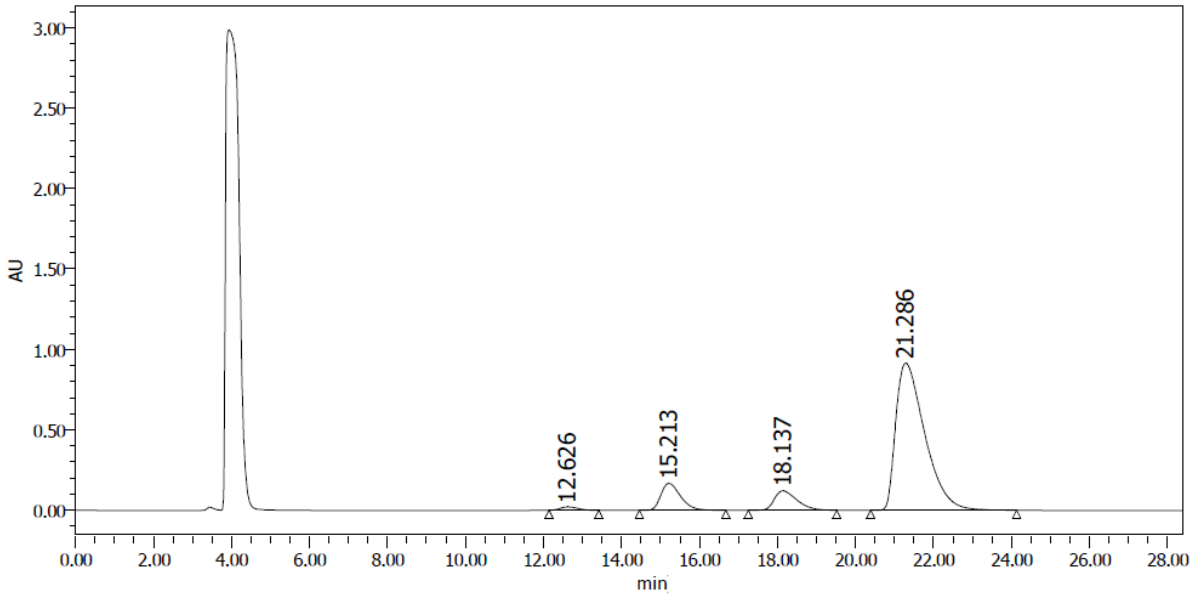
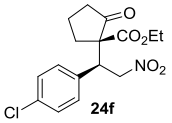


	retention time (min)	area (μV·sec)	%area
1	12.480	8318638	3.83
2	14.981	98494839	45.31
3	18.253	8761458	4.03
4	21.289	101799188	46.83



	retention time (min)	area (μV·sec)	%area
1	12.626	629814	1.08
2	15.213	5809318	9.92
3	18.137	4808431	8.21
4	21.286	47286670	80.78



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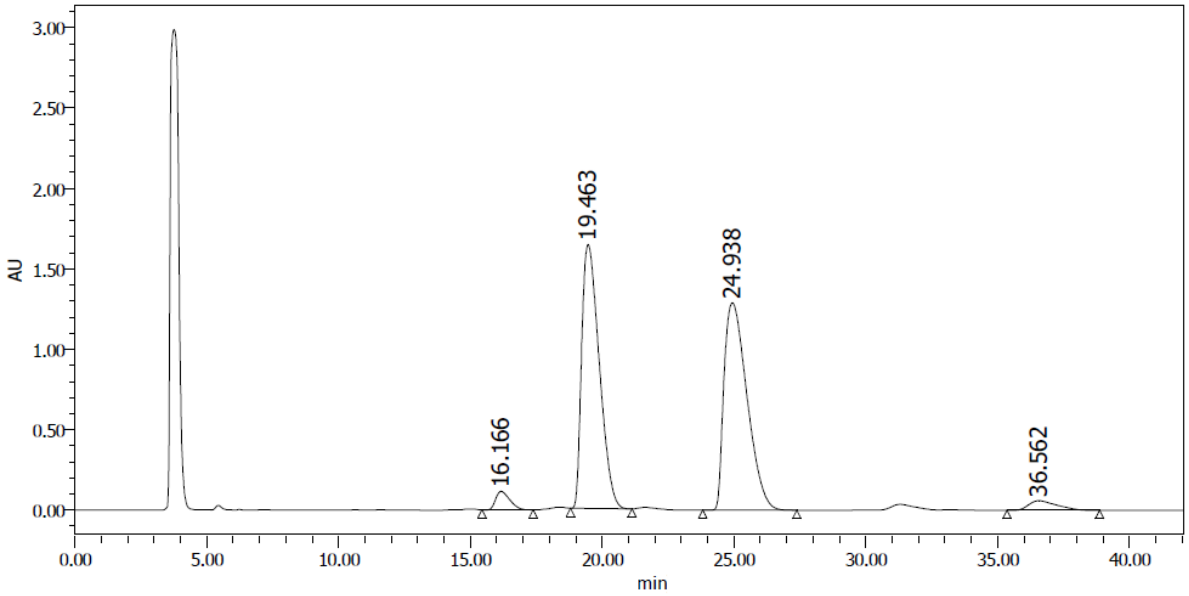
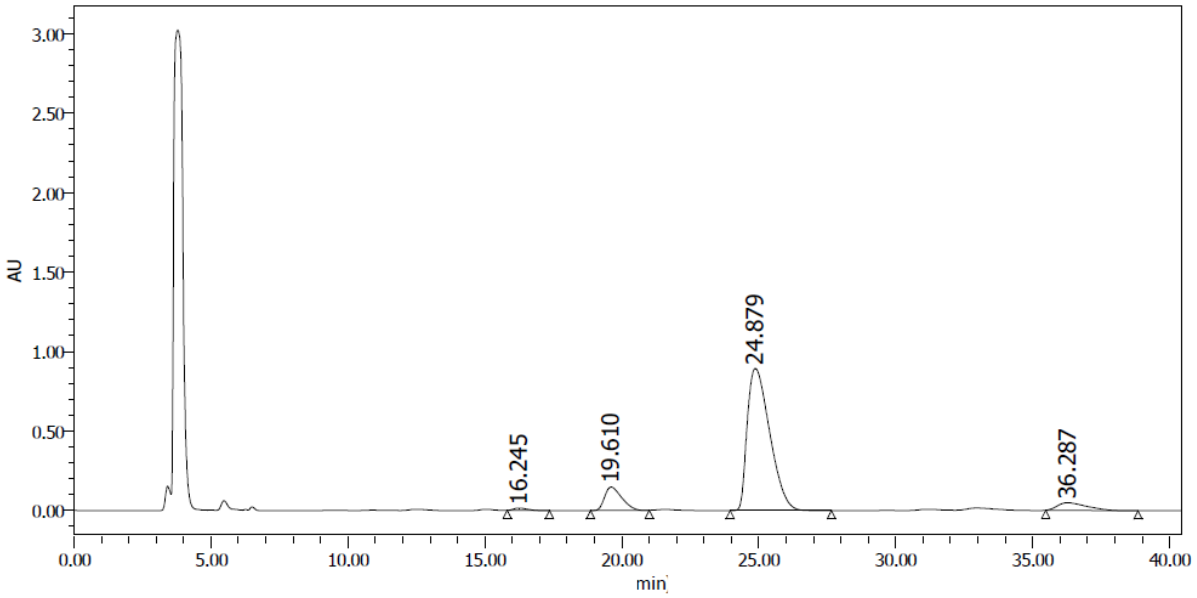
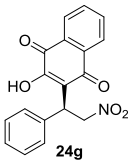


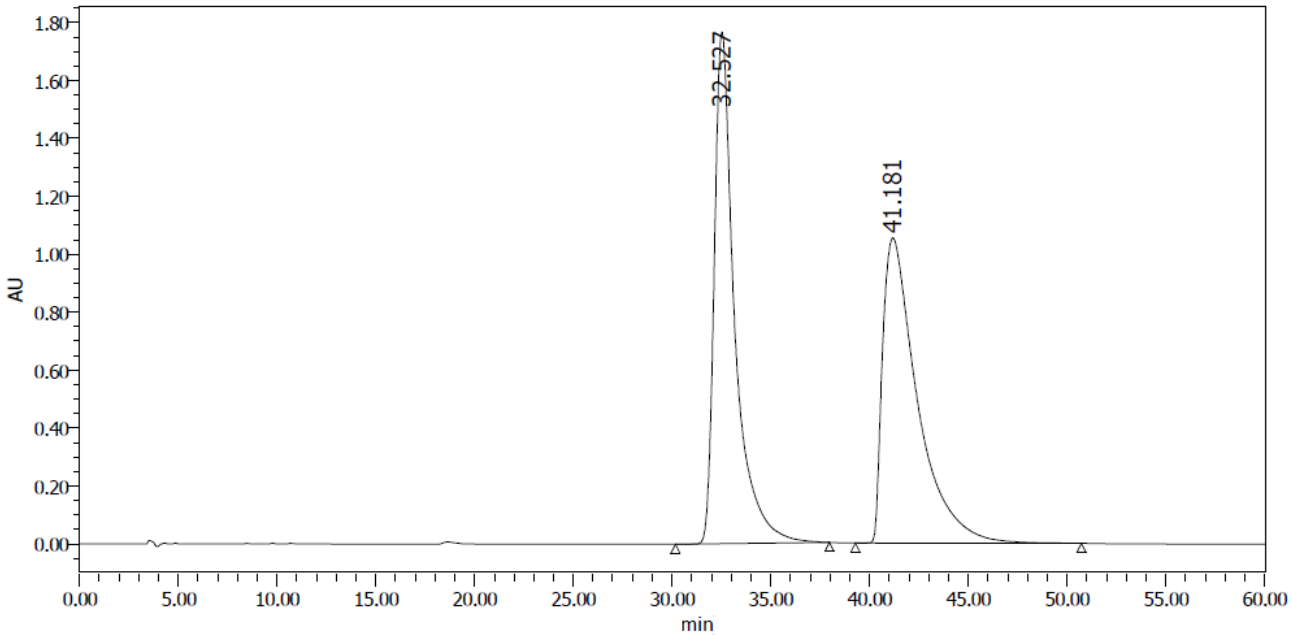
	retention time (min)	area (μV·sec)	%area
1	16.166	4185209	2.57
2	19.463	76073857	46.68
3	24.938	78193364	47.98
4	36.562	4502841	2.76



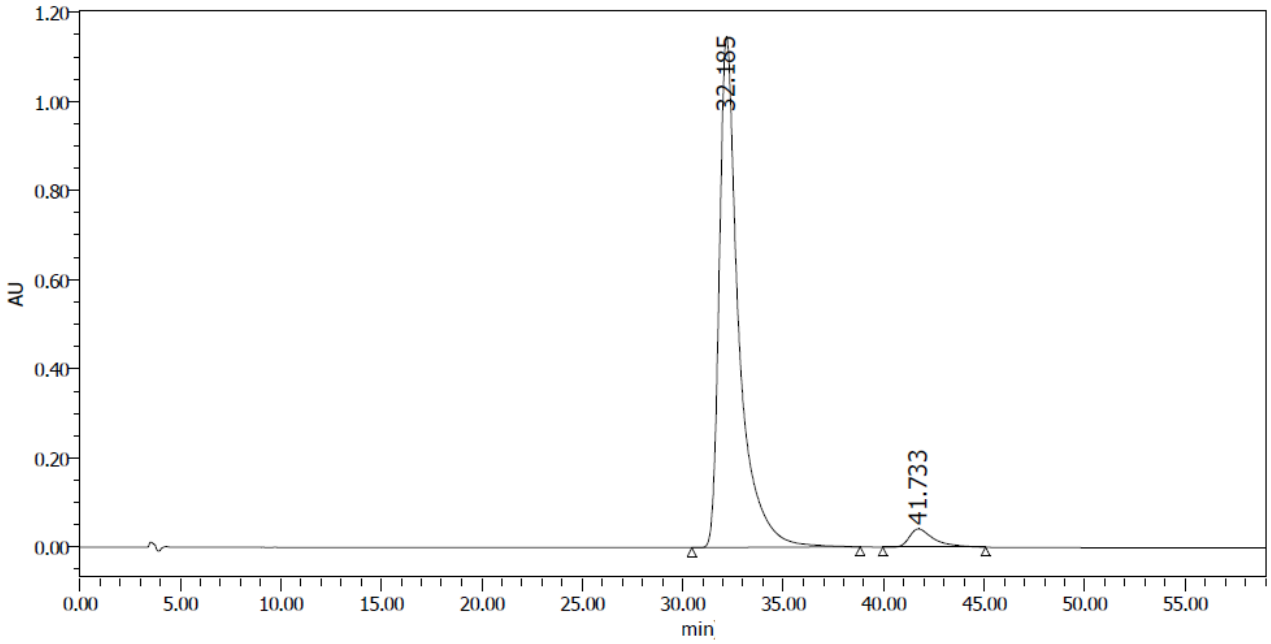
	retention time (min)	area (μV·sec)	%area
1	16.245	519052	0.84
2	19.610	6352117	10.34
3	24.879	50997074	83.01
4	36.287	3564672	5.80



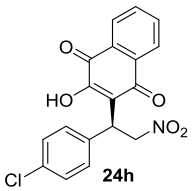
24g



	retention time (min)	area (μV·sec)	%area
1	32.527	127069635	49.58
2	41.181	129221687	50.42



	retention time (min)	area (μV·sec)	%area
1	32.185	77573419	95.75
2	41.733	3447324	4.25



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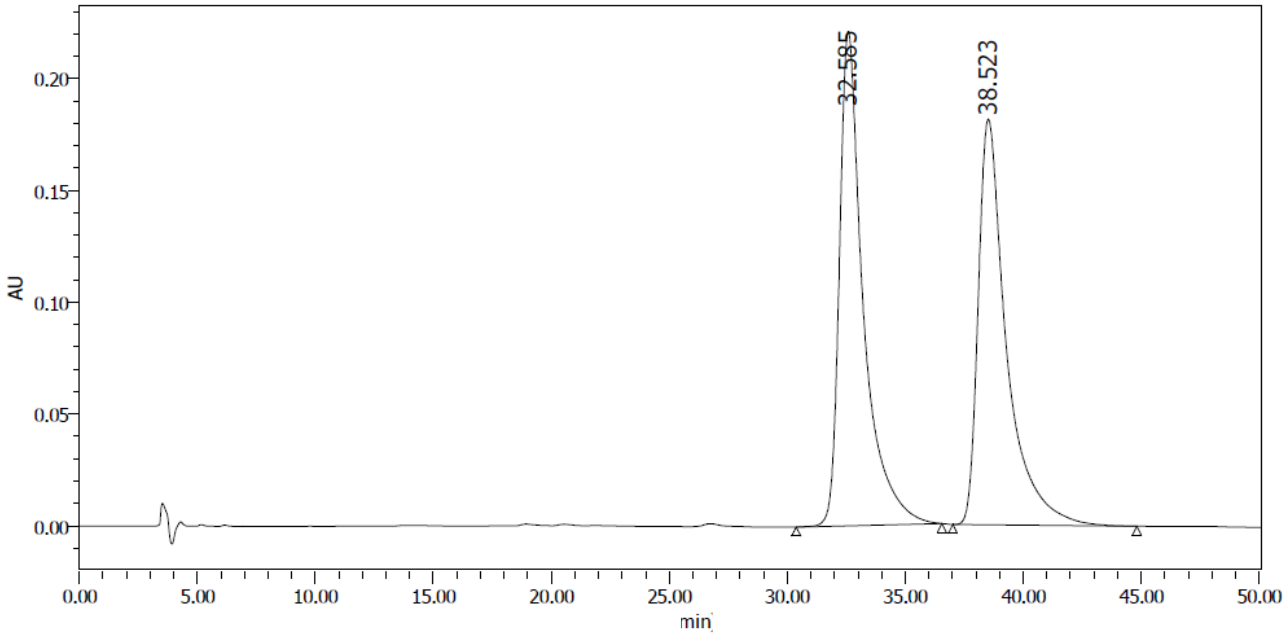
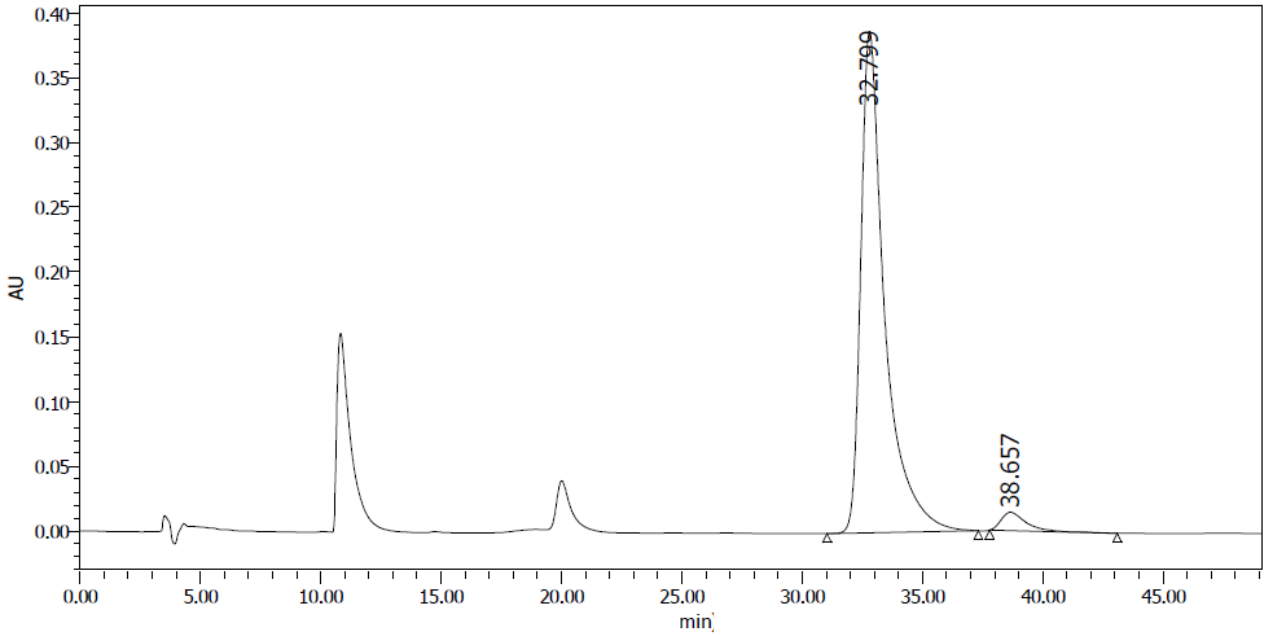


	retention time (min)	area (μV·sec)	%area
1	32.585	15561759	50.75
2	38.523	15101655	49.25



	retention time (min)	area (μV·sec)	%area
1	32.799	26823139	96.32
2	38.657	1023801	3.68