Electronic Supplementary Material (ESI) for RSC Advances.

Magnetic nanoparticles (MNPs)-supported 9-amino(9-deoxy)*epi*-quinidine organocatalyst for asymmetric α-amination of aldehydes

Tao Wu, Dandan Feng, Guangxin Xie and Xuebing Ma*

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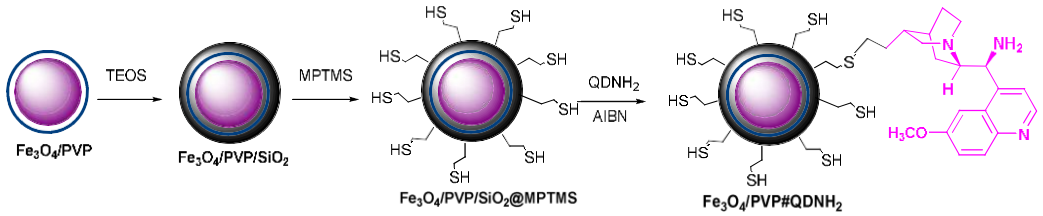
1. Preparation of Fe_3O_4/PVP#$QDNH_2$



Fe_3O_4/PVP (0.25 g) was well-dispersed in 50 mL of ethanol under ultrasound irradiation, added aqueous ammonia (1.5 mL, 23%) and tetraethyl orthosilicate (0.24 g, 1.2 mmol). After being stirred at room temperature for 3 h, MPTMS (0.26 g, 1.3 mmol) was added slowly and stirred for another 24 h. Fe_3O_4/PVP/SiO_2@MPTMS (0.44 g) was obtained by being separated magnetically, washed with ethanol (25 mL × 3) and dried at 60 °C under vacuum for 8 h. Under a N_2 atmosphere, a mixture of Fe_3O_4/PVP/SiO_2@ MPTMS (0.44 g), $QDNH_2$ (0.32 g, 1.0 mmol) and AIBN (41.0 mg, 0.25mmol, once a day) in 15 mL of $CHCl_3$ was refluxed for four days and cooled to room temperature. The mousy Fe_3O_4/PVP#$QDNH_2$ (0.5 g) was separated magnetically, washed with $CHCl_3$ (20 mL × 3), ethanol (25 mL × 3) and dried at 50 °C under vacuum for 4 h. Based on the nitrogen content determined by elemental analysis, the loaded capacity of $QDNH_2$ was 0.39 mmol g^{-1}.

The molar ratio of $QDNH_2$-attached thioether (–S–) and free sulfydryl (–SH) in the outermost shell of various heterogeneous organocatalyst covered on TEOS-modified Fe_3O_4/PVP could be ascertained by the contents of N and S elements and shown in Table s1.

Table S1 The molar ratio of $QDNH_2$-attached thioether (–S–) and free sulfydryl (–SH) in the outermost shell of TEOS-modified Fe_3O_4/PVP

Cat.	N (%)	S (%)	Molar ratio[a] (*m*/*n*)	Weight loss (%[b]/%[c])
Fe_3O_4/PVP#$QDNH_2$	1.62	6.58	1/4.3	19.7/22.9
Fe_3O_4/PVP@$QDNH_2$(1)	1.42	3.99	1/1.8	-
Fe_3O_4/PVP@$QDNH_2$(2)	1.93	5.35	1/2.6	-
Fe_3O_4/PVP@$QDNH_2$(3)	2.50	8.00	1/3.2	30.2/32.1
Fe_3O_4/PVP@$QDNH_2$(4)	1.97	6.06	1.3.0	-

[a] Molar ratio of thioether and free sulfydryl based on elemental analysis of N and S. [b] Weight loss calculated from elemental analysis. [c] Weight loss detected by TGA in the 150–800 °C range.

1. IR spectra

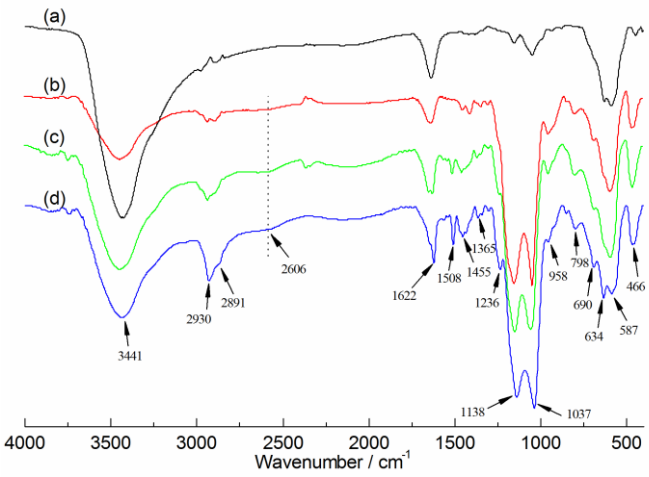


Fig. S1 IR spectra of Fe_3O_4/PVP (a), Fe_3O_4/PVP/SiO_2@MPTMS (b), Fe_3O_4/PVP#$QDNH_2$ (c) and Fe_3O_4/PVP@$QDNH_2$(3) (d)

2. TGA

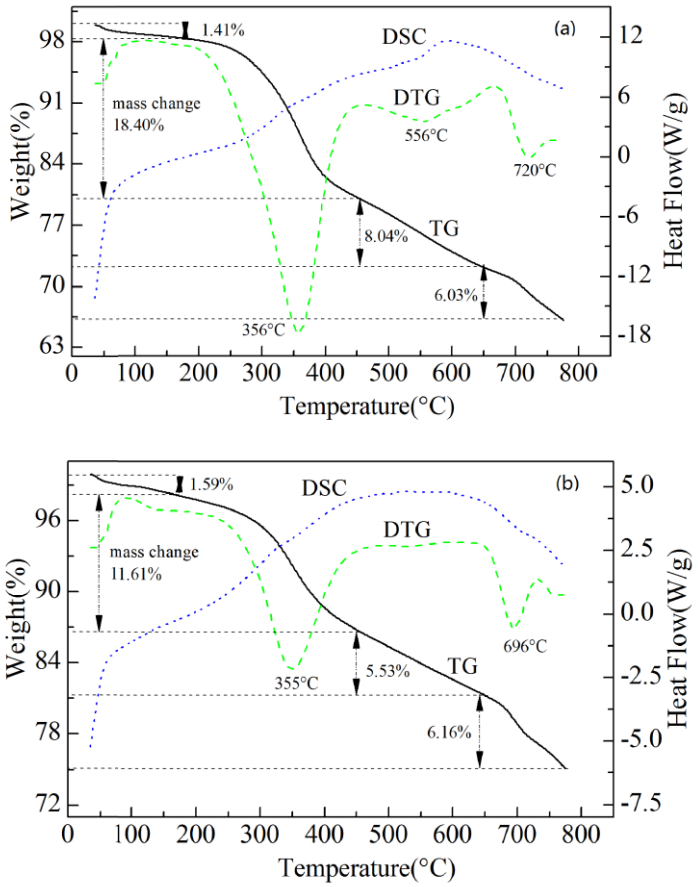
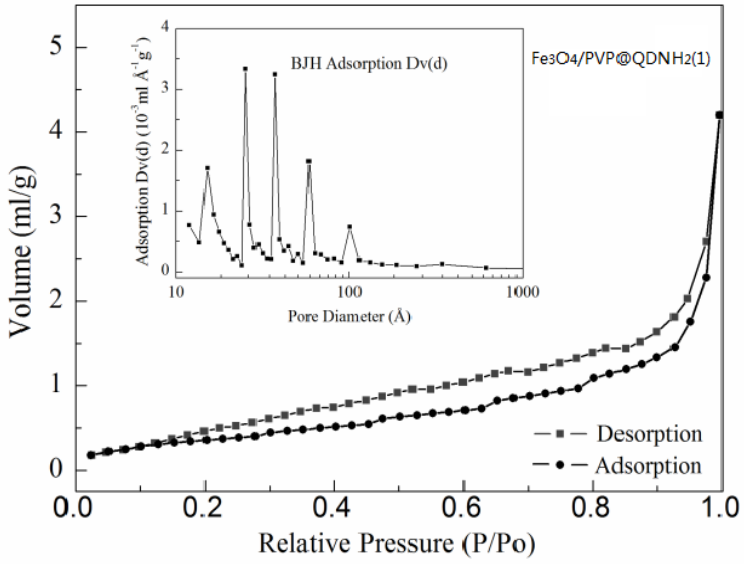
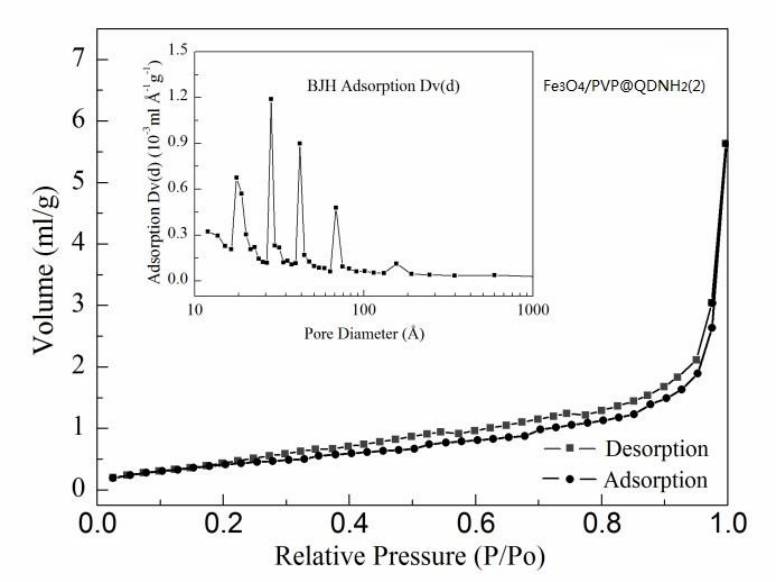
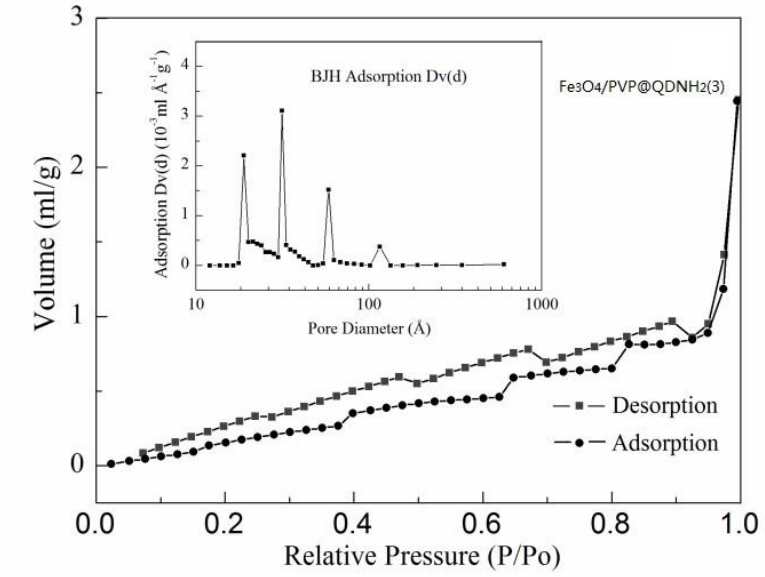


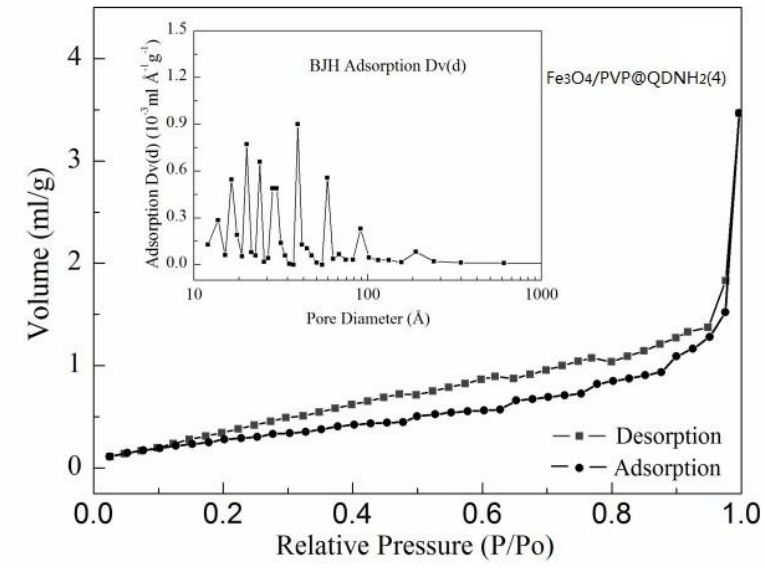
Fig. S2 Thermogravimetric curves of Fe_3O_4/PVP@QDNH$_2$(3) (a), Fe_3O_4/PVP#QDNH$_2$ (b)

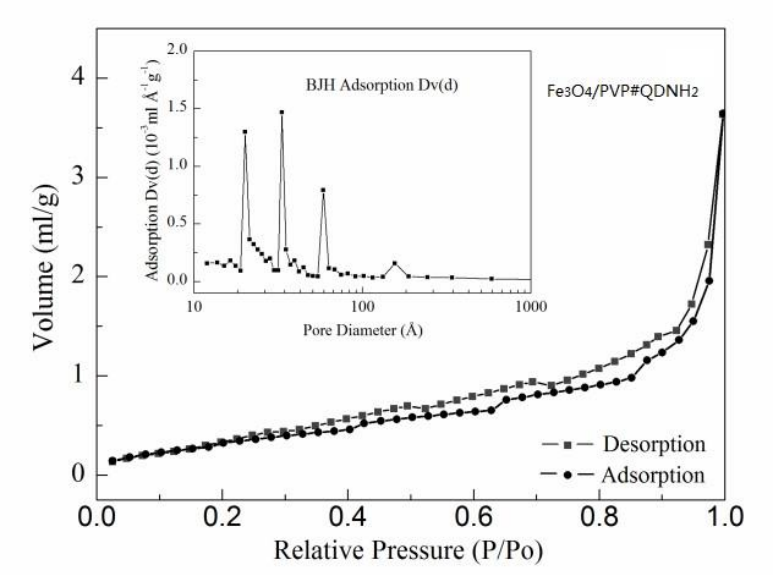
3. N_2 adsorption-desorption isotherm

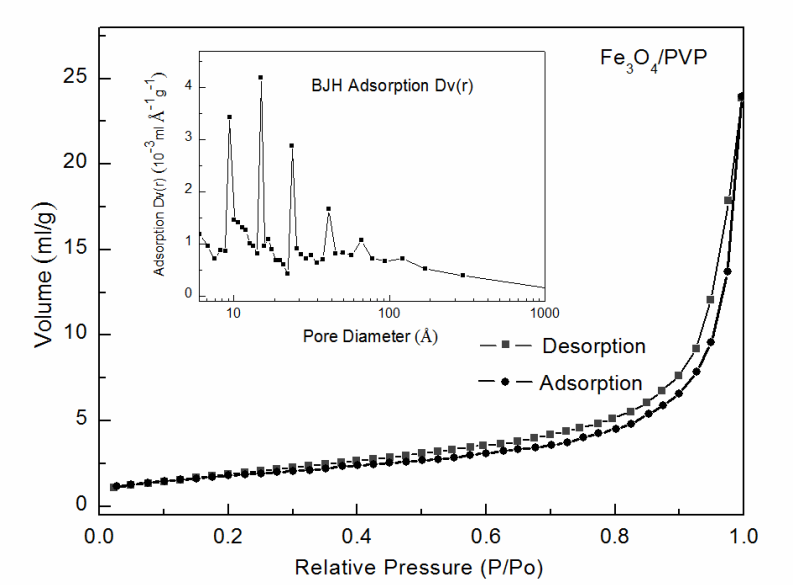



BJH Adsorption Dv(d)
Fe3O4/PVP@QDNH2(2)
Adsorption Dv(d) (10-3 ml Å-1 g-1)
Pore Diameter (Å)
Volume (ml/g)
Relative Pressure (P/Po)
Desorption
Adsorption

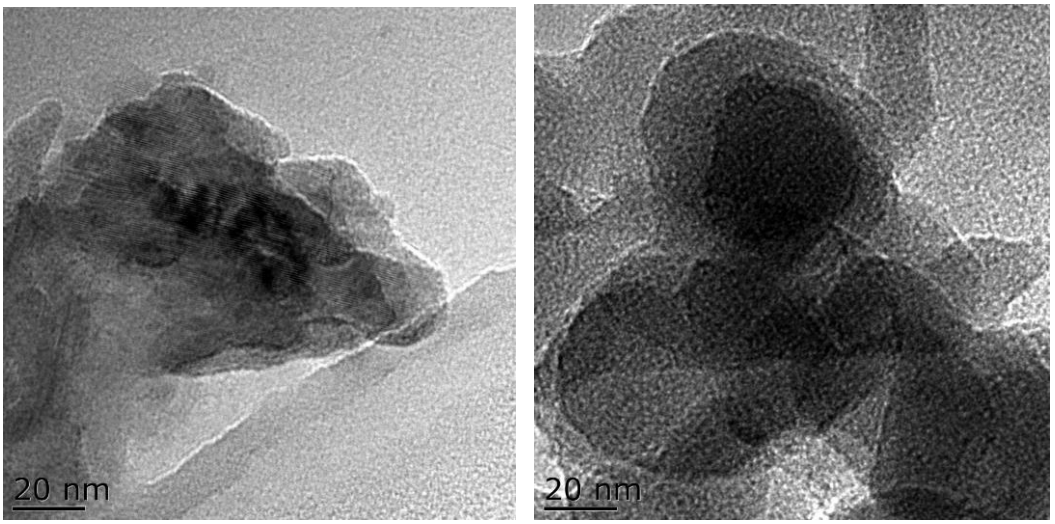

BJH Adsorption Dv(d)
Fe3O4/PVP@QDNH2(3)
Adsorption Dv(d) (10-3 ml Å-1 g-1)
Pore Diameter (Å)
Volume (ml/g)
Relative Pressure (P/Po)
Desorption
Adsorption

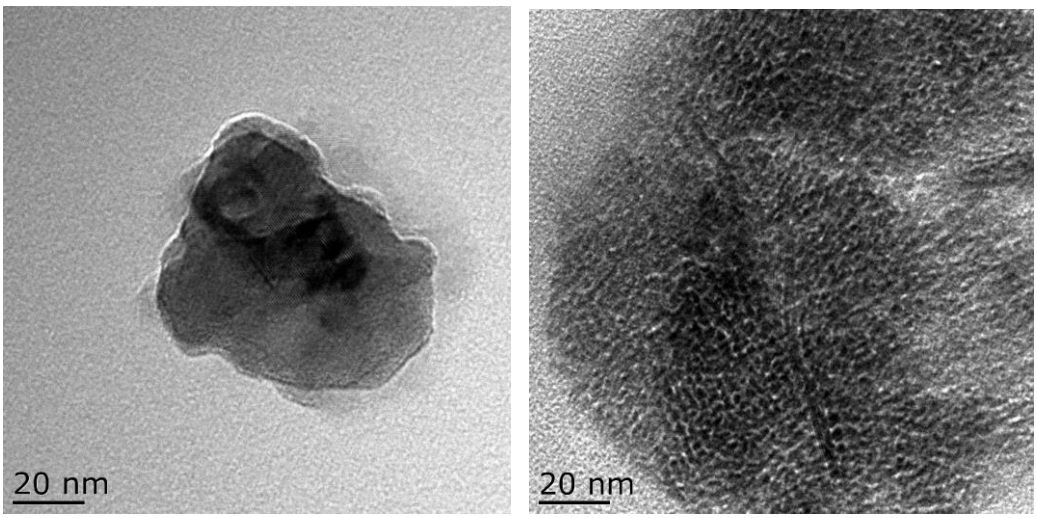

BJH Adsorption Dv(d)
Fe3O4/PVP@QDNH2(4)
Adsorption Dv(d) (10-3 ml Å-1 g-1)
Pore Diameter (Å)
Volume (ml/g)
Relative Pressure (P/Po)
Desorption
Adsorption





4. The core-shelled morphologies of Fe_3O_4/PVP@QDNH$_2$(3)





5. The characterization of raw materials

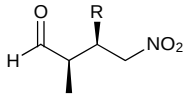
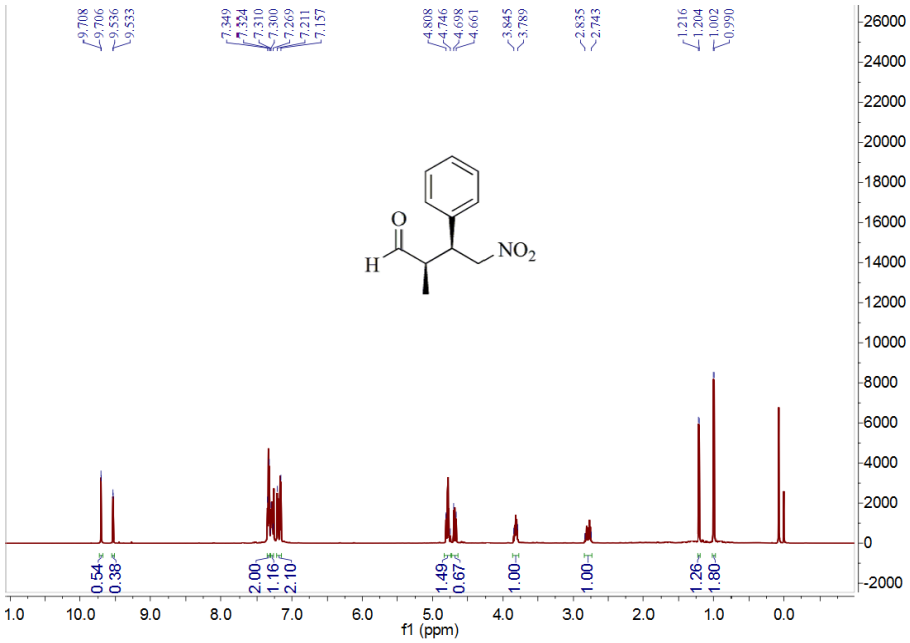
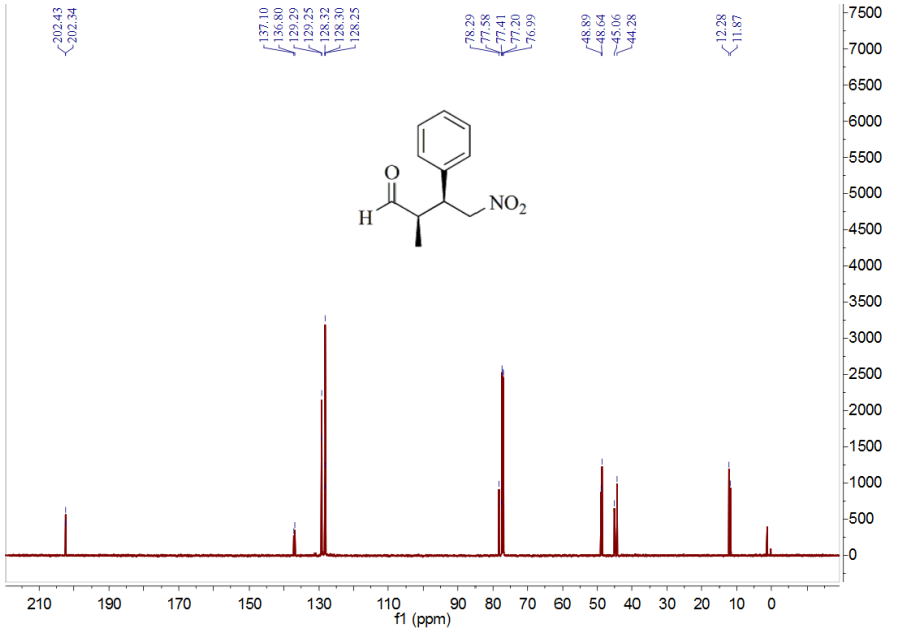


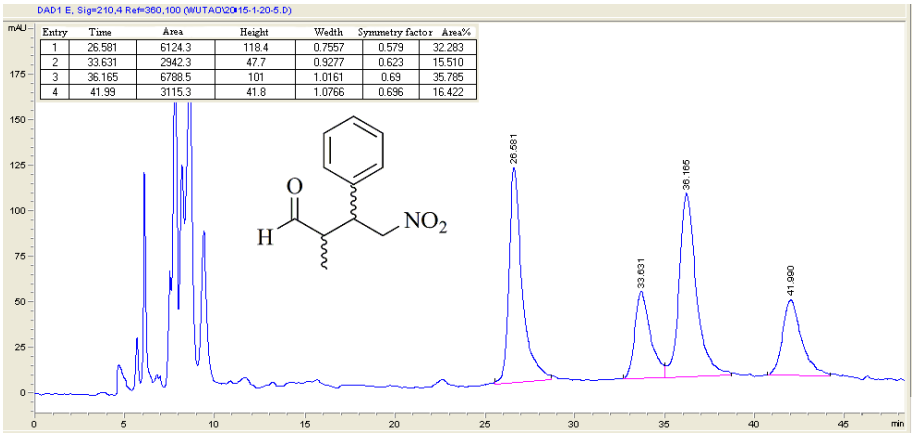
Table S2 The properties of (2R, 3S)-2-methyl-4-nitro-3-phenylbutanal and its derivatives

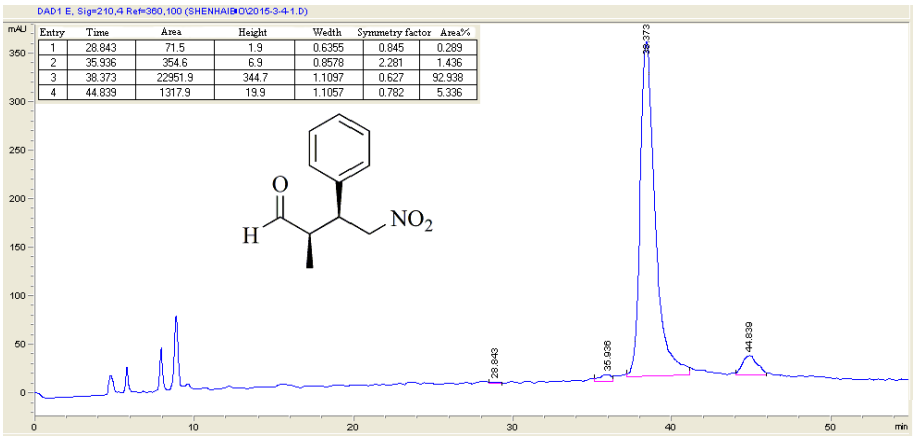
R	*Syn/Anti*	%ee *Syn*
Ph	93:7	>99
4-FPh	96:4	99
4-ClPh	96:4	>99
4-BrPh	95:5	>99
4-CH_3OPh	99:1	>99
3-CH_3OPh	96:4	98
3-CH_3Ph	94:6	>99
2-ClPh	87:13	96
2-CH_3OPh	92:8	98
2-CH_3Ph	94:6	99
1-Naphthyl	91:9	>99
2-Furyl	89:11	98

(2R, 3S)-2-methyl-4-nitro-3-phenylbutanal: *syn/anti* = 93:7, >99% ee *syn*, %ee *syn* was determined by HPLC analysis on Daicel Chiralpak OD-H column: heptane/*i*-PrOH = 80/20, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 28.8 min (minor), t_R = 38.4 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.00 (d, *J* = 7.3 Hz, 3H, C*H*$_3$), 2.74-2.84 (m, 1H, C*H*CH$_3$), 3.79-3.85 (m, 1H, C*H*CH$_2$), 4.77-4.81 (m, 2H, C*H*$_2$), 7.16–7.21 (m, 2H, Ph*H*), 7.27-7.30 (m, 1H, Ph*H*), 7.32-7.35 (m, 2H, Ph*H*), 9.71 (d, *J* = 1.5 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.3 (*C*H$_3$), 44.3 (*C*HCH$_2$), 48.6 (*C*HCH$_3$), 78.3 (*C*H$_2$), 128.2, 128.3, 129.2, 129.3, 136.8 (Ph), 202.3 (*C*HO).

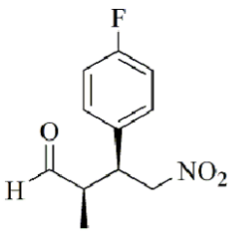


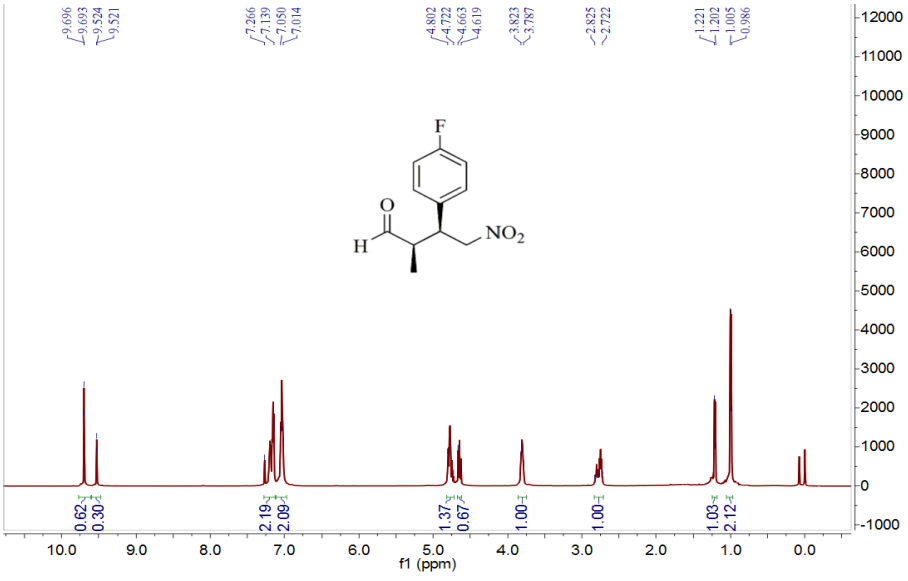


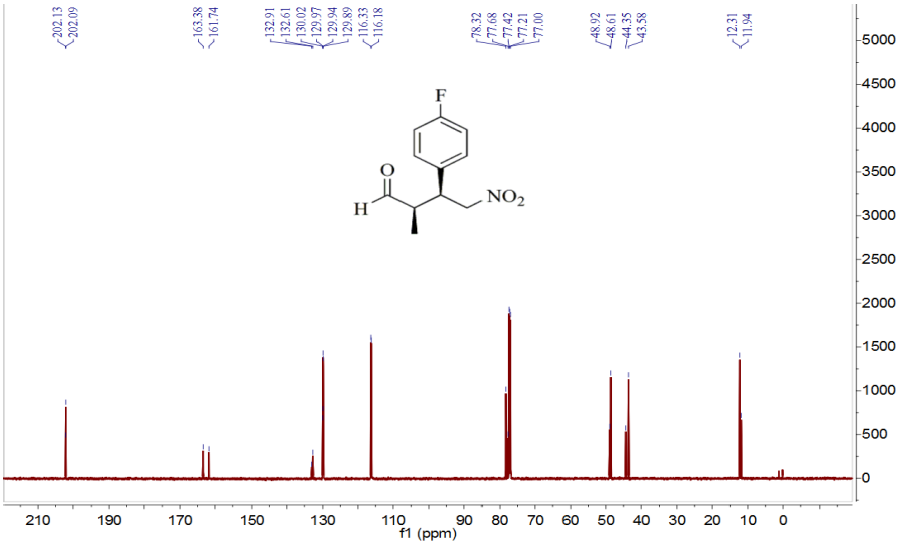


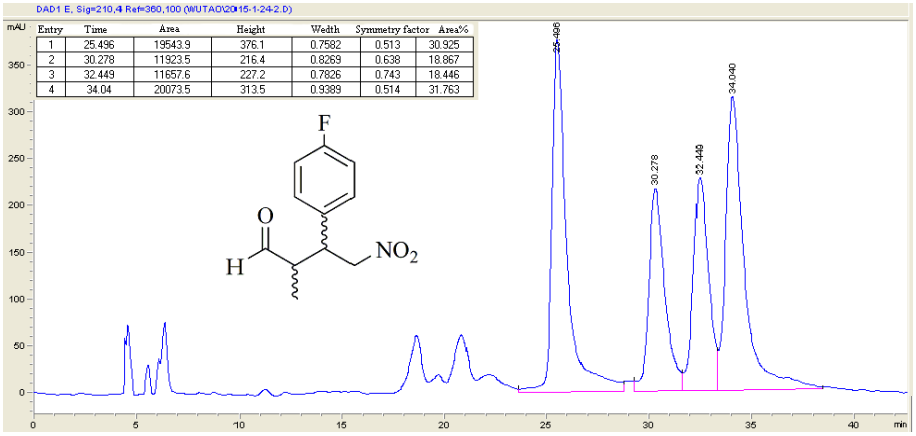


(2R, 3S)-3-(4-fluorophenyl)-2-methyl-4-nitrobutanal: *syn/anti* = 96:4, 99% ee *syn*, %ee *syn* was determined by HPLC analysis on Daicel Chiralpak AD-H column: heptane/*i*-PrOH = 95/5, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 24.8 min (major), t_R = 32.9 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.99-1.01 (m, 3H, CH_3), 2.72-2.83 (m, 1H, CHCH$_3$), 3.79-3.82 (m, 1H, CHCH$_2$), 4.72-4.80 (m, 2H, CH_2), 7.01-7.05 (m, 2H, ArH), 7.14-7.27 (m, 2H, ArH), 9.69 (s, 1H, CHO); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.3 (*C*H$_3$), 43.6 (*C*HCH$_2$), 48.6 (*C*HCH$_3$), 78.3 (*C*H$_2$), 116.2, 116.3, 129.9, 130.0, 132.6 (Ar), 202.1 (*C*HO).









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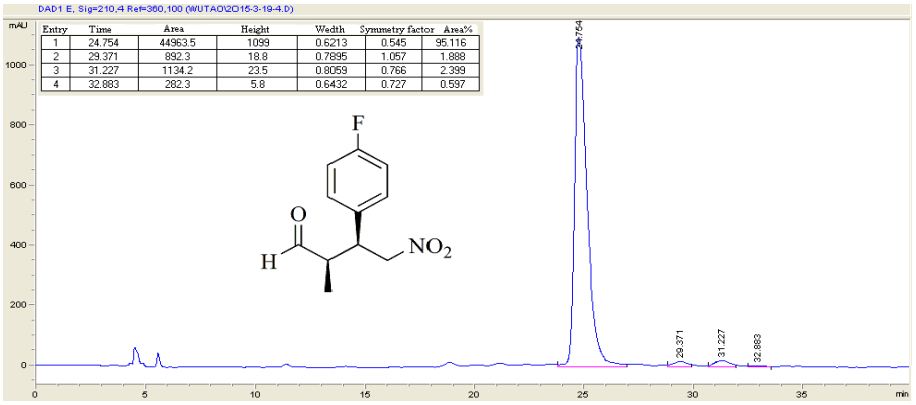

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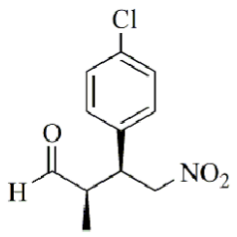
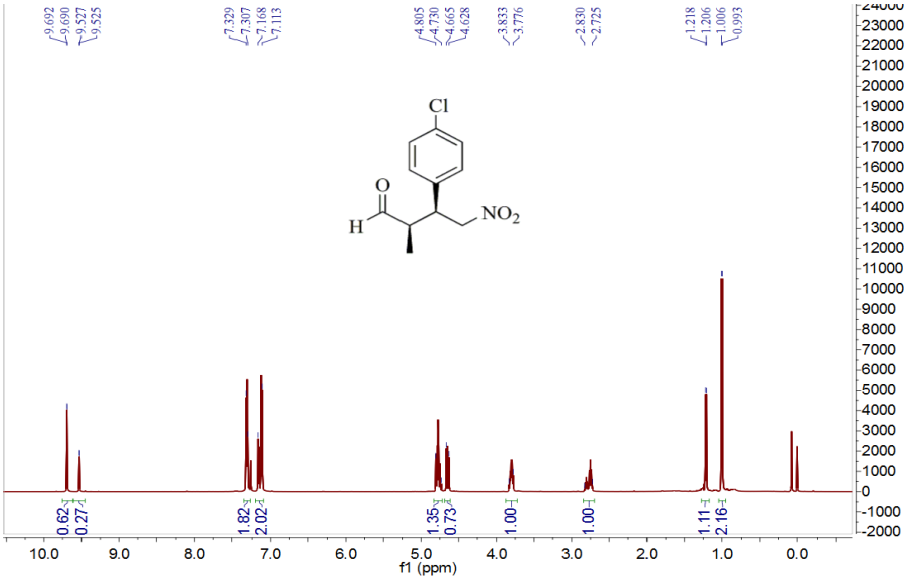
3	31.227	1134.2	23.5	0.8059	0.766	2.399
4	32.883	282.3	5.8	0.6432	0.727	0.597

(2R, 3S)-3-(4-chlorophenyl)-2-methyl-4-nitrobutanal: *syn/anti* = 96:4, >99% ee *syn*, %ee syn was determined by HPLC analysis on Daicel Chiralpak AD-H column: heptane/*i*-PrOH = 95/5, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 26.2 min (major), t_R = 35.5 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.00 (d, *J* = 7.3 Hz, 3H, CH_3), 2.73-2.83 (m, 1H, CHCH$_3$), 3.78-3.83 (m, 1H, CHCH$_2$), 4.73-4.81 (m, 2H, CH_2), 7.11-7.17 (m, 2H, ArH), 7.31-7.33 (m, 2H, ArH), 9.69 (d, *J* = 1.4 Hz, 1H, CHO); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.3 (*C*H$_3$), 43.7 (*C*HCH$_2$), 48.4 (*C*HCH$_3$), 78.1 (*C*H$_2$), 129.5, 129.6, 129.7, 134.3, 135.4 (Ar), 201.9 (*C*HO).

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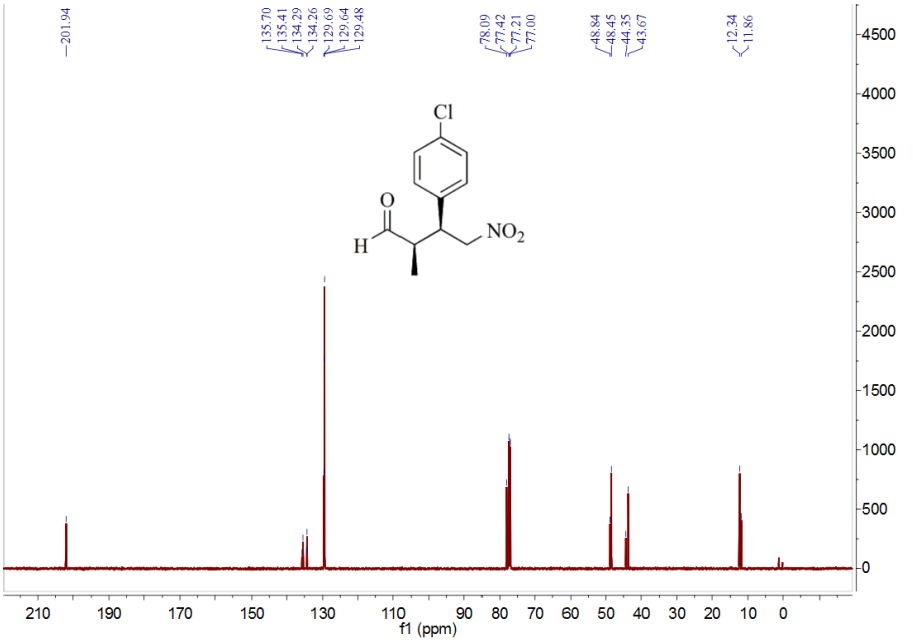
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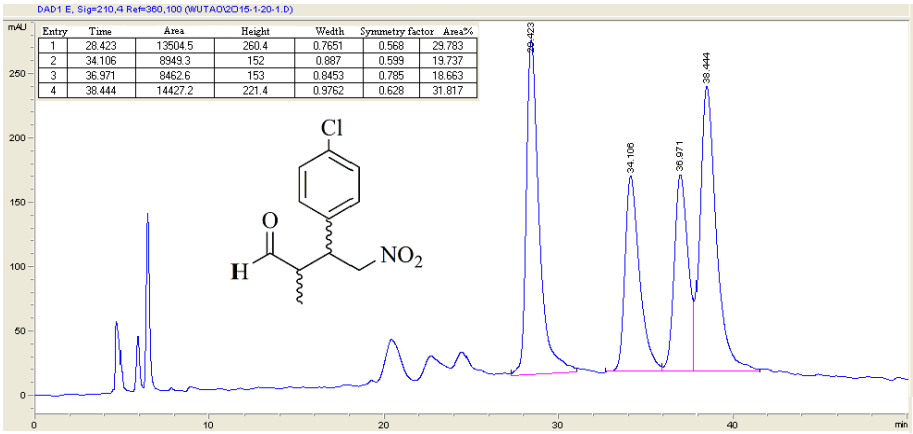
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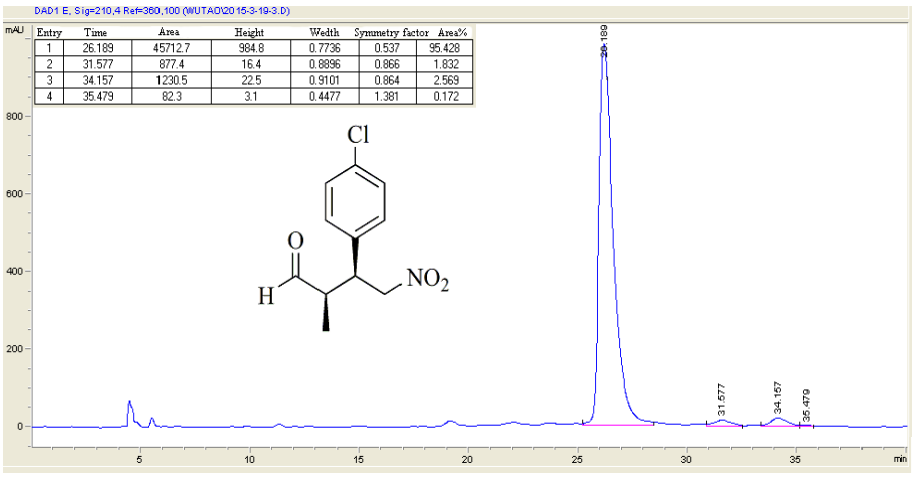
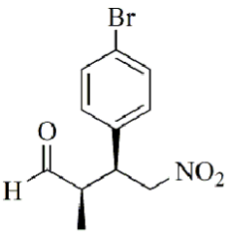
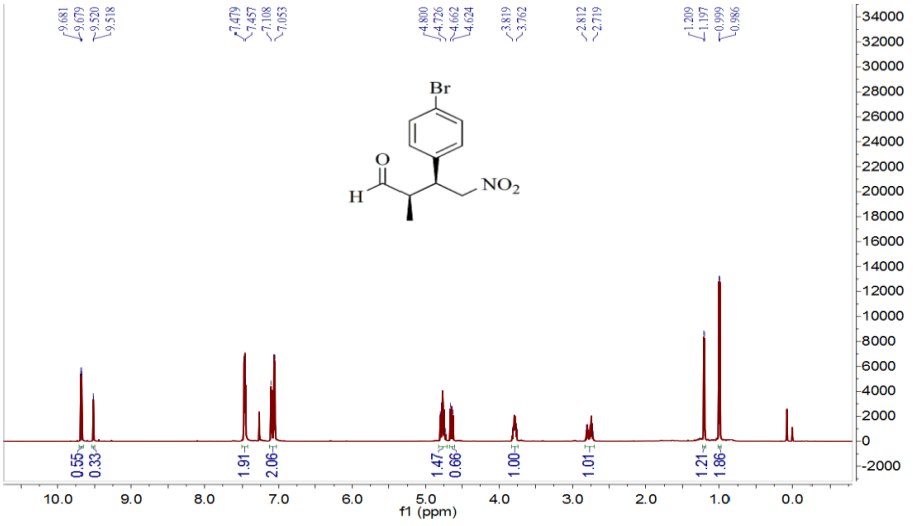
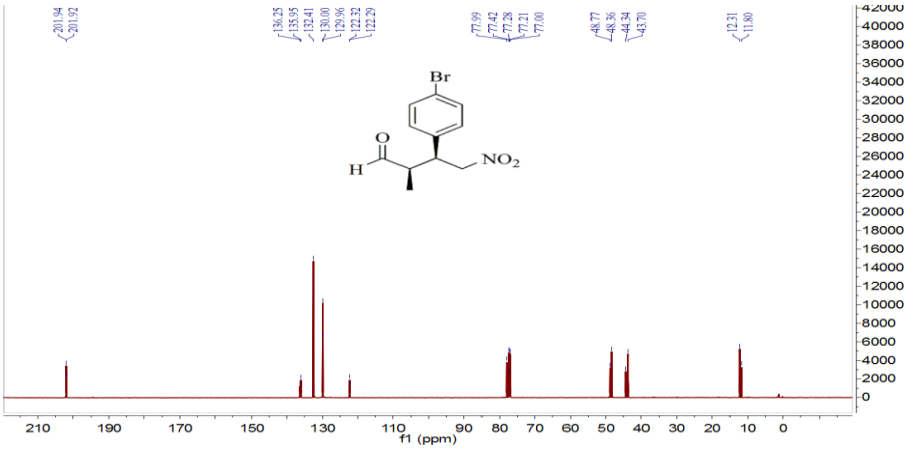
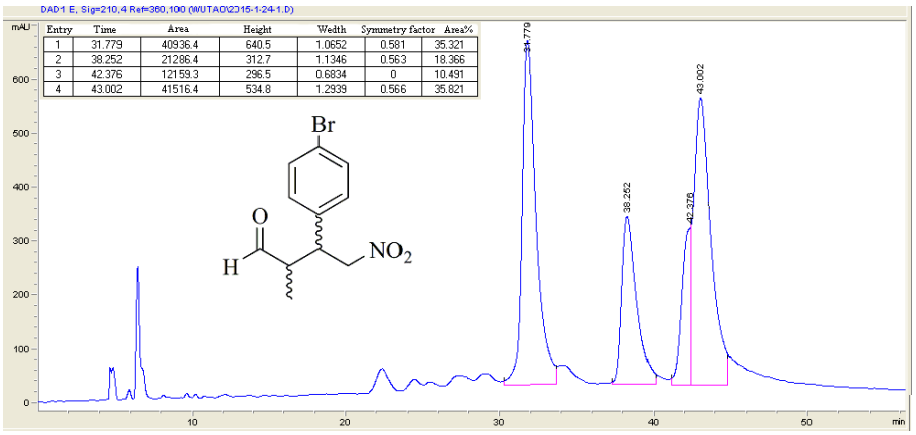


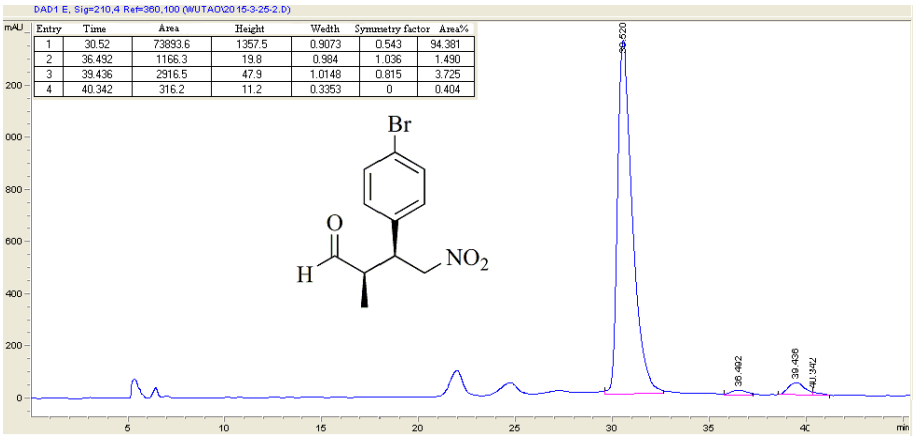
(2R, 3S)-3-(4-bromophenyl)-2-methyl-4-nitrobutanal: *syn/anti* = 95:5, >99%ee *syn*, %ee *syn* was determined by HPLC analysis on Daicel Chiralpak AD-H column: heptane/*i*-PrOH = 95/5, flow rate 0.9 mL min^{-1}, λ = 210 nm: t_R = 30.5 min (major), t_R = 40.3 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.99 (d, *J* = 7.3 Hz, 3H, C*H*$_3$), 2.72-2.81 (m, 1H, C*H*CH$_3$), 3.76-3.81 (m, 1H, C*H*CH$_2$), 4.73-4.80 (m, 2H, C*H*$_2$), 7.05-7.11 (m, 2H, Ar*H*), 7.46-7.48(m, 2H, Ar*H*), 9.68 (d, *J* = 1.3 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.3 (*C*H$_3$), 43.7 (*C*HCH$_2$), 48.4 (*C*HCH$_3$), 78.0 (*C*H$_2$), 122.3, 129.9, 130.0, 132.4, 135.9 (Ar), 201.9 (*C*HO).



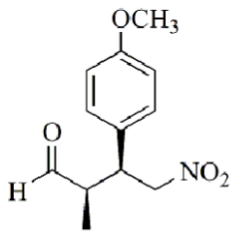




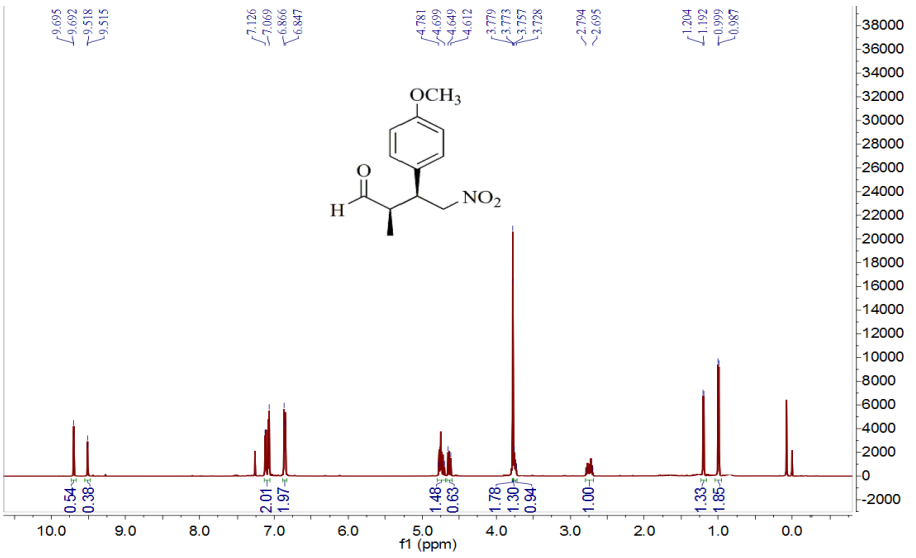


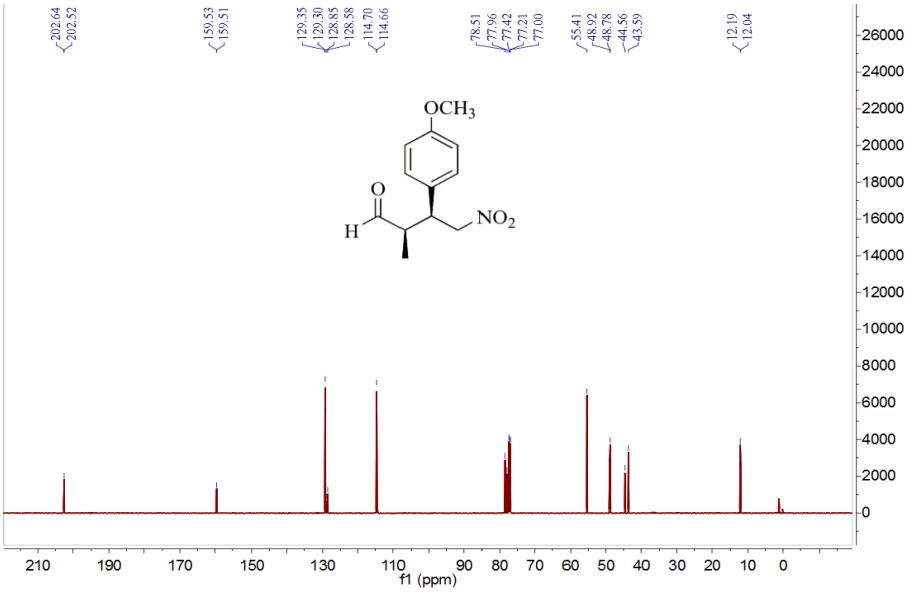


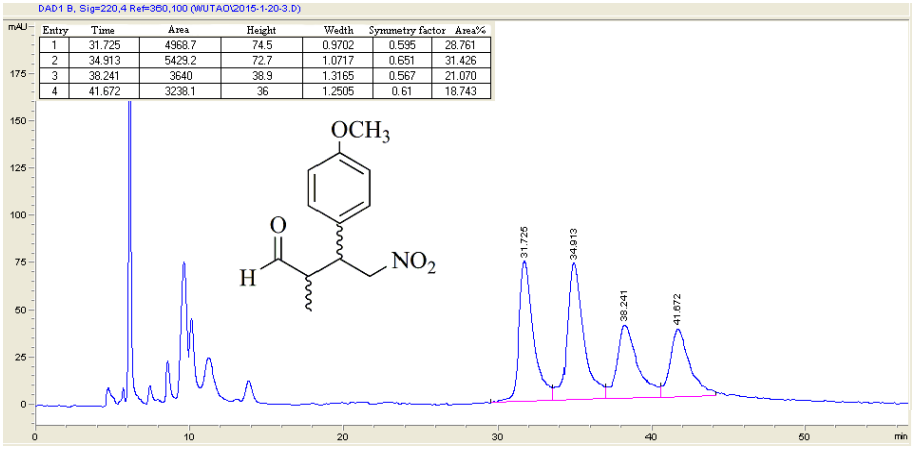
(2R, 3S)-3-(4-methoxyphenyl)-2-methyl-4-nitrobutanal: *syn/anti* = 99:1, >99 %ee *syn*, %ee *syn* was determined by

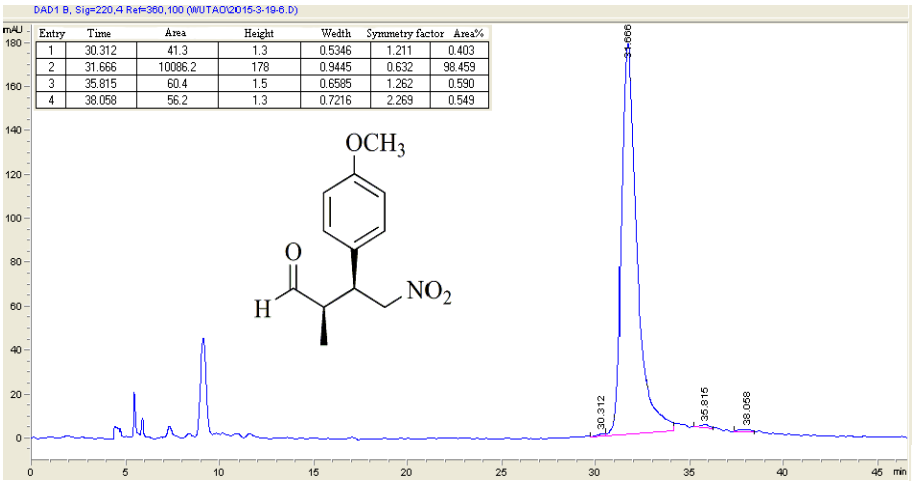


HPLC analysis on Daicel Chiralpak OD-H column: heptane/*i*-PrOH = 80/20, flow rate 1.0 mL min^{-1}, λ = 220 nm: t_R= 30.3 min (minor), 31.7 min (major); ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.2 Hz, 3H, CHC*H*$_3$), 2.70-2.79 (m, 1H, C*H*CH$_3$), 3.73-3.76 (m, 1H, C*H*CH$_2$), 3.78 (s, 3H, OC*H*$_3$), 4.70-4.78 (m, 2H, C*H*$_2$), 6.85-6.87 (m, 2H, Ar*H*), 7.07-7.13 (m, 2H, Ar*H*), 9.69 (d, *J* = 1.6 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.2 (CH*C*H$_3$), 43.6 (*C*HCH$_2$), 48.8 (*C*HCH$_3$), 55.4 (OCH$_3$), 78.5 (*C*H$_2$), 114.6, 114.7, 128.6, 129.3, 159.5 (Ar), 202.5 (*C*HO).

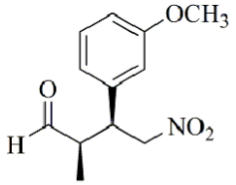




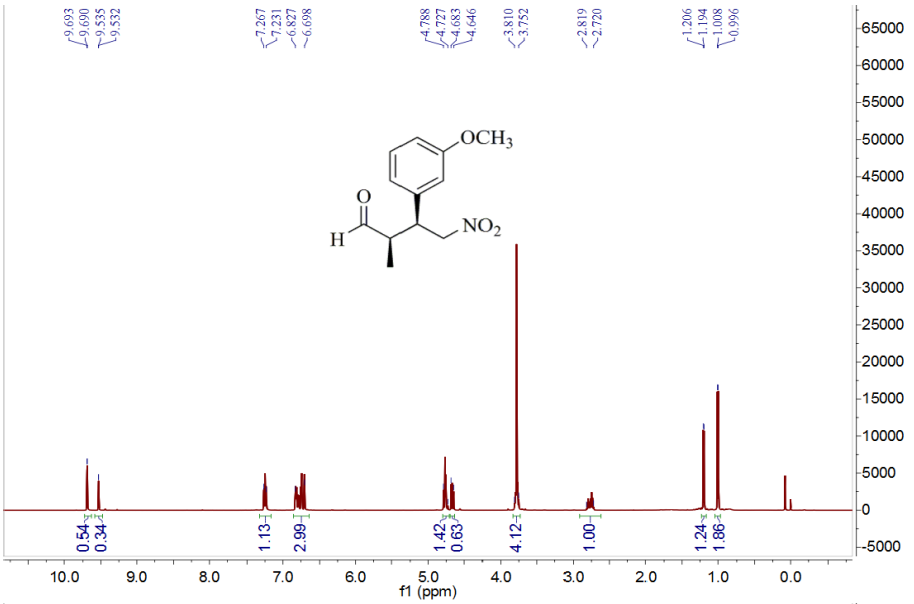


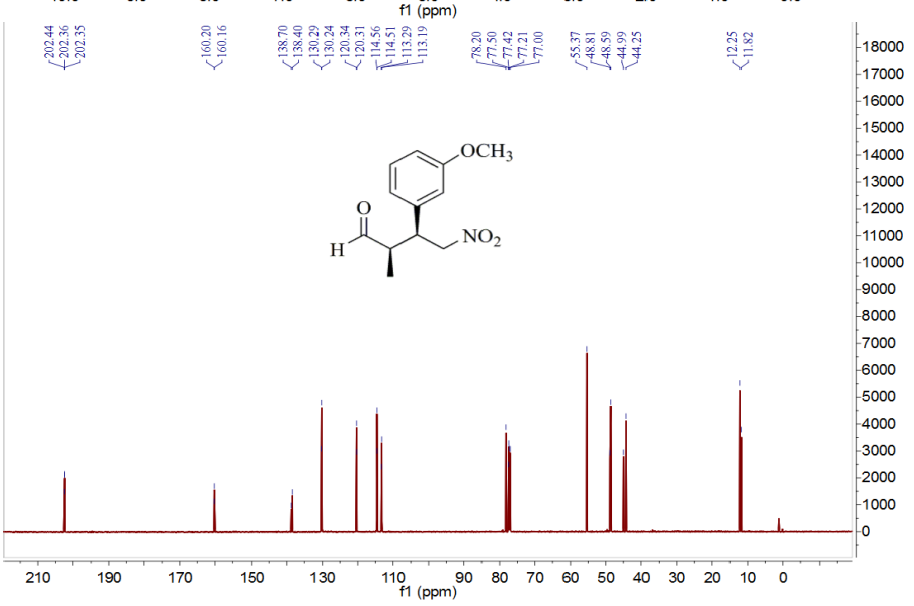


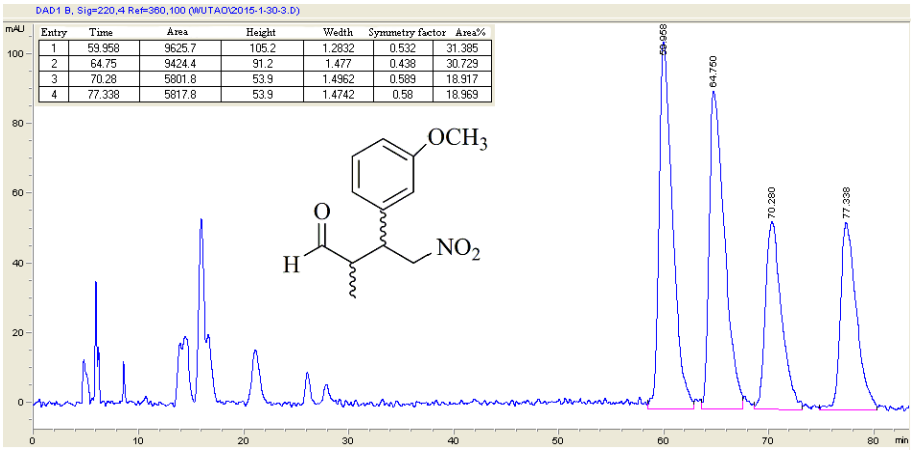
(2R, 3S)-3-(3-methoxyphenyl)-2-methyl-4-nitrobutanal: *syn/anti* = 96:4, 98 %ee *syn*, %ee *syn* was determined by HPLC analysis on Daicel Chiralpak OJ-H column: heptane/*i*-PrOH = 80/20, flow rate 1.0 mL min^{-1}, λ = 220 nm: t_R = 53.5 min (minor), t_R = 56.0 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.00 (d, *J* = 7.3 Hz, 3H, CHC*H*$_3$), 2.72-2.82 (m, 1H, C*H*CH$_3$), 3.75-3.81 (m, 4H, C*H*CH$_2$, OC*H*$_3$), 4.73-4.79 (m, 2H, C*H*$_2$), 7.70-7.83 (m, 3H, Ar*H*), 7.23-7.27



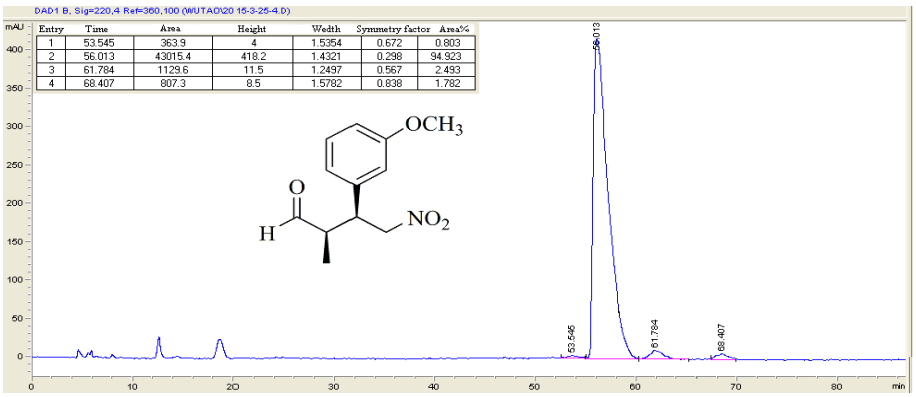
(m, 1H, Ar*H*), 9.69 (d, *J* = 1.6 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.3 (CH*C*H$_3$), 44.3 (*C*HCH$_2$), 48.6 (*C*HCH$_3$), 55.4 (O*C*H$_3$), 78.2 (*C*H$_2$), 113.2, 114.5, 120.3, 130.2, 138.4, 160.2 (Ar), 202.3 (*C*HO).



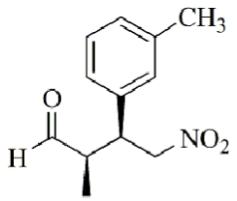




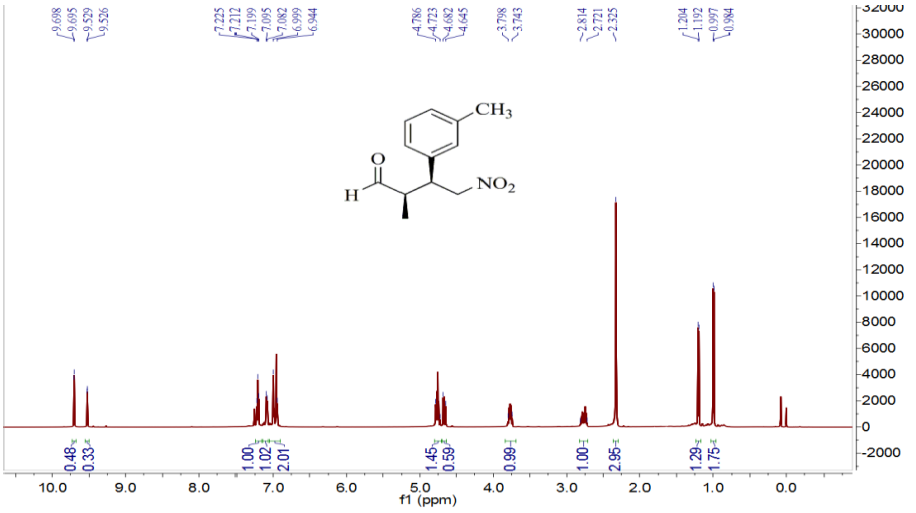
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	59.958	9625.7	105.2	1.2832	0.532	31.385
2	64.75	9424.4	91.2	1.477	0.438	30.729
3	70.28	5801.8	53.9	1.4962	0.589	18.917
4	77.338	5817.8	53.9	1.4742	0.58	18.969

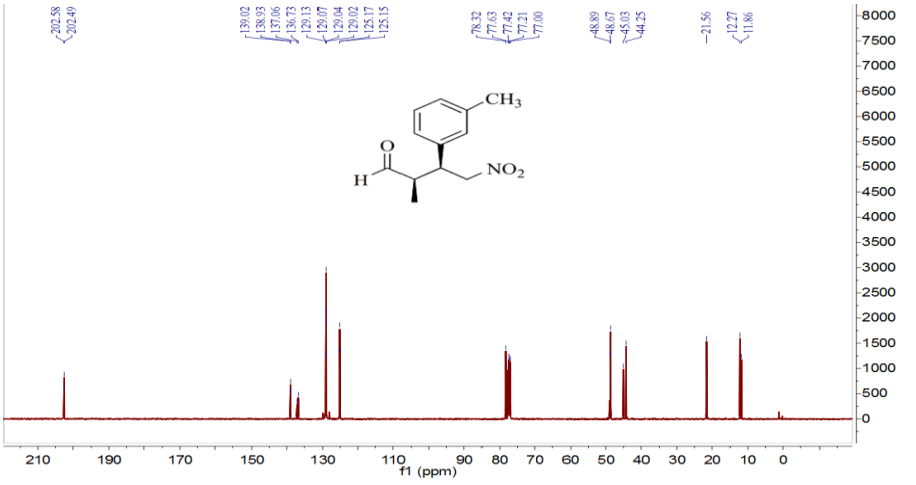


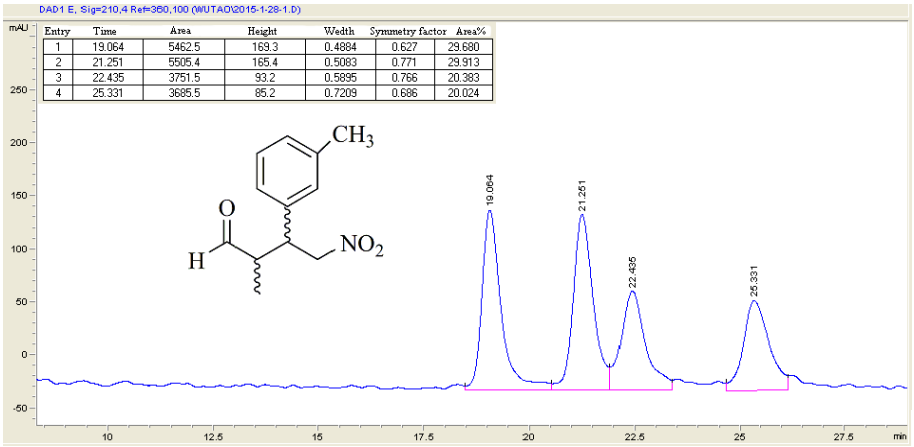
(2R, 3S)-3-(3-methylphenyl)-2-methyl-4-nitrobutanal: *syn/anti* = 94:6, >99 %ee *syn*, %ee *syn* was determined by

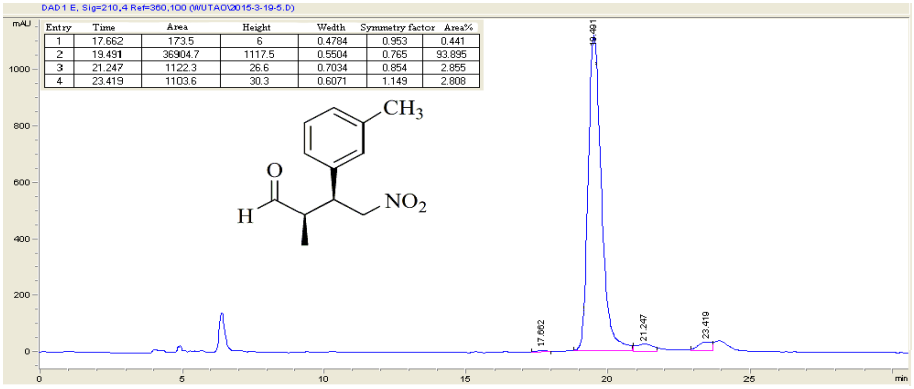


HPLC analysis on Daicel Chiralpak OD-H column: heptane/*i*-PrOH = 80/20, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 17.7 min (minor), t_R = 19.5 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, major diastereomer): δ 0.99 (d, *J* = 7.3 Hz, 3H, CHC*H*$_3$), 2.33(s, 3H, ArC*H*$_3$), 2.72-2.81 (m, 1H, C*H*CH$_3$), 3.74-3.80 (m, 1H, C*H*CH$_2$), 4.72-4.79 (m, 2H, C*H*$_2$), 6.95-7.00 (m, 2H, Ar*H*), 7.08-7.09 (m, 1H, Ar*H*), 7.20-7.23 (m, 1H, Ar*H*), 9.70 (d, *J* = 1.7 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.3 (CH*C*H$_3$), 21.6 (Ar*C*H$_3$), 44.3 (*C*HCH$_2$), 48.7 (*C*HCH$_3$), 78.3 (*C*H$_2$), 125.1, 125.2, 129.0, 129.1, 136.7, 138.9 (Ar), 202.5 (*C*HO).

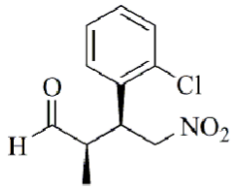


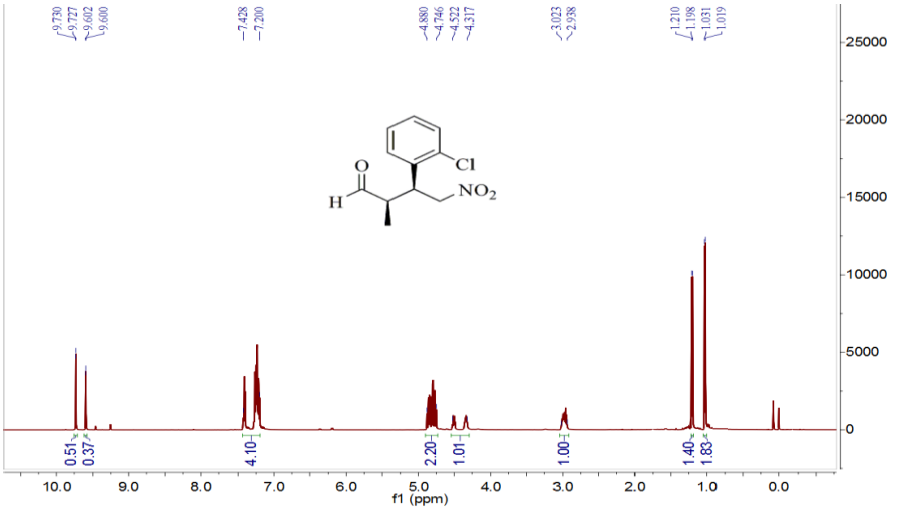


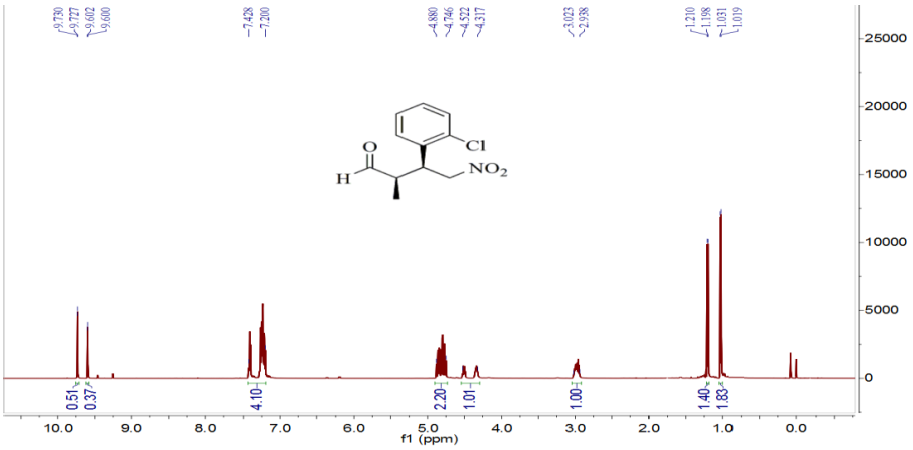


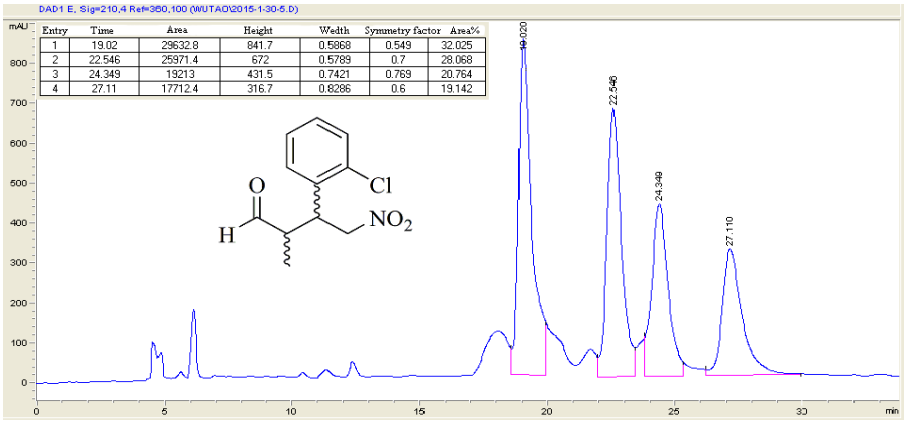


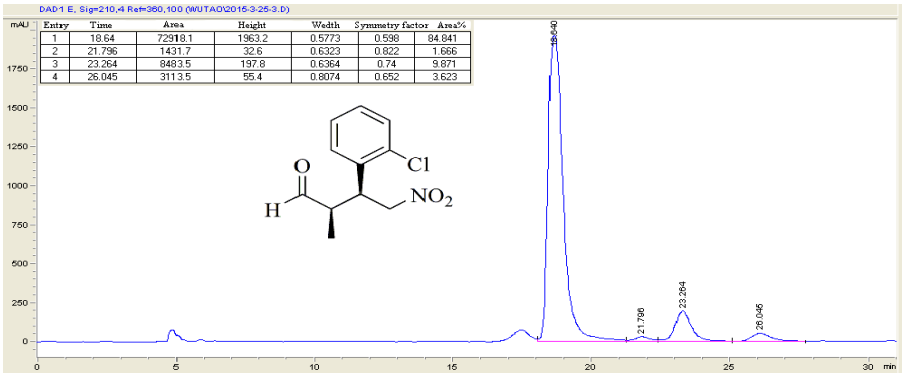
(2R, 3S)-3-(2-chlorophenyl)-2-methyl-4-nitrobutanal: *syn/anti* = 87:13, 96 %ee *syn*, %ee *syn* was determined by HPLC analysis on Daicel Chiralpak AD-H column: heptane/*i*-PrOH = 95/5, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 18.6 min (major), t_R = 21.8 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.03 (d, *J* = 7.4 Hz, 3H, C*H*$_3$), 2.94-3.02 (m, 1H, C*H*CH$_3$), 4.32-4.52 (m, 1H, C*H*CH$_2$), 4.75-4.88 (m, 2H, C*H*$_2$), 7.20-7.43 (m, 4H, Ar*H*), 9.73 (d, *J* = 1.4 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.4 (*C*H$_3$), 40.1 (*C*HCH$_2$), 48.0 (*C*HCH$_3$), 76.9 (*C*H$_2$), 127.6, 128.5, 129.4, 130.7, 134.3, 134.8 (Ar), 202.0 (*C*HO).



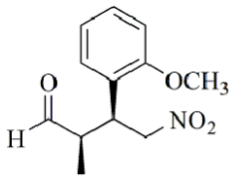


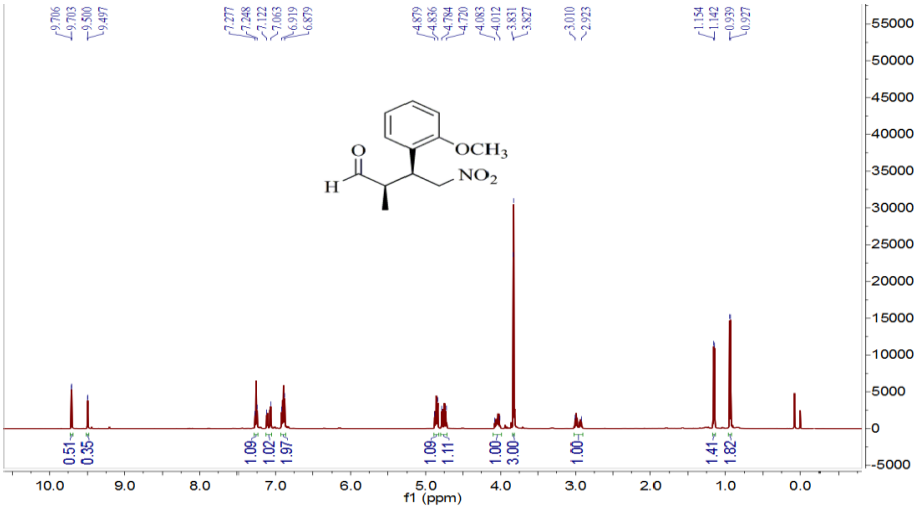


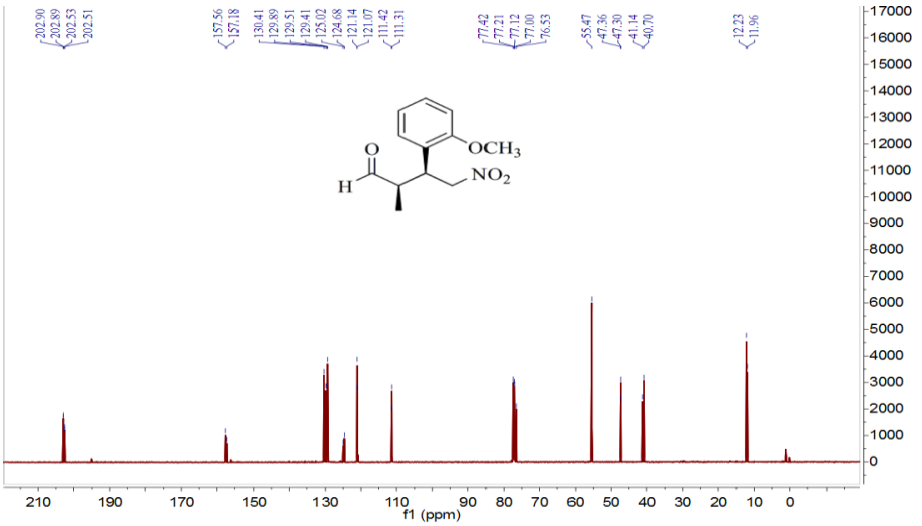


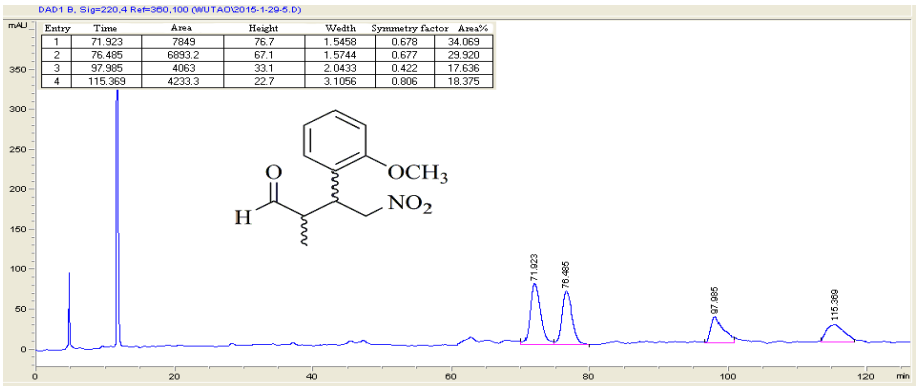


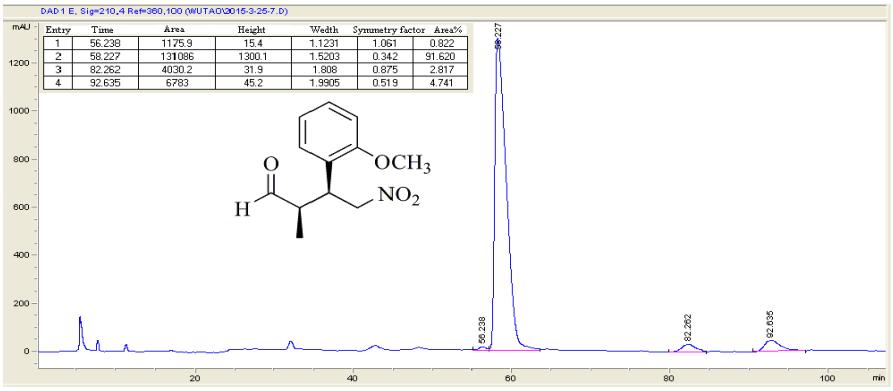
(2R, 3S)-3-(2-methoxyphenyl)-2-methyl-4-nitrobutanal: *syn/anti* = 92:8, 98 %ee *syn*, %ee *syn* was determined by HPLC analysis on Daicel Chiralpak AS-H column: heptane/*i*-PrOH = 98/2, flow rate 0.9 mL min^{-1}, λ = 220 nm: t_R = 56.2 min (minor), t_R = 58.2 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.93 (d, *J* = 7.3 Hz, 3H, CHC*H*$_3$), 2.92-3.01 (m, 1H, C*H*CH$_3$), 3.83 (s, 3H, OC*H*$_3$), 4.02-4.07 (m, 1H, C*H*CH$_2$), 4.72-4.88 (m, 2H, C*H*$_2$), 6.88-6.92 (m, 2H, Ar*H*), 7.06-7.12 (m, 1H, Ar*H*), 7.25-7.28 (m, 1H, Ar*H*), 9.70 (d, *J* = 1.8 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.2 (CH*C*H$_3$), 40.7 (*C*HCH$_2$), 47.3 (*C*HCH$_3$), 55.5 (OCH$_3$), 77.1 (*C*H$_2$), 111.3, 121.1, 124.7, 129.4, 130.4, 157.5 (Ar), 202.9 (*C*HO).



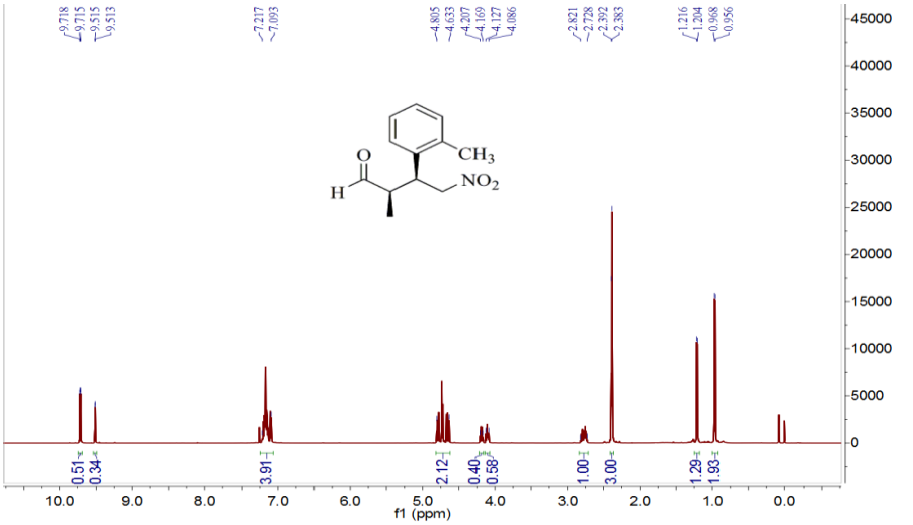

9.706
9.703
9.500
9.497
7.277
7.248
7.122
7.063
6.919
6.879
4.879
4.836
4.784
4.720
4.083
4.012
3.831
3.827
3.010
2.923
1.154
1.142
0.959
0.927
OCH3
NO2
O
H
0.51
0.35
1.09
1.02
1.97
1.09
1.11
1.00
3.00
1.00
1.41
1.82
f1 (ppm)

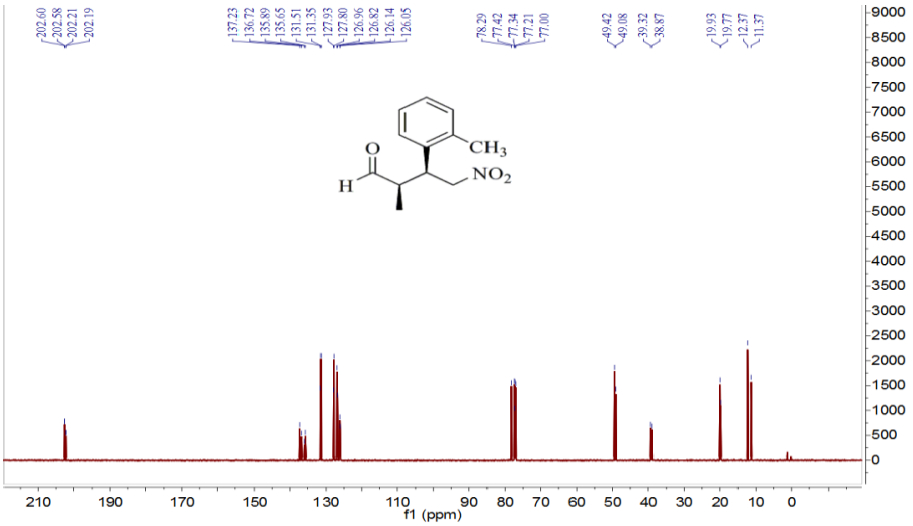

202.90
202.89
202.53
202.51
157.56
157.18
130.41
129.89
129.51
129.41
125.02
124.68
121.14
121.07
111.42
111.31
77.42
77.21
77.12
77.00
76.53
55.47
47.36
47.30
41.14
40.70
12.23
11.96
OCH3
NO2
O
H
f1 (ppm)

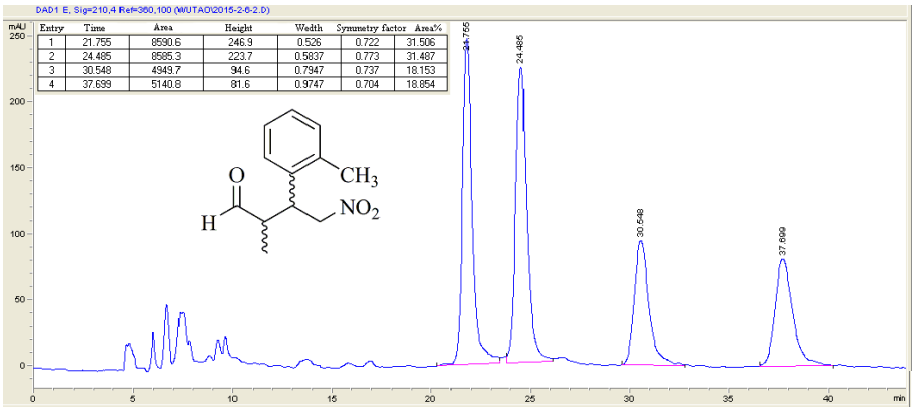

DAD1 B, Sig=220,4 Ref=360,100 (WUTAO\2015-1-29-5.D)
Entry Time Area Height Width Symmetry factor Area%
1 71.923 7849 76.7 1.5458 0.678 34.069
2 76.485 6893.2 67.1 1.5744 0.677 29.920
3 97.985 4063 33.1 2.0433 0.422 17.636
4 115.369 4233.3 22.7 3.1056 0.806 18.375
mAU
OCH3
NO2
O
H
71.923
76.485
97.985
115.369
min

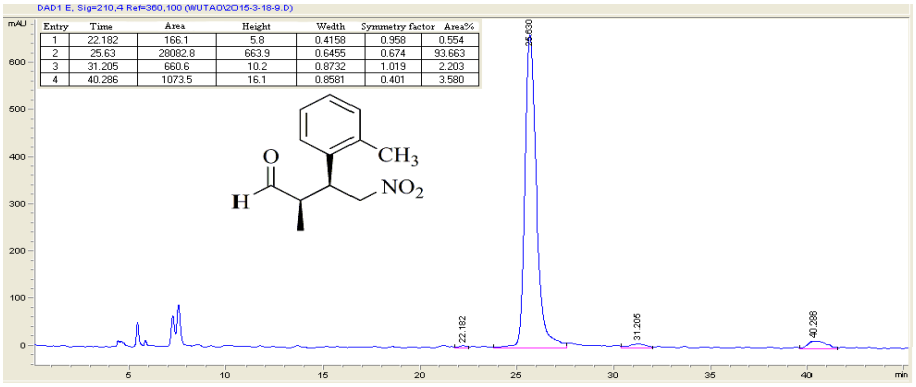

DAD1 E, Sig=210,4 Ref=360,100 (WUTAO\2015-3-25-7.D)
Entry Time Area Height Width Symmetry factor Area%
1 56.238 1175.9 15.4 1.1231 1.061 0.822
2 58.227 131086 1300.1 1.5203 0.342 91.620
3 82.262 4030.2 31.9 1.808 0.875 2.817
4 92.635 6783 45.2 1.9905 0.519 4.741
mAU
OCH3
NO2
O
H
58.227
56.238
82.262
92.635
min

(2R, 3S)-3-(2-methylphenyl)-2-methyl-4-nitrobutanal: *syn/anti* =94:6, 99 %ee *syn*, %ee *syn* was determined by HPLC analysis on Daicel Chiralpak OD-H column: heptane/*i*-PrOH = 80/20, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 22.2 min (minor), t_R = 25.6 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.96 (d, *J* = 7.3 Hz, 3H, CHC*H*$_3$), 2.39 (s, 3H, ArC*H*$_3$), 2.73-2.82 (m, 1H, C*H*CH$_3$), 4.09-4.13 (m, 1H, C*H*CH$_2$), 4.63-4.81 (m, 2H, C*H*$_2$), 7.09-7.22 (m, 4H, Ar*H*), 9.72 (d, *J* = 1.9 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.4 (CH*C*H$_3$), 19.9 (Ar*C*H$_3$), 38.9 (*C*HCH$_2$), 49.4 (*C*HCH$_3$), 78.3 (*C*H$_2$), 126.1, 126.9, 127.8, 131.3, 133.6, 137.2 (Ar), 202.6 (*C*HO).



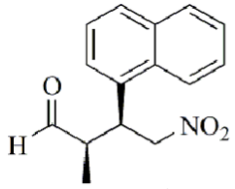




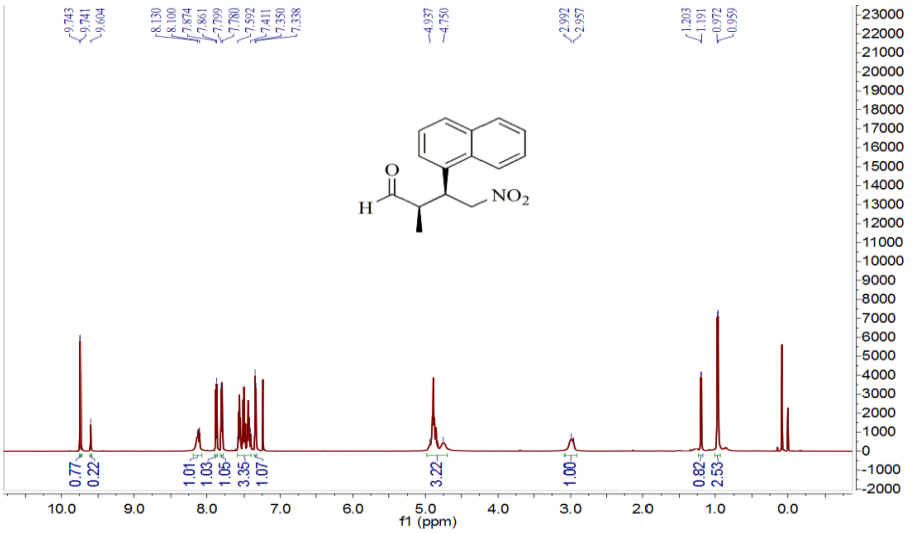


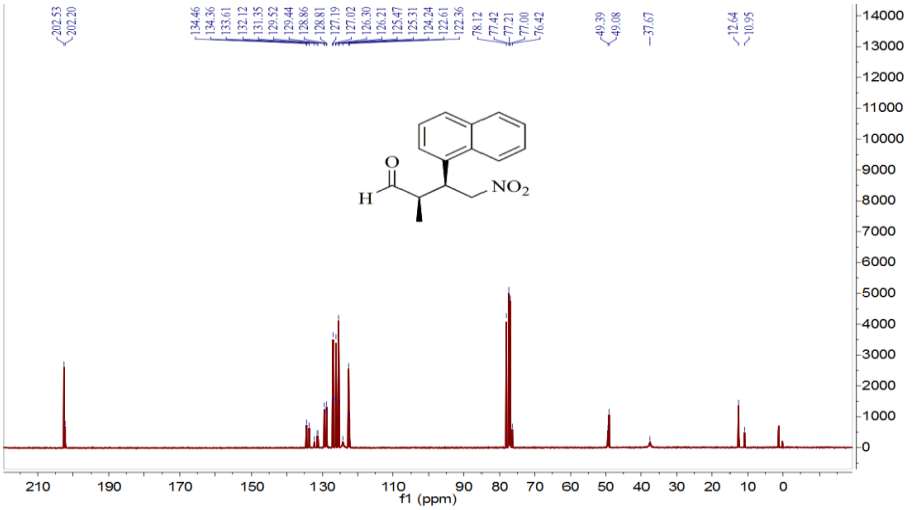
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	22.182	166.1	5.8	0.4158	0.958	0.554
2	25.63	28082.8	663.9	0.6455	0.674	93.663
3	31.205	660.6	10.2	0.8732	1.019	2.203
4	40.286	1073.5	16.1	0.8581	0.401	3.580

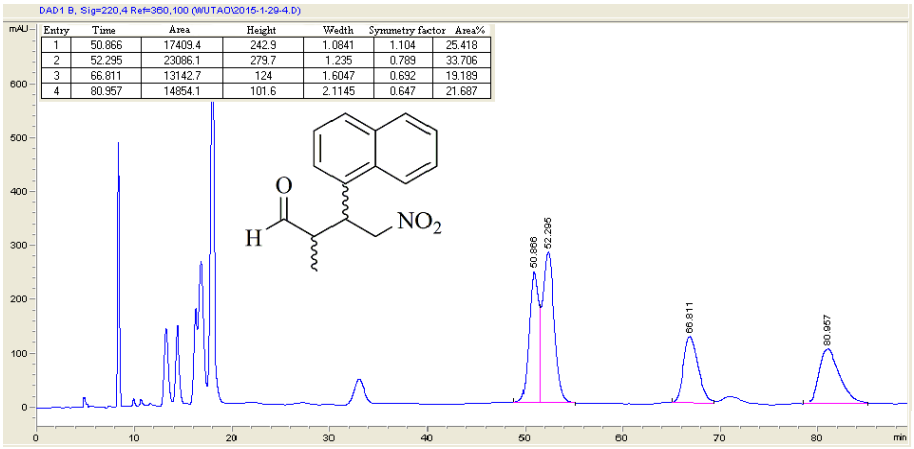
(2R, 3S)-2-methyl-3-(naphthalen-1-yl)-4-nitrobutanal: *syn/anti* = 91:9, >99 %ee *syn*, %ee *syn* was determined by

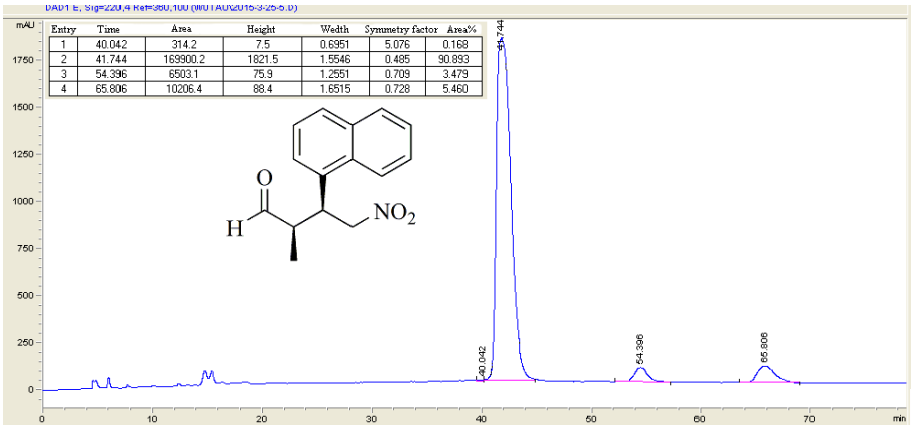


HPLC analysis on Daicel Chiralpak AS-H column: heptane/*i*-PrOH = 90/10, flow rate 1.0 mL min^{-1}, λ = 220 nm: t_R = 40.0 min (minor), t_R = 41.7 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.97 (d, *J* = 7.3 Hz, 3H, C*H*$_3$), 2.96-2.99 (m, 1H, C*H*CH$_3$), 4.75-4.94 (m, 3H, C*H*CH$_2$, C*H*$_2$), 7.34 (d, *J* = 7.1 Hz, 1H, Ar*H*), 7.41-7.59 (m, 3H, Ar*H*), 7.78-7.80 (m, 1H, Ar*H*), 7.87 (d, *J* = 8.1 Hz, 1H, Ar*H*), 8.10-8.13 (m, 1H, Ar*H*), 9.74 (d, *J* = 1.5 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereome): δ 12.6 (*C*H$_3$), 37.7 (*C*HCH$_2$), 49.1 (*C*HCH$_3$), 78.1 (*C*H$_2$), 122.6, 124.2, 125.5, 126.2, 127.0, 128.8, 129.4, 131.3, 133.6, 134.3 (Naphth), 202.5 (*C*HO).

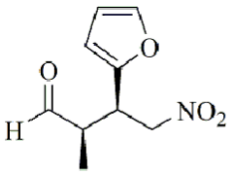


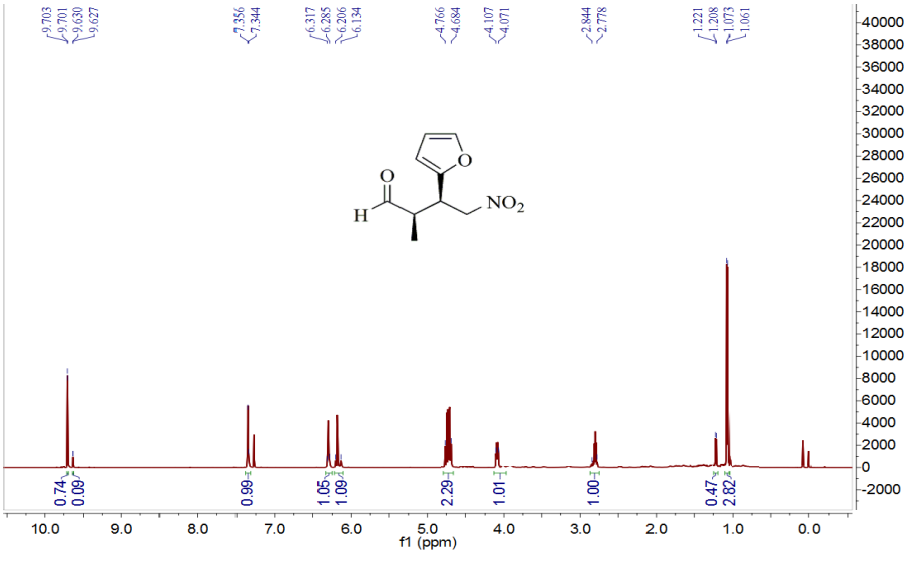


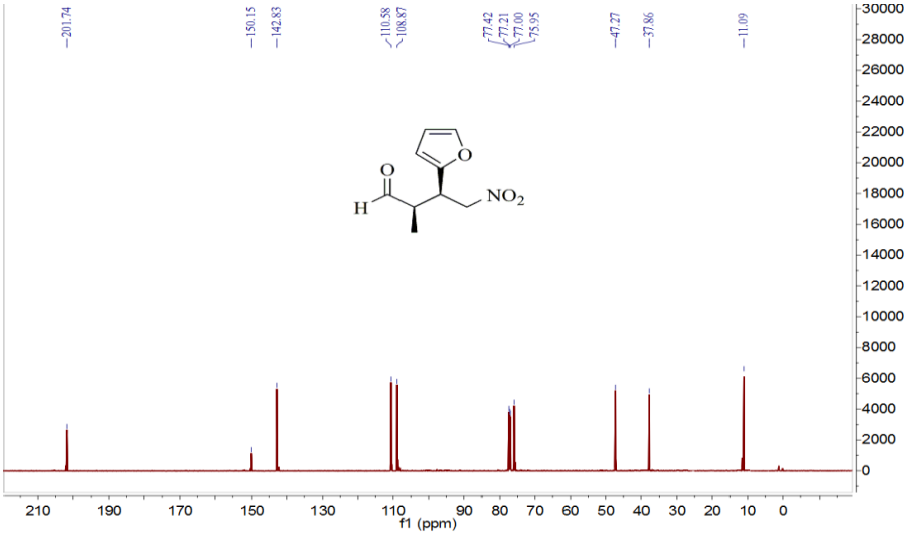


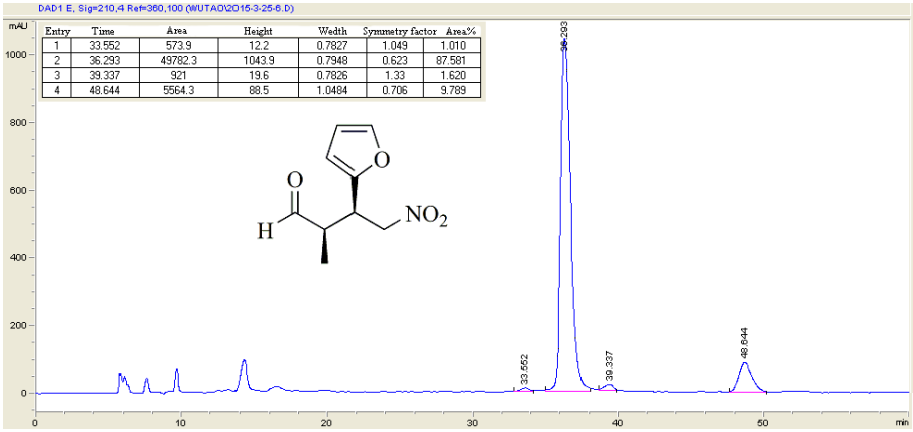


(2R, 3R)-3-(furan-2-yl)-2-methyl-4-nitrobutanal: *syn/anti* = 89:11, 98 %ee *syn*, %ee *syn* was determined by HPLC analysis on Daicel Chiralpak AS-H column: heptane/*i*-PrOH = 90/10, flow rate 0.8 mL min^{-1}, λ = 210 nm: t_R = 33.6 min (minor), t_R = 36.3 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.07 (d, *J* = 7.3 Hz, 3H, C*H*$_3$), 2.78-2.84 (m, 1H, C*H*CH$_3$), 4.07-4.11 (m, 1H, C*H*CH$_2$), 4.68-4.77 (m, 2H, C*H*$_2$), 6.13-6.21(m, 1H, =C*H*), 6.29-6.32(m, 1H, =C*H*), 7.34-7.36 (m, 1H, =C*H*), 9.70 (d, *J* = 0.8 Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 11.1 (*C*H$_3$), 37.9 (*C*HCH$_2$), 47.3 (*C*HCH$_3$), 76.0 (*C*H$_2$), 108.9, 110.6, 142.8, 150.2 (=*C*H), 201.7 (*C*HO).

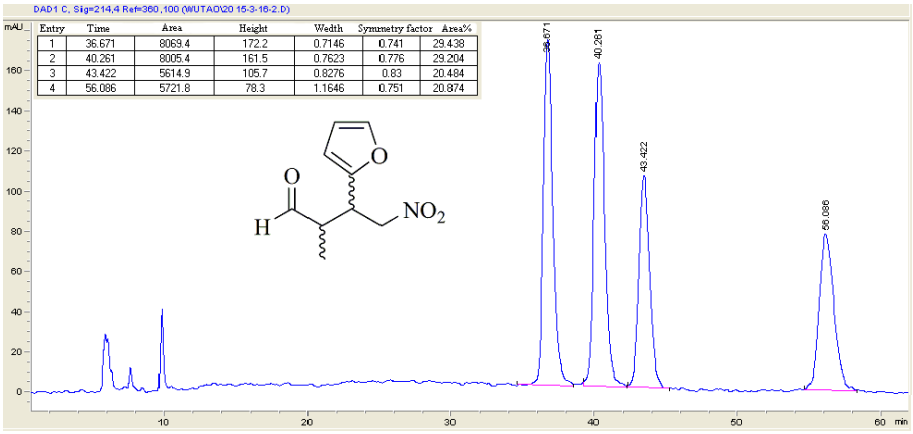








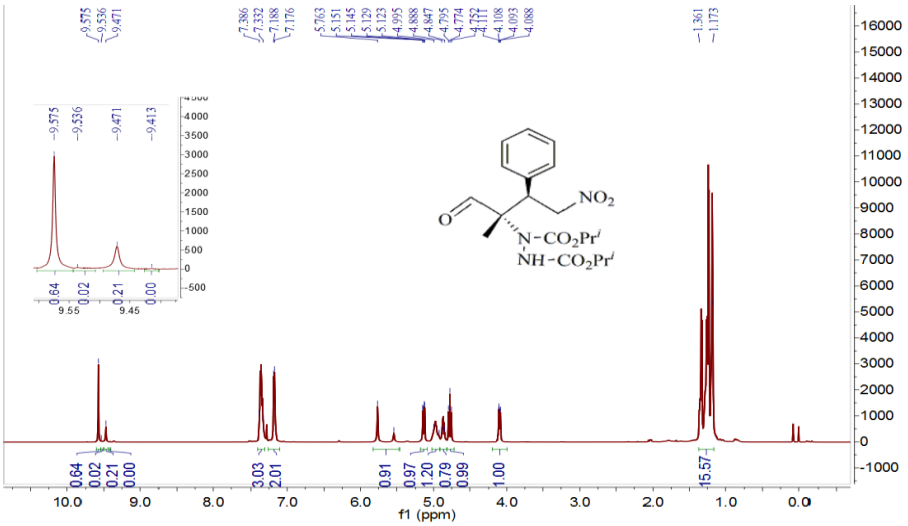
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	33.552	573.9	12.2	0.7827	1.049	1.010
2	36.293	49782.3	1043.9	0.7948	0.623	87.581
3	39.337	921	19.6	0.7826	1.33	1.620
4	48.644	5564.3	88.5	1.0484	0.706	9.789

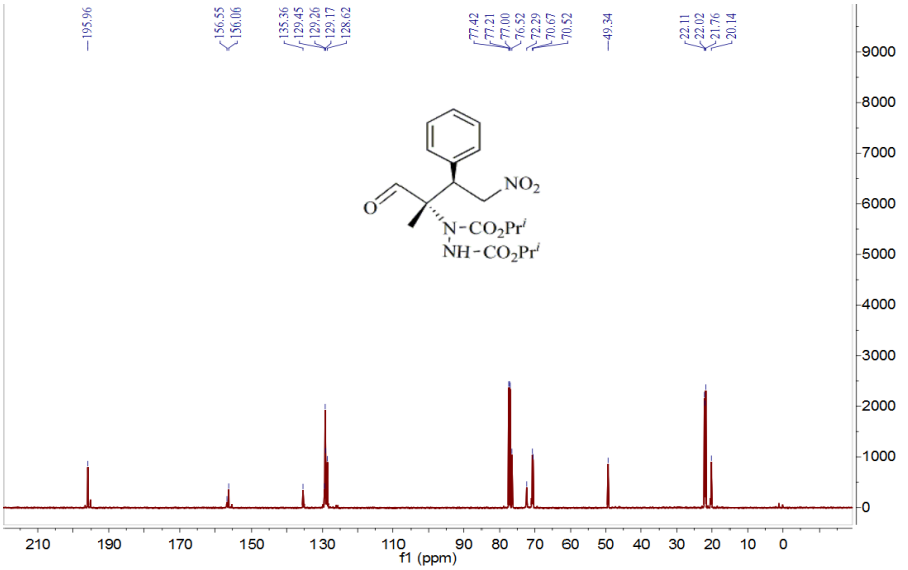


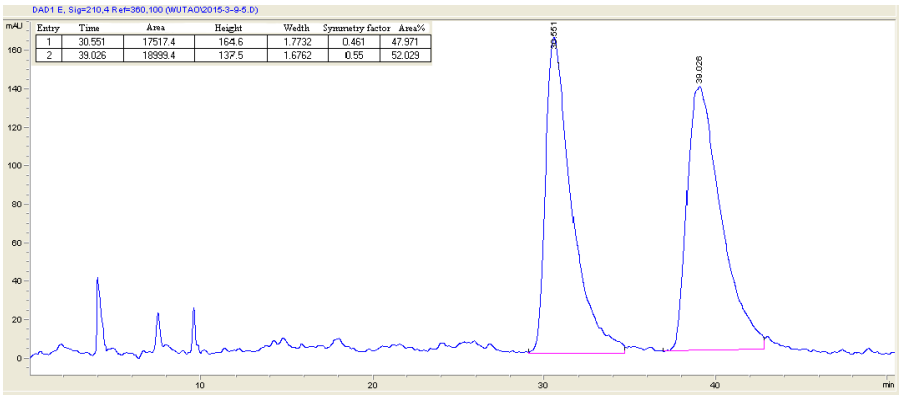
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	36.671	8069.4	172.2	0.7146	0.741	29.438
2	40.261	8005.4	161.5	0.7623	0.776	29.204
3	43.422	5614.9	105.7	0.8276	0.83	20.484
4	56.086	5721.8	78.3	1.1646	0.751	20.874

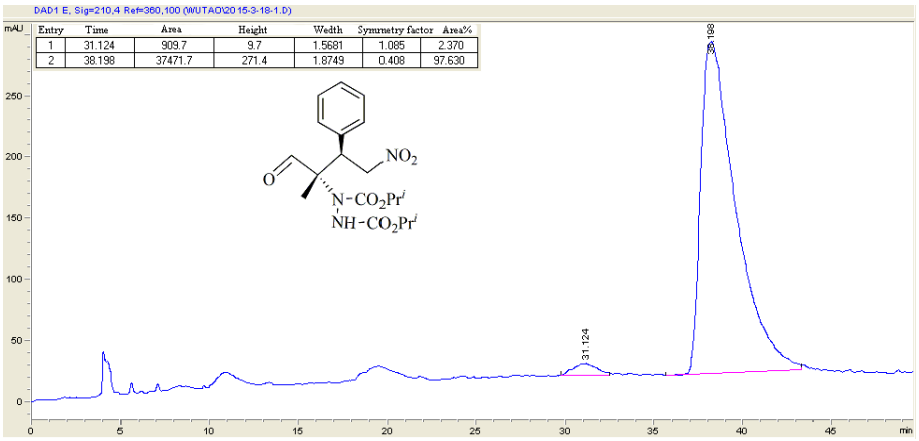
6. The NMR and HPLC characterization of α-amination products

(1) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-phenylbutan-2-yl]hydrazine-1, 2-dicarboxylate

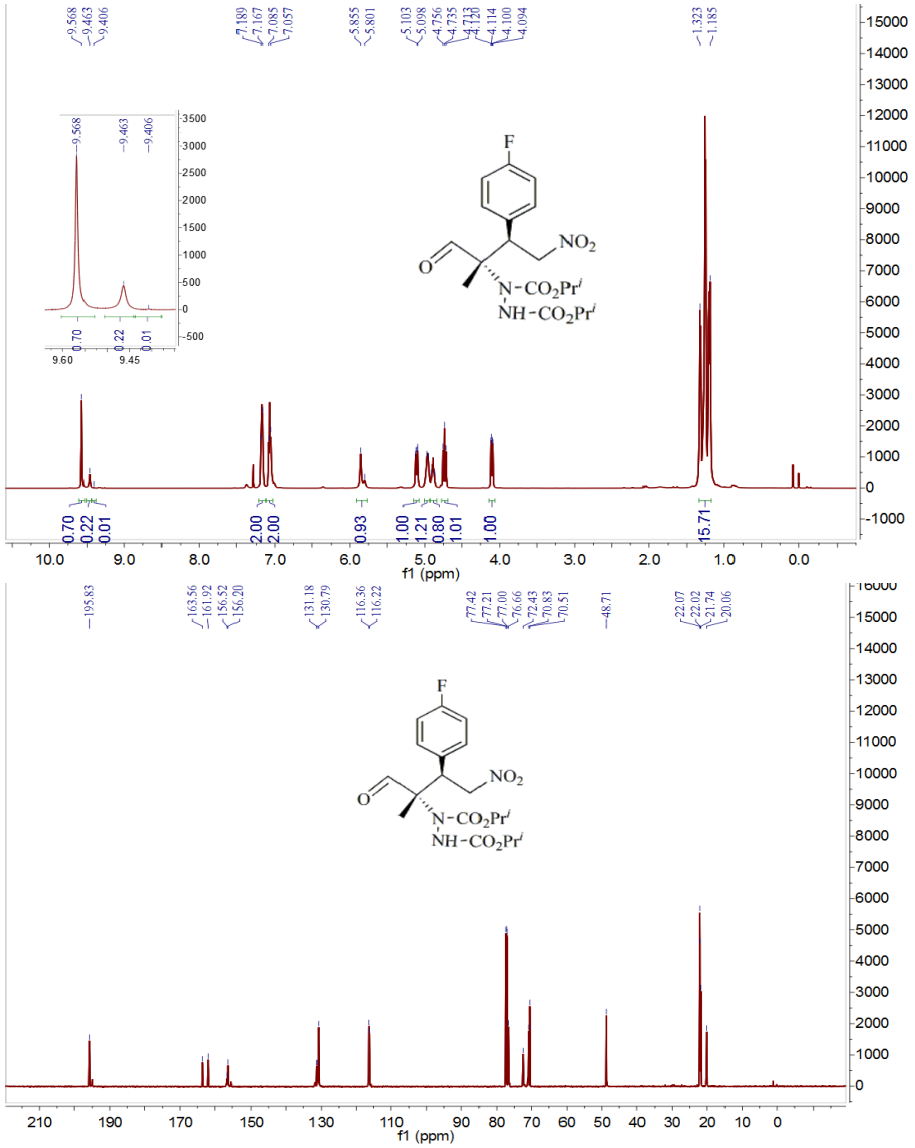


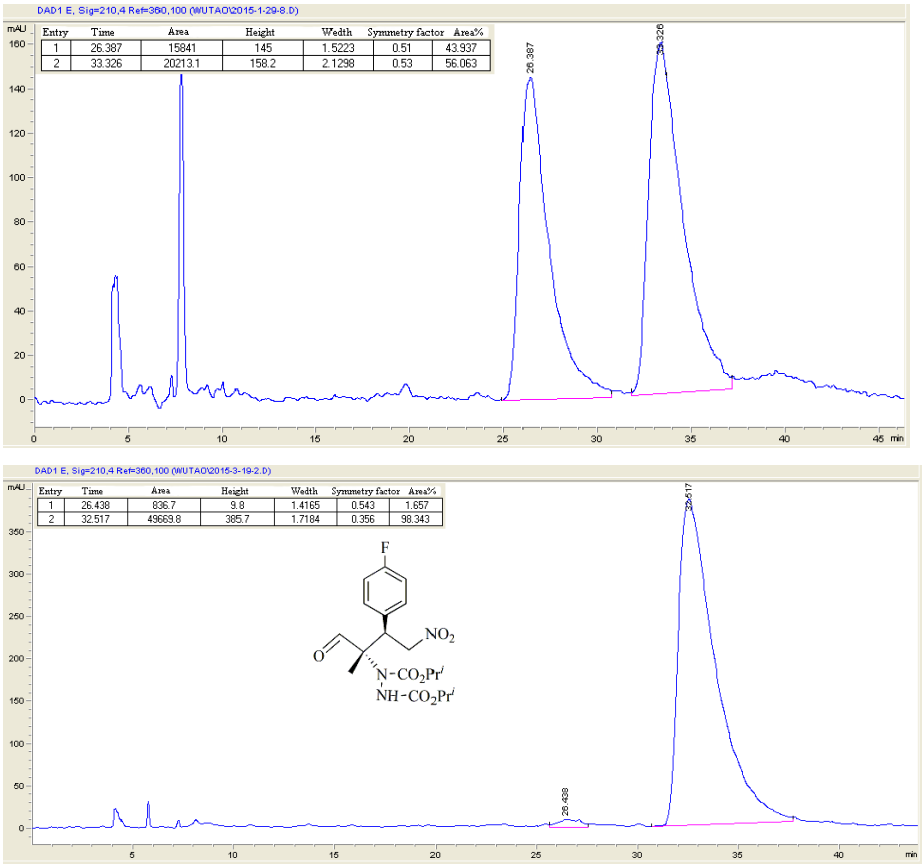




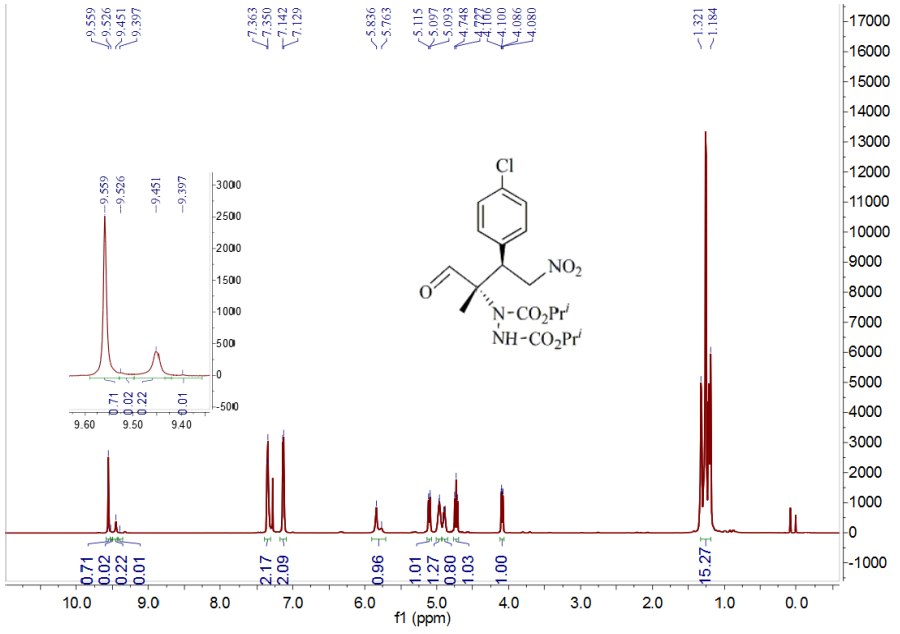


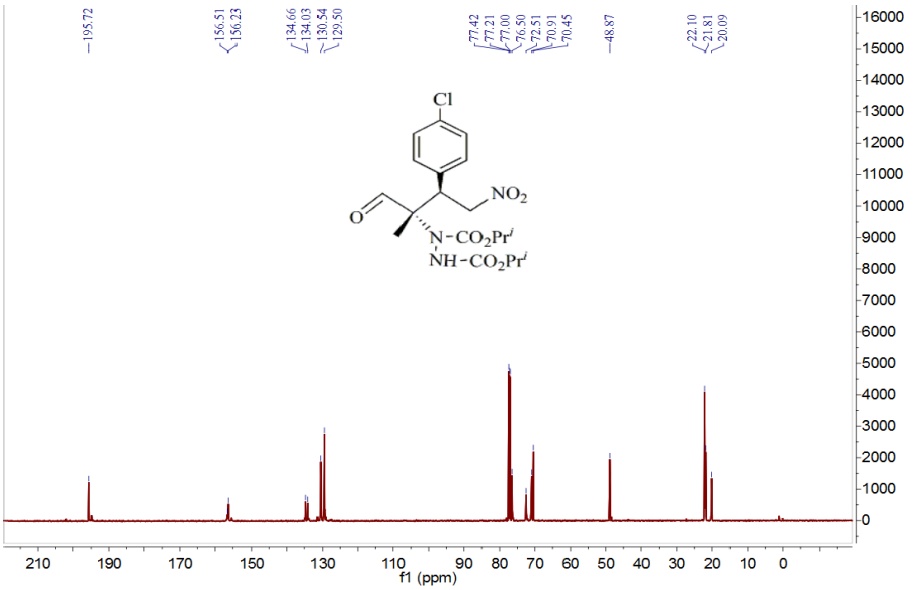
(2) Di-*iso*-propyl-1-[(2S,3S)-2-methyl-4-nitro-1-oxo-3-(4-fluorophenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate

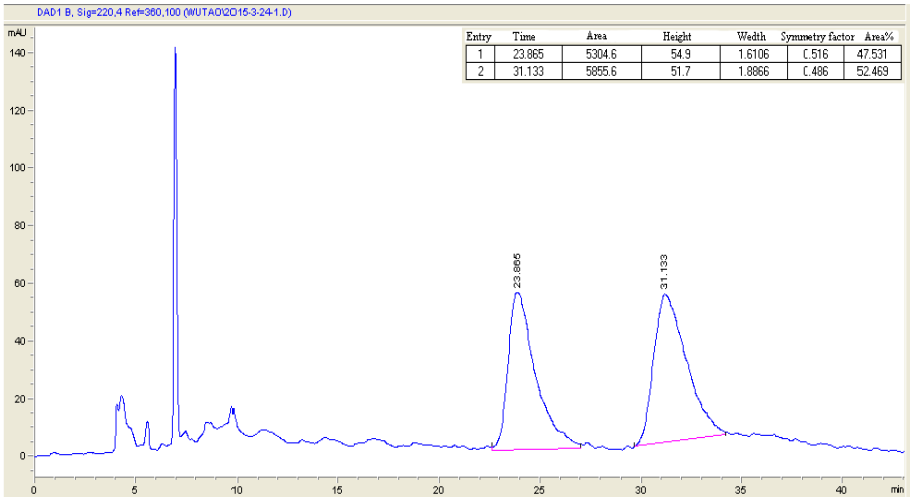




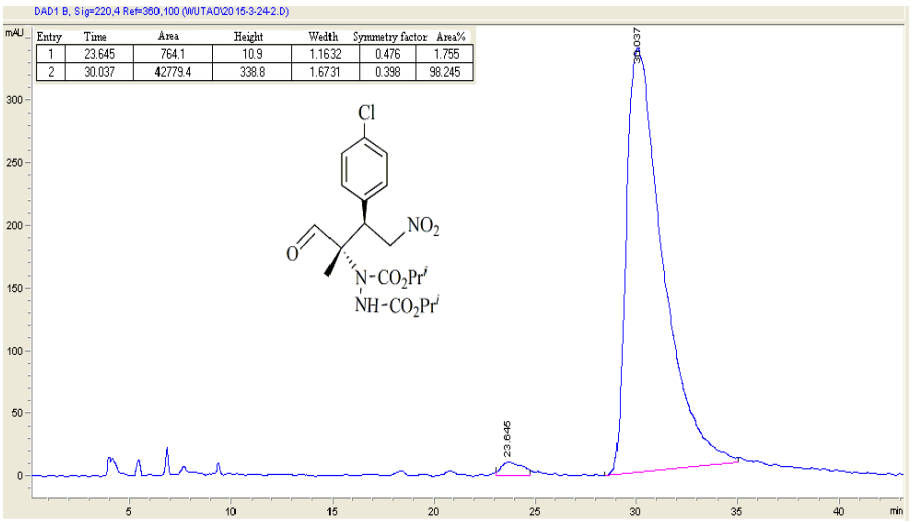
(3) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(4-chlorophenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate





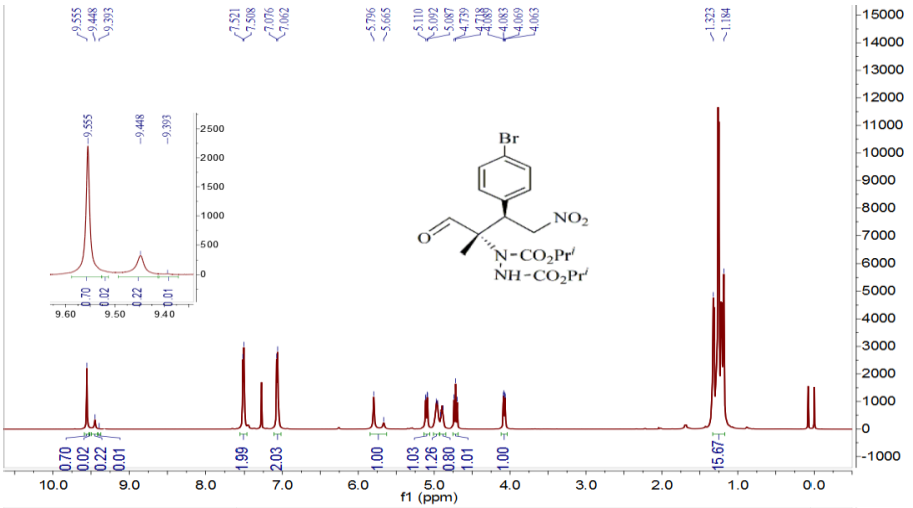


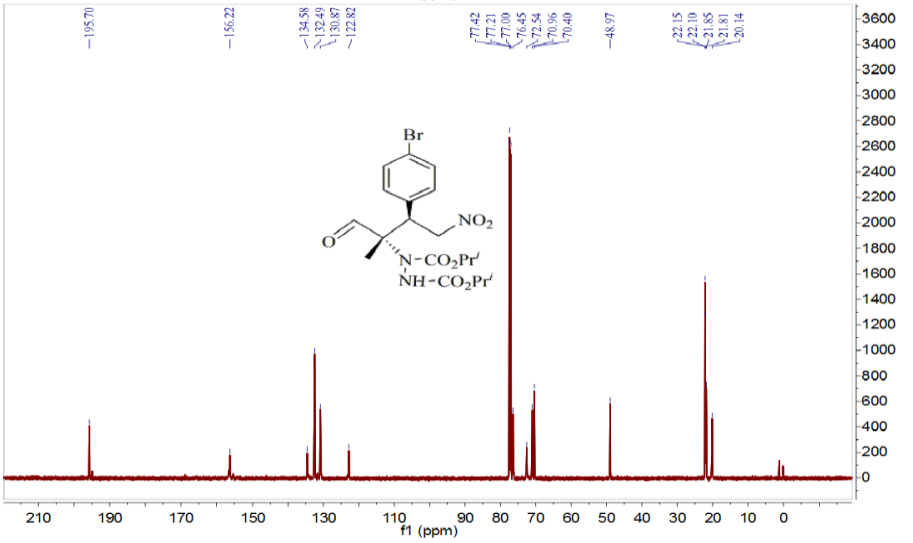
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	23.865	5304.6	54.9	1.6106	0.516	47.531
2	31.133	5855.6	51.7	1.8866	0.486	52.469

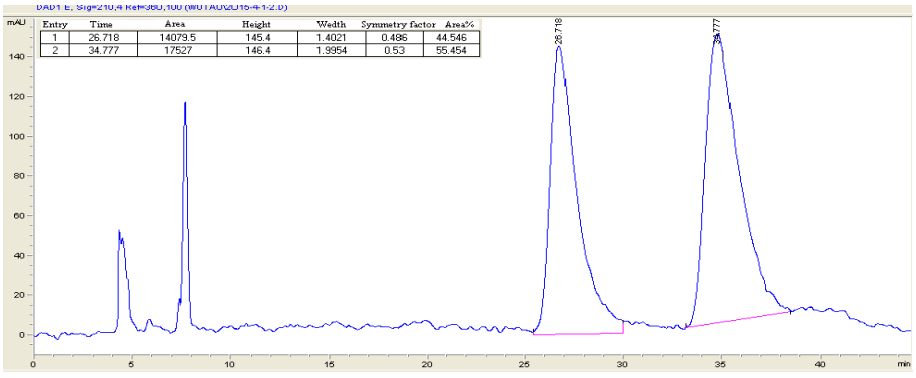


Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	23.645	764.1	10.9	1.1632	0.476	1.755
2	30.037	42779.4	338.8	1.6731	0.398	98.245

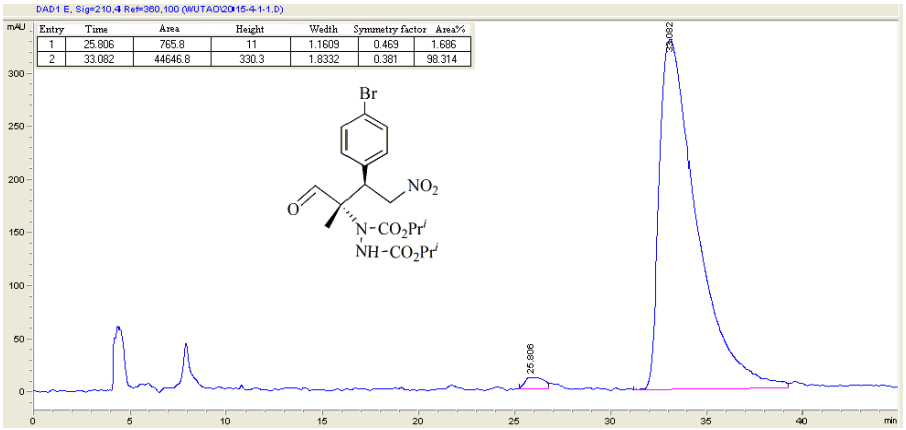
(4) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(4-bromophenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate







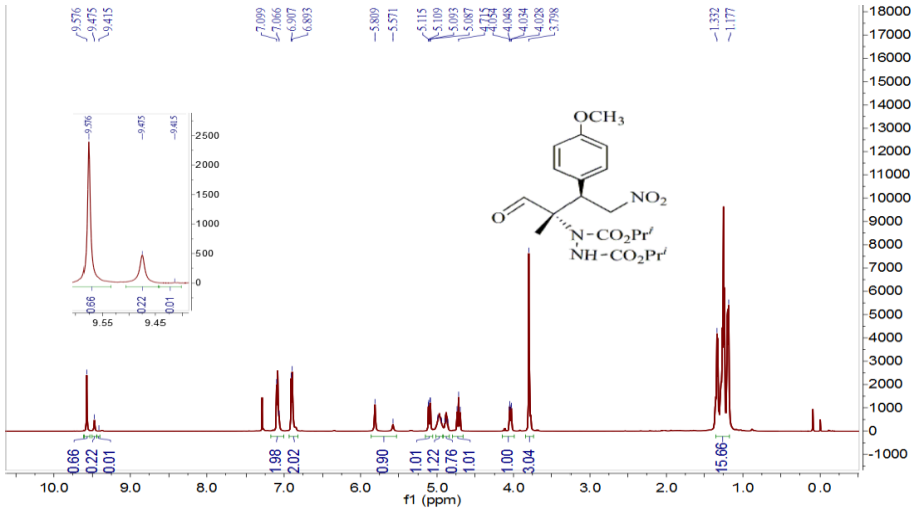
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	26.718	14079.5	145.4	1.4021	0.486	44.546
2	34.777	17527	146.4	1.9954	0.53	55.454

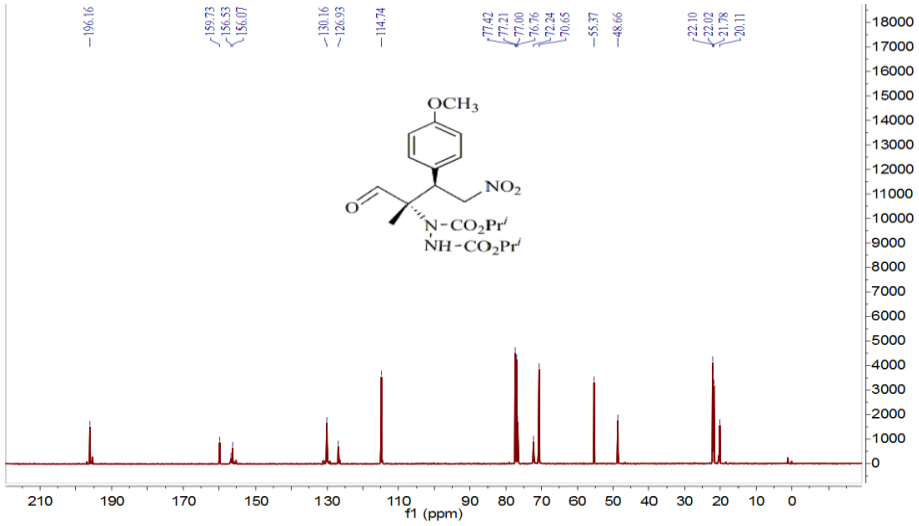


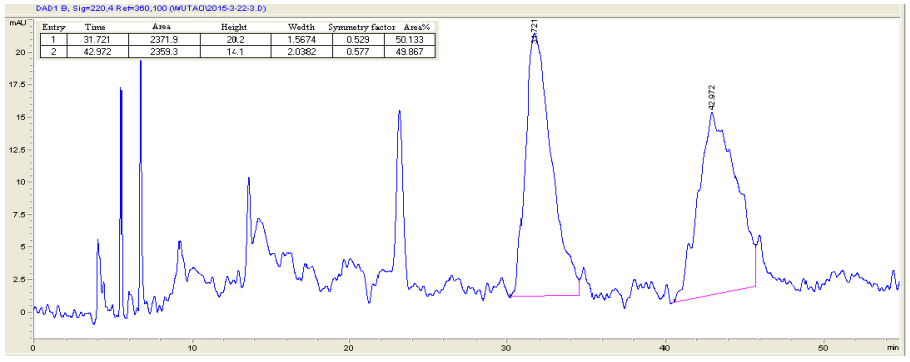
DAD1 E, Sig=210,4 Ref=360,100 (WUTAO2015-4-1-1.D)

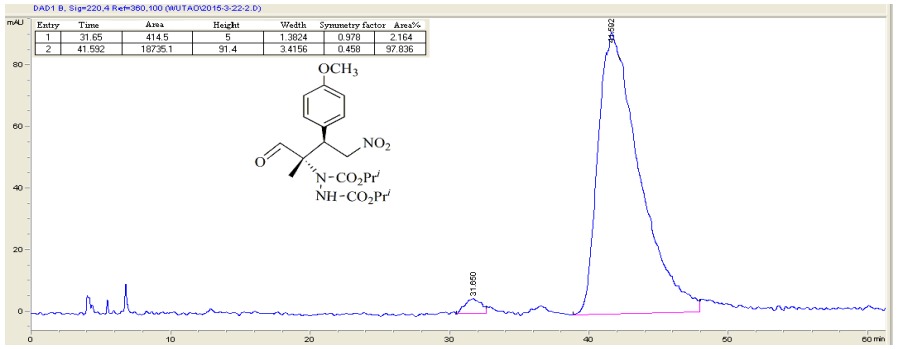
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	25.806	765.8	11	1.1609	0.469	1.686
2	33.082	44646.8	330.3	1.8332	0.381	98.314

(5) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(4-methoxyphenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate

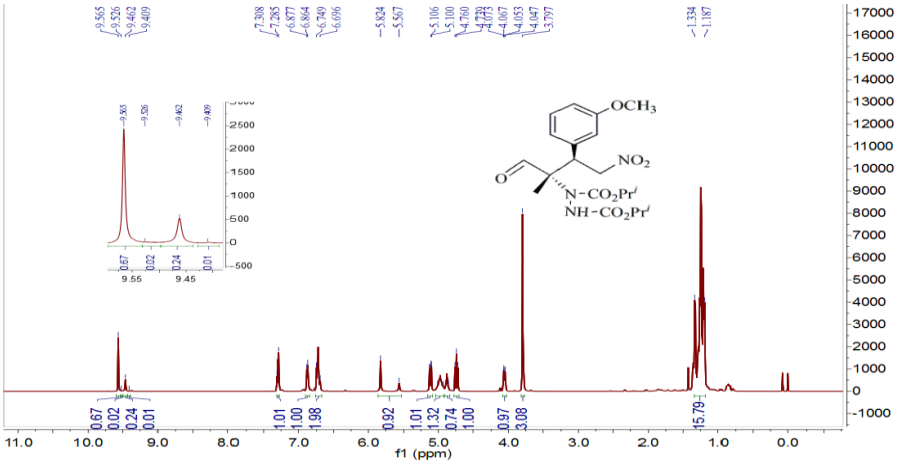


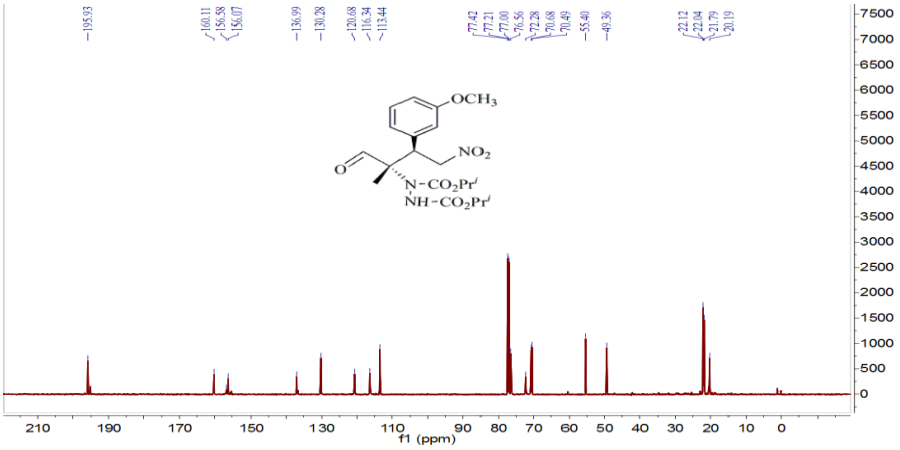


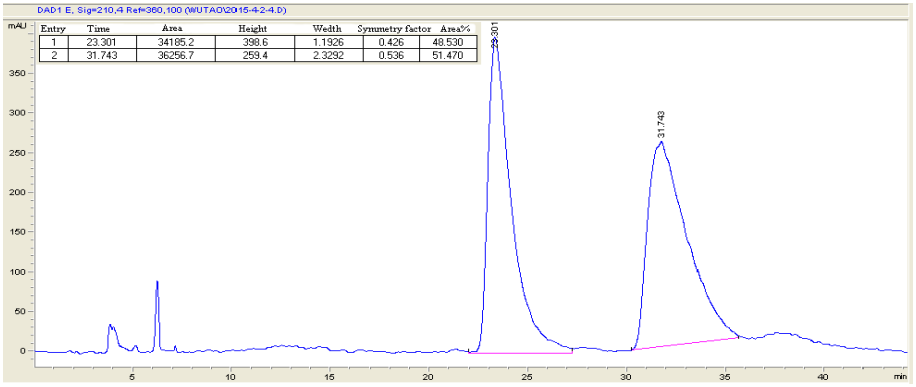


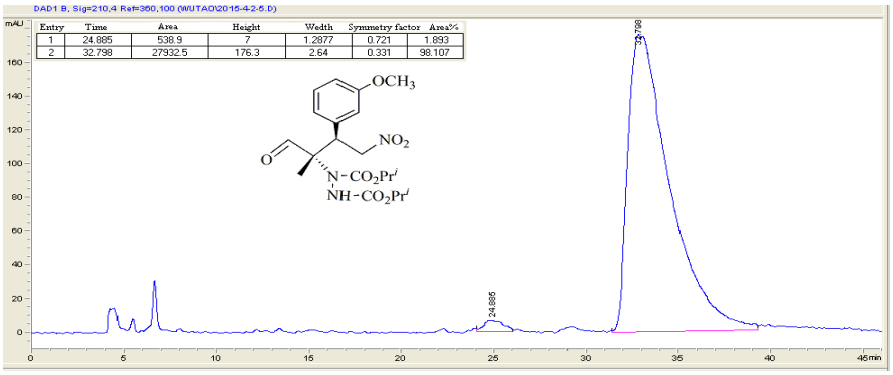


(6) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(3-methoxyphenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate

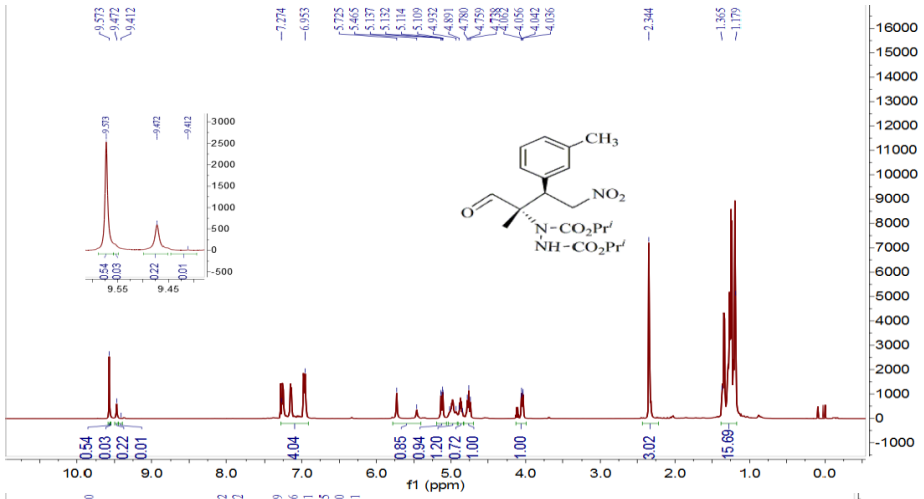


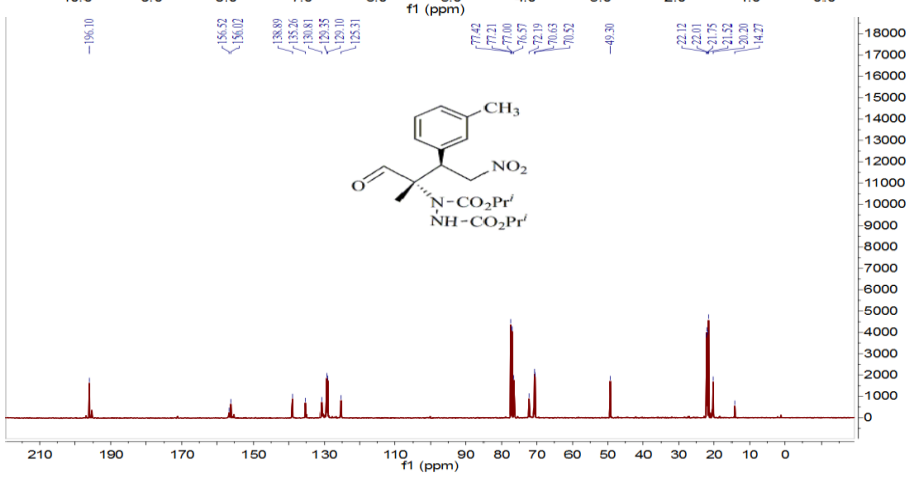


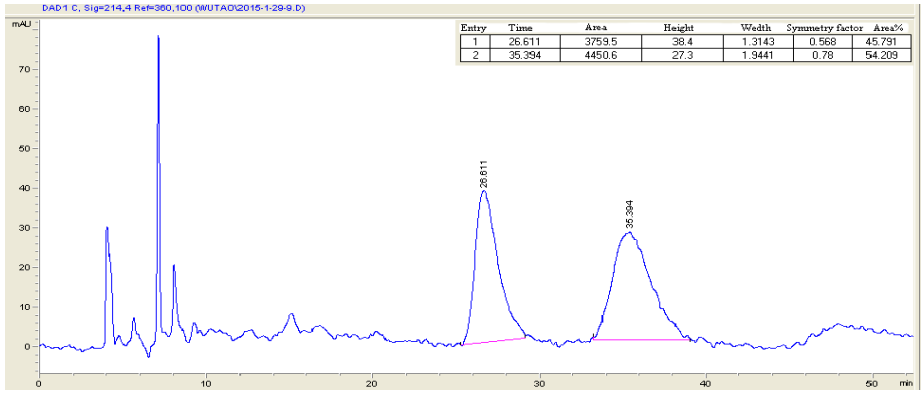




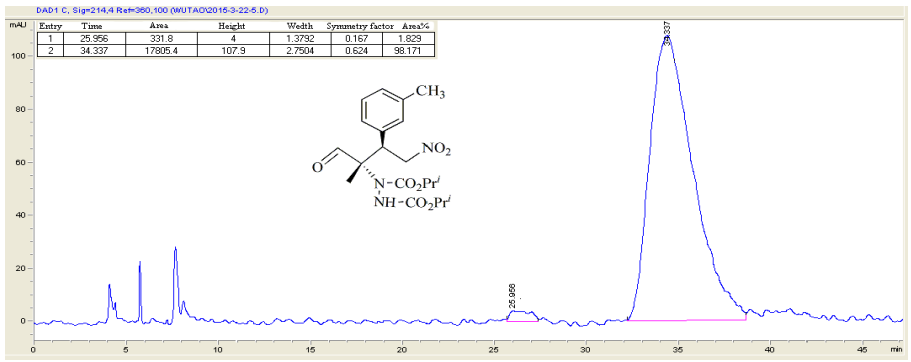
(7) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(3-methylphenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate





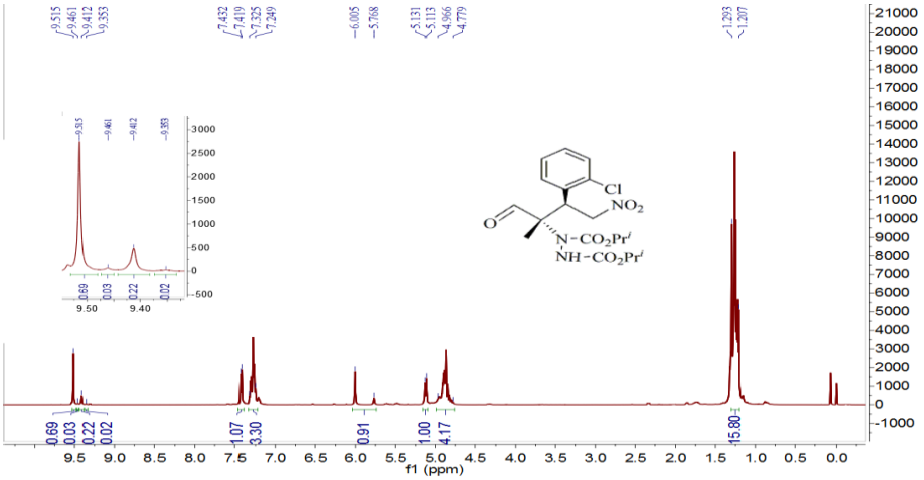


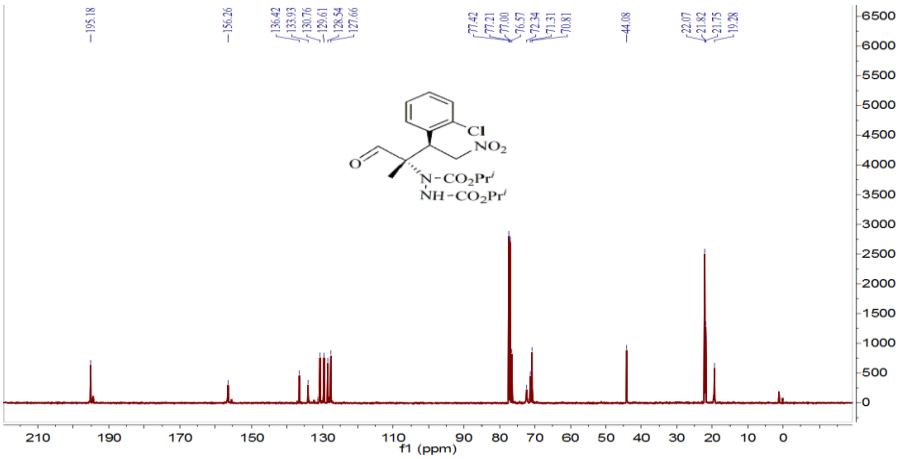
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	26.611	3759.5	38.4	1.3143	0.568	45.791
2	35.394	4450.6	27.3	1.9441	0.78	54.209

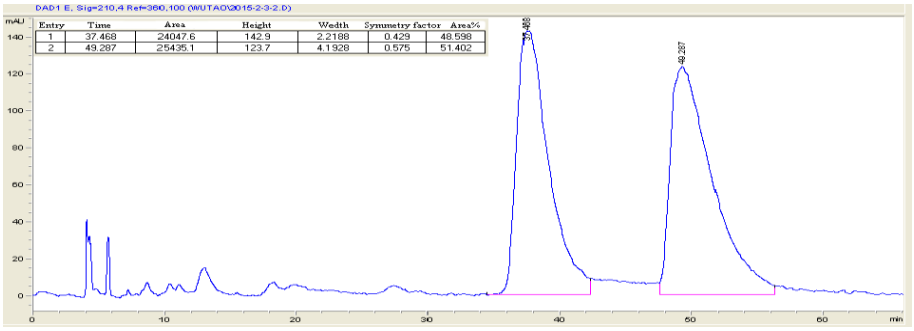


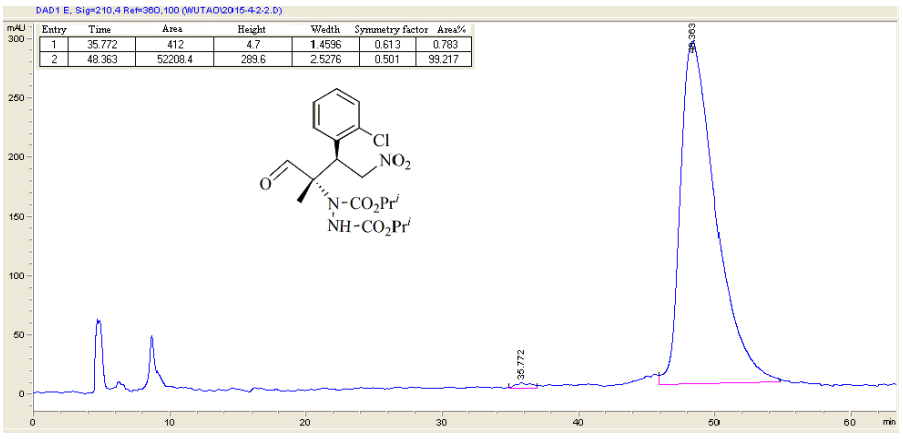
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	25.956	331.8	4	1.3792	0.167	1.829
2	34.337	17805.4	107.9	2.7504	0.624	98.171

(8) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(2-chlorophenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate

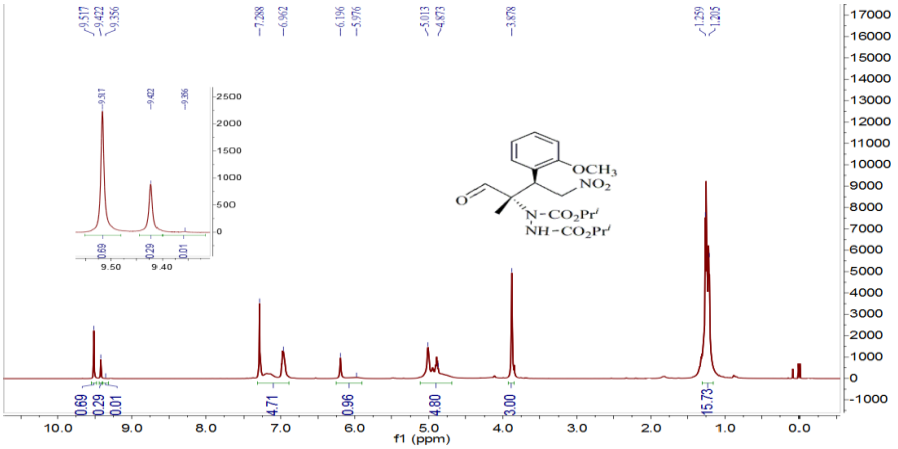


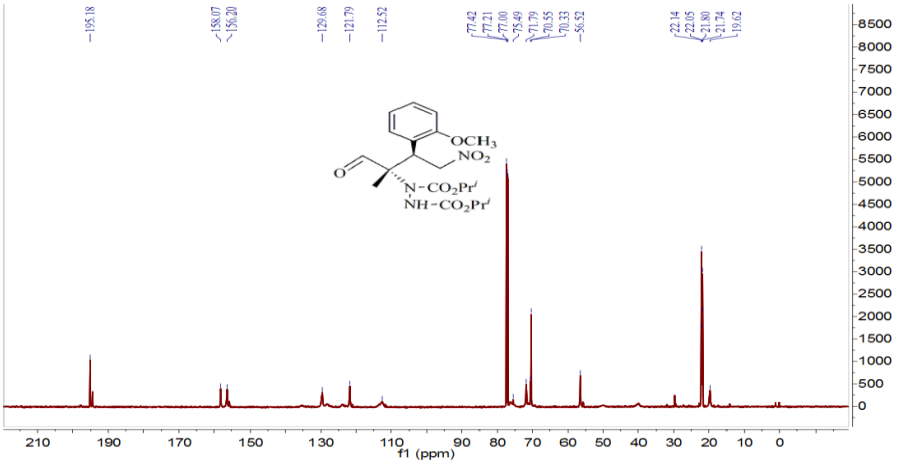


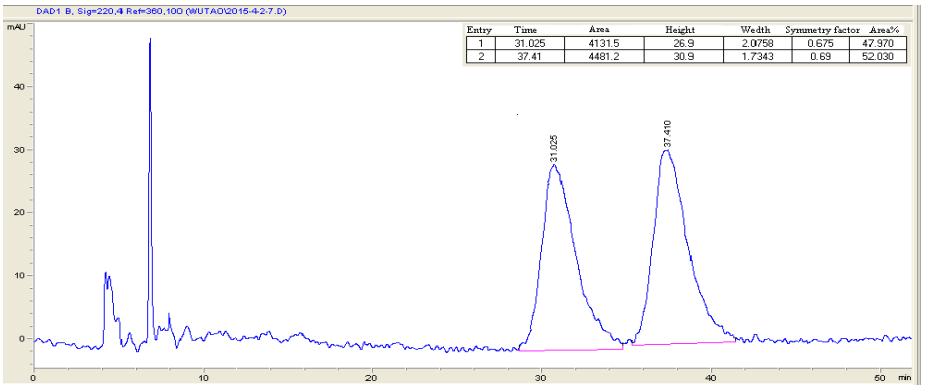




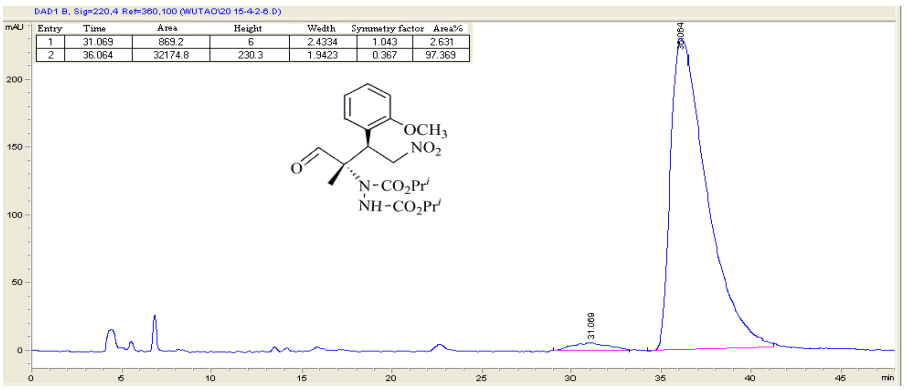
(9) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(2-methoxyphenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate





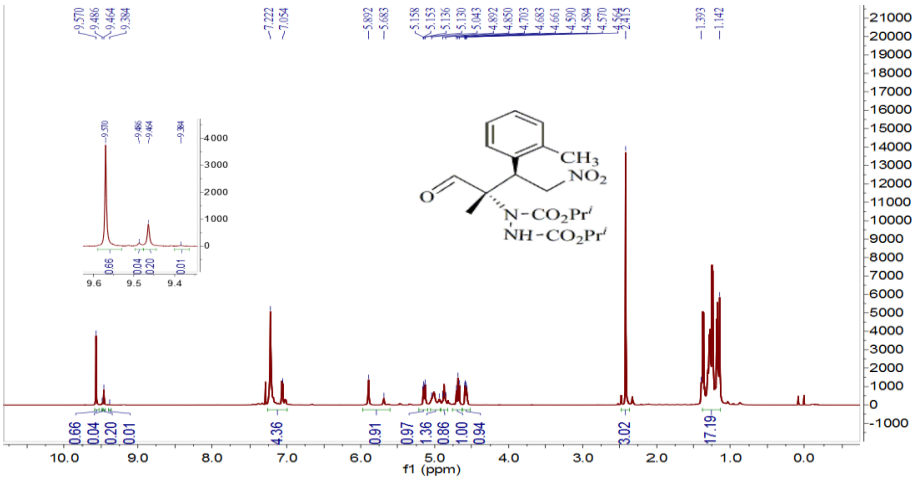


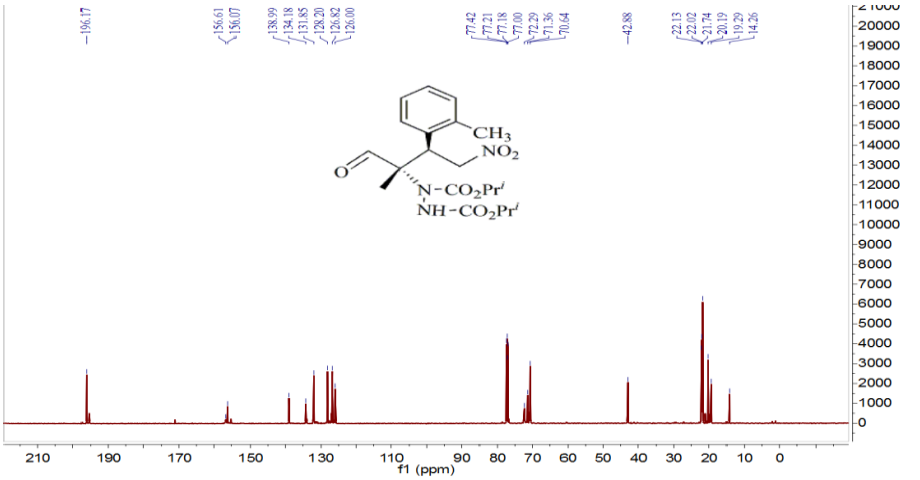
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	31.025	4131.5	26.9	2.0758	0.675	47.970
2	37.41	4481.2	30.9	1.7343	0.69	52.030

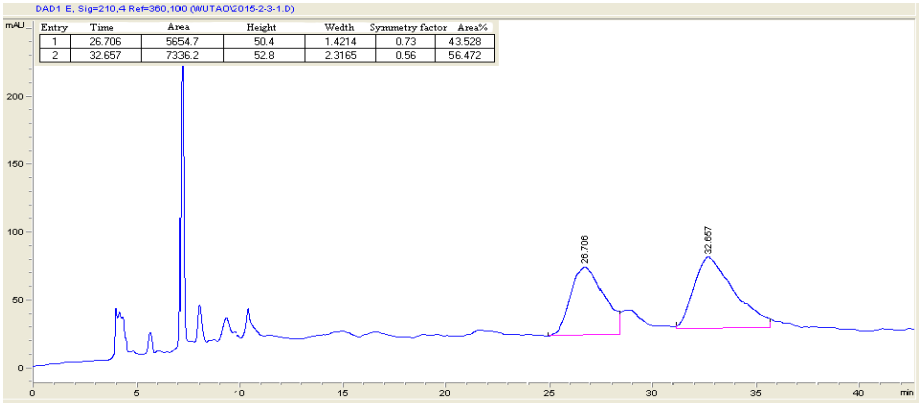


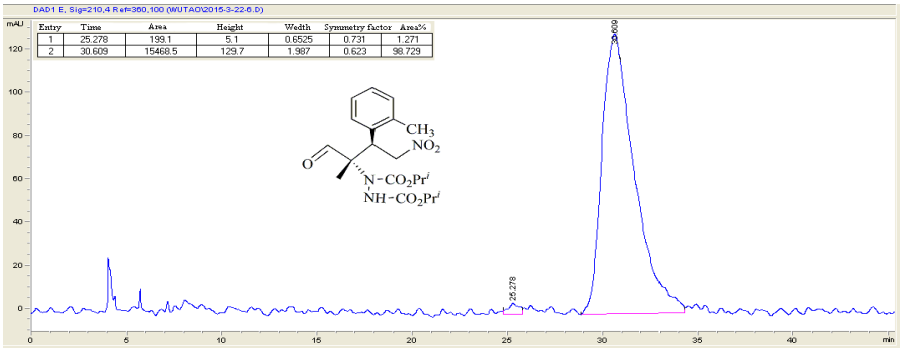
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	31.069	869.2	6	2.4334	1.043	2.631
2	36.064	32174.8	230.3	1.9423	0.367	97.369

(10) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(2-methylphenyl)butan-2-yl]hydrazine-1, 2-dicarboxylate

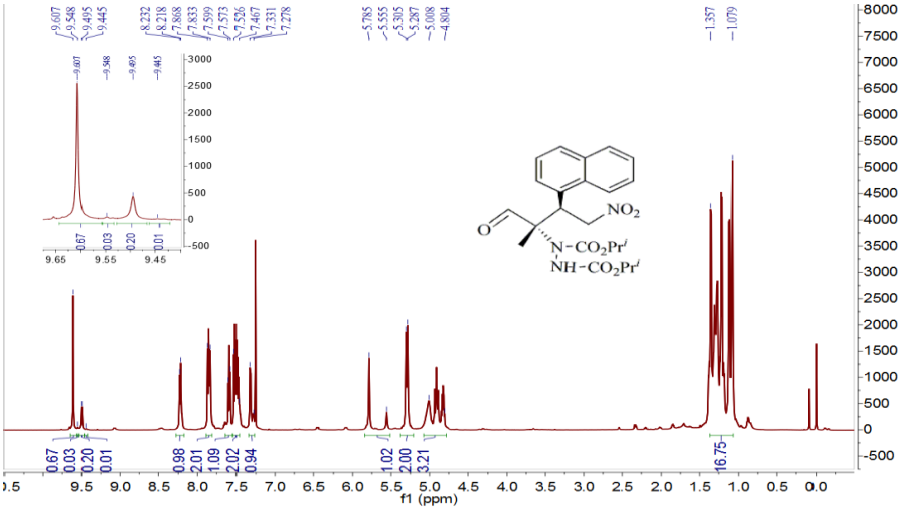


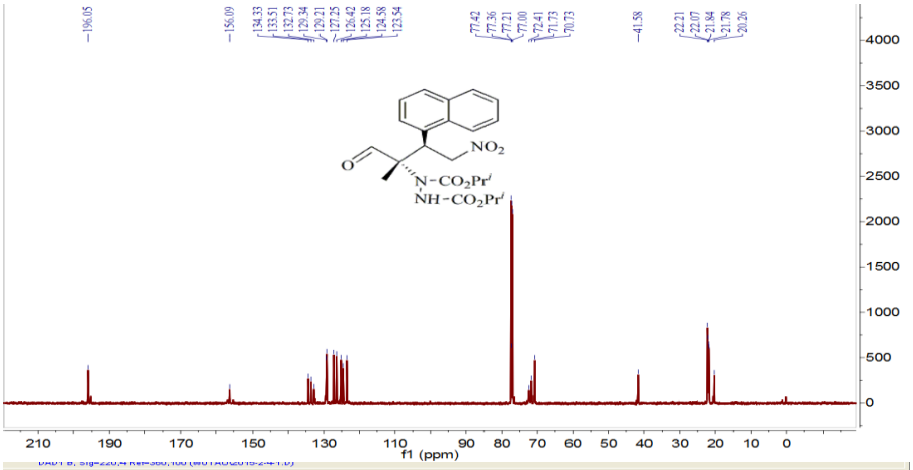


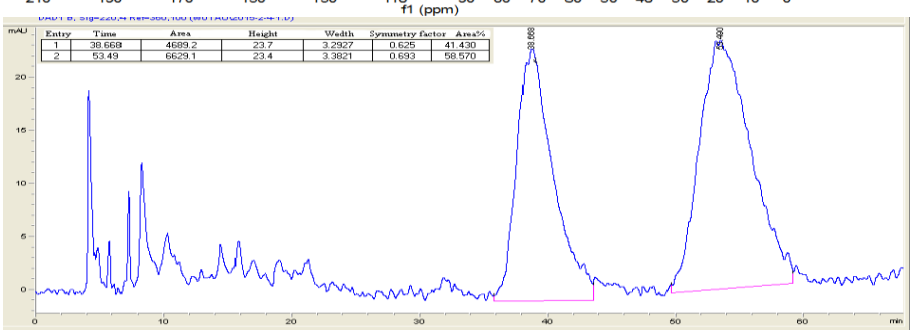


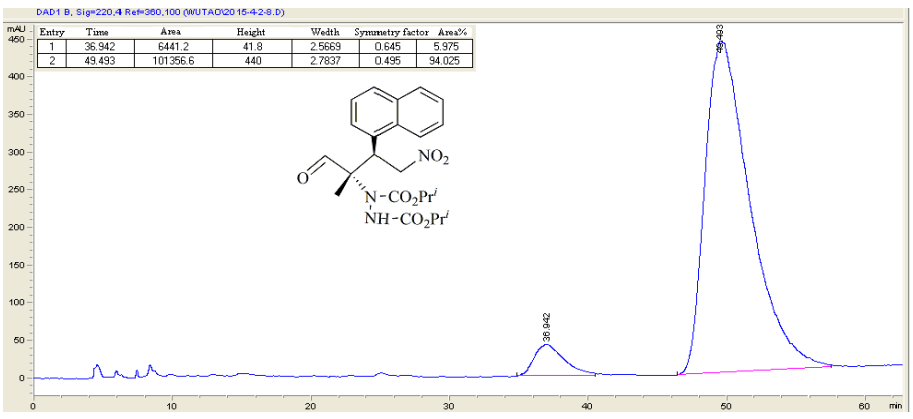


(11) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(naphthaen-1-yl)butan-2-yl]hydrazine-1, 2-dicarboxylate

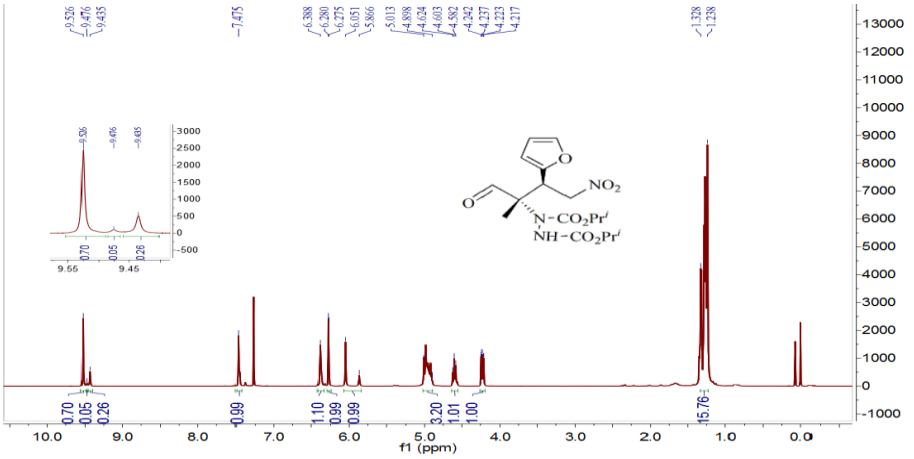


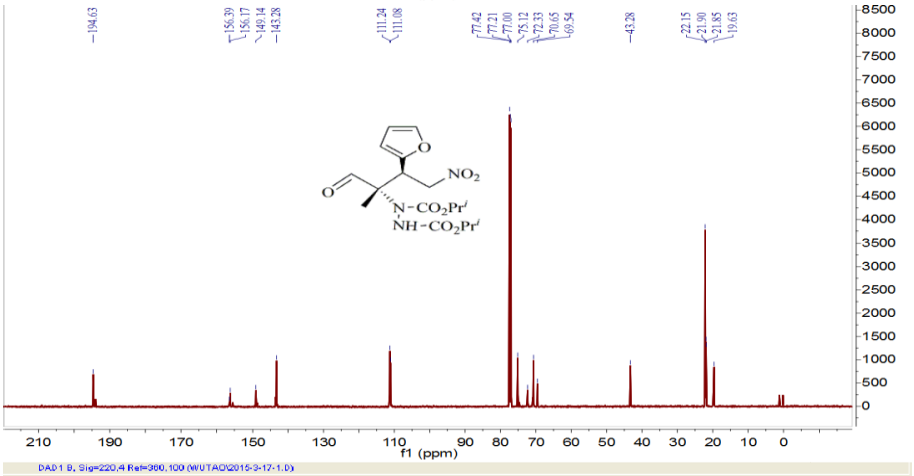


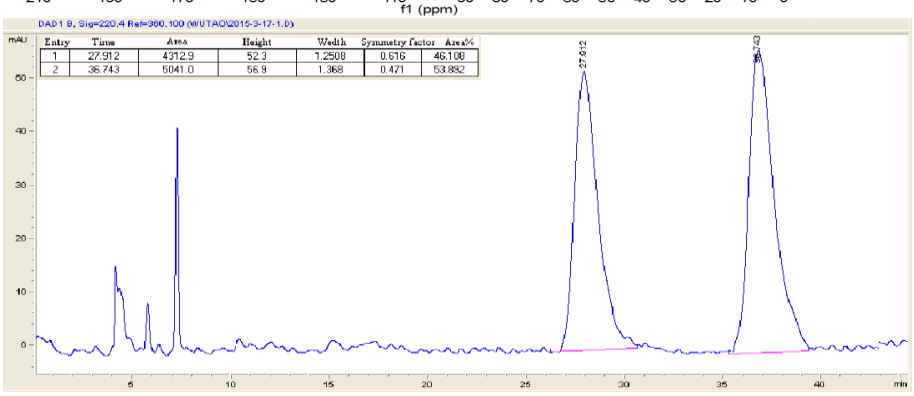


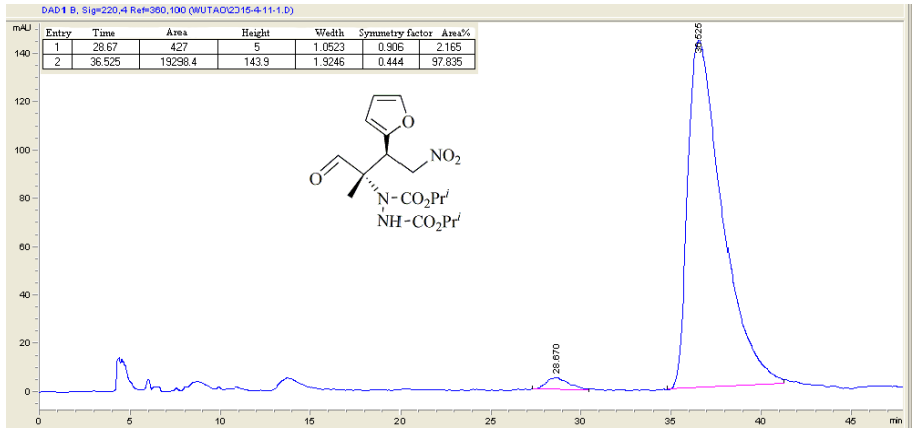


(12) Di-*iso*-propyl-1-[(2S, 3S)-2-methyl-4-nitro-1-oxo-3-(furan-2-yl)butan-2-yl]hydrazine-1, 2-dicarboxylate

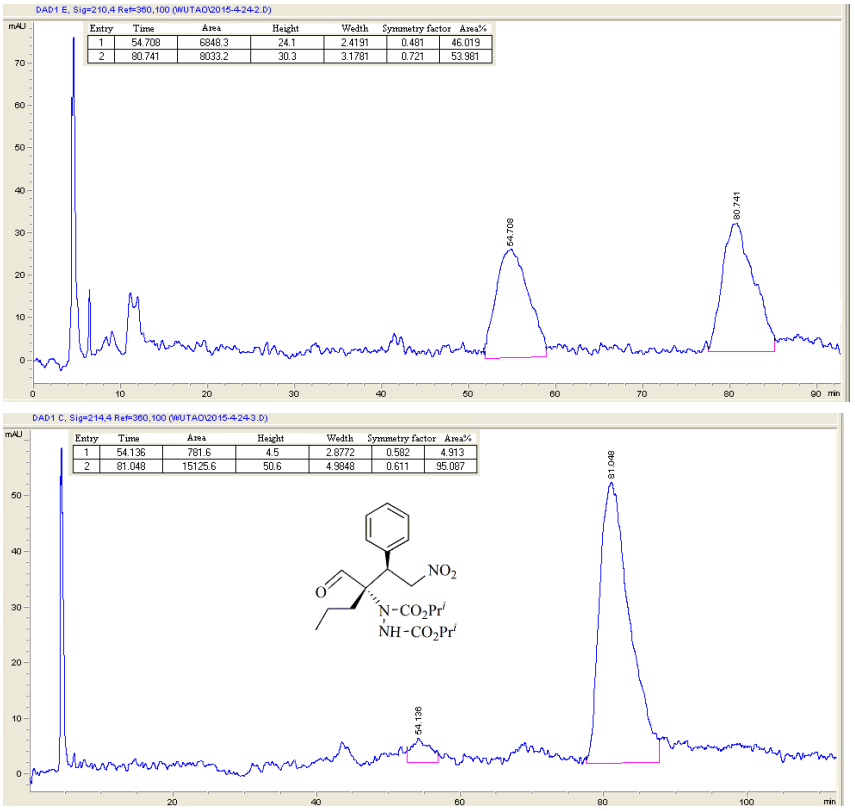








(13) Di-*iso*-propyl-1-[(2S, 3S)-2-propyl-4-nitro-1-oxo-3-(furan-2-yl)butan-2-yl]hydrazine-1, 2-dicarboxylate



7. Determination of diastereoselectivity of α-amination products

According to the reference (Org. Biomol. Chem., 2011, 9, 994–997), the *syn/anti* values of α-amination products were determined by ^{1}NMR. It was found that there are four peaks in the 9.35–9.62 ppm range, which was attributed to hydrogen in –CHO attached to two pairs of enantiomers. Using di-*iso*-propyl-1-[2-methyl-4-nitro-1-oxo-3-(4-fluorop-henyl)butan-2-yl]hydrazine-1, 2-dicarboxylate as an example shown in the following figure, the similar results of syn/anti were achieved by ^{1}H NMR and HPLC on Phenomenex column. The others were shown in above-mentioned ESI†.