Electronic Supplementary Material (ESI) for RSC Advances.

A solution to achieve good reusability of MNPs Fe_3O_4-supported (S)-Diphenylprolinoltrimethylsilyl ether catalysts in asymmetric Michael reaction

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1. Elemental analysis

Table s1. The elemental analysis of supported Jørgensen–Hayashi catalysts

Entry	Catalyst	C (%)	H (%)	N (%)	S (%)	Loaded ProTMS (%, mmol/g)	Loaded MPTMS (%, mmol/g)
1	Fe_3O_4/PVP	0.01	0.23	0.05	/	/	/
2	Fe_3O_4@SiO_2/ProTMS	31.51	4.10	1.02	6.15	37.81, 0.73	8.9, 1.18
3	Fe_3O_4/PVP@SiO_2/ProTMS	31.56	3.22	0.9	5.42	33.15, 0.64	8.0, 1.06
4	Fe_3O_4/PVP@SiO_2/ProTMS[a]	34.27	3.93	1.76	5.62	/	/

[a] 10th-recycled Fe_3O_4/PVP@ SiO_2/ProTMS

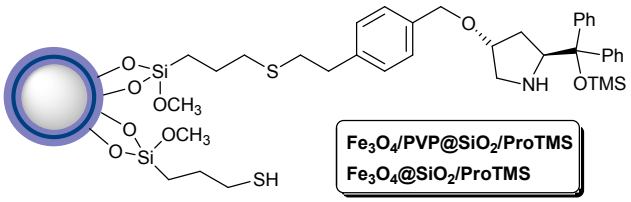
The calculation of loaded MPTMS, ProTMS and Jørgensen–Hayashi catalyst **5**:

In Fe_3O_4@SiO_2/ProTMS and Fe_3O_4/PVP@SiO_2/ProTMS catalysts, only Jørgensen–Hayashi catalyst **5** contained nitrogen element, the loading capacities of Jørgensen–Hayashi catalyst **5** was equal to that of ProTMS, and could be calculated according to elemental analysis (1.02% and 0.90%) as followed.

In Fe_3O_4@SiO_2/ProTMS: 1.02 ÷(14×100) ×1000=0.73 (mmol g^{-1})

In Fe_3O_4/PVP@SiO_2/ProTMS: 0.9÷(14×100) ×1000=0.64 (mmol g^{-1})

Furthermore, Jørgensen–Hayashi catalyst **5** was immobilized by the radical addition of sulfydryl (-SH) to C=C double bond to obtain ProTMS. It is confirmed that nitrogen in ProTMS has the same content as sulphur, and the total contents of sulphur (6.15% and 5.42%) are the sum of sulfide (-S-) and thiol (-SH).



Then, the total contents of sulphur:

In Fe_3O_4@SiO_2/ProTMS: 6.15 ÷(32×100) ×1000=1.92 (mmol g^{-1})

In Fe_3O_4/PVP@SiO_2/ProTMS: 5.42 ÷(32×100) ×1000=1.69 (mmol g^{-1})

The contents of free MPTMS unreacted with Jørgensen–Hayashi catalyst **5**:

In Fe_3O_4@SiO_2/ProTMS: 1.92-0.73=1.19 (mmol g^{-1})

In Fe_3O_4/PVP@SiO_2/ProTMS:1.69-0.64=1.05 (mmol g^{-1})

The molar ratios of free MPTMS to ProTMS:

In Fe_3O_4@SiO_2/ProTMS:1.19/0.73=1.63

In Fe_3O_4/PVP@SiO_2/ProTMS:1.05/0.64=1.64

2. TGA

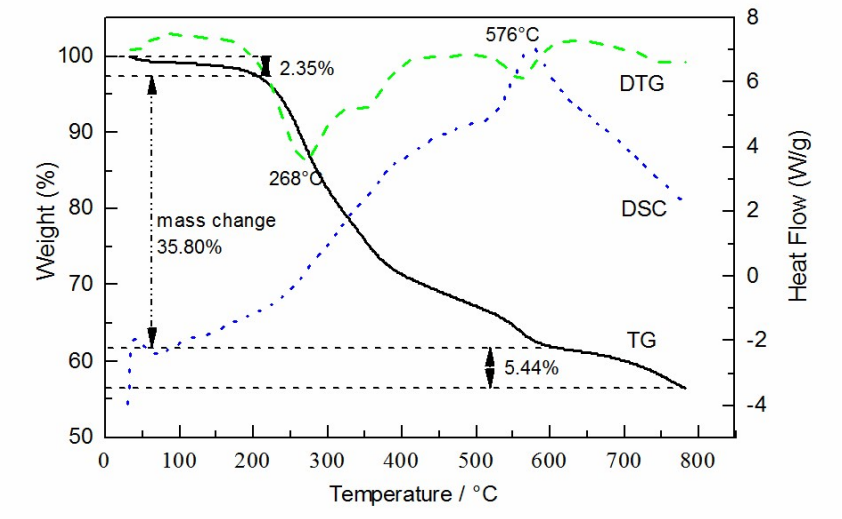


Fig. s1 TGA of Fe_3O_4@SiO_2/ProTMS

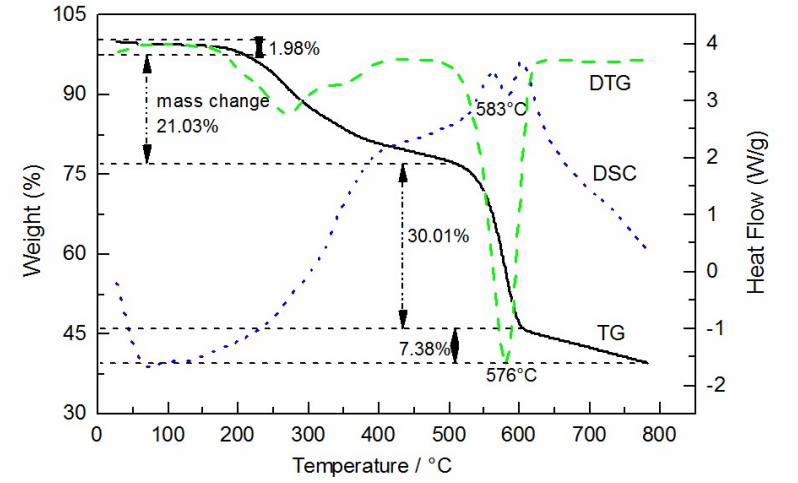


Fig. s2. TGA of Fe_3O_4/PVP@SiO_2/ProTMS

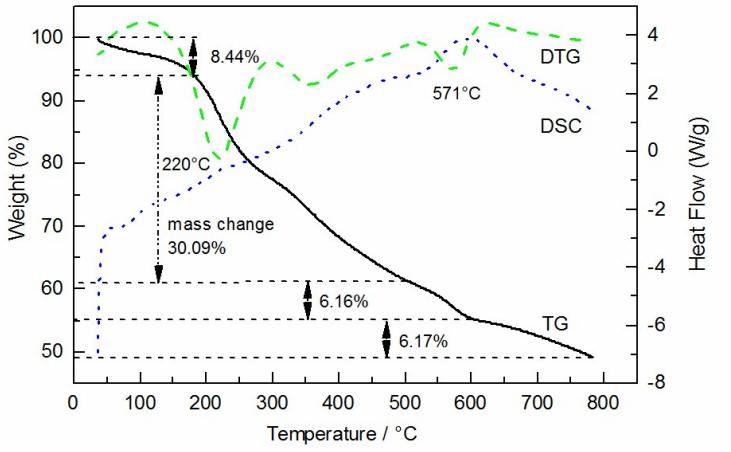


Fig. s3. TGA of 10th-recycled Fe_3O_4/PVP@SiO_2/ProTMS

3. N_2 adsorption-desorption isotherm

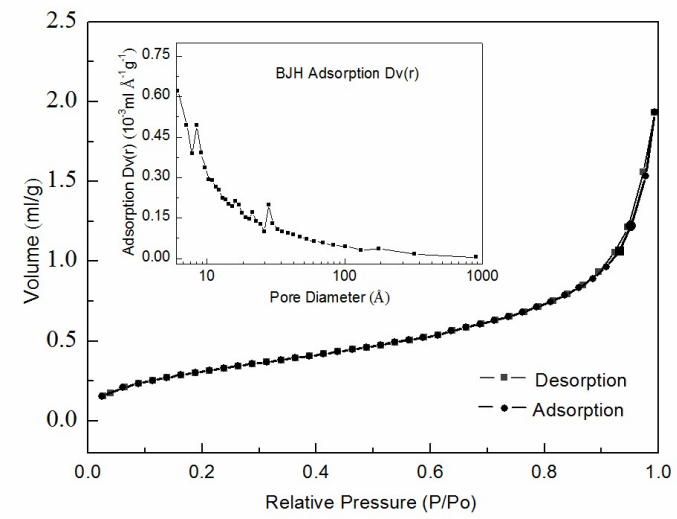


Fig. s4. N_2 adsorption-desorption isotherm and pore distribution of **Fe_3O_4**

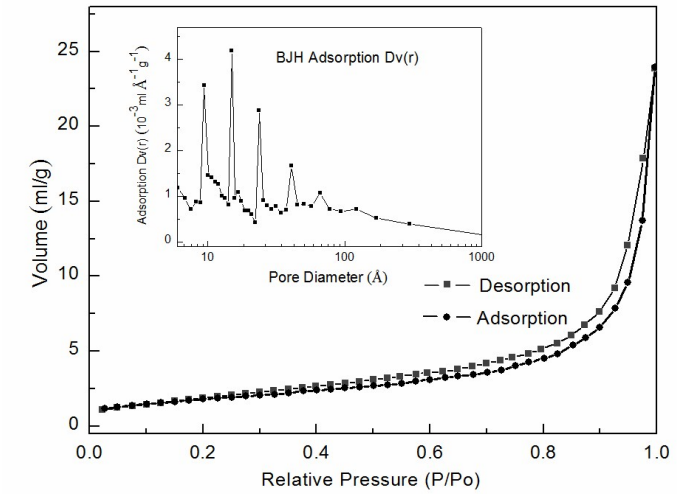


Fig. s5. N_2 adsorption-desorption isotherm and pore distribution of **Fe_3O_4/PVP**

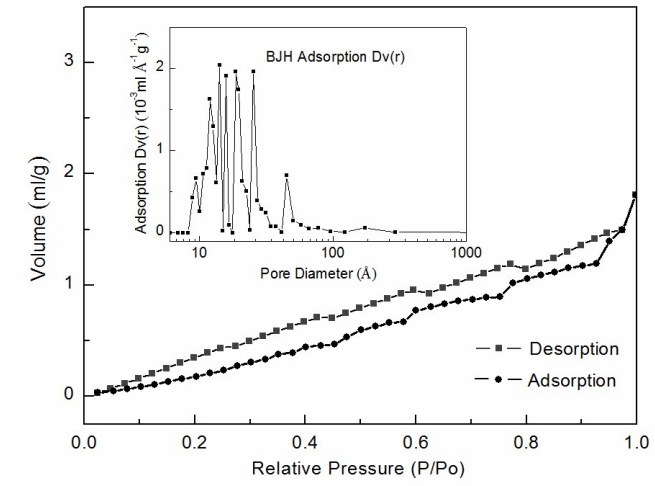


Fig. s6. N_2 adsorption-desorption isotherm and pore distribution of Fe_3O_4@SiO_2/ProTMS

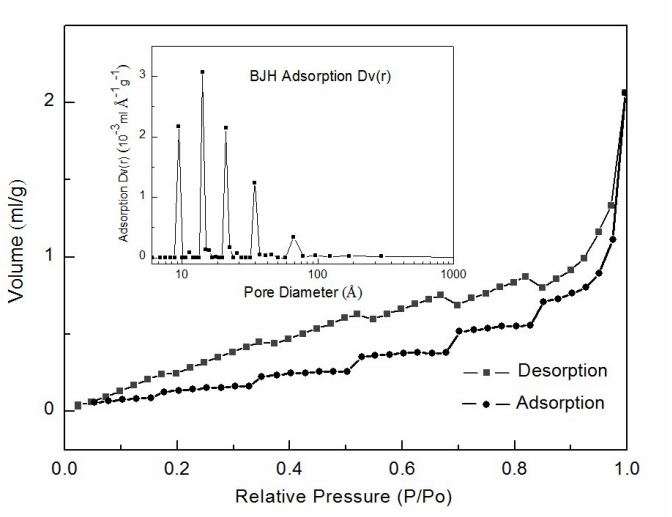


Fig. s7. N_2 adsorption-desorption isotherm and pore distribution of Fe_3O_4/PVP@SiO_2/ProTMS

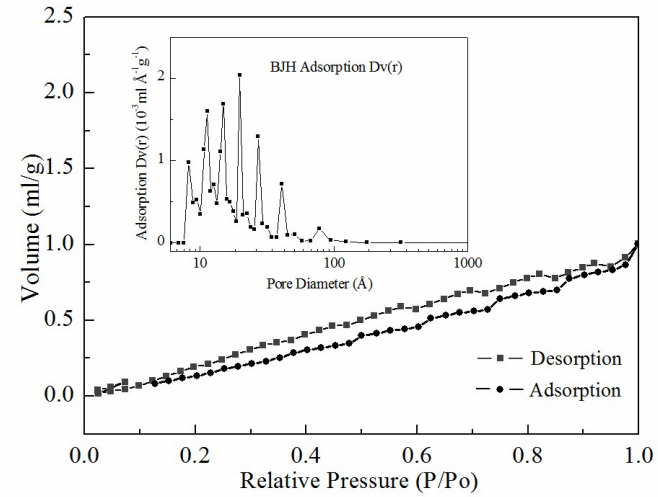


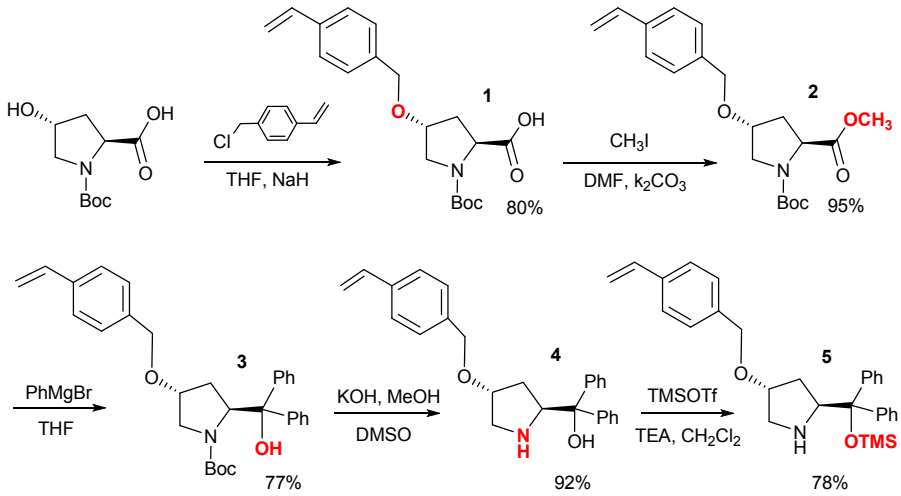
Fig. s8. N_2 adsorption-desorption isotherm and pore distribution of 10th-recycled Fe_3O_4/PVP@SiO_2/ProTMS

Table s2. The mesoporous properties of as-synthesized sample [a]

Entry	Catalyst	Surface Area [m^2/g] [b]	Average Pore Diameter [Å] [c]	Pore Volume [10^{-3}cc/g] [d]
1	Fe_3O_4	7.91	51.9	20.53
2	Fe_3O_4/PVP	65.88	117.2	385.9
3	Fe_3O_4@SiO_2/ProTMS	3.34	75.69	12.65
4	Fe_3O_4/PVP@SiO_2/ProTMS	3.92	157.1	30.77
5	Fe_3O_4/PVP@SiO_2/ProTMS [e]	16.86	25.00	21.07

[a] The sample was degassed at 100 °C for 5 h.
[b] Based on multipoint BET method.
[c] Based on the desorption data using BJH method. [d] Based on the desorption data of BJH method.
[e] 10th-recycled Fe_3O_4/PVP@SiO_2/ProTMS

4. ^{1}H and ^{13}C NMR spectra of intermediates and Jørgensen-Hayashi catalyst 5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OH
N
Boc
O
Cl
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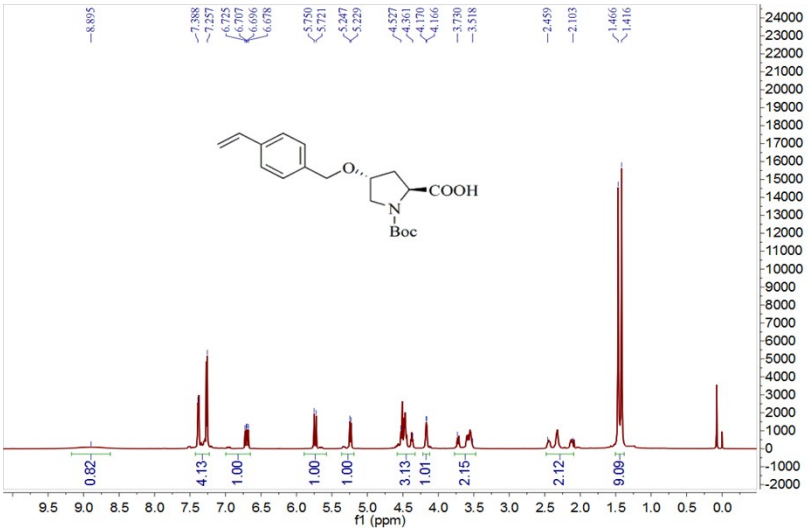
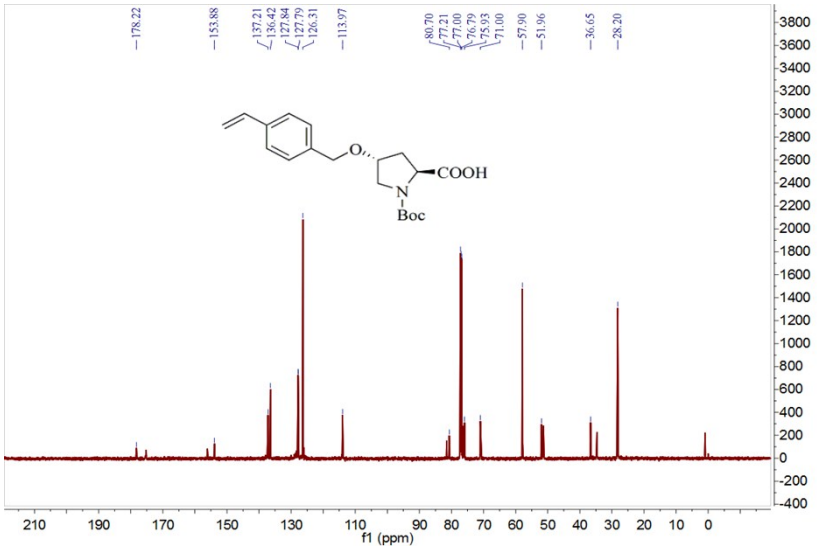
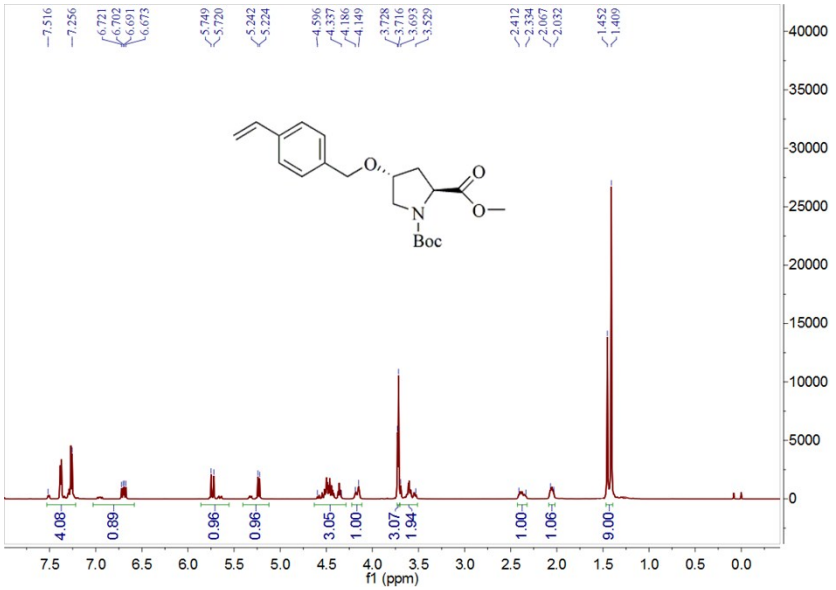
CH3I
DMF, k2CO3
2
OCH3
95%
PhMgBr
THF
3
Ph
Ph
OH
77%
KOH, MeOH
DMSO
4
92%
TMSOTf
TEA, CH2Cl2
5
OTMS
78%


COOH
Boc
f1 (ppm)


COOH
Boc
f1 (ppm)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6.702
6.691
6.673
5.749
5.720
5.242
5.224
4.596
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4.186
4.149
3.728
3.716
3.693
3.529
2.412
2.334
2.067
2.032
1.452
1.409
O
O
O
N
Boc
4.08
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0.96
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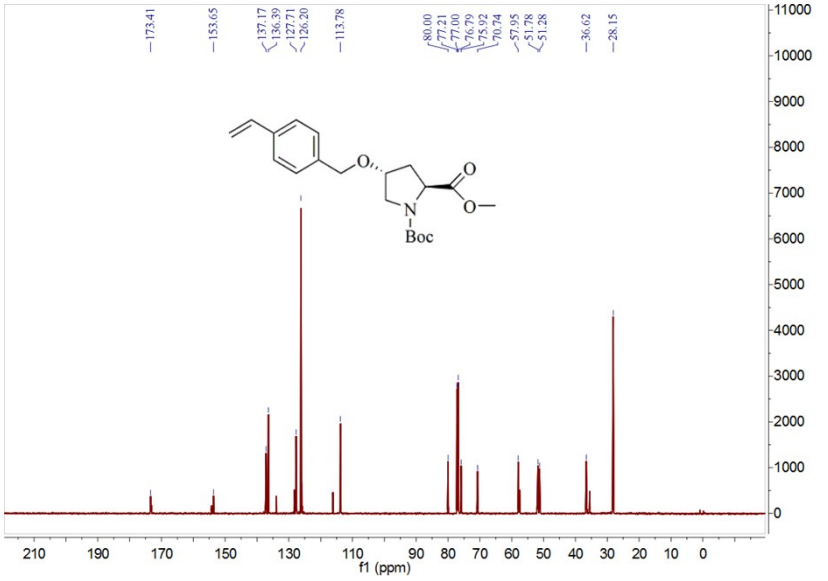
1.00
3.07
1.94
1.00
1.06
9.00
f1 (ppm)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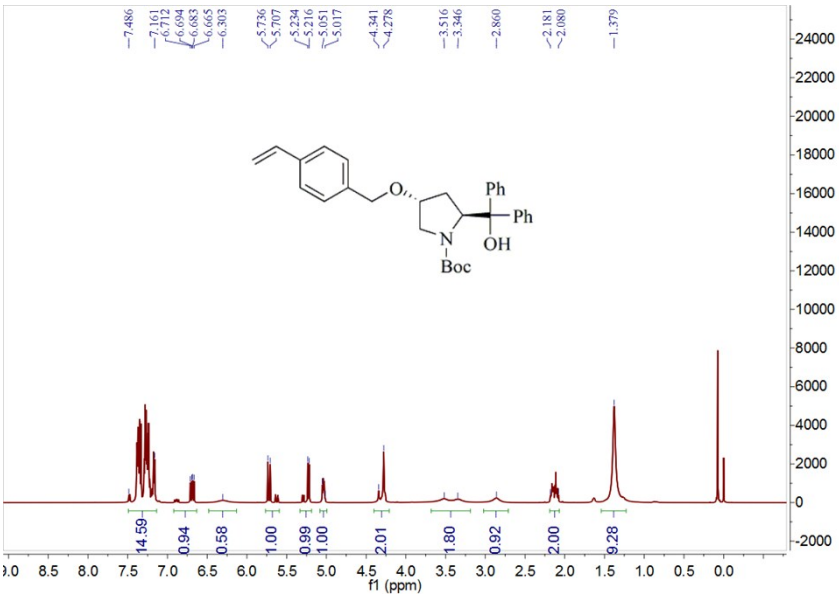
153.65
137.17
136.39
127.71
126.20
113.78
80.00
77.21
77.00
76.79
75.92
70.74
57.95
51.78
51.28
36.62
28.15
O
O
O
N
Boc
f1 (ppm)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6.694
6.683
6.665
6.303
5.736
5.707
5.234
5.216
5.051
5.017
4.341
4.278
3.516
3.346
2.860
2.181
2.080
1.379
O
Ph
Ph
N
OH
Boc
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1.00
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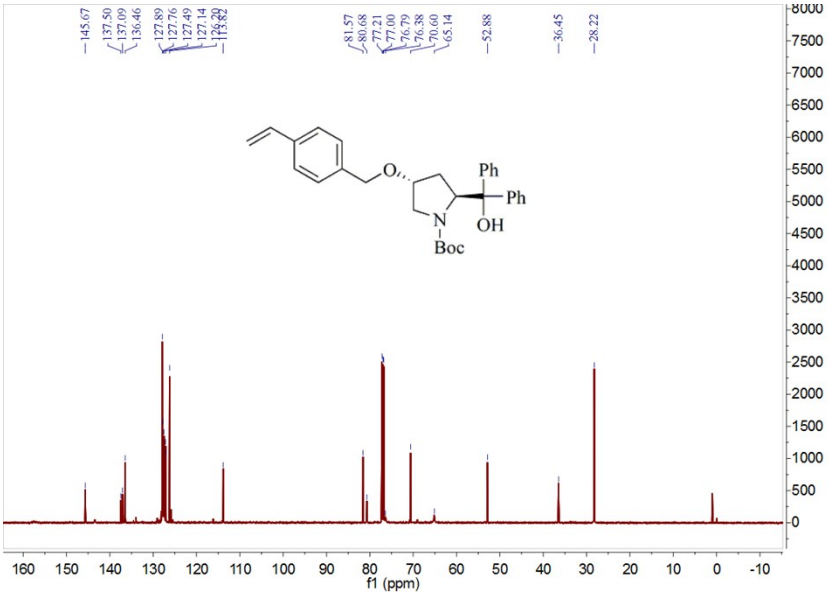
0.92
2.00
9.28
f1 (ppm)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127.76
127.49
127.14
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80.68
77.21
77.00
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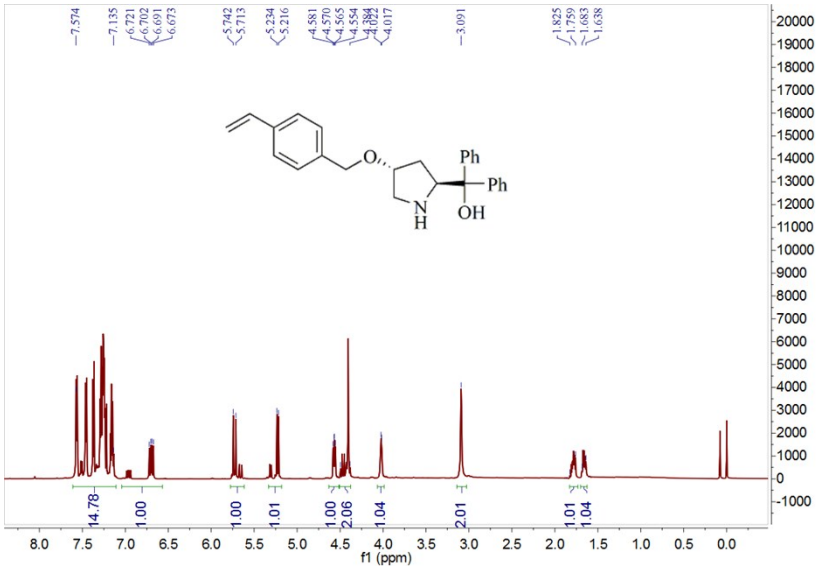
O
Ph
Ph
OH
N
Boc
f1 (ppm)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6.691
6.673
5.742
5.713
5.234
5.216
4.581
4.570
4.565
4.554
4.017
3.091
1.825
1.759
1.683
1.638
O
Ph
Ph
OH
N
H
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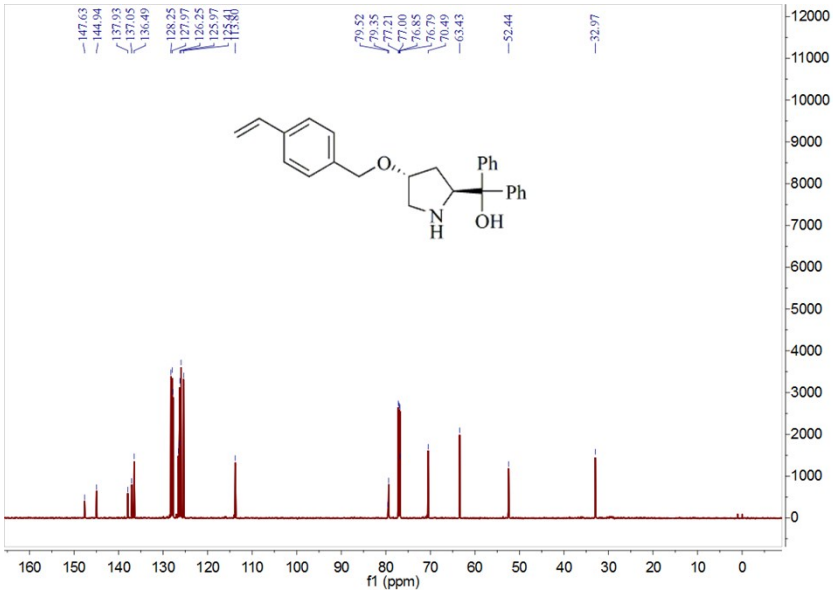
1.00
1.01
1.00
2.06
1.04
2.01
1.01
1.04
f1 (ppm)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137.93
137.05
136.49
128.25
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126.25
125.97
79.52
79.35
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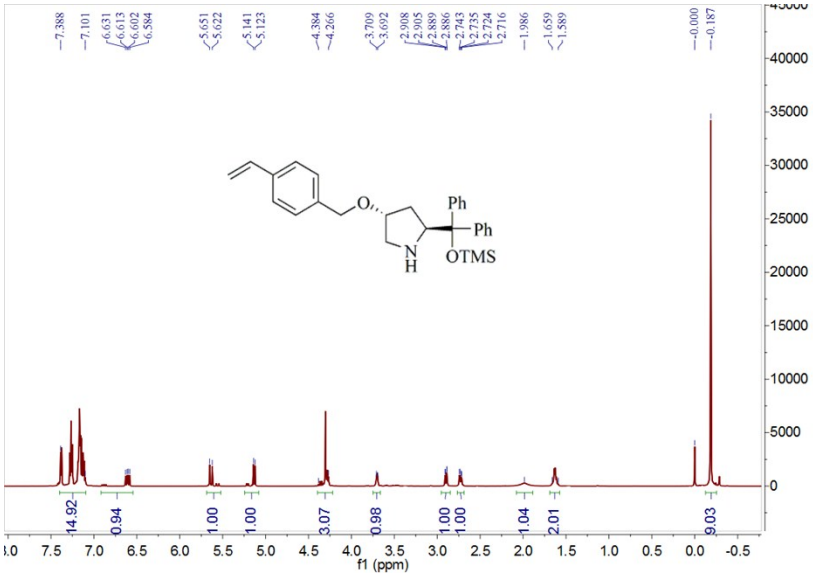
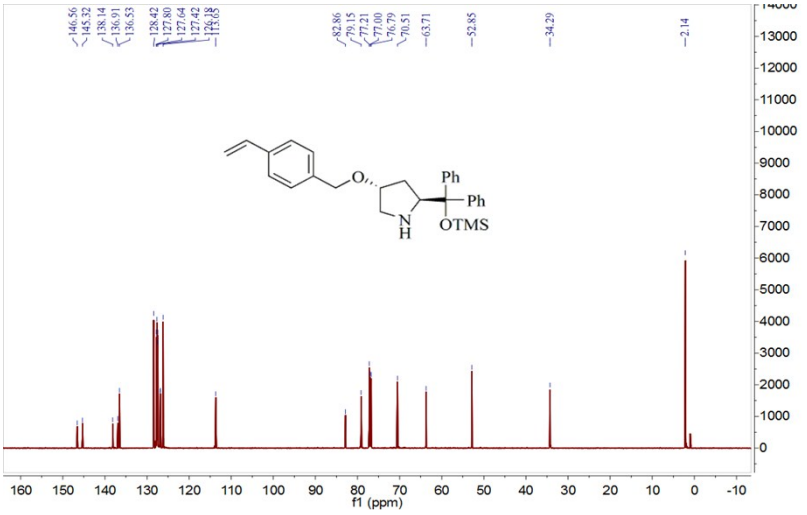
76.79
70.49
63.43
52.44
32.97
O
Ph
Ph
OH
N
H
f1 (ppm)



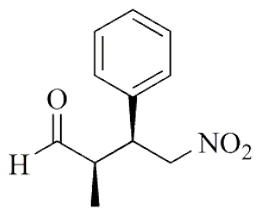


5. Characterization of asymmetric Michael reaction products

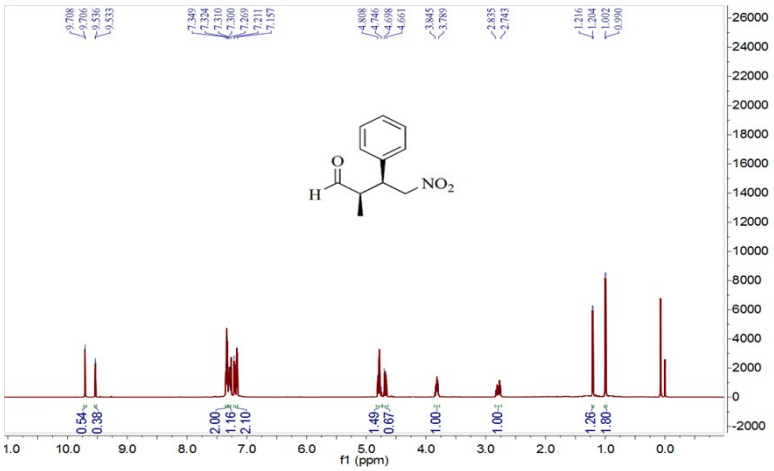
Racemic Michael adducts were prepared using pyrolidine as catalyst according to the same procedure. Nitroalkenes derivatives were synthesized according to the reported literature. [1-3]

[1] Gao S. H., et. al., *Org. Lett.*, **2006**, 8, 2373-2376.
[2] Trost B. M., et. al., *J. Am. Chem. Soc.*, **2008**, 130, 2438-2439.
[3] Lopchuk J. M., et. al., *Org. Lett.*, **2013**, 15, 5218-5221.

(2R, 3S)-2-methyl-4-nitro-3-phenylbutanal: 96:4 dr, 98.2% ee, HPLC on Daicel Chiralpak OD-H column:



heptane/*i*-PrOH = 8/2, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 26.8 min (minor), t_R = 37.5 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.00 (d, J = 7.3 Hz, 3H, CH_3), 2.74–2.84 (m, 1H, CHCH$_3$), 3.79–3.85 (m, 1H, CHCH$_2$), 4.77–4.81 (m, 2H, CH_2), 7.16–7.21 (m, 2H, Ar-*H*), 7.27–7.30 (m, 1H, Ar-*H*), 7.32–7.35 (m, 2H, Ar-*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*=O).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9.533
7.349
7.324
7.310
7.300
7.269
7.211
7.157
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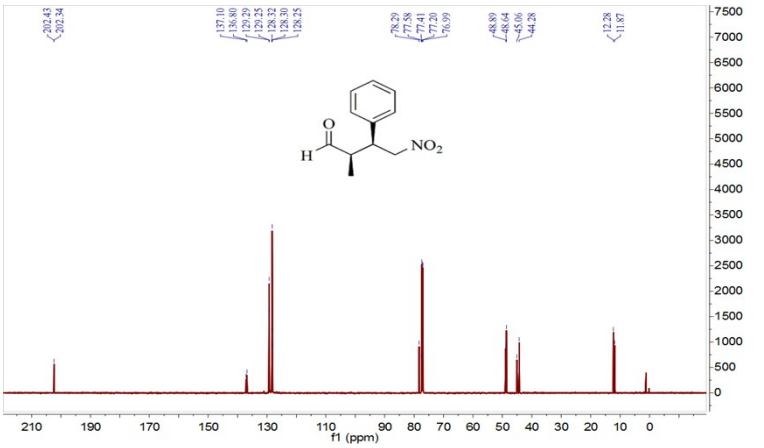
4.746
4.698
4.661
3.845
3.789
2.835
2.743
1.216
1.204
1.002
0.990
O
H
NO2
0.54
0.38
2.00
1.16
2.10
1.49
0.67
1.00
1.00
1.26
1.80
f1 (ppm)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129.29
129.25
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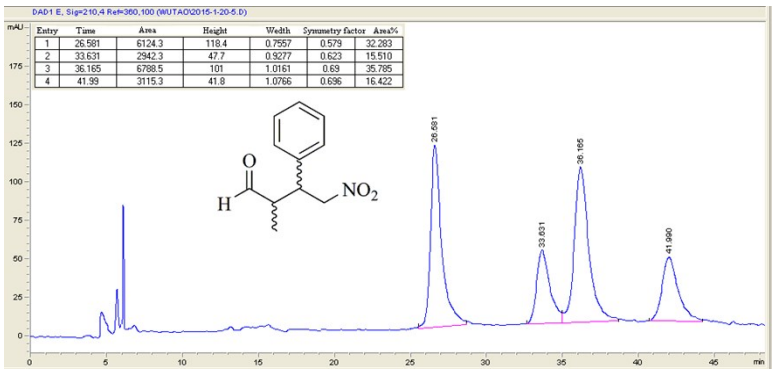
12.28
11.87
O
H
NO2
f1 (ppm)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2 33.631 2942.3 47.7 0.9277 0.623 15.510
3 36.165 6788.5 101 1.0161 0.69 35.785
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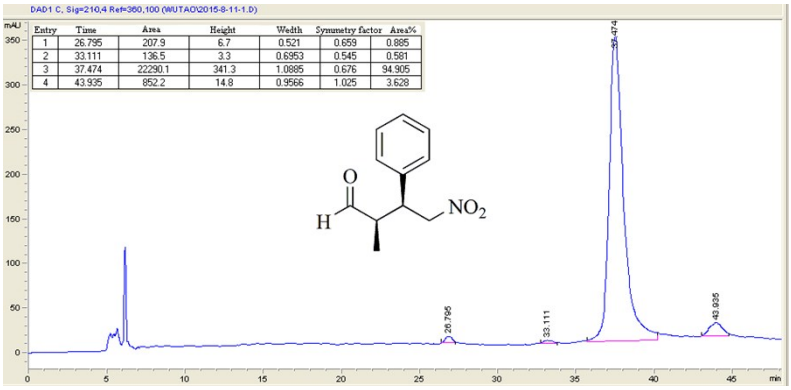
33.631
41.990
min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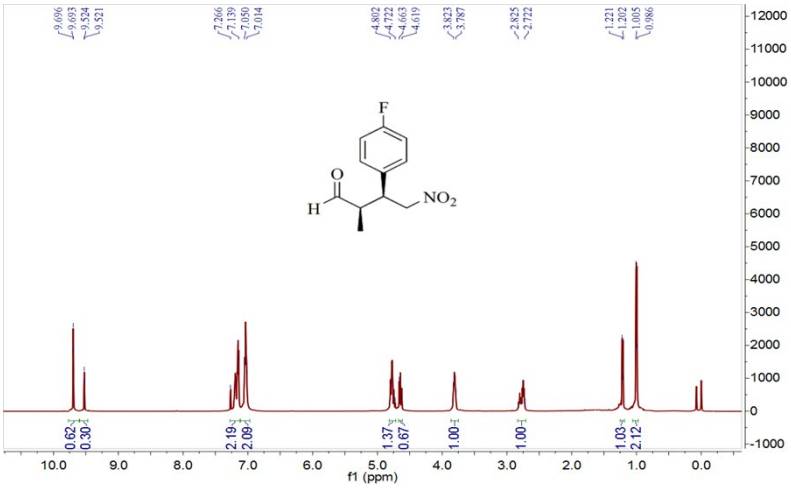
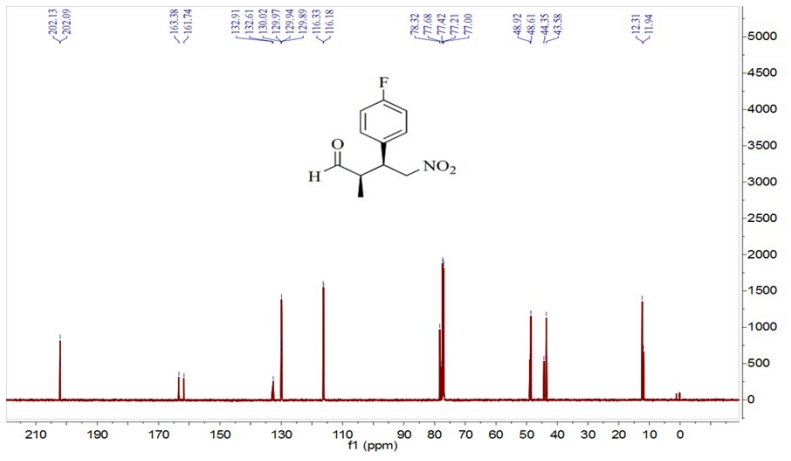
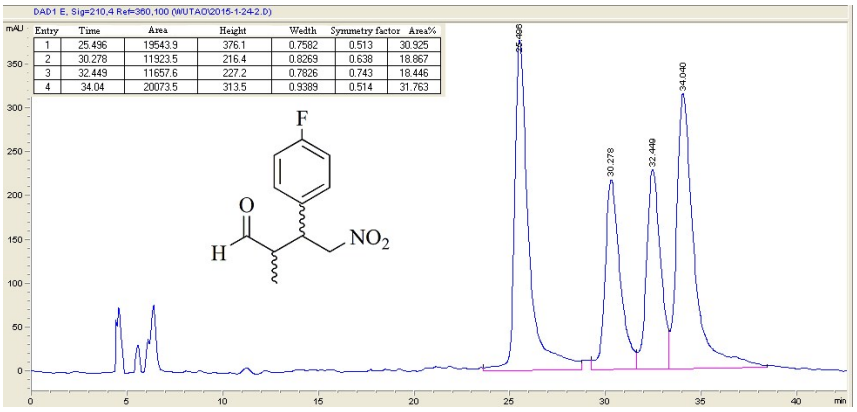
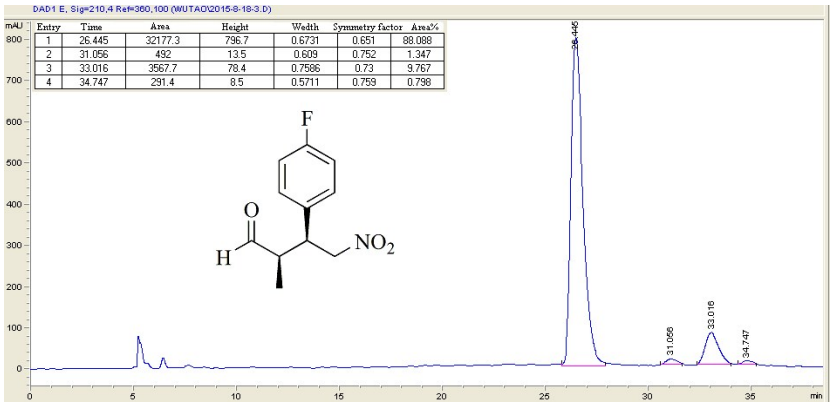
3 37.474 22290.1 341.3 1.0885 0.676 94.905
4 43.935 852.2 14.8 0.9566 1.025 3.628
mAU
O
H
NO2
37.474
26.795
33.111
43.935
min

(2R, 3S)-3-(4-fluorophenyl)-2-methyl-4-nitrobutanal: 89:11 dr, 98.2% ee, HPLC on Daicel Chiralpak AD-H column: heptane/*i*-PrOH = 19/1, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 26.4 min (major), t_R = 34.7 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, Ar-*H*), 7.14–7.27 (m, 2H, Ar-*H*), 9.69 (s, 1H, C*H*O); ^{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 (Ph), 202.1 (*C*=O).

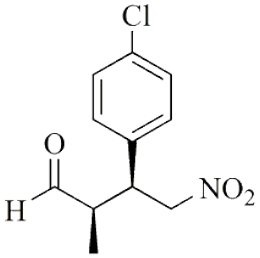


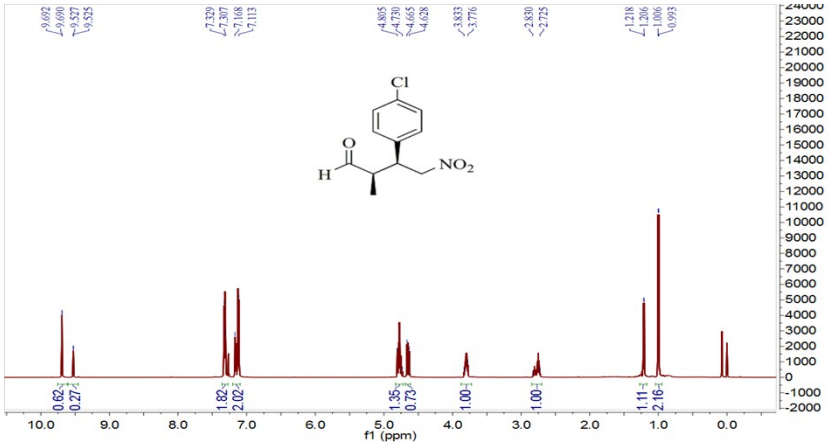


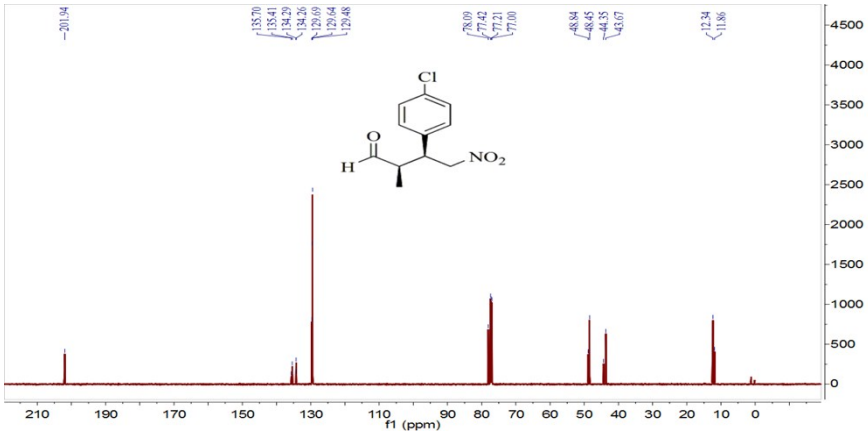


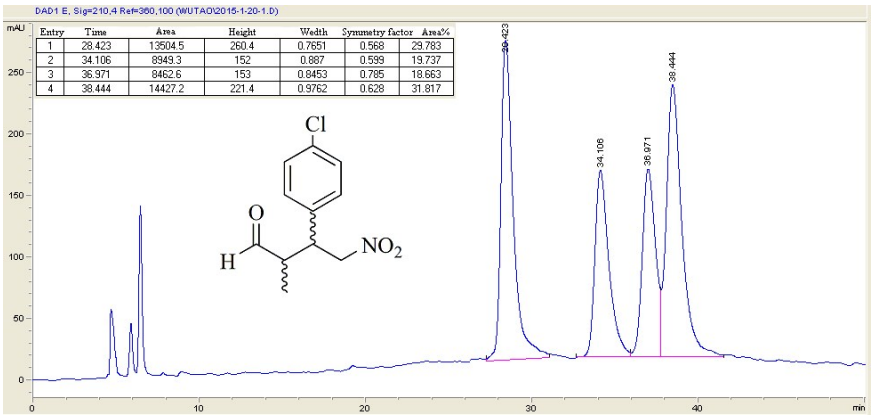


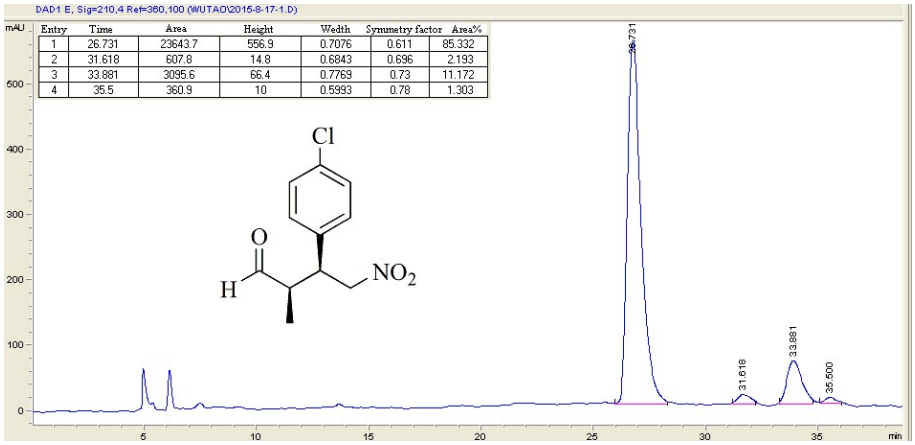
(2R, 3S)-3-(4-chlorophenyl)-2-methyl-4-nitrobutanal: 87:13 dr, 97.0% ee, HPLC on Daicel Chiralpak AD-H column: heptane/*i*-PrOH = 19/1, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 27.1 min (major), t_R = 36.2 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.00 (d, J = 7.3 Hz, 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, Ar-*H*), 7.31–7.33 (m, 2H, Ar-*H*), 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 (Ph), 201.9 (*C*=O).



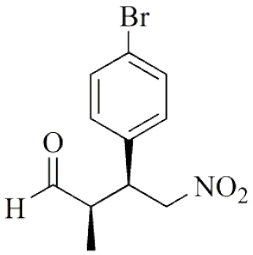




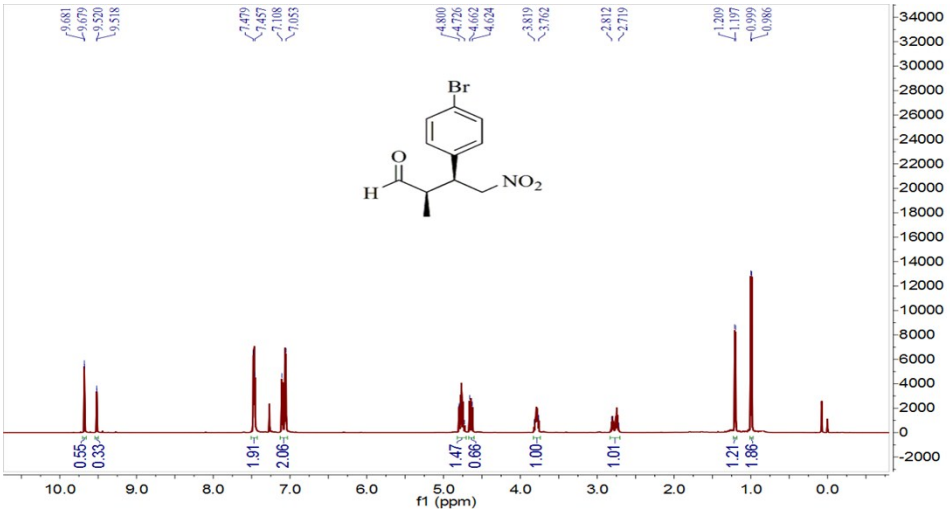


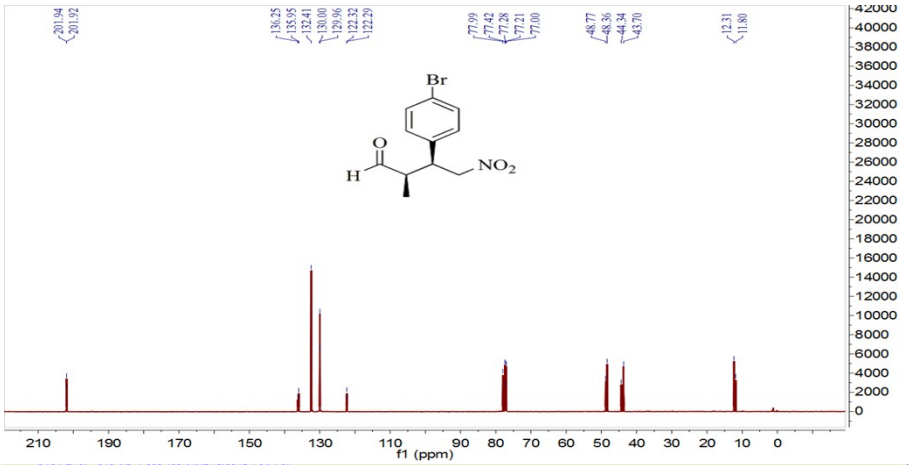


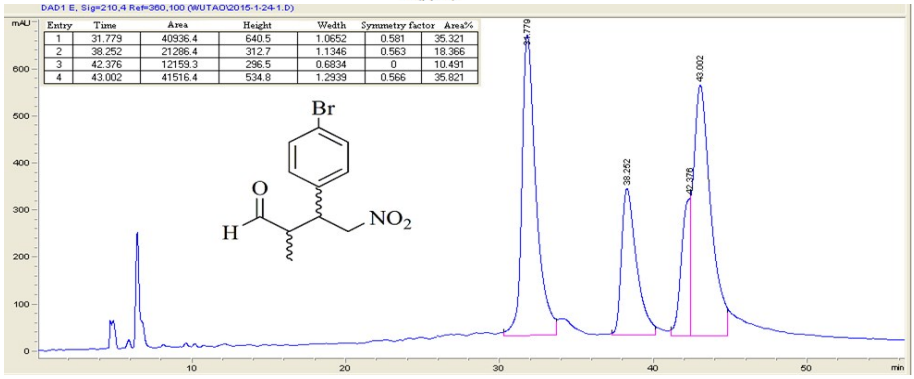
(2R, 3S)-3-(4-bromophenyl)-2-methyl-4-nitrobutanal: 86:14 dr, 96.0% ee, HPLC on Daicel Chiralpak AD-H

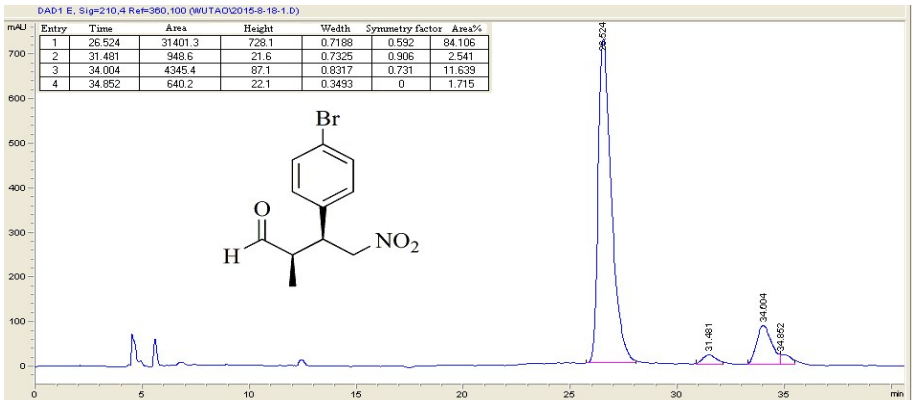


column: heptane/*i*-PrOH = 19/1, flow rate 0.9 mL min^{-1}, λ = 210 nm: t_R = 26.5 min (major), t_R = 34.9 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.99 (d, *J* = 7.3 Hz, 3H, C*H*$_3$), 2.72–2.81 (m, 1H, C*H*CH$_3$), 3.76–3.81 (m, 1H, C*H*CH$_2$), 4.73–4.80 (m, 2H, C*H*$_2$), 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 (Ph), 201.9 (*C*=O).

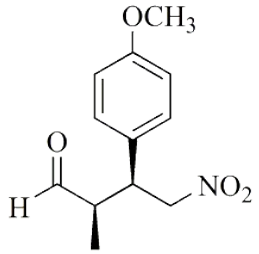




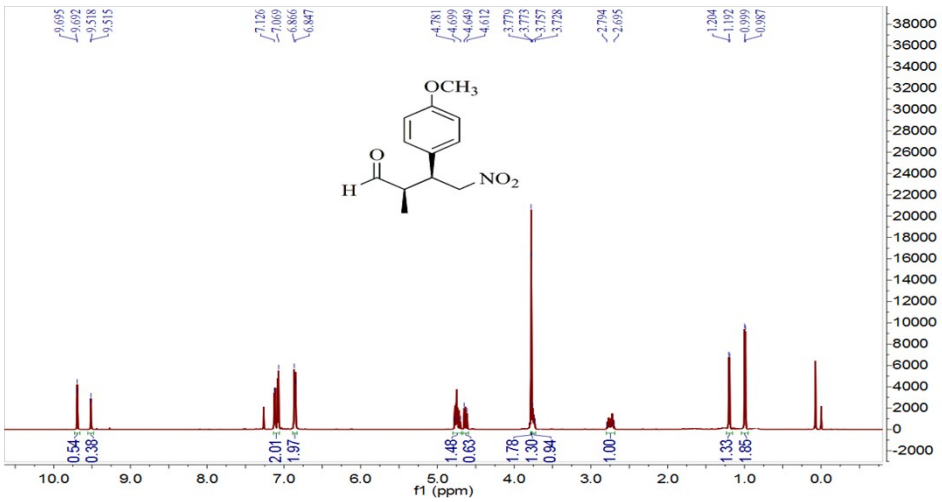


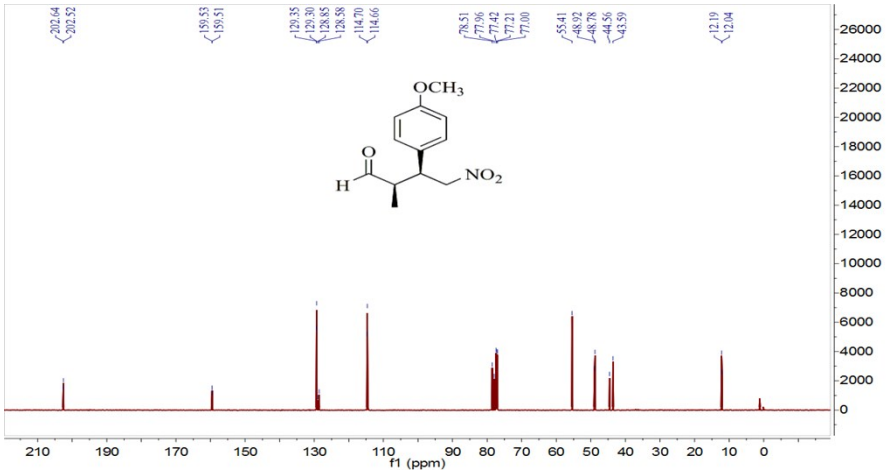


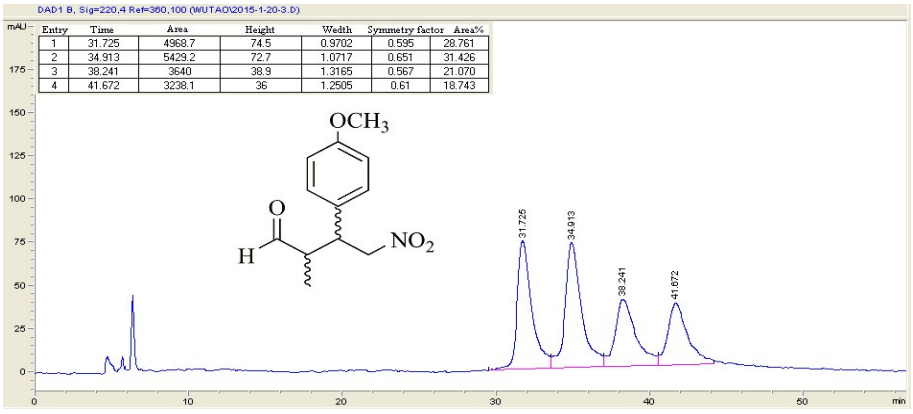
(2R,3S)-3-(4-methoxyphenyl)-2-methyl-4-nitrobutanal: 92:8 dr, 96.7% ee, HPLC on Daicel Chiralpak OD-H



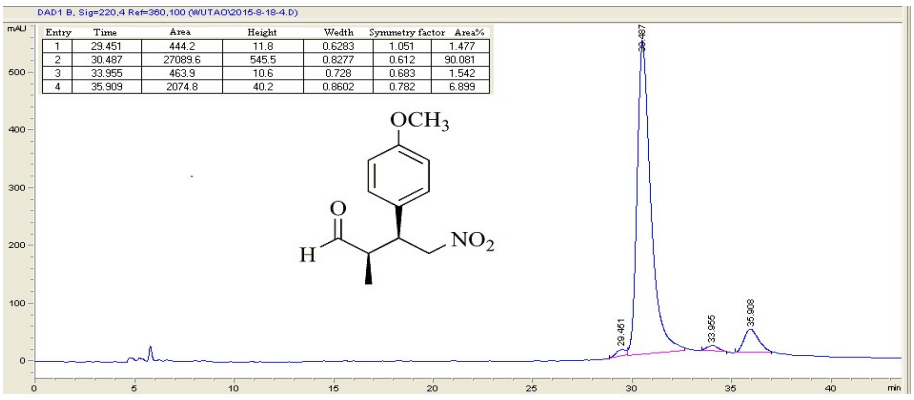
column: heptane/*i*-PrOH = 8/2, flow rate 1.0 mL min^{-1}, λ = 220 nm: t_R = 29.5 min (minor), t_R = 30.5 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.98 (d, *J* = 7.2 Hz, 3H, CHC*H*$_3$), 2.70–2.79 (m, 1H, C*H*CH$_3$), 3.73–3.76 (m, 1H, C*H*CH$_2$), 3.78(s, 3H, OC*H*$_3$), 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 (O*C*H$_3$), 78.5 (*C*H$_2$), 114.6, 114.7, 128.6, 129.3, 159.5 (Ph), 202.5 (*C*=O).





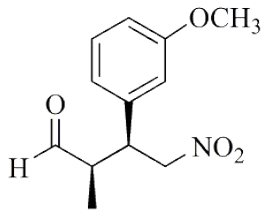


Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	31.725	4968.7	74.5	0.9702	0.595	28.761
2	34.913	5429.2	72.7	1.0717	0.651	31.426
3	38.241	3640	38.9	1.3165	0.567	21.070
4	41.672	3238.1	36	1.2505	0.61	18.743

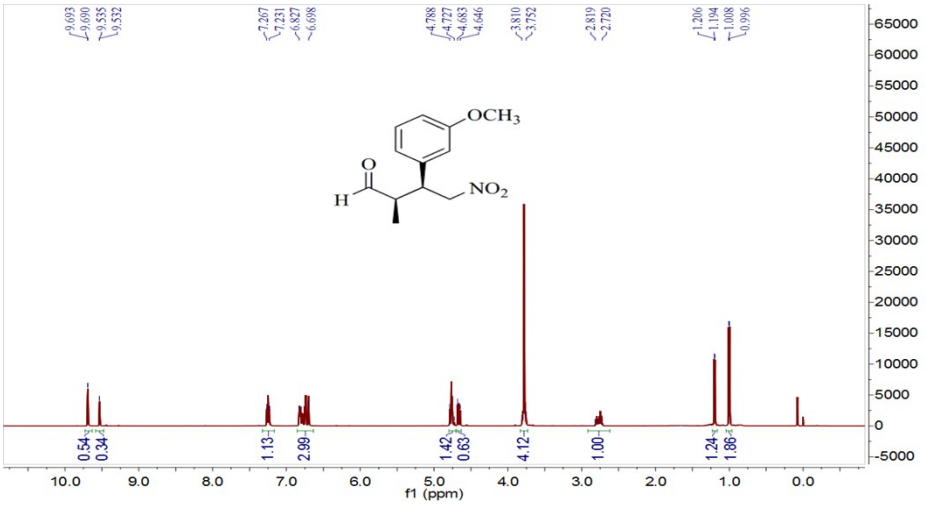


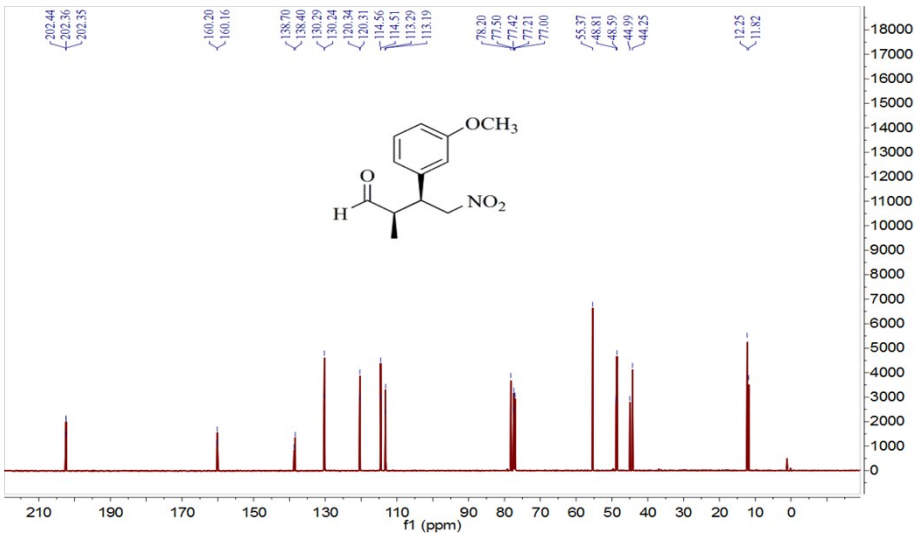
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	29.451	444.2	11.8	0.6283	1.051	1.477
2	30.487	27089.6	545.5	0.8277	0.612	90.081
3	33.955	463.9	10.6	0.728	0.683	1.542
4	35.909	2074.8	40.2	0.8602	0.782	6.899

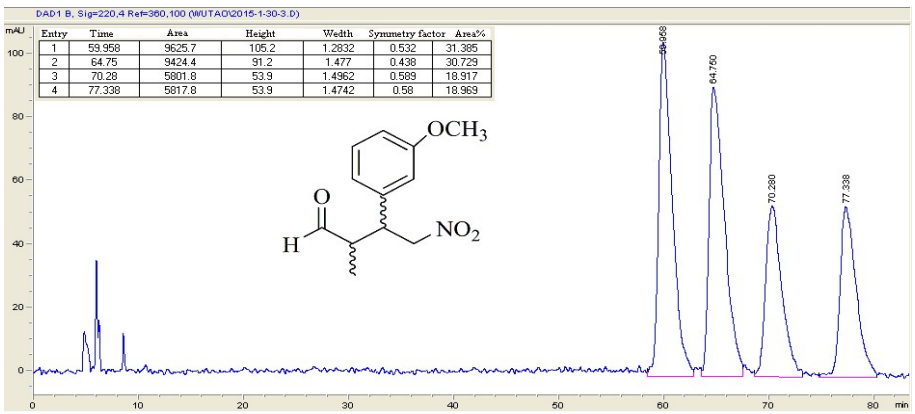
(2R,3S)-3-(3-methoxyphenyl)-2-methyl-4-nitrobutanal: 89:11 dr, 95.8% ee, HPLC on Daicel Chiralpak OJ-H



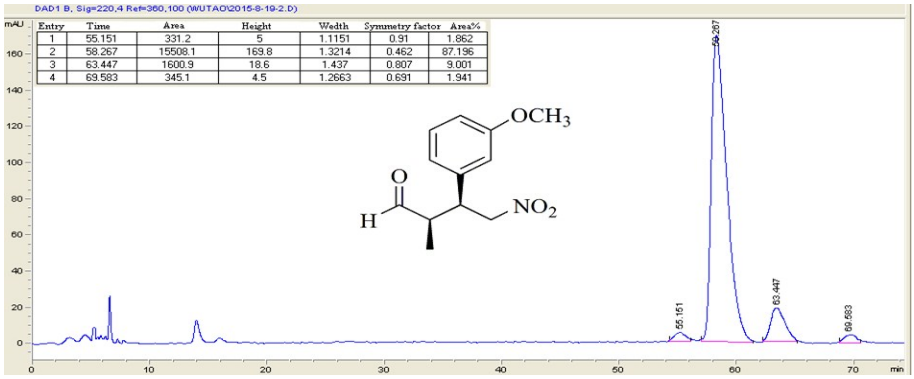
column: heptane/*i*-PrOH = 8/2, flow rate 1.0 mL min^{-1}, λ = 220 nm: t_R = 55.2 min (minor), t_R = 58.3 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.00 (d, *J* = 7.3 Hz, 3H, CH*C*H_3), 2.72–2.82 (m, 1H, C*H*CH_3), 3.75–3.81 (m, 4H, C*H*CH_2, O*C*H_3), 4.73–4.79 (m, 2H, CH_2), 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 (Ph), 202.3 (*C*=O).



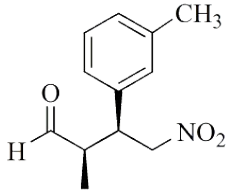




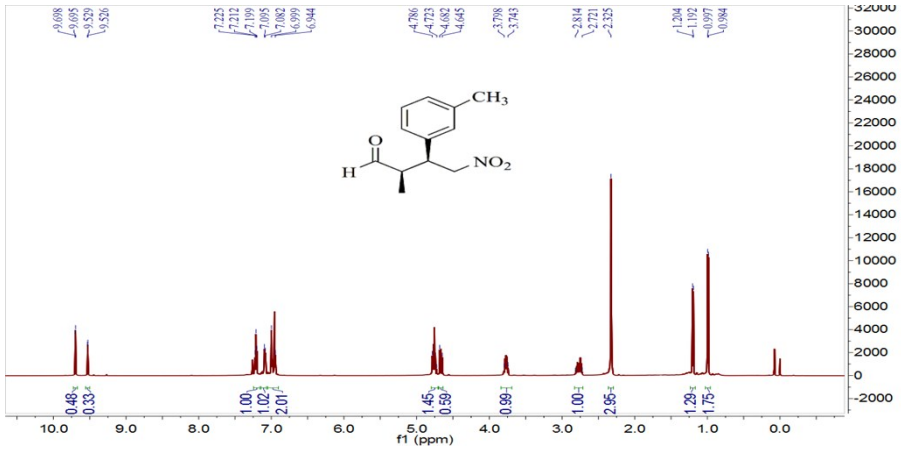
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	59.958	9625.7	105.2	1.2832	0.532	31.385
2	64.75	9424.4	91.2	1.477	0.438	30.729
3	70.28	5801.8	53.9	1.4962	0.589	18.917
4	77.338	5817.8	53.9	1.4742	0.58	18.969

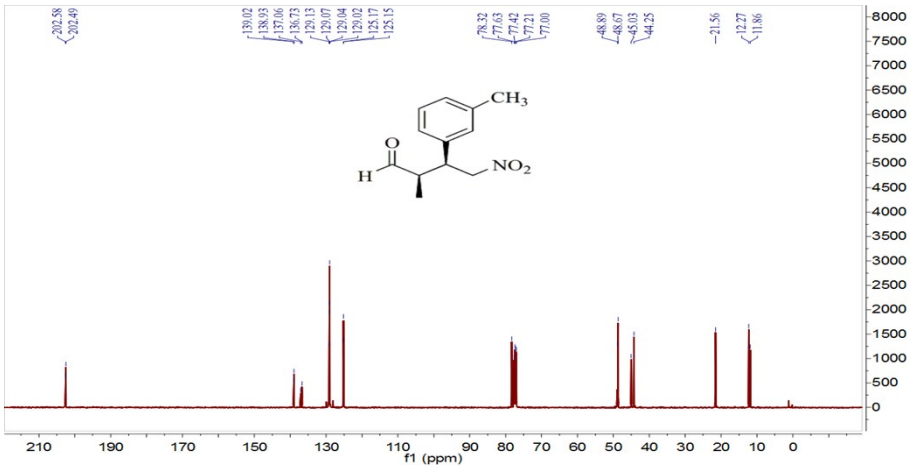


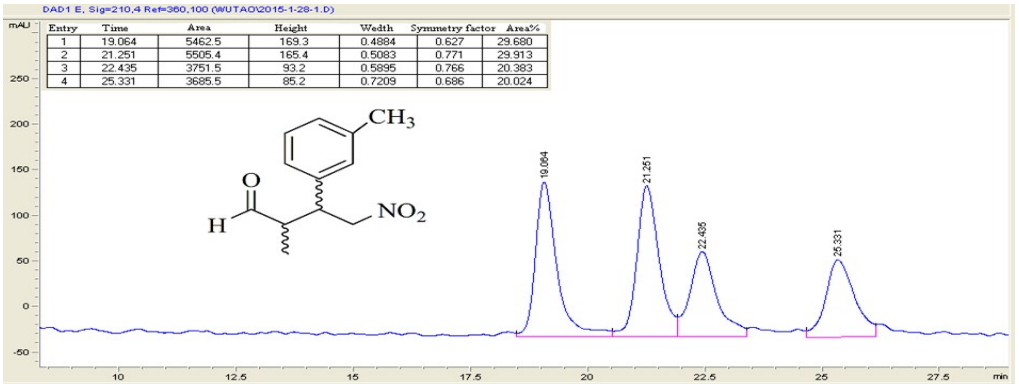
(2R,3S)-2-methyl-4-nitro-3-m-tolylbutanal: 89:11 dr, 96.4% ee, HPLC on Daicel Chiralpak OD-H column: heptane/i-PrOH = 8/2, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 19.5 min (minor), t_R = 21.5 min (major); ^{1}H NMR

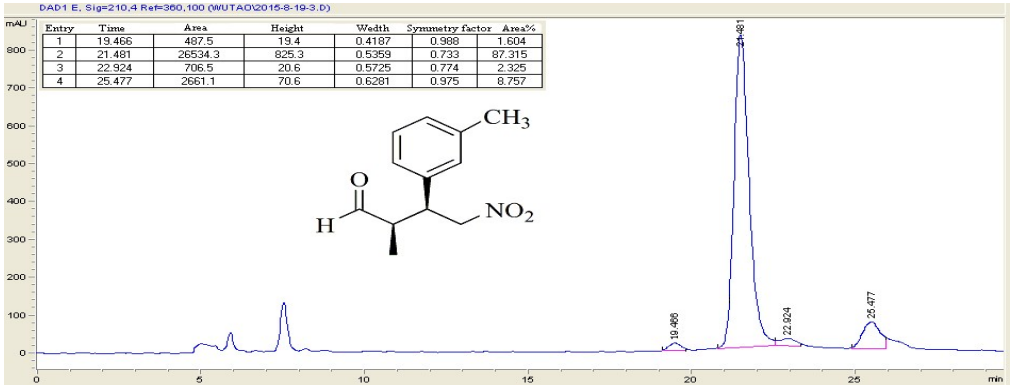


(600 MHz, $CDCl_3$, major diastereomer): δ 0.99 (d, J = 7.3 Hz, 3H, CHCH_3), 2.33(s, 3H, Ar-CH_3), 2.72–2.81 (m, 1H, CHCH$_3$), 3.74–-3.80 (m, 1H, CHCH$_2$), 4.72–4.79 (m, 2H, CH_2), 6.95–7.00 (m, 2H, Ar-H), 7.08–7.09 (m, 1H, Ar-H), 7.20–7.23 (m, 1H, Ar-H), 9.70 (d, J = 1.7 Hz, 1H, CHO); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 12.3 (CHCH$_3$), 21.6 (Ar-CH$_3$), 44.3 (CHCH$_2$), 48.7 (CHCH$_3$), 78.3 (CH$_2$), 125.1, 125.2, 129.0, 129.1, 136.7, 138.9 (Ph), 202.5 (C=O).

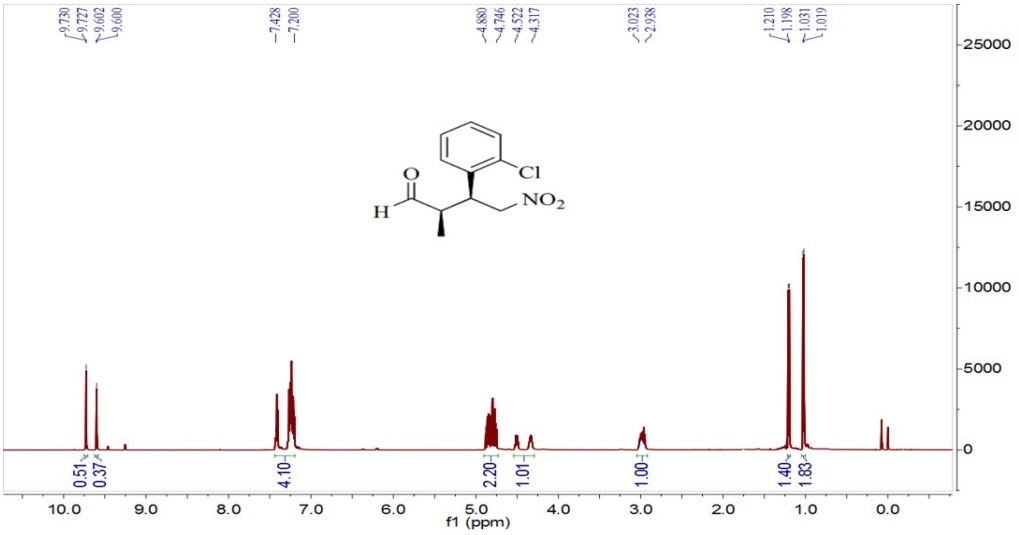


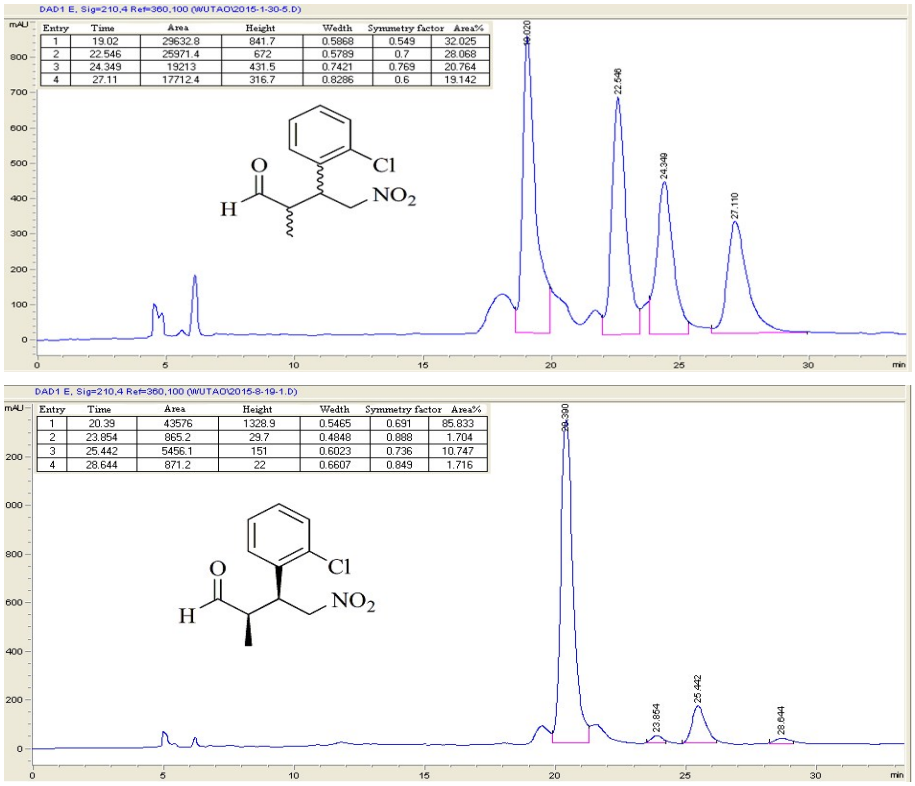




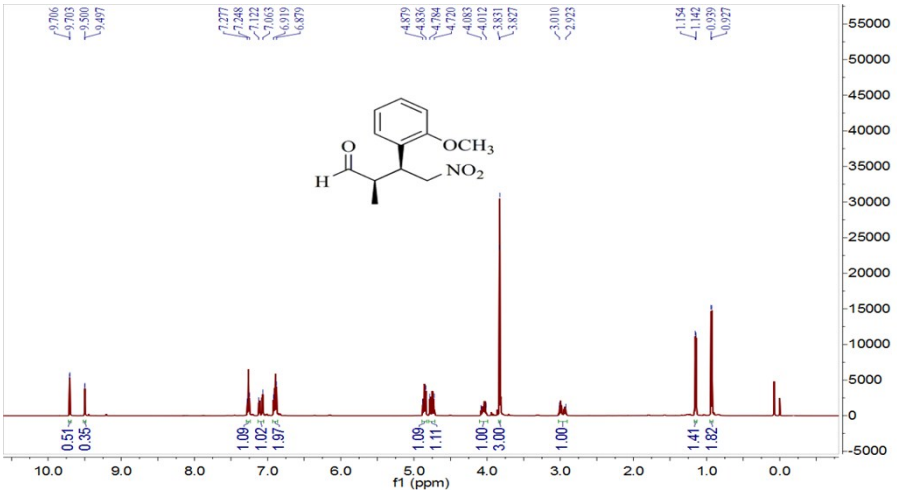


(2R,3S)-3-(2-chlorophenyl)-2-methyl-4-nitrobutanal: 88:12 dr, 96.1% ee, HPLC on Daicel Chiralpak AD-H column: heptane/i-PrOH 19/1, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 20.4 min (major), t_R = 23.9 min (minor); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 1.03 (d, J = 7.4 Hz, 3H, CH_3), 2.94–3.02 (m, 1H, CHCH$_3$), 4.32–4.52 (m, 1H, CHCH$_2$), 4.75–4.88 (m, 2H, CH_2), 7.20–7.43 (m, 4H, Ar-H), 9.73 (d, J = 1.4 Hz, 1H, CHO); ^{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 (Ph), 202.0 (*C*=O).





(2R, 3S)-3-(2-methoxyphenyl)-2-methyl-4-nitrobutanal: 92:8 dr, 95.7% ee, HPLC on Daicel Chiralpak AS-H column: heptane/i-PrOH = 98/2, flow rate 0.9 mL min^{-1}, λ = 220 nm: t_R = 72.6 min (minor), t_R = 75.3 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 (O*C*H$_3$), 77.1 (*C*H$_2$), 111.3, 121.1, 124.7, 129.4, 130.4, 157.5 (Ph), 202.9 (*C*=O).


9.706
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9.497
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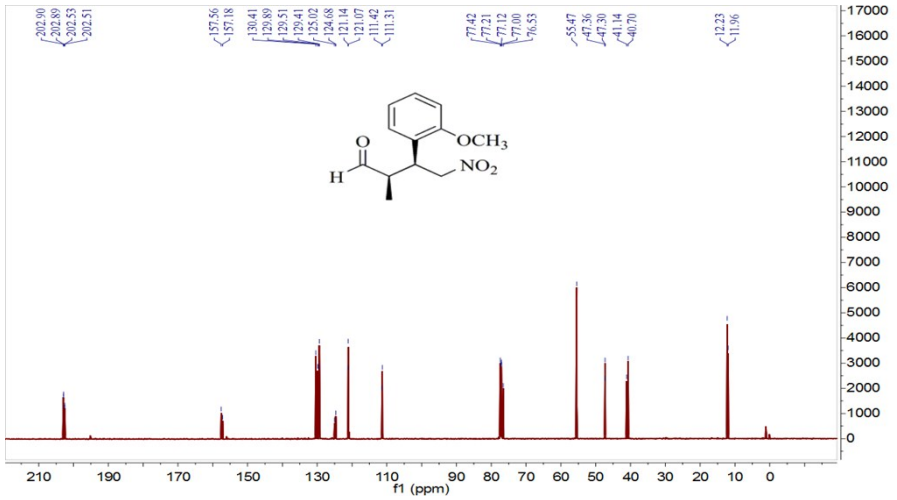
4.720
4.083
4.012
3.831
3.827
3.010
2.923
1.154
1.142
1.139
0.939
0.927
OCH3
NO2
O
H
0.51
0.35
1.09
1.02
1.97
1.09
1.11
1.00
3.00
1.00
1.41
1.82
f1 (ppm)


202.90
202.89
202.53
202.51
157.56
157.18
130.41
129.89
129.51
129.41
125.02
124.68
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121.07
111.42
111.31
77.42
77.21
77.12
77.00
76.53
55.47
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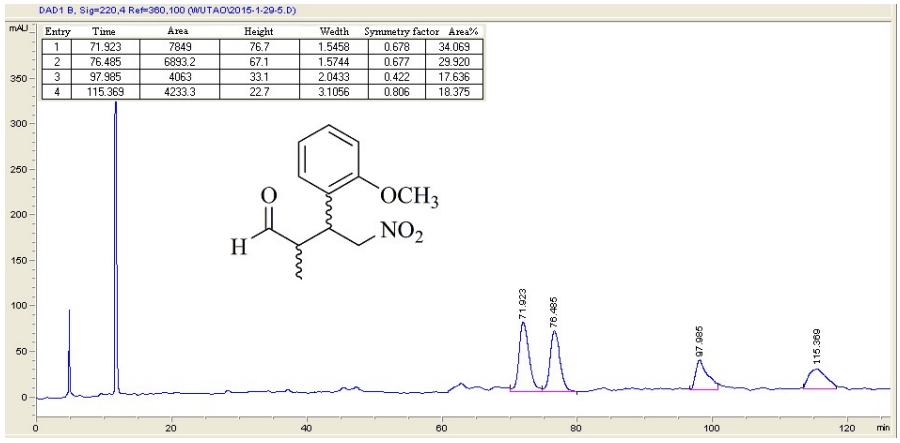
47.30
41.14
40.70
12.23
11.96
OCH3
NO2
O
H
f1 (ppm)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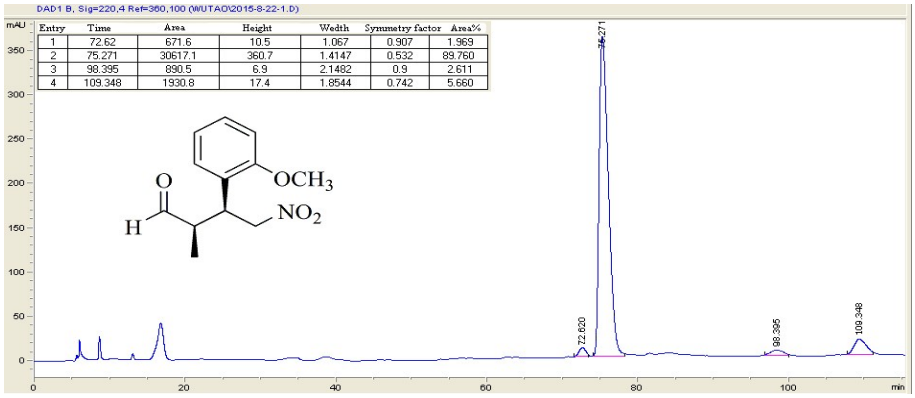
2 76.485 6893.2 67.1 1.5744 0.677 29.920
3 97.985 4063 33.1 2.0433 0.422 17.636
4 115.369 4233.3 22.7 3.1056 0.806 18.375
OCH3
NO2
O
H
71.923
76.485
97.985
115.369
min


DAD1 B, Sig=220,4 Ref=360,100 (WUTAO\2015-8-22-1.D)
mAU
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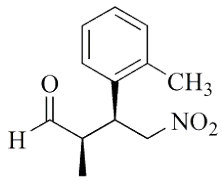
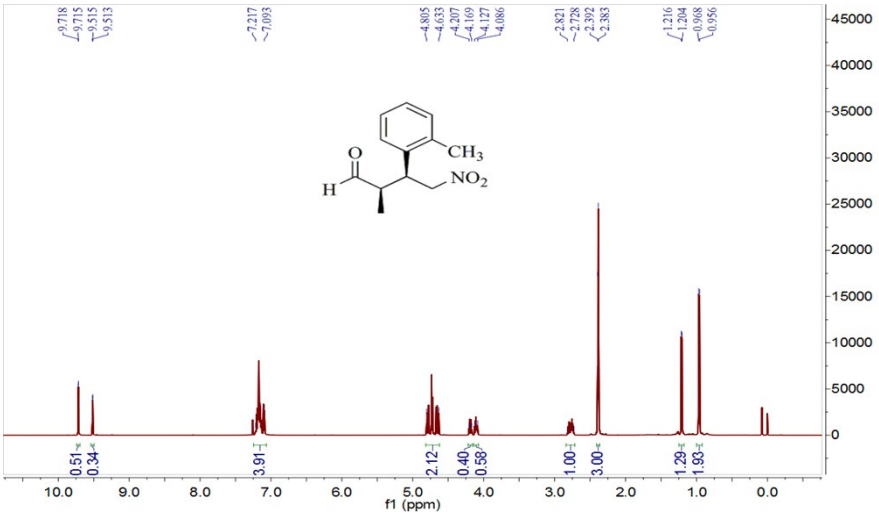
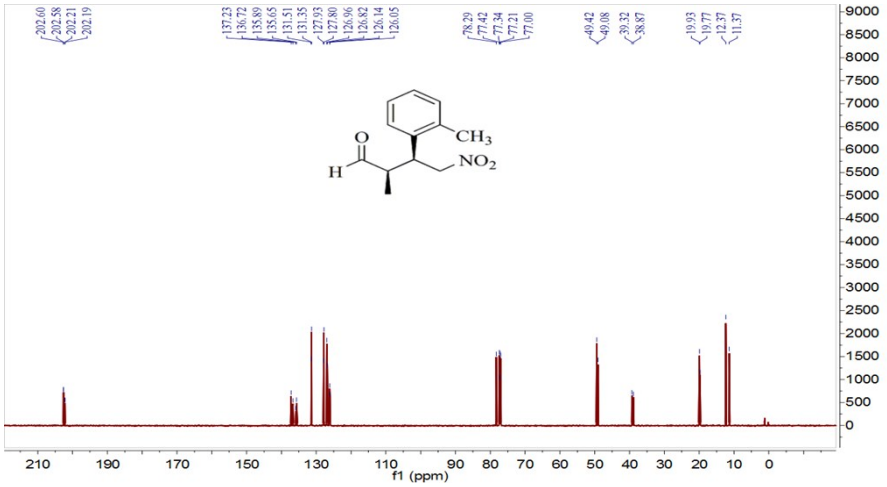
1 72.62 671.6 10.5 1.067 0.907 1.969
2 75.271 30617.1 360.7 1.4147 0.532 89.760
3 98.395 890.5 6.9 2.1482 0.9 2.611
4 109.348 1930.8 17.4 1.8544 0.742 5.660
OCH3
NO2
O
H
72.620
75.271
98.395
109.348
min

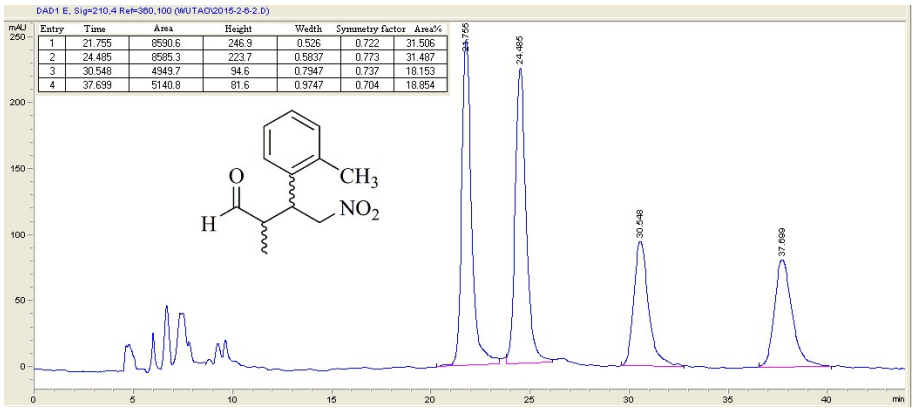
(2R, 3S)-2-methyl-4-nitro-3-*o*-tolylbutanal: 90:10 dr, 96.6% ee, HPLC on Daicel Chiralpak OD-H column:



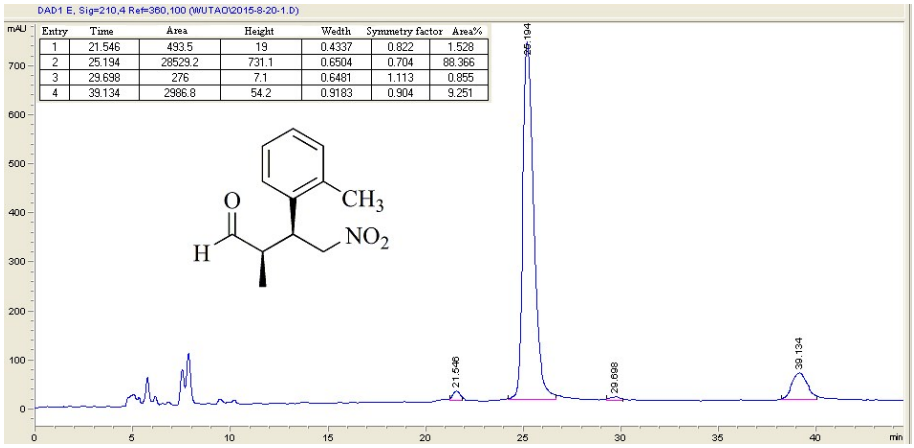
heptane/*i*-PrOH = 8/2, flow rate 1.0 mL min^{-1}, λ = 210 nm: t_R = 21.5 min (minor), t_R = 25.2 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.96 (d, *J* = 7.3 Hz, 3H, CHC*H*$_3$), 2.39 (s, 3H, ArC*H*$_3$), 2.73–2.82 (m, 1H, C*H*CH_3), 4.09–4.13 (m, 1H, C*H*CH_2NO_2), 4.63–4.81 (m, 2H, CH_2NO_2), 7.09–7.22 (m, 4H, ArH), 9.72 (d, *J* = 1.9 Hz, 1H, CHO); ^{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 (Ph), 202.6 (*C*=O).



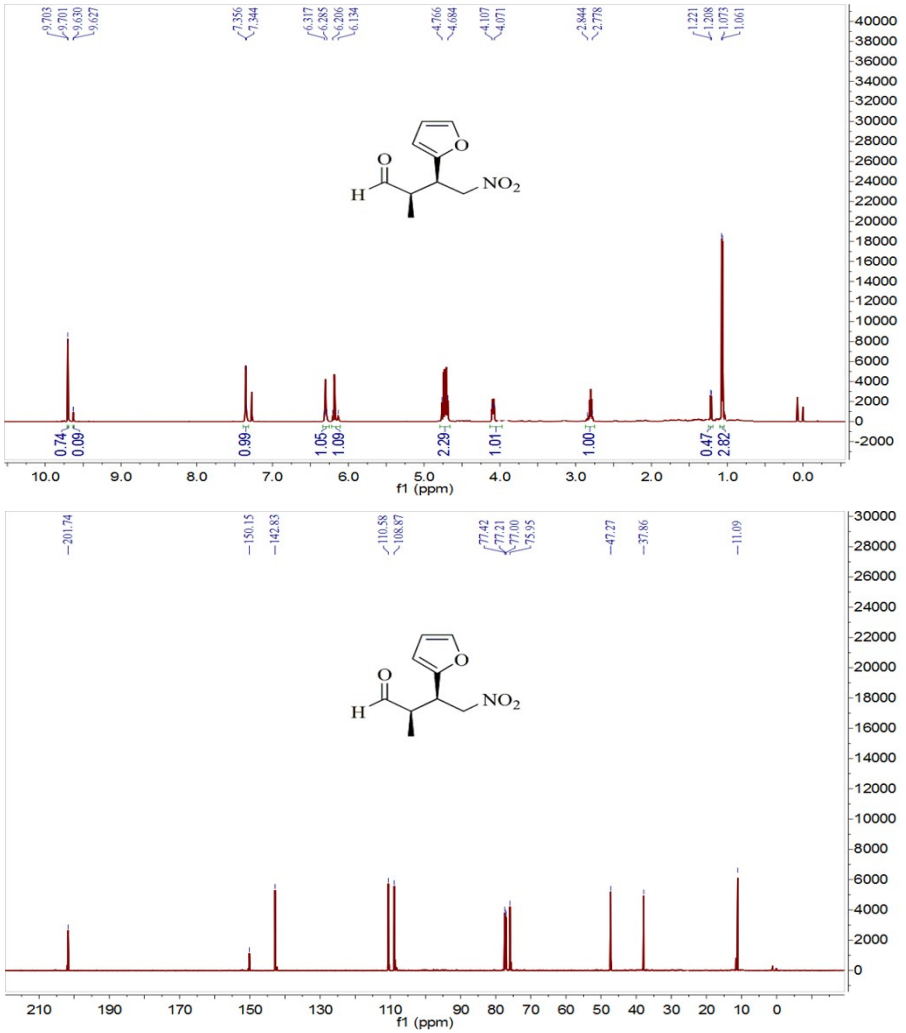


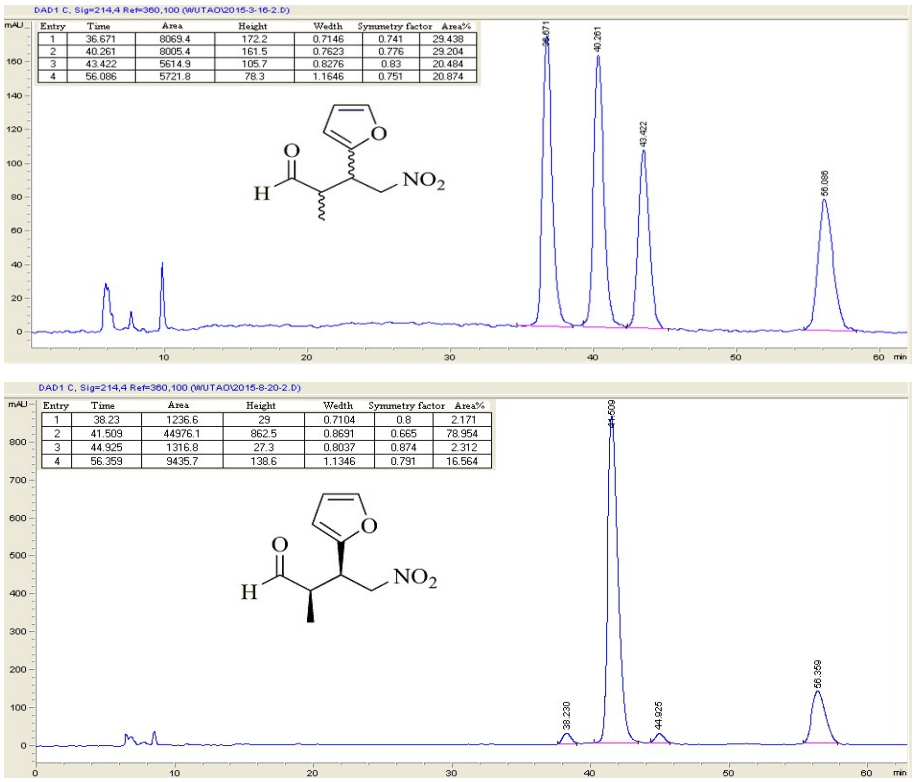


Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	21.755	8590.6	246.9	0.526	0.722	31.506
2	24.485	8585.3	223.7	0.5837	0.773	31.487
3	30.548	4949.7	34.6	0.7947	0.737	18.153
4	37.699	5140.8	81.6	0.9747	0.704	18.854

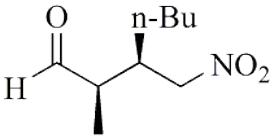


(2R, 3R)-3-(furan-2-yl)-2-methyl-4-nitrobutanal: 81:19 dr, 96.4% ee, HPLC on Daicel Chiralpak AS-H column: heptane/i-PrOH = 9/1, flow rate 0.8 mL min^{-1}, λ = 214 nm: t_R = 38.2 min (minor), t_R = 41.5 min (major); ^{1}H NMR (600 MHz, TMS, $CDCl_3$, major diastereomer): δ 1.07 (d, J = 7.3 Hz, 3H, CH_3), 2.78–2.84 (m, 1H, CHCH$_3$), 4.07–4.11 (m, 1H, CHCH$_2$), 4.68–4.77 (m, 2H, CH_2), 6.13–6.21(m, 1H, =CH), 6.29–6.32(m, 1H, =CH), 7.34–7.36 (m, 1H, =CH), 9.70 (d, J = 0.8 Hz, 1H, CHO); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 11.1 (CH$_3$), 37.9 (CHCH$_2$), 47.3 (CHCH$_3$), 76.0 (CH$_2$), 108.9, 110.6, 142.8, 150.2 (=CH), 201.7 (C=O).

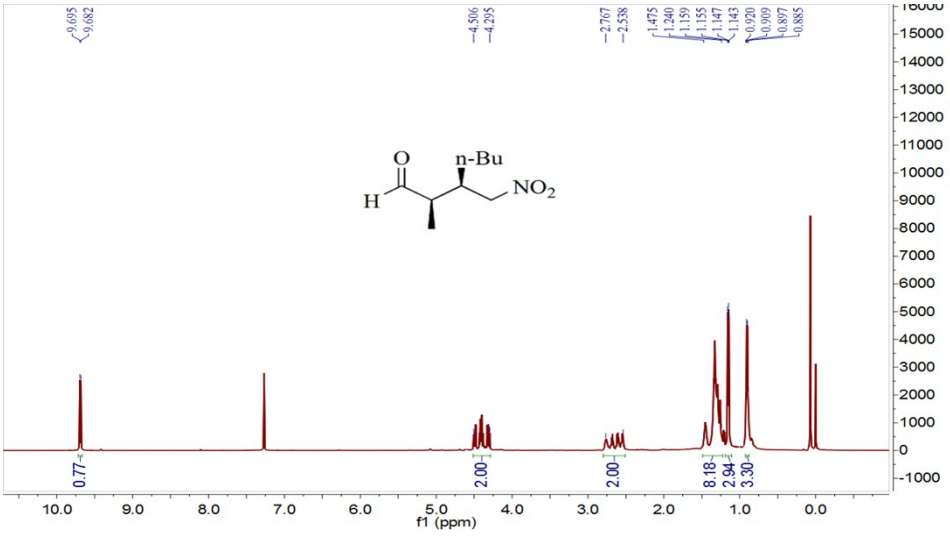


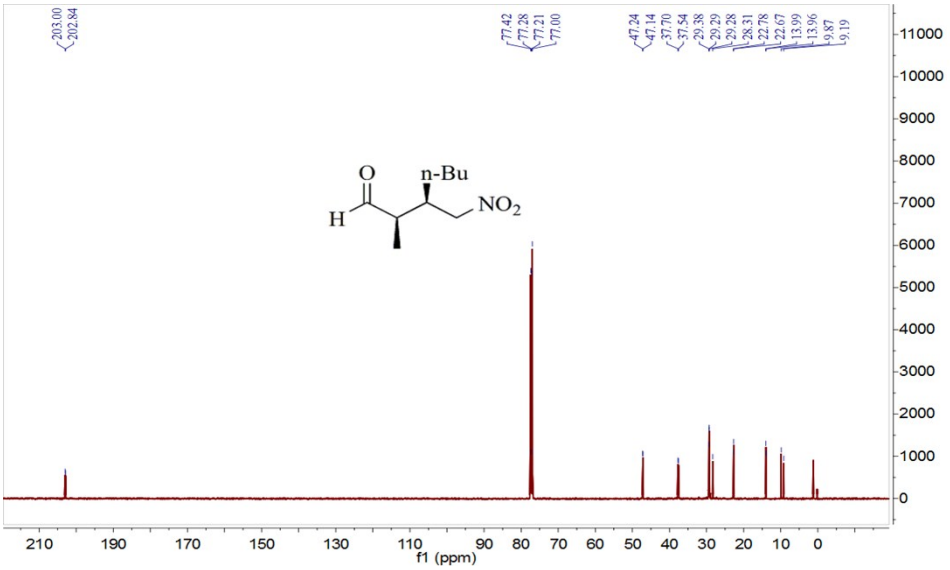


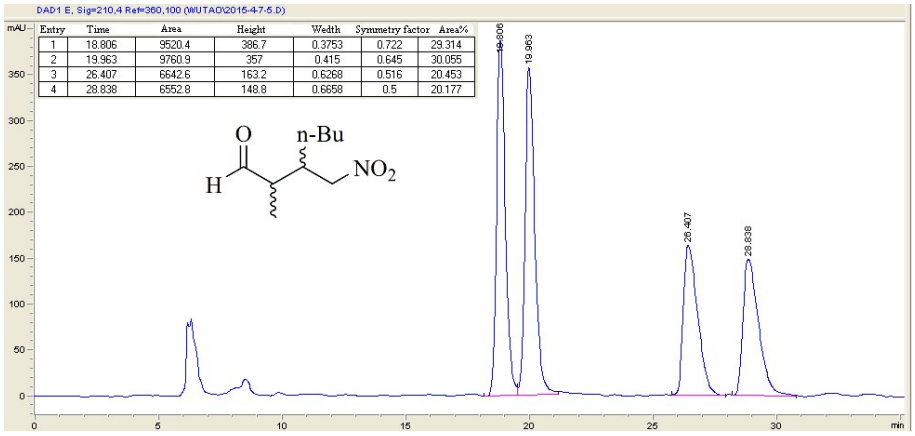
(2R, 3R)-3-n-butyl-2-methyl-4-nitrobutanal: 84:16 dr, 97.2% ee, HPLC on Daicel Chiralpak AS-H column:



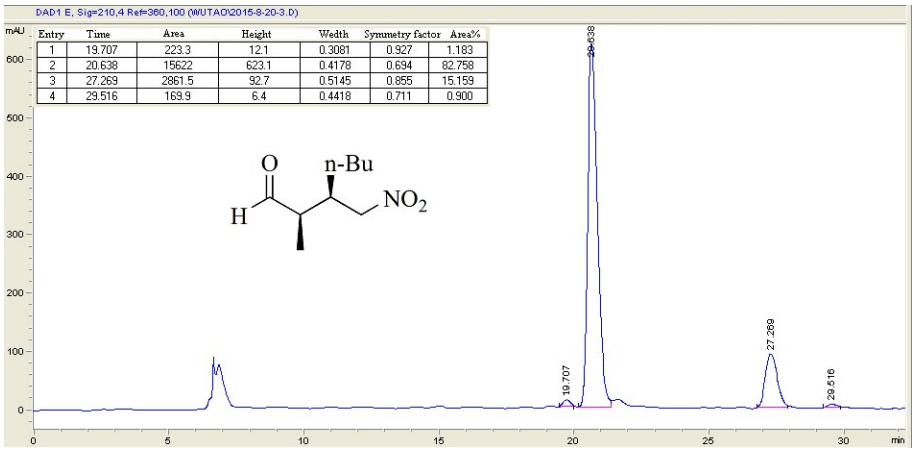
heptane/*i*-PrOH = 19/1, flow rate 0.8 mL min^{-1}, λ = 210 nm: t_R = 19.7 min (minor), t_R = 20.6 min (major); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, major diastereomer): δ 0.90 (dd, *J* = 7.0, 13.9 Hz, 3H, CHCH_3), 1.15 (dd, *J* = 2.8, 7.3 Hz, 3H, CH_2CH_3), 1.24–1.48 (m, 6H, $CH_2CH_2CH_2$), 2.54–2.77 (m, 2H, C*H*CH_3, C*H*CH_2NO_2), 4.29–4.51 (m, 2H, CH_2NO_2), 9.69 (d, *J* = 7.7Hz, 1H, C*H*O); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer): δ 9.9 (CH_3), 14.0 (CH_2CH_3), 22.7, 28.3, 29.3 ($CH_2CH_2CH_2$), 37.7 ($CHCH_2NO_2$), 47.1 ($CHCH_3$), 77.3 (CH_2NO_2), 203.0 (C=O).







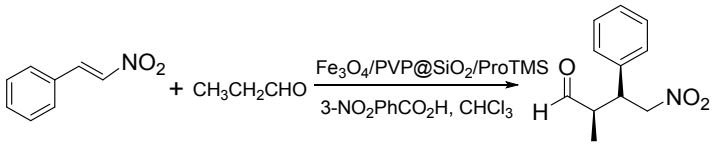
Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	18.806	9520.4	386.7	0.3753	0.722	29.314
2	19.963	9760.9	357	0.415	0.645	30.055
3	26.407	6642.6	163.2	0.6268	0.516	20.453
4	28.838	6552.8	148.8	0.6658	0.5	20.177



Entry	Time	Area	Height	Width	Symmetry factor	Area%
1	19.707	223.3	12.1	0.3081	0.927	1.183
2	20.638	15622	623.1	0.4178	0.694	82.759
3	27.269	2861.5	92.7	0.5145	0.855	15.159
4	29.516	169.9	6.4	0.4418	0.711	0.900

6. Reusability of Fe_3O_4/PVP@ SiO_2/ProTMS

Table s3. Recycling experiments of Fe_3O_4/PVP@SiO_2/ProTMS in Michael addition reaction [a]



Run	T (h)	Yield (%) [b]	% ee (*Syn*) [c]	*syn/anti* [d]

1	8	>99	98	96/4
2	12	>99	98	96/4
3	18	96	98	96/4
4	18	95	98	96/4
5	24	93	98	96/4
6	24	89	98	96/4
7	24	88	98	96/4
8	48	86	98	96/4
9	48	81	97	964
10	48	77	98	96/4

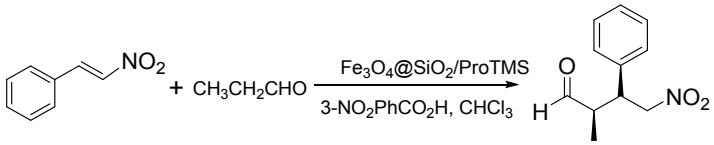
[a] Reaction conditions: *trans*-*β*-Nitrostyrene (40 mg, 0.27 mmol), propionaldehyde (94 mg, 1.62 mmol), Fe_3O_4/PVP@ProTMS (30 mg, 7 mol %), 3-NO_2PhCO_2H (10 mol %), $CHCl_3$ (2.0 mL), 0 °C.

[b] Isolated yield.

[c] Determined by ^1H NMR.

[d] Determined by chrial HPLC of crude.

Table s4. Recycling experiments of Fe_3O_4@SiO_2/ProTMS in Michael addition reaction [a]



Run	T (h)	Yield (%) [b]	%ee (*Syn*) [c]	*syn/anti* [d]
1	15	93	98	93/7
2	24	89	98	92/8
3	35	85	98	91/9
4	48	81	98	90/10
5	48	70	98	90/10
6	48	56	98	89/11

[a] Reaction conditions: *trans*-*β*-Nitrostyrene (40 mg, 0.27 mmol), propionaldehyde (94 mg, 1.62 mmol), Fe_3O_4@ProTMS (26 mg, 7 mol %), 3-NO_2PhCO_2H (10 mol %), $CHCl_3$ (2.0 mL), 0 °C.

[b] Isolated yield.

[c] Determined by ^1H NMR.

[d] Determined by chrial HPLC of crude.

7. TEM image of Fe_3O_4/PVP@SiO_2/ProTMS and 10th-recycled Fe_3O_4/PVP@ SiO_2/ProTMS

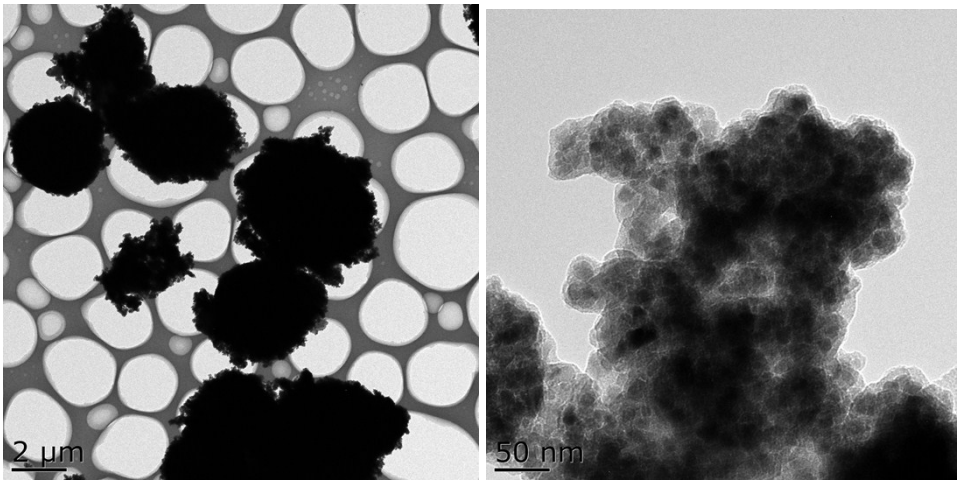


Fig. s9. TEM image of fresh Fe_3O_4/PVP@SiO_2/ProTMS

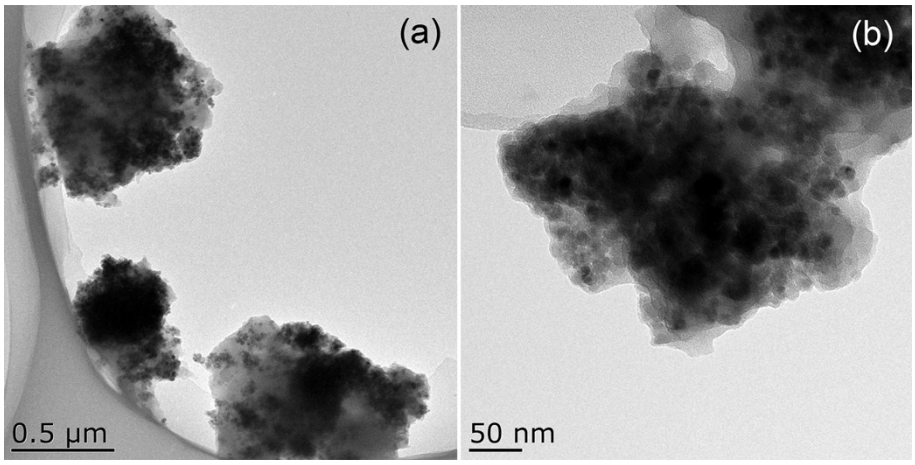


Fig. s10. TEM image of 10th-recycled Fe_3O_4/PVP@SiO_2/ProTMS