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Synthesis and Asymmetric Hydrogenation of ß-Aryl Substituted ß-Acylaminoacrylates

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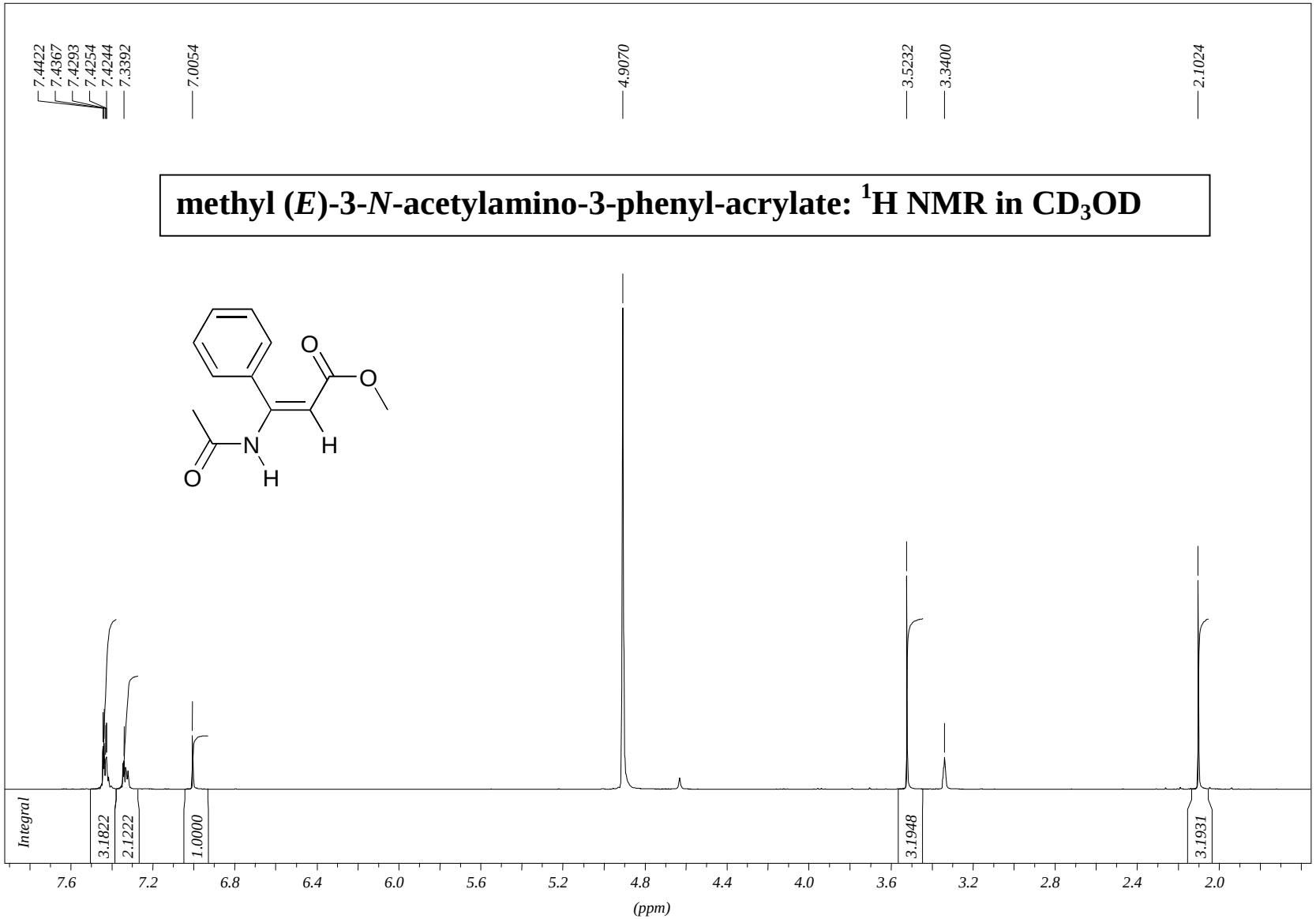
1. methyl (*E*)-3-*N*-acetylamino-3-phenyl-acrylate

^{1}H NMR (**CD_3OD**, 400 MHz): δ 2.10 (s, 3H, CH_3CO), 3.52 (s, 3H, $COOCH_3$), 7.00 (s, 1H, =CH), 7.33-7.44 (m, 5H, Ph-H) ppm (see spectrum page 2).
^{1}H NMR (**THF-d8**, 400 MHz): δ 2.00 (s, 3H, CH_3CO), 3.40 (s, 3H, $COOCH_3$), 7.12 (s, 1H, =CH), 7.26-7.34 (m, 5H, Ph-H), 8.68 (br s, 1H, NH) ppm. (see spectrum page 3).
^{13}C {^{1}H}NMR (**CD_3OD**, 100.6 MHz): δ 25.19, 52.22, 105.17, 130.05, 130.47, 131.02, 137.97, 138.42, 153.02, 170.64, 173.58 ppm.
^{13}C {^{1}H}NMR (**THF-d8**, 100.6 MHz): δ 24.39, 50.43, 103.10, 128.58, 129.28, 129.41, 138.16, 151.04, 167.58, 169.68 ppm.
Mp.: 172.1-172.9°C
MS, m/z (%): 219 (12) [M^+], 204 (100) [M^+ - CH_3]
$C_{12}H_{13}NO_3$ (219.2): calcd.: C 65.74, H 5.98, N 6.39, found: C 65.71, H 5.81, N 6.36
x-ray structure (see part 5, page 13)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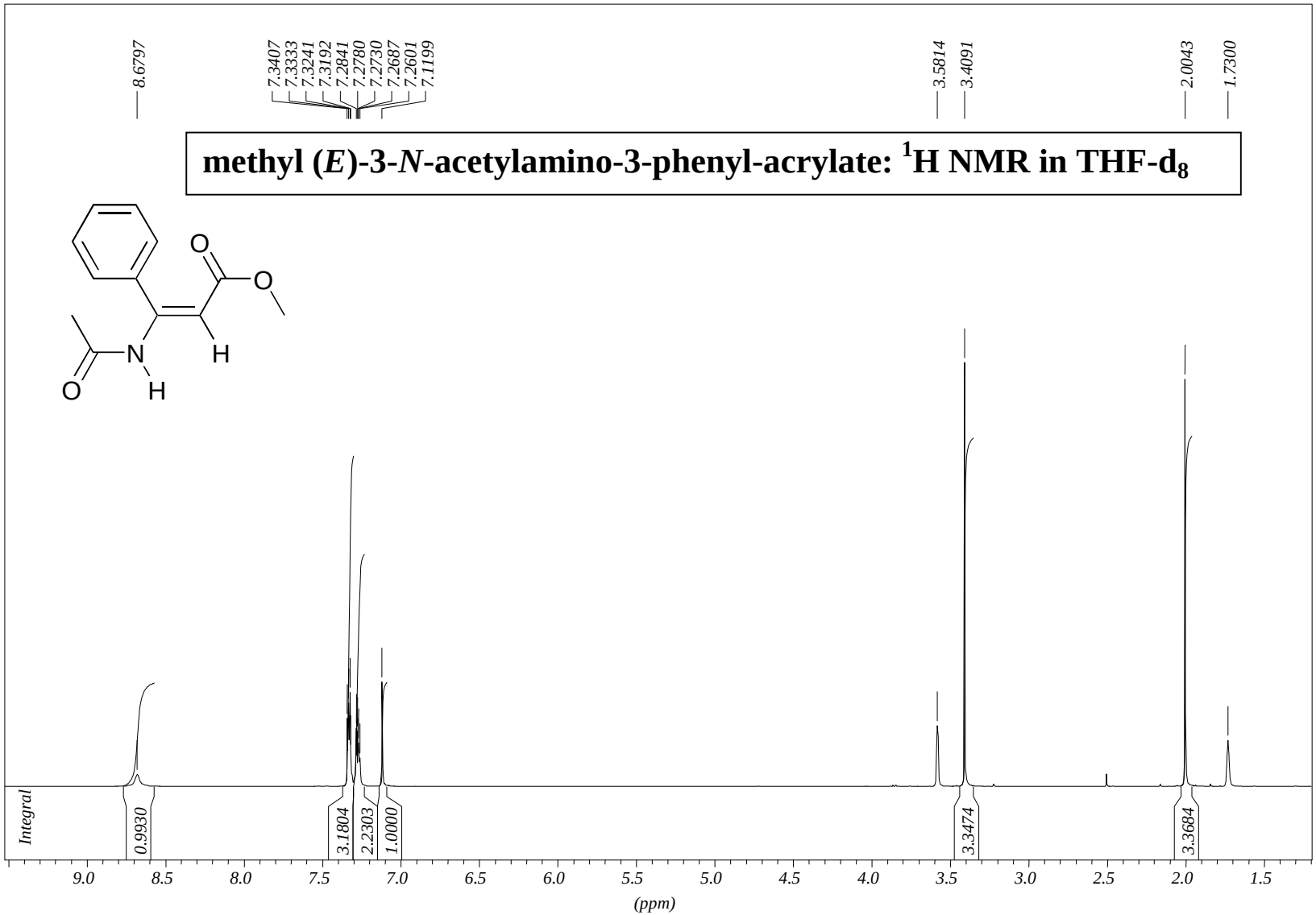
7.4254
7.4244
7.3392
7.0054
4.9070
3.5232
3.3400
2.1024
methyl (E)-3-N-acetylamino-3-phenyl-acrylate: 1H NMR in CD3OD
O
O
N
H
H
O
Integral
3.1822
2.1222
1.0000
3.1948
3.1931
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
(ppm)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7.3407
7.3333
7.3241
7.3192
7.2841
7.2780
7.2730
7.2687
7.2601
7.1199
3.5814
3.4091
2.0043
1.7300
methyl (E)-3-N-acetylamino-3-phenyl-acrylate: 1H NMR in THF-d8
O
O
N
H
O
H
Integral
0.9930
3.1804
2.2303
1.0000
3.3474
3.3684
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

2. methyl 3-*N*,*N*-bisacetylamino-3-phenyl-acrylate

^{1}H NMR (**$CDCl_3$**, 400 MHz): δ 2.36 (s, 6H, $2COCH_3$), 3.75 (s, 3H, $COOCH_3$), 6.63 (s, 1H, =CH), 7.41-7.52 (m, 5H, Ph-H) (see spectra page 5, 6 resp.).

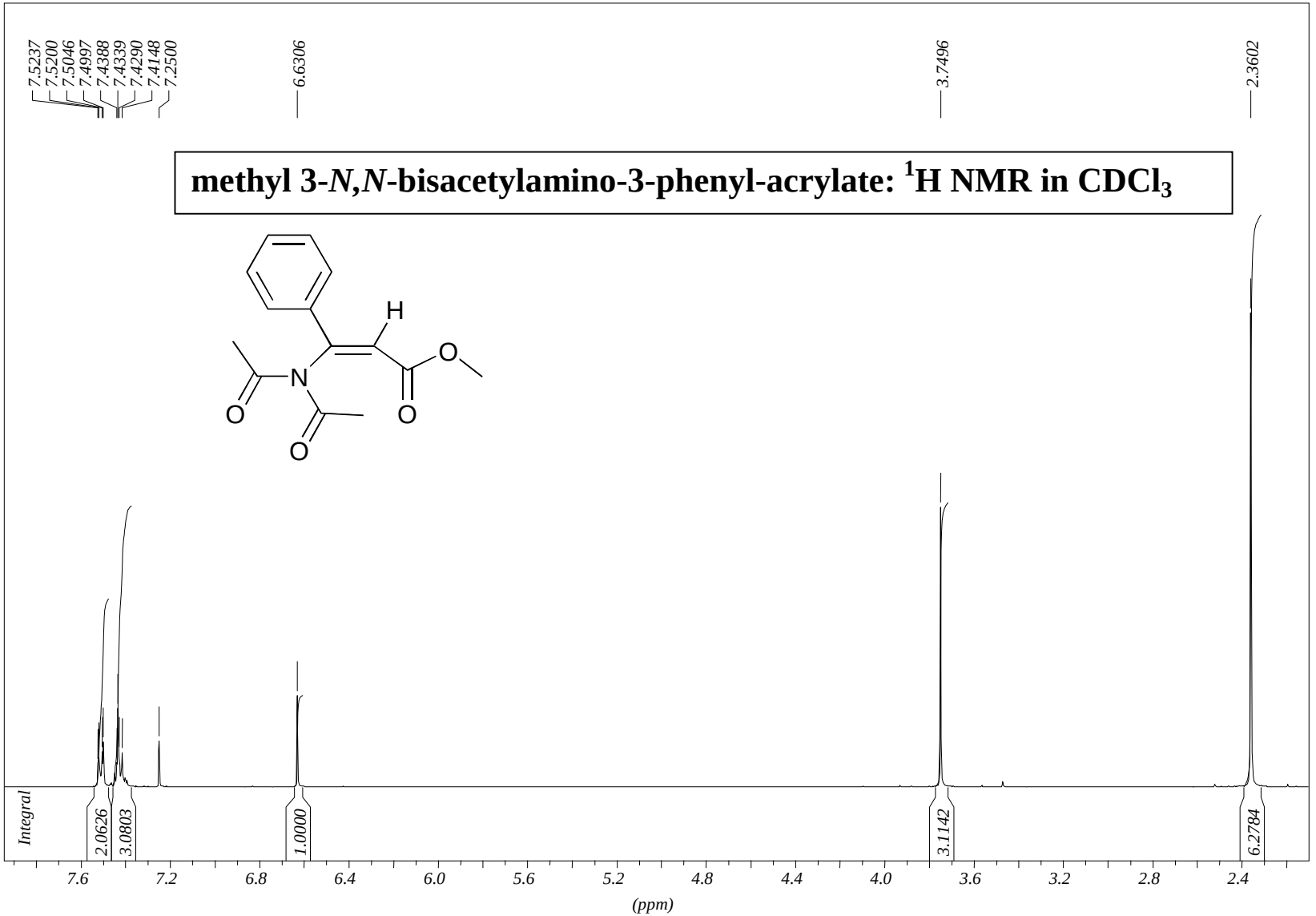
^{13}C {^{1}H}NMR (**$CDCl_3$**, 100.6 MHz): δ 26.09, 51.89, 116.50, 126.13, 129.32, 131.12, 135.01, 150.32, 164.47, 172.24 ppm.

Mp.: 93.2-93.8°C

MS, m/z (%): 261 (1) [M^+], 218 (79) [M^+ - CH_3CO], 160 (100) [MH^+ - CH_3CO - $COOCH_3$]

$C_{14}H_{15}NO_4$ (261.3): calcd.: C 64.36, H 5.79, N 5.36, found: C 63.79, H 5.49, N 5.25

x-ray structure: (see part 5, page 14)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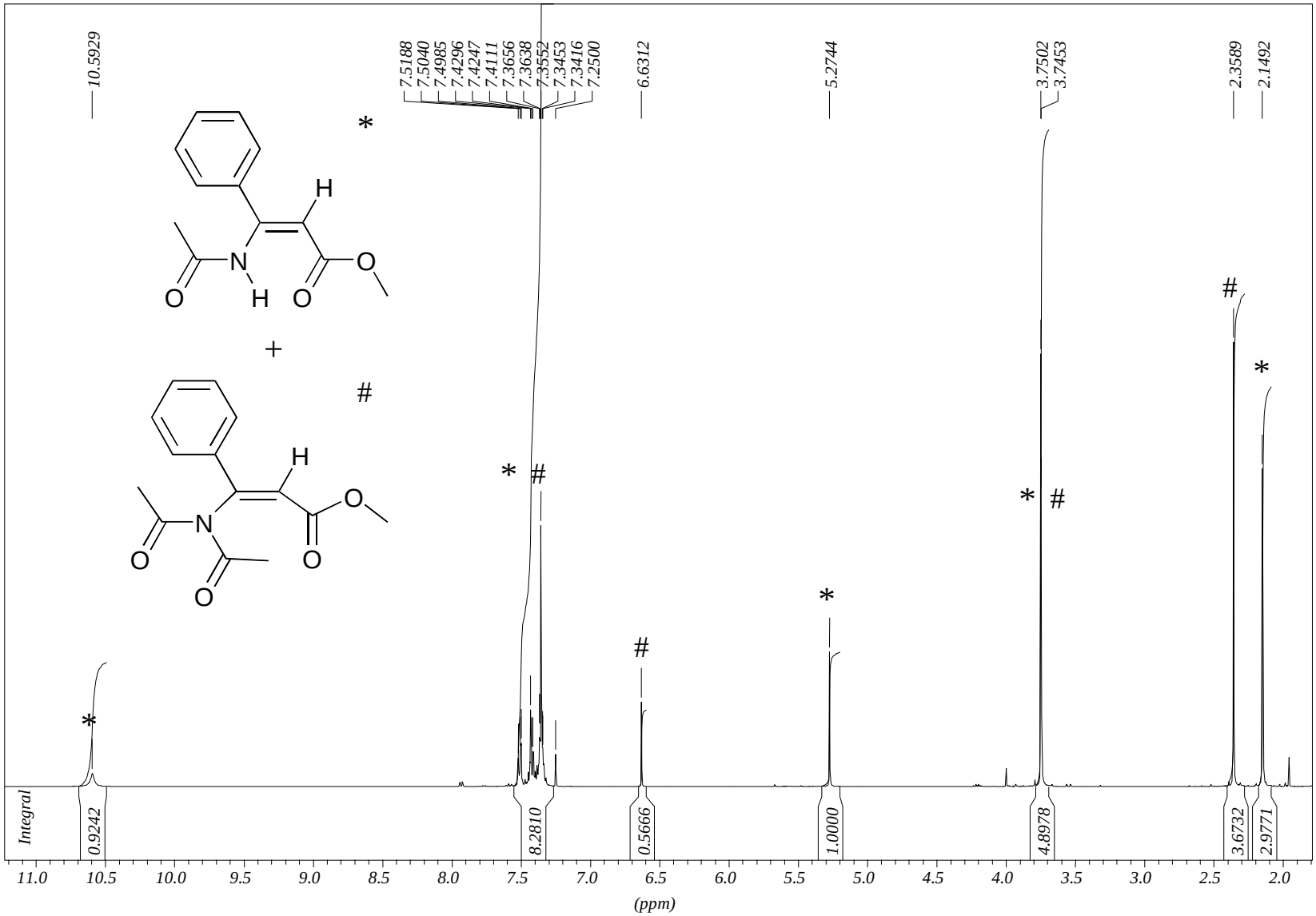
7.5200
7.5046
7.4997
7.4388
7.4339
7.4290
7.4148
7.2500
6.6306
3.7496
2.3602
methyl 3-*N*,*N*-bisacetylamino-3-phenyl-acrylate: ^{1}H NMR in $CDCl_3$
H
N
O
O
O
O
Integral
2.0626
3.0803
1.0000
3.1142
6.2784
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
(ppm)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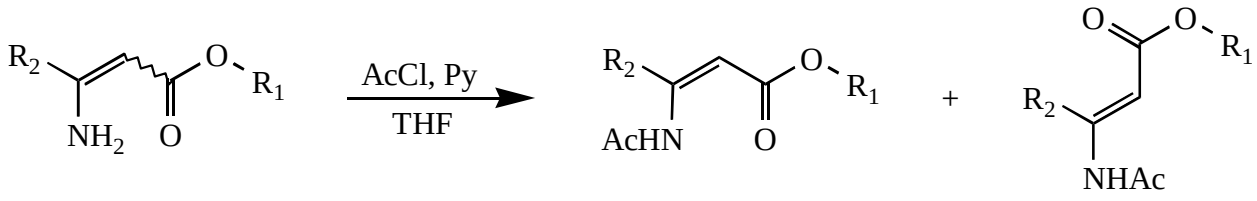
7.5188
7.5040
7.4985
7.4296
7.4247
7.4111
7.3656
7.3638
7.3552
7.3453
7.3416
7.2500
6.6312
5.2744
3.7502
3.7453
2.3589
2.1492
Integral
0.9242
8.2810
0.5666
1.0000
4.8978
3.6732
2.9771
(ppm)

Experimental Section:

General: All reactions were performed under argon by using standard Schlenk techniques. Solvents were dried and freshly distilled under Ar before use.
The spectroscopic and physical data were determined as follows:
NMR-Spectra: Bruker ARX 400,
^{1}H and ^{13}C NMR spectra are referenced to internal standards ($CHCl_3$: ^{1}H: δ 7.25, ^{13}C δ 77.0; CH_3OH: ^{1}H: δ 3.34, ^{13}C δ 49.2; THF: ^{1}H: δ 1.73, ^{13}C δ 25.4; acetone: ^{1}H: δ 2.05, ^{13}C δ 29.92).
Mass spectra: AMD 402
Melting points: Galen III, Cambridge Instruments
Elemental analyses: Leco CHNS-932
HPLC-Measurements: The enantiomeric excess of *β*-amino acid esters were analysed by HPLC with an Liquid Chromatograph 1090 equipped with DAD (Hewlett Packard) and Chiralyser (IBZ Messtechnik GmbH, Hannover). The enantiomeric resolution of all the obtained *β*-amino acid derivatives was successful on the chiral stationary phase Chiralcel OD-H (Daicel) with an eluent hexane/ethanol 95:5. In some cases other chiral phases (Chiralcel OB or *R,R*-Whelk O1) or an hexane-ethanol ratio 98:2 was more suitable in order to achieve the resolutions of the *β*-amino acid esters and starting material or by-products.

3. Synthesis of ß-Aryl Substituted ß-Acetylaminoacrylates



Z *E*

General Procedure for Synthesis of ß-Aryl Substituted ß-Acetylaminoacrylates: To a solution of 3-amino-3-aryl-acrylic acid ester (10.0 g) and pyridine (double-molecular quantity related to the used amine) in 40 - 90 ml THF acetyl chloride (double-molecular quantity related to the used amine) in 30 - 40 ml THF at 0 °C was added drop by drop. Within 6 h the reaction mixture was warmed up to ambient temperature and stirred additional 16 h.
(In some cases after cooling of the reaction solution on 0 °C, additional acetyl chloride (double-molecular quantity related to the used amine) was added. Within 4 h the reaction mixture was warmed up to ambient temperature and stirred additionel 3 - 16 h.)
Subsequently, the reaction mixture was diluted with 100 ml of a 1 M KH_2PO_4 and 100 ml ethyl acetate. The organic phase was washed with water (2×50 ml)) and dried over Na_2SO_4.
During removing the solvent a white precipitation was formed, which is filtered off and washed with EtOAc/hexane (1:7). Pure *E*-isomer is received. In the other cases the solvent was completely removed and the received oil was soluted in 10 - 20 ml ethyl acetates and stratify with 50 - 100 ml hexane. Over night a white precipitate crystallizes in the refrigerator, which is filtered off and washed with cold EtOAc/hexane (1:9).

methyl (*E*)-3-*N*-acetylamino-3-*p*-methyl-phenyl-acrylate:

Yield after crystallization: 2.1g (17.0 %)
M.p.: 159-163°C
^{1}H NMR (**acetone-d$_6$**, 400 MHz): δ 2.11(s, 3H, $COCH_3$), 2.35(s, 3H, CH_3), 3.46(s, 3H, $COOCH_3$), 7.09(s, 1H, =CH), 7.16 - 7.21(m, 4H, phenyl), 8.63(br s, 1H, NH) ppm.
^{13}C NMR(**acetone-d$_6$**, 100.6 MHz): δ 21.1, 24.5, 50.5, 102.6, 129.1, 129.3, 134.3, 136.5, 139.4, 167.7, 170.3 ppm.
MS, m/z (%): 233 (27) [M^+], 160 (100)[M^+-CH_2COOCH_3].
$C_{13}H_{15}NO_3$ (233.26): calcd. C 66.94, H 6.48, N 6.00
found C 66.83, H 6.76, N 5.88.

ethyl (*E*)-3-*N*-acetylamino-3-*p*-methyl-phenyl-acrylate:

Yield after crystallization: 1.03g (8.5 %)
M.p.: 69-71°C
^{1}H NMR (**acetone-d$_6$**, 400 MHz): δ 1.09(t, *J* = 7.1 Hz, 3H, CH_3), 2.10(s, 3H, $COCH_3$), 2.40(s, 3H, CH_3), 3.96(q, *J* = 7.1 Hz, 2H, CH_2), 6.94(s, 1H, =CH), 7.15 - 7.35(m, 4H, phenyl), 8.63(br s, 1H, NH) ppm.
^{13}C NMR(**acetone-d$_6$**, 100.6 MHz): δ 14.3, 21.4, 60.7, 104.8, 129.7, 134.8, 137.1, 140.3, 151.9, 169.6, 172.7 ppm.
MS, m/z (%): 247 (19) [M^+], 174 (100) [M^+-$COOCH_2CH_3$].
$C_{14}H_{17}NO_3$(247.29): calcd. C 68.00, H 6.93, N 5.66
found C 68.03, H 7.07, N 5.71.

methyl (*E*)-3-*N*-acetylamino-3-*p*-methoxy-phenyl-acrylate:

Yield after crystallization: 1.35g (11.0 %)
M.p.: 181-183°C
^{1}H NMR (**acetone-d$_6$**, 400 MHz): δ 2.12(s, 3H, $COCH_3$), 3.47(s, 3H, $COOCH_3$), 3.83(s, 3H, $PhOCH_3$), 6.90-6.92(m, 2H, Phenyl), 7.05(s, 1H, =CH), 7.25 - 7.27(m, 2H, phenyl), 8.61(br s, 1H, NH) ppm.
^{13}C NMR(**acetone-d$_6$**, 100.6 MHz): δ 24.3, 51.4, 55.8, 104.2, 114.5, 129.5, 131.2, 151.9, 162.1, 170.0, 172.7 ppm.
MS, m/z (%): 249 (33) [M^+], 190 (100) [M^+-$COOCH_3$].
$C_{13}H_{15}NO_4$ (249.26): calcd. C 62.64, H 6.07, N 5.62
found C 62.49, H 5.89, N 5.53.

methyl (*E*)-3-*N*-acetylamino-3-*p*-chloro-phenyl-acrylate:

Yield after crystallization: 1.2 g (9.9 %)
M.p.: 139–141°C
^{1}H NMR (**acetone-d$_6$**, 400 MHz): δ 2.10 (s, 3H, $COCH_3$), 3.47 (s, 3H, $COOCH_3$), 7.10 (s, 1H, =CH), 7.33 (m, 2H, phenyl), 7.40 (m, 2H, phenyl), 8.79 (br s, 1H, NH) ppm.
^{13}C {^{1}H}NMR (**acetone-d$_6$**, 100.6 MHz): δ 24.7, 50.9, 103.2, 128.5, 131.4, 135.1, 136.2, 150.4, 167.8, 170.5 ppm.
MS, m/z (%): 253 (17) [M^+], 194 (100) [M^+ - $COOCH_3$].
$C_{12}H_{12}ClNO_3$ (253.68): calcd. C 56.81, H 4.77, N 5.52, Cl 13.98
found C 57.11, H 5.90, N 5.56, Cl 14.07.

methyl (*E*)-3-*N*-acetylamino-3-*p*-fluoro-phenyl-acrylate:

Yield after crystallization: 2.1 g (17.3 %)
M.p.: 136–138°C
^{1}H NMR (**acetone-d$_6$**, 400 MHz): δ 2.10 (s, 3H, $COCH_3$), 3.47 (s, 3H, $COOCH_3$), 7.10 (s, 1H, =CH), 7.13 (m, 2H, phenyl), 7.37 (m, 2H, phenyl), 8.77 (br s, 1H, NH) ppm.
^{13}C {^{1}H}NMR (**acetone-d$_6$**, 100.6 MHz): δ 24.7, 50.9, 103.1, 115.5 ($2J_{CF}$ = 21.9 Hz), 131.9 ($3J_{CF}$ = 8.6 Hz), 133.6 ($4J_{CF}$ = 3.8 Hz), 150.5, 163.9 ($1J_{CF}$ = 245.1 Hz), 167.8, 170.5 ppm.
MS, m/z (%): 237 (13) [M^+], 178 (100) [M^+ - $COOCH_3$].
$C_{13}H_{12}FNO_3$ (237.23): calcd. C 61.76, H 5.10, N 5.90
found C 61.46, H 5.33, N 5.95.

ethyl (*E*)-3-*N*-acetylamino-3-*p*-fluoro-phenyl-acrylate:

Yield after crystallization: 2.6 g (21.7 %)
M.p.: 89–91°C
^{1}H NMR (**acetone-d$_6$**, 400 MHz): δ 1.06 (t, 3H, J = 7.1 Hz, CH_3), 2.10 (s, 3H, $COCH_3$), 3.91 (q, 2H, J = 7.1 Hz, $COOCH_2$), 7.08 (s, 1H, =CH), 7.13 (m, 2H, phenyl), 7.37 (m, 2H, phenyl), 8.79 (br s, 1H, NH) ppm.
^{13}C {^{1}H}NMR (**acetone-d$_6$**, 100.6 MHz): δ 14.5, 24.7, 103.7, 115.5 ($2J_{CF}$ = 21.9 Hz), 131.8 ($3J_{CF}$ = 8.6 Hz), 133.6 ($4J_{CF}$ = 2.9 Hz), 150.0, 163.9 ($1J_{CF}$ = 246.0 Hz), 167.4, 170.5 ppm.
MS, m/z (%): 251 (11) [M^+], 178 (100) [M^+ - $COOC_2H_5$].
$C_{13}H_{14}FNO_3$ (251.10): calcd. C 62.14, H 5.62, N 5.57
found C 61.66, H 5.43, N 5.62.

methyl (*E*)-3-*N*-acetylamino-3-*o*-methoxy-phenyl-acrylate:

Yield after crystallization: 0.98g (7.3%)
M.p.: 191-193.5°C
^{1}H NMR (**acetone-d$_6$**, 400 MHz): δ 2.10(s, 3H, $COCH_3$), 2.22(s, 3H, $PhOCH_3$), 3.43(s, 3H, $COOCH_3$), 7.06-7.26(m, 5, =CH, and phenyl), 8.67(b s, 1H, NH) ppm.
^{13}C NMR(**acetone-d$_6$**, 100.6 MHz): δ 19.2, 24.6, 50.7, 103.1, 126.3, 129.1, 129.3, 130.5, 136.4, 151.1, 167.5, 170.5 ppm.
MS, m/z (%): 233 (28) [M^+], 174 (100)[M^+-$COOCH_3$].
$C_{13}H_{15}NO_3$(233.26): calcd. C 66.94, H 6.48, N 6.00
found C 66.82, H 6.48, N 5.93.

ethyl (*E*)-3-*N*-acetylamino-3-*m*-nitro-phenyl-acrylate:

Yield after crystallization: 1.3g (9.3 %)
M.p.: 168-171°C
^{1}H NMR (**acetone-d$_6$**, 400 MHz): δ 1.07(t, 3H, J = 7.2 Hz, CH_3), 2.11(s, 3H, $COCH_3$), 3.93(q, 2H, J = 7.2 Hz, $COOCH_2$), 7.15(s, 1H, =CH), 7.68 - 7.81(m, 2H, phenyl), 8.20 - 8.27(m, 2H, phenyl), 8.85(br s, 1H, NH) ppm.
^{13}C NMR(**acetone-d$_6$**, 100.6 MHz): δ 14.4, 24.7, 60.0, 104.2, 124.3, 124.6, 130.3, 136.2, 136.7, 148.7, 149.0, 167.2, 170.4 ppm.
MS, m/z (%): 278 (8) [M^+], 43 (100) $[COCH_3]^+$.
$C_{13}H_{14}N_2O_5$ (278.26): calcd. C 56.11, H 5.07, N 10.07
found C 56.06, H 5.08, N 10.03.

4. Product Characterization

The reaction products of the hydrogenations were isolated as follows: After evaporation of the solvent, the catalyst was removed by filtration over a short silica gel column with ethyl acetate as eluent.

(*S*)-(-)-methyl 3-acetylamino-3-phenyl-propanoate

M.p.: 99–101°C
^{1}H NMR (**CDCl$_3$**, 400 MHz): δ 2.03 (s, 3H, $COCH_3$), 2.81 – 2.97 (m, 2H, CH_2), 3.62 (s, 3H, $COOCH_3$), 5.42 – 5.44 (m, 1H, CH), 6.61 (m, 1H, NH), 7.27 – 7.34 (m, 4H, phenyl) ppm.
^{13}C {^{1}H}NMR (**CDCl$_3$**, 100.6 MHz): δ 23.4, 39.7, 49.5, 51.8, 126.2, 127.6, 128.7, 140.4, 169.3, 171.7 ppm.
MS, m/z (%): 221(3) [M^+], 178 (100) [M^+ - $COCH_3$].
$C_{12}H_{15}NO_3$ (221.25): calcd. C 65.14, H 6.83, N 6.33
found C 64.99, H 6.72, N 6.13.
$[\alpha]^{25}_D$ = - 79.9 (c 1.00, MeOH)
ee = > 99 % ee

(*S*)-(-)-methyl 3-acetylamino-3-(*p*-methyl-phenyl)-propanoate

M.p.: 102–105°C
^{1}H NMR (**CDCl$_3$**, 400 MHz) δ 2.00(s, 3H, $COCH_3$), 2.30 (s, 3H, CH_3), 2.78-2.94 (m, 2H, CH_2), 3.61 (s, 3H, $COOCH_3$), 5.35-5.40 (m, 1H, CH), 6.47 - 6.49 (m, 1H, NH), 7.11 - 7.20 (m, 4H, phenyl) ppm.
^{13}C NMR(**CDCl$_3$**, 100.6 MHz): δ 21.0, 23.4, 39.7, 49.3, 51.8, 126.1, 129.4, 137.40, 137.41, 169.3, 171.8 ppm.
MS, m/z (%): 235 (5) [M^+], 192 (100) [M^+ - $COCH_3$].
$C_{13}H_{17}NO_3$ (235.28): calcd. C 66.36, H 7.28, N 5.95
found C 66.32, H 7.55, N 5.64.
$[\alpha]^{25}_D$ = - 89.2 (c 0.64, MeOH)
ee = > 99 % ee

(*S*)-(-)-ethyl 3-acetylamino-3-(*p*-methyl-phenyl)-propanoate

M.p.: yellow oil
^{1}H NMR (**CDCl$_3$**, 400 MHz) δ 1.16 (t, *J* = 7.2 Hz, 3H, CH_3), 2.00 (s, 3H, $COCH_3$), 2.31 (s, 3H, CH_3), 2.76 - 2.94 (m, 2H, CH_2), 4.05 (q, *J* = 7.2 Hz, 2H, $COOCH_2$), 5.35 - 5.37 (m, 1H, CH), 6.47 - 6.49 (m, 1H, NH), 7.11 - 7.20 (m, 4H, phenyl) ppm.
^{13}C NMR(**CDCl$_3$**, 100.6 MHz): δ 14.0, 21.0, 23.4, 39.9, 49.3, 60.7, 126.2, 129.3, 137.3, 137.5, 169.2, 171.4 ppm.
MS, m/z (%): 249 (6) [M^+], 206 (100) [M^+ - $COCH_3$].
$C_{14}H_{19}NO_3$ (249.31): calcd. C 67.45, H 7.68, N 5.62
found C 67.65, H 7.58, N 5.42.
$[\alpha]^{25}_D$ = - 72.2 (c 0.90, MeOH)
ee = 99 %

(*S*)-(-)-methyl 3-acetylamino-3-(*p*-methoxy-phenyl)-propanoate

M.p.: 126-130°C
^{1}H NMR (**$CDCl_3$**, 400 MHz) δ 1.99 (s, 3H, $COCH_3$), 2.72 - 2.93 (m, 2H, CH_2), 3.60 (s, 3H, $COOCH_3$), 3.77 (s, 3H, OCH_3), 5.32 - 5.38(m, 1H, CH), 6.42 - 6.44(m, 1H, NH), 6.83 - 6.85 (m, 2H, phenyl), 7.18-7.20(m, 2H, phenyl) ppm.
^{13}C NMR(**$CDCl_3$**, 100.6 MHz): δ 23.4, 39.7, 49.0, 51.8, 55.3, 114.1, 127.4, 132.5, 159.0, 169.2, 171.8 ppm.
MS, m/z (%): 251 (10) [M^+], 208 (100) [M^+ - $COCH_3$].
$C_{13}H_{17}NO_4$ (251.28): calcd. C 62.14, H 6.82, N 5.57
found C 62.40, H 6.79, N 5.29.
$[\alpha]^{25}_D$ = - 74.6 (c 0.63, MeOH)
ee = 98 % ee

(*S*)-(-)-methyl 3-acetylamino-3-(*p*-chloro-phenyl)-propanoate

M.p.: 127–129°C
^{1}H NMR (**$CDCl_3$**, 400 MHz) δ 2.01 (s, 3H, $COCH_3$), 2.77 – 2.91 (m, 2H, CH_2), 3.60 (s, 3H, $COOCH_3$), 5.34 – 5.39 (m, 1H, CH), 6.68 (m, 1H, NH), 7.20 – 7.29 (m, 4H, phenyl) ppm.
^{13}C {^{1}H}NMR (**$CDCl_3$**, 100.6 MHz): δ 23.3, 39.4, 48.9, 51.9, 127.6, 128.8, 133.4, 139.0, 169.4, 171.6 ppm.
MS, m/z (%): 255 (5) [M^+], 212 (100) [M^+ - $COCH_3$].
$C_{12}H_{12}ClNO_3$ (255.70): calcd. C 56.37, H 5.52, N 5.48, Cl 13.87
found C 56.30, H 5.49, N 5.23, Cl 13.90.
$[\alpha]^{25}_D$ = - 76.9 (c 1.00, MeOH)
ee = 98 % ee

(*S*)-(-)-methyl 3-acetylamino-3-(*p*-fluoro-phenyl)-propanoate

M.p.: 103–105°C
^{1}H NMR (**$CDCl_3$**, 400 MHz) δ 1.91 (s, 3H, $COCH_3$), 2.69 – 2.84 (m, 2H, CH_2), 3.54 (s, 3H, $COOCH_3$), 5.28 – 5.33 (m, 1H, CH), 6.80 (m, 1H, NH), 6.92 (m, 2H, phenyl), 7.19 (m, 2H, phenyl) ppm.
^{13}C {^{1}H}NMR (**$CDCl_3$**, 100.6 MHz): δ 23.2, 39.7, 48.9, 51.8, 115.4 ($2J_{CF}$ = 21.0 Hz), 127.9 ($3J_{CF}$ = 8.6 Hz), 136.6 ($4J_{CF}$ = 3.8 Hz), 162.0 ($1J_{CF}$ = 246.0 Hz), 169.4, 171.5 ppm.
MS, m/z (%): 239 (3) [M^+], 196 (100) [M^+ - $COCH_3$].
$C_{12}H_{14}FNO_3$ (239.24): calcd. C 60.23, H 5.90, N 5.86
found C 60.62, H 5.92, N 5.40.
$[\alpha]^{25}_D$ = - 69.7 (c 0.50, MeOH)
ee = > 99 % ee

(*S*)-(-)-ethyl 3-acetylamino-3-(*p*-fluoro-phenyl)-propanoate

M.p.: 28–30°C

^{1}H NMR (**$CDCl_3$**, 400 MHz) δ 1.10 (t, 3H, J = 7.1 Hz, CH_3), 1.94 (s, 3H, $COCH_3$), 2.69 – 2.84 (m, 2H, CH_2), 4.00 (q, 2H, J = 7.1 Hz, CH_2), 5.29 – 5.34 (m, 1H, CH), 6.67 (m, 1H, NH), 6.93 (m, 2H, phenyl), 7.19 (m, 2H, phenyl) ppm.
^{13}C {^{1}H}NMR (**$CDCl_3$**, 100.6 MHz): δ 13.9, 23.3, 39.9, 48.9, 60.8, 115.4 ($2J_{CF}$ = 21.9 Hz), 127.9 ($3J_{CF}$ = 8.6 Hz), 136.3 ($4J_{CF}$ = 2.8 Hz), 162.0 ($1J_{CF}$ = 246.0 Hz), 169.3, 171.2 ppm.

MS, m/z (%): 253 (4) [M^+], 210 (100) [M^+ - $COCH_3$].
$C_{13}H_{16}FNO_3$ (253.25): calcd. C 61.65, H 6.37, N 5.53
found C 61.29, H 6.02, N 5.20.
$[\alpha]^{25}_D$ = - 61.4 (c 0.20, MeOH)
ee = > 99 % ee

(*S*)-(-)-methyl 3-acetylamino-3-(*o*-methoxy-phenyl)-propanoate

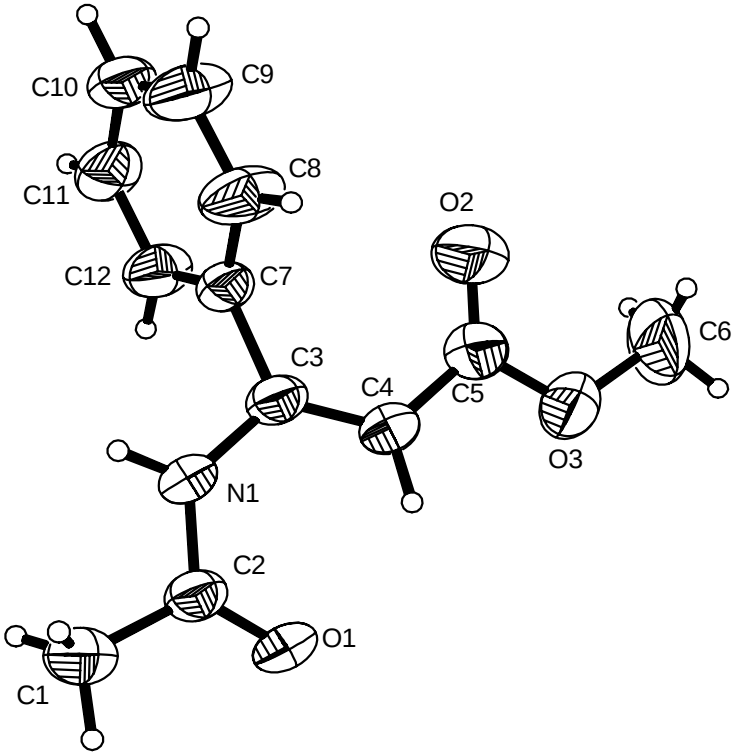
M.p.: 138.6-140°C
^{1}H NMR (**$CDCl_3$**, 400 MHz) δ 1.98 (s, 3H, $COCH_3$), 2.78 - 2.94 (m, 2H, CH_2), 3.58 (s, 3H, $COOCH_3$), 3.87 (s, 3H, CH_3), 5.54 - 5.60 (m, 1H, CH), 6.75 - 6.77 (m, 1H, NH), 6.86 - 6.92 (m, 2H, phenyl), 7.22 - 7.24 (m, 2H, phenyl) ppm.
^{13}C NMR(**$CDCl_3$**, 100.6 MHz): δ 23.5, 39.2, 47.8, 51.6, 55.3, 110.8, 120.8, 127.9, 128.6, 128.9, 156.8, 168.9, 171.8 ppm.
MS, m/z (%): 251 (5) [M^+], 208 (100) [M^+ - $COCH_3$].
$C_{13}H_{17}NO_4$ (251.28): calcd. C 62.14, H 6.82, N 5.57
found C 62.23, H 6.90, N 5.52.
$[\alpha]^{25}_D$ = - 44.4 (c 0.83, MeOH)
ee = 98 %

(*S*)-(-)-ethyl 3-acetylamino-3-(*m*-nitro-phenyl)-propanoate

M.p.: 126–129°C
^{1}H NMR (**$CDCl_3$**, 400 MHz) δ 1.17 (t, *J* = 7.16 Hz, 3H, CH_3), 2.07 (s, 3H, $COCH_3$), 2.84 - 2.95 (m, 2H, CH_2), 4.08 (q, *J* = 7.16 Hz, 2H, $COOCH_2$), 5.46 - 5.51 (m, 1H, CH), 6.87 - 6.89 (m, 1H, NH), 7.48 - 7.66 (m, 2H, phenyl), 8.10 -8.15 (m, 2H, phenyl) ppm.
^{13}C NMR(**$CDCl_3$**, 100.6 MHz): δ 14.0, 23.3, 39.5, 48.9, 61.2, 121.1, 122.6, 129.6, 132.8, 143.0, 148.4, 169.6, 170.9 ppm.
MS, m/z (%): 280 (3) [M^+], 43 (100) [$COCH_3^+$].
$C_{13}H_{16}N_2O_5$ (280.28): calcd. C 55.71, H 5.75, N 9.99
found C 55.51, H 5.91, N 9.93.
$[\alpha]^{25}_D$ = - 52.1 (c 0.48, MeOH)
ee = 99 %

5. Crystallographic Experimental Section

A



B

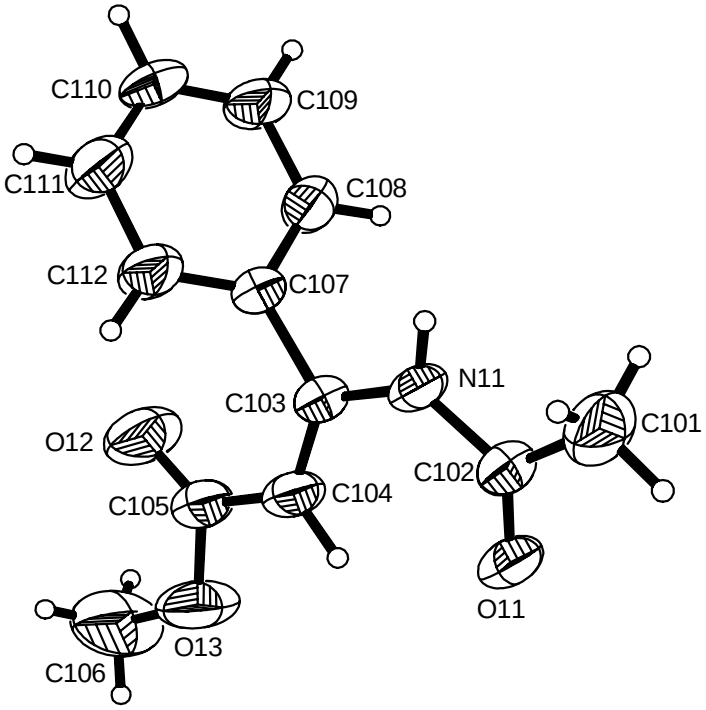


Figure 1: Molecular structures A and B (2 molecules per asymmetric unit) of methyl (*E*)-3-*N*-acetylamino-3-phenyl-acrylate in the crystal (ORTEP, 50 % probability ellipsoids).

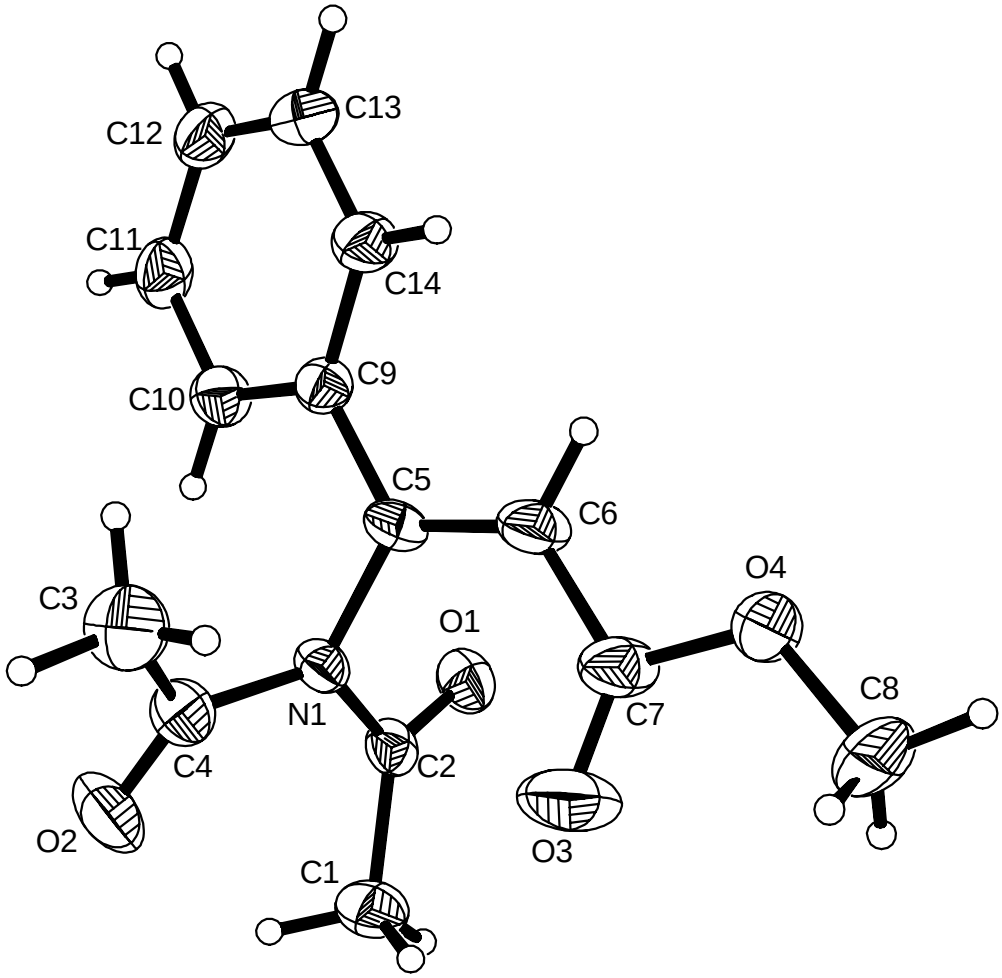


Figure 2: Molecular structure of methyl 3-*N*,*N*-bisacetylamino-3-phenyl-acrylate in the crystal (ORTEP, 50 % probability ellipsoids).

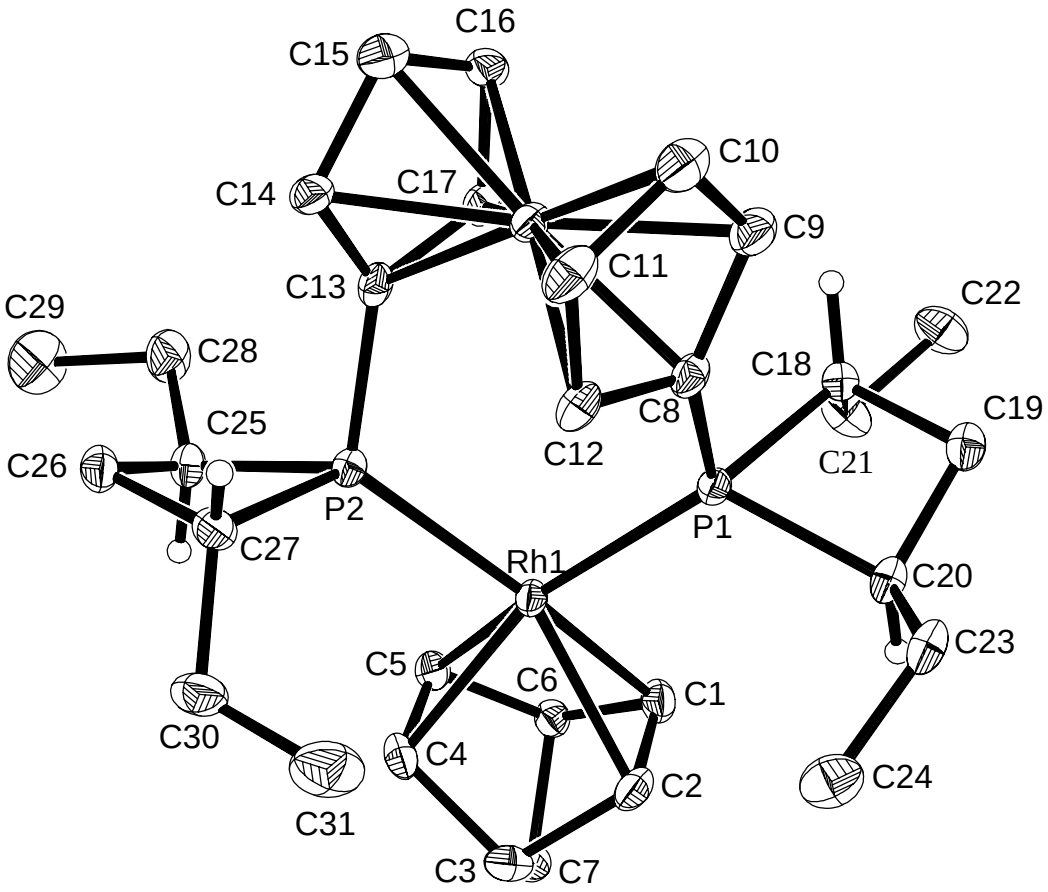


Figure 3: Molecular structure of [Rh((*R*,*R*)-Et-FerroTANE)(NBD)]$^+$ in the crystal (ORTEP, 30 % probability ellipsoids). All hydrogens except for the asymmetric carbon atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-P1 2.322(2), Rh1-P2 2.306(2); P1-Rh1-P2 98.27(5).

The best planes of the 4 atoms of the two phosphetane rings traverse themselves in an angle of 41.8 ° (middle deviation of the atoms 0.1328, 0.1421 Å resp.).

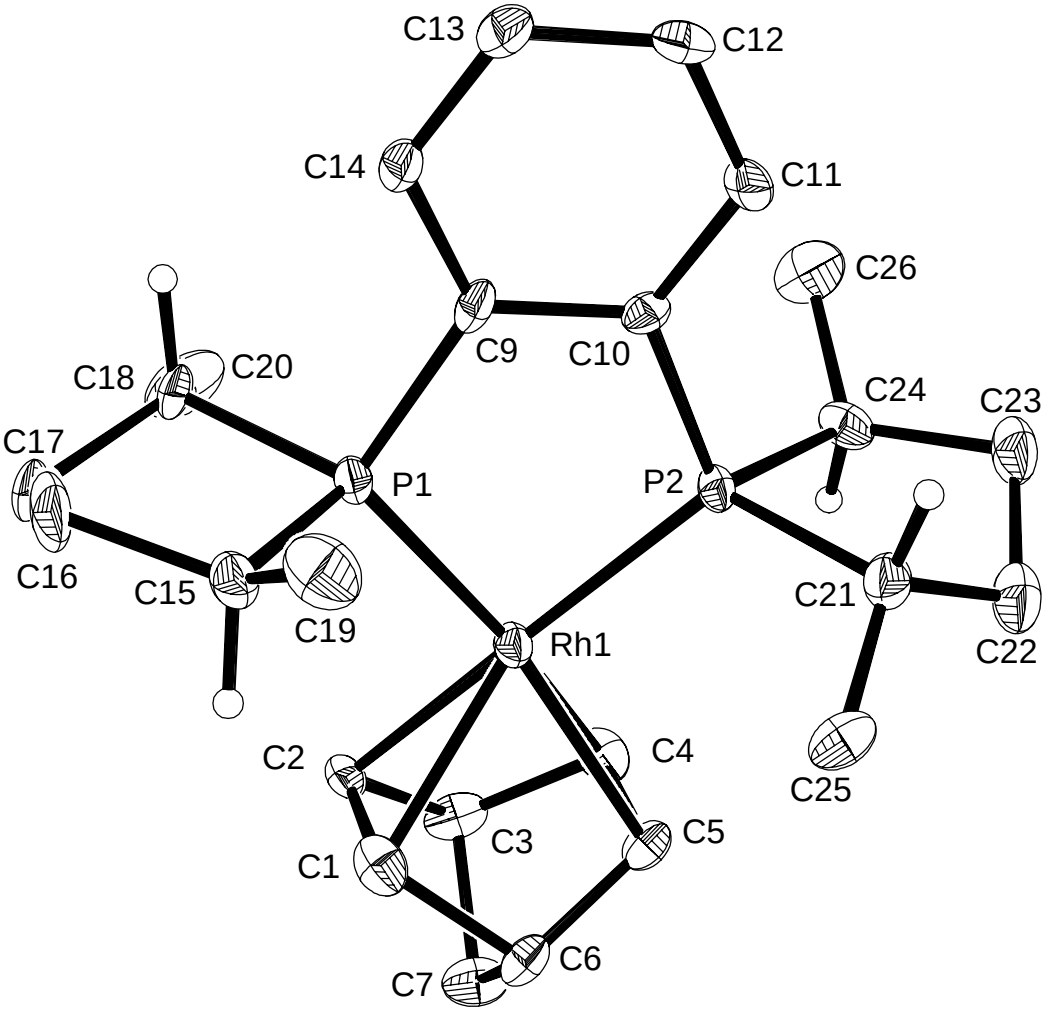


Figure 3: Molecular structure of [Rh((*S*,*S*)-Me-DuPHOS)(NBD)]$^+$ in the crystal (ORTEP, 30 % probability ellipsoids). All hydrogens except for the asymmetric carbon atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-P1 2.265(2), Rh1-P2 2.275(2); P1-Rh1-P2 84.62(5).

The best planes of the 5 atoms of the two phospholane rings traverse themselves in an angle of 7.9° (middle deviation of the atoms 0.1718, 0.1768 Å resp.).

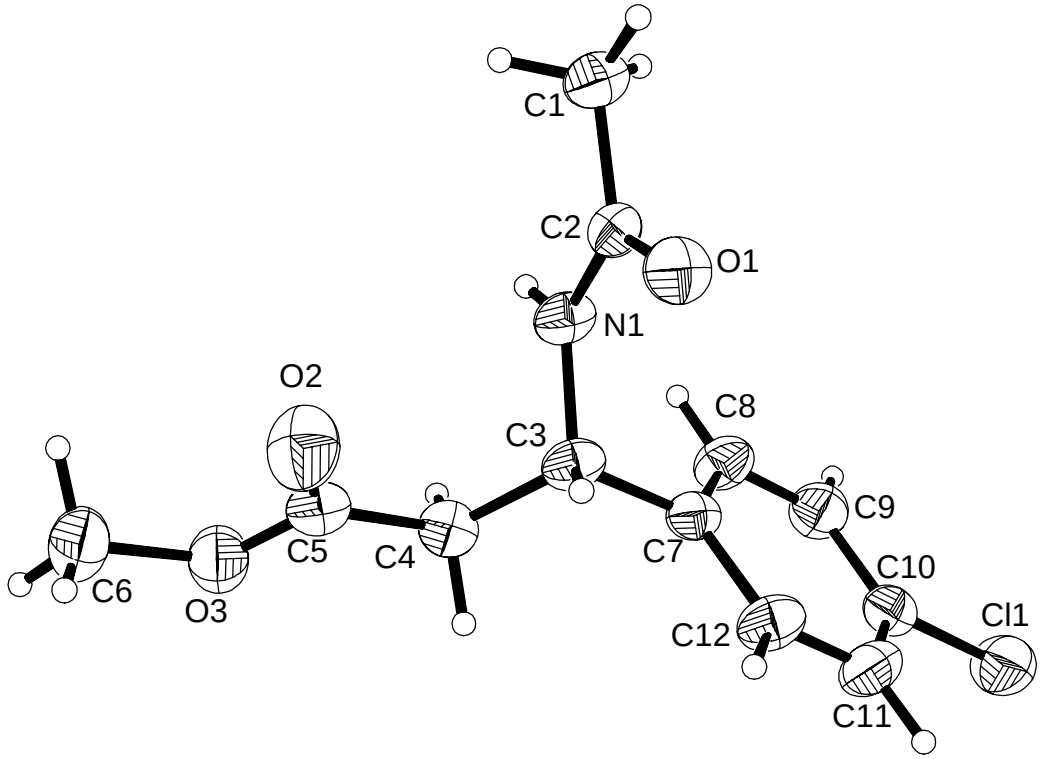


Figure 2: Molecular structure of (*S*)-(-)-methyl 3-acetylamino-3-(*p*-chloro-phenyl)-propanoate in the crystal (ORTEP, 50 % probability ellipsoids).

Diffraction data were collected on a STOE-IPDS diffractometer [λ(Mo-K_α) = 0.71073 Å]. The structure were solved by direct methods (SHELXS-97 (Sheldrick, 1997)) and refined by full matrix least square techniques against F^2 (SHELXL-97). XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. As observation criterion I > 2s(I) was used.

The nonhydrogen atoms were refined anisotropically. The hydrogen atoms (except the hydrogen atoms at the N1 and C3 of the (*S*)-(-)-methyl 3-acetylamino-3-(*p*-chloro-phenyl)-propanoate) were placed into theoretical positions and were refined by using the riding model.

Compound	methyl (*E*)-3-*N*-acetylamino-3-phenyl-acrylate	methyl 3-*N*,*N*-bisacetylamino-3-phenyl-acrylate	[Rh((*R*,*R*)-Et-FerroTANE)(NBD)]BF_4	[Rh((*S*,*S*)-Me-DuPHOS)(NBD)]BF_4	(*S*)-(-)-methyl 3-acetylamino-3-(p-chloro-phenyl)-propanoate
Empirical formula	$C_{12}H_{13}NO_3$	$C_{14}H_{15}NO_4$	$C_{31}H_{44}BF_4FeP_2Rh$	$C_{25}H_{36}BF_4P_2Rh$	$C_{12}H_{14}ClNO_3$
Formula weight	219.23	261.27	724.17	588.20	255.69
Crystal system	Triklinic	Orthorhombic	Monoklinic	Monoklinic	Monoklinic
Space group	$P\bar{1}$	Pbca	$P2_1$	$P2_1$	$P2_1$
a [Å]	8.931(2)	11.756(2)	10.581(2)	8.701(2)	5.046(1)
b [Å]	10.765(2)	7.735(2)	14.343(3)	18.374(4)	8.346(2)
c [Å]	12.868(3)	29.301(6)	10.600(2)	8.918(2)	15.246(3)
α [°]	72.19(3)	90	90	90	90
β [°]	89.67(3)	90	101.47(3)	113.40(3)	95.30(3)
γ [°]	80.51(3)	90	90	90	90
V [$Å^3$]	1160.4(4)	2664.4(9)	1576.6(5)	1308.5(5)	639.3
d_c [Mg/m^3]	1.255	1.303	1.525	1.493	1.328
Z	4	8	2	2	2
μ [mm^{-1}]	0.091	0.096	1.129	0.815	0.295
F(000)	464	1104	744	604	268
Crystal size [mm]	0.6 x 0.2 x 0.15	0.8 x 0.25 x 0.25	0.5 x 0.45 x 0.35	0.4 x 0.4 x 0.25	0.6 x 0.4 x 0.3
Temperature [K]	293	293	200	200	293
Scan range (2Θ) [°]	1.66 – 22.62	2.22 – 22.49	1.96 – 22.50	2.22 – 22.00	2.68 – 22.98
Index range (hkl)	-9/9, -11/11, -13/13	-12/12, -7/7, -31/30	-11/11, -15/15, -11/11	-9/9, -19/19, -9/9	-5/5, -9/9, -16/16
Reflection collected	5212	11043	7159	5585	3077
Independent reflections	2871	1678	4126	3097	1639
Beobachtete Reflexe	1505	1130	3974	2967	1411
Observed reflections	289	172	360	314	162
R1 (2σ(I))	0.0437	0.0463	0.0285	0.0310	0.0355
R1 (all data)	0.0911	0.0702	0.0298	0.0325	0.0413
wR2 (all data)	0.1031	0.1142	0.0709	0.0787	0.0887
Goodness of fit	0.777	0.928	1.185	0.974	0.977
Largest difference peak and hole (e/ Å)	0.158/-0.161	0.273/-0.280	0.606/-0.441	0.953/-0.319	0.151/-0.134

Table 1: Crystallographic and refinement data for methyl (*E*)-3-*N*-acetylamino-3-phenyl-acrylate, methyl 3-*N*,*N*-bisacetylamino-3-phenyl-acrylate, [Rh((*R*,*R*)-Et-FerroTANE)(NBD)]BF_4, Rh((*S*,*S*)-Me-DuPHOS)(NBD)]BF_4 and (*S*)-(-)-methyl 3-acetylamino-3-(*p*-chloro-phenyl)-propanoate