Supplementary Material (ESI) for Chemical Communications

Asymmetric Intermolecular Stetter Reactions Catalyzed by a Novel Triazolium Derived *N*-Heterocyclic Carbene

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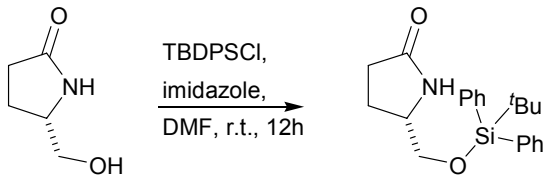
Electronic Supplementary Information

Supplementary Information

Experimental Section

General remarks: All reactions were performed in oven-dried glassware under a slight positive pressure of argon. The employed aldehydes were freshly distilled or recrystallized, the 1,3-unsaturated ketones were prepared according to standard literature procedures.[1] Other starting materials and reagents were purchased from commercial suppliers and used without further purification. All solvents were dried by conventional methods.[2] Toluene and THF were freshly distilled from Na/Pb alloy under argon. Preparative column chromatography: Merck silica gel 60, particle size 0.040–0.063 mm (230–240 mesh, flash). Analytical TLC: silica gel 60, F254 plates from Merck, Darmstadt. Optical rotation values were measured on a PerkinElmer P241 polarimeter. IR spectra were taken on a PerkinElmer FT/IR 1760 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were determined on a Gemini 300 or a Varian Inova 400 spectrometer and all measurements were performed with tetramethylsilane as internal standard. Chemical shifts for ^{1}H-NMR and ^{13}C-NMR are reported in parts per million (ppm), with coupling constants reported in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet. Mass spectra were acquired on a Finnigan SSQ 7000 spectrometer (CI 100 eV; EI 70 eV). Microanalyses were obtained with a Vario EL element analyzer. Melting points were determined with a Tottoli melting point apparatus and are uncorrected. Analytical HPLC was performed on Hewlett-Packard 1100 Series chromatographs using chiral stationary phases (Daicel Chiralcel OD, Daicel Chiralpak AD,VWR (s,s)-Whelk O1). Reaction control via gas chromatography was performed on a Varian CP-3800 (CP-Sil 8 CB) by using theoretical response factors for the determination of conversion.[3]

(*S*)-5-((tert-Butyldiphenylsilyloxy)methyl)pyrrolidin-2-one (19):

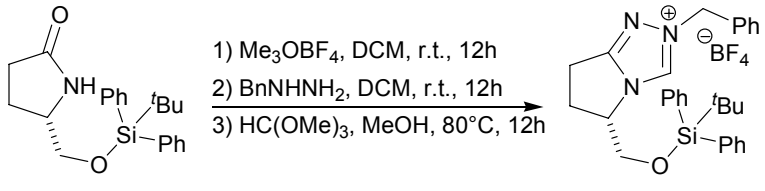


18 **19**

Imidazole (355 mg, 5.21 mmol) and tert-butyldiphenylsilylchloride (TBDPSCl) (1.35 mL, 5.21 mmol) were sequentially added to a solution of pyrrolidinone **18** (0.50 g, 4.34 mmol) in dry DMF (10 mL), at room temperature. After stirring for 18 h, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl (30 mL) and extracted with ethyl acetate (2 × 15 mL). The combined organic layers were washed with water (2 × 15 mL) and dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was then purified by silica gel flash chromatography (EtOAc) to give (*S*)-5-((tert-butyldiphenylsilyloxy)methyl)pyrrolidin-2-one (**19**) (1.52g, 99%) as a colorless oil. The analytical data were in accordance with those reported in the literature.[4]

$[\alpha]_D^{23} = -16.1$ (c 1.01, $CHCl_3$); ^{1}H-NMR (300MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.74 (m, 1H), 2.11 (m, 1H), 2.29 (m, 2H), 3.55 (m, 2H), 3.77 (m, 1H), 6.39 (s, 1H), 7.37 (m, 6H), 7.62 (m, 4H); ^{13}C-NMR (75MHz, $CDCl_3$): δ = 19.1, 22.7, 26.6, 29.7, 55.5, 67.2, 127.7, 129.7, 132.9, 135.4, 178.1.

(*S*)-2-Benzyl-5-((tert-butyldiphenylsilyloxy)methyl)-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate (9):



19 **9**

A 10 mL round bottomed flask was charged with the lactam **19** (0.35 g, 1.00 mmol) in absolut CH_2Cl_2 (10 mL). Trimethyloxonium tetrafluoroborate (0.16 g, 1.10 mmol) was added and the reaction mixture stirred for 12 hours at room temperature. Afterwards benzylhydrazine (0.11 mL, 1.10 mmol) was added and the solution was again stirred for 12 hours. The solvent was removed in vacuo and the residue was used without further purification. Trimethyl orthoformate (10 mL) was added and the reaction mixture was refluxing at 80°C for 12 hours. The solvent was removed in vacuo and the product was precipitated from ethyl acetate. Recrystallization from hot ethyl acetate afforded (*S*)-2-benzyl-5-((tert-butyldiphenylsilyloxy)methyl)-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-iumtetrafluoro-borate (**9**) (0.47g, 85%) as analytical pure colorless solid.

mp: 159°C; $[\alpha]_D^{23}$ = –3.8 (c 1.01, $CHCl_3$); IR(KBr): ν (cm^{-1}) = 3397, 3137, 3097, 3044, 2955, 2933, 2886, 2859, 2371, 2346, 1971, 1902, 1834, 1684, 1523, 1499, 1465, 1429, 1389, 1288, 862, 824, 786, 646, 614, 558; ^{1}H-NMR (300MHz, $CDCl_3$): 0.72 (s, 9H), 2.54 (m, 1H), 2.92 (m, 1H), 3.11 (m, 2H), 3.78 (dd, *J* = 3.6Hz, 11.8Hz, 1H), 4.14 (dd, *J* = 3.6Hz, 11.8Hz, 1H), 5.01 (m, 1H), 5.30 (d, *J* = 14.2Hz, 1H), 5.39 (d, *J* = 14.2Hz, 1H), 7.36 (m, 7 H), 7.44 (m, 8H), 9.43 (s, 1H). ^{13}C-NMR (75MHz, $CDCl_3$): 19.14, 22.22, 26.77, 29.79, 57.06, 61.61, 64.67, 128.00, 128.12, 129.22, 129.36, 129.62, 130.21, 130.31, 131.52, 131.75, 135.24, 135.32, 138.50, 162.55. MS (ESI): *m/z* (+) = 468.2 (100, M^+); 382.3 (5). *m/z* (-) = 87.3 (100, BF_4^-); Anal. Calcd for $C_{29}H_{34}N_3OSiBF_4$: C 62.70%, H 6.17%; N 7.56%; Found: C 63.01%; H 6.57%; N 7.54%.

General procedure for the asymmetric intermolecular Stetter reaction:

In a dry, argon-flushed Schlenk tube the precatalyst **9** (27 mg, 0.05 mmol 10 mol%), dry Cs_2CO_3 (16 mg, 0.05 mmol) and chalcone **2** (104 mg, 0.5 mmol) were dissolved in absolute THF (1 mL). The reaction mixture was cooled to 0°C and then benzaldehyde **1** (64 mg,

0.60 mmol) was added dropwise. After stirring for 8h, the reaction mixture was directly purified by flash chromatography on silca gel (pentane / diethylether = 9:1) to yield (*R*)-1,2,4-triphenylbutane-1,4-dione **12a** (102mg, 65%) as colorless solid. Recrystallization from diethylether afforded the 1,4-diketone **12a** (62mg, 40%) enantiomerically pure as colorless needles. The analytical data were in accordance with those reported in the literature.[5]

(*R*)-1,2,4-Triphenylbutane-1,4-dione (12a), $[\alpha]_D^{23}$ = –291.1 (c 1.01, $CHCl_3$); ^{1}H-NMR (300MHz, $CDCl_3$): 3.22 (dd, *J* = 18.3Hz, 3.8Hz, 1H), 4.14 (dd, *J* = 18.3 Hz, 10.2Hz, 1H), 5.24 (dd, *J* = 10.2Hz, 3.8Hz, 1H), 7.12-7.64 (m, 12H), 7.90-8.22 (m, 3H); ^{13}C-NMR (75MHz, $CDCl_3$): 43.8, 48.6, 127.3, 128.0, 128.1, 128.4, 128.5, 128.6, 128.8, 129.1, 129.9, 132.8, 133.2, 136.3, 138.5, 197.9, 198.8.

(*R*)-2,4-Diphenyl-1-*p*-tolylbutane-1,4-dione (12b), $[\alpha]_D^{23}$ = –251.4 (c 1.01, $CHCl_3$); ^{1}H-NMR (300MHz, $CDCl_3$): 2.26 (s, 3H), 3.20 (dd, *J* =17.7Hz, 3.7Hz, 1H), 4.12 (dd, *J* = 17.7Hz, 9.9Hz, 1H), 5.23 (dd, *J* = 9.9Hz, 3.7Hz, 1H), 7.11-7.56 (m, 10H), 7.82-8.04 (m, 4H); ^{13}C-NMR (75MHz, $CDCl_3$): 21.6, 43.8, 48.6, 125.4, 127.3, 128.2, 128.3, 128.6, 129.1, 129.2, 129.3, 129.6, 129.8,130.6, 131.1, 132.8, 133.2, 133.9, 136.6, 138.9, 143.7, 144.9, 198.1, 198.5.

(*R*)-2,4-Diphenyl-1-*m*-tolylbutane-1,4-dione (12c), $[\alpha]_D^{23}$ = –334.1 (c 1.01, $CHCl_3$); ^{1}H-NMR (300MHz, CDCl3): 2.28 (s, 3H), 3.22 (dd, *J* =17.7, 3.9Hz, 1H), 4.13 (dd, *J* = 17.7Hz, 10.2Hz, 1H), 5.25 (dd, *J* = 10.2Hz, 3.9Hz, 1H), 7.12-7.54 (m, 10H), 7.74-7.78 (m, 2H), 7.88-7.94 (m, 2H); ^{13}C-NMR (75MHz, $CDCl_3$): 21.4, 43.9, 48.7, 126.2, 127.3, 128.2, 128.3, 128.4, 128.6, 129.0, 129.2, 129.4, 133.2, 133.7, 134.1, 136.5, 138.3, 138.7, 198.1, 199.1.

(*R*)-1-(4-Chlorophenyl)-2,4-diphenylbutane-1,4-dione (12d), ^{1}H-NMR (400MHz, $CDCl_3$): 3.22 (dd, *J* =18.2Hz, 3.6Hz, 1H), 4.13 (dd, *J* = 18.2Hz, 10.2Hz, 1H), 5.17 (dd, *J* = 10.2Hz, 3.6Hz, 1H), 7.12-7.50 (m, 10H), 7.86-7.92 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$): 44.0, 48.9, 127.5, 128.1, 128.6, 128.8, 129.3, 130.3, 131.8, 133.3, 134.7, 136.3, 138.2, 139.3, 197.6, 197.9.

(*R*)-1-(4-Bromophenyl)-2,4-diphenylbutane-1,4-dione (12e), ^{1}H-NMR (400MHz, $CDCl_3$): 3.22 (dd, *J* = 18.2Hz, 3.6Hz, 1H), 4.13 (dd, *J* = 18.2Hz, 10.5Hz, 1H), 5.17 (dd, *J* = 10.5Hz, 3.6Hz, 1H), 7.12-7.58 (m, 10H), 7.80-7.84 (m, 2H), 7.88-7.93 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): 43.9, 48.8, 127.5, 128.1, 128.6, 129.3, 130.4, 131.8, 133.3, 135.2, 136.3, 138.2, 197.8, 197.9.

(*R*)-1-(Naphthalen-2-yl)-2,4-diphenylbutane-1,4-dione (12f), $[\alpha]_D^{23}$ = –106.7 (c 1.01, $CHCl_3$); ^{1}H-NMR (400MHz, $CDCl_3$): 3.26 (dd, *J* = 18.1Hz, 3.8Hz, 1H), 4.19 (dd, *J* = 18.1Hz, 9.8Hz, 1H), 5.40 (dd, J = 9.8Hz, 3.8Hz, 1H), 7.69-7.50 (m, 10H), 7.65-8.05 (m, 6H), 8.51 (s, 1H); ^{13}C-NMR (75MHz, $CDCl_3$): 44.0, 48.9, 124.6, 126.5, 127.3, 127.6, 128.1, 128.2, 128.3, 128.4, 128.5, 129.2, 129.7, 130.7, 132.5, 133.3, 133.8, 135.5, 136.5, 138.7, 198.0, 198.8.

(*R*)-1-(Furan-2-yl)-2,4-diphenylbutane-1,4-dione (12h), ^{1}H-NMR (300MHz, $CDCl_3$): 3.24 (dd, *J*=18.0Hz, 3.8Hz, 1H), 4.09 (dd, *J* = 18.0Hz, 10.1Hz, 1H), 5.04 (dd, *J* = 10.1Hz, 3.8Hz, 1H), 6.38 (m, 1H), 7.10-7.50 (m, 10H), 7.80-7.98 (m, 2H); ^{13}C-NMR (75MHz, CDCl3): 42.8, 48.7, 112.3, 118.0, 127.1, 127.5, 128.2, 128.3, 128.4, 128.6, 128.8, 129.0, 133.3, 136.4, 138.3, 146.5, 187.7, 197.8.

(*R*)-2-(4-Chlorophenyl)-1,4-diphenylbutane-1,4-dione (12i), $[\alpha]_D^{23}$ = –220.0 (c 1.01, $CHCl_3$); ^{1}H-NMR (400MHz, $CDCl_3$): 3.22 (dd, *J* =18.2Hz, 3.8Hz, 1H), 4.08 (dd, *J* = 18.2Hz, 9.8Hz, 1H), 5.23 (dd, *J* = 9.8Hz, 3.8Hz, 1H), 7.14-7.52 (m, 10H), 7.87-7.96 (m, 4H); ^{13}C-NMR (100MHz, $CDCl_3$): 43.8, 48.0, 128.1, 128.4, 128.5, 128.6, 128.8, 129.1, 129.3, 129.6, 129.9, 133.1, 133.3, 133.5, 136.2, 136.3, 137.1, 197.6, 198.5.

(***R*)-1,4-Diphenyl-2-p-tolylbutane-1,4-dione (12j)**, ^{1}H-NMR (300MHz, $CDCl_3$): 2.21(s, 3H), 3.20 (dd, *J* = 18.1Hz, 3.7Hz, 1H), 4.11 (dd, *J* = 18.1Hz, 10.1Hz, 1H), 5.21 (dd, *J* = 10.1Hz, 3.7Hz, 1H), 7.04-7.51 (m, 10H), 7.88-7.97 (m, 4H); ^{13}C-NMR (75MHz, $CDCl_3$): 21.0, 43.9, 48.3, 128.1, 128.2, 128.5, 128.6, 128.9, 129.9, 132.8, 133.2, 135.6, 136.5, 137.1, 198.2, 199.1.

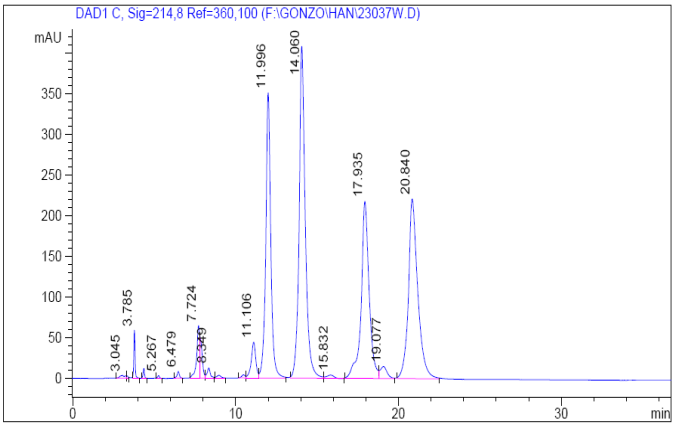
AK Enders - Analytische HPLC

Sample Name: han 23037
Data file: F:\GONZO\HAN\23037W.D
Sample Info: Laufmittel: n-Heptan/EtOH 95:5;
Probe im LM gelöst

Säule: WHELK.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 11:55:12
Injektion Date: 27.03.2007

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	29.6	30.2
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.04	0.28	3.43	75.31	0.20
2	3.34	0.10	2.69	18.51	0.05
3	3.78	0.09	58.74	319.10	0.84
4	4.36	0.09	12.01	71.57	0.19
5	5.27	0.13	3.29	26.70	0.07
6	6.48	0.16	8.15	86.12	0.23
7	7.72	0.19	64.61	830.01	2.18
8	7.89	0.17	40.85	457.79	1.20
9	8.35	0.20	12.53	175.41	0.46
10	8.97	0.27	3.45	62.41	0.16
11	10.48	0.23	3.97	60.65	0.16
12	11.11	0.29	44.11	862.81	2.27
13	12.00	0.31	350.90	7503.57	19.70
14	14.06	0.38	408.09	10702.72	28.10
15	15.83	0.47	4.10	122.56	0.32
16	17.94	0.49	217.87	7438.01	19.53
17	19.08	0.44	14.79	440.29	1.16
18	20.84	0.57	221.28	8832.91	23.19
Total				38086.45	100.00

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han 23037

Figure 1 HPLC of 1,2,4-triphenylbutane-1,4-dione (***rac*-12a**).

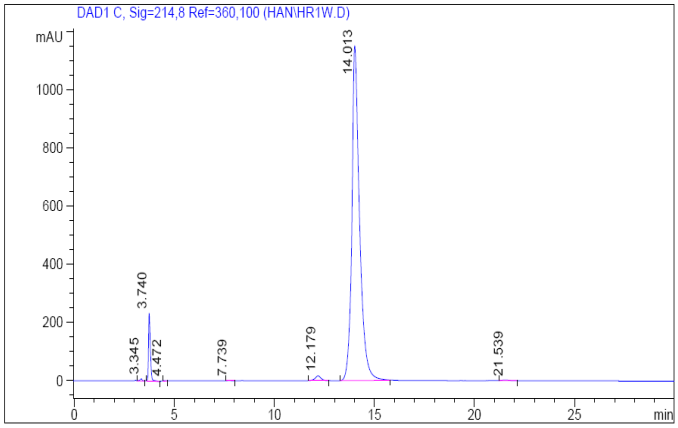
AK Enders - Analytische HPLC

Sample Name: HAN HR1
Data file: D:\GONZO\HAN\HR1W.D
Sample Info: Laufmittel: n-Heptan/ETOH 95:5;
Probe im LM gelöst

Säule: WHELK.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 15:38:36
Injektion Date: 27.03.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	32.5	32.7
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.35	0.12	7.83	67.06	0.20
2	3.74	0.10	233.36	1507.41	4.60
3	4.47	0.14	2.15	21.49	0.07
4	7.74	0.17	1.35	15.36	0.05
5	12.18	0.32	16.75	363.52	1.11
6	14.01	0.38	1149.49	30726.48	93.79
7	21.54	0.37	1.97	59.59	0.18
Total				32760.92	100.00

Figure 2 HPLC of (*R*)-1,2,4-triphenylbutane-1,4-dione (**12a**).

AK Enders - Analytische HPLC

Sample Name: Han 361
Data file: F:\BERT\HAN\361RAIA.D
Sample Info: Laufmittel:n-Heptan/IP 9:1;
Probe im LM gelöst

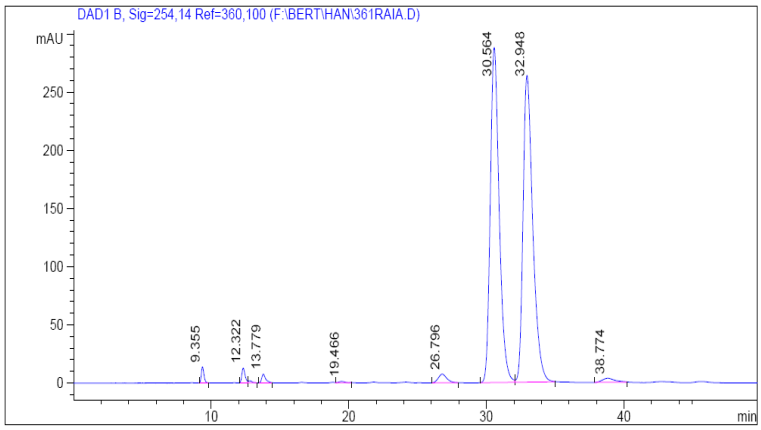
HEWLETT PACKARD

Säule: DAICELIA.M
Säuleninfo: (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 12:36:30
Injektion Date: 25.01.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	23.7	23.6
Flow in ml/min:	0.5	0.5



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.36	0.20	13.93	183.92	0.68
2	12.32	0.25	12.73	208.52	0.77
3	12.80	0.24	1.77	31.48	0.12
4	13.78	0.31	7.46	153.77	0.57
5	19.47	0.39	1.21	39.45	0.15
6	26.80	0.52	7.52	322.95	1.19
7	30.56	0.68	288.12	12950.48	47.78
8	32.95	0.75	263.79	12985.14	47.91
9	38.77	0.77	3.52	229.05	0.85
Total				27104.76	100.00

Figure 3 HPLC of 2,4-diphenyl-1-*p*-tolylbutane-1,4-dione (***rac*-12b**).

AK Enders - Analytische HPLC

Sample Name: Han HR 2
Data file: E:\BERT\HAN\HR2IA.D
Sample Info: Laufmittel:n-Heptan/IP 9:1;
Probe im LM gelöst

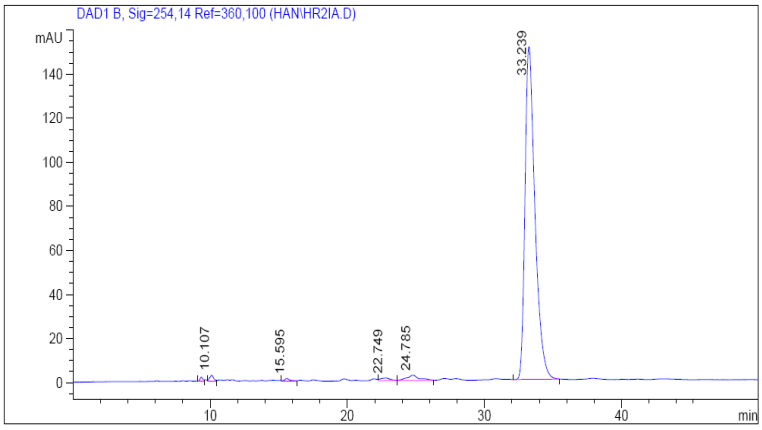
HEWLETT PACKARD

Säule: DAICELIA.M
Säuleninfo: (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 11:51:11
Injektion Date: 31.03.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	24.8	25.2
Flow in ml/min:	0.5	0.5



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.34	0.19	1.82	23.88	0.30
2	10.11	0.34	2.61	53.02	0.67
3	15.59	0.34	1.15	31.06	0.39
4	22.75	0.60	1.23	62.45	0.78
5	24.79	0.77	2.47	158.93	2.00
6	33.24	0.76	151.02	7627.03	95.86
Total				7956.37	100.00

Figure 4 HPLC of (*R*)-2,4-diphenyl-1-*p*-tolylbutane-1,4-dione (**12b**).

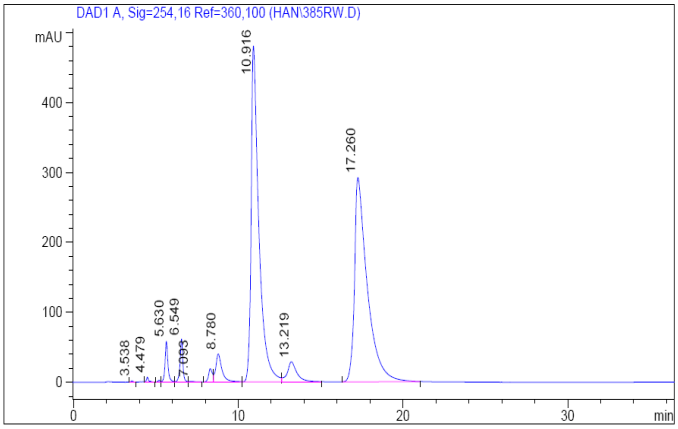
AK Enders - Analytische HPLC

Sample Name: H 385 rac
Data file: D:\GONZO\HAN\385RW.D
Sample Info: Laufmittel: n-Heptan/IP 9:1;
Probe im LM/DCM gelöst

Säule: WHELK.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 08:49:39
Injektion Date: 20.02.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	53.7	54.0
Flow in ml/min:	1.0	1.0



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.54	0.14	2.12	19.63	0.06
2	4.48	0.14	7.35	73.79	0.21
3	5.18	0.15	2.76	28.33	0.08
4	5.63	0.18	58.28	720.26	2.02
5	6.55	0.17	61.77	731.07	2.05
6	7.09	0.40	1.24	34.11	0.10
7	8.29	0.24	19.32	316.31	0.89
8	8.78	0.38	40.25	1069.57	3.00
9	10.92	0.46	480.50	15670.46	43.98
10	13.22	0.59	28.83	1190.05	3.34
11	17.26	0.76	292.06	15779.55	44.28
Total				35633.12	100.00

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H 385 rac

Figure 5 HPLC of 2,4-diphenyl-1-*m*-tolylbutane-1,4-dione (***rac*-12c**).

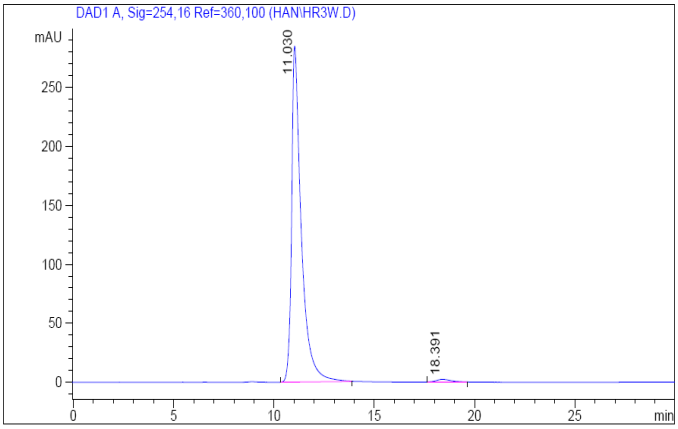
AK Enders - Analytische HPLC

Sample Name: Han HR 3
Data file: D:\GONZO\HAN\HR3W.D
Sample Info: Laufmittel: n-Heptan/IP 9:1;
Probe im LM gelöst

Säule: WHELK.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 14:08:57
Injektion Date: 31.03.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	49.0	49.6
Flow in ml/min:	1.0	1.0



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	11.03	0.48	284.83	9515.12	98.73
2	18.39	0.66	2.35	122.06	1.27
Total				9637.19	100.00

Han HR 3 Page 1 of 1

Figure 6 HPLC of (*R*)-2,4-diphenyl-1-*m*-tolylbutane-1,4-dione (**12c**).

AK Enders - Analytische HPLC

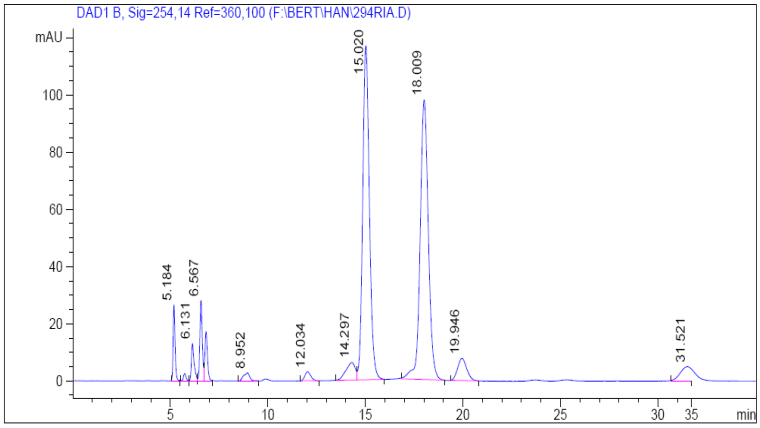
Sample Name: H 294 Rac
Data file: F:\BERT\HAN\294RIA.D
Sample Info: Laufmittel:n-Heptan/IP 9:1;
Probe im LM/DCM gelöst

Säule: DAICELIA.M
Säuleninfo: (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 09:32:24
Injektion Date: 23.11.2007

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	50.1	49.2
Flow in ml/min:	1.0	1.0



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.18	0.10	26.60	184.28	2.55
2	5.73	0.15	2.51	23.10	0.32
3	6.13	0.14	13.08	128.97	1.78
4	6.57	0.13	28.20	244.44	3.38
5	6.83	0.14	17.28	160.32	2.22
6	8.95	0.30	2.78	61.37	0.85
7	12.03	0.31	3.20	68.37	0.95
8	14.30	0.43	6.17	205.09	2.84
9	15.02	0.37	116.89	2784.40	38.49
10	18.01	0.45	97.81	2863.12	39.58
11	19.95	0.47	7.76	252.55	3.49
12	31.52	0.63	4.96	257.48	3.56
Total				7233.48	100.00

Figure 7 HPLC of 1-(4-chlorophenyl)-2,4-diphenylbutane-1,4-dione (***rac*-12d**).

AK Enders - Analytische HPLC

Sample Name: H 375
Data file: E:\BERT\HAN\375IA.D
Sample Info: Laufmittel:n-Heptan/IP 9:1;
Probe im LM gelöst

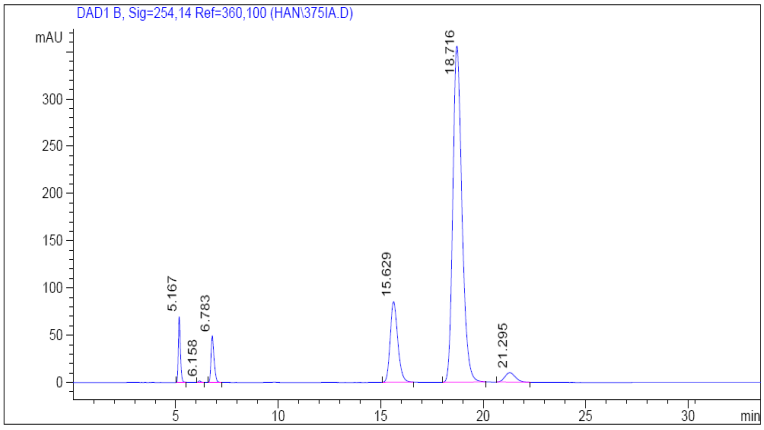
HEWLETT PACKARD

Säule: DAICELIA.M
Säuleninfo: (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 14:04:47
Injektion Date: 06.02.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	49.1	49.1
Flow in ml/min:	1.0	1.0



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.17	0.11	69.86	494.21	3.39
2	6.16	0.13	1.71	14.34	0.10
3	6.78	0.15	49.52	508.38	3.49
4	15.63	0.40	85.36	2191.35	15.03
5	18.72	0.47	355.85	11011.29	75.53
6	21.30	0.52	10.09	359.67	2.47
Total				14579.25	100.00

Figure 8 HPLC of (*R*)-1-(4-chlorophenyl)-2,4-diphenylbutane-1,4-dione (**12d**).

AK Enders - Analytische HPLC

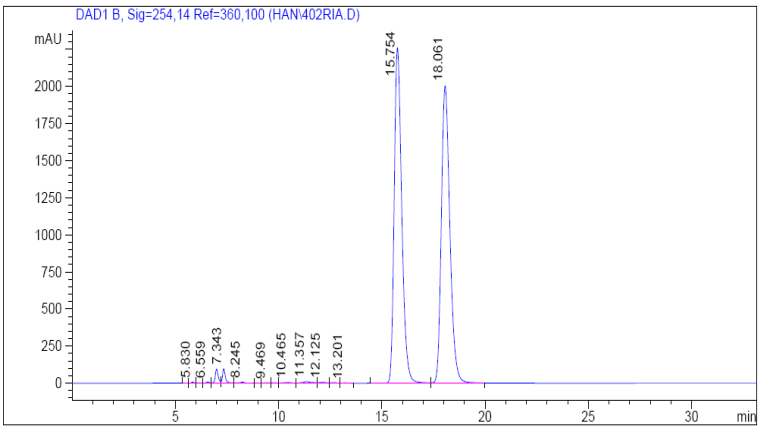
Sample Name: H 402 rac
Data file: E:\BERT\HAN\402RIA.D
Sample Info: Laufmittel:n-Heptan/IP 7:3;
Probe im LM gelöst

Säule: DAICELIA.M
Säuleninfo: (250 x 4.6) mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 13:48:53
Injektion Date: 25.02.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	43.7	43.2
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.45	0.18	1.97	25.75	0.02
2	5.83	0.14	7.97	73.39	0.06
3	6.12	0.18	3.03	37.07	0.03
4	6.56	0.17	8.32	96.65	0.08
5	6.99	0.15	95.72	959.26	0.81
6	7.34	0.15	98.01	956.66	0.81
7	8.24	0.31	7.52	167.44	0.14
8	8.99	0.20	1.82	23.94	0.02
9	9.47	0.31	2.65	51.45	0.04
10	9.78	0.24	3.07	49.92	0.04
11	10.47	0.37	4.96	133.87	0.11
12	11.36	0.42	10.62	331.47	0.28
13	12.13	0.37	6.04	150.93	0.13
14	12.67	0.29	3.70	70.75	0.06
15	13.20	0.29	1.88	37.22	0.03
16	15.75	0.39	2261.28	57382.20	48.57
17	18.06	0.44	2004.09	57600.56	48.75
Total				118148.54	100.00

Figure 9 HPLC of 1-(4-bromophenyl)-2,4-diphenylbutane-1,4-dione (***rac*-12e**).

AK Enders - Analytische HPLC

Sample Name: H 403
Data file: E:\BERT\HAN\403IA.D
Sample Info: Laufmittel:n-Heptan/IP 7:3;
Probe im LM gelöst

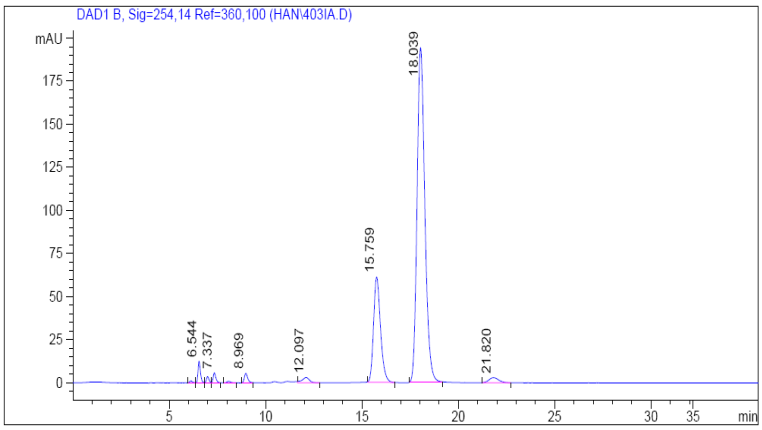
HEWLETT PACKARD

Säule: DAICELIA.M
Säuleninfo: (250 x 4.6) mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 14:25:31
Injektion Date: 25.02.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	43.1	43.1
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.12	0.15	1.14	10.91	0.15
2	6.54	0.14	12.51	109.94	1.47
3	6.99	0.14	3.65	33.79	0.45
4	7.34	0.15	5.77	57.41	0.77
5	8.07	0.21	0.85	11.38	0.15
6	8.97	0.19	5.44	66.98	0.90
7	12.10	0.39	3.04	80.96	1.08
8	15.76	0.38	61.14	1532.88	20.54
9	18.04	0.43	194.17	5455.57	73.10
10	21.82	0.54	2.94	103.70	1.39
Total				7463.51	100.00

Figure 10 HPLC of (*R*)-1-(4-bromophenyl)-2,4-diphenylbutane-1,4-dione (**12e**).

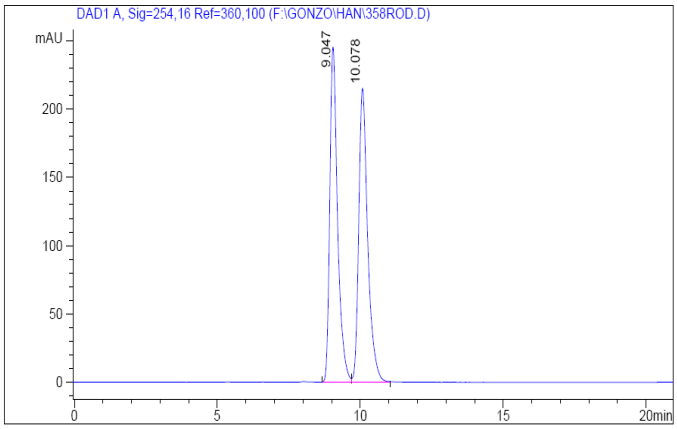
AK Enders - Analytische HPLC

Sample Name: H 358 rac
Data file: F:\GONZO\HAN\358ROD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Probe im LM gelöst

Säule: DAICELOD.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 15:26:30
Injektion Date: 24.01.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	25.4	26.1
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.05	0.28	245.55	4646.98	49.79
2	10.08	0.33	215.18	4686.45	50.21
Total				9333.43	100.00

Figure 11 HPLC of 1-(naphthalen-2-yl)-2,4-diphenylbutane-1,4-dione (***rac*-12f**).

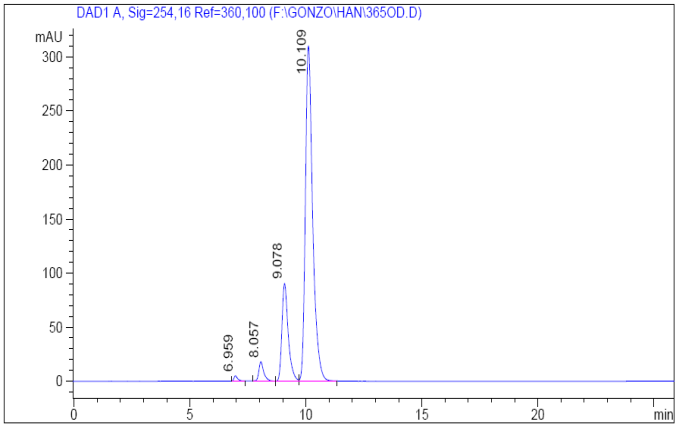
AK Enders - Analytische HPLC

Sample Name: H 365
Data file: F:\GONZO\HAN\365OD.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Probe im LM gelöst

Säule: DAICELOD.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 14:25:23
Injektion Date: 28.01.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	25.5	25.9
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.96	0.17	4.96	57.59	0.65
2	8.06	0.22	17.98	267.83	3.04
3	9.08	0.28	90.37	1705.13	19.37
4	10.11	0.33	310.19	6770.98	76.93
Total				8801.53	100.00

Figure 12 HPLC of (*R*)-1-(naphthalen-2-yl)-2,4-diphenylbutane-1,4-dione (**12f**).

AK Enders - Analytische HPLC

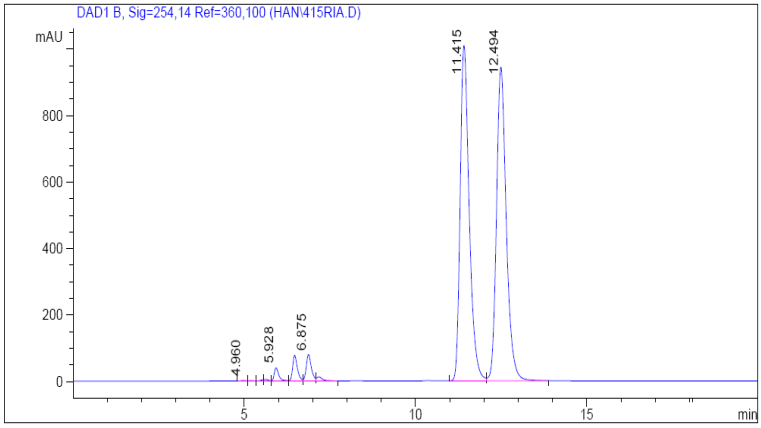
Sample Name: H 415 rac
Data file: E:\BERT\HAN\415RIA.D
Sample Info: Laufmittel:n-Heptan/IP 6:4;
Probe im LM gelöst

Säule: DAICELIA.M
Säuleninfo: (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 08:59:44
Injektion Date: 07.03.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	51.6	51.3
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.96	0.17	1.91	20.77	0.05
2	5.19	0.13	1.58	14.99	0.04
3	5.53	0.10	3.94	26.29	0.07
4	5.64	0.12	5.14	42.96	0.11
5	5.93	0.14	40.17	374.85	0.95
6	6.47	0.14	77.86	749.65	1.90
7	6.88	0.16	80.03	826.77	2.10
8	7.18	0.18	12.54	157.36	0.40
9	11.42	0.28	1009.78	18481.18	46.88
10	12.49	0.30	944.14	18727.39	47.50
Total				39422.21	100.00

Figure 13 HPLC of 1-(furan-2-yl)-2,4-diphenylbutane-1,4-dione (***rac*-12g**).

AK Enders - Analytische HPLC

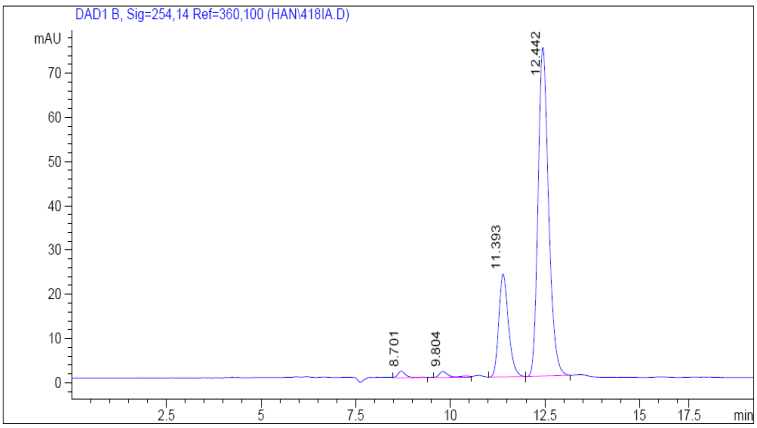
Sample Name: Han 418
Data file: E:\BERT\HAN\418IA.D
Sample Info: Laufmittel:n-Heptan/IP 6:4;
Probe im LM gelöst

Säule: DAICELIA.M
Säuleninfo: (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 11:14:15
Injektion Date: 07.03.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	51.1	51.0
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.70	0.21	1.50	23.19	1.22
2	9.80	0.28	1.36	27.42	1.44
3	11.39	0.28	23.26	413.29	21.73
4	12.44	0.29	74.34	1437.65	75.60
Total				1901.56	100.00

Figure 14 HPLC of (*R*)-1-(furan-2-yl)-2,4-diphenylbutane-1,4-dione (**12g**).

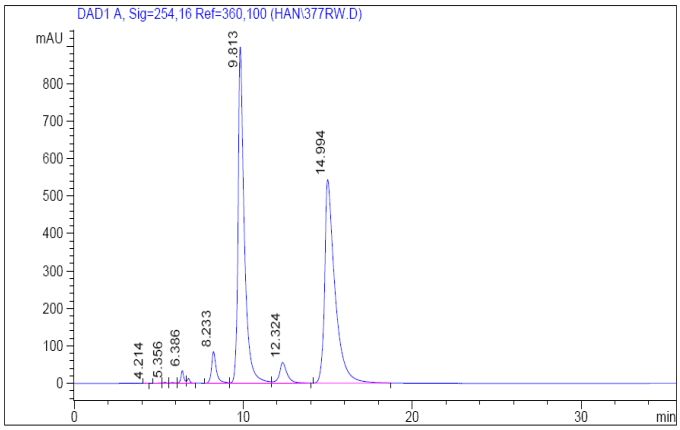
AK Enders - Analytische HPLC

Sample Name: H 377 rac
Data file: D:\GONZO\HAN\377RW.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Probe im LM gelöst

Säule: WHELK.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 13:12:54
Injektion Date: 07.02.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	42.9	44.7
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.21	0.11	1.05	7.75	0.02
2	5.06	0.20	1.15	16.64	0.03
3	5.36	0.19	2.75	37.51	0.07
4	5.79	0.26	2.32	42.85	0.09
5	6.39	0.18	34.08	410.21	0.82
6	6.75	0.18	12.89	158.17	0.31
7	8.23	0.29	84.60	1695.58	3.37
8	9.81	0.37	897.44	23008.57	45.78
9	12.32	0.46	55.47	1790.91	3.56
10	14.99	0.60	543.67	23095.53	45.95
Total				50263.73	100.00

H 377 rac Page 1 of 1

Figure 15 HPLC of 2-(4-chlorophenyl)-1,4-diphenylbutane-1,4-dione (***rac*-12i**).

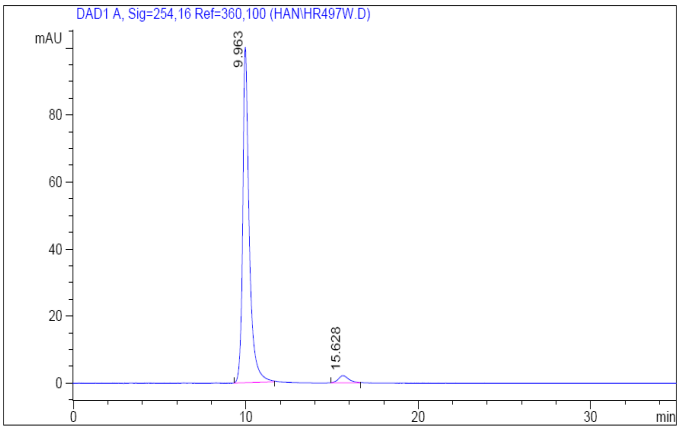
AK Enders - Analytische HPLC

Sample Name: HR 497
Data file: D:\GONZO\HAN\HR497W.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Probe im LM gelöst

Säule: WHELK.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 11:57:30
Injektion Date: 21.05.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	41.8	42.5
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.96	0.38	100.13	2626.33	96.62
2	15.63	0.55	2.17	91.95	3.38
Total				2718.28	100.00

Figure 16 HPLC of (*R*)-2-(4-chlorophenyl)-1,4-diphenylbutane-1,4-dione (**12i**).

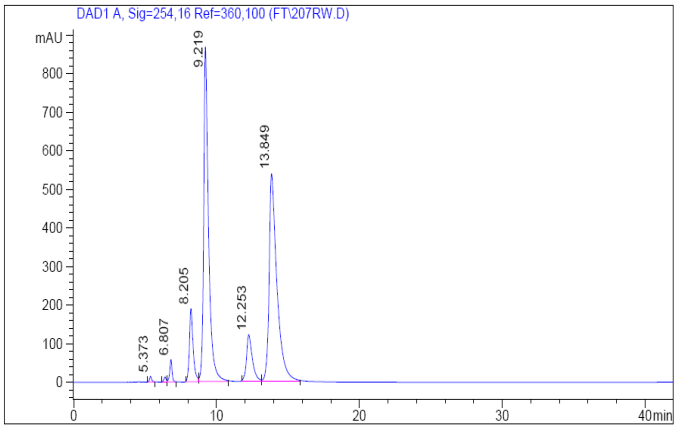
AK Enders - Analytische HPLC

Sample Name: FT 207 F1 rac
Data file: D:\GONZO\FT\207RW.D
Sample Info: Laufmittel: n-Heptan/IP 7:3;
Probe im LM gelöst

Säule: WHELK.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 08:54:35
Injektion Date: 08.02.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	44.4	45.1
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.37	0.16	14.67	151.62	0.31
2	6.39	0.17	12.86	140.10	0.29
3	6.81	0.17	57.87	641.01	1.32
4	8.21	0.27	189.45	3448.10	7.09
5	9.22	0.34	866.40	20418.68	41.99
6	12.25	0.42	120.50	3442.69	7.08
7	13.85	0.54	537.83	20379.98	41.91
Total				48622.19	100.00

Figure 17 HPLC of 1,4-diphenyl-2-p-tolylbutane-1,4-dione (***rac*-12h**).

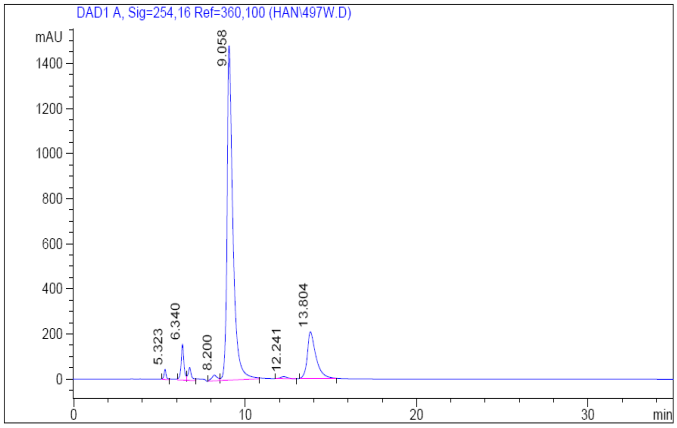
AK Enders - Analytische HPLC

Sample Name: H 497
Data file: D:\GONZO\HAN\497W.D
Sample Info: Laufmittel: n-Heptan/IP 7:3
Probe im LM gelöst

Säule: WHELK.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 12:26:17
Injektion Date: 15.05.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	41.5	42.1
Flow in ml/min:	0.7	0.7



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.32	0.13	45.23	405.22	0.87
2	6.34	0.18	159.31	1846.98	3.97
3	6.76	0.20	56.94	788.03	1.69
4	8.20	0.33	25.12	582.94	1.25
5	9.06	0.35	1482.80	35279.33	75.81
6	12.24	0.40	8.92	234.40	0.50
7	13.80	0.52	207.82	7399.40	15.90
Total				46536.31	100.00

Figure 18 HPLC of (*R*)-1,4-diphenyl-2-p-tolylbutane-1,4-dione (**12h**).

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[4] M. Hashimoto, M. Matsumoto and S. Terashima**,** *Tetrahedron.* **2003**, *59*, 3019.

[5] a) H. Stetter and H. Kuhlmann, *Chem. Ber.* **1976**, *109*, 2890; b) A. E. Mattson, A. R. Bharadwaj and K. A. Scheidt, *J. Am. Chem. Soc*. **2004**, *126*, 2314.