BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Ugi reaction-derived prolyl peptide catalysts grafted on the renewable polymer polyfurfuryl alcohol for applications in heterogeneous enamine catalysis

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^{1}H and ^{13}C NMR spectra of prolyl pseudo-peptide catalysts and chiral-phase HPLC analysis of Michael adducts

Spectra of compounds

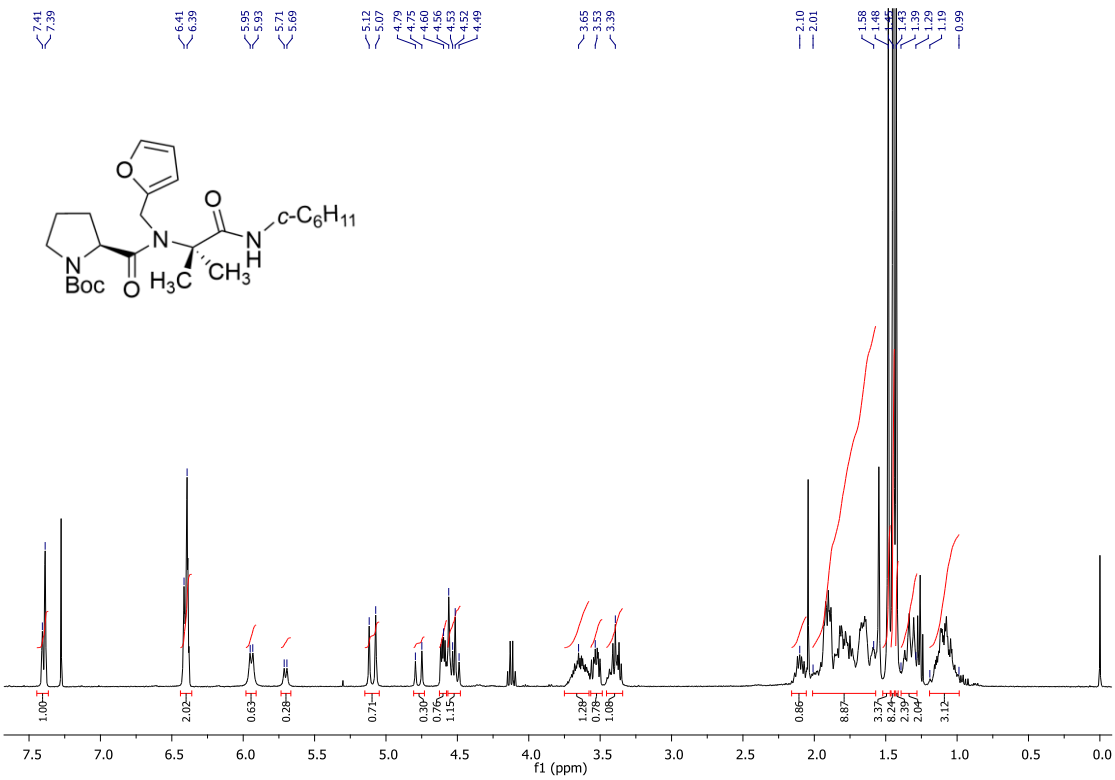


Figure S1: 400 MHz ^{1}H NMR spectrum in $CDCl_3$ of **1**.

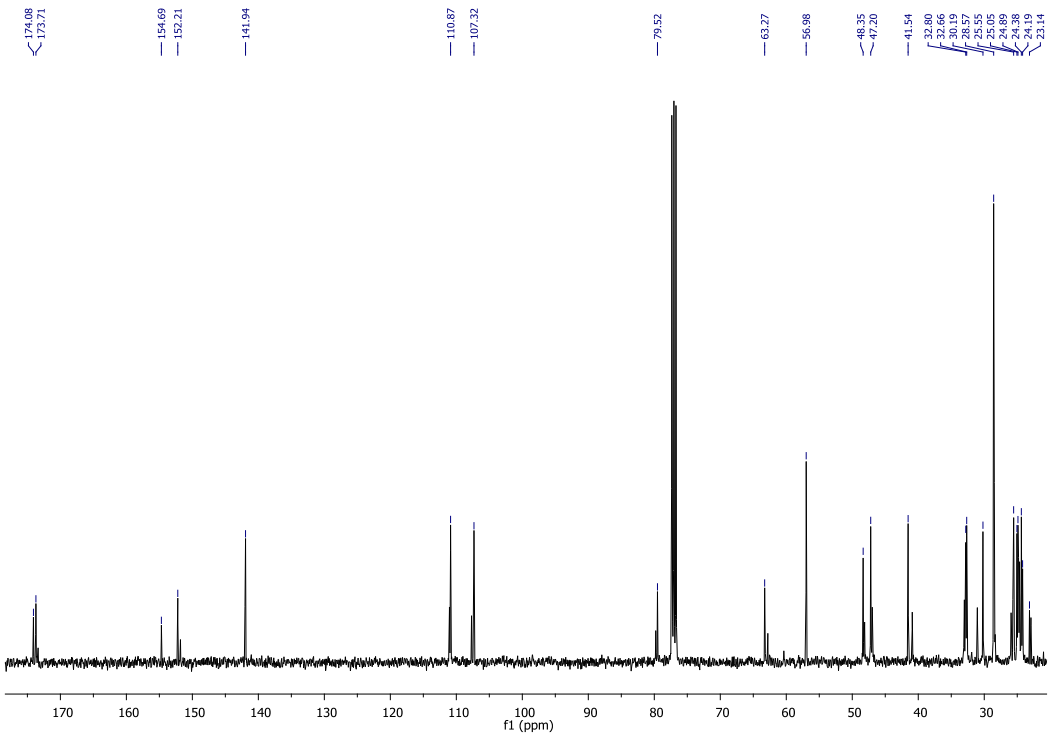


Figure S2: 100 MHz ^{13}C NMR spectrum in $CDCl_3$ of **1**.

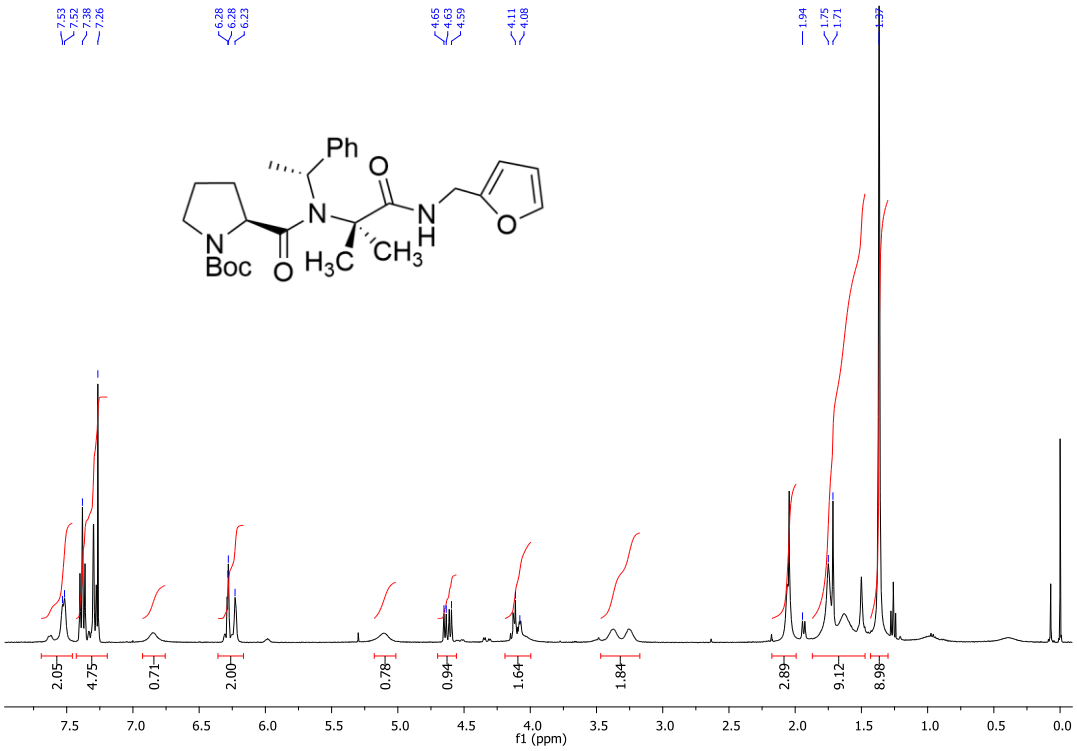


Figure S3: 400 MHz ^{1}H NMR spectrum in $CDCl_3$ of **2**.

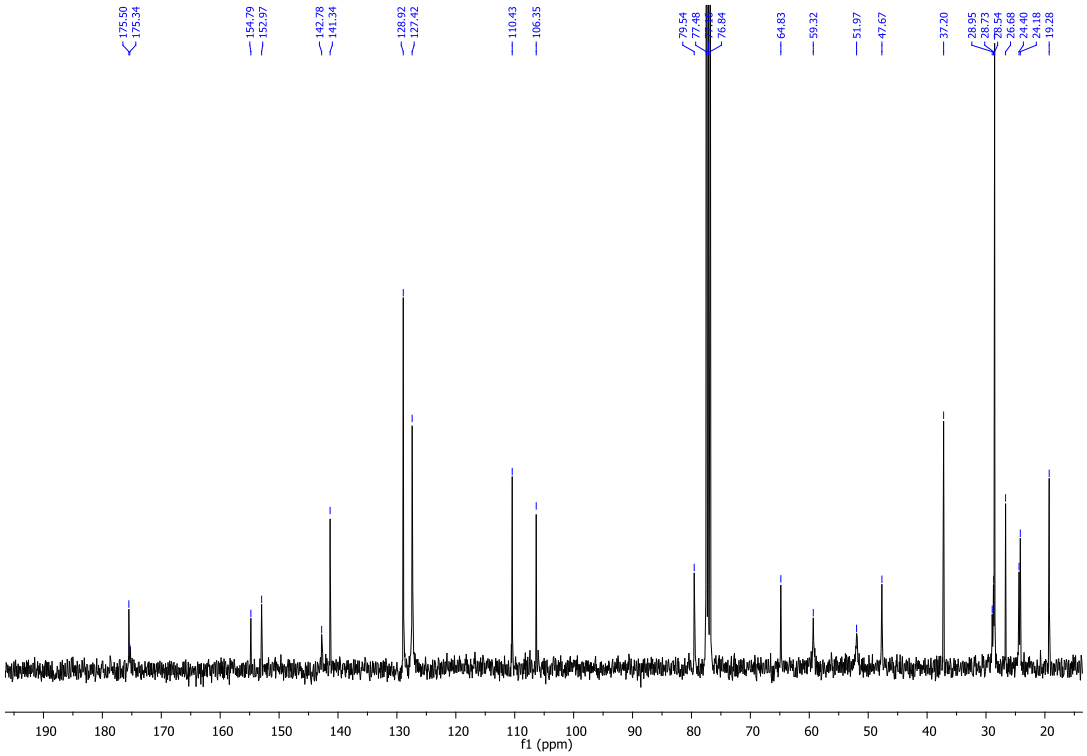


Figure S4: 100 MHz ^{13}C NMR spectrum in $CDCl_3$ of **2**.

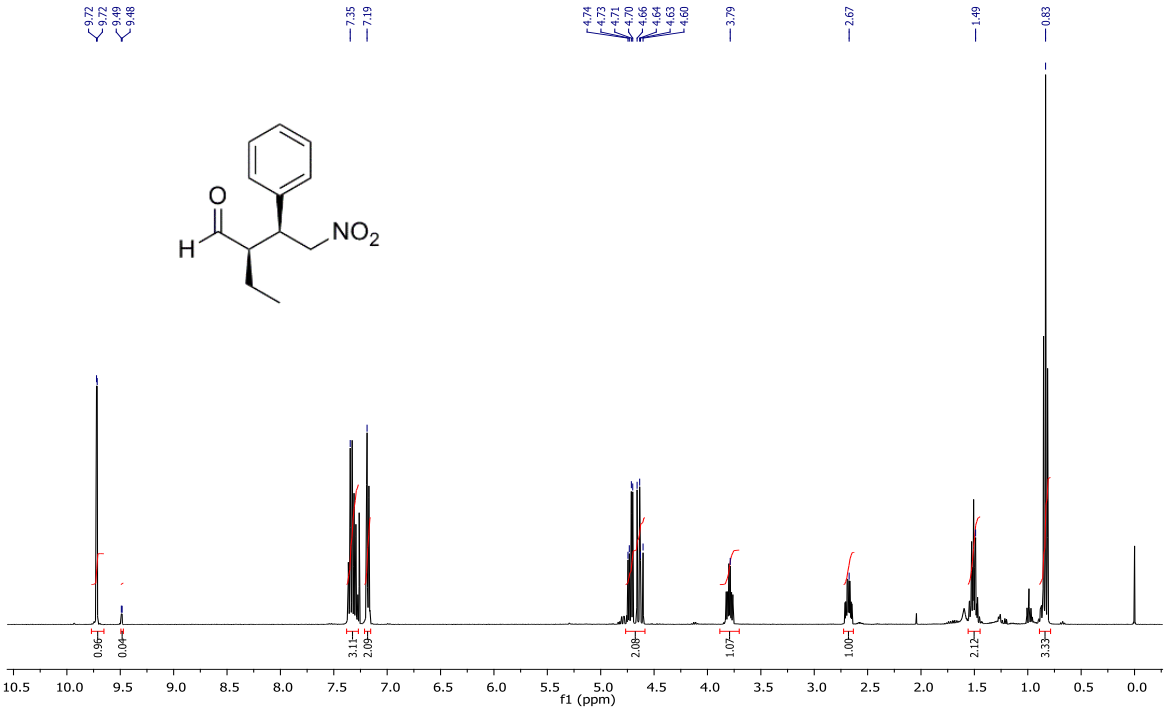


Figure S5: 400 MHz ^{1}H NMR spectrum in $CDCl_3$ of (2R,3S)-2-Ethyl-4-nitro-3-phenylbutanal (**5**).

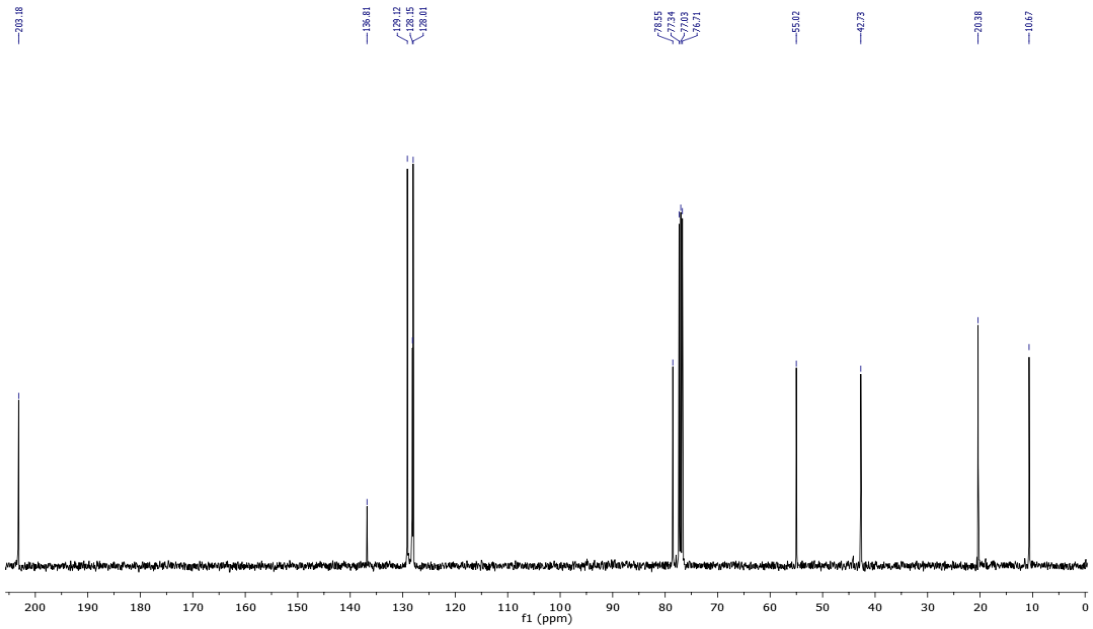


Figure S6: 100 MHz ^{13}C NMR spectrum in $CDCl_3$ of (2R,3S)-2-ethyl-4-nitro-3-phenylbutanal (**5**).

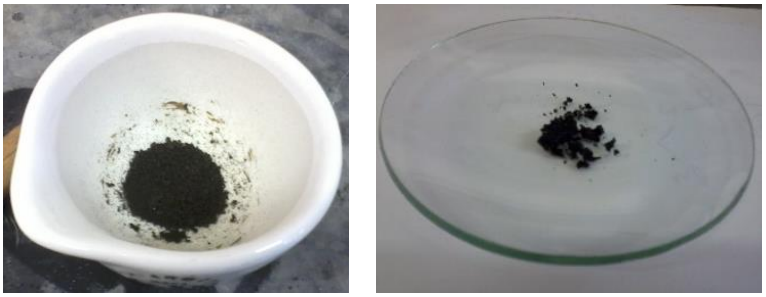


Figure S7: Photograph of PFA-supported catalysts material.

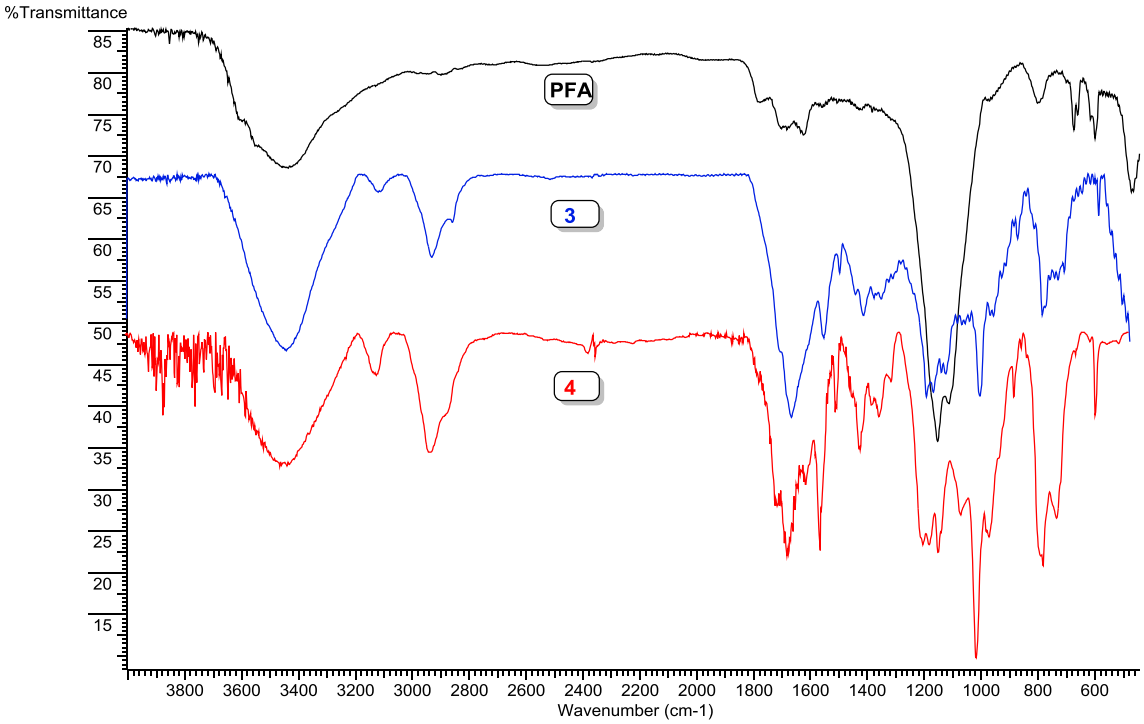


Figure S8: FT-IR spectra of polymers **PFA** (black), **3** (blue) and **4** (red) in the range of 4000–600 cm^{-1}.

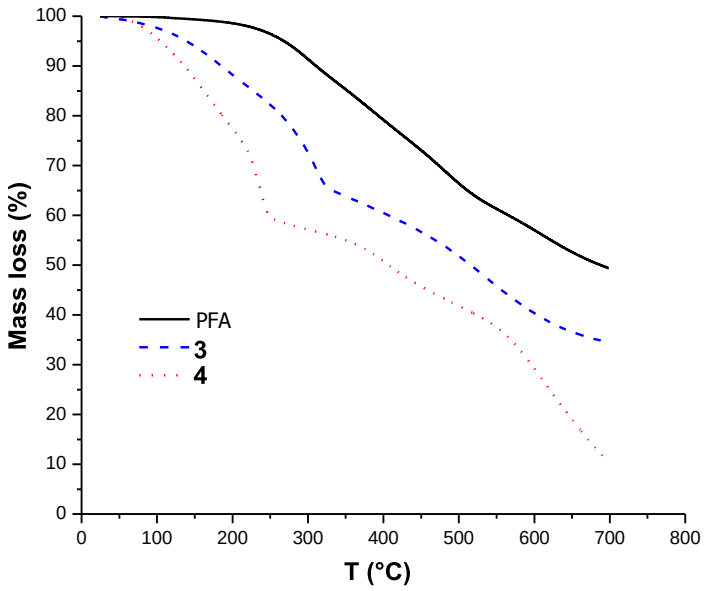
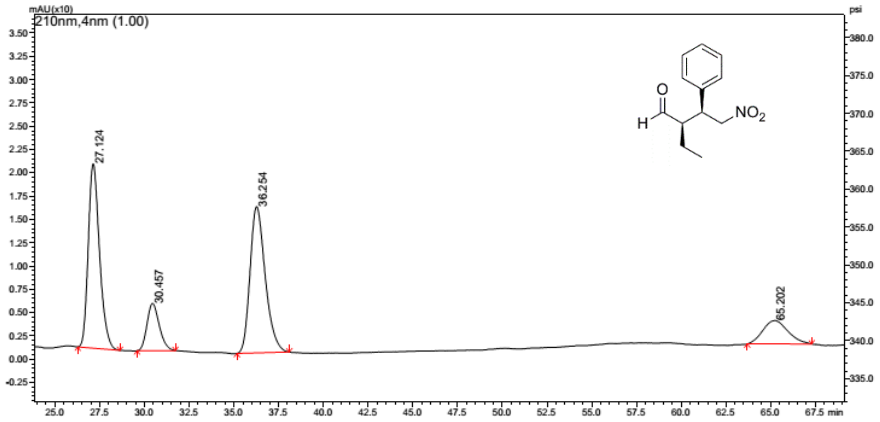


Figure S9: Variation of mass *versus* temperature measured by TGA for the **PFA**, **3** and **4** conducted under oxidative atmosphere at 10 °C min^{-1}.

Chiral HPLC results and spectra

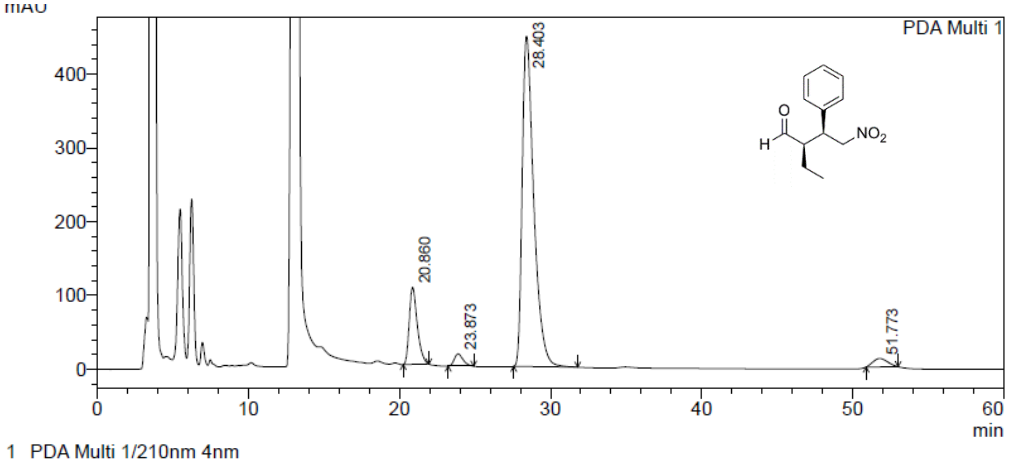


PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.124	867445	19800	37.957	45.951
2	30.457	242098	5070	10.593	11.767
3	36.254	931040	15712	40.739	36.463
4	65.202	244769	2508	10.710	5.819
Total		2285353	43090	100.000	100.000

Figure S10: Chiral HPLC of racemic 2-ethyl-4-nitro-3-phenylbutanal. Chiralpak OD-H (*n*-hexane/iPrOH 91:9), 25 °C at 0.9 ml min^{-1}, UV detection at 210 nm.



PeakTable

PDA Ch1 210nm 4nm

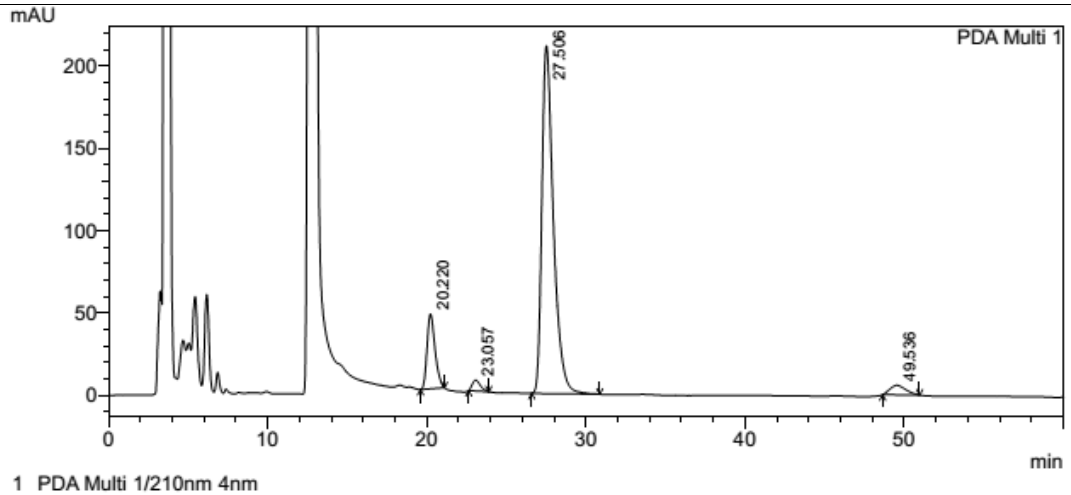
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.860	3875196	104361	13.278	17.997
2	23.873	674856	16601	2.312	2.863
3	28.403	23865884	447601	81.774	77.189
4	51.773	769271	11317	2.636	1.952
Total		29185207	579880	100.000	100.000

Figure S11: Chiral HPLC of the crude asymmetric 2-ethyl-4-nitro-3-phenylbutanal (**5**) obtained by bath reaction with PFA-supported catalyst **3**. Chiralpak OD-H (n-hexane/iPrOH 90:10), 25 °C) at 1.0 ml min^{-1}, UV detection at 210 nm of the crude reaction.

Table S1: Results of continuous flow Michael addition between *n*-butanal and β-nitrostyrene using the microreactor filled with PFA-supported catalyst **3**.

Entry [a]	Flow rate ϕ(μL min^{-1})	Running time (h)	Residence time τ(min)[b]	Conversion [c]	*dr*. (*syn:anti*) [e]	ee% [f]
1	2.5	0-10	-	-	-	-
2	2.5	10-12	140	25	95:5	74
3	2.5	12-14	140	27	95:5	75
4	2.5	14-16	140	30	95:5	74
5	2.5	16-18	140	31	95:5	73
6	2.5	18-20	140	38	95:5	74
7[d]	2.5	20-22	140	42	95:5	72
8	1	24-36	349	43	94:6	72
9	1	36-48	349	21	94:6	72
10	1	48-72	349	24	94:6	72

a) Reaction conditions: HPLC column (0.21 cm i.d. x 15 cm, containing 0.639 mmol of catalyst **3**); β-nitrostyrene (2.5 mmol, 1 equiv, 0.25 M), *n*-butanal (3 equiv, 0.75 M) in toluene. b) Residence time calculated as void volume/rate flow ($\tau = V_0/\phi$). c) Conversion determined by ^{1}H NMR spectroscopy. d) Productivities are measured in mmol product h^{-1} mmol $catalyst^{-1}$. e) dr determined by ^{1}H NMR spectroscopy. f) Determined by chiral-stationary phase HPLC analysis.

Entry	HPLCs of Table 1.
2	

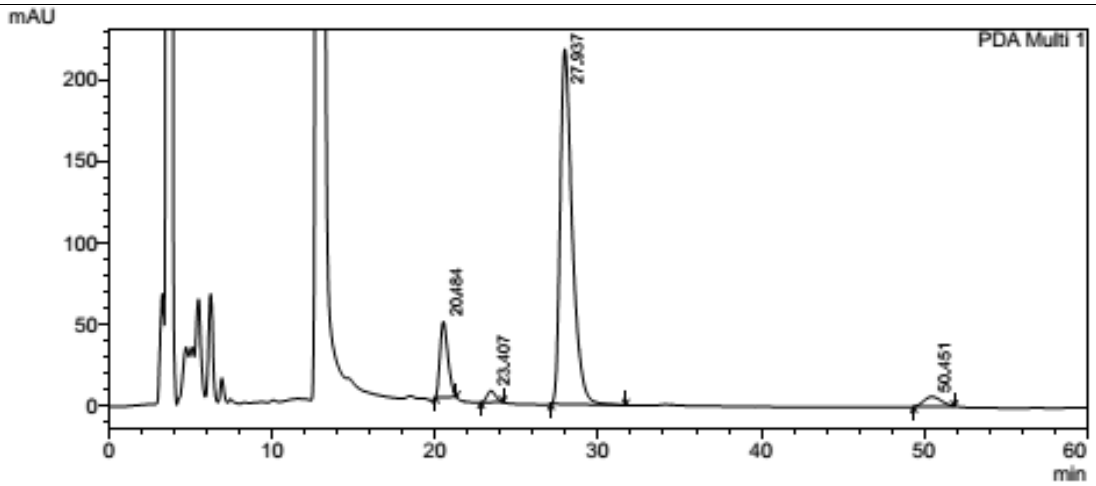
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.220	1587854	45517	12.317	16.913
2	23.057	229856	6527	1.783	2.425
3	27.506	10678706	211414	82.837	78.558
4	49.536	394748	5660	3.062	2.103
Total		12891163	269118	100.000	100.000

3



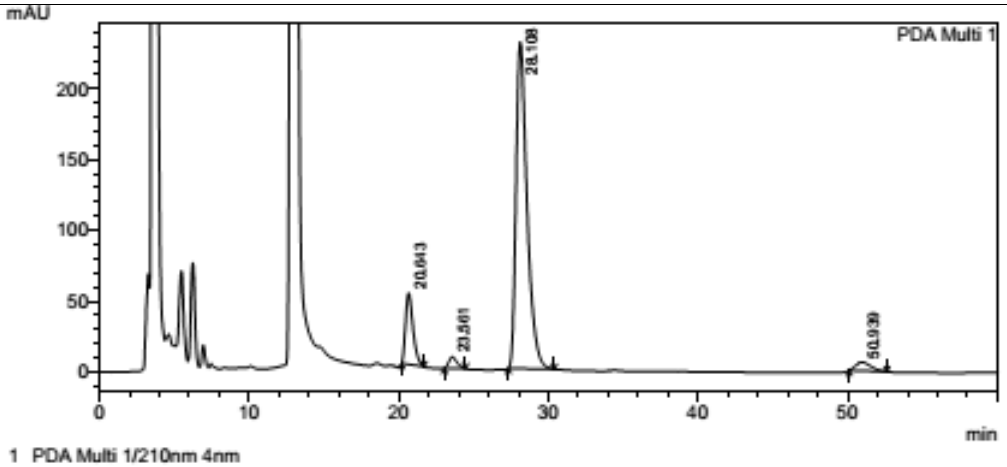
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.484	1557976	46209	11.639	16.702
2	23.407	260434	7046	1.946	2.547
3	27.937	11116474	217305	83.047	78.543
4	50.451	450875	6108	3.368	2.208
Total		13385758	276669	100.000	100.000

4



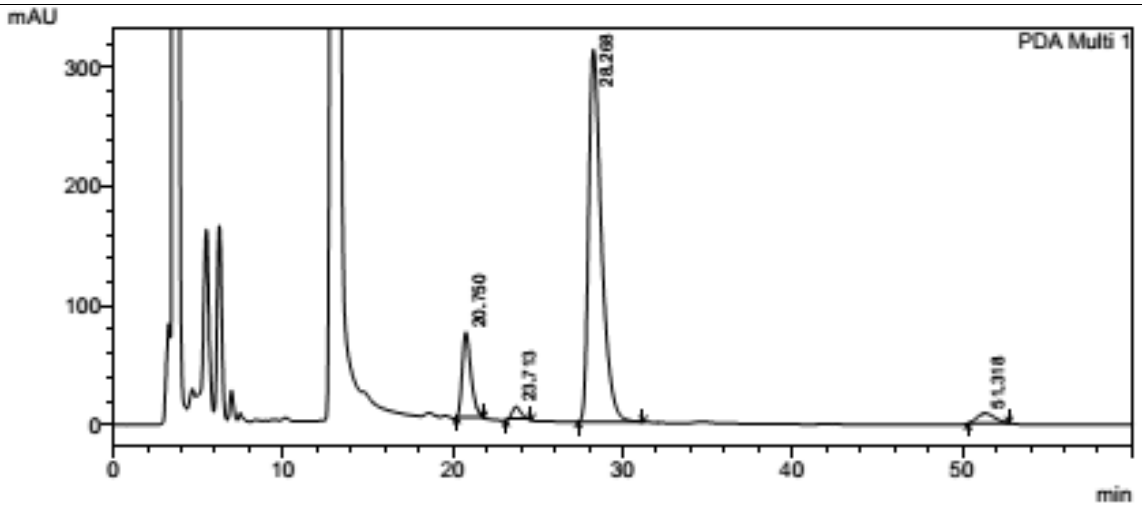
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.643	1759063	50465	12.300	17.081
2	23.561	304022	7992	2.126	2.705
3	28.108	11808725	230951	82.570	78.168
4	50.939	429640	6046	3.004	2.046
Total		14301450	295454	100.000	100.000

5



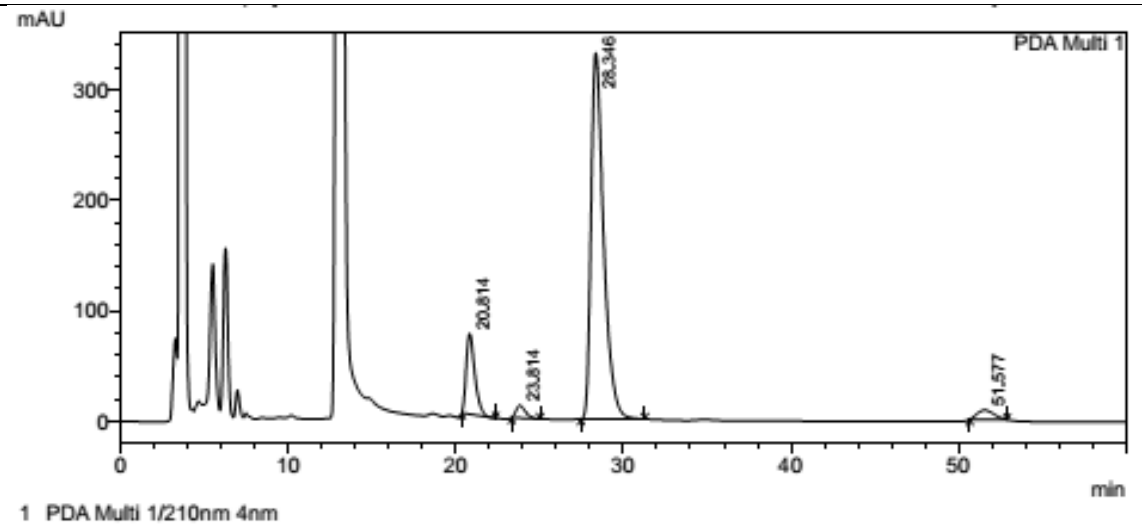
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.750	2558251	71344	12.801	17.688
2	23.713	430531	11138	2.154	2.761
3	28.268	16396233	312604	82.044	77.501
4	51.318	599641	8266	3.001	2.049
Total		19984657	403353	100.000	100.000

6



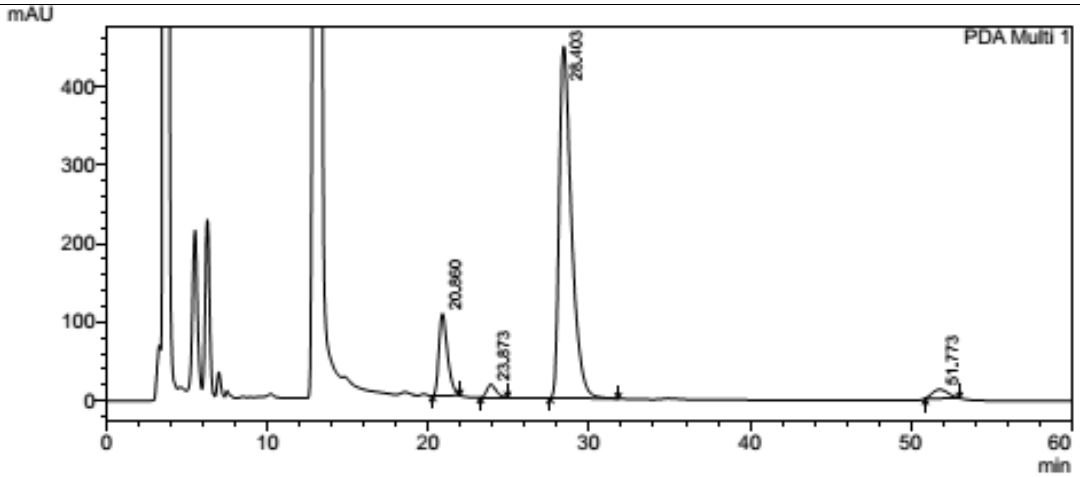
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.814	2609783	72871	12.500	17.194
2	23.814	445781	11406	2.135	2.691
3	28.346	17230466	330988	82.526	78.095
4	51.577	592685	8561	2.839	2.020
Total		20878715	423826	100.000	100.000

7



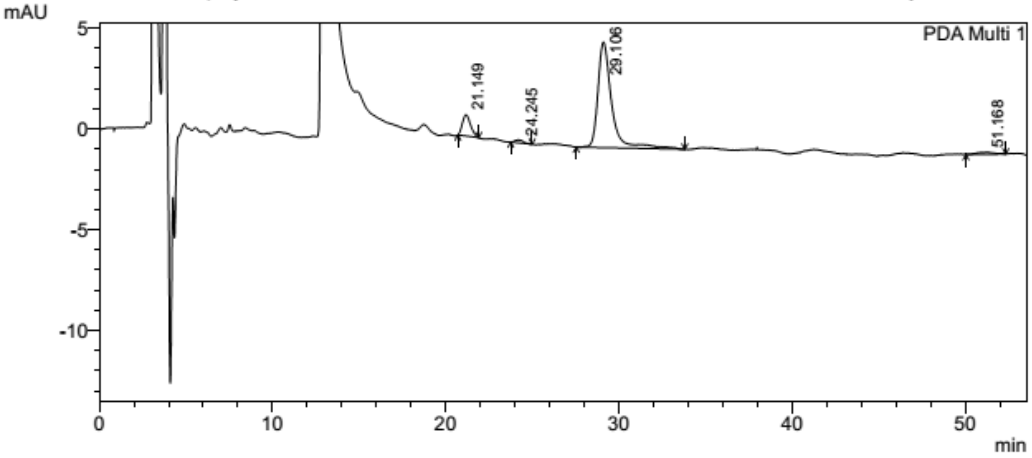
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.860	3875196	104361	13.278	17.997
2	23.873	674856	16601	2.312	2.863
3	28.403	23865884	447601	81.774	77.189
4	51.773	769271	11317	2.636	1.952
Total		29185207	579880	100.000	100.000

8



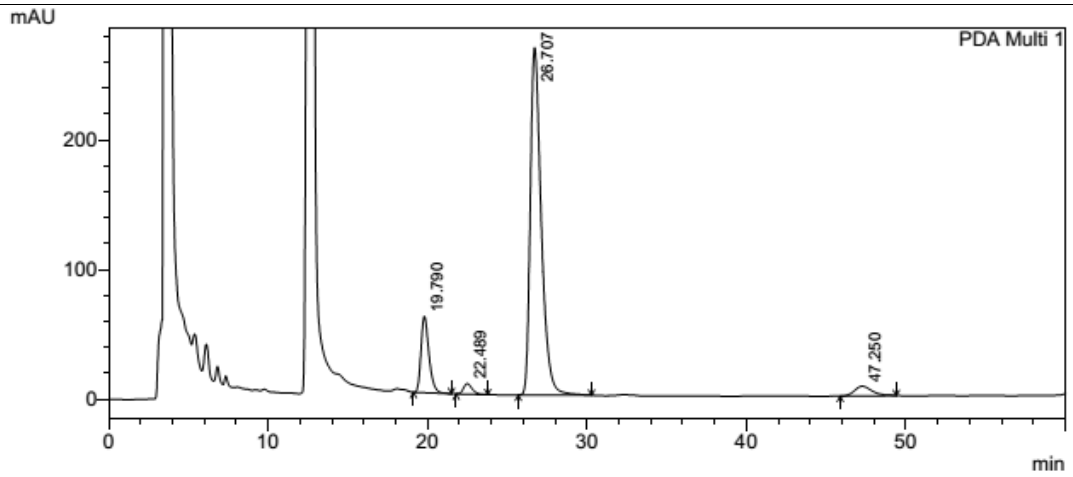
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.149	34196	1054	10.236	16.098
2	24.245	4504	148	1.348	2.267
3	29.106	288448	5240	86.342	80.030
4	51.168	6929	105	2.074	1.606
Total		334078	6547	100.000	100.000

9



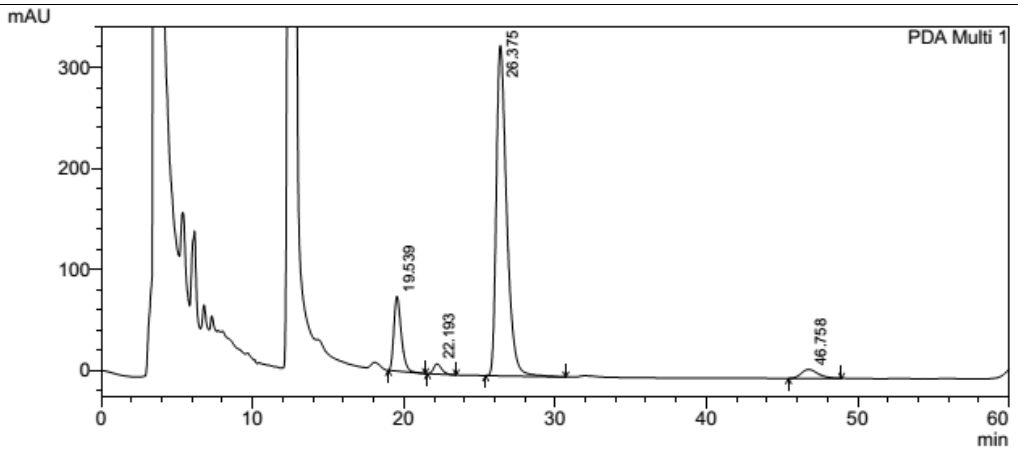
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.790	2045275	58935	13.030	17.215
2	22.489	308886	8179	1.968	2.389
3	26.707	12772745	267759	81.372	78.214
4	47.250	569814	7469	3.630	2.182
Total		15696720	342341	100.000	100.000

10



1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.539	2514588	73878	13.158	17.609
2	22.193	373640	10131	1.955	2.415
3	26.375	15533770	326639	81.282	77.855
4	46.758	688913	8902	3.605	2.122
Total		19110912	419550	100.000	100.000

Figure S12: Different examples of chiral HPLC analysis of the crude asymmetric 2-ethyl-4-nitro-3-phenylbutanal (**5**) obtained by continuous flow Michael addition reaction with PFA-supported catalyst **3 (**Table S1). Chiralpak OD-H (*n*-hexane/iPrOH 90:10), 25 °C, 1.0 ml min^{-1}, UV detection at 210 nm of the crude reaction.