Electronic supplementary Information (ESI)

Conformationally Restricted Dynamic Supramolecular Catalysts for Substrate-Selective Epoxidations

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Chromatograms and spectra and for the analysis of the competitive reactions

GC calibration curves

$$y = 0.9388x + 0.0022$$
$$R^2 = 0.99933$$

Fig. S1 GC-calibration curve for substrate **28b**.

$$y = 1.5046x - 0.0933$$
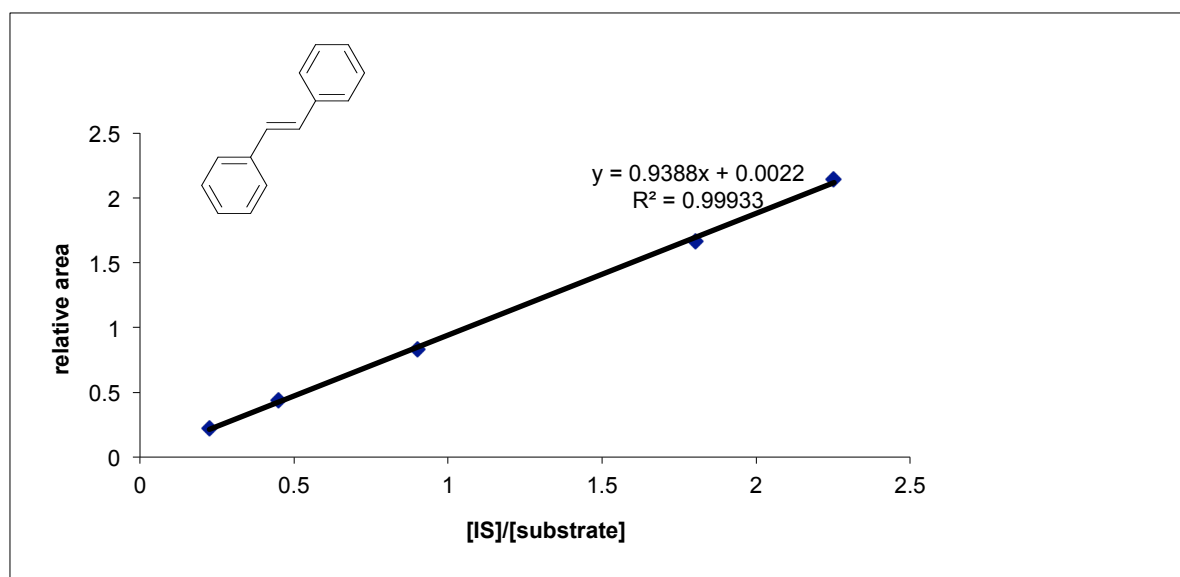$$R^2 = 0.99856$$

Fig. S2 GC-calibration curve for substrate **27b**.

Fig. S3 GC-calibration curve for substrate **26b**.

Fig. S4 GC-calibration curve for substrate **4a**.

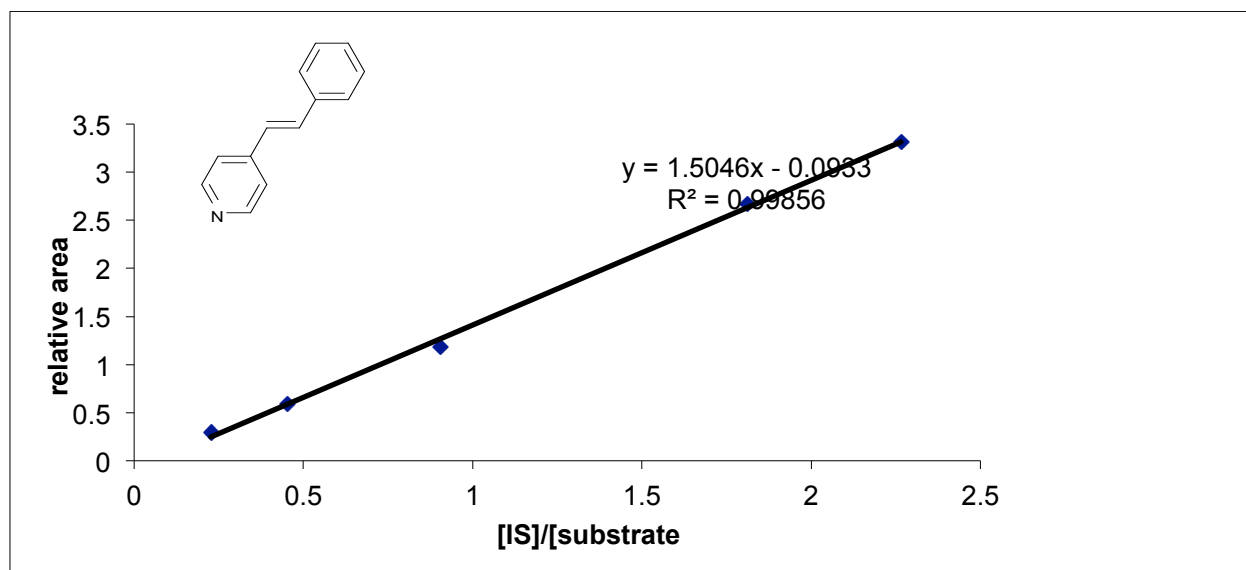**Fig. S5** GC-calibration curve for substrate **5a**.
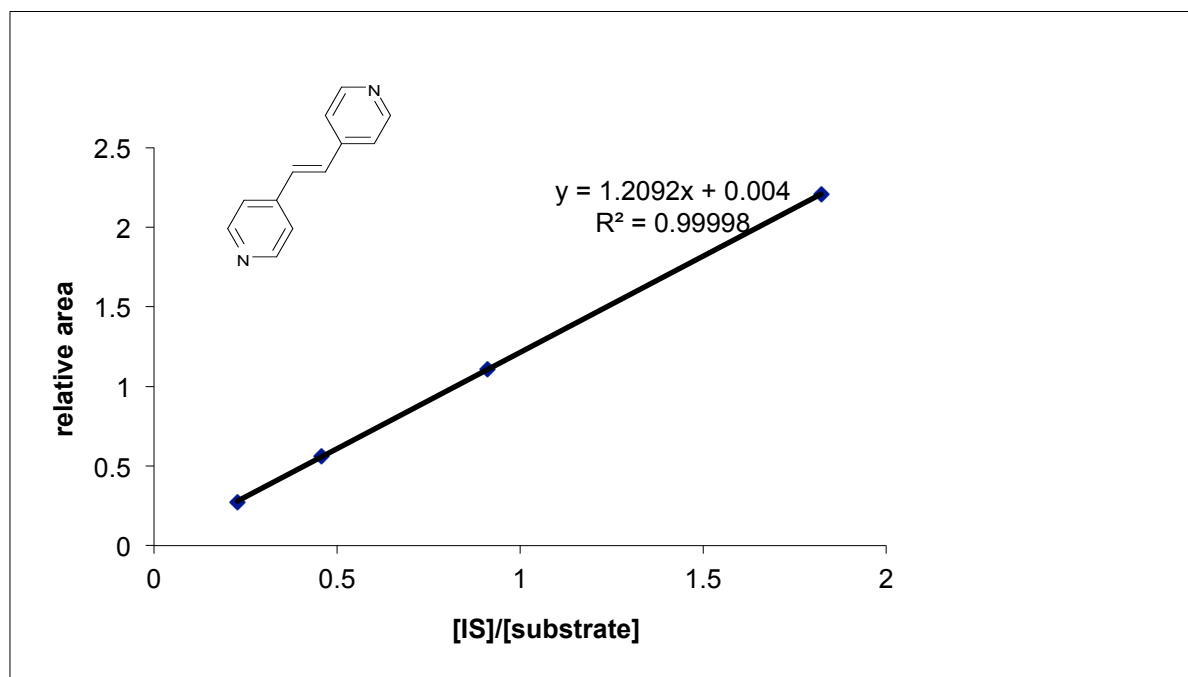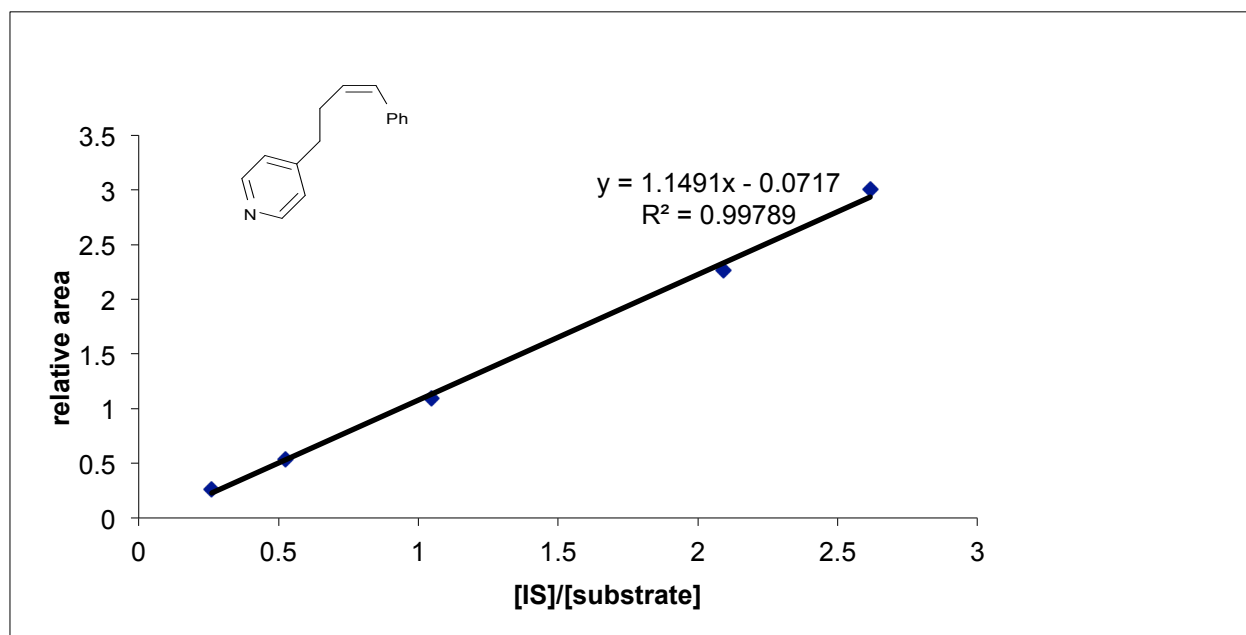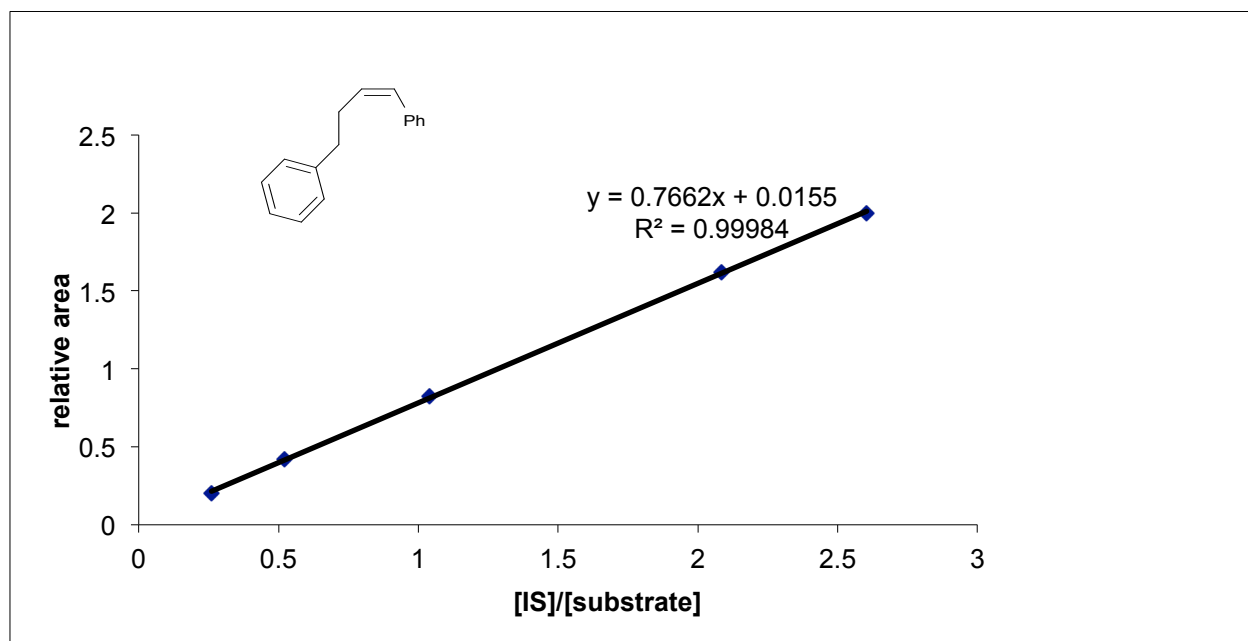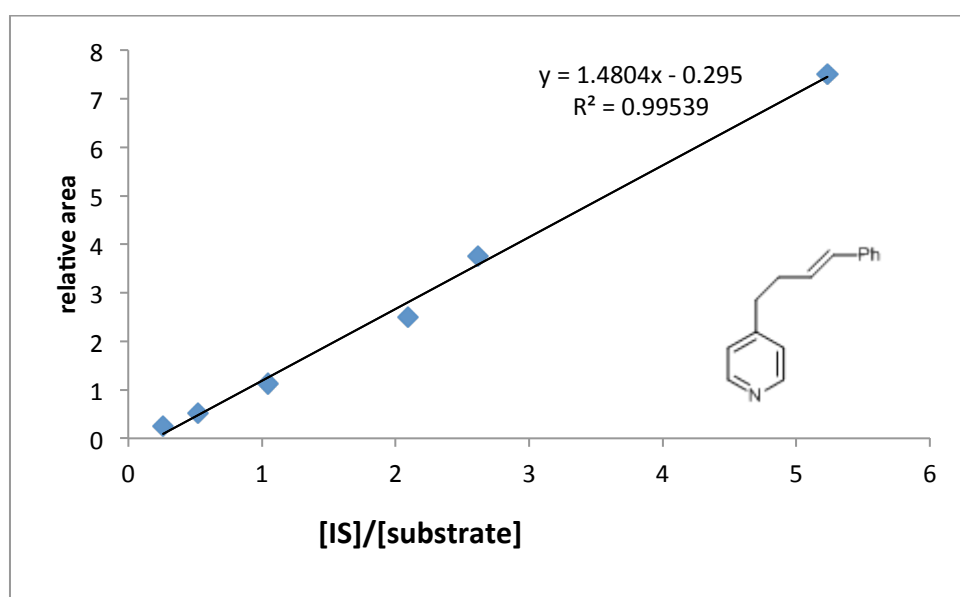

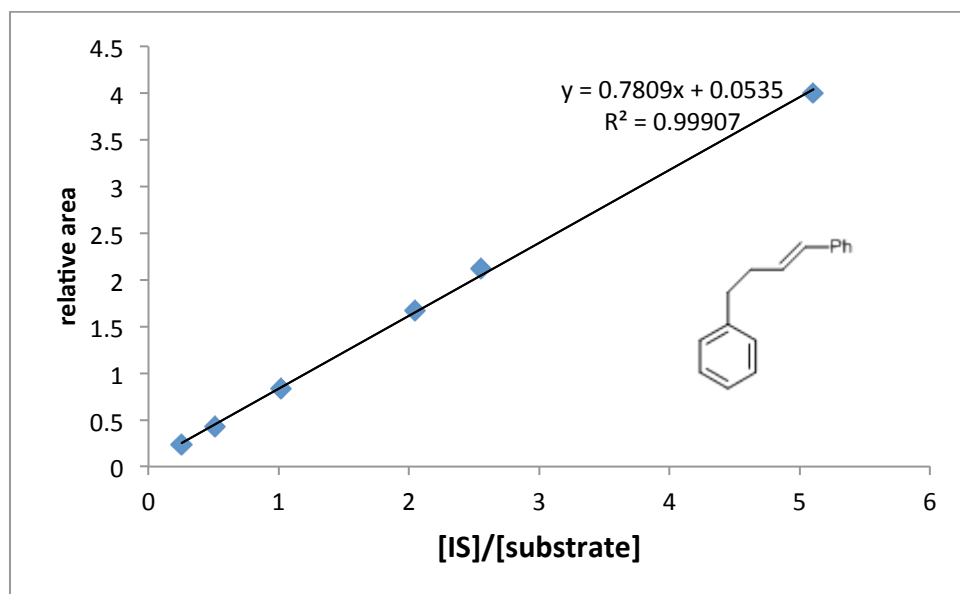**Fig. S6** GC-calibration curve for substrate **4b**.

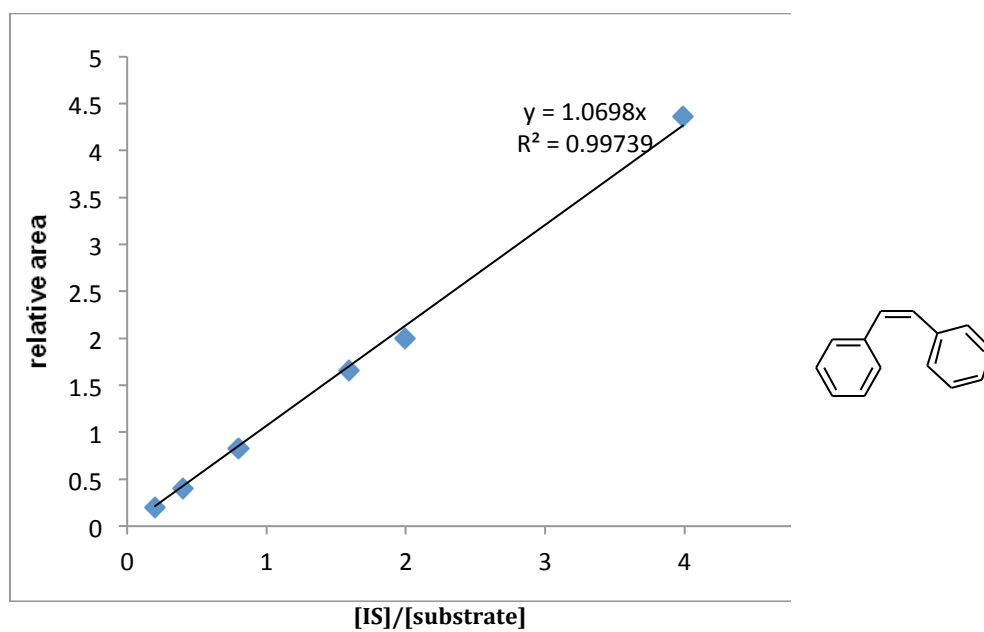**Fig. S7** GC-calibration curve for substrate **5b**.

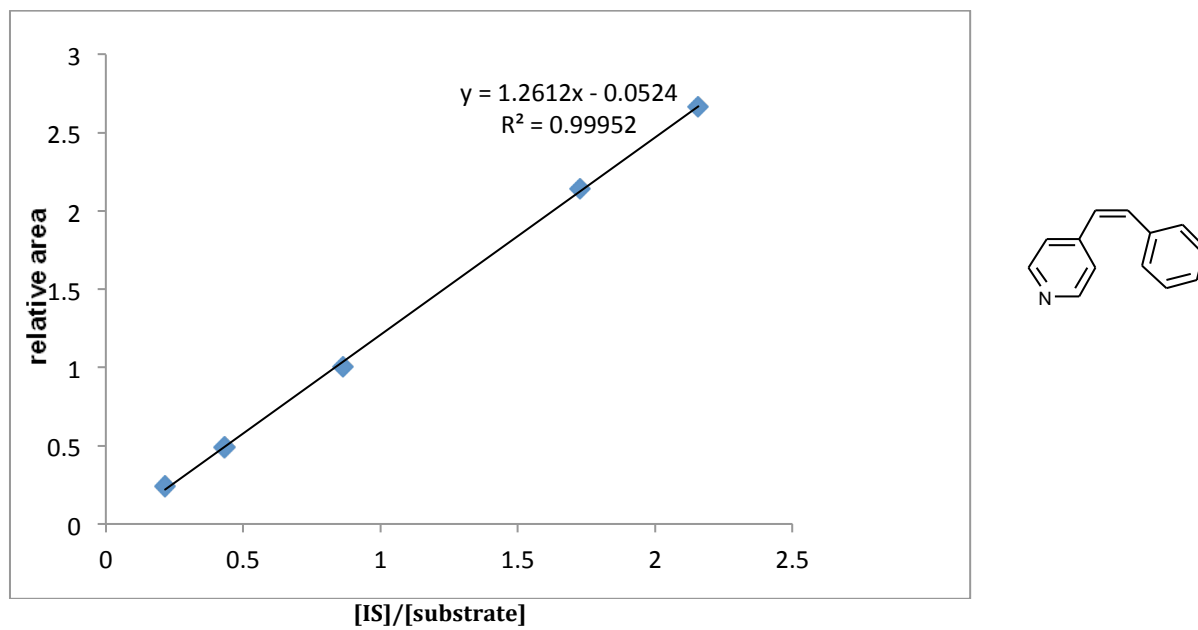**Fig. S8** GC-calibration curve for substrate **28a**.

Fig. S9 GC-calibration curve for substrate **27a**.

Examples of chromatograms and spectra used to analyse the substrate selectivity

Catalytic system **9** (5 mM) + **2** (15 mM)

Competitive epoxidation: **4b:5b**

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	1.845	1496258.63	988040.49	99.65	99.65	BB	1.5144
2	13.166	2363.05	756.22	0.16	0.16	BB	3.1248
3	13.375	1210.06	367.68	0.08	0.08	BB	3.2910
4	15.856	1419.58	330.23	0.09	0.09	BV	4.2987
5	16.116	273.58	80.58	0.02	0.02	VB	3.3950
		1501524.89	989575.21	100.00	100.00		

Fig. S10 GC chromatogram for the analysis of substrate selectivity in the competitive epoxidation **4b** *vs*. **5b** using system **9** (5 mM) + **2** (15 mM) in CH_2Cl_2.

Fig. S11 ^{1}H NMR (400 MHz, CDCl$_3$): Reference sample containing **4b**:**5b** (1:1).

Catalytic system 9 (5 mM) + 2 (15 mM)

Competitive epoxidation: 4b:5b

Fig. S12 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum for the analysis of substrate selectivity in the competitive expoxidation **4b** *vs.* **5b** using system **9** (5 mM) + **2** (15 mM) in CH$_2$Cl$_2$ as catalyst.

Fig. S13 GC-chromatogram for the analysis of substrate selectivity in the competitive expoxidation **26b** *vs.* **28b** using system **9** (5 mM) + **2** (15 mM) in CH_2Cl_2.
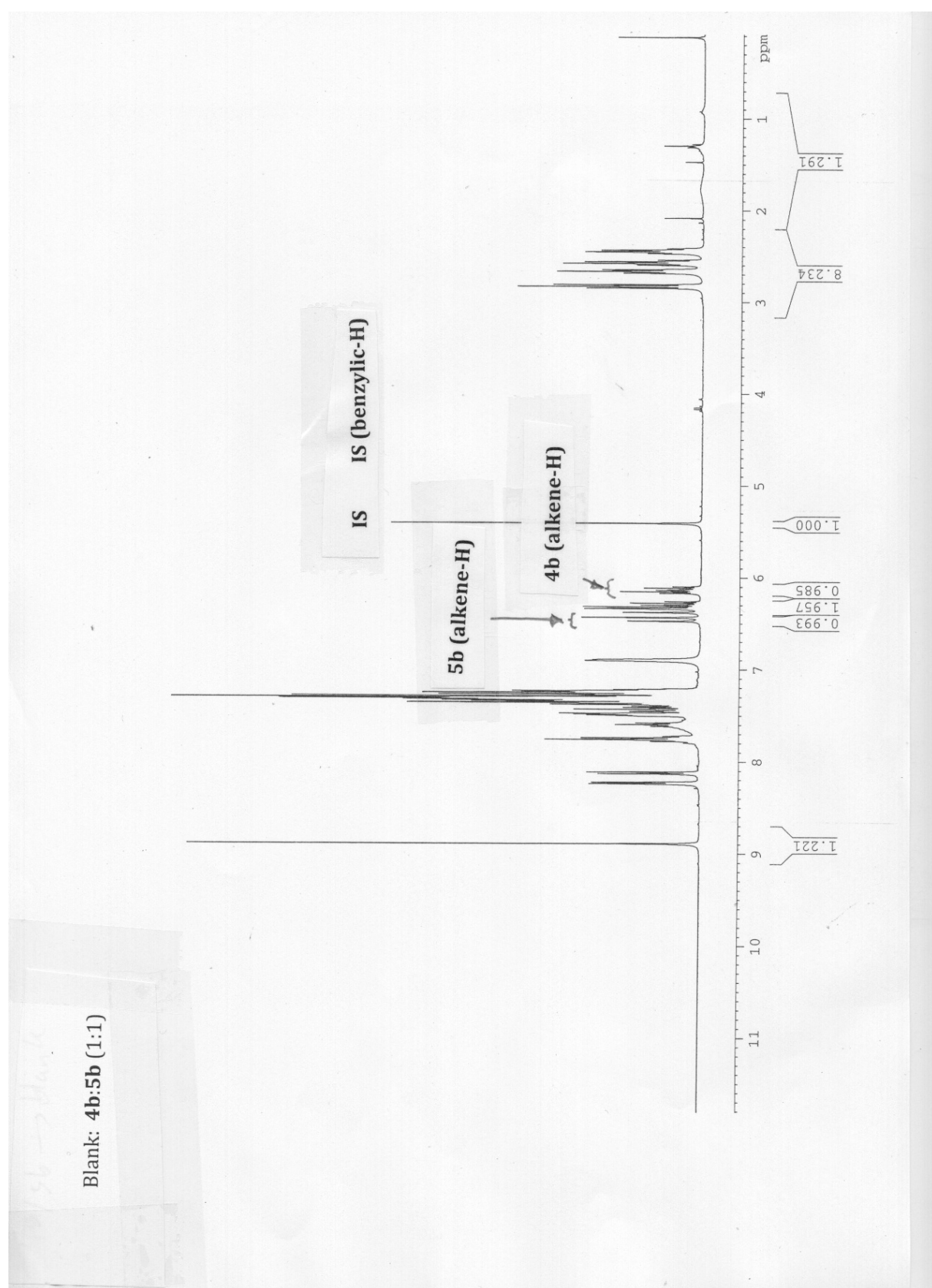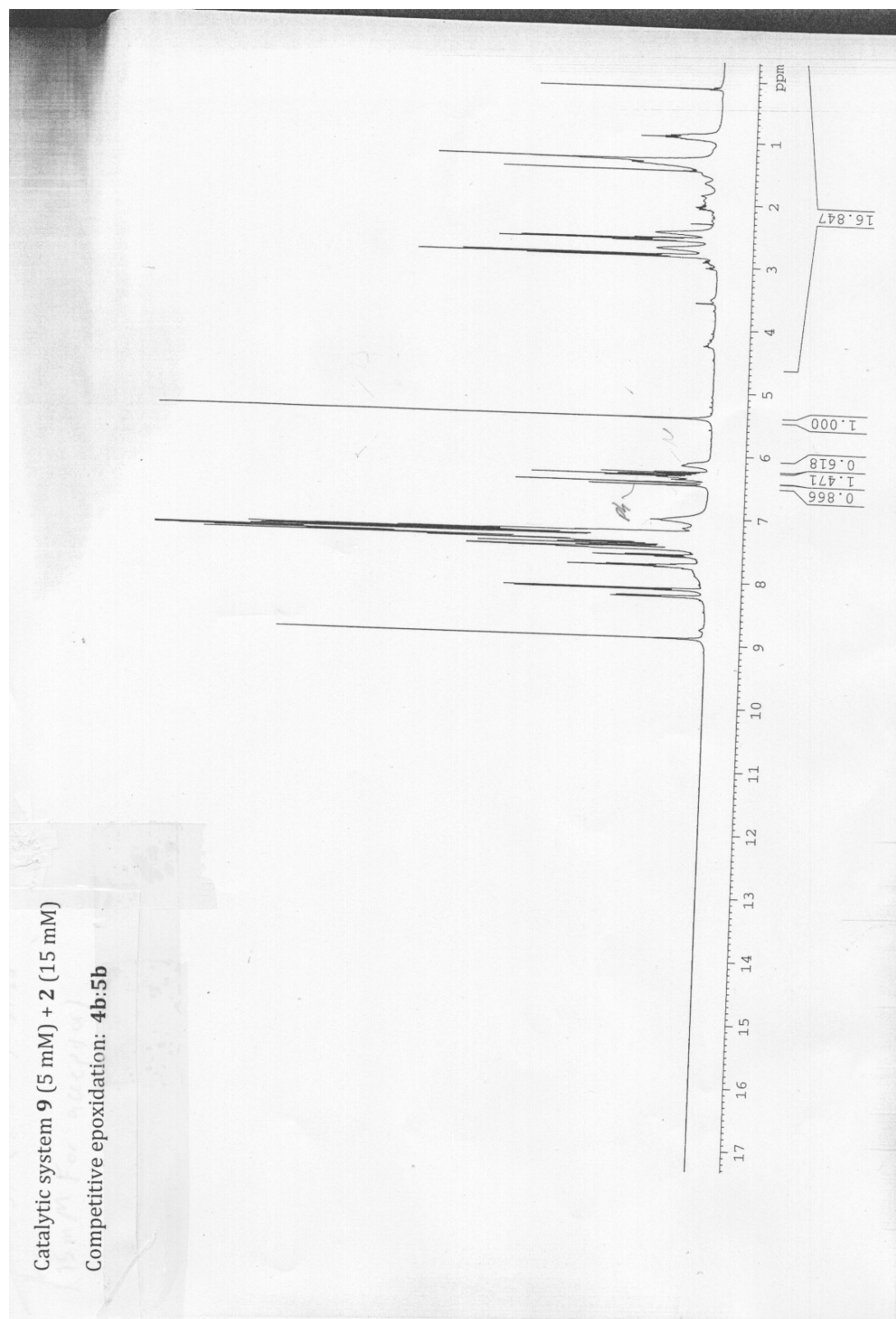
Fig. S14 ^{1}H NMR (400 MHz, CDCl$_3$): Reference sample containing **26b**:**28b** (1:1).

Fig. S15 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum for the analysis of substrate selectivity in the competitive expoxidation **26b** *vs*. **28b** using system **9** (5 mM) + **2** (15 mM) in CH$_2$Cl$_2$ as catalyst.
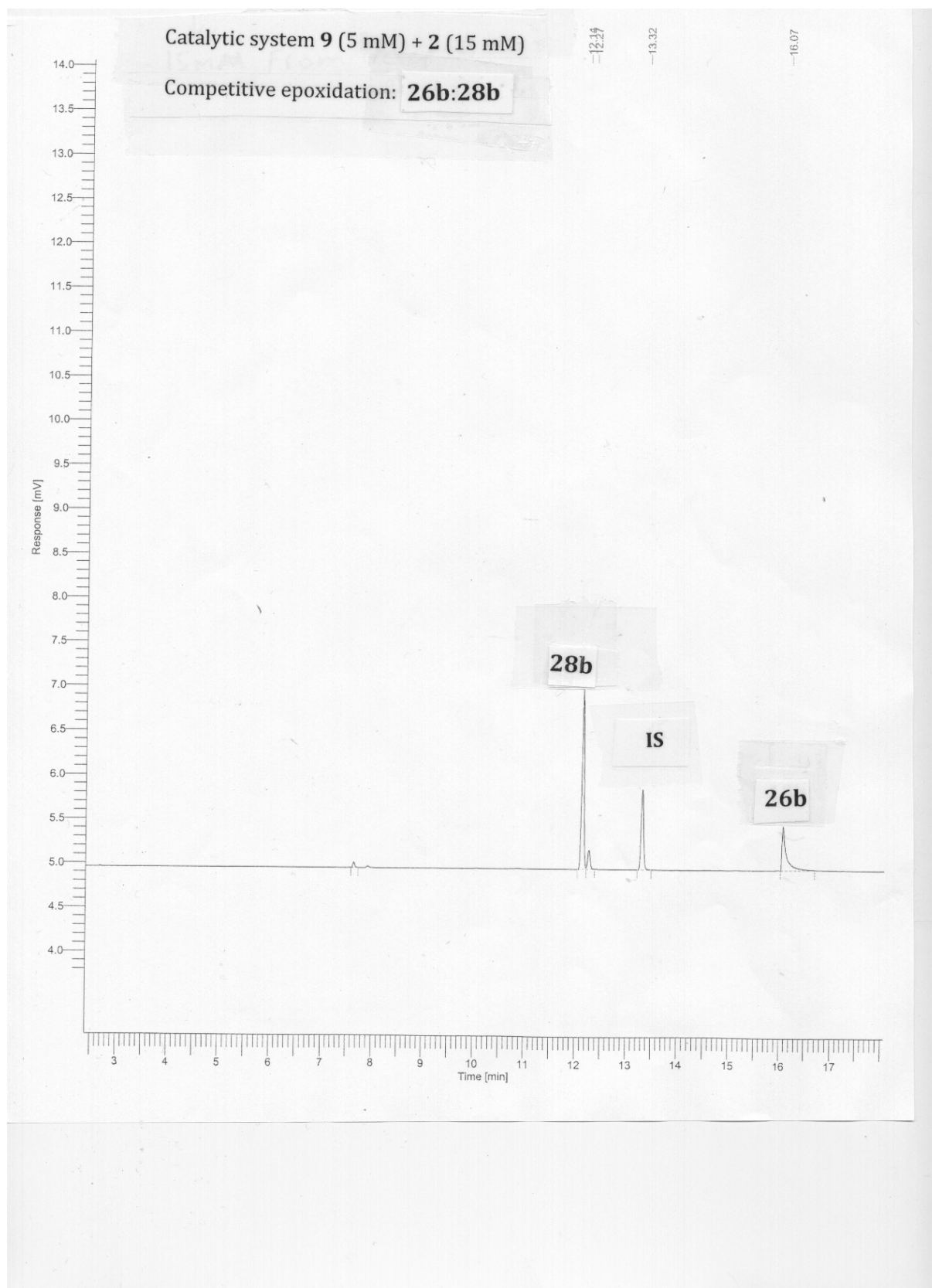
Catalytic system **9** (5 mM) + **2** (5 mM)

Competitive epoxidation: **27a:28a**

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	1.847	1444188.43	986624.13	99.77	99.77	BB	1.4638
2	7.944	1345.18	514.77	0.09	0.09	BB	2.6132
3	9.534	187.57	58.87	0.01	0.01	BB	3.1861
4	9.953	912.89	144.17	0.06	0.06	MM	6.3321
5	13.325	852.04	229.84	0.06	0.06	BB	3.7070
		1447486.11	987571.78	100.00	100.00		

Fig. S16 GC-chromatogram for the analysis of substrate selectivity in the competitive epoxidation **27a** *vs.* **28a** using system **9** (5 mM) + **2** (5 mM) in CH$_2$Cl$_2$.
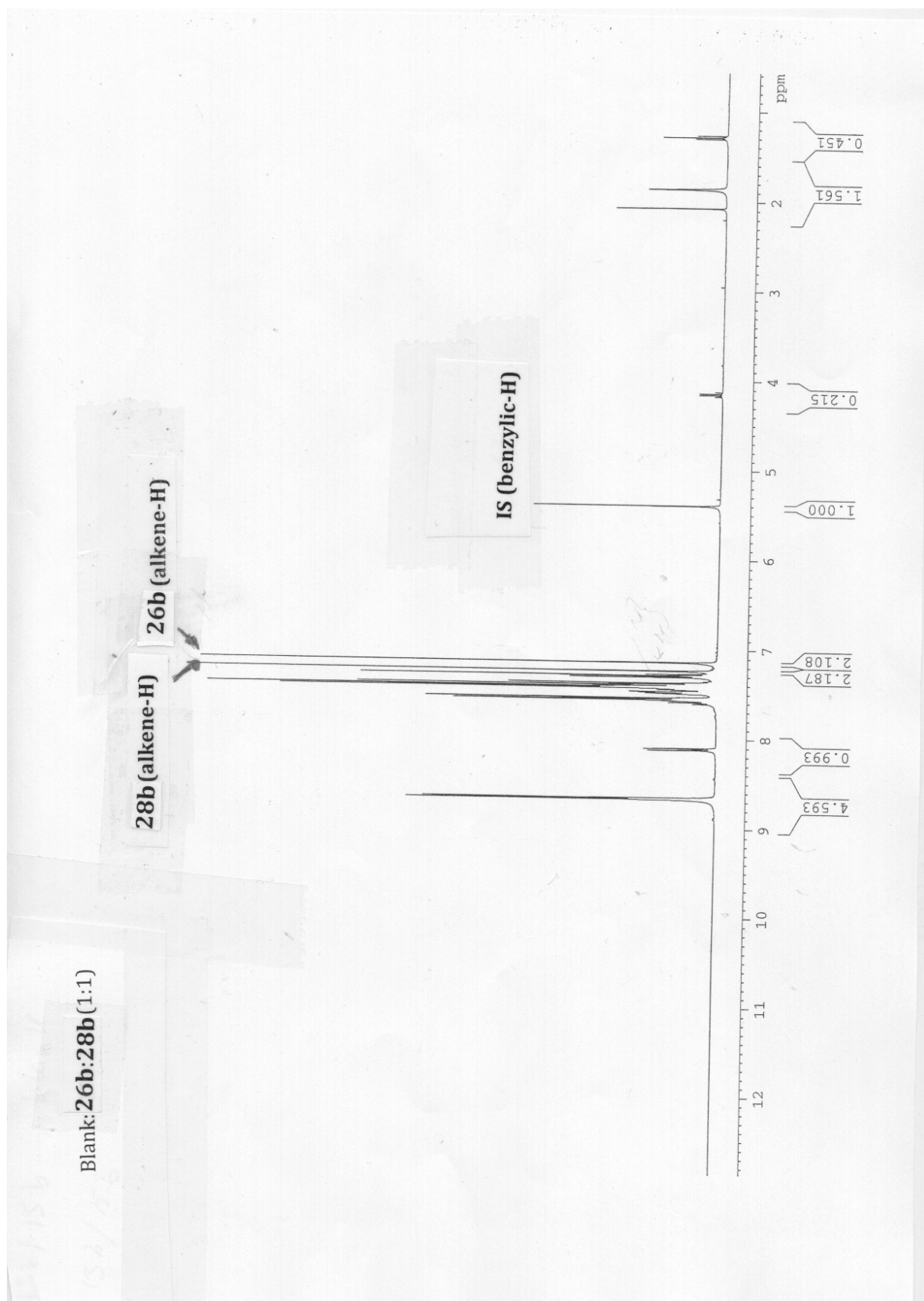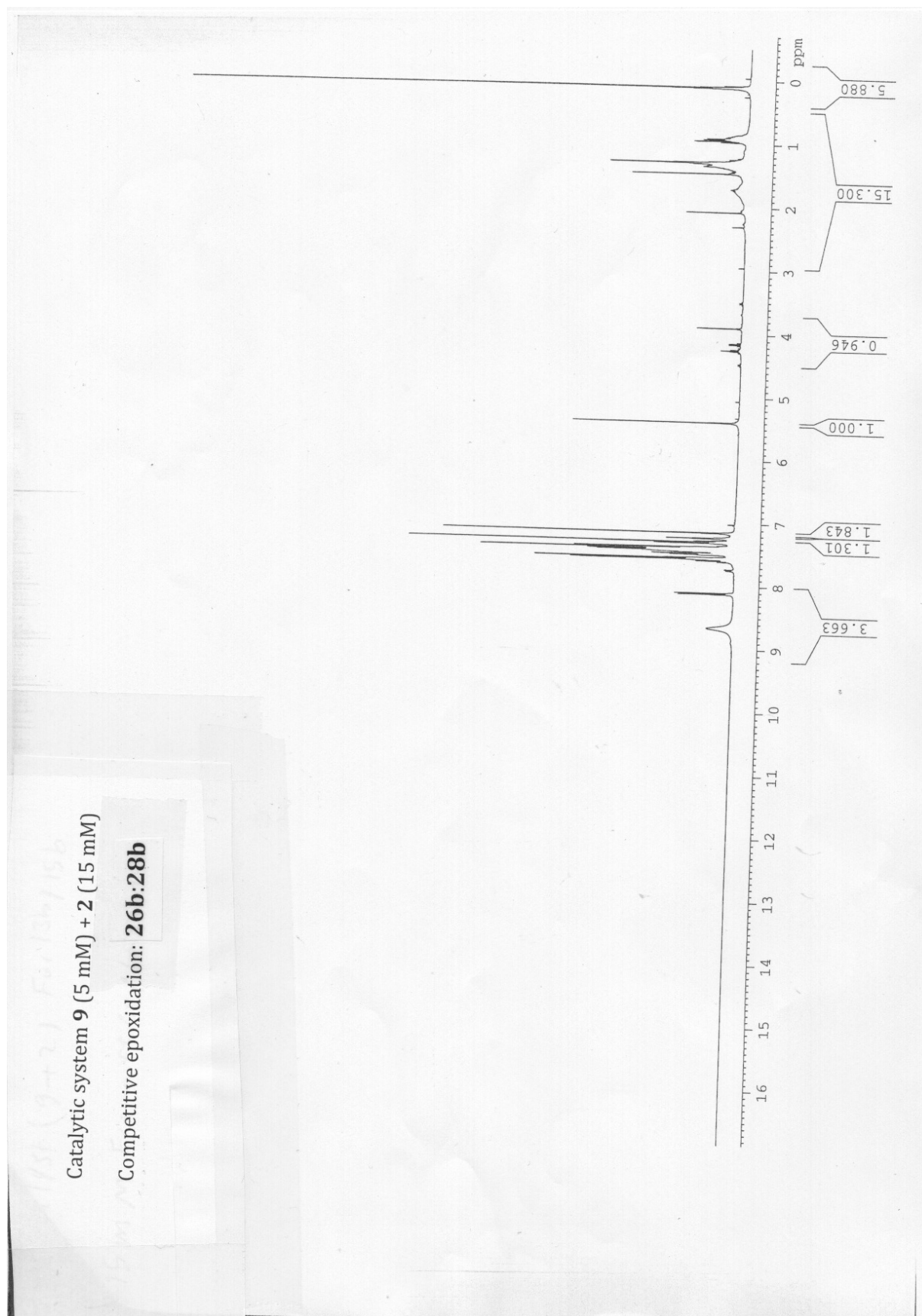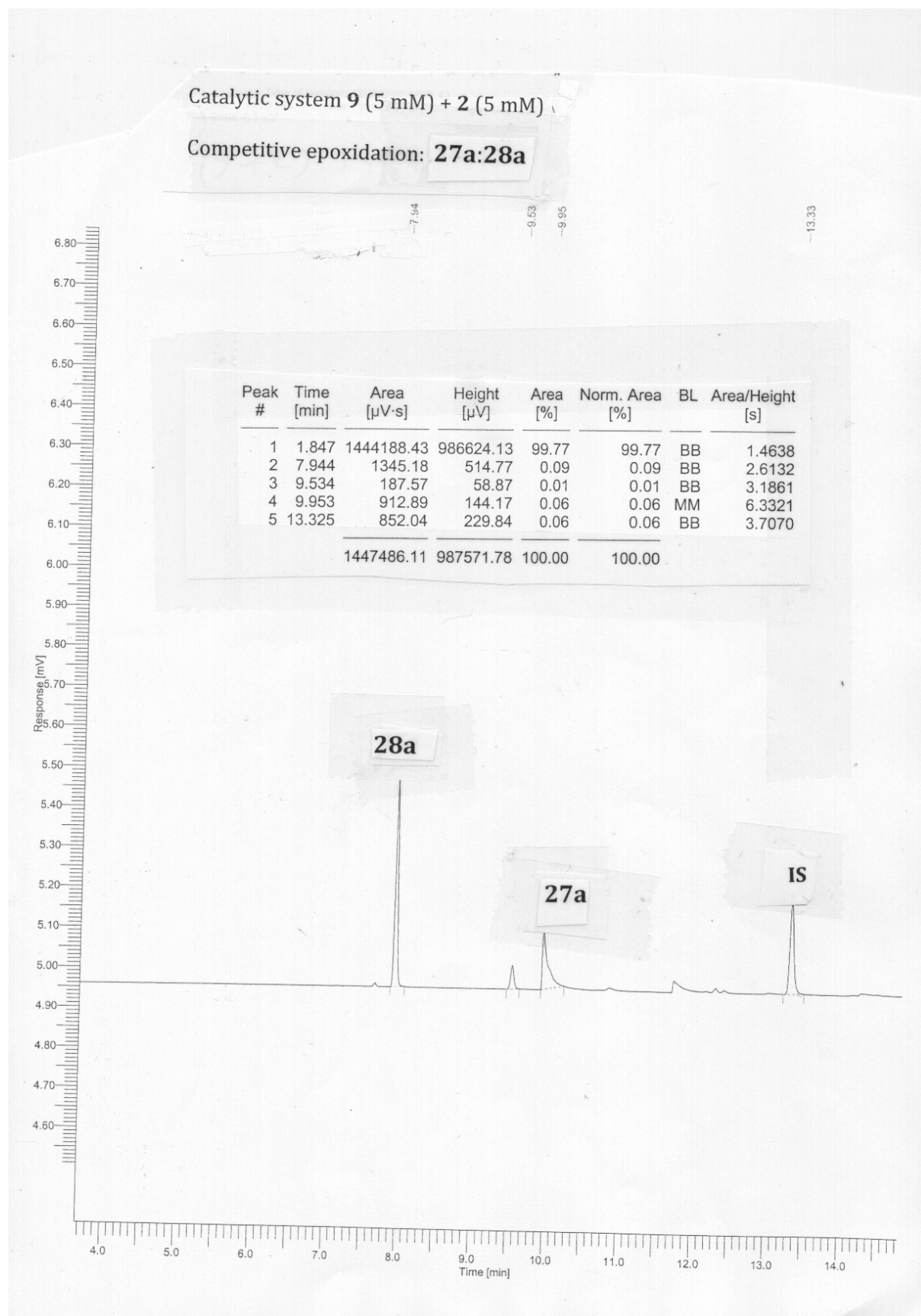
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Fig. S17 ^{1}H NMR (400 MHz, CDCl$_3$): Reference sample containing **27a**:**28a** (1:1).

Fig. S18 [^1]H NMR (400 MHz, CDCl₃) spectrum for the analysis of substrate selectivity in the competitive epoxidation **27a** *vs.* **28a** using system **9** (5 mM) + **2** (5 mM) in CH₂Cl₂ as catalyst.

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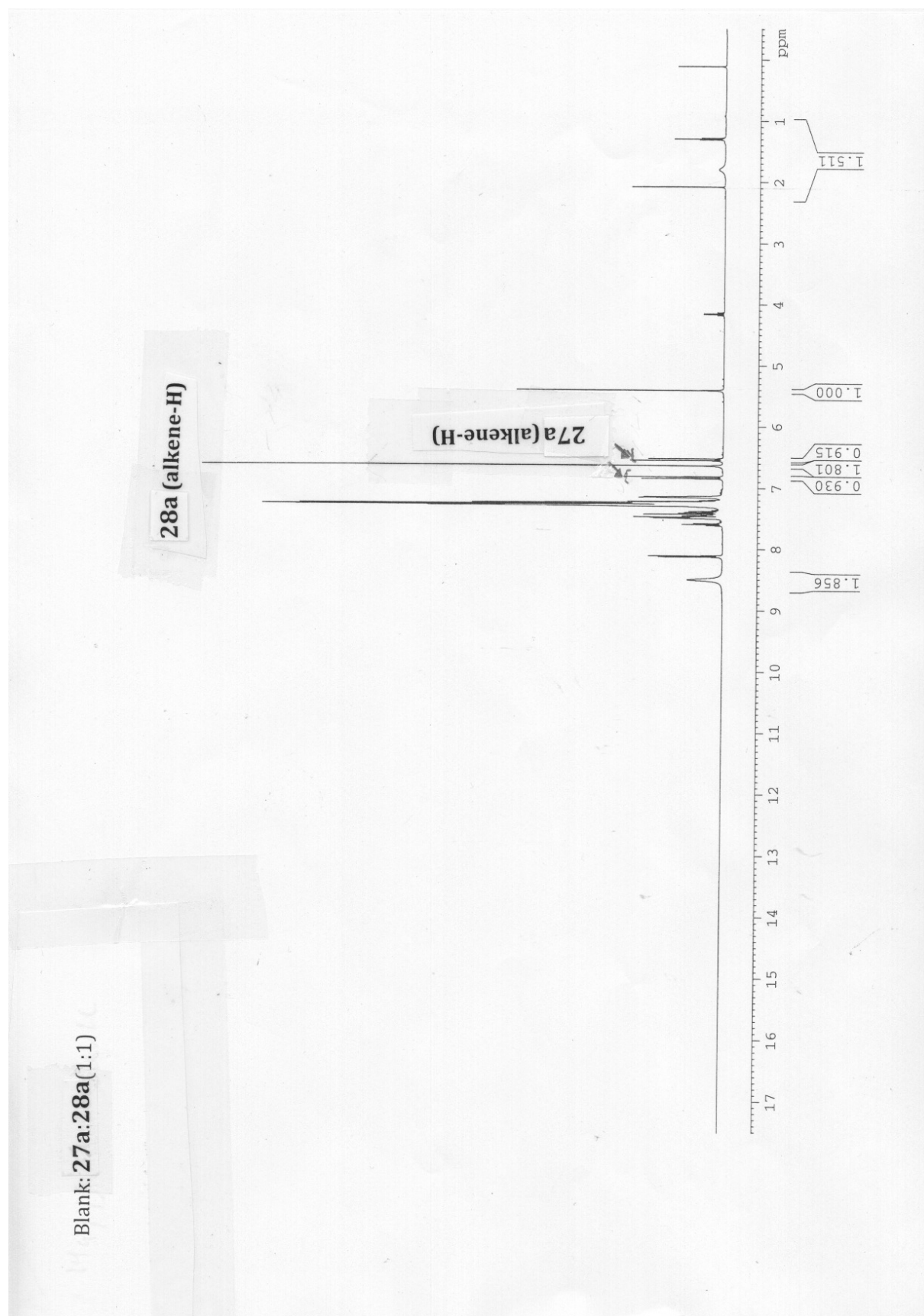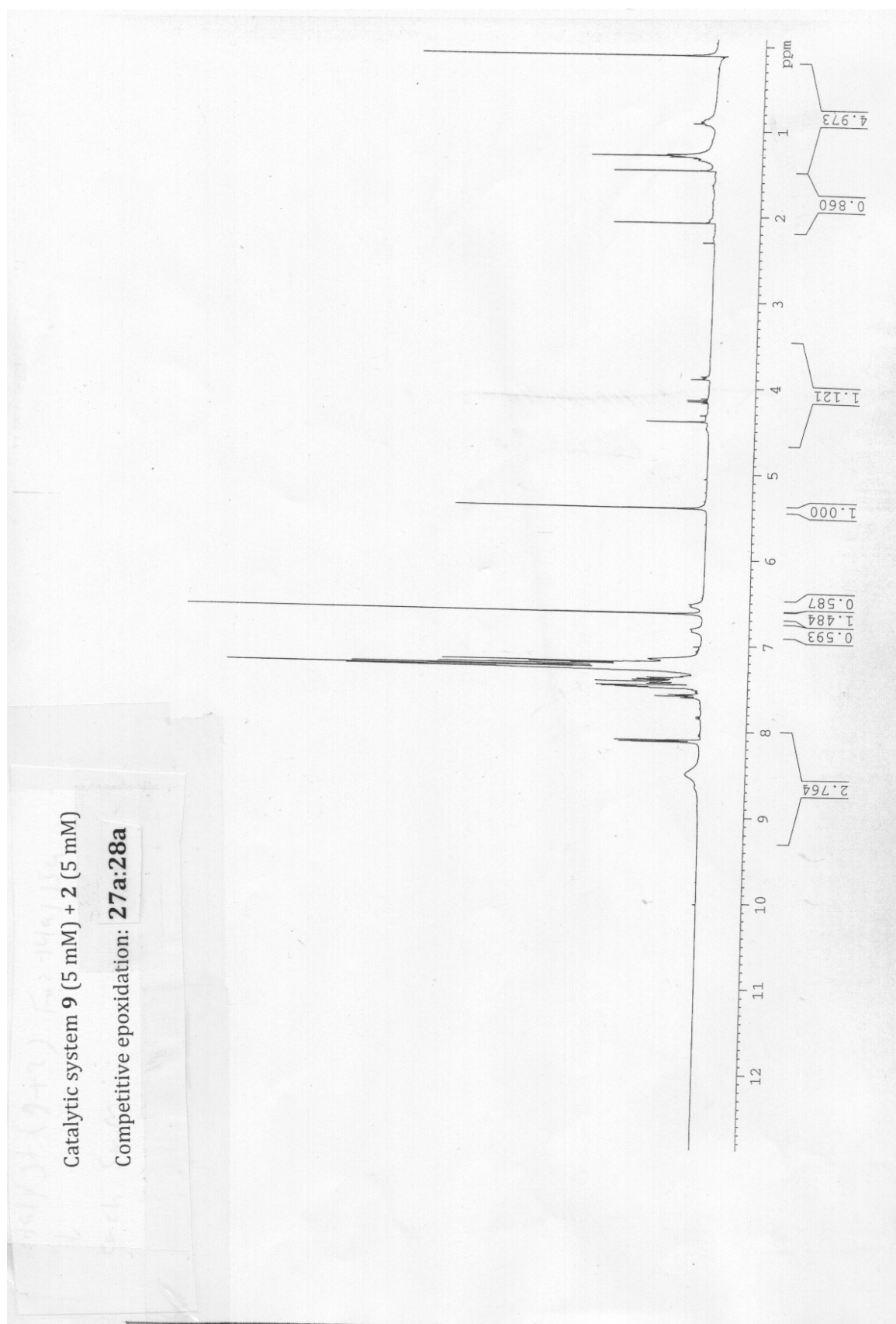
Table S1 The selectivity in the epoxidation of the styrene analogues catalysed by the different supramolecular systems.[a]

Entry	Cat. system (mM)	Selectivity by GC[b]/NMR[b] 4a:5a		4b:5b	
1	**1** (5) + **2** (5)	1.55	1.43	1.52	1.50
2	**1** (5) + **2** (15)	1.69	1.64	1.70	1.60
3	**1** (0.5) + **2** (0.5)	1.30	1.32	1.32	1.29
4	**8** (5) + **2** (5)	1.66	1.65	1.86	1.89
5	**8** (5) + **2** (15)	1.82	1.76	2.68	2.75
6	**9** (5) + **2** (5)	1.80	1.73	1.95	2.06
7	**9** (5) + **2** (15)	1.93	1.86	2.97	2.92
8	**9** (0.5) + **2** (0.5)	1.42	1.38	1.75	1.77
9	**9** (5) + ZnTPP (5)	0.99	1.08	1.02	1.06
10[c]	**9** (5) + **2** (5)	1.02	1.04	1.08	1.06
11[d]	**9** (5) + **2** (5)	1.34	1.28	1.73	1.75
12	**12** (5)	1.15	1.13	1.15	1.22
13	**12** (15)	1.24	1.23	1.30	1.34

[a] General procedure: catalyst part **1**, or **8**, or **9** (3 µmol each), receptor part **2** (3 or 9 µmol each), substrate pairs of **4** and **5** (30 µmol each), PhIO (24 µmol), internal standard benzyl bensoate (15 µmol), DCM (0.6 ml or 6 mL), and rt. Consistently 70% of the product was epoxide (GC). [b] Relative selectivity; see ref. 3d for its calculation. In this case based only on the disappearance of starting material. [c]receptor without Zn. [d]4-Ethylpyridine (90 µmol) added.
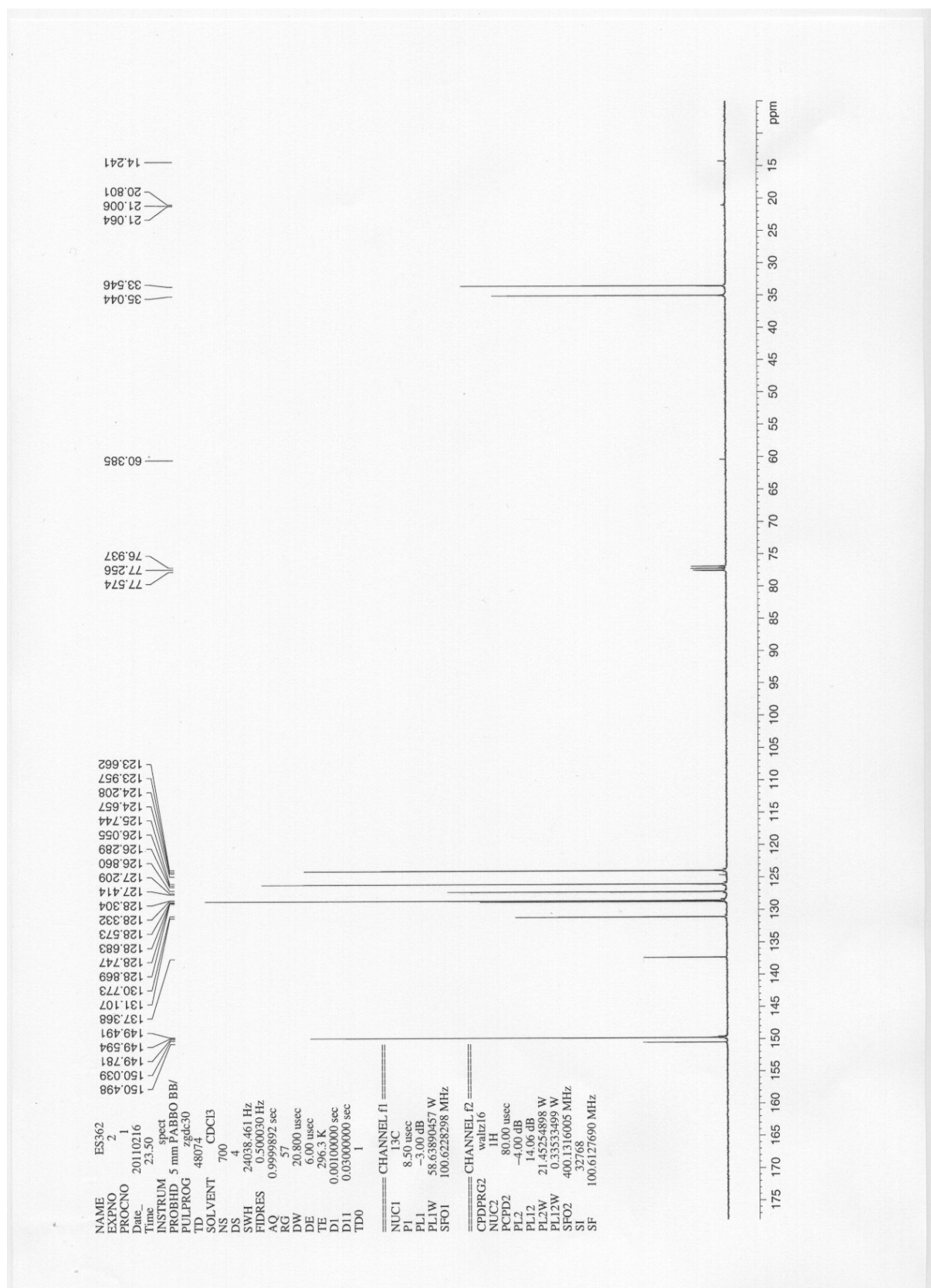
Table S2 The selectivity in the epoxidation of stilbene analogues catalysed by the different supramolecular systems.[a]

Entry	Cat. system (mM)	Selectivity by GC[b]/NMR[b] 26b:28b		27b:28b		27a:28a	
1	**1** (5) + **2** (5)	1.70	1.75	1.22	1.26	0.75	0.69
2	**1** (5) + **2** (15)	2.38	2.35	1.38	1.42	0.58	0.56
3	**8** (5) + **2** (5)	1.95	1.91	1.37	1.25	1.92	1.90
4	**8** (5) + **2** (15)	3.28	3.34	1.51	1.48	3.27	3.25
5	**9** (5) + **2** (5)	2.22	2.25	1.18	1.25	2.15	2.12
6	**9** (5) + **2** (15)	3.40	3.46	1.45	1.51	3.36	3.44
9	**12** (5)	1.36	1.34	1.08	1.06	1.06	1.09
10	**12** (15)	1.52	1.56	1.18	1.22	1.28	1.32

[a]General procedure: catalyst part **1**, or **8**, or **9** or catalyst **12** (3 µmol each), receptor part **2**, (3 or 9 µmol each), substrates pairs of **26**, **27**, **28** (30 µmol each), PhIO (24 µmol), internal standard (benzyl benzoate) (15 µmol), DCM (0.6 ml), and rt. Consistently 70% of the product was epoxide (GC). [b] Relative selectivity; see ref. 3d for its calculation. In this case based only on the disappearance of starting material. n.d = not determined.

NMR spectra

Fig. S19 ^{1}H NMR (400 MHz, CDCl₃) spectrum of **4b**.

Fig. S20 ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **4b**.

Fig. S21 ¹H NMR (400 MHz, CDCl₃) spectrum of **6b**.

Fig. S22 ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **6b**.