

# **A General Organocatalyst for Direct $\alpha$ -Functionalization of Aldehydes: Stereoselective C-C, C-N, C-F, C-Br and C-S Bond-Forming Reactions. Scope and Mechanistic Insights**

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## **Supporting Information**

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## Experimental Section

**General Methods.** The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm relative to  $\text{CHCl}_3$  ( $\delta = 7.26$ ) for  $^1\text{H}$  NMR and relative to the central  $\text{CDCl}_3$  resonance ( $\delta = 77.0$ ) for  $^{13}\text{C}$  NMR. Flash chromatography (FC) was carried out using Merck silica gel 60 (230-400 mesh). Optical rotation was measured on a Perkin-Elmer 241 polarimeter.

**Materials.** All the aldehydes **4a-i**, the azodicarboxylates **5** and *N*-fluorobenzensulfonimide (NFSI) are commercially available and used as received. Methyl vinyl keton **9**, aldehydes **4a** and **4f** were distilled prior to use. The organocatalyst **3**,<sup>1</sup> aldehydes **4j-l**,<sup>2</sup>  $\alpha$ -imino ethyl glyoxylate **7**<sup>3</sup> and 4,4-dibromo-2,6-di-tert-butyl-cyclohexa-2,5-dienone **13**<sup>4</sup> were prepared according to published procedure. All solvents were of p.a. quality and used without further purification.

**General Procedure for the  $\alpha$ -Amination of Aldehydes.** Azodicarboxylate **5** (0.2 mmol) was added to a solution of aldehyde **4** (0.24 mmol) and catalyst (*S*)-**3c** (12 mg, 0.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.1 mL) at room temperature. After 20 min, the reaction mixture was diluted with MeOH (0.5 mL) followed by careful addition of  $\text{NaBH}_4$  (12 mg, 0.3 mmol). After 20 min,  $\text{NaOH}_{\text{aq}}$  (2.5 mL 0.5 M) was added and after an additional 2 h the resulting mixture was diluted with water. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 20 mL) and the combined organic phases were dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed in vacuo followed by FC purification to give *N*-amino-oxazolidinone **6**. Separation conditions of the enantiomers and spectral data for compounds **6a-e** were in accordance with those previously reported.<sup>5</sup> Optical rotation for **6a-e** were of opposite sign to those reported with L-proline.<sup>5</sup>

**General Procedure for the Mannich Reaction with Aldehydes.**  $\alpha$ -Imino ethyl glyoxylate **7** (100 mg, 0.48 mmol) was added to a solution of aldehyde **4** (0.96 mmol) and catalyst (*S*)-**3c** (30 mg, 0.05 mmol) in  $\text{CH}_3\text{CN}$  (1.25 mL). The resulting mixture was stirred at room temperature for 16 h and then diluted with water. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 20 mL) and the combined organic phases were dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed in vacuo followed by FC purification to give the Mannich adduct **8**.

**Compound 8a:**  $^1\text{H}$  NMR  $\delta$  9.66 (*d*,  $J = 2.5$  Hz, 1H), 6.77 (*d*,  $J = 9.0$  Hz, 2H), 6.65 (*d*,  $J = 9.0$  Hz, 2H), 4.27 (*dd*,  $J = 7.1$ , 6.1 Hz, 1H), 4.17 (*q*,  $J = 7.3$  Hz, 2H) 3.74 (*s*, 3H), 2.68 (*m*, 1H), 1.76 (*m*, 1H),

1.66 (*m*, 1H), 1.22 (*t*, *J* = 7.3 Hz, 3H), 1.01 (*t*, *J* = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR  $\delta$  202.8, 172.7, 153.5, 140.7, 116.3, 115.1, 61.8, 58.3, 55.9, 55.6, 18.8, 14.4, 12.3. The enantiomers were separated according to literature procedures.<sup>6</sup>  $[\alpha]^{25}_{\text{D}} = -43.3$  (*c* = 1.0, CHCl<sub>3</sub>).

**Compound 8b:** Separation conditions of the enantiomers, spectral data and optical rotation was in accordance with those previously reported.<sup>7</sup>

**Compounds 8c:** The title compound was isolated as it corresponding diol after LiAlH<sub>4</sub> reduction by the following procedure: The crude reaction mixture was diluted with dry THF (10 mL) and cooled to 0 °C followed by careful addition of LiAlH<sub>4</sub> (30 mg, 0.76 mmol). After 2 h at ambient temperature, NH<sub>4</sub>Cl<sub>sat</sub> (20 mL) was carefully added, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The combined organic phases were dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed in vacuo followed by FC purification to give 2-allyl-3-(4-methoxy-phenylamino)-butane-1,4-diol in 63% yield (two steps).  $^1\text{H}$  NMR  $\delta$  6.78 (*d*, *J* = 9.2 Hz, 2H), 6.69 (*d*, *J* = 9.2 Hz, 2H), 5.79 (*m*, 1H), 5.08 (*bs*, 1H), 5.05 (*bs*, 1H), 3.81-3.70 (overlapping peaks including *s* at 3.75 ppm, total 6H), 3.66 (*dd*, *J* = 11.0, 3.9 Hz, 1H), 3.48 (*dd*, *J* = 9.5, 4.7 Hz, 1H), 2.23 (*dtt*, *J* = 14.0, 6.5, 1.3 Hz, 1H), 2.12 (*dtt*, *J* = 14.0, 8.0, 1.3 Hz, 1H), 1.94 (*m*, 1H).  $^{13}\text{C}$  NMR  $\delta$  153.7, 140.5, 136.4, 117.4, 117.3, 115.2, 64.1, 62.2, 60.5, 56.0, 42.0, 33.9. The enantiomers were separated by HPLC on Daicel Chiraldak AD with hexane/*i*-PrOH (95:5) as the eluent: R<sub>t</sub> (min): 44.7 (minor enantiomer); 46.5 (major enantiomer).  $[\alpha]^{25}_{\text{D}} = -33.2$  (*c* = 1.5, CHCl<sub>3</sub>).

**Compounds 8d:**  $^1\text{H}$  NMR  $\delta$  9.75 (*d*, *J* = 1.3 Hz, 1H), 7.25 (*m*, 5H), 6.76 (*d*, *J* = 8.9 Hz, 2H), 6.55 (*d*, *J* = 8.9 Hz, 2H), 4.20 (*m*, 1H), 4.22-4.05 (overlapping peaks, total 4H), 3.74 (*s*, 3H), 3.30 (*m*, 1H), 3.14 (*dd*, *J* = 14.4, 7.2 Hz, 1H), 2.93 (*dd*, *J* = 14.4, 7.2 Hz, 1H), 1.22 (*t*, *J* = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR  $\delta$  202.7, 172.5, 153.3, 140.8, 138.1, 129.3, 129.0, 127.1, 116.0, 115.0, 61.9, 57.6, 55.9, 55.5, 31.9, 25.5.  $[\alpha]^{25}_{\text{D}} = -15.2$  (*c* = 1.0, CHCl<sub>3</sub>). The enantiomeric excess was determined after LiAlH<sub>4</sub> reduction to the corresponding diol, according to the procedure described for compound 8c, to give 2-benzyl-3-(4-methoxy-phenylamino)-butane-1,4-diol in 65% yield.  $^1\text{H}$  NMR  $\delta$  7.30-7.13 (overlapping peaks, total 5H), 6.77 (*d*, *J* = 8.8 Hz, 2H), 6.62 (*d*, *J* = 8.8 Hz, 2H), 3.79-3.64 (overlapping peaks including *s* at 3.73 ppm, total 8H), 2.77 (*dd*, *J* = 14.0, 8.2 Hz, 1H), 2.64 (*dd*, *J* = 14.0, 8.2 Hz, 1H), 2.17 (*m*, 1H).  $^{13}\text{C}$  NMR  $\delta$  153.3, 140.8, 138.11, 129.3, 129.0, 127.1, 115.9, 115.0, 61.9, 57.6, 55.9, 55.5, 31.9, 14.4. The enantiomeric excess was determined by HPLC on Daicel Chiraldak AD with hexane/*i*-PrOH (95:5) as the eluent: R<sub>t</sub> (min): 48.5 (major enantiomer); 54.0 (minor enantiomer).  $[\alpha]^{25}_{\text{D}} = -4.7$  (*c* = 0.5, CHCl<sub>3</sub>).

**Compound 8e:**  $^1\text{H}$  NMR  $\delta$  9.72 (*d*, *J* = 1.3 Hz, 1H), 6.77 (*d*, *J* = 9.0 Hz, 2H), 6.65 (*d*, *J* = 9.0 Hz, 2H), 4.34 (*d*, *J* = 5.9 Hz, 1H), 4.14 (*d*, *J* = 7.4 Hz, 1H), 3.73 (*s*, 3H), 2.87 (*td*, *J* = 7.1, 5.9 Hz, 1H), 1.22 (*t*, *J* = 7.4 Hz, 3H), 1.16 (*d*, *J* = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR  $\delta$  201.7, 171.7, 153.1, 140.1, 115.6, 114.7, 61.5,

58.6, 55.6, 48.4, 14.1, 9.8. The enantiomers were separated according to literature procedures.<sup>6</sup>

**General Procedure for the Michael Addition to Aldehydes.** Methyl vinyl ketone **9** (82  $\mu$ L, 1.0 mmol) was added to a solution of aldehyde **4** (2.0 mmol) and catalyst (*S*)-**3c** (60 mg, 0.1 mmol) in EtOH (0.5 mL) and stirred at 40 °C for 64 h. The crude reaction mixture was purified by FC, without prior evaporation of the solvent, to give 2-substituted 5-oxo-hexanal **10**. Separation conditions of the enantiomers, spectral data and optical rotation for compounds **10a-c** were in accordance with those previously reported.<sup>8</sup>

**General procedure for the  $\alpha$ -Bromination of Aldehydes.** 4,4-Dibromo-2,6-di-tert-butyl-cyclohexa-2,5-dienone **13** (136 mg, 0.38 mmol) was added to a solution of aldehyde **4** (0.25 mmol), catalyst (*S*)-**3c** (0.05 mmol) benzoic acid (6 mg, 0.05 mmol) and water (10  $\mu$ L) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) at -24 °C. After 90 min at ambient temperature, the reaction mixture was diluted with MeOH (1 mL) followed by careful addition of NaBH<sub>4</sub> (15 mg, 0.38 mmol). The mixture was stirred for 10 min, quenched with sat. NH<sub>4</sub>Cl and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The combined organic phases were dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed in vacuo followed by FC purification to give the 2-bromo-alcohol **14**. Separation conditions of the enantiomers, spectral data and optical rotation for compounds **14a-b** were in accordance with those previously reported.<sup>9</sup>

**Compound 14c:** <sup>1</sup>H NMR  $\delta$  3.96 (*dd*, *J* = 9.5, 2.9 Hz, 2H), 3.80 (*dd*, *J* = 12.6, 9.5 Hz, 1H), 2.00 (*m*, 3H), 1.68 (*m*, 12H). <sup>13</sup>C NMR  $\delta$  76.2, 63.2, 40.2, 36.7, 29.7, 28.4.  $[\alpha]^{25}_D$  = -0.7 (c = 0.9 CHCl<sub>3</sub>). The ee was determined after conversion to the corresponding *m*-nitrobenzoyl ester by the following procedure: To a solution of bromo alcohol **14c** (30 mg, 0.12 mmol) and Et<sub>3</sub>N (49  $\mu$ L, 0.35 mmol) was added *m*-nitrobenzoylchloride (65 mg, 0.35 mmol) and the resulting mixture was stirred at ambient temperature for 20 min. Water was added, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL) and the combined organic phases were dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed in vacuo followed by FC purification to give 4-nitro-benzoic acid 2-adamantan-1-yl-2-bromo-ethyl ester in 76% yield. <sup>1</sup>H NMR  $\delta$  8.90 (*s*, 1H), 8.44 (*d*, *J* = 8.3 Hz, 1H), 8.40 (*d*, *J* = 7.7 Hz, 1H), 7.68 (*t*, *J* = 8.1 Hz, 1H), 4.88 (*dd*, *J* = 11.8, 3.1 Hz, 1H), 4.60 (*dd*, *J* = 11.8, 9.0 Hz, 1H), 4.05 (*dd*, *J* = 9.0, 3.1 Hz, 1H), 2.04 (*m*, 3H), 1.72 (*m*, 12H). <sup>13</sup>C NMR  $\delta$  166.4, 148.6, 135.6, 131.9, 130.0, 127.9, 125.0, 66.7, 66.0, 40.2, 36.9, 28.6. The enantiomers were separated by HPLC on Daicel Chiraldak AD with hexane/*i*-PrOH (90:10) as the eluent: R<sub>t</sub> (min): 12.5 (minor enantiomer); 14.9 (major enantiomer).  $[\alpha]^{25}_D$  = +54.3 (c = 1.4, CHCl<sub>3</sub>).

## Computational Methods

All quantum chemical calculations are carried out by using the Gaussian98<sup>10</sup> or Gaussian03<sup>11</sup> suite of programs. Using Gaussian98,<sup>10</sup> initial structures are computed at the HF/6-31G level of theory and are used as starting geometries for calculations which are computed at the B3LYP/6-31G(d) level of theory.

Full geometry optimization and frequency analysis has been performed for all stationary points, and minima structures are characterized by exactly zero imaginary vibrations.

Absolute energies and cartesian coordinates of fully gas phase optimized geometries at the B3LYP/6-31G(d) level of theory are listed below.

### **Enamine formed by 3-methyl butanal (4b) and catalyst (S)-3c**

Charge = 0

Multiplicity = 1

Stoichiometry = C<sub>29</sub>H<sub>31</sub>NOF<sub>12</sub>Si

E<sub>elec</sub>(gas phase) = -2741.40305633 Hartree

N	-1.715905	2.262085	0.859121
C	-0.299992	2.116686	0.521989
C	0.399286	3.148464	1.441821
C	-0.541609	3.295959	2.649296
C	-1.937407	3.075865	2.055221
C	0.244452	0.638319	0.701245
C	1.607841	0.432850	-0.000841
C	2.084193	-0.873436	-0.168025
C	3.339994	-1.126254	-0.719296
C	4.147381	-0.075637	-1.149046
C	3.671636	1.227925	-1.019434
C	2.420473	1.481286	-0.450443
C	3.799125	-2.557507	-0.821963
F	3.889289	-3.124970	0.407046
C	4.543747	2.385457	-1.435218
F	5.309566	2.818734	-0.408035
C	-2.686475	2.254970	-0.141042
C	-3.978787	2.599447	-0.000582

C	-5.015417	2.619511	-1.103870
C	-5.724268	3.988696	-1.140017
C	-0.789657	-0.341144	0.116917
C	-0.894596	-0.554748	-1.264171
C	-1.856186	-1.424051	-1.778559
C	-2.722755	-2.111693	-0.925311
C	-2.624453	-1.895241	0.444840
C	-1.680394	-1.002734	0.959609
C	-3.515842	-2.623669	1.415484
F	-2.780668	-3.281842	2.346451
C	-2.003296	-1.593222	-3.267542
F	-2.342158	-2.858179	-3.595942
O	0.367889	0.413724	2.098609
Si	1.285163	-0.478176	3.204353
C	1.159077	-2.348289	2.950123
C	3.092689	0.064001	3.209016
C	0.487714	-0.035350	4.852517
F	-4.303753	-3.532577	0.806599
F	-4.320130	-1.773955	2.089925
F	-2.975481	-0.787684	-3.761602
F	-0.865925	-1.288812	-3.928324
F	5.379927	2.046528	-2.438611
F	3.808748	3.440165	-1.851304
F	5.007642	-2.667348	-1.406432
F	2.928212	-3.306751	-1.531310
C	-4.472562	2.260829	-2.493247
H	-4.348478	2.889840	0.981828
H	-2.312903	1.926829	-1.106198
H	-2.414263	4.026353	1.766143
H	-0.452820	4.275029	3.129825
H	1.405203	2.849290	1.742630
H	-0.158235	2.370004	-0.536913
H	0.477141	4.100881	0.902988

H	-0.318428	2.528548	3.392553
H	-2.615455	2.575215	2.758180
H	2.094261	2.509912	-0.376778
H	5.118086	-0.269029	-1.588993
H	1.463559	-1.710727	0.129947
H	-0.216233	-0.056896	-1.948937
H	-3.448596	-2.810623	-1.323167
H	-1.630115	-0.824346	2.025868
H	3.182413	1.153954	3.284634
H	3.601733	-0.367177	4.080706
H	3.640117	-0.259328	2.318032
H	0.975121	-0.576618	5.672812
H	0.567459	1.035901	5.069228
H	-0.575802	-0.300362	4.867873
H	1.801556	-2.722878	2.146695
H	1.480478	-2.849472	3.872670
H	0.130888	-2.670826	2.749662
H	-5.786548	1.871925	-0.851008
H	-6.541712	3.990991	-1.871552
H	-6.148239	4.243439	-0.161291
H	-5.018183	4.782374	-1.413646
H	-4.030150	1.259614	-2.521959
H	-5.279540	2.285475	-3.234343
H	-3.707258	2.979264	-2.814124

### Iminium ion intermediate (*S,S*)-19

Charge = 1

Multiplicity = 1

Stoichiometry = C<sub>29</sub>H<sub>31</sub>NOF<sub>13</sub>Si

E<sub>elec</sub>(gas phase) = -2841.03040784 Hartree

C	2.360152	-1.524250	-0.800422
C	1.615061	-0.527006	-0.180761

C	2.304713	0.442332	0.539863
C	3.686227	0.415132	0.634652
C	4.422262	-0.572176	0.004637
C	3.742843	-1.540169	-0.713562
C	0.073929	-0.537880	-0.159480
O	-0.385774	-1.241975	0.988567
Si	0.081116	-1.650471	2.636700
C	-1.476266	-2.546210	3.255685
C	4.353582	1.457594	1.470122
F	5.704246	1.428838	1.353174
C	4.489782	-2.602895	-1.450185
F	3.860871	-3.812237	-1.351088
C	-0.516732	0.880163	-0.149502
C	-0.043342	1.880329	-0.993495
C	-0.625800	3.136446	-1.000218
C	-1.679541	3.439522	-0.152553
C	-2.139464	2.452432	0.698187
C	-1.569128	1.188474	0.698087
C	-3.244101	2.713875	1.666218
F	-3.840031	3.915008	1.468979
C	-0.133851	4.137270	-1.992489
F	-0.560478	5.394796	-1.719426
C	-0.497772	-1.381215	-1.353382
C	-0.180420	-0.942583	-2.791305
C	-1.401282	-0.161135	-3.309384
C	-2.591956	-0.583825	-2.445961
N	-1.998501	-1.399395	-1.325347
C	-2.635587	-2.089355	-0.465186
C	-4.114845	-2.218388	-0.293187
F	-4.764619	-1.193080	-1.016090
C	-4.667705	-3.583878	-0.749097
C	-4.006041	-4.742284	0.012945
F	-4.213754	1.750963	1.580228

F	-2.798844	2.680758	2.957587
F	-0.572325	3.825542	-3.253519
F	1.226821	4.158793	-2.059347
F	4.572801	-2.326738	-2.785338
F	5.756676	-2.756968	-0.990516
F	4.054741	1.290317	2.795445
F	3.931434	2.711537	1.141340
C	1.574335	-2.823236	2.605803
C	0.417914	-0.086270	3.661400
C	-6.191480	-3.600611	-0.566541
H	-4.343915	-2.048695	0.750561
H	-2.042679	-2.642757	0.231564
H	-3.292045	-1.206215	-2.975928
H	-1.586151	-0.386233	-4.349583
H	0.724244	-0.358432	-2.850383
H	-0.182220	-2.395616	-1.172864
H	-0.020863	-1.826313	-3.395813
H	-1.244973	0.903756	-3.241826
H	-3.127695	0.246594	-2.022084
H	-1.939402	0.443894	1.368688
H	-2.120443	4.414931	-0.153615
H	0.790990	1.696944	-1.640605
H	1.888981	-2.311779	-1.349646
H	5.490156	-0.589627	0.075514
H	1.770263	1.228395	1.033043
H	-1.668791	-3.452929	2.691568
H	-1.350496	-2.836470	4.293501
H	-2.351878	-1.907427	3.205333
H	1.722663	-3.239273	3.597397
H	1.419847	-3.652279	1.924283
H	2.491231	-2.320058	2.326194
H	-0.370421	0.651080	3.564577
H	0.467228	-0.365290	4.709773

H	1.361696	0.384736	3.417553
H	-4.445964	-3.682656	-1.807792
H	-6.458762	-3.525608	0.482125
H	-6.665789	-2.789500	-1.099277
H	-6.591626	-4.532106	-0.945300
H	-4.133221	-4.635130	1.085255
H	-4.473270	-5.674179	-0.274364
H	-2.947398	-4.842545	-0.200955

### **Iminium ion intermediate (*R,S*)-19**

Charge = 1

Multiplicity = 1

Stoichiometry = C<sub>29</sub>H<sub>31</sub>NOF<sub>13</sub>Si

E<sub>elec</sub>(gas phase) = -2841.02861921 Hartree

C	-1.604951	1.134186	0.656616
C	-0.486458	0.887402	-0.124692
C	0.017917	1.932790	-0.892732
C	-0.597244	3.173673	-0.892298
C	-1.727849	3.409799	-0.126575
C	-2.221054	2.376417	0.647319
C	0.117126	-0.524903	-0.168107
C	-0.463199	-1.333282	-1.385445
N	-1.962661	-1.362245	-1.332533
C	-2.588364	-0.569423	-2.437346
C	-1.416482	-0.031300	-3.263377
C	-0.179211	-0.827277	-2.809153
C	-2.612380	-2.010265	-0.448821
C	-4.104996	-2.039105	-0.312055
F	-4.302006	-2.318531	1.064143
C	-0.066747	4.228557	-1.805840
F	-0.519840	5.466603	-1.489188
C	-3.465905	2.534358	1.453040

F	-3.930346	3.806503	1.463093
C	1.656521	-0.505051	-0.197273
C	2.340582	0.423681	0.580125
C	3.722245	0.404943	0.666471
C	4.464435	-0.535474	-0.025787
C	3.790658	-1.461042	-0.802212
C	2.407024	-1.454853	-0.880041
C	4.536567	-2.528795	-1.532542
F	4.453312	-3.730757	-0.888532
C	4.382039	1.417245	1.544124
F	5.734396	1.322452	1.518576
O	-0.335166	-1.261465	0.958384
Si	0.120602	-1.721268	2.600395
C	-1.354426	-2.790845	3.127705
C	1.719353	-2.747107	2.564779
C	0.290626	-0.170974	3.686225
F	4.018433	-2.731072	-2.780975
F	5.853327	-2.236455	-1.673222
F	3.983838	1.272498	2.845017
F	4.046704	2.689288	1.184186
C	-4.803245	-3.127975	-1.146175
C	-6.317589	-3.057303	-0.904687
C	-4.247990	-4.524928	-0.833875
F	-0.443620	3.979552	-3.100564
F	1.294394	4.263664	-1.806055
F	-4.466879	1.739528	0.946782
F	-3.291922	2.138799	2.745594
H	-2.052621	-2.557178	0.279484
H	-3.217712	-1.230006	-3.012974
H	-1.597924	-0.167110	-4.319379
H	0.718122	-0.231013	-2.859671
H	-0.135488	-2.351035	-1.251234
H	-0.026030	-1.679480	-3.458924

H	-1.287483	1.026016	-3.097276
H	-3.194237	0.215304	-2.009080
H	-1.991151	0.358577	1.283244
H	-2.200884	4.370172	-0.129099
H	0.898545	1.795327	-1.487712
H	1.941313	-2.201348	-1.488364
H	5.533084	-0.542434	0.033350
H	1.800247	1.171453	1.124438
H	-1.396670	-3.716268	2.562632
H	-1.257904	-3.060123	4.174459
H	-2.300873	-2.276387	3.010358
H	1.863870	-3.207415	3.537374
H	1.667973	-3.545481	1.833034
H	2.597775	-2.150031	2.356787
H	-0.576704	0.475229	3.617035
H	0.377873	-0.480298	4.723406
H	1.174596	0.411099	3.456480
H	-4.611986	-2.900106	-2.191161
H	-6.551859	-3.263954	0.130924
H	-6.719674	-2.082940	-1.157456
H	-6.820933	-3.792583	-1.518570
H	-4.374421	-4.764525	0.213687
H	-4.781448	-5.268031	-1.411235
H	-3.195957	-4.620997	-1.086028
H	-4.540045	-1.066777	-0.487315

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