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Supporting Information

Organocatalytic Asymmetric Formal [3+2] Cycloaddition Reaction of Isocyanoacetates with Saccharin-Derived 1-Azadienes

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1. Optimization Reaction Conditions of Catalytic Asymmetric Formal [3+2] Cycloaddition Reaction of Isocyanoacetate 1a with Chalcone-derived Tosylimine 5a



Table S1 Catalysts screening and optimization reaction conditions^[a]

						-
Entry	Catalyst	<i>t</i> (h)	T [°C]	Yield (%)	$dr^{[b]}$	<i>ee</i> (%) ^[c]
1	3 a	0.5	r.t.	99	0.9:1	25 (4)
2	3 b	0.5	r.t.	99	2.6:1	63 (36)
3	3c	0.5	r.t.	99	2.1:1	39 (9)
4	3d	0.5	r.t.	99	2.1:1	42 (8)
5	3e	0.5	r.t.	99	1.8:1	65 (37)
6	3 e	0.5	0	99	2.2:1	55 (24)
7	3 e	0.5	40	99	2.6:1	60 (29)
8 ^[d]	3 e	0.5	r.t.	99	3.1:1	67 (28)
9 ^[e]	3e	2	r.t.	99	2.1:1	58 (41)
10 ^[f]	3e	2	r.t.	99	2.2:1	80 (52)
11 ^[f]	3e	2	10	99	4.2:1	81 (35)
12 ^[f]	3e	2	0	99	2.1:1	74 (48)
13 ^[f]	3e	2	-20	99	3.0:1	59 (43)

[a] Unless otherwise noted, all of reactions were carried out with isocyanoacetate **1a** (0.12 mmol), α , β unsaturated imine **5a** (0.10 mmol), AgOAc (5 mol%) and catalyst **3** (0.02 mmol) in 2.0 mL of CH₂Cl₂. The data in parentheses are the ee value for minor isomer. [b] Determined by ¹H NMR analysis for the pure product, the data in parenthesis was the *ee* for minor isomer. [c] Enantiomeric excesses were determined by chiral HPLC analysis. [d] 30 mg of 4Å molecular sieves was added. [e] **1a** was added dropwise. [f] **5a** was added dropwise.

2. X-Ray Crystal Data of Compound 4d

Table S2. Crystal data and structure refinement for	r 4d (CCDC 2010595).		
Empirical formula	$C_{25}H_{19}BrN_2O_4S$		
Formula weight	523.39		
Temperature	293(2) K		
Wavelength	1.54184 Å		
Crystal system	orthorhombic		
Space group	P 21 21 21		
Unit cell dimensions	a = 6.73540(10) Å	$\alpha = 90^{\circ}$.	
	b = 18.2897(2) Å	$\beta = 90^{\circ}$.	
	c = 19.0257(2) Å	$\gamma = 90^{\circ}.$	
Volume	2343.75(5) Å ³		
Z	4		
Density (calculated)	1.483 Mg/m ³		
Absorption coefficient	3.514 mm ⁻¹		
F (000)	1064.0		
Crystal size	$0.43 \ge 0.37 \ge 0.35 \text{ mm}^3$		
Theta range for data collection	4.648 to 67.073°		
Index ranges	-6<=h<=8, -16<=k<=21, -22<=	=l<=22	
Reflections collected	23450		
Independent reflections	4171 [R (int) = 0.0719]		
Data / restraints / parameters	4171 / 0 / 300		
Goodness-of-fit on F ²	1.036		
Final R indices [I>2sigma (I)]	R1 = 0.0488, wR2 = 0.1277		
R indices (all data)	R1 = 0.0499, wR2 = 0.1286		
Largest diff. peak and hole	1.077 and -0.832 e.Å ⁻³		

Figure S1. ORTEP plot of the X-ray crystal structure of 4d. Displacement ellipsoids are drawn at the 50% probability level.

3. Copies of HPLC Analysis Spectra of Compounds 4

4a (Table 3, entry 1)









Total		234326.086	13485564.681	100.0000
4	54.102	9107.561	1773365. 125	13.1501
3	34. 403	39.850	608.900	0.0045
2	29.460	3167.785	200083.656	1.4837
1	10.700	222010.091	11511507.000	00. 3017

4b (Table 3, entry 2)



Total

Racemic



	no concron crmo		ni ou	THE OWN
1	33.198	203557.453	14832495.000	31.0386
2	38.698	204110.969	14984826.000	31. 3573
3	77.032	156235. 672	17969982.000	37.6041
Total		563904.094	47787303.000	100.0000





212122. 411

20901600. 313

100.0000

4c (Table 3, entry 3)



498523.438

54484105.375

100.0000

Total

4d (Table 3, entry 4)



0 -20

ò

Peak

1

2

3

Total

5

10

21.143

24.880

41.358

15

Racemic



30

35

Area

40

45

Area% 75.7206

4.8907

19.3887 100.0000

25 (min)

20

4e (Table 3, entry 5)





Peak	Retention time	Height	Area	Area%	
1	16.615	109378.844	4955883.500	20. 2611	
2	23.215	85759.695	5074097.500	20.7444	
3	38.782	41492.289	7435519.000	30. 3985	
4	61.248	45931.684	6994635.000	28. 5961	
Total		282562. 512	24460135.000	100.000	





1	16.802	302620.000	13695628.000	81.7622
2	23. 530	6553. 463	376609.250	2.2483
3	38.098	50.934	1762.601	0.0105
4	60.770	19639. 793	2676559.000	15.9789
Total		328864.190	16750558.851	100.0000

4f (Table 3, entry 6)











Tota1		237193.683	9415542.563	100.0000
4	29.878	13475. 732	1181805.375	12.5516
3	21.365	2431.196	133643.063	1.4194
2	16.473	6121.896	299016.125	3.1758
1	11.307	215164.859	7801078.000	82.8532

4g (Table 3, entry 7)



Peak	Retention time	Height	Area	Area%
1	13.980	228819.375	9059898.000	37.1878
2	24. 438	166808.047	9706435.000	39.8417
3	44.820	45369. 629	5596195. 500	22.9705
Total		440997.051	24362528.500	100.0000



Total		532677, 516	27226130, 906	100,0000
3	43.803	89388. 383	9305614.000	34. 1790
2	24.823	8786. 945	477696.906	1.7546
1	14.955	434502.188	17442820.000	64.0665

4h (Table 3, entry 8)



Racemic



Peak	Retention time	Height	Area	Area%	
1	13.265	270299. 188	11481567.000	23.8575	
2	23.215	192775.688	11405680.000	23. 6998	
3	25.815	46635.980	12638654.000	26.2618	
4	60.882	75855.086	12599795.000	26. 1810	
Total		585565.941	48125696.000	100.0000	



275172.436

Total

11592957.675

100.0000

4i (Table 3, entry 9)



4k (Table 3, entry 11)







Total		218709.566	17723956. 406	100.0000	
4	77.682	20132. 754	4074880.750	22.9908	
3	37.535	14089.200	1165943.250	6. 5783	
2	26. 588	180916.906	12200495.000	68.8362	

4l (Table 3, entry 12)





Peak	Retention time	Height	Area	Area%
1	11.645	27423.449	1522017.125	36.9237
2	24.813	12685.854	1039606. 563	25.2206
3	30.307	17395.816	1560434. 500	37.8557
Total		57505. 120	4122058. 188	100.0000



4m (Table 3, entry 13)





Peak	Retention time	Height	Area	Area%
1	12.090	161402.922	5310817.500	30. 4710
2	13.237	51354. 984	3383643.500	19. 4138
3	41.088	51828. 617	5216984.000	29.9326
4	73.078	32181.967	3517646.250	20. 1826
Total		296768.490	17429091.250	100.0000



Tota1		462384.848	35271887.250	100.0000
4	72.238	297892.031	25478998.000	72.2360
3	41.593	17859.039	1485583.375	4.2118
2	13. 497	126119.852	7616079. 500	21. 5925
1	12.212	20513.926	691226.375	1.9597

4n (Table 4, entry 1)



40 (Table 4, entry 2)





Peak	Retention time	Height	Area	Area%	
1	15.673	285406. 281	16221143.000	37.0300	
2	24.660	260305.719	17044800.000	38.9103	
3	35.290	99082.859	10539441.000	24.0597	
Total		644794.859	43805384.000	100.0000	



4p (Table 4, entry 3)





Ican	Recention cime	neight	Alca	AI Call	
1	24.825	206742.641	15763546.000	37.1447	
2	40.140	223284. 297	15807227.000	37.2476	
3	63. 557	97926. 133	10867467.000	25.6077	
Total		527953.070	42438240.000	100.0000	



4q (Table 4, entry 4)



4r (Table 4, entry 5)





4s (Table 4, entry 6)





Total		197871.355	6520890.000	100.0000	_
3	21.790	10873.801	889637.250	13.6429	
2	12.977	88737.117	2829233.750	43. 3872	
1	9.150	98260. 438	2802019.000	42.9699	



Chiral

4t (Table 4, entry 7)

Tota1





224003.476

13413938. 938

100.0000

4u (Table 4, entry 8)



4v (Table 4, entry 9)



4w (Table 4, entry 10)





4x (Table 4, entry 11)





Peak	Retention time	Height	Area	Area%
1	19.098	251772.563	11986988.000	37.0855
2	22.398	250533.313	12249845.000	37.8987
3	38.032	30007.844	8085767.000	25.0158
Tota1		532313.719	32322600.000	100.0000



4y (Table 4, entry 12)





Peak	Retention time	Height	Area	Area%
1	19.332	21456. 334	5414917.000	16. 4350
2	23.865	158908.484	10942670.000	33. 2126
3	40.398	19204.971	5337431.500	16. 1999
4	49.198	93895.008	11252356.000	34. 1525
Total		293464.797	32947374. 500	100.0000





Peak	Retention time	Height	Area	Area%	
1	19.598	203591.016	13118973.000	38. 1022	
2	23.798	338550. 188	20067078.000	58.2820	
3	41.598	1725.702	487348.750	1.4154	
4	49.132	5627.227	631390.813	1.8338	
Total		553658. 592	34431009.664	100.0000	

4z (Table 4, entry 13)

Tota1



384944.051

36237160. 500

100.0000

S28

4. Copies of NMR Spectra for the Compounds 4











т


























1 H NMR of **4h** 5.036 2.119 3.727 3.164 2.361 N CO2Me Me 0 0=\$'-N Ph⁷⁷H 5(15 4 15 3.26 3/00 1/49 1/1<mark>1</mark>/11/12 1/40 1.04 1(01 __0.18 **p**.61 0(48 **-0**.€17 PPM 9 7 2 8 5 6 3 4

-



















 13 C NMR of **4**k



 1 H NMR of **4**l





1 H NMR of **4m**













S56





3.234















1 H NMR of 4q















Т,



S68









1 H NMR of 4v

3.229



















 1 H NMR of 4y







13 C NMR of 4z

