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CN 108610278 B

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2020.10.13

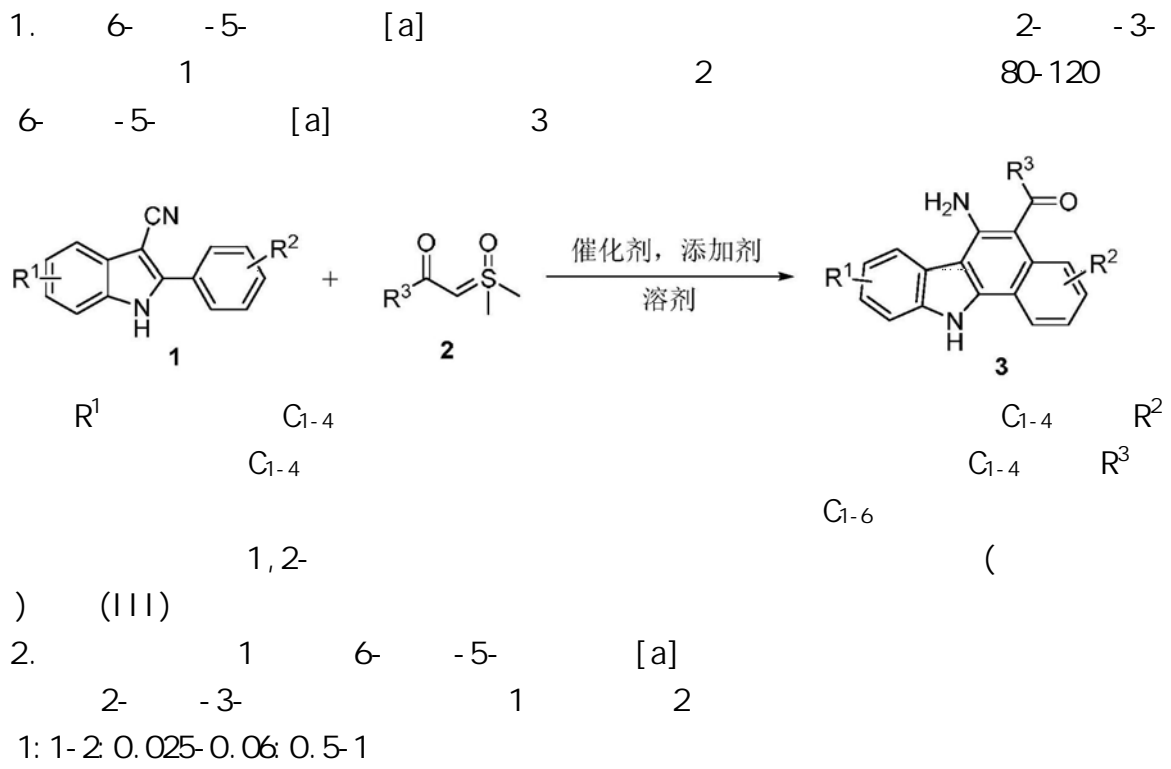
(21) 201810733102.2

(22) 2018.07.05

t # < 4 . - 2

书1

书9



6- -5- [a]

[0001] 6- -5- [a]

[0002] [a]

[a]

[a]

[a]

6- -5- [a]

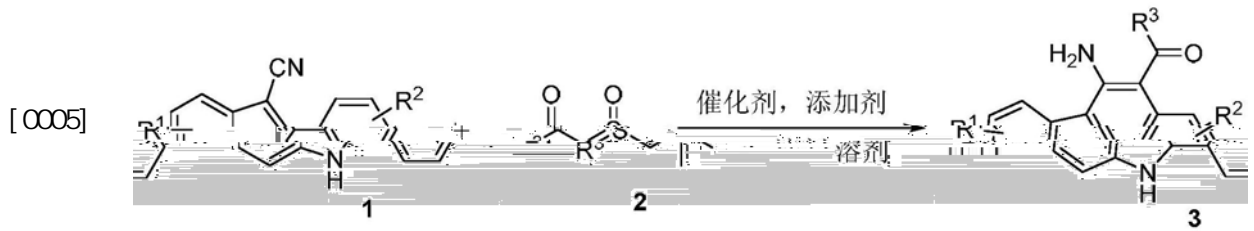
6- -5- [a]

[0003] 6- -5- [a] Rh(III)

2- -3-
6- -5- [a]

[0004] 6- -5- [a]

2 2- -3- 1
3 80-120 6- -5- [a]



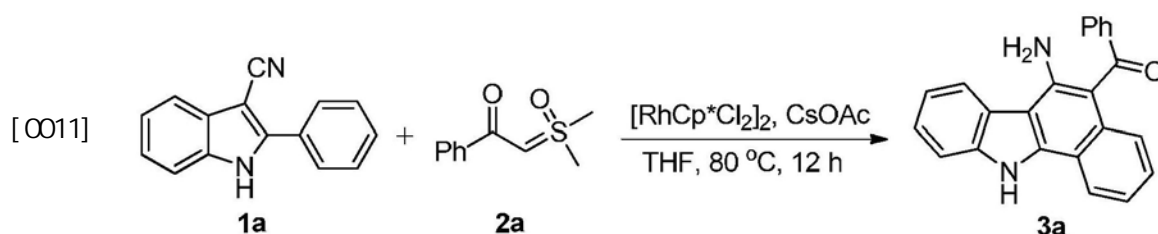
[0006] R¹ C₁₋₄ C₁₋₄ R³
R² C₁₋₄ C₁₋₄ R³
C₁₋₆
() (III) ([RhCp*Cl₂]₂)

[0007] 2- -3- 1 2
 1: 1-2 0.025-0.06: 0.5-1
 [0008] (1) (2)

2- -3-
 6- -5- [a] (3) (4)
 6- -5- [a]

[0009]

[0010] 1



[0012] 15mL 1a(0.5mmol , 109.1mg) (3mL) 2a(0.75mmol ,
 147.2mg) () (III) ([RhCp*Cl₂]₂, 0.025mmol , 15.4mg)
 (0.25mmol , 48.0mg) 80

12h 10mL (10mL× 3)
 (/
 20/1) 3a(63.9mg, 38) ¹H NMR

(400MHz, CDCl₃): 6.91(s, 2H) , 7.12(t, J 7.6Hz, 1H) , 7.20-7.31(m, 3H) , 7.39-7.47(m,
 3H) , 7.51-7.56(m, 3H) , 7.70(d, J 8.0Hz, 1H) , 8.37(d, J 8.0Hz, 1H) , 8.43(d, J 8.0Hz,
 1H) , 12.56(s, 1H) . ¹³C NMR(100MHz, CDCl₃): 105.8, 107.0, 111.5, 116.0, 120.0, 121.0,
 121.6, 122.0, 122.7, 124.1, 125.6, 126.2, 128.5, 129.1, 131.8, 132.5, 138.5, 138.7,
 141.6, 146.0, 197.1. HRMS cal cd for C₂₃H₁₆N₂O: 359.1155[M+Na]⁺, found: 359.1154

[0013] 2

[0014] 15mL 1a(0.5mmol , 109.1mg) (3mL) 2a(0.75mmol ,
 147.2mg) [RhCp*Cl₂]₂(0.025mmol , 15.4mg) (0.25mmol , 48.0mg)
 (0.25mmol , 85.9mg) 80 12h

10mL

147.2mg)	[RhCp*Cl ₂] ₂ (0.025mmol, 15.4mg)	(0.25mmol, 48.0mg)	
(0.25mmol, 85.9mg)		80	12h
	10mL	(10mL×3)	(/
20/1)	3a(55.5mg, 33)		
[0017]	4		
[0018]	15mL	1a(0.5mmol, 109.1mg)	(3mL) 2a(0.75mmol,
147.2mg)	[RhCp*Cl ₂] ₂ (0.025mmol, 15.4mg)	(0.25mmol, 48.0mg)	
	80	12h	
10mL	(10mL×3)	(/	20/1)
(45.4mg, 27)			3a
[0019]	5		
[0020]	15mL	1a(0.5mmol, 109.1mg)	(3mL) 2a(0.75mmol,
147.2mg)	[RhCp*Cl ₂] ₂ (0.025mmol, 15.4mg)	(0.25mmol, 48.0mg)	
	80	12h	
10mL	(10mL×3)	(/	20/1)
(57.2mg, 34)			3a
[0021]	6		
[0022]	15mL	1a(0.5mmol, 109.1mg)	(3mL) 2a(0.75mmol,
147.2mg)	[RhCp*Cl ₂] ₂ (0.025mmol, 15.4mg)	(0.25mmol, 48.0mg)	
	100	12h	
10mL	(10mL×3)	(/	20/1)
(70.6mg, 42)			3a
[0023]	7		
[0024]	15mL	1a(0.5mmol, 109.1mg)	(3mL) 2a(0.75mmol,
147.2mg)	[RhCp*Cl ₂] ₂ (0.025mmol, 15.4mg)	(0.25mmol, 48.0mg)	
	120	12h	
10mL	(10mL×3)	(/	20/1)
(65.6mg, 39)			3a
[0025]	8		
[0026]	15mL	1a(0.5mmol, 109.1mg)	(3mL) 2a(0.5mmol,
98.1mg)	[RhCp*Cl ₂] ₂ (0.03mmol, 18.5mg)	(0.5mmol, 96.0mg)	
	100	12h	
10mL	(10mL×3)	(/	20/1)
			3a

(62.2mg, 37)

[0027] 9

[0028] 15mL 1a(0.5mmol, 109.1mg) (3mL) 2a(1mmol, 196.2mg) [RhCp*Cl₂]₂(0.0125mmol, 7.7mg) (0.5mmol, 96.0mg)

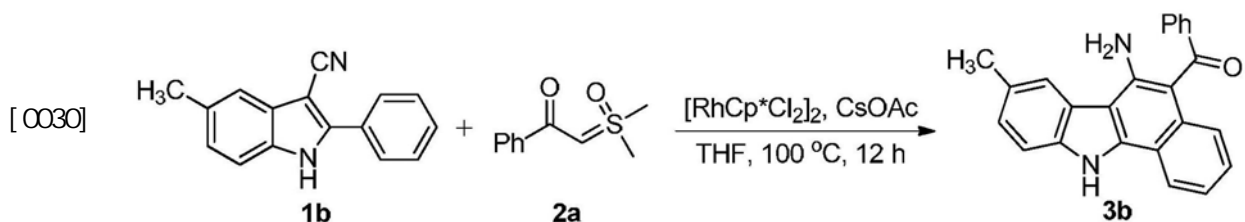
100 12h

10mL (10mL × 3)

(/ 20/1) 3a

(52.1mg, 31)

[0029] 10



[0031] 15mL 1b(0.5mmol, 116.1mg) (3mL) 2a(0.75mmol, 147.2mg) [RhCp*Cl₂]₂(0.025mmol, 15.4mg) (0.25mmol, 48.0mg)

100 12h

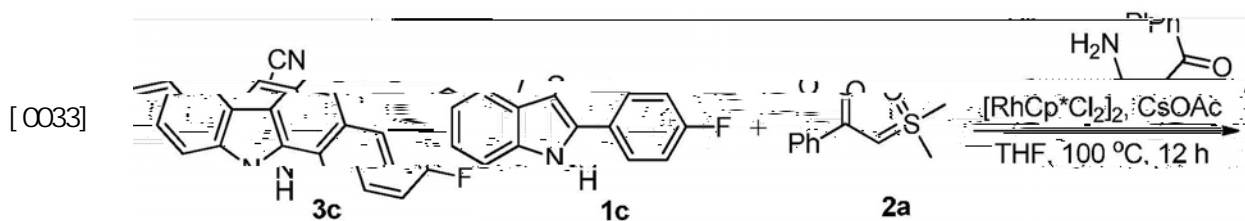
10mL (10mL × 3)

(/ 20/1) 3b

(71.8mg, 41)

¹H NMR(600MHz, DMSO-d₆): 2.53(s, 3H), 6.88(s, 2H), 7.09-7.11(m, 1H), 7.19(d, J = 8.4Hz, 1H), 7.22-7.25(m, 1H), 7.27(d, J = 8.4Hz, 1H), 7.40(t, J = 7.8Hz, 2H), 7.51-7.55(m, 3H), 7.58(d, J = 8.4Hz, 1H), 8.23(s, 1H), 8.33(d, J = 7.8Hz, 1H), 12.39(s, 1H). ¹³C NMR(150MHz, DMSO-d₆): 21.8, 106.1, 107.2, 111.7, 116.6, 121.3, 122.0, 122.4, 123.5, 125.9, 126.0, 126.7, 129.0, 129.3, 129.6, 132.2, 133.0, 137.2, 139.3, 142.2, 146.7, 197.5. HRMS calcd for C₂₄H₁₈N₂O: 373.1311[MNa]⁺, found: 373.1319

[0032] 11



[0034] 15mL 1c(0.5mmol, 118.1mg) (3mL) 2a(0.75mmol, 147.2mg) [RhCp*Cl₂]₂(0.025mmol, 15.4mg) (0.25mmol, 48.0mg)

100 12h

10mL (10mL × 3)

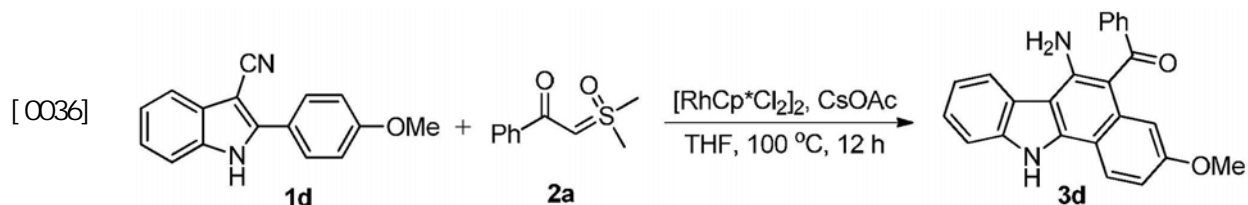
(/ 20/1) 3c

(77.8mg, 44)

¹H NMR(600MHz, DMSO-d₆): 6.84(dd, J₁ = 8.4Hz, J₂ = 2.4Hz, 1H), 7.06(s, 2H), 7.16(td, J₁ = 8.4Hz, J₂ = 2.4Hz, 1H), 7.31(t, J

7.8 Hz, 1H), 7.44-7.46(m, 3H), 7.56-7.58(m, 3H), 7.70(d, J = 8.4 Hz, 1H), 8.41-8.43(m, 2H), 12.57(s, 1H). ¹³C NMR(150MHz, DMSO-d₆): 105.7(d, ³J_{C-F} = 3.3 Hz), 107.0, 110.8, 111.0(d, ³J_{C-F} = 3.3 Hz), 112.0, 113.5, 120.7, 121.4, 123.2, 124.7, 125.1(d, ²J_{C-F} = 9.8 Hz), 129.1, 129.6, 132.4, 134.6(d, ²J_{C-F} = 9.8 Hz), 138.9, 139.2, 141.9, 118.0, 160.5(d, ¹J_{C-F} = 239.6 Hz), 197.3. ¹⁹F NMR(377MHz, DMSO) : -113.7. HRMS calcd for C₂₃H₁₅FN₂ONa: 377.1061[MNa]⁺, found: 377.1063

[0035] 12

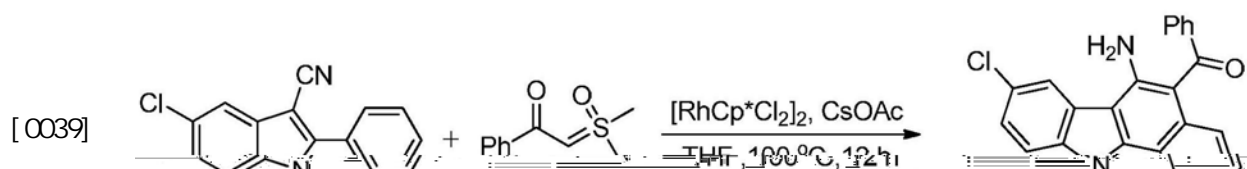


[0037] 15mL 1d(0.5mmol, 124.1mg) (3mL) 2a(0.75mmol, 147.2mg) [RhCp*Cl₂]₂(0.025mmol, 15.4mg) (0.25mmol, 48.0mg) 100 12h

10mL (10mL × 3) (/ 20/1) 3d (91.4mg, 50%) ¹H NMR(600MHz, DMSO-d₆): 3.30(s, 3H), 6.61

(d, J = 2.4 Hz, 1H), 6.91(dd, J₁ = 8.4 Hz, J₂ = 2.4 Hz, 1H), 7.23(s, 2H), 7.29(t, J = 7.8 Hz, 1H), 7.40-7.44(m, 3H), 7.51-7.54(m, 3H), 7.67(d, J = 7.8 Hz, 1H), 8.27(d, J = 9.0 Hz, 1H), 8.39(d, J = 7.8 Hz, 1H), 12.42(s, 1H). ¹³C NMR(150MHz, DMSO-d₆): 54.7, 105.7, 105.9, 108.8, 111.3, 111.9, 112.7, 120.5, 121.1, 123.5, 124.0, 124.2, 129.0, 129.3, 131.7, 135.0, 138.9, 140.0, 143.1, 148.2, 157.4, 197.4. HRMS calcd for C₂₄H₁₈N₂NaO₂: 389.1260 [MNa]⁺, found: 389.1260

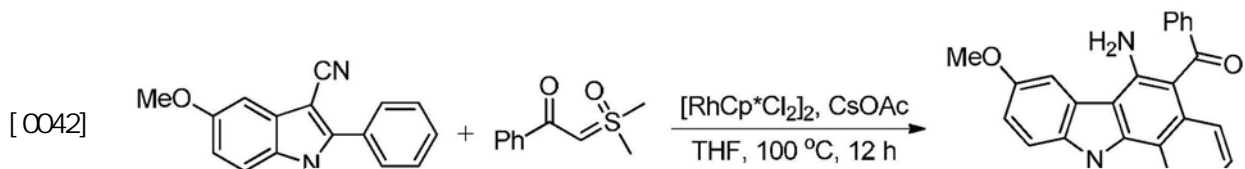
[0038] 13



[0040] 15mL 1e(0.5mmol, 126.4mg) (3mL) 2a(0.75mmol, 147.2mg) [RhCp*Cl₂]₂(0.025mmol, 15.4mg) (0.25mmol, 48.0mg) 100 12h

10mL (10mL × 3) 3e

[0041] 14



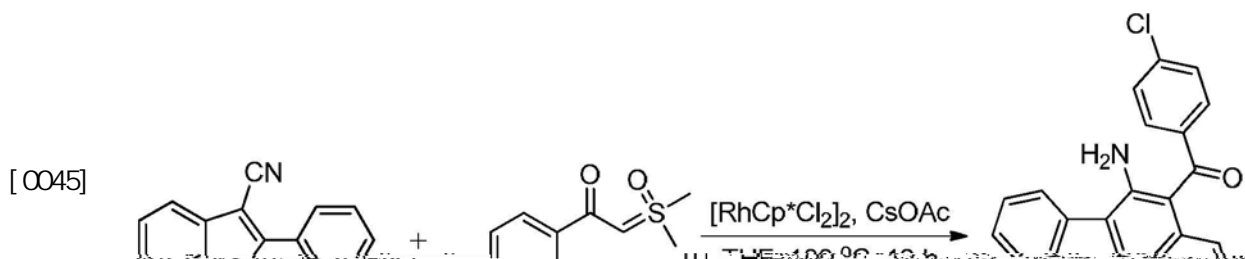
[0043] 15mL 1f (0.5mmol, 124.1mg) (3mL) 2a (0.75mmol, 147.2mg) [RhCp*Cl₂]₂ (0.025mmol, 15.4mg) (0.25mmol, 48.0mg)

100 12h

10mL (10mL × 3)

3f

[0044] 15



[0046] 15mL 1a (0.5mmol, 109.1mg) (3mL) 2b (0.75mmol, 173.0mg) [RhCp*Cl₂]₂ (0.025mmol, 15.4mg) (0.25mmol, 48.0mg)

100 12h

10mL (10mL × 3)

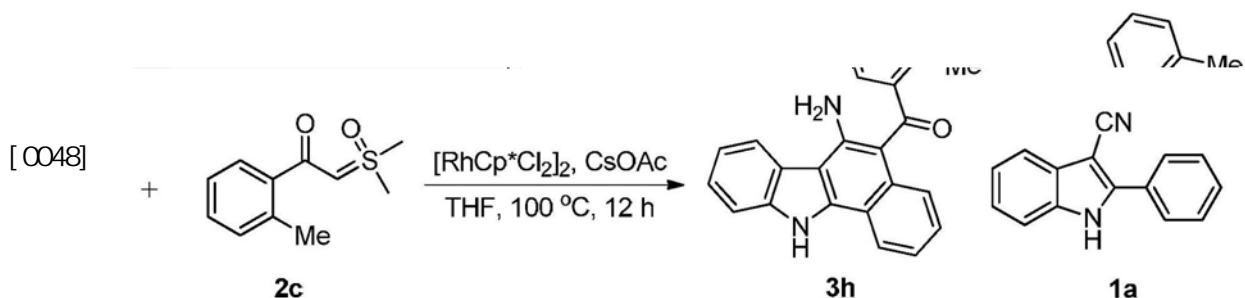
(/ 20/1)

3g

(83.2mg, 45%)

¹H NMR (400MHz, DMSO-d₆): 6.99(s, 2H), 7.16(t, J 7.6Hz, 1H), 7.22(d, J 8.4Hz, 1H), 7.27(d, J 8.4Hz, 1H), 7.31(d, J 7.6Hz, 1H), 7.45(t, J 8.8Hz, 3H), 7.55(d, J 8.0Hz, 2H), 7.71(d, J 8.0Hz, 1H), 8.38(d, J 8.0Hz, 1H), 8.43(d, J 8.4Hz, 1H), 12.55(s, 1H). ¹³C NMR (100MHz, DMSO-d₆): 105.4, 106.9, 111.6, 116.1, 120.1, 121.0, 121.7, 122.1, 122.7, 124.2, 125.7, 126.3, 128.6, 131.0, 132.4, 136.4, 138.5, 138.9, 140.4, 146.4, 195.5. HRMS calcd for C₂₃H₁₆ClN₂O 371.0946 [M+H]⁺, found: 371.0950

[0047] 16



[0049] 15mL 1a (0.5mmol, 109.1mg) (3mL) 2c (0.75mmol, 147.2mg)

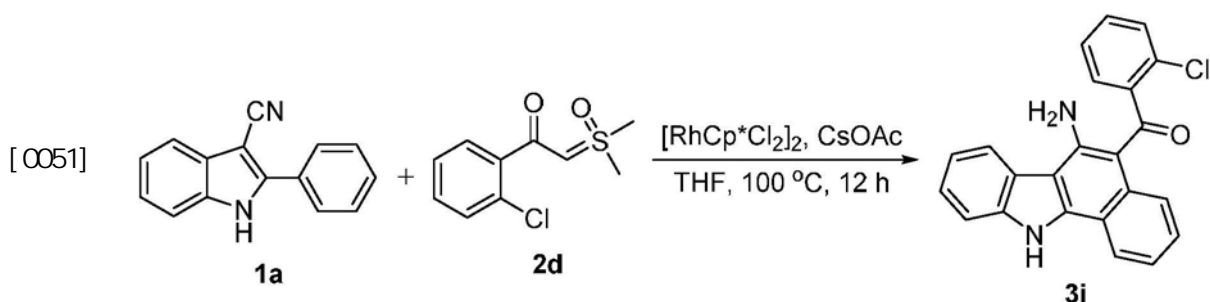
157.7mg) $[\text{RhCp}^*\text{Cl}_2]_2$ (0.025mmol, 15.4mg) (0.25mmol, 48.0mg)
100 12h

10mL (10mL × 3)

(/ 20/1) 3h

(66.6mg, 38) $^1\text{H NMR}$ (600MHz, DMSO-d_6): 2.25(s, 3H), 7.04(t, J 7.2Hz, 1H), 7.09(d, J 6.6Hz, 1H), 7.13(t, J 7.2Hz, 1H), 7.20-7.24(m, 2H), 7.27(d, J 7.8Hz, 1H), 7.31-7.34(m, 2H), 7.46(t, J 7.2Hz, 1H), 7.72(d, J 8.4Hz, 1H), 7.78(s, 2H), 8.35(d, J 7.8Hz, 1H), 8.48(d, J 7.8Hz, 1H), 12.59(s, 1H). $^{13}\text{C NMR}$ (150MHz, DMSO-d_6): 20.2, 106.7, 107.2, 112.2, 117.0, 120.8, 121.4, 122.3, 122.5, 123.4, 124.7, 126.2, 126.3, 126.4, 129.1, 130.1, 131.6, 133.5, 135.8, 139.0, 140.0, 144.2, 149.0, 198.1. HRMS calcd for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}$: 373.1311 $[\text{MNa}]^+$, found: 373.1317

[0050] 17



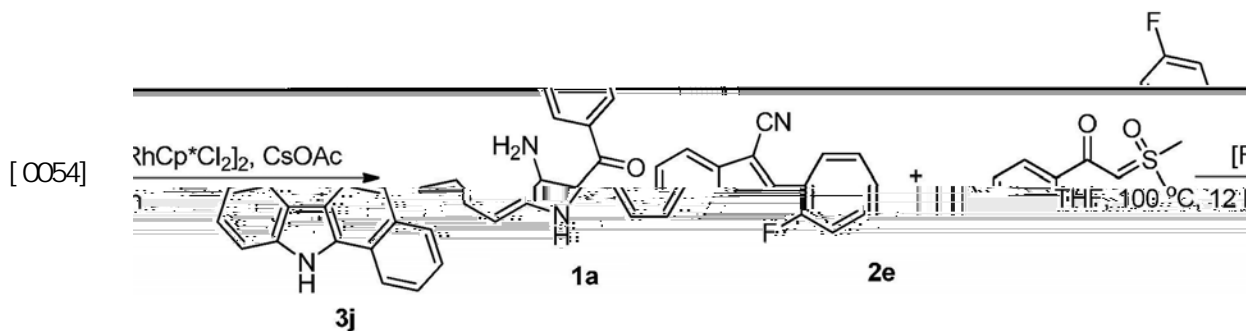
[0052] 15mL 1a (0.5mmol, 109.1mg) (3mL) 2d (0.75mmol, 173.0mg) $[\text{RhCp}^*\text{Cl}_2]_2$ (0.025mmol, 15.4mg) (0.25mmol, 48.0mg)

100 12h

10mL (10mL × 3)

3i

[0053] 18



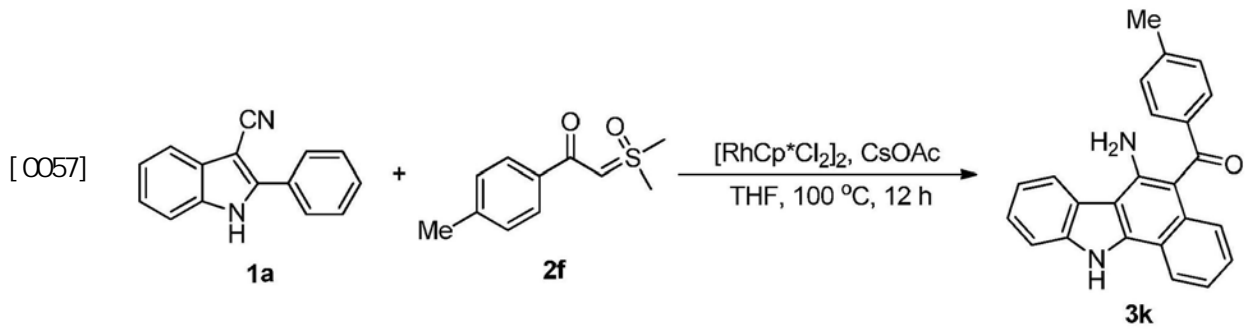
[0055] 15mL 1a (0.5mmol, 109.1mg) (3mL) 2e (0.75mmol, 160.7mg) $[\text{RhCp}^*\text{Cl}_2]_2$ (0.025mmol, 15.4mg) (0.25mmol, 48.0mg)

100 12h

10mL (10mL × 3)

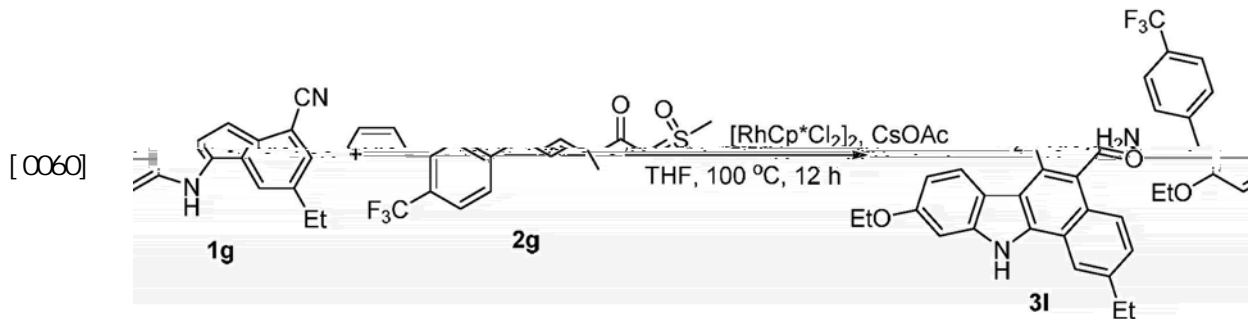
3j

[0056] 19



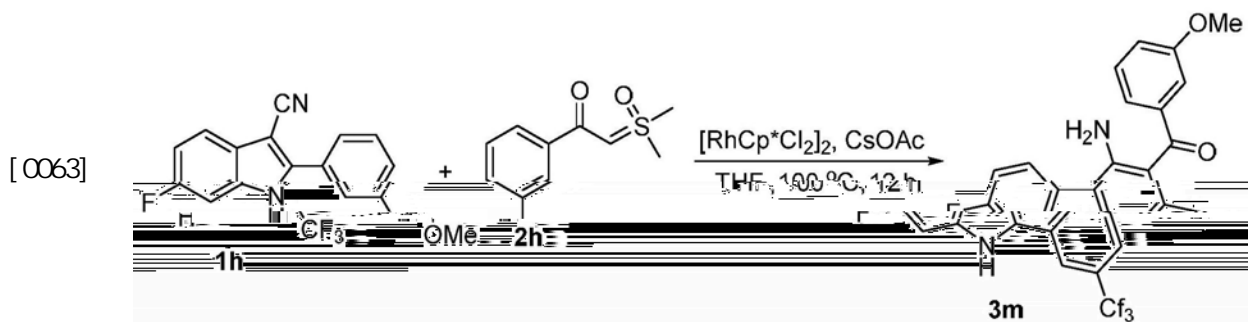
[0058] 15mL 1a (0.5mmol, 109.1mg) (3mL) 2f (0.75mmol, 157.7mg) [RhCp*Cl₂]₂ (0.025mmol, 15.4mg) (0.25mmol, 48.0mg)
100 12h
10mL (10mL × 3)
3k

[0059] 20



[0061] 15mL 1g (0.5mmol, 145.2mg) (3mL) 2g (0.75mmol, 198.2mg) [RhCp*Cl₂]₂ (0.025mmol, 15.4mg) (0.25mmol, 48.0mg)
100 12h
10mL (10mL × 3)
3l

[0062] 21



[0064] 15mL 1h (0.5mmol, 152.1mg) (3mL) 2h (0.75mmol, 169.7mg) [RhCp*Cl₂]₂ (0.025mmol, 15.4mg) (0.25mmol, 48.0mg)
100 12h
10mL (10mL × 3)
3m

[0065]

