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(45) 2020.10.13

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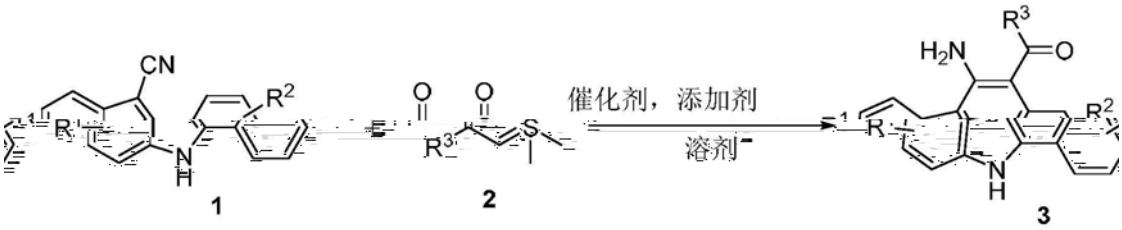
书1 书9

CN 108610278 B

1. 6- -5- [a] ο մե . ... ὶ ضي 2- -3- Ч ش . ... 1 ╕ U ш ѵ ~ ˆ 2 Ỳ. ╕ ė ѵ ╕ 80-120 ὔ └ 6- -5- [a] ο մե . ... 3 ... ὶ



ὶ R^1 C_{1-4} C_{1-4} R^2 C_{1-4} C_{1-4} R^3 ὔ ὔ ὔ C_{1-6} ╕ ضم ժ ً 1 ,2- Ỳ. ╕ ( ) ... (III) ѵ ╕ Ė ... 2. ≠ 1 6- -5- [a] ο մե . ... ὶ ضي 2- -3- Ч ش . ... 1 ˆ 2 Ỳ. ╕ ė ѵ ╕ 1:1-2:0 .025-0 .06:0 .5-1

6- -5- [a]

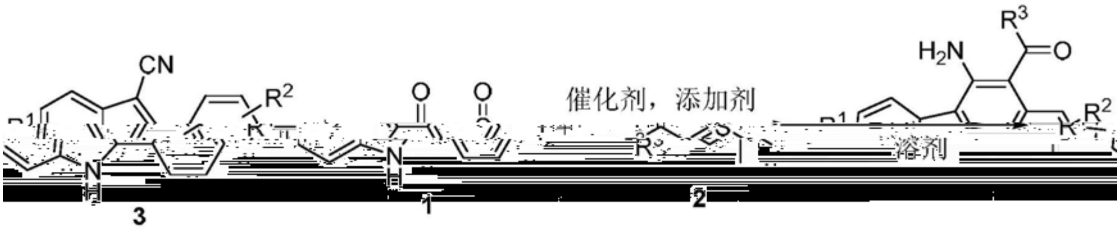
[0001] 6- -5- [a]

[0002] [a] [a] [a] [a] 6- -5- [a] 6- -5- [a]

[0003] 6- -5- [a] 2- -3- Rh(III) 6- -5- [a]

[0004] 6- -5- [a] 2- -3- 1 2 80-120 6- -5- [a] 3

[0005]



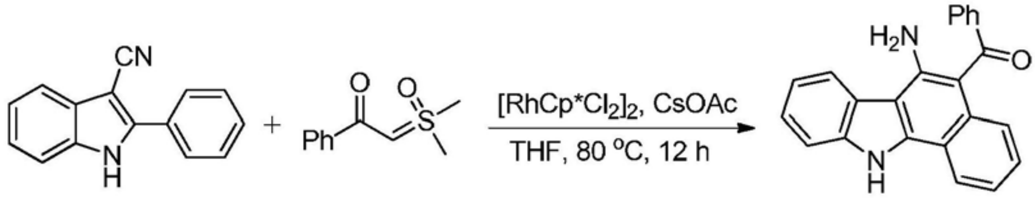
[0006] R^1 C_{1-4} C_{1-4} R^2 C_{1-4} C_{1-4} R^3 C_{1-6} 1,2- ( ) (III) ($[RhCp^*Cl_2]_2$)

[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] 4

[0010] 1

[0011] 

1a 2a 3a

[0012] 15mL 1a(0.5mmol,109.1mg) (3mL) 2a(0.75mmol,147.2mg) ( ) (III) ([RhCp*Cl$_2$]$_2$,0.025mmol,15.4mg) (0.25mmol,48.0mg) 80 12h 10mL (10mL×3) (/ 20/1) 3a(63.9mg,38) . ^{1}H NMR (400MHz,CDCl$_3$):δ6.91(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).^{13}C NMR(100MHz,CDCl$_3$):δ105.8,107.0,111.5,116.0,120.0,121.0,121.6,122.0,122.7,124.1,125.6,126.2,128.5,129.1,131.8,132.5,138.5,138.7,141.6,146.0,197.1.HRMS calcd for $C_{23}H_{16}N_2ONa$:359.1155[M+Na]$^+$,found:359.1154

[0013] 2

[0014] 15mL 1a(0.5mmol,109.1mg) (3mL) 2a(0.75mmol,147.2mg) [RhCp*Cl$_2$]$_2$(0.025mmol,15.4mg) (0.25mmol,48.0mg) (0.25mmol,85.9mg) 80 12h 10m? 2

147 .2mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) (0 .25mmol ,48 .0mg) غ ´E
(0 .25mmol ,85 .9mg) ضي ï U 80 ï 12h ï
U ï ' ↓ ₰ ~ 10mL U ŭ (10mL × 3) U
غ غ ш № (/
20/1) ﻫ 3a(55 .5mg ,33)

[0017] 4

[0018] ضي15mL ï ш ₰ ~ 1a(0 .5mmol ,109 .1mg) (3mL) 2a(0 .75mmol ,
147 .2mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي
ï U 80 ï 12h ï U ï ' ↓ ₰ ~
10mL U ŭ (10mL × 3) U غ غ ш
№ (/ 20/1) ﻫ 3a
(45 .4mg ,27)

[0019] 5

[0020] ضي15mL ï ш ₰ ~ 1a(0 .5mmol ,109 .1mg) (3mL) 2a(0 .75mmol ,
147 .2mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي
ï U 80 ï 12h ï U ï ' ↓ ₰ ~
10mL U ŭ (10mL × 3) U غ غ ш
№ (/ 20/1) ﻫ 3a
(57 .2mg ,34)

[0021] 6

[0022] ضي15mL ï ш ₰ ~ 1a(0 .5mmol ,109 .1mg) ضم ơ ً (3mL) 2a(0 .75mmol ,
147 .2mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي
ï U 100 ï 12h ï U ï ' ↓ ₰ ~
10mL U ŭ (10mL × 3) U غ غ ш
№ (/ 20/1) ﻫ 3a
(70 .6mg ,42)

[0023] 7

[0024] ضي15mL ï ш ₰ ~ 1a(0 .5mmol ,109 .1mg) ضم ơ ً (3mL) 2a(0 .75mmol ,
147 .2mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي
ï U 120 ï 12h ï U ï ' ↓ ₰ ~
10mL U ŭ (10mL × 3) U غ غ ш
№ (/ 20/1) ﻫ 3a
(65 .6mg ,39)

[0025] 8

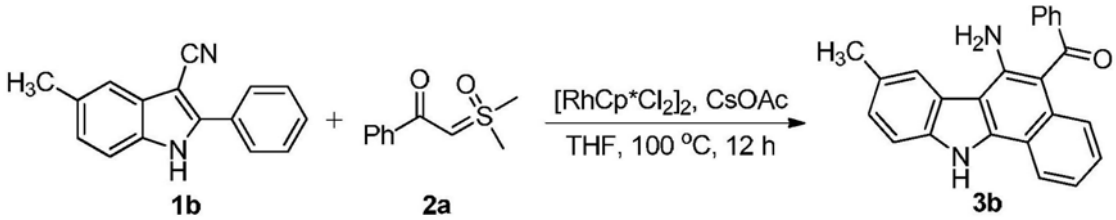
[0026] ضي15mL ï ш ₰ ~ 1a(0 .5mmol ,109 .1mg) ضم ơ ً (3mL) 2a(0 .5mmol ,
98 .1mg) [RhCp*Cl2]2(0 .03mmol ,18 .5mg) غ (0 .5mmol ,96 .0mg) ضي ï
U 100 ï 12h ï U ï ' ↓ ₰ ~
10mL U ŭ (10mL × 3) U غ غ ш
№ (/ 20/1) ﻫ 3a

(62.2mg,37)

[0027] 9

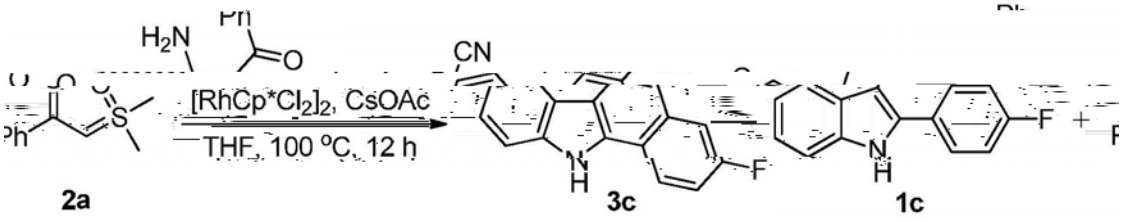
[0028] ضي15mL ǐ ч ѵ ~ 1a(0.5mmol,109.1mg) ضم ժ ً (3mL) 2a(1mmol, 196.2mg) [RhCp*Cl2]2(0.0125mmol,7.7mg) غ (0.5mmol,96.0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ㄴ ѵ ~ 10mL U ŭ (10mL×3) U غ غ ч № (/ 20/1) ﻫ 3a (52.1mg,31)

[0029] 10

[0030] 

[0031] ضي15mL ǐ ч ѵ ~ 1b(0.5mmol,116.1mg) ضم ժ ً (3mL) 2a(0.75mmol, 147.2mg) [RhCp*Cl2]2(0.025mmol,15.4mg) غ (0.25mmol,48.0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ㄴ ѵ ~ 10mL U ŭ (10mL×3) U غ غ ч № (/ 20/1) ﻫ 3b (71.8mg,41) . ... ^{1}H NMR(600MHz,DMSO-d_6):δ2.53(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). ^{13}C NMR(150MHz,DMSO-d_6):δ21.8,106.1,107.2,111.7, 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 $C_{24}H_{18}N_2ONa$:373.1311[M+Na]$^+$, found:373.1319

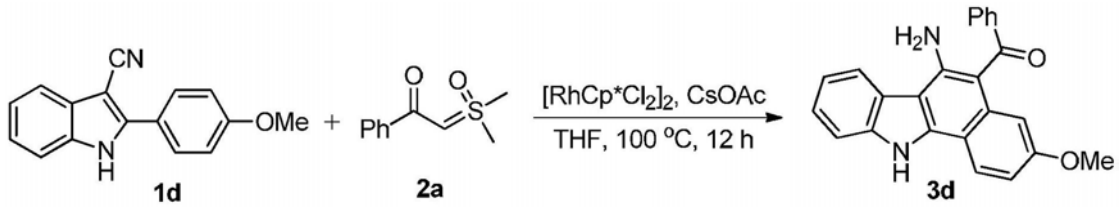
[0032] 11

[0033] 

[0034] ضي15mL ǐ ч ѵ ~ 1c(0.5mmol,118.1mg) ضم ժ ً (3mL) 2a(0.75mmol, 147.2mg) [RhCp*Cl2]2(0.025mmol,15.4mg) غ (0.25mmol,48.0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ㄴ ѵ ~ 10mL U ŭ (10mL×3) U غ غ ч № (/ 20/1) ﻫ 3c (77.8mg,44) . ... ^{1}H NMR(600MHz,DMSO-d_6):δ6.84(dd,J_1 8.4Hz,J_2 2.4Hz,1H),7.06(s,2H),7.16(td,J_1 8.4Hz,J_2 2.4Hz,1H),7.31(t,J

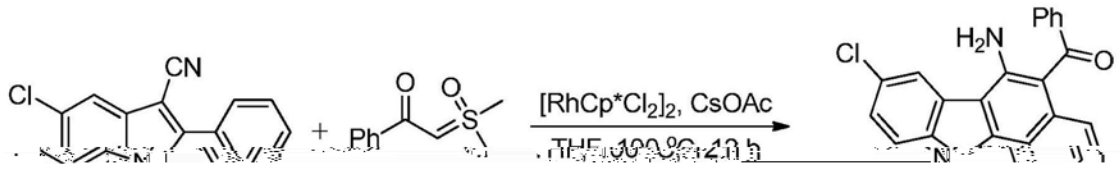
7 .8Hz ,1H) ,7 .44-7 .46(m ,3H) ,7 .56-7 .58(m ,3H) ,7 .70(d ,J 8 .4Hz ,1H) ,8 .41-8 .43(m , 2H) ,12 .57(s ,1H) .^{13}C NMR(150MHz ,DMSO-d_6) :δ105 .7(d ,$^{3}J_{C-F}$ 3 .3Hz) ,107 .0 ,110 .8 , 111 .0(d ,$^{3}J_{C-F}$ 3 .3Hz) ,112 .0 ,113 .5 ,120 .7 ,121 .4 ,123 .2 ,124 .7 ,125 .1(d ,$^{2}J_{C-F}$ 9 .8Hz) , 129 .1 ,129 .6 ,132 .4 ,134 .6(d ,$^{2}J_{C-F}$ 9 .8Hz) ,138 .9 ,139 .2 ,141 .9 ,118 .0 ,160 .5(d ,$^{1}J_{C-F}$ 239 .6Hz) ,197 .3 .^{19}F NMR(377MHz ,DMSO)δ: -113 .7 .HRMS calcd for $C_{23}H_{15}FN_2ONa$: 377 .1061[M+Na]$^+$,found:377 .1063

[0035] 12

[0036] 

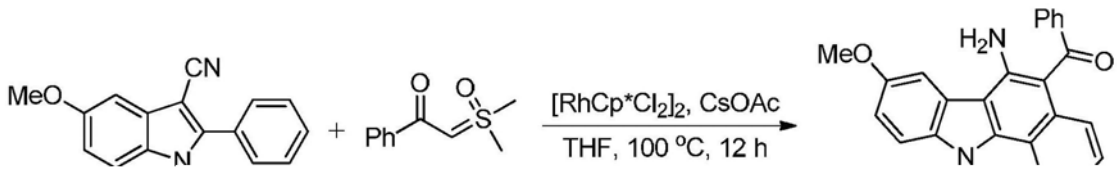
[0037] ضي15mL ǐ ч ѵ ~ 1d(0 .5mmol ,124 .1mg) ضم ժ ً (3mL) 2a(0 .75mmol , 147 .2mg) [RhCp*Cl_2]$_2$(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ㄴ ѵ ~ 10mL U ŭ (10mL × 3) U غ غ ч № (/ 20/1) ﻫ 3d (91 .4mg ,50) . ... ^{1}H NMR(600MHz ,DMSO-d_6) :δ3 .30(s ,3H) ,6 .61 (d ,J 2 .4Hz ,1H) ,6 .91(dd ,J_1 8 .4Hz ,J_2 2 .4Hz ,1H) ,7 .23(s ,2H) ,7 .29(t ,J 7 .8Hz , 1H) ,7 .40-7 .44(m ,3H) ,7 .51-7 .54(m ,3H) ,7 .67(d ,J 7 .8Hz ,1H) ,8 .27(d ,J 9 .0Hz ,1H) , 8 .39(d ,J 7 .8Hz ,1H) ,12 .42(s ,1H) .^{13}C NMR(150MHz ,DMSO-d_6) :δ54 .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 $C_{24}H_{18}N_2NaO_2$:389 .1260 [M+Na]$^+$,found:389 .1260

[0038] 13

[0039] 

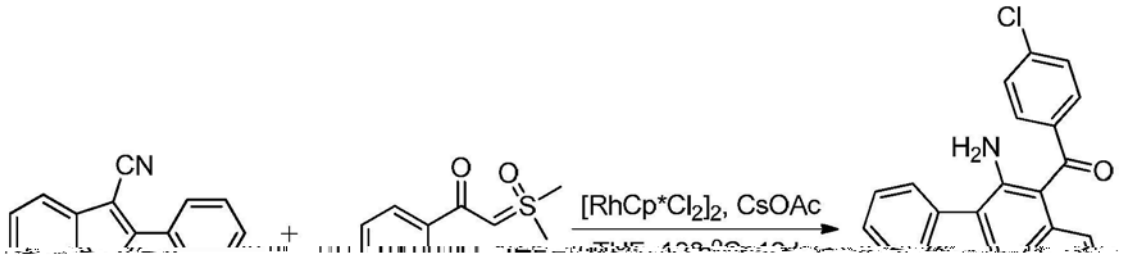
[0040] ضي15mL ǐ ч ѵ ~ 1e(0 .5mmol ,126 .4mg) ضم ժ ً (3mL) 2a(0 .75mmol , 147 .2mg) [RhCp*Cl_2]$_2$(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ㄴ ѵ ~ 10mL U ŭ (10mL × 3) U غ غ ч № ⌠ 3e

[0041] 14

[0042] 

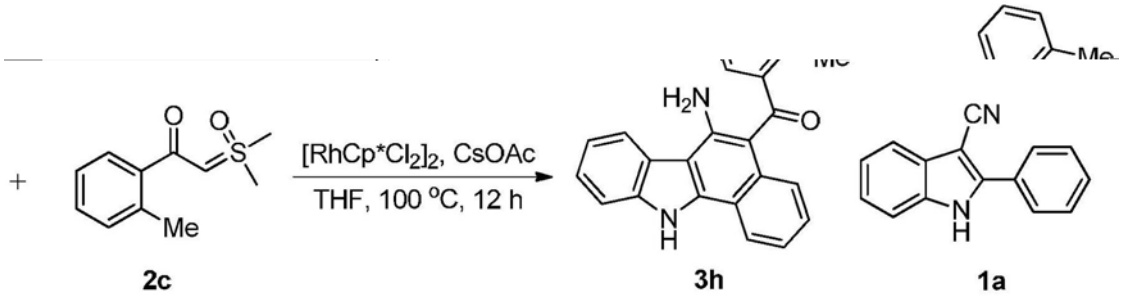
[0043] ضي15mL ǐ ч ѵ ~ 1f(0 .5mmol ,124 .1mg) ضم ժ ً (3mL) 2a(0 .75mmol , 147 .2mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ч ѵ ~ 10mL U ŭ (10mL × 3) U غ غ ч № ⌠ 3f

[0044] 15

[0045] 

[0046] ضي15mL ǐ ч ѵ ~ 1a(0 .5mmol ,109 .1mg) ضم ժ ً (3mL) 2b(0 .75mmol , 173 .0mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ч ѵ ~ 10mL U ŭ (10mL × 3) U غ غ ч № (/ 20/1) ڡ 3g (83 .2mg ,45) . ... ^{1}H NMR(400MHz ,DMSO-d_6) :δ6 .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) .^{13}C NMR(100MHz ,DMSO-d_6) :δ105 .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 $C_{23}H_{16}ClN_2O$:371 .0946[M +H]$^{+}$,found:371 .0950

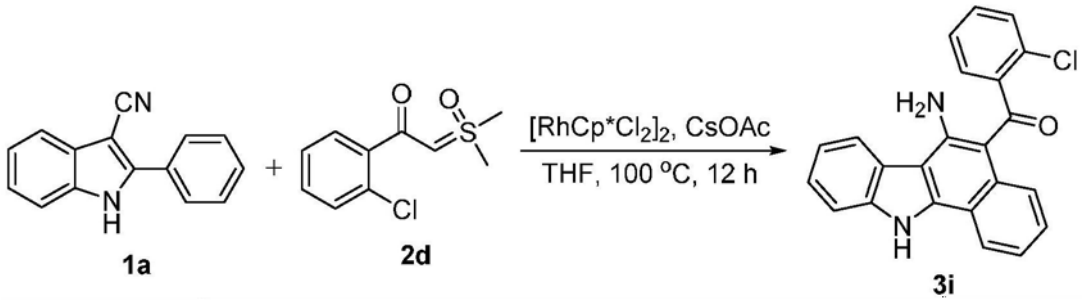
[0047] 16

[0048] 

[0049] ضي15mL ǐ ч ѵ ~ 1a(0 .5mmol ,109 .1mg) ضم ժ ً (3mL) 2c(0 .75mmol ,

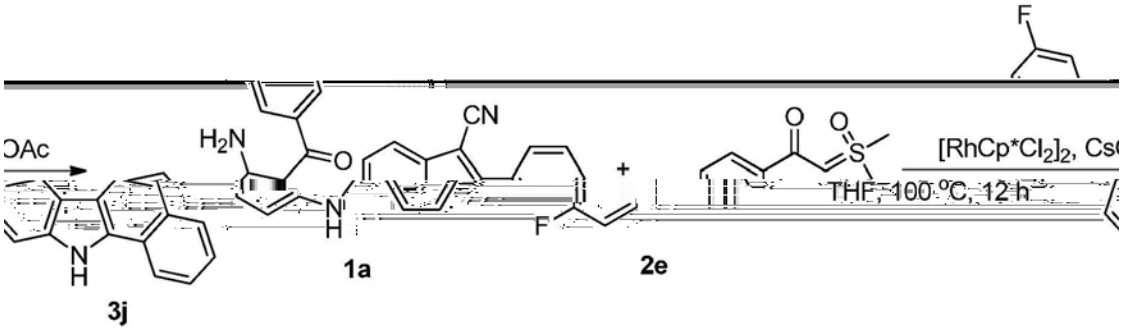
157 .7mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي
ّ U 100 ّ 12h ّ U ّ ' ل ٧ ~
10mL U ُّ (10mL × 3) U غ غ ش
№ (/ 20/1) ٿ 3h
(66 .6mg ,38) . ... 1H NMR(600MHz ,DMSO-d6) :δ2 .25(s ,3H) ,7 .04
(t ,J 7 .2Hz ,1H) ,7 .09(d ,J 6 .6Hz ,1H) ,7 .13(t ,J 7 .2Hz ,1H) ,7 .20-7 .24(m ,2H) ,7 .27
(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) .13C NMR(150MHz ,
DMSO-d6) :δ20 .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 C24H18N2ONa:373 .1311[M+Na]+ ,found:373 .1317

[0050] 17

[0051] 

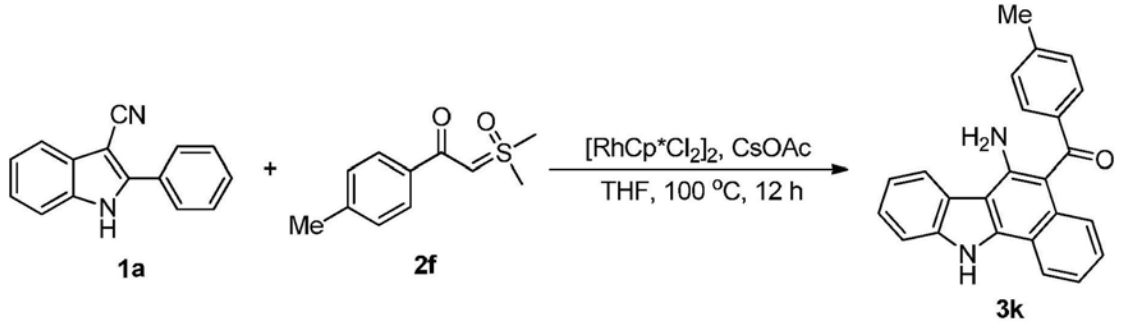
[0052] ضي15mL ّ ش ٧ ~ 1a(0 .5mmol ,109 .1mg) ضه ك ً (3mL) 2d(0 .75mmol ,
173 .0mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي
ّ U 100 ّ 12h ّ U ّ ' ل ٧ ~
10mL U ُّ (10mL × 3) U غ غ ش
№ ∫ 3i

[0053] 18

[0054] 

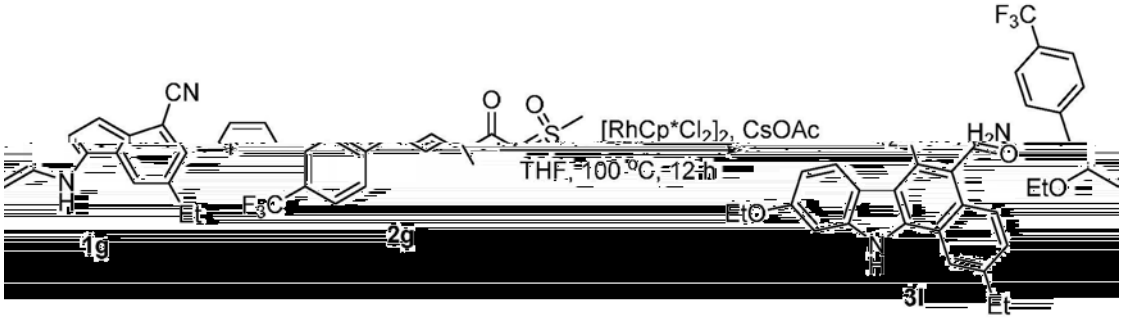
[0055] ضي15mL ّ ش ٧ ~ 1a(0 .5mmol ,109 .1mg) ضه ك ً (3mL) 2e(0 .75mmol ,
160 .7mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي
ّ U 100 ّ 12h ّ U ّ ' ل ٧ ~
10mL U ُّ (10mL × 3) U غ غ ش
№ ∫ 3j

[0056] 19

[0057] 

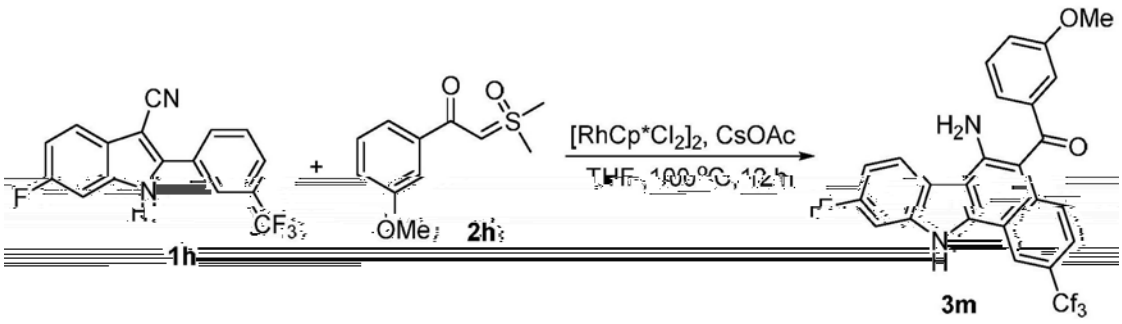
[0058] ضي15mL ǐ ч ѵ ~ 1a(0 .5mmol ,109 .1mg) ضم ժ ً (3mL) 2f(0 .75mmol , 157 .7mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ㄴ ѵ ~ 10mL U ŭ (10mL × 3) U غ غ ч № ⌡ 3k

[0059] 20

[0060] 

[0061] ضي15mL ǐ ч ѵ ~ 1g(0 .5mmol ,145 .2mg) ضم ժ ً (3mL) 2g(0 .75mmol , 198 .2mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ㄴ ѵ ~ 10mL U ŭ (10mL × 3) U غ غ ч № ⌡ 3l

[0062] 21

[0063] 

[0064] ضي15mL ǐ ч ѵ ~ 1h(0 .5mmol ,152 .1mg) ضم ժ ً (3mL) 2h(0 .75mmol , 169 .7mg) [RhCp*Cl2]2(0 .025mmol ,15 .4mg) غ (0 .25mmol ,48 .0mg) ضي ǐ U 100 ǐ 12h ǐ U ǐ ' ㄴ ѵ ~ 10mL U ŭ (10mL × 3) U غ غ ч № ⌡ 3m

[0065] ŭ ⁄ ǐ 2