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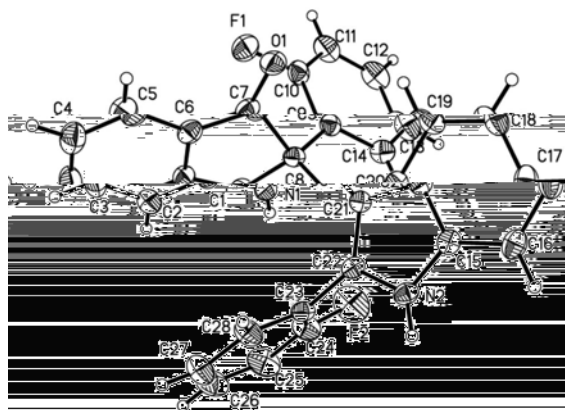
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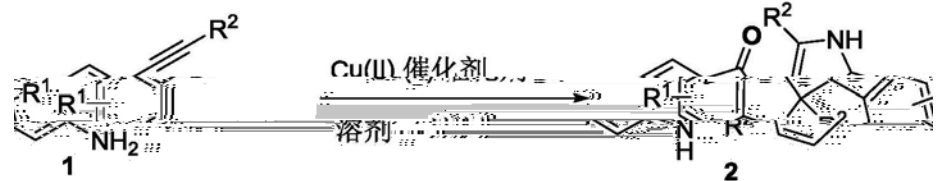
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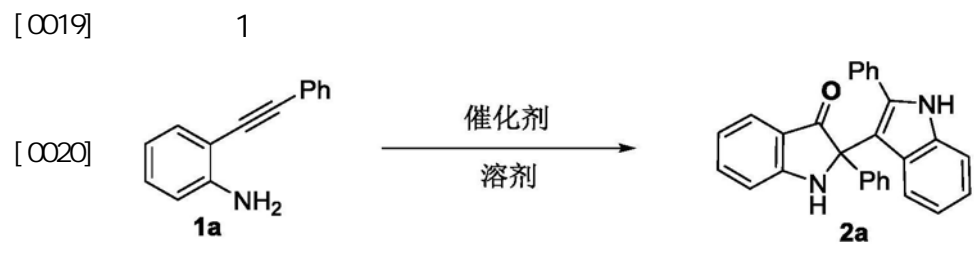


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[0009]	(HFIP) 1, 2	(DCE)		(TFE)	(HFIP)
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[0010]		{Cu(OAc) ₂ · H ₂ O}		{CuCl ₂ · 2H ₂ O}	{Cu(OAc) ₂ }
[0011]		(m CPBA)		(TBHP)	
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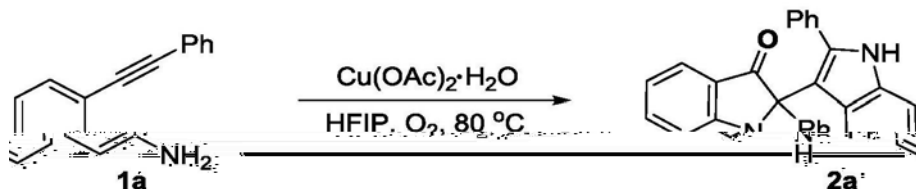
序号	催化剂	额外条件	温度(°C)	溶剂	产率(%) ^b	
1	Cu(OAc) ₂		80	HFIP	42	
2	Cu(OAc) ₂		80	TFE	32	
3	Cu(OAc) ₂		80	MeOH	trace	
4	Cu(OAc) ₂		80	DCE	15	
5	Cu(OAc) ₂		80	THF	trace	
6	Cu(OAc) ₂		80	dioxane	trace	
7	Cu(OAc) ₂ ·H ₂ O		80	HFIP	53	
8	CuCl ₂ ·2H ₂ O		80	HFIP	22	
9	CuBr ₂		80	HFIP	trace	
[0024] trace	10	Cu(OTf) ₂		80	HFIP	
trace	11	CuSO ₄		80	HFIP	
28	12	Cu(OAc) ₂ ·H ₂ O	<i>m</i> -CPBA ^c	80	HFIP	
24	13	Cu(OAc) ₂ ·H ₂ O	TBHP ^c	80	HFIP	
26	14 ^d	Cu(OAc) ₂ ·H ₂ O		80	HFIP	
36	15 ^e	Cu(OAc) ₂ ·H ₂ O		80	HFIP	
61	16	Cu(OAc) ₂ ·H ₂ O	O ₂	80	HFIP	
23	17	Cu(OAc) ₂ ·H ₂ O	O ₂	60	HFIP	
P	41	18	Cu(OAc) ₂ ·H ₂ O	O ₂	100	HFIP

^a mCPBA, 20 min, 0.15 mmol; ^b 产率; ^c 0.3 mmol; ^d 催化剂(0.0075 mmol); ^e 催化剂(0.03 mmol)。

[0025]

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[0026]



[0027]

15mL 1a (57.9mg, 0.3mmol) (3.0mg, 0.015mmol) (2mL) 80

20h (/ 5/1)

2a (36.6mg, 61%) ¹H NMR(400MHz, DMSO d₆): 6.61

(d, J = 8.0Hz, 1H), 6.70-6.77(m 2H), 6.98(d, J = 8.4Hz, 1H), 7.01-7.07(m 6H), 7.12-7.17(m 3H), 7.25(d, J = 7.6Hz, 1H), 7.34(d, J = 8.4Hz, 1H), 7.38-7.40(m 2H), 7.51(t, J = 7.6Hz, 1H), 8.33(s, 1H), 11.34(s, 1H). ¹³C NMR(150MHz, DMSO d₆): 71.6, 111.5, 111.7, 112.4, 118.0, 118.9, 119.1, 120.8, 121.6, 124.9, 127.46, 127.51, 127.6, 127.8, 127.9, 128.1, 130.0, 133.7, 136.3, 138.0, 138.5, 140.3, 160.6, 201.0. HRMS calcd for C₂₈H₂₀N₂O 423.1468[MNa]⁺, found: 423.1466.

[0028]

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[0029]

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[0030]

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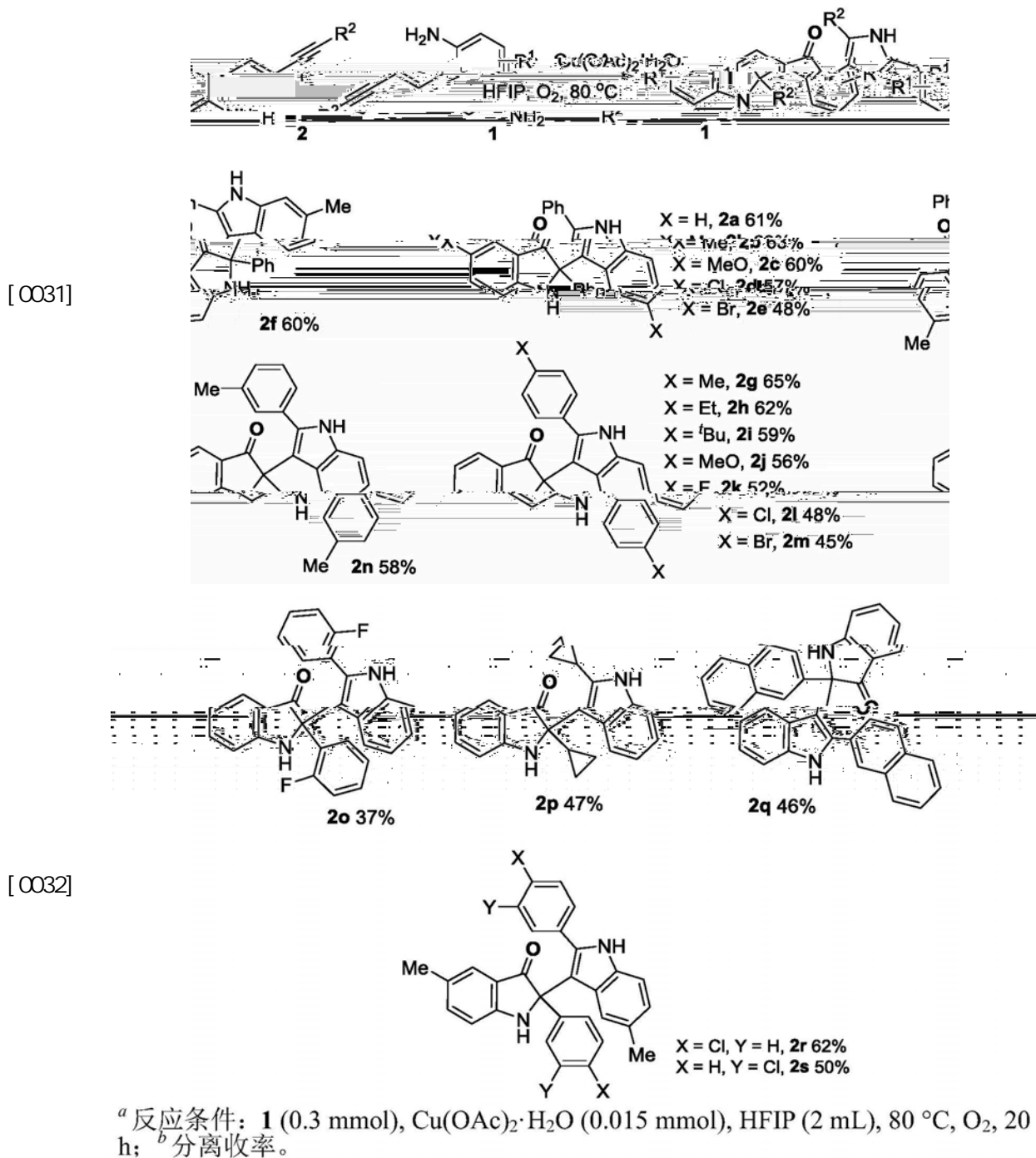
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a, b



[0033]

[0034] 5 Methyl 2 (5 methyl 2 phenyl 1H indol 3 yl) 2 phenyl indolin 3 one (2b)

[0035] Yellow solid (40.5 mg, 63%). ¹H NMR (600 MHz, DMSO-*d*₆): 2.11 (s, 3H), 2.22 (s, 3H), 6.40 (s, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 7.03–7.06 (m, 6H), 7.11–7.15 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.35–7.37 (m, 3H), 8.06 (s, 1H), 11.18 (s, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆): 20.6, 22.0, 72.1, 111.2, 111.4, 112.4, 119.2, 120.6, 123.1, 124.0, 126.9, 127.2, 127.3, 127.5, 127.7, 128.0, 128.2, 130.0, 133.9, 134.7, 138.4, 139.3, 140.7, 159.1, 201.0. HRMS calcd for C₃₀H₂₄N₂O 451.1781 [MNa]⁺, found: 451.1776.

[0036] 5 Methoxy 2 (5 methoxy 2 phenyl 1H indol 3 yl) 2 phenyl indol in 3 one (2c)

[0037] Yellow solid (41.4mg, 60). $^1\text{H NMR}$ (600MHz, DMSO d_6): 3.38(s, 3H), 3.67(s, 3H), 6.01(d, J 1.8Hz, 1H), 6.67 6.70(m 2H), 6.97(d, J 9.0Hz, 1H), 7.05(t, J 7.8Hz, 2H), 7.08 7.10(m 3H), 7.13 7.15(m 3H), 7.22(dd, J₁ 9.0Hz, J₂ 3.6Hz, 2H), 7.43 7.44(m 2H), 7.94(s, 1H), 11.18(s, 1H). $^{13}\text{C NMR}$ (150MHz, DMSO d_6): 55.2, 56.1, 72.5, 103.2, 105.0, 111.2, 111.6, 112.2, 114.1, 119.3, 127.4, 127.57, 127.62, 127.8, 128.0, 128.1, 128.4, 129.9, 131.5, 133.8, 138.8, 140.7, 152.7, 153.1, 156.5, 201.1. HRMS cal cd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{NaO}$ 483.1679[MNa]⁺, found: 483.1676.

[0038] 5 Chloro 2 (5 chloro 2 phenyl 1H indol 3 yl) 2 phenyl indol in 3 one (2d)

[0039] Yellow solid (40.0mg, 57). $^1\text{H NMR}$ (600MHz, DMSO d_6): 6.42(s, 1H), 6.99(d, J 8.4Hz, 1H), 7.05(dd, J₁ 8.4Hz, J₂ 1.2Hz, 1H), 7.11(t, J 7.2Hz, 2H), 7.16 7.19(m 6H), 7.22(t, J 7.2Hz, 1H), 7.36(d, J 8.4Hz, 1H), 7.39 7.40(m 2H), 7.53(dd, J₁ 9.0Hz, J₂ 1.8Hz, 1H), 8.60(s, 1H), 11.66(s, 1H). $^{13}\text{C NMR}$ (150MHz, DMSO d_6): 72.2, 111.0, 113.3, 114.1, 119.8, 121.7, 121.8, 123.8, 127.4, 127.8, 128.0, 128.4, 128.5, 128.9, 130.0, 133.1, 134.7, 137.8, 139.7, 140.0, 158.8, 199.5. HRMS cal cd for $\text{C}_{28}\text{H}_{18}\text{Cl}_2\text{N}_2\text{NaO}$ 491.0688[MNa]⁺, found: 491.0680.

[0040] 6 Methyl 2 (6 methyl 2 phenyl 1H indol 3 yl) 2 phenyl indol in 3 one (2f)

[0041] Yellow solid (38.5mg, 60). $^1\text{H NMR}$ (400MHz, DMSO d_6): 2.33(s, 3H), 2.35(s, 3H), 6.49(d, J 8.4Hz, 1H), 6.54(d, J 8.0Hz, 1H), 6.58(d, J 8.0Hz, 1H), 6.77(s, 1H), 7.02 7.06(m 5H), 7.10 7.15(m 5H), 7.34 7.36(m 2H), 8.23(s, 1H), 11.15(s, 1H). $^{13}\text{C NMR}$ (100MHz, DMSO d_6): 21.7, 22.6, 71.8, 111.39, 111.43, 112.1, 116.8, 119.7, 120.6, 120.8, 124.7, 125.9, 127.3, 127.48, 127.53, 127.6, 127.9, 130.0, 130.6, 133.8, 136.7, 137.7, 140.6, 148.8, 160.9, 200.1. HRMS cal cd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{NaO}$ 451.1781[MNa]⁺, found: 451.1781.

[0042] 2 (4 Ethyl phenyl) 2 (2 (4 ethyl phenyl) 1H indol 3 yl) indol in 3 one (2h)

[0043] Yellow solid (42.4mg, 62). $^1\text{H NMR}$ (600MHz, DMSO d_6): 1.04(t, J 7.8Hz, 3H), 1.11(t, J 7.8Hz, 3H), 2.42(q, J 7.8Hz, 2H), 2.49(q, J 7.8Hz, 2H), 6.63(d, J 8.4Hz, 1H), 6.70(t, J 7.2Hz, 1H), 6.75(t, J 7.8Hz, 1H), 6.84 6.87(m 4H), 6.96(d, J 8.4Hz, 1H), 7.00 7.04(m 3H), 7.26(d, J 8.4Hz, 3H), 7.32(d, J 8.4Hz, 1H), 7.50(t, J 7.2Hz, 1H), 8.28(s, 1H), 11.25(s, 1H). $^{13}\text{C NMR}$ (150MHz, DMSO d_6): 16.10, 16.11, 28.2, 28.4, 71.5, 111.4, 111.6, 112.3, 117.8, 118.9, 119.1, 120.7, 121.5, 124.9, 126.9, 127.3, 127.6, 127.9, 130.0, 131.0, 136.1, 137.3, 137.9, 138.7, 142.8, 143.2, 160.5, 201.3. HRMS cal cd for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{NaO}$ 479.2094[MNa]⁺, found: 479.2094.

[0044] 2 (4 (tert Butyl) phenyl) 2 (2 (4 (tert butyl) phenyl) 1H indol 3 yl) indol in 3 one (2i)

[0045] Yellow solid (45.3mg, 59%). $^1\text{H NMR}$ (400MHz, DMSO d_6): 1.14(s, 9H), 1.20(s, 9H), 6.65-6.71(m, 2H), 6.75(t, J = 7.6Hz, 1H), 6.95(d, J = 8.4Hz, 1H), 7.00-7.06(m, 5H), 7.10(d, J = 8.0Hz, 2H), 7.26-7.33(m, 4H), 7.49(t, J = 7.2Hz, 1H), 8.25(s, 1H), 11.25(s, 1H). $^{13}\text{C NMR}$ (150MHz, DMSO d_6): 31.5, 31.6, 34.4, 34.6, 71.5, 111.5, 111.6, 112.3, 117.8, 118.9, 119.1, 120.7, 121.4, 124.1, 124.6, 124.9, 127.2, 127.8, 129.9, 130.7, 136.1, 136.9, 137.9, 138.9, 149.7, 149.9, 160.8, 201.5. HRMS calcd for $\text{C}_{36}\text{H}_{36}\text{N}_2\text{NaO}$ 535.2720 [MNa] $^+$, found: 535.2704.

[0046] 2-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-1H-indol-3-yl)indolin-3-one (2k)

[0047] Yellow solid (34.0mg, 52%). $^1\text{H NMR}$ (600MHz, DMSO d_6): 6.68(d, J = 8.4Hz, 1H), 6.75(t, J = 7.2Hz, 1H), 6.80(t, J = 7.8Hz, 1H), 6.87(t, J = 9.0Hz, 2H), 6.92(t, J = 8.4Hz, 2H), 6.98(d, J = 8.4Hz, 1H), 7.06(t, J = 7.8Hz, 1H), 7.17-7.20(m, 2H), 7.33(d, J = 7.8Hz, 1H), 7.35(d, J = 8.4Hz, 1H), 7.37-7.40(m, 2H), 7.53(t, J = 7.8Hz, 1H), 8.38(s, 1H), 11.40(s, 1H). $^{13}\text{C NMR}$ (150MHz, DMSO d_6): 71.0, 111.76, 111.81, 112.5, 114.4(d, $^2\text{J}_{\text{CF}}$ 21.9Hz), 114.8(d, $^2\text{J}_{\text{CF}}$ 20.7Hz), 118.3, 118.7, 119.4, 120.5, 121.9, 125.0, 127.5, 129.5(d, $^3\text{J}_{\text{CF}}$ 7.7Hz), 130.0(d, $^4\text{J}_{\text{CF}}$ 3.3Hz), 132.2(d, $^3\text{J}_{\text{CF}}$ 8.7Hz), 136.1, 137.6, 138.3, 160.7, 161.9(d, $^1\text{J}_{\text{CF}}$ 242.9Hz), 162.0(d, $^1\text{J}_{\text{CF}}$ 243.9Hz), 201.2. $^{19}\text{F NMR}$ (376MHz, DMSO d_6): 114.4-114.5(m), 116.1-116.2(m). HRMS calcd for $\text{C}_{28}\text{H}_{19}\text{F}_2\text{N}_2\text{O}$ 437.1460 [MH] $^+$, found: 437.1451.

[0048] 2-(4-bromophenyl)-2-(2-(4-bromophenyl)-1H-indol-3-yl)indolin-3-one (2m)

[0049] Yellow solid (37.5mg, 45%). $^1\text{H NMR}$ (600MHz, DMSO d_6): 6.69(d, J = 7.8Hz, 1H), 6.77(t, J = 7.8Hz, 1H), 6.82(t, J = 7.8Hz, 1H), 6.99(d, J = 8.4Hz, 1H), 7.06-7.08(m, 3H), 7.24(d, J = 8.4Hz, 2H), 7.27-7.30(m, 4H), 7.33(d, J = 7.8Hz, 1H), 7.36(d, J = 8.4Hz, 1H), 7.53-7.56(m, 1H), 8.41(s, 1H), 11.45(s, 1H). u

6.69(t, J 7.2, 1H), 6.80-6.83(m 1H), 6.89-6.93(m 1H), 6.94(t, J 7.8, 1H), 6.98-7.02(m 2H), 7.03-7.07(m 2H), 7.17-7.20(m 2H), 7.25-7.29(m 1H), 7.30-7.32(m 2H), 7.38-7.42(m 2H), 7.69(s, 1H), 11.34(s, 1H). ^{13}C NMR(150MHz, DMSO d_6): 69.7, 110.4, 111.6, 112.3, 115.2(d, $^2J_{\text{CF}}$ 20.7Hz), 116.4(d, $^2J_{\text{CF}}$ 21.9Hz), 117.9, 118.3, 119.1, 121.3, 121.6(d, $^2J_{\text{CF}}$ 15.3Hz), 121.9, 123.5(d, $^4J_{\text{CF}}$ 3.2Hz), 124.1(d, $^4J_{\text{CF}}$ 2.3Hz), 124.8, 126.5, 127.3(d, $^2J_{\text{CF}}$ 12.0Hz), 129.2(d, $^4J_{\text{CF}}$ 3.3Hz), 130.2(d, $^3J_{\text{CF}}$ 7.7Hz), 130.5(d, $^3J_{\text{CF}}$ 7.7Hz), 130.8, 133.1, 136.4, 137.8, 159.8(d, $^1J_{\text{CF}}$ 243.9Hz), 160.5, 161.6(d, $^1J_{\text{CF}}$ 247.2Hz), 200.3. ^{19}F NMR(565MHz, DMSO d_6): 112.4(s), 107.7(s). HRMS cal cd for $\text{C}_{28}\text{H}_{18}\text{F}_2\text{N}_2\text{NaO}$ 459.1279[MNa] $^+$, found: 459.1272.

[0054] 2-Cyclopropyl-2-(2-cyclopropyl-1H-indol-3-yl)indolin-3-one(2p)

[0055] Yellow solid(23.1mg, 47%). ^1H NMR(400MHz, DMSO d_6): 0.02-0.08(m 1H), 0.33-0.39(m 1H), 0.68-0.74(m 2H), 0.81(d, J 8.0Hz, 2H), 0.85-0.88(m 2H), 1.77-1.83(m 1H), 2.19-2.26(m 1H), 6.70(t, J 7.6Hz, 1H), 6.75-6.80(m 2H), 6.94(t, J 8.0Hz, 1H), 7.20-7.25(m 2H), 7.38(s, 1H), 7.44-7.47(m 2H), 10.54(s, 1H). ^{13}C NMR(150MHz, DMSO d_6): 1.0, 4.6, 8.0, 8.3, 9.7, 16.8, 68.1, 110.7, 111.3, 111.5, 117.3, 119.1, 119.5, 119.8, 120.5, 124.6, 128.0, 134.9, 137.8, 139.3, 161.4, 204.2. HRMS cal cd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{NaO}$ 351.1468[MNa] $^+$, found: 351.1466.

[0056] 2-(Naphthalen-2-yl)-2-(2-(naphthalen-2-yl)-1H-indol-3-yl)indolin-3-one(2q)

[0057] Yellow solid(34.5mg, 46%). ^1H NMR(400MHz, DMSO d_6): 6.54(d, J 8.0Hz, 1H), 6.67-6.72(m 2H), 7.02-7.07(m 2H), 7.13(d, J 8.4Hz, 1H), 7.29-7.40(m 6H), 7.43-7.46(m 2H), 7.54(d, J 8.8Hz, 1H), 7.57-7.61(m 3H), 7.65(d, J 8.0Hz, 1H), 7.75(t, J 8.0Hz, 2H), 8.06(s, 1H), 8.62(s, 1H), 11.55(s, 1H). ^{13}C NMR(150MHz, DMSO d_6): 71.7, 111.8, 111.9, 112.7, 118.1, 119.2, 119.3, 120.8, 121.8, 124.7, 124.9, 126.3, 126.36, 126.43, 126.5, 126.8, 127.0, 127.5, 127.6, 127.7, 127.8, 128.1, 128.3, 129.3, 131.0, 132.3, 132.4, 132.6, 132.7, 136.6, 138.07, 138.09, 138.3, 160.1, 200.6. HRMS cal cd for $\text{C}_{36}\text{H}_{24}\text{N}_2\text{NaO}$ 523.1781[MNa] $^+$, found: 523.1767.

[0058] 2-(4-Chlorophenyl)-2-(2-(4-chlorophenyl)-5-methyl-1H-indol-3-yl)-5-methylindolin-3-one(2r)

[0059] Yellow solid(46.1mg, 62%). ^1H NMR(600MHz, DMSO d_6): 2.16(s, 3H), 2.26(s, 3H), 6.50(s, 1H), 6.91(d, J 8.4Hz, 1H), 6.94(d, J 7.8Hz, 1H), 7.11(d, J 8.4Hz, 2H), 7.14(s, 5H), 7.26(d, J 8.4Hz, 1H), 7.34(d, J 8.4Hz, 2H), 7.41(d, J 8.4Hz, 1H), 8.15(s, 1H), 11.31(s, 1H). ^{13}C NMR(150MHz, DMSO d_6): 20.6, 22.0, 71.5, 111.5, 111.6, 112.6, 118.9, 120.3, 123.6, 124.1, 127.4, 127.5, 127.6, 127.7, 127.9, 128.9, 129.4, 130.8, 131.8, 132.3, 132.5, 132.7, 134.7, 137.2, 139.5, 139.7, 159.4, 200.8. HRMS cal cd for $\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{N}_2\text{NaO}$ 519.1001[MNa] $^+$, found: 519.0989.

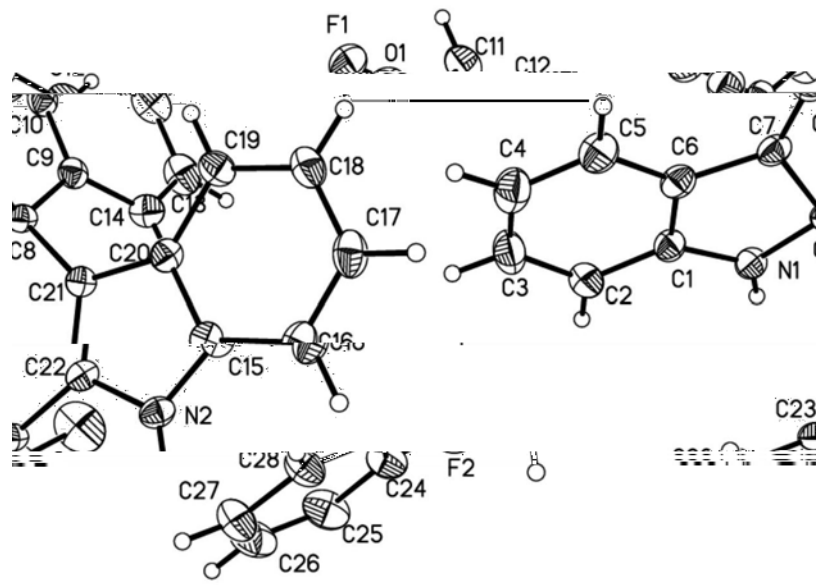
[0060] 2-(3-Chlorophenyl)-2-(2-(3-chlorophenyl)-5-methyl-1H-indol-3-yl)-5-methylindolin-3-one(2s)

[0061] Yellow solid(37.2mg, 0

0 0

3H), 6.49(s, 1H), 6.91(d, J = 8.4 Hz, 1H), 6.97(d, J = 8.4 Hz, 1H), 7.05-7.09(m, 2H), 7.13-7.14(m, 1H), 7.15-7.17(m, 3H), 7.19-7.21(m, 1H), 7.26(d, J = 8.4 Hz, 1H), 7.31-7.32(m, 2H), 7.41(dd, J₁ = 8.4 Hz, J₂ = 1.8 Hz, 1H), 8.23(s, 1H), 11.36(s, 1H). ¹³C NMR (150 MHz, DMSO-d₆): 20.6, 22.0, 71.5, 111.3, 111.7, 112.6, 118.8, 120.2, 123.7, 124.1, 126.0, 127.3, 127.5, 127.6, 127.67, 127.73, 128.3, 129.4, 129.8, 129.9, 132.6, 132.9, 134.7, 135.5, 137.1, 139.9, 142.8, 159.3, 200.7. HRMS calcd for C₃₀H₂₂Cl₂N₂NaO 519.1001 [M+Na]⁺, found: 519.0997.

[0062]



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