

Supporting Information for

Copper-Catalyzed Cascade Double C3-Indolations of 3-Diazoindolin-2-imines with Indoles:

Convenient Access to 3,3-Diaryl-2-iminoindoles

Zao Du, Yanpeng Xing, Ping Lu, Yanguang Wang**

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

pinglu@zju.edu.cn; orgwyg@zju.edu.cn

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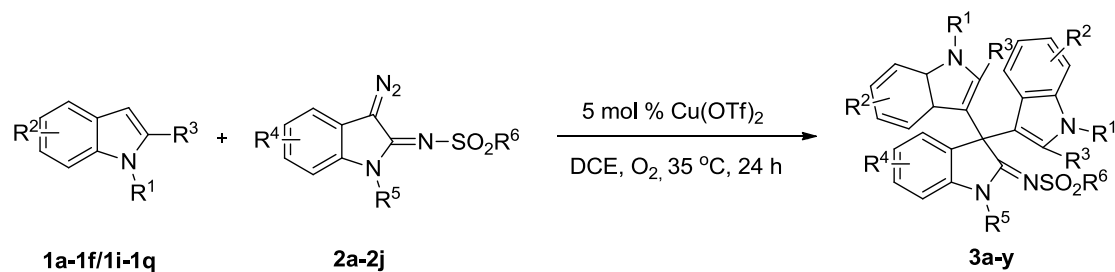
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General Information

^1H NMR spectra were recorded on 400 MHz spectrometer. The chemical shifts were reported relative to internal standard TMS (0 ppm) in CDCl_3 . The following abbreviations were used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants were reported in Hertz (Hz). ^{13}C NMR spectra were recorded on 100 MHz or 150 MHz and referenced to the internal solvent signals (77.00 ppm for CDCl_3 , 39.50 ppm for $(\text{CD}_3)_2\text{SO}$). Infrared spectra were obtained on an FTIR spectrometer. High-resolution mass spectra (HRMS) data were obtained by using an electron ionization time-of-flight (EI-TOF) mass spectrometer. MALDI-TOF data were obtained by using a matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer. Melting points were measured with a micro melting point apparatus. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254. CH_3CN and 1, 2-dichloroethane were dried by distillation over CaH_2 . THF and toluene were dried by distillation over Na. DMF was dried over 4 Å molecular sieves.

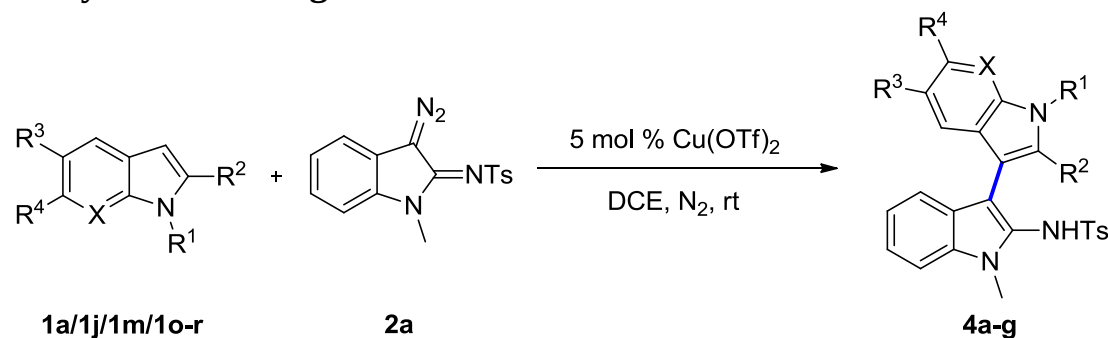
The 3-diazoindolin-2-imines and its analogues were prepared according to the published methods.^{1, 2}

General Procedure for the Synthesis of 3a-y



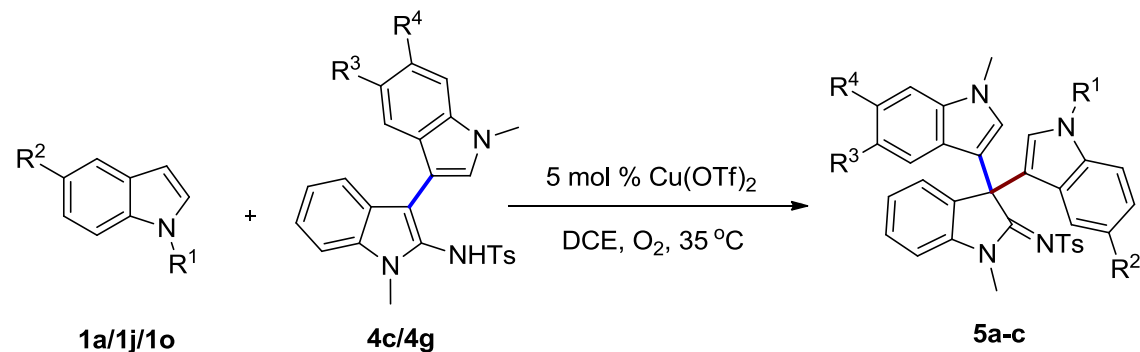
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **1** (0.4 mmol), **2** (0.2 mmol), Cu(OTf)₂ (0.01 mmol) and DCE (2 mL) at room temperature under O₂ atmosphere. The reaction mixture was stirred for about 24 hours at 35 °C. Upon completion, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to give the product **3** as a solid.

General Procedure for the Synthesis of **4a-g**



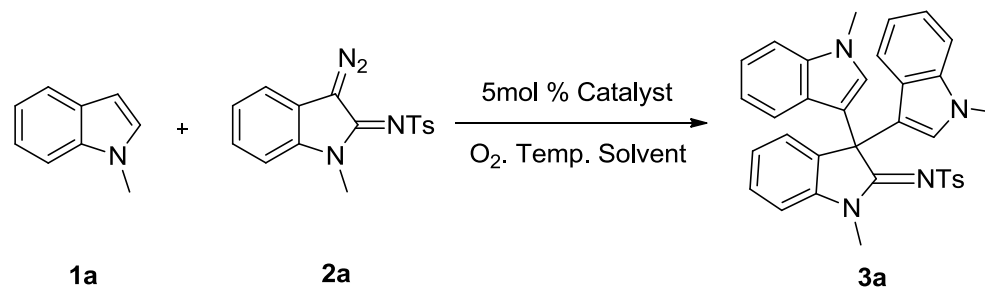
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **1a/1r/1m/1o-r** (0.2 mmol), **2a** (0.2 mmol), Cu(OTf)₂ (0.01 mmol) and DCE (2 mL) at room temperature in nitrogen atmosphere. The reaction mixture was stirred for about 3 to 24 hours at room temperature. Upon completion, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to give the product **4a-g**.

General Procedure for the Synthesis of 5a-c



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **1a/1j/1o** (0.2 mmol), **4c/4g** (0.1 mmol), Cu(OTf)₂ (0.005 mmol) and DCE (1 mL) at 35 °C under O₂ atmosphere. The reaction mixture was stirred for about 5 to 16 hours for **5a-c**. Upon completion, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to give the product **5a-c**.

Table S1. Optimization of Reaction Conditions for 3a



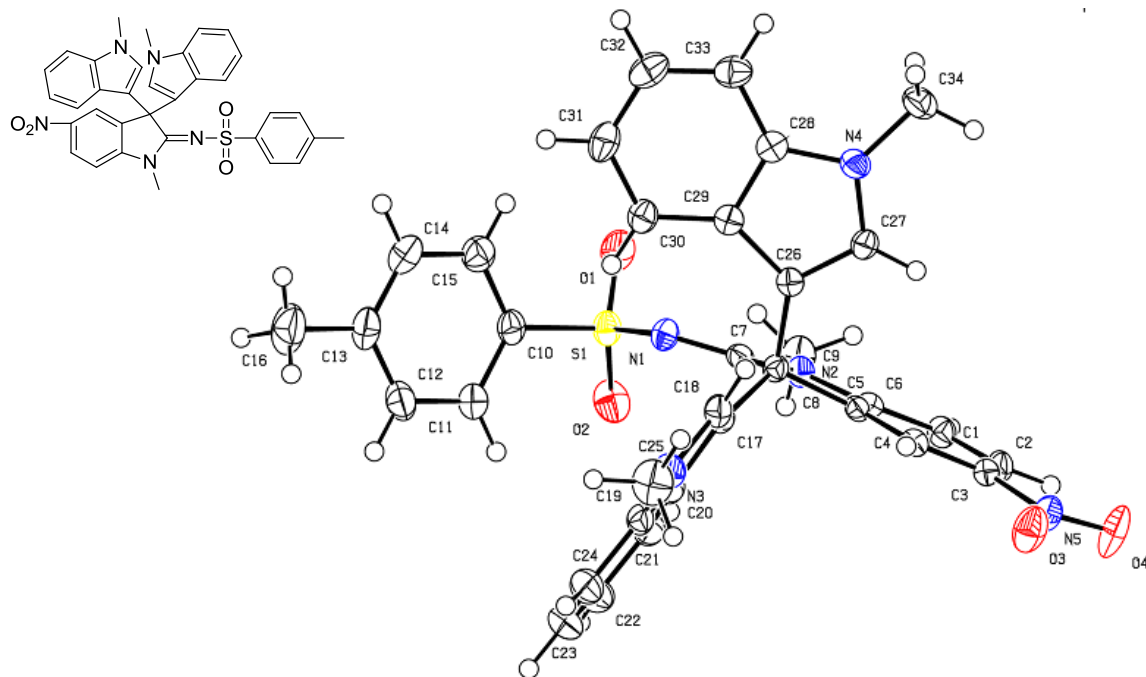
entry	catalyst	solvent	temp (°C)	time	yield ^b (%)
1	Cu(OTf) ₂	DCE	50	8	81
2	Cu(acac) ₂	DCE	50	8	64
3	Cu(NO ₃) ₂ ·3H ₂ O	DCE	50	8	66
4	CuCl ₂ ·2H ₂ O	DCE	50	8	54
5	Cu(OAc) ₂ ·H ₂ O	DCE	50	8	63
6	CuBr ₂	DCE	50	36	18
7	Cu ₂ O	DCE	50	36	40
8	CuOTf	DCE	50	8	78
9	Cu(OTf) ₂	toluene	50	8	76
10	Cu(OTf) ₂	THF	50	8	64
11	Cu(OTf) ₂	CH ₃ CN	50	8	trace
12	Cu(OTf) ₂	DMF	50	8	trace
13	Cu(OTf) ₂	DMSO	50	8	trace
14	Cu(OTf) ₂	DCE	80	8	60
15	Cu(OTf) ₂	DCE	50	24	86
16	Cu(OTf)₂	DCE	35	24	98
17	Cu(OTf) ₂	DCE	35	16	65
18	Cu(OTf) ₂	DCE	35	8	32
19	Cu(OTf) ₂	DCE	rt	36	79
20	Cu(OTf) ₂	DCE	35	24	58 ^c

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), catalyst (0.005 mmol), solvent (1 mL), O₂. ^b Isolated yield referred to **2a**. ^c Air.

Reference

1. Xing, Y. P.; Sheng, G. R.; Wang, J.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, *16*, 1244.
2. Sheng, G. R.; Huang, K.; Chi, Z. H.; Ding, H. L.; Xing, Y. P.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, *16*, 5096.

The ORTEP diagram and Crystal Parameters of 3s



Bond precision: C-C = 0.0031 Å Wavelength=0.71073

Cell: a=9.7972(7) b=10.5090(8) c=15.4371(11)
 alpha=72.931(7) beta=74.564(6) gamma=84.268(6)
 Temperature: 170 K

	Calculated	Reported
Volume	1464.2(2)	1464.16(18)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C34 H29 N5 O4 S	C34 H29 N5 O4 S
Sum formula	C34 H29 N5 O4 S	C34 H29 N5 O4 S
Mr	603.69	603.68
Dx, g cm-3	1.369	1.369
Z	2	2
Mu (mm-1)	0.160	0.160
F000	632.0	632.0
F000'	632.50	
h, k, lmax	11, 12, 18	11, 12, 18
Nref	5370	5350
Tmin, Tmax	0.946, 0.969	0.929, 1.000
Tmin'	0.946	

Correction method= MULTI-SCAN

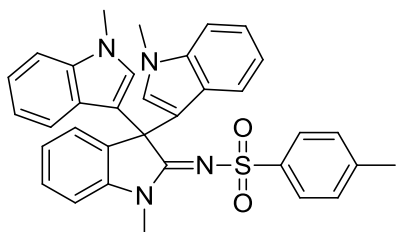
Data completeness= 0.996 Theta(max)= 25.350

R(reflections)= 0.0430(4138) wR2(reflections)= 0.1066(5350)

S = 1.027 Npar= Npar = 401

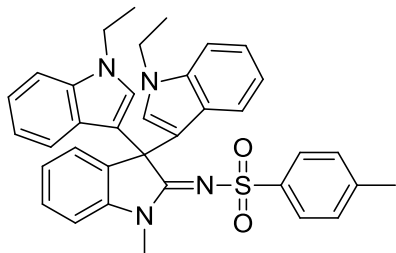
Characterization Data for Products

4-methyl-N-(1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)benzenesulfonamide (**3a**):



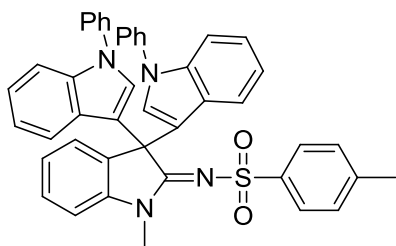
109.4 mg; yield: 98%; gray solid, m.p. 246-247 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 7.2 Hz, 1H), 7.35-7.30 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.12-7.08 (m, 3H), 7.05-6.99 (m, 3H), 6.93 (d, J = 8.0 Hz, 2H), 6.88 (s, 2H), 6.76 (t, J = 7.6 Hz, 2H), 3.89 (s, 3H), 3.67 (s, 6H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 142.7, 141.3, 140.9, 137.4, 136.6, 129.2, 128.4, 128.1, 126.2, 125.8, 124.9, 124.3, 121.35, 121.25, 118.9, 113.0, 109.8, 109.2, 56.5, 32.8, 32.6, 21.4 ppm; IR (film): 3050, 2926, 1589, 1484, 1466, 1280, 1144, 1084, 738 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{30}\text{N}_4\text{O}_2\text{S}$: 558.2089; found: 558.2095.

N-(1,1''-diethyl-1'-methyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3b**)



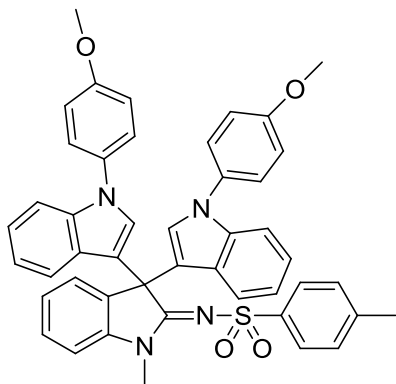
106.7 mg; yield: 91%; pale yellow solid, m.p. 227 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, J = 6.8 Hz, 1H), 7.35-7.31 (m, 3H), 7.26-7.24 (m, 2H), 7.12-7.01 (m, 4H), 6.98-6.94 (m, 6H), 6.78-6.74 (m, 2H), 4.06 (q, J = 4.8 Hz, 4H), 3.87 (s, 3H), 2.29 (s, 3H), 1.36 (t, J = 7.4 Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 142.7, 141.2, 141.1, 136.6, 136.4, 128.4, 128.1, 127.8, 126.4, 125.8, 124.9, 124.3, 121.4, 121.1, 118.7, 113.1, 109.7, 109.2, 56.5, 40.9, 32.5, 21.3, 15.4 ppm; IR (film): 3048, 2977, 2934, 1590, 1464, 1280, 1145, 1084, 738 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{36}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$: 586.2402; found: 586.2407.

4-methyl-N-(1'-methyl-1,1"-diphenyl-[3,3':3',3"-terindolin]-2'-ylidene)benzenesulfonamide (**3c**)



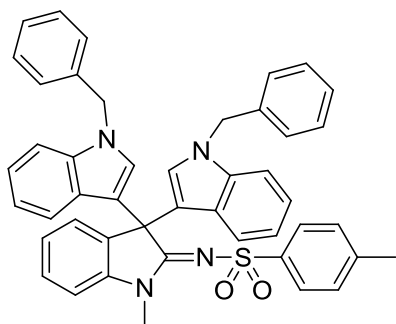
118.7 mg; yield: 87%; yellow solid, m.p. 136-137 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.46-7.39 (m, 10H), 7.33 (td, J = 7.6, 1.2 Hz, 1H), 7.31-7.27 (m, 2H), 7.224-7.221 (m, 2H), 7.15-7.05 (m, 6H), 6.97 (d, J = 8.0 Hz, 2H), 6.85 (t, J = 7.6 Hz, 2H), 3.88 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 143.0, 141.5, 141.0, 139.3, 136.7, 135.7, 129.4, 128.6, 128.5, 127.0, 126.4, 126.0, 125.0, 124.5, 124.4, 122.2, 121.6, 120.0, 115.4, 110.5, 109.9, 56.3, 32.7, 21.3 ppm; IR (film): 3060, 2923, 1595, 1500, 1457, 1144, 1084, 739 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{44}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$: 682.2402; found: 682.2405.

N-(1,1''-bis(4-methoxyphenyl)-1'-methyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3d**)



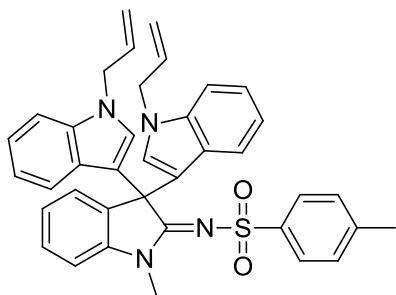
123.2 mg; yield: 83%; yellow solid, m.p. 139-140 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 7.2$ Hz, 1H), 7.42-7.35 (m, 5H), 7.33-7.32 (m, 2H), 7.31-7.30 (m, 2H), 7.16 (s, 2H), 7.13-7.06 (m, 6H), 6.99-6.95 (m, 6H), 6.83 (t, $J = 7.6$ Hz, 2H), 3.88 (s, 3H), 3.83 (s, 6H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.3, 158.2, 142.9, 141.4, 141.1, 137.1, 135.9, 132.4, 128.9, 128.6, 128.4, 126.7, 126.1, 126.0, 125.0, 124.4, 122.0, 121.5, 119.7, 114.8, 114.6, 110.4, 109.9, 56.4, 55.5, 32.6, 21.4 ppm; IR (film): 3047, 2933, 2837, 1588, 1514, 1460, 1249, 1143, 1084, 835, 739 cm^{-1} ; HRMS (MALDI-TOF) calcd for $\text{C}_{46}\text{H}_{38}\text{N}_4\text{O}_4\text{S}$: 742.2614; found: 743.269 ($[\text{M}+\text{H}]^+$).

N-(1,1''-dibenzyl-1'-methyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3e**)



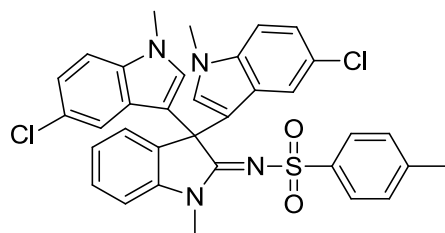
81.0 mg; yield: 57%; dark yellow solid, m.p. 113-115 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, J = 7.6 Hz, 1H), 7.36-7.32 (m, 3H), 7.23-7.22 (m, 6H), 7.15-7.10 (m, 3H), 7.06-7.00 (m, 11H), 6.90 (d, J = 8.4 Hz, 2H), 6.73 (t, J = 7.6 Hz, 2H), 5.20 (s, 4H), 3.89 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 143.0, 141.2, 141.1, 137.4, 137.0, 136.0, 128.9, 128.6, 128.5, 128.3, 127.4, 126.53, 126.50, 125.9, 125.0, 124.3, 121.7, 121.5, 119.1, 114.0, 109.9, 109.8, 56.4, 50.1, 32.8, 21.4 ppm; IR (film): 3049, 2928, 1589, 1512, 1465, 1282, 1144, 1084, 737 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{46}\text{H}_{38}\text{N}_4\text{O}_2\text{S}$: 710.2715; found: 710.2716.

N-(1,1''-diallyl-1'-methyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3f**)



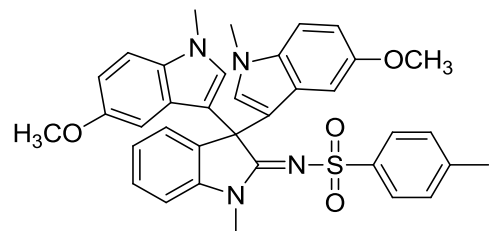
73.2 mg; yield: 60%; yellow solid, m.p. 96-97 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.36-7.31 (m, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.12-7.03 (m, 4H), 6.98 (t, J = 8.2 Hz, 4H), 6.91 (s, 2H), 6.75 (t, J = 7.6 Hz, 2H), 5.94-5.85 (m, 2H), 5.13-5.10 (m, 2H), 5.01-4.97 (m, 2H), 4.60 (d, J = 5.2 Hz, 4H), 3.88 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 142.9, 141.3, 141.1, 136.8, 136.2, 133.3, 128.5, 128.3, 128.2, 126.4, 125.9, 124.9, 124.3, 121.5, 121.3, 118.9, 117.0, 113.6, 109.8, 109.5, 56.4, 48.7, 32.7, 21.3 ppm; IR (film): 3048, 2922, 1589, 1465, 1280, 1144, 1083, 994, 911, 738 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{38}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$: 610.2402; found: 610.2408.

N-(5,5"-dichloro-1,1',1"-trimethyl-[3,3':3',3"-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3g**)



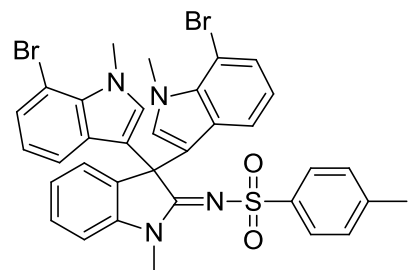
100.2 mg; yield: 80%; gray solid, m.p. 216-217 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, J = 8.4 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.12-7.07 (m, 4H), 7.04-7.01 (m, 4H), 6.94 (d, J = 2.0 Hz, 2H), 6.84 (s, 2H), 3.89 (s, 3H), 3.64 (s, 6H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 169.0, 142.8, 141.6, 140.6, 135.9, 135.6, 130.1, 128.8, 128.5, 127.0, 125.6, 124.8, 124.6, 124.4, 121.8, 120.5, 112.7, 110.4, 110.0, 56.0, 32.98, 32.96, 21.4 ppm; IR (film): 3063, 2922, 1589, 1475, 1371, 1282, 1145, 1085, 789, 734 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{28}\text{Cl}_2\text{N}_4\text{O}_2\text{S}$: 626.1310; found: 626.1314.

N-(5,5''-dimethoxy-1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3h**)



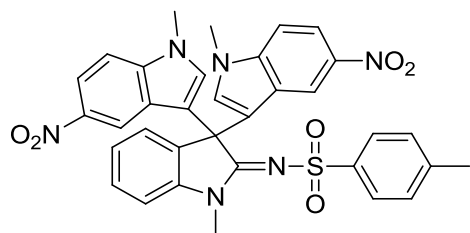
115.0 mg; yield: 93%; dark yellow solid, m.p. 102-104 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.37-7.33 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 2H), 7.10-7.06 (m, 2H), 6.90 (d, J = 8.0 Hz, 2H), 6.78 (s, 3H), 6.76 (d, J = 2.0 Hz, 1H), 6.53 (s, 2H), 3.90 (s, 3H), 3.63 (s, 6H), 3.35 (s, 6H), 2.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.3, 153.2, 143.2, 141.3, 141.0, 136.1, 132.9, 129.8, 128.4, 128.3, 126.5, 125.9, 125.0, 124.3, 112.5, 111.7, 109.8, 109.6, 103.4, 56.5, 55.3, 33.1, 32.9, 21.3 ppm; IR (film): 2943, 2832, 1588, 1488, 1227, 1143, 1084, 911, 822, 734 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{36}\text{H}_{34}\text{N}_4\text{O}_4\text{S}$: 618.2301; found: 618.2295.

N-(7,7''-dibromo-1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3i**)



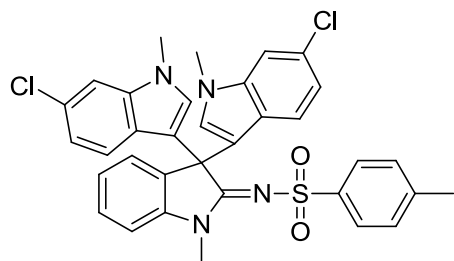
85.7 mg; yield: 60%; white solid, m.p. 319-320 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.37-7.29(m, 4H), 7.20 (d, J = 0.8 Hz, 1H), 7.18 (d, J = 0.8 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.04 (td, J = 7.6, 0.8 Hz, 1H), 6.98-6.92 (m, 4H), 6.78 (s, 2H), 6.54 (t, J = 7.8 Hz, 2H), 4.03 (s, 6H), 3.88 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 169.1, 142.5, 141.6, 140.5, 135.7, 133.7, 132.2, 129.2, 128.5, 128.4, 126.5, 125.5, 124.50, 124.45, 120.7, 120.1, 112.4, 110.0, 103.8, 55.9, 37.0, 32.6, 21.4 ppm; IR (film): 2948, 1592, 1487, 1363, 1306, 1145, 1084, 909, 775, 729 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{28}\text{Br}_2\text{N}_4\text{O}_2\text{S}$: 714.0300; found: 714.0304.

4-methyl-N-(1,1',1''-trimethyl-5,5''-dinitro-[3,3':3',3''-terindolin]-2'-ylidene)benzenesulfonamide (**3j**)



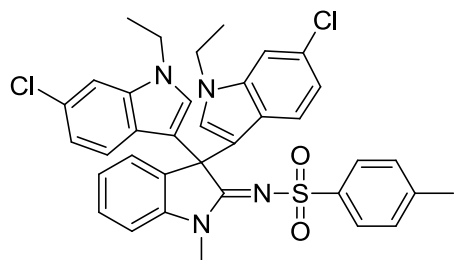
92.0 mg; yield: 71%; dark yellow solid, m.p. 176-177 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 2.0 Hz, 1H), 7.95 (d, J = 2.4 Hz, 1H), 7.84 (d, J = 2.0 Hz, 2H), 7.44-7.40 (m, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.26 (s, 1H), 7.24 (s, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.15-7.11 (m, 1H), 7.08 (s, 2H), 6.94 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H), 3.79 (s, 6H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.8, 142.9, 142.3, 141.2, 140.2, 139.9, 134.6, 131.4, 129.1, 128.6, 125.6, 125.3, 124.8, 124.5, 118.1, 117.3, 115.9, 110.5, 109.5, 55.6, 33.4, 33.1, 21.3 ppm; IR (film): 3115, 2946, 1590, 1486, 1332, 1295, 1146, 1084, 911, 735 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{28}\text{N}_6\text{O}_6\text{S}$: 648.1791; found: 648.1790.

N-(6,6''-dichloro-1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3k**)



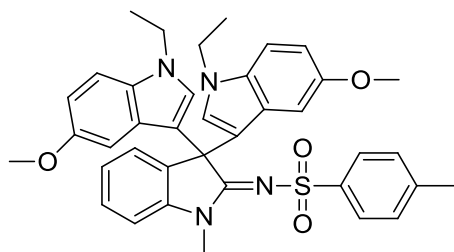
102.7 mg; yield: 82%; gray solid, m.p. 247-249 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.30 (m, 4H), 7.17 (d, J = 1.6 Hz, 2H), 7.11-7.04 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.79 (s, 2H), 6.65 (dd, J = 8.4, 1.6 Hz, 2H), 3.89 (s, 3H), 3.62 (s, 6H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 142.9, 141.8, 140.7, 137.9, 135.8, 129.4, 128.6, 127.6, 125.8, 124.8, 124.6, 124.5, 122.3, 119.7, 113.6, 110.1, 109.3, 56.1, 32.9, 21.4 ppm; IR (film): 3063, 2934, 1589, 1485, 1278, 1145, 1084, 804 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{28}\text{Cl}_2\text{N}_4\text{O}_2\text{S}$: 626.1310; found: 626.1313.

N-(6,6''-dichloro-1,1''-diethyl-1'-methyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3l**)



108.6 mg; yield: 83%; pale yellow solid, m.p. 248-249 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.34 (m, 4H), 7.22 (d, J = 1.6 Hz, 2H), 7.11 (d, J = 7.6 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.86-6.83 (m, 4H), 6.66 (dd, J = 8.8, 1.6 Hz, 2H), 4.00 (q, J = 7.2 Hz, 4H), 3.88 (s, 3H), 2.34 (s, 3H), 1.36 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 142.8, 141.7, 140.8, 136.9, 135.8, 128.5, 128.4, 127.9, 127.4, 125.8, 124.9, 124.6, 124.4, 122.3, 119.5, 113.6, 110.0, 109.3, 56.1, 41.1, 32.8, 21.4, 15.3 ppm; IR (film): 3062, 2977, 2933, 1592, 1467, 1145, 1084, 804, 734 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{36}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}_2\text{S}$: 654.1623; found: 654.1624.

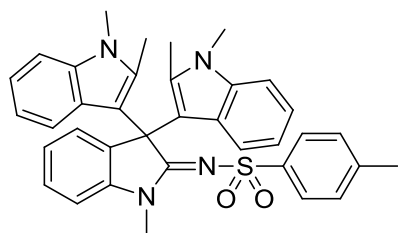
N-(1,1'-diethyl-5,5'-dimethoxy-1'-methyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3m**)



109.9 mg; yield: 85%; pale yellow solid, m.p. 200-201 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.35 (m, 2H), 7.26-7.24 (m, 2H), 7.16 (s, 1H),

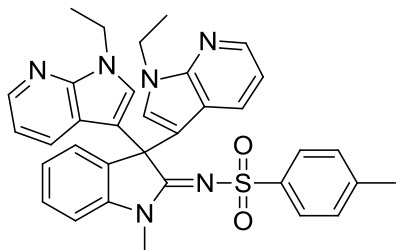
7.14-7.12 (m, 2H), 7.11-7.09 (m, 1H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.84 (s, 2H), 6.76 (d, $J = 2.4$ Hz, 1H), 6.74 (d, $J = 2.4$ Hz, 1H), 6.52 (d, $J = 2.4$ Hz, 2H), 4.02 (q, $J = 7.2$ Hz, 4H), 3.90 (s, 3H), 3.31 (s, 6H), 2.27 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 170.4, 153.2, 143.3, 141.3, 141.2, 136.1, 131.8, 128.5, 128.2, 128.1, 126.7, 126.0, 125.0, 124.3, 112.6, 111.8, 109.9, 109.7, 103.3, 56.5, 55.1, 41.0, 33.2, 21.3, 15.5 ppm; IR (film): 2978, 2936, 2832, 1589, 1488, 1224, 1143, 1084, 822 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{38}\text{H}_{38}\text{N}_4\text{O}_4\text{S}$: 646.2614; found: 646.2617.

4-methyl-N-(1,1',1'',2,2''-pentamethyl-[3,3':3',3''-terindolin]-2'-ylidene)benzenesulfonamide (**3n**):



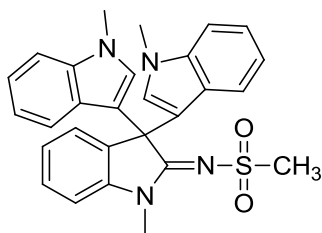
107.9 mg; yield: 92%; yellow solid, m.p. 121-122 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.0$ Hz, 2H), 7.38 (td, $J = 7.6, 1.2$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.24-7.22 (m, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.08-6.99 (m, 5H), 6.73-6.68 (m, 3H), 6.07 (s, 1H), 3.96 (s, 3H), 3.57 (s, 3H), 3.50 (s, 3H), 2.33 (s, 3H), 2.09 (s, 3H), 1.67 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 143.3, 141.5, 141.3, 136.61, 136.59, 136.3, 129.3, 128.6, 128.4, 128.2, 127.0, 126.7, 126.5, 126.1, 126.0, 125.7, 124.4, 120.4, 120.3, 120.0, 119.8, 118.8, 118.7, 112.0, 109.8, 108.4, 108.4, 57.3, 33.9, 29.5, 29.4, 21.4, 12.3, 11.9 ppm; IR (film): 3047, 2939, 1589, 1467, 1364, 1278, 1144, 1084, 737 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{36}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$: 586.2402; found: 586.2405.

N-(3,3-bis(1-ethyl-1H-pyrrolo[2,3-b]pyridin-3-yl)-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (**3o**)



67.1 mg; yield: 57%; yellow solid, m.p. 123 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (dd, $J = 4.8, 1.6$ Hz, 2H), 7.41-7.38 (m, 3H), 7.34-7.32 (m, 1H), 7.21 (dd, $J = 8.0, 1.6$ Hz, 2H), 7.17-7.10 (m, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.98 (s, 2H), 6.69-6.66 (m, 2H), 4.33-4.17 (m, 4H), 3.93 (s, 3H), 2.34 (s, 3H), 1.40 (t, $J = 7.2$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 147.5, 143.2, 142.6, 141.8, 140.7, 134.9, 129.5, 128.7, 126.8, 125.9, 124.8, 124.4, 118.7, 115.2, 112.2, 110.2, 56.3, 39.3, 33.1, 21.3, 15.6 ppm; IR (film): 2977, 2934, 1593, 1433, 1282, 1146, 1085, 783, 731 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{32}\text{N}_6\text{O}_2\text{S}$: 588.2307; found: 588.2305.

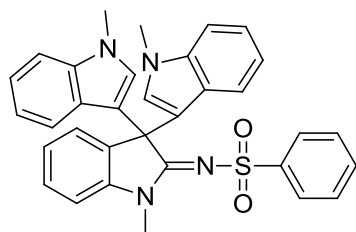
N-(1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)methanesulfonamide (**3p**):



86.8 mg; yield: 90%; pale yellow solid, m.p. 292-293 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.31 (m, 2H), 7.26-7.24 (m, 4H), 7.13 (t, $J = 7.6$ Hz,

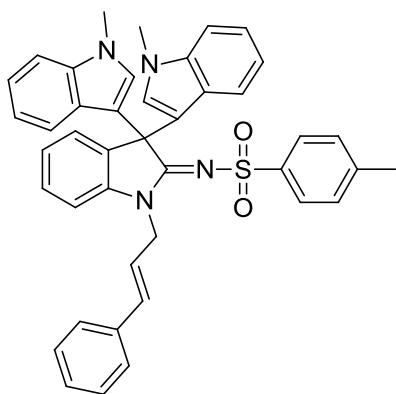
2H), 7.08-7.03 (m, 2H), 6.89 (t, $J = 7.6$ Hz, 2H), 6.81 (s, 2H), 3.83 (s, 3H), 3.69 (s, 6H), 2.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 143.2, 137.6, 135.9, 128.7, 128.2, 126.3, 124.9, 124.2, 121.7, 121.5, 118.8, 113.7, 109.8, 109.3, 56.4, 43.7, 32.9, 32.8 ppm; IR (film): 3051, 2935, 1593, 1486, 1331, 1283, 1117, 911, 803, 736 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_2\text{S}$: 482.1776; found: 482.1774.

N-(1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)benzenesulfonamide (**3q**)



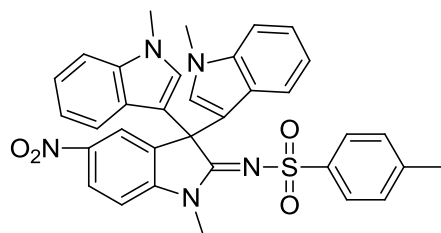
91.4 mg; yield: 84%; yellow solid, m.p. 266-267 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.41 (m, 3H), 7.32-7.27 (m, 2H), 7.23-7.19 (m, 2H), 7.15-7.03 (m, 6H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.86 (s, 2H), 6.78-6.74 (m, 2H), 3.89 (s, 3H), 3.63 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 143.6, 142.7, 137.4, 136.5, 130.9, 129.1, 128.1, 127.8, 126.2, 125.8, 124.9, 124.4, 121.33, 121.29, 118.9, 113.0, 109.8, 109.2, 56.5, 32.7 ppm; IR (film): 3054, 2934, 1592, 1486, 1284, 1145, 1084, 911, 796, 738 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{33}\text{H}_{28}\text{N}_4\text{O}_2\text{S}$: 544.1933; found: 544.1936.

N-(1'-cinnamyl-1,1''-dimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3r**)



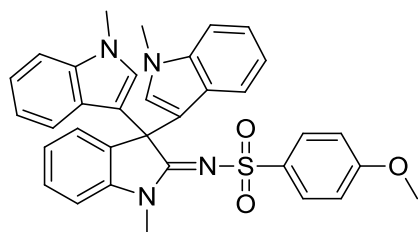
125.4 mg; yield: 95%; pale yellow solid, m.p. 129-130 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, J = 7.2 Hz, 1H), 7.31-7.08 (m, 15H), 6.98-6.93 (m, 3H), 6.80-6.76 (m, 4H), 6.69 (d, J = 16.0 Hz, 1H), 6.40-6.36 (m, 1H), 5.06 (d, J = 5.6 Hz, 2H), 3.69 (s, 6H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 141.1, 140.7, 140.6, 137.4, 137.3, 136.1, 133.8, 130.4, 128.5, 128.2, 127.94, 127.92, 126.5, 126.1, 125.3, 124.8, 124.3, 122.0, 121.1, 120.8, 118.9, 111.5, 110.2, 109.4, 56.5, 45.8, 32.9, 21.3 ppm; IR (film): 3049, 2927, 1587, 1465, 1282, 1146, 1084, 910, 737 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{42}\text{H}_{36}\text{N}_4\text{O}_2\text{S}$: 660.2559; found: 660.2562.

4-methyl-N-(1,1',1''-trimethyl-5'-nitro-[3,3':3',3''-terindolin]-2'-ylidene)benzenesulfonamide (**3s**)



96.5 mg; yield: 80%; yellow solid, m.p. 283-284 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.27-8.24 (m, 1H), 8.20 (d, J = 2.0 Hz, 1H), 7.28 (s, 1H), 7.26-7.24 (m, 2H), 7.16-7.12 (m, 3H), 7.02 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.92 (s, 2H), 6.84-6.80 (m, 2H), 3.90 (s, 3H), 3.70 (s, 6H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 147.9, 144.4, 141.9, 140.0, 137.5, 137.3, 129.4, 128.6, 125.9, 125.7, 125.2, 121.7, 120.8, 120.4, 119.3, 111.5, 109.5, 109.4, 56.1, 32.9, 32.7, 21.4 ppm; IR (film): 3050, 2926, 1590, 1524, 1484, 1335, 1147, 1086, 737 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{29}\text{N}_5\text{O}_4\text{S}$: 603.1940; found: 603.1942.

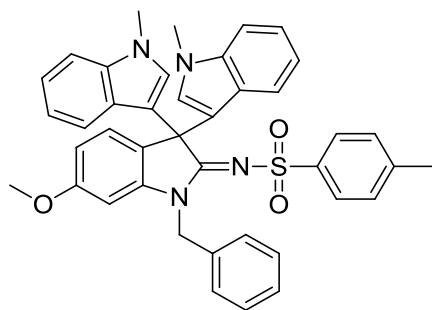
4-methoxy-N-(1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)benzenesulfonamide (**3t**)



91.9 mg; yield: 80%; pale yellow solid, m.p. 270-271 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 7.2 Hz, 1H), 7.34-7.30 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.12-7.08 (m, 3H), 7.05-7.01 (m, 3H), 6.88 (s, 2H), 6.79-6.76 (m, 2H), 6.62-6.60 (m, 2H), 3.89 (s, 3H), 3.76 (s, 3H), 3.67 (s, 6H) ppm; ^{13}C

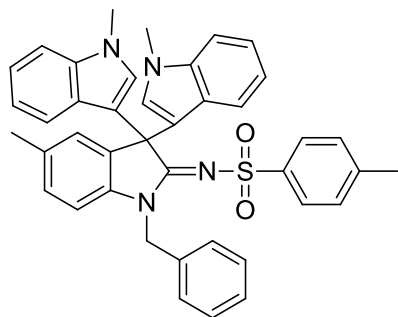
NMR (100 MHz, CDCl₃) δ 169.7, 161.4, 142.8, 137.4, 136.5, 136.0, 129.2, 128.1, 127.8, 126.2, 124.9, 124.3, 121.4, 121.3, 118.9, 113.1, 112.9, 109.7, 109.2, 56.5, 55.3, 32.8, 32.7 ppm; IR (film): 3042, 2928, 1588, 1484, 1254, 1145, 1085, 807, 737 cm⁻¹; HRMS (EI) calcd for C₃₄H₃₀N₄O₃S: 574.2039; found: 574.2033.

N-(1'-benzyl-6'-methoxy-1,1"-dimethyl-[3,3':3',3"-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3u**)



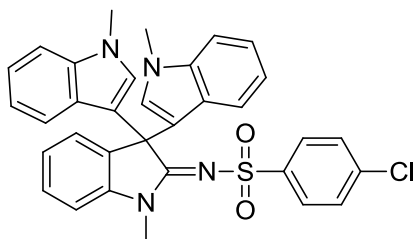
130.2 mg; yield: 98%; pale yellow solid, m.p. 136 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.28 (m, 3H), 7.26-7.24 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.14-7.08 (m, 6H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.95-6.89 (m, 3H), 6.81-6.77 (m, 4H), 6.69-6.66 (m, 1H), 5.42 (s, 2H), 3.70 (s, 6H), 3.53 (s, 3H), 2.23 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 157.0, 141.0, 140.7, 138.8, 137.3, 135.0, 134.0, 130.7, 128.6, 128.1, 127.83, 127.76, 126.1, 125.3, 121.1, 120.8, 118.8, 112.5, 111.5, 111.2, 110.9, 109.4, 56.7, 55.4, 47.5, 32.8, 21.3 ppm; IR (film): 3049, 2926, 1568, 1491, 1274, 1147, 1087, 1022, 737 cm⁻¹; HRMS (EI) calcd for C₄₁H₃₆N₄O₃S: 664.2508; found: 664.2504.

N-(1'-benzyl-1,1'',5'-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3v**)



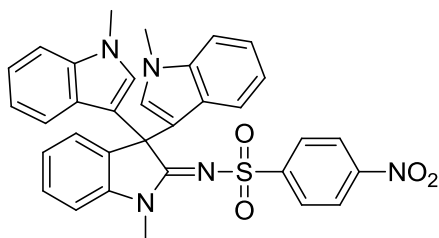
127.1 mg; yield: 98%; pale yellow solid, m.p. 275-276 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.32 (m, 2H), 7.28-7.21 (m, 5H), 7.19 (s, 1H), 7.15 (s, 2H), 7.12-7.08 (m, 4H), 6.97-6.95 (m, 1H), 6.92-6.89 (m, 3H), 6.81-6.77 (m, 4H), 5.41 (s, 2H), 3.70 (s, 6H), 2.23 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 141.0, 140.7, 138.2, 137.5, 137.3, 135.1, 133.9, 130.7, 128.6, 128.3, 128.1, 127.9, 127.7, 126.1, 125.4, 125.3, 121.0, 120.8, 118.7, 111.3, 110.1, 109.4, 56.4, 47.3, 32.9, 21.3, 21.2 ppm; IR (film): 3049, 2923, 1568, 1494, 1330, 1149, 1087, 736 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{41}\text{H}_{36}\text{N}_4\text{O}_2\text{S}$: 648.2559; found: 648.2559.

4-chloro-N-(1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)benzenesulfonamide (**3w**)



109.8 mg; yield: 95%; pale gray solid, m.p. 261-262 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 7.6 Hz, 1H), 7.33 (td, J = 7.6, 1.1 Hz, 1H), 7.28-7.25 (m, 2H), 7.24-7.20 (m, 2H), 7.13-7.09 (m, 3H), 7.06-7.02 (m, 3H), 6.99 (d, J = 8.4 Hz, 2H), 6.86 (s, 2H), 6.80-6.76 (m, 2H), 3.88 (s, 3H), 3.66 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 170.4, 142.5, 142.1, 137.4, 137.0, 136.5, 129.2, 128.2, 127.9, 127.2, 126.1, 124.9, 124.6, 121.4, 121.2, 118.9, 112.7, 109.9, 109.3, 56.6, 32.8, 32.7 ppm; IR (film): 3050, 2937, 1586, 1298, 1146, 1085, 910, 737 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{33}\text{H}_{27}\text{ClN}_4\text{O}_2\text{S}$: 578.1543; found: 578.1545.

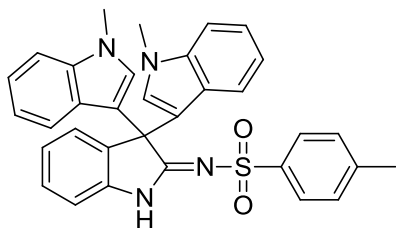
4-nitro-N-(1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)benzenesulfonamide (**3x**)



116.7 mg; yield: 99%; yellow solid, m.p. 252 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.82 (m, 2H), 7.42-7.39 (m, 3H), 7.34 (td, J = 7.8, 1.1 Hz, 1H), 7.20-7.14 (m, 3H), 7.11-7.03 (m, 3H), 6.95 (d, J = 8.0 Hz, 2H), 6.89 (s, 2H), 6.79-6.75 (m, 2H), 3.89 (s, 3H), 3.67 (s, 6H) ppm; ^{13}C NMR (100 MHz,

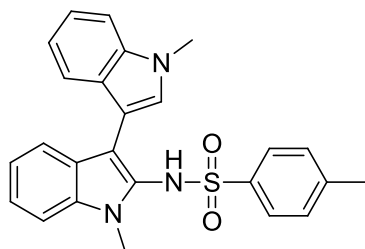
CDCl_3) δ 171.4, 148.8, 148.6, 142.0, 137.4, 136.7, 129.5, 128.3, 126.6, 125.9, 125.0, 124.8, 122.9, 121.5, 120.9, 119.0, 112.0, 110.1, 109.4, 56.8, 32.8, 32.5 ppm; IR (film): 3053, 2938, 1581, 1348, 1295, 1148, 1085, 737 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{33}\text{H}_{27}\text{N}_5\text{O}_4\text{S}$: 589.1784; found: 589.1780.

N-(1,1'-dimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**3y**)



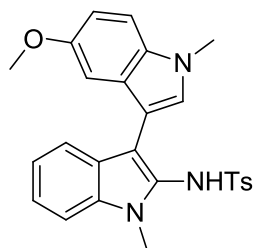
84.9 mg; yield: 78%; pale yellow solid, m.p. 293 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.10 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.37-7.35 (m, 2H), 7.29 (td, J = 7.8, 1.1 Hz, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 7.19-7.12 (m, 5H), 7.03 (td, J = 7.6, 0.8 Hz, 1H), 6.88-6.82 (m, 4H), 6.77 (s, 2H), 3.64 (s, 6H), 2.27 (s, 3H) ppm; ^{13}C NMR (150 MHz, DMSO) δ 171.6, 142.4, 141.1, 138.8, 137.2, 134.9, 129.1, 128.6, 128.3, 125.9, 125.6, 124.4, 123.4, 121.1, 120.8, 118.5, 112.8, 112.5, 109.8, 56.3, 32.3, 20.9 ppm; IR (film): 3049, 2924, 1594, 1466, 1143, 1083, 910, 813, 738 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{33}\text{H}_{28}\text{N}_4\text{O}_2\text{S}$: 544.1933; found: 544.1936.

N-(1,1'-dimethyl-1H,1'H-[3,3'-biindol]-2-yl)-4-methylbenzenesulfonamide (**4a**)



62.7 mg; yield: 73%; gray solid, m.p. 112-113 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.32-7.29 (m, 1H), 7.25-7.23 (m, 1H), 7.22-7.19 (m, 2H), 7.11 (d, J = 8.5 Hz, 2H), 7.10-7.06 (m, 1H), 7.05-7.01 (m, 2H), 6.61 (d, J = 8.0 Hz, 2H), 6.50 (s, 1H), 3.92 (s, 3H), 3.66 (s, 3H), 2.10 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 143.1, 136.7, 135.5, 135.3, 128.5, 127.1, 127.0, 126.6, 126.5, 125.9, 122.7, 121.7, 120.6, 120.0, 119.6, 119.2, 109.8, 109.1, 106.5, 105.7, 32.6, 30.0, 21.5 ppm; IR (film): 3289 (br), 3054, 2929, 1472, 1404, 1377, 1328, 1161, 1091, 737 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$: 429.1511; found: 429.1515.

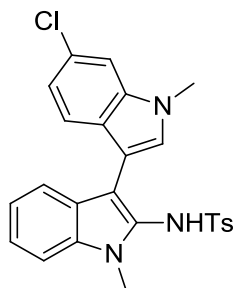
N-(5'-methoxy-1,1'-dimethyl-1H,1'H-[3,3'-biindol]-2-yl)-4-methylbenzenesulfonamide (**4b**)



65.2 mg; yield: 71%; yellow solid, m.p. 204-205 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.33-7.28 (m, 1H), 7.14 (d, J = 8.4 Hz, 3H), 7.08 (t, J = 7.2 Hz, 1H), 6.95 (s, 1H), 6.87 (dd, J = 8.8, 2.4 Hz, 1H), 6.66 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 2.0 Hz, 1H),

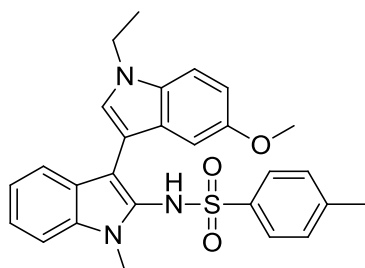
6.44 (s, 1H), 3.94 (s, 3H), 3.73 (s, 3H), 3.65 (s, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 143.3, 135.5, 135.3, 132.1, 128.5, 127.5, 127.1, 127.0, 126.7, 125.9, 122.7, 120.5, 119.7, 112.2, 109.9, 109.8, 106.0, 105.6, 101.4, 55.8, 32.8, 30.1, 21.5 ppm; IR (film): 3272 (br), 2941, 1574, 1490, 1225, 1160, 1090, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_3\text{S}$: 459.1617; found: 459.1608.

N-(6'-chloro-1,1'-dimethyl-1H,1'H-[3,3'-biindol]-2-yl)-4-methylbenzenesulfonamide (**4c**)



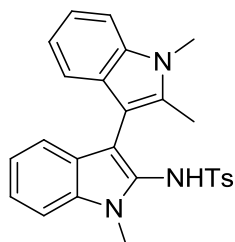
80.6 mg; yield: 87%; pale yellow solid, m.p. 197-198 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.39 (m, 2H), 7.34-7.29 (m, 1H), 7.22 (d, J = 1.6 Hz, 1H), 7.16-7.11 (m, 3H), 7.10-7.06 (m, 2H), 6.96 (dd, J = 8.4, 1.6 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 6.59 (s, 1H), 3.93 (s, 3H), 3.66 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.3, 137.1, 135.4, 135.2, 128.5, 127.8, 127.04, 126.97, 126.6, 125.8, 125.7, 122.9, 121.4, 120.4, 119.8, 119.6, 109.9, 109.0, 107.1, 105.3, 32.7, 30.0, 21.4 ppm; IR (film): 3272 (br), 2933, 1595, 1474, 1318, 1161, 1090, 912, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{22}\text{ClN}_3\text{O}_2\text{S}$: 463.1121; found: 463.1115.

N-(1'-ethyl-5'-methoxy-1-methyl-1H,1'H-[3,3'-biindol]-2-yl)-4-methylbenzenesulfonamide (**4d**)



66.2 mg; yield: 70%; pale gray solid, m.p. 200-201 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.35 (s, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.19-7.14 (m, 3H), 7.07 (t, J = 7.5 Hz, 1H), 6.84 (dd, J = 8.8, 2.3 Hz, 1H), 6.66 (s, 1H), 6.60-6.57 (m, 3H), 4.01 (q, J = 7.3 Hz, 2H), 3.94 (s, 3H), 3.70 (s, 3H), 2.05 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 153.6, 143.3, 135.4, 135.3, 131.1, 128.5, 127.7, 126.9, 126.6, 125.9, 125.3, 122.6, 120.7, 119.6, 112.0, 109.7, 106.2, 105.8, 101.9, 55.8, 40.9, 30.1, 21.3, 15.5 ppm; IR (film): 3272 (br), 2978, 2937, 1488, 1222, 1161, 1091, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_3\text{S}$: 473.1773; found: 473.1771.

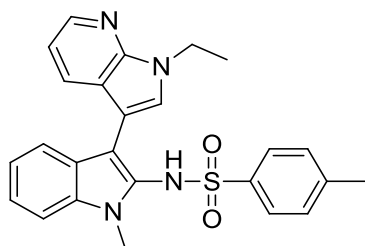
4-methyl-N-(1,1',2'-trimethyl-1H,1'H-[3,3'-biindol]-2-yl)benzenesulfonamide (**4e**)



76.2 mg; yield: 86%; dark yellow solid, m.p. 173-174 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.40 (m, 1H), 7.31-7.28 (m, 2H), 7.21 (s, 1H),

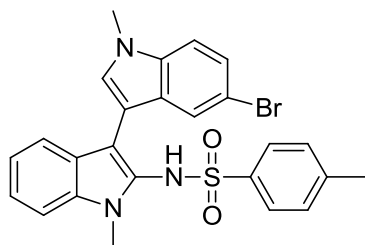
7.19-7.15 (m, 1H), 7.09-7.02 (m, 3H), 6.98 (d, $J = 8.4$ Hz, 2H), 6.63-6.60 (m, 3H), 3.96 (s, 3H), 3.56 (s, 3H), 2.19 (s, 3H), 1.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 142.6, 136.6, 136.1, 135.4, 133.5, 128.4, 126.9, 126.5, 125.9, 122.6, 120.9, 120.7, 119.61, 119.56, 118.1, 109.9, 108.7, 105.5, 103.8, 29.9, 29.4, 21.6, 11.4 ppm; IR (film): 3305 (br), 2937, 1597, 1471, 1389, 1339, 1160, 1092, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_2\text{S}$: 443.1667; found: 443.1663.

N-(3-(1-ethyl-1H-pyrrolo[2,3-b]pyridin-3-yl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide (**4f**)



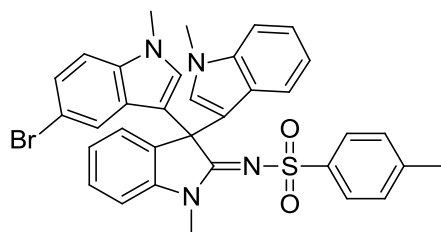
57.7 mg; yield: 65%; brown solid, m.p. 175-176 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.29 (dd, $J = 4.6, 1.4$ Hz, 1H), 7.60-7.57 (m, 1H), 7.49 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.42 (d, $J = 8.8$ Hz, 2H), 7.35-7.31 (m, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.12-7.08 (m, 1H), 6.95-6.91 (m, 2H), 6.58 (d, $J = 8.4$ Hz, 2H), 4.25 (q, $J = 7.2$ Hz, 2H), 3.95 (s, 3H), 2.01 (s, 3H), 1.48 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 147.1, 143.4, 142.7, 135.5, 135.2, 128.6, 127.0, 126.6, 125.7, 124.8, 122.9, 120.4, 119.9, 119.7, 115.1, 109.9, 105.5, 105.4, 39.1, 30.0, 21.3, 15.7 ppm; IR (film): 3275 (br), 2977, 2933, 1597, 1467, 1388, 1331, 1162, 1090, 735 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_2\text{S}$: 444.1620; found: 444.1619.

N-(5'-bromo-1,1'-dimethyl-1H,1'H-[3,3'-biindol]-2-yl)-4-methylbenzenesulfonamide (**4g**)



96.3 mg; yield: 95%; pale gray solid, m.p. 185-186 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (t, J = 7.4 Hz, 2H), 7.34-7.28 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.12-7.09 (m, 2H), 7.06 (s, 1H), 6.66 (d, J = 8.0 Hz, 2H), 6.59 (s, 1H), 3.93 (s, 3H), 3.69 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 135.43, 135.36, 135.2, 128.8, 128.5, 127.6, 127.0, 126.8, 125.8, 124.7, 122.9, 120.4, 120.0, 112.5, 110.5, 109.9, 106.5, 105.0, 32.8, 30.1, 21.5 ppm; IR (film): 3363 (br), 2922, 1580, 1471, 1372, 1282, 1145, 1083, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{22}\text{BrN}_3\text{O}_2\text{S}$: 507.0616; found: 507.0636.

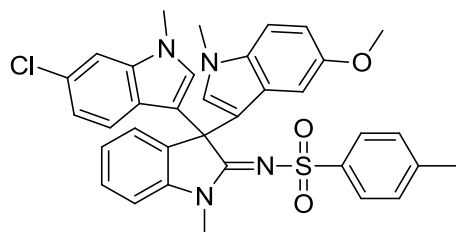
N-(5-bromo-1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**5a**)



63.0 mg; yield: 99%; pale yellow solid, m.p. 254-255 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, J = 7.6 Hz, 1H), 7.36-7.32 (m, 3H), 7.22 (d, J = 8.0 Hz, 1H), 7.18-7.09 (m, 4H), 7.08-7.04 (m, 2H), 6.97 (d, J = 8.4 Hz, 3H), 6.88 (s, 1H), 6.83-6.79 (m, 2H), 3.88 (s, 3H), 3.67 (s, 3H), 3.64 (s, 3H),

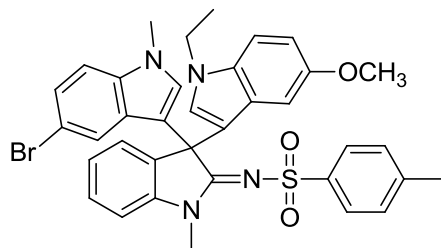
2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 142.7, 141.5, 140.7, 137.4, 136.2, 136.1, 130.2, 129.2, 128.6, 128.3, 127.8, 126.0, 125.7, 124.7, 124.4, 124.3, 124.0, 121.4, 120.8, 119.0, 112.9, 112.6, 112.4, 110.7, 109.9, 109.3, 56.2, 33.0, 32.8, 32.7, 21.4 ppm; IR (film): 3054, 2922, 1588, 1471, 1280, 1144, 1084, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{29}\text{BrN}_4\text{O}_2\text{S}$: 636.1195; found: 636.1199.

N-(6''-chloro-5-methoxy-1,1',1''-trimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**5b**)



60.4 mg; yield: 97%; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 1.6 Hz, 1H), 7.13-7.05 (m, 3H), 6.96-6.91 (m, 3H), 6.82 (s, 1H), 6.78-6.75 (m, 2H), 6.66 (dd, J = 8.6, 1.8 Hz, 1H), 6.46 (d, J = 2.4 Hz, 1H), 3.90 (s, 3H), 3.64-3.63 (m, 6H), 3.39 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 153.3, 143.0, 141.5, 140.8, 137.9, 136.0, 132.8, 129.7, 129.5, 128.5, 128.4, 127.5, 126.4, 126.0, 125.8, 124.83, 124.77, 124.4, 122.5, 119.6, 113.6, 112.4, 111.7, 111.5, 109.9, 109.8, 109.1, 103.4, 103.3, 56.3, 55.4, 33.0, 32.9, 21.3 ppm; IR (film): 2939, 1622, 1590, 1488, 1280, 1227, 1144, 1084, 734 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{35}\text{H}_{31}\text{ClN}_4\text{O}_3\text{S}$: 622.1805; found: 622.1804.

N-(5-bromo-1''-ethyl-5''-methoxy-1,1'-dimethyl-[3,3':3',3''-terindolin]-2'-ylidene)-4-methylbenzenesulfonamide (**5c**)



67.3 mg; yield: 99%; pale gray solid, m.p. 143-144 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 2H), 7.32-7.29 (m, 2H), 7.24 (d, J = 2.0 Hz, 1H), 7.19-7.16 (m, 1H), 7.15-7.11 (m, 2H), 7.09-7.06 (m, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 6.80 (s, 1H), 6.77-6.75 (m, 1H), 6.33 (d, J = 2.4 Hz, 1H), 4.00 (q, J = 7.3 Hz, 2H), 3.88 (s, 3H), 3.64 (s, 3H), 3.47 (s, 3H), 2.28 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 153.3, 142.9, 141.4, 140.8, 136.3, 135.9, 131.7, 129.8, 128.8, 128.7, 128.4, 127.8, 126.5, 125.7, 124.8, 124.5, 124.4, 124.3, 113.2, 112.3, 111.7, 111.4, 110.7, 110.0, 109.8, 102.7, 56.2, 55.4, 41.1, 32.9, 32.8, 21.4, 15.5 ppm; IR (film): 2937, 1589, 1487, 1280, 1144, 1084, 790, 734 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{36}\text{H}_{33}\text{BrN}_4\text{O}_3\text{S}$: 680.1457; found: 680.1459.

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