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Axially chiral *N*-heterocyclic carbene gold(I) complex catalyzed asymmetric Friedel–Crafts/cyclization reaction of nitrogen-tethered 1,6-enynes with indole derivatives

Jinming Yang [a], Rui Zhang [a], Wenfeng Wang [a], Zhen Zhang [a], Min Shi [a,b,*]

[a] *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei-Long Road, Shanghai 200237, China*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China*

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ABSTRACT

A class of axially chiral NHC–Au(I) complexes has been applied to the asymmetric Friedel–Crafts/cyclization reaction of nitrogen-tethered 1,6-enynes **14** with indole derivatives **15**, affording the corresponding Friedel–Crafts and intramolecular cyclization products **16** in good yields and with moderate ee values under mild conditions.

1. Introduction

Over the past decade, homogeneous gold catalysis has seen rapid growth for C–C, C–O or C–N bond forming reactions mainly due to the soft carbophilic Lewis acid properties of gold complexes toward C–C multiple bonds.[1] In comparison to other transition metal catalysts, gold complexes can efficiently catalyze reactions under very mild conditions that are tolerant of air or moisture to give excellent chemoselectivity and wide functional group compatibility. Although the first example of a gold-catalyzed enantioselective reaction was reported by Hayashi and Ito in 1986 for the aldol condensation between isocyanates and aldehydes,[2] gold-catalyzed asymmetric transformations still remains a challenging topic although there have been a few investigations at the present stage[3] despite the rapid development of several synthetic applications.[4] To the best of our knowledge, most studies on this topic have been focused on the gold activation of allenes toward nucleophilic attack, such as the asymmetric hydrofunctionalization of allenes,[4b–f] [2+2] cycloaddition and cycloisomerization of enallenes.[5] Only a few reports have addressed the asymmetric activation of substrates containing an alkyne functional group.[4a,6] The difficulty of enantioselective gold(I)-catalyzed transformations is probably due to the linear coordination geometry of the Au(I) center with the reaction site far away from the chiral environment, thus special strategies or chiral ligands are needed to deliver spatial arrangements to the opposite site of the metal cation.[3,7]

N-Heterocyclic carbenes (NHCs) represent a growing class of ligands in transition-metal catalysis,[8] which have several typical features such as stability to air and moisture, low toxicity, strong σ-donor and poor π-acceptor properties.[9] So far, in almost all of the successful systems for asymmetric gold catalysis, chiral phosphines were employed as ligands,[2–6] while the number of chiral NHC–Au(I) complexes reported as catalysts remains rare[6f,g,10] although NHCs have emerged as an effective alternative for a number of homogeneous gold catalysts.[8k,11] During our ongoing survey of the literature, there is only one relevant paper reported by Tomioka et al. using C_2-symmetric NHC–Au(I) complexes in the cycloisomerization of 1,6-enynes, providing the corresponding cyclopentane products in high yields but along with moderate enantioselectivities (up to 59% ee).[6g] Based upon our previous successful examples of NHC–metal complex-catalyzed asymmetric transformations,[12] we reported that the sterically less hindered gold(I) complex (a*R*)-**6** shown in Scheme 1 with a pyrrolidin-1-yl group, was the best catalyst in the gold(I)-catalyzed asymmetric acetoxycyclization of 1,6-enyne, giving products in >99% yield and with (−)59% ee at 0 °C. The sterically less hindered gold(I) catalyst (a*S*)-**2a** (Scheme 1) as well was the best catalyst in the asymmetric oxidative rearrangement of 1,6-enynes, affording the corresponding aldehydes in excellent yields (up to >99%) and with low to modest enantioselectivities (3.1–70% ee) using PhCl as the solvent at 10 °C.[13] The steric environment around the gold center can significantly affect the product's enantioselectivity while the substrates used can also impact to a large extent, the reaction outcome; we thus attempted asymmetric catalysis with these chiral NHC–Au complexes. Herein we report that these axially chiral gold complexes are also reasonably effective in the asymmetric Friedel–Crafts/cyclization reaction of nitrogen-tethered 1,6-enynes **14** with

* Corresponding author. Fax: +86 21 64166128.
E-mail address: Mshi@mail.sioc.ac.cn (M. Shi).

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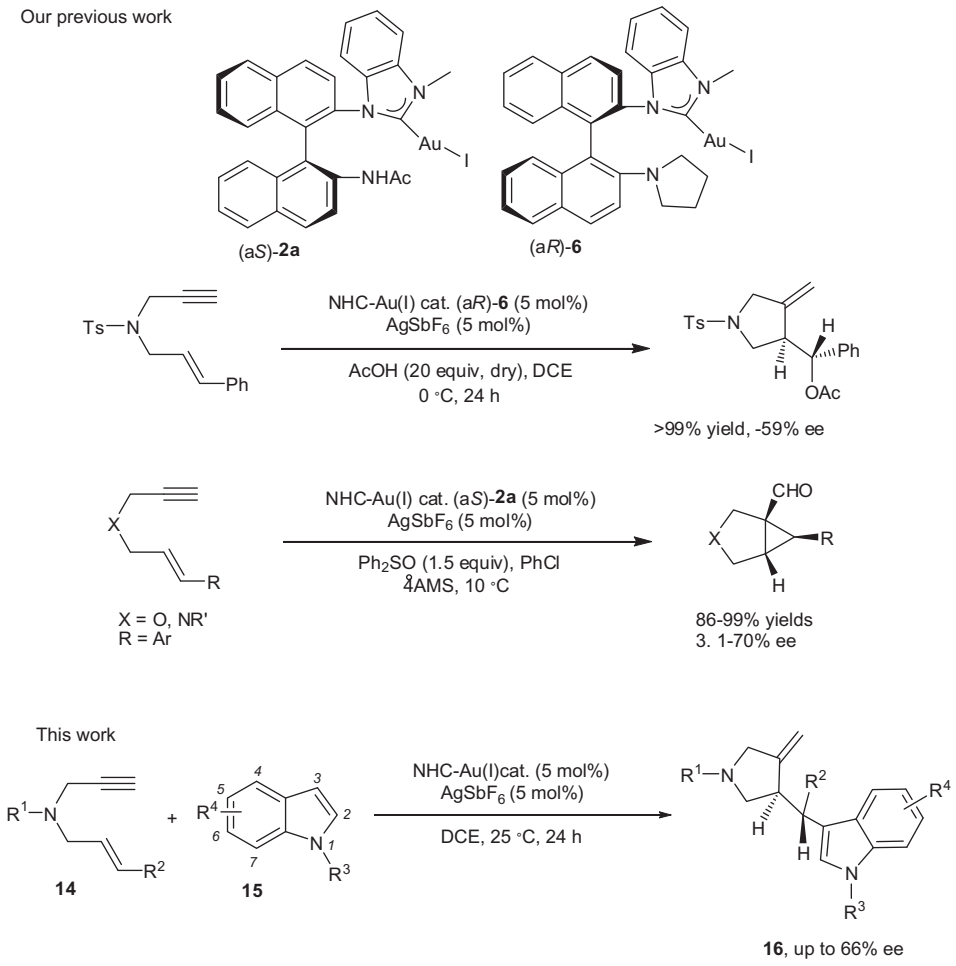


Scheme 1. Axially chiral NHC–Au complex catalyzed asymmetric reactions.

indole derivatives **15**, giving the corresponding Friedel–Crafts and intramolecular cyclization products **16** in good yields and with moderate ee values under mild conditions (Scheme 1).[14]

2. Results and discussion

Axially chiral NHC–Au(I) complexes **1**–**11**[13] and the intermediates **12** and **13** (Fig. 1) derived from optically active binaphthyl-2,2′-diamine (BINAM) (see Scheme 2 in the Section 4), which were employed in the asymmetric Friedel–Crafts/cyclization reaction of 1,6-enynes **14** with indole derivatives **15**. The new NHC–Au(I) complex (a*R*)-**4** was characterized by NMR, MALDI-MS, and IR spectroscopic data and its structure has been further confirmed by the X-ray diffraction study of single crystals grown from a solution of mixed petroleum ether/CH_3CO_2Et/CH_2Cl_2 (1:1:1). Its ORTEP drawing is shown in Figure 2.[15]

Initial examination of the asymmetric Friedel–Crafts/cyclization reaction of 1,6-enyne **14a** with indole derivative **15a** was carried out in various solvents using gold complex (a*R*)-**6** as the catalyst in the presence of silver salts and the results are summarized in Table 1. As can be seen from Table 1, the desired product **16a** was obtained in good yields in 1,2-dichloroethane (DCE), chlorobenzene, toluene, and dichloromethane using gold complex (a*R*)-**6** as the catalyst in the presence of $AgSbF_6$ (Table 1, entries 1–4). In acetonitrile, tetrahydrofuran (THF), and ether, the desired product **16a** was formed in lower yields, indicating that the reaction could not proceed efficiently in electron-donating solvents (Table 1, entries 5–7). The examination of other silver salts and other counter ions, such as NaBARF, revealed that $AgSbF_6$ was the best cocatalyst in this reaction (Table 1, entries 8–13). This may be due to the counter anion of SbF_6 making the gold cationic species more stable in this reaction. In terms of the yield, we found that using DCE as the solvent, **16a** was formed in a 73% yield and 37% ee value with a 99:1 dr value (Table 1, entry 1). Since the solvents employed could significantly affect the reaction rates, all of the reactions shown in Table 1 were quenched until when they were complete, based on the TLC monitoring.

We next examined various axially chiral gold complexes in the asymmetric Friedel–Crafts/cyclization reaction of 1,6-enyne **14a** with indole derivative **15a** in DCE at 25 °C and the results are shown in Table 2. These gold complexes are all fairly effective catalysts in this reaction to afford **16a** in moderate to good yields along with 4–46% ee values (Table 2, entries 1–14). Axially chiral gold complex (a*S*)-**7** produced **16a** in an 89% yield along with 46% ee and 12:1 dr, this was the best result in this reaction (Table 2, entry 10).

Having determined the optimal reaction conditions, the generality of this gold(I) complex-catalyzed asymmetric Friedel–Crafts/cyclization reaction was next examined using a variety of 1,6-enynes **14** and indole derivatives **15** and the results are summarized in Table 3. When the R^1 sulfonyl group was 4-bromobenzenesulfonyl (Bs), 4-nitrobenzenesulfonyl (Ns) or 2,4,6-triisopropylbenzenesulfonyl, the reaction proceeded smoothly to afford the corresponding products **16b**–**16d** in good yields but along with 2–44% ee values, suggesting that the electronic properties and steric effects of the sulfonyl group play a significant role in this reaction (Table 3, entries 1–3). Moreover, when R^2 was either an electron-rich or -poor aromatic group, the reaction proceeded

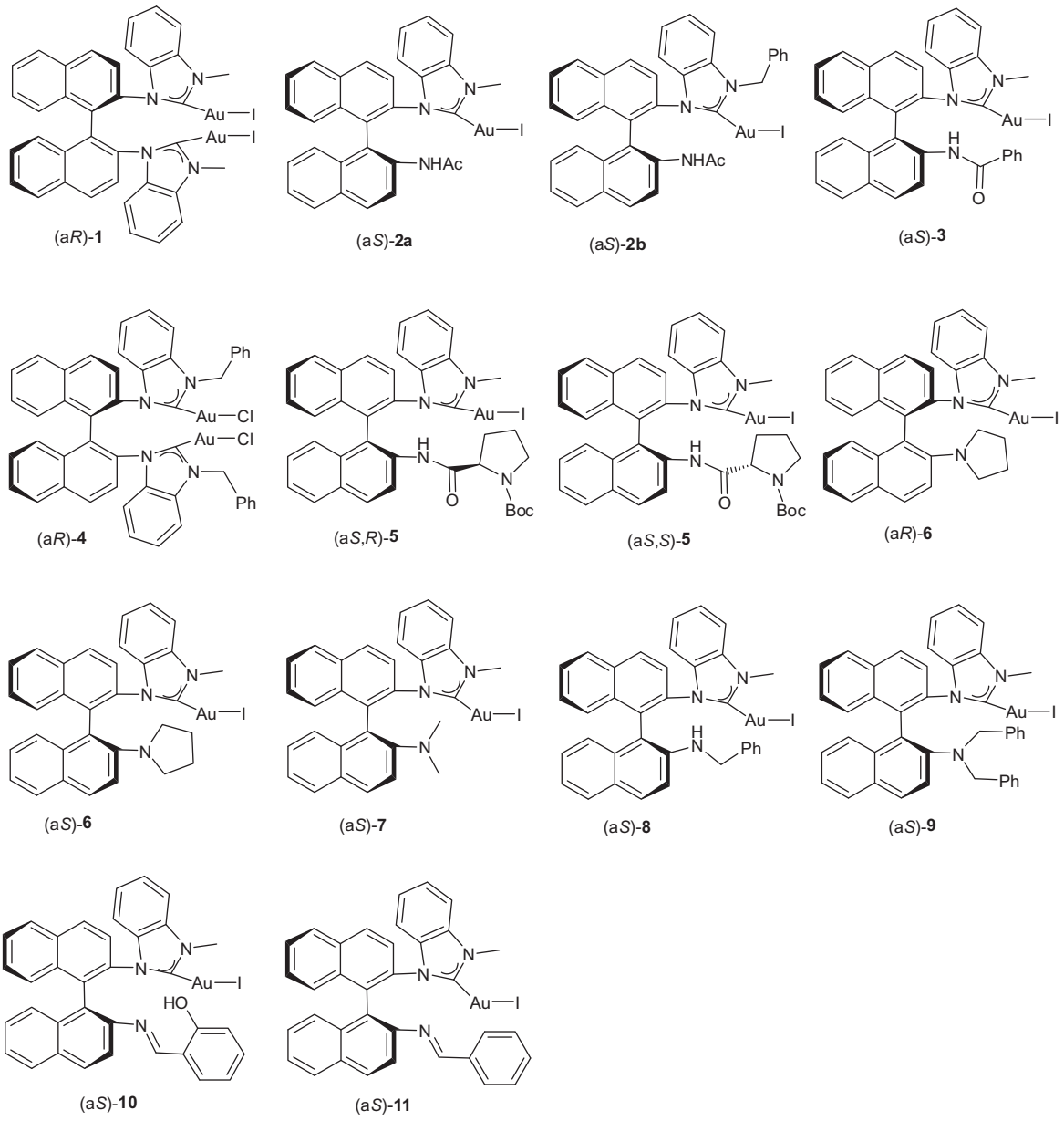
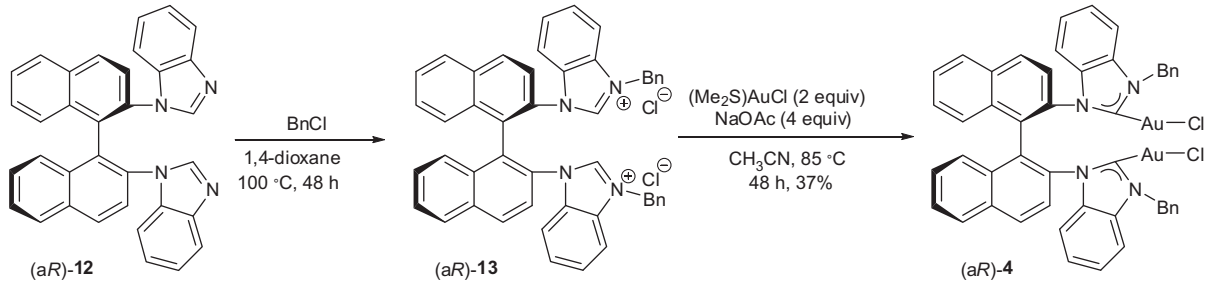


Figure 1. Axially chiral gold complexes employed in the asymmetric Friedel–Crafts/cyclization reaction of 1,6-enynes **14** with indole derivatives **15**.



Scheme 2.

efficiently to give the corresponding adducts **16e**–**16i** in good yields along with 42–62% ee values and high dr values, indicating that the electronic properties of the R^2 group did not have a significant impact on the reaction outcome (Table 3, entries 4–8). Furthermore, the R^3 group on the indole derivative could also be an H atom, Bn group or Boc-protecting group, giving the corresponding products

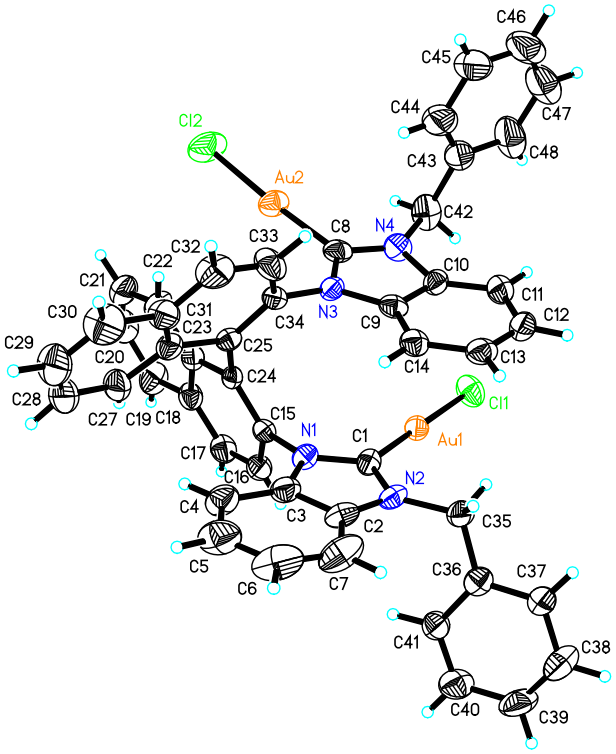


Figure 2. ORTEP drawing of NHC–Au(I) complex **4**.

16j–**16n** in good yields along with 54–66% ee values and high dr values under the standard conditions (Table 3, entries 9–13). Only when R^2 was a hydrogen atom or an aliphatic group such as substrates **14j** (R^2 = H), **14k** (2 × R^2 = Me), or **14l** (2 × R^2 = Me), did the reaction provide complex product mixtures under the standard conditions (Table 3, entries 14–16). Their spectroscopic data have been summarized in Section 4 and the major product of **16** was unambiguously assigned as having the *anti*-configuration on the basis of X-ray diffraction data of **16l**. Its ORTEP drawing is shown in Figure 3.[16] We used **16l** of 66% ee for recrystallization from CH_2Cl_2/petroleum ether (1:1). The single crystal obtained is a racemic product. Therefore, while the relative configuration can be determined, the absolute configuration cannot be determined at the present stage.

3. Conclusion

In conclusion, axially chiral gold(I) complex **7** prepared from optically active BINAM was found to be a fairly effective catalyst for the asymmetric Friedel–Crafts/cyclization reaction of 1,6-enynes **14** with indole derivatives **15** in DCE under mild conditions to give the corresponding products **16** in good yields along with moderate to good enantioselectivities. Efforts are currently underway to elucidate the mechanistic details of this asymmetric reaction and to find further applications for these axially chiral gold complexes.

4. Experimental

4.1. General

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. Melting points were determined on a digital melting point apparatus and temperatures are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 or AM-400 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to 0.00 ppm (TMS) and 77.0 ppm ($CDCl_3$), respectively; coupling constants J are given in Hz. Optical rotations were determined at 589 nm (sodium D line) using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in units of 10 deg^{-1} cm^2 g^{-1}. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Chiral HPLC was performed by using a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H, OD-H and IC-H columns, 4.6 × 250 mm, Daicel Chemical Ind., Ltd). Mass spectra were recorded by EI, ESI, and MALDI and HRMS was measured on a HP-5989 instrument. Flash column chromatography was performed using 300–400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. The single crystals for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/petroleum ether (1:1).

4.2. Preparation of axially chiral NHC–Au(I) complexes 1, 2a, 2b, 3 and 5–11

Complexes **1**, **2a**, **2b**, **3** and **5**–**11** are the known compounds and were synthesized according to the literature.[17]

4.2.1. Complex (a*R*)-1

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.24 (s, 6H), 6.54 (t, J = 8.0 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 7.14 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.55–7.70 (m, 8H), 7.95 (d, J = 9.2 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H).

4.2.2. Complex (a*S*)-2a

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.07 (s, 3H), 3.94 (s, 3H), 6.82 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 7.12–7.22 (m, 5H), 7.25–7.29 (m, 1H), 7.39–7.46 (m, 2H), 7.64–7.69 (m, 3H), 7.80 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 9.2 Hz, 1H).

4.2.3. Complex (a*S*)-2b

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.99 (s, 3H), 5.37 (d, J = 15.6 Hz, 1H), 5.84 (d, J = 15.6 Hz, 1H), 6.82–6.84 (m, 2H), 6.89 (t, J = 7.2 Hz, 1H), 6.95–7.09 (m, 5H), 7.19 (t, J = 7.2 Hz, 1H), 7.28–7.29 (m, 4H), 7.48–7.49 (m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.68–7.72 (m, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H).

4.2.4. Complex (a*S*)-3

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.77 (s, 3H), 6.79 (d, J = 8.4 Hz, 1H), 7.02 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.20–7.30 (m, 5H), 7.36 (t, J = 7.2 Hz, 1H), 7.43–7.47 (m, 2H), 7.56–7.66 (m, 3H), 7.72 (d, J = 9.2 Hz, 2H), 7.76–7.81 (m, 3H), 8.21 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.40 (d, J = 9.2 Hz, 1H).

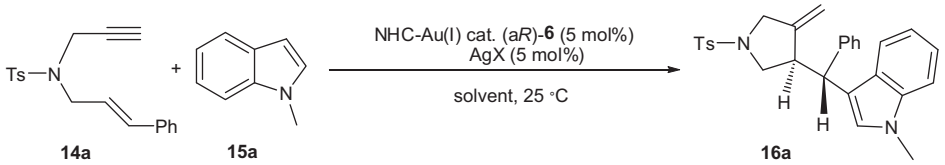
4.2.5. Complex (a*S*,*S*)-5

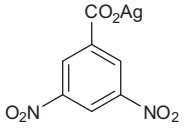
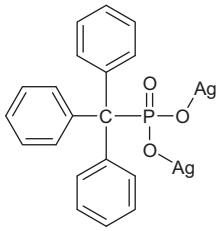
This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.20 (s, 9H), 1.62–2.10 (m, 6H), 2.86 (s, 1H), 3.77 (s, 3H), 4.31 (br, 1H), 7.10–7.13 (m, 1H), 7.21–7.32 (m, 3H), 7.38 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.50–7.54 (m, 1H), 7.59 (t, J = 7.2 Hz, 2H), 7.63 (d, J = 9.2 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 8.08 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 9.2 Hz, 1H), 8.53 (s, 1H).

4.2.6. Complex (a*S*)-6

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80–1.83 (m, 2H), 1.95–2.01 (m, 2H), 2.61 (t, J = 8.0 Hz, 2H),

Table 1
Asymmetric Friedel–Crafts/cyclization reaction of 1,6-enyne **14a** with indole derivative **15a** in various solvents in the presence of (a*R*)-**6** and silver salts



Entry[a]	AgX	Solvent	Time (d)	Yield[b](%)	dr[c]	ee[d](%)
1	$AgSbF_6$	DCE	1	73	>99:1	(−)37
2	$AgSbF_6$	PhCl	2	83	12:1	(−)14
3	$AgSbF_6$	Toluene	2	69	>99:1	(−)24
4	$AgSbF_6$	CH_2Cl_2	1.5	77	53:1	(−)22
5	$AgSbF_6$	CH_3CN	7	40	>99:1	(−)13
6	$AgSbF_6$	THF	2.5	35	>99:1	(−)18
7	$AgSbF_6$	Et_2O	5	46	26:1	(−)20
8	AgOTf	DCE	1	59	>99:1	(−)5
9	$AgClO_4$	DCE	2.5	44	>99:1	(−)37
10	4-NO_2PhCO_2Ag	DCE	7	NR	—[e]	—[e]
11		DCE	6	NR	—[e]	—[e]
12		DCE	5	NR	—[e]	—[e]
13	NaBARF	DCE	5	Trace	—[e]	—[e]

[a] Reaction conditions: 5 mol % of catalyst; 5 mol % of AgX; 0.1 mmol of **14a**; 3.0 equiv of **15a**; 1.0 mL of dry solvent.
[b] Isolated yields.
[c] Determined by ^{1}H NMR spectroscopy.
[d] Determined by chiral HPLC using a Chiralpak AD-H column.
[e] Not determined.

2.99–3.05 (m, 2H), 4.06 (s, 3H), 6.19 (d, *J* = 8.4 Hz, 1H), 6.36 (t, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.12–7.17 (m, 3H), 7.19–7.23 (m, 1H), 7.27 (d, *J* = 9.2 Hz, 1H), 7.47–7.53 (m, 2H), 7.63–7.67 (m, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H).

4.2.7. Complex (a*S*)-7

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.46 (s, 6H), 4.07 (s, 3H), 6.33 (d, *J* = 8.0 Hz, 1H), 6.41 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.16–7.27 (m, 4H), 7.42–7.45 (m, 2H), 7.58–7.65 (m, 3H), 7.85 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H).

4.2.8. Complex (a*S*)-8

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.95 (s, 3H), 4.38 (dd, *J* = 6.0, 16.0 Hz, 1H), 4.56 (t, *J* = 5.6 Hz, 1H), 4.62 (dd, *J* = 5.6, 16.0 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 7.02–7.05 (m, 4H), 7.08–7.17 (m, 5H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.42–7.45 (m, 3H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.67 (ddd, *J* = 2.8, 5.6, 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H).

4.2.9. Complex (a*S*)-9

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.75 (s, 3H), 4.32 (s, 4H), 6.58 (d, *J* = 7.2 Hz, 4H), 6.67 (t, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 4H), 7.00 (t, *J* = 7.2 Hz, 2H), 7.15–7.20 (m, 2H), 7.25–7.34 (m, 5H), 7.42 (d, *J* = 9.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.65–7.67 (m, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H).

4.2.10. Complex (a*S*)-10

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.76 (s, 3H), 6.68 (ddd, *J* = 2.8, 6.0, 8.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.90 (dt, *J* = 1.2, 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 7.16–7.17 (m, 2H), 7.25–7.40 (m, 5H), 7.43–7.47 (m, 1H), 7.55 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.59–7.65 (m, 2H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.48 (s, 1H), 11.82 (s, 1H).

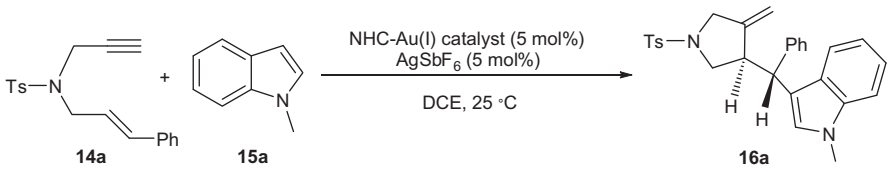
4.2.11. Complex (a*S*)-11

This is a known compound.[17] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.80 (s, 3H), 6.86 (ddd, *J* = 1.6, 6.0, 7.6 Hz, 1H), 7.15–7.26 (m, 4H), 7.29–7.34 (m, 3H), 7.36–7.41 (m, 2H), 7.46–7.55 (m, 4H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.39 (s, 1H).

4.3. Preparation of axially chiral NHC–Au(I) complex (a*R*)-4

Compound **12**[12f] (195 mg, 0.40 mmol) and benzyl chloride (0.93 mL, 8.0 mmol) were refluxed in 1,4-dioxane (6.0 mL) until **12** was completely consumed as seen by TLC monitoring. When a

Table 2
Axially chiral gold complex catalyzed asymmetric Friedel–Crafts/cyclization reaction of 1,6-enyne **14a** with indole derivative **15a** in DCE



Entry[a]	Catalyst	Time (d)	Yield[b](%)	dr[c]	ee[d] (%)
1	(a*R*)-**1**	1.0	84	68:1	(+)33
2	(a*S*)-**2a**	1.0	87	6:1	(+)44
3	(a*S*)-**2b**	1.0	88	>99:1	(+)20
4	(a*S*)-**3**	1.5	53	25:1	(−)4
5	(a*R*)-**4**	2.0	70	35:1	(+)38
6	(a*S*,*S*)-**5**	1.5	44	42:1	(−)11
7	(a*S*,*R*)-**5**	1.0	63	42:1	(+)17
8	(a*S*)-**6**	1.0	89	>99:1	(+)34
9	(a*R*)-**6**	2.0	73	>99:1	(−)37
10	(a*S*)-**7**	1.0	89	12:1	(+)46
11	(a*S*)-**8**	2.5	42	36:1	(+)12
12	(a*S*)-**9**	1.0	67	>99:1	(+)20
13	(a*S*)-**10**	1.0	85	30:1	(−)4
14	(a*S*)-**11**	1.0	82	50:1	(−)10

[a] Reaction conditions: 5 mol % of catalyst; 5 mol % of $AgSbF_6$; 0.1 mmol of **14a**; 3.0 equiv of **15a**; 1.0 mL of DCE.
[b] Isolated yields.
[c] Determined by ^1H NMR spectroscopy.
[d] Determined by chiral HPLC using a Chiralpak AD-H column.

white solid precipitated in the reaction system, the resulting suspension was cooled to room temperature and filtered to obtain the solid, which was then washed with *n*-hexane three times to give benzimidazolium salt **13** in almost quantitative yield without any further purification.

Under an argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirrer bar were added NHC precursor **13** (74 mg, 0.10 mmol), NaOAc (33 mg, 0.40 mmol), and [(Me_2S)AuCl] (59 mg, 0.20 mmol) followed by the addition of dry CH_3CN (5.0 mL) as the solvent. After refluxing at 85 °C for about 48 h, the reaction mixture was cooled to room temperature and filtered through Celite. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 3/1) to give complex **4** as a white solid in a 37% yield (Scheme 2).

4.3.1. Compound (a*R*)-12

This is a known compound.[12f] ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 6.11 (d, J = 7.8 Hz, 2H), 6.50 (t, J = 7.5 Hz, 2H), 6.93–6.99 (m, 2H), 6.99 (s, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.48–7.56 (m, 6H), 7.63–7.69 (m, 2H), 8.07 (d, J = 8.4 Hz, 4H).

4.3.2. Complex (a*R*)-4

A colorless solid. Mp 325–327 °C (dec.). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 5.82 (d, J = 15.6 Hz, 2H), 6.22 (d, J = 15.2 Hz, 2H), 6.48 (t, J = 8.0 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 7.00 (t, J = 8.0 Hz, 2H), 7.27–7.36 (m, 8H), 7.47 (d, J = 7.2 Hz, 4H), 7.56–7.60 (m, 2H), 7.65–7.71 (m, 6H), 7.98 (dd, J = 8.0, 5.6 Hz, 4H). IR (KBr) ν 2359, 2342, 1749, 1734, 1698, 1684, 1559, 1534, 1522, 1508, 1489, 1474, 1276, 1261, 764, 749, 689, 684, 669, 651 cm^{-1}. $[\alpha]_D^{20} = +60$ (c 0.45, $CHCl_3$). LRMS (MALDI) m/e 1095.5 [M^+-Cl]; HRMS (MALDI) calcd for [$C_{48}H_{34}N_4{}^{197}$Au-Cl_2Au] requires 863.2444, found 863.2429 [M^+-Cl_2Au].

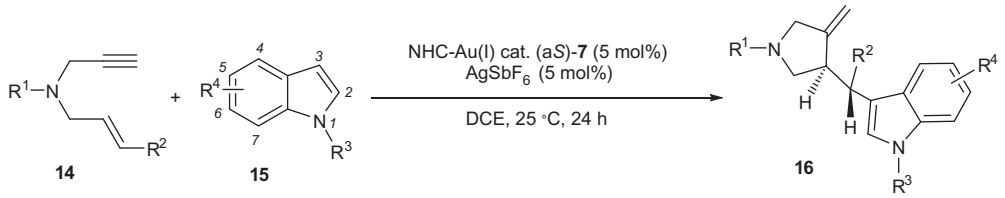
4.4. Preparation of 1,6-enynes and indole derivatives

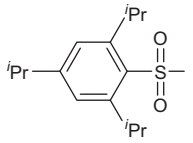
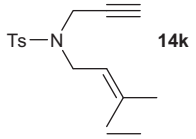
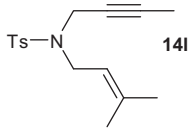
4.4.1. Preparation of 1,6-enyne 14i

To a mixture of propargylamine (412 μL, 6.0 mmol) and Et_3N (0.92 mL, 6.6 mmol) in CH_2Cl_2 (4.0 mL) was added dropwise the solution of TsCl (1258 mg, 6.6 mmol) in CH_2Cl_2 (12.0 mL) at 0 °C. The reaction system was then warmed to room temperature and stirred for 5 h followed by quenching with 20 mL of water. After extraction with CH_2Cl_2 for three times, the combined organic phases were washed with saturated brine and then dried over anhydrous Na_2SO_4. The crude product was concentrated under reduced pressure and then purified by silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 5/1; containing minor Et_3N) to give 4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide as a white solid in an 84% yield. It is a known compound.[18] ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.11 (t, J = 2.4 Hz, 1H), 2.43 (s, 3H), 3.83 (dd, J = 6.0, 2.4 Hz, 2H), 4.73 (t, J = 6.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H).

Under an argon atmosphere, to a solution of 4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (418 mg, 2.0 mmol), 3-(4-methoxyphenyl)-prop-2-en-1-ol (362 mg, 2.2 mmol), and Ph_3P (630 mg, 2.4 mmol) in THF (10 mL) was added dropwise DEAD (0.47 mL, 2.4 mmol) at 0 °C. The reaction was warmed to room temperature and stirred for 24 h. The volatiles were then removed under reduced pressure and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 10/1) to give **14i** as a yellow solid in a 90% yield. Mp 85–87 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.05 (t, J = 2.4 Hz, 1H), 2.42 (s, 3H), 3.79 (s, 3H), 3.96 (d, J = 6.6 Hz, 2H), 4.11 (d, J = 1.8 Hz, 2H), 5.92 (dt, J = 15.3, 7.5 Hz, 1H), 6.51 (d, J = 15.3 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 9.0 Hz, 4H), 7.76 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 35.7, 48.6, 55.2, 73.7, 76.5, 113.9, 120.4, 127.7, 128.8, 129.4, 134.4, 135.9, 143.5, 159.4. IR (KBr) ν 3033, 2957, 2925, 2838, 1607, 1577, 1512, 1495, 1464, 1456, 1442, 1421, 1347, 1305,

Table 3
The scope and limitations of the axially chiral gold complex catalyzed asymmetric Friedel–Crafts/cyclization reaction of 1,6-enynes **14** with indole derivatives **15** in DCE



Entry[a]	R^1	R^2	R^3, R^4	Yield[b](%)	dr[c]	ee[d](%)
1	Bs	Ph, **14b**	1-Me, H, **15a**	**16b**, 40	66:1	(+)6
2	Ns	Ph, **14c**	1-Me, H, **15a**	**16c**, 80	57:1	(+)44
3		Ph, **14d**	1-Me, H, **15a**	**16d**, 67	>99:1	(+)2
4	Ts	1-Naph, **14e**	1-Me, H, **15a**	**16e**, 87	>99:1	(+)62
5	Ts	Mes, **14f**	1-Me, H, **15a**	**16f**, 90	>99:1	(+)62
6	Ts	4-ClC_6H_4,**14g**	1-Me, H, **15a**	**16g**, 83	>99:1	(+)62
7	Ts	4-MeC_6H_4,**14h**	1-Me, H, **15a**	**16h**, 87	>99:1	(+)60
8	Ts	4-$MeOC_6H_4$, **14i**	1-Me, H, **15a**	**16i**, 86	>99:1	(+)42
9	Ts	Ph, **14a**	H, 2-Me, **15b**	**16j**, 88	9:1	(+)65
10	Ts	Ph, **14a**	1-Bn, 2-Me, **15c**	**16k**, 73	10:1	(+)56
11	Ts	Ph, **14a**	H, 5-Br, **15d**	**16l**, 86	13:1	(+)66
12	Ts	Ph, **14a**	1-Bn, H, **15e**	**16m**, 81	>99:1	(+)63
13	Ts	Ph, **14a**	1-Boc, H, **15f**	**16n**, 72	>99:1	(+)54
14	Ts	H, **14j**	1-Me, H, **15a**	Complex	—[e]	—[e]
15	 **14k**	**14k**	1-Me, H, **15a**	Complex	—[e]	—[e]
16	 **14l**	**14l**	1-Me, H, **15a**	Complex	—[e]	—[e]

[a] Reaction conditions: 5 mol % of (a*S*)-**7**; 5 mol % of $AgSbF_6$. 0.1 mmol of **14**; 3.0 equiv of **15**; 1.0 mL of dry DCE at 25 °C for 24 h.
[b] Isolated yields.
[c] Determined by ^1H NMR spectroscopy.
[d] Determined by chiral HPLC.
[e] Not determined.

1282, 1252, 1175, 1161, 1119, 1095, 1059, 1032, 926, 898, 854, 814, 763, 738, 715, 703, 659, 580, 564, 543 cm^{-1}. LRMS (EI) *m*/*e* 355, 200 (65.69%), 199 (20.29%), 198 (100%), 184 (22.53%), HRMS (EI) calcd for [$C_{20}H_{21}NO_3S$] requires 355.1242, found 355.1246 [M^+].

4.4.2. 1,6-Enynes 14a–14h, 14j–14m and indole derivatives 15a, 15d, and 15f are known compounds and have been synthesized according to the literature procedures[17,19–22]

4.5. General procedure for NHC–Au(I) complex-catalyzed asymmetric Friedel–Crafts/cyclization reaction of 1,6-enynes with indole derivatives and analytical data for the products

A mixture of NHC–Au(I) complex (5 mol %), 1,6-enyne **14a** (0.10 mmol), 1-methyl-1*H*-indole **15a** (0.30 mmol), and $AgSbF_6$ (2.0 mg, 0.0050 mmol) in dry 1,2-dichloroethane (DCE) (1.0 mL) was stirred at 25 °C until **14a** was completely consumed by TLC monitoring. Then the reaction mixture was quenched by filtering through Celite and the volatiles were removed under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 8/1) to give the corresponding product **16a** as a white solid.

4.5.1. 1-Methyl-3-((4-methylene-1-tosylpyrrolidin-3-yl)(phenyl)methyl)-1*H*-indole 16a

This is a known compound.[1a] ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.43 (s, 3H), 3.31 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.40–3.47 (m, 2H), 3.74 (s, 3H), 3.83 (d, *J* = 14.0 Hz, 1H), 3.88 (d, *J* = 16.0 Hz, 1H), 3.95 (d, *J* = 10.4 Hz, 1H), 4.23 (d, *J* = 1.2 Hz, 1H), 4.73 (d, *J* = 1.2 Hz, 1H), 6.87 (s, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 7.08–7.11 (m, 1H), 7.16–7.25 (m, 8H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), $[\alpha]_D^{20} = -43$ (*c* 2.0, $CHCl_3$) [(+)46% ee].

4.5.2. 3-{[1-(4-Bromo-benzenesulfonyl)-4-methylene-pyrrolidin-3-yl]-phenyl-methyl}-1-methyl-1*H*-indole 16b

A colorless solid. 40% yield. Mp 197–199 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 3.30 (dd, *J* = 9.3, 3.9 Hz, 1H), 3.45 (dd, *J* = 18.9, 9.6 Hz, 1H), 3.40–3.50 (m, 1H), 3.73 (s, 3H), 3.85 (s, 2H), 3.94 (d, *J* = 9.9 Hz, 1H), 4.28 (s, 1H), 4.76 (s, 1H), 6.85 (s, 1H), 7.02–7.13 (m, 2H), 7.18–7.27 (m, 6H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 9.0 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.8, 45.7, 47.8, 52.2, 53.1, 109.2, 110.4, 116.1, 119.0, 119.4, 121.8, 125.8, 126.3, 127.1, 127.8, 128.1, 128.2, 129.1, 132.3, 134.7, 137.0, 143.1, 144.6. IR (KBr) ν 3056, 2928, 2883, 2360, 1574, 1541, 1472, 1457, 1388, 1373, 1348, 1120, 1092, 1032, 1008, 901, 823, 738, 703, 613, 577 cm^{-1}.

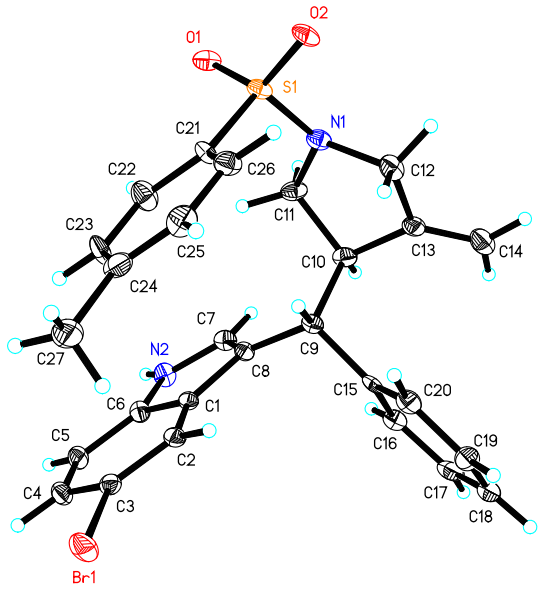


Figure 3. ORTEP drawing of **16l**.

$[\alpha]_D^{20} = -4.0$ (*c* 0.20, $CHCl_3$), $[\alpha]_D^{20} = -2.0$ (*c* 1.0, $CHCl_3$) [(+)6% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 9.15 min, t_{minor} = 12.23 min. LRMS (ESI) *m*/*e* 521.0 [M$^+$+H]; HRMS (ESI) calcd for [$C_{27}H_{26}N_2O_2SBr$] requires 521.0893, found 521.0893 [M$^+$+H].

4.5.3. 1-Methyl-3-{[4-methylene-1-(4-nitro-benzenesulfonyl)-pyrrolidin-3-yl]-phenyl-methyl}-1*H*-indole 16c

A yellow solid. 80% yield. Mp 192–194 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.33–3.38 (m, 1H), 3.47–3.52 (m, 2H), 3.74 (s, 3H), 3.91–3.94 (m, 3H), 4.33 (d, *J* = 1.6 Hz, 1H), 4.80 (d, *J* = 1.2 Hz, 1H), 6.86 (s, 1H), 6.97–7.01 (m, 1H), 7.09–7.12 (m, 1H), 7.16–7.21 (m, 5H), 7.23–7.27 (m, 2H), 7.82–7.85 (m, 2H), 8.21–8.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.8, 45.8, 47.9, 52.2, 53.0, 109.3, 110.8, 116.0, 119.1, 119.2, 122.0, 124.3, 125.8, 126.4, 127.1, 128.1, 128.2, 128.3, 128.6, 137.0, 142.9, 144.3, 150.1. IR (KBr) *v* 3058, 2923, 2854, 2360, 2343, 1527, 1505, 1458, 1349, 1166, 1098, 736, 615 cm^{-1}. $[\alpha]_D^{20} = -27$ (*c* 0.45, $CHCl_3$) [(+)44% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 12.12 -min, t_{minor} = 21.89 min. LRMS (ESI) *m*/*e* 488.1 [M$^+$+H]; HRMS (ESI) calcd for [$C_{27}H_{25}N_3O_4S$+Na] requires 510.1458, found 510.1463 [M$^+$+Na].

4.5.4. 1-Methyl-3-{[4-methylene-1-(2,4,6-triisopropyl-benzene-sulfonyl)-pyrrolidin-3-yl]-phenyl-methyl}-1*H*-indole 16d

A colorless solid. 67% yield. Mp 194–195 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (d, *J* = 6.4 Hz, 6H), 1.19 (d, *J* = 6.8 Hz, 6H), 1.23 (d, *J* = 6.8 Hz, 6H), 2.82–2.93 (m, 1H), 3.41 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.51 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.59–3.65 (m, 1H), 3.72 (s, 3H), 3.86 (dt, *J* = 13.2, 1.6 Hz, 1H), 3.94 (dq, *J* = 13.6, 2.0 Hz, 1H), 4.09–4.19 (m, 2H), 4.24 (d, *J* = 10.8 Hz, 1H), 4.28 (dd, *J* = 4.0, 2.0 Hz, 1H), 4.78 (dd, *J* = 3.6, 1.6 Hz, 1H), 6.94 (s, 1H), 6.98–7.02 (m, 1H), 7.08–7.24 (m, 7H), 7.28–7.31 (m, 2H), 7.49–7.51 (dt, *J* = 8.0, 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 24.6, 24.9, 32.7, 34.1, 45.8, 47.8, 51.4, 109.1, 110.0, 116.7, 118.9, 119.4, 121.7, 123.8, 125.7, 126.2, 127.2, 128.2, 128.3, 130.8, 137.0, 143.6, 145.6, 151.3, 153.0. IR (KBr) *v* 2958, 2928, 2868, 1600, 1483, 1465, 1424, 1363, 1316, 1263, 1151, 1134, 1061, 1043, 1031, 899, 883, 765, 703, 675, 670, 588, 562 cm^{-1}. $[\alpha]_D^{20} = +2.0$ (*c* 1.0, $CHCl_3$) [(+)2% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 6.25 min, t_{minor} = 8.45 min. LRMS (ESI) *m*/*e* 569.2 [M$^+$+H]; HRMS (ESI) calcd for [$C_{36}H_{44}N_2O_2S$+Na] requires 591.3016, found 591.3021 [M$^+$+Na].

4.5.5. 1-Methyl-3-{[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-naphthalen-1-yl-methyl}-1*H*-indole 16e

A colorless solid. 87% yield. Mp 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.44 (s, 3H), 3.42 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.51–3.64 (m, 2H), 3.69 (s, 3H), 3.84 (t, *J* = 14.7 Hz, 2H), 4.21 (s, 1H), 4.54 (s, 1H), 4.92 (d, *J* = 9.3 Hz, 1H), 6.85 (s, 1H), 6.95 (dd, *J* = 7.5, 6.9 Hz, 1H), 7.15 (t, *J* = 6.6 Hz, 1H), 7.21–7.28 (m, 4H), 7.31–7.45 (m, 4H), 7.63 (dd, *J* = 7.8, 4.2 Hz, 3H), 7.77–7.80 (m, 1H), 7.90–7.93 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 22.6, 32.7, 48.2, 52.4, 53.3, 109.2, 109.8, 116.3, 118.8, 119.4, 121.7, 122.9, 124.7, 125.2, 125.8, 126.5, 126.8, 127.3, 127.8, 128.9, 129.7, 132.0, 132.6, 133.7, 137.0, 139.3, 143.6, 145.1. IR (KBr) *v* 3048, 2923, 2853, 2359, 2343, 1596, 1541, 1508, 1472, 1458, 1344, 1160, 10995, 793, 777, 738, 663, 587, 548 cm^{-1}. $[\alpha]_D^{20} = -95$ (*c* 0.50, $CHCl_3$) [(+)62% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 9.03 min, t_{minor} = 10.31 min. LRMS (ESI) *m*/*e* 507.1 [M$^+$+H]; HRMS (ESI) calcd for [$C_{32}H_{30}N_2O_2S$+Na] requires 529.1920, found 529.1936 [M$^+$+Na].

4.5.6. 1-Methyl-3-[[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-(2,4,6-trimethyl-phenyl)-methyl]-1*H*-indole 16f

A colorless solid. 90% yield. Mp 225–227 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.97 (s, 3H), 2.20 (d, *J* = 23.4 Hz, 6H), 2.40 (s, 3H), 3.57–3.73 (m, 4H), 3.78 (s, 3H), 3.95 (d, *J* = 13.5 Hz, 1H), 4.09 (s, 1H), 4.45 (d, *J* = 10.5 Hz, 1H), 4.70 (s, 1H), 6.57 (s, 1H), 6.77 (s, 2H), 6.88 (d, *J* = 5.4 Hz, 2H), 7.11–7.16 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 3H), 7.65 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 21.5, 29.6, 32.8, 41.2, 44.1, 52.4, 54.2, 108.9, 110.6, 115.7, 118.7, 119.9, 121.5, 126.0, 127.76, 127.78, 129.7, 132.4, 135.3, 135.6, 137.0, 143.6, 144.1. IR (KBr) *v* 2922, 2855, 1613, 1597, 1471, 1424, 1346, 1306, 1180, 1096, 1045, 1013, 815, 738, 664, 591, 549 cm^{-1}. $[\alpha]_D^{20} = -94$ (*c* 0.80, $CHCl_3$) [(+)62% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 6.36 min, t_{minor} = 6.86 min. LRMS (ESI) *m*/*e* 499.1 [M$^+$+H]; HRMS (ESI) calcd for [$C_{31}H_{34}N_2O_2S$+Na] requires 521.2233, found 521.2223 [M$^+$+Na].

4.5.7. 3-{(4-Chlorophenyl)-[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-methyl}-1-methyl-1*H*-indole 16g

A colorless solid. 83% yield. Mp 202–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.23 (s, 3H), 3.34–3.40 (m, 3H), 3.75 (s, 3H), 3.80–3.93 (m, 3H), 4.23 (s, 1H), 4.76 (s, 1H), 6.86 (s, 1H), 7.00–7.04 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.13–7.28 (m, 7H), 7.59 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.8, 45.1, 47.8, 52.1, 53.0, 109.3, 110.5, 115.8, 119.0, 119.3, 121.9, 125.8, 127.0, 127.7, 128.3, 129.5, 129.7, 131.8, 132.6, 137.1, 141.9, 143.6, 144.8. IR (KBr) *v* 2922, 1733, 1698, 1684, 1653, 1647, 1558, 1541, 1489, 1473, 1457, 1340, 1161, 1092, 1013, 739, 663, 591, 549 cm^{-1}. $[\alpha]_D^{20} = -46$ (*c* 0.35, $CHCl_3$) [(+)62% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 10.79 min, t_{minor} = 13.21 min. LRMS (ESI) *m*/*e* 491.1 [M$^+$+H]; HRMS (ESI) calcd for [$C_{28}H_{27}N_2O_2SCl$+Na] requires 513.1374, found 513.1366 [M$^+$+Na].

4.5.8. 1-Methyl-3-{[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-*p*-tolyl-methyl}-1*H*-indole 16h

A colorless solid. 87% yield. Mp 178–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.23 (s, 3H), 2.43 (s, 3H), 3.27 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.39–3.46 (m, 2H), 3.73 (s, 3H), 3.85 (s, 2H), 3.92 (d, *J* = 10.4 Hz, 1H), 4.28 (d, *J* = 1.2 Hz, 1H), 4.74 (d, *J* = 0.8 Hz, 1H), 6.85 (s, 1H), 7.00 (dd, *J* = 12.0, 7.2 Hz, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 6.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 32.7, 45.2, 47.7, 52.4, 53.1, 109.2, 110.0, 116.6, 118.8, 119.5, 121.6, 125.7, 127.2, 127.7, 127.9, 128.8, 129.7, 132.6, 135.6, 137.0, 140.3, 143.5, 145.2. IR (KBr) *v* 3048, 2922, 2856, 2360, 2343, 2331, 1541, 1509, 1482, 1473, 1458, 1373, 1344, 1161, 1132, 1118, 1095, 1044, 814, 739, 663, 591, 549 cm^{-1}.

$[\alpha]_D^{20} = -26$ (*c* 0.50, $CHCl_3$) [(+)60% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 8.73 min, t_{minor} = 11.30 min. LRMS (ESI) *m*/*e* 471.1 [M$^+$+H]; HRMS (ESI) calcd for [$C_{29}H_{30}N_2O_2S$+Na] requires 493.1920, found 493.1923 [M$^+$+Na].

4.5.9. 3-{(4-Methoxy-phenyl)-[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-methyl}-1-methyl-1*H*-indole 16i

A yellow solid. 86% yield. Mp 190–192 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.42 (s, 3H), 3.29 (dd, *J* = 13.5, 8.4 Hz, 1H), 3.38–3.42 (m, 2H), 3.71 (s, 3H), 3.73 (s, 3H), 3.85 (s, 2H), 3.90 (d, *J* = 9.0 Hz, 1H), 4.26 (s, 1H), 4.75 (s, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 5.7 Hz, 3H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 32.7, 44.8, 47.9, 52.3, 53.1, 55.1, 109.2, 110.1, 113.4, 116.6, 118.7, 119.5, 121.7, 125.6, 127.1, 127.7, 129.0, 129.6, 132.6, 135.5, 137.0, 143.5, 145.1, 157.8. IR (KBr) *v* 3057, 3027, 2926, 2854, 2360, 2343, 1610, 1542, 1509, 1473, 1466, 1459, 1344, 1247, 1161, 1095, 742, 664, 591, 549 cm^{-1}. $[\alpha]_D^{20} = -21$ (*c* 0.45, $CHCl_3$) [(+)42% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 11.40 min, t_{minor} = 15.38 min. LRMS (ESI) *m*/*e* 487.1 [M$^+$+H]; HRMS (ESI) calcd for [$C_{29}H_{30}N_2O_3S$+Na] requires 509.1869, found 509.1856 [M$^+$+Na].

4.5.10. 2-Methyl-3-{[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-phenyl-methyl}-1*H*-indole 16j

A colorless solid. 88% yield. Mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.34 (s, 3H), 2.42 (s, 3H), 3.11 (dd, *J* = 6.8, 1.2 Hz, 2H), 3.78 (dt, *J* = 14.0, 2.0 Hz, 2H), 4.02 (dd, *J* = 14.4, 1.2 Hz, 1H), 4.08 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 1.6 Hz, 1H), 4.79 (d, *J* = 1.6 Hz, 1H), 7.01–7.11 (m, 3H), 7.18–7.34 (m, 7H), 7.57 (dd, *J* = 8.4, 6.4 Hz, 3H), 7.84 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 21.5, 45.5, 46.0, 52.4, 53.0, 109.9, 110.6, 113.0, 119.0, 119.3, 120.8, 126.0, 126.9, 127.7, 128.1, 128.3, 129.6, 132.0, 132.7, 135.5, 143.1, 143.5, 145.9. IR (KBr) *v* 3055, 2922, 2854, 1716, 1697, 1684, 1558, 1541, 1472, 1458. 1436, 1430, 1339, 1304, 1184, 1160, 1094, 1065, 1045, 1032, 899, 813, 737, 664, 588, 549. cm^{-1}. $[\alpha]_D^{20} = -45$ (*c* 0.20, $CHCl_3$) [(+)65% ee]. Chiralcel OD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{minor} = 10.76 min t_{major} = 13.14 min,. LRMS (ESI) *m*/*e* 457.1 [M$^+$+H]; HRMS (ESI) calcd for [$C_{28}H_{29}N_2O_2S$] requires 457.1944, found 457.1943 [M$^+$+H].

4.5.11. 1-Benzyl-2-methyl-3-{[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-phenyl-methyl}-1*H*-indole 16k

A colorless solid. 73% yield. Mp 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.27 (s, 3H), 2.38 (s, 3H), 3.05 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.17 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.84 (dt, *J* = 14.0, 2.0 Hz, 2H), 3.97 (dd, *J* = 14.0, 1.6 Hz, 1H), 4.11 (d, *J* = 11.2 Hz, 1H), 4.44 (dd, *J* = 4.0, 2.0 Hz, 1H), 4.81 (dd, *J* = 4.0, 2.0 Hz, 1H), 5.28 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 6.8 Hz, 2H), 7.02–7.35 (m, 13H), 7.55 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.61 (dd, *J* = 7.2, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.6, 21.5, 45.7, 45.9, 46.5, 52.5, 53.1, 109.4, 109.9, 113.3, 119.2, 119.3, 120.9, 125.8, 126.0, 126.2, 127.3, 127.7, 128.1, 128.3, 128.8, 129.6, 132.8, 133.7, 136.9, 137.7, 143.1, 143.4, 146.0. IR (KBr) *v* 3085, 3059, 3027, 2924, 2855, 2360, 2343, 1655, 1597, 1560, 1541, 1508, 1496, 1466, 1453, 1412, 1346, 1162, 1095, 739, 699, 664, 589, 549. cm^{-1}. $[\alpha]_D^{20} = -21$ (*c* 0.15, $CHCl_3$) [(+)56% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 8.05 -min, t_{minor} = 10.11 min. LRMS (ESI) *m*/*e* 547.2 [M$^+$+H]; HRMS (ESI) calcd for [$C_{35}H_{35}N_2O_2S$] requires 547.2414, found 547.2394 [M$^+$+H].

4.5.12. 5-Bromo-3-{[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-phenyl-methyl}-1*H*-indole 16l

A yellow solid. 86% yield. Mp 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.45 (s, 3H), 3.28–3.32 (m, 1H), 3.40–3.44 (m, 2H), 3.81–3.85 (m, 3H), 4.22 (d, *J* = 1.2 Hz, 1H), 4.74 (d, *J* = 1.6 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 7.10–7.13 (m, 3H), 7.16–7.23 (m, 4H), 7.27 (dd, *J* = 8.4, 7.6 Hz, 2H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 8.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 45.5, 47.7, 52.2, 53.1, 110.3, 112.68, 112.73, 117.5, 121.7, 122.4, 125.1, 126.5, 127.6, 128.1, 128.3, 128.5, 129.8, 132.5, 134.9, 142.6, 143.8, 144.7. IR (KBr) *v* 3085, 3065, 2924, 1653, 1647, 1636, 1457, 1339, 1170, 1097, 814, 737, 702, 548 cm^{-1}. $[\alpha]_D^{20} = -6.0$ (*c* 0.25, $CHCl_3$).), $[\alpha]_D^{20} = -4.0$ (*c* 1.0, $CHCl_3$) [(+)66% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 8.56 min, t_{minor} = 9.54 min. LRMS (ESI) *m*/*e* 521.0 [M$^+$+H]; HRMS (ESI) calcd for [$C_{27}H_{25}N_2O_2SBr$+Na] requires 543.0712, found 543.0725 [M$^+$+Na].

4.5.13. 1-Benzyl-3-{[4-methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-phenyl-methyl}-1*H*-indole 16m

A colorless solid. 81% yield. Mp 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.40 (s, 3H), 3.31–3.36 (m, 1H), 3.38–3.42 (m, 1H), 3.41 (dd, *J* = 6.0, 3.6 Hz, 1H), 3.82–3.90 (m, 2H), 3.95 (d, *J* = 9.6 Hz, 1H), 4.22 (d, *J* = 1.2 Hz, 1H), 4.73 (d, *J* = 1.6 Hz, 1H), 5.28 (d, *J* = 1.6 Hz, 2H), 6.93 (s, 1H), 6.99–7.21 (m, 11H), 7.27–7.35 (m, 4H), 7.59 (dt, *J* = 8.4, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 45.6, 47.8, 49.9, 52.3, 53.0, 109.7, 110.1, 117.1, 119.2, 119.7, 122.0, 125.3, 126.2, 126.5, 127.5, 127.6, 127.7, 128.1, 128.2, 128.8, 129.7, 132.7, 136.8, 137.5, 143.1, 143.5, 145.0. IR (KBr) *v* 3059, 2923, 2854, 2360, 1598, 1495, 1480, 1466, 1453, 1345, 1160, 1094, 766, 741, 663, 589, 549 cm^{-1}. $[\alpha]_D^{20} = -41$ (*c* 0.30, $CHCl_3$) [(+)63% ee]. Chiralcel AD-H, hexane/^{i}PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 10.04 min, t_{minor} = 13.18 min. LRMS (ESI) *m*/*e* 533.1 [M$^+$+H]; HRMS (ESI) calcd for [$C_{34}H_{32}N_2O_2S$+Na] requires 555.2077, found 555.2064 [M$^+$+Na].

4.5.14. 3-{[4-Methylene-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-phenyl-methyl}-indole-1-carboxylic acid *tert*-butyl ester (16n)

A colorless solid. 72% yield. Mp 90–92 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.71 (s, 9H), 2.43 (s, 3H), 3.34–3.39 (m, 1H), 3.43 (d, *J* = 5.1 Hz, 2H), 3.76–3.87 (m, 2H), 3.96 (d, *J* = 13.8 Hz, 1H), 4.13 (s, 1H), 4.72 (s, 1H), 7.09–7.29 (m, 10H), 7.48 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 8.05 (d, *J* = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 28.2, 29.7, 45.3, 47.7, 52.0, 53.1, 84.0, 110.7, 115.2, 119.7, 121.9, 122.3, 124.6, 126.7, 127.7, 128.26, 128.33, 129.8, 132.7, 141.6, 143.6, 144.3. IR (KBr) *v* 2956, 2926, 2855, 1732, 1474, 1453, 1371, 1350, 1309, 1256, 1215, 1162, 1121, 1070, 1050, 1032, 1015, 815, 767, 762, 746, 663, 590, 549 cm^{-1}. $[\alpha]_D^{20} = -58$ (*c* 0.50, $CHCl_3$) [(+)54% ee]. Chiralcel IC-H, hexane/^{i}PrOH = 60/40, 0.7 mL/min, 230 nm, t_{minor} = 24.11 min t_{major} = 37.90 min. LRMS (ESI) *m*/*e* 565.0 [M$^+$+Na]; HRMS (ESI) calcd for [$C_{32}H_{34}N_2O_4S$+Na] requires 565.2132, found 565.2118 [M$^+$+Na].

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15. The crystal data for **4** have been deposited in CCDC with number 831588. Empirical Formula: $C_{49}H_{36}Au_2Cl_4N_4$; Formula Weight: 1216.55; Crystal Color, Habit: colorless, Crystal Dimensions: 0.157 × 0.086 × 0.071 mm; Crystal System: Monoclinic; Lattice Parameters: a = 13.578(7)Å, b = 11.721(6)Å, c = 14.055(7)Å, α = 90°, β = 105.038(8)°, γ = 90°, V = 2160.2(19)Å^3; Space group: $P2(1)$; Z = 2; D_{calc} = 1.870 g/cm^3; F_{000} = 1168; Final R induces [$I > 2\sigma(I)$]: R1 = 0.0408; wR2 = 0.0834.
16. The crystal data for **16l** have been deposited in CCDC with number 844605. Empirical Formula: $C_{27}H_{25}BrN_2O_2S$; Formula Weight: 521.46; Crystal Color, Habit: colorless, Crystal Dimensions: 0.25 × 0.15 × 0.10 mm; Crystal System: Triclinic; Lattice Parameters: a = 9.3548(13)Å, b = 12.6226(17)Å, c = 20.103(3)Å, α = 80.248(3)°, β = 89.184(3)°, γ = 89.857(3)°, V = 2339.2(5)Å^3; Space group: P-1; Z = 4; D_{calc} = 1.481 g/cm^3; F_{000} = 1072; Final R indices [$I > 2\sigma(I)$] R1 = 0.0844, wR2 = 0.2445.
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