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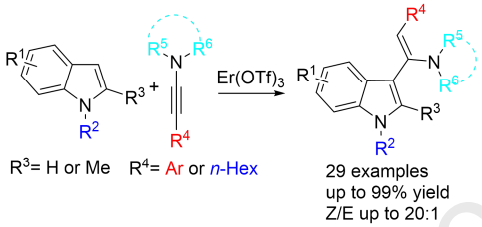

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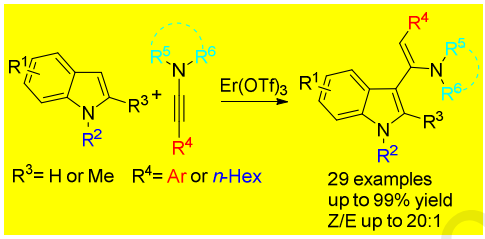

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Er(OTf)$_3$-Catalyzed Approach to 3-Alkenylindoles Through Regioselective Addition of Ynamides and Indoles

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ABSTRACT

An efficient approach to access functionalized 3-alkenylindoles has been developed through Er(OTf)$_3$-catalyzed addition of ynamides and indoles. A number of C- aryl substituted ynamides **7a-7k** could react with indoles **6a-6s**, affording the desired products **8aa-8sa, 8ab-8ak, 8bd, 8bk** and **8tc** in moderate to excellent yields with high regioselectivities.

1. Introduction

Indoles exist as subunits for many natural products and pharmaceuticals.[1] For instance, Vinblastine (**1**) and Vincristine (**2**), isolated from *Vinca rosea*,[2] exhibit potent anti-tumor effect by altering the physiological activity of cell mitosis through tubulin inhibition, and have been used in clinical.[3] Sunitinib (**3**), a multi-target inhibitor developed by Sugen in 2006, is currently applied in the clinical treatment of malignant stromal tumor or metastatic renal cell carcinoma.[4] Indirubin (**4**), a Chinese medicine extracted from indigo, displays an excellent inhibitory effect on CML leukemia with the characteristics of reliable curative effect, small toxic and side effects.[5] In addition, Melatonin (**5**), can effectively inhibit a variety of tumors, including colon, breast, and prostate cancers (**Figure 1**).[6] As a result, development of efficient methodologies based on indole skeleton is of great importance.

Over the past decade, ynamides have been widely used in organic synthesis and many important transformations have been achieved with high regio- and stereoselectivities.[7,8] For example, a variety of skeletons including functional indoles,[9,17] benzofurans,[10] quinolines,[11] oxazoles,[12] pyridines,[13] carbolines,[9b,14] enamides,[15] and amidines[16] have been successfully synthesized from ynamides. Among them, *cis*-hydroarylation of ynamides with indoles, which was first achieved by Zhang and co-workers, is one of the most interesting and important methods in preparing alkenylpyrroles, alkenylfurans and alkenylindoles. In this case, Tf_2NH served as an alternative Brønsted acid to catalyze the regioselective *cis*-hydroarylation at C-3 position of 1H-indole with ynamides, affording the desired products in moderate to excellent selectivities, in which the acetylene-terminal substituent of ynamides is *n*-hexyl. Aryl substituted ynamides have not been reported (**Figure 2**, a).[17] Interestingly, the additive

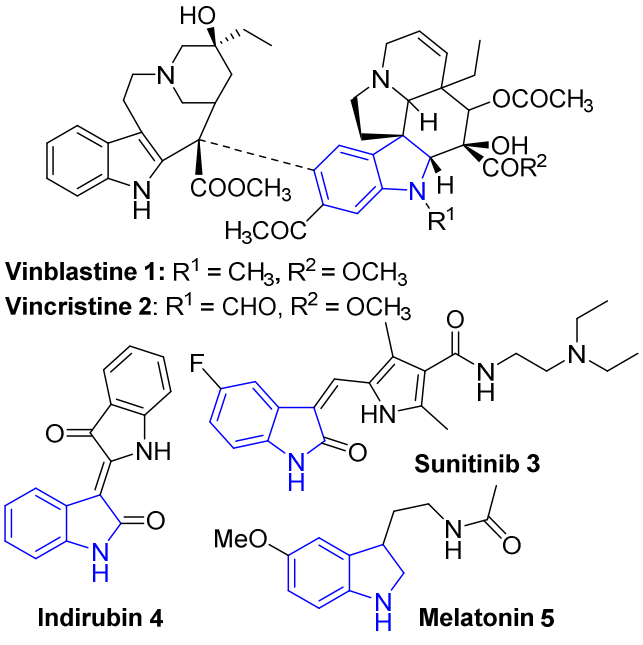

Figure 1. Structures of several natural products and drug molecules.

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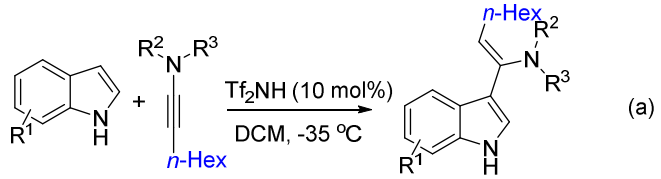
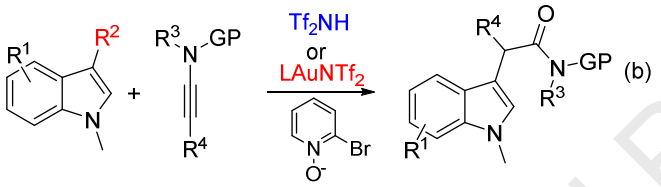
2-...Tf)$_3$ leading to amide products in excellent yield.[9c] Similar results were also obtained under LAuNTf$_2$/2-Br pyridine-N-oxide conditions (**Figure 2**, b).[9g] It is worth mentioning that gold complex could catalyze *cis*-hydroarylation of ynamides with indoles, affording 2-alkenyl products (**Figure 2**, c).[18] Very recently, we successfully established a diastereoselective approach to *trans*-pyrido and pyrrolo[1,2-c][1,3]oxazin-1-ones through Sc(OTf)$_3$-catalyzed addition of ynamides with *N,O*-acetals[19a] or ketones.[19b] On the basis of our continuous efforts in tombarthite Lewis acid catalyzed chemical transformations, we envisioned that *cis*-hydroarylation of ynamides could occur with indoles (**Figure 2**, d). Herein we present an efficient approach for the synthesis of 3-alkenylindoles through Er(OTf)$_3$-catalyzed regioselective addition of ynamides and indoles (**Figure 2**, d).

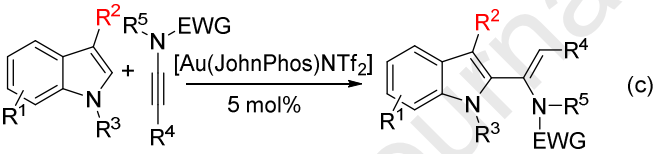
Tf$_2$NH catalyzed *cis*-hydroarylation[17]



Tf$_2$NH or LAuNTf$_2$ catalyzed *addition*[9e,9g]



Gold-Catalyzed *cis*-Hydroarylation[18]



Er(OTf)$_3$-Catalyzed *cis*-Hydroarylation (This work)

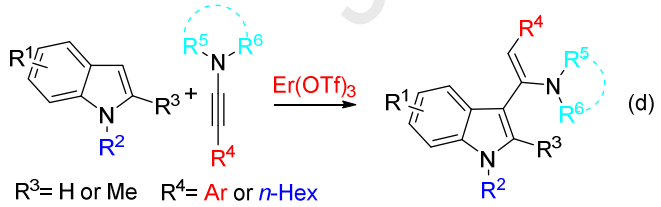
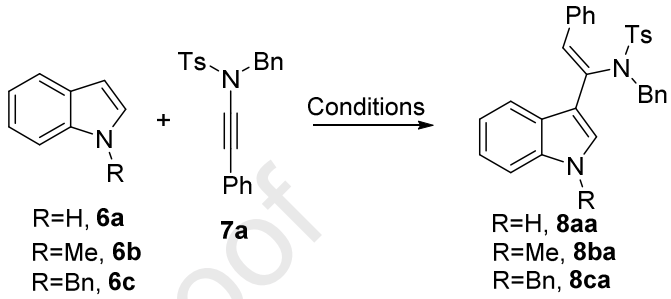


Figure 2. *cis*-Hydroarylation of Ynamides with Indoles.

2. Results and Discussion

Our investigation commenced with the reaction of ynamide **7a** with indole **6** under Brønsted acid or Lewis acid-promoted conditions. When the mixture of **7a** and **6a** was treated with Tf$_2$NH (conditions used by Zhang)[17] at room temperature or -35^{o}C for 2 h, **8aa** was produced in 83% and 81% yield separately. This hydroarylation was highly regioselective in C-3, but the ratio of Z/E isomers was low (Table 1, entries 1-2). To improve the Z/E selectivity, various Lewis acids were screened, and the results were summarized in Table 1. Lewis acid BF$_3$·Et$_2$O could promote the selective formation of E isomer in 85% yield (Table 1, entry 3). In(OTf)$_3$ could afford the product in 80% yield, but with 1:1 ratio of Z/E isomers (Table 1, entry 4); Cu(OTf)$_2$ also predominately produced E isomer (Z/E = 1:8) in 75% yield could afford the Z isomer as the main product, and Er(OTf)$_3$ turned out to be the most effective catalyst, producing **8aa** not only in extremely high yield (up to 92%), but also with excellent stereoselectivity (Table 1, entries 6-8). Different N-substituted indoles were also examined for this Er(OTf)$_3$ catalyzed transformation (entries 9-11). *N*-Me indole **6b** could react well to produce **8ba**, but *N*-Ts and *N*-Boc indoles failed to deliver the desired products, due to the deficiency of electron density at indole nitrogen. *N*-Bn indole **6c** could react well to produce **8ca**, but with poor stereoselectivity (Table 1, entry 12).

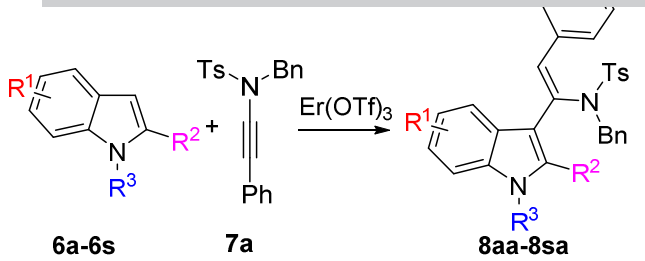
Table 1. Optimization of reaction conditions.

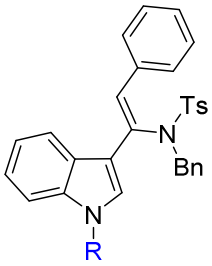


Entry[a]	R	Lewis acid	T/(^{o}C)	Y%[b]	*Z*:*E*[c]
1[d]	H	Tf$_2$NH (Brønsted acid)	rt	83	5:1
2[d]	H	Tf$_2$NH	-35	81	10:1
3	H	BF$_3$·Et$_2$O	70	85	1:20
4	H	In(OTf)$_3$	70	80	1:1
5	H	Cu(OTf)$_2$	70	75	1:8
6	H	Y(OTf)$_3$	70	76	12:1
7	H	Sc(OTf)$_3$	70	79	20:1
8	H	Er(OTf)$_3$	70	92	20:1
9	Me	Er(OTf)$_3$	70	83	20:1
10	Ts	Er(OTf)$_3$	70	-	-
11	Boc	Er(OTf)$_3$	70	-	-
12	Bn	Er(OTf)$_3$	70	78	55:45

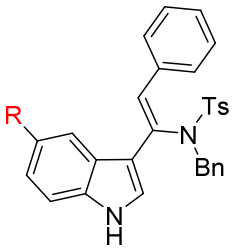
[a] A solution of compound **6** (0.25 mmol), LA (0.05 mmol) and **7** (0.30 mmol) in anhydrous DCE (1.5 mL) was stirred for 2 h. The mixture was quenched with a saturated aqueous solution of NaHCO$_3$ and extracted with EtOAc. [b]Isolated yield. [c]*Z*:*E* was determined by ^{1}H NMR. [d] Tf$_2$NH was 0.025 mmol.

Next, we turned to investigate the scope and limitation of the addition of ynamide **7a** with different indoles **6a-6s** (**Scheme 1**). Different substituted indoles were surveyed under the optimal conditions, as summarized in Scheme 1. In general, all these 5-, 6-, 4-substituted indoles could smoothly react with ynamide **7a**, affording the desired 3-alkenylindoles **8da-8ha, 8ja-8ma** in moderate to excellent yields with high regioselectivities. When 5-OTIPS indole were used, the desired products **8ia** was obtained in 72% yield with a reduced regioselectivity (*Z*/*E*=7:1). 5-Azaindole or 5-hydroxyl indoles could not obtain the desired products, the reactions were complex. When 5,6-disubstituted indoles were used, the desired products **8na-8pa** were also obtained in moderate to excellent yields with high regioselectivities. In addition, 5- and 2-substituted *N*-Me indoles **6q-6s** also proved to be suitable substrates, affording the desired products **8qa-8sa** in moderate to excellent yields with high regioselectivities. It is worth mentioning that 1-Methyl-1H-indol-5-amine could successfully provide the product **8sa** in 72% yield with high regioselectivities. Azaindole substrates could not react.

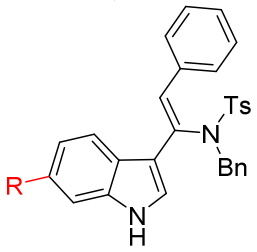




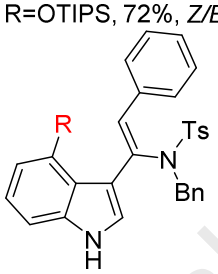
8aa, R=H, 92%, *Z*/*E*=20:1
8ba, R=Me, 64%, *Z*/*E*=20:1
8ca, R=Me, 78%, *Z*/*E*=3:2



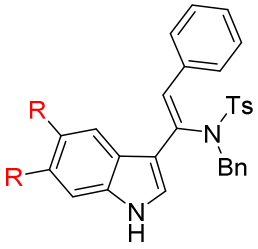
8da, R=OCF_3, 92%, *Z*/*E*=20:1
8ea, R=CF_3, 82%, *Z*/*E*=20:1
8fa, R=OMe, 90%, *Z*/*E*=20:1
8ga, R=OBn, 63%, *Z*/*E*=20:1
8ha, R=Cl, 66%, *Z*/*E*=20:1
8ia, R=OTIPS, 72%, *Z*/*E*=7:1



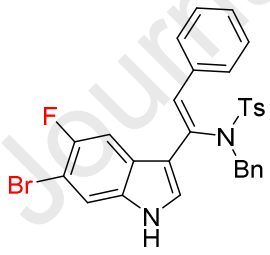
8ja, R=Br, 87%, *Z*/*E*=20:1
8ka, R=Cl, 95%, *Z*/*E*=20:1



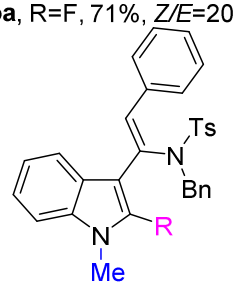
8la, R=OMe, 93%, *Z*/*E*=20:1
8ma, R=Me, 75%, *Z*/*E*=20:1



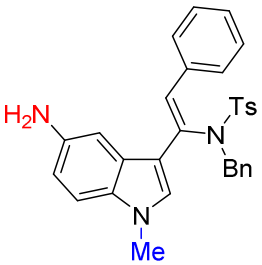
8na, R=Cl, 79%, *Z*/*E*=20:1
8oa, R=F, 71%, *Z*/*E*=20:1



8pa, 95%, *Z*/*E*=20:1



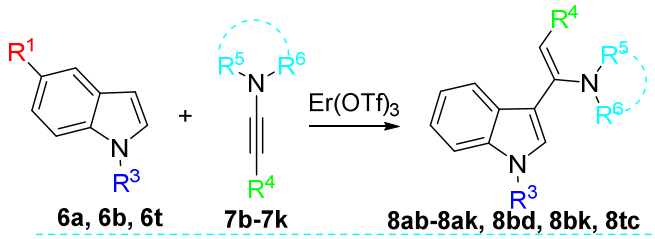
8qa, R=Ph, 98%, *Z*/*E*=20:1
8ra, R=Me, 99%, *Z*/*E*=20:1

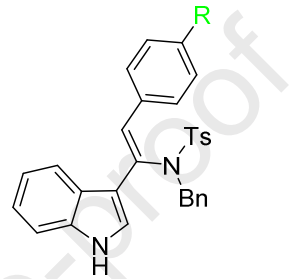


8sa, 72%, *Z*/*E*=20:1

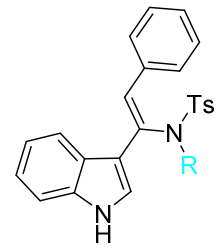
Scheme 1. The reactions of ynamide **7a** with different indoles **6a-6s**. [a] A solution of compound **6a-6s** (0.25 mmol), $Er(OTf)_3$ (30 mg, 0.05 mmol) and **7a** (0.30 mmol) in anhydrous DCE (1.5 mL) was stirred at 70 °C for 2 h. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with EtOAc. [b]Isolated yield. [c]*Z*:*E* was determined by ^1H NMR.

A variety of substitutions at the acetylene phenyl ring and nitrogen of ynamide **7** were also investigated, and the results are summarized in **Scheme 2**. Various *N*-Ts ynamides with *N*-Bn, *N*-Me and *N*-Ph substitution could afford the desired products in moderate to good yields with high regioselectivities (**8ab-8af,** for *N*-Me ynamide (**8af**). It is worth mentioning that the replacement of -NBnTs with other groups like oxazolidone ring or -NBnCOOEt could also lead to the desired products **8ag-8ak**, **8bk**, but the yields and selectivities were slightly reduced in these cases. We speculate that the reason for the low yields of **8ag-8ak, 8bk** may be the decreased activity of ynamides. Specifically, substrate containing aliphatic R^4 groups could not obtain the product.

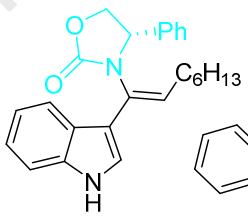




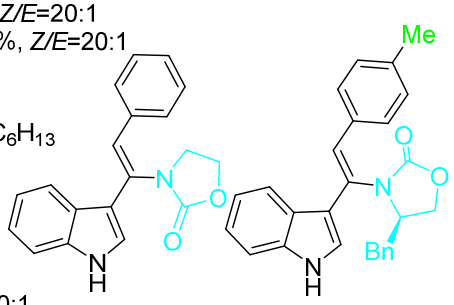
8ab, R=Br, 85%, *Z*/*E*=20:1
8ac, R=Cl, 76%, *Z*/*E*=20:1
8ad, R=OMe, 92%, *Z*/*E*=20:1



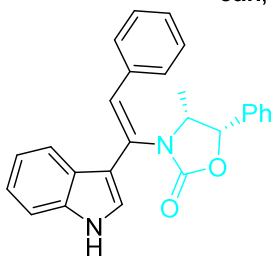
8ae, R=Ph, 83%, *Z*/*E*=20:1
8af, R=Me, 47%, *Z*/*E*=5:1



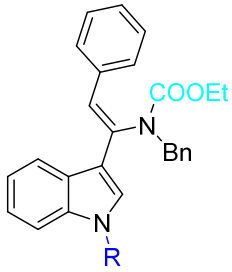
8ag, 36%, *Z*/*E*=20:1



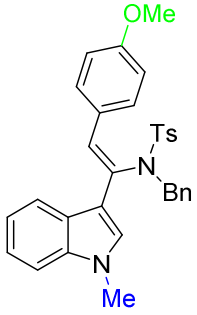
8ah, 35%, *Z*/*E*=20:1 **8ai**, 72%, *Z*/*E*=6:1



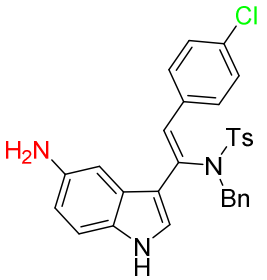
8aj, 42%, *Z*/*E*=10:1



8ak, R=H, 48%, *Z*/*E*=20:1
8bk, R=Me, R= 50%, *Z*/*E*=20:1



8bd, 79%, *Z*/*E*=20:1



8tc, 74%, *Z*/*E*=20:1

Scheme 2. The reactions of ynamides **7b-7k** with indoles **6a, 6b** and **6t**. [a] A solution of **6a/6b/6t** (0.25 mmol), $Er(OTf)_3$ (30 mg, 0.05 mmol) and **7b-7k** (0.30 mmol) in anhydrous DCE (1.5 mL) was stirred at 70 °C for 2 h. The

mi
extracted with EtOAc. Isolated yield. Z:E was determined by ^{1}H NMR.

The stereochemistry of alkenyl products were unambiguously determined as *Z*-form based on the X-ray crystallography of **8aa**[20] (**Figure 3** and see Supporting Information).

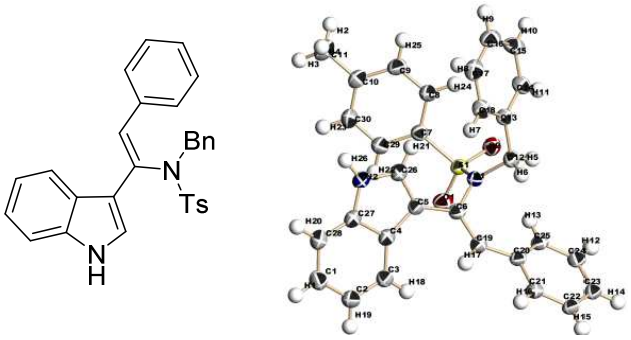


Figure 3. The X-ray crystallography of **8aa**.

On the basis of our experimental results and the precedent ynamide chemistry,[19] a possible mechanism for this $Er(OTf)_3$-catalyzed transformation was illustrated in **Figure 4**. First, the triple bond in ynamide **7** was activated by $Er(OTf)_3$. The resulting alkenyl Er(III) intermediate **int-1** was subsequently attacked by indoles from the same side of the metal Er due to the electronegativity,[21] giving (*Z*)-indole **int-2**. Finally, the **int-2** was hydrolyzed to yield the desired *cis*-hydroarylation 3-alkenylindoles and regenerate $Er(OTf)_3$ for the catalytic cycle. The formation of (*E*)-indole of boron trifluoride and copper triflate conditions is due to the large intermolecular interaction between aryl R^4 and indole, which makes indole attack from the same side of aryl R^4.

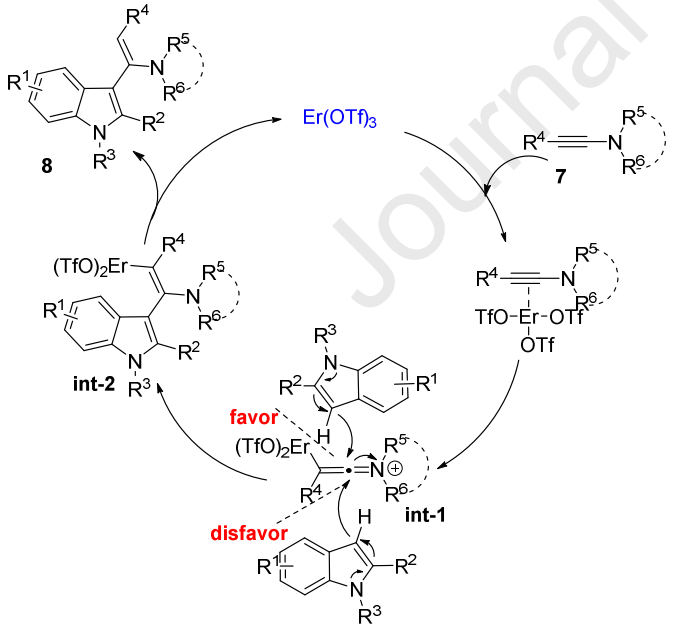


Figure 4. The proposed reaction mechanism

3. Conclusions

In summary, we have established an efficient approach to access functionalized 3-alkenylindoles through $Er(OTf)_3$-catalyzed regioselective addition of ynamides **7a-7k** with indoles **6a-6s**. $Er(OTf)_3$ was found to be an effective catalyst for this tranformation, and a variety of C-aryl substituted ynamides were successfully introduced to indoles, affording the desired products **8aa-8sa, 8ab-8ak, 8bd**, **8bk** and **8tc** in moderate to excellent yields with high regioselectivities.

4.1 *General Methods.*

Reactions were monitored by thin layer chromatography (TLC) on glass plates coated with silica gel with fluorescent indicator. Flash chromatography was performed on silica gel (300−400) with Petroleum/EtOAc as eluent. Optical rotations were measured on a polarimeter with a sodium lamp. HRMS were measured on a LCMSIT apparatus. IR spectra were recorded using film on a Fourier Transform Infrared Spectrometer. NMR spectra were recorded at 400 or 600 MHz, and chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (77.16 ppm) for ^{13}C NMR.

4.1.1 *General Procedure for Synthesis of ynamide* 7.[19]

To a mixture of an amide (2 mmol), K_3PO_4 (4 mmol), $CuSO_4$•$5H_2O$ (0.2mmol,) and 1,10-phenanthroline (0.4 mmol,) in toluene at N_2 atmosphere was added a solution 1-bromoalkyne (2.2 mmol) in toluene. The reaction was stirred at 75 °C for 24 h at N_2 atmosphere. The reaction mixture was cooled to room temperature and diluted with EtOAc and filtered through Celite and the filtrate was concentrated in vacuo. The crude products were purified by silica gel flash chromatography to afford the desired ynamide.

4.1.2 *General procedure for synthesis of* **8**.

To a solution of compound **6** (0.25 mmol), $Er(OTf)_3$ (30 mg, 0.05 mmol) and **7** (0.30 mmol) in anhydrous DCE (1.5 mL) at 70 °C for 2 h. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried, filtrated and concentrated. The residue was purified by flash chromatography on silica gel to give **8**.

4.2 *(Z)-N-(1-(1H-Indol-3-yl)-2-phenylvinyl)-N-benzyl-4-methylbenzenesulfonamide* (**8aa**).

White solid. (110 mg, 92%, PE/EA = 4:1); mp 174-176 °C; IR (film): ν_{max} 3394, 2955, 2924, 1458, 1377, 1340, 1156, 1090, 761, 696, 671 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.18 (m, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.43- 7.38 (m, 2H), 7.37- 7.32 (m, 1H), 7.24-7.12 (m, 9H), 7.11-7.08 (m, 3H), 7.04-6.98 (m, 2H), 6.90-6.85 (m, 1H), 6.71 (s, 1H), 4.65-4.51 (m, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 137.7, 136.5, 136.0, 135.8, 130.4, 130.2, 129.2, 128.9, 128.6, 128.4, 128.3, 128.1, 127.2, 126.3, 125.3, 122.6, 120.7, 120.1, 115.3, 111.6, 52.0, 29.8, 21.7 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{30}H_{27}N_2O_2S^+$: 479.1788, found: 479.1790.

4.3 *(Z)-N-Benzyl-4-methyl-N-(1-(1-methyl-1H-indol-3-yl)-2-phenylvinyl)benzenesulfonamide* (**8ba**).

White solid. (78 mg, 64%, PE/EA = 10:1); mp 170-172 °C; IR (film): ν_{max} 3028, 1597, 1471, 1344, 1091, 1049, 754, 697, 669, 546 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.79 (m, 1H), 7.39-7.34 (m, 2H), 7.29-7.24 (m, 2H), 7.20-7.11 (m, 9H), 7.07-7.01 (m, 4H), 6.83 (s, 1H), 6.43 (s, 1H), 4.59 (brs, 2H), 3.55 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.0, 137.3, 136.1, 135.9, 130.5, 130.3, 130.0, 129.1, 128.6, 128.4, 128.2, 128.1, 128.1, 127.0, 126.9, 122.2, 120.4, 120.2, 113.5, 109.6, 52.3, 32.9, 21.6 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{30}N_3O_2S^+$: 493.1944, found: 493.1941.

4.4 *(Z)-N-Benzyl-4-methyl-N-(2-phenyl-1-(5-(trifluoromethoxy)-1H-indol-3-yl)vinyl) benzenesulfonamide* (**8da**).

White solid. (129 mg, 92%, PE/EA = 4:1); mp 160-162 °C; IR (film): ν_{max} 3368, 2925, 1457, 1255, 1220, 1155, 1089, 747,

698 ... nd:

11.52-11.45 (m, 1H), 7.54-7.45 (m, 4H), 7.38-7.28 (m, 4H), 7.25-7.10 (m, 7H), 7.03-6.96 (m, 2H), 6.74-6.69 (m, 1H), 6.44-6.40 (m, 1H),4.52 (brs, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (101 MHz, DMSO-*d6*) δ 143.5, 142.4, 137.3, 135.5, 135.4, 134.8, 129.8, 129.7, 129.4, 128.3, 128.1, 128.0, 128.0, 127.7, 127.4, 127.2, 126.9, 125.6, 121.7, 119.1, 115.4, 114.3, 113.0, 111.7, 51.3, 21.0 ppm; ^{19}F NMR (376 MHz, DMSO-*d6*) δ -56.9 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{26}F_3N_2O_3S^+$: 563.1611, found: 563.1611.

4.5 *(Z)-N-Benzyl-4-methyl-N-(2-phenyl-1-(5-(trifluoromethyl)-1H-indol-3-yl)vinyl) benzenesulfonamide* (**8ea**).

White solid. (112 mg, 82%, PE/EA = 4:1); mp 191-193 °C; IR (film): ν_{max} 3362, 2926, 1432, 1330, 1155, 1113, 813, 745, 696, 664, 546 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.64 (brs, 1H), 7.90-7.81 (m, 1H), 7.62-7.53 (m, 1H), 7.52-7.40 (m, 5H), 7.32-7.24 (m, 5H), 7.23-7.12 (m, 3H), 7.06-6.98 (m, 2H), 6.76 (s, 1H), 6.43 (s, 1H), 4.65-4.40 (m, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 143.5, 137.3, 135.5, 135.3, 129.7, 129.6, 129.4, 128.4, 128.1, 128.0, 127.5, 127.4, 127.3, 127.2, 126.3, 124.9, 124.5, 120.6 (t, *J* = 20.6, 41.3 Hz), 118.1, 116.6, 114.9, 112.7, 51.3, 21.0 ppm; ^{19}F NMR (376 MHz, DMSO-*d6*, rotamers) δ -60.2, -60.8 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{26}F_3N_2O_2S^+$: 547.1662, found: 547.1668.

4.6 *(Z)-N-Benzyl-N-(1-(5-methoxy-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8fa**).

White solid. (114 mg, 90%, PE/EA = 4:1); mp 186-188 °C; IR (film): ν_{max} 3386, 2920, 1342, 1196, 1180, 1132, 1076, 1041, 703, 636, 544 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.16 (m, 1H), 7.44-7.35 (m, 2H), 7.25-7.21 (m, 2H), 7.20-7.13 (m, 7H), 7.12-7.06 (m, 2H), 7.03-6.96 (m, 2H), 6.90-6.82 (m, 1H), 6.81-6.76 (m, 1H), 6.66 (s, 1H), 4.62-4.48 (m, 2H), 3.80 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 154.1, 143.4, 137.6, 135.6, 131.5, 130.7, 129.7, 129.4, 128.3, 128.1, 128.0, 127.5, 126.9, 126.3, 125.8, 113.2, 112.6, 111.7, 101.4, 55.4, 51.4, 21.1 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{29}N_2O_3S^+$: 509.1893, found: 509.1896.

4.7 *(Z)-N-Benzyl-N-(1-(5-(benzyloxy)-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8ga**).

White solid. (92 mg, 63%, PE/EA = 4:1); mp 160-162 °C; IR (film): ν_{max} 3379, 3030, 2925, 2853, 1623, 1481, 1455, 1338, 1216, 1026, 736 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.10-11.00 (m, 1H), 7.54-7.49 (m, 2H), 7.47-7.42 (m, 2H), 7.38-7.26 (m, 8H), 7.22-7.13 (m, 7H), 7.02-6.97 (m, 2H), 6.91-6.85 (m, 1H), 6.64 (s, 1H), 6.22-6.18 (m, 1H), 5.08 (brs, 2H), 4.70-4.40 (m, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 153.1, 143.4, 137.7, 137.6, 135.7, 135.6, 131.7, 130.7, 129.7, 129.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.6, 127.5, 126.9, 126.4, 125.7, 125.7, 113.2, 112.5, 112.3, 103.2, 69.9, 51.4, 21.0 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{37}H_{33}N_2O_3S^+$: 585.2206, found: 585.2205.

4.8 *(Z)-N-Benzyl-N-(1-(5-chloro-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8ha**).

White solid. (85 mg, 66%, PE/EA = 4:1); mp 224-226 °C; IR (film): ν_{max} 3439, 2924, 1196, 1180, 1132, 1054, 1007, 822, 760, 615 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.46-11.33 (m, 1H), 7.55-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.44-7.34 (m, 3H), 7.30-7.10 (m, 9H), 7.05-6.96 (m, 2H), 6.72 (s, 1H), 6.33 (s, 1H), 4.65-4.42 (m, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 143.5, 137.4, 135.6, 135.5, 134.8, 129.9, 129.7, 129.4, 128.4, 128.2, 128.1, 128.1, 127.4, 127.3, 127.1, 126.6, 126.6, 124.6, 121.8, 118.5, 113.6, 113.4, 51.3, 21.1 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{26}ClN_2O_3S^+$: 513.1396.

4.9 *(Z)-N-benzyl-4-methyl-N-(2-phenyl-1-(5-((triisopropylsilyl)oxy)-1H-indol-3-yl)vinyl)benzenesulfonamide* (**8ia**)

Yellow oil. (117 mg, 72%, PE/EA = 4:1); IR (film): ν_{max} 2960, 2921, 1490, 1390, 1335, 1097, 1076, 750, 702 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*, Z/E=7:1, major) δ 11.13-11.09 (m, 1H), 7.58-7.53 (m, 2H), 7.34-7.29 (m, 2H), 7.28-7.25 (m, 1H), 7.24-7.20 (m, 3H), 7.18-7.13 (m, 6H), 7.01-6.98 (m, 2H), 6.77 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.61 (s, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 4.62-4.50 (m, 2H), 2.42 (s, 3H), 1.27-1.19 (m, 3H), 1.07-1.03 (m, 18H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*, Z/E=7:1, major) δ 149.9, 143.9, 137.9, 136.0, 132.3, 130.7, 130.1, 129.9, 128.5, 128.5, 128.4, 128.0, 127.4, 126.7, 126.6, 116.0, 113.0, 112.9, 108.7, 51.9, 21.5, 18.3, 12.5 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{39}H_{47}N_2O_3SSi^+$: 651.3071, found: 651.3071.

4.10 *(Z)-N-Benzyl-N-(1-(6-bromo-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8ja**).

White solid. (121 mg, 87%, PE/EA = 4:1); mp 153-155 °C; IR (film): ν_{max} 3364, 2955, 2924, 1454, 1337, 1155, 1090, 804, 748, 695, 548 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.35-11.24 (m, 1H), 7.64-7.45 (m, 4H), 7.36-7.26 (m, 4H), 7.23-7.11 (m, 7H), 7.04-6.95 (m, 2H), 6.77-6.66 (m, 1H), 6.24 (s, 1H), 4.60-4.41 (m, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 143.5, 137.4, 137.2, 135.5, 135.4, 129.9, 129.7, 129.5, 128.3, 128.2, 128.0, 127.4, 127.2, 127.0, 126.4, 124.5, 122.7, 121.2, 114.4, 113.9, 51.4, 21.1 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{30}H_{26}BrN_2O_2S^+$: 557.0893, 559.0872, found: 557.0898, 559.0886.

4.11 *(Z)-N-Benzyl-N-(1-(6-chloro-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8ka**).

White solid. (122 mg, 95%, PE/EA = 4:1); mp 144-146 °C; IR (film): ν_{max} 3371, 2926, 1455, 1338, 1155, 1090, 1025, 806, 753,700, 539 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.24 (m, 1H), 7.65-7.59 (m, 1H), 7.42-7.38 (m, 2H), 7.31-7.28 (m, 1H), 7.23-7.14 (m, 7H), 7.13-7.06 (m, 5H), 7.00-6.94 (m, 2H), 6.79 (s, 1H), 6.69 (s, 1H), 4.59-4.46 (m, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.5, 136.8, 135.9, 135.6, 130.2, 130.0, 129.3, 129.0, 128.6, 128.5, 128.3, 128.2, 128.1, 127.4, 125.8, 124.9, 121.3, 120.8, 115.6, 111.5, 52.0, 21.6 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{30}H_{26}ClN_2O_2S^+$: 513.1398, found: 513.1393.

4.12 *(Z)-N-Benzyl-N-(1-(4-methoxy-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8la**).

White solid. (118 mg, 93%, PE/EA = 4:1); mp 154-156 °C; IR (film): ν_{max} 3355, 2973, 2865, 2843, 1454, 1346, 1055, 1033, 1015 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.36-8.27 (m, 1H), 7.34-7.27 (m, 2H), 7.16-7.08 (m, 6H), 7.07-7.03 (m, 2H), 7.00-6.93 (m, 5H), 6.87-6.84 (m, 2H), 6.58-6.53 (m, 1H), 4.52-4.48 (m, 2H), 3.76 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 142.9, 138.4, 138.3, 137.5, 137.0, 132.0, 130.5, 129.2, 128.9, 128.5, 128.3, 127.7, 127.6, 127.3, 126.4, 124.7, 123.3, 116.9, 112.0, 104.2, 100.2, 77.2, 54.3, 53.4, 21.6 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{29}N_2O_3S^+$: 509.1893, found: 509.1896.

4.13 *(Z)-N-Benzyl-4-methyl-N-(1-(4-methyl-1H-indol-3-yl)-2-phenylvinyl)benzenesulfonamide* (**8ma**).

White solid. (92 mg, 75%, PE/EA = 4:1); mp 155-157 °C; IR (film): ν_{max} 3388, 2923, 1597, 1445, 1340, 1181, 1132, 1025, 749, 697, 544 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.93 (m,

1H 7.24-7.20 (m, 3H), 7.19-7.15 (m, 3H), 7.13-7.08 (m, 1H), 7.07-7.02 (m, 2H), 6.97-6.90 (m, 3H), 6.40-6.35 (m, 1H), 6.09 (s, 1H), 4.55-4.48 (m, 2H), 2.55 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.3, 136.4, 136.2, 135.9, 131.9, 130.2, 130.1, 130.0, 129.0, 128.7, 128.5, 128.4, 128.2, 127.9, 127.4, 125.6, 125.1, 123.1, 122.4, 116.5, 109.0, 51.8, 21.6, 21.5 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{29}N_2O_2S^+$: 493.1944, found: 493.1949.

4.14 *(Z)-N-Benzyl-N-(1-(5,6-dichloro-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8na**).

White solid. (108 mg, 79%, PE/EA = 4:1); mp 219-221 °C; IR (film): ν_{max} 3439, 1342, 1156, 1055, 1026, 1009, 821, 758, 703, 616, 545 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.54-11.46 (m, 1H), 7.61 (s, 1H), 7.53 (s, 1H), 7.48-7.43 (m, 2H), 7.42-7.36 (m, 2H), 7.28-7.23 (m, 5H), 7.22-7.13 (m, 3H), 7.05-7.00 (m, 2H), 6.72 (s, 1H), 6.48-6.43 (m, 1H), 4.65-4.40 (m, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.3, 135.6, 135.3, 135.1, 129.7, 129.4, 128.4, 128.3, 128.1, 127.4, 127.3, 126.9, 125.4, 124.0, 122.5, 120.3, 113.8, 113.3, 51.3, 21.0 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{30}H_{25}Cl_2N_2O_2S^+$: 547.1008, found: 547.1008.

4.15 *(Z)-N-Benzyl-N-(1-(5,6-difluoro-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8oa**).

White solid. (91 mg, 71%，PE/EA = 4:1); mp 200-202 °C; IR (film): ν_{max} 3363, 2925, 1476, 1338, 1196, 1154, 1076, 852, 744, 696, 543 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.40-11.31 (m, 1H), 7.51-7.46 (m, 2H), 7.45-7.41 (m, 1H), 7.40-7.32 (m, 3H), 7.31-7.26 (m, 2H), 7.25-7.15 (m, 6H), 7.05-6.98 (m, 2H), 6.75-6.68 (m, 1H), 6.35 (s, 1H), 4.66-4.40 (m, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 143.5, 137.4, 135.5, 135.4, 131.4, 131.3, 129.9, 129.7, 129.4, 128.4, 128.2, 128.0, 127.4, 127.3, 126.6, 120.8, 114.2, 106.1 (d, *J* = 19.5 Hz), 99.7 (d, *J* = 21.2 Hz), 51.4, 21.0 ppm; ^{19}F NMR (376 MHz, DMSO-*d6*, rotamers) δ -144.60 (d, *J* = 233.1 Hz), -145.17 (d, *J* = 218.1 Hz), -147.55 (d, *J* = 214.3 Hz), -148.15 (d, *J* = 214.3 Hz) ppm; HRMS (ESI): $[M + Na]^+$ Calcd for $C_{31}H_{26}F_2N_2O_2SNa^+$: 551.1575, found: 551.1571.

4.16 *(Z)-N-Benzyl-N-(1-(6-bromo-5-fluoro-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8pa**).

White solid. (137 mg, 95%, PE/EA = 4:1); mp 186-188 °C; IR (film): ν_{max} 3360, 2925, 1457, 1338, 1154, 1089, 1026, 751, 696, 673, 545 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.33-11.22 (m, 1H), 7.76-7.65 (m, 1H), 7.60-7.50 (m, 2H), 7.44-7.35 (m, 1H), 7.34-7.23 (m, 4H), 7.21-7.14 (m, 5H), 7.12-7.09 (m, 1H), 7.08-7.00 (m, 2H), 6.77 (s, 1H), 6.30 (s, 1H), 4.69-4.48 (m, 2H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.6, 136.6, 135.5, 134.6, 131.3, 131.2, 129.9, 129.8, 129.5, 128.2, 128.1, 127.8, 127.4, 125.8, 125.5, 125.3, 121.9, 120.1, 119.5, 112.8, 112.0, 51.8, 21.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.9 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{30}H_{25}BrFN_2O_2S^+$: 575.0799, 577.0778, found: 575.0799, 577.0771.

4.17 *(Z)-N-Benzyl-4-methyl-N-(1-(1-methyl-2-phenyl-1H-indol-3-yl)-2-phenylvinyl)benzenesulfonamide* (**8qa**).

Colourless oil. (139 mg, 98%, PE/EA = 10:1); IR (film): ν_{max} 2955, 2923, 1494, 1405, 1338, 1153, 1098, 1076, 741, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.36 (m, 3H), 7.33-7.29 (m, 1H), 7.28-7.20 (m, 4H), 7.17-7.13 (m, 1H), 7.12-7.06 (m, 4H),7.06-7.01 (m, 3H), 6.94-6.86 (m, 3H), 6.67-6.62 (m, 2H), 6.53 (s, 1H), 6.45-6.40 (m, 2H), 4.88 (d, *J* = 15.6 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.41 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR 7.0, 132.8, 131.0, 130.1, 129.2, 128.6, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.2, 127.0, 126.2, 122.3, 120.7, 120.6, 109.4, 107.8, 51.9, 31.0, 21.5 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{37}H_{33}N_2O_2S^+$: 569.2257, found: 569.2253.

4.18 *(Z)-N-Benzyl-N-(1-(1,2-dimethyl-1H-indol-3-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide* (**8ra**).

White solid. (135 mg, 99%, PE/EA = 10:1); mp 155-157 °C; IR (film): ν_{max} 2955, 2923, 2851, 1467, 1405, 1338, 1153, 1076, 1021, 740, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 2H), 7.30-7.20 (m, 6H), 7.17-7.12 (m, 2H), 7.10-7.05 (m, 1H), 7.04-6.97 (m, 3H), 6.75-6.67 (m, 4H), 6.34 (s, 1H), 4,70-4.63 (m, 2H), 3.57 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 138.5, 137.7, 137.0, 136.5, 136.0, 131.4, 130.6, 128.7, 128.5, 128.3, 128.2, 128.1, 127.2, 127.0, 126.9, 126.8, 119.6, 119.4, 111.3, 108.2, 52.2, 29.6, 21.4, 11.1 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{32}H_{31}N_2O_2S^+$: 507.2101, found: 507.2104.

4.19 *(Z)-N-(1-(5-Amino-1-methyl-1H-indol-3-yl)-2-phenylvinyl)-N-benzyl-4-methylbenzenesulfonamide* (**8sa**).

White solid. (91 mg, 72%, PE/EA = 4:1); mp 150-152 °C; IR (film): ν_{max} 3063, 2925, 1646, 1455, 1349, 1283, 1157, 1090, 1028, 799, 549 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 2H), 7.37-7.32 (m, 2H), 7.22-7.18 (m, 2H), 7.17-7.11 (m, 3H), 7.10-7.05 (m, 2H), 7.04-7.00 (m, 3H), 6.83-6.78 (m, 2H), 6.70 (s, 1H), 6.40-6.35 (m, 2H), 4.67-4.63 (m, 2H), 3.97-3.94 (m, 2H), 3.73 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 144.1, 141.0, 136.0, 135.5, 135.2, 134.1, 129.6, 129.5, 129.1, 128.8, 128.4, 128.3, 128.1, 127.2, 126.4, 115.1, 110.3, 109.7, 100.7, 51.2, 37.8, 33.1, 29.8, 21.8 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{30}N_3O_2S^+$: 508.2053, found: 508.2055.

4.20 *(Z)-N-Benzyl-N-(2-(4-bromophenyl)-1-(1H-indol-3-yl)vinyl)-4-methylbenzenesulfonamide* (**8ab**).

White solid. (118 mg, 85%, PE/EA = 4:1); mp 185-187 °C; IR (film): ν_{max} 3386, 2924, 1484, 1333, 1155, 1089, 1011, 813, 745, 703, 545 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.35-11.26 (m, 1H), 7.77-7.68 (m, 1H), 7.60-7.51 (m, 2H), 7.44-7.36 (m, 1H), 7.34-7.25 (m, 4H), 7.22-7.13 (m, 6H), 7.13-7.08 (m, 1H), 7.07-7.00 (m, 2H), 6.76 (s, 1H), 6.36-6.27 (m, 1H), 4,68-4.50 (m, 2H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 143.5, 137.6, 136.6, 135.4, 135.0, 131.2, 130.7, 130.1, 129.8, 129.5, 128.2, 128.0, 127.4, 125.9, 125.5, 125.3, 121.9, 120.1, 119.8, 119.4, 112.8, 112.0, 51.8, 21.1 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{30}H_{26}BrN_2O_2S^+$: 557.0893, 559.0872, found: 557.0900, 559.0863.

4.21 *(Z)-N-Benzyl-N-(2-(4-chlorophenyl)-1-(1H-indol-3-yl)vinyl)-4-methylbenzenesulfonamide* (**8ac**).

White solid. (97 mg, 76%, PE/EA = 4:1); mp 189-191 °C; IR (film): ν_{max} 3387, 2922, 1607, 1196, 1142, 1180, 1132, 1076, 745, 636, 572 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.34-8.25 (m, 1H), 7.82-7.78 (m, 1H), 7.43-7.36 (m, 3H), 7.26-7.23 (m, 1H), 7.22-7.16 (m, 4H), 7.15-7.10 (m, 2H), 7.07-7.00 (m, 4H), 6.95-6.90 (m, 2H), 6.86-6.84 (m, 1H), 6.81 (s, 1H), 4.65-4.57 (m, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 143.5, 137.6, 136.5, 135.4, 134.6, 131.2, 131.1, 129.8, 129.5, 128.2, 128.0, 127.8, 127.4, 125.8, 125.5, 125.3, 121.9, 120.1, 119.4, 112.8, 112.0, 51.8, 21.1 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{30}H_{26}ClN_2O_2S^+$: 513.1398, found: 513.1400.

4.22 *(Z)-N-(1-(1H-Indol-3-yl)-2-(4-methoxyphenyl)vinyl)-N-benzyl-4-methylbenzenesulfonamide* (**8ad**).

IR (film): ν_{max} 3387, 2924, 1506, 1332, 1196, 1143, 1076, 1027, 744, 671, 546 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d6*) δ 11.19-11.09 (m, 1H), 7.75-7.65 (m, 1H), 7.61-7.50 (m, 2H), 7.40-7.26 (m, 5H), 7.25-7.11 (m, 4H), 7.10-6.97 (m, 3H), 6.85-6.73 (m, 2H), 6.72-6.67 (m, 1H), 6.15 (s, 1H), 4.65-4.48 (m, 2H), 3.78 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 158.4, 143.4, 137.8, 136.4, 135.7, 129.8, 129.7, 129.4, 128.6, 128.2, 128.0, 127.5, 126.2, 125.4, 125.2, 121.7, 119.8, 119.4, 113.7, 113.5, 111.9, 55.1, 51.4, 21.1 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{31}H_{29}N_2O_3S^+$: 509.1893, found: 509.1896.

4.23 *(Z)-N-(1-(1H-Indol-3-yl)-2-phenylvinyl)-4-methyl-N-phenylbenzenesulfonamide* (**8ae**).

Colourless oil. (96 mg, 83%，PE/EA = 4:1); IR (film): ν_{max} 3386, 2955, 2924, 1458, 1356, 1161, 1088, 1015, 745, 692, 559 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26-8.22 (m, 1H), 7.98-7.92 (m, 1H), 7.64-7.58 (m, 2H), 7.50-7.46 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 1H), 7.21-7.17 (m, 8H), 7.11-7.08 (m, 1H), 7.04-7.00 (m, 1H), 6.97-6.92 (m, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 141.0, 137.1, 136.8, 135.4, 132.1, 129.2, 129.0, 128.9, 128.5, 128.3, 127.6, 126.1, 125.4, 124.1, 122.8, 121.0, 120.8, 120.2, 116.1, 111.8, 21.6 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{29}H_{25}N_2O_2S^+$: 465.1631, found: 465.1635.

4.24 *(Z)-N-(1-(1H-Indol-3-yl)-2-phenylvinyl)-N,4-dimethylbenzenesulfonamide* (**8af**).

Colourless oil. (47 mg, 47%，PE/EA = 4:1); IR (film): ν_{max} 3379, 2925, 1692, 1457, 1337, 1160, 1087, 961, 749, 674, 547 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, Z/E=5:1, major) δ 8.33-8.22 (m, 1H), 7.80-7.71 (m, 1H), 7.43-7.35 (m, 2H), 7.34-7.28 (m, 3H), 7.25-7.16 (m, 5H), 7.11-7.05 (m, 1H), 7.01-6.96 (m, 2H), 6.87-6.84 (m, 1H), 3.17 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, Z/E=5:1, major) δ 143.0, 136.9, 136.8, 135.9, 133.7, 129.1, 128.7, 128.5, 127.6, 127.2, 126.7, 125.8, 125.4, 122.6, 120.6, 120.0, 37.2, 21.5 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{24}H_{23}N_2O_2S^+$: 403.1475, found: 403.1477.

4.25 *(S,Z)-3-(1-(1H-Indol-3-yl)oct-1-en-1-yl)-4-phenyloxazolidin-2-one* (**8ag**).

Colourless oil. (35 mg, 36%, PE/EA = 2:1); IR (film): ν_{max} 3302, 2925, 1740, 1455, 1411, 1241, 1098, 1042, 770, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.72-8.65 (m, 1H), 7.70-7.63 (m, 1H), 7.42-7.36 (m, 1H), 7.23-7.16 (m, 4H), 7.15-7.10 (m, 1H), 7.08-7.04 (m, 1H), 6.93-6.86 (m, 2H), 5.97 (dd, *J* = 6.4, 7.2 Hz, 1H), 4.23 (dd, *J* = 8.0, 8.8 Hz, 1H), 4.15-4.09 (m, 1H), 4.08-4.01 (m, 1H), 3.06-3.00 (m, 1H), 2.62-2.54 (m, 1H), 2.40-2.22 (m, 2H), 1.62-1.46 (m, 2H), 1.37-1.30 (m, 4H), 0.95-0.87 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 136.7, 135.6, 129.8, 129.0, 128.8, 127.1, 126.7, 125.4, 123.5, 122.6, 120.6, 119.5, 113.0, 111.9, 67.9, 39.8, 31.9, 29.5, 29.4, 28.4, 22.8, 14.3 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{26}H_{31}N_2O_2^+$: 403.2380, found:403.2385.

4.26 *(Z)-3-(1-(1H-Indol-3-yl)-2-phenylvinyl)oxazolidin-2-one* (**8ah**).

White solid. (27 mg, 35%, PE/EA = 4:1); mp 85-87 °C; IR (film): ν_{max} 3302, 2922, 1739, 1629, 1419, 1243, 1132, 1032, 747, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.12-9.05 (m, 1H), 7.80-7.70 (m, 1H), 7.43-7.34 (m, 4H), 7.29-7.23 (m, 2H), 7.17-7.10 (m, 2H), 6.97-6.93 (m, 1H), 6.78 (s, 1H), 4.43-4.35 (m, 2H), 3.72-3.65 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 137.2, 135.9, 129.8, 128.9, 128.2, 127.5, 124.8, 124.5, 123.5, 122.6, 120.7, 119.6, 113.2, 112.3, 62.7, 45.7 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_2^+$: 305.1284, found: 305.1287.

4.27 *(4R,5S)-3-((Z)-1-(1H-Indol-3-yl)-2-phenylvinyl)-4-benzyloxazolidin-2-one* (**8ai**).

Colourless oil. (73 mg, 72%, PE/EA = 2:1); IR (film): ν_{max} 3320, 2922, 1747, 1402, 1219, 1180, 1076, 1044, 809, 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, Z/E=6:1, major) δ 8.87-8.81 (m, 1H), 7.90-7.81 (m, 1H), 7.42-7.37 (m, 2H), 7.36-7.32 (m, 1H), 7.22-7.18 (m, 3H), 7.17-7.13 (m, 5H), 6.99-6.95 (m, 1H), 6.82-6.78 (m, 2H), 4.23-4.13 (m, 2H), 4.09-4.02 (m, 1H), 3.10-3.04 (m, 1H), 2.62-2.53 (m, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, Z/E=6:1, major) δ 156.9, 137.6, 137.2, 135.7, 133.1, 129.6, 128.9, 128.81, 128.5, 127.0, 124.5, 122.8, 120.8, 119.9, 112.2, 68.6, 57.6, 39.4, 21.5 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{27}H_{25}N_2O_2^+$: 409.1910, found: 409.1914.

4.28 *(4R,5S)-3-((Z)-1-(1H-Indol-3-yl)-2-phenylvinyl)-4-methyl-5-phenyloxazolidin-2-one* (**8aj**).

Colourless oil. (41 mg, 42%, PE/EA = 2:1); IR (film): ν_{max} 3315, 2900, 1705, 1402, 1350, 1280, 1076, 968, 567 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, Z/E=10:1, major) δ 9.14-9.00 (m, 1H), 7.94-7.80 (m, 1H), 7.52-7.45 (m, 2H), 7.42-7.34 (m, 6H), 7.33-7.29 (m, 1H), 7.24-7.14 (m, 5H), 7.02-6.97 (m, 1H), 5.56 (d, *J* = 7.6 Hz, 1H), 4.31-4.17 (m, 1H), 0.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, Z/E=10:1, major) δ 156.0, 136.4, 135.3, 134.8, 127.9, 127.8, 127.7, 126.8, 125.6, 123.9, 122.0, 120.1, 111.5, 78.4, 55.4 14.8 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O_2^+$: 395.1754, found: 395.1756.

4.29 *Ethyl (Z)-(1-(1H-indol-3-yl)-2-phenylvinyl)(benzyl)carbamate* (**8ak**).

Colourless oil. (48 mg, 48%, PE/EA = 4:1); IR (film): ν_{max} 3312, 2926, 1692, 1626, 1456, 1319, 1196, 1131, 1018, 741, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.38-8.27 (m, 1H), 7.90-7.81 (m, 1H), 7.45-7.31 (m, 4H), 7.26-7.18 (m, 9H), 6.80-6.72 (m, 2H), 4.65 (d, *J* = 14.0 Hz, 1H), 4.54 (d, *J* = 14.4 Hz, 1H), 4.02-3.87 (m, 2H), 0.86-0.75 (m, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.4, 137.5, 136.9, 136.3, 133.3, 130.2, 128.5, 128.4, 128.0, 127.8, 127.1, 125.5, 124.1, 123.0, 122.7, 120.7, 120.2, 116.6, 111.6, 61.8, 52.1, 14.4 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{26}H_{25}N_2O_2^+$: 397.1910, found: 397.1910.

4.30 *Ethyl (Z)-benzyl(1-(1-methyl-1H-indol-3-yl)-2-phenylvinyl)carbamate* (**8bk**).

Colourless oil. (51 mg, 50%); IR (film): ν_{max} 3313, 3058, 2927, 1692, 1626, 1531, 1409, 1244, 1132, 1076, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.89-7.81 (m, 1H), 7.40-7.34 (m, 2H), 7.31-7.17 (m, 8H), 7.17-7.12 (m, 3H), 6.71 (s, 1H), 6.63 (s, 1H), 4.70-4.63 (m, 1H), 4.57-4.50 (m, 1H), 3.00-3.90 (m, 2H), 3.66 (s, 3H), 0.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 137.7, 137.6, 136.4, 133.3, 130.2, 128.9, 128.5, 128.3, 127.9, 127.7, 126.9, 126.1, 122.6, 122.3, 120.4, 114.9, 109.7, 61.8, 52.2, 33.0, 14.4 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{27}H_{27}N_2O_2^+$: 411.2067, found 411.2066.

4.31 *(Z)-N-benzyl-N-(2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-3-yl)vinyl)-4-methylbenzenesulfonamide* (**8bd**).

White solid. (103 mg, 79%); mp 156-158 °C; IR (film): ν_{max} 3456, 2918, 1604, 1507, 1333, 1248, 1154, 1035, 742, 544 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.77 (m, 1H), 7.46-7.39 (m, 2H), 7.28-7.23 (m, 2H), 7.21-7.15 (m, 4H), 7.13-7.05 (m, 6H), 6.78 (s, 1H), 6.72-6.66 (m, 2H), 6.29 (s, 1H), 4.69-4.59 (m, 2H), 3.80 (s, 3H), 3.54 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 143.1, 138.2, 137.2, 136.3, 130.3, 129.9, 129.6, 129.0, 128.8, 128.5, 128.3, 128.1, 128.0, 127.0, 122.2, 120.3, 120.2, 113.7, 113.6, 109.5, 55.3, 52.3, 32.8, 21.6 ppm; HRMS

(E . V.; 523.2050.

4.32 *(Z)-N-(1-(5-amino-1H-indol-3-yl)-2-(4-chlorophenyl)vinyl)-N-benzyl-4-methylbenzenesulfonamide* (**8tc**).

Pale yellow foam solid. (98 mg, 74%); IR (film): ν_{max} 3028, 1597, 1471, 1344, 1091, 1049, 754, 697, 669 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d6*) δ 11.07-11.01 (m, 1H), 7.85-7.79 (m, 2H), 7.51-7.45 (m, 2H), 7.34-7.30 (m, 2H), 7.28-7.17 (m, 3H), 7.13-7.09 (m, 2H), 7.06-7.01 (m, 2H), 6.73-6.65 (m, 3H), 6.36-6.25 (m, 2H), 4.64 (s, 2H), 3.92 (s, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*) δ 155.1, 144.7, 140.3, 136.4, 135.1, 134.3, 133.5, 131.6, 130.9, 130.2, 129.0, 128.6, 128.4, 128.2, 127.7, 126.7, 114.6, 112.4, 109.6, 101.4, 51.0, 36.6, 21.6 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{30}H_{27}ClN_3O_2S^+$: 528.1507, found 528.1507.

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Highlights

- An efficient approach to access functionalized 3-alkenylindoles
- $Er(OTf)_3$-catalyzed addition of ynamides and indoles
- A variety of C-aryl substituted ynamides were successfully introduced to indoles

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: