DOI: 10.1002/adsc.200900614

Gold Catalysis: Anellated Heterocycles and Dependency of the Reaction Pathway on the Tether Length

A. Stephen K. Hashmi,[a,*] Sreekumar Pankajakshan,[b] Matthias Rudolph,[a] Elisabeth Enns,[a] Thomas Bander,[b] Frank Rominger,[a] and Wolfgang Frey[b]

[a] Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: (+49)6221-54-4205; e-mail: hashmi@hashmi.de
[b] Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Received: September 4, 2009; Published online: November 18, 2009

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900614.

Abstract: A series of furan-yne substrates with an arylalkynylamide substructure were prepared and subjected to catalytic amounts of phosphanegold(I) complexes. With two carbon atoms in the tether between the arylalkynylamide and the furan subunits, the formation of benzoanellated heterocycles was observed, a number of interesting heterocyclic framworks could be accessed in this way. With three carbon atoms in the tether, the outcome was quite different, cyclopentadiene derivatives anellated to tetrahydropyridine rings were isolated. The two different pathways suggested are supported by calculations regarding the selectivity-determining step.

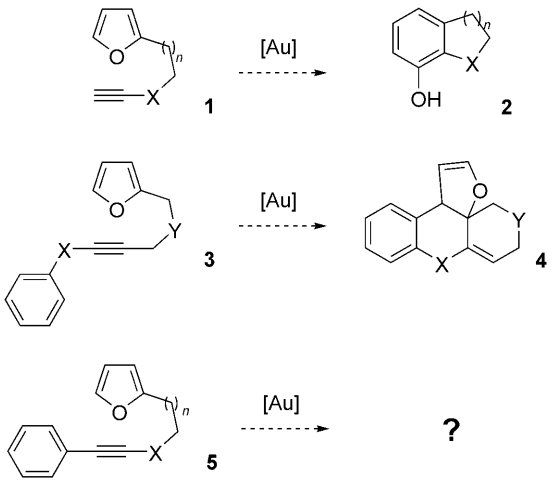
Keywords: alkynes; arenes; benzanellation; gold; heterocycles; homogeneous catalysis

Introduction

The importance of gold in homogeneous catalysis is still increasing, offering a plethora of catalytic conversions and rearrangements which lead to impressive structural diversity.[1] Most of these transformations are perfectly atom economic and very user-friendly as no precautions like the exclusion of moisture or oxygen are necessary.

In most cases alkynes are used as substrates, but donor-substituted alkynes like ene-ynamides also form an interesting but little explored class of substrates.[2]

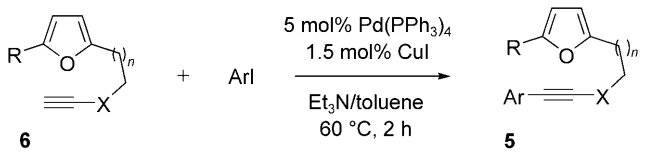
Last year, we reported the gold-catalyzed synthesis of benzoanellated heterocycles from furan substrates with ynamides and ynol ether groups possessing the heteroatom in the tether (Scheme 1, **1**).[2f] With gold catalysts, these substrates followed the pathway of the normal phenol synthesis (in the case of three atoms in the tether reacting with the proximal carbon atom to deliver a *five-membered* ring in **2**), but the reactions were superior in both conversion time and selectivity. Just recently, we investigated related substrates with an aryl ether moiety on the other side of the alkyne (**3**), leading to an inversion of the regioselectivity in the cyclization; the alkyne now closed the ring with the distal carbon atom to a *six-membered* ring and provided the new tetracyclic framework **4**, again in fast reactions.[3] This raised our interest in the behaviour of substrates **5** with the phenyl group on the alkyne[4] and the activating heteroatom on the other side in the tether.



Scheme 1. Different types of alkynyl-furan substrates with heteroatoms on the alkyne.

Results and Discussion

These substrates **5** were synthesized by Sonogashira coupling of the terminal ynamides **6**[2f] with the corresponding aryl iodides (Scheme 2). The failure of the Sonogashira coupling with bulky substrates (for example, 2-*i*-PrC_6H_4I), ethynyl ethers, and the failure to couple aryl bromides and aryl chlorides were the limitations of this substrate synthesis.



Scheme 2. Synthesis of the substrates by Sonogashira coupling.

Compound **5a** (R = Me, Ar = tolyl) was subjected to 5 mol% of the $Ph_3PAuNTf_2$ catalyst in CD_2Cl_2 in an NMR tube and the reaction was monitored by *in situ* ^1H NMR spectroscopy. The conversion was slow but selective, only one product was formed, and took 16 h at 45 °C. $Mes_3PAuNTf_2$ showed similar activity, while with $AuCl_3$ only decomposition of the substrate was observed. Finally, a combination of Ph_3PAuCl and $AgBF_4$ (5 mol%, 1:1) was found to catalyze the reaction much faster (complete conversion in 4 h at room temperature in CD_2Cl_2). Control experiments with $AgBF_4$ and with trifluoroacetic acid gave no conversion while trifluoromethanesulfonic acid decomposed the substrate.

Characterization of the purified product showed it to be the benzanellated dihydroindole derivative **7a** (Table 1, entry 1, 53% yield). Particularly pleasing was the observation that the enol ether part of the furan moiety was eliminated from the central six-membered ring (as an enol then equilibrating to the more stable ketone), establishing the synthetically important anellated arene unit. Scope and reactivity of further substrates were explored (Table 1, **5b**–**5x**).

The substrate **5b** with a more electron-donating methoxy group initially was reacted at slightly higher temperature (45 °C) in only 1 h to furnish the product **7b** in 57% yield (entry 2), but also delivered **7b** in 3.5 h at room temperature in quite similar yield (entry 3). The naphthyl-substituted **5c** furnished the tetracyclic compound **7c** in 53% yield with a reaction time of 7 h at room temperature (entry 4). The substrate **5d** with a heteroaryl group attached to the alkyne gave the benzofuran derivative **7d** in an excellent yield of 79% after 6 h at room temperature (entry 5). Even thiophene **5e** also led to the benzothiophene product **7e** in 65% yield (entry 6).[5] We then switched to **5f**, a brosyl (Bs)-substituted ynamide, and the product **7f** was isolated with a significantly improved yield of 75% (entry 7). Similarly, **5g** gave the benzothiophene product **7g** in a yield of 74% (entry 8). An X-ray crystallographic analysis of **7g** proved the structure unambiguously and gave conclusive support for the benzanellation chemistry (Figure 1, *left*).[6] The substrate **5h**, where the thiophene moiety is connected to the alkyne at the 3-position, selectively at 0 °C (2 h) furnished **7h** – a constitutional isomer of **7g** – in 60% yield (entry 9). The influence of the protection group is a minor one, **5i** which differs from **5h** by the protection group only, gives a quite similar result (entry 10). The substrate **5j** with two not symmetry-equivalent *ortho*-positions on the arene reacted regioselectively to give the product **7j** in 53% yield (entry 11). The regioselectivity is particularly noteworthy when compared to the arylalkyne substrates reported by Echavarren et al., where *meta*-substitution of the arene produced regioisomeric mixtures.[7] The deactivated substrate **5k** with a *p*-nitro group on the arene, failed to react and decomposed when exposed for prolonged reaction times (entry 12). Compound **5l** with a pyridine substitution at the alkyne had a similar fate (entry 13). The substrate **5m** only underwent partial addition of water, the amide **8** was isolated in 18% yield (entry 14). The naphthyl-substituted **5n** with the brosyl (Bs) protecting group gave the phenanthrene derivative **7n** in 72% yield (entry 15). The substrate **5o**, with a benzofuran group on the alkyne and an ethyl group on C-5 of the furan reacted beautifully to give the dibenzofuran derivative **7o** in 76% yield (entry 16). So did the substrate **5p** with an *N*-methylindole moiety and the benzoindole product was isolated in 41% yield (entry 17). A substrate with a bulky substituent like phenanthrene on the alkyne (**5q**) was also converted – albeit slower – and the triphenylene derivative **7q** was isolated in 43% yield (entry 18). We also examined the reactivity of unsubstituted furan substrate **5r**, but the system was too passive to react (entry 19). Typical ^1H NMR shifts indicating a successful conversion are the two triplets of the *N*-tosylpyrrolidine substructure, appearing around 2.79–3.06 ppm and 3.98–4.06 ppm with a coupling constant of 8.2 Hz, as well as the methylene group in the side chain (between the carbonyl group and the arene) as a characteristic singlet at 3.63–4.01 ppm (only with further anellated arenes in **7o** and **7q** this signal appears at 4.10 ppm and 4.23 ppm, respectively).

Having established the generality of arene nucleophiles, the substrate **5s** with a hydroxy group as a potential nucleophile was subjected to the catalyst. But then only the formation of the Meyer–Schuster-type α,β-unsaturated amide **9** was observed (Scheme 3).

The gold-catalyzed conversion of arylynamides with one additional carbon atom in the tether had a completely different outcome. With **5t** selectively a new

Table 1. Gold-catalyzed reaction of arylynamides **5a–5r** (two-carbon tether).

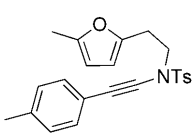
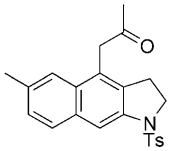
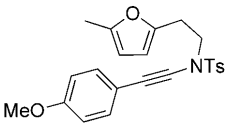
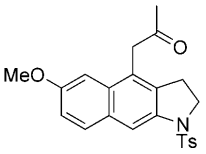
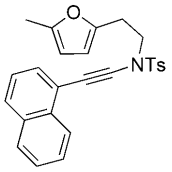
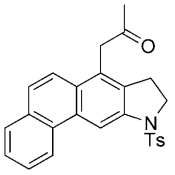
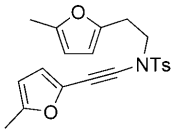
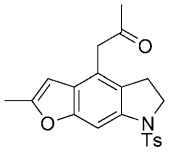
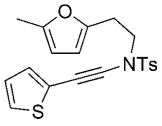
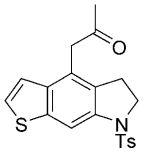
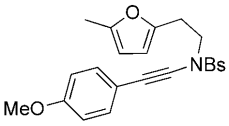
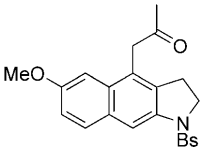
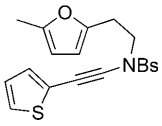
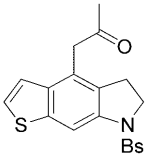
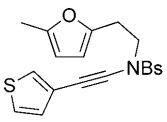
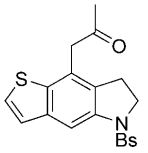
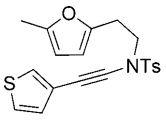
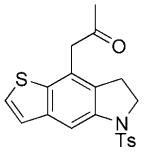
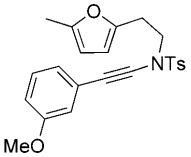
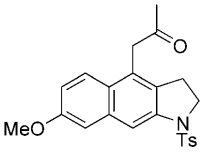
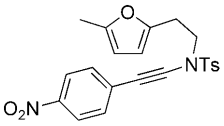
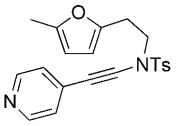
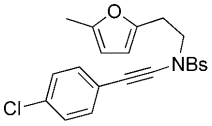
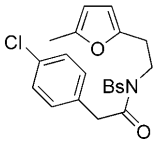
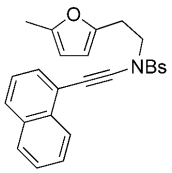
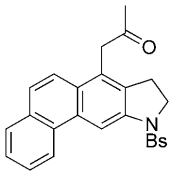
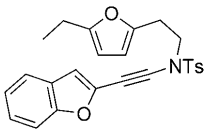
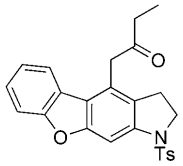
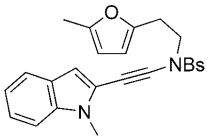
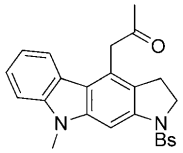
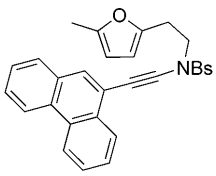
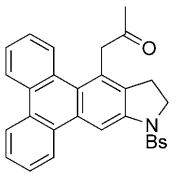
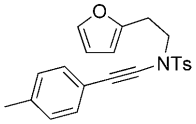
Entry		Substrate **5**	Time [h]	Temperature [°C]		Product	Yield [%]
1[a]	**5a**		4	r.t.	**7a**		53
2[b]	**5b**		1	45	**7b**		57
3[b]	**5b**		3.5	r.t.	**7b**		54
4[a]	**5c**		7	r.t.	**7c**		53
5[a]	**5d**		6	r.t.	**7d**		79
6[a]	**5e**		1	r.t.	**7e**		65
7[a]	**5f**		4	r.t.	**7f**		75
8[a]	**5g**		3	r.t.	**7g**		74
9[a]	**5h**		2	0	**7h**		60
10[a]	**5i**		1	r.t.	**7i**		66
11[a]	**5j**		1	50	**7j**		53

Table 1. (Continued)

Entry	Substrate **5**	Time [h]	Temperature [°C]	Product	Yield [%]
12[b]	**5k** 	24	50	substrate decomposes	-
13[b]	**5l** 	20	65	no reaction	-
14[a]	**5m** 	1	r.t.	**8** 	18
15[a]	**5n** 	8	r.t.	**7n** 	72
16[a]	**5o** 	3	r.t.	**7o** 	76
17[a]	**5p** 	12	r.t.	**7p** 	41
18[a]	**5q** 	20	45	**7q** 	43
19[a]	**5r** 	48	45	no reaction	

[a] In CH_2Cl_2.
[b] In $CHCl_3$.

product was formed. Again the control experiments with $AgBF_4$ or trifluoroacetic acid gave no conversion, trifluoromethanesulfonic acid led to an unspecific decomposition of the substrate.

The 1D and 2D NMR spectra combined with mass spectroscopic data led to the assumption that the product would be **10t**, a cyclic unsaturated ketone with a stereogenic centre (Table 2, entry 1). The reaction was much faster (finished in 45 min at room temperature) and no trace of the benzanellated product **7t** was detected in the reaction mixture. This indicates that a completely different mechanistic pathway is involved. The substrate **5u** with a *p*-tolyl substitution on the alkyne followed and a similar reaction, product **10u** was isolated in 52% yield (entry 2). We have managed to obtain an X-ray structure analysis of this compound, thereby unambiguously proving the product identity (Figure 1, *right*).[6]

A heteroaryl ynamide substrate **5v** also furnished the cyclopentenone derivative **10v** in 50% yield (entry 3). An electron-withdrawing group on the alkyne was not tolerated and hence the pyridinyl substituted **5w** remained unreactive (entry 4). Typical ^{1}H NMR shifts for the products **10** are the resonance

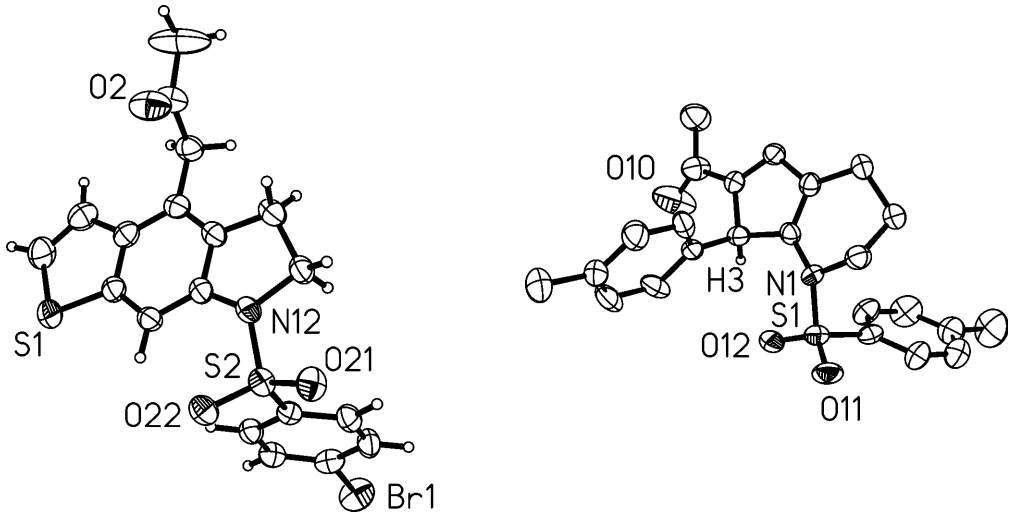
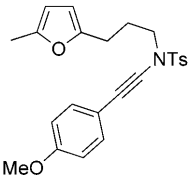
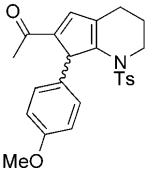
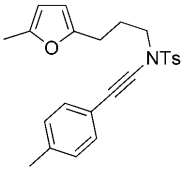
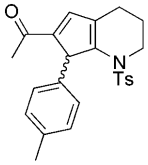
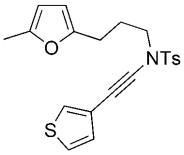
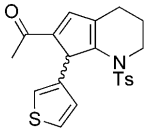
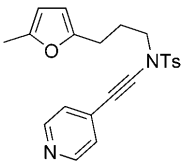
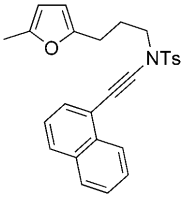


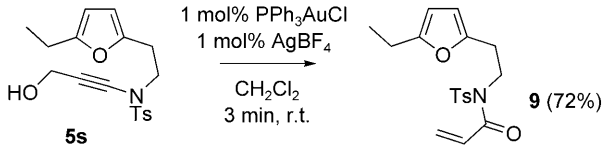
Figure 1. Solid state molecular structure of the benzanellated product **7g** (*left*) and the cyclopentenone product **10u** (*right*).

of the acetyl group (CH_3CO) at the cyclopentadiene, a singlet at 2.19–2.23 ppm, and the vinylic methine group of the cyclopentadiene ring, a doublet with a coupling constant of 1.3–1.5 Hz at 7.11–7.12 Hz.

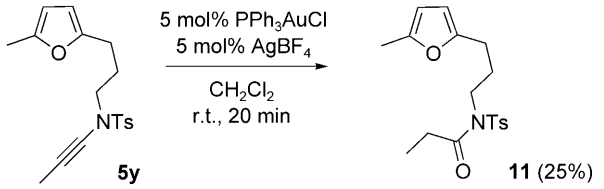
Table 2. Gold-catalyzed conversion of arylynamides **5s**–**5w** (three-carbon tether).[a]

Entry	Substrate **5**	Time [h]	Temperature [°C]	Product	Yield [%]
1	**5t** 	0.7	r.t.	**10t** 	56
2	**5u** 	1	r.t.	**10u** 	52
3	**5v** 	4	r.t.	**10v** 	50
4	**5w** 	20	50	no reaction	–
5	**5x** 	1.5	r.t.	complex mixture	–

[a] All the reactions were done in CH_2Cl_2.



Scheme 3. Gold-catalyzed conversion of **5s**.



Scheme 4. Gold-catalyzed conversion of methylynamide **5y**.

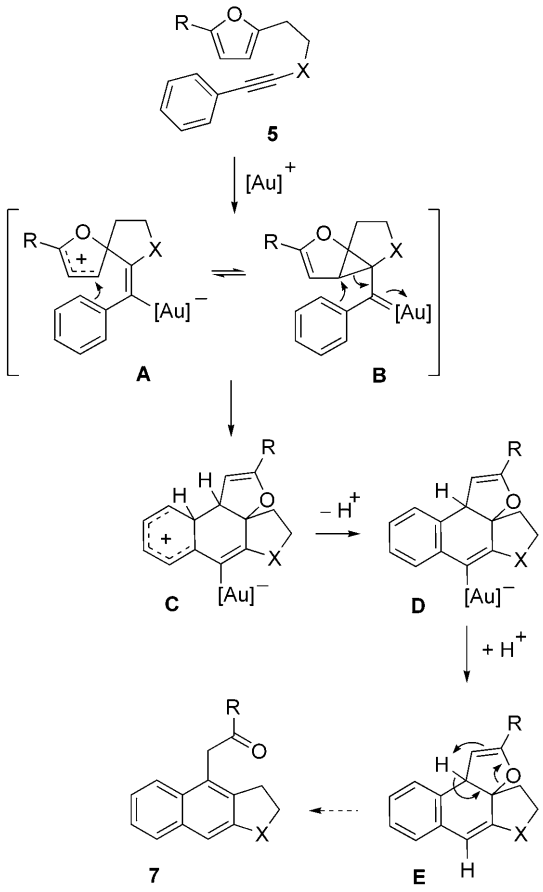
The substrate **5x** yielded a complicated mixture of products (entry 5). The NMR spectra of the crude reaction mixture showed the presence of both cyclopentenone and benzanellated products, as identified in the mixture by the characteristic signals mentioned for products **7** and **10** above, but these could not be separated.

Compared to the known gold-catalyzed reactions of arylalkynes,[7] which did not always react selectively, the arylalkynyl*amides* due to the directing properties of the amide group showed improved selectivities.

We also investigated if an alkyl group attached to the alkyne would lead to similar transformations but the substrate **5y** underwent water addition to form the amide **11**, in 25% yield (Scheme 4).

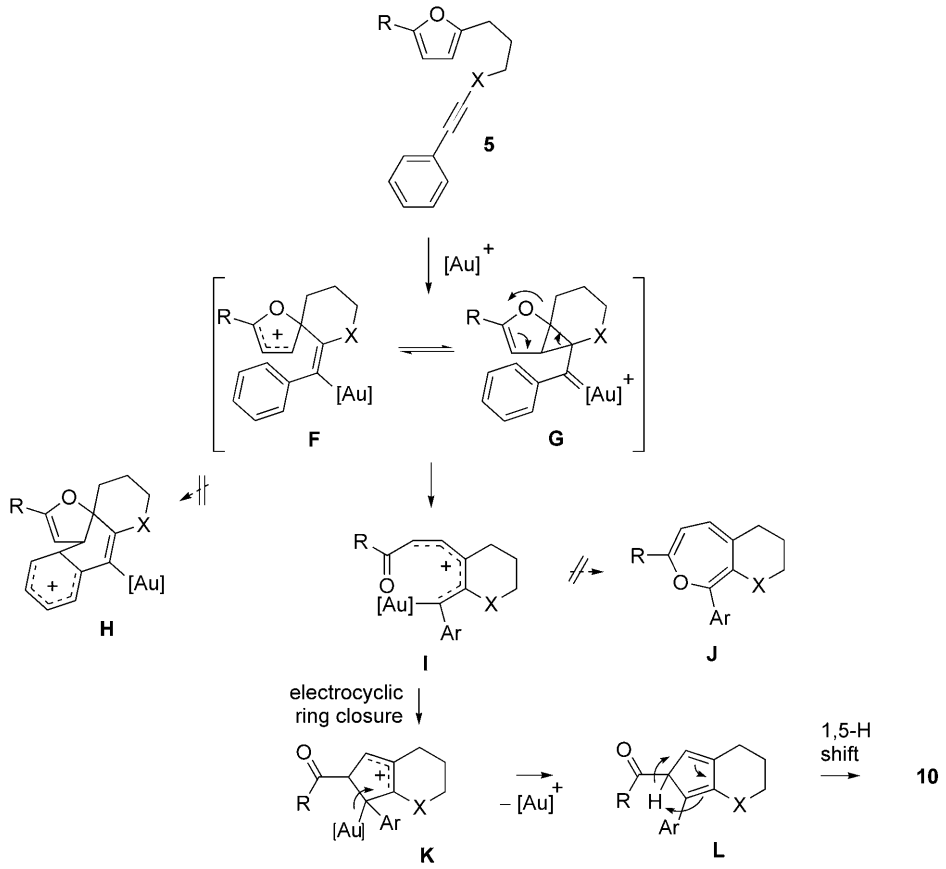
The mechanistic pathway for the formation of benzanellated products **7** from arylynamides **5a–5p** seems straightforward and proceeds through the classical *exo*-1,6-enyne cyclization mode[8] (Scheme 5). The activation of the alkyne by gold leads to the formation of intermediates **A** or **B** having a cationic or carbene identity,[9] respectively. A Friedel–Crafts type[10] electrophilic attack (**C**) followed by rearomatization of the arene unit leads to the cyclized intermediate **D**. This intermediate could protodeaurate (**E**), then undergo the crucial second aromatization process by elimination of the furyl enol ether bridge to deliver the final product **7**.

The mechanistic route for the cyclopentenone structures **10** from arylynamides **5s–5x** with the longer tether is shown in Scheme 6. The reaction is initiated by 6-*exo-dig* attack to give the cation **F** or carbene **G** intermediate. Ring-opening forms the conjugated monocyclic intermediate **I**. Species **I** resembles the crucial carbene intermediate in gold- and platinum-catalyzed phenol synthesis from furyl alkynes (the latter differs from **I** only by lack of the aryl group).[4,11] Such an intermediate was reported[4] to be incapable (due to the presence of the arene moiety on the carbene/carbocation substructure) of further



Scheme 5. Proposed mechanism for the gold-catalyzed benzannelation of arylynamides **2**.

reaction (to **J**), and this lack of reactivity is considered to be the main reason behind the failure of gold/platinum-catalyzed phenol synthesis from terminally substituted furyl alkynes. The proposed intermediate **I** might undergo electrocyclization to the heteroatom-stabilized intermediate **K** followed by elimination to form the cyclopentenone compound **L**, which eventually is transformed to the final product **10** by a 1,5-H shift, this sequence **I**/**K**/**L** resembles the mechanism of the gold-catalyszd synthesis of acylindenes, which shows a similar electrocyclization/elimination/1,5-H shift sequence.[12] The activity of the intermediate **I**, compared to its analogue in phenol synthesis is attributed to the presence of the heteroatom (nitrogen here) which would assist to stabilize the formation of charges in the allylic cation **K**, but not in the pentadienyl cation **I**. The absence of benzanellation pathway possibly goes back to a different conformation caused by the different length of the tether in raising the distance of the arene moiety and the electrophilic C-3 of the furan unit (comparing the five-membered ring in **A** and the six-membered ring in **F**). The assumption is supported by the fact that the substrate **5x** with a naphthyl moiety (offering a second aromatic



Scheme 6. Proposed mechanism for the formation of cyclopentenones from gold catalysis of arylynamides **2** with three-carbon tether.

ring which still can be reached by C-3 of the furan) was found to show signals of both types of products (**7** and **10**) in the ^{1}H NMR of the crude product as discussed above.

In order to evaluate the feasibility of the mechanistic pathways, we conducted DFT calculations including zero point corrections of selected key intermediates. First we calculated the intermediates **A** and **F** from Scheme 5 and Scheme 6, which are the intermediates before the selectivity-determining step. They are depicted in Figure 2. There is no evidence for a major contribution of the cyclopropyl-forms **B** and **G**. For both **A** and **F** we found two different conformers **A1/A2** and **F1/F2**. All these conformers are local minima, interestingly for both **A** and **F** the thermodynamically more stable conformer is the one with a shorter distance between the potentially reacting centers (details of the calculations in the Supporting Information). **A1** has a carbon-carbon distance between the reacting centers of 3.08 Å, **A2** is 8.8 kJ mol^{-1} higher in energy and shows a much bigger distance of 3.64 Å. The corresponding value for **F1** is 2.99 Å, **F2** is 20.6 kJ mol^{-1} higher in energy with a distance of 3.87 Å. This would indicate that in both intermediates, **A1** for the two-carbon-tether and **F1** for the three-carbon-tether, the electrophilic carbon of the furan ring could attack the phenyl group and deliver an intermediate **C** and **H**. But calculating the corresponding σ-complexes after the attack at the benzene ring reveals the difference, **C** is a stable intermediate, while **H** does turn out not to be a stable structure. We could only find a local minimum (45.0 kJ mol^{-1} higher than **F1**) in which a C–C interaction starts to form (1.65 Å), but due to the geometrical restraints in the molecule cannot form a stable bond. On the other hand the open-chained intermediate **I** is a minimum energetically only 26.0 kJ mol^{-1} higher than **F1**. The calculation also shows the additional conjugative stabilization of the cation in intermediate **I** by the phenyl group, part of the explanation for not seeing the cyclization to **J**.

Conclusions

Over all, we have explored gold-catalyzed reactions of furanyne substrates with an aryl group on the distal end of the triple bond and an amide group on the proximal end for the first time. The outcome of the reaction selectively depends on the length of the

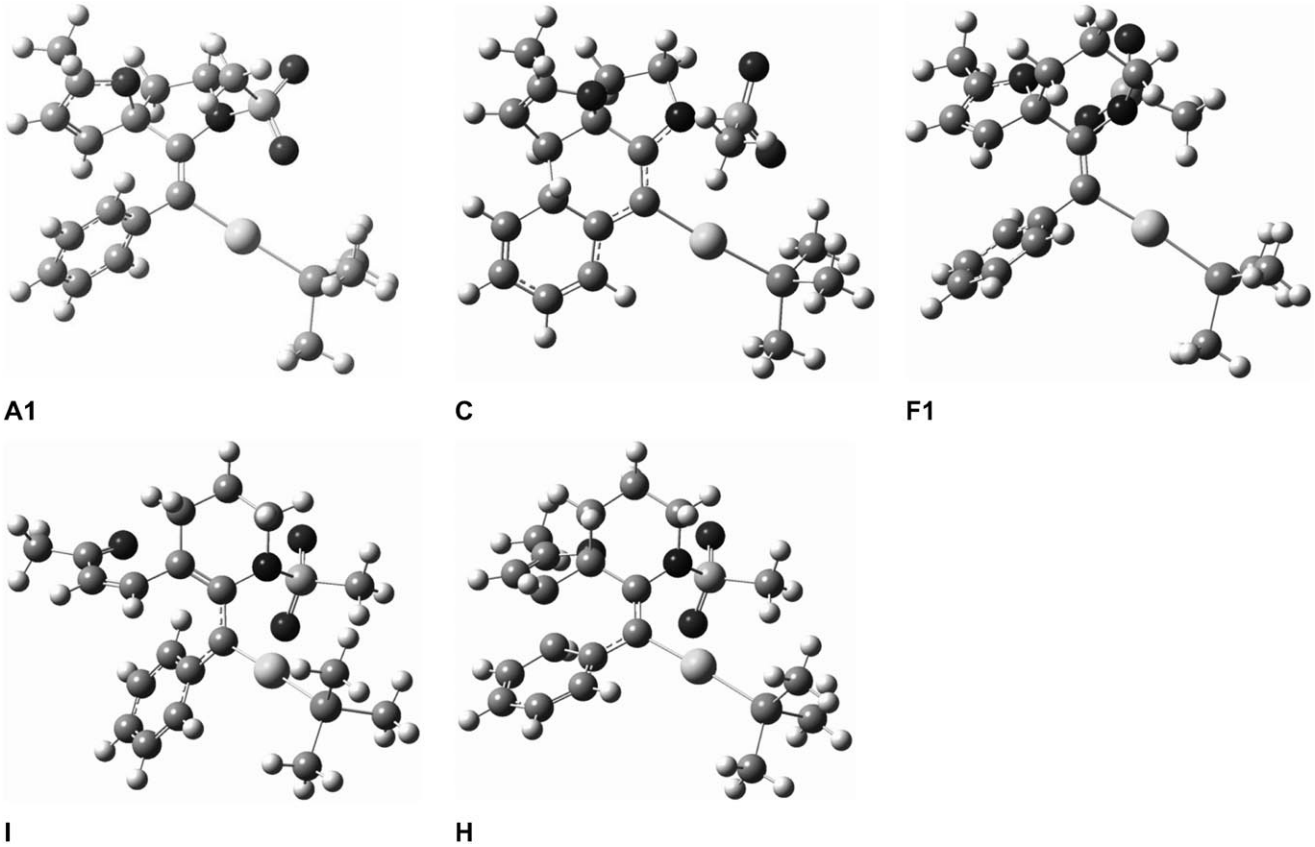
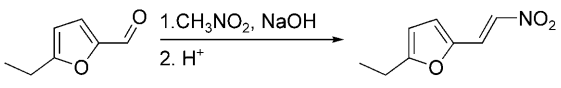


Figure 2. Molecular geometries for key intermediates obtained from DFT calculations.

tether, in the case of three atoms in the tether between the furan and the alkyne, anellated systems composing of the aryl group, a new benzene ring with a side chain and a five-membered nitrogen heterocycle are formed. In the case of four atoms in the tether, acylcyclopentadienes anellated to a six-membered nitrogen heterocycle are isolated. Both observed routes open new possibilities for the synthesis of important anellated arenes and anellated heteroarenes under very mild reaction conditions. The keto group present at the beta-carbon atom of the side-chain of the products **7** will allow a wide spectrum of further functionalizations.

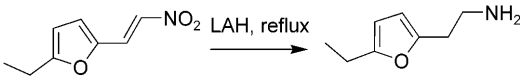
Experimental Section

2-Ethyl-5-(2-nitrovinyl)furan[13]



124 mg (1 mmol, 1 equiv.) of 5-ethylfurfural were added to an ice-cold solution of 1 mL methanol and 0.13 mL of nitromethane (2 mmol, 2 equiv.). Aqueous 1 M NaOH (2.5 equiv.) was added followed by 4 mL of ice/water. The reaction mixture was stirred for 20 min at 0 °C and then slowly added to 8 M HCl (1.6 equiv.) and was stirred for 1.5 h at room temperature. The organic part was extracted with dichloromethane and then dried over $MgSO_4$. Column chromatography (silica gel, petroleum ether:ethyl acetate) furnished the nitroalkene product as yellow crystals; yield: 144 mg (84%). R_f (petroleum ether:ethyl acetate, 1:1) = 0.44; IR (neat): $\tilde{\nu}$ = 3129, 2992, 2919, 1670, 1552, 1520, 1498, 1070, 970, 826, 821, 725, 558 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.6 Hz, 3H), 2.65 (q, J = 7.6 Hz, 2H), 6.24 (d, J = 3.5 Hz, 1H), 6.82 (d, J = 3.5 Hz, 1H), 7.44 (d, J = 13.2 Hz, 1H), 7.72 (d, J = 13.2 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.74 (q), 21.81 (t), 108.7 (d), 122.0 (d), 125.6 (d), 133.3 (d), 145.1 (s), 163.8 (s); MS (EI): m/z (%) = 167 (100) (M^+), 138 (35), 124 (60), 105 (76), 83 (60), 77 (40), 55 (30); anal. calcd. for $C_8H_9NO_3$: C 57.48, H 5.43, N 8.38; found: C 57.70, H 5.49, N 8.27.

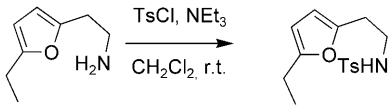
2-(5-Ethylfuran-2-yl)ethylamine



3.00 g (18.0 mmol, 1 equiv.) of **1** were dissolved in 50 mL of anhydrous ether. The solution was slowly added to 2.00 g (54.0 mmol, 3 equiv.) of $LiAlH_4$ in 150 mL of anhydrous ether under nitrogen at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then refluxed for 18 h. After cooling to 0 °C, the reaction was quenched with 10 mL of NH_4Cl. The solid was filtered off and the organic

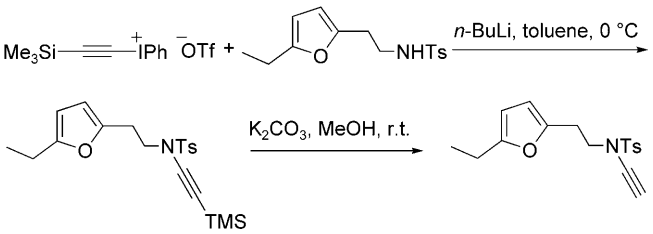
layer was extracted with ether, the combined organic phases dried over $MgSO_4$. Column chromatography (silica gel, petroleum ether:ethyl acetate:1% NEt_3) furnished the pure amine as a light brown oil; yield: 1.52 g (64%); R_f (petroleum ether:ethyl acetate, 1:1) = 0.05; IR (film): $\tilde{\nu}$ = 2970, 2937, 1566, 1464, 1325, 1211, 1011, 934, 777 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, J = 8.0 Hz, 3H) 1.43 (bs, 1H), 2.60 (q, J = 8.0 Hz, 2H), 2.72 (t, J = 6.8 Hz, 2H), 2.94 (t, J = 7.24 Hz, 2H), 5.86 (d, J = 3.2 Hz, 1H), 5.93 (d, J = 3.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.13 (q), 21.34 (t), 32.50 (t), 40.83 (t), 104.2 (t), 106.3 (t), 151.9 (s), 156.5 (s); MS (EI): m/z (%) = 140 (10) (M+1), 123 (100); HR-MS (ESI): m/z = 140.1070, calcd. for $C_8H_{13}NO$: 140.1079.

2-(5-Ethylfuran-2-yl)-*N*-tosylethanamine



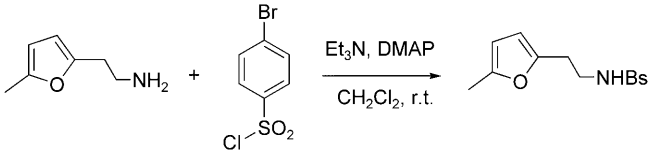
1.30 g (9.40 mmol, 1 equiv.) of the amine **2** were dissolved in 20 mL of dichloromethane. 1.4 mL (10.4 mmol, 1.1 equiv.) of triethylamine and 1.80 g (9.40 mmol, 1 equiv.) of tosyl chloride were added to this solution. The reaction mixture was stirred at room temperature for 24 h.The reaction was quenched with 10 mL of water, and the organic layer was extracted with dichloromethane. After drying over $MgSO_4$, column chromatography (silica gel, petroleum ether:ethyl acetate) gave the product as a yellow oil; yield: 1.87 g (70%); R_f (petroleum ether:ethyl acetate, 4:1) = 0.30; IR (film): $\tilde{\nu}$ = 3282, 2971, 2937, 1566, 1420, 1322, 1153, 1092, 1009, 795, 660, 549 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.3 Hz, 3H), 2.41 (s, 3H), 2.53 (q, J = 8.0 Hz, 2H), 2.71 (t, J = 7.0 Hz, 2H), 3.20 (q, J = 6.8 Hz, 2H), 4.71 (t, J = 6.9 Hz , 1H), 5.82 (d, J = 3.2 Hz, 1H), 5.88 (d, J = 3.2 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.09 (q), 21.30 (t), 21.54 (q), 28.31(t), 41.77 (t), 104.4 (d), 107.4 (d), 127.1 (d, 2C), 129.7 (d, 2C), 136.9 (s), 143.4 (s), 149.7 (s), 157.1 (s); MS (EI): m/z (%) = 293 (40) (M^+), 184 (30), 155 (95), 122 (70), 109 (100), 91 (60); anal. calcd. for $C_{15}H_{19}NSO_3$: C 61.41, H 6.53, N 4.77; found: C 61.35, H 6.55, N 4.92.

N-[2-(5-Ethylfuran-2-yl)-ethyl]-*N*-ethynyl-4-methylbenzenesulfonamide[14]



2.65 g (9.00 mmol, 1 equiv.) of the amine **3** were dissolved in 70 mL of dry toluene under nitrogen. The solution was cooled to 0 °C and 4.00 mL (10 mmol, 1.1 equiv.) *n*-butyllithium (2.5 M solution in hexane) were added drop by drop. The reaction mixture was stirred for 1 h at the same temperature. 4.90 g (10.8 mmol, 1.2 equiv.) of trimethylsilylethynyliodonium triflate was added in portions and the reaction mixture was warmed to room temperature for 36 h. The solvent was removed under vacuum and the crude product was passed through a pad of silica gel to remove all residual impurities. The crude TMS-protected alkyne obtained as brownish-yellow oil (yield: 2.80 g, 7.20 mmol) was dissolved in 20 mL of methanol and 1.26 g (9.00 mmol, 1.2 equiv.) of K_2CO_3 were added in portions. The suspension was stirred at room temperature for 1 h after which the solvent was removed and column chromatography done (silica gel, petroleum ether:ethyl acetate). The pure product was isolated as a yellow oil; overall yield: 1.20 g (42%); R_f (petroleum ether:ethyl acetate, 4:1) = 0.50; IR (film): $\tilde{\nu}$ = 3296, 2972, 2936, 2135, 1698, 1596, 1566, 1453, 1362, 1166, 1090, 950, 683 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.19 (t, J = 7.6 Hz, 3H), 2.44 (s, 3H), 2.57 (q, J = 7.6 Hz, 2H), 2.75 (s, 1H), 2.92 (t, J = 7.5 Hz, 2H), 3.58 (t, J = 7.6 Hz, 2H), 5.81–5.84 (m, 1H), 5.92 (d, J = 3.1 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 12.14 (q), 21.29 (t), 21.67 (q), 26.99 (t), 49.78 (t), 59.48 (d), 75.66 (s), 104.4 (d), 107.3 (d), 127.6 (d, 2C), 129.8 (d, 2C), 134.5 (s), 144.7 (s), 149.0 (s), 156.9 (s); MS (APCI): m/z (%) = 318 (100) $(M+1)^+$, 123 (24); HR-MS (APCI): m/z = 317.1079, calcd. for $C_{17}H_{19}NO_3S$: 317.1086.

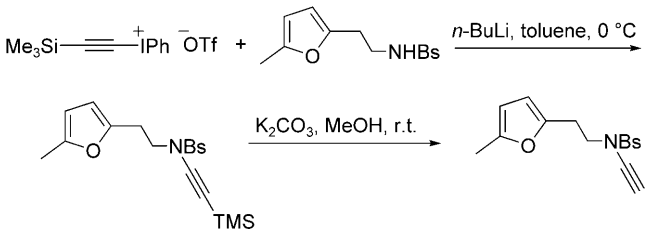
4-Bromo-*N*-[2-(5-methyl-furan-2-yl)-ethyl]benzenesulfonamide



1.30 g (9.40 mmol, 1 equiv.) of 2-(5-methylfuran-2-yl)ethylamine[15] were dissolved in 20 mL of dichloromethane. Cooled to 0 °C and 1.40 mL (10.4 mmol, 1.1 equiv.) of triethylamine, a pinch of DMAP and 2.60 g (10.3 mmol, 1.1 equiv.) of brosyl chloride were added to this solution. The reaction mixture was stirred at toom temperature for 12 h.The reaction was quenched with 10 mL of water, and the organic layer was extracted with dichloromethane and the extract dried over $MgSO_4$. Column chromatography (silica gel, petroleum ether:ethyl acetate) gave the product as a pale-yellow solid; yield: 2.60 g (72%); mp: 56–58 °C; R_f (petroleum ether:ethyl acetate, 1:1) = 0.45; IR (film): $\tilde{\nu}$ = 3275, 2918, 1573, 1471, 1388, 1320, 1155, 1065, 1009, 927, 821, 783, 738, 655, 602 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.20 (s, 3H), 2.73 (t, J = 6.5 Hz, 2H), 3.23 (q, J = 6.4 Hz, 2H), 4.61 (t, J = 6.3 Hz, 1H), 5.80–5.84 (m, 1H), 5.88 (d, J = 3.0 Hz, 1H), 7.59–7.72 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.49 (q), 28.30 (t), 41.79 (t), 106.1 (d), (107.9 (d), 127.6 (s), 128.6 (d, 2C), 132.3 (d, 2C), 139.0 (s), 149.5 (s), 151.5 (s); MS (APCI): m/z (%) = 344 (7) (M+1), 109 (100); HR-MS (APCI): m/z = 342.9876, calcd. for $C_{13}H_{14}BrNO_3S$: 342.9878; anal. calcd. for $C_{13}H_{14}BrNO_3S$: C 45.36, H 4.10, N 4.07; found: C 45.49, H 4.13, N 4.04.

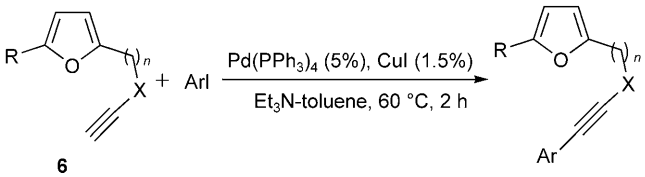
4-Bromo-*N*-ethynyl-*N*-[2-(5-methyl-furan-2-yl)ethyl]benzenesulfonamide

4.00 g (11.6 mmol, 1 equiv.) of amine **5** were dissolved in 100 mL of dry toluene under nitrogen. The solution was



cooled to 0 °C and *n*-butyllithium was added drop by drop. The reaction mixture was stirred for 1 h at the same temperature. 6.20 g (13.8 mol, 1.2 equiv.) of trimethylsilylethynyliodonium triflate were added in portions and the reaction mixture was warmed to room temperature for 36 h. The solvent was removed under vacuum and the product was passed through a short pad of silica gel. The crude TMS-protected alkyne thus obtained (yield: 4.00 g, 9.00 mmol) was dissolved in 20 mL of methanol and 1.50 g (10.8 mmol, 1.2 equiv.) of K_2CO_3 were added in portions. The suspension was stirred at room temperature for 1 h after which the solvent was removed and column chromatography done (silica gel, petroleum ether:ethyl acetate). The pure product was isolated as a colourless solid; overall yield: 2.80 g (65%); mp: 70–72 °C; R_f (petroleum ether:ethyl acetate, 4:1) = 0.53; IR (film): $\tilde{\nu}$ = 3296, 2137, 1573, 1367, 1169, 1068, 965, 785, 744, 664 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.78 (s, 1H), 2.92 (t, J = 7.5 Hz, 2H), 3.60 (t, J = 7.5 Hz, 2H), 5.79–5.82 (m, 1H), 5.90 (d, J = 3.1 Hz, 1H), 7.64–7.76 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.59 (q), 26.97 (t), 49.96 (t), 60.00 (d), 75.02 (s), 106.1 (d), 107.7 (d), 128.9 (d, 2C), 132.5 (d, 2 C), 136.4 (s), 148.8 (s), 151.2 (s), 161.1 (s); MS (ESI^+): m/z (%) = 390 (100) $(M+Na)^+$, 368 $(M+1)^+$, 186 (16); HR-MS (ESI^+): m/z = 366.9885, calcd. for $C_{15}H_{14}BrNO_3S$: 366.9878.

General Procedure for the Sonogashira Couplings



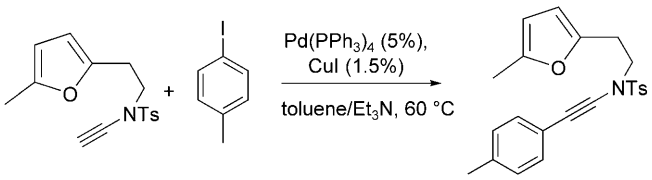
6 **5**

n = 2, 3
R = H, Me, Et
X = NTs, NBs

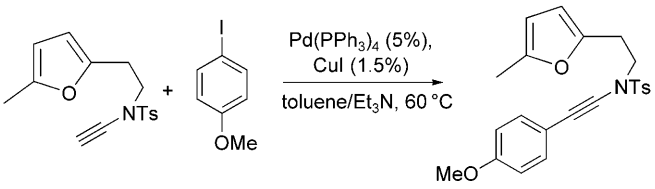
1.00 mmol (1 equiv.) of the ynamide[16] and 1.10 mmol of the aryl iodide were added to a mixture of 2 mL dry toluene and 2 mL triethylamine. 5 mol% of tetrakis(triphenylphosphine)palladium(0) was added and the mixture was degassed. After being stirred for 10 min at room temperature 1.5 mol% copper(I) iodide was added. The reaction mixture was heated at 60 °C for 2 h. The solvent was removed under vacuum and the crude product was purified over flash column chromatography (silica gel, petroleum ether/ethyl acetate).

4-Methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-*p*-tolylethynylbenzenesulfonamide (5a)

Yield: 31%, pale brown oil, R_f (petroleum ether:ethyl acetate, 4:1) = 0.44; IR (film): $\tilde{\nu}$ = 2922, 2235, 1365, 1168, 903, 722, 649 cm^{-1}; ^1H NMR (CD_2Cl_2, 250 MHz): δ = 2.20 (s, 3H), 2.34 (s, 3H), 2.44 (s, 3H), 2.96 (t, J = 7.6 Hz, 2H), 3.65 (t, J = 7.6 Hz, 2H), 5.83–5.85 (m, 1H), 5.94 (d, J = 3.2 Hz, 1H), 7.10 (dd, J = 8.6 Hz, 0.7 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.33 (dd, J = 8.6 Hz, 0.7 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.47 (q), 21.45 (q), 21.65 (q), 27.18 (t), 50.22 (t), 70.94 (s), 81.18 (s), 106.1 (d), 107.5 (d), 119.6 (s), 127.6 (d, 2C), 127.8 (d, 2C), 129.7 (d, 2C), 131.5 (d, 2C), 134.6 (s), 138.0 (s), 144.5 (s), 149.3 (s), 151.2 (s); MS (EI^+): m/z (%) = 394 $(M+1)^+$ (14), 393 (M^+) (41), 246 (55), 214 (57), 108 (96), 91 (100); HR-MS (ESI^+): m/z = 394.1396, calcd. for $C_{23}H_{23}NO_3S$: 393.1399.

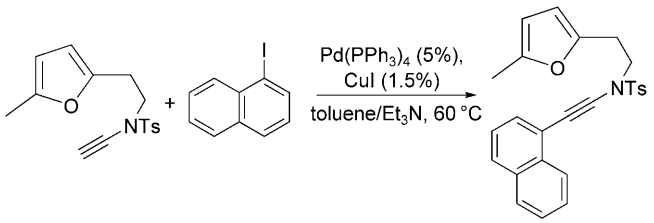


N-(4-Methoxyphenylethynyl)-4-methyl-*N*-[2-(5-methyl-furan-2-yl)ethyl]benzenesulfonamide (5b)



Yield: 31%, brown oil; R_f (petroleum ether:ethyl acetate, 4:1) = 0.42; IR (film): $\tilde{\nu}$ = 2923, 2235, 1605, 1511, 1363, 1247, 1167, 904, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.45 (s, 3H), 2.96 (t, J = 7.8 Hz, 2H), 3.65 (t, J = 7.8 Hz, 2H), 3.81 (s, 3H), 5.81–5.83 (m, 1H), 5.92 (d, J = 3.2 Hz, 1H), 6.8 (d, J = 8.8 Hz, 2H), 7.29–7.35 (m, 4H), 7.81 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.59 (q), 21.71 (q), 27.28 (t), 29.48 (q); 50.40 (t), 55.35 (q), 70.71 (s), 80.5 (s), 106.1 (d), 107.5 (d), 113.8 (d, 2C), 114.7 (s), 127.6 (d, 2C), 129.6 (d, 2C), 133.4 (d, 2C), 144.5 (s), 149.4 (s), 151.1 (s), 159.6 (s); MS (ESI^+): m/z (%) = 432 (100) $(M+Na)^+$; HR-MS (EI^+): m/z = 409.1349, calcd. for $C_{23}H_{23}NO_4S$: 409.1348.

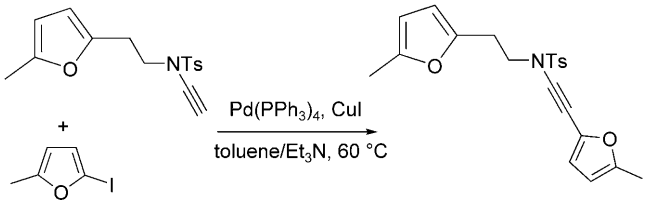
4-Methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-naphthalen-1-ylethynylbenzenesulfonamide (5c)



Yield: 29%, yellow oil; R_f (petroleum ether:ethyl acetate, 4:1) = 0.33; IR (film): $\tilde{\nu}$ = 3057, 2921, 2230, 1364, 1167, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.44 (s, 3H), 3.06 (t, J = 7.6 Hz, 2H), 3.78 (t, J = 7.6 Hz, 2H), 5.82–5.85 (m, 1H), 5.96 (d, J = 3.1 Hz, 1H), 7.33 (d, J =

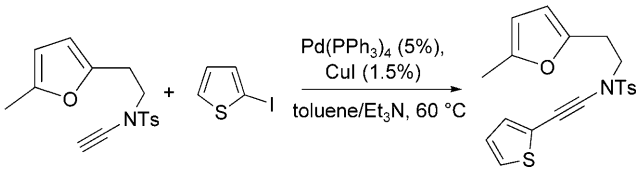
8.3 Hz, 2H), 7.38–7.42 (m, 1H), 7.50–7.58 (m, 3H), 7.79 (d, J=8.3 Hz, 2H), 7.86 (d, J=8.4 Hz, 2H), 8.18–8.22 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.54 (q), 21.74 (q), 27.31 (t), 50.37 (t), 69.5 (s), 86.6 (s), 106.2 (d), 107.6 (d), 120.5 (s), 125.1 (d), 126.2 (d), 126.3 (d), 126.7 (d), 127.7 (d, 2C), 128.2 (d), 129.7 (d), 129.8 (d, 2C), 130.9 (d), 133.1 (s), 133.2 (s), 134.7 (s), 144.7 (s), 149.2 (s), 151.2 (s); MS (ESI$^+$): m/z (%)=452 (100) $(M+Na)^+$; HR-MS (ESI$^+$): m/z=430.1479, $C_{26}H_{23}NO_3S$: calcd: 430.1469.

4-Methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-(5-methylfuran-2-ylethynyl)benzenesulfonamide (5d)



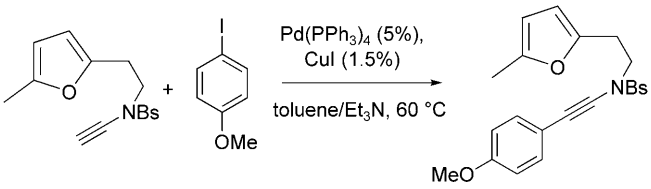
Yield: 20%, yellow oil; R_f (petroleum ether:ethyl acetate, 8:1)=0.25; IR (film): $\tilde{\nu}$=2922, 2220, 1543, 1436, 1365, 1264, 1167, 1090, 1019, 920, 786, 712 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ=2.20 (s, 3H), 2.29 (s, 3H), 2.44 (s, 3H), 2.94 (t, J=7.8 Hz, 2H), 3.65 (t, J=7.9 Hz, 2H), 5.79–5.82 (m, 1H), 5.91 (d, J=5.9 Hz, 1H), 5.96–5.99 (m, 1H), 6.51 (d, J=3.2 Hz, 1H), 7.33 (d, J=8.2 Hz, 2H), 7.79 (d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.46 (q), 13.95 (q), 21.70 (q), 27.18 (t), 50.36 (t), 62.41 (s), 85.78 (s), 106.1 (d), 107.3 (d), 107.6 (d), 118.8 (d), 127.6 (d, 2C), 129.8 (d, 2C), 134.8 (s), 134.9 (s), 144.7 (s), 149.2 (s), 151.2 (s), 154.2 (s); MS (ESI$^+$): m/z (%)=406 (72) $(M+Na)^+$, 301 (100); HR-MS (ESI): m/z=406.1078, calcd. for $C_{21}H_{21}NO_4S$: 406.1088.

4-Methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-thiophen-2-ylethynylbenzenesulfonamide (5e)



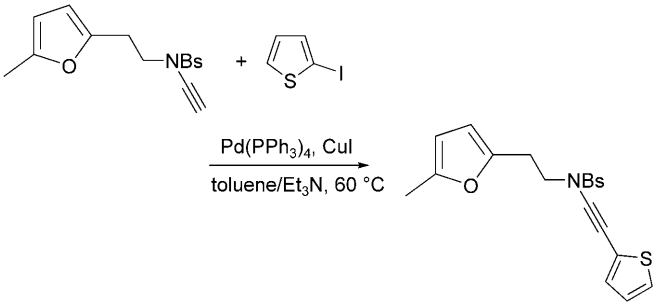
Yield: 41%, yellow oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.26; IR (film): $\tilde{\nu}$=2922, 2227, 1366, 1167, 1090, 709, 662, 547 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.20 (s, 3H), 2.45 (s, 3H), 2.94 (t, J=7.6 Hz, 2H), 3.67 (t, J=7.6 Hz, 2H), 5.81–5.83 (m, 1H), 5.92 (d, J=3.2 Hz, 1H), 6.95–6.98 (m, 1H), 7.17 (dd, J=3.7 Hz, 1.1 Hz, 1H), 7.26–7.28 (m, 1H), 7.35 (d, J=8.3 Hz, 2H), 7.80 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.47 (q), 21.69 (q), 27.26 (t), 50.35 (t), 64.24 (s), 85.46 (s), 106.1 (d), 107.6 (d), 122.8 (s), 127.0 (d), 127.6 (d, 2C), 127.8 (d), 129.8 (d, 2C), 133.1 (d), 134.5 (s), 144.7 (s), 149.2 (s), 151.1(s); MS (EI$^+$): m/z (%)=386 (52) $(M+H)^+$, 231 (100); HR-MS (ESI$^+$): m/z= 386.0879, calcd. for $C_{20}H_{19}NO_3S_2$: 386.0886.

4-Bromo-*N*-(4-methoxyphenylethynyl)-*N*-[2-(5-methylfuran-2-yl)ethyl]benzenesulfonamide (5f)



Yield: 17%, yellow oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.35; IR (film): $\tilde{\nu}$=2925, 1605, 1573, 1367, 1248, 1170, 902, 725, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.21 (s, 3H), 2.96 (t, J=7.4 Hz, 2H), 3.67 (t, J=7.5 Hz, 2H), 3.81 (s, 3H), 5.80–5.83 (m, 1H), 5.92 (d, J=3.1 Hz, 1H), 6.83 (d, J=8.8 Hz, 2H), 7.31 (d, J=8.9 Hz, 2H), 7.67 (d, J=8.6 Hz, 2H), 7.76 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.57 (q), 27.15 (t), 50.46 (t), 55.40 (q), 71.03 (s), 79.78 (s), 106.1 (d), 107.7 (d), 114.0 (d, 2C), 114.3 (s), 128.7 (s), 129.0 (d, 2C), 132.3 (d, 2C), 133.6 (d, 2C), 136.6 (s), 149.2 (s), 151.3 (s), 159.7 (s); MS (ESI): m/z (%)=473 (3) (M^+), 255 (100), 212 (42); HR-MS (ESI): m/z=474.0375, calcd. for $C_{22}H_{20}BrNO_4S$: 474.0371.

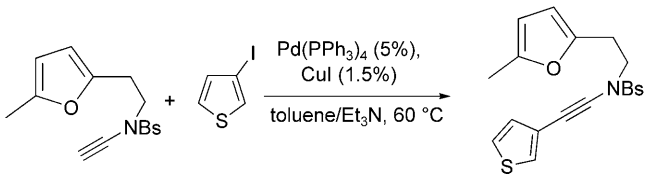
4-Bromo-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-thiophen-2-ylethynylbenzenesulfonamide (5g)



Yield: 36%, yellow oil; R_f (petroleum ether:ethyl acetate, 8:1)=0.50; IR (film): $\tilde{\nu}$=3102, 2920, 2226, 1572, 1368, 1168, 1088, 1067, 783, 742, 703, 592, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.20 (s, 3H), 2.95 (t, J=7.4 Hz, 2H), 3.69 (t, J=7.4 Hz, 2H), 5.80–5.83 (m, 1H), 5.91 (d, J=3.2 Hz, 1H), 6.96–7.00 (m, 1H), 7.18 (dd, J=3.8 Hz, 1.3 Hz, 1H), 7.29 (dd, J=5.2 Hz, 1.2 Hz, 1H), 7.65–7–78 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ=13.49 (q), 27.16 (t), 50.51 (t), 64.68 (s), 84.82 (s), 106.1 (d), 106.8 (d), 122.4 (s), 127.0 (d), 128.1 (d), 128.9 (s), 129.0 (d, 2C), 132.4 (d, 2C), 133.4 (d), 136.4 (s), 148.9 (s), 151.2 (s); MS (ESI$^+$): m/z (%)=471 (100) $(M+Na)^+$, 231 (59); HR-MS (ESI): m/z=448.9746, calcd. for $C_{19}H_{16}BrNO_3S_2$: 448.9750.

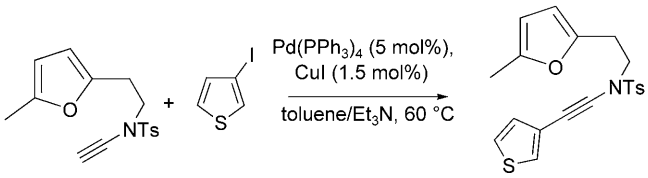
4-Bromo-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-thiophen-2-ylethynylbenzenesulfonamide (5h)

Yield: 27%, brown oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.62; IR (film): $\tilde{\nu}$=3106, 2920, 2238, 1572, 1367, 1169, 1068, 901, 863, 782, 744, 592, 569 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.20 (s, 3H), 2.98 (t, J=7.4 Hz, 2H), 3.68 (t, J=7.4 Hz, 2H), 5.81–5.83 (m, 1H), 5.92 (d, J=3.1 Hz, 1H), 7.05 (dd, J=5.0 Hz, 1.0 Hz, 1H), 7.25–7.29 (m, 1H), 7.41 (dd, J=3.0 Hz, 1.1 Hz, 1H), 7.68 (d, J=8.7 Hz, 2H), 7.76 (d,



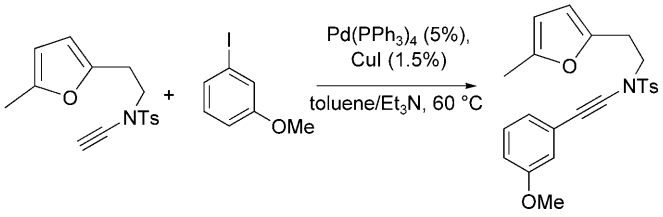
J=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.54 (q), 27.17 (t), 50.38 (t), 66.30 (s), 80.58 (s), 106.1 (d), 107.7 (d), 121.1 (s), 125.3(d), 128.8 (s), 129.0 (d, 2C), 129.3 (d), 130.3 (d), 132.5 (d, 2C), 136.6 (s), 149.0 (s), 151.3 (s); MS (APCI): m/z (%)=451 (100) $(M+H)^+$, 450 (98) (M^+), 231 (99); HR-MS (APCI): m/z=449.9845, calcd. for $C_{19}H_{16}BrNO_3S_2$: 448.9879.

4-Methyl-*N*-[2-(5-methyl-furan-2-yl)ethyl]-*N*-thiophen-3-ylethynyl-benzenesulfonamide (5i)



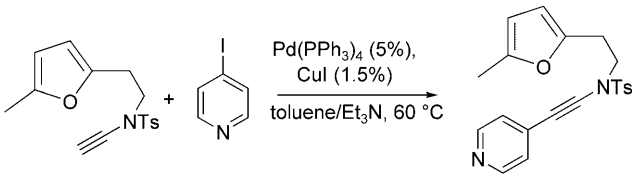
Yield: 31% brown oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.59; IR (film): $\tilde{\nu}$=2934, 2235, 1739, 1365, 1168, 1090, 1019, 984, 901, 863, 783, 709, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.20 (s, 3H), 2.44 (s, 3H), 2.91 (t, J=7.6 Hz, 2H), 3.65 (t, J=7.7 Hz, 2H), 5.80–5.83 (m, 1H), 5.92 (d, J=2.9 Hz, d), 7.04 (dd, J=4.9 Hz, 1H), 7.23–7.26 (m, 1H), 7.33 (d, J=8.2 Hz, 2H), 7.37 (dd, J=3.0 Hz, 1H), 7.80 (d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.53 (q), 21.67 (q), 27.23 (t), 50.36 (t), 65.94 (s), 81.25 (s), 106.1 (d), 107.6 (d), 121.5 (s), 125.1 (d), 127.6 (d, 2C), 128.9 (s), 129.8 (d, 2C), 130.3 (d), 134.7 (d), 144.6 (s), 149.3 (s), 151.1 (s); MS (ESI): m/z (%)=408 (100) $(M+Na)^+$, 345 (26), 301 (38); HR-MS (APCI): m/z=385.0806, calcd. for $C_{20}H_{19}rNO_3S_2$: 385.0806.

N-(3-Methoxyphenylethynyl)-4-methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]benzenesulfonamide (5j)



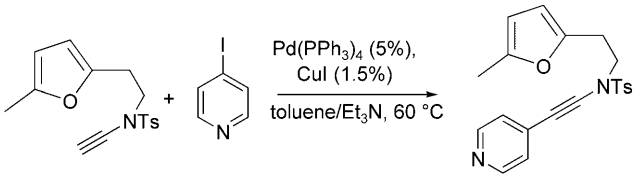
Yield: 40%, brown oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.43; IR (film): $\tilde{\nu}$=2921, 2549, 2236, 1365, 1168, 873, 785 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.21 (s, 3H), 2.43 (s, 3H), 2.99 (t, J=7.5 Hz, 2H), 3.67 (t, J=7.6 Hz, 2H), 3.81 (s, 3H), 5.81–5.83 (m, 1H), 5.93 (d, J=3.2 Hz, 1H), 76.81–6.95 (m, 3H), 7.19 (t, J=8.1 Hz, 1H), 7.35 (d, J=8.4 Hz, 2H), 7.82 (d, J=8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.55 (q), 21.76 (q), 27.35 (t), 50.21 (t), 55.29 (q), 106.1 (d), 107.6 (d), 114.1 (d), 116.3 (d), 123.9 (d), 127.7 (d, 2C), 129.3 (d), 129.8 (d, 2C), 134.6 (s), 144.7 (s), 149.2 (s), 151.1 (s), 159.3 (s); MS (ESI$^+$): m/z (%)=432 (100) $(M+Na)^+$; HR-MS (EI$^+$): m/z=409.1348, calcd. for $C_{23}H_{23}NO_4S$: 409.1345.

4-Methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-(4-nitrophenylethynyl)benzenesulfonamide (5k)



Yield: 43%, brown oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.41; IR (film): $\tilde{\nu}$=2923, 2225, 1593, 1514, 1368, 1337, 1167, 1090, 852, 748, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.20 (s, 3H), 2.42 (s, 3H), 2.97 (t, J=7.5 Hz, 2H), 3.72 (t, J=7.5 Hz, 2H), 5.82–5.85 (m, 1H), 5.92 (d, J=3.2 Hz, 1H), 7.36 (d, J=8.4 Hz, 2H), 7.43 (d, J=8.8 Hz, 2H), 7.81 (d, J=8.3 Hz, 2H), 8.16 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.53 (q), 21.75 (q), 27.41 (t), 50.27 (t), 70.79 (s), 88.60 (s), 106.2 (d), 107.8 (d), 123.6 (d, 2C), 127.7 (d, 2C), 129.9 (d, 2C), 130.2 (s), 130.9 (d, 2C), 134.5 (s), 145.1 (s), 146.2 (s), 148.9 (s), 151.2 (s); MS (ESI$^+$): m/z (%)=425 (100) $(M+H)^+$, 155 (25); HRMS (EI$^+$): m/z=425.1183, calcd. for $C_{22}H_{20}N_2O_5S$: 425.1179.

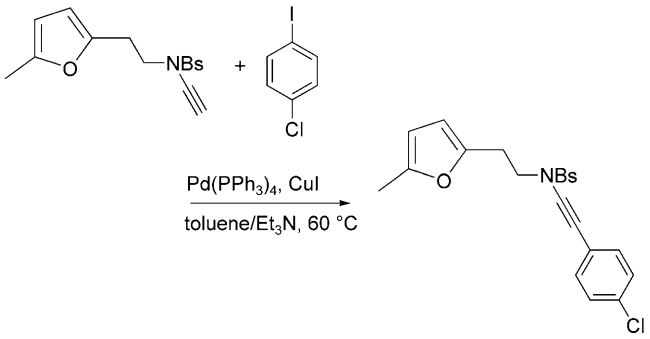
4-Methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-pyridin-4-ylethynylbenzenesulfonamide (5l)



Yield: 34%, dark oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.11; IR (film): $\tilde{\nu}$=2922, 2229, 1592, 1365, 1166, 1088, 815, 779, 676 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.20 (s, 3H), 2.45 (s, 3H), 2.98 (t, J=7.6 Hz, 2H), 3.70 (t, J=7.6 Hz, 2H), 5.81–5.83 (m, 1H), 5.93 (d, J=3.1 Hz, 1H), 7.18 (dd, J=6.1 Hz, 1.4 Hz, 2H), 7.35 (d, J=8.3 Hz, 2H), 7.81 (d, J=8.3 Hz, 2H), 8.51 (dd, J=6.1 Hz, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.49 (q), 21.75 (q), 27.47 (t), 50.26 (t), 70.82 (s), 88.03 (s), 106.3 (d), 107.8 (d), 123.6 (d, 2C), 127.6 (d, 2C), 129.9 (d, 2C), 130.3 (s), 130.9 (d, 2C), 134.5 (s), 145.2 (s), 146.3 (s), 148.8 (s), 151.3 (s); MS (EI$^+$): m/z (%)=380 (15) (M^+), 225 (35), 109 (50), 95 (100); HR-MS (ESI$^+$): m/z=380.1195, calcd. for $C_{21}H_{20}N_2O_3S$: 380.1195.

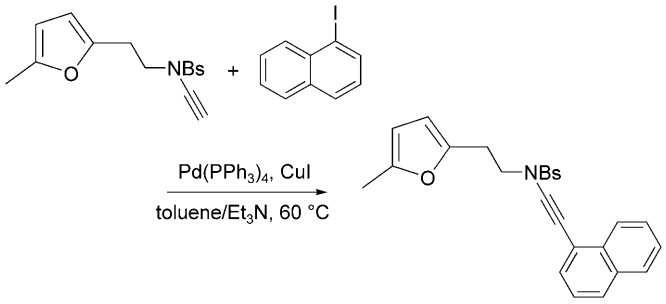
4-Bromo-*N*-(4-chlorophenylethynyl)-*N*-[2-(5-methylfuran-2-yl)ethyl]benzenesulfonamide (5m)

Yield: 25%, yellow solid; mp 64–66°C; R_f (petroleum ether:ethyl acetate, 4:1)=0.60; IR (film): $\tilde{\nu}$=2920, 2236, 1573, 1370, 1170, 1088, 1011, 825, 743, 600 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.20 (s, 3H), 2.96 (t, J=7.5 Hz, 2H), 3.69 (t, J=7.5 Hz, 2H), 5.80–5.83 (m, 1H), 5.92 (d, J=3.2 Hz, 1H), 7.28 (s, 4H), 7.66–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.50 (q), 27.24 (t), 50.40 (t), 70.42



(s), 82.14 (s), 106.2 (d), 107.9 (d), 120.9 (s), 128.6 (d, 2C), 129.0 (d, 2C), 132.5 (d, 2C), 132.7 (d, 2C), 134.1 (s), 136.5 (s), 148.9 (s), 151.3 (s); MS (ESI$^+$): *m/z* (%) = 479 (6) (M + 2), 258 (30), 139 (58), 109 (46), 95 (100); anal. calcd. for $C_{21}H_{17}BrClNO_3S$: C 52.68, H 3.58, N 2.93; found: C 52.50, H 3.66, N 2.93. A crystal structure analysis was obtained.[6]

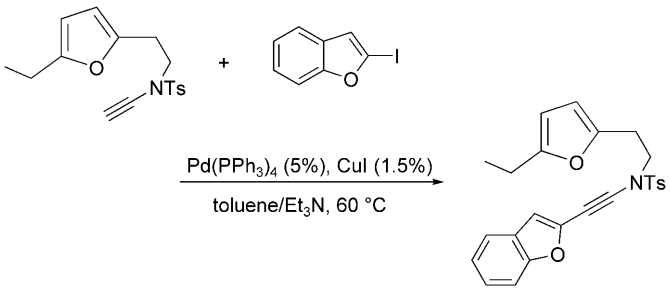
4-Bromo-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-naphthalen-1-ylethynylbenzenesulfonamide (5n)



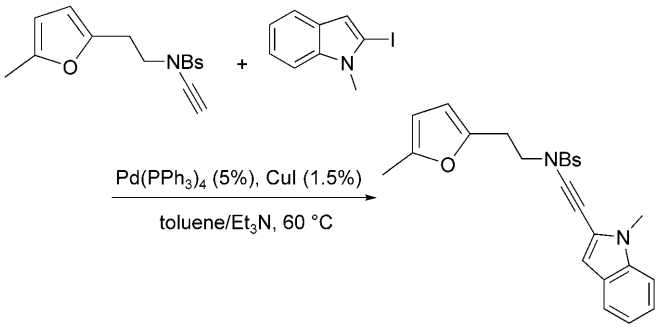
Yield: 27%, yellow oil; R_f (petroleum ether:ethyl acetate, 4:1) = 0.60; IR (film): $\tilde{\nu}$ = 3058, 2920, 2231, 1572, 1366, 1168, 1067, 1010, 932, 743, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.21 (s, 3H), 3.07 (t, J = 7.3 Hz, 2H), 3.80 (t, J = 7.3 Hz, 2H), 5.81–5.83 (m, 1H), 5.96 (d, J = 3.2 Hz, 1H), 7.38–7.44 (m, 1H), 7.50–7.59 (m, 3H), 7.66 (d, J = 8.6 Hz, 2H), 7.77–7.86 (m, 4H) , 8.13–8.16 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 13.50 (q), 27.29 (t), 50.46 (t), 106.2 (d), 107.9 (d), 120.1 (s), 125.1 (s), 126.0 (d), 126.4 (d), 126.8 (d), 128.3 (d), 128.5 (d), 128.9 (s), 129.1 (d, 2C), 130.0 (d), 132.5 (d, 2C), 133.1 (s), 133.2 (s), 136.5 (s), 149.0 (s), 151.0 (s); MS (ESI$^+$): *m/z* (%) = 495 (18) (M + 2)$^+$, 274 (100), 155 (46), 109 (44), 95 (52); HR-MS (ESI): *m/z* = 493.0347, calcd. for $C_{25}H_{20}BrNO_3S$: 493.0338.

N-Benzofuran-2-ylethynyl-*N*-[2-(5-ethylfuran-2-yl)ethyl]-4-methylbenzenesulfonamide (5o)

Yield: 20%, brown oil; R_f (petroleum ether:ethyl acetate, 4:1) = 0.32; IR (film): $\tilde{\nu}$ = 2253, 1368, 1168, 1090, 902, 723, 649 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 1.16 (t, J = 7.6 Hz, 3H), 2.46 (s, 3H), 2.55 (q, J = 7.6 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 3.70 (t, J = 7.4 Hz, 2H), 5.84–5.86 (m, 1H), 5.96 (d, J = 3.1 Hz, 1H), 6.96 (d, J = 1.1 Hz, 1H), 7.22–7.47 (m, 5H), 7.56 (d, J = 7.7 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 12.09 (q), 21.33 (t), 21.78 (q), 27.27 (t), 50.41 (t), 62.17 (s), 87.5 (s), 104.5 (d), 107.3 (s), 107.6 (d), 111.1 (d), 113.1 (d), 121.1 (d), 123.2 (d), 125.6 (d), 127.7 (d, 2C), 129.7 (s), 130.0 (d, 2C), 134.5 (s), 135.3 (s), 145.0 (s), 148.8 (s), 157.1 (s); MS (APCI): *m/z* (%) = 434 (M + 1)$^+$ (34), 279 (100), 222 (31); HR-MS (APCI): *m/z* = 434.1422, calcd. for $C_{24}H_{23}NO_4S$: 434.1428.



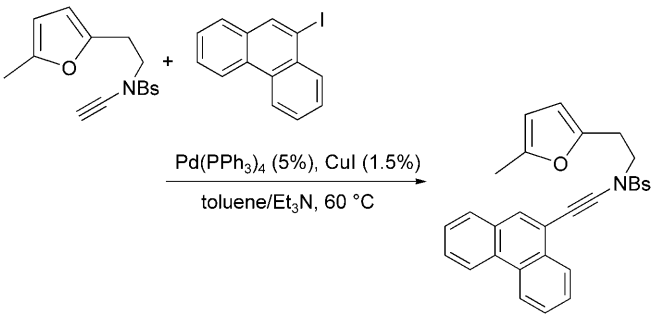
4-Bromo-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-(1-methyl-1*H*-indol-2-ylethynyl)benzenesulfonamide (5p)



Yield: 30%, colourless solid; mp 122–124 °C; R_f (petroleum ether:ethyl acetate, 4:1) = 0.52; IR (film): $\tilde{\nu}$ = 2218, 1572, 1365, 1169, 966 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 3.00 (t, J = 7.1 Hz, 2H), 3.72 (s, 3H), 3.76 (t, J = 7.2 Hz, 2H), 5.81–5.84 (m, 1H), 5.94 (d, J = 3.0 Hz, 1H), 6.73 (s, 1H), 7.08–7.14 (m, 1H), 7.27 (dd, J = 4.9 Hz, 1.0 Hz, 2H), 7.57 (td, J = 7.7 Hz, 0.8 Hz, 1H), 7.68 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.50 (q), 27.24 (t), 30.45 (q), 50.45 (t), 63.46 (s), 86.68 (s), 106.2 (d), 107.9 (d), 108.7 (d), 109.5 (d), 120.1 (d), 121.0 (d), 123.2 (d), 126.9 (s), 129.1 (d, 2C), 132.5 (d, 2C), 136.5 (s), 137.3 (s), 148.9 (s), 151.3 (s); MS (APCI): *m/z* (%) = 499 (100) (M + 1)$^+$, 278 (46); HR-MS (APCI): *m/z* = 496.0480, calcd. for $C_{24}H_{21}BrN_2O_3S$: 496.0456.

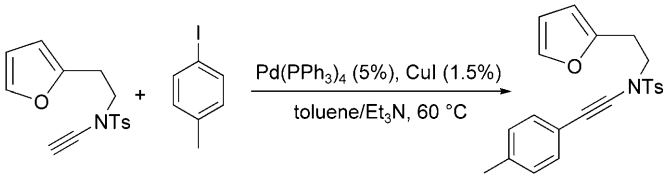
4-Bromo-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-phenanthren-9-ylethynylbenzenesulfonamide (5q)

Yield: 31%, sticky brown oil; R_f (petroleum ether:ethyl acetate, 4:1) = 0.42; IR (film): $\tilde{\nu}$ = 3061, 2921, 2230, 1572, 1365, 1168, 1067, 906, 742, 724, 567 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.22 (s, 3H), 7.40 (t, J = 7.4 Hz, 2H), 3.83 (t, J = 7.4 Hz, 2H), 5.81–5.83 (m, 1H), 5.98 (d, J = 3.1 Hz, 1H), 7.56–7.73 (m, 6H), 7.80–7.85 (m, 3H), 7.88 (s, 1H), 8.24–8.28 (m, 1H), 8.62–8.71 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.61 (q), 27.36 (t), 50.54 (t), 70.02 (s), 85.37 (s), 106.2 (d), 107.9 (d), 118.9 (s), 122.6 (d), 122.9 (d), 126.7 (d), 127.0 (d), 127.1 (d), 127.2 (d), 127.4 (d), 128.3 (d), 128.9



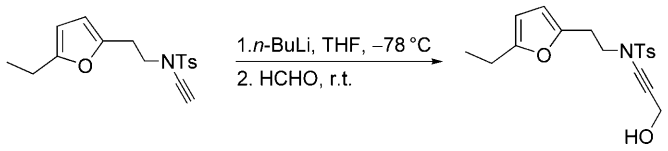
(s), 129.1 (d, 2C), 130.0 (s), 131.1 (s), 131.3 (d), 132.5 (d, 2C), 136.5 (s), 149.0 (s), 151.3 (s); MS (APCI): *m/z* (%) = 544 (8) (M^+), 325 (100), 282 (42); HR-MS (APCI): *m/z* = 544.0573, $C_{29}H_{22}BrNO_3S$: 544.0579.

N-(2-Furan-2-ylethyl)-4-methyl-*N*-4-tolylethynylbenzenesulfonamide (5r)



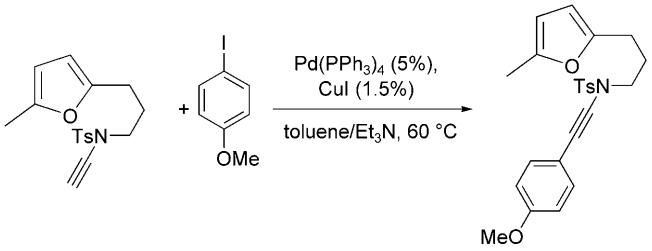
Yield: 41%, brown oil; R_f (petroleum ether:ethyl acetate, 8:1) = 0.34; IR (film): $\tilde{\nu}$ = 2922, 2235, 1597, 1363, 1167, 1090, 814, 735, 664 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz): δ = 2.34 (s, 3H), 2.44 (s, 3H), 3.01 (t, J = 7.4 Hz, 2H), 3.66 (t, J = 7.4 Hz, 2H), 6.08–6.10 (m, 1H), 6.27–6.30 (m, 1H), 7.12 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.31 (dd, J = 1.9, 0.7 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 21.47 (q), 21.73 (q), 27.15 (t), 50.06 (t), 71.01 (s), 81.13 (s), 106.9 (d), 109.3 (d), 127.7 (d, 2C), 129.0 (d, 2C), 129.8 (d, 2C), 131.5 (d, 2C), 134.5 (s), 138.1 (s), 141.6 (d), 144.6 (d), 151.3 (d); MS (ESI^+): *m/z* (%) = 375 (7), 360 (6), 304 (100); HR-MS (APCI): *m/z* = 402.1635, calcd. for $C_{22}H_{21}NO_3S$: 402.1639.

N-[2-(5-Ethylfuran-2-yl)ethyl]-*N*-(3-hydroxyprop-1-ynyl)-4-methylbenzenesulfonamide (5s)



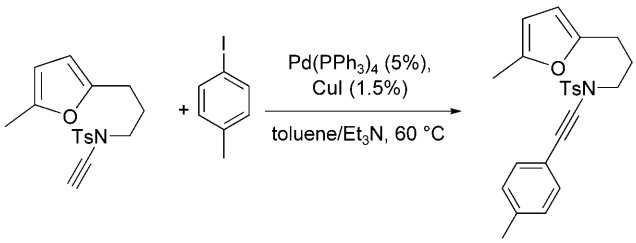
210 mg (0.66 mmol, 1 equiv.) of the alkyne **1c** were dissolved in 10 mL dry THF taken in a flame-dried-round bottom flask under nitrogen. The solution was cooled to −78 °C and 0.29 mL (0.73 mmol, 1.1 equiv.) *n*-butyllithium (2.5 M solution in hexane) were added dropwise. The solution was stirred for 45 min at the same temperature and then 40 mg (1.2 mmol, 2 equiv.) of paraformaldehyde were added in portions. The reaction mixture was warmed to room temperature and stirred for overnight. After being quenched with ammonium chloride solution the mixture was extracted with ether. After being dried over magnesium sulfate the solvent was removed under vacuum. Column chromatography (silica gel, petroleum ether:ethyl acetate) furnished the pure product as a light brown oil; yield: 110 mg (48%); R_f (petroleum ether:ethyl acetate, 2:1) = 0.23; IR (film): $\tilde{\nu}$ = 3523, 2972, 2241, 1360, 1165, 998, 847, 813, 677, 573 cm^{-1}; ^1H NMR (CD_2Cl_2, 250 MHz): δ = 1.18 (t, J = 7.6 Hz, 3H), 2.43 (s, 3H), 2.56 (q, J = 7.6 Hz, 2H), 2.88 (t, J = 7.2 Hz, 2H), 3.57 (t, J = 7.3 Hz, 2H), 4.33 (d, J = 5.5 Hz, 2H), 5.83–5.86 (m, 1H), 5.91 (d, J = 3.1 Hz, 1H), 7.35 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 12.12 (q), 21.32 (t), 21.65 (q), 27.26 (t), 50.09 (t), 51.22 (t), 69.95 (s), 78.87 (s), 104.4 (d), 107.4 (d), 127.5 (d, 2C), 129.9 (d, 2C), 134.6 (s), 144.7 (s), 149.1 (s), 157.0 (s); MS (APCI): *m/z* (%) = 348 (6) $(M+1)^+$, 330 (100); HR-MS (ESI): *m/z* = 330.1145 (water molecule lost), cacd. for $C_{18}H_{21}NO_4S$: 347.1191.

N-(4-Methoxyphenylethynyl)-4-methyl-*N*-[3-(5-methylfuran-2-yl)propyl]benzenesulfonamide (5t)



Yield: 37%, brown oil; R_f (petroleum ether:ethyl acetate, 4:1) = 0.47; IR (film): $\tilde{\nu}$ = 2922, 2235, 1604, 1511, 1361, 1287, 1246, 1166, 1090, 1020, 831, 722, 663, 577 cm^{-1}; ^1H NMR (CD_2Cl_2, 250 MHz): δ = 2.01 (qu, J = 7.2 Hz, 2H), 2.23 (s, 3H), 2.45 (s, 3H), 2.65 (t, J = 7.3 Hz, 2H), 3.42 (t, J = 7.1 Hz, 2H), 3.80 (s, 3H), 5.81–5.85 (m, 1H), 5.88 (d, J = 3.0 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 7.28–7.38 (m, 4H), 7.82 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.56 (q), 21.74 (q), 24.92 (t), 26.61 (t), 51.07 (t), 55.35 (q), 70.41 (s), 80.92 (s), 105.8 (d), 106.1 (d), 113.9 (d, 2C), 114.7 (s), 127.7 (d, 2C), 129.7 (d, 2C), 133.4 (d, 2C), 134.5 (s), 144.5 (s), 150.5 (s), 152.6 (s), 159.5 (s); MS (APCI): *m/z* (%) = 424 (100) $(M+1)^+$; HR-MS (ESI): *m/z* = 423.1499, calcd. for $C_{24}H_{25}NO_4S$: 423.1504.

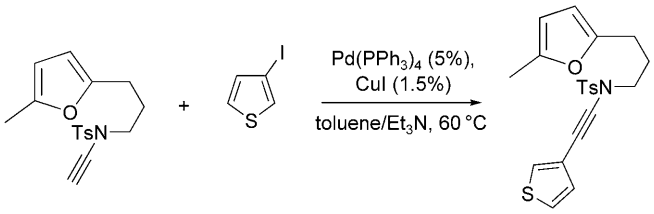
4-Methyl-*N*-[3-(5-methylfuran-2-yl)propyl]-*N*-p-tolylethynylbenzenesulfonamide (5u)



Yield: 24%, yellow oil; R_f (petroleum ether:ethyl acetate, 4:1) = 0.55; IR (film): $\tilde{\nu}$ = 2924, 2235, 1448, 1363, 1166, 1090, 907, 814, 727, 662, 576 cm^{-1}; ^1H NMR (CD_2Cl_2, 250 MHz): δ = 1.99 (qu, J = 7.3 Hz, 2H), 2.21 (s, 3H), 2.33 (s, 3H), 2.44 (s, 3H), 2.63 (t, J = 7.3 Hz, 2H), 3.41 (t, J = 7.3 Hz, 2H),

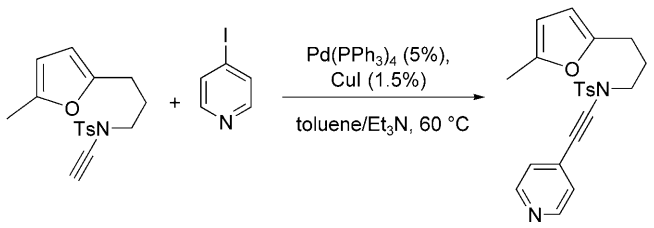
5.82–5.85 (m, 1H), 5.87 (d, J=3.1 Hz, 1H), 7.11 (d, J=8.4 Hz, 2H), 7.25 (d, J=8.3 Hz, 2H), 7.37 (d, J=8.4 Hz, 2H), 7.80 (d, J=8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.47 (q), 21.43 (q), 21.67 (q), 24.87 (t), 26.60 (t), 50.99 (t), 70.72 (s), 81.61 (s), 105.8 (d), 106.1 (d), 119.7 (s), 127.7 (d, 2C), 129.0 (d, 2C), 129.7 (d, 2C), 131.5 (d, 2C), 134.5 (s), 138.0 (s), 144.5 (s), 150.5 (s), 152.6 (s); MS (ESI): m/z (%)=430 $(M+Na)^+$ 408 (18); HR-MS (ESI): m/z=407.1550, calcd. for $C_{24}H_{25}NO_3S$: 407.1555.

4-Methyl-*N*-[3-(5-methylfuran-2-yl)propyl]-*N*-thiophen-3-ylethynylbenzenesulfonamide (5v)



Yield: 39%, yellow oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.55; IR (film): $\tilde{\nu}$=3106, 2921, 2236, 1597, 1569, 1363, 1167, 1091, 781 658, 579 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.97 (quint, J=7.2 Hz, 2H), 2.21 (s, 3H), 2.45 (s, 3H), 2.62 (t, J=7.4 Hz, 2H), 3.41 (t, J=7.2 Hz, 2H), 5.82–5.85 (m, 1H), 5.87 (d, J=3.0 Hz, 1H), 7.06 (dd, J=5.1 Hz, 1.1 Hz, 1H), 7.27–7.31 (m, 1H), 7.35–7.41 (m,3H), 7.79 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.49 (q), 21.65 (q), 24.83 (t), 26.57 (t), 50.98 (t), 65.74 (s), 81.59 (s), 105.8 (d), 106.1 (d), 121.5 (s), 125.1 (d), 127.7 (d, 2C), 128.7 (d), 129.7 (d, 2C), 130.2 (d), 134.5 (s), 144.5 (s), 150.5 (s), 152.5 (s); MS (ESI): m/z (%)=422 (100) $(M+Na)^+$, 400 (23); HR-MS (ESI): m/z=399.0958, calcd. for $C_{21}H_{21}NO_3S_2$: 399.0963.

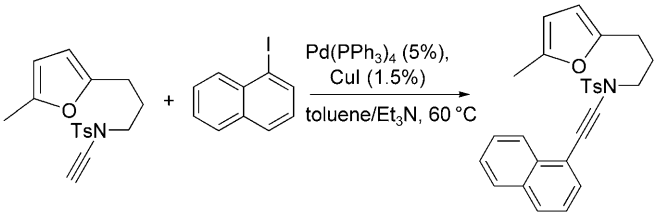
4-Methyl-*N*-[3-(5-methylfuran-2-yl)propyl]-*N*-pyridin-4-ylethynylbenzenesulfonamide (5w)



Yield: 46%, dark brown oil; R_f (petroleum ether:ethyl acetate, 4:1)=0.10; IR (film): $\tilde{\nu}$=2922, 2229, 1592, 1366, 1167, 1089, 815, 675, 579, 545 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.95–2.06 (m, 2H), 2.22 (s, 3H), 2.45 (s, 3H), 2.63 (t, J=7.4 Hz, 2H), 3.47 (t, J=7.4 Hz, 2H), 5.83–5.86 (m, 1H), 5.88 (d, J=3.1 Hz, 1H), 7.17–7.20 (m, 2H), 7.39 (d, J=8.4 Hz, 2H), 7.80 (d, J=8.5 Hz, 2H), 8.47–8.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.57 (q), 21.75 (q), 24.80 (t), 26.71 (t), 50.81 (t), 69.80 (s), 87.80 (s), 106.0 (d), 106.4 (d), 124.3 (d, 2C), 127.6 (d, 2C), 130.0 (d, 2C), 131.7 (s), 134.4 (s), 145.3 (s), 149.6 (d, 2C), 150.8 (s), 152.5 (s); MS (ESI): m/z (%)=417 (90) $(M+Na)^+$, 395 (100) $(M+1)^+$, 240 (62); HR-MS (ESI): m/z=394.1349, calcd. for $C_{22}H_{22}N_2O_3S$: 394.1351.

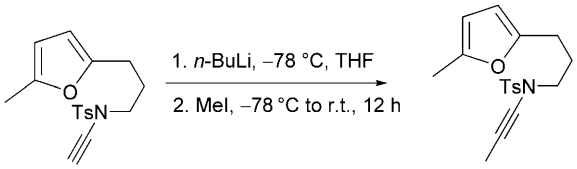
4-Methyl-*N*-[3-(5-methylfuran-2-yl)propyl]-*N*-naphthalen-1-ylethynylbenzenesulfonamide (5x)

Yield: 35%, brown oil; R_f (petroleum ether:ethyl acetate,



4:1)=0.54; IR (film): $\tilde{\nu}$=3058, 2922, 2230, 1596, 1569, 1448, 1363, 1167, 1090, 1018, 951, 774, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.03–2.15 (m, 2H), 2.22 (s, 3H), 2.44 (s, 3H), 2.70 (t, J=7.6 Hz, 2H), 3.54 (t, J=7.2 Hz, 2H), 5.83–5.87 (m, 1H), 5.91 (d, J=3.1 Hz, 1H), 7.38 (d, J=7.8 Hz, 2H), 7.43 (d, J=7.8 Hz, 1H), 7.50–7.59 (m, 3H), 7.81 (d, J=8.6 Hz, 2H), 7.87 (d, J=8.3 Hz, 2H), 8.15–8.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=13.62 (q), 21.74 (q), 24.92 (t), 26.70 (t), 50.99 (t), 69.26 (s), 86.82 (s), 105.8 (d), 106.2 (d), 120.5 (s), 125.2 (d), 126.2 (d), 126.3 (d), 126.7 (d), 127.0 (s), 127.7 (d, 2C), 128.1 (d), 128.2 (d), 129.6 (d), 129.8 (d, 2C), 133.1 (s), 134.5 (s), 144.7 (s), 150.6 (s), 152.5 (s); MS (ESI): m/z (%)=466 (26) $(M+Na)^+$, 444 (100) $(M+1)^+$; HR-MS (ESI): m/z=443.1550, calcd. for $C_{27}H_{25}NO_3S$: 443.1555.

4-Methyl-*N*-[3-(5-methylfuran-2-yl)propyl]-*N*-prop-1-ynylbenzenesulfonamide (5y)



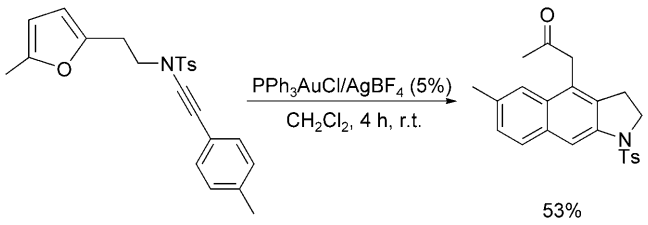
300 mg (0.95 mmol, 1 equiv.) of the ynamide were dissolved in 10 mL of dry THF under nitrogen. The system was cooled to −78 °C and 0.44 mL (1.1 mmol, 1.1 equiv.) of *n*-butyllithium were added slowly. The reaction mixture was stirred for 45 min at the same temperature and then 0.31 mL (5 mmol, 5 equiv.) of methyl iodide were added. The reaction mixture was warmed to room temperature in 12 h, and then quenched with saturated aqueous ammonium chloride. The organic layer was extracted with ether, and the extract dried over magnesium sulfate. The solvent was removed under vacuum leaving the product as a yellow oil which was directly used without further purification; yield: 307 mg (98%); R_f (petroleum ether:ethyl acetate, 8:1)=0.54; IR (film): $\tilde{\nu}$=2253, 1968, 1360, 1169, 902, 723, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.89 (s, 3H), 1.93 (quint, J=7.4 Hz , 2H), 2.24 (s, 3H), 2.44 (s, 3H), 2.60 (t, J=7.4 Hz, 2H), 3.29 (t, J=7.4 Hz, 2H), 5.81–5.84 (m, 1H), 5.87 (d, J=3.1 Hz, 1H), 7.33 (d, J=8.4 Hz, 2H), 7.76 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ=3.31 (q), 13.51 (q), 21.62 (q), 24.82 (t), 26.42 (t), 50.81 (t), 65.78 (s),

71.84 (s), 105.8 (d), 106.0 (d), 127.5 (d, 2C), 129.6 (d, 2C), 134.6 (s), 144.3 (s), 150.5 (s), 152.8 (s); MS (APCI): *m/z* (%) = 332 (100) $(M+1)^+$, 177 (25); HR-MS (ESI): *m/z* = 331.1239, calcd. for $C_{18}H_{21}NO_3S$: 331.1241.

Catalysis; General Procedure

500 μmol (1 equiv.) of the substrate **5** was dissolved in CH_2Cl_2 or $CHCl_3$ and 25 μmol (5 mol%) of Ph_3PAuCl were added, followed by 25 μmol (5 mol%) of $AgBF_4$. The reaction mixture was stirred at room temperature or as mentioned until the starting material was consumed. The solvent was removed under vacuum and the product was purified over flash column chromatography (silica gel, petroleum ether:ethyl acetate).

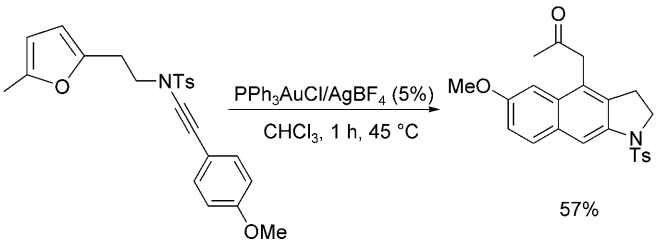
1-[6-Methyl-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-benzo[*f*]indol-4-yl]propan-2-one (7a)



53%

White solid; mp 158–160 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.18; IR (film): $\tilde{\nu}$ = 2923, 1717, 1351, 1163, 1091, 914, 814, 664, 596 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.02 (s, 3H), 2.33 (s, 3H), 2.48 (s, 3H), 2.98 (t, J = 8.2 Hz, 2H), 3.91 (s, 2H), 4.00 (t, J = 8.2 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.47 (s, 1H), 7.69–7.77 (m, 3H), 7.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.54 (q), 21.99 (q), 27.19 (t), 29.24 (q), 45.01 (t), 47.02 (t), 110.8 (d), 122.2 (d), 126.2 (s), 127.3 (d, 2C), 128.2 (d), 128.5 (d), 129.7 (d, 2C), 132.2 (s), 132.4 (s), 133.9 (s), 135.0 (s), 138.9 (s), 144.2 (s), 205.5 (s); MS (ESI^+): *m/z* (%) = 416 $(M+Na)^+$(100), 394 (7); HRMS (ESI^+): *m/z* = 416.1298, calcd. for $C_{23}H_{23}NO_3S$: 416.1296.

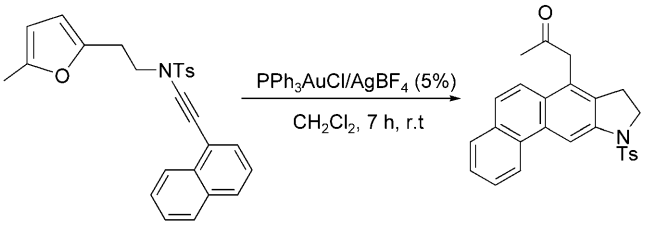
1-[6-Methoxy-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-benzo[*f*]indol-4-yl]propan-2-one (7b)



57%

Yellow solid; mp 122–124 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.17; IR (film): $\tilde{\nu}$ = 2922, 1706, 1613, 1413, 1347, 1233, 1160, 1088, 812, 662, 593, 543 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.98 (s, 3H), 2.34 (s, 3H), 2.99 (t, J = 8.1 Hz, 2H), 3.88 (s, 5H), 4.01 (t, J = 8.1 Hz, 2H), 7.03 (d, J = 2.4 Hz, 1H), 7.14 (dd, J = 8.9 Hz, 2.5 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.9 Hz, 1H), 7.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 21.51 (q), 27.40 (t), 29.08 (q), 45.56 (t), 49.67 (t), 55.39 (q), 102.6 (d), 111.3 (d), 118.0 (d), 125.6 (s), 127.3 (d, 2C), 129.3 (s), 129.7 (d, 2C), 130.1 (d), 130.6 (s), 132.7 (s), 133.9 (s), 137.9 (s), 144.2 (s), 157.5 (s), 205.5 (s); MS (ESI^+): *m/z* (%) = 432 $(M+Na)^+$ (100), 276 (39), 254 (41); HR-MS (ESI^+): *m/z* = 432.1240, calcd. for $C_{23}H_{23}NO_4S$: 432.1245.

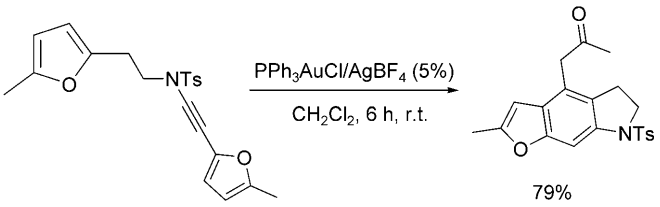
1-[10-(Toluene-4-sulfonyl)-9,10-dihydro-8*H*-10-azacyclopenta[*b*]phenanthren-7-yl]propan-2-one (7c)



53%

White solid; mp 202–205 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.11; IR (film): $\tilde{\nu}$ = 2923, 2253, 1711, 1454, 1352, 1162, 1090, 905, 670 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.04 (s, 3H), 2.31 (s, 3H), 3.04 (t, J = 8.2 Hz, 2H), 3.99 (s, 2H), 4.07 (t, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 7.58–7.73 (m, 4H), 7.76 (d, J = 8.3 Hz, 2H), 7.88 (dd, J = 7.8 Hz, 1.3 Hz, 1H), 8.77 (d, J = 8.4 Hz, 1H), 8.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 21.52 (q), 27.30 (t), 29.31 (q), 45.48 (t), 49.92 (t), 106.8 (d), 121.5 (d), 123.2 (d), 126.4 (d), 126.8 (d), 127.3 (d, 2C), 127.4 (s), 127.8 (s), 128.4 (d), 129.7 (d, 2C), 130.4 (s), 131.4 (s), 131.7 (s), 132.0 (s), 133.9 (s), 140.7 (s), 144.3 (s), 205.2 (s); MS (ESI^+): *m/z* (%) = 430 $(M+1)^+$ (29), 429 (M^+) (100), 217 (45); HR-MS (ESI^+): *m/z* = 430.1479, calcd. for $C_{26}H_{23}NO_3S$: 430.1469.

1-[2-Methyl-7-(toluene-4-sulfonyl)-6,7-dihydro-5*H*-1-oxa-7-aza-*s*-indacen-4-yl]propan-2-one (7d)

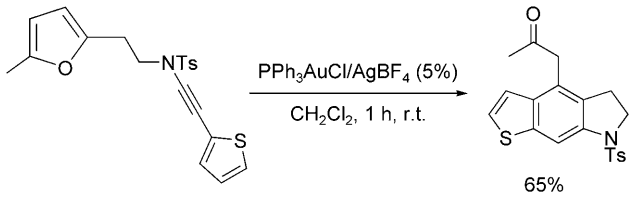


79%

Yellow oil; R_f (petroleum ether:ethyl acetate, 2:1) = 0.11; IR (film): $\tilde{\nu}$ = 2923, 2253, 1978, 1711, 1355, 1163, 1093, 902, 723, 649 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.99 (s, 3H), 2.35 (s, 3H), 2.43 (s, 3H), 2.79 (t, J = 8.3 Hz, 2H), 3.63 (s, 2H), 3.98 (t, J = 8.3 Hz, 2H), 6.24 (s,1H), 7.19 (d, J = 8.2 Hz, 2H), 7.63–7.68 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.23 (q), 21.50 (q), 26.40 (t), 29.14 (q), 46.11 (t), 5058 (t), 98.29 (d), 100.7 (d), 121.4 (s), 125.6 (s), 126.5 (s), 127.3 (d, 2C), 129.6 (d, 2C), 134.0 (s), 138.8 (s), 144.1 (s), 154.6 (s), 155.9 (s), 204.7 (s); MS (ESI^+): *m/z* (%) = 406 (89) $(M+Na)^+$, 250 (85), 228 (100); HR-MS (ESI): *m/z* = 406.1091, calcd. for $C_{21}H_{21}NO_4S$: 406.1088.

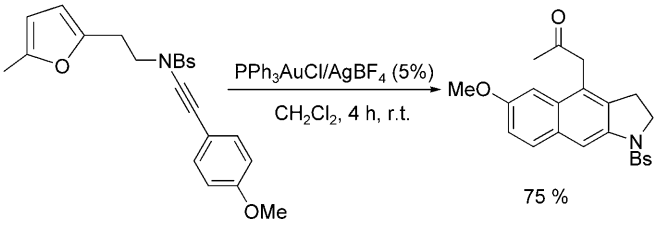
1-[7-(Toluene-4-sulfonyl)-6,7-dihydro-5*H*-1-thia-7-aza-*s*-indacen-4-yl]propan-2-one (7e)

Yellow oil; R_f (petroleum ether:ethyl acetate, 2:1) = 0.19; IR (film): $\tilde{\nu}$ = 2924, 1710, 1597, 1430, 1353, 1253, 1161, 1091,



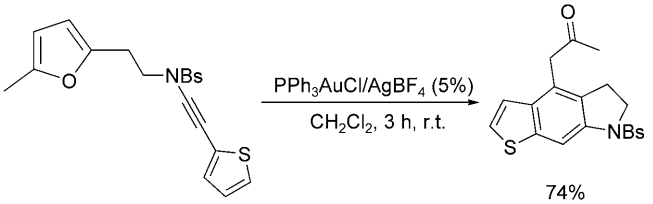
1065, 905, 729, 662 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.03 (s, 3H), 2.35 (s, 3H), 2.89 (t, J = 8.2 Hz, 2H), 3.82 (s, 2H), 4.01 (t, J = 8.2 Hz, 2H), 7.19–7.24 (m, 3H), 7.38 (d, J = 5.6 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 8.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 21.56 (q), 26.60 (t), 29.28 (q), 46.39 (t), 50.39 (t), 107.4 (d), 120.8 (d), 125.0 (s), 125.9 (d), 127.3 (d, 2C), 129.5 (s), 129.7 (d, 2C), 133.9 (s), 135.7 (s), 139.7 (s), 140.5 (s), 144.3 (s), 204.6 (s); MS (ESI^+): m/z (%): 408 $(M+Na)^+$ (27), 253 (50), 230 (71), 188 (100); HR-MS (ESI^+): m/z = 386.0879, calcd. for $C_{20}H_{19}NO_3S_2$: 386.0886.

1-[1-(4-Bromobenzenesulfonyl)-6-methoxy-2,3-dihydro-1*H*-benzo[*f*]indol-4-yl]propan-2-one (7f)



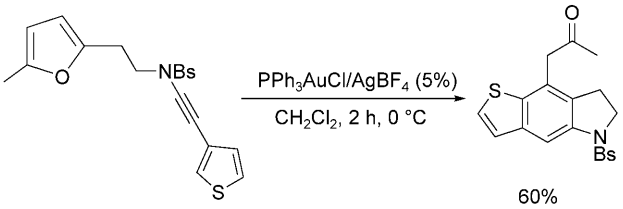
Pale yellow solid; mp 110–114 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.14; IR (film): $\tilde{\nu}$ = 2935, 1707, 1614, 1573, 1355, 1235, 1168, 1091, 738 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.01 (s, 3H), 2.99 (t, J = 8.1 Hz, 2H), 3.89 (s, 5H), 4.01 (t, J = 8.1 Hz, 2H), 7.03–7.05 (m, 1H), 7.15 (dd, J = 8.6 Hz, 2.4 Hz, 1H), 7.55 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.7 Hz, 1H), 7.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 27.36 (t), 29.18 (q), 45.53 (t), 49.86 (t), 55.47 (q), 102.6 (d), 111.3 (d), 118.2 (d), 125.9 (s), 128.4 (s), 128.7 (d, 2C), 129.3 (s), 130.1 (d), 130.8 (s), 132.4 (d, 2C), 135.9 (s), 137.5 (s), 157.9 (s), 205.1 (s); MS (ESI): m/z (%) = 473 (5) (M^+), 255 (100); HR-MS (ESI): m/z = 496.0189, calcd. for $C_{22}H_{20}BrNO_4S$: 496.0189.

1-[7-(4-Bromobenzenesulfonyl)-6,7-dihydro-5*H*-1-thia-7-aza-*s*-indacen-4-yl]propan-2-one (7g)



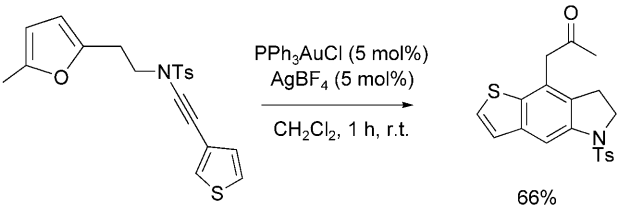
Yellow solid; mp 182–185 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.20; IR (film): $\tilde{\nu}$ = 2922, 2851, 1710, 1574, 1430, 1353, 1164, 1067 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.06 (s, 3H), 2.92 (t, J = 8.4 Hz, 2H), 3.84 (s, 2H), 4.01 (t, J = 8.4 Hz, 2H), 7.22 (d, J = 5.5 Hz, 1H), 7.40 (d, J = 5.6 Hz, 1H), 7.56 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 8.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 26.54 (t), 29.33 (q), 46.33 (t), 50.43 (t), 107.4 (d), 120.8 (d), 125.2 (s), 126.2 (d), 128.5 (s), 128.6 (d, 2C), 129.4 (s), 132.4 (d, 2C), 135.9 (s), 136.0 (s), 139.2 (s), 140.5 (s), 204.5 (s); MS (ESI^+): m/z (%) = 471 (100) $(M+Na)^+$, 231 (78); HR-MS (ESI): m/z = 448.9752, calcd. for $C_{19}H_{16}BrNO_3S_2$: 448.9750.

1-[5-(4-Bromobenzenesulfonyl)-6,7-dihydro-5*H*-1-thia-5-aza-*s*-indacen-8-yl]propan-2-one (7h)



Yellow oil; R_f (petroleum ether:ethyl acetate, 2:1) = 0.17; IR (film): $\tilde{\nu}$ = 3086, 1873, 1716, 1573, 1357, 1253, 1168, 1093, 1067, 909, 826, 738, 612 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.12 (s,3H), 2.89 (t, J = 8.2 Hz; 2H), 3.79 (s, 2H), 4.00 (t, J = 8.2 Hz, 2H), 7.34 (d, J = 5.5 Hz, 1H), 7.43 (d, J = 5.5 Hz, 1H), 7.56 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 26.58 (t), 29.67 (q), 47.41 (t), 50.41 (t), 108.5 (d), 124.8 (s), 125.0 (d), 126.4 (d), 128.4 (s), 128.6 (d, 2C), 129.5 (s), 132.4 (d, 2C), 135.9 (s), 136.6 (s), 139.8 (s), 139.9 (s), 203.9 (s); MS (APCI): m/z (%) = 452 (27) $(M+1)^+$, 246 (22), 231 (100); HR-MS (APCI): m/z = 449.9829, calcd. for $C_{19}H_{16}BrNO_3S_2$: 449.9834.

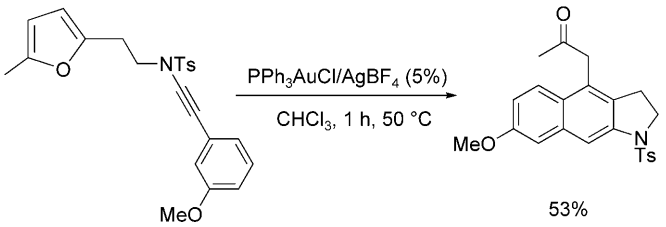
1-[5-(Toluene-4-sulfonyl)-6,7-dihydro-5*H*-1-thia-5-aza-*s*-indacen-8-yl]propan-2-one (7i)



Yellow oil; R_f (petroleum ether:ethyl acetate, 2:1) = 0.18; IR (film): $\tilde{\nu}$ = 2958, 2924, 1713, 1597, 1402, 1352, 1253, 1160, 1089, 909, 813, 729, 664, 588 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.09 (s, 3H), 2.35 (s, 3H), 2.86 (t, J = 8.1 Hz, 2H), 3.77 (s, 2H), 4.00 (t, J = 8.1 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 5.4 Hz, 1H), 7.41 (d, J = 5.4 Hz, 1H), 7.68 (d, J = 8.3 Hz, 2H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 21.54 (q), 26.61 (t), 29.51 (q), 47.48 (t), 50.45 (t), 108.5 (d), 124.5 (s), 125.0 (d), 126.1 (d), 127.3 (d, 2C), 129.7 (d, 2C), 130.2 (s), 134.0 (s), 137.4 (s), 139.9 (s), 144.1 (s), 204.3 (s); MS (ESI): m/z (%) = 408 (100) $(M+Na)^+$; HR-MS (APCI): m/z = 385.0802, calcd, for $C_{20}H_{19}rNO_3S_2$: 385.0806.

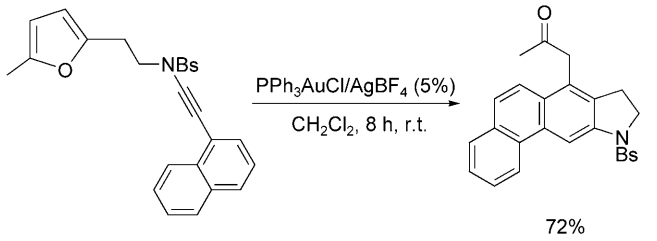
1-[7-Methoxy-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-benzo[*f*]indol-4-yl]propan-2-one (7j)

Yellow solid; mp 116–118 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.16; IR (film): $\tilde{\nu}$ = 2924, 1707, 1625, 1418, 1350, 1156, 1089, 813, 663, 596, 545 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.01 (s, 3H), 2.35 (s, 3H), 2.98 (t, J = 8.2 Hz,



2H), 3.90 (s, 2H), 3.93 (s, 3H), 4.00 (t, $J=8.2$ Hz, 2H), 7.06 (dd, $J=8.9$ Hz, 2.6 Hz, 1H), 7.17 (d, $J=2.7$ Hz, 1H), 7.22 (d, $J=8.2$ Hz, 2H), 7.63 (d, $J=8.9$ Hz, 1H), 7.74 (d, $J=8.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta=21.53$ (q), 26.86 (t), 29.24 (q), 45.19 (t), 49.83 (t), 55.34 (q), 107.1 (d), 109.8 (d), 117.6 (d), 124.5 (d), 124.6 (s), 126.#) (s), 127.3 (d, 2C), 129.7 (d, 2C), 134.0 (s), 135.8 (s), 140.4 (s), 144.3 (s), 157.8 (s), 205.3 (s); MS (ESI$^+$): m/z (%) = 410 (M^+) (12), 255 (100); HR-MS (ESI$^+$): $m/z=432.1243$, calcd. for $C_{23}H_{23}NO_4S$: 432.1245.

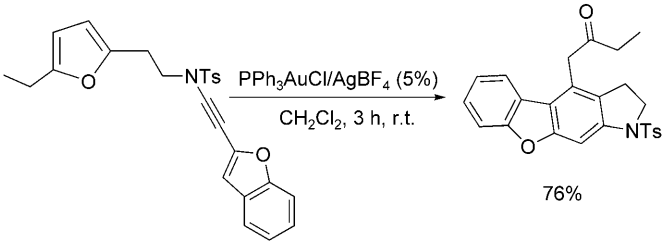
1-[10-(4-Bromobenzenesulfonyl)-9,10-dihydro-8*H*-10-azacyclopenta[*b*]phenanthren-7-yl]propan-2-one (7n)



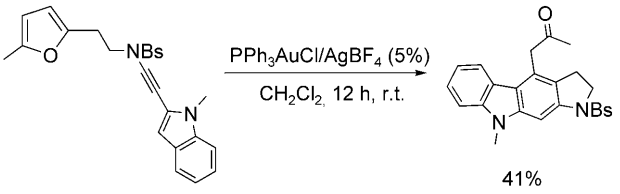
Colourless solid; mp 186–188 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.16; IR (film): $\tilde{\nu}=2924$, 1713, 1359, 1164, 1066, 821, 748, 615 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=$ 2.07 (s, 3H), 3.06 (t, $J=8.2$ Hz, 2H), 4.01 (s, 2H), 4.06 (t, $J=8.2$ Hz, 2H), 7.53 (d, $J=8.6$ Hz, 2H), 7.59–7.75 (m, 6H), 7.88 (dd, $J=7.8$ Hz, 1.1 Hz, 1H), 8.75 (d, $J=8.3$ Hz, 1H), 8.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta=27.25$ (t), 29.44 (q), 45.37 (t), 49.93 (t), 106.9 (d), 121.5 (d), 123.1 (d), 126.6 (d), 126.9 (d), 127.0 (d), 127.6 (s), 128.0 (s), 128.5 (d), 128.6 (d, 2C), 130.3 (s), 131.3 (s), 131.7 (s), 131.8 (s), 132.4 (d, 2C), 135.8 (s), 140.1 (s), 205.1 (s); MS (APCI): m/z (%) = 494 (11) (M^+), 275 (100); HR-MS (ESI): $m/z=$ 493.0352, calcd, for $C_{25}H_{20}BrNO_3S$: 493.0347.

1-[1-(Toluene-4-sulfonyl)-2,3-dihydro-1*H*-9-oxa-1-azacyclopenta[*b*]fluoren-4-yl]butan-2-one (7o)

Yellow solid; mp 134–137 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.25, IR (film): $\tilde{\nu}=2924$, 1712, 1598, 1449, 1353, 1332, 1162, 1090,904, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=0.95$ (t, $J=7.2$ Hz, 3H), 2.33–2.39 (m, 5H), 2.94 (t, $J=$ 8.5 Hz, 2H), 4.00 (s, 2H), 4.05 (t, $J=8.5$ Hz, 2H), 7.22 (d, $J=8.4$ Hz, 2H), 7.29 (dt, $J=7.6$ Hz, 1.1 Hz, 1H), 7.40 (dt, $J=7.8$ Hz, 1.2 Hz, 1H), 7.56 (d, $J=8.4$ Hz, 1H), 7.72 (d, $J=$ 8.3 Hz, 2H), 7.79 (d, $J=8.1$ Hz, 1H), 7.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta=7.65$ (q), 21.53 (q), 26.41 (t), 35.23 (t), 45.23 (t), 50.54 (t), 98.29 (d), 111.7 (d), 119.2 (s), 121.1 (d), 123.0 (d), 123.7 (s), 125.6 (s), 126.2 (d), 126.9 (s), 127.3 (d, 2C), 129.8 (d, 2C), 133.9 (s), 141.7 (s), 144.3 (s), 156.6 (s), 156.7 (s), 206.9 (s); MS (ESI$^+$): m/z (%) = 456 (100) $(M+Na)^+$, 300 (54), 278 (34), 222 (46), 179 (54); HR-MS (ESI): $m/z=456.1250$. calcd. for $C_{24}H_{23}NO_4S$: 456.1245.

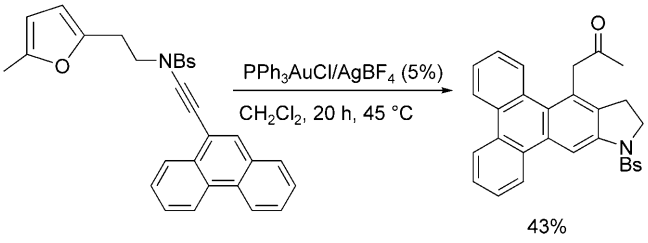


1-[1-(4-Bromobenzenesulfonyl)-9-methyl-1,2,3,9-tetrahydropyrrolo[2,3-*b*]carbazol-4-yl]propan-2-one (7p)



Pale yellow solid; mp 186–188 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.23; IR (film): $\tilde{\nu}=2925$, 1722, 1599, 1570, 1469, 1440, 1354, 1318, 1160, 1065, 840, 816, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=2.03$ (s, 3H), 2.93 (t, $J=$ 8.2 Hz, 2H), 3.88 (s, 3H), 4.05 (t, $J=8.2$ Hz, 2H), 4.10 (s, 2H), 7.18–7.24 (m, 1H), 7.39–7.48 (m, 2H), 7.53 (d, $J=$ 8.6 Hz, 2H), 7.65 (d, $J=8.7$ Hz, 2H), 7.95 (d, $J=7.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta=26.44$ (t), 29.14 (q), 29.49 (q), 46.58 (t), 50.65 (t), 95.25 (d), 108.6 (d), 119.5 (d), 121.3 (d), 121.9 (s), 123.7 (s), 125.1 (d), 125.7 (s), 126.3 (s), 128.6 (d, 2C), 132.4 (d, 2C), 136.1 (s), 140.1 (s), 141.5 (s), 141.8 (s), 160.2 (s), 205.2 (s); MS (APCI): m/z (%) = 497 (90) (M^+), 278 (100); HR-MS (APCI): $m/z=496.0449$, calcd. for $C_{24}H_{21}BrN_2O_3S$: 496.0456.

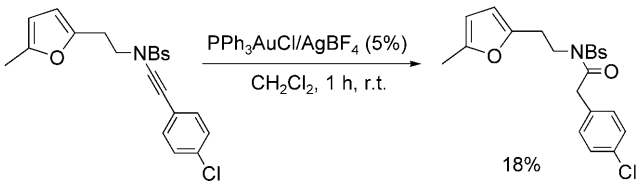
1-[10-(4-Bromobenzenesulfonyl)-11,12-dihydro-10*H*-10-azacyclopenta[*b*]triphenylen-13-yl]propan-2-one (7q)



Pale yellow solid; mp 108–110 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.13; IR (film): $\tilde{\nu}=3056$, 2923, 1716, 1573, 1356, 1263, 1164, 733, 702, 568 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=2.29$ (s, 3H), 2.93 (t, $J=8.3$ Hz, 2H), 4.02 (t, $J=8.3$ Hz, 2H), 4.23 (s, 2H), 7.41–7.49 (m, 1H), 7.52–7.59 (m, 8H), 8.54–8.66 (m, 3H), 8.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta=27.46$ (t), 29.80 (q), 49.86 (t), 106.7 (d), 123.0

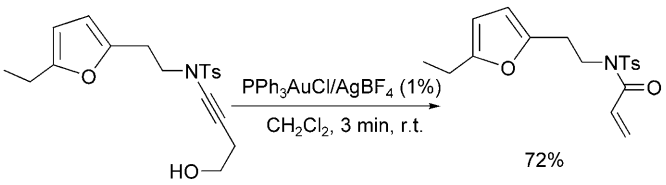
(d), 123.7 (d), 125.7 (d), 126.3 (s), 126.7 (d), 126.9 (d), 127.5 (d), 127.6 (d), 128.6 (s), 128.7 (d, 2C), 129.1 (s), 129.9 (s), 130.0 (s), 130.6 (s), 132.1 (s), 132.5 (d, 2C), 133.5 (s), 135.7 (s), 140.6 (s), 165.2 (s), 205.6 (s); MS (APCI): *m/z* (%) = 545 (62) $(M+1)^+$, 306 (100), 280 (54); HR-MS (APCI): *m/z* = 544.0573, calcd. for $C_{29}H_{22}BrNO_3S$: 544.0579.

4-Bromo-*N*-[2-(4-chlorophenyl)acetyl]-*N*-[2-(5-methylfuran-2-yl)ethyl]benzenesulfonamide (8)



Yellow oil; R_f (petroleum ether:ethyl acetate, 2:1) = 0.38; IR (film): $\tilde{\nu}$ = 2365, 2253, 1974, 1698, 1360, 1089, 902 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.21 (s, 3H), 3.00 (t, *J* = 7.1 Hz, 2H), 3.63 (s, 2H), 4.01 (t, *J* = 7.1 Hz, 2H), 5.86–5.89 (m, 1H), 5.94 (d, *J* = 3.0 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.51 (q), 28.76 (t), 41.70 (t), 46.21 (t), 106.4 (d), 108.3 (d), 128.8 (d, 2C), 129.1 (s), 129.6 (d, 2C), 130.7 (d, 2C), 131.3 (s), 132.3 (d, 2C), 133.3 (s), 138.2 (s), 149.2 (s), 151.5 (s), 170.5 (s); MS (APCI): *m/z* (%) = 498 (9) $(M+2)^+$, 479 (20), 109 (100); HR-MS (APCI): *m/z* = 494.9900, calcd. for $C_{21}H_{19}BrClNO_4S$: 494.9907.

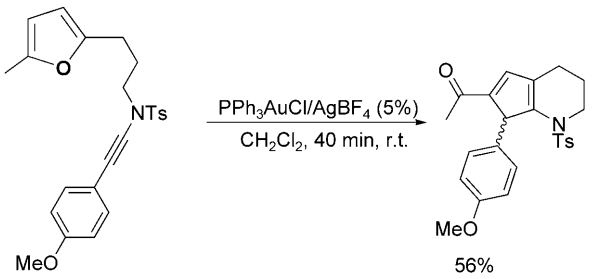
N-Acryloyl-*N*-[2-(5-ethylfuran-2-yl)ethyl]-4-methylbenzenesulfonamide (9)



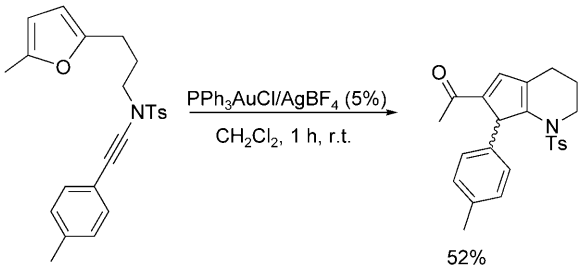
Colourless oil; R_f (petroleum ether:ethyl acetate, 2:1) = 0.35; IR (film): $\tilde{\nu}$ = 2970, 2934, 1684, 1346, 1159, 1087, 812, 709, 662 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (t, *J* = 7.8 Hz, 3H), 2.43 (s, 3H), 2.58 (q, *J* = 7.8 Hz, 2H), 2.97–3.05 (m, 2H), 4.02–4.07 (m, 2H), 5.72 (dd, *J* = 10.4 Hz, 1.8 Hz, 1H), 5.83–5.86 (m, 1H), 5.96 (d, *J* = 3.1 Hz, 1H), 6.37 (dd, *J* = 16.7 Hz, 1.8 Hz, 1H), 6.72–6.82 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 12.40 (q), 21.70 (q), 29.17 (t), 46.00 (t), 104.9 (d), 107.7 (d), 128.0 (d, 2C), 128.7 (d), 130.1 (d, 2C), 131.1 (t), 137.1 (s), 145.6 (s), 150.0 (s), 157.5 (s), 165.6 (s); MS (APCI): *m/z* (%) = 348 (15) $(M+1)^+$, 177 (22), 123 (100); HR-MS (APCI): *m/z* = 347.1172, calcd. for $C_{18}H_{21}NO_4S$: 347.1191.

1-[7-(4-Methoxyphenyl)-1-(toluene-4-sulfonyl)-2,3,4,7-tetrahydro-1*H*-[1]pyrindin-6-yl]ethanone (10t)

Yellow solid; mp 188–193 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.23; IR (film): $\tilde{\nu}$ = 2932, 1646, 1509, 1362, 1299, 1247, 1168, 907, 820, 729, 672 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.21–1.31 (m, 1H), 1.66–1.72 (m, 1H), 2.20 (s, 3H), 2.24–2.37 (m, 2H), 2.38 (s, 3H), 2.96–3–02 (m, 1H), 3.77 (s, 3H), 3.87 (td, *J* = 13.6 Hz, 1H), 5.27 (s, 1H), 6.76 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 1.3 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.33 (t), 21.59 (q), 22.01 (q), 26.46 (q), 46.87 (t), 55.18 (q), 56.86 (d), 113.8 (d, 2C), 126.5 (s), 127.3 (d, 2C), 128.8 (s), 129.3 (d, 2C), 129.6 (d, 2C), 135.7 (s), 142.1 (d), 143.8 (s), 146.3 (s), 150.3 (s), 158.4 (s), 192.8 (s); MS (ESI): *m/z* (%) = 424 (23) $(M+1)^+$, 268 (100); HR-MS (ESI): *m/z* = 446.1407, calcd. for $C_{24}H_{25}NO_4S$: 446.1401.



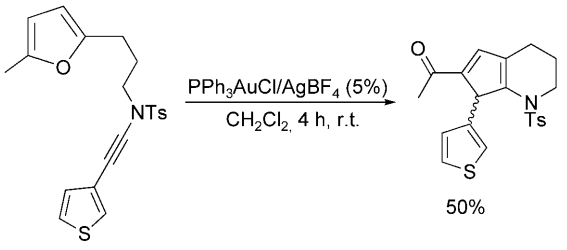
1-[1-(Toluene-4-sulfonyl)-7-(4-tolyl)-2,3,4,7-tetrahydro-1*H*-[1]pyrindin-6-yl]ethanone (10u)



Colourless solid; mp 165–168 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.13; IR (film): $\tilde{\nu}$ = 2922, 2549, 2190, 1974, 1643, 1521, 1167, 809, 672, 552 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.22–1.31 (m, 1H), 1.66–1.73 (m, 1H), 2.19 (s, 3H), 2.30 (s, 3H), 2.38 (s, 3H), 2.31–2.37 (m, 2H), 2.95–3.02 (m, 1H), 3.86 (td, *J* = 13.4 Hz, 3.7 Hz, 1H), 5.29 (s, 1H), 7.11 (d, *J* = 1.5 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.34 (t), 21.16 (q), 21.55 (q), 21.92 (t), 26.46 (q), 46.99 (t), 126.7 (s), 127.4 (d, 2C), 128.2 (d, 2C), 129.1 (d, 2C), 129.6 (d, 2C), 133.8 (s), 135.7 (s), 136.1 (s), 142.2 (d), 143.8 (s), 146.2 (s), 150.3 (s), 192.3 (s); MS (ESI): *m/z* (%) = 430 $(M+Na)^+$, 275 (28); HR-MS (ESI): *m/z* = 407.1550, calcd. for $C_{24}H_{25}NO_3S$: 407.1555.

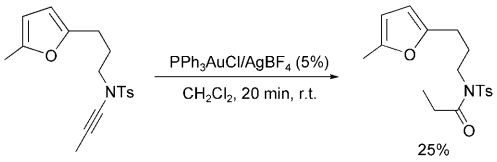
1-[7-Thiophen-3-yl-1-(toluene-4-sulfonyl)-2,3,4,7-tetrahydro-1*H*-[1]pyrindin-6-yl]ethanone (10v)

Yellow solid; mp 180–183 °C; R_f (petroleum ether:ethyl acetate, 2:1) = 0.08; IR (film): $\tilde{\nu}$ = 2926, 1647, 1520, 1361, 1169, 1088, 1049, 831, 784, 731, 671 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.22–1.30 (m, 1H), 1.66–1.72 (m, 1H), 2.23 (s, 3H), 2.25–2.36 (m, 2H), 2.40 (s, 3H), 2.97–3.03 (m, 1H), 3.88 (td, *J* = 13.6 Hz, 3.6 Hz, 1H), 5.50 (s, 1H), 6.77 (dd, *J* = 5.0 Hz, 1.3 Hz, 1H), 7.12 (d, *J* = 1.3 Hz, 1H), 7.13–7.15 (m,



1H), 7.17–7.18 (m, 1H), 7.21 (d, $J=8.5$ Hz, 2H), 7.38 (d, $J=8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta=20.29$ (t), 21.55 (q), 21.90 (t), 26.41 (q), 46.85 (t), 52.87 (d), 122.9 (d), 124.7 (d), 126.4 (s), 126.7 (d), 127.3 (d, 2C), 129.7 (d, 2C), 135.6 (s), 136.5 (s), 142.2 (d), 143.9 (s), 144.9 (s), 149.3 (s), 192.3 (s); MS (ESI): *m/z* (%) = 422 (100) $(M+Na^+)^+$, 400 (35) $(M+1)^+$, 245 (12); HR-MS (ESI): *m/z* = 399.0958, calcd. for $C_{21}H_{21}NO_3S_2$: 399.0963.

4-Methyl-*N*-[3-(5-methylfuran-2-yl)propyl]-*N*-propionylbenzenesulfonamide (11)



Colourless oil; R_f (petroleum ether:ethyl acetate, 8:1) = 0.62; IR (film): $\tilde{\nu}=2923$, 1700, 1350, 1159, 903, 724 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=1.04$ (t, $J=7.2$ Hz, 3H), 1.99–2.12 (m, 2H), 2.25 (s, 3H), 2.44 (s, 3H), 2.56 (q, $J=7.3$ Hz, 2H), 2.64 (t, $J=7.4$ Hz, 2H), 3.83 (t, $J=7.8$ Hz, 2H), 7.32 (d, $J=8.2$ Hz, 2H), 7.76 (d, $J=8.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=8.840$ (q), 13.52 (q), 21.59 (q), 23.45 (t), 28.27 (t), 29.68 (t), 59.04 (t), 105.3 (d), 105.9 (d), 127.5 (d, 2C), 129.8 (d, 2C), 133.7 (s); 143.2 (s), 151.7 (s), 157.8 (s), 180.0 (s); MS (ESI): *m/z* (%) = 350 (24) $(M+1)^+$, 332 (92), 294 (100); HR-MS (APCI): *m/z* = 349.1334, calcd. for $C_{18}H_{23}NO_4S$: 349.1438.

Acknowledgements

Gold salts were generously donated by Umicore AG & Co. KG. T. Bender is grateful for support by the RISE program.

References

[1] For recent reviews, see: a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8604–8605; *Angew. Chem. Int. Ed.* **2006**, 45, 7896–7936; b) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; c) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; d) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; e) N. Bongers, N. Krause, *Angew. Chem.* **2008**, 120, 2208–2211; *Angew. Chem. Int. Ed.* **2008**, 47, 2178–2181; f) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; g) E. Jiménez-Núnez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; h) Z. G. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265.

[2] a) F. Marion, J. Coulomb, C. Courillon, L. Fensterbank, M. Malacria, *Org. Lett.* **2004**, *6*, 1509–1511; b) L. Zhang, S. A. Kozmin, *J. Am. Chem. Soc.* **2004**, *126*, 11806–11807; c) S. Couty, C. Meyer, J. Cossy , *Angew. Chem.* **2006**, *118*, 6878–68882; *Angew. Chem. Int. Ed.* **2006**, *45*, 6726–6730; d) A. S. K. Hashmi, R. Salathé, W. Frey, *Synlett* **2007**, 1763–1766; e) F. Istrate, A. Buzas, I. Dias Jurberg, Y. Odabachian, F. Gagosz, *Org. Lett.* **2008**, *10*, 925–928; f) A. S. K. Hashmi, M. Rudolph, J. W. Bats, W. Frey, F. Rominger, T. Oeser, *Chem. Eur. J.* **2008**, *14*, 6672–6678.

[3] A. S. K. Hashmi, M. Rudolph, J. Huck, W. Frey, J. W. Bats, M. Hamzic, *Angew. Chem.* **2009**, *121*, 5962–5966; *Angew. Chem. Int. Ed.* **2009**, *48*, 5848–5852.

[4] For one other reaction with a phenyl group on the alkyne, see: B. M. Matute, C. Nevado, D. J. Cardenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2003**, *125*, 5757–5766.

[5] For the few gold-catalyzed reactions with sulfur-containing substrates, see: a) A. Arcadi, G. Bianchi, S. Di Giuseppe, F. Marinelli, *Green Chem.* **2003**, *5*, 64–67; b) I. Nakamura, T. Sato, Y. Yamamoto, *Angew. Chem.* **2006**, *118*, 4585–4587; *Angew. Chem. Int. Ed.* **2006**, *45*, 4473–4475; c) N. Morita, N. Krause, *Angew. Chem.* **2006**, *118*,1930–1932; *Angew. Chem. Int. Ed.* **2006**, *45*, 1897–1899; d) L. Peng, X. Zhang, S. Zhang, J. Wang, *J. Org. Chem.* **2007**, *72*, 1192–1197; e) G. Li, L. Zhang, *Angew. Chem.* **2007**, *119*, 5248–5251; *Angew. Chem. Int. Ed.* **2007**, *46*, 5156–5159; f) P. W. Davies, S. J.-C. Albrecht, *Chem. Commun.* **2008**, 238–240.

[6] CCDC 734056 (**5m**), 734057 (**7g**) and 734058 (**10u**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[7] C. N. Oberhuber, P. P. Galn, E. H. Gmez, T. Lauterbach, C. Rodrguez, S. Lopez, C. Bour, A. Roselin, D. J. Creenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2008**, *130*, 269–279.

[8] For a recent review, see: E. Jimenez-Nunez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350.

[9] Recently, a strong argument in favour of the cationic form of the intermediates in noble metal-catalyzed enyne cyclizations came up see : a) G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem.* **2009**, *121*, 2548–2551; *Angew. Chem. Int. Ed.* **2009**, 48, 2510–2513; b) A. Fürstner, L. Morency, *Angew. Chem.* **2008**, *120*, 5108–5111; *Angew. Chem. Int. Ed.* **2008**, *47*, 5030–5033. See also discussion in: c) A. S. K. Hashmi, *Angew. Chem.* **2008**, *120*, 6856–6858; *Angew. Chem. Int. Ed.* **2008**, *47*, 6754–6756.

[10] For representative examples of gold-catalyzed aromatic addition to alkynes and alkenes, see: a) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem.* **2000**, *112*, 2382–2385; *Angew. Chem. Int. Ed.* **2000**, *39*, 2285–2288; b) M. T. Reetz, K. Sommer, *Eur. J. Org. Chem.* **2003**, 3485–3496; c) C. Nieto-Oberhuber, S. Lopez, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179; d) P .Y. Toullec, E. Genin, L. Leseurre, J.-P. Genêt, V. Michelet, *Angew. Chem.* **2006**, *118*,

7587–7590; *Angew. Chem. Int. Ed.* **2006**, *45*, 7427–7430; e) C. H. M. Amijs, C. Ferrer, A. M. Echavarren, *Chem. Commun.* **2007**, 698–700.

[11] a) A. S. K. Hashmi, M. Rudolph, J. P. Weyrauch, M. Wölfle, W. Frey, J. W. Bats, *Angew. Chem.* **2005**, *117*, 2858–2861; *Angew. Chem. Int. Ed.* **2005**, *44*, 2798–2801; b) A. S. K. Hashmi, M. Rudolph, H.-U. Siehl, M. Tanaka, J. W. Bats, W. Frey, *Chem. Eur. J.* **2008**, *14*, 3703–3708.

[12] A. S. K. Hashmi, M. Bührle, R. Salathé, J. W. Bats, *Adv. Synth. Catal.* **2008**, *350*, 2059–2064.

[13] D. M. Mampreian, A. H. Hoveyda. *Org. Lett.* **2004**, 6, 2829–2832.

[14] B. Witulski, T. Stengel, *Angew. Chem.* **1998**, *110*, 495–498; *Angew. Chem. Int. Ed.* **1998**, *37*, 489–492.

[15] A. S. K. Hashmi, F. Ata, E. Kurpejovic, J. Huck, M. Rudolph, *Top. Catal.* **2007**, *44*, 245–251.

[16] A. S. K. Hashmi, M. Rudolph, J. W. Bats, W. Frey, F. Rominger, T. Oeser, *Chem. Eur. J.* **2008**, *14*, 6672–6678.

