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AN EFFICIENT SYNTHESIS OF (ARYL)(4-(2-(ARYLETHYNYL)-PHENYL)-1*H*-PYRROL-3-YL)METHANONE FROM THE REACTION OF (*E*)-1-ARYL-3-(2-(ARYLETHYNYL)PHENYL)PROP-2-EN-1-ONE AND *p*-TOLUENESULFONYLMETHYL ISOCYANIDE

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Abstract – Herein we reported a facile approach to synthesize pyrrole derivatives under mild conditions. The reaction proceeds cycloaddition reactions between (*E*)-1-aryl-3-(2-(arylethynyl)phenyl)prop-2-en-1-one and commercially available *p*-toluenesulfonylmethyl isocyanide. Although the triple bond in the substrate was not involved in the reaction process, this work still provided a method for the synthesis of pyrrole derivatives.

INTRODUCTION

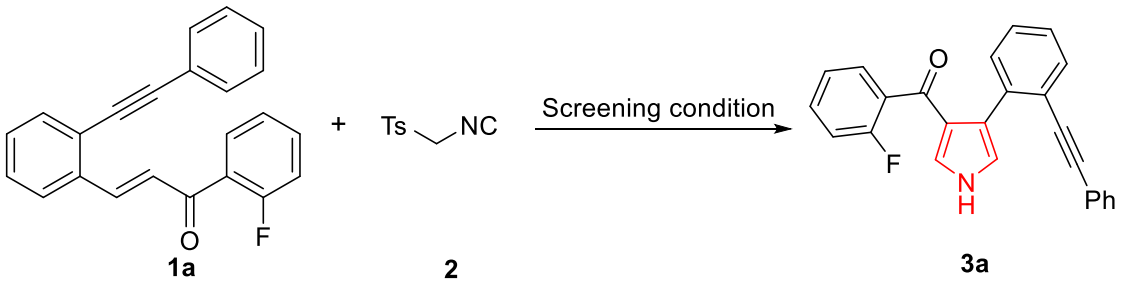
As the five-membered *N*-containing heterocyclic scaffolds, pyrroles and their derivatives show the important biological and pharmaceutical activities, wide applying in medicinal chemistry,[1] material science,[2] and natural products,[3] which are also the mother nucleus of numerous natural products, such as chlorophyll, vitamin B_{12}, heme and several cytochrome enzymes.[4]

p-Toluenesulfonylmethyl isocyanide (TosMIC), a useful building block, has been widely used in organic synthesis, especially for the construction of pyrrole derivatives.[5] In addition, it was found that (*E*)-1-aryl-3-(2-(arylethynyl)phenyl)prop-2-en-1-one derivatives were gained popularity as versatile building blocks and have been used for access to various compounds such as 3-haloindene derivatives,[6] ketonitrones,[7] functionalized indenes,[8] benzo[*b*]fluorenes,[9] pyrazole derivatives,[10] 1*H*-benzo[*g*]indazoles and naphtho[2,1-*d*]isoxazoles,[11] methylenecyclopentane derivatives,[12] anti-indeno[1,2-*d*]pyridazines,[13] and so on. In 2011, Wu used (*E*)-2-alkynylphenylchalcone and 2-isocyanoacetate for the synthesis of tetrahydroindeno[2,1-*b*]pyrroles.[14] In 2015, the similar reaction was reported by Xu to give benz[*e*]indole and spiro[indene-1,3′-pyrrole] derivatives.[15] Recently, we have been committed to the synthesis of

heterocyclic compounds using alkyne substrates.[16] Herein, we would like to provide the pyrrole derivatives from the reaction of (*E*)-1-aryl-3-(2-(arylethynyl)phenyl)prop-2-en-1-one and *p*-toluene-sul fonylmethyl isocyanide under mild condition.

RESULTS AND DISCUSSION

In order to achieve our purpose, the (*E*)-1-(2-fluorophenyl)-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one **1a**, and *p*-toluenesulfonylmethyl isocyanide **2** were chosen as the starting materials to screen the reaction conditions (Scheme 1). First, when the mixture of the **1a** and **2** was reacted in MeCN in the presence of 0.4 equiv of ^{t}BuOK under 80 ^{o}C about 12 h, the target compound **3a** was effectively obtained in 33% yield (Table 1, entry 1). This result encouraged us to further explore the reaction conditions. Then, the others bases, including Et_3N, KOH, Cs_2CO_3, and DBU were incorporated in the model reaction, the product **3a** was gained with the different yields, respectively (Table 1, entries 2-5). However, the best result was found as DBU was used in the reaction. The different solvents, such as EtOH, THF, DMF, and DMSO were also tested in the synthesis of **3a**, and the results showed the inferior yeilds were gained compared to the reaction in MeCN (Table 1, entries 6-9). Subsequently, we investigated the usage amount of DBU in the reaction. We found when the loading amount of DBU was 0.05 mmol, the yield of **3a** decreased rapidly, however when the dosage of DBU was increased to 0.2 mmol, the yield of the reaction was improved distinctly, but more dosage of DBU had little effect on the reaction (Table 1, entries 10-12). The reaction time had the great influence on the reaction. When the reaction time was extended to 18 h, the highest yield could be obtained (Table 1, entry 13). However, the further extension of the reaction time had little effect on the reaction (Table 1, entry 14). Finally, the screening of the reaction temperature showed that the reaction could not operate at lower temperature. As the temperature was decreased to 60 °C and 40 °C, the obtained yields were only 31% and trace, respectively (Table 1, entries 15, 16). Moreover, we also found that the yield of the reaction decreased when the reaction temperature was raised (Table 1, entries 17, 18). The results were summarized in Table 1.



Scheme 1. The model reaction of **1a** and **2**

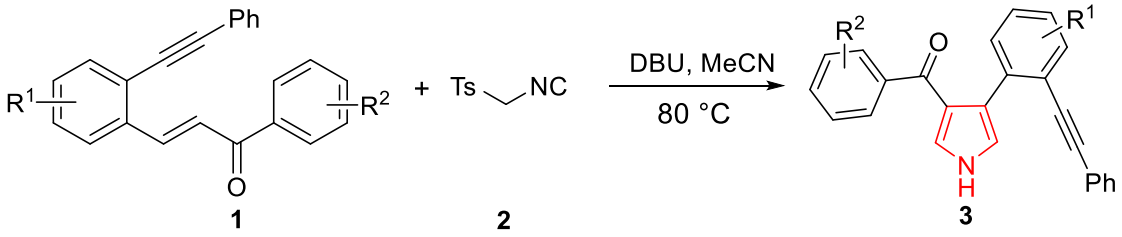
Table 1. The reaction results of model reaction

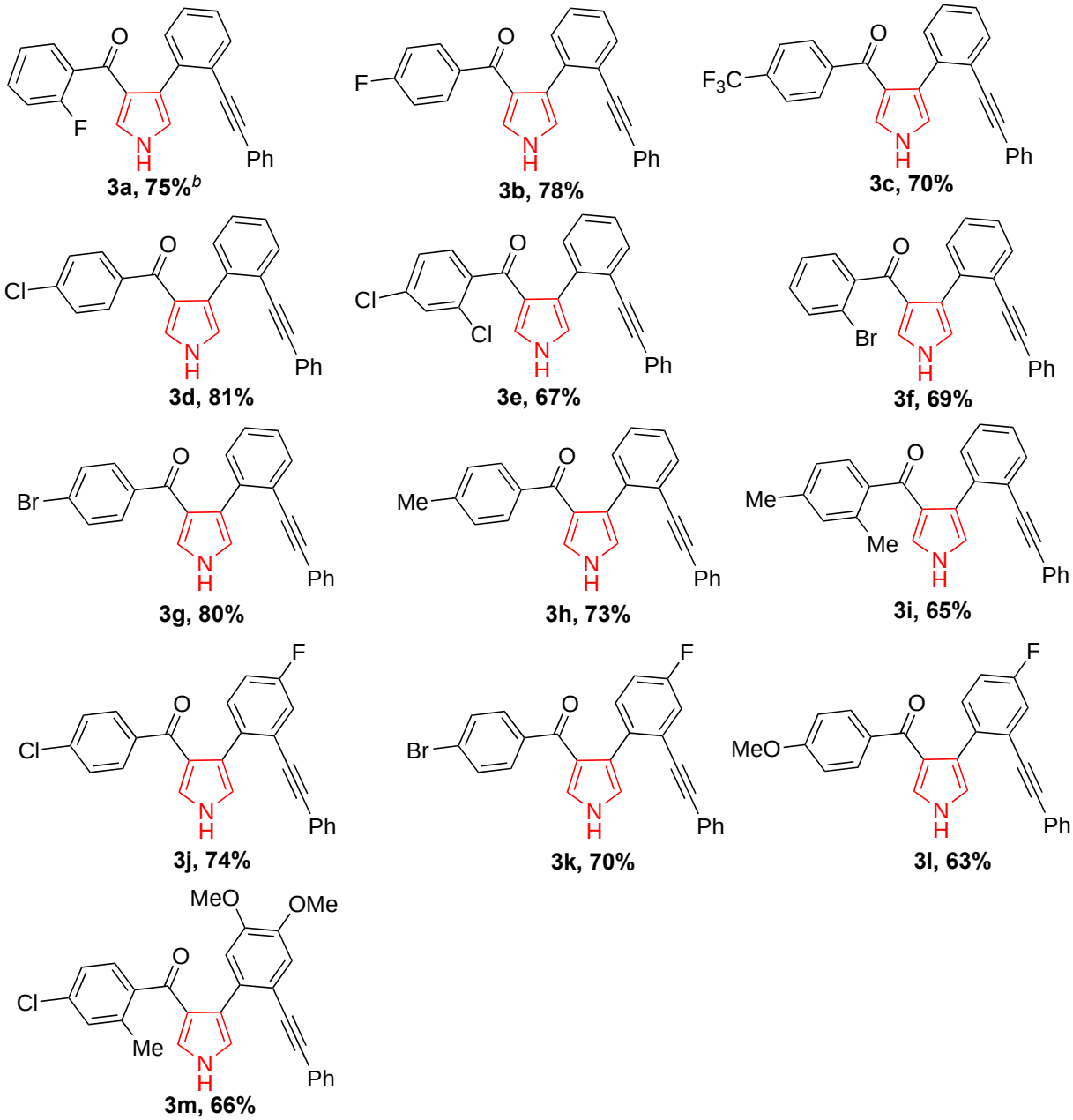
Entry	Solvent	Base (mmol)	Temp (^{o}C)	Yield (%)[b]
1	MeCN	^{t}BuOK (0.1)	80	33
2	MeCN	Et_3N (0.1)	80	45
3	MeCN	KOH (0.1)	80	24
4	MeCN	Cs_2CO_3 (0.1)	80	37
5	MeCN	DBU (0.1)	80	58
6	EtOH	DBU (0.1)	80	37
7	THF	DBU (0.1)	80	40
8	DMF	DBU (0.1)	80	36
9	DMSO	DBU (0.1)	80	39
10	MeCN	DBU (0.05)	80	15
11	MeCN	DBU (0.2)	80	65
12	MeCN	DBU (0.3)	80	61
13	MeCN	DBU (0.2)	80	75[c]
14	MeCN	DBU (0.2)	80	70[d]
15	MeCN	DBU (0.2)	60	31
16	MeCN	DBU (0.2)	40	trace
17	MeCN	DBU (0.2)	90	71
18	MeCN	DBU (0.2)	100	62

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), solvent (2.0 mL), [b] Isolated yield, [c] Time, 18 h, [c] Time, 24 h.

With the optimal reaction conditions in hand, the substrate scope of the (*E*)-1-aryl-3-(2-(arylethynyl)phenyl)prop-2-en-1-one was investigated to synthesize pyrrole derivatives. It was found when the (*E*)-1-aryl-3-(2-(arylethynyl)phenyl)prop-2-en-1-one with the strong electron-withdrawing group (such as F-, CF_3-) was used in the reaction, the corresponding products **3a**-**3c** were obtained with good yields (75%, 78%, and 70%), respectively. When there were other halogen atoms (such as Cl and Br) on the substrate **1**, the reactions were also carried out smoothly with products **3d**-**3g** in excellent yields (67-81%). The electron-donating group methyl located in substrate **1** to give **3h** and **3i** in good yield, which showed that the electronic properties of the substituents had little effect on the reaction. In addition, it was also found when the (*E*)-1-aryl-3-(2-(arylethynyl)phenyl)prop-2-en-1-one with the multiple substituents, the reaction performed very well, obtained target products **3j**-**3m** in good yields. The results were listed in Table 2.

Table 2. Synthesis of (aryl)(4-(2-(arylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone





[a] Conditions: **1** (0.2 mmol), **2** (0.2 mmol), DBU (1 eq.), MeCN (2.0 mL), 80 °C, 18 h; [b] Isolated yield.

The structure of **3** was determined by ^{1}H, ^{13}C NMR, and high-resolution mass spectrometry (HRMS) analysis. And crucially, the X-ray diffraction data of **3e** were gained, which additionally confirmed the product structure. The molecular perspective was shown in Figure **1**.

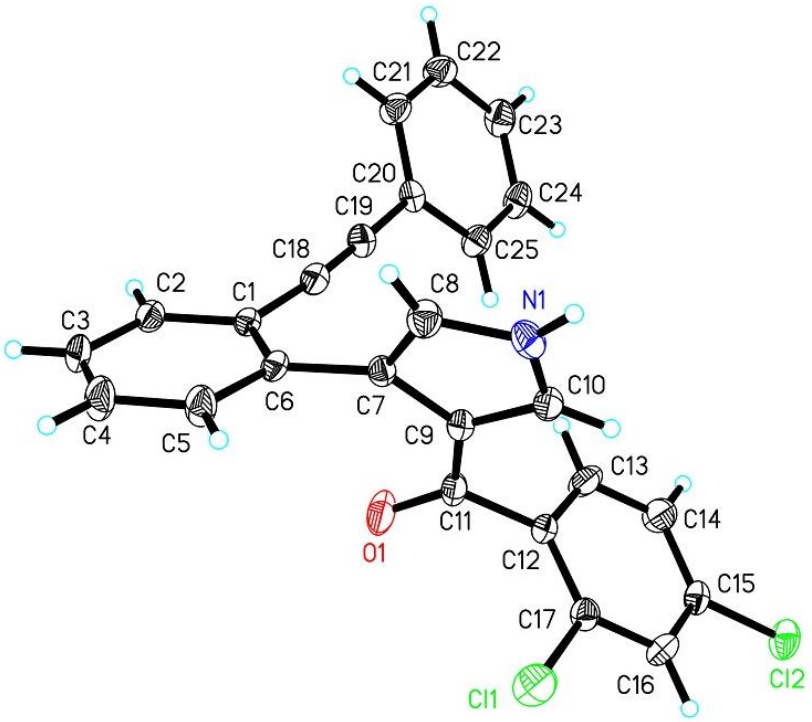
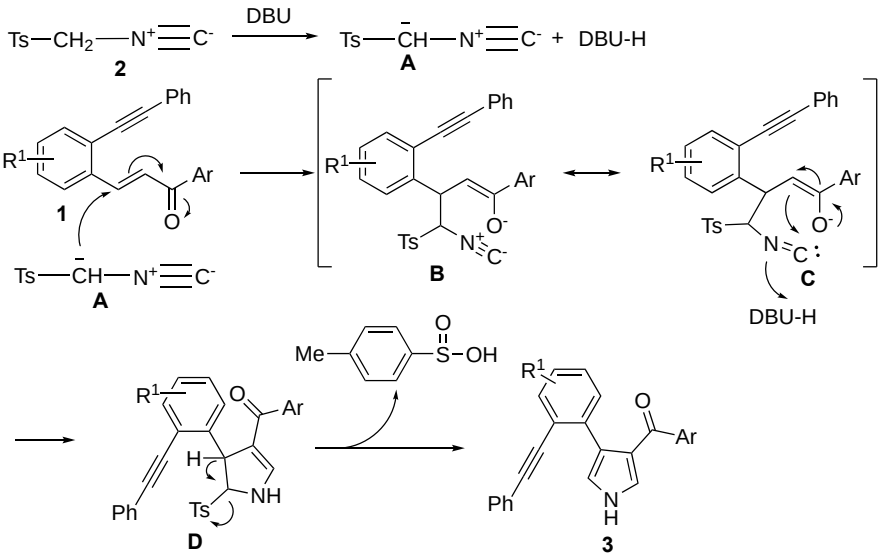


Figure 1. The crystal structure of **3e** (CCDC: 2161393)

The possible reaction mechanism was shown in Scheme **2**. At first, under the promotion of DBU, the Michael addition reaction took place between **1** and TosMIC **2** to give the intermediate **B**, which resonance formula was structure C. Subsequently, **C** underwent intramolecular cyclization reaction to form intermediate **D**. At last, **D** removed 4-methylbenzenesulfinic acid to give product **3**.



Scheme 2. The possible reaction mechanism of product **3**

In conclusion, an efficient protocol for the synthesis of pyrrole derivatives form various (*E*)-1-aryl-3-(2-(arylethynyl)phenyl)prop-2-en-1-one and *p*-toluenesulfonylmethyl isocyanide via intermolecular cascade reaction was developed in this research. Although the triple bond in the substrate **1** was not involved in the reaction, this study still provided a simple method for the synthesis of pyrrole derivatives.

EXPERIMENTAL

1. General Information

Unless otherwise special indicated, all the reagents were purchased from commercial supplies unless otherwise stated. All the solvents were used as anhydrous treatment. Melting points were determined on XT-5 microscopic melting-point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained from solution in $CDCl_3$ (DMSO-d_6) with Me_4Si as internal standard using a Bruker-400 spectrometer operating at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). The HRMS were obtained on a Bruker micrOTOF-Q 134 instrument; X-ray diffraction was recorded on a Siemens P4 or Simart-1000 diffractometer. Copies of the ^{1}H NMR and ^{13}C NMR spectra are provided in the Supporting Information. CCDC 2161393 (**3e**) contains 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.

2. General Procedure for the Synthesis of product 3

To a 10 mL Schlenk tube, the mixture of (*E*)-1-aryl-3-(2-(arylethynyl)phenyl)prop-2-en-1-one **1** (0.2 mmol), *p*-toluenesulfonylmethyl isocyanide **2** (0.2 mmol), DBU (0.2 mmol) and MeCN (2 mL) were added. The system was stirred at 80 ^{o}C using an oil bath for 18 h (monitored by TLC), and then the reaction was quenched by saturated brine (5 mL) and extracted with EtOAc twice (2 x 6 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. The concentrated residue was purified by column chromatography over silica gel using petroleum ether/EtOAc to afford the desired product **3**.

(2-Fluorophenyl)(4-(2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3a)

White solid, mp 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.47 – 7.41 (m, 2H), 7.38 – 7.35 (m, 3H), 7.31 – 7.22 (m, 6H), 7.15 (td, J = 7.6, 2.0 Hz, 1H), 6.92 (t, J = 9.6 Hz, 1H), 6.85 (t, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz), δ 188.3, 159.9 (d, J_{C-F} = 251.0 Hz), 137.3, 132.1, 132.0, 131.5, 130.9 (d, J_{C-F} = 2.4 Hz), 130.3, 128.7 (d, J_{C-F} = 13.8 Hz), 128.2, 128.0, 127.9, 127.3, 126.5, 124.5, 123.9, 123.7, 123.4 (d, J_{C-F} = 3.2 Hz), 123.0, 120.2, 115.8 (d, J_{C-F} = 21.9 Hz), 91.9, 89.9; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{16}FNNaO$: 388.1114; found: 388.1120.

(4-Fluorophenyl)(4-(2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3b)

White solid, mp 177-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.76 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.30 (m, 8H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 6.89 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$)δ 190.5, 164.8 (d, J_{C-F} = 251.8 Hz), 137.4, 135.5 (d, J_{C-F} = 2.6 Hz), 132.7, 132.2 (d, J_{C-F} = 8.9 Hz), 131.5, 130.1, 128.3, 128.2, 128.0, 126.5, 125.7, 124.9, 123.6, 123.2, 122.6, 119.8, 114.7 (d, J_{C-F} = 21.4 Hz), 91.9, 89.9; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{16}FNONa$: 388.1114; found: 388.1122.

(4-(2-(Phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)(4-(trifluoromethyl)phenyl)methanone (3c)

Yellow solid, mp 171-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.71 (t, *J* = 1.6 Hz, 1H), 7.64 (d, 1H), 7.45 (dd, *J* = 8.4, 5.6 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.29 – 7.20 (m, 7H), 7.10 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.96 (t, *J* = 1.6 Hz, 1H), 6.93 (td, *J* = 8.4, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 162.2 (d, J_{C-F} = 247.8 Hz), 140.7, 139.6 (d, J_{C-F} = 8.9 Hz), 134.3 (d, J_{C-F} = 8.7 Hz), 133.9, 131.5, 131.3, 129.7, 129.2, 128.2, 128.1, 127.6, 126.3, 124.1 (d, J_{C-F} = 1.9 Hz), 123.2, 122.8, 120.1, 118.8, (d, J_{C-F} = 3.1 Hz), 116.9 (d, J_{C-F} = 22.3 Hz), 113.8 (d, J_{C-F} = 21.7 Hz), 91.5, 88.9. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{16}F_3NONa$: 438.1082; found: 438.1078.

(4-Chlorophenyl)(4-(2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3d)

White solid, mp 151-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.49 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.33 – 7.29 (m, 6H), 7.24 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.05 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 137.7, 137.5, 137.1, 132.6, 131.5, 131.1, 130.1, 128.2, 128.0, 127.9, 126.6, 125.3, 125.1, 123.6, 123.4, 122.6, 119.5, 91.9, 89.9; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{16}ClNONa$: 404.0818; found: 404.0813.

(2,4-Dichlorophenyl)(4-(2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3e)

Yellow solid, mp 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.46 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.40 – 7.33 (m, 6H), 7.29 – 7.21 (m, 3H), 7.06 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.01 (t, *J* = 2.4 Hz, 1H); ^{13}CNMR (101 MHz, $CDCl_3$) δ 190.2, 166.1, 163.6, 137.3, 135.5, 132.6, 132.2, 132.1, 131.5, 130.1, 128.28, 128.0, 126.5, 125.3, 125.0, 123.6, 122.6, 119.6, 114.7, 114.5, 91.9, 89.9; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{15}Cl_2NONa$: 438.0428; found: 438.0422.

(2-Bromophenyl)(4-(2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3f)

White solid, mp 168-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.23 (m, 7H), 7.20 – 7.14 (m, 3H), 7.08 (s, 1H), 6.95 (s, 1H); ^{13}C NMR (100 MHz,) δ 190.5, 141.9, 136.9, 132.9, 132.0, 131.6, 130.7, 130.5, 129.6, 128.3, 128.0, 127.8, 127.6, 126.6, 126.5, 124.6, 123.8, 123.5, 122.9, 120.5, 119.9, 91.8, 90.1; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{16}BrNONa$: 448.0313; found: 448.1320.

(4-Bromophenyl)(4-(2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3g)

White solid, mp 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.38 – 7.34 (m, 3H), 7.30 – 7.24 (m, 6H), 7.24 – 7.18 (m, 2H), 6.92 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 138.0, 137.3, 132.6, 131.4, 131.2, 130.9, 130.0, 128.3, 128.2, 128.0, 126.5, 126.4, 126.2, 124.8, 123.4, 122.5, 122.7, 122.5, 120.0, 91.8, 90.0; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{16}BrNONa$: 448.0313; found: 448.0316.

(4-(2-(Phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)(*p*-tolyl)methanone (3h)

White solid, mp 156-158 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.65 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.45 (dd, *J* = 7.6 Hz, 1H), 7.34 – 7.28 (m, 6H), 7.25 – 7.21 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 2.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 141.8, 138.7, 137.1, 132.6, 131.5, 130.6, 129.7, 128.8, 128.7, 126.5, 126.4, 124.1, 123.2, 122.6, 122.1, 120.7, 91.4, 90.7, 21.5; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{19}NNaO$: 384.1364; found: 384.1376.

(2,4-Dimethylphenyl)(4-(2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3i)

White solid, mp 203-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.51 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.38 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.31 – 7.27 (m, 5H), 7.20 (td, *J* = 7.6, 1.6 Hz, 1H), 7.05 (t, *J* = 2.4 Hz, 1H), 6.97 (s, 1H), 6.93 (t, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 2.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz), δ 193.1, 139.7, 137.4, 137.2, 137.1, 132.3, 131.6, 131.5, 130.4, 129.8, 128.18, 127.9, 126.7, 126.4, 125.2, 125.0, 124.8, 123.9, 122.7, 119.9, 91.6, 90.2, 21.3, 20.1; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{21}NONa$: 398.1521; found: 398.1533.

(4-Chlorophenyl)(4-(4-fluoro-2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3j)

White solid, mp 169-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.71 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 14.4, 8.4 Hz, 1H), 7.30 – 7.26 (m, 6H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.96 (t, *J* = 2.0 Hz, 1H), 6.93 (td, *J* = 7.6, 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 162.4 (d, J_{C-F} = 289.0 Hz), 140.7, 136.5, 135.2, 134.3 (d, J_{C-F} = 8.6 Hz), 133.8, 131.5, 131.4, 129.8, 129.2, 128.2, 128.1, 127.6, 125.6, 124.4 (d, J_{C-F} = 4.9 Hz), 123.3 (d, J_{C-F} = 11.3 Hz), 119.7, 117.1, 116.9, 113.9 (d, J_{C-F} = 21.8 Hz), 91.5, 88.9; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{15}ClFNONa$: 422.0724; found: 422.0732.

(4-Bromophenyl)(4-(4-fluoro-2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3k)

White solid, mp 181-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 10.4, 8.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.22 (m, 6H), 7.09 (dd, *J* = 9.6, 2.8 Hz, 1H), 7.00 (t, *J* = 1.6 Hz, 1H), 6.94 (td, *J* = 8.4, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 162.2 (d, J_{C-F} = 247.7 Hz), 139.6 (d, J_{C-F} = 8.8 Hz), 137.8, 134.4 (d, J_{C-F} = 8.7 Hz), 131.4, 131.2, 131.0, 128.2, 128.1, 126.6, 125.8, 124.1, 123.3, 123.0, 120.0, 118.8, 117.0, 116.8, 113.8 (d, J_{C-F} = 21.8 Hz), 91.5, 88.9; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{15}BrFNNaO$: 466.0219; found: 466.0225.

(4-(4-Fluoro-2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)(4-methoxyphenyl)methanone (3l)

Yellow solid, mp 190-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.35 – 7.27 (m, 7H), 7.22 (dd, *J* = 9.6, 2.8 Hz, 1H), 7.04 (t, *J* = 2.4 Hz, 1H), 7.01 (td, *J* = 8.4, 2.8 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 161.2 (d, J_{C-F} = 259.1 Hz), 138.4, 135.3, 134.8 (d, J_{C-F} = 6.8 Hz), 133.6, 131.8 (d, J_{C-F} = 31.8 Hz), 128.2, 124.8, 124.1, 123.7, 123.3, 119.3, 119.9 (d, J_{C-F} = 22.9 Hz), 115.4 (d, J_{C-F} = 21.1 Hz), 113.0, 92.5, 89.2, 55.4; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{18}FNO_2Na$: 418.1219; found: 418.1222.

(4-Chloro-2-methylphenyl)(4-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-1*H*-pyrrol-3-yl)methanone (3m)

Yellow solid, mp 152-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.69 (t, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.33 – 7.27 (m, 5H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 2.0 Hz, 1H), 7.00 (s, 1H), 6.85 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 149.1, 147.5, 141.0, 133.8, 131.4, 130.8, 129.9, 129.2, 128.3, 127.9, 127.6, 125.8, 124.8, 123.7, 123.0, 119.7, 115.0, 114.7, 113.2, 90.5, 90.0, 56.0; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{20}ClNO_3Na$: 464.1029; found: 464.1036.

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