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Marie Betou, a Raphaël J. Durand, a Antoine Sallustrau, a Claire Gousset, a Erwann Le Coz, a Yann R. Leroux, a Loïc Toupet, b Elzbieta Trzop, b Thierry Roisnel, a Yann Trolez* a

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Abstract: The reactivity of functionalized ynamides and arylamines with tetracyanoethylene at room temperature has been evaluated. In most cases, the corresponding 1,1,4,4-tetracyanobutadienes (TCBDs) have been obtained in good to excellent yields, following a sequence of [2+2]cycloaddition and [2+2]retroelectrocyclization. The influence of diverse functional groups on the yield of the reaction has been investigated, in particular concerning multiple ynamides. These TCBDs have been characterized by various spectroscopic techniques, electrochemistry and X-Ray diffraction for some of them.

Introduction

The synthesis of 1,1,4,4-tetracyanobutadienes (TCBDs) has met an increasing interest over the last years.[1] Actually, the properties of such molecules could be of particular interest given their exceptional electron-accepting ability and their intense non-linear absorption in some cases.[2] Moreover, their ease of synthesis could also explain their recent rise. Indeed, a certain number of research groups have shown that some organic alkynes activated by an electron-donating group (EDG) could readily react with tetracyanoethylene (TCNE) according to a sequence of [2+2]cycloaddition-retroelectrocyclization (CA-RE) to afford the corresponding TCBDs in variable yields.[3, 4] In some examples (p-aniline, azulene, heteroazulene and rich porphyrin substituted alkynes), there is no need for heating the reaction or using an excess of TCNE to reach yields over 90%.[4] Therefore, this type of
reaction seems to meet the requirements of the “click” reactions as defined by Sharpless and coworkers in 2001.\[5\]

However, this reaction is very dependent on the nature of the EDG. There is a right balance to find between using an EDG which is rich enough to make the CC triple bond react with TCNE, and an EDG which is too rich and induces an over-reaction of the alkyne with the TCBD itself, producing thus a complex mixture with the formation of multiple oligomers and / or the desired TCBD in bad yield. Following this idea, we recently reported that ynamides\[6\] could be incorporated in the list of compounds which readily react with TCNE in generally high yields, the nitrogen playing the role of the EDG (scheme 1).\[7\]

We now report on the extension of the scope of the reaction with differently functionalized ynamides, including unsaturated groups that could potentially also react with TCBD or the formed TCBD.\[8\] Moreover, systems bearing two ynamide functions conjugated to each other were investigated. This study also conducted us to investigate the reactivity of aromatic ynamines.

![Scheme 1. Reaction between an ynamide and TCNE.](image)

### Results and discussion

We first evaluated the influence of the different three groups of an ynamide (EWG, R$_1$ and R$_2$ in Table 1). All the experiments used 1 equivalent of TCNE and were carried out in dichloromethane at room temperature during 16 hours (unless otherwise stated).

We started by evaluating the influence of aromatic and heteroaromatic moieties conjugated to the triple bond (R$_1$ in table 1). When the phenyl was used, ynamide 1,\[9\] which can be considered in this study as a model compound, allowed for the formation of the corresponding TCBD 2 in 98% yield (table 1, entry 1) as already reported. The phenyl can be substituted by a naphthyl (ynamide 3) or a p-fluorophenyl group (ynamide 23)\[10\] without any dramatic effect on the yield of the reaction (entries 2 and 12). Heteroaromatic substituents can also be used since furanyl (ynamide 5) and thiophene (ynamide 19)\[10\] gave the corresponding TCBDs 6 and 20 in 97% and 87% yields respectively (entries 3 and 10).

Surprisingly, when an anthracenyl substituted in 9-position (ynamide 7) was reacted, no TCBD could be obtained (entry 4). Only the starting material was recovered. No other side-reaction (such as a Diels-Alder cycloaddition) was observed. The rational for such a poor reactivity might come from steric hindrance of protons located in 1 and 8-positions that "protect" the triple bond.

As already observed, the nature of the EWG does not seem to have an influence since replacing the tosyl group by a Boc group (ynamide 21)\[11\] led to TCBD 22 quantitatively (entry 11).
We also evaluated the influence of the group linked to the nitrogen (R₂ in table 1). When using a phenyl group (compound 9) instead of benzyl group, the reaction was completely inhibited and the corresponding TCBD 10 was not obtained (entry 5). This observation could be explained by a partial delocalization of the electron doublet of the nitrogen over this phenyl ring, which makes it less available to enrich the CC triple bond. In this case, we thus deduced that the triple bond was not electron-rich enough to react with TCNE. This group could also be replaced by an allyl function (ynamide 11) without any detrimental effect (formation of TCBD 12 in 94% yield, entry 6). It is noteworthy that there was no further cycloaddition involving the allylic double bond and the TCBD group. One might have anticipated that a Diels-Alder reaction was possible as observed in other similar compounds.[8,13] This system is probably too strained to allow for any further reactions,[14] at least at room temperature. This reaction is also compatible with a propargylic group (ynamide 13) since the corresponding TCBD 14 was obtained in 64% yield (entry 7). Contrary to what was observed with the allylic group, a significant decrease of the yield was observed. Nevertheless, the conversion could be improved to 91% by stirring the reaction mixture during 58 hours instead of the standard 16 hours. Therefore, a propargylic group does not inhibit the reaction but only slows it down. No further reaction with the terminal triple bond was observed, and as one could have anticipated, the selectivity between the two CC triple bonds present in ynamide 13 is total.

Then, we tested the influence of a non-aromatic system linked to the triple bond on the CA-RE sequence (R₁ in table 1). After observing that a propargylic group could slow down the reaction, we wanted to evaluate the influence of a CC triple bond conjugated to the CC triple bond of an ynamide. Surprisingly, when a phenylacetylene unit was conjugated (ynamide 15), the reaction was completely inhibited and the corresponding TCBD 16 has never been obtained: 95% of the starting material was recovered after purification (entry 8). Heating the reaction mixture did not change the result. A possible reason for this non-reactivity could be that electron density of the CC triple bond linked to the nitrogen might be decreased because of the conjugation with the second triple bond. On the contrary, when a vinyl group was conjugated (ynamide 17), the reaction worked perfectly and gave the expected TCBD 18 in 94% yield (entry 9). Once again, the presence of the double bond did not induce the formation of by-products or over-reactions. These figures show that the presence of CC double bonds is not detrimental to the formation of TCBDs, contrary to conjugated CC triple bonds. A cyclopropyl group (ynamide 25) could also be used to lead to the corresponding TCBD 26 in 86% yield (entry 13).

**Table 1.** Influence of the different substituents on the reaction of ynamides with TCNE.

<table>
<thead>
<tr>
<th>entry</th>
<th>ynamide</th>
<th>EWG</th>
<th>R₁</th>
<th>R₂</th>
<th>TCBD</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Ts</td>
<td>Ph</td>
<td>Bn</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>Ts</td>
<td>naphtalen-2-yl</td>
<td>Bn</td>
<td>4</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>Ts</td>
<td>furan-2-yl</td>
<td>Bn</td>
<td>6</td>
<td>97</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>Ts</td>
<td>anthracen-9-yl</td>
<td>Bn</td>
<td>8</td>
<td>0\textsuperscript{a}</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>Ts</td>
<td>Ph</td>
<td>Ph</td>
<td>10</td>
<td>0\textsuperscript{a}</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>Ts</td>
<td>Ph</td>
<td>allyl</td>
<td>12</td>
<td>94</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>Ts</td>
<td>Ph</td>
<td>propargyl</td>
<td>14</td>
<td>64\textsuperscript{b}</td>
</tr>
<tr>
<td>8</td>
<td>15</td>
<td>Ts</td>
<td>thiophen-2-yl</td>
<td>Bn</td>
<td>16</td>
<td>0\textsuperscript{a}</td>
</tr>
<tr>
<td>9</td>
<td>17</td>
<td>Ts</td>
<td></td>
<td>Bn</td>
<td>18</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>19</td>
<td>Ts</td>
<td>p-fluorophenyl</td>
<td>Bn</td>
<td>20</td>
<td>87</td>
</tr>
<tr>
<td>11</td>
<td>21</td>
<td>Boc</td>
<td></td>
<td>Bn</td>
<td>22</td>
<td>99</td>
</tr>
<tr>
<td>12</td>
<td>23</td>
<td>Ts</td>
<td>cyclopropyl</td>
<td>Bn</td>
<td>24</td>
<td>99</td>
</tr>
<tr>
<td>13</td>
<td>25</td>
<td>Ts</td>
<td></td>
<td>Bn</td>
<td>26</td>
<td>86</td>
</tr>
</tbody>
</table>

\textsuperscript{a}No conversion, the starting material was recovered. \textsuperscript{b}When the solution was stirred during 58 h instead of 16 h, the yield was increased to 91%.

Taking into account that a phenyl group directly linked to the nitrogen of an ynamide completely inhibits the reaction with TCNE, we wondered whether similar compounds without EWG but only aromatic groups could react. For this purpose, three compounds were investigated (Scheme 2). The first one was the acridinone derivative 27.\textsuperscript{[17]} No reaction was observed in this case. The electronic doublet of the nitrogen is probably too delocalized over the aromatic rings rather than the CC triple bond so that it is not reactive enough. The presence of the ketone in addition to aromatic systems conjugated with the nitrogen is probably detrimental to the reaction. This is the reason why another similar compound was tested without this ketone, namely the carbazole ynamine 29.\textsuperscript{[18]} The corresponding TCBD 30 was obtained in a very good yield of 83%. This experiment completes the observation recently made by Kato and collaborators that carbazole is also a good activating group for initiating CA-RE with TCNE.\textsuperscript{[3]} Similarly the indole ynamine 31\textsuperscript{[19]} was also reacted and provided TCBD 32 in 59% yield. Concerning the formation of both TCBDs 30 and 32, no by-products were isolated. The yield is therefore significantly lower than with ynamides, even though it is important to note that no optimisation of these reactions was attempted. Nevertheless, these last two experiments confirm that arylated ynamines can also provide TCBDs in good yields,\textsuperscript{[20]} contrary to alkylated ynamines that probably over-react with TCNE to lead to a mixture of numerous products in low yields.\textsuperscript{[7]} This observation opens new prospects in the field of optoelectronics for this reaction since compounds 30 and 32 both absorb light in the visible range (Figure 2).
It is noteworthy to notice that 7,7,8,8-tetracyanoquinodimethane (TCNQ) can also be a good reactant for CA-RE with some activated alkynes, although not as reactive as TCNE.\textsuperscript{3c,Ad,21} We tested the reactivity of this compound with someynamides orynamines described in this paper, but we never observed the expected reactivity, neither at room temperature nor at higher temperature. The majority of the starting material was recovered. Consequently, we conclude that namides are able to react with TCNE but not TCNQ.

TCBDs 4, 6, 14, 18, 20, 24, 26 and 30 were characterized by X-ray diffraction (Figure 1), additionally to NMR spectroscopy and high-resolution mass spectrometry. As already observed for other TCBDs, the two dicyanovinyls are not in the same plane. The torsion angle measured for the first seven TCBDs is below 90° (between 60° and 86°) as usually observed for TCBDs whereas for compound 30 it is over 90° (136°). This is probably due to steric hindrance that precludes the TCBD moiety to stand in s-cis conformation. The orientation of the unsaturated group (R\textsubscript{1} in Table 1) linked to the TCBD group differs from one another, depending on their nature. In the case of naphtyl, phenyl fluoro phenyl and carbazole groups (compounds 4, 14, 24 and 30 respectively), the torsion angle between the dicyanovinyl and the aromatic group is comprised between 43 and 63°. In these cases, this observation means that the aromatic groups are fairly conjugated to the TCBD, which can be explained by steric hindrance. On the contrary, in the case of the furanyl, vinyl and thiophenyl groups (compounds 6, 18 and 20), the torsion angle is comprised between 10° and 20°, meaning that these groups are much more conjugated to the TCBD. This can be explained by their geometrical nature that allows for a less congested conformation. Moreover, an intramolecular π-stacking is observed between the tosyl group and the aromatic group for naphtyl 4 and for thiophenyl 20. The distance between the tosyl and the aromatic group is 3.4 and 3.5 Å respectively. Intermolecularly, some recurrent interactions can be observed. Numerous N-H bond between nitriles and aromatic or benzylic protons are at stake. Tosyl groups also participate to interactions with O-H bonds between oxygens of the sulfonamide function and aromatic protons. In only two cases dipole-dipole interactions can be observed between TCBDs in compounds 4 and 20. Intermolecular π-stacking could not been evidenced, probably because of a too important steric congestion.
In order to evaluate the possibility to perform multiple TCNE additions on the same molecule, we reacted conjugated bis-ynamides with two equivalents of TCNE in the same conditions as previously described (Scheme 3). We started with mono-phenyl bis-ynamide 33 which was reacted overnight at room temperature with two equivalents of TCNE. The major product obtained was the mono-adduct 34 in 79% yield. Trace amount of the bis-adduct was observed by $^1$H NMR spectroscopy. The first addition of TCNE probably deactivates the second CC triple bond because of the strong electron-withdrawing properties of the TCBD moiety. Therefore, the second ynamide function was much less reactive. The same reaction was tested with bis-ynamide 35 containing a thiophene unit instead of the phenyl group. In that case, the mono-adduct 36 was exclusively formed in 97% yield, despite the presence of two equivalents of TCNE. The same phenomenon as with bis-ynamide 33 is at stake and is even reinforced by the fact that a thiophene is a better conducting unit than a phenyl so that the effect of the presence of one TCBD on the second triple bond is much stronger. This deactivation of the second conjugated triple bond is in major contrast with what has been observed with other good activating groups,^{4b,4c,23} except with porphyrins where such a behavior has also been observed.$^{4d}$ On the contrary, when using bis-ynamide 37 containing a triphenylamine spacer, the only isolated product was bis-adduct 38 (92% yield). It can be explained by the fact that this unit itself is a strong activating unit$^{21c,24}$ and that the distance between the two triple bonds (two phenyls and one nitrogen atom) is longer than in the previous cases. The fact that multiple additions of TCNE are possible on the same molecule offers interesting opportunities for the synthesis of larger molecular systems, such as dendrimers$^{25}$ or polymers$^{26}$ in the future.
Scheme 3. Evaluation of the reactivity of conjugated bis-ynamides with two equivalents of TCNE.

Most of the new TCBDs were characterized by cyclic voltammetry (figure S1). In general, they exhibit two reversible reduction waves around -0.5 and -1.0 V vs ferrocene, which are reminiscent to their electron super-accepting properties (Table 2). Both dicyanovinyl moieties are subsequently reduced with one electron each time. Particularly noteworthy is the case of compound 38 where two distinct waves were observed around -0.5 V vs ferrocene, indicating a significant electronic coupling concerning the first reduction of the two TCBD moieties. The second reduction wave around -1.0 V vs ferrocene does not exhibit such a coupling since this reduction appears as one reversible two-electron wave.

Table 2. Reduction potentials of TCBDs 4, 6, 14, 18, 22, 24, 26, 30, 32, 34, 36 and 38. They were measured from cyclic voltammograms presented in figure S3.

<table>
<thead>
<tr>
<th>TCBD</th>
<th>$E_{1/2}^1$ (V vs Fc)</th>
<th>$E_{1/2}^2$ (V vs Fc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-0.584</td>
<td>-1.015</td>
</tr>
<tr>
<td>6</td>
<td>-0.611</td>
<td>-1.028</td>
</tr>
<tr>
<td>14</td>
<td>-0.541</td>
<td>-1.065</td>
</tr>
<tr>
<td>18</td>
<td>-0.623</td>
<td>-0.962</td>
</tr>
<tr>
<td>22</td>
<td>-0.611</td>
<td>-1.172</td>
</tr>
<tr>
<td>24</td>
<td>-0.570</td>
<td>-1.027</td>
</tr>
<tr>
<td>26</td>
<td>-0.702</td>
<td>-1.134</td>
</tr>
<tr>
<td>30</td>
<td>-0.483</td>
<td>-1.044</td>
</tr>
<tr>
<td>32</td>
<td>-0.522</td>
<td>-1.021</td>
</tr>
<tr>
<td>34</td>
<td>-0.542</td>
<td>-1.053</td>
</tr>
<tr>
<td>36</td>
<td>-0.521</td>
<td>-0.905</td>
</tr>
<tr>
<td>38</td>
<td>-0.520/-0.630</td>
<td>-1.039</td>
</tr>
</tbody>
</table>

The UV-vis absorption properties of these new compounds are very dependent on the nature of the group linked to the TCBD moieties. As indicated in figure 3, compounds 34, 36 and 38 exhibit very different absorption spectra in the visible range, with respective
absorption maxima at 417, 468 and 604 nm. In particular, compound 38 absorbs in the whole visible range, which allow to envisage different applications in opto-electronic devices. The maximum absorption coefficients of these three species are comprised between $1.2 \times 10^4$ and $1.8 \times 10^4 \text{ mol}^{-1}.\text{L.cm}^{-1}$ in this region.

Figure 2. UV-vis spectra of compounds 4 (in purple), 6 (in red), 30 (in green) and 32 (in blue) in dichloromethane.

Figure 3. UV-vis spectra of compounds 34 (in blue), 36 (in red) and 38 (in black) in dichloromethane.

To conclude, we have explored the scope and limitations of the reaction between functionalized ynamides or arylynamines and TCNE. In most cases, TCBDs were obtained in good to excellent yields. Only steric hindrance and conjugated triple bonds inhibit the reaction. This study was crucial to evaluate the compatibility of this reactivity with the elaboration of diversely functionalized structures. The possibility to run the reaction several times on the same substrate allows us to potentially build more complex systems for diverse
applications in different fields such as photovoltaic devices[27] or non-linear absorbers[28] to exploit the exceptional electron-accepting properties of such TCBD moieties.

CCDC 1004149 (4), CCDC 1010768 (6), CCDC 1021633 (14), CCDC 1480922 (18), CCDC 960489 (20), CCDC 1406171 (24), CCDC 1429182 (26) and CCDC 1429183 (30) 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.

**Experimental Section**

**General information**

Reactions were monitored by thin layer chromatography (Merck TLC silica gel 60 F254 on aluminum sheets) and visualized under UV irradiation at 254 nm or KMnO4 staining solution. Compounds were purified by column chromatography using Geduran® silica gel 60 (0.040 – 0.063 nm). NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Spectra were recorded in deuterochloroform referenced to residual CHCl3 (1H, 7.26 ppm) or CDCl3 (13C, 77.2 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hz. The following abbreviations are used to describe multiplicity: s-singlet, d-doublet, t-triplet, dt-doublet of triplet, td-triplet of doublet, tt-triplet of triplet, ddt-doublet of doublet of triplet and m-multiplet. HRMS experiments were carried out on a Waters Q-Tof 2 (ESI) spectrometer.

**Electrochemical experiments**

**Electrochemical Setup and Procedure**

All electrochemical measurements were performed with an Autolab PGSTAT 12 (Metrohm) and a conventional three-electrode system, comprising a glassy carbon (GC) electrode as working electrode, a platinum wire as the auxiliary electrode, and SCE electrode (Metrohm) as reference electrode. Ferrocene/ferrocenium redox couple was used as an internal reference and all potential are indicated versus this redox couple for clarity. The GC electrodes were purchased from CH Instrument, Inc. (Tx, USA) as 2-mm-diameter rods. The electrodes were polished with grit 4000 SiC paper (Struers) wetted with Milli-Q water. The electrodes were thoroughly rinsed with Milli-Q water and acetone. The electrodes were dried with an argon gas stream, before measurements.

**Crystallography**

All measurements were made in the x-scan technique on a CCD Saphire 3 Xcalibur (Oxford Diffraction) or an APEXII Bruker-AXS diffractometer with graphite monochromatized Mo Kα radiation. The structure was solved by direct methods.[29] The non-hydrogen atoms were refined anisotropically by the full-matrix least-square techniques using the program
SHELXL97. All the hydrogen atoms bonded to C atoms were located geometrically and treated using a riding model, with C–H = 0.95–1.00 Å and Uiso(H) = 1.2 or 1.5Ueq(C).

**Synthesis**

**Compound 4**

A solution of ynamide 3 (200 mg, 0.486 mmol) and TCNE (62.0 mg, 0.486 mmol) in CH₂Cl₂ (5 mL) was stirred at r.t. for 16 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane:EtOAc 8:2) to give TCBD 4 (260 mg, 0.482 mmol, 99%) as an orange solid. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.1 Hz, 1H), 7.87 (dt, J = 8.7, 2.5 Hz, 3H), 7.73 – 7.59 (m, 3H), 7.47 (d, J = 1.8 Hz, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.33 – 7.25 (m, 2H), 7.09 (t, J = 7.8 Hz, 2H), 6.99 (dd, J = 8.2, 1.1 Hz, 2H), 4.74 (s, 2H), 2.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 158.7, 147.4, 135.2, 132.4, 131.1, 130.9, 130.3, 129.9, 129.8, 129.6, 129.5, 129.3, 129.2, 128.4, 128.1, 127.6, 124.3, 111.7, 111.6, 111.3, 111.2, 93.7, 81.9, 52.8, 21.9. HRMS (ESI) calculated for C₁₂H₁₈N₂O₅S [M+Na]⁺ 562.13137, found 562.1315. **UV-visible spectroscopy** (CH₂Cl₂): λ max (log ε) = 263 (4.47), 349 (3.93) nm. Crystal data: Crystallization: liquid diffusion from a CH₂Cl₂ solution into cyclohexane; Formula: C₆H₁₂N₂O₅S; Temperature: 130(2) K, Wavelength: 0.71073 Å, Crystal system: Monoclinic, space group, P2₁/c, Unit cell dimensions: a = 13.4821(2) Å, b = 16.6381(3) Å, c = 13.6268(2) Å, α = 90°, β = 119.292(2)°, γ = 90°, Volume: 2665.88(9) Å³, Z = 4, Calculated density: 1.344 Mg/m³, Absorption coefficient 0.161 mm⁻¹, F(000): 1120, Crystal size: 0.224 x 0.169 x 0.109 mm³, Theta range for data collection: 2.99 to 27.00°, Limiting indices: -17<=h<=16, -21<=k<=12, -17<=l<=17, Reflections collected / unique: 23487 / 5247 [R(int) = 0.0856], Completeness to theta = 27.00°, 99.9%, Absorption correction: None, Refinement method: Full-matrix least-squares on F², Data / restraints / parameters: 5821 / 0 / 362, Goodness-of-fit on F²: 1.020, Final R indices [I>2sigma(I)]: R1 = 0.0641, wR2 = 0.1492, R indices (all data) : R1 = 0.1092, wR2 = 0.1799, Largest diff. peak and hole : 0.615 and -0.460 e.A⁻³.

**Compound 6**

A solution of ynamide 5 (200 mg, 0.569 mmol) and TCNE (72.9 mg, 0.569 mmol) in CH₂Cl₂ (5.5 mL) was stirred at r.t. for 16 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane:EtOAc 7:3) to give TCBD 6 (266 mg, 0.555 mmol, 97%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.5 Hz, 2H), 7.66 (dd, J = 1.8, 0.5 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.39 (dd, J = 5.0, 1.8 Hz, 3H), 7.27 (d, J = 3.9 Hz, 2H), 6.72 – 6.69 (m, 1H), 4.93 (s, 2H), 2.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.1, 150.0, 148.2, 147.5, 145.2, 133.2, 132.5, 130.9, 129.6, 129.4, 128.9, 128.8, 123.5, 115.2, 111.9, 111.5, 111.5, 111.4, 83.3, 80.5, 53.7, 21.9. HRMS (ESI) calculated for C₂₆H₁₇N₃O₅S [M+Na]⁺ 502.09498, found 502.0948. **UV-visible spectroscopy** (CH₂Cl₂): λ max (log ε) = 281 (4.31), 380 (4.25) nm. Crystal data: Crystallization: liquid diffusion from a CH₂Cl₂ solution into cyclohexane; Formula: C₂₆H₁₇N₃O₅S; Temperature: 250 K, Wavelength: 0.71073 Å, Crystal system: Triclinic, space group: P-1, Unit cell dimensions: a = 8.0434(6) Å, b = 9.1866(8) Å, c = 17.657(10) Å, α = 92.121(7)°, β = 99.213(7)°, γ = 110.069(7)°, Volume: 1203.71(15) Å³, Z = 2, Calculated density: 1.323 Mg/m³, Absorption coefficient 0.172 mm⁻¹, F(000): 496, Crystal size: 0.263 x 0.131 x 0.081 mm³, Theta range for data collection: 3.05 to 27.00°, Limiting indices: -9<=h<=10, -11<=k<=11, -22<=l<=20, Reflections collected / unique: 9231 / 5247
Compound 12

A solution of ynamide 11 (105 mg, 0.337 mmol) and TCNE (43.3 mg, 0.337 mmol) in CH$_2$Cl$_2$ (3.4 mL) was stirred at r.t. for 16 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane to pentane:EtOAc 8:2) to give TCBD 12 (140 mg, 0.318 mmol, 94%) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 (dt, $J = 8.8$, 1.6 Hz, 2H), 7.68 (tt, $J = 7.2$, 1.6 Hz, 1H), 7.58 – 7.63 (m, 2H), 7.53 – 7.56 (m, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 5.41 – 5.45 (m, 2H), 5.30 (ddt, $J = 17.2$, 9.6, 6.4 Hz, 1H), 4.28 (d, $J = 6.4$ Hz, 2H), 2.49 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.2, 159.4, 147.4, 133.7, 133.0, 131.1, 130.9, 129.8, 129.4, 128.3, 128.1, 111.8, 111.3, 111.2, 110.6, 93.0, 82.7, 53.2, 21.9. HRMS (ESI) calculated for C$_{24}$H$_{17}$N$_5$NaO$_2$S [M+Na]$^+$ 462.1001, found 462.1006; calculated for C$_{24}$H$_{17}$KN$_5$O$_2$S [M+K]$^+$ 478.0740, found 478.0766.

Compound 14

A solution of ynamide 13 (82.1 mg, 0.265 mmol) and TCNE (33.9 mg, 0.265 mmol) in CH$_2$Cl$_2$ (8 mL) was stirred overnight at r.t. for 16 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane:EtOAc 8:2) to give TCBD 12 (72.2 mg, 0.167 mmol, 64%) as a beige solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.71 (m, 2H), 7.68 – 7.64 (m, 3H), 7.60 – 7.55 (m, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 4.48 (d, $J = 2.5$ Hz, 2H), 2.70 (t, $J = 2.5$ Hz, 1H), 2.48 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.4, 158.2, 147.7, 133.9, 132.3, 131.2, 130.8, 129.9, 129.7, 128.1, 111.8, 111.6, 110.7, 110.1, 92.2, 85.1, 79.9, 73.7, 41.1, 21.9. HRMS (ESI) calculated for C$_{24}$H$_{15}$N$_5$NaO$_2$S [M+Na]$^+$ 460.0844, found 460.0844. Crystal data: Crystallogeeness: liquid diffusion from a CH$_2$Cl$_2$ solution into cyclohexane; Formula: C$_{24}$H$_{15}$N$_5$O$_2$S, Temperature: 140 K, Wavelength: 0.71073 Å, Crystal system: monoclinic, space group: P 21/c, Unit cell dimensions: a = 8.6183(2) Å, b = 13.0256(3) Å, c = 20.2405(5) Å, α = 90°, β = 100.456(2)°, γ = 90°, Volume: 2234.44(9) Å$^3$, Z = 4, Calculated density: 1.30 Mg/m$^3$, Absorption coefficient 0.176 mm$^{-1}$, F(000): 904, Crystal size: 0.218 x 0.167 x 0.114 mm$^3$, Theta range for data collection: 3.188 to 26.999°, Limiting indices: -10<=h<=11, -16<=k<=16, -25<=l<=25, Reflections collected / unique: 17112 / 4857 [R(int) = 0.0495], Completeness to theta = 25.242°, 99.8%, Absorption correction: None, Refinement method: Full-matrix least-squares on F2, Data / restraints / parameters: 4857 / 0 / 290, Goodness-of-fit on F2: 0.975, Final R indices [I>2sigma(I)]: R1 = 0.0428, wR2 = 0.0920, R indices (all data) : R1 = 0.0709, wR2 = 0.1079, Largest diff. peak and hole : 0.251 and -0.369 e.A$^{-3}$.

Compound 18

A solution of ynamide 17 (88.3 mg, 0.228 mmol) and TCNE (29.2 mg, 0.228 mmol) in CH$_2$Cl$_2$ (2.3 mL) was stirred at r.t. for 16 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane to pentane:EtOAc 8:2) to give TCBD 12 (111 mg, 0.215 mmol, 94%) as an orange solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, $J = 8.5$ Hz, 1H), 7.55 – 7.35 (m, 1H), 7.26 – 7.21 (m, 3H), 7.04 (d, $J = 16.1$ Hz, 1H), 4.88 (s, 2H), 2.48 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.4, 157.7, 148.2, 147.7, 133.4, 132.9, 132.8, 132.7, 132.4, 124.7, 111.8, 111.3, 111.2, 110.6, 93.0, 82.7, 53.2, 21.9. HRMS (ESI) calculated for C$_{24}$H$_{17}$K$_2$N$_5$O$_2$S [M+K]$^+$ 509.1029, found 509.1034; calculated for C$_{24}$H$_{17}$K$_2$N$_5$O$_2$S [M+K]$^+$ 509.1034, found 509.1034.
109.9, 129.9, 129.7, 129.6, 129.5, 129.1, 128.4, 119.6, 111.6, 111.3, 111.0, 110.9, 88.6, 53.0, 52.9, 21.9. **HRMS (ESI)** calculated for C$_{30}$H$_{21}$N$_{5}$NaO$_{2}$S [M+Na]$^+$ 538.1314, found 538.1321; calculated for C$_{30}$H$_{22}$KN$_{5}$O$_{2}$S [M+K]$^+$ 554.1053, found 554.1054. **Crystal data:** Crystallogenesis: slow evaporation of a CH$_2$Cl$_2$ solution; Formula: C$_{30}$H$_{21}$N$_{5}$O$_{2}$S, Temperature: 295 K, Wavelength: 0.71073 Å, Crystal system: Monoclinic, space group, P 21/c, Unit cell dimensions: a = 16.6788(6) Å, b = 17.3511(9) Å, c = 9.4234(5) Å, α = 90°, β = 94.829(2)°, γ = 90°, Volume: 2717.4(2) Å$^3$, Z = 4, Calculated density: 1.260 g.cm$^{-3}$, Absorption coefficient 0.155 mm$^{-1}$, F(000): 1072, Crystal size: 0.340 x 0.160 x 0.090 mm$^3$, Theta range for data collection: 3.197 to 27.483°, Limiting indices: -18≤h≤21, -13≤k≤22, -11≤l≤12, Reflections collected / unique: 18561 / 6197 [R(int) = 0.0297], Completeness to theta = 99.5%, Absorption correction: multi-scan, Refinement method: Full-matrix least-squares on F2, Data / restraints / parameters: 6197 / 0 / 248, Goodness-of-fit: 1.059, Final R indices [I>2sigma(I)]: R1a = 0.0858, wR2b = 0.2778, R indices (all data) : R1a = 0.1445, wR2b = 0.3319, Largest diff. peak and hole : 0.626 and -0.501 e.A$^{-3}$.

**Compound 20**

The spectroscopic data are similar to those reported in the literature.[7] **Crystal data:** Crystallogenesis: liquid diffusion from a CH$_2$Cl$_2$ solution into cyclohexane; Formula: C$_{26}$H$_{17}$N$_{5}$O$_{2}$S$_{2}$, Temperature: 100 K, Wavelength: 0.71073 Å, Crystal system: Monoclinic, space group, P 21/n, Unit cell dimensions: a = 13.5158(3) Å, b = 10.2890(2) Å, c = 17.4575(3) Å, α = 90°, β = 108.622(2)°, γ = 90°, Volume: 2300.61(8) Å$^3$, Z = 4, Calculated density: 1.431 g.cm$^{-3}$, Absorption coefficient 0.267 mm$^{-1}$, F(000): 1024, Crystal size: 0.268 x 0.154 x 0.147 mm, Theta range for data collection: 3.04 to 26.99°, Limiting indices: -14≤h≤17, -11≤k≤13, -22≤l≤22, Reflections collected / unique: 17883 / 5013 [R(int) = 0.0246], Completeness to theta = 99.8%, Absorption correction: none, Refinement method: Full-matrix least-squares on F$^2$, Data / restraints / parameters: 5013 / 0 / 316, Goodness-of-fit: 1.084, Final R indices [I>2sigma(I)]: R1a = 0.0375, wR2b = 0.1057, R indices (all data) : R1a = 0.0494, wR2b = 0.1091, Largest diff. peak and hole : 0.465 and -0.485 e.A$^{-3}$.

**Compound 22**

A solution of ynamide 21 (200 mg, 0.651 mmol) and TCNE (83 mg, 0.651 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred at r.t. for 18 h. The mixture was concentrated under reduced pressure and purified by column chromatography (petroleum ether:Et$_2$O 1:0 to 1:1) to give TCBD 22 (285 mg, 0.650 mmol, 99%) as a brown solid. **$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.64 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.9 Hz, 2H), 7.43 (dd, J = 8.5, 1.2 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.10 – 7.13 (m, 2H), 4.87 (s, 2H), 1.45 (s, 9H). **$^{13}$C NMR** (100 MHz, CDCl$_3$) 164.3, 161.4, 150.4, 134.5, 134.4, 130.3, 129.8, 129.6, 129.3, 128.8, 127.2, 111.6, 111.3, 111.0, 111.0, 90.3, 87.5, 82.3, 53.4, 27.7. **HRMS (ESI)** calculated for C$_{26}$H$_{21}$N$_{5}$NaO$_2$ [M+Na]$^+$ 458.15929, found 458.1591.

**Compound 24**

A solution of ynamide 23 (105 mg, 0.277 mmol) and TCNE (35 mg, 0.276 mmol) in CH$_2$Cl$_2$ (3 mL) was stirred at r.t. for 18 h. The mixture was concentrated under reduced pressure to give TCBD 24 (140 mg, 0.276 mmol, 99%) as a bright yellow powder. **$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.90 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.7
A solution of ynamide 25 (291 mg, 0.894 mmol) and TCNE (116 mg, 0.906 mmol) in CH₂Cl₂ (10 mL) was stirred at r.t. for 18 h. The mixture was first dark red and then turned orange with white precipitate. The mixture was concentrated under reduced pressure and purified by column chromatography (n-pentane:CH₂Cl₂ 1:0 to 0:1) to give TCBD 26 (350 mg, 0.772 mmol, 86%) as a dark yellow solid. \(^1\)H NMR (400 MHz, CDCl₃) δ 7.94 (dt, J = 8.4, 1.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.43 – 7.38 (m, 5H), 4.94 (s, 2H), 2.51 (s, 3H), 1.85 (tt, J = 8.5, 5.5 Hz, 1H), 1.14 – 1.08 (m, 2H), 0.99 – 0.94 (m, 2H). \(^13\)C NMR (100 MHz, CDCl₃) δ 172.1, 159.5, 147.6, 133.2, 131.9, 131.1, 130.0, 129.6, 129.5, 128.5, 111.3, 111.1, 110.4, 93.3, 79.7, 52.9, 22.0, 18.2, 11.8. HRMS (ESI) calculated for C₂₅H₁₉N₅O₂S [M+Na]^+ 476.1157, found 476.1154. Crystal data: liquid diffusion from a CH₂Cl₂ solution into cyclohexane; Formula: C₂₅H₁₉N₅O₂S, Formula weight: 453.52, Temperature: 150 K, Wavelength: 1.54184 Å, Crystal system: Triclinic, space group: P-1, Unit cell dimensions: a = 10.1604(3) Å, b = 11.6936(5) Å, c = 13.2402(5) Å, \(a = 115.472(4)^\circ\), \(\beta = 97.027(3)^\circ\), \(\gamma = 94.319(3)^\circ\), Volume = 1395.07(10) Å³, Unit cell least-squares on F², Data / restraints / parameters: 5330 / 0 / 363, Goodness-of-fit on F²: 1.054, Final R indices [I>2sigma(I)]: R1 = 0.0522, wR2 = 0.1413, R indices (all data) : R1 = 0.0555, wR2 = 0.1473, Extinction coefficient: 0.0036(5), Largest diff. peak and hole: 1.888 and -0.387 e.Å⁻³. Compound 26
Compound 30

A solution of ynamide 29 (43.0 mg, 0.161 mmol) and TCNE (23.0 mg, 0.178 mmol) in CH₂Cl₂ (10 mL) was stirred at r.t. for 18 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane:CH₂Cl₂ 1:1 to CH₂Cl₂) to give TCBD 30 (53.0 mg, 0.134 mmol, 83%) as a purple solid. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, J = 7.6, 1.4, 0.7 Hz, 2H), 7.75 – 7.71 (m, 2H), 7.69 – 7.64 (m, 1H), 7.54 (dd, J = 8.3, 7.3, 1.3 Hz, 4H), 7.48 (td, J = 7.5, 1.0 Hz, 2H), 7.44 (dt, J = 8.2, 0.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.8, 156.3, 138.2, 135.1, 131.3, 130.4, 130.2, 127.6, 126.7, 125.6, 121.6, 112.7, 112.0, 111.2, 110.8, 110.7, 91.6, 83.3. HRMS (ESI) calculated for C₂₆H₁₄N₅ [M+H]⁺ 396.12492, found 396.1249.

UV-visible spectroscopy (CH₂Cl₂): λ_max (log ε) = 279 (4.08), 315 (3.84), 511 (3.20) nm. Crystal data: Crystallization: liquid diffusion from a CH₂Cl₂ solution into cyclohexane, Formula: C₂₆H₁₃N₅, Temperature: 250 K, Wavelength: 1.54184 Å, Crystal system: Orthorhombic, space group, P2₁2₁2₁, Unit cell dimensions: a = 7.9516(3) Å, b = 12.0897(4) Å, c = 21.5176(7) Å, α = 90°, β = 90°, γ = 90°, Volume: 2068.54(12) Å³, Z = 4, Calculated density: 1.270 Mg/m³, Absorption coefficient 0.621 mm⁻¹, F(000): 816, Crystal size: 0.2708 x 0.0668 x 0.0367 mm³, Theta range for data collection: 4.194 to 72.112°, Limiting indices: -9<=h<=9, -14<=k<=13, -26<=l<=25, Reflections collected / unique: 8409 / 4043 [R(int) = 0.0220], Completeness to theta = 67.684°, 99.9 %, Absorption correction: Gaussian, Max. and min. transmission: 0.979 and 0.910, Refinement method: Full-matrix least-squares on F², Data / restraints / parameters: 4043 / 0 / 280, Goodness-of-fit on F²: 1.052, Final R indices [I>2sigma(I)]: R1 = 0.0339, wR2 = 0.0870, R indices (all data) : R1 = 0.0377, wR2 = 0.0870, Absolute structure parameter: -0.1(2), Extinction coefficient: n/a, Largest diff. peak and hole: 0.089 and -0.176 e.Å⁻³.

Compound 32

A solution of ynamide 31 (91.0 mg, 0.419 mmol) and TCNE (53.7 mg, 0.419 mmol) in CH₂Cl₂ (10 mL) was stirred at r.t. for 18 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane:CH₂Cl₂ 1:1 to CH₂Cl₂) to give TCBD 32 (85.0 mg, 0.246 mmol, 59%) as a very slimy dark red liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (dt, J = 8.6, 1.8 Hz, 2H), 7.74 (dd, J = 7.6, 2.0, 1.2 Hz, 1H), 7.68 – 7.60 (m, 4H), 7.40 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 7.00 (dd, J = 3.7, 0.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 162.2, 157.3, 153.4, 134.9, 131.2, 130.9, 130.4, 130.3, 127.6, 125.8, 125.7, 123.3, 114.0, 112.8, 111.7, 111.6, 110.3, 90.4, 76.6. HRMS (ESI) calculated for C₂₂H₁₂N₂ [M+H]⁺ 346.10927, found 346.1096. UV-visible spectroscopy (CH₂Cl₂): λ_max (log ε) = 258 (4.25), 336 (4.18), 443 (3.57) nm.

Compound 34

A solution of ynamide 33 (50 mg, 0.10 mmol) and TCNE (26 mg, 0.20 mmol) in CH₂Cl₂ (2 mL) was stirred at r.t. for 16 h. The mixture was concentrated under reduced pressure and purified by column chromatography (CH₂Cl₂:cyclohexane 9:1) to give TCBD 34 (49 mg, 0.080 mmol, 79%) as an orange-red solid. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 3.45 (s, 3H), 3.21 (s, 3H), 2.51 (s, 3H), 2.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 163.6, 147.7, 145.5, 133.4, 132.3, 131.5, 131.1, 130.3, 130.2, 129.6, 128.3, 127.9, 111.9, 111.9, 110.8, 110.5, 90.7, 88.8, 80.2, 69.8, 41.2, 39.3, 27.1, 22.0, 21.9. HRMS
(ESI) calculated for C_{32}H_{24}N_{6}NaO_{4}S_{2} [M+Na]^+ 643.1198, found 643.1198. **UV-visible spectroscopy** (CH_{2}Cl_{2}): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 276 (4.48), 313 (4.41), 416 (4.17) nm.

**Compound 36**

A solution of ynamide 35 (52 mg, 0.080 mmol) and TCNE (20 mg, 0.16 mmol) in CH_{2}Cl_{2} (0.8 ml) was stirred at r.t. for 16 h. The reaction mixture was purified by column chromatography (pentane:EtOAc 8:2 to 7:3) to give TCBD 36 (61 mg, 0.078 mmol, 98%) as a red solid. \(^1\)H NMR (400 MHz, CDCl_{3}) \( \delta \) 7.75 (d, \( J = 8.3 \) Hz, 2H), 7.62 (d, \( J = 8.2 \) Hz, 2H), 7.31 – 7.03 (m, 14H), 6.73 – 6.64 (m, 2H), 4.74 (s, 2H), 4.46 (s, 2H), 2.31 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl_{3}) \( \delta \) 158.9, 154.4, 148.1, 146.1, 137.6, 136.2, 134.6, 134.0, 133.3, 132.4, 132.3, 131.9, 131.3, 130.6, 130.1, 130.0, 129.8, 129.3, 129.2, 128.1, 126.4, 126.2, 112.8, 112.2, 111.7, 111.6, 95.4, 84.4, 65.5, 55.7, 53.2, 21.6, 21.5. HRMS (ESI) calculated for C_{42}H_{30}N_{6}NaO_{4}S_{3} [M+Na]^+ 801.1388, found 801.1376. **UV-visible spectroscopy** (CH_{2}Cl_{2}): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 285 (4.26), 337 (4.08), 468 (4.25) nm.

**Compound 38**

A solution of ynamide 37 (37 mg, 0.045 mmol) and TCNE (12 mg, 0.091 mmol) in CH_{2}Cl_{2} (0.5 ml) was stirred at r.t. for 16 h. The reaction mixture was purified by column chromatography (CH_{2}Cl_{2} to CH_{2}Cl_{2}:Et_{2}O 9:1) to give TCBD 38 (45 mg, 42 mmol, 92%) as a purple solid. \(^1\)H NMR (400 MHz, CDCl_{3}) \( \delta \) 7.96 (d, \( J = 8.3 \) Hz, 4H), 7.55 (t, \( J = 7.6 \) Hz, 2H), 7.49 (d, \( J = 8.3 \) Hz, 4H), 7.43 (t, \( J = 7.6 \) Hz, 1H), 7.38 – 7.18 (m, 12H), 7.08 – 6.97 (m, 8H), 4.82 (s, 4H), 2.52 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl_{3}) \( \delta \) 164.0, 159.2, 150.8, 147.6, 144.5, 133.2, 131.4, 131.2, 131.1, 130.8, 130.0, 129.7, 129.4, 128.6, 127.8, 127.7, 123.9, 122.8, 122.2, 111.4, 90.0, 81.2, 52.7, 22.0. HRMS (ESI) calculated for C_{52}H_{42}N_{12}NaO_{4}S_{2} [M+H+Na]^+ 1090.26821, found 1090.26766. **UV-visible spectroscopy** (CH_{2}Cl_{2}): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 306 (5.05), 335 (4.98), 579 (4.49) nm.

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