CHEMISTRY
AN ASIAN JOURNAL
www.chemasianj.org

Accepted Article

Title: Reactivity of functionalized ynamides with tetracyanoethylene: scope, limitations and optoelectronic properties of the adducts

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

To be cited as: *Chem. Asian J.* 10.1002/asia.201700353

Link to VoR: http://dx.doi.org/10.1002/asia.201700353

A Journal of

ACES
Asian Chemical Editorial Society

A sister journal of **Angewandte Chemie** and **Chemistry – A European Journal**

WILEY-VCH

10.1002/asia.201700353

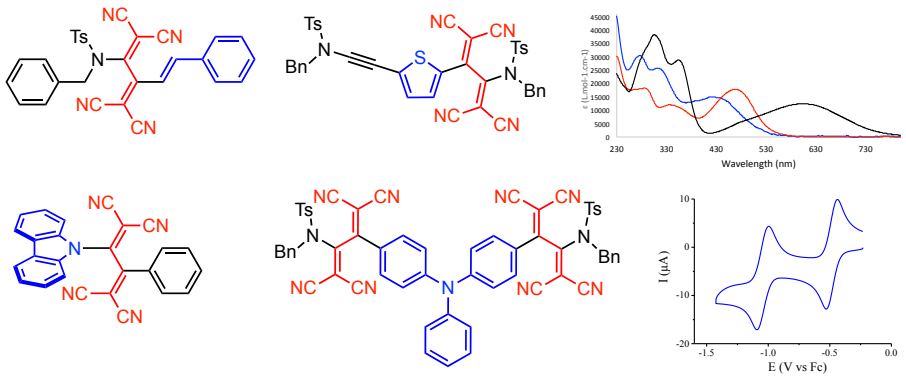
Reactivity of functionalized ynamides with tetracyanoethylene: scope, limitations and optoelectronic properties of the adducts

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]

[a] Institut des Sciences Chimiques de Rennes, UMR 6226, CNRS, Ecole Nationale Supérieure de Chimie de Rennes, Université de Rennes 1, 35708 Rennes Cedex (France)

[b] Institut de Physique de Rennes, CNRS, UMR 6251, Université de Rennes 1, 263 avenue du Général Leclerc, 35042 Rennes Cedex (France)

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



Abstract: The reactivity of functionalized ynamides and arylynamines 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

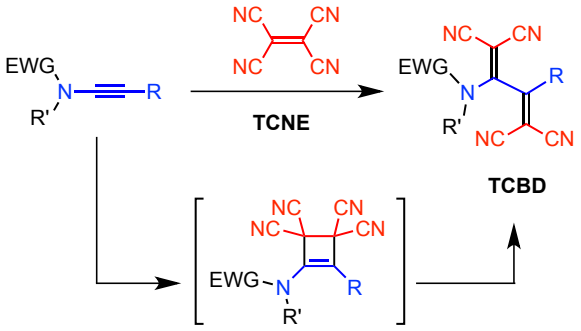
The synthesis of 1,1,4,4-tetracyanobutadienes (TCBDs) has met an increasing interest over the last years.[1] Actually, the properties of such molecules could be of particular interest given their exceptional electron-accepting ability and their intense non-linear absorption in some cases.[2] Moreover, 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

10.1002/asia.201700353

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 TCNE 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.

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 naphtyl (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.

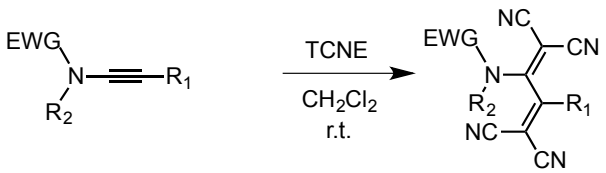
As already observed, the nature of the EWG does not seem to have an influence since replacing the tosyl group by a Boc group (ynamide **21**)[11] led to TCBD **22** quantitatively (entry 11).

10.1002/asia.201700353

We also evaluated the influence of the group linked to the nitrogen (R_2 in table 1). When using a phenyl group (compound **9**)[12] 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**)[10] 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**)[15] 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.

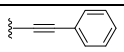
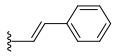
Then, we tested the influence of a non-aromatic system linked to the triple bond on the CA-RE sequence (R_1 in table 1). After observing that a propargylic group could slow down the reaction, we wanted to evaluate the influence of a CC triple bond conjugated to the CC triple bond of an ynamide. Surprisingly, 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**),[10] 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**)[16] 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.



entry	ynamide	EWG	R_1	R_2	TCBD	yield (%)
1	**1**	Ts	Ph	Bn	**2**	98
2	**3**	Ts	naphtalen-2-yl	Bn	**4**	99
3	**5**	Ts	furan-2-yl	Bn	**6**	97

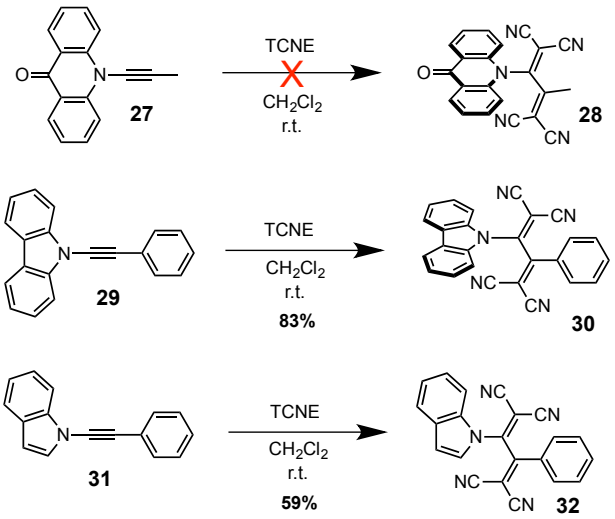
10.1002/asia.201700353

4	**7**	Ts	anthracen-9-yl	Bn	**8**	0[a]
5	**9**	Ts	Ph	Ph	**10**	0[a]
6	**11**	Ts	Ph	allyl	**12**	94
7	**13**	Ts	Ph	propargyl	**14**	64[b]
8	**15**	Ts		Bn	**16**	0[a]
9	**17**	Ts		Bn	**18**	94
10	**19**	Ts	thiophen-2-yl	Bn	**20**	87
11	**21**	Boc	Ph	Bn	**22**	99
12	**23**	Ts	p-fluorophenyl	Bn	**24**	99
13	**25**	Ts	cyclopropyl	Bn	**26**	86

[a]No conversion, the starting material was recovered. [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**.[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**.[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.[3f] Similarly the indole ynamine **31**[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,[20] contrary to alkylated ynamines that probably over-react with TCNE to lead to a mixture of numerous products in low yields.[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).

10.1002/asia.201700353



Scheme 2. Evaluation of the reactivity of arylated ynamines.

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.[3c,4d,21] We tested the reactivity of this compound with some ynamides or ynamines 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 ynamides 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_1 in Table 1) linked to the TCBD group differs from one another, depending on their nature. In the case of naphtyl, phenyl fluorophenyl 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.

10.1002/asia.201700353

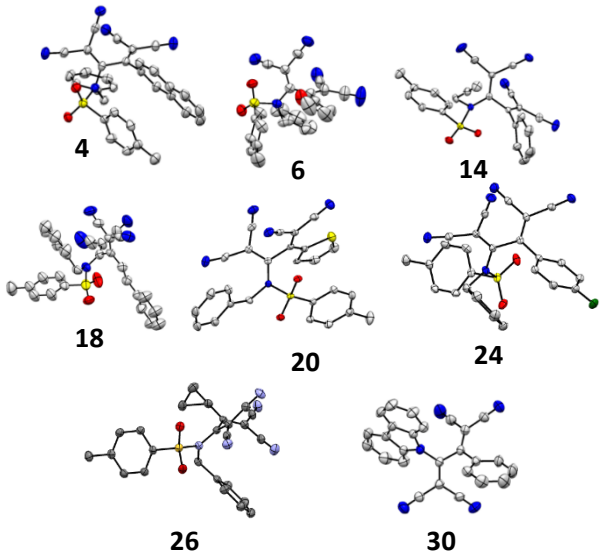
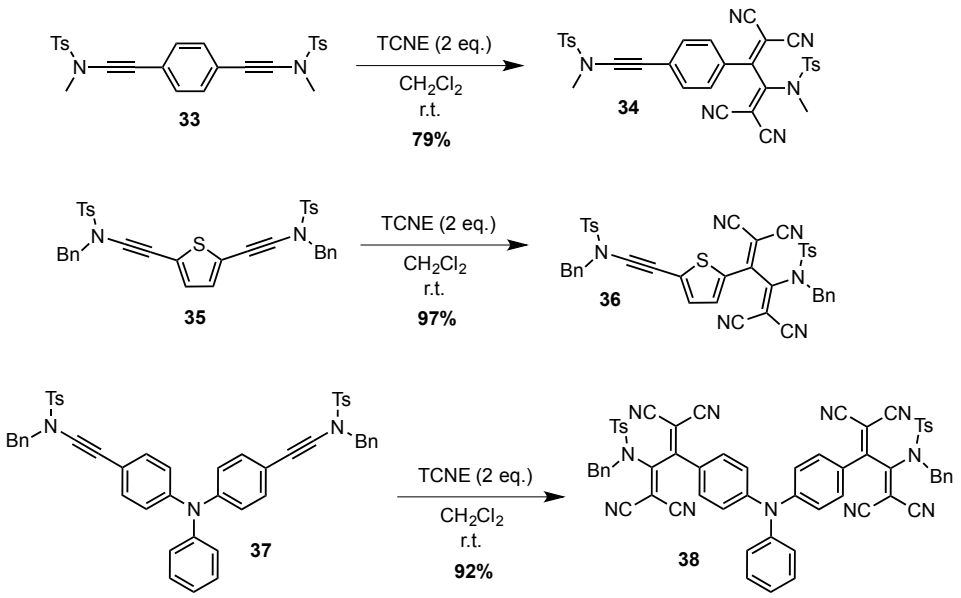


Figure 1. X-ray structure of TCBDs **4**, **6**, **14**, **18**, **20**, **24**, **26** and **30**; protons and solvent molecules have been omitted for clarity.

In order to evaluate the possibility to perform multiple TCNE additions on the same molecule, we reacted conjugated bis-ynamides[22] 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.

10.1002/asia.201700353



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.

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

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

10.1002/asia.201700353

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 x 10^4 and 1.8 x 10^4 $mol^{-1}.L.cm^{-1}$ in this region.

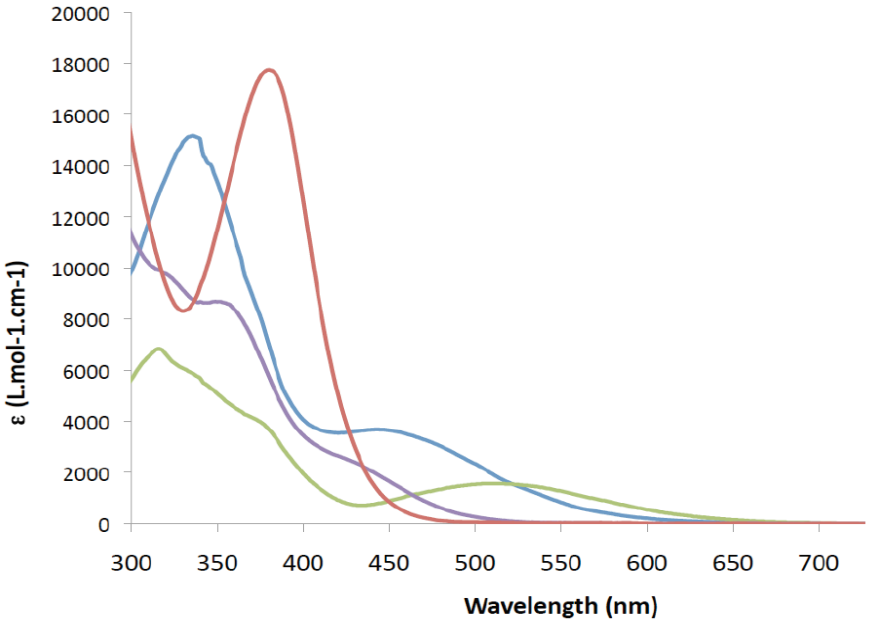


Figure 2. UV-vis spectra of compounds **4** (in purple), **6** (in red), **30** (in green) and **32** (in blue) in dichloromethane.

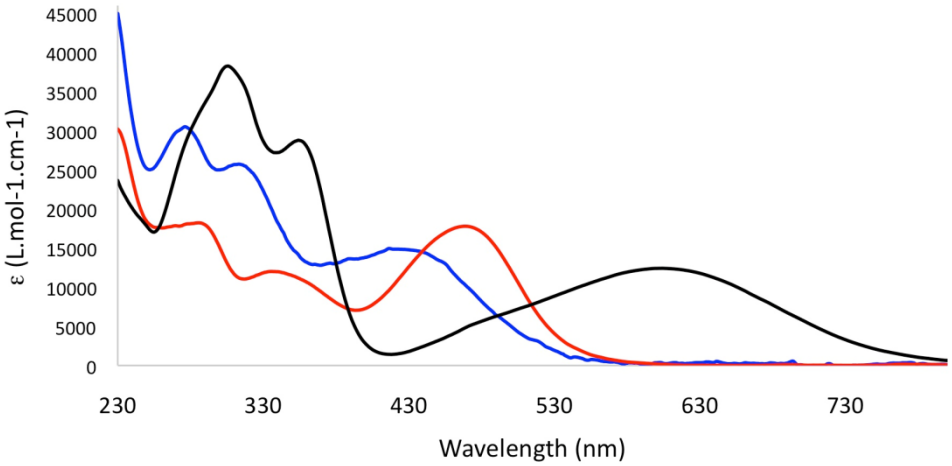


Figure 3. UV-vis spectra of compounds **34** (in blue), **36** (in red) and **38** (in black) in dichloromethane.

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 F_{254} on aluminum sheets) and visualized under UV irradiation at 254 nm or $KMnO_4$ 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 $CHCl_3$ (^{1}H, 7.26 ppm) or $CDCl_3$ (^{13}C, 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, ddd-doublet of doublet of doublet, 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.[30] 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 CH_2Cl_2 (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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 158.7, 147.4, 135.2, 133.3, 132.4, 131.1, 130.9, 130.2, 129.9, 129.8, 129.6, 129.5, 129.3, 129.2, 128.4, 128.1, 127.6, 127.0, 124.3, 111.7, 111.6, 111.3, 111.2, 93.7, 81.9, 52.8, 21.9. **HRMS** (ESI) calculated for $C_{32}H_{21}N_5NaO_2S$ $[M+Na]^+$ 562.13137, found 562.1315. **UV-visible spectroscopy** (CH_2Cl_2): λ_{max} (log ε) = 263 (4.47), 349 (3.93) nm. **Crystal data**: Crystallogenesis: liquid diffusion from a CH_2Cl_2 solution into cyclohexane; Formula: $C_{32}H_{21}N_5O_2S$, 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) Å^3, Z = 4, Calculated density: 1.344 Mg/m^3, Absorption coefficient 0.161 mm^{-1}, F(000): 1120, Crystal size: 0.224 x 0.169 x 0.109 mm^3, 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 / 5821 [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 CH_2Cl_2 (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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{26}H_{17}N_5NaO_3S$ $[M+Na]^+$ 502.09498, found 502.0948. **UV-visible spectroscopy** (CH_2Cl_2): λ_{max} (log ε) = 281 (4.31), 380 (4.25) nm. **Crystal data**: Crystallogenesis: liquid diffusion from a CH_2Cl_2 solution into cyclohexane; Formula: $C_{26}H_{17}N_5O_3S$, 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) Å^3, Z = 2, Calculated density: 1.323 Mg/m^3, Absorption coefficient 0.172 mm^{-1}, F(000): 496, Crystal size: 0.263 x 0.131 x 0.081 mm^3, 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

[R(int) = 0.0449], Completeness to theta = 27.00°, 99.8%, Absorption correction: None, Refinement method: Full-matrix least-squares on F2, Data / restraints / parameters: 5247 / 0 / 316, Goodness-of-fit on F2: 1.002, Final R indices [I>2sigma(I)]: R1 = 0.0634, wR2 = 0.1384, R indices (all data) : R1 = 0.1216, wR2 = 0.1767, Largest diff. peak and hole : 0.317 and -0.238 e.A^{-3}.

Compound 12

A solution of ynamide **11** (105 mg, 0.337 mmol) and TCNE (43.3 mg, 0.337 mmol) in CH_2Cl_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, 124.4, 111.8, 111.3, 111.2, 110.6, 93.0, 82.7, 53.2, 21.9. **HRMS** (ESI) calculated for $C_{24}H_{17}N_5NaO_2S$ $[M+Na]^+$ 462.1001, found 462.1006; calculated for $C_{24}H_{17}KN_5O_2S$ $[M+K]^+$ 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_2Cl_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 $C_{24}H_{15}N_5NaO_2S$ $[M+Na]^+$ 460.0844, found 460.0844. **Crystal data**: Crystallogenesis: liquid diffusion from a CH_2Cl_2 solution into cyclohexane; Formula: $C_{24}H_{15}N_5O_2S$, 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: 1.300 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_2Cl_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, 11H), 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,

130.9, 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 $C_{30}H_{21}N_5NaO_2S$ $[M+Na]^+$ 538.1314, found 538.1321; calculated for $C_{30}H_{21}KN_5O_2S$ $[M+K]^+$ 554.1053, found 554.1054. **Crystal data**: Crystallogenesis: slow evaporation of a CH_2Cl_2 solution; Formula: $C_{30}H_{21}N_5O_2S$, 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_2Cl_2 solution into cyclohexane; Formula: $C_{26}H_{17}N_5O_2S_2$, 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, 0.651mmol) and TCNE (83 mg, 0.651 mmol) in CH_2Cl_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_2O 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 $C_{26}H_{21}N_5NaO_2$ $[M+Na]^+$ 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_2Cl_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

Hz, 2H), 7.10 (d, *J* = 7.1 Hz, 2H), 7.04 (d, *J* = 7.1 Hz, 4H), 4.79 (s, 2H), 2.52 (s, 3H). **^{1}H NMR {^{19}F}** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.02 (s, 4H), 4.79 (s, 2H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2 (t, J_{C-F} = 128 Hz), 158.5, 147.5, 133.1, 131.5 (d, *J* = 9.4 Hz), 131.1, 131.0, 129.6, 129.5, 129.4, 128.2, 125.7 (d, *J* = 3.3 Hz), 117.2, 117.0, 111.5, 111.4, 111.0, 110.9, 93.6 (d, *J* = 1.3 Hz), 81.7, 52.6, 21.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.2. **HRMS** (ESI) calculated for $C_{28}H_{18}FKN_5O_2S$ $[M+K]^+$ 546.08023, found 546.0801; calculated for $C_{28}H_{18}FN_5NaO_2S$ $[M+Na]^+$ 530.10629, found 530.1058. **Crystal data**: Crystallogenesis: liquid diffusion from a CH_2Cl_2 solution into cyclohexane; Formula: $C_{31}H_{24}FN_5O_2S$, Formula weight: 549.61, 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, α = 115.472(4)°, β = 97.027(3)°, γ = 94.319(3)°, Volume: 1395.07(10) $Å^3$, Z = 2, Calculated density: 1.308 Mg/m^3, Absorption coefficient: 1.397 mm^{-1}, F(000): 572, Crystal size: 0.296 x 0.210 x 0.207 mm^3, Theta range for data collection: 3.754 to 70.729°, Limiting indices: -12<=h<=9, -14<=k<=14, -16<=l<=15, Reflections collected / unique: 13777 / 5330 [R(int) = 0.0230], Completeness to theta = 67.684°, 99.9 %, Absorption correction: Semi-empirical from equivalents, Max. and min. transmission: 1.00000 and 0.90963, Refinement method: Full-matrix least-squares on F^2, Data / restraints / parameters: 5330 / 0 / 363, Goodness-of-fit on F^2: 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 $e.A^{-3}$.

Compound 26

A solution of ynamide **25** (291 mg, 0.894 mmol) and TCNE (116 mg, 0.906 mmol) in CH_2Cl_2 (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:CH_2Cl_2 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, $CDCl_3$) 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, $CDCl_3$) δ 172.1, 159.5, 147.6, 133.2, 131.9, 131.1, 130.0, 129.6, 129.5, 128.5, 111.3, 111.3, 111.1, 110.4, 93.3, 79.7, 52.9, 22.0, 18.2, 11.8. **HRMS** (ESI) calculated for $C_{25}H_{19}N_5NaO_2S$ $[M+Na]^+$ 476.1157, found 476.1154. **Crystal data**: Crystallogenesis: liquid diffusion from a CH_2Cl_2 solution into cyclohexane; Formula: $C_{25}H_{19}N_5O_2S$, Formula weight: 453.52, Temperature: 150 K, Wavelength: 1.54184 Å, Crystal system: Triclinic, space group: P_{-1}, Unit cell dimensions: a = 8.1626(4) Å, b = 8.7035(5) Å, c = 16.8844(8) Å, α = 91.953(4)°, β = 95.786(4)°, γ = 111.987(5)°, Volume: 1103.25(11) $Å^3$, Z = 2, Calculated density: 1.365 Mg/m^3, Absorption coefficient: 1.578 mm^{-1}, F(000): 472, Crystal size: 0.5653 x 0.0548 x 0.0418 mm^3, Theta range for data collection: 5.282 to 71.217°, Index ranges: -10<=h<=6, -10<=k<=10, -20<=l<=20, Reflections collected: 8920, Independent reflections: 4217 [R(int) = 0.0274], Completeness to theta = 67.684°, 99.9 %, Absorption correction: Gaussian, Max. and min. transmission: 0.943 and 0.684, Refinement method: Full-matrix least-squares on F^2, Data / restraints / parameters: 4217 / 0 / 299, Goodness-of-fit on F^2: 1.031, Final R indices [I>2sigma(I)]: R1 = 0.0387, wR2 = 0.1037, R indices (all data) : R1 = 0.0452, wR2 = 0.1086, Extinction coefficient: n/a, Largest diff. peak and hole: 0.641 and -0.407 $e.A^{-3}$.

Compound 30

A solution of ynamide **29** (43.0 mg, 0.161 mmol) and TCNE (23.0 mg, 0.178 mmol) in CH_2Cl_2 (10 mL) was stirred at r.t. for 18 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane:CH_2Cl_2 1:1 to CH_2Cl_2) to give TCBD **30** (53.0 mg, 0.134 mmol, 83%) as a purple solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (ddd, *J* = 7.6, 1.4, 0.7 Hz, 2H), 7.75 – 7.71 (m, 2H), 7.69 – 7.64 (m, 1H), 7.54 (ddd, *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). **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{26}H_{14}N_5$ $[M+H]^+$ 396.12492, found 396.1249. **UV-visible spectroscopy** (CH_2Cl_2): λ_{max} (log ε) = 279 (4.08), 315 (3.84), 511 (3.20) nm. **Crystal data**: Crystallogenesis: liquid diffusion from a CH_2Cl_2 solution into cyclohexane, Formula: $C_{26}H_{13}N_5$, Temperature: 250 K, Wavelength: 1.54184 Å, Crystal system: Orthorhombic, space group, $P2_12_12_1$, 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) Å^3, Z = 4, Calculated density: 1.270 Mg/m^3, Absorption coefficient 0.621 mm^{-1}, F(000): 816, Crystal size: 0.2708 x 0.0668 x 0.0367 mm^3, Theta range for data collection: 4.194 to 72.112°, Limiting indices: -9<=h<=6, -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.A^{-3}.

Compound 32

A solution of ynamide **31** (91.0 mg, 0.419 mmol) and TCNE (53.7 mg, 0.419 mmol) in CH_2Cl_2 (10 mL) was stirred at r.t. for 18 h. The mixture was concentrated under reduced pressure and purified by column chromatography (pentane:CH_2Cl_2 1:1 to CH_2Cl_2) to give TCBD **32** (85.0 mg, 0.246 mmol, 59%) as a very slimy dark red liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dt, *J* = 8.6, 1.8 Hz, 2H), 7.74 (ddd, *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). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.2, 157.3, 135.4, 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, 111.0, 110.3, 90.4, 76.6. **HRMS** (ESI) calculated for $C_{22}H_{12}N_5$ $[M+H]^+$ 346.10927, found 346.1096. **UV-visible spectroscopy** (CH_2Cl_2): 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 CH_2Cl_2 (2 mL) was stirred at r.t. for 16 h. The mixture was concentrated under reduced pressure and purified by column chromatography (CH_2Cl_2:cyclohexane 9:1) to give TCBD **34** (49 mg, 0.080 mmol, 79%) as an orange-red solid. **^{1}H NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{32}H_{24}N_6NaO_4S_2$ $[M+Na]^+$ 643.1198, found 643.1198. **UV-visible spectroscopy** (CH_2Cl_2): λ_{max} (log ε) = 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_2Cl_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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 129.3, 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 $C_{42}H_{30}N_6NaO_4S_3$ $[M+Na]^+$ 801.1388, found 801.1376. **UV-visible spectroscopy** (CH_2Cl_2): λ_{max} (log ε) = 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_2Cl_2 (0.5 mL) was stirred at r.t. for 16 h. The reaction mixture was purified by column chromatography (CH_2Cl_2 to CH_2Cl_2:Et_2O 9:1) to give TCBD **38** (45 mg, 42 mmol, 92%) as a purple solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 112.2, 112.1, 111.6, 111.4, 90.0, 81.2, 52.7, 22.0. **HRMS** (ESI) calculated for $C_{62}H_{42}N_{11}NaO_4S_2$ $[M+H+Na]^+$ 1090.26821, found 1090.26766. **UV-visible spectroscopy** (CH_2Cl_2): λ_{max} (log ε) = 306 (5.05), 335 (4.98), 579 (4.49) nm.

Acknowledgments

M. Betou and A. Sallustrau thank the Région Bretagne for a post-doctoral grant. J.-C. Guillemin is acknowledged for proofreading the manuscript.

[1] a) M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009,** *42,* 235–248; b) S.-i. Kato, F. Diederich, *Chem. Commun.* **2010,** *46,* 1994–2006.

[2] a) X. Wu, J. Wu, Y. Liu, A. K. Y. Jen, *J. Am. Chem. Soc.* **1998,** *121,* 472–473; b) C. Cai, I. Liakatas, M.-S. Wong, M. Bösch, C. Bosshard, P. Günter, S. Concilio, N. Tirelli, U. W. Suter, *Org. Lett.* **1999,** *1,* 1847–1849; c) M. T. Beels, M. S. Fleischman, I. Biaggio, B. Breiten, M. Jordan, F. Diederich, *Opt. Mater. Express* **2012,** *2,* 294–303; d) Y. Mi, P. Liang, Z. Yang, D. Wang, H. Cao, W. He, H. Yang, Lian Yu, *ChemistryOpen* **2016**, *5*, 71–77.

[3] a) T. Mochida, S. Yamazaki, *J. Chem. Soc. Dalton Trans.* **2002,** 3559–3564; b) Y. Morioka, N. Yoshizawa, J.-i. Nishida, Y. Yamashita, *Chem. Lett.* **2004,** *33,* 1190–1191; c) S.-i. Kato, M. Kivala, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, F. Diederich, *Chem. Eur. J.* **2009,** *15,* 8687–8691; d) R. Garcia, M. A. Herranz, M. R. Torres, P.-A. Bouit, J. L. Delgado, J. Calbo, P. M. Viruela, E. Orti, N. Martin, *J. Org. Chem.* **2012,** *77,* 10707–10717; e) F. G. Perrin, G. Kiefer, L. Jeanbourquin, S. Racine, D. Perrotta, J. Waser, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.*

2015, *54,* 13393–13396; f) S.-i. Kato, H. Noguchi, S. Jin, Y. Nakamura, *Asian J. Org. Chem.* **2016**, *5*, 246 – 256; g) T. Shoji, S. Ito, T. Okujima, N. Morita, *Eur. J. Org. Chem.* **2011**, 5134–5140; h) S. Niu, G. Ulrich, P. Retailleau, R. Ziessel, *Tetrahedron Lett.* **2011**, *52*, 4848–4853; i) A. Leliège, P. Blanchard, T. Rousseau, J. Roncali, *Org. Lett.* **2011**, *13*, 3098–3101; j) Z. Jin, D. Wanga, X. Wanga, P. Liang, Y. Mi, H. Yang *Tetrahedron Lett.* **2013**, *54*, 4859–4864.

[4] a) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* **2005,** 737–739; b) T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Chem. Eur. J.* **2008,** *14,* 8398–8408; c) T. Shoji, J. Higashi, S. Ito, T. Okujima, M. Yasunami, N. Morita, *Chem. Eur. J.* **2011,** *17,* 5116–5129; (d) D. Koszelewski, A. Nowak-Król, D. T. Gryko, *Chem. Asian J.* **2012,** *7,* 1887–1894.

[5] H.C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001,** *40,* 2004–2021.

[6] a) G. Evano, A. Coste, K. Jouvin, *Angew. Chem. Int. Ed.* **2010,** *49,* 2840–2859; b) K. A. DeKorver, H. Li, A. G. Lohse, R. Hayashi, Z. Lu, Y. Zhang, R. P. Hsung, *Chem. Rev.* **2010,** *110,* 5064 –5106.

[7] M. Betou, N. Kerisit, E. Meledje, Y. R. Leroux, C. Katan, J.-F. Halet, J.-C. Guillemin, Y. Trolez, *Chem. Eur. J.* **2014,** *20,* 9553–9557.

[8] C. M. Reisinger, P. Rivera-Fuentes, S. Lampart, W. B. Schweizer, F. Diederich, *Chem. Eur. J.* **2011,** *17,* 12906–12911.

[9] Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz, E. L. Vera, *Org. Lett.* **2004,** *6,* 1151–1154.

[10] K. Jouvin, A. Coste, A. Bayle, F. Legrand, G. Karthikeyan, K. Tadiparthi, G. Evano, *Organometallics* **2012,** *31,* 7933–7947.

[11] J. R. Dunetz, R. L. Danheiser, *Org. Lett.* **2003**, *5*, 4011-4014.

[12] T. Hamada, X. Ye, S. S. Stahl, *J. Am. Chem. Soc.* **2008,** *130,* 833–835.

[13] T. Shoji, S. Ito, T. Okujima, N. Morita, *Org. Biomol. Chem.* **2012,** *10,* 8308–8313.

[14] a) G. Jayamurugan, J.-P. Gisselbrecht, C. Boudon, F. Schoenebeck, W. B. Schweizer, B. Bernet, F. Diederich, *Chem. Commun.* **2011,** *47,* 4520–4522; b) G. Jayamurugan, A. D. Finke, J.-P. Gisselbrecht, C. Boudon, W. B. Schweizer, F. Diederich, *J. Org. Chem.* **2014,** *79,* 426–431; c) N. Kerisit, A. D. Finke, N. Trapp, Y. R. Leroux, J.-C. Guillemin, Y. Trolez, F. Diederich, *Tetrahedron* **2015,** *71,* 4393–4399.

[15] Y. Tokimizu, M. Wieteck, M. Rudolph, S. Oishi, N. Fujii, A. S. K. Hashmi, H. Ohno, *Org. Lett.* **2015,** *17,* 604−607.

[16] L. V. Graux, H. Clavier, G. Buono, *ChemCatChem* **2014**, *6*, 2544 – 2548.

[17] A. R. Katritzky, W. H. Ramer, *J. Org. Chem.* **1985,** *50,* 852–856.

[18] A. Sagadevan, A. Ragupathi, C.-C. Li, J. R. Hwu, K. C. Hwang, *Green Chem.* **2015,** *17,* 1113–1119.

[19] A. H. Sato, K. Ohashi, K. Ito, T. Iwasawa, *Tetrahedron Lett.* **2013,** 54, 2878–2881.

[20] T. Okuno, H. Iwahashi, *Acta Cryst.* **2013,** *E69,* o665.

[21] a) M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun.* **2007**, 4731–4733; b) T. Shoji, S. Ito, K. Toyota, T. Iwamoto, M. Yasunami, Noboru Morita, *Eur. J. Org. Chem.* **2009**, 4316–4324; c) X. Tang, W. Liu, J. Wu, C.-S. Lee, J. You, P. Wang, *J. Org. Chem.* **2010,** *75,* 7273–7278; d) T. Shoji, J. Higashi, S. Ito, T. Okujima, M. Yasunamie, N. Morita, *Org. Biomol. Chem.* **2012**, *10*, 2431–2438.

[22] M. Betou, A. Sallustrau, Y. Trolez, *Tetrahedron Lett.* **2015,** *56,* 4627–4630.

[23] a) T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006,** *12,* 1889–1905; b) N. Krauße, M. Kielmann, J. Ma, H. Butenschön, *Eur. J. Org. Chem.* **2015**, 2622–2631.
[24] a) T Shoji, E. Shimomura, M. Maruyama, A. Maruyama, S. Ito, T. Okujima, K. Toyota, N. Morita, *Eur. J. Org. Chem.* **2013**, 7785–7799; b) T. Shoji, N. Kamata, A. Maruyama, S. Ito, T. Okujima, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1338–1346.
[25] C. Dengiz, B. Breiten, J.-P. Gisselbrecht, C. Boudon, N. Trapp, W. B. Schweizer, F. Diederich, *J. Org. Chem.* **2015**, *80*, 882−896.
[26] J. Ohshita, T. Kajihara, D. Tanaka, Y. Ooyama, *J. Organomet. Chem.* **2014**, *749*, 255–260.
[27] M. Sekita, B. Ballesteros, F. Diederich, D. M. Guldi, G. Bottari, T. Torres, *Angew. Chem. Int. Ed.* **2016**, *55*, 5560–5564.
[28] Z. Pokladek, N. Ripoche, M. Betou, Y. Trolez, O. Mongin, J. Olesiak-Banska, K. Matczyszyn, M. Samoc, M. G. Humphrey, M. Blanchard-Desce, F. Paul, *Chem. Eur. J.* **2016,** *22*, 10155-10167.
[29] a) A. Altomare, M. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, G. Spagna, G. *J. Appl. Crystallogr.* **1999**, *32*, 115−119; b) G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.
[30] G. M. Sheldrick (**1997**) SHELXL97. Program for the refinement of crystal structures. University of Göttingen, Germany.