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Approaching ambient temperatures in 1,2-DCE to deliver efficient intermolecular Dötz benzannulation processes

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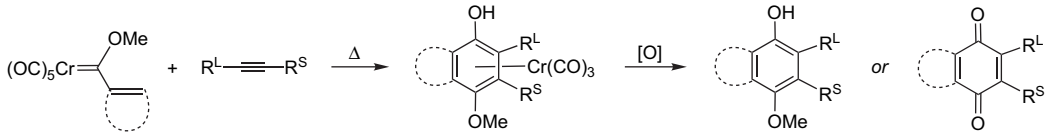
Abstract

Conditions have been developed that enable intermolecular Dötz benzannulations to be carried out under extremely mild conditions, using 1,2-DCE as the reaction solvent and without the requirement for any additional reaction promoters. The new protocols, at temperatures close to ambient, have been applied successfully to a range of internal and terminal alkynes with a series of aryl and alkenyl carbene complexes, resulting in good to high yields of the benzannulation products. The developed conditions did, however, return lower benzannulation yields when utilised with the traditionally more troublesome 2-furyl carbene complex. It was found that increased reaction temperatures in 1,2-DCE did deliver high yields for the processes with this heteroaryl species.

Keywords: Carbene; Chromium; 1,2-Dichloroethane; Dötz benzannulation; Quinone

1. Introduction

Since their discovery in 1964,[1] transition metal carbene complexes have become widely utilised synthetic tools for the preparative chemist, delivering a rich array of valuable transformations and desirable product classes.[2] Amongst the most extensively developed and applied methods with Fischer carbene complexes is the Dötz benzannulation process, originally divulged in 1975.[3] This annulation, between an α,β-unsaturated Fischer carbene complex and an alkyne, has become an established synthetic technique for the preparation of highly functionalised phenols and quinones (Scheme 1).[2,4] Such processes are normally performed by heating the substrates in an ethereal donor solvent,[4,5] and high levels of regioselectivity, with respect to the alkyne insertion, are generally delivered.[4,6] Having stated this, there are two common drawbacks associated with this type of reaction: only moderate yields of products often result, and long reaction times can be required. Due to these practical issues, considerable work has been devoted towards enhancing the efficacy of the Dötz benzannulation process. In this regard, studies carried out by Yamashita led to the serendipitous discovery of a method for promoting these metal carbene-mediated cyclisations,[6e,7] with the use of acetic anhydride and triethylamine as additives resulting in the pro-



Scheme 1. Dötz benzannulation process.

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motion of some reactions which were otherwise unsuccessful under conventional conditions. Subsequent to this, Boger noted that certain transformations could be effectively promoted with acetic anhydride alone.[8]

Work within our own laboratory has led to the development of further methods for the promotion of the Dötz annulation reaction. In particular, the application of ultrasonication techniques facilitate the benzannulation process and allow reactions to proceed very rapidly to completion.[9] Perhaps more importantly, we have also exploited the use of dry state adsorption techniques to considerably enhance the yields obtained in a series of Dötz reactions.[9,10] Additionally, further work within our laboratory has shown that microwave technology can be applied as a direct source of thermal energy to successfully promote the Dötz benzannulation.[11]

In common with the Pauson–Khand reaction, the first step in the Dötz benzannulation is believed to be decarbonylation of the transition metal centre.[12] Moreover, it has been well documented in the literature that the addition of alkyl methyl sulfides can very effectively enhance Pauson–Khand cyclisations, perhaps by promotion of key steps in the reaction mechanism or by stabilisation of coordinatively unsaturated intermediates.[13] Furthermore, recent work within our own laboratory has now shown that dodecyl methyl sulfide (DodSMe) can be readily used as an odourless replacement for the more traditional *n*-butyl methyl sulfide in Pauson–Khand processes.[14] Based on all of these, we proposed that addition of alkyl methyl sulfides to Dötz reaction mixtures could lead to positive promotional effects and we now report on our attempts to formulate further enhanced benzannulation protocols of this class.

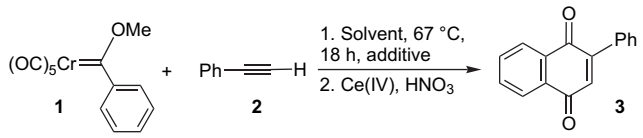
2. Results and discussion

2.1. Exploring the use of a sulfide additive in the Dötz benzannulation process

As part of this programme, a model reaction was firstly selected on which to base the initial studies. Due to the robust nature of the phenyl methoxy carbene **1**, this complex was chosen for reaction with commercially available phenylacetylene **2**; in all reactions performed, oxidative work-up, with ceric ammonium nitrate (Ce(IV)) to produce the naphthoquinone product was applied as standard. As can be seen from Table 1 (Entry 1), reaction in THF produced a good yield of the benzannulation product **3**; this 80% yield, following standard reflux conditions in THF under an atmosphere of nitrogen, is in line with that achieved by Wulff (67%) using optimised conditions in degassed THF under argon at 45 °C.[5a,15]

Investigations into the use of the odourless sulfide, DodSMe, as an additive were then initiated. This preliminary study was performed in three different reaction solvents: THF, *n*-Bu_2O and 1,2-DCE. The ethereal solvents, THF and *n*-Bu_2O, are commonly utilised to provide optimal yields in Dötz benzannulation reactions,[4,5] whilst 1,2-DCE is the solvent of choice for the DodSMe-promoted Pauson–Khand reaction.[14] At the outset, in each case and in line with that employed in our previous studies, 3 equiv of the sulfide promoter was used. As can be seen from Table 1, in every instance the sulfide additive had a detrimental effect on the isolated yield of the naphthoquinone product.

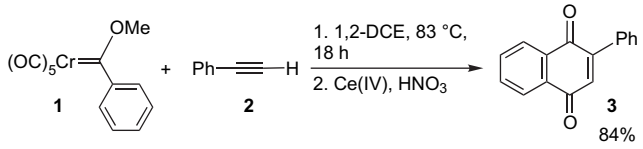
Table 1
Initial benzannulation reactions probing sulfide additive effects



Entry	Solvent	DodSMe (equiv)	Yield[a] (%)
1	THF	0	80
2	THF	3	58
3	*n*-Bu_2O	0	35
4	*n*-Bu_2O	3	22
5	1,2-DCE	0	77
6	1,2-DCE	3	50

[a] Isolated yield.

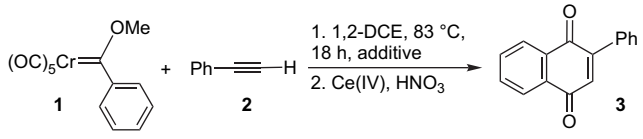
Despite these disappointing outcomes with the chosen sulfide additive, the potential for the use of 1,2-DCE as an effective reaction solvent was noted (Entry 5, Table 1). Consequently, an annulation was attempted at the higher reflux temperature of 1,2-DCE (83 °C). As shown in Scheme 2, an elevated yield of 84% was obtained, which compared favourably with the equivalent and previously described process in THF.



Scheme 2. 1,2-DCE as an effective Dötz benzannulation solvent.

At this stage and undeterred by the results displayed in Table 1, a marginally more extended investigation into the sulfide additive methods was considered appropriate. Based on the promising use of 1,2-DCE, as shown in Scheme 2, this solvent was used as the basis for a sulfide additive equivalent study. From the results displayed in Table 2, it is again clear that

Table 2
Benzannulation reactions with increasing sulfide additive levels



Entry	DodSMe (equiv)	Yield[a] (%)
1	0	84
2	1	80
3	2	77
4	3	53
5	5	48

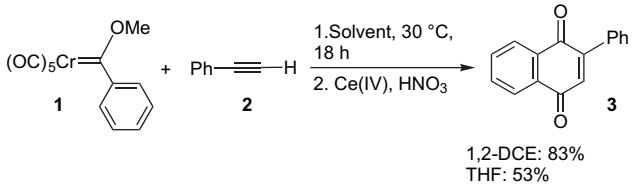
[a] Isolated yield.

the sulfide additive has a (progressively) negative impact on the benzannulation reaction outcomes.

2.2. Probing the potential of 1,2-DCE as a promoting solvent in Dötz benzannulations

From the results accumulated to this stage, it was apparent that the use of the sulfide additive was hindering rather than promoting the desired carbene-mediated cyclisations. Having stated this, the potential for 1,2-DCE to act as an effective solvent, which could enhance the efficiency of Dötz benzannulations, had started to emerge. In this regard and to probe the scope of 1,2-DCE as an annulation promoting solvent, lower temperature processes were explored. Initially and in line with previously published studies,[5a] reactions were performed at 45 °C, with THF being used as a comparator. Pleasingly, when 1,2-DCE was used at this lower temperature the efficiency of the benzannulation process was almost equivalent to that at 83 °C and an excellent 79% yield of the naphthoquinone product resulted (Entry 2, Table 3). By comparison, the reaction performed in THF was considerably less effective (Entry 3). Somewhat disappointingly, when 1,2-DCE was employed at room temperature, the reaction yield was significantly reduced to 32% (Entry 4), with no increase being observed over a longer reaction period of 72 h in the same solvent (Entry 5). Despite this, once again, the reaction run in THF at room temperature led to a significantly lower yield (Entry 6) than that obtained with 1,2-DCE.

At this stage, it should be pointed out that the laboratory (room) temperature during the studies detailed above was in the range 14–17 °C, i.e., somewhat lower than the 20–25 °C commonly regarded as room temperature. Based on this, it was envisaged that gentle warming of the reaction mixture might be beneficial. In order to investigate this, a simple study was performed at 30 °C with 1,2-DCE and THF as solvents (Scheme 3). Remarkably, in 1,2-DCE an excellent 83% yield of benzannulated product **3** was obtained (cf. 53% in THF). Taking into account that intermolecular Dötz annulations normally require moderate to high temperatures in order to produce high yields of cyclisation products, this 1,2-DCE process at 30 °C constitutes an appreciable and encouraging practical advance in this area, with the desired process being achieved successfully and efficiently at near ambient temperature without the aid of mechanical promotion.[10b]



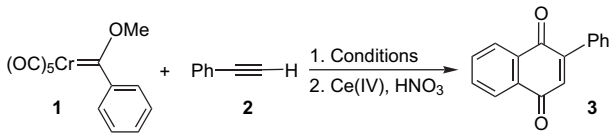
Scheme 3. Effective Dötz benzannulation at near ambient temperature.

2.3. Establishing the scope of low temperature Dötz benzannulations in 1,2-DCE

To test the more general effectiveness of the developing low temperature benzannulation protocol in 1,2-DCE, a range of reactions between a series of carbene complexes and alkyne substrates were probed. The first set of reactions performed used the phenyl carbene **1**, as shown in Table 4. As can be seen, excellent yields were obtained from the reactions involving each of the terminal alkynes (Entries 1 and 3). The moderate yield of naphthoquinone from diphenylacetylene (Entry 2) could be attributed to the greater steric hindrance around this alkyne.

The second series of reactions were performed employing the generally less robust cyclohexenyl carbene **6** (Table 5). As with complex **1**, excellent yields were obtained for the reactions involving both terminal alkynes (Entries 1 and 3).

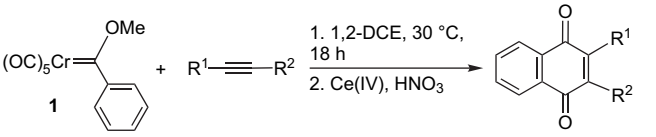
Table 3
Solvent examination over a range of benzannulation reaction temperatures



Entry	Solvent	Temp (°C)	Time (h)	Yield[a] (%)
1	1,2-DCE	83	18	84
2	1,2-DCE	45	18	79
3	THF	45	18	65
4	1,2-DCE	rt	18	32
5	1,2-DCE	rt	72	32
6	THF	rt	18	16

[a] Isolated yield.

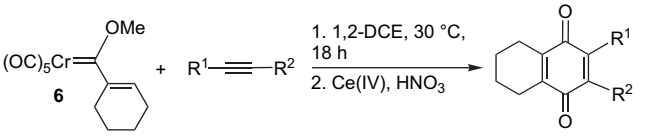
Table 4
Low temperature use of phenyl carbene complex **1** with alkynes in 1,2-DCE



Entry	R^1	R^2	Product	Yield[a] (%)
1	Ph	H	**3**	83
2	Ph	Ph	**4**	53
3	*n*-Bu	H	**5**	82

[a] Isolated yield.

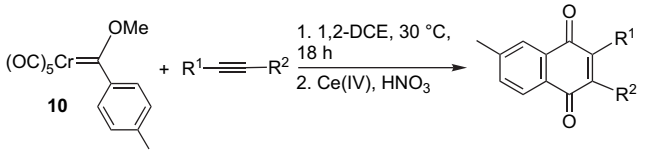
Table 5
Low temperature use of cyclohexenyl carbene complex **6** with alkynes in 1,2-DCE



Entry	R^1	R^2	Product	Yield[a] (%)
1	Ph	H	**7**	92
2	Ph	Ph	**8**	55
3	*n*-Bu	H	**9**	80

[a] Isolated yield.

Table 6
Low temperature use of *p*-tolyl carbene complex **10** with alkynes in 1,2-DCE



Entry	R^1	R^2	Product	Yield[a] (%)
1	Ph	H	**11**	65
2	Ph	Ph	**12**	38
3	*n*-Bu	H	**13**	42

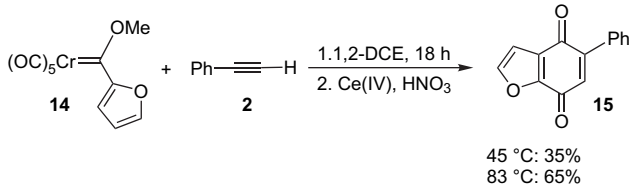
[a] Isolated yield.

Once again, a more moderate yield was obtained for the internal alkyne (Entry 2).

It has previously been shown that Dötz benzannulation reactions carried out with the *p*-tolyl carbene **10** generally tend to be lower yielding than reactions carried out with the equivalent phenyl complex.[4,5c,11] This trend was, indeed, observed using the methodology developed here (Table 6). Despite this, good to moderate yields of the naphthoquinone products were obtained under what are considered to be remarkably mild conditions for such intermolecular annulations, and with excellent levels of regioselection.

The results obtained from the reactions involving the phenyl **1**, cyclohexenyl **6** and *p*-tolyl **10** carbene complexes pleasingly demonstrated that our optimised conditions were successful for a range of Dötz benzannulations at near ambient temperature. The next series of reactions to be performed involved the traditionally less effective 2-furyl carbene **14**.[4,5b,c,11] Disappointingly, only very modest yields resulted from the use of this heteroaryl complex (Table 7), clearly demonstrating that the developed protocols with 1,2-DCE are not compatible with all carbenes at such low reaction temperatures.

Undeterred by the poor reactivity of this complex, a further series of reactions was investigated in order to ascertain whether an increase in temperature in 1,2-DCE would result in higher yields with the 2-furyl carbene **14**. As shown in Scheme 4, using phenylacetylene as the alkyne substrate, a significantly increased, yet still moderate, 35% yield was obtained at 45 °C, whilst a considerably more respectable yield of 65% was obtained at 83 °C in 1,2-DCE with the same alkyne.

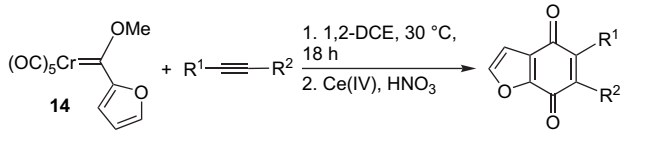


Scheme 4. Benzannulation with the 2-furyl carbene complex **14** at more elevated temperatures.

Based on these positive outcomes in refluxing 1,2-DCE, reactions with the remaining alkynes were performed under similar conditions. As shown in Table 8, when compared to the yields at 30 °C (3–9%), a significant increase in reaction efficiency was recorded with the three alkyne substrates employed to this stage. In this regard, the outcome of the reaction between the 2-furyl carbene **14** and the sterically encumbered internal alkyne (entry 2) was particularly noteworthy. It had been observed from our studies thus far that, with each of the previously employed complexes, the lowest yields had been obtained with diphenylacetylene. In contrast, with complex **14** this alkyne substrate had clearly delivered the most efficient cyclisation. Interestingly, this reactivity trend with the 2-furyl carbene **14**, whereby higher yields are obtained from more encumbered internal alkynes, has been noted previously both in seminal studies by Wulff[5b] and from work within our own laboratory.[11] Overall and from that shown in Table 8, the 2-furyl complex **14** could now be applied effectively with a series of alkyne substrates with 1,2-DCE as the reaction solvent.

From the results obtained so far, other than with the 2-furyl carbene complex **14**, the yields from reactions involving diphenylacetylene had been somewhat lower than those resulting from the terminal alkynes which had been investigated. As mentioned previously, this lowered reactivity profile with the internal diaryl alkyne is attributed to the increased steric hindrance around the key triple bond within this substrate. To investigate this further, a set of reactions using a less encumbered internal alkyne were performed to ascertain if this would result in an increase in the observed cyclisation yields. In this regard, 3-hexyne **18** was selected as a less sterically demanding internal alkyne and annulations attempted with the four carbene complexes used to this stage in this study.

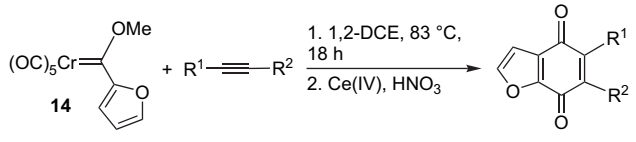
Table 7
Low temperature use of 2-furyl carbene complex **14** with alkynes in 1,2-DCE



Entry	R^1	R^2	Product	Yield[a] (%)
1	Ph	H	**15**	5
2	Ph	Ph	**16**	3
3	*n*-Bu	H	**17**	9

[a] Isolated yield.

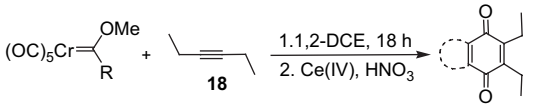
Table 8
Dötz benzannulation reactions with 2-furyl carbene complex **14** in 1,2-DCE at 83 °C



Entry	R^1	R^2	Product	Yield[a] (%)
1	Ph	H	**15**	65
2	Ph	Ph	**16**	88
3	*n*-Bu	H	**17**	56

[a] Isolated yield.

Table 9
Dötz benzannulation reactions of internal alkyne **18** in 1,2-DCE



Entry	R	Temp (°C)	Product	Yield[a] (%)
1	Ph **1**	30	**19**	72
2	1-Cyclohexenyl **6**	30	**20**	65
3	*p*-Tolyl **10**	30	**21**	69
4	2-Furyl **14**	83	**22**	71

[a] Isolated yield.

Reactions with phenyl **1**, cyclohexenyl **6** and *p*-tolyl **10** complexes were all carried out at 30 °C; the reaction with 2-furyl carbene **14** was performed at 83 °C (Table 9). Pleasingly, in most cases the observed yields were appreciably greater than those obtained with diphenylacetylene. The 72% yield for the reaction with phenyl carbene **1** showed a significant improvement over the 53% yield previously obtained with diphenylacetylene. This trend was mirrored by the results from the reactions involving the cyclohexenyl complex **6** (65% cf. 55%), and the *p*-tolyl carbene **10** (69% cf. 38%). In contrast, the 71% yield with the 2-furyl complex **14**, despite being more than acceptable for a process with such a heteroaryl carbene, was lower than the 88% yield obtained with diphenylacetylene. This result, again, fits with the pattern that lower yields seem to be obtained with the 2-furyl carbene when more accessible alkynes are employed.

It should also be noted at this stage that, in attempts to obtain higher yields from the annulation processes involving diphenylacetylene and the non-heteroaryl complexes, reactions were performed with the phenyl carbene **1** and this diaryl alkyne at more elevated temperatures. Unfortunately, runs at 50 °C and 83 °C failed to deliver yields that were greater than the 53% achieved between these substrates at 30 °C (see, Table 4, Entry 2).

2.4. Rationalisation of 1,2-DCE as a promoting solvent for Dötz benzannulation processes

The possibility of using 1,2-DCE as the reaction solvent in order to perform intermolecular Dötz benzannulations with such levels of efficiency, especially at relatively low temperatures, was unexpected and intriguing. In this regard, despite the role of this solvent not currently being well defined, it is suggested that 1,2-DCE could act as a bidentate ligand within the reaction manifold and, in turn, could serve to stabilise coordinatively unsaturated chromium species which occur along the mechanistic pathway, following the initial decarbonylation step. If 1,2-DCE was to act in this fashion, it is envisaged that such a ligating species would be readily displaced to allow the continuation of the desired annulation reaction process. This rationalisation is analogous to that proposed by Boger,[8] who postulated that acetic anhydride was acting as a similar bidentate ligand which serves to stabilise metal-based intermediates in such carbene-mediated annulation processes. In further support of (reversible) halide ligation, Guerchais has shown how chelate chloro coordination stabilises an iron carbene complex, whilst being sufficiently labile to allow further reaction at the iron centre following ready dissociation.[16] In addition, Nayak and Burkey have described how 1,2-DCE can be employed in effective CO photodissociation processes with $Cr(CO)_6$, with the rationalisation being that solvent coordination with the resulting $Cr(CO)_5$ inhibits re-association of CO, prior to reaction of the pentacarbonylchromium unit with added ligand.[17] As stated above, loss of CO from the starting carbene complex is believed to be the first step in the Dötz benzannulation.[12]

With respect to the lack of success of the sulfide additive in the benzannulation processes attempted, it has been widely assumed that the role of such Lewis base promoters in the Pauson–Khand reaction is to facilitate CO ligand loss from the requisite parent and intermediate cobalt complexes.[18] However, a recent publication has proposed that the root of Lewis base promotion within such Pauson–Khand processes is not centred around the mediation of CO extrusion.[19] This theoretical study has concluded that such Lewis base promoters actually serve to confer irreversibility on the key alkene insertion process within Pauson–Khand annulations and, hence, drive the reaction process forward. Based on this more recent observation and with no directly equivalent olefin insertion step present within the Dötz reaction pathway, it is perhaps not so surprising that Lewis basic sulfide additives do not serve to promote this class of metal carbene-mediated benzannulation process.

3. Conclusions

The initial proposal, to develop a sulfide-promoted Dötz benzannulation process, proved to be unsuccessful. However, it became apparent that 1,2-DCE was acting to promote the desired cyclisation reactions and, consequently, our focus turned to developing conditions for use with this readily accessible solvent. Following optimisation, reaction conditions have now been formulated which allow intermolecular Dötz benzannulations to be performed under remarkably mild low temperature conditions and without the requirement for any further reaction promoters. This methodology has been applied to a series of substrates to successfully deliver the products of Dötz annulation in generally good to excellent yields.

4. Experimental

4.1. General experimental methods

All reagents were obtained from commercial suppliers and used without further purification, unless otherwise stated. Tetrahydrofuran and ether were dried by heating to reflux over sodium wire, using benzophenone ketyl as an indicator, then distilled under nitrogen. 1,2-DCE was dried by heating to reflux over calcium hydride and then distilled under nitrogen. Petroleum ether was distilled prior to use and refers to

fractions boiling between 30 and 40 °C. *n*-Bu_2O, 1-hexyne and phenylacetylene were purified by distillation under nitrogen. Fischer carbene complexes **1**,[20] **6**,[6c,21] **10**[20] and **14**[5b,22] were readily synthesised by published methods. Flash chromatography was carried out using Prolabo silica gel (230–400 mesh). IR spectra were obtained on a Perkin Elmer Spectrum 1 machine. ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz or a Joel Ex 270 MHz spectrometer at 270 MHz. ^{13}C NMR spectra were recorded on a Bruker DPX 400 spectrometer at 100 MHz. Chemical shifts are reported in parts per million. Coupling constants are reported in hertz and refer to $^3J_{H-H}$ interactions unless otherwise specified. Accurate mass measurements were performed at the University of Wales, Swansea using a Finnigan MAT 95XP high resolution double focusing mass spectrometer.

4.2. Preparation of dodecylmethylsulfide[23]

To a stirred suspension of K_2CO_3 (15.01 g, 108.6 mmol) in DMF (60 mL), cooled to 0 °C in an ice-water bath, was added a solution of MeI (6.46 mL, 103.8 mmol) and dodecanethiol (23.67 mL, 98.8 mmol) in DMF (20 mL), via cannula. The resulting mixture was stirred at room temperature for 18 h. The reaction mixture was filtered and HCl (1 M, 50 mL) was slowly added. Distilled water (50 mL) was then added, followed by EtOAc (50 mL). The organic layer was separated and washed with water (5×50 mL). The organic layer was washed with sodium thiosulfate solution (1×30 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude reaction product was purified by distillation (bp=162–164 °C at 18 mmHg) to afford the desired product as a colourless oil (19.85 g, 93%). FTIR (CH_2Cl_2): 2927, 2855 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (t, J=7.4 Hz, 2H, SCH_2), 2.10 (s, 3H, SCH_3), 1.60 (quintet, J=7.4 Hz, 2H, CH_2), 1.43–1.21 (m, 18H, CH_2), 0.89 (t, J=6.8 Hz, 3H, CH_3).

4.3. General procedures

4.3.1. General procedure A—Dötz benzannulation reaction

To a stirred solution of chromium carbene complex in the reaction solvent under an atmosphere of N_2, was added the alkyne. The reaction vessel was fitted with a reflux condenser, if necessary, and the reaction mixture warmed to the appropriate temperature for the time stated. The reaction mixture was then cooled and was added to a solution of ceric ammonium nitrate (CAN) in HNO_3 (0.1 M). The resulting solution was stirred for 30 min before being extracted with ether. The organic extracts were combined, washed with water, dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash chromatography (eluent: 1:11 ether in petroleum ether).

Following *general procedure A*, data are reported as (a) alkyne, (b) chromium carbene complex, (c) solvent, (d) reaction temperature, (e) reaction time, (f) quantity of CAN, (g) quantity of HNO_3 and (h) product yield.

4.3.2. General procedure B—Dötz benzannulation reaction with DodSMe additive

To a stirred solution of chromium carbene complex in the reaction solvent under an atmosphere of N_2, were added the alkyne and DodSMe, sequentially. The reaction vessel was fitted with a reflux condenser, if necessary, and the reaction mixture was warmed to the appropriate temperature for the time stated. The reaction mixture was then cooled and was added to a solution of CAN in HNO_3 (0.1 M). The resulting solution was stirred for 30 min before being extracted with ether. The organic extracts were combined, washed with water, dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash chromatography (eluent: 1:11 ether in petroleum ether).

Following *general procedure B*, data are reported as (a) alkyne, (b) DodSMe, (c) chromium carbene complex, (d) solvent, (e) reaction temperature, (f) reaction time, (g) quantity of CAN, (h) quantity of HNO_3 and (i) product yield.

4.4. 2-Phenyl-1,4-naphthoquinone, 3[5a]

Following general procedure A:

Reaction carried out in THF at 67 °C: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c) THF, 5 mL, (d) 67 °C, (e) 18 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 60 mg, 80%.

Reaction carried out in n-Bu_2O at 67 °C: (a) phenylacetylene **2**, 138 μL, 1.26 mmol, (b) carbene **1**, 250 mg, 0.8 mmol, (c) *n*-Bu_2O, 5 mL, (d) 67 °C, (e) 18 h, (f) 3.180 g, 5.8 mmol, (g) 11 mL and (h) **3**, 66 mg, 35%.

Reaction carried out in 1,2-DCE at 67 °C: (a) phenylacetylene **2**, 138 μL, 1.26 mmol, (b) carbene **1**, 250 mg, 0.8 mmol, (c) 1,2-DCE, 5 mL, (d) 67 °C, (e) 18 h, (f) 3.180 g, 5.8 mmol, (g) 11 mL and (h) **3**, 144 mg, 77%.

Reaction carried out in 1,2-DCE at 83 °C: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c) 1,2-DCE, 5 mL, (d) 83 °C, (e) 18 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 63 mg, 84%.

Reaction carried out in 1,2-DCE at 45 °C: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c) 1,2-DCE, 5 mL, (d) 45 °C, (e) 18 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 59 mg, 79%.

Reaction carried out in THF at 45 °C: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c) THF, 5 mL, (d) 45 °C, (e) 18 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 49 mg, 65%.

Reaction carried out in 1,2-DCE at rt over 18 h: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c) 1,2-DCE, 5 mL, (d) rt, (e) 18 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 24 mg, 32%.

Reaction carried out in 1,2-DCE at rt over 72 h: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c) 1,2-DCE, 5 mL, (d) rt, (e) 72 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 24 mg, 32%.

Reaction carried out in THF at rt: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c)

THF, 5 mL, (d) rt, (e) 18 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 12 mg, 16%.

Reaction carried out in 1,2-DCE at 30 °C: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c) 1,2-DCE, 5 mL, (d) 30 °C, (e) 18 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 62 mg, 83%.

Reaction carried out in THF at 30 °C: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) carbene **1**, 100 mg, 0.32 mmol, (c) THF, 5 mL, (d) 30 °C, (e) 18 h, (f) 1.272 g, 2.32 mmol, (g) 11 mL and (h) **3**, 40 mg, 53%.

Following the Wulff-based process[5a,b] using freeze–thaw degassed THF in a sealed tube at 75 °C; see, Ref. 15.

To a stirred solution of carbene **1** (250 mg. 0.8 mmol) in dry THF (5 mL) was added phenylacetylene **2** (138 μL, 1.26 mmol). The solution was degassed by the freeze–thaw method (−196 °C to 25 °C; three cycles). The reaction vessel was placed under an atmosphere of N_2 and heated to 75 °C for 18 h in a one-necked flask fitted with a threaded vacuum stopcock. After this time, the reaction mixture was cooled and was added to a solution of CAN (3.18 g, 5.8 mmol) in HNO_3 (0.1 M, 11 mL). The solution was stirred for 30 min and then extracted with ether (3×20 mL). The ether extracts were combined, washed with water (3×20 mL), dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash chromatography (eluent: 1:11 ether in petroleum ether) to afford the desired product **3** (133 mg, 71%).

Following general procedure B:

Reaction carried out in THF at 67 °C with 3 equiv of DodSMe: (a) phenylacetylene **2**, 138 μL, 1.26 mmol, (b) 636 μL, 2.4 mmol, (c) carbene **1**, 250 mg, 0.8 mmol, (d) THF, 5 mL, (e) 67 °C, (f) 18 h, (g) 3.180 g, 5.8 mmol, (h) 11 mL and (i) **3**, 108 mg, 58%.

Reaction carried out in n-Bu_2O at 67 °C with 3 equiv of DodSMe: (a) phenylacetylene **2**, 138 μL, 1.26 mmol, (b) 636 μL, 2.4 mmol, (c) carbene **1**, 250 mg, 0.8 mmol, (d) *n*-Bu_2O, 5 mL, (e) 67 °C, (f) 18 h, (g) 3.180 g, 5.8 mmol, (h) 11 mL and (i) **3**, 41 mg, 22%.

Reaction carried out in 1,2-DCE at 67 °C with 3 equiv of DodSMe: (a) phenylacetylene **2**, 138 μL, 1.26 mmol, (b) 636 μL, 2.4 mmol, (c) carbene **1**, 250 mg, 0.8 mmol, (d) 1,2-DCE, 5 mL, (e) 67 °C, (f) 18 h, (g) CAN, 3.180 g, 5.8 mmol, (h) 11 mL and (i) **3**, 94 mg, 50%.

Reaction carried out in 1,2-DCE at 83 °C with 1 equiv of DodSMe: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) 85 μL, 0.32 mmol, (c) carbene **1**, 100 mg, 0.32 mmol, (d) 1,2-DCE, 5 mL, (e) 83 °C, (f) 18 h, (g) 1.272 g, 2.32 mmol, (h) 11 mL and (i) **3**, 60 mg, 80%.

Reaction carried out in 1,2-DCE at 83 °C with 2 equiv of DodSMe: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) 170 μL, 0.64 mmol, (c) carbene **1**, 100 mg, 0.32 mmol, (d) 1,2-DCE, 5 mL, (e) 83 °C, (f) 18 h, (g) 1.272 g, 2.32 mmol, (h) 11 mL and (i) **3**, 58 mg, 77%.

Reaction carried out in 1,2-DCE at 83 °C with 3 equiv of DodSMe: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) 254 μL, 0.96 mmol, (c) carbene **1**, 100 mg, 0.32 mmol, (d) 1,2-DCE, 5 mL, (e) 83 °C, (f) 18 h, (g) 1.272 g, 2.32 mmol, (h) 11 mL and (i) **3**, 40 mg, 53%.

Reaction carried out in 1,2-DCE at 83 °C with 5 equiv of DodSMe: (a) phenylacetylene **2**, 55 μL, 0.5 mmol, (b) 424 μL, 1.6 mmol, (c) carbene **1**, 100 mg, 0.32 mmol, (d) 1,2-DCE, 5 mL, (e) 83 °C, (f) 18 h, (g) 1.272 g, 2.32 mmol, (h) 11 mL and (i) **3**, 36 mg, 48%.

Yellow solid. Mp 108–110 °C. FTIR (CH_2Cl_2): 1666, 1598 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.22–8.12 (m, 2H), 7.81–7.77 (m, 2H), 7.60–7.57 (m, 2H), 7.50–7.47 (m, 3H), 7.10 (s, 1H).

4.5. 2,3-Diphenyl-1,4-naphthoquinone, **4**[5a]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) diphenylacetylene, 178 mg, 1 mmol, (b) carbene **1**, 200 mg, 0.64 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.544 g, 4.64 mmol, (g) 11 mL and (h) **4**, 104 mg, 53%.

Reaction carried out in 1,2-DCE at 50 °C: (a) diphenylacetylene, 187 mg, 1.05 mmol, (b) carbene **1**, 210 mg, 0.67 mmol, (c) 1,2-DCE, 10 mL, (d) 50 °C, (e) 18 h, (f) 2.664 g, 4.86 mmol, (g) 11 mL and (h) **4**, 103 mg, 50%.

Reaction carried out in 1,2-DCE at 83 °C: (a) diphenylacetylene, 185 mg, 1.04 mmol, (b) carbene **1**, 206 mg, 0.66 mmol, (c) 1,2-DCE, 10 mL, (d) 83 °C, (e) 18 h, (f) 2.626 g, 4.79 mmol, (g) 11 mL and (h) **4**, 88 mg, 43%.

Yellow solid. Mp 134–135 °C. FTIR (CH_2Cl_2): 1664, 1597 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.24–8.19 (m, 2H), 7.82–7.78 (m, 2H,), 7.28–7.21 (m, 6H), 7.14–7.09 (m, 4H).

4.6. 2-Butyl-1,4-naphthoquinone, **5**[24]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) 1-hexyne, 115 μL, 1 mmol, (b) carbene **1**, 200 mg, 0.64 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.544 g, 4.64 mmol, (g) 11 mL and (h) **5**, 98 mg, 82%.

Yellow oil. FTIR (CH_2Cl_2): 1664, 1596 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.13–8.04 (m, 2H), 7.76–7.71 (m, 2H), 6.80 (t, $^4J_{H-H}$=1.2 Hz, 1H), 2.59 (td, J=7.6 Hz, $^4J_{H-H}$= 1.2 Hz, 2H), 1.58 (quintet, J=7.6 Hz, 2H), 1.44 (sextet, J=7.3 Hz, 2H), 0.97 (t, J=7.3 Hz, 3H).

4.7. 5,6,7,8-Tetrahydro-2-phenyl-1,4-naphthoquinone, **7**[11]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) phenylacetylene **2**, 122 μL, 1.11 mmol, (b) carbene **6**, 224 mg, 0.71 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.878 g, 5.15 mmol, (g) 11 mL and (h) **7**, 155 mg, 92%.

Yellow solid. Mp 57–58 °C. FTIR (CH_2Cl_2): 1651, 1605 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.42 (m, 5H), 6.79 (s, 1H), 2.51–2.49 (m, 4H), 1.77–1.73 (m, 4H).

4.8. 5,6,7,8-Tetrahydro-2,3-diphenyl-1,4-naphthoquinone, **8**

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) diphenylacetylene, 196 mg, 1.1 mmol, (b) carbene **6**, 220 mg, 0.70 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.785 g, 5.08 mmol, (g) 11 mL and (h) **8**, 120 mg, 55%.

Yellow/orange solid. Mp 166–168 °C. FTIR (CH_2Cl_2): 1650, 1606 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.25 (m, 6H), 7.09–7.06 (m, 4H), 2.63–2.60 (m, 4H), 1.86–1.82 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 143.2, 142.5, 133.3, 130.8, 128.3, 127.8, 23.1, 21.4. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%. Found: C, 84.05; H, 5.54%. High resolution mass spectrum (EI) *m/z*: 314.1298; $C_{22}H_{18}O_2$ ($[M]^+$) requires 314.1301.

4.9. 2-Butyl-5,6,7,8-tetrahydro-1,4-naphthoquinone, **9**[25]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) 1-hexyne, 132 μL, 1.15 mmol, (b) carbene **6**, 230 mg, 0.73 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.9 g, 5.29 mmol, (g) 11 mL and (h) **9**, 125 mg, 80%.

Brown oil. FTIR (CH_2Cl_2): 1650, 1615 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.47 (t, $^4J_{H-H}$=1.4 Hz, 1H), 2.42–2.38 (m, 6H), 1.69–1.68 (m, 4H), 1.51–1.44 (m, 2H), 1.42–1.33 (m, 2H), 0.93 (t, *J*=7.2 Hz, 3H).

4.10. 7-Methyl-2-phenyl-1,4-naphthoquinone, **11**[26]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) phenylacetylene **2**, 105 μL, 0.96 mmol, (b) carbene **10**, 200 mg, 0.61 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.423 g, 4.42 mmol, (g) 11 mL and (h) **11**, 98 mg, 65%.

Yellow solid. Mp 101–102 °C. FTIR (CH_2Cl_2): 1659, 1603 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 8.08–7.47 (m, 8H), 7.03 (s, 1H), 2.52 (s, 3H).

4.11. 6-Methyl-2,3-diphenyl-1,4-naphthoquinone, **12**[9a]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) diphenylacetylene, 171 mg, 0.96 mmol, (b) carbene **10**, 200 mg, 0.61 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.423 g, 4.42 mmol, (g) 11 mL and (h) **12**, 75 mg, 38%.

Yellow solid. Mp 107–109 °C. FTIR (CH_2Cl_2): 1664, 1603 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 8.11–7.06 (m, 13H), 2.55 (s, 3H).

4.12. 2-Butyl-7-methyl-1,4-naphthoquinone, **13**[27]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) 1-hexyne, 110 μL, 0.96 mmol, (b) carbene **10**, 200 mg, 0.61 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.423 g, 4.42 mmol, (g) 11 mL and (h) **13**, 58 mg, 42%.

Brown oil. FTIR (CH_2Cl_2): 1664, 1603 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.95 (d, *J*=7.8 Hz, 1H), 7.89 (s, 1H), 7.52 (dd, *J*=7.9 Hz, $^4J_{H-H}$=1.0 Hz, 1H), 6.75 (t, $^4J_{H-H}$=1.3 Hz, 1H), 2.56 (td, *J*=7.6 Hz, $^4J_{H-H}$=1.2 Hz, 2H), 2.50 (s, 3H), 1.62–1.51 (m, 2H), 1.49–1.35 (m, 2H), 0.96 (t, *J*=7.2 Hz, 3H).

4.13. 5-Phenylbenzo[b]furan-4,7-dione, **15**[6i]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) phenylacetylene **2**, 114 μL, 1.04 mmol, (b) carbene **14**, 200 mg, 0.66 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.626 g, 4.79 mmol, (g) 11 mL and (h) **15**, 7 mg, 5%.

Reaction carried out in 1,2-DCE at 45 °C: (a) phenylacetylene **2**, 57 μL, 0.52 mmol, (b) carbene **14**, 100 mg, 0.33 mmol, (c) 1,2-DCE, 5 mL, (d) 45 °C, (e) 18 h, (f) 1.311 g, 2.39 mmol, (g) 11 mL and (h) **15**, 26 mg, 35%.

Reaction carried out in 1,2-DCE at 83 °C: (a) phenylacetylene **2**, 57 μL, 0.52 mmol, (b) carbene **14**, 100 mg, 0.33 mmol, (c) 1,2-DCE, 5 mL, (d) 83 °C, (e) 18 h, (f) 1.311 g, 2.39 mmol, (g) 11 mL and (h) **15**, 48 mg, 65%.

Yellow/orange solid. Mp 145–147 °C. FTIR (CH_2Cl_2): 1670, 1567, 1371 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J*=1.8 Hz, 1H), 7.52–7.44 (m, 5H), 6.94 (d, *J*=1.8 Hz, 1H), 6.81 (s, 1H).

4.14. 5,6-Diphenylbenzo[b]furan-4,7-dione, **16**[9a]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) diphenylacetylene, 185 mg, 1.04 mmol, (b) carbene **14**, 200 mg, 0.66 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.626 g, 4.79 mmol, (g) 11 mL and (h) **16**, 6 mg, 3%.

Reaction carried out in 1,2-DCE at 83 °C: (a) diphenylacetylene, 185 mg, 1.04 mmol, (b) carbene **14**, 200 mg, 0.66 mmol, (c) 1,2-DCE, 10 mL, (d) 83 °C, (e) 18 h, (f) 2.626 g, 4.79 mmol, (g) 11 mL and (h) **16**, 175 mg, 88%.

Orange solid. Mp 170–171 °C. FTIR (CH_2Cl_2): 1670, 1598, 1360 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J*=1.7 Hz, 1H), 7.23–7.21 (m, 6H), 7.05–7.02 (td, *J*=6.8 Hz, $^4J_{H-H}$=1.9 Hz, 4H), 6.96 (d, *J*=1.7 Hz, 1H).

4.15. 5-Butylbenzo[b]furan-4,7-dione, **17**[28]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) 1-hexyne, 119 μL, 1.04 mmol, (b) carbene **14**, 200 mg, 0.66 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.626 g, 4.79 mmol, (g) 11 mL and (h) **17**, 12 mg, 9%.

Reaction carried out in 1,2-DCE at 83 °C: (a) 1-hexyne, 119 μL, 1.04 mmol, (b) carbene **14**, 200 mg, 0.66 mmol, (c) 1,2-DCE, 10 mL, (d) 83 °C, (e) 18 h, (f) 2.626 g, 4.79 mmol, (g) 11 mL and (h) **17**, 75 mg, 56%.

Yellow oil. FTIR (CH_2Cl_2): 1659, 1608, 1370 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J=1.8 Hz, 1H), 6.84 (d, J=1.8 Hz, 1H), 6.49 (t, $^4J_{H-H}$=1.3 Hz, 1H), 2.50 (td, J=7.6 Hz, $^4J_{H-H}$=1.3 Hz, 2H), 1.57–1.49 (m, 2H), 1.45–1.36 (m, 2H), 0.95 (t, J=7.3 Hz, 3H).

4.16. 2,3-Diethyl-1,4-naphthoquinone, **19**[5a]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) 3-hexyne **18**, 115 μL, 1 mmol, (b) carbene **1**, 200 mg, 0.64 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.544 g, 4.64 mmol, (g) 11 mL and (h) **19**, 112 mg, 72%.

Yellow solid. Mp 64–66 °C. FTIR (CH_2Cl_2): 1659, 1596 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.11–8.07 (m, 2H), 7.72–7.68 (m, 2H), 2.66 (q, J=7.5 Hz, 4H), 1.17 (t, J=7.5 Hz, 6H).

4.17. 2,3-Diethyl-5,6,7,8-tetrahydro-1,4-naphthoquinone, **20**[29]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) 3-hexyne **18**, 113 μL, 0.99 mmol, (b) carbene **6**, 200 mg, 0.63 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.505 g, 4.57 mmol, (g) 11 mL and (h) **20**, 89 mg, 65%.

Yellow solid. Mp 78–80 °C. FTIR (CH_2Cl_2): 1635 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.49 (q, J=7.5 Hz, 4H), 2.44–2.41 (m, 4H), 1.70–1.67 (m, 4H), 1.08 (t, J=7.5 Hz, 6H).

4.18. 2,3-Diethyl-6-methyl-1,4-naphthoquinone, **21**[27]

Following general procedure A:

Reaction carried out in 1,2-DCE at 30 °C: (a) 3-hexyne **18**, 109 μL, 0.96 mmol, (b) carbene **10**, 200 mg, 0.61 mmol, (c) 1,2-DCE, 10 mL, (d) 30 °C, (e) 18 h, (f) 2.423 g, 4.42 mmol, (g) 11 mL and (h) **21**, 96 mg, 69%.

Yellow solid. Mp 58–59 °C. FTIR (CH_2Cl_2): 1648, 1606 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J=7.9 Hz, 1H), 7.87 (s, 1H), 7.48 (d, J=7.9 Hz, 1H), 2.67–2.62 (m, 4H), 2.48 (s, 3H), 1.17–1.13 (m, 6H).

4.19. 5,6-Diethylbenzo[b]furan-4,7-dione, **22**[5b]

Following general procedure A:

Reaction carried out in 1,2-DCE at 83 °C: (a) 3-hexyne **18**, 131 μL, 1.15 mmol, (b) carbene **14**, 220 mg, 0.73 mmol, (c) 1,2-DCE, 10 mL, (d) 83 °C, (e) 18 h, (f) 2.9 g, 5.29 mmol, (g) 11 mL and (h) **22**, 106 mg, 71%.

Yellow solid. Mp 62–63 °C. FTIR (CH_2Cl_2): 1663, 1578, 1364 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J=1.8 Hz, 1H), 6.82 (d, J=1.8 Hz, 1H), 2.62–2.54 (m, 4H), 1.15–1.10 (m, 6H).

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15. It should be noted that, as part of this programme and by following a Wulff-based process,[5a,b] a 71% yield of naphthoquinone **3** was obtained from reaction of carbene complex **1** and phenylacetylene **2** at 75 °C in a sealed tube under nitrogen with degassed THF (freeze–thaw method; −196 °C to 25 °C; three cycles), and following Ce(IV) work-up. Accordingly, all further reactions within this programme were performed under more standard inert (nitrogen) gas conditions in routinely dried THF (Na, benzophenone ketyl).
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