

Carbon-carbon bond formation and reduction of aldehydes, ketones and acetals with silylated nucleophiles catalysed by tetracyanoethylene

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Tetracyanoethylene catalyses the reactions of aldehydes, ketones and acetals with silylated nucleophiles such as trimethylsilyl cyanide, allyltrimethylsilane, aryl methyl ketone trimethylsilylenol ethers and triethylsilane to promote carbon-carbon bond formation and reduction under neutral conditions. All the evidence strongly suggested that the reactions occur through single electron transfer (SET) mechanism based on UV spectroscopic measurements.

In recent years, a variety of efficient catalysts or promoters have been developed to induce carbon-carbon bond-forming reactions and the reduction of aldehyde, ketone and acetals with silylated nucleophiles.¹ Because most of these catalysts are highly acidic and moisture sensitive, the development of new efficient catalysts which can be easily prepared, handled and used under mild conditions is still of interest. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), a representative one-electron oxidant, has been reported to catalyse alcoholysis of epoxides,^{2a} tetrahydropyranylation of alcohols,^{2b} glycosidation using glycals^{2c} and deprotection of acetals,^{2d} silyl ethers^{2e} and ortho esters.^{2f} In this context, we recently reported that a catalytic amount of tetracyanoethylene (TCNE), a representative π -acid and one-electron acceptor,³ accelerates substrate-specific rearrangement, acetonidation and alkanolysis of epoxides⁴ and Mukaiyama aldol reaction of acetals,⁵ in preliminary communications. Here we disclose full details of the reaction of aldehydes, ketones and acetals with silylated nucleophiles such as trimethylsilyl cyanide (TMS-CN), allyltrimethylsilane (TMS-allyl), aryl methyl ketone TMS-enol ethers and triethylsilane (TES-H) catalysed by TCNE to afford the corresponding adducts or substitution products in high yields under mild and neutral conditions.

Results and discussion

Decanal **1** when heated under reflux with TMS-CN (1.5 equiv.) in MeCN in the presence of a catalytic amount of TCNE (0.2 equiv.) gave the corresponding cyanohydrin **2** in 87% yield after acidic hydrolysis. Similarly, benzaldehyde **3**, octan-2-one **7** and acetophenone **9**, also reacted with TMS-CN to give the corresponding cyanohydrins (**4**, **8**, **10**) in good to high yield under the same conditions. Unexpectedly, TCNE was a poor catalyst for the reaction of these carbonyl compounds with other silylated nucleophiles (TMS-allyl and acetophenone TMS-enol ether), except for the reaction of benzaldehyde **3** with acetophenone TMS-enol ether to give carbon-carbon bond formation (Table 1).

In turn, attention was focused on the reactivities of acetals with silylated nucleophiles. As shown in Table 2, the dimethyl acetals (**11**, **17**, **23**) derived from aryl aldehydes, *p*-anisaldehyde, benzaldehyde and 2-furfuraldehyde, when treated with TMS-CN, TMS-allyl, aryl methyl ketone TMS-enol ethers and TES-H in the presence of a catalytic amount of TCNE afforded the corresponding substitution products (**12-16**, **18-22**, **24-26**) in good yields. In the reaction of *p*-anisaldehyde dimethyl acetal **11** with acetophenone TMS-enol ether, the disubstitution

product **43**, which is obtained by overreaction, was isolated as by-product in 5% yield (entry 3). In the reaction of benzaldehyde dimethyl acetal **17** with acetophenone TMS-enol ether, the adducts (**44**, **45**) of TCNE, acetophenone silyl enol ether and the starting acetal (**17**) or the product (**20**) were isolated as by-products in 2 or 12% yields, respectively (entry 8). These adducts are thought to be formed by reactions involving a nucleophilic substitution of TCNE with the silyl enol ether. The dimethyl acetals (**27**, **32**) derived from α,β -unsaturated aldehydes, *trans*-cinnamaldehyde and *trans*-hex-2-enal, when treated with silylated nucleophiles under the same conditions gave the corresponding substitution products (**28-31**, **33-35**) in good yields. Saturated acetals appear less reactive than α,β -unsaturated ones under the present conditions. Thus, decanal dimethyl acetal **36** can react with TMS-CN and TMS-allyl under same conditions to afford the corresponding substitution products (**37**, **38**) in 87 or 66% yields, respectively, while the reaction of **36** with acetophenone TMS-enol ether afforded the corresponding substitution product (**39**) in only 38% yield, and the starting acetal was recovered in 47% yield. The low reactivity is attributable to the consumption of catalyst TCNE due to nucleophilic attack of silyl enol ether to TCNE. We isolated in 8% yield the adduct (**46**) of TCNE, acetophenone silyl enol ether and decanal dimethyl acetal (**36**). The dimethyl acetal (**40**) derived from octan-2-one can react with TMS-CN or TMS-enol ether to afford the corresponding substitution products (**41**, **42**) in 63 or 55% yield, respectively.

The UV spectroscopic measurement on the mixture of TCNE and decanal dimethyl acetal **36** in MeCN showed significant charge transfer (CT) absorption bands as a shoulder at 285-300

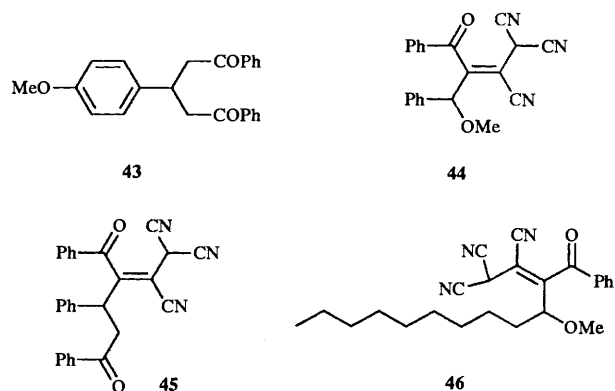

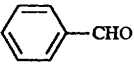
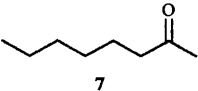
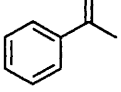
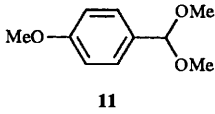
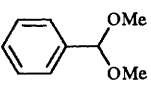
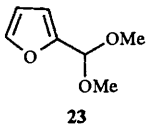
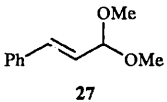
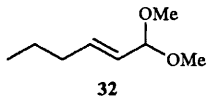
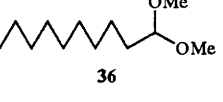
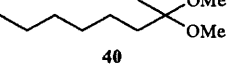


Table 1 The reaction of aldehydes with silylated nucleophiles catalysed by TCNE
$$R,R'C=O \xrightarrow[\text{MeCN, reflux}]{\text{TCNE (0.2 equiv.), TMS-Nu (1.5 equiv.)}} \xrightarrow{3\% \text{ HCl}} R,R'C(\text{OH})\text{Nu}$$

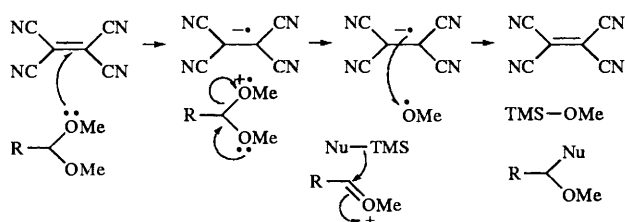
Entry	Aldehyde	TMS-Nu	Time (h)	Product	Yield (%)
1		TMS-CN	1	2 Nu = CN	87
2		TMS-CH ₂ CH=CH ₂	4	No reaction	
3		TMS-O-C(=CH ₂)Ph	4	No reaction	
4		TMS-CN	3	4 Nu = CN	93
5		TMS-CH ₂ CH=CH ₂	4	5 Nu = CH ₂ CH=CH ₂	10 ^a
6		TMS-O-C(=CH ₂)Ph	4	6 Nu = CH ₂ COPh	97
7		TMS-CN	2	8 Nu = CN	87 ^b
8		TMS-CH ₂ CH=CH ₂	4	No reaction	
9		TMS-O-C(=CH ₂)Ph	4	No reaction	
10		TMS-CN	2	10 Nu = CN	74 ^b
11		TMS-CH ₂ CH=CH ₂	4	No reaction	
12		TMS-O-C(=CH ₂)Ph	4	No reaction	

^a The starting material was recovered in 80% yields. ^b The corresponding TMS ether of the cyanohydrin was isolated.

Table 2 The reaction of acetals with silylated nucleophiles catalysed by TCNE
$$RR'C(\text{OMe})_2 \xrightarrow[\text{MeCN, reflux}]{\text{TCNE (0.2 equiv.), TMS-Nu (1.5 equiv.)}} RR'C(\text{OMe})\text{Nu}$$

Entry	Acetal	TMS-Nu	Time (h)	Product	Yield (%)
1		TMS-CN	2	12 Nu = CN	91
2		TMS-CH ₂ CH=CH ₂	1	13 Nu = CH ₂ CH=CH ₂	70
3		TMS-O-C(=CH ₂)Ph	1	14 Nu = CH ₂ COPh	88
4		TMS-O-C(=CH ₂)-2-Furyl	1	15 Nu = CH ₂ CO-2-Furyl	91
5		Et ₃ SiH	3	16 Nu = H	85 ^a
6		TMS-CN	5	18 Nu = CN	72
7		TMS-CH ₂ CH=CH ₂	1	19 Nu = CH ₂ CH=CH ₂	68
8		TMS-O-C(=CH ₂)Ph	1	20 Nu = CH ₂ COPh	83
9		TMS-O-C(=CH ₂)-2-Furyl	1	21 Nu = CH ₂ CO-2-Furyl	94
10		Et ₃ SiH	3	22 Nu = H	46 ^{a,b}
11		TMS-CN	4	24 Nu = CN	78
12		TMS-CH ₂ CH=CH ₂	4	No reaction	
13		TMS-O-C(=CH ₂)Ph	1	25 Nu = CH ₂ COPh	51
14		TMS-O-C(=CH ₂)-2-Furyl	3	26 Nu = CH ₂ CO-2-Furyl	60
15		TMS-CN	1	28 Nu = CN	80
16		TMS-CH ₂ CH=CH ₂	4	No reaction	
17		TMS-O-C(=CH ₂)Ph	1	29 Nu = CH ₂ COPh	79
18		TMS-O-C(=CH ₂)-2-Furyl	1	30 Nu = CH ₂ CO-2-Furyl	93
19		Et ₃ SiH	5	31 Nu = H	70 ^a
20		TMS-CN	1	33 Nu = CN	66
21		TMS-O-C(=CH ₂)Ph	2	34 Nu = CH ₂ COPh	75
22		TMS-O-C(=CH ₂)-2-Furyl	1	35 Nu = CH ₂ CO-2-Furyl	85
23		TMS-CN	5	37 Nu = CN	87
24		TMS-CH ₂ CH=CH ₂	5	38 Nu = CH ₂ CH=CH ₂	66
25		TMS-O-C(=CH ₂)Ph	4	39 Nu = CH ₂ COPh	38
26		TMS-CN	2	41 Nu = CN	63
27		TMS-O-C(=CH ₂)Ph	1	42 Nu = CH ₂ COPh	55

^a TCNE (0.3 equiv.) and Et₃SiH (4 equiv.) were used in this reaction. ^b Considerable loss of product occurred during work-up because of its low boiling point; the yield indicated stands for a tentative isolated yield.



Scheme 1

nm. The intensity of CT absorption bands were dependent on the concentration of decanal dimethyl acetal **36**. A strong acid, tricyanovinyl alcohol generated from TCNE and water,⁶ appears to be ruled out as a catalyst, because all of these reactions proceed under anhydrous conditions. Therefore, as shown in Scheme 1, the activation of the C=O and C-O bond of carbonyl and acetal groups for attack of silylated nucleophiles is presumed to be initiated by single electron transfer (SET)³ to the electron-deficient double bond of TCNE from the carbonyl and acetal oxygen.

Conclusion

In addition to the previously reported isomerization, acetonidation and alkanolysis of epoxides,⁴ the high efficiency of TCNE in the coupling reactions between silylated nucleophiles and carbonyl compounds and acetals demonstrated that a π -acid, TCNE, seems to promise much as a versatile and mild catalyst for Lewis acid-promoted reactions.

Experimental

Mps were measured with a Yanagimoto micromelting point apparatus and are uncorrected. IR absorption spectra were recorded on a JASCO IRA-1 spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) and a JEOL JNM-EX-400 (400 MHz) spectrometer with SiMe₄ as internal standards; *J* values are given in Hz. Mass spectra (MS) and high-resolution MS (HRMS) were recorded on a JEOL JMS-D300 or a JEOL JMS-SX102A spectrometer. UV-visible absorption spectra were recorded on a Shimadzu UV-260 instrument. Products were purified by column chromatography on silica gel (Merck, Kieselgel 60, 70–230 mesh). Acetonitrile was distilled from CaH₂ and stored over molecular sieve.

TCNE was purified by recrystallization from 1,2-dichloroethane. Decanal **1**, benzaldehyde **3** octan-2-one **7** and acetophenone **9** were purified by distillation. Dimethyl acetals were prepared by transacetalization of the corresponding aldehydes or ketones with trimethyl orthoformate in the presence of *p*-TsOH·H₂O,⁷ and purified by distillation. Trimethylsilyl cyanide, allyl trimethylsilane, and triethylsilane were purified by distillation. Silyl enol ethers were prepared by silylation of the corresponding enolates of ketones,⁸ and purified by distillation.

General procedure for the reactions of aldehydes and ketones with silylated nucleophiles catalysed by TCNE

Decanal (58.1 mg, 0.372 mmol) and TMS-CN (55 mg, 0.558 mmol) were added to a solution of TCNE (9.5 mg, 0.074 mmol) in MeCN (2 cm³) under argon atmosphere, and the mixture was stirred at the reflux temperature for 1 h. Hydrochloric acid (3%) was added to the reaction mixture which was then extracted with diethyl ether. After work-up, the crude product was purified by silica gel column chromatography (AcOEt-hexane, 1:6) to give 2-hydroxyundecanenitrile **2** (59.0 mg, 87%) as a low-melting solid, mp 27 °C (Found: C, 72.0; H, 11.7; N, 7.6. C₁₁H₂₁NO requires C, 72.08; H, 11.55; N, 7.64%);

$\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3370 (OH), 1450 and 1060; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.88 (3 H, t, *J* 6.8, CH₃), 1.27 (12 H, m), 1.50 (2 H, m, HOCHCH₂CH₂), 1.85 (2 H, m, HOCHCH₂), 2.59 (1 H, d, *J* 6.4, OH) and 4.47 (1 H, td, *J* 6.4, 6.8, CH); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.1 (q), 22.7 (t), 24.6 (t), 29.0 (t), 29.3 (t), 29.37 (t), 29.44 (t), 31.9 (t), 35.2 (t), 61.3 (d) and 120.2 (s).

Compounds (**4**, **16**, **19**, **22**),⁹ (**8**, **10**, **41**)¹⁰ and (**12**, **14**, **20**, **28**, **33**, **37**, **43**)^{1b} were identified by comparison of their spectroscopic behaviour with those described in the references. The yields and reaction conditions of other products are shown in Table 1. Other analytical data are presented:

1-Phenylbut-3-en-1-ol **5**.¹¹—Colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3360 (OH), 1640, 1490, 1450, 1040, 910, 750 and 690; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.10 (1 H, d, *J* 3.2, OH), 2.51 (2 H, m, PhCHCH₂), 4.73 (1 H, m, OCH), 5.12–5.20 (2 H, m, =CH₂), 5.73–5.88 (1 H, m, =CH) and 7.34 (5 H, m, ArH).

3-Hydroxy-1,3-diphenylpropan-1-one **6**.¹²—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3500 (OH), 1670 (C=O), 1450 and 680; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.38 (2 H, d, *J* 5.9, CH₂), 3.63 (1 H, d, *J* 2.9, OH), 5.35 (1 H, dt, *J* 2.9, 5.9, CH), 7.25–7.62 (8 H, m, ArH) and 7.95 (2 H, m, ArH); *m/z* (EI) 226.1005 (M⁺; C₁₅H₁₄O₂ requires *m/z* 226.0994).

General procedure for the reactions of acetals with silylated nucleophiles catalysed by TCNE

p-Anisaldehyde dimethyl acetal **11** (100 mg, 0.549 mmol) and TMS-CN (82 mg, 0.824 mmol) were added to a solution of TCNE (14.1 mg, 0.110 mmol) in MeCN (2 cm³) under an argon atmosphere, and the mixture was stirred at the reflux temperature for 2 h. The reaction mixture was extracted with ether and the extent was worked up to give a crude product which was purified by silica gel column chromatography (EtOAc-hexane, 1:6) to afford 2-methoxy-2-(4-methoxyphenyl)ethanenitrile **12**^{1b} (88.1 mg, 91%) as a colourless oil.

The yields and reaction conditions of other products are shown in Table 2. Other analytical data are presented here.

4-Methoxy-4-(4-methoxyphenyl)but-1-ene **13**.⁹—Colourless oil (Found: C, 75.0; H, 8.5. C₁₂H₁₆O₂ requires C, 74.97; H, 8.39 %); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1610, 1510, 1090 and 830; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.34–2.62 (2 H, m, =CHCH₂), 3.19 (3 H, s, OCH₃), 3.81 (3 H, s, ArOCH₃), 4.12 (1 H, t, *J* 6.8, OCH), 5.04 (2 H, m, =CH₂), 5.75 (1 H, m, =CH) and 6.89 and 7.21 (4 H, each d, *J* 8.8, ArH).

1-(2-Furyl)-3-methoxy-3-(4-methoxyphenyl)propan-1-one **15**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1650 (C=O), 1465, 1205 and 1090; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.92 (1 H, dd, *J* 15.6, 4.9, CHH), 3.19 (3 H, s, OCH₃), 3.43 (1 H, dd, *J* 15.6, 8.8, CHH), 3.81 (3 H, s, ArOCH₃), 4.79 (1 H, dd, *J* 8.8, 4.9, OCH), 6.51 (1 H, d, *J* 3.4, 1.5, ArH), 6.90 (2 H, dd, *J* 6.8, 2.0, ArH), 7.18 (1 H, d, *J* 3.4, ArH), 7.31 (2 H, m, ArH) and 7.57 (1 H, d, *J* 1.0, ArH); *m/z* (EI) 260.1063 (M⁺; C₁₅H₁₆O₄ requires *m/z* 260.1049).

2-Methoxy-2-phenylethanenitrile **18**.¹⁰—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2240 (CN), 1450, 1085 and 970; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.54 (3 H, s, OCH₃), 5.20 (1 H, s, CH) and 7.41–7.52 (5 H, m, ArH); *m/z* (EI) 147.0674 (M⁺; C₉H₉NO requires *m/z* 147.0683).

1-(2-Furyl)-3-methoxy-3-phenylpropan-1-one **21**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1660 (C=O), 1570, 1470, 1100 and 1010; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.92 (1 H, dd, *J* 16.1, 4.4, CHH), 3.22 (3 H, s, OCH₃), 3.44 (1 H, dd, *J* 16.1, 9.3, CHH), 4.85 (1 H, dd, *J* 9.3, 4.4, OCH), 6.51 (1 H, m, ArH) and 7.17–7.58 (7 H, m, ArH); *m/z* (EI) 230.0929 (M⁺; C₁₄H₁₄O₃ requires *m/z* 230.0942).

2-(2-Furyl)-2-methoxyethanenitrile **24**.⁹—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1140, 1080, 1015 and 960; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.49 (3 H, s, OCH₃), 5.32 (1 H, s, CH), 6.45 (1 H, m, ArH), 6.65 (1 H, m, ArH) and 7.49 (1 H, m, ArH); *m/z* (EI) 137.0489 (M⁺, C₇H₇NO₂ requires *m/z* 137.0478).

3-(2-Furyl)-3-methoxy-1-phenylpropan-1-one **25**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1675 (C=O), 1280, 1090 and 1010; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.29 (3 H, s, OCH₃), 3.31 (1 H, dd, *J* 17.1, 4.9,

COCHH), 3.71 (1 H, dd, *J* 17.1, 8.9, CHH), 4.92 (1 H, dd, *J* 8.9, 4.9, OCH), 6.35 (2 H, m, ArH), 7.41–7.59 (4 H, m, ArH) and 7.98 (2 H, m, ArH); *m/z* (EI) 230.0969 (M^+ ; $C_{14}H_{14}O_3$ requires *m/z* 230.0943).

1,3-(2,2-Difuryl)-3-methoxypropan-1-one **26**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1650 (C=O), 1460, 1090 and 1010; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.11 (1 H, dd, *J* 16.1, 4.9, CHH), 3.27 (3 H, s, OCH₃), 3.58 (1 H, dd, *J* 16.1, 8.8, CHH), 4.89 (1 H, dd, *J* 8.8, 4.9, OCH), 6.34 (2 H, m, ArH), 6.54 (1 H, m, ArH), 7.23 (1 H, d, *J* 4.4, ArH), 7.41 (1 H, d, *J* 1.4, ArH) and 7.60 (1 H, d, *J* 1.0, ArH); *m/z* (EI) 220.0746 (M^+ ; $C_{12}H_{12}O_4$ requires *m/z* 220.0736).

(E)-3-Methoxy-1,5-diphenylpent-4-en-1-one **29**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1675 (C=O), 1450, 1090 and 970; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.07 (1 H, dd, *J* 16.1, 4.9, CHH), 3.35 (3 H, s, OCH₃), 3.47 (1 H, dd, *J* 16.1, 7.8, CHH), 4.46 (1 H, m, OCH), 6.17 (1 H, dd, *J* 16.1, 7.8, PhCH=CH), 6.67 (1 H, d, *J* 15.6, PhCH), 7.22–7.59 (8 H, m, ArH) and 7.95–7.98 (2 H, m, ArH); *m/z* (EI) 226.1333 (M^+ ; $C_{18}H_{18}O_2$ requires *m/z* 226.1307).

1-(2-Furyl)-3-methoxy-5-phenylpent-4-en-1-one **30**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1655 (C=O), 1465 and 1090; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.92 (1 H, dd, *J* 15.6, 4.9, CHH), 3.31 (1 H, dd, *J* 15.6, 7.8, CHH), 3.33 (3 H, s, OCH₃), 4.43 (1 H, m, OCH), 6.14 (1 H, dd, *J* 16.1, 7.8, PhCH=CH), 6.53 (1 H, m, ArH), 6.65 (1 H, d, *J* 16.1, PhCH), 7.21–7.41 (6 H, m, ArH) and 7.59 (1 H, m, ArH); *m/z* (EI) 256.1111 (M^+ ; $C_{16}H_{16}O_3$ requires *m/z* 256.1100).

(E)-1-Methoxy-3-phenylprop-2-ene **31**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1450, 1370, 1180, 1110 and 960; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.39 (3 H, s, OCH₃), 4.10 (2 H, d, *J* 6.4, OCH₂), 6.28 (1 H, dt, *J* 15.6, 5.9, PhCH=CH), 6.61 (1 H, d, *J* 16.1, PhCH) and 7.21–7.41 (5 H, m, ArH); *m/z* (EI) 148.0875 (M^+ ; $C_{10}H_{12}O$ requires *m/z* 148.0887).

(E)-3-Methoxy-1-phenyloct-4-en-1-one **34**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1670 (C=O), 1600, 1450, 1090 and 970; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.88 (3 H, t, *J* 7.7, CH₂CH₃), 1.39 (2 H, m, CH₂CH₃), 2.03 (2 H, m, =CHCH₂), 2.97 (1 H, dd, *J* 16.2, 5.1, COCHH), 3.27 (3 H, s, OCH₃), 3.35 (1 H, dd, *J* 16.2, 7.5, COCHH), 4.21 (1 H, m, OCH), 5.36 (1 H, m, =CHCH), 5.72 (1 H, dt, *J* 15.4, 6.8, CH₂CH=), 7.43–7.58 (3 H, m, ArH) and 7.91–7.97 (2 H, m, ArH); *m/z* (EI) 232.1472 (M^+ ; $C_{15}H_{20}O_2$ requires *m/z* 232.1463).

1-(2-Furyl)-3-methoxyoct-4-en-1-one **35**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1650 (C=O), 1465 and 1090; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.87 (3 H, t, *J* 7.3, CH₂CH₃), 1.39 (2 H, m, CH₂CH₃), 2.02 (2 H, m, =CHCH₂), 2.82 (1 H, dd, *J* 15.1, 5.4, COCHH), 3.19 (1 H, dd, *J* 15.1, 8.3, COCHH), 3.25 (3 H, s, OCH₃), 4.18 (1 H, td, *J* 8.3, 4.9, OCH), 5.34 (1 H, dd, *J* 15.6, 8.3, CH₂CH=), 5.71 (1 H, m, =CHCH), 6.53 (1 H, dd, *J* 3.4, 1.5, ArH), 7.20 (1 H, d, *J* 3.4, ArH) and 7.59 (1 H, d, *J* 1.0, ArH); *m/z* (EI) 222.1237 (M^+ ; $C_{13}H_{18}O_3$ requires *m/z* 222.1255).

4-Methoxytridec-1-ene **38**.¹³—Colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1465, 1090 and 910; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.88 (3 H, t, *J* 6.8, CH₂CH₃), 1.27 (14 H, br s), 1.45 (2 H, m, OCHCH₂), 2.26 (2 H, m, =CHCH₂), 3.20 (1 H, m, OCH), 3.34 (3 H, s, OCH₃), 5.03–5.12 (2 H, m, =CH₂) and 5.74–5.90 (1 H, m, =CH).

3-Methoxy-1-phenyldodecan-1-one **39**.—Colourless oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1670 (C=O), 1450 and 1090; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.88 (3 H, t, *J* 6.8, CH₂CH₃), 1.26 (14 H, br s), 1.57 (2 H, m, OCHCH₂), 2.94 (1 H, dd, *J* 16.1, 5.4, COCHH), 3.29 (1 H, dd, *J* 16.6, 6.8, COCHH), 3.34 (3 H, s, OCH₃), 3.87 (1 H, m, OCH), 7.44–7.60 (3 H, m, ArH) and 7.97 (2 H, m, ArH); *m/z* (EI) 290.2237 (M^+ ; $C_{19}H_{30}O_2$ requires *m/z* 290.2245).

3-Methoxy-3-methyl-1-phenylnonan-1-one **42**.—Colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1670 (C=O), 1450, 1075 and 685; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.87 (3 H, t, *J* 6.8, CH₂CH₃), 1.26 (8 H, br s), 1.29 (3 H, s, CCH₃), 1.65 (2 H, m, OCCH₂CH₂), 3.07 (1 H, d, *J* 14.6, COCHH), 3.19 (3 H, s, OCH₃), 3.20 (1 H, d, *J* 14.6,

COCHH), 7.42–7.58 (3 H, m, ArH) and 7.96 (2 H, m, ArH); *m/z* (FAB) 263.2022 (M^+ + H; $C_{17}H_{27}O_2$ requires *m/z* 263.2011).

3-Benzoyl-4-methoxy-4-phenylbut-2-ene-1,1,2-trinitrile **44**.—Brown viscous oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2230 (CN), 1660 (C=O), 1610, 1530 and 1090; $\delta_{\text{H}}(\text{CDCl}_3)$, 3.45 (3 H, s, OCH₃), 5.90 (1 H, s, OCH), 6.38 (1 H, s, NCCH) and 7.34–7.59 (10 H, m, ArH); *m/z* (EI) 341.1145 (M^+ ; $C_{21}H_{15}N_3O_2$ requires *m/z* 341.1163).

3,5-Dibenzoyl-4-phenylprop-2-ene-1,1,2-trinitrile **45**.—Brown viscous oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2240 (CN), 1650 (C=O), 1610 and 1525; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.31 (1 H, dd, *J* 17.1, 3.9, COCHH), 3.86 (1 H, dd, *J* 17.1, 9.3, COCHH), 5.69 (1 H, dd, *J* 9.3, 3.9, PhCH), 6.29 (1 H, s, NCCH), 7.28–7.69 (13 H, m, ArH) and 7.96 (2 H, m, ArH); *m/z* (EI) 429.1495 (M^+ ; $C_{28}H_{19}N_3O_2$ requires *m/z* 429.1477).

3-Benzoyl-4-methoxytridec-2-ene-1,1,2-trinitrile **46**.—Red viscous oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2230 (CN), 1650 (C=O), 1610, 1530 and 1100; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.87 (3 H, t, *J* 7.3, CH₂CH₃), 1.24 (12 H, m), 1.47–1.82 (4 H, m, OCHCH₂CH₂), 3.37 (3 H, s, OCH₃), 5.03 (1 H, dd, *J* 6.8, 3.9, OCH), 6.44 (1 H, s, NCCH), 7.50–7.63 (3 H, m, ArH) and 7.70 (2 H, m, ArH); *m/z* (EI) 391.2241 (M^+ ; $C_{24}H_{29}N_3O_2$ requires *m/z* 391.2259).

Charge-transfer interaction between TCNE and decanal dimethyl acetal

CT complex formation between TCNE and decanal dimethyl acetal was evidenced by a shoulder at 285–300 nm in the UV-visible absorption spectrum of a mixture of TCNE (3.6×10^{-3} mol dm⁻³) and decanal (54×10^{-3} mol dm⁻³) which was absent in the spectrum of TCNE (3.6×10^{-3} mol dm⁻³) in dry acetonitrile.

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