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Inter- and intramolecular isocarbon couplings of cobalt-complexed propargyl radicals: challenging the consensus

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ABSTRACT

Intermolecular coupling reactions of $Co_2(CO)_6$-complexed, γ-ethyl propargyl radicals occurred with higher DL-diastereoselectivity than intramolecular cyclizations of isocarbon analogues (de_{inter}–$de_{intra} \leq 52\%$). The observed phenomenon was interpreted in terms of a tandem action of two main determinants—sterics and CH/π coordination—with the latter being enabled by the methoxy groups located on the periphery of the aromatic nuclei (4-, 3,4-, 3,4,5-).

1. Introduction

An incorporation of rigidity elements, restriction of conformational freedoms, and increase in steric hindrance are recognized in synthetic chemistry as effective tools for controlling the stereoselectivity of the C–C bond formation.[1] In particular, intramolecular reactions, both ionic and radical, exhibit a higher level of stereocontrol when compared to their intermolecular counterparts.[2] Among representative examples is the pinacol coupling, affording acyclic *threo*- and *erythro*-diols with low diastereoselectivity in intermolecular reactions (de 0–40%) and cyclic *threo*-diols with an excellent stereoselectivity (de 82–100%) in intramolecular cyclizations.[2a] The trend is further underscored by [4+2] cycloadditions of nitroalkenes to olefins[2b] and electrooxidative alkylation of ethers.[2c] Shortening the carbon tether also enhances the diastereoselectivity of cyclization reactions due to a lesser degree of conformational freedoms (de C_5 90% vs C_6 40%).[2d] As a part of the ongoing systematic studies on the chemistry of π-bonded organic molecules,[3] we reported on intramolecular cyclizations of $Co_2(CO)_6$-complexed propargyl radicals, affording 1,5-cyclodecadiynes.[4] The stereoselectivity was dependent upon topology and substitution pattern; in particular, cyclization occurred stereorandomly when the α-aromatic substituents of C_{2v}-symmetry were heavily populated with methoxy groups. Thus, DL- and *meso*-1,5-cyclodecadiynes were formed in the ratio of 54:46 with methoxy groups arranged in a 3,4,5-pattern on the periphery of the aromatic rings. The concept of CH/π coordination was invoked to account for an unusually high amount of *meso*-diastereomer (**1**, Fig. 1). In intermolecular reactions—with the substitution topology preserved—much higher DL-diastereoselectivity was observed (DL/*meso*, 80:20), presumably due to the tandem action of CH/π coordination and repulsion between γ-alkyl groups. The hypothesis put forth was that aromatic rings could be coordinatively held together, while cobalt/alkyne units are forced away from each other, giving rise to the respective DL-diastereomer (**2**, Fig. 1).[4]

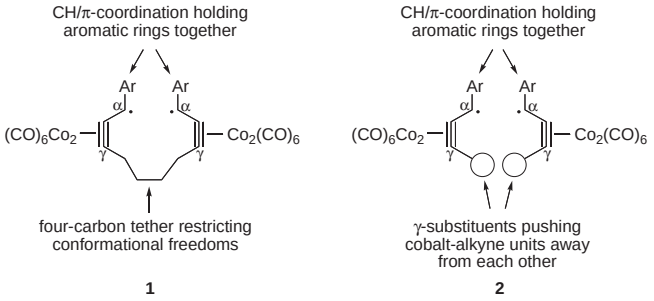

Figure 1. The CH/π-coordination and γ-substituents impacting the disposition of converging propargyl radicals.

The notion that intermolecular reactions can be more stereoselective than their intramolecular counterparts runs contrary to the general consensus and could not have been predicted on the

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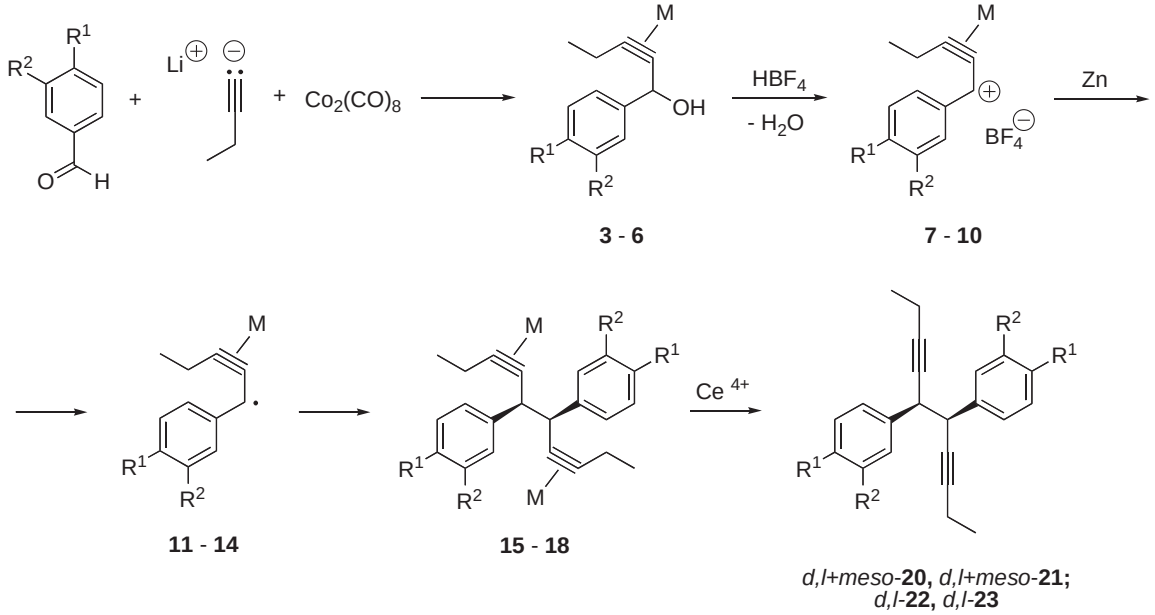
basis of the literature precedence.[1,2] The current study was undertaken to examine this phenomenon in order to determine its scope and generality, as well as the stereoelectronic and topological parameters involved. Another objective was to establish the stereoselectivity of radical coupling reactions of γ-alkyl-substituted $Co_2(CO)_6$-complexed propargyl radicals for which only two examples—γ-ethyl,[4] γ-phenyl[3e]—have been reported thus far.

2. Results and discussion

2.1. Intermolecular coupling reactions of γ-ethyl-substituted propargyl alcohols

To compare the stereoselectivities of inter- and intramolecular radical reactions mediated by a $Co_2(CO)_6$-metal core, a series of isocarbon analogues of bis-propargyl diols[4] were synthesized with ethyl groups positioned gamma to the cationic centers. Requisite γ-ethyl-substituted propargyl alcohols **3**–**6** were synthesized by the condensation of lithium 1-butynylide with benzaldehyde and its derivatives,[5a] followed by the complexation with $Co_2(CO)_8$[5b] (Scheme 1). These complexes were treated with HBF_4 to release metal-stabilized propargyl cations **7**–**10**.[4,6] The reduction was carried out with Zn[3b,h,4] to generate propargyl radicals **11**–**14**, which then underwent intermolecular dimerization to form bis-clusters **15**–**18**. Independent from topology and substitution pattern — 0-, 4-*i*-Pr, 4-OMe, 3,4-$(OMe)_2$ — DL-diastereomers are predominantly formed, varying from DL/*meso*, 73:27 for parent dimer **15** (R^1=R^2=H) to 90:10 for aromatic substituents. In the case of the parent dimer with unsubstituted aromatic ring **15** and 4-isopropyl derivative **16**, diastereomers exhibited a comparable mobility on inorganic sorbents and could hardly be separated. To the contrary, the presence of methoxy groups—4-OMe, 3,4-$(OMe)_2$—facilitated separation allowing for isolation of individual DL- and *meso*-diastereomers (**17**, **18**). Decomplexation was carried out with cerium(IV) ammonium nitrate[3,4,6] (8–11 equiv, −78 °C), affording metal-free 5,6-disubstituted 3,7-decadiynes represented either by the DL- and *meso*-diastereomeric mixtures (**20**, **21**), or by the individual DL-diastereomers (**22**, **23**). The latter belong to the class of 1,5-alkadiynes that represents a key entry point to several common types of organic molecules, such as 1,5-alkadienes, 1,4-diketones, 1,6-diketones, and 3-ene-1,5-alkadiynes, and for which stereo- and regioselective methods of synthesis are still lacking. The 'classical' propargyl—propargyl coupling reaction exhibited a poor regioselectivity due to acetylene/allene rearrangement.[7a] Metal-catalyzed processes (Ru, Pd) are limited in scope,[7b,c] with their yields and diastereoselectivities drastically decreasing in the presence of bulky, electron-withdrawing (CF_3) and electron-donating substituents (Me; OMe).[7b] In addition, metal-promoted dimerizations exhibited a low regioselectivity because of the formation of isomeric allene-ynes.[7c] The mediation of intermolecular coupling of propargyl alcohols with $Ti(O^iPr)_2Cl_2$/Mg suffered from the low conversions (~70%), poor diastereo- and regioselectivities with the end products being 'contaminated' by the substantial quantities of isomeric allenes (45–50%).[7d]



M = $Co_2(CO)_6$; **3**, **7**, **11**, **15**, **20** R^1=R^2=H; **4**, **8**, **12**, **16**, **21** R^1=i-Pr, R^2=H; **5**, **9**, **13**, **17**, **22** R^1=OMe, R^2=H; **6**, **10**, **14**, **18**, **23** R^1=R^2=OMe.

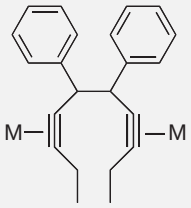
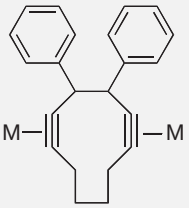
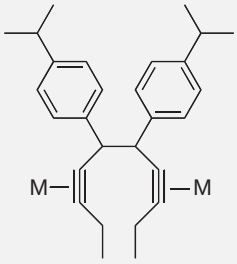
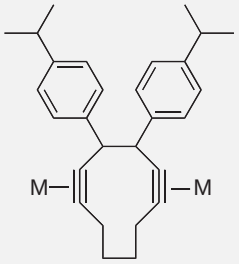
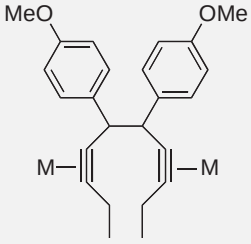
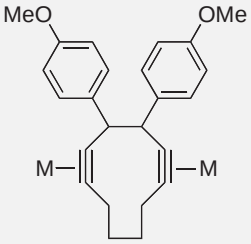
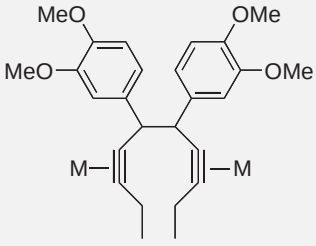
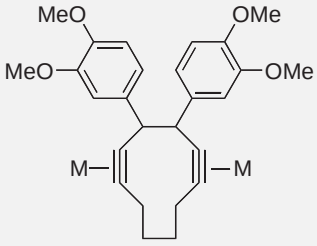
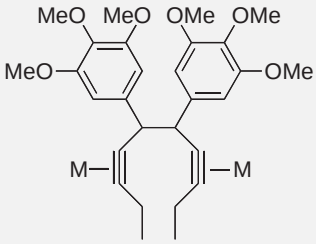
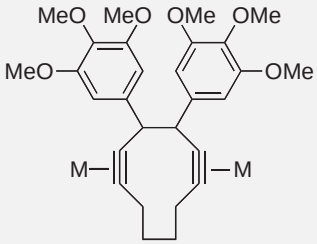
Scheme 1. A four-step synthesis of DL- and *meso*-5,6-diaryl-3,7-decadiynes via intermolecular coupling of metal-enhanced propargyl radicals (major DL-stereoisomers are shown).

3,4-dimethoxy derivative **18**, with 3,4,5-trimethoxy derivative **19** falling within the same range (DL-**19**/*meso*-**19**, 80:20; Table 1).[4] The yields for key radical C–C forming steps, lying in the range of 56.0–78.9%, exceeded by far those for intramolecular reactions of isocarbon analogues (28.7–43.3%).[4] Chromatographic separability was dependent upon the nature and topology of

2.2. Relative configurations of 5,6-diaryl-3,7-decadiynes 15–18

The diastereomeric composition of 3,4-diaryl-1,5-hexadiynes with terminal triple bonds was determined by using the NMR signatures of $Co_2(CO)_6$-complexed acetylenic hydrogens.[3b,c,e,g] Due

Table 1
Diastereoselectivity of inter- versus intramolecular coupling reactions

Intermolecular coupling products	DL/*meso* ratio (de)	Intramolecular cyclization products	DL/*meso* ratio (de)	$de_{inter}-de_{intra}$
 **15**	73:27 (46)	 **24**	67:33 (34)	12
 **16**	74:26 (48)	 **25**	80:20 (60)	−12
 **17**	85:15 (70)	 **26**	67:33 (34)	36
 **18**	90:10 (80)	 **27**	67:33 (34)	46
 **19**	80:20[4] (60)	 **28**	54:46[4] (8)	52

to magnetic anisotropy of aromatic substituents, in *meso*-diastereomers, a significant up-field shift was observed (~1.27 ppm) relative to analogous resonances in DL-counterparts (*meso*- 4.96-5.21 ppm; DL- 6.28-6.43 ppm). In the case of internal triple bonds (**15**–**18**), stereochemical assignment was carried out by means of X-ray crystallography by using DL-**18** as a model compound (Fig. 2).[8]

The disposition of substituents around the central C_5–C_6 bond unambiguously establishes DL-configuration, along with substantial deviation from ideal *gauche* arrangement. Thus, methine hydrogens are nearly perpendicular to each other (H_5–C_5–C_6–H_6 87.57°), with phenyl groups being forced into a closer proximity (C_{11}–C_5–C_6–C_{19} 40.3°). An *anti*-disposition of cobalt/alkyne units is also significantly affected by the steric constraints imposed by the bulky metal cores (C_4–C_5–C_6–C_7 142.0°). Radical dimers with terminal triple bonds were shown to arrange methine hydrogens in *anti*-fashion, with cobalt/alkyne moieties being positioned opposite to each other, in a distorted *gauche* mode.[3b] The presence of γ-ethyl substituents in DL-**18** pushed the metal/alkyne cores away from each other, the phenomenon previously observed by us[3e] for γ-phenyl-substituted 1,5-hexadiynes. To further minimize the repulsion, γ-ethyl groups also adopt nearly ideal *anti*-conformation relative to internal triple bonds (C_1–C_2–C_3–C_4 173.6°; C_7–C_8–C_9–C_{10} 173.7°). Another manifestation of the internal strain of the DL-stereoisomer is an extended carbon–carbon bond formed by converging propargyl radicals (C_5–C_6 1.616 Å). The metal cores—Co_2C_2—represent undistorted tetrahedrons wherein the Co–Co and C–C triple bonds are arranged perpendicular to each other (89.51°; 89.69°).[6] Other noteworthy structural features of DL-**18** include: (a) a lengthened coordinated C–C triple bond (~1.29 Å vs 1.21 Å for the free ligand) and bent geometry for coordinated alkyne units (141–148°), both indicative of the nature of bonding between transition metal and π-bonded unsaturated ligand;[6] (b) inequivalency of alkyne units attested by the different degree of planarity (C_2–C_3–C_4–C_5 8.0°; C_6–C_7–C_8–C_9 0.0°); (c) inequivalency of alkyne units attested by the bond angles around the coordinated triple bonds with somewhat smaller angles for acetylenic termini (C_4–C_3–C_2 143.1°; C_3–C_4–C_5 147.4°; C_7–C_8–C_9 140.8°; C_8–C_7–C_6 148.5°).

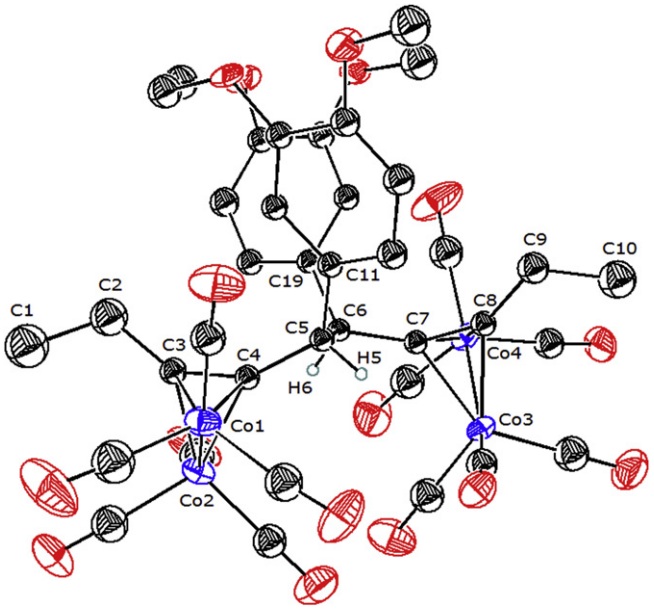


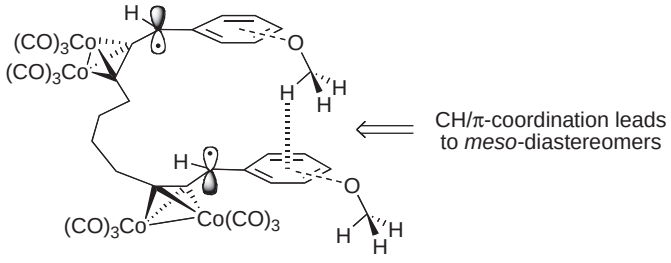
Figure 2. ORTEP diagram of molecular structure of DL-**18** with 20% probability ellipsoids.

2.3. Why are intermolecular reactions more diastereoselective than intramolecular cyclizations?

Intermolecular radical coupling of γ-ethyl, $Co_2(CO)_6$-complexed propargyl alcohols occurred with diastereoselectivity ranging from 73:27 to 90:10 and featured the preponderant formation of the respective DL-diastereomers **15**–**19** (Table 1). Comparison with diastereomeric data on isocarbon intramolecular reactions affording 1,5-cyclodecadiynes **24**–**28** revealed that the disparity on stereoisomeric composition is dependent upon functionality and topology of the substrates (Table 1). In particular, radical dimers fall into one of two distinct categories: (1) diastereoselectivity of inter- and intramolecular reactions does not show any identifiable trends (**15**, **16**), or (2) the level of diastereoselection in intramolecular cyclizations is inferior to that of intermolecular reactions (**17**–**19**). Thus, in the case of the parent dimer **15**, a DL/*meso* ratio equal to 73:27 represents the modest increase in stereoselectivity with respect to its isocarbon counterpart **24** (DL/*meso*, 73:27; Table 1, line 1). Introducing a 4-isopropyl group into the aromatic ring did not affect the stereoselectivity of the intermolecular process (**16**; DL/*meso*, 74:26); however, there is a slight decrease in DL-diastereoselectivity when compared to its intramolecular counterpart **25** (DL/*meso*, 80:20). The differences in diastereoselectivities (de_{inter}–de_{intra}) have the same absolute magnitude (Table 1, col. 5; 12 vs −12), thus indicating that there is no clear trend as to how the diastereoselectivity would change when the carbon tether is compromised. The main structural difference between the substrates belonging to two different categories (**15**, **16** vs **17**–**19**) is the presence of methoxy groups on the periphery of the aromatic nuclei. Intermolecular coupling reactions leading to dimers **17**–**19** feature DL-diastereoselectivities that exceed, by far, those observed in respective intramolecular cyclizations (ΔDL 18–26%). Furthermore, the difference in diastereoselectivities (de_{inter}–de_{intra}) is found to be directly proportional to the number of methoxy groups present (4-OMe 36%; 3,4-$(OMe)_2$ 46%; 3,4,5-$(OMe)_3$ 52%; Table 1, col. 5).

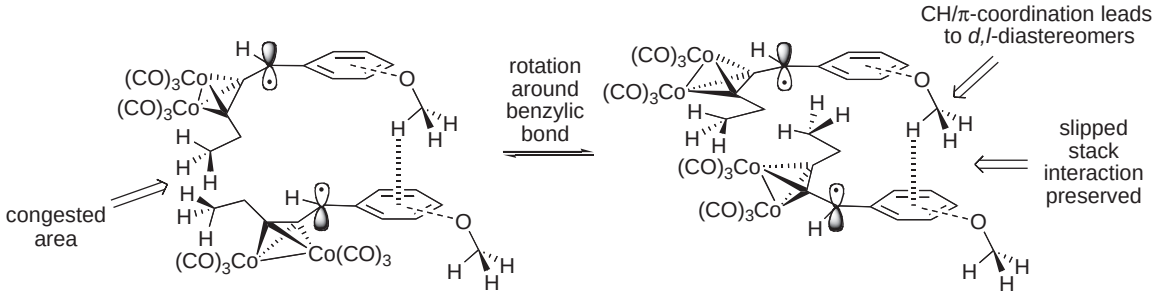
The phenomenon observed—higher DL-diastereoselectivity in intermolecular radical reactions with respect to intramolecular cyclizations when one, or more, methoxy groups are attached to the aromatic nuclei—is best interpreted by invoking the concept of CH/π coordination.[9,10] It is a well established fact that a $C^{-\delta}$–$H^{+\delta}$ bond can coordinate to the face of the aromatic ring, which represents a negative end of the electric quadrupole moment.[10a–c] In energetic terms, it is a weak inter- or intramolecular interaction, although it has a profound effect on molecular recognition, selectivity of organic reactions, stability of inclusion complexes, three-dimensional structure of proteins, and topology of protein/ligand complexes.[10b,c] Low-polarity C–H bonds in diverse hydrocarbon structures, such as methane,[10b] ethane,[10c] acetylene,[10b,c] benzene,[10a,b] methyl,[10b] methylene[10b] or isopropyl[10c] groups are capable of coordinating with the centroid of the aromatic rings. Most relevant to the current context are the reports in which OMe-groups coordinate their weakly polar C–H bonds with the aromatic moieties.[10d–f] Depicted in Figure 3 is a pre-*meso*-conformation of diradical **A** in which a MeO-group is shown as coordinated with the aromatic nucleus in CH/π coordination mode. Kinetically, such coordination is consequential since it holds the aromatic hexagons next to each other, in a slipped stack fashion, thus limiting conformational freedoms and avoiding a destabilizing face-to-face repulsion between negatively charged aromatic surfaces. A short, four-carbon tether does not allow for rotation around a benzylic bond that would give rise to an opposite, DL-diastereomer. In intermolecular reactions, γ-ethyl groups, due to repulsion, can destabilize conformation **B** that would give rise to *meso*-diastereomer (Fig. 3). Rotation around a benzylic bond will put bulky γ-substituents further apart from each other while preserving the CH/π coordination between a C–H bond, a soft acid, and an aromatic ring, a soft base. A higher concentration of conformation **C** will increase the amount of DL-diastereomer, thus enhancing the stereoselectivity of the overall process. Paradoxically, the same process—CH/π coordination—promotes the formation of *meso*-diastereomer in intramolecular cyclizations and, to the contrary, increases the amount of DL-diastereomer in

Intramolecular reactions



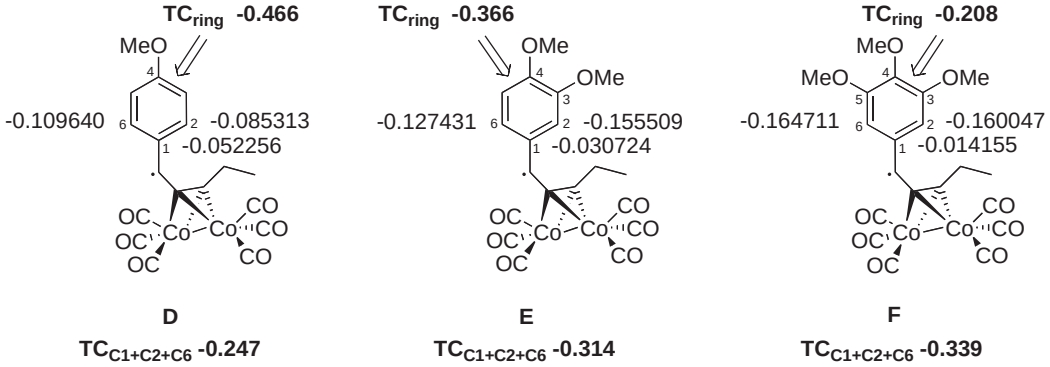
pre-*meso*-conformation **A**

Intermolecular reactions



pre-*meso*-conformation **B** pre-*d,l*-conformation **C**

Figure 3. The impact of CH/π-coordination upon diastereoselectivity in intra- and intermolecular coupling reactions.



D **E** **F**

$TC_{C1+C2+C6}$ **-0.247** $TC_{C1+C2+C6}$ **-0.314** $TC_{C1+C2+C6}$ **-0.339**

Figure 4. Charge distribution and total charges of the aromatic rings (TC_{ring}; $TC_{C1+C2+C6}$) derived from PM3 calculations.

intermolecular reactions (pre-DL-conformation **C**). Computation data[11] on charge distribution in requisite cobalt-complexed radicals **D**, **E**, and **F** revealed that the aromatic rings are negatively charged with the numerical values being dependent upon the number of MeO-groups (1–3) and substitution pattern (4-; 3,4-; 3,4,5-; Figure 4). Thus, the total charge of the aromatic ring (TC_{ring}) is the highest in 4-OMe derivative (**D**) and the lowest in 3,4,5-$(OMe)_3$ derivative **F** (−0.466; −0.208). Introduction of MeO-groups polarizes the aromatic hexagons with the carbon atoms bearing substituents becoming more positive (C_3, C_4, C_5) and those at the bottom of the hexagon (C_1, C_2, C_6) maintaining their negative charges. The sum of negative charges ($TC_{C1+C2+C6}$) varies from −0.247 (4-OMe), via −0.314 (3,4-$(OMe)_2$), to −0.339 (3,4,5-$(OMe)_3$), clearly indicating that an alleged CH/π coordination can take place for all three substrates with the bottom of the aromatic ring acting as a soft base. It is worthy to mention that by X-ray data, a more efficient interaction was observed in case of the aromatic ring bearing three MeO-groups of various topology (2,4,6-,[10d,e] 1,3,5-[10f]). Overall, an observed increase in DL-diastereoselectivity (de_{inter}–de_{intra} 36–52%) is probably determined by the relative strength of CH/π coordination that, in turn, can be influenced by several confounding factors, i.e., negative charge of the aromatic coordinating site, topology of the electrophilic C–H bonds, conformational flexibility, and steric factor.

3. Conclusion

In conclusion, we found that, despite the general consensus, intermolecular radical coupling reactions can be more diastereoselective than isocarbon intramolecular cyclizations. The functional parameter enhancing intermolecular reactions is the presence of MeO-groups on the periphery of the aromatic nuclei, which act as soft acids and coordinate with the negative sites of the aromatic hexagons, in a slipped stack mode. Such an acid/base coordination restricts conformational freedoms and enhances the stereochemical outcome of the radical reactions. This finding

allows us to stereoselectively (up to 90%) synthesize 5,6-disubstituted DL-3,7-decadiynes that belong to a class of 1,5-alkadiynes, otherwise inaccessible. The knowledge thus acquired also has a predictive power: intermolecular radical reactions can be made more stereoselective by exploiting a CH/π coordination between negatively charged, alternative aromatic, heteroaromatic, or carbocyclic systems (soft bases) and O-, N-, and S-atom-based coordinating moieties (soft acids).

4. Experimental section

4.1. General

All manipulations of air-sensitive materials were carried out in flame-dried Schlenk-type glassware on a dual-manifold Schlenk line interfaced to a vacuum line. Nitrogen (Airgas, ultrahigh purity) was dried by passing through a Drierite tube (Hammond). All solvents were distilled before use under dry nitrogen over appropriate drying agents (ether, THF, from sodium benzophenone ketyl; CH_2Cl_2, from CaH_2; benzene, from sodium). All reagents were purchased from Sigma/Aldrich and Acros and used as received. $Co_2(CO)_8$ and $Ce(NH_4)_2(NO_3)_6$ were purchased from Strem. NMR solvents were supplied by Cambridge Isotope Laboratories. ^1H and ^{13}C NMR spectra were recorded on Bruker DRX-400 (^1H, 400 MHz) spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported relative to tetramethylsilane. Spin/spin coupling constants (J) are given in hertz. Melting temperatures (uncorrected) were measured on a Mel-Temp II (Laboratory Devices) apparatus and Optimelt Automated Meltemp. Silica Gel S735-1 (60–100 mesh; Fisher) was used for flash column chromatography. Analytical and preparative TLC analysis (PTLC) were conducted on Silica gel 60 F_{254} (EM Science; aluminum sheets) and Silica Gel 60 PF_{254} (EM Science; w/gypsum; 20×20 cm), respectively. Eluents are ether (E) and petroleum ether (PE). Mass spectra (TOF, ESI) were run at the Regional Center on Mass-Spectroscopy, UC Riverside, Riverside, CA (Agilent 6210 LCTOF instrument with a Multimode source). The X-ray analysis was carried out by the crystallographic center at the Emory University, Atlanta, GA.

4.2. Synthesis of $Co_2(CO)_6$-complexed propargyl alcohols 3–6

*4.2.1. μ-η²-(1-Phenyl-2-pentyn-1-ol)dicobalt hexacarbonyl (**3**)*[3g].

*4.2.2. μ-η²-[1-(4′-Isopropylphenyl)-2-pentyn-1-ol]dicobalt hexacarbonyl (**4**) (protocol A).* Under an atmosphere of nitrogen, 1-butyne (5.94 g, 110 mmol) was bubbled through a solution of *n*-BuLi (9 mmol, 5.6 mL/1.6 M) in dry THF (50 mL) at −10 °C and stirred for 5 h. A solution of 4-isopropylbenzaldehyde (888 mg, 6 mmol) in dry THF (15 mL) was added dropwise (15 min) at −10 °C, and the mixture was warmed to 20 °C and stirred for 20 h. The suspension was cooled to 0 °C and quenched with saturated NH_4Cl_{aq} (50 mL). An aqueous layer was extracted with ether (3×50 mL), and combined ethereal fractions were dried (Na_2SO_4). Upon concentration under reduced pressure (1/2 of the initial volume), under an atmosphere of nitrogen, the crude alcohol (1.21 g, 6 mmol; assuming 100% yield) was added to a solution of dicobaltoctacarbonyl (3.08 g, 9 mmol) in dry ether (100 mL). The reaction mixture was stirred at room temperature for 16 h, concentrated under reduced pressure, and fractionated on a silica gel column (400 g, PE/E, 5:1) to give **4** (1.90 g, 64.8%) as a dark red oil. TLC (PE/E, 3:1): R_f 0.50. ^1H NMR (400 MHz, $CDCl_3$): δ 1.23 (6H, d, $2CH_3$, J=6.8), 1.28 (3H, t, CH_3, J=7.4), 2.29 (1H, d, OH, J=3.6), 2.79 (2H, ABX_3, CH_AH_B, J (H_AH_B)=15.6), 2.90 (1H, septet, CH), 5.90 (1H, d, CH), 7.23 (2H, m, aromatic H), 7.36 (2H, m, aromatic H). MS TOF: m/z calcd for $C_{20}H_{17}O_7Co_2$ $[M-H]^-$ 486.9644, found 486.9654.

*4.2.3. μ-η²-[1-(4′-Methoxyphenyl)-2-pentyn-1-ol]dicobalt hexacarbonyl (**5**).* Analogous to protocol A, 1-butyne (5.94 g, 110 mmol), *n*-BuLi (6.6 mmol, 4.1 mL/1.6 M; dry THF, 50 mL), 4-methoxybenzaldehyde (816 mg, 6 mmol; dry THF, 15 mL) (20 °C, 16 h), and dicobaltoctacarbonyl (2.26 g, 6.6 mmol; dry ether, 100 mL) afforded, after fractionation on a silica gel column (400 g, PE/E, 10:1), **5** (1.12 g, 39.3%) as a dark red oil. TLC (PE/E, 1:1): R_f 0.58. ^1H NMR (400 MHz, $CDCl_3$): δ 1.27 (3H, t, CH_3, J=7.2), 2.27 (1H, d, OH, J=3.2), 2.76 (2H, ABX_3, CH_AH_B, J (H_AH_B)=15.6), 5.88 (1H, d, CH, J=2.8), 6.91 (2H, m, aromatic H), 7.36 (2H, m, aromatic H). MS TOF: m/z calcd for $C_{18}H_{13}O_8Co_2$ $[M-H]^-$ 474.9280, found 474.9287.

*4.2.4. μ-η²-[1-(3′,4′-Dimethoxyphenyl)-2-pentyn-1-ol]dicobalt hexacarbonyl (**6**).* Analogous to protocol A, 1-butyne (5.94 g, 110 mmol), *n*-BuLi (9 mmol, 5.6 mL/1.6 M; dry THF, 50 mL), 3,4-dimethoxybenzaldehyde (996 mg, 6 mmol; dry THF, 15 mL) (20 °C, 16 h), and dicobaltoctacarbonyl (2.26 g, 6.60 mmol; dry ether, 100 mL) afforded, after fractionation on a silica gel column (400 g, PE/E, 3:1), **6** (1.25 g, 41.4%) as light red crystals. Mp 90–108 °C (w/ decomp.; sealed capillary; dried by co-evaporation with benzene, 3×1 mL). TLC (PE/E, 1:1): R_f 0.32. ^1H NMR (400 MHz, $CDCl_3$): δ 1.28 (3H, t, CH_3, J=7.4), 2.29 (1H, d, OH, J=3.2), 2.78 (2H, ABX_3, CH_AH_B, J (H_AH_B)=15.6), 3.88 (3H, s, OMe), 3.92 (3H, s, OMe), 5.88 (1H, d, CH), 6.92 (2H, ABX, aromatic CH_ACH_B, J (H_AH_B)=8.4, J (H_AH_X)=2.0), 7.03 (1H, d, aromatic H_X). MS TOF: m/z calcd for $C_{19}H_{15}O_9Co_2$ $[M-H]^-$ 504.9386, found 504.9401.

4.3. Zinc-induced intermolecular dimerization of $Co_2(CO)_6$-complexed propargyl alcohols 3–6

*4.3.1. DL- and meso-μ-η²-(5,6-Diphenyl-3,7-decadiyne)bis(dicobalt hexacarbonyl) (**15**) (protocol B).* Under an atmosphere of nitrogen, a solution of **3** (89.2 mg, 0.2 mmol) in dry ether (5 mL) was added dropwise (8 min) to a solution of $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol) in dry ether (20 mL) at 0 °C and stirred for 1 h. An additional amount of $HBF_4 \cdot Me_2O$ (53.6 mg, 0.40 mmol) was added at 0 °C and stirred for another 30 min. The ethereal layer was removed, and the cation was washed with dry ether (2×15 mL) at −30 °C. The residual amount of ether was removed under reduced pressure at −30 °C, the cation was dissolved in dry CH_2Cl_2 (20 mL), cooled to −50 °C and stirred for 15 min. Zinc (650 mg, 10 mmol) was added at −50 °C, the reaction mixture was stirred for 5 min, then warmed to 20 °C and stirred for additional 30 min (TLC control). The crude mixture was filtered through a short bed of Florisil (1 cm), concentrated under reduced pressure (NMR: DL-**15**/*meso*-**15**, 73:27) to give inseparable DL-**15** and *meso*-**15** (57 mg, 66.4%). Spectral and physico-chemical data were reported previously.[3g]

*4.3.2. DL- and meso-μ-η²-[5,6-Di(4′-isopropylphenyl)-3,7-decadiyne] bis(dicobalthexacarbonyl) (**16**).* Analogous to protocol B, an interaction of **4** (97.6 mg, 0.2 mmol; dry ether, 5 mL) and $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol+26.8 mg, 0.20 mmol; in dry ether, 20 mL), followed by the treatment with zinc (650 mg, 10 mmol; dry CH_2Cl_2, 20 mL), afforded, after filtration though a short bed of Florisil (1 cm), an inseparable mixture of DL-**16** and *meso*-**16** (53 mg, 56.0%; DL-**16**/*meso*-**16**, 74:26) as red crystals. TLC (PE/E, 5:1): R_f 0.70. ^1H NMR (400 MHz, $CDCl_3$): *meso*- 0.90 (6H, t, $2CH_3$, J=7.2), DL- 1.20 (6H, t, $2CH_3$, J=7.2), 1.228 (6H, d, $2CH_3$, J=6.8), 1.230 (6H, d, $2CH_3$, J=6.8), *meso*- 1.25, 1.26 (6H, low-field components of two doublets, $2CH_3$), 1.50 (4H, ABX_3, $2CH_AH_B$, J (H_AH_B)=16.0), DL- 2.64 (4H, ABX_3, $2CH_AH_B$, J (H_AH_B)=16.0), 2.89 (2H, septet, 2CH), *meso*- 2.93 (2H, septet, 2CH, J=7.2), 4.52 (2H, s, 2CH), DL- 4.75 (2H, s, 2CH), 6.81 (4H, d, aromatic H, J=7.2), 7.06 (4H, d, aromatic H, J=8.4), *meso*- 7.19 (4H, ABX, aromatic H, J (H_AH_B)=7.6, J (H_AH_X)=0.8, J (H_BH_X)=0.8), 7.36 (2H, dd, aromatic H, J=8.0, J=0.8), 7.54 (2H, dd, aromatic H, J=8.0, J=0.8). ^{13}C NMR (100 MHz, $CDCl_3$): δ DL- 15.7 (CH_3CH_2), *meso*- 16.1

(CH_3CH_2), DL- 23.8, 24.1 ((CH_3)$_2$CH), *meso*- 24.0 ((CH_3)$_2$CH), 25.9 (CH_3CH_2), DL- 26.7 (CH_3CH_2), 33.7 ((CH_3)$_2$CH), *meso*-34.0 ((CH_3)$_2$CH), 54.0 (C5, C6), DL- 60.2 (C5, C6), 101.3, 101.6 (C3, C4, C7, C8), *meso*- 105.4, 106.6 (C3, C4, C7, C8), DL- 125.5, 130.8, 138.9, 148.7 (aromatic C), *meso*- 126.7, 127.1, 127.7, 131.2, 140.7, 148.8 (aromatic C), DL+*meso*- 199.4, 200.6 (C=O). Assignments are based on dept 45 and HSQC. MS TOF: *m*/*z* calcd for $C_{41}H_{37}O_{13}Co_4$ $[M+MeO]^-$ 972.9568, found 972.9534.

*4.3.3. DL- and meso-μ-η²-[5,6-Di(4′-methoxyphenyl)-3,7-decadiyne] bis(dicobalthexacarbonyl) (**17**).* Analogous to protocol B, an interaction of **5** (95.2 mg, 0.2 mmol; dry ether, 5 mL) and $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol; dry ether, 20 mL), followed by the treatment with zinc (650 mg, 10 mmol; dry CH_2Cl_2, 20 mL), afforded, after filtration through a short bed of Florisil (1 cm), a mixture of DL-**17**/*meso*-**17** (NMR: 85:15). Fractionation on preparative TLC (PE/E, 3:1) yielded DL-**17** (55.1 mg, 60.0%) as dark red crystals and *meso*-**17** (6 mg, 6.5%) as brown crystals.

Compound DL-**17**. Mp: 89–100 °C (w/decomp.; sealed capillary; dried by co-evaporation with benzene, 3×1 mL). TLC (PE/E, 1:1): R_f 0.65. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (6H, t, $2CH_3$, J=7.2), 2.68 (4H, ABX_3, $2CH_AH_B$, J (H_AH_B)=16.0), 3.81 (6H, s, $2OCH_3$), 4.74 (2H, s, 2CH), 6.76 (8H, m, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8 (C1, C10), 26.7 (C2, C9), 55.3 (2OMe), 59.9 (C5, C6), 101.2, 101.7 (C3, C4, C7, C8), 112.9, 131.9, 133.7, 159.2 (aromatic C), 199.4, 200.5 (C=O). MS TOF: *m*/*z* calcd for $C_{37}H_{29}O_{15}Co_4$ $[M+MeO]^-$ 948.8829, found 948.8818.

Compound *meso*-**17**. Mp: 133–143 °C (w/decomp.; sealed capillary; dried by co-evaporation with benzene, 3×1 mL). TLC (PE/E, 1:1): R_f 0.64. ^{1}H NMR (400 MHz, C_6D_6): δ 0.96 (6H, t, $2CH_3$, J=7.4), 1.70 (4H, ABX_3, $2CH_AH_B$, J (H_AH_B)=15.6), 3.46 (6H, s, $2CH_3$), 4.71 (2H, s, 2CH), 6.88 (2H, dd, aromatic H, J=8.2, J=2.6), 7.02 (2H, dd, aromatic H, J=8.4, 2.8), 7.34 (2H, dd, aromatic H, J=8.4, 2.4), 7.63 (2H, dd, aromatic H, J=8.4, 2.4). MS TOF: *m*/*z* calcd for $C_{37}H_{29}O_{15}Co_4$ $[M+MeO]^-$ 948.8829, found 948.8832.

*4.3.4. DL- and meso-μ-η²-[5,6-Di(3′,4′-dimethoxyphenyl)-3,7-decadiyne]bis(dicobalthexacarbonyl) (**18**).* Analogous to protocol B, an interaction of **6** (101.2 mg, 0.2 mmol; dry ether, 5 mL) and $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol; dry ether, 20 mL), followed by the treatment with zinc (650 mg, 10 mmol; dry CH_2Cl_2, 20 mL), afforded, after filtration through a short bed of Florisil (1 cm), a mixture of DL-**18**/*meso*-**18** (NMR: 90:10). Fractionation on preparative TLC (PE/E, 1:1) yielded DL-**18** (69.2 mg, 70.7%) as dark red crystals and *meso*-**18** (8.0 mg, 8.2%) as brown amorphous solid.

Compound DL-**18**. Mp: 120–121 °C (sealed capillary; dried by co-evaporation with benzene, 3×1 mL). TLC (E): R_f 0.60. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (6H, t, $2CH_3$, J=7.2), 2.70 (4H, ABX_3, $2CH_AH_B$, J (H_AH_B)=15.6), 3.59 (6H, br s, $2OCH_3$), 3.87 (6H, s, $2OCH_3$), 4.72 (2H, s, 2CH), 6.30 (2H, br s, aromatic H), 6.61 (2H, br s, aromatic H), 6.77 (2H, d, aromatic H, J=8.0). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8 (C1, C10), 26.8 (C2, C9), 55.3 (2OMe), 56.0 (2OMe), 60.1 (C5, C6), 101.0, 101.5 (C3, C4, C7, C8), 110.3, 114.5, 134.0, 147.7, 148.7 (aromatic C), 199.5, 200.5 (C=O). MS TOF: *m*/*z* calcd for $C_{39}H_{33}O_{17}Co_4$ $[M+MeO]^-$ 1008.9051, found 1008.9037. Single crystals suitable for X-ray structure analysis were obtained by methanol vapor diffusion into a solution of DL-**18** in CH_2Cl_2 (48 h, +5 °C).

Compound *meso*-**18** TLC (PE/E, 1:2): R_f 0.62. ^{1}H NMR (400 MHz, C_6D_6): δ two atropoisomers, 51:49 0.95 (3H, t, CH_3, J=7.6), 0.96 (3H, t, CH_3, J=7.2), 0.98 (6H, t, $2CH_3$, J=6.8), 1.59–1.99 (8H, m, $4CH_2$), 3.53 (6H, s, $2OCH_3$), 3.575 (3H, s, OCH_3), 3.579 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 4.67 (1H, s, CH), 4.79 (1H, s, CH), 4.73 (2H, AB, CH_AH_B, J (H_AH_B) 11.6), 6.68–6.85 (4H, m, aromatic H), 6.95–7.06 (4H, m, aromatic H), 7.18–7.36 (4H, m, aromatic H). MS TOF: *m*/*z* calcd for $C_{39}H_{33}O_{17}Co_4$ $[M+MeO]^-$ 1008.9051, found 1008.9029.

4.4. X-ray crystallography of DL-18[8]

A suitable crystal of DL-**18** was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 APEX II CCD sealed tube diffractometer with graphite monochromated Mo K_α (0.71073 Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.5° frame widths. Data collection, indexing and initial cell refinements were all carried out using APEX II[8a] software. Frame integration and final cell refinements were done using SAINT[8b] software. The final cell parameters were determined from least-squares refinement on 1142 reflections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).[8c] Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij}'s related to the atom's ridden upon. Only the cobalt and oxygen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the International Tables for X-ray Crystallography.[8d] Structure solution, refinement, graphics, and generation of publication materials were performed by using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Supplementary data.

4.5. Decomplexation protocol: synthesis of DL- and *meso*-5,6-diaryl-3,7-decadiynes 20–23

*4.5.1. DL- and meso-5,6-Diphenyl-3,7-decadiyne (**20**).* Decomplexation of DL- and *meso*-**15** was reported previously,[3g] affording DL-**20**/*meso*-**20**, in the ratio of 70:30 (69.3%).

*4.5.2. DL- and meso-5,6-Di(4′-isopropylphenyl)-3,7-decadiyne (**21**) (protocol C).* Under an atmosphere of nitrogen, at −78 °C, a solution of degassed $Ce(NH_4)_2(NO_3)_6$ (131.0 mg, 0.24 mmol) in acetone (8 mL, degassed) was added (10 min) to a solution of DL-**16**+*meso*-**16** (28.3 mg, 0.03 mmol; DL-**16**/*meso*-**16**, 74:26) in acetone (10 mL, degassed). The reaction mixture was stirred at −78 °C for 15 min, then at −50 °C for 30 min. Additional portions of $Ce(NH_4)_2(NO_3)_6$ (3×16.4 mg, 0.03 mmol; acetone, 1 mL) were added at −78 °C, the reaction mixture was stirred for 15 min, and then at −50 °C for 30 min (TLC control). The crude product was treated (−78 °C, N_2) with a degassed saturated solution of $NaCl_{aq}$ (20 mL), transferred to a separatory funnel and extracted with ether (2×15 mL). The combined organic layers were dried (molecular sieves 4 Å), filtered, concentrated under reduced pressure, and fractionated on preparative TLC (1/2 plate, PE/E, 10:1) to afford DL-**21**+*meso*-**21** (8.2 mg, 73.9%; NMR: DL-**21**/*meso*-**21**, 71:29) as a light yellow oil. TLC (PE/E, 10:1): R_f 0.54 (visualized in phosphomolybdic acid). ^{1}H NMR (400 MHz, $CDCl_3$): δ *meso*- 1.07 (6H, t, $2CH_3$, J=7.6), DL- 1.18 (6H, t, $2CH_3$, J=7.4) DL+*meso*- 1.25 (24H, d, $4(CH_3)_2CH$, J=6.4), *meso*- 2.16 (4H, q, $2CH_2$), DL- 2.25 (4H, q, $2CH_2$), DL+*meso*- 2.89 (4H, septet, 4CH), *meso*- 3.81 (2H, s, 2CH), DL- 3.86 (2H, s, 2CH), DL+*meso*- 7.09–7.29 (16H, m, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ *meso*- 12.5 (C2, C9), DL- 12.6 (C2, C9), *meso*- 14.0 (C1, C10), DL- 14.2 (C1, C10), DL+*meso*- 24.00, 24.04, 24.07 ((CH_3)$_2$CH), DL+*meso*- 33.7 ((CH_3)$_2$CH), *meso*- 45.7 (C5, C6), DL- 45.8 (C5, C6), DL- 78.8 (C4, C7), *meso*- 79.7 (C4, C7), DL- 86.3 (C3, C8), *meso*- 86.4 (C3, C8), *meso*- 125.7, 128.6, 137.3 (aromatic C), DL- 125.8, 128.3, 137.6 (aromatic C), DL+*meso*- 147.4 (aromatic C). MS ESI(+): *m*/*z* calcd for $C_{28}H_{35}$ $[MH]^+$ 371.2733, found 371.2740.

*4.5.3. DL-5,6-Di(4′-methoxyphenyl)-3,7-decadiyne (**22**).* Analogous to protocol C, treatment of DL-**17** (37 mg, 0.04 mmol; acetone, 10 mL) with $Ce(NH_4)_2(NO_3)_6$ (175.4 mg, 0.24 mmol+21.9 mg, 0.04 mmol) in acetone (8 mL, 1 mL, degassed), followed by an

aqueous work-up and fractionation on preparative TLC (PE/E, 3:1), afforded DL-**22** (11 mg, 79.7%) as a light yellow oil. TLC (PE/E, 2:1): R_f 0.50 (visualized in phosphomolybdic acid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (6H, t, $2CH_3$, J=7.6), 2.25 (4H, q, $2CH_2$), 3.80 (6H, s, $2OCH_3$), 3.85 (2H, s, 2CH), 6.75–6.82 (4H, six lines, aromatic H), 7.11–7.18 (4H, six lines, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6 (C2, C9), 14.2 (C1, C10), 45.2 (C5, C6), 55.2 (OCH_3), 79.2 (C4, C7), 86.4 (C3, C8), 113.1, 129.7, 131.9, 158.5 (aromatic C). MS ESI(+): m/z calcd for $C_{24}H_{27}O_2$ $[MH]^+$ 347.2006, found 347.2012.

*4.5.4. DL-5,6-Di(3′,4′-dimethoxyphenyl)-3,7-decadiyne (**23**).* Analogous to protocol C, treatment of DL-**18** (48.9 mg, 0.05 mmol) with Ce $(NH_4)_2(NO_3)_6$ (219.2 mg, 0.40 mmol+27.4 mg, 0.05 mmol+27.4 mg, 0.05 mmol) in acetone (8 mL+1 mL+1 mL, degassed), followed by an aqueous work-up and filtration through a short bed of Florisil (1 cm), afforded DL-**23** (16.6 mg, 81.7%) as light yellow crystals. Mp: 123–125 °C (sealed capillary; dried by co-evaporation with benzene, 3×1 mL). TLC (E): R_f 0.40. ^{1}H NMR (400 MHz, C_6D_6): δ 1.16 (3H, t, $2CH_3$, J=7.4), 2.23 (2H, q, $2CH_2$), 3.50 (6H, s, $2OCH_3$), 3.60 (6H, s, $2OCH_3$), 4.24 (2H, s, 2CH), 6.70 (2H, d, aromatic H, J=8.0), 7.08 (2H, s, aromatic H), ~7.09 (2H, dd, aromatic H, J=2.0). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6 (C2, C9), 14.3 (C1, C10), 45.5 (C5, C6), 55.7, 55.9 (4OMe), 79.3, 86.5 (C3, C4, C7, C8), 110.4, 112.2, 120.9, 132.1, 148.0, 148.1 (aromatic C). MS TOF: m/z calcd for $C_{26}H_{31}O_4$ $[MH]^+$ 407.2217, found 407.2230.

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Supplementary data

Tables of crystallographic details, bond distances, angles, atomic coordinates, equivalent isotropic displacement parameters, and torsion angles for DL-**18**. Crystallographic data (excluding structure factors) for DL-**18** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 763505. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.05.011.

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