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Synthesis of 7-silanorbornene electron donor-acceptor polycyclic dyads

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Abstract. High pressure cycloaddition synthesis of electron donor-acceptor dyads possessing rigid polynorbornene framework and 7-silanorbornadiene moiety is described.

Introduction. Organometallic compounds, particularly those with metal-metal σ -bonds as electron-rich species are excellent electron donors.[1] Studies with group-14 elements (silicon and germanium) catenanes showed electron transfer to electron acceptor.[2] Furthermore, it was shown that C_{60} is good electron acceptor for photoinduced electron transfer from cyclic organogermanium[3] or organosilicon[4,5] compounds. Preparation of electron-transfer dyads[1,6] (donor-acceptor molecules) with novel molecular architectures and ED/EA geometrical orientations is the current synthetic challenge.

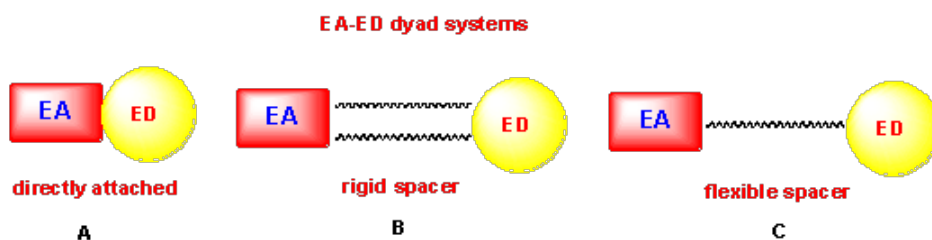


Figure 1. The architecture of acceptor-donor couples (dyads)

Figure 1 illustrates schematic representation of dyads involving electron-donor (ED) and electron-acceptor (EA) electrophores: A) directly attached, B) separated by rigid spacer and C) separated by flexible spacer. A viable approach to artificial models for the mimicry of natural photosynthesis is to organize the donor-acceptor couple *via* controlling the distance and the electronic coupling (Figure 2). We describe here the synthesis of new electron acceptor and silicon-donor dyads by facile and irreversible [4+2]cycloadditions of polynorbornenes and siloles.

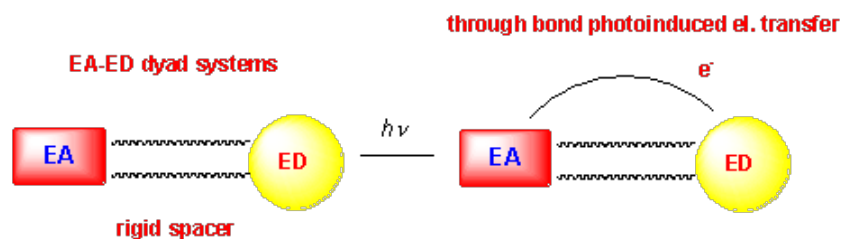


Figure 2. Through bond photoinduced electron transfer

Use of rigid alicyclic systems for the construction of spacers, possessing precise separation and orientation of effector groups on rigid frameworks has been achieved in our previous synthetic work. A variety of rigid polycyclic spacers based on the polynorbornene framework[7-11] is available and some representative examples are shown in Figure 3. Based on our previous studies on the cycloaddition reactivity of metalloles[12], it was necessary to choose molecules containing 7-oxanorbornene or 7-oxabenzonorbornene moiety such as **1**[13] and **2** in order to retain dienophilic reactivity towards siloles. For instance, diene **1** was used recently as a rigid spacer in the synthesis of U-shaped dyads and the study of electron transfer.[14] Alicyclic spacers containing bicyclo[2.2.2]octene moiety have been also prepared,[15][16] however, they have not been employed for preparation of dyads, since they showed smaller reactivity towards dienes.

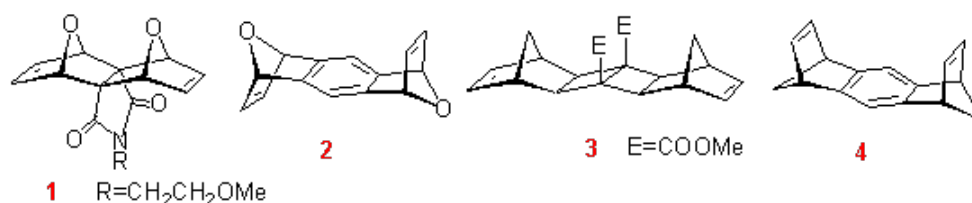
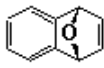
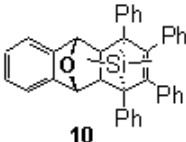
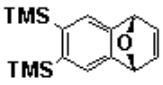
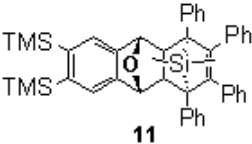
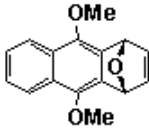
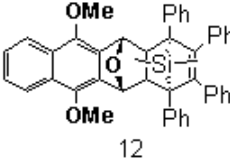
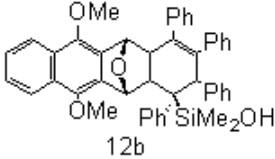
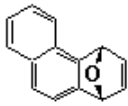
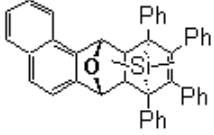
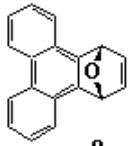
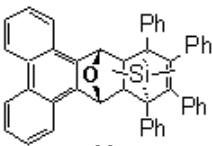


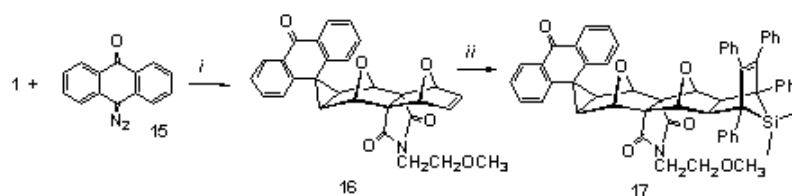
Figure 3. Polycyclic rigid spacers

In order to synthesize polycyclic dyads which were designed by AM1 modeling, a single-step cycloaddition methodology was employed. Firstly a series of ED/EA dyads with short intramolecular separation was prepared. Table 1 summarizes the results of high pressure cycloadditions of 1,1-dimethyl-2,3,4,5-tetraphenylsilole to 7-oxabenzonorbornenes: 1,4-epoxy-1,4-dihydronaphthalene **5**, 5,6-bis(trimethylsilyl)-1,4-epoxy-1,4-dihydronaphthalene **6**[17], 9,10-dimethoxy-1,4-oxa-1,4-dihydroanthracene **7**[18], 1,4-oxa-1,4-dihydro-phenanthrene **8**[19] and 1,4-epoxy-1,4-dihydrotriphenylene **9**[19]. All reactions were highly stereospecific and *exo,endo*- cycloadducts were formed exclusively.[20] Products **10**[21] and **11**[22] also incorporated in Table 1 were known from our previous studies. It was interesting to mention that in the reaction of 1,1-dimethyl-2,3,4,5-tetraphenylsilole with 9,10-dimethoxy-1,4-oxa-1,4-dihydro-anthracene **7**, ring opening product **12b** was also obtained. This acid catalysed 7-silanorbornene ring cleavage was known previously to happen only in the 1,1-dimethyl-2,3-diphenylsilole cycloadducts.[21]

Table 1. Addition of 1,1-dimethyl-2,3,4,5-tetraphenylsilole to 7-benzonorbornadienes

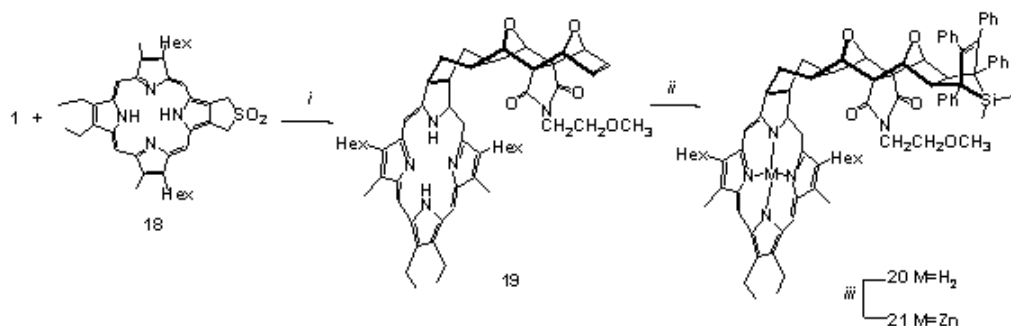
Entry	Substrate	Product	Conditions	Yield (%)
1			1 GPa, 20 h, RT	92
2			0.8 GPa, 24 h, 70 °C	31
3			0.8 GPa, 24 h, 80 °C	16
				3
4			0.8 GPa, 24 h, 80 °C	49
5			0.8 GPa, 24 h, 80 °C	62

Two-step cycloaddition protocol was employed for the synthesis of longer separated dyad depicted in Scheme 1. This reaction has followed the report by Warrener *et al.* for the 9-diazo-4,5-diazafluorene addition to norbornenes.[23] When 9-diazoanthrone[24] was allowed to react with bis-alkene **1** in 1,3-dipolar cycloaddition reaction, a symmetrical 1:1 spiro-cycloadduct **16** was formed. Initially formed pyrazoline adduct was not observed in the reaction conditions (toluene reflux), due to its facile thermal deazetisation and formation of cyclopropane ring. After chromatographic separation monoadduct **16** was allowed to react with 1,1-dimethyl-2,3,4,5-tetraphenylsilole under high pressure (0.8 GPa, at 80 °C) to obtain dyad **17** in 64% yield.



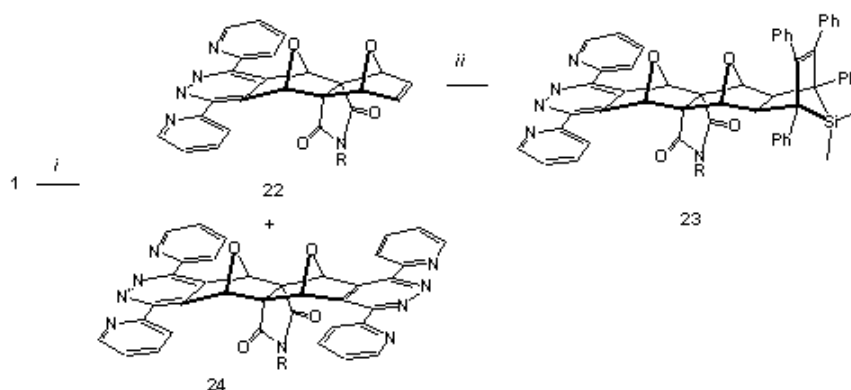
Scheme 1. Reagents and conditions *i*) 120 oC, 16h, toluene; *ii*) 1,1-dimethyl-2,3,4,5-tetraphenylsilole, 0.8 GPa, 1 d, 80 oC, DCM

There are some interesting features noted in the proton NMR spectra of the new adducts. Steric compression[25] of aromatic signals caused by the proximity of oxygen atom and aromatic protons in adduct **16** causes an up-field chemical shift of H₁ anthrone proton by 0.3 ppm, as compared to 9-diazoanthrone. Furthermore, the magnetic shielding of anthrone ring causes the up-field chemical shift for methoxy resonance of methoxyethyl substituent in **1** by 0.25 ppm and could be used as an indicator for stereochemical assignments of these adducts.



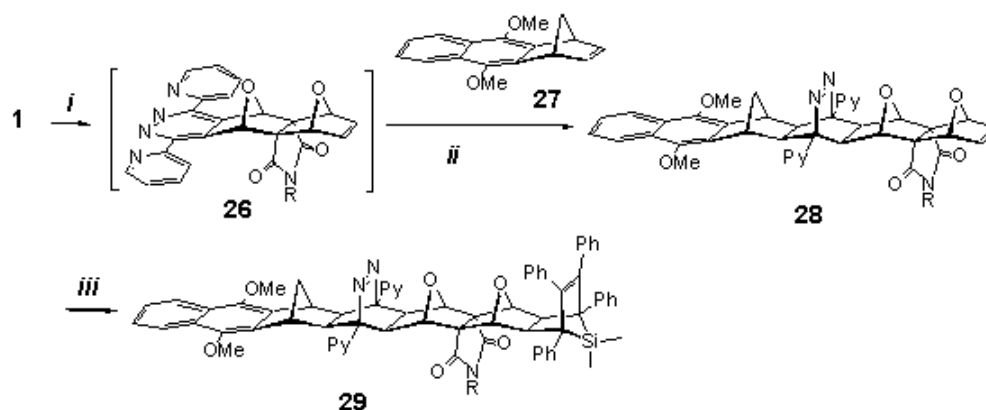
Scheme 2. Reagents and conditions *i*) 120 °C, 2h, toluene; *ii*) 1,1-dimethyl-2,3,4,5-tetraphenylsilole, 0.8 GPa, 3 d, 100 °C, DCM; *iii*) ZnOAc, CHCl₃, MeOH

In a similar manner dyad system containing porphyrine ring has been synthesised (Scheme 2). A solution of porphyrine sulfone **18** [26] and alkene **1** in toluene was heated at reflux. In these reaction conditions, molecule of SO₂ was eliminated and reactive porphyrine-1,3-diene formed. It was trapped *in situ* with **1** in Diels-Alder reaction to form adduct **19** in 28 % yield. Under high pressure 1,1-dimethyl-2,3,4,5-tetraphenylsilole reacts readily with **19** forming cycloadduct **20** (26%), which was subsequently metallated with zinc acetate.



Scheme 3. Reagents and conditions *i*) 2-pyridyl-*s*-tetrazine, CHCl₃, 60 °C, 3h //DDQ 16h, *ii*) 1,1-dimethyl-2,3,4,5-tetraphenylsilole, 0.8 GPa, 3 d, 80 °C, DCM

Furthermore, reaction of diene **1** and 2-pyridyl-*s*-tetrazine in chloroform followed by DDQ oxidation afforded adduct **22** as a major, and bis-adduct **24** as a minor product (in 41 % and 5 % yield, respectively). After chromatographic separation, alkene **22** was further reacted with 1,1-dimethyl-2,3,4,5-tetraphenylsilole under high pressure to form dyad **23** in 73% yield (Scheme 3).



Scheme 4. Reagents and conditions *i*) 2-pyridyl-*s*-tetrazine, DCM 1h/0.8 GPa, 1 d, DCM; *ii*) **27**, 0.8 GPa, 3 d, DCM; *iii*) 1,1-dimethyl-2,3,4,5-tetraphenylsilole, 0.8 GPa, 3 d, 80 °C, DCM

Dyad **29** possessing longer molecular separation was prepared by the set of Diels-Alder reactions shown in Scheme 4. In

order to assembly this larger system, BLOCK synthetic protocols were used[27] employing tetrazine coupling method[28] in the first step. Reaction of diene **1** and 2-pyridyl-*s*-tetrazine in the presence of triethyl amine gave after high pressure promoted reaction at 8 kbar intermediate 1,3-diene **26**. Intermediate **26** was reacted under high pressure with alkene **27** to obtain 1:1 adduct **28** in 32 % yield. Finally, high pressure reaction of 1,1-dimethyl-2,3,4,5-tetraphenylsilole with **28** afforded adduct **29** in 45 % yield. AM1 structure depicted in Figure 4 reveals the geometrical features of this dyad.

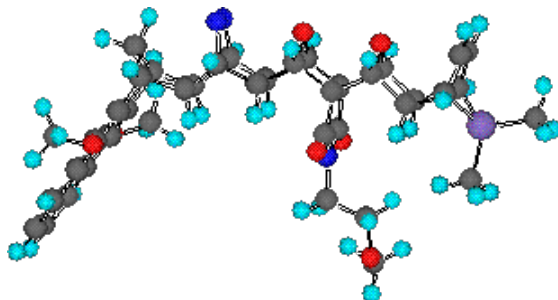
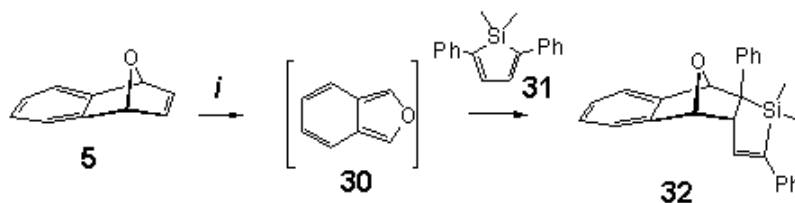


Figure 4. AM1 model of dyad **29**, phenyl and pyridyl substituents are omitted for clarity

The shortest dyad separation could be achieved by direct connection of ED and EA units. The fact that siloles could also act as dienophile[29] was employed in order to prepare directly attached ED/EA dyads. However, reactions with cyclic dienes such as isobenzofuran (IBF) with 1,1-dimethyl-2,3,4,5-tetraphenylsilole were unsuccessful. When 1,1-dimethyl-2,5-diphenylsilole **31** was used as a dienophile in the reaction with IBF, adduct **32** was obtained in 25 % yield (Scheme 5). Here IBF was generated *in situ* by reaction of 2-pyridyl-*s*-tetrazine and 7-oxabenzonornbornadiene **5** and trapped with **31** using the standard tetrazine method.[30]



Scheme 5. Reagents and conditions *i*) 2-pyridyl-*s*-tetrazine, CHCl₃, DCM, 1,1-dimethyl-2,5-diphenylsilole, 1 d, RT

The investigation of the electrochemical and photophysical properties of novel adducts described in this paper is currently being undertaken and these results will be reported in due course.

Selected spectroscopic data for new compounds

12: ¹H (CDCl₃), δ/ppm: 0.16 (3H, s), 0.61 (3H, s), 3.41 (2H, s), 3.99 (6H, s), 6.14 (2H, s), 6.79-7.18 (20H, m), 7.51 (2H, dd, *J*=6.4 Hz, *J*=3.3 Hz), 8.14 (2H, dd, *J*=6.4 Hz, *J*=3.3 Hz),

12b: ¹H (CDCl₃), δ/ppm: -0.31 (3H, s), 0.53 (3H, s), 2.99 (1H, t, *J*=6.8 Hz), 3.22 (3H, s), 3.37 (1H, d, *J*=8.9 Hz), 4.18 (3H, s), 5.01 (1H, d, *J*=6.4 Hz), 5.98 (1H, s), 6.21 (1H, s), 6.72 (1H, br s), 6.89-7.14 (20H, m), 7.46 (1H, td, *J*=6.7 Hz, *J*=1.4 Hz), 7.55 (1H, td, *J*=6.7 Hz, *J*=1.4 Hz), 8.12 (1H, d, *J*=8.2 Hz), 8.17 (1H, d, *J*=8.2 Hz),

13: ¹H (CDCl₃), δ/ppm: 0.08 (3H, s), 0.66 (3H, s), 3.32 (1H, d, *J*=7.2 Hz), 3.37 (1H, d, *J*=7.2 Hz), 5.96 (2H, s), 6.31 (2H, d, *J*=4.3 Hz), 6.87-8.00 (24H, m),

14: ¹H (CDCl₃), δ/ppm: 0.18 (3H, s), 0.69 (3H, s), 3.36 (2H, s), 6.38 (2H, s), 8.86-7.74 (28H, m),

16: ¹H (CDCl₃), δ/ppm: 2.22 (2H, s), 3.22 (3H, s), 3.43 (2H, t, *J*=4.9 Hz), 3.53 (2H, t, *J*=4.9 Hz), 5.15 (2H, s), 5.24 (2H, s), 6.51 (2H, s), 7.17 (2H, dd, *J*=7.44 Hz, *J*=0.39 Hz), 7.30-7.43 (5H, m), 7.98 (1H, dd, *J*=2.82 Hz, *J*=1.14 Hz), 8.05 (1H, dd, *J*=7.5 Hz, *J*=1.62 Hz),

17: ¹H (CDCl₃), δ/ppm: 0.05 (3H, s), 0.59 (3H, s), 2.23 (2H, s), 3.19 (3H, s), 3.39 (2H, s), 3.67 (2H, t, *J*=8.4 Hz), 3.74 (2H, t, *J*=8.4 Hz), 5.21 (2H, s), 5.26 (2H, s), 6.71-7.43 (H, m), 7.95 (1H, d, *J*=7.0 Hz), 8.08 (1H, d, *J*=7.0 Hz),

19: ^1H (CDCl_3), d/ppm: -0.71 (2H, s), 0.88 (6H, t, $J=7.3$ Hz), 1.19 (4H, t, $J=7.1$ Hz), 1.33-1.37 (4H, m), 1.46-1.51 (4H, m), 1.69-1.75 (4H, m), 1.83 (6H, t, $J=7.4$ Hz), 1.98 (3H, s), 2.22-2.27 (4H, m), 2.89 (2H, t, $J=6.1$ Hz), 3.04 (2H, t, $J=6.1$ Hz), 3.54 (6H, s), 4.01 (4H, t, $J=3.7$ Hz), 4.07 (4H, t, $J=7.1$ Hz), 4.66-4.69 (4H, m), 5.17 (2H, s), 5.43 (2H, s), 6.57 (2H, s), 10.02 (2H, s), 10.06 (2H, s),

20: ^1H (CDCl_3), d/ppm: -0.71 (2H, s), 0.06 (3H, s), 0.62 (3H, s), 0.97 (6H, t, $J=7.3$ Hz), 1.19 (4H, t, $J=7.1$ Hz), 1.33-1.37 (4H, m), 1.46-1.51 (4H, m), 1.69-1.75 (4H, m), 1.93 (6H, t, $J=7.4$ Hz), 1.95 (3H, s), 2.28-2.39 (4H, m), 2.89 (2H, t, $J=6.1$ Hz), 3.04 (2H, t, $J=6.1$ Hz), 3.54 (6H, s), 4.01 (4H, t, $J=3.7$ Hz), 4.07 (4H, t, $J=7.1$ Hz), 4.66-4.69 (4H, m), 5.17 (2H, s), 5.43 (2H, s), 6.57 (2H, s), 6.77-7.21 (20H, m), 10.00 (2H, s), 10.01 (2H, s),

21: ^1H (CDCl_3), d/ppm: 0.04 (3H, s), 0.60 (3H, s), 0.96 (6H, t, $J=7.3$ Hz), 1.19 (4H, t, $J=7.1$ Hz), 1.33-1.37 (4H, m), 1.46-1.51 (4H, m), 1.69-1.75 (4H, m), 1.91 (6H, t, $J=7.4$ Hz), 1.93 (3H, s), 2.28-2.39 (4H, m), 2.89 (2H, t, $J=6.1$ Hz), 3.04 (2H, t, $J=6.1$ Hz), 3.54 (6H, s), 4.01 (4H, t, $J=3.7$ Hz), 4.07 (4H, t, $J=7.1$ Hz), 4.66-4.69 (4H, m), 5.17 (2H, s), 5.43 (2H, s), 6.57 (2H, s), 6.77-7.21 (20H, m), 10.00 (2H, s), 10.20 (2H, s),

22: ^1H (CDCl_3), d/ppm: 2.63 (2H, t, $J=5.5$ Hz), 2.94 (2H, t, $J=5.5$ Hz), 2.96 (3H, s), 5.63 (2H, s), 6.60 (2H, s), 7.44 (2H, dd, $J=3.8$ Hz, $J=1.6$ Hz), 7.46 (2H, dd, $J=4.8$ Hz, $J=1.1$ Hz), 7.92 (2H, dt, $J=7.7$ Hz, $J=1.8$ Hz), 8.75 (2H, td, $J=8.0$ Hz, $J=0.9$ Hz), 8.87-8.89 (2H, m),

23: ^1H (CDCl_3), d/ppm: 2.18 (2H, t, $J=5.3$ Hz), 2.24 (2H, t, $J=5.3$ Hz), 2.27 (3H, s), 7.38 (4H, s), 7.40-7.45 (4H, m), 7.84 (2H, dt, $J=7.9$ Hz, $J=1.8$ Hz), 8.64 (2H, td, $J=7.9$ Hz, $J=0.9$ Hz), 8.87-8.90 (2H, m),

24: ^1H (CDCl_3), d/ppm: -0.08 (3H, s), 0.59 (3H, s), 2.83 (2H, t, $J=5.2$ Hz), 2.96 (3H, s), 3.06 (2H, t, $J=5.2$ Hz), 3.41 (2H, s), 5.56 (2H, s), 6.89-7.22 (20H, m), 7.16 (2H, s), 7.49 (2H, t, $J=5.4$ Hz), 7.95 (2H, t, $J=7.7$ Hz), 8.77 (2H, d, $J=7.9$ Hz), 8.96 (2H, d, $J=2.0$ Hz),

28: ^1H (CDCl_3), d/ppm: 1.08 (1H, d, $J=10.3$ Hz), 1.71 (1H, d, $J=10.3$ Hz), 2.84 (2H, s), 2.99 (3H, s), 3.22 (2H, s), 3.45 (2H, t, $J=3.7$ Hz), 3.48 (2H, t, $J=3.7$ Hz), 3.65 (2H, s), 3.71 (6H, s), 4.35 (2H, s), 4.97 (2H, t, $J=0.8$ Hz), 6.33 (2H, t, $J=0.8$ Hz), 7.37 (2H, dd, $J=6.6$ Hz, $J=3.3$ Hz), 7.44 (1H, dd, $J=4.8$ Hz, $J=1.2$ Hz), 7.47 (2H, dd, $J=4.8$ Hz, $J=1.2$ Hz), 7.97 (2H, dd, $J=7.7$ Hz, $J=1.9$ Hz), 8.4 (2H, dt, $J=7.7$ Hz, $J=1.9$ Hz), 8.83-8.85 (4H, m),

29: ^1H (CDCl_3), d/ppm: -0.08 (3H, s), 0.52 (3H, s), 1.03 (1H, d, $J=10.4$ Hz), 1.71 (1H, d, $J=10.4$ Hz), 3.02 (2H, s), 3.05 (3H, s), 3.21 (2H, s), 3.22 (2H, s), 3.23 (2H, s), 3.58 (2H, t, $J=5$ Hz), 3.72 (2H, t, $J=5.1$ Hz), 3.78 (3H, s), 4.43 (2H, s), 4.89 (2H, s), 6.64-6.67 (4H, m), 6.80-6.84 (6H, m), 6.87-6.92 (4H, m), 6.99-7.05 (2H, m), 7.10 (4H, t, $J=7.1$ Hz), 7.40 (2H, dd, $J=6.4$ Hz, $J=3.3$ Hz), 7.49 (2H, ddd, $J=6.9$ Hz, $J=1.7$ Hz, $J=0.9$ Hz), 8.05 (2H, dd, $J=6.4$ Hz, $J=3.3$ Hz), 8.07 (2H, dt, $J=7.8$ Hz, $J=1.6$ Hz), 8.8 (2H, d, $J=4.4$ Hz), 8.89 (2H, dd, $J=5.3$ Hz, $J=2.4$ Hz),

32: ^1H (CDCl_3), d/ppm: -0.32 (3H, s), 0.55 (3H, s), 3.10 (1H, d, $J=3.3$ Hz), 5.11 (1H, s), 5.68 (1H, s), 6.88 (3H, dt, $J=7.7$ Hz, $J=0.7$ Hz), 6.91 (2H, dt, $J=7.7$ Hz, $J=1.3$ Hz), 7.01 (1H, d, $J=7.1$ Hz), 7.11 (1H, d, $J=3.3$ Hz), 7.17-7.21 (4H, m), 7.27 (2H, t, $J=7.7$ Hz), 7.34-7.37 (2H, m),

Conclusion. Cycloaddition protocols were used in conjunction with high pressure conditions for synthesis of novel dyads in whose effector groups are separated by polycyclic norbornane framework.

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