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Cycloaddition reactions of tetracyclones, benzo[*b*]thiophene *S*-oxides, and benzo[*b*]thiophene *S*,*S*-dioxides with alkynes

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Abstract *: Tetracyclones have been submitted to Diels-Alder reactions with alkynes to give oligoarylbenzenes. The reactions were performed under diverse conditions, such as in diphenyl ether, under solventless conditions and under microwave irradiation. Also, 3-substituted benzo[b]thiophene S-oxides and benzo[b]thiophene S,S-dioxides have been subjected to [4+2]-cycloaddition reactions with alkynes and alkenes to give aryl substituted extended aromatic systems.*

Keywords *– tetracyclone,benzo[b]thiophene S-oxide,benzo[b]thiophene S,S-dioxide, thiophene S,S-dioxide, thiophene S-oxide, Diels-Alder reaction, cycloaddition, solventless reaction*

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Abbreviations used:

Bzl:	benzyl	EI:	electron ionization
CPBA:	chloroperoxybenzoic acid	FAB:	fast atom bombardment
DCC:	dicyclohexylcarbodiimide	NBS:	N-bromosuccinimide
DDQ:	2,3-dichloro-5,6-dicyanobenzoquinone	Ph:	phenyl
DIPA:	diisopropylamine	TBAF:	tetrabutylammonium fluoride
DMAP:	4-dimethylaminopyridine	THF:	tetrahydrofuran
DME:	1,2-dimethoxyethane	TMS:	trimethylsilyl

I. Introduction

Arenes can be synthesized facilely through [4+2]-cycloaddition reactions. The approaches include the reactions of alkynes with cyclic dienes that possess within the ring a function that can be extruded, eg., as CO_2, CO, SO or SO_2. Such cyclic dienes are thiophene *S*-oxides **1**, thiophene *S*,*S*-dioxides **2**, cyclopentadienones **3** (eg., tetracyclones) and α-pyrones **4**, among others (Figure 1). Also, arenoannelated cyclic dienes such as benzo[*b*]thiophene *S*-oxides **5** and benzo[*b*]thiophene *S*,*S*-dioxides **6** (Figure 1) belong to this group of reactants that furnish arenes in cycloadditions with alkynes, in this case leading to more extended aromatic π-systems. Furthermore, cycloaddition of these reactants with alkenes can lead to aromatic systems upon a subsequent dehydrogenation step, where with certain alkenes such as quinones an externally added oxidant is not always a necessity.

Within this context, tetraarylcyclopentadienones (tetracyclones, **7**) are commonly used to construct oligoarylbenzenes of considerable complexity, with an easy access to tetra-, penta- and hexaarylbenzenes [1,2]. Molecules with hexaarylbenzene units have been used as sensors [3], as components in organic light emitting diodes (OLEDs) [4] and in molecular switches [5]. A recent comprehensive review of hexaarylbenzenes can be found in ref. 6. We have noted that cycloaddition of tetracyclones at higher temperatures in the presence of air leads to α-pyrones as side products [7]. While α-pyrones lend themselves to cycloaddition reactions with alkynes [8], oftentimes they are less reactive dienes than the cyclopentadienones (tetracyclones). In the following, tetracyclones have been reacted with substituted tolanes (diphenylacetylenes) under diverse reaction conditions such as under solventless conditions, in diphenyl ether as solvent and under microwave irradiation. These reactions are set in juxtaposition and compared with the example of a reaction of a thiophene S-oxide with an alkyne.

In cycloaddition reactions, benzo[*b*]thiophene *S*-oxides **5** (R=H) have been found to react as the ene-component in [3+2]-cycloadditions with 1,3-dipoles such as mesitonitrile oxide [9], in Diels-Alder type [4+2]-cycloadditions [10], just as benzo[*b*]thiophene *S*,*S*-dioxides **6** (R=H) [10], and photochemically in [2+2]-cycloadditions [11]. In [4+2]-cycloaddition reactions, benzo[*b*]thiophene *S*-oxides **5** (R=H) can act as diene component, also, as is shown by the dimerization of the unsubstituted benzo[*b*]thiophene *S*-oxide with itself

[12]. Also, the author has shown previously that certain 2-substituted benzothiophene S-oxides can function as dienes in cycloaddition reactions [13]. In the following, the viability of 3-substituted benzo[*b*]thiophene *S*-oxides **5** and 3-substituted benzo[*b*]thiophene *S*,*S*-dioxides **6** as dienes in [4+2]-cycloaddition with selected alkynes and alkenes is examined.

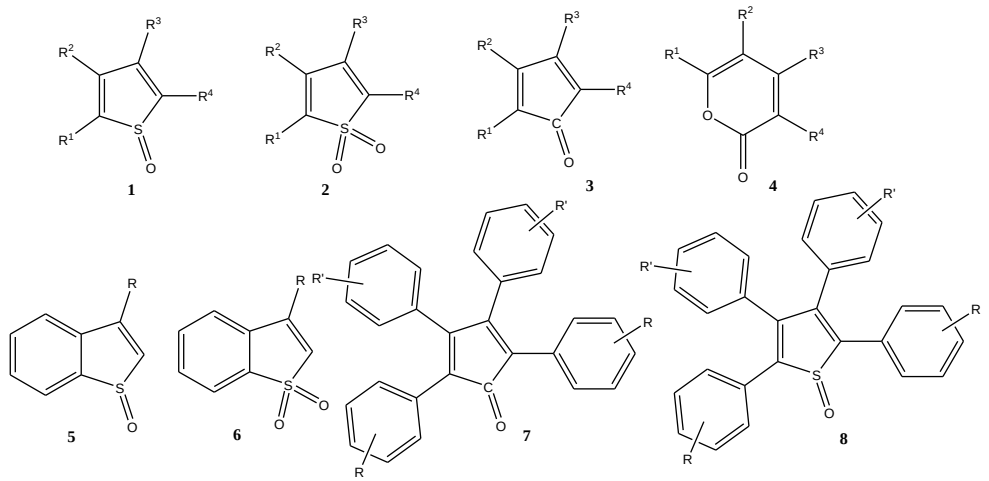


Figure 1. Structure of thiophene *S*-oxide **1**, thiophene *S*,*S*-dioxide **2**, cyclopentadienone **3**, α-pyrone **4**, benzo[*b*]thiophene *S*-oxide **5**, benzo[*b*]thiophene *S*,*S*-dioxide **6**, tetraarylcyclopentadienone (tetracyclone) **7**, and tetraarylthiophene-*S*-oxide **8**

II. Experimental

General. – Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. Infrared spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM instruments. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^{1}H at 270 MHz, ^{13}C at 67.8 MHz) and with a JEOL 600 spectrometer (^{1}H at 600 MHz, ^{13}C at 150.9 MHz). The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). The assignment in the ^{13}C-NMR spectra was aided by DEPT experiments (DEPT = distortionless enhancement by polarization transfer), where (CH_3) denotes methyl, (CH_2) secondary carbon, (CH) tertiary carbon and (C_{quat}) a quaternary carbon. Mass spectra were measured with a JMS-01-SG-2 spectrometer. Column chromatography was carried out on Wakogel 300. Elemental analysis was carried out at Kyushu University, Hakozaki Campus, Fukuoka, Japan. All cycloaddition reactions with tetracyclones were carried out under de-aerated conditions (under argon).

Chemicals. – 3-Tetraarylcyclopentadienones were prepared via Weiss reaction (1,3-diarylpropan-2-one **9**, substituted benzil **10**, benzyltributylammonium hydroxide, dioxane [Scheme 1]) [7,14]. *p*,*p*'-Dicyanotolane (**17**) and 4-(phenylethynyl)benzonitrile (**15**) [MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 203 (67.4)] were prepared from *p*-cyanophenylacetylene (**10**) and *p*-bromobenzonitrile (**11**) and bromobenzene (**14**), respectively, by Sonogashira coupling reaction (Scheme 2). 3-Ethynyldibenzo[*b*,*d*]thiophene (**20**) [MS (EI, 70 eV) m/z (%) 208 (100)] was synthesized by reaction of 3-bromodibenzo[*b*,*d*]thiophene (**18**) with TMS-acetylene (**12**) (Sonogashira coupling reaction) with subsequent desilylation (Bu_4NF, THF) (Scheme 3). Di-*n*-propyl acetylenedicarboxylate (**23**) was prepared from acetylenedicarboxylic acid (**22**) (PrOH, benzene, conc. H_2SO_4), while benzyl propiolate (**26**) was synthesized from propiolic acid (**24**) (benzyl alcohol (**25**), DMAP, DCC, CH_2Cl_2) (Scheme 4). *N*-4-iodophenylmaleimide (43) was prepared by reaction of maleic anhydride with 4-iodoaniline (THF) and subsequent cyclization [15]. Benzo[*b*]thiophene (**27**) (TCI) and benzo[*b*]thien-3-ylboronic acid (**31**) (TCI) were acquired commercially. 3-Bromobenzo[*b*]thiophene (**28**) was both acquired commercially and synthesized from benzo[*b*]thiophene (**27**) according to ref. 16. 3-Phenylbenzo[*b*]thiophene (**30a**), 3-(4-methoxyphenyl)benzo[*b*]thiophene (**30b**) and 3-(4-ethoxyphenyl)benzo[*b*]thiophene (**30c**) were prepared from 3-bromobenzo[*b*]thiophene (**28**) by Suzuki reaction with phenyl-, 4-methoxyphenyl, and 4-ethoxyphenylboronic acids **29** ($Pd(PPh_3)_2Cl_2$, PPh_3, aq. Na_2CO_3, DME) [for analogous preparation, please see: ref. 17-19]. 3-(4-Acetylphenyl)benzo[b]thiophene (**30d**) was prepared by Suzuki reaction between benzo[b]thienylboronic acid (**31**) and 4-bromoacetophenone (**32**) ($Pd(PPh_3)_2Cl_2$, PPh_3, aq. Na_2CO_3, DME) [for analogous preparation, please see: ref. 20] (Scheme 5). 3-Phenylbenzo[*b*]thiophene *S*-oxide (**33**) was prepared from **30a** analogous to the literature [H_2O_2, CF_3CO_2H, spectroscopic data: IR (KBr) υ1605, 1560, 1086, 1060, 1030, 762, 735, 700 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.01 (1H, s), 7.50 – 7.56 (8H, m), 8.00 – 8.02 (1H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 124.4, 126.6, 128.0 (2C), 129.0 (2C), 129.9, 131.7, 132.5, 132.6, 137.2, 146.5, 148.5; ref. 21,22] (Scheme 6). 3-(4-Methoxyphenyl)benzo[*b*]thiophene *S*,*S*-dioxide (**35a**) [20], 3-(4-

ethoxyphenyl)benzo[*b*]thiophene *S*,*S*-dioxide (**35b**), 3-bromobenzo[*b*]thiophene *S*,*S*-dioxide (**34b**) [23], 4-acetylphenylbenzo[*b*]thiophene *S*,*S*-dioxide (**35c**) and 3-phenylbenzo[b]thiophene S,S-dioxide (**35d**) were prepared by oxidation of the corresponding benzo[*b*]thiophenes (m-CPBA, CH_2Cl_2) (Scheme 7).

4-(Phenylethynyl)benzamide (16). –To **15** (850 mg, 4.2 mmol) and tetrabutylammonium hydrogensulfate (Bu_4NHSO_4, 1,0 g) in CH_2Cl_2 (45 mL) were added 30w% aq. H_2O_2 (10 mL) and a 20w% aq. NaOH solution (10 mL), and the resulting reaction mixture was stirred for 12h at rt. Thereafter, it was poured into water (20 mL) and extracted with $CHCl_3$. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel ($CHCl_3$-ethyl acetate: 9:1) to give **16** (500 mg, 54%) as a colorless solid, mp. 250 °C [24]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.80 – 6.15 (2H, bs, NH_2), 7.35 – 7.38(5) (3H, m), 7.53 – 7.57 (2H, m), 7.60 (2H, d, ^3J = 8.4 Hz), 7.79 (2H, d, ^3J = 8.4 Hz); ^{1}H-NMR (270 MHz, DMSO-d^6) δ 7.40 – 7.43 (4H, m), 7.53 – 7.58 (2H, m), 7.60 (2H, d, ^3J = 8.4 Hz), 7.87 (2H, d, ^3J = 8.4 Hz), 8.08 (1H, bs, NH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 92.0(5) (C_{quat}, $\underline{C}\equiv$), 108.0 (C_{quat}, $\equiv\underline{C}$), 127.2 (C_{quat}), 127.4 (2C, CH), 127.7 (C_{quat}), 128.4 (2C, CH), 128.5 (CH), 131.7 (2C, CH), 131.7(5) (2C, CH), 132.5 (C_{quat}), 168.5 (C_{quat}, CO); ^{13}C-NMR (67.8 MHz, DMSO-d^6) δ 89.8 (C_{quat}, $\underline{C}\equiv$), 92.5 (C_{quat}, $\equiv\underline{C}$), 122.9(5) (C_{quat}), 126.3 (C_{quat}), 129.0 (2C, CH), 130.0 (2C, CH), 130.3(5) (CH), 133.4(5) (2C, CH), 132.6 (2C, CH), 134.9(5) (C_{quat}), 168.8 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 221 (M^+, 19.1), 205 (13.7), 149 (12.9), 77 (12.8, $C_6H_5^+$), 58 (100). HRMS Found: 221.0840. Calcd. for $C_{15}H_{11}ON$: 221.0841. Found: C, 81.19; H, 5.05; N, 6.27%. Calcd. for $C_{15}H_{11}ON$: C, 81.43; H, 5.01; N, 6.33%.

3-Ethynyldibenzo[*b*,*d*]thiophene *S*,*S*-dioxide (**21**) To 3-ethynyldibenzo[*b*,*d*]thiophene (**20**, 165 mg, 0.79 mmol) in CH_2Cl_2 (5 mL) was added at 0 °C *m*-CPBA (550 mg, 70w%, 2.23 mmol) as a colorless solid. Thereafter, the suspension was stirred at rt for 12h. The reaction mixture was poured in aq. Na_2CO_3 (5 w%, 15 mL) and extracted with CH_2Cl_2 (3 X 15 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (CH_2Cl_2/ether 7:1) to give **21** (147 mg, 77%) as a colorless solid; mp. 252 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.31 (1H, s, C≡C$\underline{H}$), 7.53-7.69 (3H, m), 7.77-7.85 (4H, m), 7.88 (1H, s); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 81.1 ($CH_{ethynyl}$), 81.8 (C_{quat}), 121.7 (CH), 122.2 (CH), 122.3 (CH), 125.0 (CH), 128.1 (C_{quat}), 130.8 (CH), 131.9 (C_{quat}), 133.9 (CH), 134.0 (CH), 137.5 (C_{quat}), 137.9 (C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 241 (MH^+, 9.4). HRMS Found: 241.0324. Calcd. for $C_{14}H_9O_2S$: 241.0323.

1-(4-Cyanophenyl)-2,3,4,5-tetraphenylbenzene (36a). – A mixture of tetracyclone (**7a**, 216 mg, 0.59 mmol) and 4-cyanophenylacetylene (**13**, 150 mg, 1.18 mmol) was heated to 175 °C for 5 min. Thereafter, the excess 4-cyanophenylacetylene is sublimated off and the remaining mass is taken up in hexane/ether (10:1) to give **36a** (255 mg, 90%) as a colorless solid, mp. 203 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.75 – 6.97 (16H, m), 7.15 (4H, m), 7.25 (2H, d, ^3J = 8.6 Hz), 7.44 (2H, d, ^3J = 8.6 Hz), 7.51 (1H, s); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 110.0 (C_{quat}), 118.9 (C_{quat}, CN), 125.5[5] (CH), 126.1 (CH), 126.5 (CH), 126.7 (2C, CH), 127.0 (2C, CH), 127.2 (2C, CH), 127.7 (2C, CH), 129.8 (2C, CH), 130.6 (2C, CH), 130.9 (CH), 131.3 (2C, CH), 131.3 (4C, CH), 131.4 (2C, CH), 132.6(5) 138.9 (C_{quat}), 139.2 (2C, C_{quat}), 139.5 (C_{quat}), 139.8 (C_{quat}), 140.4 (C_{quat}), 141.2 (C_{quat}), 141.3 (C_{quat}), 142.1 (C_{quat}), 146.7 (C_{quat}).

1-(4-Carboxamidophenyl)-2,3,4,5-tetraphenylbenzene (37a). – To **36a** (285 mg, 0.59 mmol) and tetrabutylammonium hydrogensulfate (Bu_4NHSO_4, 150 mg) in CH_2Cl_2 (10 mL) were added 30w% aq. H_2O_2 (2 mL) and a 20w% aq. NaOH solution (2 mL), and the resulting reaction mixture was stirred for 12h at rt. Thereafter, it was poured into water (20 mL) and extracted with $CHCl_3$. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel ($CHCl_3$-ethyl acetate: 9:1) to give **37a** (257 mg, 87%) as a colorless solid; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.70 – 6.00 (2H, b, NH_2), 6.76 – 6.94 (15H, m), 7.16 (5H, bs), 7.24 (2H, d, ^3J = 8.4 Hz), 7.55 (1H, s), 7.62 (2H, d, ^3J = 8.4 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 125.4 (CH), 125.7 (CH), 125.9 (CH), 126.4 (CH), 126.7 (2C, CH), 126.7(5) (2C, CH), 127.1 (2C, CH), 127.6 (2C, CH), 129.9 (2C, CH), 130.2 (2C, CH), 130.9 (C_{quat}), 131.1 (CH), 131.4 (2C, CH), 131.4 (2C, CH), 131.4(5) (4C, CH), 139.2(5) (C_{quat}), 139.5(5) (2C, C_{quat}), 139.7 (C_{quat}), 139.9(5) (C_{quat}), 140.0 (C_{quat}), 141.0 (C_{quat}), 141.5 (C_{quat}), 142.0 (C_{quat}), 145.7 (C_{quat}), 169.1 (C_{quat}, C(O)N).

4-(4-Cyanophenyl)-1,2-bis-(4-fluorophenyl)-3,5,6-triphenylbenzene (36b). – A mixture of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadienone (**7b**, 378 mg, 0.9 mmol) and 1-(4-cyanophenyl)-2-phenylacetylene (**15**, 244 mg, 1.2 mmol) in diphenyl ether (1.5 g) was heated at 175 ^{o}C for 14h. The cooled mixture was subjected to column chromatography on silica gel (hexane – CH_2Cl_2 1:1) to give **36b** (475 mg, 89%) colorless solid, mp. 353 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.55 – 6.62 (4H, m), 6.72 – 6.91 (19H, m), 6.92 (2H, d, ^3J = 8.4 Hz), 7.14 (2H, d, ^3J = 8.4 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 109.1 (C_{quat}), 113.9 (2C,

CH, J_{CF} = 21.8 Hz), 113.9(5) (2C, CH, J_{CF} = 21.2 Hz), 119.0 (CN), 125.6 (CH), 125.8(5) (CH), 125.9 (CH), 126.9 (4C, CH), 127.0 (4C, CH), 127.1 (5) (4C, CH), 130.5 (2C, CH), 131.0(5) (2C, CH), 131.1 (CH) 132.6 (4C, CH, J_{CF} = 7.8 Hz), 135.9 (C_{quat}, J_{CF} = 3.9 Hz), 136.0(5) (C_{quat}, J_{CF} = 3.9 Hz), 138.8 (C_{quat}), 139.5(5) (C_{quat}), 139.6 (C_{quat}), 139.7 (C_{quat}), 139.8 (C_{quat}), 140.1(5) (C_{quat}), 140.2(6) (C_{quat}), 140.3 (C_{quat}), 140.9 (C_{quat}), 145.9 (2C, C_{quat}), 160.7 (2C, C_{quat}, $^1J_{CF}$ = 244.3 Hz).

4-(4-Carboxamidophenyl)-1,2-bis(4-fluorophenyl)-3,5,6-triphenylbenzene (37b). – **36b** (450 mg, 0.76 mmol) and tetrabutylammonium hydrogensulfate (Bu_4NHSO_4, 195 mg) in CH_2Cl_2 (12 mL) were added 30w% aq. H_2O_2 (2.6 mL) and a 20w% aq. NaOH solution (2.6 mL), and the resulting reaction mixture was stirred for 12h at rt. Thereafter, it was poured into water (20 mL) and extracted with $CHCl_3$. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel ($CHCl_3$-ethyl acetate: 9:1) to give **37b** (340 mg, 73%) as a colorless solid, mp. 345 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.65 (2H, bd, NH_2), 6.56 (2H, d, ^3J = 8.9 Hz), 6.60 (2H, d, ^3J = 8.9 Hz), 6.74 – 6.90 (19H, m), 6.91 (2H, d, ^3J = 8.4 Hz), 7.32 (2H, d, ^3J = 8.4 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 614 (MH^+, 15.2), 613 (M^+, 13.6). HRMS Found: 614.2294. Calcd. for $C_{43}H_{30}ONF_2$: 614.2295 (MH^+).

1,2-Bis(4-cyanophenyl)-3,4,5,6-tetraphenylbenzene (**36c**). – A mixture of *p*,*p*'dicyanotolane (**17**, 228 mg, 1.0 mmol) and tetracyclone (**7a**, 192 mg, 0.5 mmol) in diphenylether (1.1 mL) was heated at 175 °C for 24h.* The cooled solution was subjected to column chromatography on silica gel (hexane → CH_2Cl_2) to give **36c** (272 mg, 93%) as a colorless solid; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.75 – 6.82 (8H, m), 6.84 – 6.90 (12H, m), 6.91 (4H, d, ^3J = 8.1 Hz), 7.18 (4H, d, ^3J = 8.1 Hz), ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 109.4 (C_{quat}, 2C, CN), 118.3 (C_{quat}, 2C), 125.3 (2C, CH), 125.6 (2C, CH), 126.4 (4C, CH), 126.7 (4C, CH), 130.5 (4C, CH), 130.7 (4C, CH), 130.7(5) (4C, CH), 137.7 (2C, C_{quat}), 138.9 (2C, C_{quat}), 139.3 (2C, C_{quat}), 140.0 (2C, C_{quat}), 141.3 (2C, C_{quat}), 144.9 (2C, C_{quat}); MS (EI) *m/z* (%) 585 (M^++1, 11,2), 584 (M^+, 114.). HRMS Found: 584.2260. Calcd. for $C_{44}H_{28}N_2$: 584.2252. *The solventless reaction did not work under the conditions as the reaction mixture was not molten at 175 °C.

1-(4-Cyanophenyl)-2,3,4,5,6-pentaphenylbenzene (36d) and 1-(4-carboxamidophenyl)-2,3,4,5,6-pentaphenylbenzene (37c). – A mixture of tetracyclone (**7a**, 216 mg, 0.59 mmol) and 1-(4-cyanophenyl)-2-phenylacetylene (**15**, 145 mg, 0.72 mmol) in diphenyl ether (1 g) was heated to 175 °C for 15h. The cooled mixture was submitted to column chromatography on silica gel (hexane → hexane / ether 10:1) to give **36d** (280 mg, 85%) as a colorless solid; mp. 355 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.77 – 6.88 (25H, m), 6.94 (2H, d, ^3J = 8.6 Hz), 7.14 (2H, d, ^3J = 8.6 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 108.9(5) (C_{quat}), 119.1 (C_{quat}, CN), 126.7 (5C, CH), 126.9 (4C, CH), 131.2 (6C, CH), 131.2(5) (6C, CH), 138.5 (C_{quat}), 139.8 (2C, C_{quat}), 139.9 (2C, C_{quat}), 140.0(5) (2C, C_{quat}), 140.2 (C_{quat}), 140.6(5) (2C, C_{quat}), 141.3 (C_{quat}), 146.2 (C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 559 (M+, 100). HRMS Found: 559.2296. Calcd. for $C_{43}H_{29}N$: 559.2300. **36d** (250 mg, 0.45 mmol) and tetrabutylammonium hydrogensulfate (Bu_4NHSO_4, 115 mg) in CH_2Cl_2 (10 mL) were added 30w% aq. H_2O_2 (2.0 mL) and a 20w% aq. NaOH solution (2.0 mL), and the resulting reaction mixture was stirred for 12h at rt. Thereafter, it was poured into water (20 mL) and extracted with $CHCl_3$. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel ($CHCl_3$-ethyl acetate: 9:1) to give **37c** (185 mg, 71%) as a colorless solid, MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 578 (MH^+, 1.2), 559 (2.4). HRMS Found: 578.2487. Calcd. for $C_{43}H_{32}ON$: 578.2484.

1,2-Bis(4-methoxyphenyl)-3,4,5,6-tetraphenylbenzene (**36e**). – A solventless mixture of 4,4'-dimethoxytolane (**38a**, 171 mg, 0.72 mmol) and tetracyclone (**7a**, 138 mg, 0.36 mmol) was heated at 175 °C for 18h. The cooled mixture was subjected to column chromatography on silica gel (hexane-CH_2Cl_2: 2:1) to give **36e** (189 mg, 88%) as a colorless solid, mp. 292 °C (Lit. 292 – 293 °C [Lit. 1]);^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.59 (6H, s, 2 OCH_3), 6.41 (4H, d, ^3J = 8.9 Hz), 6.71 (4H, d, ^3J = 8.9 Hz), 6.82-6.84 (20H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 54.9 (2C, 2 OCH_3), 112.2 (4C, CH), 125.0(5) (2C, CH), 125.1 (2C, CH), 126.5 (4C, CH), 126.6 (4C, CH), 131.4 (8C, CH), 132.4 (4C, CH), 133.2 (2C, C_{quat}), 140.1 (2C, C_{quat}), 140.6 (2C, C_{quat}), 140.8 (2C, C_{quat}), 140.9 (2C, C_{quat}), 156.9 (2C, C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 595 (M^++1, 5.9), 594 (M^+, 7.6). HRMS Found: 594.2554. Calcd. for $C_{44}H_{34}O_2$: 594.2559 (FAB).

1,2-Bis(*p*-tolyl)-3,4,5,6-tetraphenylbenzene (36f). – A mixture of bis(p-tolyl)acetylene (**38b**, 589 mg, 2.86 mmol) and tetracyclone (**7a**, 220 mg, 0.57 mmol) was heated at 175 °C for 3h. Thereafter, the cooled solution was subjected to column chromatography (CH_2Cl_2 – hexane 1:1) to give **36f** as a solid (292 mg, 91%), mp. 355°C (Lit. 357 – 358 °C [1]); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.32 (6H, s, 2 CH_3), 6.65 (4H, d, ^3J = 8.1 Hz), 6.69 (4H, d, ^3J = 8.1 Hz), 6.82 (20H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.0 (2C, CH_3), 125.0 (2C, CH), 125.0(5) (2C, CH), 126.5 (8C, CH), 127.3 (4C, CH), 131.2(5) (4C, CH), 131.4(5) (8C, CH), 134.3 (2C, C_{quat}),

137.6 (2C, C_{quat}), 140.1 (2C, C_{quat}), 140.4 (2C, C_{quat}), 140.8 (2C, C_{quat}), 140.9 (2C, C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 562 (M^+, 5.1), 563 (MH^+, 3.2). HRMS: Found: 562.2668. Calcd. for $C_{44}H_{34}$: 562.2661 (M^+).

1-(Dibenzo[*b,d*]thien-3-yl)-2,3,4,5-tetraphenylbenzene (36g) and **1-(1,1-dioxo-dibenzo[*b,d*]thien-3-yl)-2,3,4,5-tetraphenylbenzene (37d).** – A mixture of 3-ethynyldibenzo[*b,d*]thiophene (**20**, 104 mg, 0.5 mmol) and tetracyclone (**7a**, 192 mg, 0.5 mmol) in diphenylether (1.5 mL) was heated at 175 °C for 30 min. Thereafter, the cooled solution was subjected to column chromatographic separation on silica gel (hexane → hexane/toluene 3:1) to give **36g** (180 mg, 64%) as colorless solid, mp. 237 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.80 – 6.95 (14H, m), 7.15 – 7.23 (7H, m), 7.39 – 7.41 (2H, m), 7.57 (1H, d, ^3J = 7.0 Hz), 7.69 (1H, s), 7.77 – 7.83 (1H, m), 7.93 – 7.96 (1H, m), 8.02(5) (1H, d, ^4J = 1.6 Hz). To a solution of **36g** (222 mg, 0.31 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (215 mg, 0.87 mmol). The resulting mixture was stirred at rt for 12h. The reaction mixture was poured in aq. Na_2CO_3 (5 w%, 15 mL) and extracted with CH_2Cl_2 (3 X 15 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (CH_2Cl_2/ether 7:1) to give **37d** (210 mg, 91%) as a pale yellow solid, mp. > 250 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 121.4 (CH), 121.8 (CH), 122.8 (CH), 122.9 (CH), 124.3 (CH), 125.4 (CH), 125.6 (CH), 125.7 (CH), 126.3 (CH), 126.6 (CH), 126.7 (2C, CH), 126.9 (2C, CH), 127.1 (2C, CH), 127.6 (2C, CH), 128.2 (C_{quat}), 128.9 (CH), 129.0 (C_{quat}), 130.0 (2C, CH), 131.5 (2C, CH), 131.5[5] (2C, CH), 131.6 (2C, CH), 131.7 (CH), 135.2 (C_{quat}), 135.6 (C_{quat}), 137.5 (C_{quat}), 138.1 (C_{quat}), 139.5 (C_{quat}), 139.7 (C_{quat}), 139.9 (C_{quat}), 140.3 (C_{quat}), 140.4 (C_{quat}), 140.9 (C_{quat}), 141.7 (C_{quat}), 141.9 (C_{quat}).

2",3"-Bis(4-fluorophenyl)-5"-(4-cyanophenyl)-*p*-quinquephenyl (**36h**). – A mixture of 2,5-bis(p-biphenyl)-3,4-bis(4-fluorophenyl)cyclopentadienone (**7c**, 58 mg, 0.10 mmol) and 4-cyanotolane (**13**, 50 mg, 0.39 mmol) in diphenyl ether (150 mg) has been heated at 175 °C for 10h. The cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/ether/$CHCl_3$ 1:1:1) to give **36h** (54 mg, 81%) as a colorless solid, mp. 300 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.58 – 6.87 (8H, m), 6.71 (2H, d, ^3J = 8.6 Hz), 7.19 (2H, d, ^3J = 8.1 Hz), 7.24 – 7.52 (16H, m), 7.56 (2H, d, ^3J = 7.3 Hz), 7.58 (1H, s); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 110.3 (C_{quat}), 114.3 (4C, CH, $^2J_{CF}$ = 20.7 Hz), 118.8 (C_{quat}), 126.0 (2C, CH), 126.5 (2C, CH), 126.8 (2C, CH), 126.9(5) (2C, CH), 127.4 (CH), 128.7 (2C, CH), 128.8 (2C, CH), 130.2 (2C, CH), 130.6 (2C, CH), 131.2(5) (CH), 131.6 (2C, CH), 131.7 (2C, CH), 132.7(5) (2C, CH, J_{CF} = 7.8 Hz), 132.8 (2C, CH, J_{CF} = 7.8 Hz), 137.9 (C_{quat}), 138.8 (C_{quat}), 139.1 (C_{quat}), 139.3 (C_{quat}), 139.4(5) (C_{quat}), 139.5 (C_{quat}), 139.7 (C_{quat}), 140.1(5) C_{quat}), 140.4 (C_{quat}), 141.0 (C_{quat}), 141.3 (C_{quat}), 161.7 (2C, C_{quat}, $^1J_{CF}$ = 245.9 Hz), 162.3 7 (2C, C_{quat}, $^1J_{CF}$ = 245.9 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 671 (M^+, 15.1). HRMS: Found: 671.2426. Calcd. for $C_{49}H_{31}NF_2$: 671.2425.

1-(Phenylethynyl)-2,3,4,5,6-pentaphenylbenzene (36i). – A mixture of tetracyclone (**7a**, 123 mg, 0.33 mmol) and diphenyldiacetylene (**38c**, 258 mg, 1.28 mmol) was heated for 3h at 150 °C. The reaction mixture was directly crystallized and recrystallized from ether/hexane 1:1 to yield **36i** (175 mg, 94%) as a colorless solid, mp. 283 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.68 (2H, d, ^3J = 6.0 Hz), 6.83 – 7.35 (26H, m), 7.52 (2H, d, ^3J = 7.6 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 89.4 (C≡), 96.9 (≡C), 125.4 (2C, C_{quat}), 125.5 (2C, CH), 126.3 (2C, CH), 126.6 (2C, CH), 126.7 (4C, CH), 127.0 (4C, CH), 127.6 (2C, C_{quat}), 127.9 (2C, CH), 128.4 (CH), 130.9 (4C, CH), 131.1 (2C, CH), 131.2 (2C, CH), 131.3 (4C, CH), 132.5 (CH), 139.9 (2C, C_{quat}), 140.0 (C_{quat}), 140.2 (C_{quat}), 140.5 (2C, C_{quat}), 141.2 (C_{quat}), 143.2 (C_{quat}). MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 558 (M^+, 8.1), 559 (M^++1, 4.8). HRMS: Found: 558.2342. Calcd. for $C_{44}H_{30}$: 558.2348.

4,5-Bis-(4-cyanophenyl)-1,2-bis(4-fluorophenyl)-3,6-diphenylbenzene (**36j**). – A mixture of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadienone (**7b**, 378 mg, 0.9 mmol) and bis-(4-cyanophenyl)acetylene (**17**, 198 mg, 0.9 mmol) was heated at 175 °C for 12h. The cooled mixture was subjected to column chromatography on silica gel (hexane – CH_2Cl_2 1:1) to give **36j** (475 mg, 85%) as colorless plates, mp. 380 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.59 (4H, dd, ^3J = 8.1 Hz, ^3J = 8.1 Hz), 6.71 – 6.77 (8H, m), 6.89 – 6.92 (10H, m), 7.18 (4H, d, ^3J = 8.1 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 110.7 (2C, C_{quat}), 114.9 (4C, CH, $^2J_{CF}$ = 21.2 Hz), 119.4 (2C, C_{quat}), 127.1 (2C, CH), 128.2 (4C, CH), 131.7 (4C, CH), 131.8 (4C, CH), 132.7 (4C, CH), 133.4 (4C, CH, $^3J_{CF}$ = 8.4 Hz), 136.4 (2C, C_{quat}, $^4J_{CF}$ = 3.4 Hz), 139.2 (2C, C_{quat}), 139.9 (2C, C_{quat}), 141.5 (2C, C_{quat}), 141.6 (2C, C_{quat}), 145.9 (2C, C_{quat}), 161.7 (2C, C_{quat}, $^1J_{CF}$ = 245.9 Hz); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 621 (MH^+, 87), 620 (M^+, 92). HRMS Found: 620.2057. Calcd. for $C_{44}H_{26}N_2F_2$: 620.2064.

4,5-Bis(4-fluorophenyl)-1,2-bis(4-methoxyphenyl)-3,6-diphenyl-benzene (**36k**). – A solventless mixture of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadienone (**7b**, 483 mg, 1.16 mmol) and p,p'-dimethoxytolane (**38a**, 600 mg, 2.52 mmol) was heated at 175 °C for 23h. The cooled mixture is subjected to column chromatography on silica gel (hexane/$CHCl_3$/ether 10:1:1) to give **36k** (690 mg, 94%) as a colorless solid; ^{1}H-

NMR (270 MHz, $CDCl_3$) δ ; ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 54.9 (2C, OCH_3), 112.2 (4C, CH), 113.7 (2C, C_{quat}, J_{CF} = 21.2 Hz), 125.2 (2C), 126.8 (4C, CH), 131.3 (4C, CH), 132.3 (4C, CH), 132.7 (4C, CH, J_{CF} = 7.9 Hz), 132.9 (C_{quat}), 136.6 (2C, C_{quat}, J_{CF} = 4.5 Hz), 139.2 (C_{quat}), 140.5 (C_{quat}), 140.6 (C_{quat}), 140.8 (C_{quat}), 157.0 (C_{quat}), 160.6 (2C, C_{quat}, $^1J_{CF}$ = 242.6 Hz); MS (70 eV) *m/z* (%) 630 (M^+, 100). HRMS Found: 630.2378. Calcd. for $C_{44}H_{32}O_2F_2$: 630.2370.

4,5-Bis-(4-nitrophenyl)-1,2-bis(4-fluorophenyl)-3,6-diphenylbenzene (**36L**). – A mixture of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadienone (**7b**, 142 mg, 0.34 mmol) and p,p'-dinitrotolane (**38d**, 64 mg, 0.225 mmol) in diphenyl ether (500 mg) was heated to 175 °C for 10h. The cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/$CHCl_3$/ether 5:1:1) to give **36L** (94 mg, 63%) colorless solid; mp. 340 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.61 (4H, dd, ^3J = 8.6 Hz, ^3J = 8.6 Hz), 6.73 – 6.79 (8H, m), 6.90 – 6.93 (6H, m), 6.99 (4H, d, ^3J = 8.6 Hz), 7.77 (4H, d, ^3J = 8.6 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 114.1 (4C, CH, $^2J_{CF}$ = 21.2 Hz), 122.4 (4C, CH), 126.4 (2C, CH), 127.4 (4C, CH), 130.9 (4C, CH), 131.9 (4C, CH), 132.4(5) (4C, CH, $^3J_{CF}$ = 8.4 Hz), 135.4 (2C, C_{quat}, $^4J_{CF}$ = 3.9 Hz), 138.9 (2C, C_{quat}), 140.7 (2C, C_{quat}), 140.9 (2C, C_{quat}) 145.8 (2C, C_{quat}), 147.0 (2C, C_{quat}), 161.7 (2C, C_{quat}, $^1J_{CF}$ = 245.9 Hz).

1-(4-Cyanophenyl)-3,4-bis-(4-fluorophenyl)-2,5-diphenylbenzene (36m). – A mixture of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadienone (**7b**, 420 mg, 1.0 mmol) and 4-cyanophenylacetylene (**13**, 128 mg, 1.0 mmol) was heated to 175 °C for 9h.* The cooled mixture was subjected to column chromatography on silica gel (hexane – ether – CH_2Cl_2: 10 : 1 : 1) to give **36m** (390 mg, 75%) as a colorless solid, mp. 300 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.60 – 6.81 (9H, m), 6.97 – 6.99 (3H, m), 7.18 – 7.20 (6H, m), 7.24 (2H, d, ^3J = 8.1 Hz), 7.44 (2H, d, ^3J = 8.1 Hz), 7.51 (1H, s); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 110.2 (C_{quat}), 114.0 (2C, CH, J_{CF} = 21.2 Hz), 114.3 (2C, CH, J_{CF} = 21.2 Hz), 118.8 (C_{quat}, CN), 126.3 (CH), 126.7 (CH), 127.4(5) (2C, CH), 127.8(5) (2C, CH), 129.8 (2C, CH), 131.1 (CH), 131.2 (2C, CH), 131.5 (2C, CH), 132.7 (2C, CH, J_{CF} = 7.7 Hz), 132.8 (2C, CH, J_{CF} = 7.9 Hz), 135.4 (C_{quat}, J_{CF} = 3.4 Hz), 135.6 (C_{quat}, J_{CF} = 3.9 Hz), 138.9(5) (C_{quat}), 139.2 (C_{quat}), 139.5 (C_{quat}), 140.9 (C_{quat}), 141.1(5) C_{quat}), 141.4 (C_{quat}), 146.4 (2C, C_{quat}); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 519 (M^+) (100). HRMS Found: 519.1799. Calcd. for $C_{37}H_{23}NF_2$: 519.1799. *Care has to be taken to heat the reaction vessel completely as 4-cyanophenylacetylene sublimates under the conditions.

2,4-Bis(4-fluorophenyl)-1,3,5-triphenylbenzene (36n). – A neat melt of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadienone (**7b**, 274 mg, 0.65 mmol) and phenylacetylene (**38e**, 663 mg, 6.5 mmol) was heated at 175 °C for 3 min. The cooled mixture was taken up in hexane-ether (9:1) to give **36n** (310 mg, 97%) as a colorless solid, mp. 233 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.55 – 6.96 (15H, m), 7.14 – 7.18 (8H, bs), 7.56 (1H, s). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 113.6 (2C, CH, d, J_{CF} = 21.2 Hz), 113.9 (2C, CH, d, J_{CF} = 21.2 Hz), 125.5 (CH), 126.1 (CH), 126.2 (CH), 126.8 (2C, CH), 127.4 (2C, CH), 127.5 (2C, CH), 129.6 (4C, CH), 131.1 (2C, CH), 131.3 (CH), 132.5 (2C, CH, d, J_{CF} = 8.0 Hz), 132.6 (2C, CH, d, J_{CF} = 6.7 Hz), 131.3 (CH), 134.4 (C_{quat}), 135.5 (C_{quat}, d, J_{CF} = 3.4 Hz), 135.9 (C_{quat}, d, J_{CF} = 1.6 Hz), 138.1 (C_{quat}), 139.2 (C_{quat}), 140.5 (C_{quat}), 140.7 (C_{quat}), 140.8 (C_{quat}), 141.1 (C_{quat}), 141.2 (C_{quat}), 162.0 (2C, C_{quat}, d, J_{CF} = 246.0 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 494 (M^+, 100). HRMS Found: 494.1853. Calcd. for $C_{36}H_{24}F_2$: 496.1846 (FAB).

1,2-Bis(4-fluorophenyl)-3,6-diphenyl-4,5-bis(*p*-tolyl)benzene (36o). – A solution of 3,4-bis-(4-fluorophenyl)-2,5-diphenylcyclopentadienone (**7b**, 210 mg, 0.5 mmol) and *p*,*p*'-dimethyltolane (**38b**, 206 mg, 1.0 mmol) in diphenyl ether (1.5 mL) was heated at 175 °C for 9h. The cooled reaction mixture was subjected to column chromatography on silica gel (hexane → hexane/ether/$CHCl_3$ (10:1:1)) to give **36o** (260 mg, 87%) as colorless plates, mp. 339 °C - ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.09 (6H, s, 2 CH_3), 6.52 – 6.89 (26H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.0 (2C, CH_3), 113.7 (4C, CH, J_{CF} = 20.7 Hz), 125.2 (2C, CH), 126.7 (4C, CH), 127.3 (4C, CH), 131.1[5] (4C, CH), 131.3 (4C, CH), 132.7 (4C, CH, J_{CF} = 7.8 Hz), 134.5 (2C, CH), 136.6[5] (C_{quat}), 137.4 (C_{quat}), 139.2 (C_{quat}), 139.7 (C_{quat}), 140.7 (C_{quat}), 140.7 (C_{quat}), 162.4 (2C, C_{quat}, $^1J_{CF}$ = 245 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 598 (M^+, 27.2). HRMS Found: 598.2471. Calcd. for $C_{44}H_{32}F_2$: 598.2472.

1,2-Bis(4-bromophenyl)-3,4,5,6-tetraphenylbenzene (36p). – A solution of p,p'-dibromotolane (**38f**, 81 mg, 0.24 mmol) and tetracyclone (**7a**, 92 mg, 0.24 mmol) in diphenyl ether (0.3 mL) was held at 175 °C for 36h.* Column chromatography on silica gel (hexane → hexane/toluene 1:1) gave **36p** (140 mg, 85%) as a colorless solid, mp. 350 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.68 (4H, d, ^3J = 8.6 Hz), 6.77 – 6.89 (20H, m), 7.02 (4H, d, ^3J = 8.6 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 119.7 (2C, C_{quat}), 125.3 (2C, CH), 125.5 (2C, CH), 126.6 (4C, CH), 126.8 (4C, CH), 130.0 (4C, CH), 131.2 (8C, CH), 132.9 (4C, CH), 138.8 (2C, C_{quat}), 139.3 (2C, C_{quat}), 140.1 (2C, C_{quat}), 140.2 (2C, C_{quat}), 140.4 (2C, C_{quat}), 140.9 (2C, C_{quat}); MS (3-nitrobenzyl alcohol) m/z (%) 694 ($[^{81}Br]_2M^+$, 21.3), 692 ($[^{81}Br^{79}Br]M^+$, 36), 690 ($[^{79}Br]_2M^+$, 17.6). HRMS Found: 692.0543. Calcd. for

$C_{42}H_{28}{}^{79}Br^{81}Br$: 692.0542. *The solventless reaction at similar temperatures did not work because of the sublimation of p,p'-dibromotolane under the conditions.

Dimethyl naphthalene-1,2-dicarboxylate (**39a**). – A mixture of benzo[*b*]thiophene *S*,*S*-dioxide (**34a**, 194 mg, 1.17 mmol) and dimethyl acetylenedicarboxylate (**23b**, 1.2 g, 8.4(5) mmol) in diphenyl ether (1.5 g) was heated at 135 °C for 16h. Thereafter the cooled reaction mixture was subjected to column chromatography to give **39a** (140 mg, 49%) as a colorless oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.98 (3H, s, CO_2CH_3), 4.10 (3H, s, CO_2CH_3), 7.60 – 7.65 (2H, m), 7.89 - 7.93 (2H, m), 7.96 (1H, d, ^3J = 8.6 Hz), 8.04 (1H, d, ^3J = 8.6 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 52.8 (OCH_3), 52.9 (OCH_3), 124.8 (C_{quat}), 125.0 (CH), 126.2 (CH), 127.8 (CH), 128.1 (CH), 128.6 (CH), 129.4 (C_{quat}), 129.6 (CH), 135.0 (C_{quat}), 135.2 (C_{quat}), 166.4 (C_{quat}, CO), 169.7 (C_{quat}, CO). MS (EI, 70 eV) m/z (%) 244 (M^+, 21).

Dimethyl 4-phenylnapthalene-1,2-dicarboxylate (39b). – A mixture of 3-phenylbenzo[b]thiophene *S*,*S*-dioxide (**35d**, 233 mg, 0.82 mmol) and dimethyl acetylenedicarboxylate (**23b**, 2.56 g, 17.7 mmol) in diphenyl ether (2.5 g) was heated at 140 ^{o}C for 15 h. The cooled mixture was submitted to chromatography on silica gel (hexane → hexane /CH_2Cl_2 1:1) to give **39b** (70%) as a colorless oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.96 (3H, s, $CO_2C\underline{H}_3$), 4.11 (3H, s, $CO_2C\underline{H}_3$), 7.46 – 7.62 (7H, m), 7.94 (2H, d, ^3J = 8.6 Hz), 7.98 (1H, s); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 52.7 (CO_2CH_3), 53.0 (CO_2CH_3), 125.9 (CH), 126.5 (2C, CH), 127.6 (CH), 128.0 (CH), 128.5 (2C, CH), 128.6 (CH), 129.6 (2C, CH), 133.6 (C_{quat}), 134.3 (C_{quat}), 136.7 (C_{quat}), 138.7 (C_{quat}), 139.0 (C_{quat}), 142.1 (C_{quat}), 166.3 (C_{quat}, CO), 169.7 (C_{quat}, CO).

Dimethyl 4-(acetylphenyl)naphthalene-1,2-dicarboxylate (39c). – A solution of 3-(4-acetylphenyl)benzo[*b*]thiophene *S*,*S*-dioxide (**35c**, 225 mg, 0.79 mmol) and dimethyl acetylenedicarboxylate (**23b**, 800 mg, 5.54 mmol) in diphenyl ether (1.5 g) was heated at 135 ^{o}C for 26 h. The cooled solution was subjected directly to column chromatography on silica gel (hexane → $CHCl_3$/ether/hexane 2:1:1) to give **39c** as a colorless solid (157 mg, 55%), mp. 143 °C; 2.70 (3H, s, $COC\underline{H}_3$). 3.97 (3H, s, $CO_2C\underline{H}_3$), 4.12 (3H, s, $CO_2C\underline{H}_3$), 7.55 – 7.65 (2H, m), 7.59 (2H, d, ^3J = 8.4 Hz), 7.86 (1H, d, ^3J = 7.8 Hz), 7.95 (1H, d, ^3J = 8.4 Hz), 7.99 (1H, s), 8.10 (2H, d, ^3J = 8.4 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 26.7(5) (CH_3), 52.8 (OCH_3), 53.0 (OCH_3), 124.0 (C_{quat}), 125.8 (CH), 126.0 (CH), 126.6 (CH), 127.8 (CH), 128.5 (2C, CH), 128.9 (CH), 129.7(5) (C_{quat}), 130.2 (2C, CH), 133.1 (C_{quat}), 134.8(5) (C_{quat}), 136.4(5) (C_{quat}), 140.7 (C_{quat}), 144.2 (C_{quat}), 165.9 ($\underline{C}O_2CH_3$), 169.4 ($\underline{C}O_2CH_3$), 197.7 (C_{quat}, CO).

Di-*n*-propyl 4-phenylnaphthalene-1,2-dicarboxylate (39d). – A mixture of 3-phenylbenzo[*b*]thiophene *S*-oxide (**33**, 160 mg, 0.70(5) mmol) and dipropyl acetylenedicarboxylate (**23a**, 1.19 g, 6.0 mmol) was heated at 135 ^{o}C for 8h. Thereafter, the cooled solution was separated by column chromatography on silica gel (hexane → hexane/CH_2Cl_2 1:1) to give **39d** (162 mg, 61%) as a slowly solidifying oil;^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.02 (6H, q, ^3J = 6.2 Hz, 2 CH_3), 1.76 - 1.87 (4H, m), 4.32 (2H, t, ^3J = 7.0 Hz, OCH_2), 4.49 (2H, t, ^3J = 7.0 Hz, OCH_2), 7.46 - - 7.67 (7H, m), 7.93 (1H, d, ^3J = 8.6 Hz), 7.98 (1H, s); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 10.4(5) (CH_3), 10.5 (CH_3), 21.9 (CH_2), 22.0 (CH_2), 67.3 (OCH_2), 67.6 (OCH_2), 124.5 (C_{quat}), 125.8 (CH), 126.4 (CH), 127.4(5) (CH), 127.8(5) (CH), 128.3(5) (CH), 128.4 (2C, CH), 129.8(5) (C_{quat}), 129.9 (2C, CH), 133.5 (C_{quat}), 134.4 (C_{quat}), 139.5 (C_{quat}), 141.8 (C_{quat}), 165.8 (C_{quat}, CO), 169.2 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 377 (MH^+, 15.9), 376 (M^+, 45.3), 317 (32.3), 275 (100. MH^+-C_3H_7-C_3H_7O). HRMS Found: 376.1671. Calcd. for $C_{24}H_{24}O_4$: 376.1675 (FAB).

5-Phenyl)-benz[*a*]anthracene-7,12-dione (**40a**). – A solution of 3-phenylbenzo[*b*]thiophene *S*-oxide (**33**, 142 mg, 0.64 mmol) and naphthoquinone (**41**, 120 mg, 0.75 mmol) in diphenyl ether (900 mg) was heated at 135 ^{o}C for 9h. Thereafter, the cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/CH_2Cl_2 1:1) to give **40a** (143 mg, 67%) as a colorless solid, mp. 167 °C [Lit. 167-167.5 °C[25,26]] ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.54 (5H, bs), 7.57 – 7.63 (1H, m), 7.74 – 7.84 (3H, m), 8.00 (1H, d, ^3J = 8.6 Hz), 8.27 (1H, d, ^3J = 7.0 Hz), 8.33 (1H, d, ^3J = 6.0 Hz), 8.35 (1H, s), 9.81 (1H, d, ^3J = 8.9 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 123.5 (CH), 126.4 (CH), 126.9 (CH), 127.3 (CH), 128.3 (CH), 128.5 (2C, CH), 128.7 (CH), 128.9 (CH), 129.5 (CH), 129.8 (2C, CH), 131.2(5) (C_{quat}), 132.2(5) (C_{quat}), 133.3 (C_{quat}), 133.4 (CH), 134.3 (CH), 135.0 (C_{quat}), 135.2 (2C, C_{quat}), 139.5 (2C, C_{quat}), 184.0 (C_{quat}, CO), 186.0 (C_{quat}, CO).

5-(4-Methoxyphenyl)-benz[*a*]anthracene-7,12-dione (**40b**). A solution of 3-(4-methoxyphenyl)benzo[*b*]thiophene *S*,*S*-dioxide (**35a**, 174 mg, 0.64 mmol) and naphthoquinone (**41**, 120 mg, 0.75 mmol) in diphenyl ether (900 mg) was heated at 135 ^{o}C for 42h. Thereafter, the cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/CH_2Cl_2 1:1) to give **40b** (151 mg, 65%) as a colorless solid [27] – ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.93 (3H, s, OCH_3), 7.09 (2H, d ^3J = 8.6 Hz), 7.48 (2H, d,

^3J = 8.6 Hz), 7.58 – 7.64 (1H, m), 7.74 – 7.86 (4H, m), 8.05 (1H, d, ^3J = 8.6 Hz), 8.27 (1H, d, ^3J = 7.6 Hz), 8.34 (1H, s), 9.81 (1H, d, ^3J = 8.9 Hz);); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 55.4 (OCH_3), 114.0 (2C, CH), 123.5 (CH), 126.4 (CH), 127.0 (CH), 127.3 (CH) 128.2 (C_{quat}), 128.6 (CH), 128.9 (CH), 129.5 (CH), 131.1 (2C, CH), 131.4 (C_{quat}), 131.8 (C_{quat}), 132.3 (C_{quat}), 133.3 (C_{quat}), 133.4 (CH), 134.2 (CH), 135.1 (C_{quat}), 135.3 (C_{quat}), 147.3 (C_{quat}), 159.7 (C_{quat}), 184.6 (C_{quat}, CO), 186.0 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 364 (M^+, 48.5), 248 (100), 203 (71.9), 202 (71.7). HRMS Found: 364.1102. Calcd. for $C_{25}H_{16}O_3$: 364.1099.

5-Bromobenz[*a*]anthracene-7,12-dione (**40c**). – A solution of 3-bromobenzo[*b*]thiophene *S*,*S*-dioxide (**34b**, 245 mg, 1.0 mmol) and naphthoquinone (**41**, 198 mg, 1.25 mmol) in diphenyl ether (1.2 g) was heated at 135 °C for 34h. Thereafter, the cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/CH_2Cl_2 1:1) to give **40c** (190 mg, 56%) as a solid; mp. 198 °C [28,29]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.77 – 7.84 (4H, m), 8.25 – 8.32 (2H, m), 8.39 – 8.43 (1H, m), 8.71 (1H, s), 9.75 (1H, d, ^3J = 9.7 Hz);); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 126.6 (CH), 126.9 (CH), 127.4 (CH), 128.0 (CH), 128.7 (C_{quat}), 129.2 (CH), 130.0 (CH), 130.5 (CH), 131.4 (C_{quat}), 131.7 (C_{quat}), 131.8 (C_{quat}), 135.0 (3C, C_{quat}), 133.7 (CH), 134.5 (CH), 182.4 (C_{quat}, CO), 185.6 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 338 ([^{81}Br]M^+, 97.1), 336 ([^{79}Br]M^+, 100), 257 (M^+-Br, 29.5), 200 (62.1). HRMS Found: 335.9788. Calcd. for $C_{18}H_9O_2{}^{79}Br$: 335.9786.

1-(4-Ethoxyphenyl)-4-phenylnaphthalene (42). – A solution of 3-(4-ethoxyphenyl)benzo[*b*]thiophene *S*,*S*-dioxide (**35b**, 143 mg, 0.5 mmol) and phenylacetylene (**38e**, 500 mg, 5.0 mmol) in diphenyl ether (500 mg) was heated to 175 °C for 13h. The cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/CH_2Cl_2 1:1) to give **42** (78%) as a colorless solid, mp. 125 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.52 (3H, t, ^3J = 6.9 Hz, CH_3), 4.14 (2H, q, ^3J = 6.9 Hz, OCH_2), 7.04 (2H, d, ^3J = 8.4 Hz), 7.42 – 7.54 (11H, m), 7.95 – 7.96 (1H, m), 7.99 – 8.00 (1H, m) ^{13}C-NMR (150.9 MHz, $CDCl_3$, DEPT) δ 14.9 (CH_3), 63.5 (OCH_2), 114.3 (2C, CH), 125.7 (CH), 125.7(5) (CH), 126.3 (CH), 126.4 (CH), 126.4(5) (CH), 126.5 (CH), 127.2 (CH), 128.3 (2C, CH), 130.1 (2C, CH), 131.1 (2C, CH), 131.9(5) (C_{quat}), 132.1 (C_{quat}), 133.0 (C_{quat}), 139.5 (C_{quat}), 139.5(5) (C_{quat}), 140.9 (C_{quat}), 158.3(5) (C_{quat}). MS (EI, 70 eV) *m/z* (%) 324 (M^+, 8.6), 83 (100). HRMS Found: 324.1517. Calcd. for $C_{24}H_{20}O$: 324.1514.

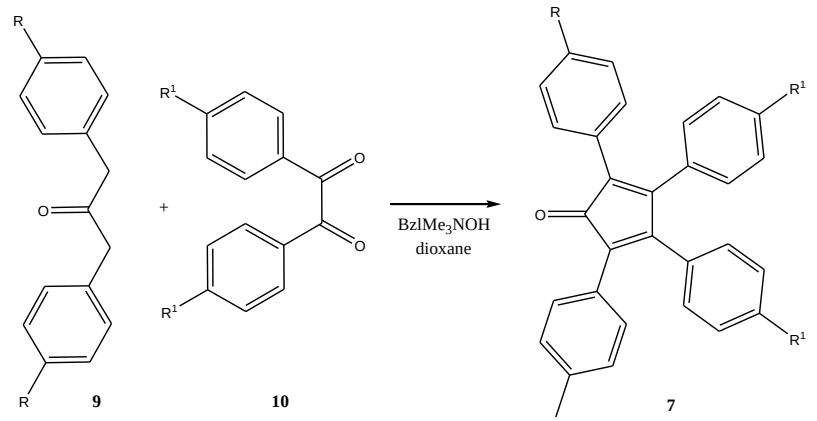
2-(4-Iodophenyl)-5-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-dione (45). – A solution of 3-phenylbenzo[*b*]thiophene *S*-oxide (**33**, 120 mg, 0.54 mmol) and *N*-(4-iodophenyl)maleimide (**43**, 323 mg, 1.08 mmol) in diphenyl ether (1.0 g) was heated at 135 °C for 13h. The mixture was subjected to column chromatography on silica gel (hexane → hexane/CH_2Cl_2 1:1) to give the cycloadduct **44**. To the cycloadduct **44** was added DDQ (2,3-dichloro-5,6-dicyanobenzoquinone, 227 mg, 1.0 mmol) in benzene (5 mL), and the mixture was kept under reflux for 3h. The cooled mixture was subjected to column chromatography on silica gel (hexane/CH_2Cl_2 1:1) to give **45** (120 mg, 47%) ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.31 (2H, d, ^3J = 7.6 Hz), 7.52 – 7.55 (4H, m), 7.57 (1H, dd, ^3J = 8.6 Hz, ^3J = 7.3 Hz), 7.77 (1H, d, ^3J = 8.4 Hz, ^3J = 7.3 Hz), 7.86 (2H, d, ^3J = 7.6 Hz), 7.91 (1H, s), 8.03 (1H, d, ^3J = 8.6 Hz), 9.09 (1H, d, ^3J = 8.4 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 91.2 (C_{quat}), 120.5 (CH), 126.1 (CH), 128.2 (CH), 129.0 (2C, CH), 129.3 (CH), 129.5 (2C, CH), 129.6 (C_{quat}), 129.8 (CH), 130.3 (CH), 130.4 (C_{quat}), 130.6 (2C, CH), 131.3 (C_{quat}), 135.9 (C_{quat}), 139.1 (2C, CH), 139.9(5) (C_{quat}), 149.3 (C_{quat}), 157.6 (C_{quat}), 165.9 (C_{quat}, CO), 168.4 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 475 (M^+, 100), 431 (7.9), 430 (6.8), 334 (20.7), 304 (12.8), 276 (8.0), 202 (25). HRMS Found: 475.0063. Calcd. for $C_{24}H_{14}O_2NI$: 475.0069.

B**enzyl 2,6-bis(*tert*-butyl)benzoate** (**47**). – A solution of 2,5-bis(*tert*-butyl)thiophene *S*,*S*-dioxide (**46**, 250 mg, 1.1 mmol) and benzyl propiolate (**26**, 120 mg, 0.75 mmol) in diphenyl ether (500 mg) was heated at 170°C for 1h. The cooled solution was subjected to column chromatography on silica gel to give **46** (177 mg, 73%) as a colorless oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.25 (9H, s, Bu^t), 1.35 (9H, s, Bu^t), 5.35 (2H, s), 7.27 (1H, m), 7.33 – 7.47 (6H, m), 7.34 (1H, s); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 31.1 (3 CH_3, Bu^t), 31.4 (3CH_3, Bu^t), 34.2 (C_{quat}), 35.5 (C_{quat}), 125.5 (CH), 126.7 (CH), 126.9 (CH), 128.3 (CH), 128.5 (2C, CH), 128.6 (2C, CH), 132.2 (C_{quat}), 135.5 (C_{quat}), 144.5 (C_{quat}), 148.1 (C_{quat}), 172.1 (C_{quat}, CO), MS (EI, 70 eV) m/z (%) 324 (M^+), 309 (M^+-CH_3, 30), 217 (31), 91 ($C_6H_5CH_2{}^+$, 100). HRMS Found: 324.2086. Calcd. for $C_{22}H_{28}O_2$: 324.2089.

III. Results and Discussion

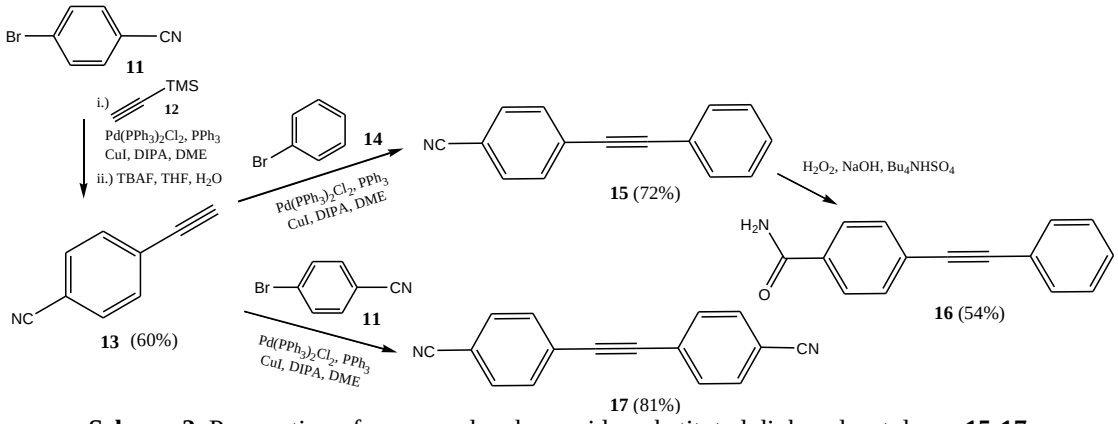
Preparation of starting materials

Tetraarylcyclopentadienones (tetracyclones) **7** were prepared according to a known strategy [14,30] via Weiss reaction with a concomitant double dehydration. The preparation of the tetracyclones used in this study, utilizing benzyltrimethylammonium hydroxide ($BzlMe_3NOH$), has been published earlier [7] (Scheme 1).

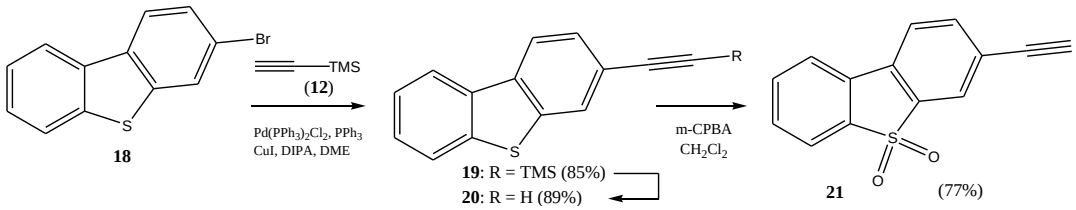


Scheme 1. Preparation of tetraarylcyclopentadienones (tetracyclones) **7** via Weiss reaction [7.14].

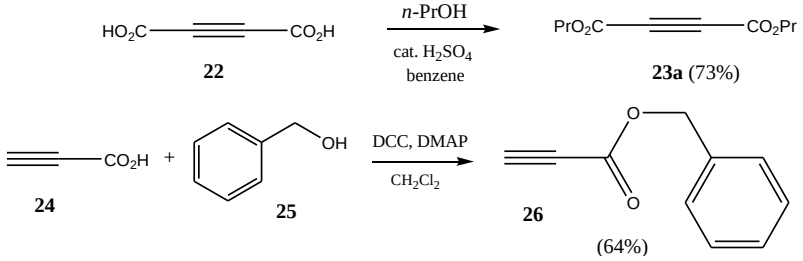
The preparation of substituted diphenylacetylenes, where not commercially available to us, proceeded via double Sonogashira coupling reaction, using trimethylsilylacetylene as a mono-protected acetylene, where the TMS group was removed routinely (TBAF, THF, H_2O) and the deprotection was followed by a second Sonogoshira coupling reaction (Scheme 2). A similar strategy was followed in preparing 3-ethynyldibenzo[*b*,*d*]thiophene (**20**). In the case of mono-*p*-cyanotolane **15** and 3-ethynyldibenzo[*b*,*d*]thiophene (**20**), further derivatisation occurred by hydrolysis of the cyano group in **15** to the amide **16** and by oxidation of the sulfur function in **20** to the *S*,*S*-dioxide **21**, in order to have further tolane and arylacetylene derivatives available that could function as dienophiles in the subsequent [4+2]-cycloaddition reactions (Scheme 3). Lateron it was realized that it is more facile to derivatize these functions after the cycloaddition reactions, ie. using alkynes **15** and **20**, respectively, has been completed. Dipropyl acetylenedicarboxylate (**23a**) was best prepared by sulfuric acid catalyzed esterification of acetylenedicarboxylic acid (**22**), while DMAP catalyzed esterification of **22** in the presence of DCC gave very poor results. This in contrast to benzyl propiolate (**26**), which could be prepared from propiolic acid (**24**) in the presence of DMAP/DCC [31] (Scheme 4).



Scheme 2. Preparation of cyano and carboxamido-substituted diphenylacetylenes **15**-**17**.

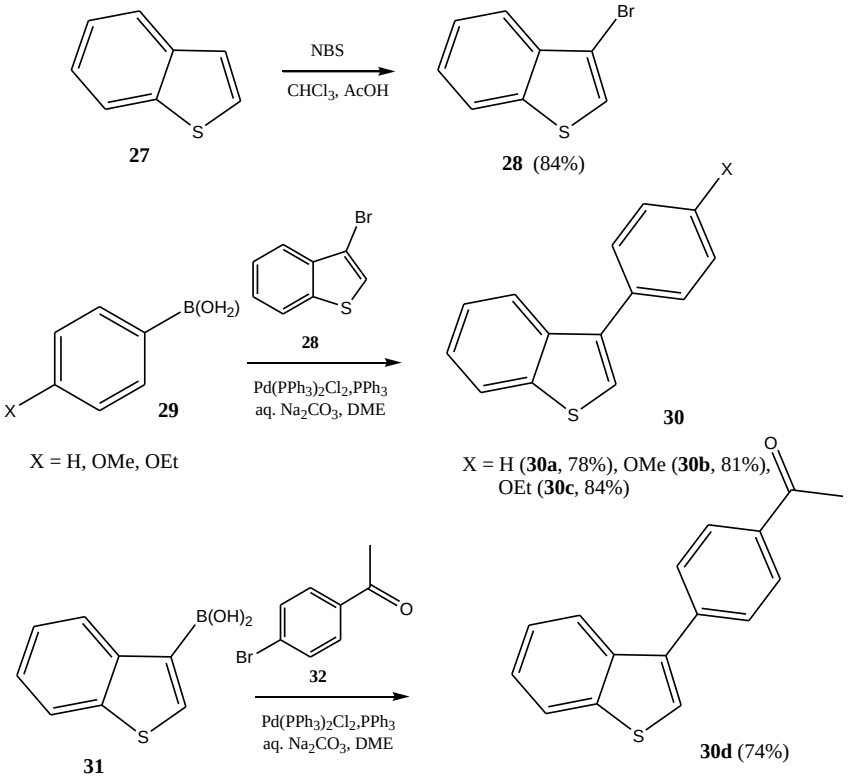


Scheme 3. Preparation of 3-ethynyldibenzo[*b*,*d*]thiophenes **20** and **21**.

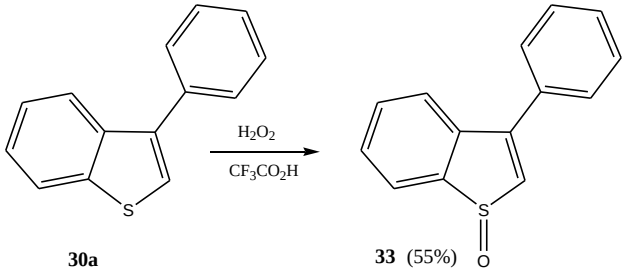


Scheme 4. Preparation of dipropyl acetylenedicarboxylate (**23**) and benzyl propiolate (**26**).

3-Substituted benzo[*b*]thiophenes **30** were synthesized by Suzuki-Miyaura reaction of either benzo[*b*]thienyl-3-boronic acid (**31**) and bromoarenes such as **32** or of 3-bromobenzo[*b*]thiophene (**28**), which can be synthesized directly from the commercially available benzo[*b*]thiophene (Br_2, $CHCl_3$ [32] or NBS, AcOH, $CHCl_3$ [16]), with commercially available arylboronic acids **29** (Scheme 5). The preparation of 3-phenylbenzo[*b*]thiophene *S*-oxide **33** from 3-phenylbenzo[*b*]thiophene **30a** followed an established route. Mostly, benzo[*b*]thiophene *S*-oxides have been prepared from benzo[*b*]thiophenes by oxidation, where it is important to avoid over-oxidation to the respective benzo[*b*]thiophene *S*,*S*-dioxide. This can be achieved by using the oxidizing reagents H_2O_2 – AcOH [33], H_2O_2 – SeO_2 [33], dimethyldioxirane (DMD, albeit in low yields), oxaziridines [33], Bu^{t}OCl – MeOH [34,35], *m*-CPBA-BF_3·etherate [13,36], or by using enzymatic oxidation (*P. putida* UV4) [37,38]. In the present case, the benzo[*b*]thiophene **30a** was oxidized to the benzo[*b*]thiophene *S*-oxide **33** with H_2O_2 – CF_3CO_2H [39] (Scheme 6), under conditions also used to oxidize thiophenes to thiophene *S*-oxides [40,41]. Benzo[*b*]thiophene *S*-oxide **33** could be obtained in acceptable yield (Scheme 6). The benzo[*b*]thiophene *S*-oxide is stable over an extended period of time. It should kept away from light, however, because as is in the case of thiophene *S*-oxides [36], photoirradiation can lead to deoxygenation to revert the compounds back to the benzo[*b*]thiophene **30a**. Benzo[*b*]thiophene *S*,*S*-dioxides **34**/**35** are formed by oxidation of benzo[*b*]thiophenes **27**,**28**,**30a-d** with *m*-CPBA at room temperature (Scheme 7). In the same way, 2,5-*tert*-butylthiophene *S*,*S*-dioxide [42,43] was prepared.

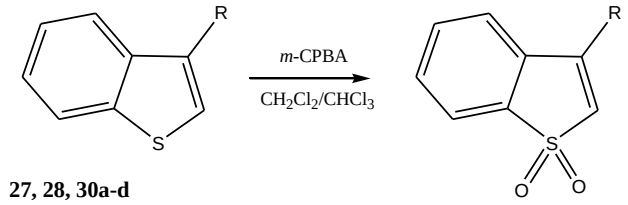


Scheme 5. Preparation of 3-arylbenzo[*b*]thiophenes **30** by Suzuki-Miyaura reaction



30a **33** (55%)

Scheme 6. Preparation of 3-phenylbenzo[*b*]thiophene S-oxide (**33**) according to ref. 21.



27, 28, 30a-d

(R = H, Br, Ph, 4-MeO-Ph, 4-EtO-Ph, 4-CH_3COPh)

34a: R = H (67%)
34b: R = Br (63%)
35a: R = 4-MeO-Ph (78%)
35b: R = 4-EtO-Ph (79%)
35c: R = 4-CH_3COPh (71%)
35d: R = Ph (81%)

Scheme 7. Preparation of 3-substituted benzo[*b*]thiophene *S,S*-dioxides **34a,b** and **35a-d**.

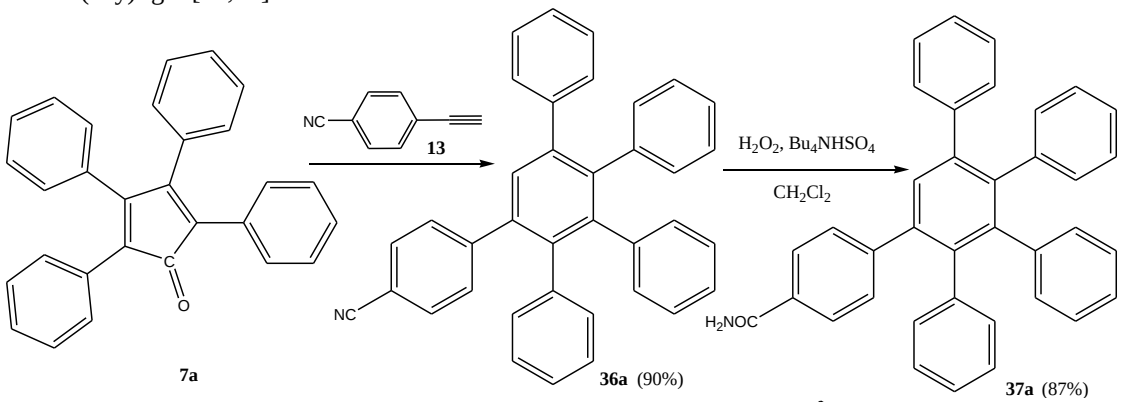
Cycloaddition reactions

Tetraarylcyclopentadienones (tetracyclones) **7** are known to be excellent dienes in a Diels-Alder type reaction leading to cycloadducts decorated with neighboring bulky substituents [44-46], with the reaction possessing a long history [47]. Nevertheless, the cycloaddition reactions often necessitate high temperatures. A typical solvent suitable for such high temperatures is diphenyl ether, which the author had used previously in cycloaddition reactions with bulky substituted cyclic dienes [43]. Diphenyl ether had also been used before in cycloaddition reactions with tetracyclones [46]. However, it has also been found that under the high temperatures used (>160 °C), tetracyclones convert to α-tetraarylpyrones, when the reactions are run in air [7].

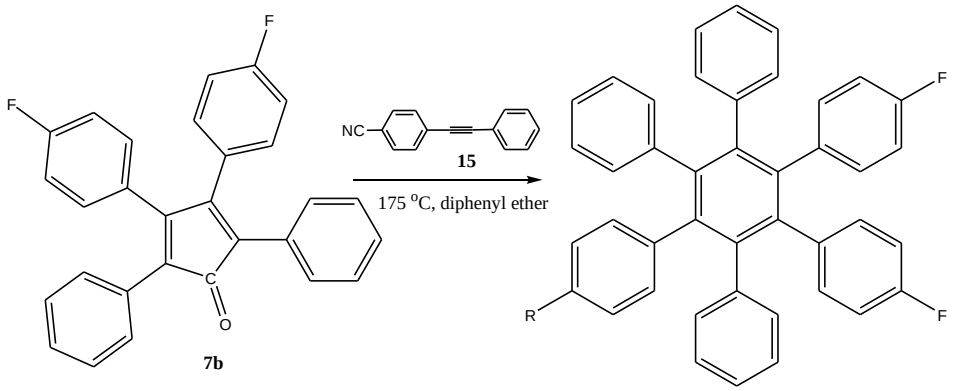
The current experiments showed a very clear dependence of the reaction on the steric demand of the cycloaddends, namely on whether the alkyne used was mono- or disubstituted, where mono-substituted alkynes were very quick to react. This included the 1,4-diphenylbuta-1,3-diyne, where the reaction was complete after 3 hours. Nevertheless, in the cases studied, a reaction temperature of 175°C seemed optimal. In those cases, where microwave irradiation was used, the reaction time could be shortened, but the yields were generally not improved. Exclusion of air is necessary, especially when working with solvents such as diphenyl ether. In a number of cases, sublimation of the alkyne was found to be an issue. In those cases, it was advantageous to use diphenyl ether as solvent. In a number of cases, the mixture of cycloaddends did not form a homogeneous melt at 175 °C. Again, in these cases diphenyl ether was used as solvent. In cases, where functionalities were to be transformed by hydrolysis or oxidation, it was advantageous to undertake the cycloaddition reaction first and carry out the functional transformation second. This held true in both the cases where a carboxamidohexaarylbenzene was targeted and where a *S,S*-dioxodibenzothienylpentaphenylbenzene was to be prepared. The amido-substituted tolanes such as **16** are less soluble than the respective cyano-substituted tolanes, and they also have higher melting points. Both of these characteristics are detrimental to the cycloaddition reaction. In the case of sulfone **21**, the stability of the alkyne at elevated temperatures is a further impediment. Overall, the novel oligoarylbenzenes **36** were prepared in good yield (Scheme 8).

Having worked with both tetracyclones and tetraarylthiophene *S*-oxides [43,48], the query always comes up – which is the better building block for hexaarylbenzenes and similar compounds? Competitive experiments in the cycloaddition of tetraphenylcyclopenta-1,3-dienone and tetraphenylthiophene *S*-oxide with N-phenylmaleimide have shown that tetraphenylthiophene *S*-oxide is the more reactive diene [43]. Nevertheless, where extended reaction times are needed, thiophene *S*-oxides tend to give more side-products, which include the respective thiophenes as deoxygenation products. The preparation procedures of tetraarylthiophene *S*-oxide and tetracyclone complement each other – while both can be prepared by the reaction of zirconapentadienes, the more robust route is the Weiss reaction for tetracyclones, which is complemented by the oxidation reaction of

thiophenes to thiophene *S*-oxides. Yields can be comparable. Tetracyclones can be stored over longer periods of time than tetraarylthiophene *S*-oxides which deoxygenate slowly even at room temperature, especially when exposed to (day)light [36,49].

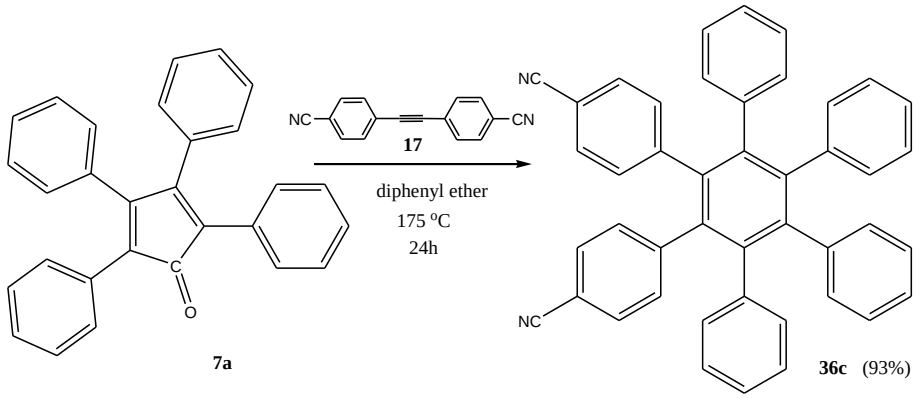


7a **36a** (90%) **37a** (87%)

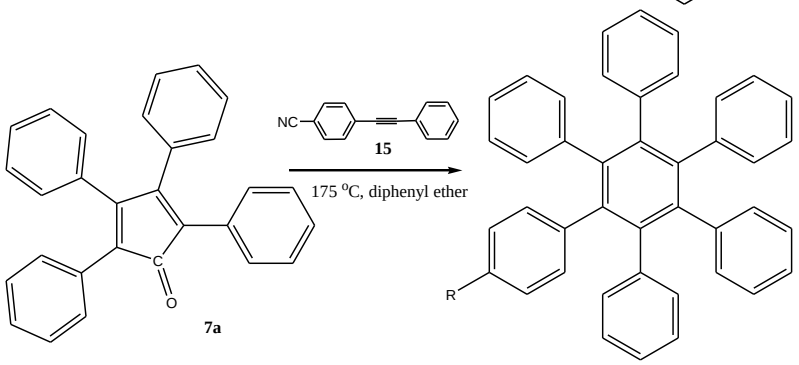


7b

36b: R= CN (89%)
37b: R = $CONH_2$ (73%)
H_2O_2, Bu_4NHSO_4
CH_2Cl_2

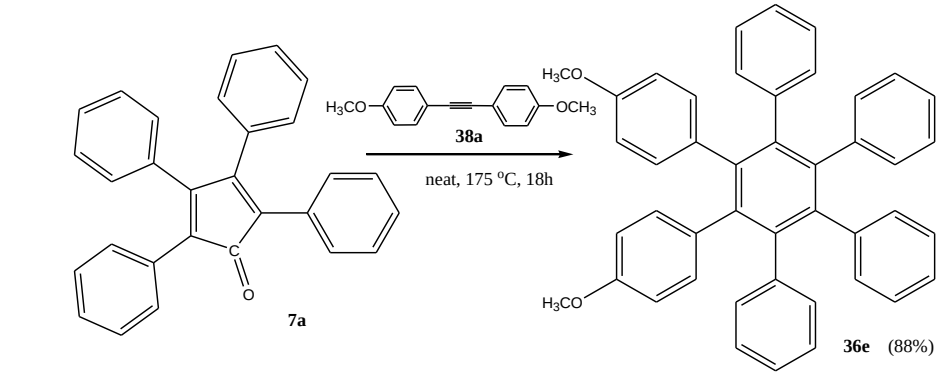


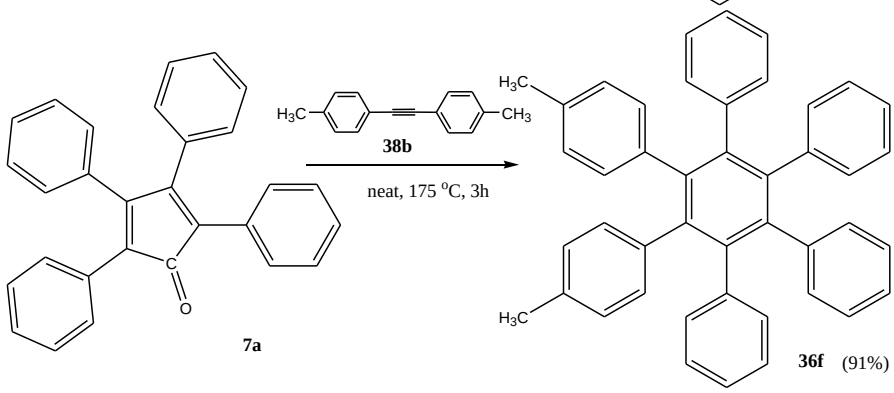
7a **36c** (93%)

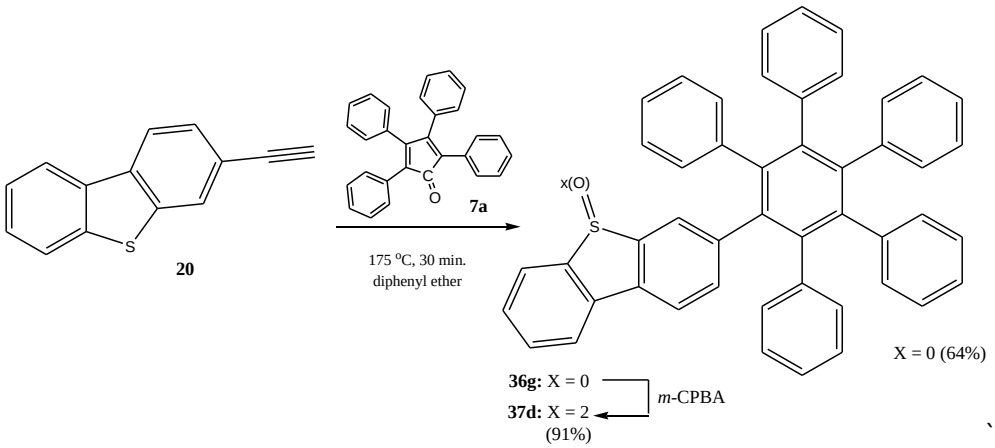


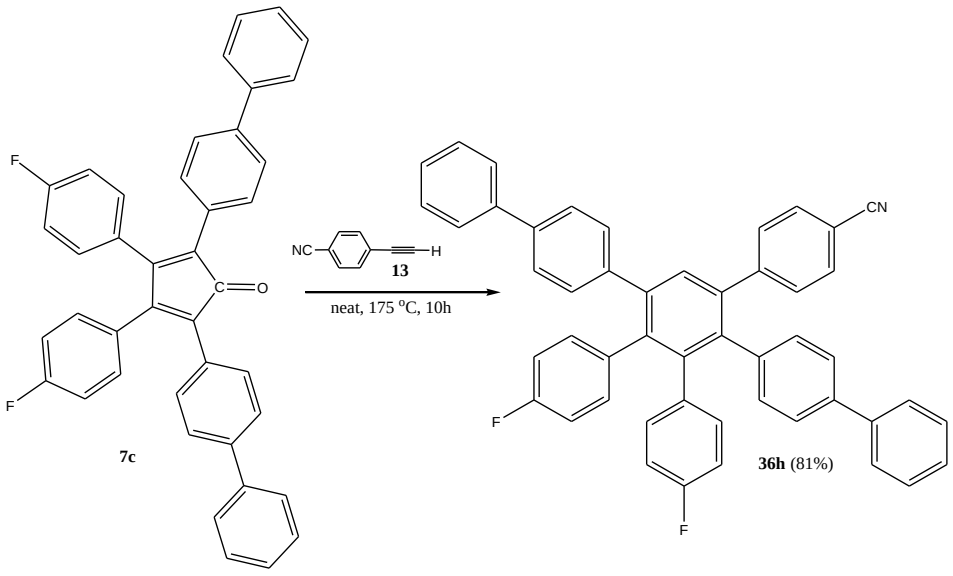
7a

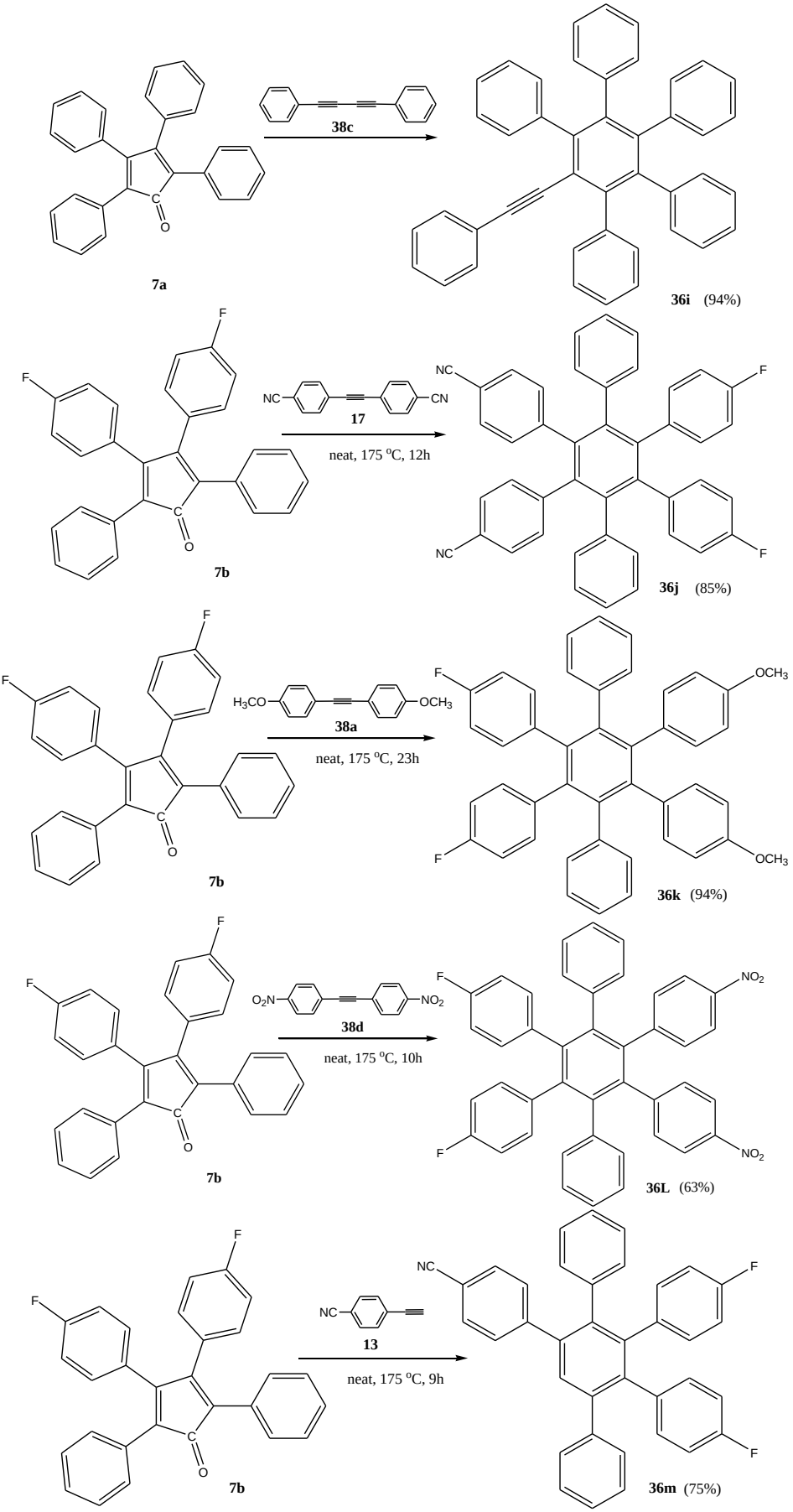
36d: R= CN (85%)
37c: R = $CONH_2$ (71%)
H_2O_2, Bu_4NHSO_4
CH_2Cl_2

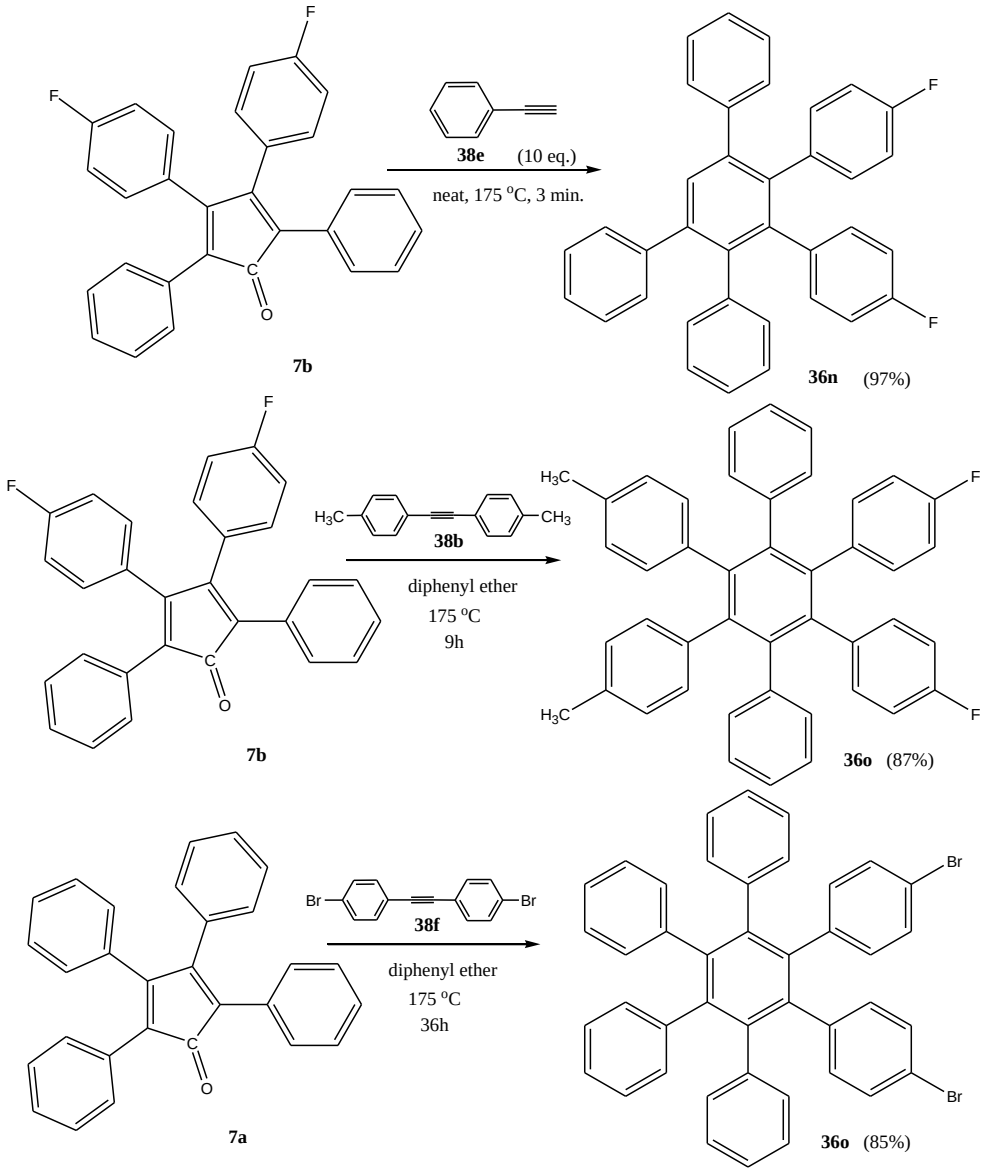

H3CO
OCH3
38a
neat, 175 °C, 18h
7a
36e (88%)


H3C
CH3
38b
neat, 175 °C, 3h
7a
36f (91%)


20
7a
175 °C, 30 min.
diphenyl ether
x(O)
X = 0 (64%)
36g: X = 0
37d: X = 2
(91%)
m-CPBA


NC
H
13
neat, 175 °C, 10h
7c
36h (81%)


38c
7a
36i (94%)
F
NC
CN
17
neat, 175 °C, 12h
7b
36j (85%)
H3CO
OCH3
38a
neat, 175 °C, 23h
36k (94%)
O2N
NO2
38d
neat, 175 °C, 10h
36L (63%)
13
neat, 175 °C, 9h
36m (75%)
O

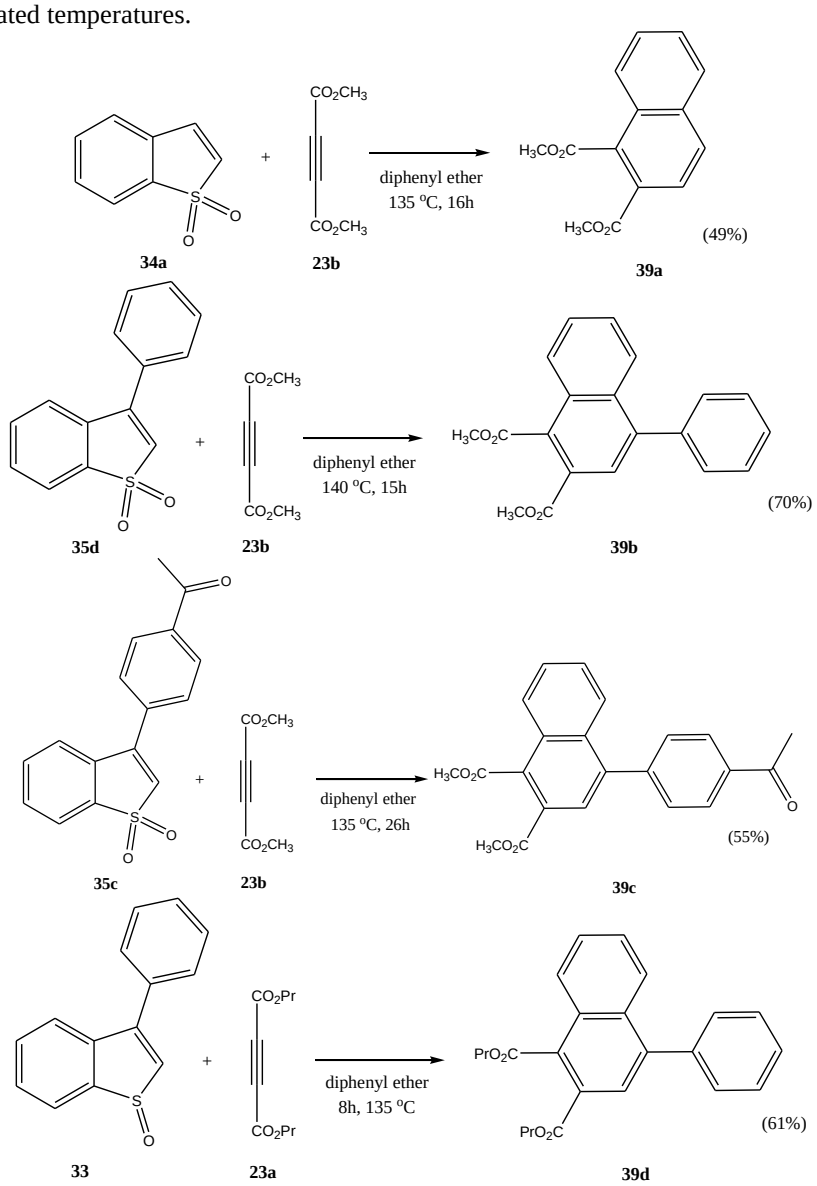


Scheme 8. Cycloaddition of tetracyclones **7** to diarylacetylenes and arylacetylenes.

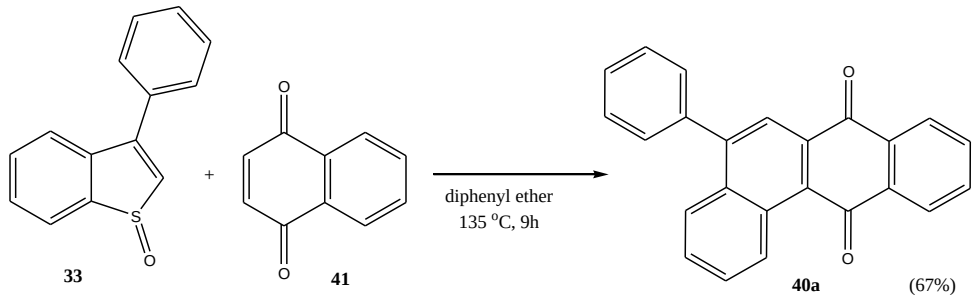
Furthermore, 3-substituted benzo[*b*]thiophene *S*,*S*-dioxides **34a**, and **35b-d** as well as benzo[*b*]thiophene *S*-oxide **33** were tested as dienes in cycloaddition reactions with alkynes. A number of 2-substituted benzo[*b*[thiophenes had been tested as dienes, previously [13]. Again, the benzo[b]thiophene *S*-oxide **33** was seen to be more reactive than the corresponding benzo[*b*]thiophene *S*,*S*-dioxides, eg. **34a**, **35c** , and **35d**, which is reflected in the reaction times (Scheme 9). The reaction of benzo[*b*]thiophene *S*-oxide **33** and benzo[*b*]thiophene *S*,*S*-dioxides **35a** and **35b** with *p*-naphthoquinone (**41**) gave 5-substituted benz[*a*]anthracene-7,12-diones **40**. The long reaction times in diphenyl ether in the presence of air leads to the oxidation of the primary cycloadducts to produce compounds **40** (Scheme 10). This does not happen in the cycloaddition with other alkenes such as exemplified by the cycloaddition of benzo[*b*]thiophene *S*-oxide **33** with *N*-(*p*-iodophenyl)maleimide (**43**), where the cycloadduct **44** is stable under the reaction conditions and an oxidant (in this case, DDQ) is needed for a subsequent dehydrogenation (Scheme 12). Interestingly, the cycloaddition of benzo[*b*]thiophene *S*,*S*-dioxide **35b** to phenylacetylene (**38e**) only gave one isolable product, showing a very regioselective reaction (Scheme 11). The structure of the compound was confirmed by an HMQC-NOESY sequence, where an NOE effect was detected between the ortho protons of the aryl substituents with the inner protons of the napthalenyl-unit as shown in Figure 2. It is believed that the regioselectivity of this reaction stems from a secondary overlap of frontier orbitals of the phenyl group of the phenyl acetylene and the benzo unit of

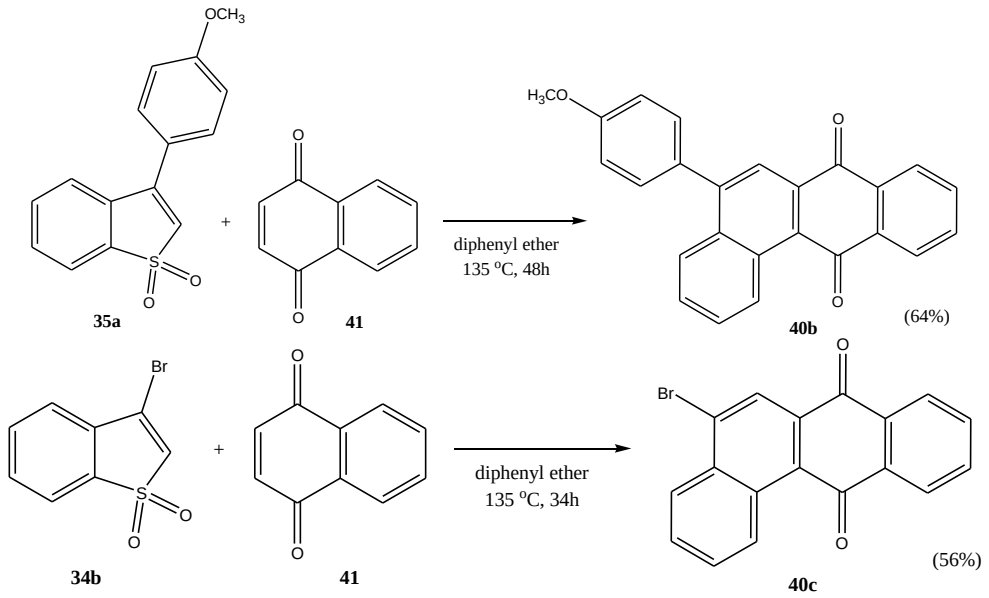
the benzo[*b*]thiophene *S*,*S*-dioxide as shown in Figure 2. A similar regioselectivity had been noted in the cycloaddition of phenylacetylene with phenyl-substituted 2-pyrones [50].

Finally, the reactivity of 2.5-*tert*-butylthiophene *S*,*S*-dioxide (**47**) as a cyclic diene with two sterically exacting alkyl substituents towards propiolate **26** was investigated (Scheme 13) and compared to the reactivity of the corresponding thiophene S-oxide [43]. It was seen that **47** reacts facilely with mono-substituted alkynes such as **26** at elevated temperatures.

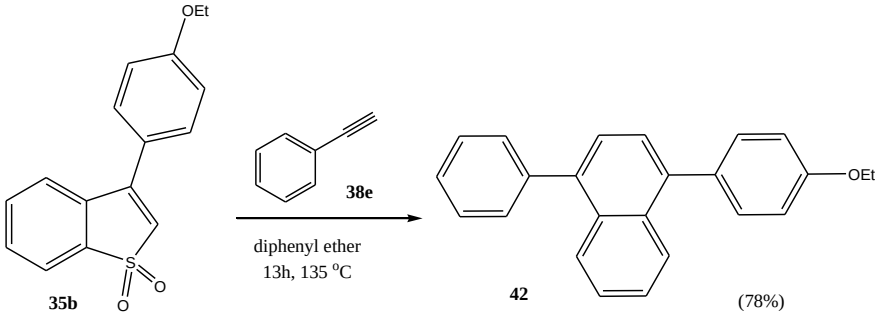


Scheme 9. Benzo[*b*]thiophene *S*,*S*-dioxides and benzo[*b*]thiophene *S*-oxide as dienes in Diels Alder type reactions with acetylene dicarboxylates.





Scheme 10. Benzo[*b*]thiophene *S*,*S*-dioxides and benzo[*b*]thiophene *S*-oxide as dienes in Diels Alder type reactions with acetylene dicarboxylates



Scheme 11. Regioselective Diels-Alder reaction of benzo[*b*]thiophene *S*,*S*-dioxide **35b** with phenylacetylene

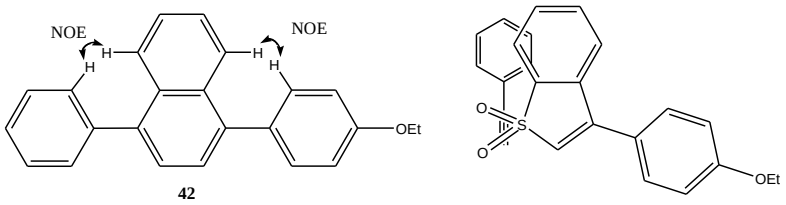
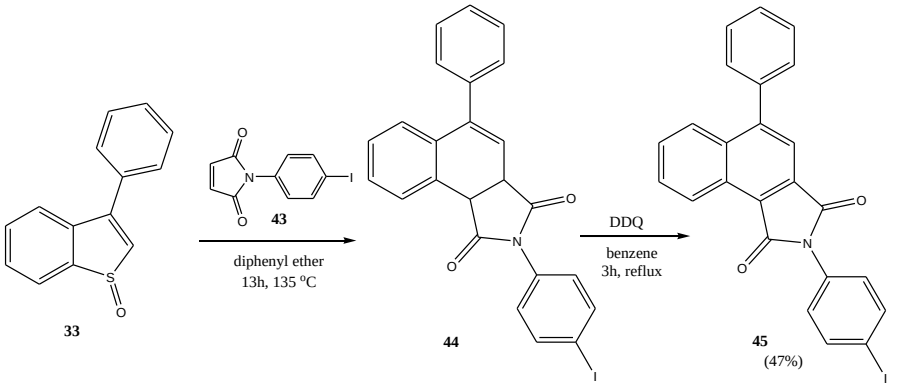
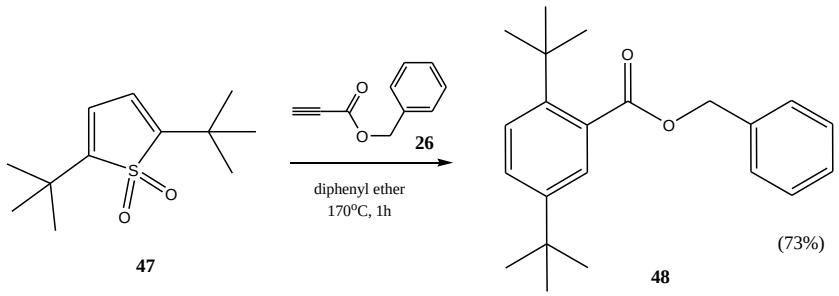


Figure 2. Regioselective formation of 1-(4-ethoxyphenyl)-4-phenylnaphthalene (**42**)



Scheme 12. Cycloaddition of benzo[*b*]thiophene *S*-oxide **33** and phenylmaleimide **43** with subsequent oxidative dehydrogenation of the cycloadduct



Scheme 13. Cycloaddition of 2,5-bis(*tert*-butyl)thiophene *S*,*S*-dioxide (**47**) to alkyne **26**

IV. Conclusion

A number of tetraarylcyclopentadienones (tetracyclones) **7** were reacted with alkynes to generate oligoarylbenzenes **36**/**37**, among them the novel compounds **36b**/**37b**, **36g**/**37d**, **36h**, **36j**, **36k**, **36L**, **36m**, **36n**, and **36o**. The reactions were carried out under inert atmosphere. These reactions were performed under solventless conditions unless the reaction mixtures did not give homogeneous melt or the alkyne was easily sublimated. In those cases, de-aerated diphenyl ether was used as a solvent. A 3-arylbenzo[*b*]thiophene *S*-oxide and a number of 3-arylbenzo[b]thiophene *S*,*S*-dioxides were prepared by a Suzuki cross-coupling reaction / oxidation sequence. These compounds were used as dienes in their reaction with alkynes, leading to substituted naphthalenes. Their reactions with *p*-naphthoquinone at elevated temperatures using diphenyl ether as solvent lead to benz[*a*]anthracene-7,12-diones. With phenylacetylene, 3-arylbenzo[b]thiophene S,S-dioxide **35b** leads to a regioselective cycloaddition, most likely governed by secondary interactions between the phenyl group of the alkyne and the benzo unit of the benzo[*b*]thiophene *S*,*S*-dioxide.

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