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Synthesis and Diels-Alder Reactions of Furo[2,3-*c*]pyrroles and Benzofuro[2,3-*c*]pyrroles

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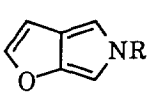
Abstract: Furo[2,3-*c*]pyrroles **1a-d** and benzofuro[2,3-*c*]pyrroles **6a-e** were synthesized. Diels-Alder reactions of **1b** and **6b** gave *1:2* cycloadduct **13** and *1:1* cycloadduct **20**, respectively. Parent compound **17** of benzofuro[2,3-*c*]pyrrole ring system was trapped as *N-tert*-butoxycarbonyl derivative **18**. Oxidative extrusion of the *N*-bridge in Diels-Alder adduct **20** gave dibenzofuran **22**.

Furo[2,3-*c*]pyrroles **1** and benzofuro[2,3-*c*]pyrroles **6** are highly labile heterocyclic ring systems according to theoretical calculation.[1] Their synthesis and reaction are unknown. Among the related ring systems **2-5**, **7**, and **8**, only **3**[2] and **7**[3] were synthesized. However, the method used in these syntheses are unsuitable for the preparation of furo[2,3-*c*]pyrrole **1** and benzofuro[2,3-*c*]pyrrole **6** ring systems. We developed three methods for the synthesis of iso-condensed heteroaromatic pyrroles.[4] In our preliminary communication, we have reported the synthesis of benzo[2,3-*c*]pyrrole **6**.[4b] Herein we report the preparation of furo[2,3-*c*]pyrrole **1** and benzofuro[2,3-*c*]pyrrole **6** in detail, as well as Diels-Alder reactions of these heterocycles.



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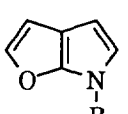

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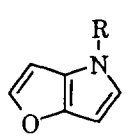

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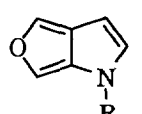

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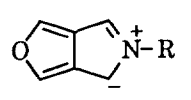

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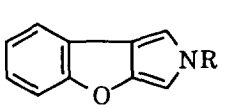

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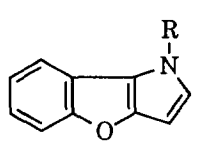

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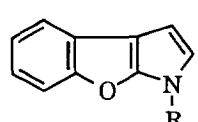

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Knoevenagel condensation of 3-methyl-2-furocarboxaldehyde (**9**) with diethyl malonate gave alkylidenemalonate **10**.[4] Bromination of **10** with *N*-bromosuccinimide in the presence of dibenzoyl peroxide afforded bromide **11**. Treatment of **11** with benzylamine, isopropylamine, *tert*-butylamine and 3-hydroxypropylamine in ethanol yielded furo[2,3-*c*]pyrroles **1a**, **1b**, **1c** and **1d**, respectively. The yields are only moderate (16-46%) because these compounds are highly sensitive to acid, and partially polymerized upon silica gel chromatography. Subsequently, Diels-Alder reaction of **1b** with two equiv. dimethyl acetylenedicarboxylate (DMAD) at room temperature in benzene gave a *1:2* cycloadduct **13**. The expected *1:1* cycloadduct **12** was not detected. Diels-Alder reaction of **1b** with 0.9 equiv. DMAD also gave only *1:2* cycloadduct **13** and recovered **1b**. Apparently, the reactive furan moiety of *1:1* cycloadduct **12** underwent a second Diels-Alder reaction with DMAD very rapidly, Scheme 1. A structure of **13** from *X*-ray crystallographic analysis is shown in Figure 1.[5]

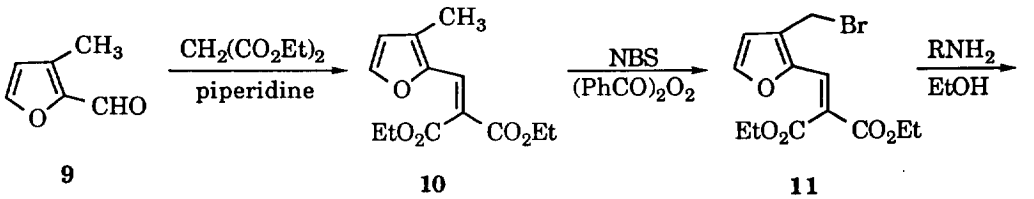
We applied the same method for synthesis of benzofuro[2,3-*c*]pyrroles **6**. Knoevenagel condensation of 2-methyl-3-benzofurocarboxaldehyde (**14**) with diethyl malonate gave **15**. Bromination of **15** with *N*-bromosuccinimide afforded bromide **16**. Treatment of bromide **16** with methylamine, isopropylamine, benzylamine, phenylamine and p-toluidine afforded benzofuro[2,3-*c*]pyrroles **6a-e** respectively. In addition, treatment of **16** with ammonia in ethanol gave parent compound **17**, which was not isolable, but reacted immediately with di-*tert*-butyl dicarboxylate and 4-dimethylaminopyridine to give stable derivative **18**.[6] Diels-Alder reactions of compounds **6** and **18** with DMAD afforded cycloadducts **20** and **19** smoothly. *m*-Chloroperbenzoic acid oxidation of **20** with spontaneous extrusion of the R-N=O group gave 3,4-dimethoxycarbonyldibenzofuran (**22**) *via* intermediate **21**.[7]

In summary, we have succeeded in synthesis of two new heterocyclic ring systems, furo[2,3-*c*]pyrrole **1** and benzofuro[2,3-*c*]pyrrole **6**. Diels-Alder reactions of **1b** and **6b** with DMAD gave *1:2* cycloadduct **13** and *1:1* cycloadduct **20** respectively. Oxidative extrusion of the nitrogen bridge in Diels-Alder adduct **20** afforded dibenzofuran **22**. Parent system **6** was also prepared and trapped with di-*tert*-butyl dicarbonate to give **18**, which also underwent Diels-Alder reaction with DMAD.

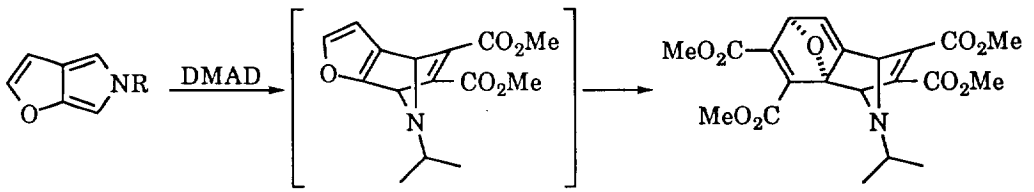
Experimental Section

General. ^{1}H NMR spectra were recorded on a Varian EM-390, a JEOL HX-100 or a Bruker AM-400 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer. Mass spectra refer to the electron impact mass spectra and were recorded on a JEOL TMS-D-100 mass spectrometer. High-resolution mass spectra were recorded on

Scheme 1



9 **10** **11**



12 **13**

1a R = CH_2Ph
1b R = $CH(CH_3)_2$
1c R = $C(CH_3)_3$
1d R = $(CH_2)_3OH$

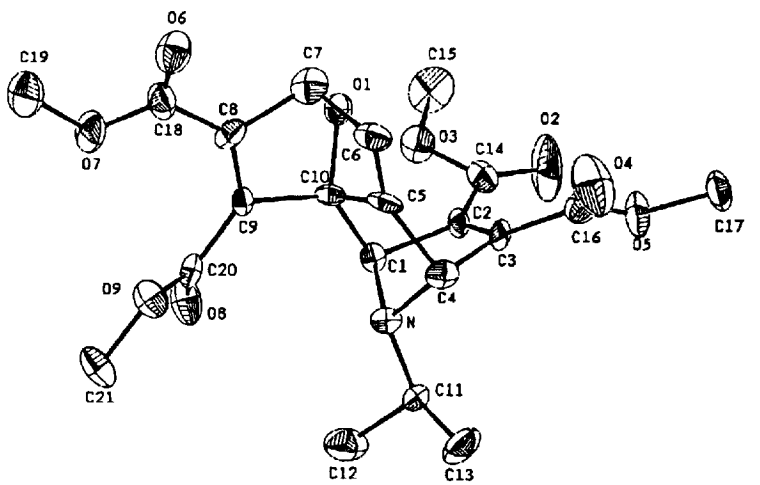
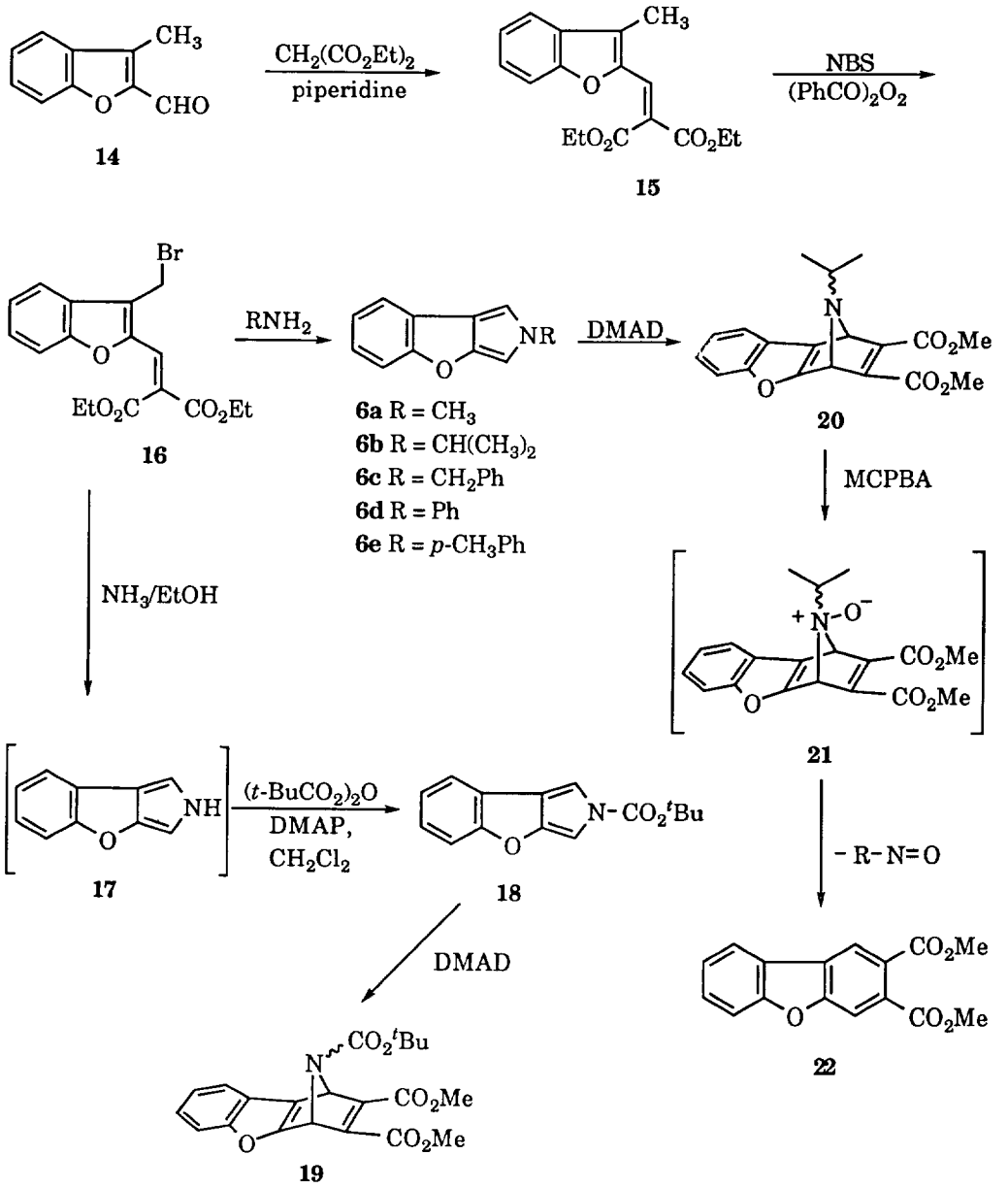


Figure 1 Crystal Structure of **13**

Scheme 2


CH3
CHO
14
CH2(CO2Et)2
piperidine
CH3
EtO2C
CO2Et
15
NBS
(PhCO)2O2
Br
EtO2C
CO2Et
16
RNH2
NR
6a R = CH3
6b R = CH(CH3)2
6c R = CH2Ph
6d R = Ph
6e R = p-CH3Ph
DMAD
N
CO2Me
CO2Me
20
MCPBA
NH3/EtOH
+N-O−
21
NH
17
(t-BuCO2)2O
DMAP,
CH2Cl2
N-CO2tBu
18
- R-N=O
DMAD
CO2tBu
19
22

a JEOL HX-110 mass spectrometer. IR spectra were recorded on a Perkin-Elmer 781 spectrometer, and UV spectra on a Perkin-Elmer Lambda 5 UV-VIS spectrometer. Single crystal *X*-ray analysis was performed on a Enraf-Nonius CAD-4 diffractometer. Melting points determined with a Büchi 530 melting-point apparatus and are uncorrected. Flash-column chromatography was performed as follows: silica gel, Merck No. 7736 Kieselgel 60H, was placed in a sintered-glass column packed dry. Solvent was flushed through the silica gel under a water-aspirator vacuum. The compound was then deposited with a minimal amount of solvent and eluted with solvent under a water aspirator vacuum. Diethyl ether and tetrahydrofuran (THF) were distilled from potassium/sodium metal under a nitrogen atmosphere with benzophenone ketyl as the indicator. All reactions were conducted under a nitrogen atmosphere.

Diethyl [(3-Bromomethyl-2-furyl)methylene]propanedioate (11). To a solution of **10** (290 mg, 1.2 mmol) in carbon tetrachloride (25 ml) was added *N*-bromosuccinimide (204 mg, 1.2 mmol) and dibenzoyl peroxide (10 mg). The reaction mixture was stirred and heated at reflux for 1 h. After the mixture was cooled in an ice bath, the solid was removed by filtration and washed with carbon tetrachloride. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 10:1) gave **11** (209 mg, 55%) as a yellow oil: IR (neat) 2980, 1730, 1635 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 1 H, J = 1.7 Hz), 7.38 (s,1 H), 6.49 (d, 1 H, J = 1.7 Hz), 4.56 (s, 2 H), 4.34 (q, 2 H, J = 7.2 Hz), 4.23 (q, 2 H, J = 7.2 Hz), 1.30 (t, 3 H, J = 7.2 Hz), 1.26 (t, 3 H, J = 7.2 Hz); MS *m/z* (relative intensity) 322 (M^++2, 44%), 330 (M^+, 48%), 251 (100%).

***N*-Benzylfuro[2,3-*c*]pyrrole (1a).** To a solution of benzylamine (114 mg, 1.1 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **11** (160 mg, 0.48 mmol) in 95% ethanol (7ml). The reaction mixture was stirred at room temperature for 31 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 20:1) gave **1a** (19mg, 20%) as a yellow oil: IR (neat) 3120, 3030, 2930, 1605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 4 H), 7.12 (s, 1 H), 7.11 (d, 1 H, J = 4.1 Hz), 6.50 (d, 1 H, J = 4.1 Hz), 6.49 (s, 1 H), 6.40 (s, 1 H), 5.13 (s,2 H); MS *m/z* (relative intensity) 197 (M^+,77), 91 (100); HRMS calcd $C_{13}H_{11}NO$ 197.0834, found 197.0841.

***N*-Isopropylfuro[2,3-*c*]pyrrole (1b).** To a solution of isopropylamine (38 mg, 0.64 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **11** (96 mg, 0.29 mmol) in 95% ethanol (10 ml). The reaction mixture was stirred at room temperature for 32 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 20:1) gave **1b** (10.8 mg, 25%) as a yellow oil: IR (Neat) 3115, 2920, 1380 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.18 (bd, 1 H), 6.90 (bd, 1 H), 6.41 (d, 1 H, J = 3.0 Hz), 6.32 (d, 1 H, J = 3.0 Hz), 4.24 (m, 1 H), 1.45 (d, 6 H, J = 6.0 Hz); MS *m/z* (relative intensity) 149 (M^+,100), 107 (45).

***N*-*tert*-Butylfuro[2,3-*c*]pyrrole (1c).** To a solution of *tert*-butylamine (36 mg, 0.49 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **11** (73 mg, 0.22 mmol) in

95% ethanol (10 ml). The reaction mixture was stirred and heated at reflex for 24 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 20:1) gave **1c** (7.1 mg, 20%) as a yellow oil: IR (neat) 3120, 2940, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 1 H, J = 2.1 Hz), 6.66 (d, 1 H, J = 1.6 Hz), 6.62 (d, 1 H, J = 1.6 Hz), 6.39 (d, 1 H, J = 2.1 Hz), 1.65 (s, 9 H); MS m/z (relative intensity) 163 (M^+, 77), 107 (100).

***N*-(3-Hydroxypropyl)furo[2,3-*c*]pyrrole (1d).** To a solution of 3-hydroxypropylamine (145 mg, 1.49 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **11** (128 mg, 0.39 mmol) in 95% ethanol (10 ml). The reaction mixture was stirred at room temperature for 18 h. Concentration and silica gel flash column charomatography (hexane-ethyl acetate, 5:1) gave **1d** (6 mg, 10%) as a yellow oil: IR (neat) 3415, 3010, 1376 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.26 (d, 1 H, J = 1.5 Hz), 6.48 (d, 1 H, J = 1.5 Hz), 6.42 (d, 1 H, J = 2.4 Hz), 6.36 (d, 1 H, J = 2.4 Hz), 4.11 (t, 2 H, J = 6.0 Hz), 4.61 (t, 2 H, J = 6.0 Hz), 2.09 (quintet, 2 H, J = 6.0 Hz), 1.59 (bs, 1 H); MS m/z (relative intensity) 165 (M^+, 100), 121 (54).

Cycloadduct 13 of *N*-Isopropylfuro[2,3-*c*]pyrrole (1b) and Dimethyl Acetylenedicarboxylate. A solution of **1b** (6 mg, 0.04 mmol) and dimethyl acetylenedicarboxylate (11.4 mg, 0.08 mmol) in benzene (3 ml) were stirred at room temperature for 5 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 5:1) gave **13** (15.3 mg, 88%) as a white solid: mp 107-108°C; IR (neat) 3130, 1732, 1718, 1635 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.47 (s, 1 H), 5.67 (d, 1 H, J = 1.4 Hz), 5.01 (s, 1 H), 4.98 (s, 1 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.77 (s, 3 H), 2.76 (m, 1 H), 0.97 (d, 3 H, J = 6.2 Hz), 0.94 (d, 3 H, J = 6.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 163.70 (s), 163.48 (s), 163.29 (s), 162.40 (s), 157.31 (s), 151.09 (s), 149.58 (s), 143.10 (s), 140.52 (s), 126.21 (s), 98.59 (s), 87.20 (d), 66.33 (d), 65.91 (d), 52.50 (q), 52.42 (q), 52.19 (q), 52.11 (q), 45.40 (q), 22.01 (q), 21.90 (q); MS m/z (relative intensity) 433 (M^+, 27), 401 (100), 358 (27); HRMS calcd $C_{21}H_{23}NO_9$ 433.1376, found 433.1373.

Diethyl [(3-Methyl-2-benzofuryl)methylene]propanedioate (15). To a solution of **14** (1g, 6.25 mmol) in dry benzene (30 ml) was added diethyl malonate (3 g, 18.75 mmol), piperidine (0.15 ml) and acetic acid (0.1 ml). The reaction mixture was refluxed for 26 h with a Dean-Stark water separator attached. After the mixture were washed with H_2O (20 ml x 2), 5% hydrochloride acid (10 ml x 2), saturated sodium carbonate (15 ml) and then dried ($MgSO_4$). Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 10:1) gave **15** (1.76g, 94%) as a yellow solid: mp 89-90°C; IR (KBr) 2965, 1745, 1690, 1620 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.61 (s, 1 H), 7.40-7.12 (m, 4 H), 4.45 (q, 2 H, J = 6.8 Hz), 4.28 (q, 2 H, J = 6.8 Hz), 2.41 (s, 3 H), 1.41 (t, 3 H, J = 6.8 Hz), 1.30 (t, 3 H, J = 6.8 Hz); MS m/z (relative intensity) 302 (M^+, 93), 256 (100), 184 (33); HRMS calcd $C_{17}H_{18}O_5$ 302.1149, found 302.1154.

Diethyl [(3-Bromomethyl-2-benzofuryl)methylene]propanedioate (16). To a solution of **15** (1.65 g, 5.4 mmol) in carbon tetrachloride (50 ml) was added *N*-bromosuccinimide

(970 mg, 5.4 mmol) and dibenzoyl peroxide (80 mg). The reaction mixture was stirred and heated at reflux for 1 h. After the mixture was cooled in an ice bath, the solid was removed by filtration and washed with carbon tetrachloride. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 10:1) gave **16** (1.85 g, 90%) as a yellow solid: mp 115-116°C; IR (KBr) 2985, 1732, 1718, 1636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, 1 H, *J* = 7.2, 0.8 Hz), 7.41-7.27 (m, 4 H), 4.69 (s, 2 H), 4.46 (q, 2 H, *J* = 7.3 Hz), 4.31 (q, 2 H, *J* = 7.3 Hz), 1.41 (t, 3 H, *J* = 7.3 Hz), 1.33 (t, 3 H, *J* = 7.3 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.70 (s), 163.71 (s), 155.29 (s), 147.21 (s), 127.78 (d), 126.80 (s), 125.91 (s), 123.70 (d), 123.63 (d), 123.00 (s), 120.68 (d), 111.59 (d), 62.01 (t), 61.80 (t), 20.01 (t), 14.09 (q), 14.02 (q); MS *m/z* (relative intensity) 382 (M^++2, 26), 380 (M^+, 26), 301 (100), 255 (35); HRMS calcd $C_{17}H_{17}BrO_5$ 380.0259, found 380.0224.

N-Methylbenzofuro[2,3-*c*]pyrrole (6a). To a solution of 35% methylamine (29.7 mg, 0.96 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **16** (166 mg, 0.44 mmol) in 95% and ethanol-tetrahydrofuran (1:1, 6 ml). The reaction mixture was stirred at room emperature for 16 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 20:1) gave **6a** (41 mg, 55%) as a white solid: mp 102-103°C; IR (KBr) 3118, 2935, 1635, 1580, 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, 1 H, *J* = 7.3, 1.0 Hz), 7.40 (d, 1 H, *J* = 7.3Hz), 7.22 (m, 2 H), 6.72 (d, 1 H, *J* = 1.3Hz), 6.49 (d, 1 H, *J* = 1.3 Hz), 3.77 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 161.10 (s), 150.29 (s), 121.41 (d), 122.70 (s), 122.01 (d), 120.33 (d), 114.74 (s), 111.39 (d), 108.50 (d), 97.58 (d), 37.40 (q); MS *m/z* (relative intensity) 171 (M^+, 100); HRMS calcd $C_{11}H_9NO$ 171.0684, found 171.0674.

***N*-Isopropylbenzofuro[2,3-*c*]pyrrole (6b)**. To a solution of isopropylamine (38 mg, 0.64 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **16** (110 mg, 0.29 mmol) in 95% ethanol-tetrahydrofuran (2:1, 15 ml). The reaction mixture was stirred at room temperature for 18 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 20:1) gave **6b** (34 mg, 80%) as a white solid: mp 54-55°C; IR (KBr) 2975, 1625, 1570, 1405, 1370 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.53 (m, 1 H), 7.39-7.04 (m, 3 H), 6.81 (d, 1 H, *J* = 2.7Hz), 6.51 (d, 1 H, *J* = 2.7 Hz), 4.25 (m, 1 H), 1.56 (d, 6 H, *J*= 6.0 Hz); MS *m/z* (relative intensity) 199 (M^+, 100); HRMS calcd $C_{13}H_{13}NO$ 199.0998, found 199.0997.

***N*-Benzylbenzofuro[2,3-*c*]pyrrole (6c)**. To a solution of benzylamine (102 mg, 0.95 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **16** (165 mg, 0.43 mmol) in 95% ethanol-tetrahydrofuran (1:1, 6 ml). The reaction mixture was stirred at room temperature for 22 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 20:1) gave **6c** (84.5 mg, 79%) as a white solid: mp 88-89°C; IR (KBr) 3025, 1630, 1580, 1395, 1198cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 1 H, *J* = 7.4Hz), 7.41 (d, 1 H, *J* = 7.4 Hz), 7.36-7.15 (m, 7 H), 6.85 (d, 1 H, *J* = 1.4 Hz), 6.57 (d, 1 H, *J* = 1.4 Hz), 5.16 (s, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 161.40 (s), 150.50 (s), 138.01 (s), 128.90 (d, 2c), 127.91 (d), 127.12 (d, 2c), 124.50 (d), 122.73 (s), 122.20 (d), 120.59 (d), 115.09 (s), 111.61 (d), 108.19 (d),

97.40 (d), 54.81 (t); MS *m/z* (relative intensity) 247(M^+, 100); HRMS calcd $C_{17}H_{13}NO$ 247.0998, found 247.0982.

***N*-Phenylbenzofuro[2,3-*c*]pyrrole (6d).** To a solution of aniline (88.7 mg, 0.95 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **16** (165 mg, 0.43 mmol) in 95% ethanol-tetrahydrofuran (1:1, 6 ml). The reaction mixture was stirred and heated at 65°C for 20 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 20:1) gave **6d** (39.6 mg, 17%). IR (KBr) 3031, 1640, 1382, 1220, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67(d, 1 H, J = 7.5Hz), 7.45 (d, 4 H, J = 4.2 Hz), 7,39 (d, 1 H, J = 7.5 Hz), 7.27 (m, 2 H), 7.20 (m, 1 H), 7.20 (d, 1 H, J = 1.4Hz), 6.95 (d, 1 H, J = 1.4 Hz); MS *m/z* (relative intensity) 233 (M^+, 100); HRMS calcd $C_{16}H_{11}NO$ 233.0851, found 233.0840.

***N*-*p*-Tolylbenzofuro[2,3-*c*]pyrrole (6e).** To a solution of p-toluidine (98 mg, 0.91 mmol) in 95% ethanol (2 ml) was added dropwise a solution of **16** (134 mg, 0.35 mmol) in 95% ethanol (6 ml). The reaction mixture was stirred at room temperature for 34 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 20:1) gave **6e** (17.2 mg, 20%) as a yellow solid: mp 137-138°C; IR (KBr) 3008, 1645, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, 1 H, J = 6.8 Hz), 7.39 (d, 1 H, J = 7.8 Hz), 7.34 (d, 2 H, J = 6.8 Hz), 7.25 (m, 3 H), 7.20 (d, 1 H, J = 7.8 Hz), 7.16 (d, 1 H, J = 1.9Hz), 6.91 (d, 1 H, J = 1.9 Hz), 2.38 (s, 3 H); MS *m/z* (relative intensity) 247 (M^+, 100), 232 (31); HRMS calcd for $C_{17}H_{13}NO$ 247.1003, found 247.0997.

***N*-*tert*-Butoxycarbonylbenzofuro[2,3-*c*]pyrrole (18).** To a solution of **16** (78 mg, 0.21 mmol) in 95% ethanol (10 ml) was added dropwise 25% ammonia water (0.15 ml). The reaction mixture was stirred at room temperature for 52 h. After concentration, a solution of 4-dimethylaminopyridine (50 mg, 0.41 mmol), di-*tert*-butyl dicarbonate (134 mg, 0.61 mmol) in dry dichloromethane (10 ml) was added. The reaction mixture was stirred at room temperature for 2 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 5:1) gave **18** (12.6 mg, 25%) as a yellow oil: IR (neat) 2980, 1740, 1415, 1360, 1250, 1160 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.66 (dd, 1 H, J = 6.6, 1.5 Hz), 7.40-7.18 (m, 4 H), 7.04 (d, 1 H, J = 1.5 Hz), 1.65 (s, 9 H); MS *m/z* (relative intensity) 257 (M^+, 56), 201 (100), 157 (63); HRMS calcd for $C_{15}H_{15}NO_3$ 257.1053, found 257.1051.

Cycloadduct 19 of *N*-*tert*-butoxycarbonylbenzofuro[2,3-*c*]pyrrole (18) and Dimethyl Acetylenedicarboxylate. A solution of **18** (14 mg, 0.05 mmol) and dimethyl acetylenedicarboxylate (15.5 mg, 0.11 mmol) in benzene (5 ml) were refluxed for 9 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 7:1) gave **19** (17.8mg, 82%) as a yellow oil: IR (neat) 2945, 1770-1710, 1530, 1385, 1255 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.75 (s, 2 H), 7.30 (s, 2 H), 3.78 (s, 6 H), 3.69 (m, 2 H), 1.57 (s, 9 H); MS *m/z* (relative intensity) 399 (M^+, 24), 283 (50), 227 (32), 183 (100); HRMS calcd for $C_{21}H_{21}NO_7$ 399.1318, found 399.1330.

Cycloadduct 20 of *N*-isopropylbenzofuro[2,3-c]pyrrole (6b) and Dimethyl Acetylenedicarboxylate. A solution of **6b** (18 mg, 0.09 mmol) and dimethyl acetylenedicarboxylate (15.4 mg, 0.11 mmol) in benzene (5 ml) were stirred at room temperature for 60 h. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 5:1) gave **20** (22.9 mg, 75%) as a yellow oil: IR (neat) 1950, 1740, 1715, 1580, 1572, 1432 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.50-7.30 (m, 2 H), 7.28-7.08 (m, 2 H), 5.55 (d, 1 H, J = 0.2 Hz), 5.09 (d, 1 H, J = 0.2 Hz), 3.79 (s, 3 H), 3.72 (s, 3 H), 2.88 (m, 1 H), 1.10 (d, 6 H, J = 6.0 Hz); MS m/z (relative intensity) 341 (M^+, 90), 225 (100), 199 (70).

Dimethyl Dibenzofuran-2,3-dicarboxylate (22). To a solution of **20** (22 mg, 0.06 mmol) in dichloromethane (5 ml) was added dropwise a solution of *m*-chloroperbenzoic acid (15.3 mg, 0.07 mmol) in dichloromethane (3 ml). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was then washed with saturated sodium thiosulfate solution, water and brine. Concentration and silica gel flash column chromatography (hexane-ethyl acetate, 2:1) gave **22** (9.5 mg, 56%) as a yellow oil: IR (neat) 3100, 2900, 1720, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1 H), 7.98 (d, 1 H, J = 7.6 Hz), 7.88 (s, 1 H), 7.61 (d, 1 H, J = 8.3Hz), 7.54 (dd, 1 H, J = 8.3, 7.2 Hz), 7.40 (dd, 1 H, J = 7.6, 7.2 Hz), 3.9 (s, 6 H); MS m/z (relative intensity) 284 (M^+, 100), 253 (26), 236 (27); HRMS calcd for $C_{16}H_{12}O_5$ 284.0685, found 284.0684.

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5. Crystal data of **13**: $C_{21}H_{23}NO_9$: M=433.41, monoclinic, space group $P2_{1/c}$, a=9.819(7), b=8.906(4), c=23.503(7) Å, α=90°, β=91.72°, Z=4. 2712 Unique reflections were measured of which 892 were considered observed [I > 1.5 σ (I)]. The structure was solved by direct

method to an R value of 0.066. All calculations were performed with the NRCC-SDP package. The supplementary materials have been deposited at the Cambridge Crystallographic Data Center.

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