

# Synthesis of Bridged Heteroaromatic Compounds as Reference Standards for Coal Degradation Products

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The synthesis of 2-naphthyl 2'-dibenzothieryl ether, 1-(1'-naphthyl)-2-(4''-acridinyl)ethane and a series of naphthylethyldibenzothiophenes is reported.

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Since a major portion of coal and coal-derived products is aromatic and heteroaromatic in nature, there is much concern about potential environmental and health hazards stemming from the utilization of coal resources as alternative fuel sources. As a result our research efforts have focused on the synthesis of polycyclic aromatic thiophenes and related heterocycles occurring in coal-derived products [2a-z]. From a recently proposed structure for coal [3], Figure 1, one can observe a composite of simple to complex aromatic and heteroaromatic structures linked by a wide variety of bridging groups. Therefore, in this study we wish to report the synthesis of several aromatic and heteroaromatic-linked constituents of coal as reference compounds to aid in the identification of potential coal degradation products.

When 2-bromodibenzothiophene (**1**) was allowed to react under modified Ullmann conditions [4] in the presence of pyridine, potassium carbonate, and cuprous iodide, only a small amount (5.3%) of 2-naphthyl 2'-dibenzothieryl ether (**3**) was isolated (Scheme 1).

The naphthyldibenzothiethylene **4**, **5**, **6**, and **7** prepared as described [5] were hydrogenated in the presence of 10% Pd/C as the catalyst in benzene solution to yield the corresponding substituted ethanes **8**, **9**, **10**, and **11**. Thus 1-(1'-naphthyl)-2-(2''-dibenzothieryl)ethene (**4**) provided 1-(1'-naphthyl)-2-(2''-dibenzothieryl)ethane (**8**) in 55% yield. 1-(2'-Naphthyl)-2-(2''-dibenzothieryl)ethene (**5**) afforded 1-(2'-naphthyl)-2-(2''-dibenzothieryl)ethane (**9**) in 64% yield. 1-(1'-Naphthyl)-2-(4''-dibenzothieryl)ethene (**6**) gave 1-(1'-naphthyl)-2-(4''-dibenzothieryl)ethane (**10**) in

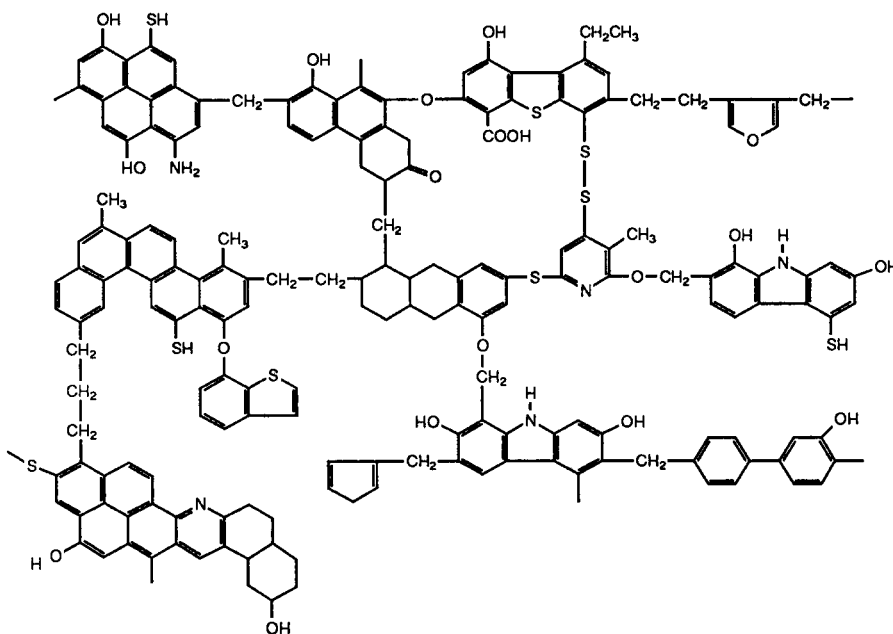
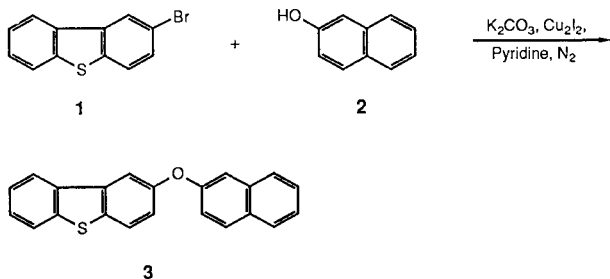
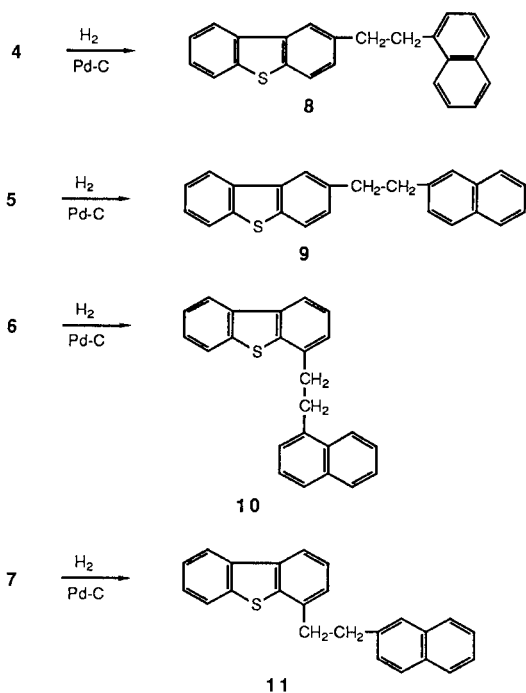


Figure 1

Scheme 1



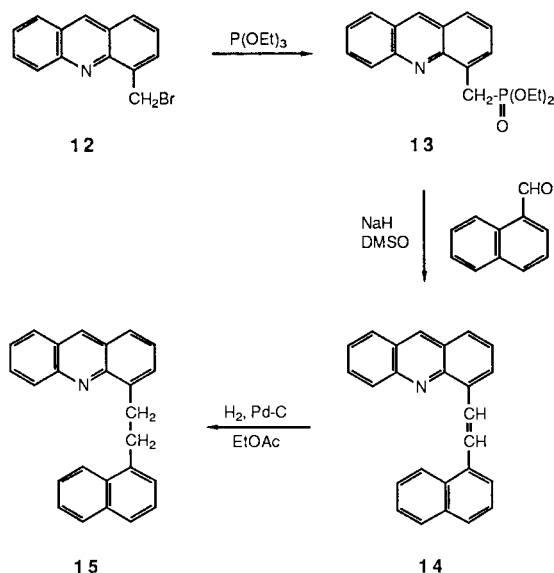
Scheme 2



80% yield. 1-(2'-Naphthyl)-2-(4"-dibenzothiényl)ethene (**7**) produced 1-(2'-naphthyl)-2-(4"-dibenzothiényl)ethane (**11**) in 33% yield. The above transformations are illustrated in Scheme 2.

4-Bromomethylacridine (**12**) [6] was allowed to react with triethyl phosphite to afford diethyl 4-acridinylmethyl phosphonate (**13**) in 55% yield. Treatment of **13** with sodium hydride in dimethyl sulfoxide solution gave the carbanion which when allowed to react with 1-naphthalene-carboxaldehyde gave 1-(1'-naphthyl)-2-(4"-acridinyl)ethene (**14**) in 66% yield. When **14** was subjected to catalytic hydrogenation in ethyl acetate solution using 10% Pd/C as the catalyst, 1-(1'-naphthyl)-2-(4"-acridinyl)ethane (**15**) was obtained in 4% yield, Scheme 3.

Scheme 3



These compounds are being used as analytical standards to search for **3**, **8**, **9**, **10**, **11**, and **15** in coal-derived products. The results of these analytical studies will be reported elsewhere.

## EXPERIMENTAL

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. The ir spectra were recorded on a Beckmann FT 1100 spectrophotometer as potassium bromide pellets. Routine <sup>1</sup>H nmr spectra were obtained on a JEOL FX-90Q spectrometer in the solvent indicated with TMS as the internal standard. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

### 2-Naphthyl 2'-Dibenzothiényl Ether (**3**).

2-Bromodibenzothiophene (**1**) (2.63 g, 10 mmoles) was added to a stirred mixture of 2-naphthol (**2**) (1.44 g, 10 mmoles) and powdered potassium carbonate (1.38 g, 10 mmoles) in pyridine (10 ml) under a nitrogen atmosphere. When the mixture began to reflux, copper(I) iodide (1.5 g) was added and heating and reflux was continued for 137 hours. The mixture was evaporated to dryness *in vacuo* and the residue was distilled in a Kugelrohr apparatus to give 1.93 g of crude product containing 2-bromodibenzothiophene (**1**). Recrystallization from ethanol yielded 1.1 g of 2-bromodibenzothiophene (**1**). The filtrate was evaporated to dryness and the residue was subjected to column chromatography with dichloromethane/petroleum ether (1:10) as the eluent. The fractions containing the product were pooled, evaporated to dryness, then recrystallized from ethanol to give **3** (100 mg, 5.3%) as colorless crystals, mp 162-163°; *R<sub>f</sub>* = 0.54 (chloroform/petroleum ether, 1:4); ir (potassium bromide):  $\nu$  max 3050, 1252, 1213  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{22}\text{H}_{14}\text{OS}$ : C, 80.95; H, 4.3; S, 9.8. Found: C, 80.9; H, 4.4; S, 9.7.

### 1-(1'-Naphthyl)-2-(2"-dibenzothiényl)ethene (**4**).

Compound **4** was obtained as described [5], mp 159-160°, softens *ca.* 138°, lit [5] mp 155-156°; <sup>1</sup>H nmr (deuteriochloroform): δ 7.18-7.72 (5H, m), 7.74-7.93 (6H, m), 8.07-8.32 (3H, m).

*Anal.* Calcd. for C<sub>24</sub>H<sub>16</sub>S: C, 85.7; H, 4.8; S, 9.5. Found: C, 85.9; H, 4.9; S, 9.3.

1-(2'-Naphthyl)-2-(2"-dibenzothienyl)ethene (**5**).

Compound **5** was obtained as described [5], mp 229-231°, lit [5] mp 208-209°; <sup>1</sup>H nmr (DMSO-d<sub>6</sub>): 100°, δ 7.34-7.58 (5H, m), 7.76-8.05 (7H, m), 8.35-8.46 (1H, m), 8.59 (1H, d, J = 0.7 Hz).

*Anal.* Calcd. for C<sub>24</sub>H<sub>16</sub>S: C, 85.7; H, 4.8; S, 9.5. Found: C, 85.9; H, 4.5; S, 9.4.

1-(1'-Naphthyl)-2-(4"-dibenzothienyl)ethene (**6**).

Compound **6** was obtained as described [5], mp 171-173°, lit [5] mp 181-182°; <sup>1</sup>H nmr (deuteriochloroform): δ 7.32-7.61 (7H, m), 7.71-7.97 (5H, m), 8.08-8.25 (4H, m).

1-(2'-Naphthyl)-2-(4"-dibenzothienyl)ethene (**7**).

Compound **7** was obtained as described [5], mp 146-148°, lit [5] mp 163-164°; <sup>1</sup>H nmr (deuteriochloroform): δ 7.39-7.54 (7H, m), 7.68-8.21 (9H, m).

1-(1'-Naphthyl)-2-(2"-dibenzothienyl)ethane (**8**).

This compound was prepared from 1-(1'-naphthyl)-2-(2"-dibenzothienyl)ethene (**4**) (2 g, 5.9 mmoles) in benzene (250 ml) and 10% Pd/C as the catalyst (0.1 g). It was allowed to stir at room temperature under a hydrogen atmosphere for 36 hours. Removal of excess solvent under reduced pressure resulted in a light yellow oil which solidified upon standing overnight at room temperature. The solid was dissolved in hot ethanol (*ca.* 100 ml), treated with charcoal, then allowed to cool to room temperature whereupon the precipitate was collected by filtration. This material was recrystallized from ethanol to afford **8** (1.1 g, 55%) as white branches, mp 99-100°; <sup>1</sup>H nmr (deuteriochloroform): δ 3.17-3.29 (2H, m), 3.38-3.47 (2H, m), 7.22-8.16 (14H, m).

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>S: C, 85.2; H, 5.4; S, 9.5. Found: C, 85.1; H, 5.45; S, 9.5.

1-(2'-Naphthyl)-2-(2"-dibenzothienyl)ethane (**9**).

This compound was prepared from 1-(2'-naphthyl)-2-(2"-dibenzothienyl)ethene (**5**), (1.5 g, 4.5 mmoles) in benzene (300 ml) and 10% Pd/C catalyst (0.1 g) in a manner similar to that described for the synthesis of **8** above. The crude isolated product was dissolved in hot ethanol (*ca.* 200 ml), treated with charcoal, allowed to cool to room temperature whereupon the precipitate was collected by filtration. This material was recrystallized (2x) from ethanol to afford **9** (1 g, 64%) as fine white clusters, mp 131-133°; <sup>1</sup>H nmr (deuteriochloroform): δ 3.19 (4H, s), 7.23-7.52 (6H, m), 7.65-7.89 (6H, m), 7.98-8.15 (2H, m).

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>S: C, 85.2; H, 5.4; S, 9.5. Found: C, 85.4; H, 5.15; S, 9.7.

1-(1'-Naphthyl)-2-(4"-dibenzothienyl)ethane (**10**).

This compound was prepared from 1-(1'-naphthyl)-2-(4"-dibenzothienyl)ethene (**6**) (1 g, 3 mmoles) in benzene (100 ml) and 10% Pd/C catalyst (0.1 g) in a manner similar to that described for the synthesis of **8**. Removal of excess solvent *in vacuo* resulted in a viscous liquid which solidified upon standing at room temperature. This solid was dissolved in hot ethanol (100 ml), treated with charcoal, then allowed to cool to room temperature. The precipitate was collected by filtration and dried to give **10** (0.8 g, 80%)

as short white branches, mp 115-116°; <sup>1</sup>H nmr (deuteriochloroform): δ 3.27-3.40 (2H, m), 3.48-3.62 (2H, m), 7.29-7.60 (8H, m), 7.65-8.01 (4H, m), 8.07-8.26 (2H, m).

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>S: C, 85.2; H, 5.4; S, 9.5. Found: C, 85.4; H, 5.6; S, 9.4.

1-(2'-Naphthyl)-2-(4"-dibenzothienyl)ethane (**11**).

This compound was prepared from 1-(2'-naphthyl)-2-(4"-dibenzothienyl)ethene (**7**) (1 g, 3 mmoles) in benzene (100 ml) and 10% Pd/C catalyst (0.1 g) in a manner similar to that described for the synthesis of **8** except that the mixture was stirred for 72 hours. Excess solvent was removed under reduced pressure to afford an off-white oil. This oil was dissolved in hot benzene:hexane (1:1, *ca.* 100 ml), treated with charcoal, then allowed to cool and stand overnight at -15°. The precipitate was collected by filtration and recrystallized from benzene:hexane (1:1, *ca.* 50 ml) to give, after standing 72 hours at room temperature, **11** (0.34 g, 33%) as thick irregular plates having a faint purple tint, mp 71-72°; <sup>1</sup>H nmr (deuteriochloroform): δ 3.25 (4H, s), 7.17-7.51 (7H, m), 7.64-8.16 (7H, m).

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>S: C, 85.2; H, 5.4; S, 9.5. Found: C, 85.0; H, 5.3; S, 9.2.

Diethyl 4-Acridinylmethyl Phosphonate (**13**).

4-Bromomethylacridine (**12**) [6] (3 g, 11 mmoles) and triethyl phosphite (6 ml, 37 mmoles) were heated under reflux for 4 hours. Excess triethyl phosphite was removed under reduced pressure and the residue was subjected to vacuum distillation whereupon **13** (2 g, 55% yield) was collected, bp 216-219° at 2 mm Hg. This product was utilized without further purification in the next reaction.

1-(1'-Naphthyl)-2-(4"-acridinyl)ethene (**14**).

A 60% oil dispersion of sodium hydride (0.2 g, prewashed with hexane) was added portionwise to a stirred solution of diethyl 4-acridinylmethyl phosphonate (**13**) (1.8 g, 5.5 mmoles) and 1-naphthalenecarboxaldehyde (1 g, 6.4 mmoles) in 30 ml of dimethyl sulfoxide at ice bath temperature under an atmosphere of nitrogen. The mixture was stirred for 20 minutes, then allowed to warm to room temperature and stirring was continued for 2 hours. The resulting mixture was poured onto crushed ice and water. The precipitate was collected and dried to give **14** (1.2 g, 66% yield) as a yellow solid, mp 186-187°; <sup>1</sup>H nmr (deuteriochloroform): δ 7.20-8.90 (17H, m).

*Anal.* Calcd. for C<sub>25</sub>H<sub>17</sub>N: C, 90.6; H, 5.2; N, 4.2. Found: C, 90.9; H, 5.3; N, 4.0.

1-(1'-Naphthyl)-2-(4"-acridinyl)ethane (**15**).

This compound was prepared from 1-(1'-naphthyl)-2-(4"-acridinyl)ethene (**14**), (0.3 g, 0.9 mmole) in ethyl acetate (200 ml) and 10% Pd/C catalyst (1 g) in a manner similar to that described for the synthesis of **8** except that the mixture was stirred for 4 days. Excess solvent was removed under reduced pressure and the residue chromatographed on an alumina column with hexane as the eluent to give **15** (11.8 mg, 4%) as pale green needles, mp 105-106°; <sup>1</sup>H nmr (deuteriochloroform): δ 3.54-3.88 (4H, m), 7.28-8.03 (12H, m), 8.40 (1H, d, J = 5.8 Hz), 8.70 (1H, s), 8.91 (1H, d, J = 5.8 Hz).

*Anal.* Calcd. for C<sub>25</sub>H<sub>19</sub>N: C, 90.1; H, 5.7; N, 4.2. Found: C, 89.9; H, 5.8; N, 4.2.

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