Supporting Information

Direct construction of 2,3-unsubstituted benzofurans and benzothiophenes via metal-free catalyzed intramolecular Friedel-Crafts reaction

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## 1. Screening of acids as the catalyst

**Table S1.** Screening of acids as the catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>T [ºC]</th>
<th>GC yield&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>H₂SO₄</td>
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<sup>a</sup> Reaction conditions: unless otherwise noted, all reactions were performed with 1d (1 mmol), catalyst (100 µL) in 2.0 mL toluene at 110 ºC for 12 h. <sup>b</sup> GC yield with TCE as internal standard. <sup>c</sup> 100 mg PPA was used.
2. GC Standard curve of 2d

**Table S2.** GC standard curve of 7-bromobenzofuran (2d) with TCE as internal reference.

GC Method: 50°C hold for 1 min, followed by a temperature increase of 10°C/min to 200°C, and 30°C/min to 300°C, hold for 2 min (total run time: 21.3 min). Retention time: TCE 5.72 min, 2d 12.1 min.

<table>
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<th>Mass of TCE (mg)</th>
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<th>Area of 2d</th>
<th>Area of TCE</th>
<th>( x = \frac{\text{Area of 2d}}{\text{Area of TCE}} )</th>
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**Figure S1:** The standard curve of 2d with TCE.
3. Mechanism study for the synthesis of 2d

3.1 Mechanism study for the synthesis of 2d by GC-MS

Taking 2d as an example, when the reaction mixture was stirred for 3 h at 130 °C, we took small amount of sample for testing, and the GC-MS spectra are shown below (Figure S2).

GC (TIC):

MS spectra:

Figure S2: GC-MS data of the reaction mixture for synthesis of 2d.
3.2 Further verification of the proposed mechanism

To a 50 mL round-bottomed flask was added 1-bromo-2-(2,2-diethoxyethoxy)benzene (1d) (1.4 g, 5 mmol), phosphoric acid (1.5 ml, 4.8 equiv) and chlorobenzene (15 mL). The mixture was stirred at 80 °C for 3 h. Then the mixture was cooled to room temperature, the organic layer was separated and concentrated under reduced pressure. The residue was finally purified by flash silica gel column chromatography (eluting with petroleum ether/ethyl acetate) to afford the desired intermediate I: 2-(2-bromophenoxy)acetaldehyde (360 mg, 1.67 mmol, 33% yield) as yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1H), 7.59 (dd, J = 7.9, 1.6 Hz, 1H), 7.29-7.25 (m, 1H), 6.92 (m, 1H), 6.79 (dd, J = 8.2, 1.3 Hz, 1H), 4.62 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 199.04, 154.23, 133.99, 128.75, 123.40, 113.67, 112.44, 73.64. GC-MS (EI) m/z 214. IR: 3069, 2826, 2717 (νC-H of aldehyde group), 1731 (νC=O), 1586, 1442, 1282, 1240, 1055, 1028, 740, 657 cm⁻¹.

To a 10 mL Schleck tube was added 2-(2-bromophenoxy)acetaldehyde (108 mg, 0.5 mmol) isolated above, phosphoric acid (150 µL, 4.8 equiv) and chlorobenzene (1.5 mL). The mixture was stirred at 130 °C for 8 h. The GC yield is 90%. As we predicted, intermediate product I can be converted into the target product 2d efficiently.
4. General information

All reagents were purchased from commercial suppliers and used without further purification unless otherwise specified. Thin layer chromatography (TLC) was performed using TLC silica gel 60 F254 glass plates. Silica gel 60 (200-300 mesh) was used for column chromatography. Proton nuclear magnetic resonance (\(^1\)H NMR) and carbon nuclear magnetic resonance (\(^{13}\)C NMR) spectra were measured on JEOL 400YH spectrometers. Chemical shifts for hydrogens are reported in parts per million (ppm, \(\delta\) scale) downfield from tetramethylsilane (\(\delta = 0\)), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). Detection and analysis of compounds by gas chromatography (Shimazu GC-2010 plus) and gas chromatography mass spectrometry were performed (Shimazu GC-2010 plus and Shimazu GCMS-TQ8040). HRMS spectra were determined on a Bruker Apex IV Fourier Transform Mass Spectrometer (EI) or Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (ESI).
5. General procedure A for the preparation of starting materials

To a mixture of phenol 1 (1.0 equiv.) and K₂CO₃ or KOH (2.0 equiv.) was added DMF, and it was stirred at 60 °C for 1 h. Then 2-bromo-acetaldehyde ethyl acetal (1.5 equiv.) was added. The mixture was stirred for about 6 h under reflux until the reaction was completed based on TLC analysis. It was cooled to room temperature and extracted with EtOAc (50 mL × 3). The combined organic layers were subsequently washed with 5% NaOH aqueous solution and water, dried over MgSO₄ and concentrated under reduced pressure. The residual crude product was finally purified by flash silica gel column chromatography (eluting with petroleum ether/ethyl acetate) to afford the desired 2-aryloxyacetaldehyde diethyl acetals.

(2,2-Diethoxyethoxy)benzene (1a)

The general procedure A was followed with phenol (1.0 g, 10.6 mmol), KOH (1.19 g, 21.2 mmol) and 2-bromoacetaldehyde diethyl acetal (3.13 g, 15.9 mmol) in DMF (15 mL). 1a was afforded as a colorless liquid (1.9 g, 9.05 mmol, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.23 (m, 2H), 6.97 – 6.89 (m, 3H), 4.84 (t, J = 5.2 Hz, 1H), 4.00 (d, J = 5.2 Hz, 2H), 3.80 – 3.72 (m, 2H), 3.67 – 3.59 (m, 2H), 1.24 (t, J = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 158.86, 129.51, 121.06, 114.73, 100.61, 68.54, 62.53, 15.43.

1-(2,2-Diethoxyethoxy)-2-fluorobenzene (1b)

The general procedure A was followed with 2-fluorophenol (5.0 g, 44.6 mmol), K₂CO₃ (12.3 g, 89.2 mmol) and 2-bromoacetaldehyde diethyl acetal (13.18 g, 66.9 mmol) in DMF (35 mL). 1b was afforded as a colorless liquid (7.98 g, 38 mmol, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.09 – 6.99 (m, 3H), 6.91 – 6.89 (m, 1H), 4.86 (t, J = 5.2 Hz, 1H), 4.07 (d, J = 5.2 Hz, 2H), 3.82 – 3.75 (m, 2H), 3.69 – 3.61 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 152.76 (d, J = 246 Hz), 146.68 (d, J = 11.1 Hz), 124.16 (d, J = 3.0 Hz), 121.46 (d, J = 7.1 Hz), 116.15 (d, J = 18.2 Hz), 110.19, 100.61, 70.16, 62.93, 15.41.

1-Chloro-2-(2,2-diethoxyethoxy)benzene (1c)

The general procedure A was followed with 2-chlorophenol (5.0 g, 38.9 mmol), K₂CO₃ (10.74 g, 77.8 mmol) and 2-bromoacetaldehyde diethyl acetal (11.5 g, 58.4 mmol) in DMF (35 mL). 1c was afforded as a colorless liquid (6.55 g, 26.7 mmol, 69%). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (dd, J = 7.9, 1.6 Hz, 1H), 7.29 – 7.20 (m, 1H), 6.97 – 6.90 (m, 2H), 4.90 (t, J = 5.2 Hz, 1H), 4.08 (d, J = 5.3 Hz, 2H), 3.87 – 3.80 (m, 2H), 3.75 – 3.68 (m, 2H), 1.28 (t, J = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 154.15, 130.15, 127.71, 122.89, 121.65, 113.78, 100.53, 70.04, 63.22, 15.24.

1-Bromo-2-(2,2-diethoxyethoxy)benzene (1d)

The general procedure A was followed with 2-bromophenol (10.50 g, 60.7 mmol), K₂CO₃ (16.80 g, 121.4 mmol) and 2-bromoacetaldehyde diethyl acetal (17.95 g, 91.1 mmol) in DMF (35 mL). 1d was afforded as a colorless liquid (14.05 g, 48.6 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (dd, J = 7.8, 1.7 Hz, 1H), 7.24 – 7.23 (m, 1H), 6.91 – 6.89 (m, 1H), 6.86 – 6.81 (m, 1H), 4.88 (t, J = 5.2 Hz, 1H), 4.05 (d, J = 5.2 Hz, 2H), 3.85 – 3.77 (m,

...
2H), 3.74 – 3.67 (m, 2H), 1.26 (t, J = 7.1 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 154.89, 113.20, 128.32, 122.02, 113.26, 112.05, 100.99, 69.96, 63.29, 15.25.

1-(2,2-Diethoxyethoxy)-2-iodobenzene (1e)

The general procedure A was followed with 2-iodophenol (5 g, 22.7 mmol), K2CO3 (6.27 g, 45.4 mmol) and 2-bromoacetaldehyde diethyl acetal (6.7 g, 34 mmol) in DMF (35 mL). 1e was afforded as a colorless liquid (4.74 g, 14.08 mmol, 62%). 1H NMR (400 MHz, CDCl3) δ 7.76 (dd, J = 7.8, 1.7 Hz, 1H), 7.28 – 7.25 (m, 1H), 6.81 (dd, J = 8.2, 1.2 Hz, 1H), 6.73 – 6.69 (m, 1H), 4.89 (t, J = 5.2 Hz, 1H), 4.03 (d, J = 5.2 Hz, 2H), 3.86 – 3.78 (m, 2H), 3.76 – 3.69 (m, 2H), 1.27 (t, J = 7.1 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 157.06, 139.31, 129.32, 122.66, 112.14, 100.57, 86.32, 70.00, 63.31, 15.29.

1-(Tert-butyl)-2-(2,2-diethoxyethoxy) benzene (1f)

The general procedure A was followed with 2-tert-butylphenol (2.9 g, 19.3 mmol), K2CO3 (2.2 g, 38.9 mmol) and 2-bromoacetaldehyde diethyl acetal (5.7 g, 28.9 mmol) in DMF (35 mL). 1f was afforded as a colorless liquid (2.33 g, 8.76 mmol, 45%). 1H NMR (400 MHz, CDCl3) δ 7.29 (dd, J = 7.7, 1.6 Hz, 1H), 7.18 – 7.14 (m, 1H), 6.92 – 6.88 (m, 1H), 6.84 (dd, J = 8.2, 1.1 Hz, 1H), 4.95 (t, J = 5.4 Hz, 1H), 4.02 (d, J = 5.4 Hz, 2H), 3.81 – 3.74 (m, 2H), 3.69 – 3.62 (m, 2H), 1.40 (s, 9H), 1.25 (t, J = 7.0 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 157.33, 138.17, 127.17, 126.80, 111.82, 100.63, 67.80, 62.28, 34.99, 29.86, 15.47. HRMS (EI) m/z calcd for C16H26O3 [M]+ 266.1882, found 266.1876.

1-(2,2-Diethoxyethoxy)-2-methylbenzene (1g)

The general procedure A was followed with o-cresol (5.0 g, 46.3 mmol), K2CO3 (12.8 g, 92.6 mmol) and 2-bromoacetaldehyde diethyl acetal (13.7 g, 69.5 mmol) in DMF (35 mL). 1g was afforded as a colorless liquid (6.7 g, 29.9 mmol, 65%). 1H NMR (400 MHz, CDCl3) δ 7.15 (t, J = 7.0 Hz, 2H), 6.88 (td, J = 7.4, 0.6 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 4.88 (t, J = 5.3 Hz, 1H), 4.03 (d, J = 5.3 Hz, 2H), 3.86 – 3.74 (m, 2H), 3.73 – 3.62 (m, 2H), 2.26 (s, 3H), 1.28 (t, J = 7.1 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 156.61, 130.55, 126.74, 126.66, 120.54, 111.01, 100.68, 68.72, 62.62, 16.11, 15.25.

2-(2,2-Diethoxyethoxy)-1,1'-biphenyl (1h)

The general procedure A was followed with 2-phenylphenol (4.0 g, 23.5 mmol), K2CO3 (6.5 g, 47 mmol) and 2-bromoacetaldehyde diethyl acetal (6.95 g, 35.3 mmol) in DMF (35 mL). 1h was afforded as a colorless liquid (5.5 g, 19.2 mmol, 82%). 1H NMR (400 MHz, CDCl3) δ 7.57 (dd, J = 5.2, 3.3 Hz, 2H), 7.39 – 7.26 (m, 5H), 7.05 – 7.01 (m, 1H), 6.96 (dd, J = 8.2, 0.7 Hz, 1H), 4.71 (t, J = 5.3 Hz, 1H), 3.98 (d, J = 5.2 Hz, 2H), 3.71 – 3.64 (m, 2H), 3.55 – 3.47 (m, 2H), 1.17 (t, J = 7.0 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 155.57, 138.51, 131.04, 130.99, 129.77, 128.72, 127.90, 126.93, 121.38, 112.65, 100.87, 69.43, 63.17, 15.42. HRMS (EI) m/z calcd for C16H12O3 [M]+ 286.1569, found 286.1633.
1-(2,2-Diethoxyethoxy)-4-nitrobenzene (Ii)

The general procedure A was followed with 4-nitrophenol (5.0 g, 36 mmol), \( \text{K}_2\text{CO}_3 \) (10 g, 72 mmol) and 2-bromoacetaldehyde diethyl acetal (10.64 g, 54 mmol) in DMF (70 mL). Ii was afforded as a pale-yellow liquid (3.7 g, 14.5 mmol, 40%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.22 – 8.15 (m, 2H), 7.02 – 6.97 (m, 2H), 4.86 (t, \( J = 5.1 \text{ Hz, 1H} \)), 4.10 (d, \( J = 5.2 \text{ Hz, 2H} \)), 3.85 – 3.74 (m, 2H), 3.70 – 3.60 (m, 2H), 1.25 (q, \( J = 7.0 \text{ Hz, 6H} \)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 163.60, 141.63, 125.81, 114.64, 100.20, 69.08, 63.02, 15.30.

Isopropyl 4-(2,2-diethoxyethoxy) benzoate (Ij)

The general procedure A was followed with isopropyl 4-hydroxybenzoate (5.0 g, 27.8 mmol), \( \text{K}_2\text{CO}_3 \) (7.67 g, 55.6 mmol) and 2-bromoacetaldehyde diethyl acetal (8.2 g, 41.7 mmol) in DMF (35 mL). Ij was afforded as a colorless liquid (6.5 g, 21.9 mmol, 79%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.00 – 7.96 (m, 2H), 6.94 – 6.92 (m, 2H), 5.25 – 5.19 (m, 1H), 4.85 (t, \( J = 5.2 \text{ Hz, 1H} \)), 4.05 (d, \( J = 5.1 \text{ Hz, 2H} \)), 3.81 – 3.74 (m, 2H), 3.68 – 3.60 (m, 2H), 1.35 (d, \( J = 8.0 \text{ Hz, 6H} \)), 1.25 (t, \( J = 7.1 \text{ Hz, 6H} \)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 165.89, 162.21, 131.54, 123.69, 114.18, 100.42, 68.60, 68.04, 62.87, 22.09, 15.42. HRMS (ESI) \( m/z \) calcd for C\(_{18}\)H\(_{24}\)O\(_5\) [M + H]\(^+\) 297.1702, found 297.1694.

1-Bromo-4-(2,2-diethoxyethoxy)benzene (Ik)

The general procedure A was followed with 4-bromophenol (3.0 g, 17.3 mmol), KOH (1.94 g, 34.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.1 g, 25.9 mmol) in DMF (30 mL). Ik was afforded as a colorless liquid (3.3 g, 11.4 mmol, 66%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.38 – 7.35 (m, 2H), 6.82 – 6.80 (m, 2H), 4.82 (t, \( J = 5.2 \text{ Hz, 1H} \)), 3.97 (d, \( J = 5.2 \text{ Hz, 2H} \)), 3.80 – 3.72 (m, 2H), 3.67 – 3.59 (m, 2H), 1.25 (t, \( J = 7.1 \text{ Hz, 6H} \)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 157.64, 132.15, 116.38, 113.09, 100.29, 68.63, 62.62, 15.28.

1-(2,2-Diethoxyethoxy)-4-methoxybenzene (Il)

The general procedure A was followed with 4-methoxyphenol (3.0 g, 24.2 mmol), KOH (2.7 g, 48.4 mmol) and 2-bromoacetaldehyde diethyl acetal (7.15 g, 36.3 mmol) in DMF (30 mL). Il was afforded as a colorless liquid (5.1 g, 21.3 mmol, 88%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.88 – 6.80 (m, 4H), 4.82 (t, \( J = 5.2 \text{ Hz, 1H} \)), 3.97 (d, \( J = 5.2 \text{ Hz, 2H} \)), 3.81 – 3.72 (m, 5H), 3.67 – 3.59 (m, 2H), 1.25 (t, \( J = 7.1 \text{ Hz, 6H} \)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 153.87, 152.65, 115.49, 114.41, 100.41, 69.10, 62.32, 55.48, 15.19.

1-(2,2-Diethoxyethoxy)naphthalene (Im)
The general procedure A was followed with 1-naphthol (5.0 g, 34.7 mmol), K₂CO₃ (9.6 g, 69.4 mmol) and 2-bromoacetaldehyde diethyl acetal (10.26 g, 52.1 mmol) in DMF (35 mL). **1m** was afforded as a colorless liquid (6.25 g, 24 mmol, 69%). **1H NMR** (400 MHz, CDCl₃) δ 8.31 – 8.29 (m, 1H), 7.82 – 7.79 (m, 1H), 7.52 – 7.44 (m, 3H), 7.37 (t, J = 8.0 Hz, 1H), 6.83 (dd, J = 7.2 Hz, 1H), 5.02 (t, J = 5.3 Hz, 1H), 4.20 (d, J = 5.2 Hz, 2H), 3.88 – 3.81 (m, 2H), 3.76 – 3.68 (m, 2H), 1.30 (t, J = 8.0 Hz, 6H). **13C NMR** (101 MHz, CDCl₃) δ 154.21, 134.40, 127.32, 126.28, 125.70, 125.55, 125.07, 121.92, 120.46, 104.80, 100.56, 68.77, 62.60, 15.30.

2-(2,2-Diethoxyethoxy)-1,4-dichlorobenzene (**1n**)![Image](Image)

The general procedure A was followed with 2,5-dichlorophenol (5.0 g, 30.67 mmol), K₂CO₃ (8.46 g, 61.34 mmol) and 2-bromoacetaldehyde diethyl acetal (9.06 g, 46 mmol) in DMF (35 mL). **1n** was afforded as a colorless liquid (6.2 g, 22.2 mmol, 72%). **1H NMR** (400 MHz, CDCl₃) δ 7.26 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 2.3 Hz, 1H), 6.88 (dd, J = 8.3, 2.3 Hz, 1H), 4.86 (t, J = 5.2 Hz, 1H), 4.03 (d, J = 5.2 Hz, 2H), 3.84 – 3.76 (m, 2H), 3.71 – 3.64 (m, 2H), 1.25 (t, J = 8.0 Hz, 6H). **13C NMR** (101 MHz, CDCl₃) δ 154.70, 133.06, 130.78, 121.69, 121.50, 114.23, 100.60, 70.27, 63.53, 15.43. HRMS (ESI) m/z calcd for C₁₂H₁₆Cl₂O₃ [M + Na]⁺ 301.0374, found 301.0374.

2-(2,2-Diethoxyethoxy)-1,4-dimethylbenzene (**1o**)![Image](Image)

The general procedure A was followed with 2, 5-dimethylphenol (5.0 g, 40.98 mmol), K₂CO₃ (11.3 g, 81.96 mmol) and 2-bromoacetaldehyde diethyl acetal (9.06 g, 46 mmol) in DMF (35 mL). **1o** was afforded as a colorless liquid (12.1 g, 61.5 mmol, 43%). **1H NMR** (400 MHz, CDCl₃) δ 7.00 (d, J = 7.5 Hz, 1H), 6.67 (d, J = 7.5 Hz, 1H), 6.45 (s, 1H), 4.85 (t, J = 5.3 Hz, 1H), 3.99 (d, J = 5.3 Hz, 2H), 3.82 – 3.74 (m, 2H), 3.69 – 3.61 (m, 2H), 2.30 (s, 3H), 2.19 (s, 3H), 1.25 (t, J = 6 Hz, 6H). **13C NMR** (101 MHz, CDCl₃) δ 156.49, 136.48, 130.30, 123.58, 121.07, 112.08, 100.74, 68.72, 62.67, 21.32, 15.77, 15.32.

1,2-Dichloro-3-(2,2-diethoxyethoxy) benzene (**1p**)![Image](Image)

The general procedure A was followed with 2,3-dichlorophenol (3.0 g, 18.4 mmol), Cs₂CO₃ (9.0 g, 27.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.4 g, 27.6 mmol) in DMF (35 mL). **1p** was afforded as a colorless liquid (3.78 g, 13.55 mmol, 74%). **1H NMR** (400 MHz, CDCl₃) δ 7.10 (t, J = 8.1 Hz, 1H), 7.05 (dd, J = 8.2, 1.5 Hz, 1H), 6.82 (dd, J = 8.1, 1.5 Hz, 1H), 4.85 (t, J = 5.2 Hz, 1H), 4.03 (d, J = 5.2 Hz, 2H), 3.82 – 3.75 (m, 2H), 3.70 – 3.63 (m, 2H), 1.23 (t, J = 7.1 Hz, 6H). **13C NMR** (101 MHz, CDCl₃) δ 154.70, 133.06, 130.78, 121.69, 121.50, 114.23, 100.60, 70.27, 63.53, 15.43. HRMS (EI) m/z calcd for C₁₂H₁₆Cl₂O₃ [M⁺] 278.0476, found 278.0472.

1,2-Dichloro-3-(2,2-diethoxyethoxy) benzene (**1q**)![Image](Image)

The general procedure A was followed with 2,5-dimethylphenol (5.0 g, 40.98 mmol), K₂CO₃ (11.3 g, 81.96 mmol) and 2-bromoacetaldehyde diethyl acetal (12.1 g, 61.5 mmol) in DMF (55 mL). **1q** was afforded as a colorless liquid (4.65 g, 19.54 mmol, 48%). **1H NMR** (400 MHz, CDCl₃) δ 6.94 – 6.92 (m, 2H), 6.70 (d, J = 8.1 Hz, 1H), 4.84 (t, J = 5.3 Hz, 1H), 3.88 (d, J = 5.3 Hz, 2H), 3.81 – 3.74 (m, 2H), 3.69 – 3.61 (m, 2H), 2.25 (s, 3H), 2.20 (s, 3H), 1.25 (t, J = 8 Hz, 6H). **13C NMR** (101 MHz, CDCl₃) δ 154.72, 131.60, 129.94, 127.03, 126.75, 111.29, 100.87, 69.10, 62.81, 20.56, 15.48. HRMS (EI) m/z calcd for C₁₄H₂₂O₃ [M⁺] 238.1569, found 238.1563.

2,4-Dibromo-1-(2,2-diethoxyethoxy) benzene (**1r**)
The general procedure A was followed with 2, 4-dibromophenol (3.0 g, 11.9 mmol), K₂CO₃ (3.28 g, 23.8 mmol) and 2-bromoacetaldehyde diethyl acetal (3.53 g, 17.9 mmol) in DMF (55 mL). 1r was afforded as a colorless liquid (2.7 g, 7.34 mmol, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 4.2 Hz, 1H), 7.35 (d, J = 8.7, 2.3 Hz, 1H), 6.79 (d, J = 8.8 Hz, 1H), 4.86 (t, J = 5.2 Hz, 1H), 4.02 (d, J = 5.2 Hz, 2H), 3.84 – 3.77 (m, 2H), 3.72 – 3.65 (m, 2H), 1.25 (t, J = 6.7 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 154.51, 135.57, 131.29, 114.67, 113.37, 113.17, 106.68, 70.41, 63.63, 15.46. HRMS (EI) m/z calcd for C₁₂H₁₆Br₂O₃ [M+2]⁺ 367.9466, found 367.9435.

1,4-Dibromo-2,5-bis(2,2-diethoxyethoxy)benzene (1s)

The general procedure A was followed with hydroquinone (10 g, 37.3 mmol), KOH (8.36 g, 149.2 mmol) and 2-bromoacetaldehyde diethyl acetal (3.53 g, 17.9 mmol) in DMSO (125 mL). 1s was afforded as a white solid (13.1 g, 26.2 mmol, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.14 (s, 2H), 4.84 (t, J = 5.2 Hz, 2H), 3.99 (d, J = 5.2 Hz, 4H), 3.83 – 3.75 (m, 4H), 3.71 –3.65 (m, 4H), 1.25 (t, J = 7.1 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃ ) δ 150.04, 118.85, 111.10, 100.48, 71.00, 63.17, 15.27.

1,5-Bis(2,2-diethoxyethoxy)naphthalene (1t)

The general procedure A was followed with 1,5-dihydroxynaphthalene (5.0 g, 31.25 mmol), KOH (7 g, 125 mmol) and 2-bromoacetaldehyde diethyl acetal (9.24 g, 46.9 mmol) in DMF (125 mL). 1t was afforded as a pale-yellow solid (2.04 g, 5.19 mmol, 17%). Mp 140.6 - 141.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 6.85 (d, J = 7.6 Hz, 2H), 5.01 (t, J = 5.2 Hz, 2H), 4.18 (d, J = 5.2 Hz, 4H), 3.89 - 3.79 (m, 4H), 1.29 (t, J = 7.0 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 154.08, 126.82, 125.08, 114.63, 105.67, 100.65, 68.94, 62.72, 15.36.

1-(2,2-Diethoxyethoxy)-3-fluorobenzene (1u)

The general procedure A was followed with 3-fluorophenol (3.6 g, 32.1 mmol), K₂CO₃ (6.8 g, 49 mmol) and 2-bromoacetaldehyde diethyl acetal (5.5 g, 24.1 mmol) in DMF (15 mL). 1u was afforded as a colorless liquid (5.5 g, 24.1 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.18 (m, 1H), 6.72 – 6.62 (m, 3H), 4.83 (t, J = 5.2 Hz, 1H), 3.99 (d, J = 5.2 Hz, 2H), 3.81 – 3.73 (m, 2H), 3.67 – 3.60 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 163.62 (d, J = 246 Hz), 160.00 (d, J = 10.8 Hz), 130.26 (d, J = 10.1 Hz), 110.38 (d, J = 2.5 Hz), 107.86 (d, J = 21.3 Hz), 102.52 (d, J = 25.0 Hz), 100.40, 68.77, 62.75, 15.39. HRMS (EI) m/z calcd for C₁₂H₁₁FO₃ [M⁺] 228.1162, found 228.1164.

1-Chloro-3-(2,2-diethoxyethoxy)benzene (1v)
The general procedure A was followed with 3-chlorophenol (5.0 g, 38.8 mmol), KOH (4.37 g, 78 mmol) and 2-bromoacetaldehyde diethyl acetal (11.5 g, 58.4 mmol) in N,N-dimethylacetamide (DMAC) (50 mL). **1v** was afforded as a colorless liquid (5.2 g, 21.2 mmol, 55%). 1H NMR (400 MHz, CDCl3) δ 7.21-7.16 (m, 1H), 6.96 – 6.91 (m, 2H), 6.83 – 6.78 (m, 1H), 4.82 (t, J = 5.2 Hz, 1H), 3.99 (d, J = 5.2 Hz, 2H), 3.81 – 3.70 (m, 2H), 3.69 – 3.58 (m, 2H), 1.25 (dd, J = 8.8, 5.3 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 159.25, 134.72, 130.10, 121.08, 115.10, 112.97, 100.27, 68.64, 62.60, 15.24.

1-Bromo-3-(2,2-diethoxyethoxy)benzene (1w)

The general procedure A was followed with 3-bromophenol (3.26 g, 18.8 mmol), KOH (2.11 g, 37.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.6 g, 28.2 mmol) in DMAC (35 mL). **1w** was afforded as a colorless liquid (3.8 g, 13.1 mmol, 70%). 1H NMR (400 MHz, CDCl3) δ 7.16 – 7.07 (m, 3H), 6.87 – 6.84 (m, 1H), 4.82 (t, J = 5.2 Hz, 1H), 3.98 (d, J = 5.2 Hz, 2H), 3.80 – 3.73 (m, 2H), 3.67 – 3.59 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 159.16, 130.35, 123.88, 122.54, 117.84, 113.34, 100.14, 68.48, 62.48, 15.18.

1-(Tert-butyl)-3-(2,2-diethoxyethoxy)benzene (**1x**)}

The general procedure A was followed with 3-tert-butylphenol (2.9 g, 19.3 mmol), KOH (2.16 g, 38.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.7 g, 28.95 mmol) in DMF (35 mL). **1x** was afforded as a colorless liquid (1.81 g, 6.80 mmol, 35%). 1H NMR (400 MHz, CDCl3) δ 7.22 – 7.18 (m, 1H), 6.99 – 6.97 (m, 2H), 6.73 – 6.70 (m, 1H), 4.84 (t, J = 5.2 Hz, 1H), 4.00 (d, J = 5.2 Hz, 2H), 3.80 – 3.72 (m, 2H), 3.67 – 3.60 (m, 2H), 1.29 (s, 9H), 1.25 (t, J = 7.1 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 158.53, 153.02, 129.03, 118.23, 117.74, 110.90, 100.63, 68.41, 62.52, 34.86, 31.43, 15.47. HRMS (EI) m/z calcd for C16H26O3 [M]+ 266.1882, found 266.1885.

1-(2,2-Diethoxyethyl)-3-methylbenzene (**1y**)}

The general procedure A was followed with 3-methylphenol (5 g, 46.3 mmol), KOH (5.2 g, 92.6 mmol) and 2-bromoacetaldehyde diethyl acetal (4.7 g, 28.95 mmol) in DMF (50 mL). **1y** was afforded as a colorless liquid (7.8 g, 35 mmol, 76%). 1H NMR (400 MHz, CDCl3) δ 7.13-7.16 (m, 1H), 6.70 – 6.76 (m, 3H), 4.82 (t, J = 5.2 Hz, 1H), 3.98 (d, J = 5.3 Hz, 2H), 3.80 – 3.68 (m, 2H), 3.68 – 3.56 (m, 2H), 3.09 (d, J = 5.5 Hz, 2H), 2.30 (s, 3H), 2.37 – 1.20 (m, 6H); 13C NMR (101 MHz, CDCl3) δ 158.50, 139.40, 129.13, 121.61, 115.58, 111.53, 100.43, 68.51, 62.48, 21.36, 15.32.

(2,2-Diethoxyethyl)(p-tolyl)sulfane (**3a**)}

The general procedure A was followed with 4-methylbenzenethiol (2.48 g, 20 mmol), K2CO3 (3.3 g, 24 mmol) and 2-bromoacetaldehyde diethyl acetal (4.7 g, 24 mmol) in DMF (50 mL). **3a** was afforded as a colorless liquid (4.08 g, 17 mmol, 85%). 1H NMR (400 MHz, CDCl3) δ 7.29 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 4.62 (t, J = 5.6 Hz, 1H), 3.70 – 3.62 (m, 2H), 3.57 – 3.50 (m, 2H), 3.09 (d, J = 5.5 Hz, 2H), 2.31 (s, 3H), 1.19 (t, J = 6.0 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 136.38, 132.70, 130.24, 129.78, 101.86, 62.17, 38.17, 21.13, 15.37.
The general procedure A was followed with 4-chlorothiophenol (4.3 g, 30 mmol), K₂CO₃ (3.3 g, 24 mmol) and 2-bromoacetaldehyde diethyl acetal (4.7 g, 24 mmol) in DMF (50 mL). 1H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 7.9 Hz, 1H), 7.18 – 7.06 (m, 3H), 4.66 (t, J = 5.6 Hz, 1H), 3.71 – 3.64 (m, 2H), 3.59 – 3.51 (m, 2H), 3.11 (d, J = 5.6 Hz, 2H), 2.39 (s, 3H), 1.21 (t, J = 7.0 Hz, 6H); 13C NMR (101 MHz, CDCl₃) δ 137.86, 135.71, 130.22, 128.52, 126.53, 125.99, 101.66, 62.11, 36.79, 20.57, 15.38.

(2-Chlorophenyl) (2,2-diethoxyethyl) sulfane (3d)₉

The general procedure A was followed with 2-chlorothiophenol (4.30 g, 30 mmol), K₂CO₃ (8.30 g, 60 mmol) and 2-bromoacetaldehyde diethyl acetal (8.9 g, 45 mmol) in DMF (50 mL). 3d was afforded as a colorless liquid (7.52 g, 28.8 mmol, 96%). 1H NMR (400 MHz, CDCl₃) δ 7.40 – 7.35 (m, 2H), 7.20 (td, J = 7.6, 1.4 Hz, 1H), 7.14 – 7.09 (m, 1H), 4.69 (t, J = 5.5 Hz, 1H), 3.73 – 3.65 (m, 2H), 3.60 – 3.52 (m, 2H), 3.15 (d, J = 5.5 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H); 13C NMR (101 MHz, CDCl₃) δ 135.77, 133.89, 129.79, 129.28, 127.16, 126.86, 101.74, 62.38, 36.45, 15.35.

(2-Bromophenyl)(2,2-diethoxyethyl)sulfane (3e)₁₁

The general procedure A was followed with 2-bromothiophenol (5.67 g, 30 mmol), K₂CO₃ (8.28 g, 60 mmol) and 2-bromoacetaldehyde diethyl acetal (8.9 g, 45 mmol) in DMF (50 mL). 3e was afforded as a colorless liquid (8.7 g, 28.5 mmol, 95%). 1H NMR (400 MHz, CDCl₃) δ 7.53 (dd, J = 8.0, 1.3 Hz, 1H), 7.36 (dd, J = 7.9, 1.5 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.06 – 6.99 (m, 1H), 4.70 (t, J = 5.6 Hz, 1H), 3.73 – 3.66 (m, 2H), 3.60 – 3.54 (m, 2H), 3.15 (d, J = 5.5 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H); 13C NMR (101 MHz, CDCl₃) δ 137.81, 133.05, 128.88, 127.77, 126.89, 123.90, 101.65, 62.39, 36.86, 15.34.
6. General procedure B for the preparation of benzofurans and benzothiophenes

To a 25 mL Schlenk tube was added compound 1 or 3 (1 mmol), phosphoric acid (300 µL, 4.8 equiv) and chlorobenzene (3 mL). The mixture was stirred at 130 °C for 12 h. Then the mixture was cooled to room temperature, the organic layer was separated and concentrated under reduced pressure. The residual was finally purified by flash silica gel column chromatography (eluting with petroleum ether/ethyl acetate) to afford the desired products.

Benzofuran (2a)\(^\text{12}\)

\[
\text{2a was afforded as a colorless liquid (104 mg, 0.88 mmol, 88%).}^{12}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 7.64 - 7.58 (m, 2H), 7.54 - 7.49 (m, 1H), 7.34 - 7.28 (m, 1H), 7.23 (dd, } J = 7.3, 1.0 \text{ Hz, 1H), 6.78 (dd, } J = 2.2, 0.8 \text{ Hz, 1H); }^{13}\text{C NMR (101 MHz, CDCl}_3\text{) }\delta 155.04, 144.99, 127.50, 124.32, 122.82, 121.28, 111.51, 106.65.
\]

7-Fluorobenzofuran (2b)\(^\text{13}\)

\[
\text{2b was afforded as a colorless liquid (67 mg, 0.49 mmol, 49%). Due to the relatively low boiling point of the compound, some products evaporated away with the chlorobenzene solvent, resulting in low yield. }^{1}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 7.66 (d, } J = 2.1 \text{ Hz, 1H), 7.37 (dd, } J = 7.8, 0.8 \text{ Hz, 1H), 7.19 - 7.14 (m, 1H), 7.06 - 7.01 (m, 1H), 6.83 - 6.81 (m, 1H); }^{13}\text{C NMR (101 MHz, CDCl}_3\text{) }\delta 148.42 (d, } J = 124 \text{ Hz), 145.86, 141.92, 130.96, 123.42, 116.88, 110.67, 107.12.
\]

7-Chlorobenzofuran (2c)\(^\text{1}\)

\[
\text{2c was afforded as a colorless liquid (108 mg, 0.71 mmol, 71%). }^{1}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 7.69 (d, } J = 2.2 \text{ Hz, 1H), 7.50 (dd, } J = 7.8, 0.9 \text{ Hz, 1H), 7.30 (dd, } J = 7.8, 0.9 \text{ Hz, 1H), 7.17 (t, } J = 7.8 \text{ Hz, 1H), 6.82 (d, } J = 2.1 \text{ Hz, 1H); }^{13}\text{C NMR (101 MHz, CDCl}_3\text{) }\delta 150.70, 145.64, 129.02, 124.42, 123.66, 119.74, 116.90, 107.11.
\]

7-Bromobenzofuran (2d)\(^\text{14}\)

\[
\text{2d was afforded as a colorless liquid (173 mg, 0.88 mmol, 88%). }^{1}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 7.70 (d, } J = 2.2 \text{ Hz, 1H), 7.56 - 7.46 (m, 2H), 7.13 (t, } J = 7.8 \text{ Hz, 1H), 6.85 (d, } J = 2.2 \text{ Hz, 1H); }^{13}\text{C NMR (101 MHz, CDCl}_3\text{) }\delta 152.05, 145.82, 128.71, 127.60, 124.18, 120.52, 107.42, 104.59.
\]

7-Iodobenzofuran (2e)\(^\text{3}\)

\[
\text{2e was afforded as a pale-yellow liquid (137 mg, 0.56 mmol, 56%). }^{1}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 7.69 (d, } J = 2.2 \text{ Hz, 1H), 7.66 (dd, } J = 7.7, 0.9 \text{ Hz, 1H), 7.55 (dd, } J = 7.7, 1.0 \text{ Hz, 1H), 7.00 (t, } J = 7.6 \text{ Hz, 1H), 6.88 (d, } J = 2.3 \text{ Hz, 1H); }^{13}\text{C NMR (101 MHz, CDCl}_3\text{) }\delta 155.30, 145.34, 133.39, 127.54, 124.66, 121.45, 107.79, 75.19.
\]

7-(Tert-butyl)benzofuran (2f)
2f was afforded as a colorless liquid (148 mg, 0.85 mmol, 85%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 2.2$ Hz, 1H), 7.46 (dd, $J = 7.0$, 2.0 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.75 (d, $J = 2.1$ Hz, 1H), 1.50 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.36, 144.06, 135.09, 127.99, 122.77, 120.90, 119.28, 106.49, 34.45, 29.95. HRMS (EI) $m/z$ calcd for C$_{12}$H$_{14}$O [M]+ 174.1045, found 174.1037.

7-Methylbenzofuran (2g)$^3$

2g was afforded as a colorless liquid (96 mg, 0.73 mmol, 73%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 2.2$ Hz, 1H), 7.45 – 7.40 (m, 1H), 7.16 – 7.05 (m, 2H), 6.75 (d, $J = 2.2$ Hz, 1H), 2.53 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.11, 144.67, 126.94, 125.14, 122.85, 121.73, 118.70, 106.86, 15.08.

7-Phenylbenzofuran (2h)$^3$

2h was afforded as a colorless liquid (121 mg, 0.62 mmol, 62%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 – 7.85 (m, 2H), 7.68 (d, $J = 2.2$ Hz, 1H), 7.58 (dd, $J = 7.7$, 1.2 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.46 (dd, $J = 7.5$, 1.1 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.34 – 7.30 (m, 1H), 6.83 (d, $J = 2.1$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.35, 145.14, 136.67, 128.78, 128.75, 128.33, 127.82, 125.76, 123.98, 123.46, 120.56, 106.93.

7-Nitrobenzofuran (2i)$^5$

2i was afforded as a pale-yellow liquid (64 mg, 0.39 mmol, 39%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.55 (d, $J = 2.0$ Hz, 1H), 8.25 (dd, $J = 9.2$, 2.4 Hz, 1H), 7.79 (d, $J = 2.4$ Hz, 1H), 7.60 (d, $J = 9.2$ Hz, 1H), 6.94 (dd, $J = 2.4$, 1.2 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.69, 147.98, 144.20, 127.80, 120.22, 117.86, 111.78, 107.59.

Isopropyl benzofuran-5-carboxylate (2j)$^7$

2j was afforded as a white solid (91 mg, 0.44 mmol, 44%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (d, $J = 1.6$ Hz, 1H), 8.03 (dd, $J = 8.7$, 1.8 Hz, 1H), 7.69 (d, $J = 2.2$ Hz, 1H), 7.53 (d, $J = 8.7$ Hz, 1H), 6.85 (dd, $J = 2.2$, 0.7 Hz, 1H), 5.31 – 5.25 (m, 1H), 1.40 (d, $J = 4$Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.42, 157.50, 146.29, 127.47, 126.13, 126.02, 123.75, 111.28, 107.26, 68.44, 22.17. HRMS (ESI) $m/z$ calcd for C$_{12}$H$_{12}$O$_3$ [M + H]$^+$ 205.0865, found 205.0864.

5-Bromobenzofuran (2k)$^1$

2k was afforded as a colorless liquid (185 mg, 0.94 mmol, 94%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 1.2$ Hz, 1H), 7.61 (d, $J = 2.2$ Hz, 1H), 7.38 (d, $J = 1.5$ Hz, 2H), 6.71 (d, $J = 2.2$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.66, 146.12, 129.39, 127.14, 123.81, 115.77, 112.82, 106.11.

5-Methoxybenzofuran (2l)$^1$

2l was afforded as a colorless liquid (70 mg, 0.47 mmol, 47%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 2.2$ Hz, 1H), 7.39 (d, $J = 9.0$ Hz, 1H), 7.06 (d, $J = 2.5$ Hz, 1H), 6.90 (dd, $J = 9.0$, 2.6 Hz, 1H), 6.71 (dd, $J = 2.2$, 0.7 Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.99, 149.99, 145.80, 127.86, 113.14, 111.88, 106.77, 103.57, 29.79.
Naphtho[1,2-h]furan (2m)<sup>1</sup>

![Naphtho[1,2-h]furan](image)

2m was afforded as a colorless liquid (138 mg, 0.82 mmol, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (d, <i>J</i> = 8.2 Hz, 1H), 7.93 (d, <i>J</i> = 8.2 Hz, 1H), 7.76 (d, <i>J</i> = 2.1 Hz, 1H), 7.66 (s, 2H), 7.31 – 7.46 (m, 1H), 7.51 – 7.46 (m, 1H), 6.90 (d, <i>J</i> = 2.0 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.71, 144.23, 131.56, 128.45, 126.45, 125.22, 123.55, 123.08, 121.64, 120.14, 119.87, 107.73.

4,7-Dichlorobenzofuran (2n)<sup>1</sup>

![4,7-Dichlorobenzofuran](image)

2n was afforded as a white solid (129 mg, 0.69 mmol, 69%), Mp 56.5-57.0 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, <i>J</i> = 2.2 Hz, 1H), 7.25 (d, <i>J</i> = 8.4 Hz, 1H), 7.19 (d, <i>J</i> = 8.3 Hz, 1H), 6.92 (d, <i>J</i> = 2.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.77, 146.21, 128.19, 124.92, 124.82, 123.53, 115.66, 106.19.

4,7-Dimethylbenzofuran (2o)<sup>6</sup>

![4,7-Dimethylbenzofuran](image)

2o was afforded as a colorless liquid (108 mg, 0.74 mmol, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, <i>J</i> = 2.2 Hz, 1H), 7.00 (d, <i>J</i> = 7.4 Hz, 1H), 6.94 (d, <i>J</i> = 7.4 Hz, 1H), 6.78 (d, <i>J</i> = 2.1 Hz, 1H), 2.50 (s, 3H), 2.49 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.69, 144.09, 128.31, 126.60, 124.88, 122.89, 118.78, 105.39, 18.34, 14.82.

6,7-Dichlorobenzofuran (2p)<sup>16</sup>

![6,7-Dichlorobenzofuran](image)

2p was afforded as a white solid (119 mg, 0.64 mmol, 64%), Mp 40.3-41.2 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d, <i>J</i> = 2.2 Hz, 1H), 7.43 (d, <i>J</i> = 8.3 Hz, 1H), 7.34 (d, <i>J</i> = 8.4 Hz, 1H), 6.81 (d, <i>J</i> = 2.2 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.67, 146.49, 128.74, 127.40, 125.02, 119.69, 116.26, 107.48. HRMS (EI) <i>m/z</i> calcd for C<sub>8</sub>H<sub>4</sub>Cl<sub>2</sub>O [M]+ 185.9639, found 185.9633.

5,7-Dimethylbenzofuran (2q)<sup>17</sup>

![5,7-Dimethylbenzofuran](image)

2q was afforded as a colorless liquid (124 mg, 0.85 mmol, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (d, <i>J</i> = 2.1 Hz, 1H), 7.20 (s, 1H), 6.91 (s, 1H), 6.67 (d, <i>J</i> = 2.2 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.44, 144.67, 132.13, 126.94, 126.45, 120.98, 118.31, 106.32, 21.22, 15.00.

5,7-Dibromobenzofuran (2r)<sup>16</sup>

![5,7-Dibromobenzofuran](image)

2r was afforded as a white solid (153 mg, 0.56 mmol, 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 (d, <i>J</i> = 2.2 Hz, 1H), 7.68 (d, <i>J</i> = 1.8 Hz, 1H), 7.60 (d, <i>J</i> = 1.8 Hz, 1H), 6.80 (d, <i>J</i> = 2.1 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.29, 146.88, 130.11, 129.73, 123.23, 116.06, 107.13, 105.06. HRMS (EI) <i>m/z</i> calcd for C<sub>8</sub>H<sub>4</sub>Br<sub>2</sub>O [M]+ 273.8629, found 273.8622.

4,8-Dibromobenzo[1,2-b:4,5-b']difuran (2s)<sup>7</sup>
2s was afforded as a yellow solid (177 mg, 0.56 mmol, 56%). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \ 7.76 \ (d, \ J = 2.2 \ Hz, \ 2H), \ 6.98 \ (d, \ J = 2.2 \ Hz, \ 2H); \ ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \ 148.94, \ 146.60, \ 127.19, \ 107.53, \ 93.94. \)

Naphtho[1,2-b:5,6-b']difuran (2t)

2t was afforded as a white solid (93 mg, 0.45 mmol, 45%). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \ 8.16 \ (d, \ J = 8.3 \ Hz, \ 2H), \ 7.79 - 7.77 \ (m, \ 4H), \ 6.94 \ (d, \ J = 1.9 \ Hz, \ 2H); \ ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \ 151.07, \ 143.98, \ 122.62, \ 120.22, \ 119.01, \ 105.70. \)

6- And 4-fluorobenzofuran (2u+2u')

A mixture of 2u and 2u' were afforded as a colorless liquid (78 mg, 0.57 mmol, 57%). Due to the relatively low boiling point of the compounds, some products evaporated away with the chlorobenzene solvent, resulting in low yield. 2u: 2u' = 83:17. 2u \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \ 7.60 \ (d, \ J = 2.3 \ Hz, \ 1H), \ 7.50 \ (dd, \ J = 8.7, \ 5.5 \ Hz, \ 1H), \ 7.21 \ (dd, \ J = 9.6, \ 2.3 \ Hz, \ 1H), \ 7.02 - 6.97 \ (m, \ 1H), \ 6.74 \ (dd, \ J = 2.0, \ 0.8 \ Hz, \ 1H). \)

2u' \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \ 7.59 \ (d, \ J = 2.2 \ Hz, \ 1H), \ 7.30 \ (d, \ J = 8.4Hz, \ 1H) \ 7.13 - 7.05 \ (m, \ 1H), \ 6.94 - 6.98 \ (m, \ 1H), \ 6.86 \ (dd, \ J = 2.2, \ 0.7 Hz, \ 1H). \)

2u \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \ 160.99 \ (d, \ J = 290 \ Hz), \ 155.05, \ 145.59 \ (d, \ J = 5.0Hz), \ 121.35 \ (d, \ J = 10.1Hz), \ 113.80, \ 111.12 \ (d, \ J = 24.2Hz), \ 106.37, \ 99.08 \ (d, \ J = 27.3Hz). \)

6- And 4-chlorobenzofuran (2v+2v')

A mixture of 2v and 2v' were afforded as a colorless liquid (124 mg, 0.81 mmol, 81%). 2v: 2v' = 66:34. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \ 7.65 \ (d, \ J = 2.2 \ Hz, \ 1H), \ 7.61 \ (2v, \ d, \ J = 2.2 \ Hz, \ 1H), \ 7.52 \ (2v, \ s, \ 1H), \ 7.50 \ (2v', \ d, \ J = 8.0 \ Hz, \ 2H), \ 7.44 - 7.40 \ (2v', \ m, \ 1H), \ 7.25 - 7.20 \ (2v, \ m, \ 2H), \ 6.87 \ (2v', \ dd, \ J = 2.2, \ 0.8 \ Hz, \ 1H), \ 6.75 \ (2v, \ dd, \ J = 2.1, \ 0.9 \ Hz, \ 1H). \)

\( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \ 145.71, \ 145.52, \ 134.27, \ 129.81, \ 128.71, \ 126.53, \ 124.95, \ 123.61, \ 122.79, \ 121.76, \ 110.11, \ 105.38. \)

6- And 4-bromobenzofuran (2w+2w')

A mixture of 2w and 2w' were afforded as a colorless liquid (169 mg, 0.86 mmol, 86%). 2w: 2w' = 57:47. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \ 7.68 \ (s, \ 1H), \ 7.66 \ (d, \ J = 2.2 \ Hz, \ 1H), \ 7.59 \ (d, \ J = 2.2 \ Hz, \ 1H), \ 7.47 - 7.45 \ (m, \ 1H), \ 7.45 - 7.43 \ (m, \ 1H), \ 7.39 \ (d, \ J = 7.7 \ Hz, \ 1H), \ 7.35 \ (dd, \ J = 8.3, \ 1.5 \ Hz, \ 1H), \ 7.16 \ (t, \ J = 8.0 \ Hz, \ 1H), \ 6.81 \ (2w', \ dd, \ J = 2.3, \ 0.9 \ Hz, \ 1H), \ 6.74 \ (2w, \ dd, \ J = 2.0, \ 1.0 \ Hz, \ 1H); \ ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \ 155.34, \ 154.81, \ 145.64, \ 145.47, \ 129.10, \ 126.56, \ 125.86, \ 125.32, \ 122.21, \ 117.64, \ 114.98, \ 114.35, \ 110.64, \ 106.94, \ 106.64. \)

6- And 4- (tert-butyl)benzofuran (2x+2x')

A mixture of 2x and 2x' were afforded as a colorless liquid (169 mg, 0.86 mmol, 86%). 2x: 2x' = 57:47. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \ 7.68 \ (s, \ 1H), \ 7.66 \ (d, \ J = 2.2 \ Hz, \ 1H), \ 7.59 \ (d, \ J = 2.2 \ Hz, \ 1H), \ 7.47 - 7.45 \ (m, \ 1H), \ 7.45 - 7.43 \ (m, \ 1H), \ 7.39 \ (d, \ J = 7.7 \ Hz, \ 1H), \ 7.35 \ (dd, \ J = 8.3, \ 1.5 \ Hz, \ 1H), \ 7.16 \ (t, \ J = 8.0 \ Hz, \ 1H), \ 6.81 \ (2x', \ dd, \ J = 2.3, \ 0.9 \ Hz, \ 1H), \ 6.74 \ (2x, \ dd, \ J = 2.0, \ 1.0 \ Hz, \ 1H); \ ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \ 155.34, \ 154.81, \ 145.64, \ 145.47, \ 129.10, \ 126.56, \ 125.86, \ 125.32, \ 122.21, \ 117.64, \ 114.98, \ 114.35, \ 110.64, \ 106.94, \ 106.64. \)
A mixture of 2x and 2x′ was afforded as a colorless liquid (143 mg, 0.82 mmol, 82%). \(2x:2x' = 84:16\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61 (2x′, d, \(J = 2.3\) Hz, 1H), 7.58 (2x, dd, \(J = 8.2\), 1.4 Hz, 1H), 7.23 (2x′, t, \(J = 8.0\) Hz, 1H), 7.16 (2x, dd, \(J = 7.5\), 1.1 Hz, 1H), 7.01 (2x′, dd, \(J = 2.3\), 0.9 Hz, 1H), 6.71 (2x, dd, \(J = 2.2\), 1.0 Hz, 1H), 1.47 (2x′, s, 9H), 1.38 (2x, s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 155.40, 148.27, 144.77, 143.54, 124.78, 124.00, 120.71, 120.63, 120.46, 118.78, 109.56, 108.11, 107.63, 106.57, 35.02, 31.79, 30.79.

6- And 4-methylbenzofuran (2y+2y′)\(^1\)

A mixture of 2y and 2y′ were afforded as a colorless liquid (102 mg, 0.77 mmol, 77%). \(2y:2y' = 64:36\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 (2y′, d, \(J = 2.2\) Hz, 1H), 7.55 (2y, d, \(J = 2.2\) Hz, 1H), 7.47 (2y′, d, \(J = 7.9\) Hz, 1H), 7.33 – 7.29 (m, 2H), 7.19 (2y′, t, \(J = 7.8\) Hz, 1H), 7.05 (dd, \(J = 13.2\), 7.7 Hz, 2H), 6.82 – 6.77 (2y′, m, 1H), 6.76 – 6.68 (2y, m, 1H), 2.53 (2y′, s, 3H), 2.47 (2y, s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 155.46, 154.82, 144.43, 134.51, 131.22, 127.29, 124.93, 124.24, 123.05, 120.68, 111.69, 108.89, 106.44, 105.27, 21.74, 18.73.

5-Methylbenzothiophene (4a)\(^2\)

\(4a\) was afforded as a colorless liquid (80 mg, 0.54 mmol, 54%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 (d, \(J = 8.2\) Hz, 1H), 7.60 (d, \(J = 6.6\) Hz, 1H), 7.38 (d, \(J = 5.4\) Hz, 1H), 7.24 (d, \(J = 5.4\) Hz, 1H), 7.16 (d, \(J = 8.2\) Hz, 1H), 2.46 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 140.07, 137.01, 133.96, 126.51, 126.11, 123.66, 123.17, 123.11.

7-Methylbenzothiophene (4c)\(^3\)

\(4c\) was afforded as a colorless liquid (80 mg, 0.50 mmol, 50%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (dd, \(J = 6.9\), 5.3 Hz, 2H), 7.48 (d, \(J = 5.5\) Hz, 1H), 7.29 (dd, \(J = 8.6\), 2.0 Hz, 1H), 7.25 (d, \(J = 5.5\) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 140.69, 137.81, 130.42, 128.27, 124.65, 123.40, 123.17, 123.11.

5-Chlorobenzothiophene (4b)\(^3\)

\(4b\) was afforded as a colorless liquid (80 mg, 0.50 mmol, 50%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, \(J = 7.9\) Hz, 1H), 7.41 (d, \(J = 5.4\) Hz, 1H), 7.35 (d, \(J = 5.4\) Hz, 1H), 7.29 (t, \(J = 7.5\) Hz, 1H), 7.14 (d, \(J = 7.2\) Hz, 1H), 2.57 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 140.12, 139.54, 132.14, 125.91, 124.70, 124.67, 124.51, 121.35, 20.56.

7-Chlorobenzothiophene (4d)\(^3\)

\(4d\) was afforded as a colorless liquid (123 mg, 0.73 mmol, 73%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.71 (dd, \(J = 7.3\), 1.6 Hz, 1H), 7.48 (d, \(J = 5.4\) Hz, 1H), 7.38 – 7.27 (m, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 141.14, 139.20, 128.06, 127.50, 125.51, 124.70, 123.99, 122.14.
7-Bromobenzothiophene (4e)\(^1\)

\[
\begin{array}{c}
\text{Br} \\
\text{S}
\end{array}
\]

was afforded as a colorless liquid (170 mg, 0.8 mmol, 80\%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 8.0\) Hz, 1H), 7.51 – 7.46 (m, 2H), 7.42 (d, \(J = 5.5\) Hz, 1H), 7.24 (t, \(J = 7.8\) Hz, 1H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 141.58, 140.51, 127.29, 127.12, 125.57, 124.83, 122.61, 115.94.
7. $^1$H and $^{13}$C NMR spectra and HRMS spectra

$^1$H NMR spectrum for 1a

$^{13}$C NMR spectrum for 1a
$^1$H NMR spectrum for 1b

$^{13}$C NMR spectrum for 1b
$^1$H NMR spectrum for 1c

$^{13}$C NMR spectrum for 1c
$^1$H NMR spectrum for 1d

$^{13}$C NMR spectrum for 1d
$^1$H NMR spectrum for 1e

$^{13}$C NMR spectrum for 1e
$^1$H NMR spectrum for 1f

$^{13}$C NMR spectrum for 1f
HRMS (EI) spectrum for 1f

$^{1}$H NMR spectrum for 1g
$^{13}$C NMR spectrum for 1g

$^1$H NMR spectrum for 1h
$^{13}$C NMR spectrum for 1h
HRMS (EI) spectrum for 1h

Elemental Composition Report

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
5 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

| Minimum: 70.00 | Maximum: 100.00 |
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| Calc. Mass | 286.1629 | 286.1629 | 286.1629 | 286.1629 |
| mDa | 0.4 | 1.2 | 7.5 | 1 |
| PPM | 200.0 | 100.0 | 50.0 |
| DBE | Score | Formula |
| | | C18 H24 N S |
$^{1}$H NMR spectrum for 1i

$^{13}$C NMR spectrum for 1i
$^1$H NMR spectrum for 1j

$^{13}$C NMR spectrum for 1j
HRMS (ESI) spectrum for 1j

Xevo G2 Q-TOF/YCA166#

11-19 12 (0.233) Cm (10:16-(2:6+23:27))

19-Mar-2018

Waters Xevo G2 Q-TOF/YCA166#

m/z

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0 100

163.0387 205.0861 209.0822 251.1270 279.0949 279.1589 297.1694 298.1728 316.1410 324.1296 353.1218 381.1205 397.1293 425.1172 447.2301 455.2169

1H NMR spectrum for 1k

13C NMR spectrum for 1k
$^1$H NMR spectrum for 1l

$^{13}$C NMR spectrum for 1l
$^1$H NMR spectrum for 1m

$^{13}$C NMR spectrum for 1m
$^{1}H$ NMR spectrum for 1n

$^{13}C$ NMR spectrum for 1n
HRMS (ESI) spectrum for 1n

Waters Xevo G2 Q-TOF/YCA166#
10-27 POS 12 (0.233) Cm (9:15-(2.5+24:40))

19-Mar-2018

1: TOF MS ES+

2.75e4

1H NMR spectrum for 1o
$^{13}$C NMR spectrum for 1o

$^1$H NMR spectrum for 1p
**13C NMR spectrum for 1p**

**HRMS (EI) spectrum for 1p**
Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 100.0 PPM / DBE, min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
22 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

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$^1$H NMR spectrum for 1q
$^{13}$C NMR spectrum for 1q
HRMS (EI) spectrum for 1q

$^{1}$H NMR spectrum for 1r
$^{13}$C NMR spectrum for 1r

HRMS (EI) spectrum for 1r

$^1$H NMR spectrum for 1s
$^{13}$C NMR spectrum for 1s
$^1$H NMR spectrum for 1t

$^{13}$C NMR spectrum for 1t
$^1$H NMR spectrum for 1u

$^{13}$C NMR spectrum for 1u
HRMS (EI) spectrum for 1u

Elemental Composition Report

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
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$^1$H NMR spectrum for 1v

13C NMR spectrum for 1v
$^1$H NMR spectrum for 1w

$^{13}$C NMR spectrum for 1w
$^1$H NMR spectrum for 1x

$^{13}$C NMR spectrum for 1x
HRMS (EI) spectrum for 1x

Elemental Composition Report

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
9 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)

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$^1$H NMR spectrum for 1y

$^{13}$C NMR spectrum for 1y
$^{1}$H NMR spectrum for 3a

$^{13}$C NMR spectrum for 3a
$^1$H NMR spectrum for 3b

$^{13}$C NMR spectrum for 3b
$^1$H NMR spectrum for 3c

$^{13}$C NMR spectrum for 3c
$^1$H NMR spectrum for 3d

$^{13}$C NMR spectrum for 3d
$^1$H NMR spectrum for 3e

$^{13}$C NMR spectrum for 3e
$^1$H NMR spectrum for 2a

$^{13}$C NMR spectrum for 2a
$^1$H NMR spectrum for 2b

13C NMR spectrum for 2b
$^1$H NMR spectrum for 2c

$^{13}$C NMR spectrum for 2c
$^1$H NMR spectrum for 2d

$^{13}$C NMR spectrum for 2d
\textbf{$^1$H NMR spectrum for 2e}

\textbf{$^{13}$C NMR spectrum for 2e}
$^1$H NMR spectrum for 2f

$^{13}$C NMR spectrum for 2f
HRMS (EI) spectrum for 2f

1H NMR spectrum for 2g

13C NMR spectrum for 2g
${}^1$H NMR spectrum for 2h

${}^{13}$C NMR spectrum for 2h
$^1$H NMR spectrum for 2i

$^{13}$C NMR spectrum for 2i
$^{1}H$ NMR spectrum for 2j

$^{13}C$ NMR spectrum for 2j
HRMS (ESI) spectrum for 2j

Waters Xevo G2 Q-TOF/YCA166#
11-19B 11 (0.216) Cm (9:18-2:5)

19-Mar-2018

m/z

1H NMR spectrum for 2k
$^{13}$C NMR spectrum for 2k
$^1$H NMR spectrum for 2l

$^{13}$C NMR spectrum for 2l
$^1$H NMR spectrum for 2m

$^{13}$C NMR spectrum for 2m
$^1$H NMR spectrum for 2n

$^{13}$C NMR spectrum for 2n
$^1$H NMR spectrum for 2o

$^{13}$C NMR spectrum for 2o
$^1$H NMR spectrum for 2p

HRMS (EI) spectrum for 2p
\(^1\)H NMR spectrum for 2q

\[^{13}\text{C} \text{NMR spectrum for 2q}\]
$^1$H NMR spectrum for 2r

$^{13}$C NMR spectrum for 2r
HRMS (EI) spectrum for 2r

^1H NMR spectrum for 2s
$^{13}$C NMR spectrum for 2s

$^1$H NMR spectrum for 2t
$^{13}$C NMR spectrum for 2t

$^1$H NMR spectrum for 2u and 2u'
$^{13}$C NMR spectrum for 2u and 2u'

$^1$H NMR spectrum for 2v and 2v'
$^{13}$C NMR spectrum for 2v and 2v′

$^1$H NMR spectrum for 2w and 2w′
13C NMR spectrum for 2w and 2w′

1H NMR spectrum for 2x and 2x′
$^{13}$C NMR spectrum for 2x and 2x′

$^1$H NMR spectrum for 2y and 2y′
$^{13}$C NMR spectrum for 2$y$ and 2$y'$
$^1$H NMR spectrum for 4a

$^{13}$C NMR spectrum for 4a
$^1$H NMR spectrum for 4b

$^{13}$C NMR spectrum for 4b
$^1$H NMR spectrum for 4c

$^{13}$C NMR spectrum for 4c
$^1$H NMR spectrum for 4d

$^{13}$C NMR spectrum for 4d
$^1$H NMR spectrum for 4e

$^{13}$C NMR spectrum for 4e
$^{1}$H NMR spectrum for aldehyde intermediate I

$^{13}$C NMR spectrum for aldehyde intermediate I
Infrared absorption spectrum of aldehyde intermediate I

8. REFERENCES


