Supporting Information

for

Halogenated volatiles from the fungus

*Geniculosporium* and the actinomycete

*Streptomyces chartreusis*

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Synthetic procedures, characterization data, mass spectra of all isomers of chlorodimethoxybenzene and dichlorodimethoxybenzene and ¹H, ¹³C, and DEPT spectra of all synthetic compounds
Synthetic procedures

General methods: Chemicals were purchased from Acros Organics (Geel, Belgium) or Sigma Aldrich Chemie GmbH (Steinheim, Germany). All non-aqueous reactions were performed under an inert atmosphere (N₂) in flame-dried flasks. Solvents were purified by distillation and dried according to standard methods. For general procedures, relative quantities of reagents are given in equivalents (equiv), and the amounts of solvents are indicated by the final concentrations of the starting material (set to 1.0 equiv). Thin-layer chromatography was performed with 0.2 mm precoated plastic sheets Polygram® Sil G/UV254 (Machery-Nagel). Column chromatography was carried out using Merck silica gel 60 (70–200 mesh). ¹H NMR and ¹³C NMR spectra were recorded on Bruker DRX-400 (400 MHz) and AV III-400 (400 MHz) spectrometers, and were referenced against TMS (δ = 0.00 ppm) for ¹H NMR and CDCl₃ (δ = 77.01 ppm) for ¹³C NMR. NMR data of all commercially available and synthetic chlorodimethoxybenzenes 4a–4f and dichlorodimethoxybenzenes 10a–10k are listed in Tables 2 and 3 (main text). ¹H NMR, ¹³C NMR, and DEPT spectra of synthetic compounds are shown in Figures S3–S53. UV spectra were obtained using a Varian Cary 100 Bio, and IR spectra were recorded with a Bruker Tensor 27 ATR.

General procedure for the methylation of phenols: Similar to the procedure by An et al. [1], to a solution of the catechol (13), resorcinol (8 or 14), or hydroquinone (crude 16, cf. below, or 18) (1.0 equiv) in acetone (0.1 M), potassium carbonate (5.0 equiv) was added and the mixture was stirred for 10 min. Methyl iodide (2.6 equiv) was added and the reaction mixture was stirred under reflux for 16 h. After cooling to room temperature water was added and the mixture was extracted three times with diethyl ether. The combined organic extracts were dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the pure compounds 4c (from 8), 10b (from 13), 10h (from 14), 10i (from crude 16), and 10k (from 18).

2-Chloro-1,3-dimethoxybenzene (4c): Pale yellow solid (76 mg, 0.44 mmol, 88%). TLC (hexane/ethyl acetate 10:1) Rᵣ 0.38; IR (ATR) ʋ 3011 (w), 2966 (w), 2947 (w), 2840 (w), 1594 (m), 1472 (m), 1435 (m), 1299 (m), 1253 (m), 1191 (w), 1174 (w), 1099 (m), 1053 (m), 1025 (m), 849 (w), 764 (m), 709 (m), 654 (m), 597 (m); UV–vis λᵥmax (log ε) 280 (3.08), 274 (3.10), 230 (3.79) nm.

1,5-Dichloro-2,3-dimethoxybenzene (10b): Colourless solid (50 mg, 0.24 mmol, 80%). TLC (hexane/ethyl acetate 10:1) Rᵣ 0.55; IR (ATR) ʋ 3089 cm⁻¹ (w), 3005 (w), 2967 (w), 2939 (w), 2831 (w), 1572 (m), 1480 (m), 1425 (m), 1399 (m), 1292 (m), 1263 (m), 1229 (m), 1171 (m), 1102 (m), 1043 (m), 999 (m), 895 (m), 830 (m), 760 (m), 718 (m), 589 (m); UV–vis (CH₂Cl₂) λᵥmax (log ε) 286 (3.22), 280 (3.20), 231 (3.83) nm.

1,5-Dichloro-2,4-dimethoxybenzene (10h): Pale yellow solid (49 mg, 0.24 mmol, 80%). TLC (hexane/ethyl acetate 10:1) Rᵣ 0.37; IR (ATR) ʋ 2976 (w), 2946 (w), 2879 (w), 2847 (w), 1575 (m), 1494 (m), 1470 (m), 1455 (m), 1428 (m), 1373 (m), 1294
(m), 1231 (m), 1207 (m), 1087 (m), 1055 (m), 1020 (m), 860 (m), 803 (m), 741 (m), 579 (m) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 292 (3.59), 233 (3.89) nm.

2,3-Dichloro-1,4-dimethoxybenzene (10i): Pale yellow solid (1.03 g, 5.0 mmol, 13% over two steps from 15). TLC (hexane/ethyl acetate 10:1) \(R_f\) 0.42; IR (ATR) \(\tilde{\nu}\) 3094 (w), 2967 (w), 2946 (w), 2914 (w), 2873 (w), 2840 (w), 1591 (w), 1570 (w), 1479 (m), 1457 (m), 1406 (w), 1303 (w), 1262 (m), 1192 (w), 1116 (w), 1038 (s), 900 (w), 790 (s), 711 (w), 608 (m) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 296 (3.59), 229 (3.76) nm.

1,3-Dichloro-2,5-dimethoxybenzene (10k): Colourless solid (49 mg, 0.24 mmol, 48%). TLC (hexane/ethyl acetate 10:1) \(R_f\) 0.56; IR (ATR) \(\tilde{\nu}\) 3087 (w), 2992 (w), 2949 (w), 2903 (w), 2835 (w), 1704 (w), 1663 (w), 1610 (m), 1594 (m), 1559 (m), 1480 (s), 1420 (m), 1403 (m), 1306 (m), 1257 (m), 1222 (s), 1175 (m), 1074 (m), 1042 (s), 984 (s), 909 (w), 909 (m), 850 (m), 831 (m), 804 (s), 761 (s), 717 (m), 606 (m) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 292 (3.56), 287 (3.45), 230 (3.78) nm.

1-Chloro-2,3-dimethoxybenzene (4a): To a solution of veratrole (5) (1.38 g, 1.00 mmol, 1.0 equiv) in dry ether (2.00 mL), 1.6 M n-butyllithium in hexane (1.25 mL) was added slowly and the mixture was stirred at room temperature for 48 h [2]. The resulting solution of (2,3-dimethoxyphenyl)lithium was diluted with dry diethyl ether (12 mL), triethylamine (101 mg, 1.00 mmol, 1.0 equiv) was added, and the mixture was further stirred for 10 min. Trifluoromethanesulfonyl chloride (169 mg, 1.00 mmol, 1.0 equiv) was added dropwise to the mixture [3]. After stirring at room temperature for 1 h, the reaction was quenched by the addition of water. The aqueous phase was extracted three times with diethyl ether. The combined extracts were dried over MgSO\(_4\), concentrated in vacuo and purified by column chromatography on silica gel to afford 1-chloro-2,3-dimethoxybenzene (4a, 80 mg, 0.47 mmol, 47%) as a pale yellow oil. TLC (hexane/ethyl acetate 10:1) \(R_f\) 0.40; IR (ATR) \(\tilde{\nu}\) 3003 (w), 2936 (w), 2835 (w), 1582 (w), 1481 (m), 1460 (m), 1427 (m), 1295 (w), 1263 (m), 1237 (m), 1173 (w), 2253 (w), 1079 (w), 1041 (s), 1001 (s), 855 (m), 799 (w), 771 (m), 736 (m), 654 (w), 556 (w) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 280 (3.15), 273 (3.17), 231 (3.55) nm.

4-Chloro-1,2-dimethoxybenzene (4b): To a cooled solution (0 °C) of 3,4-dimethoxianiline (6) (3.10 g, 20.0 mmol, 1.0 equiv) in 6 M HCl (30 mL) was added a 2.5 M solution of NaNO\(_2\) (1.40 g, 20.0 mmol, 1.0 equiv) in H\(_2\)O (8 mL), resulting in solution A. In a separate flask CuSO\(_4\) (5.80 g, 26.7 mmol, 1.3 equiv) was dissolved in H\(_2\)O (25 mL) and NaCl (2.30 g, 40.0 mmol, 2.0 equiv) was added. To this solution was added Na\(_2\)SO\(_3\) (1.70 g, 13.4 mmol, 0.7 equiv) in H\(_2\)O (6 mL). The precipitate was filtered off, washed with H\(_2\)O, dissolved in concentrated HCl (11 mL) and cooled to 0 °C. Solution A was added dropwise and the mixture was stirred for 1 h at room temperature, followed by 30 min at 100 °C. After cooling to room temperature the mixture was extracted three times with EtOAc. The combined extracts were dried over MgSO\(_4\) and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel yielding 4b (2.10 g, 12.20 mmol, 61%) as colourless oil. TLC (hexane/ethyl acetate 10:1) \(R_f\) 0.22; IR (ATR) \(\tilde{\nu}\) 3003 (w), 2956 nm.
(w), 2908 (w), 1591 (m), 1500 (s), 1441 (m), 1402 (w), 1252 (s), 1226 (s), 1177 (m), 1131 (m), 1022 (s), 873 (m), 838 (m), 797 (m), 763 (m), 643 (m) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 283 (3.47), 235 (3.91) nm.

**General procedure for ipso-substitutions of chlorobenzenes to methoxybenzenes:** According to the method of Testaferri et al. [4], sodium methoxide (4.0 equiv) was added to a stirred solution of the tetrachlorobenzene 11 or 12 (1.0 equiv) in hexamethylphosphoramide (0.3 M). The reaction mixture was stirred at 120 °C for 3 h and then cooled to room temperature. At this stage the mixture contains some minor amounts of phenols that are subsequently methylated by the addition of methyl iodide (1.5 equiv). The mixture was stirred for 1 h at room temperature and then poured into 2 M HCl. The aqueous phase was extracted three times with diethyl ether. The combined organic layers were dried over MgSO\(_4\) and concentrated in vacuo. Column chromatography on silica gel yielded the target compounds 10a, 10c, and 10e (from 11), and 10f and 10g (from 12).

1,2-Dichloro-3,4-dimethoxybenzene (10a), 1,4-dichloro-2,3-dimethoxybenzene (10c), and 1,3-dichloro-2,4-dimethoxybenzene (10e): The crude product contained mainly monosubstitution products, but small amounts of disubstitution products could be isolated by rigorous purification via column chromatography. The yields were: 10a (40 mg, 0.19 mmol, 4%, pale yellow oil), 10c (100 mg, 0.48 mmol, 10%, colourless solid), and 10e (40 mg, 0.19 mmol, 4%, colourless oil).

10a: TLC (hexane/ethyl acetate 5:1) \(R_f\) 0.25; IR (ATR) \(\tilde{\nu}\) 3005 (w), 2939 (w), 2840 (w), 1579 (w), 1474 (m), 1431 (m), 1400 (m), 1291 (m), 1262 (m), 1169 (w), 1140 (w), 1043 (m), 1007 (m), 889 (w), 834 (m), 796 (m), 752 (w), 672 (m), 644 (w), 598 (w) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 288 (3.23), 283 (3.22), 230 (3.84).

10c: TLC (hexane/ethyl acetate 5:1) \(R_f\) 0.47; IR (ATR) \(\tilde{\nu}\) 3003 (w), 2973 (w), 2941 (w), 2876 (w), 1579 (w), 1459 (m), 1430 (m), 1403 (m), 1239 (m), 1152 (w), 1128 (m), 1004 (s), 865 (m), 797 (m), 645 (m), 627 (m) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 274 (2.60), 231 (3.87) nm.

10e: TLC (hexane/ethyl acetate 5:1) \(R_f\) 0.56; IR (ATR) \(\tilde{\nu}\) 3007 (w), 2968 (w), 2941 (w), 2873 (w), 2840 (w), 1579 (w), 1466 (m), 1433 (m), 1402 (m), 1294 (m), 1270 (w), 1227 (m), 1151 (w), 1081 (s), 1008 (m), 914 (m), 750 (m), 686 (m), 644 (w), 576 (w) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 288 (3.22), 283 (3.21), 230 (3.84).

2,5-Dichloro-1,3-dimethoxybenzene (10f) and 1,2-dichloro-3,5-dimethoxybenzene (10g): The yields were: 10f (120 mg, 0.58 mmol, 29%, colourless solid) and 10g (72 mg, 0.35 mmol, 17%, colourless solid).

10f: TLC (hexane/ethyl acetate 10:1) \(R_f\) 0.27; IR (ATR) \(\tilde{\nu}\) 3092 (w), 3032 (w), 2976 (w), 2942 (w), 2909 (w), 2839 (w), 1590 (m), 1567 (m), 1459 (m), 1439 (m), 1404 (m), 1315 (m), 1296 (m), 1230 (m), 1119 (m), 1061 (m), 914 (m), 869 (m), 820 (m), 669 (s), 633 (m), 582 (m) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 276 (3.01), 231 (3.90) nm.
10g: TLC (hexane/ethyl acetate 10:1) \( R_f \) 0.45; IR (ATR) \( \tilde{\nu} \) 3092 (w), 2983 (w), 2954 (w), 2939 (w), 2837 (w), 1594 (m), 1569 (m), 1463 (m), 1429 (m), 1410 (m), 1323 (m), 1274 (m), 1214 (m), 1185 (m), 1159 (m), 1095 (m), 1030 (m), 933 (m), 857 (m), 825 (m), 782 (m), 697 (s), 658 (m), 639 (m), 621 (m); UV–vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}} \) (log \( \varepsilon \)) 289 (3.42), 229 (3.91) nm.

2-Chloro-1,4-dimethoxybenzene (4f): Following the procedure of Kajigaeshi et al. [5], a solution of 1,4-dimethoxybenzene (9, 414 mg, 3.00 mmol, 1.0 equiv) in CH\(_2\)Cl\(_2\) was treated with Bn\((\text{Me})_3\text{N}^+\text{ICl}_4^-\) (1.30 g, 3.00 mmol, 1.0 equiv) and stirred overnight at room temperature. The reaction mixture was diluted with H\(_2\)O and extracted three times with EtOAc. The combined organic layers were dried over MgSO\(_4\) and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel yielding 4f (174 mg, 1.00 mmol, 34%) as yellow oil. TLC (hexane/ethyl acetate 20:1) \( R_f \) 0.31; IR (ATR) \( \tilde{\nu} \) 3003 (w), 2948 (w), 2836 (w), 1581 (w), 1496 (s), 1461 (m), 1438 (m), 1271 (m), 1213 (s), 1180 (m), 1039 (s), 882 (m), 797 (m), 735 (s) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}} \) (log \( \varepsilon \)) 294 (3.56), 230 (3.78) nm.

**General procedure for the bis-chlorination of dimethoxybenzenes:** A solution of the dimethoxybenzene 5 or 9 (1.0 equiv) in acetic acid (0.3 M) was treated with Bn\((\text{Me})_3\text{N}^+\text{ICl}_4^-\) (2.0 equiv) [5]. The mixture was stirred for 1 h at room temperature, diluted with H\(_2\)O, and extracted three times with EtOAc. The combined extracts were dried over MgSO\(_4\) and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield 10d (from 5) and 10j (from 9).

1,2-Dichloro-4,5-dimethoxybenzene (10d): Pale yellow oil (466 mg, 2.25 mmol, 45%). TLC (hexane/ethyl acetate 10:1) \( R_f \) 0.39; IR (ATR) \( \tilde{\nu} \) 3004 (w), 2966 (w), 2906 (w), 2839 (w), 1594 (m), 1503 (s), 1432 (s), 1362 (m), 1337 (m), 1253 (s), 1210 (s), 1178 (s), 1131 (s), 1025 (s), 919 (s), 838 (s), 793 (s), 676 (s) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}} \) (log \( \varepsilon \)) 290 (3.51), 235 (3.91) nm.

1,4-Dichloro-2,5-dimethoxybenzene (10j): Colourless oil (118 mg, 0.57 mmol, 38%). TLC (hexane/ethyl acetate 20:1) \( R_f \) 0.30; IR (ATR) \( \tilde{\nu} \) 3029 (w), 2909 (w), 1501 (s), 1481 (m), 1439 (s), 1367 (m), 1279 (m), 1213 (s), 1187 (m), 1079 (s), 1025 (s), 858 (s), 775 (s) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}} \) (log \( \varepsilon \)) 299 (3.69), 230 (3.90) nm.

2,3-Dichlorohydroquinone (16): To a solution of 1,4-benzoquinone (15, 4.32 g, 40.0 mmol, 1.0 equiv) in dry ether (35 mL), sulfuryl chloride (6.50 mL, 80.0 mmol, 2.0 equiv) was added and stirred for 16 h at room temperature. The mixture was cooled with ice and the dark brown precipitate was filtered off, washed with cold diethyl ether (10 mL), and dried in vacuo. A suspension of the obtained solid was treated with glacial AcOH (20 mL) and concentrated H\(_2\)SO\(_4\) (2 mL). The mixture was stirred for 24 h at 60 °C and then poured on ice, followed by extraction (3×) with diethyl ether. The collected organic layers were washed with brine, dried over MgSO\(_4\) and concentrated to yield a brown solid (3.10 g) containing 16 (GC–MS) that was used in the methylation step (cf. above) without further purification.
2,6-Dichlorobenzene-1,4-diol (18): To a solution of 2,6-dichloro-\(p\)-benzoquinone (17, 1.00 g, 5.70 mmol) in ethyl acetate (20 mL), phosphate buffer (10 mL, 10 mmol \(\text{Na}_2\text{HPO}_4\), 10 mmol \(\text{KH}_2\text{PO}_4\), pH 7.0) and L-ascorbic acid (4.0 g) were added. The mixture was shaken in a separatory funnel for 5 min. The mixture was extracted three times with ethyl acetate, the combined extracts were dried over MgSO\(_4\) and concentrated in vacuo to yield pure 2,6-dichlorobenzene-1,4-diol (18, 1.00 g, 5.60 mmol, 99%) as a colourless solid [6]. TLC (hexane/ethyl acetate 10:1) \(R_f\) 0.56. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.72 (s, 2H, 2 × CH), 4.86 (s, 2H, 2 × OH) ppm. 

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.9 (C\(_q\)), 143.5 (C\(_q\)), 123.9 (2 × C\(_q\)), 116.4 (2 × CH) ppm; IR (ATR) \(\tilde{\nu}\) 3384 cm\(^{-1}\) (br), 3075 (w), 2517 (m), 2415 (m), 2077 (w), 1791 (m), 1746 (w), 1687 (w), 1614 (w), 1577 (m), 1477 (s), 1430 (m), 1344 (m), 1275 (w), 1213 (m), 1112 (m), 1095 (m), 971 (s), 947 (s), 844 (m), 803 (s), 700 (w), 599 (w) cm\(^{-1}\); UV–vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 296 (3.58), 229 (3.49) nm. MS (EI, 70 eV) \(m/z\) (%): 178 (100) [M]+, 142 (12), 114 (59), 86 (41), 79 (44), 61 (16), 53 (48).

References

Mass spectra of chlorodimethoxybenzenes and dichlorodimethoxybenzenes

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Figure 1: Mass spectra of chlorodimethoxybenzenes 4a–4c.
Figure 1 (continued): Mass spectra of chlorodimethoxybenzenes 4d–4f.
Figure 2: Mass spectra of dichlorodimethoxybenzenes 10a–10c.
Figure 2 (continued): Mass spectra of dichlorodimethoxybenzenes 10d–10f.
Figure 2 (continued): Mass spectra of dichlorodimethoxybenzenes 10g–10i.
Figure 2 (continued): Mass spectra of dichlorodimethoxybenzenes 10j–10k.
NMR spectra of synthetic compounds

Figure 3: $^1$H NMR spectrum of compound 4a.

Figure 4: $^{13}$C NMR spectrum of compound 4a.
Figure 5: $^{13}$C DEPT spectrum of compound 4a.

Figure 6: $^1$H NMR spectrum of compound 4b.
Figure 7: $^{13}$C NMR spectrum of compound 4b.

Figure 8: $^{13}$C DEPT spectrum of compound 4b.
Figure 9: $^1$H NMR spectrum of compound 4c.

Figure 10: $^{13}$C NMR spectrum of compound 4c.
**Figure 11:** $^{13}$C DEPT spectrum of compound 4c.

**Figure 12:** $^1$H NMR spectrum of compound 4d.
Figure 13: $^{13}$C NMR spectrum of compound 4d.

Figure 14: $^{13}$C DEPT spectrum of compound 4d.
Figure 15: $^1$H NMR spectrum of compound 4e.

Figure 16: $^{13}$C NMR spectrum of compound 4e.
Figure 17: $^{13}$C DEPT spectrum of compound 4e.

Figure 18: $^1$H NMR spectrum of compound 4f.
Figure 19: $^{13}$C NMR spectrum of compound 4f.

Figure 20: $^{13}$C DEPT spectrum of compound 4f.
Figure 21: $^1$H NMR spectrum of compound 10a.

Figure 22: $^{13}$C NMR spectrum of compound 10a.
Figure 23: $^{13}$C DEPT spectrum of compound 10a.

Figure 24: $^1$H NMR spectrum of compound 10b.
Figure 25: $^{13}$C NMR spectrum of compound 10b.

Figure 26: $^{13}$C DEPT spectrum of compound 10b.
Figure 27: $^1$H NMR spectrum of compound 10c.

Figure 28: $^{13}$C NMR spectrum of compound 10c.
Figure 29: $^{13}$C DEPT spectrum of compound 10c.

Figure 30: $^1$H NMR spectrum of compound 10d.
Figure 31: $^{13}$C NMR spectrum of compound 10d.

Figure 32: $^{13}$C DEPT spectrum of compound 10d.
Figure 33: $^1$H NMR spectrum of compound 10e.

Figure 34: $^{13}$C NMR spectrum of compound 10e.
Figure 35: $^{13}$C DEPT spectrum of compound 10e.

Figure 36: $^1$H NMR spectrum of compound 10f.
Figure 37: $^{13}$C NMR spectrum of compound 10f.

Figure 38: $^{13}$C DEPT spectrum of compound 10f.
Figure 39: $^1$H NMR spectrum of compound 10g.

Figure 40: $^{13}$C NMR spectrum of compound 10g.
Figure 41: $^{13}$C DEPT spectrum of compound 10g.

Figure 42: $^1$H NMR spectrum of compound 10h.
Figure 43: $^{13}$C NMR spectrum of compound 10h.

Figure 44: $^{13}$C DEPT spectrum of compound 10h.
Figure 45: $^1$H NMR spectrum of compound 10i.

Figure 46: $^{13}$C NMR spectrum of compound 10i.
**Figure 47:** $^{13}$C DEPT spectrum of compound 10i.

**Figure 48:** $^1$H NMR spectrum of compound 10j.
Figure 49: $^{13}$C NMR spectrum of compound 10j.

Figure 50: $^{13}$C DEPT spectrum of compound 10j.
Figure 51: $^1$H NMR spectrum of compound 10k.

Figure 52: $^{13}$C NMR spectrum of compound 10a.
Figure 53: $^{13}$C DEPT spectrum of compound 10k.

Figure 54: $^1$H NMR spectrum of compound 18.
Figure 55: $^{13}$C NMR spectrum of compound 18.

Figure 56: $^{13}$C DEPT spectrum of compound 18.