

Supplementary Material

An Efficient Approach to Sulfate Metabolites of Polychlorinated Biphenyls

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1. TCE PCB/Phenol sulfate diesters

1.1. Sulfuric acid 4-bromo-2-chlorophenyl 2,2,2-trichloroethyl ester (2a)

White solid; mp: 58-60 °C; ^1H NMR (400 MHz, CDCl_3): δ /ppm 4.92 (s, 2H, CH_2), 7.39 (dd, 1H, $J = 8.8$ Hz, $J = 0.4$ Hz), 7.46 (dd, 1H, $J = 8.8$ Hz, $J = 2.3$ Hz), 7.65 (dd, 1H, $J = 2.3$ Hz, $J = 0.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ /ppm 80.8 (CH_2), 92.2 (CCl_3), 121.3, 124.0 (CH), 127.9, 131.4 (CH), 133.7 (CH), 145.1 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3092, 3019, 2966, 1472, 1424, 1187, 1001, 886 cm^{-1} . EI-MS m/z (relative intensity, %): 416 (9, $\text{C}_8\text{H}_5\text{BrCl}_4\text{O}_4\text{S}^{*+}$), 286 (8), 206 (80), 177 (22), 131 (11), 63 (20).

1.2. Sulfuric acid 2,6-dichlorophenyl 2,2,2-trichloroethyl ester (2b)

White solid; mp: 50-51 °C; ^1H NMR (400 MHz, CDCl_3): δ /ppm 5.03 (s, 2H, CH_2), 7.21 (dd, 1H, $J = 7.7$ Hz, $J = 8.6$ Hz), 7.39 (d, 2H, $J \sim 8.6$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ /ppm 80.8 (CH_2), 92.4 (CCl_3), 128.8 (CH), 129.5 ($2\times\text{CH}$ and $2\times\text{C}$), 143.4 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3085, 3017, 2964, 1442, 1423, 1203, 1005, 882 cm^{-1} . EI-MS m/z (relative intensity, %): 372 (9, $\text{C}_8\text{H}_5\text{Cl}_5\text{O}_4\text{S}^{*+}$), 162 (100), 131 (12), 73 (13), 63 (17).

1.3. Sulfuric acid biphenyl-4-yl 2,2,2-trichloroethyl ester (8a)

White solid; mp: 89-90 °C; ^1H NMR (400 MHz, CDCl_3): δ /ppm 4.86 (s, 2H, CH_2), 7.37 (m, 1H, $J \sim 7.7$ Hz), 7.41 (AA'XX' system, 2H, $J \sim 8.0$ Hz), 7.45 (AA'XX' system, 2H, $J \sim 8.0$ Hz), 7.54 (AA'XX' system, 2H, $J \sim 8.0$ Hz), 7.62 (AA'XX' system, 2H, $J \sim 8.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ /ppm 80.5 (CH_2), 92.5 (CCl_3), 121.3 ($2\times\text{CH}$), 127.2 ($2\times\text{CH}$), 127.9 (CH), 128.8 ($2\times\text{CH}$), 129.0 ($2\times\text{CH}$), 139.6, 141.2, 149.6 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3077, 2969, 1414,

1204, 1091, 989, 869, 845, 794 cm^{-1} . EI-MS m/z (relative intensity, %): 380 (25, $\text{C}_{14}\text{H}_{11}\text{Cl}_3\text{O}_4\text{S}^{+}$), 250 (15), 169 (100), 139 (14), 115 (50).

1.4. Sulfuric acid 4'-chloro-biphenyl-3-yl 2,2,2-trichloroethyl ester (8c)

White solid; mp: 79-80 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ/ppm 4.85 (s, 2H, CH_2), 7.34 (ddd, 1H, $J = 1.5$ Hz, $J = 2.5$ Hz, $J = 7.8$ Hz), 7.42 (AA'XX' system, 2H, $J \sim 8.7$ Hz), 7.49 (AA'XX' system, 2H, $J \sim 8.7$ Hz), 7.48-7.54 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 80.4 (CH_2), 92.3 (CCl_3), 119.6 (CH), 119.9 (CH), 126.4 (CH), 128.4 ($2\times\text{CH}$), 129.2 ($2\times\text{CH}$), 130.5 (CH), 134.5, 137.7, 142.5, 150.5 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3077, 3063, 3022, 2975, 1418, 1197, 991 cm^{-1} . EI-MS m/z (relative intensity, %): 414 (25, $\text{C}_{14}\text{H}_{10}\text{Cl}_4\text{O}_4\text{S}^{+}$), 284 (20), 217 (10), 204 (100), 175 (35), 149 (15), 139 (30).

1.5. Sulfuric acid 4'-chloro-biphenyl-2-yl 2,2,2-trichloroethyl ester (8d)

White solid; mp: 70-71 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ/ppm 4.22 (s, 2H, CH_2), 7.41-7.47 (m, 7H), 7.56 (ddd, 1H, $J = 0.9$ Hz, $J = 1.2$ Hz, $J = 7.5$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 79.9 (CH_2), 92.3 (CCl_3), 122.1 (CH), 128.1 (CH), 128.9 ($2\times\text{CH}$), 129.5 (CH), 130.8 ($2\times\text{CH}$), 131.5 (CH), 133.9, 134.6, 134.7, 147.0 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3070, 3031, 2960, 1474, 1423, 1208, 1159, 1090, 1009, 884, 835 cm^{-1} . EI-MS m/z (relative intensity, %): 414 (29, $\text{C}_{14}\text{H}_{10}\text{Cl}_4\text{O}_4\text{S}^{+}$), 284 (15), 203 (50), 168 (100), 139 (30).

1.6. Sulfuric acid 2',5'-dichloro-biphenyl-4-yl 2,2,2-trichloroethyl ester (8e)

White solid; mp: 89-90 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ/ppm 4.85 (s, 2H, CH_2), 7.28 (dd, 1H, $J = 2.4$ Hz, $J = 8.5$ Hz), 7.32 (d, 1H, $J = 2.4$ Hz), 7.40 (d, 1H, $J = 8.5$ Hz), 7.43

(AA'XX' system, 2H, $J \sim 8.9$ Hz), 7.48 (AA'XX' system, 2H, $J \sim 8.9$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 80.5 (CH_2), 92.4 (CCl_3), 120.9 ($2\times\text{CH}$), 129.1 (CH), 130.8, 131.0 (CH), 131.1 ($2\times\text{CH}$), 131.2 (CH), 132.9, 137.9, 140.3, 149.9 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3075, 3010, 2954, 1459, 1423, 1213, 1181, 1149, 1098, 1026, 1005, 889 cm^{-1} . EI-MS m/z (relative intensity, %): 448 (25, $\text{C}_{14}\text{H}_9\text{Cl}_5\text{O}_4\text{S}^{+}$), 318 (35), 238 (100), 209 (35), 183 (16), 173 (20), 149 (17), 139 (35).

1.7. Sulfuric acid 2,4'-dichloro-biphenyl-4-yl 2,2,2-trichloroethyl ester (8f)

Viscous liquid; ^1H NMR (400 MHz, CDCl_3): δ/ppm 4.88 (s, 2H, CH_2), 7.32-7.42 (m, 6H), 7.51 (d, 1H, $J = 2.5$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 80.6 (CH_2), 92.3 (CCl_3), 119.7 (CH), 122.9 (CH), 128.5 ($2\times\text{CH}$), 130.6 ($2\times\text{CH}$), 132.2 (CH), 133.7, 134.5, 136.2, 139.3, 149.3 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3094, 2958, 1587, 1475, 1423, 1215, 1171, 1003 cm^{-1} . EI-MS m/z (relative intensity, %): 448 (30, $\text{C}_{14}\text{H}_9\text{Cl}_5\text{O}_4\text{S}^{+}$), 318 (36), 251 (12), 238 (100), 209 (38), 173 (18), 139 (45).

1.8. Sulfuric acid 3',4'-dichloro-biphenyl-4-yl 2,2,2-trichloroethyl ester (8g)

White solid; mp: 84-85 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ/ppm 4.87 (s, 2H, CH_2), 7.38 (dm, 1H, $J \sim 9.0$ Hz), 7.45 (AA'XX' system, 2H, $J \sim 8.5$ Hz), 7.52 (d, 1H, $J \sim 8.4$ Hz), 7.59 (AA'XX' system, 2H, $J \sim 8.6$ Hz), 7.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 80.5 (CH_2), 92.4 (CCl_3), 121.7 ($2\times\text{CH}$), 126.3 (CH), 128.7 ($2\times\text{CH}$), 129.0 (CH), 130.9 (CH), 132.3, 133.2, 138.7, 139.5, 150.0 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3070, 3007, 2955, 1478, 1417, 1375, 1217, 1141, 1087, 1013, 901, 881 cm^{-1} . EI-MS m/z (relative intensity, %): 448 (23, $\text{C}_{14}\text{H}_9\text{Cl}_5\text{O}_4\text{S}^{+}$), 318 (30), 238 (100), 209 (47), 183 (15), 173 (16), 139 (40).

1.9. Sulfuric acid 2,3',4'-trichloro-biphenyl-4-yl 2,2,2-trichloroethyl ester (8h)

Viscous liquid; ^1H NMR (400 MHz, CDCl_3): δ/ppm 4.90 (s, 2H, CH_2), 7.26 (dd, 1H, $J = 2.3$ Hz, $J = 8.4$ Hz), 7.36 (dd, 1H, $J = 2.3$ Hz, $J = 8.6$ Hz), 7.39 (dd, 1H, $J = 0.4$ Hz, $J = 8.6$ Hz), 7.50-7.50 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 80.5 (CH_2), 92.1 (CCl_3), 119.8 (CH), 122.9 (CH), 128.7 (CH), 130.2 (CH), 131.1 (CH), 132.1 (CH), 132.4, 132.5, 133.5, 137.5, 137.9, 149.3 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 2954, 2919, 1458, 1429, 1212, 1177, 1000, 919 cm^{-1} . EI-MS m/z (relative intensity, %): 482 (15, $\text{C}_{14}\text{H}_8\text{Cl}_6\text{O}_4\text{S}^{*+}$), 352 (31), 272 (100), 243 (33), 173 (47).

1.10. Sulfuric acid 2',3,5'-trichloro-biphenyl-4-yl 2,2,2-trichloroethyl ester (8i)

Viscous liquid; ^1H NMR (400 MHz, CDCl_3): δ/ppm 5.00 (s, 2H, CH_2), 7.29-7.32 (m, 2H), 7.40 (dd, 1H, $J = 2.2$ Hz, $J = 8.4$ Hz), 7.41 (d, 1H, $J \sim 9.0$ Hz), 7.56 (d, 1H, $J \sim 2.2$ Hz), 7.61 (d, 1H, $J \sim 8.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 80.6 (CH_2), 92.1 (CCl_3), 122.5 (CH), 126.4, 129.3 (CH), 129.5 (CH), 130.6, 130.8 (CH), 131.2 (CH), 131.8 (CH), 132.9, 138.8, 138.9, 145.4 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3072, 3024, 2961, 1460, 1424, 1218, 1190, 1002, 886 cm^{-1} . EI-MS m/z (relative intensity, %): 482 (23, $\text{C}_{14}\text{H}_8\text{Cl}_6\text{O}_4\text{S}^{*+}$), 352 (12), 272 (100), 243 (30), 173 (42).

1.11. Sulfuric acid 2',3,4'-trichloro-biphenyl-4-yl 2,2,2-trichloroethyl ester (8j)

White solid; mp: 38-40 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ/ppm 4.98 (s, 2H, CH_2), 7.25 (d, 1H, $J = 8.5$ Hz), 7.32 (dd, 1H, $J = 2.1$ Hz, $J = 8.5$ Hz), 7.39 (dd, 1H, $J = 2.1$ Hz, $J = 8.5$ Hz), 7.49 (d, 1H, $J = 2.1$ Hz), 7.55 (d, 1H, $J = 2.1$ Hz), 7.60 (d, 1H, $J = 8.5$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 80.6 (CH_2), 92.1 (CCl_3), 122.5 (CH), 126.3, 127.4 (CH), 129.3 (CH), 129.9 (CH), 131.7 (CH), 131.8 (CH), 132.9, 134.8, 136.0, 138.9, 145.3 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 2966,

2914, 1463, 1425, 1191, 1003 cm^{-1} . EI-MS m/z (relative intensity, %): 482 (15, $\text{C}_{14}\text{H}_8\text{Cl}_6\text{O}_4\text{S}^{++}$), 272 (100), 243 (36), 173 (43).

1.12. Sulfuric acid 2',3,5,5'-tetrachloro-biphenyl-4-yl 2,2,2-trichloroethyl ester (8k)

White solid; mp: 120-121 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ/ppm 5.07 (s, 2H, CH_2), 7.31-7.36 (m, 2H), 7.43 (m, 1H), 7.49 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 81.0 (CH_2), 92.4 (CCl_3), 129.4, 130.0 (CH), 130.3 ($2\times\text{CH}$), 130.7, 130.8 (CH), 131.4 (CH), 133.2, 138.1, 139.1 ($2\times\text{C}$), 143.2 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3096, 3018, 2967, 1454, 1425, 1196, 1010, 902, 873, 854 cm^{-1} . EI-MS m/z (relative intensity, %): 516 (13, $\text{C}_{14}\text{H}_7\text{Cl}_7\text{O}_4\text{S}^{++}$), 305 (85), 279 (23), 207 (37). HRMS (EI): found m/z 515.7855, calculated for ($\text{C}_{14}\text{H}_7(35)\text{Cl}_7\text{O}_4\text{S}^{++}$) 515.7885.

1.13. Sulfuric acid 2',3,4',5-tetrachloro-biphenyl-4-yl 2,2,2-trichloroethyl ester (8l)

White solid; mp: 94-95 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ/ppm 5.05 (s, 2H, CH_2), 7.24 (d, 1H, $J = 8.2$ Hz), 7.34 (dd, 1H, $J = 2.0$ Hz, $J = 8.2$ Hz), 7.46 (s, 2H), 7.52 (d, 1H, $J = 2.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 81.0 (CH_2), 92.4 (CCl_3), 127.6 (CH), 129.3, 130.2 (CH), 130.4 ($2\times\text{CH}$), 131.7 (CH), 133.1, 135.2, 135.5, 139.3 ($2\times\text{C}$), 143.0 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (film): 3066, 2971, 1450, 1199, 1009, 871, 841 cm^{-1} . EI-MS m/z (relative intensity, %): 516 (6, $\text{C}_{14}\text{H}_7\text{Cl}_7\text{O}_4\text{S}^{++}$), 305 (82), 279 (20), 207 (30). HRMS (EI): found m/z 515.7884, calculated for ($\text{C}_{14}\text{H}_7(35)\text{Cl}_7\text{O}_4\text{S}^{++}$) 515.7885.

2. PCB sulfate monoesters

2.1. Sulfuric acid mono-biphenyl-4-yl ester, ammonium salt (9a)

White solid; mp: 250 °C (dec.); ^1H NMR (400 MHz, CD_3OD): δ/ppm 7.30 (tm, 1H, $J = 7.5$ Hz), 7.35-7.43 (m, 4H), 7.55-7.58 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD): δ/ppm 122.8 (2 \times CH), 127.9 (2 \times CH), 128.2 (CH), 128.7 (2 \times CH), 129.8 (2 \times CH), 139.2, 141.2, 153.6 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (KBr): 3194, 3076, 1237, 1071 cm^{-1} . UV/Vis: $\lambda_{9\text{a,max}}(\text{MeOH}) = 252$ nm, $\epsilon_{9\text{a}} = 1.50 \times 10^4$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ($\lambda_{7\text{a,max}}(\text{MeOH}) = 260$ nm, $\epsilon_{7\text{a}} = 3.08 \times 10^4$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). HRMS (ESI, negative): $[\text{M-NH}_4]^-$ found m/z 249.0242, calculated for $\text{C}_{12}\text{H}_9\text{O}_4\text{S}$ 249.0222.

2.2. Sulfuric acid mono-(4'-chloro-biphenyl-3-yl) ester, ammonium salt (9c)

White solid; mp: 250 °C (dec.); ^1H NMR (400 MHz, CD_3OD): δ/ppm 7.28-7.31 (m, 1H), 7.39-7.41 (m, 2H), 7.42 (AA'XX' system, 2H, $J \sim 8.8$ Hz), 7.55-7.57 (m, 1H), 7.61 (AA'XX', 2H, $J \sim 8.8$ Hz). ^{13}C NMR (100 MHz, CD_3OD): δ/ppm 121.0 (CH), 121.7 (CH), 124.2 (CH), 129.6 (2 \times CH), 129.9 (2 \times CH), 130.7 (CH), 134.7, 140.6, 142.4, 154.7 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (KBr): 3231, 3084, 1251, 1212, 1066 cm^{-1} . UV/Vis: $\lambda_{9\text{c,max}}(\text{MeOH}) = 254$ nm, $\epsilon_{9\text{c}} = 2.05 \times 10^4$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ($\lambda_{7\text{c,max}}(\text{MeOH}) = 256$ nm, $\epsilon_{7\text{c}} = 2.00 \times 10^4$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). HRMS (ESI, negative): $[\text{M-NH}_4]^-$ found m/z 282.9836, calculated for $\text{C}_{12}\text{H}_8(35)\text{ClO}_4\text{S}$ 282.9832.

2.3. Sulfuric acid mono-(4'-chloro-biphenyl-2-yl) ester, ammonium salt (9d)

White solid; mp: 186-188 °C; ^1H NMR (400 MHz, CD_3OD): δ/ppm 7.21 (d"t", 1H, $J = 1.3$ Hz, $J = 7.6$ Hz), 7.30-7.35 (m, 2H), 7.37 (AA'XX' system, 2H, $J \sim 8.8$ Hz), 7.57 (AA'XX' system, 2H, $J \sim 8.8$ Hz), 7.71 (ddd, 1H, $J = 0.6$ Hz, $J = 1.3$ Hz, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, CD_3OD): δ/ppm 122.7 (CH), 126.0 (CH), 129.1 (2 \times CH), 129.5 (CH), 131.6 (CH), 132.2

(2×CH), 134.0, 134.4, 138.4, 151.1 (C_{Ar} -OSO₃). IR (KBr): 3180, 3072, 1254, 1046 cm⁻¹. UV/Vis: $\lambda_{9d,max}$ (MeOH) = 247 nm, ϵ_{9d} = 1.68×10⁴ L·mol⁻¹·cm⁻¹ ($\lambda_{7d,max}$ (MeOH) = 251 nm, ϵ_{7d} = 1.50×10⁴ L·mol⁻¹·cm⁻¹). HRMS (ESI, negative): [M-NH₄]⁻ found m/z 282.9825, calculated for C₁₂H₈(35)ClO₄S 282.9832.

2.4. Sulfuric acid mono-(2',5'-dichloro-biphenyl-4-yl) ester, ammonium salt (9e)

White solid; mp: 230 °C (dec.); ¹H NMR (400 MHz, CD₃OD): δ /ppm 7.33 (dd, 1H, J = 2.6 Hz, J = 8.6 Hz), 7.36 (dd, 1H, J = 2.6 Hz, J = 0.4 Hz), 7.39 (m, 4H), 7.46 (dd, 1H, J = 0.4 Hz, J = 8.6 Hz). ¹³C NMR (100 MHz, CD₃OD): δ /ppm 122.2 (2×CH), 129.7 (CH), 131.2 (2×CH), 132.1 (CH and C), 132.3 (CH), 133.9, 136.0, 143.0, 154.1 (C_{Ar} -OSO₃). IR (KBr): 3496, 3272, 1242, 1070, 1020 cm⁻¹. UV/Vis: $\lambda_{9e,max}$ (MeOH) = 250 nm, ϵ_{9e} = 1.03×10⁴ L·mol⁻¹·cm⁻¹ ($\lambda_{7e,max}$ (MeOH) = 263 nm, ϵ_{7e} = 1.49×10⁴ L·mol⁻¹·cm⁻¹). HRMS (ESI, negative): [M-NH₄]⁻ found m/z 316.9443, calculated for C₁₂H₇(35)Cl₂O₄S 316.9442.

2.5. Sulfuric acid mono-(2,4'-dichloro-biphenyl-4-yl) ester, ammonium salt (9f)

White solid; mp: 190-192 °C; ¹H NMR (400 MHz, CD₃OD): δ /ppm 7.30 (m, 2H), 7.34-7.43 (m, 4H), 7.47 (dd, 1H, J = 0.9 Hz, J = 1.7 Hz). ¹³C NMR (100 MHz, CD₃OD): δ /ppm 121.3 (CH), 123.7 (CH), 129.3 (2×CH), 132.1 (2×CH), 132.6 (CH), 133.3, 134.7, 137.0, 139.0, 154.2 (C_{Ar} -OSO₃). IR (KBr): 3240, 3072, 1263, 1212, 1054, 924, 811 cm⁻¹. UV/Vis: $\lambda_{9f,max}$ (MeOH) = 247 nm, ϵ_{9f} = 1.58×10⁴ L·mol⁻¹·cm⁻¹ ($\lambda_{7f,max}$ (MeOH) = 255 nm, ϵ_{7f} = 1.66×10⁴ L·mol⁻¹·cm⁻¹). HRMS (ESI, negative): [M-NH₄]⁻ found m/z 316.9452, calculated for C₁₂H₇(35)Cl₂O₄S 316.9442.

2.6. Sulfuric acid mono-(3',4'-dichloro-biphenyl-4-yl) ester, ammonium salt (9g)

White solid; mp: 230 °C (dec.); ^1H NMR (400 MHz, CD_3OD): δ/ppm 7.40 (AA'XX' system, 2H, $J \sim 9.0$ Hz), 7.51 (dd, 1H, $J = 2.0$ Hz, $J = 8.3$ Hz), 7.54 (dd, 1H, $J = 0.4$ Hz, $J = 8.3$ Hz), 7.57 (AA'XX' system, 2H, $J \sim 9.0$ Hz), 7.73 (dd, 1H, $J = 0.4$ Hz, $J = 2.0$ Hz). ^{13}C NMR (100 MHz, CD_3OD): δ/ppm 122.9 (2 \times CH), 127.6 (CH), 128.7 (2 \times CH), 129.7 (CH), 131.9 (CH), 132.1, 133.7, 136.3, 142.3, 154.3 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (KBr): 3222, 3075, 1256, 1057 cm^{-1} . UV/Vis: $\lambda_{9\text{g,max}}(\text{MeOH}) = 262$ nm, $\epsilon_{9\text{g}} = 2.56 \times 10^4$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ($\lambda_{7\text{g,max}}(\text{MeOH}) = 272$ nm, $\epsilon_{7\text{g}} = 2.32 \times 10^4$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). HRMS (ESI, negative): $[\text{M-NH}_4]^-$ found m/z 316.9451, calculated for $\text{C}_{12}\text{H}_7(35)\text{Cl}_2\text{O}_4\text{S}$ 316.9442.

2.7. Sulfuric acid mono-(2,3',4'-trichloro-biphenyl-4-yl) ester, ammonium salt (9h)

White solid; mp: 160-162 °C; ^1H NMR (400 MHz, CD_3OD): δ/ppm 7.30-7.35 (m, 3H), 7.50 (m, 1H), 7.54-7.58 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ/ppm 121.4 (CH), 123.7 (CH), 130.5 (CH), 131.3 (CH), 132.5 (CH), 132.5 (CH), 132.7, 133.0, 133.3, 135.6, 140.6, 154.5 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (KBr): 3240, 3086, 1269, 1256, 1209, 1056 cm^{-1} . HRMS (ESI, negative): $[\text{M-NH}_4]^-$ found m/z 350.9053, calculated for $\text{C}_{12}\text{H}_6(35)\text{Cl}_3\text{O}_4\text{S}$ 350.9052.

2.8. Sulfuric acid mono-(2',3,5'-trichloro-biphenyl-4-yl) ester, ammonium salt (9i)

White solid; mp: 200 °C (dec.); ^1H NMR (400 MHz, CD_3OD): δ/ppm 7.31 (dd, 1H, $J = 2.2$ Hz, $J = 8.5$ Hz), 7.35 (dd, 1H, $J = 2.2$ Hz, $J = 8.5$ Hz), 7.38 (dd, 1H, $J = 0.4$ Hz, $J = 2.2$ Hz), 7.47 (d, 1H, $J = 2.2$ Hz), 7.48 (dd, 1H, $J = 0.4$ Hz, $J \sim 8.0$ Hz), 7.71 (dd, 1H, $J = 0.3$ Hz, $J = 8.5$ Hz). ^{13}C NMR (100 MHz, CD_3OD): δ/ppm 123.4 (CH), 127.4, 129.6 (CH), 130.2 (CH), 131.9 (CH), 132.0, 132.1 (CH), 132.5 (CH), 134.0, 136.7, 141.7, 150.0 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (KBr): 3495,

3270, 1246, 1051 cm^{-1} . UV/Vis: $\lambda_{9i,\text{max}}(\text{MeOH}) = 249 \text{ nm}$, $\epsilon_{9i} = 1.17 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$
($\lambda_{7i,\text{max}}(\text{MeOH}) = 259 \text{ nm}$, $\epsilon_{7i} = 1.11 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). HRMS (ESI, negative): $[\text{M}\text{-NH}_4]^-$
found m/z 350.9062, calculated for $\text{C}_{12}\text{H}_6(35)\text{Cl}_3\text{O}_4\text{S}$ 350.9052.

2.9. Sulfuric acid mono-(2',3,4'-trichloro-biphenyl-4-yl) ester, ammonium salt (9j)

White solid; mp: 185 °C (dec.); ^1H NMR (400 MHz, CD_3OD): δ/ppm 7.27-7.38 (m, 3H),
7.45 (d, 1H, $J = 2.1 \text{ Hz}$), 7.54 (d, 1H, $J = 2.1 \text{ Hz}$), 7.70 (d, 1H, $J = 8.5 \text{ Hz}$). ^{13}C NMR (100 MHz,
 CD_3OD): δ/ppm 123.4 (CH), 127.3, 128.6 (CH), 129.6 (CH), 130.7 (CH), 131.9 (CH), 133.5
(CH), 134.3, 135.3, 136.8, 138.9, 150.0 ($\text{C}_{\text{Ar}}\text{-OSO}_3$). IR (KBr): 3464, 1249, 1080, 1057, 822 cm^{-1} .
 1 . UV/Vis: $\lambda_{9a,\text{max}}(\text{MeOH}) = 251 \text{ nm}$, $\epsilon_{9a} = 1.38 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ($\lambda_{7a,\text{max}}(\text{MeOH}) = 260 \text{ nm}$,
 $\epsilon_{7a} = 1.52 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). HRMS (ESI, negative): $[\text{M}\text{-NH}_4]^-$ found m/z 350.9045, calculated
for $\text{C}_{12}\text{H}_6(35)\text{Cl}_3\text{O}_4\text{S}$ 350.9052.