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Polystyrene-supported bifunctional resorcinarenes as cheap, metalfree and recyclable catalysts for epoxide/CO₂ coupling reactions

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1. General information

Unless otherwise noted, all commercial reagents were used as received without futher purification or drying, including CO₂ (purchased from PRAX- 38 AIR). Flash chromatography was carried out using 60 mesh silica gel and dry-packed columns. Thin layer chromatography was carried out using Merck TLC Silicagel 60 F254 aluminum sheets. Components were visualized by UV light (λ = 254 nm) and stained with *p*-anisaldehyde or phosphomolybdic dip. NMR spectra were recorded at 298 K on a Fourier 300 MHz Bruker, a Bruker Avance 400 Ultrashield or a Bruker Avance 500 Ultrashield apparatus. Chemical shifts are reported in ppm relative to the residual solvent peaks in CDCl₃ (δ = 7.26 ppm) and (CD₃)₂CO (δ = 2.05 ppm). Elemental analysis was performed by MEDAC Ltd, United Kingdom. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer.

2. General Protocol for the Carbonate Synthesis (COC1-12)



Typically, the reaction was performed in a 30 mL steel autoclave where the epoxide (S1-12) (8.3 mmol, 1 equiv.) and catalyst 14 (1.0 mol %) were added as liquid and solid respectively. The autoclave was then subjected to three cycles of pressurization and depressurization with CO₂. Finally, the autoclave was charged with 0.5 Mpa (5 bar) of CO₂, heated to 80 °C, and the contents was stirred for 18 hours. Upon complation of the reaction, the autoclave was cooled to room temperature and carefully depressurized. The volatiles were removed under reduced pressure, and the product was purified by flash column chromatography (typically 1:1 cyclohexane/ethyl acetate as eluent) to afford the pure cyclic carbonate COC1-12.

2.1. Characterization of Cyclic Carbonates



1,2-hexylene carbonate, COC1: Following the general procedure using 1,2epoxyhexane S1 (8.3 mmol, 1 equiv.), catalyst **14** (0.083 mmol, 0.01 equiv.) and CO₂ (0.5 MPa) to afford 1,2-hexylene carbonate COC1 (7.72 mmol, 93% yield) as a colorless oil. The spectroscopic data correspond to those previously reported in the literature.^{1,2,3} **¹H-NMR** (400 MHz, CDCl₃): δ = 0.90 (t, J = 6.0 Hz, 3H), 1.25-

1.48 (m, 4H), 1.59-1.83 (m, 2H), 4.05 (t, J = 8.0 Hz, 1H), 4.51 (dd, J = 8.0 Hz, 1H), 4.68 (m, 7.5 Hz, 1H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 13.9, 22.3, 26.6, 33.7, 69.5, 77.2, 155.1. **IR**: 1784 cm⁻¹ (C=O).



Allyl glycidyl carbonate, COC2: Following the general procedure using allyl glycidyl oxirane S2 (8.3 mmol, 1 equiv.), catalyst 14 (0.083 mmol, 0.01 equiv.) and CO₂ (0.5 MPa) to afford allyl glycidyl carbonate COC2 (8.05 mmol, 97% yield) as a colorless oil. The spectroscopic data correspond to those previously reported in the literature.^{1,3} ¹H-NMR (400

MHz, CDCl₃): δ = 3.62 (dd, J = 3.8; 11.0 Hz, 1H), 3.69 (dd, J = 4.1; 11.0 Hz, 1H), 3.99-4.12 (m, 2H), 4.40 (dd, J = 6.1; 8.4 Hz, 1H), 4.50 (t, 8.4 Hz, 1H), 4.82 (m, 1H), 5.20-5.32 (m, 2H), 5.81-5.92 (m, 1H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 66.4, 69.0, 72.8, 75.1, 118.1, 133.7, 155.1. **IR**: 1782 cm⁻¹ (C=O)



Styrene carbonate, COC3: Following the general procedure using styrene oxide S3 (8.3 mmol, 1 equiv.), catalyst **14** (0.083 mmol, 0.01 equiv.) and CO₂ (0.5 MPa) to afford styrene carbonate COC**3** (6.72 mmol, 81% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.^{1,3} **1H**-**NMR** (400 MHz, CDCl₃): δ = 4.35 (dd, J = 7.8; 8.6 Hz, 1H), 4.80 (t, J = 8.4 Hz, 1H), 5.68 (t, J = 8.0 Hz, 1H), 7.33-7.49 (m, 5H). ¹³**C**-**NMR** (100 MHz,

CDCl₃): δ = 71.3, 78.1, 126.0, 129.8, 129.9, 135.9, 155.9. **IR**: 1776 cm⁻¹ (C=O)



Propylene carbonate, COC4: Following the general procedure using propylene oxide S4 (8.3 mmol, 1 equiv.), catalyst **14** (0.083 mmol, 0.01 equiv.) and CO₂ (0.5 MPa) to afford propylene carbonate COC4 (7.30 mmol, 88% yield) as a colorless oil. The spectroscopic data correspond to those previously reported in the literature.^{1,3} ¹**H-NMR** (400 MHz, CDCl₃): δ = 1.49 (d, J = 6.3 Hz, 3H), 4.02 (dd, J =

7.2; 8.4 Hz, 1H), 4.55 (dd, J = 7.7; 8.4 Hz, 1H), 4.80-4.90 (m, 1H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 19.5, 70.8, 73.6, 155.1. **IR**: 1782 cm⁻¹ (C=O)



3-phenoxypropylene carbonate, COC5: Following the general procedure using 3-phenoxypropylene oxide S5 (8.3 mmol, 1 equiv.), catalyst **14** (0.083 mmol, 0.01 equiv.) and CO₂ (0.5 MPa) to afford 3-phenoxypropylene carbonate COC5 (7.89 mmol, 95% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.³ **1H-NMR** (400 MHz, CDCl₃): δ = 4.18 (dd, J = 10.5, 3.6 Hz,

1H), 4.27 (dd, J = 10.6, 4.4 Hz, 1H), 4.53–4.67 (m, 2H), 5.02–5.09 (m, 1H), 6.94 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 2H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 66.4, 67.0, 74.2, 114.8, 122.2, 129.8, 157.9. **IR**: 1781 cm⁻¹ (C=O).



COC6

3-methoxypropylene carbonate, COC6: Following the general procedure using 3-methoxypropylene oxide S6 (8.3 mmol, 1 equiv.), catalyst **14** (0.083 mmol, 0.01 equiv.) and CO_2 (0.5 MPa) to afford 3-methoxypropylene carbonate S6 (7.55 mmol, 91% yield) as a colorless oil. The spectroscopic data correspond to those previously reported in the literature.^{1,2,3} ¹**H-NMR** (400

MHz, $CDCl_3$): δ = 3.42 (s, 3H), 3.59 (dd, J= 11.0, 3.8 Hz, 1H), 3.66 (dd, J= 11.0, 3.8 Hz, 1H), 4.37 (dd, J = 6.1; 8.4 Hz, 1H), 4.49 (t, J = 8.4 Hz, 1H), 4.76-4.84 (m, 1H). ¹³**C-NMR** (100 MHz, $CDCl_3$): δ = 59.8, 66.4, 71.8, 75.1, 155.1. **IR**: 1780 cm⁻¹ (C=O)



1,2-octylene carbonate, COC7: Following the general procedure using 1,2-octylene oxide S7 (8.3 mmol, 1 equiv.), catalyst **14** (0.083 mmol, 0.01 equiv.) and CO₂ (0.5 MPa) to afford 1,2-octylene carbonate COC7 (7.05 mmol, 85% yield) as a yellow oil. The spectroscopic data correspond to those previously reported in the literature.³ **¹H-NMR** (400 MHz, CDCl₃): δ = 0.88 (t, J = 7.0 Hz, 3H), 1.22-1.54

(m, 8H), 1.62-1.87 (m, 2H), 4.06 (dd, J = 7.2; 8.4 Hz, 1H), 4.52 (dd, J = 7.8; 8.4, Hz, 1H), 4.70 (m, 7.5 Hz, 1H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 14.2, 22.7, 24.3, 28.9, 31.7, 33.9, 69.6, 155.2. **IR**: 1788 cm⁻¹ (C=O).



COC8

3-chloropropylene carbonate, COC8: Following the general procedure using 3-chloropropylene oxide S8 (8.3 mmol, 1 equiv.), catalyst **14** (0.083 mmol, 0.01 equiv.) and CO₂ (0.5 MPa) to afford 3-chloropropylene carbonate COC**8** (7.80 mmol, 94% yield) as a colorless oil. The spectroscopic data correspond to those previously reported in the literature.^{1,2,3} **1H-NMR** (400 MHz, CDCl₃): δ = 3.68-

3.80 (m, 2H), 4.41 (dd, J = 5.7; 8.9 Hz, 1H), 4.59 (dd, J = 8.2; 8.9 Hz, 1H), 4.91-5.0 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ = 43.5, 66.9, 74.3, 154.0. **IR**: 1778 cm⁻¹ (C=O).



COC9

Glycerol carbonate, COC9: Following the general procedure using glycidol S9 (8.3 mmol, 1 equiv.), catalyst **14** (0.083 mmol, 0.01 equiv.) and CO₂ (0.5 MPa) to afford glycerol carbonate COC**9** (6.64 mmol, 80% yield) as a colorless oil. The spectroscopic data correspond to those previously reported in the literature.^{2,3} **1H**-**NMR** (400 MHz, CDCl₃): δ = 2.68 (dd, J = 7.0; 5.8 Hz, 1H), 3.70

(ddd, J = 12.9; 6.8; 3.5 Hz, 1H), 3.98 (ddd, J = 12.8; 5.5; 3.0 Hz, 1H), 4.45 (dd, J = 9.3; 5.8 Hz, 1H), 4.52 (t, J = 8.3 Hz, 1H), 4.77–4.89 (m, 1H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 61.8, 66.1, 76.7, 155.6. **IR**: 1762 cm⁻¹ (C=O).

Cyclohexene carbonate, COC10: Following the general procedure using cyclohexene oxide S10 (8.3 mmol, 1 equiv.), catalyst 14 (0.249 mmol, 0.03 equiv.) and CO₂ (0.5 MPa) at 100 °C for 64 hours to afford cyclohexene carbonate COC10 (3.40 mmol, 41% yield, 68% selectivity, 65% conversion) as a yellow oil. The spectroscopic data correspond to those previously reported in the literature.^{1,2} ¹H-NMR (400 MHz, CDCl₃): δ = 1.29-1.50 (m, 2H), 1.56-1.72 (m, 2H), 1.84-1.93 (m, 4H), 4.65-4.71 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ = 19.1, 26.8, 75.9, 155.5. IR: 1785 cm⁻¹ (C=O).



Cyclopentene carbonate, COC11: Following the general procedure using cyclopentene oxide S11 (8.3 mmol, 1 equiv.), catalyst 14 (0.249 mmol, 0.03 equiv.) and CO_2 (0.5 MPa) at 100 °C for 64 hours to afford cyclopentene carbonate COC11 (5.73 mmol, 69% yield, 76% selectivity, 95% conversion) as a white solid. The

COC11 spectroscopic data correspond to those previously reported in the literature.¹ ¹H-NMR (400 MHz, CDCl₃): δ = 1.60-1.87 (m, 4H), 2.08-2.22 (m, 2H), 5.01-5.14 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ = 21.7, 33.3, 81.9, 155.6. **IR**: 1780 cm⁻¹ (C=O). **Tetrahydrofuro[3,4-***d***][1,3]dioxol-2-one, COC12**: Following the general procedure using 3,4-epoxytetrahydrofuran S12 (8.3 mmol, 1 equiv.), catalyst 14 (0.249 mmol, 0.03 equiv.) and CO₂ (0.5 MPa) at 100 °C for 64 hours to afford tetrahydrofuro[3,4*d*][1,3]dioxol-2-one COC12 (4.90 mmol, 59% yield, 86% selectivity, 71% conversion) as a white solid. The spectroscopic data correspond to those previously reported in the literature.¹ ¹H-NMR (400 MHz, CDCl₃): δ = 3.53-3.61 (m, 2H), 4.09-4.36 (m, 2H), 5.20 (d, J = 2.2 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ = 73.1, 80.1, 154.5. IR: 1779 cm⁻¹ (C=O).

3. General Protocol for the Synthesis of Resorcin[4]arenes (1-4)



In a two neck 100 mL round bottom flask, one equivalent of resorcinol (50 mmol) in a solution of ethanol (10 mL) and water (10 mL) and concentrated HCl (5 mL) were added and cooled to 0 °C. Then the aldehyde reagent (50 mmol, 1 equiv.) was added dropwise to the reaction mixture. The resulting solution was stirred at 75 °C for 48 hours. Upon cooling to room temperature, the desired resorcin[4]arene precipitated. The solid product was filtred and washed with water and ethanol.

3.1. Characterization of Resorcin[4]arenes



Resorcin[4]arene 1: Following the general procedure using resorcinol (50 mmol, 1 equiv.) and butyraldehyde (50 mmol, 1 equiv.) to afford resorcin[4]arene **1** (6.0 mmol, 48% yield) as a pale yellow solid. ¹**H-NMR** (400 MHz, Acetone-d₆): δ = 0.95 (t, J = 7.4 Hz, 12 H), 1.36 – 1.24 (m, 8 H), 2.35 – 2.22 (m, 8 H), 4.33 (t, J = 7.9 Hz, 4 H), 6.23 (s, 4 H), 7.58 (s, 4 H), 8.42 (s, 8 H). ¹³**C-NMR** (100 MHz,

Acetone-d₆): δ = 14.4, 22.0, 33.0, 36.5, 103.8, 125.3, 125.7, 152.7. Elemental analysis: Calculated for C₄₀H₄₈O₈·¼H₂O: C, 72.65; H, 7.39. Found: C, 72.88; H, 7.38. Melting point: >350 °C.



Resorcin[4]arene 2: Following the general procedure using resorcinol (50 mmol, 1 equiv.) and valeraldehyde (50 mmol, 1 equiv.) to afford resorcin[4]arene **2** (6.4 mmol, 51% yield) as a yellow solid. ¹**H-NMR** (400 MHz, Acetone-d₆): δ = 0.89 (t, J = 7.2 Hz, 12 H), 1.50 – 1.17 (m, 16 H), 2.3 (m, 8 H), 4.3 (t, J = 7.9 Hz, 4 H), 6.24 (s, 4 H), 7.56 (s, 4 H), 8.43 (s, 8 H). ¹³C-NMR (100 MHz, Acetone-d₆): δ = 14.6, 23.4, 31.3, 34.0, 34.4, 103.9, 125.3, 125.5,

152.7. Elemental analysis: Calculated for C₄₄H₅₆O₈·½H₂O: C, 73.20; H, 7.97. Found: C, 73.03; H, 8.80. Melting point: >350 °C.



Resorcin[4]arene 3: Following the general procedure using resorcinol (50 mmol, 1 equiv.) and heptaldehyde (50 mmol, 1 equiv.) to afford resorcin[4]arene **3** (5.9 mmol, 47% yield) as a yellow solid. ¹**H-NMR** (400 MHz, Acetone-d₆): δ = 0.89 (t, J = 6.8 Hz, 12 H), 1.45 – 1.23 (m, 32 H), 2.36-2.21 (m, 8 H), 4.31 (t, J = 7.9 Hz, 4 H), 6.24 (s, 4 H), 7.55 (s, 4 H), 8.48 (s, 8 H). ¹³**C-NMR** (100 MHz, Acetone-d₆): δ = 14.3, 23.3, 28.9, 30.0, 32.7, 34.2, 34.3, 103.5,

125.1, 125.3, 152.6. **Elemental analysis**: Calculated for C₅₂H₇₂O₈⋅½H₂O: C, 74.88; H, 8.82. Found: C, 74.50; H, 8.46. **Melting point**: 323 °C.



Resorcin[4]arene 4: Following the general procedure using resorcinol (50 mmol, 1 equiv.) and lauric aldehyde (50 mmol, 1 equiv.) to afford resorcin[4]arene **4** (6.5 mmol, 52% yield) as a yellow solid. ¹**H-NMR** (400 MHz, Acetone-d₆): δ = 0.89 (t, J = 6.7 Hz, 12 H), 1.30 (m, 72 H), 2.09 (m, 8 H), 2.39 (M, 8 H), 4.30 (t, J = 7.9 Hz, 4 H), 6.24 (s, 4 H), 7.53 (s, 4 H), 8.51 (s, 8 H). ¹³**C-NMR** (100 MHz, Acetone-d₆): δ = 14.4, 23.4, 29.1, 29.3, 30.2, 30.4, 30.5,

30.6, 30.7, 32.7, 34.4, 34.5, 103.6, 125.5, 125.6, 152.9. **Elemental analysis**: Calculated for C₇₂H₁₁₂O₈·H₂O: C, 78.14; H, 10.29. Found: C, 77.99; H, 9.43. **Melting point**: 304 °C.



4. General Protocol for the Synthesis of Tetrabenzoxazines (5-11)

Into a solution of resorcin[4]arene **1-4** (2 mmol, 1 equiv.) and excess of formaldehyde (5 ml) in ethanol (50 ml), the corresponding primary amine (10 mmol, 1.25 equiv.) was added dropwise. The reaction mixture was stirred at room temperature for 24 hours. The solid product was filtered off, washed with cold ethanol/water (9:1 v/v) and dried to give the tetrabenzoxazine **5-11**.

4.1. Characterization of Tetrabenzoxazines



Tetrabenzoxazine 5: Following the general procedure using propyl resorcin[4]arene **1** (2 mmol, 1 equiv.) and butylamine (10 mmol, 1.25 equiv.) to afford tetrabenzoxazine **5** (1.48 mmol, 74% yield) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.90 (t, J = 7.3 Hz, 12 H), 0.97 (t, J = 7.3 Hz, 12 H), 1.2 – 1.41 (m, 16 H), 1.42 – 1.61 (m, 8 H), 2.18 (m, 8 H), 2.63 (m, 8 H), 3.78 (d, J = 17.3 Hz, 4 H), 3.98 (d, J = 17.3 Hz, 4 H), 4.24 (t, J = 7.9 Hz 4 H), 4.91 (q, J = 8.0 Hz, 8 H), 7.12 (s, 4 H), 7.74 (s, 4 H).

¹³**C-NMR** (100 MHz, CDCl₃): δ = 14.1, 14.2, 20.4, 21.2, 30.1, 32.4, 35.7, 46.5, 51.4, 82.9, 108.5, 121.3, 123.5, 124.4, 148.0, 149.8. **Elemental analysis**: Calculated for C₆₄H₉₂N₄O₈·H₂O: C, 72.28; H, 8.91; N, 5.27. Found: C, 72.57; H, 8.76; N, 4.87.



Tetrabenzoxazine 6: Following the general procedure using butyl resorcin[4]arene **2** (2 mmol, 1 equiv.) and propylamine (10 mmol, 1.25 equiv.) to afford tetrabenzoxazine **6** (1.52 mmol, 76% yield) as an orange solid. ¹**H-NMR** (400 MHz, CDCl₃): δ = 0.90 (m, 24H), 1.18 – 1.61 (m, 24 H), 2.18 (m, 8 H), 2.58 (m, 8 H), 3.77 (d, J = 17.3 Hz, 4 H), 3.95 (d, J = 17.3 Hz 4 H), 4.21 (t, J = 7.8 Hz, 4 H), 4.90 (q, J = 9.6 Hz, 8 H), 7.11 (s, 4 H), 7.78 (s, 4 H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 11.7, 14.3, 21.3, 22.9, 30.4, 32.8, 33.4,

46.5, 53.6, 83.3, 108.6, 121.2, 123.6, 124.4, 148.2, 149.8. **Elemental analysis**: Calculated for C₆₄H₉₂N₄O₈·1/3H₂O: C, 73.11; H, 8.88; N, 5.33. Found: C, 72.93; H, 9.51; N, 4.89.



Tetrabenzoxazine **7**: Following the general procedure using resorcin[4]arene **2** (2 mmol, 1 equiv.) and butylamine (10 mmol, 1.25 equiv.) to afford tetrabenzoxazine **7** (1.76 mmol, 88% yield) as a pinkish yellow solid. ¹H-NMR (400 MHz, CDCl₃): $\delta = 0.93$ (m, 24 H), 1.19 – 1.6 (m, 32 H), 2.18 (m, 8 H), 2.62 (m, 8 H), 3.76 (d, J = 17.3 Hz, 4 H), 3.96 (d, J = 17.3 Hz, 4 H), 4.21 (t, J = 7.8 Hz, 4 H), 4.91 (q, J = 8.0 Hz, 8 H), 7.11 (s, 4 H), 7.78 (s, 4 H). ¹³C-NMR (100 MHz, CDCl₃): $\delta = 13.9$, 14.2, 20.3, 22.7, 30.1,

30.3, 32.7, 33.3, 46.4, 51.2, 83.9, 108.5, 121.1, 123.5, 124.3, 148.0, 149.7. **Elemental analysis**: Calculated for C₆₈H₁₀₀N₄O₈·½H₂O: C, 73.54; H, 9.17; N, 5.04. Found: C, 73.69; H, 9.25; N, 4.74.



Tetrabenzoxazine 8: Following the general procedure using resorcin[4]arene **2** (2 mmol, 1 equiv.) and hexylamine (10 mmol, 1.25 equiv.) to afford tetrabenzoxazine **8** (1.74 mmol, 87% yield) as a pinkish yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.88 (m, 24 H), 1.21 – 1.56 (m, 48 H), 2.16 (m, 8 H), 2.62 (m, 8 H), 3.76 (d, J = 17.3 Hz, 4 H), 3.96 (d, J = 17.3 Hz, 4 H), 4.21 (t, J = 7.8 Hz, 4 H), 4.9 (q, J = 9.6 Hz, 8 H), 7.10 (s, 4 H), 7.79 (s, 4

H). ¹³C-NMR (100 MHz, CDCl₃): δ = 14.0, 14.2, 22.6, 22.7, 26.8, 28.0, 30.3, 31.7, 32.7, 33.3, 46.4, 51.6, 83.0, 108.6, 121.0, 123.5, 124.3, 148.0, 149.6. Elemental analysis: Calculated for C₇₆H₁₁₆N₄O₈: C, 75.21; H, 9.63; N, 4.62. Found: C, 74.78; H, 9.21; N, 4.60.



Tetrabenzoxazine 9: Following the general procedure using resorcin[4]arene 2 (2 mmol, 1 equiv.) and benzylamine (10 mmol, 1.25 equiv.) to afford tetrabenzoxazine 9 (1.66 mmol, 83% yield) as a orange solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.95 (t, J = 7.2 Hz, 12 H), 1.25 - 1.49 (m, 16 H), 2.23 (m, 8 H), 3.68 – 410 (m, 16 H), 4.27 (t, J = 7.7 Hz, 4 H), 4.87 (q, J = 9.6 Hz, 8 H), 7.16 - 7.35 (m, 20 H), 7.72 (s, 4 H). ¹³C-NMR (100 MHz, CDCl₃): δ = 14.2, 22.7, 30.6, 32.7, 33.6, 46.7, 55.9, 82.4, 108.6,

121.4, 123.9, 124.4, 127.5, 128.5, 129.1, 137.9, 148.2, 149.9. **Elemental analysis**: Calculated for C₈₀H₉₂N₄O₈·H₂O: C, 76.52; H, 7.55; N, 4.46. Found: C, 76.75; H, 7.41; N, 4.69.



Tetrabenzoxazine 10: Following the general procedure using resorcin[4]arene **3** (2 mmol, 1 equiv.) and butylamine (10 mmol, 1.25 equiv.) to afford tetrabenzoxazine **10** (1.6 mmol, 80% yield) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.88 (m, 24 H), 1.17 – 1.57 (m, 48 H), 2.17 (m, 8 H), 2.61 (m, 8 H), 3.76 (d, J = 17.3 Hz, 4 H), 3.96 (d, J = 17.3 Hz, 4 H), 4.21 (t, J = 7.8 Hz, 4 H), 4.90 (q, J = 9.6 Hz, 8 H), 7.10 (s, 4 H), 7.77 (s, 4 H). ¹³C-NMR (100 MHz, CDCl₃): δ = 14.1, 14.2, 20.5, 22.8, 28.2, 29.5, 30.3, 32.1, 32.8,

33.8, 46.6, 51.4, 83.3, 108.6, 121.2, 123.6, 124.5, 148.2, 149.8. **Elemental analysis**: Calculated for C₇₆H₁₁₆N₄O₈: C, 75.21; H, 9.63; N, 4.62. Found: C, 74.85; H, 9.79; N, 4.73.



Tetrabenzoxazine 11: Following the general procedure using resorcin[4]arene **4** (2 mmol, 1 equiv.) and butylamine (10 mmol, 1.25 equiv.) to afford tetrabenzoxazine **11** (1.56 mmol, 78% yield) as a red solid. ¹**H-NMR** (400 MHz, CDCl₃): δ = 0.89 (m, 24 H), 1.13 – 1.57 (m, 88 H), 2.15 (m, 8 H), 2.60 (m, 8 H), 3.76 (d, J = 17.1 Hz, 4 H), 3.95 (d, J = 17.1 Hz, 4 H), 4.20 (t, J = 8.0 Hz, 4 H), 4.90 (q, J = 9.3 Hz, 8 H), 7.08 (s, 4 H), 7.78 (s, 4 H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 14.1, 14.3, 20.5, 22.9, 28.3, 29.5, 29.6,

29.8, 29.9, 30.3, 32.1, 32.2, 32.8, 33.7, 33.8, 46.4, 51.2, 83.9, 108.5, 121.1, 123.5, 124.3, 148.0, 149.7. **Elemental analysis**: Calculated for C₉₆H₁₅₆N₄O₈·H₂O: C, 76.24; H, 10.53; N, 3.70. Found: C, 76.55; H, 9.85; N, 3.31.

5. Synthesis of Ammonium Resorcin[4]arene Halides (12-19)



Into a solution of the tetrabenzoxazine **5-11** (1.5 mmols) in isopropanol (40 ml), concentrated HX (9 ml) and water (20 ml) were added. The mixture was refluxed for 4 hours. The crude product was triturated with diethyl ether, the solid was filtered off and dried to give the desired ammonium resorcin[4]arene halide salts **12-19**.

5.1. Characterization of Ammonium Resorcin[4]arene Halides



Resorcin[4]arene Ammonium Halide **12**: the Following general procedure using tetrabenzoxazine 5 (1.5 mmol) and hydrobromic acid (9 mL) to afford the ammonium resorcin[4]arene bromide 12 (1.38 mmol, 92% yield) as a pale yellow solid. ¹H-NMR (400 MHz, $CDCI_3$): δ = 0.99 (m, 24 H), 1.26 – 1.50 (m, 16 H), 1.98 (m, 8 H), 2.21 (m, 8 H), 3.19 (m, 8 H), 4.21 (m, 8), 4.37 (t, J = 7.8 Hz, 4 H), 7.26 (s, 4 H), 7.48 (br, 8 H), 8.95 (s, 8 H). ¹³C-NMR (100 MHz, CDCl₃): $\delta=13.6,\,14.1,\,20.2,\,21.2,\,27.6,\,33.9,\,34.9,\,43.9,$

49.5, 108.1, 125.4, 126.1, 150.2. **Elemental analysis**: Calculated for C₆₀H₉₆Br₄N₄O₈⋅H₂O: C, 53.82 H, 7.38; N, 4.18; O, 10.75; Br, 23.87. Found: C, 54.11; H, 7.50; N, 3.95; O, 9.61; Br, 21.86. **Melting point**: 237 °C.



Ammonium Resorcin[4]arene 13: Halide Following the general procedure using tetrabenzoxazine 6 (1.5 mmol) and hydrobromic acid (9 mL) to afford the ammonium resorcin[4]arene bromide 14 (1.23 mmol, 82% yield) as a pale yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.91 (t, J = 7.8 Hz, 12 H), 0.99 (t, J = 7.8 Hz, 12 H), 1.21 – 1.48 (m, 16 H), 2.0 (m, 8 H), 2.18 (m, 8 H), 3.12 (m, 8 H), 4.18 (m, 8), 4.32 (t, J = 7.8 Hz, 4 H), 7.22 (s, 4 H), 7.46 (br, 8 H), 8.90 (s, 8 H). ¹³**C-NMR** (100 MHz, CDCl₃): δ = 11.2, 14.2, 19.4,

22.7, 30.3, 32.5, 34.4, 43.7, 51.1, 108.3, 125.2, 126.1, 150.3. **Elemental analysis**: Calculated for C₆₀H₉₆Br₄N₄O₈·H₂O: C, 53.82; H, 7.38; N, 4.18; O, 10.75; Br, 23.87. Found: C, 53.68; H, 7.41; N, 4.07; O, 10.14; Br, 22.73. **Melting point**: 260 °C.



Ammonium Resorcin[4]arene Halide 14: Following the general procedure using tetrabenzoxazine 7 (1.5 mmol) and hydrobromic acid (9 mL) to afford the ammonium resorcin[4]arene bromide 14 (1.31 mmol, 87% yield) as a pinkish yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.92 (m, 24 H), 1.15 – 1.52 (m, 24 H), 1.96 (m, 8 H), 2.19 (m, 8 H), 3.15 (m, 8 H), 4.18 (m, 8), 4.31 (t, J = 7.9 Hz, 4 H), 7.22 (s, 4 H), 7.44 (br, 8 H), 8.91 (s, 8 H). ¹³C-NMR (100 MHz, CDCl₃): δ = 13.6, 14.2, 20.1, 22.8, 27.6, 30.3, 32.5,

34.3, 43.9, 49.5, 108.2, 125.3, 126.2, 150.3. Elemental analysis: Calculated for C₆₄H₁₀₄Br₄N₄O₈:
C, 55.10; H, 7.66; N, 4.02; O, 10.32; Br, 22.91. Found: C, 54.77; H, 7.27; N, 3.78; O, 9.09; Br, 22.34. Melting point: 241 °C.



Ammonium Resorcin[4]arene Halide 15: Following the general procedure using tetrabenzoxazine **8** (1.5 mmol) and hydrobromic acid (9 mL) to afford the ammonium resorcin[4]arene bromide **15** (1.16 mmol, 77% yield) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.89 (m, 24 H), 1.2 – 1.48 (m, 40 H), 1.95 (m, 8 H), 2.19 (m, 8 H), 3.14 (m, 8 H), 4.17 (m, 8), 4.32 (t, J = 7.8 Hz, 4 H), 7.22 (s, 4 H), 7.45 (br, 8 H), 8.90 (s, 8 H). ¹³C-NMR (100 MHz, CDCl₃): δ = 14.1, 14.3,

22.5, 22.8, 25.7, 26.5, 30.4, 31.2, 32.6, 34.3, 43.9, 49.8, 108.2, 125.3, 126.2, 150.1. Elemental analysis: Calculated for C₇₂H₁₂₀Br₄N₄O₈·2H₂O: C, 56.69; H, 8.19; N, 3.67; O, 10.49; Br, 20.95. Found: C, 56.88; H, 8.19; N, 3.63; O, 9.37; Br, 20.19. Melting point: 248 °C.



Ammonium Resorcin[4]arene Halide 16: Following the general procedure using tetrabenzoxazine 9 (1.5 mmol) and hydrobromic acid (9 mL) to afford the ammonium resorcin[4]arene bromide 16 (1.01 mmol, 67% yield) as a pale pink solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.86 (t, J = 7.3 Hz, 12 H), 1.13 – 1.43 (m, 16 H), 2.12 (m, 8 H), 4.03 (m, 8), 4.24 (t, J = 7.9 Hz, 4 H), 4.42 (br, 8 H), 7.16 (s, 4 H), 7.4 (m, 8 H), 7.70 (m, 8 H), 8.87 (s, 8 H). ¹³C-NMR (100 MHz, CDCl₃): δ = 14.2, 22.7, 30.3, 32.6, 34.2, 42.5, 52.1,

108.0, 125.1 126.2, 129.1, 129.4, 129.9, 130.0, 130.9, 150.1. **Elemental analysis**: Calculated for C₇₆H₉₆Br₄N₄O₈: C, 60.32; H, 6.39; N, 3.70; O, 8.47; Br, 21.12. Found: C, 57.83; H, 6.03; N, 3.46; O, 8.23; Br, 20.92. **Melting point**: 209 °C.



Ammonium Resorcin[4]arene 17: Halide Following the general procedure using tetrabenzoxazine 9 (1.5 mmol) and hydrochloric acid (9 mL) to afford the ammonium resorcin[4]arene chloride 17 (1.07 mmol, 71% yield) as a pale pink solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.86 (t, J = 7.3 Hz, 12 H), 1.14 – 1.42 (m, 16 H), 2.10 (m, 8 H), 4.05 (m, 8), 4.24 (t, J = 7.8 Hz, 4 H), 4.3 (br, 4 H), 7.12 (s, 4 H), 7.40 (m, 8 H), 7.7 (m, 8 H), 8.18 (br, 8 H), 8.9 (s, 8 H). ¹³C-NMR $(100 \text{ MHz}, \text{CDCl}_3)$: $\delta = 14.2, 22.8, 30.2, 32.7, 34.4,$

42.2, 52.0, 108.8, 124.8, 126.6, 129.3, 129.7, 129.8, 130.7, 150.4. **Elemental analysis**: Calculated for C₇₆H₉₆Cl₄N₄O₈·2H₂O: C, 66.56; H, 7.35; N, 4.09; O, 11.67; Cl, 10.34. Found: C, 66.25; H, 7.66; N, 4.38; O, 9.04; Cl, 10.14. **Melting point**: 228 °C.



Ammonium Resorcin[4]arene 18: Halide Following the general procedure using tetrabenzoxazine 10 (1.5 mmol) and hydrobromic acid (9 mL) to afford the ammonium resorcin[4]arene bromide 18 (1.17 mmol, 78% yield) as a pale yellow solid. ¹H-NMR (400 MHz, $CDCI_3$): $\delta = 0.88$ (t, J = 6.9 Hz, 12 H), 0.94 (t, J = 7.4 Hz, 12 H), 1.10 - 1.50 (m, 40 H), 1.95 (m, 8 H), 2.18 (m, 8 H), 3.16 (m, 8 H), 4.17 (m, 8), 4.32 (t, J = 7.8 Hz, 4 H), 7.20 (s, 4 H), 7.45 (br, 8 H), 8.90 (s, 8 H). ¹³C-NMR (100 MHz, CDCl₃): $\delta = 13.7, 14.2, 20.1, 22.8, 27.6, 28.1, 29.5, 32.0,$

32.9, 34.4, 43.9, 49.5, 108.2, 125.3, 126.2, 150.1. **Elemental analysis**: Calculated for C₇₂H₁₂₀Br₄N₄O₈·H₂O: C, 57.37; H, 8.16; N, 3.72; O, 9.55; Br, 21.20. Found: C, 57.22; H, 8.50; N, 3.53; O, 9.66; Br, 20.58. **Melting point**: 223 °C.



Ammonium Resorcin[4]arene Halide **19**: Following the general procedure using tetrabenzoxazine 11 (1.5 mmol) and hydrobromic acid (9 mL) to afford the ammonium resorcin[4]arene bromide 19 (1.11 mmol, 74% yield) as a red solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.91 (m, 24 H), 1.15 – 1.45 (m, 80 H), 1.95 (m, 8 H), 2.18 (m, 8 H), 3.14 (m, 8 H), 4.17 (m, 8), 4.32 (t, J = 7.8 Hz, 4 H), 7.22 (s, 4 H), 7.46 (br, 8 H), 8.94 (s, 8 H). ¹³C-NMR (100 MHz, CDCl₃): δ = 13.7, 14.3, 20.1, 22.9, 27.6, 28.2, 29.6,

29.7, 29.8, 29.9, 30.0, 30.2, 32.1, 32.9, 34.4, 43.9, 49.5, 108.1, 125.4, 126.2, 150.2. Elemental analysis: Calculated for C₉₂H₁₆₀Br₄N₄O₈: C, 62.43; H, 9.11; N, 3.17; O, 7.23; Br, 18.06. Found: C, 63.01; H, 9.78; N, 2.86; O, 7.08; Br, 16.23. Melting point: 210 °C.

6. Synthesis and Characterization of PS-Supported Resorcin[4]arenes 21-





a) In an oven-dried 250 mL round-bottom flask, Merrifield resin (1.0 g, f = 1.09 mmol/g) was added as solid. DMF (50 mL) was added and gently shaked under argon atmosphere for 30 min at room temperature. In a separate oven-dried flask, NaH (60%, 10 mmol) and tetrabenzoxazine **7** (2 mmol) were added as solid. THF (50 mL) was added and this solution was stirred for 30 min at room temperature. Afterwards, the tetrabenzoxazin solution was added over the Merrifield resin suspension and the reaction mixture was heated up to 70 °C under argon atmosphere using a continuous shaking for 96 hours. The reaction mixture was then filtered and the resin was washed with water, water/MeOH (1:1), MeOH, MeOH/THF (1:1) and THF (50 mL each). The solid was dried under reduced pressure at 40 °C for 24 hours to obtain the desired PS-supported tetrabenzoxazine **21** ($f_N = 0.26 \text{ mmol/g}$, $f_{max} = 0.50 \text{ mmol/g}$, 52% yield).



Elemental analysis (%): N, 1.48; C, 86.13; H, 7.88; O, 4.35. f_N = 0.26 mmol/g (f_{max} = 0.50 mmol/g). **IR (cm⁻¹)**: 538, 696, 755, 905, 1028, 1068, 1111, 1181, 1223, 1375, 1451, 1492, 1601, 2857, 2923, 3003, 3025, 3059, 3083.

b) PS-supported tetrabenzoxazine **21** (0.145 mmol, 1.0 equiv., $f_N = 0.26$ mmol/g) was placed into a pressure tube. Methyl iodide (0.725 mmol, 5.0 equiv.) as solution in acetonitrile (2.5 mL) was added and the reaction mixture was heated to 75 °C, continuously shaked for 48 hours. The reaction mixture was filtered off, and the resin was washed with water, water/MeOH (1:1), MeOH, MeOH/THF (1:1) and THF (50 mL each). The solid was dried under reduced pressure at 40 °C for 24 hours to obtain the desired PS-supported resorcin[4]arene iodide salt **22** ($f_N = 0.23$ mmol/g, $f_{max} = 0.25$ mmol/g, 92% yield).



Elemental analysis (%): N, 1.26; C, 76.58; H, 7.04; O, 3.70; I, 12.28. *f*_N = 0.23 mmol/g (*f*_{max} = 0.25 mmol/g). IR (cm⁻¹): 696, 754, 1131, 1217, 1375, 1451, 1492, 1601, 2871, 2921, 3024, 3059, 3082, 3408.





In a 10 mL vial, a suspension of N-Benzyl-*n*-butylamine (100 mg, 0.613 mmol) in diethylether (2.4 mL) was prepared. Then, hydrobromic acid (48%, 73 μ L, 0.643 mmol) was added and the reaction was stirred for 1 hour observing the solution of the starting material. Afterwards, the solvent was removed under reduced pressure and the obtained orangish solid was washed with pentane to render the desired *N*-Benzyl-*N*-butylammonium bromide **20** as a white solid (138.0 mg, 0.564 mmol, 92% yield).



¹**H-NMR** (500 MHz, CDCl₃): δ = 0.89 (t, J = 7.4 Hz, 3 H), 1.36 (h, J = 7.4 Hz, 2 H), 1.86 (p, J = 7.9 Hz, 2 H), 2.75 – 2.85 (m, 2 H), 4.08 (t, J = 5.3 Hz, 2 H), 7.34 – 7.48 (m, 3 H), 7.59 – 7.65 (m, 2 H), 9.34 (br, 2 H). ¹³**C-NMR** (125 MHz, CDCl₃): δ = 13.6,

20.2, 27.8, 45.8, 50.6, 129.4, 129.7, 129.8, 130.7. **IR (cm⁻¹)**: 509, 596, 696, 746, 1010, 1214, 1431, 1462, 1501, 2414, 2574, 2799, 2936. **Melting point**: 220 °C.

8. Recycling Studies

Table S1.	Background	reactions
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Entry	Catalyst	COC1 Yield (%)*	
1	Merrifield resin (PS-Cl)	0	
2	Iodomethane	13	
3	21	25	
4	22	>99	

Reaction conditions: 1,2-epoxyhexane S1 (8.3 mmol), CO_2 (0.5 MPa), catalyst (1 mol%), time = 18 h, temperature = 80 °C. Selectivity in all cases is >99%. *NMR Yields based on mesitylene as internal standard.

Table S2. Elemental analysis for the recycled catalyst 22.

	C (%)	H (%)	N (%)	O (%)	I (%)
Fresh	76.58	7.04	1.26	3.70	12.28
After 12 th run	82.74	7.74	0.91	4.25	3.86

Table S3. Data points relating to Fig. 2.

Run nº	Catalyst loading (%)	COC1 Yield (%)*
1	0.89	100
2	n.d.	100
3	n.d.	100
4	0.80	100
5	n.d.	95
6	0.75	91
7	n.d.	91
8	n.d.	92
9	0.69	90
10	n.d.	85
11	n.d.	84
12	n.d.	85

Reaction conditions: 1,2-epoxyhexane S1 (8.3 mmol), CO_2 (0.5 MPa), catalyst 14 (1 mol%), time = 18 h, temperature = 80 °C. Selectivity in all cases is >99%. *NMR Yields based on mesitylene as internal standard.

9. Copies of IR, ¹H-NMR and ¹³C-NMR Spectra

9.1. COC1



9.2. COC2



9.3. COC3



9.4. COC4

¹H-NMR spectrum

COC4 (1H-NMR)



9.5. COC5

¹H-NMR spectrum

COC5 (1H-NMR)

9.6. COC6

9.7. COC7

¹H-NMR spectrum

COC7 (1H-NMR)

9.8. COC8

¹H-NMR spectrum

COC8 (1H-NMR)

9.9. COC9

9.10. COC10

9.11. COC11

9.12. COC12

9.13. Resorcin[4]arene 1

¹H-NMR spectrum

9.14. Resorcin[4]arene 2

¹H-NMR spectrum

¹³C-NMR spectrum

Resorcinarene 2 (13C-NMR)

9.15. Resorcin[4]arene 3

¹H-NMR spectrum

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

9.16. Resorcin[4]arene 4

¹H-NMR spectrum

9.17. Tetrabenzoxazine 5

¹H-NMR spectrum

5 (1H-NMR)

¹³C-NMR spectrum

5 (13C-NMR)

9.18. Tetrabenzoxazine 6

¹H-NMR spectrum

6 (1H-NMR)

9.19. Tetrabenzoxazine 7

¹H-NMR spectrum

7 (1H-NMR)

¹³C-NMR spectrum

7 (13C-NMR)

9.20. Tetrabenzoxazine 8

¹H-NMR spectrum

8 (1H-NMR)

110 100 90 f1 (ppm)

9.21. Tetrabenzoxazine 9

¹H-NMR spectrum

¹³C-NMR spectrum

9 (13C-NMR)

9.22. Tetrabenzoxazine 10

¹H-NMR spectrum

9.23. Tetrabenzoxazine 11

¹H-NMR spectrum

110 100 f1 (ppm)

9.24. Ammonium Resorcin[4]arene Halide 12

¹H-NMR spectrum 12 (1H-NMR) -8.92 -7.45 Bu Br H₂N HO .OH HQ OH Br[⊖] Pr Pr Bu B Pr Pr ∙<mark>Ń⊕</mark> H₂ Bu Ó ю но ЪΗ Đ Br[⊖] ŇΗ₂ | Bu 12 H H H. H Ч 25.96-28.24-.48 7.03 3.89 4.65 8 7.95 .0 8.0 6.0 5.5 4.0 3.5 3.0 2.5 1.5 1.0 0.5 0. 9.5 9.0 8.5 7.5 7.0 6.5 4.5 5.0 f1 (ppm) 2.0 ¹³C-NMR spectrum 12 (13C-NMR) ~77.48 CDCl3 -77.16 CDCl3 ~76.84 CDCl3 <126.16 <125.30 -108.11-150.13 -49.51 -43.92 → 34.32 32.55 30.33 → 27.58 → 27.58 → 27.58 → 27.58 → 27.58 Bu B H₂N .OH HO OH H₂ (⊕N-HQ \mathbf{Br}^{Θ} [″]Pr Pr ·Bu Pr Pr -Ń⊕ H₂ Bu Ó юн но ЮΗ Đ NH₂ e | Bu Br 12

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9.25. Ammonium Resorcin[4]arene Halide 13

9.26. Ammonium Resorcin[4]arene Halide 14

9.27. Ammonium Resorcin[4]arene Halide 15

¹H-NMR spectrum 15 (1H-NMR) --8.84 -7.39 Hex ⊖ H₂N^IBr æ ſ .OH HO. HQ \mathbf{Br}^{Θ} ้BuBนั้ Hex Br BuBu -<mark>Ń⊕</mark> H₂ Hex-Ó юн но ЮН Đ NH₂ Θ | ⁻ Hex Br 15 4.52 -H 24.38-.22 7.68 3.61 8.00 8.16 8.13 .0 6.0 5.5 3.5 3.0 2.5 1.5 1.0 0.5 0. 9.5 9.0 8.5 8.0 7.5 7.0 6.5 4.5 4.0 5.0 f1 (ppm) 2.0 ¹³C-NMR spectrum 15 (13C-NMR) -77.48 CDCl3 -77.16 CDCl3 -76.84 CDCl3 $< \frac{126.20}{125.29}$ -108.15 -150.14 22.54 22.54 22.54 22.54 22.54 22.54 22.54 22.54 22.54 22.54 22.54 22.54 -49.76 -43.93 Hex Θ B H₂N но .OH OH H₂ ∕ ⊕<mark>N</mark>−Hex HO Br[⊖] ้ BuBu BuBu -<mark>Ń⊕</mark> H₂ Hex Ó юн но ЮΗ Đ NH2 e | Hex Br 15

110 100 f1 (ppm)

80

70

60

50

40

30

20

90

10

(

150

160

140

130

120

)0 190

180

170

9.28. Ammonium Resorcin[4]arene Halide 16

9.29. Ammonium Resorcin[4]arene Halide 17

¹H-NMR spectrum

17 (13C-NMR)

9.30. Ammonium Resorcin[4]arene Halide 18

¹H-NMR spectrum

9.31. Ammonium Resorcin[4]arene Halide 19

¹H-NMR spectrum

19 (1H-NMR) -7.21 4.13 4.13 4.19 4.19 Bu e ₁ H₂<mark>N</mark> R HO OH. OH H₂ ∕ <mark>⊕N</mark>−Bu HO \mathbf{Br}^{Θ} ^{ั้ท}ี่ Un Un Br^Θ UnUn -<mark>Ń⊕</mark> H₂ Bu-Ó Ю но ЮН Đ NH₂ ∣ Bu Θ Br 19 ------**++**+ 81.77-0 4.27 3.97 90 2.71 6.92 8.22 7.08 .0 5.5 3.5 3.0 2.5 0.5 0. 9.0 8.0 7.5 6.0 4.5 4.0 2.0 1.5 1.0 9.5 8.5 7.0 6.5 5.0 f1 (ppm)

19 (13C-NMR)

9.32. N-Benzyl-*n*-butylammonium bromide 20

110 100 f1 (ppm) Ċ

9.33. PS-supported Tetrabenzoxazine 21

IR spectrum

9.34. PS-supported Resorcin[4]arene Halide 22

IR spectrum

10. References

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