

Electronic Supplementary Information for:

An Artificial Organosilicon Receptor

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S1. GC-FID quantification

Dodecane was used as an internal standard to gravimetrically quantitate the chromatographic analyses. The samples were prepared at ~1% (w/w) product in a THF solution containing 1% (w/w) dodecane. Based on triplicate measurements, the response factors for the analytes were calculated (Equation 1), and found to be linear as a function of concentration over four orders of magnitude (i.e. 0.01-10% (w/w), Figure S1 and Tables S1).

$$RF_{\text{analyte}} = ([\text{analyte}]/\text{Area}_{\text{analyte}}) \times (\text{Area}_{\text{IS}}/[\text{IS}]) \times RF_{\text{IS}} \quad (1)$$

The linearity of a set of response factors is illustrated in Figure S1.

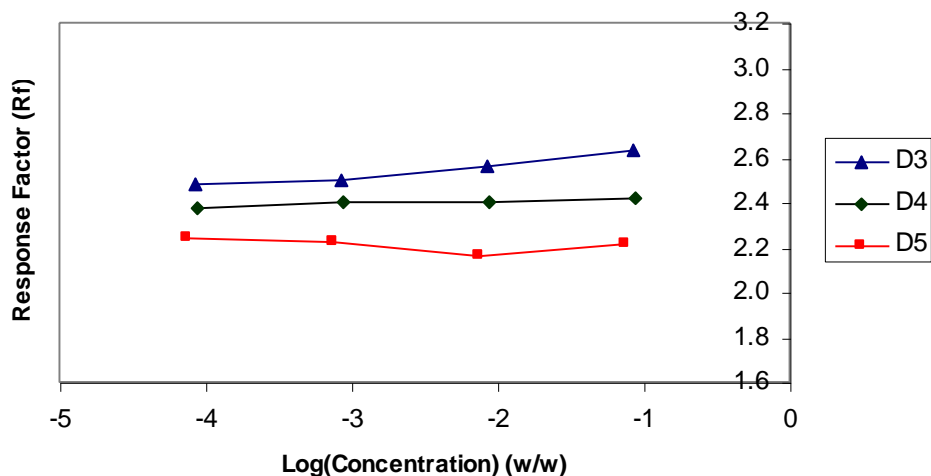


Figure S1: Evaluation of the experimental measurement of a response factor versus the concentration of an analyte over four orders of magnitude.

The terms in Equation 1 are defined as follows: RF_{analyte} = response factor for the analyte, $[\text{analyte}]$ = concentration of the analyte, $\text{Area}_{\text{analyte}}$ = peak area of the analyte, Area_{IS} = peak area of the internal standard, $[\text{IS}]$ = concentration of the internal standard, RF_{IS} = response factor for the internal standard = 1. Subsequently, Equation 1 was solved to quantitatively calculate the concentration of an analyte in the presence of an internal standard (Equation 2).

$$[\text{analyte}] = (Rf_{\text{analyte}} \times \text{Area}_{\text{analyte}}) \times ([\text{IS}]/\text{Area}_{\text{IS}}) \quad (2)$$

Table S1: GC-FID cyclic siloxane retention times and response factors.

Analyte	Retention Time (m)	Average	Response Factor (RF)	
			Standard Deviation	RSD
D ₃	5.011	2.692	0.04	1.5%
D ₄	7.916	2.516	0.014	0.6%
D ₅	10.360	2.479	0.008	0.3%

S2. Synthesis of MIP- α_1

α -D₃ complex (0.67g, 0.77mmol of α -cyclodextrin based on the calculated stoichiometry) was dried *in vacuo* over silica gel prior to reaction, and dissolved in dried DMSO (6.7ml). The stirred solution was treated with excess 2,4-TDI (0.973ml, 6.77mmol) at room temperature, and the subsequent mixture heated to 70 °C while magnetically stirred. After approximately 2 hours, the gel formed was chopped into small pieces and poured into acetone. The resultant polymer was ground with a mortar and pestle and refluxed for one hour in water to remove any free α -cyclodextrin and to allow the dissociation of the complex, one hour in THF, and then one hour in EtOH to further remove the template molecule as well as any unreacted TDI. Finally, the polymer was dried in a vacuum oven at 70 °C for 24 hours. During the drying process, the polymer was further ground to achieve a better particle size distribution. The urethane linkages in the polymer were confirmed from the CP MAS ¹³C NMR spectroscopy, which also confirmed the complete removal of the cyclic template, due to the disappearance of the silicon peak. The

mole ratio of TDI to α -cyclodextrin in the imprinted polymer was estimated from the elemental analysis.

CP MAS ^{13}C NMR (100.56 MHz): δ 155.7 (carbonyl C of TDI), 136.7, 130.7 and 119.6 (aromatic C of TDI), 102.3 (C_1 of α -CD), 82.6 (C_4 of α -CD), 73.2 (C_2 , C_3 and C_5 of α -CD), 63.7 (C_6 of α -CD) and 17.8 (CH_3 of TDI) ppm. Found: C, 52.4; H, 5.75; N, 9.56 %. Calculated for TDI/ α -CD = 8.5: C, 54.74; H, 5.15; N, 9.65 %.

S3. Synthesis of MIP- α_2

A “non-imprinted” (blank) polymer was prepared in an identical manner to MIP- α_1 , but in the absence of any preformed complex by treating free α -CD with 2,4-TDI in DMSO. α -CD (0.58g, 0.6mmol) was dried *in vacuo* at 70 °C for 24 hours prior to reaction, and dissolved in dried DMSO (5.8ml). The stirred solution was treated with excess 2,4-TDI (0.604mL, 4.2mmol) at room temperature and the subsequent mixture was heated to 70 °C while magnetically stirred. After approximately 2 hours, the gel formed was chopped into small pieces and poured into acetone. The resultant polymer was ground with a mortar and pestle and refluxed for one hour in water, one hour in THF, and then one hour in EtOH. Finally, the polymer was dried in a vacuum oven at 70 °C for 24 hours. During the drying process, the polymer was further ground to achieve a better particle size distribution. The urethane linkages in the polymer were confirmed from the CP MAS ^{13}C NMR spectroscopy. The mole ratio of TDI to β -cyclodextrin in the imprinted polymer was evaluated by elemental analysis.

CP MAS ^{13}C NMR (100.56 MHz): δ 155.6 (carbonyl C of TDI), 136.8, 130.8 and 117.5 (aromatic C of TDI), 102.2 (C_1 of α -CD), 83.3 (C_4 of α -CD), 72.8 (C_2 , C_3 and C_5 of α -CD), 63.5 (C_6 of α -CD) and 18.1 (CH_3 of TDI) ppm. Found: C, 53.31; H, 6.3; N, 8.62 %. Calculated for TDI/ α -CD = 6.5: C, 53.64; H, 5.24; N, 8.61 %.

S4. Synthesis of MIP- β_1

β -D₃ complex (1.9g, 1.5mmol of β -cyclodextrin based on the calculated stoichiometry) was dried *in vacuo* over silica gel prior to reaction and dissolved in dried DMSO (20ml). The stirred solution was treated with excess 2,4-TDI (1.6ml, 11.1mmol) at room temperature and the

subsequent mixture heated to 70 °C while magnetically stirred. After approximately 2 hours, the gel formed was chopped into small pieces and poured into acetone. The resultant polymer was ground with a mortar and pestle and refluxed for one hour in water to remove any free β -cyclodextrin and to allow the dissociation of the complex, one hour in THF, and then one hour in EtOH to further remove the template molecule as well as any unreacted TDI. Finally the polymer was dried in a vacuum oven at 70 °C for 24 hours. During the drying process, the polymer was further ground to achieve a better particle size distribution. The urethane linkages in the polymer were confirmed from the CP MAS ^{13}C NMR spectroscopy, which also confirmed the complete removal of the cyclic template due to the disappearance of the silicon peak. The mole ratio of TDI to β -cyclodextrin in the imprinted polymer was evaluated by elemental analysis.

CP MAS ^{13}C NMR (100.56 MHz): δ 155.8 (carbonyl C of TDI), 136.4, 130.5 and 118.1 (aromatic C of TDI), 102.5 (C_1 of β -CD), 82.9 (C_4 of β -CD), 72.9 (C_2 , C_3 and C_5 of β -CD), 64.3 (C_6 of β -CD) and 17.1 (CH_3 of TDI) ppm. Found: C, 53.08; H, 5.73; N, 8.85 %. Calculated for TDI/ β -CD = 7.5: C, 53.66; H, 5.25; N, 8.55 %.

S5. Synthesis of MIP- β_2

A “non-imprinted” (blank) polymer was prepared in an identical manner to MIP- β_1 , but in the absence of any preformed complex, by treating free β -CD with 2,4-TDI in DMSO. β -CD (0.94g, 0.83mmol) was dried in vacuo at 70 °C for 24 hours prior to reaction and dissolved in dried DMSO (9.4ml). The stirred solution was treated with excess 2,4-TDI (0.884ml, 6.15mmol) at room temperature and the subsequent mixture was heated to 70 °C while magnetically stirred. After approximately 2 hours, the gel formed was chopped into small pieces and poured into acetone. The resultant polymer was ground with a mortar and pestle and refluxed for one hour in water, one hour in THF, and then one hour in EtOH. Finally the polymer was dried in a vacuum oven at 70 °C for 24 hours. During the drying process, the polymer was further ground to achieve a better particle size distribution. The urethane linkages in the polymer were confirmed from the CP MAS ^{13}C NMR spectroscopy. The mole ratio of TDI to β -cyclodextrin in the imprinted polymer was evaluated by elemental analysis.

CP MAS ^{13}C NMR (100.56 MHz): δ 155.5 (carbonyl C of TDI), 136.4, 130.9 and 118.8 (aromatic C of TDI), 102.7 (C_1 of β -CD), 82.6 (C_4 of β -CD), 73.0 (C_2 , C_3 and C_5 of β -CD), 64.6

(C₆ of β -CD) and 17.9 (CH₃ of TDI) ppm. Found: C, 53.31; H, 5.92; N, 7.96 %. Calculated for TDI/ β -CD = 7: C, 53.30; H, 5.28; N, 8.29 %.

S6. Synthesis of MIP- γ_1

γ -D₅ complex (1.05g, 0.75mmol of γ -cyclodextrin based on the calculated stoichiometry) was dried *in vacuo* over silica gel prior to reaction and dissolved in dried DMSO (10.5ml). The stirred solution was treated with 2,4-TDI (0.8ml, 5.5mmol) at room temperature and the subsequent mixture was heated to 70 °C while magnetically stirred. After approximately 2 hours, the gel formed was chopped into small pieces and poured into acetone. The resultant polymer was ground with a mortar and pestle and refluxed for one hour in water to remove any free γ -cyclodextrin and allow the dissociation of the complex, one hour in THF, and then one hour in EtOH to further remove the template molecule as well as unreacted TDI. Finally, the polymer was dried in a vacuum oven at 70 °C for 24 hours. During the drying process, the polymer was further ground to achieve a better particle size distribution. The urethane linkages in the polymer were confirmed from the CP MAS ¹³C NMR spectroscopy, which also confirmed the complete removal of the cyclic template due to the disappearance of the silicon peak. The mole ratio of TDI to γ -cyclodextrin in the imprinted polymer was evaluated by elemental analysis.

CP MAS ¹³C NMR (100.56 MHz): δ 155.3 (carbonyl C of TDI), 138.0, 130.7 and 118.7 (aromatic C of TDI), 102.8 (C₁ of γ -CD), 83.4 (C₄ of γ -CD), 73.4 (C₂, C₃ and C₅ of γ -CD), 68.0 (C₄ of γ -CD) and 18.3 (CH₃ of TDI) ppm. Found: C, 53.78; H, 6.33; N, 7.61 %. Calcd for TDI/ β CD = 7: C, 52.73; H, 5.34; N, 7.76 %.

S7. Synthesis of MIP- γ_2

γ -D₄ complex (1.3g, 0.93mmol of γ -cyclodextrin based on the calculated stoichiometry) was dried *in vacuo* over silica gel prior to reaction, and dissolved in dried DMSO (13ml). The stirred solution was treated with excess 2,4-TDI (1ml, 7mmol) at room temperature and the subsequent mixture heated to 70 °C while magnetically stirred. After approximately 2 hours, the gel formed was chopped into small pieces and poured into acetone. The resultant polymer was ground with a mortar and pestle and refluxed for one hour in water to remove any free γ -cyclodextrin and allow

the dissociation of the complex, one hour in THF, and then one hour in EtOH to further remove the template molecule as well as any unreacted TDI. Finally, the polymer was dried in a vacuum oven at 70 °C for 24 hours. During the drying process, the polymer was further ground to achieve a better particle size distribution. The urethane linkages in the polymer were confirmed from the CP MAS ^{13}C NMR spectroscopy, which also confirmed the complete removal of the cyclic template due to the disappearance of the silicon peak. The mole ratio of TDI to γ -cyclodextrin in the imprinted polymer was evaluated by elemental analysis.

CP MAS ^{13}C NMR (100.56 MHz): δ 155.7 (carbonyl C of TDI), 137.6, 135.1 and 125.3 (aromatic C of TDI), 103.0 (C_1 of γ -CD), 83.4 (C_4 of γ -CD), 72.9 (C_2 , C_3 and C_5 of γ -CD), 57.0 (C_4 of γ -CD) and 17.6 (CH_3 of TDI) ppm. Found: C, 52.76; H, 5.34; N, 8.72 %. Calculated for TDI/ β -CD = 8: C, 53.29; H, 5.29; N, 8.29 %.

S8. Synthesis of MIP- γ_3

γ -D₃ complex (0.6g, approximately 0.4mmol of γ -cyclodextrin based on the calculated stoichiometry) was dried *in vacuo* over silica gel prior to reaction, and dissolved in dried DMSO (6ml). The stirred solution was treated with excess 2,4-TDI (0.403ml, 2.8mmol) at room temperature and the subsequent mixture was heated to 70 °C while magnetically stirred. After approximately 2 hours, the gel formed was chopped into small pieces and poured into acetone. The resultant polymer was ground with a mortar and pestle and refluxed for one hour in water to remove any free γ -cyclodextrin and allow the dissociation of the complex, one hour in THF, and then one hour in EtOH to further remove the template molecule as well as any unreacted TDI. Finally, the polymer was dried in vacuum oven at 70 °C for 24 hours. During the drying process, the polymer was further ground to achieve a better particle size distribution. The urethane linkages in the polymer were confirmed from the CP MAS ^{13}C NMR spectroscopy, which also confirmed the complete removal of the cyclic template due to the disappearance of the silicon peak. The mole ratio of TDI to γ -cyclodextrin in the imprinted polymer was evaluated by elemental analysis.

CP MAS ^{13}C NMR (100.56 MHz): δ 154.7 (carbonyl C of TDI), 135.6, 130.2 and 117.3 (aromatic C of TDI), 102.0 (C_1 of γ -CD), 81.6 (C_4 of γ -CD), 72.4 (C_2 , C_3 and C_5 of γ -CD), 61.5

(C₆ of γ -CD) and 16.5 (CH₃ of TDI) ppm. Found: C, 51.2; H, 5.73; N, 7.96 %. Calculated for TDI/ β -CD = 7: C, 52.73; H, 5.34; N, 7.76 %.

S9. Synthesis of MIP- γ_4

A “non-imprinted” (blank) polymer was prepared in an identical manner to MIPs- γ_{1-3} but in the absence of any preformed complex by treating free γ -CD with 2,4-TDI in DMSO. γ -CD (1g, 0.77mmol) was dried *in vacuo* at 70 °C for 24 hours prior to reaction, and dissolved in dried DMSO (10 ml). The stirred solution was treated with 2,4-TDI (0.77ml, 5.4mmol) at room temperature and the subsequent mixture heated to 70 °C while magnetically stirred. After approximately 2 hours, the gel formed was chopped into pieces and poured into acetone. The resultant polymer was ground with a mortar and pestle and refluxed for one hour in water, one hour in THF, and then one hour in EtOH. Finally, the polymer was dried in a vacuum oven at 70 °C for 24 hours. During the drying process, the polymer was further ground to achieve a better particle size distribution. The urethane linkages in the polymer were confirmed from the CP MAS ¹³C NMR spectroscopy. The mole ratio of TDI to β -cyclodextrin in the imprinted polymer was evaluated by elemental analysis.

CP MAS ¹³C NMR (100.56 MHz): δ 154.5 (carbonyl C of TDI), 135.9, 130.0 and 117.4 (aromatic C of TDI), 102.2 (C₁ of γ -CD), 82.0 (C₄ of γ -CD), 72.6 (C₂, C₃ and C₅ of γ -CD), 62.0 (C₆ of γ -CD) and 17.1 (CH₃ of TDI) ppm. Found: C, 51.29; H, 5.8; N, 7.87 %. Calculated for TDI/ β -CD = 7: C, 52.73; H, 5.34; N, 7.76 %.

S10 . Binding Studies

Table S2: Batch rebinding of the template and structural analogues to molecular imprinted cyclodextrins (MICDs).

Reaction	initial μmol	μmol adsorbed	% recovery ¹
MIP- α , 1mM D ₃ in acetonitrile	0.5	0.0	100.0
MIP- α , 1mM D ₃ in 95% acetonitrile	0.5	0.06	89.0
NIP- α , 1mM D ₃ in acetonitrile	0.5	0.0	100.0
NIP- α , 1mM D ₃ in 95% acetonitrile	0.5	0.03	95.0
MIP- β , 1mM D ₃ in acetonitrile	0.5	0.03	95.0
MIP- β , 1mM D ₃ in 95% acetonitrile	0.5	0.24	51.8
MIP- β , 1mM D ₄ in acetonitrile	0.5	0.005	99.1
MIP- β , 1mM D ₄ in 95% acetonitrile	0.5	0.01	97.2
MIP- β , 1mM D ₅ in acetonitrile	0.5	0.008	98.5
MIP- β , 1mM D ₅ in 95% acetonitrile	0.5	0.001	97.7
NIP- β , 1mM D ₃ in acetonitrile	0.5	0.001	99.8
NIP- β , 1mM D ₃ in 95% acetonitrile	0.5	0.1	79.6
MIP- γ_1 , 1mM D ₅ in acetonitrile	0.5	0.0	100.0
MIP- γ_1 , 1mM D ₅ in 95% acetonitrile	0.5	0.0	100.0
MIP- γ_1 , 1mM D ₅ in 90% acetonitrile	0.5	0.002	99.7
MIP- γ_1 , 1mM D ₄ in acetonitrile	0.5	0.002	99.6
MIP- γ_1 , 1mM D ₄ in 95% acetonitrile	0.5	0.002	97.7
MIP- γ_1 , 1mM D ₃ in acetonitrile	0.5	0.0	100.0
MIP- γ_1 , 1mM D ₃ in 95% acetonitrile	0.5	0.0005	99.9

MIP- γ_2 , 1mM D ₄ in acetonitrile	0.5	0.0	100.0
MIP- γ_2 , 1mM D ₄ in 95% acetonitrile	0.5	0.0	100.0
MIP- γ_2 , 1mM D ₃ in acetonitrile	0.5	0.005	99.0
MIP- γ_2 , 1mM D ₃ ³ in 95% acetonitrile	0.5	0.02	96.0
MIP- γ_2 , 1mM D ₅ in acetonitrile	0.5	0.009	98.2
MIP- γ_3 , 1mM D ₃ in acetonitrile	0.5	0.002	99.7
MIP- γ_3 , 1mM D ₃ in 95% acetonitrile	0.5	0.06	89.7
MIP- γ_3 , 1mM D ₄ in acetonitrile	0.5	0.0	100
MIP- γ_3 , 1mM D ₄ in 95% acetonitrile	0.5	0.07	85.7
MIP- γ_3 , 1mM D ₅ in acetonitrile	0.5	0.001	97.2
MIP- γ_3 , 1mM D ₅ in 95% acetonitrile	0.5	0.02	97.0
NIP- γ , 1mM D ₃ in acetonitrile	0.5	0.01	97.6
NIP- γ , 1mM D ₃ in 95% acetonitrile	0.5	0.04	92.3
NIP- γ , 1mM D ₄ in acetonitrile	0.5	0.05	90.2
NIP- γ , 1mM D ₄ in 95% acetonitrile	0.5	0.06	87.3
NIP- γ , 1mM D ₅ in acetonitrile	0.5	0.0	100.0
NIP- γ , 1mM D ₅ in 95% acetonitrile	0.5	0.04	92.5

¹ % of free (unbound) analyte (average value).

S11. Polymer Characterization

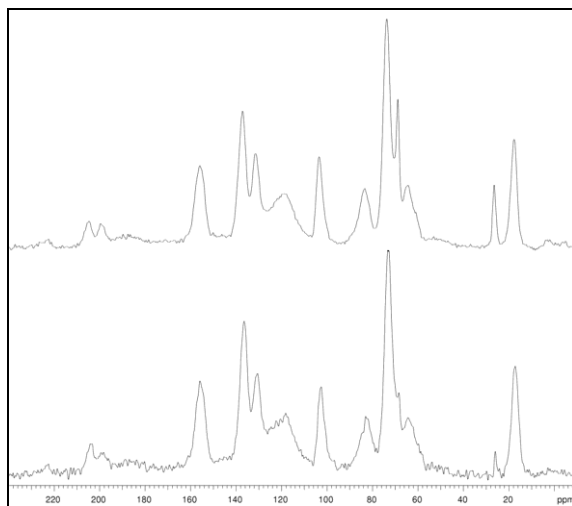


Figure S1: ^{13}C CP MAS NMR of MIP- β after its preparation (bottom), and after the extensive wash to restore its activity (top).