Electronic Supplementary Material (ESI) for ChemComm.

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1 General Information

All reagents and deuterated solvents were purchased from commercial suppliers and used without further purification. HPLC solvents and deuterated solvent were further dried over 4 Å molecular sieves and treated with silver foil to remove chloride anions. Mono-functionalized bambus[6]uril was prepared according to previously published procedure[1].

NMR spectra were recorded on a Bruker Avance III 300, Bruker Avance III 500, and MHz spectrometer. Chemical shifts (in ppm) are referenced to residual solvent peaks of deuterated solvent. Standard abbreviations for multiplicity are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, and br = broad.

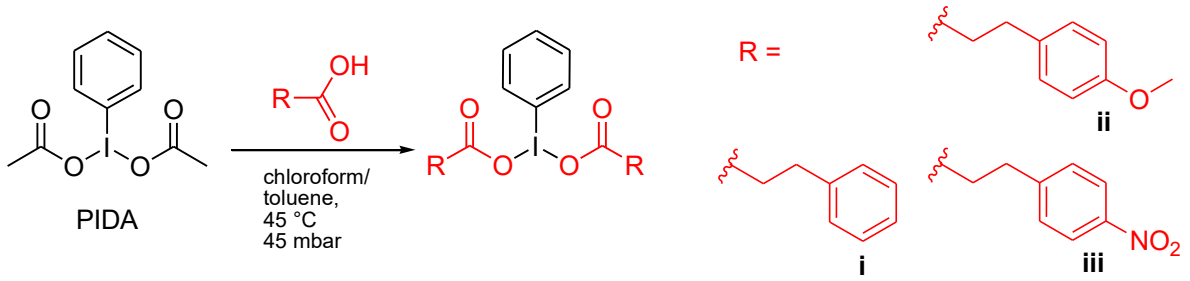
HRMS analysis was recorded on Agilent 6224 Accurate-Mass TOF LC-MS. Samples were ionized by electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI).

[1] Maršálek, K.; Šindelář, V. Monofunctionalized Bambus[6]Urils and Their Conjugates with Crown Ethers for Liquid–Liquid Extraction of Inorganic Salts. *Organic Letters* **2020**, *22* (4), 1633–1637

2 Synthetic Procedures

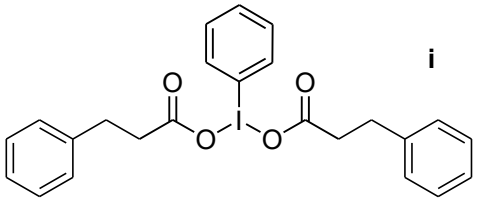
2.1 Preparation of (bis(acyloxy)iodo)benzenes

Acoording to Scheme S 1, (diacetoxyiodo)benzene (2 equiv.) and the corresponding acid (1 equiv.) were dissolved in chloroform:toluene (1:1) mixture, and the volatiles (i.e. solvent and acetic acid) were azeotropically removed by rotary evaporation with toluene at 45 °C.



Scheme S 1. Preparation of (bis(acyloxy)iodo)benzenes.

2.1.1 Preparation of i

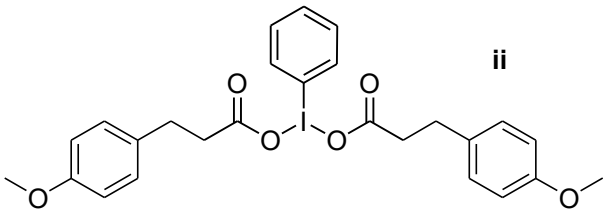


$C_{24}H_{23}IO_4$
Mol. Wt.: 502.34

According to the literature procedure,[2] 3-phenylpropionic acid (107.5 mg, 0.72 mmol) and (diacetoxyiodo)benzene (115.3 mg, 0.36 mmol) were dissolved in chloroform/toluene mixture (1:1, 5 mL) and the volatiles removed azeotropically by rotary evaporator with toluene (45°C, 45 mbar, 5 times). The product contained 3-phenylpropionic acid (≈ 6 %), and was used in subsequent reactions without further purification. Yield: 163 mg (90 %)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.28 – 7.13 (m, 10H), 2.88 (t, J = 7.7 Hz, 4H), 2.58 (t, J = 7.7 Hz, 4H).

2.1.2 Preparation of ii

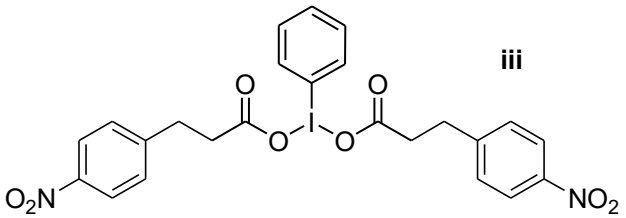


$C_{26}H_{27}IO_6$
Mol. Wt.: 562.39

3-(4-methoxyphenyl)propionic acid (111.9 mg, 0.62 mmol) and (diacetoxyiodo)benzene (100 mg, 0.31 mmol) were dissolved in chloroform/toluene mixture (1:1, 5 mL) and the volatiles removed azeotropically by rotary evaporator with toluene (45°C, 45 mbar, 15 times). The product contained 3-(4-methoxyphenyl)propionic acid (≈ 7 %), and was used in subsequent reactions without further purification. Yield: 148 mg (85 %)

^{1}H NMR (300 MHz, CDCl3) δ 7.94 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.05 (d, J = 8.5 Hz, 4H), 6.79 (d, J = 8.6 Hz, 4H), 3.78 (s, 6H), 2.81 (t, J = 7.6 Hz, 4H), 2.54 (t, J = 7.6 Hz, 4H).

2.1.3 Preparation of **iii**



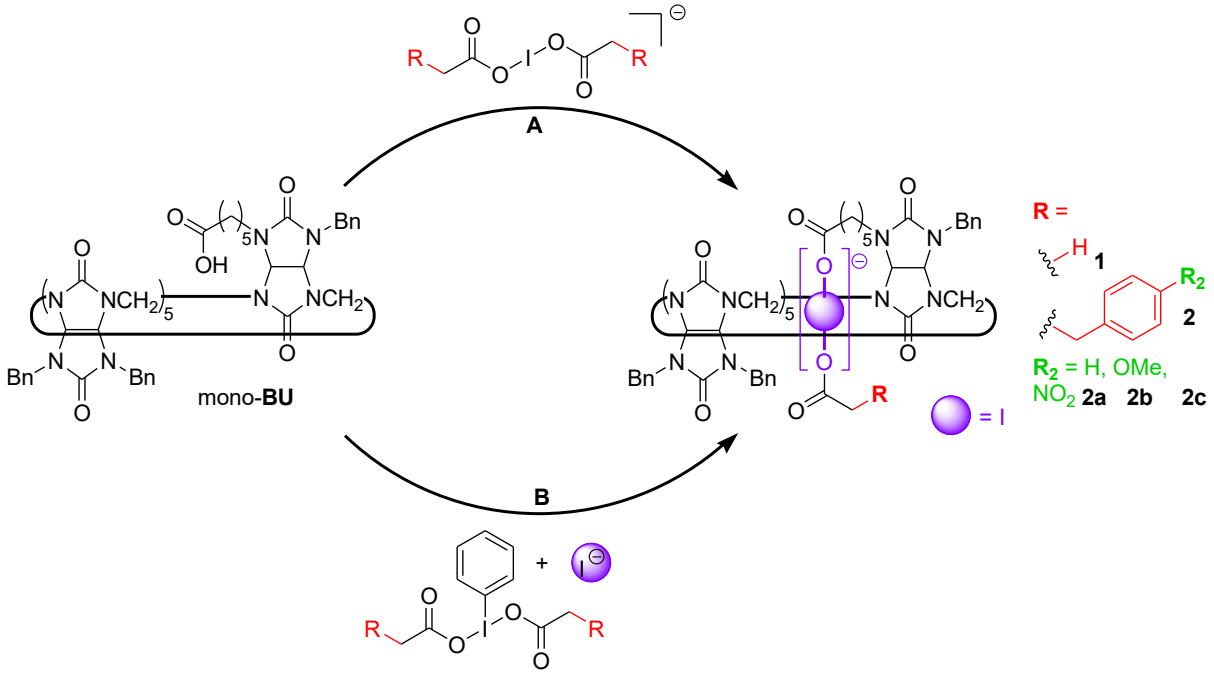
$C_{24}H_{21}IN_2O_8$
Mol. Wt.: 592.34

3-(4-nitrophenyl)phenylpropionic acid (121.2 mg, 0.62 mmol) and (diacetoxyiodo)benzene (100 mg, 0.31 mmol) were dissolved in chloroform/toluene mixture (1:1, 5 mL) and the volatiles removed azeotropically by rotary evaporator with toluene (45°C, 45 mbar, 15 times). The product contained 3-(4-nitrophenyl)propionic acid (≈ 6 %), and was used in subsequent reactions without further purification. Yield: 165 mg (90 %)

^{1}H NMR (300 MHz, CDCl3) δ 8.08 (d, J = 8.5 Hz, 4H), 7.95 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.27 (d, J = 8.5 Hz, 4H), 2.96 (t, J = 7.3 Hz, 4H), 2.62 (t, J = 7.3 Hz, 4H).

2.2 Preparation of [1]rotaxanes

[1]rotaxanes could be prepared in two different ways shown in Scheme S 2, *in situ* from the isolated iodate(I) axle or from the iodate(III) axle precursors. Due to its simplicity, without needing to isolate the iodate(I) axles, route B involving iodate(III) axle precursors was used when isolating [1]rotaxanes. The known mono-**BU**[1] and the iodate(I) axle[2] precursors were prepared according to published procedures.

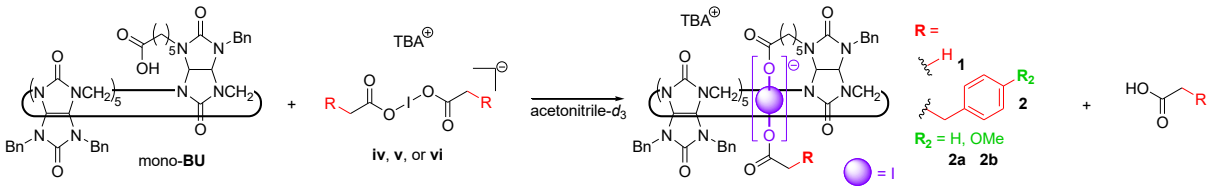


Scheme S 2. Different approaches to [1]rotaxane synthesis.

[2] Kandrnálová, M.; Kokan, Z.; Havel, V.; Nečas, M.; Šindelář, V. Hypervalent Iodine Based Reversible Covalent Bond in Rotaxane Synthesis. *Angew. Chem. Int. Ed.* **2019**, *58* (50), 18182–18185.

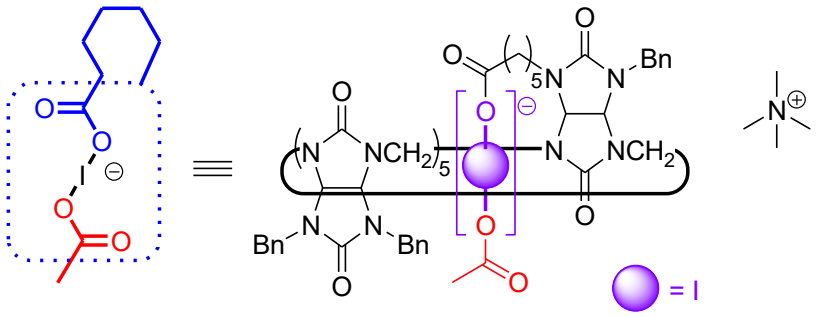
2.2.1 *In situ* [1]rotaxane Preparation

Rotaxanes **1**, **2a**, and **2b** could be prepared quantitatively *in situ* after just a few minutes upon adding to the mono-**BU** (5 mg, 2.5 µmol) a solution (0.5 mL, 5 mM, 1 equiv.) of tetrabutylammonium iodate(I) precursors (**iv**, **v**, and **vi** respectively) in acetonitrile-d_3. The obtained spectra were in excellent agreement with the spectra of isolated [1]rotaxanes (slight discrepancies in chemical shifts < 0.01 ppm were evident, likely due to the presence of an acid from the *in situ* preparation). The **2c** could not be prepared in this way because we could not obtain its iodate(I) precursor in sufficient purity.



Scheme S 3. The *in situ* formation of [1]rotaxanes.

2.2.2 Preparation of 1



Mono-**BU** (50.4 mg, 0.025 mmol) and and TMAI (5.0 mg, 0.025 mmol) were weighed in a vial and evacuated, flushed with argon 5 times. The same was done for the (Diacetoxyiodo)benzene (9.8 mg 0.030 mmol) in a separate vial, and 0.6 mL of dry $CDCl_3$ was added and transfered with a double-tipped needle to the vial containing mono-**BU** and TMAI. The solution was stirred at room temperature under argon atmosphere overnight. The reaction was quenched by adding two drops of dry diethyl ether. Solution was transferred into 12 mL of dra diethyl ether, resulting in slightly yellow precipitate formation, which was separated using 5 cycles of centrifugation (8000 rpm, 5 min) and washing with dry diethyl ether, and lastly dried under high vacuum.

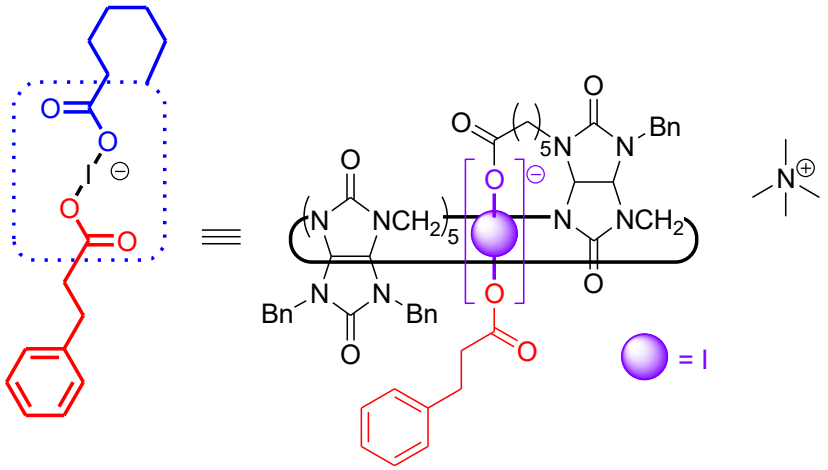
Yield: 53 mg (93 %)

^{1}H NMR (500 MHz Acetonitrile-d_3) δ 7.38 – 7.11 (m, 55H), 5.93 (dd, J = 29.4, 8.5 Hz, 2H), 5.71 (d, J = 8.8 Hz, 2H), 5.64 – 5.56 (m, 3H), 5.50 (dd, J = 13.4, 8.6 Hz, 2H), 5.42 (d, J = 8.5 Hz, 1H), 5.31 (dd, J = 16.2, 8.5 Hz, 2H), 5.04 – 4.35 (m, 24H), 4.29 – 4.04 (m, 12H), 3.83 (ddd, J = 14.1, 7.5, 4.0 Hz, 1H), 3.67 – 3.58 (m, 1H), 3.06 (s, 12H), 1.72 – 1.54 (m, 3H), 1.49 – 1.39 (m, 1H), 1.30 (dt, J = 12.7, 6.5 Hz, 2H), 1.17 – 1.10 (m, 1H), 1.07 (s, 3H), 0.92 – 0.82 (m, 1H).

^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 178.4, 175.9, 161.5, 161.3, 161.1, 161.1, 161.0, 160.7, 159.7, 159.6, 159.6, 159.5, 159.5, 159.5, 140.5, 140.2, 140.1, 140.1, 140.1, 139.9, 129.5, 129.4, 129.4, 129.4, 129.3, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 118.3, 71.3, 71.2, 71.1, 71.0, 70.9, 70.9, 70.7, 70.4, 70.2, 68.5, 56.3, 56.2, 48.7, 48.7, 48.7, 48.6, 48.5, 48.5, 48.4, 34.8, 25.7, 25.1, 20.7, 1.3.

(–)ESI-HRMS (m/z): calculated mass 2214.7925; observed mass 2214.7967.

2.2.3 Preparation of **2a**



Mono-**BU** (100.9 mg, 0.050 mmol) and and TMAI (10 mg, 0.050 mmol) were weighed in a vial and evacuated, flushed with argon 5 times. The same was done for **i** (30 mg with 95% purity, 0.060 mmol) in a separate vial, and 0.6 mL of dry $CDCl_3$ was added and transfered with a double-tipped needle to the vial containing mono-**BU** and TMAI. The solution was stirred at room temperature under argon atmosphere overnight. The reaction was quenched by adding two drops of dry diethyl ether. Solution was transferred into 12 mL of dra diethyl ether, resulting in slightly yellow precipitate formation, which was separated using 5 cycles of centrifugation (8000 rpm, 5 min) and washing with dry diethyl ether, and lastly dried under high vacuum. The final product contained small amounts (≈ 6 %) of 3-phenylpropionic acid.

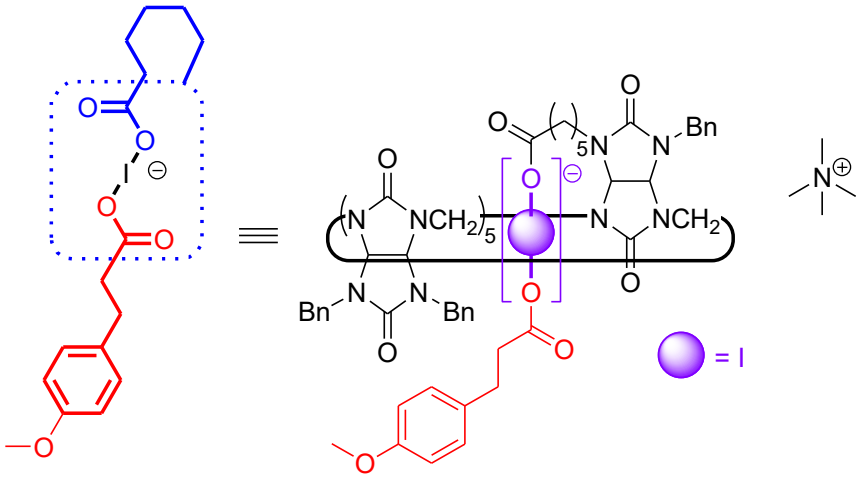
Yield: 109 mg (92 %)

^{1}H NMR (500 MHz Acetonitrile-d_3) δ 7.35 (d, J = 7.4 Hz, 2H), 7.32 – 7.13 (m, 55H), 7.05 (d, J = 7.4 Hz, 2H), 5.96 (dd, J = 8.5, 4.7 Hz, 2H), 5.75 (dd, J = 10.8, 8.5 Hz, 2H), 5.70 – 5.66 (m, 2H), 5.63 (d, J = 8.4 Hz, 1H), 5.58 (d, J = 8.6 Hz, 1H), 5.55 (d, J = 8.5 Hz, 1H), 5.45 (d, J = 8.7 Hz, 1H), 5.39 (d, J = 8.5 Hz, 1H), 5.22 (d, J = 8.3 Hz, 1H), 5.00 – 4.32 (m, 24H), 4.29 – 3.98 (m, 12H), 3.82 (d, J = 25.6 Hz, 1H), 3.63 (d, J = 25.2 Hz, 1H), 3.05 (s, 12H), 2.43 (d, J = 16.5 Hz, 2H), 1.86 (t, J = 16.6 Hz, 2H), 1.66 (m, 1H), 1.56 (m, 2H), 1.42 (m, 2H), 1.32 (m, 2H), 1.13 (m, 1H), 0.90 (m, 1H).

^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 178.4, 177.9, 161.5, 161.3, 161.1, 160.6, 159.7, 159.6, 159.5, 159.5, 142.1, 141.8, 140.5, 140.2, 140.2, 140.1, 140.1, 139.9, 129.5, 129.5, 129.4, 129.4, 129.4, 129.4, 129.3, 129.3, 129.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 127.0, 118.3, 71.3, 71.3, 71.3, 71.1, 71.0, 71.0, 71.0, 70.8, 70.7, 70.6, 70.5, 68.4, 67.1, 56.3, 56.2, 49.0, 48.9, 48.8, 48.7, 48.6, 48.6, 48.5, 48.4, 48.4, 48.2, 43.9, 36.4, 34.5, 33.0, 25.6, 25.0, 24.5, 23.9, 1.8, 1.6, 1.5, 1.3, 1.2, 1.0, 0.8.

(–)ESI-HRMS (m/z): calculated mass 2303.8364; observed mass 2303.8352.

2.2.4 Preparation of **2b**



Mono-**BU** (50 mg, 0.025 mmol) and and TMAI (5 mg, 0.025 mmol) were weighed in a vial and evacuated, flushed with argon 5 times. The same was done for **ii** (13.8 mg with 93% purity, 0.025 mmol) in a separate vial, and 0.6 mL of dry $CDCl_3$ was added and transfered with a double-tipped needle to the vial containing mono-**BU** and TMAI. The solution was stirred at room temperature under argon atmosphere overnight. The reaction was quenched by adding two drops of dry diethyl ether. Solution was transferred into 12 mL of dra diethyl ether, resulting in slightly yellow precipitate formation, which was separated using 5 cycles of centrifugation (8000 rpm, 5 min) and washing with dry diethyl ether, and lastly dried under high vacuum. The final product contained small amounts (≈ 7 %) of 3-phenylpropionic acid.

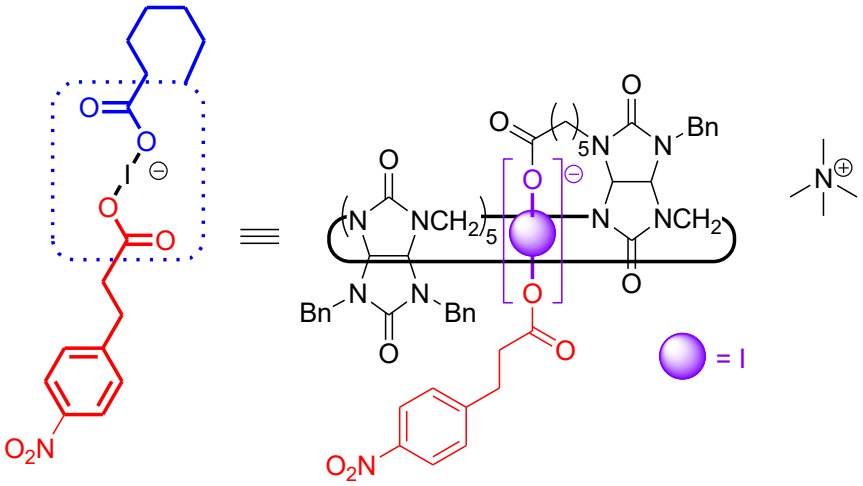
Yield=54.2 mg (90%)

^{1}H NMR (500 MHz Acetonitrile-d_3) δ 7.36 – 7.09 (m, 12H), 6.96 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.96 (dd, J = 8.5, 1.2 Hz, 2H), 5.74 (t, J = 8.8 Hz, 2H), 5.69 – 5.66 (m, 2H), 5.63 (d, J = 8.3 Hz, 1H), 5.58 (d, J = 8.7 Hz, 1H), 5.53 (d, J = 8.6 Hz, 1H), 5.44 (d, J = 8.6 Hz, 1H), 5.39 (d, J = 8.5 Hz, 1H), 5.23 (d, J = 8.3 Hz, 1H), 4.98 – 4.32 (m, 24H), 4.28 – 3.98 (m, 12H), 3.82 (m, 1H), 3.74 (s, 3H), 3.63 (m, 0H), 3.07 – 3.05 (m, 1H), 2.39 – 2.33 (t, J = 8.61, 3H), 1.86 – 1.81 (t, J = 8.61, 3H), 1.68 – 1.63(m, 1H), 1.58 –1.53 (m, 2H), 1.48 –1.43 (m, 1H), 1.29 –1.25 (m, 1H), 1.14 – 1.09 (m, 2H), 0.93 –0.87 (m, 1H).

^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 178.4, 177.3, 161.5, 161.0, 160.6, 159.9, 159.7, 150.4, 147.5, 140.6, 140.2, 140.1, 139.9, 130.5, 130.3, 129.4, 128.0, 127.9, 127.6, 127.2, 124.7, 124.4, 71.4, 71.2, 71.0, 70.7, 70.4, 68.5, 56.3, 48.9, 48.8, 48.7, 48.5, 48.4, 48.3, 48.2, 48.0, 44.0, 35.0, 34.5, 32.6, 31.4, 27.2, 25.6, 25.5, 25.0, 24.6, 1.3.

(–)ESI-HRMS (m/z): calculated mass 2334.8500; observed mass 2334.8469.

2.2.5 Preparation of **2c**



Mono-**BU** (50 mg, 0.025 mmol) and and TMAI (5 mg, 0.025 mmol) were weighed in a vial and evacuated, flushed with argon 5 times. The same was done for **iii** (14.6 mg with 94% purity, 0.025 mmol) in a separate vial, and 0.6 mL of dry $CDCl_3$ was added and transfered with a double-tipped needle to the vial containing mono-**BU** and TMAI. The solution was stirred at room temperature under argon atmosphere overnight. The reaction was quenched by adding two drops of dry diethyl ether. Solution was transferred into 12 mL of dra diethyl ether, resulting in slightly yellow precipitate formation, which was separated using 5 cycles of centrifugation (8000 rpm, 5 min) and washing with dry diethyl ether, and lastly dried under high vacuum. The final product contained small amounts (≈ 5 %) of 3-(4-nitrophenyl)propionic acid.

Yield: 55mg (90 %)

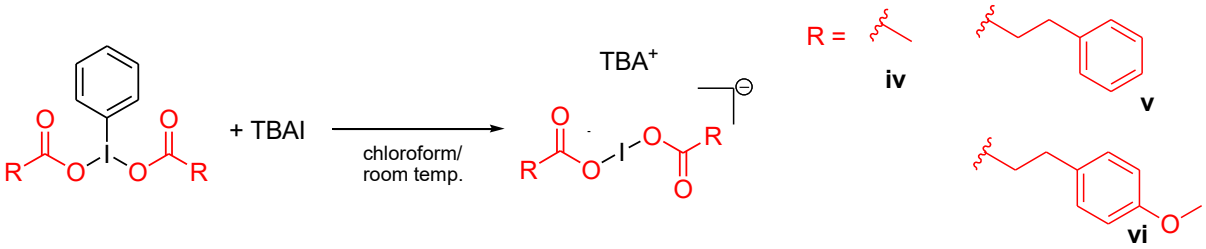
^{1}H NMR (500 MHz Acetonitrile-d_3) δ 8.14 (d, J = 8.7 Hz, 1H), 7.46 – 7.02 (m, 55H), 5.91 (dd, J = 16.6, 8.5 Hz, 2H), 5.70 – 5.64 (m, 4H), 5.62 (d, J = 8.4 Hz, 1H), 5.55 (d, J = 8.6 Hz, 1H), 5.49 (d, J = 8.5 Hz, 1H), 5.45–5.40 (m, 1H), 5.35 (d, J = 8.5 Hz, 1H), 5.20 (d, J = 8.3 Hz, 1H), 4.96 – 4.41 (m, 24H), 4.28 – 4.01 (m, 12H), 3.83–3.78 (m, 1H), 3.65–3.59 (m, 1H), 3.05 (s, 12H), 2.46 (t, J = 7.5 Hz, 1H), 1.82 (t, J = 7.6 Hz, 1H), 1.66 – 1.62 (m, 1H), 1.57 –1.52 (m, 2H), 1.43–1.38 (m, 1H), 1.35 – 1.22 (m, 2H), 1.16 – 1.10 (m, 1H), 0.92–0.86 (m, 1H).

^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 178.3, 177.3, 161.5, 161.3, 161.0, 161.0, 160.6, 159.9, 159.7, 159.7, 159.5, 159.4, 150.4, 147.5, 140.5, 140.5, 140.4, 140.2, 140.2, 140.1, 140.1, 139.9, 130.5, 130.3, 129.5, 129.4, 129.4, 129.4, 129.4, 129.3, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.2, 127.2, 124.6, 124.4, 118.3, 71.4, 71.3, 71.2, 71.1, 71.0, 70.9, 70.9, 70.7, 70.5, 70.4, 68.4, 56.3, 56.2, 56.2, 48.9, 48.8, 48.7, 48.7, 48.5, 48.5, 48.3, 48.3, 48.2, 48.0, 43.9, 35.0, 34.4, 32.6, 25.6, 25.0, 24.6.

(–)ESI-HRMS (m/z): calculated mass 2349.8245; observed mass 2349.8206.

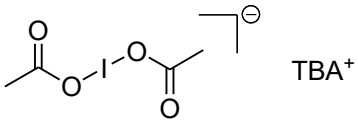
2.3 Preparation of bis(acyloxy)iodates(I)

Acoording to Scheme S 4, (diacyloxyiodo)benzene (1 equiv.) and tetrabutylammonium iodide (1 equiv.) were dissolved in chloroform-d_1, and the product precipitated with dry diethyl ether. For the isolation of compounds, TBA counter cation was used instead TMA, due to increased stability of the products. The nitro derivative could not be prepared due to decomposition, regardless of the counterion.



Scheme S 4. Preparation of bis(acyloxy)iodates(I).

2.3.1 Preparation of **iv**

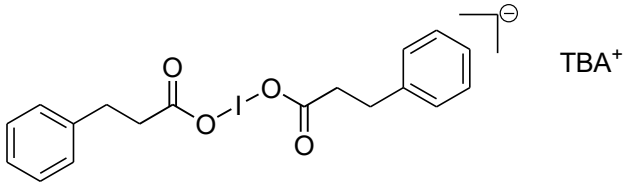


According to the literature procedure,[2] (diacetoxyiodo)benzene (100 mg , 0.31 mmol) and tetrabutylammonium iodide (137.61 mg 0.37 mmol) were weighted in separate vials . evacuated and flushed with argon 5 times. TBAI was dissolved with 1 ml of $CDCl_3$ dry and transfer with a double-tipped needle to (Bis[3-phenylpropionic]iodo)benzene vial. The solution was stirred at room temperature under argon atmosphere overnight. The reaction was quenched by adding 1 mL of dry diethyl ether, and the solution was transferred to 12 mL of dry diethyl ether, when slightly yellow precipitate formed. The precipitate was was isolated using 5 cycles of centrifugation (8000 rpm, 5 min). washing with dry diethyl ether, and dried under high vacuum. The spectra conform to the literature.

Yield: 145 mg (96 %)

^{1}H NMR (300 MHz Acetonitrile-d_3) δ 3.13 – 3.02 (m, 8H), 1.82 (s, 6H), 1.59 (m, J = 7.9 Hz, 8H), 1.43 – 1.26 (m, 9H), 0.97 (t, J = 7.3 Hz, 12H).

2.3.2 Preparation of **v**

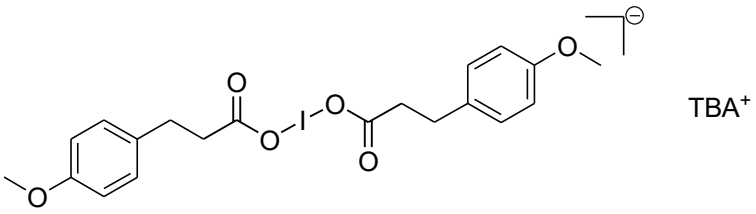


According to the literature procedure,[2] **i** (100 mg with 94% purity, 0.19 mmol) and tetrabutylammonium iodide, TBAI, (89.81 mg 0.20 mmol) were weighted in separate vials . evacuated and flushed with argon 5 times. TBAI was dissolved with 1 ml of $CDCl_3$ dry and transfer with a double-tipped needle to (Bis[3-phenylpropionic]iodo)benzene vial. The solution was stirred at room temperature under argon atmosphere overnight. The reaction was quenched by adding 1 mL of dry diethyl ether, and the solution was transferred to 12 mL of dry diethyl ether, when slightly yellow precipitate formed. The precipitate was was isolated using 5 cycles of centrifugation (8000 rpm, 5 min). washing with dry diethyl ether, and dried under high vacuum. The spectra conform to the literature.

Yield: 119 mg (94%)

^{1}H NMR (300 MHz Acetonitrile-d_3) δ 7.22 (m, 10H), 3.13 – 3.02 (m, 8H), 2.79 (t, J = 7.8 Hz, 4H), 2.41 (t, J = 7.8 Hz, 4H), 1.67 – 1.52 (m, 8H), 1.34 (m, J = 7.4 Hz, 9H), 0.97 (m, J = 7.3 Hz, 12H).

2.3.3 Preparation of **vi**



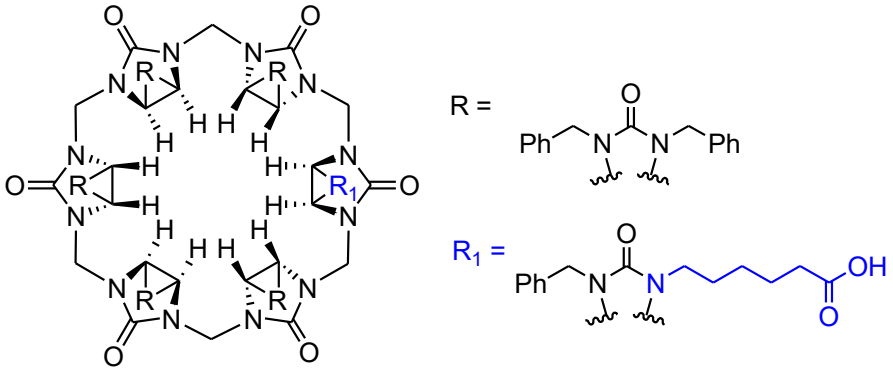
According to the literature procedure,[2] **ii** (50 mg with 93% purity, 0.084 mmol) and tetrabutylammonium iodide, TBAI, (37.2 mg 0.100 mmol) were weighted in separate vials . evacuated and flushed with argon 5 times. TBAI was dissolved with 1 ml of $CDCl_3$ dry and transfer with a double-tipped needle to (Bis[3-phenylpropionic]iodo)benzene vial. The solution was stirred at room temperature under argon atmosphere overnight. The reaction was quenched by adding 1 mL of dry diethyl ether, and the solution was transferred to 12 mL of dry diethyl ether, when slightly yellow precipitate formed. The precipitate was was isolated using 5 cycles of centrifugation (8000 rpm, 5 min). washing with dry diethyl ether, and dried under high vacuum.

Yield: 54 mg (89 %)

^{1}H NMR (500 MHz Acetonitrile-d_3) δ 7.11 (d, J = 8.6 Hz, 4H), 6.81 (d, J = 8.7 Hz, 4H), 3.74 (s, 6H), 3.11 – 3.05 (m, 8H), 2.72 (t, J = 7.8 Hz, 4H), 2.37 (t, J = 7.8 Hz, 4H), 1.60 (dt, J = 16.1, 7.8 Hz, 12H), 1.36 (h, J = 7.4 Hz, 8H), 0.97 (t, J = 7.4 Hz, 12H).

^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 177.3, 158.9, 135.5, 130.3, 114.6, 101.0, 94.3, 59.4, 55.8, 37.0, 32.5, 24.3, 20.4, 13.8, 1.3.

2.4 Preparation of mono-**BU**



According to previously published procedure,[1] mono-functionalized bambus[6]uril was prepared from 2,4-dibenzylglycoluril (33.78 g, 104.8 mmol, 0.98 eq), mono-benzylhexanoicglycoluril acid (0.741 g, 2.14 mmol, 0.02 eq), paraformaldehyde (4.01 g, 133.7 mmol, 1.25 eq.) and dioxane (150 mL). A round bottomed flask was charged with all the reagents while stirring. Concentrated sulphuric acid (4.5 mL) was added dropwise. Then, the reaction mixture was heated to 80 °C for 6 hours. After cooling to room temperature, diethyl-ether (300 mL) was added and the suspension was filtered. White precipitate was washed with diethyl-ether and then resuspended in a mixture of water (200 mL), methanol (200

mL) and aqueous ammonia (7.5 mL). This suspension was heated to reflux for 1 h. The suspension was filtered at room temperature and the solid was washed with diethyl-ether. This mixture of anion-free dodekabenzylbambus[6]uril and monofunctionalized bambusuril was separated by silica gel column chromatography with 2 % methanol in dichloromethane as the mobile phase. After the separation, the product was dissolved in dichloromethane (100 mL) and treated with trifluoroacetic acid (300 µl). The solution was washed with ultrapure water (100 mL) and evaporated in vacuo. The residue was dispersed in acetonitrile by sonication, filtered and washed three times with acetonitrile. After drying, a white solid was obtained. The spectra conform to the literature.

Yield: 2.13 g (49%)

^{1}H NMR (300 MHz DMSO-*d*) δ 11.99 (s, 1H), 7.31 – 7.16 (m, 55H), 5.23 – 5.12 (m, 12H), 4.74 – 4.45 (m, 24H), 4.21 – 4.11 (m, 10H), 3.53 – 3.44 (m, 2H), 2.18 (t, J = 7.3 Hz, 2H), 1.65 – 1.63 (m, 2H), 1.54 – 1.41 (m, 4H), 1.25 – 1.20 (m, 2H).

3 NMR Spectra

3.1 NMR spectrum of **i**

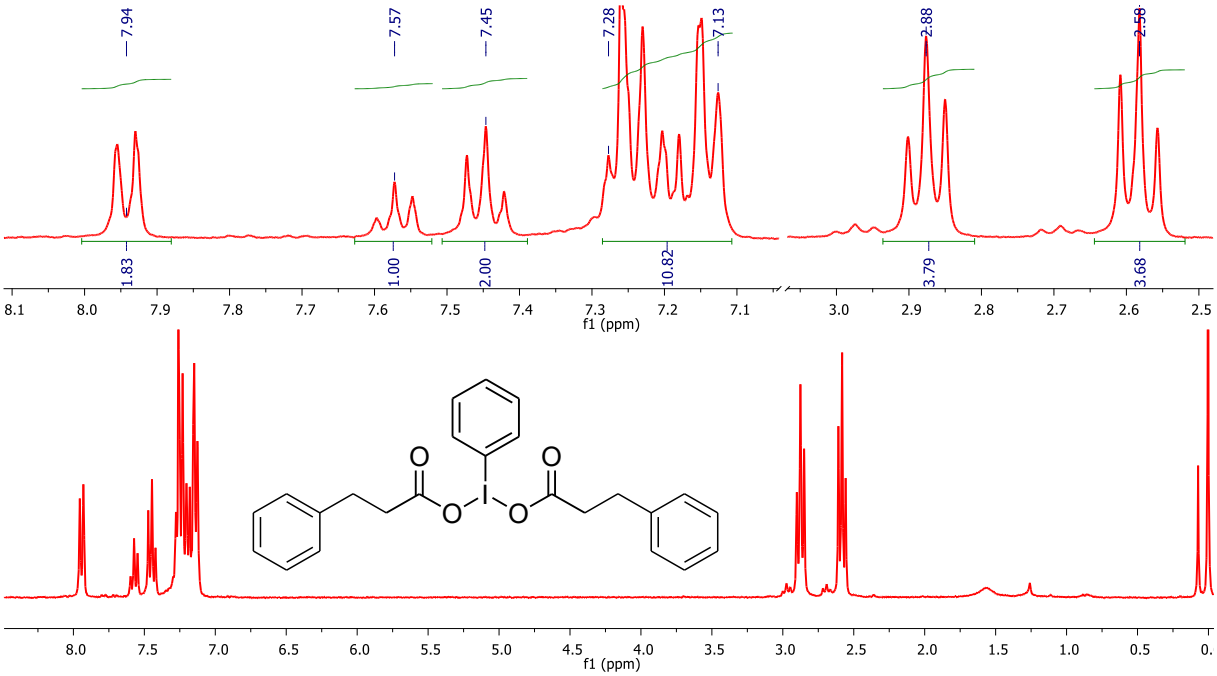


Figure S 1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **i**.

3.2 NMR spectrum of **ii**

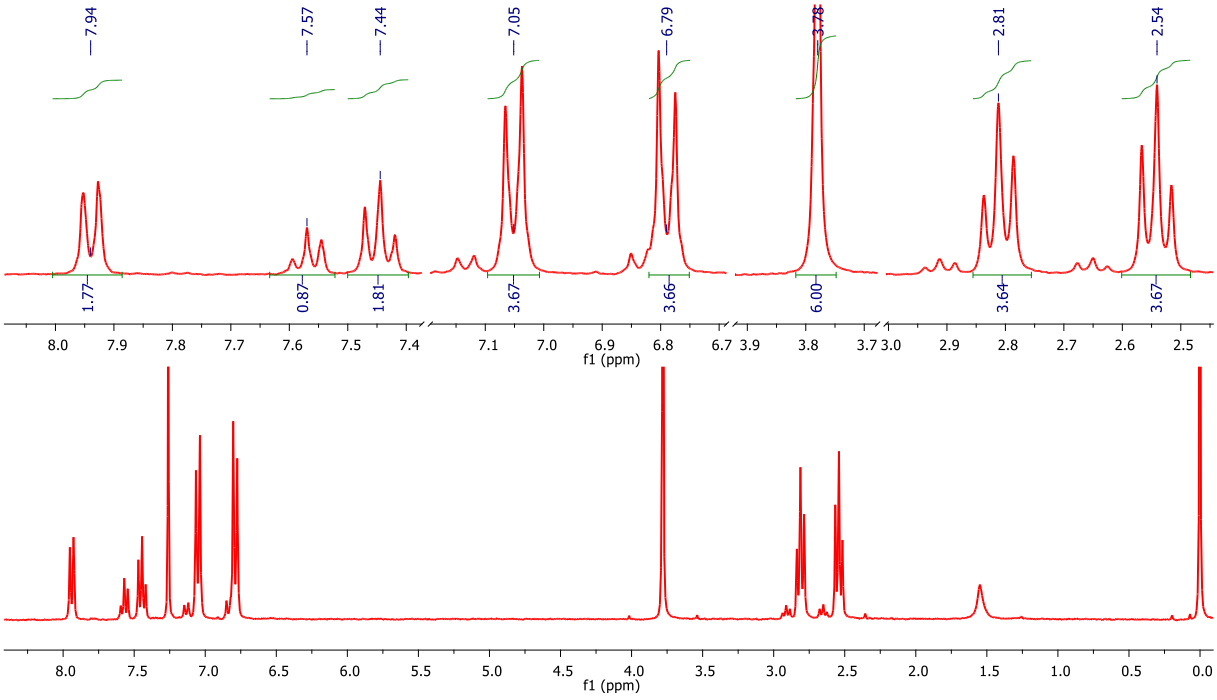


Figure S 2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **ii**.

3.3 NMR spectrum of **iii**

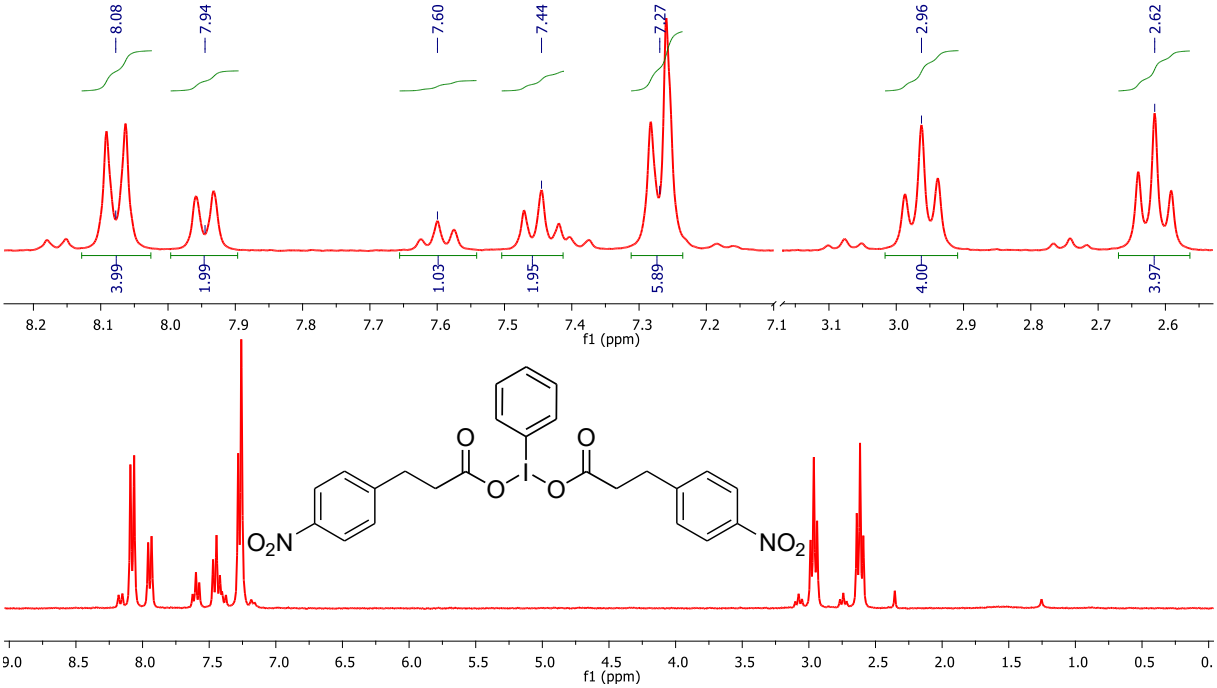


Figure S 3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **iii**.

3.4 NMR spectrum of **iv**

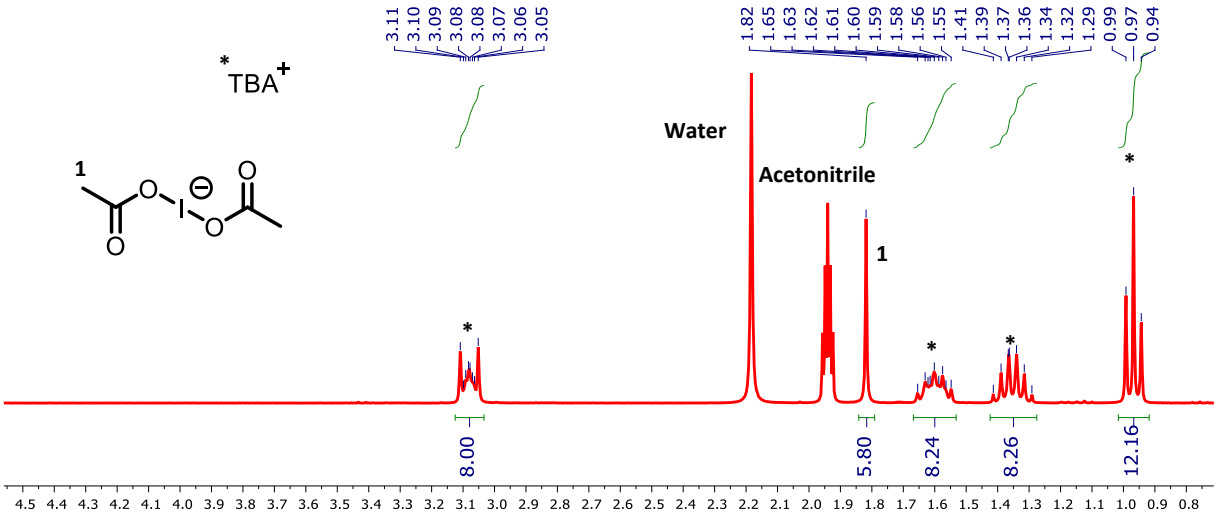


Figure S 4. ^{1}H NMR spectrum (300 MHz, CD_3CN, 298 K) of Tetrabutylammonium bis(acetoxy)iodate.

3.5 NMR spectrum of v

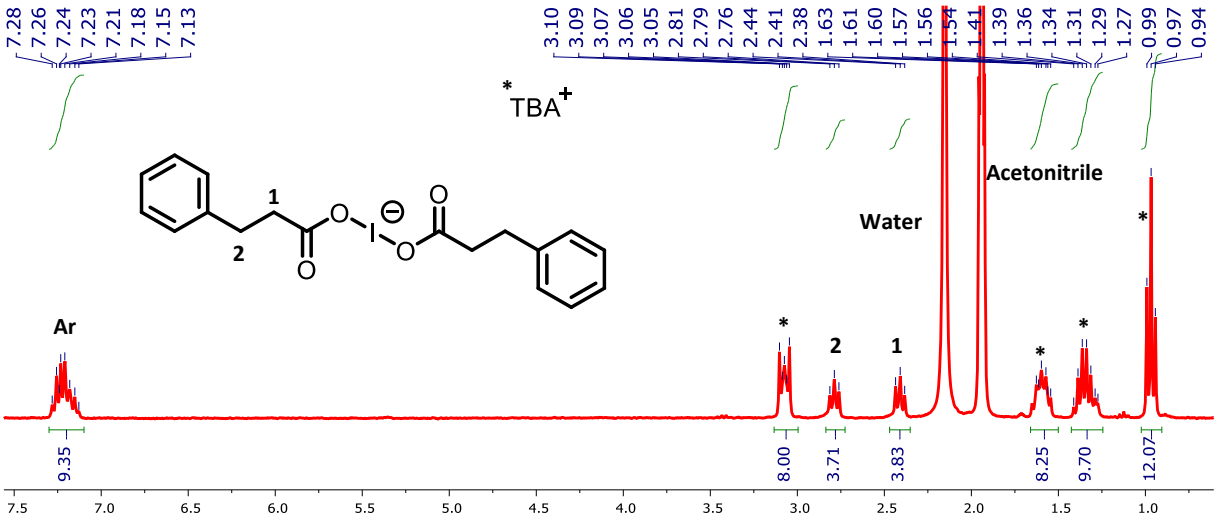


Figure S 5. ^{1}H NMR spectrum (300 MHz, CD_3CN, 298 K) of Tetrabutylammonium (Bis[3-phenylpropanoyloxy]iodate).

3.6 NMR spectra of vi

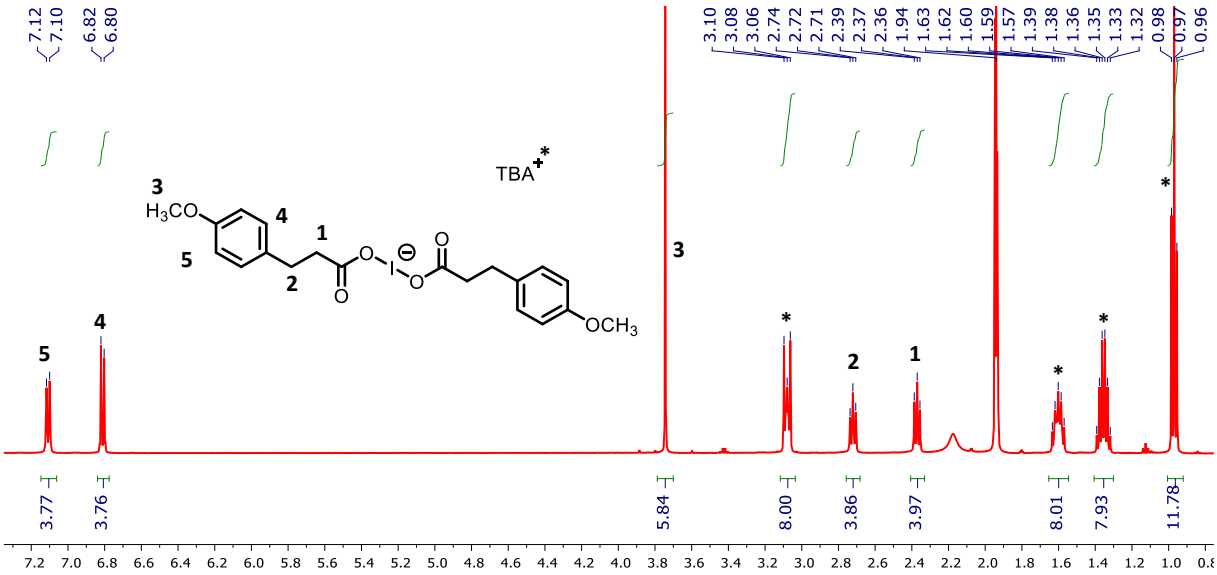


Figure S 6. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of Tetrabutylammonium Bis[3-(4-MetoxyPhenylpropanoyloxy)iodate.

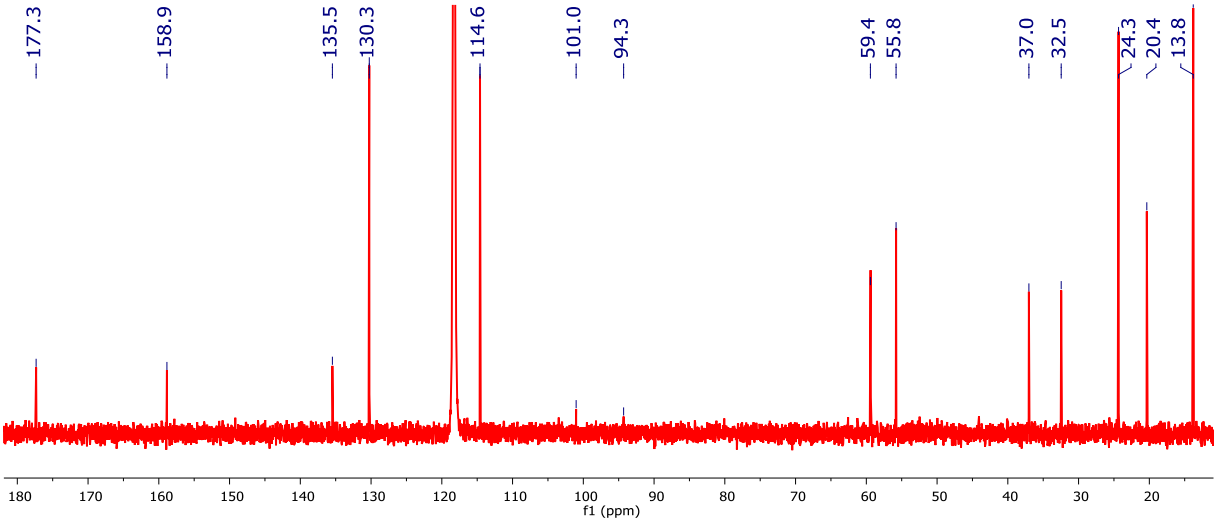


Figure S 7. ^{13}C NMR spectrum (500 MHz, CD_3CN, 298 K) of Tetrabutylammonium Bis[3-(4-MetoxyPhenylpropanoyloxy)iodate.

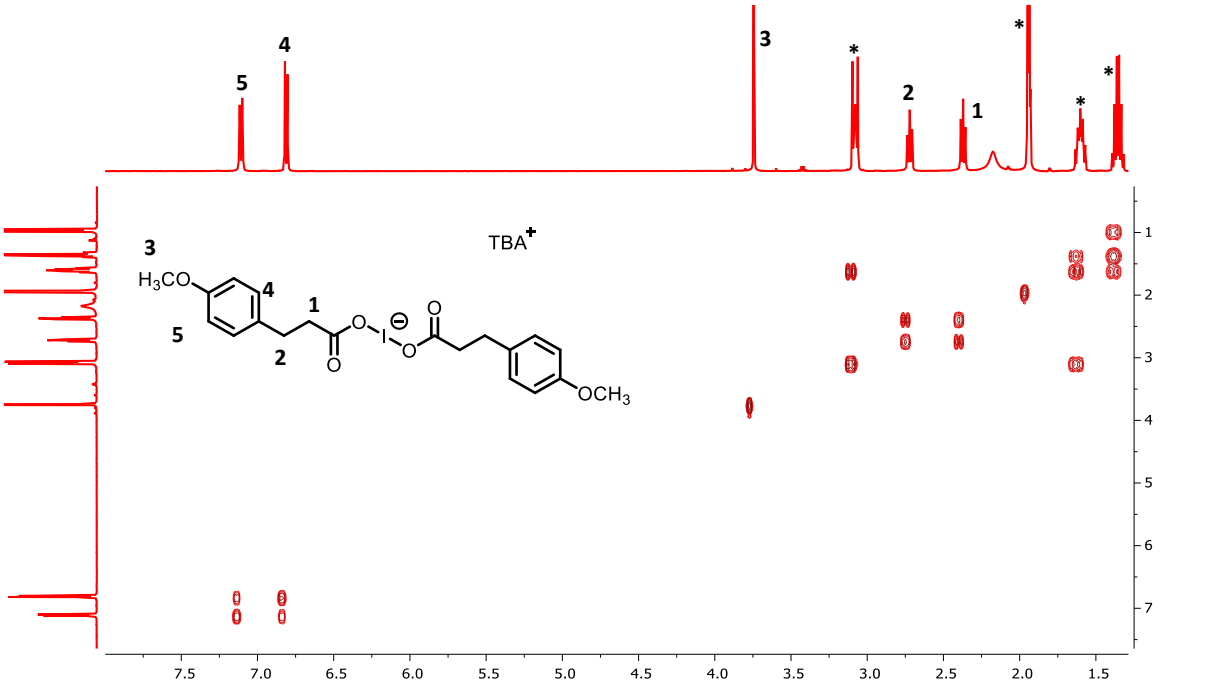


Figure S 8. COSY NMR spectrum (500 MHz, CD_3CN, 298) K of Tetrabutylammonium Bis[3-(4-MetoxyPhenylpropanoxy)iodate.

3.7 NMR spectrum of mono-**BU**

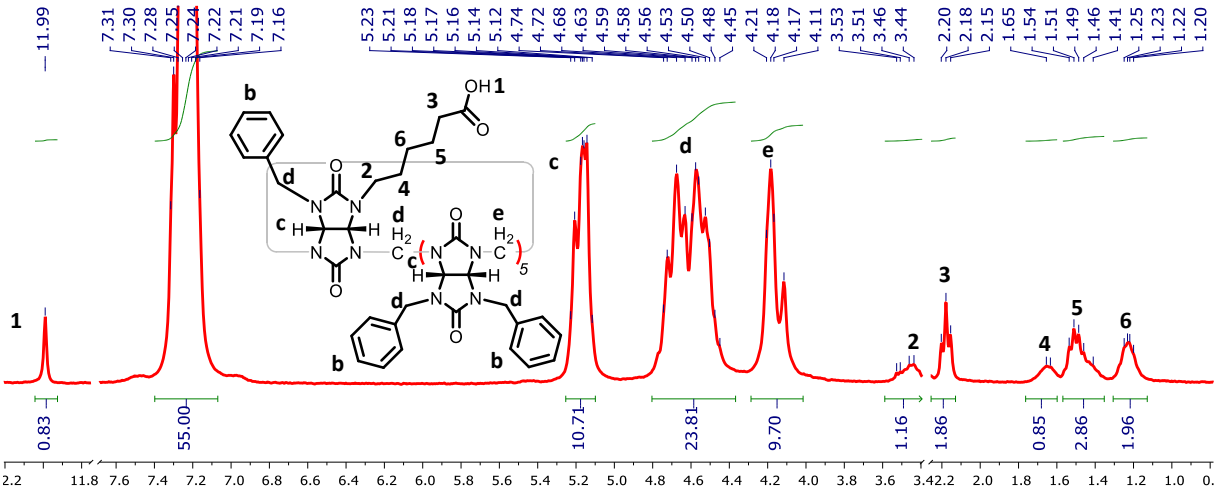


Figure S 9. ^{1}H NMR spectrum (300 MHz, DMSO, 298 K) of mono-functionalized bambus[6]uril.

3.8 NMR spectra of **1**

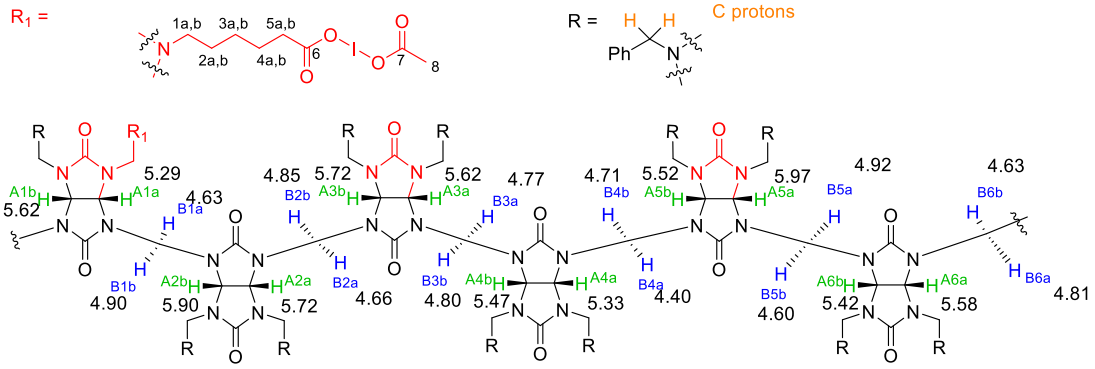


Figure S 10. Numbering scheme for the NMR spectra.

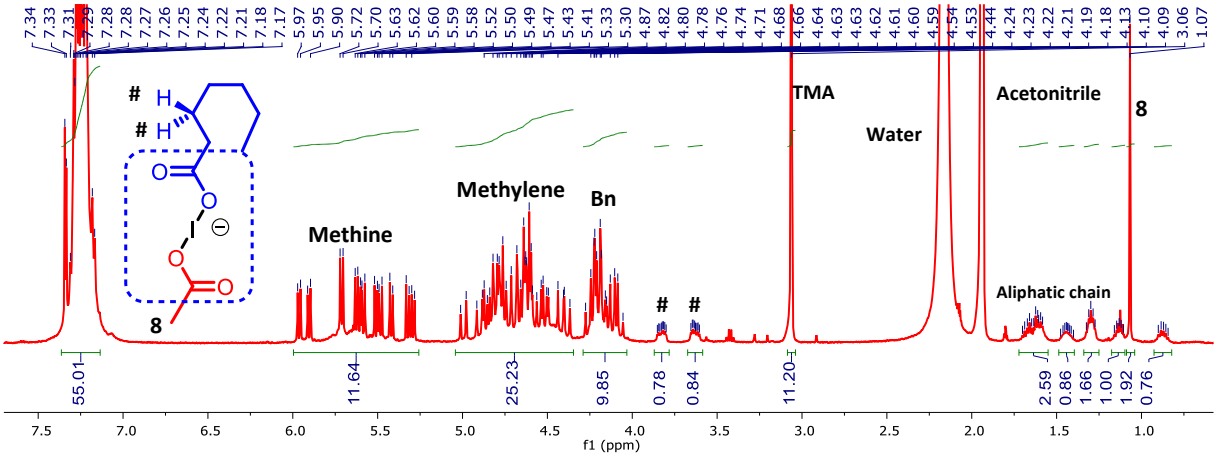


Figure S 11. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of **1**.

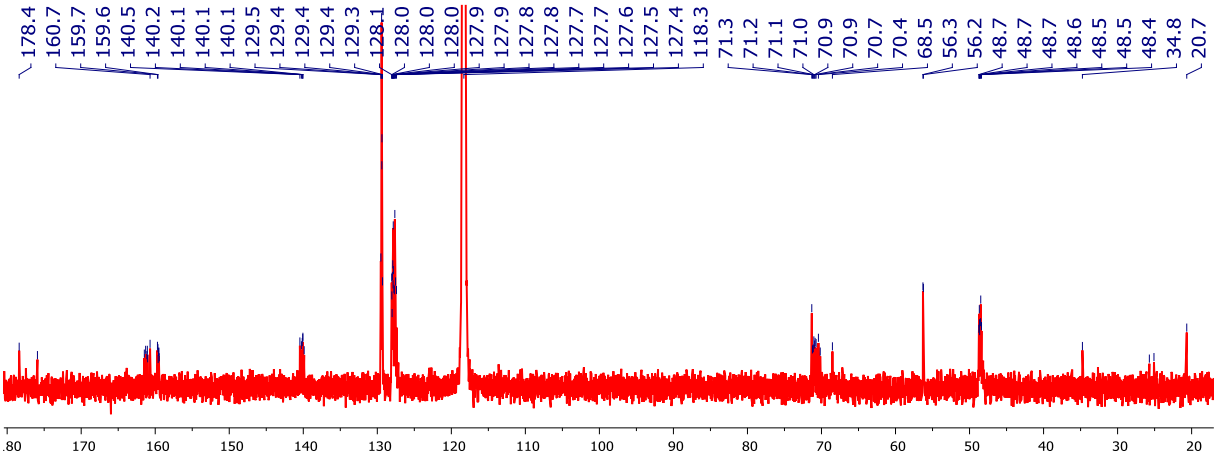


Figure S 12. ^{13}C NMR spectrum 500 MHz, CD_3CN, 298 K of **1**.

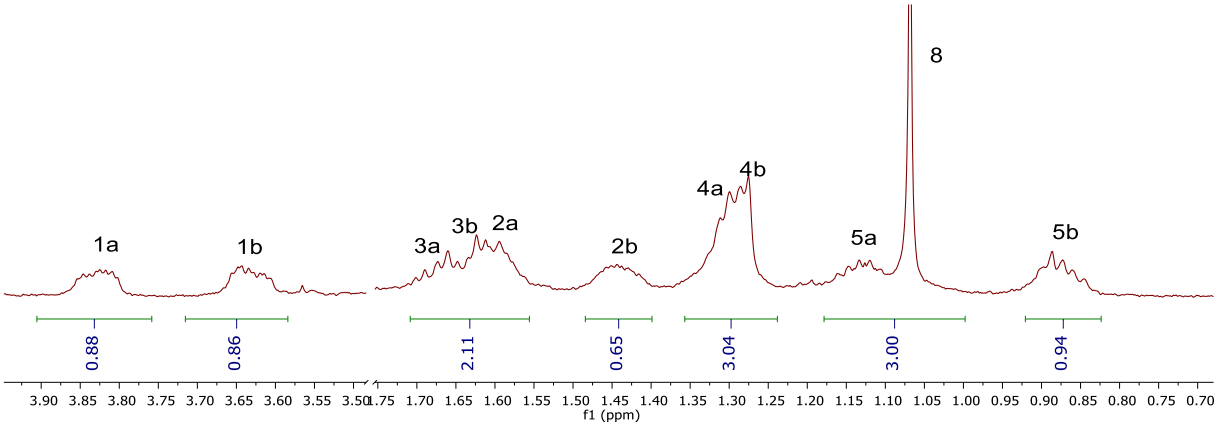


Figure S 13. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) intercept of **1**, showing aliphatic region.

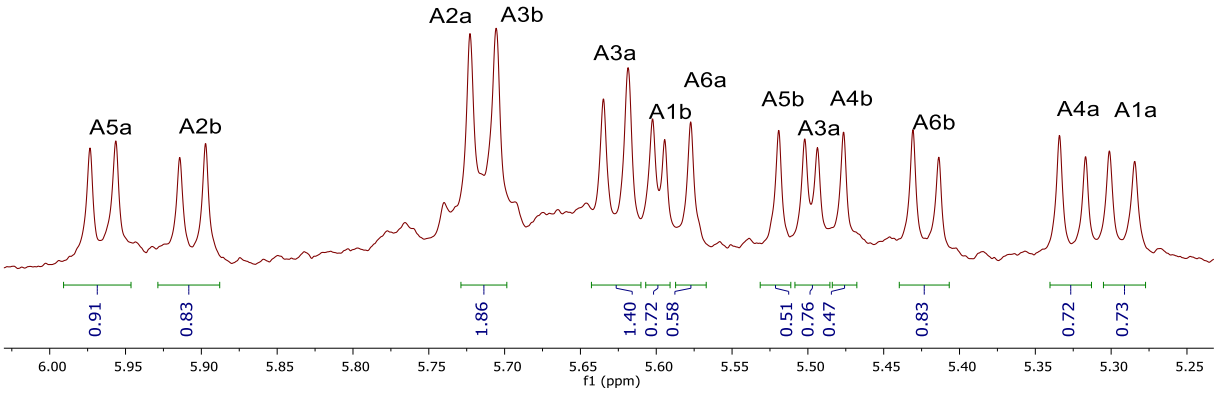


Figure S 14. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) intercept of **1**, showing methine proton region.

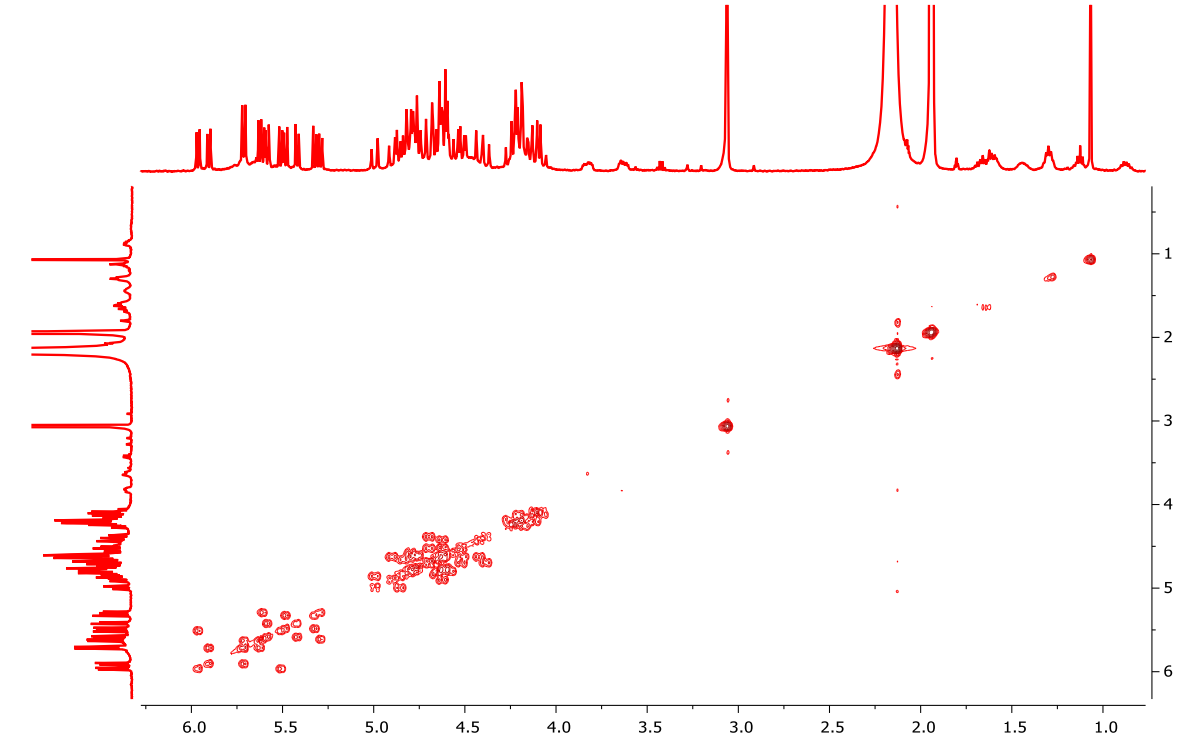


Figure S 15. COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of **1**.

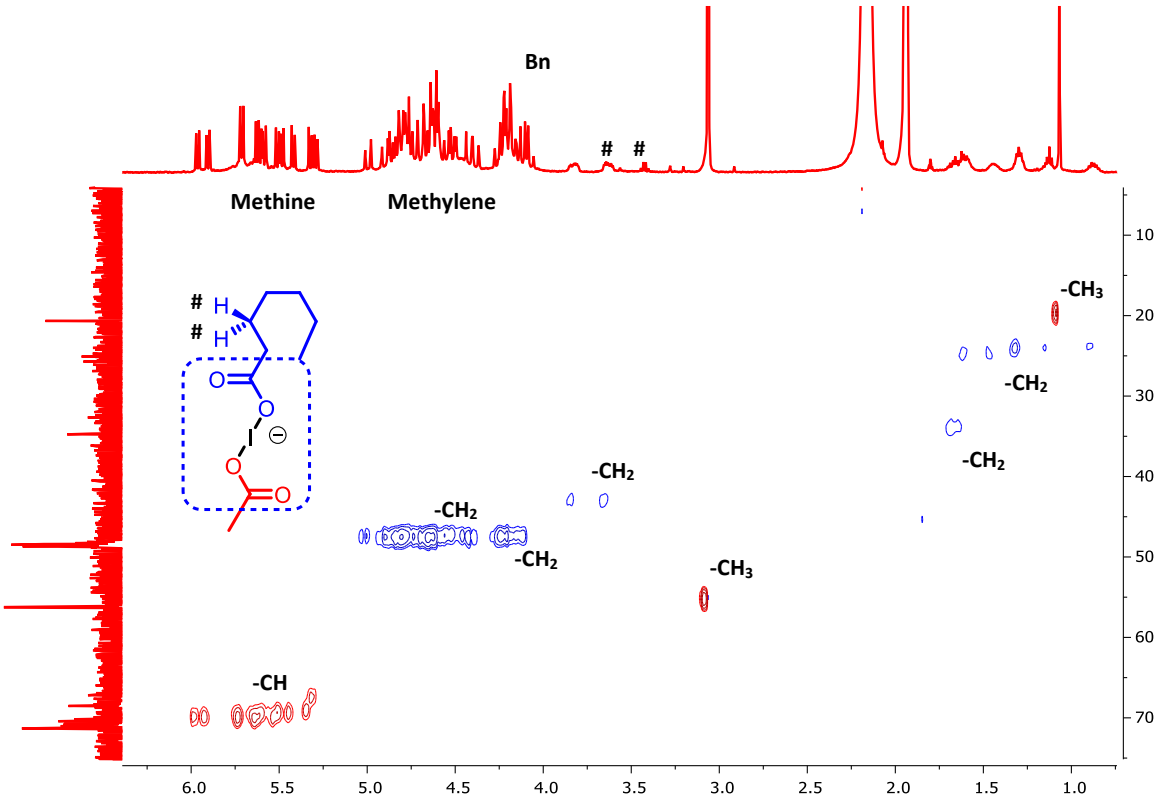


Figure S 16. HSQC NMR spectrum (500 MHz, CD_3CN, 298 K) of **1**.

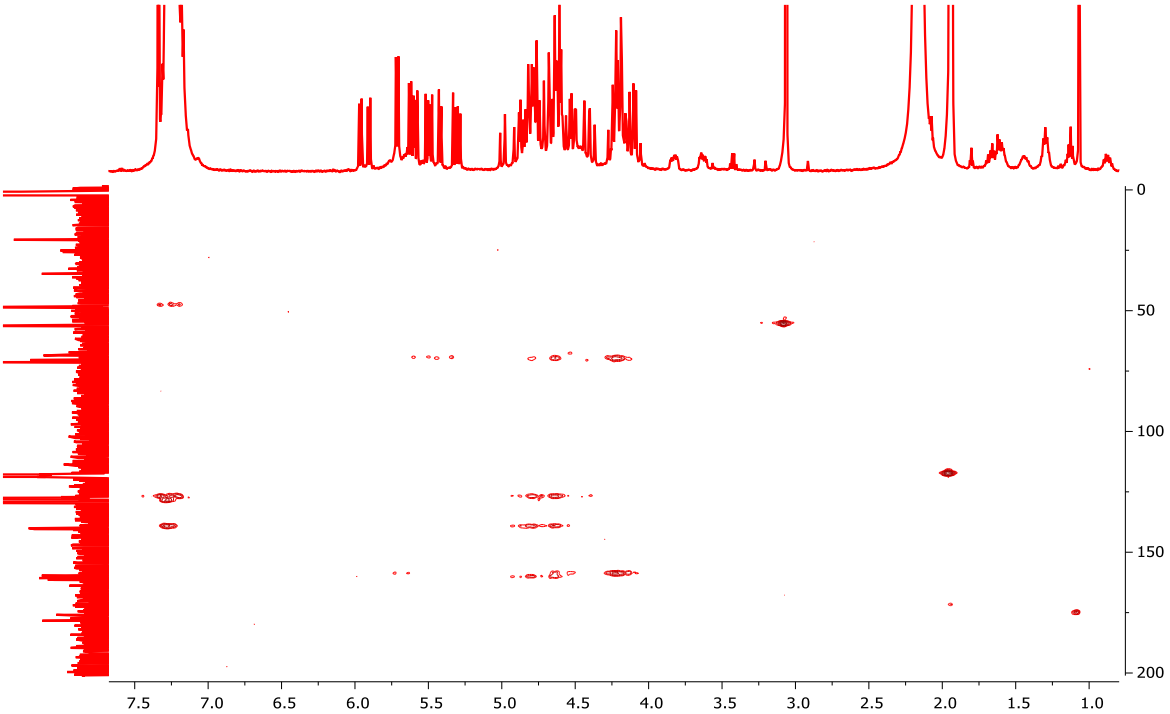


Figure S 17. HMBC NMR spectrum (500 MHz, CD_3CN, 298 K) of **1**.

3.9 NMR spectra of **2a**

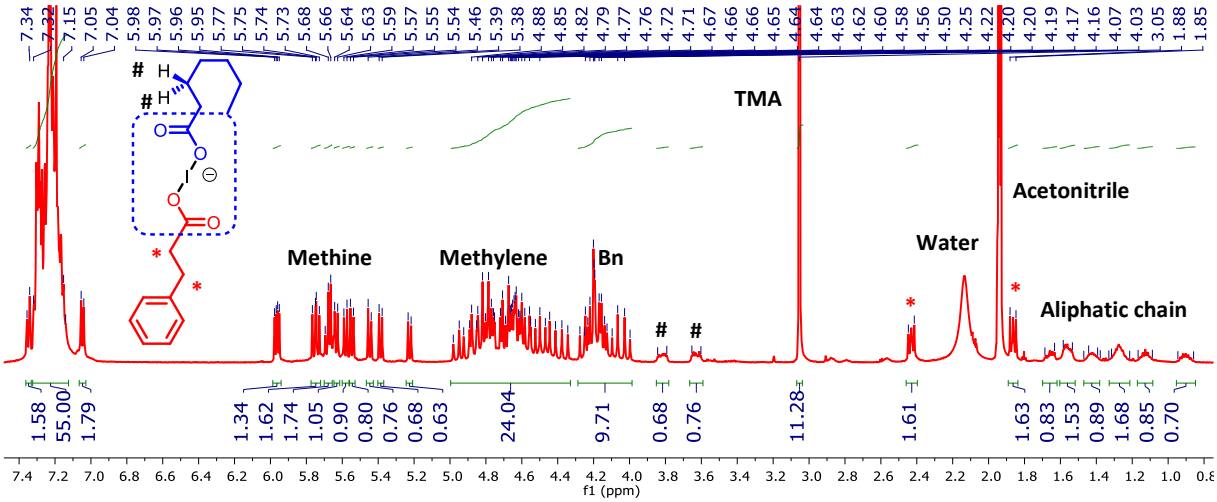


Figure S 18. ^1H NMR spectrum (500 MHz, CD_3CN, 298 K) of **2a**.

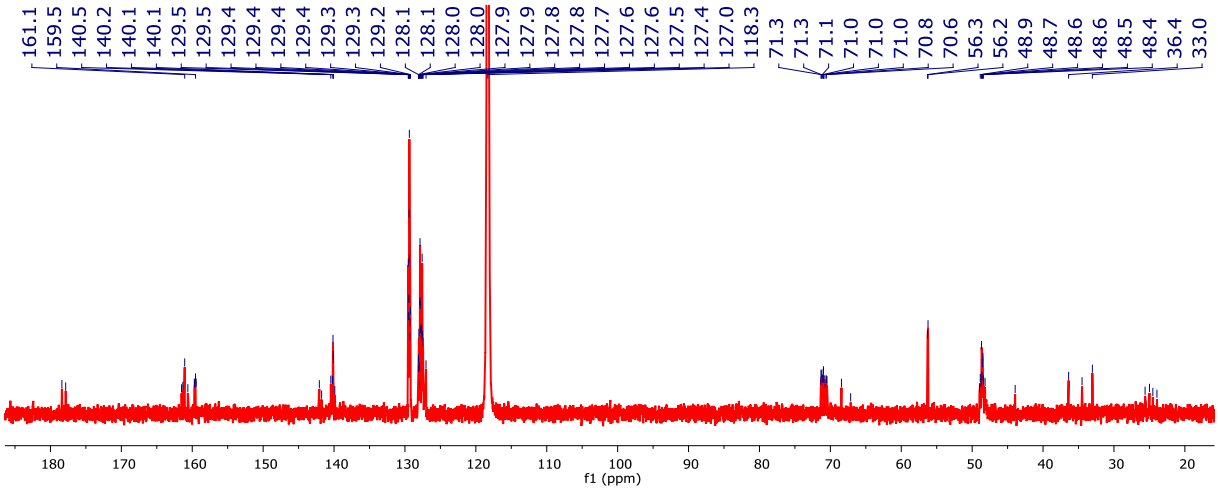


Figure S 19. ^{13}C NMR spectrum (500 MHz, CD_3CN, 298 K) of **2a**.

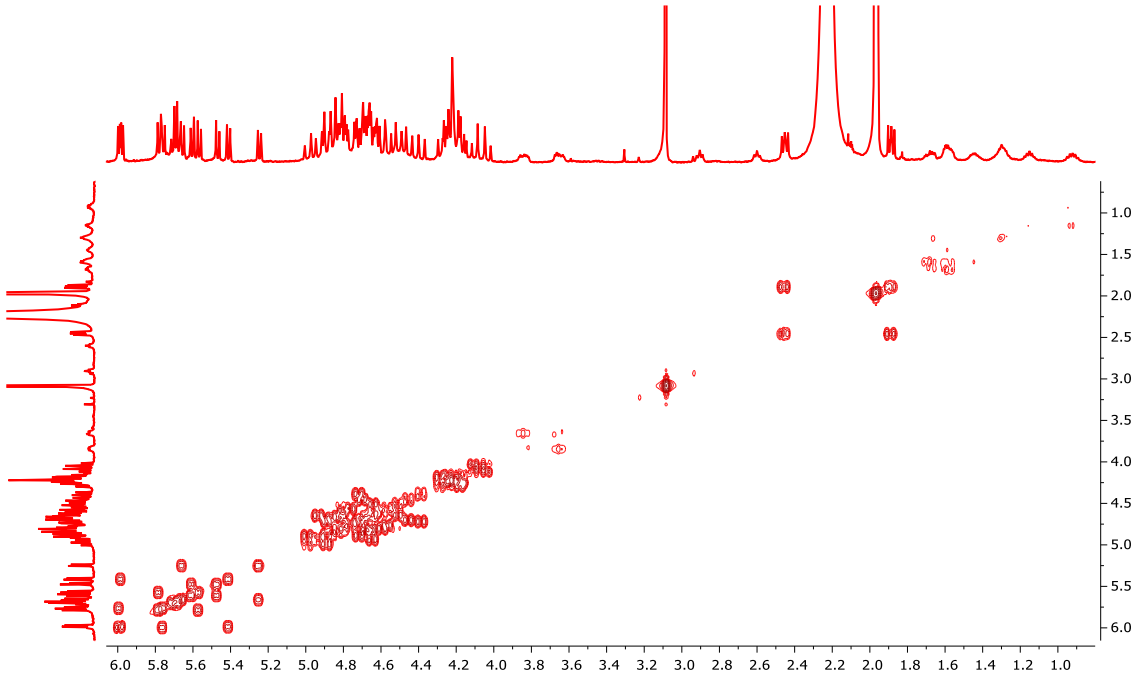


Figure S 20. COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of **2a**.

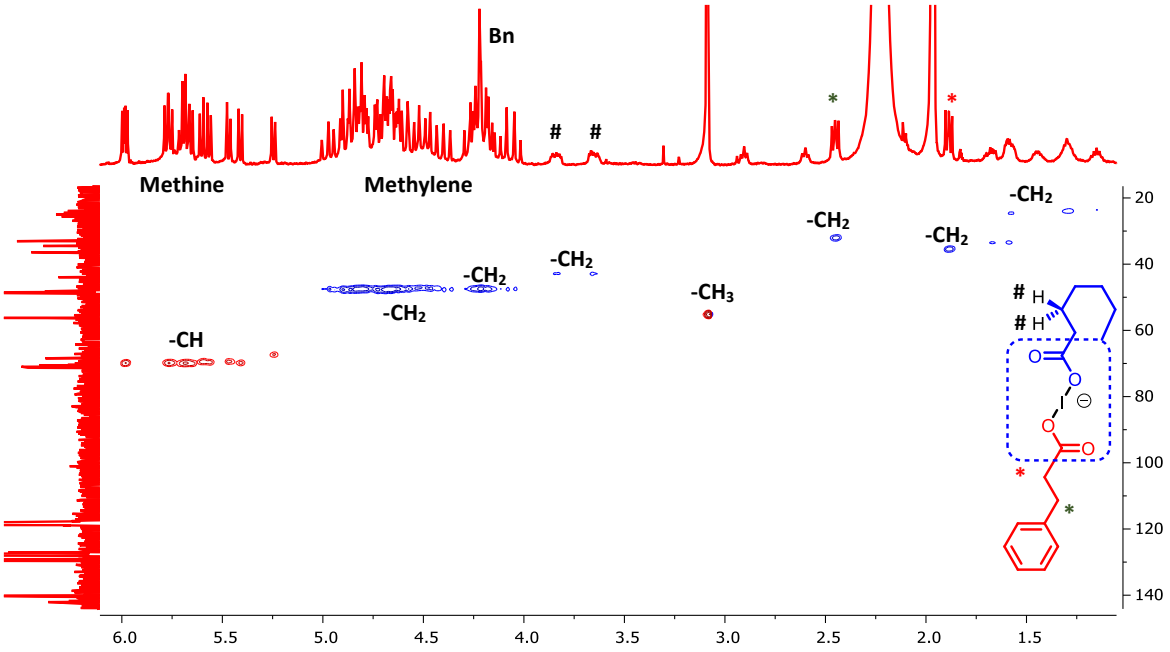


Figure S 21. HSQC NMR spectrum (500 MHz, CD_3CN, 298 K) of **2a**.

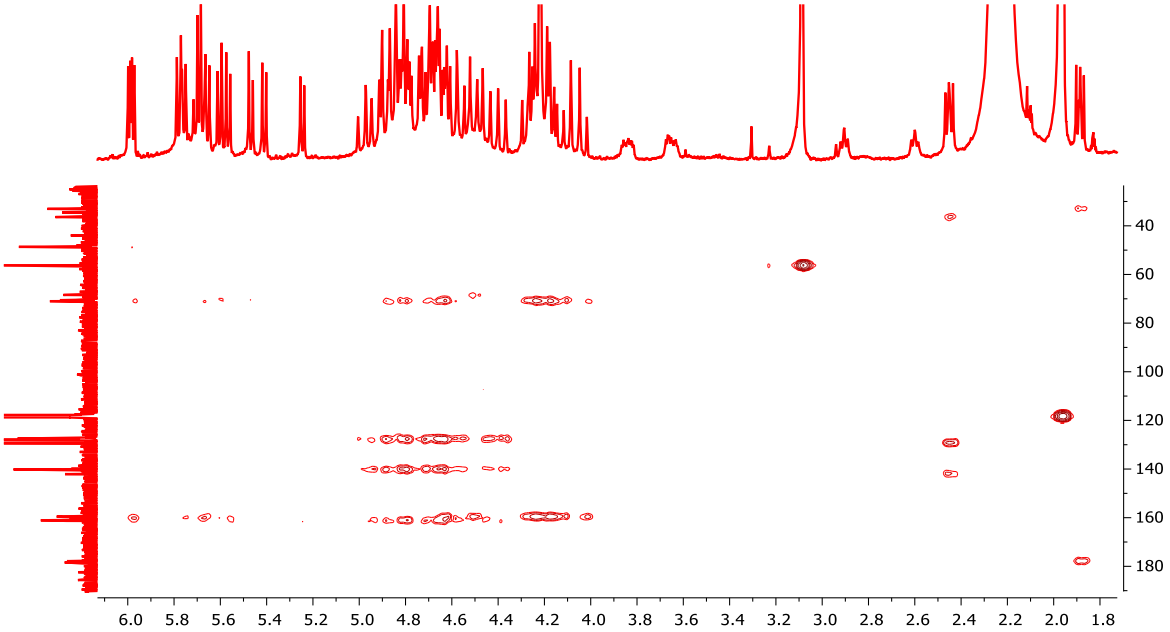


Figure S 22. HMBC NMR spectrum (500 MHz, CD_3CN, 298 K) of **2a**.

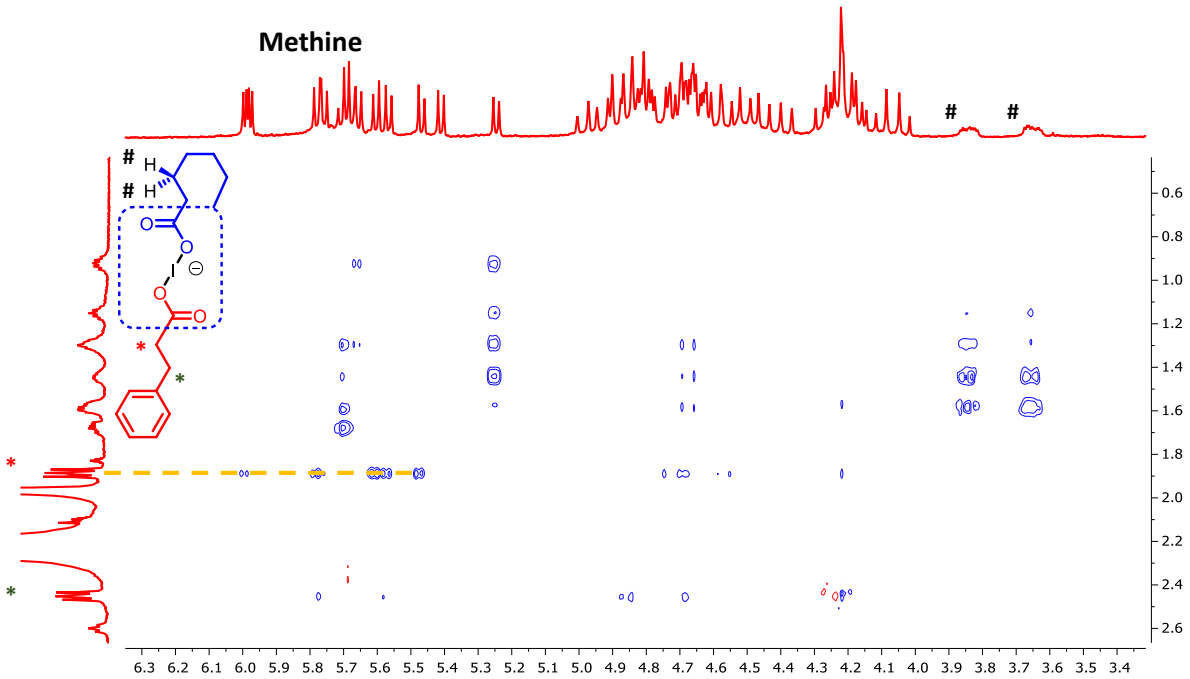


Figure S 23. ROESY NMR spectrum (500 MHz, CD_3CN, 298 K) of **2a**.

3.10 NMR spectra of **2b**

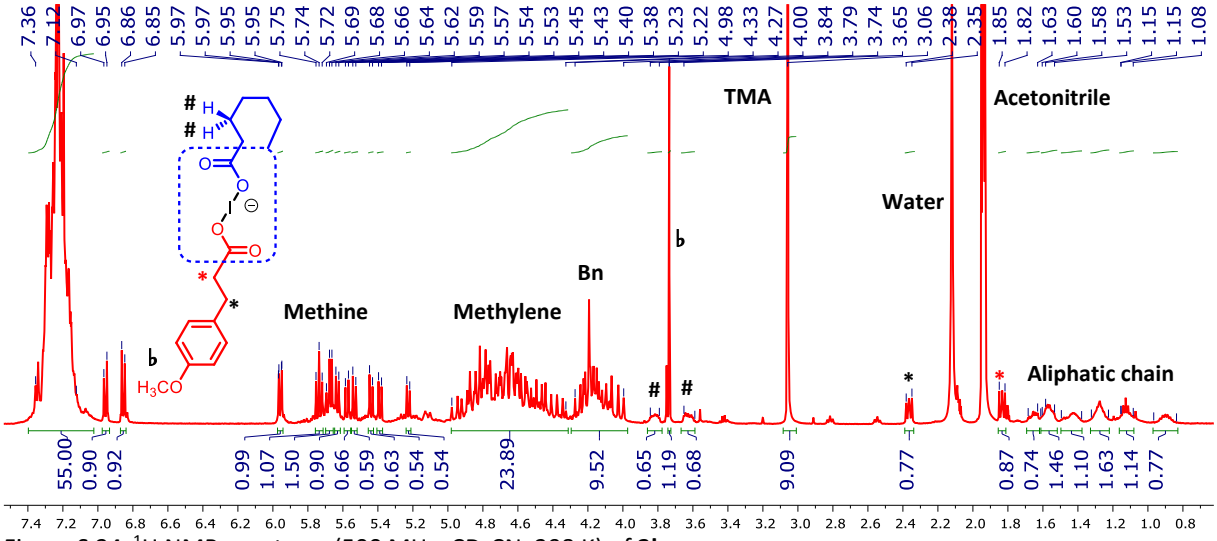


Figure S 24. ^1H NMR spectrum (500 MHz, CD_3CN, 298 K) of **2b**.

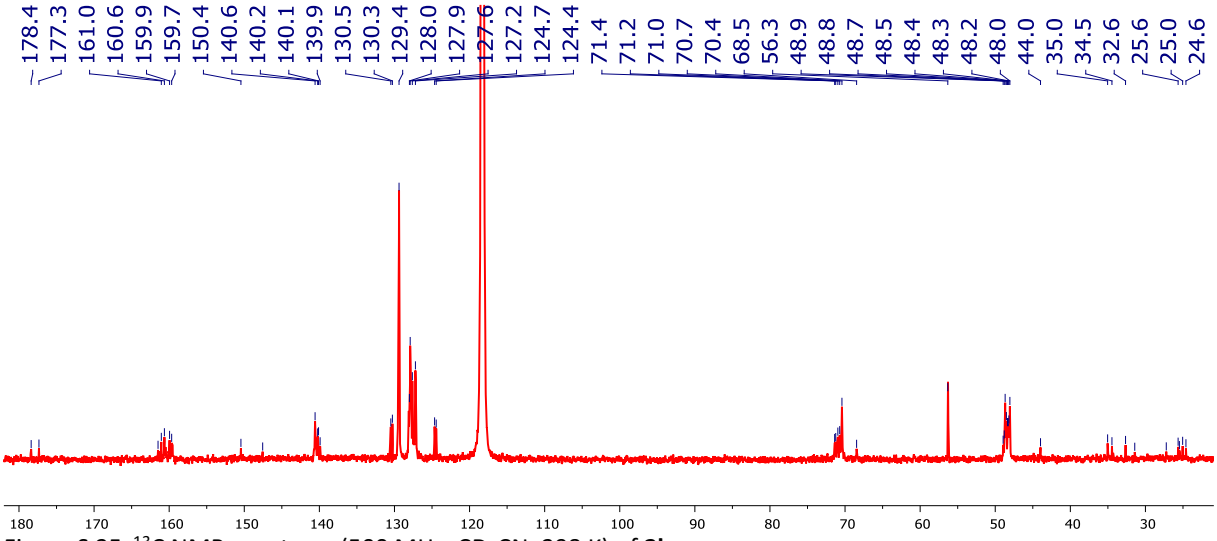


Figure S 25. ^{13}C NMR spectrum (500 MHz, CD_3CN, 298 K) of **2b**.

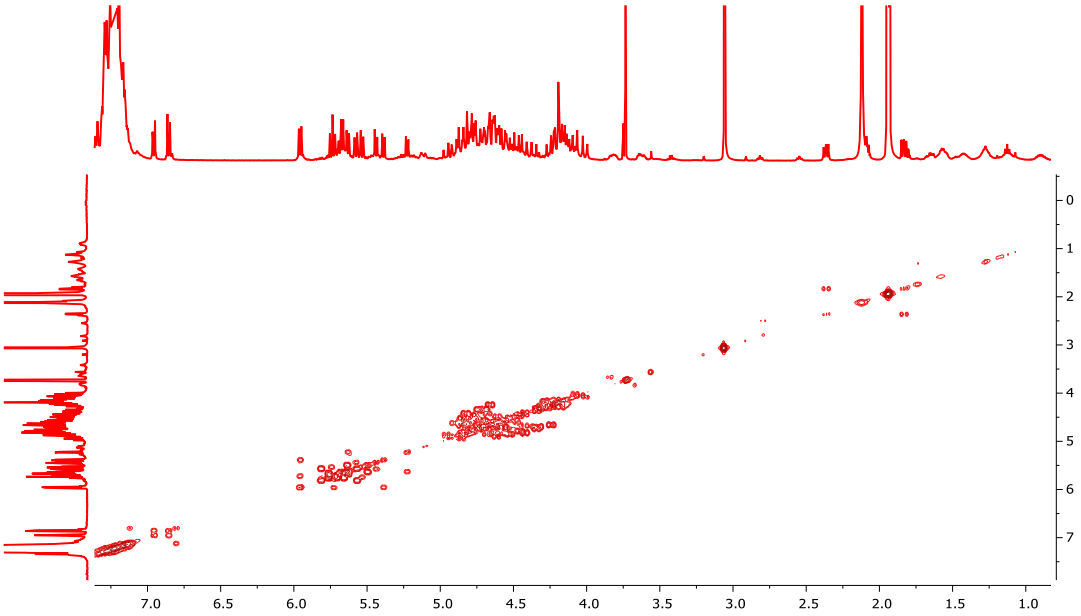


Figure S 26. COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of **2b**.

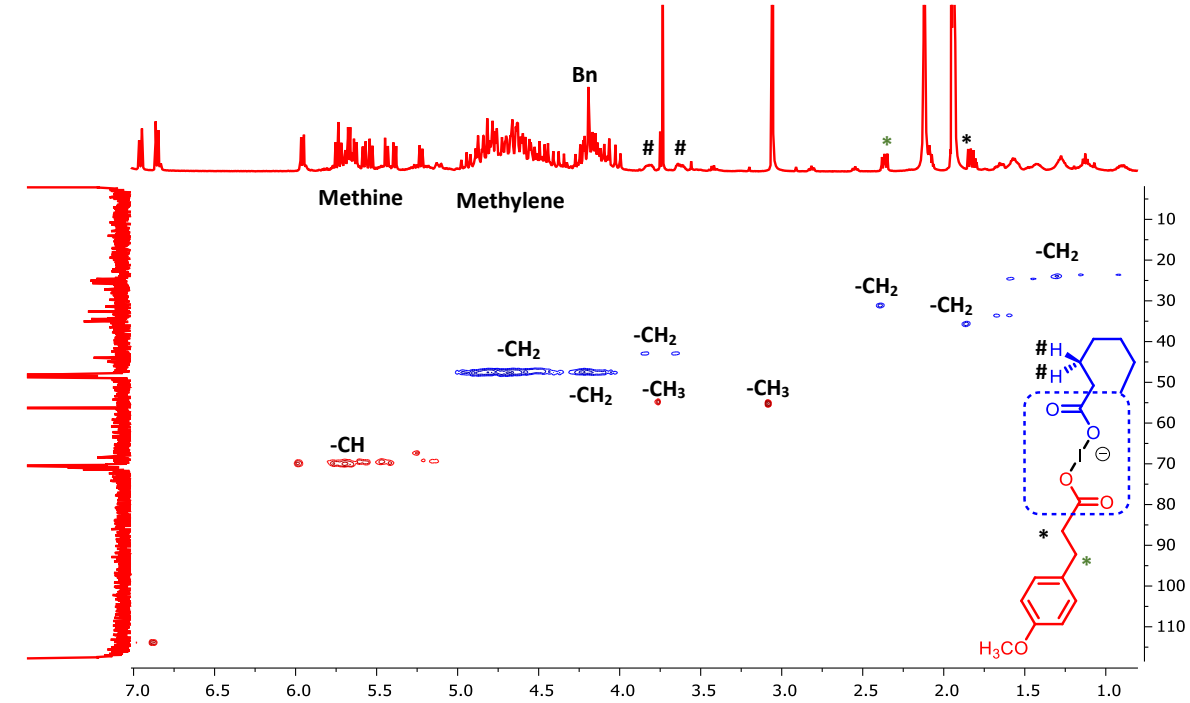


Figure S 27. HSQC NMR spectrum (500 MHz, CD_3CN, 298 K) of **2b**.

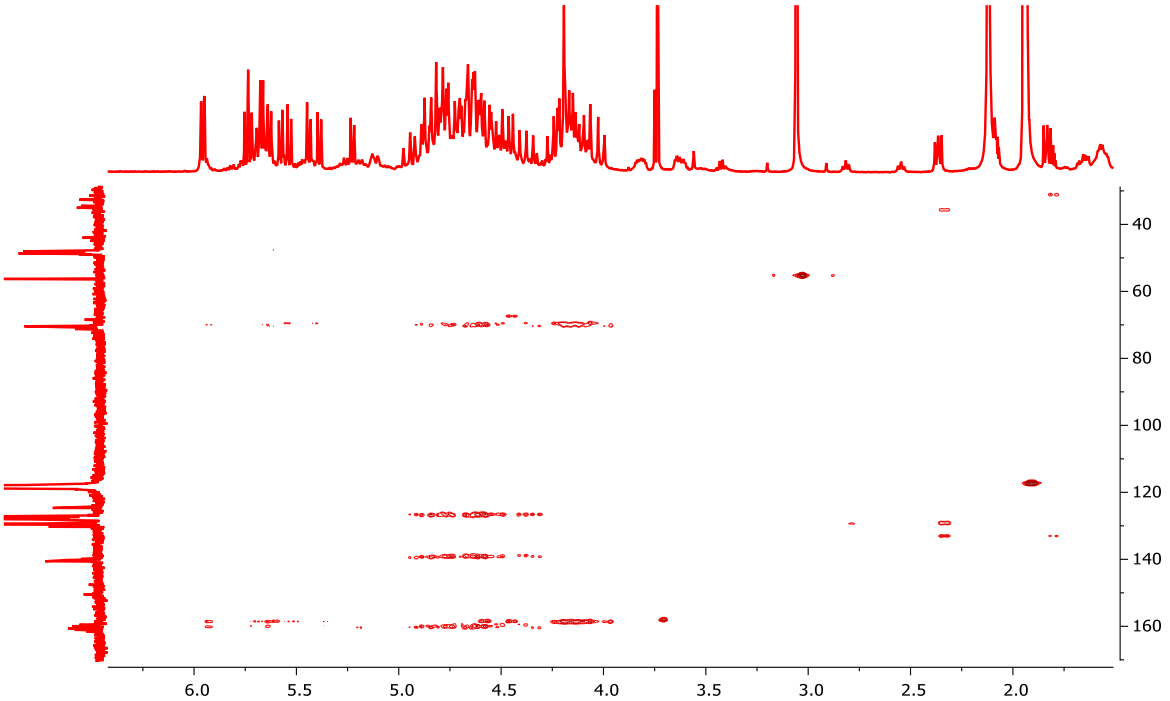


Figure S 28. HMBC NMR spectrum (500 MHz, CD_3CN, 298 K) of **2b**.

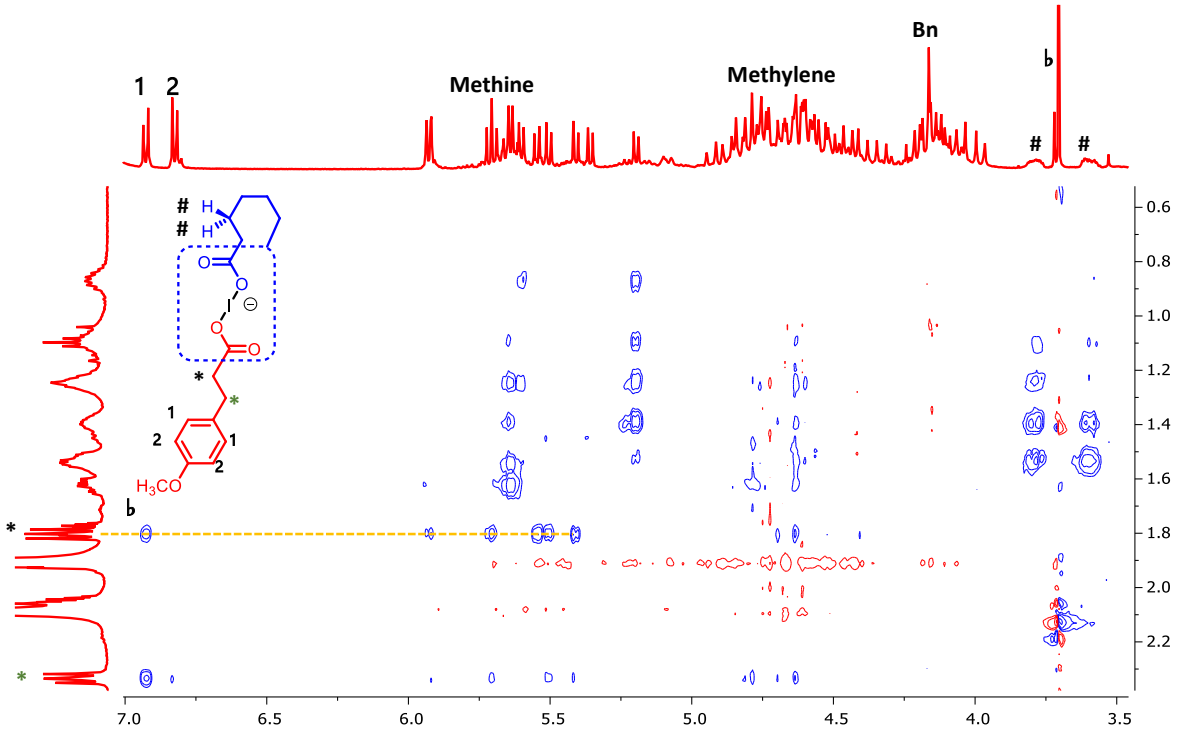


Figure S 29. ROESY NMR spectrum (500 MHz, CD_3CN, 298 K) of **2b**.

3.11 NMR spectra of **2c**

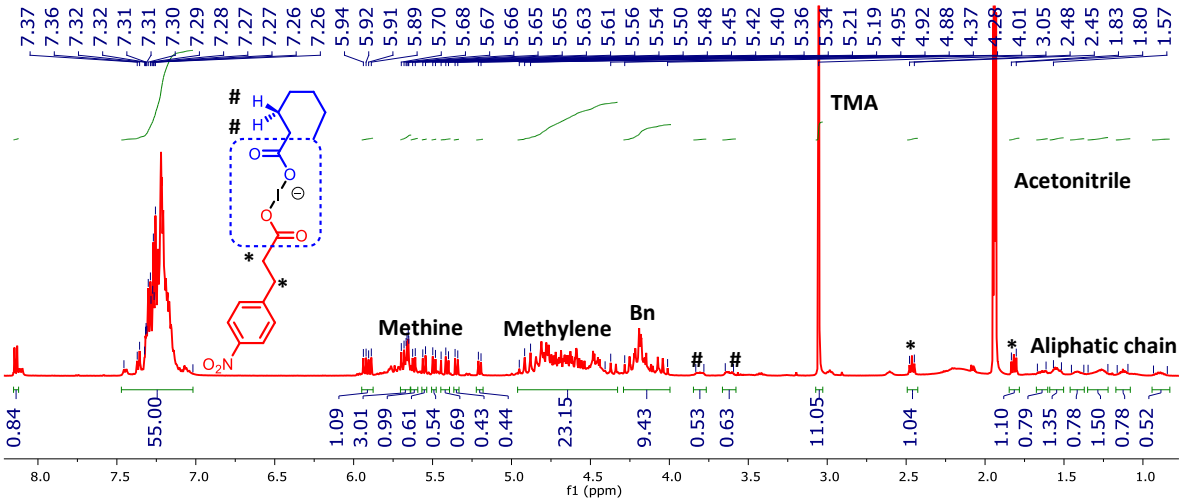


Figure S 30. ^1H NMR spectrum (500 MHz, CD_3CN, 298 K) of **2c**.

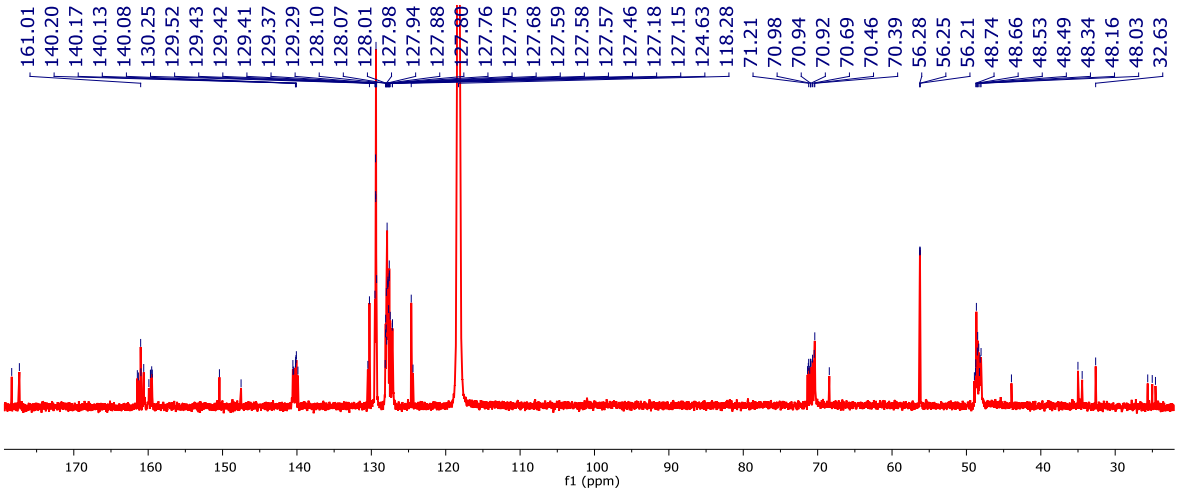


Figure S 31. ^{13}C NMR spectrum (500 MHz, CD_3CN, 298 K) of **2c**.

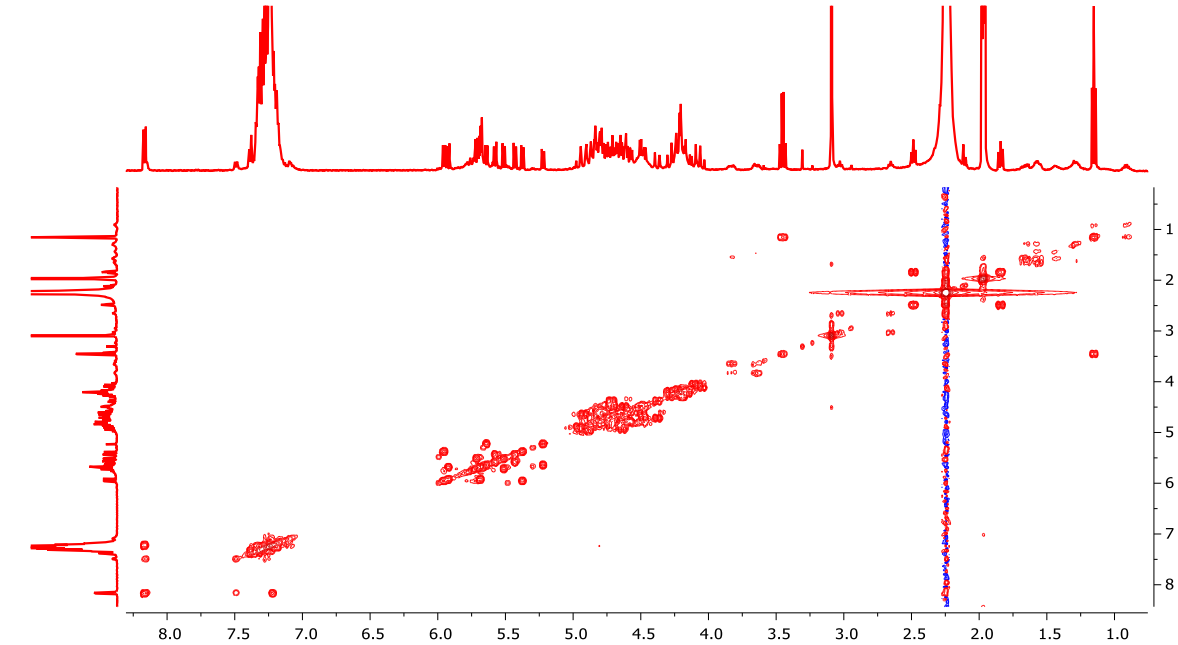


Figure S 32. COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of **2c**.

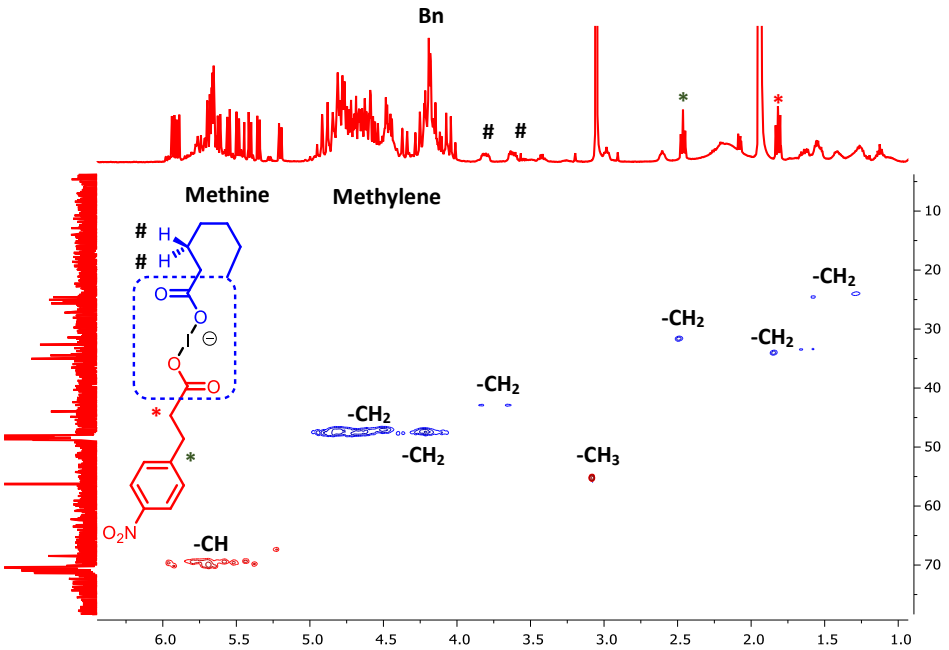


Figure S 33. HSQC NMR spectrum (500 MHz, CD_3CN, 298 K) of **2c**.

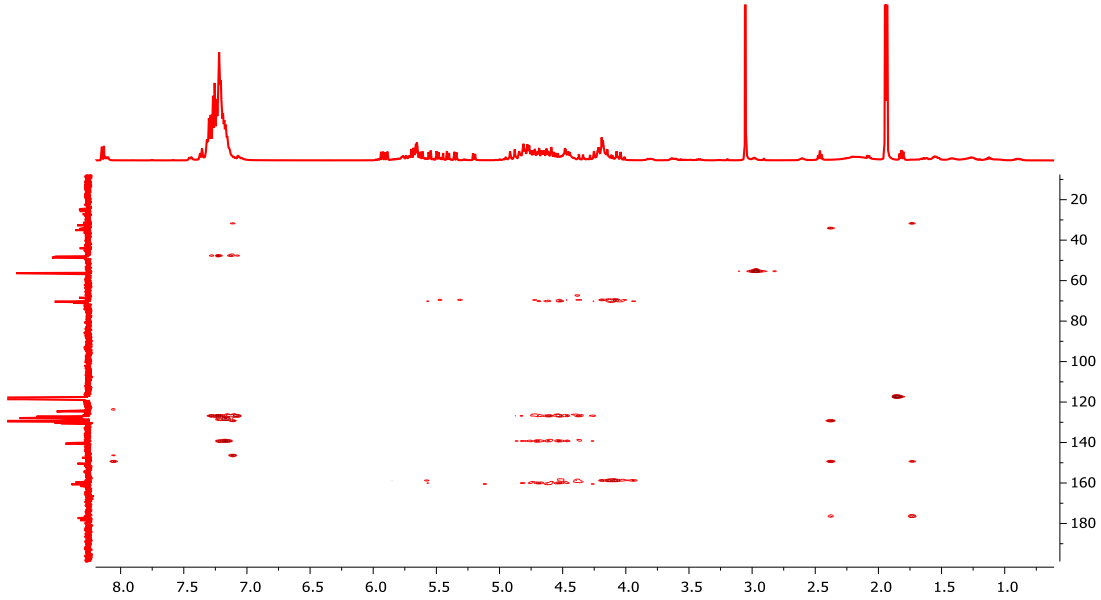


Figure S 34. HMBC NMR spectrum (500 MHz, CD_3CN, 298 K) of **2c**.

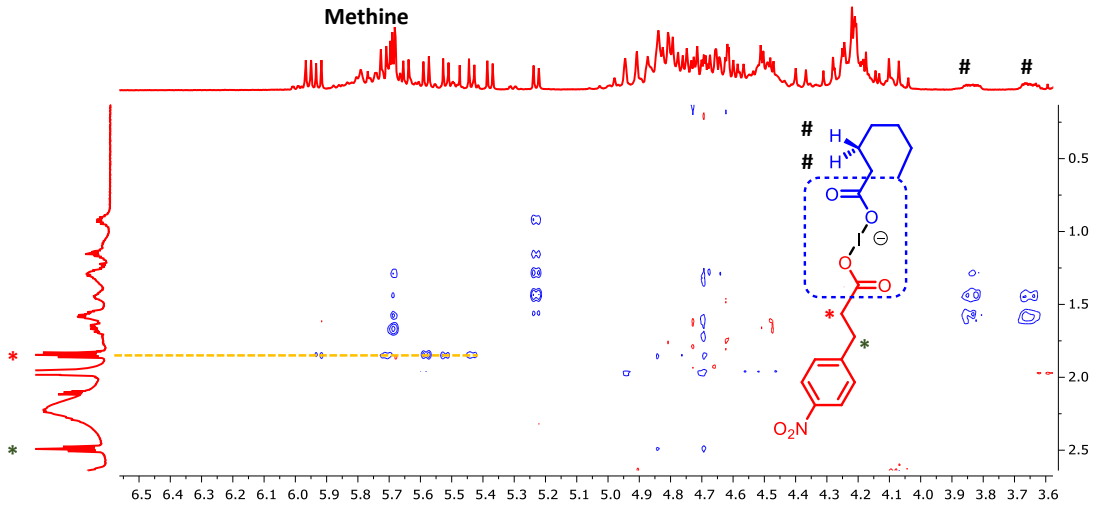


Figure S 35. ROESY NMR spectrum (500 MHz, CD_3CN, 298 K) of **2c**.

3.12 *In situ* NMR Spectra of 1, 2a, and 2b

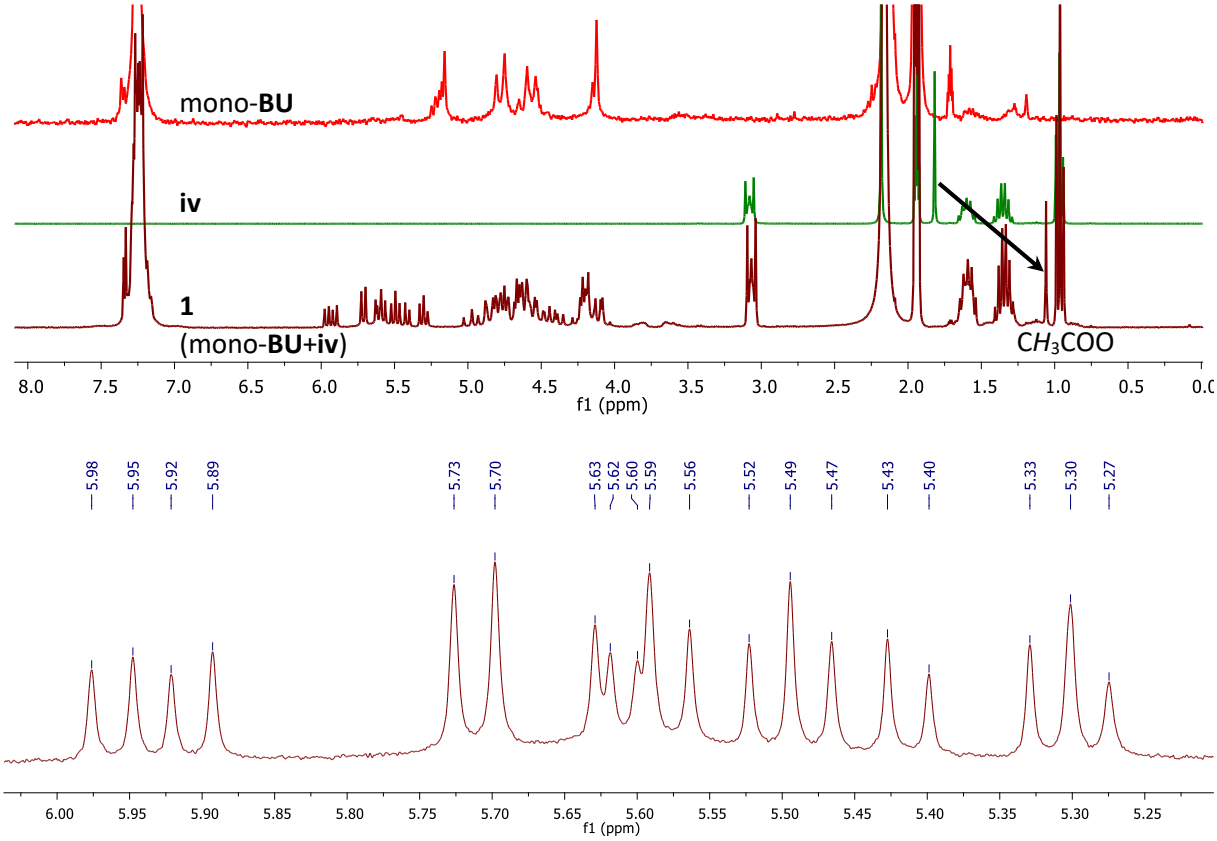


Figure S 36. ^1H NMR (acetonitrile-d_3) spectrum of the *in situ* quantitatively formed **1**, showing enlarged methine proton region. The arrow shows strong shielding of α-protons (CH_3) of the appended acetate moiety in **1** compared to **iv**, indicating inclusion of the acetate into the [1]rotaxane structure.

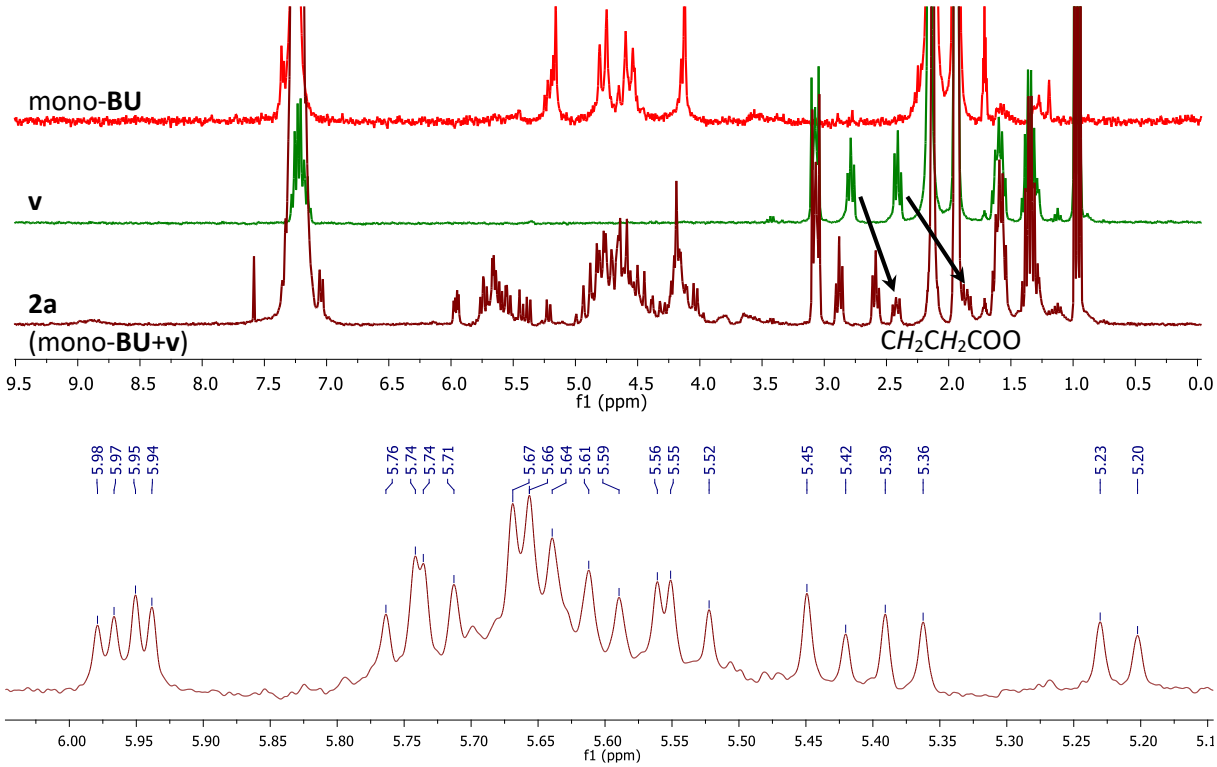


Figure S 37. ^{1}H NMR (acetonitrile-d_3) spectrum of the *in situ* quantitatively formed **2a**, showing enlarged methine proton region. The arrows shows strong shielding of α- and β-protons (CH_2CH_2COO) of the appended hydrocinnamate moiety in **2a** compared to **v**, indicating inclusion of the hydrocinnamate into the [1]rotaxane structure.

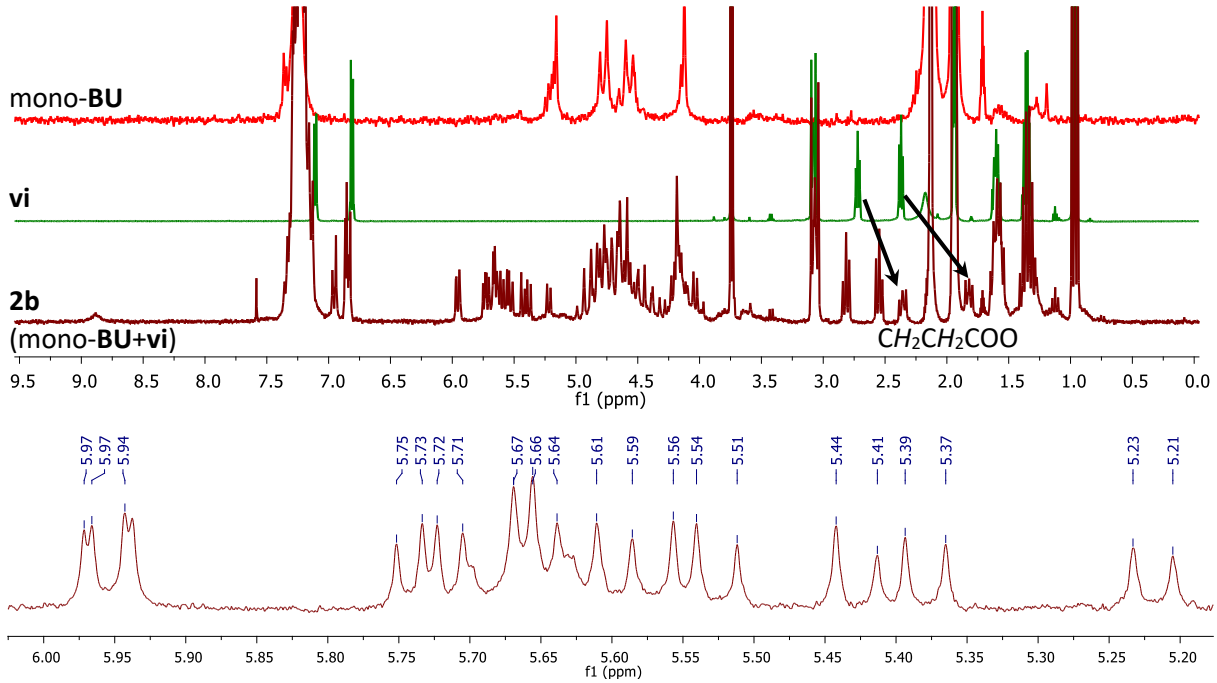
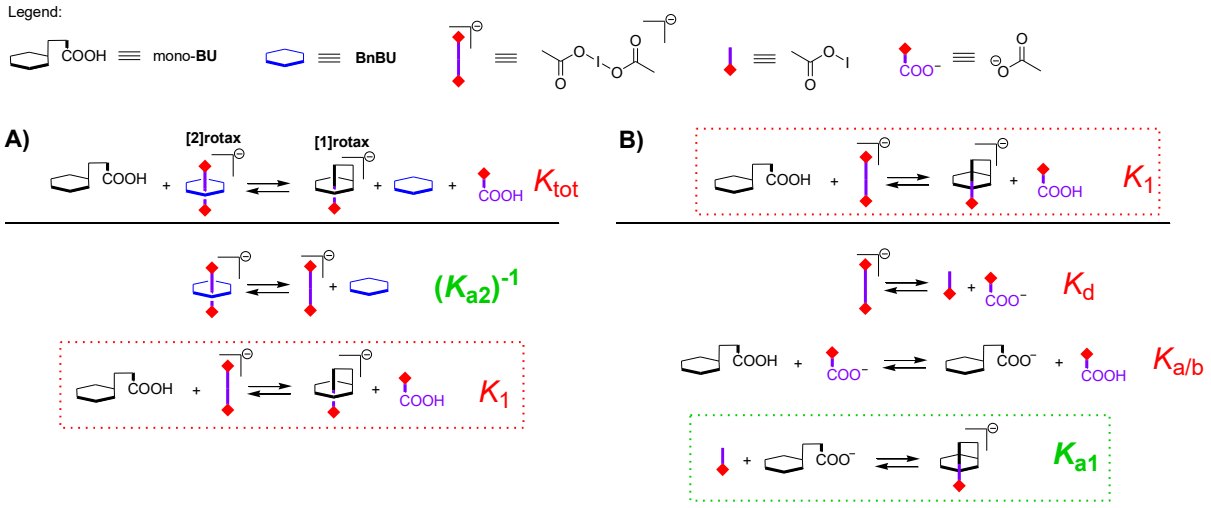


Figure S 38. ^{1}H NMR (acetonitrile-d_3) spectrum of the *in situ* quantitatively formed **2b**, showing enlarged methine proton region. The arrows shows strong shielding of α- and β-protons (CH_2CH_2COO) of the appended *p*-methoxyhydrocinnamate moiety in **2b** compared to **vi**, indicating inclusion of the *p*-methoxyhydrocinnamate into the [1]rotaxane structure.

4 Competition Experiments

To obtain a sense of the [1]rotaxane stability, an experiment was designed where [1]rotaxane and [2]rotaxane are competing for their formation in a mixture of mono-**BU**, **BnBU**, and **iv** in chloroform-d_1. The equilibrium was achieved in minutes and is described in Scheme S 5. Self-association of deprotonated mono-**BU** was omitted for simplicity. Strong preference for the equilibrium A to shift towards the formation of [1]rotaxane (Figure S 39) implies that K_{a1} describing the stability of [1]rotaxane is substantially larger than K_{a2} describing the stability of [2]rotaxane (K_{a2} = 1.4 × 10^7 M^{-1}).



Scheme S 5. Chemical equations describing the competition experiment.

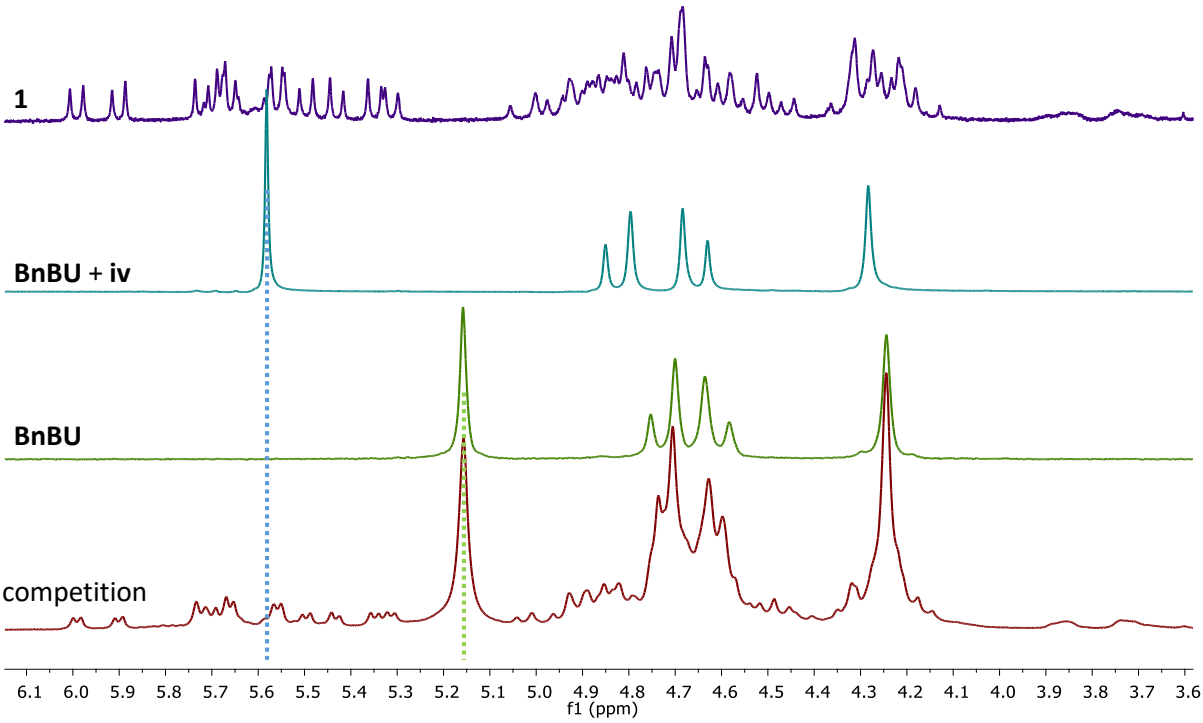


Figure S 39. ^{1}H NMR (chloroform-d_1) spectra of competion experiment where mono-**BU** and **BnBU** are compeeting for the tetrabutylammonium (diacetoxy)iodate(I) or its components, **iv**, to form [1]- and [2]rotaxanes, respectively. The resulting bottom spectra indicate strong shift of the equilibrium towards the formation of empty **BnBU** and **1**, with negligible amounts of [2]rotaxane (i.e. **BnBU** + **iv** mixture). The spectra were recorded at 300 MHz, except the bottom spectra which was recorded at 500 MHz.

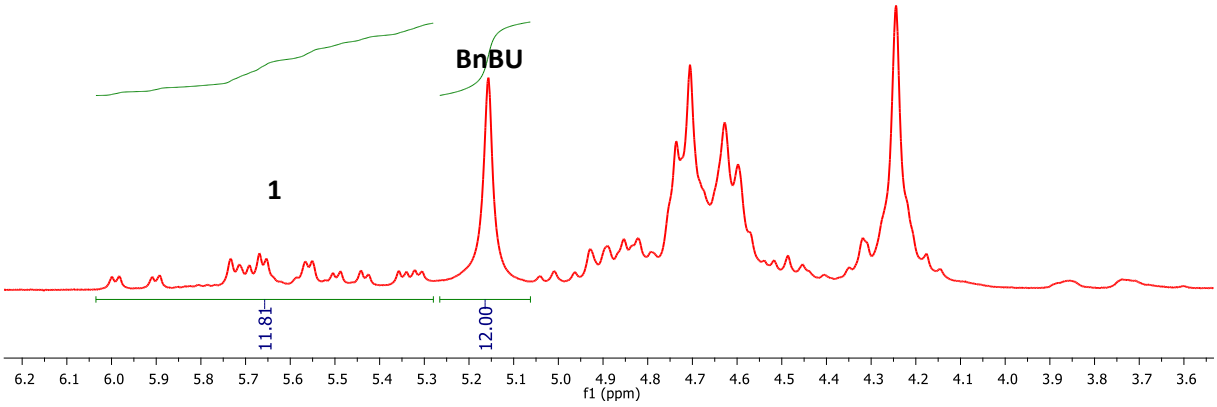
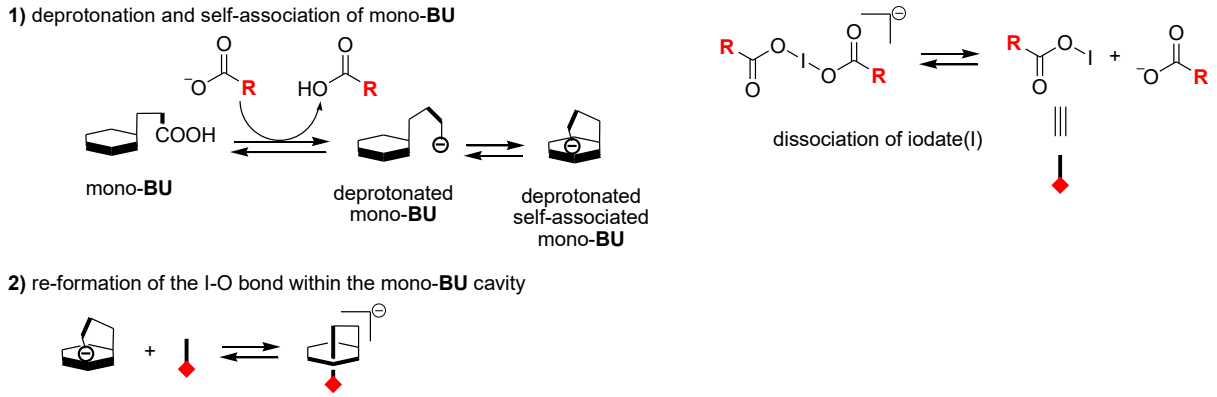


Figure S 40. ^{1}H NMR (500 MHz, chloroform-d_1) of the above competition experiment, indicating twelve methine protons in **BnBU** and in **1**. The integration suggests the final mixture is composed almost exclusively of **BnBU** and **1**, indicating strong preference for the formation of [1]rotaxanes.

5 The Mechanism of [1]rotaxane Formation

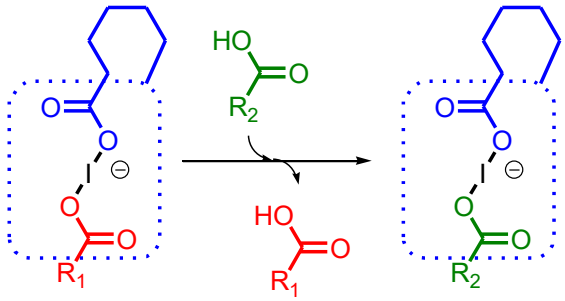
A plausible mechanism of [1]rotaxane formation involves intramolecular anion recognition of the appended carboxylate in mono-**BU**, followed by the re-formation of the I–O bond within the cavity of mono-**BU**.



Scheme S 6. Plausible mechanism of [1]rotaxane formation in two major steps.

6 Exchange Experiments

Carboxylate exchange experiments were performed in acetonitrile-d_3, by forming the [1]rotaxane *in situ*, and subsequent addition of 2 equivalents (i.e. with respect to bambusuril) of the exchanging carboxylic acid. Two equivalents of the added acid is equimolar with respect to the exchanged acid (i.e. two equivalents of the carboxylate moieties are present in the bis(acyloxy)iodate(I) precursor from the *in situ* reaction of [1]rotaxane formation).



Scheme S 7. General scheme for the carboxylate exchange experiments of [1]rotaxanes in acetonitrile-d_3.

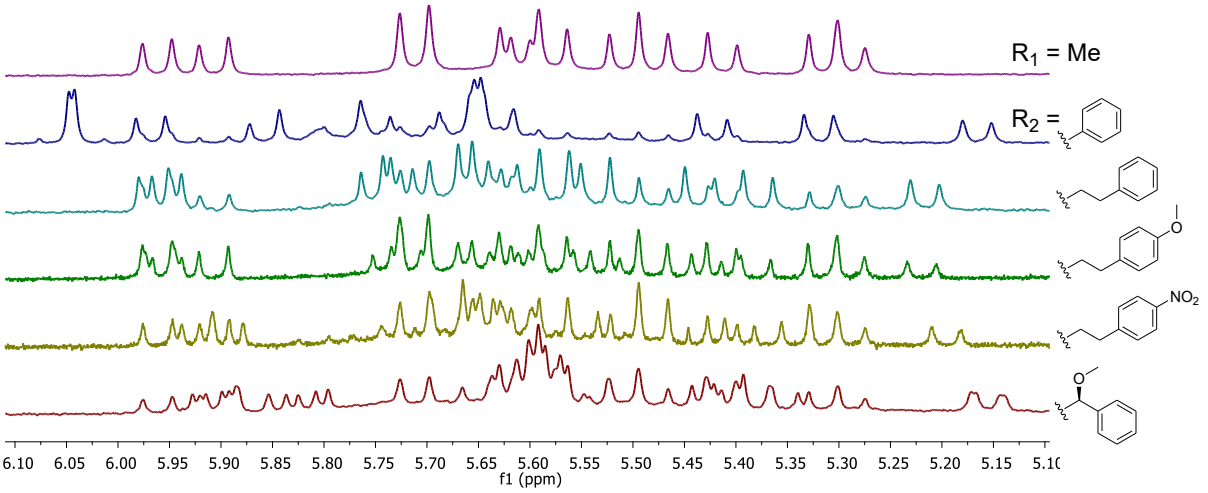


Figure S 41. ^{1}H NMR (300 MHz, acetonitrile-d_3) intercept of the methine proton region in the carboxylate exchange reactions where a particular carboxylic acid was added to the *in situ* formed **1** (R_1 = Me). Inegrated peaks used for calculating relative ratios were those at 5.30 ppm for **1**, and between 5.10–5.25 ppm for the formed [1]rotaxanes.

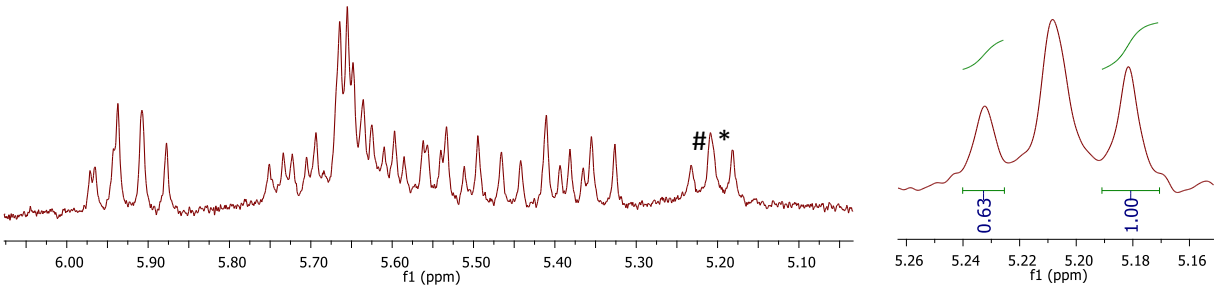


Figure S 42. ^{1}H NMR (300 MHz, acetonitrile-d_3) intercept of the methine proton region in the carboxylate exchange reactions where a *p*-nitrophenylpropionic acid was added to the *in situ* formed **2b** (the *p*-OMe derivative) to form **2c** (the *p*-NO_2 derivative). Inegrated peaks used for calculating relative ratios were those at 5.20 ppm, i.e. halves of doublets of **2b** (hashtag) and **2c** (asterisk), and the obtained ratios are in very good agreement with the ratio (i.e. **2b**:**2c** = 0.6) from the independent experiments starting from **1**.

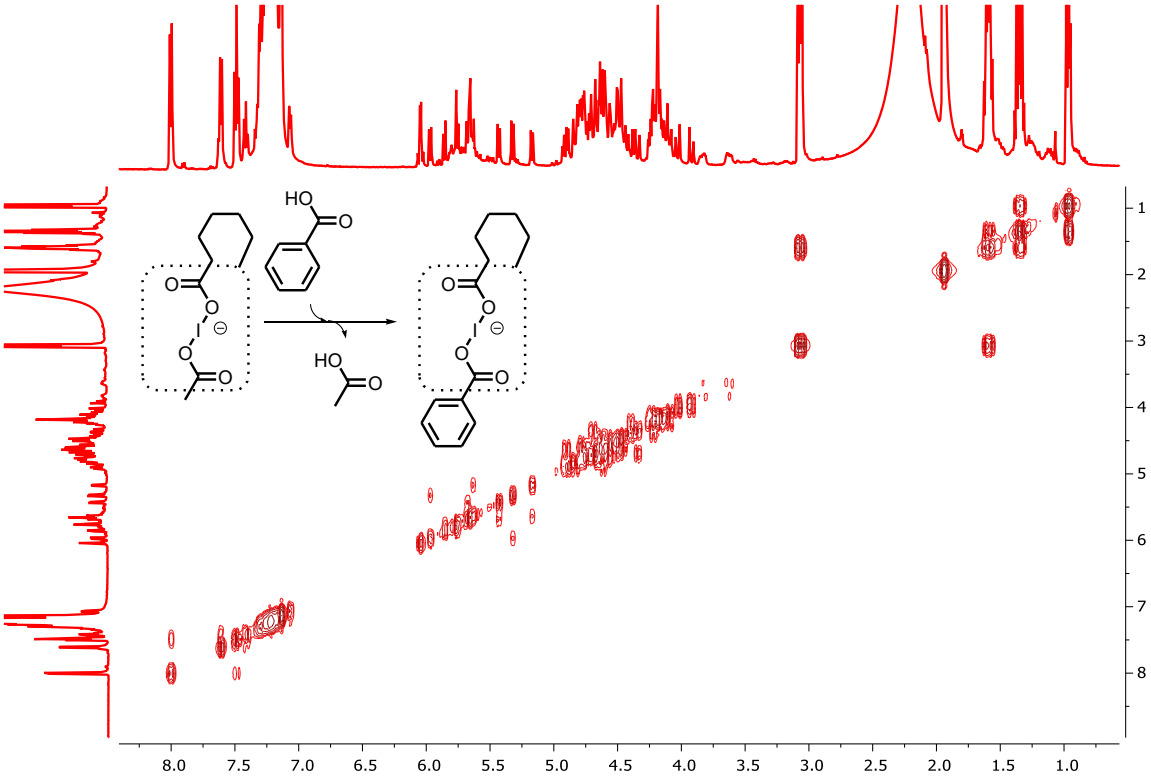


Figure S 43. COSY spectrum (500 MHz, CD_3CN, 298 K) of the benzoate exchange reaction.

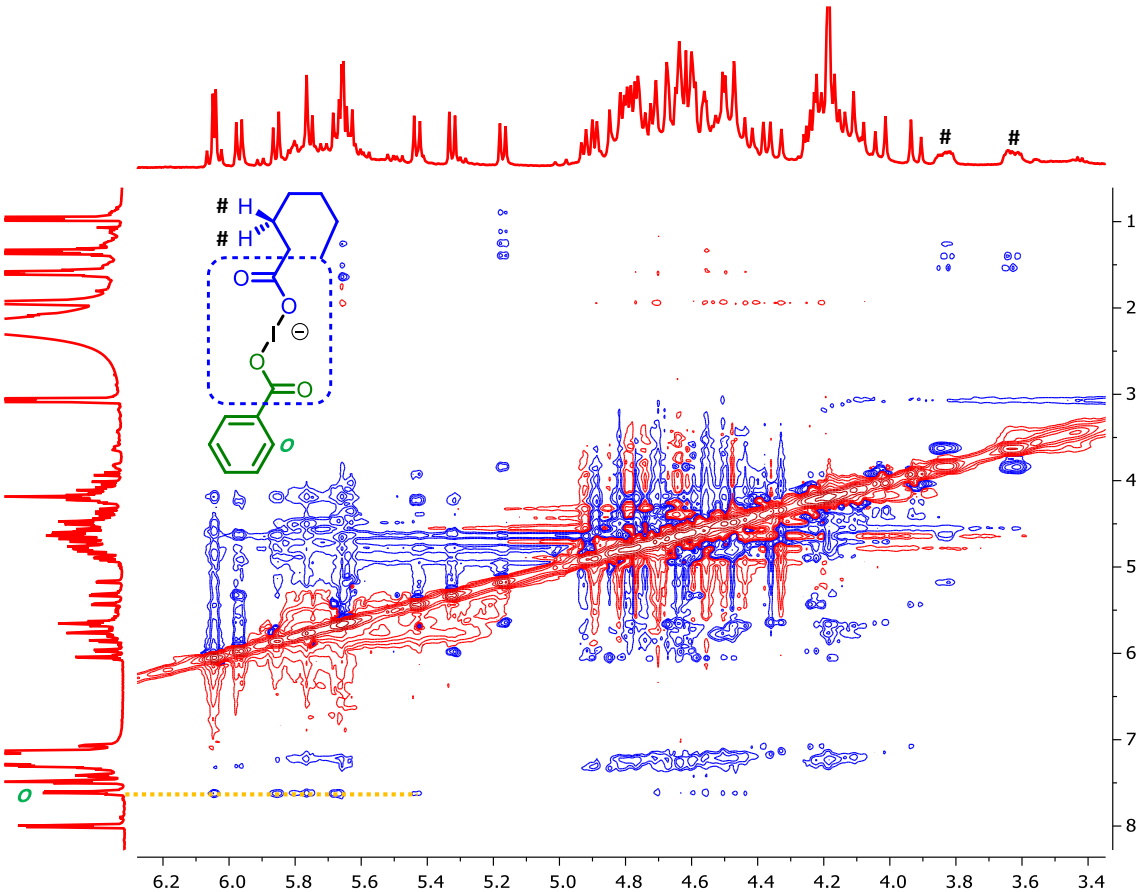


Figure S 44. ROESY spectrum (500 MHz, CD_3CN, 298 K) of the benzoate exchange reaction, showing that the benzoate is indeed incorporated into the [1]rotaxane structure. This is evident from the dotted orange line indicating ROE contacts of phenyl with only one set of methine protons, as observed for the [1]rotaxanes herein.