Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Pillar[5]arenes with an introverted amino group: a hydrogen bonding tuning effect

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Contents

1. General:

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz with a Mercury plus 400 spectrometer at 298 K. Chemical shifts were referenced to $CHCl_3$ residue (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR). Mass spectra were recorded with Bruker MicroTOF II spectrometer. For single crystal growing, **IP**-DA-3 (3 mg) was dissolved in chloroform (0.3 ml). The single crystals were obtained by slow evaporation the solutions under 25 ^{o}C for 2 weeks. The data set was treated with the SQUEEZE program to remove highly disordered solvent molecules. The crystallographic formulae include the number of solvent molecules suggested by the SQUEEZE program.

2. Synthetic procedure and characterization data for 1 and 2:

Compound **2** was synthesized according to our earlier work.[1] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.03-6.99 (m, 8 H), 6.92 (s, 1 H), 6.84 (s, 1 H), 4.55-4.90 (m, 20 H), 4.09-3.84 (m, 28 H), 1.06-0.80 (m, 27 H). HR-MS (ESI-TOF): Calcd. for $C_{73}H_{86}O_{30}Na$: 1465.5102. Found: 1465.4522.

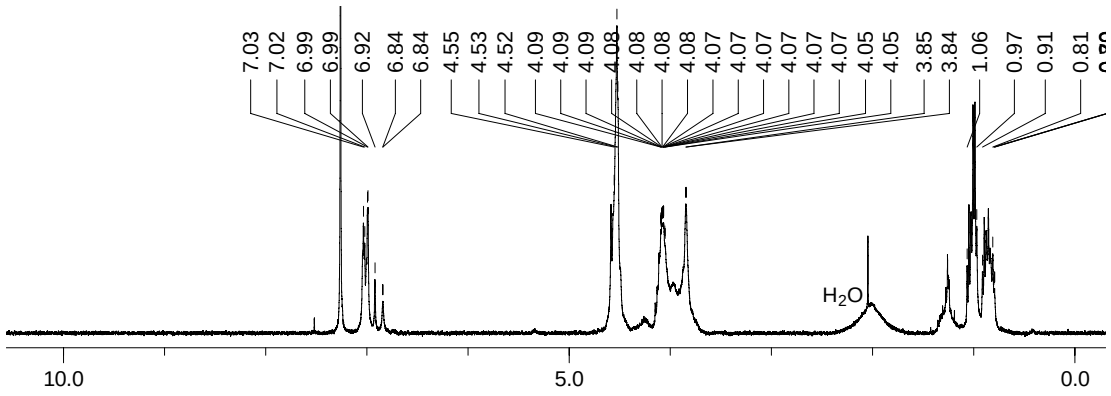

Figure S1. ^{1}H NMR spectrum of **2** in $CDCl_3$.

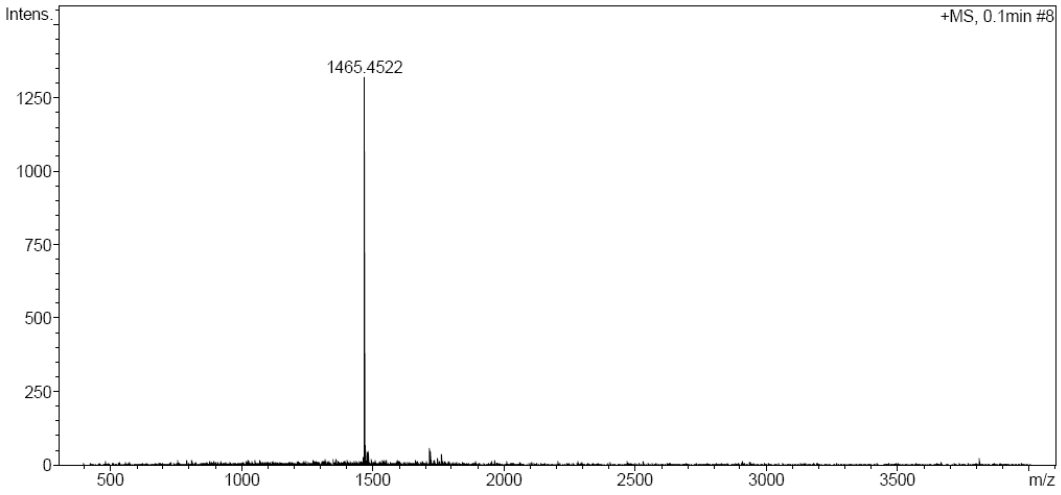

Figure S2. HR ESI-MS of **2**.

To the solution of **2** (200 mg, 0.14 mmol) in CH_2Cl_2 (8 mL) was added oxalyl chloride (96 μL, 1.12 mmol) and DMF (2 μL). The mixture was stirred at 25 °C for 3 h and then subject to distill under reduced pressure. The residue was redissolved in anhydrous CH_2Cl_2 (2 mL), and then phenol (40 mg, 0.42 mmol) and anhydrous pyridine (67 μL, 0.84 mmol) was added to such a solution. After stirred at 25 °C for 12 h, the mixture was washed with saturated Na_2CO_3 and aqueous HCl (5%). The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 40/1) to give **1** as white solid (88 mg, 42%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (t, *J* = 7.2 Hz, 1 H), 7.17-7.04 (m, 14 H), 4.82 (q, *J* = 14.8 Hz, 1 H), 4.53 (m, 19 H), 4.07 (m, 18 H), 3.87 (m, 10 H), 0.97-0.91 (m, 24), 0.69 (t, *J* = 6.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 168.1, 150.4, 149.3, 149.1, 149.0, 148.9, 148.7, 129.5, 129.1, 128.9, 128.7, 128.6, 126.1, 121.5, 114.8, 114.7, 114.6, 114.5, 114.4, 114.2, 66.0, 65.9, 65.7, 61.0, 60.8, 29.6, 29.4, 29.1, 29.0, 13.9, 13.8, 13.6. MS (ESI): *m/z* 1541 $[M+Na]^+$, HR-MS (ESI-TOF): Calcd. for $C_{79}H_{90}O_{30}Na$: 1541.5415. Found: 1541.5425.

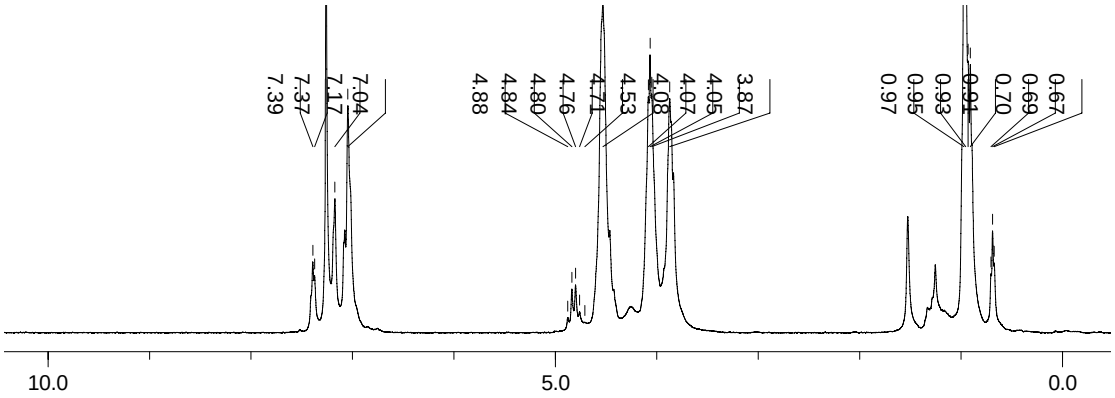

Figure S3. ^{1}H NMR spectrum of **1** in $CDCl_3$.

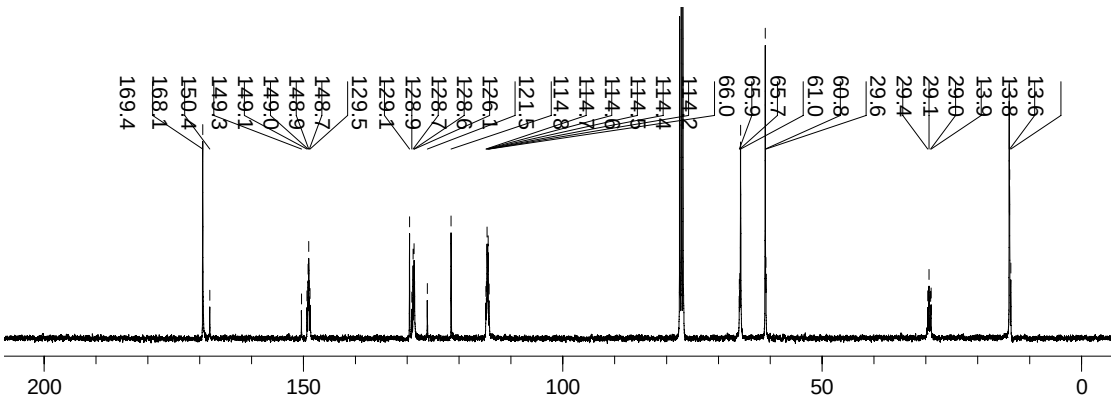

Figure S4. ^{13}C NMR spectrum of **1** in $CDCl_3$.

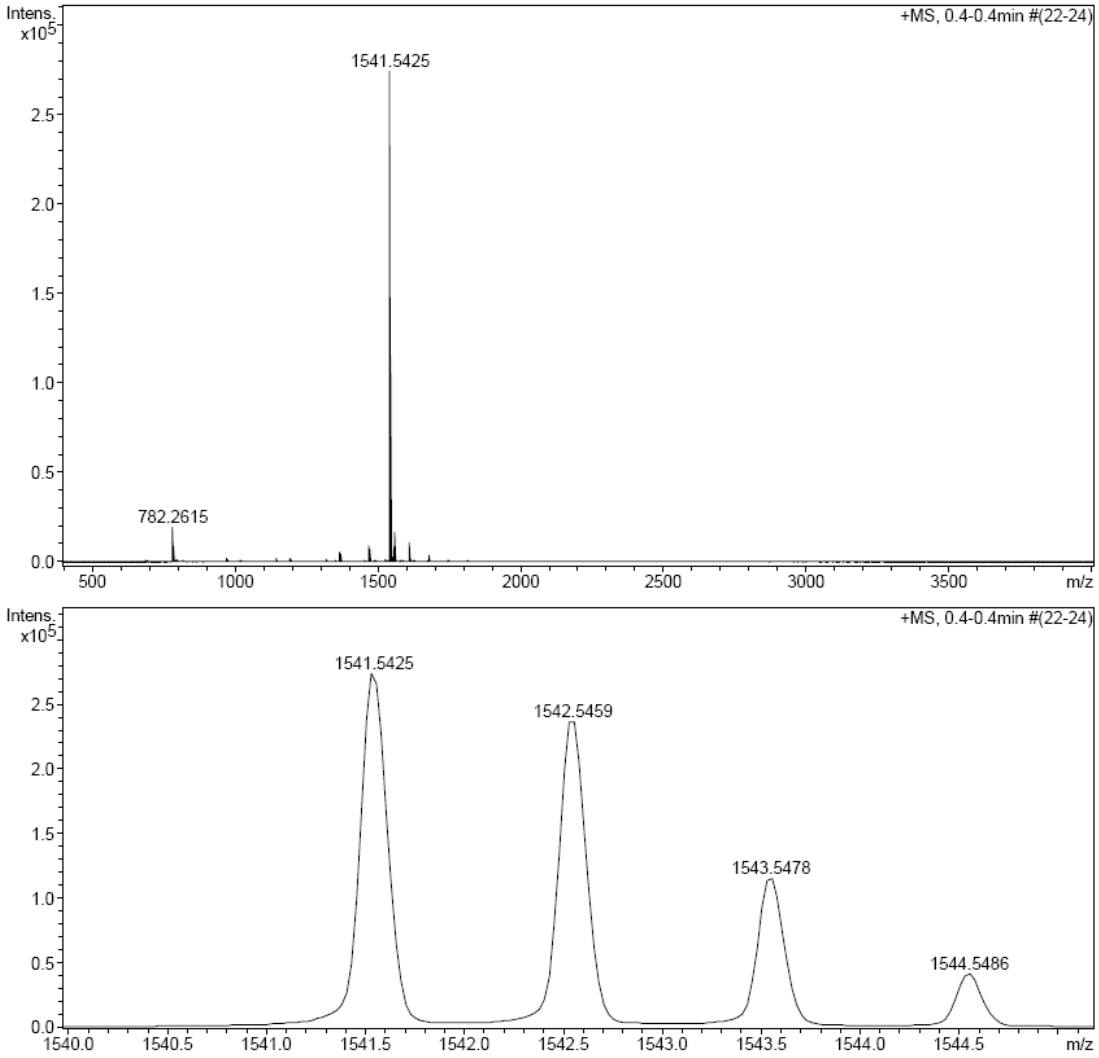

Figure S5. HR ESI-MS of **1**.

3. Synthetic procedure and characterization data for authentic sample of IP-DA-3 and IP-MA-3:

General procedure for the synthesis of **IP**-DA-3 and **IP**-MA-3: To the solution of **2** (100 mg, 0.07 mmol) in CH_2Cl_2 (5 mL) was added oxalyl chloride (48 μL, 0.56) and DMF (2 μL). The mixture was stirred at 25 ^oC for 3 h and then subject to distill under reduced pressure. The residue was redissolved in anhydrous CH_2Cl_2 (2 mL), and then **DA**-3 or **MA**-3 (0.70 mmol) and anhydrous pyridine (67 μL, 0.84 mmol) was added to such a solution. After stirred at 25 ^oC for 5 h, the mixture was washed with aqueous HCl (5%). The crude product was purified by column chromatography to give **IP**-DA-3 or **IP**-MA-3 as white solid.

IP-DA-3 (35%) ^1H NMR ($CDCl_3$, 400 MHz): δ 7.19-6.74 (m, 10 H), 5.92 (br, 1 H), 4.51-3.64 (m, 49 H), 2.45 (br, 1 H), 1.12-1.08 (m, 27 H), -0.42 (br, 2 H), -0.69 (br, 1 H), -0.83 (br, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6-168.0 (m), 149.2-148.3 (m),

129.9-127.1 (m), 115.4-113.6 (m), 66.2-65.4 (m), 61.4-61.0 (m), 30.2-28.5 (m), 14.2. MS (ESI): *m/z* 1499 $[M+H]^+$, HR-MS (ESI-TOF): Calcd. for $C_{76}H_{95}O_{29}N_2$: 1499.6021. Found: 1499.6000.

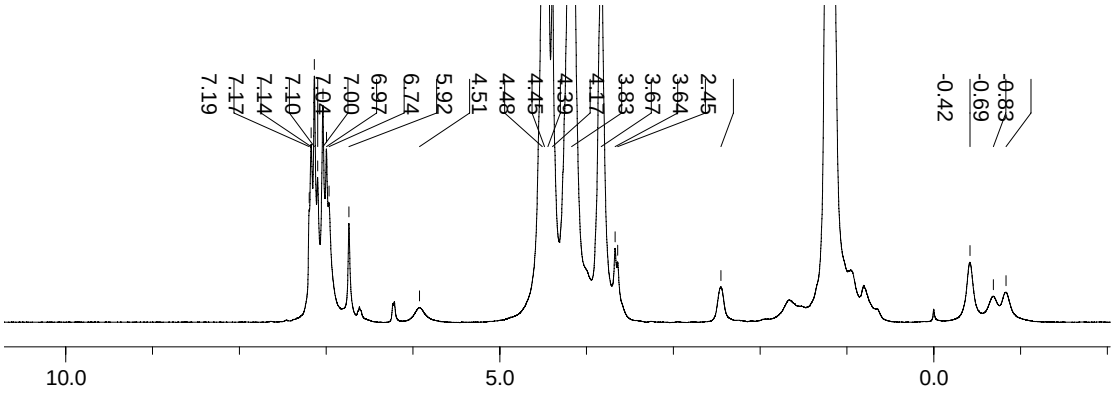

Figure S6. ^{1}H NMR spectrum of **IP**-DA-3 in $CDCl_3$.

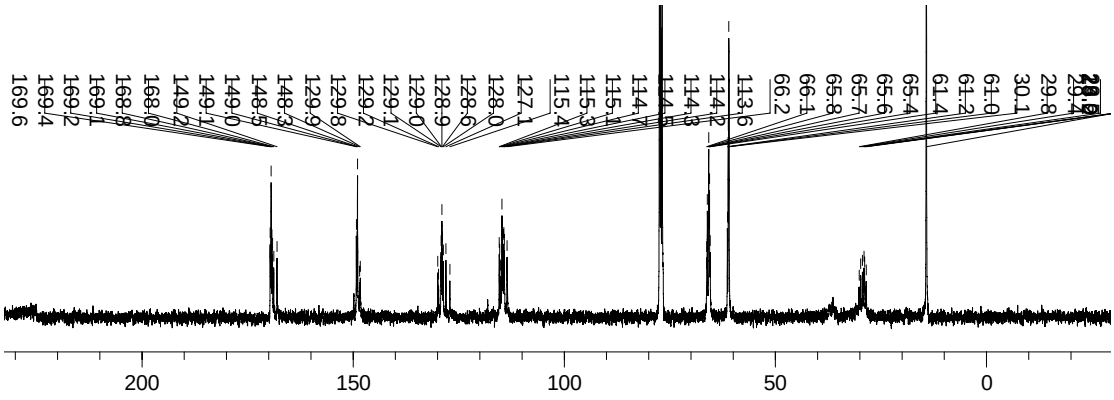

Figure S7. ^{13}C NMR spectrum of **IP**-DA-3 in $CDCl_3$.

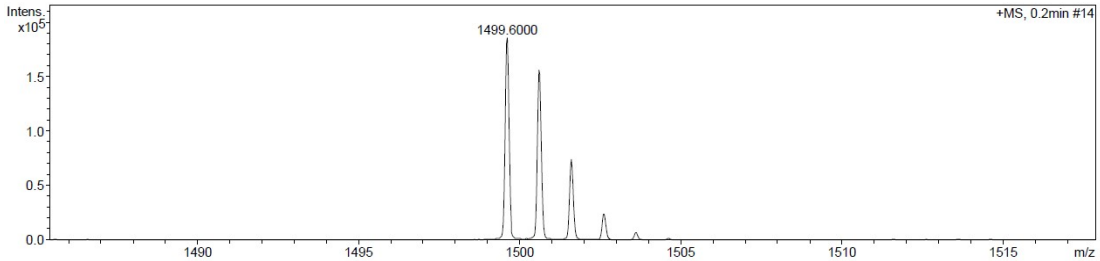

Figure S8. HR ESI-MS of **IP**-DA-3.

IP-MA-3 (48%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.14-6.71 (m, 10 H), 5.70 (br, 1 H), 4.54-3.87 (m, 48 H), 2.67 (br, 1 H), 2.09 (br, 1 H), 1.14-1.10 (m, 27 H), -0.02 (br, 2 H), -0.74 (br, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6-168.4 (m), 149.6-148.5 (m), 129.9-127.6 (m), 115.4-113.5 (m), 66.1-65.6 (m), 61.3-61.0 (m), 39.8, 30.0-28.8 (m), 21.1, 14.1, 9.4. MS (ESI): *m/z* 1484 $[M+H]^+$, HR-MS (ESI-TOF): Calcd. for $C_{76}H_{94}O_{29}N$: 1484.5912. Found: 1484.5916.

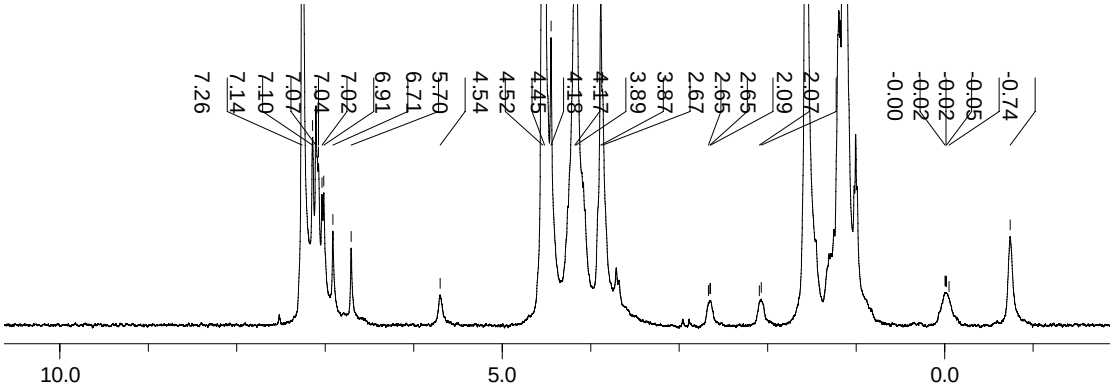

Figure S9. ^{1}H NMR spectrum of **IP**-MA-3 in $CDCl_3$.

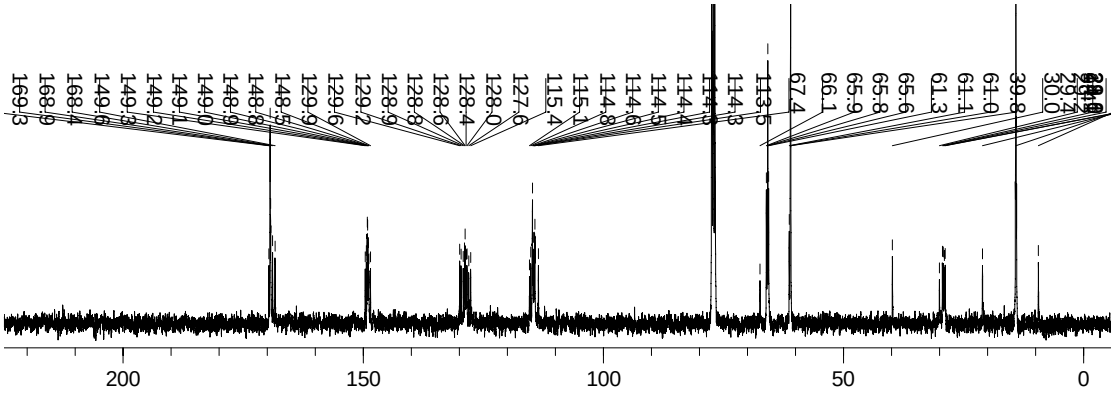

Figure S10. ^{13}C NMR spectrum of **IP**-MA-3 in $CDCl_3$.

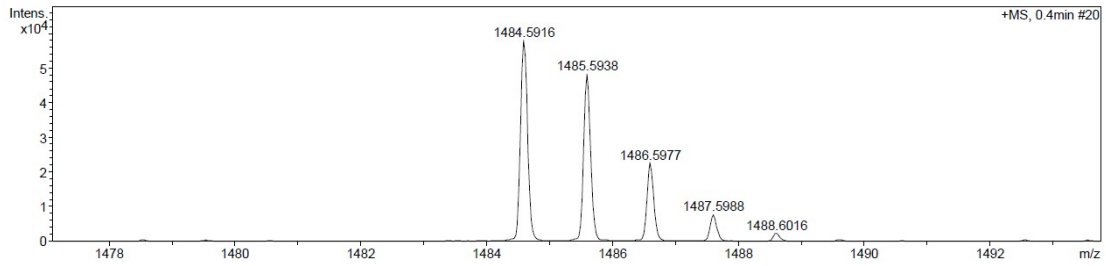

Figure S11. HR ESI-MS of **IP**-MA-3.

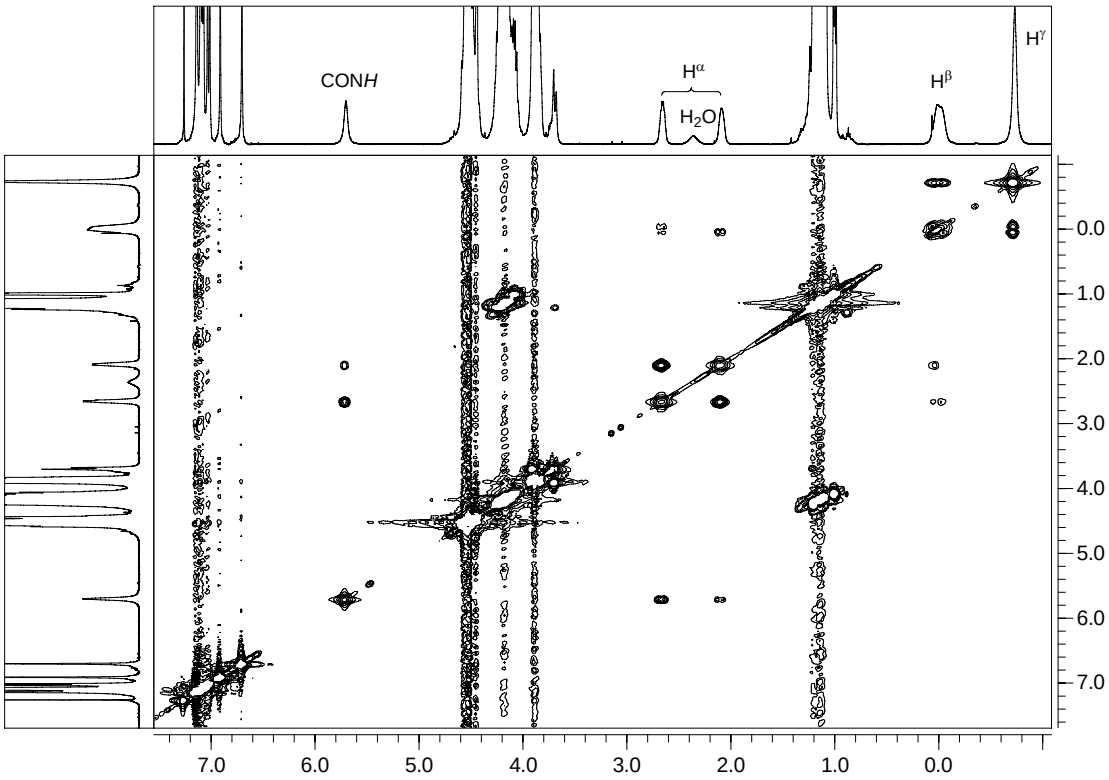

Figure S12. 2D COSY ^{1}H NMR spectrum of **IP**-MA-3 (10 mM) in $CDCl_3$.

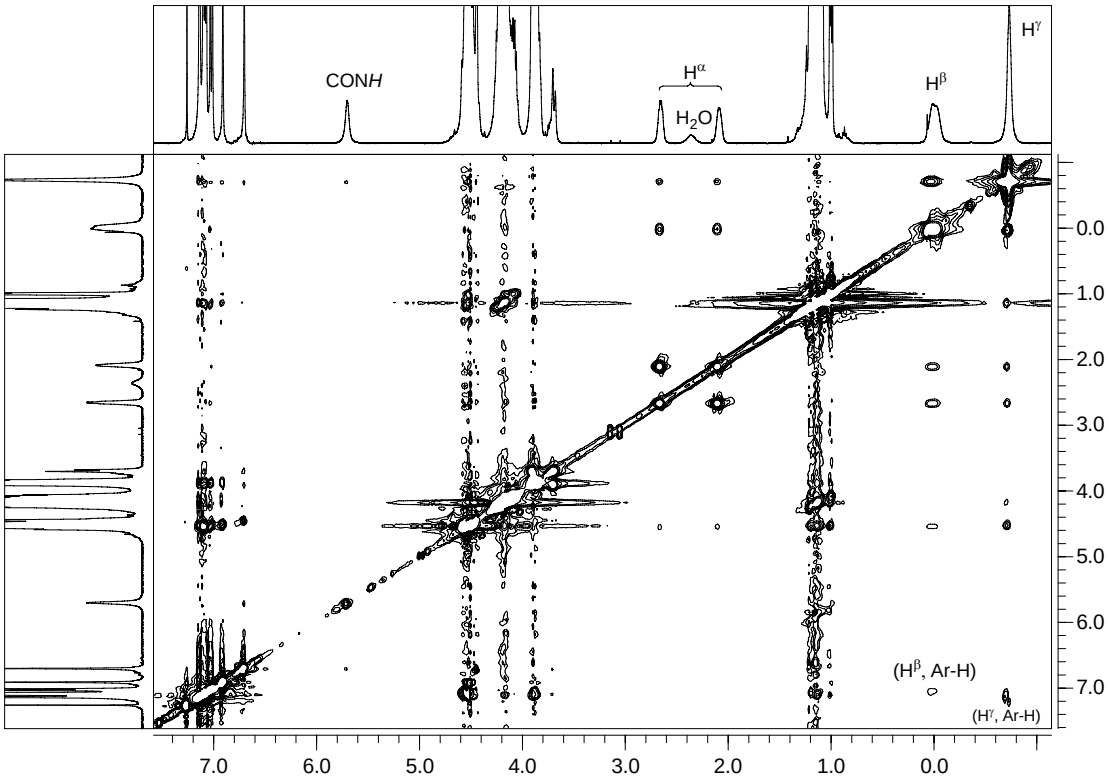

Figure S13. 2D NOESY ^{1}H NMR spectrum (mixing time = 0.6 s) of **IP**-MA-3 (10 mM) in $CDCl_3$.

4. Kinetic experiments for measurement the reaction rate constants:

For the kinetic experiments, **1** ([**1**$_0$] = 4.0 mM) and **DA**-n (80 mM) or **MA**-n (160 mM) was dissolved in $CDCl_3$. The reactions were then monitored by ^{1}H NMR. The ratio of **1** and introverted pillar[5]arene or phenol in the reaction mixture was determined by their integration and thus the concentration of **1** ([**1**]) could be calculated. By fitting the values of ln([**1**$_0$]/[**1**]) or ln([**3**$_0$]/[**3**]) versus time plots with a linear model, the reaction rate constants (*k*s) were obtained, which equal to the slop of the line.

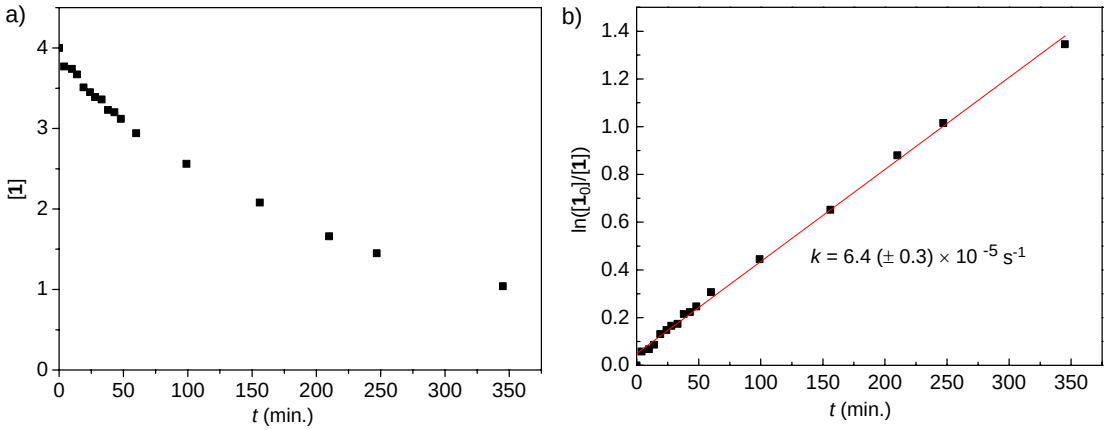

Figure S14. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **DA**-2 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

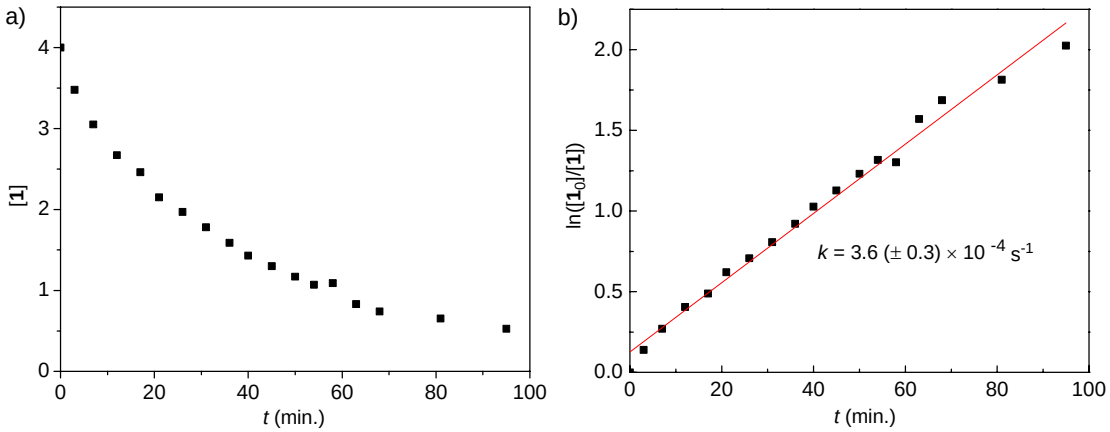

Figure S15. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **DA**-3 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

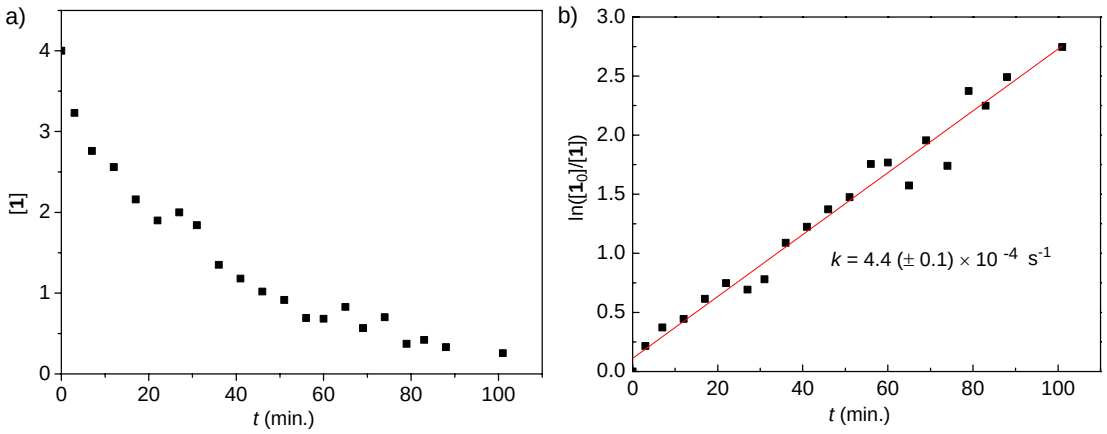

Figure S16. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **DA**-4 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

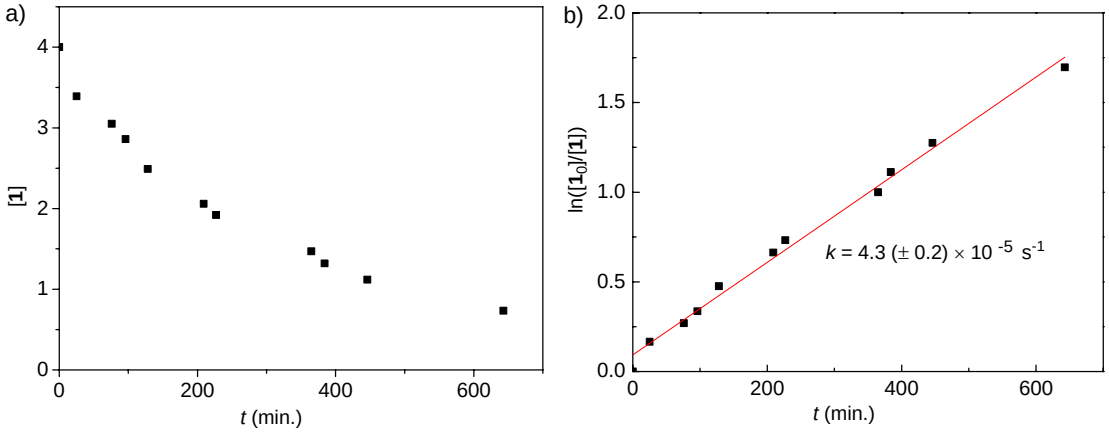

Figure S17. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **DA**-5 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

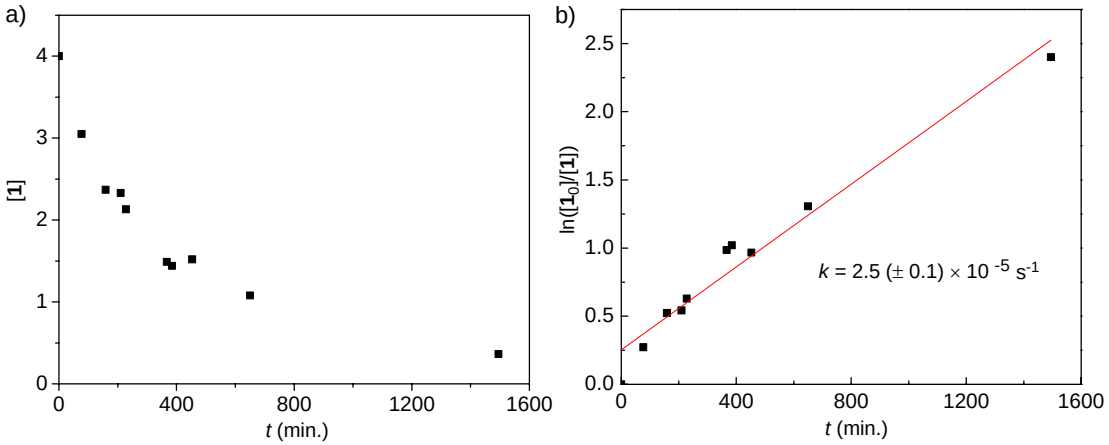

Figure S18. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **DA**-6 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

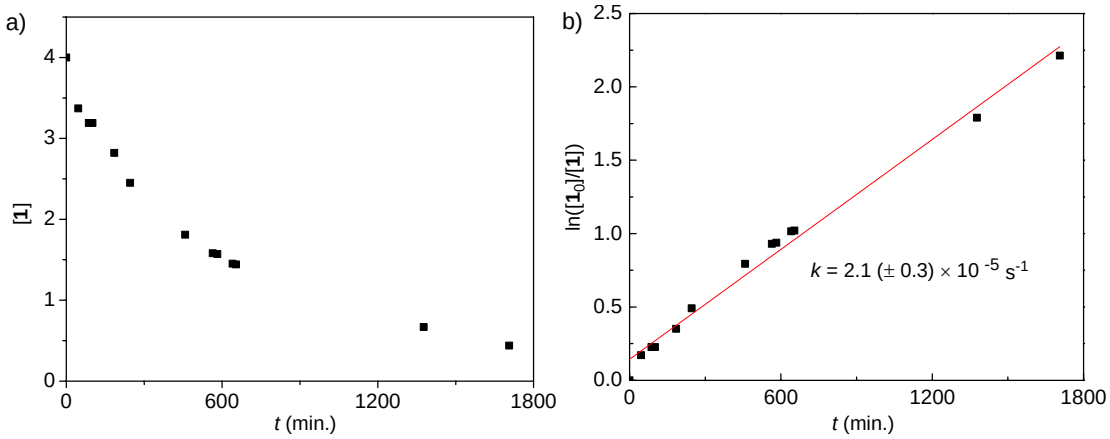

Figure S19. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **DA**-7 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

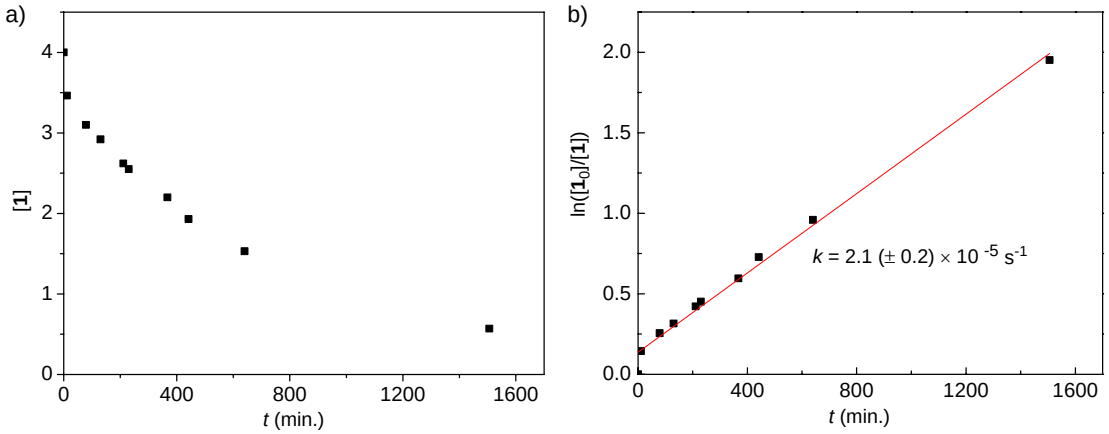

Figure S20. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **MA**-3 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

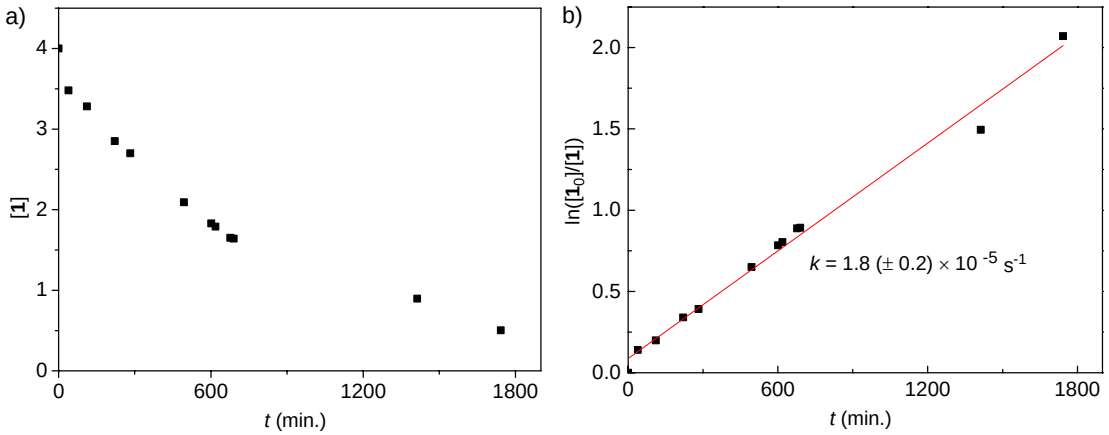

Figure S21. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **MA**-4 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

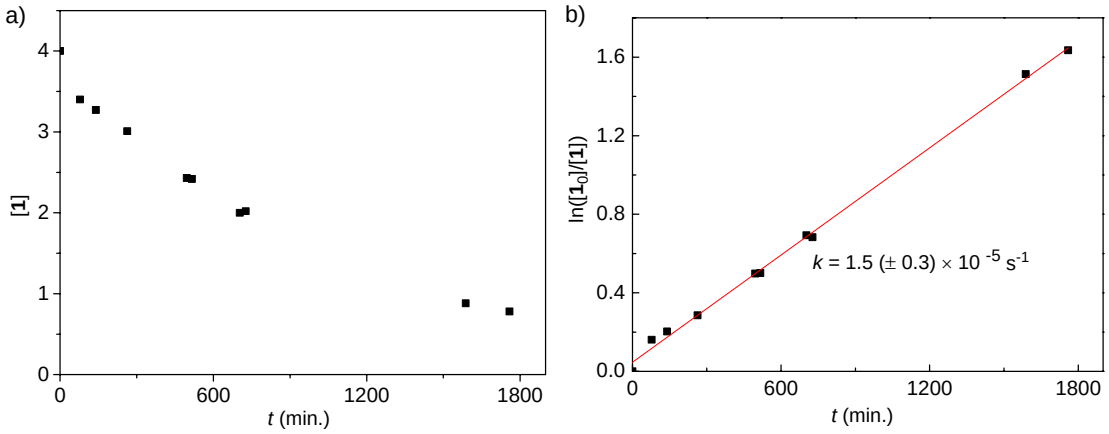

Figure S22. (a) Changes in [**1**] and (b) ln([**1**$_0$]/[**1**]) of the reaction mixture with time (*t*) after mixing of **1** and **MA**-6 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

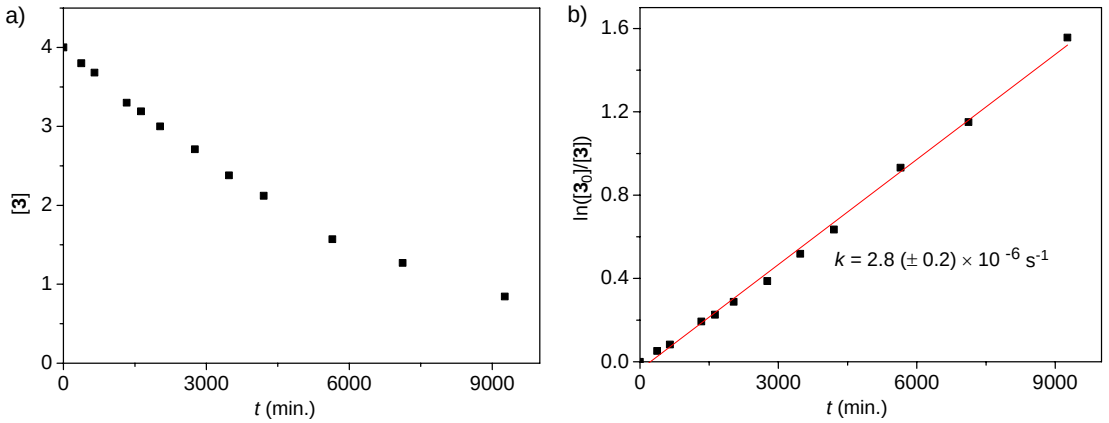

Figure S23. (a) Changes in [**3**] and (b) ln([**3**$_0$]/[**3**]) of the reaction mixture with time (*t*) after mixing of **3** and **MA**-3 in $CDCl_3$. The solid line represents the linear simulation of measured data points.

5. Full ^{1}H NMR spectra of IP-DA-n and IP-MA-n:

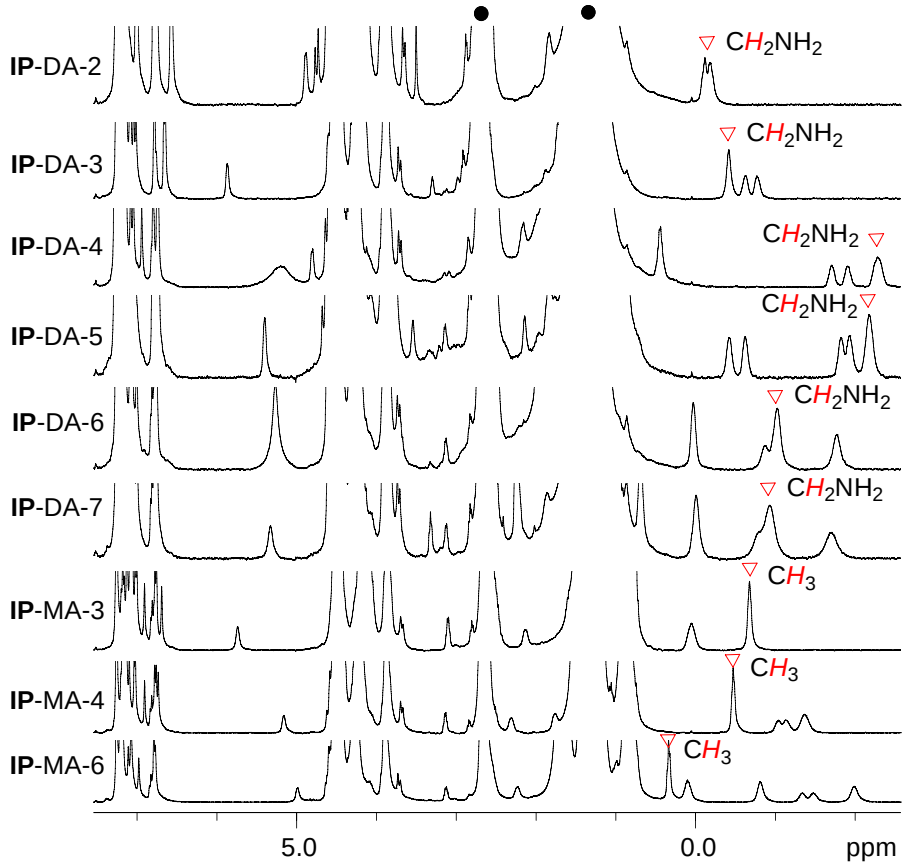

Figure S24. ^{1}H NMR spectra of **IP**-DA-n (n = 2-7) and **IP**-MA-n (n = 3, 4, 6) produced in situ by the reaction of **1** with **DA**-n and **MA**-n. • indicates the signals from the excess **DA**-n or **MA**-n. The assignment of the proton signals of CH_2NH_2 and CH_3 based on their integration and non-anisotropic properties.

6. Reference

[1] W. Si, L. Chen, X.-B. Hu, G. Tang, Z. Chen, J.-L. Hou, Z.-T. Li, *Angew. Chem. Int. Ed.* **2011**, *50*, 12564-12568.