Electronic Supplementary Material (ESI) for RSC Advances.

New Multiple-Layered 3D Polymers Showing Aggregation-Induced Emission and Polarization

Sai Zhang[a*], Qingkai Yuan[b] and Guigen Li[b]*

[a]*School of Pharmacy, Continuous Flow Engineering Laboratory of National Petroleum and Chemical Industry, Changzhou University,Changzhou, Jiangsu 213164, China.*

[b]*Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, 79409-1061, USA. Email: Guigen.li@ttu.edu*

Supporting Information

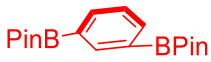
Section S1.General Information

All processes were magnetically stirred in oven-dried glassware with anhydrous solvents under Ar. Syringes, stainless steel or polyethylene cannulas, rubber septa, or a weak Ar counter-flow adding solvents, liquids, and solutions. Ice/water (0 °C) or dry ice/acetone (-78 °C) cooling baths were created in Dewar vessels. High-temperature processes used heated oil baths. Rotavapors at 40-65 °C eliminated solvents. All yields are separate chromatographic and NMR yields.

Without additional purification, all commercially accessible compounds were utilized as received. Without further purification, solvents such CH_3OH, toluene, EA, ether, DCM, dioxane, and acetone were employed. An Innovation Technology solvent system delivers THF and DCM.

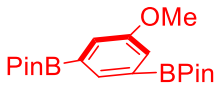
On 400 MHz and 500 MHz instruments with TMS as an internal standard, the ^{1}H and ^{13}C NMR spectra were captured. The residual solvent signal (= 7.26 for CDCl3) was utilized to reference the 1H NMR spectra. The signal of the solvents was employed in the 13C NMR spectra (= 7.16 for CDCl3 and). Chemical shifts () with regard to TMS were reported in ppm. Chemical shift, multiplicity (singlet, doublet, triplet, multiplet), coupling constant (J, Hz), and integration are used to describe the data. The TOSOH EcoSEC HLC-8420 GPC, which has a dual-flow refractive index detector, was used to collect GPC data. Along with the RI detector, a UV detector is also provided for usage with UV visible polymers. The range of the installed columns is 500-107 Da. Samples were conducted at a flow rate of 0.7 mL/min for 25 minutes. Our investigations used polystyrene (PS) standards for calibration.

Section S2. Synthetic Procedure



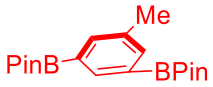
1

1 was synthesized from 1,3-dibromobenzene following the reported procedure [1] with very minor modification. **1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1):** White solid, 50% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.44 – 7.34 (m, 1H), 1.45 – 1.29 (m, 24H).



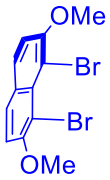
2

2 was synthesized from 1,3-dibromobenzene following the reported procedure [2]. **2,2'-(5-methoxy-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2):** White solid, 77% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.86 (d, *J* = 0.8 Hz, 1H), 7.41 (d, *J* = 0.9 Hz, 2H), 3.85 – 3.81 (m, 3H), 1.32 (s, 24H).



3

3 was synthesized from 1,3-dibromobenzene following the reported procedure [3]. **2,2'-(5-methyl-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1-3):** White solid, 77% yield. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.44 – 7.34 (m, 1H), 1.45 – 1.29 (m, 24H).

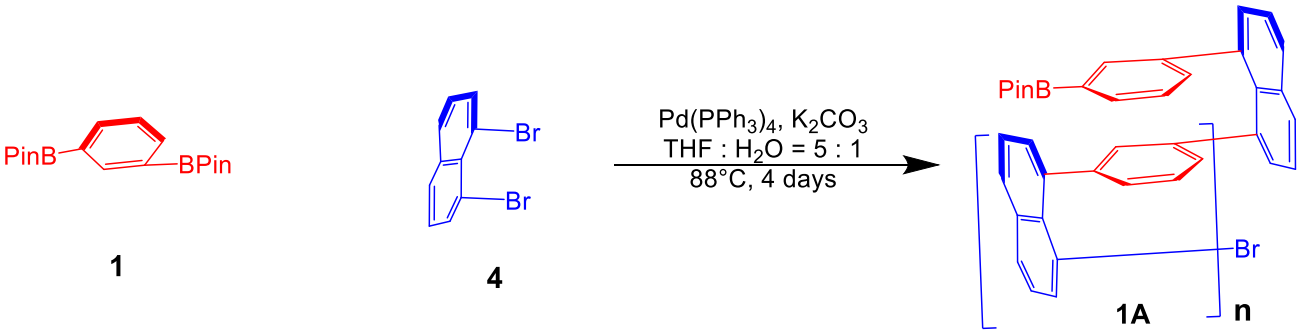


5

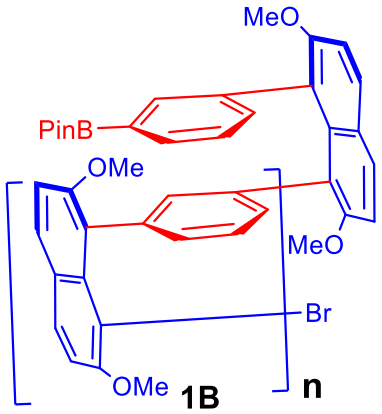
5 was synthesized from 1,3-dibromobenzene following the reported procedure. **1,8-dibromo-2,7-dimethoxynaphthalene (5):** Yellow solid, 85%, ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.74 (dd, *J* = 8.9, 1.6 Hz, 2H), 7.18 – 7.12 (m, 2H), 4.01 (d, *J* = 1.6 Hz, 6H).

General Procedure for **Polymer 1A-1C, 2A-2C.**

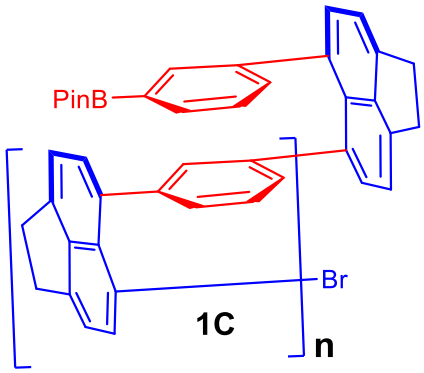
Take Polymer **1A** as an example for synthesis from 2,7-diethoxynaphthalene following the reported procedure.



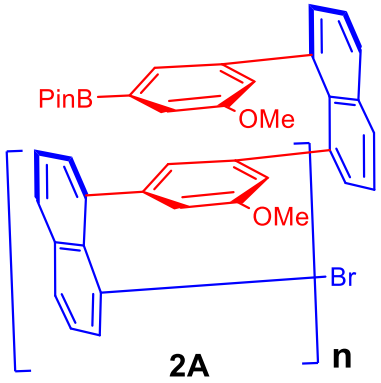
A 50 mL oven-dried round-bottom flask was filled with 1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene **1** (132.0 mg, 0.4 mmol, 1 equiv), 1,8-dibromonaphthalene **4**(114.4 mg, 0.4 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), The round-bottom flask was filled with 2 mL H_2O and 10 mL THF. Argon was added after the round bottom flask had been vacuum-degassed. Then, for more than 96 hours, it was heated at 88°C. To reach room temperature, the mixture was chilled. In a single pot, the resultant mixture was then added to MeOH/HCl. The components that had precipitated were collected by filtration through a Buchner funnel and repeatedly rinsed with methanol and water. The solid was further dried to produce earthy yellow solid (149mg, 60% yield, M_n=9427, M_w=9792, PDI=1.039). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.18-7.24 (m, 656H), 7.19-5.80(m,340H), 1.27(br, 12H).



The same synthesis procedure as Polymer **1A**, **1B** was obtained as yellow solid (205 mg, 81% yield, M_n=8318, M_w=8808, PDI=1.059). ^{1}H NMR (400 MHz, CHOLOFORM-D) δ 7.80-7.24 (m, 133H), 7.19-6.25(m, 57H), 4.20 – 2.99 (m,123H), 1.23(br, 12H).

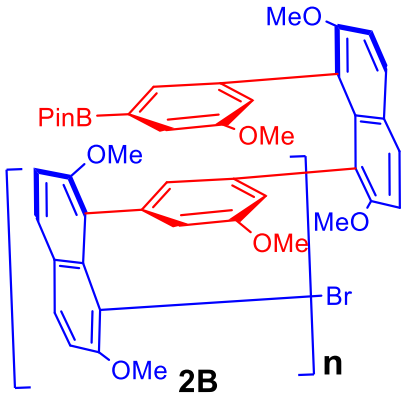


The same synthesis procedure as Polymer **1A**, **1C** was obtained as yellow solid (151 mg, 63% yield, M_n=8847, M_w=9226, PDI=1.043). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.75-7.24 (m, 641H), 7.19-5.90(m, 458H), 3.60 – 2.80 (m, 337H), 1.29(br, 12H)



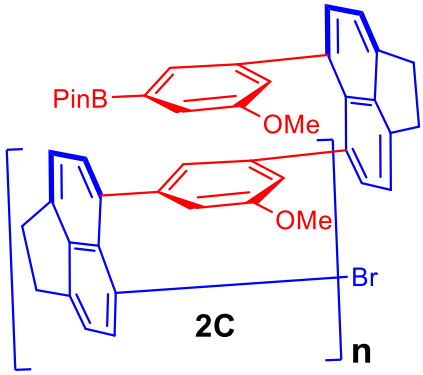
2A

The same synthesis procedure as Polymer **1A**, **2A** was obtained as yellow solid (210 mg, 81% yield, M_n= 1885, M_w=2576, PDI= 1.366). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.40-7.24 (m, 1314H), 7.19-5.50(m, 735H), 3.90 – 2.50 (m, 609H),1.27(br, 12H).



2B

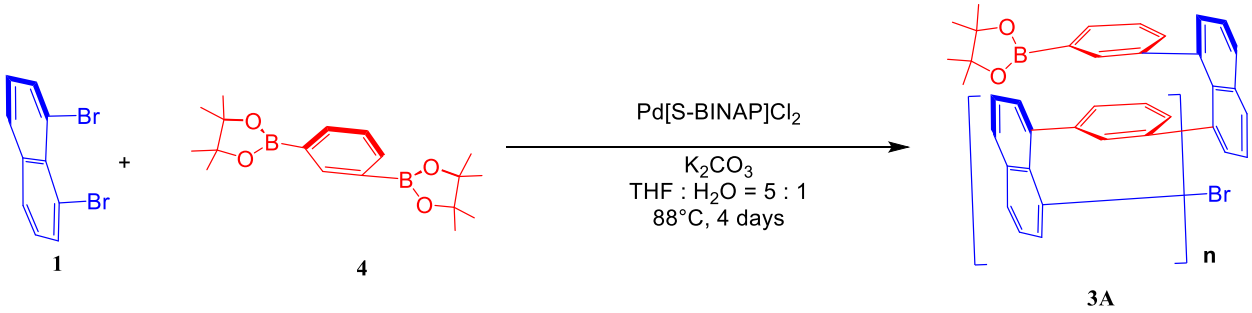
The same synthesis procedure as Polymer **1A**, **2B** was obtained as yellow solid (205 mg, 82% yield, Mn=7216, Mw=8086, PDI=1.121). ^{1}H NMR (400 MHz,CHLOROFORM-D) δ 7.90–7.24 (m, 891H), 7.19-5.75(m, 1018H), 4.21 – 2.80 (m, 1526H), 1.28(m, br).



The same synthesis procedure as Polymer **1A**, **2C** was obtained as yellow solid (90 mg, 38% yield, Mn=2629, Mw=2916, PDI=1.109). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.25-7.24 (m, 353H), 7.19-5.60(m,180H), 3.80 – 2.55 (m, 304H), 1.28(br, 12H)

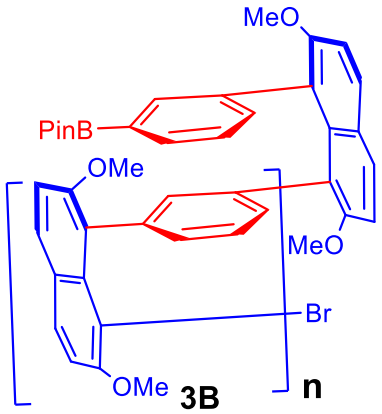
General Procedure for **polymer 3A-3C, 4A-4C, 5A-5C**

Take Polymer **3A** as an example for synthesis from 2,7-diethoxynaphthalene following the reported procedure.



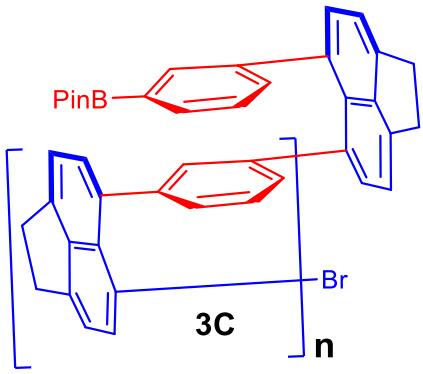
A 50 mL oven-dried round-bottom flask was filled with 1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (132.0 mg, 0.4 mmol, 1 equiv), 1,8-dibromonaphthalene (114.4 mg, 0.4 mmol, 1.0 equiv), Pd(S-BINAP)Cl_2 (16 mg, 0.02 mmol), The round-bottom flask was filled with 2 mL H2O and 10 mL THF. Argon was added after the round bottom flask had been vacuum-degassed. Then, for more than 96 hours, it was heated at 85℃. To reach room temperature, the mixture was chilled. In a single pot, the resultant mixture was then added to MeOH/HCl. The components that had precipitated were collected by filtration through a Buchner funnel and repeatedly rinsed with methanol and water. The solid was further dried to produce earthy yellow solid (149mg, 60% yield, $[\alpha]_D^{RT}$= +4(c=0.05, THF), Mn=51362, Mw=88548, PDI=1.724). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.39 – 5.73 (Ar-H).

Synthesis of **Polymer 3B**



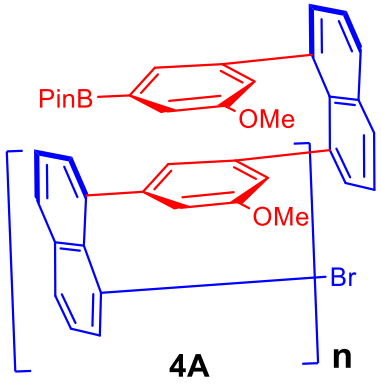
The same synthesis procedure as Polymer **3A**, **3B** was obtained as light yellow solid (188mg, 69% yield, $[\alpha]_D^{RT}$= +4(c=0.1, THF), Mn=65599, Mw=116905, PDI=1.782). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.43 – 5.74 (Ar-H), 4.26 – 3.24 (OCH_3-H).

Synthesis of **Polymer 3C**



The same synthesis procedure as Polymer **3A**, **3C** was obtained as yellow solid (182mg, 71%,$[\alpha]_D^{RT}$= 43,(c=0.0325, THF), Mn=68002, Mw=115241, PDI=1.695). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.93 – 5.93 (Ar-H), 3.80 – 3.15 (CH_2CH_2-H).

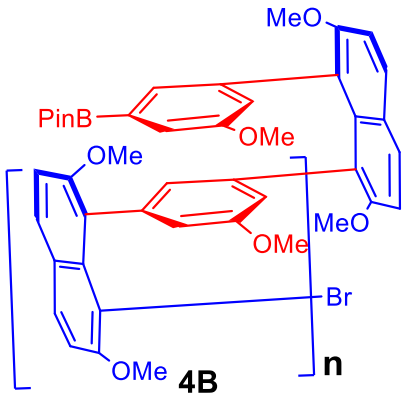
Synthesis of **Polymer 4A**



4A

The same synthesis procedure as Polymer **3A**, **4A** was obtained as yellow solid (120mg, 47% yield, $[\alpha]_D^{RT} = +8, c = 0.1, THF), Mn = 66765, Mw = 105730, PDI = 1.584$). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.29 – 5.50 (m, Ar-H), 4.04 – 2.64 (m, OCH_3-H).

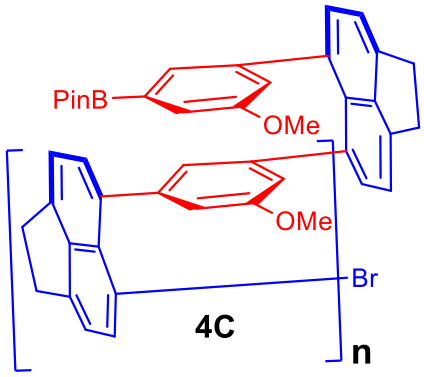
Synthesis of **Polymer 4B**



4B

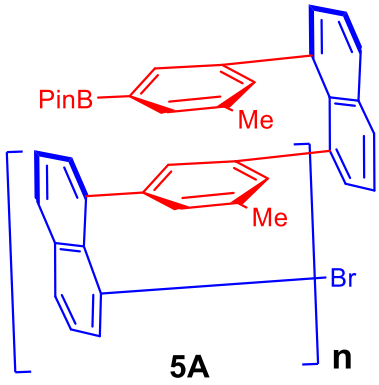
The same synthesis procedure as Polymer **3A**, **4B** was obtained as yellow solid (143mg, 51% yield, $[\alpha]_D^{RT} = +2, (c = 0.1, THF), Mn = 64469, Mw = 102227, PDI = 1.585$). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.32 – 5.15 (m, Ar-H), 4.15 – 2.44 (m, OCH_3-H,).

Synthesis of **Polymer 2C**



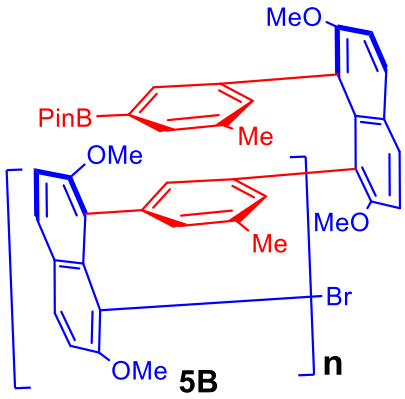
The same synthesis procedure as Polymer **3A**, **4C** was obtained as yellow solid (119mg, 44% yield, $[\alpha]_D^{RT} = -12.5, (c = 0.1, THF), Mn = 49209, Mw = 77682, PDI = 1.579)$. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.00 – 5.46 (m, Ar-H), 4.21 – 2.34 (m, OCH_3H, CH_2CH_2-H).

Synthesis of **Polymer 5A**



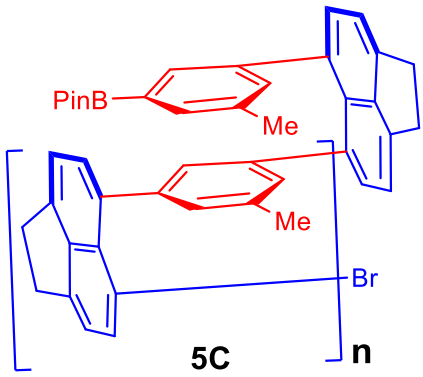
The same synthesis procedure as Polymer **3A**, **5A** was obtained as yellow solid (131mg, 46% yield, $[\alpha]_D^{RT} = -40, (c = 0.025, THF), Mn = 57119, Mw = 95336, PDI = 1.669)$. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.13 – 5.71 (m, Ar-H), 2.52 – 1.64 (m, CH_3-H).

Synthesis of **Polymer 3B**



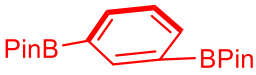
The same synthesis procedure as Polymer **3A**, **5B** was obtained as yellow solid (198mg,72% yield, $[\alpha]_D^{RT} = +3, (c = 0.1, THF), Mn = 50202, Mw = 70448, PDI = 1.403)$. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.98 – 6.20 (m, Ar-H), 4.32 – 2.88 (m, OCH_3-H), 2.58 – 1.66 (m, CH_3-H).

Synthesis of **Polymer 5C**



The same synthesis procedure as Polymer **3A**, **5C** was obtained as yellow solid(187mg, 71%, $[\alpha]_D^{RT} = -2,\ (c = 0.05, THF), Mn = 40101, Mw = 54189, PDI = 1.351)$. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.24 – 5.91 (m, Ar-H), 3.85 – 2.89 (m, CH_2CH_2-H), 2.59 – 2.00 (m, CH_3-H).

Section S3. NMR Spectras and GPC data



1

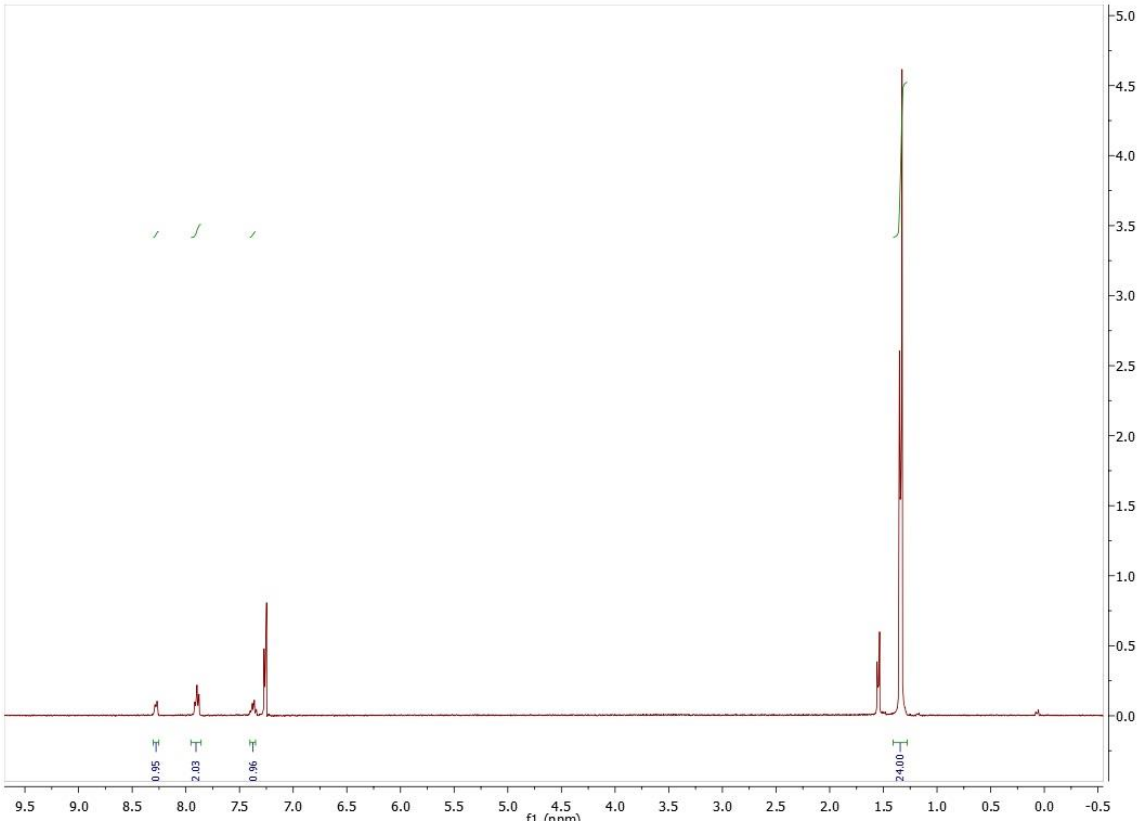
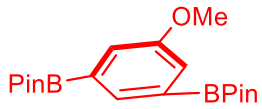


Figure S1.[1]H NMR spectrum of **1**



2

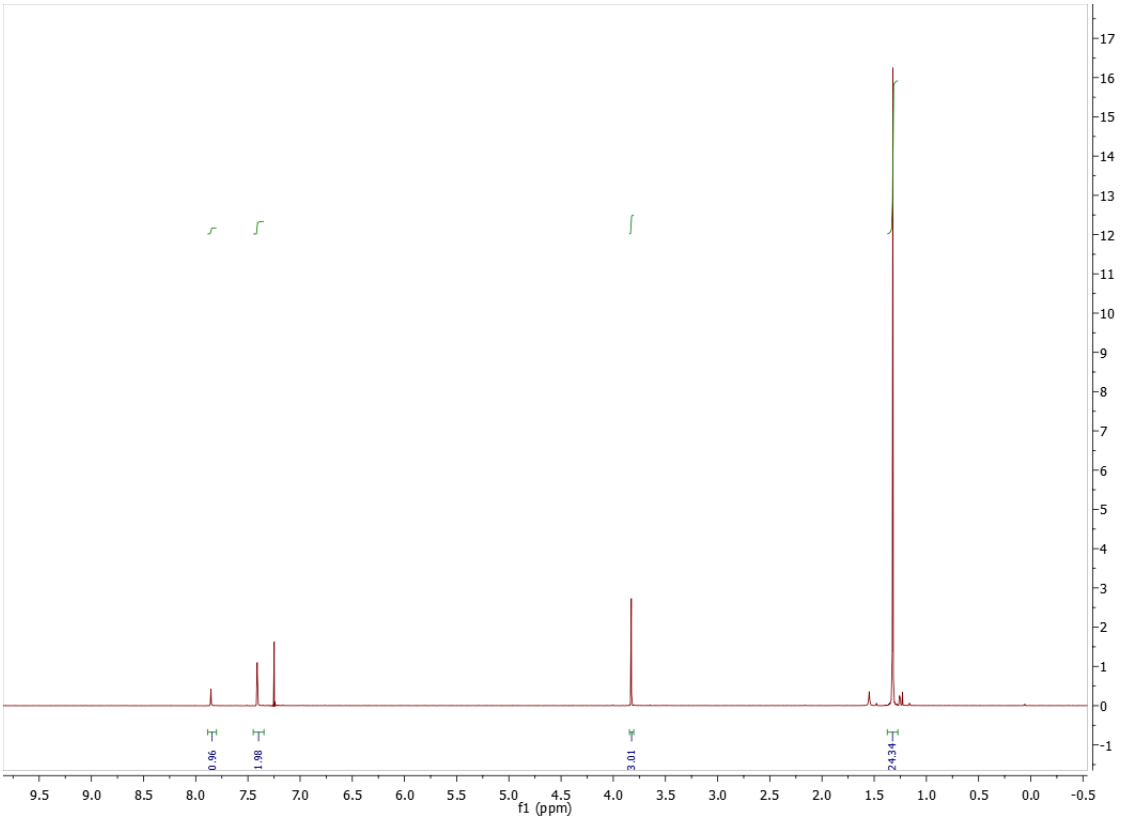
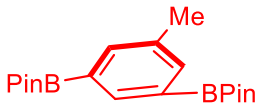


Figure S2.[1]H NMR spectrum of **2**



3

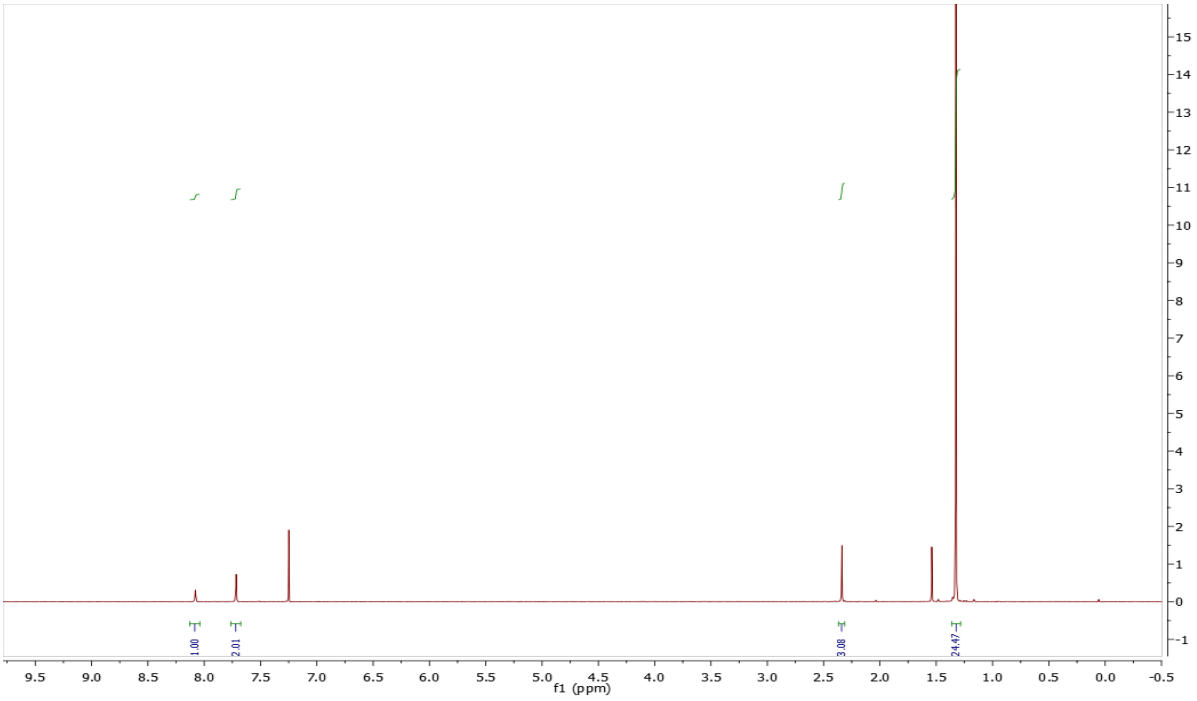


Figure S3.^{1}H NMR spectrum of **3**

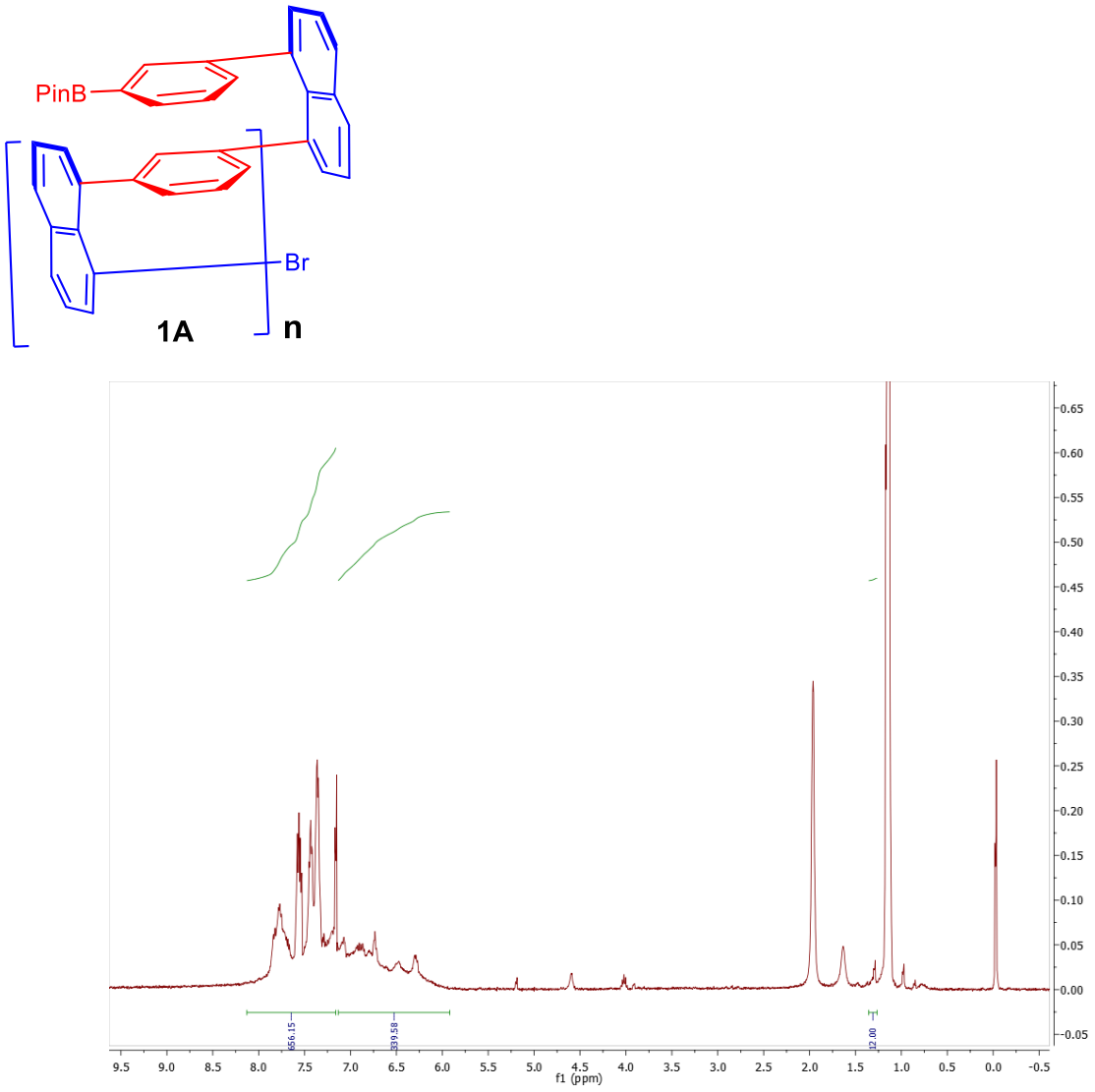
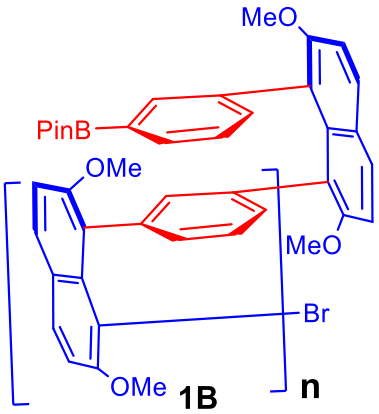


Figure S4.^{1}H NMR spectrum of **1A**



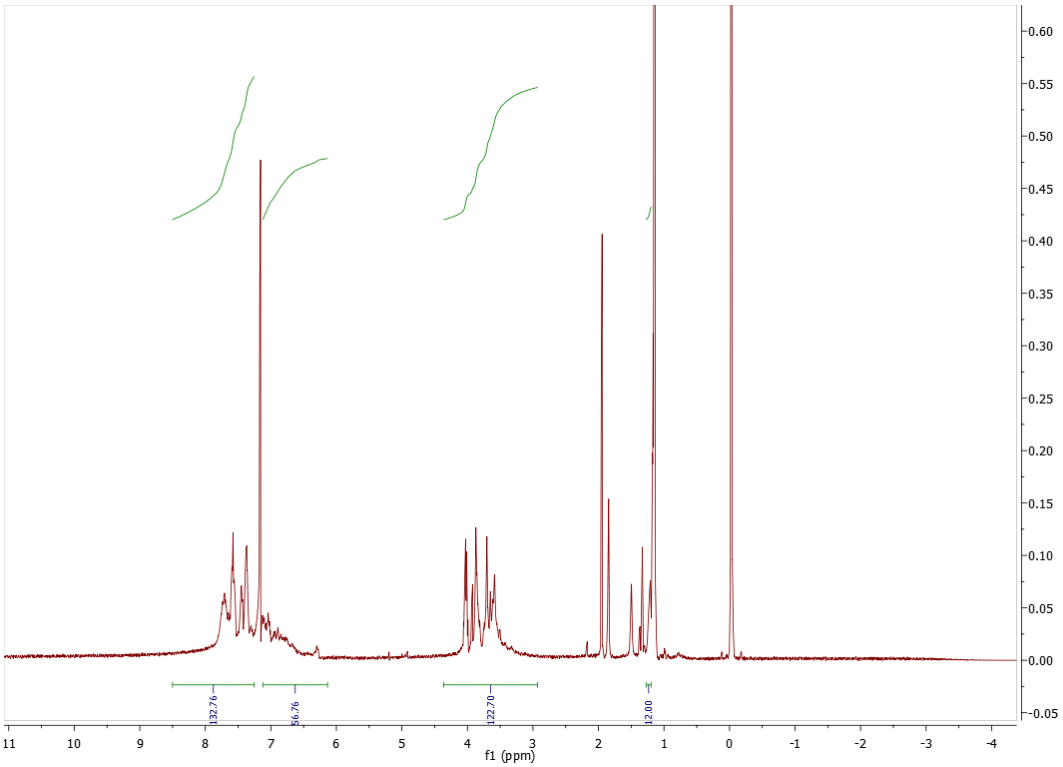
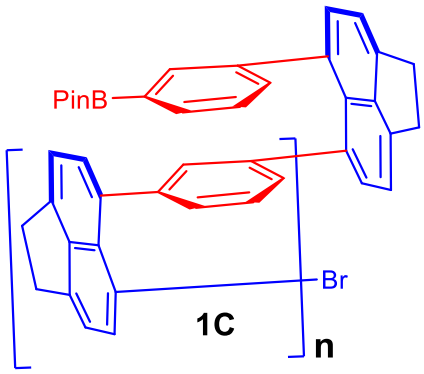


Figure S5.[1]H NMR spectrum of **1B**



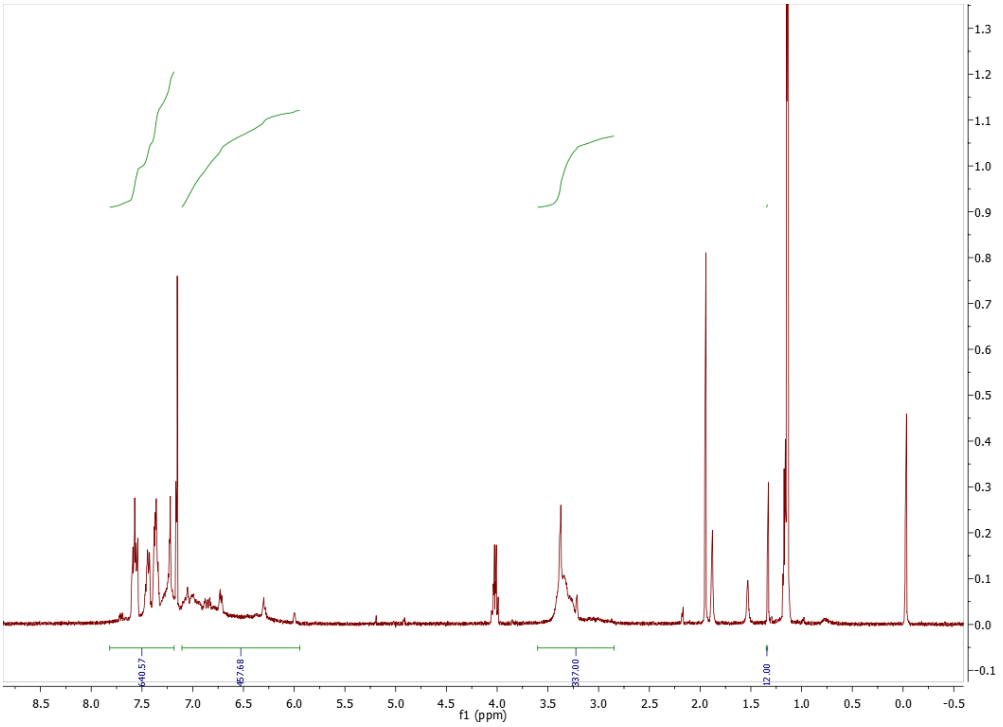
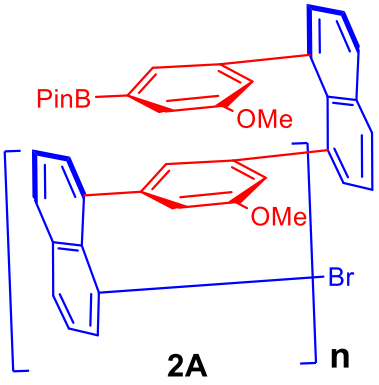


Figure S6. ^{1}H NMR spectrum of **1C**



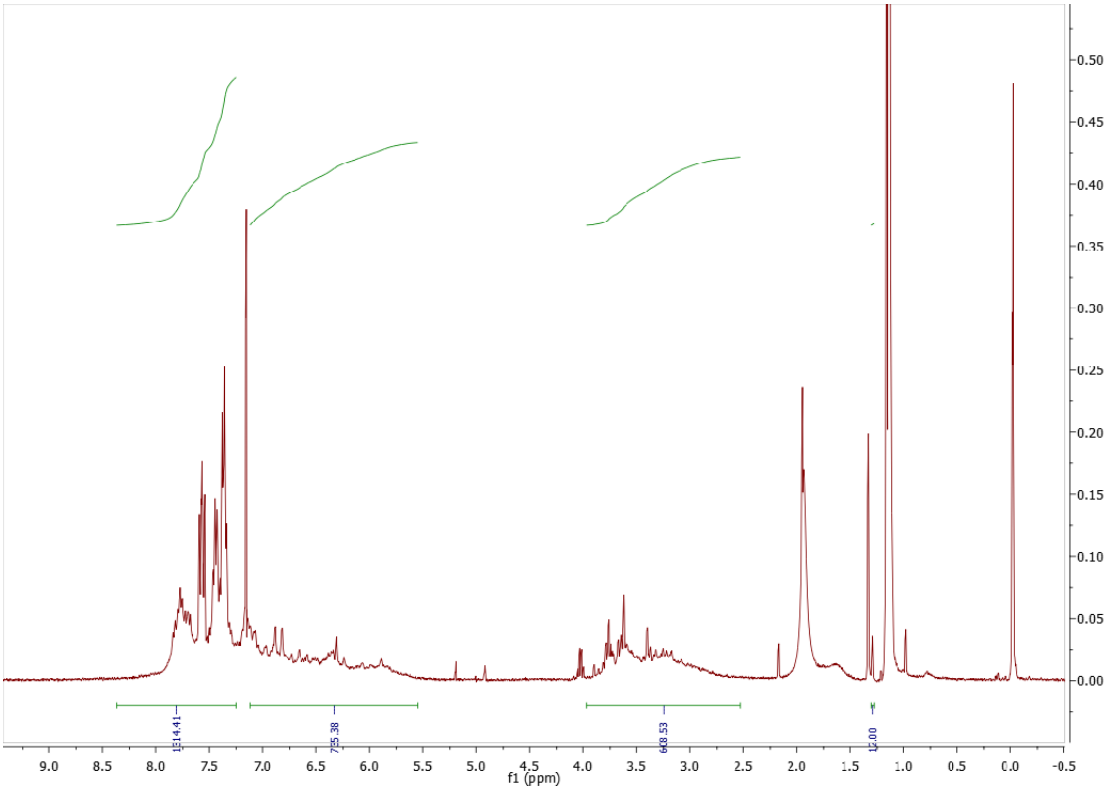
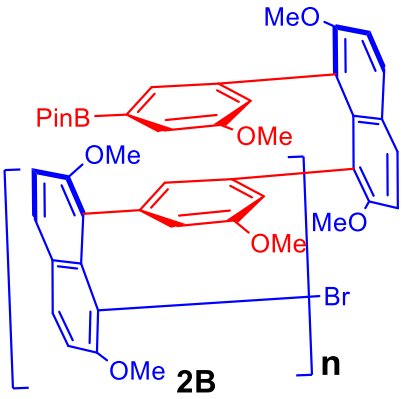


Figure S7.^{1}H NMR spectrum of **2A**



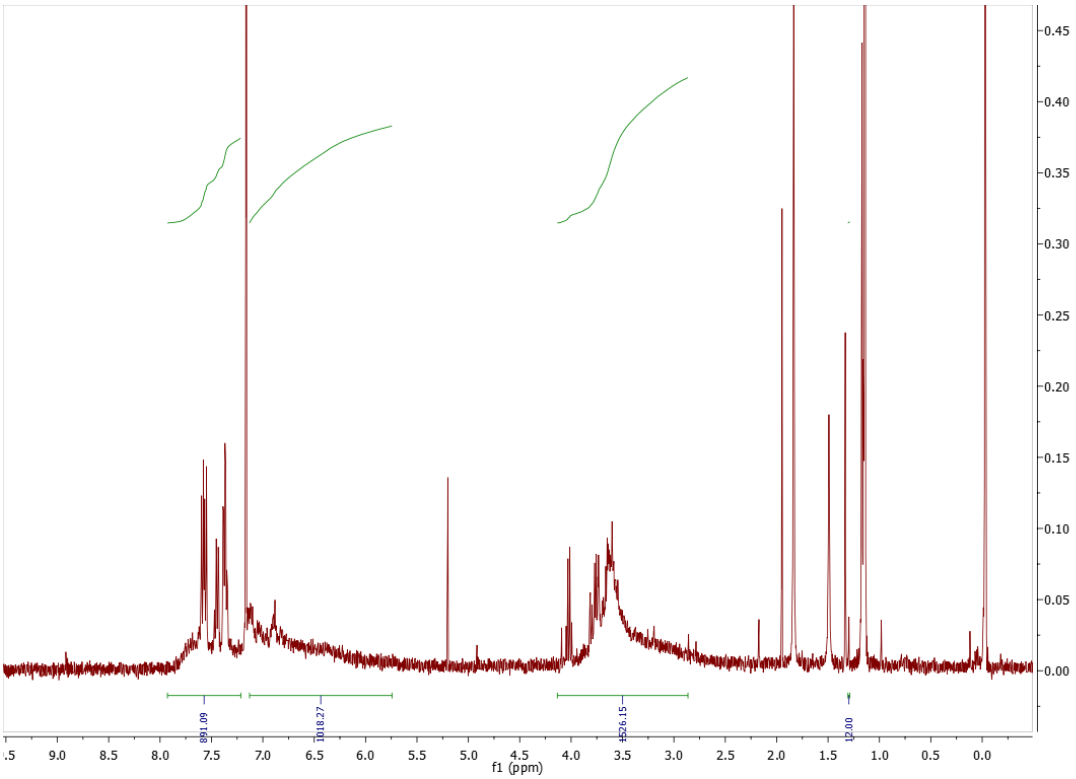
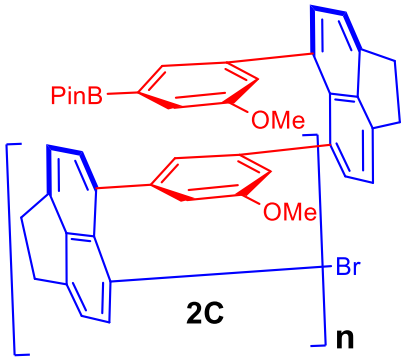


Figure S8. ^{1}H NMR spectrum of **2B**



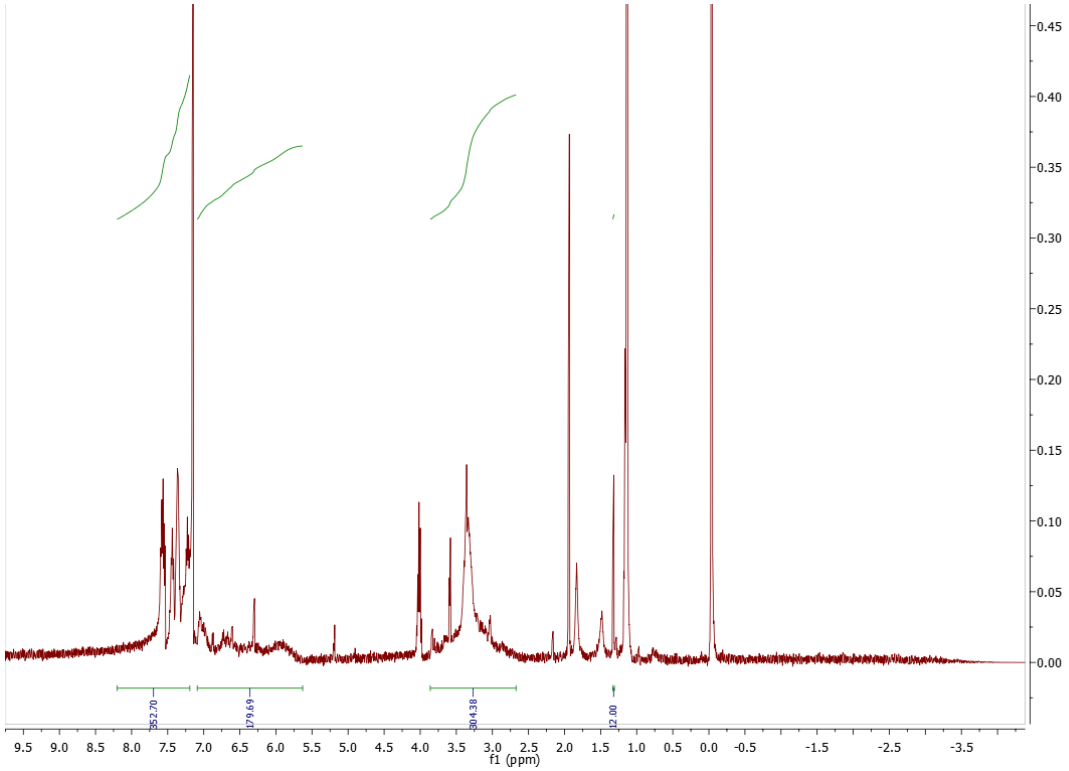


Figure S9.[1]H NMR spectrum of **2C**

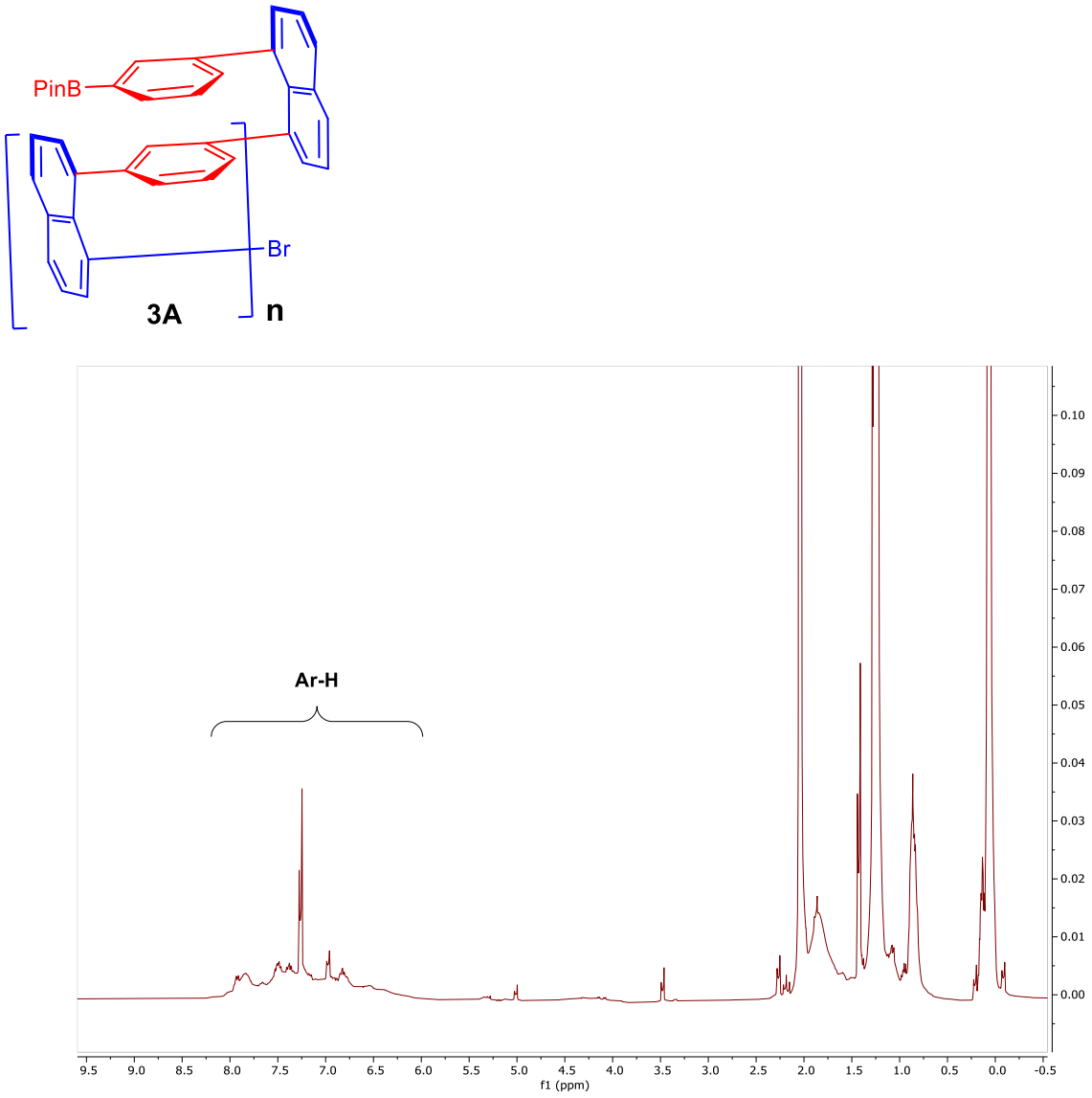
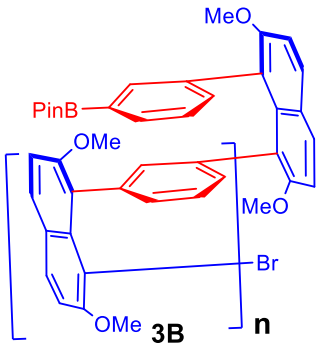


Figure S10.^{1}H NMR spectrum of **3A**



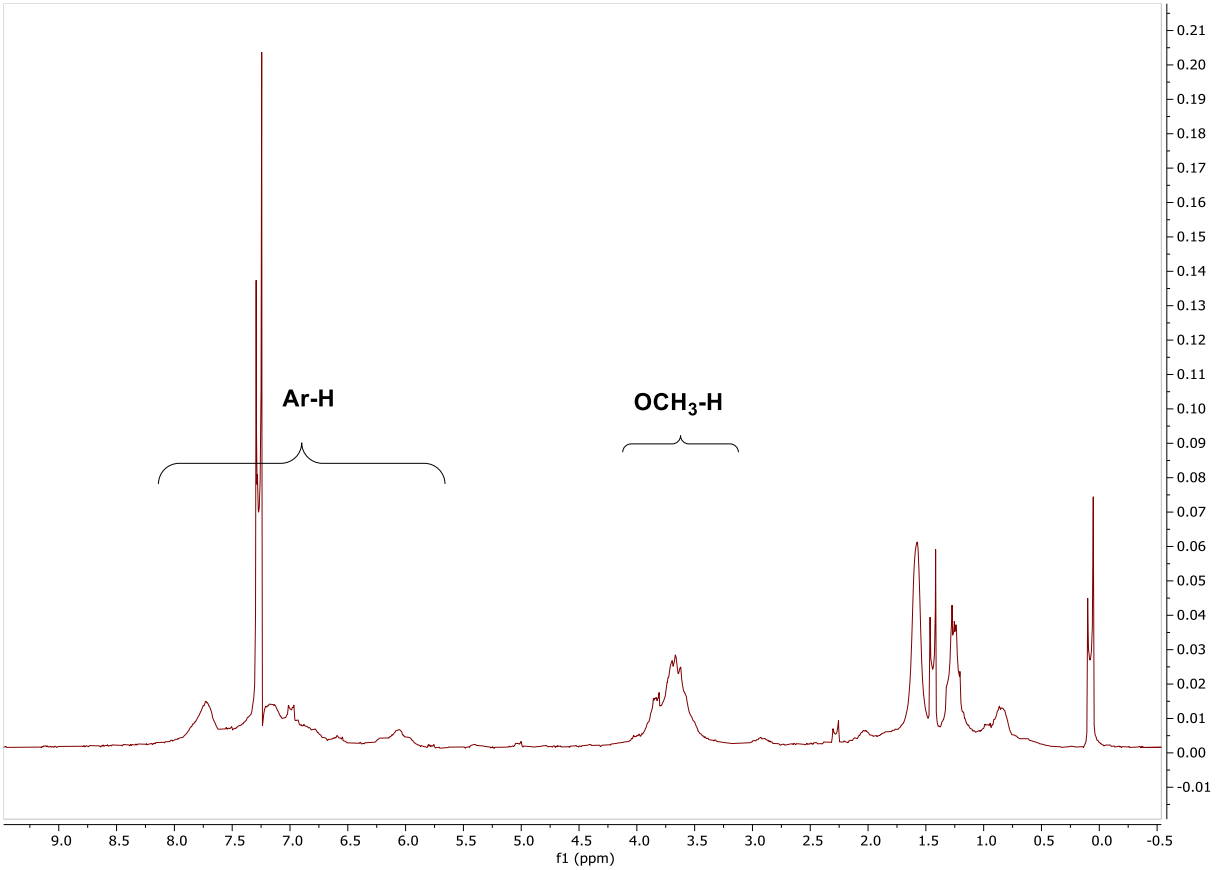


Figure S11.^{1}H NMR spectrum of **3B**

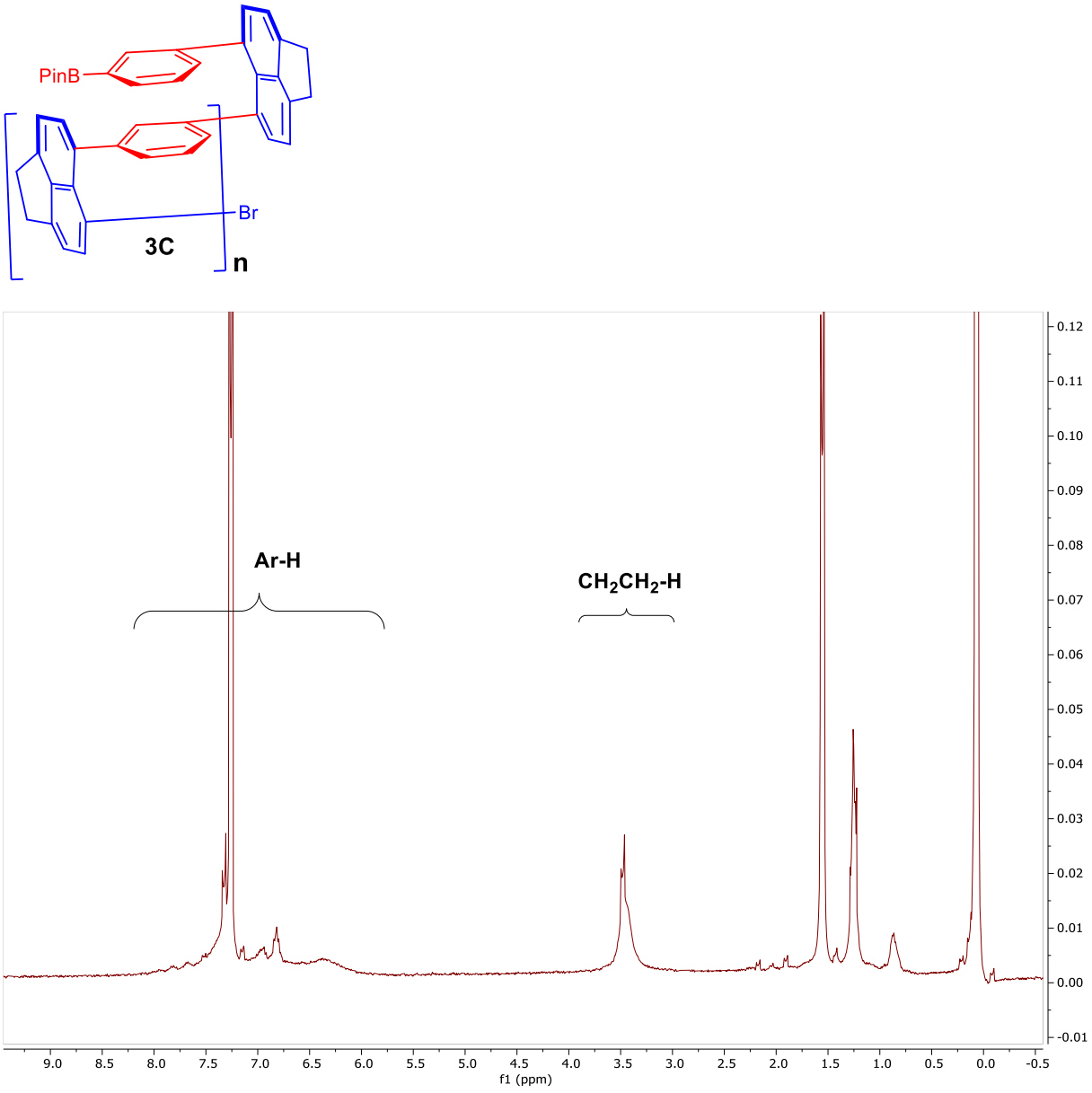


Figure S12.[1]H NMR spectrum of **3C**

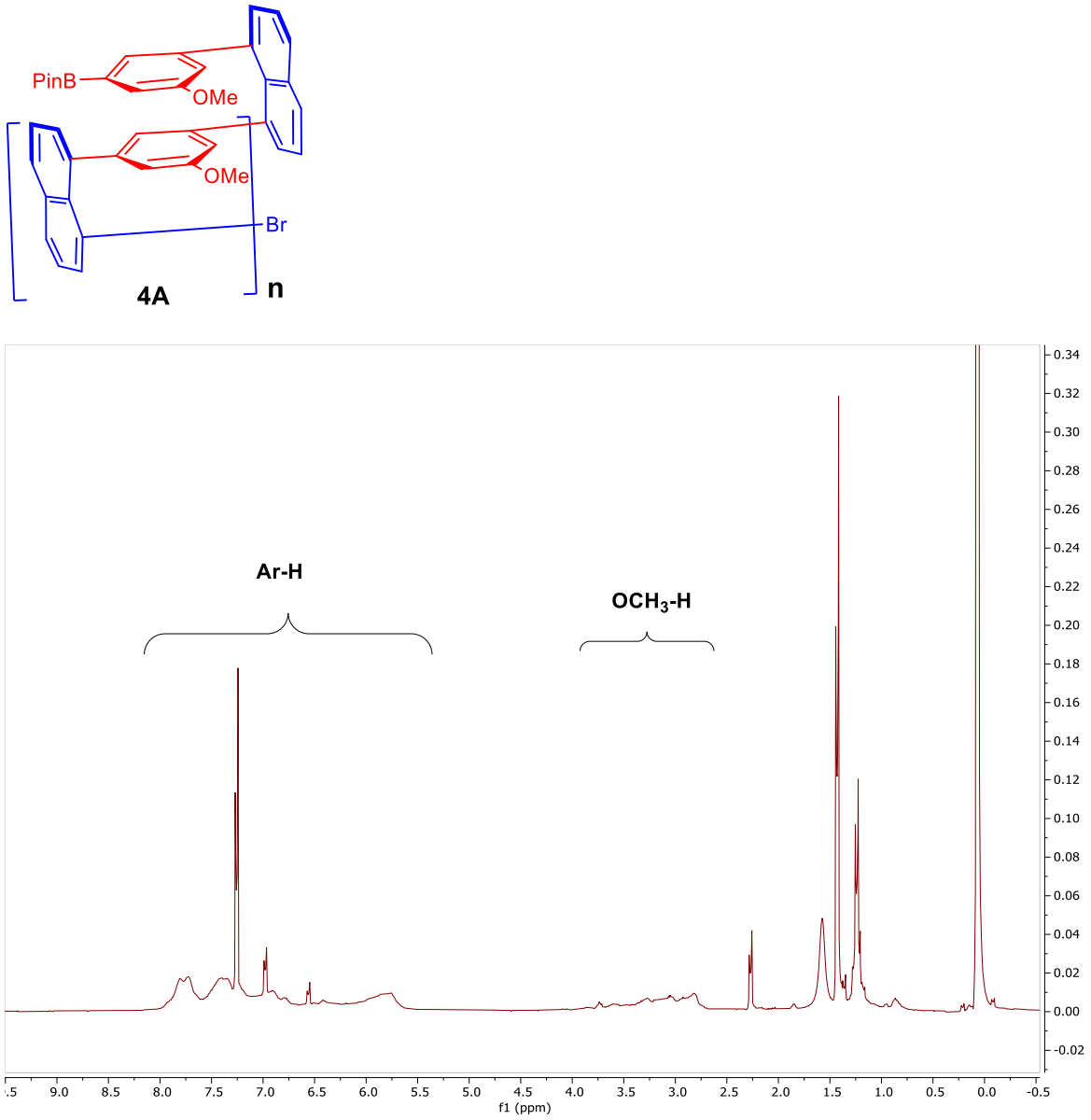
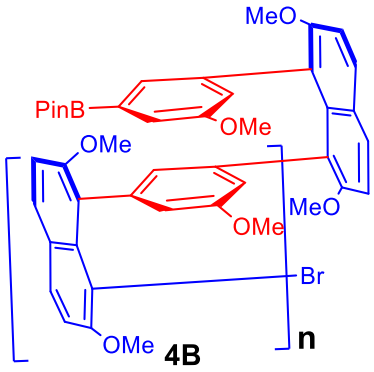


Figure S13.[1]H NMR spectrum of **4A**



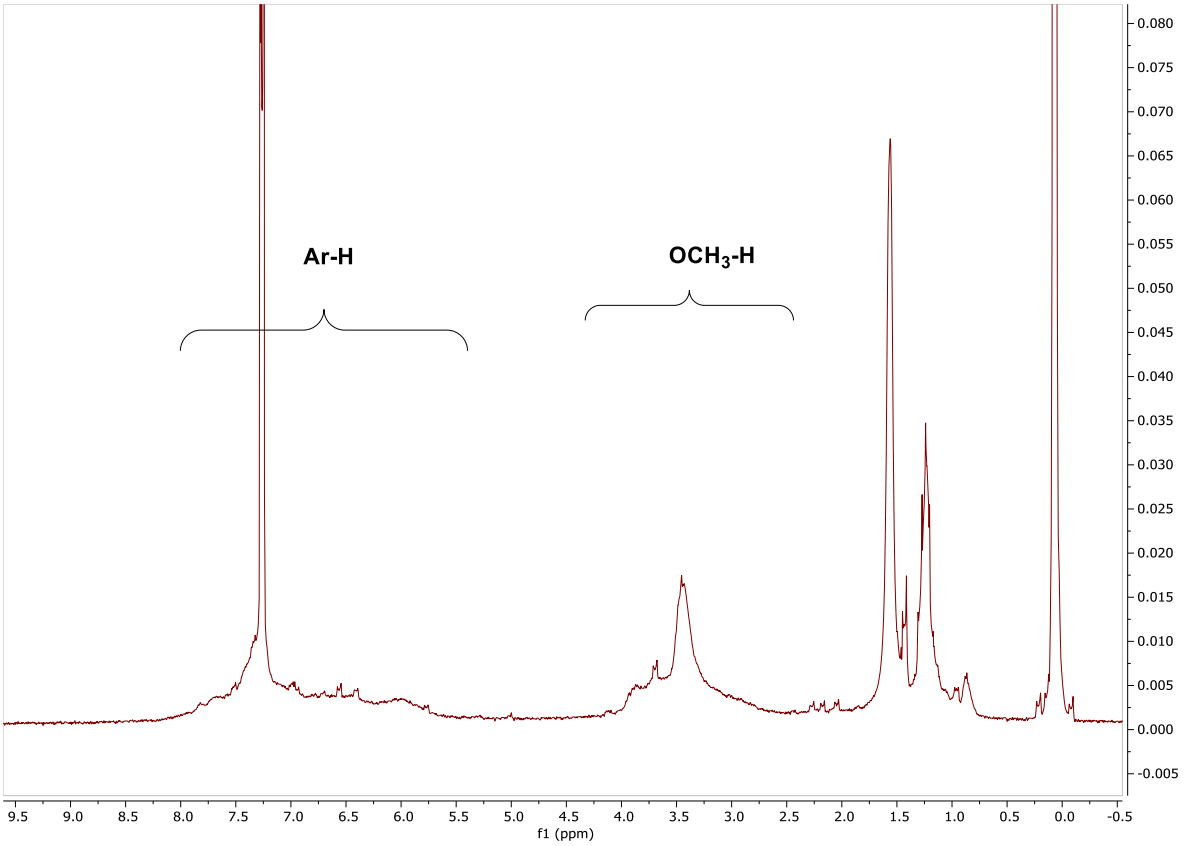


Figure S14.^{1}H NMR spectrum of **4B**

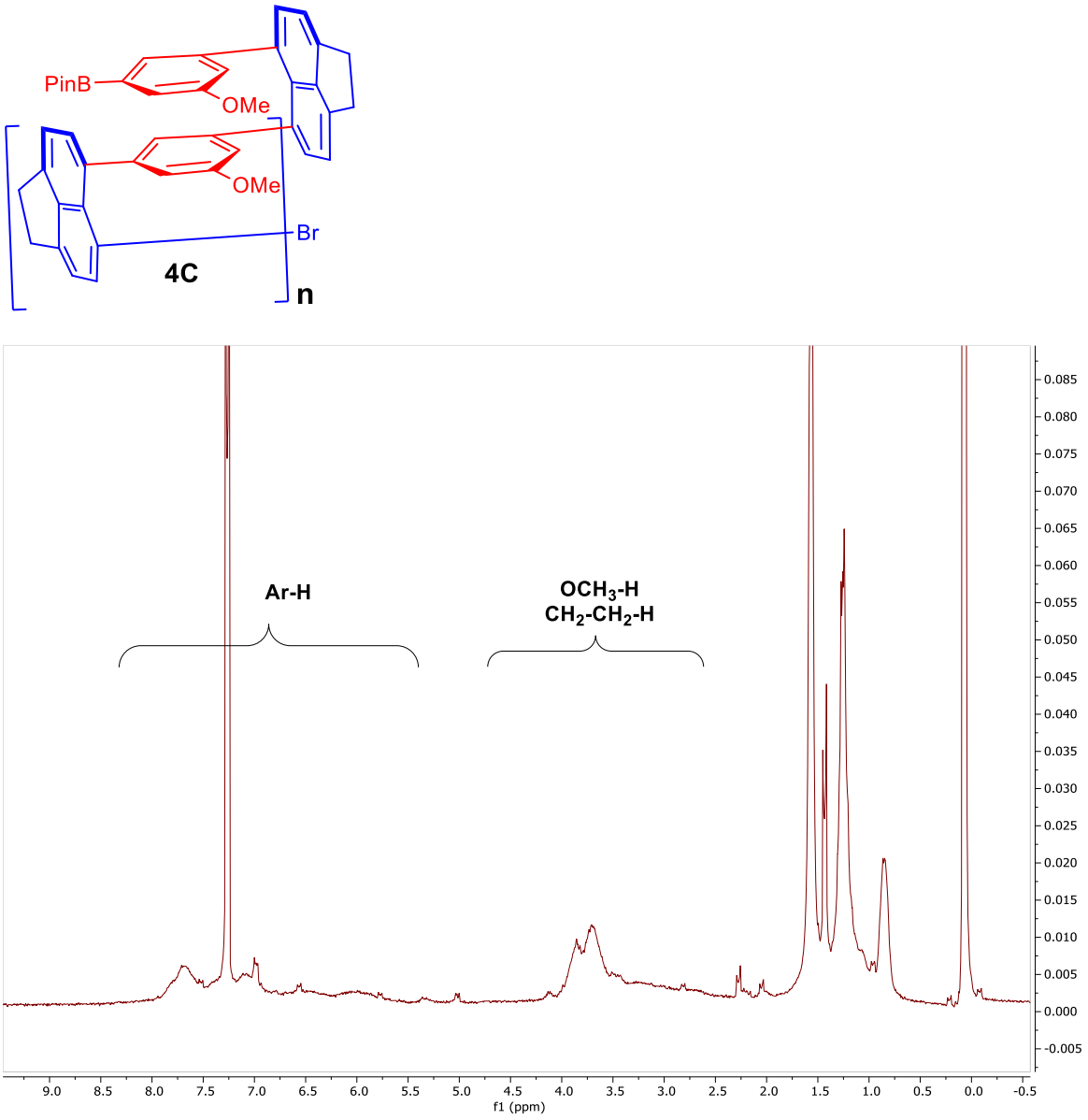
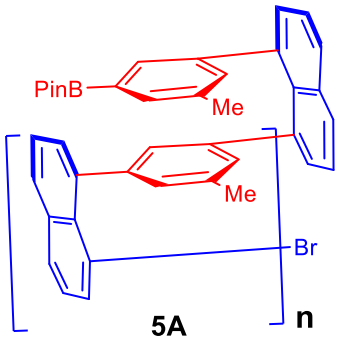


Figure S15.^{1}H NMR spectrum of **4C**



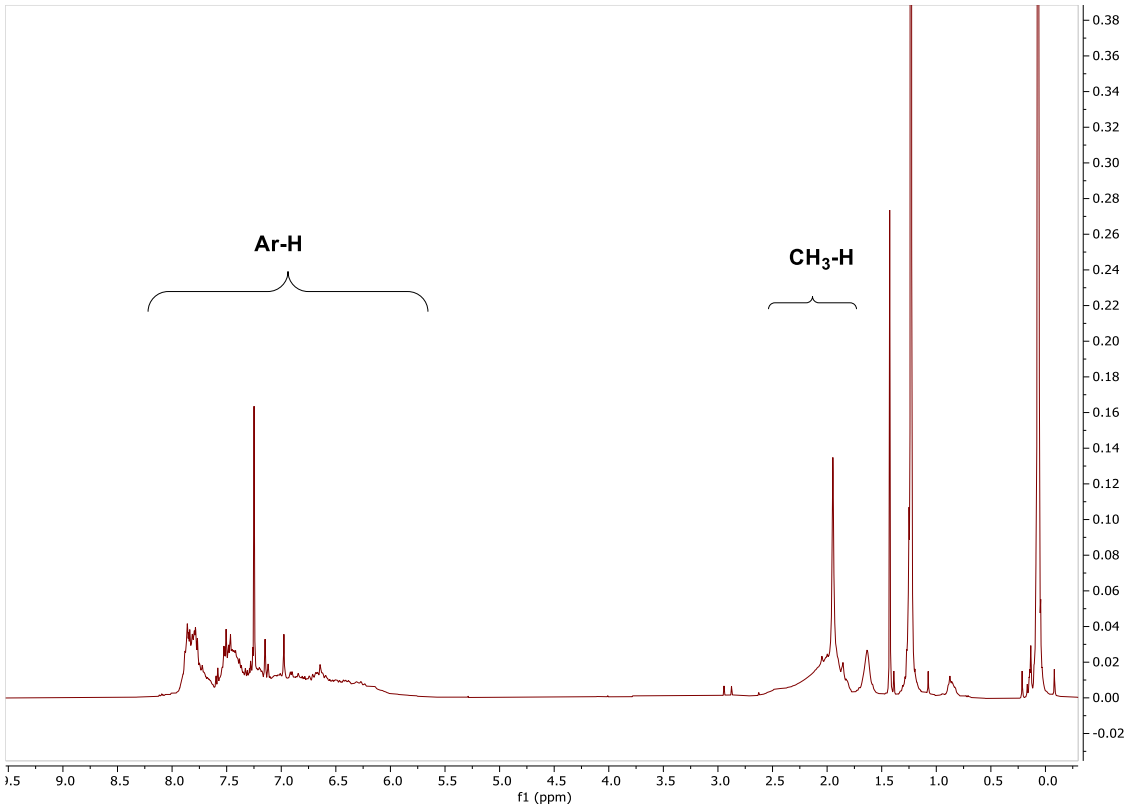
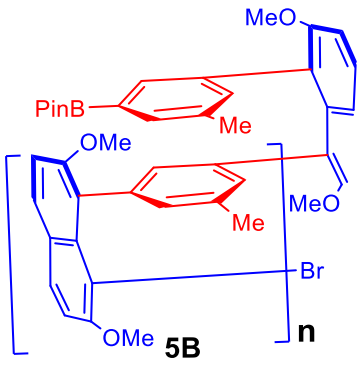


Figure S16.[1]H NMR spectrum of **5A**



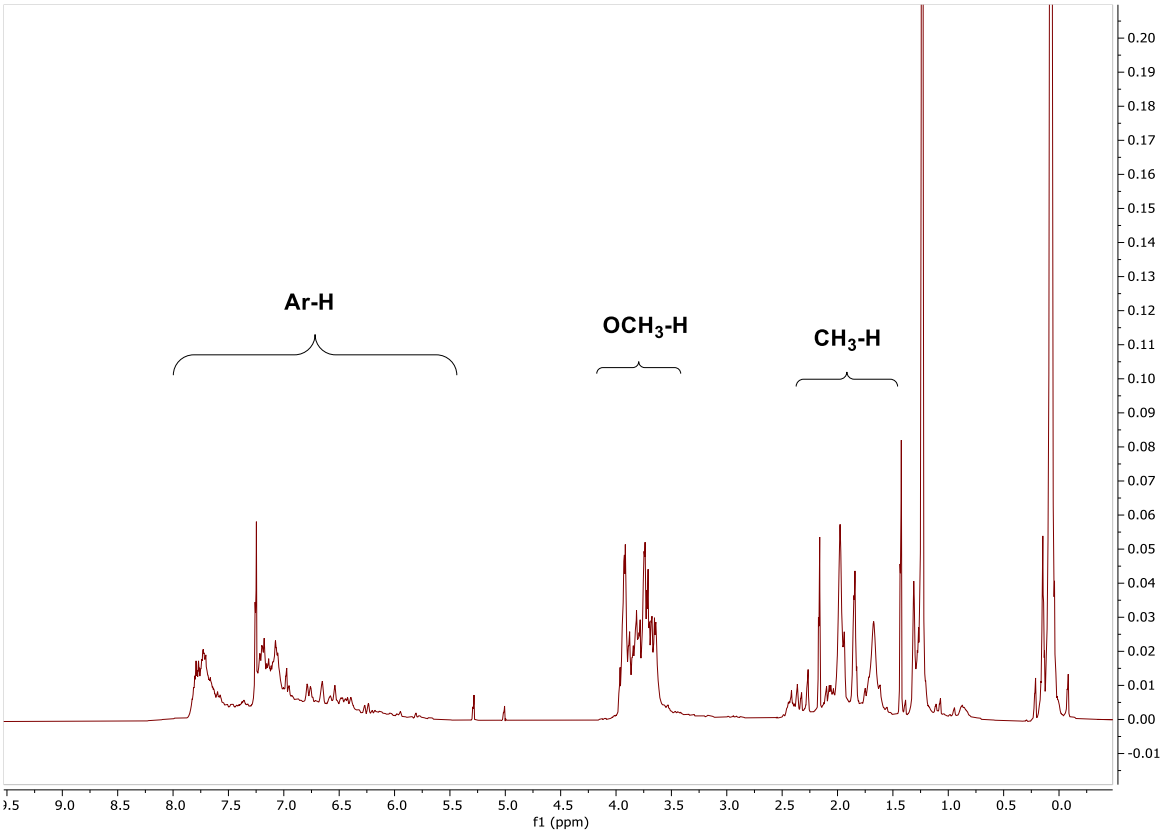
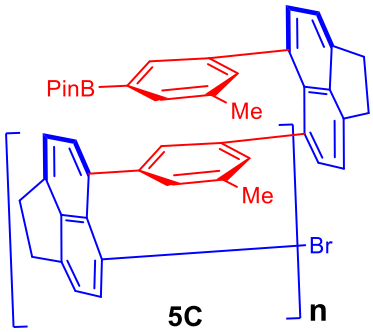


Figure S17.[1]H NMR spectrum of **5B**



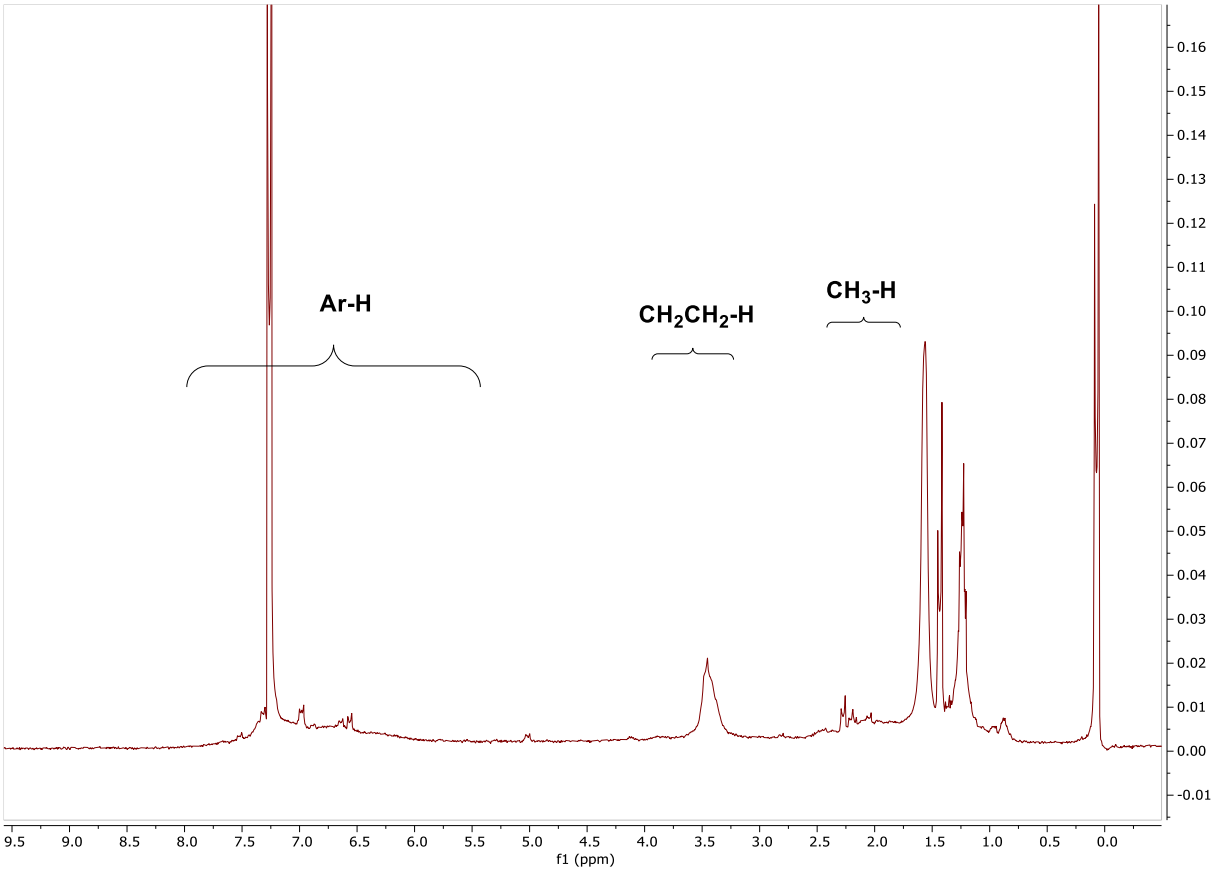


Figure S18.[1]H NMR spectrum of **5C**

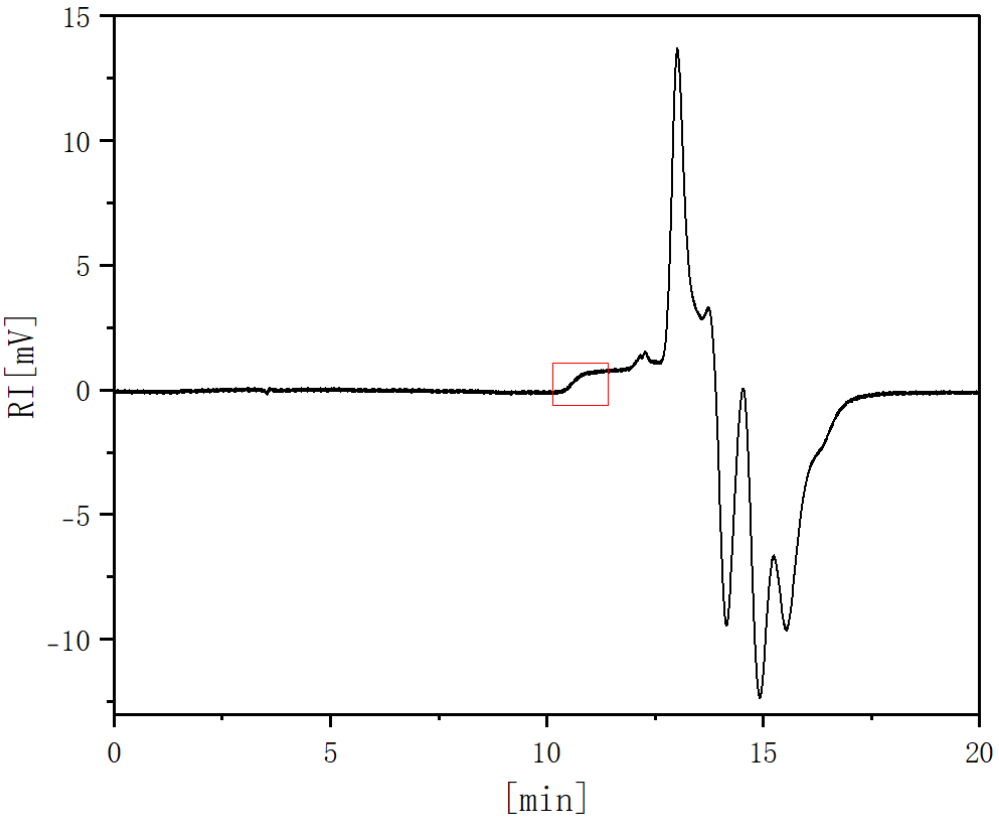


Figure S19. GPC data of **1A**

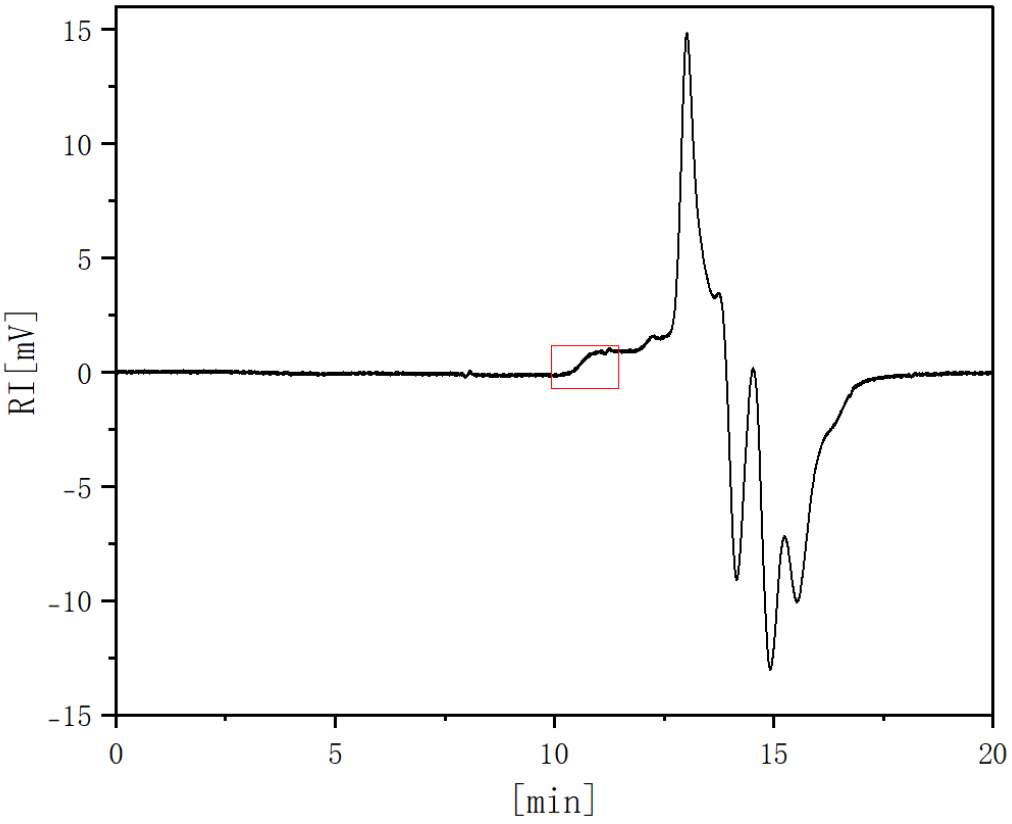


Figure S20. GPC data of **1B**

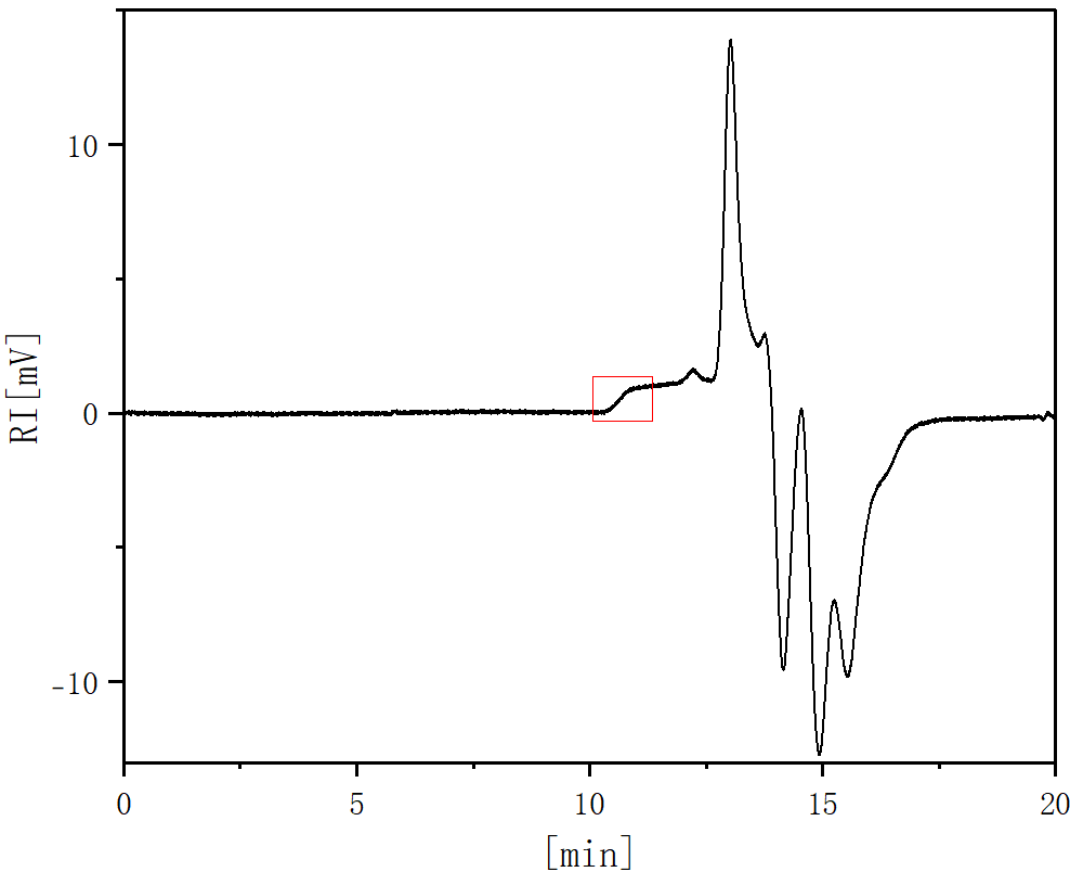


Figure S21. GPC data of **1C**

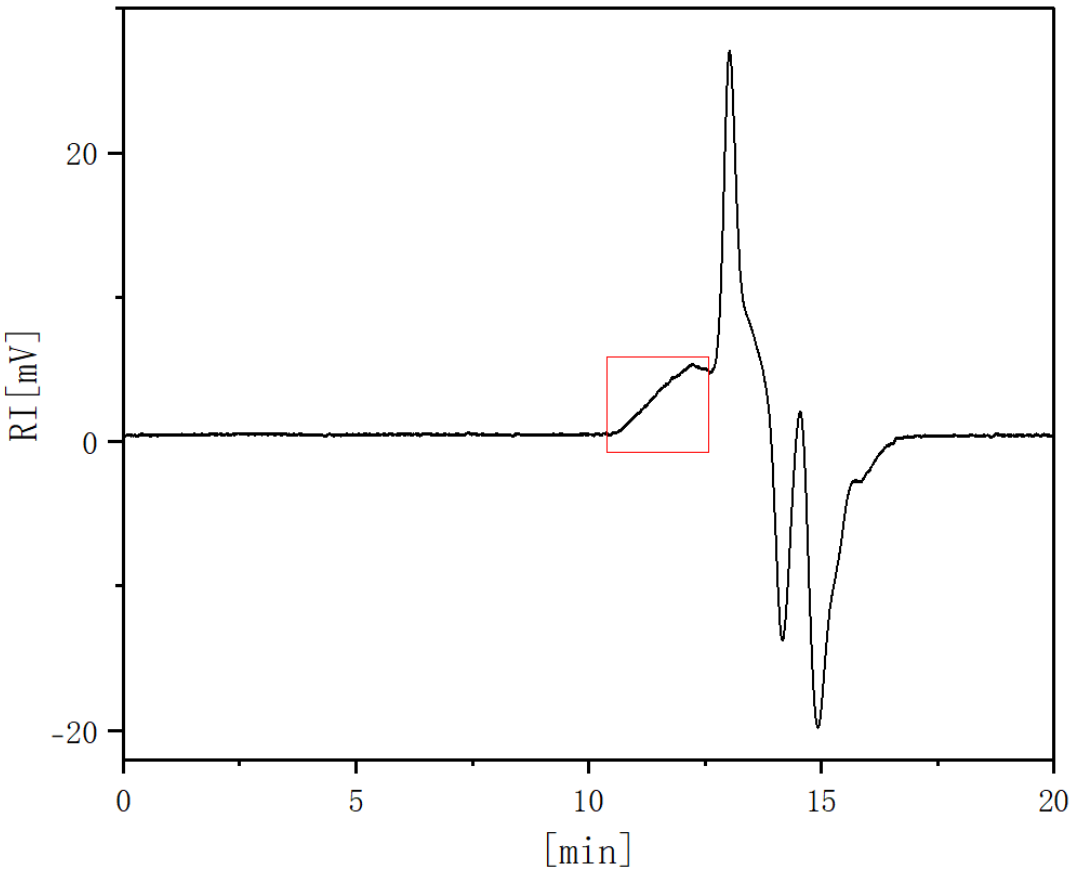


Figure S22. GPC data of **2A**

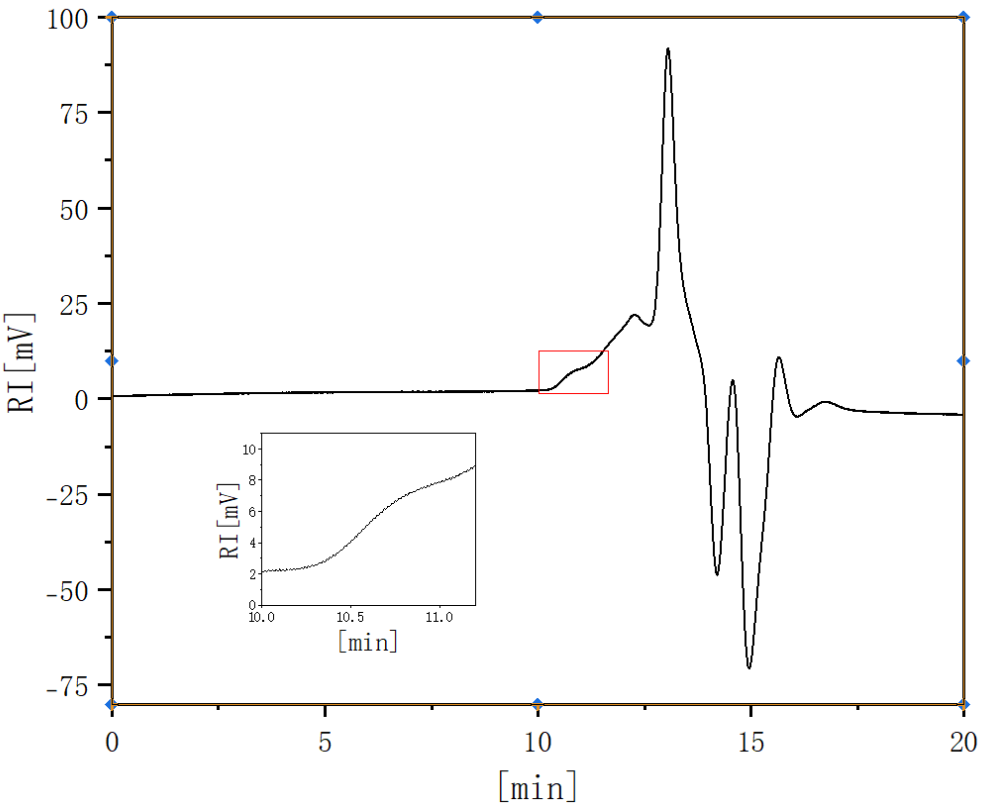


Figure S23. GPC data of **2B**

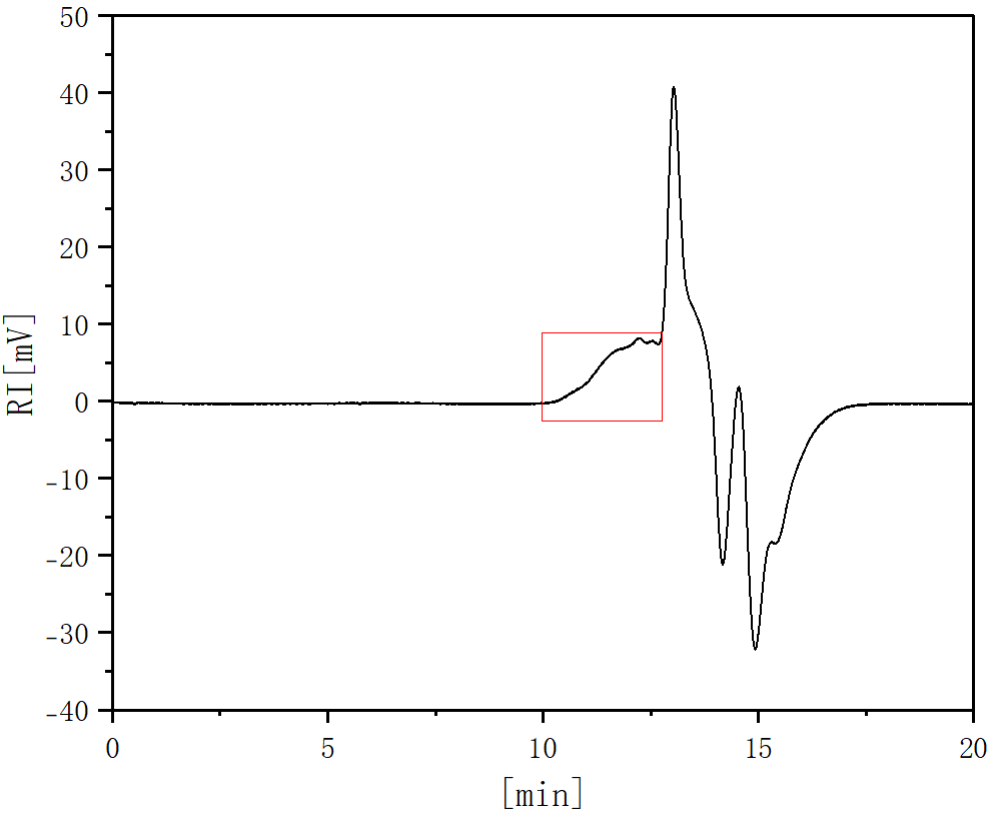


Figure S24. GPC data o**f 2C**

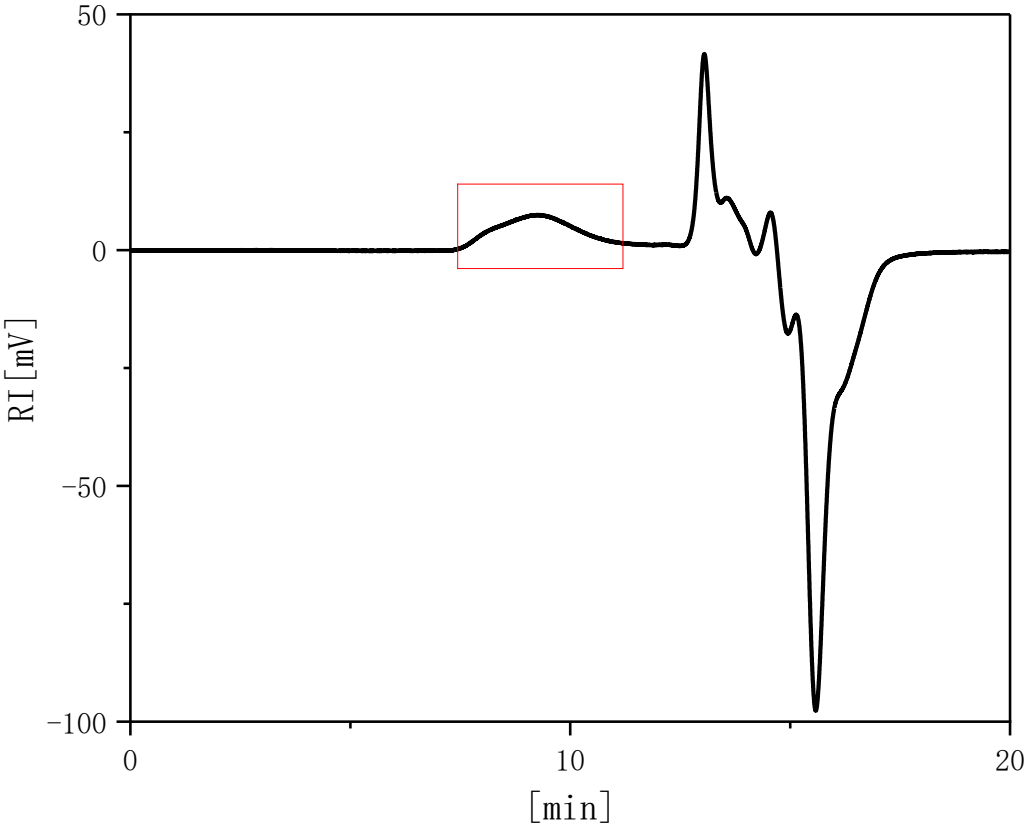


Figure S25. GPC data of **3A**

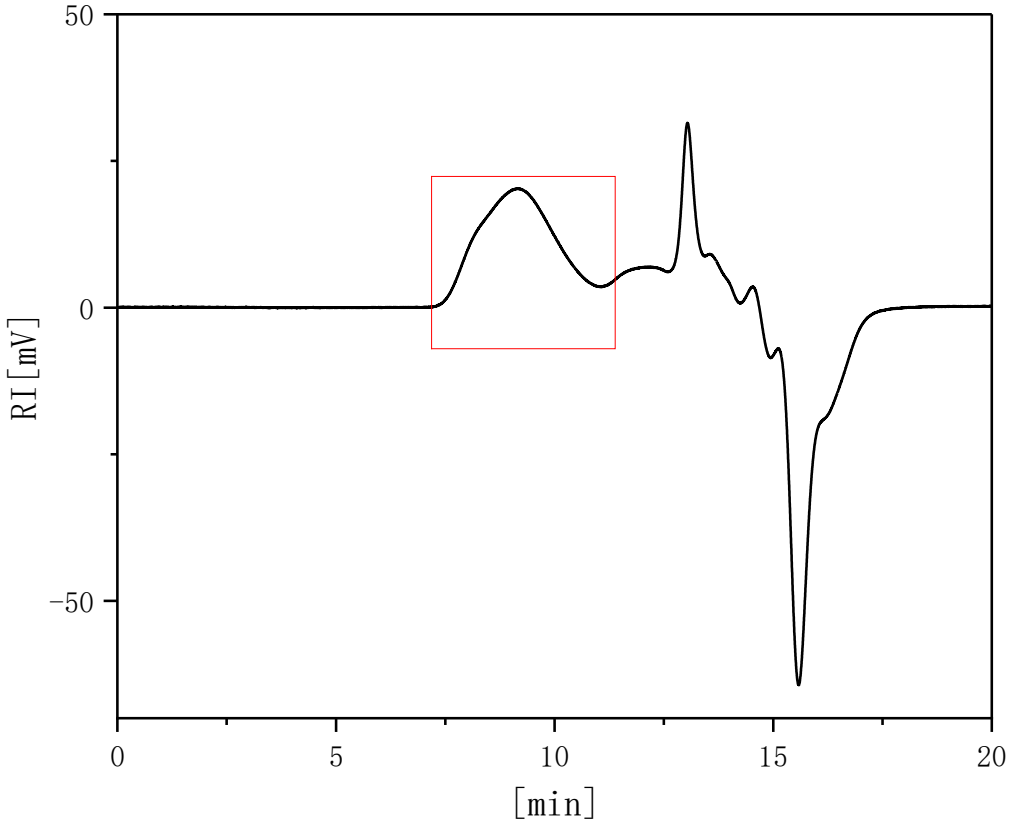


Figure S26. GPC data of **3B**

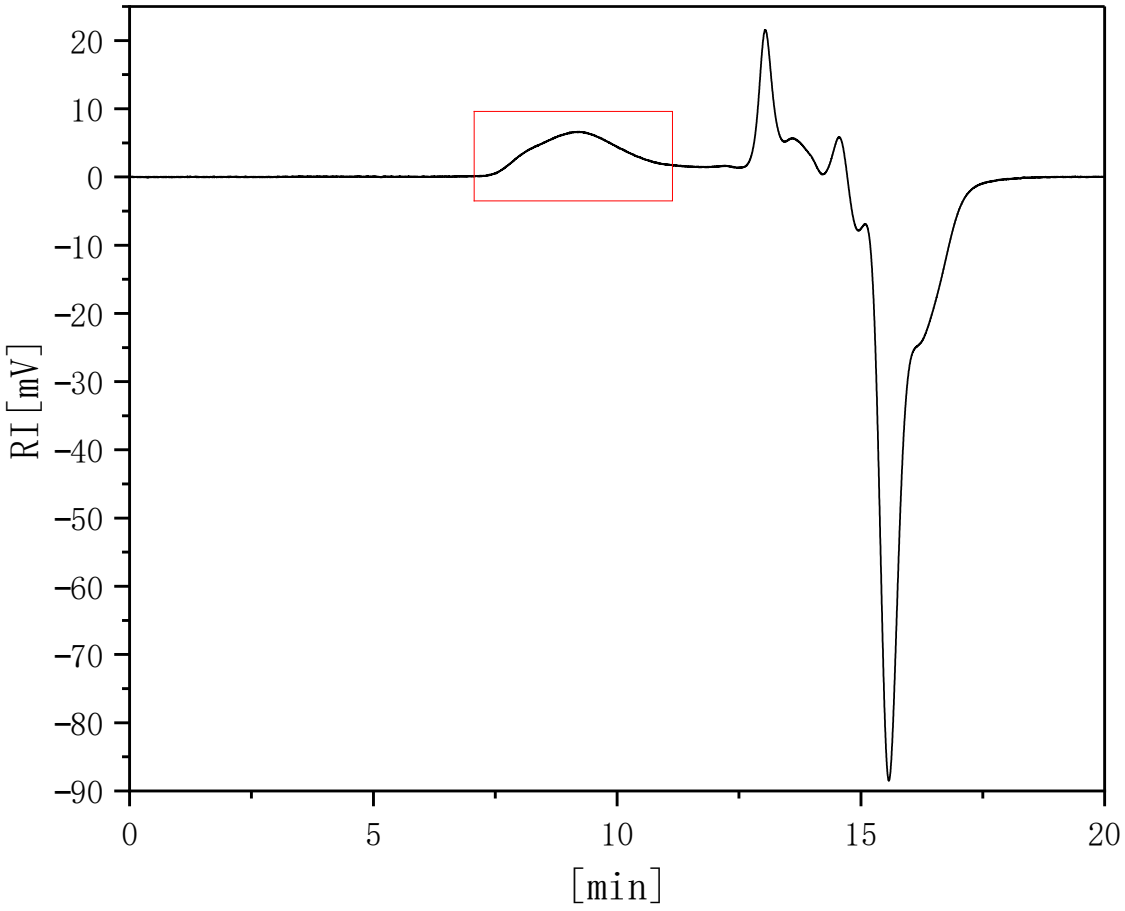


Figure S27. GPC data of **3C**

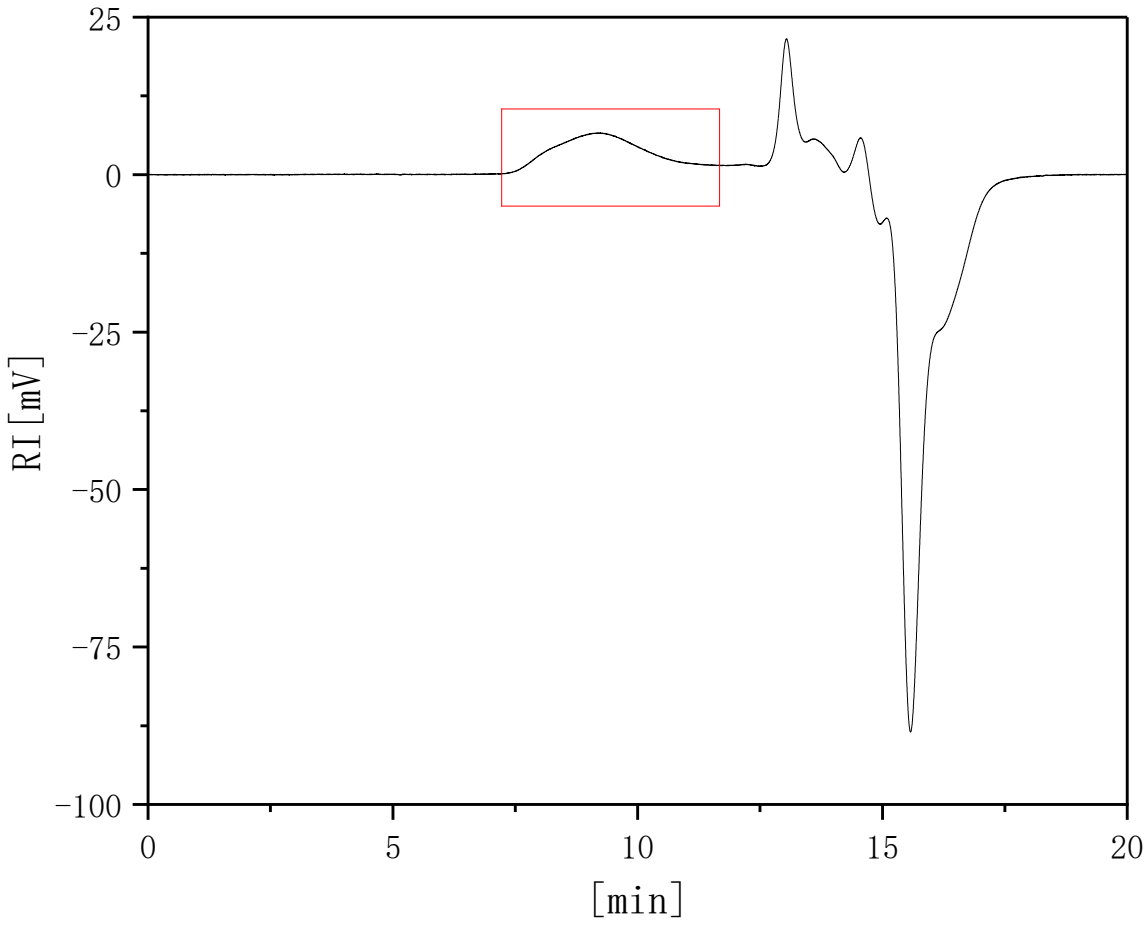


Figure S28. GPC data of **4A**

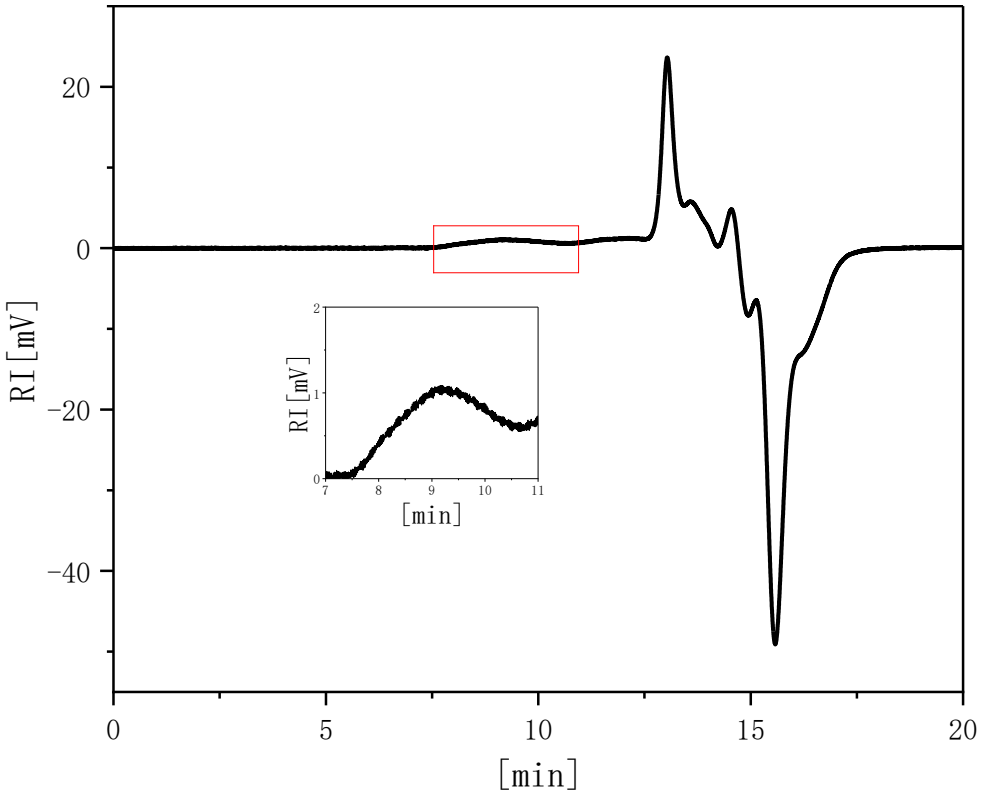


Figure S29. GPC data of **4B**

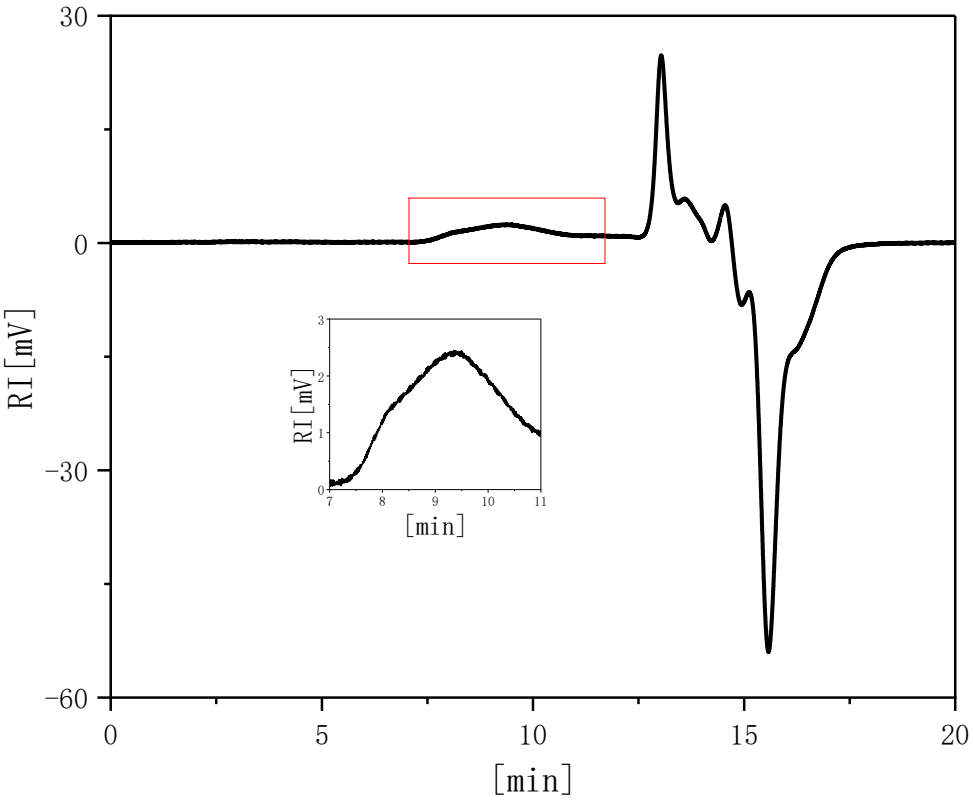


Figure S30. GPC data of **4C**

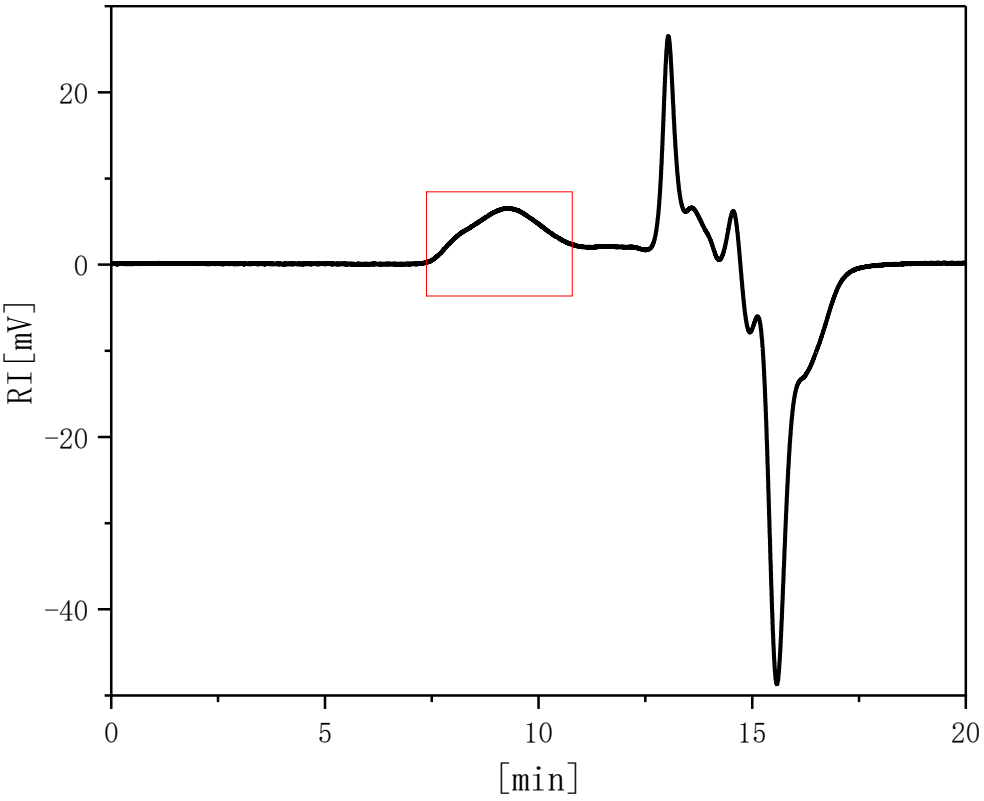


Figure S31. GPC data of **5A**

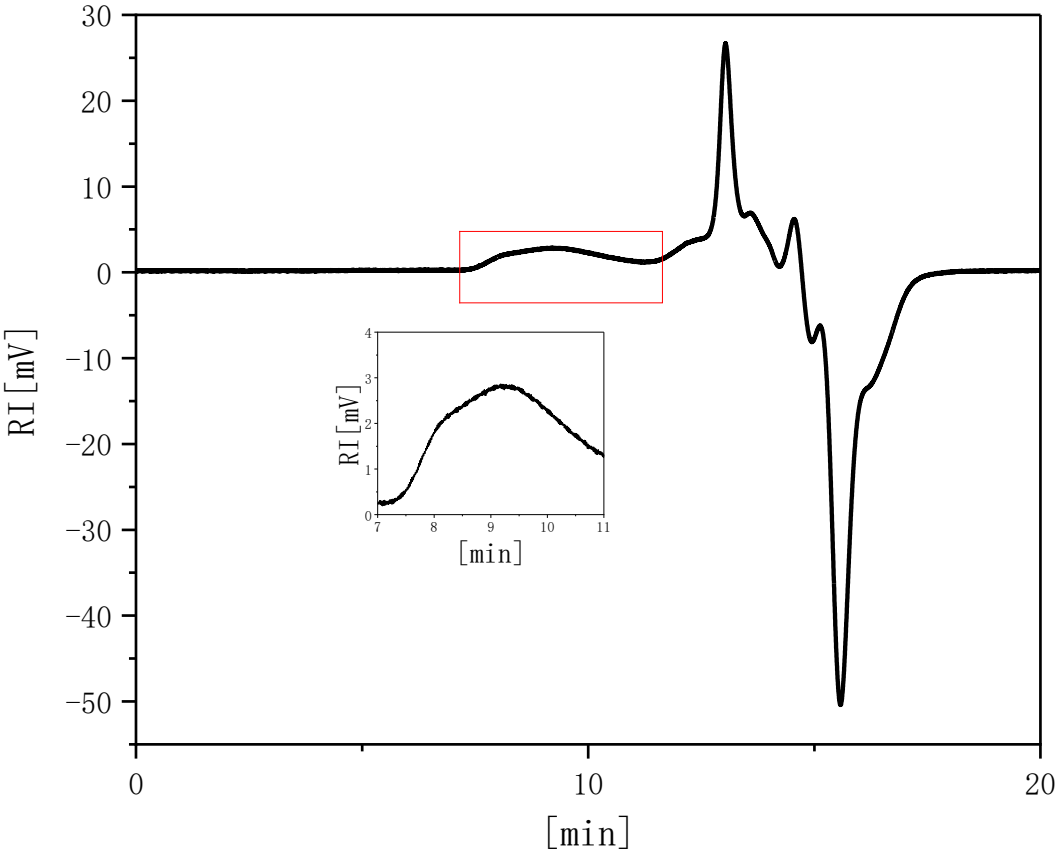


Figure S32. GPC data of **5B**

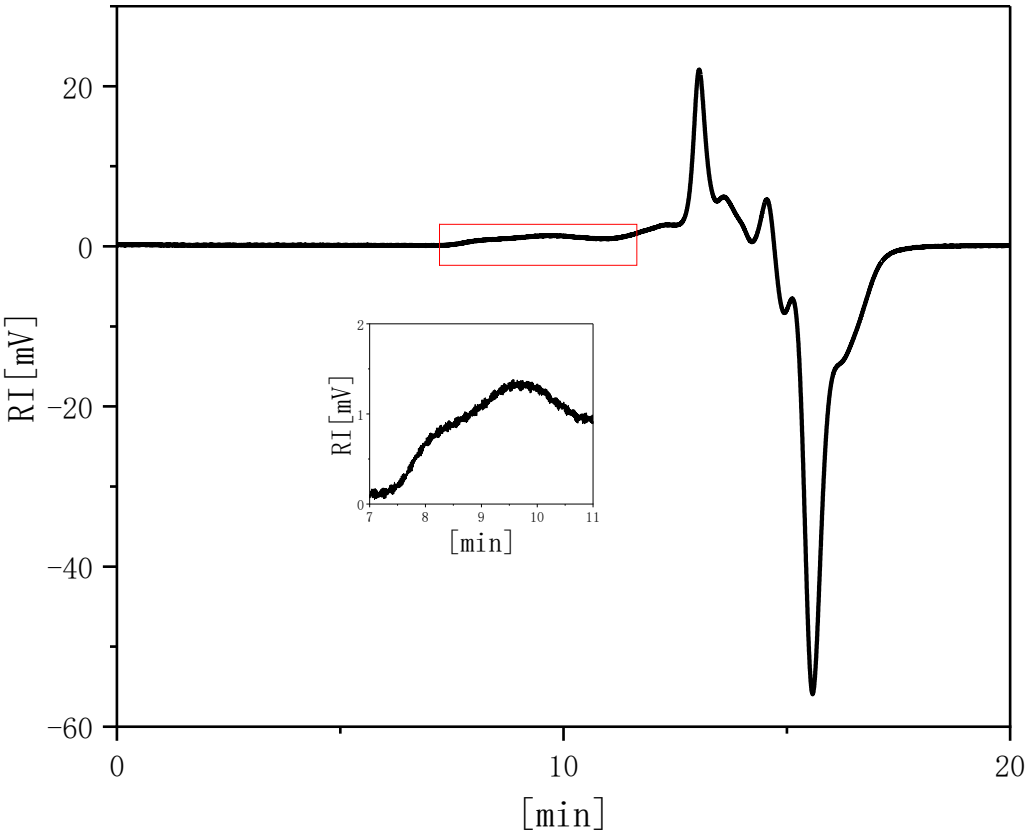
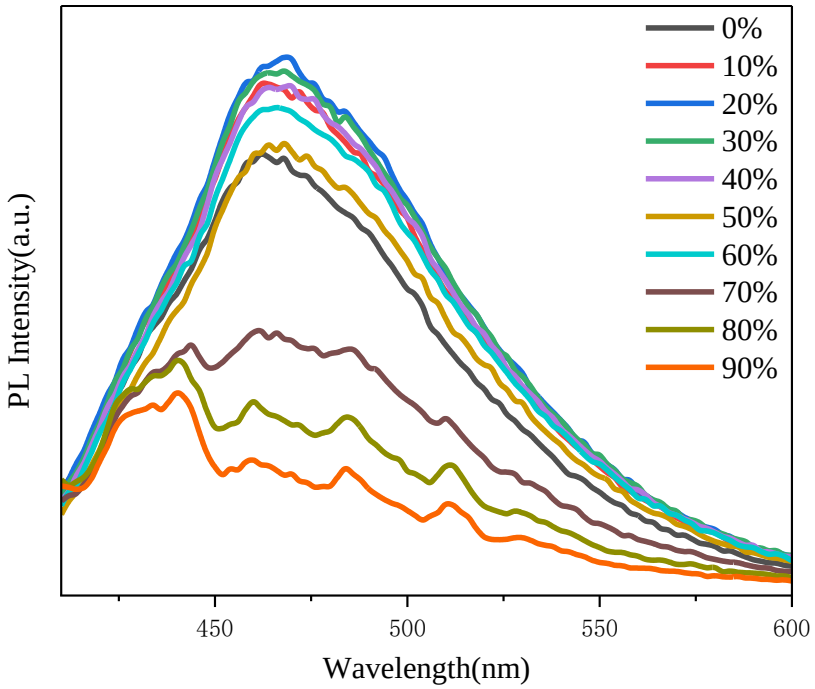
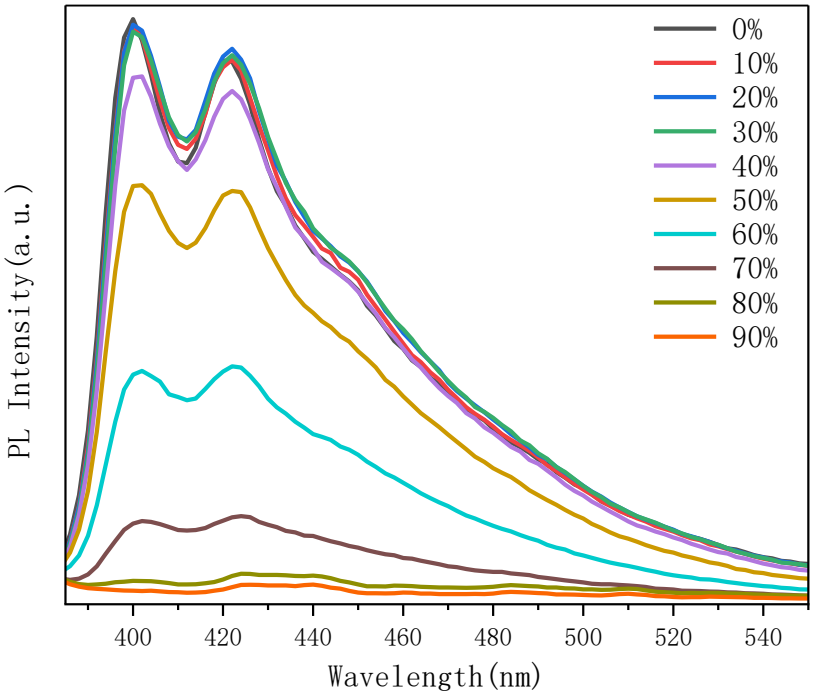


Figure S33. GPC data of **5C**

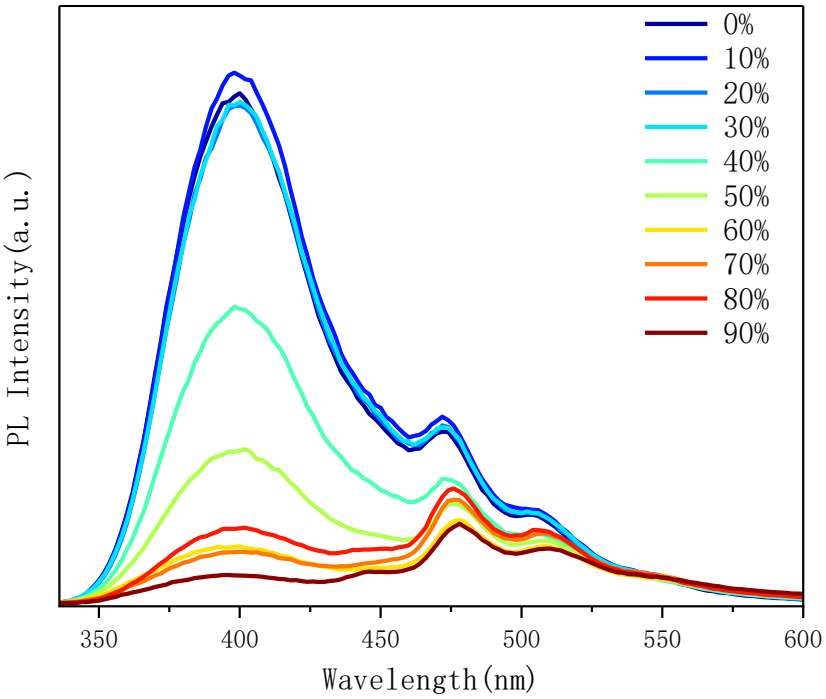
Section S4: Fluorescence Spectra



Figire S34. Fluorescence spectra of **1A** in THF-H_2O cosolvent



Figire S35. Fluorescence spectra of **1C** in THF-H_2O cosolvent



Figire S36. Fluorescence spectra of **2A** in THF-H_2O cosolvent

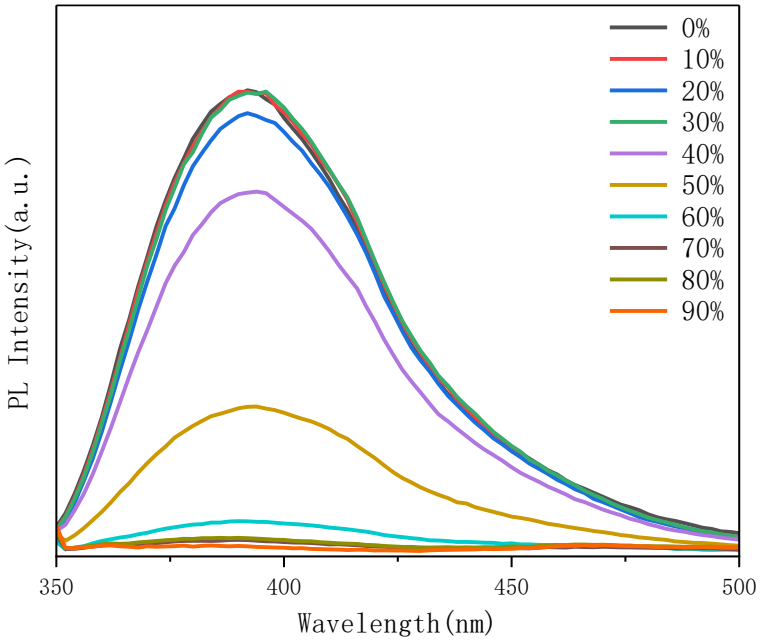


Figure S37. Fluorescence spectra **2C** in THF-H_2O cosolvent

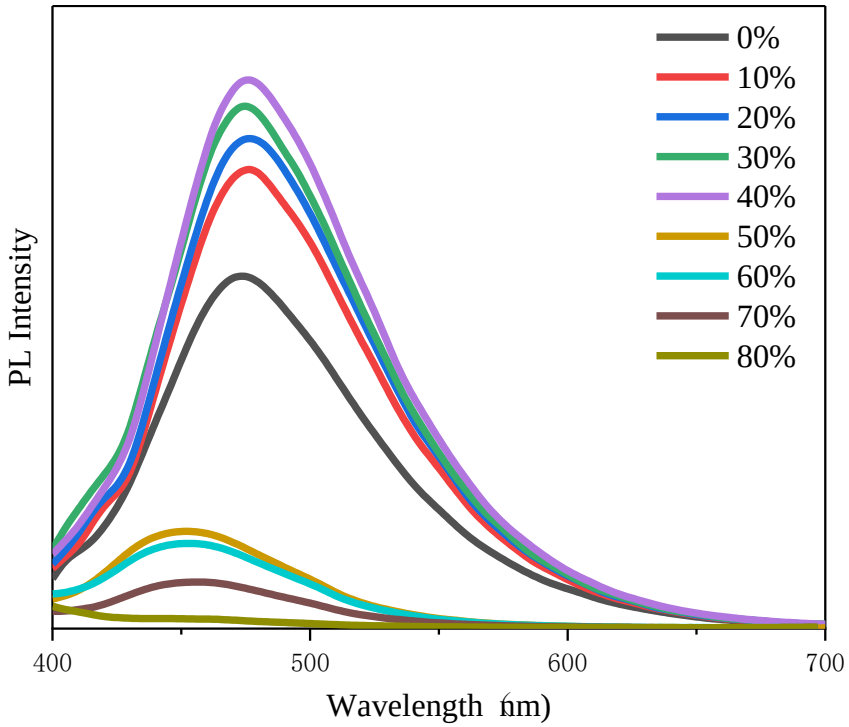
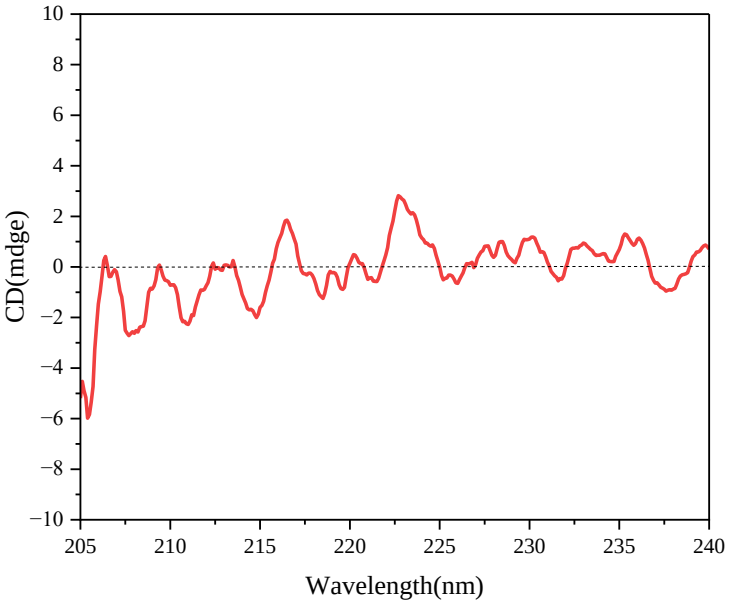


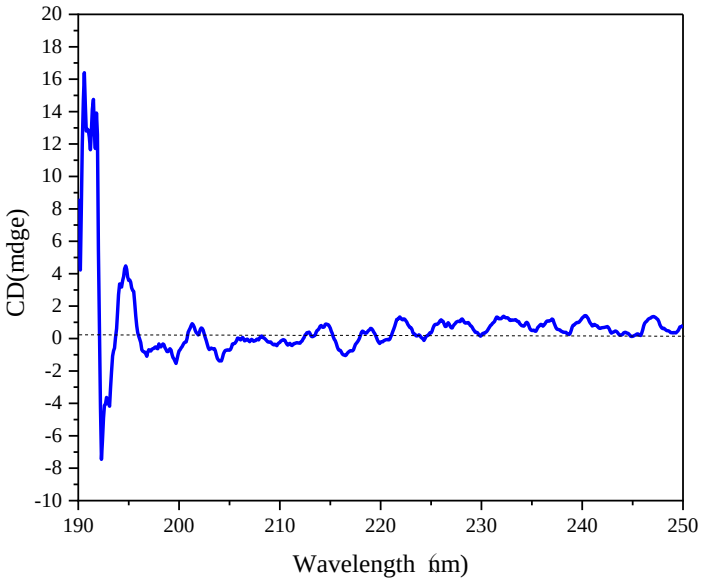
Figure S38. Fluorescence spectra **4C** in THF-H_2O cosolvent

Section S4: CD Spectra



0.2 mg/mL in methanol

Figure S39. CD spectra of **4A**



0.2 mg/mL in methanol

Figure S40. CD spectra of **5A**