Selective halide ion binding of templation effect for quadruple stranded-helicate enabling the activation of C-Br bond

Lei Fu, Yang Liu, Zhiyuan Jiang, Zhe Zhang,* Qixia Bai, Yu-Qing Li, Zhi Chen, Xiaopeng Li, Pingshan Wang,* Tun Wu*

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1. Experimental section

General procedures. Chemicals were purchased from Sigma/Aldrich, Fisher Scientific, Energy Chemical, Alfa Aesar and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker- flex) precoated with Al_2O_3 (IB-F) or SiO_2 (IB_2-F). Column chromatography was conducted using basic Al_2O_3 Brockman Activity I (60-325 mesh) or SiO_2 (60-200 mesh) from Fisher Scientific. NMR spectra were recorded on a Bruker NMR 400, 500 MHz spectrometer, using $CDCl_3$ for ligands and CD_3CN for metallo-products. Different NMR solvents were purchased from J&K scientific and Sigma/Aldrich. Electrospray ionization-mass spectrometry (ESI-MS) experiments were performed on a Waters Synapt G2-Si quadrupole/time-of-flight (Q/ToF) tandem mass spectrometer. This instrument contains atriwave device between the Q and ToF analyzers, consisting of three collision cells in the order trap cell, ion mobility cell, and transfer cell. Trap and transfer cells are pressurized with Ar, and the ion mobility cell is pressurized with N_2 flowing in a direction opposite to that of the entering ions.

ESI-MS. ESI-MS was recorded with a Waters Synapt G2-Si tandem mass spectrometer, using solutions of 0.01 mg sample in 1 mL of $CHCl_3/CH_3OH$ (1:3, v/v) for ligands, 2 mg sample in 1 mL of CH_3CN/CH_3OH (5:1, v/v) for complexes.

Molecular Modeling. Energy minimization of the macrocycles was conducted with the Materials Studio version 6.0 program, using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted. Geometry optimization used a universal forcefield with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals parameters.

Single crystal X-ray diffraction. Single crystals suitable for X-ray crystallography were all obtained by slow vapor diffusion of isopropyl ether into a concentrated acetonitrile solution of the library containing 3 equiv. TBAX (10 mg/mL) at 15 °C. Single-crystals X-ray diffraction data for quadruple stranded-helicate **D** was collected on a Bruker D8 VENTURE diffractometer using a mirror monochromated Cu-Kα radiation. Using Olex2, the structures were solved with the SIR2004 [2] structure

solution program using Direct Methods and refined with the XH [3] refinement package using CGLS minimisation. Data refinement and reduction were undertaken with Bruker SAINT. The structures were solved by direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement using the SHELXTL software package. Details on crystals data collection and refinement were summarized in Table S1. CCDC: 2310483, 2173968-2173970.

Computing Method. The calculations were based on spin-polarized density functional theory (DFT) using projector augmented wave (PAW) methods, as implemented in the Vienna ab initial simulation package (VASP).[1] A plane-wave basis set with a kinetic-energy cut-off of 400 eV was used to expand the wave function of valence electrons. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used for describing the exchange-correlation interactions.[2-3]

Herein, a 20 Å vacuum space was set in every direction to prevent the interaction between two nearest quadruple-stranded helicate **D**. The Brillouin-zone integration was sampled by single Γ point. The structural relaxations were performed by computing the Hellmann–Feynman forces within the total energy and force convergences of 10^{-4} eV and 0.05 eV/Å, respectively.

The binding energy ΔE of interaction between the quadruple-stranded helicate **D** and Bromine ion (Br^-) were expressed as follows:

$$E = E_{\text{T - Br}} - E_T - E_{Br}$$

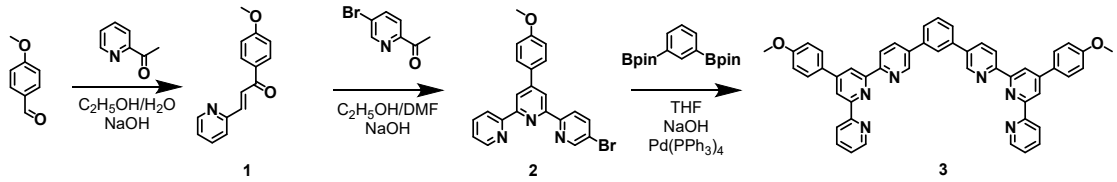
where $E_{T\text{-}Br}$ and E_T were the total energy of the quadruple-stranded helicate **D** with and without Bromine ion, respectively. E_{Br} was the energy of Bromine ion. The binding energy of interaction between the Dibenzyl and Bromine ion (Br^-) were same as above.

Table S1. The binding energy of quadruple-stranded helicate **D** and Br^- is compared

structure	E_x^+	E_{Br}^+	E_{total}^+	E_b^+
bromodiphenylmethane **3**	-151.65	-4.61	-159.68	-3.43
helicate **D**	-1339.71	-4.61	-1347.87	-3.56

2. Synthesis of strand 3

1[4] were synthesized according to the reported procedures and showed identical ^{1}H NMR spectra to those reported.



Compound **2**: **1** (2.0 g, 8.3 mmol) and 5-bromo-2-acetylpyridine (1.7 g, 8.3 mmol) were dissolved in a mixed solvent of EtOH : DMF = 4 : 1 (150 mL), NaOH (0.5 g, 12.5 mmol) in water (10 mL) was added. After being stirred at 25 °C for 12 h, NH_4OH (aq) (28 wt%, 15 mL) was added into the mixture slowly, which was refluxed at 85°C for additional 24 h. After cooling to room temperature, the crude product was filtrated and washed by EtOH to give Compound **2** as a white solid (2.8 g, 3.7 mmol) in 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.76-8.75 (d, *J* = 4 Hz, 1H, Tpy-H$^{6''}$), 8.73-8.72 (m, 1H, Tpy-H^6), 8.71-8.70 (d, *J* = 4 Hz, 1H, Tpy-H$^{5'}$), 8.66-8.65 (m, 1H, Tpy-H$^{3'}$), 8.63-8.61 (d, *J* = 8 Hz,1H, Tpy-H^3), 8.57-8.55 (d, *J* = 8 Hz, 1H, Tpy-H$^{3''}$), 7.99-7.96 (dd, *J* = 8, 4 Hz, 1H, Tpy-H$^{4''}$), 7.89-7.85 (m, 3H, Tpy-H$_4$, Ph-H^d), 7.37-7.34 (t, *J* = 6 Hz, 1H, Tpy-H^5), 7.04-7.02(d, *J* = 8 Hz, 2H, Ph-H^3) 3.88 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 160.6, 156.1, 155.9, 154.8, 150.1, 149.9, 149.1, 139.4, 136.9, 130.5, 128.5, 123.9, 122.6, 121.3, 121.1, 118.5, 118.1, 114.3, 55.4; ESI-MS (*m/z*): Calcd $[M+H]^+$: 419.294, Found $[M+H]^+$: 419.294.

Strand **3**: To a degassed flask containing Compound **2** (836.6 mg, 2.0 mmol), 1,3-bis(4,4,5,5- tetramethyl-1,3,2- dioxaborolan-2-yl)benzene (330.0 mg, 1.0 mmol), and NaOH (240.0 mg, 6.0 mmol), a solvent (80 mL) of THF was added. After being purged with N_2 for 10 min, $Pd(PPh_3)_4$ (138.5 mg, 0.12 mmol) was added into the mixture, which was then refluxed for 2 day under N_2. The solvent was removed in vacuo to give a residue that was dissolved in $CHCl_3$ and washed with water. The organic layer was dried (anhydrous $MgSO_4$), concentrated in vacuum to give a residue that was purified by flash column chromatography (Al_2O_3) with CH_2Cl_2 as an eluent to give strand **3**, as a white solid: 414.1 mg (Yield: 55%); m.p. > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$, 298

K) δ: 9.04-9.03 (d, *J* = 4 Hz, 2H, Tpy-$H^{6''}$), 8.79-8.86 (m, 4H, Tpy-$H^{3'',5'}$), 8.75-8.74 (d, *J* = 4 Hz, 2H, Tpy-H^{6}), 8.73-8.72 (d, *J* = 4 Hz, 2H, Tpy-$H^{3'}$), 8.71-8.69 (d, *J* = 8 Hz, 2H, Tpy-H^{3}), 8.15-8.13 (dd, *J* = 8 Hz, 2H, Tpy-$H^{4''}$), 7.95 (s, 1H, Ph-H^{c}), 7.92-7.88 (m, 6H, Tpy-H_4 , Ph-H^{d}), 7.75-7.73 (d, *J* = 8 Hz, 2H, Ph-H^{b}), 7.68-7.65 (t, *J* = 6 Hz, 1H, Ph-H^{a}), 7.38-7.35 (t, *J* = 6 Hz, 4H, Tpy-H^{5}), 7.06-7.03 (d, *J* = 12 Hz, 4H, Ph-H^{e}), 3.89 (s, 6H, OCH_3); 13C NMR (101 MHz, $CDCl_3$, 298 K) δ: 160.6, 156.4, 155.9, 155.6, 155.5, 149.8, 149.1, 147.6, 138.8, 136.9, 136.1, 135.3, 130.7, 130.1, 128.6, 127.0, 125.9, 123.9, 121.4, 118.4, 118.3, 114.4, 55.4; ESI-MS (*m/z*): Calcd $[M+H]^+$: 753.878, Found $[M+H]^+$: 753.878.

3. NMR and ESI- MS Spectra of Compound 2 and Strand 3

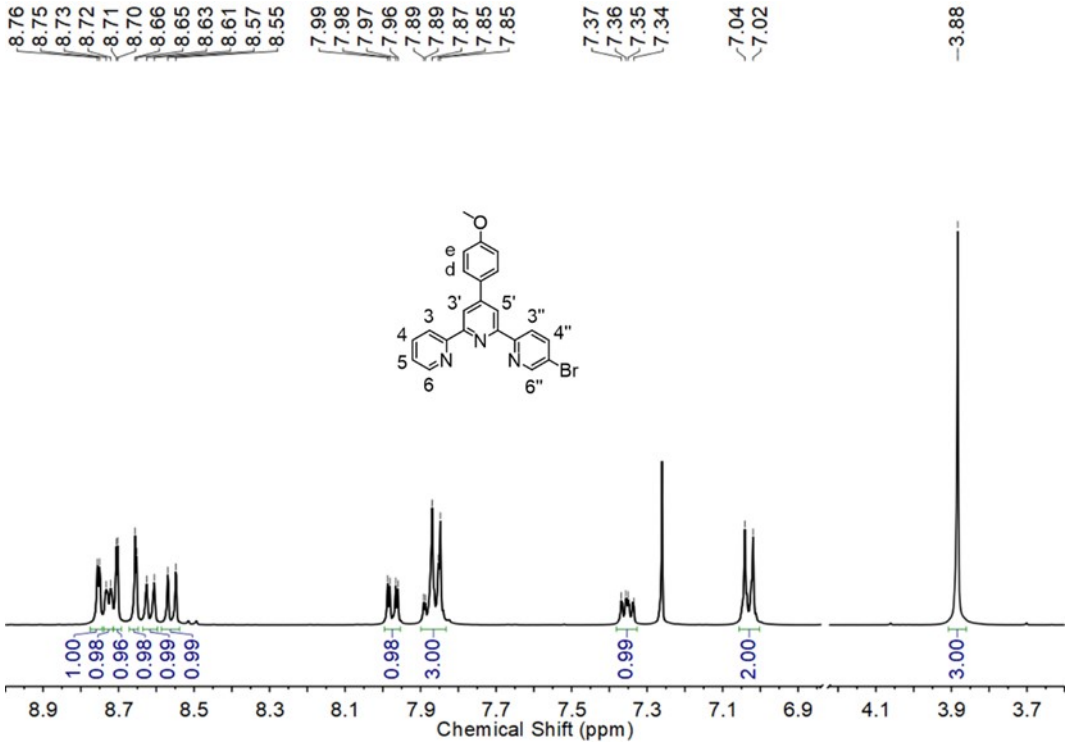


Figure S1. ^{1}H NMR spectrum (400 MHz, 298 K) of Compound **2** in $CDCl_3$.

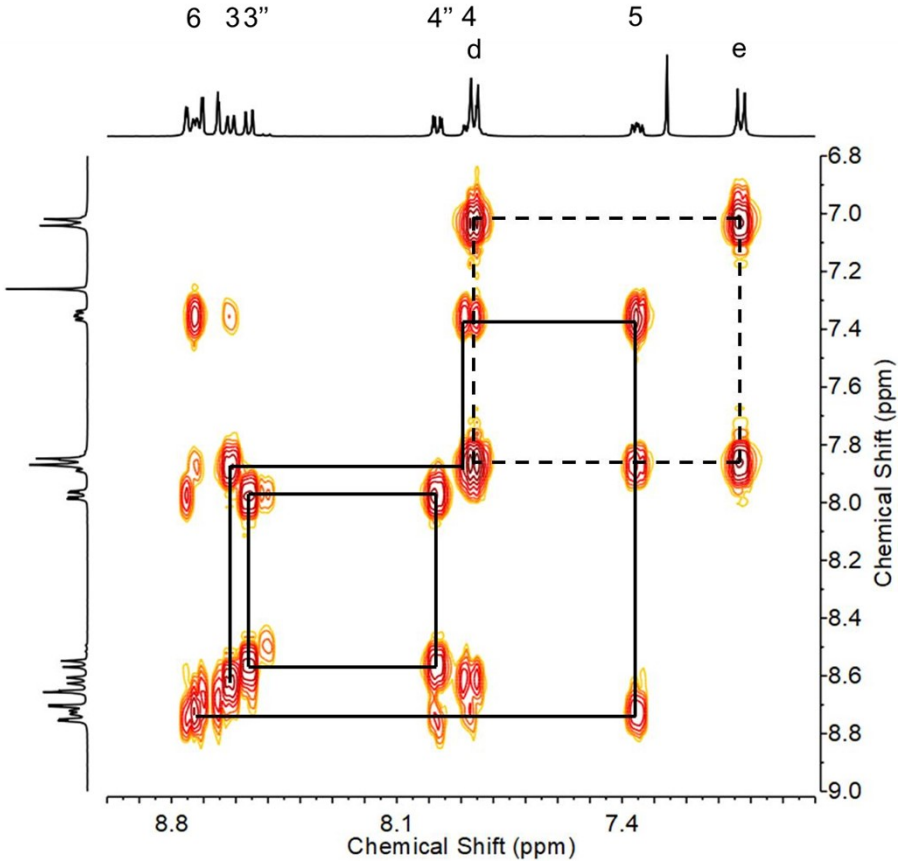


Figure S2. 2D COSY NMR spectrum (400 MHz, 298 K) of Compound **2** in $CDCl_3$.

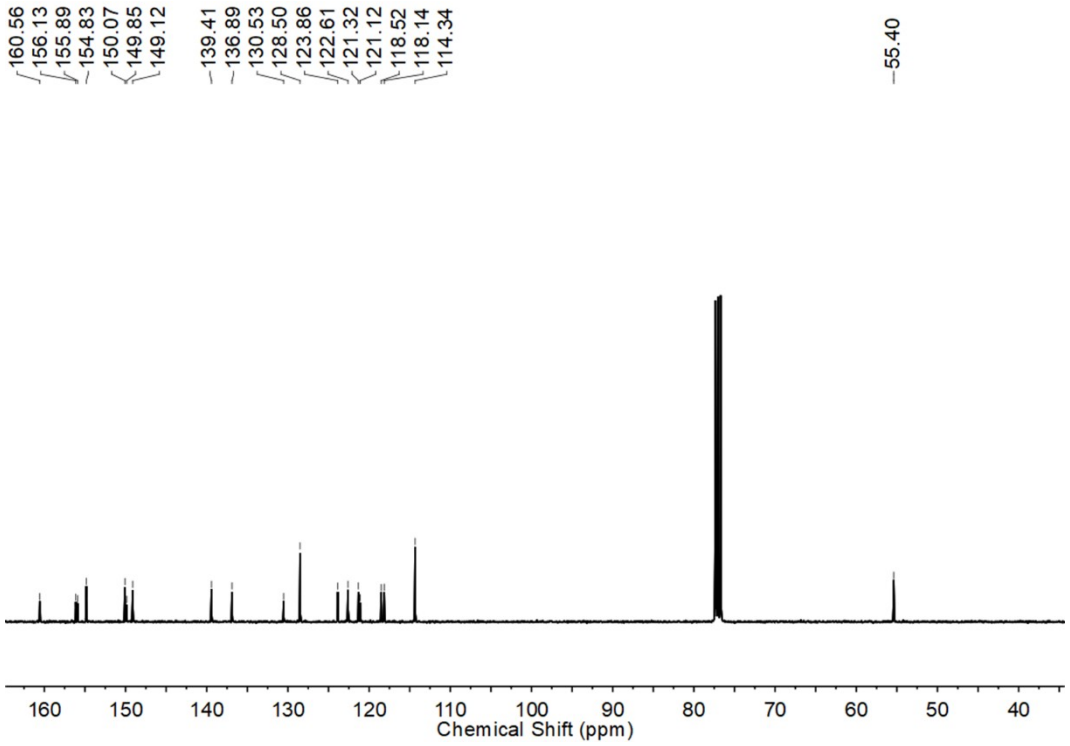


Figure S3. ^{13}C NMR spectrum (101 MHz, 298 K) of Compound **2** in $CDCl_3$

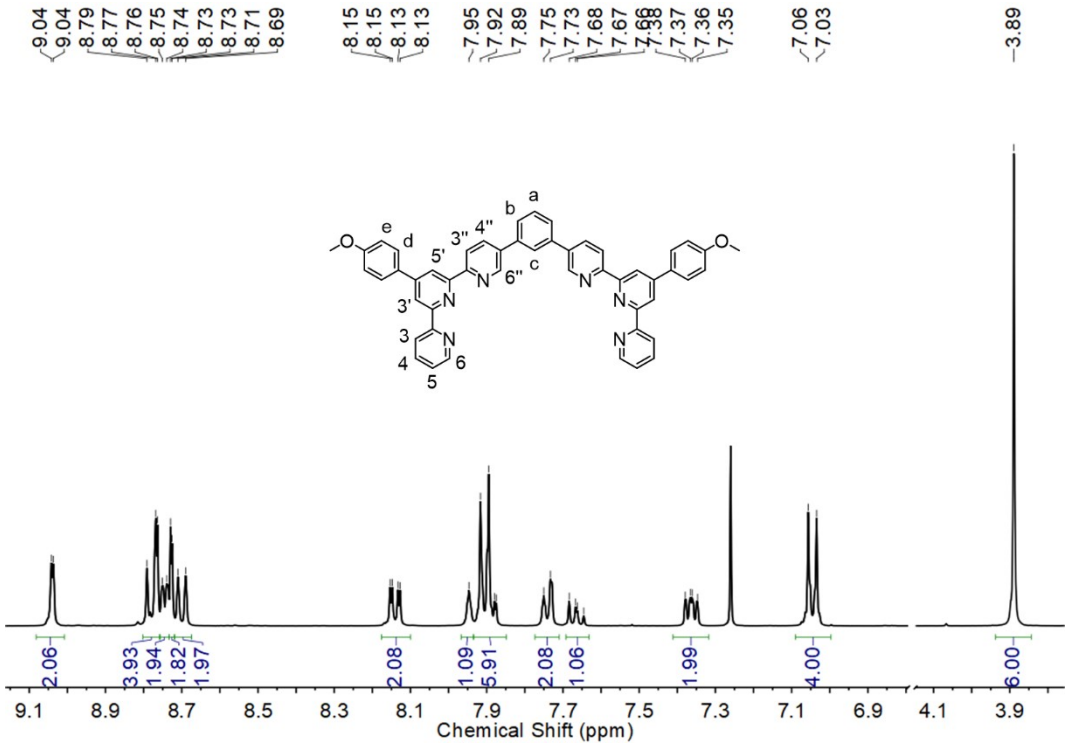


Figure S4. ^{1}H NMR spectrum (500 MHz, 298 K) of strand **3** in $CDCl_3$.

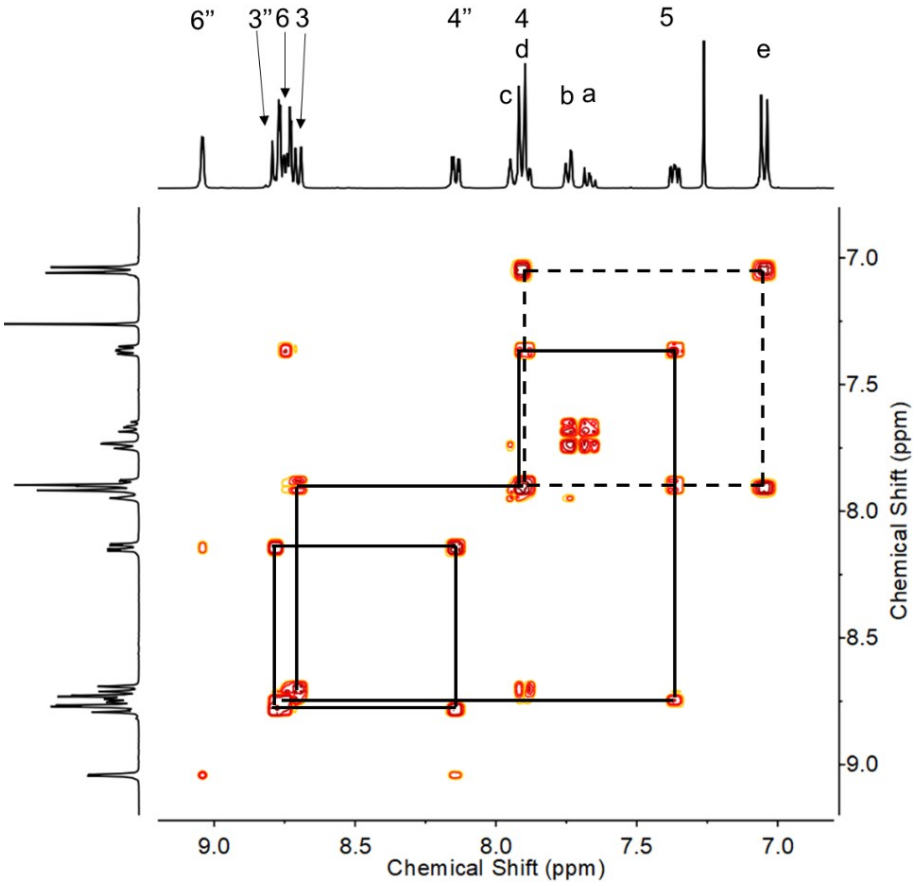


Figure S5. 2D COSY NMR spectrum (500 MHz, 298 K) of strand **3** in $CDCl_3$.

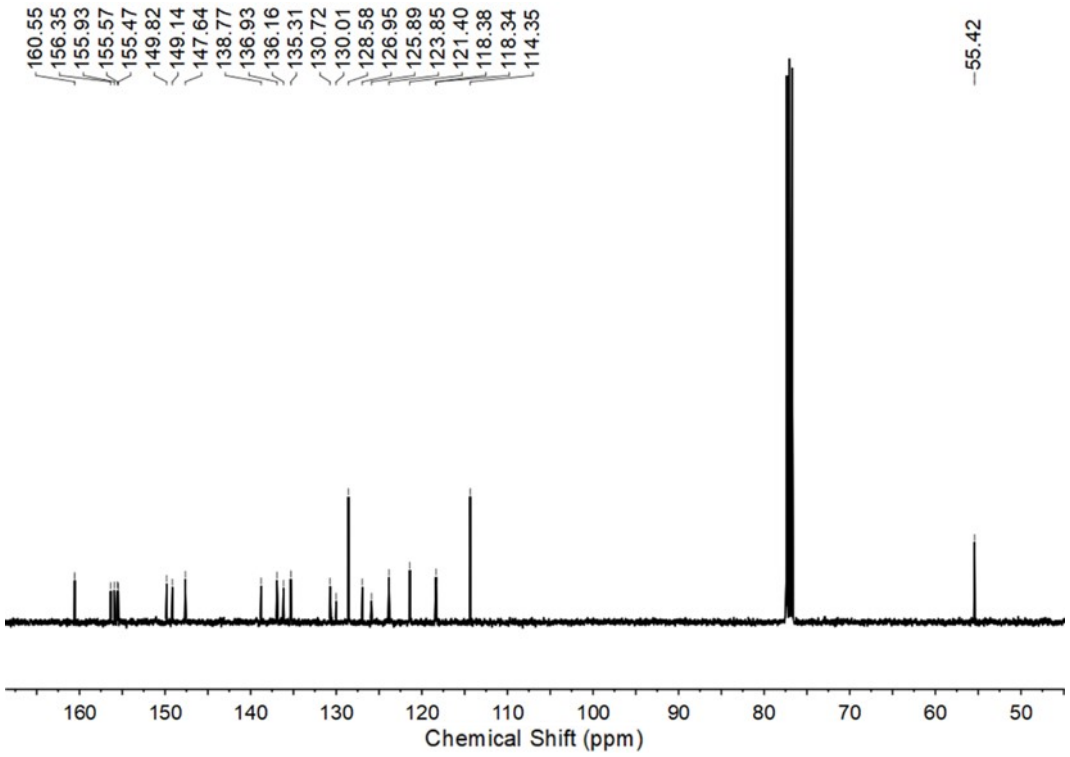


Figure S6. ^{13}C NMR spectrum (126 MHz, 298 K) of strand **3** in $CDCl_3$.

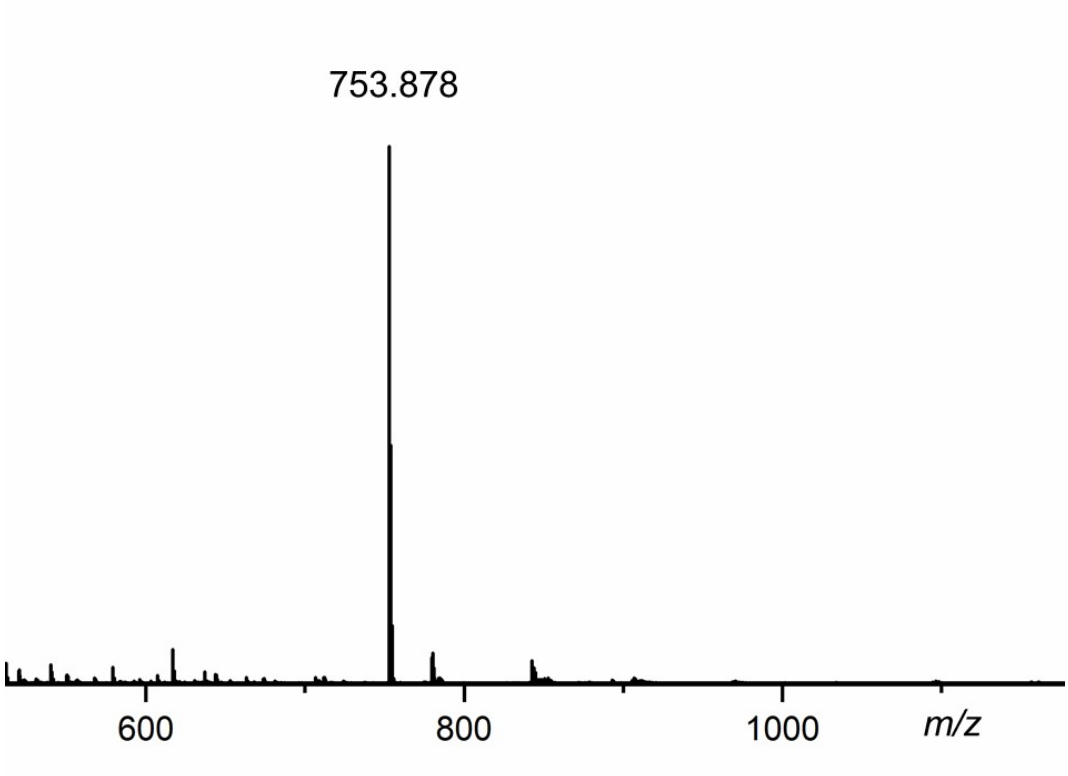


Figure S7. The ESI-MS spectrum of strand **3**.

4. Synthesis and characterizations of a library of metallo-macrocycles

To a solution of strand **3** (30.1 mg, 40 mmol) in a mixed solvent (methanol : chloroform = 1 : 1, 20 mL) was added a solution of $Zn(NO_3)_2 \cdot 6H_2O$ in methanol (12.0 mg, 40 mmol in 5 mL), and the resulting mixture was stirred at 60 °C for 8 h. After cooling to room temperature, the addition of excess NH_4PF_6 afforded a precipitate which was washed thoroughly by D.I. water and methanol. Drying in vacuo at 50 °C for 8 h gave a pale white solid with quantitative yield.

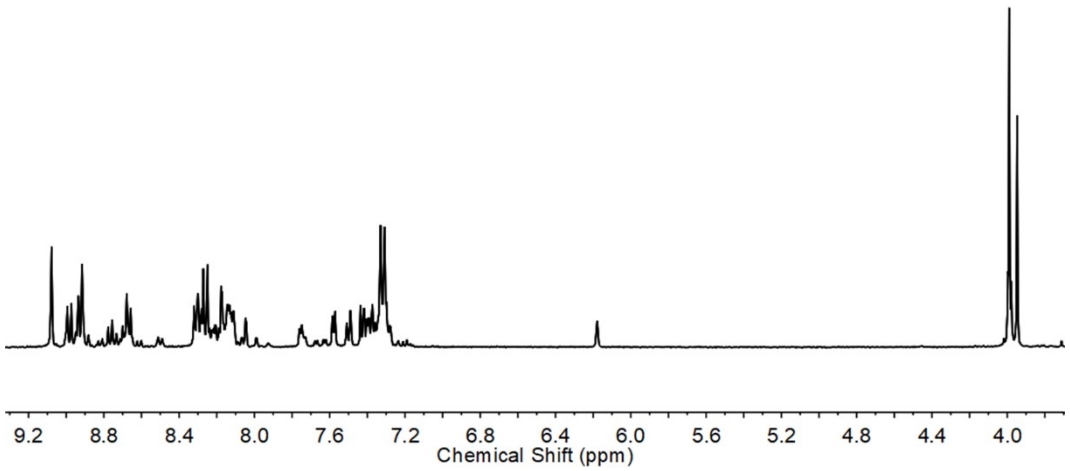


Figure S8. ^{1}H NMR spectrum (400 MHz, 298 K) of metallo-macrocycles([Zn_2**3**$_2$], [Zn_3**3**$_3$], [Zn_4**3**$_4$]) in CD_3CN-d_3.

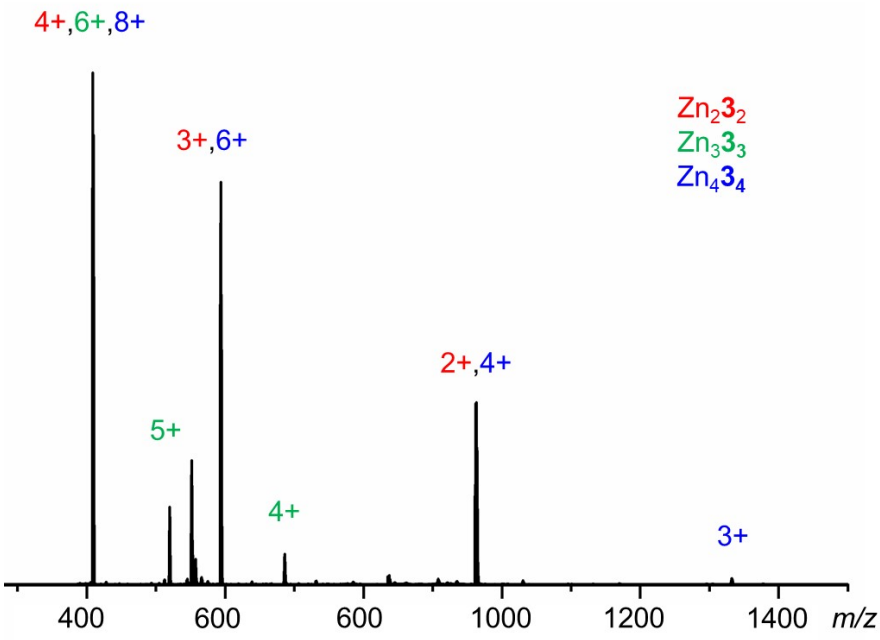


Figure S9. ESI-MS spectrum for the mixture of metallo-macrocycles([Zn_2**3**$_2$], [Zn_3**3**$_3$], [Zn_4**3**$_4$]) at CH_3CN.

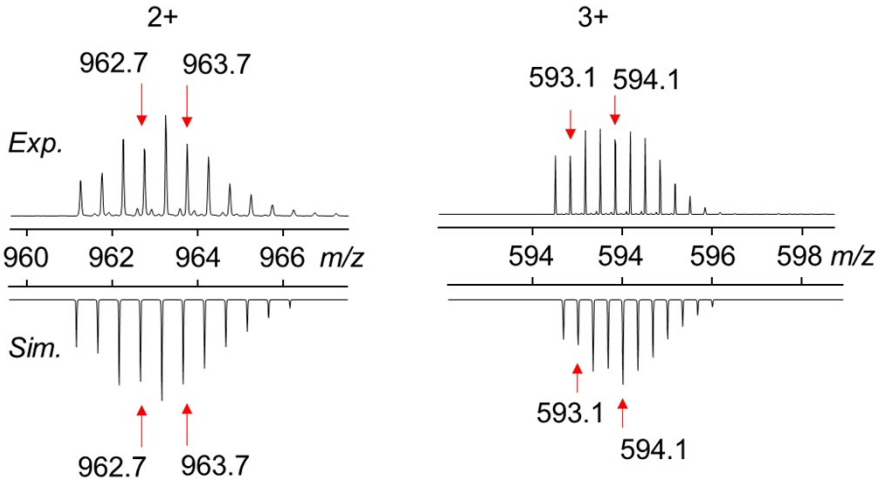


Figure S10. Two charge states of [Zn_2**3**$_2$].

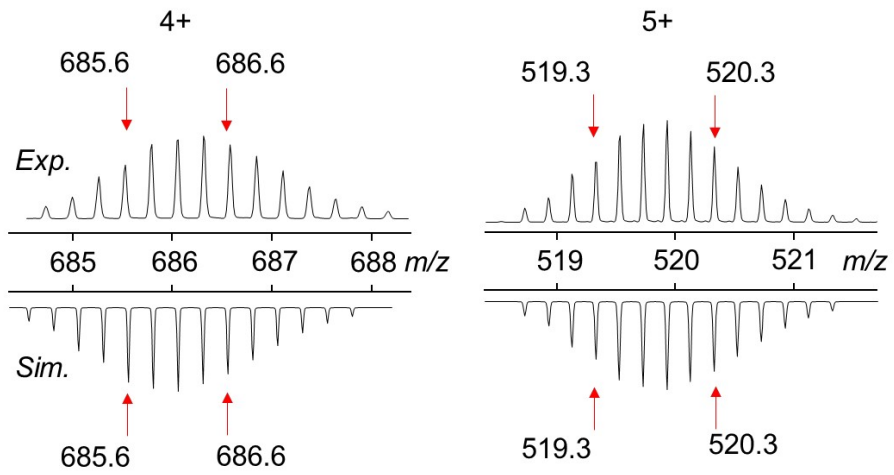


Figure S11. Two charge states of [Zn_3**3**$_3$].

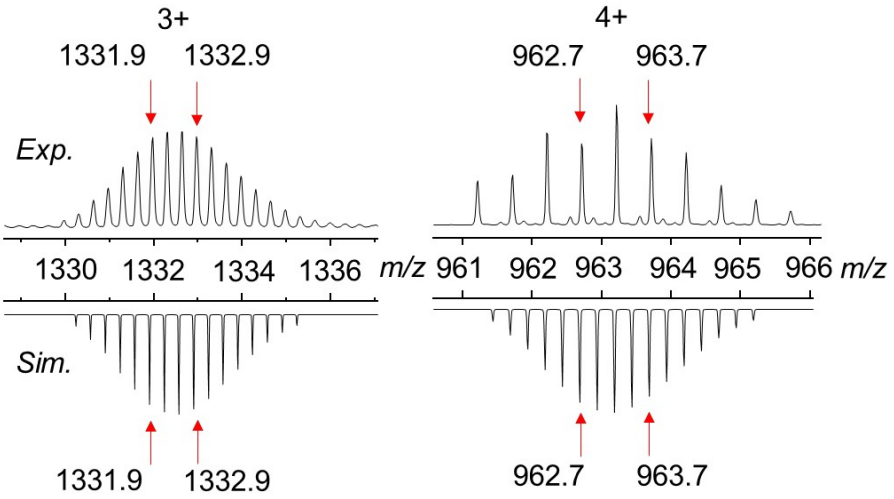


Figure S12. Two charge states of [Zn_4**3**$_4$].

5. Synthesis and characterizations of quadruple stranded helicate D

In a NMR tube, a CD_3CN-d_3 solution (0.5 mL) of the metallo-macrocycles (2.2 mg, 1 μmol) was added along with a solution of TBAX (3 μmol, TBA: tetrabutylammonium, X^-= SCN^-, N_3^-, NO_2^-, HCO_3^-, SO_4^{2-}, PO_4^{3-}, H_2PO_4) in CD_3CN-d_3. The quadruple-stranded helicate **D** was obtained quantitatively. ^{1}H NMR (400 MHz, CD_3CN-d_3, 298 K): δ (ppm) 10.13 (s, 4H, Tpy^B-$H^{6''}$), 9.57 (s, 4H, Ph-H^c), 9.43 (s, 4H, Tpy^B-$H^{5'}$), 8.72-8.71 (d, J = 8 Hz, 4H, Tpy^B-H^6), 8.54-8.54 (m, 12H, Tpy^A-$H^{3'',5'}$, Tpy^B-$H^{3'}$), 8.12-8.10 (d, J = 4 Hz, 8H, Tpy^A-$H^{3'}$, Tpy^B-$H^{3''}$), 7.87-7.85 (m, 8H, Ph-H^b), 7.82 (m, 4H, Tpy^B-H^3), 7.87-7.82 (dd, J = 8, 2 Hz, 8H, $Tpy^{A,B}$-$H^{4''}$), 7.62-7.59 (m, 8H, Ph^A-H^d), 7.55-7.40 (t, J = 8 Hz, 4H, Tpy^B-H^4), 7.48-7.38 (m, 16H, Tpy^A-$H^{3,6''}$, Tpy^B-H^5, Ph-H^a), 7.20-7.16 (t, J = 10 Hz, 4H, Tpy^A-H^4), 6.94-6.90 (m, 12H, Tpy^A-H^6, Ph^A-H^e), 6.82-6.79 (d, J = 8 Hz, 8H, Ph^B-H^d), 6.62-6.59 (t, J = 6 Hz, 4H, Tpy^A-H^5), 6.43-6.41 (d, J = 8 Hz, 8H, Ph^B-H^e), 3.86 (s, 12H, A-OCH_3), 3.73 (s, 12H, B-OCH_3); ESI-MS (*m/z*): 1073.98 [M-$3PF_6^-$]$^{3+}$ (calcd. *m/z* = 1073.98), 1683.45 [M-$2PF_6^-$]$^{2+}$ (calcd. *m/z* = 1683.45).

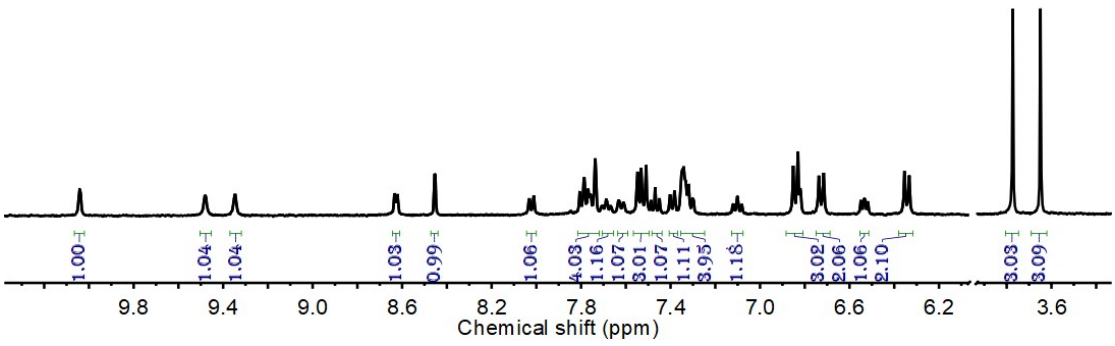


Figure S13. ^{1}H NMR spectrum (500 MHz, 298 K) of quadruple-stranded helicate **D** in CD_3CN-d_3.

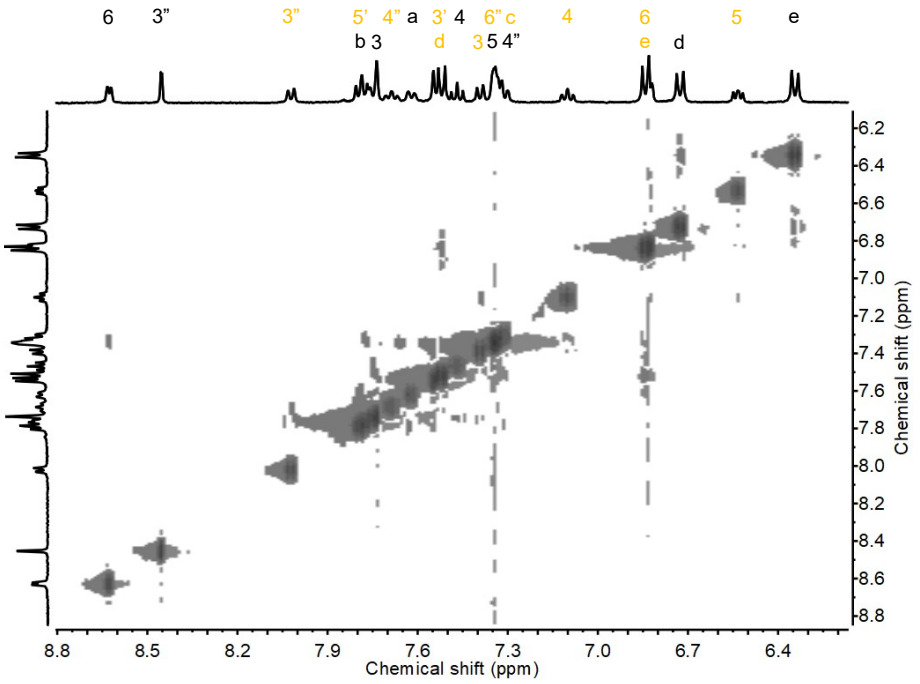


Figure S14. 2D COSY NMR spectrum (500 MHz, 298 K) of quadruple-stranded helicate **D** in CD_3CN-d_3.

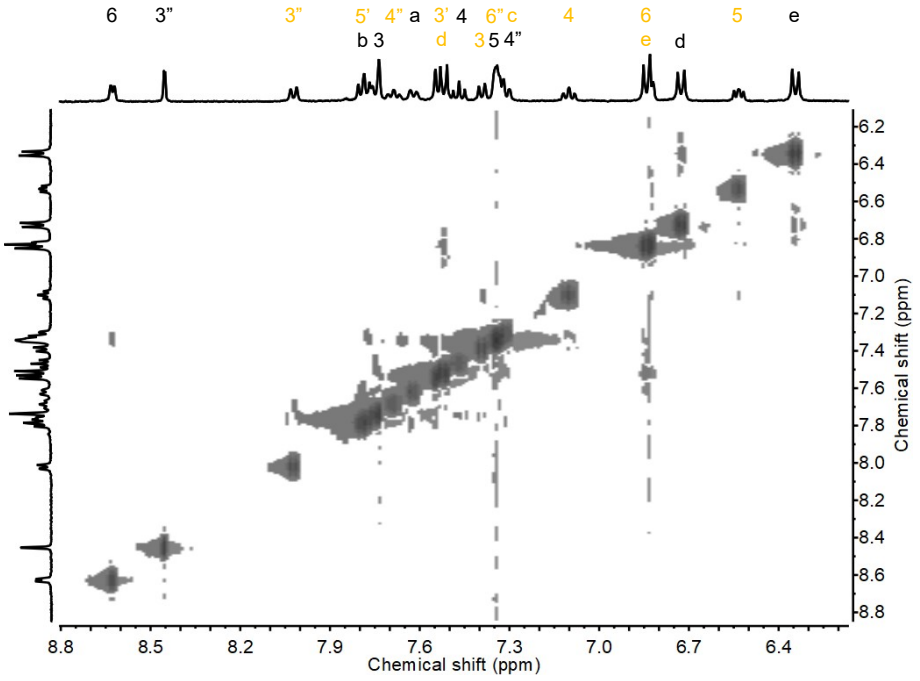


Figure S15. 2D NOESY NMR spectrum (500 MHz, 298 K) of quadruple-stranded helicate **D** in CD_3CN-d_3.

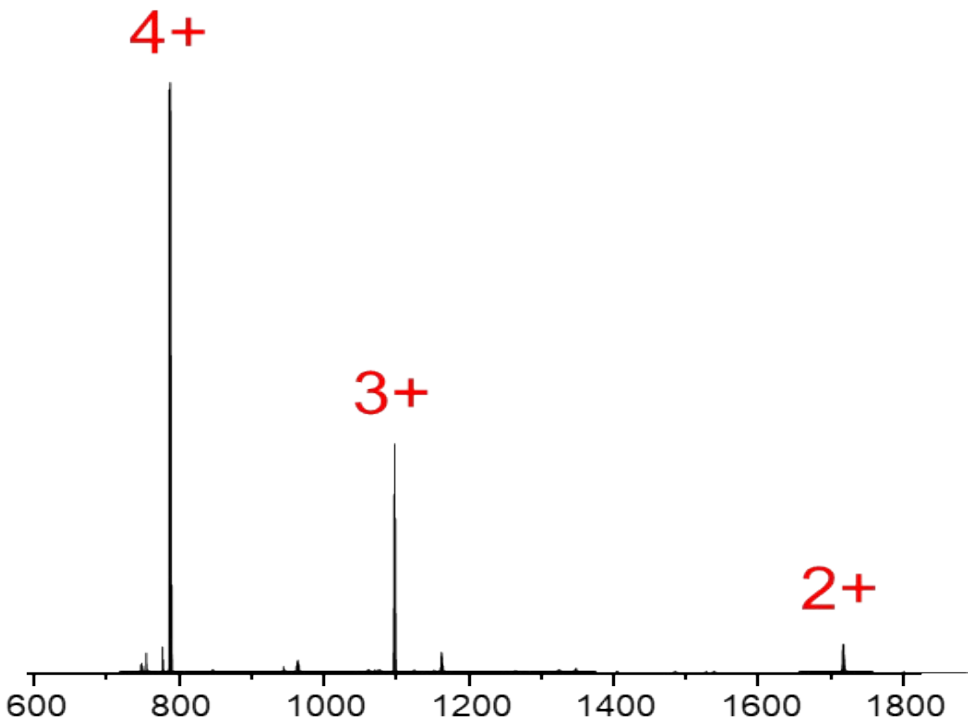


Figure S16. ESI-MS spectrum for the quadruple-stranded helicate **D** at CH_3CN.

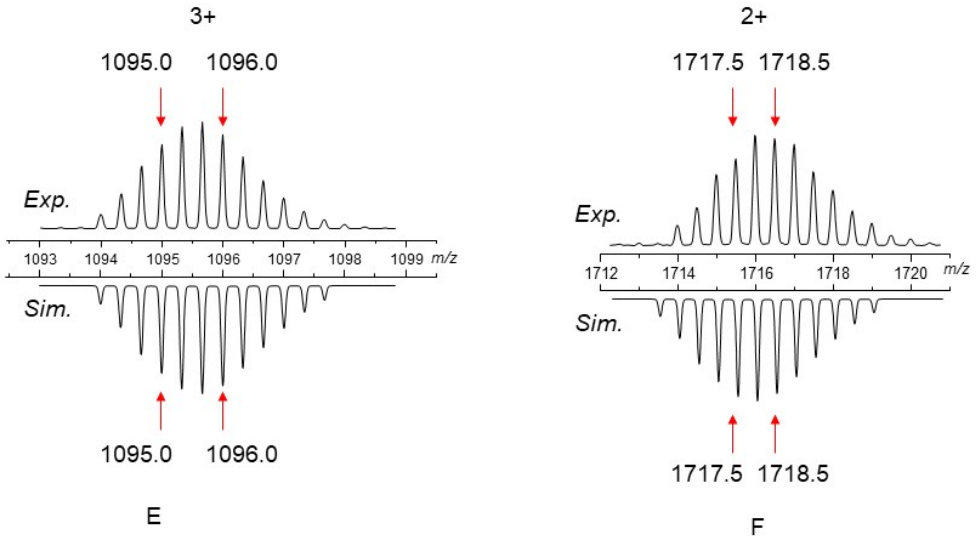


Figure S17. Isotope pattern of quadruple-stranded helicate **D**.

In a NMR tube, a CD_3CN-d_3 solution (0.5 mL) of the metallo-macrocycles (2.2 mg, 1 μmol) was added along with a solution of TBAX (3 μmol, TBA: tetrabutylammonium, X^-= F^-, NO_3^-, ClO_4^-, ReO_4^-, BF_4^-, PF_6^-, OTf^-, NTf_2^-) in CD_3CN-d_3. The quadruple-stranded helicate **D** cannot be obtained, shown as below.

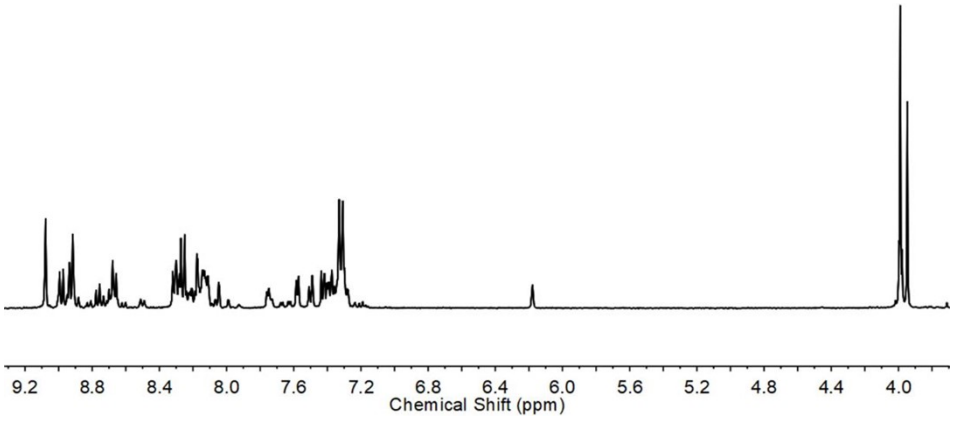


Figure S18. ^1H NMR spectrum (400 MHz, 298 K) of metallo-macrocycles with the additions of non-nucleophilic anions.

6. X-ray crystallographic data and structures

Table S2. Crystal Data and Structure Refinement for quadruple-stranded helicate **D**.

Identification code	Quadruple-stranded helicate **D**
Empirical formula	$C_{1002}H_{723}F_{120}N_{121}O_{40}P_{20}Zn_{10}$
Formula weight	18651.07
Temperature/K	100.0
Crystal system	triclinic
Space group	*P*-1
a/Å	25.9132(12)
b/Å	44.757(2)
c/Å	50.585(2)
α/°	64.778(2)
β/°	78.694(2)
γ/°	89.831(2)
Volume/Å^3	51829(4)
Z	2
ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	1.250
F(000)	19164.0
Crystal size/mm^3	0.4 × 0.15 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection /°	3.492 to 117.862
Index ranges	-26≤h≤28, -49≤k≤49, -56≤l≤56
Reflections collected	711443
Independent reflections	148780 [R_{int} = 0.0923, R_{sigma} = 0.0872]
Data/restraints/parameters	148780/42/11703
Goodness-of-fit on F^2	2.479
Final R indexes [I>=2σ (I)]	R_1 = 0.2333, wR_2 = 0.5725
Final R indexes [all data]	R_1 = 0.2803, wR_2 = 0.6131
Largest diff. peak/hole / e Å^{-3}	4.74/-5.37

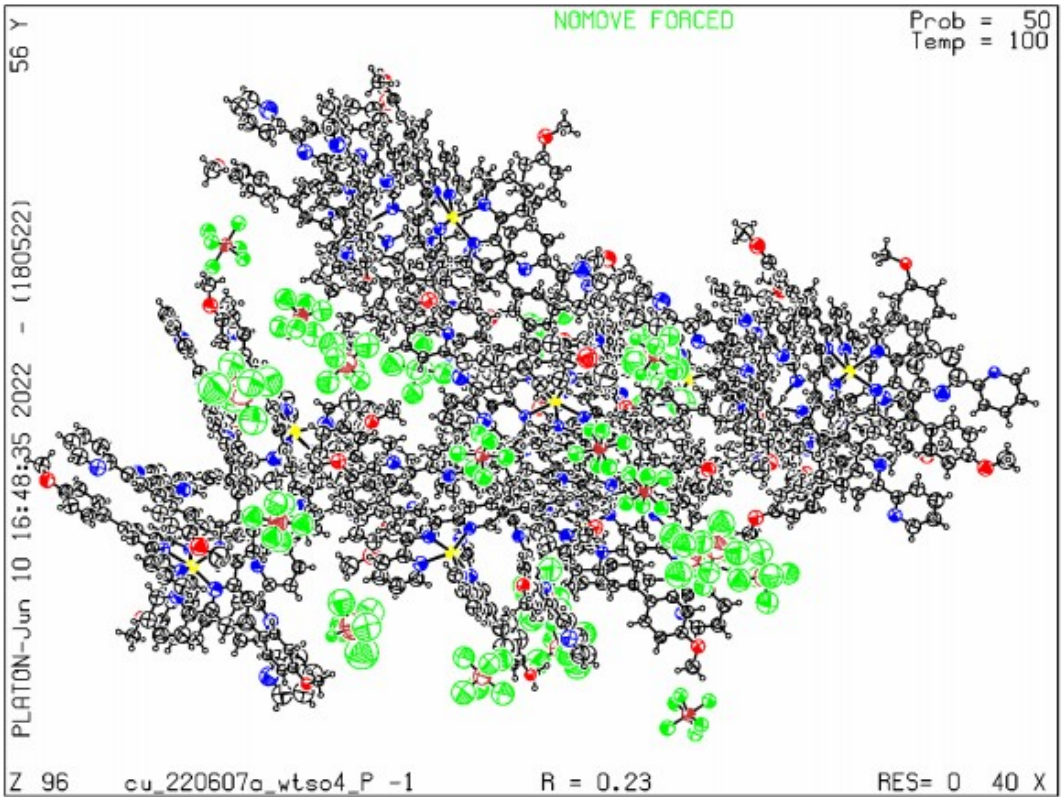


Figure S19. The crystal structure of quadruple-stranded helicate **D**.

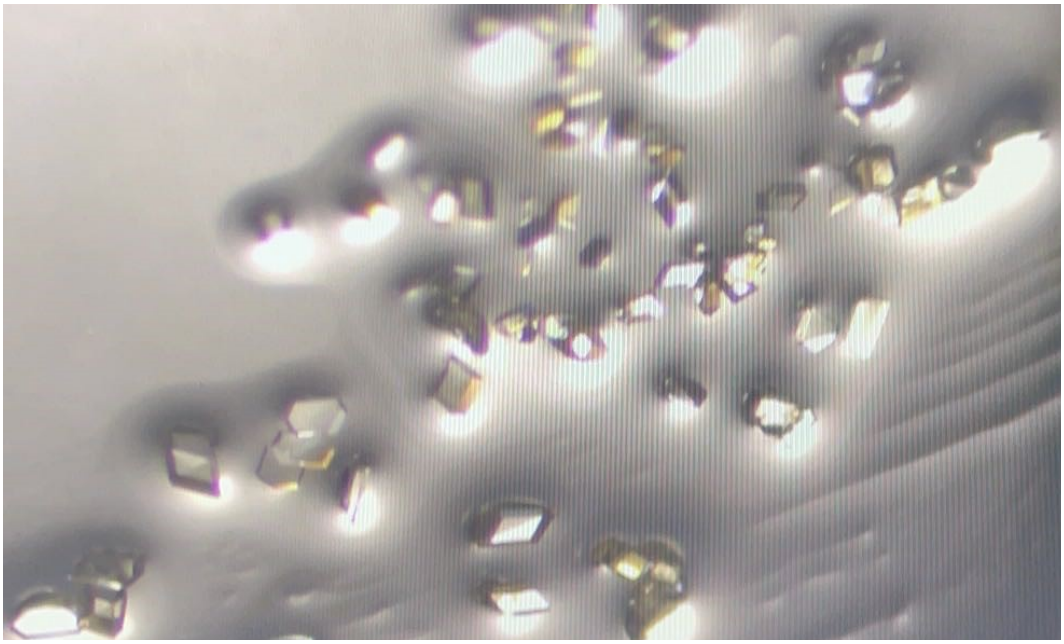


Figure S20.The macroscopic crystal photograph of quadruple-stranded helicate **D**

7. Catalyzed Hydrolysis of halogenated-diphenylmethane

In a sealed glass reactor, to a solution of catalysis **1** (9 μmol, 10 mol%) in CH_3CN (10 mL), Ph_2CHBr (90 μmol, 1 equiv) and H_2O (0.9 mmol) were added and the reaction was stirred at 40 °C for 1 h. Then, the solvent was removed in vacuo to give a residue which was subject to ^1H NMR test directly. The control experiments followed the above procedure. The difference lies in the use of different catalysts (quadruple-stranded helicate Br, $Zn(NO_3)_2$, $Zn(Tpy)_2$ or without catalyst) or substrates (Ph_2CHCl). The structure of $Zn(Tpy)_2$ was shown as Figure S21.

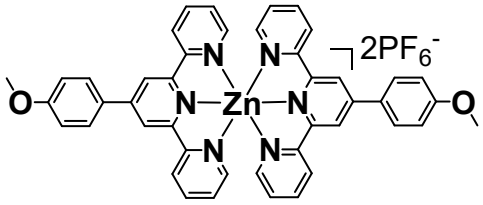


Figure S21. The chemical structure of $Zn(Tpy)_2$.

8. The Catalyzed Hydrolysis

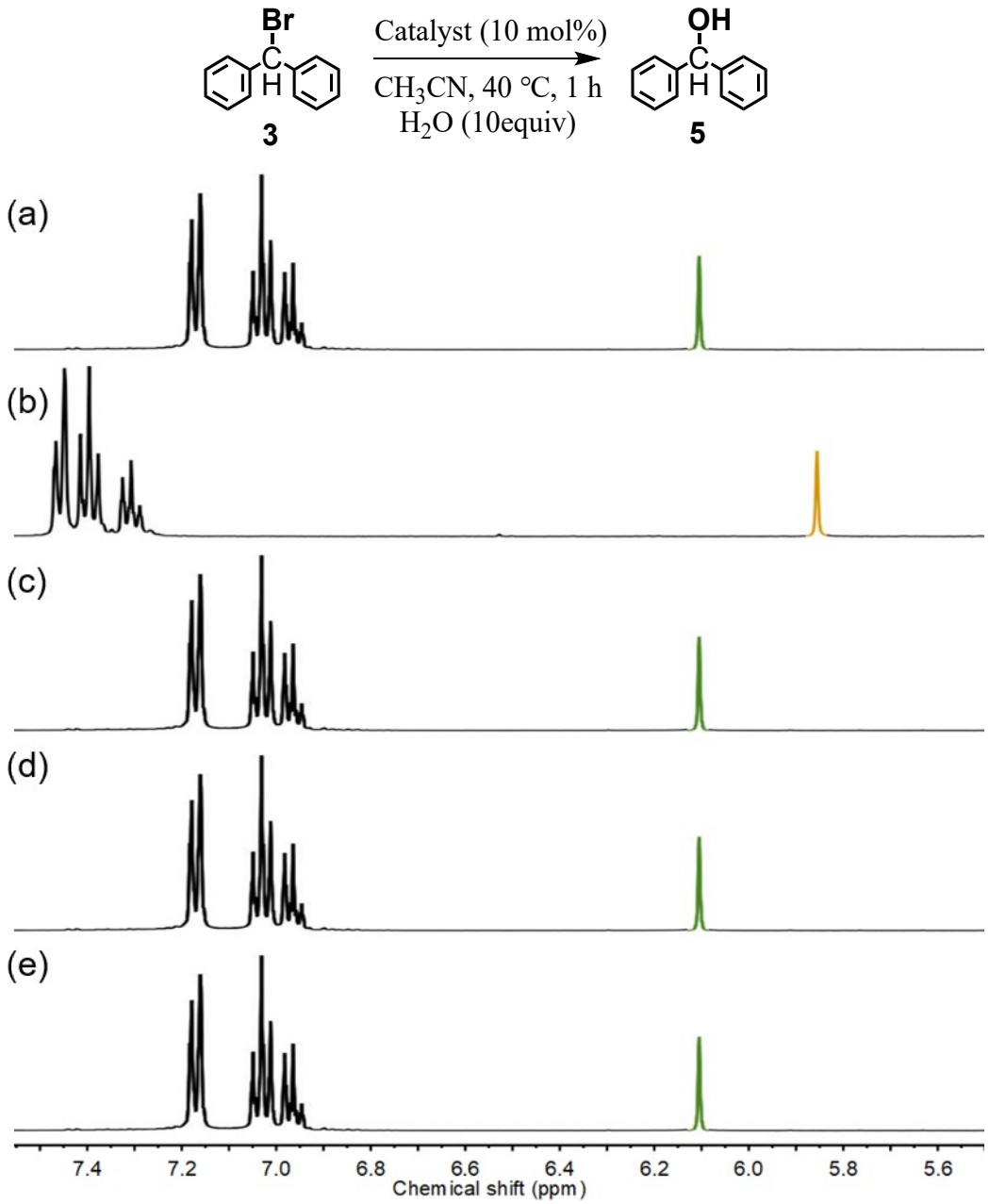


Figure S22. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) bromodiphenylmethane **3**. (b) The reaction mixture of 90 μmol of **3** in presence of 10 mol% of the library (9 μmol) and 0.9 mmol H_2O in 10 mL of CH_3CN after stirring for 1 h at 40 ℃. The reaction mixture of 90 μmol of **3**, 0.9 mmol H_2O in 10 mL of CH_3CN after stirring for 1 h at 40 ℃ in presence of 10 mol% of (c) Helicate-Br, (d) $Zn(Tpy)_2$, (e) $Zn(NO_3)_2$.

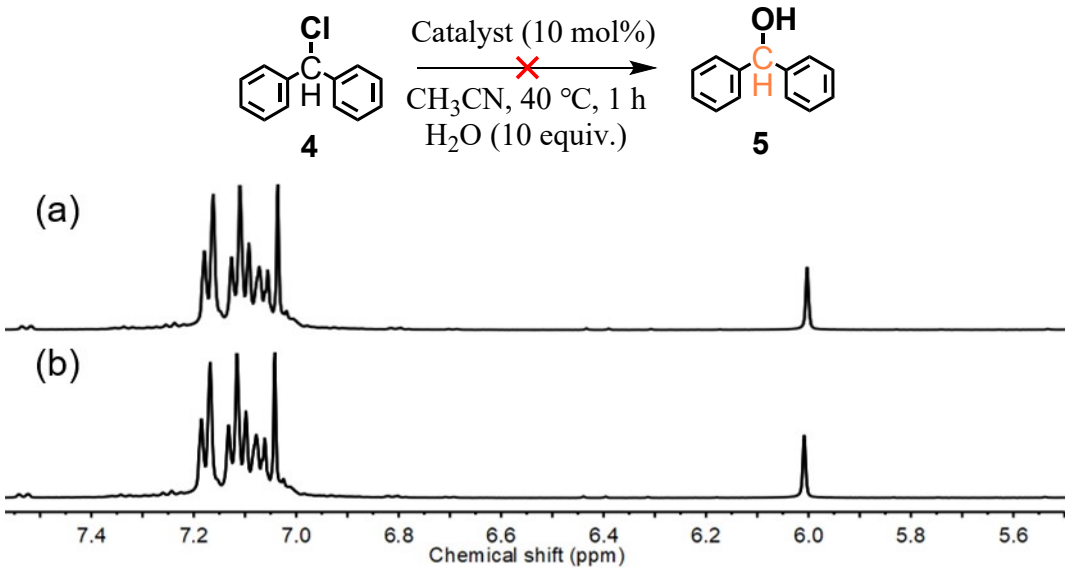
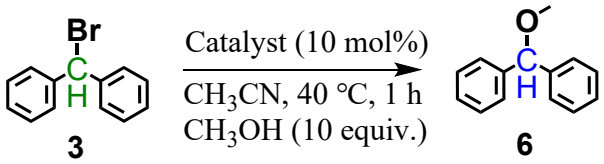


Figure S23 Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) (chloromethylene)dibenzene **4**. (b) The reaction mixture of 90 μmol of (chloromethylene)dibenzene **4** in presence of 10 mol% of the library (9 μmol) and 0.9 mmol H_2O in 10 mL of CH_3CN after stirring for 1 h at 40 °C.

9. The Catalyzed Alcoholysis



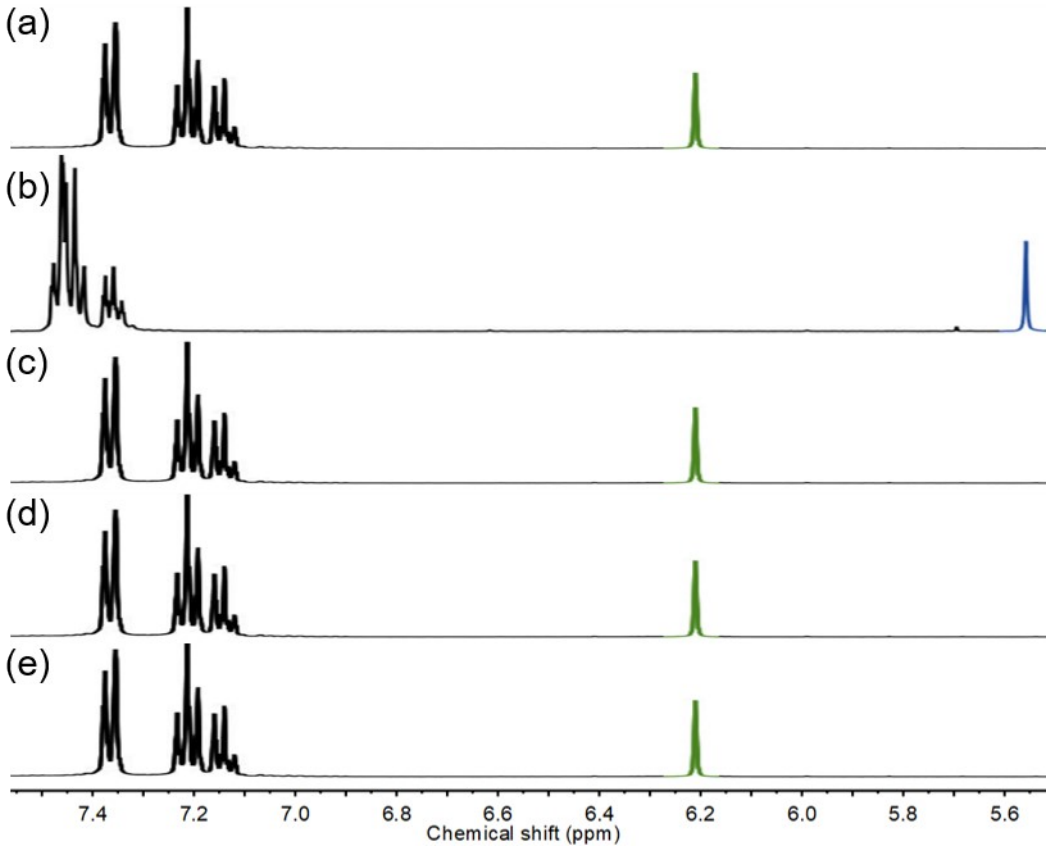


Figure S24. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) bromodiphenylmethane **3**. (b) the reaction mixture of 90 μmol of **3** in presence of 10 mol% of the library (9 μmol) and 0.9 mmol MeOH in 10 mL of CH_3CN after stirring for 1 h at 40 °C. The reaction mixture of 90 μmol of **3**, 0.9 mmol MeOH in 10 mL of CH_3CN after stirring for 1 h at 40 °C in presence of 10 mol% of (c) Helicate-Br, (d) $Zn(Tpy)_2$, (e) $Zn(NO_3)_2$.

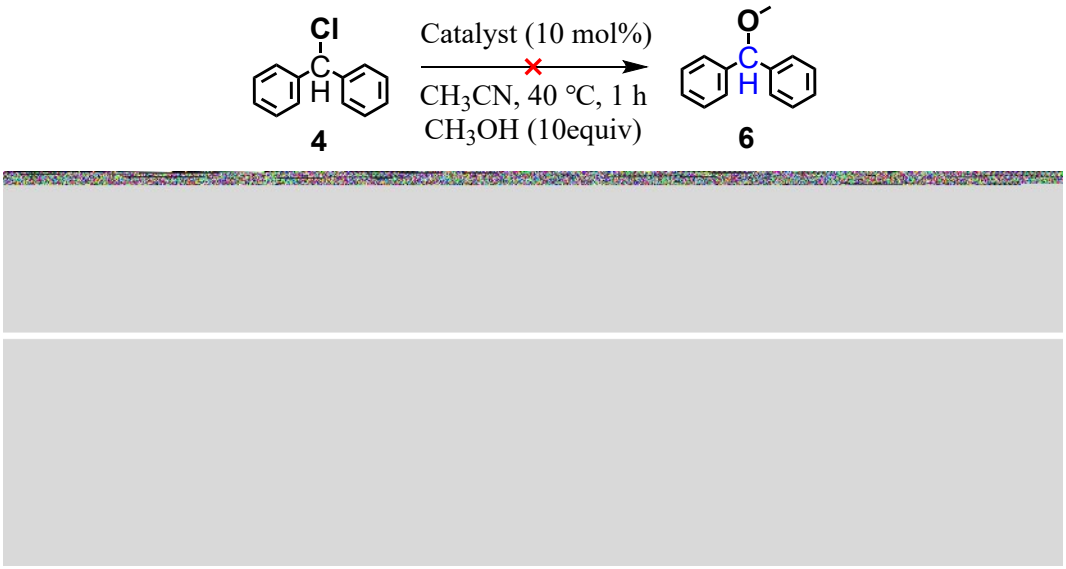


Figure S25. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) (chloromethylene)dibenzene **4**. (b) The reaction mixture of 90 μmol of (chloromethylene)dibenzene **4** in presence of 10 mol% of the library (9 μmol) and 0.9 mmol CH_3OH in 10 mL of CH_3CN after stirring for 1 h at 40 °C.

10. The Catalyzed Competitive Reaction

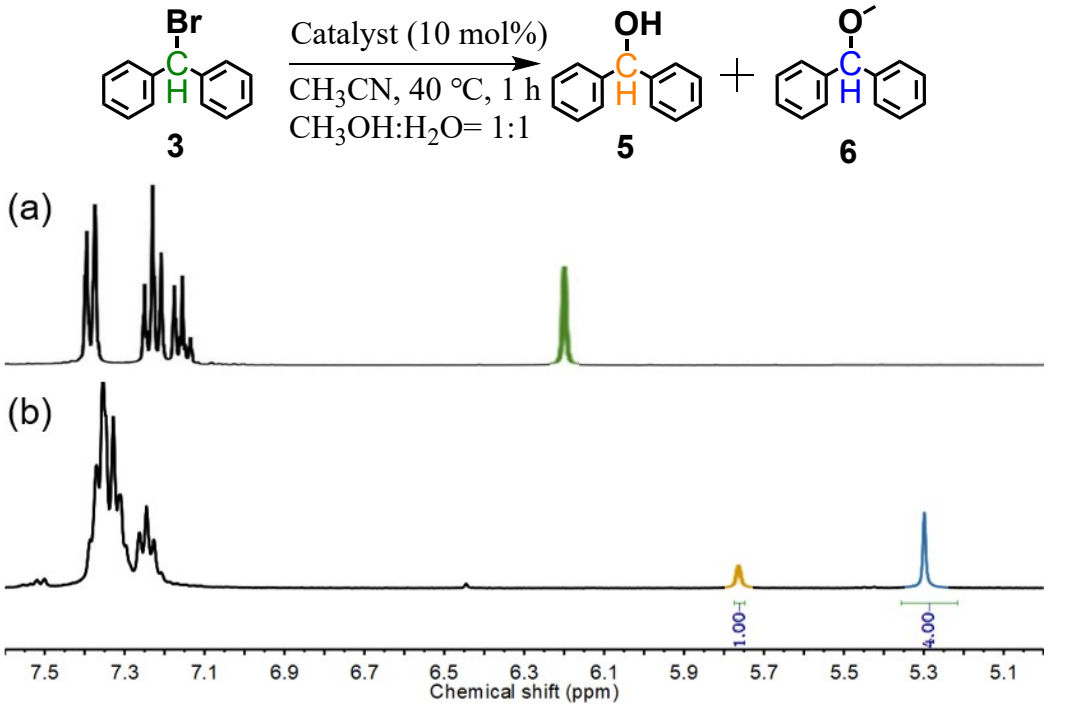


Figure S26. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) bromodiphenylmethane **3**; (b) the reaction mixture of 90 μmol of **3** in presence of 10 mol% of the library (9 μmol), 0.9 mmol H_2O and 0.9 mmol MeOH in 10 mL of CH_3CN after stirring for 1 h at 40 °C.

11. The Catalyzed Ritter Reaction

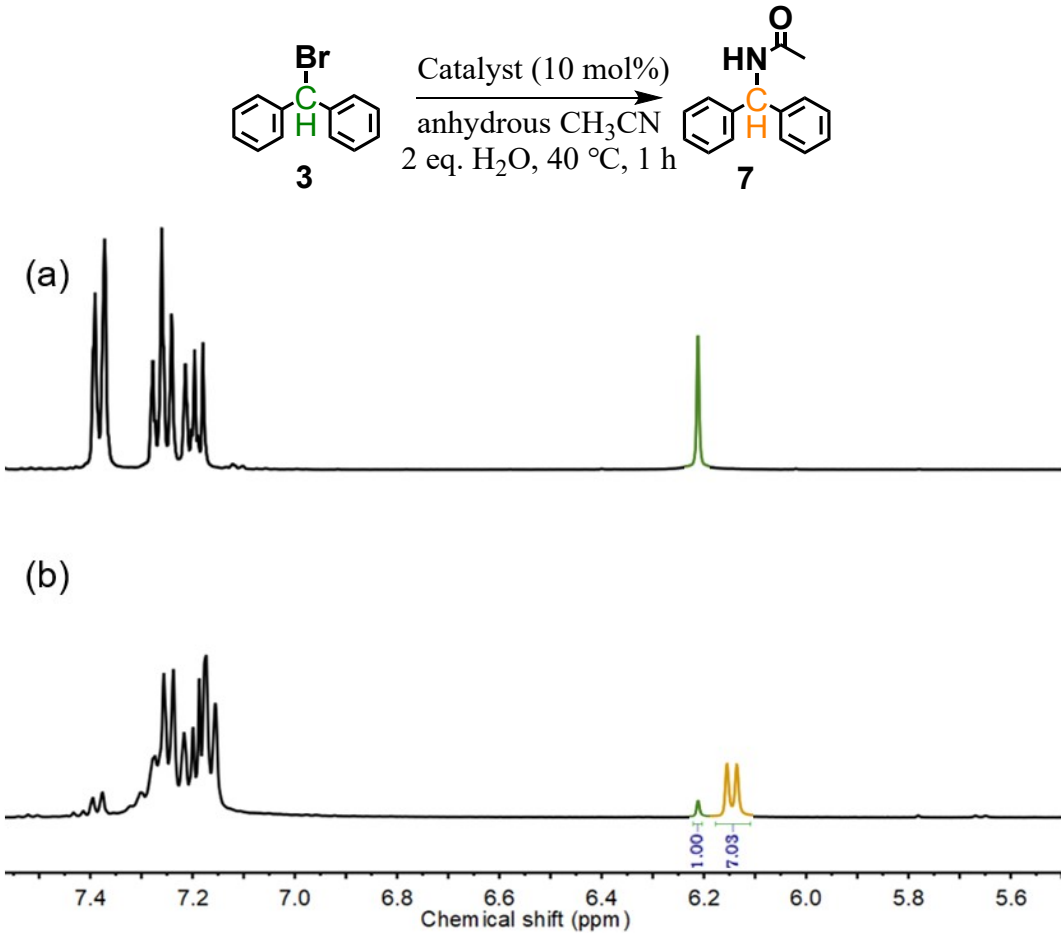


Figure S27. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) bromodiphenylmethane **3**; (b) the reaction mixture of 90 μmol of **3** in presence of 10 mol% of the library (9 μmol) and 0.18 mmol H_2O in 10 mL of anhydrous CH_3CN after stirring for 1 h at 40 °C.

12. The Catalyzed Friedel–Crafts Benzylation

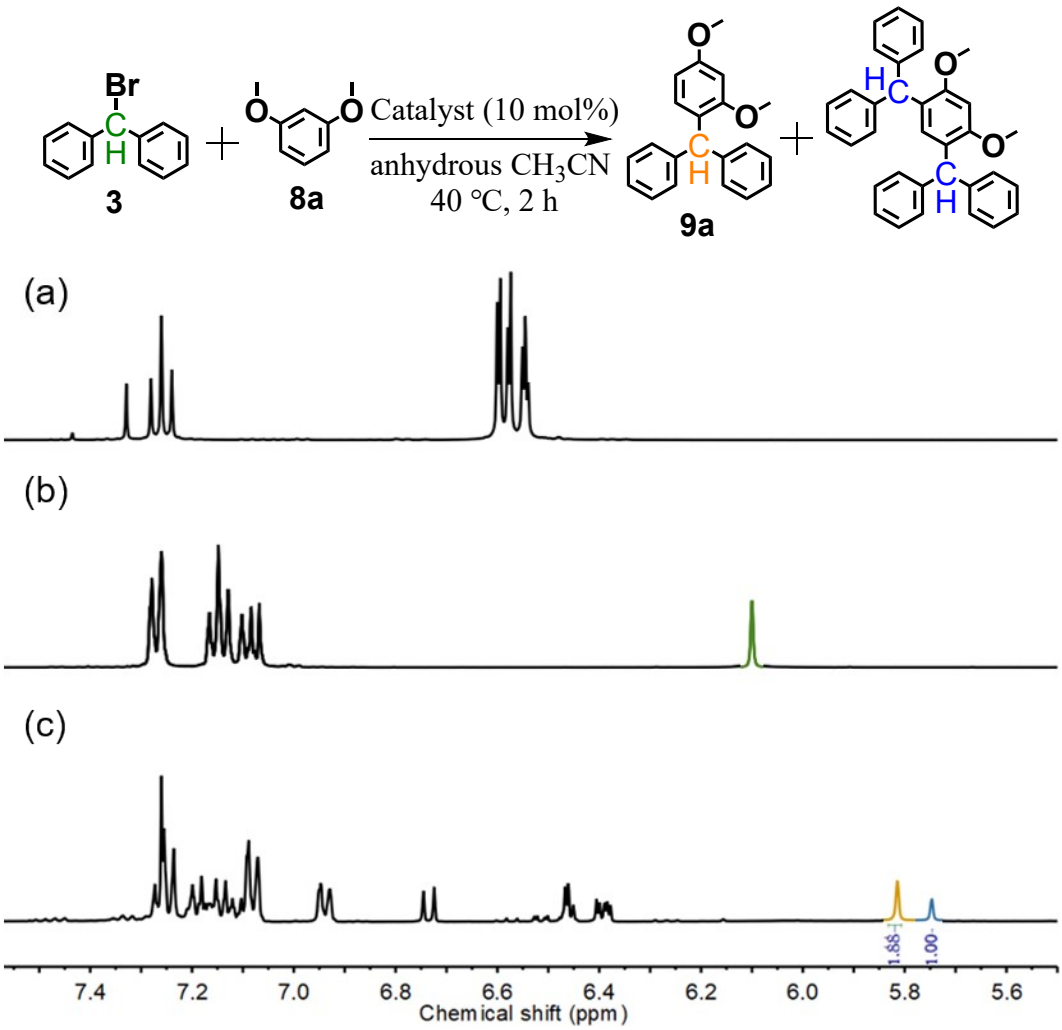


Figure S28. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) 1,3-dimethoxybenzene **8a**; (b) bromodiphenylmethane **3**; (c) the reaction mixture of 90 μmol of **3** and 135 μmol **8a** in presence of 10 mol% of the library in 10 mL of anhydrous CH_3CN after stirring for 2 h at 40℃.

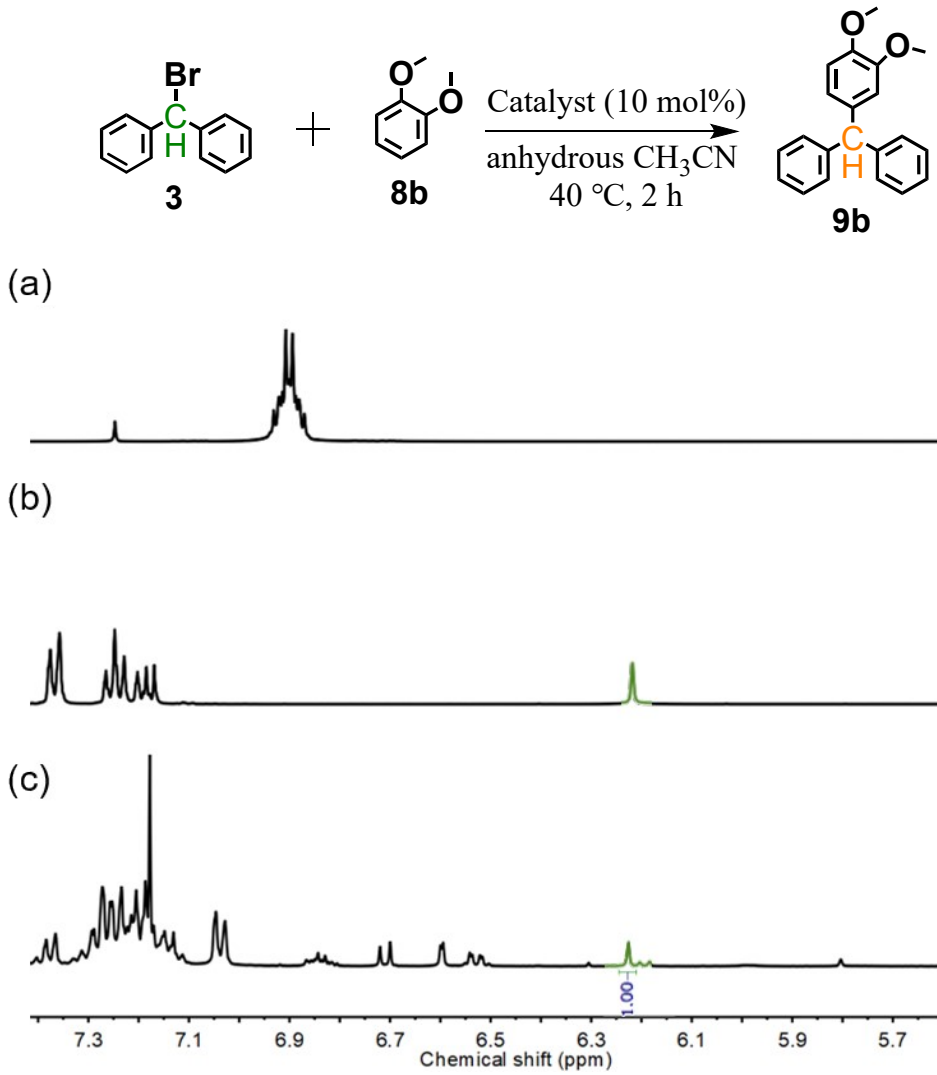


Figure S29. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) 1,2-dimethoxybenzene **8b**; (b) bromodiphenylmethane **3**; (c) the reaction mixture of 90 µmol of **3** and 135 µmol **8b** in presence of 10 mol% of the library in 10 mL of anhydrous CH_3CN after stirring for 2 h at 40°C.

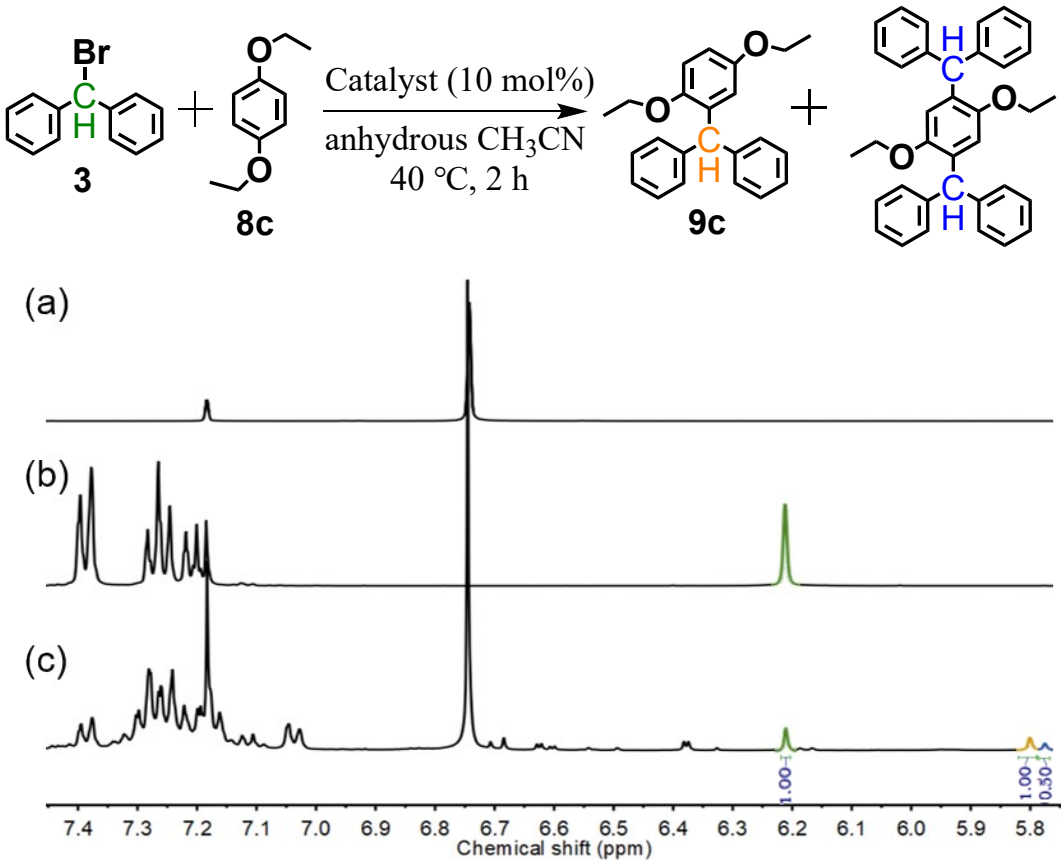


Figure S30. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) 1,4-trimethoxybenzene **8c**; (b) bromodiphenylmethane **3**; (c) the reaction mixture of 90 µmol of **3** and 135 µmol **8c** in presence of 10 mol% of the library in 10 mL of anhydrous CH_3CN after stirring for 2 h at 40°C.

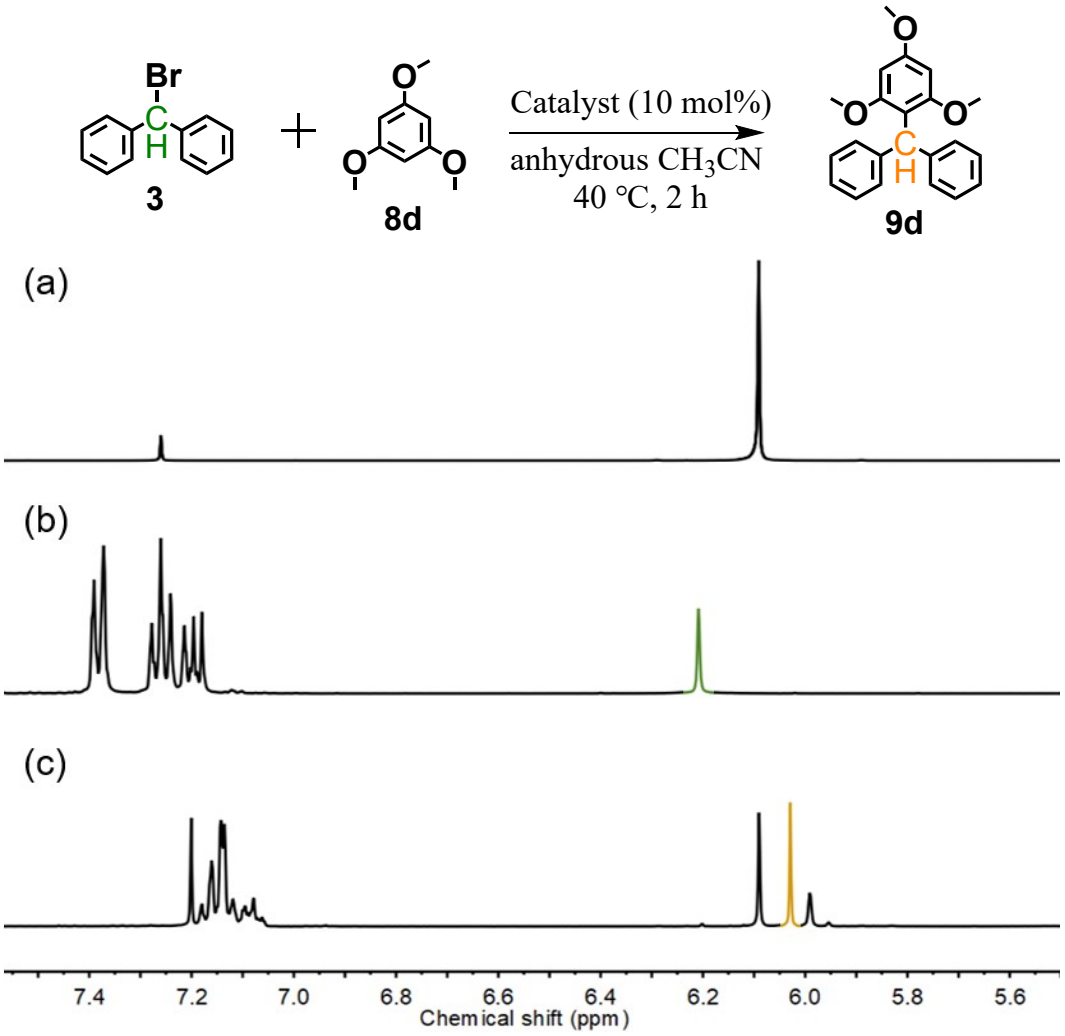


Figure S31. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) 1,3,5-trimethoxybenzene **8d**; (b) bromodiphenylmethane **3**; (c) the reaction mixture of 90 µmol of **3** and 135 µmol **8d** in presence of 10 mol% of the library in 10 mL of anhydrous CH_3CN after stirring for 2 h at 40 °C.

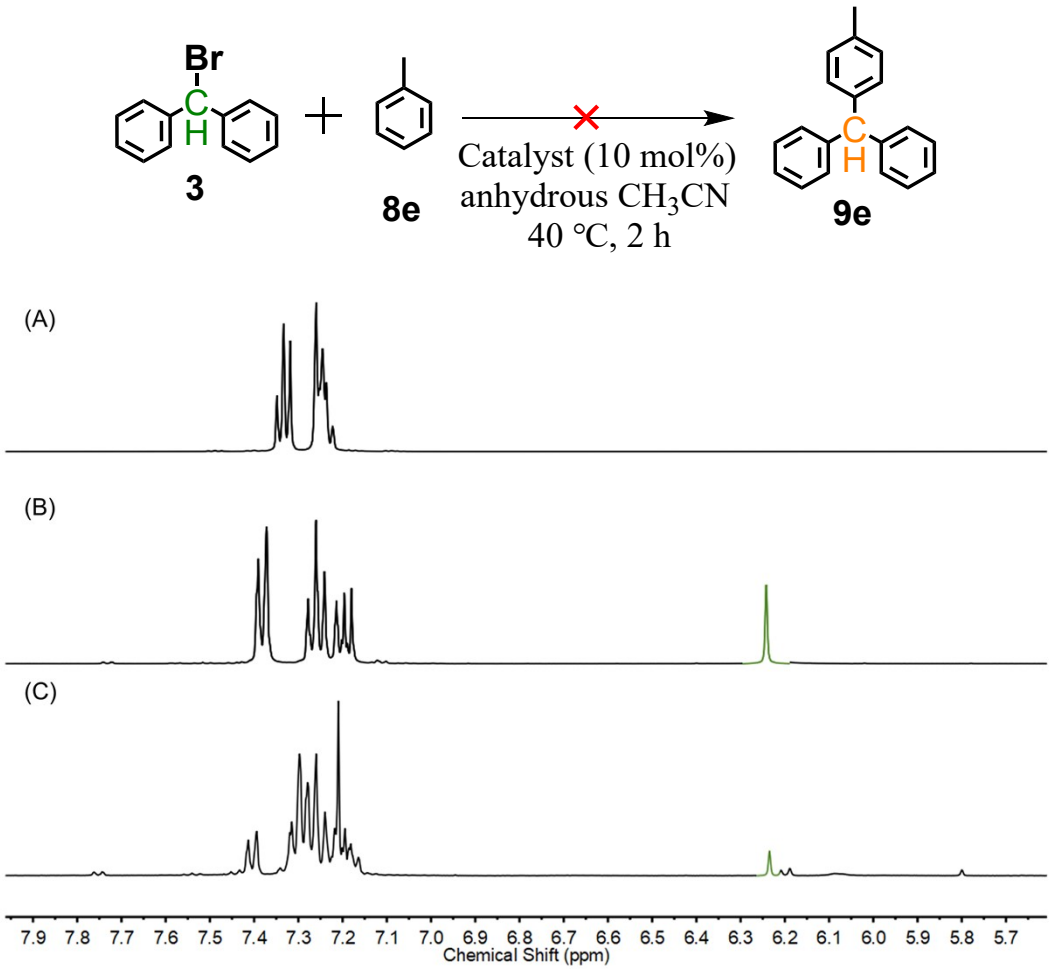


Figure S32. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) toluene **8e**; (b) bromodiphenylmethane **3**; (c) the reaction mixture of 90 µmol of **3** and 135 µmol **8e** in presence of 10 mol% of the library in 10 mL of anhydrous CH_3CN after stirring for 2 h at 40 °C.

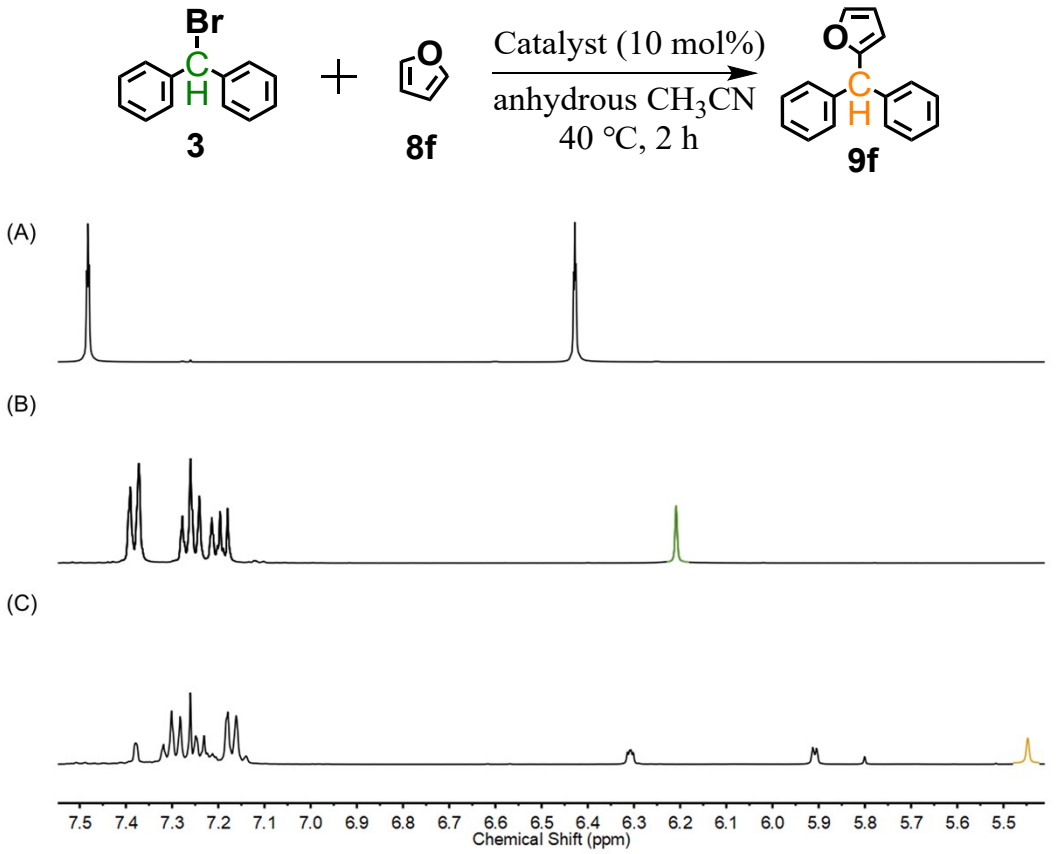


Figure S33. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) furan **8f**; (b) bromodiphenylmethane **3**; (c) the reaction mixture of 90 µmol of **3** and 135 µmol **8f** in presence of 10 mol% of the library in 10 mL of anhydrous CH_3CN after stirring for 2 h at 40 °C.

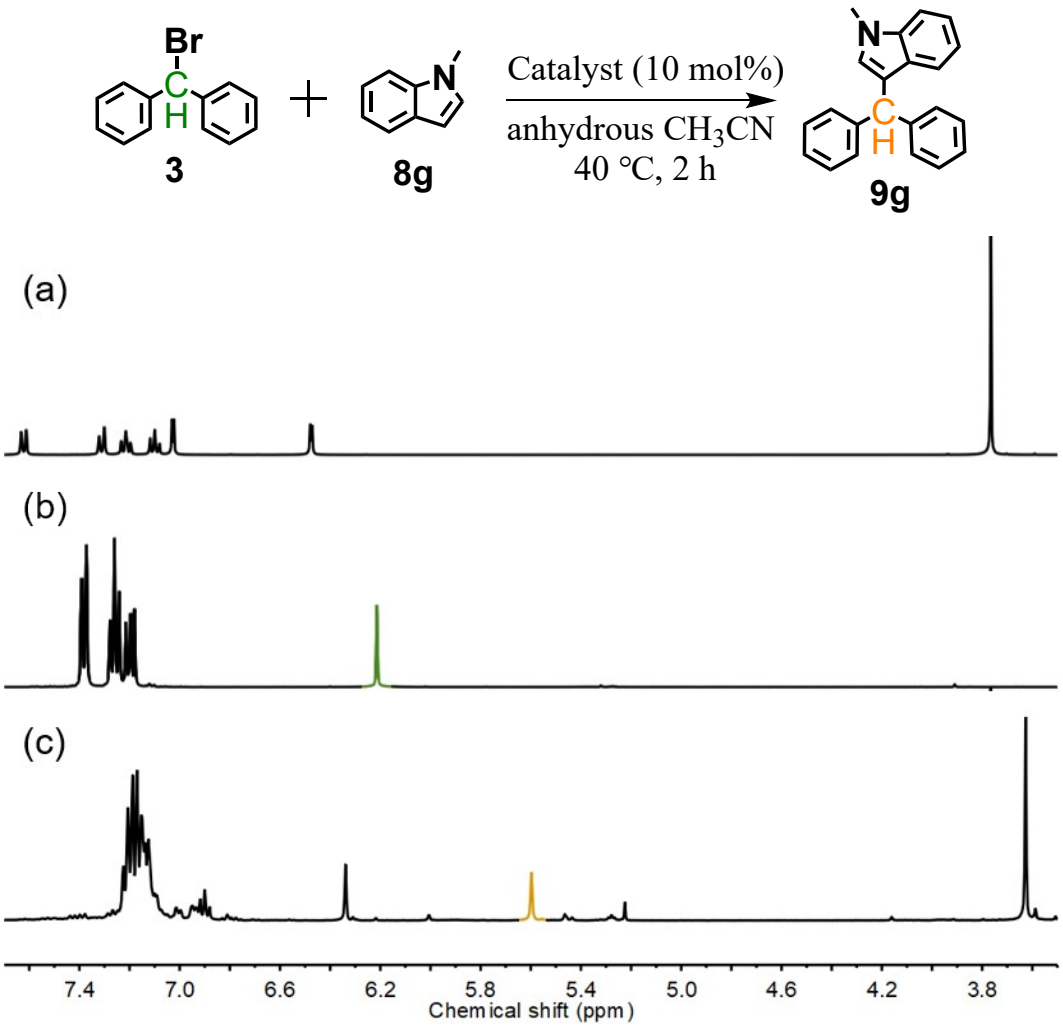


Figure S34. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) 1-methyl-1H-indole **8g**; (b) bromodiphenylmethane **3**; (c) the reaction mixture of 90 μmol of **3** and 135 μmol **8g** in presence of 10 mol% of the library in 10 mL of anhydrous CH_3CN after stirring for 2 h at 40 °C.

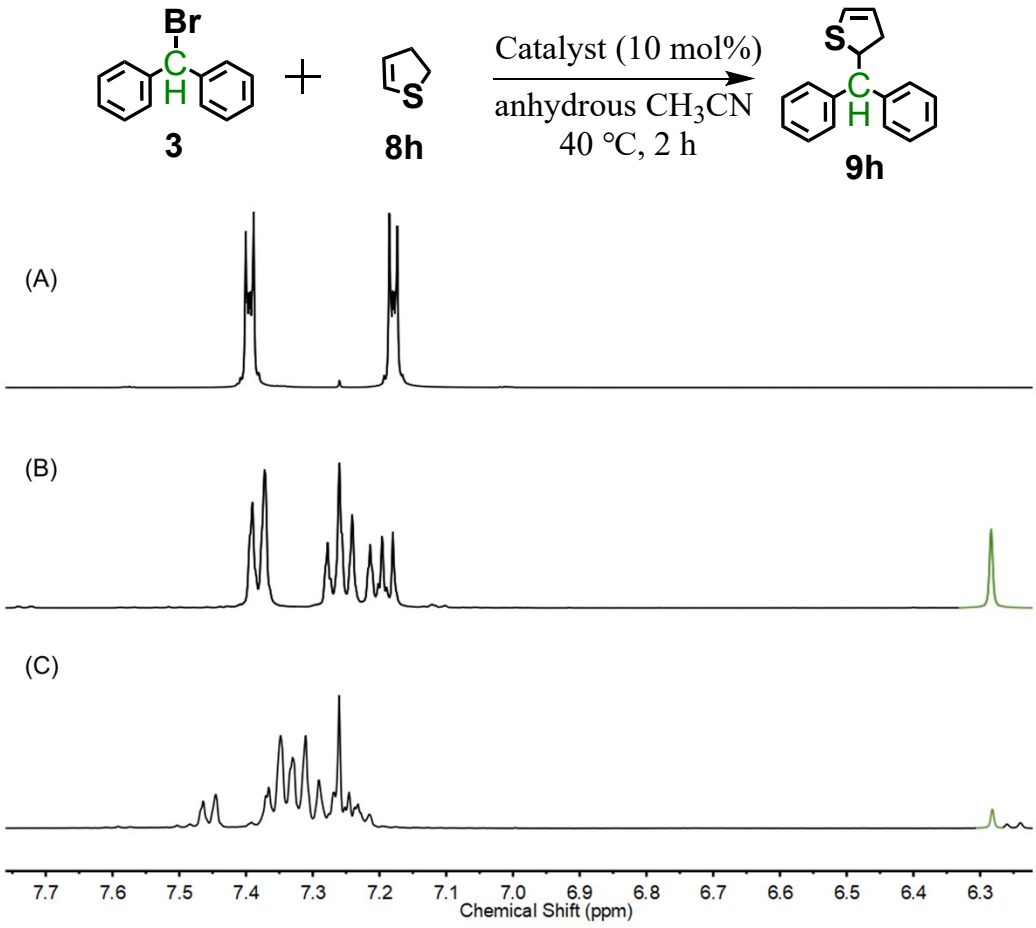


Figure S35. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) thiophene **8h**; (b) bromodiphenylmethane **3**; (c) the reaction mixture of 90 µmol of **3** and 135 µmol **8h** in presence of 10 mol% of the library in 10 mL of anhydrous CH_3CN after stirring for 2 h at 40 °C.

13. Mechanism experiment

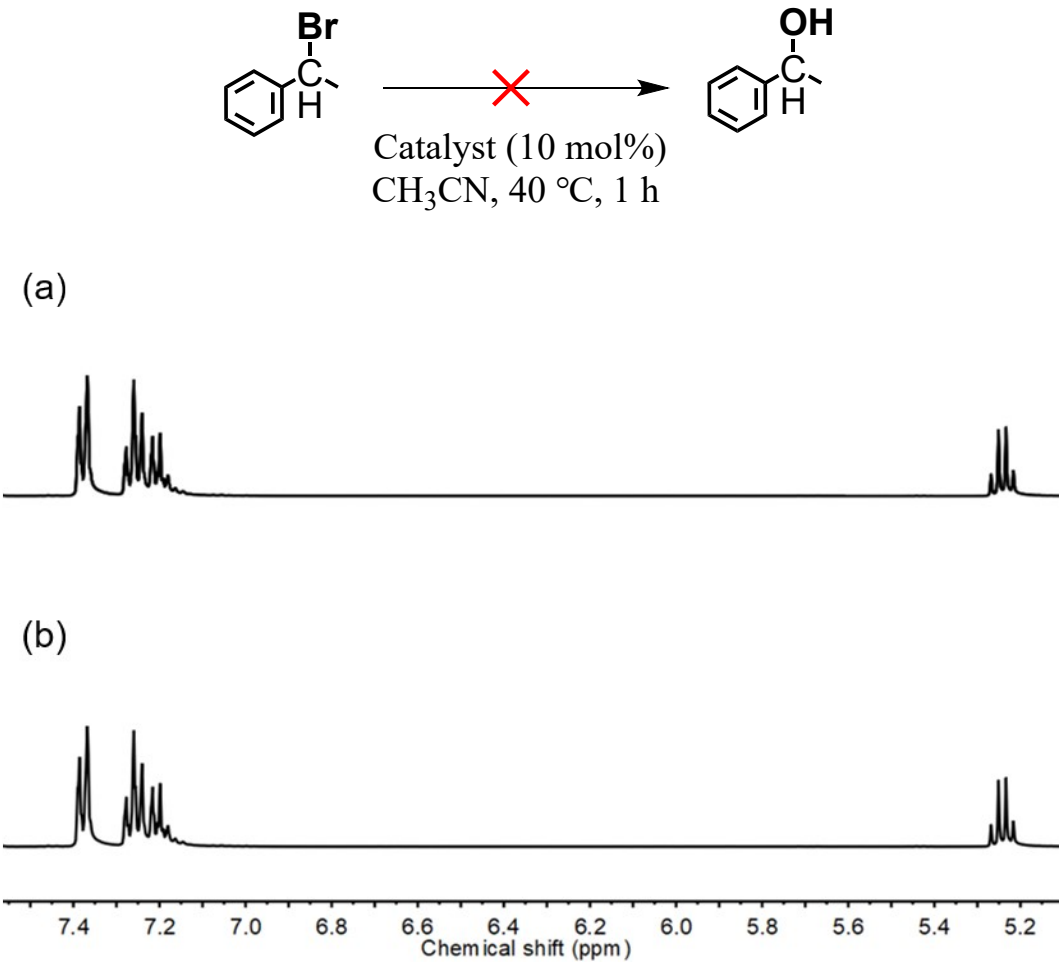


Figure S36. Partial ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of: (a) (1-bromoethyl)benzene; (b) the reaction mixture of 90 μmol of (1-bromoethyl)benzene in presence of 10 mol% of the library and 0.9 mmol H_2O in 10 mL of CH_3CN after stirring for 1 h at 40 °C.

14. Single-crystal X-ray structures of quadruple-stranded helicate E, F, G

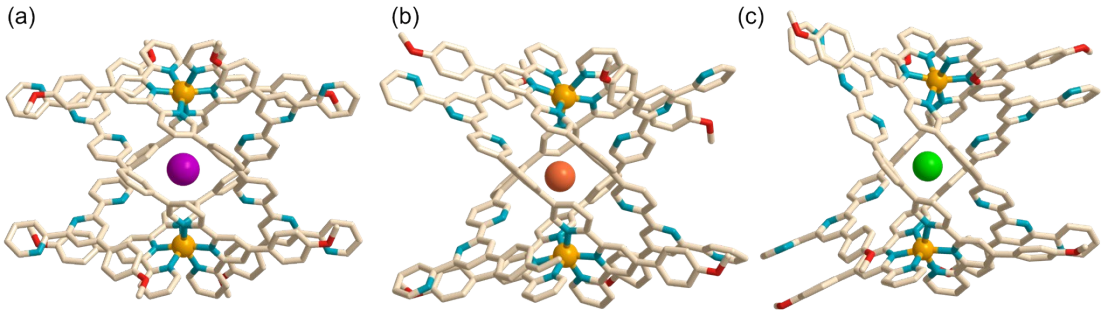


Figure S37. Single-crystal X-ray structures of (a) quadruple-stranded helicate E ($I^-\subset$**D**), (b) quadruple-stranded helicate **F** ($Br^-\subset$**D**) (c) quadruple-stranded helicate **G** ($Cl^-\subset$**D**).

15. The titration of HCO_3^-

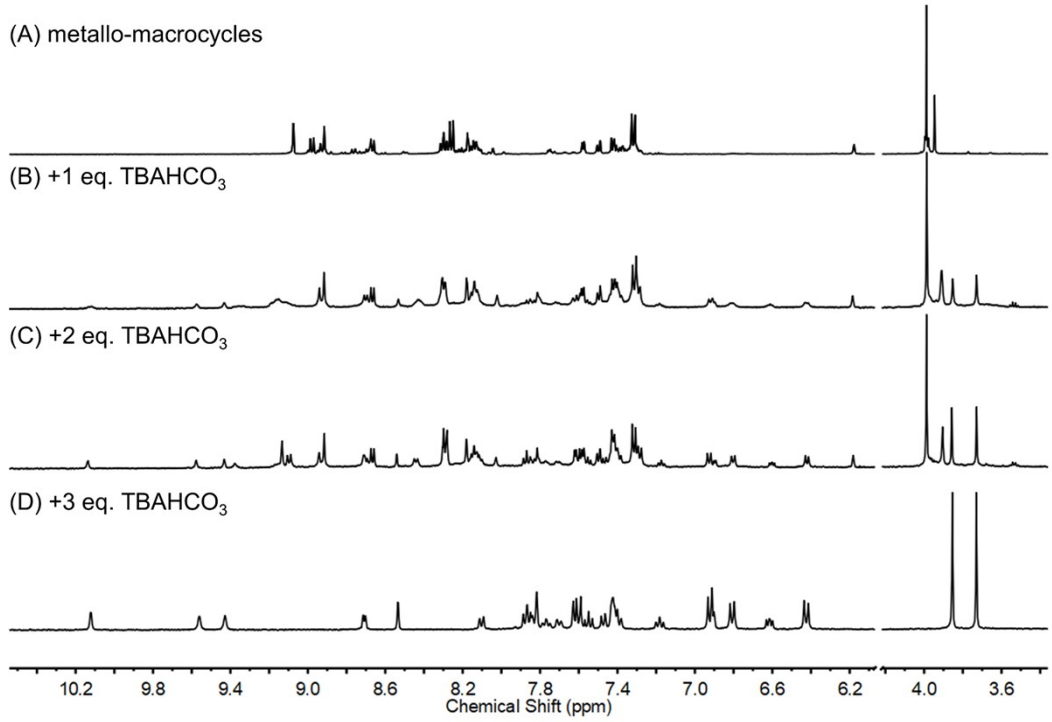


Figure S38. ^{1}H NMR spectra (400 MHz, CD_3CN-d_3, 298 K) showing the conversion of a library of metallo-macrocycles to quadruple stranded helicate **D**-HCO_3^- upon addition of tetrabutylammonium hydrogen carbonate: (A) a library of metallo-macrocycles, addition of (B) 1.0 equiv. of tetrabutylammonium hydrogen carbonate; (C) 2.0 equiv. of tetrabutylammonium hydrogen carbonate; (D) 3.0 equiv. of tetrabutylammonium hydrogen carbonate.

16. The *in-situ* hydrolysis and alcoholysis reactions

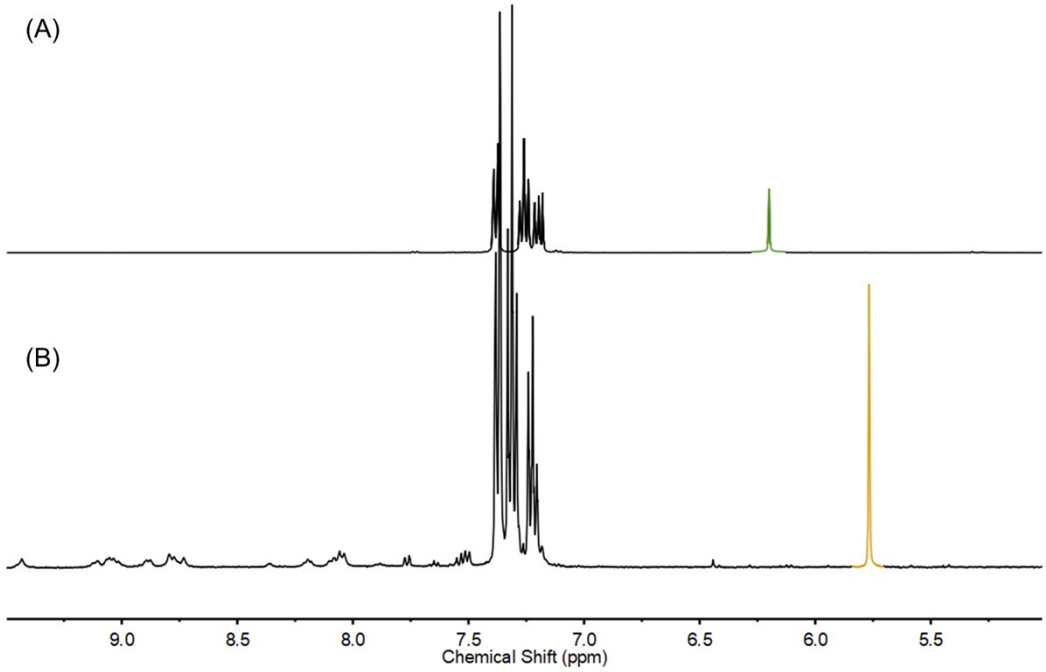


Figure S39. Partial ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of: (a) bromodiphenylmethane **3**; (b) The reaction mixture of 9 μmol of **3** in presence of 10 mol% of the library (0.9 μmol) and 0.09 mmol H_2O in 0.5 mL of CH_3CN after stirring for 1 h at 40 °C.

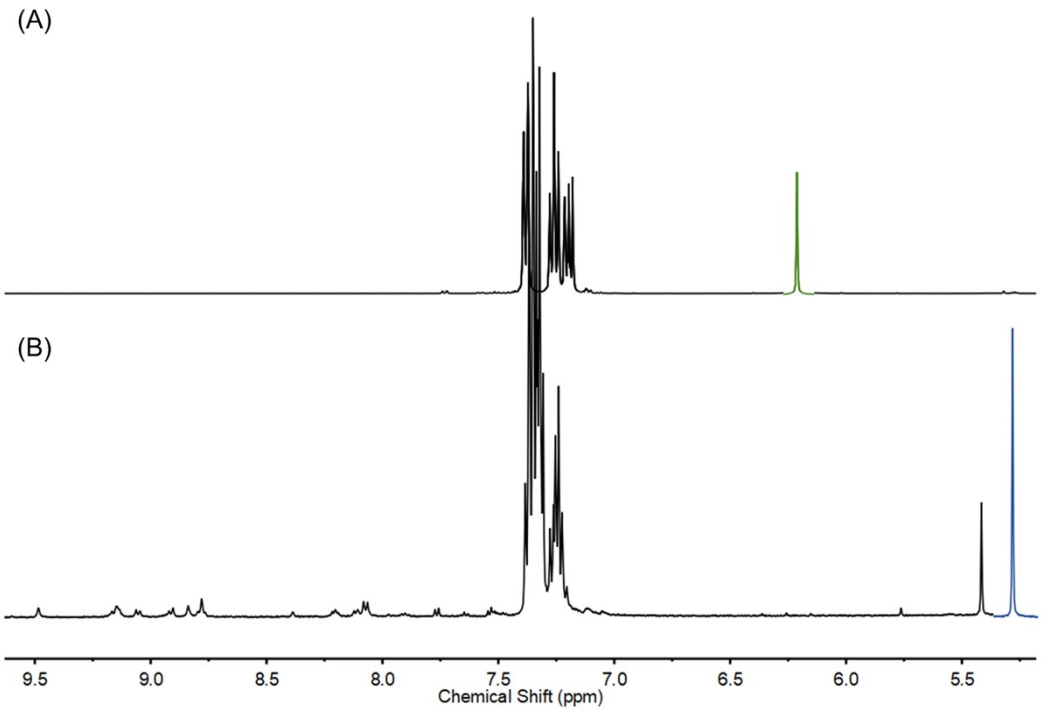
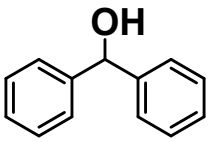


Figure S40. Partial ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of: (A) bromodiphenylmethane **3**; (B) The reaction mixture of 9 μmol of **3** in presence of 10 mol% of the library (0.9 μmol) and 0.09 mmol CH_3OH in 0.5 mL of CD_3CN after stirring for 1 h at 40 °C.

17. Characterizations of the catalytic products



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ(ppm) : 7.35-7.34 (d, J= 4 Hz, 4H), 7.31-7.28 (t, J= 6 Hz, 4H), 7.23-7.20 (t, J= 6 Hz, 2H), 5.80 (s, 1H). ^{1}H NMR spectra is consistent with previous report[5].

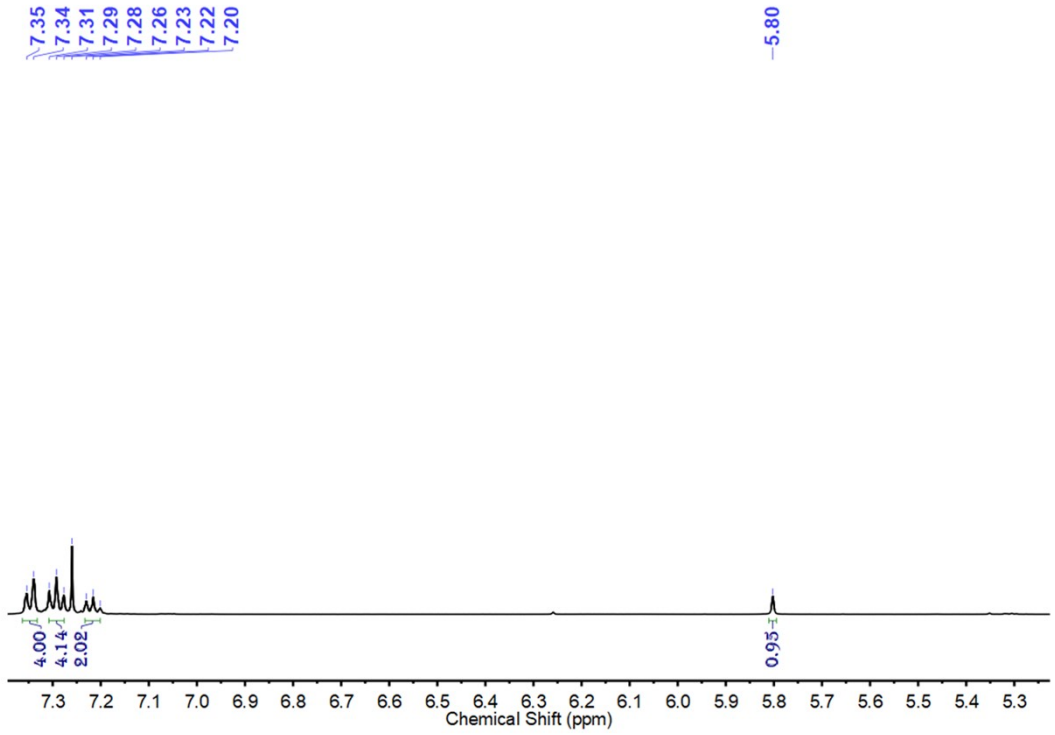
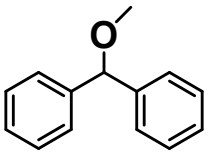


Figure R41. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **5**.



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ(ppm) : 7.30-7.19 (m, 9H), 7.18-7.16 (t, J= 4 Hz,

2H), 5.23 (s, 1H). ^{1}H NMR spectra is consistent with previous report[5].

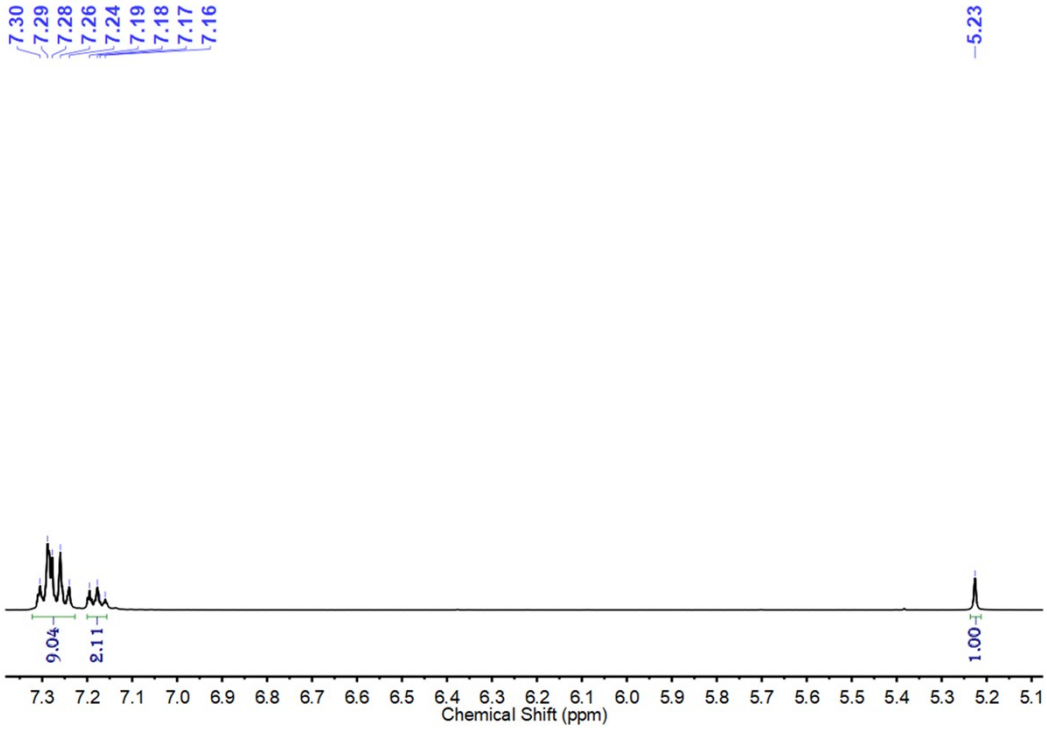
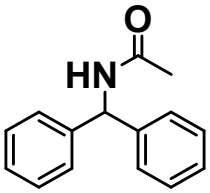


Figure S42. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **6**.



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ (ppm) : 7.27-7.16 (m, 10H), 6.16-6.14 (d, J= 8 Hz, 1H), 2.1 (s, 3H). ^{1}H NMR spectra is consistent with previous report[5].

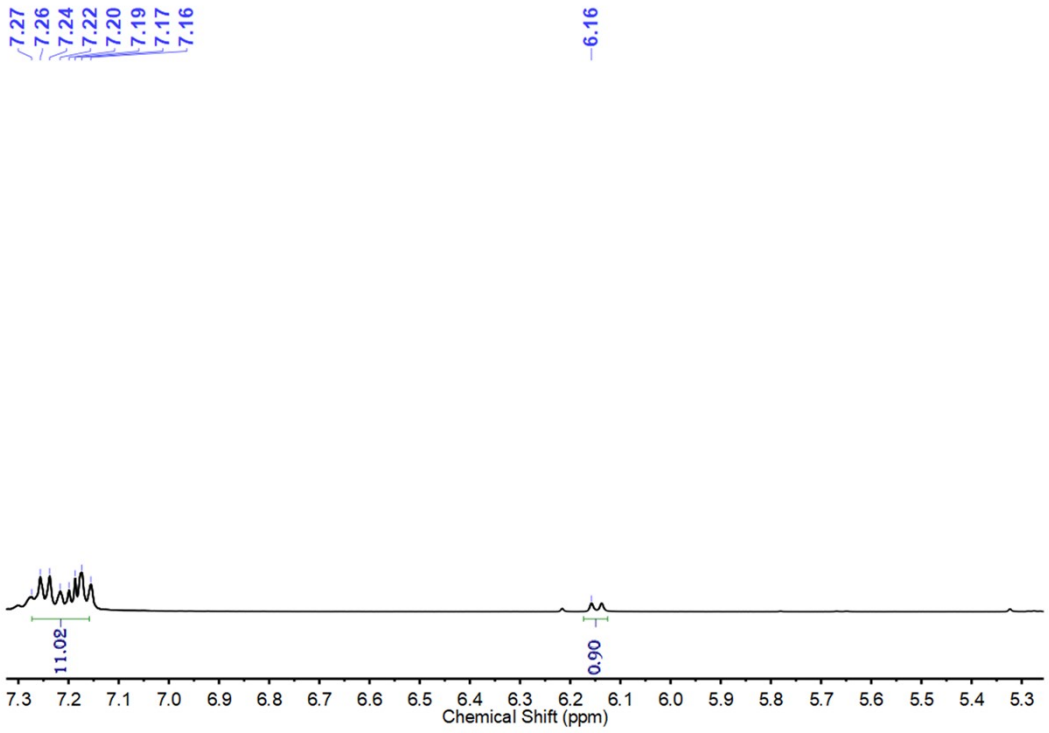
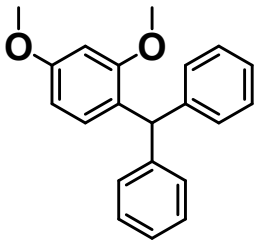


Figure R43. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **7.**



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ(ppm) : 7.23-7.06 (m, 6H), 6.99-6.97 (d, J= 8 Hz, 4H), 6.65-6.63 (d, J= 8 Hz, 1H), 6.37 (s, 1H), 6.30-6.28 (d, J= 8 Hz, 1H), 5.73 (s, 1H), 3.68 (s, 3H), 3.59 (s, 3H). ^{1}H NMR spectra is consistent with previous report[6].

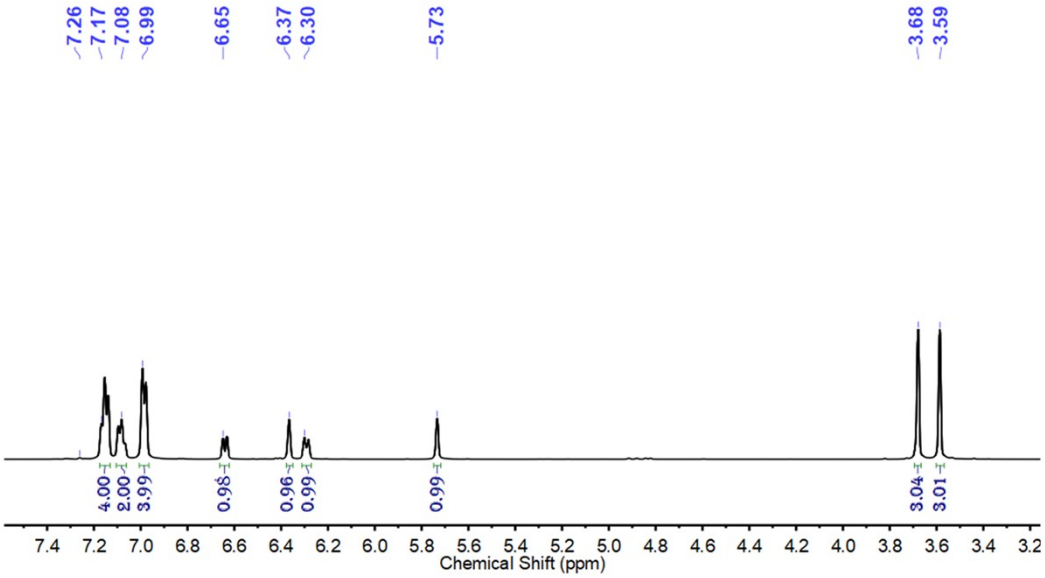
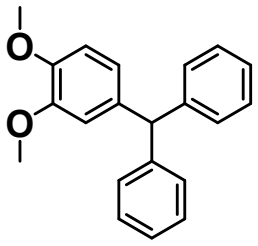


Figure R44. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **9a**.



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ(ppm) : 7.30-7.26 (m, 4H), 7.23-7.21 (m, 2H), 7.13-7.12 (d, J= 4 Hz, 4H), 6.80-7.79 (d, J= 4 Hz, 1H), 6.68 (s, 1H), 6.62-6.61 (d, J=4 Hz, 1H), 5.51 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H). ^{1}H NMR spectra is consistent with previous report[6].

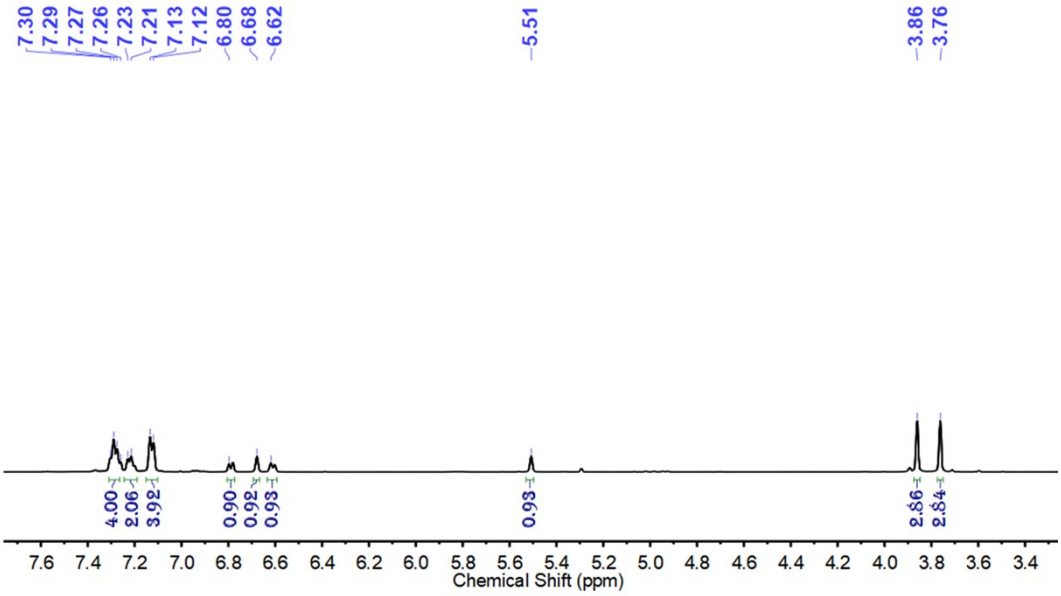
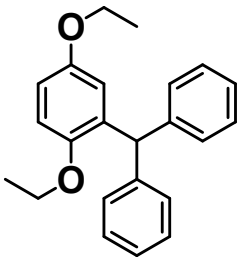


Figure R45. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **9b**.



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ(ppm) : 7.32-7.26 (m, 4H), 7.21-7.19 (m, 2H), 7.14-7.13 (m, 4H), 6.84 (m, 1H), 6.72 (m, 1H), 6.50-6.48 (d, J=8 Hz, 1H), 5.90-5.89 (d, J= 4 Hz, 1H), 3.81 (m, 3H), 3.62 (m, 3H).

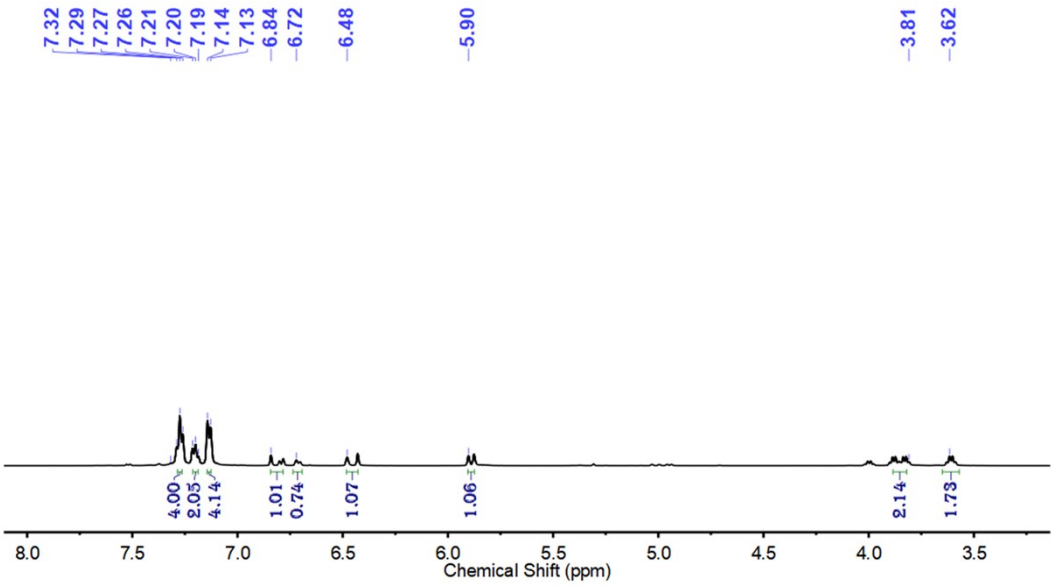


Figure R46. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **9c**.

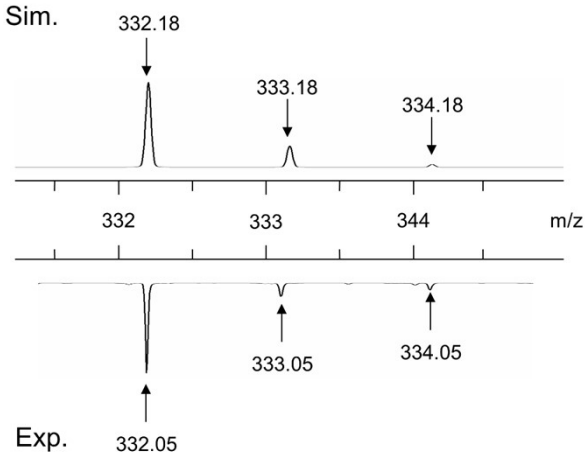
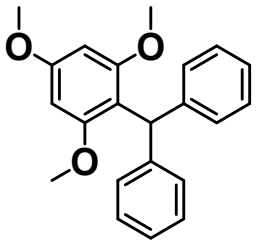


Figure R47. ESI-MS and isotopic pattern of **9c** indicated a charge ion [**9c** + H]$^+$.



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ(ppm) : 7.11-7.08 (m, 10H), 6.05 (s, 2H), 5.97 (s, 1H), 3.68 (s, 3H), 3.47 (s, 6H). ^{1}H NMR spectra is consistent with previous report[6].

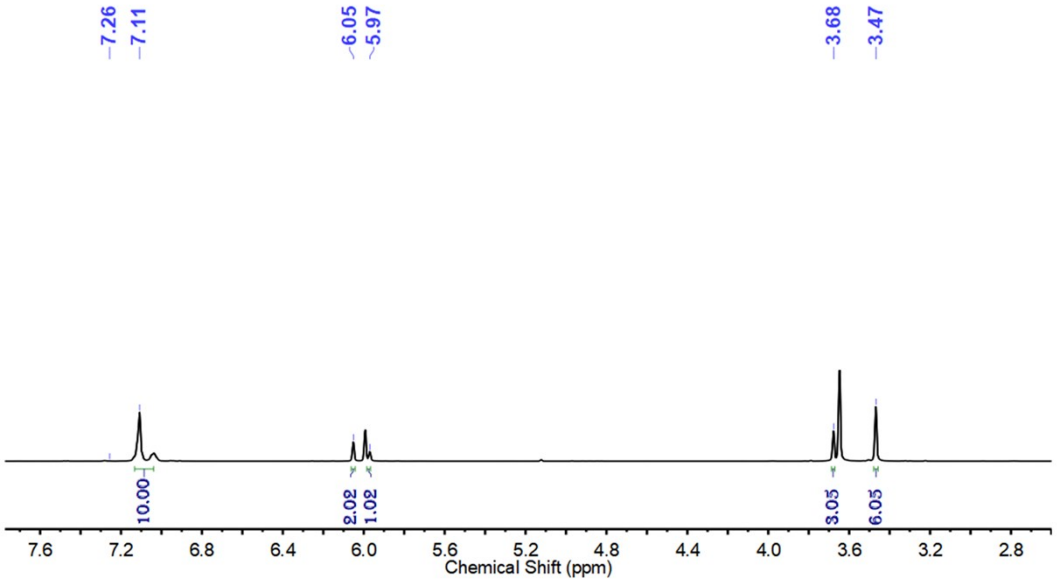
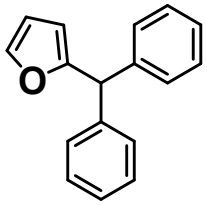


Figure R48. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **9d**.



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ(ppm) : 7.38 (s, 1H), 7.30-7.23 (m, 6H), 7.16-7.14 (d, J = 8 Hz, 4H), 6.31 (m, 1H), 5.91-5.90 (d, J = 4 Hz, 1H), 5.45 (s, 1H). ^{1}H NMR spectra is consistent with previous report[7].

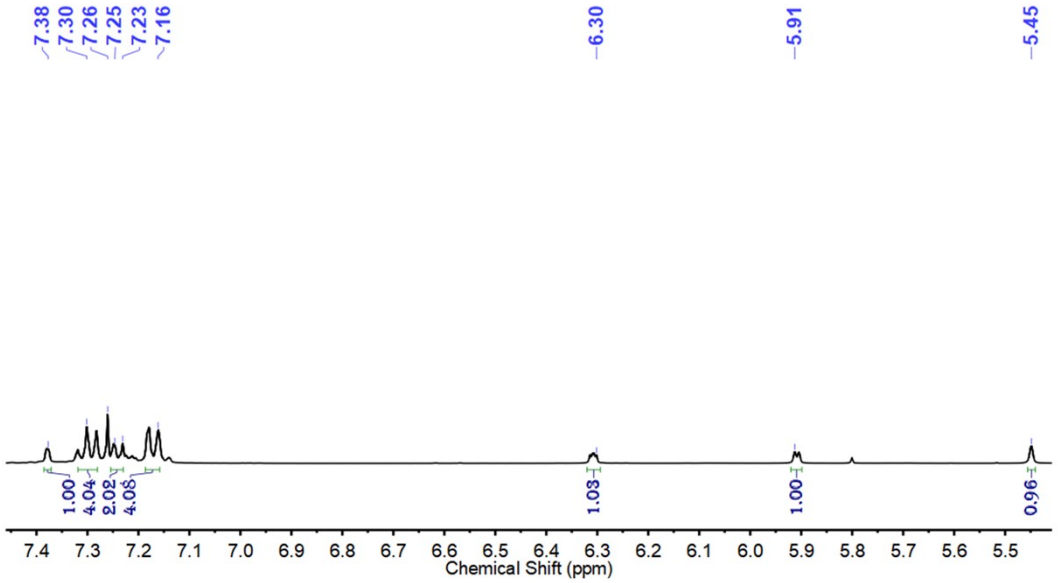
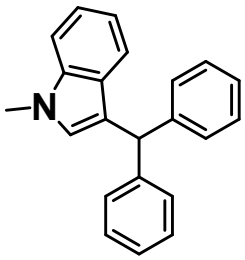


Figure R49. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **9f**.



^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ(ppm) : 7.29–7.22 (m, 13H), 6.99-6.96 (t, J = 6 Hz, 1H), 6.42 (s, 1H), 5.68 (s, 1H), 3.70 (s, 3H). ^{1}H NMR spectra is consistent with previous report[7].

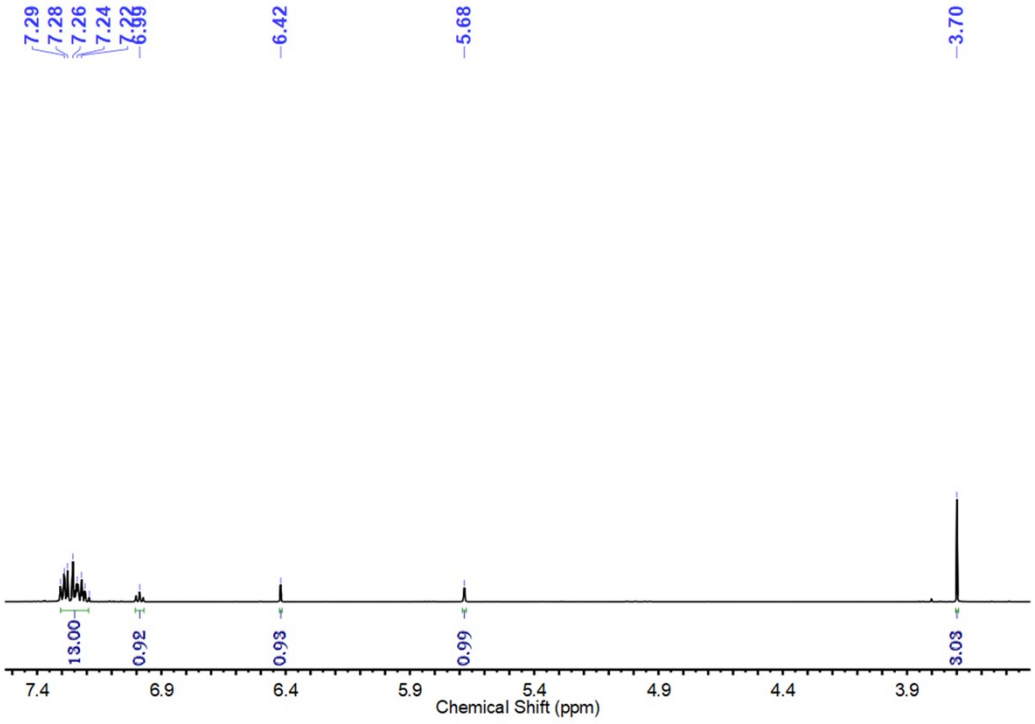


Figure R50. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **9g**.

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