Supporting information for

Mechanochemical Synthesis of Biphenyl-Derived Organic Fluorescent Materials via Solvent-Free and Ligand-Free Oxidative Homocouplings

Zefeng Li[a], Caihang Zhang[a], Yingxuan Zheng[a], Ping Deng[a,*], Yan Yu[a,*]

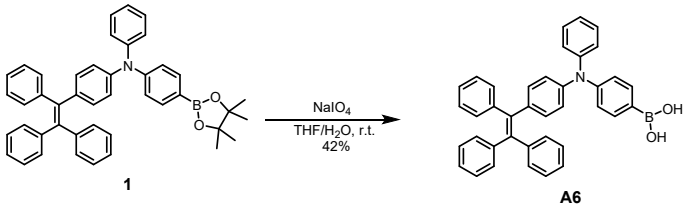
[a] *Key Laboratory of Advanced Materials Technologies, International (HongKong Macao and Taiwan) Joint Laboratory on Advanced Materials Technologies, College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian, 350108, China*

** E-mail: pingdeng@fzu.edu.cn (Ping Deng); yuyan@fzu.edu.cn (Yan Yu)*

1. Experimental supplementary information

1.1 General methods and materials

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Ultrashield 600 Plus NMR spectrometer. Thermogravimetric analysis (TGA) was performed using NETZSCH STA449C analyzer under nitrogen gas flow with a heating rate of 20 °C min^{-1}. Photoluminescence (PL) spectra were taken on Horiba Jobin yvon FluoroMax-4 spectrometer. UV-vis spectra were measured by Perkinelmer LAMBDA 950 UV-vis spectrophotometer. MALDI-TOF mass spectrum (MS) was recorded on an Applied Biosystems-Sciex 5800 MALDI-TOF/TOF mass spectrometer. Gel permeation chromatography (GPC) measurements were carried out on a GPC system equipped with polystyrene gel columns using tetrahydrofuran as an eluent at 40 °C after calibration with polystyrene standards. Cyclic voltammetry (CV) measurements were carried out on a CHI 600 electrochemical analyzer with a three-electrode cell in a deoxygenated anhydrous acetonitrile solution of tetra-n-butylammonium- hexafluorophosphate (0.1 M) under nitrogen atmosphere. A platinum disk electrode, platinum-wire, and $Ag/AgNO_3$ electrode were used as a working electrode, a counter electrode, and a reference electrode, respectively, with the polymer thin film for evaluation coated on the surface of the platinum disk electrode. The CV curves were calibrated using ferrocene/ferrocenium (Fc/Fc^+) redox couple as an external standard, which was measured under the same condition before and after the measurement of samples. $E_{1/2}^{Fc,Fc+} = 0.09$ V. The HOMO and LUMO energy levels were respectively estimated according to the equations: $E_{HOMO} = -e(E_{ox} + 4.71)$ (eV), where E_{ox} is the onset oxidation, and the unit of potential is V versus $Ag/AgNO_3$.



1 A6

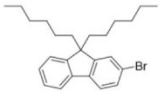
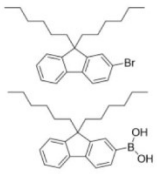
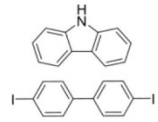
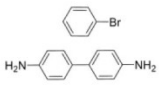
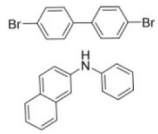
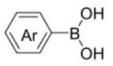
1.2 Synthesis of compound A6

Compound A6: In a 250 mL round-bottom flask, compound **1** (0.68 g, 1.09 mmol), sodium

periodate (0.71 g, 3.27 mmol), tetrahydrofuran (15 mL), and water (4 mL) were added and stirred overnight at room temperature, then 2 M dilute hydrochloric acid (1.8 mL) was added and the reaction was continued for 24 h. The solution was extracted with ethyl acetate and the combined organic layer was washed with brine. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The crude product was dissolved in ethyl acetate followed by precipitation with hexane to give a precipitate. The precipitate was filtered and washed with hot petroleum ether to obtain a green solid **A6** (0.25 g, 42%).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.16-7.01 (m, 26H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.89-6.83 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.5, 147.0, 145.2, 143.9, 143.7, 143.5, 140.9, 140.6, 139.2, 136.6, 134.5, 132.3, 131.4, 129.3, 127.7, 127.6, 127.6, 126.5, 126.4, 125.4, 125.1, 124.2, 123.9, 123.8, 122.8, 121.2. **HPLC-ESI-MS** m/z: $[M + H]^+$ Calcd for $C_{38}H_{30}BO_2$: 544.2442, Found 544.2466.

2 Supporting data

Table S1 Comparison of synthetic methods of biphenyl-based materials

Products	Raw materials	Catalyst	Additive/Base	Solvent	Temperature (°C)	Atomsphere	Time (h)	Yield (%)
B2[1]		$Ni(COD)_2$	COD/BiPy	DMF	75	Inert gas	3	75
B2[2]		$Pd(PPh_3)_4$	K_2CO_3	EtOH	90	Inert gas	48	80
B3[3]		$PdCl_2(Ph_3P)_2$	Ligand/NaH/ ^{t}BuONa	*o*-Xylene	145	Inert gas	24	93
B4[4]		$PdCl_2(Ph_3P)_2$	PPh_3/^{t}BuONa	*o*-Xylene	145	Inert gas	48	93
B5[5]		Cu	18-crown-6 /K_2CO_3	Dichloro-benzene	180	Inert gas	48	67
This work		$Pd(OAc_2)$	$AgNO_3$/K_2CO_3	—	rt	Air	3	35-73

References

[1] N. Fomina, S.E. Bradforth, T.E. Hogen-Esch, *Macromolecules*. 2009, 42, 6440–6447.

[2] Z. Lin, X. Yang, H. Xu, T. Sakurai, W. Matsuda, S. Seki, Y. Zhou, J. Sun, K.Y. Wu, X.Y. Yan, *et al.*, *J. Am. Chem. Soc*. 2017, 139, 18616–18622.

[3] X. Tao, L. Li, Y. Zhou, X. Qian, M. Zhao, L. Cai, X. Xie, *Chinese J. Chem*. 2017, 35, 1749–1754.

[4] L. Cai, X. Qian, W. Song, T. Liu, X. Tao, W. Li, X. Xie, *Tetrahedron.* 2014, 70, 4754–4759.

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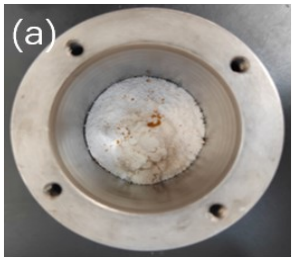
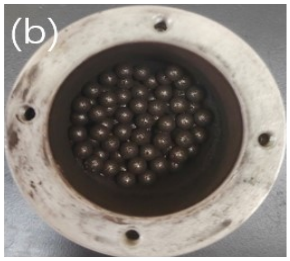




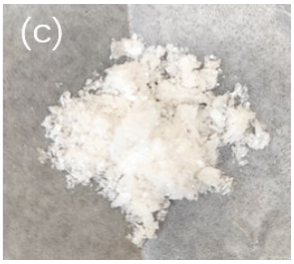


Figure S1 Solid-state homocoupling on a large scale using 56 mL stainless-steel jar with a hundred stainless-steel balls (diameter: 5mm). reaction mixture (a) before ball milling, (b) after ball milling, (c) isolate product.

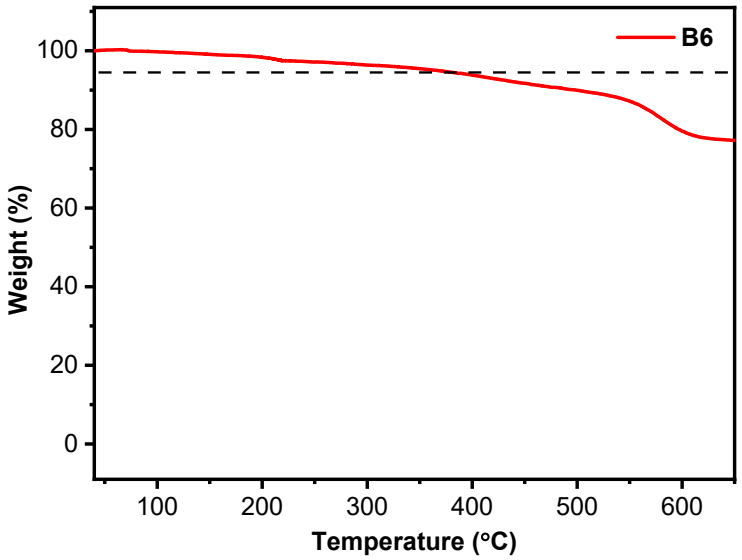


Figure S2 The TGA plot of **B6**.

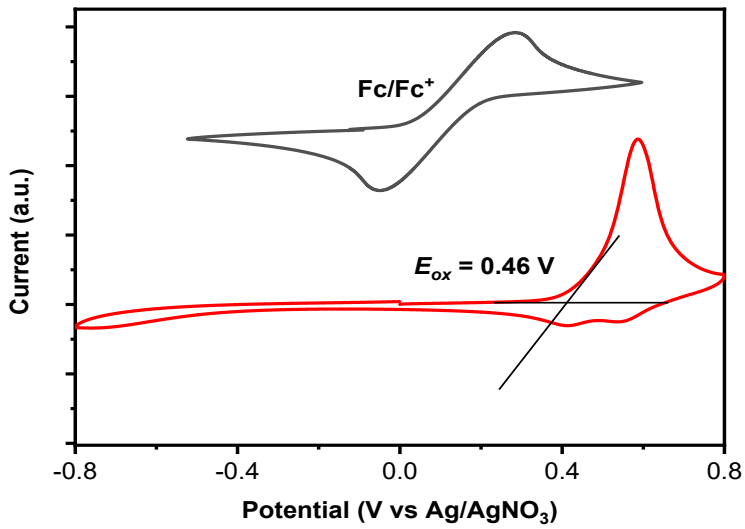


Figure S3 Cyclic voltammogram of the **B6** thin film.

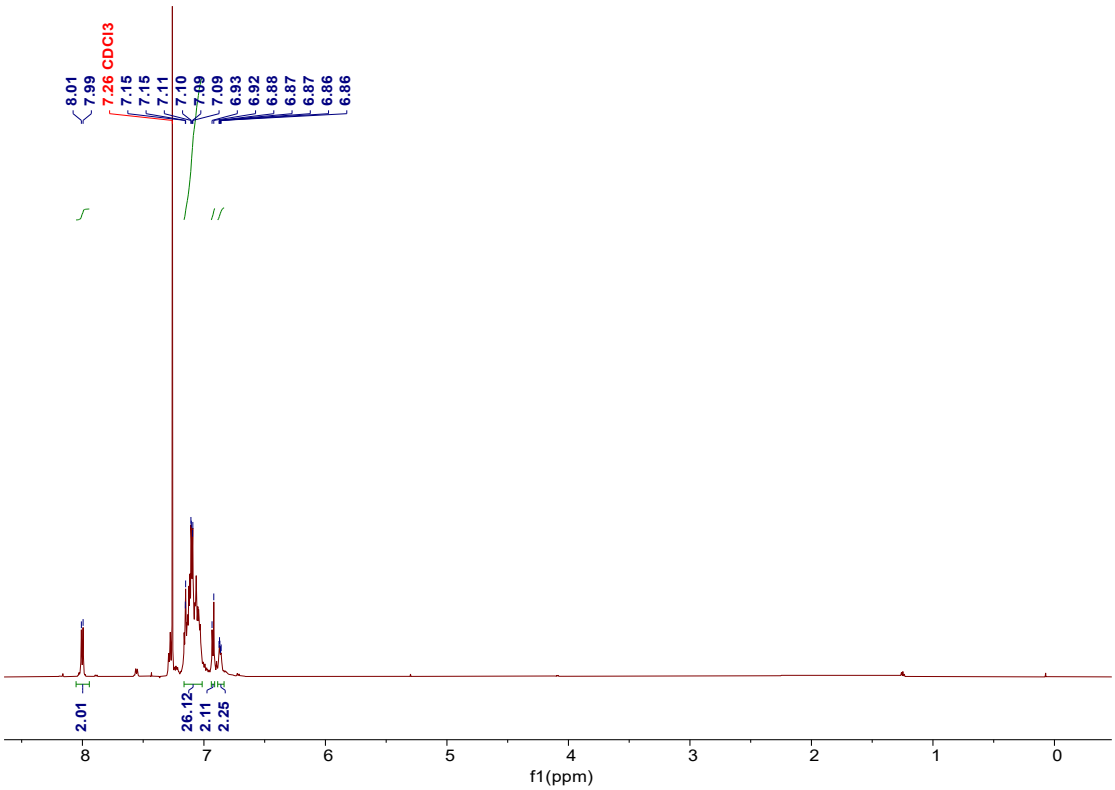


Figure S4 ^{1}H NMR spectrum of **A6** in $CDCl_3$.

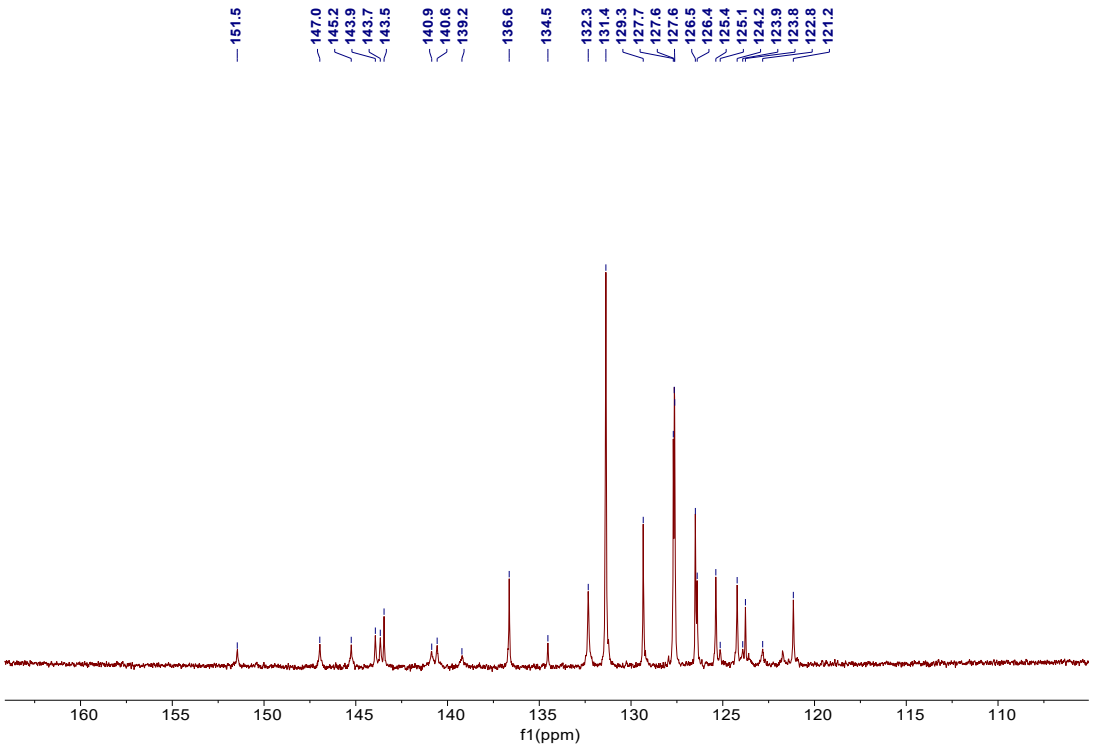


Figure S5 ^{13}C NMR spectrum of **A6** in $CDCl_3$.

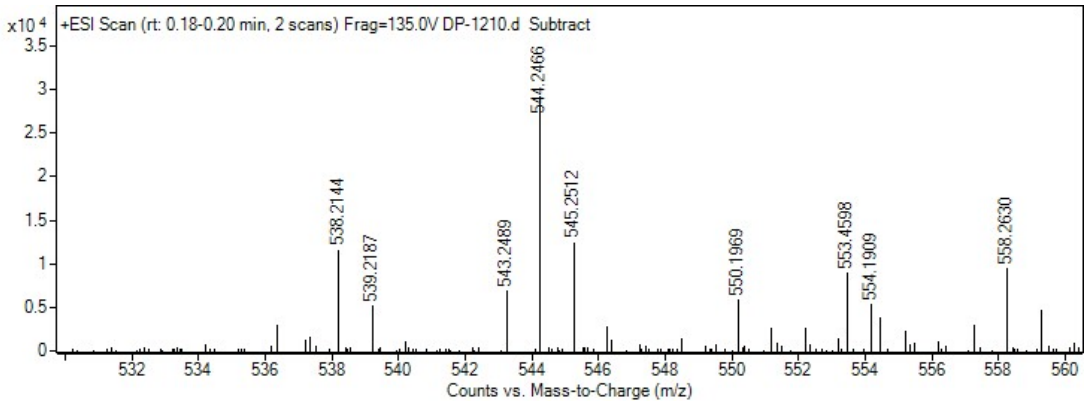


Figure S6 Mass spectrum (HPLC-ESI-MS) of **A6**

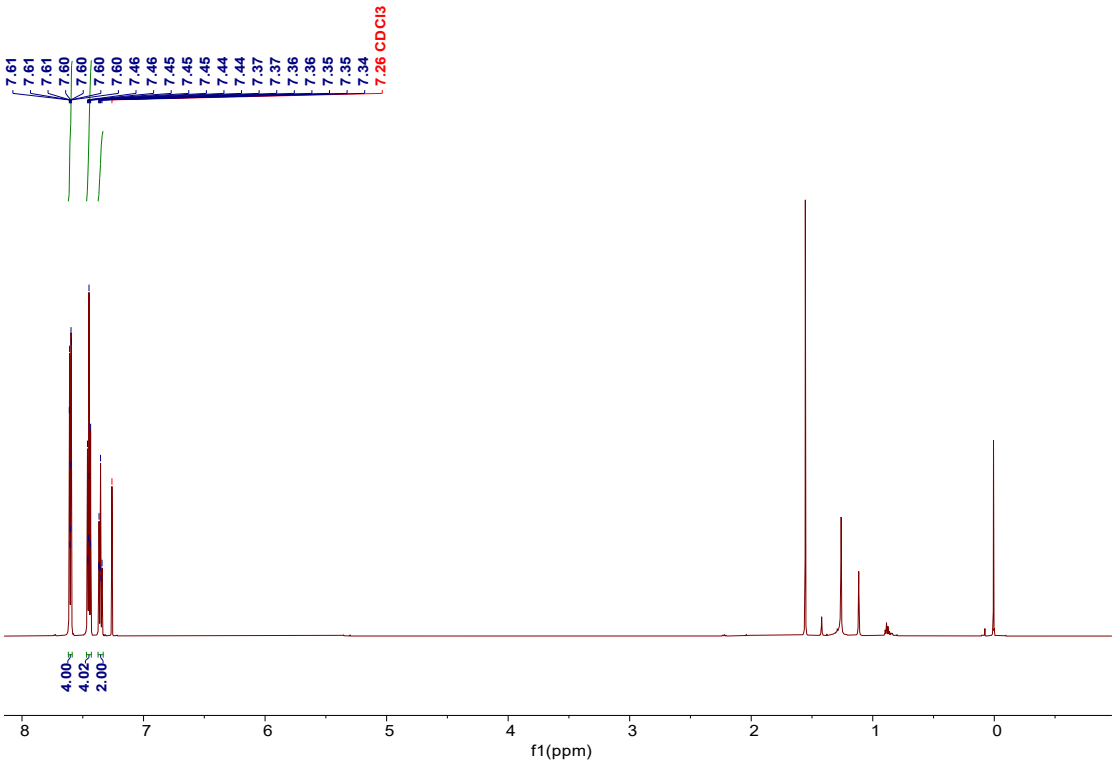


Figure S7 ^{1}H NMR spectrum of **B1** in $CDCl_3$.

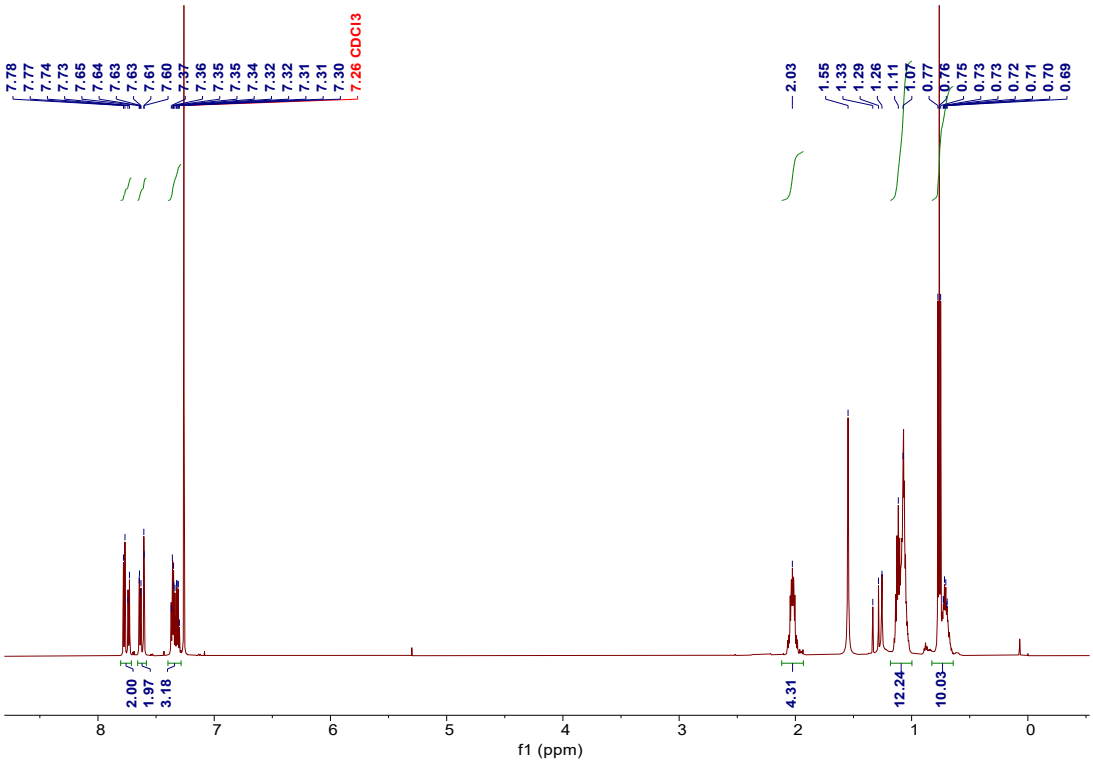


Figure S8 ^{1}H NMR spectrum of the compound **B2** in $CDCl_3$.

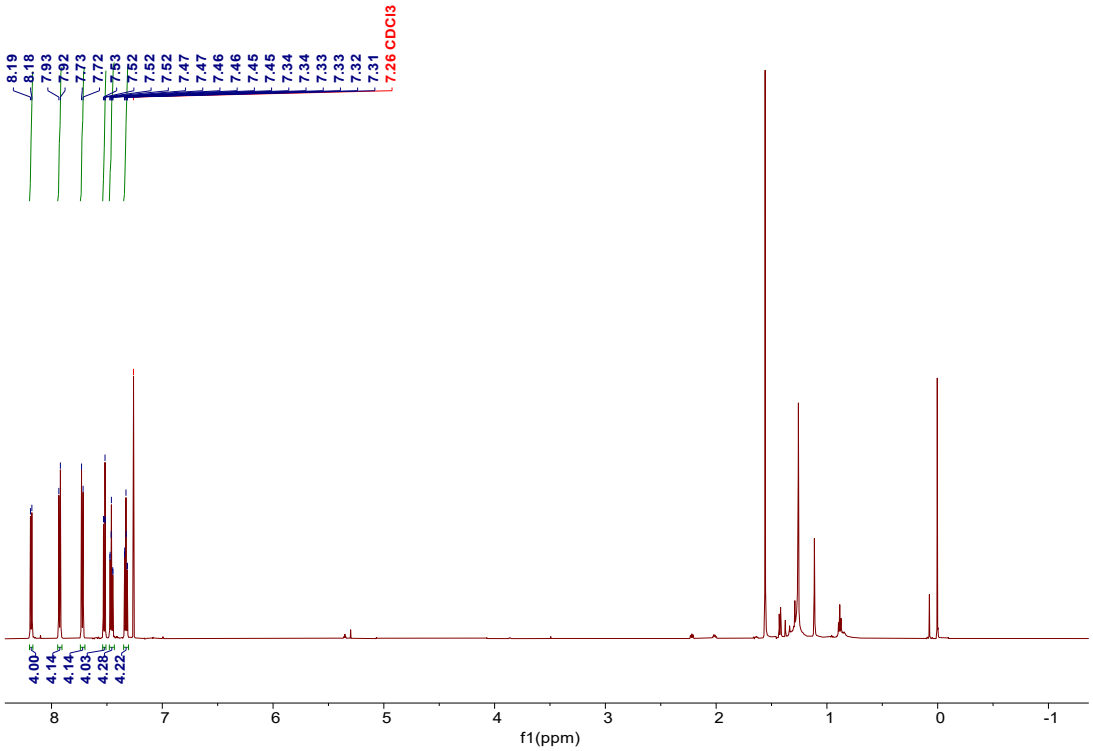


Figure S9 ^{1}H NMR spectrum of the compound **B3** in $CDCl_3$.

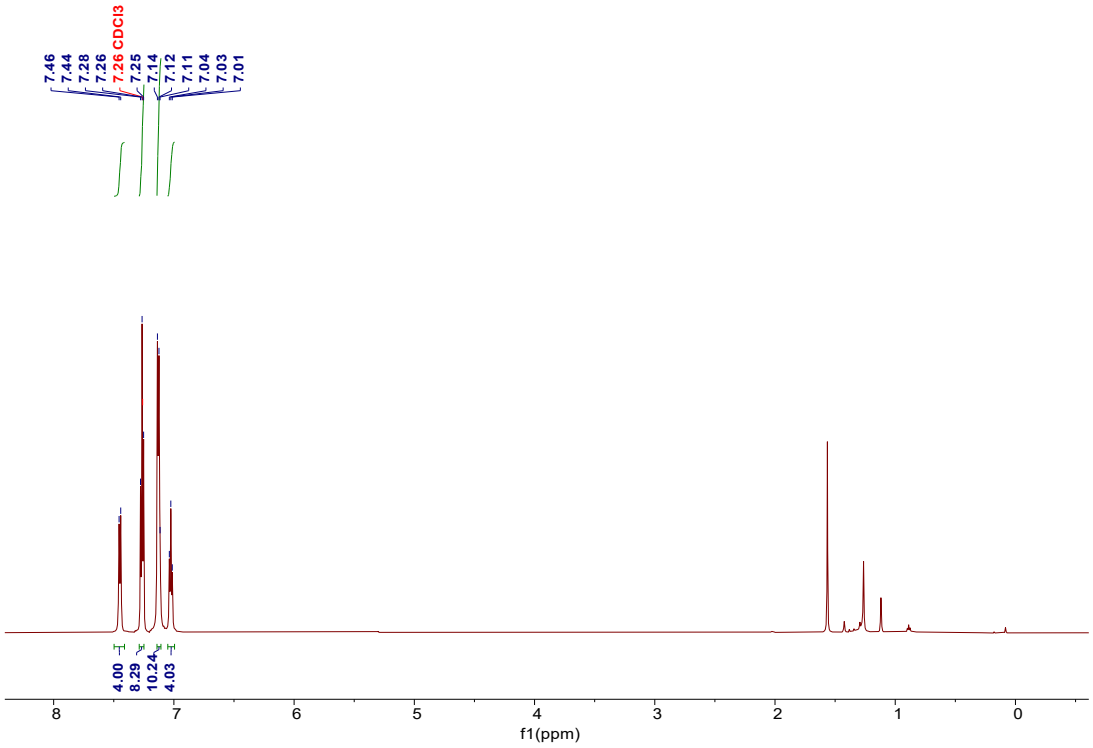


Figure S10 ^{1}H NMR spectrum of the compound **B4** in $CDCl_3$.

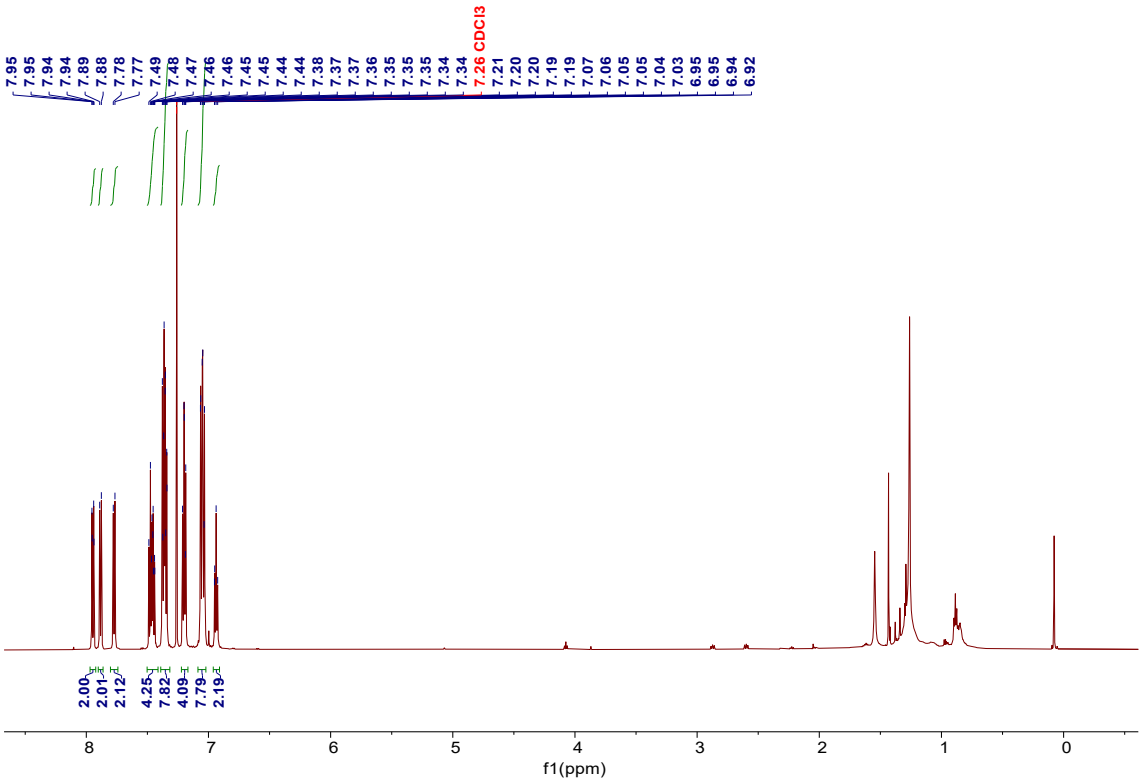


Figure S11 ^{1}H NMR spectrum of the compound **B5** in $CDCl_3$.

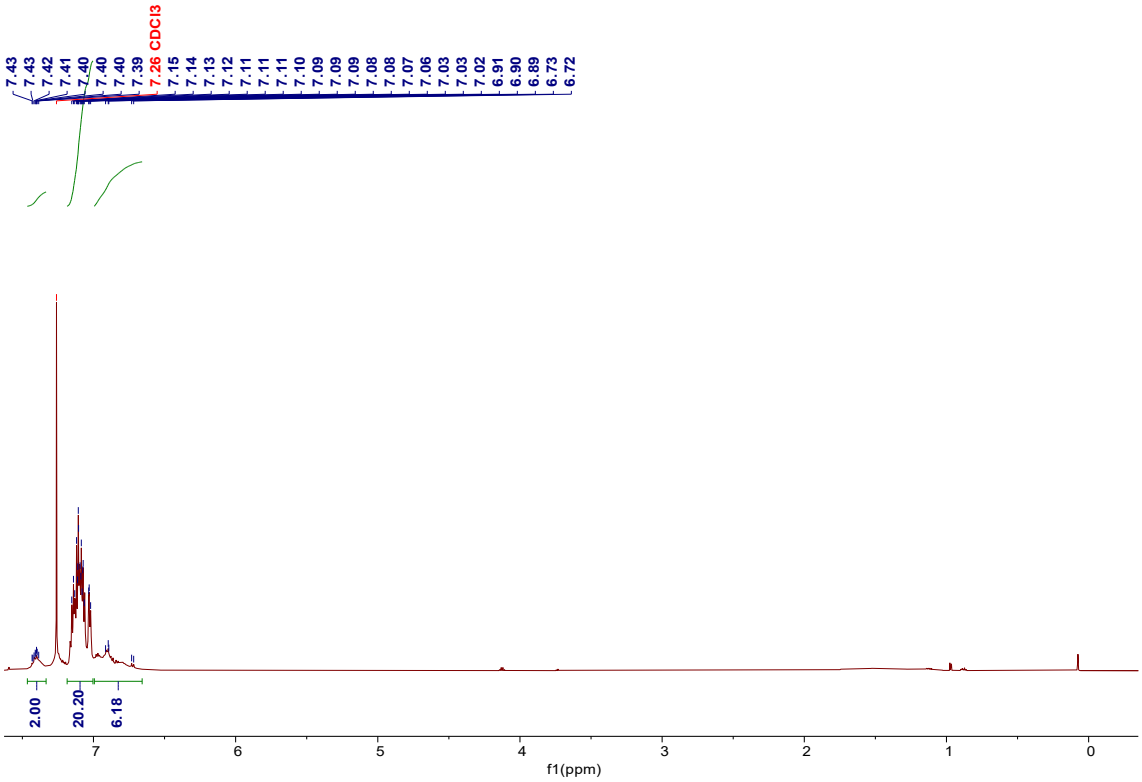
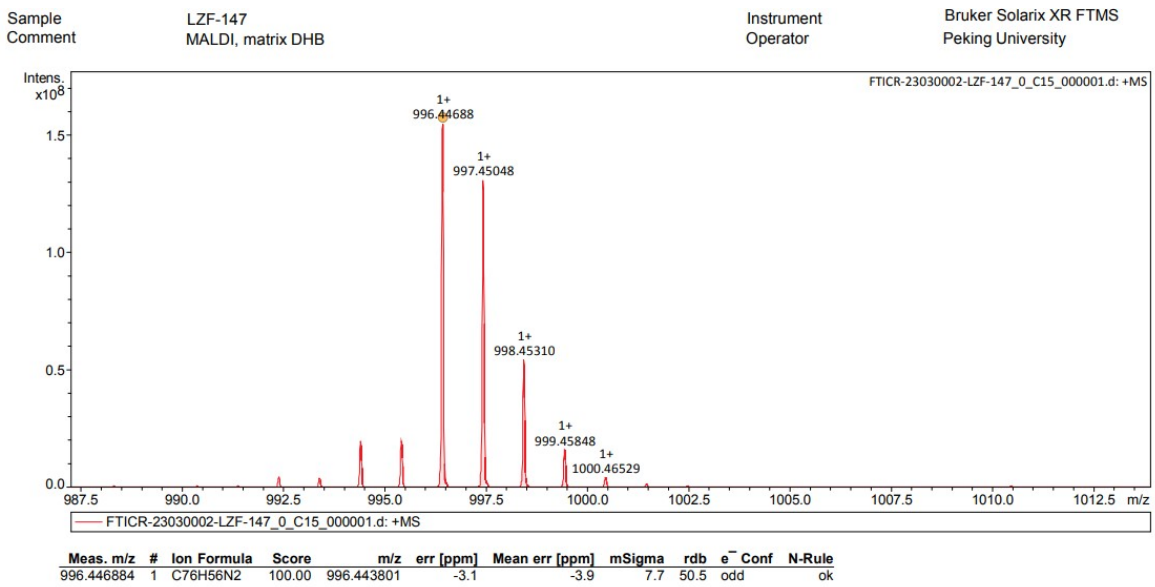


Figure S12 ^{1}H NMR spectrum of the compound **B6** in $CDCl_3$.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
996.446884	1	C76H56N2	100.00	996.443801	-3.1	-3.9	7.7	50.5	odd	ok

Figure S13 HRMS (MALDI FT-ICR) of **B6**.