# Electronic Supplementary Information for

## How Side-Chain Substituents and Substrates Influence Mechanochromic Luminescence: Case Study with Pyrene

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## Materials and Methods

**Materials.** $CH_2Cl_2$ were dried refluxing over $CaH_2$ for at least 6 h prior to use. THF was dried by KOH for overnight first and then refluxing over sodium using benzophenone as an indicator. Water was deionized with a Milli2Q SP reagent water system (Millipore) to a specific resistivity of 18.2 MΩ.cm. All other reagents and solvents were obtained from Aladdin Reagent (Shanghai) and were used as received.

**Methods.** $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AV400 NMR spectrometer operated in the Fourier transform mode. $^1H$ NMR spectra were referenced to the signal for residual protio chloroform at 7.26 ppm and coupling constants are given in hertz. ESI-MS experiments were performed on Thermo Scientific LTQ Orbitrap Mass Spectrometer equipped with an electrospray interface. Melting point was recorded on a SGW2X4 (Shanghai Precision and Scientific Instrument Co., Ltd.) illuminated microscope melting point apparatus. Differential scanning calorimetry (DSC) measurements were conducted at 20 °C/min under nitrogen atmosphere on Mettler-Toledo DSC (Mettler-Toledo Co., Ltd., Zurich, Switzerland). UV-Vis

absorption spectra were recorded on a Beijing Persee TU-1901 UV-vis spectrometer. Photographs were taken by a Cannon 500D digital camera. Micrographs were taken on an Olympus DP72 color camera mounted on a BX51 microscope. Steady-state emission spectra were recorded on a Horiba FluoroMax-4 spectrofluorometer (Japan). Fluorescence lifetime data were acquired with a 1MHz LED laser with the excitation peak at 369 nm (NanoLED-370). Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific). Absolute quantum yields were measured with HORIBA Quanta-ϕ integrating sphere in combination with Horiba FluoroMax-4 spectrofluorometer. Powder X-ray diffraction patterns (PXRD) were collected on a Siemens D-500 diffractometer using Cu-Kα radiation. Single crystal data were acquired with a Gemini S Ultra Single Crystal Diffractometer. Mechanochromic fluorescence spectra in the solid state were recorded on an Ocean Optics USB4000-VIS-NIR Spectrometer equipped with an optical fiber with an integrated LED excitation module ($\lambda_{ex}$ = 365 nm). The spectra were analyzed in SpectraSuite (Ocean Optics, v2008).

## Synthesis

**1P1F**

1,1,2,2-Tetrahydroperfluoro-1-decanol (3.2 g, 6.9 mmol), 1-pyrenebutyric acid (1.0 g, 3.5 mmol), EDC•HCl (1.32 g, 6.9 mmol), and dry THF (60 ml) were added to a round bottom flask equipped with a magnetic stir bar. After cooling to 0 °C in an ice-water bath, DMAP (1.68 g, 13.8 mmol) was added. The reaction was conducted under 25 °C for 12 h, and THF was removed in vacuo, the resulting solid was dissolved in ethyl acetate, washed with aqueous 1 M HCl and brine, dried over $MgSO_4$, and filtered. The crude product was purified by silica gel column chromatography, yielding a white powder (2.0 g, 80 %). $^1$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.32-7.82 (9H, pyrene, -Ar*H*), 4.37 (2H, b, -OC*H*$_2$CH$_2$CF$_2$), 3.40 (2H, e, -ArC*H*$_2$CH$_2$CH$_2$COO), 2.52-2.37 (4H, a+c, -OCH$_2$C*H*$_2$CF$_2$ and -ArCH$_2$CH$_2$C*H*$_2$COO), 2.21 (2H, d, -ArCH$_2$C*H*$_2$CH$_2$COO). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.06, 135.44, 131.42, 130.89, 130.04, 128.76, 127.48, 127.45, 127.35, 126.79, 125.89, 125.11, 124.99, 124.82, 123.22, 56.28, 33.58, 32.68, 30.50, 26.53. M.P.: 89-90 °C. ESI-MS (m/z): $[M+Na]^+$ calcd. for $C_{30}H_{19}F_{17}NaO_2$ 757.101, found 757.103 (Relative Abundance: 100).

**1P1A**

Decan-1-ol (0.88 g, 5.56 mmol), 1-pyrenebutyric acid (0.8 g, 2.78 mmol), EDC•HCl (1.06 g, 5.56 mmol), and dry THF (60 ml) were added to a round bottom flask equipped with a magnetic stir bar. After cooling to 0 °C in an ice-water bath, DMAP (1.35 g, 11.12 mmol) was added. The reaction was conducted under 25 °C for 12 h, and THF was removed in vacuo, the resulting liquid was dissolved in ethyl acetate, washed with aqueous 1 M HCl and brine, dried over $MgSO_4$, and filtered. The crude product was purified by silica gel column chromatography to obtain the pure product as viscous liquid (0.98 g, 82 %). $^1$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.32-7.82 (9H, pyrene, -Ar*H*), 4.07 (2H, d, -OC*H*$_2$CH$_2$), 3.35 (2H, a, -ArC*H*$_2$CH$_2$CH$_2$COO), 2.44 (2H, c, -ArCH$_2$CH$_2$C*H*$_2$COO), 2.18 (2H, b, -ArCH$_2$C*H*$_2$CH$_2$COO), 1.62 (2H, e, -OCH$_2$C*H*$_2$), 1.40-1.15 (14H, f, -OCH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.86 (3H, g, -CH$_2$CH$_2$C*H*$_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.64, 135.80, 131.44, 130.93, 129.99, 128.78, 127.51, 127.40, 127.38, 126.73, 125.86, 125.12, 125.02, 124.93, 124.83, 124.79, 123.37, 64.69, 33.99, 32.84, 31.94, 29.58, 29.36, 29.32, 28.71, 26.88, 26.00, 22.73, 14.18. ESI-MS (m/z): $[M+Na]^+$ calcd. for $C_{30}H_{36}NaO_2$ 451.261, found 451.262 (Relative Abundance: 100).

**3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl (4-nitrophenyl) carbonate**

To a THF solution of 1,1,2,2-tetrahydroperfluoro-1-decanol (5.0 g, 10.77 mmol) was successively added dry pyridine (1 ml) and 4-nitrophenyl carbonochloridate (2.6 g, 12.92 mmol). The mixture was stirred for 12 h at room temperature. The solid was filtered off and the solvent THF was removed in vacuo, the resulting solid was dissolved in ethyl acetate, washed with aqueous $NaHCO_3$ (1.0 M). The organic phase was separated, dried with $MgSO_4$, and filtered off. The crude product was purified by silica gel column chromatography, yielding a white solid (6.0 g, 90 %). $^1$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.30 (2H, d, -Ar*H*), 7.40 (2H, c, -Ar*H*), 4.61 (2H, b, -OC*H*$_2$CH$_2$CF$_2$), 2.63 (2H, a, -OCH$_2$C*H*$_2$CF$_2$).

**decyl (4-nitrophenyl) carbonate**

To a THF solution of decan-1-ol (5.0 g, 31.6 mmol) was successively added dry pyridine (2.94 ml) and 4-nitrophenyl carbonochloridate (7.62 g, 37.92 mmol). The mixture was stirred for 12 h at room temperature. The solid was filtered off and the solvent THF was removed in vacuo, the resulting liquid was dissolved in ethyl acetate, washed with aqueous $NaHCO_3$ (1.0 M). The organic phase was separated, dried with $MgSO_4$, and filtered off. The crude product was purified by silica gel column chromatography, yielding a viscous liquid (9.18 g, 90 %). $^1$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.28 (2H, a, -Ar*H*), 7.39 (2H, b, -Ar*H*), 4.29 (2H, c, -OC*H*$_2$CH$_2$), 1.76 (2H, d, -OCH$_2$C*H*$_2$CH$_2$), 1.30 (14H, e, -OCH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.88 (3H, f, -CH$_2$ CH$_2$C*H*$_3$).

**1P2F**

The THF (30 ml) solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl (4-nitrophenyl) carbonate (2.13 g, 3.38 mmol) was added 1,3-diaminopropan-2-ol (138 mg, 1.53 mmol) and $Et_3N$ (0.9 ml). The mixture was stirred for 18 h at room temperature, and THF was removed in vacuo, the resulting mixture was dissolved in ethyl acetate, and washed with aqueous $Na_2CO_3$ (1.0 M) until the aqueous phase became colorless. The organic phase was separated, dried with $MgSO_4$, and filtered off. Then, the filtrate was evaporated to obtain the crude solid product and used directly in the next step. The crude solid product and 1-pyrenebutyric acid (662 mg, 2.3 mmol), EDC•HCl (883 mg, 4.6 mmol), and dry THF (30 ml) were added to a round bottom flask equipped with a magnetic stir bar. After cooling to 0 °C in an ice-water bath, DMAP (1.16 g, 9.5 mmol) was added. The reaction was conducted under 25 °C for 12 h, and THF was removed in vacuo, the resulting solid was dissolved in ethyl acetate, washed with aqueous 1 M HCl and brine, dried over $MgSO_4$, and filtered. The crude product was purified by silica gel column chromatography, yielding a white powder (1.48 g, 72 %). $^1$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.32-7.82 (9H, pyrene, -Ar*H*), 5.20 (2H, h, -CH$_2$N*H*COO), 4.88 (1H, g, -NHCH$_2$C*H*CH$_2$NH), 4.31 (4H, b, -OC*H*$_2$CH$_2$CF$_2$), 3.45-3.20 (6H, f+c, -NHC*H*$_2$CHC*H*$_2$NH and -ArC*H*$_2$CH$_2$CH$_2$COO), 2.55-2.30 (6H, a+e, -OCH$_2$C*H*$_2$CF$_2$ and -ArCH$_2$CH$_2$C*H*$_2$COO), 2.20 (2H, d, -ArCH$_2$C*H*$_2$CH$_2$COO). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.75, 156.24, 135.40, 131.41, 130.85, 130.05, 128.75, 127.49, 127.44, 127.38, 126.82, 125.92, 125.09, 125.03, 124.95, 124.84, 124.80, 123.19,

71.20, 57.10, 40.74, 33.62, 32.56, 30.73, 26.47. M.P.: 89-90 °C. ESI-MS (m/z): $[M+Na]^+$ calcd. for $C_{45}H_{30}F_{34}N_2NaO_6$ 1363.146, found 1363.150 (Relative Abundance: 100).

**1P2A**

Compound **1P2A** was synthesized according to the same general procedure described for the synthesis **1P2F**. Finally, the obtained pure product **1P2A** was viscous liquid. $^1$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.32-7.82 (9H, pyrene, -Ar*H*), 5.16 (2H, f, -$CH_2$N*H*COO), 4.90 (1H, e, -NHC$H_2$C*H*C$H_2$NH), 3.99 (4H, g, -$CH_2$C*H*$_2$O), 3.45-3.20 (6H, d+a, -NHC*H*$_2$CHC*H*$_2$NH and -ArC*H*$_2$C$H_2$C$H_2$COO), 2.43 (2H, c, -ArC$H_2$C$H_2$C*H*$_2$COO), 2.18 (2H, b, -ArC$H_2$C*H*$_2$C$H_2$COO), 1.53 (4H, h, -OC$H_2$C*H*$_2$C$H_2$ ), 1.32-1.15 (28H, i, -OC$H_2$C$H_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C$H_3$), 0.87 (3H, j, -C$H_2$C$H_2$C*H*$_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.82, 157.24, 135.56, 131.42, 130.89, 130.02, 128.76, 127.48, 127.39, 126.78, 125.88, 125.10, 124.98, 124.83, 123.26, 122.26, 71.62, 65.42, 40.66, 33.75, 32.64, 31.92, 29.57, 29.34, 29.31, 29.00, 26.59, 26.39, 25.83, 22.72, 14.17. ESI-MS (m/z): $[M+Na]^+$ calcd. for $C_{45}H_{64}N_2NaO_6$ 751.466, found 751.465 (Relative Abundance: 100).

**2P1F**

The THF (20 ml) solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl (4-nitrophenyl) carbonate (1.0 g, 1.59 mmol) was added diethanolamine (334 mg, 3.18 mmol) and $Et_3N$ (0.44 ml). The mixture was stirred for 18 h at room temperature, and THF was removed in vacuo, the resulting mixture was dissolved in ethyl acetate, and washed with aqueous $Na_2CO_3$ (1.0 M) until the aqueous phase became colorless. The organic phase was separated, dried with $MgSO_4$, and filtered off. Then, the filtrate was evaporated to obtain the crude product and used directly in the next step. The crude product (0.6 g) and 1-pyrenebutyric acid (0.8 g, 2.8 mmol), EDC•HCl (0.74 g, 3.85 mmol), and dry THF (20 ml) were added to a round bottom flask equipped with a magnetic stir bar. After cooling to 0 °C in an ice-water bath, DMAP (1.02 g, 8.4 mmol) was added. The reaction was conducted under 25 °C for 12 h, and THF was removed in vacuo, the resulting mixture was dissolved in ethyl acetate, washed with aqueous 1 M HCl and brine, dried over $MgSO_4$, and filtered. The crude product was purified by silica gel column chromatography to

obtain the pure product as viscous solid (0.77 g, 68 %). $^{1}$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.32-7.82 (9H, pyrene, -Ar*H*), 4.30 (2H, a, -OC*H*$_2$CH$_2$CF$_2$), 4.23-4.06 (4H, d, -NCH$_2$C*H*$_2$O), 3.54-3.38 (4H, c, -NC*H*$_2$CH$_2$O), 3.33 (4H, g, -ArC*H*$_2$CH$_2$CH$_2$COO), 2.45-2.27 (6H, b+e, -OCH$_2$C*H*$_2$CF$_2$ and -ArCH$_2$CH$_2$C*H*$_2$COO), 2.15 (4H, f, -ArCH$_2$C*H*$_2$CH$_2$COO). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.24, 173.16, 155.36, 135.55, 135.43, 131.42, 130.88, 130.01, 128.73, 127.47, 127.43, 127.30, 126.77, 125.89, 125.09, 124.97, 124.81, 123.25, 123.20, 62.37, 62.06, 57.59, 47.56, 46.83, 33.70, 33.61, 32.69, 30.68, 29.80, 26.63, 26.60. ESI-MS (m/z): $[M+Na]^+$ calcd. for $C_{55}H_{42}F_{17}NNaO_6$ 1158.264, found 1158.261 (Relative Abundance: 100).

**2P1A**

Compound **2P1A** was synthesized according to the same general procedure described for the synthesis **2P1F**. Finally, the obtained pure product **2P1A** was viscous liquid. $^{1}$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.32-7.82 (9H, pyrene, -Ar*H*), 4.25-4.25 (4H, f, -NCH$_2$C*H*$_2$O), 3.98 (2H, a, -OC*H*$_2$CH$_2$CH$_2$), 3.55-3.40 (4H, e, -NC*H*$_2$CH$_2$O), 3.30 (4H, i, -ArC*H*$_2$CH$_2$CH$_2$COO), 2.40 (4H, g, -ArCH$_2$CH$_2$C*H*$_2$COO), 2.13 (4H, h, -ArCH$_2$C*H*$_2$CH$_2$COO), 1.50 (2H, b, -OCH$_2$C*H*$_2$CH$_2$), 1.35-1.05 (14H, c, -OCH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.85 (3H, d, -CH$_2$CH$_2$C*H*$_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.27, 173.22, 156.26, 135.60, 135.47, 131.41, 130.88, 130.00, 128.73, 127.49, 127.43, 127.31, 126.76, 125.88, 125.09, 124.97, 124.82, 123.27, 65.98, 62.56, 62.33, 47.35, 46.80, 33.77, 33.69, 32.72, 31.94, 29.58, 29.55, 29.35, 29.29, 28.94, 26.66, 25.91, 22.74, 14.20. ESI-MS (m/z): $[M+Na]^+$ calcd. for $C_{55}H_{59}NNaO_6$ 852.424, found 852.424 (Relative Abundance: 100).

## Supporting Figures

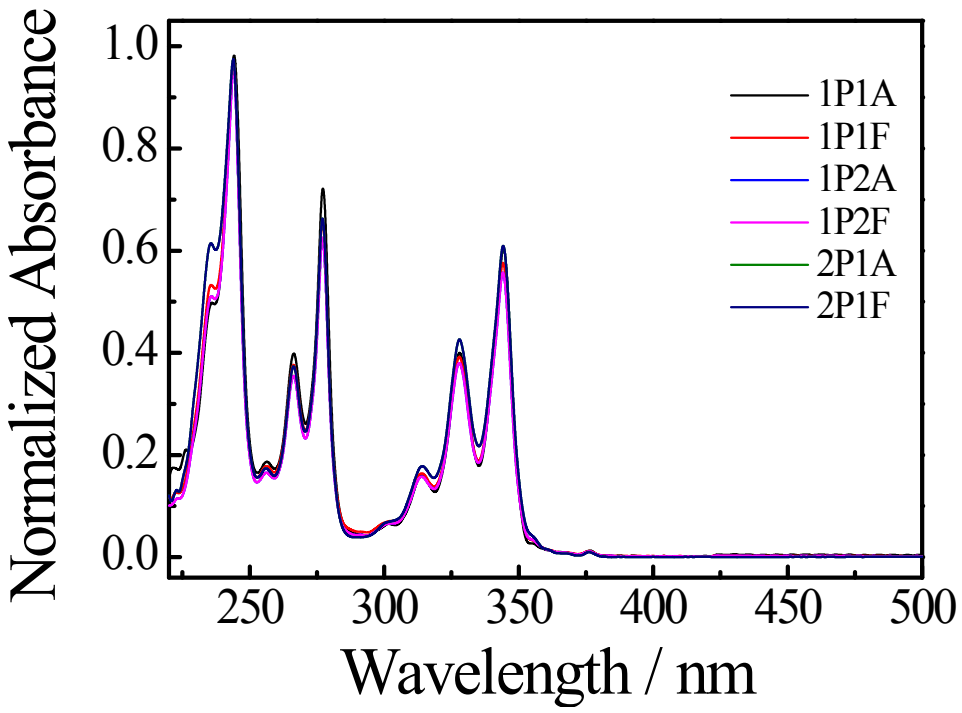



**Fig. S1** Normalized absorption spectra of **1P1A**, **1P1F**, **1P2A**, **1P2F**, **2P1A** and **2P1F** in $CH_2Cl_2$.

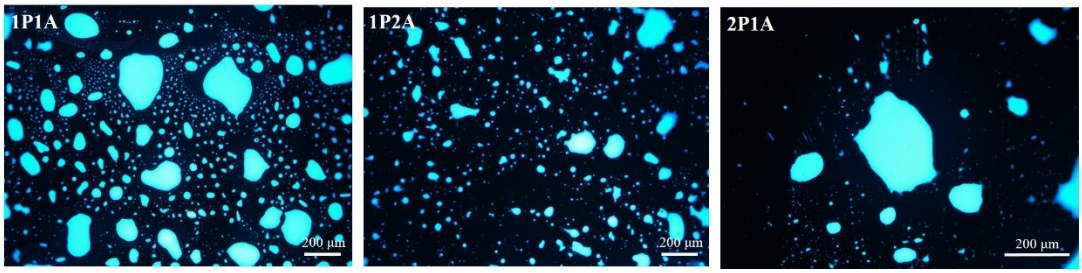
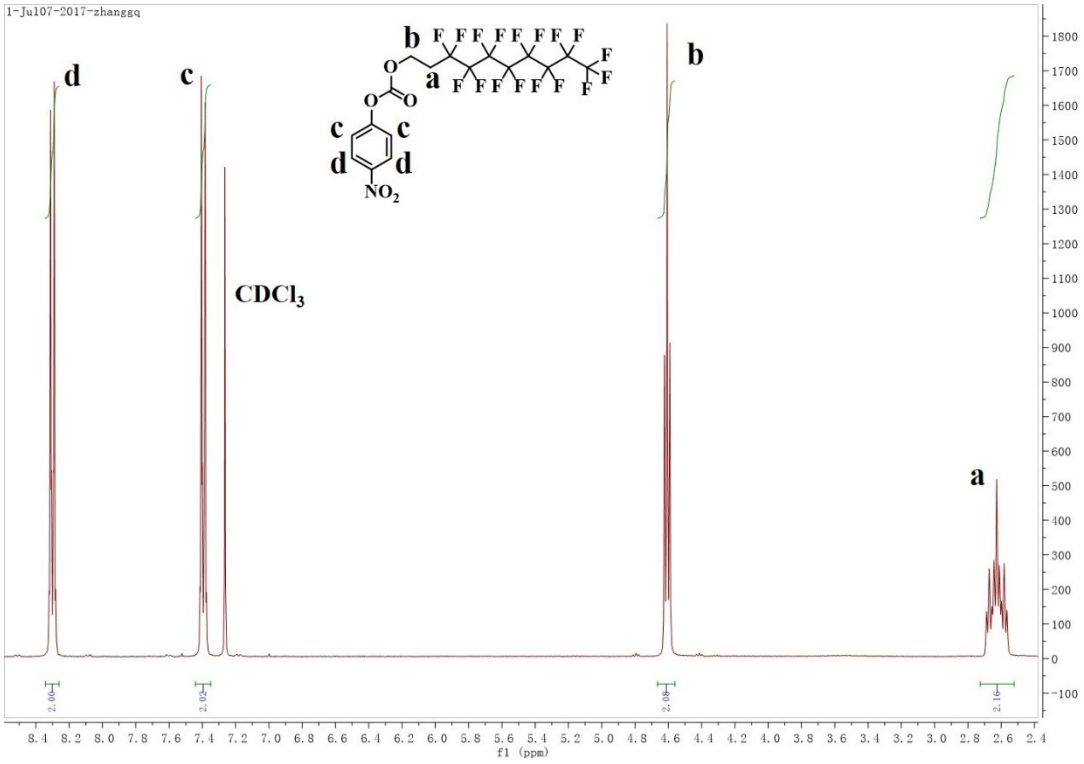
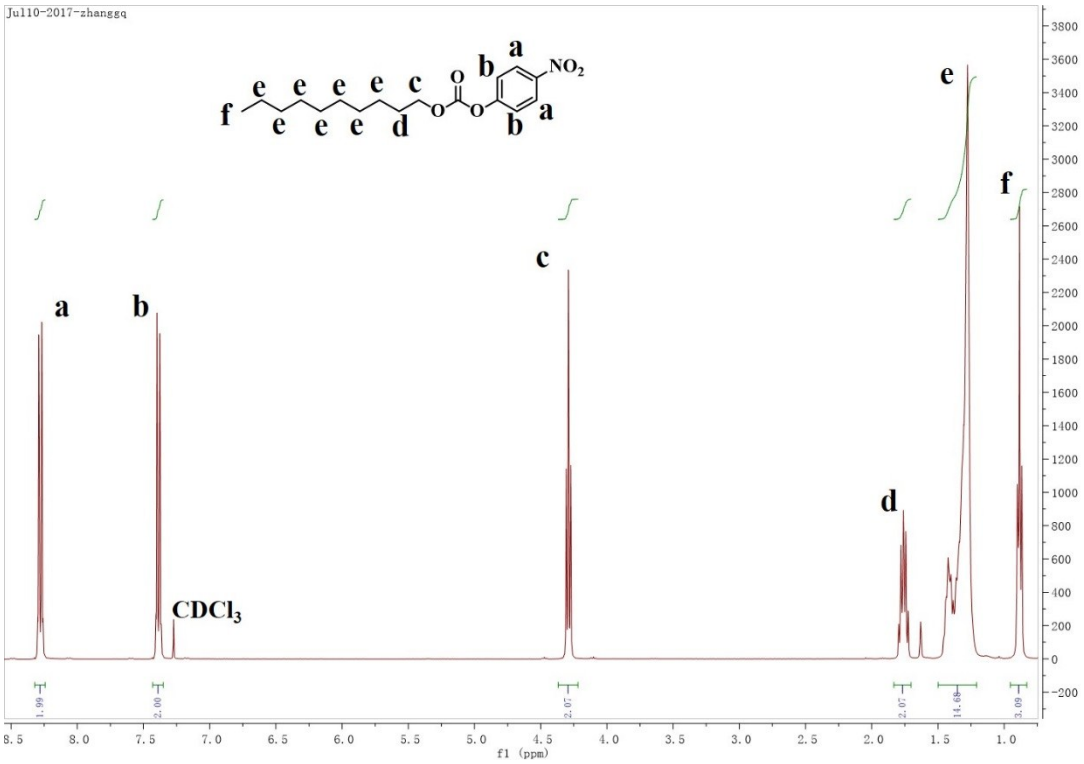



**Fig. S2** Fluorescence microscopy images showing liquid-state morphologies of non-fluorinated pyrene derivatives **1P1A**, **1P2A** and **2P1A**.

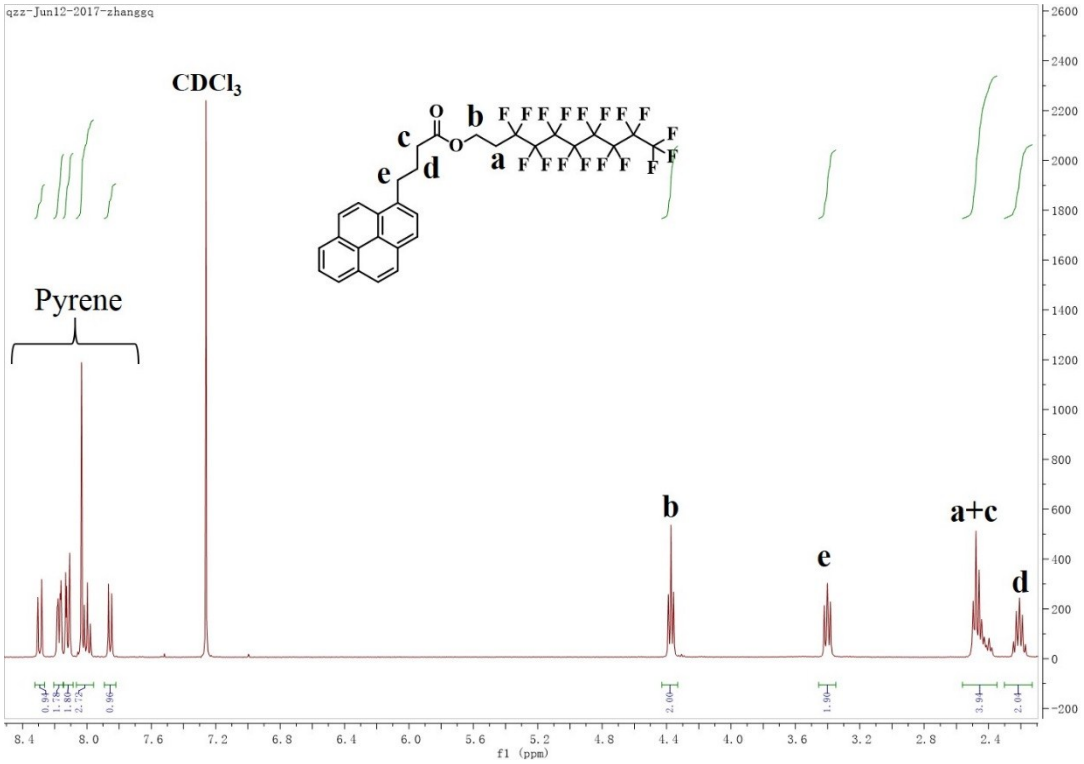
# $^{1}$H NMR, $^{13}$C NMR and ESI-MS Spectra



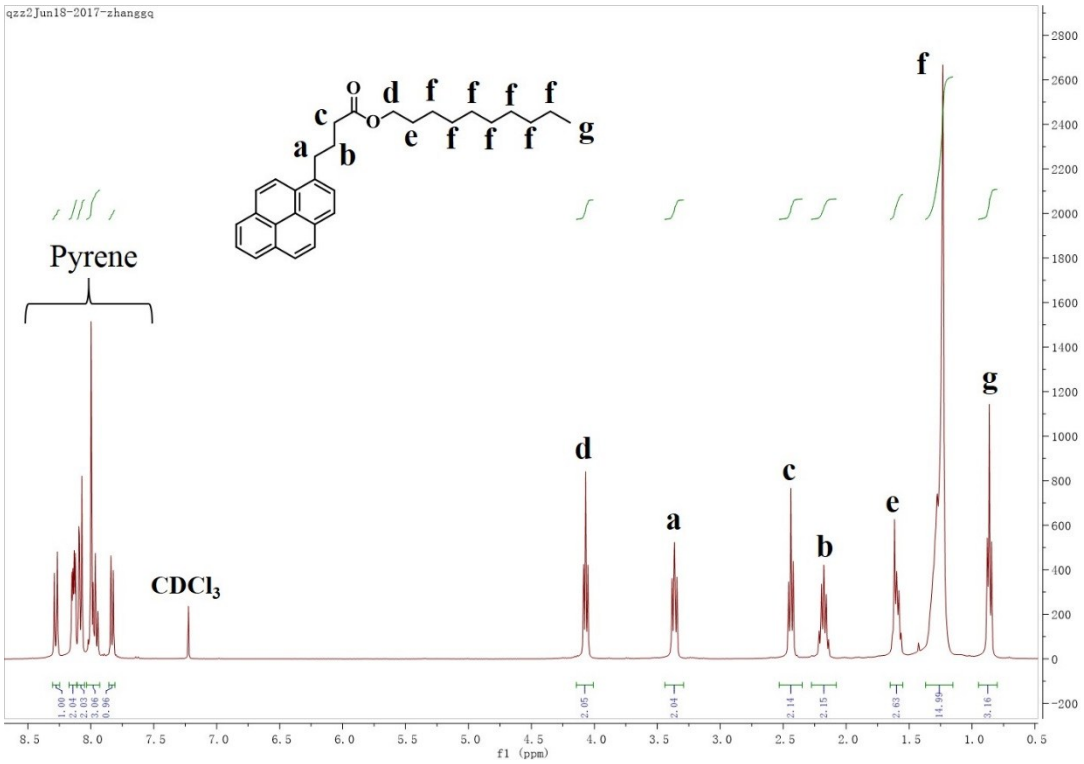

$^{1}$H NMR spectrum of **3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl (4-nitrophenyl) carbonate** in $CDCl_3$.



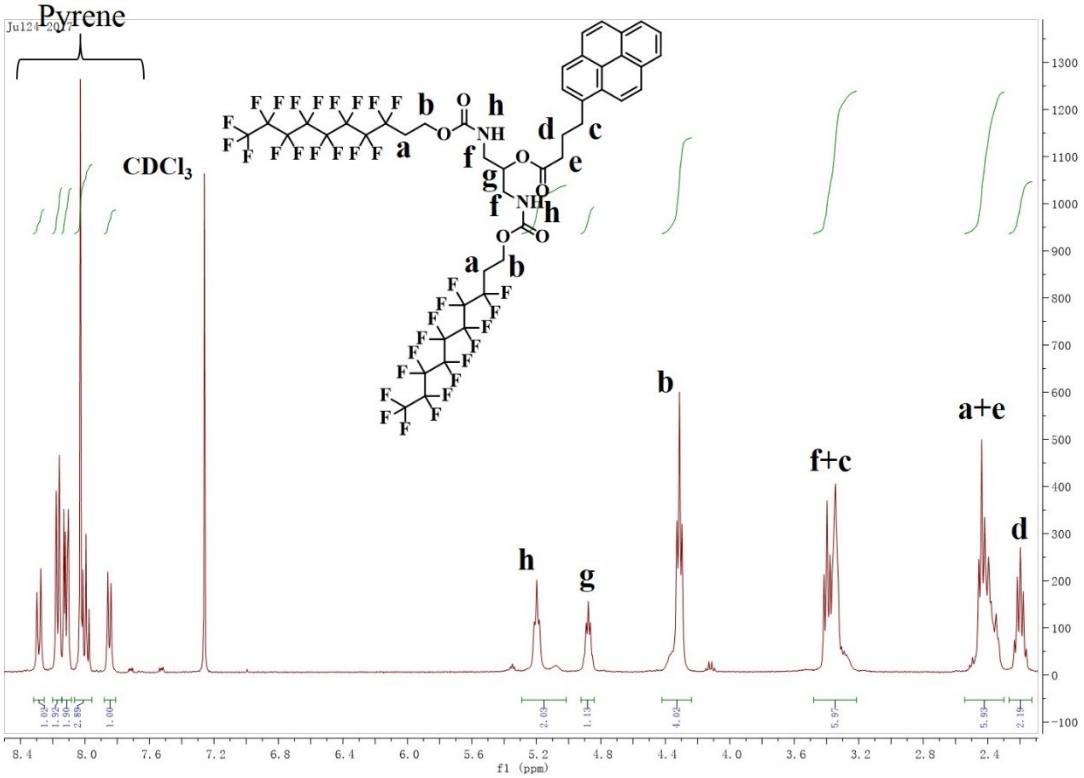

$^1$H NMR spectrum of **decyl (4-nitrophenyl) carbonate** in $CDCl_3$.



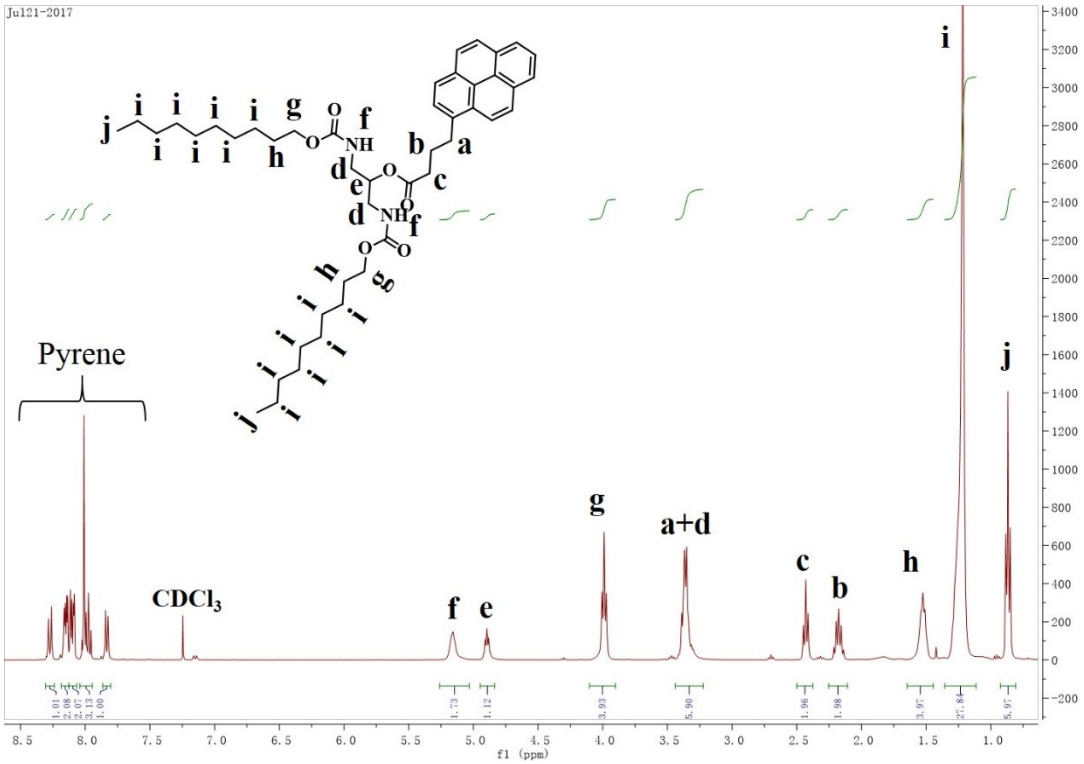

$^1$H NMR spectrum of **1P1F** in $CDCl_3$.



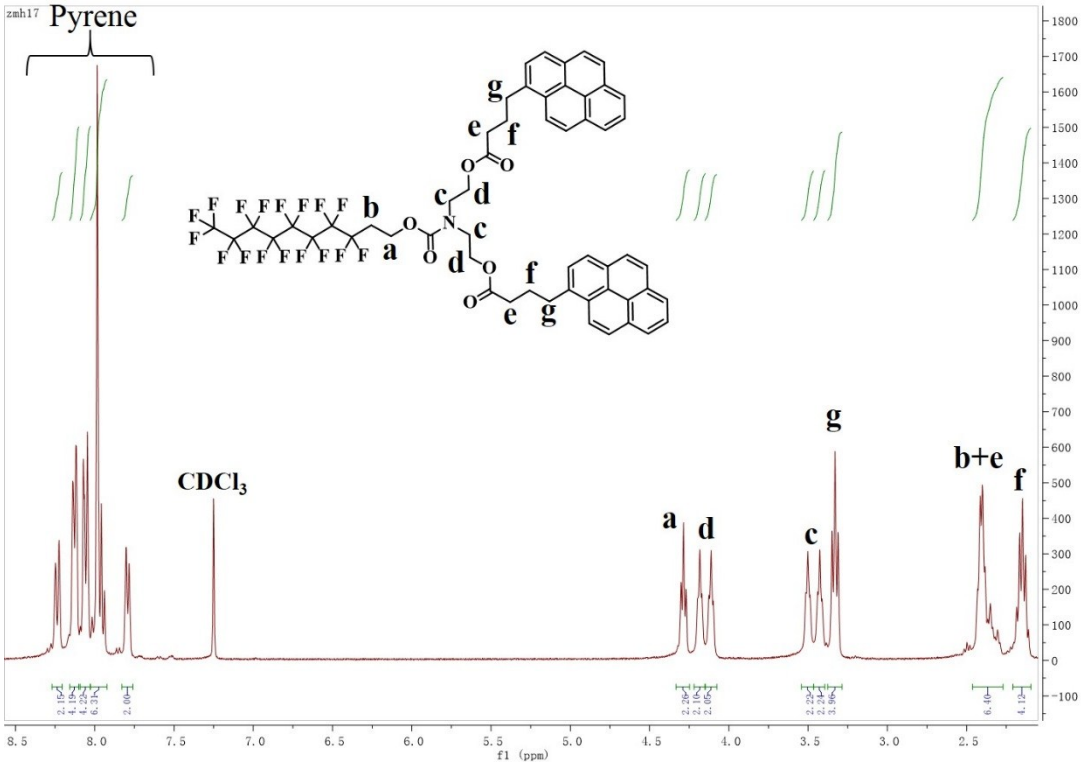

$^1$H NMR spectrum of **1P1A** in $CDCl_3$.



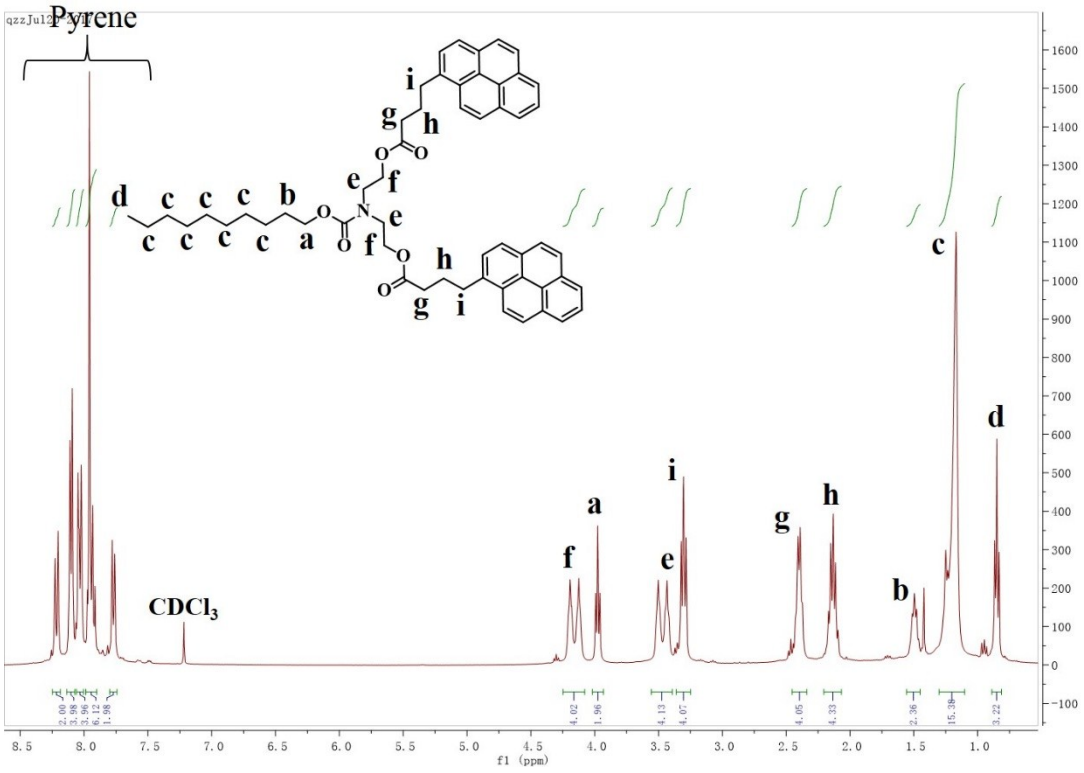

$^1$H NMR spectrum of **1P2F** in $CDCl_3$.



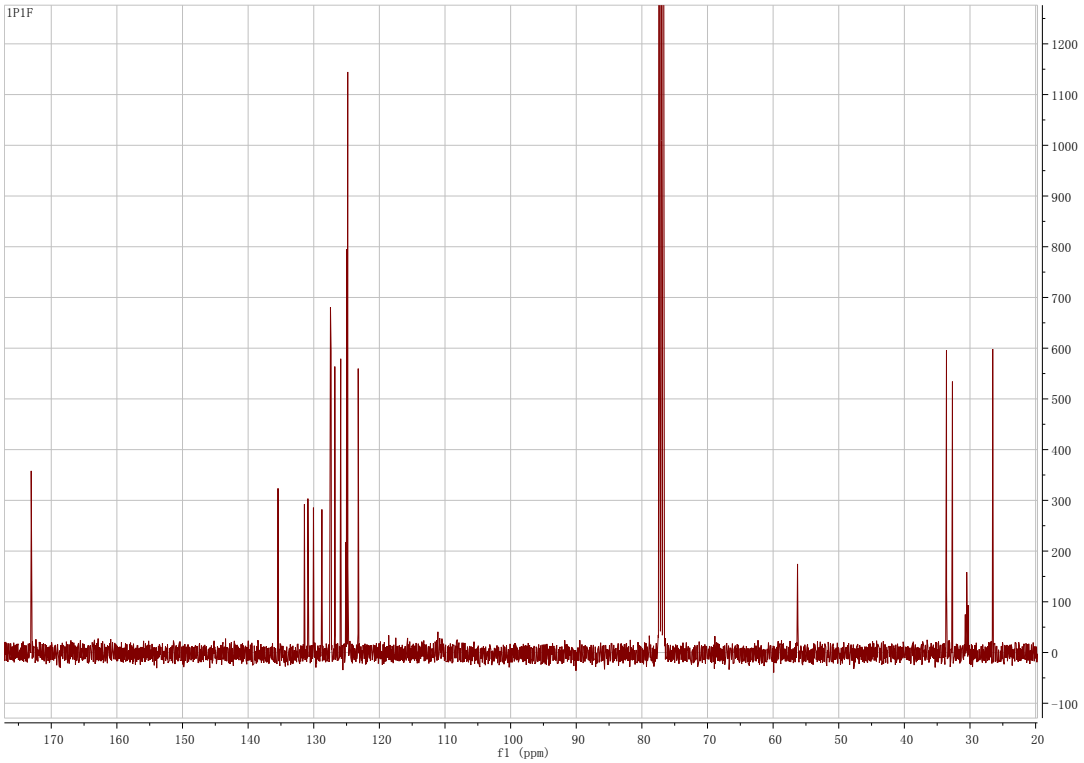

$^1$H NMR spectrum of **1P2A** in $CDCl_3$.



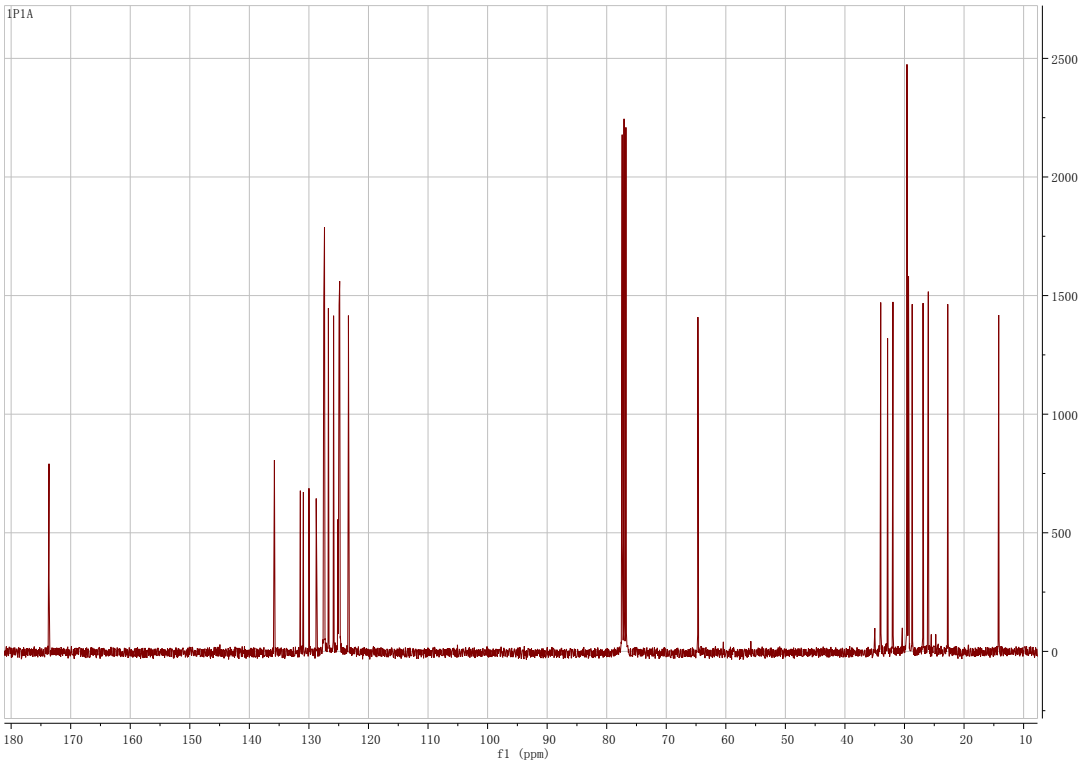

$^1$H NMR spectrum of **2P1F** in $CDCl_3$.



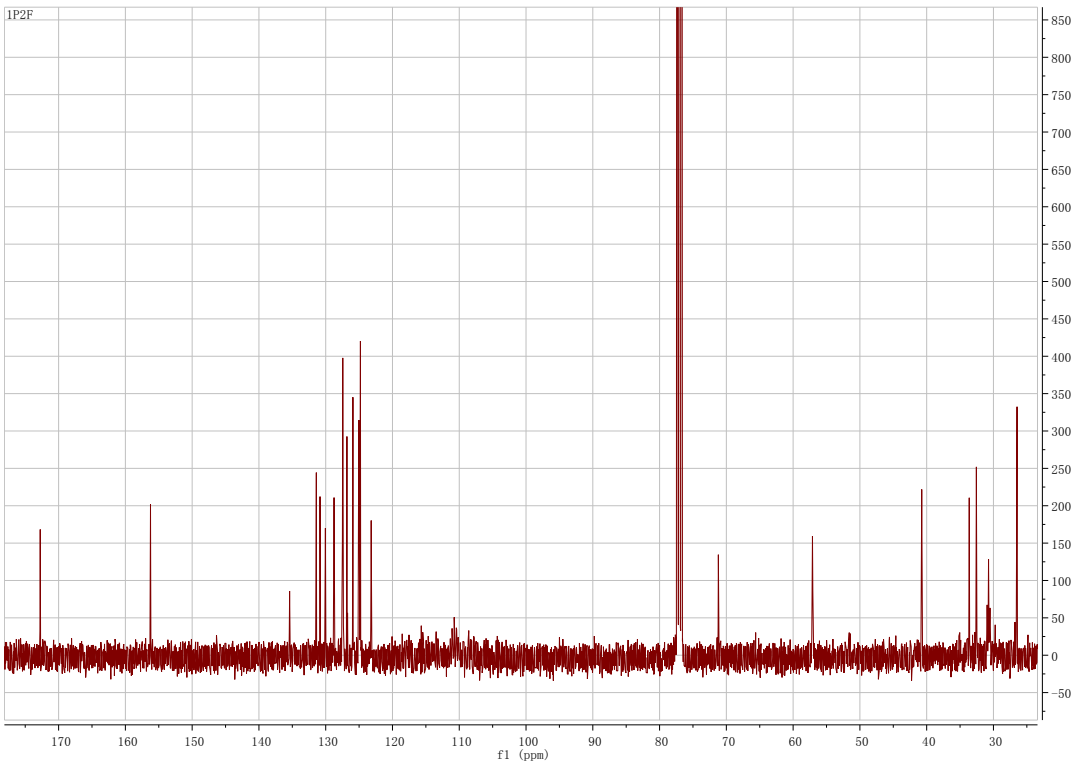

$^{1}$H NMR spectrum of **2P1A** in $CDCl_3$.



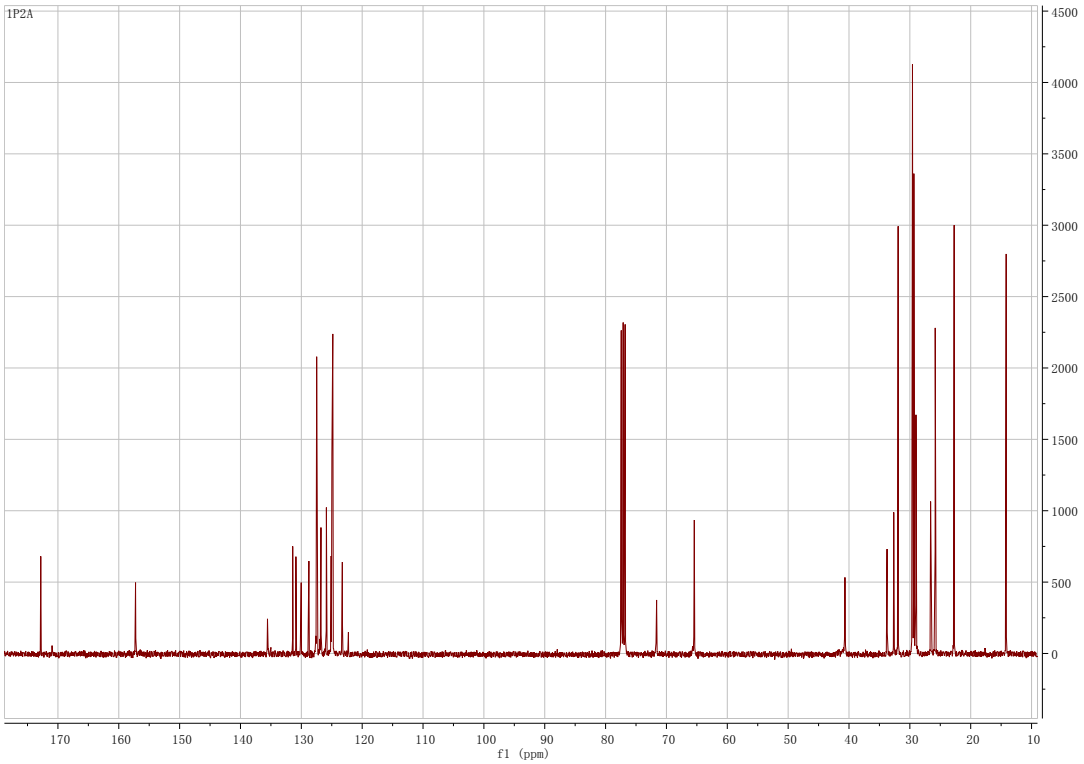

$^{13}$C NMR spectrum of **1P1F** in $CDCl_3$.



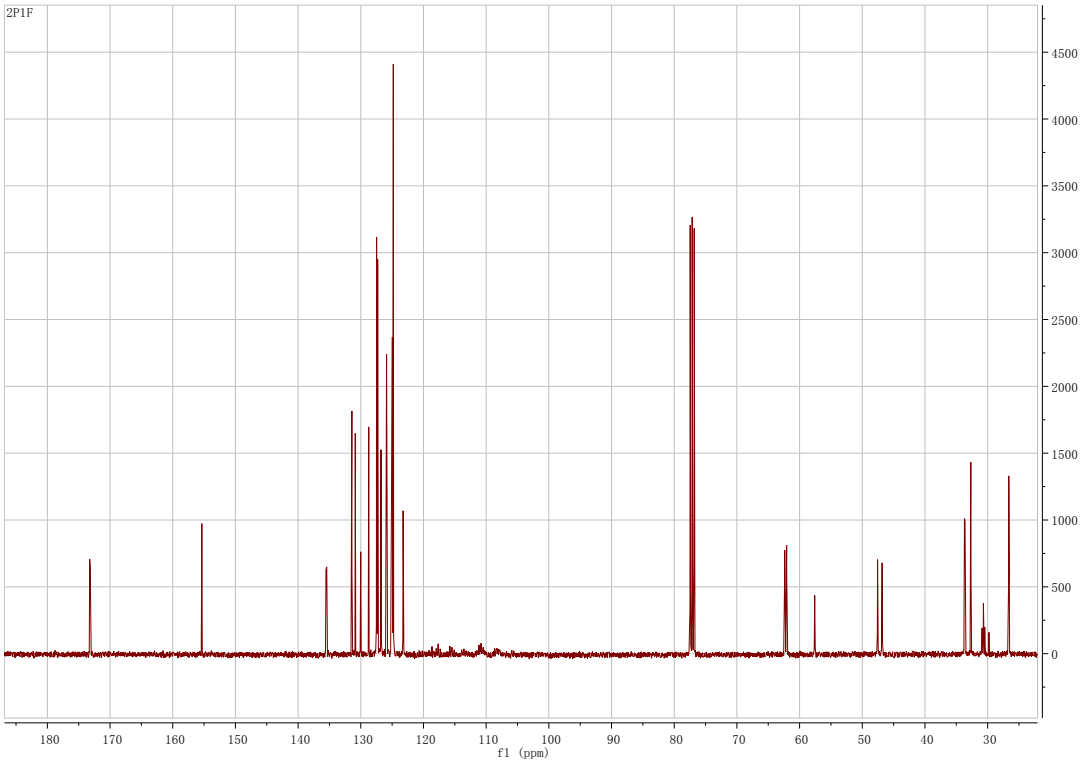

$^{13}C$ NMR spectrum of **1P1A** in $CDCl_3$.



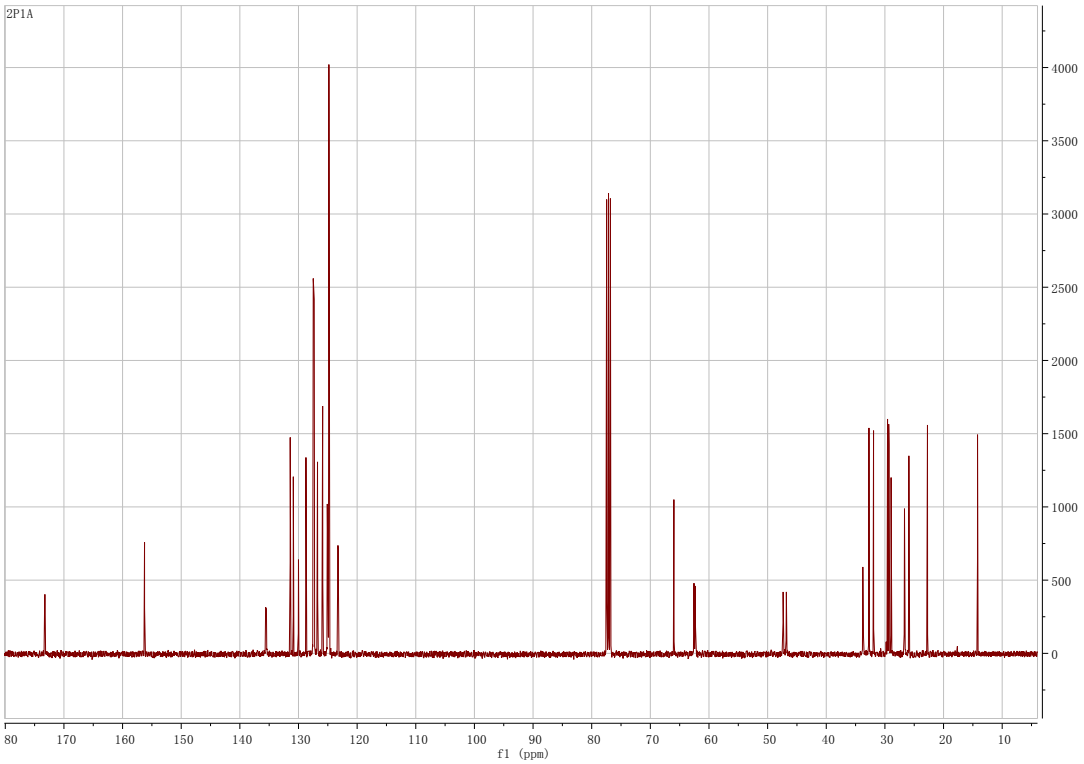

$^{13}C$ NMR spectrum of **1P2F** in $CDCl_3$.



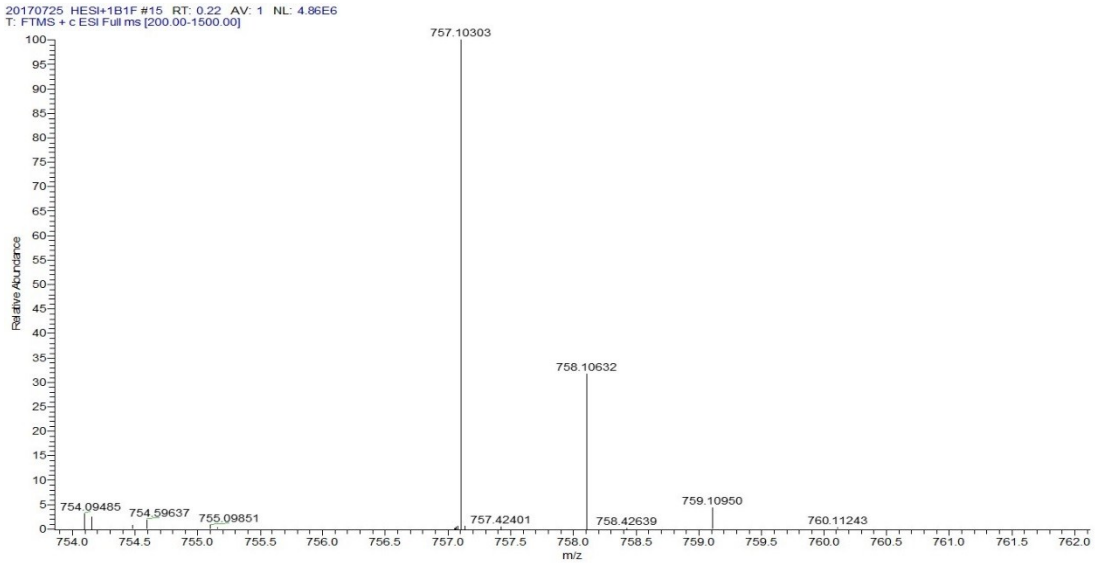

$^{13}C$ NMR spectrum of **1P2A** in $CDCl_3$.



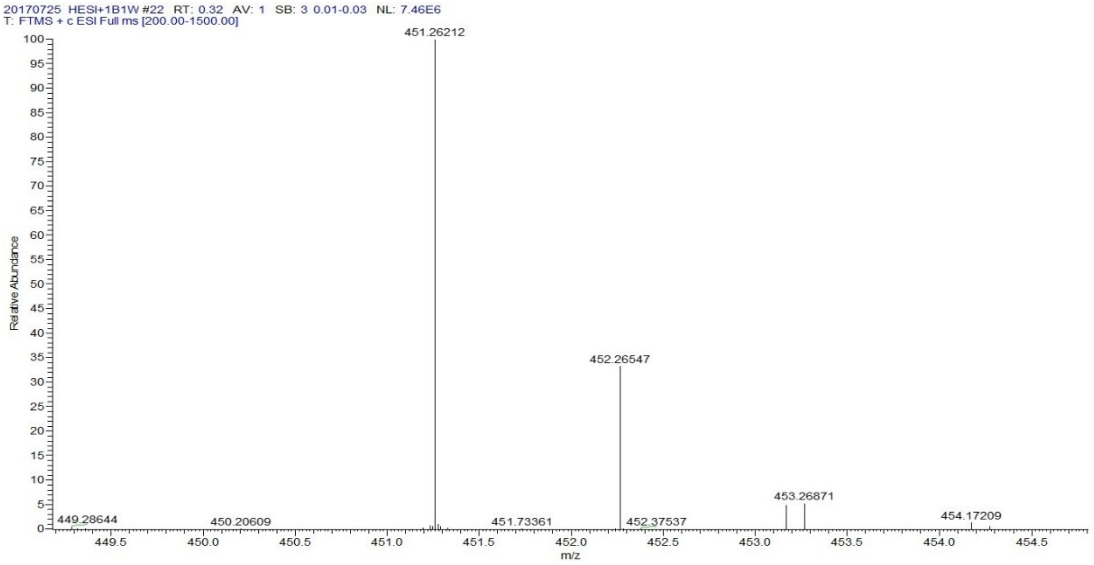

$^{13}C$ NMR spectrum of **2P1F** in $CDCl_3$.



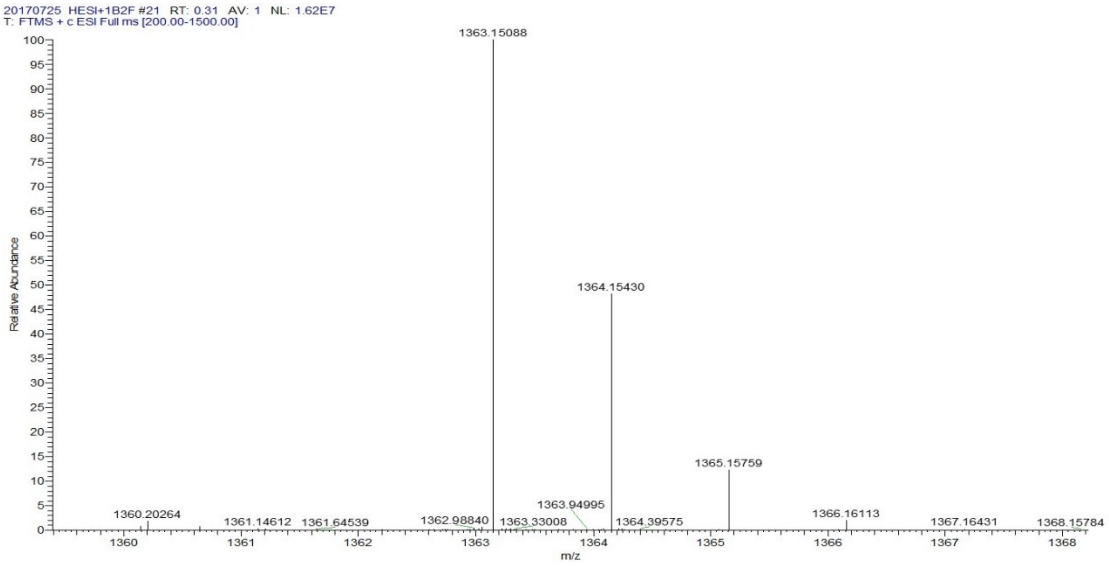

$^{13}C$ NMR spectrum of **2P1A** in $CDCl_3$.



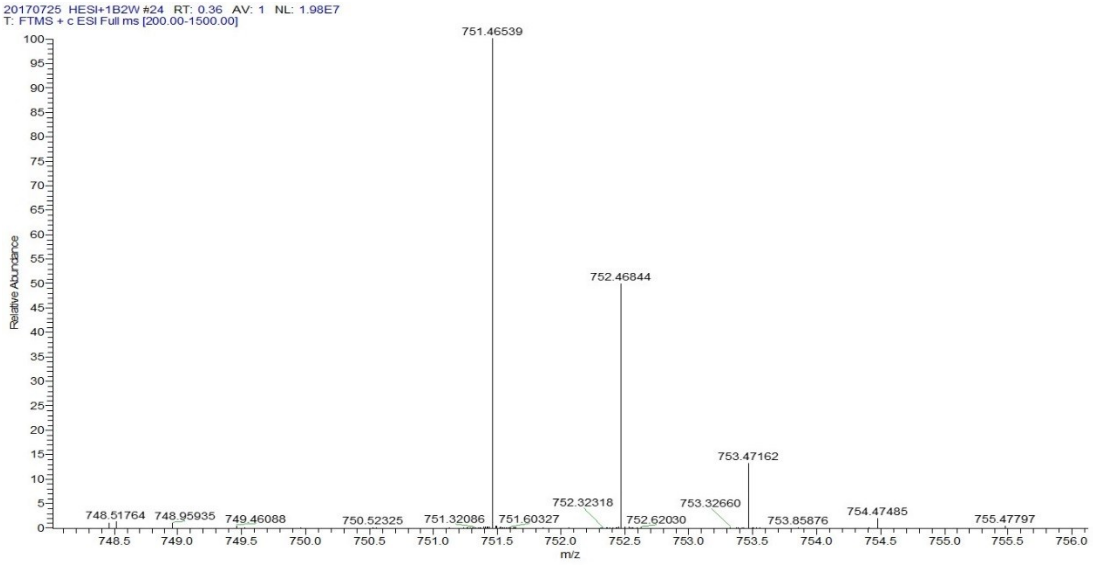

ESI-MS spectrum of **1P1F**.




ESI-MS spectrum of **1P1A**.

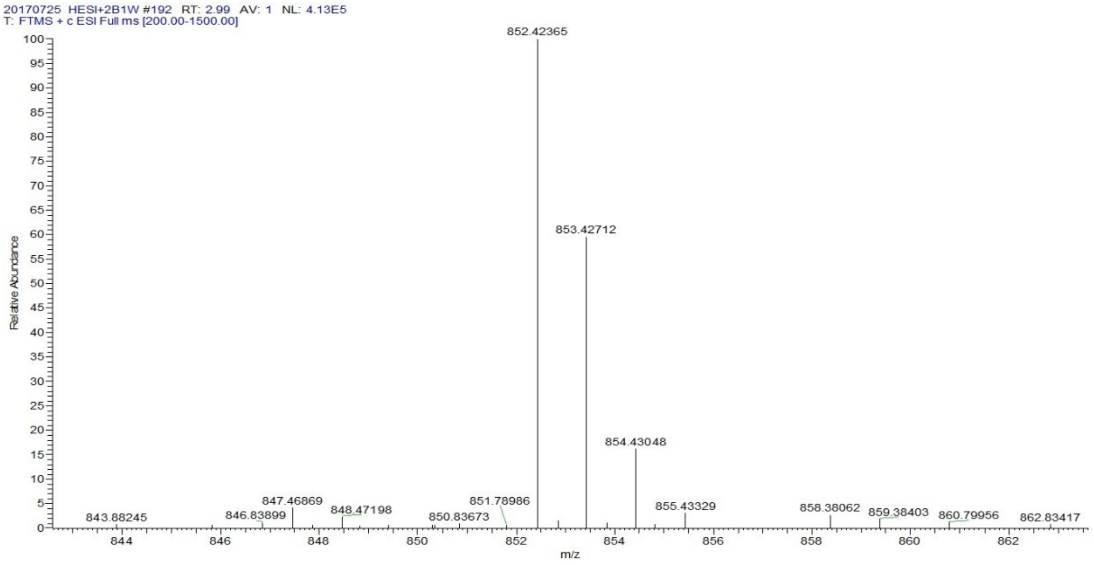



ESI-MS spectrum of **1P2F**.




ESI-MS spectrum of **1P2A**.


ESI-MS spectrum of **2P1F**.




ESI-MS spectrum of **2P1A**.