Supporting Information

Pd(II)-Catalyzed Enantioselective C-H Olefination and Photoregulation of Sterically-Hindered Diarylethenes

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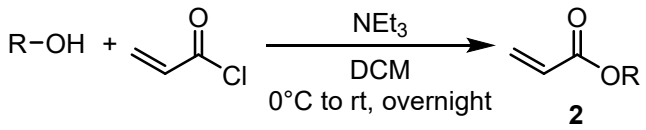
1. General Information

All the materials and solvents were purchased from commercial suppliers and used without additional purification. $Pd(OAc)_2$ was purchased from Laajoo (China). NMR spectra were recorded on a Bruke Avance operating for ^1H NMR at 400 MHz, ^{13}C NMR at 101 MHz, ^{19}F NMR at 376 MHz using TMS as internal standard. The peaks were internally referenced to $CDCl_3$ (7.26 ppm) or residual undeuterated solvent signal of $CDCl_3$ (77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument. The ee value was determined on Shimadzu HPLC using CHIRALPAK column with hexane and 2-propanol as eluent, Wavelength = 254 nm. UV-Vis spectra were recorded on Agilent Cary 60 (1 cm quartz cell) at 293K. CD spectra were recorded using Jasco J-819 spectropolarimeter (1 cm quartz cell) at 293K. The photochromic reaction was conducted by continuous irradiation of an Hg/Xe lamp (Hamamatsu, LC8 Lightningcure, 200W) equipped with a narrow band interference filter (Shenyang HB optical Technology) for λ_{irr} = 313 nm, a broad band interference filters (Anford) for λ_{irr} > 490 nm, or a monochromator (monoscan 2000, OceanOptics) for λ_{irr} = 517 ± 10 nm. Quantum yields of photoisomerization were measure by the standard procedures using 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6) as the reference[S1-S2]. BTTE was prepared according to previous reference[13].

2. Experiment Details and Characterization

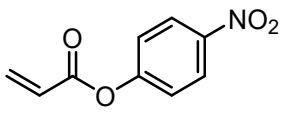
2.1 Preparation of Substrates

2.1.1 General procedure for the synthesis of olenfins:



General Procedure A: In a round bottom flask, acryloyl chloride (1.2 equiv., 12 mmol) was added dropwise to a solution of corresponding alcohol (1.0 equiv., 10 mmol) and NEt_3 (1.5 equiv., 15 mmol) in DCM (40 mL) at 0 °C under argon atmosphere. After the addition was completed, the ice bath was removed, and the reaction mixture was stirred at room temperature overnight. Upon completion of the reaction, the reaction mixture was diluted with water and extracted with DCM. The combined organic layer was washed with saturated aqueous $NaHCO_3$. The organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo. The crude mixture was purified by silica gel column chromatography using petroleum ether: ethyl acetate as the eluent to afford the desired compound **2**.

Compound **2a**, **2k**, **2l**, **2m**, **2n**, **2o**, **2p**, **2q**, **2r**, **2s**, **2t**, **2u**, **2v**, **2w**, **2x, 2y** are commercially available and were used directly without further purification.

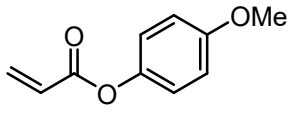


4-nitrophenyl acrylate 2b:

2b was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 24 : 1 to give as white solid(1.73 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.0 Hz, 2 H), 7.34 (d, *J* = 9.1 Hz, 2 H), 6.67 (d, *J* = 17.3 Hz, 1 H), 6.34 (dd, *J* = 17.3, 10.5 Hz, 1 H), 6.11 (d, *J* = 10.5 Hz, 1 H). m.p. 63.7-64.3℃

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 155.3, 145.4, 134.0, 127.1, 125.2, 122.4.

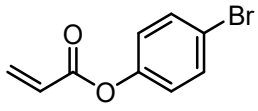


4-methoxyphenyl acrylate 2c:

2c was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 100 : 1 to give as colorless liquid(1.62 g, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 9.0 Hz, 2 H), 6.90 (d, *J* = 9.0 Hz, 2 H), 6.59 (d, *J* = 17.1 Hz, 1 H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1 H), 5.99 (d, *J* = 10.2 Hz, 1 H), 3.80 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 157.3, 144.1, 132.4, 128.0, 122.3, 114.5, 55.6.

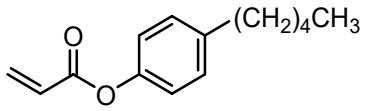


4-bromophenyl acrylate 2d:

2d was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 100 : 1 to give as colorless liquid(1.54 g, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 2 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.61 (d, *J* = 17.3 Hz, 1 H), 6.30 (dd, *J* = 17.3, 10.4 Hz, 1 H), 6.03 (d, *J* = 10.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 149.6, 133.0, 132.5, 127.6, 123.4, 119.0.

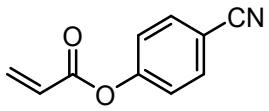


4-pentylphenyl acrylate 2e:

2e was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 100 : 1 to give as colorless liquid(1.96 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.2 Hz, 2 H), 7.03 (d, *J* = 8.5 Hz, 2 H), 6.59 (d, *J* = 17.4 Hz, 1 H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1 H), 5.99 (d, *J* = 10.5 Hz, 1 H), 2.64 - 2.55 (m, 2 H), 1.58 - 1.65 (m, 2 H), 1.37 - 1.29 (m, 4 H), 0.89 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 148.5, 140.6, 132.3, 129.3, 128.1, 121.1, 35.3, 31.5, 31.2, 22.5, 14.0.

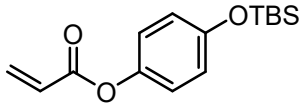


4-cyanophenyl acrylate 2f:

2f was prepared following **General Procedure A** and purified by flash in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give as white solid(0.91 g, 52% yield). m.p. 65.6-66.7℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 6.65 (d, *J* = 17.3 Hz, 1 H), 6.32 (dd, *J* = 17.3, 10.4 Hz, 1 H), 6.09 (d, *J* = 10.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 153.9, 133.9, 133.7, 127.3, 122.8, 118.3, 109.9.

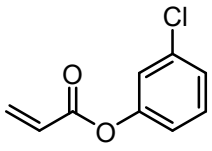


4-((*tert*-butyldimethylsilyl)oxy)phenyl acrylate 2g:

In an oven-dried 100 mL two-necked round-bottom flask, under Ar atmosphere, hydroquinone (1.10 g, 10 mmol) was dissolved in EtOAc (50 mL). Imidazole (1.70 g, 25 mmol) and TBDMSCl (1.66 g, 11.0mmol) were added to the solution and the resulting mixture was stirred for 4 h at 20 °C. The reaction was quenched by adding water and extracted with EtOAc for three times. The combined organic layers were washed brine, dried over Na_2SO_4, and concentrated in vacuo to afford the crude product without further purification.
In a round bottom flask, acryloyl chloride (948 μL, 12 mmol) was added dropwise to a solution of the crude product and NEt_3 (2.1 mL, 15 mmol) in DCM (40 mL) at 0 °C under argon atmosphere. After the addition was completed, the ice bath was removed, and the reaction mixture was stirred at room temperature overnight. Upon completion of the reaction, the reaction mixture was diluted with water and extracted with DCM. The combined organic layer was washed with saturated aqueous $NaHCO_3$. The organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo. The crude mixture was purified by silica gel column chromatography using petroleum ether: ethyl acetate = 100 : 1 as the eluent to give **2g** as colorless liquid(1.09 g, 39%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.9 Hz, 2 H), 6.83 (d, *J* = 8.9 Hz, 2 H), 6.58 (d, *J* = 17.3 Hz, 1 H), 6.30 (dd, *J* = 17.3, 10.5 Hz, 1 H), 5.98 (d, *J* = 10.4 Hz, 1 H), 0.98 (s, 9 H), 0.20 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 153.4, 144.6, 132.4, 128.1, 122.2, 120.6, 25.7, 18.2, -4.4.

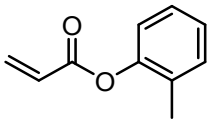


3-chlorophenyl acrylate 2h:

2h was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 100 : 1 to give as colorless liquid(1.70 g, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 1 H), 7.20 - 7.13 (m, 1 H), 7.11 (s, 1 H), 6.98 (d, *J* = 8.1 Hz, 1 H), 6.54 (d, *J* = 17.3 Hz, 1 H), 6.23 (dd, *J* = 17.2, 10.3 Hz, 1 H), 5.96 (d, *J* = 10.5 Hz, 1 H).

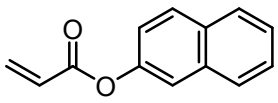
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 150.0, 133.7, 132.1, 129.1, 126.5, 125.2, 121.2, 118.9.



***o*-tolyl acrylate 2i:**

2i was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 100 : 1 to give as colorless liquid(1.08 g, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.17 (m, 3 H), 7.09 (d, *J* = 7.9 Hz, 1 H), 6.67 (d, *J* = 17.3 Hz, 1 H), 6.39 (dd, *J* = 17.3, 10.4 Hz, 1 H), 6.06 (d, *J* = 10.5 Hz, 1 H), 2.23 (s, 3 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 149.2, 132.6, 131.2, 130.2, 127.8, 127.0, 126.1, 121.9, 16.2.

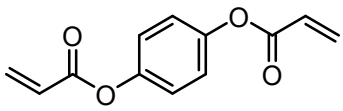


naphthalen-2-yl acrylate 2j:

2j was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 50 : 1 to give as colorless liquid(1.78 g, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.77 (m, 3 H), 7.61 (d, *J* = 2.3 Hz, 1 H), 7.51 - 7.44 (m, 2 H), 7.31 - 7.22 (m, 1 H), 6.65 (d, *J* = 17.3 Hz, 1 H), 6.37 (dd, *J* = 17.3, 10.4 Hz, 1 H), 6.04 (d, *J* = 10.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 148.3, 133.8, 132.7, 131.5, 129.5, 128.0, 127.8, 127.7, 126.6, 125.8, 121.1, 118.6.

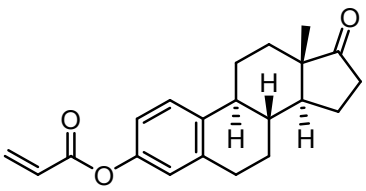


1,4-phenylene diacrylate 2z:

In a round bottom flask, acryloyl chloride (1.9 mL, 24 mmol) was added dropwise to a solution of hydroquinone (1.10 g, 10 mmol) and NEt_3 (4.2 mL, 30 mmol) in DCM (40 mL) at 0 °C under argon atmosphere. After the addition was completed, the ice bath was removed, and the reaction mixture was stirred at room temperature overnight. Upon completion of the reaction, the reaction mixture was diluted with water and extracted with DCM. The combined organic layer was washed with saturated aqueous $NaHCO_3$. The organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo. The crude mixture was purified by silica gel column chromatography using petroleum ether: ethyl acetate = 100 : 1 as the eluent to give **2g** as white solid(1.92 g, 88%). m.p. 84.7-86.5℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 4H), 6.61 (d, *J* = 17.4 Hz, 2 H), 6.32 (dd, *J* = 17.3, 10.4 Hz, 2 H), 6.02 (d, *J* = 10.4 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 148.1, 132.9, 127.8, 122.5.

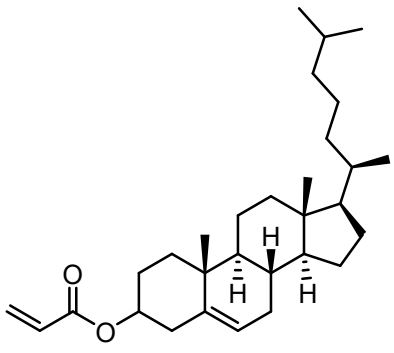


(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl acrylate 2aa:

2aa was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 50 : 1 to give as colorless liquid(2.9 g, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 1 H), 6.93 - 6.84 (m, 2 H), 6.59 (d, *J* = 17.3 Hz, 1 H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1 H), 6.00 (d, *J* = 10.1 Hz, 1 H), 2.95 - 2.88 (m, 2 H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1 H), 2.44 - 2.39 (m, 1 H), 2.29 (td, *J* = 11.0, 4.1 Hz, 1 H), 2.21 - 1.91 (m, 4 H), 1.70 - 1.38 (m, 6 H), 0.91 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.9, 164.9, 148.5, 138.1, 137.5, 132.5, 128.1, 126.5, 121.6, 118.8, 50.5, 48.0, 44.2, 38.0, 35.9, 31.6, 29.5, 26.4, 25.8, 21.7, 13.9.



(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acrylate 2ab:

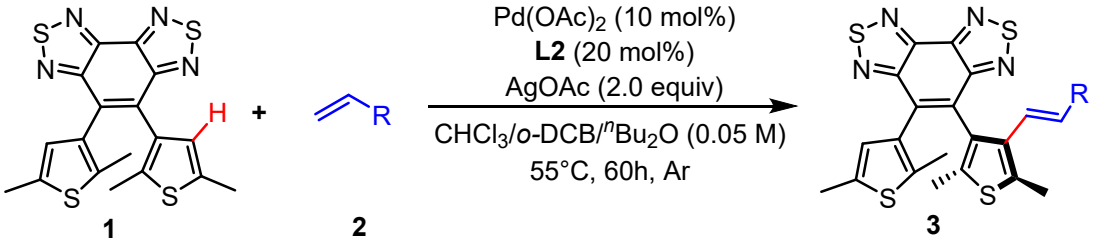
2ab was prepared following **General Procedure A** and purified by flash in petroleum ether : ethyl acetate = 50 : 1 to give as white solid (3.79 g, 86% yield). m.p. 122.5-124.1℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (d, *J* = 17.4 Hz, 1 H), 6.14 (dd, *J* = 17.3, 10.4 Hz, 1 H), 5.83 (d, *J* = 10.4 Hz, 1 H), 5.42 (d, *J* = 5.0 Hz, 1 H), 4.73 (tq, *J* = 11.5, 4.4 Hz, 1 H), 2.40 (d, *J* = 8.0 Hz, 2 H), 2.09 - 1.80 (m, 5 H), 1.74 - 0.98 (m, 24 H), 0.95 (d, *J* = 6.5 Hz, 3 H), 0.90 (d, *J* = 6.6 Hz, 6 H), 0.71 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 139.6, 130.3, 129.1, 122.8, 74.2, 56.7, 56.2, 50.1, 42.3, 39.8, 39.6, 38.2, 37.0, 36.7, 36.2, 35.9, 32.0, 31.9, 28.3, 28.1, 27.8, 24.3, 23.9, 22.9, 22.6, 21.1, 19.4, 18.8, 11.9.

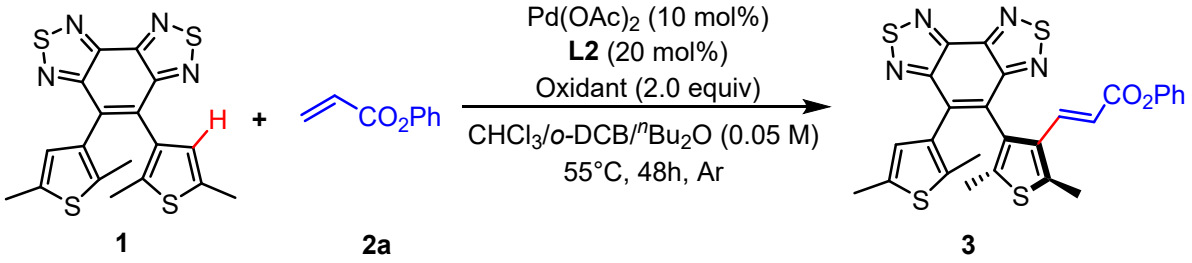
2.2 General Procedure for the Enantioselective C-H Olefination.

Note: Because of the coexistence of parallel conformer and anti-parallel conformer of sterically hindered diarylethenes, the integrals of some H-atoms may not be integers in ^{1}H NMR spectra. But the sum of the integrals of H atoms is integers for the parallel and anti-parallel conformer at the same position.



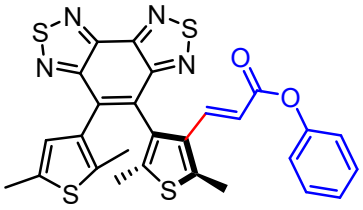
A 10 mL Schlenk tube was added **1** (41.4 mg, 0.10 mmol), **2** (0.15 mmol), **L2** (14.4 mg, 20 mmol%), AgOAc (33.4 mg, 0.20 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mol%) and $CHCl_3$/*o*-DCB/^{n}Bu$_2$O (0.67 mL/0.67 mL/0.67 mL). The reaction mixture was stirred at 55 °C (aluminum heat transfer block) for 60 h in the dark. After cooling to room temperature, the mixture was diluted with dichloromethane, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC using Hexane/EtOAc/DCM or Hexane/Acetone/DCM as the eluent to afford the desired product.

Table S1. Screening of Ag salt.



Entry	Oxidant	Yield[b] (%)	er[c]
1	AgOAc	78	95:5
2	Ag_2CO_3	16	90:10
3	Ag_3PO_4	10	91:9
4	AgTFA	39	50:50
5	$AgNO_3$	22	75.5:24.5
6	$PhCO_2Ag$	71	83.5:16.5
7	Ag_2SO_4	17	90:10
8	Ag_2O	N.R.	-
9	$AgBF_4$	N.R.	-

[a]Reaction conditions: **1** (0.10 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol %), **L2** (20 mol %), Oxidant (2.0 equiv) in solvent (2 mL), 55 °C, 48 h, under Ar. [b]Isolated yield. [c]The er value was determined by chiral HPLC. *o*-DCB = 1,2-dichlorobenzene.



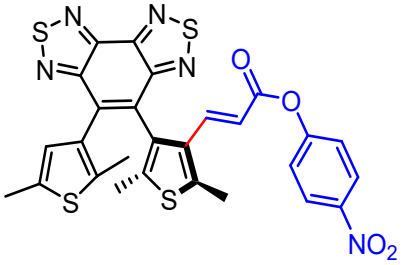
Phenyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3a:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3a** as red oil (47.7 mg, 85%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 97/3, flow = 1.0 mL/min, 254 nm) with tr = 9.0 min (major), 10.7 min (minor): 95.5 : 4.5 er. $[\alpha]_D^{20}$ = 110.0 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 16 Hz, 1 H), 7.43 (d, *J* = 16 Hz, 1 H), 7.27 - 7.34 (m, 4 H), 7.13 - 7.21 (m, 2 H), 6.92 - 7.02 (m, 4 H), 6.44 (s, 1 H), 6.30 (s, 1 H), 5.86 (d, *J* = 16.1 Hz, 1 H), 5.81 (d, *J* = 16 Hz, 1 H), 2.62 (s, 3 H), 2.58 (s, 3 H), 2.36 (s, 6 H), 2.14 (s, 3 H), 2.11 (s, 3 H), 2.10 (s, 3 H), 2.06 (s, 3 H). ap/p=46/54.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 165.6, 156.8, 156.8, 156.7, 150.7, 150.6, 147.7, 147.4, 140.0, 139.9, 139.6, 139.4, 137.3, 136.8, 135.9, 135.8, 135.2, 134.7, 132.9, 132.9, 132.7, 132.5, 131.5, 131.3, 131.0, 130.6, 129.9, 129.9, 129.4, 127.5, 126.5, 125.7, 121.5, 117.1, 116.6, 15.6, 15.5, 15.3, 15.2, 14.9, 14.4, 14.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{27}H_{20}N_4O_2S_4Na^+$: 583.0361; found: 583.0363.



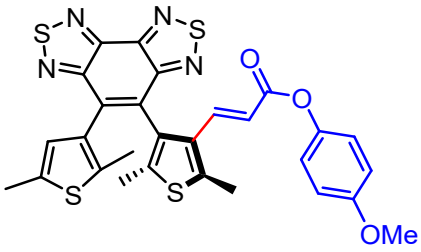
4-nitrophenyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3b:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3b** as red oil (42.4 mg, 70%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 97/3, flow = 1.0 mL/min, 254 nm) with tr = 35.2 min (major), 42.2 min (minor): 93.5 : 6.5 er. $[\alpha]_D^{20}$ = 127.6 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (m, 4 H), 7.52 (d, *J* = 16.1 Hz, 1 H), 7.42 (d, *J* = 16.1 Hz, 1 H), 7.18 (m, 4 H), 6.40 (s, 1 H), 6.31 (s, 1 H), 5.86 (d, *J* = 16.1 Hz, 1 H), 5.79 (d, *J* = 16.1 Hz, 1 H), 2.64 (s, 3 H), 2.60 (s, 3 H), 2.37 (s, 3 H), 2.34 (s, 3 H), 2.12 (s, 6 H), 2.11 (s, 3 H), 2.06 (s, 3 H). ap/p=42/58.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 164.6, 156.7, 156.7, 156.6, 155.4, 155.4, 147.6, 147.3, 147.3, 145.1, 145.1, 141.2, 141.0, 140.8, 140.6, 137.1, 137.0, 136.0, 135.8, 135.5, 135.0, 132.9, 132.8, 132.7, 132.3, 131.2, 131.0, 130.8, 130.5, 129.7, 127.2, 126.5, 125.2, 122.4, 122.3, 115.6, 115.0, 15.7, 15.5, 15.3, 15.2, 15.2, 14.9, 14.4, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{27}H_{19}N_5O_4S_4Na^+$: 628.0212; found: 628.0213.



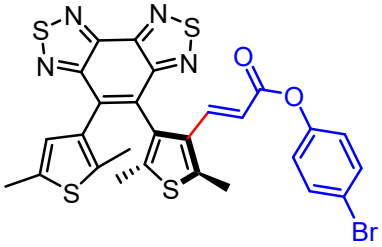
4-methoxyphenyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3c:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3c** as red oil (40.2 mg, 68%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 11.2 min (major), 13.8 min (minor): 95 : 5 er. $[\alpha]_D^{20}$ = 108.6 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 16 Hz, 1 H), 7.35 (d, *J* = 16 Hz, 1 H), 6.78 - 6.94 (m, 8 H), 6.44 (s, 1 H), 6.30 (s, 1 H), 5.85 (d, *J* = 16.1 Hz, 1 H), 5.79 (d, *J* = 16.1 Hz, 1 H), 3.77 (s, 3 H), 3.76 (s, 3 H), 2.61 (s, 3 H), 2.58 (s, 3 H), 2.36 (s, 6 H), 2.13 (s, 3 H), 2.10 (s, 6 H), 2.06 (s, 3 H). ap/p=43/57.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 166.0, 157.1, 156.8, 156.7, 156.6, 147.6, 147.3, 147.3, 144.1, 144.0, 140.0, 139.8, 139.4, 139.2, 137.3, 136.8, 135.9, 135.7, 135.1, 134.6, 132.8, 132.8, 132.7, 132.4, 131.5, 131.3, 130.9, 130.5, 129.9, 129.8, 127.4, 126.5, 122.2, 117.1, 116.6, 114.4, 55.6, 15.6, 15.4, 15.3, 15.2, 14.8, 14.4, 14.3, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{28}H_{23}N_4O_3S_4^+$: 591.0647; found: 591.0650.



4-methoxyphenyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3d:

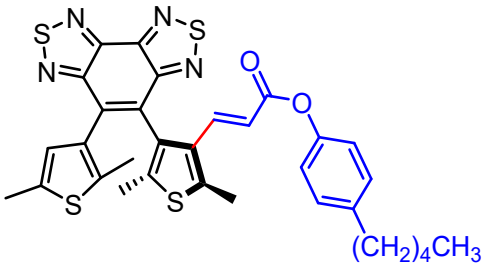
A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3d** as red oil (27.5 mg, 43%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol =

97/3, flow = 1.0 mL/min, 254 nm) with tr = 12.6 min (major), 17.7 min (minor): 94 : 6 er. $[\alpha]_D^{20}$ = 101.5 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.50 (m, 6 H), 6.82 - 6.94 (m, 4 H), 6.41 (s, 1 H), 6.30 (s, 1 H), 5.84 (d, *J* = 16.1 Hz, 1 H), 5.78 (d, *J* = 16.1 Hz, 1 H), 2.62 (s, 3 H), 2.58 (s, 3 H), 2.36 (s, 3 H), 2.34 (s, 3 H), 2.11 (s, 3 H), 2.10 (s, 6 H), 2.06 (s, 3 H). ap/p=43/57.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 165.3, 156.8, 156.7, 156.7, 156.6, 149.6, 149.6, 147.6, 147.3, 140.4, 140.2, 140.0, 139.7, 137.2, 136.9, 135.9, 135.8, 135.3, 134.8, 132.9, 132.8, 132.7, 132.4, 131.3, 131.1, 130.9, 130.5, 129.8, 129.7, 127.3, 126.5, 123.3, 123.3, 118.8, 118.8, 116.5, 115.9, 15.6, 15.4, 15.3, 15.2, 15.2, 14.9, 14.4, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{27}H_{20}BrN_4O_2S_4^+$: 638.9647; found: 638.9644.



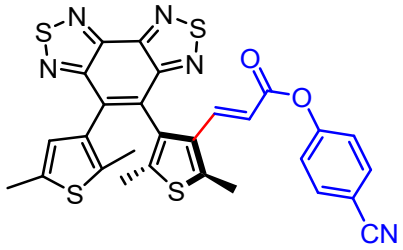
4-pentylphenyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3e:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3e** as red oil (40.4 mg, 64%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 97/3, flow = 1.0 mL/min, 254 nm) with tr = 12.6 min (major), 15.7 min (minor): 94.5 : 5.5 er. $[\alpha]_D^{20}$ = 107.3 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 16 Hz, 1 H), 7.36 (d, *J* = 16 Hz, 1 H), 7.07 - 7.15 (m, 4 H), 6.82 - 6.92 (m, 4 H), 6.45 (s, 1 H), 6.29 (s, 1 H), 5.87 (d, *J* = 16.1 Hz, 1 H), 5.81 (d, *J* = 16.1 Hz, 1 H), 2.61 (s, 3 H), 2.58 (s, 3 H), 2.50 - 2.56 (m, 4 H), 2.36 (s, 6 H), 2.13 (s, 3 H), 2.10 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 1.51 -1.61 (m, 4 H), 1.2 - 1.35 (m, 8 H), 0.82 - 0.92 (m, 6 H). ap/p=43/57.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 165.7, 156.8, 156.7, 156.6, 148.4, 148.4, 147.6, 147.3, 147.3, 140.4, 140.3, 139.8, 139.7, 139.3, 139.1, 137.3, 136.7, 135.8, 135.7, 135.1, 134.6, 132.8, 132.8, 132.7, 132.4, 131.4, 131.2, 130.9, 130.5, 129.8, 129.8, 129.2, 127.4, 126.4, 121.0, 117.2, 116.7, 35.3, 31.4, 31.1, 22.5, 15.5, 15.4, 15.2, 15.2, 14.8, 14.3, 14.1, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{32}H_{31}N_4O_2S_4^+$: 631.1324; found: 631.1326.



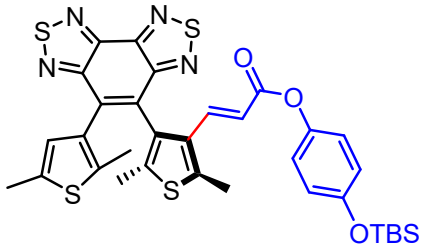
4-cyanophenyl (*E*)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3f:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 7 : 2 : 1 to give **3f** as red oil (32.7 mg, 56%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 15.3 min (major), 17.9 min (minor): 93.5 : 6.5 er. $[\alpha]_D^{20}$ = 158.6 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 - 7.66 (m, 4 H), 7.52 (d, *J* = 16 Hz, 1 H), 7.40 (d, *J* = 16 Hz, 1 H), 7.07 - 7.17 (m, 4 H), 6.39 (s, 1 H), 6.30 (s, 1 H), 5.84 (d, *J* = 16.1 Hz, 1 H), 5.77 (d, *J* = 16.1 Hz, 1 H), 2.63 (s, 3 H), 2.59 (s, 3 H), 2.36 (s, 3 H), 2.34 (s, 3 H), 2.12 (s, 6 H), 2.11 (s, 3 H), 2.06 (s, 3 H). ap/p=43/57.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 164.7, 156.8, 156.7, 156.6, 154.0, 154.0, 147.6, 147.4, 141.0, 140.8, 140.6, 140.5, 137.2, 137.0, 136.0, 135.8, 135.5, 135.0, 133.6, 133.0, 132.9, 132.7, 132.4, 131.3, 131.1, 130.9, 130.6, 129.7, 127.2, 126.5, 122.7, 122.7, 118.3, 115.8, 115.2, 109.6, 109.6, 15.7, 15.5, 15.3, 15.2, 15.0, 14.4, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{28}H_{20}N_5O_2S_4^+$: 586.0494; found: 586.0498.



4-((tert-butyldimethylsilyl)oxy)phenyl (*E*)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3g:

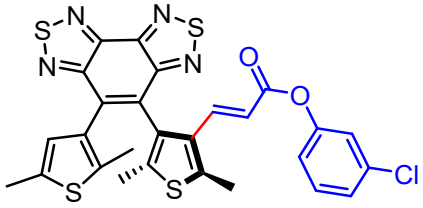
A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3g** as red oil (60.8 mg, 88%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 95/5, flow = 1.0 mL/min, 254 nm) with tr = 5.3 min (major), 7.6 min (minor): 95 : 5 er. $[\alpha]_D^{20}$ = 153.8 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 16.2 Hz, 1 H), 7.34 (d, *J* = 16.2 Hz, 1 H), 6.70 - 6.89 (m, 8 H), 6.44 (s, 1 H), 6.30 (s, 1 H), 5.85 (d, *J* = 16.1 Hz, 1 H), 5.79 (d, *J* = 16.1 Hz, 1 H), 2.61 (s, 3 H), 2.57 (s, 3 H), 2.36 (s, 6 H), 2.13 (s, 3 H), 2.10 (s, 3 H), 2.06 (s, 6 H), 0.95 (m, 18 H), 0.16 (m, 12 H). ap/p=46/54.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.9, 156.8, 156.8, 156.7, 153.2, 147.7, 147.4, 144.6, 144.6, 139.9, 139.7, 139.4,

139.2, 137.3, 136.8, 135.9, 135.8, 135.2, 134.7, 132.9, 132.9, 132.7, 132.5, 131.6, 131.4, 131.0, 130.6, 130.0, 129.9, 127.5, 126.5, 122.1, 120.5, 117.3, 116.8, 25.7, 18.2, 15.6, 15.5, 15.3, 15.2, 14.9, 14.4, 14.4, -4.4.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{33}H_{35}N_4O_3S_4Si^+$: 691.1356; found: 691.1359.



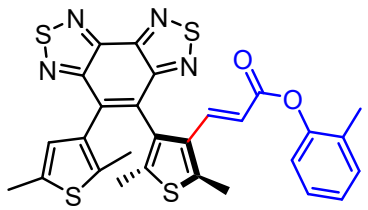
3-chlorophenyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3h:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3h** as red oil (34.0 mg, 57%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 97/3, flow = 1.0 mL/min, 254 nm) with tr = 9.3 min (major), 10.8 min (minor): 94 : 6 er. $[\alpha]_D^{20}$ = 159.8 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 16 Hz, 1 H), 7.37 (d, *J* = 16 Hz, 1 H), 7.20 - 7.26 (m, 4 H), 6.98 - 7.07 (m, 2 H), 6.85 - 6.94 (m, 2 H), 6.42 (s, 1 H), 6.30 (s, 1 H), 5.85 (d, *J* = 16.1 Hz, 1 H), 5.78 (d, *J* = 16.1 Hz, 1 H), 2.62 (s, 3 H), 2.58 (s, 3 H), 2.36 (s, 6 H), 2.12 (s, 3 H), 2.10 (s, 6 H), 2.06 (s, 3 H). ap/p=46/54.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 165.2, 156.8, 156.7, 156.7, 156.6, 151.1, 151.0, 147.6, 147.3, 140.5, 140.3, 140.0, 139.8, 137.2, 136.9, 135.9, 135.8, 135.3, 134.8, 134.6, 132.9, 132.8, 132.7, 132.4, 131.3, 131.1, 130.9, 130.5, 130.1, 129.8, 129.7, 127.3, 126.5, 126.0, 126.0, 122.2, 120.0, 119.9, 116.4, 115.8, 15.6, 15.5, 15.3, 15.2, 14.9, 14.4, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{27}H_{20}N_4O_2S_4Cl^+$: 595.0152; found: 595.0157.



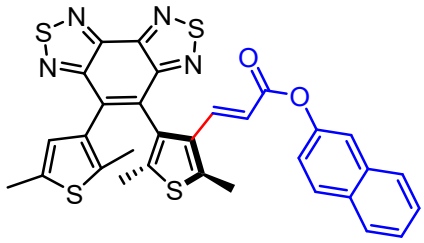
***o*-tolyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3i:**

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3i** as red oil (38.5 mg, 67%,). The ee value was determined by HPLC analysis on a Chiralcel IBN-5 column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 8.8 min (major), 9.7 min (minor): 88.5 : 11.5 er. $[\alpha]_D^{20}$ = 107.2 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 16 Hz, 1 H), 7.41 (d, *J* = 16 Hz, 1 H), 7.04 - 7.19 (m, 6 H), 6.84 - 6.93 (m, 2 H), 6.41 (s, 1 H), 6.34 (s, 1 H), 5.90 (d, *J* = 16.1 Hz, 1 H), 5.84 (d, *J* = 16.1 Hz, 1 H), 2.63 (s, 3 H), 2.60 (s, 3 H), 2.37 (s, 3 H), 2.36 (s, 3 H), 2.13 (s, 3 H), 2.12 (s, 3 H), 2.09 (s, 3 H) 2.06 (s, 3 H), 2.00 (s, 3 H), 1.98 (s, 3 H). ap/p=46/54.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 156.8, 156.8, 156.7, 156.7, 149.2, 149.2, 147.6, 147.6, 147.3, 147.3, 140.2, 140.1, 139.5, 139.3, 137.2, 136.7, 135.9, 135.8, 135.2, 134.7, 132.9, 132.9, 132.7, 132.4, 131.4, 131.2, 131.1, 131.0, 130.5, 130.1, 130.0, 129.9, 129.9, 127.2, 126.9, 126.6, 125.9, 121.7, 121.7, 116.7, 116.2, 16.1, 16.1, 15.6, 15.5, 15.3, 15.3, 15.2, 14.9, 14.4, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{28}H_{23}N_4O_2S_4^+$: 575.0698; found: 575.0699.



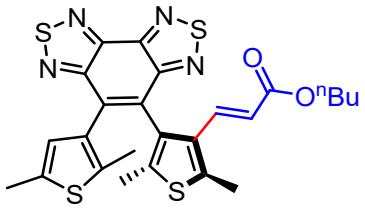
naphthalen-2-yl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3j:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 17 : 2 : 1 to give **3j** as red oil (41.5 mg, 68%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 97/3, flow = 1.0 mL/min, 254 nm) with tr = 25.8 min (major), 29.6 min (minor): 95 : 5 er. $[\alpha]_D^{20}$ = 165.8 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 - 7.85 (m, 6 H), 7.38 - 7.56 (m, 8 H), 7.13 (dd, *J* = 8.9, 2.3 Hz, 1 H), 7.10 (dd, *J* = 8.9, 2.3 Hz, 1 H), 6.47 (s, 1 H), 6.31 (s, 1 H), 5.92 (d, *J* = 16.1 Hz, 1 H), 5.86 (d, *J* = 16.1 Hz, 1 H), 2.64 (s, 3 H), 2.60 (s, 3 H), 2.38 (s, 3 H), 2.37 (s, 3 H), 2.17 (s, 3 H), 2.11 (s, 3 H), 2.07 (s, 6 H). ap/p=44/56.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 165.8, 156.8, 156.8, 156.7, 156.6, 148.6, 148.2, 147.6, 147.3, 147.3, 140.2, 140.0, 139.7, 139.5, 137.3, 136.8, 135.9, 135.8, 135.2, 134.7, 133.7, 132.9, 132.8, 132.7, 132.4, 131.5, 131.4, 131.3, 131.0, 130.5, 129.9, 129.8, 129.3, 127.8, 127.6, 127.4, 126.6, 126.5, 125.7, 121.1, 118.4, 117.0, 116.5, 15.6, 15.5, 15.3, 15.3, 15.2, 14.9, 14.4, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{31}H_{23}N_4O_2S_4^+$: 611.0698; found: 611.0703.



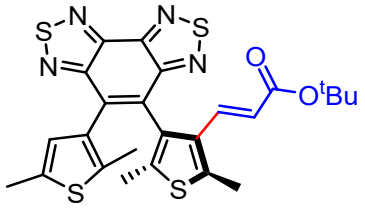
butyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3k:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3k** as red oil (33.5 mg, 62%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 95/5, flow = 1.0 mL/min, 254 nm) with tr = 7.3 min (major), 8.4 min (minor): 94 : 6 er. $[\alpha]_D^{20}$ = 90.8 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 16 Hz, 1 H), 7.19 (d, *J* = 16 Hz, 1 H), 6.36 (d, *J* = 16 Hz, 1 H), 6.32 (d, *J* = 16 Hz, 1 H), 5.67 (d, *J* = 16.1 Hz, 1 H), 5.63 (d, *J* = 16.1 Hz, 1 H), 3.94 - 4.06 (m, 4 H), 2.57 (s, 3 H), 2.53 (s, 3 H), 2.36 (s, 3 H), 2.32 (s, 3 H), 2.10 (s, 3 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 1.45 - 1.57 (m, 4 H), 1.20 - 1.33 (m, 4 H), 0.80 - 0.91 (t, *J* = 7.2 Hz, 6 H). ap/p=44/56.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 167.2, 156.8, 156.8, 156.7, 147.6, 147.3, 147.3, 138.8, 138.8, 137.7, 137.5, 137.2, 136.7, 135.7, 135.6, 134.9, 134.4, 132.8, 132.7, 132.6, 132.3, 131.7, 131.4, 131.0, 130.5, 130.0, 130.0, 127.4, 126.5, 118.4, 117.9, 64.3, 64.2, 30.6, 19.1, 19.1, 15.5, 15.3, 15.2, 15.1, 15.0, 14.9, 14.3, 14.3, 14.2, 13.7.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{25}H_{25}N_4O_2S_4^+$: 541.0855; found: 541.0856.



***tert*-butyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3l:**

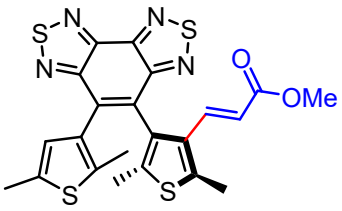
A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3l** as red oil (44.3 mg, 62%,). The ee value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr =6.7 min (major)，5.9 min (minor): 88 : 12 er. $[\alpha]_D^{20}$ = 110.6 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 16 Hz, 1 H), 7.09 (d, *J* = 16 Hz, 1 H), 6.40 (s, 1 H), 6.29 (s, 1 H), 5.63 (d, *J* = 16.1 Hz, 1 H), 5.59 (d, *J* = 16.1 Hz, 1 H), 2.56 (s, 3 H), 2.51 (s, 3 H), 2.35 (s, 3 H), 2.33 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.04 (s, 6 H), 1.37 (s, 18 H). ap/p=44/56.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.5, 156.8, 156.8, 156.7, 147.6, 147.3, 147.3, 138.4, 138.2, 137.3, 136.8, 136.6,

136.6, 135.6, 135.5, 134.6, 134.1, 132.8, 132.8, 132.7, 132.5, 131.6, 131.5, 131.0, 130.5, 130.1, 130.1, 127.5, 126.5, 120.2, 119.7, 80.3, 80.3, 28.1, 28.1, 15.5, 15.4, 15.2, 15.2, 15.1, 14.8, 14.3, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{25}H_{24}N_4O_2S_4Na^+$: 563.0674; found: 563.0673.



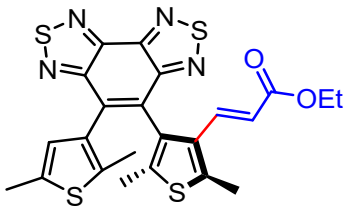
methyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3m:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3m** as red oil (37.9 mg, 76%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 95/5, flow = 0.8 mL/min, 254 nm) with tr = 6.2 min (major), 6.9 min (minor): 86.5 : 13.5 er. $[\alpha]_D^{20}$ = 80.7 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 16 Hz, 1 H), 7.22 (d, *J* = 16 Hz, 1 H), 6.35 (s, 1 H), 6.32 (s, 1 H), 5.67 (d, *J* = 16.1 Hz, 1 H), 5.60 (d, *J* = 16.1 Hz, 1 H), 3.61 (s, 3 H), 3.60 (s, 3 H), 2.57 (s, 3 H), 2.53 (s, 3 H), 2.36 (s, 3 H), 2.31 (s, 3 H), 2.10 (s, 3 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H). ap/p=44/56.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 167.5, 156.8, 156.8, 156.7, 147.6, 147.3, 147.3, 139.1, 139.0, 137.9, 137.7, 137.2, 136.7, 135.8, 135.7, 135.0, 134.5, 132.8, 132.7, 132.5, 132.2, 131.6, 131.4, 131.0, 130.5, 130.0, 130.0, 127.4, 126.5, 117.8, 117.2, 51.5, 15.4, 15.2, 15.1, 15.0, 14.9, 14.3, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{22}H_{19}N_4O_2S_4^+$: 499.0385; found: 499.0384.



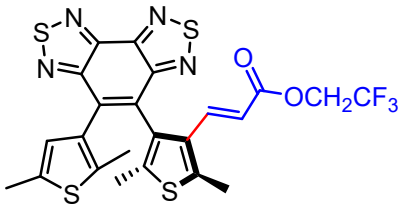
ethyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3n:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3n** as red oil (40.5 mg, 79%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 95/5, flow = 0.8 mL/min, 254 nm) with tr =8.6 min (major), 10.0 min (minor): 92.5 : 7.5 er. $[\alpha]_D^{20}$ = 159.9 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 16 Hz, 1 H), 7.20 (d, *J* = 16 Hz, 1 H), 6.37 (s, 1 H), 6.31 (s, 1 H), 5.67 (d, *J* = 16.1 Hz, 1 H), 5.61 (d, *J* = 16.1 Hz, 1 H), 4.00 - 4.15 (m, 4 H), 2.56 (s, 3 H), 2.53 (s, 3 H), 2.35 (s, 3 H), 2.32 (s, 3 H), 2.10 (s, 3 H), 2.08 (s, 3 H), 2.07 (s, 3 H), 2.04 (s, 3 H), 1.14 - 1.23 (m, 6 H). ap/p=44/56.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 167.1, 156.8, 156.8, 156.8, 156.7, 147.6, 147.3, 147.3, 138.9, 138.8, 137.7, 137.5, 137.3, 136.7, 135.7, 135.6, 134.9, 134.4, 132.8, 132.7, 132.6, 132.3, 131.7, 131.5, 131.0, 130.5, 130.0, 130.0, 127.4, 126.5, 118.4, 117.8, 60.3, 60.3, 15.4, 15.3, 15.2, 15.1, 15.0, 14.8, 14.3, 14.3, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{21}N_4O_2S_4^+$: 513.0542; found: 513.0546.



2,2,2-trifluoroethyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3o:

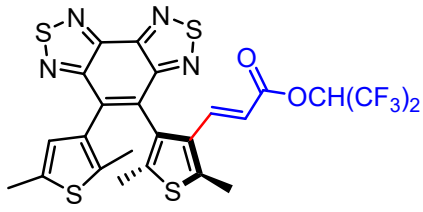
A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3o** as red oil (40.8 mg, 72%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 95/5, flow = 0.8 mL/min, 254 nm) with tr =5.2 min (major), 6.0 min (minor): 89 : 11 er. $[\alpha]_D^{20}$ = 133.5 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 16 Hz, 1 H), 7.29 (d, *J* = 16 Hz, 1 H), 6.38 (s, 1 H), 6.30 (s, 1 H), 5.74 (d, *J* = 16.1 Hz, 1 H), 5.69 (d, *J* = 16.1 Hz, 1 H), 4.33 - 4.47 (m, 4 H), 2.59 (s, 3 H), 2.56 (s, 3 H), 2.35 (s, 3 H), 2.32 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 6 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 156.8, 156.7, 156.7, 156.6, 147.6, 147.3, 147.3, 140.3, 140.2, 140.2, 140.0, 137.3, 136.8, 135.9, 135.8, 135.3, 134.7, 132.9, 132.8, 132.7, 132.5, 131.1, 131.0, 130.8, 130.4, 129.7, 129.6, 127.4, 126.4, 124.3, 124.3, 121.6, 121.6, 115.6, 115.2, 60.7, 60.6, 60.4, 60.3, 60.2, 59.9, 59.9, 59.6, 59.5, 15.6, 15.5, 15.2, 15.0, 14.9, 14.8, 14.4, 14.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6, -73.7 (both s, total 3 F)

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{18}F_3N_4O_2S_4^+$: 567.0259; found: 567.0265.



1,1,1,3,3,3-hexafluoropropan-2-yl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3p:

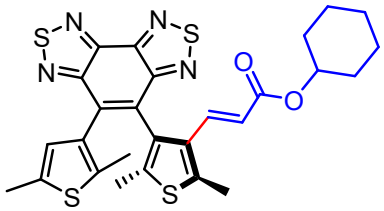
A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 40 : 10 : 1 to give **3p** as red oil (44.4 mg, 70%,). The ee value was determined by HPLC analysis on a Chiralcel A05 column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 5.2 min (major), 4.6 min (minor): 89 : 11 er. $[\alpha]_D^{20}$ = 125.9 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 16 Hz, 1 H), 7.37 (d, *J* = 16 Hz, 1 H), 6.40 (s, 1 H), 6.25 (s, 1 H), 5.66 - 5.82 (m, 4 H), 2.61 (s, 3 H), 2.58 (s, 3 H), 2.34 (s, 3 H), 2.31 (s, 3 H), 2.11 (s, 3 H), 2.10 (s, 3 H), 2.05 (s, 6 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 163.7, 156.8, 156.6, 156.6, 156.5, 147.6, 147.3, 147.3, 142.2, 142.0, 141.6, 141.5, 137.4, 136.9, 136.0, 135.5, 135.0, 133.0, 132.9, 132.8, 130.7, 130.4, 129.4, 129.3, 127.3, 126.3, 121.9, 119.0, 113.4, 113.2, 66.6, 66.3, 65.9, 15.8, 15.8, 15.2, 15.0, 14.9, 14.7, 14.5, 14.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.2 (m, 6 F).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{24}H_{17}F_6N_4O_2S_4^+$: 635.0133; found: 635.0133.



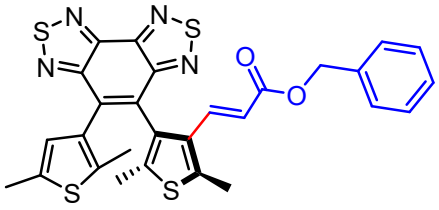
cyclohexyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3q:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3q** as red oil (48.7 mg, 86%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 95/5, flow = 1.0 mL/min, 254 nm) with tr =5.3 min (major), 6.8 min (minor): 90.5 : 9.5 er. $[\alpha]_D^{20}$ = 78.9 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 16.1 Hz, 1 H), 7.16 (d, *J* = 16.1 Hz, 1 H), 6.34 (s, 1 H), 6.29 (s, 1 H), 5.67 (d, *J* = 14 Hz, 1 H), 5.63 (d, *J* = 14 Hz, 1 H), 4.62 - 4.73 (m, 2 H), 2.56 (s, 3 H), 2.52 (s, 3 H), 2.35 (s, 3 H), 2.32 (s, 3 H), 2.10 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 1.68 - 1.80 (m, 4 H), 1.44 - 1.63 (m, 6 H), 1.10 - 1.38 (m, 10 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.5, 156.8, 156.8, 156.7, 147.6, 147.3, 138.5, 138.4, 137.4, 137.3, 136.6, 135.6, 135.5, 134.7, 134.3, 132.8, 132.7, 132.7, 132.4, 131.7, 131.5, 131.0, 130.5, 130.1, 130.0, 127.4, 126.5, 119.0, 118.5, 72.6, 72.5, 31.6, 31.6, 25.3, 23.7, 23.7, 15.4, 15.3, 15.1, 15.1, 14.8, 14.3, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{27}H_{27}N_4O_2S_4^+$: 567.1011; found: 567.1015.

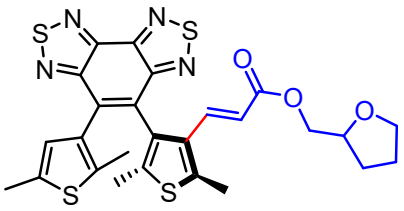


benzyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3r:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3r** as red oil (41.4 mg, 72%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 85/15, flow = 1.0 mL/min, 254 nm) with tr = 7.0 min (major), 6.5 min (minor): 93.5 : 6.5 er. $[\alpha]_D^{20}$ = 134.5 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 - 7.35 (m, 12 H), 6.33 (s, 1 H), 6.30 (s, 1 H), 5.74 (d, *J* = 16.1 Hz, 1 H), 5.69 (d, *J* = 16.1 Hz, 1 H), 5.00 - 5.10 (m, 4 H), 2.56 (s, 3 H), 2.52 (s, 3 H), 2.35 (s, 3 H), 2.26 (s, 3 H), 2.08 (s, 3 H), 2.07 (s, 3 H), 2.04 (s, 3 H), 1.98 (s, 3 H). ap/p=47/53.
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.9, 156.8, 156.8, 156.7, 156.7, 147.6, 147.3, 147.3, 139.1, 139.0, 138.3, 138.2, 137.3, 136.7, 135.9, 135.9, 135.7, 135.6, 135.0, 134.4, 132.8, 132.8, 132.7, 132.4, 131.5, 131.4, 130.9, 130.5, 129.9, 129.8, 128.6, 128.5, 128.3, 128.3, 128.2, 128.2, 127.5, 126.5, 117.9, 117.4, 66.2, 66.1, 15.5, 15.4, 15.2, 15.1, 15.0, 14.8, 14.3, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{28}H_{23}N_4O_2S_4^+$: 575.0698; found: 575.0701.



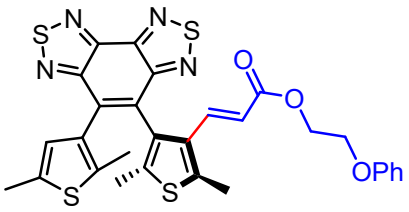
(tetrahydrofuran-2-yl)methyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3s:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 7 : 2 : 1 to give **3s** as red oil (37.0 mg, 65%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 10.7 min (major), 12.7 min (minor): 89.5 : 10.5 dr. $[\alpha]_D^{20}$ = 123.1 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 - 7.32 (m, 2 H), 6.37 (s, 1 H), 6.32 (s, 1 H), 5.76 (dd, *J* = 16.1, 2.8 Hz, 1 H), 5.71 (dd, *J* = 16.1, 2.8 Hz, 1 H), 3.88 - 4.18 (m, 6 H), 3.66 - 3.82 (m, 4 H), 2.56 (s, 3 H), 2.53 (s, 3 H), 2.36 (s, 3 H), 2.32 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 1.75 - 1.98 (m, 6 H), 1.40 - 1.55 (m, 2 H). ap/p=47/53.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 167.2, 156.8, 156.8, 156.7, 147.6, 147.3, 139.1, 139.1, 139.0, 138.3, 138.2, 138.1, 138.1, 137.3, 137.3, 136.6, 135.7, 135.7, 135.6, 134.9, 134.3, 132.8, 132.8, 132.8, 132.7, 132.4, 132.4, 131.6, 131.6, 131.4, 131.3, 131.0, 131.0, 130.5, 130.5, 130.0, 129.9, 129.9, 127.5, 126.5, 126.5, 117.8, 117.8, 117.4, 117.3, 68.4, 68.4, 66.5, 66.5, 66.4, 27.9, 27.9, 25.6, 25.6, 15.6, 15.6, 15.4, 15.4, 15.2, 15.1, 15.0, 14.8, 14.3, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{26}H_{25}N_4O_3S_4^+$: 569.0804; found: 569.0807.



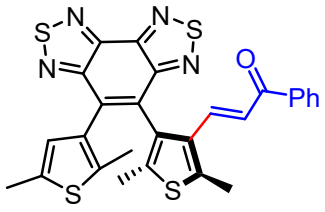
2-phenoxyethyl *(E)*-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3t:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 7 : 2 : 1 to give **3t** as red oil (33.2 mg, 55%,). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 92/8, flow = 0.8 mL/min, 254 nm) with tr = 16.0 min (major), 14.5 min (minor): 88 : 12 er. $[\alpha]_D^{20}$ = 118.4 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 - 7.31 (m, 6 H), 6.92 - 6.98 (m, 2 H), 6.86 - 6.78 (m, 4 H), 6.42 (d, *J* = 16.3 Hz, 1 H), 6.28 (d, *J* = 16.3 Hz, 1 H), 5.65 - 5.77 (m, 2 H), 4.32 - 4.46 (m, 4 H), 4.06 - 4.16 (m, 4 H), 2.56 (s, 3 H), 2.52 (s, 3 H), 2.34 (s, 3 H), 2.30 (s, 3 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H). ap/p=47/53.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 167.0, 158.3, 156.8, 156.8, 156.7, 156.7, 147.6, 147.6, 147.3, 147.3, 139.2, 139.1, 138.5, 138.3, 137.3, 136.7, 135.8, 135.6, 135.0, 134.5, 132.8, 132.8, 132.7, 132.5, 131.5, 131.4, 130.9, 130.5, 129.9, 129.8, 129.6, 127.6, 126.5, 121.2, 121.2, 117.7, 117.2, 114.5, 114.5, 65.7, 62.8, 62.7, 15.5, 15.4, 15.2, 15.1, 15.1, 14.8, 14.4, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{29}H_{25}N_4O_3S_4^+$: 605.0804; found: 605.0805.



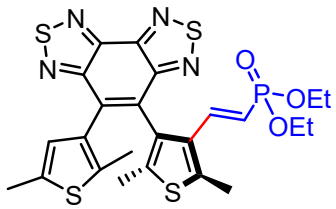
(E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)-1-phenylprop-2-en-1-one 3u:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 15 : 4 : 1 to give **3u** as red oil (26.1 mg, 48%,). The ee value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 12.7 min (major), 9.0 min (minor): 87 : 13 er. $[\alpha]_D^{20}$ = 146.0 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.62 (m, 12 H), 6.80 (d, *J* = 16.3 Hz, 1 H), 6.72 (d, *J* = 16.3 Hz, 1 H), 6.36 (s, 1 H), 6.34 (s, 1 H), 2.66 (s, 3 H), 2.62 (s, 3 H), 2.37 (s, 3 H), 2.18 (s, 3 H), 2.13 (s, 3 H), 2.12 (s, 3 H), 2.08 (s, 3 H), 1.99 (s, 3 H). ap/p=42/58.

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 190.0, 156.9, 156.8, 156.8, 147.6, 147.6, 147.3, 147.3, 140.2, 139.6, 138.1, 138.0, 137.7, 137.5, 137.4, 136.6, 135.8, 135.7, 135.1, 134.6, 133.0, 133.0, 132.8, 132.7, 132.7, 132.5, 132.4, 132.3, 131.0, 130.5, 130.2, 130.1, 128.6, 128.5, 128.0, 127.9, 127.2, 126.6, 122.4, 121.4, 15.7, 15.4, 15.2, 15.1, 15.1, 14.9, 14.4, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{27}H_{21}N_4OS_4^+$: 545.0593; found: 545.0597.



diethyl (*E*)-(2-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)vinyl)phosphonate 3v:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 4 : 3 : 3 to give **3v** as red oil (42.6 mg, 74%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 85/15, flow = 1.0 mL/min, 254 nm) with tr = 7.0 min (minor), 6.5 min (major): 93.5 : 6.5 er. $[\alpha]_D^{20}$ = 84.7 (c = 1.0, $CHCl_3$)

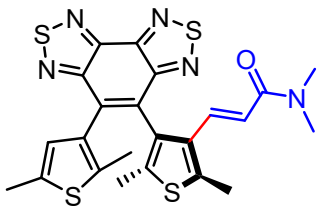
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 24.1, 17.7 Hz, 1 H), 7.07 (dd, *J* = 24.1, 17.7 Hz, 1 H), 6.45 (s, 1 H), 6.32 (s, 1 H), 5.27 - 5.50 (m, 2 H), 3.70 - 3.95 (m, 8 H), 2.56 (s, 3 H), 2.55 (s, 3 H), 2.39 (s, 3 H), 2.33 (s, 3 H), 2.19 (s, 3 H), 2.09 (s, 3 H), 2.02 (s, 3 H), 1.98 (s, 3 H), 1.08 - 1.21 (m, 12 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 156.9, 156.8, 156.6, 147.6, 147.5, 147.3, 147.3, 141.6, 141.6, 141.4, 141.4, 139.0, 138.7, 137.1, 136.6, 135.9, 135.7, 134.9, 134.4, 132.8, 132.8, 132.5, 132.2, 132.1, 132.0, 131.8, 131.6, 131.0, 130.4,

130.1, 130.0, 127.0, 126.9, 115.2, 114.5, 113.3, 112.7, 61.5, 61.5, 61.5, 61.4, 16.3, 16.2, 15.3, 15.3, 15.2, 15.1, 15.0, 14.9, 14.3, 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.5.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{24}H_{26}N_4O_3S_4P^+$: 577.0620; found: 577.0620.



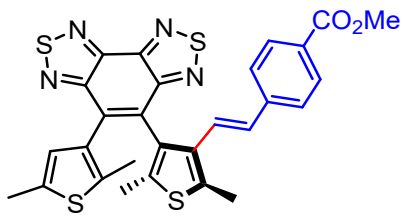
(E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)-N,N-dimethylacrylamide 3w:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 5 : 2 : 3 to give **3w** as red oil (43.5 mg, 85%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 85/15, flow = 1.0 mL/min, 254 nm) with tr = 14.6 min (major), 16.6 min (minor): 90 : 10 er. $[\alpha]_D^{20}$ = 98.6 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 15.6 Hz, 1 H), 7.17 (d, *J* = 15.6 Hz, 1 H), 6.37 (s, 1 H), 6.33 (s, 1 H), 6.11 (d, *J* = 16 Hz, 1 H), 6.00 (d, *J* = 16 Hz, 1 H), 2.88 (s, 3 H), 2.85 (s, 3 H), 2.75 (s, 3 H), 2.56 (s, 3 H), 2.52 (s, 3 H), 2.49 (s, 3 H), 2.37 (s, 3 H), 2.30 (s, 3 H), 2.18 (s, 3 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.00 (s, 3 H). ap/p=40/60.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.5, 157.0, 156.9, 156.8, 156.6, 147.5, 147.4, 147.2, 137.9, 137.2, 136.8, 136.4, 135.7, 135.6, 135.5, 135.2, 134.5, 134.1, 132.8, 132.7, 132.6, 132.6, 132.6, 131.9, 131.1, 130.7, 130.6, 130.4, 127.1, 126.7, 118.4, 117.0, 37.0, 36.6, 35.8, 35.7, 15.3, 15.2, 15.1, 15.0, 14.9, 14.3, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{22}N_5OS_4^+$: 512.0702; found: 512.0700.



methyl (*E*)-4-(2-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)vinyl)benzoate 3x:

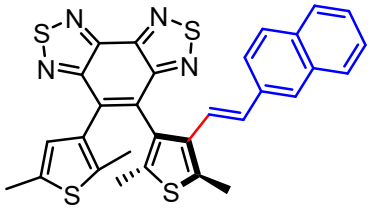
A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 7 : 2 : 1 to give **3x** as red oil (37.0 mg, 65%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol =

97/3, flow = 1.0 mL/min, 254 nm) with tr = 9.4 min (major), 10.6 min (minor): 92.5 : 7.5 er. $[\alpha]_D^{20}$ = 115.8 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) 7.80 - 7.89 (m, 4 H), 7.06 - 7.17 (m, 4 H), 6.65 (d, *J* = 16 Hz, 1 H), 6.62 (d, *J* = 16 Hz, 1 H), 6.25 - 6.37 (m, 4 H), 3.87 (s, 3 H), 3.86 (s, 3 H), 2.56 (s, 3 H), 2.54 (s, 3 H), 2.37 (s, 3 H), 2.18 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.07 (s, 3 H), 1.84 (s, 3 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) 166.8, 157.0, 156.8, 147.5, 147.2, 142.0, 137.1, 136.7, 135.4, 134.7, 134.0, 133.8, 132.6, 132.3, 132.1, 132.0, 131.1, 130.7, 130.6, 130.6, 129.9, 129.8, 129.6, 129.1, 128.6, 128.5, 126.7, 125.8, 125.1, 52.1, 15.2, 15.1, 14.8, 14.5, 14.4.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{28}H_{23}N_4O_2S_4^+$: 575.0698; found: 575.0700.



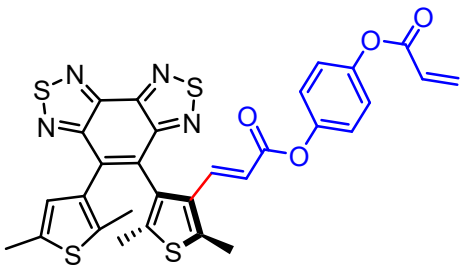
(E)-4-(2,5-dimethyl-4-(2-(naphthalen-2-yl)vinyl)thiophen-3-yl)-5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole) 3y:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 90 : 10 : 1 to give **3y** as red oil (36.8 mg, 65%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 92/8, flow = 0.8 mL/min, 254 nm) with tr = 4.9 min (major), 5.5 min (minor): 87.5 : 12.5 er. $[\alpha]_D^{20}$ = 134.8 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 - 7.76 (m, 6 H), 7.34 - 7.48 (m, 6 H), 7.27 - 7.30 (m, 2 H), 6.60 - 6.70 (m, 2 H), 6.34 - 6.47 (m, 4 H), 2.58 (s, 3 H), 2.56 (s, 3 H), 2.39 (s, 3 H), 2.19 (s, 3 H), 2.10 (s, 6 H), 2.08 (s, 3 H), 1.87 (s, 3 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 157.1, 157.0, 147.5, 147.3, 147.3, 137.1, 136.5, 135.4, 135.4, 135.0, 134.9, 134.4, 133.8, 133.5, 133.0, 132.8, 132.5, 132.3, 132.1, 132.0, 131.3, 131.0, 130.8, 130.5, 128.1, 127.8, 127.7, 127.6, 126.7, 126.3, 126.3, 126.0, 125.8, 123.0, 122.9, 15.3, 15.2, 15.1, 15.0, 14.8, 14.5, 14.5, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{30}H_{23}N_4S_4^+$: 567.0800; found: 567.0805.



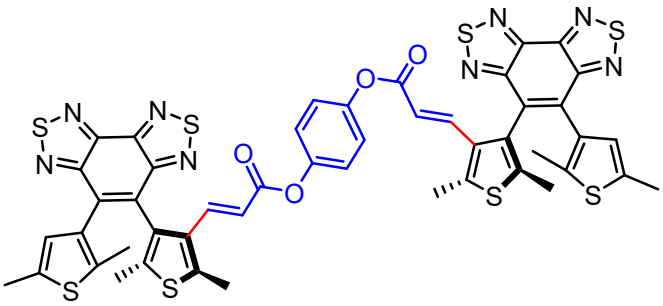
4-(acryloyloxy)phenyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3z-mono:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 7 : 2 : 1 to give **3z-mono** as red oil (47.3 mg, 75%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 95/5, flow = 1.0 mL/min, 254 nm) with tr = 20.5 min (major), 32.4 min (minor): 95.5 : 4.5 er. $[\alpha]_D^{20}$ = 162.8 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 16.2 Hz, 1 H), 7.37 (d, *J* = 16.2 Hz, 1 H), 6.96 - 7.14 (m, 8 H), 6.54 - 6.63 (m, 2 H), 6.24 - 6.46 (m, 4 H), 5.97 - 6.01 (m, 2 H), 5.87 (d, *J* = 16.2 Hz, 1 H), 5.81 (d, *J* = 16.2 Hz, 1 H), 2.63 (s, 3 H), 2.59 (s, 3 H), 2.36 (s, 6 H), 2.13 (s, 3 H), 2.11 (s, 3 H), 2.10 (s, 3 H), 2.07 (s, 3 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.4, 164.4, 156.8, 156.7, 156.6, 148.1, 148.0, 147.8, 147.6, 147.3, 140.2, 140.0, 139.8, 139.6, 137.3, 136.8, 135.9, 135.8, 135.2, 134.7, 132.9, 132.8, 132.7, 132.5, 131.4, 131.2, 130.9, 130.5, 129.8, 129.7, 127.7, 127.4, 126.5, 122.4, 122.3, 116.8, 116.3, 15.6, 15.5, 15.3, 15.2, 14.8, 14.4, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{30}H_{23}N_4O_4S_4^+$: 631.0597; found: 631.0595.



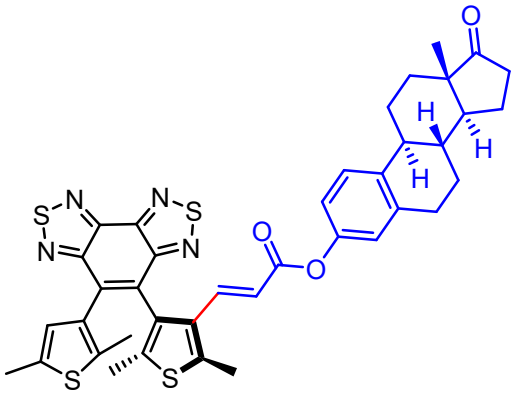
4-(acryloyloxy)phenyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3z-di:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 7 : 2 : 1 to give **3z-di** as red oil (57.4 mg, 55%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 85/15, flow = 1.0 mL/min, 254 nm) with tr = 28.4 min, 40.3 min, 56.1 min: 92 : 7.9 : 0.1. $[\alpha]_D^{20}$ = 130.1 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 16.1, 2.4 Hz, 2 H), 7.34 (dd, *J* = 16.1, 2.4 Hz, 2 H), 6.88 - 6.97 (m, 8 H), 6.40 (s, 2 H), 6.28 (s, 2 H), 5.83 (dd, *J* = 16.1, 1.6 Hz, 2 H), 5.77 (dd, *J* = 16.1, 1.6 Hz, 2 H), 2.60 (s, 6 H), 2.57 (s, 6 H), 2.35 (s, 6 H), 2.33 (s, 6 H), 2.11 (s, 6 H), 2.10 (s, 6 H), 2.09 (s, 6 H), 2.06 (s, 6 H). ap/p=45/55 (calculated based on single DAE unit).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.4, 156.7, 156.6, 147.9, 147.8, 147.8, 147.6, 147.3, 147.3, 140.1, 140.0, 139.7, 139.5, 137.3, 136.8, 135.9, 135.7, 135.2, 134.7, 132.9, 132.8, 132.7, 132.4, 131.3, 131.2, 130.9, 130.5, 129.8, 129.7, 127.4, 126.4, 122.2, 122.2, 116.8, 116.2, 15.6, 15.5, 15.3, 15.2, 14.8, 14.4, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{48}H_{34}N_8O_4S_8Na^+$: 1065.0361; found: 1065.0360.



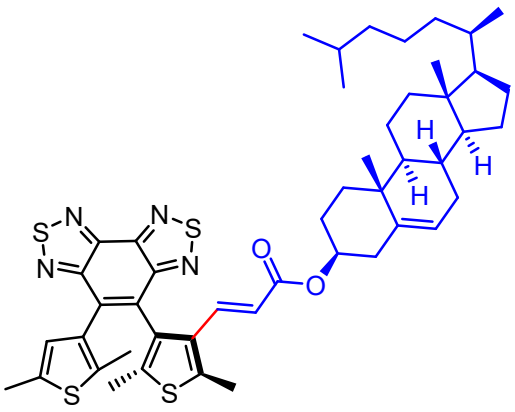
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (*E*)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3aa:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 7 : 2 : 1 to give **3aa** as red oil (49.4 mg, 67%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 35.9 min (major), 45.7 min (minor): 94 : 6 er. $[\alpha]_D^{20}$ = 175.9 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 16.1 Hz, 1 H), 7.35 (d, *J* = 16.1 Hz, 1 H), 7.19 - 7.25 (m, 2 H), 6.67 - 6.81 (m, 4 H), 6.40 (s, 1 H), 6.30 (s, 1 H), 5.87 (d, *J* = 16.1 Hz, 1 H), 5.81 (d, *J* = 16.1 Hz, 1 H), 2.80 - 2.93 (m, 4 H), 2.62 (s, 3 H), 2.58 (s, 3 H), 2.52 (d, *J* = 8.8 Hz, 1 H), 2.47 (d, *J* = 8.8 Hz, 1 H), 2.33 - 2.41 (m, 8 H), 2.20 - 2.30 (m, 2 H), 1.90 - 2.20 (m, 20 H), 1.36 - 1.68 (m, 12 H), 0.85 - 0.93 (m, 6 H). ap/p=44/56.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.8, 156.8, 156.7, 156.6, 148.5, 148.4, 147.6, 147.3, 147.3, 140.0, 139.8, 139.4, 139.2, 138.0, 137.3, 137.3, 136.8, 135.9, 135.7, 135.2, 134.6, 132.9, 132.8, 132.7, 132.4, 131.4, 131.2, 130.9, 130.5, 129.9, 129.8, 127.4, 126.5, 126.4, 121.5, 118.6, 117.2, 116.6, 50.4, 48.0, 44.1, 38.0, 35.9, 31.5, 29.4, 26.3, 25.7, 21.6, 15.6, 15.5, 15.3, 15.2, 14.9, 14.4, 14.3, 13.8.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{39}H_{37}N_4O_3S_4^+$: 737.1743; found: 737.1745.



(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 3ab:

A purification by flash chromatography in petroleum ether : dichloromethane : ethyl acetate = 7 : 2 : 1 to give **3ab** as red oil (55.5 mg, 65%,). The ee value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 97/3, flow = 1.0 mL/min, 254 nm) with tr = 6.8 min (major), 10.4 min (minor): 93 : 7 er. $[\alpha]_D^{20}$ = 99.2 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 - 7.28 (m, 2 H), 6.38 (s, 1 H), 6.28 (s, 1 H), 5.57 - 5.68 (m, 2 H), 5.28 - 5.35 (m, 2 H), 4.45 - 4.60 (m, 2 H), 2.56 (s, 3 H), 2.51 (s, 3 H), 2.34 (s, 3 H), 2.32 (s, 3 H), 2.17 - 2.27 (m, 4 H), 2.02 - 2.13 (m, 12 H), 1.89 - 2.02 (m, 4 H), 1.70 - 1.89 (m, 6 H), 0.80 - 1.60 (m, 66 H), 0.66 (s, 6 H). ap/p=44/56.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.6, 156.9, 156.8, 156.7, 147.7, 147.3, 139.7, 138.8, 138.6, 137.6, 137.4, 137.3, 136.7, 135.7, 135.6, 134.8, 134.4, 132.8, 132.8, 132.7, 132.4, 131.8, 131.6, 131.0, 130.5, 130.1, 130.1, 127.5, 126.5, 122.7, 118.8, 118.3, 74.1, 74.0, 56.7, 56.2, 50.0, 42.3, 39.8, 39.6, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.9, 29.8, 29.4, 28.3, 28.1, 27.8, 24.3, 23.9, 22.9, 22.6, 21.1, 19.4, 18.8, 15.4, 15.2, 15.1, 14.9, 14.4, 14.6, 11.9.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{48}H_{61}N_4O_2S_4^+$: 853.3672; found: 853.3673.

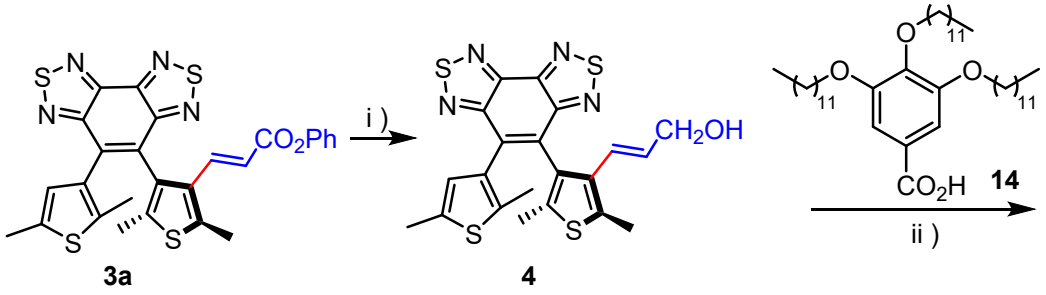
2.3 Synthetic Application

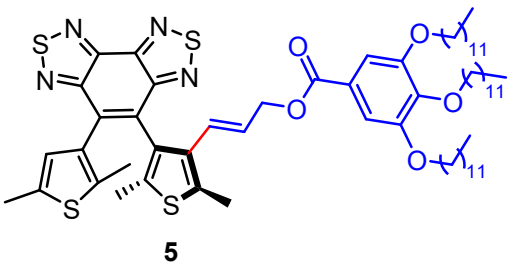
2.3.1 Scale-up of C-H Olefination for 3a

To an oven-dried 100 mL Schlenk tube containing a stirring bar was added **1** (829.2 mg, 2 mmol), **2a** (444.5 mg, 3 mmol), $Pd(OAc)_2$ (44.8 mg, 0.2 mmol), **L2** (287.6 mg, 0.4 mmol), AgOAc (667.6 mg, 4 mmol), and $CHCl_3$/*o*-DCB/$^nBu_2O$ (13.3 mL/13.3 mL/13.3 mL). The reaction flask was degassed three times with Ar. The reaction mixture was then stirred at 55 °C (aluminum heat transfer block) for 60 h in the dark. After cooling to room temperature, the mixture was diluted with dichloromethane, filtrated through celite. After concentration, the resulting residue was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 15: 4: 1 to afford the product **3a** as red foam (829.9 mg, 74% yield, 95.5:4.5 er). The er value was determined by chiral HPLC.

2.3.2 Derivatizations of 3a

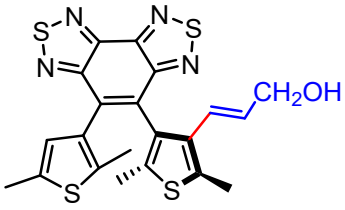
a) Synthesis of 5





i. Synthesis of **4**

To an oven-dried 10 mL tube was added **3a** (112.1mg, 0.2 mmol), dry THF (4.0 mL). The tube was charged with Ar for more than three times and cooled to -78°C. Then DIBAL-H (5.0 equiv) was added slowly at this temperature. After completed, the reaction mixture was allowed to stir at -78 °C overnight. Then the reaction was quenched by saturated NH_4Cl solution, extracted by EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by preparative TLC using petroleum ether: dichloromethane: ethyl acetate = 3: 1: 1 to afford the product **4** as a red foam (81.9 mg, 87% yield, 97:3 er). The er value was determined by chiral HPLC.



(E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)allyl 3,4,5-tris(dodecyloxy)benzoate 4:

The er value was determined by HPLC analysis on a Chiralcel AS-H column (hexane/isopropanol = 95/5, flow = 0.8 mL/min, 254 nm) with tr = 25.5 min (minor), 28.8 min (major): 97 : 3 er. $[\alpha]_D^{20}$ = 95.6 (c = 1.0, $CHCl_3$)

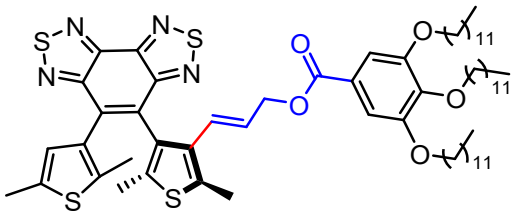
^{1}H NMR (400 MHz, DMSO-d6) δ 6.46 (s, 1 H), 6.33 (s, 1 H), 6.13 (s, 1 H), 6.03 (s, 1 H), 5.43 - 5.53 (m, 2 H), 4.42 - 4.53 (m, 2 H), 3.71 - 3.78 (m, 4 H), 2.41 (s, 3 H), 2.37 (s, 3 H), 2.32 (s, 3 H), 2.27 (s, 3 H), 2.12 (s, 3 H), 2.01 (s, 3 H), 2.00 (s, 3 H), 1.92 (s, 3 H). ap/p=46/54.

^{13}C NMR (101 MHz, DMSO-d6) δ 157.3, 157.2, 157.2, 156.9, 147.8, 147.8, 147.6, 147.5, 136.1, 136.1, 134.6, 134.5, 134.4, 134.2, 133.2, 132.9, 132.7, 132.6, 132.5, 132.2, 132.1, 132.0, 131.7, 131.3, 131.2, 131.1, 127.8, 127.7, 122.7, 122.5, 62.1, 15.3, 15.0, 14.8, 14.6, 14.3, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{21}H_{18}N4OS_4Na^+$: 493.0256; found: 493.0255.

ii. Synthesis of **5**

To a solution of **4** (81.9 mg, 0.17 mmol) in dry CH_2Cl_2 (2 mL) at room temperature were sequentially added and **14** (236.3 mg, 0.35 mmol, 2.0 equiv), DMAP (11.0 mg, 0.09 mmol, 0.5 equiv), DCC (72.2 mg, 0.35 mmol, 2.0 equiv) under argon atmosphere. The reaction mixture was stirred at that temperature. The progress of the reaction was monitored by TLC. The reaction was quenched by adding water and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 40: 10: 1 to afford the product **5** as red oil (178.3 mg, 93% yield, 96:4 er).



(E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)allyl 3,4,5-tris(dodecyloxy)benzoate 5:

The er value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 98/2, flow = 0.4

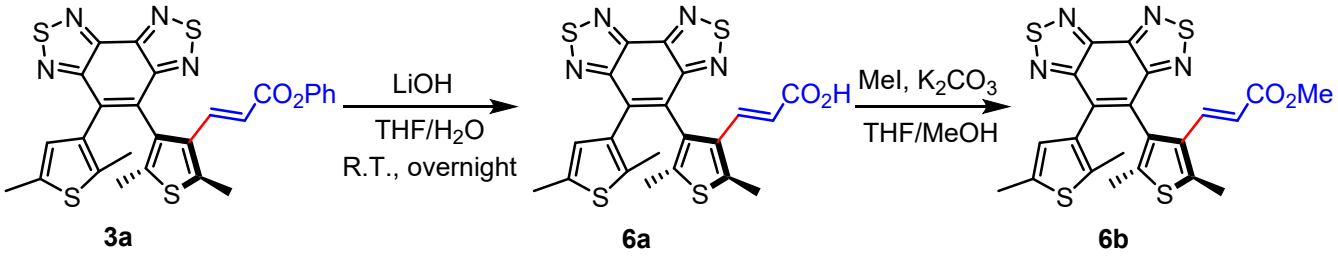
mL/min, 254 nm) with tr = 27.2 min (minor), 30.4 min (major): 96 : 4 er. $[\alpha]_D^{20}$ = 40.0 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 2 H), 7.04 (s, 2 H), 6.44 (s, 1 H), 6.33 (s, 1 H), 6.29 (d, *J* = 16 Hz, 1 H), 6.20 (d, *J* = 16 Hz, 1 H), 5.53 - 5.69 (m, 2 H), 4.50 - 4.65 (m, 4 H), 3.90 - 4.08 (m, 12 H), 2.50 (s, 3 H), 2.47 (s, 3 H), 2.39 (s, 3 H), 2.37 (s, 3 H), 2.16 (s, 3 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 1.98 (s, 3 H), 1.70 - 1.88 (m, 12 H), 1.20 - 1.54 (m, 108 H), 0.85 - 0.92 (m, 18 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 157.0, 156.9, 156.6, 152.8, 147.5, 147.4, 147.2, 142.4, 142.3, 136.5, 136.4, 135.5, 135.4, 134.1, 133.8, 133.7, 133.3, 133.0, 132.4, 132.3, 131.9, 131.7, 131.3, 130.9, 128.2, 128.1, 127.0, 125.2, 124.7, 124.3, 107.7, 73.5, 69.1, 65.8, 65.7, 32.0, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 26.1, 22.7, 15.2, 15.0, 14.8, 14.6, 14.3, 14.2, 14.0.

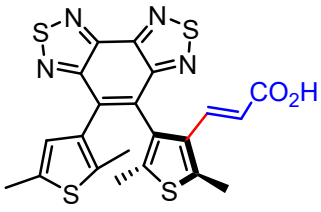
HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{64}H_{94}N_4O_5S_4Na^+$: 1149.5999; found: 1149.5998.

b) Synthesis of 6



3a **6a** **6b**

To an oven-dried 10 mL Schlenk tube was added **3a** (112.1 mg, 0.2 mmol), LiOH (14.4 mg, 3.0 equiv), THF/H_2O (1:1, 4.0 mL). The reaction was allowed to stir at room temperature under argon overnight. Then the reaction was quenched by water, extracted by EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by preparative TLC using petroleum ether: dichloromethane: ethyl acetate : acetic acid = 80: 20: 20: 3 to afford the product **6a** as a red foam(89.2 mg, 92% yield).
Then the methylation of acid **6b** was produced by adding K_2CO_3 (3.0 equiv), MeI (2.0 equiv), in THF/MeOH (2:1, 5 mL), at room temperature stirring for overnight.



(E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylic acid 6a:

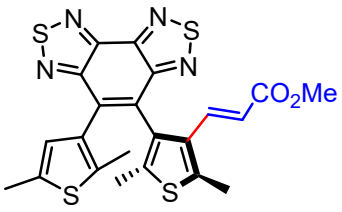
$[\alpha]_D^{20}$ = 144.9 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.10 (s, 2 H), 7.22 (d, *J* = 16.1 Hz, 1 H), 7.13 (d, *J* = 16.1 Hz, 1 H), 6.44 (s, 1 H), 6.31 (s, 1 H), 5.57 (t, *J* = 16.3 Hz, 2 H), 2.49 (s, 3 H), 2.32 (s, 3 H), 2.27 (s, 3 H), 2.10 (s, 3 H), 2.06 (s, 3 H), 2.01 (s, 3

H), 2.00 (s, 3 H), 1.93 (s, 3 H). ap/p=46/54.

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.5, 167.9, 156.9, 156.8, 147.8, 147.8, 147.6, 147.5, 138.6, 138.5, 137.2, 137.0, 7136.5, 136.3, 134.9, 134.8, 134.5, 132.9, 132.7, 132.5, 132.4, 132.0, 131.7, 131.5, 130.1, 127.7, 127.6, 119.2, 118.7, 21.5, 15.2, 15.0, 14.9, 14.3, 14.1.

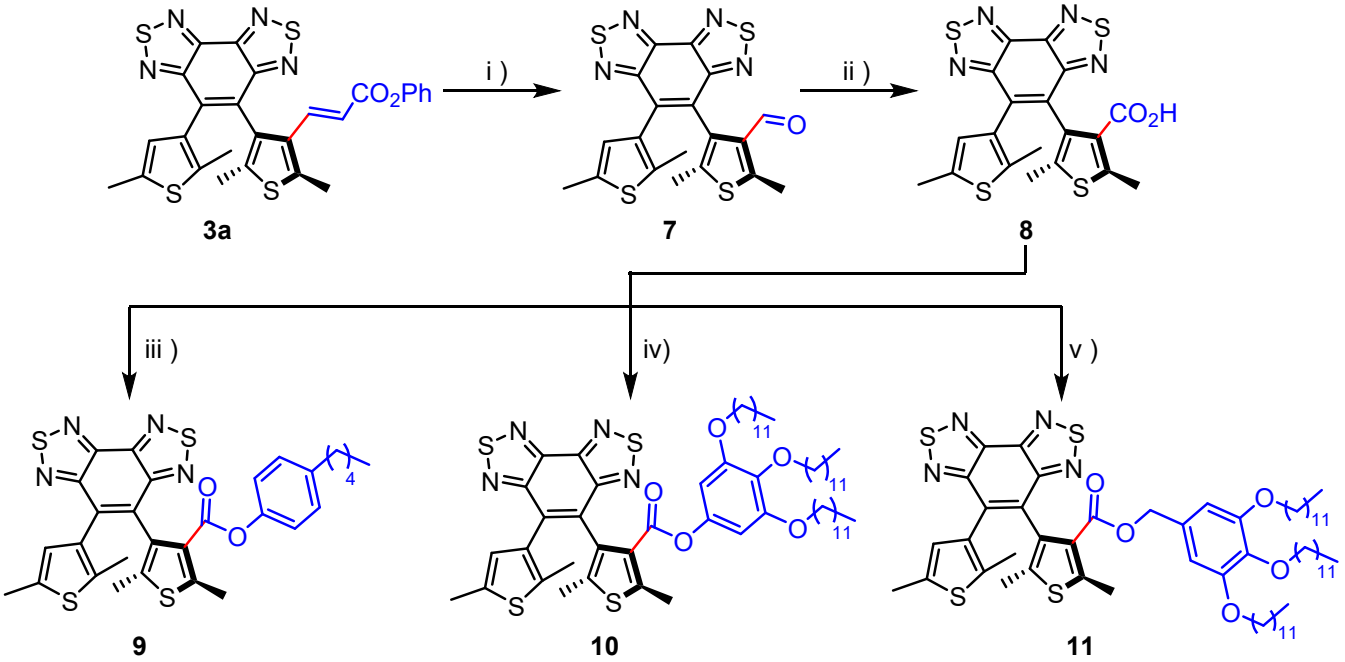
HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{21}H_{17}N_4O_2S_4$: 485.0229; found: 485.0227.



methyl (E)-3-(4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophen-3-yl)acrylate 6b:

The er value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 7.1 min (major), 5.9 min (minor): 96 : 4 er.

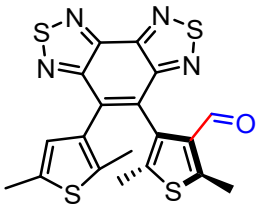
c) Synthesis of 9, 10, 11



i. Synthesis of **7**

To a solution of **3a** (829.9 mg, 1.48 mmol) in THF (38 mL) and H_2O (19 mL), K_2OsO_4•$2H_2O$ (81.8 mg, 0.22 mmol, 15 mol%) and $NaIO_4$ (3.17g, 14.8 mmol, 10 equiv) were added at 25 °C. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. The reaction mixture was then quenched with saturated

aqueous $Na_2S_2O_3$ and stirred vigorously for 30 min. The reaction mixture was extracted with EtOAc and then the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 15: 4: 1 to afford product **7** as red oil (563.3 mg, 86% yield, 95:5 er).



4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophene-3-carbaldehyde 7:

The er value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol = 97/3, flow = 1.0 mL/min, 254 nm) with tr = 10.5 min (major), 15.0 min (minor): 95 : 5 er. $[\alpha]_D^{20}$ = -6.3 (c = 1.0, $CHCl_3$)

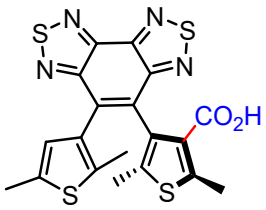
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, *J* = 3.6 Hz, 2 H), 6.61 (d, *J* = 1.3 Hz, 1 H), 6.19 (d, *J* = 1.3 Hz, 1 H), 2.80 (s, 3 H), 2.78 (s, 3 H), 2.44 (s, 3 H), 2.32 (s, 3 H), 2.23 (s, 3 H), 2.00 (s, 6 H), 1.96 (s, 3 H). ap/p=50/50.

^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4, 184.2, 157.3, 156.6, 150.9, 150.8, 147.7, 147.6, 147.2, 147.1, 136.7, 136.2, 136.1, 136.1, 135.4, 135.1, 131.8, 131.6, 131.5, 131.4, 131.3, 130.8, 130.0, 129.9, 126.9, 15.4, 15.2, 15.0, 14.4, 14.2, 14.1, 14.0, 13.5.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{19}H_{15}N_4OS_4^+$: 443.0123; found: 443.0123.

ii. Synthesis of **8**

To a stirred solution of **7** (543.7 mg, 1.23 mmol) in *t*-BuOH : THF (12 : 5 mL) at room temperature were sequentially added 2-methyl-2-butene (862.6mg, 12.3 mmol, 10 equiv), NaH_2PO_4 solution (12.3 mL, 0.5 M, 6.25 mmol, 5.0 equiv), and $NaClO_2$ solution (3.7 mL, 1.0 M, 3.7 mmol, 3.0 equiv). The reaction mixture was stirred at that temperature. The progress of the reaction was monitored by TLC. The reaction mixture was then quenched with saturated aqueous $NaHSO_3$. The resulting mixture was extracted with EtOAc. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate : acetic acid= 80: 20: 20: 3 to afford the product **8** as red solid (473.8 mg, 84% yield). m.p. >200°C.



4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophene-3-

carboxylic acid 8:

$[\alpha]_D^{20}$ = 28.2 (c = 1.0, $CHCl_3$)

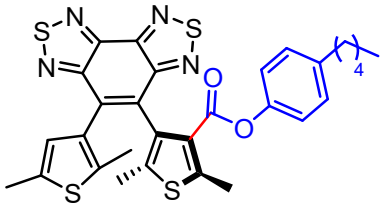
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.39 (s, 2 H), 6.76 (s, 1 H), 6.29 (s, 1 H), 2.69 (s, 3 H), 2.66 (s, 3 H), 2.43 (s, 3 H), 2.30 (s, 3 H), 2.29 (s, 3 H), 2.00 (s, 3 H), 1.96 (s, 3 H), 1.94 (s, 3 H). ap/p=47/53.

^{13}C NMR (101 MHz, DMSO-d_6) δ 164.9, 164.8, 158.0, 157.9, 157.6, 156.8, 147.5, 147.4, 147.2, 147.0, 144.6, 144.5, 136.3, 135.7, 135.0, 134.8, 134.0, 133.7, 133.2, 132.3, 132.1, 131.9, 131.8, 130.5, 130.3, 130.2, 130.0, 128.4, 127.3, 16.1, 15.9, 15.3, 15.2, 14.2, 14.0, 13.5.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{19}H_{15}N_4O_2S_4^+$: 459.0072; found: 459.0075.

iii. Synthesis of **9**

To a solution of **8** (355.4 mg, 0.77 mmol) in dry CH_2Cl_2 (7 mL) at room temperature were sequentially added and 4-Pentylphenol (189.7 mg, 1.16 mmol, 1.5 equiv), DMAP (47.0 mg, 0.39 mmol, 0.5 equiv), DCC (317.7 g, 1.54 mmol, 2.0 equiv) under argon atmosphere. The reaction mixture was stirred at that temperature. The progress of the reaction was monitored by TLC. The reaction was quenched by adding water and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 15: 4: 1 to afford product **9** as red foam (375.0 mg, 81% yield, 94 : 6 er).



4-pentylphenyl 4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophene-3-carboxylate 9:

The er value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 6.7 min (major), 7.7 min (minor): 94 : 6 er. $[\alpha]_D^{20}$ = 6.4 (c = 1.0, $CHCl_3$)

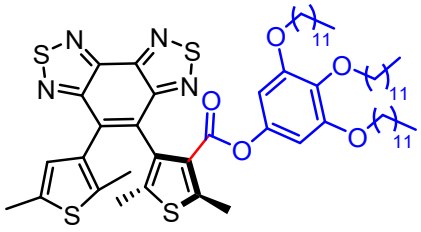
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (m, 4 H), 6.67 (s, 1 H), 6.35 (s, 1 H), 6.58 (m, 4 H), 2.82 (s, 3 H), 2.80 (s, 3 H), 2.48 - 2.52 (m, 4 H), 2.46 (s, 3 H), 2.35 (s, 3 H), 2.28 (s, 3 H), 2.04 (s, 3 H), 1.99 (s, 3 H), 1.98 (s, 3 H), 1.45 - 1.56 (m, 4 H), 1.20 - 1.33 (m, 8 H), 0.84 (t, *J* = 6.8 Hz, 6 H). ap/p=45/55.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 162.0, 157.9, 157.7, 157.5, 156.7, 147.9, 147.5, 147.4, 147.3, 147.2, 140.6, 140.5, 136.7, 136.2, 135.9, 135.8, 134.8, 134.5, 132.7, 131.3, 131.3, 131.0, 130.9, 129.2, 128.1, 127.7, 127.3, 127.1, 120.8, 35.2, 31.4, 31.1, 22.5, 16.4, 16.2, 15.4, 15.3, 15.2, 14.3, 14.1, 14.0, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{30}H_{28}N_4O_2S_4Na^+$: 627.0987; found: 627.0994.

iv. Synthesis of **10**

To a solution of **8** (78.2 mg, 0.17 mmol) in dry CH_2Cl_2 (2 mL) at room temperature were sequentially added and **19** (168.2 mg, 0.26 mmol, 1.5 equiv), DMAP (11.0 mg, 0.09 mmol, 0.5 equiv), DCC (70.2 g, 0.34 mmol, 2.0 equiv) under argon atmosphere. The reaction mixture was stirred at that temperature. The progress of the reaction was monitored by TLC. The reaction was quenched by adding water and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 15: 4: 1 to afford the product **10** as red oil (166.4 mg, 90% yield, 94.5 : 5.5 er).



3,4,5-tris(dodecyloxy)phenyl 4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-c:3,4-c']bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophene-3-carboxylate 10:

The er value was determined by HPLC analysis on a Chiralcel IF-3 column (hexane/isopropanol = 95/5, flow = 1.0 mL/min, 254 nm) with tr = 10.0 min (major), 13.6 min (minor): 94.5 : 5.5 er. $[\alpha]_D^{20}$ = 30.4 (c = 1.0, $CHCl_3$)

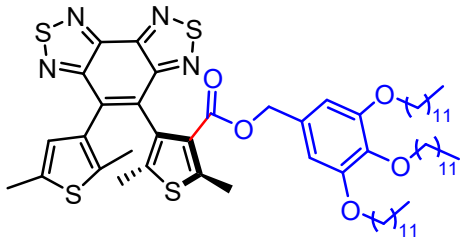
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1 H), 6.34 (s, 1 H), 5.82 (s, 1 H), 5.75 (s, 1 H), 3.65 - 3.94 (m, 12 H), 2.82 (s, 3 H), 2.80 (s, 3 H), 2.47 (s, 3 H), 2.35 (s, 3 H), 2.30 (s, 3 H), 2.04 (s, 3 H), 1.98 (s, 6 H), 1.60 - 1.78 (m, 12 H), 1.20 - 1.48 (m, 108 H), 0.84 - 0.92 (m, 18 H). ap/p=46/54.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 161.9, 157.9, 157.9, 157.5, 156.7, 153.2, 147.5, 147.4, 147.3, 145.6, 136.7, 136.3, 135.9, 135.8, 135.6, 134.9, 134.6, 132.6, 132.4, 131.7, 131.3, 131.2, 131.1, 131.0, 130.8, 128.1, 127.6, 127.3, 127.0, 99.4, 99.3, 73.4, 69.0, 32.0, 30.3, 29.8, 29.7, 29.6, 29.4, 29.3, 26.1, 22.7, 16.4, 16.2, 15.4, 15.3, 14.3, 14.2, 13.7.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{61}H_{91}N_4O_5S_4^+$: 1087.5868; found: 1087.5867.

v. Synthesis of **11**

To a solution of **8** (78.2 mg, 0.17 mmol) in dry CH_2Cl_2 (2 mL) at room temperature were sequentially added and **15** (171.9 mg, 0.26 mmol, 1.5 equiv), DMAP (11.0 mg, 0.09 mmol, 0.5 equiv), DCC (70.2 g, 0.34 mmol, 2.0 equiv) under argon atmosphere. The reaction mixture was stirred at that temperature. The progress of the reaction was monitored by TLC. The reaction was quenched by adding water and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 15: 4: 1 to afford the product **11** as red oil (146.1 mg, 78 % yield, 94.5:5.5 er).



3,4,5-tris(dodecyloxy)benzyl 4-(5-(2,5-dimethylthiophen-3-yl)benzo[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazole)-4-yl)-2,5-dimethylthiophene-3-carboxylate 11:

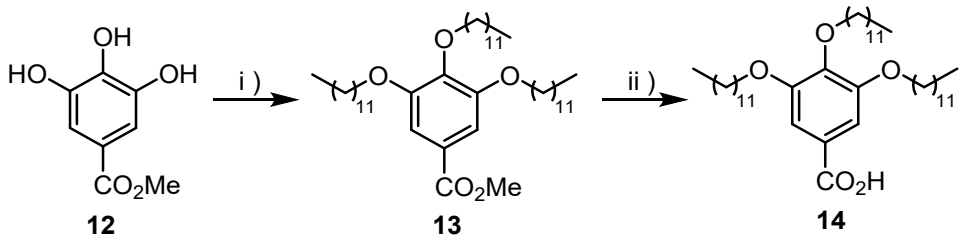
The ee value was determined by HPLC analysis on a Chiralcel IC column (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr = 4.8 min (major), 23.3 min (minor): 94.5 : 5.5 er. $[\alpha]_D^{20}$ = 22.2 (c = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 1 H), 6.20 (s, 1 H), 5.97 (s, 2 H), 5.85 (s, 2 H), 4.45 - 4.67 (m, 4 H), 3.50 - 3.97 (m, 12 H), 2.68 (s, 3 H), 2.64 (s, 3 H), 2.37 (s, 3 H), 2.24 (s, 3 H), 2.16 (s, 3 H), 1.94 (s, 3 H),1.83 (s, 3 H), 1.82 (s, 3 H), 1.60 - 1.78 (m, 12 H), 1.20 - 1.48 (m, 108 H), 0.74 - 0.86 (m, 18 H). ap/p=40/60.

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 163.2, 157.7, 157.6, 157.3, 156.2, 152.9, 152.7, 147.2, 147.0, 146.9, 146.8, 146.5, 146.4, 138.0, 137.7, 136.3, 136.2, 135.7, 135.5, 134.4, 134.1, 132.3, 132.2, 131.7, 131.5, 131.4, 130.9, 130.4, 129.5, 129.3, 128.6, 128.2, 127.4, 126.8, 106.5, 106.1, 73.4, 73.3, 68.9, 68.7, 66.6, 66.5, 32.0, 30.4, 29.8, 29.7, 29.5, 29.4, 26.2, 26.1, 22.7, 16.0, 15.8, 15.3, 15.2, 14.2, 14.0, 13.6.

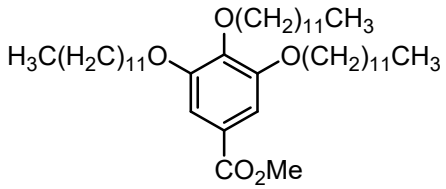
HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{62}H_{92}N_4O_5S_4Na^+$: 1123.5843; found: 1123.5845.

d) Synthesis of 14



i. Synthesis of **13**

To an oven-dried 100 mL round-bottom flask was added **12** (3.68 g, 20 mmol) and K_2CO_3 (11.06 g, 80 mmol, 4.0 equiv), dry DMF (60 mL). The flask was charged with Ar for more than three times. Treat the suspension with 1-bromododecane (17.94 g, 72 mmol, 3.6 equiv). The reaction mixture was allowed to stir vigorously at 70 °C overnight. The reaction was quenched by adding water and extracted with Et_2O for three times. The combined organic layers were washed with 0.5M HCl, water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 90: 10: 1 to afford the product **13** as white solid (10.34 g, 75%). m.p. 43.4-43.8°C.



methyl 3,4,5-tris(dodecyloxy)benzoate 13:

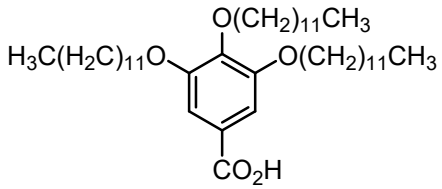
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2 H), 4.06 - 3.97 (m, 6 H), 3.88 (s, 3 H), 1.85 - 1.71 (m, 6 H), 1.51 - 1.44 (m, 6 H), 1.37 - 1.27 (m, 48 H), 0.88 (t, *J* = 6.7 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.97, 152.86, 142.33, 124.69, 107.93, 73.51, 69.15, 52.13, 32.01, 30.40, 29.83, 29.81, 29.78, 29.74, 29.71, 29.64, 29.47, 29.45, 29.36, 26.15, 26.13, 22.77, 14.18.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{44}H_{81}O_5$: 689.6079; found: 689.6082.

ii. Synthesis of **14**

To an oven-dried 50 mL round-bottom flask was added **13** (3.45 g, 5 mmol) and NaOH (0.40 g, 10 mmol, 2.0 equiv), MeOH/H_2O (1:2, 6 mL). A reflux condenser was affixed to the flask, and the mixture was heated to reflux overnight. After completion, the mixture was concentrated in vacuo. The mixture was neutralized by 2M HCl and extracted with DCM. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: ethyl acetate: acetic acid = 180: 20: 1 to afford the product **14** as white solid (2.94 g, 87%). m.p. 56.8-58.2℃.



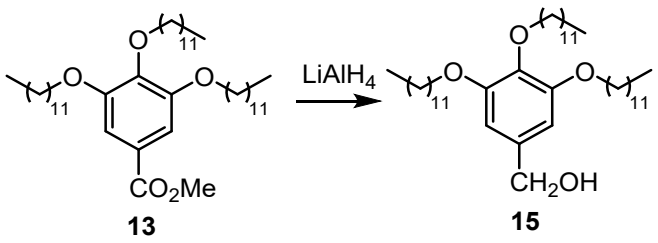
3,4,5-tris(dodecyloxy)benzoic acid 14:

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1 H), 7.37 (s, 2 H), 4.12 - 4.02 (m, 6 H), 1.89 - 1.76 (m, 6 H), 1.55 - 1.48 (m, 6 H), 1.41 - 1.30 (m, 48 H), 0.92 (t, *J* = 6.6 Hz, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 152.9, 143.2, 123.7, 108.6, 73.6, 69.2, 32.0, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 26.1, 22.8, 14.2.

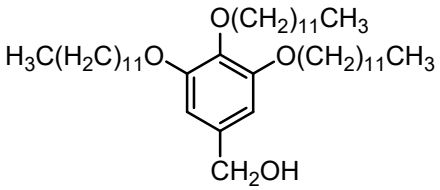
HRMS (ESI) m/z: $[M-H]^-$ Calculated for $C_{43}H_{77}O_5$: 673.5776; found: 673.5775.

e) Synthesis of 15



13 **15**

To an oven-dried 100 mL round-bottom flask was added $LiAlH_4$ (493.4 mg, 13 mmol), dry THF (20 mL). The flask was charged with Ar for more than three times. Treat the suspension dropwise with a solution of **13** (6.89 g, 10mmol) in THF (30 mL) at 0 °C over a period of 10 minutes. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. The reaction was quenched by slow addition of isopropyl alcohol (2 mL), water (3 mL) and 15% NaOH solution (2 mL). Filter the insoluble salts through a pad of Celite and concentrate the tiltrate under reduced pressure. The residue obtained was dissolved in CH_2Cl_2. The organic layers were washed with water, brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 15: 4: 1 to afford the product **15** as white solid (5.62 g, 85%). m.p. 47.2-49℃.



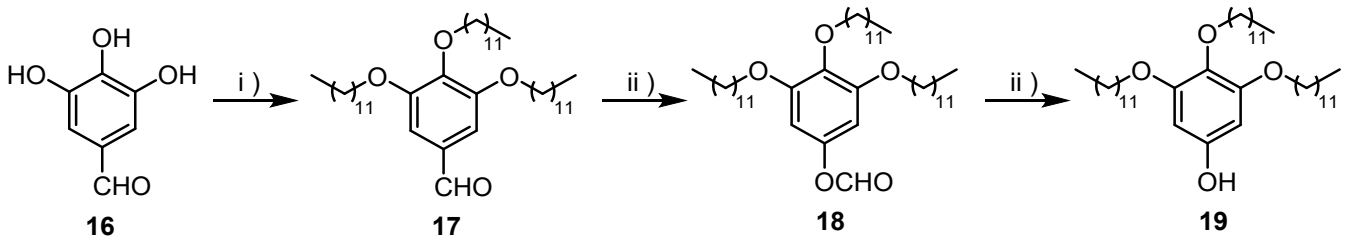
<u>(3,4,5-tris(dodecyloxy)phenyl)methanol 15:</u>

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 2 H), 4.58 (s, 2 H), 3.98 - 3.91 (m, 6 H), 1.83 - 1.70 (m, 7 H), 1.50 - 1.42 (m, 6 H), 1.36 - 1.30 (m, 48 H), 0.88 (t, *J* = 6.6 Hz, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 137.5, 136.1, 105.3, 73.5, 69.1, 65.7, 32.0, 30.4, 29.8, 29.7, 29.5, 29.4, 26.2, 22.8, 14.2.

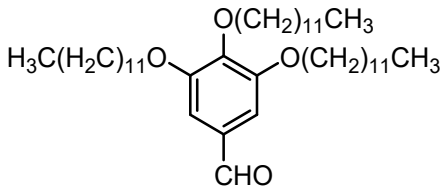
HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{43}H_{81}O_4$: 661.6129; found: 661.6131.

f) Synthesis of 19



i. Synthesis of **17**

To an oven-dried 100 mL round-bottom flask was added **16** (3.08 g, 20 mmol) and K_2CO_3 (11.06 g, 80 mmol, 4.0 equiv), dry DMF (60 mL). The flask was charged with Ar for more than three times. Treat the suspension with 1-bromododecane (17.94 g, 72 mmol, 3.6 equiv). The reaction mixture was allowed to stir vigorously at 70 °C overnight. The reaction was quenched by adding water and extracted with Et_2O for three times. The combined organic layers were washed with 0.5M HCl, water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: ethyl acetate = 200 : 1 to afford the product **17** as white solid(8.96 g, 68%). m.p. 49.1-49.8℃.



3,4,5-tris(dodecyloxy)benzaldehyde 17:

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1 H), 7.08 (s, 2 H), 4.16 - 3.97 (m, 6 H), 1.86 - 1.72 (m, 6 H), 1.51 - 1.44 (m, 6 H), 1.37 - 1.26 (m, 48 H), 0.88 (t, *J* = 6.7 Hz, 10 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 153.6, 143.8, 131.5, 107.8, 73.7, 69.3, 32.0, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 22.8, 14.2.

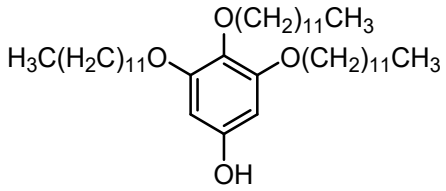
HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{43}H_{79}O_4$: 659.5973; found: 659.5976.

ii. Synthesis of **19**

To a stirred solution of **17** (659.1 mg, 1 mmol) in dry CH_2Cl_2 (5 mL) was added m-CPBA (85%, 304.5 mg, 1.5 mmol, 1.5 equiv) in portions at 0 °C over a period of 10 minutes. After 1 h, cooling was removed and the mixture was stirred at 50 °C overnight. The mixture was diluted with CH_2Cl_2 and washed with sat. $NaHCO_3$. The organic layers were washed with water, brine, dried over Na_2SO_4, and concentrated in vacuo to afford the crude product **18** without further purification.

To a stirred solution of **18** in MeOH (1 mL) was added KOH (56.1 mg, 1 mmol). The reaction mixture was stirred at room temperature for 30 min. The progress of the reaction was monitored by TLC. The residue obtained was dissolved in H_2O, and acidified with 1 M HCl to pH 5-6. The mixture was extracted with CH_2Cl_2 for three times. The combined

organic layers were washed with brine, dried over Na2SO4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography in petroleum ether: dichloromethane: ethyl acetate = 9:1 to afford the product **19** as brown solid (401.8 mg, 62%). m.p. 52.3-53.5℃.



3,4,5-tris(dodecyloxy)phenol 19:

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (s, 2 H), 5.34 (s, 1 H), 3.88 - 3.82 (m, 6 H), 1.79 - 1.66 (m, 6 H), 1.46 - 1.41 (m, 6 H), 1.32 - 1.26 (m, 48 H), 0.88 (t, *J* = 6.6 Hz, 9 H).

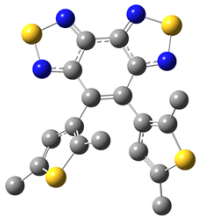
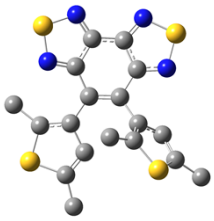
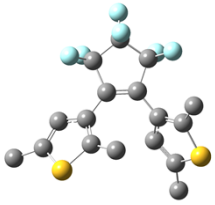
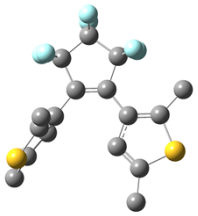
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 152.1, 131.5, 94.1, 73.8, 68.9, 32.0, 30.3, 29.9, 29.8, 29.7, 29.5, 29.4, 26.2, 22.79, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{42}H_{79}O_4$: 647.5976; found: 647.5973.

3. Computational Data of BTTE and 1b

The rotation barrier of the parallel conformers of BTTE and **1b** was calculated. Density functional theory (DFT) geometry optimization calculations were performed with M06-2X functional and def2-SVP basis set using Gaussian 16[S3]. THF was used in the SMD solvation model for energy calculation of optimized geometries. Gibbs free energy was calculated at 298.15K using Shermo 2.6[S4].

Table S2. Computational data and structures of BTTE-p and **1b**.

	BTTE-p	BTTE-TS	**1b-p**	**1b-TS**
Structure				
E/Hartree	-2506.0974870	-2506.0682780	-2051.7228040	-2051.7153000
G/Hartree	-2505.8580611	-2505.8277326	-2051.4948196	-2051.4866946
ΔG/(kcal mol^{-1})	19.03		5.10	

4. Crystallographic Data of 8

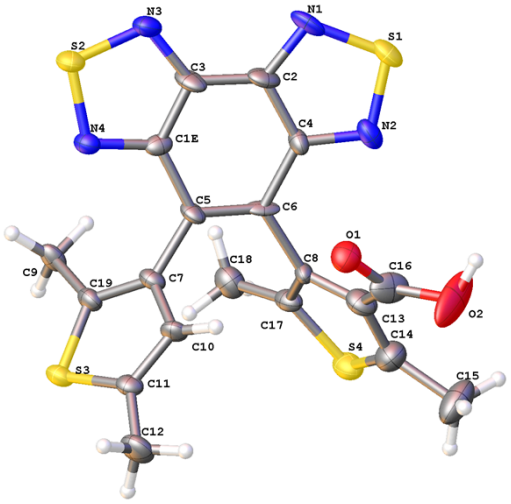


Fig. S1. Single crystal structure of **8**.

Table S3. Crystal data and structure refinement for **8**.

Compound	**8**
CCDC Number	2359686
Empirical formula	$C_{19}H_{14}N_4O_2S_4$
Formula weight	458.58
Temperature / K	170.00
Wavelength / Å	1.34139
Crystal system	Triclinic
Space group	P1
a / Å	7.7696(4)
b / Å	15.7256(8)
c / Å	19.9214(10)
α / deg	97.434(2)

β / deg	92.683(2)
γ / deg	90.008(2)
Volume / $Å^3$	2410.9(2)
Z	4
Density (calculated) / mg/mm^3	1.263
Absorption coefficient / mm^{-1}	2.505
F(000)	944
Crystal size / mm^3	0.17 x 0.17 x 0.05
Theta range for data collection / deg	2.465 to 54.876
Index ranges	-9<=h<=9, -19<=k<=19, 0<=l<=24
Reflections collected	8958
Independent reflections	8958 [R(int) = ?]
Completeness to theta = 53.594°	98.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5502
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	8958 / 33 / 1065
Goodness-of-fit on F2	1.037
Final R indices [I>2sigma(I)]	R_1 = 0.0665, wR_2 = 0.1691
R indices (all data)	R_1 = 0.0936, wR_2 = 0.1890
Absolute structure parameter	0.02(2)

5. 2D Spectra and ^{13}C NMR Assignments of 9

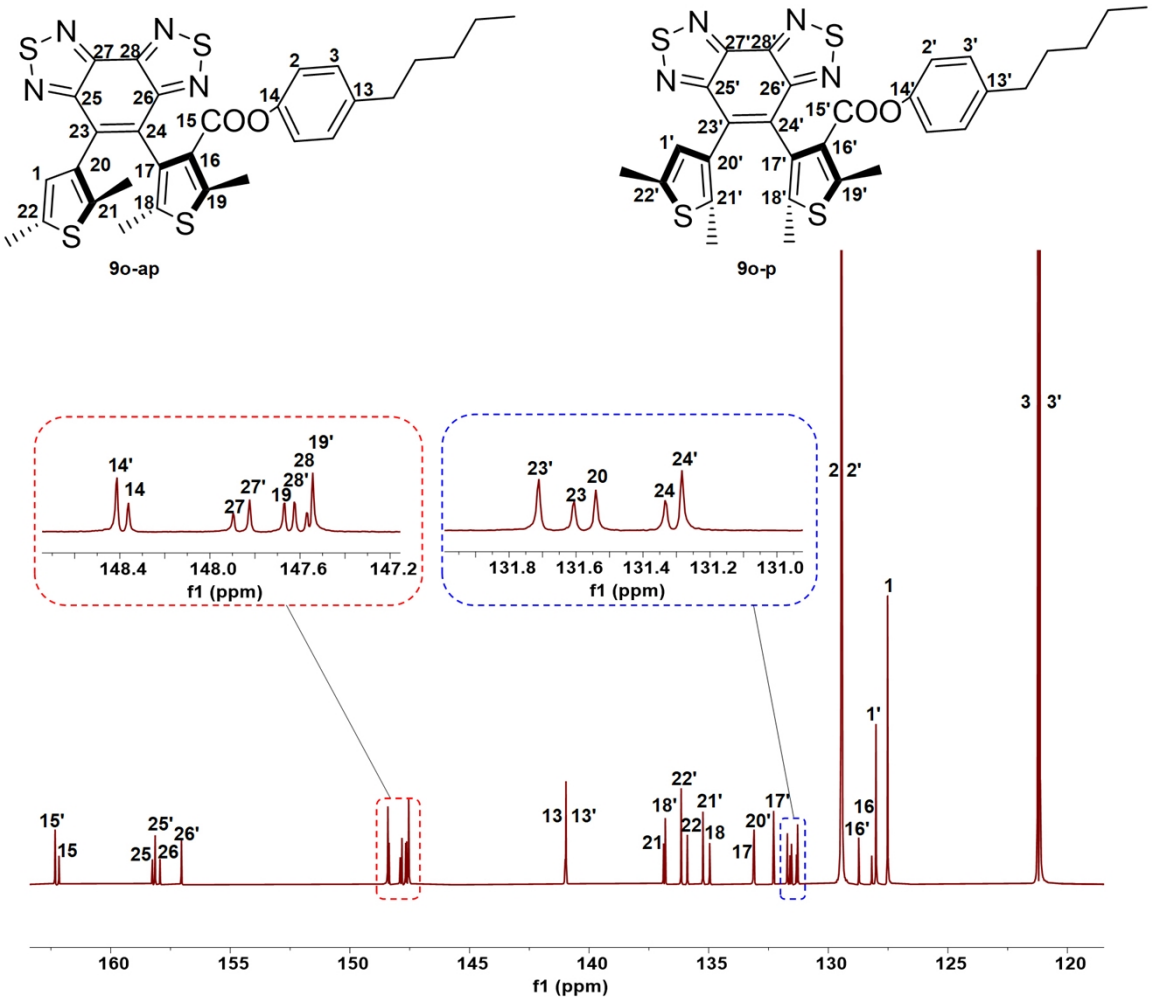


Fig. S2. Assignment of ^{13}C NMR spectrum of **9** in low field.

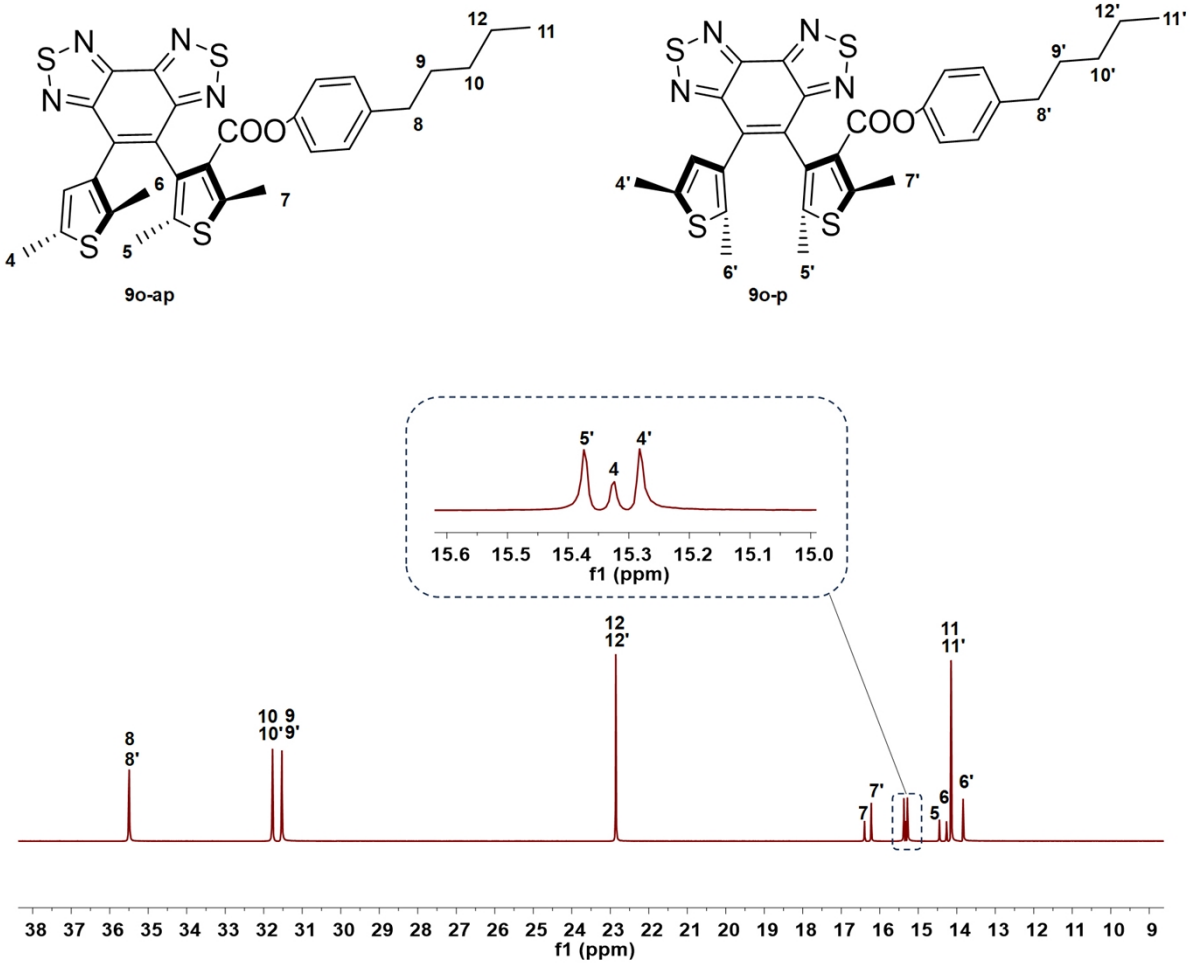


Fig. S3. Assignment of ^{13}C NMR spectrum of **9** in high field.

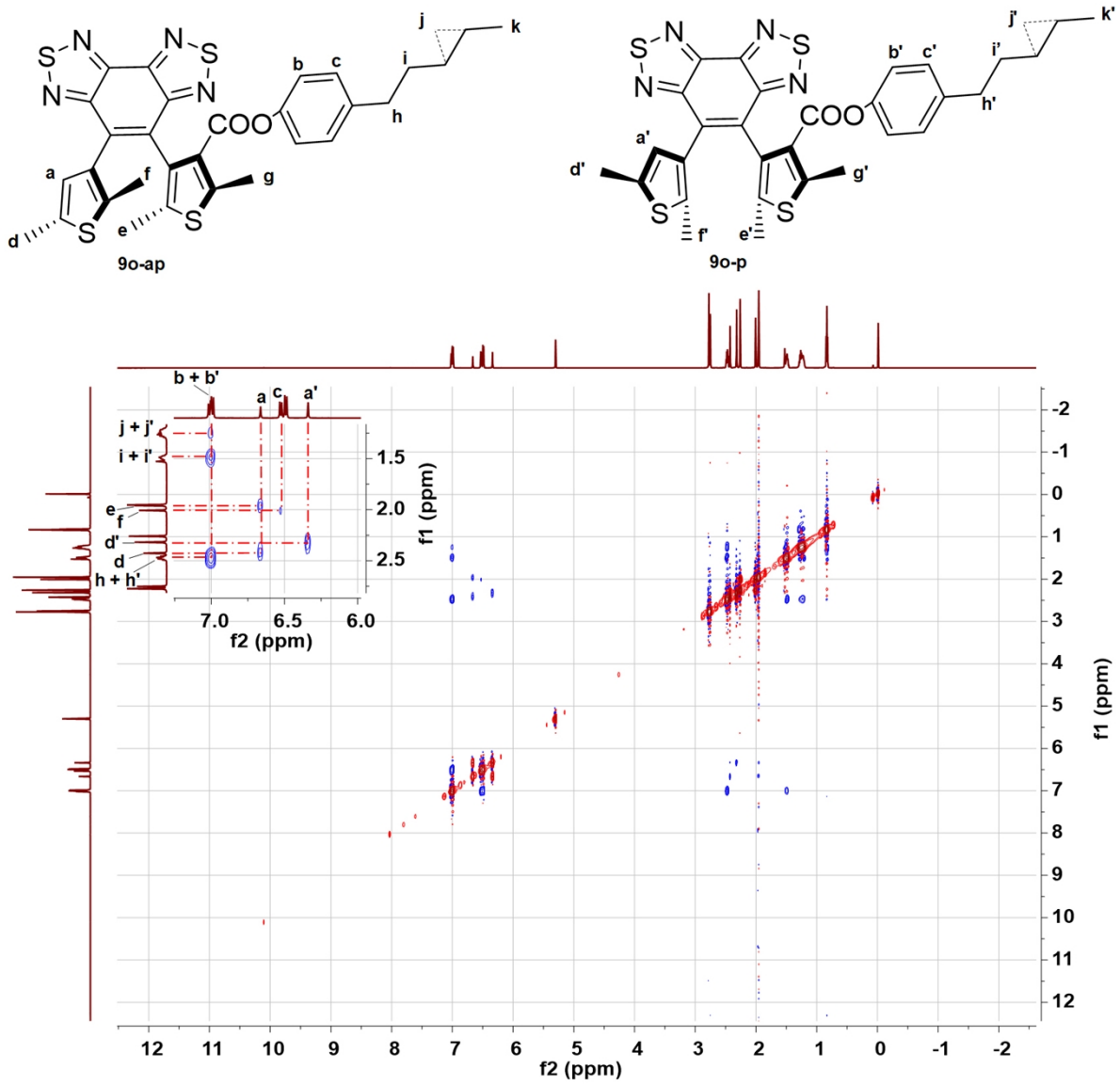


Fig. S4. 2D NOESY spectrum of **9**.

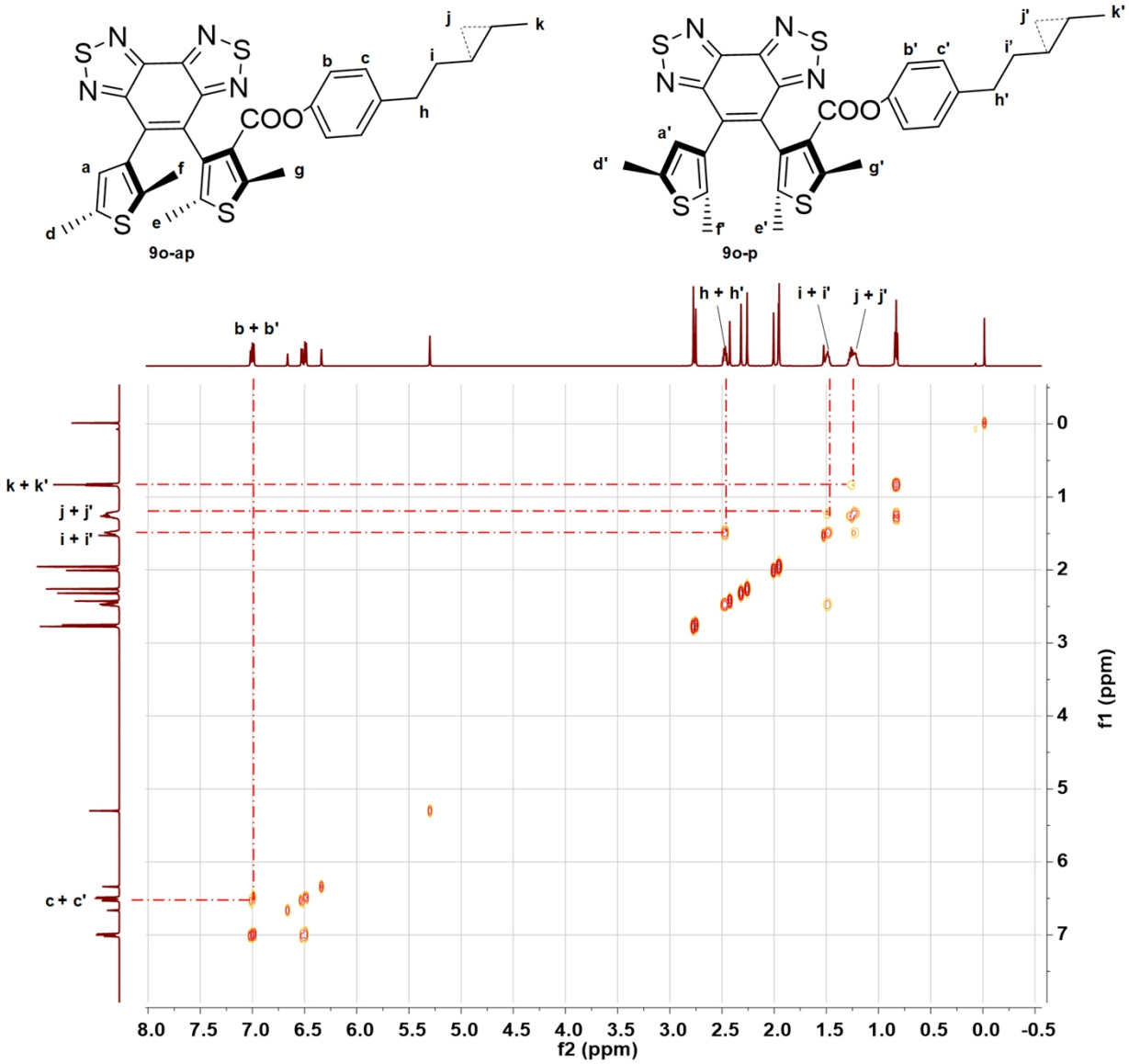


Fig. S5. 2D COSY spectrum of **9**.

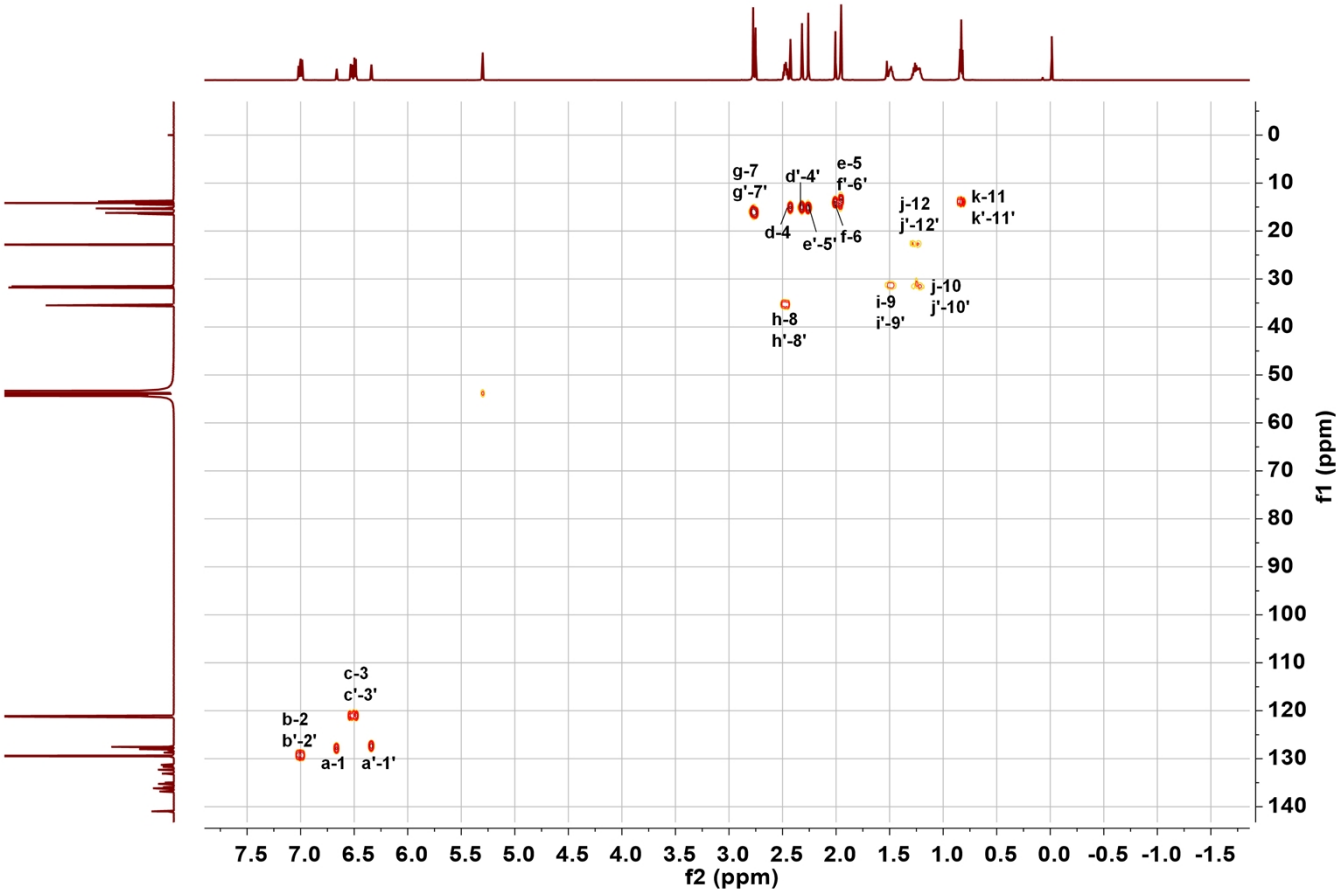


Fig. S6. 2D HMQC spectrum of **9**.

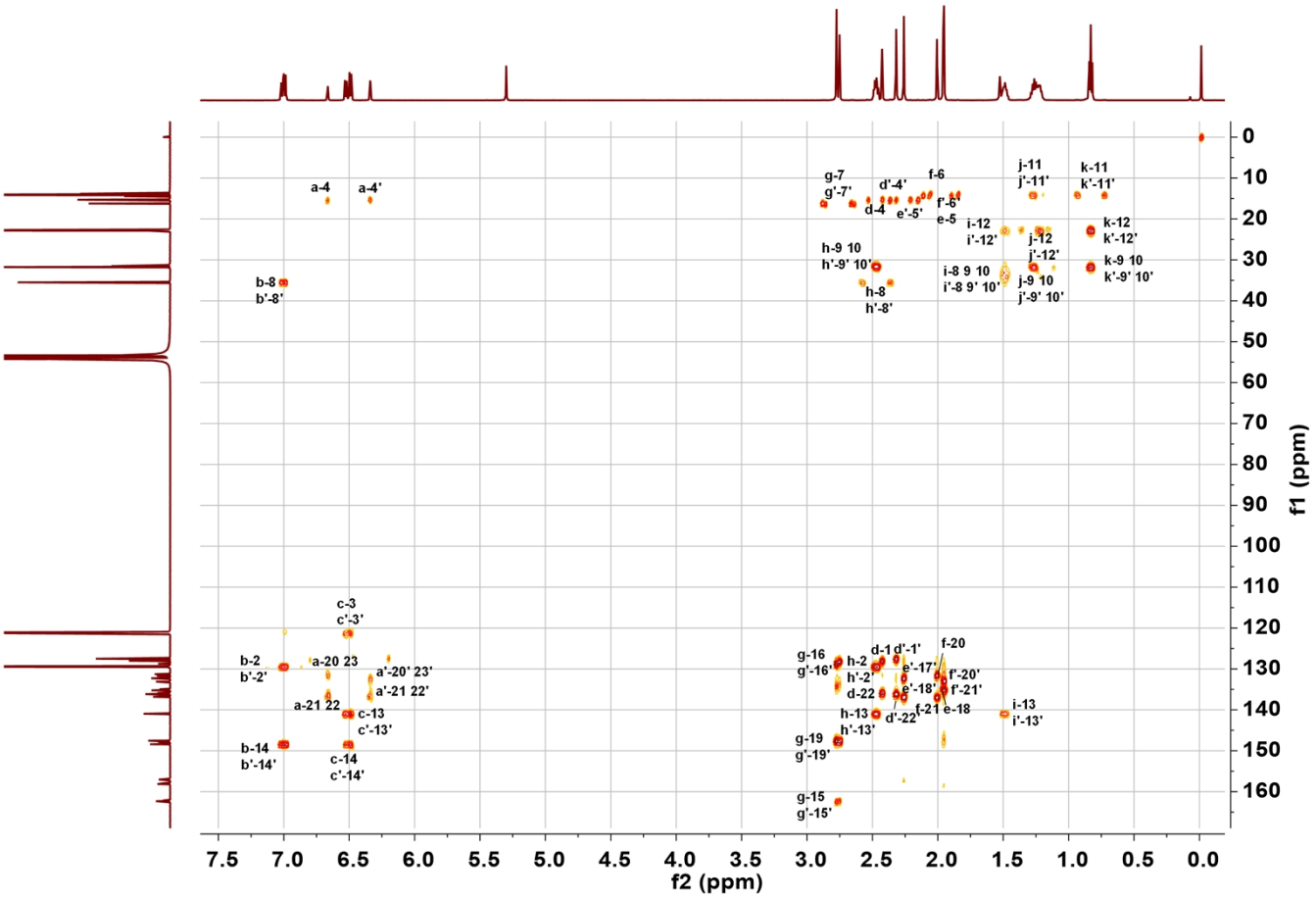


Fig. S7. 2D HMBC spectrum of **9**.

6. Photochromic and Chiral Regulation Properties

6.1 Absorption Changes of 10 and 11

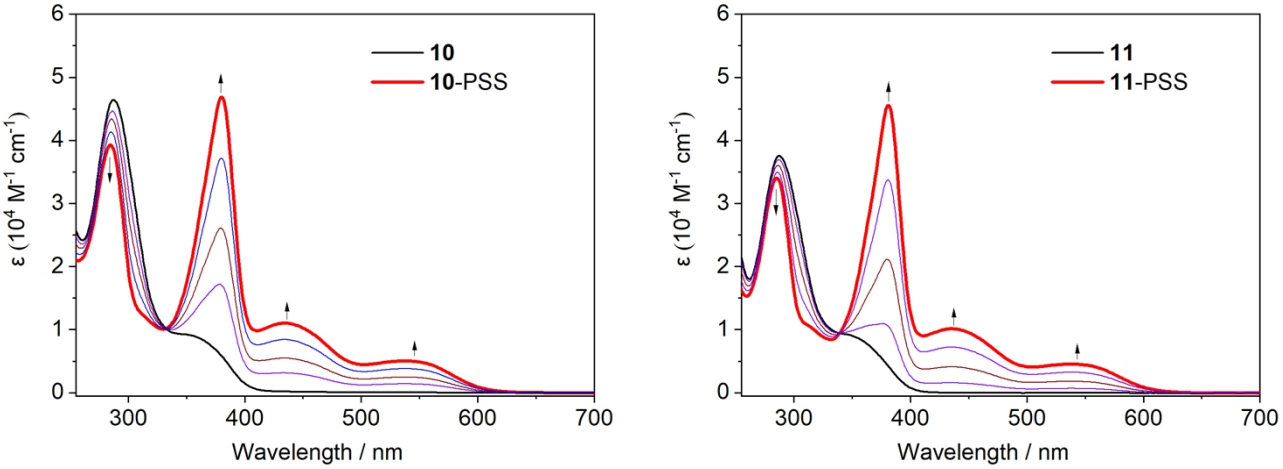


Fig. S8. UV-Vis spectra of **10** and **11** during irradiation of UV light (λ = 313 nm) ($c = 4 \times 10^{-5}$ M, THF).

6.2 Fatigue Resistance Experiments

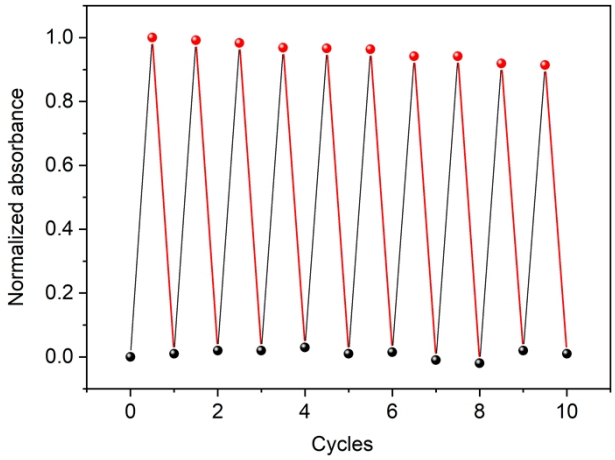


Fig. S9. Absorbance changes at 535 nm of **9** alternatively irradiated by UV light (λ = 313 nm) and visible light (λ > 490 nm) ($c = 4 \times 10^{-5}$ M, THF).

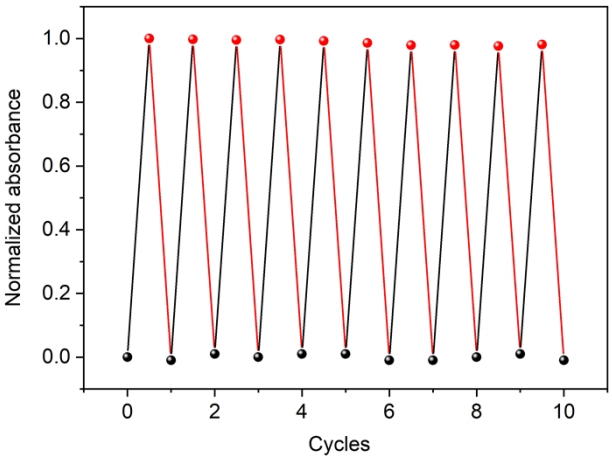


Fig. S10. Absorbance changes at 535 nm of **10** alternatively irradiated by UV light (λ = 313 nm) and visible light (λ > 490 nm) ($c = 4 \times 10^{-5}$ M, THF).

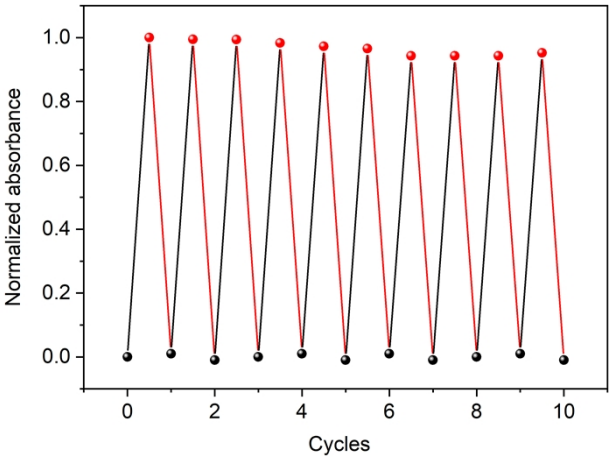


Fig. S11. Absorbance changes at 535 nm of **11** alternatively irradiated by UV light (λ = 313 nm) and visible light (λ > 490 nm) ($c = 4 \times 10^{-5}$ M, THF).

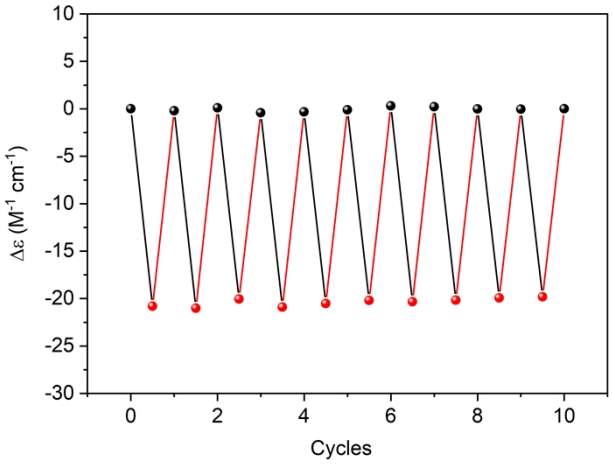


Fig. S12. Changes of CD signals of **10** at 535 nm during alternatively irradiation with UV light (λ = 313 nm) and visible light (λ > 490 nm) ($c = 4 \times 10^{-5}$ M, THF).

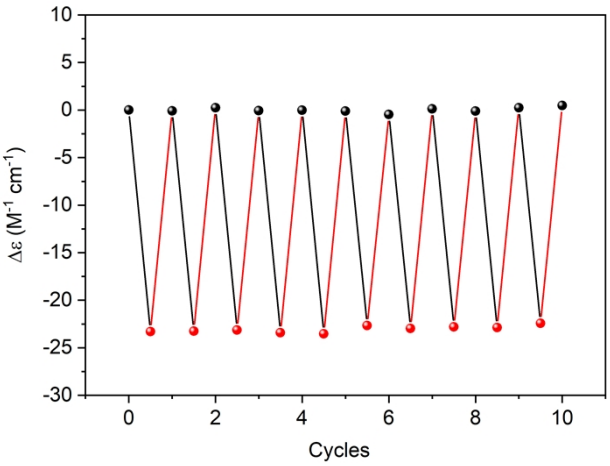


Fig. S13. Changes of CD signals of **11** at 535 nm during alternatively irradiation with UV light (λ = 313 nm) and visible light (λ > 490 nm) ($c = 4 \times 10^{-5}$ M, THF).

6.3 Thermal Stability Tests

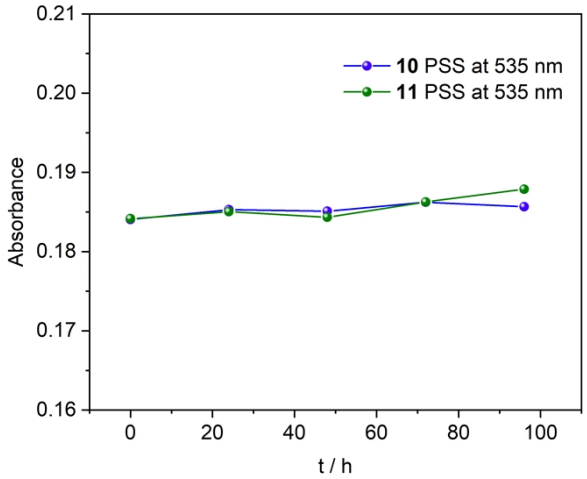


Fig. S14. Absorbance changes of **10** and **11** at PSS at 535 nm during 96 h (T = 298K) ($c = 4 \times 10^{-5}$ M, THF).

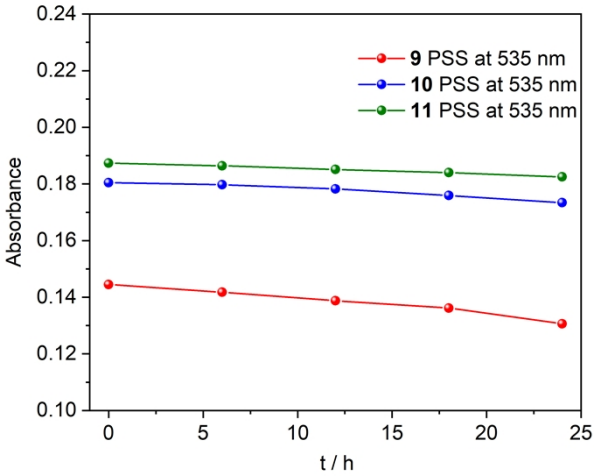


Fig. S15. Absorbance changes of **9**, **10** and **11** at PSS at 535 nm during 24 h (T = 333K) ($c = 4 \times 10^{-5}$ M, THF).

6.4 Conversion Ratio of 9, 10 and 11 under UV Light Irradiation (λ = 313 nm)

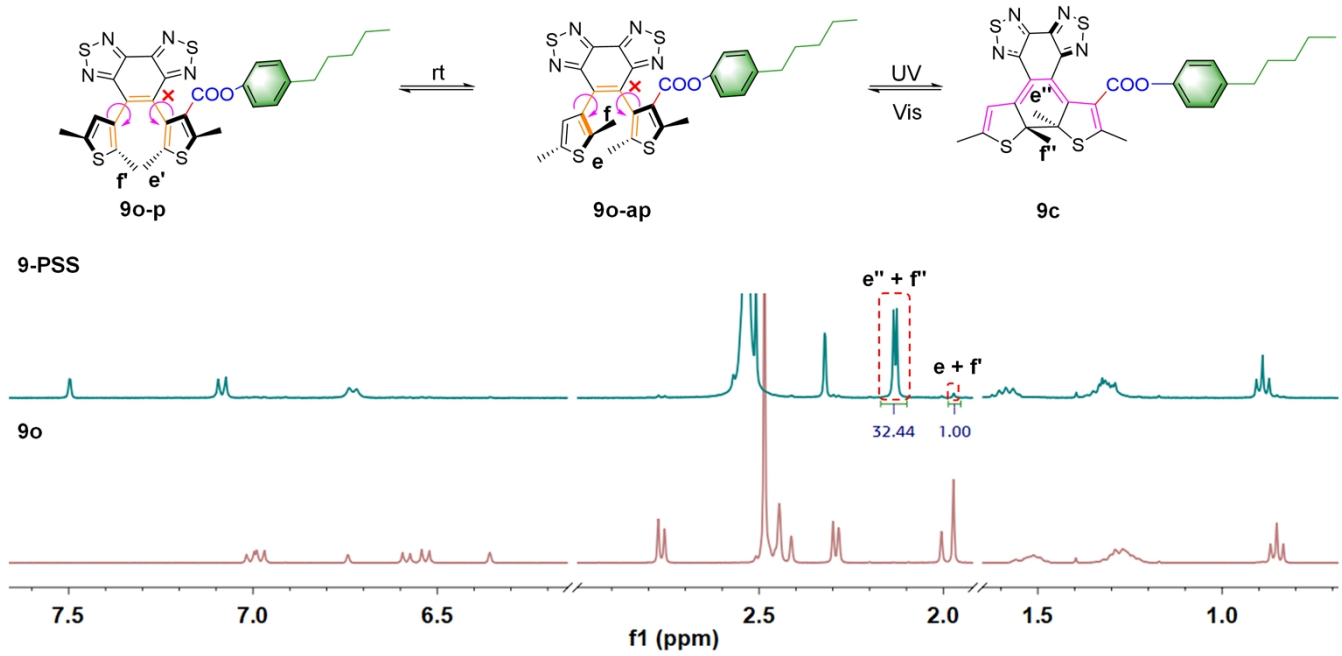


Fig. S16. Changes of ^{1}H NMR spectra of **9** at open state and PSS (c = 5 × 10^{-3} M, THF-d8). The integration of H_e + H_f' should represent 3 actual protons of **9o** and the integration of H_e'' + H_f'' should represent 6 actual protons of **9c**. Thus, the conversion ratio should be 32.44/[2*(32.44/2+1)]= 94%

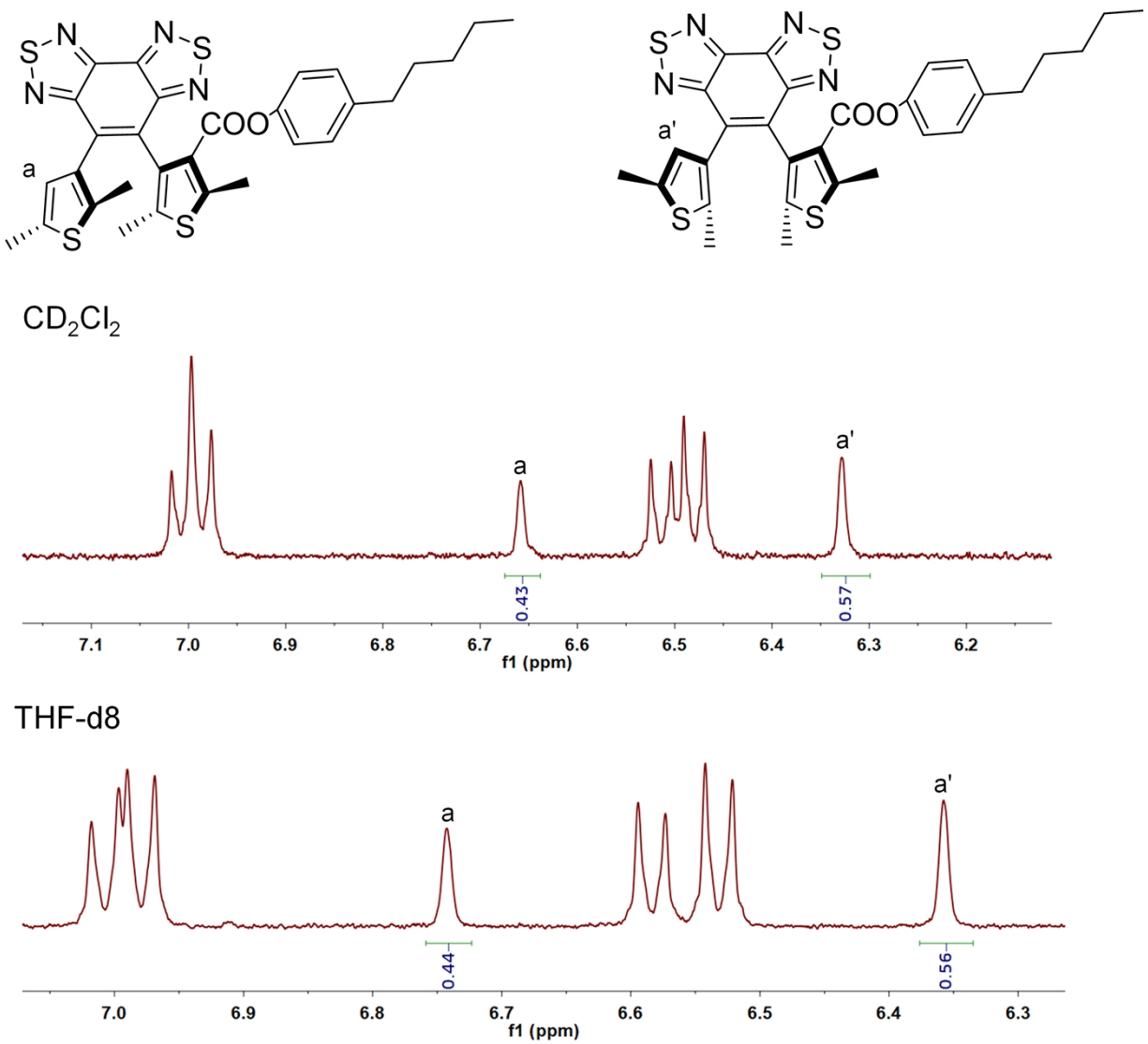


Fig. S17. Partial ^{1}H NMR spectra of **9** in CD_2Cl_2 and THF-d8. The ratio of 9o-ap and 9o-p is 43/57 in CD_2Cl_2 and 44/56 in THF-d8.

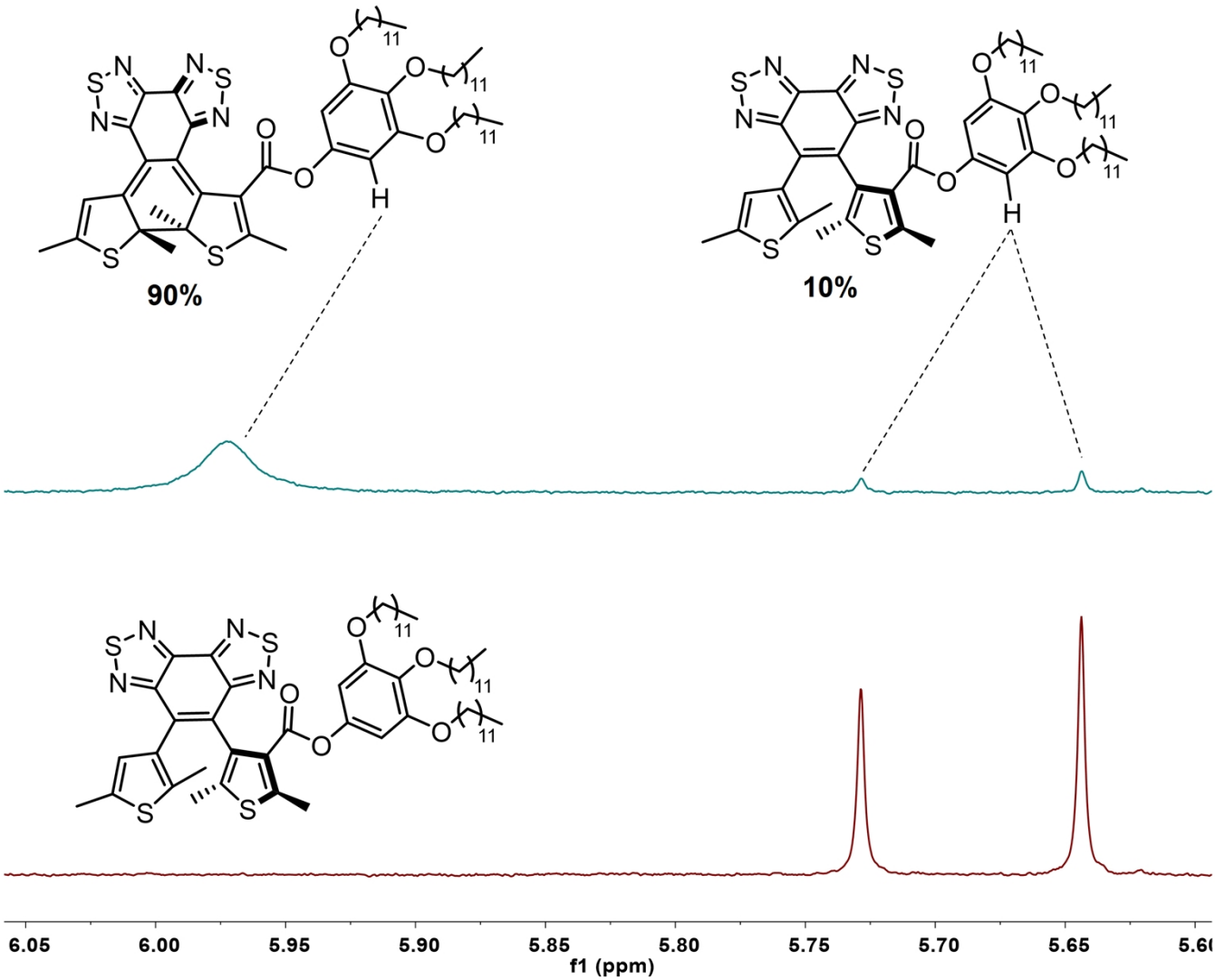


Fig. S18. Partial ^{1}H NMR spectra changes of **10** at open state and PSS (c = 5 × 10^{-3} M, CD_2Cl_2).

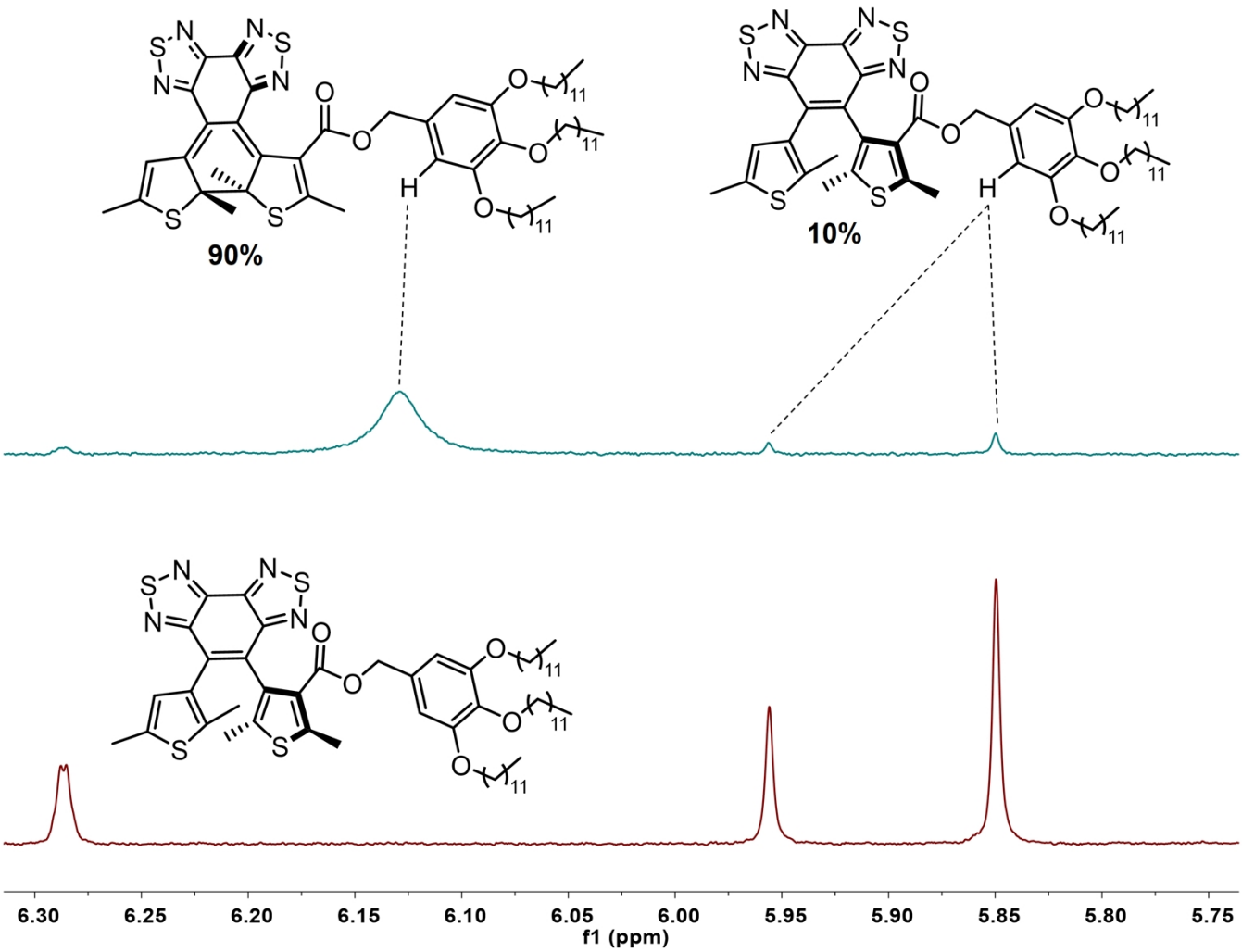


Fig. S19. Partial ^{1}H NMR spectra changes of **11** at open state and PSS (c = 5 × 10^{-3} M, CD_2Cl_2).

6.5 CD Spectra of 10 and 11

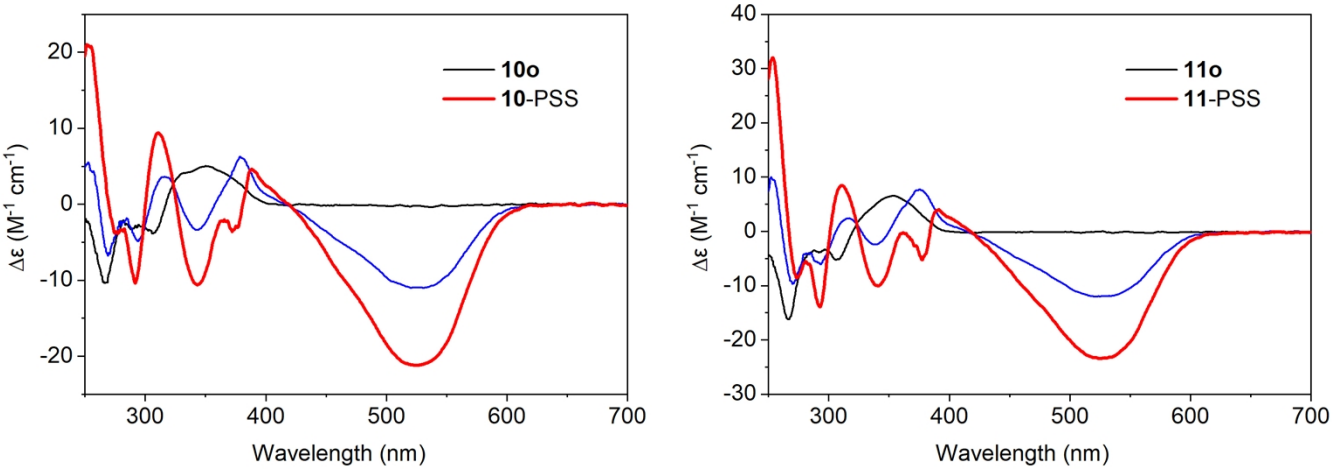


Fig. S20. CD spectra of **10**, **11** during irradiation with UV light (λ = 313 nm) (c = 4 × 10^{-5} M, THF).

6.6 Experiments of Photocyclization and Photocycloreversion Quantum Yields

Photocyclization quantum yield ($\Phi_{o\text{-}c}$) and photocycloreversion quantum yield ($\Phi_{c\text{-}o}$) were measured by monitoring the absorption changes at 517 nm during irradiation with UV light (λ = 313 nm) ($\Phi_{o\text{-}c}$) or visible light (λ = 517 nm) ($\Phi_{c\text{-}o}$) in THF according to standard procedure using BTF6 as reference[S1] whose $\Phi_{o\text{-}c}$ and $\Phi_{c\text{-}o}$ are both known as 0.35[S2], respectively. At the beginning of irradiation, $\Phi_{o\text{-}c}$ and $\Phi_{c\text{-}o}$ should follow eq. S1 and eq. S2. See supporting information of reference S1 for the detailed derivation process of equations.

$$\Phi_{o-c} = \frac{k_{o-c}V}{l\varepsilon_1 I(1-10^{-l\varepsilon_2 c_o})} \qquad \text{eq. S1}$$

$$\Phi_{c-o} = \frac{|k_{c-o}|V}{l\varepsilon_1 I(1-10^{-l\varepsilon_3 c})} \qquad \text{eq. S2}$$

c_o is the concentration of ring-open isomer. c is the concentration of ring-closed isomer. l is the optical path. V is the volume of the test solution. I is the intensity of incident light calculated from the known data of BTF6. ε_1 is the extinction coefficient of ring-closed isomer at the detection wavelength (that is, 517 nm). ε_2 is the extinction coefficient of ring-open isomer at irradiation wavelength (that is, 313 nm). ε_3 is the extinction coefficient of ring-closed isomer at irradiation wavelength (that is, 517 nm).

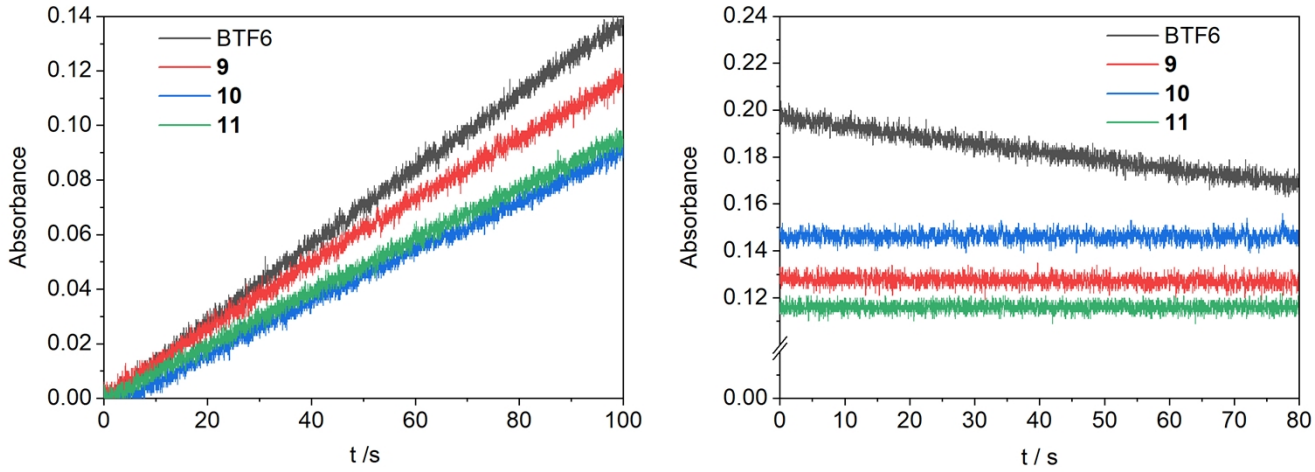


Figure S21. Absorption changes of **BTF6**, **9**, **10**, **11** during irradiation with UV light (λ = 313 nm) and visible light (λ > 490 nm) ($c = 2 \times 10^{-4}$ M, THF).

Table S4. Photochromic data of **9**, **10** and **11**.

Molecular	ε_{max}[a]	CR[b]	$\Phi_{o\text{-}c}$[c]	$\Phi_{c\text{-}o}$[d]
9	37758	0.90	0.37	-
9c	5511	>0.99	-	0.042
10	46430	0.90	0.29	-
10c	5626	>0.99	-	0.0058
11	37620	0.90	0.32	-
11c	5052	>0.99	-	0.0023

[a]Typical absorption maxima ε_{max} of ring-open isomer in the UV region and ring-closed isomer in the visible region,

respectively. [b]Caculated from ^{1}H NMR in CD_2Cl_2. [c]Quantum yields of photocyclization ($\Phi_{o\text{-}c}$) at 313 nm and cycloreversion ($\Phi_{c\text{-}o}$) at 517 nm.

7. Measurements of the HTPs of 9, 10, 11

The HTPs of **9, 10, 11** were calculated using the Grandjean-Cano wedge technique[S5] according to the equation: $\beta_M = (P\ c)^{-1}$, where β_M is HTP, P is the pitch length of the helical structure, and c is the concentration of dopants. P was determined using a Cano wedge cell. P satisfies the following formula: $P = 2\ L\ \tan\theta$, where L is the distance between two disclination lines and θ is the wedge angle. L was observed under the polarizing optical microscope before and after irradiation at 365 nm light. **9**, **10**, **11** were mixed with TEB300, heated to melt, and subsequently injected into a wedge cell respectively for HTP measurements.

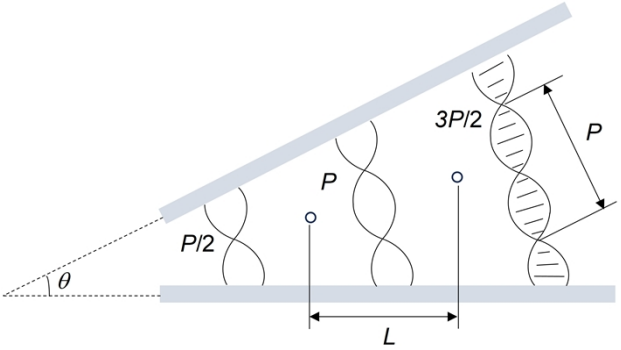


Fig. S22. Scheme of the Grandjean-Cano wedge technique.

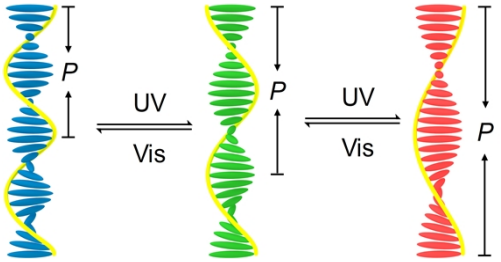


Fig. S23. Schematic illustration of pitch length modulation.

Table S5. Data for calculation of the HTPs of **9**, **10** and **11**.

Dopant	$\tan\theta$	L / μm	P / μm	c (mol%)	β_M / μm^{-1}
9	0.0183	108.5	3.9711	0.36	69.8
9 at PSS	0.0183	159.6	5.8413	0.36	47.4
10	0.0183	510.1	18.6697	0.12	44.5
10 at PSS	0.0183	408.0	14.9328	0.12	55.9
11	0.0183	438.9	16.0637	0.12	52.1
11 at PSS	0.0183	396.7	14.5192	0.12	57.5

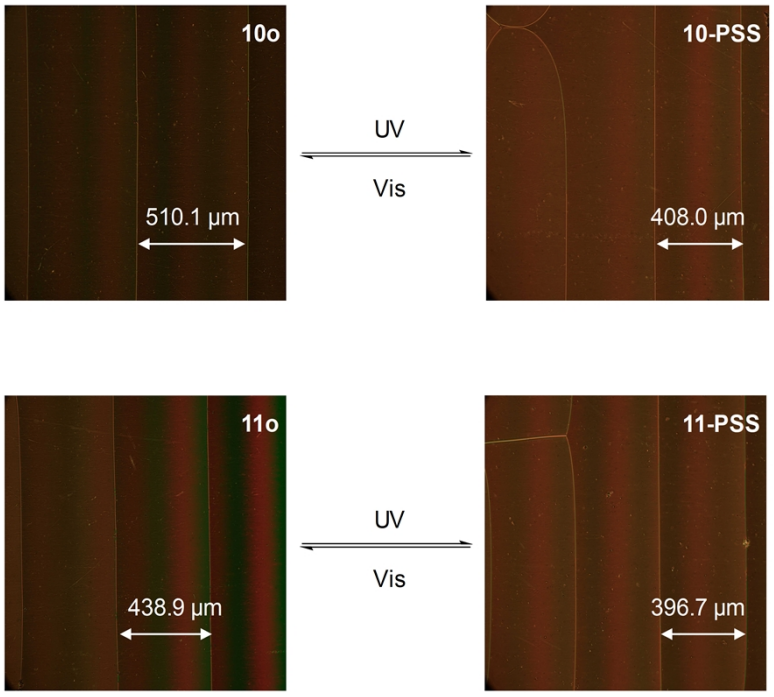
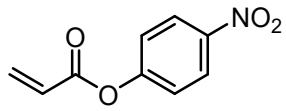
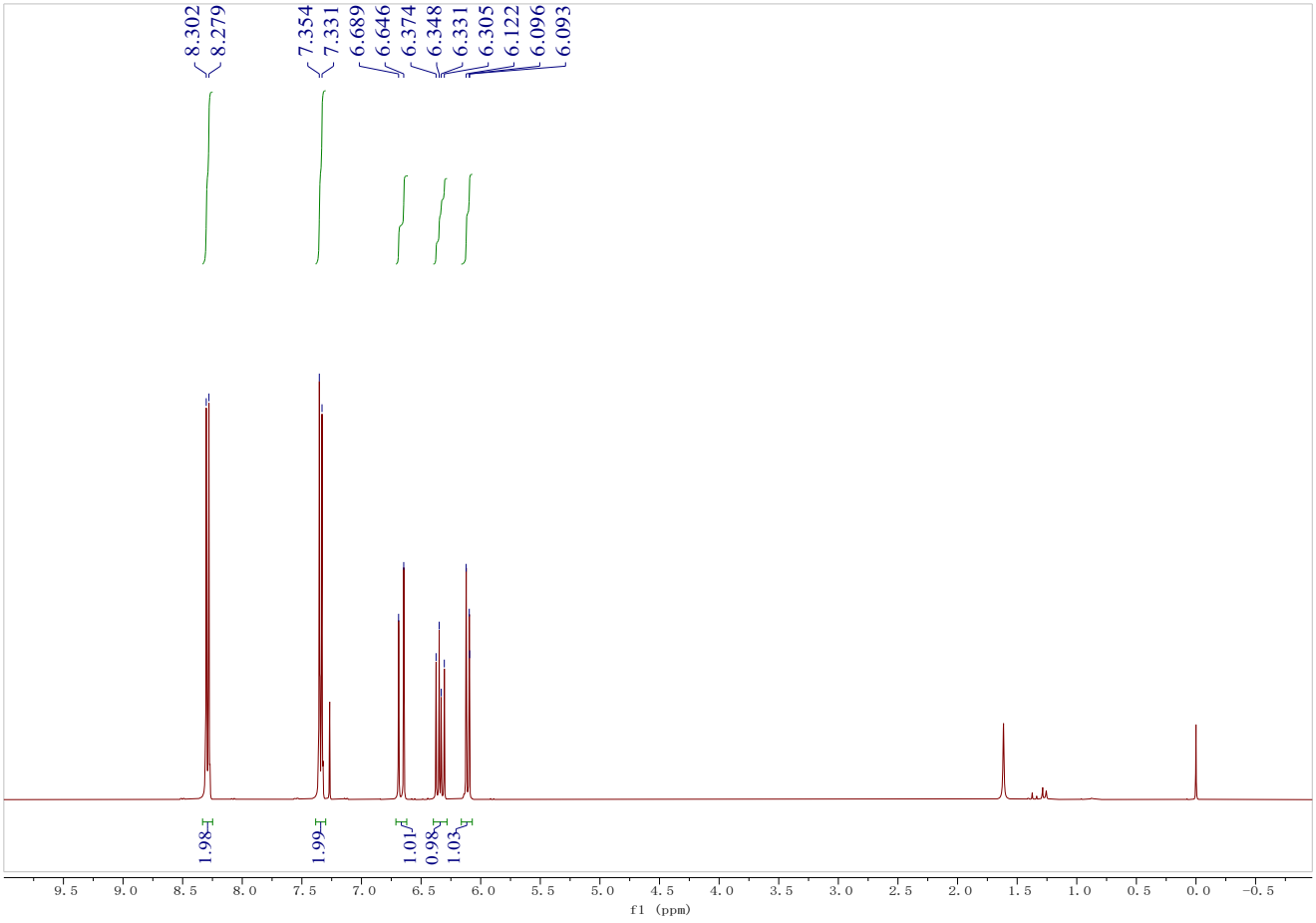


Fig. S24. Distance changes between two disclination lines changes of **10** or **11**.

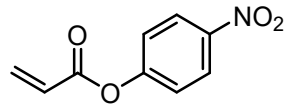
8. NMR Spectra

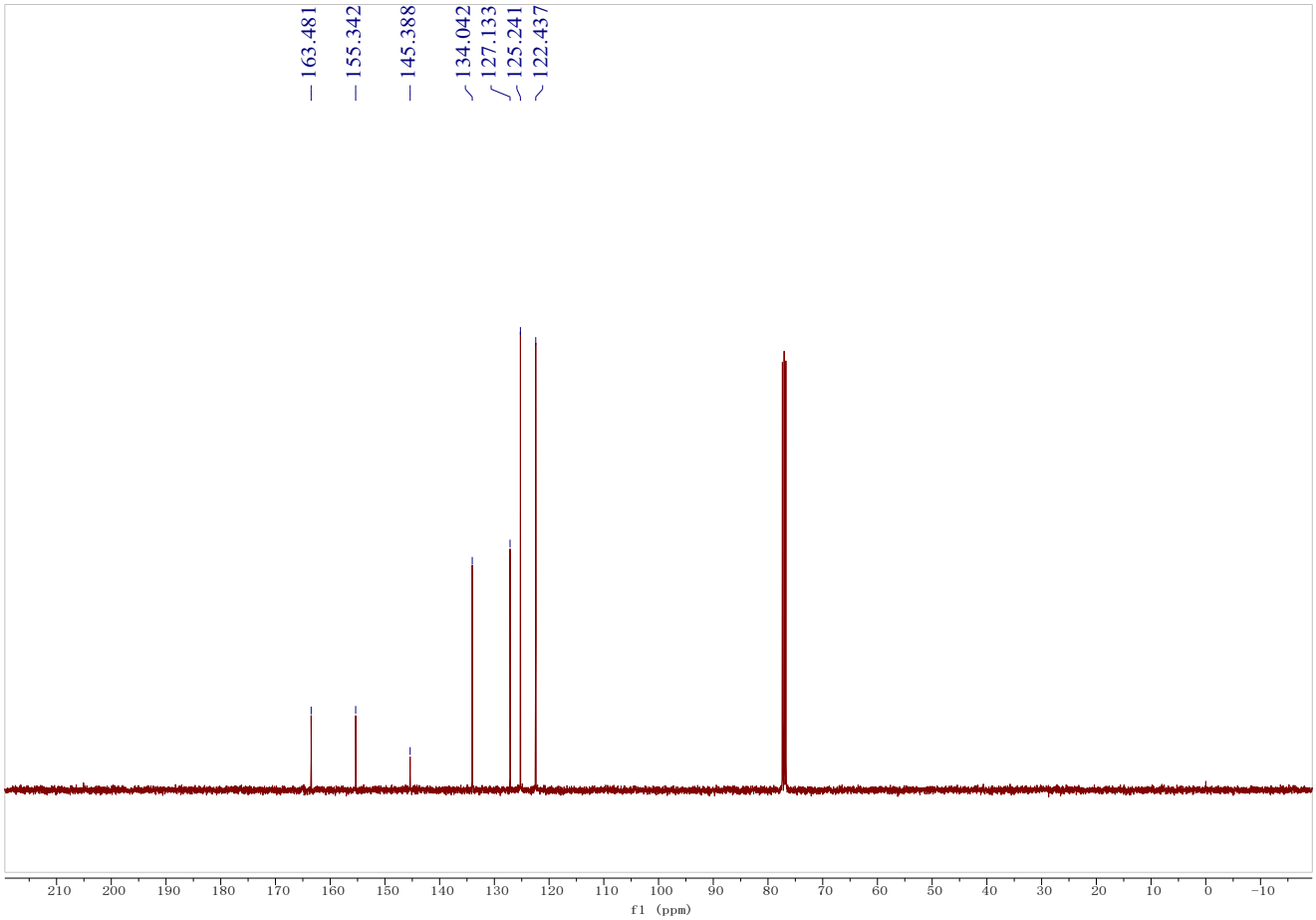
2b, ^{1}H NMR, 400 MHz, $CDCl_3$



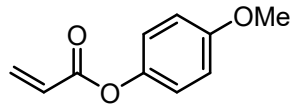


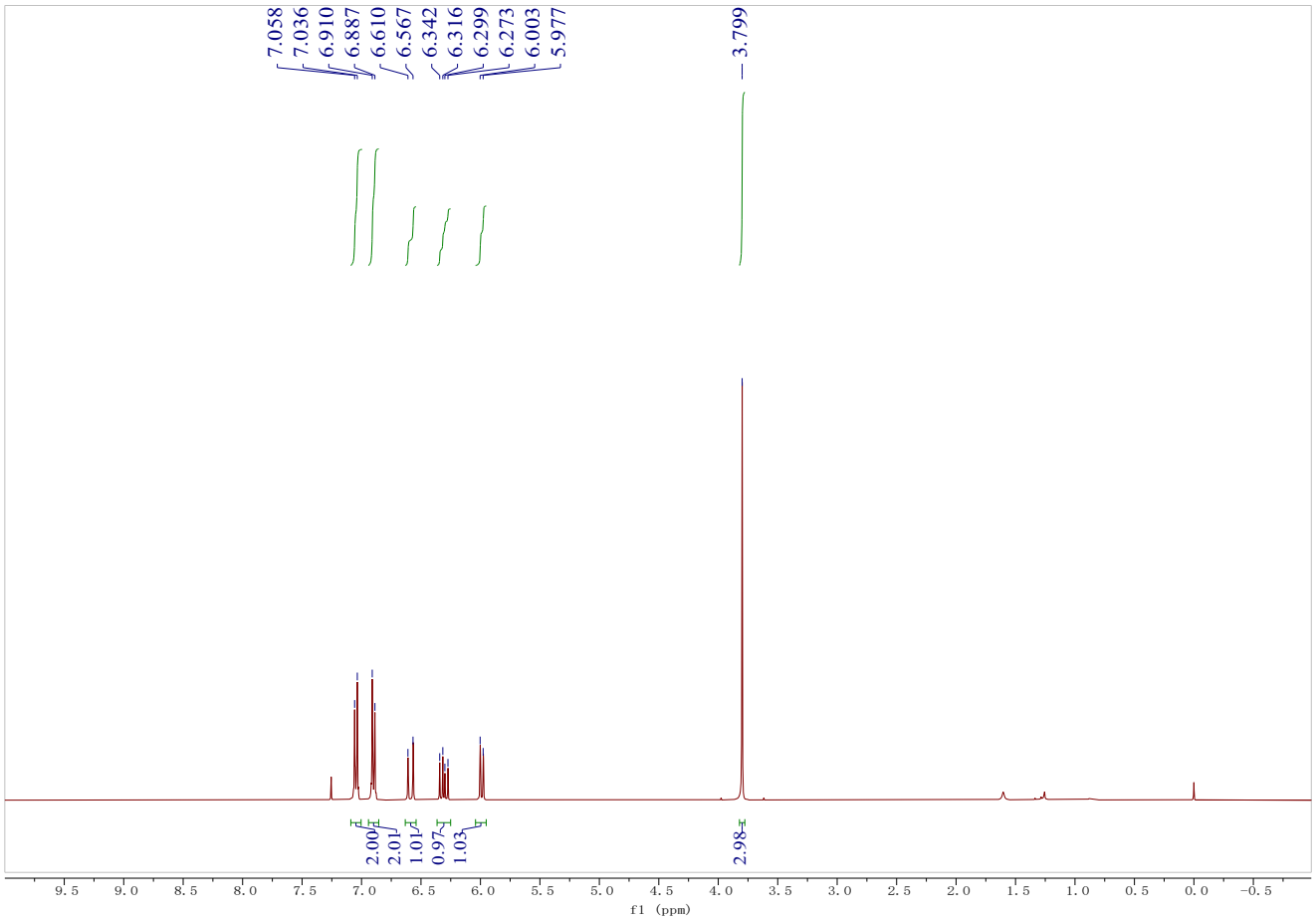
2b,^{13}C NMR, 101 MHz, $CDCl_3$



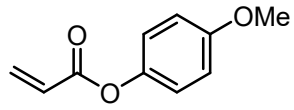


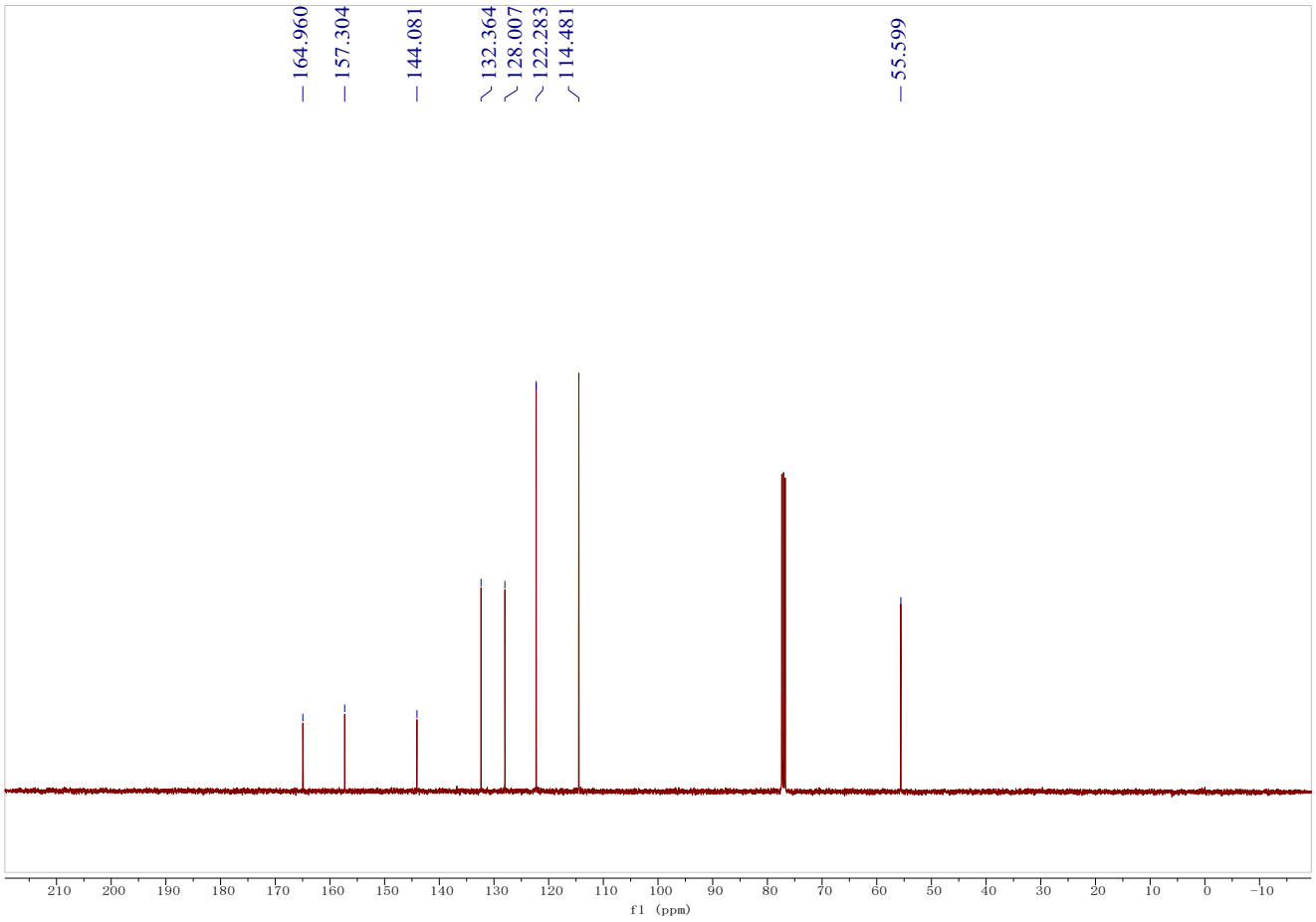
2c, ^{1}H NMR, 400 MHz, $CDCl_3$



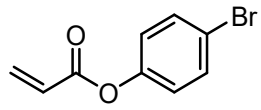


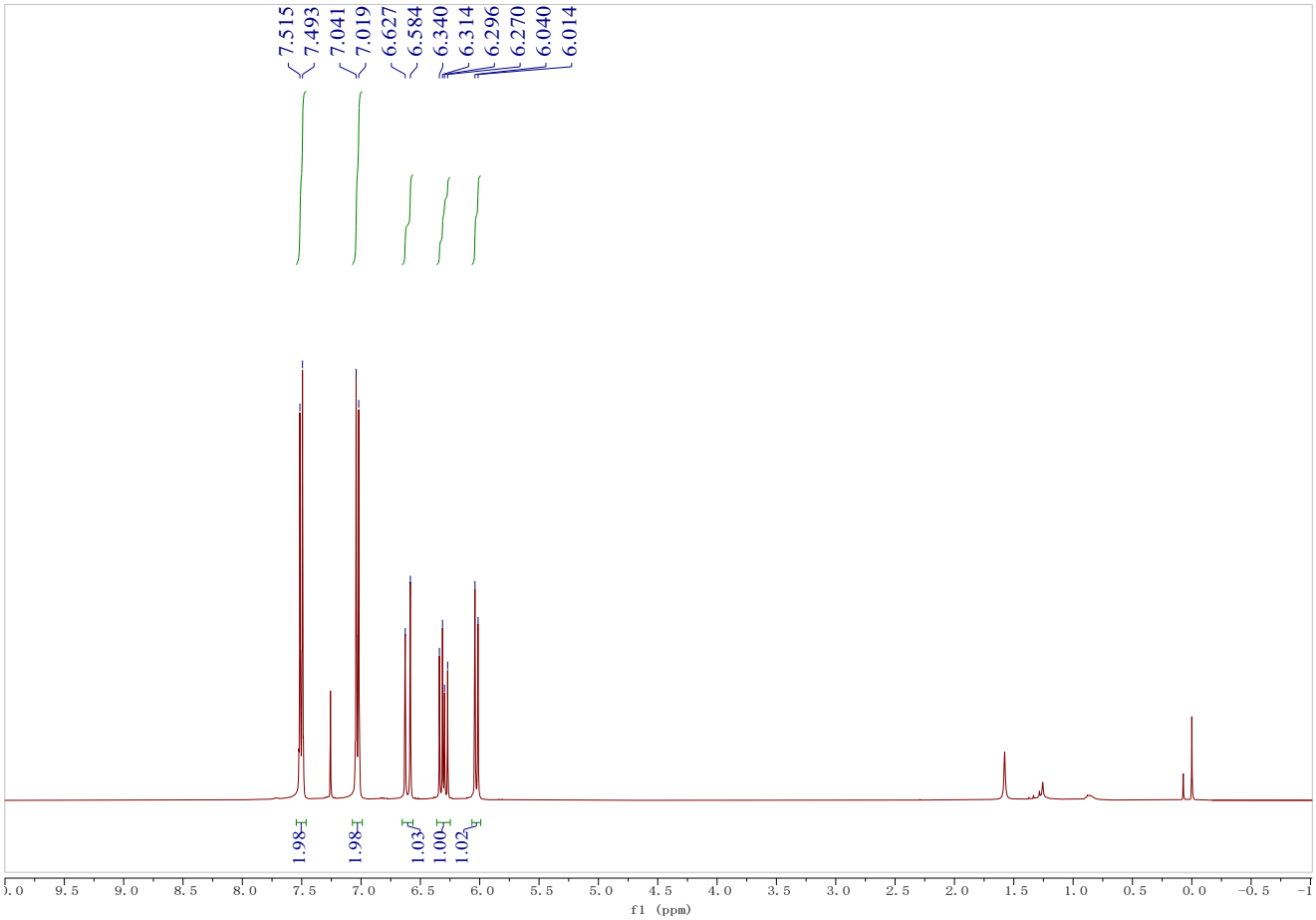
2c,^{13}C NMR, 101 MHz, $CDCl_3$



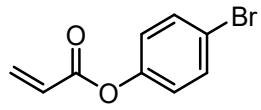


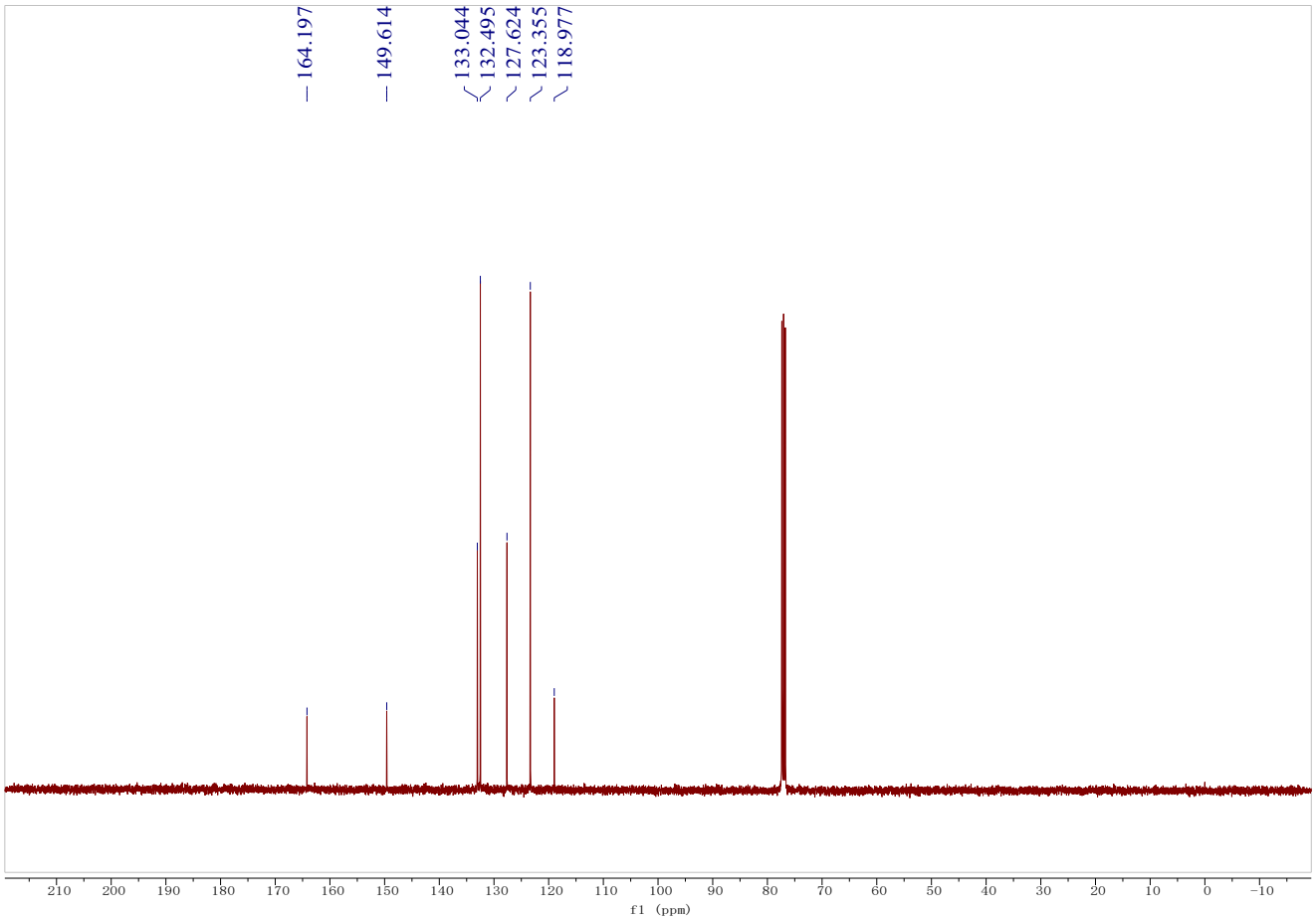
2d, ^{1}H NMR, 400 MHz, $CDCl_3$



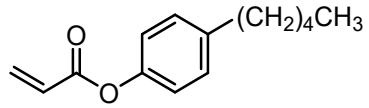


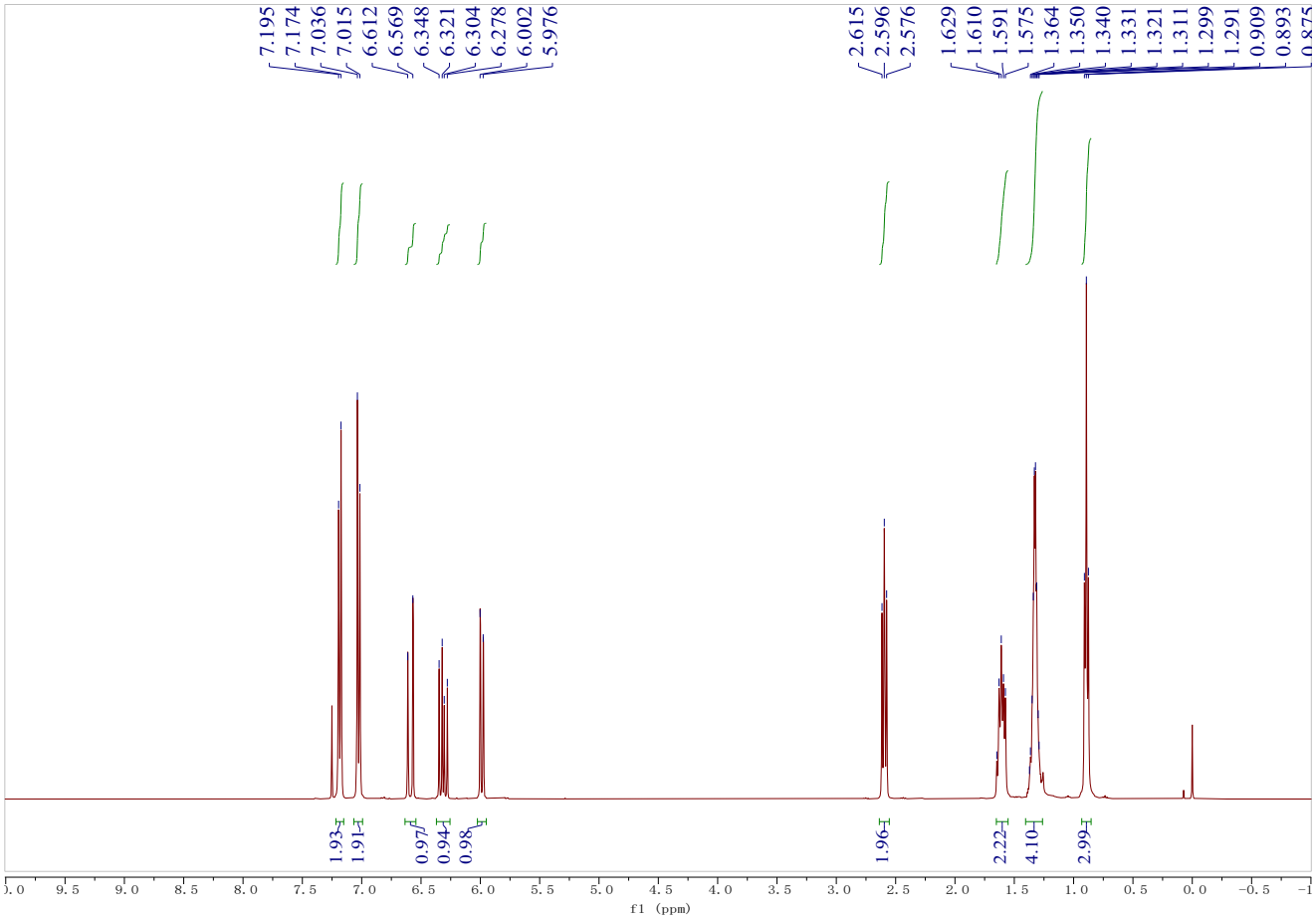
2d,^{13}C NMR, 101 MHz, $CDCl_3$



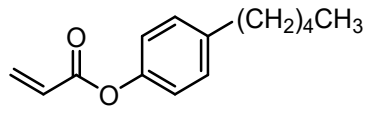


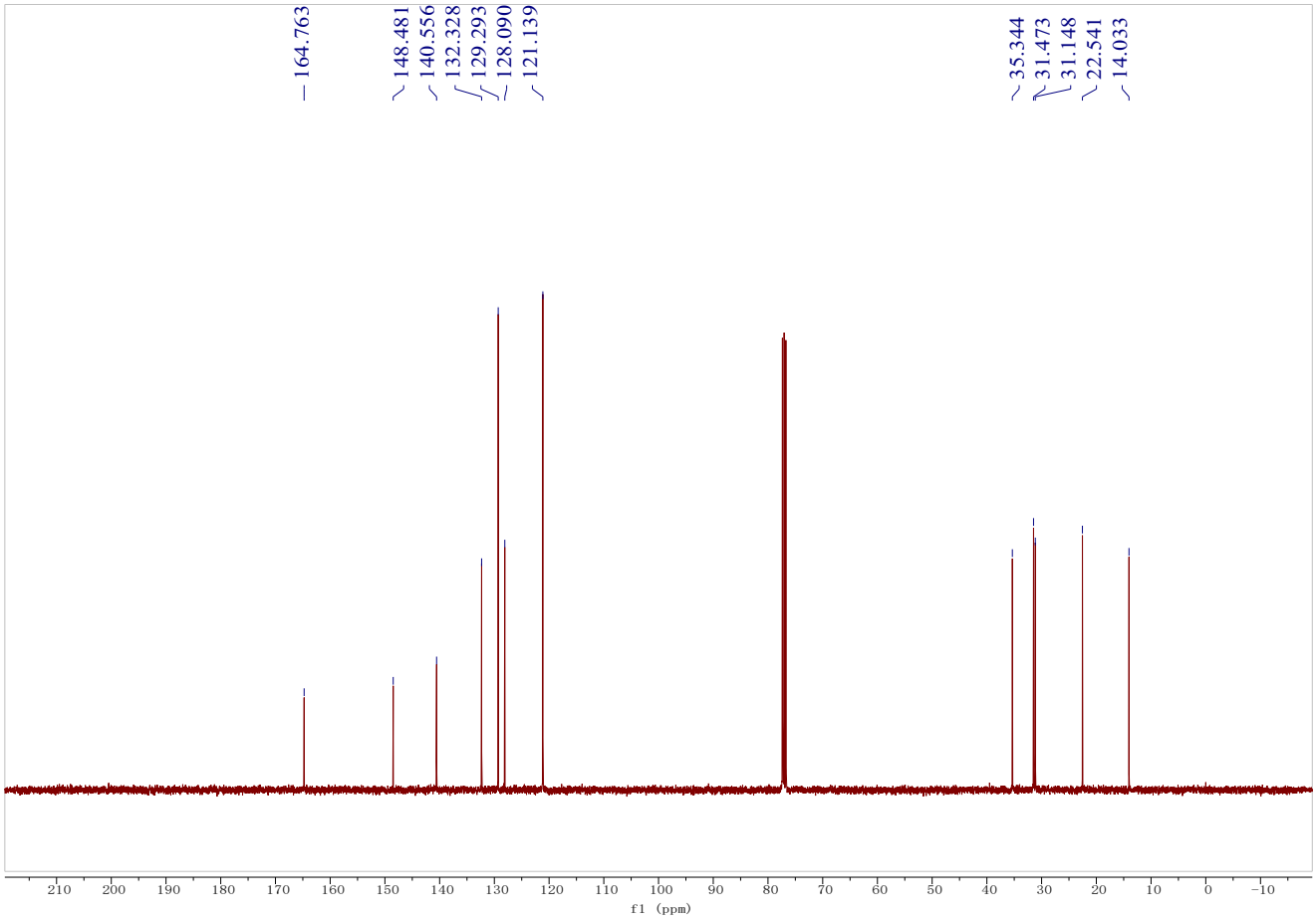
2e, ^{1}H NMR, 400 MHz, $CDCl_3$



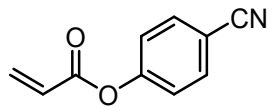


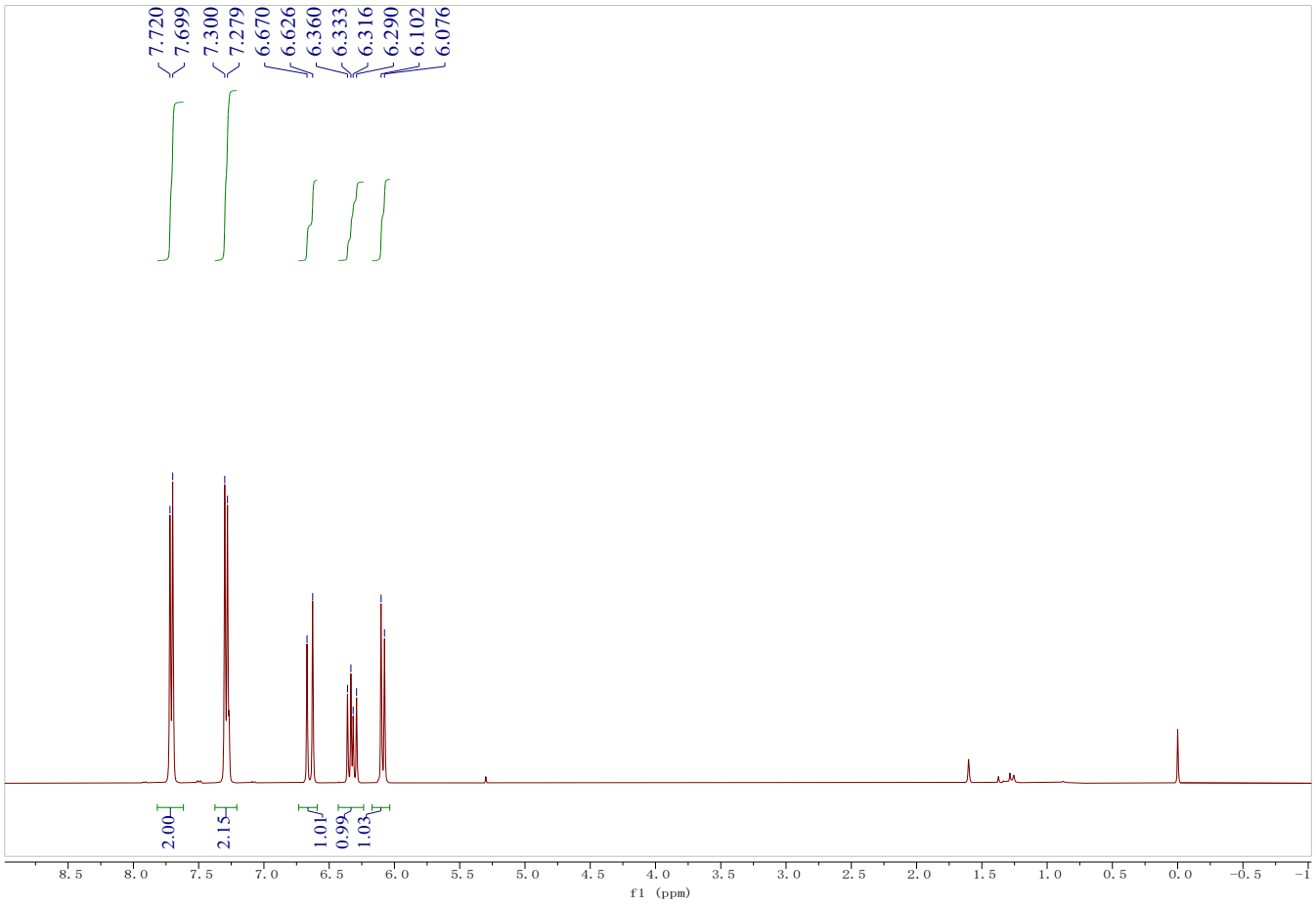
2e,^{13}C NMR, 101 MHz, $CDCl_3$



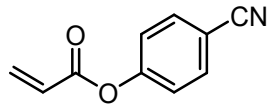


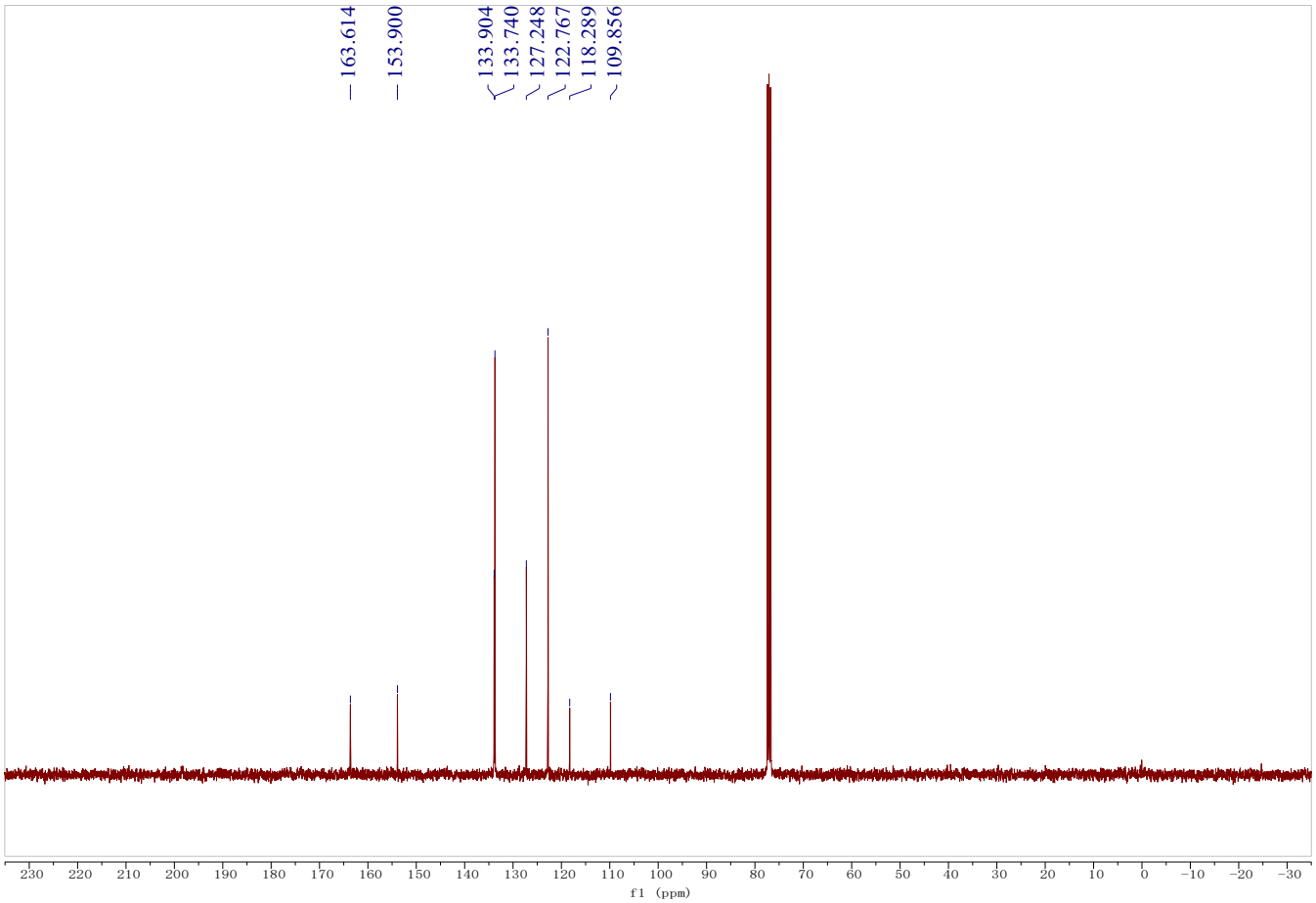
2f, ^{1}H NMR, 400 MHz, $CDCl_3$



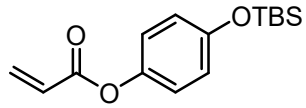


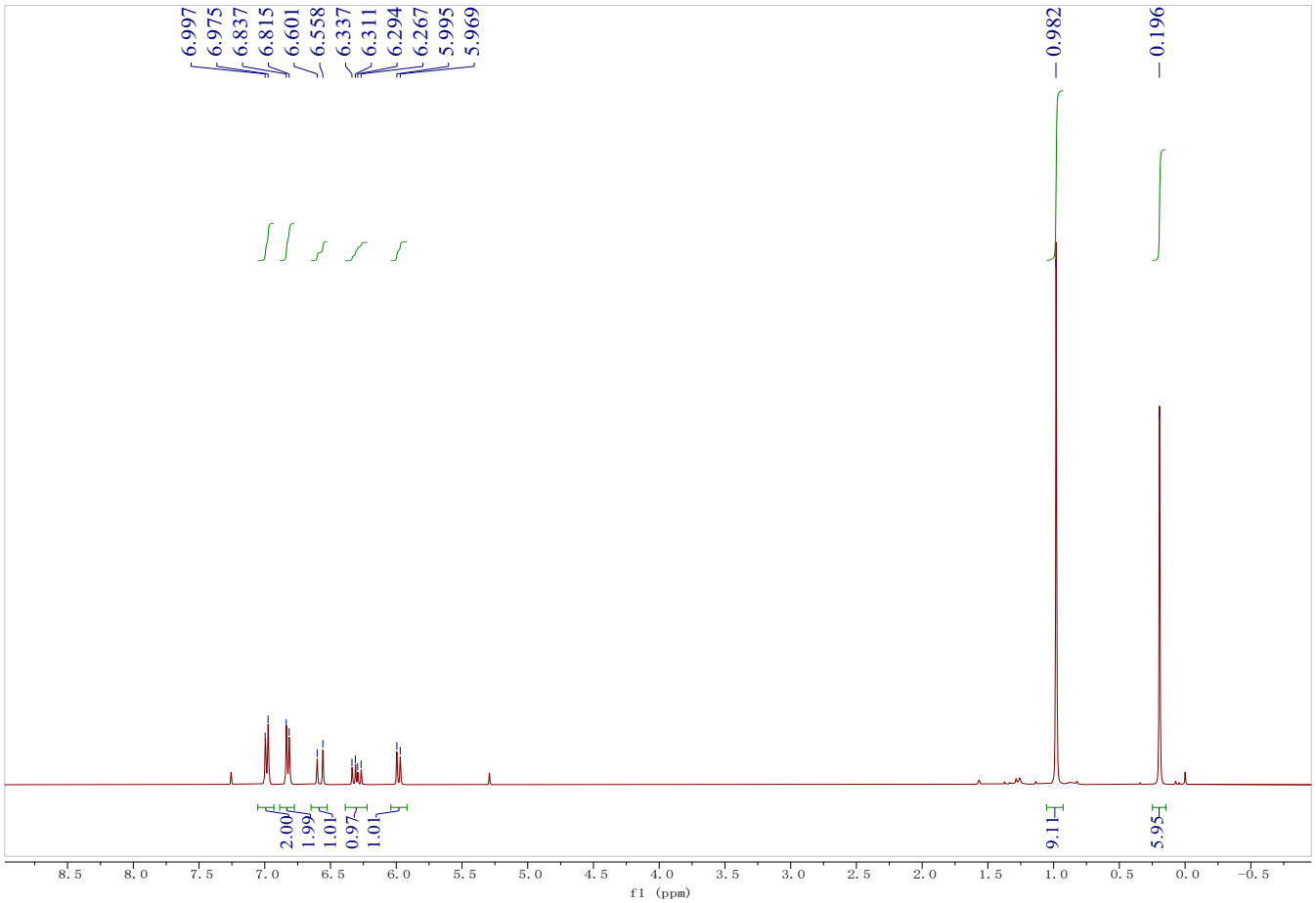
2f,^{13}C NMR, 101 MHz, $CDCl_3$



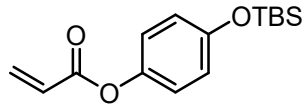


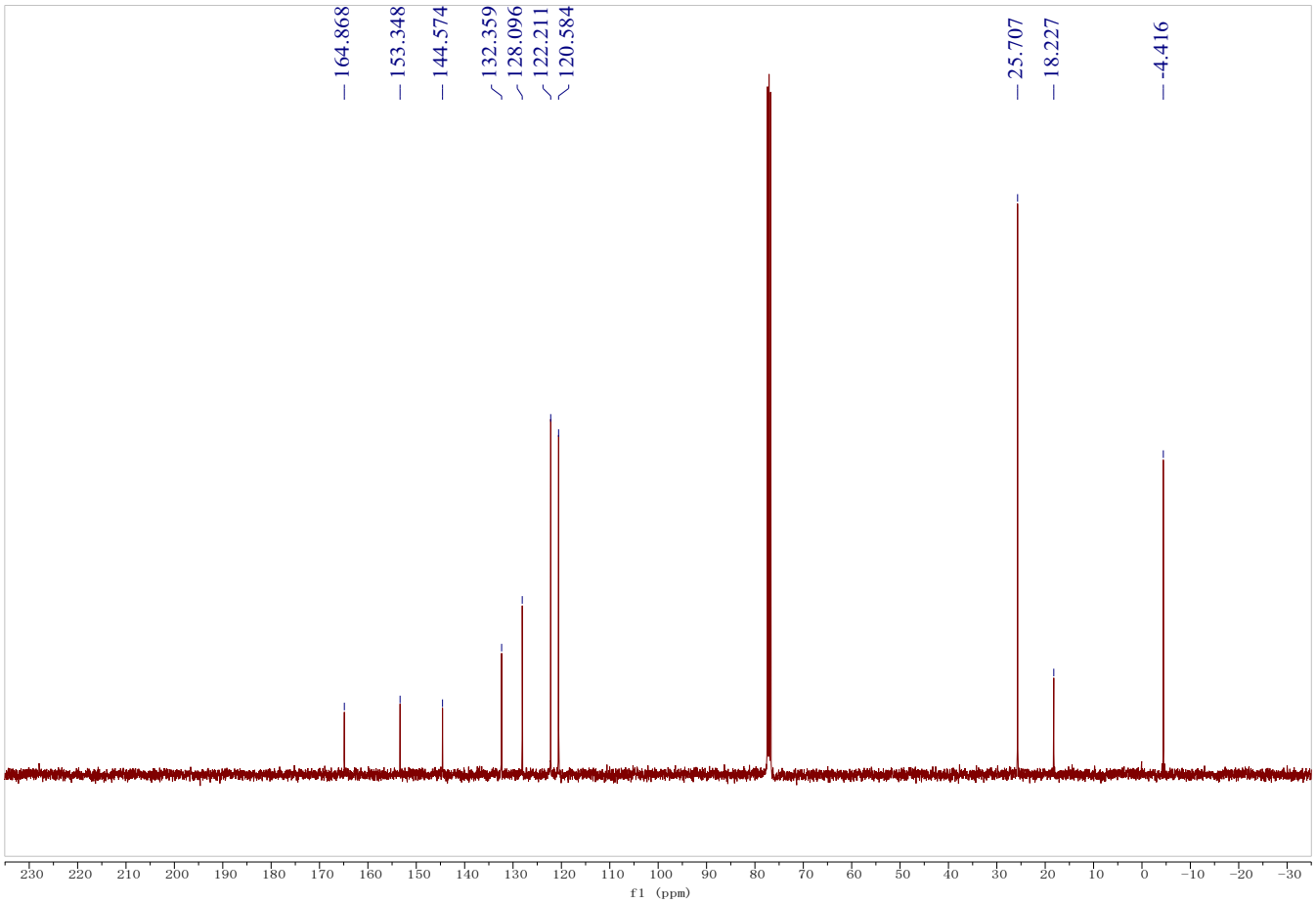
2g, ^{1}H NMR, 400 MHz, $CDCl_3$



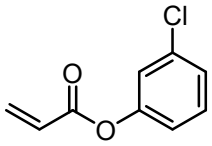


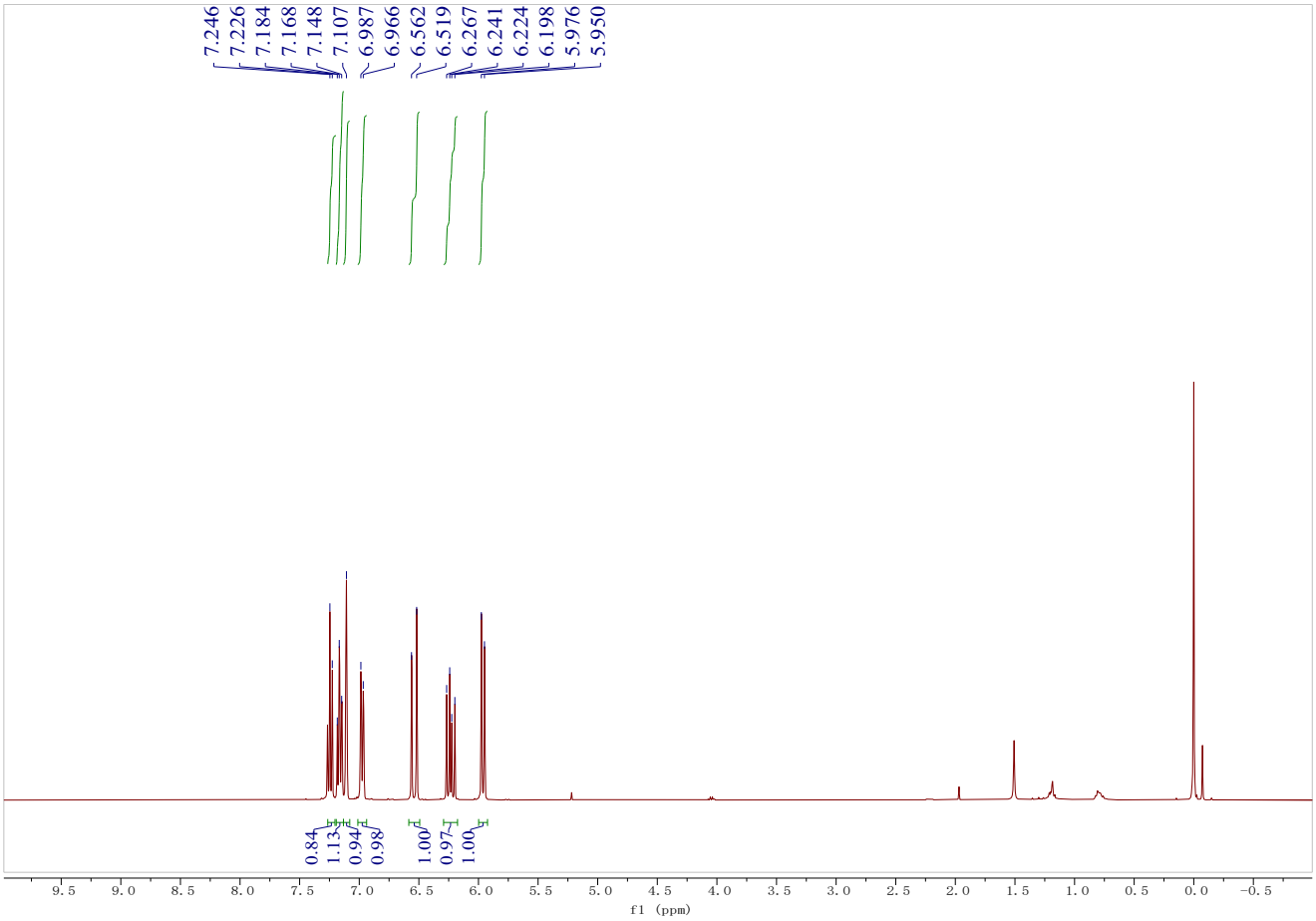
2g,^{13}C NMR, 101 MHz, $CDCl_3$





2h, ^{1}H NMR, 400 MHz, $CDCl_3$





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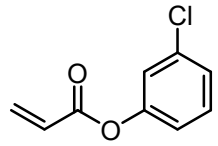

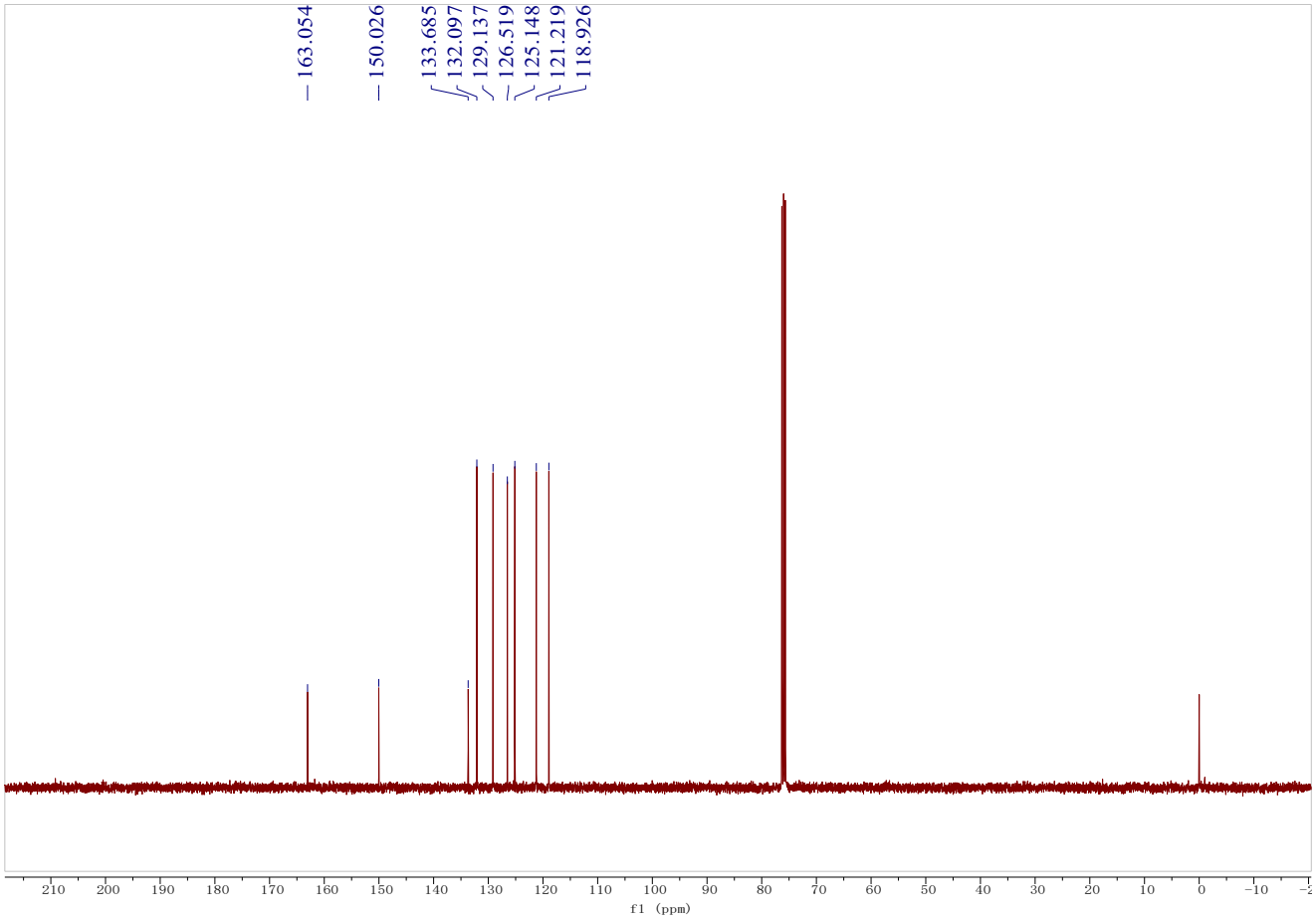

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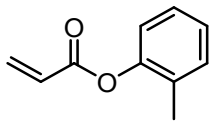
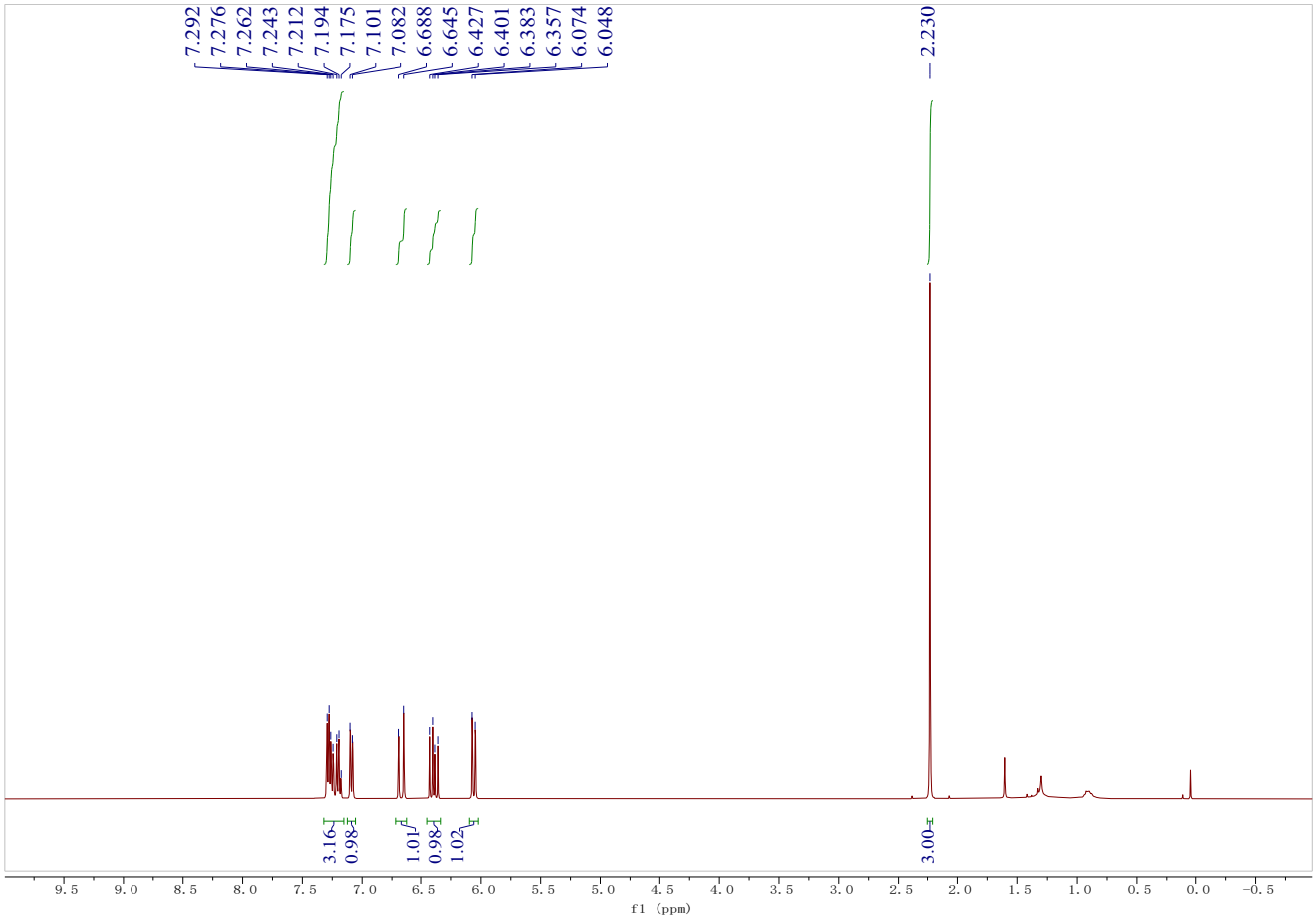
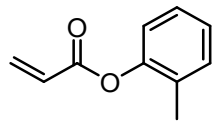
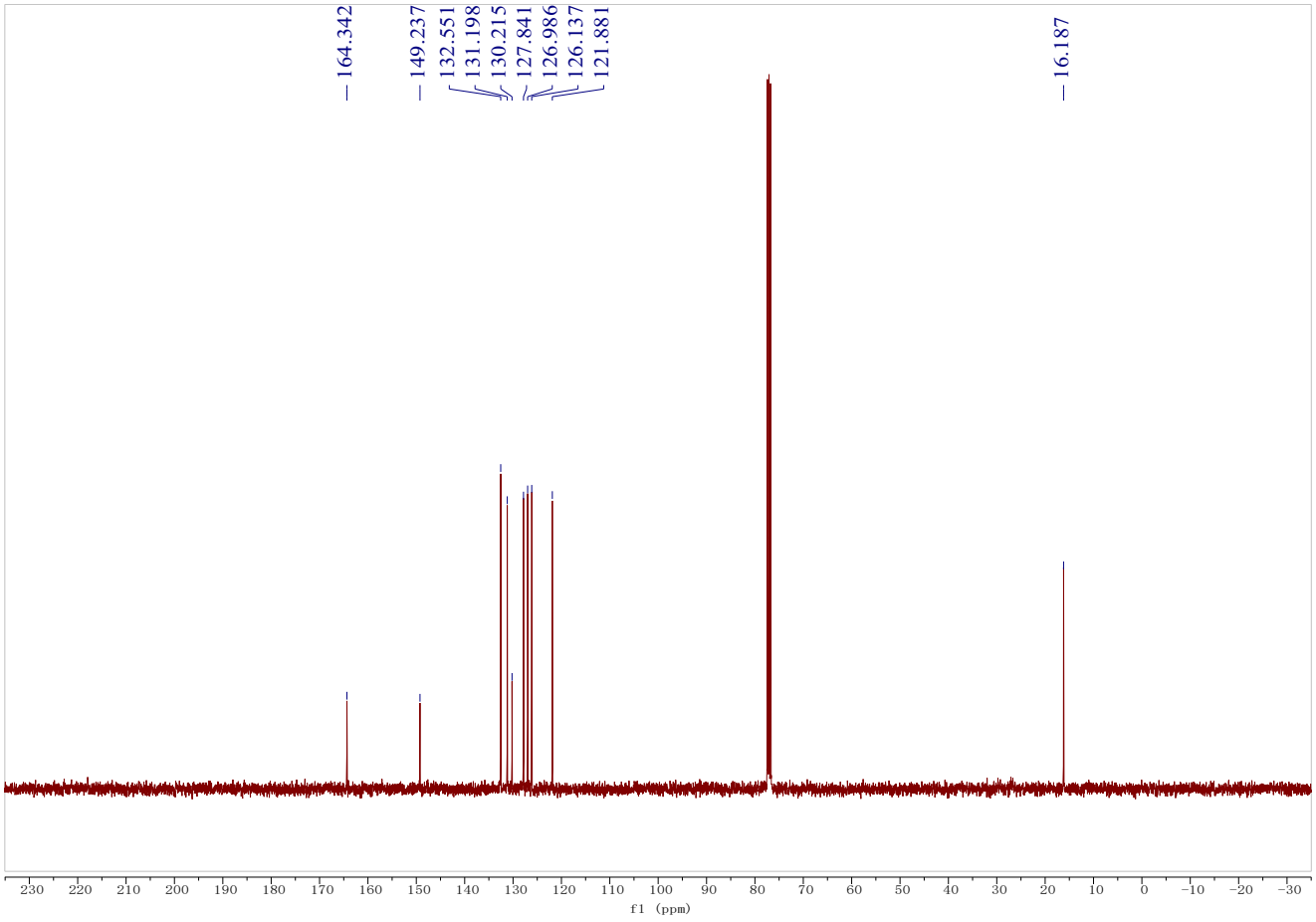


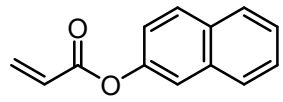


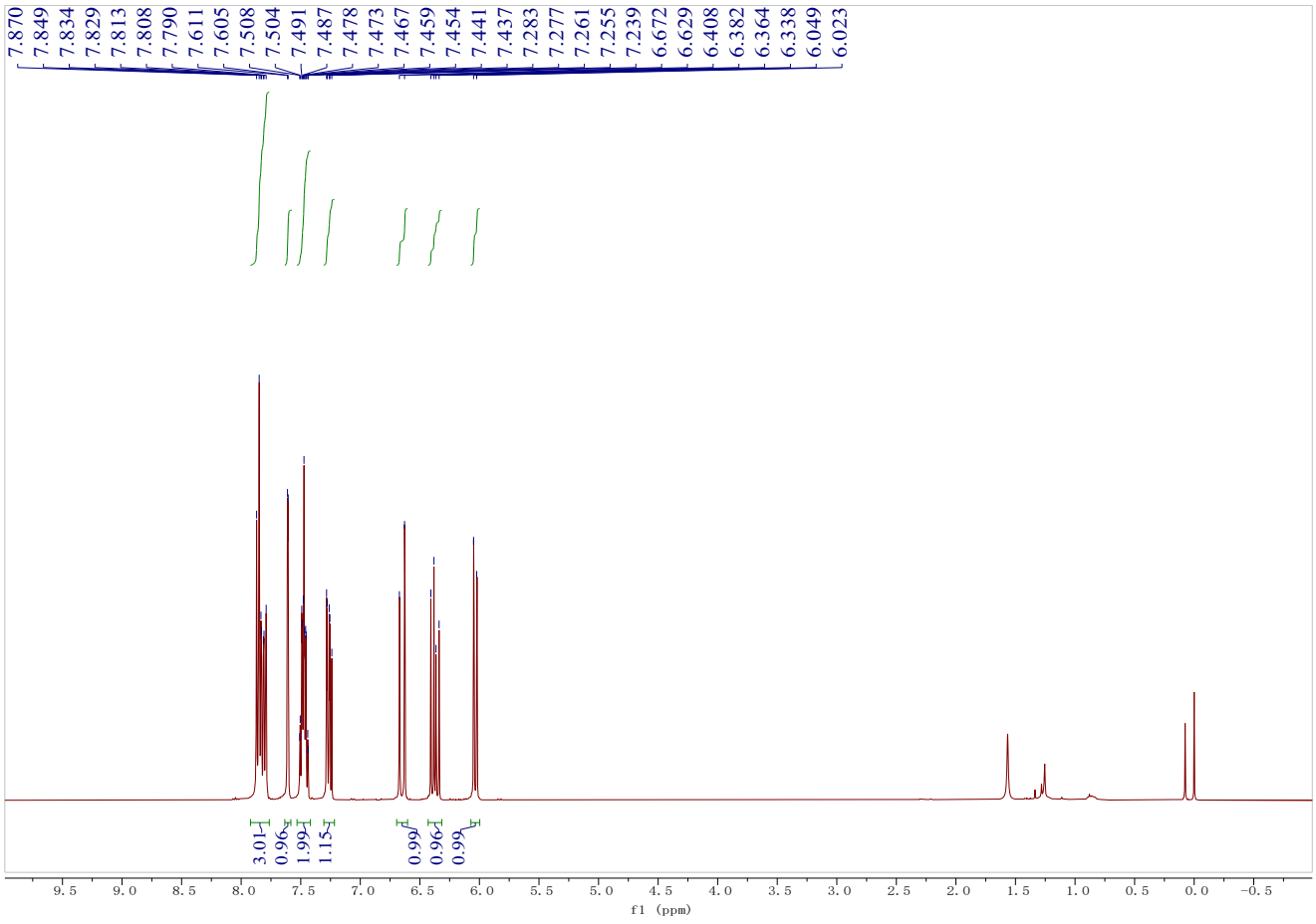
2i,^{13}C NMR, 101 MHz, $CDCl_3$



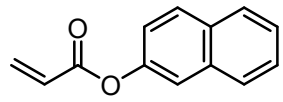


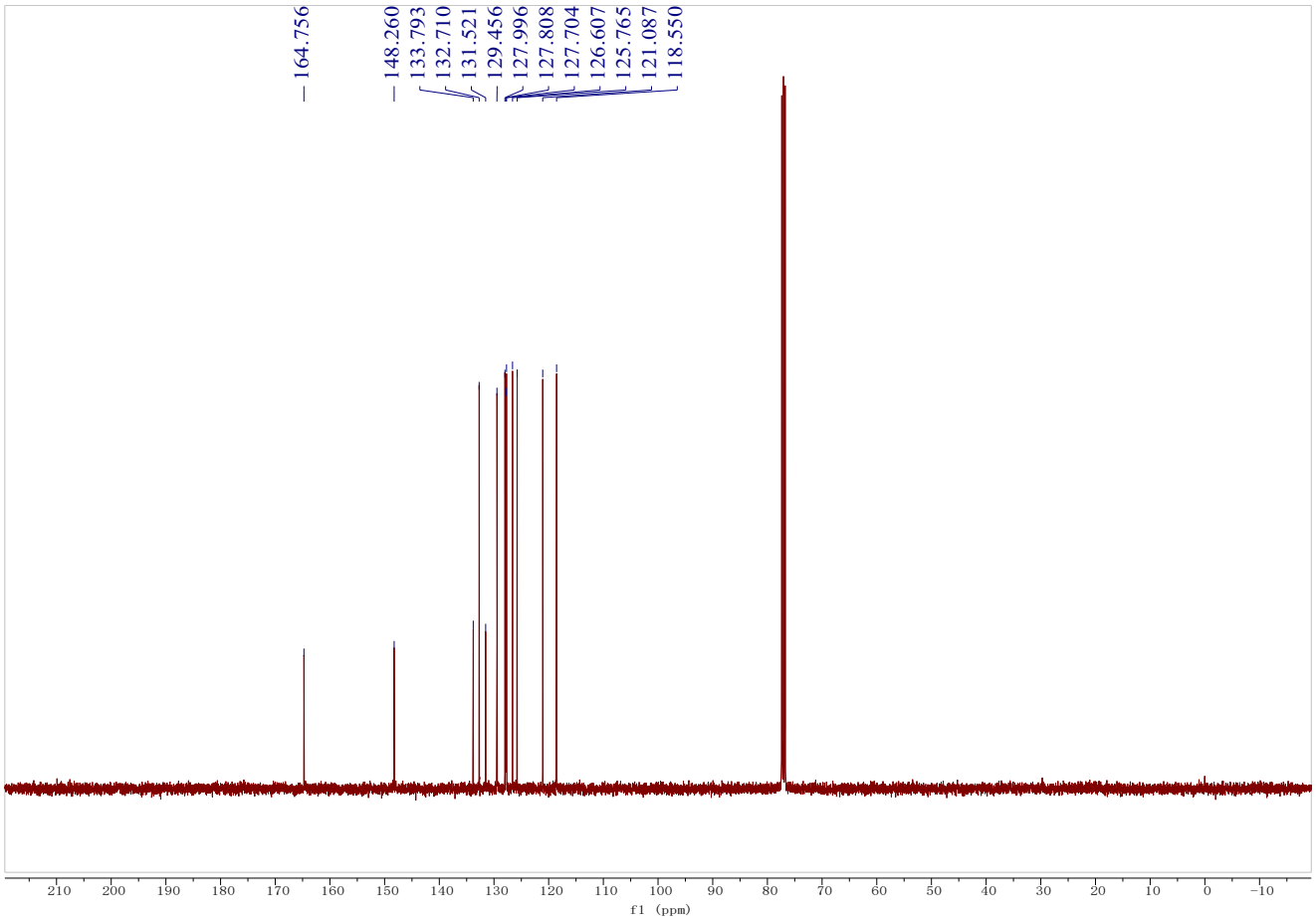
2j, ^{1}H NMR, 400 MHz, $CDCl_3$



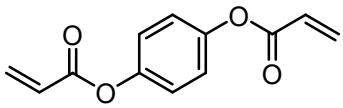


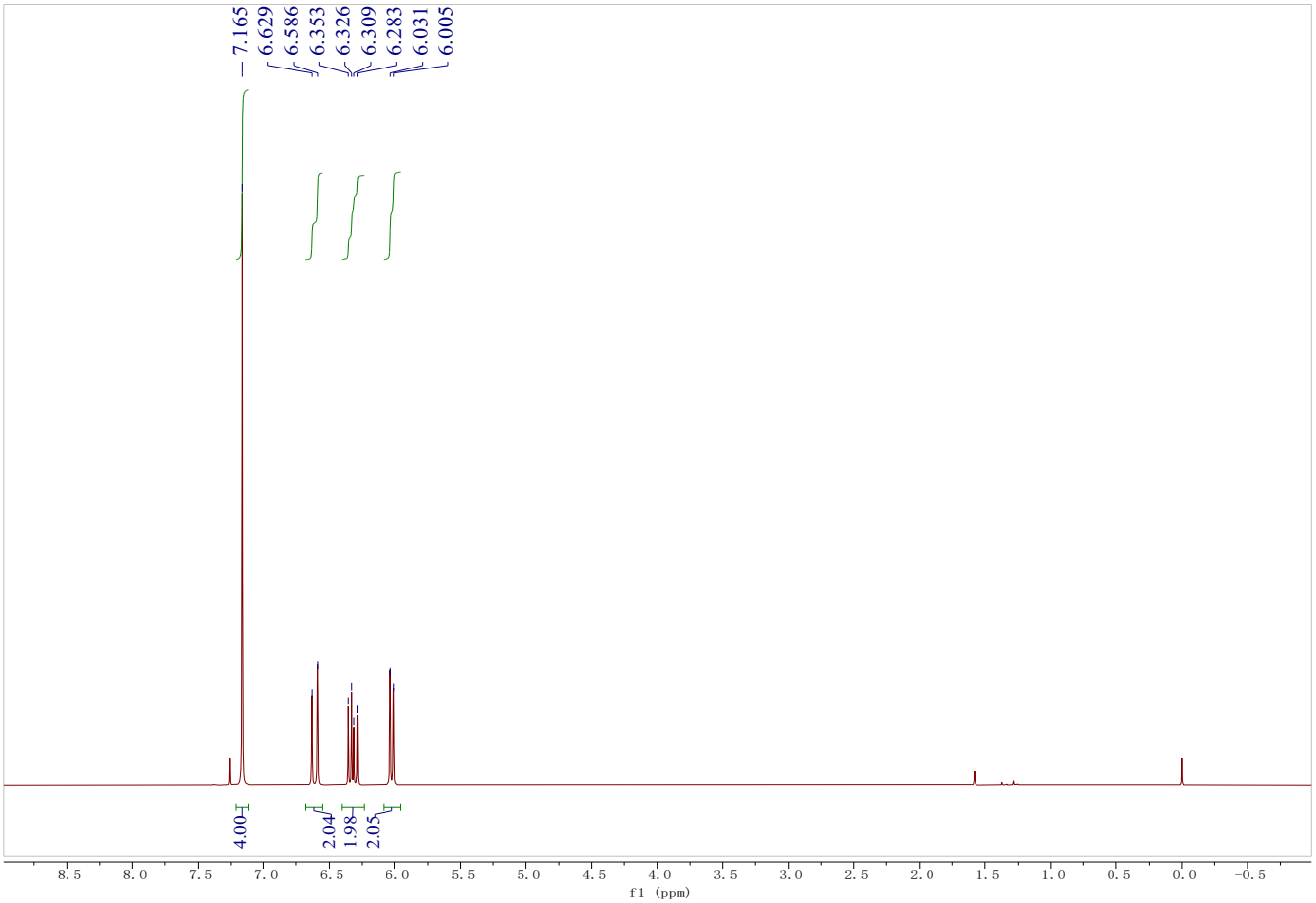
2j,^{13}C NMR, 101 MHz, $CDCl_3$



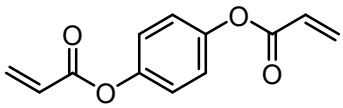


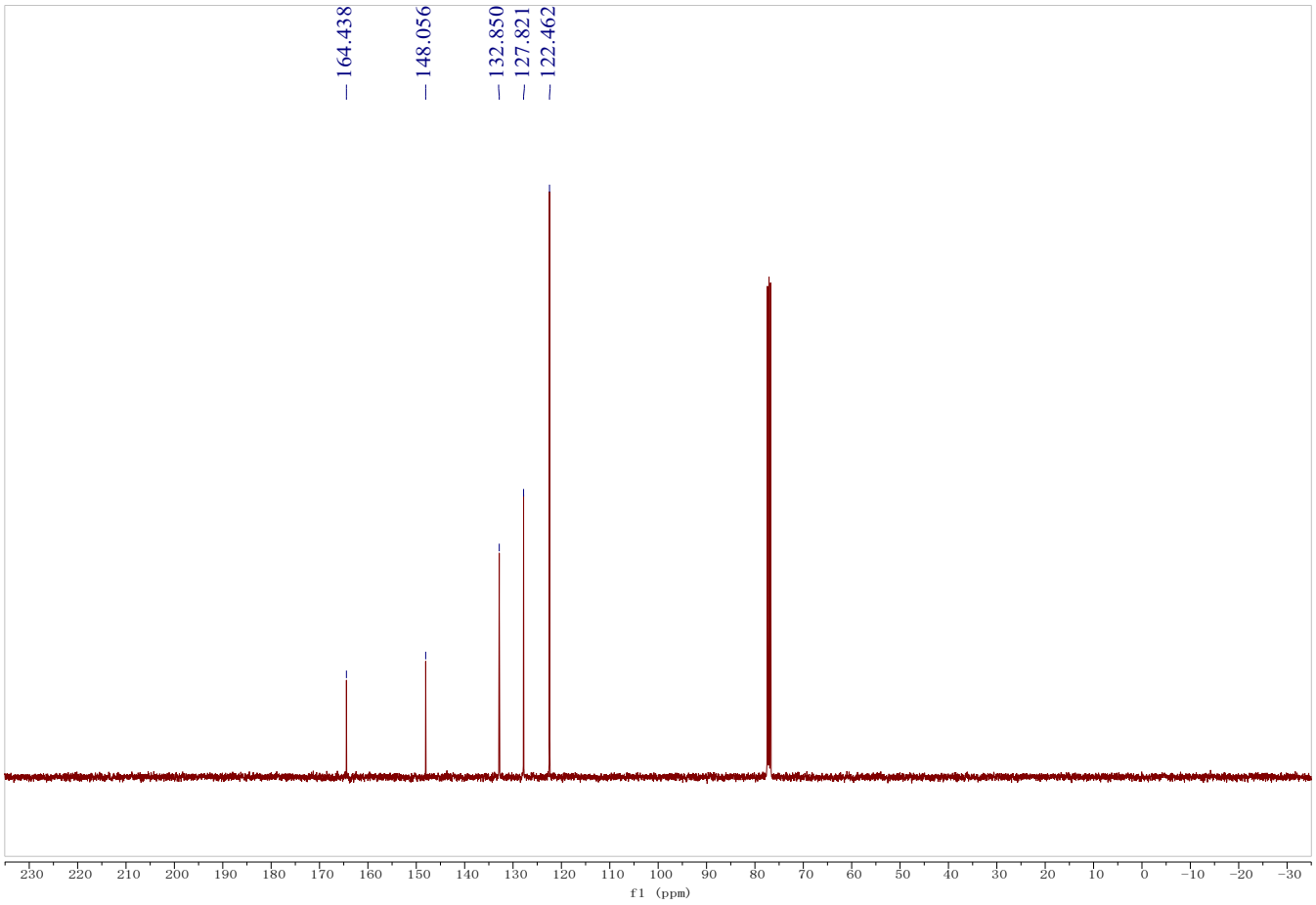
2z, ^{1}H NMR, 400 MHz, $CDCl_3$



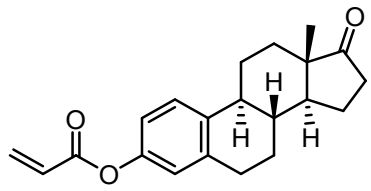


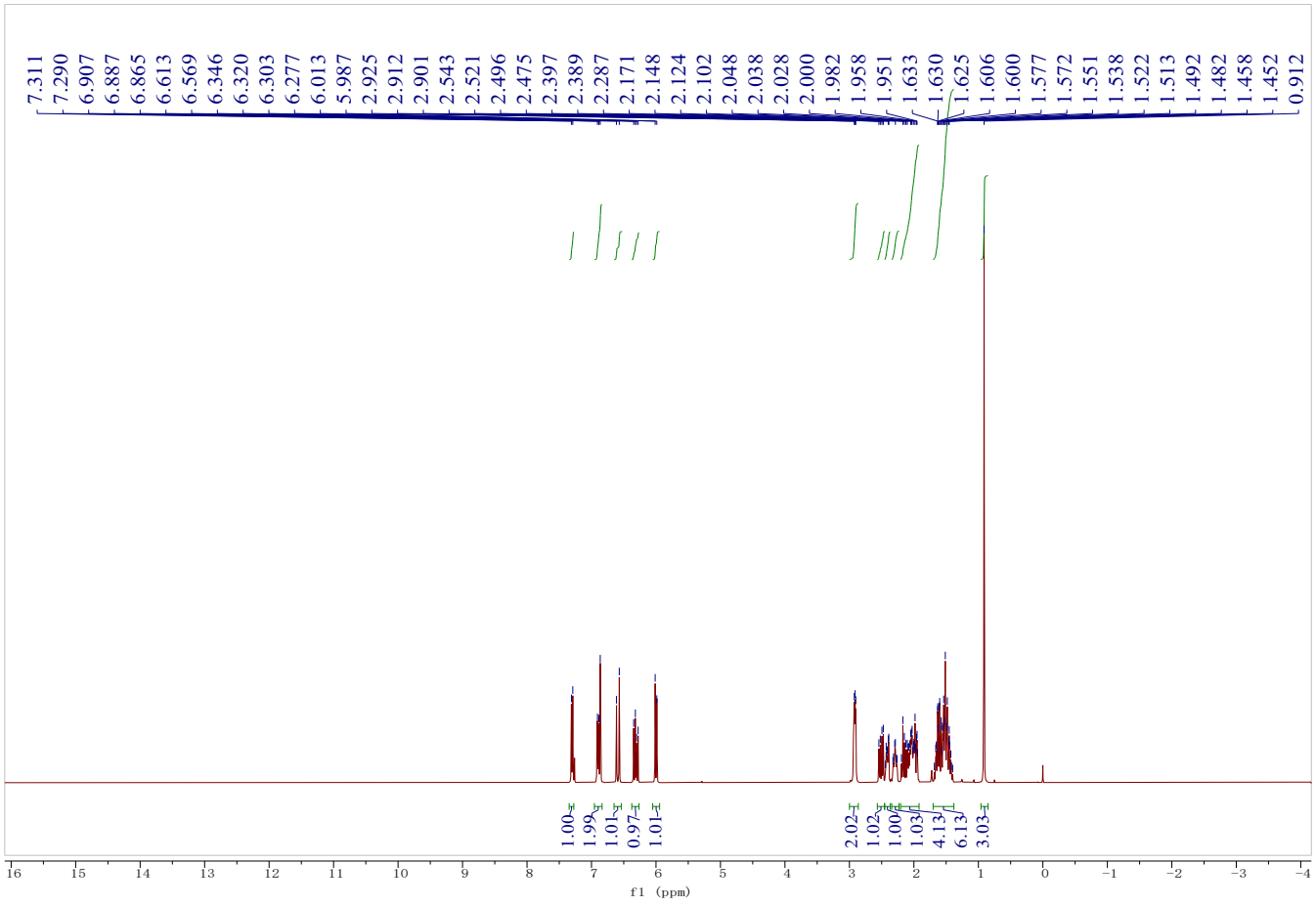
2z,^{13}C NMR, 101 MHz, $CDCl_3$



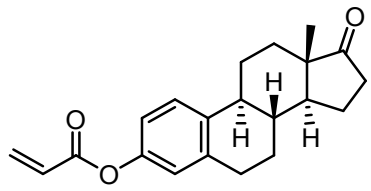


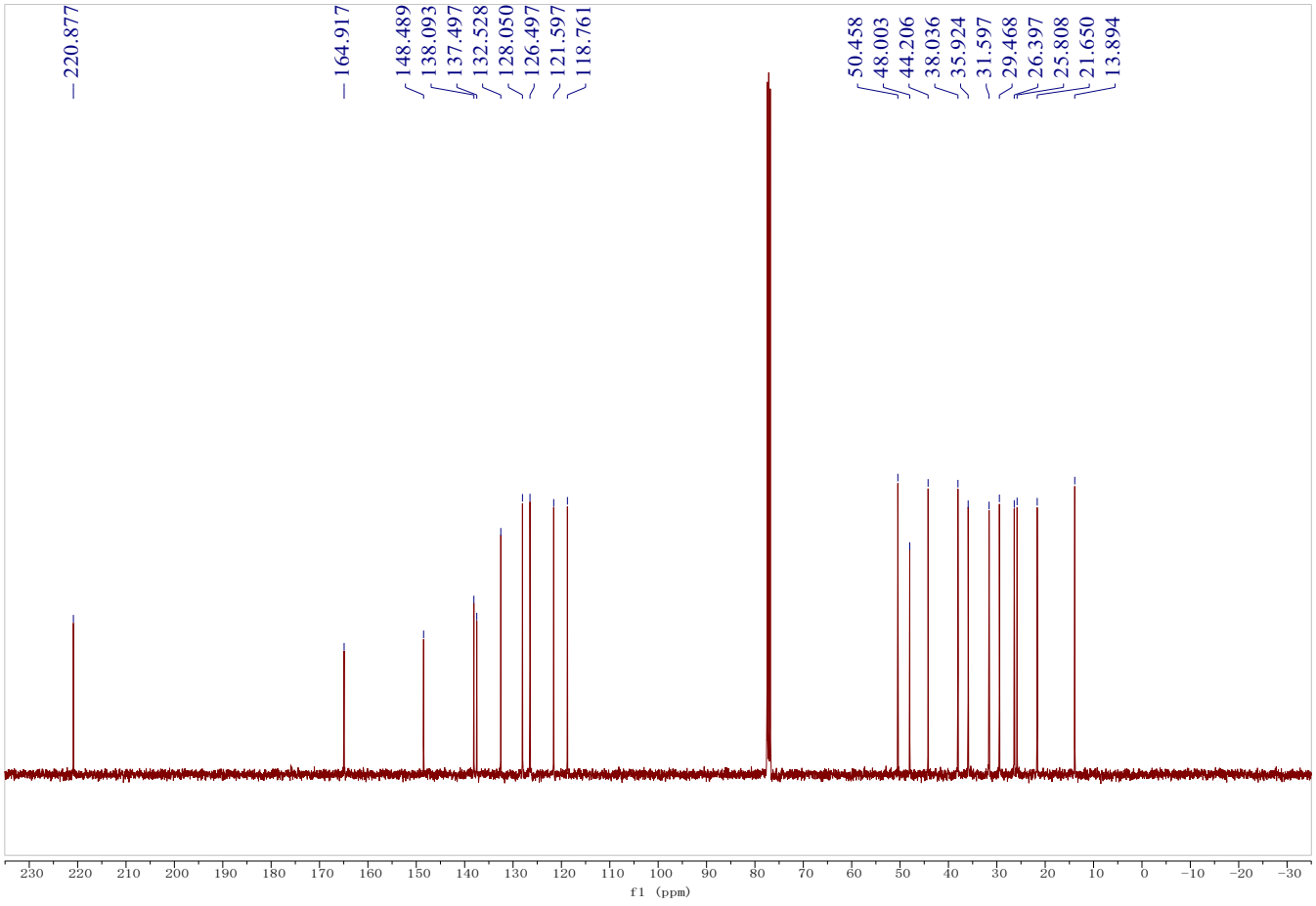
2aa, ^{1}H NMR, 400 MHz, $CDCl_3$



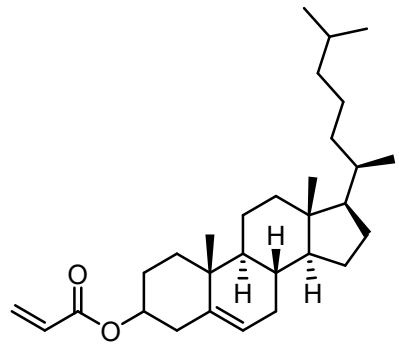


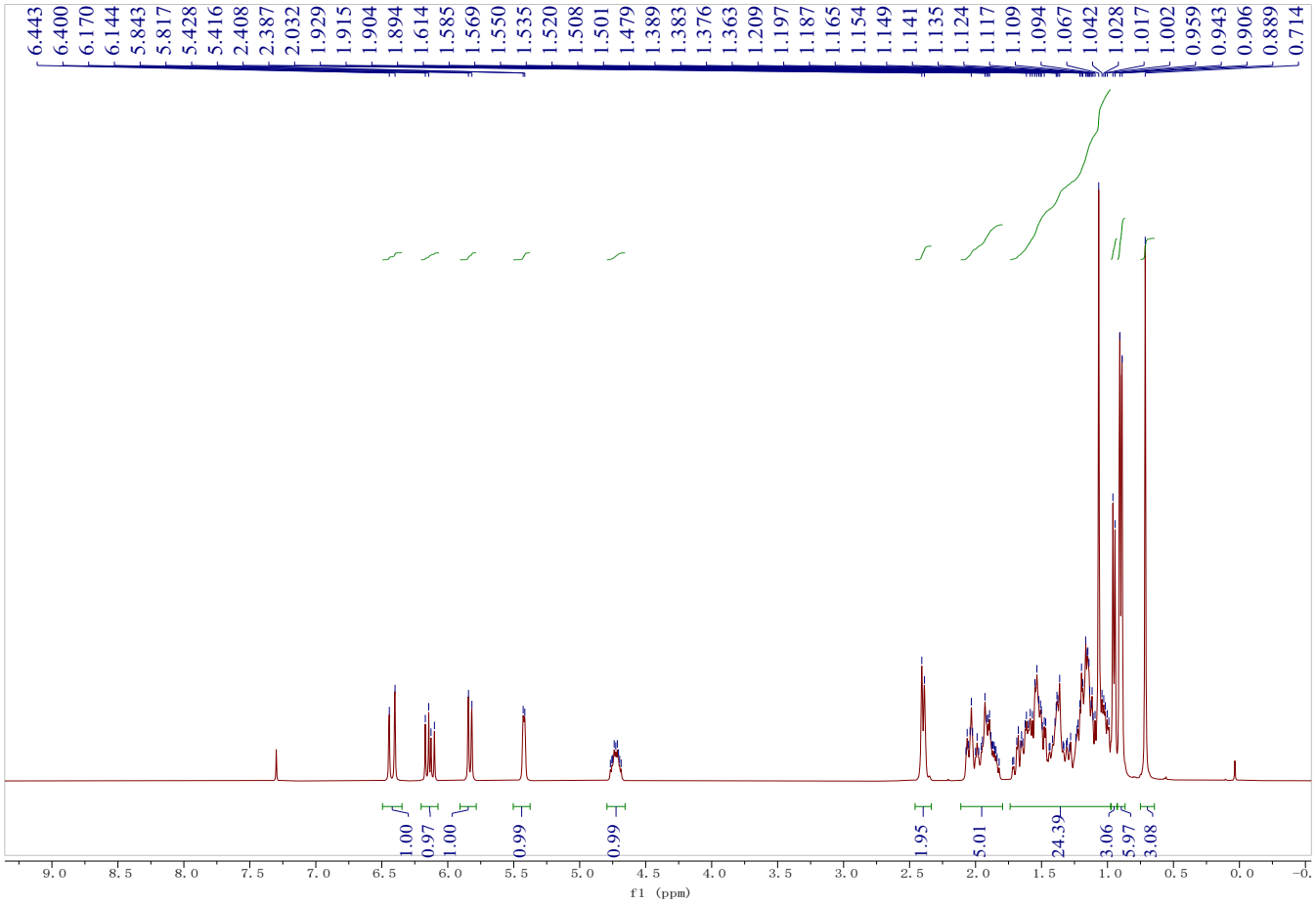
2aa,^{13}C NMR, 101 MHz, $CDCl_3$



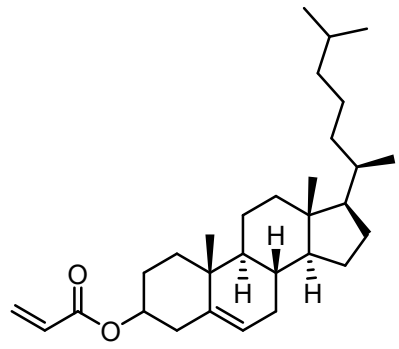


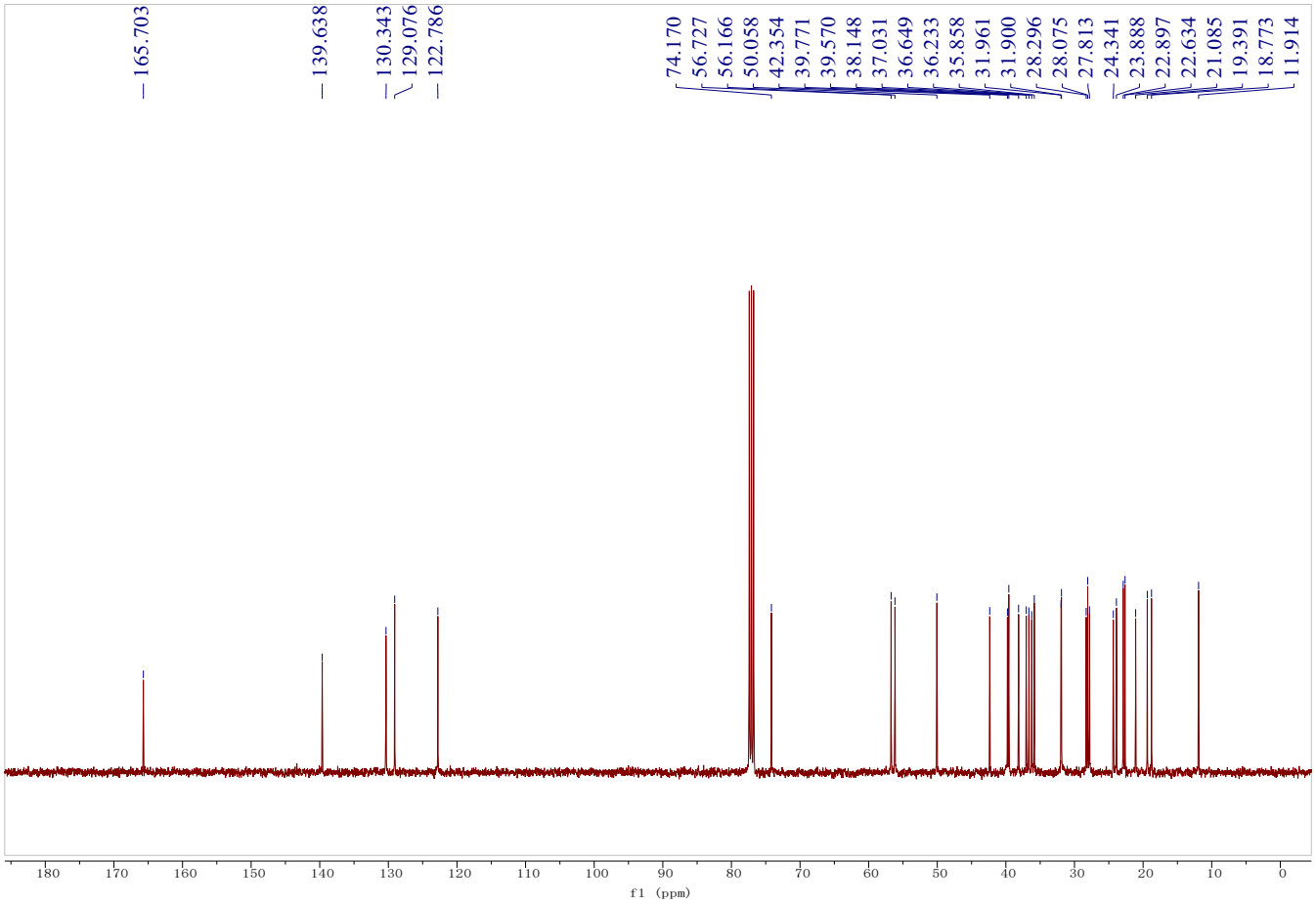
2ab, ^{1}H NMR, 400 MHz, $CDCl_3$



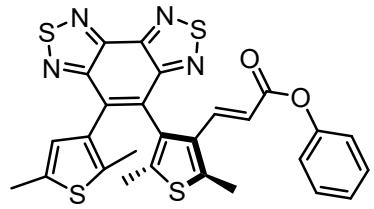


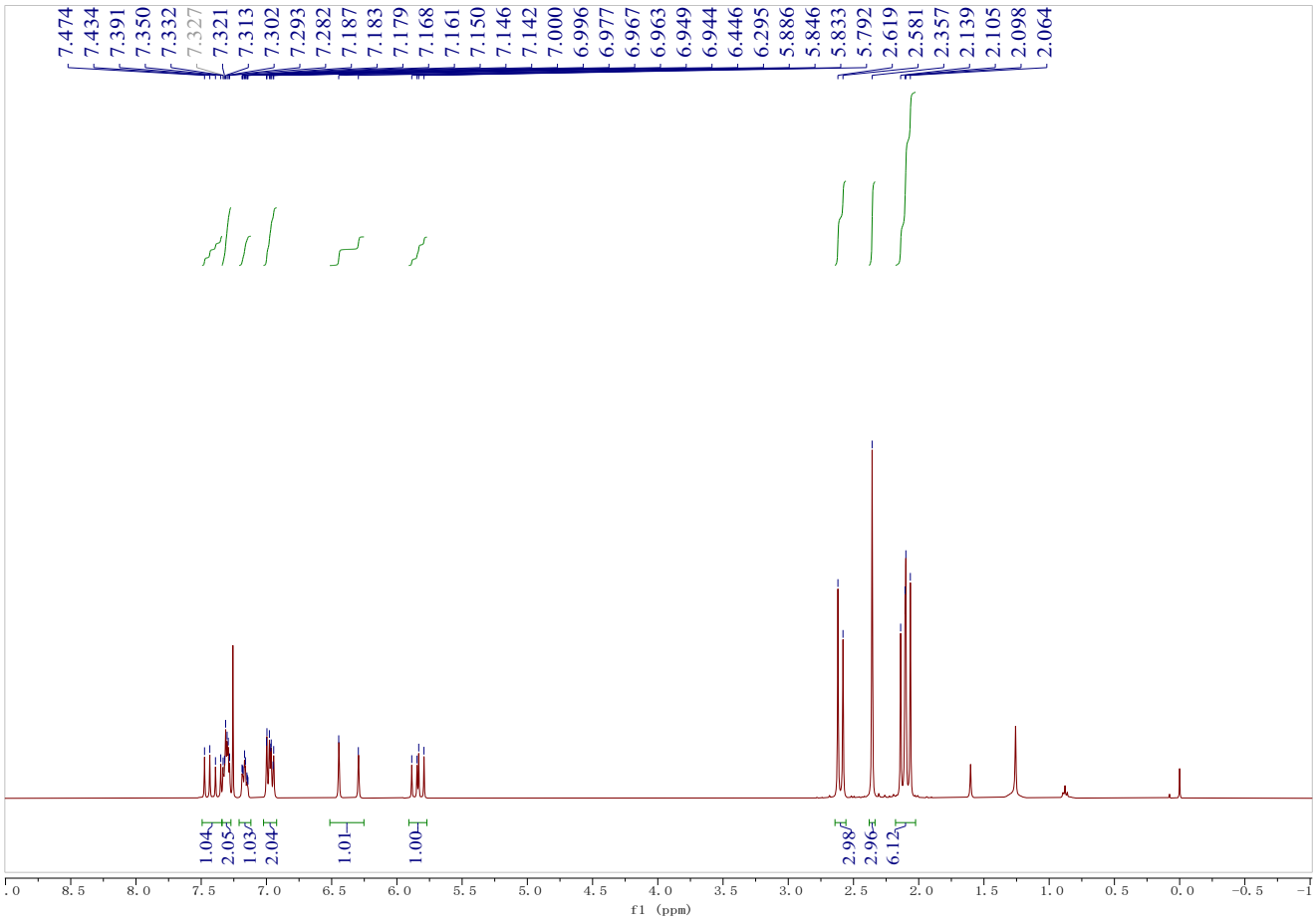
2ab,^{13}C NMR, 101 MHz, $CDCl_3$



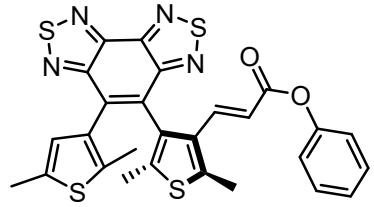


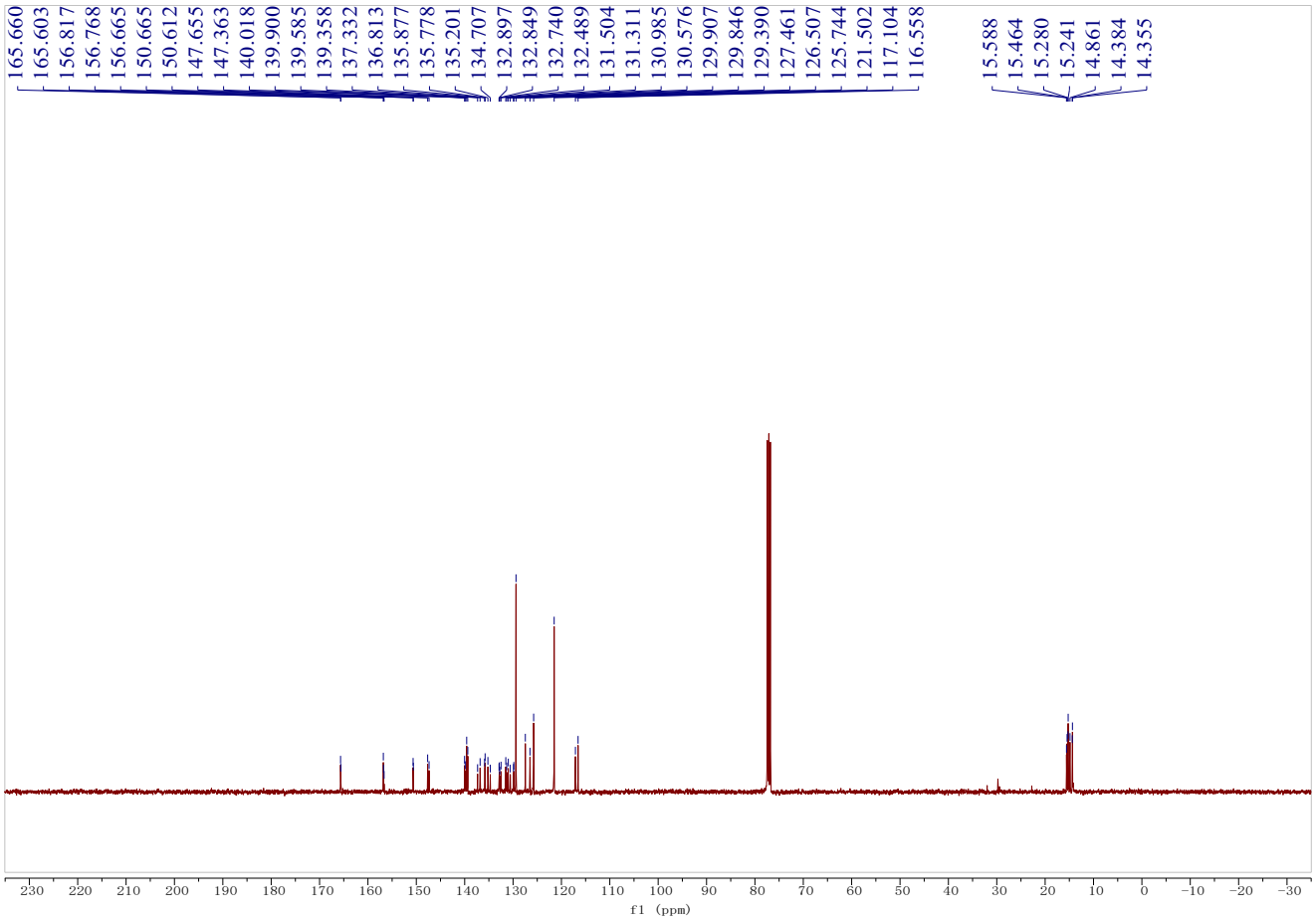
3a, ^{1}H NMR, 400 MHz, $CDCl_3$



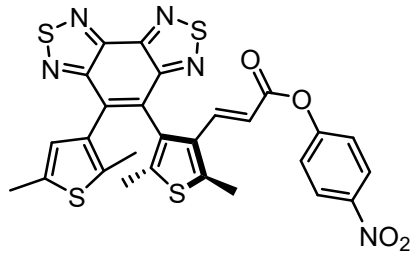


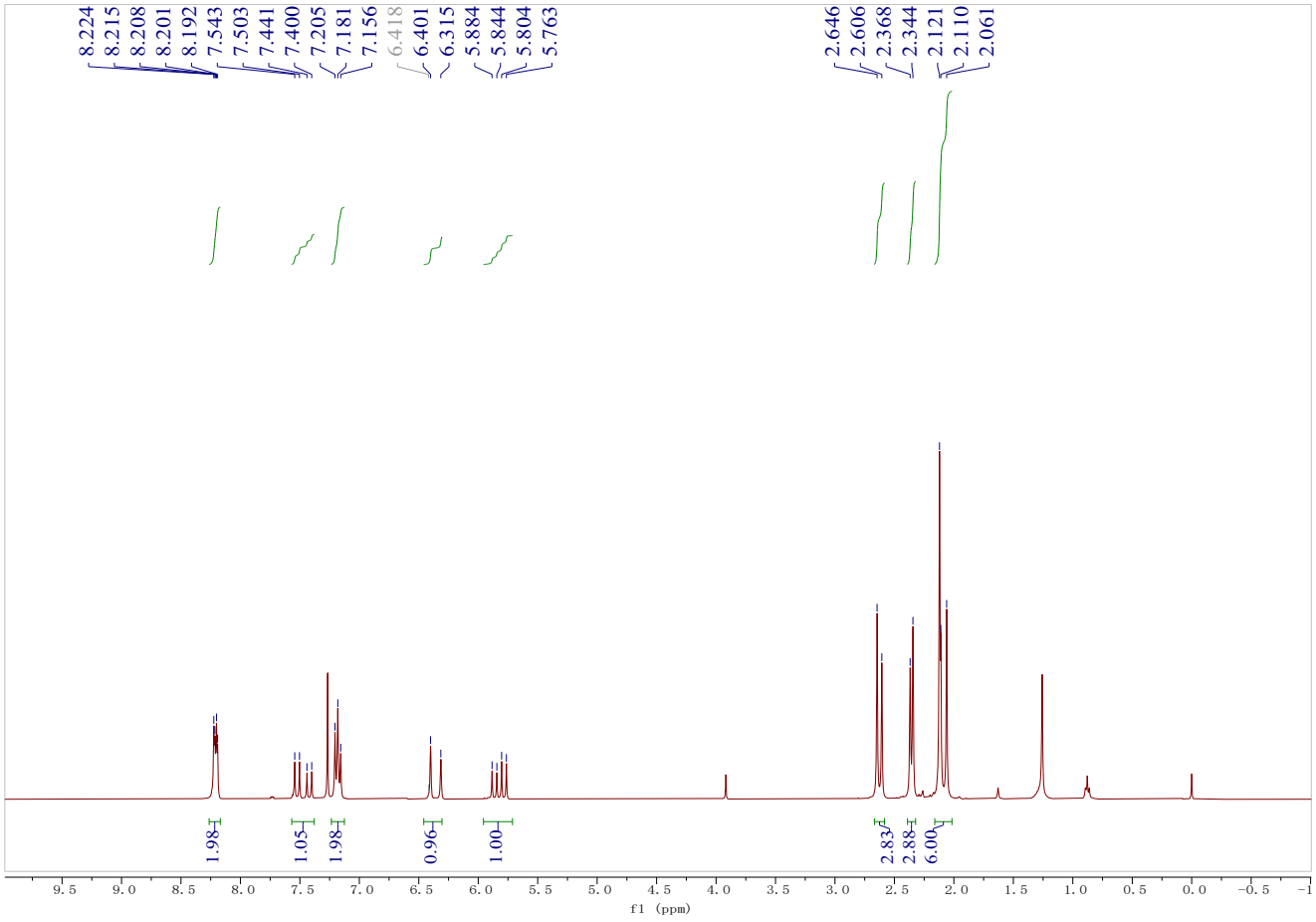
3a,^{13}C NMR, 101 MHz, $CDCl_3$



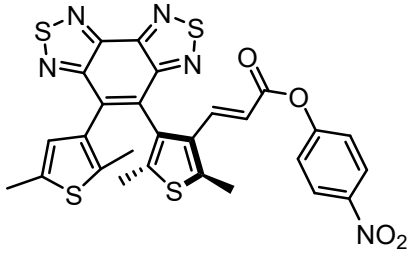


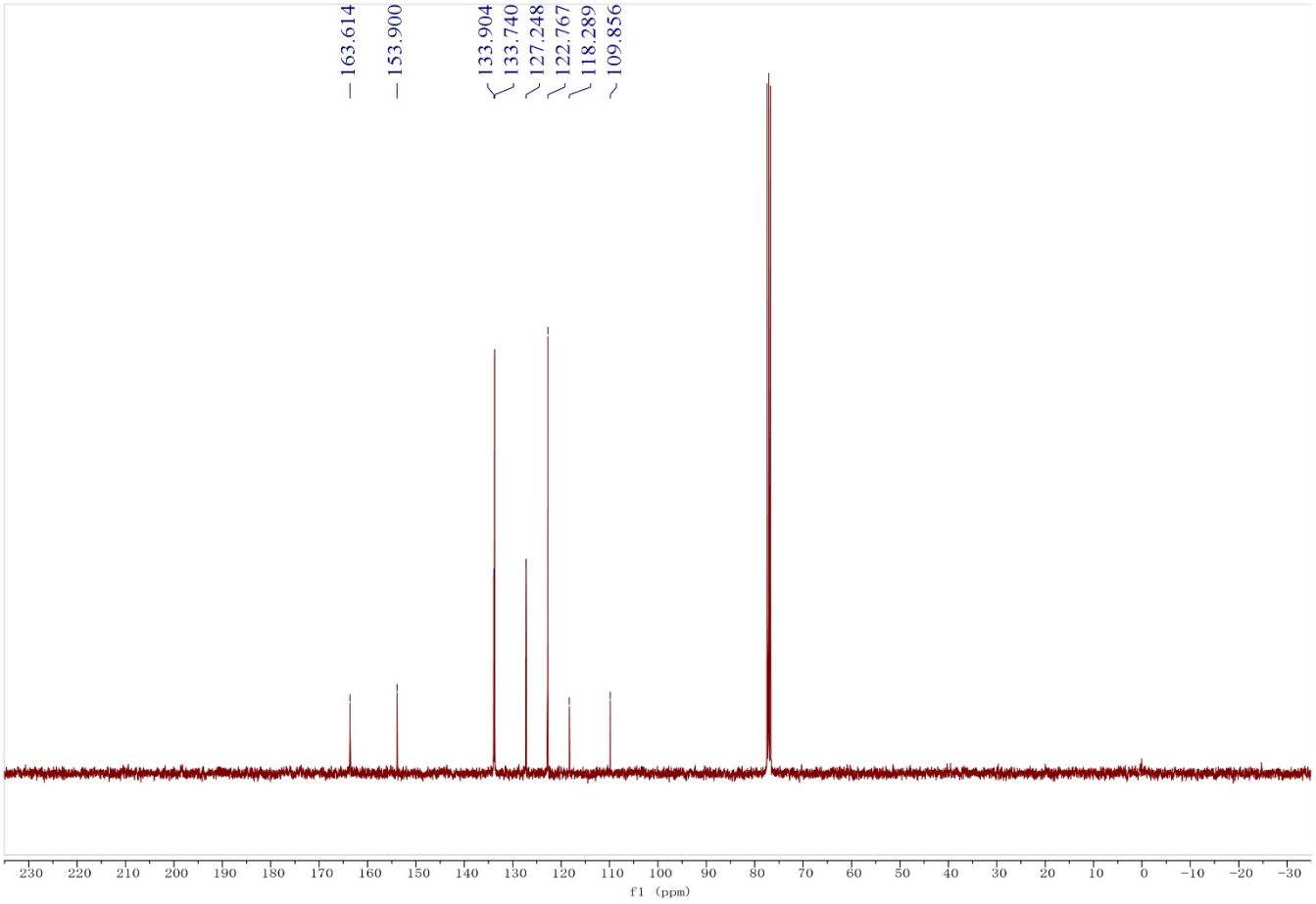
3b, ^{1}H NMR, 400 MHz, $CDCl_3$



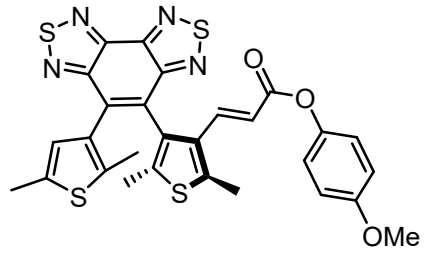


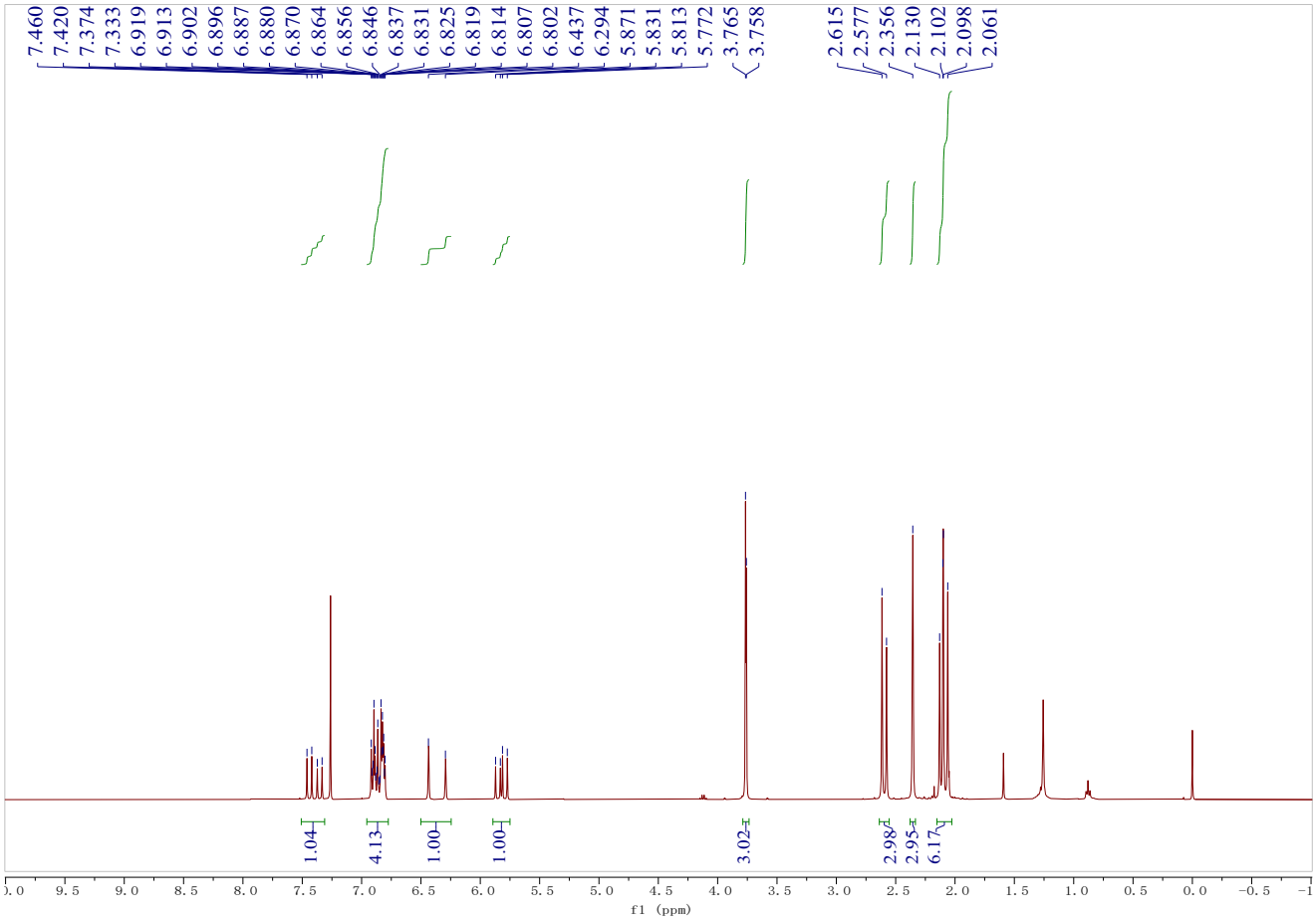
3b,^{13}C NMR, 101 MHz, $CDCl_3$



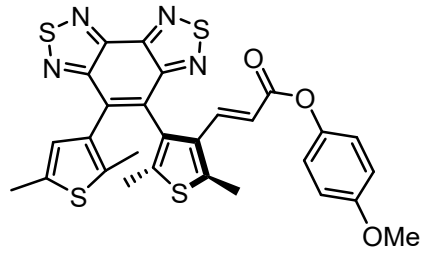


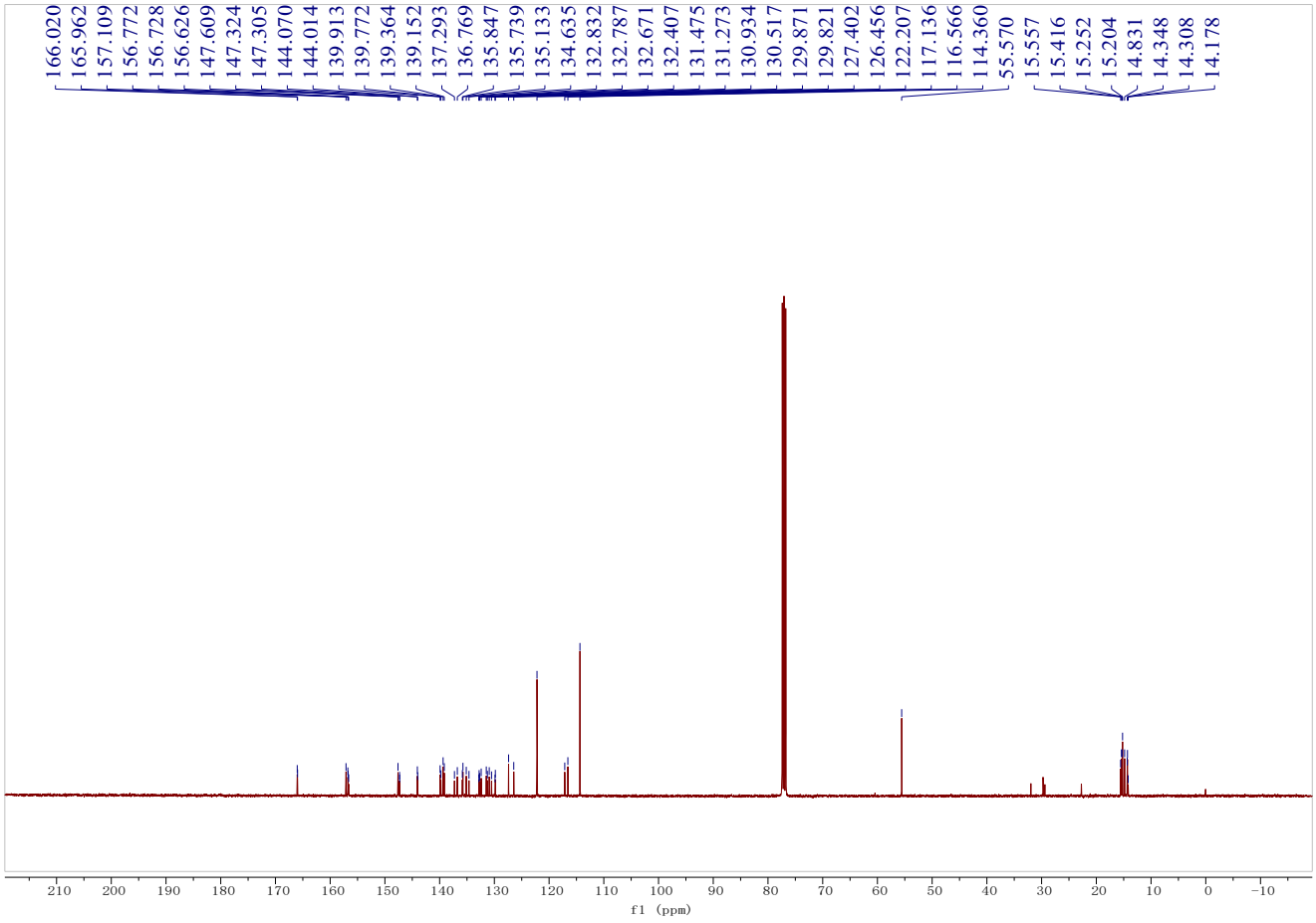
3c, ^{1}H NMR, 400 MHz, $CDCl_3$





3c,^{13}C NMR, 101 MHz, $CDCl_3$





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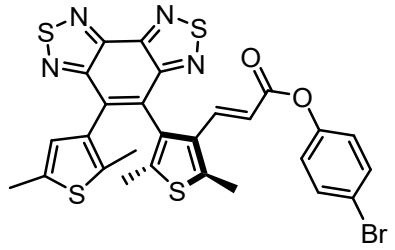
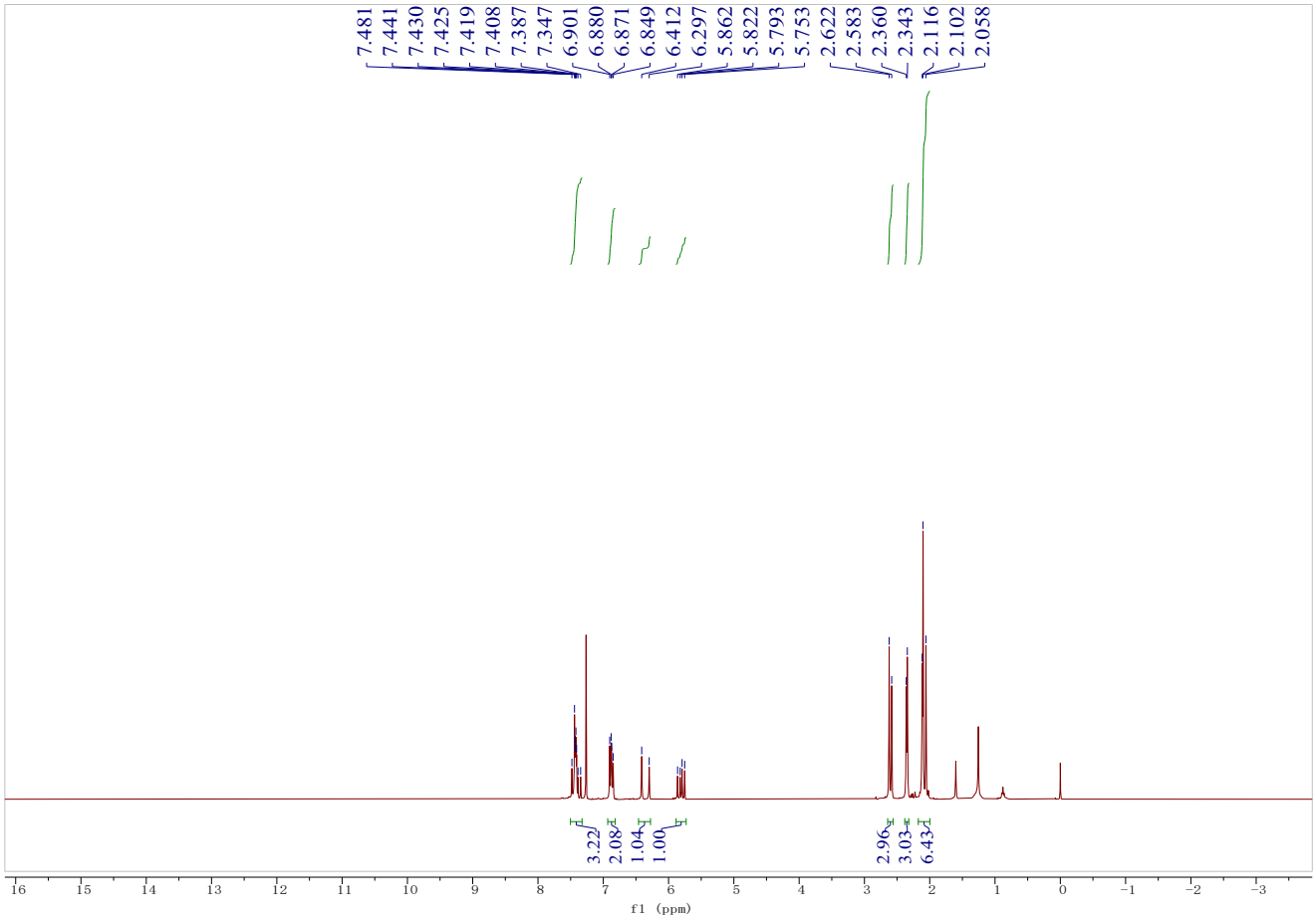
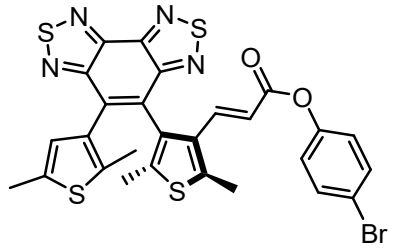
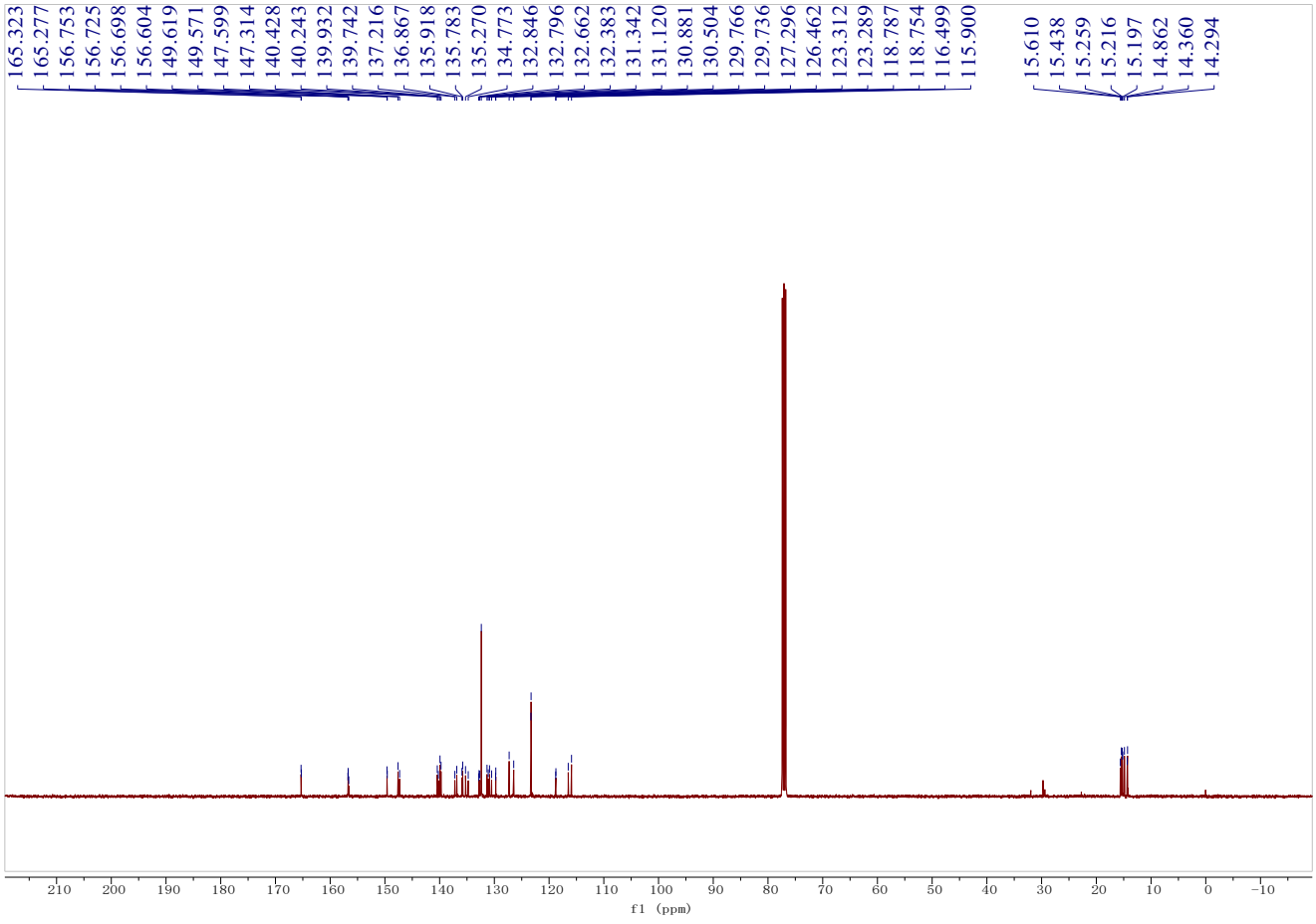


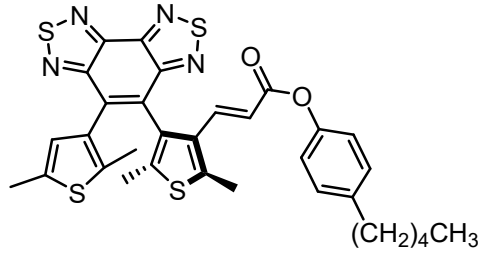


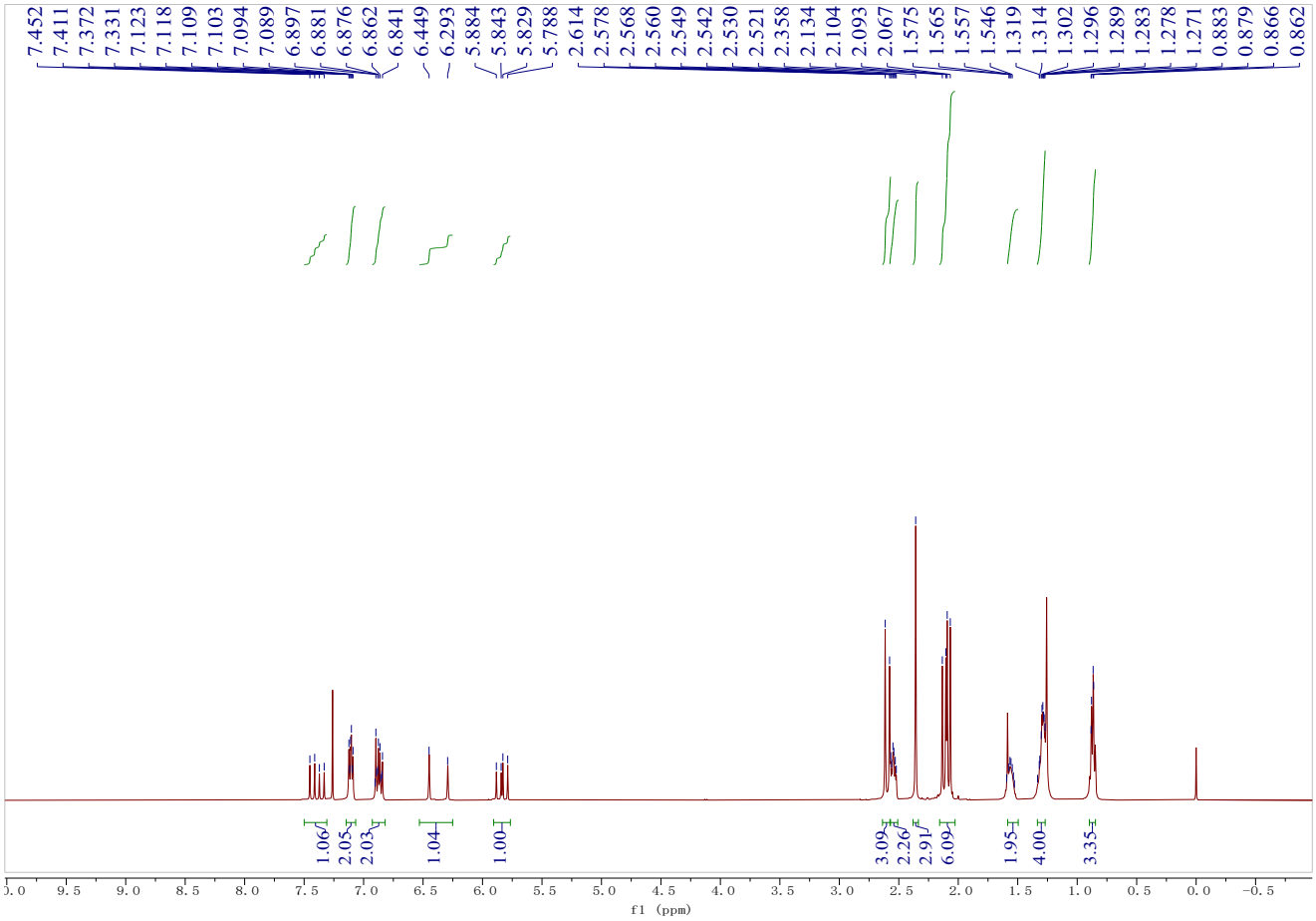
3d,^{13}C NMR, 101 MHz, $CDCl_3$



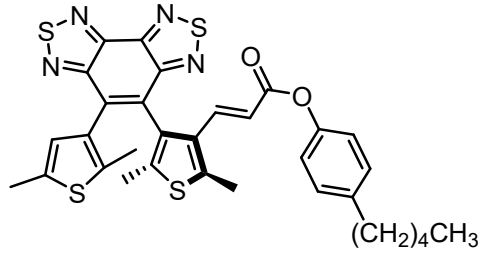


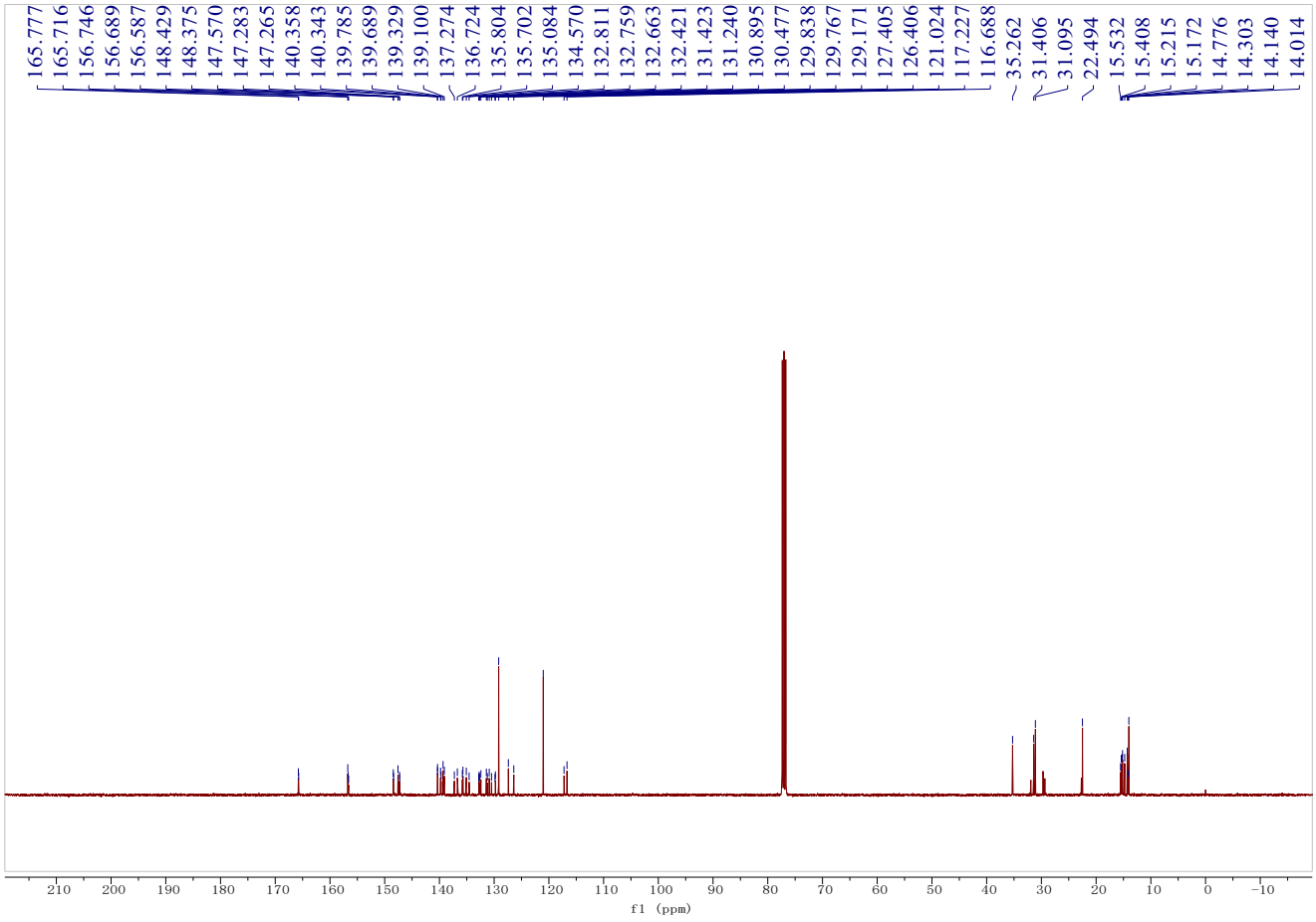
3e, ^{1}H NMR, 400 MHz, $CDCl_3$



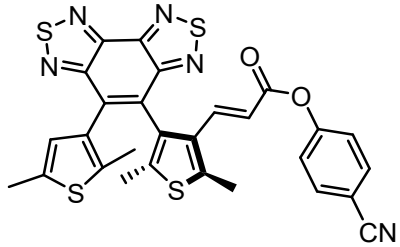


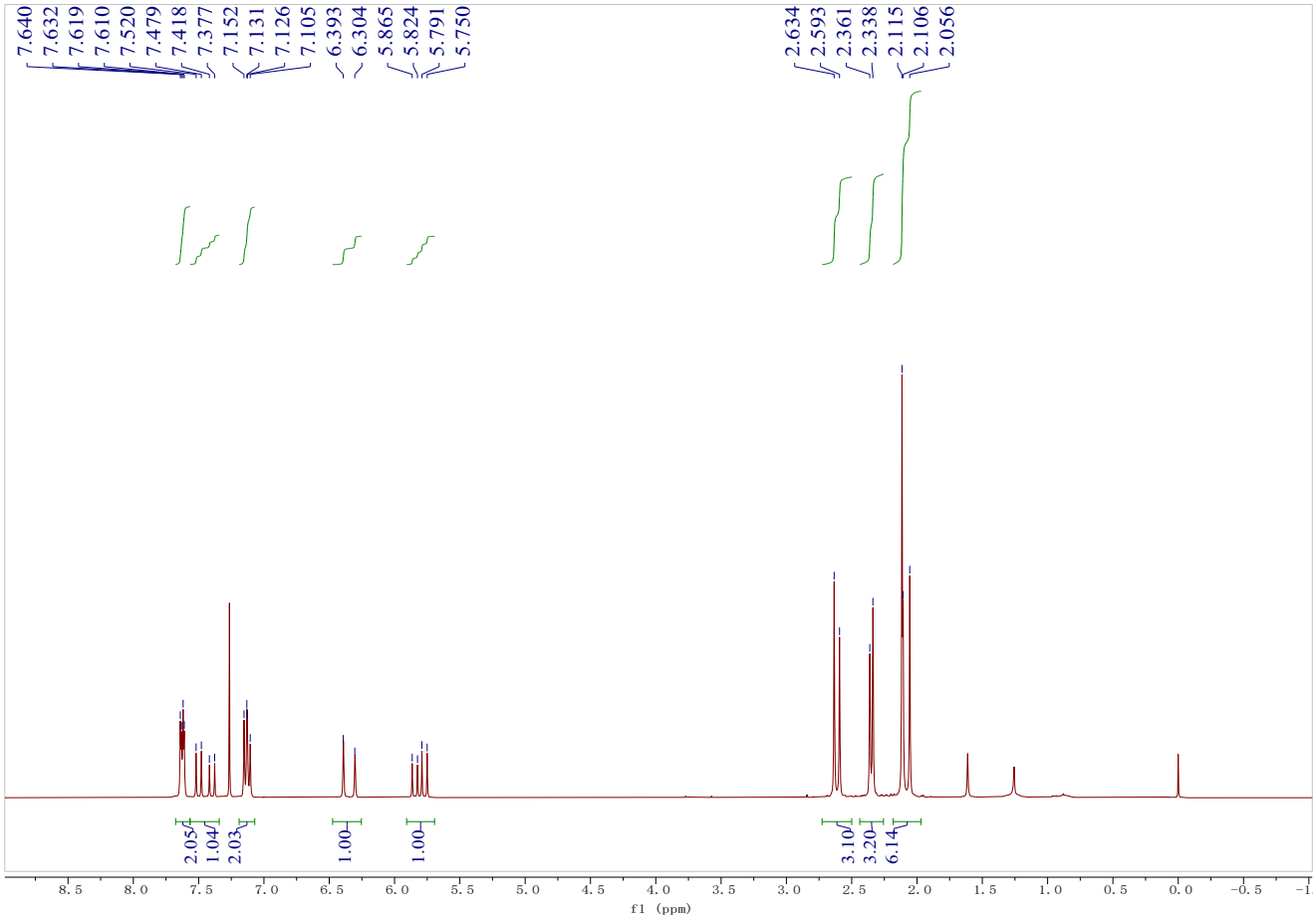
3e,^{13}C NMR, 101 MHz, $CDCl_3$



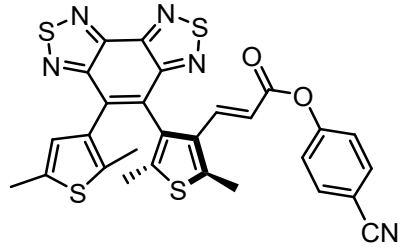


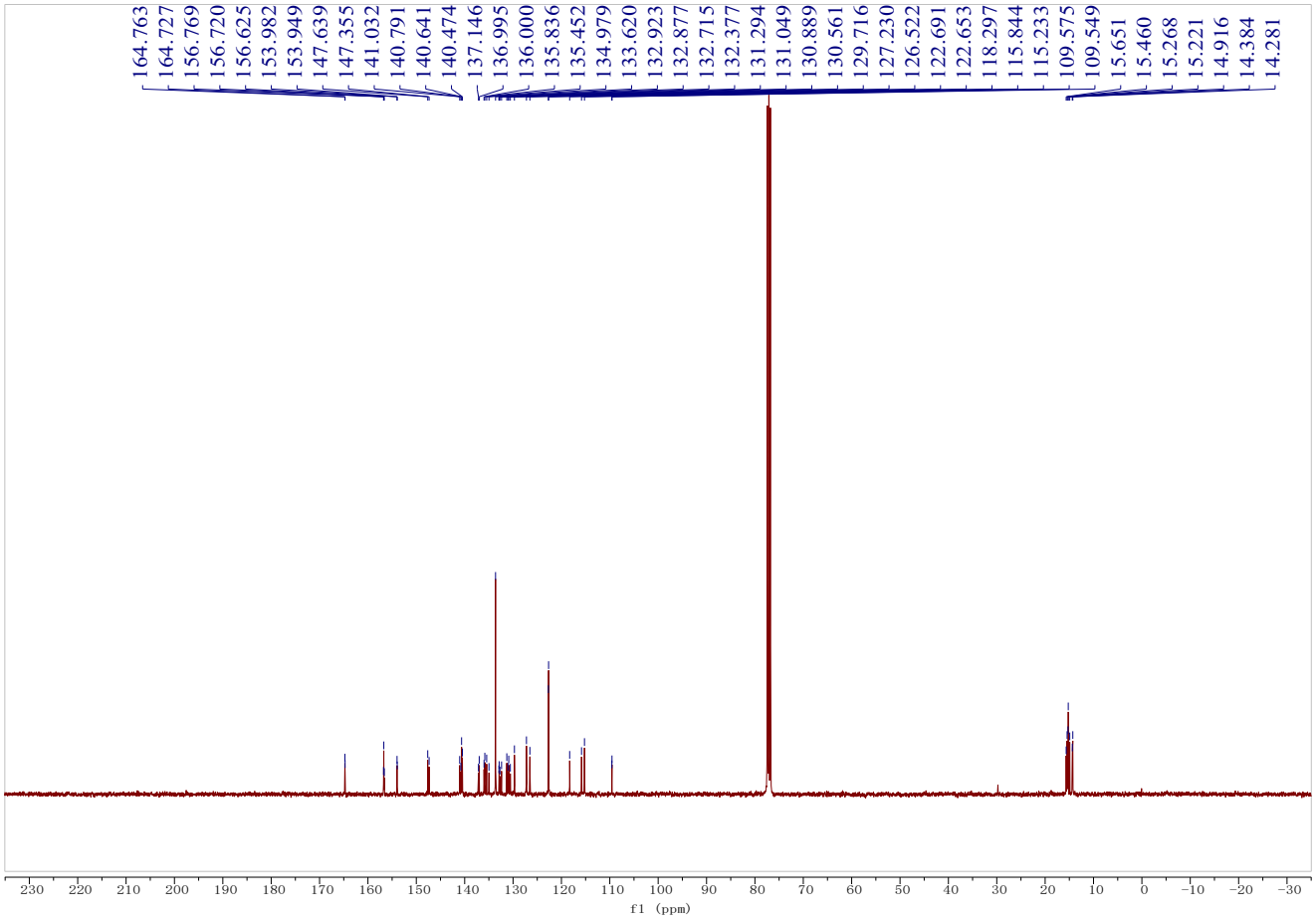
3f, ^{1}H NMR, 400 MHz, $CDCl_3$



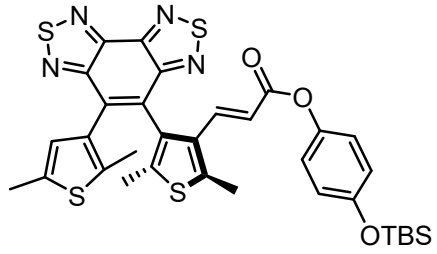


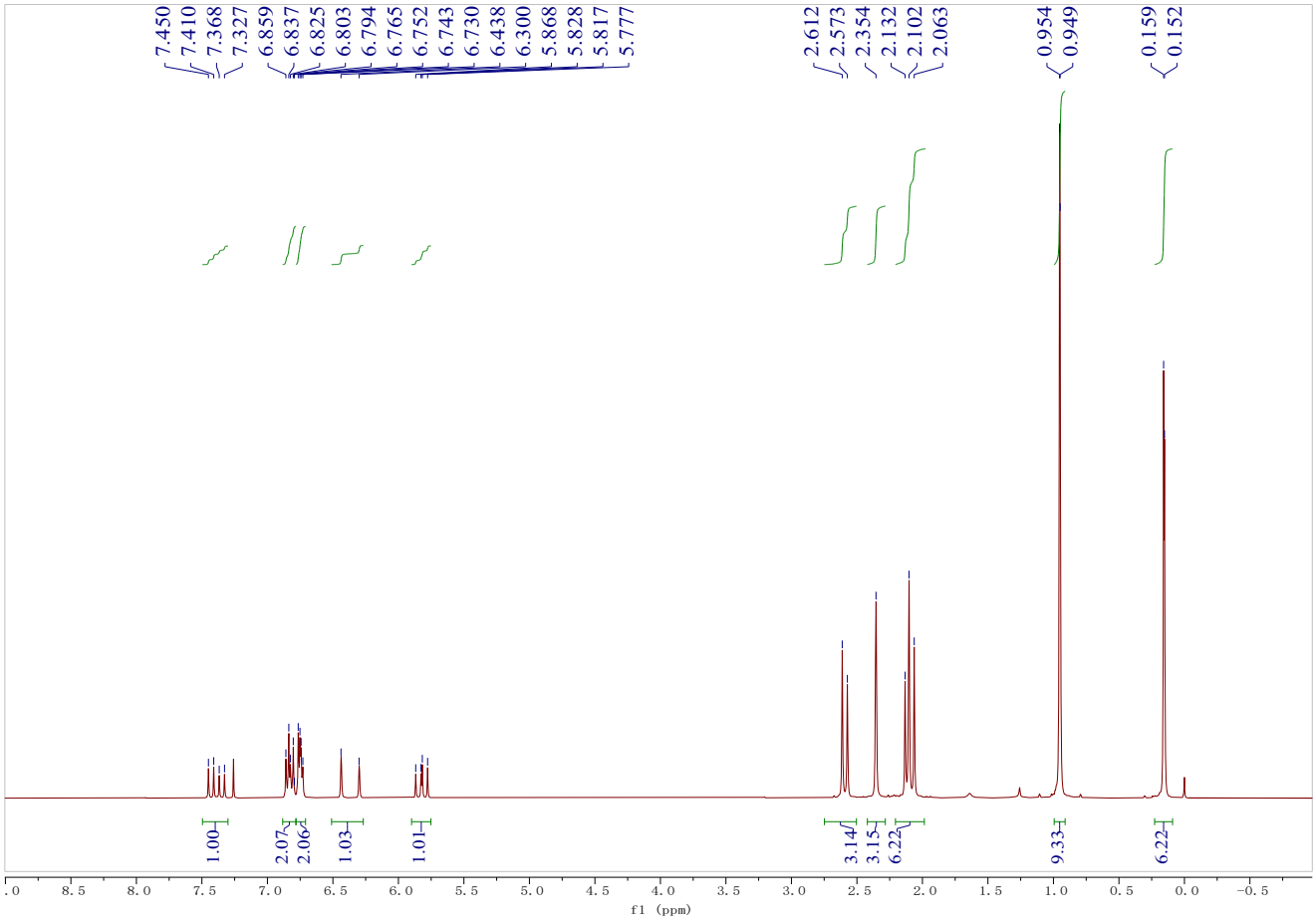
3f,^{13}C NMR, 101 MHz, $CDCl_3$



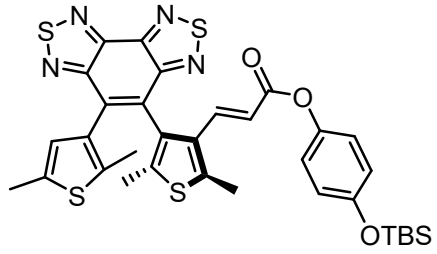


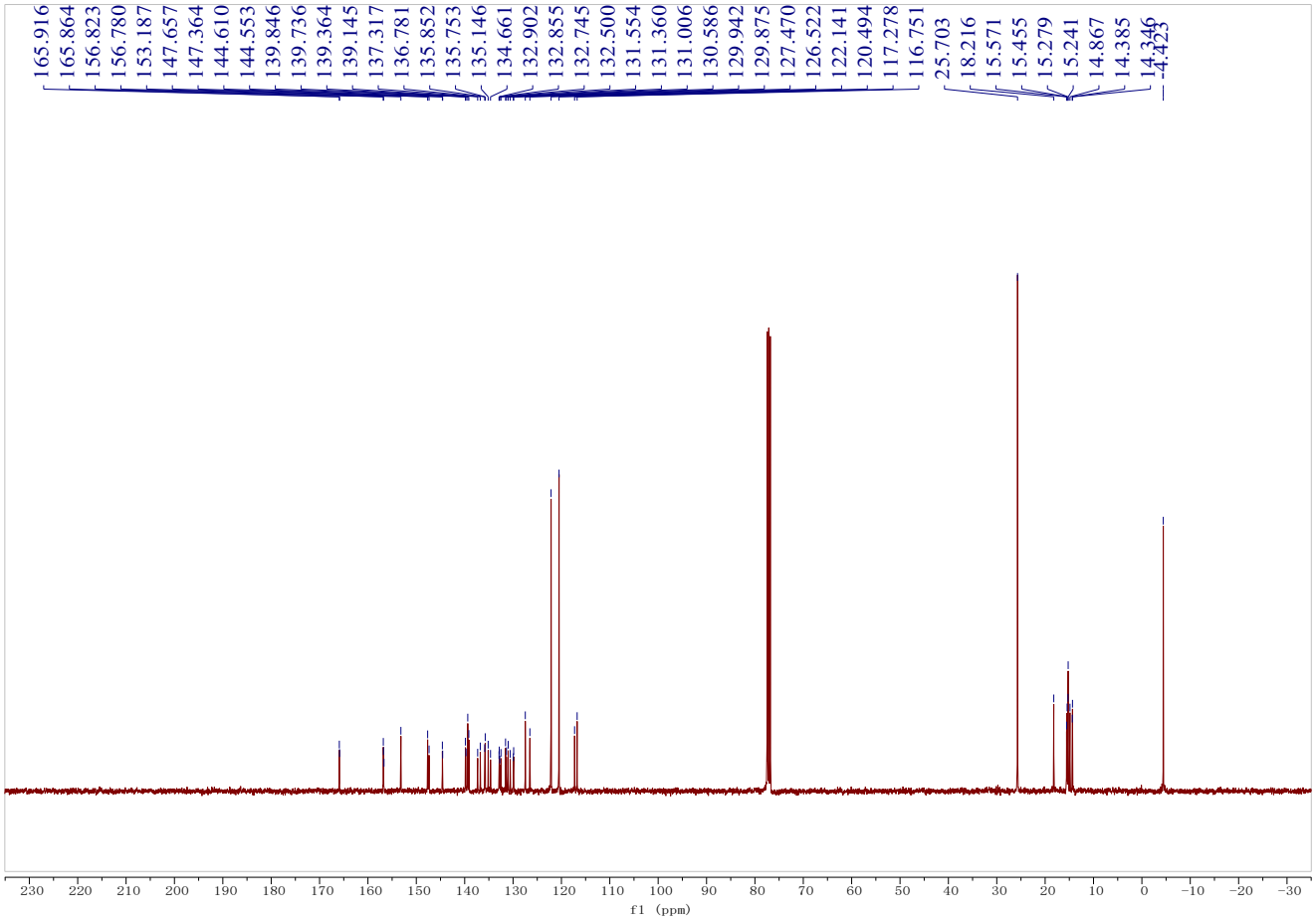
3g, ^{1}H NMR, 400 MHz, $CDCl_3$



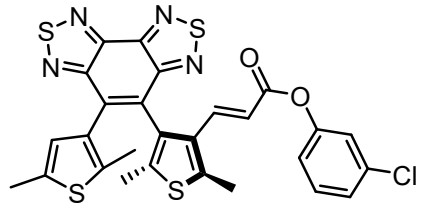


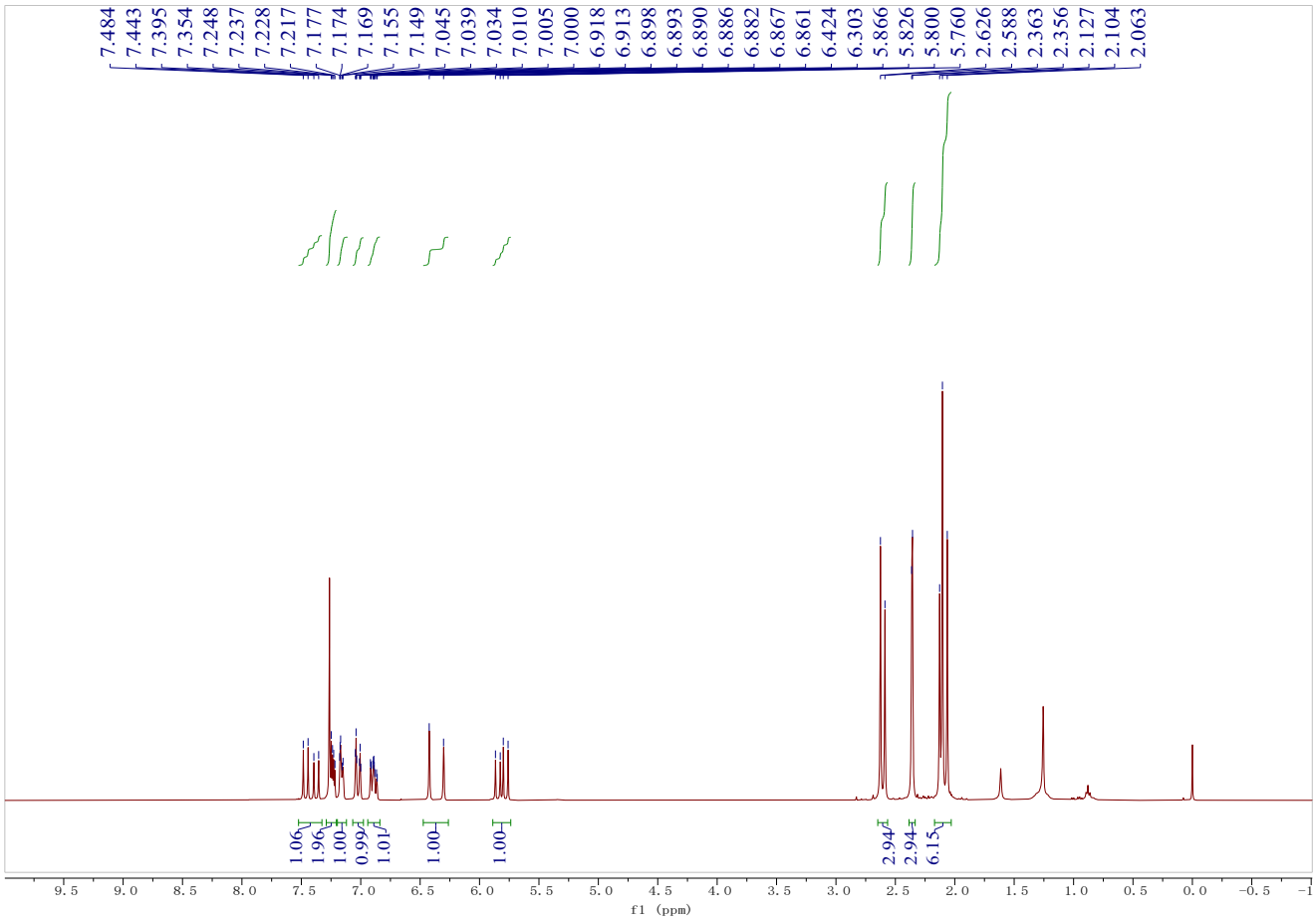
3g,^{13}C NMR, 101 MHz, $CDCl_3$



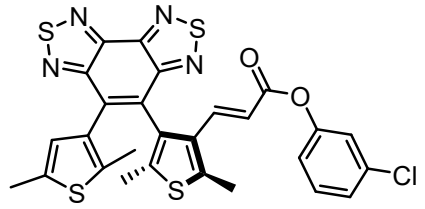


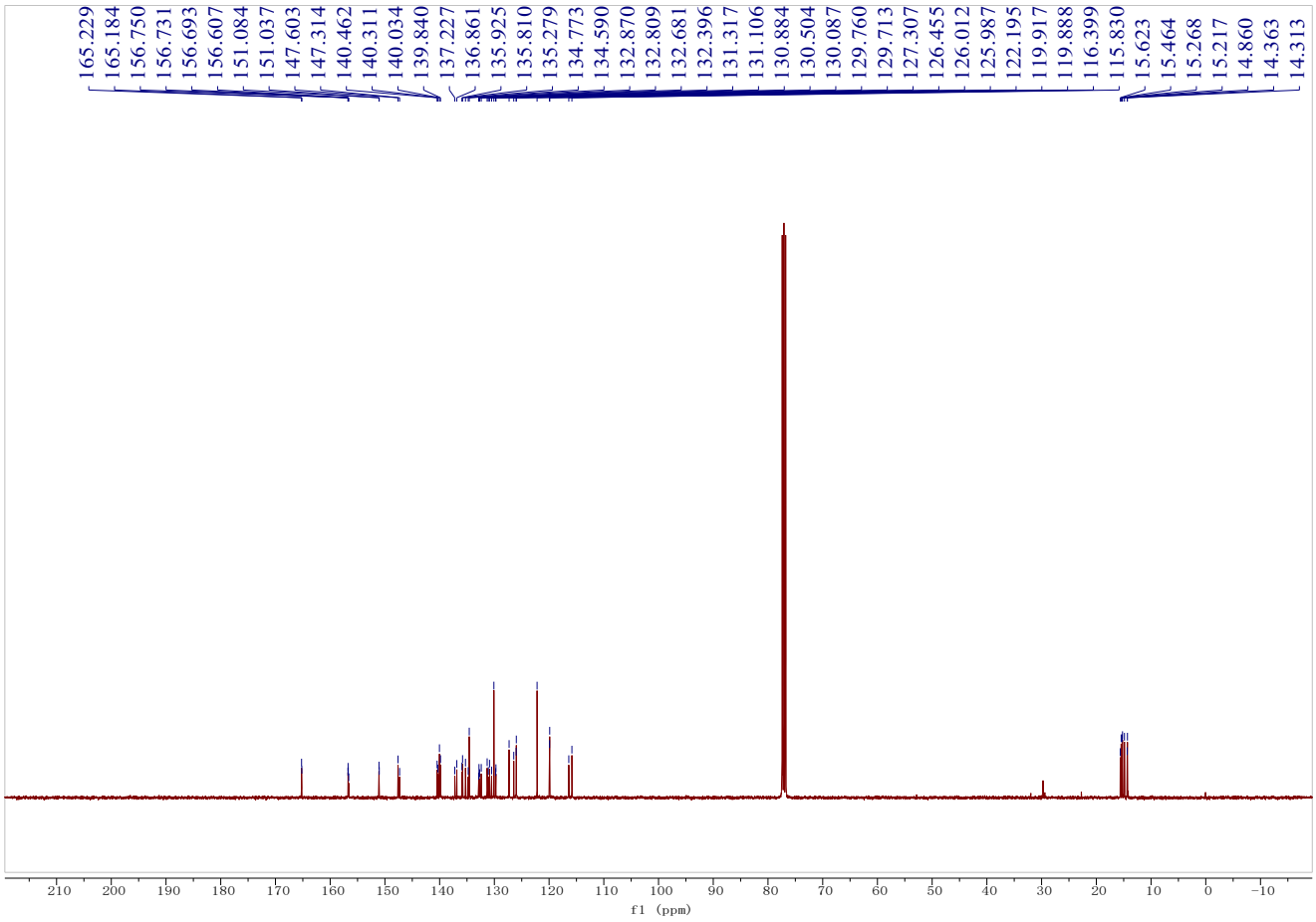
3h, ^{1}H NMR, 400 MHz, $CDCl_3$



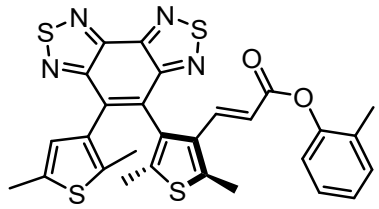


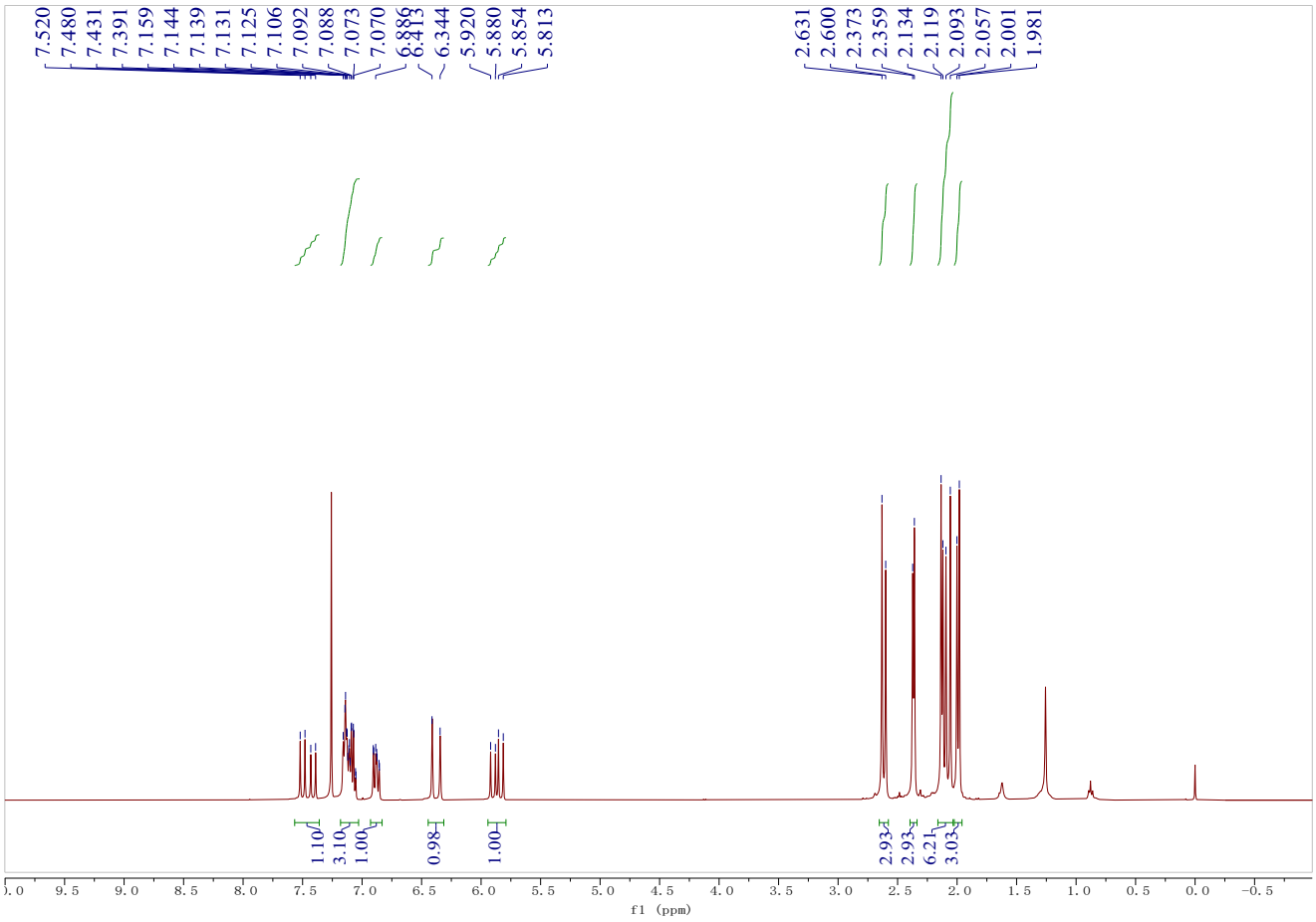
3h,^{13}C NMR, 101 MHz, $CDCl_3$



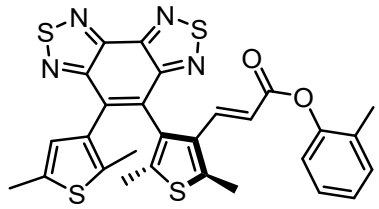


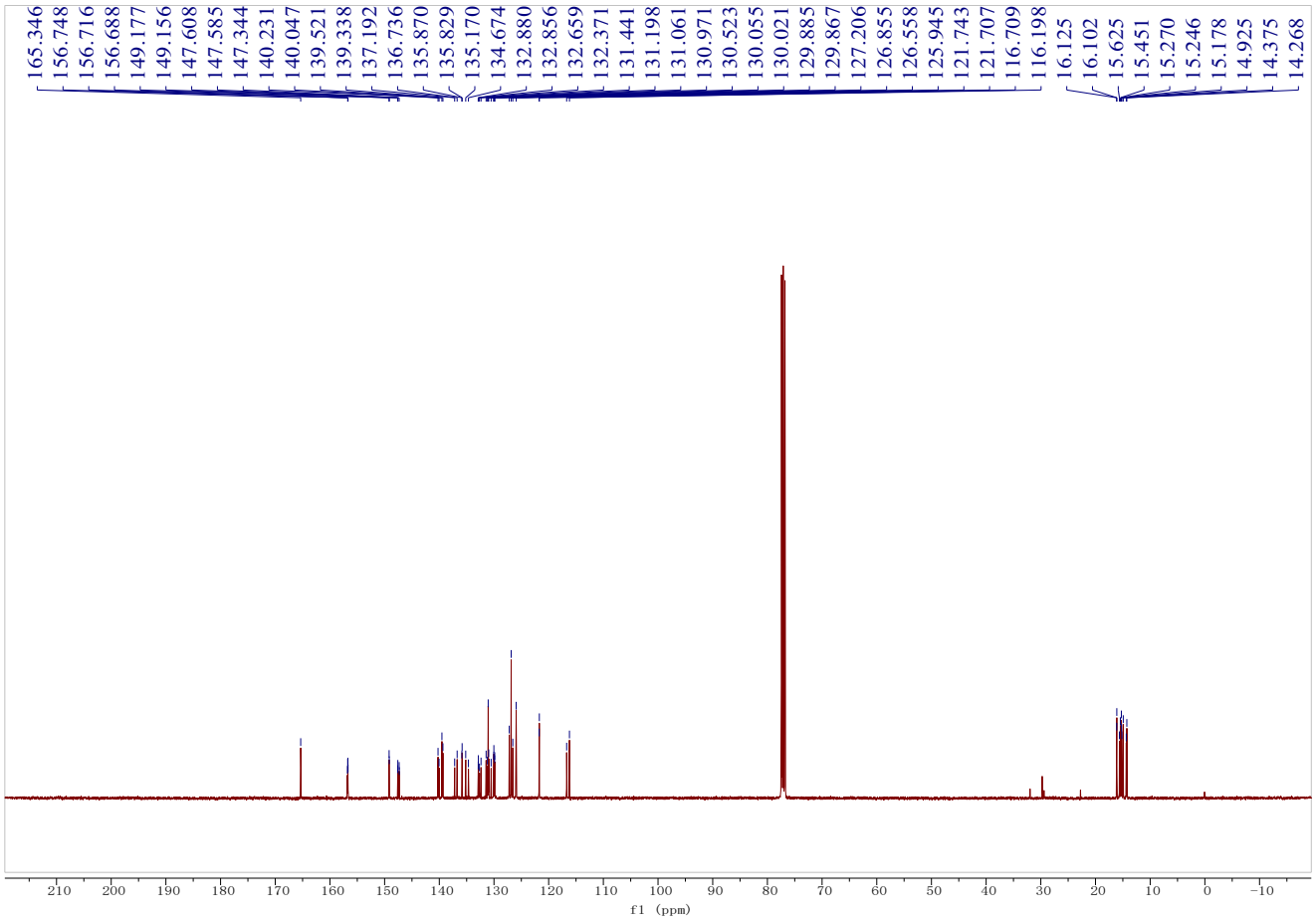
3i, ^{1}H NMR, 400 MHz, $CDCl_3$



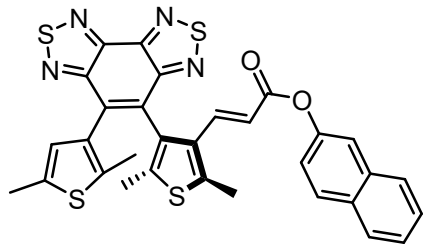


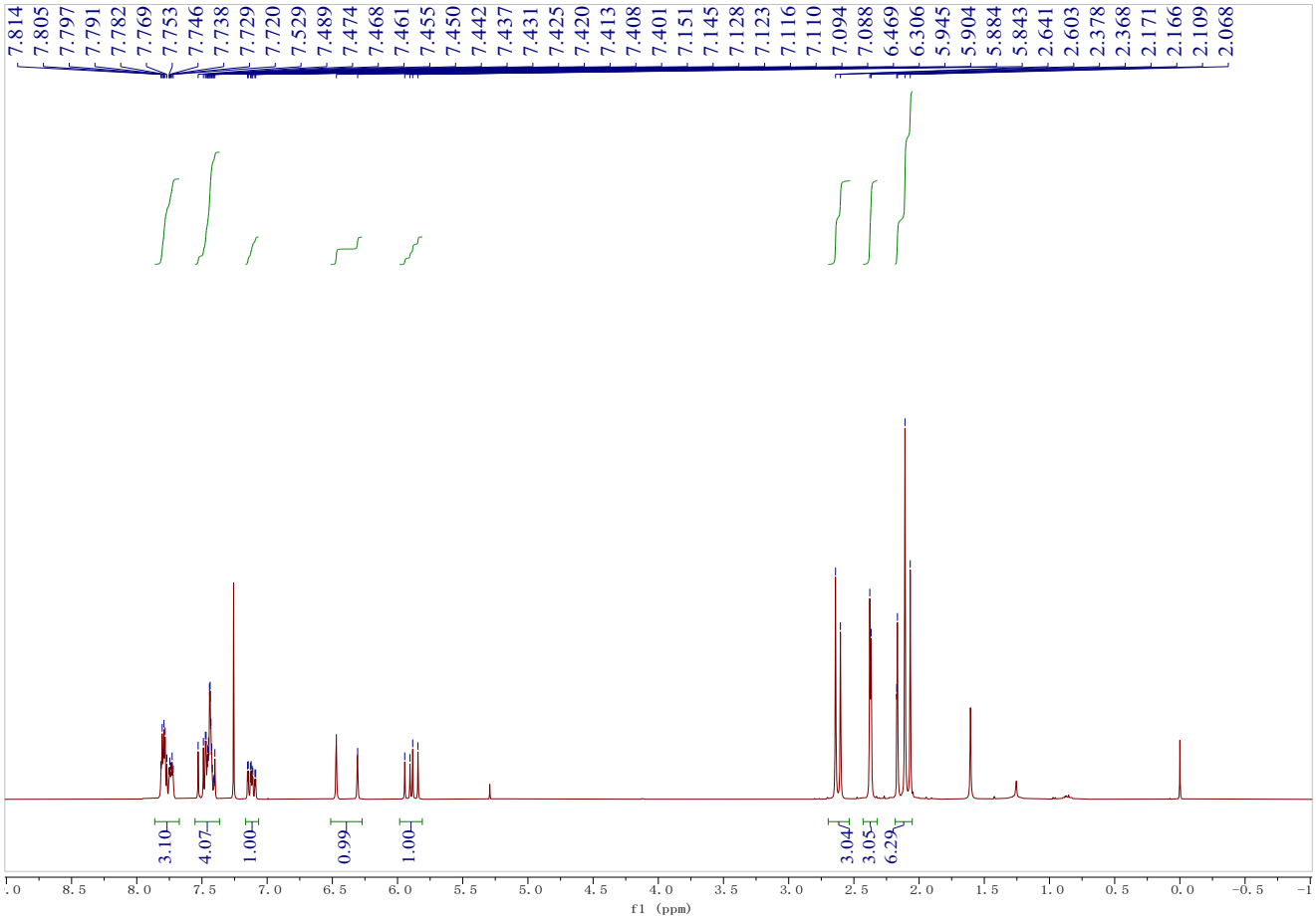
3i,^{13}C NMR, 101 MHz, $CDCl_3$



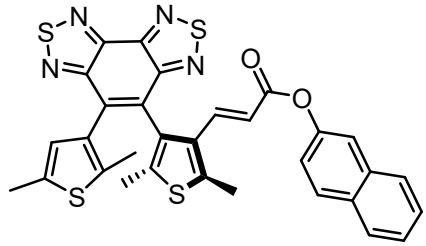


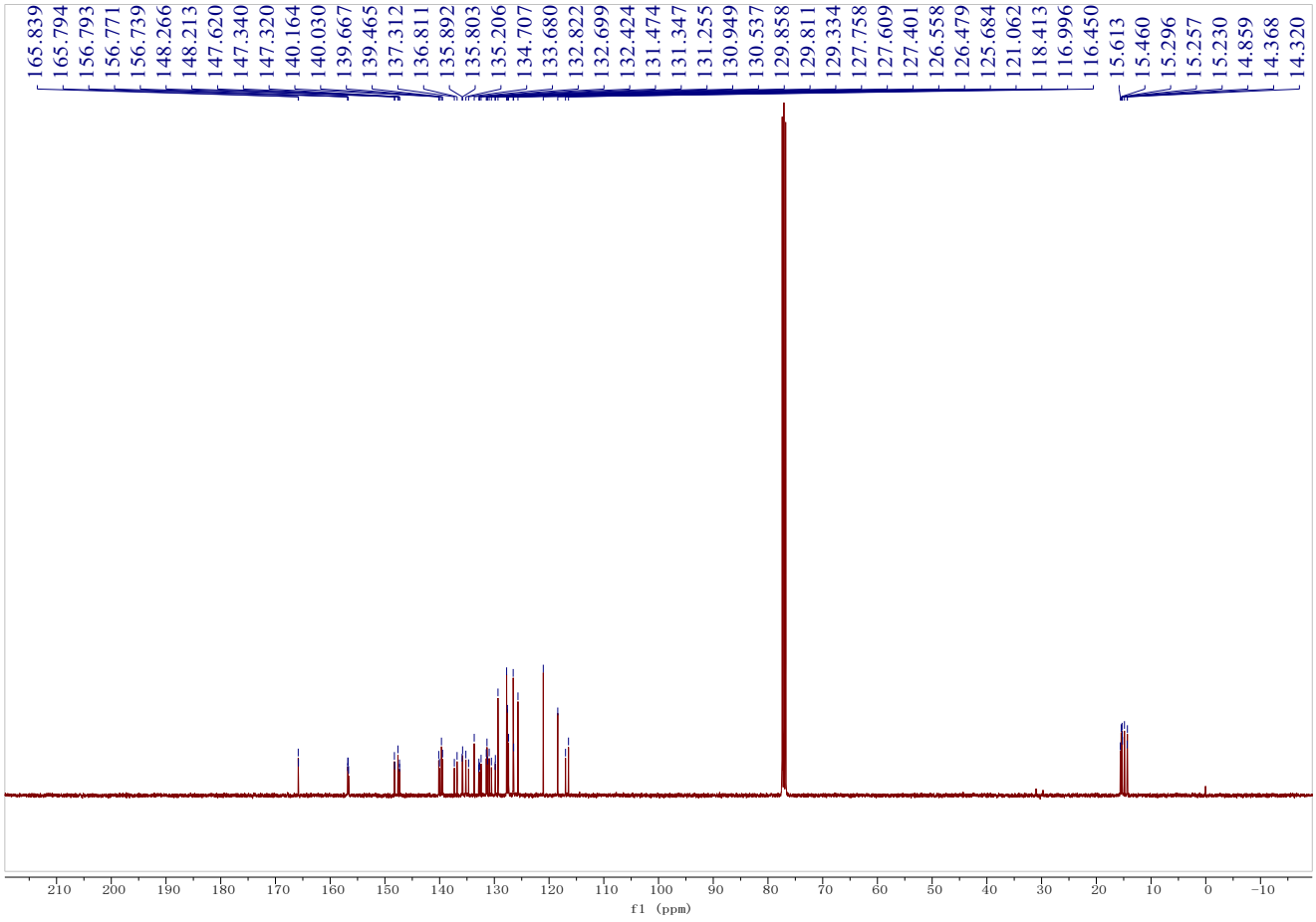
3j, ^{1}H NMR, 400 MHz, $CDCl_3$



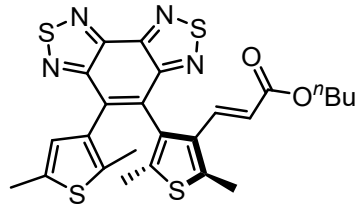


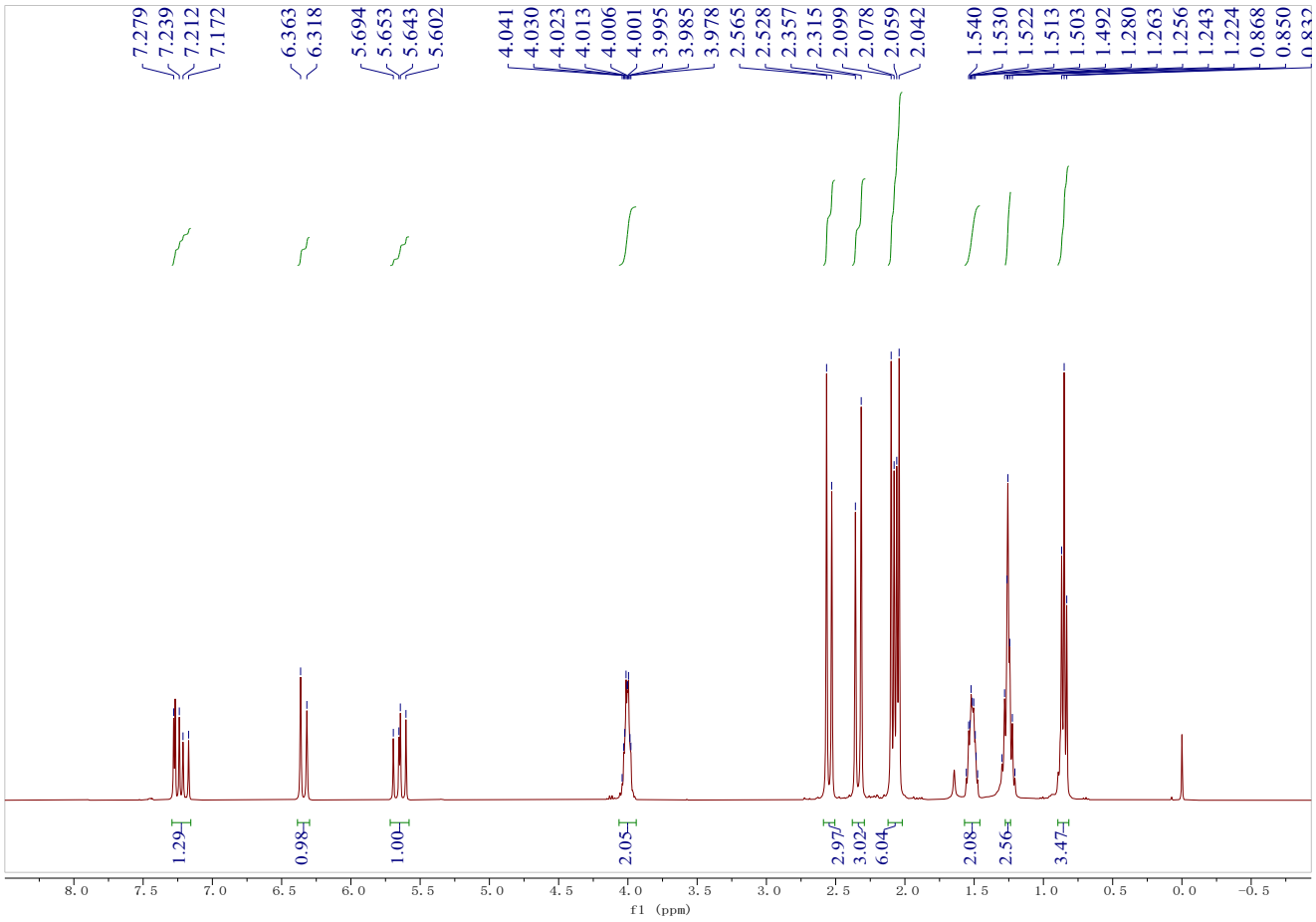
3j,^{13}C NMR, 101 MHz, $CDCl_3$



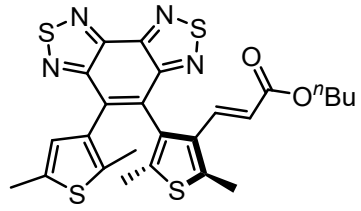


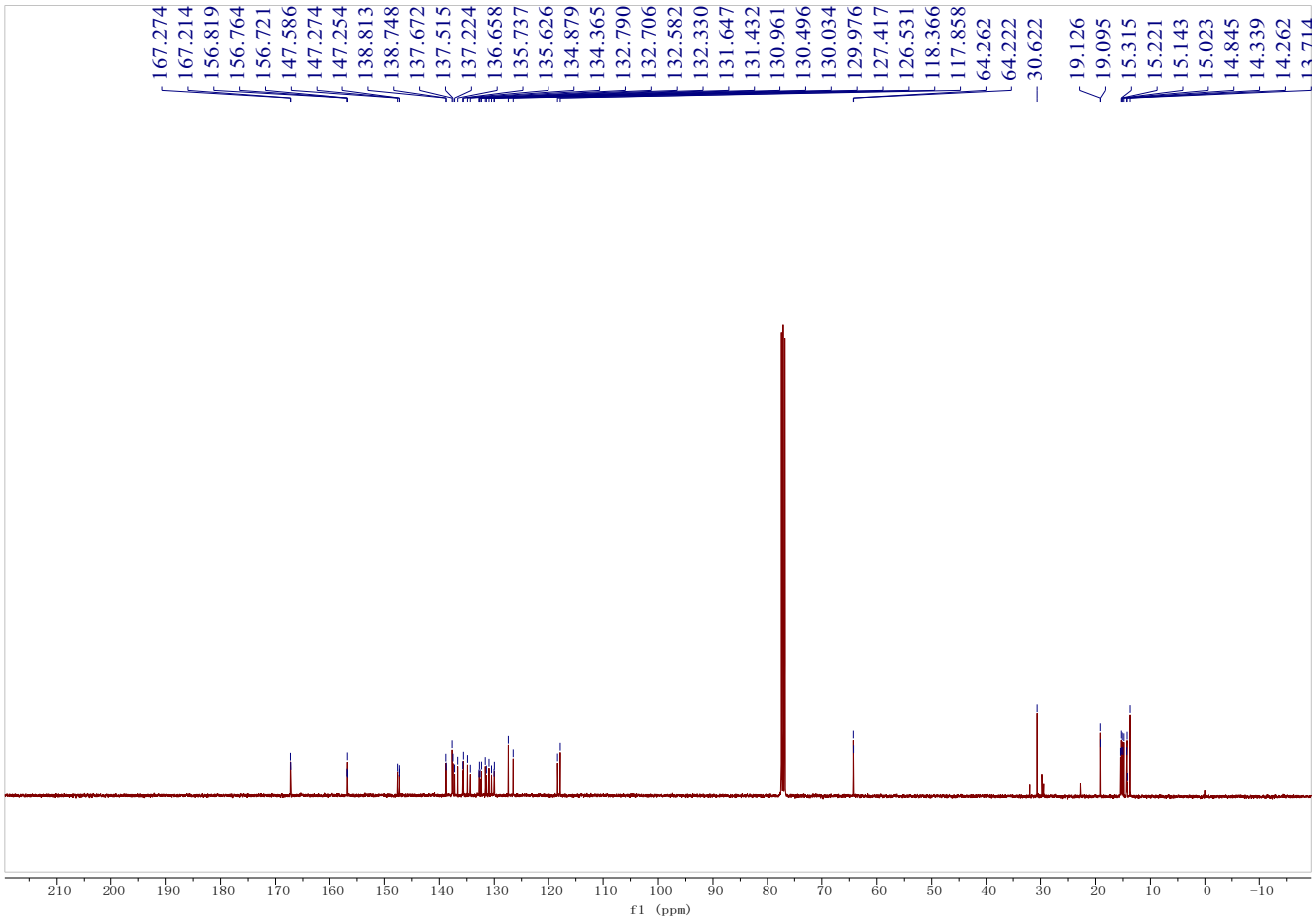
3k, ^{1}H NMR, 400 MHz, $CDCl_3$



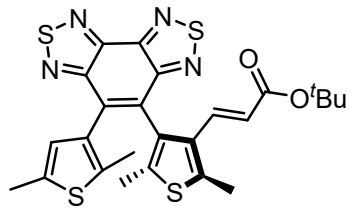


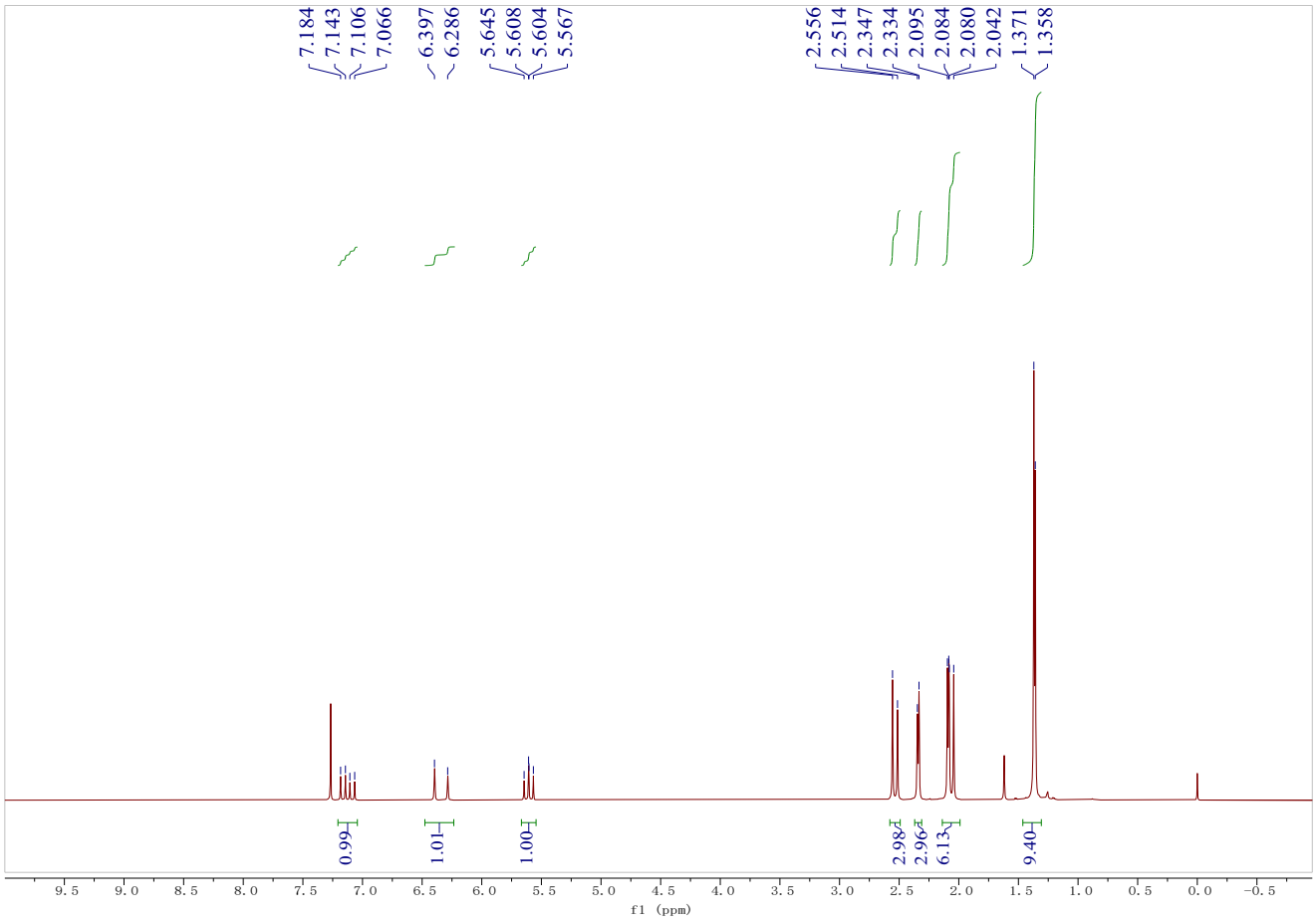
3k,^{13}C NMR, 101 MHz, $CDCl_3$



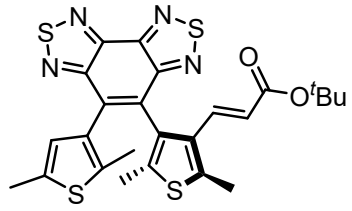


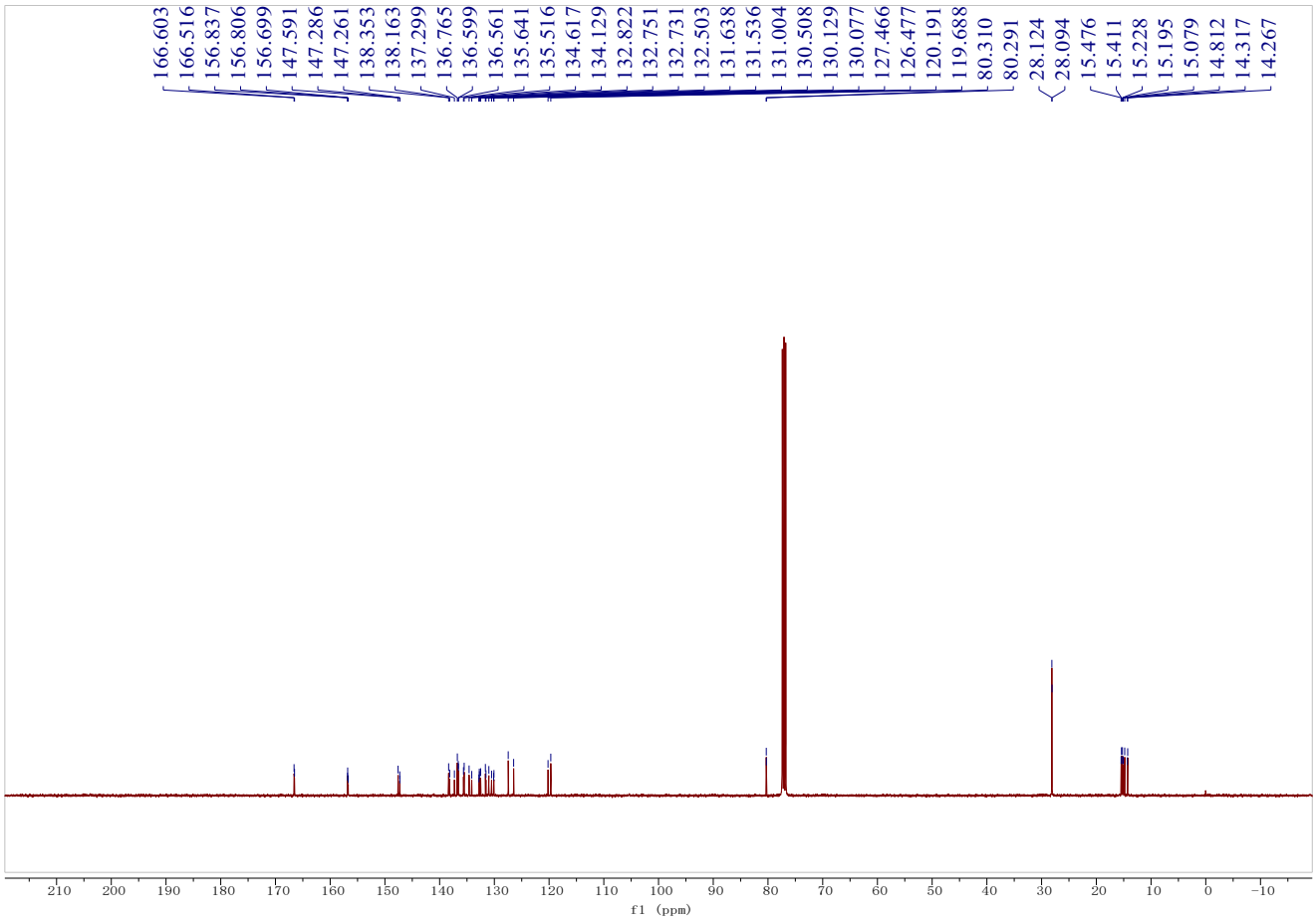
3l, ^{1}H NMR, 400 MHz, $CDCl_3$



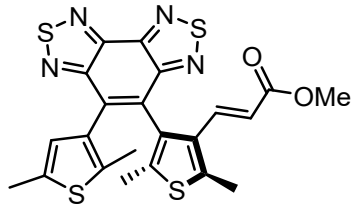


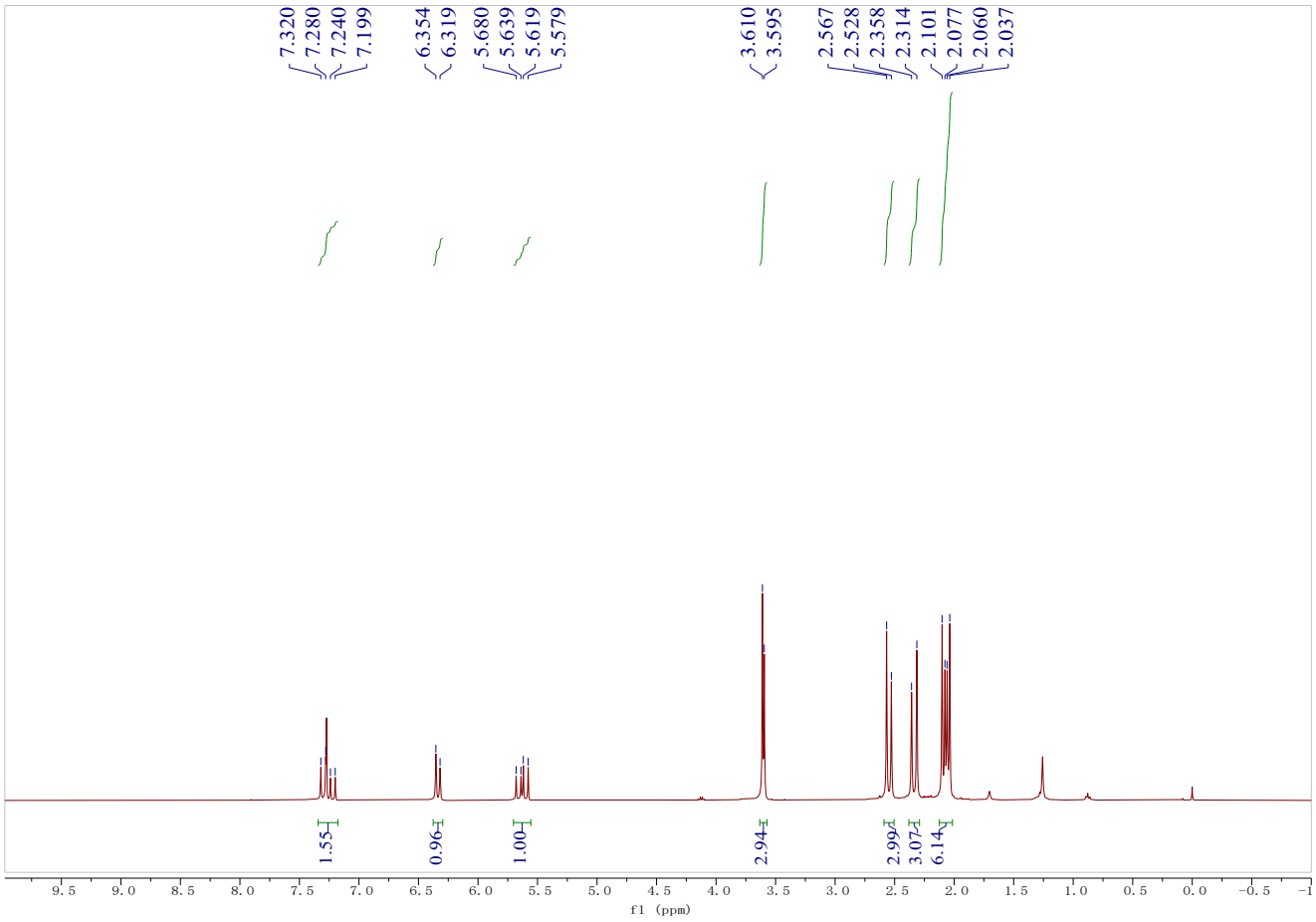
3l,^{13}C NMR, 101 MHz, $CDCl_3$



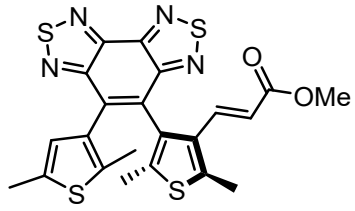


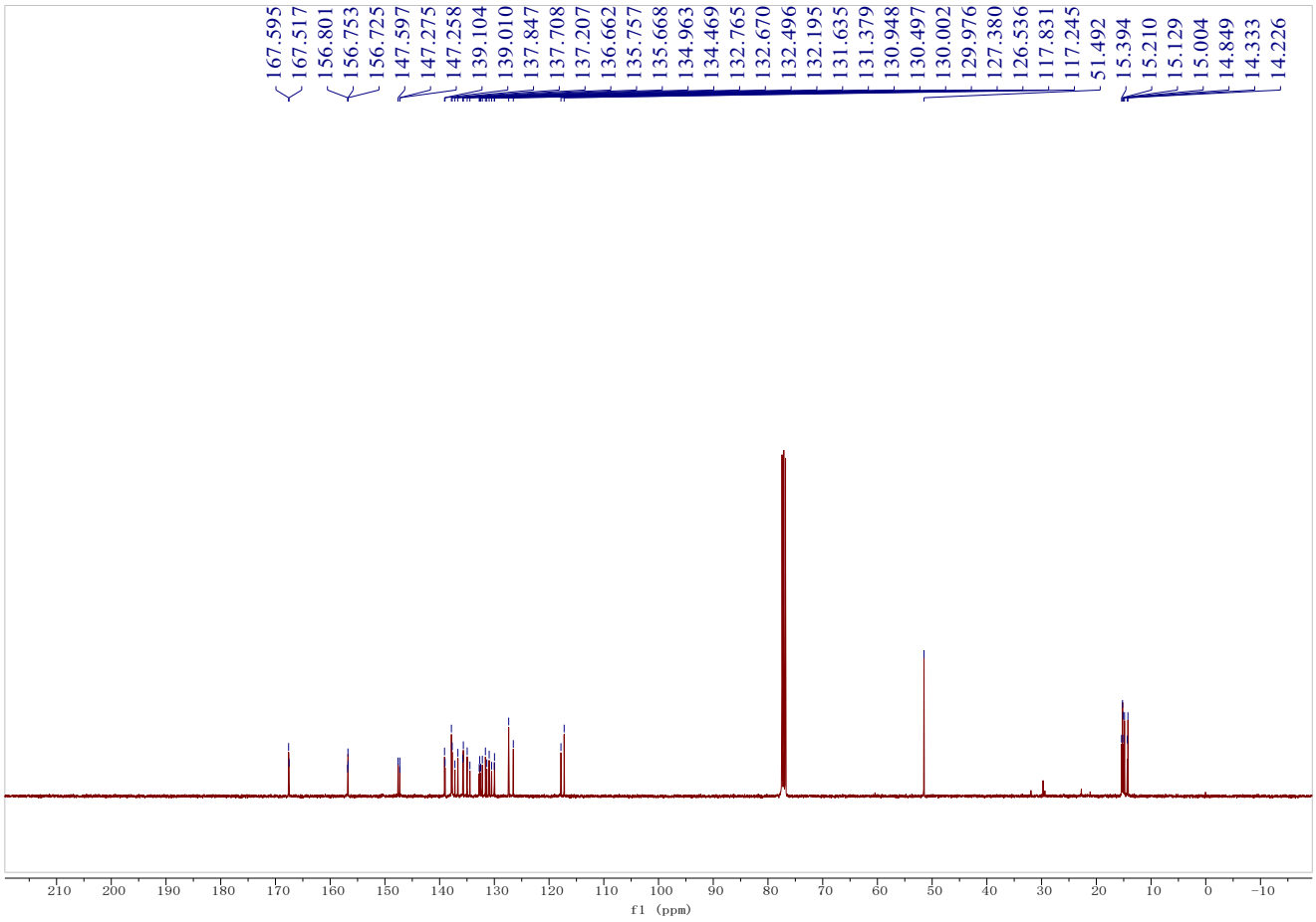
3m, ^{1}H NMR, 400 MHz, $CDCl_3$



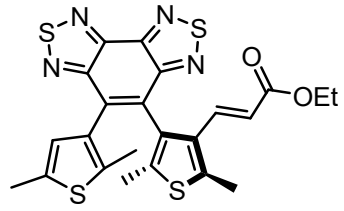


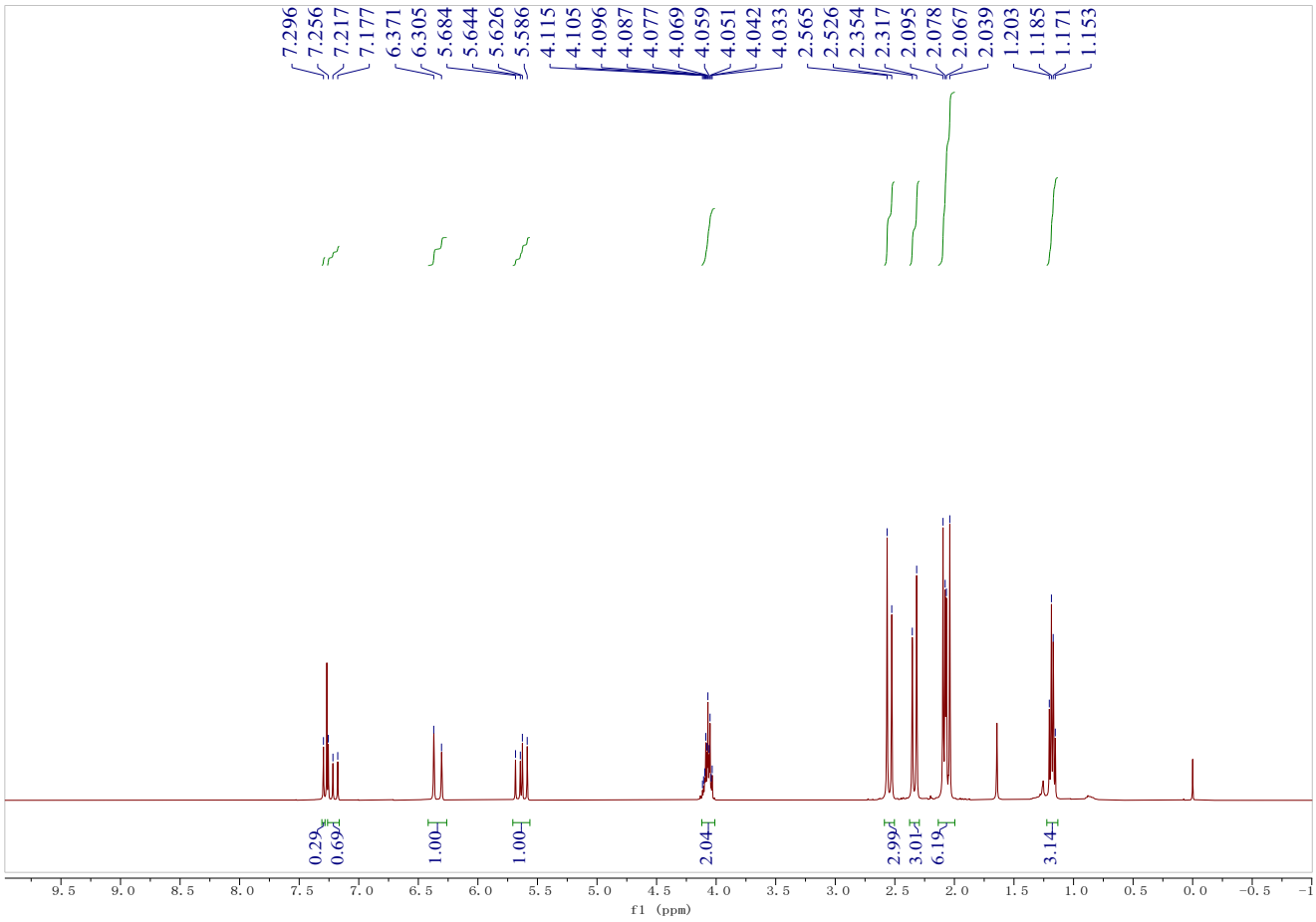
3m,^{13}C NMR, 101 MHz, $CDCl_3$



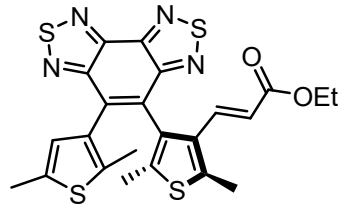


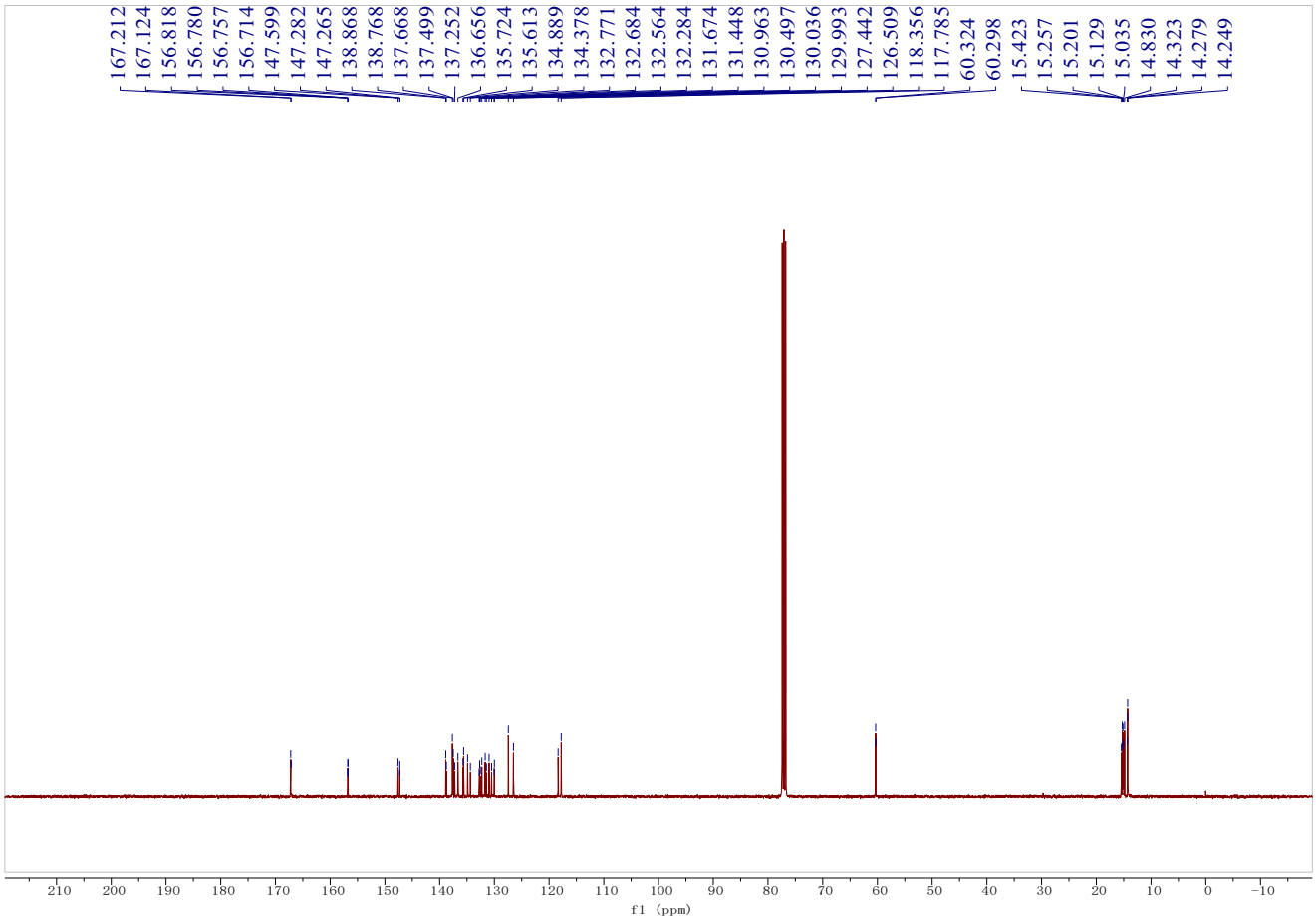
3n, ^{1}H NMR, 400 MHz, $CDCl_3$



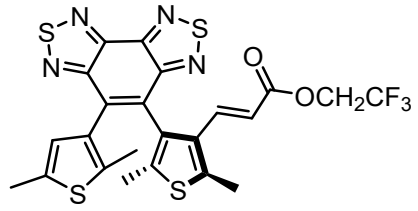


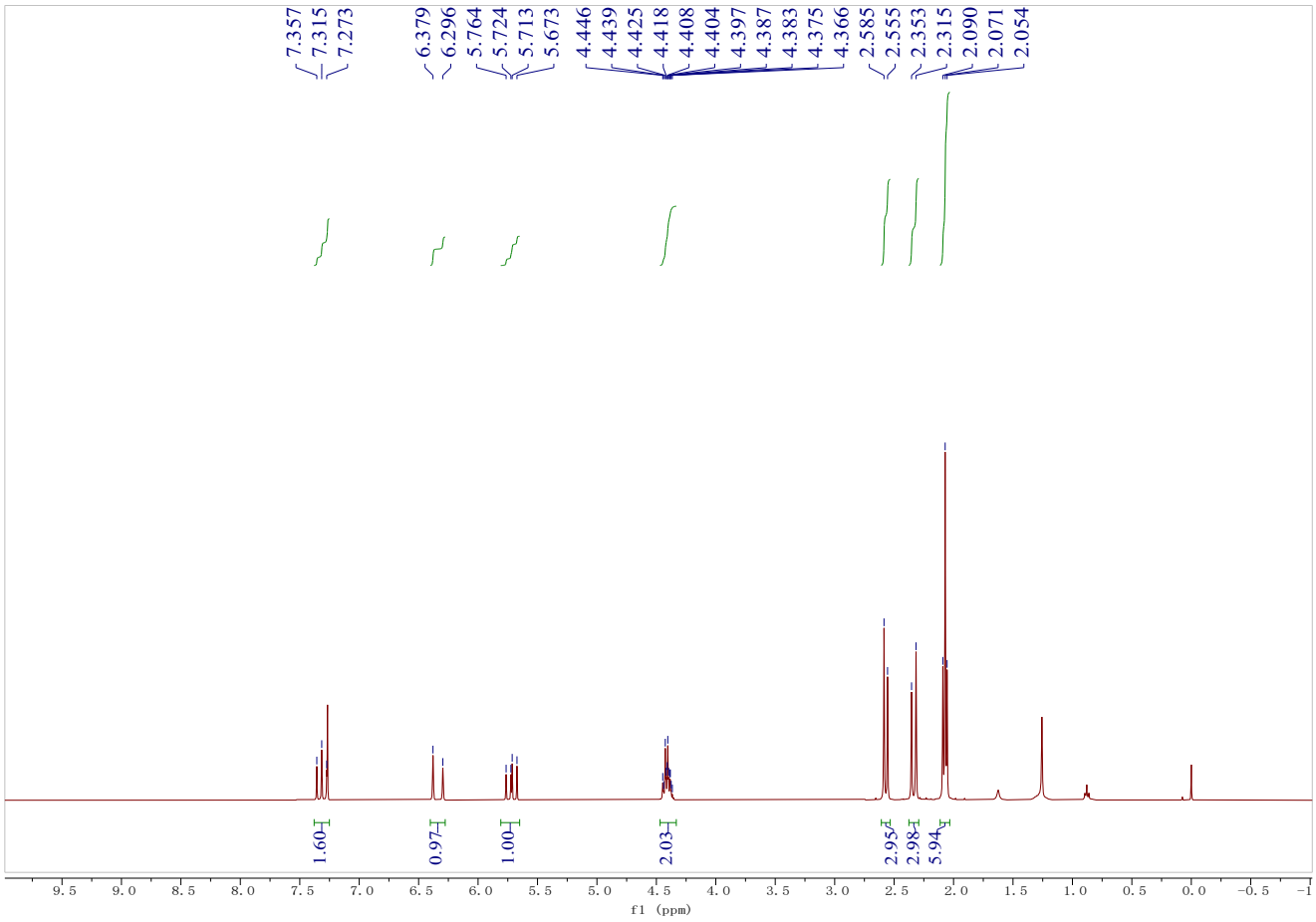
3n,^{13}C NMR, 101 MHz, $CDCl_3$



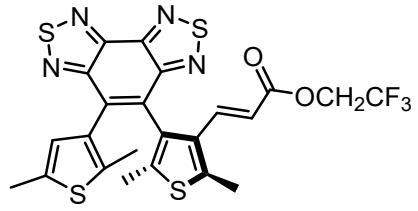


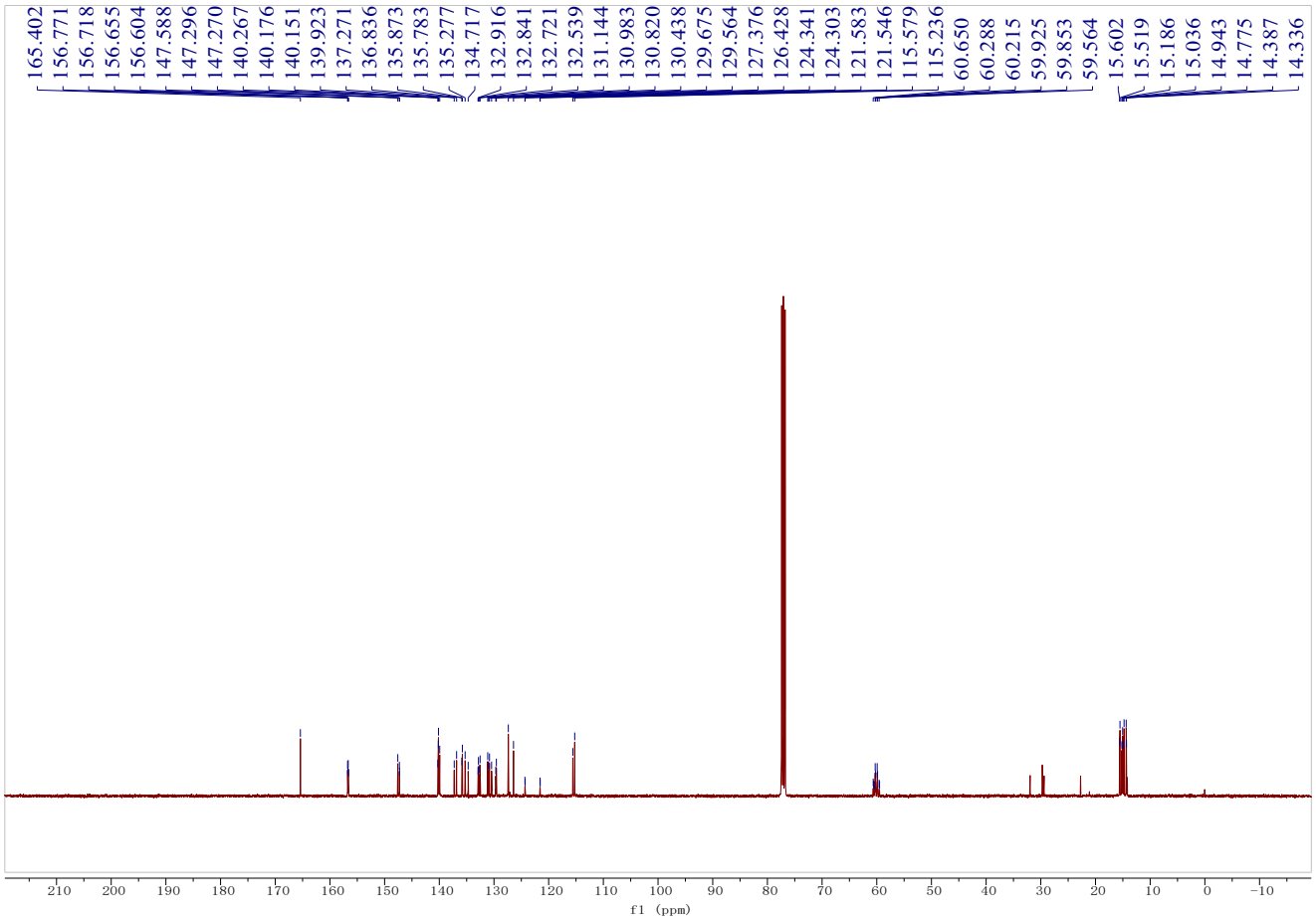
3o, ^{1}H NMR, 400 MHz, $CDCl_3$



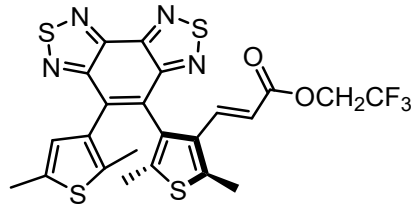


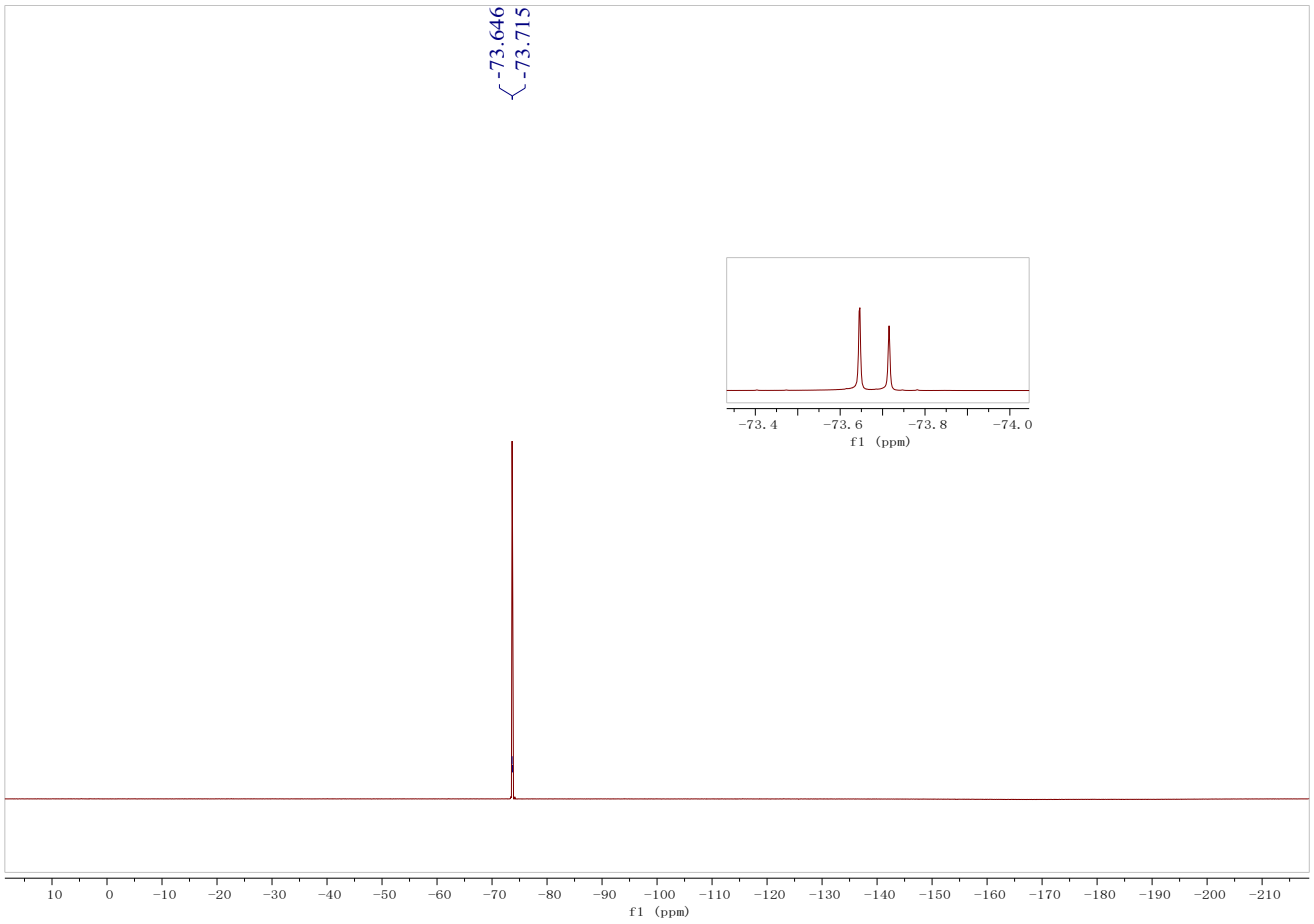
3o,^{13}C NMR, 101 MHz, $CDCl_3$



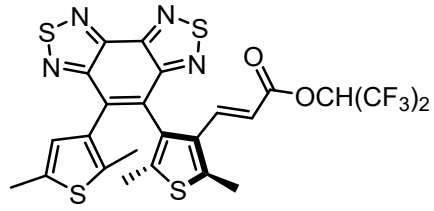


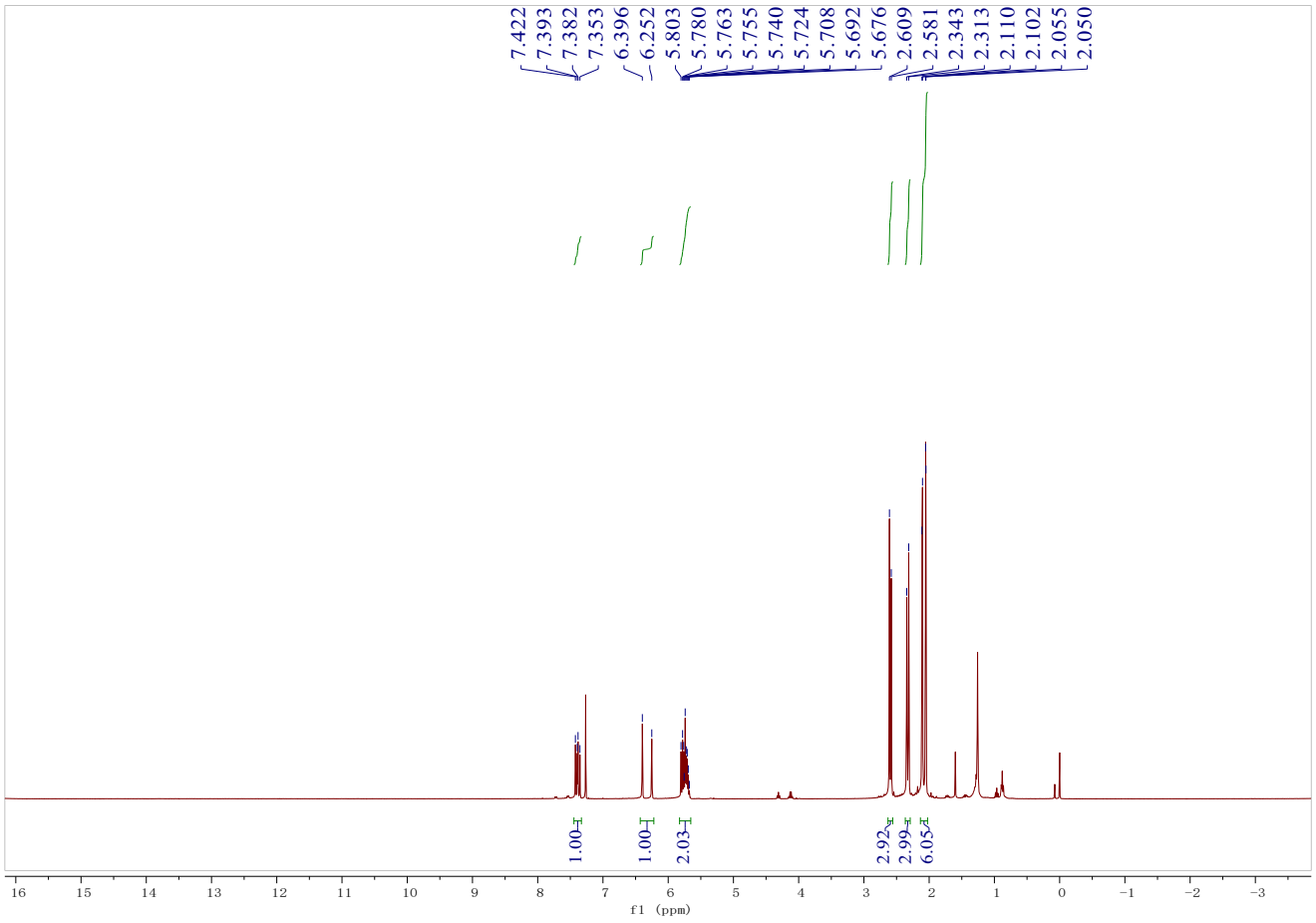
3o,^{19}F NMR, 376 MHz, $CDCl_3$



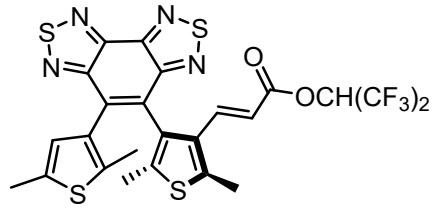


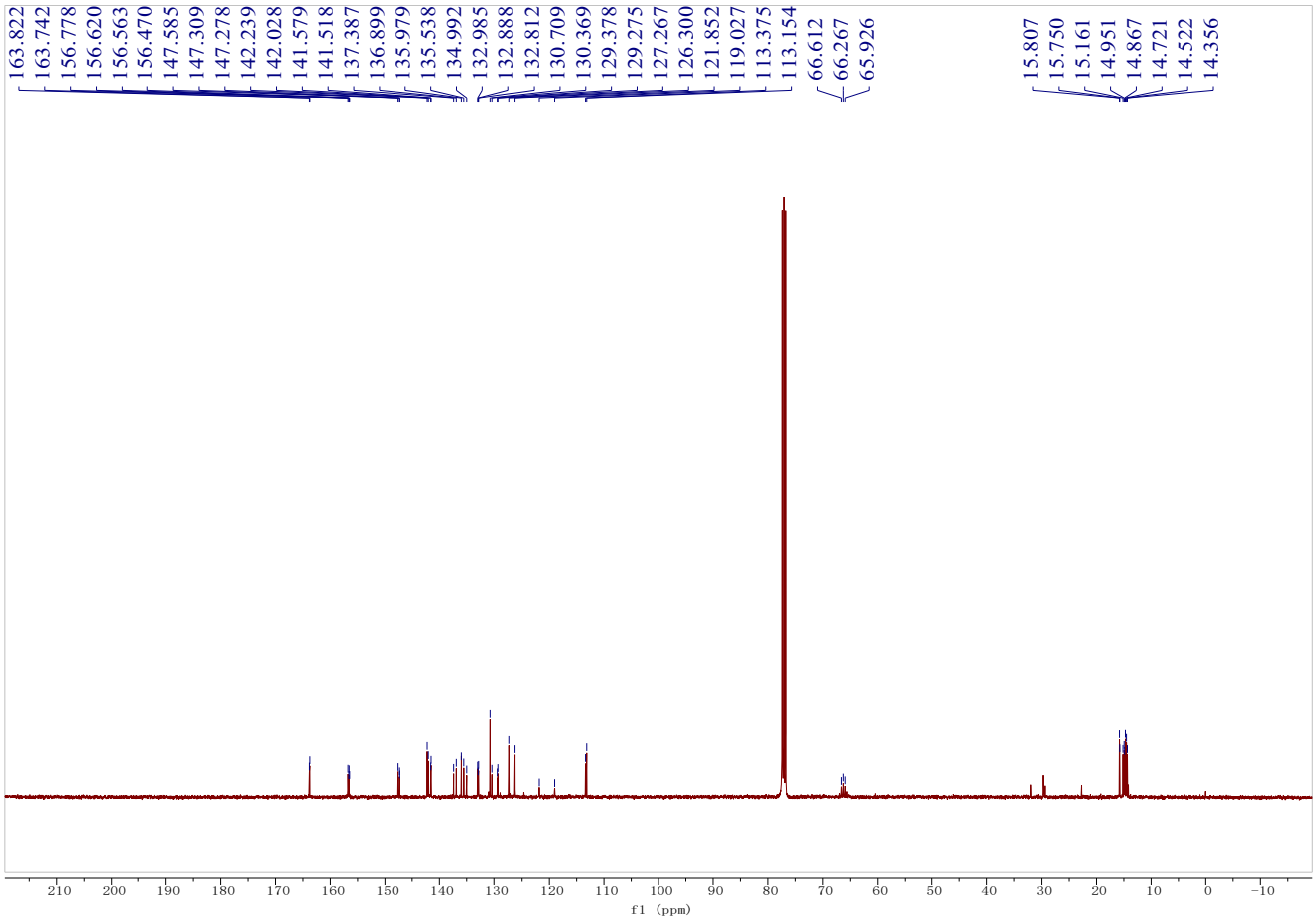
3p, ^{1}H NMR, 400 MHz, $CDCl_3$



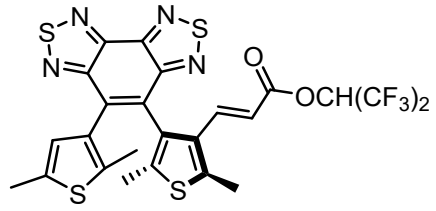


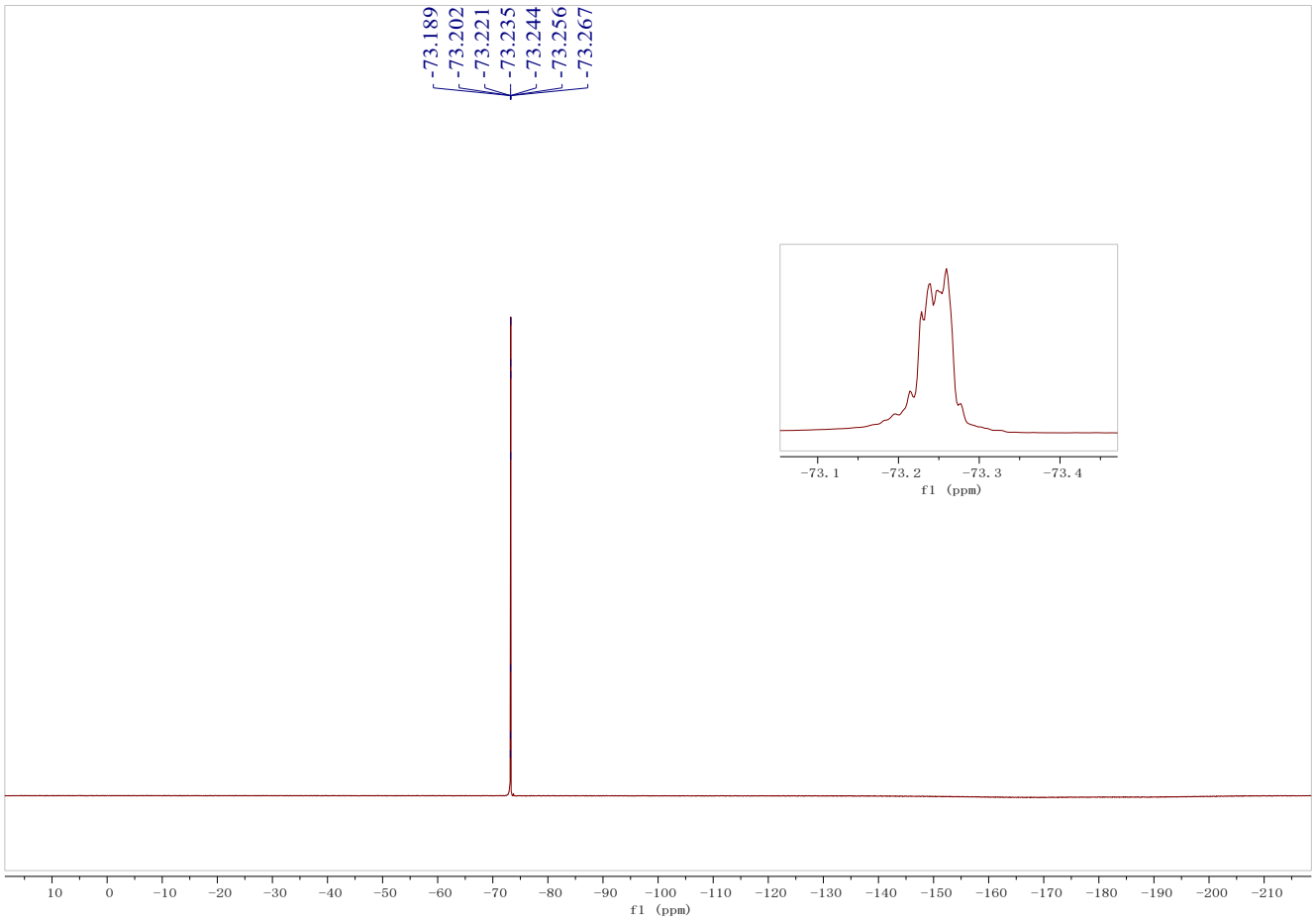
3p,^{13}C NMR, 101 MHz, $CDCl_3$



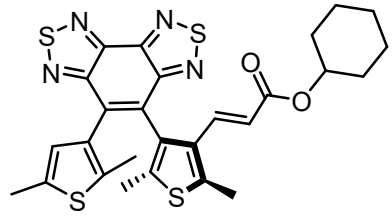


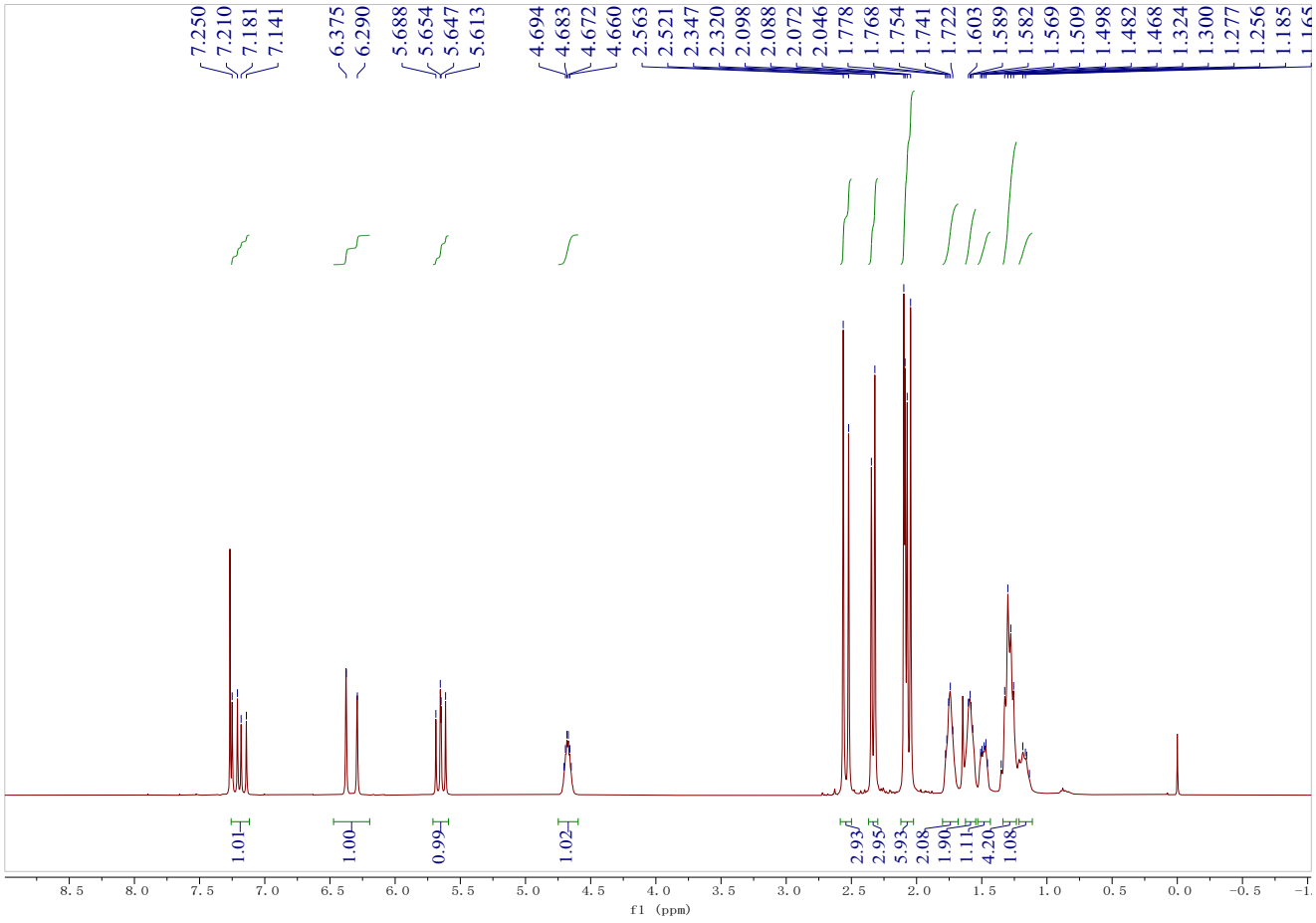
3p,^{19}F NMR, 376 MHz, $CDCl_3$



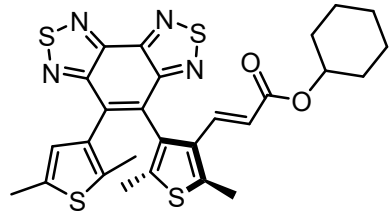


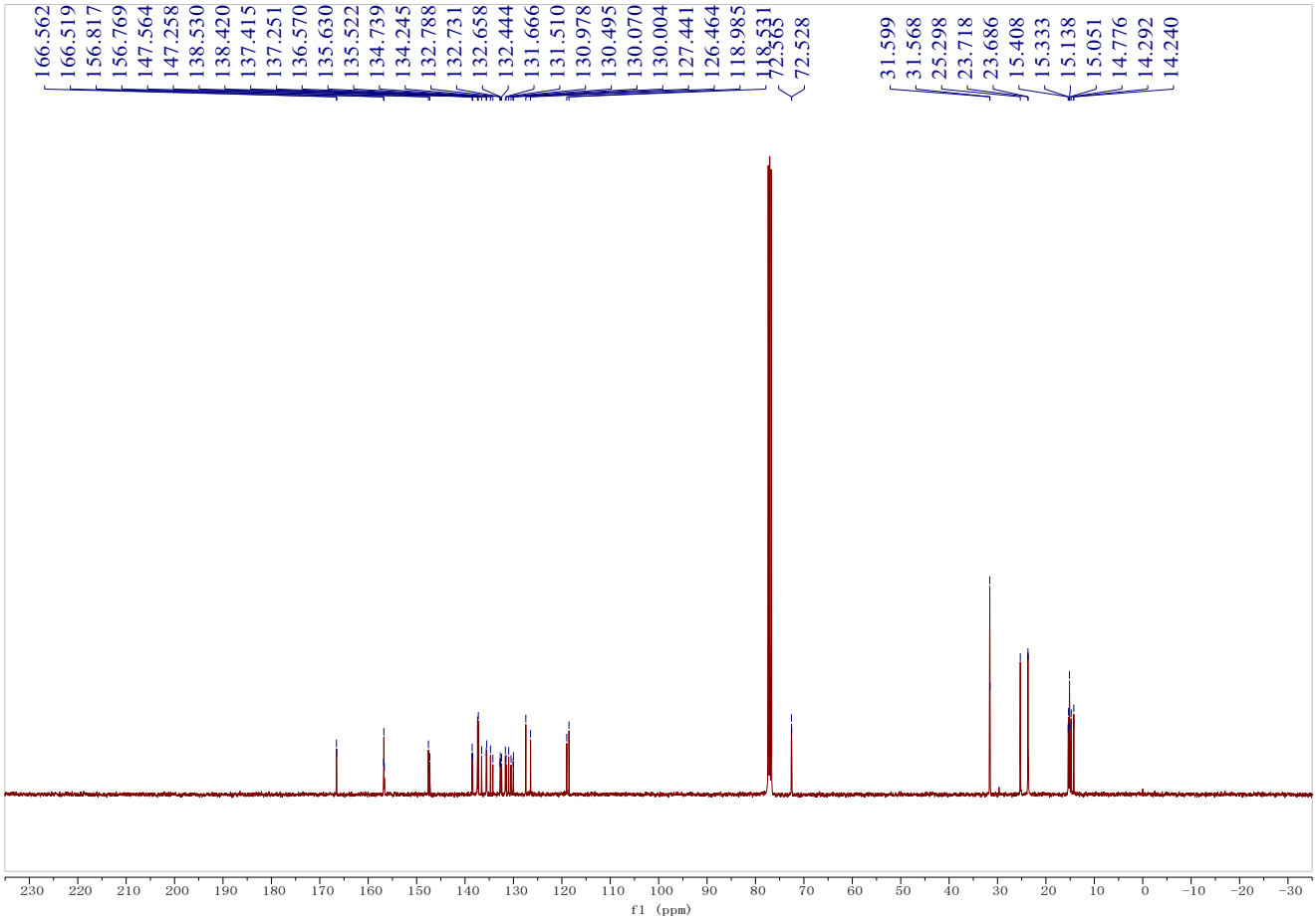
3q, ^{1}H NMR, 400 MHz, $CDCl_3$



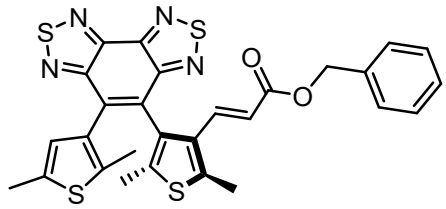


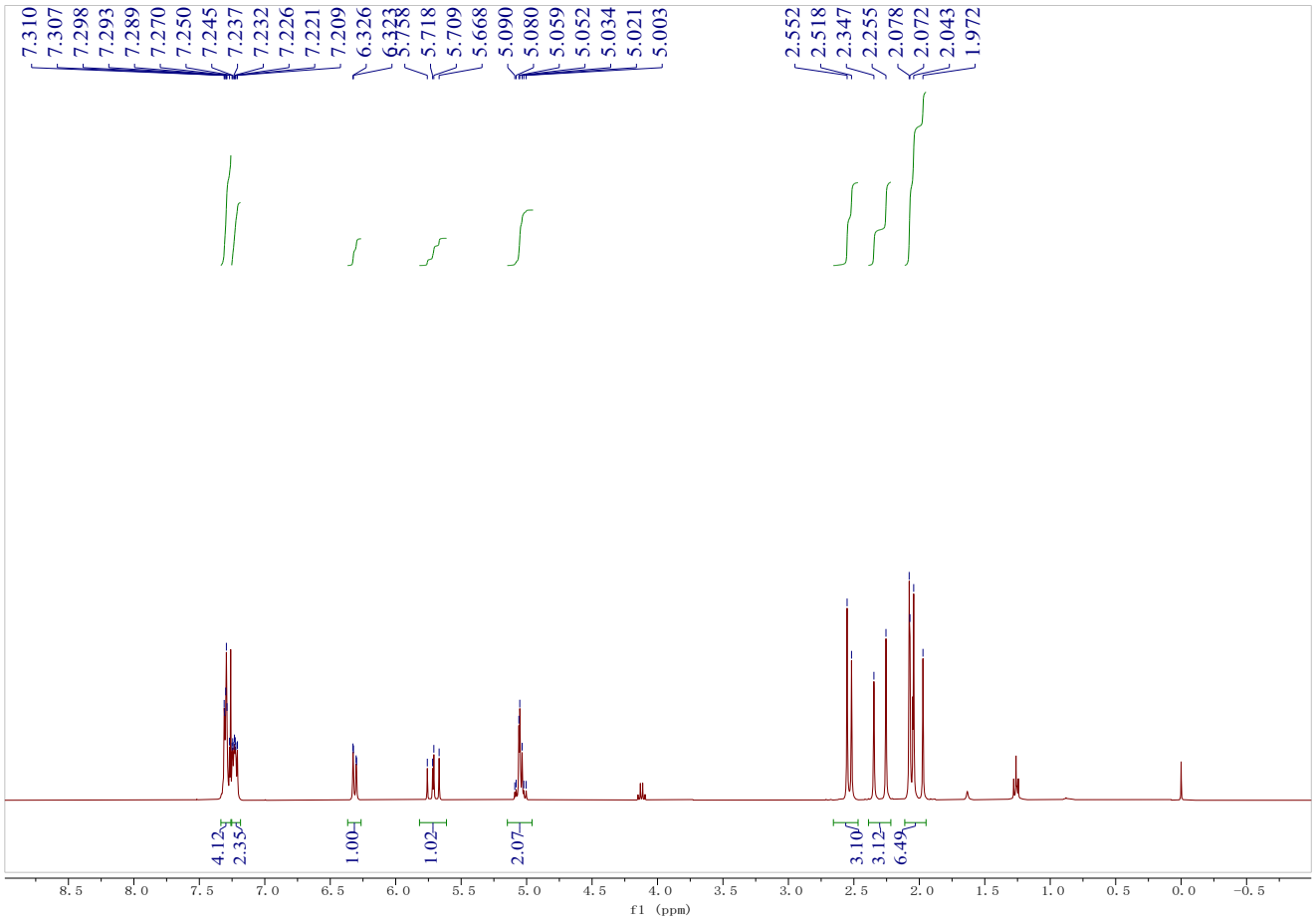
3q,^{13}C NMR, 101 MHz, $CDCl_3$



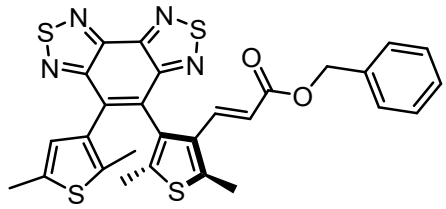


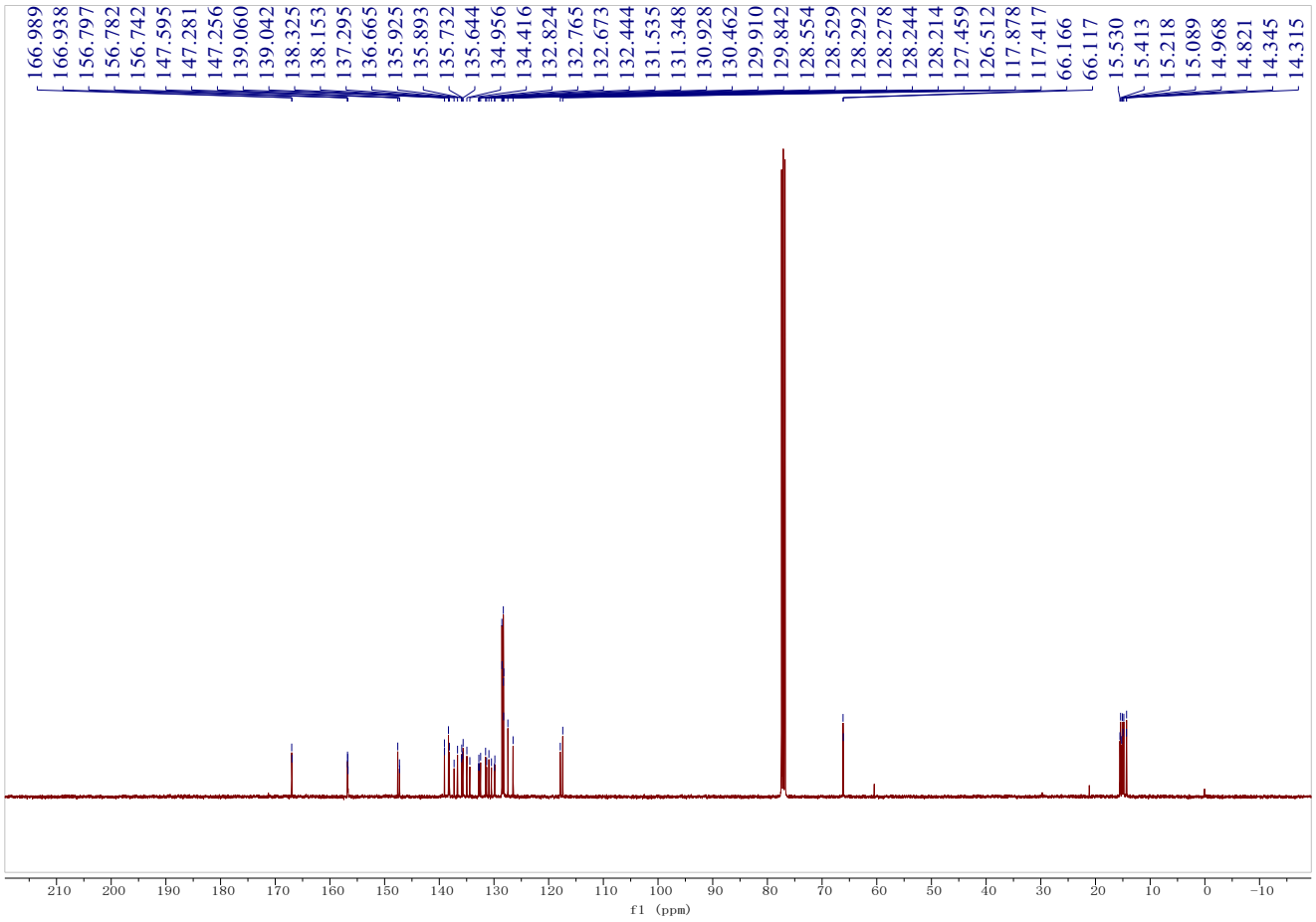
3r, ^{1}H NMR, 400 MHz, $CDCl_3$



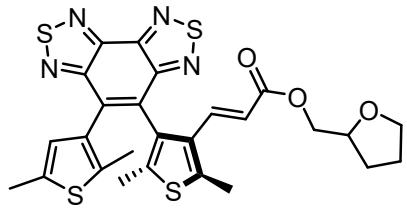


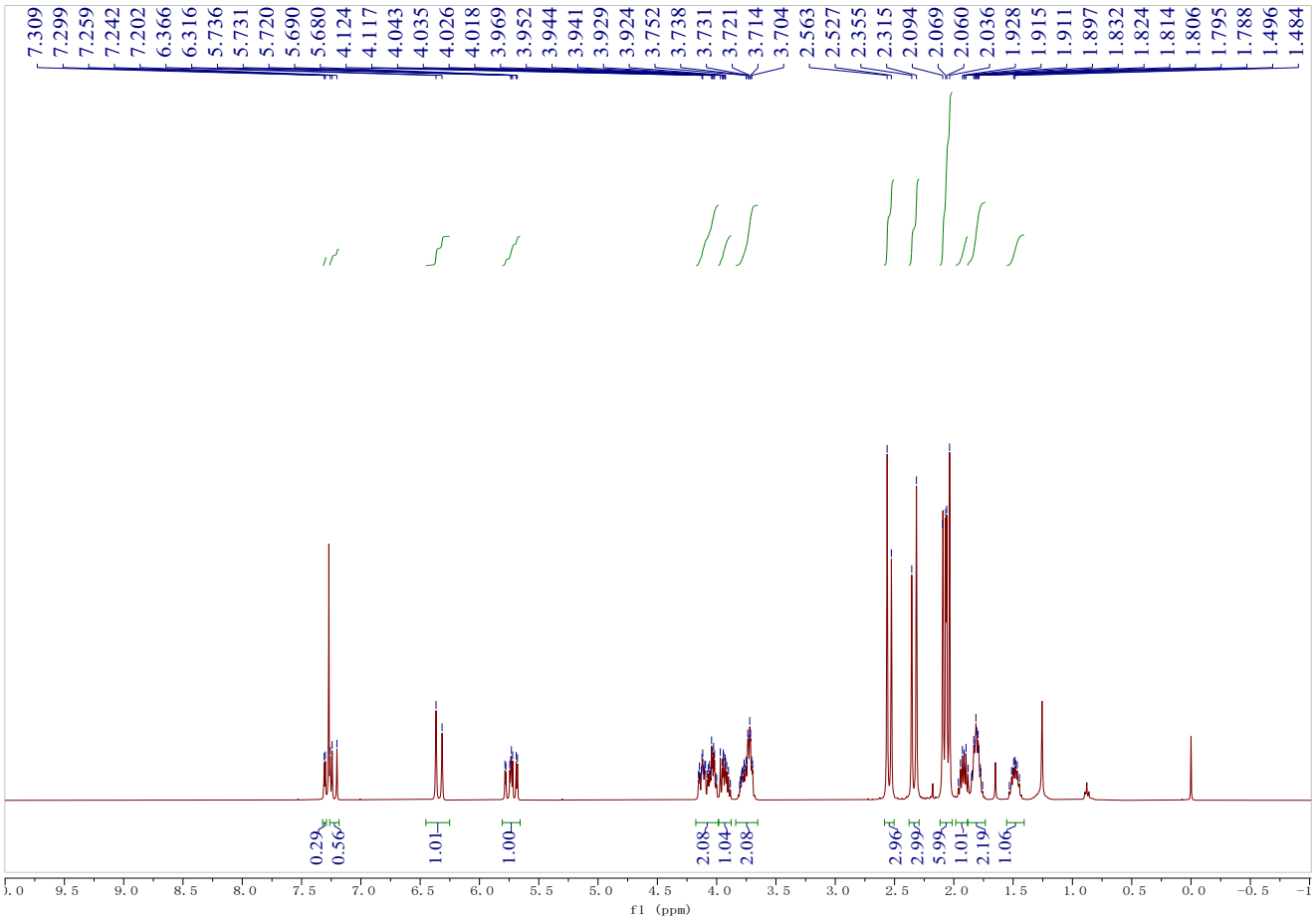
3r,^{13}C NMR, 101 MHz, $CDCl_3$



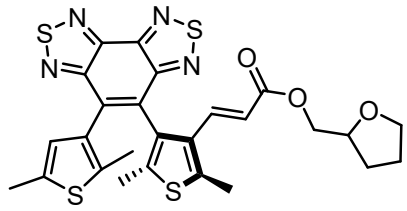


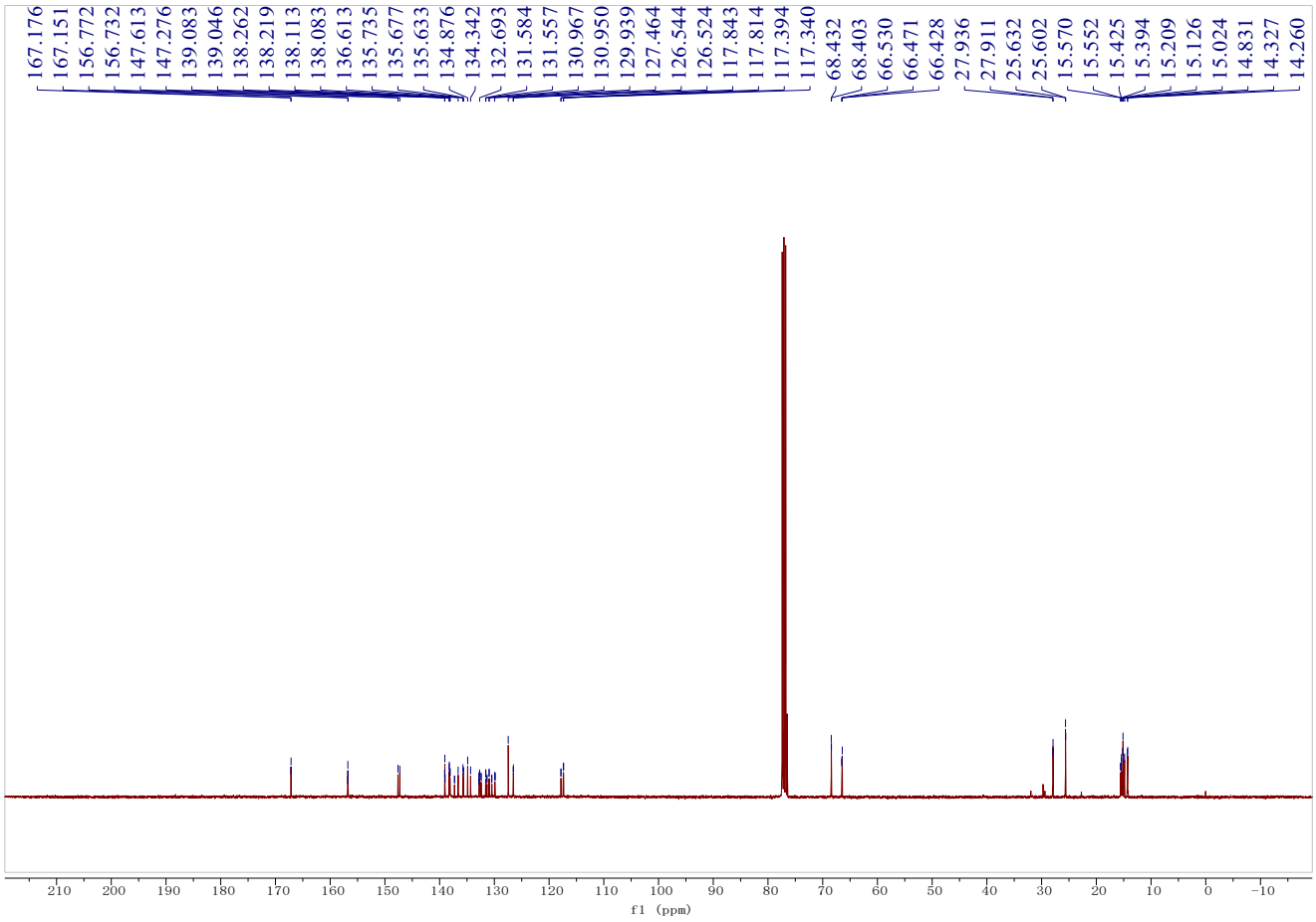
3s, ^{1}H NMR, 400 MHz, $CDCl_3$



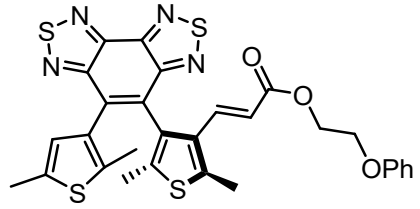


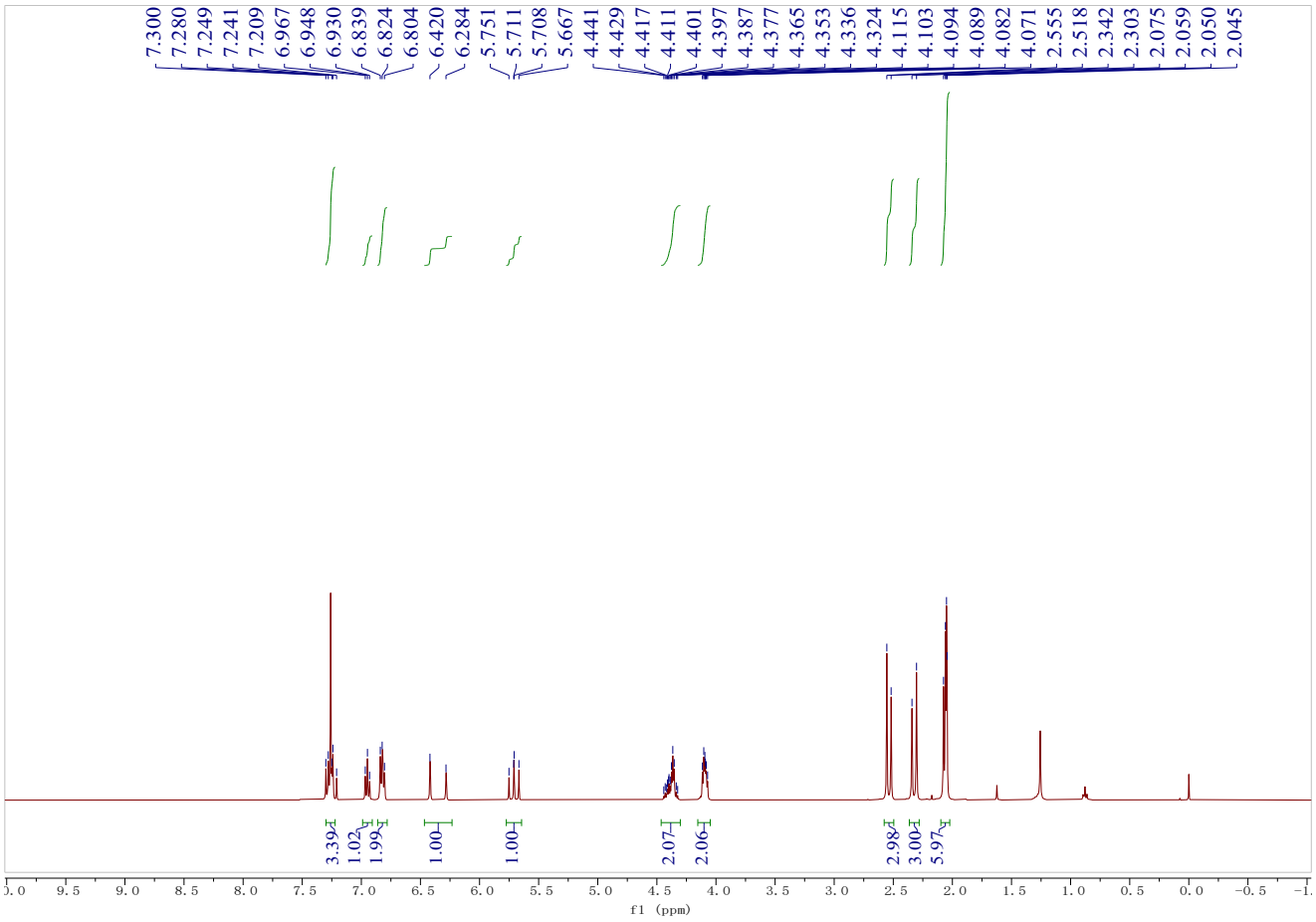
3s,^{13}C NMR, 101 MHz, $CDCl_3$



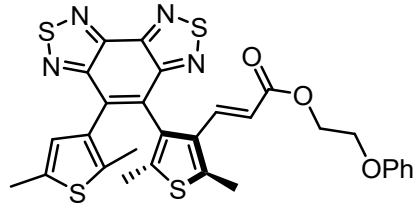


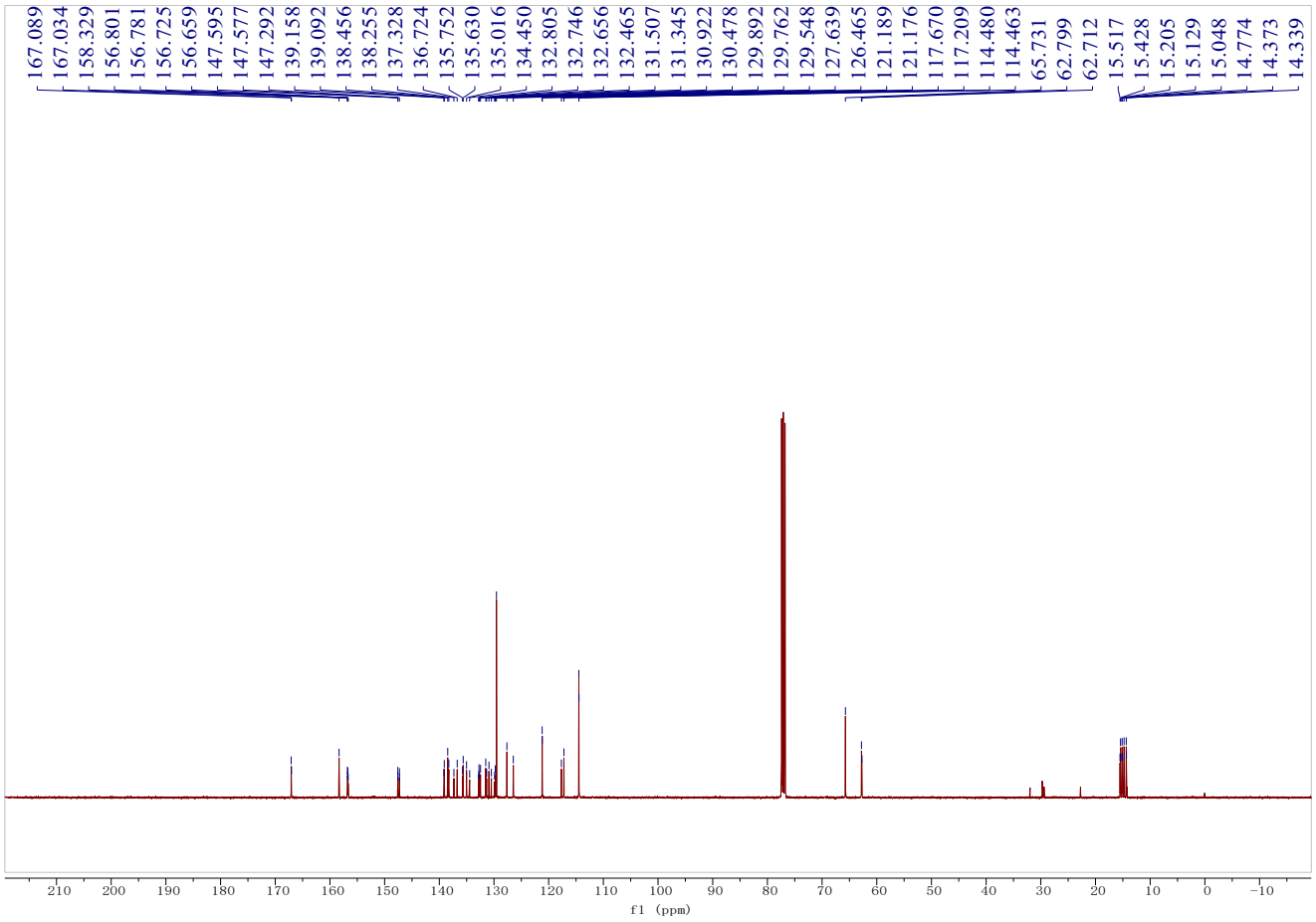
3t, ^{1}H NMR, 400 MHz, $CDCl_3$



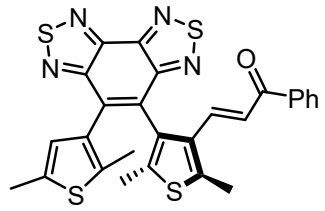


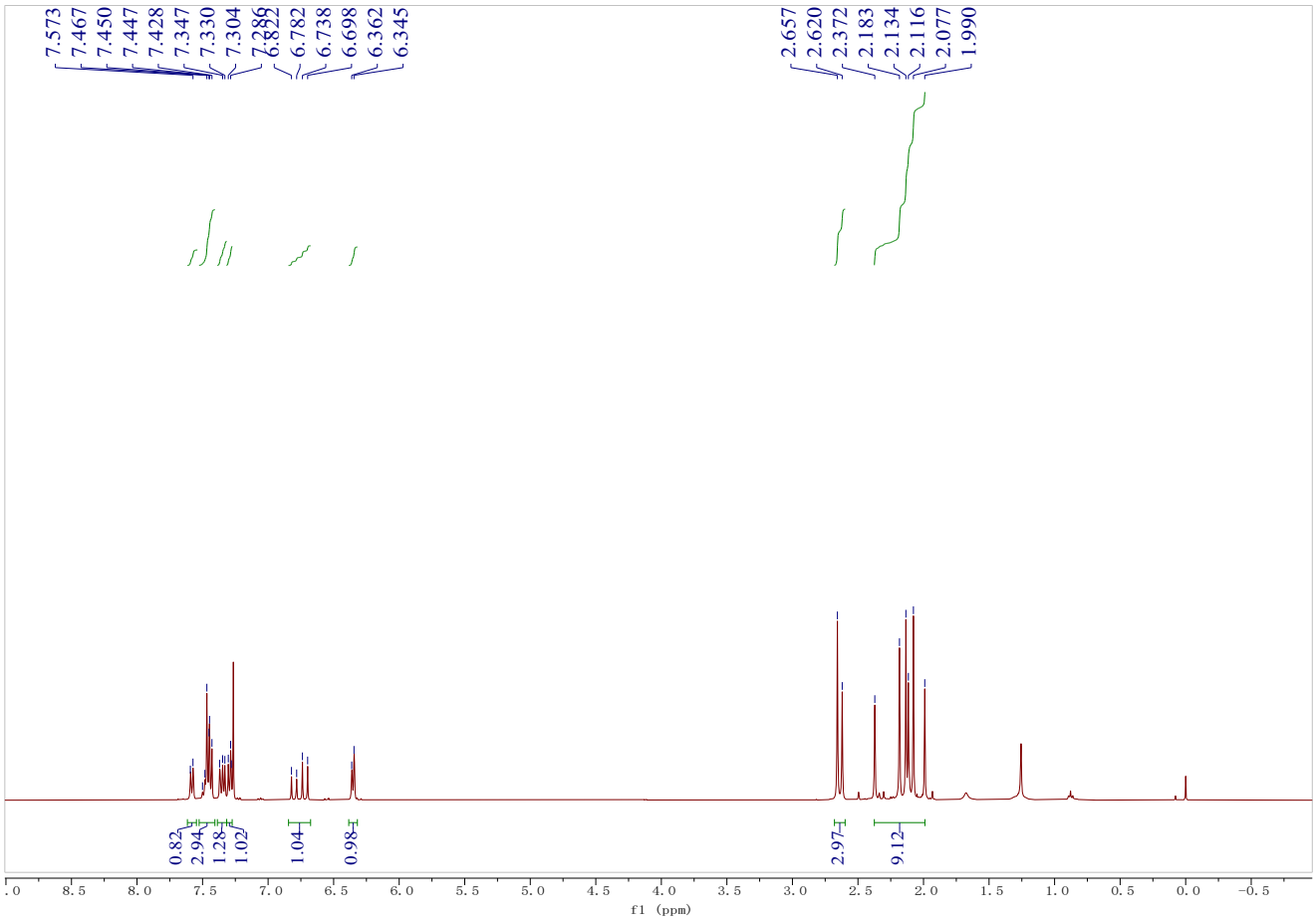
3t,^{13}C NMR, 101 MHz, $CDCl_3$



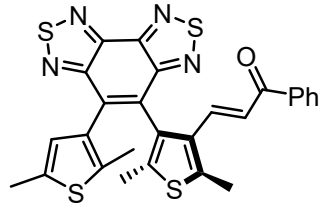


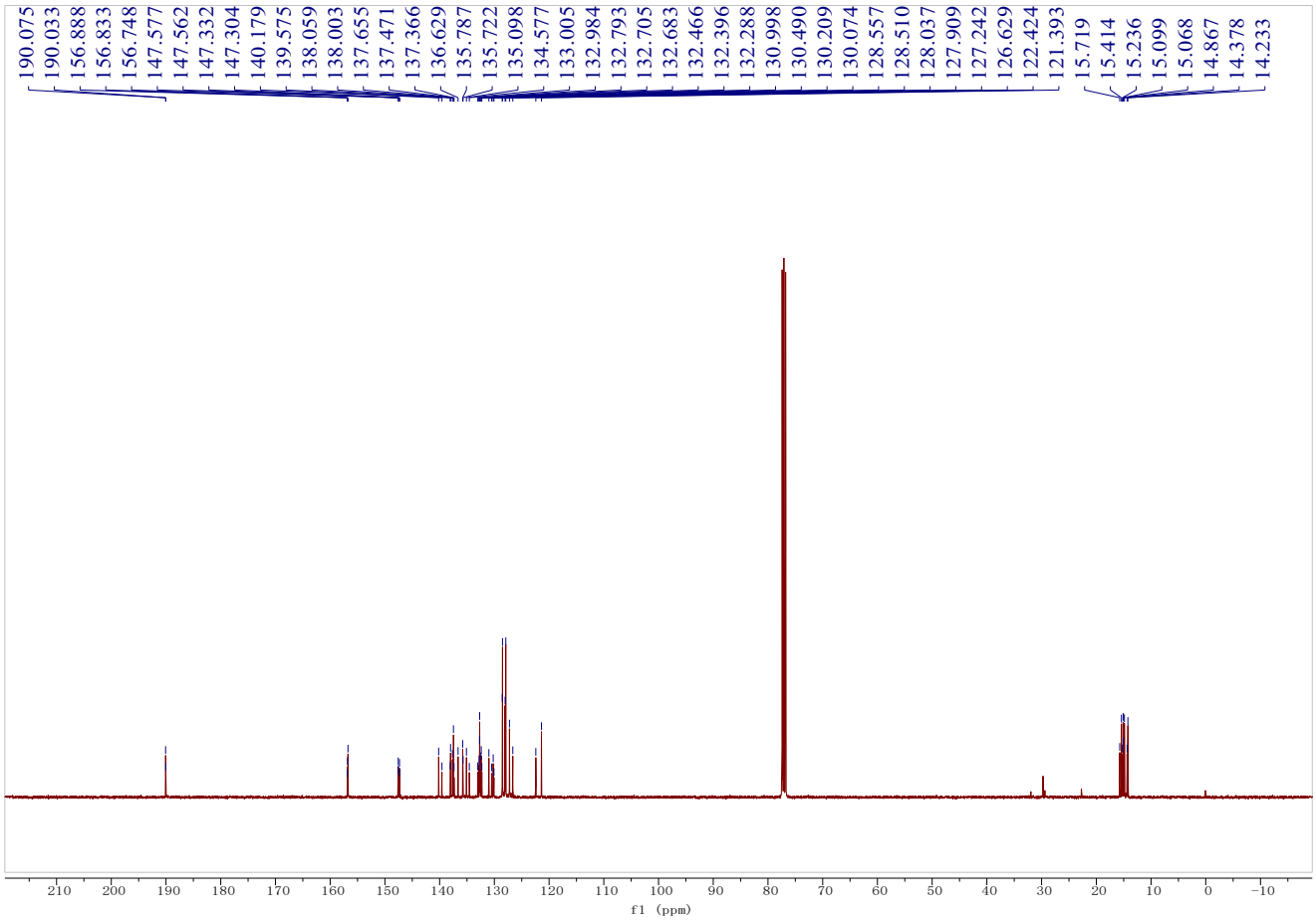
3u, ^{1}H NMR, 400 MHz, $CDCl_3$



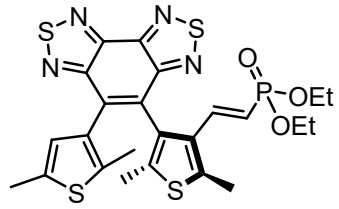


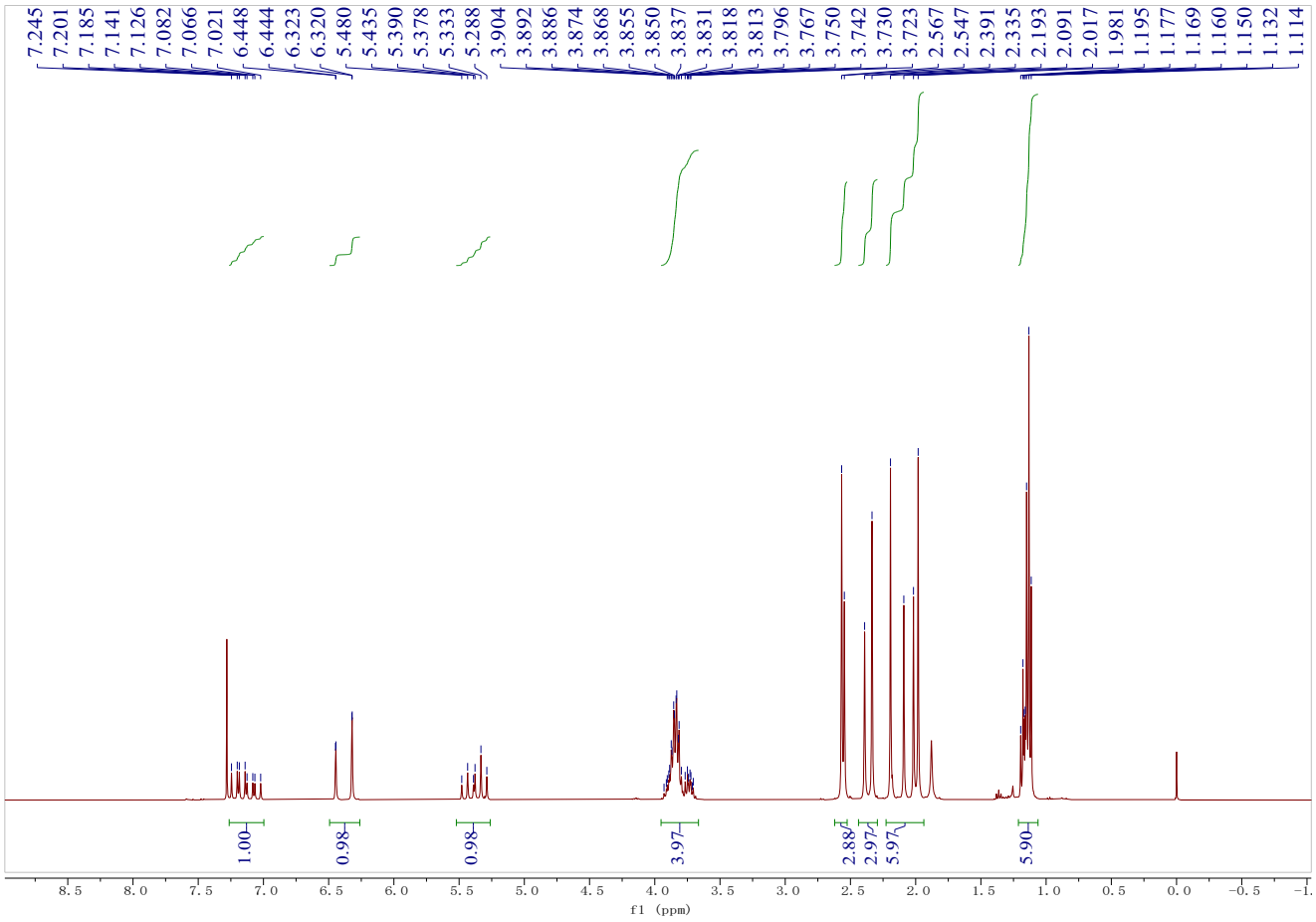
3u,^{13}C NMR, 101 MHz, $CDCl_3$



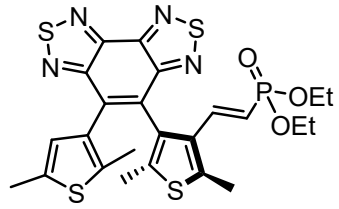


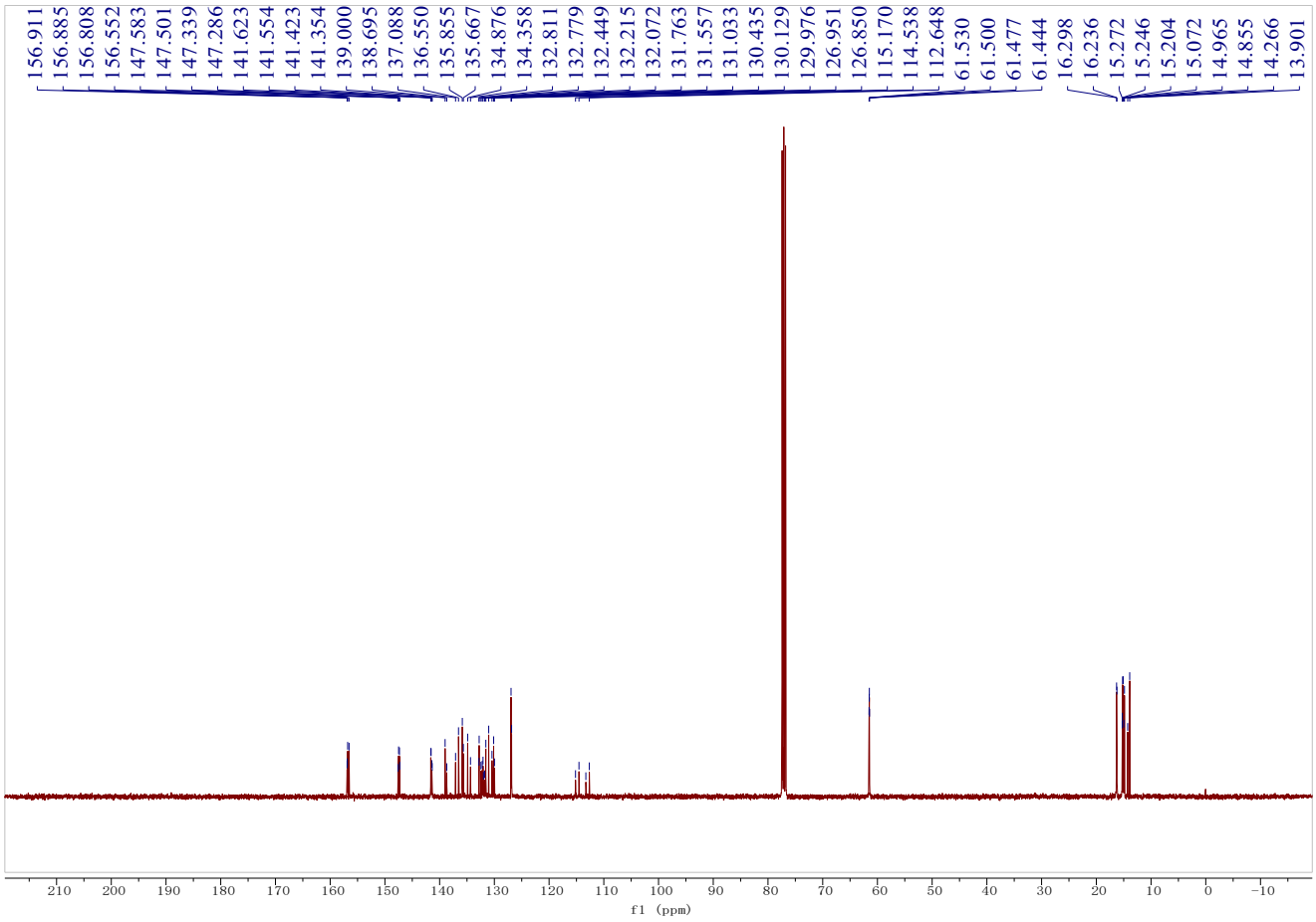
3v, ^{1}H NMR, 400 MHz, $CDCl_3$



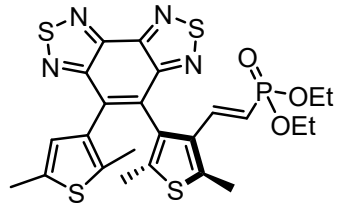


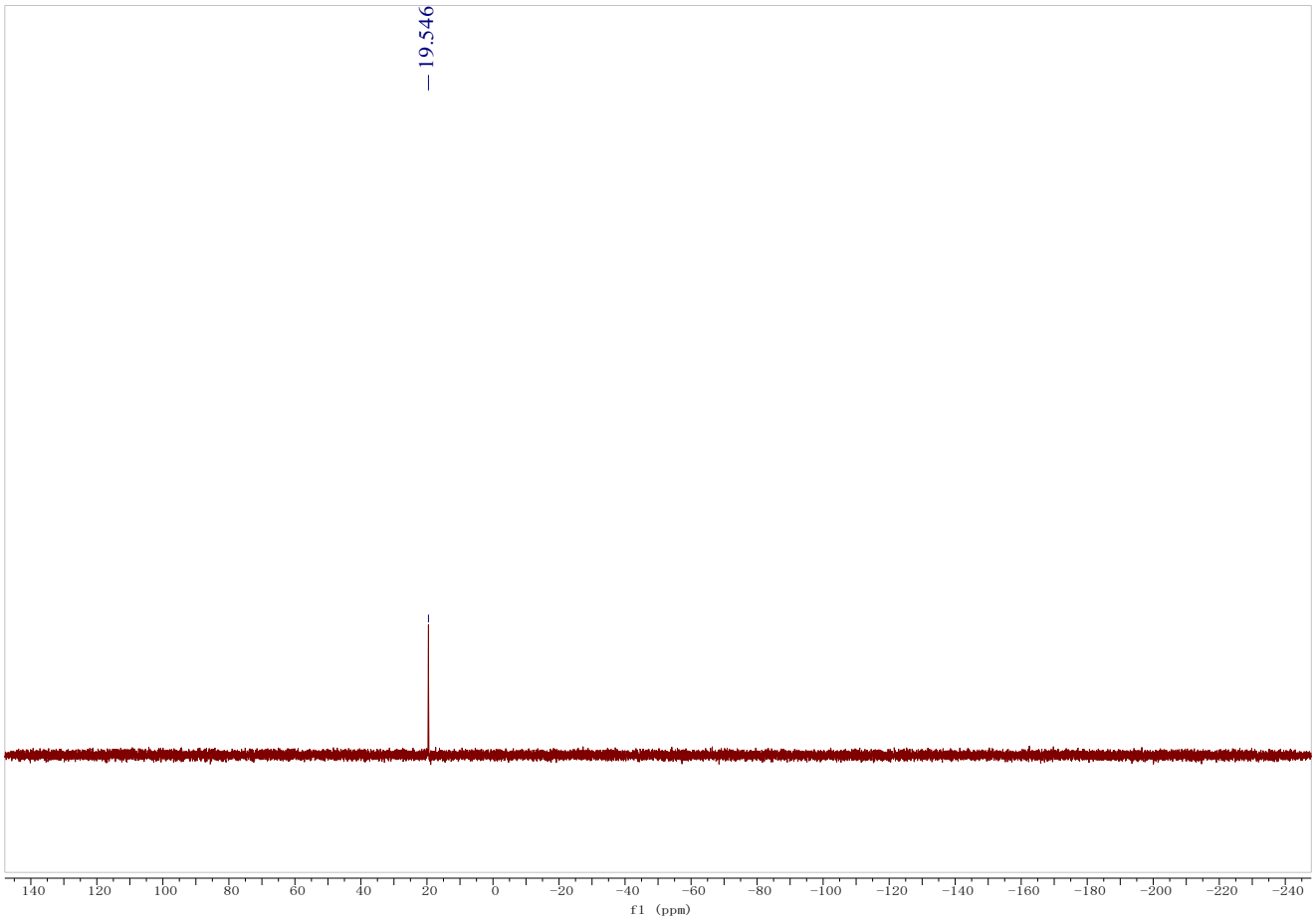
3v,^{13}C NMR, 101 MHz, $CDCl_3$



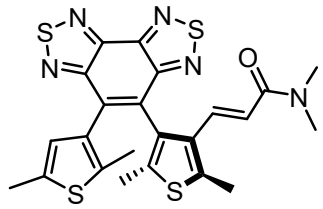


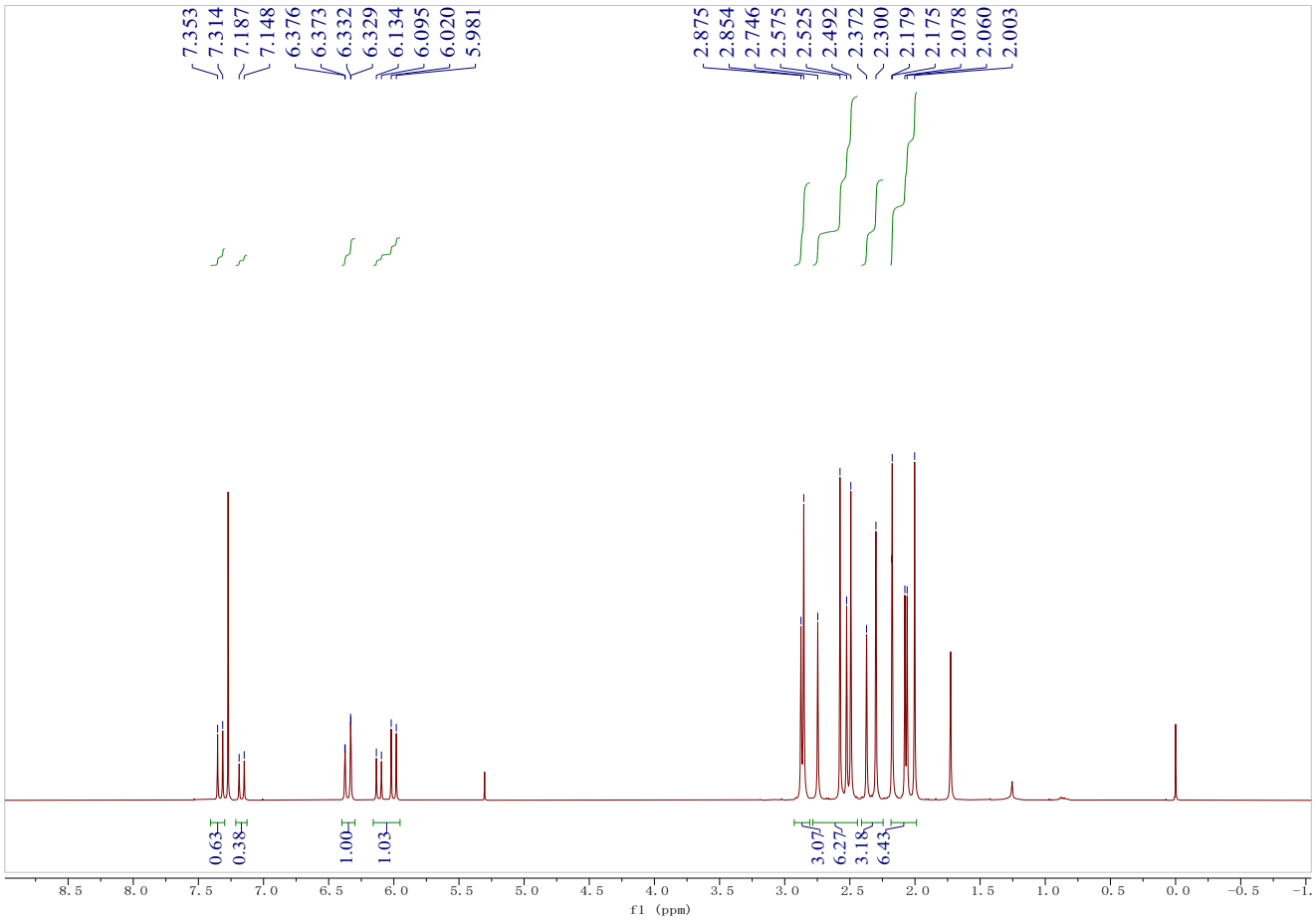
3v,^{31}P NMR, 162 MHz, $CDCl_3$



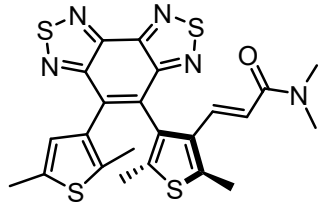


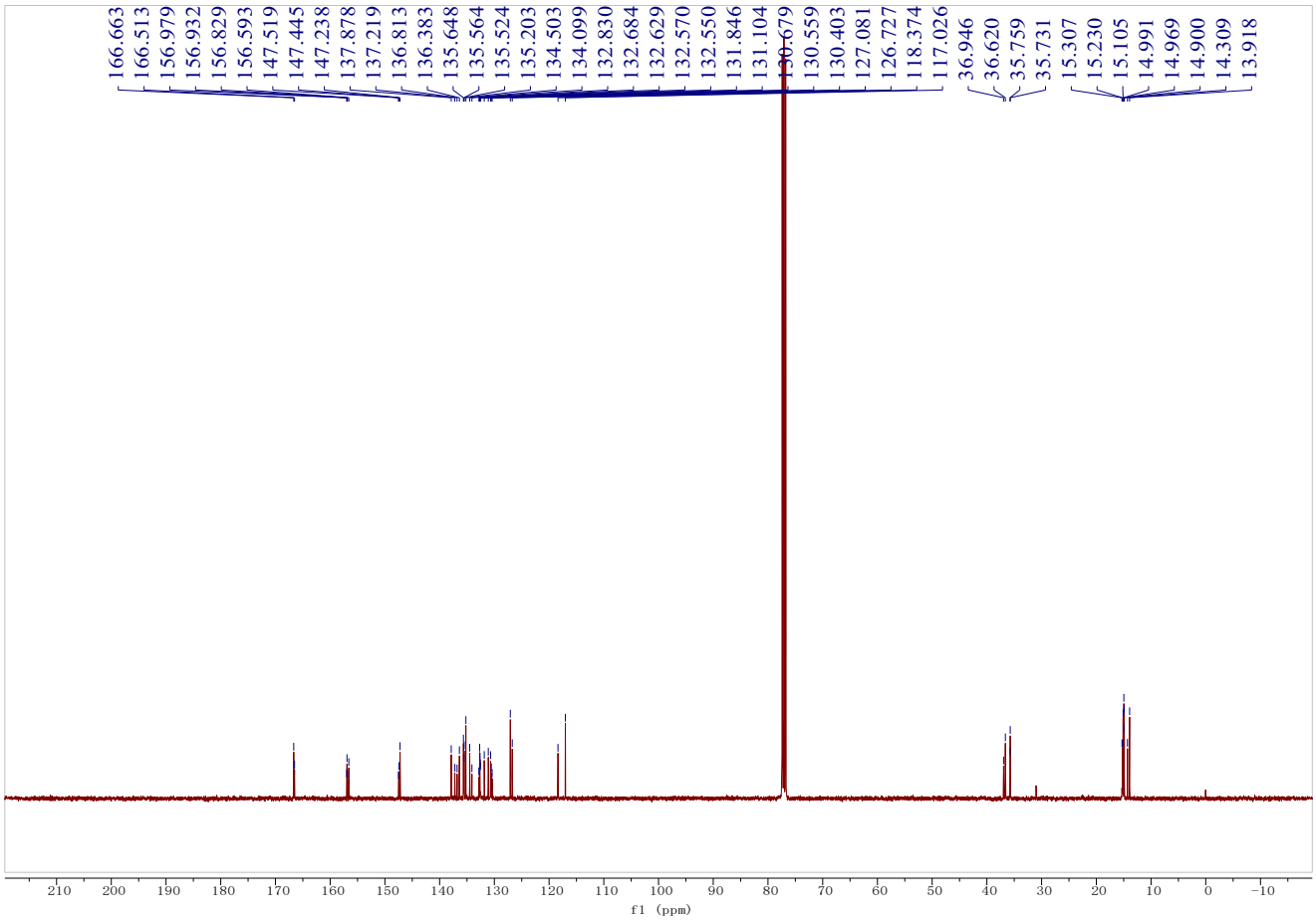
3w, ^{1}H NMR, 400 MHz, $CDCl_3$



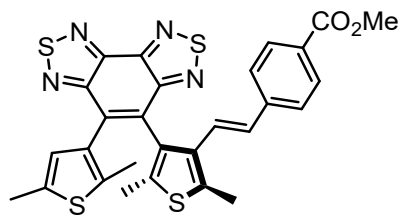


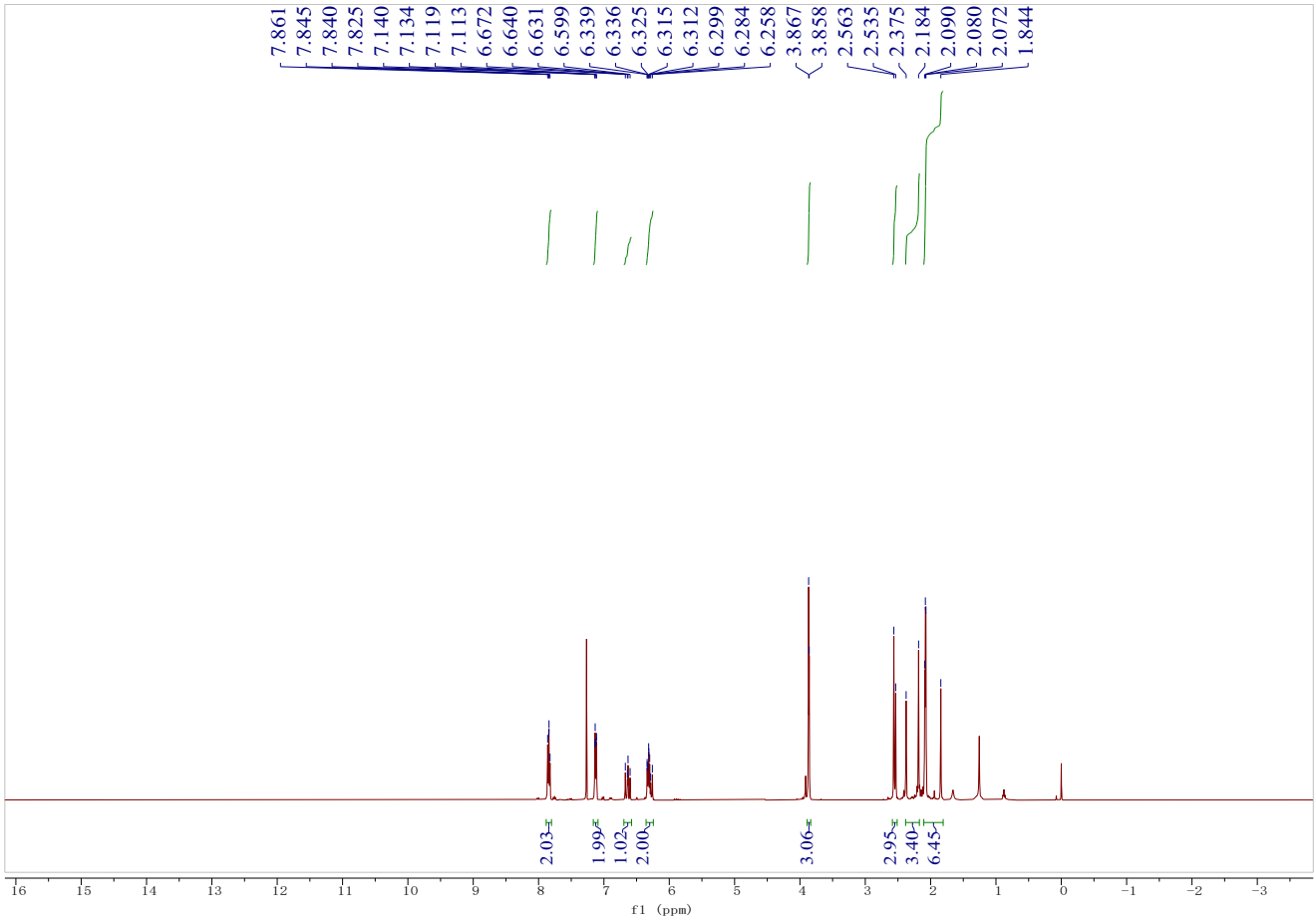
3w,^{13}C NMR, 101 MHz, $CDCl_3$



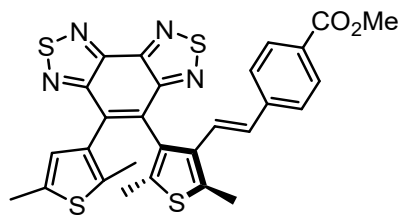


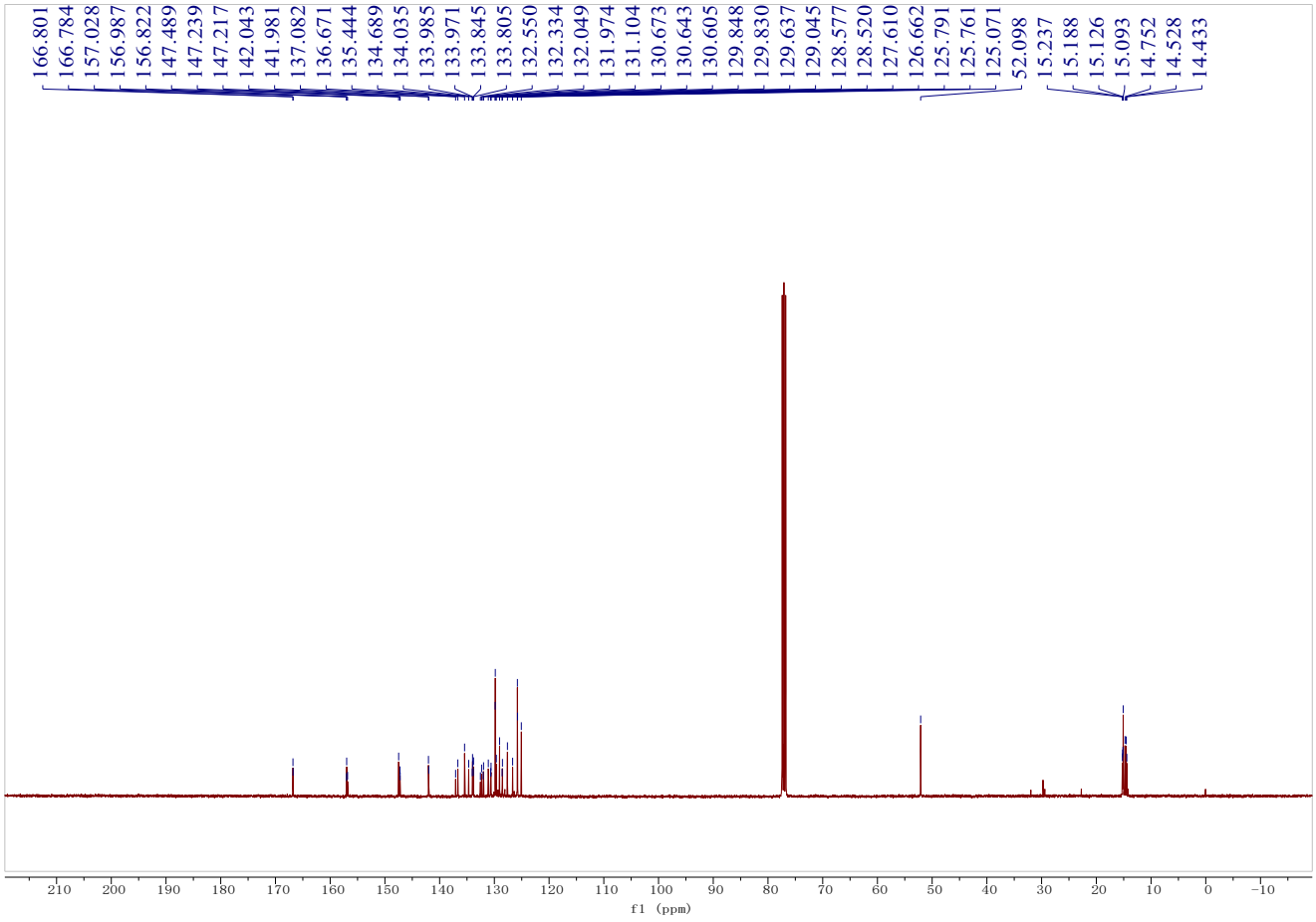
3x, ^{1}H NMR, 400 MHz, $CDCl_3$



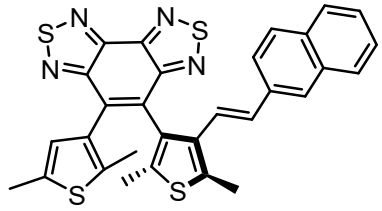


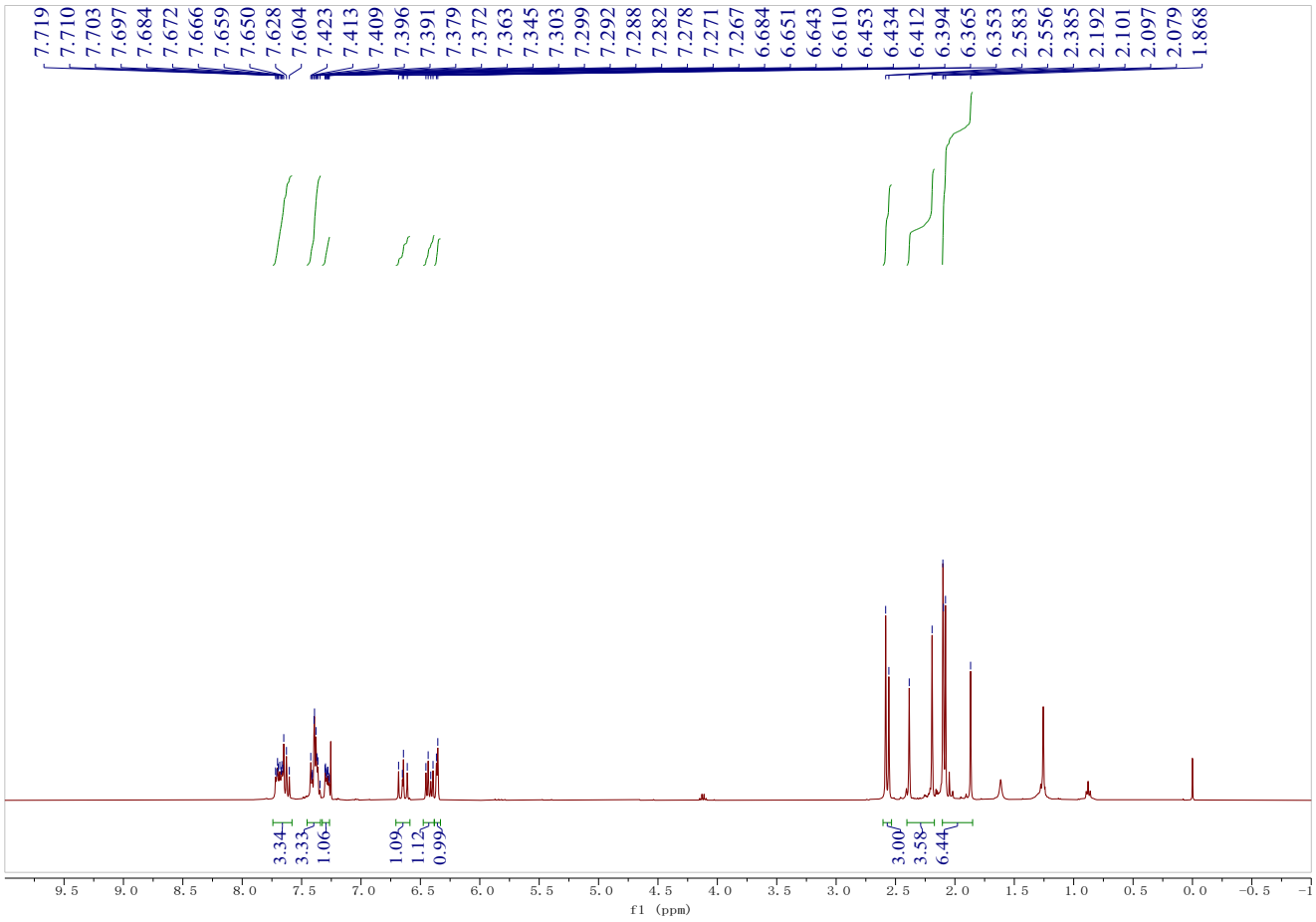
3x,^{13}C NMR, 101 MHz, $CDCl_3$



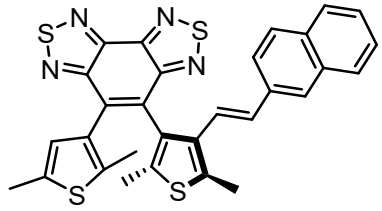


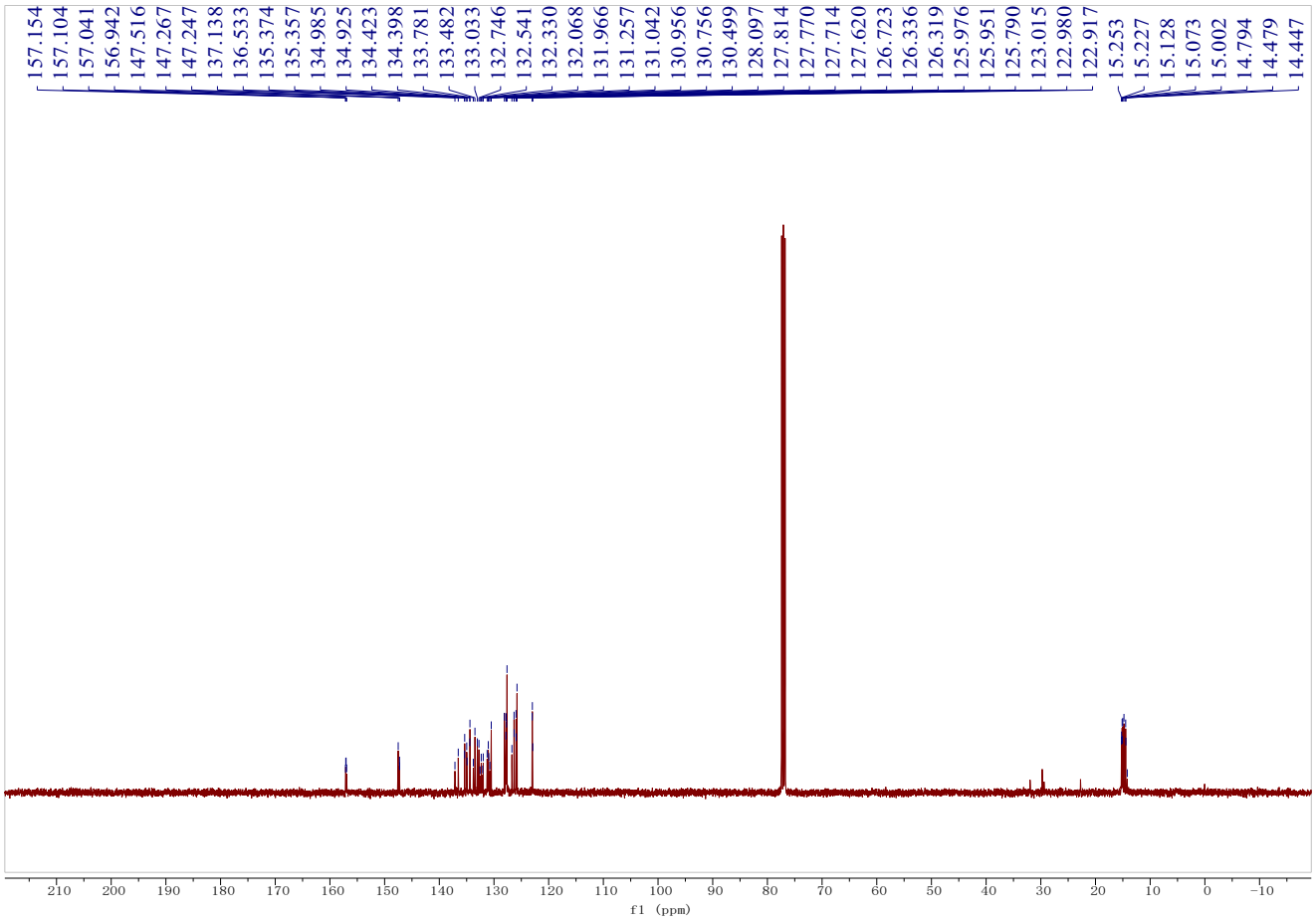
3y, ^{1}H NMR, 400 MHz, $CDCl_3$



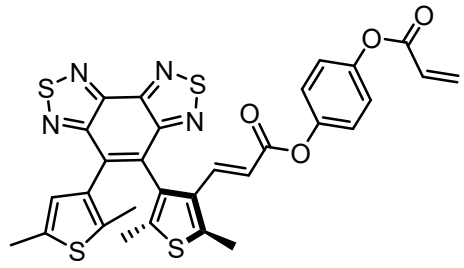


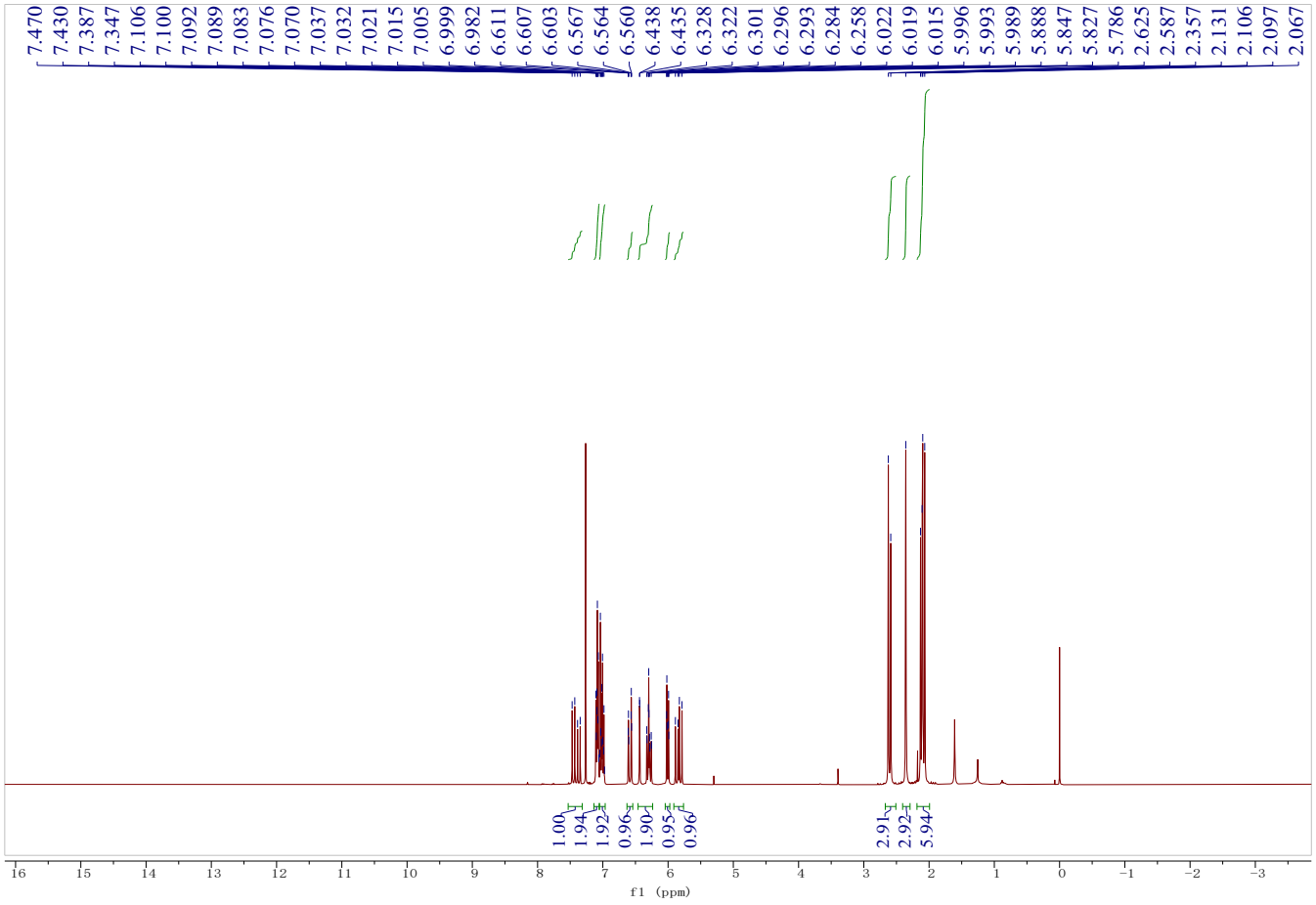
3y,^{13}C NMR, 101 MHz, $CDCl_3$



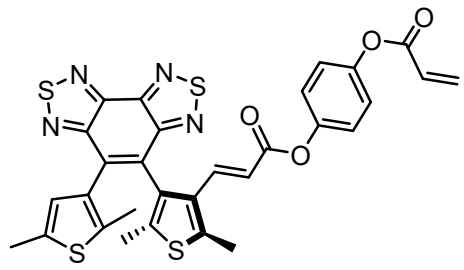


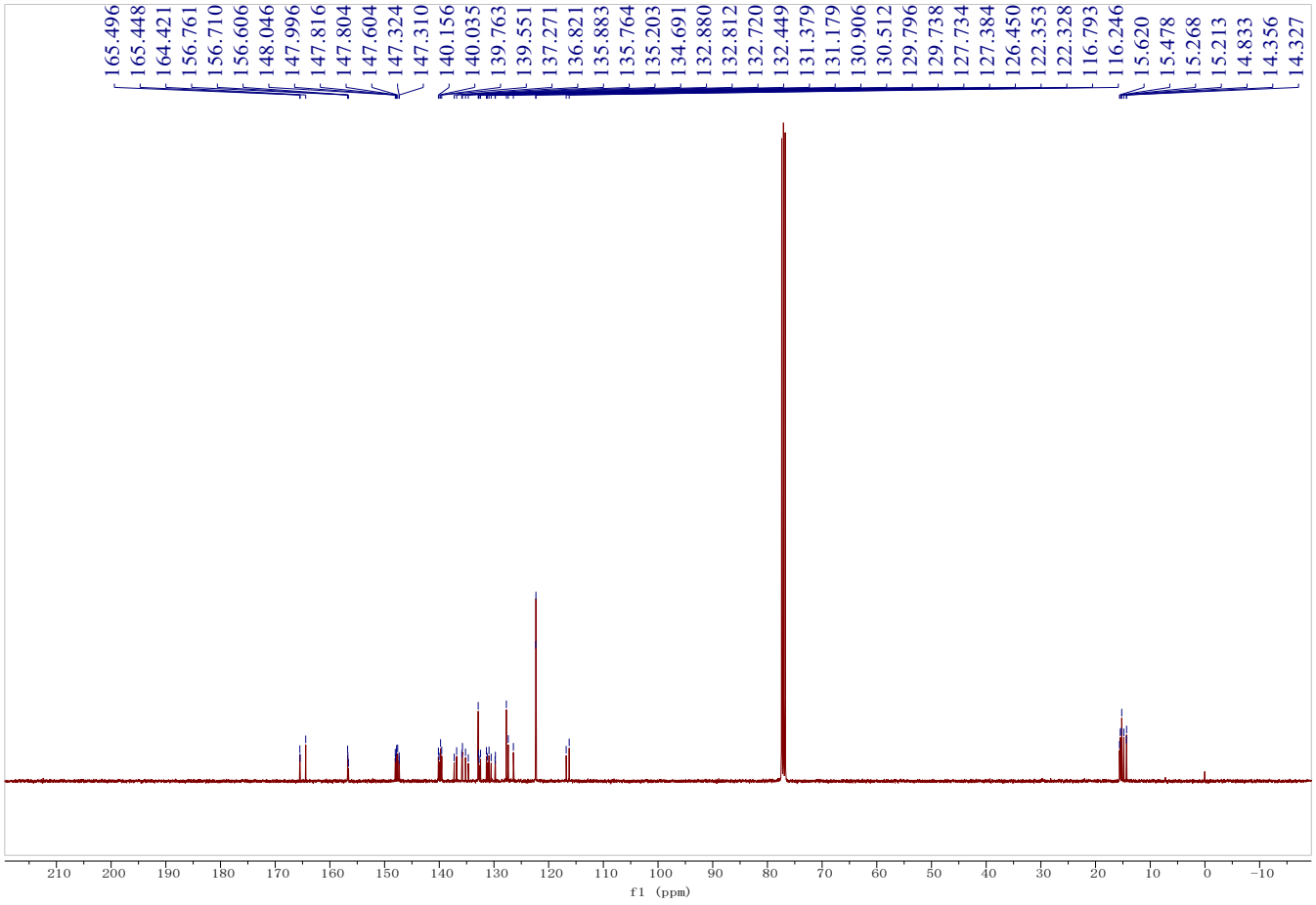
3z-mono, ^{1}H NMR, 400 MHz, $CDCl_3$



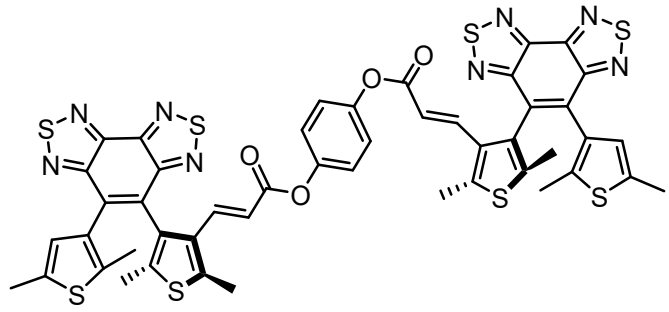


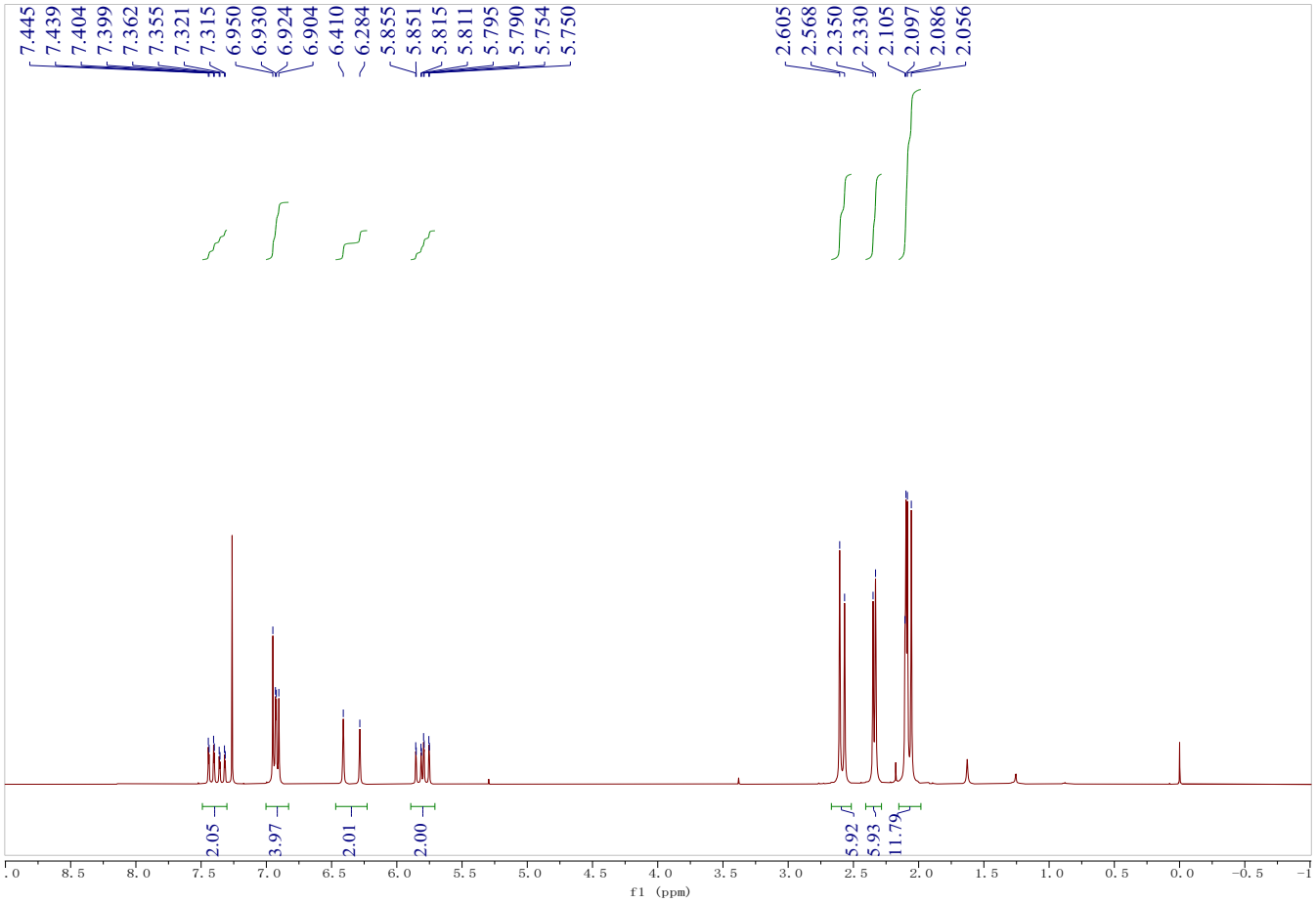
3z-mono,^{13}C NMR, 101 MHz, $CDCl_3$



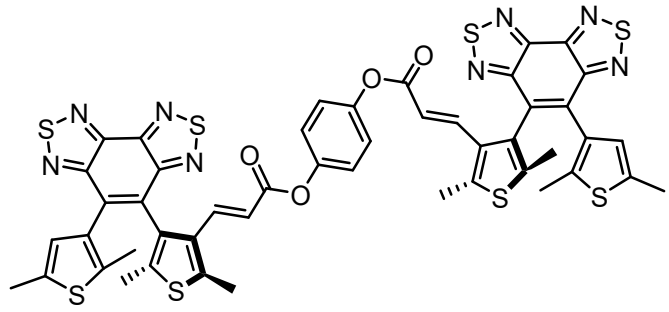


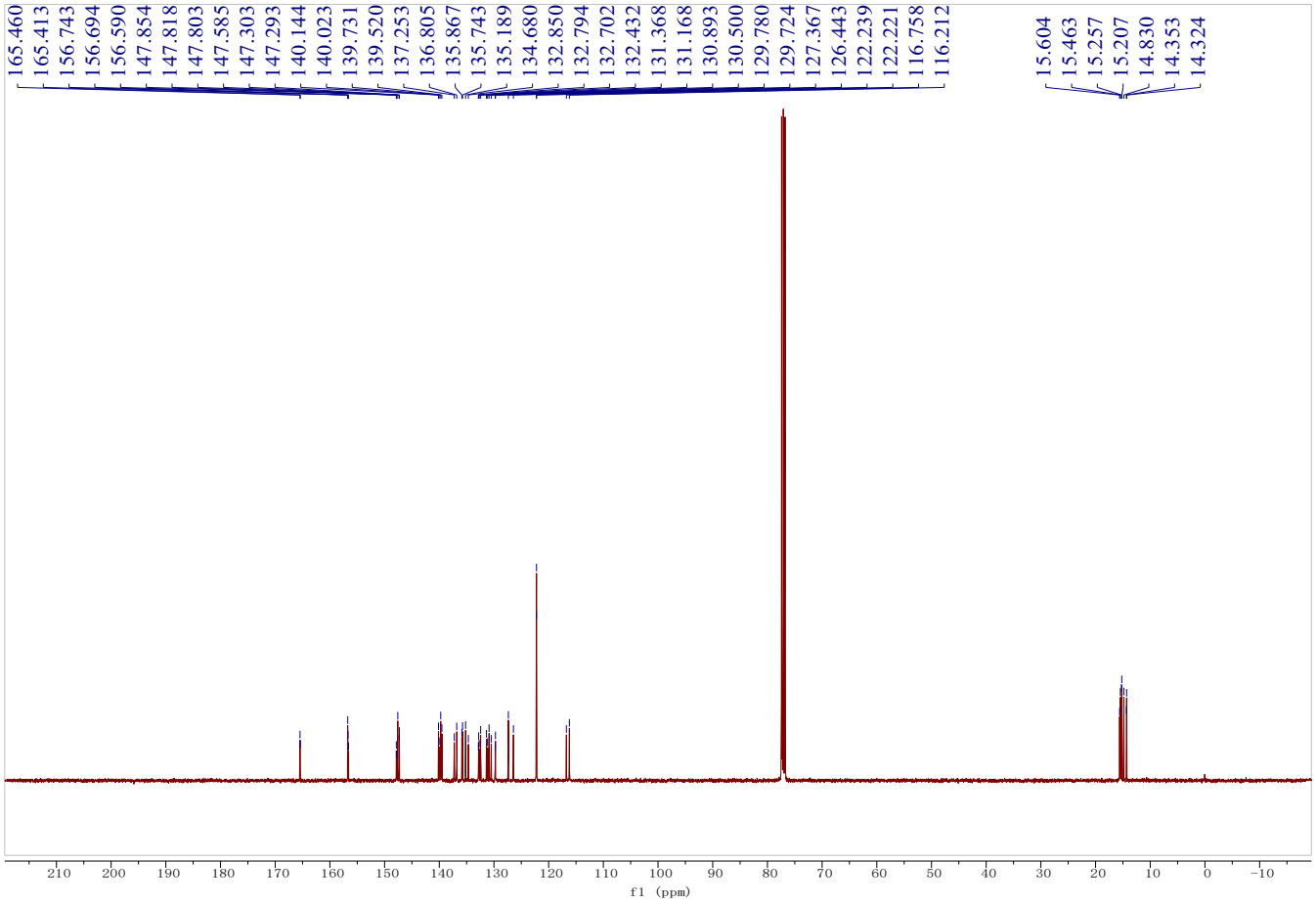
3z-di, ^{1}H NMR, 400 MHz, $CDCl_3$



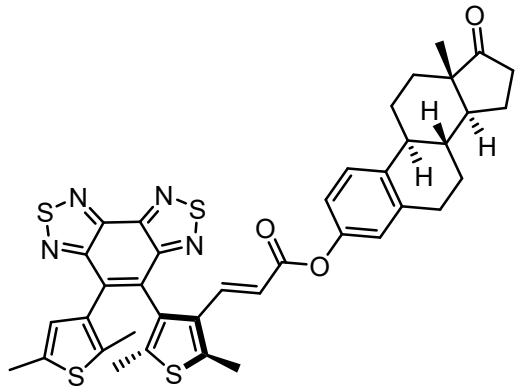


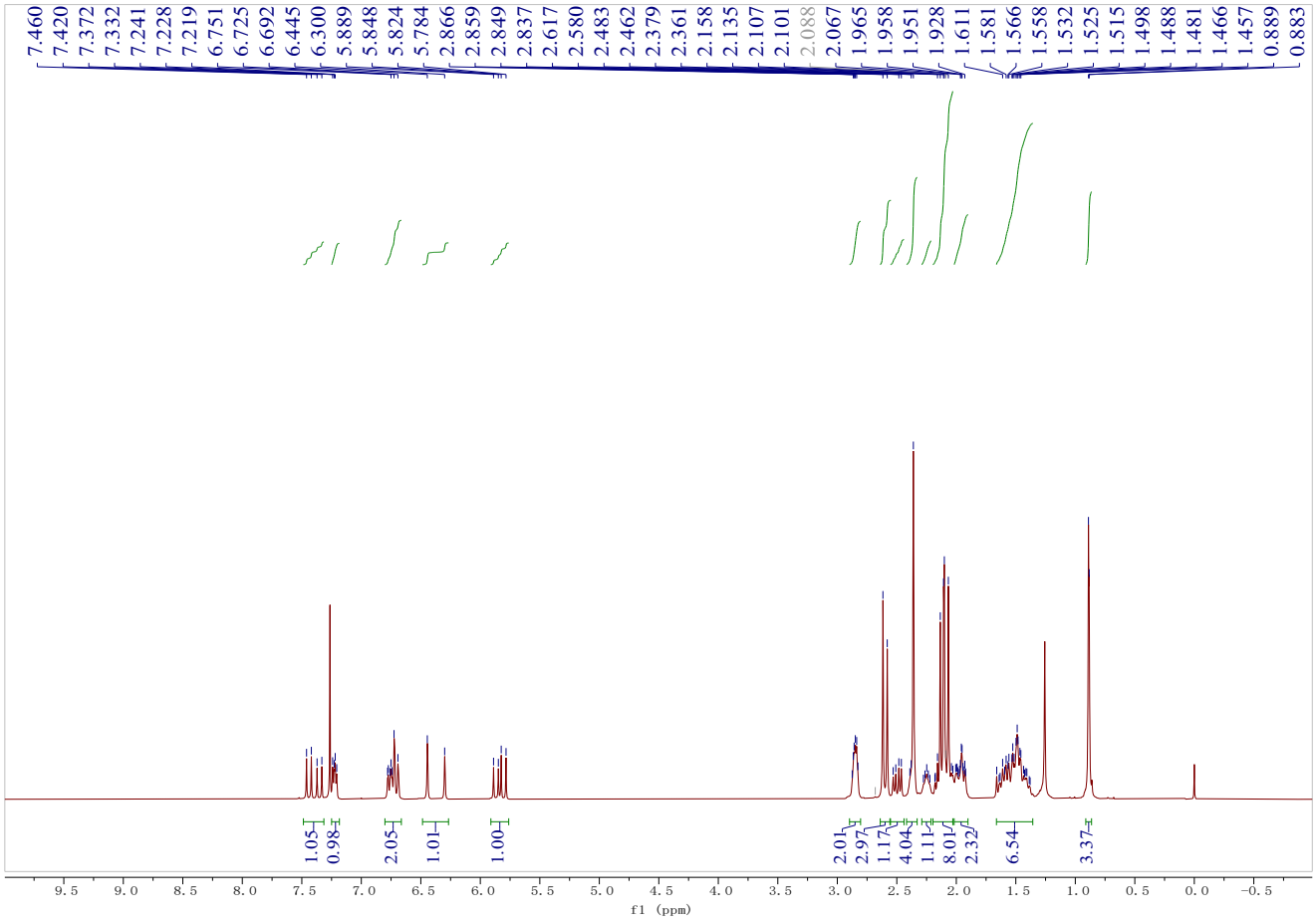
3z-di,^{13}C NMR, 101 MHz, $CDCl_3$



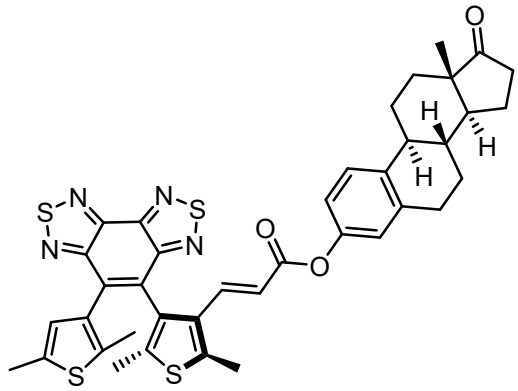


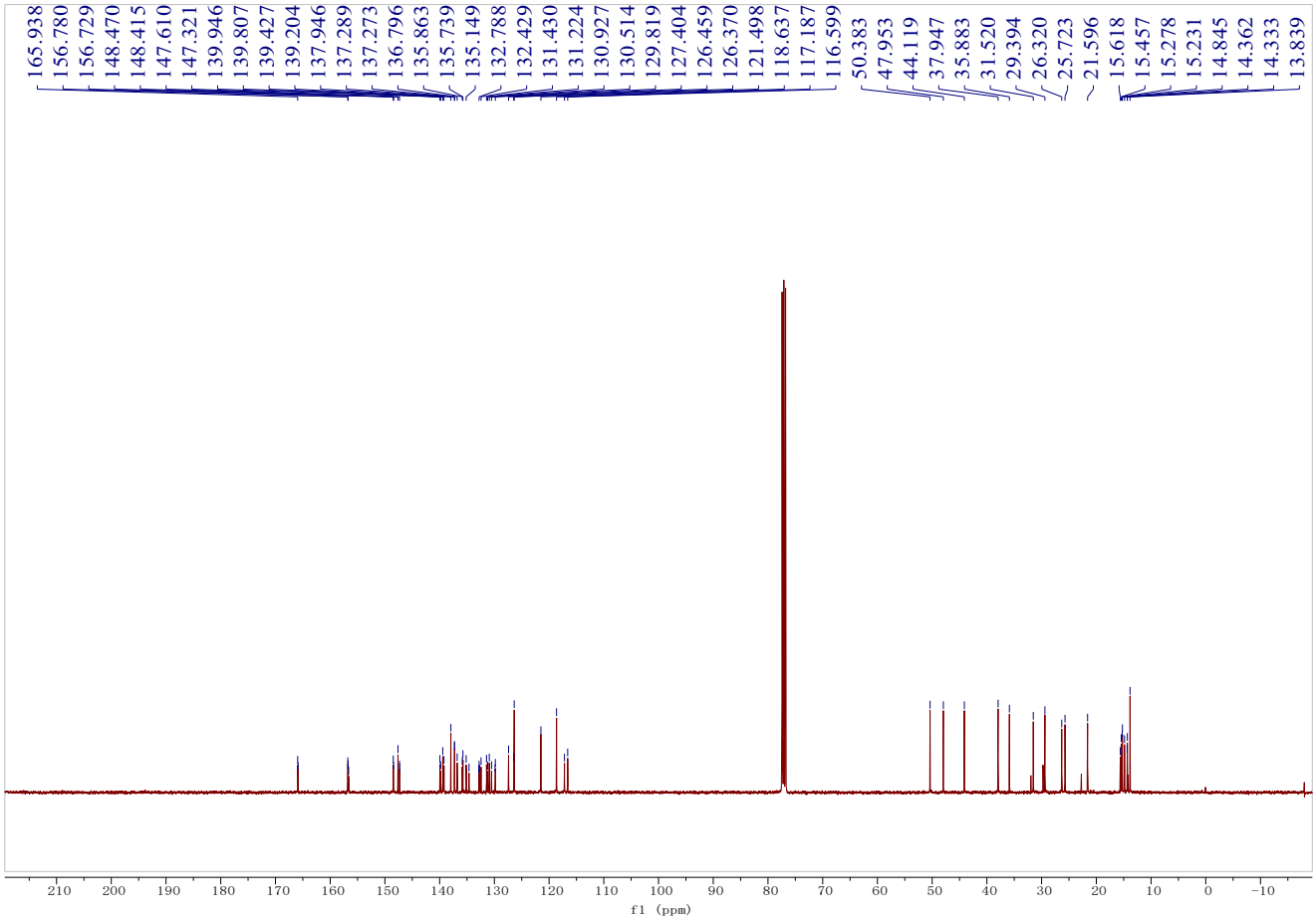
3aa, ^{1}H NMR, 400 MHz, $CDCl_3$



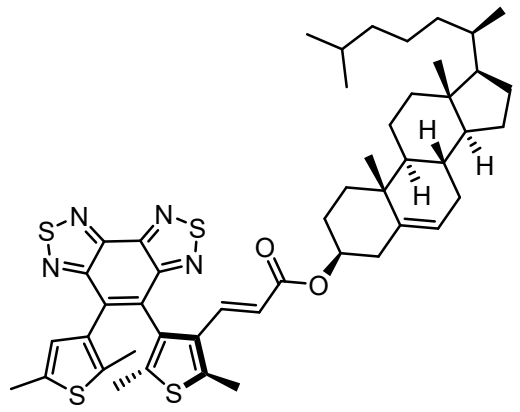


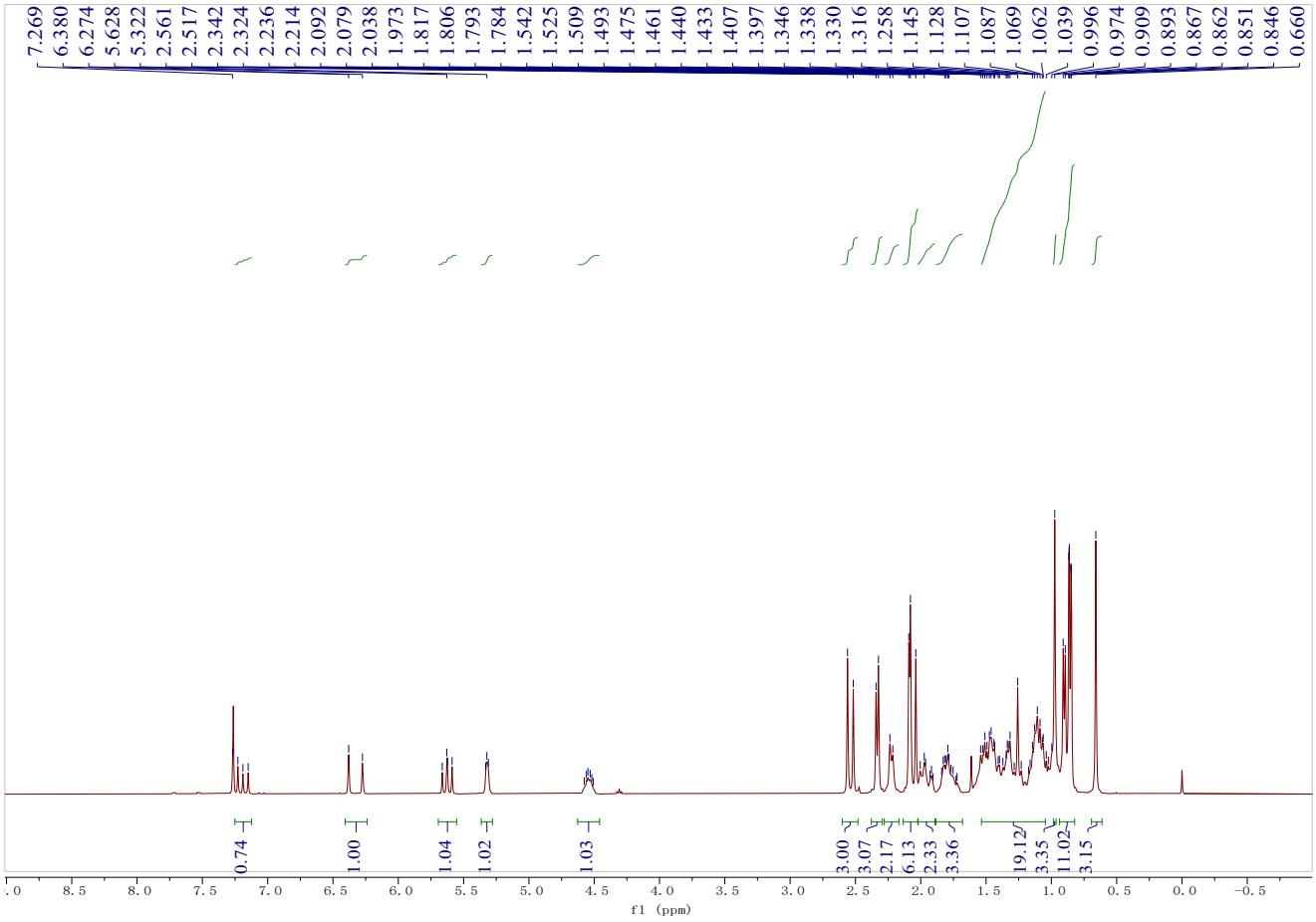
3aa,^{13}C NMR, 101 MHz, $CDCl_3$



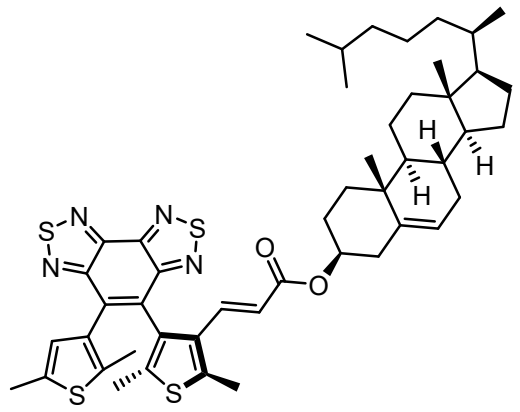


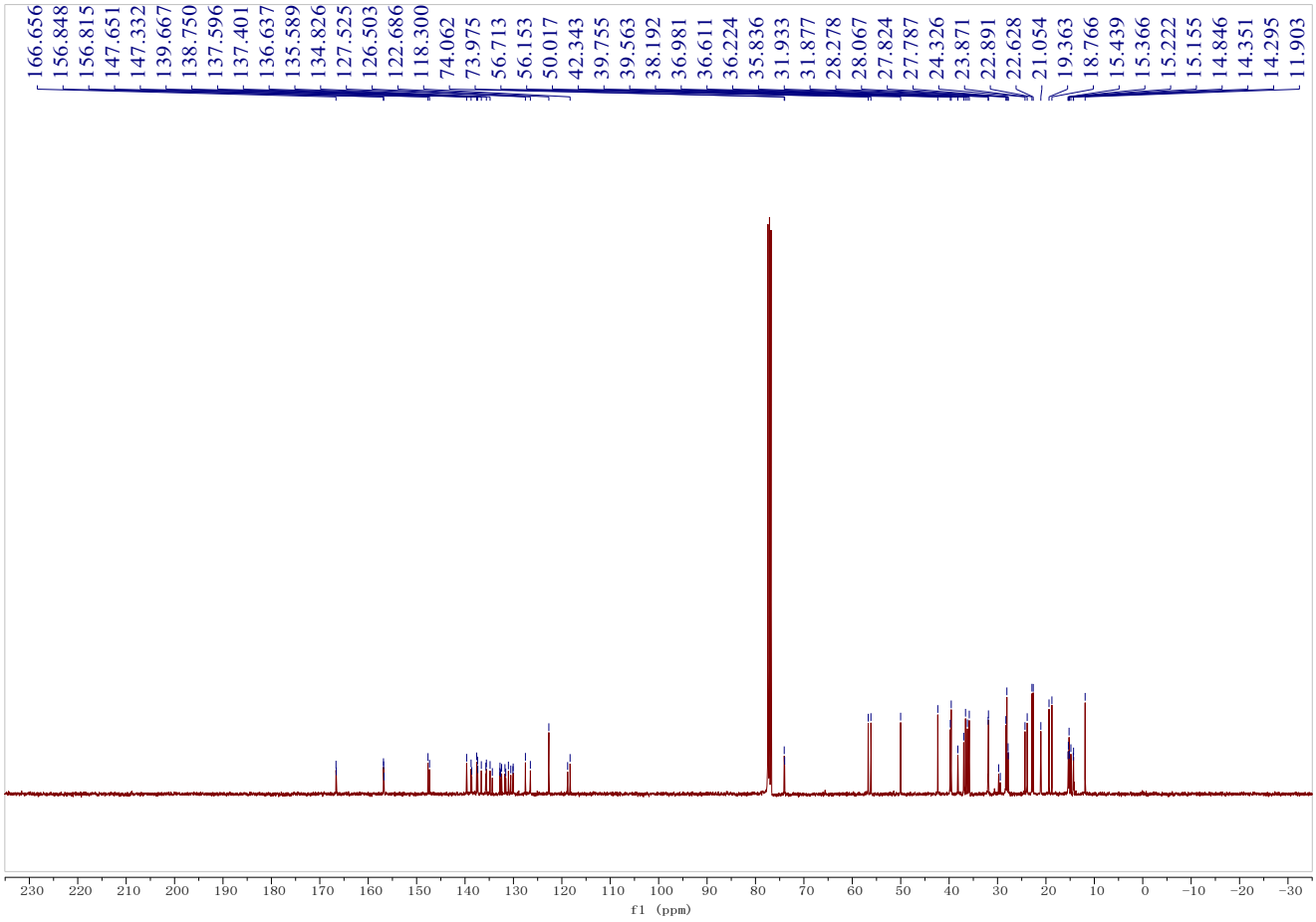
3ab, ^{1}H NMR, 400 MHz, $CDCl_3$



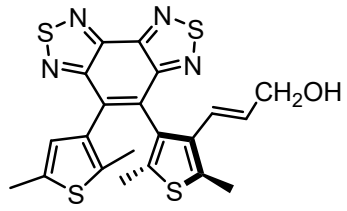


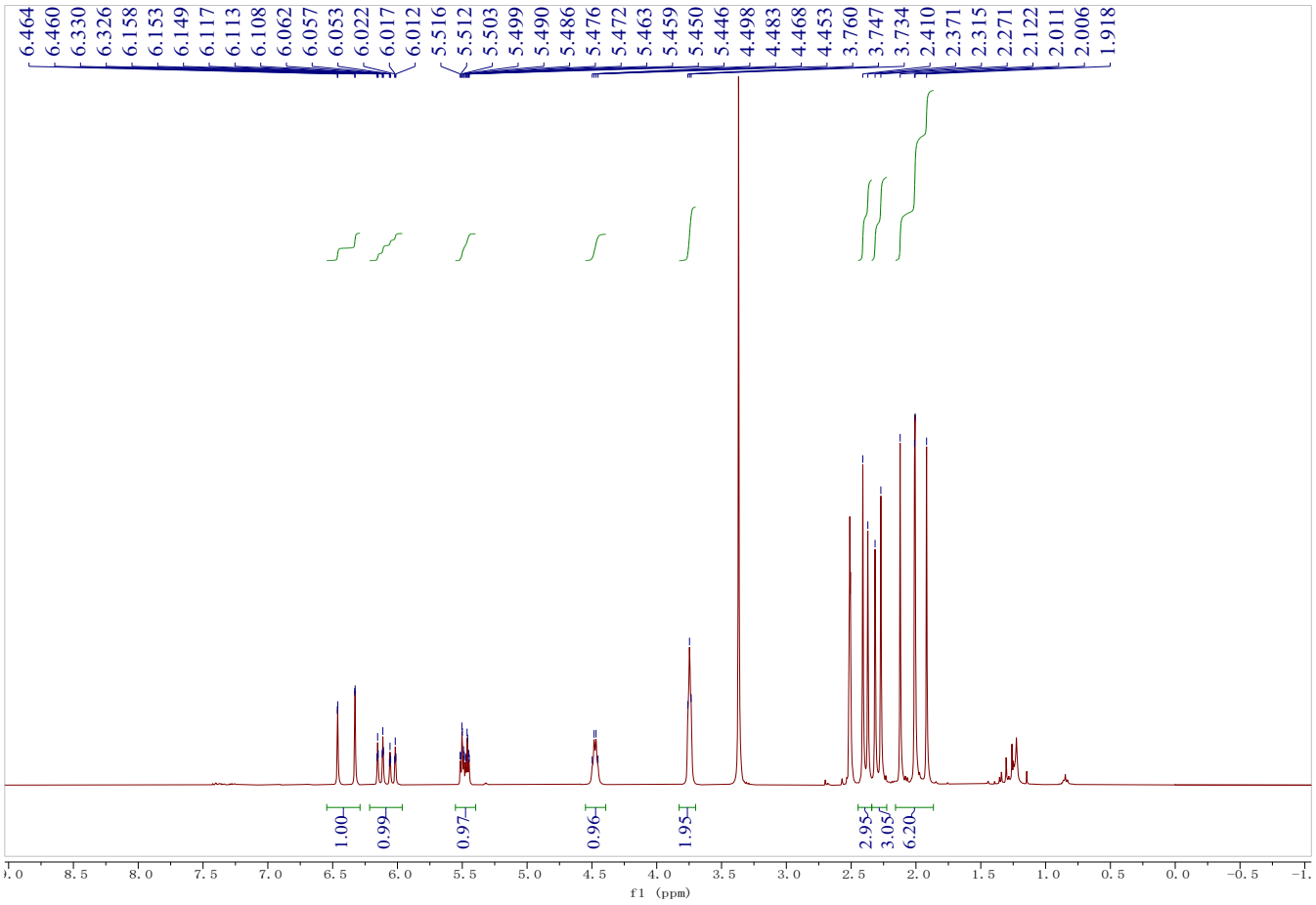
3ab,^{13}C NMR, 101 MHz, $CDCl_3$



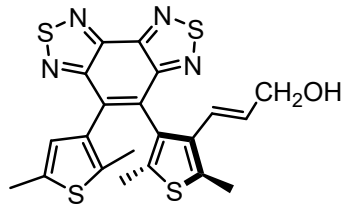


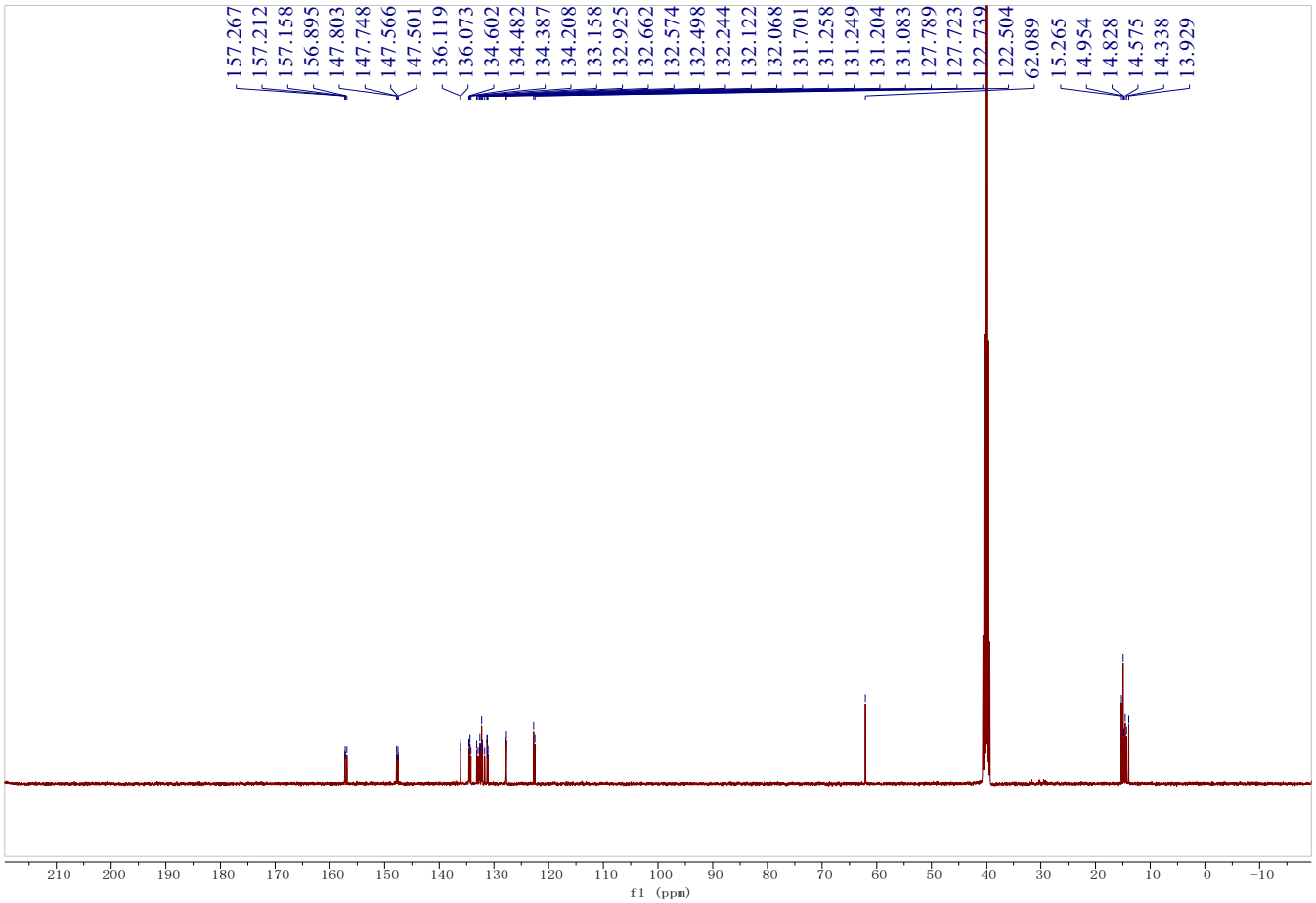
4, ^{1}H NMR, 400 MHz, DMSO-d_6



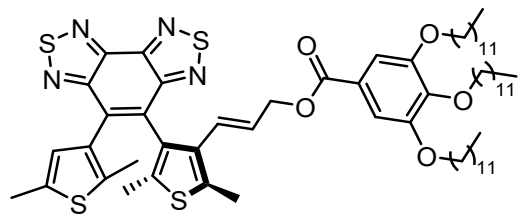


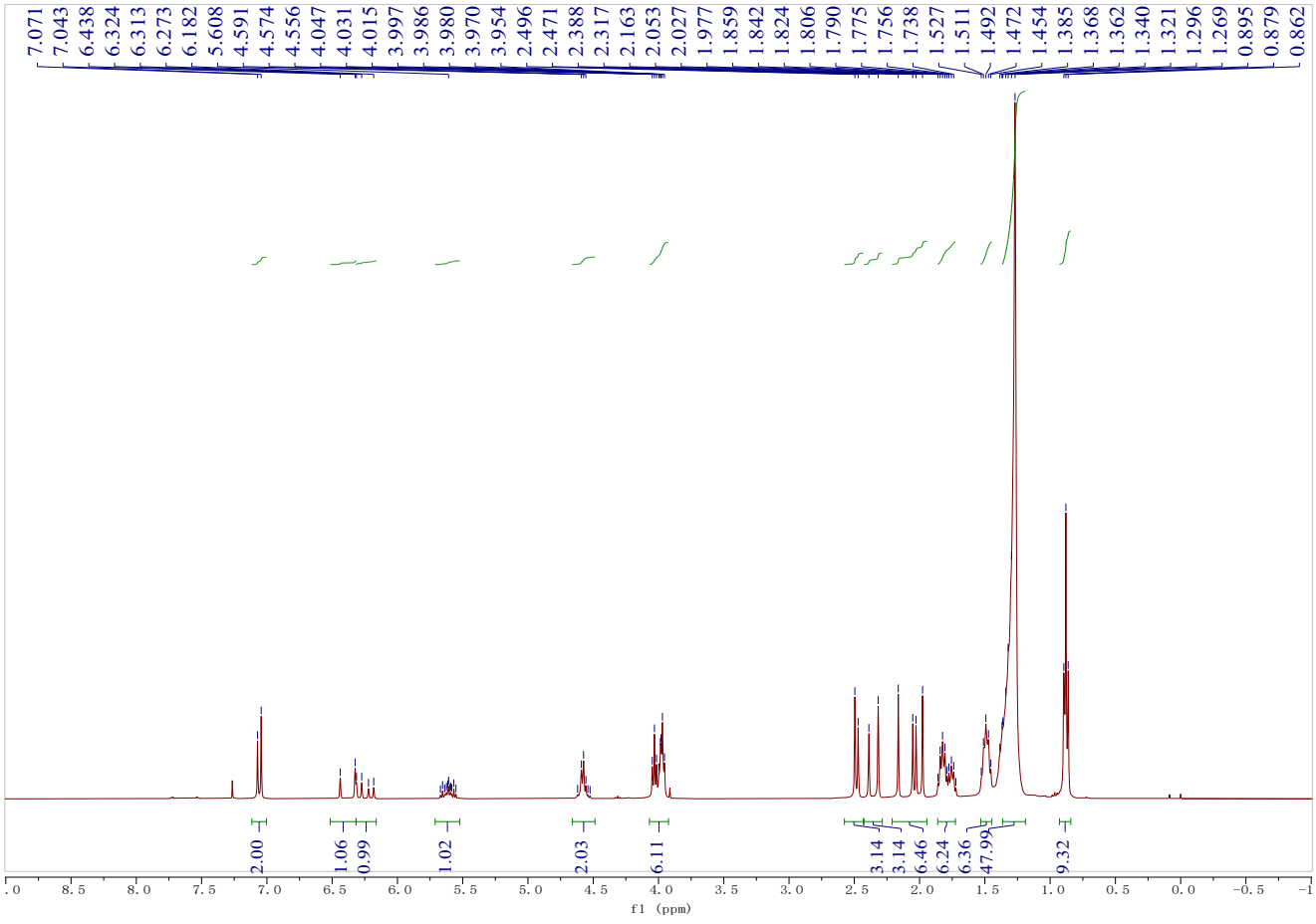
4,^{13}C NMR, 101 MHz, DMSO-d_6



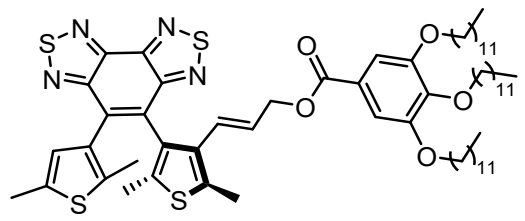


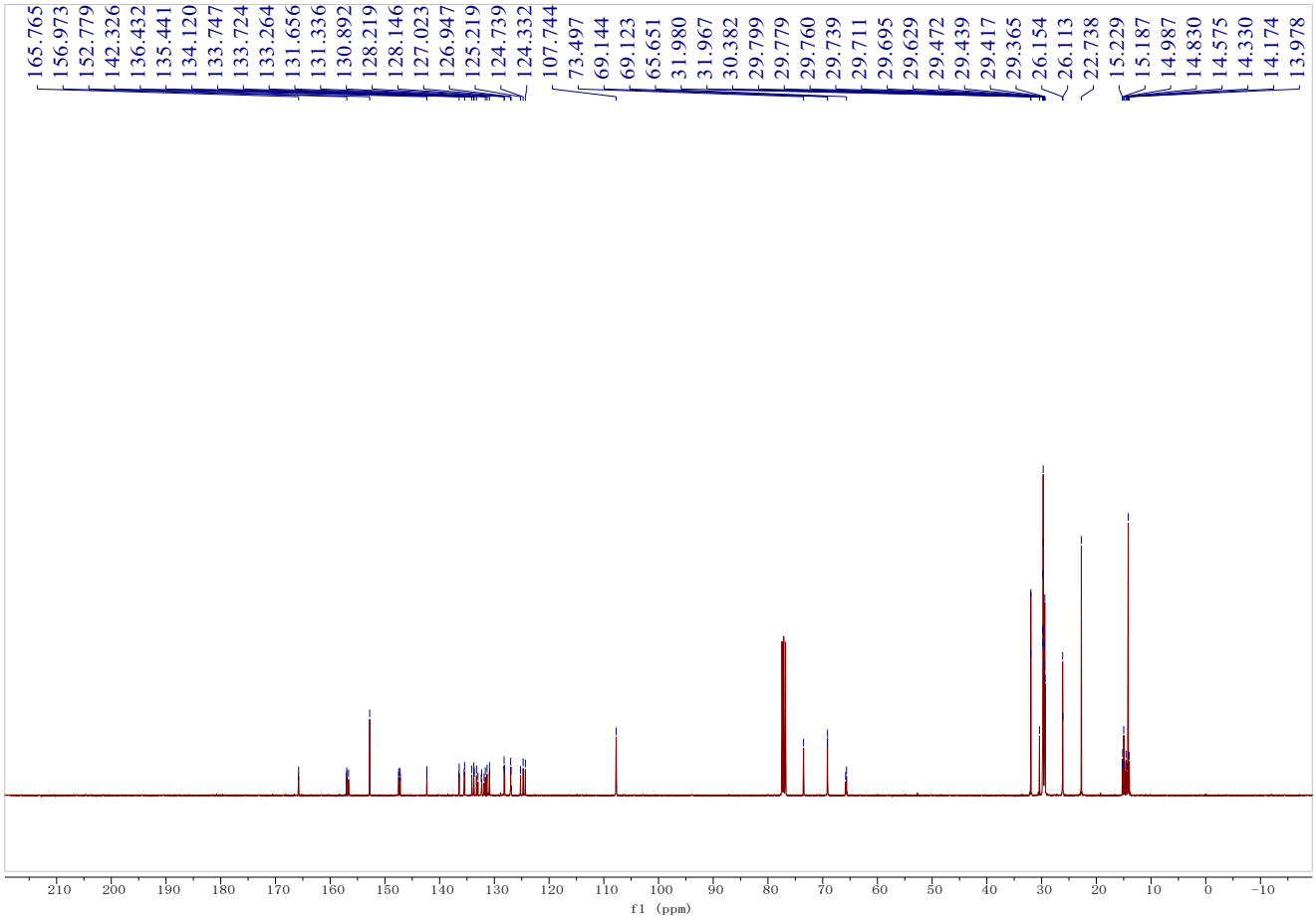
5, ^{1}H NMR, 400 MHz, $CDCl_3$



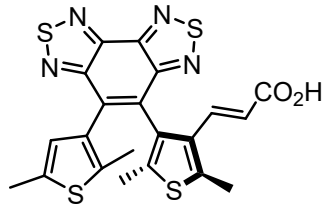


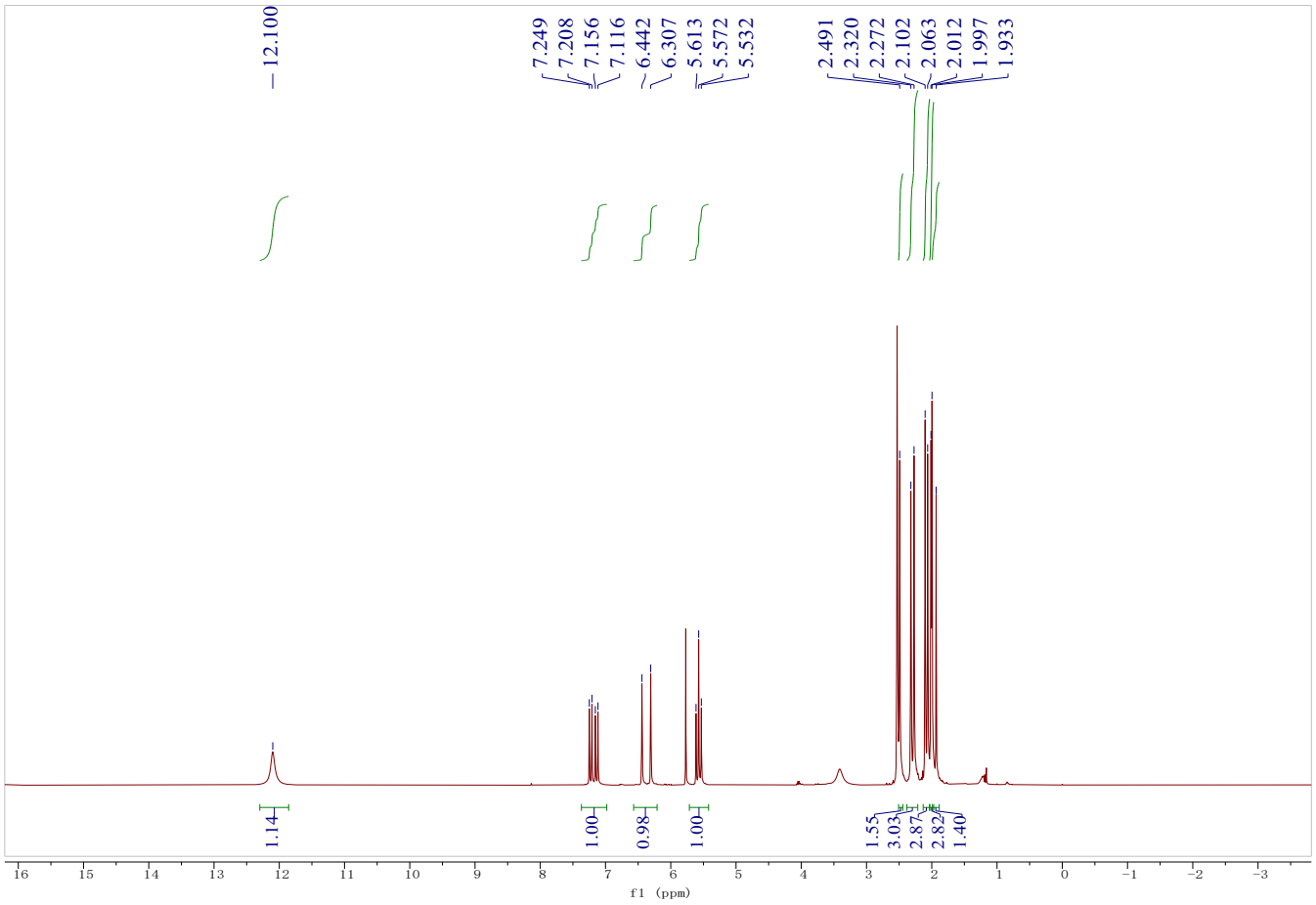
5,^{13}C NMR, 101 MHz, $CDCl_3$



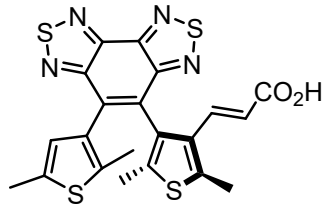


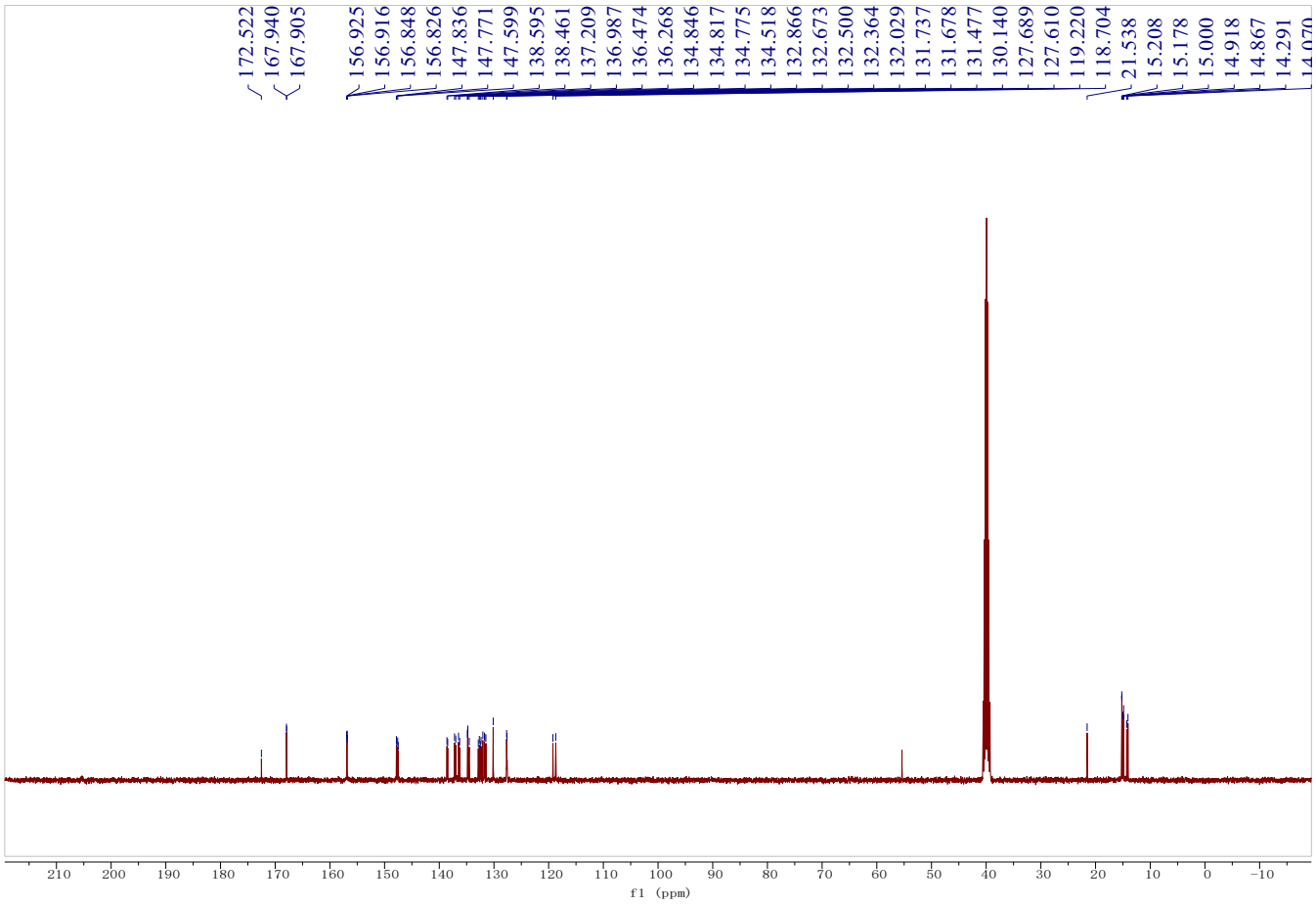
6a, ^{1}H NMR, 400 MHz, DMSO-d_6



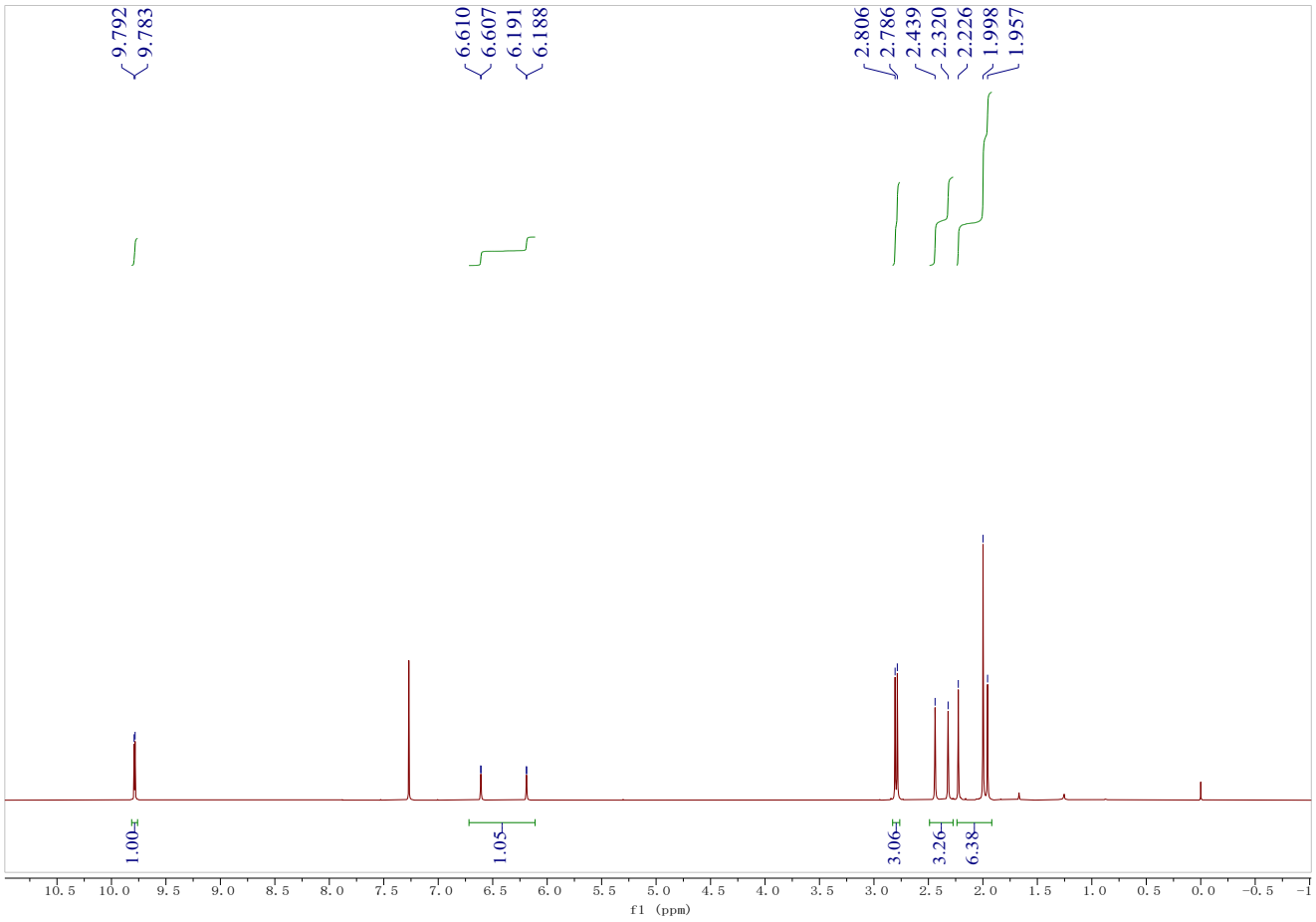


6a, ^{13}C NMR, 101 MHz, DMSO-d_6

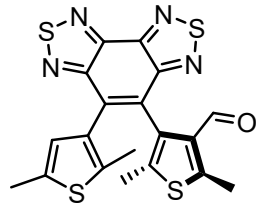


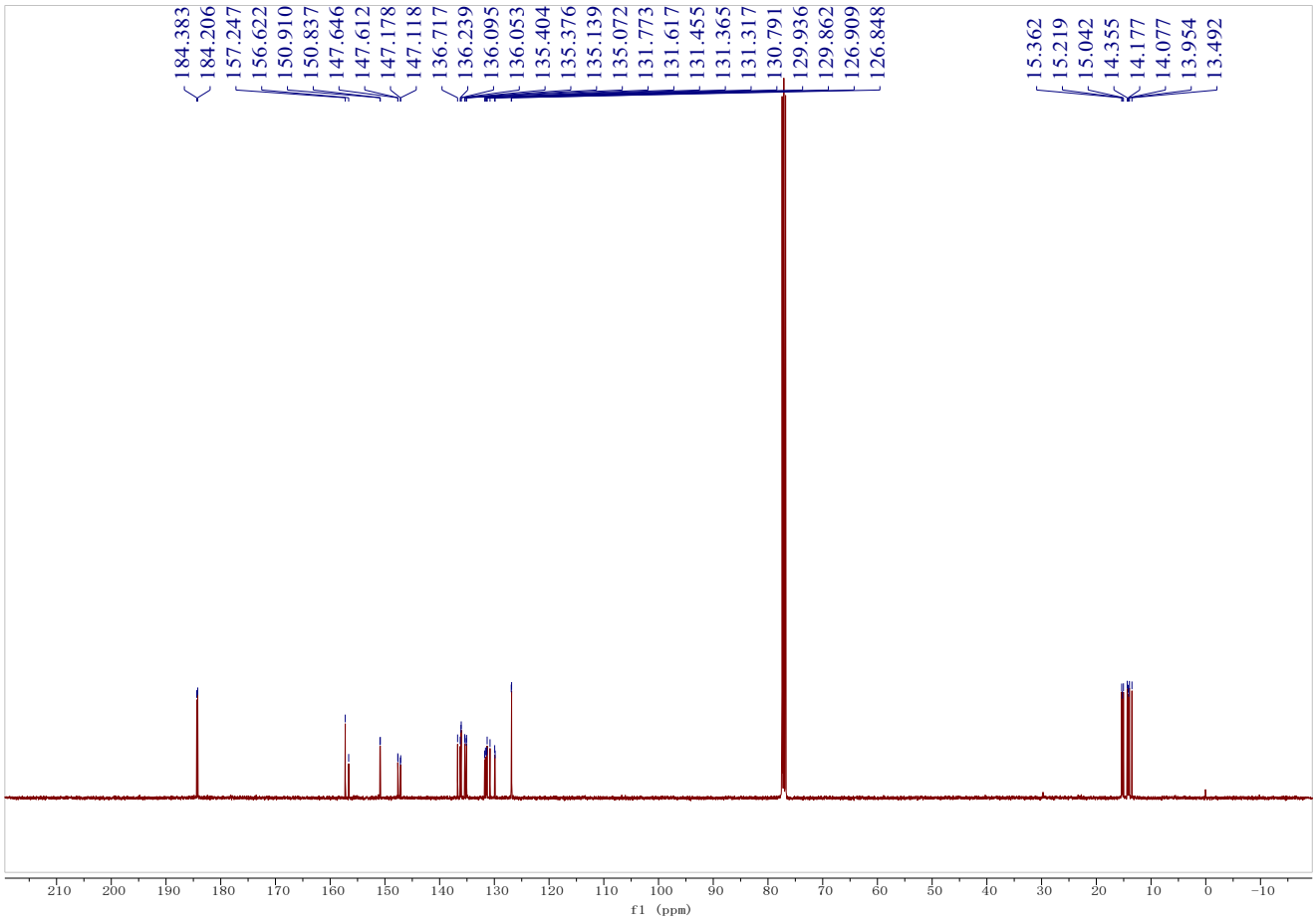


7, ^{1}H NMR, 400 MHz, $CDCl_3$

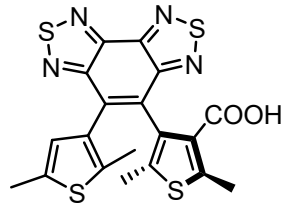


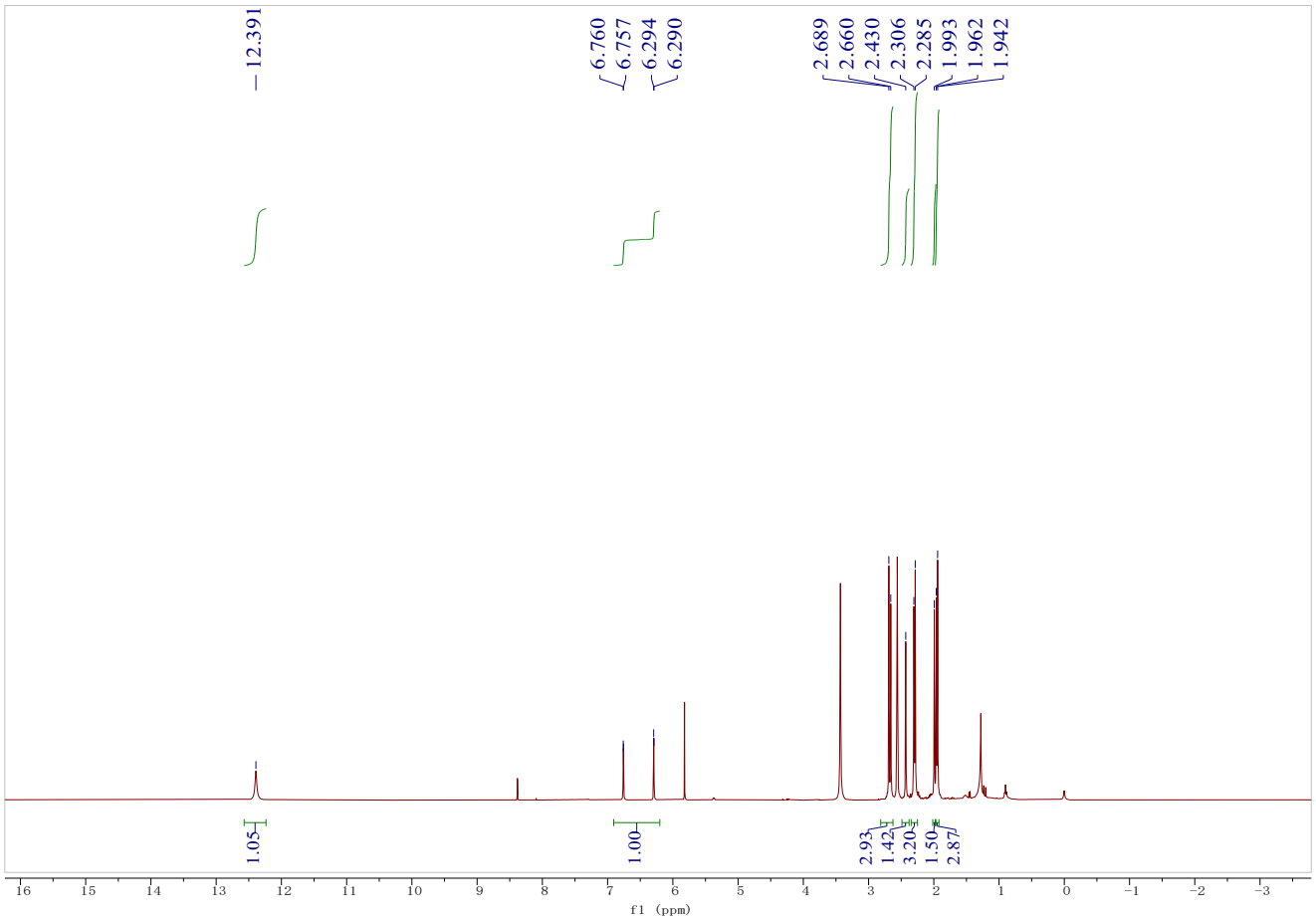
7,^{13}C NMR, 101 MHz, $CDCl_3$



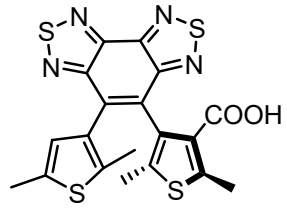


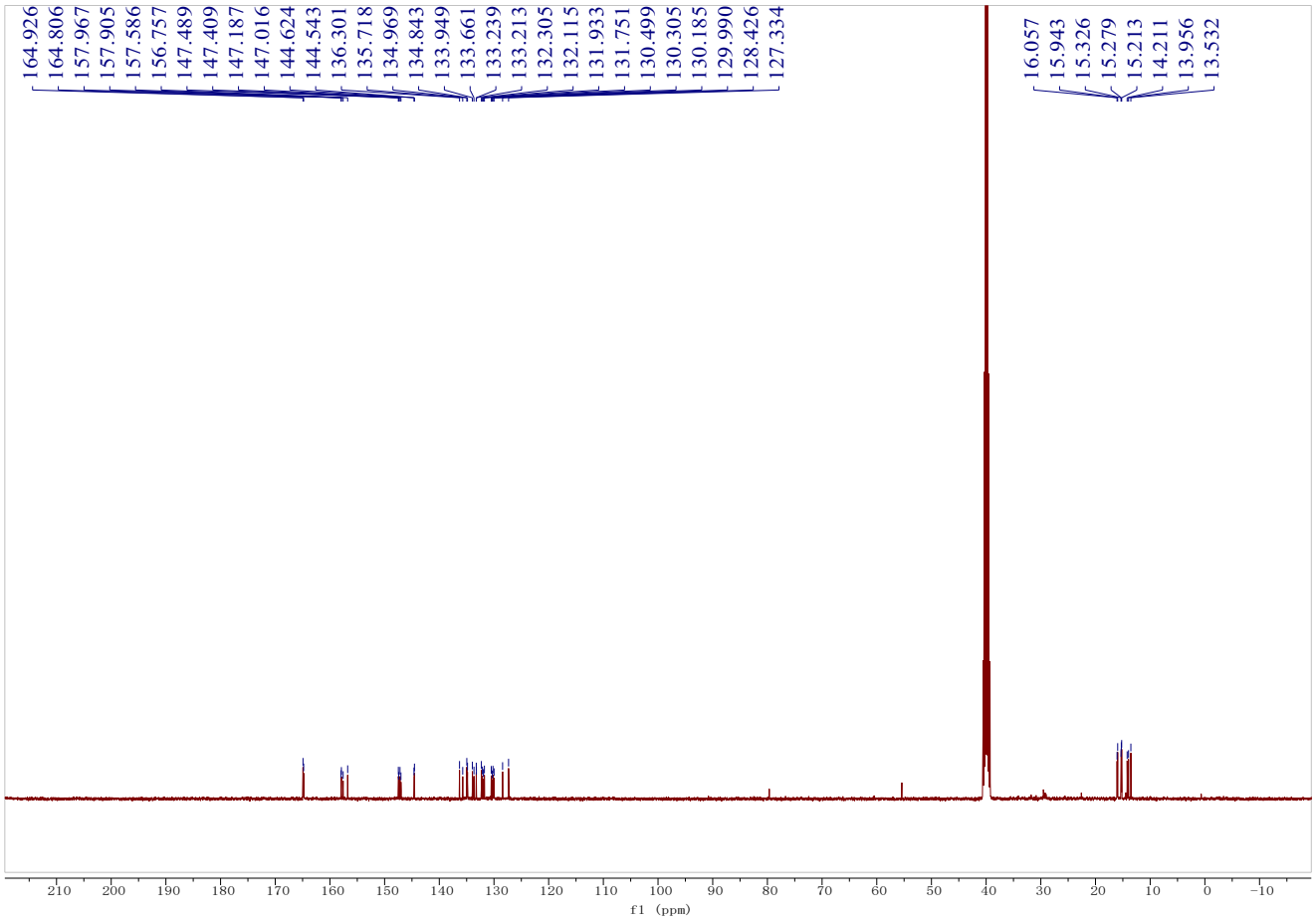
8, ^{1}H NMR, 400 MHz, DMSO-d_6



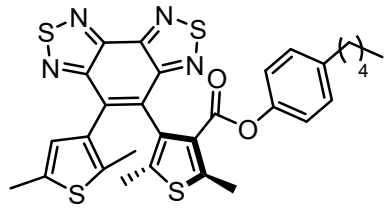


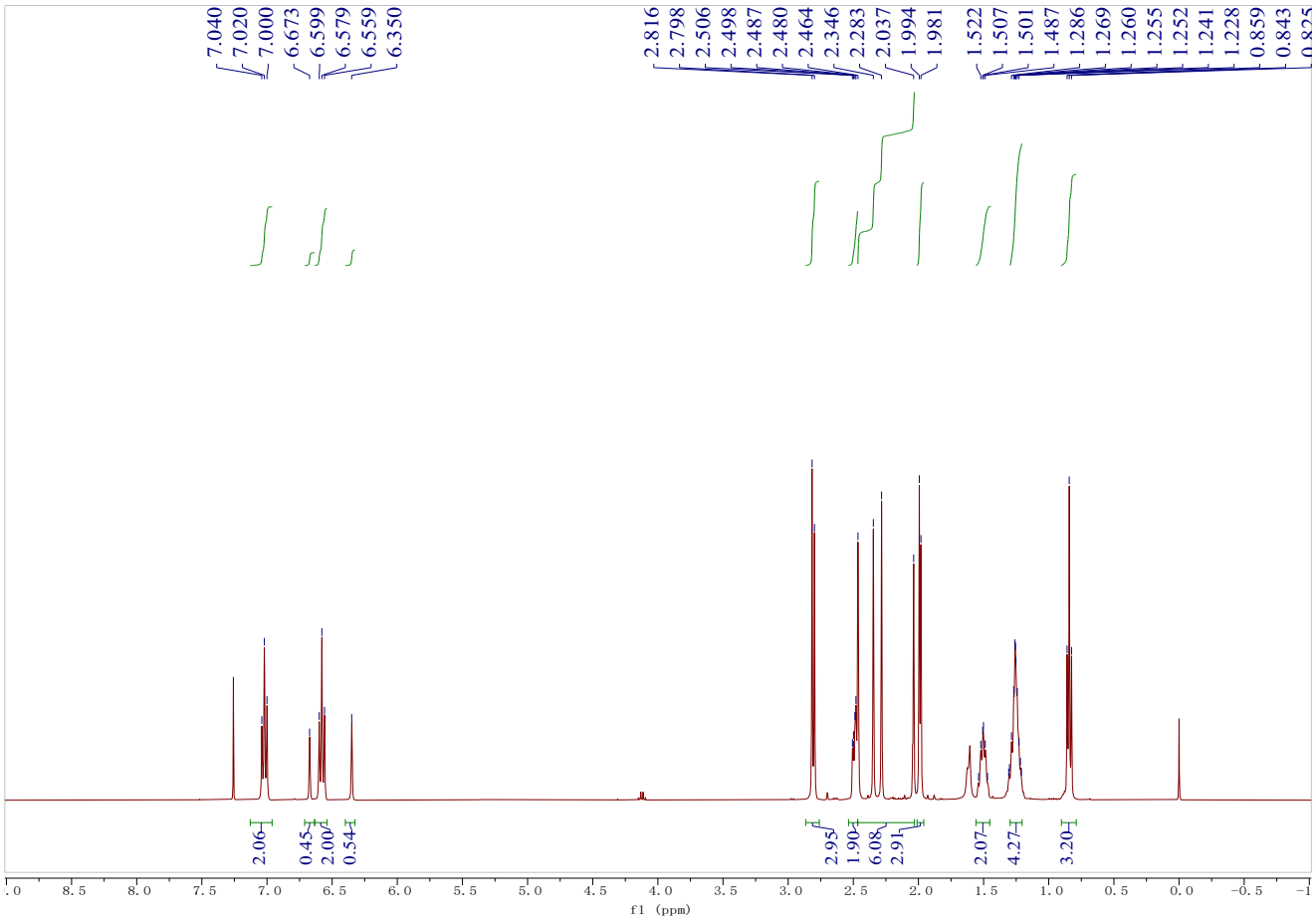
8,^{13}C NMR, 101 MHz, DMSO-d_6



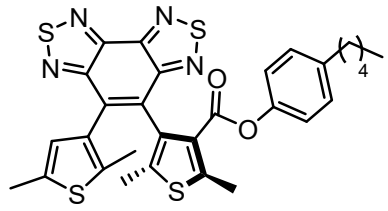


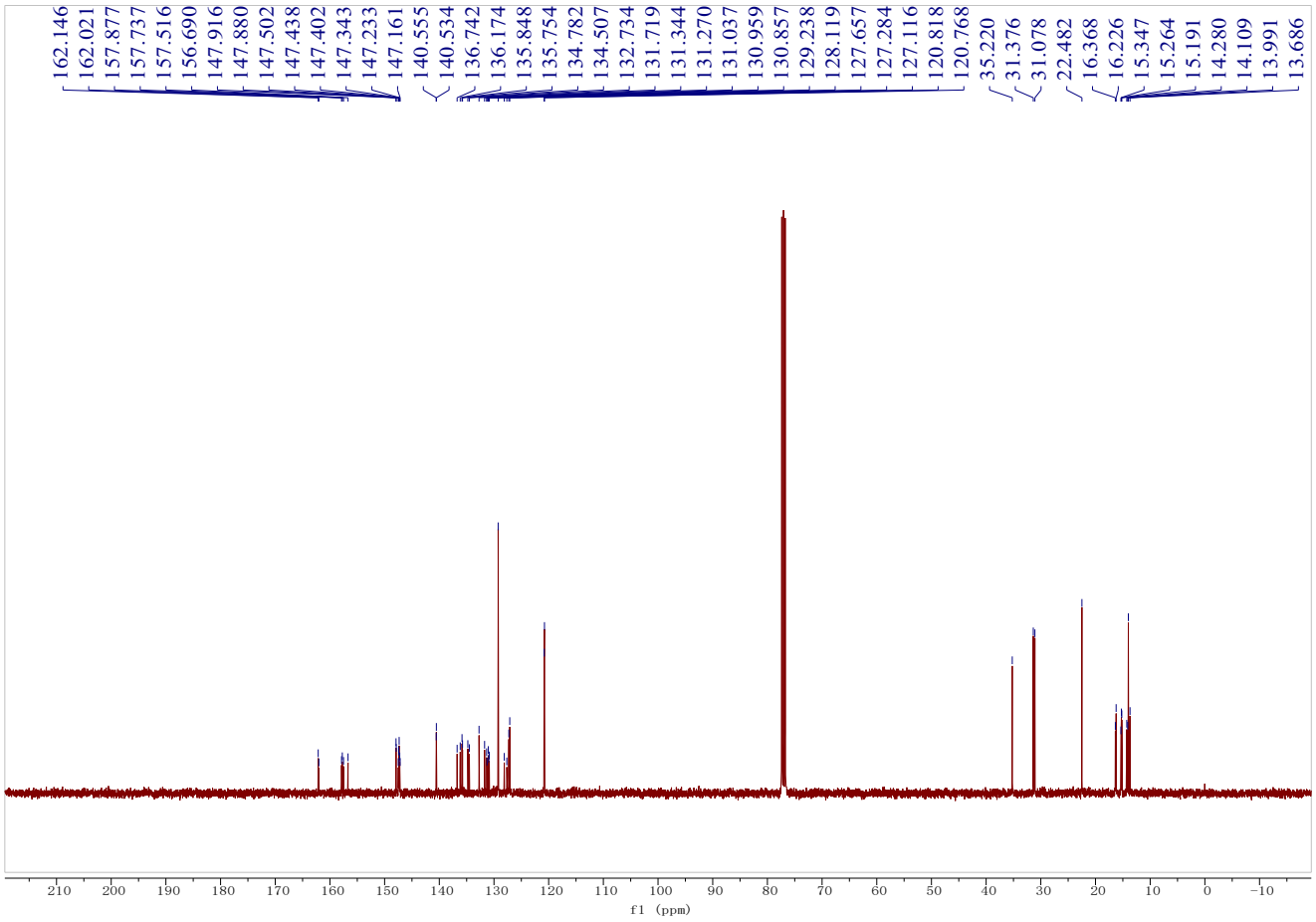
9, ^{1}H NMR, 400 MHz, $CDCl_3$



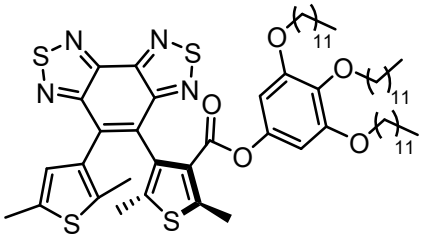


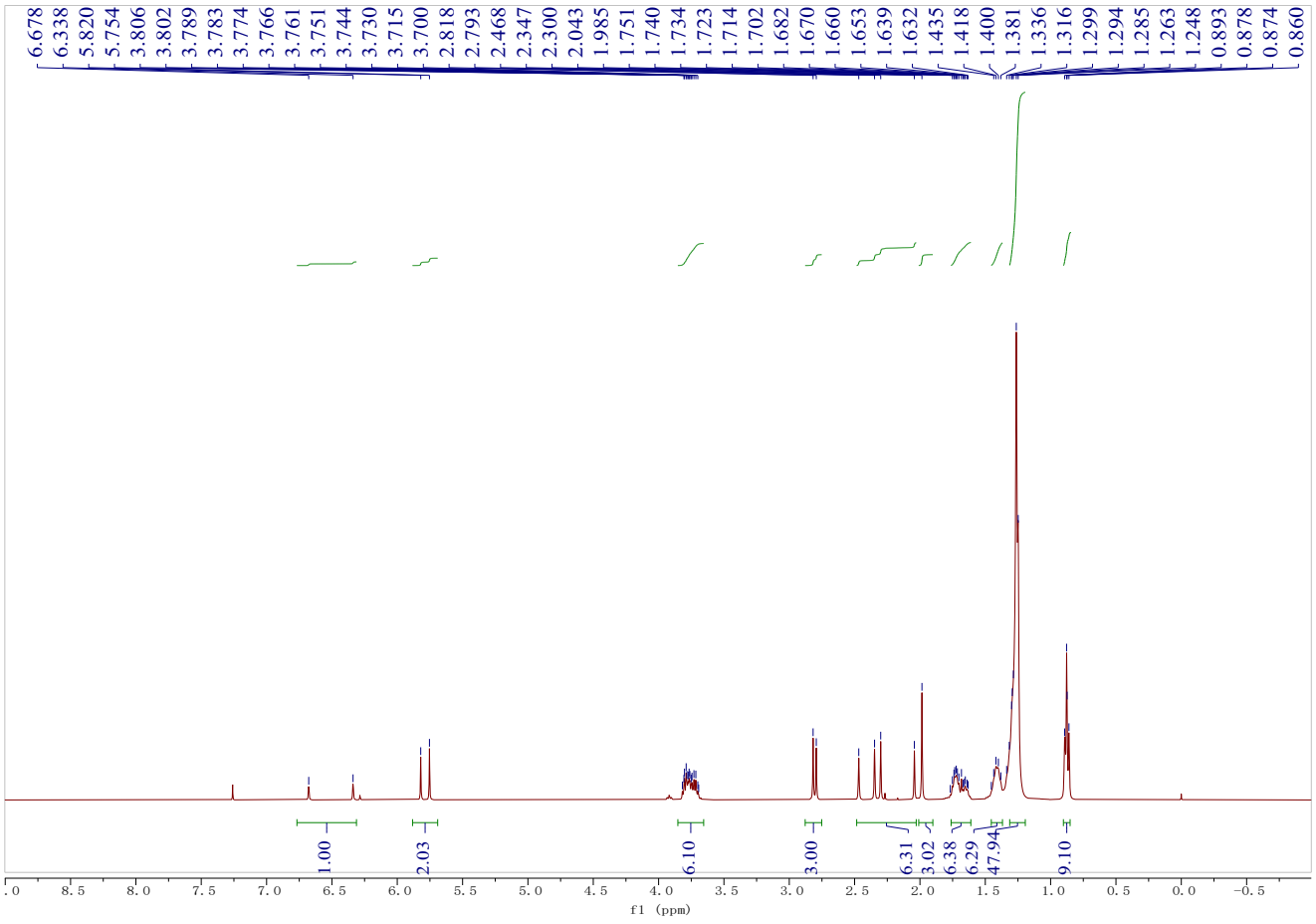
9,^{13}C NMR, 101 MHz, $CDCl_3$



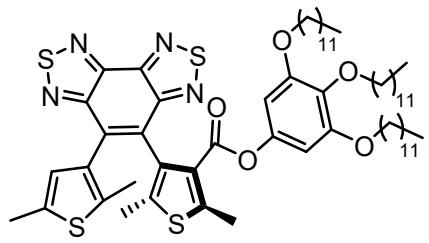


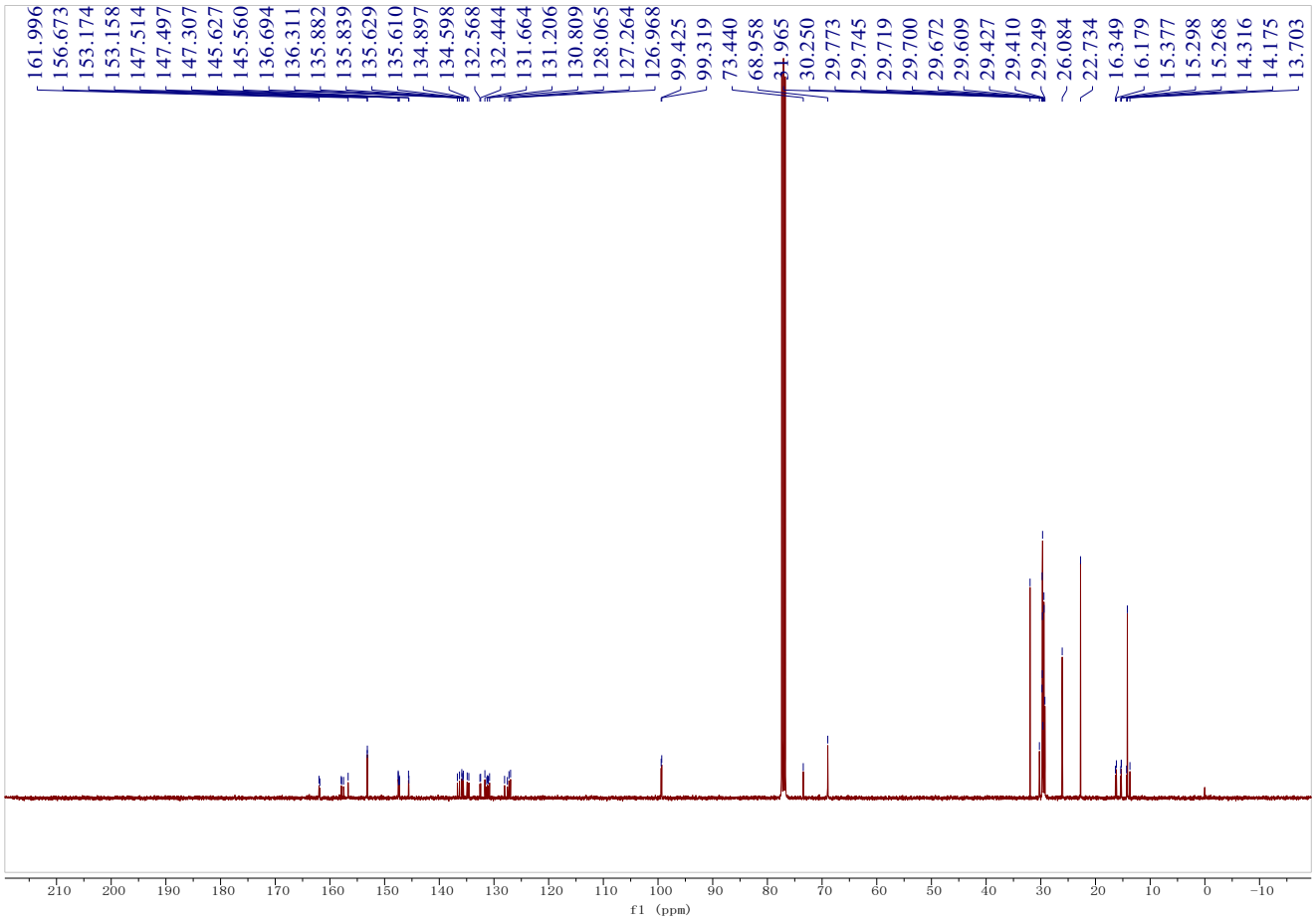
10, ^{1}H NMR, 400 MHz, $CDCl_3$



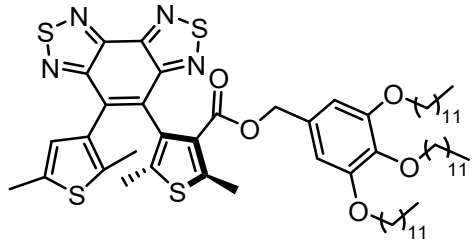


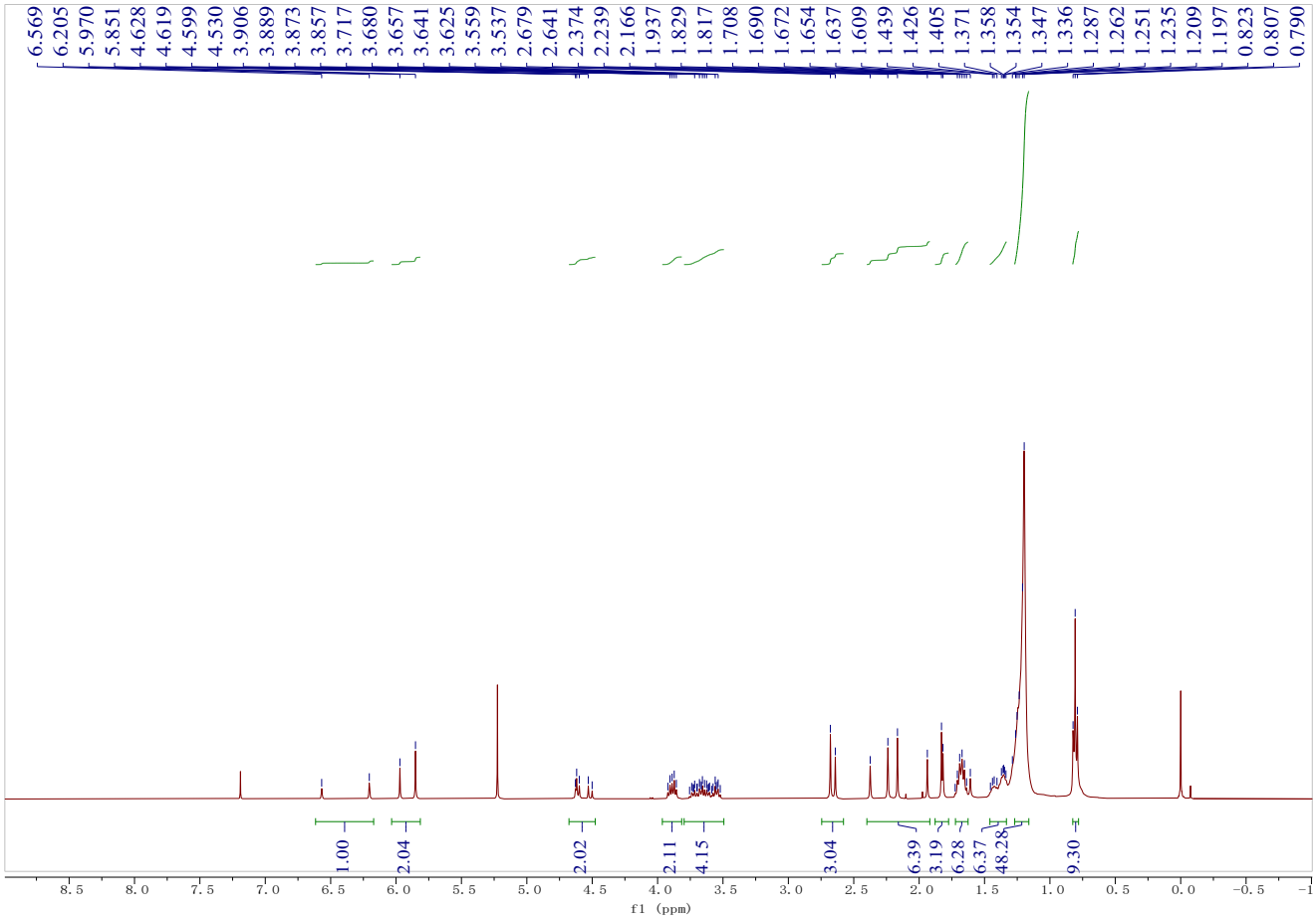
10,^{13}C NMR, 101 MHz, $CDCl_3$



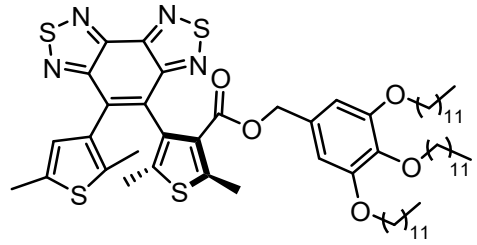


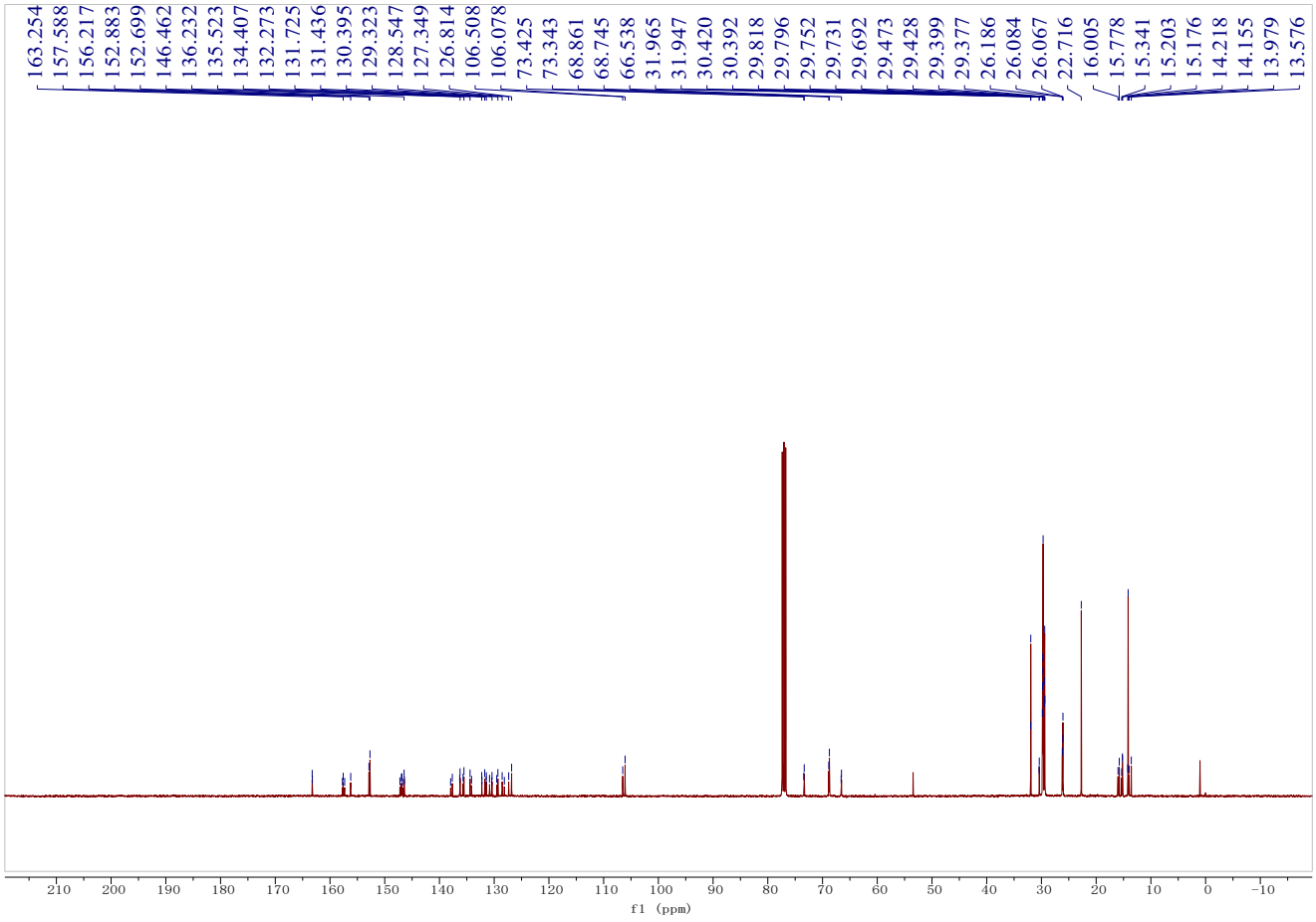
11, ^{1}H NMR, 400 MHz, $CDCl_3$



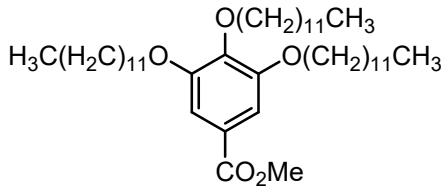


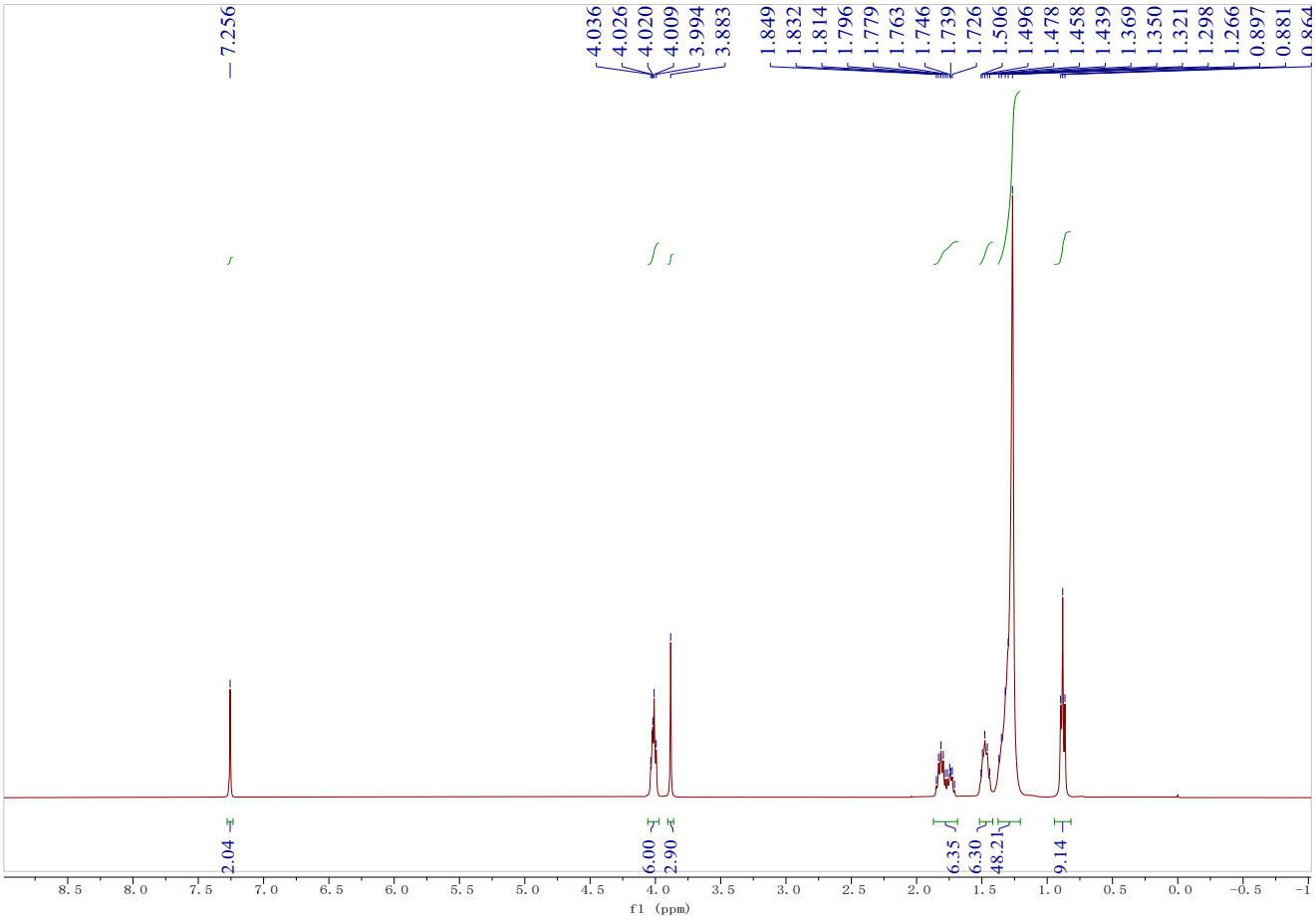
11,^{13}C NMR, 101 MHz, $CDCl_3$



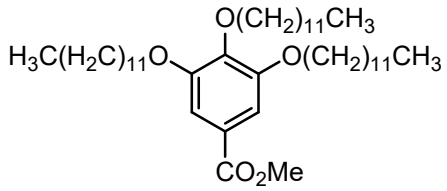


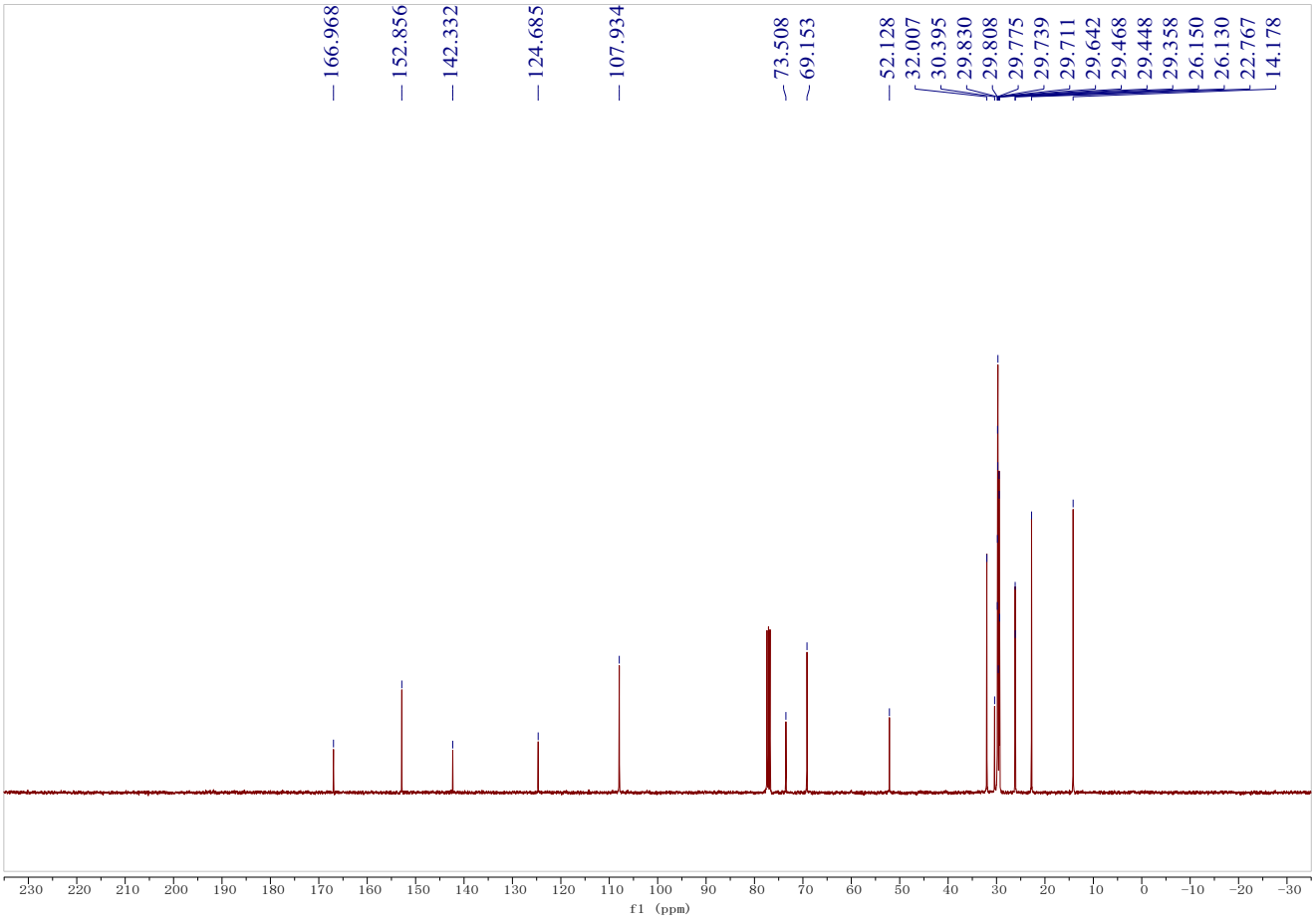
13, ^{1}H NMR, 400 MHz, $CDCl_3$



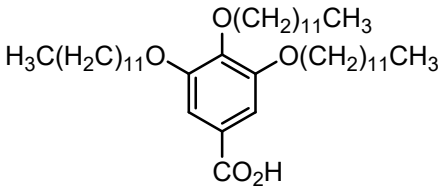


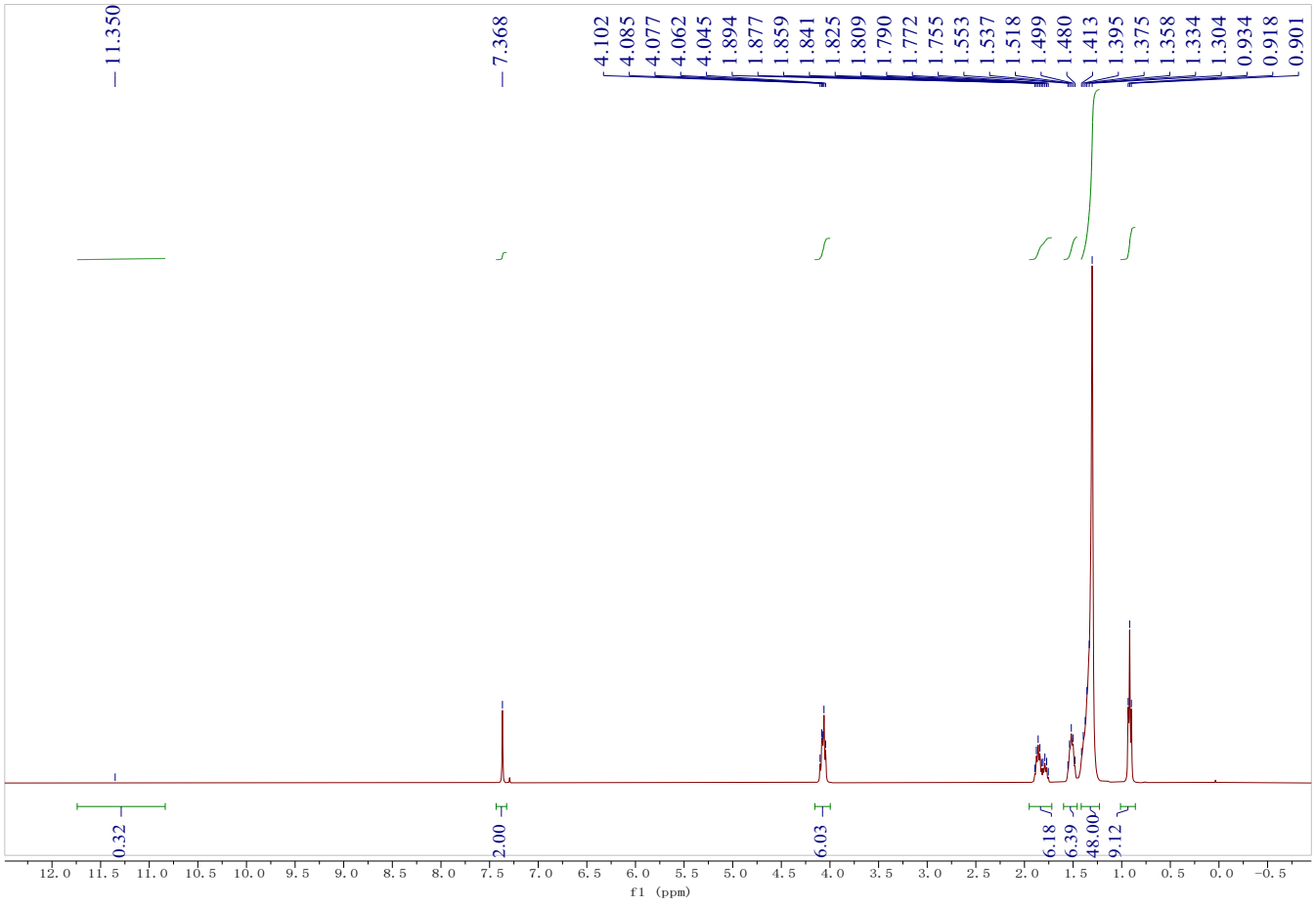
13,^{13}C NMR, 101 MHz, $CDCl_3$



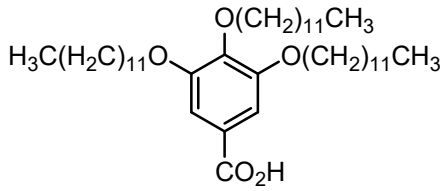


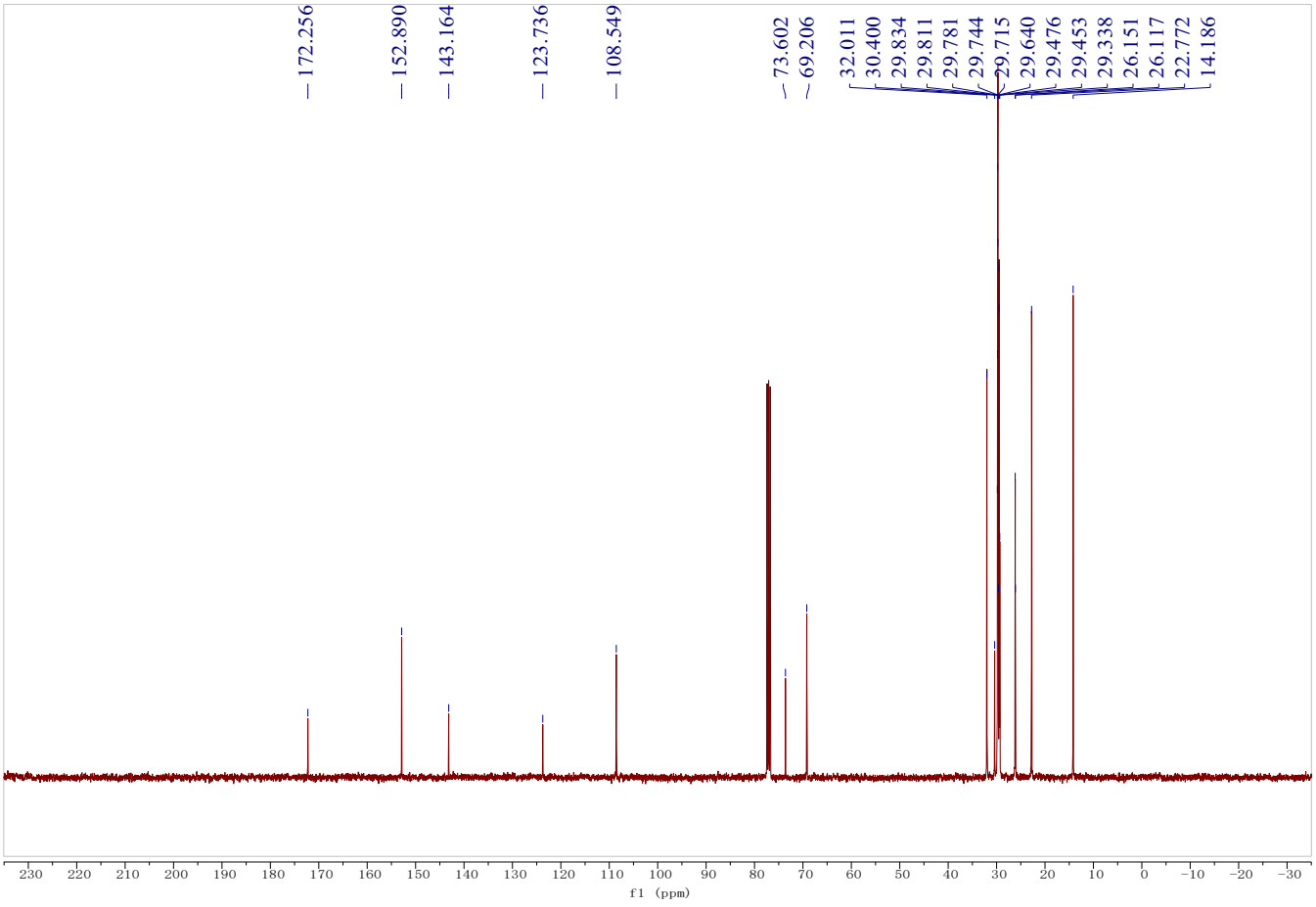
14, ^{1}H NMR, 400 MHz, $CDCl_3$



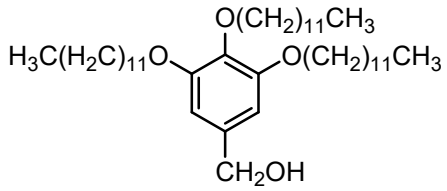


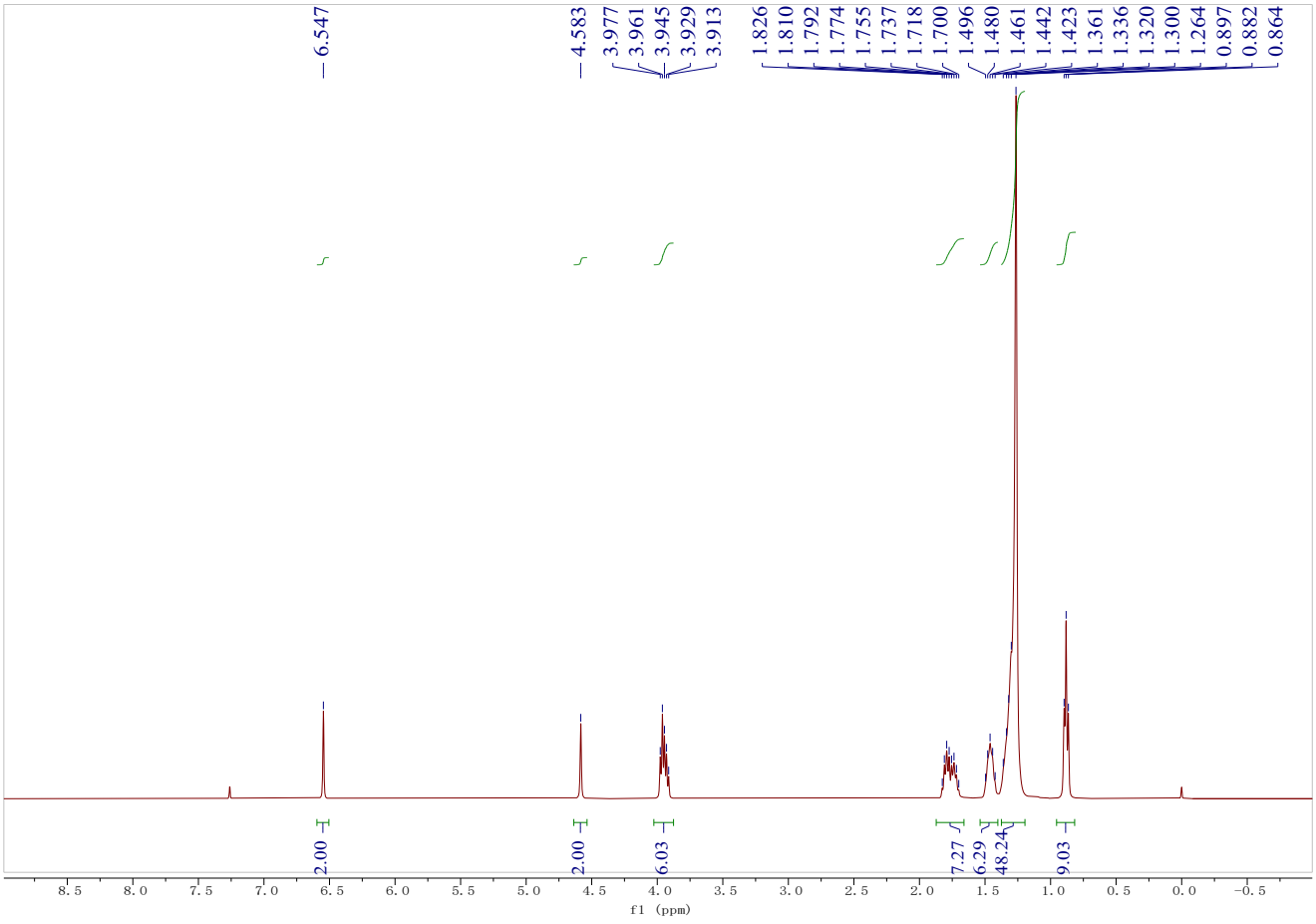
14,^{13}C NMR, 101 MHz, $CDCl_3$



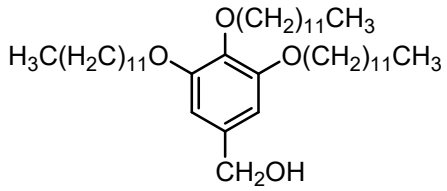


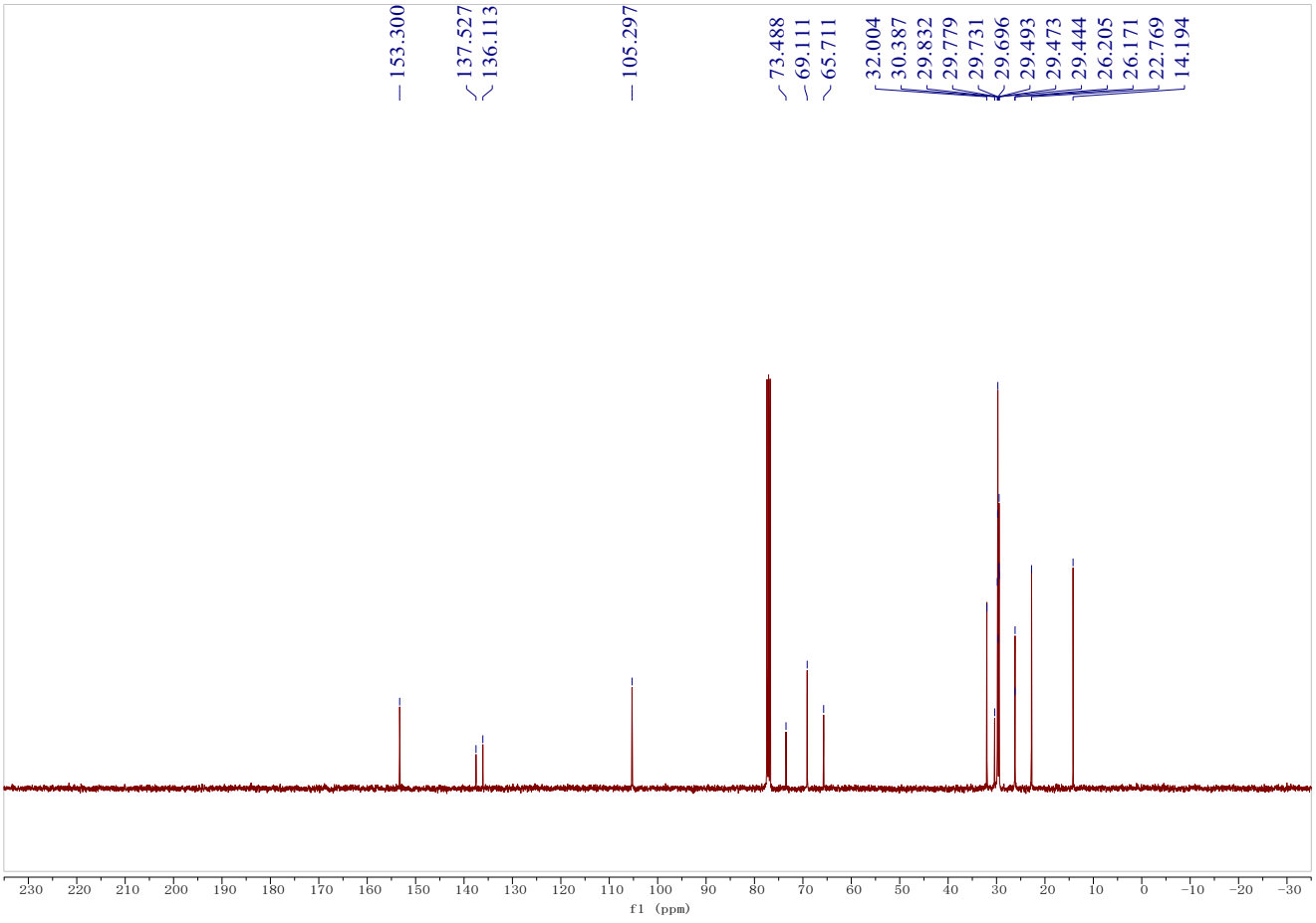
15, ^{1}H NMR, 400 MHz, $CDCl_3$



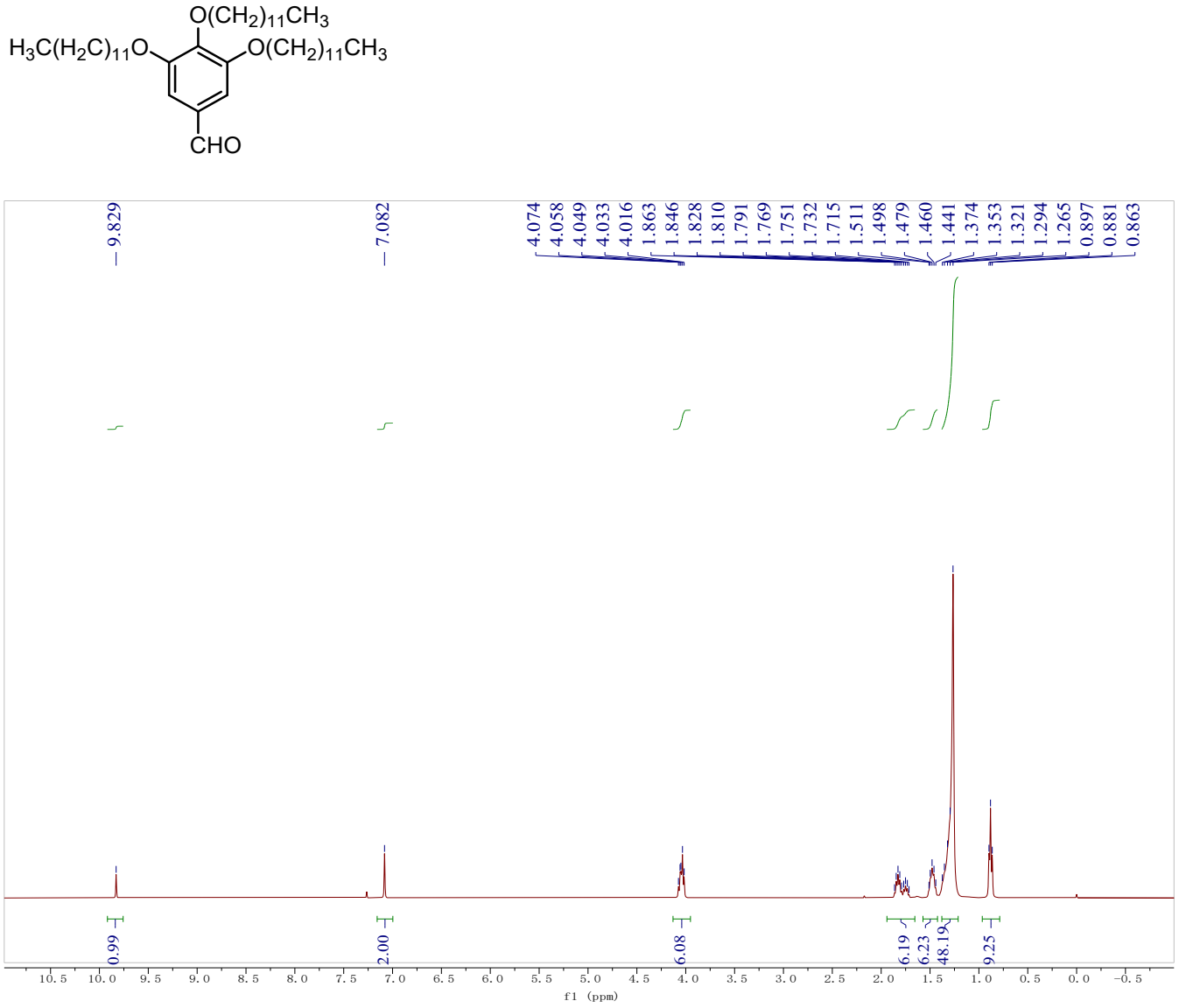


15,^{13}C NMR, 101 MHz, $CDCl_3$

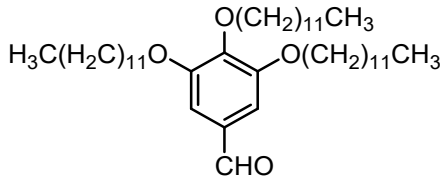


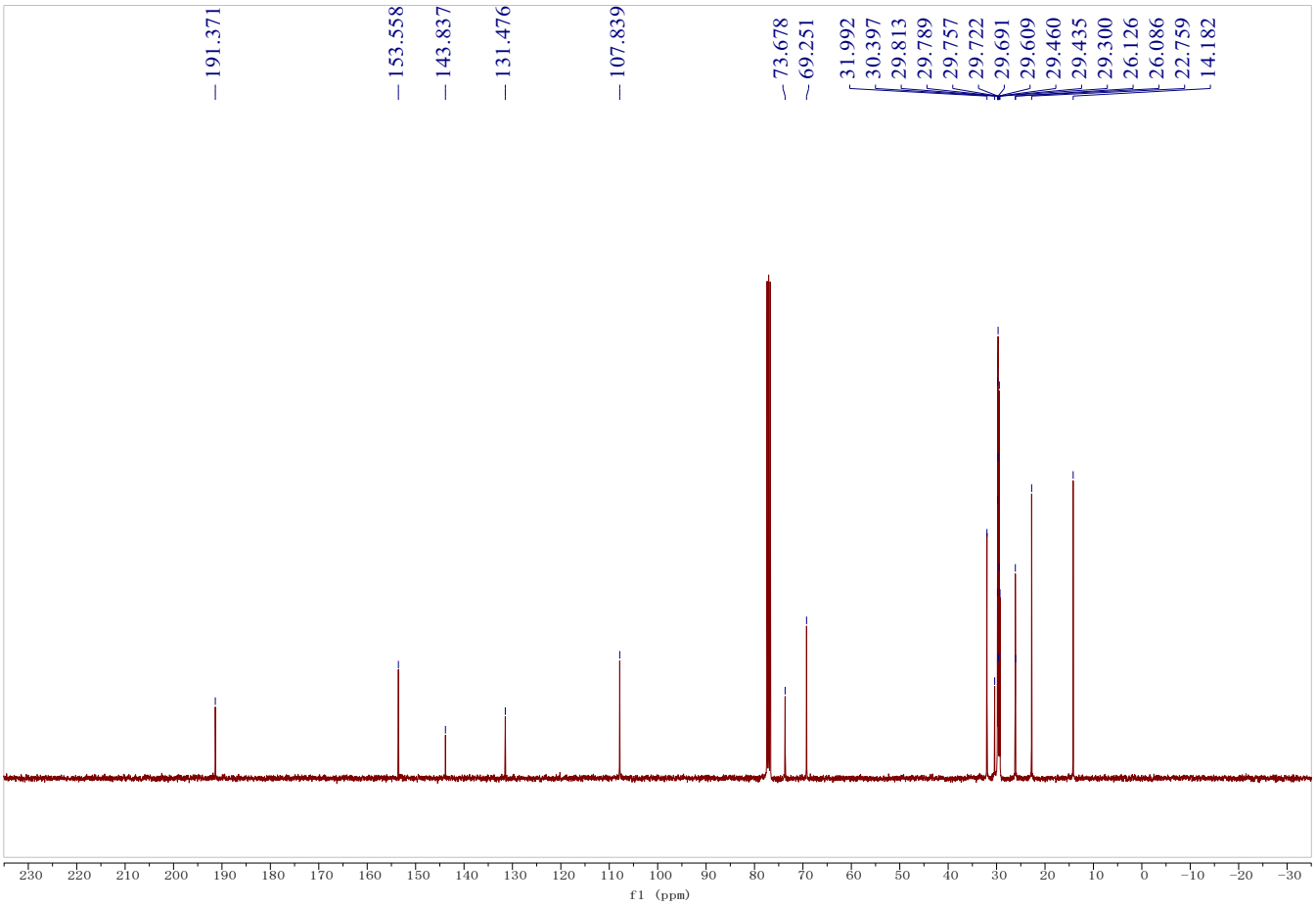


17, ^{1}H NMR, 400 MHz, $CDCl_3$

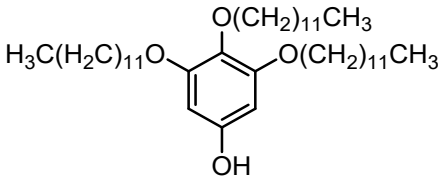


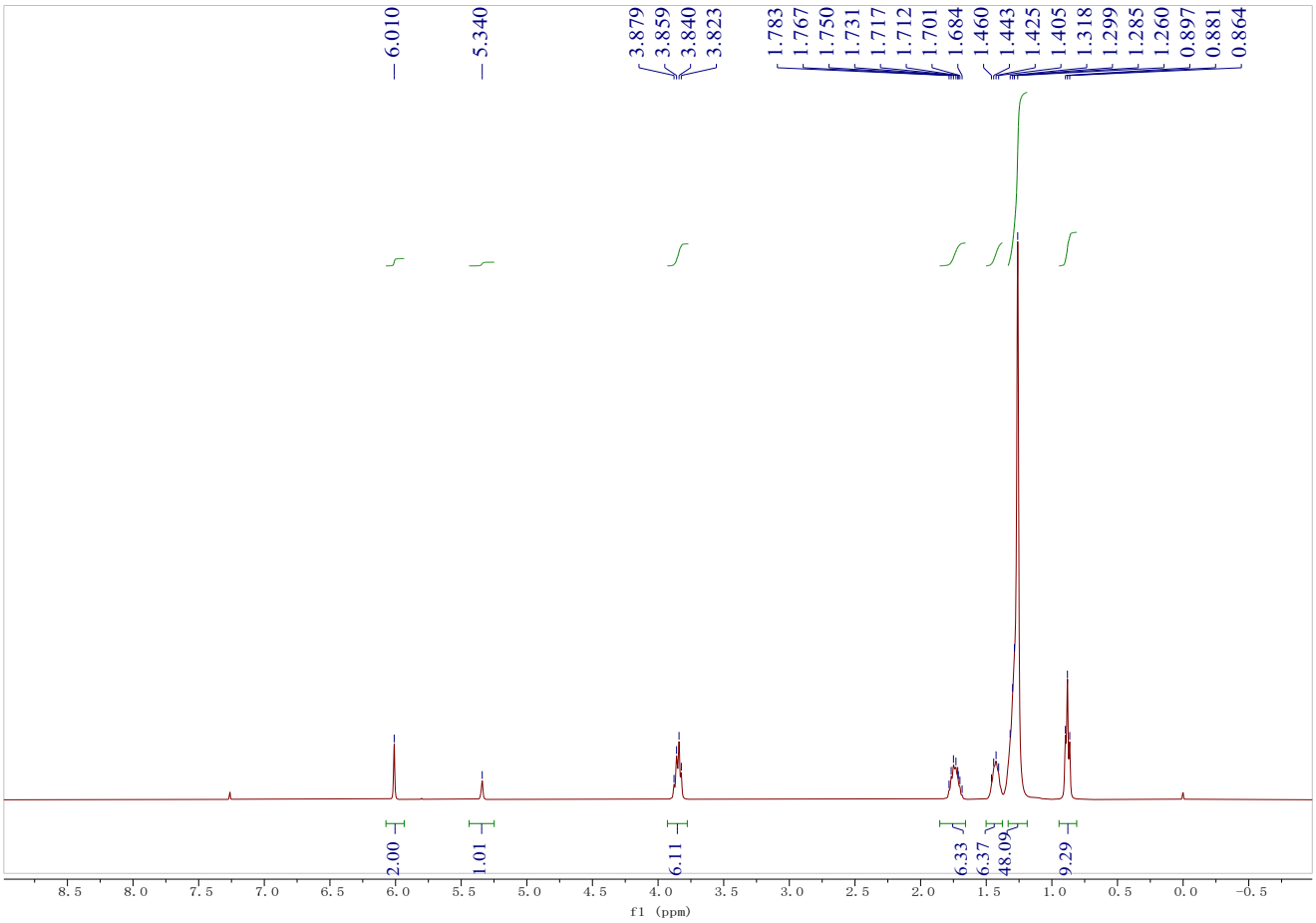
17,^{13}C NMR, 101 MHz, $CDCl_3$



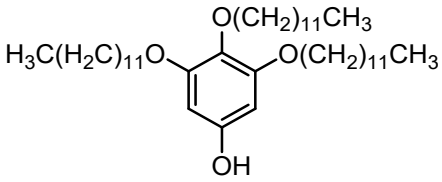


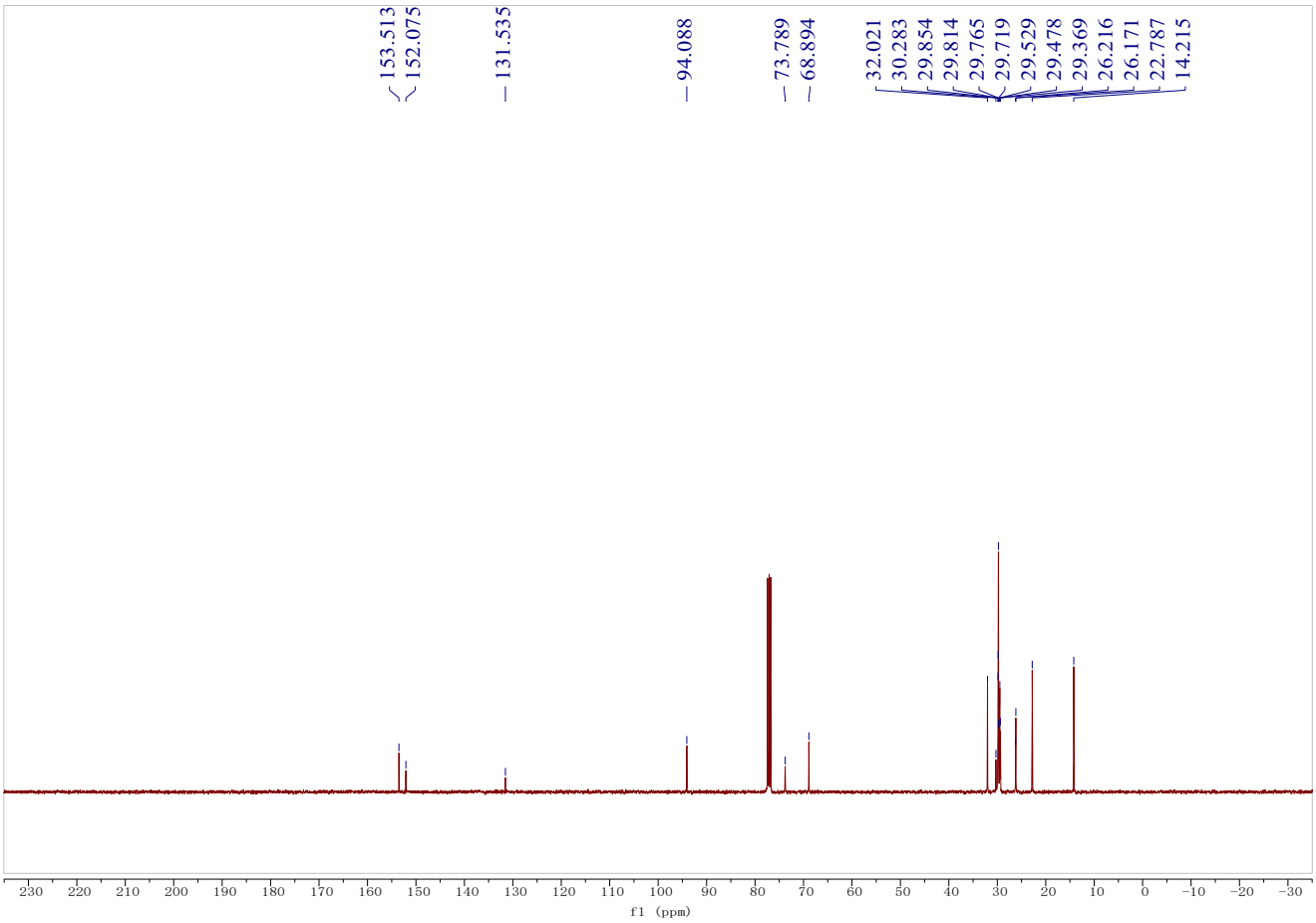
19, ^{1}H NMR, 400 MHz, $CDCl_3$





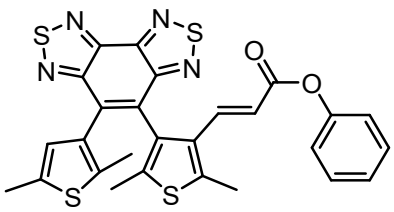
19,^{13}C NMR, 101 MHz, $CDCl_3$



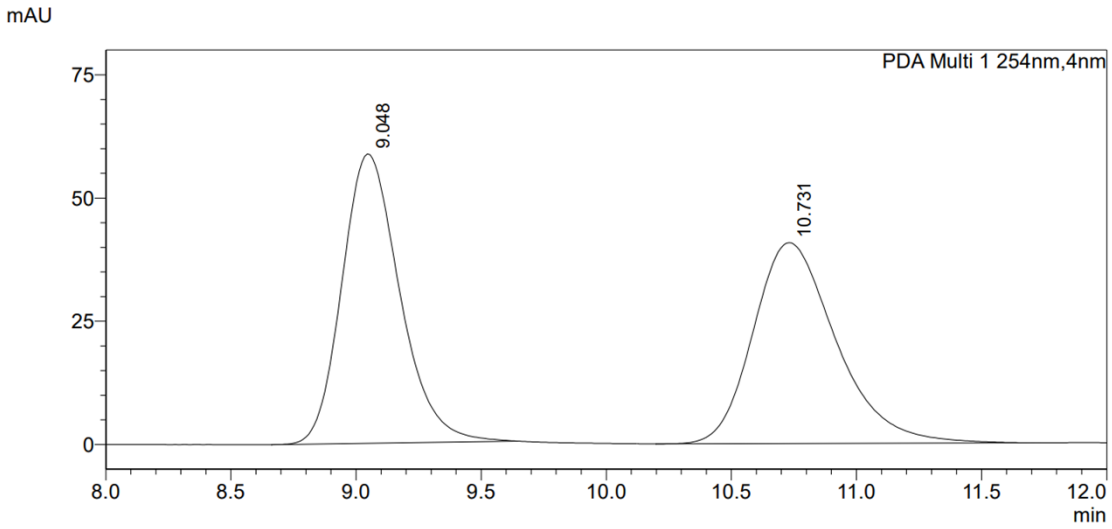


9. HPLC Charts

3a: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



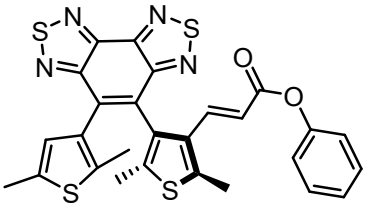
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.048	942165	58655	50.071
2	10.731	939498	40745	49.929
Total		1881663	99400	100.000



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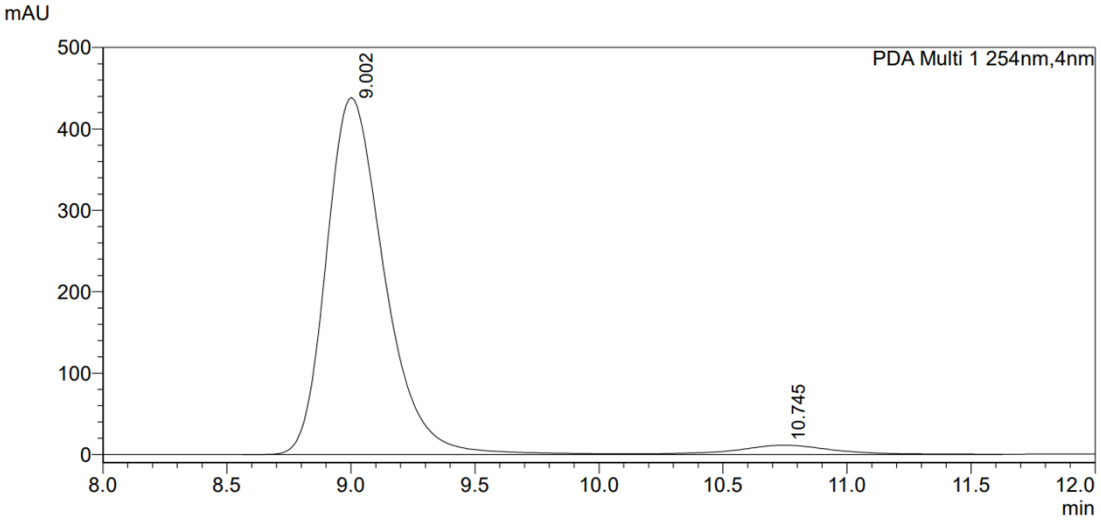
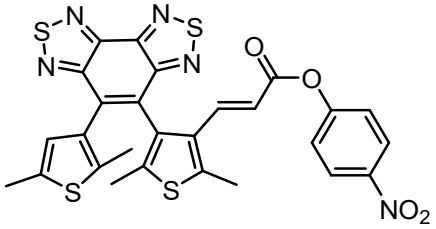


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.002	7121299	438560	95.649
2	10.745	323968	11437	4.351
Total		7445267	449997	100.000

3b: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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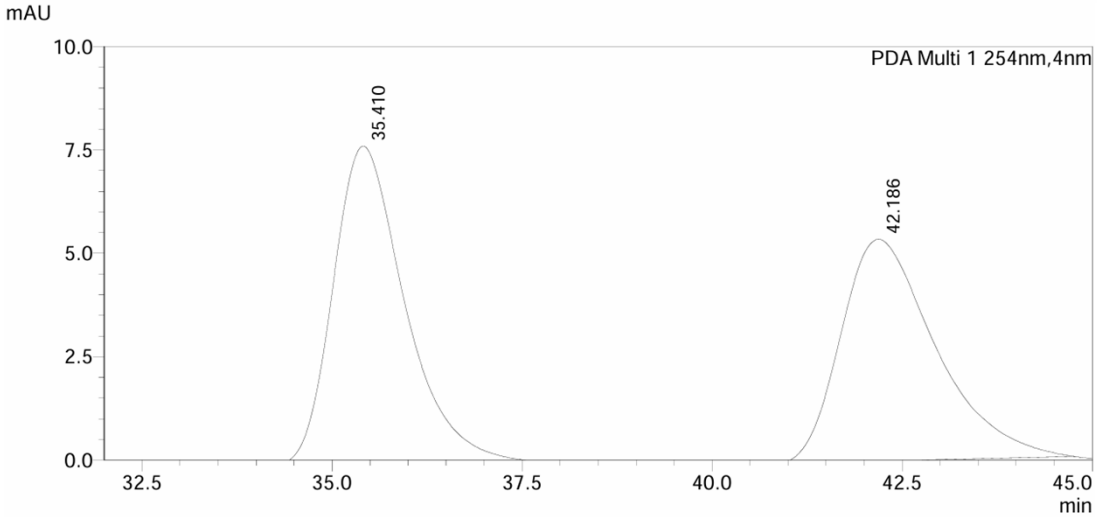
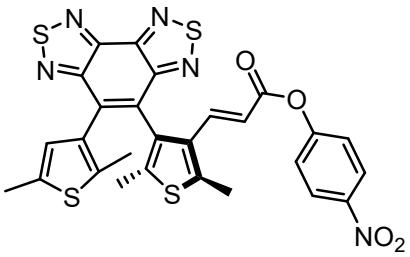


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	35.410	501022	7673	51.863
2	42.186	465034	5368	48.137
Total		966056	13041	100.000



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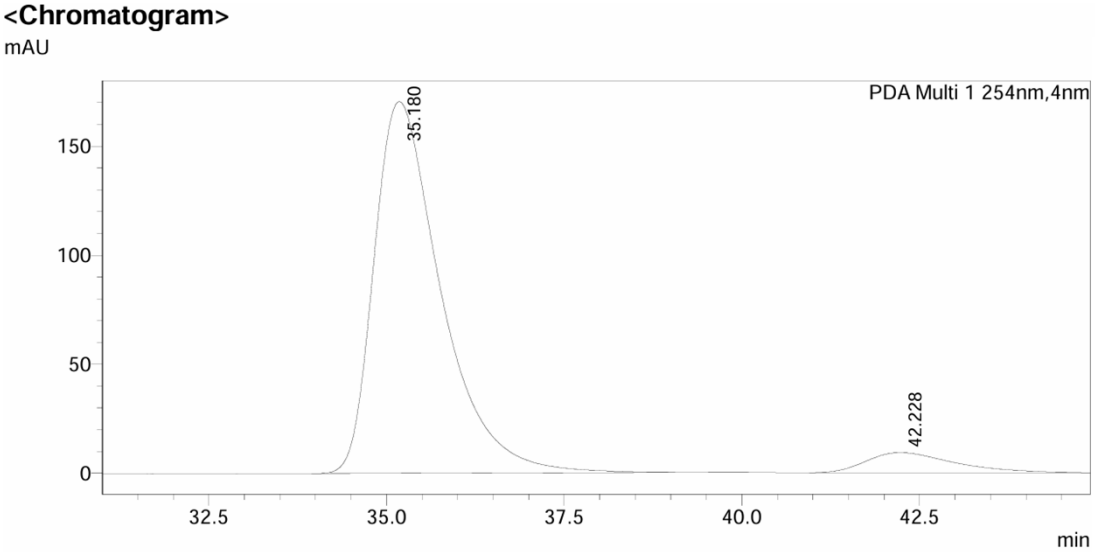
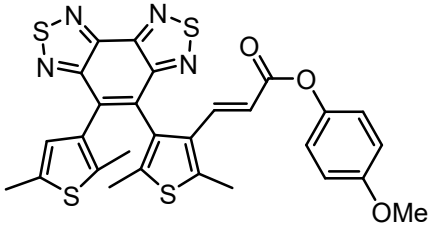


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	35.180	11169174	170491	93.293
2	42.228	802972	9243	6.707
Total		11972146	179734	100.000

3c: IF-3, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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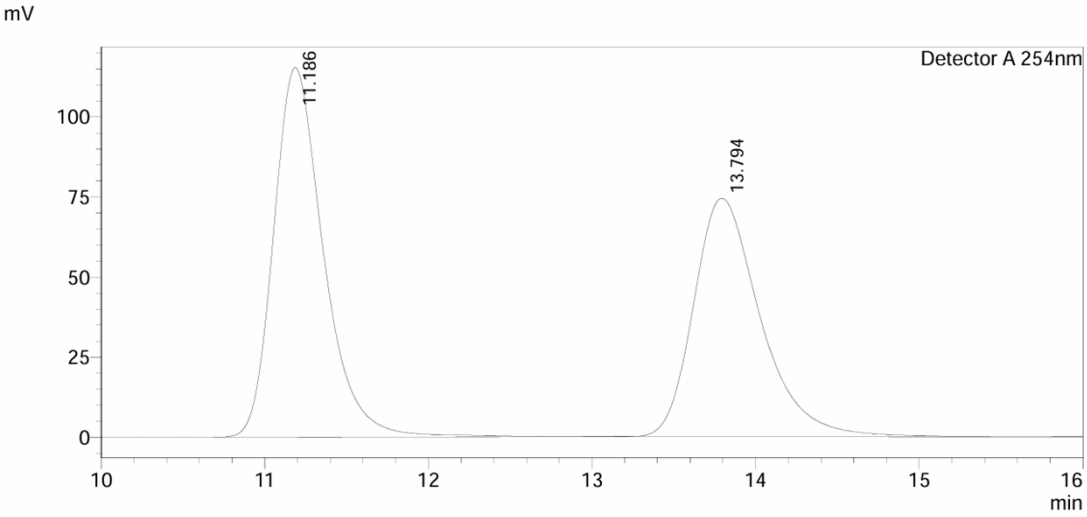
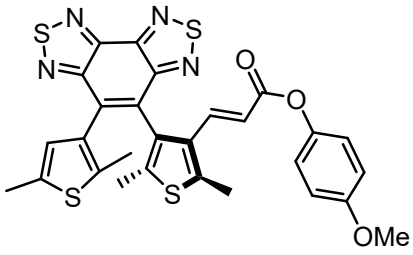


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.186	2449638	115293	53.472
2	13.794	2131520	74453	46.528
Total		4581159	189746	



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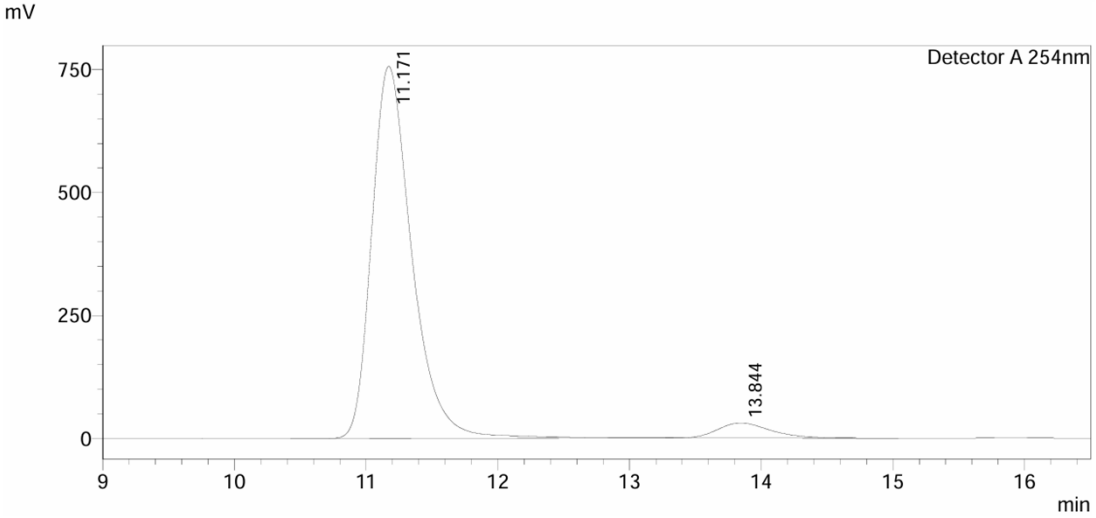
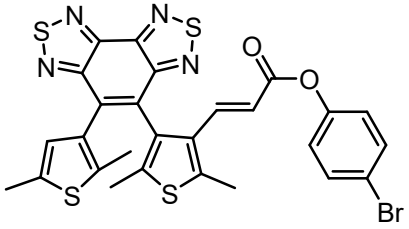


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.171	16017930	756244	94.799
2	13.844	878761	30919	5.201
Total		16896691	787163	

3d: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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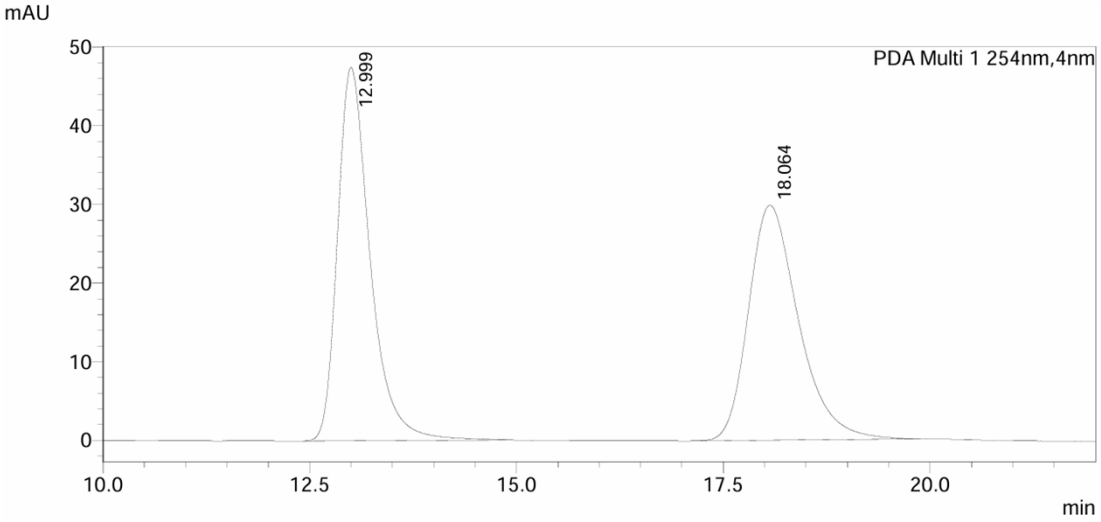
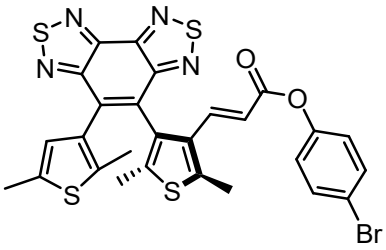


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.999	1302172	47472	50.871
2	18.064	1257582	29873	49.129
Total		2559754	77345	100.000



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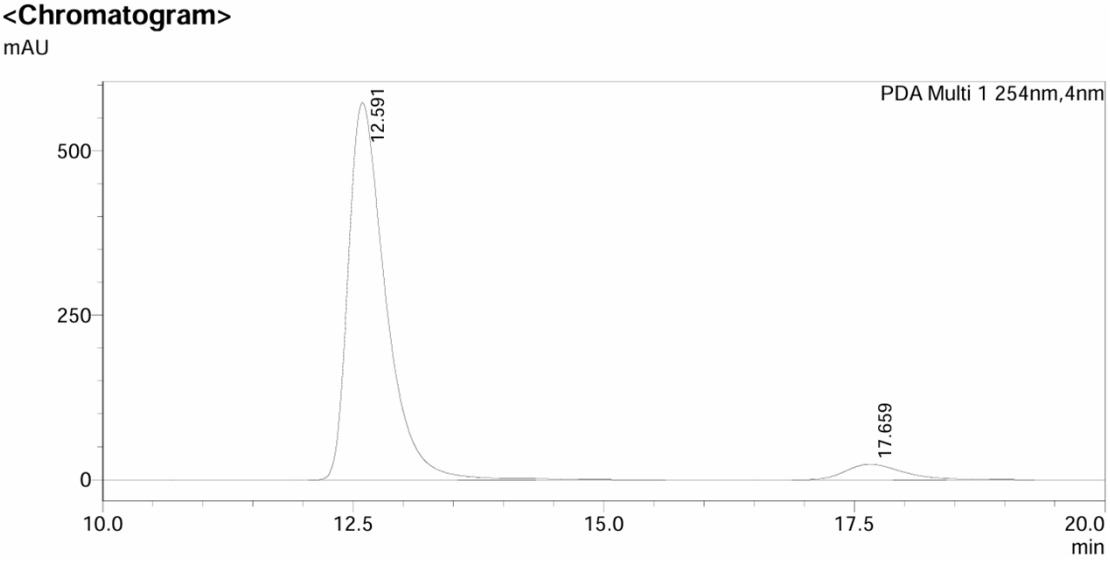
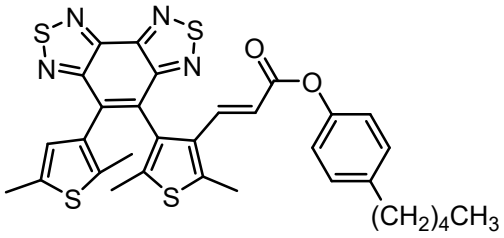


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.591	14876806	573440	93.942
2	17.659	959307	23736	6.058
Total		15836113	597176	100.000

3e: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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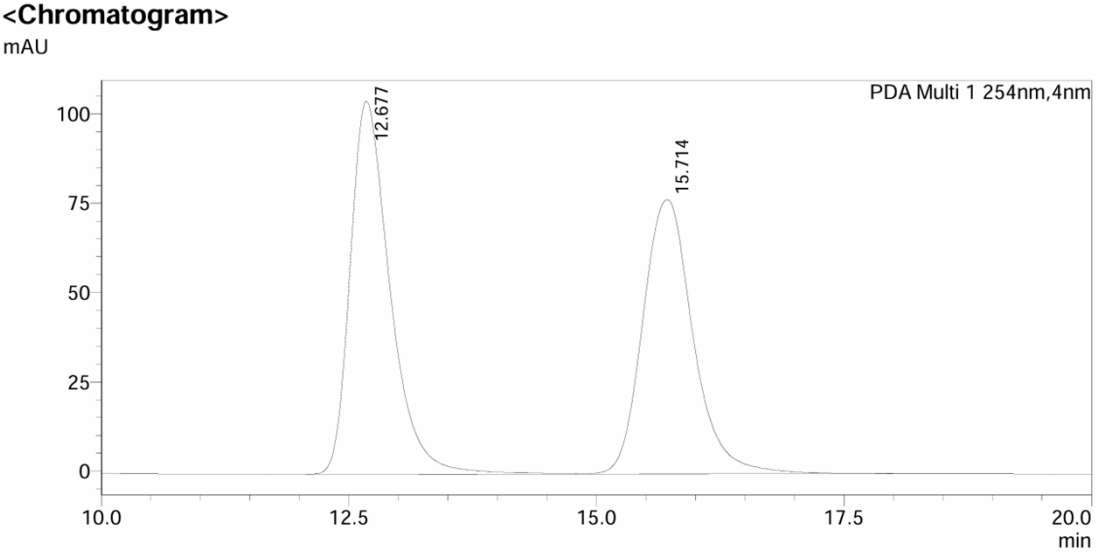
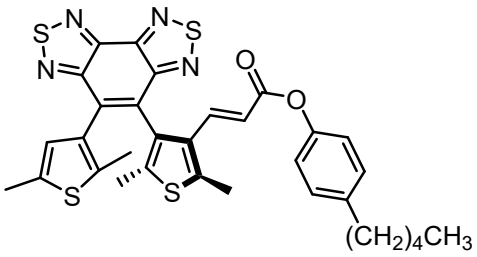


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.677	2928336	104392	51.850
2	15.714	2719408	76798	48.150
Total		5647744	181190	100.000



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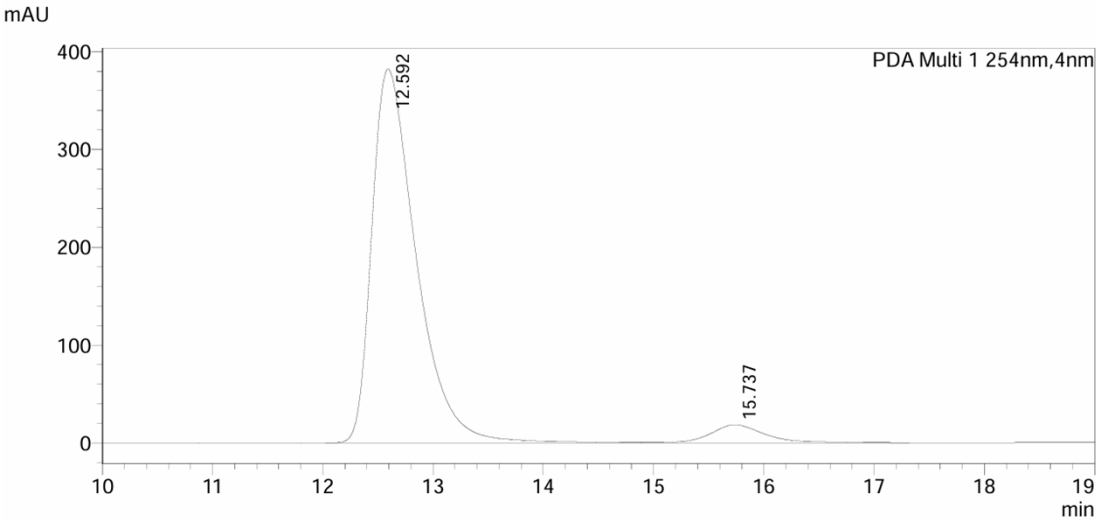
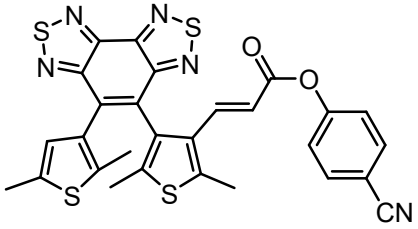


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.592	10675119	382122	94.429
2	15.737	629829	18316	5.571
Total		11304948	400437	100.000

3f: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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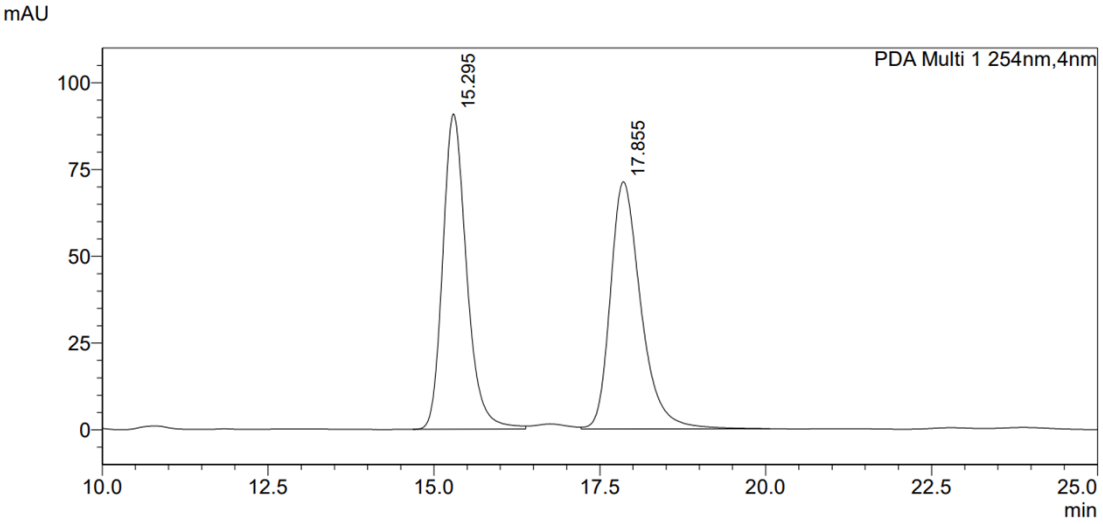
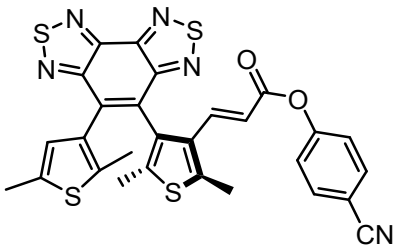


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.295	2270552	90807	49.892
2	17.855	2280380	71190	50.108
Total		4550932	161997	100.000



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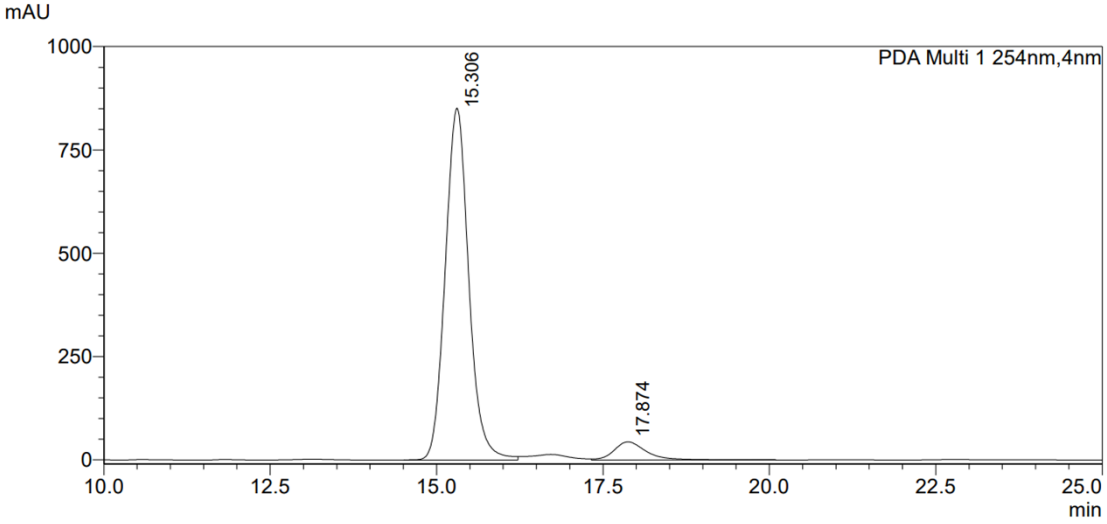
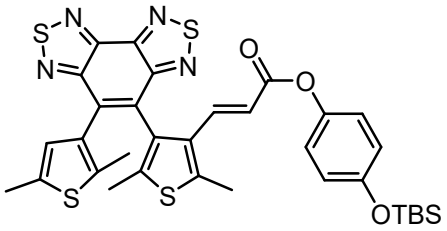


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.306	20933276	851157	93.419
2	17.874	1474598	43767	6.581
Total		22407873	894924	100.000

3g: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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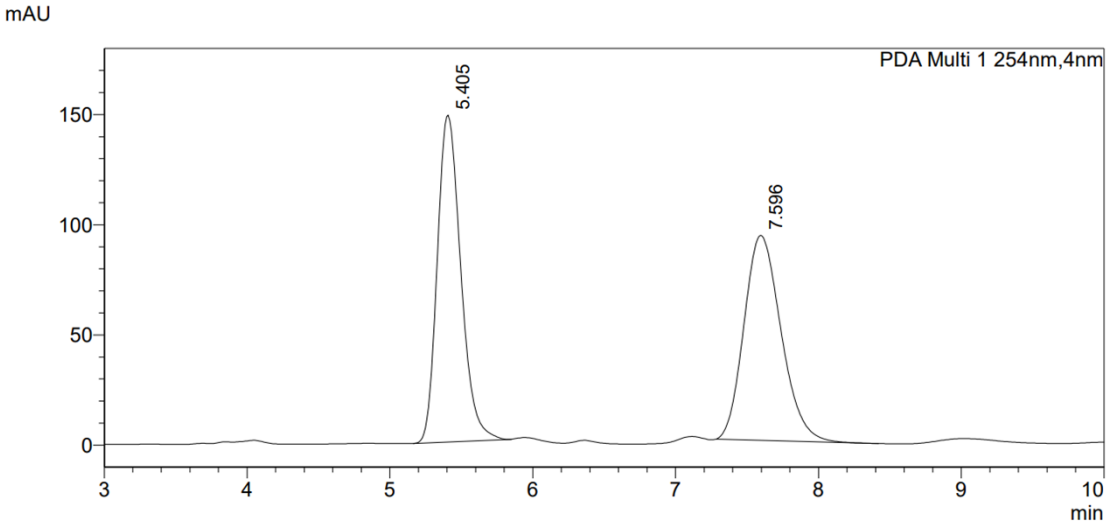
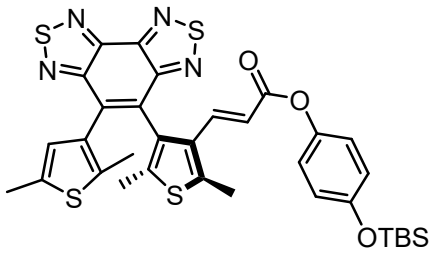


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.405	1697497	148354	50.325
2	7.596	1675591	93012	49.675
Total		3373088	241366	100.000



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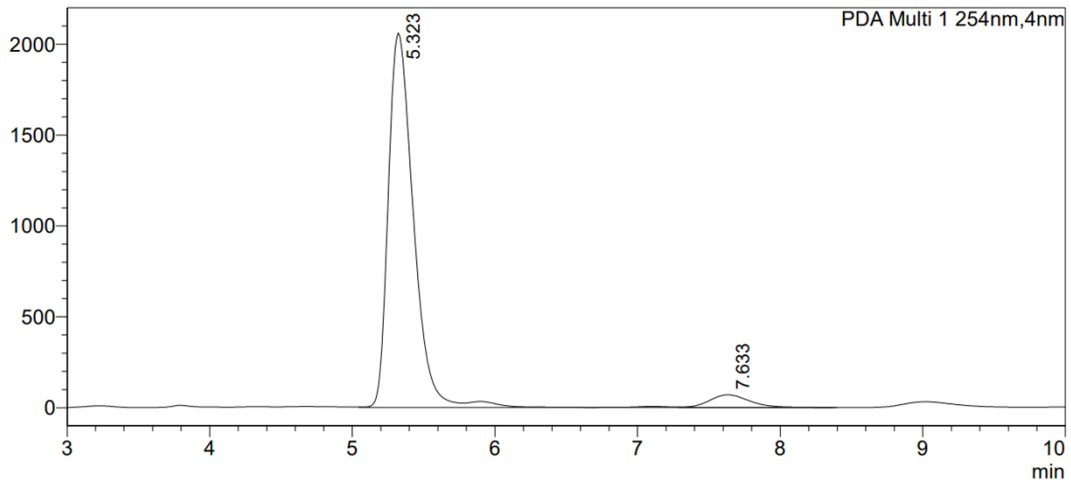
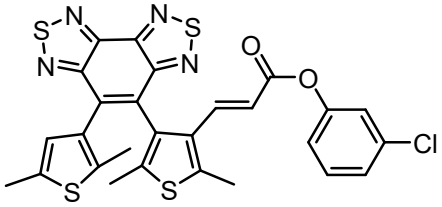


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.323	25528969	2060232	94.996
2	7.633	1344707	69379	5.004
Total		26873676	2129611	100.000

3h: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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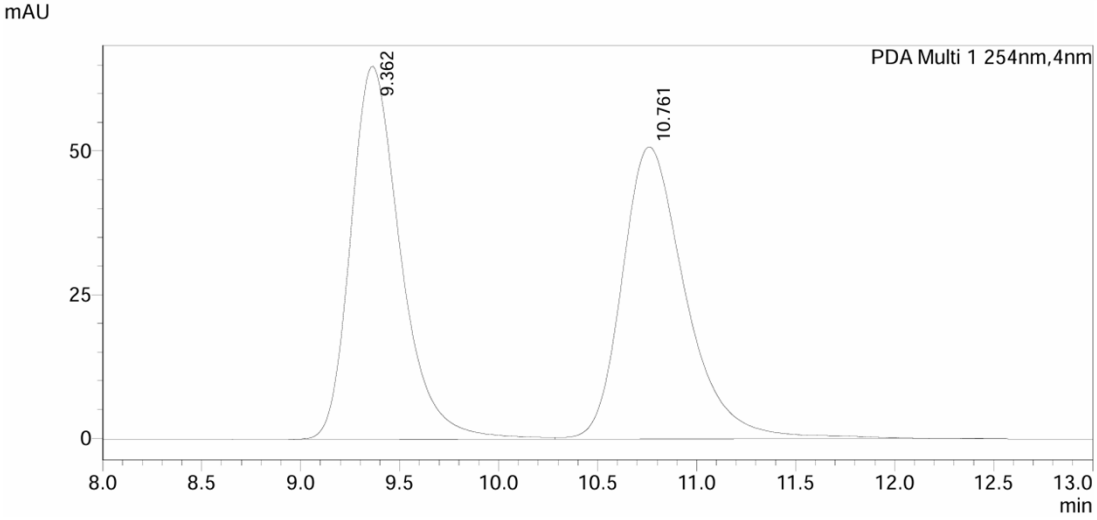
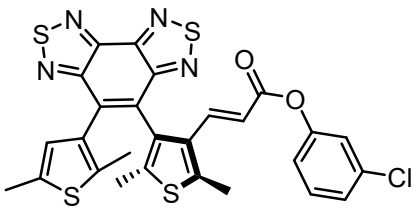


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.362	1136200	64908	49.889
2	10.761	1141252	50879	50.111
Total		2277452	115786	100.000



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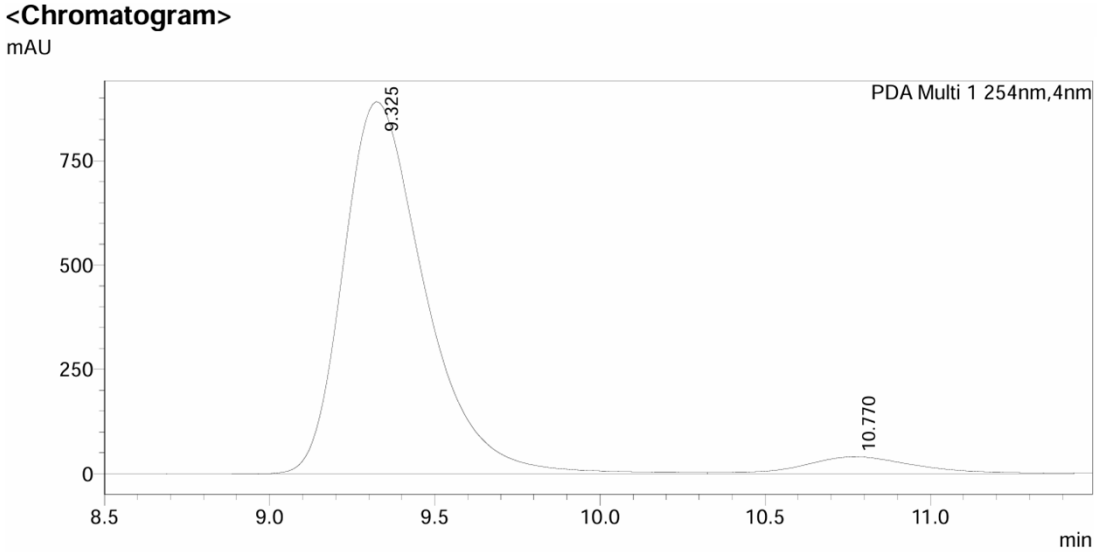
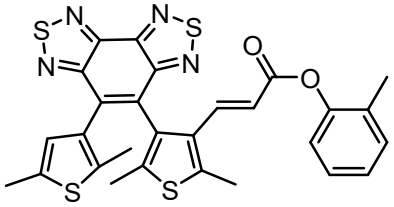


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.325	15274658	891281	94.084
2	10.770	960533	40618	5.916
Total		16235191	931899	100.000

3i: IBN-5, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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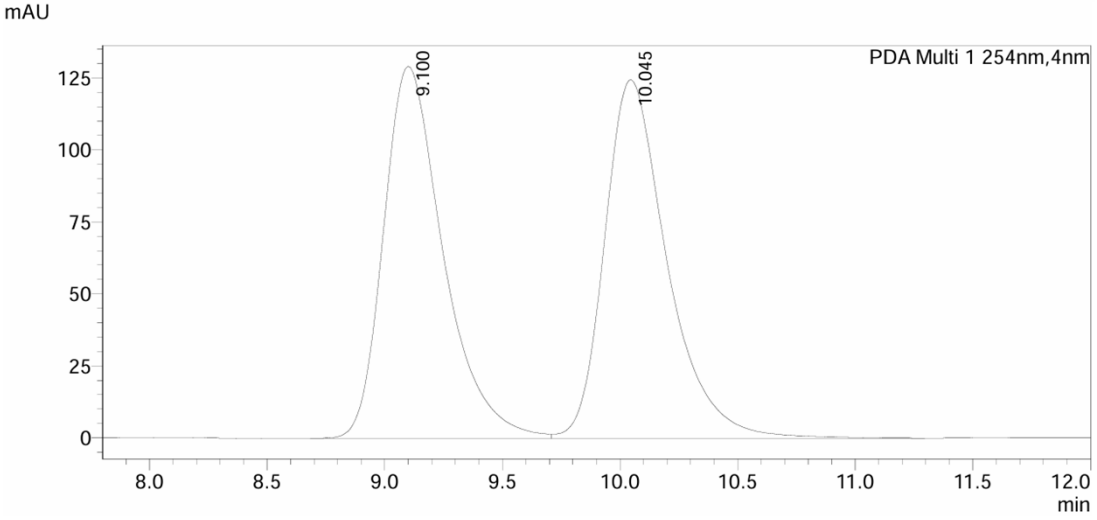
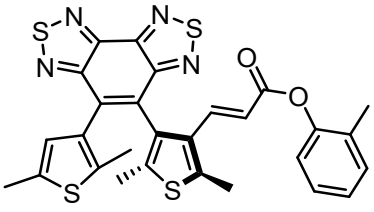


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.100	2275026	129158	49.699
2	10.045	2302580	124517	50.301
Total		4577606	253675	100.000



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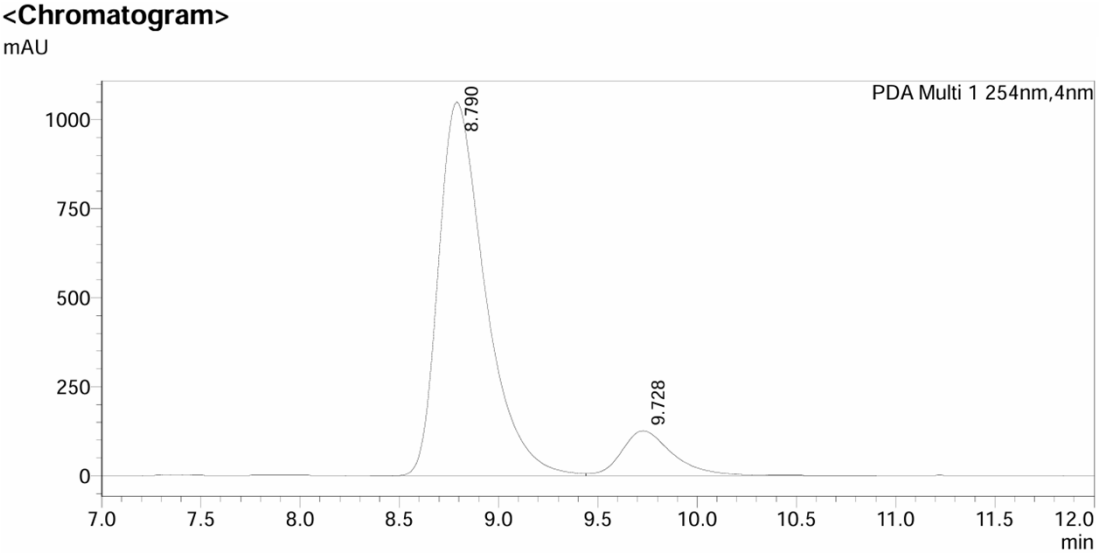
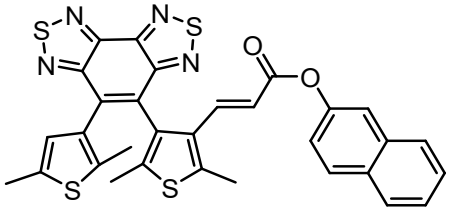


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.790	17144496	1050333	88.275
2	9.728	2277143	126241	11.725
Total		19421639	1176573	100.000

3j: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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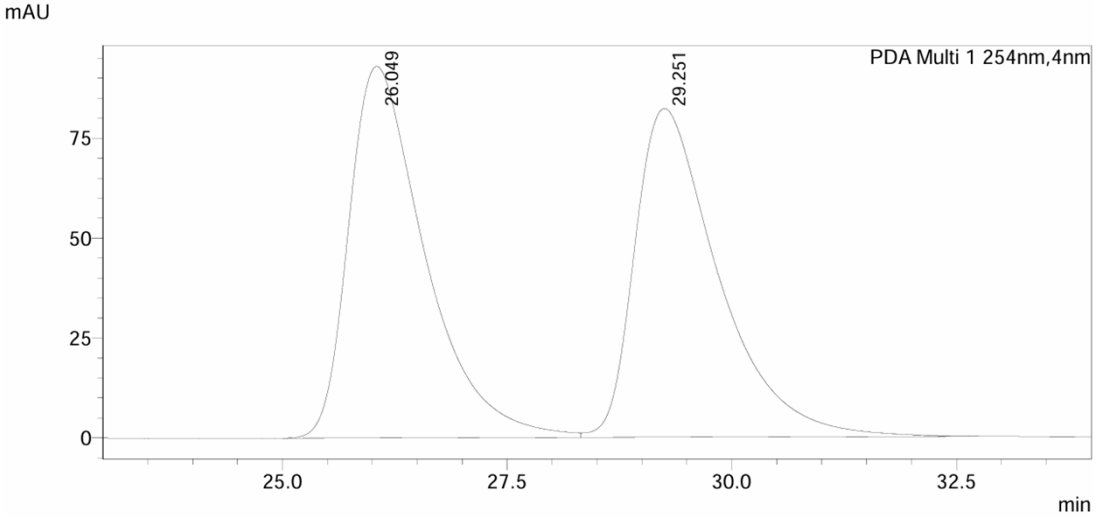
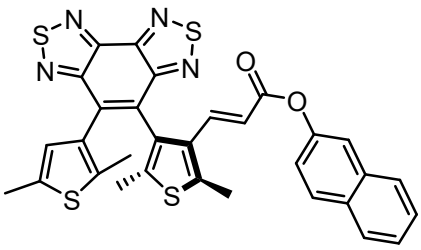


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.049	5495915	93036	50.715
2	29.251	5340845	82270	49.285
Total		10836761	175306	100.000



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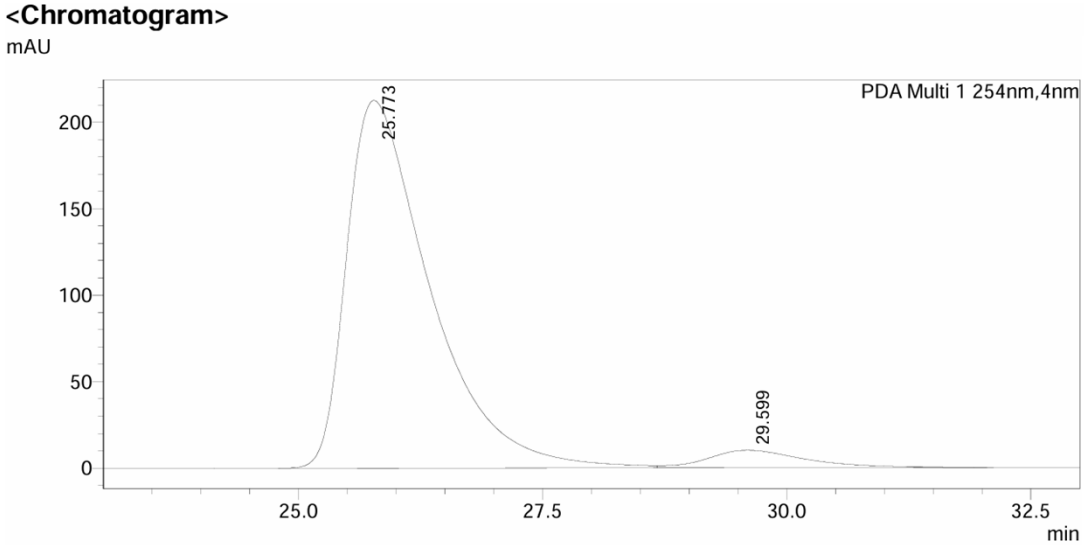
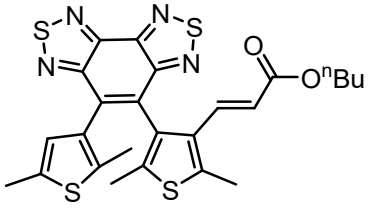


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	25.773	12658764	212739	94.699
2	29.599	708618	10194	5.301
Total		13367382	222932	100.000

3k: IF-3, Hex/iPrOH=95/5, rate=1.000 mL/min, 254 nm



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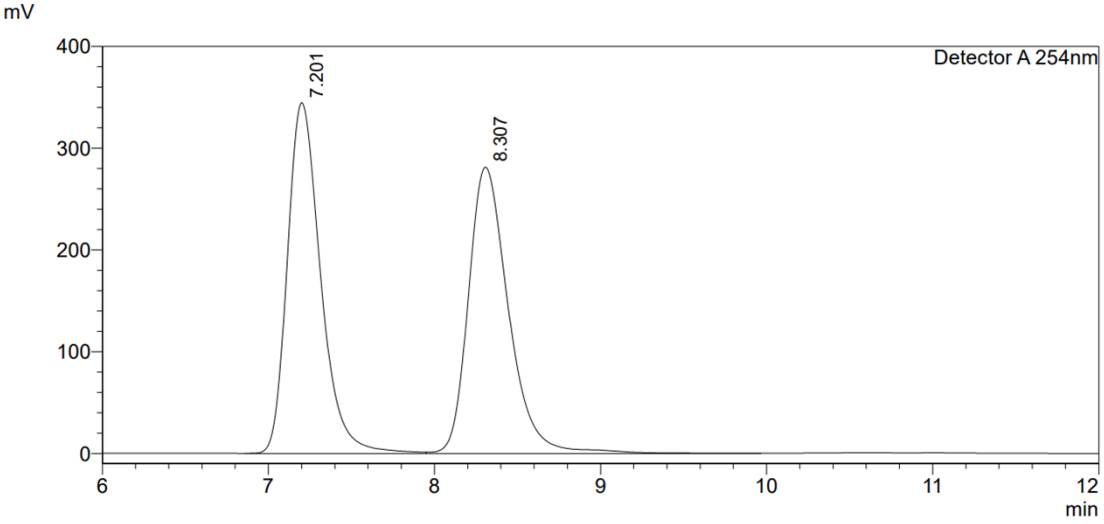
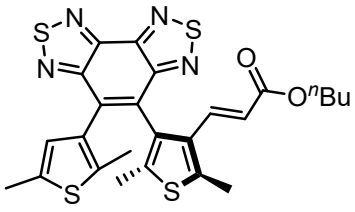


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.201	4819505	345095	50.408
2	8.307	4741411	281607	49.592
Total		9560917	626702	100.000



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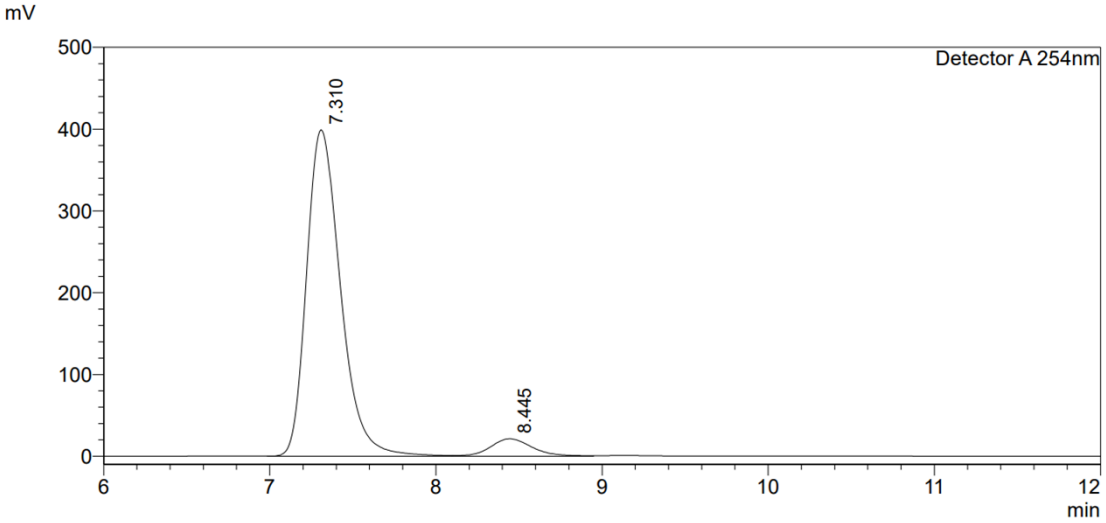
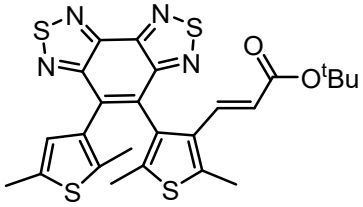


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.310	5673231	399119	93.763
2	8.445	377365	21333	6.237
Total		6050596	420452	100.000

3l: OD-H, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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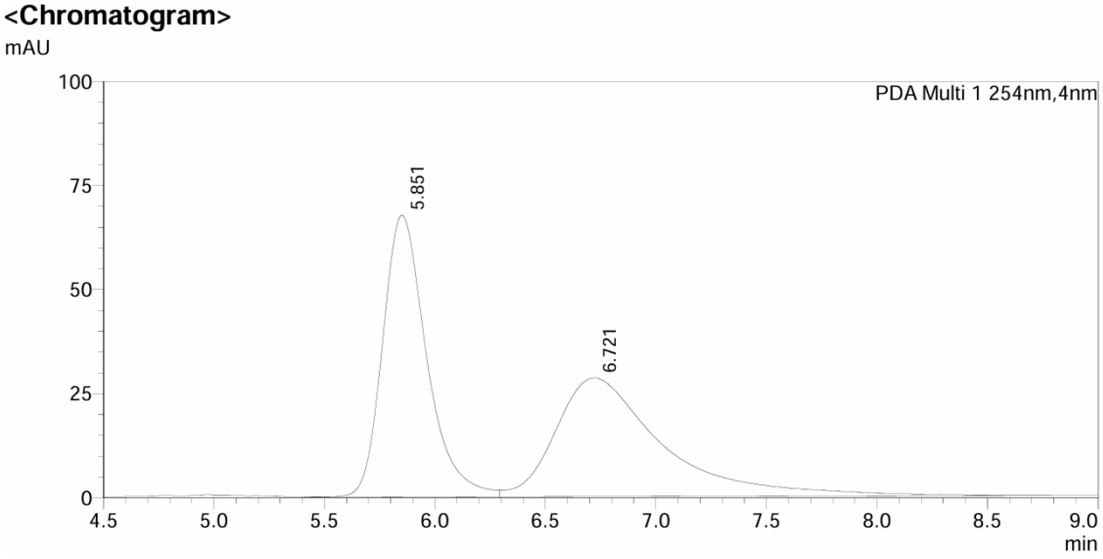
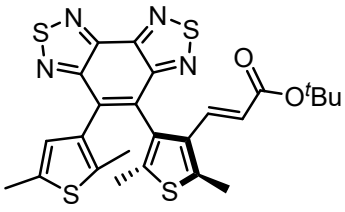


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.851	935354	67639	49.474
2	6.721	955260	28469	50.526
Total		1890614	96108	100.000



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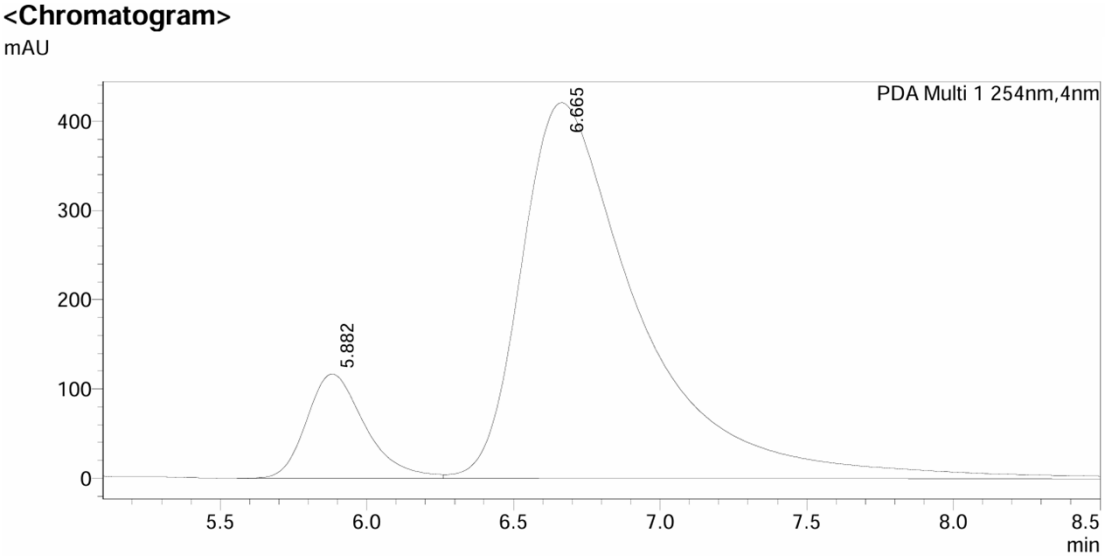
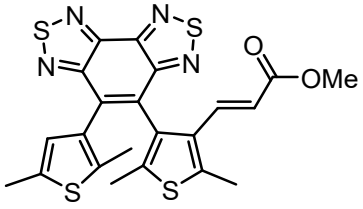


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.882	1634430	117069	11.932
2	6.665	12063373	421233	88.068
Total		13697802	538302	100.000

3m: IF-3, Hex/iPrOH=95/5, rate=0.800 mL/min, 254 nm



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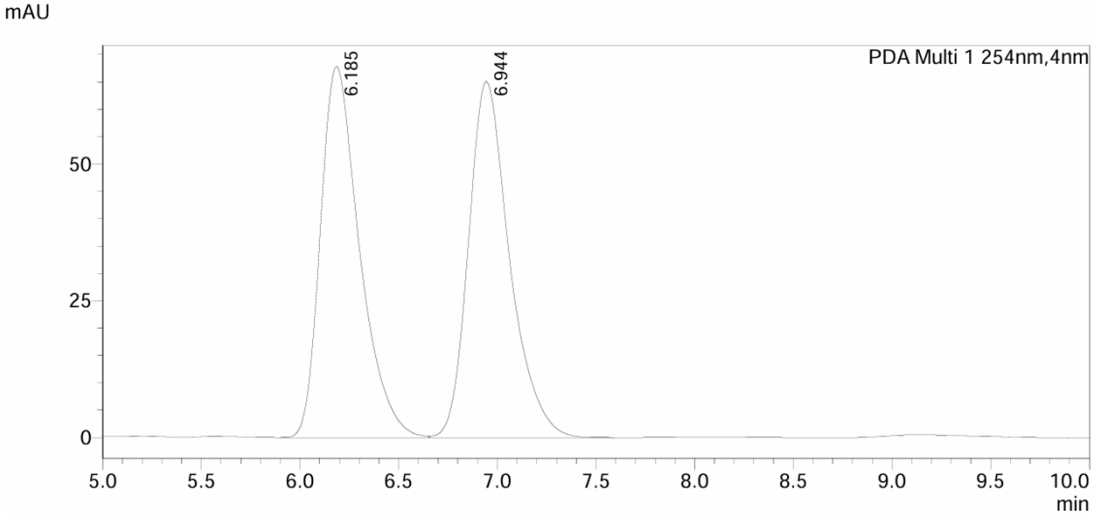
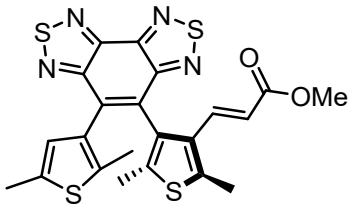


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.185	933057	67844	49.789
2	6.944	940951	65107	50.211
Total		1874008	132951	100.000



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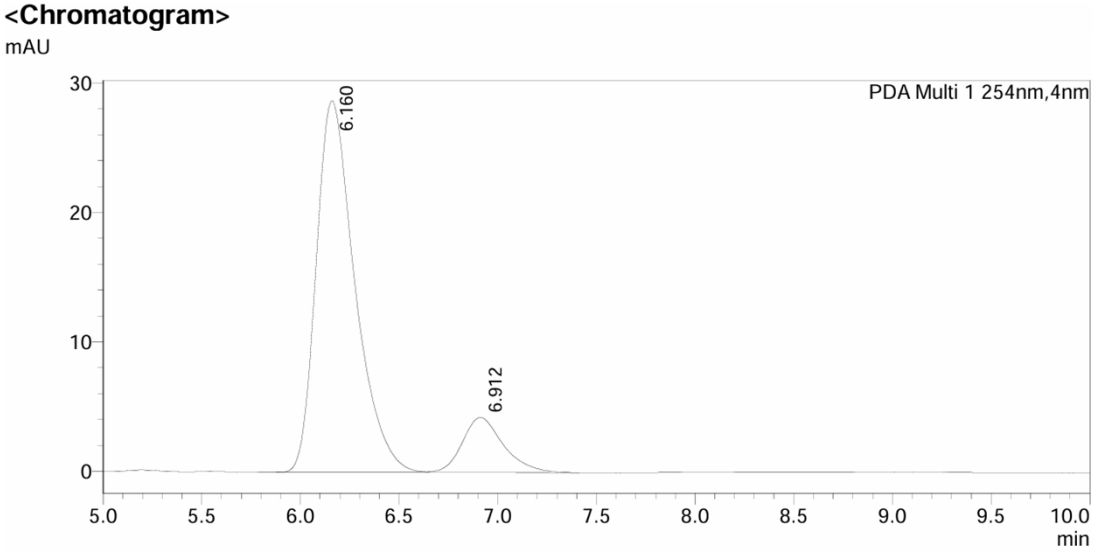
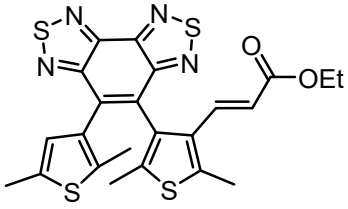


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.160	391362	28686	86.403
2	6.912	61588	4250	13.597
Total		452950	32935	100.000

3n: IF-3, Hex/iPrOH=95/5, rate=0.800 mL/min, 254 nm



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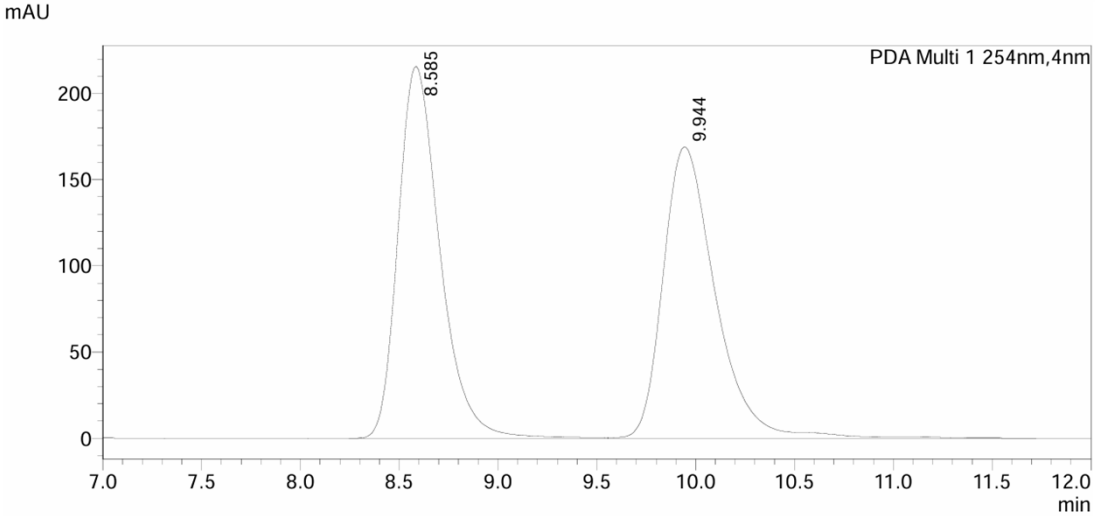
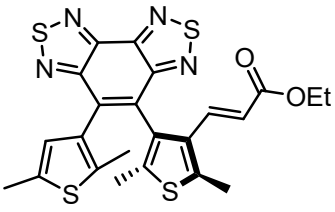


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.585	3173117	215558	50.375
2	9.944	3125860	168859	49.625
Total		6298977	384417	100.000



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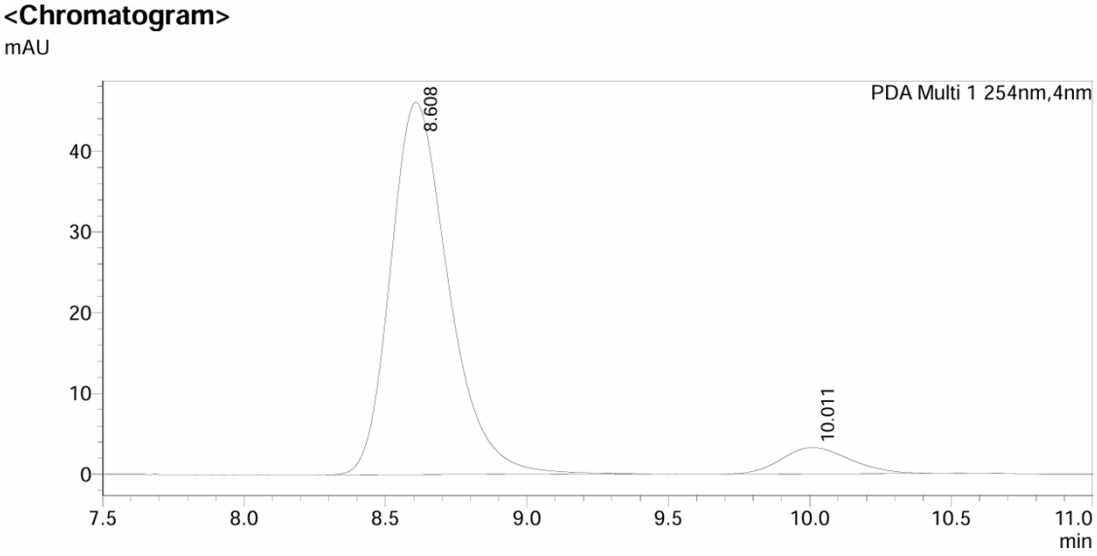
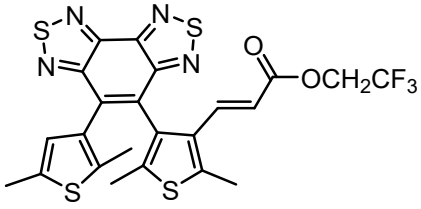


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.608	658876	46122	92.278
2	10.011	55140	3250	7.722
Total		714016	49372	100.000

3o: IF-3, Hex/iPrOH=95/5, rate=0.800 mL/min, 254 nm



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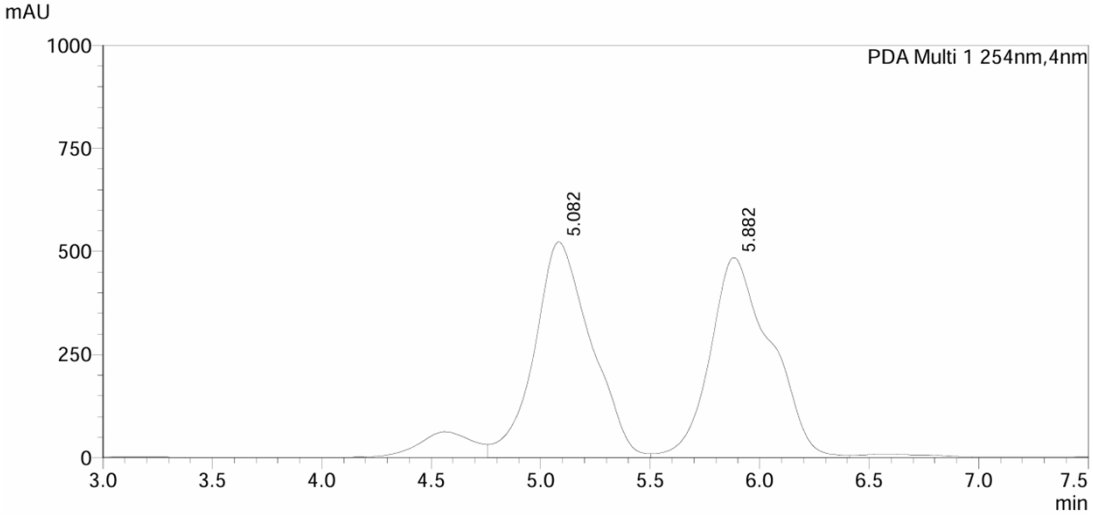
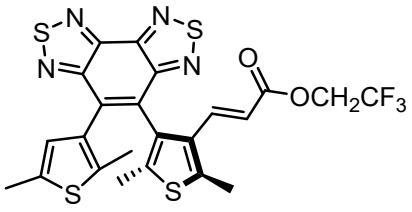


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.082	9416262	522636	50.065
2	5.882	9391960	484726	49.935
Total		18808222	1007362	100.000



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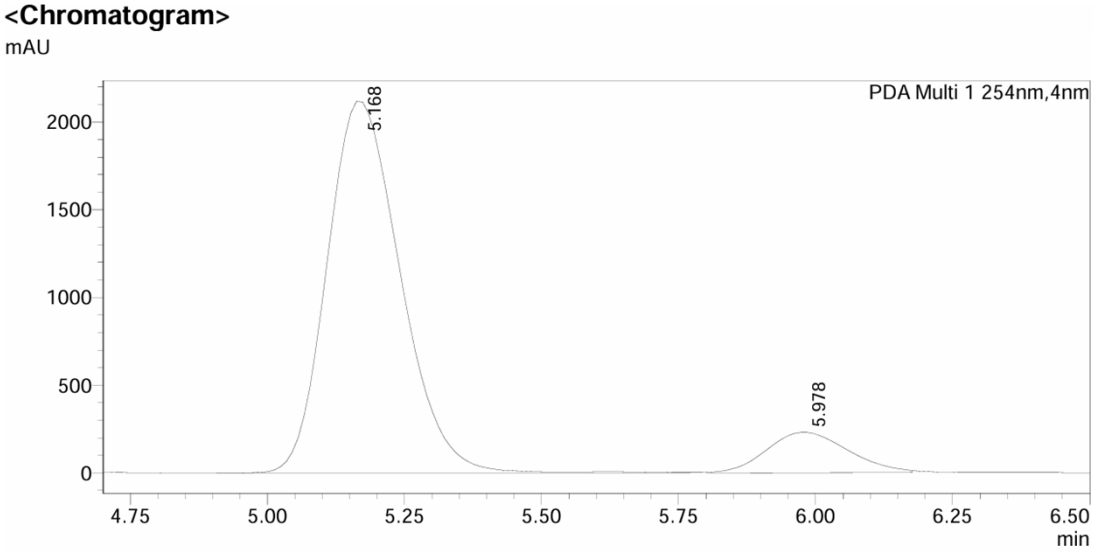
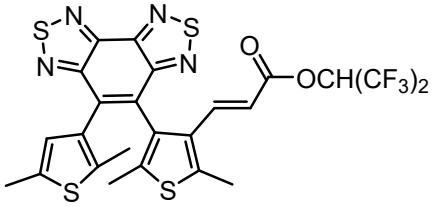


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.168	19726911	2117271	89.236
2	5.978	2379564	229971	10.764
Total		22106475	2347243	100.000

3p: A05, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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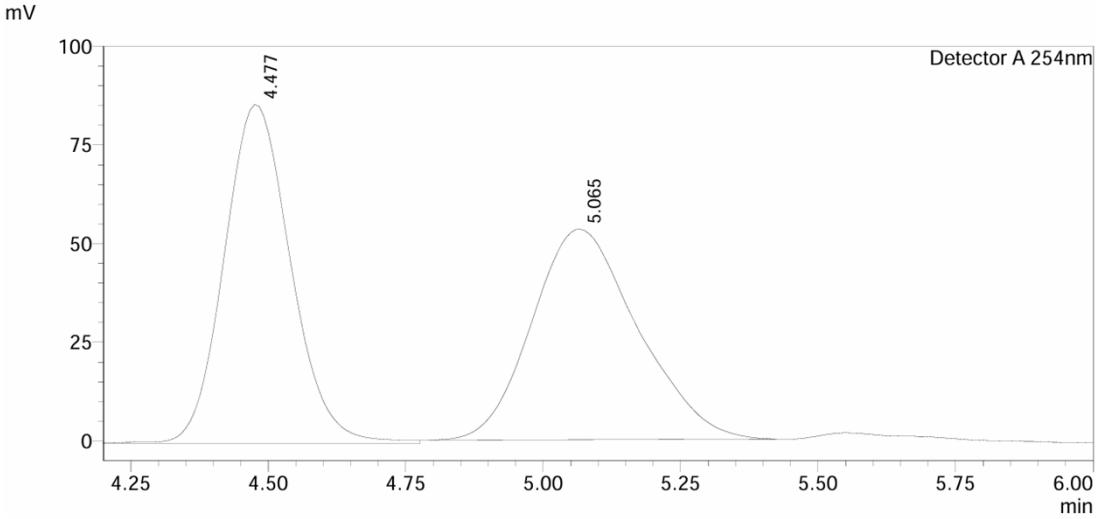
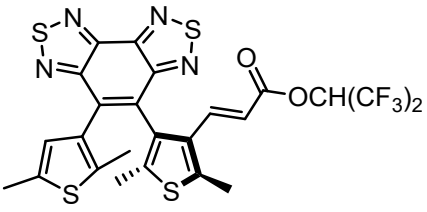


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	4.477	727020	86022	50.477
2	5.065	713292	53411	49.523
Total		1440312	139434	



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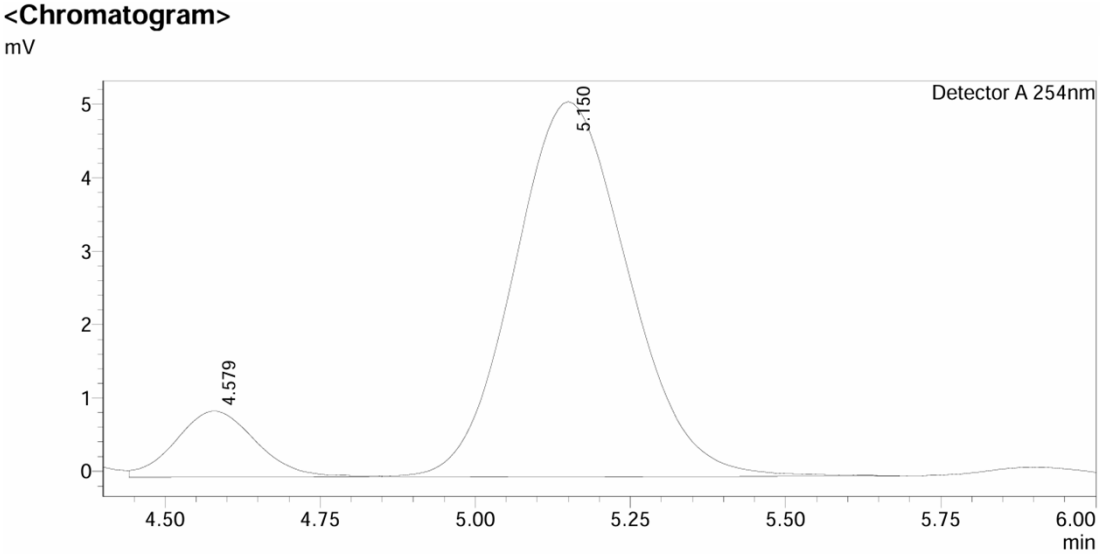
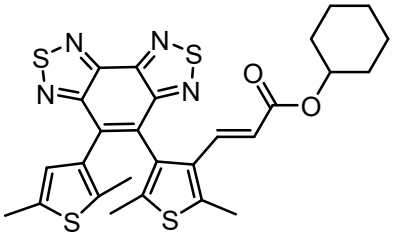


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	4.579	8120	897	11.030
2	5.150	65499	5110	88.970
Total		73618	6007	

3q: IF-3, Hex/iPrOH=95/5, rate=1.000 mL/min, 254 nm



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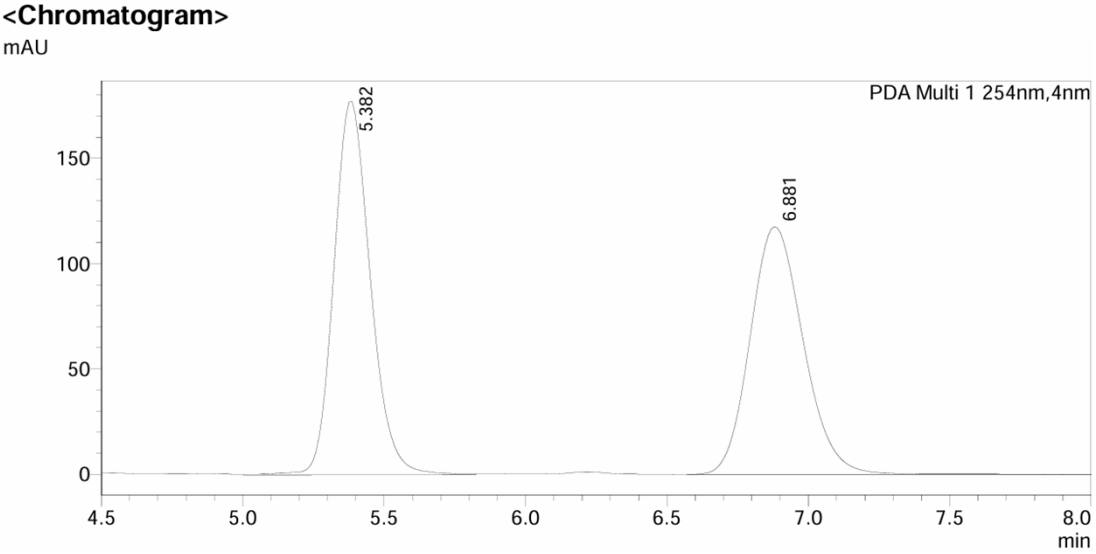
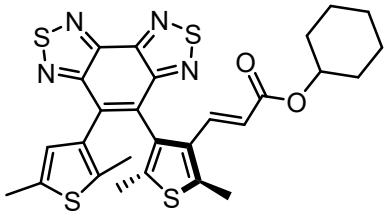


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.382	1599725	177074	50.646
2	6.881	1558918	117834	49.354
Total		3158643	294908	100.000



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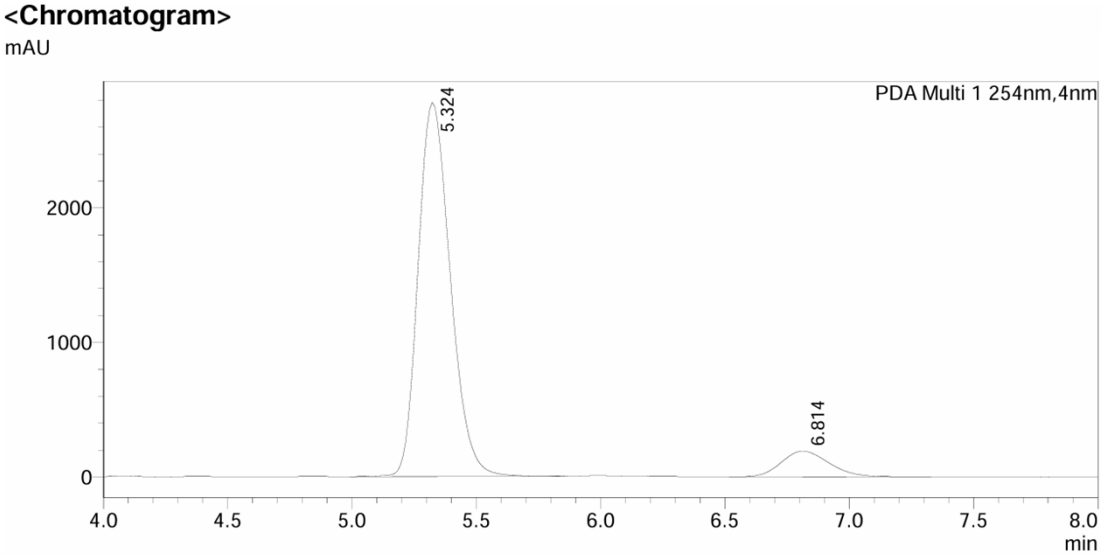
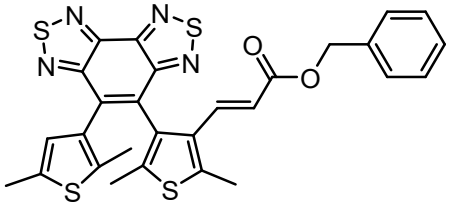


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.324	25068256	2781412	90.745
2	6.814	2556702	191480	9.255
Total		27624958	2972892	100.000

3r: IF-3, Hex/iPrOH=85/15, rate=1.000 mL/min, 254 nm



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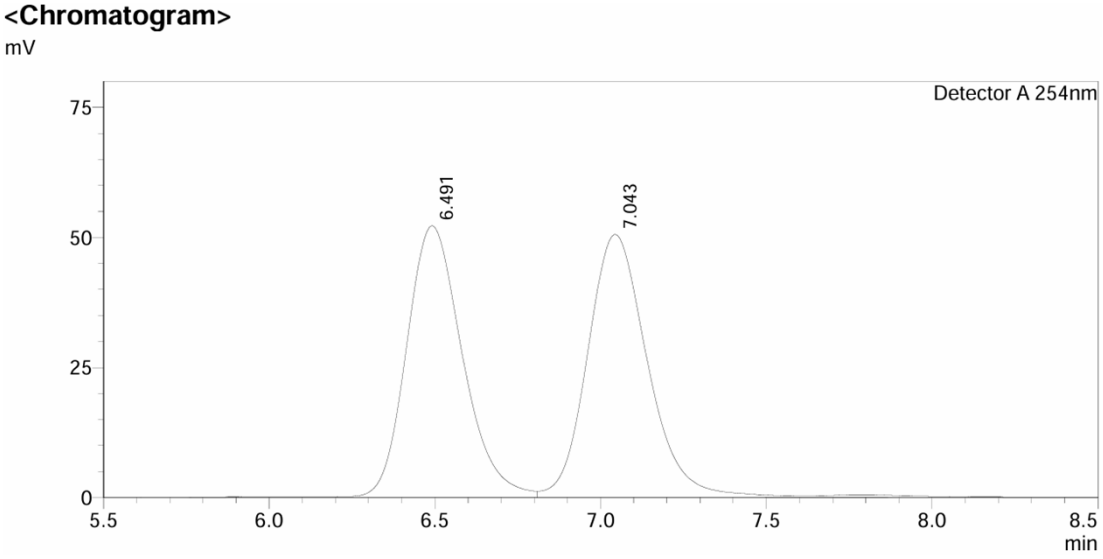
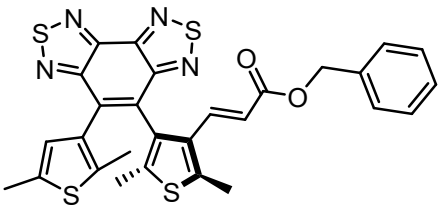


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	6.491	616870	52307	48.783
2	7.043	647651	50635	51.217
Total		1264521	102941	



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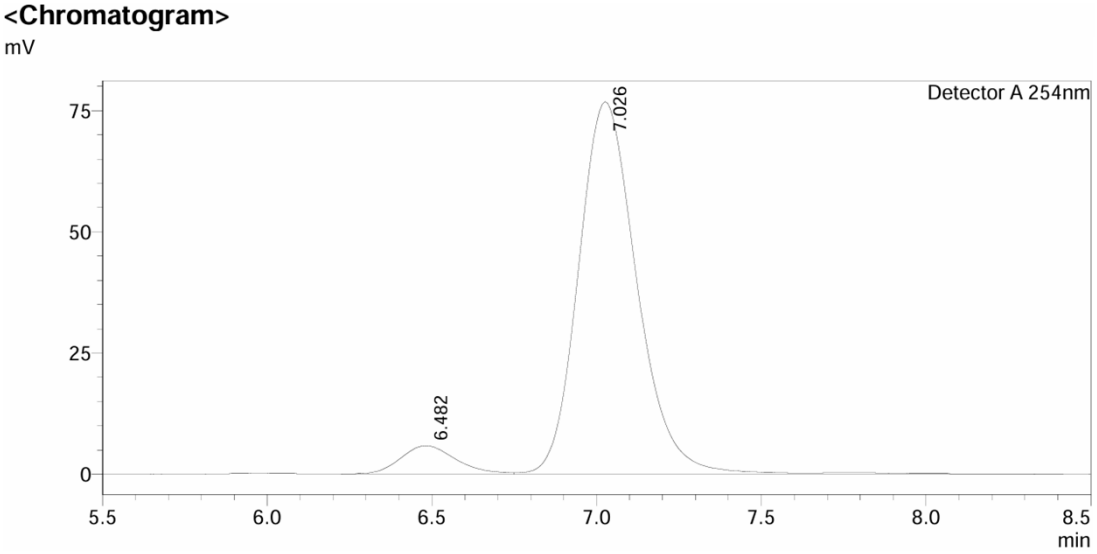
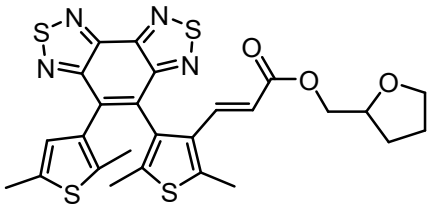


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	6.482	67856	5816	6.675
2	7.026	948759	76765	93.325
Total		1016615	82581	

3s: IF-3, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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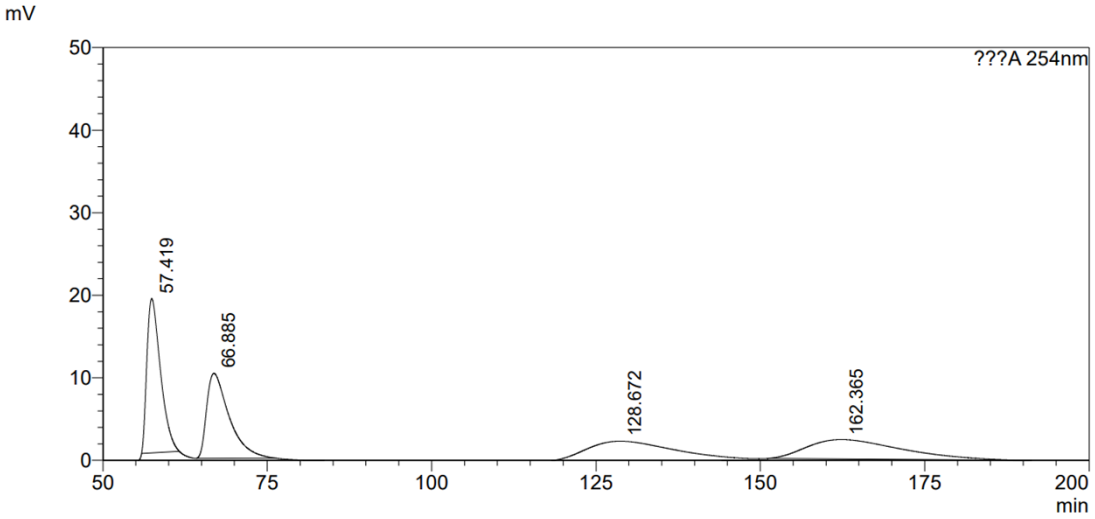
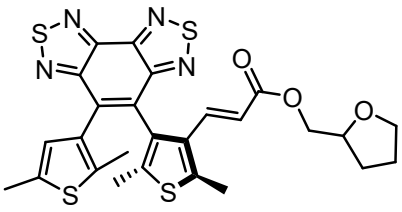


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Area%
1	57.419	2699254	27.439
2	66.885	2452058	24.926
3	128.672	2301817	23.399
4	162.365	2384219	24.236
Total		9837348	100.000



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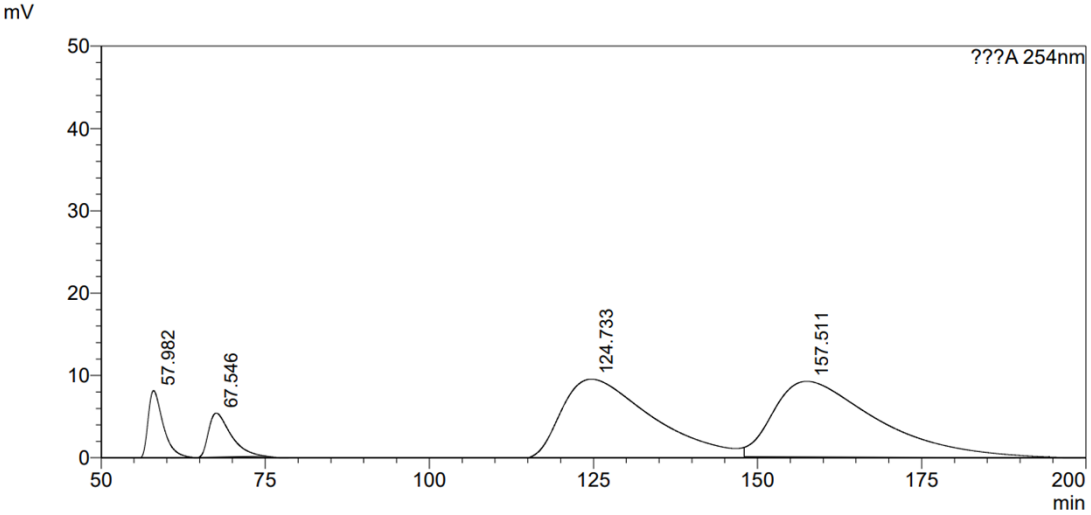
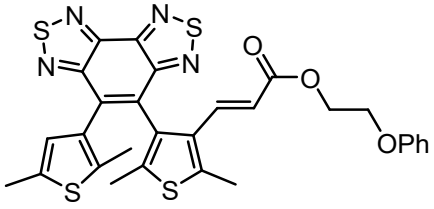


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Area%
1	57.982	1310597	5.908
2	67.546	1254565	5.656
3	124.733	9473540	42.709
4	157.511	10143043	45.727
Total		22181745	100.000

3t: AD-H, Hex/iPrOH=92/8, rate=0.800 mL/min, 254 nm



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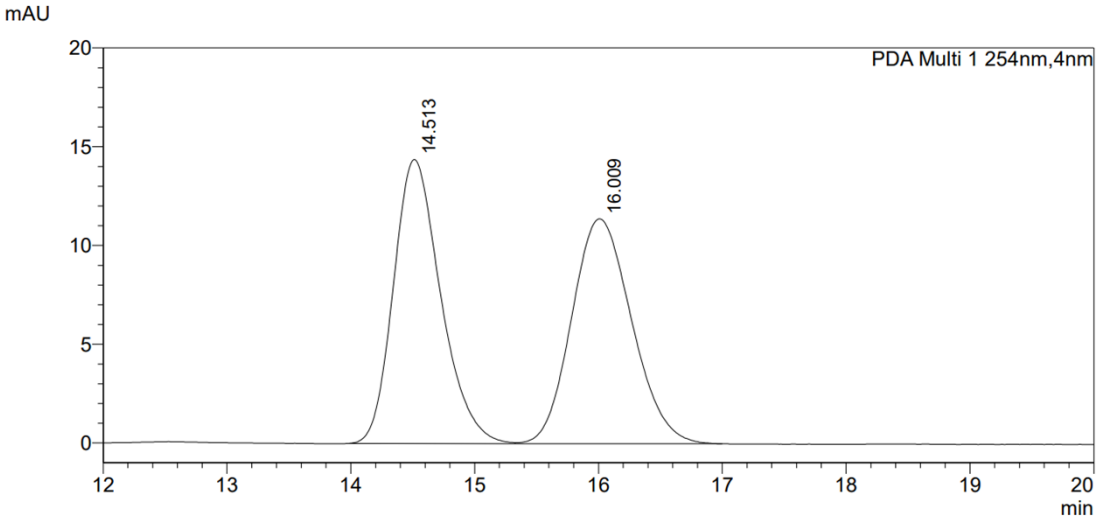
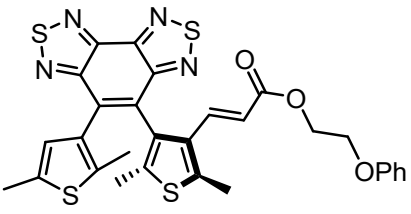


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.513	381520	14384	49.895
2	16.009	383120	11391	50.105
Total		764640	25775	100.000



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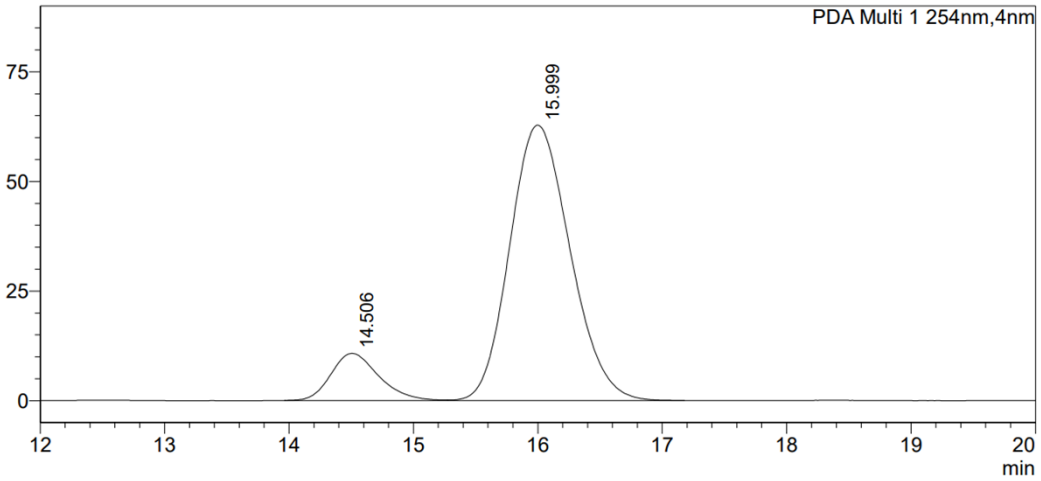
mAU

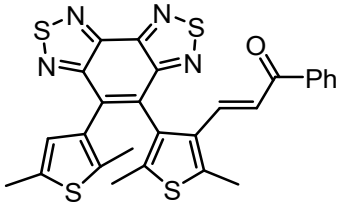


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.506	286512	10755	11.912
2	15.999	2118684	62813	88.088
Total		2405196	73568	100.000

3u: AD-H, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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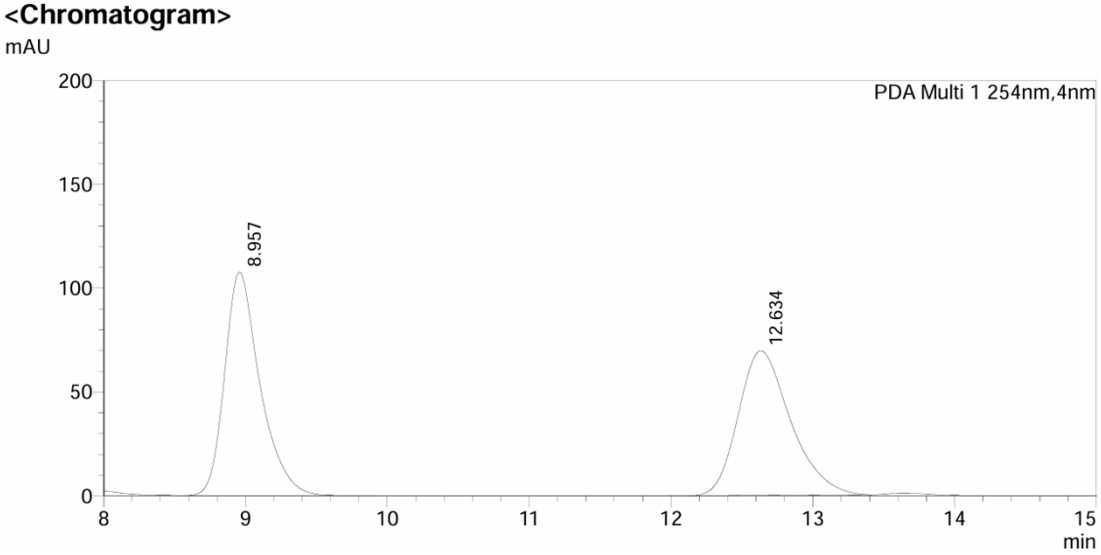
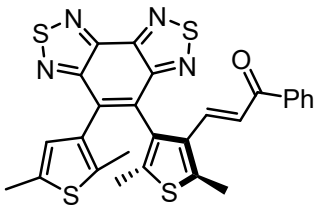


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.957	1871689	107720	51.179
2	12.634	1785451	69618	48.821
Total		3657139	177338	100.000



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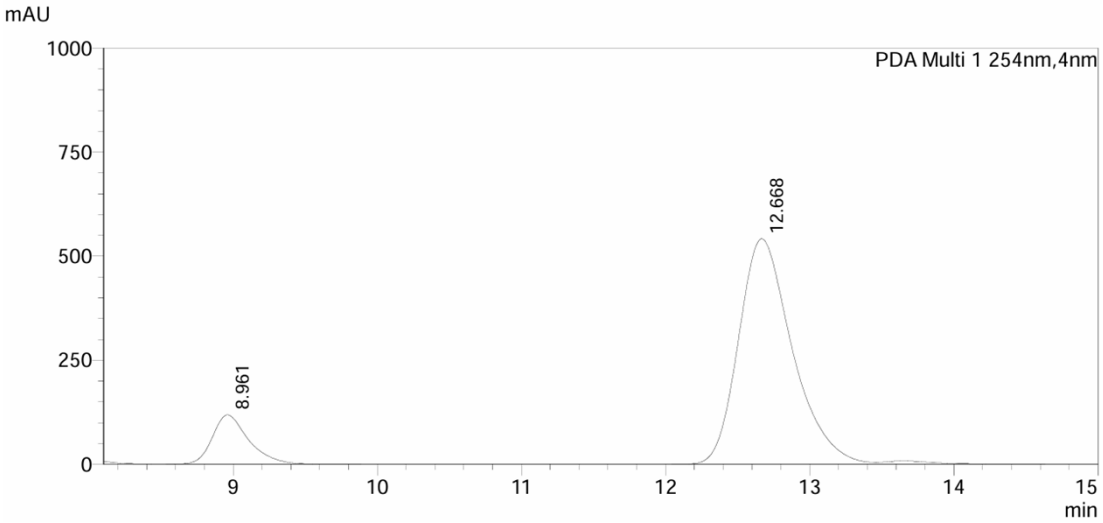
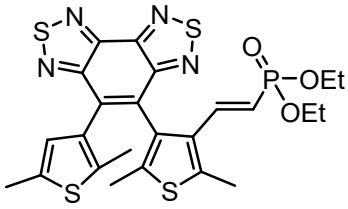


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.961	2085737	118719	12.783
2	12.668	14230756	541831	87.217
Total		16316493	660550	100.000

3v: IF-3, Hex/iPrOH=85/15, rate=1.000 mL/min, 254 nm



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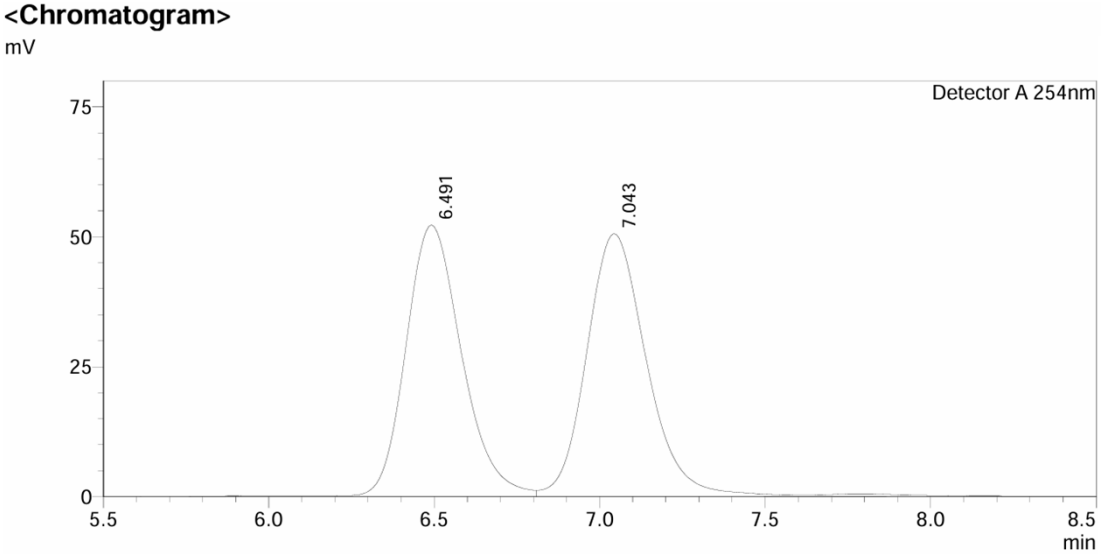
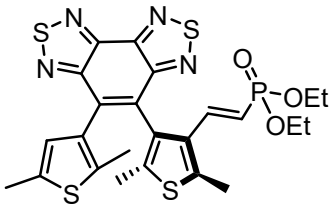


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	6.491	616870	52307	48.783
2	7.043	647651	50635	51.217
Total		1264521	102941	



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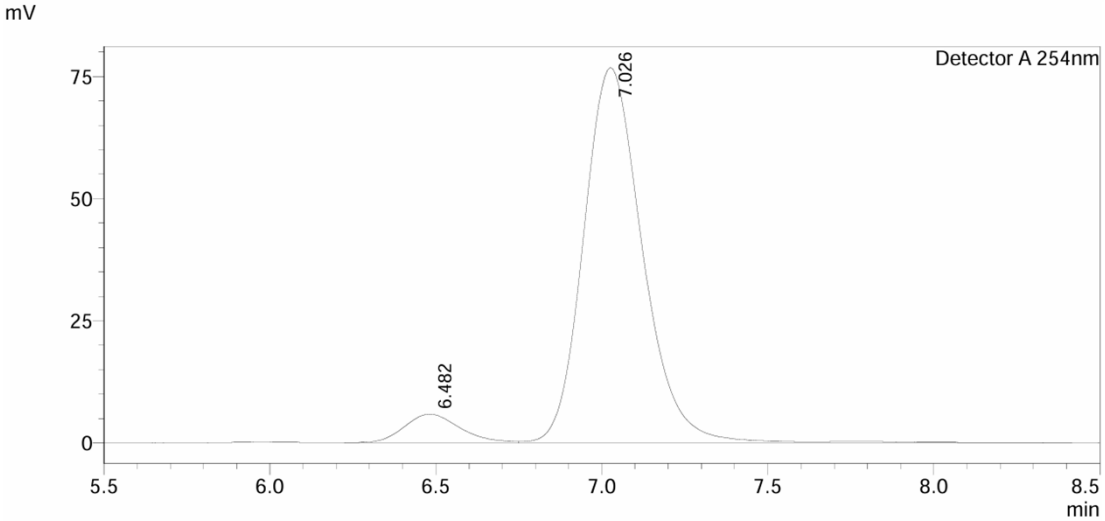
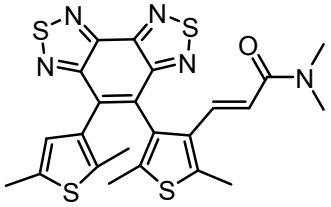


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	6.482	67856	5816	6.675
2	7.026	948759	76765	93.325
Total		1016615	82581	

3w: IF-3, Hex/iPrOH=85/15, rate=1.000 mL/min, 254 nm



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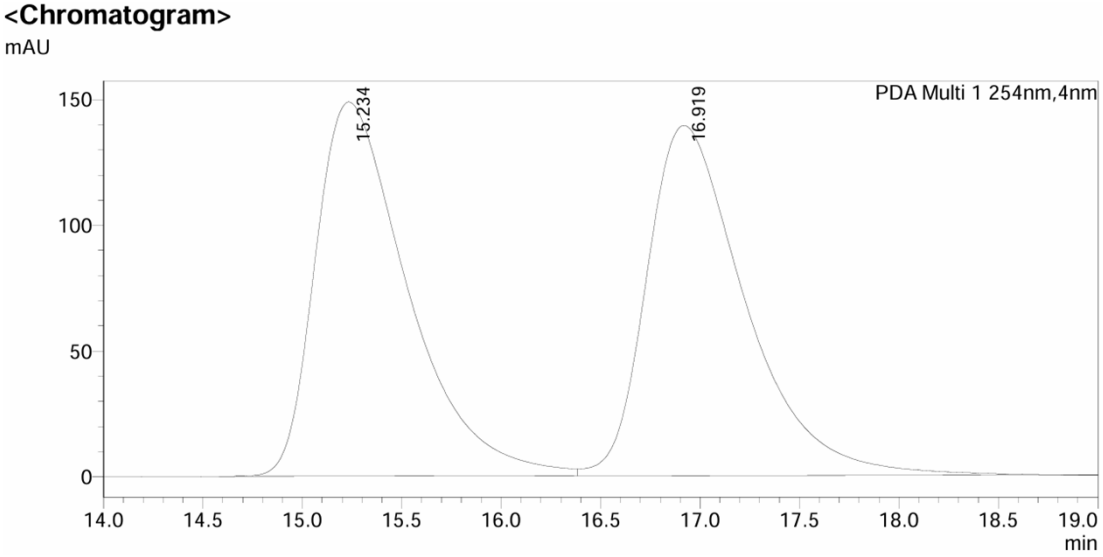
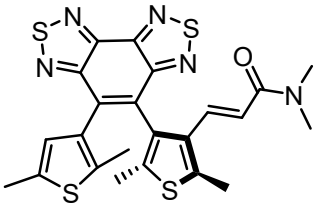


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.234	4820787	148818	49.977
2	16.919	4825173	139277	50.023
Total		9645960	288095	100.000



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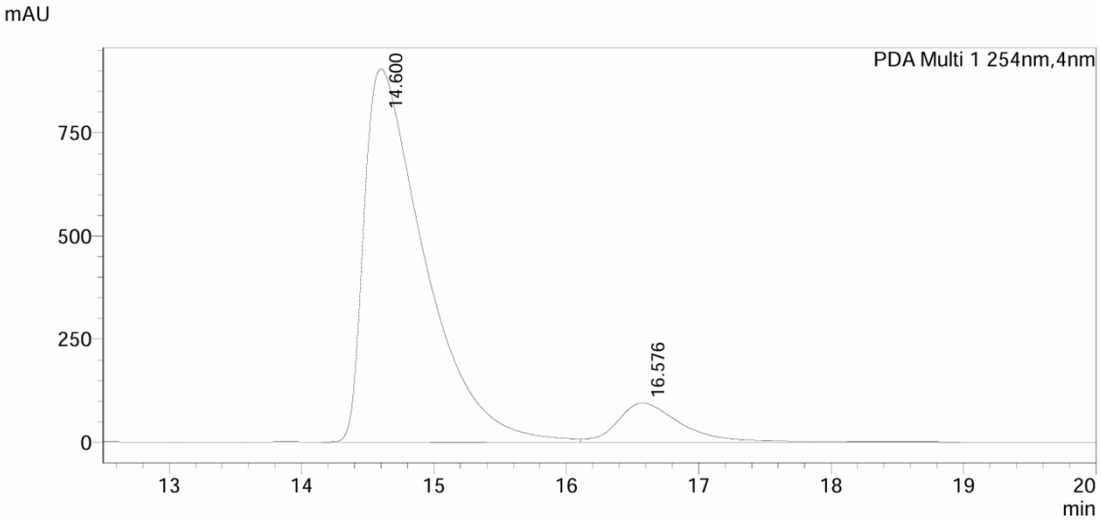
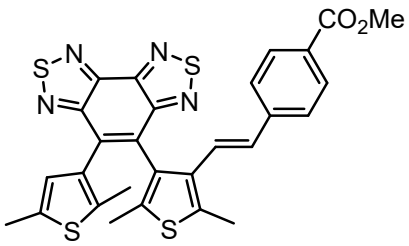


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.600	28791490	905695	90.143
2	16.576	3148281	94787	9.857
Total		31939771	1000482	100.000

3x: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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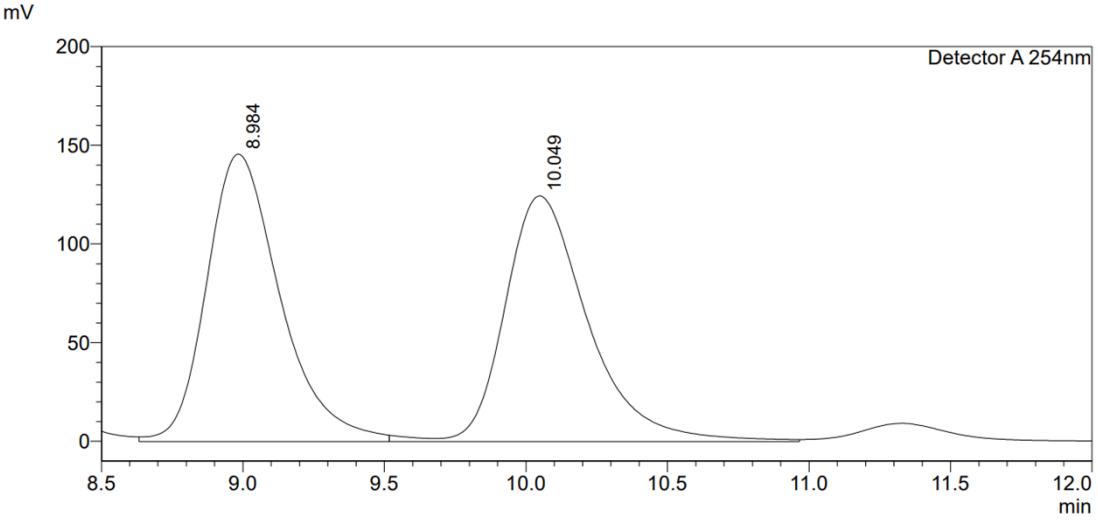
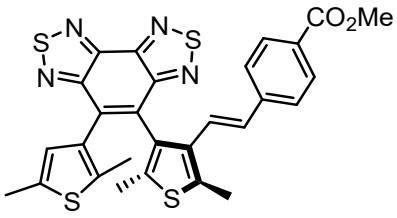


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.984	2635881	145705	50.839
2	10.049	2548876	124480	49.161
Total		5184757	270185	100.000



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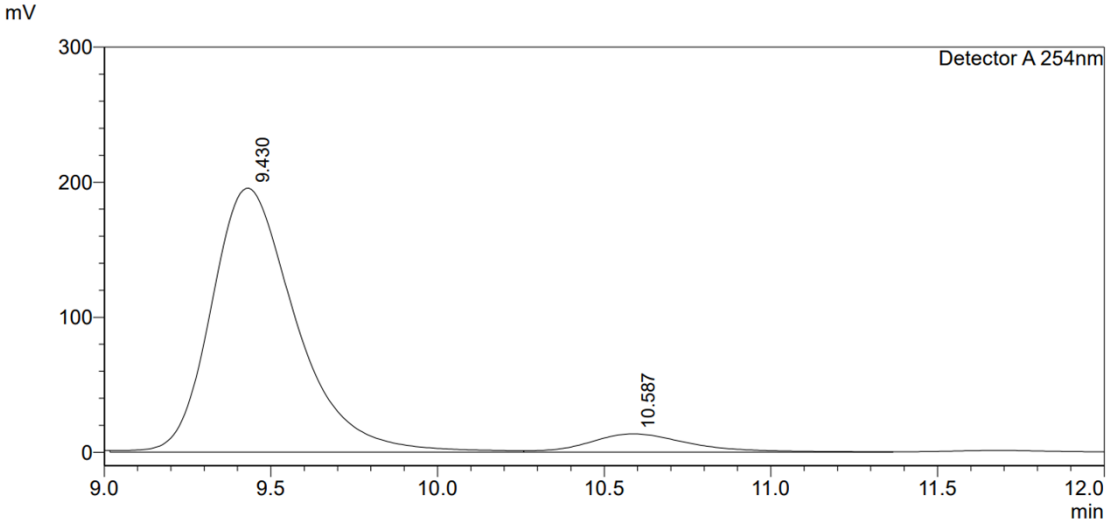
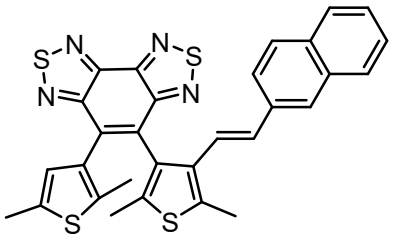


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.430	3464387	195543	92.340
2	10.587	287368	13600	7.660
Total		3751755	209143	100.000

3y: IF-3, Hex/iPrOH=92/8, rate=0.800 mL/min, 254 nm



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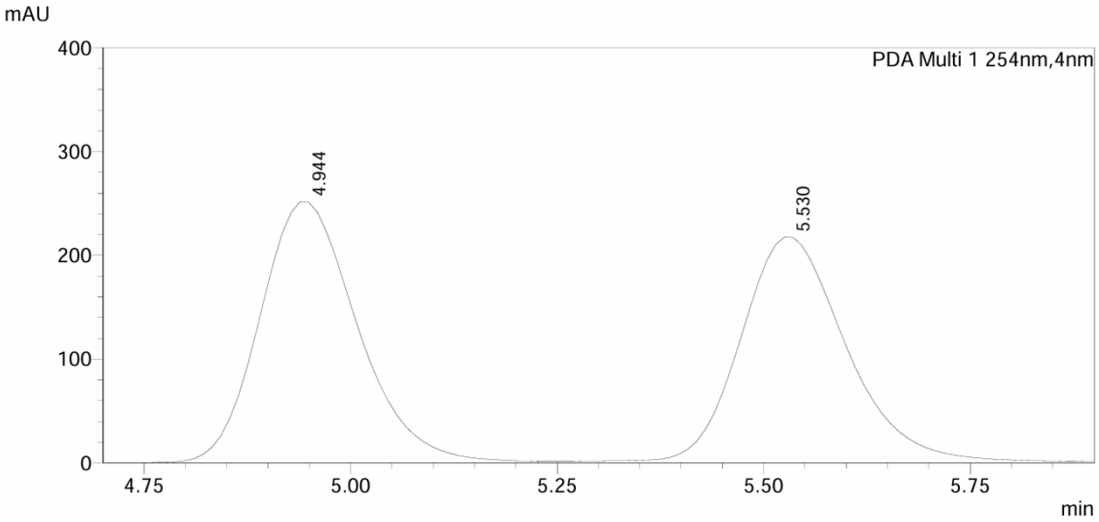
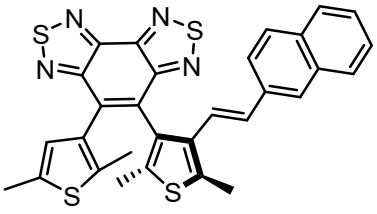


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	4.944	2069641	251635	50.984
2	5.530	1989759	217989	49.016
Total		4059399	469624	100.000



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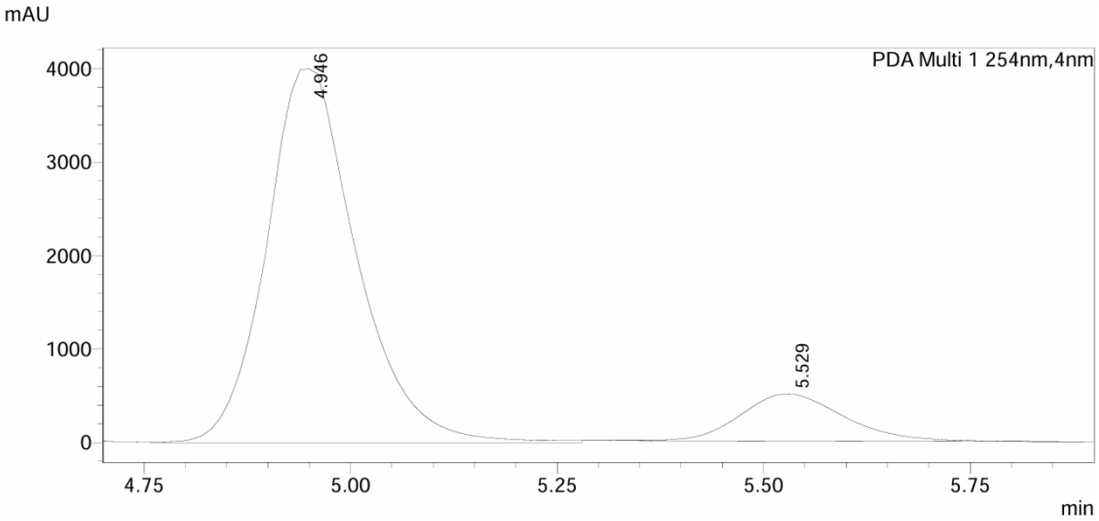
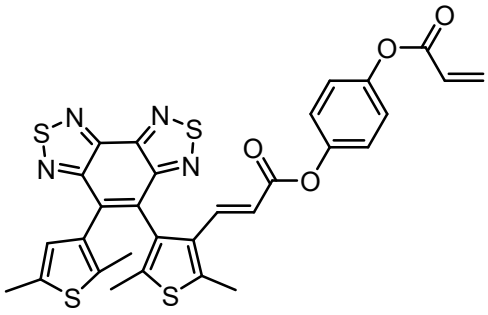


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	4.946	30380998	3999526	87.317
2	5.529	4412749	505687	12.683
Total		34793746	4505213	100.000

3z-mono: IF-3, Hex/iPrOH=95/5, rate=1.000 mL/min, 254 nm



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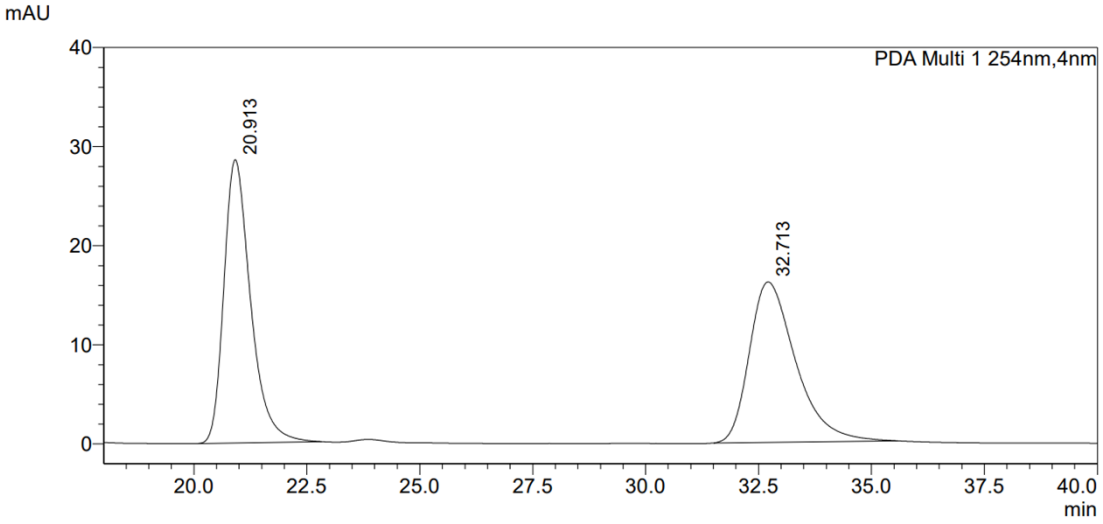
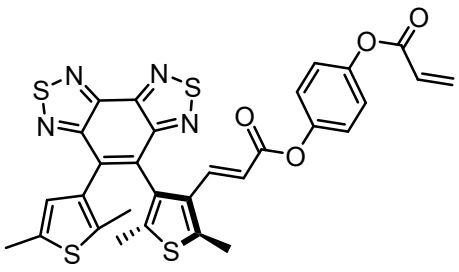


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.913	1174465	28590	50.435
2	32.713	1154195	16187	49.565
Total		2328660	44777	100.000



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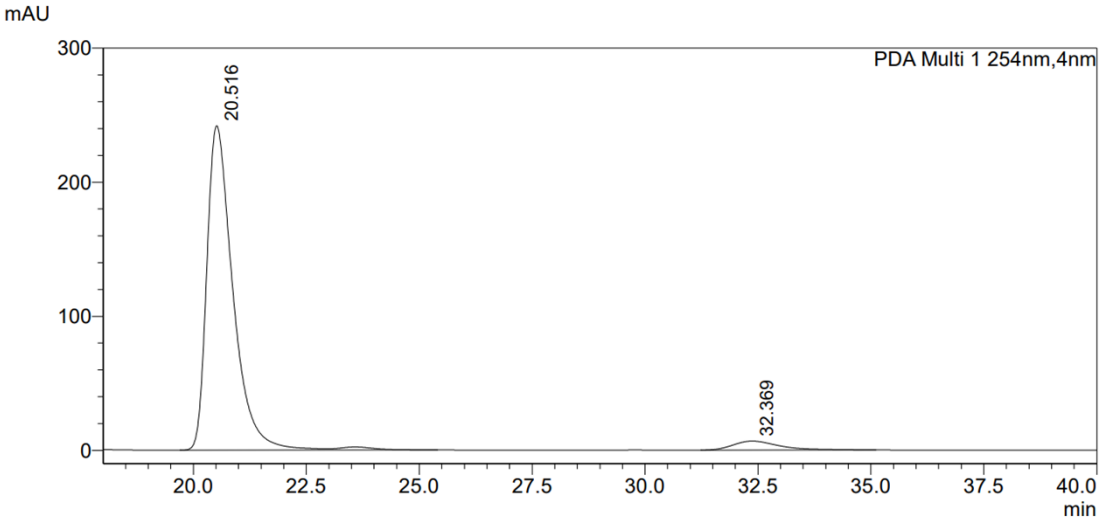
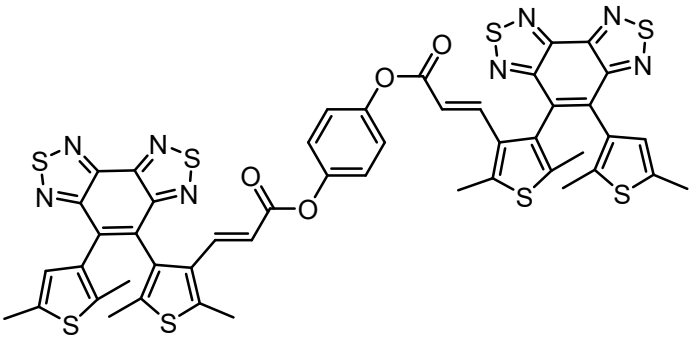


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.516	9832123	241994	95.348
2	32.369	479652	6699	4.652
Total		10311775	248692	100.000

3z-di: IF-3, Hex/iPrOH=85/15, rate=1.000 mL/min, 254 nm



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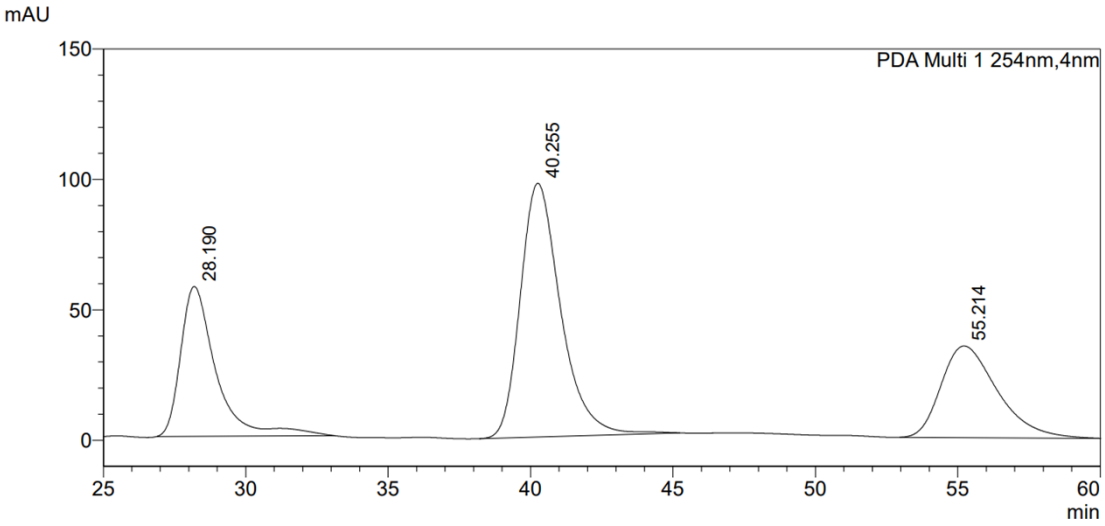
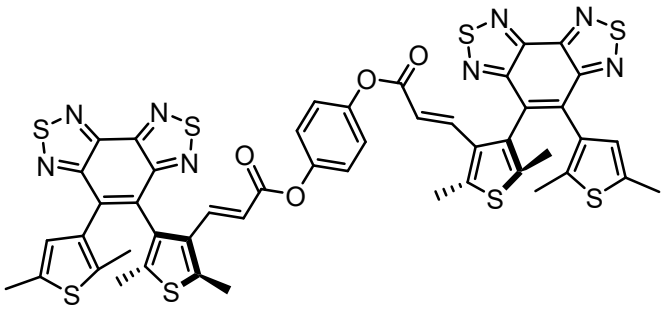


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	28.190	4965637	57419	25.614
2	40.255	9589051	97267	49.463
3	55.214	4831500	35142	24.922
Total		19386188	189829	100.000



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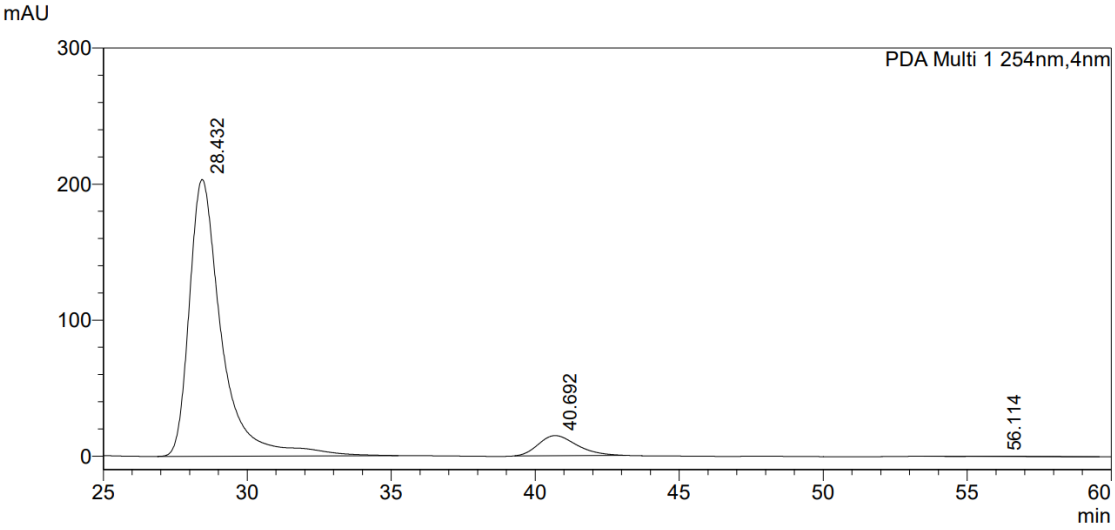
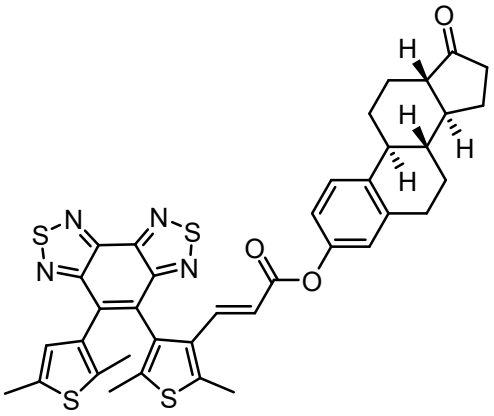


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	28.432	15909407	203527	91.975
2	40.692	1366446	14770	7.900
3	56.114	21690	244	0.125
Total		17297544	218541	100.000

3aa: IF-3, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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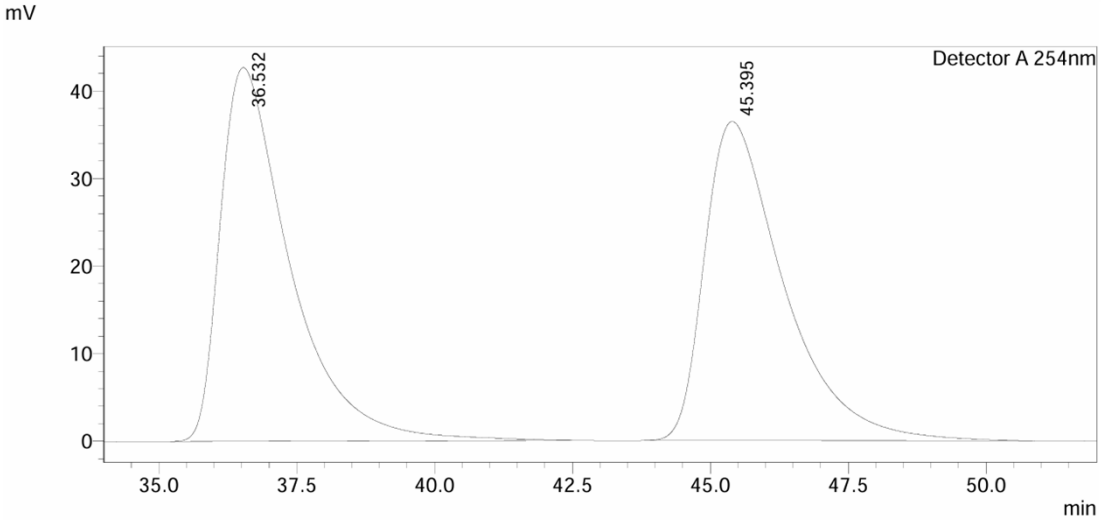
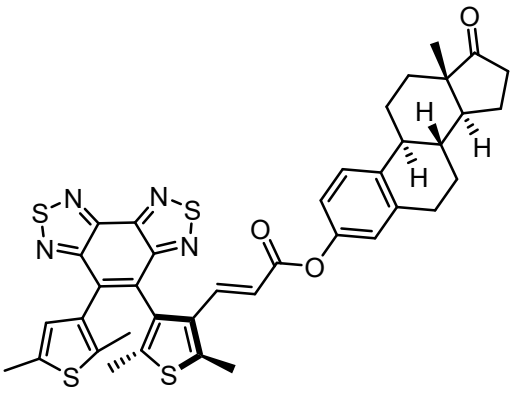


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	36.532	3758110	42666	50.719
2	45.395	3651534	36429	49.281
Total		7409644	79096	



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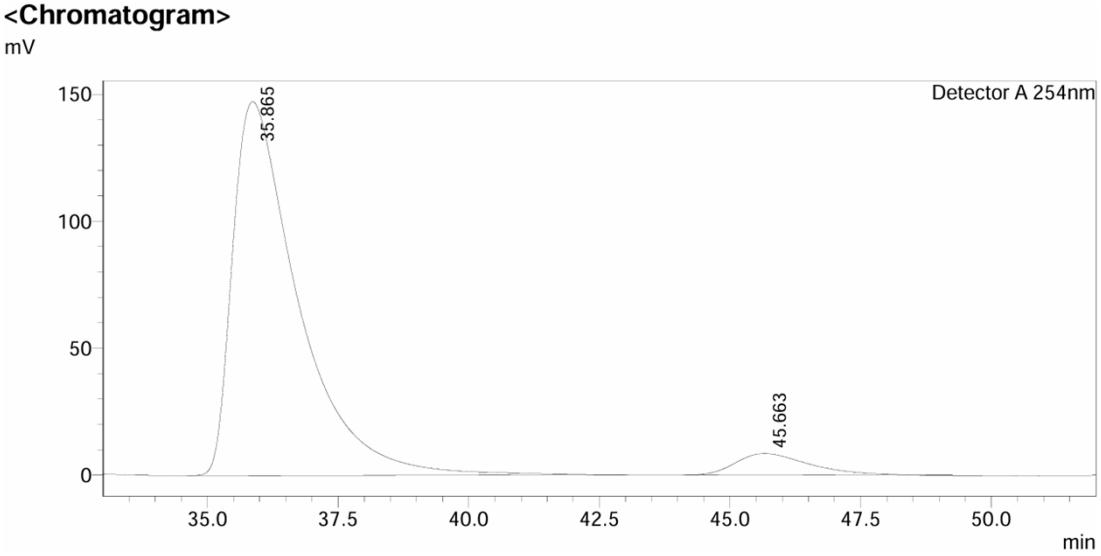
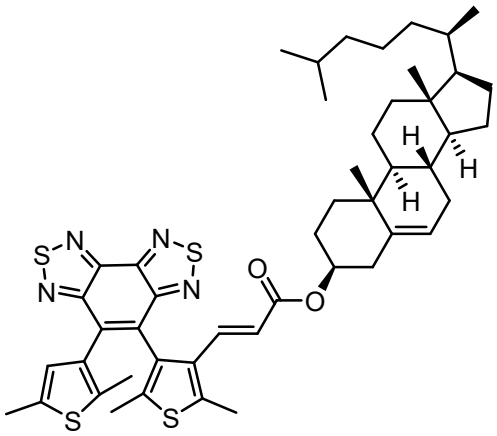


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	35.865	12854753	147142	93.838
2	45.663	844138	8468	6.162
Total		13698891	155610	

3ab: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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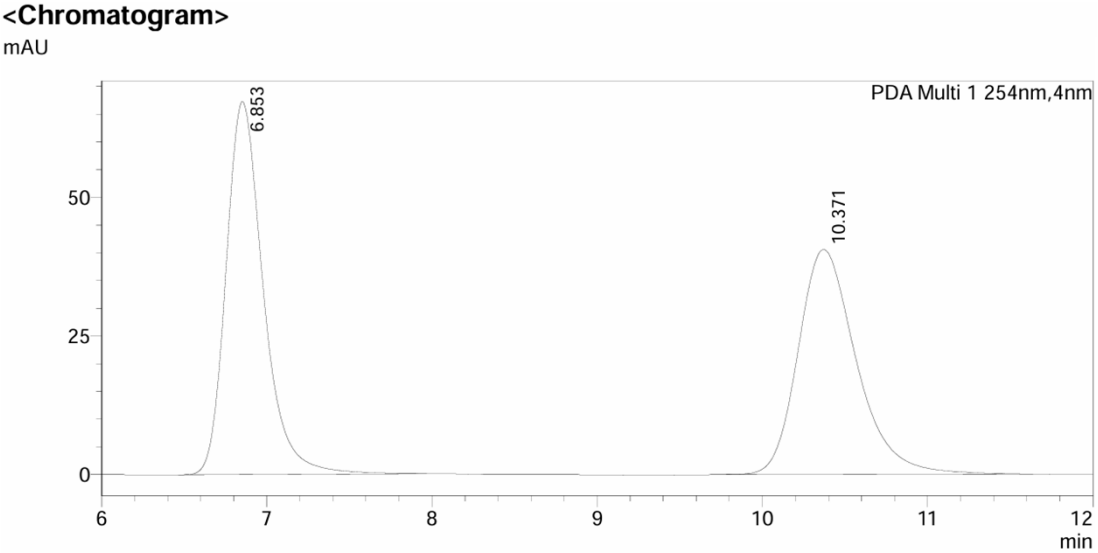
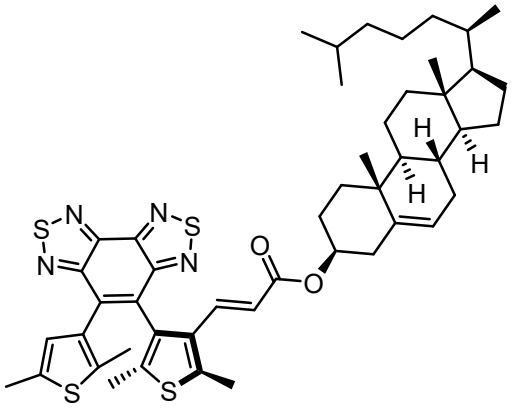


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.853	1054702	67219	51.511
2	10.371	992813	40581	48.489
Total		2047515	107800	100.000



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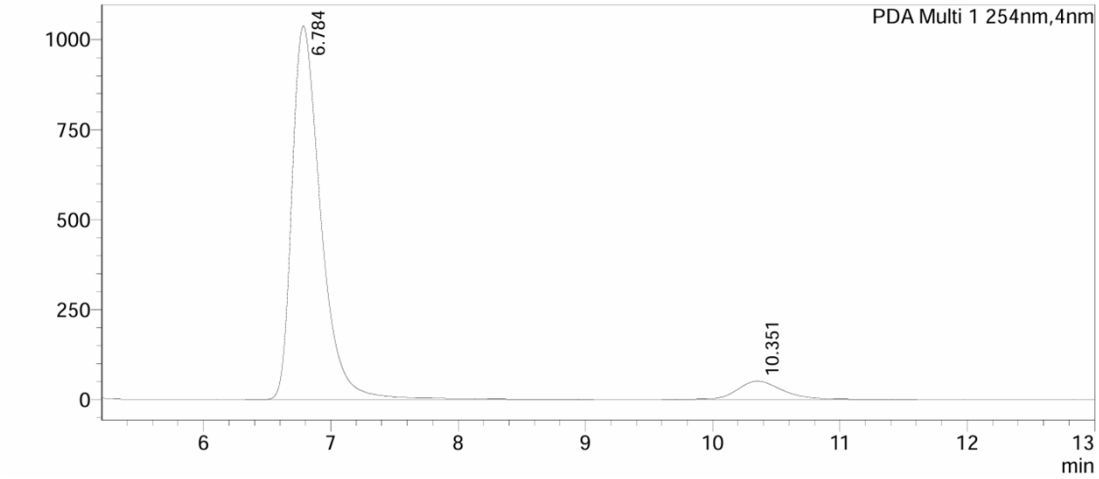
mAU

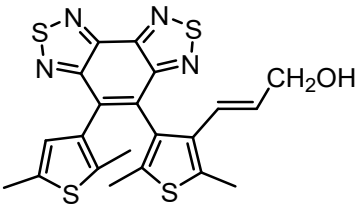


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.784	16315771	1038674	92.858
2	10.351	1254819	50703	7.142
Total		17570590	1089378	100.000

4: IF-3, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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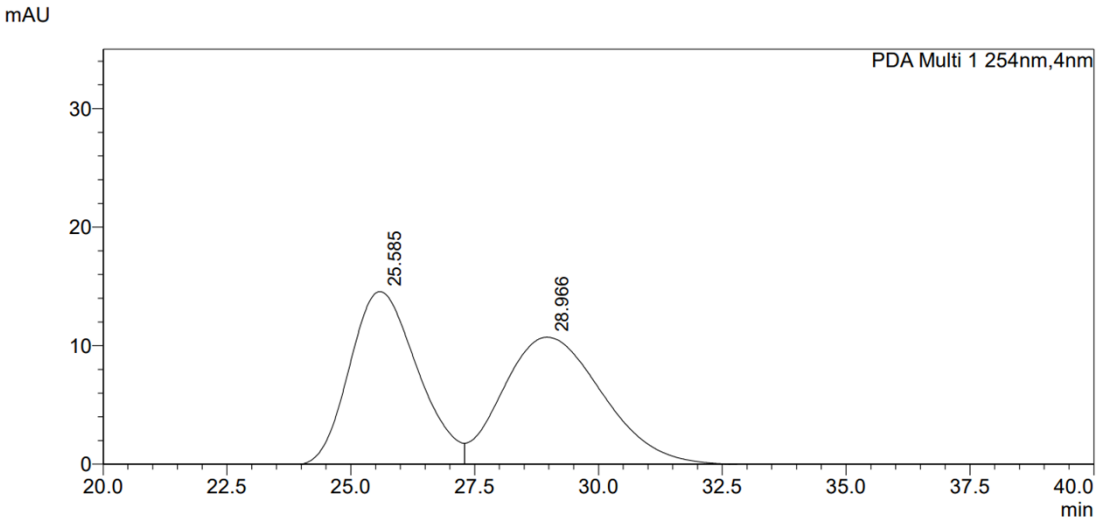
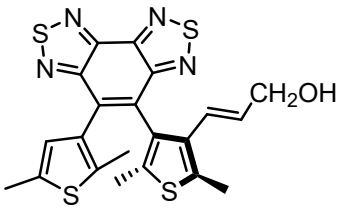


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	25.585	1395202	14612	48.161
2	28.966	1501754	10737	51.839
Total		2896957	25349	100.000



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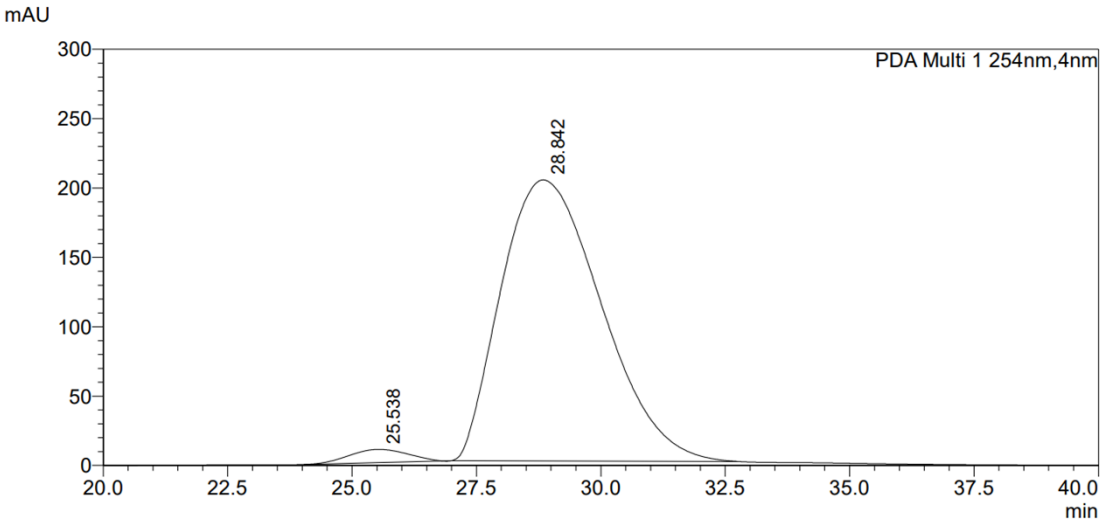
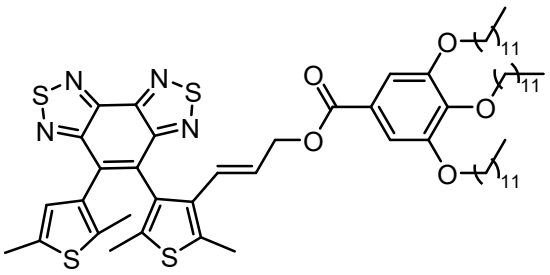


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	25.538	770953	9467	2.642
2	28.842	28404565	202483	97.358
Total		29175518	211951	100.000

5: IF-3, Hex/iPrOH=98/2, rate=0.400 mL/min, 254 nm



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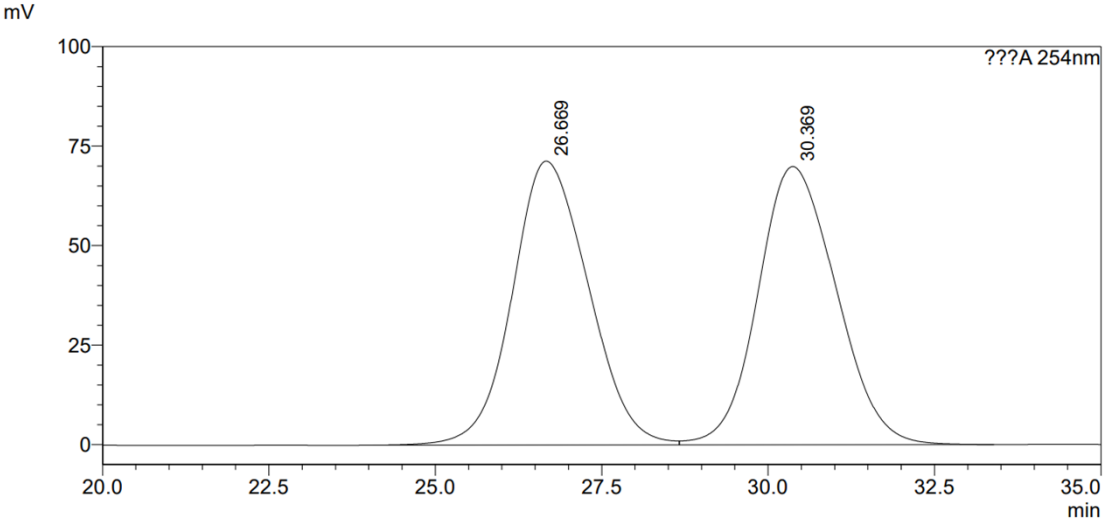
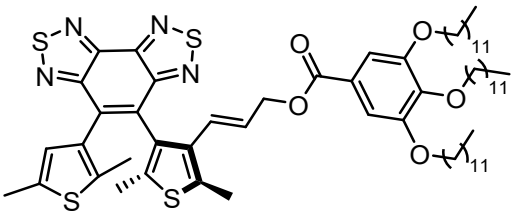


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.669	5683765	71329	49.847
2	30.369	5718585	69901	50.153
Total		11402351	141230	100.000



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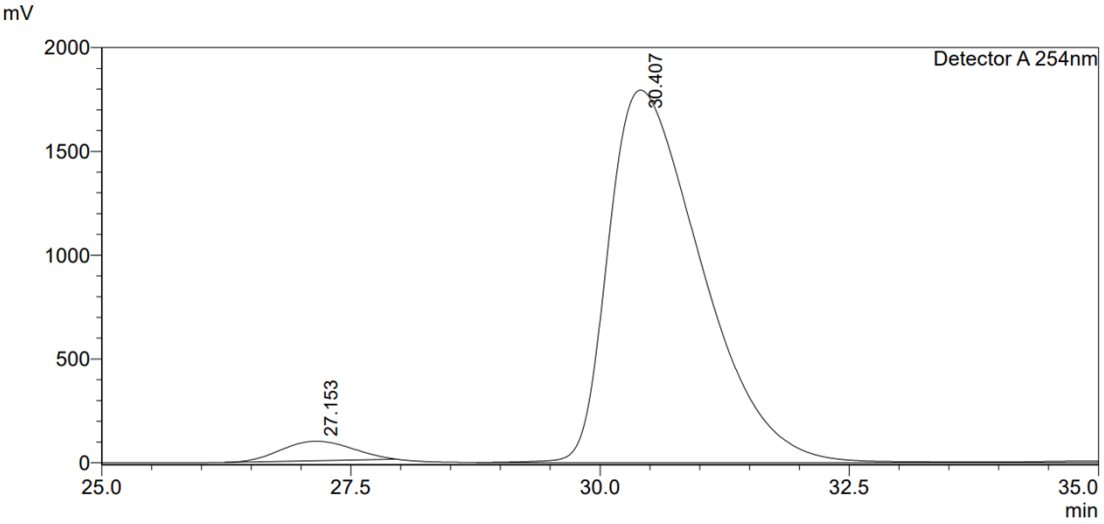
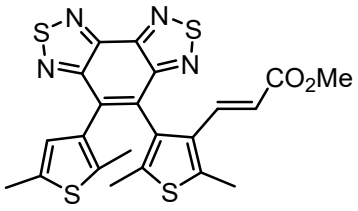


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	27.153	4675716	94014	3.840
2	30.407	117082244	1795199	96.160
Total		121757960	1889213	100.000

6b: AD-H, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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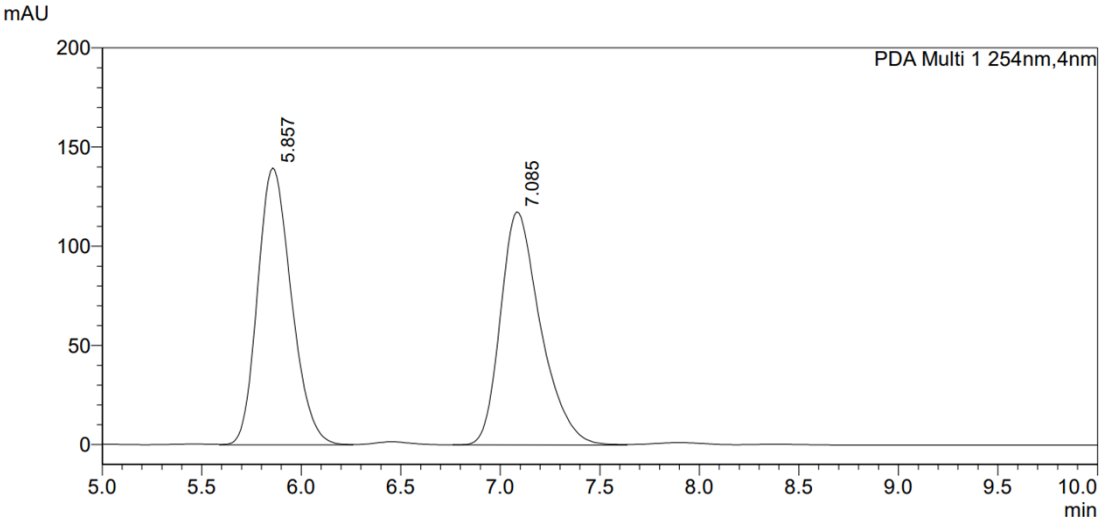
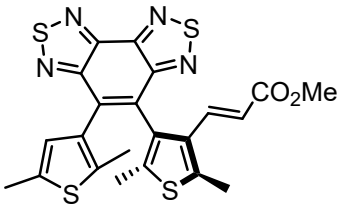


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.857	1649183	139657	50.026
2	7.085	1647497	117472	49.974
Total		3296680	257129	100.000



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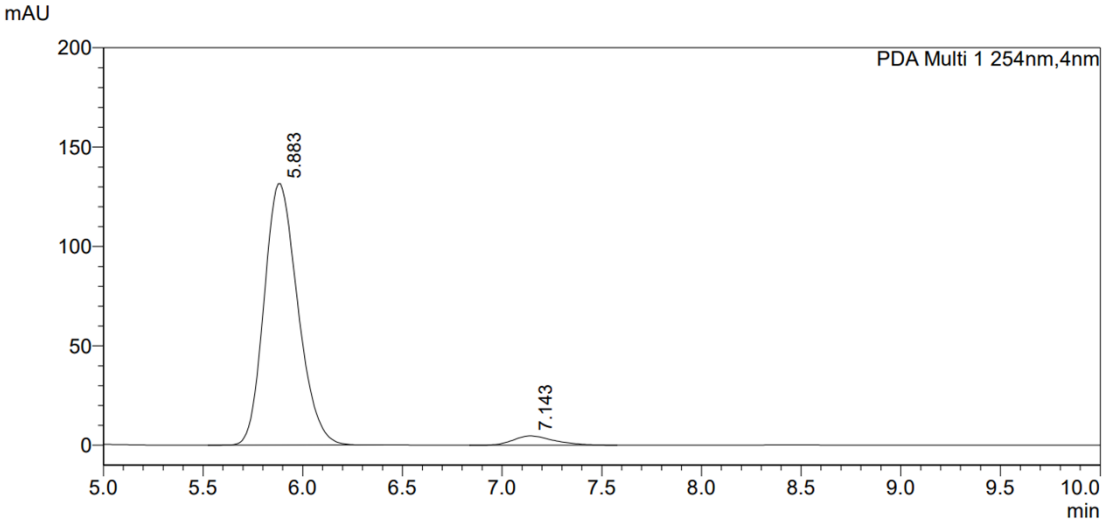
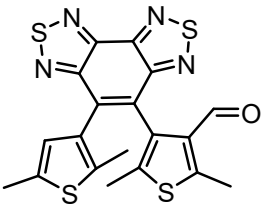


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.883	1544026	131520	95.916
2	7.143	65735	4665	4.084
Total		1609761	136185	100.000

7: OD-H, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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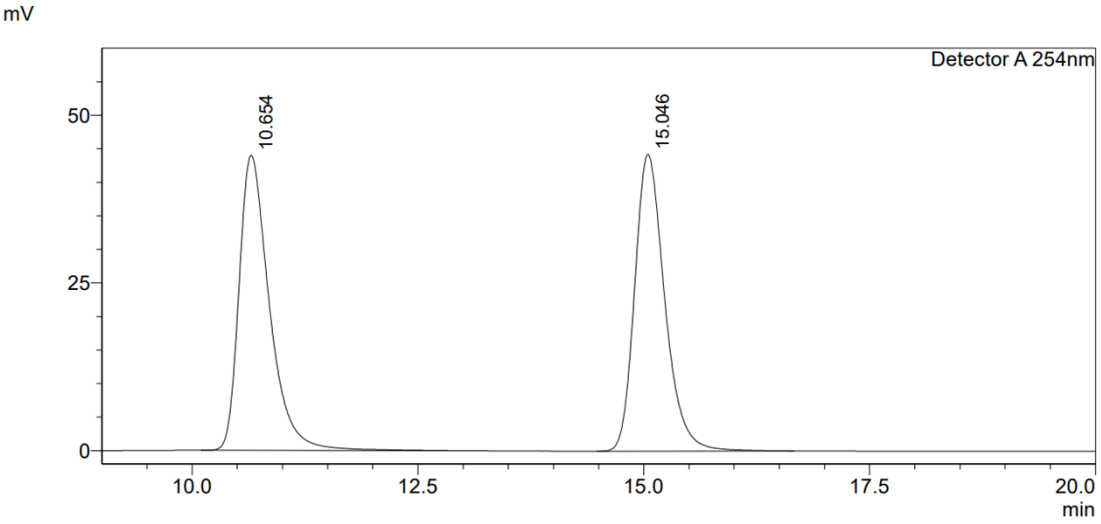
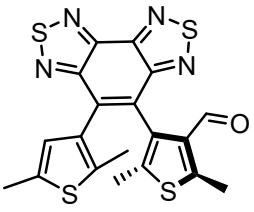


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.654	1028936	43985	50.120
2	15.046	1024024	44236	49.880
Total		2052960	88221	100.000



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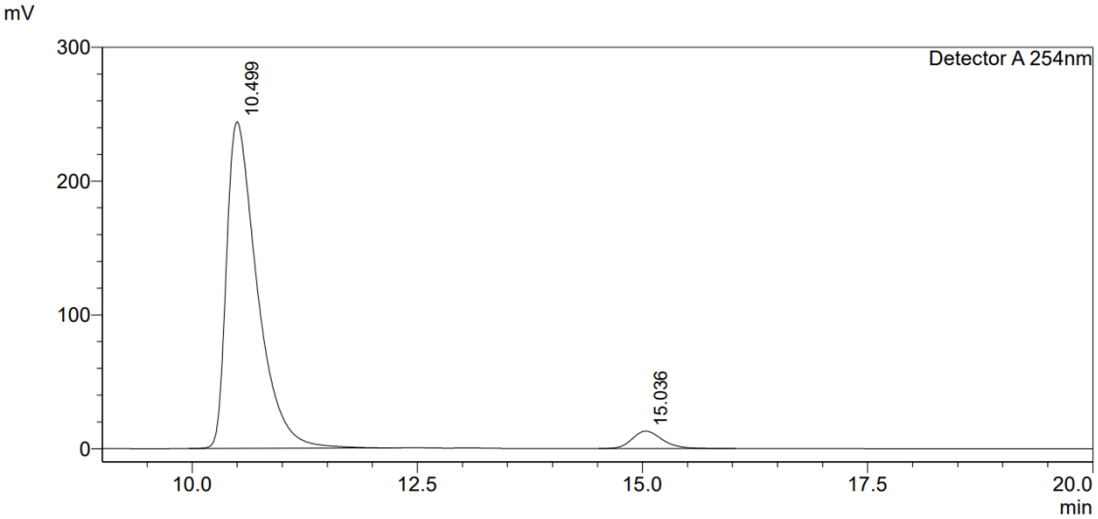
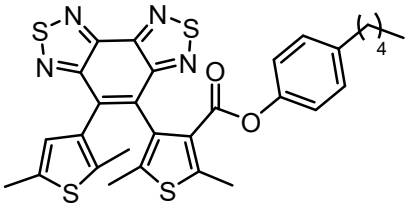


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.499	5780798	244253	95.071
2	15.036	299735	12974	4.929
Total		6080534	257227	100.000

9: AD-H, Hex/iPrOH=90/10, rate=1.000 mL/min, 254 nm



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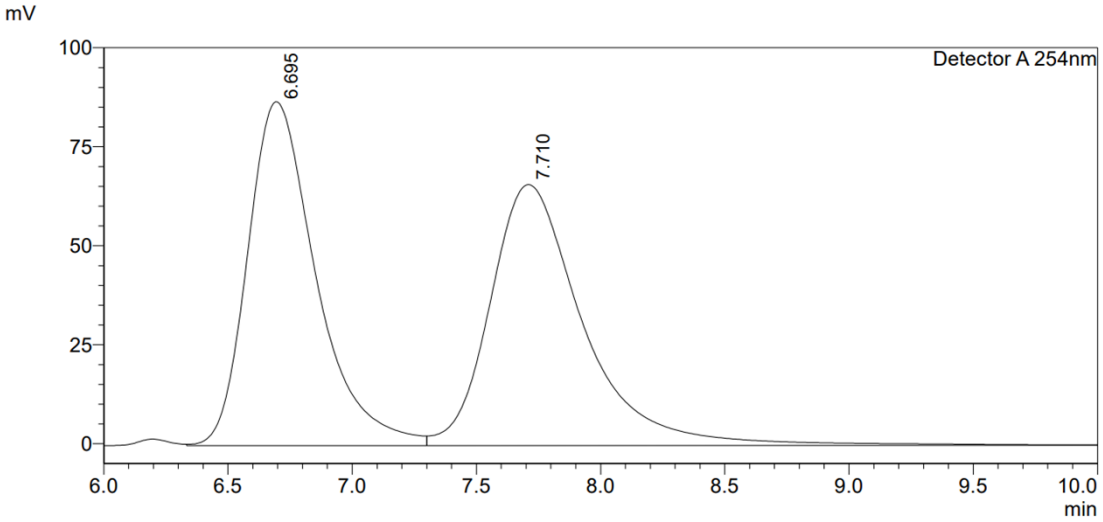
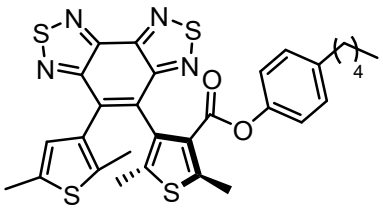


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.695	1661849	86839	49.054
2	7.710	1725966	65905	50.946
Total		3387815	152744	100.000



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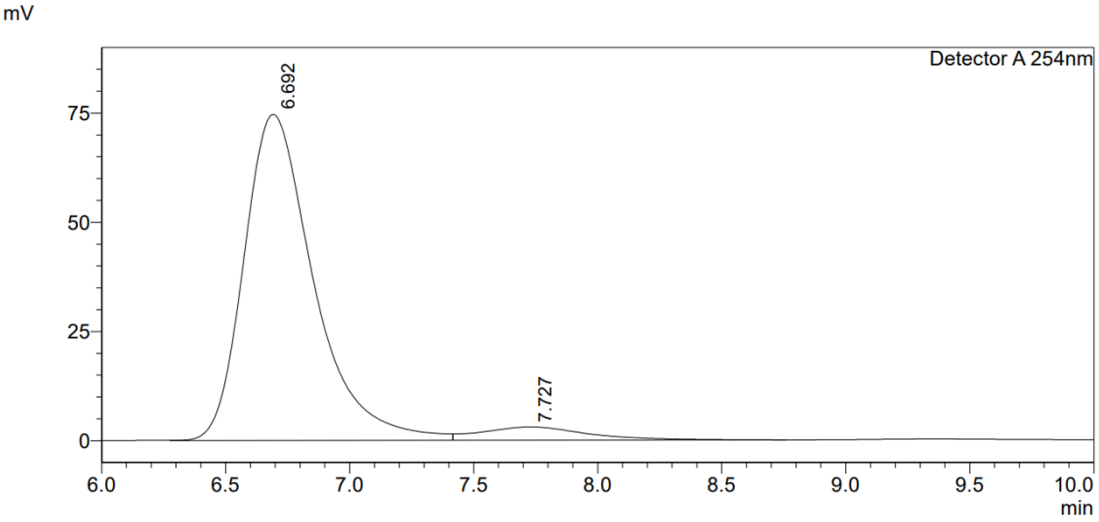
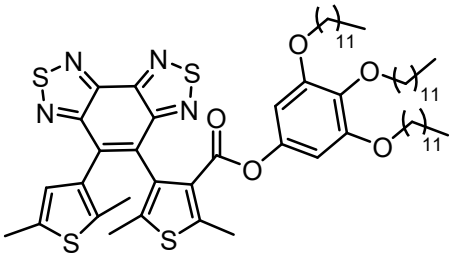


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.692	1458519	74668	94.223
2	7.727	89425	3004	5.777
Total		1547945	77672	100.000

10: IF-3, Hex/iPrOH=95/5, rate=1.000 mL/min, 254 nm



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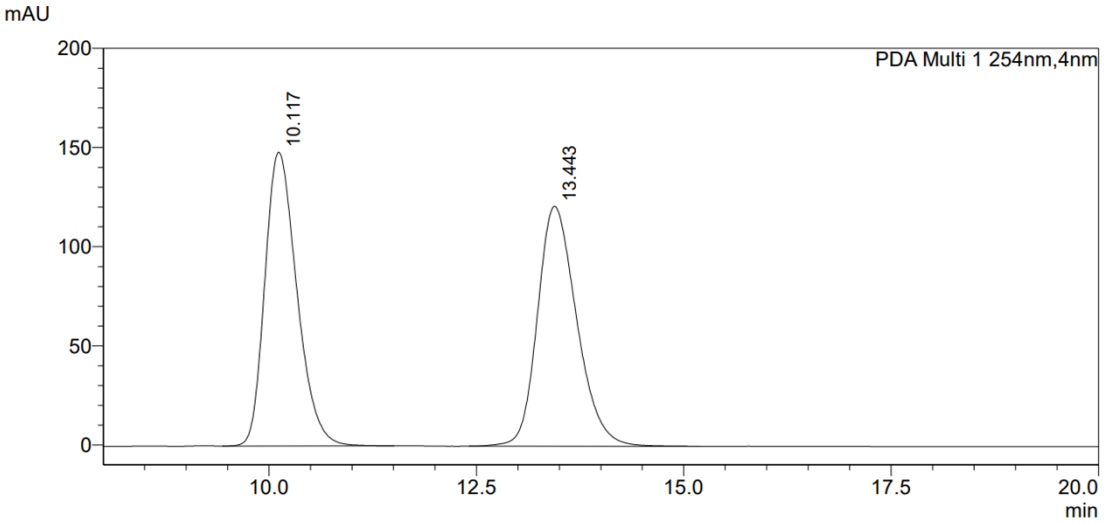
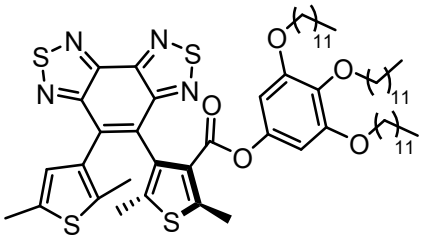


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.117	3984818	148185	50.018
2	13.443	3981882	120943	49.982
Total		7966700	269128	100.000



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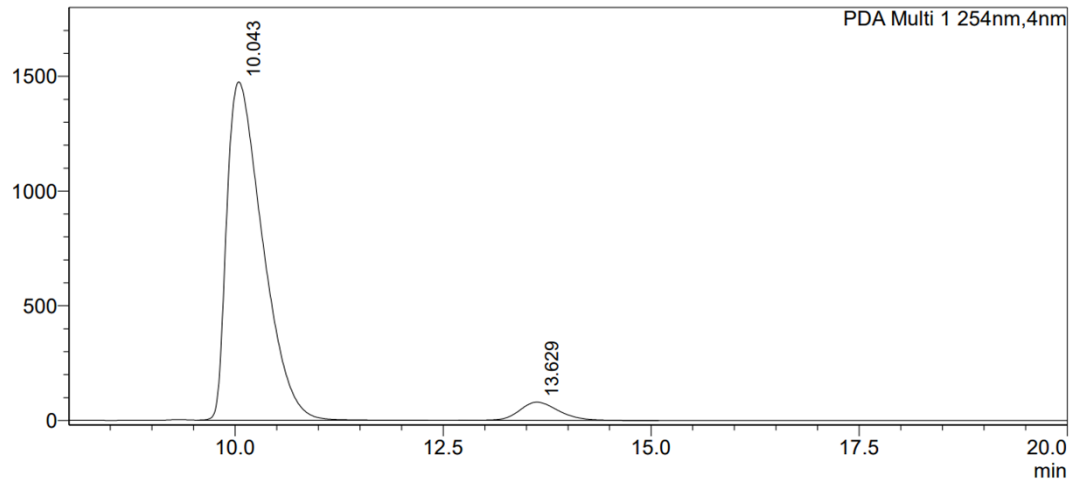
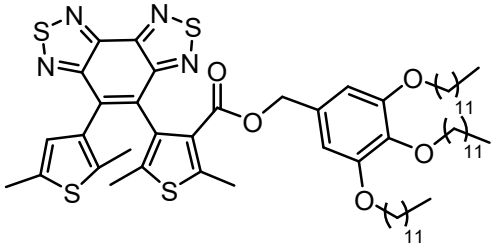


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.043	44301553	1475386	94.444
2	13.629	2606179	79666	5.556
Total		46907732	1555051	100.000

11: IC, Hex/iPrOH=97/3, rate=1.000 mL/min, 254 nm



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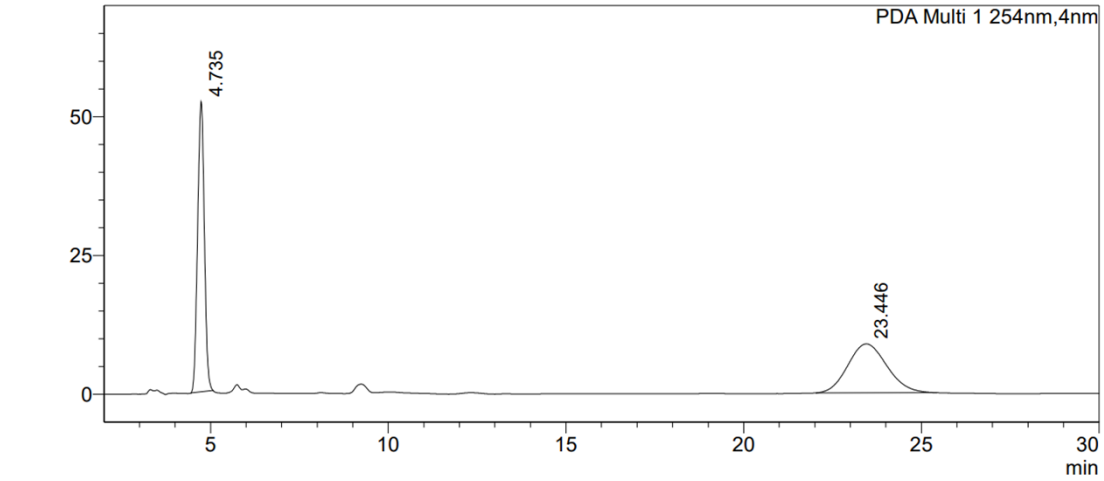
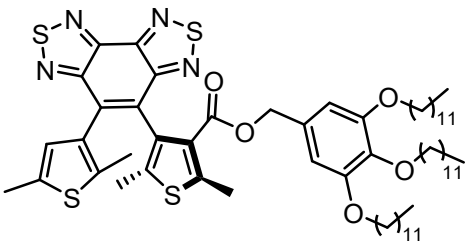


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	4.735	689505	52219	50.605
2	23.446	673015	8809	49.395
Total		1362520	61028	100.000



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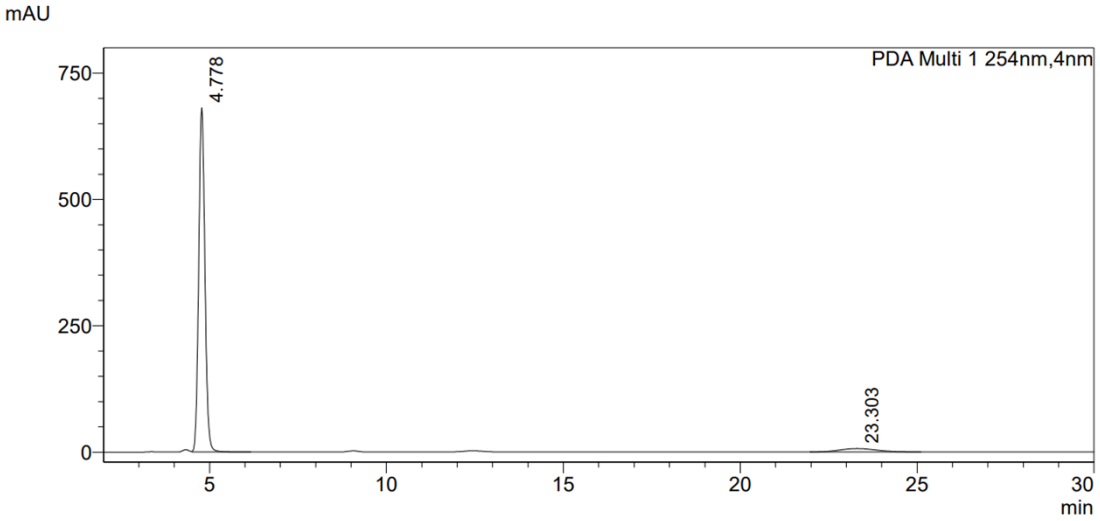

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	4.778	8322975	681713	94.438
2	23.303	490225	6783	5.562
Total		8813199	688496	100.000

10. References

S1 T. Sumi, Y. Takagi, A. Yagi, M. Morimotoa and M. Irie, *Chem. Commun.* 2014, **50**, 3928-3930.

S2 K. Uchida, E. Tsuchida, Y. Aoi and S. Nakamura, Irie, M. *Chem. Lett.* 1999, **28**, 63-64.

S3 Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

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S5 D. Podolskyy, O. Banji, and P. Rudquist, *Liquid Crystals.* 2008, **35**, 789-791.