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Supporting information

Thermal-induced reversible solid-state transformation of novel *s*-indacene 1,3,5,7-tetraone derivatives

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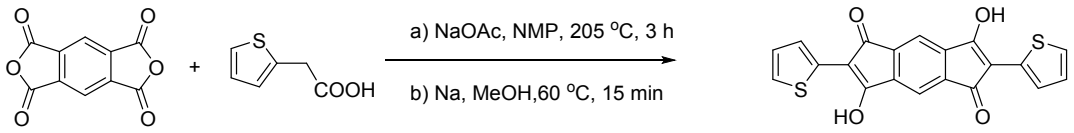
Experimental Section:

Preparation of 2,6-di(thiophen-2-yl)-s-indacene-*1,5*-dione-*3,7*-diol (DTID-diol)

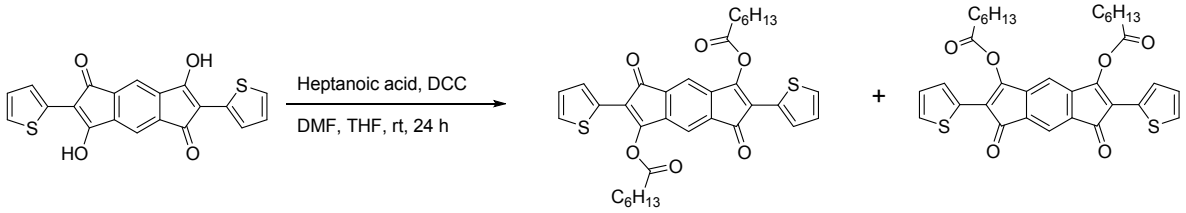


The mixture of pyromellitic anhydride (4.36 g, 20 mmol) and 2-thienyl-acetic acid (7.10 g, 50 mmol), anhydrous sodium acetate (0.82 g, 10 mmol) and 20 ml of 1-methyl-2-pyrrolidone (NMP) was stirred and heated at 205 °C under nitrogen atmosphere for 3 hours. After cooled down to room temperature, the formed solid was filtered off and wash with ethanol and then dried. The solid mixture without further purification was directly used in next step. (3.5g, 46%). MS (FD) m/z: 378.00 (M^+).

The dried solid was added into a sodium methoxide solution (methanol (25 ml) with sodium (1.0 g)) and heated to 60 °C with stirring for 15 min. After cooling down to room temperature, 100 ml water was added into the solution. Then the solution was filtered and the

filtrate was acidified by diluted HCl solution. The formed solid was collected and washed with water, dried under vacuum (DTID-diol) (3.0 g). ^{1}H NMR (DMSO-d_6, 600 MHz): 7.59 (s, 2H), 7.34 (s, 2H), 7.22 (s, 2H), 6.99 (t, J = 3.8 Hz, 2H). MS (FD) m/z: 378.00 (M^+) [cal. 378.00].

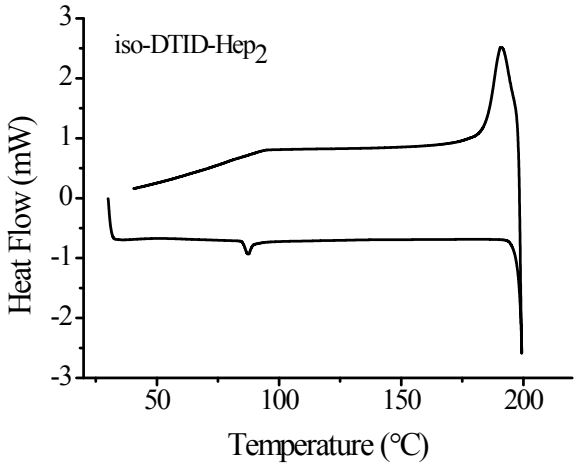
Preparation of 2,6-di(thiophen-2-yl)-s-indacene-*1,5*-dione-*3,7*-diyl diheptanoate (DTID-Hep$_2$) and 3,5-dioxo-2,6-di(thiophen-2-yl)-*3,5*-dihydro-s-indacene-*1,7*-diyl diheptanoate (iso-DTID-Hep$_2$)



To a solution of 2,6-di(thiophen-2-yl)-s-indacene-1,5-dione-3,7-diol (1.0g, 2.56 mmol) in THF (50 mL), heptanoic acid (0.72g, 5.56 mmol), N,N'-dicyclohexyylcarbodiimide (1.2 g, 5.82 mmol) and one drop of DMF was added. The solution was stirred at room temperature for 24 hours and the solid formed was filtered, and the filtrate was dried, followed purification by silica chromoatography to afford a dark blue solid (DTID-Hep$_2$) (DCM/Hexane:3/7) (0.28 g, 18%). mp: 176-179 °C. ^{1}H NMR ($CDCl_3$, 600MHz): 7.83 (d, J = 3.7 Hz, 2H), 7.42 (d, J = 5.0 Hz, 2H), 7.11 (t, J = 4.4 Hz, 2H), 7.04 (s, 2H), 2.79 (t, J = 7.5 Hz, 4H), 2.03 – 1.78 (m, 4H), 1.47 (dd, J = 14.6, 6.8 Hz, 4H), 1.43 – 1.32 (m, 8H), 1.01 – 0.88 (m, 6H). ^{13}C NMR ($CDCl_3$, 150MHz): 190.70, 169.27, 159.61, 141.93, 134.53, 129.91, 128.16, 127.59, 127.55, 117.02, 113.65, 34.29, 31.35, 28.76, 24.56, 22.45, 14.00. MS (FD) m/z: 602.15 (M^+) [cal. 602.18].

An isomer of the product with two ester side chains syn to each other (dark brown solid) was also obtained (iso-DTID-Hep$_2$) (0.29 g, 19%), mp: 195-197 °C. ^{1}H NMR ($CDCl_3$, 600MHz): 7.88 (d, J = 3.7 Hz, 2H), 7.58 (s, 1H), 7.45 (d, J = 5.1 Hz, 2H), 7.12 (t, J = 4.4 Hz,

2H), 6.50 (s, 1H), 2.78 (t, J = 7.5 Hz, 4H), 1.95 – 1.78 (m,4H), 1.47 (dd, J = 14.5, 6.7 Hz, 4H), 1.42-1.32 (m, 8H), 0.99 – 0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 150MHz): 189.80, 169.37, 157.73, 147.22, 129.96, 129.94, 128.89, 128.22, 127.68, 118.68, 116.45, 111.14, 34.32, 31.38, 28.79, 24.68, 22.46, 14.00. MS (FD) m/z: 602.16 (M^+) [cal. 602.18].



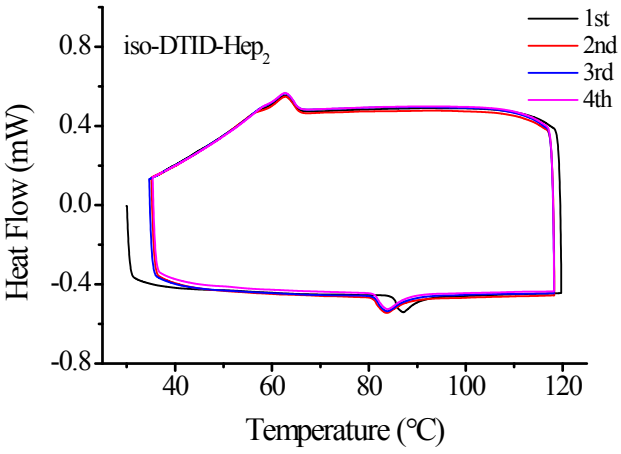


Figure S1. DSC data of iso-DTID-Hep$_2$. (a) first cyclic scan, heating from 30 °C to 200 °C. (b) four cyclic scans, heating from 30 °C to 120 °C. Heating and cooling rate: 5 °C/min

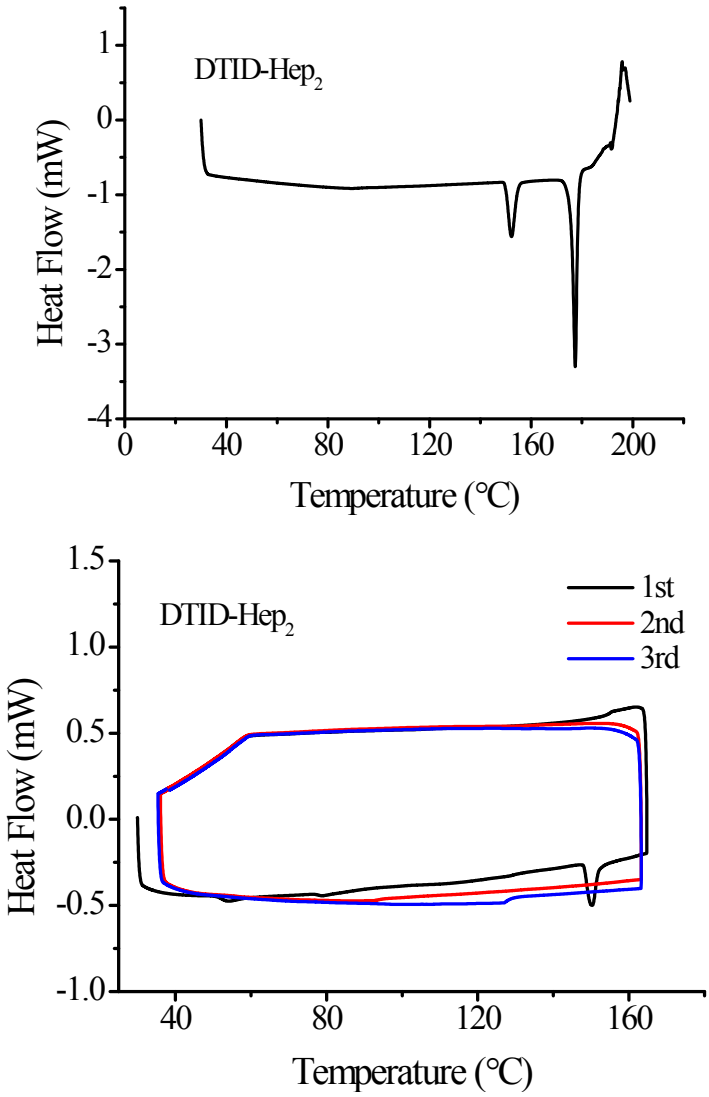
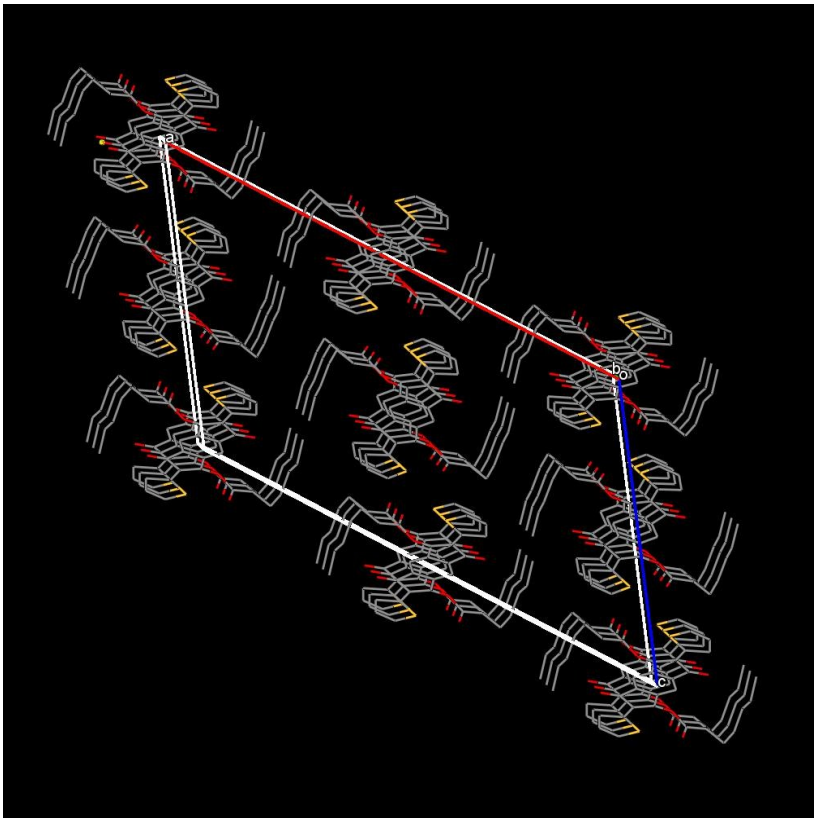


Figure S2. DSC data of DTID-Hep$_2$. (a) first cyclic scan, heating from 30 °C to 200 °C. (b) three cyclic scans, heating from 30 °C to 165 °C. Heating and cooling rate: 5 °C/min

Table S1: Single-crystal X-ray diffraction data of DTID-Hep_2 and iso-DTID-Hep_2

	Space group	**Cell lengths (Å)**	**Cell angles (°)**	**Cell volume (Å)**	**d $^{\pi-\pi}$ (Å)**	**R-factor**
DTID-Hep_2 (Form1)	C2/c	a = 31.156(5) b = 6.3506(9) c = 18.772(3)	α = 90.00 β = 124.840(11) γ = 90.00	3048.44 (Z=4)	3.228	8.08%
DTID-Hep_2 (Form2)	P 2_1/c	a = 17.6560(14) b = 5.4631(5) c = 15.1854(12)	α = 90.00 β = 91.22 γ = 90.00	1464.4 (Z=2)	--	5.18%
iso-DTID-Hep_2	P 2_12_12	a = 20.427 (18) b = 28.01(3) c = 5.260(5)	α = 90.00 β = 90.00 γ = 90.00	3009.56 (Z = 4)	3.401	6.86%

(a)



(b)

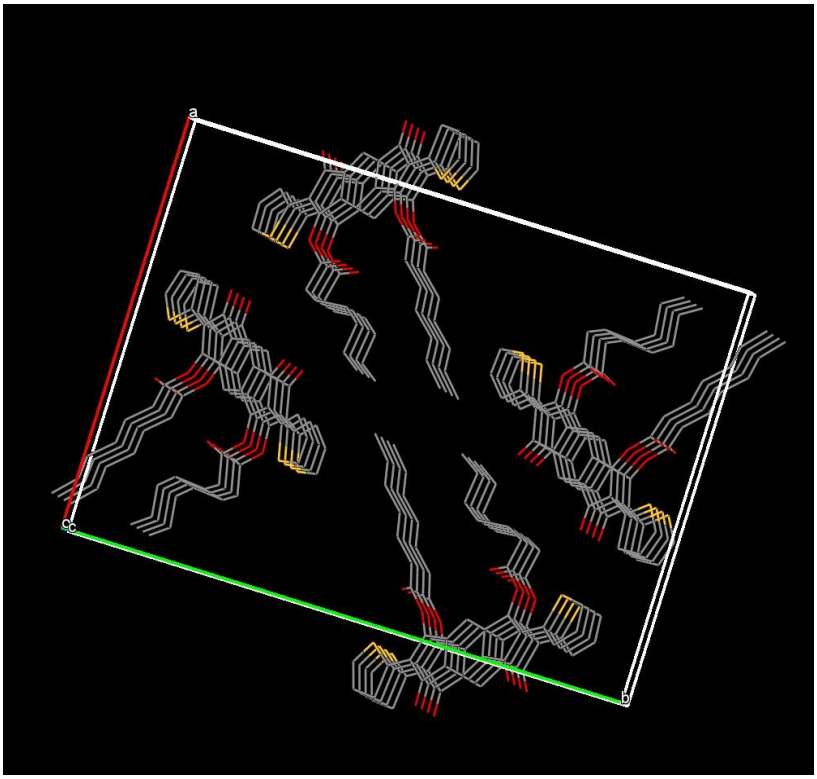
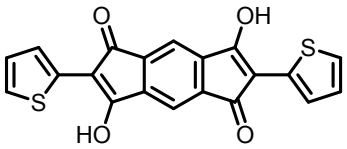


Figure S4. X-ray crystallographic packing of Form 2 of DTID-Hep$_2$ (a) and iso-DTID-Hep$_2$ (b).

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Data collected on: Jan 17 2014

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Sample #1, Operator: xshen

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 Pulse 45.0 degrees
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Total time 0 min 43 sec
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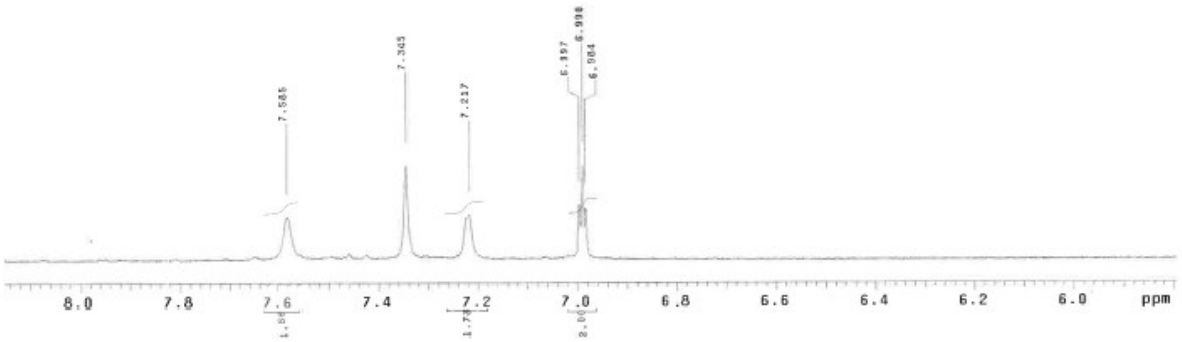

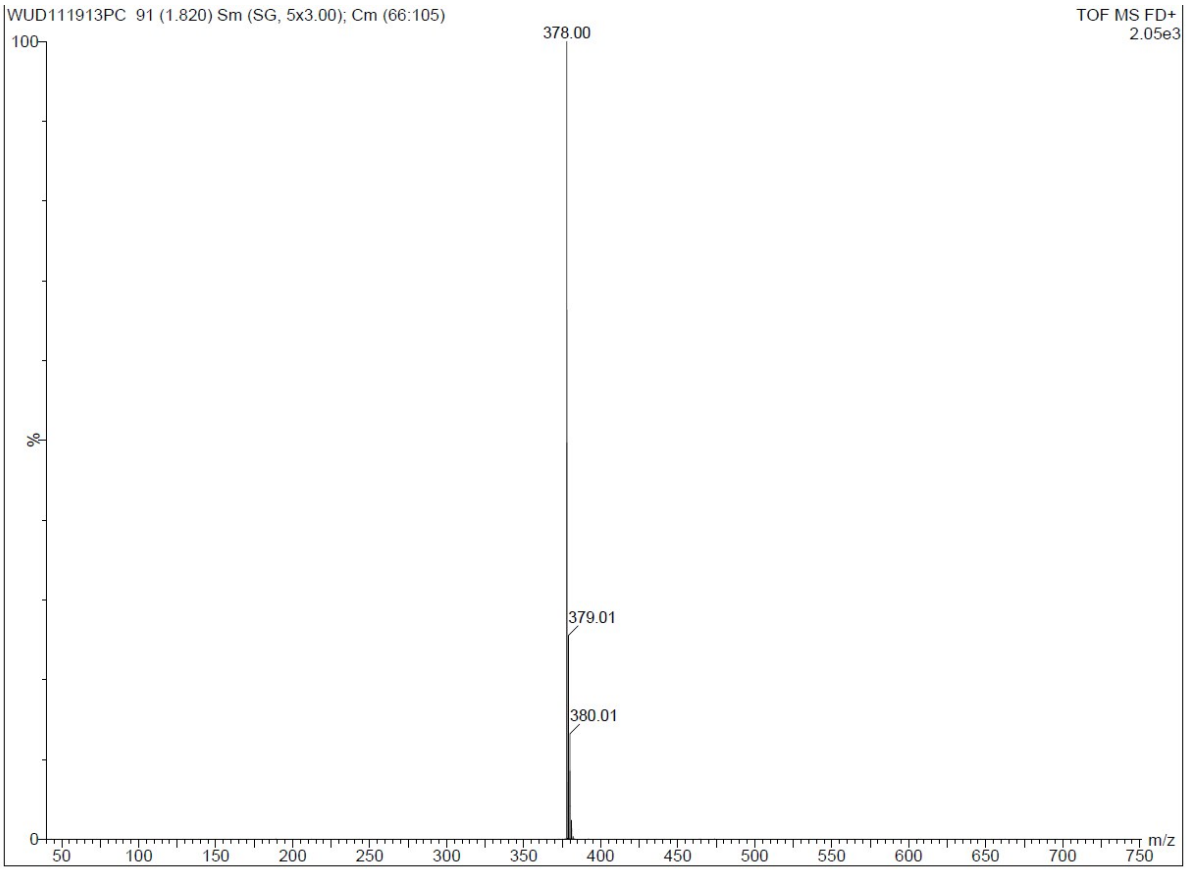

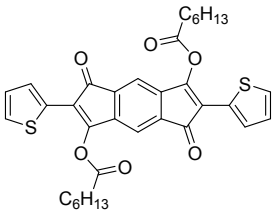
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O
S
S
O
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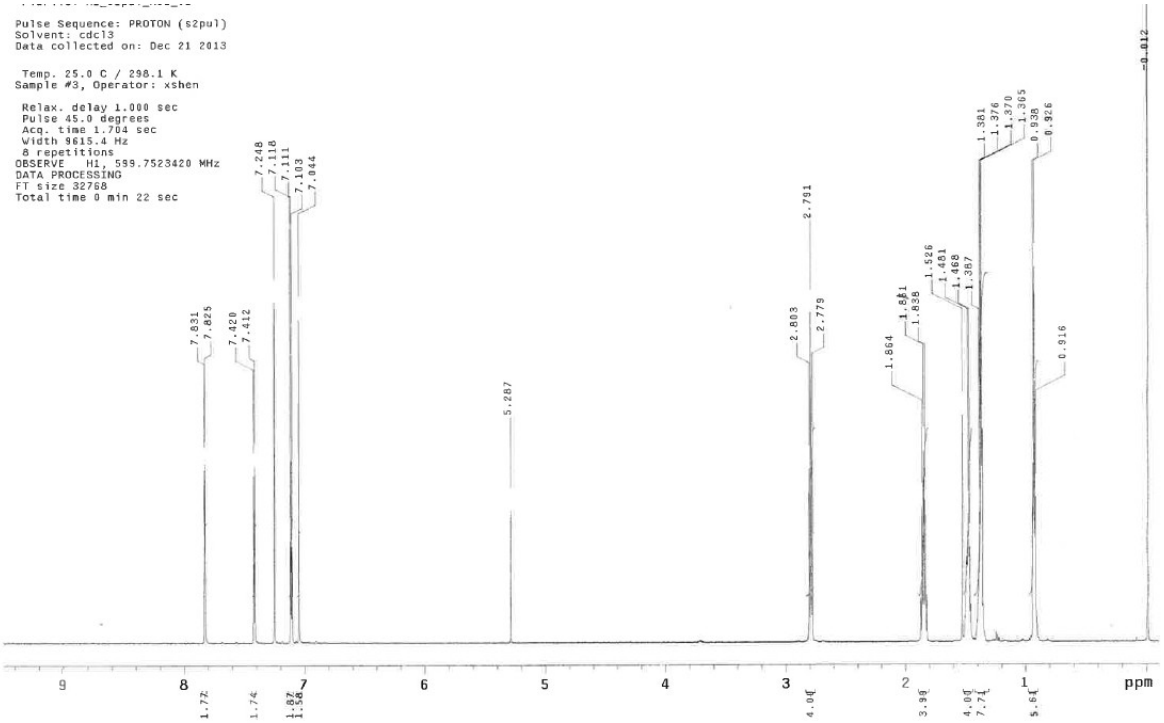
O
C6H13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Pulse 45.0 degrees
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Width 9615.4 Hz
8 repetitions
OBSERVE H1, 599.7523420 MHz
DATA PROCESSING
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Total time 0 min 22 sec
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7.412
7.248
7.118
7.111
7.103
7.044
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2.779
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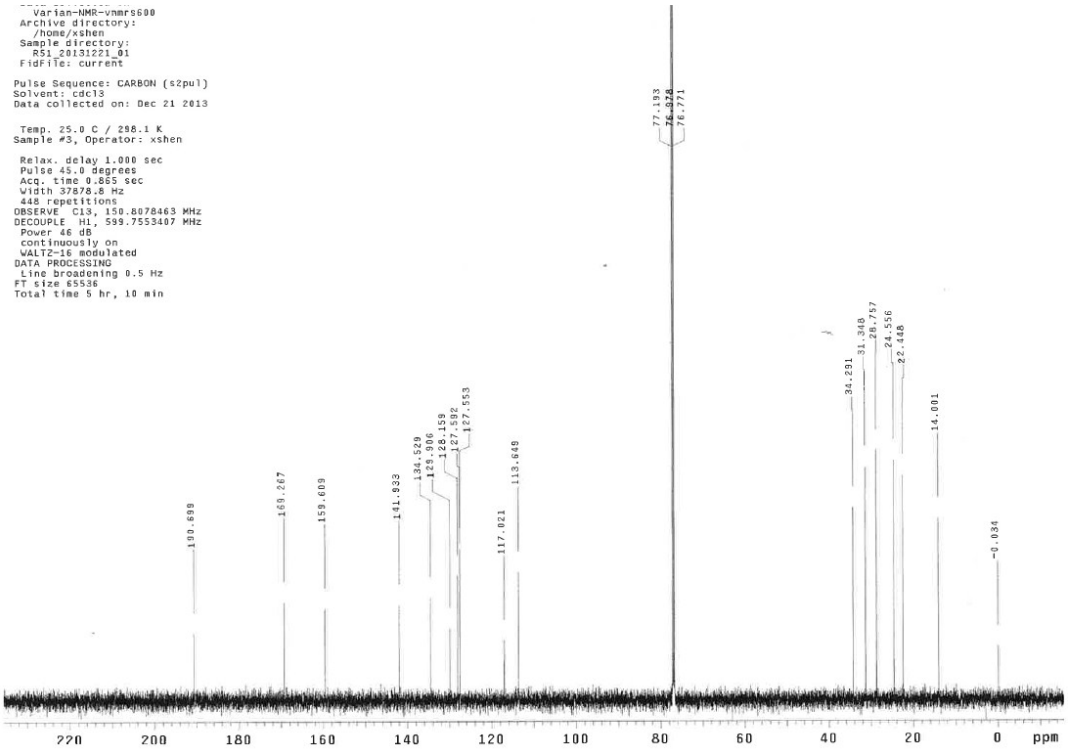
Varian-NMR-vnmrs600
Archive directory:
/home/xshen
Sample directory:
R51_20131221_01
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Solvent: cdcl3
Data collected on: Dec 21 2013
Temp. 25.0 C / 298.1 K
Sample #3, Operator: xshen
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.865 sec
Width 37878.8 Hz
448 repetitions
OBSERVE C13, 150.8078463 MHz
DECOUPLE H1, 599.7553407 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
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190.698
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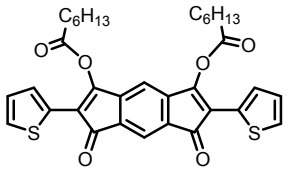
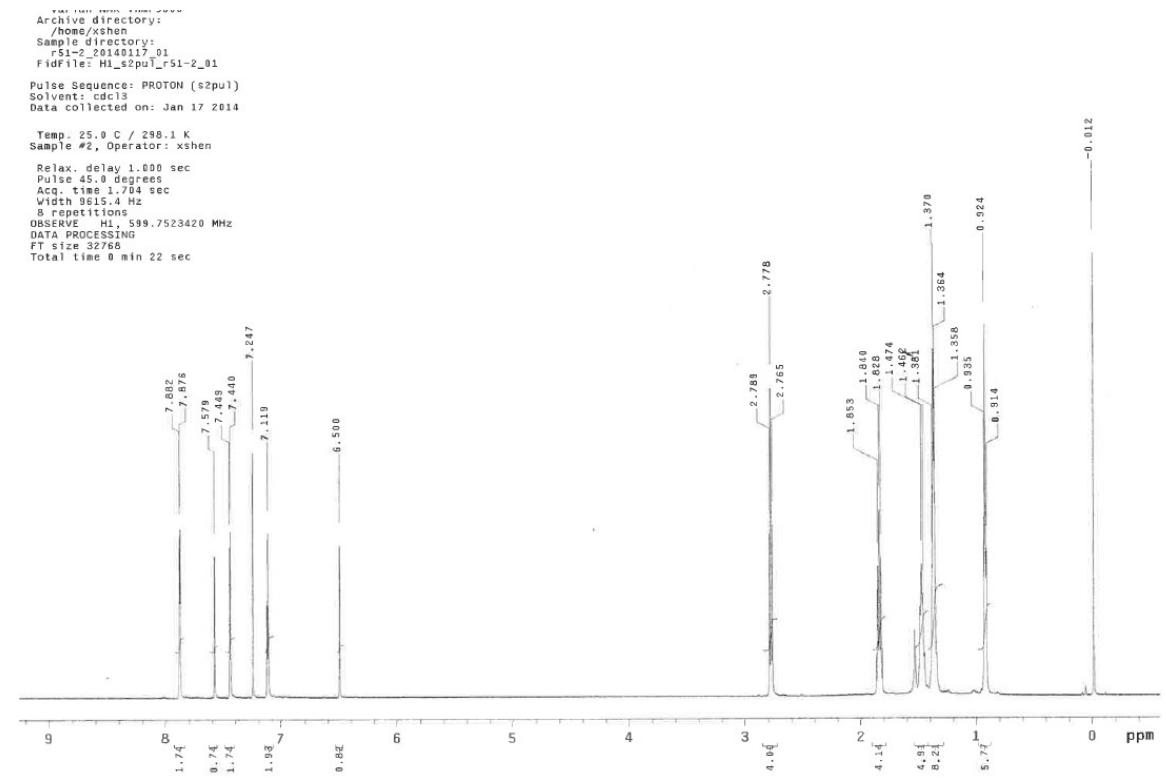

C6H13
C6H13
O
O
O
O
O
O
S
S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Solvent: cdcl3
Data collected on: Jan 17 2014
Temp. 25.0 C / 298.1 K
Sample #2, Operator: xshen
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.704 sec
Width 9615.4 Hz
8 repetitions
OBSERVE H1, 599.7523420 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 22 sec
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7.579
7.449
7.440
7.247
7.119
6.500
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2.789
2.765
1.853
1.840
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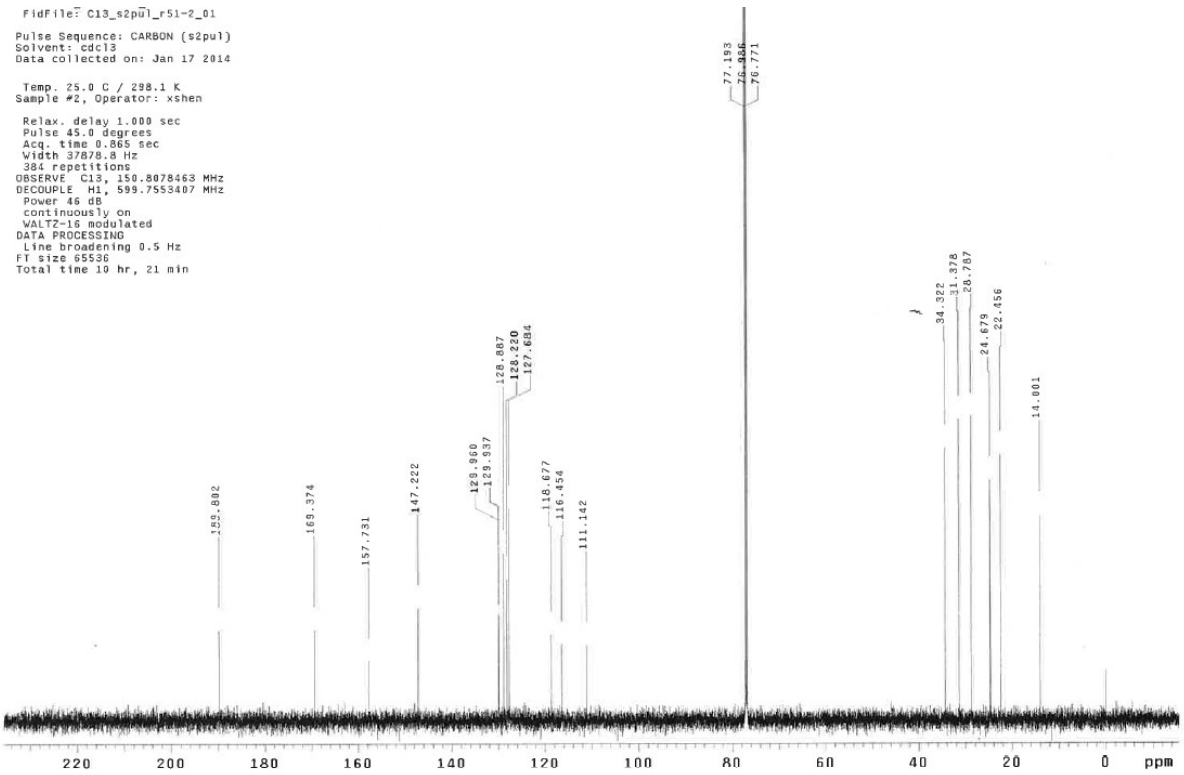
ppm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Solvent: cdcl3
Data collected on: Jan 17 2014
Temp. 25.0 C / 298.1 K
Sample #2, Operator: xshen
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.865 sec
Width 37878.8 Hz
384 repetitions
OBSERVE C13, 150.8078463 MHz
DECOUPLE H1, 599.7553407 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
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ppm