A spiro-bifluorene based 3D electron acceptor with dicyanovinylene substitution for solution processed non-fullerene organic solar cells

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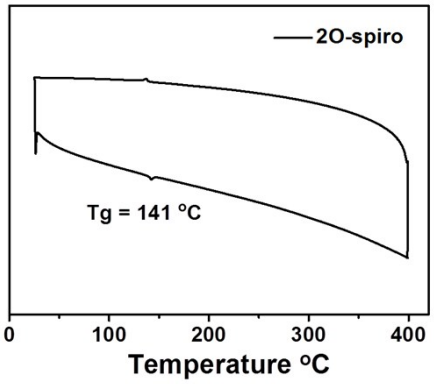
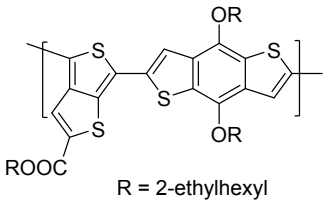


Figure S1. DSC thermograms of the **2O-spiro** on heating and cooling cycles, heating/cooling rate = 10 °C/min.



PTB7

Scheme S1. The chemical structure of **PTB7**

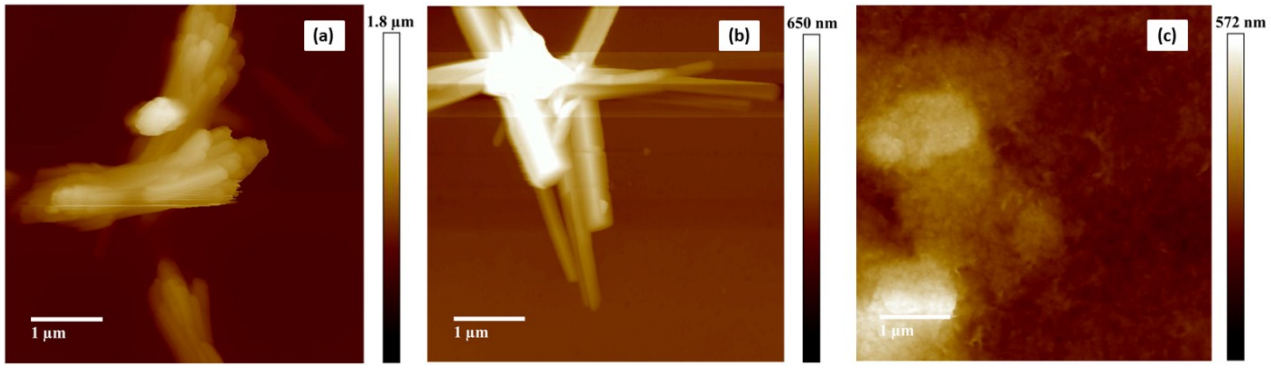


Figure S2. AFM height images of PTB7:4CN-spiro (1:1, w/w) blend processed by different solvents: (a) tetrachloroethane/DCB; (b) DCB; (c) tetrachloroethane/3%DIO.

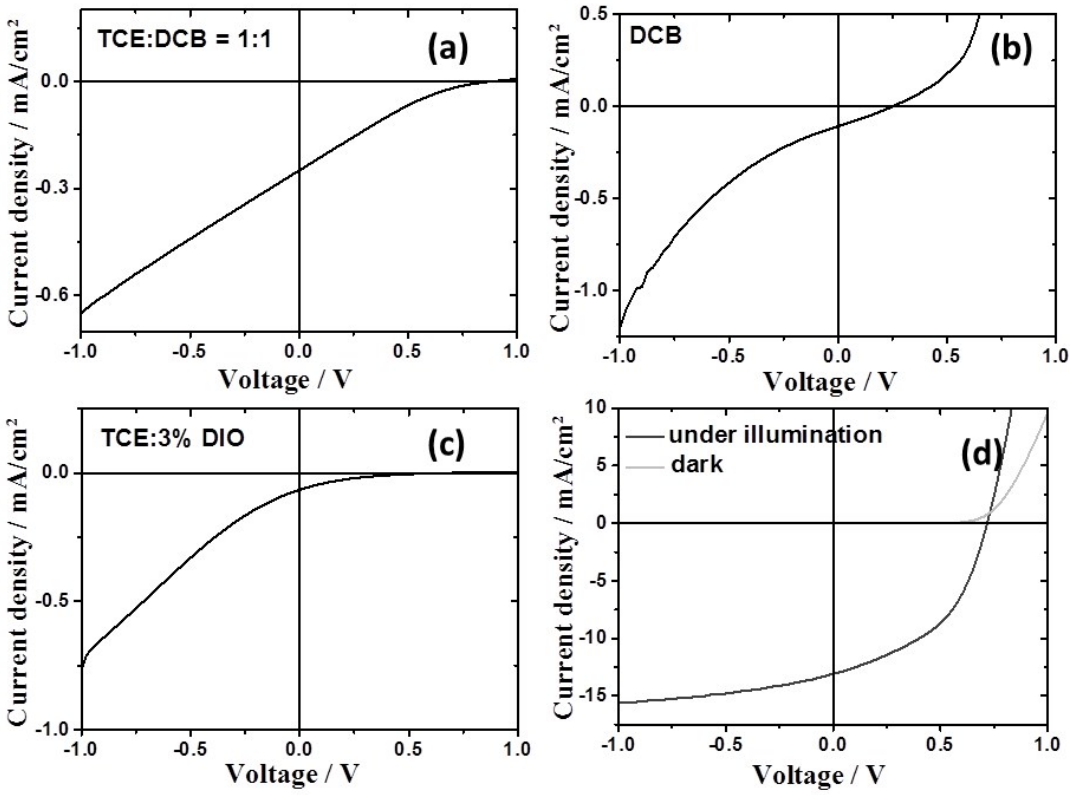
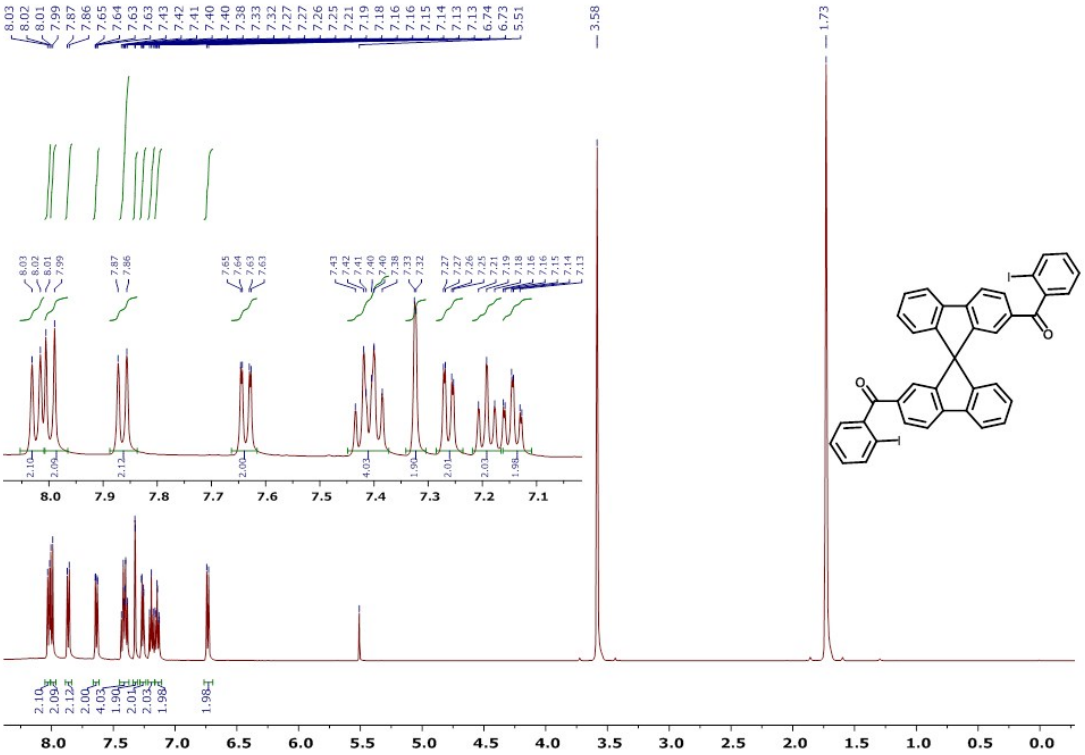


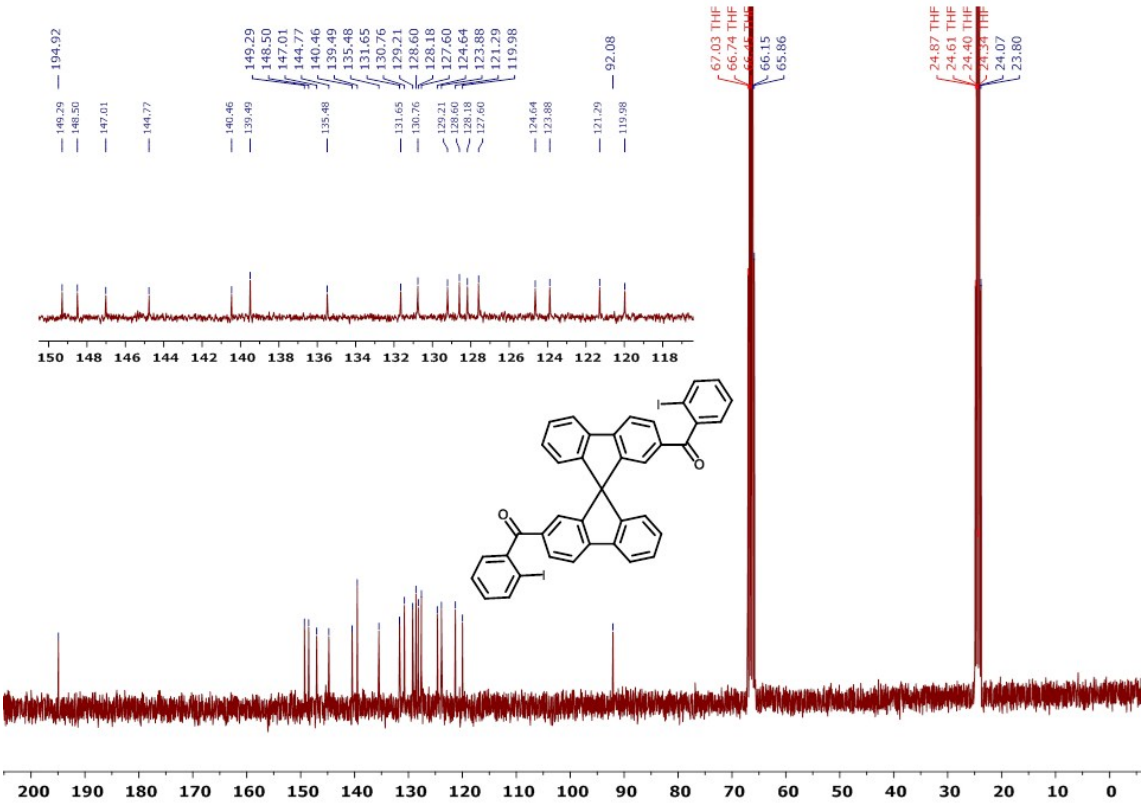
Figure S3. Current density-voltage (J-V) curves of the OPVs processed by different solvents: (a) tetrachloroethane/DCB; (b) DCB; (c) tetrachloroethane/3%DIO; (d) PTB7:$PC_{70}BM$ solar cell processed from CB/3%DIO.

^{1}H−NMR and ^{13}C−NMR Spectrum

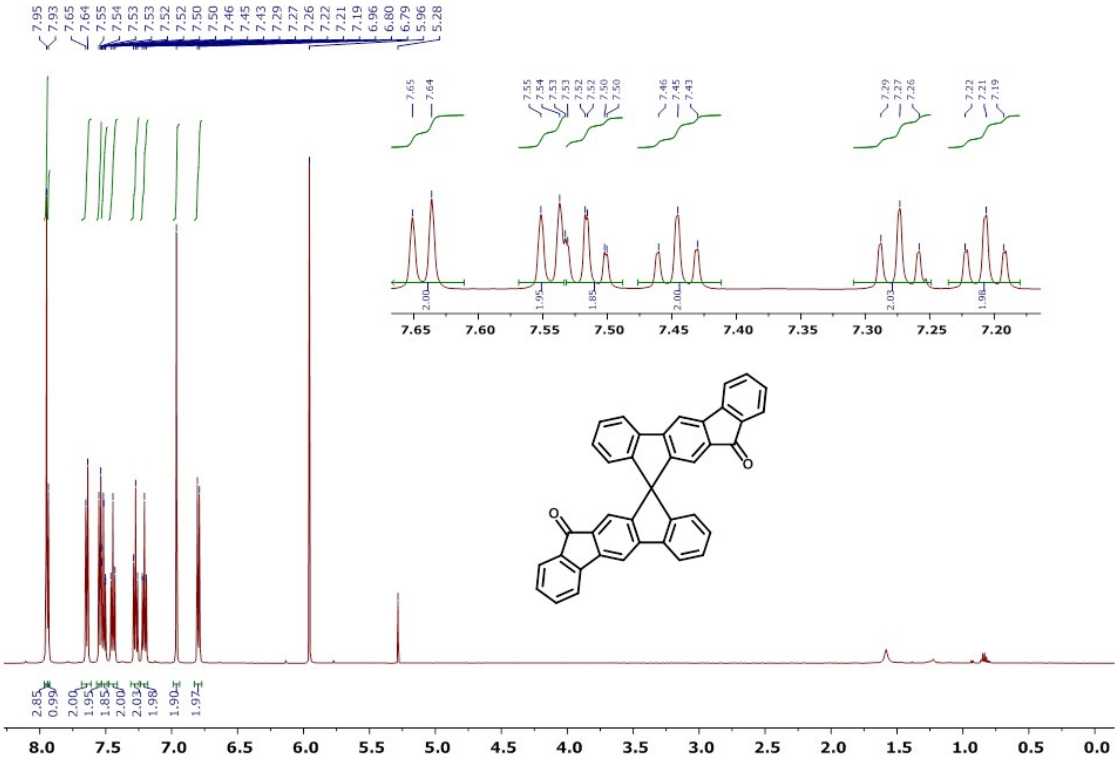
^{1}H NMR spectrum of Compound 1 in $C_2D_2Cl_4$



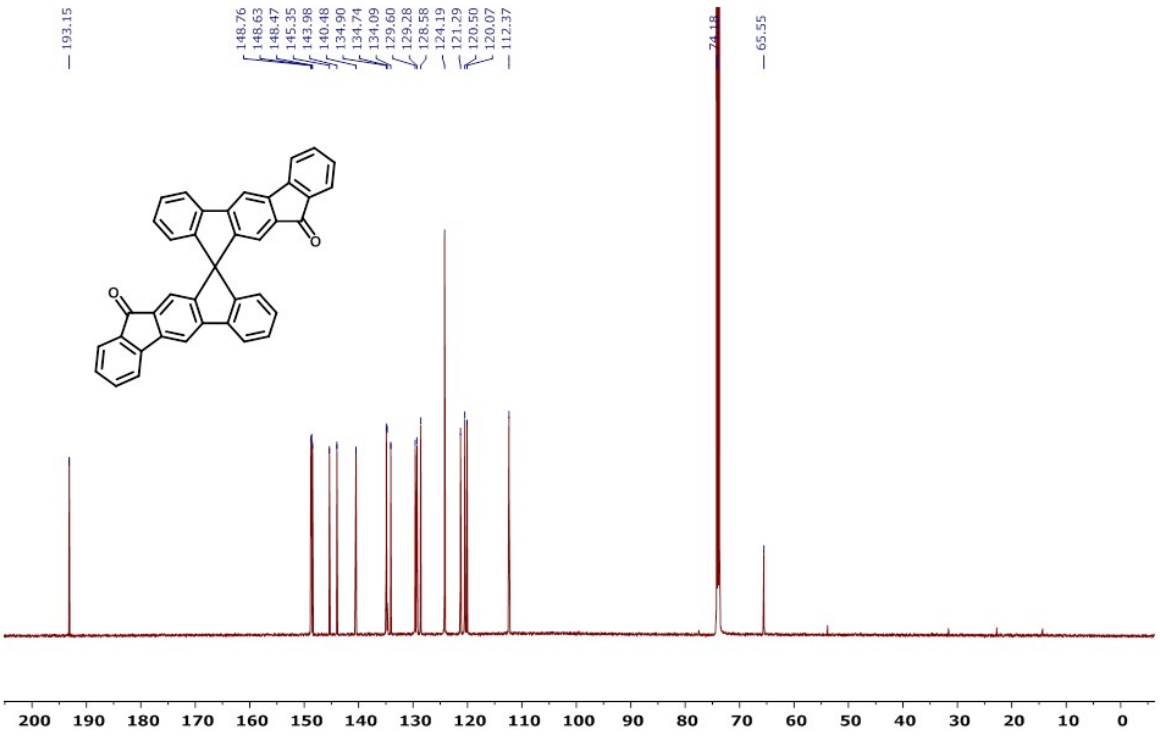
^{13}C NMR spectrum of Compound 1 in $C_2D_2Cl_4$



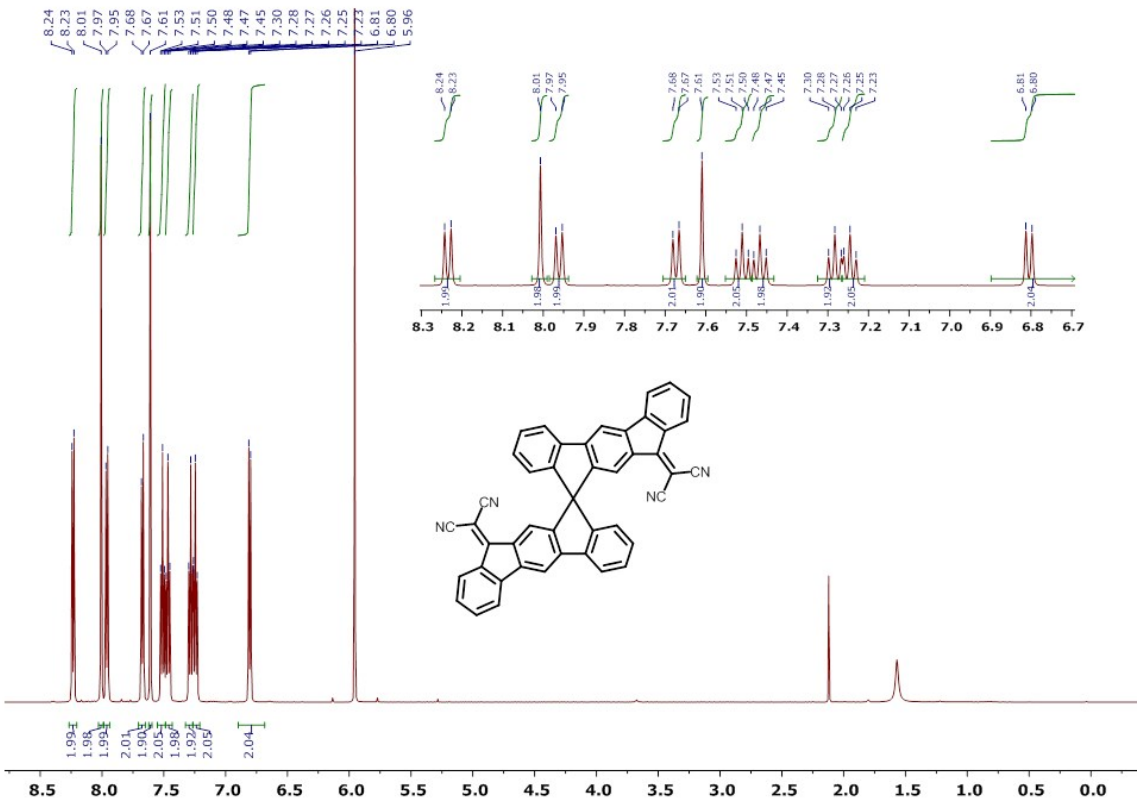
^{1}H NMR spectrum of Compound 2O-spiro in $C_2D_2Cl_4$



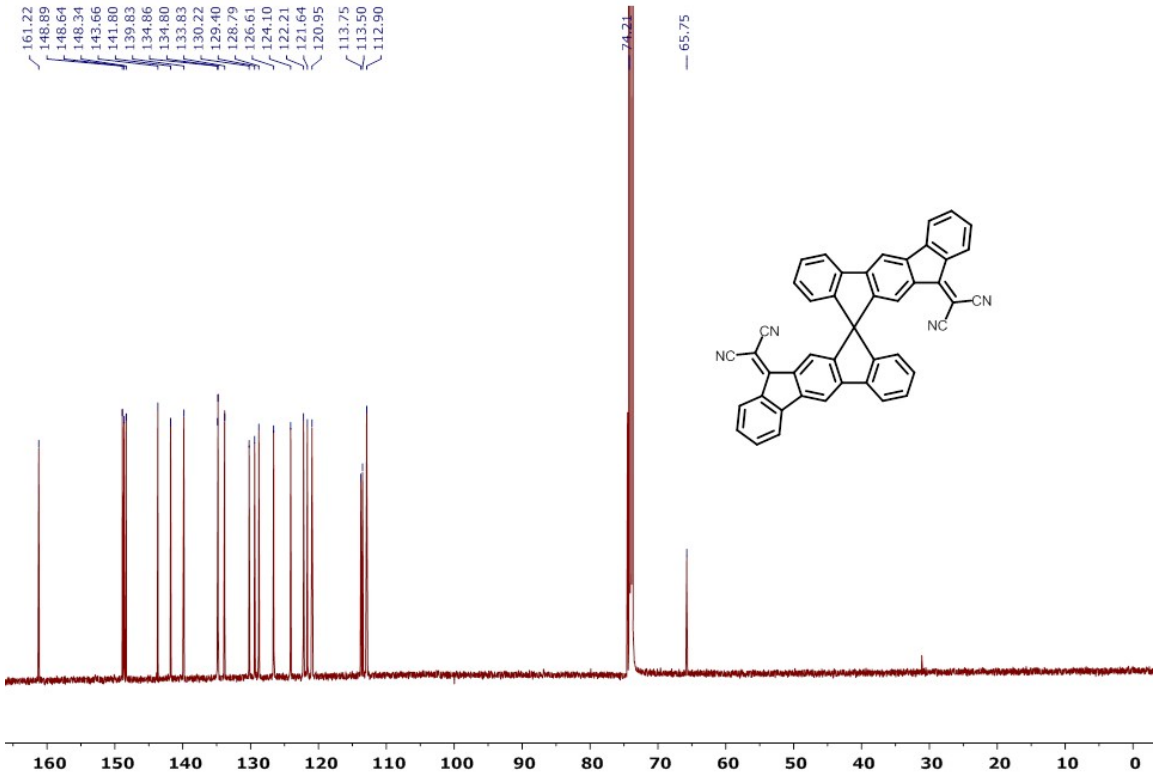
^{13}C NMR spectrum of Compound 2O-spiro in $C_2D_2Cl_4$



^{1}H NMR spectrum of Compound 4CN-spiro in $C_2D_2Cl_4$



^{13}C NMR spectrum of Compound 4CN-spiro in $C_2D_2Cl_4$



HRMS spectra

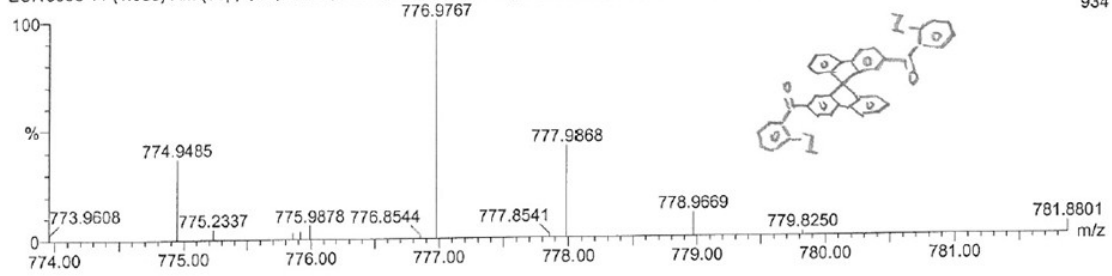
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Xia, 2I-2O-Spiro, Muellen
ESI15938 41 (1.039) AM (Top,4, Ar,8000.0,772.46,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (39:53)

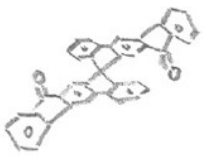
1: TOF MS ES+
934



Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
776.9767	776.9788	-2.1	-2.7	27.5	1	C39 H23 O2 127I2

Elemental Composition Report

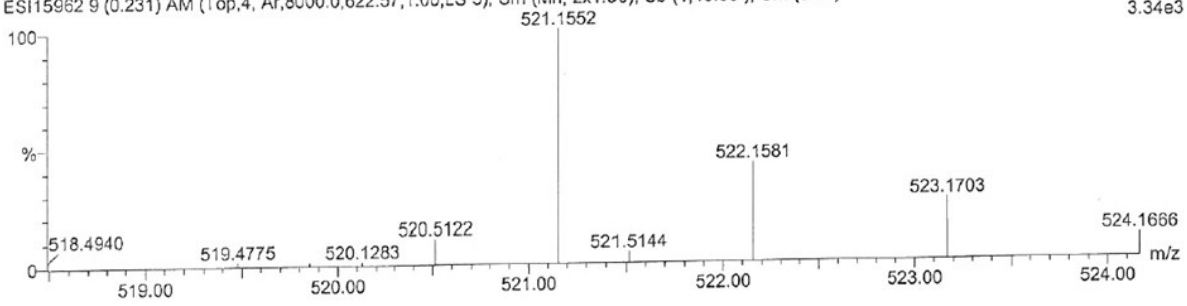
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%



Monoisotopic Mass, Odd and Even Electron Ions
14 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Xia, 2O-Spiro, Muellen
ESI15962 9 (0.231) AM (Top,4, Ar,8000.0,622.57,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (9:19)

1: TOF MS ES+
3.34e3



Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
521.1552	521.1542	1.0	2.0	29.5	1	C39 H21 O2

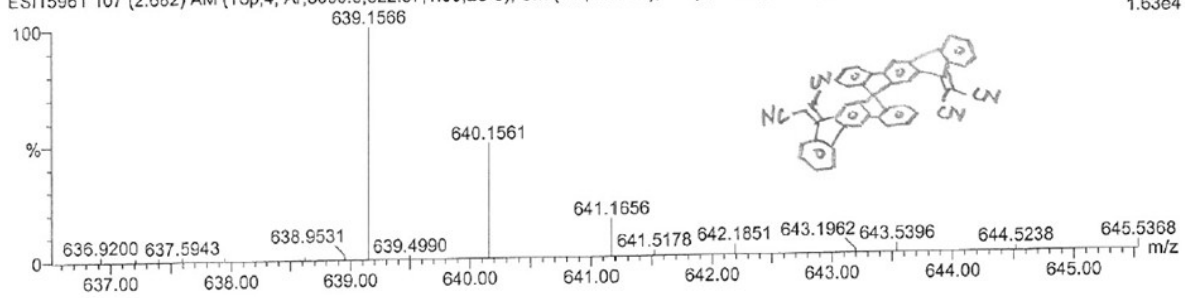
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Xia, 4CN-Spiro, Muellen
ESI15961 107 (2.682) AM (Top,4, Ar,8000.0,622.57,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (95:107)

1: TOF MS ES+
1.63e4



Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
639.1566	639.1586	-2.0	-3.1	37.5	1	C45 H20 N4 23Na

Crystal data of 2O-spiro and 4CN-spiro

The crystal structures were solved by the software Mercury 3.1 and the crystal images were created with the software PowerPoint 2010.

Table 1. Crystal data and structure refinement for compound 2O-spiro.

formula	$C_{39}H_{20}O_2$		
molecular weight	520.55 $gmol^{-1}$		
absorption	μ = 0.08 mm^{-1}		
crystal size	0.26 x 0.27 x 0.3 mm^3 yellow block		
space group	P $2_1/c$ (monoclinic)		
lattice parameters	a = 17.6736(8)Å		
(calculate from	b = 15.8144(5)Å	ß = 109.009(3)°	
21390 reflections with	c = 19.7873(9)Å		
2.5° < θ < 28.4°)	V = 5228.9(4)$Å^3$	z = 8	F(000) = 2160
temperature	-80°C		
density	d_{xray} = 1.322 gcm^{-3}		

<u>data collection</u>

diffractometer	STOE IPDS 2T
radiation	Mo-K_α Graphitmonochromator
Scan – type	ω scans
Scan – width	1°
scan range	2° ≤ θ < 28°
	-18 ≤ h ≤ 23 -20 ≤ k ≤ 18 -26 ≤ l ≤ 26
number of reflections:	
measured	34000
unique	12573 (R_{int} = 0.0551)
observed	7447 (|F|/σ(F) > 4.0)

daten correction, structure solution and refinement

corrections	Lorentz and polarisation correction.
Structure solution	Program: SIR-2004 (Direct methods)
refinement	Program: SHELXL-2014 (full matrix). 739 refined parameters, weighting scheme:
	$w=1/[\sigma^2(F_o^2) + (0.0514*P)^2+0.24*P]$ with $(Max(F_o^2,0)+2*F_c^2)/3$. H-atoms at calculated positions and refined with isotropic displacement parameters, non H-atoms refined anisotropically.
R-values	wR2 = 0.1168 (R1 = 0.048 for observed reflections, 0.0975 for all reflections)
goodness of fit	S = 1.003
maximum deviation of parameters	0.001 * e.s.d
maximum peak height in diff. Fourier synthesis	0.27, -0.17 eÅ^{-3}

Table 2. Crystal data and structure refinement for compound 4CN-spiro.

formula	$2(C_{45}H_{20}N_4), CH_2Cl_2$
molecular weight	1318.23 gmol^{-1}
absorption	μ = 1.273 mm^{-1} correction with 6 faces

transmission	T_{min} = 0.785, T_{max} = 0.987
crystal size	0.01 x 0.01 x 0.2 mm^3 brown needle
space group	P -1 (triclinic)
lattice parameters	a = 14.0610(12)Å α = 99.814(7)°
(calculate from	b = 15.0528(14)Å ß = 90.613(7)°
15604 reflections with	c = 33.272(3)Å γ = 92.172(7)°
2.7° < θ < 51.2°)	V = 6933.3(11)$Å^3$ z = 4 F(000) = 2712
temperature	-60°C
density	d_{xray} = 1.263 gcm^{-3}

data collection

diffractometer	STOE IPDS 2T
radiation	Cu-K_α mirror system IμS
Scan – type	ω scans
Scan – width	1°
scan range	3° ≤ θ < 68°
	-15 ≤ h ≤ 15 -18 ≤ k ≤ 17 -39 ≤ l ≤ 39
number of reflections:	
measured	94677
unique	23561 (R_{int} = 0.3682)
observed	3389 (|F|/σ(F) > 4.0)

daten correction, structure solution and refinement

corrections	Lorentz and polarisation correction.
Structure solution	Program: SHELXD-2013
refinement	Program: SHELXL-2013 (full matrix). 1819 refined parameters, weighting scheme:
	$w=1/[\sigma^2(F_o^2) + (0.0486*P)^2]$ with $(Max(F_o^2,0)+2*F_c^2)/3$. H-atoms at calculated positions and refined with isotropic displacement parameters, non H-atoms refined anisotropically.
R-values	wR2 = 0.2318 (R1 = 0.0725 for observed reflections, 0.3689 for all reflections)
goodness of fit	S = 0.68

maximum deviation of parameters	0.001 * e.s.d
maximum peak height in diff. Fourier synthesis	0.32, -0.32 eÅ^{-3}
remark	structure contains four different molecules and a number of solvent molecules. One potential place for solvent molecules could not be located. Squeeze was use for moldelling the electron density.