

Supporting Information

Highly Soluble Indigo Derivatives as Practical Diesel Absorption Markers

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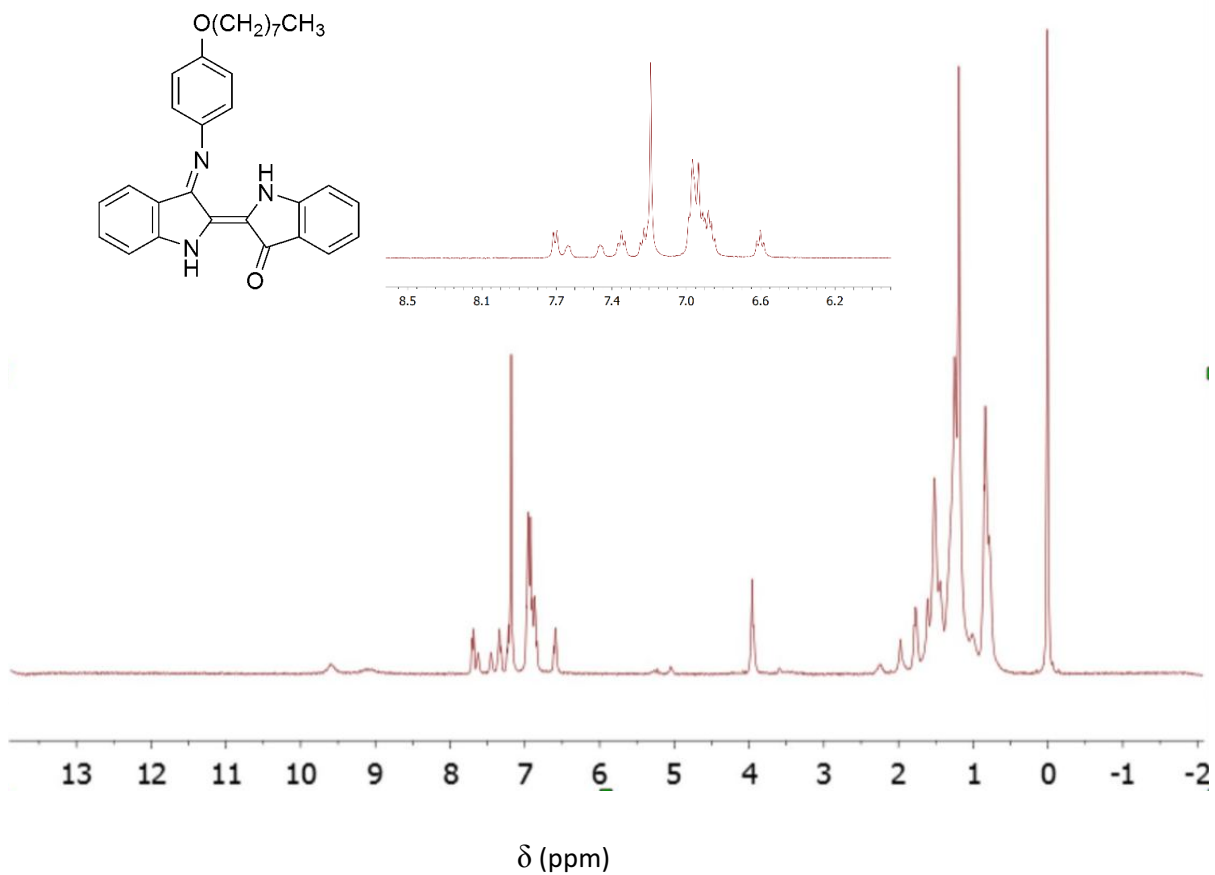


Figure S1. ^1H -NMR spectrum of compound **1** in CDCl_3

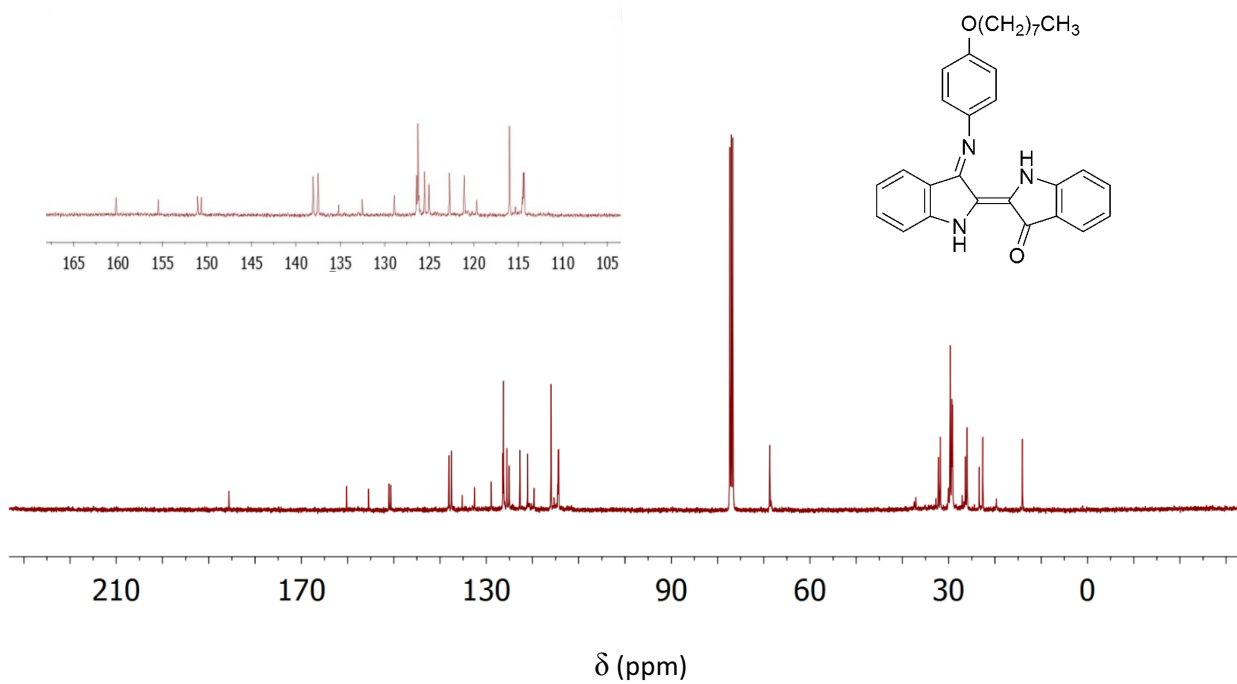


Figure S2. ^{13}C -NMR spectrum of compound **1** in CDCl_3

Mass Spectrum List Report

Analysis Info

Analysis Name OSSM580908001.d
 Method MKE_tune_wide_20130204.m
 Sample Name mono-octa-indigo
 mono-octa-indigo

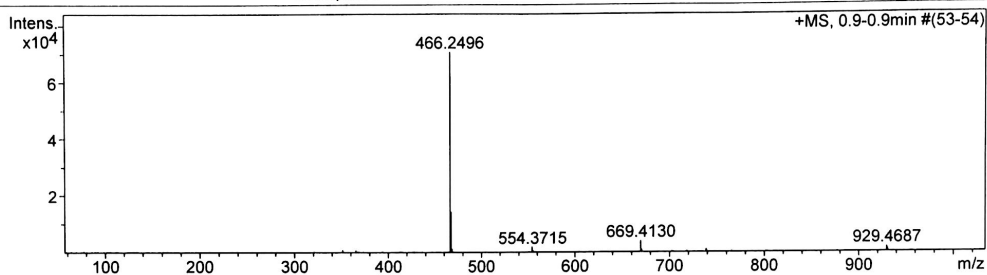
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 Operator Administrator
 Instrument micrOTOF 72

Acquisition Parameter

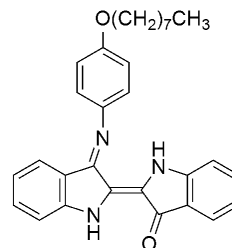
Source Type ESI
 Scan Range n/a
 Scan Begin 50 m/z
 Scan End 3000 m/z

Ion Polarity Positive
 Capillary Exit 150.0 V
 Hexapole RF 400.0 V
 Skimmer 1 54.4 V
 Hexapole 1 22.3 V

Set Corrector Fill 79 V
 Set Pulsar Pull 406 V
 Set Pulsar Push 388 V
 Set Reflector 1300 V
 Set Flight Tube 9000 V
 Set Detector TOF 1910 V



#	m/z	I	I %	S/N	FWHM	Res.
1	56.1203	452	0.6	113.6	0.0051	11012
2	58.5853	275	0.4	69.0	0.0052	11249
3	77.3119	444	0.6	111.6	0.0061	12726
4	129.8628	326	0.5	81.7	0.0078	16749
5	161.2223	277	0.4	68.8	0.0087	18470
6	165.3812	305	0.4	75.8	0.0087	19078
7	351.2127	809	1.1	175.3	0.0427	8224
8	365.2252	705	1.0	142.1	0.0434	8415
9	367.2420	274	0.4	54.7	0.0520	7059
10	413.2630	303	0.4	49.2	0.0474	8726
11	466.2496	70618	100.0	9505.3	0.0601	7761
12	467.2524	14411	20.4	1933.2	0.0542	8613
13	468.2531	1165	1.6	155.5	0.0545	8590
14	554.3715	1706	2.4	189.0	0.0555	9990
15	555.3760	564	0.8	62.4	0.0538	10331
16	669.4130	3855	5.5	495.7	0.0738	9072
17	670.4198	930	1.3	119.5	0.0828	8100
18	702.2994	370	0.5	49.6	0.0742	9465
19	718.2689	502	0.7	69.0	0.0561	12795
20	738.3037	1065	1.5	150.9	0.1171	6303
21	739.3093	508	0.7	71.9	0.0671	11013
22	765.2539	286	0.4	41.1	0.0179	42686
23	929.4687	1716	2.4	282.9	0.0784	11855
24	930.4742	982	1.4	162.0	0.0725	12837
25	1449.7210	279	0.4	73.8	0.0263	55034
26	1615.3928	275	0.4	82.7	0.0265	61038
27	1708.2307	296	0.4	96.0	0.0276	61804
28	2351.0449	797	1.1	255.5	0.0311	75650
29	2414.7219	273	0.4	88.7	0.0327	73834
30	2544.3511	300	0.4	99.7	0.0337	75412



Chemical Formula: C₃₀H₃₁N₃O₂
 Exact Mass: 465.2416
 Molecular Weight: 465.5860
 [M+H]⁺: 466.2495

Figure S3. HR-ESI mass spectrum of compound 1

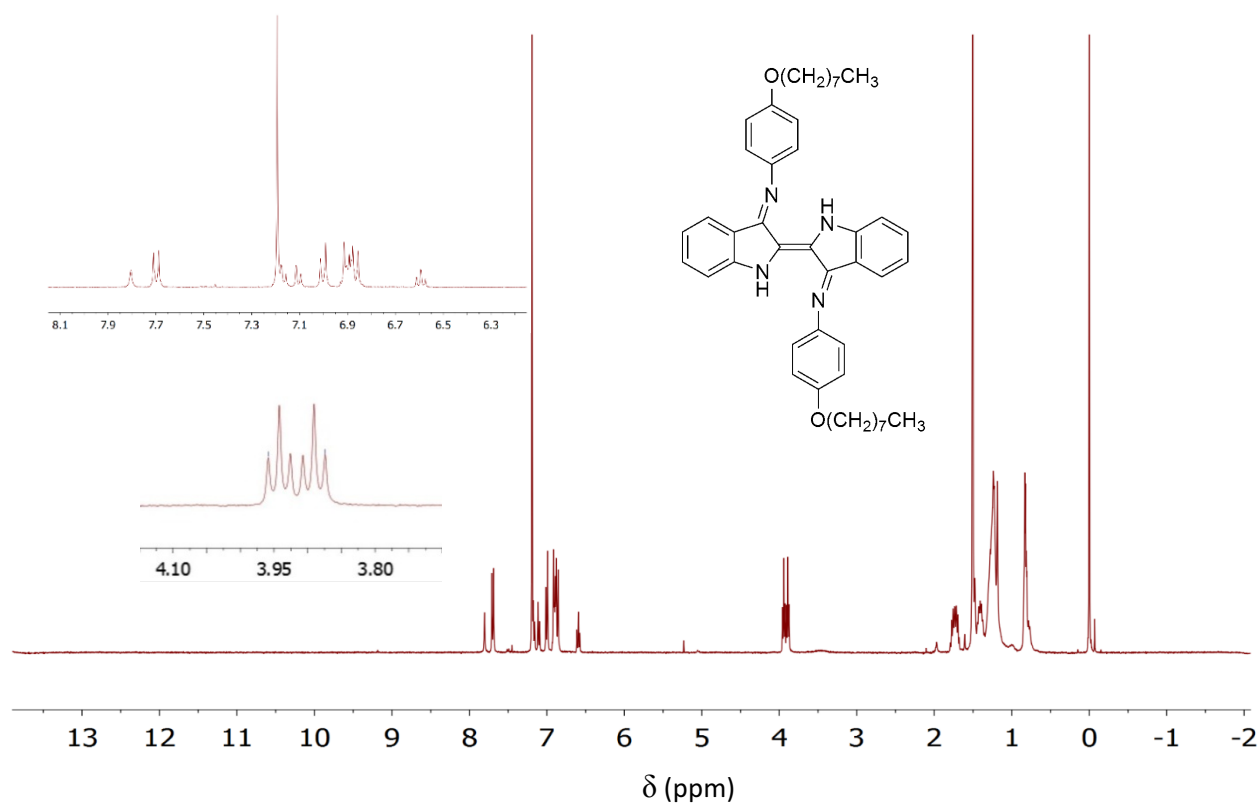


Figure S4. $^1\text{H-NMR}$ spectrum of compound **2** in CDCl_3

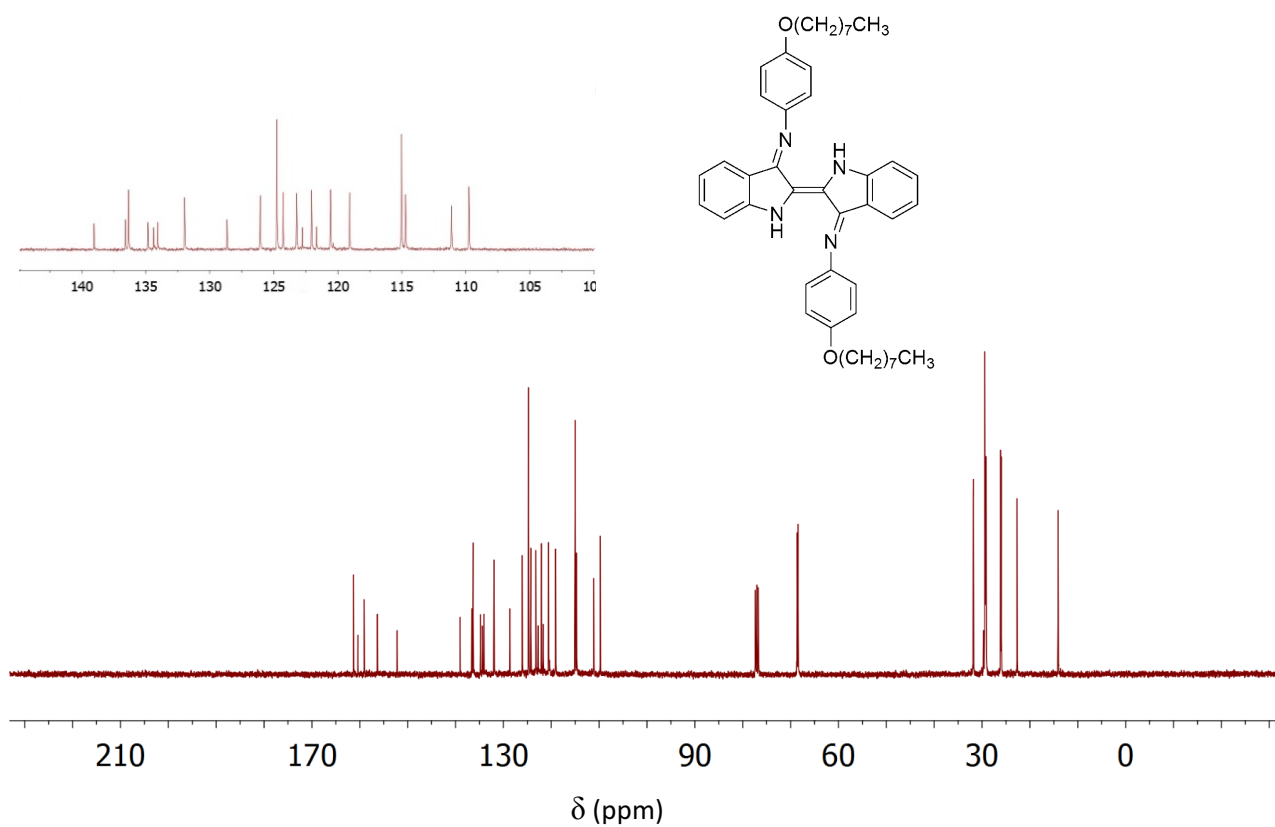


Figure S5. $^{13}\text{C-NMR}$ spectrum of compound **2** in CDCl_3

Mass Spectrum List Report

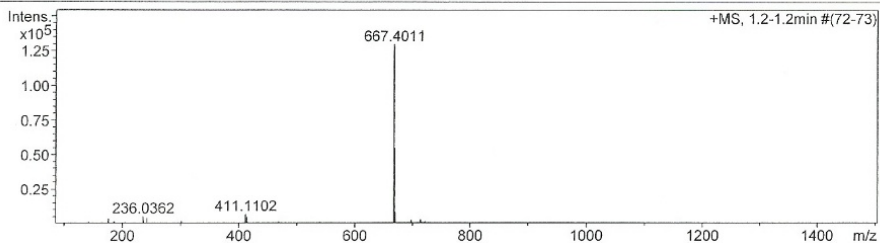
Analysis Info

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 Method Tune_low_POS_Natee20130403.m
 Sample Name Octyl-indigo
 Octyl-indigo

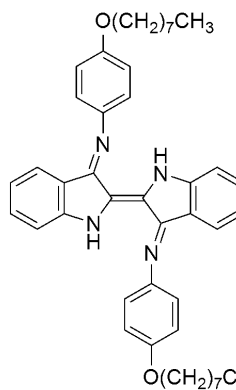
Acquisition Date 2/18/2015 12:41:51 AM
 Operator Administrator
 Instrument micrOTOF 72

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	79 V
Scan Range	n/a	Capillary Exit	150.0 V	Set Pulsar Pull	406 V
Scan Begin	50 m/z	Hexapole RF	120.0 V	Set Pulsar Push	388 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	1910 V



#	m/z	I	I%	S/N	FWHM	Res.
1	142.1620	1156	0.9	73.5	0.0254	5600
2	176.0837	3410	2.6	216.9	0.0318	5534
3	184.2065	882	0.7	55.7	0.0306	6022
4	186.2233	1396	1.1	88.4	0.0294	6343
5	204.0639	794	0.6	50.0	0.0308	6620
6	205.0722	885	0.7	55.8	0.0330	6217
7	236.0362	5198	4.0	328.9	0.0352	6704
8	242.2839	3834	3.0	242.4	0.0348	6957
9	243.2874	597	0.5	37.3	0.0397	6123
10	301.1432	1686	1.3	105.7	0.0419	7179
11	378.1307	628	0.5	38.3	0.0586	6458
12	411.1102	6874	5.3	418.8	0.0519	7917
13	412.1152	1278	1.0	77.4	0.0534	7722
14	413.2682	4849	3.8	294.9	0.0504	8196
15	414.2719	1006	0.8	60.7	0.0576	7197
16	429.3158	597	0.5	35.6	0.0597	7188
17	468.2285	1384	1.1	82.0	0.0583	8033
18	539.2797	852	0.7	48.8	0.0700	7706
19	667.4011	129147	100.0	6391.5	0.0951	7020
20	668.4044	54784	42.4	2707.8	0.0933	7166
21	669.4046	8322	6.4	410.4	0.0832	8047
22	670.4117	877	0.7	42.6	0.0919	7294
23	697.4112	2359	1.8	112.2	0.0920	7581
24	698.4115	1038	0.8	49.0	0.0968	7218
25	699.4071	632	0.5	29.6	0.0922	7586
26	713.4057	2635	2.0	123.3	0.1004	7106
27	714.4105	1286	1.0	59.8	0.0901	7931
28	715.4112	787	0.6	36.4	0.0851	8411
29	721.3740	1446	1.1	66.8	0.1011	7135
30	722.3719	636	0.5	29.1	0.0836	8641



Chemical Formula: C₄₄H₅₂N₄O₂
 Exact Mass: 668.4090
 Molecular Weight: 668.9093
 [M-H]⁺: 667.4012

Figure S6. HR-ESI mass spectrum of compound **2**

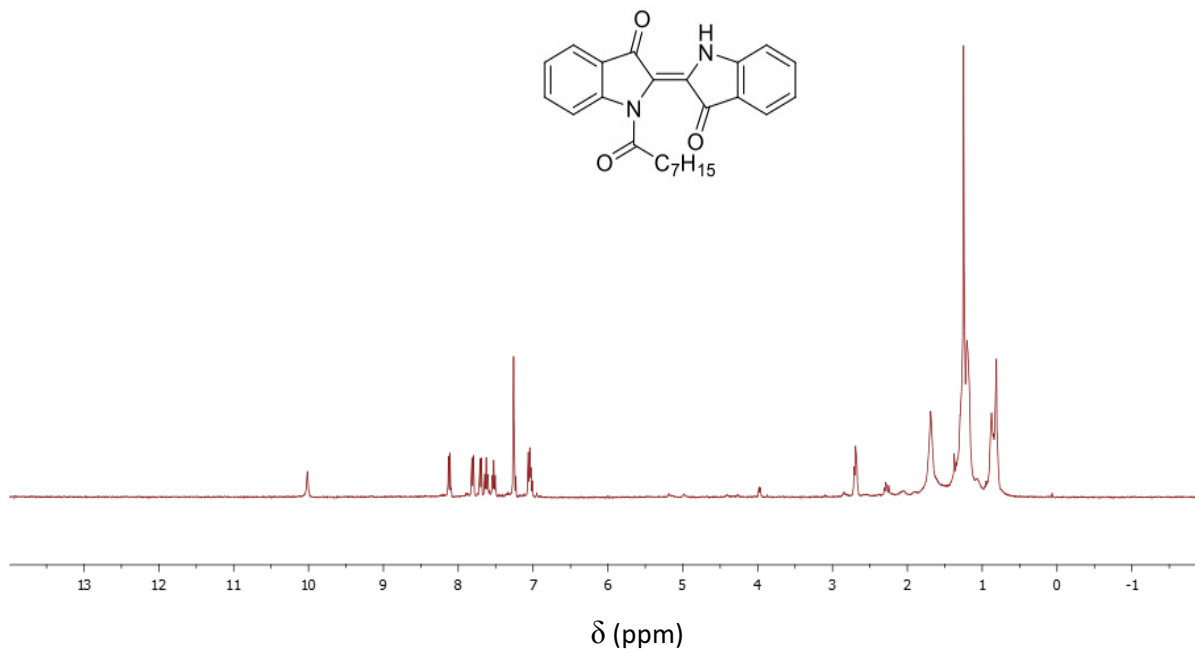


Figure S7. ¹H-NMR spectrum of compound **3** in CDCl₃

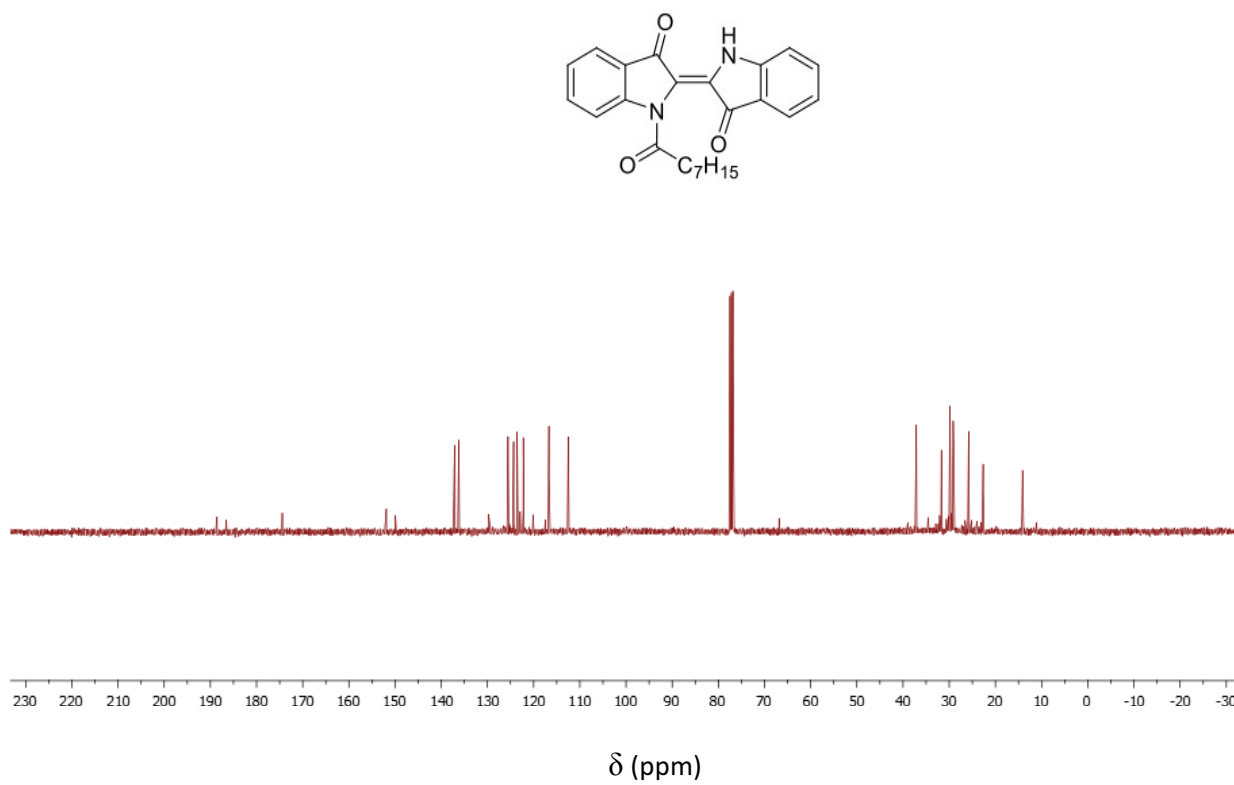


Figure S8. ¹³C-NMR spectrum of compound **3** in CDCl₃

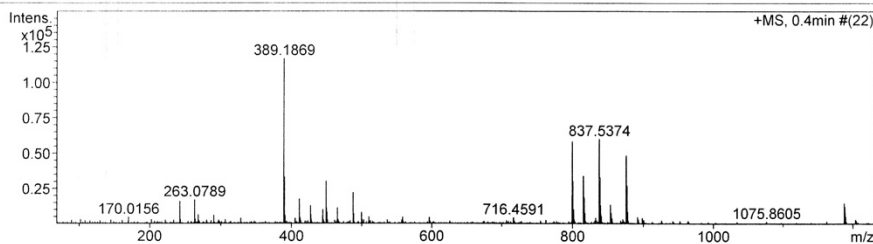
Mass Spectrum List Report

Analysis Info

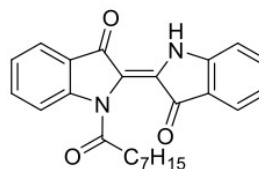
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Sample Name	mono-octaindigo	Instrument	micrOTOF 72
	mono-octaindigo		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	120.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	150.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V



#	m/z	I	I %	S/N	FWHM	Res.
1	242.2806	16253	13.9	60.3	0.0492	4926
2	263.0789	17150	14.7	63.7	0.0570	4613
3	389.1869	116737	100.0	444.8	0.0810	4803
4	390.1903	33151	28.4	125.9	0.0764	5108
5	411.1693	17895	15.3	67.9	0.0821	5008
6	427.1464	13199	11.3	50.1	0.0910	4694
7	427.3785	6961	6.0	26.1	0.0874	4889
8	444.4075	10331	8.8	39.2	0.0861	5160
9	449.3452	30451	26.1	117.1	0.1271	3536
10	450.3419	9092	7.8	34.4	0.1224	3678
11	465.3295	11051	10.0	44.5	0.1060	4390
12	487.4489	22177	19.0	85.8	0.0967	5042
13	488.4512	7528	6.4	28.6	0.0976	5003
14	499.4479	8404	7.2	32.1	0.1013	4928
15	799.3552	58431	50.1	232.2	0.1582	5051
16	800.3596	30422	26.1	120.3	0.1635	4896
17	801.3883	10539	9.0	40.8	0.2175	3684
18	815.3333	34135	29.2	135.8	0.1652	4936
19	816.3357	19127	16.4	75.5	0.1637	4988
20	817.3379	7988	6.8	30.7	0.1959	4172
21	837.5374	60255	51.6	242.7	0.1829	4580
22	838.5427	33159	28.4	133.0	0.1887	4444
23	839.5884	13406	11.5	52.9	0.2412	3481
24	853.5232	13747	11.8	54.6	0.1770	4824
25	854.5271	8006	6.9	31.2	0.1745	4897
26	875.7395	48672	41.7	198.4	0.1716	5102
27	876.7419	27356	23.4	111.0	0.1762	4975
28	877.7465	8844	7.6	34.9	0.1807	4858
29	1187.5343	15096	12.9	75.6	0.2417	4913
30	1188.5380	12503	10.7	62.5	0.2511	4733



Chemical Formula:
 $C_{24}H_{24}N_2O_3$
 Exact Mass: 388.1787
 Molecular Weight:
 388.4590
 $[M+H]^+$: 389.1865

Figure S9. HR-ESI mass spectrum of compound 3

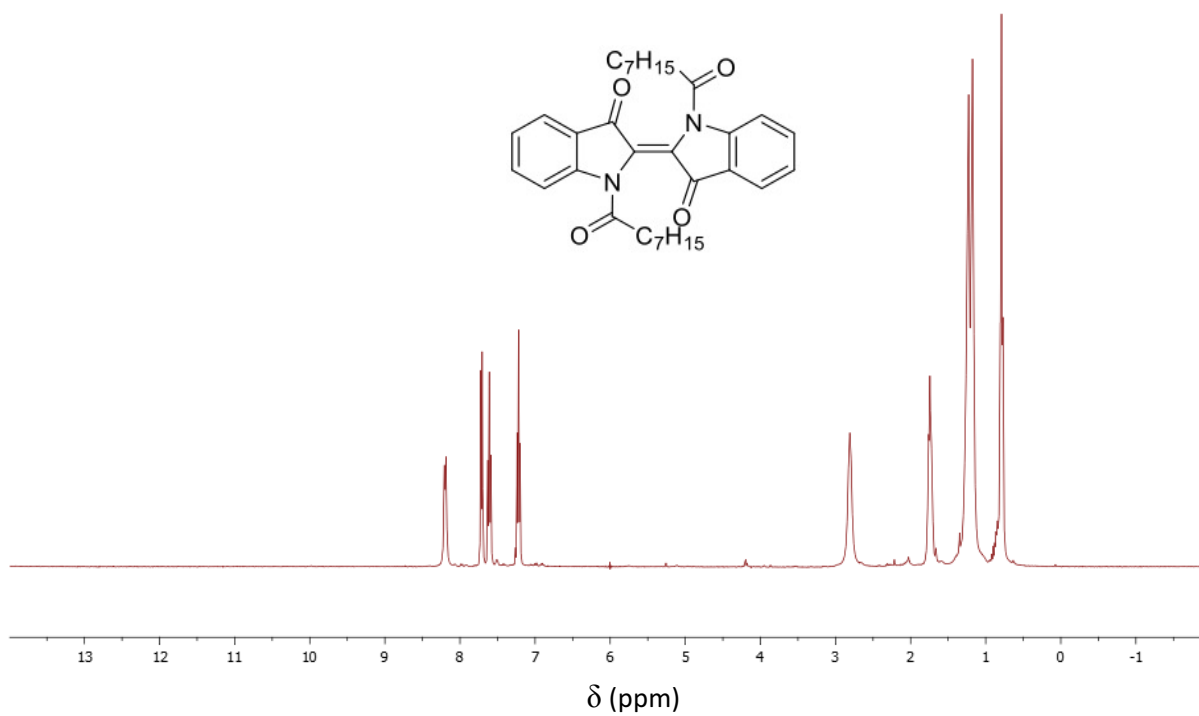


Figure S10. ^1H -NMR spectrum of compound **4** in CDCl_3 .

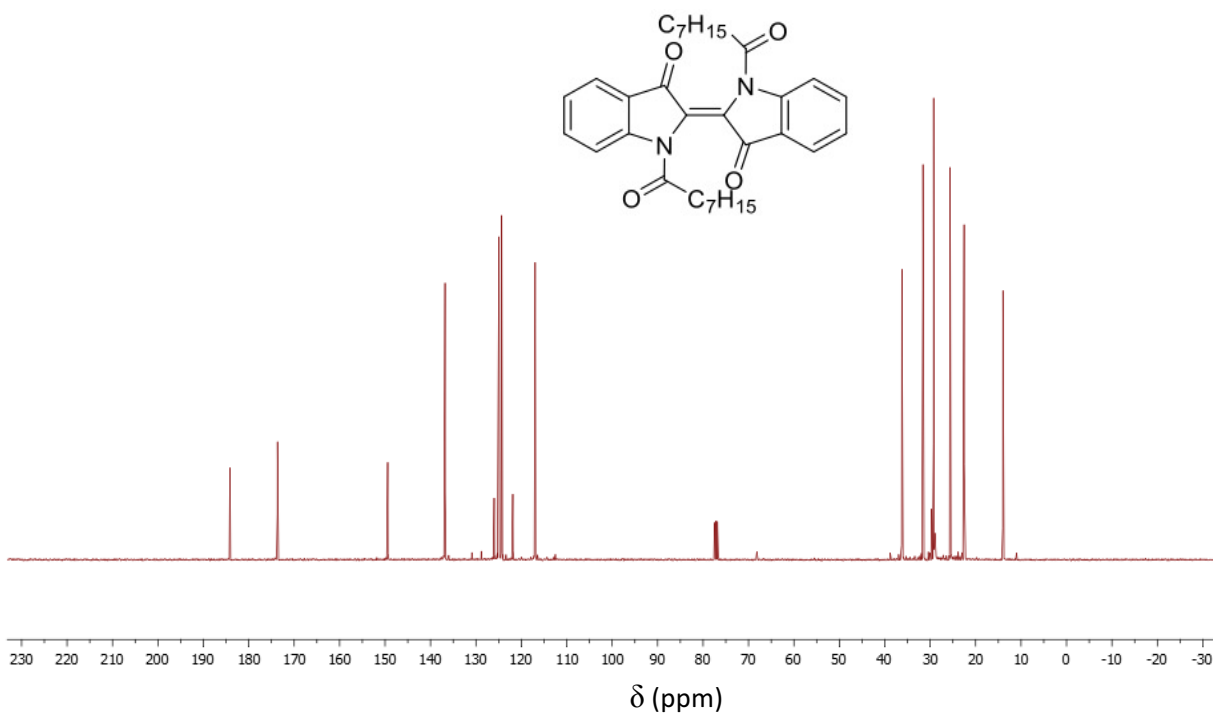


Figure S11. ^{13}C -NMR spectrum of compound **4** in CDCl_3 .

Mass Spectrum List Report

Analysis Info

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 di-octa indigo

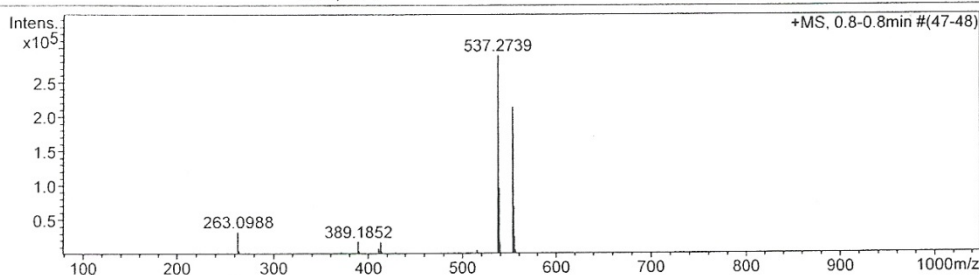
Acquisition Date 11/10/2015 10:28:43 AM
 Operator Administrator
 Instrument micrOTOF 72

Acquisition Parameter

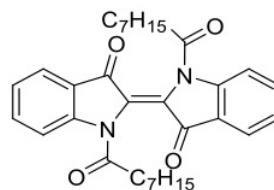
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 Scan Range n/a
 Scan Begin 50 m/z
 Scan End 3000 m/z

Ion Polarity Positive
 Capillary Exit 180.0 V
 Hexapole RF 90.0 V
 Skimmer 1 45.5 V
 Hexapole 1 25.0 V

Set Corrector Fill 50 V
 Set Pulsar Pull 337 V
 Set Pulsar Push 337 V
 Set Reflector 1300 V
 Set Flight Tube 9000 V
 Set Detector TOF 2093 V



#	m/z	I	I%	S/N	FWHM	Res.
1	263.0988	33186	11.5	1555.2	0.0886	2971
2	264.1003	5649	2.0	263.1	0.0926	2853
3	301.1449	1820	0.6	72.3	0.1071	2813
4	371.1719	3891	1.3	122.8	0.1001	3709
5	384.2461	1193	0.4	35.4	0.0853	4507
6	389.1852	18889	6.5	570.6	0.1012	3847
7	390.1878	4965	1.7	148.7	0.1060	3680
8	411.1686	9092	3.1	258.4	0.1131	3634
9	412.1713	2629	0.9	73.5	0.1190	3464
10	413.2636	17922	6.2	507.8	0.1083	3814
11	414.2668	4377	1.5	122.7	0.1136	3647
12	425.2090	2496	0.9	67.4	0.1241	3426
13	427.1636	1429	0.5	37.8	0.1712	2494
14	429.2364	3449	1.2	92.7	0.1166	3683
15	441.2859	1675	0.6	42.9	0.1442	3059
16	449.3544	2132	0.7	53.9	0.1206	3727
17	513.2779	1318	0.5	28.2	0.1623	3162
18	515.2903	6440	2.2	143.5	0.1431	3601
19	516.2940	2355	0.8	51.3	0.1352	3818
20	527.2911	2871	1.0	61.5	0.1468	3591
21	537.2739	289411	100.0	6242.2	0.1423	3777
22	538.2768	96356	33.3	2074.5	0.1397	3854
23	539.2771	17396	6.0	374.3	0.1415	3812
24	540.2792	2649	0.9	55.8	0.1429	3782
25	553.2478	213831	73.9	4813.0	0.1441	3840
26	554.2500	68814	23.8	1552.4	0.1442	3845
27	555.2493	25992	9.0	587.1	0.1438	3862
28	556.2514	6186	2.1	138.9	0.1513	3677
29	557.2653	1306	0.5	28.1	0.1613	3455
30	567.2873	1287	0.4	28.5	0.1616	3511



Chemical Formula:
 $C_{32}H_{38}N_2O_4$
 Exact Mass: 514.2832
 Molecular Weight:
 514.6551
 $[M+Na]^+$: 537.2729

Figure S12. HR-ESI mass spectrum of compound 4

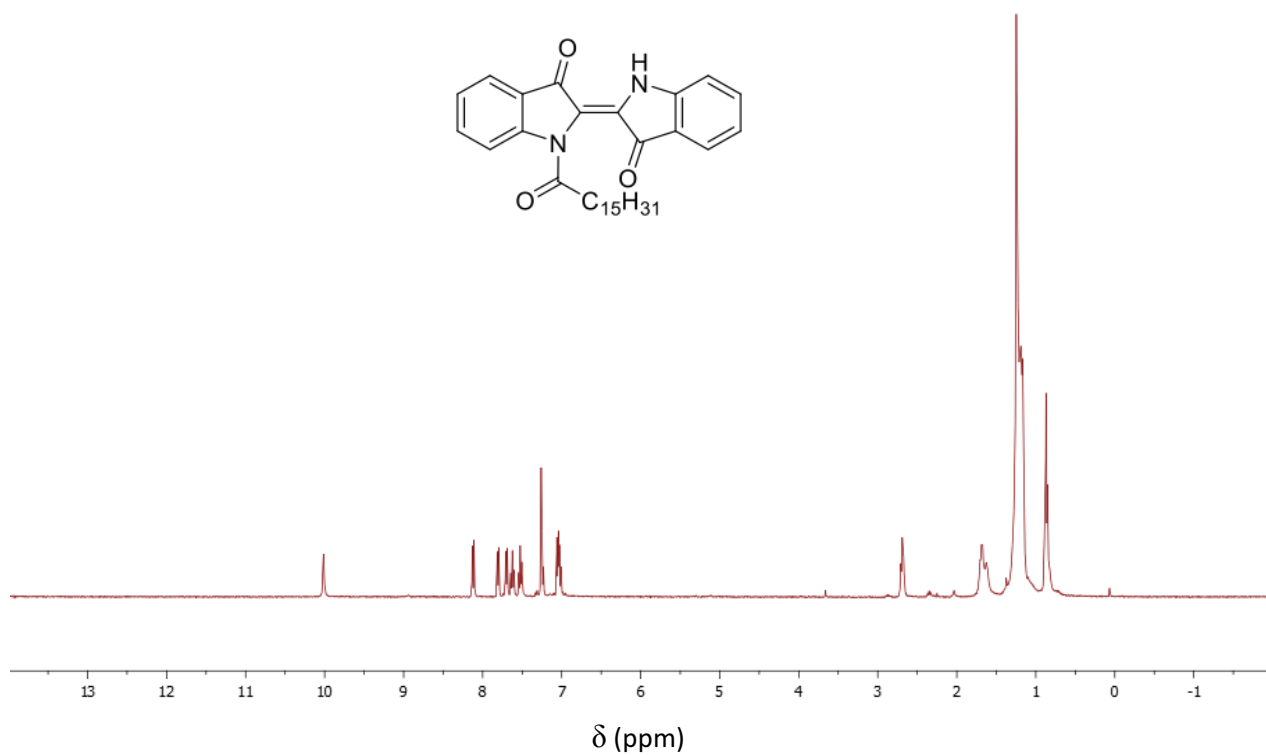


Figure S13. ^1H -NMR spectrum of compound **5** in CDCl_3 .

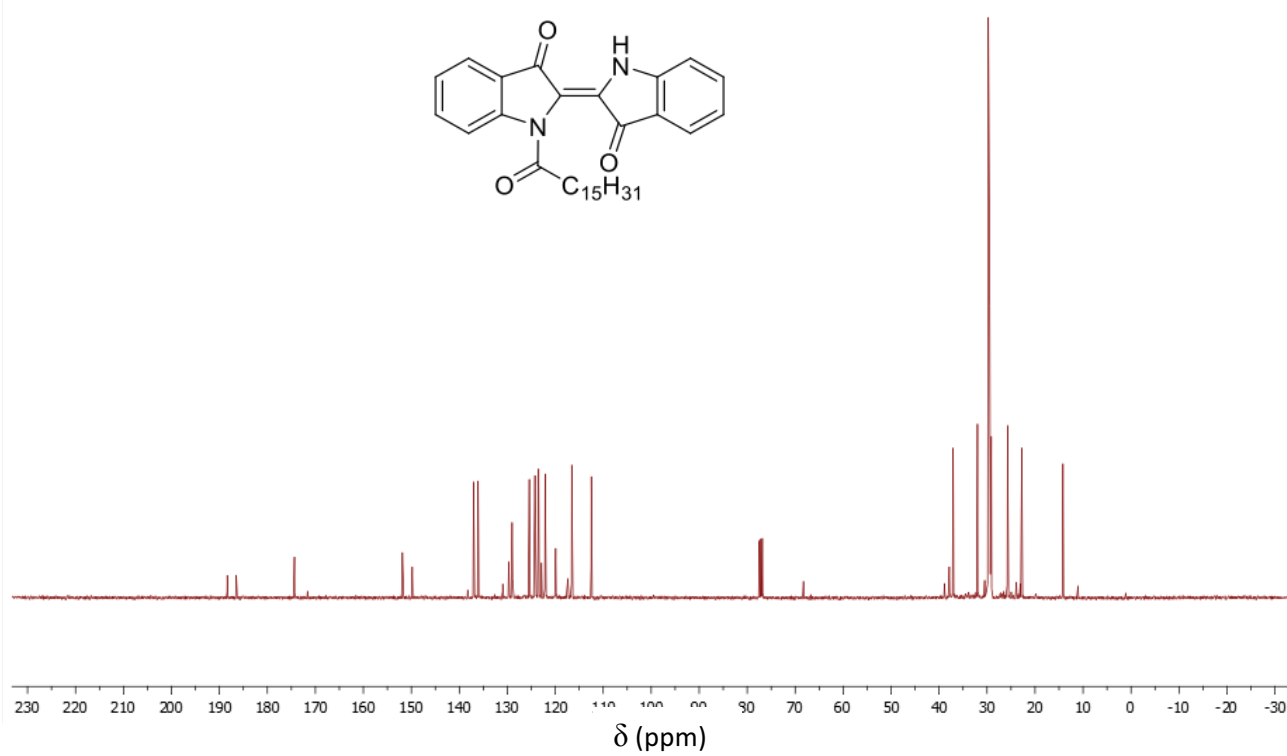


Figure S14. ^{13}C -NMR spectrum of compound **5** in CDCl_3 .

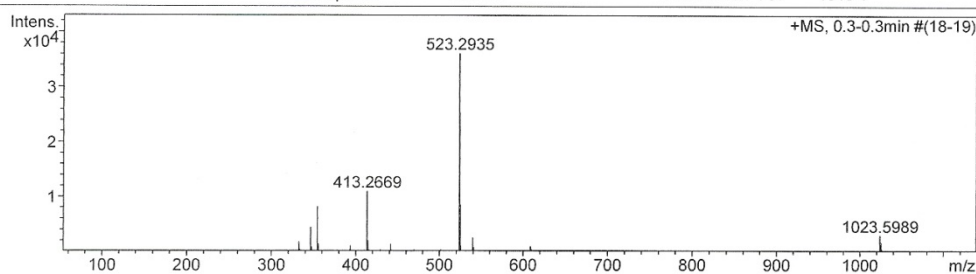
Mass Spectrum List Report

Analysis Info

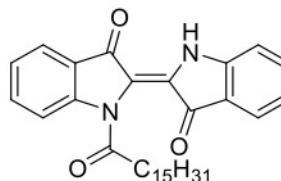
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Method	MKE_tune_wide_20130204.m	Operator	Administrator
Sample Name	mono-indigo	Instrument	micrOTOF 72
	mono-indigo		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	79 V
Scan Range	n/a	Capillary Exit	200.0 V	Set Pulsar Pull	406 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	388 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	25.0 V	Set Flight Tube	9000 V
				Set Detector TOF	1910 V



#	m/z	I	I%	S/N	FWHM	Res.
1	332.2937	1773	4.9	508.8	0.0406	8181
2	333.2965	407	1.1	116.2	0.0411	8116
3	346.2710	4434	12.3	1213.4	0.0387	8950
4	347.2738	813	2.3	221.5	0.0405	8566
5	348.2819	181	0.5	49.1	0.0497	7011
6	354.2760	8193	22.8	2165.5	0.0403	8799
7	355.2790	1444	4.0	379.9	0.0432	8229
8	393.2958	1036	2.9	234.7	0.0461	8529
9	394.2990	250	0.7	56.1	0.0455	8672
10	413.2669	10957	30.4	2313.5	0.0509	8121
11	414.2702	2056	5.7	432.4	0.0492	8417
12	415.2717	268	0.7	56.0	0.0473	8772
13	429.2475	324	0.9	64.6	0.0536	8014
14	441.2984	1381	3.8	266.0	0.0542	8139
15	442.3038	289	0.8	55.2	0.0633	6987
16	449.3610	172	0.5	32.1	0.0641	7005
17	469.3377	268	0.7	47.3	0.0879	5338
18	501.3128	268	0.7	43.1	0.0717	6992
19	523.2935	35992	100.0	5526.5	0.0624	8384
20	524.2966	8546	23.7	1308.7	0.0577	9083
21	525.3006	985	2.7	150.2	0.0627	8376
22	539.2676	2510	7.0	372.0	0.0585	9221
23	540.2704	733	2.0	108.6	0.0594	9102
24	541.2696	247	0.7	36.4	0.0630	8594
25	608.5011	980	2.7	163.1	0.0702	8669
26	609.5020	388	1.1	64.4	0.0674	9037
27	661.5327	202	0.6	36.7	0.0821	8062
28	1023.5989	2949	8.2	866.5	0.1036	9878
29	1024.5966	1705	4.7	501.3	0.1131	9061
30	1025.5989	394	1.1	115.7	0.1205	8508



Chemical Formula:
 $C_{32}H_{40}N_2O_3$
Exact Mass: 500.3039
Molecular Weight:
 500.6716
[M+Na]⁺: 523.2937

Figure S15. HR-ESI mass spectrum of compound **5**

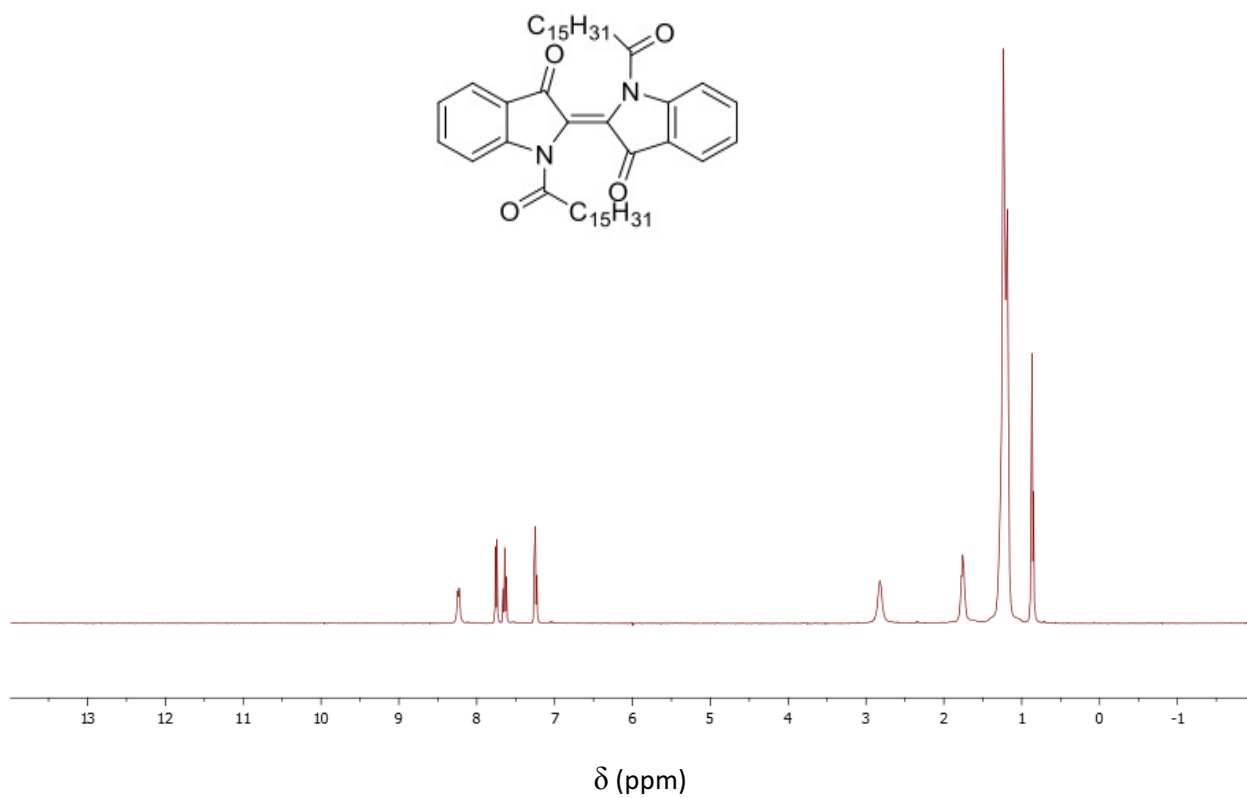


Figure S16. ¹H-NMR spectrum of compound **6** in CDCl₃

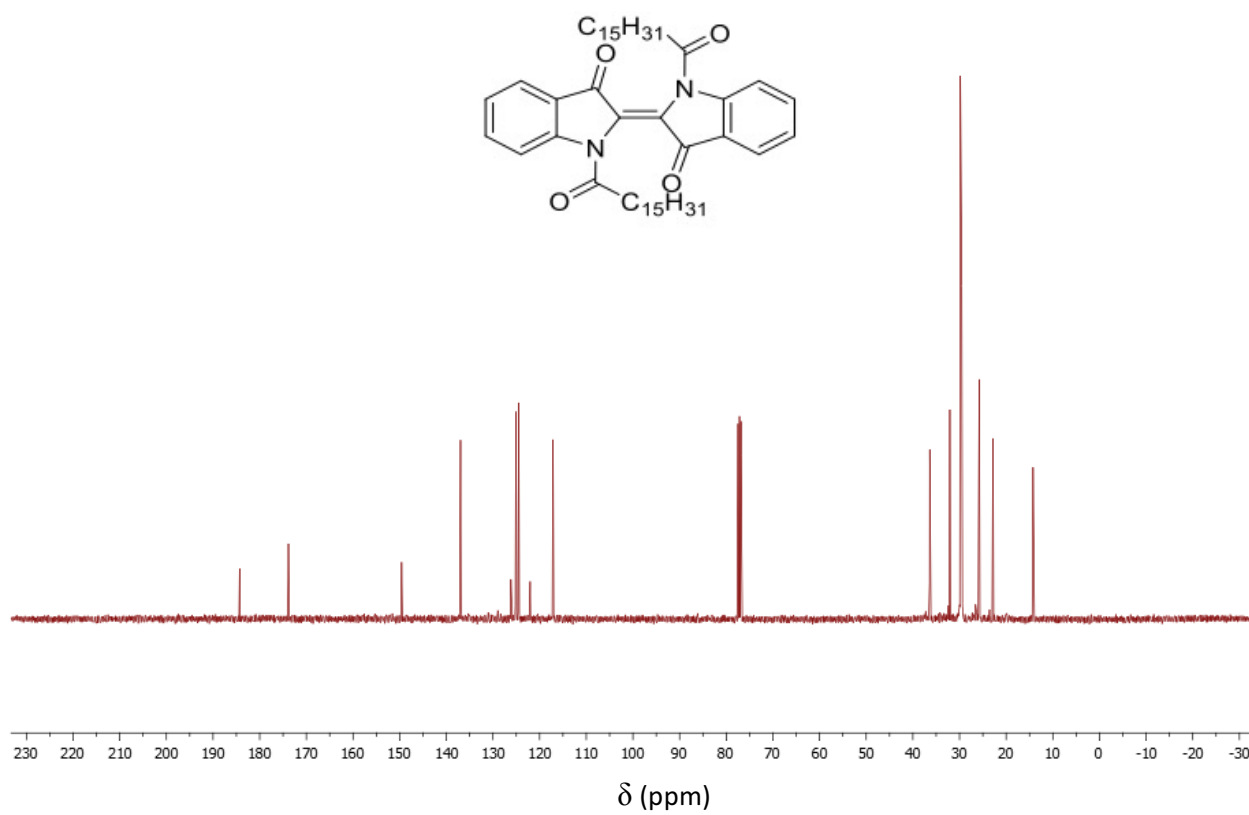


Figure S17. ¹³C-NMR spectrum of compound **6** in CDCl₃

Mass Spectrum List Report

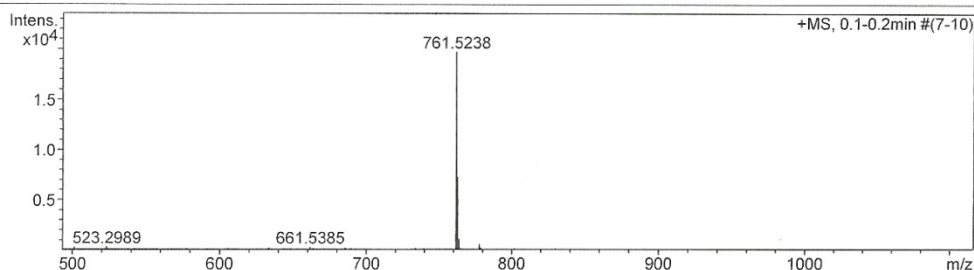
Analysis Info

Analysis Name OSCUPP580211001.d
 Method MKE_tune_wide_20130204.m
 Sample Name di-indigo
 di-indigo

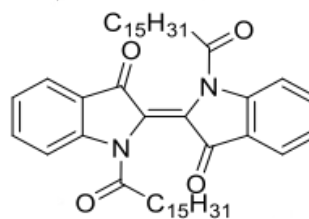
Acquisition Date 2/11/2015 11:10:22 AM
 Operator Administrator
 Instrument micrOTOF 72

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	79 V
Scan Range	n/a	Capillary Exit	200.0 V	Set Pulsar Pull	406 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	388 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	25.0 V	Set Flight Tube	9000 V
				Set Detector TOF	1910 V



#	m/z	I	I%	S/N	FWHM	Res.
1	318.2378	168	0.9	55.3	0.0456	6975
2	346.2705	744	3.8	-231.8	0.0386	8967
3	347.2712	160	0.8	49.4	0.0450	7714
4	393.2943	295	1.5	77.9	0.0458	8582
5	413.2661	9011	45.9	2243.3	0.0504	8195
6	414.2696	1674	8.5	415.2	0.0520	7965
7	415.2691	254	1.3	62.6	0.0455	9127
8	441.1143	976	5.0	223.8	0.0549	8033
9	441.2969	1372	7.0	314.6	0.0551	8012
10	442.1157	208	1.1	47.3	0.0566	7810
11	442.3009	306	1.6	69.6	0.0585	7565
12	463.0964	232	1.2	49.9	0.0513	9028
13	469.3333	245	1.2	51.8	0.0699	6713
14	501.3109	294	1.5	57.4	0.0751	6674
15	523.2989	317	1.6	58.9	0.0834	6274
16	605.4789	229	1.2	37.6	0.0873	6937
17	633.5056	216	1.1	34.3	0.0852	7438
18	661.5385	315	1.6	48.7	0.0867	7629
19	685.4319	207	1.1	30.9	0.0761	9003
20	689.5655	159	0.8	23.6	0.0829	8314
21	733.5275	176	0.9	24.9	0.1181	6210
22	761.5238	19646	100.0	2986.6	0.0863	8822
23	762.5257	7294	37.1	1110.7	0.0874	8720
24	763.5307	1133	5.8	172.3	0.0918	8315
25	764.5334	145	0.7	21.6	0.1150	6649
26	777.4943	577	2.9	90.1	0.0882	8816
27	778.4996	256	1.3	39.6	0.0906	8594
28	1500.0498	620	3.2	192.6	0.1660	9037
29	1501.0585	640	3.3	198.9	0.1848	8121
30	1502.0532	262	1.3	81.0	0.1337	11237



Chemical Formula:
 $C_{48}H_{70}N_2O_4$
 Exact Mass: 738.5336
 Molecular Weight:
 739.0804
 $[M+Na]^+$: 761.5233

Figure S18. HR-ESI mass spectrum of compound **6**

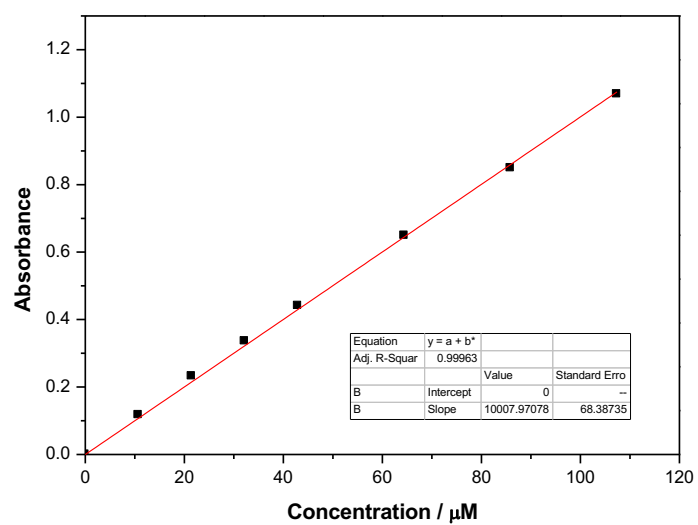


Figure S19. Standard calibration curve of compound **1** in toluene at 595 nm

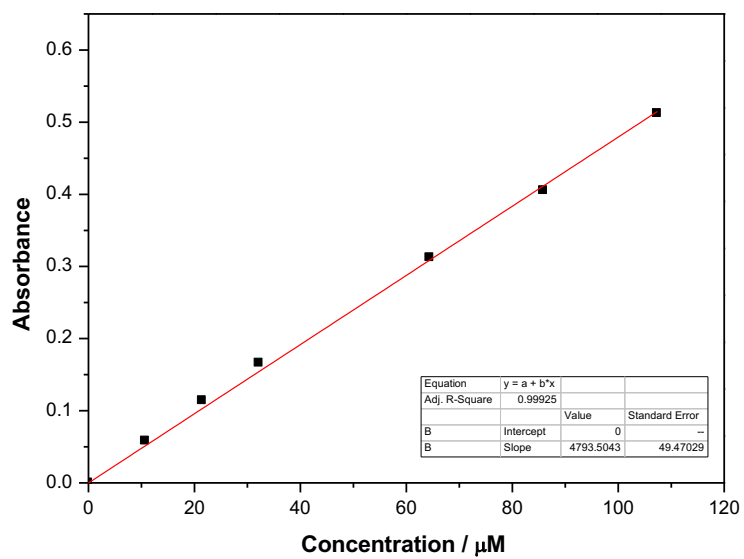


Figure S20. Standard calibration curve of compound **1** in diesel at 590 nm

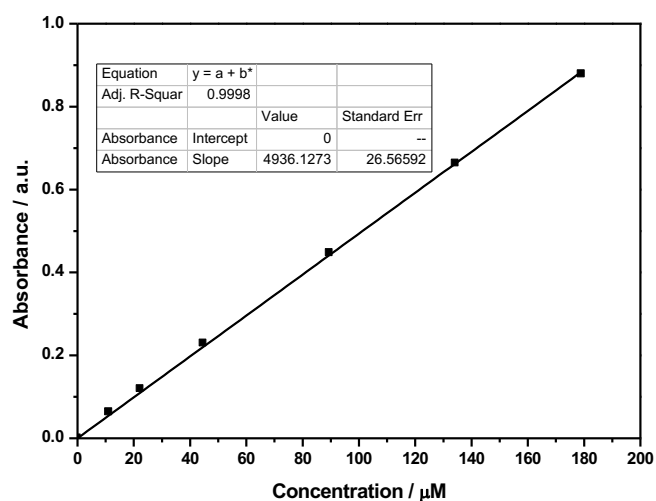


Figure S21. Standard calibration curve of compound **3** in toluene at 575 nm

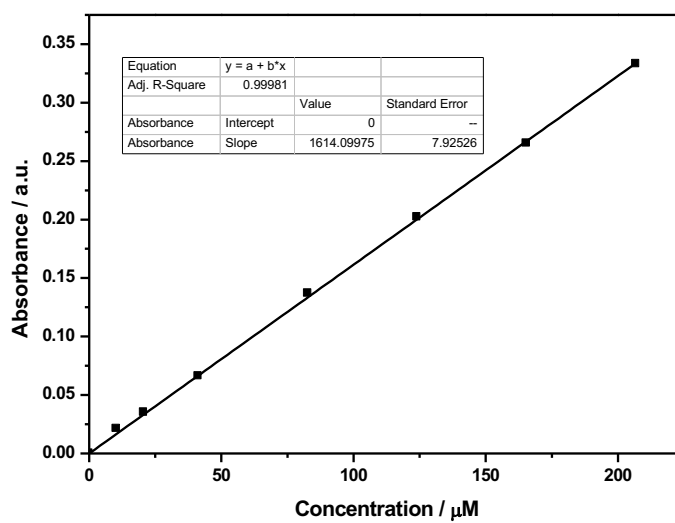


Figure S22. Standard calibration curve of compound **3** in diesel at 570 nm

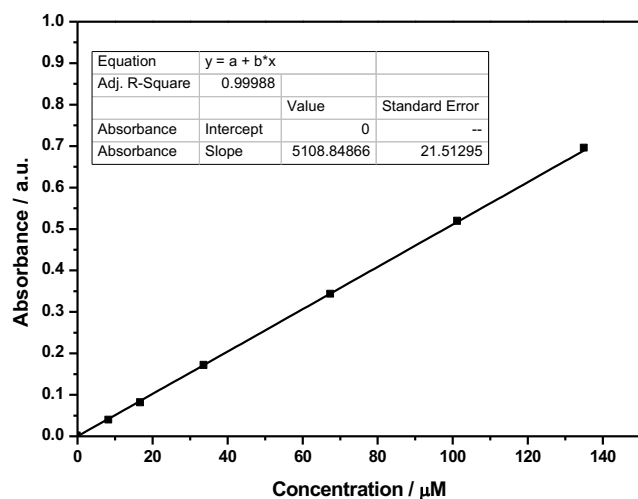


Figure S23. Standard calibration curve of compound **4** in toluene at 570 nm

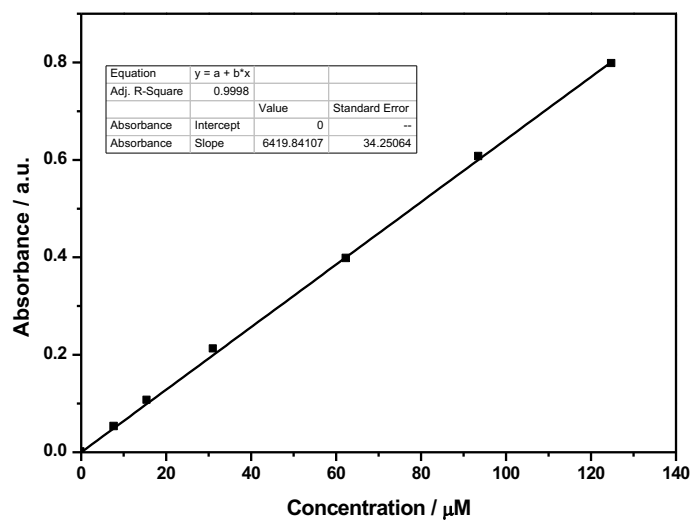


Figure S24. Standard calibration curve of compound **4** in diesel at 570 nm

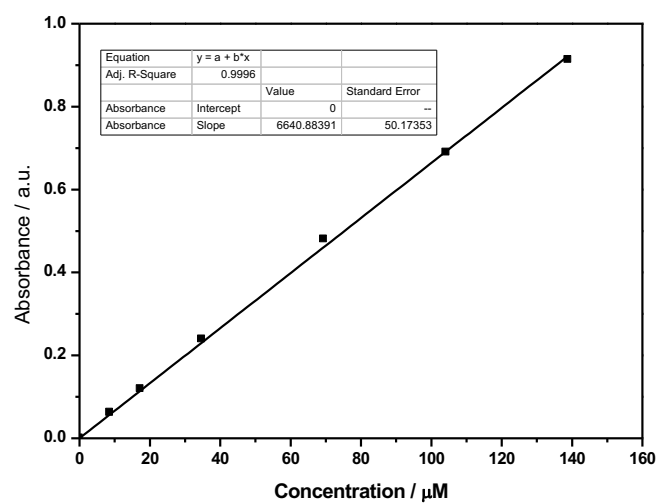


Figure S25. Standard calibration curve of compound **5** in toluene at 575 nm

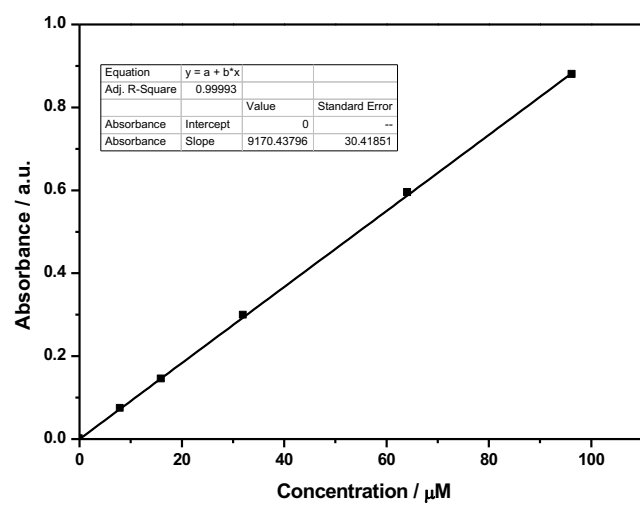


Figure S26. Standard calibration curve of compound **5** in diesel at 575 nm

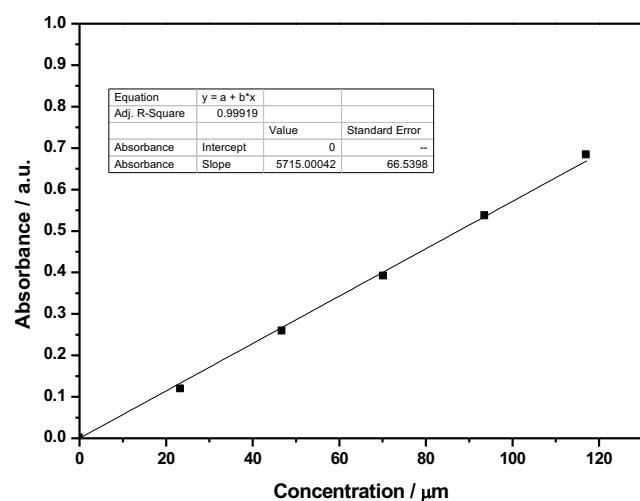


Figure S27. Standard calibration curve of compound **6** in toluene at 570 nm

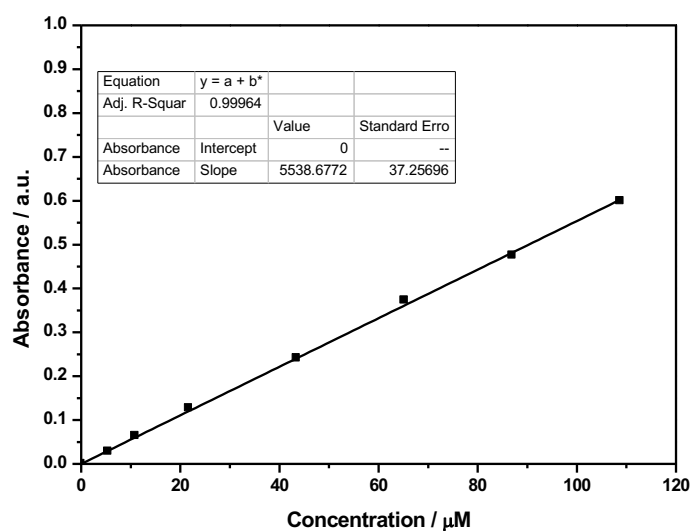


Figure S28. Standard calibration curve of compound **6** in diesel at 570 nm