Supplementary Information

The Influence of the Acyl Side Chain on Pyrene Excimer Formation as a Model for Asphaltene Aggregation

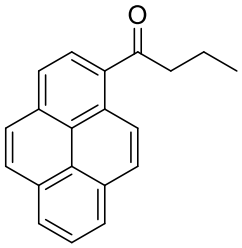
Suyane D. S. de Alvarenga,[a,b] Simon J. Garden,[b] Josué S. B. Forero,[b] Raquel S. P. Teixeira,[b] Rodrigo S. Souza,[b] Yan M. H. Gonçalves,[b] Bruno A. C. Horta,[b] Javier A. G. Gomez,[c] Luiz H. C. dos Santos,[b] Emerson S. Ribeiro *,[b] and Rodrigo J. Corrêa *,[b]

[a]*Centro Federal de Educação Tecnológica Celso Suckow da Fonseca (CEFET/RJ), 20271-110 Rio de Janeiro-RJ, Brazil*

[b]*Instituto de Química, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco A, Cidade Universitária, 21941-909 Rio de Janeiro-RJ, Brazil*

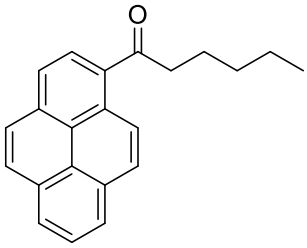
[c]*Instituto de Química, Universidade Federal Fluminense, Campus do Valonguinho, Centro, 24020-141 Niterói-RJ, Brazil*

1-(Pyren-1-yl)butan-1-one (**PC4**)



mp 70-71 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.06 (t, 3H, *J* 7.3 Hz, CH_3), 1,88 (qt, 2H, *J* 7.3, 7.6 Hz, CH_2), 3.15 (t, 1H, *J* 7.3 Hz, CH_2), 7.94-8.04 (m, 2H, H_{Ar}), 8.05-8.28 (m, 6H, H_{Ar}), 8.84 (d, 1H, *J* 9.4 Hz, H_{Ar}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 14.8, 44.5, 124.0, 124.3, 124.8, 125.0, 125.9, 125.9, 126.1, 126.3, 127.0, 129.2, 129.3, 129.4, 130.6, 131.1, 132.9, 133.5, 205.2.

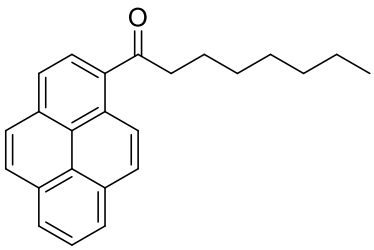
1-(Pyren-1-yl)hexan-1-one (**PC6**)



mp 90-91 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (t, 3H, *J* 6.8 Hz, CH_3), 1.29-1.52 (m, 2H, CH_2), 1.74-1.97 (m, 2H, CH_2), 3.18 (t, 2H, *J* 7.3 Hz, CH_2), 7.96-8.03 (m, 1H, H_{Ar}), 8.04-8.32 (m, 7H, H_{Ar}), 8.84 (d, 1H, *J* 9.3, H_{Ar}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.6, 24.7, 31.6, 42.7, 124.0, 124.4, 124.8, 125.0, 125.9, 126.1, 126.3, 127.1, 129.2, 129.3, 129.4, 130.6, 131.1, 133.0, 133.6, 205.4.

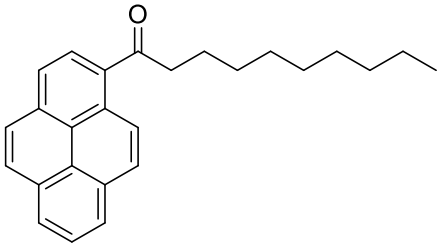
*e-mail: emersonsr@iq.ufrj.br; rodrigojosecorrea@gmail.com

1-(Pyren-1-yl)octan-1-one (**PC8**)



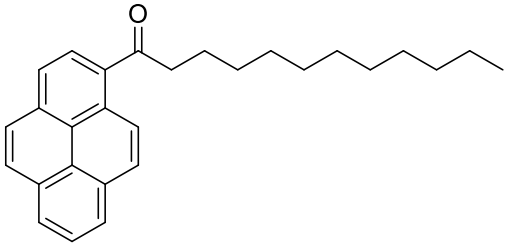
mp 72-74 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3H, *J* 6.8 Hz, CH_3), 1.17-1.51 (m, 8H, CH_2), 1.84 (m, 2H, CH_2), 3.16 (t, 2H, *J* 7.4 Hz, CH_2), 7.92-8.05 (m, 2H, H_{Ar}), 8.06-8.30 (m, 6H, H_{Ar}), 8.84 (d, 1H, *J* 9.5, H_{Ar}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.6, 25.0, 29.2, 29.4, 31.7, 42.7, 124.0, 124.4, 124.8, 125.0, 125.9, 126.1, 126.3, 127.1, 129.2, 129.3, 129.4, 130.6, 131.1, 133.0, 133.5, 205.4.

1-(Pyren-1-yl)decan-1-one (**PC10**)



mp 61-63 °C (59-61 °C lit);[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, *J* 6.8 Hz, CH_3), 1.17-1.52 (m, 12H, CH_2), 1.85 (m, 2H, CH_2), 3.20 (t, 2H, *J* 7.5 Hz, CH_2), 8.02-8.09 (m, 2H, H_{Ar}), 8.13-8.21 (m, 3H, H_{Ar}), 8.22-8.26 (m, 2H, H_{Ar}) 8.30 (d, 1H, *J* 8.1, H_{Ar}), 8.85 (d, 1H, *J* 9.4, H_{Ar}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.0, 29.3, 29.4, 29.5, 29.5, 31.9, 42.7, 124.0, 124.4, 124.8, 125.0, 125.9, 126.0, 126.2, 127.1, 129.2, 129.4, 129.5, 130.6, 131.1, 133.0, 133.6, 205.6.

1-(Pyren-1-yl)dodecan-1-one (**PC12**)



mp 58-59 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3H, *J* 6.8 Hz, CH_3), 1.18-1.51 (m, 16H, CH_2), 1.74-1.93 (m, 2H, CH_2), 3.17 (t, 2H, *J* 7.4 Hz, CH_2), 7.94-8.32 (m, 8H, H_{Ar}), 8.84 (d, 1H, *J* 9.5 Hz, H_{Ar}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.7, 25.0, 29.3, 29.4, 29.5, 29.6, 31.9, 42.7, 124.0, 124.4, 124.8, 125.0, 125.9, 126.1, 126.3, 127.1, 129.2, 129.3, 129.4, 130.6, 131.1, 133.0, 133.5, 205.4.

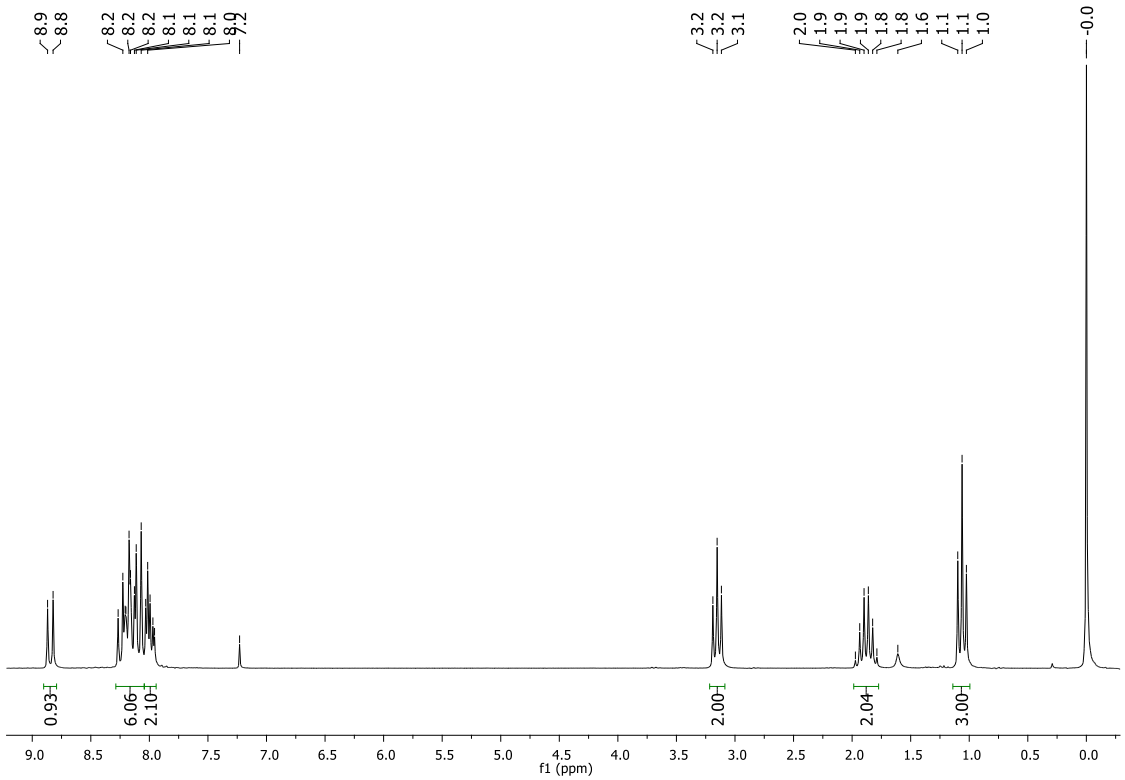


Figure S1. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **PC4**.

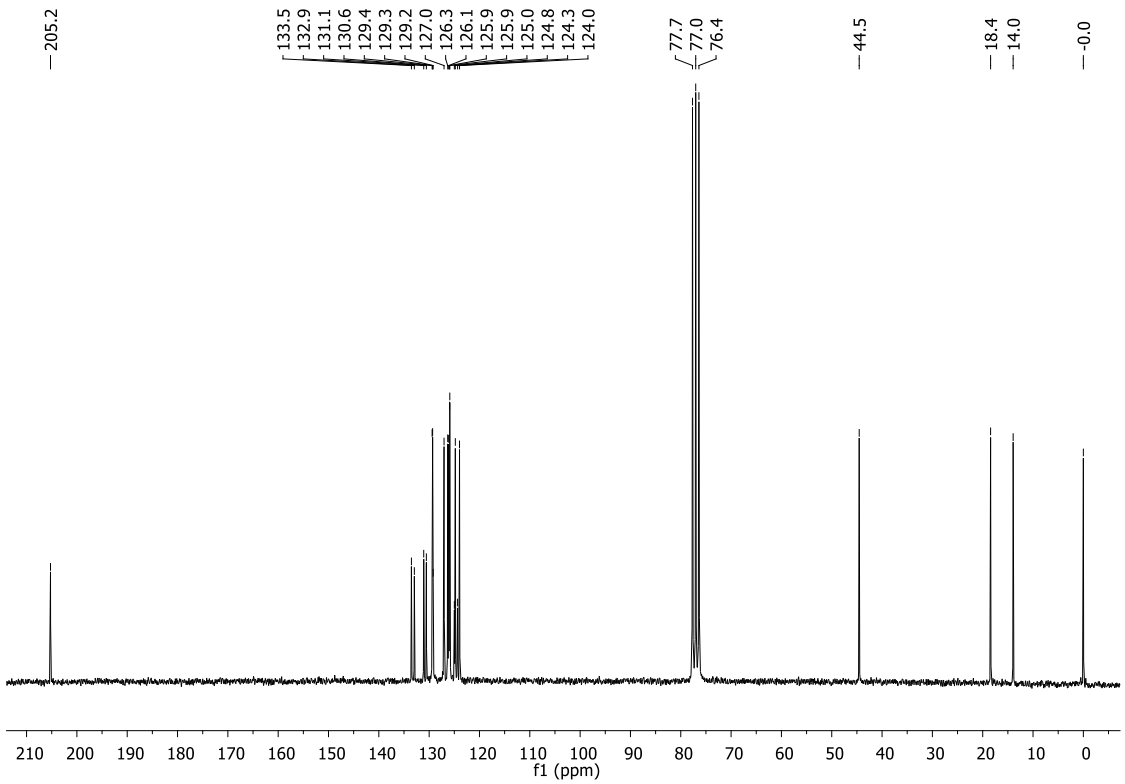


Figure S2. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **PC4**.

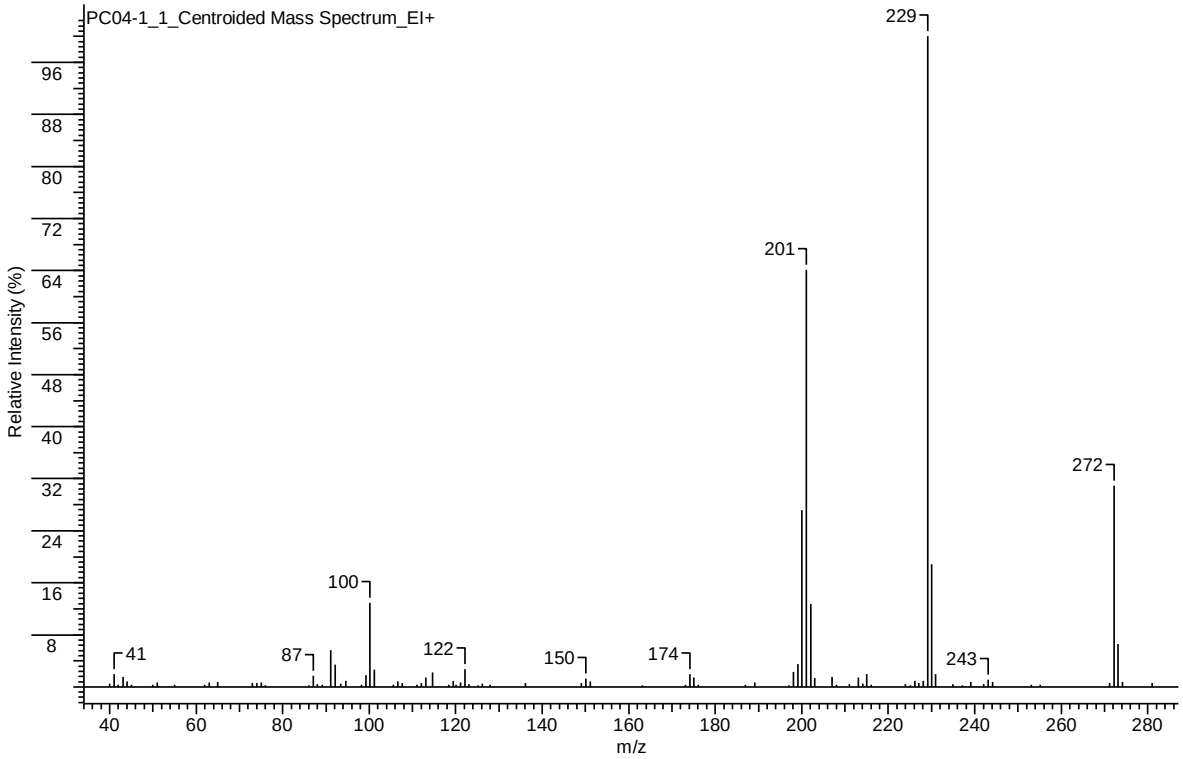


Figure S3. Mass spectrum of compound **PC4**.

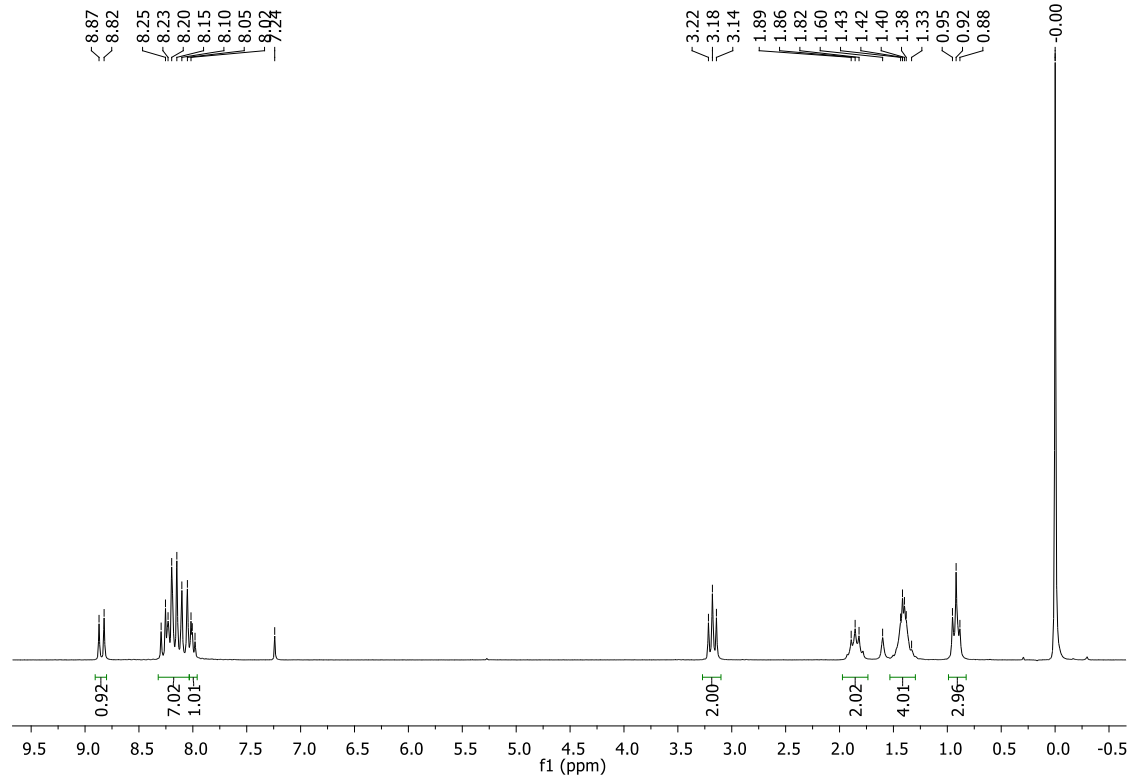


Figure S4. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **PC6**.

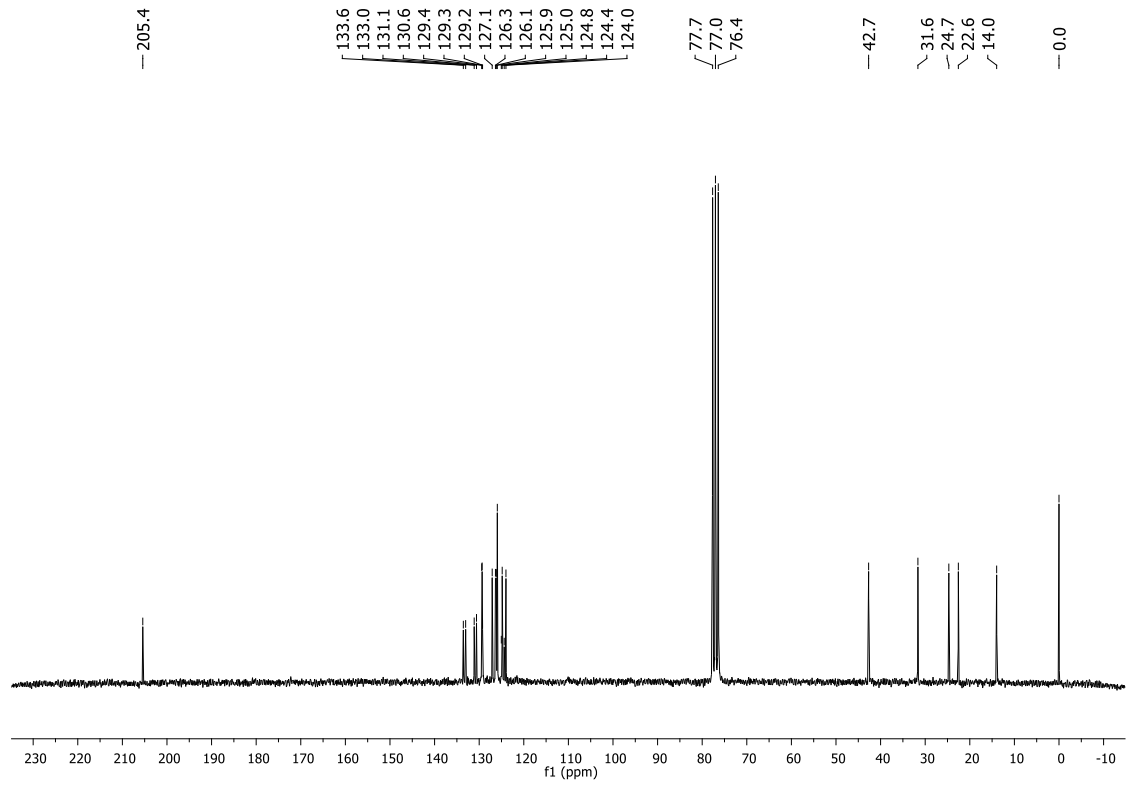


Figure S5. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **PC6**.

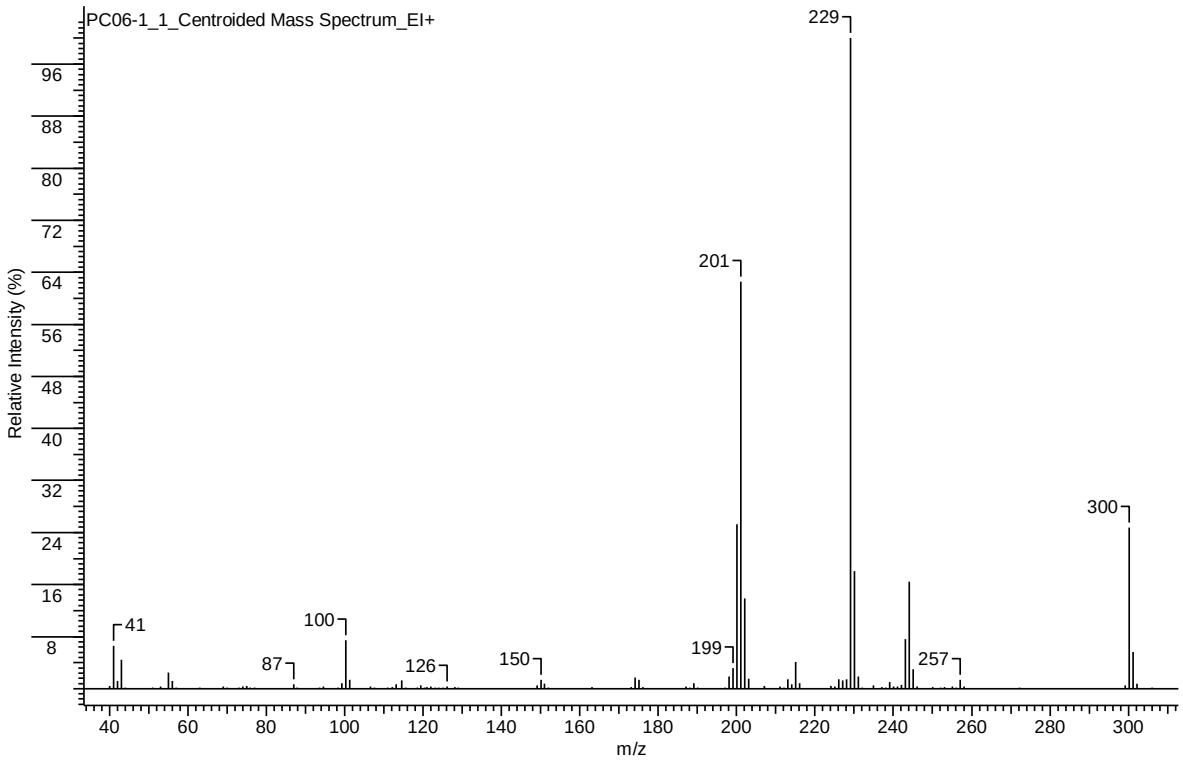


Figure S6. Mass spectrum of compound **PC6**.

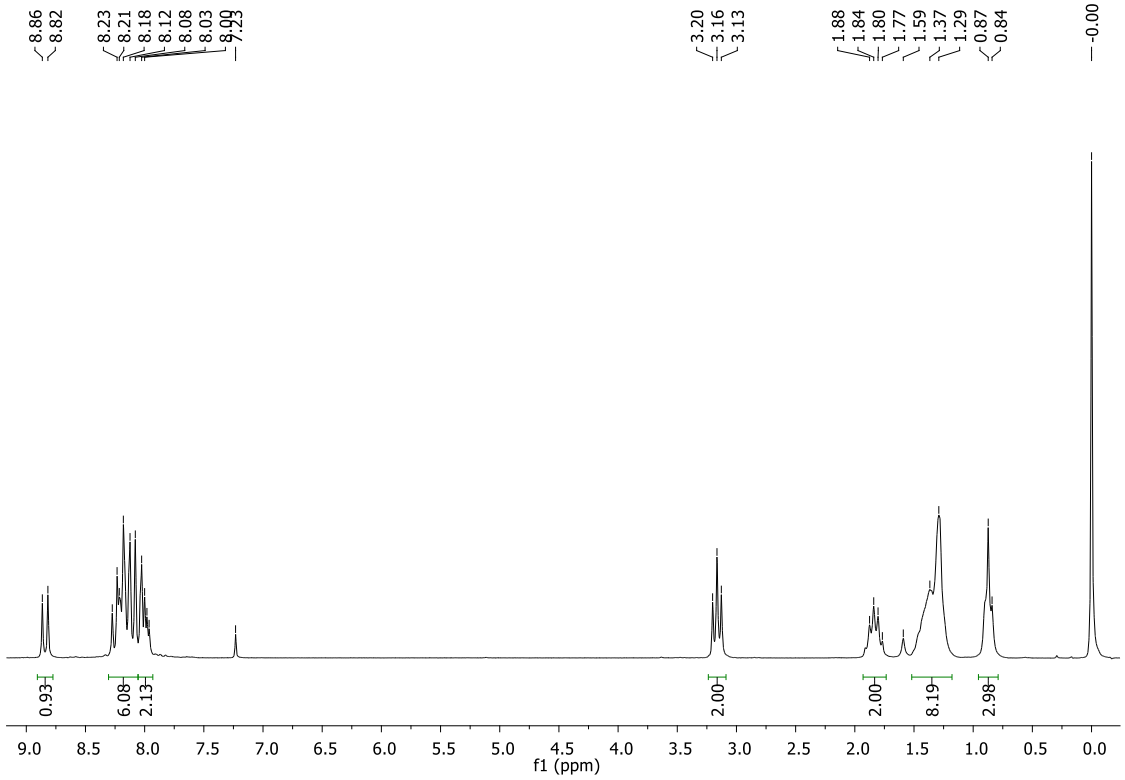


Figure S7. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **PC8**.

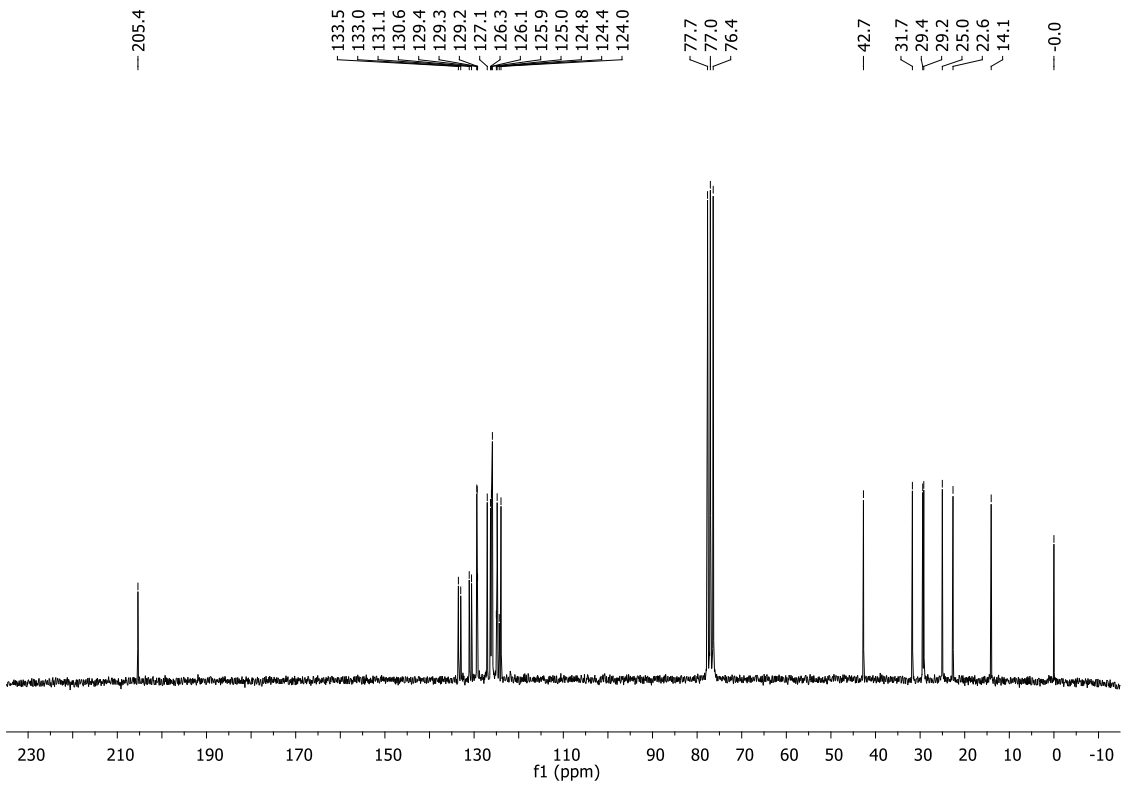


Figure S8. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **PC8**.

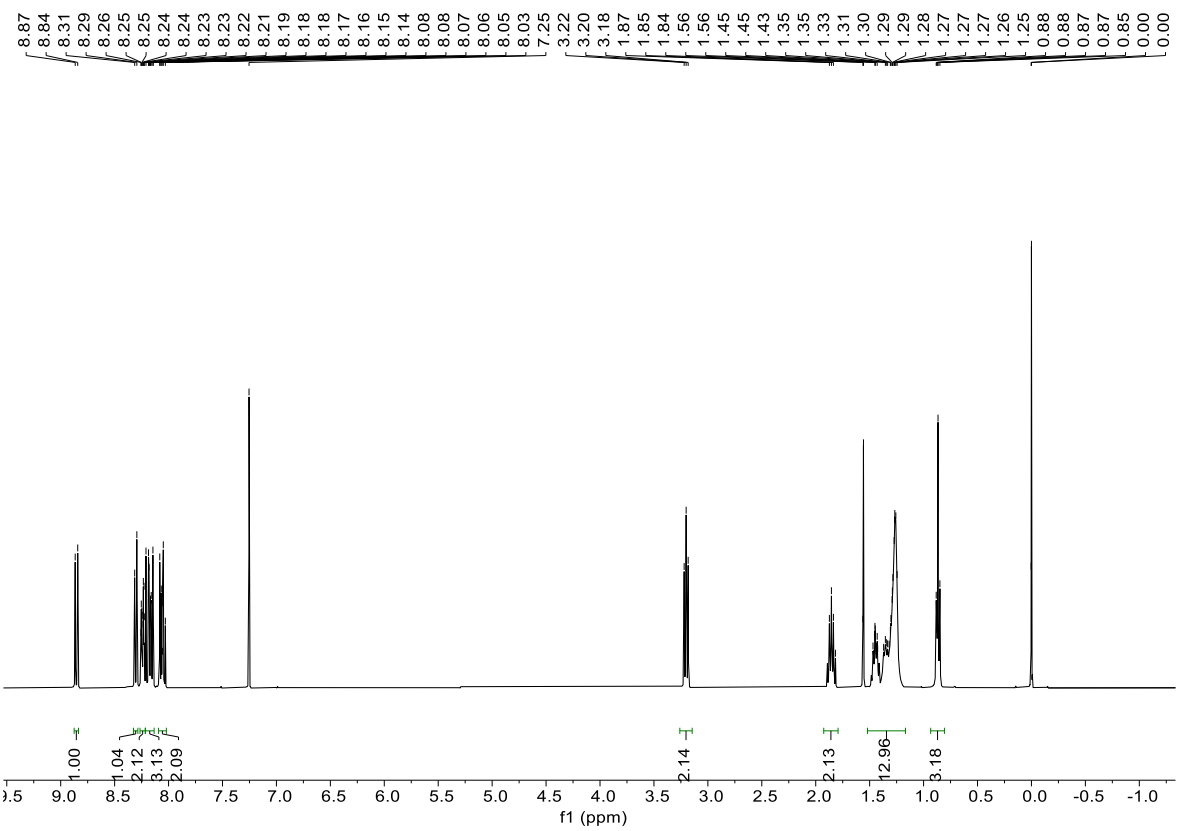


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **PC10**.

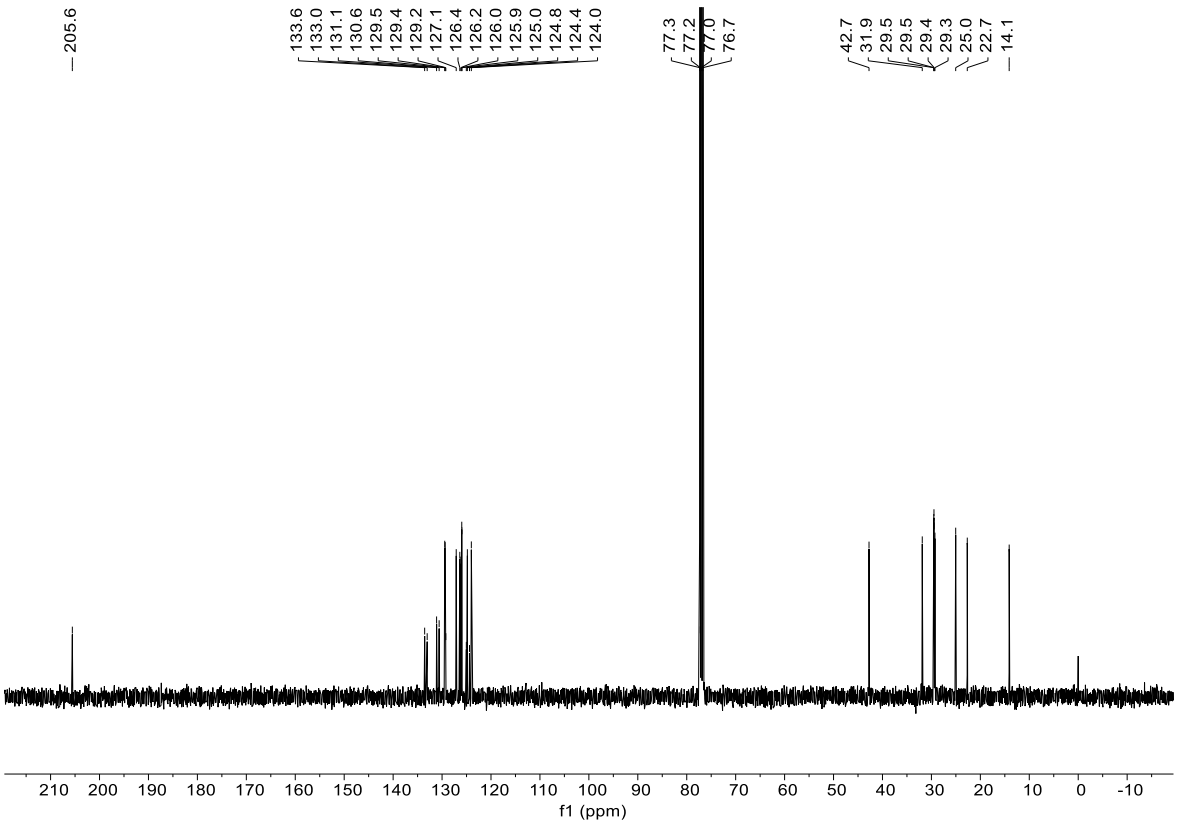


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **PC10**.

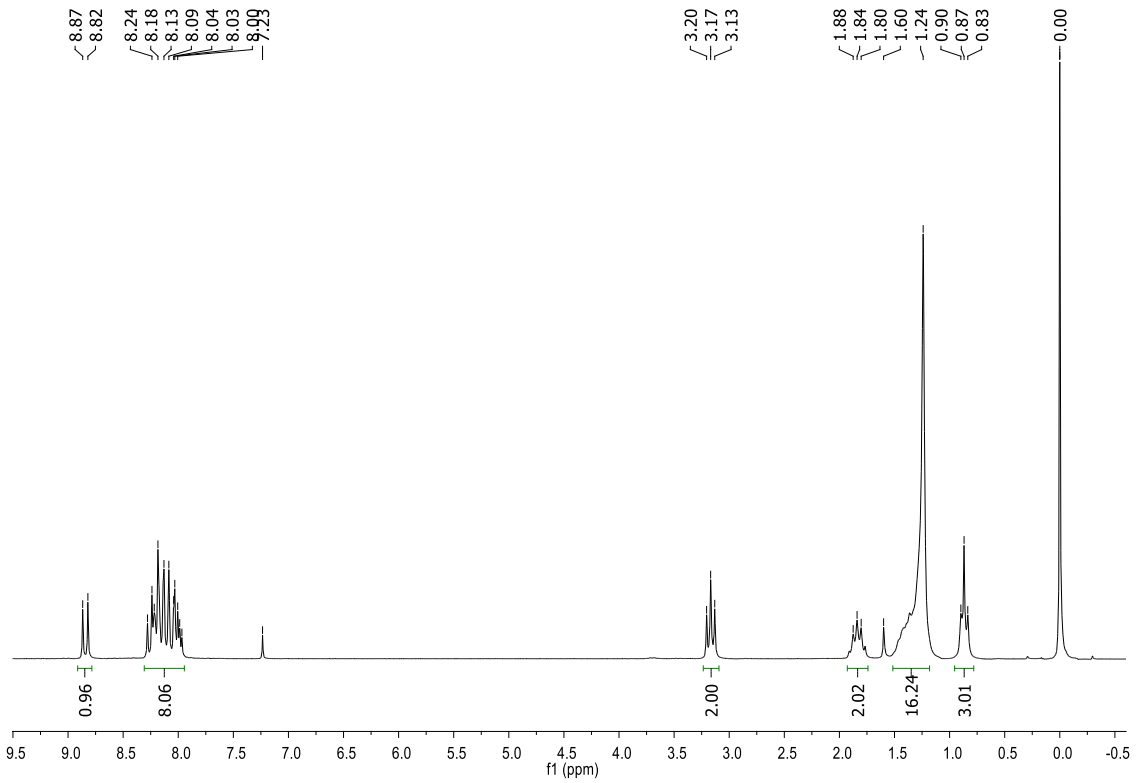


Figure S11. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **PC12**.

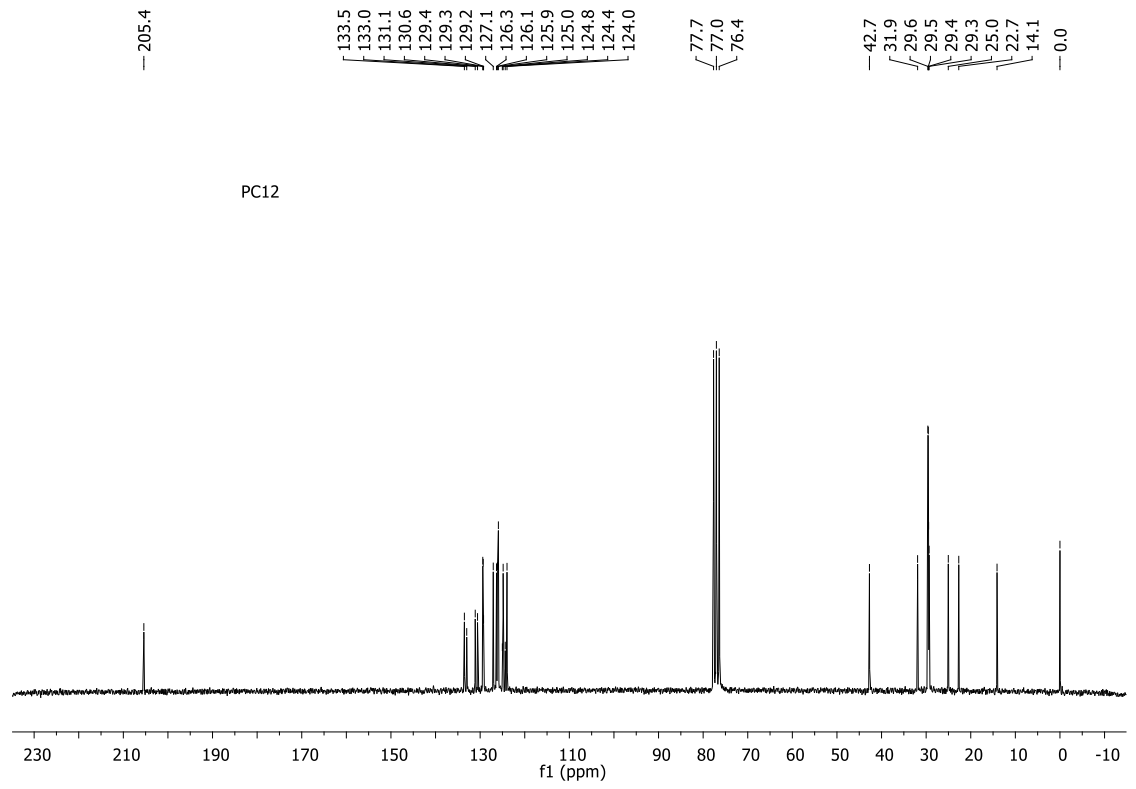


Figure S12. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **PC12**.

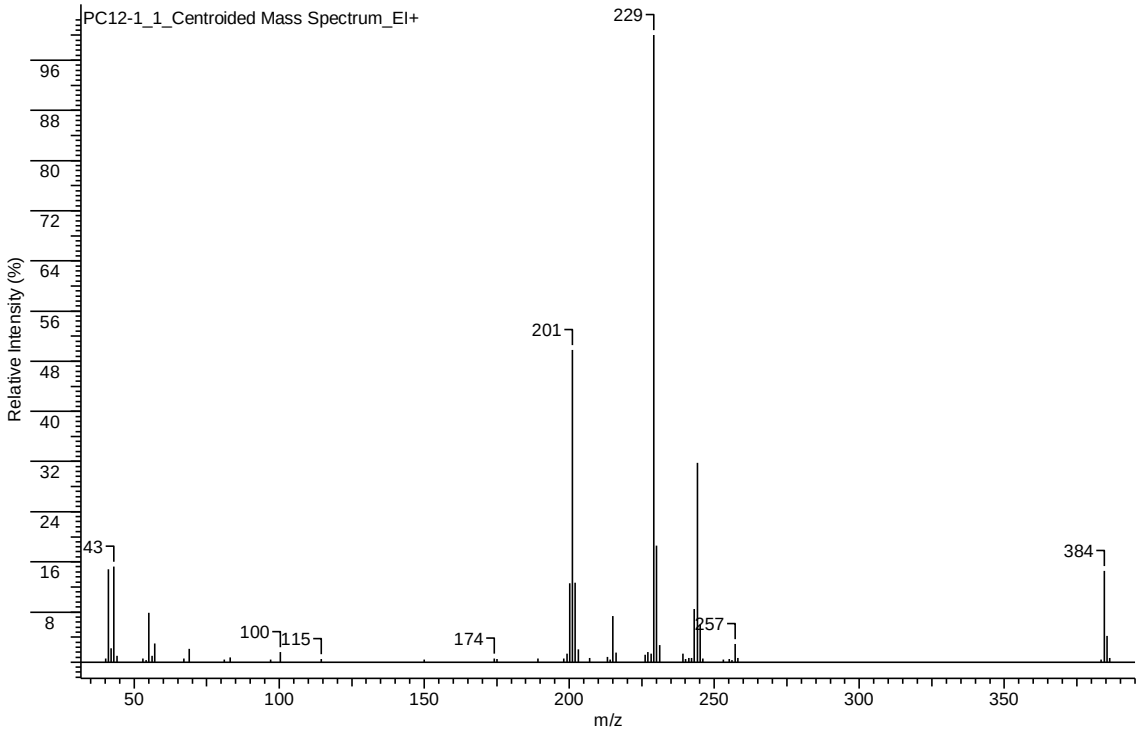


Figure S13. Mass spectrum of compound **PC12**.

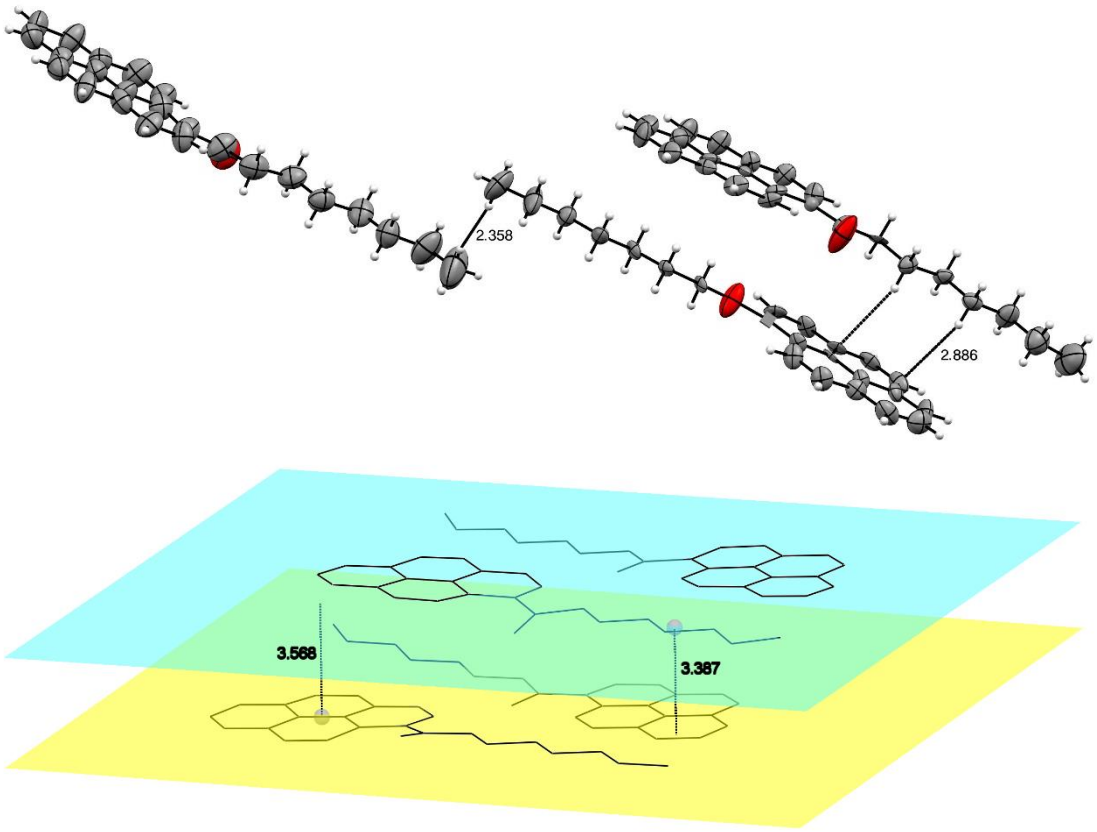


Figure S14. Molecular packing of **PC8**.

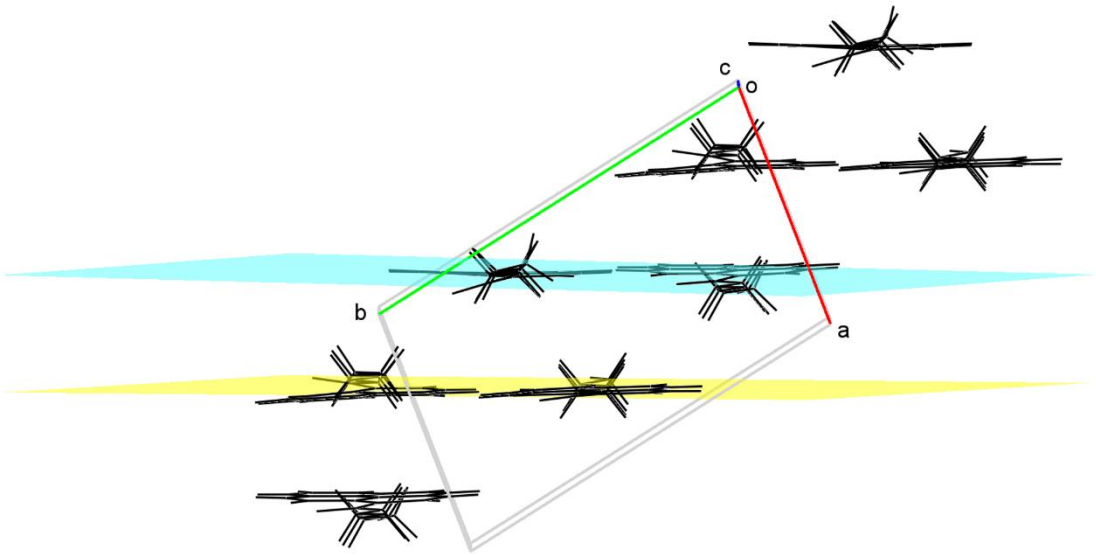
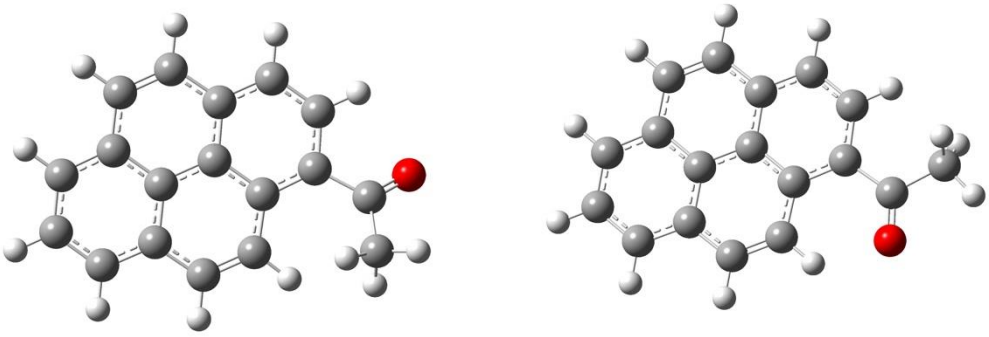


Figure S15. Molecular packing of **PC8** viewed along *bc* diagonal line.



Conformer 01 $\Delta G = 0.00$ kcal mol^{-1} Conformer 02 $\Delta G = -3.30$ kcal mol^{-1}

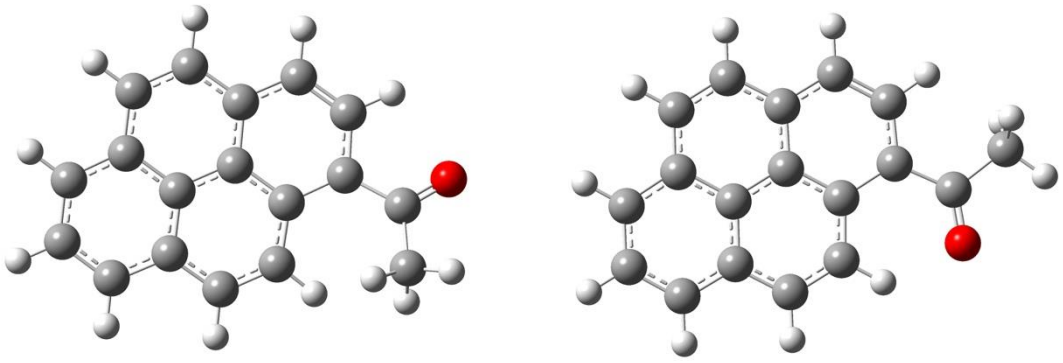
Figure S16. Conformers (S_0) for acyl pyrene **PC2**.

Table S1. Calculations parameter for **PC2** conformers (S_0)-B3LYP/def2svp/gd3bj/[IEFPCM (DCM)]

	Conformer 01	Conformer 02
Imaginary freq	0	0
Temperature / Kelvin	298.15	298.15
Pressure / atm	1	1
Frequencies scaled by	1	1
Electronic energy (EE-DFT) / Hartree	–767.86681	–767.87117
Zero-point energy correction / Hartree	0.245201	0.245385
Thermal correction to energy / Hartree	0.258676	0.258887
Thermal correction to enthalpy / Hartree	0.25962	0.259831
Thermal correction to free energy / Hartree	0.205103	0.2042
EE + zero-point energy / Hartree	–767.62161	–767.62579
EE + thermal energy correction / Hartree	–767.60813	–767.61229
EE + thermal enthalpy correction / Hartree	–767.60719	–767.61134
EE + thermal free energy correction / Hartree	–767.66171	–767.66697
E (Thermal) / (kcal mol^{-1})	162.322	162.454
Heat capacity (Cv) / (cal mol-$kelvin^{-1}$)	56.4	56.27
Entropy (S) / (cal mol-$kelvin^{-1}$)	114.741	117.085

Table S2. Geometry S_0 – conformer 01 and conformer 02-B3LYP/def2svp/gd3bj/[IEFPCM (DCM)]

Atom number	Atomic number	Conformer 01			Conformer 02		
		X	Y	Z	X	Y	Z
1	6	4.076692	−1.266225	−0.048546	−4.141497	−1.211055	−0.102877
2	6	2.959093	−2.091411	0.085683	−3.041418	−2.067250	−0.045517
3	6	1.662686	−1.543984	0.125633	−1.731427	−1.552961	0.013425
4	6	1.492489	−0.128293	0.028855	−1.529712	−0.138845	0.014353
5	6	2.647110	0.709479	−0.099882	−2.666465	0.730540	−0.044802
6	6	3.924249	0.118902	−0.139602	−3.957586	0.173634	−0.102600
7	6	0.490384	−2.357339	0.277315	−0.575863	−2.399370	0.073365
8	6	0.180304	0.446140	0.063150	−0.203546	0.401548	0.073882
9	6	−0.982710	−0.394111	0.171133	0.939869	−0.469394	0.133325
10	6	−0.761853	−1.813630	0.302147	0.690849	−1.890464	0.130243
11	6	−2.269474	0.216988	0.193404	2.250095	0.109103	0.191807
12	6	−2.364177	1.621799	0.171724	2.366233	1.514558	0.188815
13	6	−1.244664	2.433607	0.062754	1.263247	2.354487	0.131510
14	6	0.042427	1.869657	−0.005630	−0.036700	1.824050	0.073149
15	6	1.218646	2.687075	−0.133972	−1.194436	2.674614	0.013136
16	6	2.464520	2.133503	−0.182657	−2.453365	2.152559	−0.043347
17	1	3.349231	2.767973	−0.281163	−3.324987	2.810762	−0.088646
18	1	1.091046	3.771092	−0.190536	−1.041740	3.756797	0.013808
19	1	0.615790	−3.438061	0.383904	−0.724805	−3.482746	0.072972
20	1	5.076602	−1.705729	−0.079919	−5.151723	−1.624978	−0.148236
21	1	3.081130	−3.174938	0.162614	−3.186690	−3.150680	−0.045786
22	1	4.802553	0.761542	−0.241975	−4.821547	0.841783	−0.147617
23	1	−1.609844	−2.477832	0.447259	1.548331	−2.554718	0.174920
24	1	−3.360113	2.064612	0.221259	3.353058	1.973457	0.232753
25	1	−1.356207	3.520047	0.022574	1.401325	3.438357	0.131497
26	6	−3.596606	−0.497049	0.228297	3.512213	−0.702211	0.256377
27	6	−3.795587	−1.834496	−0.463732	4.846102	0.030479	0.315212
28	1	−3.079701	−2.019645	−1.275379	4.998900	0.667087	−0.570125
29	1	−3.711158	−2.653611	0.269667	4.914915	0.677567	1.203459
30	1	−4.823271	−1.857574	−0.852919	5.642685	−0.722756	0.357373
31	8	−4.555786	0.047610	0.752081	3.522846	−1.925520	0.264079



Conformer 01 $\Delta G = 0.00$ kcal mol^{-1} Conformer 02 $\Delta G = -4.37$ kcal mol^{-1}

Figure S17. Conformers (S_1) for acyl pyrene **PC2**.

Table S3. Calculations parameter for **PC2** conformers (S_1)-TD-B3LYP/def2svp/gd3bj/[IEFPCM (DCM)]

	Conformer 01	Conformer 02
Imaginary freq	0	0
Temperature / Kelvin	298.15	298.15
Pressure / atm	1	1
Frequencies scaled by	1	1
Electronic energy (EE-TD-DFT) / Hartree	–767.75662	–767.76276
Zero-point energy correction / Hartree	0.242243	0.242048
Thermal correction to energy / Hartree	0.25598	0.255941
Thermal correction to enthalpy / Hartree	0.256924	0.256885
Thermal correction to free energy / Hartree	0.202019	0.201185
EE + zero-point energy / Hartree	–767.51437	–767.52071
EE + thermal energy correction / Hartree	–767.50064	–767.50682
EE + thermal enthalpy correction / Hartree	–767.49969	–767.50587
EE + thermal free energy correction / Hartree	–767.5546	–767.56157
E (Thermal) / (kcal mol^{-1})	160.63	160.606
Heat capacity (Cv) / (cal mol-kelvin^{-1})	57.597	57.721
Entropy (S) / (cal mol-kelvin^{-1})	115.557	117.233

Table S4. Geometry S_1-conformer 01 and conformer 02-TD-B3LYP/def2svp/gd3bj/[IEFPCM (DCM)]

Atom number	Atomic number	Conformer 01			Conformer 02		
		X	Y	Z	X	Y	Z
1	6	–4.094539	–1.262404	0.051883	–4.151147	–1.182441	0.000071
2	6	–2.978628	–2.087673	–0.065064	–3.053541	–2.040577	0.000036
3	6	–1.659812	–1.532984	–0.102607	–1.720382	–1.521590	–0.000007
4	6	–1.488774	–0.113455	–0.010066	–1.515162	–0.103556	–0.000013
5	6	–2.648167	0.728126	0.094548	–2.653600	0.770997	0.000026
6	6	–3.943310	0.122639	0.127619	–3.965021	0.199915	0.000067
7	6	–0.508693	–2.337176	–0.252223	–0.586137	–2.362886	–0.000044
8	6	–0.180127	0.457740	–0.029804	–0.190680	0.432459	–0.000056
9	6	0.985585	–0.383091	–0.105409	0.950856	–0.439693	–0.000099
10	6	0.769093	–1.774719	–0.260426	0.707758	–1.836800	–0.000090
11	6	2.311697	0.233670	–0.076588	2.302167	0.133814	–0.000150
12	6	2.384959	1.646767	–0.144647	2.408362	1.546465	–0.000123
13	6	1.263431	2.451261	–0.095144	1.303872	2.381817	–0.000082
14	6	–0.050400	1.885905	–0.000911	–0.026374	1.857894	–0.000052
15	6	–1.204749	2.694464	0.090686	–1.161852	2.700087	–0.000013
16	6	–2.479304	2.134701	0.151453	–2.451069	2.176061	0.000023
17	1	–3.359483	2.776520	0.231580	–3.317706	2.840725	0.000051
18	1	–1.086368	3.780846	0.111168	–1.013567	3.783035	–0.000010
19	1	–0.621413	–3.418031	–0.364598	–0.725763	–3.446778	–0.000042
20	1	–5.094892	–1.700981	0.078996	–5.163403	–1.593744	0.000103
21	1	–3.095537	–3.172280	–0.132483	–3.196526	–3.124146	0.000041
22	1	–4.821524	0.768516	0.206786	–4.827828	0.871013	0.000095
23	1	1.613931	–2.442252	–0.406132	1.570802	–2.498137	–0.000126
24	1	3.381173	2.088566	–0.187602	3.394566	2.009426	–0.000140
25	1	1.367526	3.539628	–0.108062	1.442729	3.466181	–0.000071
26	6	3.619775	–0.456148	0.052158	3.535816	–0.678625	–0.000217
27	6	3.739563	–1.861966	0.616134	4.881208	0.039713	0.000208
28	1	2.958332	–2.110052	1.348956	5.012397	0.681061	–0.887128
29	1	3.707233	–2.619612	–0.186978	5.011801	0.681183	0.887543
30	1	4.728646	–1.940550	1.089997	5.668260	–0.725600	0.000523
31	8	4.662098	0.146968	–0.241397	3.536724	–1.919738	0.000175

Table S5. Crystallographic data and structure refinement of **PC8**

Chemical formula	$C_{24}H_{24}O$
Fw	328.43
Crystal system, space group	triclinic, P-1
Temperature / K	298
a, b, c / Å	7.736 (2), 12.906 (4), 37.644 (11)
A, β, y / degree	86.541 (9), 84.299 (9), 78.600 (8)
V / $Å^3$	3662.9 (19)
Z	8
Density (calculated) / (mg m^{-3})	1.191
Radiation type	Mo Kα
μ / mm^{-1}	0.07
F(000)	1408
Crystal size / mm	0.35 × 0.26 × 0.07
Theta range for data / Collection	2.3-24.9º
Index ranges	–9 < h < 9, –15 < k < 15, –45 < l < 45
Absorption correction	multi-scan
Tmin, Tmax	0.687, 0.745
Refinement method	full-matrix least-squares on F^2
No. of measured, independent and observed [I > 2σ(I)] reflections	196676, 13452, 7071
Rint	0.107
Extinction coefficient	0.013 (2)
R[F2 > 2σ(F2)], wR(F2), S	0.149, 0.494, 1.11
No. of reflections	13452
No. of parameters	906
H-atom treatment	H-atom parameters constrained
Δρmax, Δρmin / (e $Å^{-3}$)	0.34, –0.41

Fw: formula weight; Tmin, Tmax: transmission factors; V: volume; a-c and α-γ: unit cell parameters; R(int): internal R-value; R1: R-value; wR2: R-value for F2; ρ: number of electrons *per* unit volume.

No syntax errors found.
Please wait while processing ....

CIF dictionary
Interpreting this report

Datablock: pc08

Bond precision: C-C = 0.0102 A Wavelength=0.71073
Cell: a=7.736(2) b=12.906(4) c=37.644(11)
alpha=86.541(9) beta=84.299(9) gamma=78.600(8)
Temperature : 298 K

	Calculated	Reported
Volume	3662.8(18)	3662.9(19)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C24 H24 O	C24 H24 O
Sum formula	C24 H24 O	C24 H24 O
Mr	328.43	328.43
Dx,g cm-3	1.191	1.191
Z	8	8
Mu (mm-1)	0.071	0.071
F000	1408.0	1408.0
F000'	1408.55	
h,k,lmax	9,15,45	9,15,45
Nref	13558	13452
Tmin,Tmax	0.978,0.995	0.687,0.745
Tmin'	0.976	

Correction method= # Reported T Limits: Tmin=0.687
Tmax=0.745 AbsCorr = MULTI-SCAN
Data completeness= 0.992 Theta(max)= 25.419
R(reflections)= 0.1485(7071) wR2(reflections)= 0.4944(13452)
S = 1.106 Npar= 906

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT084_ALERT_3_A	High wR2 Value (i.e. > 0.25)	0.49 Report

Alert level B

PLAT340_ALERT_3_B	Low Bond Precision on C-C Bonds	0.01017 Ang.
PLAT930_ALERT_2_B	Check Twin Law (0 1 0)[-1 3 0] Estimated BASF	0.22
PLAT934_ALERT_3_B	Number of (Iobs-Icalc)/SigmaW > 10 Outliers	10 Check

Alert level C

PLAT082_ALERT_2_C	High R1 Value	0.15 Report
PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	3.1 Ratio
PLAT220_ALERT_2_C	Non-Solvent Resd 2 C Ueq(max)/Ueq(min) Range	3.3 Ratio
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C17 Check
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C65 Check
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	99.890 Check

And 4 other PLAT906 Alerts

PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	11.148 Check
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	4.373 Check
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	2.879 Check
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	2.277 Check
PLAT910_ALERT_3_C	Missing # of FCF Reflection(s) Below Theta(Min).	8 Note
PLAT911_ALERT_3_C	Missing # FCF Refl Between THmin & STh/L= 0.600	12 Report

Alert level G

```
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.17 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      16.84 Why ?
PLAT802_ALERT_4_G CIF Input Record(s) with more than 80 Characters         1 Info
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..         ! Info
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        90 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....         3 Note
PLAT931_ALERT_5_G Found Twin Law ( 0 1  0)[       ] Estimated BASF       0.22 Check
```

```
  1 ALERT level A = Most likely a serious problem - resolve or explain
  3 ALERT level B = A potentially serious problem, consider carefully
 12 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  7 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  8 ALERT type 2 Indicator that the structure model may be wrong or deficient
 11 ALERT type 3 Indicator that the structure quality may be low
  3 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

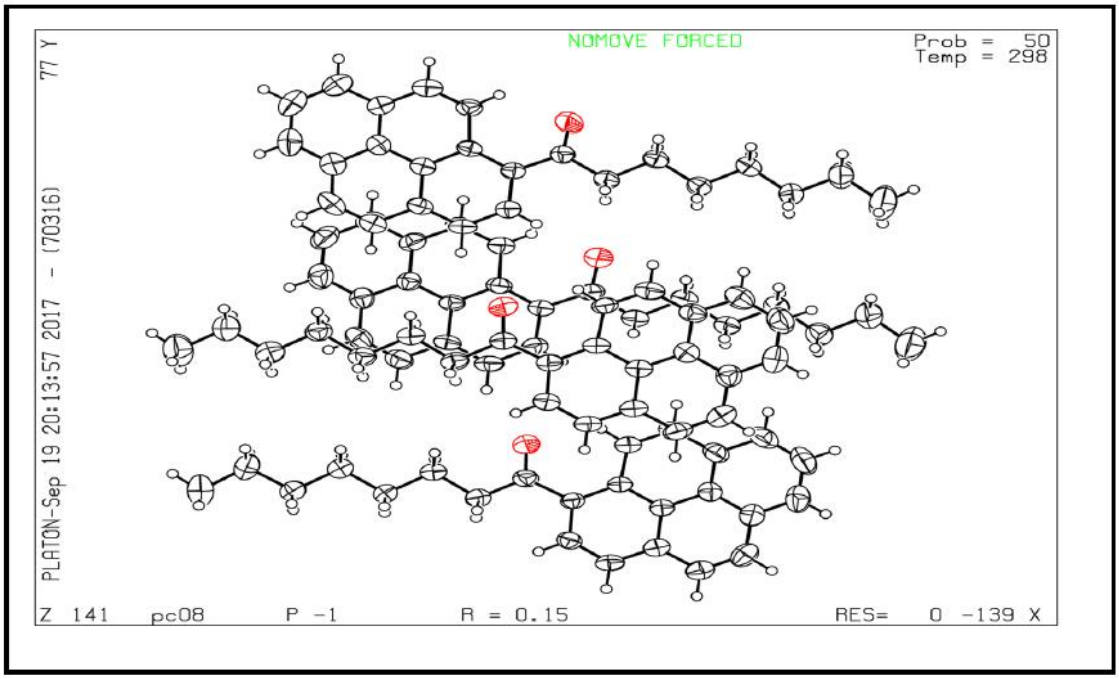
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/08/2017; check.def file version of 27/07/2017

Datablock pc08 - ellipsoid plot



Download CIF editor (publCIF) from the IUCr
Download CIF editor (enCIFer) from the CCDC
Test a new CIF entry