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Supporting Information

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Supporting Information

The direct conversion of light into continuous mechanical energy *via* photoreversible self-assembly: a light-powered engine prototype.

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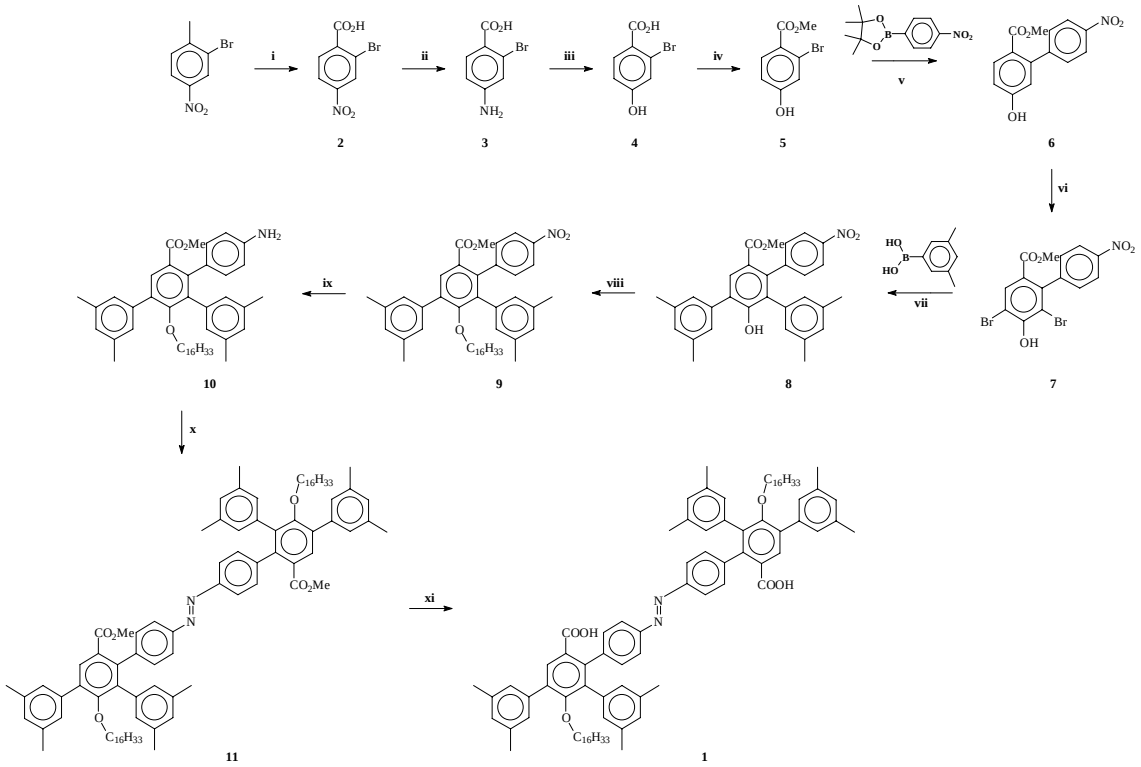


Scheme S1: **i**) $KMnO_4$ / pyr. / H_2O / Δ, 70%; **ii**) $SnCl_2$ / EtOH / Δ, 71%; **iii**) $NaNO_2$ / H_2O /H^+ / 2°C, then H_2O / H^+ / Δ, 94%; **iv**) MeOH / H^+ / Δ, 96%; **v**) K_3PO_4 / $Pd[(C_6H_5)_3P]_4$ / DMF / Δ, 78%; **vi**) $Bu_4NBr{\cdot}Br_2$ / CH_2Cl_2 / MeOH, 88%; **vii**) K_3PO_4 / $Pd[(C_6H_5)_3P]_4$ / dioxane / H_2O / Δ, 84%; **viii**) n-$C_{16}H_{33}I$ / Cs_2CO_3 / DMF / Δ, 97%; **ix**) $SnCl_2$ / EtOH / Δ, 94%; **x**) $KMnO_4$ / $CuSO_4$ / CH_2Cl_2, 27%; **xi**) t-BuOK / H_2O / Et_2O, 96%.

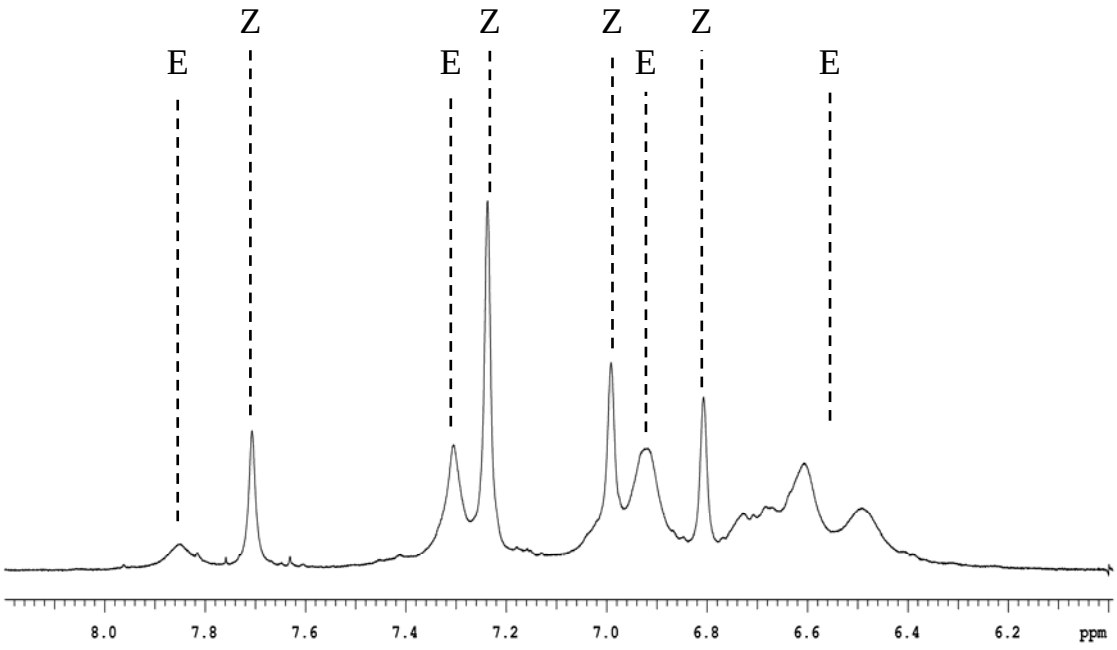


Fig. S1: downfield region of the ^{1}H-NMR spectrum of partially photoisomerized **1** in CD_2Cl_2.

Experiments on the aggregation of *E*-1 and *Z*-1

The photoisomerization process can be followed by ^{1}H-NMR spectroscopy. The spectrum of a freshly prepared sample of *E*-**1** in acetone-d_6 (6.8 mg in 0.75 mL) shows signals arising from the dissolved fraction of the compound (Figure S2 **A**). By adding to this mixture a measured amount of 1,2-dichloroethane (1 μL) as an internal standard, it has been possible to measure by ^{1}H-NMR a solubility of 2.6 mg/mL (i.e. the saturated solution concentration is $2 \cdot 10^{-3}$ M). Upon irradiation at 365 nm, the spectrum changes dramatically and a new set of signals due to the *Z* isomer starts to grow and a photostationary state (91% *Z* in solution) can be reached after 2 hrs (Figure S2 **B**).

Although compound *E*-**1** has failed to afford crystals suitable for X-ray analysis, the existence of aggregation via H-bonding in the solid state is confirmed by FT-IR spectroscopy. Spectra recorded on solid unirradiated *E*-**1** (crystallized from acetone) (Figure S3) show the characteristic features of hydrogen bonded carboxylic acids.[1] Because of the molecular structure of *E*-**1**, these hydrogen bonds must be intermolecular.

ESI-MS spectra (negative mode) of unirradiated *E*-**1** in acetone (Figure S4, top) show, besides the monocharged and bicharged (base peak) monomer, a large number of signals arising from either mono- or bicharged associated oligomeric species; within the instrumental range (4000 *m/z*), up to a bicharged hexamer can be detected. This suggests that the association observed for the *E* isomer in the solid state survives to some extent in solution. Under the same conditions, an acetone solution of **1** at the *Z* photostationary state (91% *Z*) originates markedly different spectra (Figure S4, bottom). In particular, although dimeric and trimeric monocharged species are still detected, the monocharged monomer is now the most intense peak and all the signals arising from bicharged aggregates have disappeared, suggesting that no supramolecular species

possessing two carboxylic groups capable of independent deprotonation are present in solution.

Direct evidence of the different extent of association for the two isomers in solution can be obtained by NOESY. It is well known that the sign of the NOE is related to the rotational correlation time,[2] which in turn depends on the molecular weight: small molecules show positive NOEs whilst large, slowly tumbling molecules show negative NOEs, the reversal falling in the 1000-2000 Da range. The NOESY spectrum of *E*-**1** (m.w. 1320 Da) in acetone-d_6 (Figure S5) shows no signals suggestive of stacked aggregates. The cross peaks have the same sign as the diagonal (negative), confirming that the soluble fraction of the *E* isomer forms supramolecular assemblies via intermolecular H-bonding. On the contrary, the NOESY spectrum of *Z*-**1** in acetone-d_6 (Figure S6) shows the same contacts as positive cross peaks. This cross-peak sign inversion strongly suggests that the *Z* isomer exists mainly as a fast tumbling, unassociated monomer in solution.

DOSY experiments on mixtures of *E* and *Z*-**1** in acetone showed self-diffusion coefficients ratios D_E/D_Z in the 0.9-0.95 range, depending on *E*/*Z* relative amount and concentration. The ratio drops to 0.64 when the experiment is performed in CD_2Cl_2, where both isomers are readily soluble and *E*-**1** appears much more associated. This suggests that, as far as the soluble fraction of the *E* isomer in acetone is concerned, the extent of aggregation is low, while larger aggregates are not observed due to their insolubility.

Further evidence of the existence of intramolecular hydrogen bonding for the *Z* isomer comes from kinetic measurements. The thermal *Z* to *E* back-isomerization of *Z*-**1** in acetone is very slow: a sample, at the *Z*-photostationary equilibrium, left for nine days in the dark at room temperature, still contained the *Z* isomer as the main species in solution (60%). The rate of disappearance of the *Z* isomer, measured by ^{1}H-NMR, resulted in a k =

$2.7\pm0.5\cdot10^{-4}$ min^{-1} at 25°C. Analogous measurements in the more competing solvent, methanol, gave a $k = 2.0\pm0.1\cdot10^{-2}$ min^{-1} at 25°C. The very low rate constant measured for the thermal *Z* to *E* back-isomerization in acetone is in line with previously reported data on hydrogen-bonded azodibenzoic acids [3] and, as the compound appears to be monomeric, can be explained in terms of intramolecular hydrogen bond stabilization of the *Z* isomer.

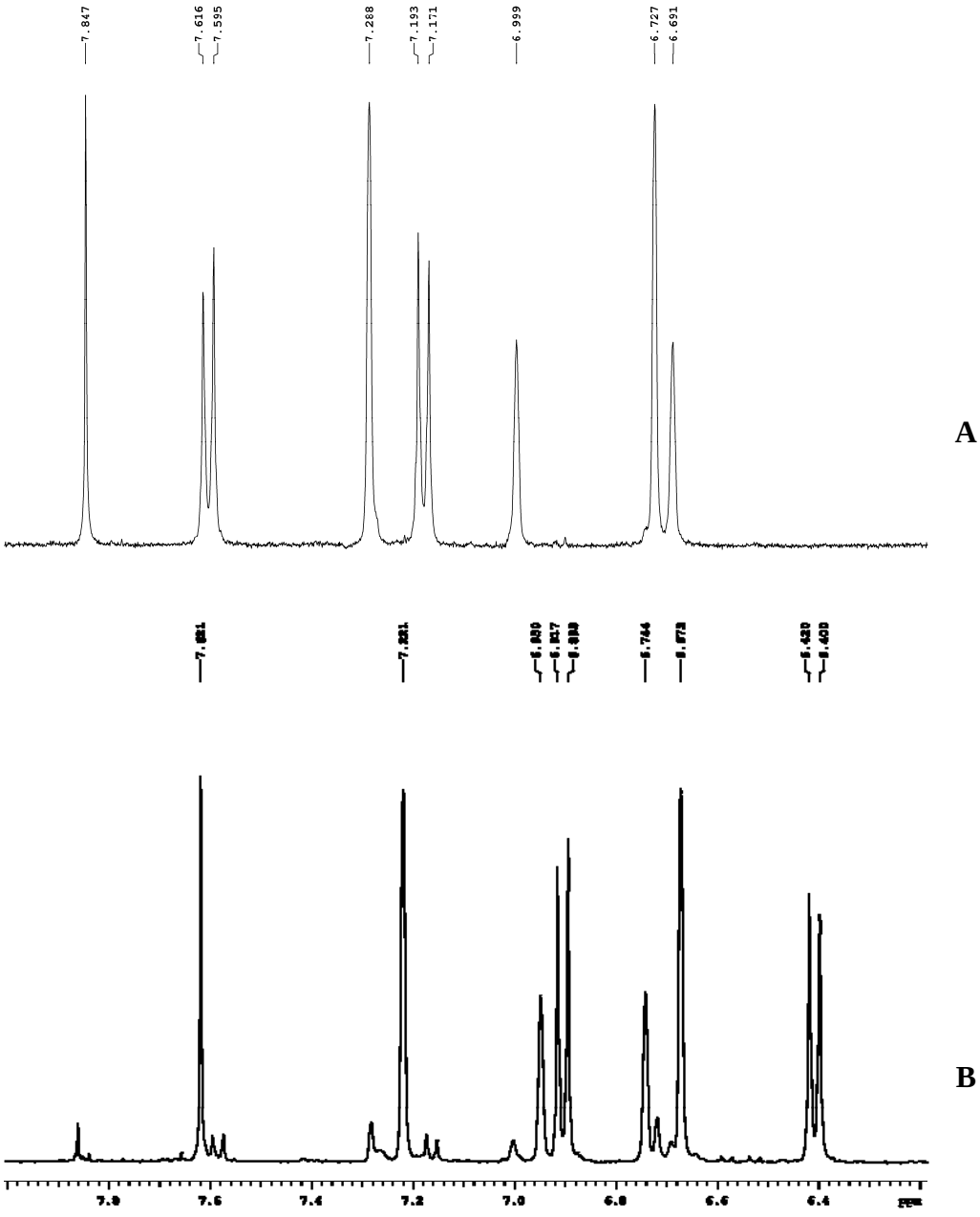


Figure S2: downfield region of the ^{1}H-NMR spectrum of **1** in acetone-d_6: a) non-irradiated *E*-**1**; b) irradiated (356 nm) **1** (*Z* photostationary state).

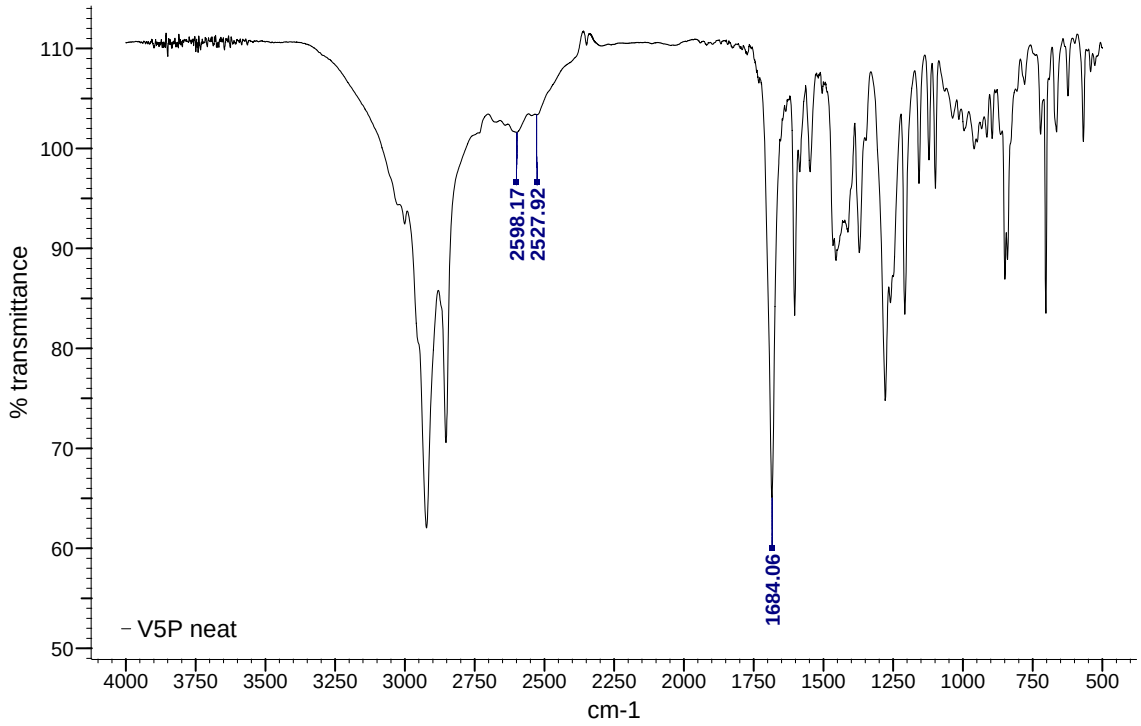


Figure S3: FT-IR spectrum of neat *E*-**1**.

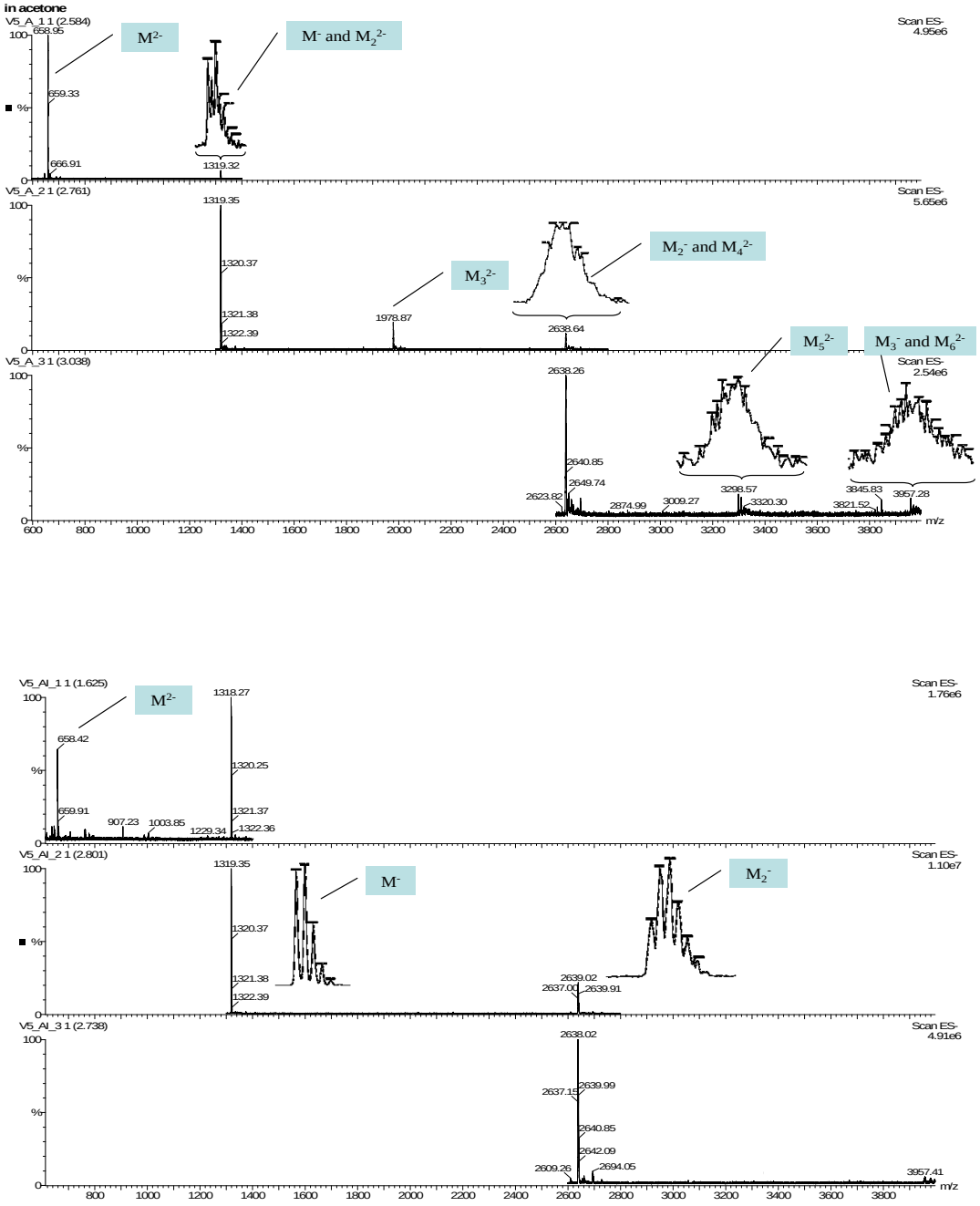


Figure S4. **Top:** ESI-MS spectra (negative mode) of non-irradiated *E*-**1** in acetone. For a better resolution, three overlapping 1500 *m/z* ranges were scanned. **Bottom**: ESI-MS spectra (negative mode) of *Z* photostationary state of **1** in acetone.

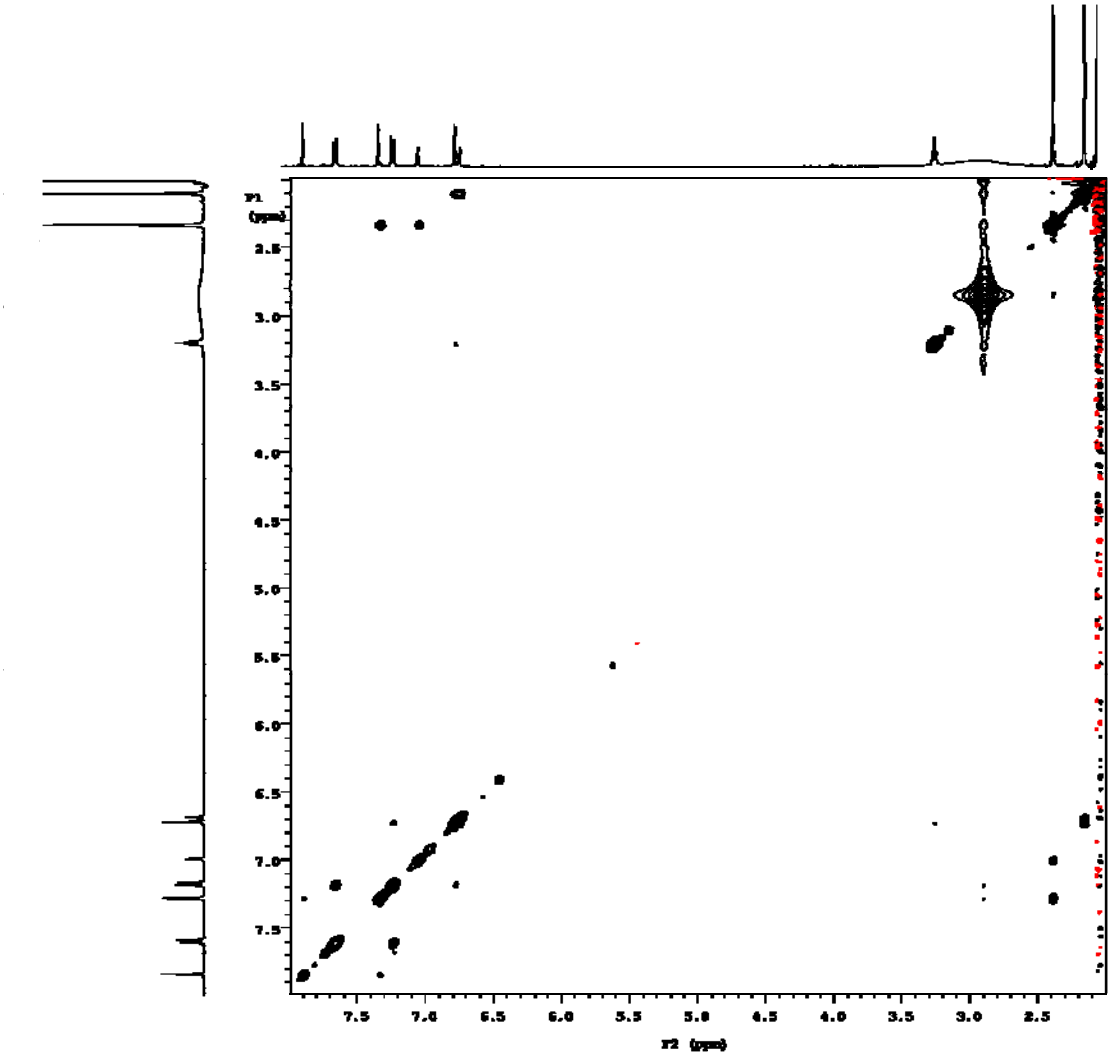


Fig. S5. NOESY spectrum of *E*-**1** in acetone-d_6 (7 mg/0.6 mL): mixing time 200 ms, black = negative, red = positive.

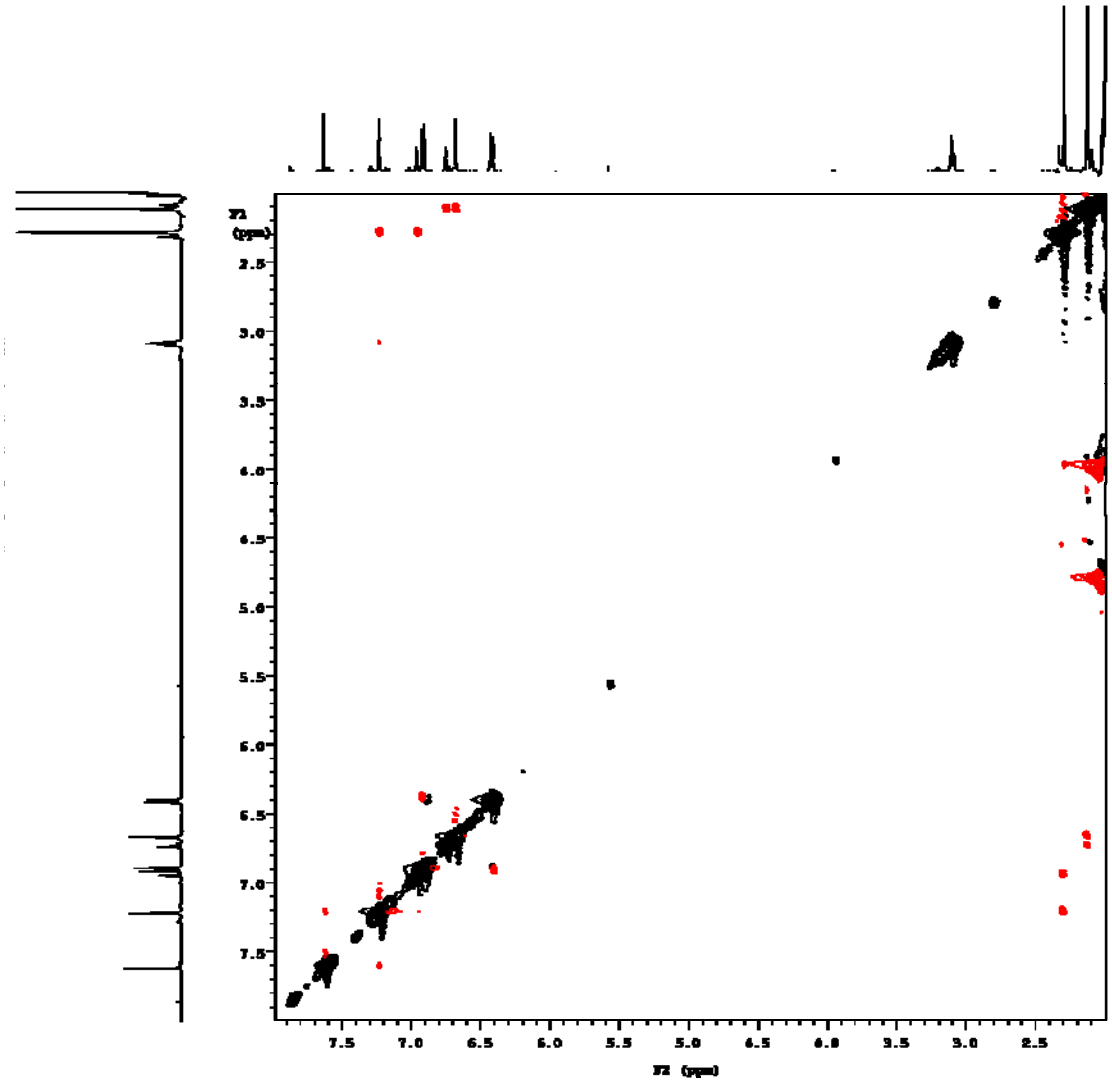


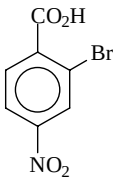
Fig. S6. NOESY spectrum of *Z*-**1** (photostationary state) in acetone-d_6 (7 mg/0.6 mL): mixing time 200 ms, black = negative, red = positive.

Materials and methods

Synthetic procedures

General.

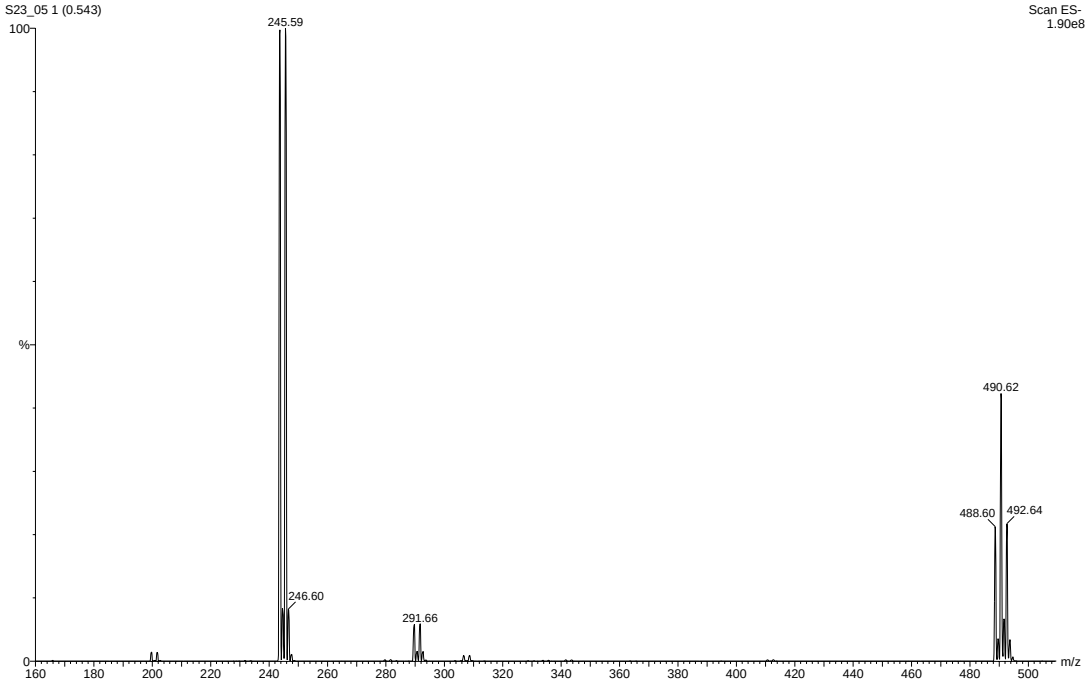
All reactions were carried out under magnetic or mechanical stirring. Reactions requiring anhydrous conditions were carried out in oven-dried glassware under dry argon atmosphere. Degassing, when necessary, was accomplished by means of an ultrasonic bath. For TLC analyses, Baker IB2-F silica gel plates were used. Column chromatography was performed on Aldrich silica gel 230-400 mesh. Reagents and solvents, including dry solvents, were purchased from Aldrich or Fluka. Melting points were determined using open glass capillaries and are uncorrected. NMR spectra were recorded with Varian Gemini 200, Mercury 300 or 400 MHz instruments; decoupled ^{13}C NMR spectra were usually recorded. To assign carbons, DEPT spectra (multiplicity 1.5) were recorded. All NMR spectra were referenced relative to residual solvent peaks. FT-IR spectra were recorded with a Nicolet 460 spectrometer. Electrospray (ES) ionization mass spectra were obtained with a Micromass ZMD 4000. High resolution mass spectra (electronic impact) were recorded with a Thermo Finnigan MAT 95 XP spectrometer.



2

2-Bromo-4-nitrobenzoic acid.

To a boiling solution of 2-bromo-4-nitrotoluene (21.3 g, 98.6 mmol) in pyridine (260 mL) and water (300 mL) were added 66.0 g (0.42 mol) of $KMnO_4$ in six portions over 6 hrs. Refluxing was continued for two additional hrs. The resulting slurry was filtered and the precipitate was washed with 1N NaOH (4x100 mL) and Et_2O (3x70 mL). The resulting filtrate was extracted with Et_2O (4x100 mL) and the combined organic phases were washed with 0.5N NaOH (30 mL). The combined aqueous phases were cooled in ice/water and acidified to pH 2 with a 20% H_2SO_4 solution. The resulting suspension was extracted with Et_20 (3x80 mL). The solvent was distilled off and the resulting solid was crystallized from water, affording 16.89 g (70%) of the title compound as a white solid. M.p. 169-171°C (lit. [4] 166°C). HRMS (EI): Calcd. for $C_7H_4BrNO_4$: 244.9324, Found: 244.9325.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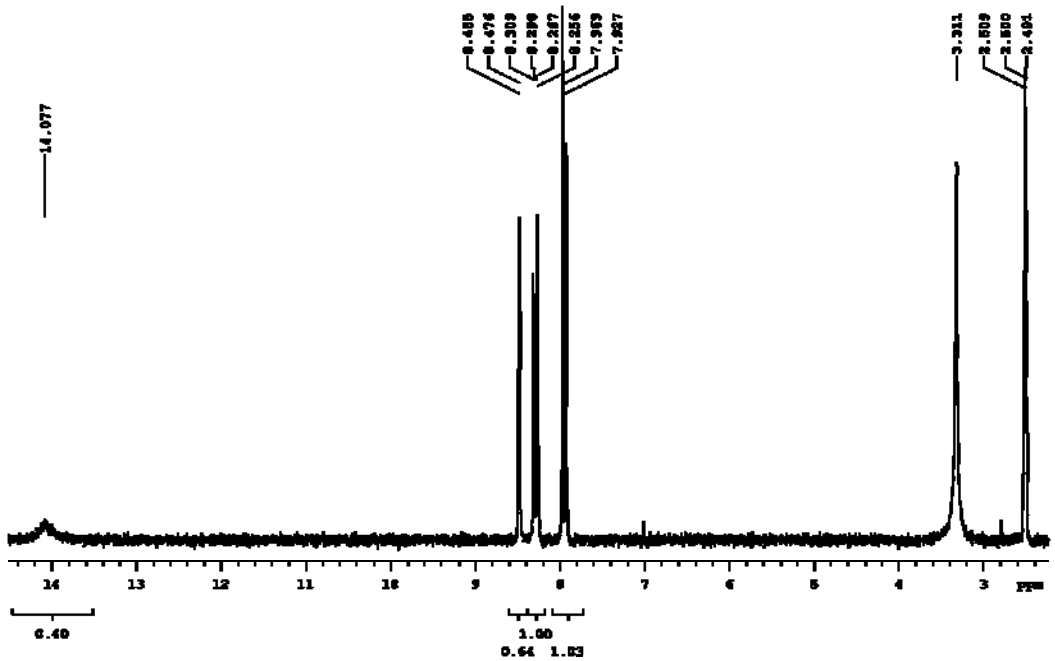
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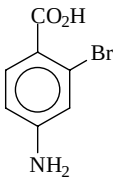
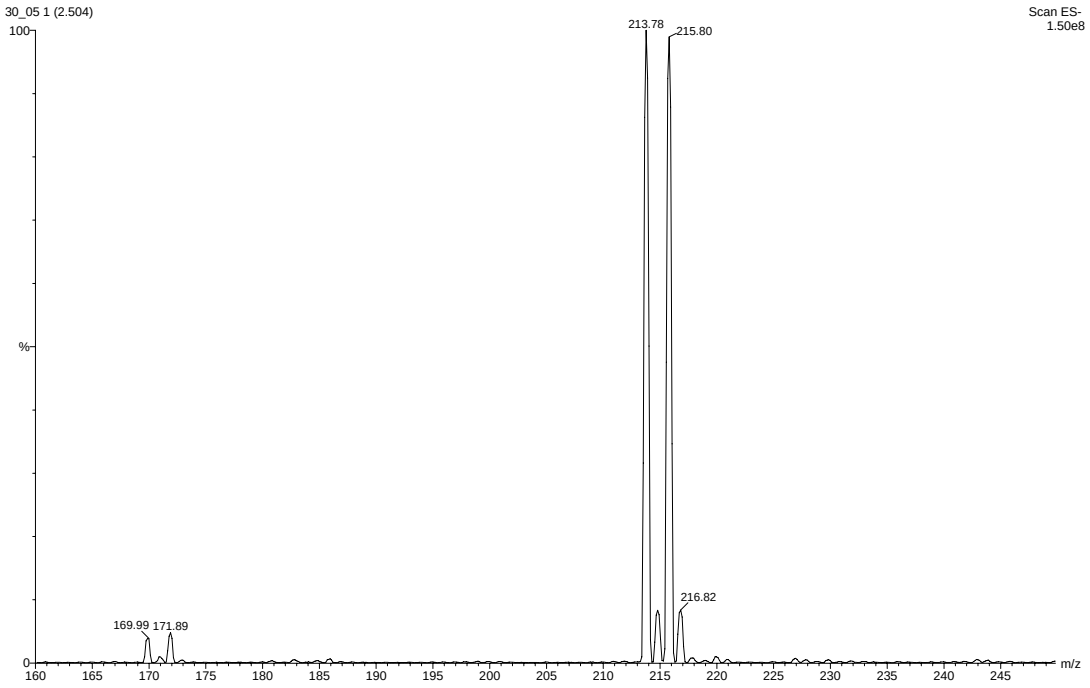
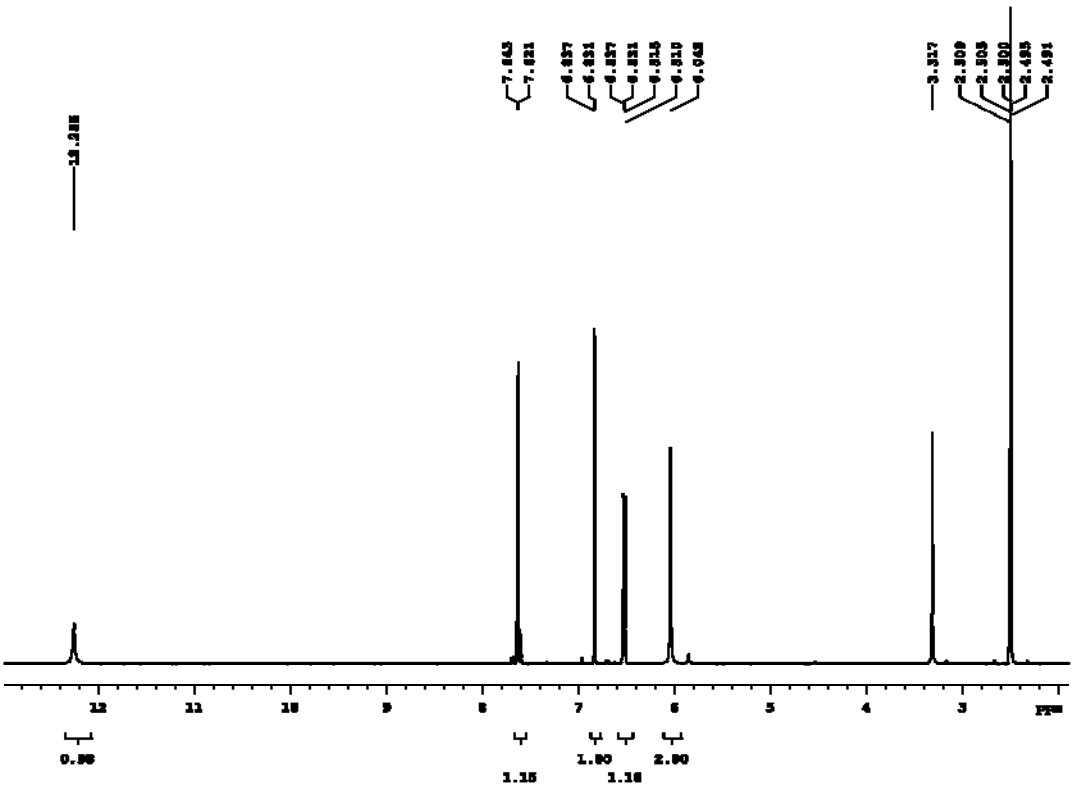


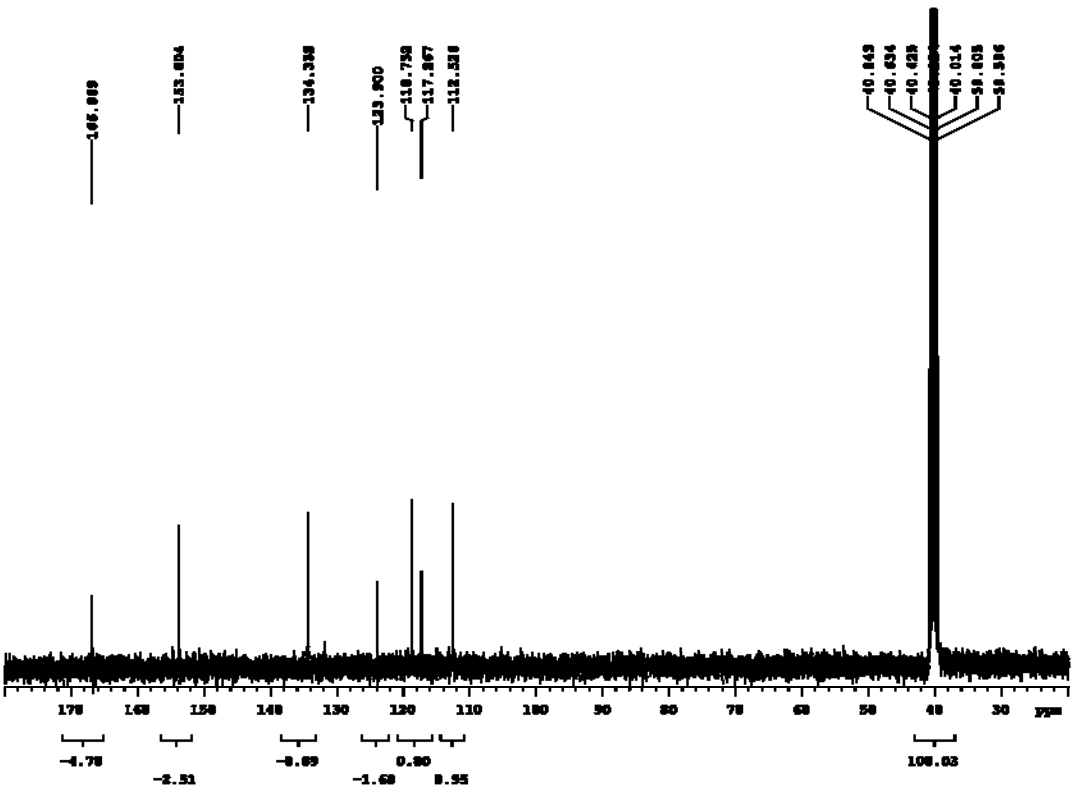
3

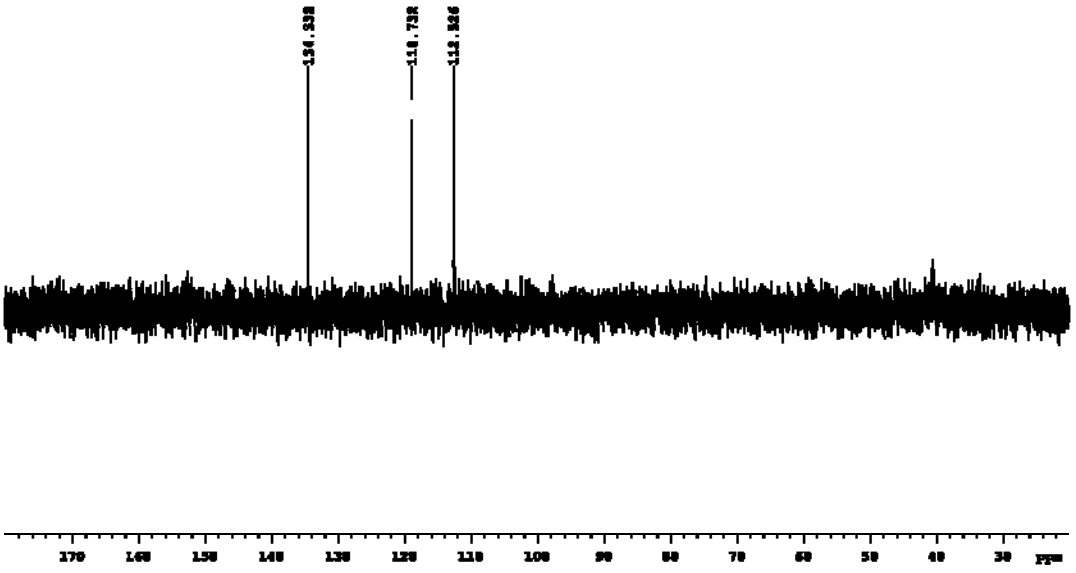
4-Amino-2-bromobenzoic acid.

To a solution of **2** (15.53 g, 63.4 mmol) in abs. EtOH (125 mL) were added 60.01 g (0.317 mol) of $SnCl_2$, and the resulting suspension was gently refluxed for 1 hr. After cooling, the reaction mixture was diluted with ice, made slightly alkaline with 5% $NaHCO_3$ and filtered. The precipitate was washed with ethyl acetate and water. The filtrate was partitioned and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was distilled off affording 10.17 g (71%) of **3** as a white solid. M.p. (H_2O) 200-202°C dec. (lit. [5] 204°C). HRMS (EI): Calcd. for $C_7H_6BrNO_2$: 214.9582, Found: 214.9582.





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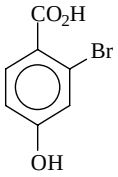
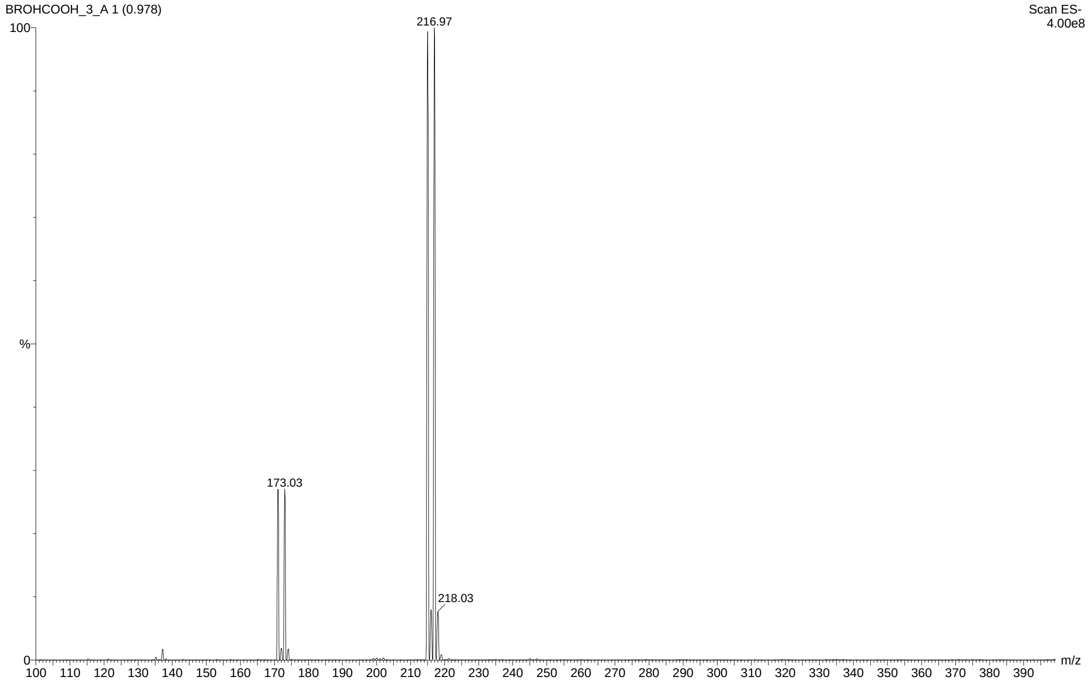


4

2-Bromo-4-hydroxybenzoic acid.

Aminoacid **3** (10.17 g, 47 mmol) was dissolved in a mixture of water (180 mL) and conc. sulfuric acid (40 g) and cooled to 2°C. A solution of $NaNO_2$ (3.24 g, 47 mmol) in 20 mL of water was then added over 0.5 h. Stirring was continued for additional 0.5 hrs. This mixture was then cautiously added to a hot (65°C) solution containing 94 g of conc. sulfuric acid in 700 mL of water. The resulting solution was kept for 48 hrs. at this temperature under vigorous stirring and was then extracted with ethyl ether (5x100 mL). The combined organic layers were dried over $MgSO_4$ and the crude obtained after removal of the solvent was purified by column chromatography over silica (CH_2Cl_2/MeOH 95:5 as the eluant), affording the title compound as a white solid in a 94% yield (9.61 g.). M.p 206-208°C (Lit. [6] 206-208°C). HRMS (EI): Calcd. for $C_7H_5BrO_3$: 215.9422, Found: 215.9421.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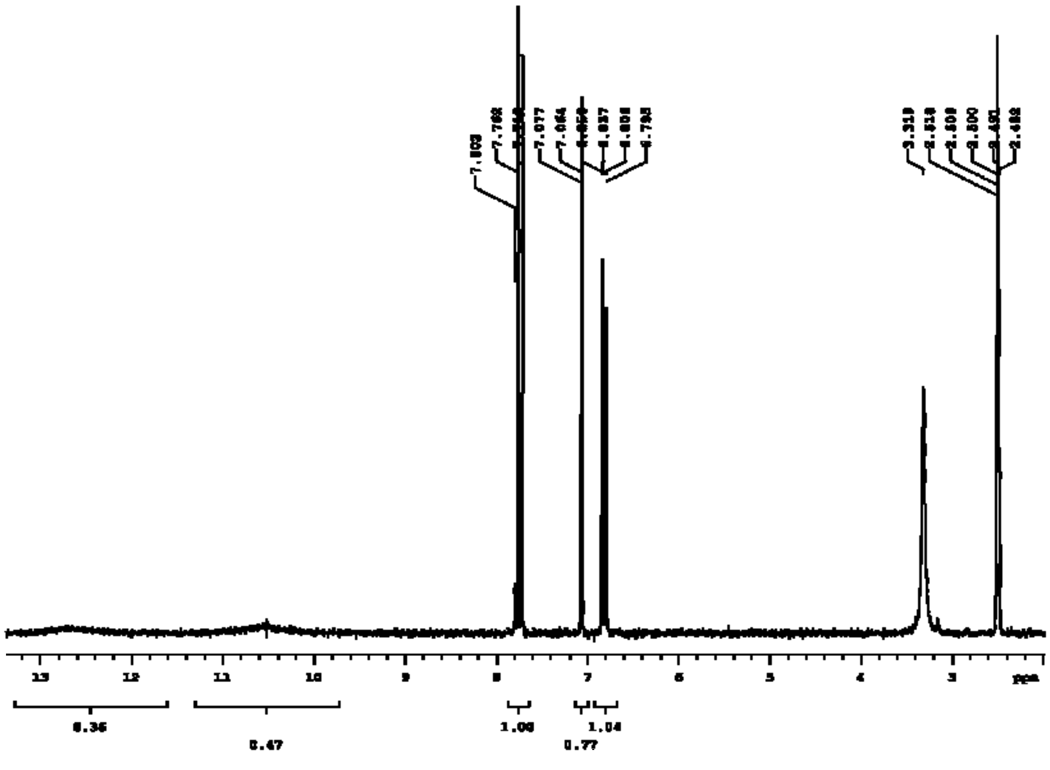
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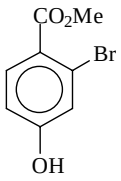
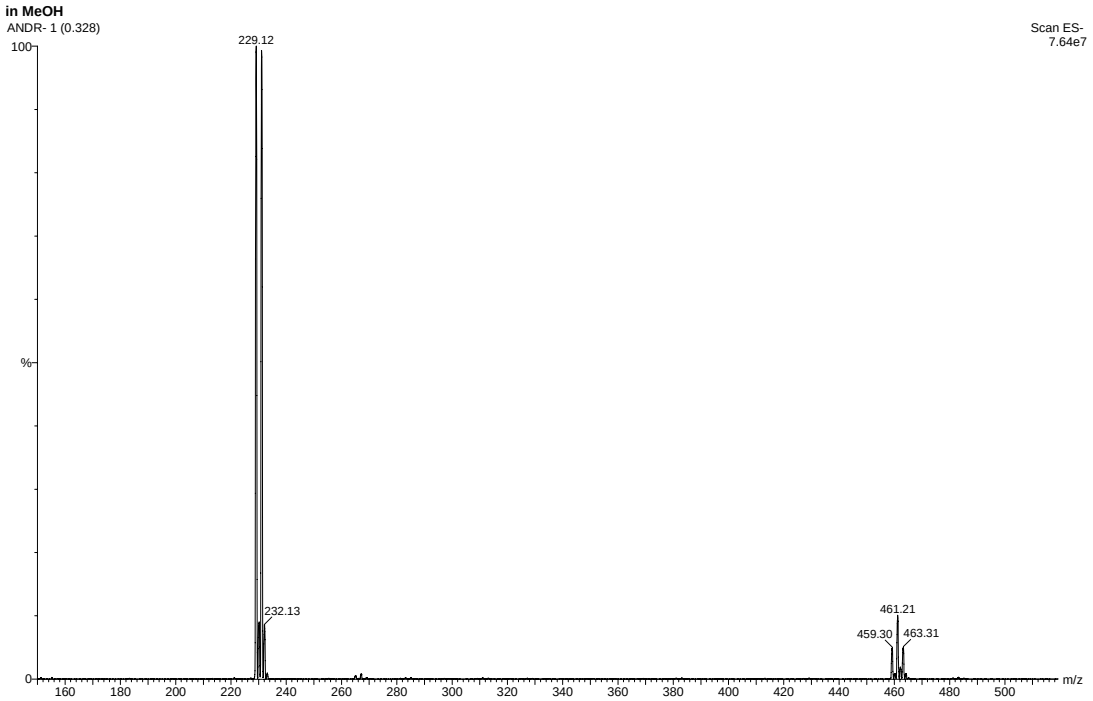
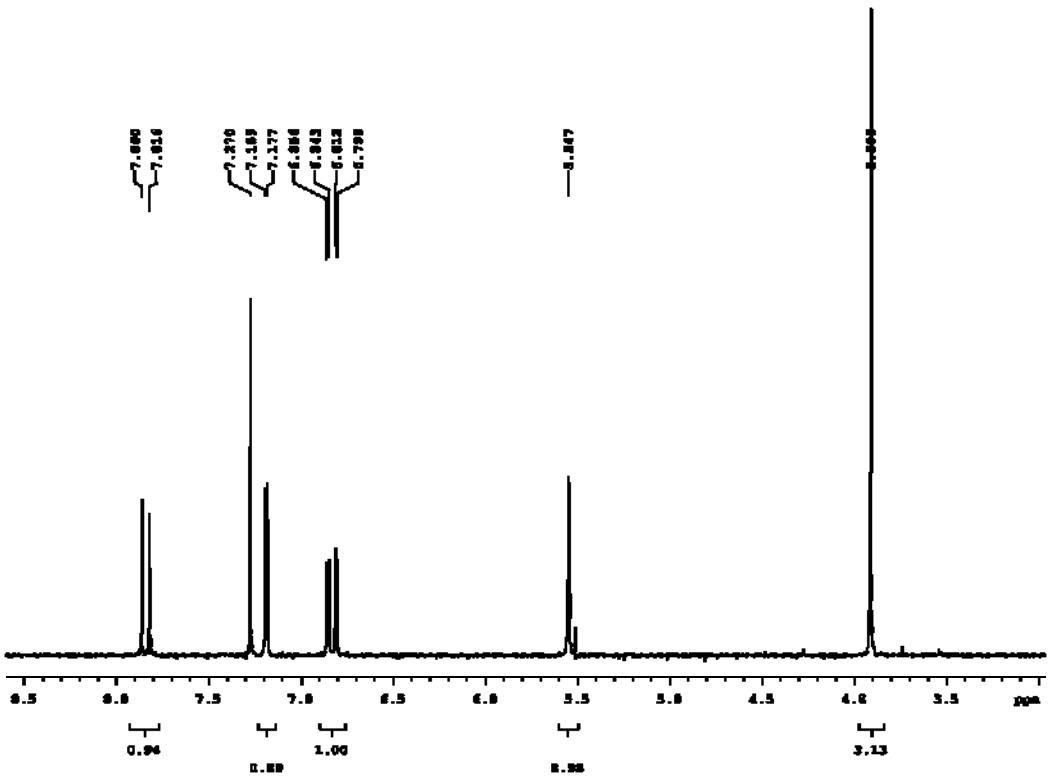


5

2-Bromo-4-hydroxybenzoic acid methyl ester.

Acid **4** (10.24 g, 47.2 mmol) was dissolved in dry MeOH and 1 mL of conc. sulfuric acid was added. The mixture was refluxed overnight, cooled to r.t. and the solvent was removed under reduced pressure. The crude was partitioned between Et_2O (100 mL) and 2.5% $NaHCO_3$ (100 mL). The aqueous layer was washed twice with Et_2O and the combined organic fractions were dried over $MgSO_4$. Filtration and removal of the solvent left a solid, which was crystallized from water/ethanol. The title compound was obtained as white crystals in a 96% yield (10.42 g). M.p. 149-151°C (Lit. [6] 152°C). HRMS (EI): Calcd. for $C_8H_7BrO_3$: 229.9578, Found: 229.9579.

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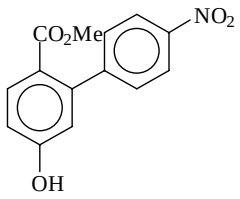
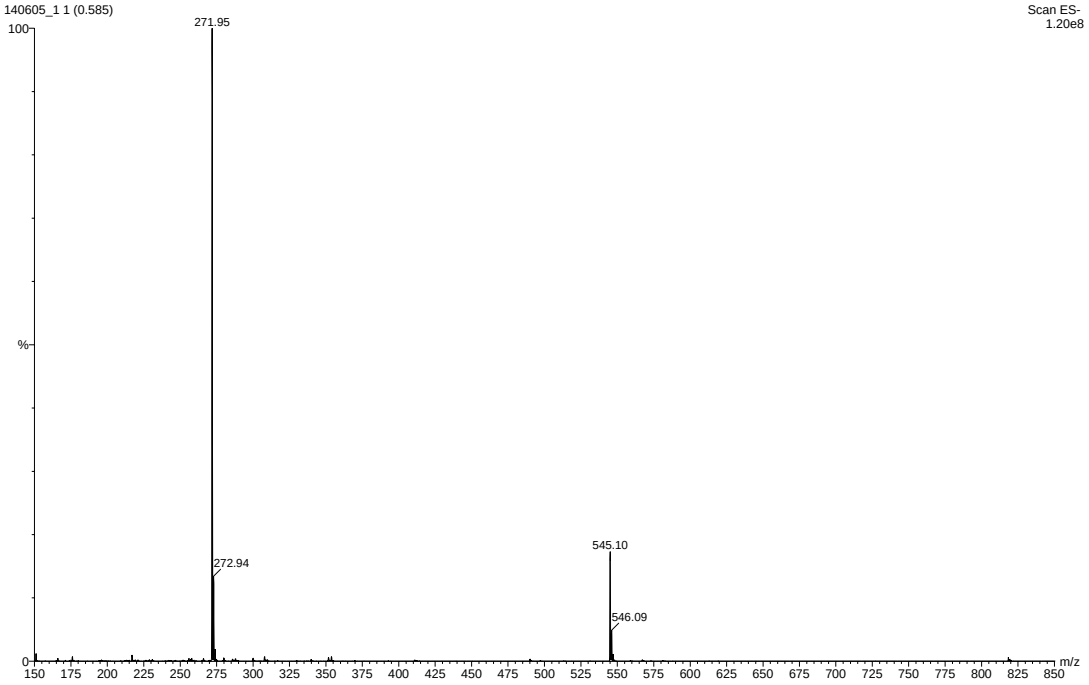


6

5-Hydroxy-2-methoxycarbonyl-4'-nitrobiphenyl.

To a degassed mixture of K_3PO_4 (5.00 g, 23.5 mmol), 4,4,5,5-tetramethyl-2-(4-nitro-phenyl)-[1,3,2]dioxaborolane (4.40 g, 17.7 mmol) and tetrakis(triphenylphosphine) palladium (0.51 g, 0.44 mmol) in DMF (85 mL) were added 3.02 g (13.1 mmol) of ester **5** and the mixture was heated overnight at 100°C under Argon. After cooling, the crude was diluted with brine (120 mL) and the pH was adjusted to neutrality with 1N HCl (10 mL). The mixture was then extracted with Et_2O (5x100 mL) and the combined organic layers were concentrated in vacuo to give a brown syrup. Treatment of this oil with hot acetone produced a precipitate which was collected, while the filtrate was reduced to a small volume and washed again with hot aqueous acetone to afford a second crop of solid. The combined precipitates were applied to a silica gel column (eluant: gradient from pure CH_2Cl_2 to CH_2Cl_2/MeOH 98:2) and the title compound was isolated as a pale yellow solid in a 78% yield (2.79 g.). M.p. 229-231°C. HRMS (EI): Calcd. for $C_{14}H_{11}NO_5$: 273.0637, Found: 273.0636.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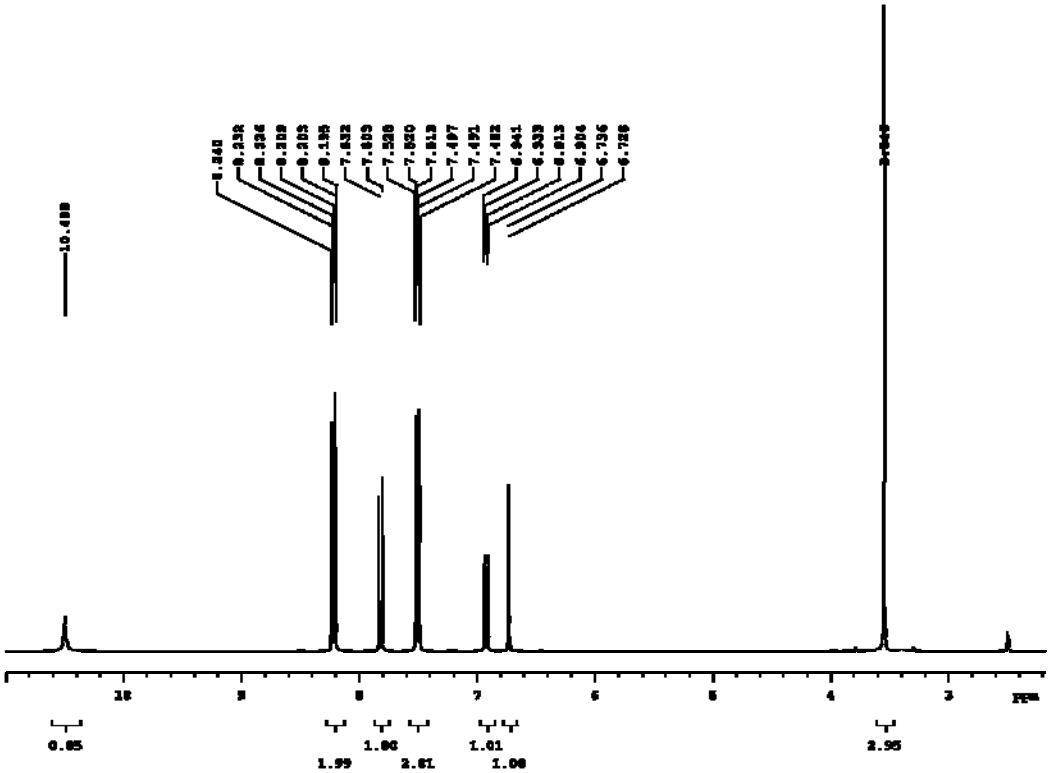
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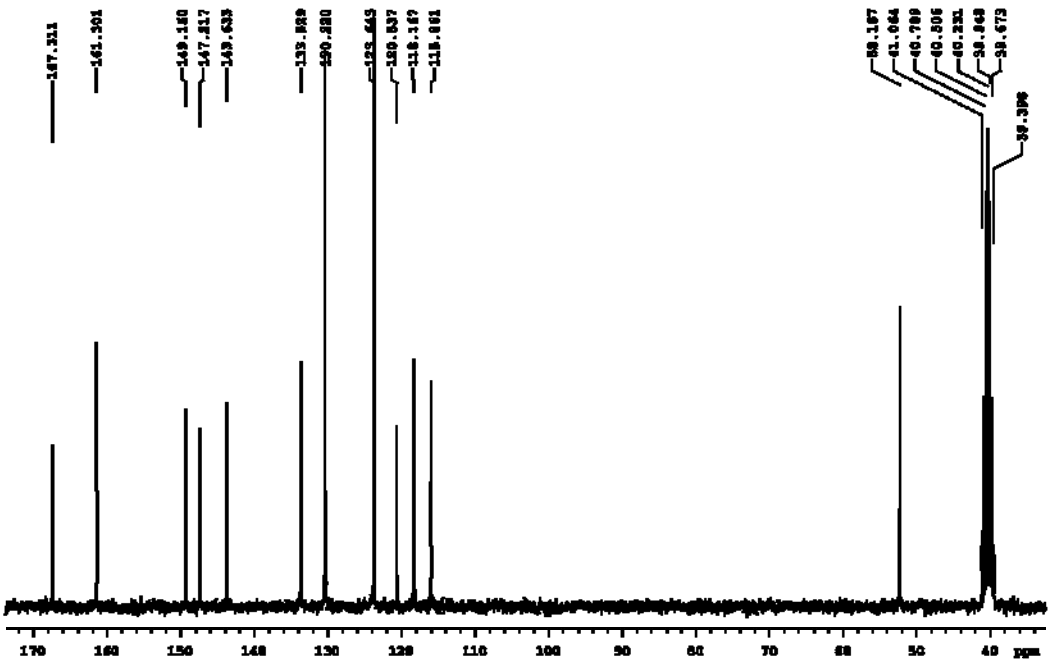
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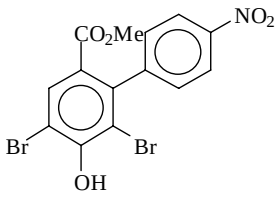
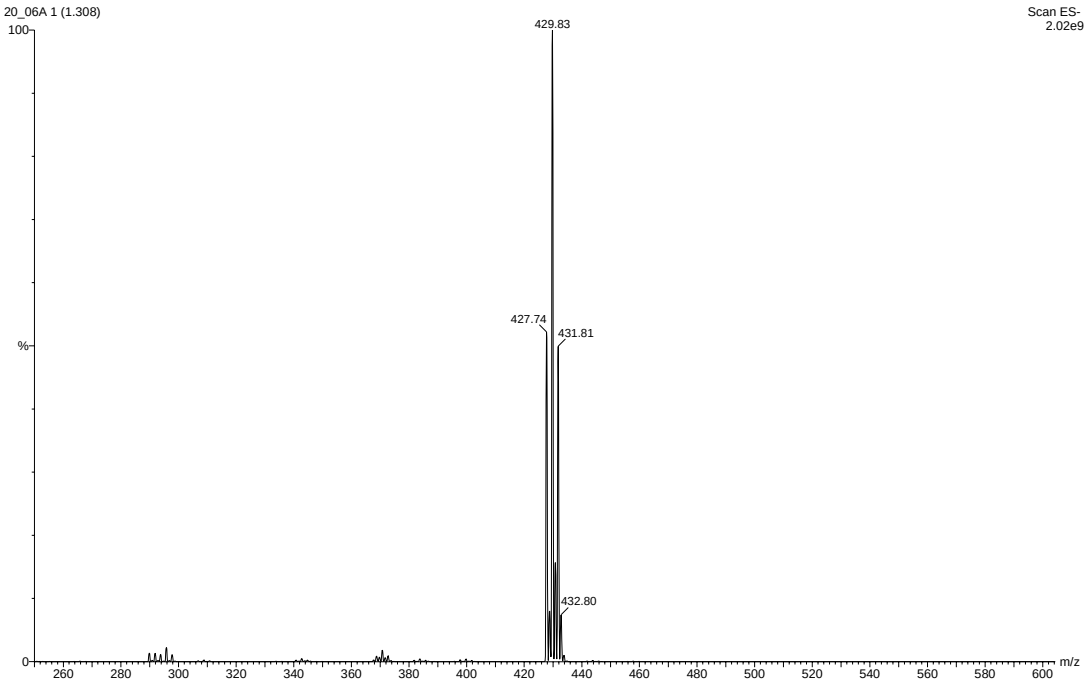
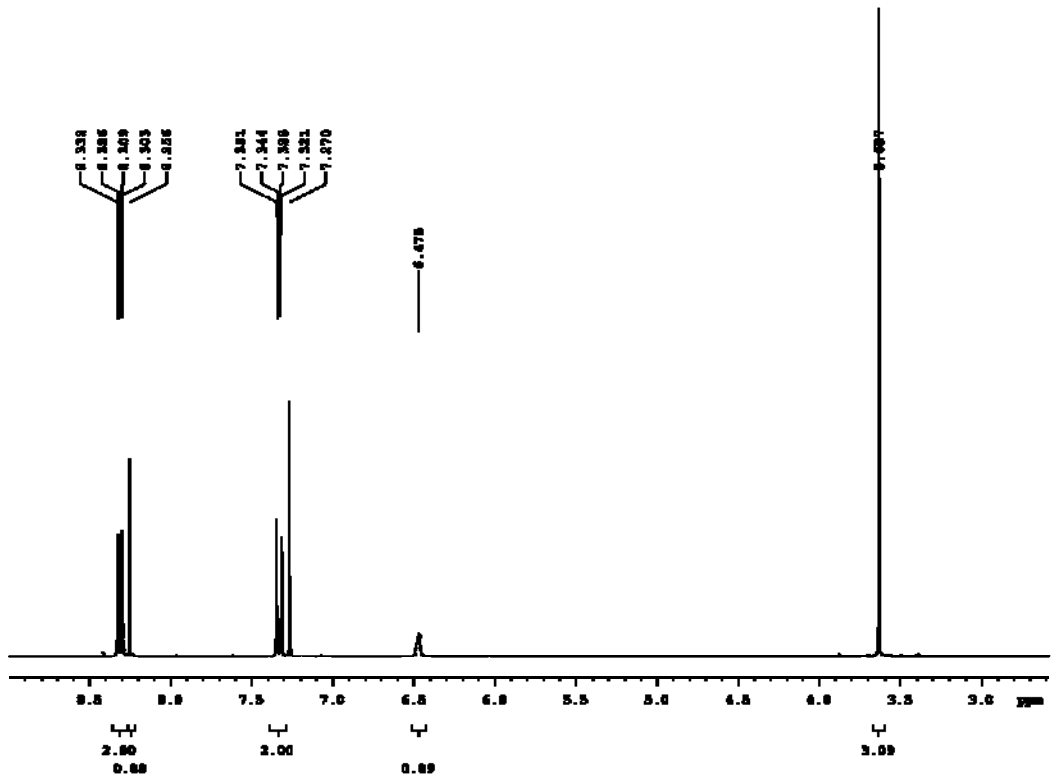


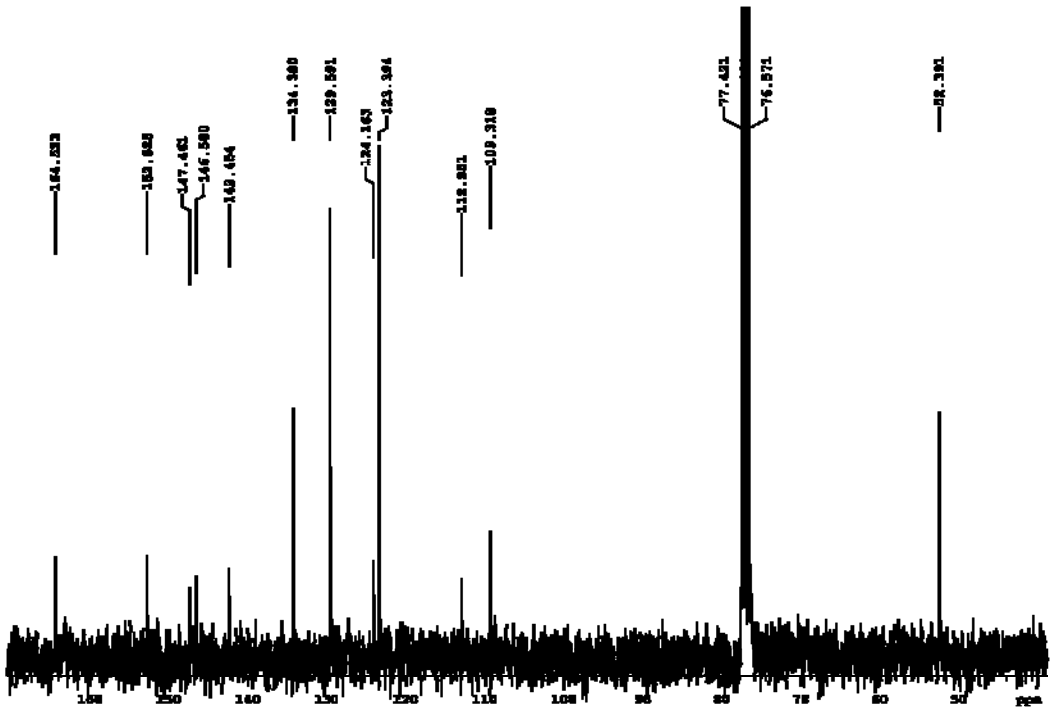
7

2,4-Dibromo-3-hydroxy-6-methoxycarbonyl-4'-nitrobiphenyl.

To a solution of **6** (1.188 g, 4.35 mmol) in CH_2Cl_2 (21 mL) and MeOH (15 mL) were added 4.41 g (9.15 mmol) of tetrabutylammonium tribromide and the solution was stirred at r.t. for 3 days. After removal of solvents under reduced pressure, the crude was partitioned between Et_2O (30 mL) and 2.5% $Na_2S_2O_3$ (30 mL). The aqueous layer was extracted twice with Et_2O and the combined organic fractions were washed with water and dried over $MgSO_4$. Removal of the solvent afforded a pale orange oil, which solidified on standing. This crude was purified by chromatography over silica ($CHCl_3$/petroleum ether 1:1 as the eluant) and the title compound was isolated as a white solid in an 88% yield (1.650 g.). M.p. 147-148°C. HRMS (EI): Calcd. for $C_{14}H_9Br_2NO_5$: 428.8847, Found: 428.8847.


20_06A 1 (1.308)
Scan ES-
2.02e9
100
%
0
429.83
427.74
431.81
432.80
m/z
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
2.00
2.00
0.89
3.00


164.233
153.642
147.461
146.560
143.454
134.380
129.591
124.163
123.304
118.881
109.310
77.421
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58.391
160
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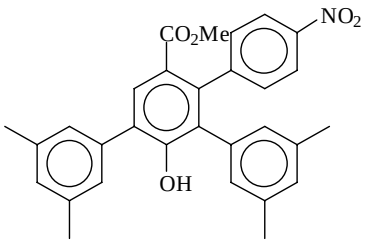
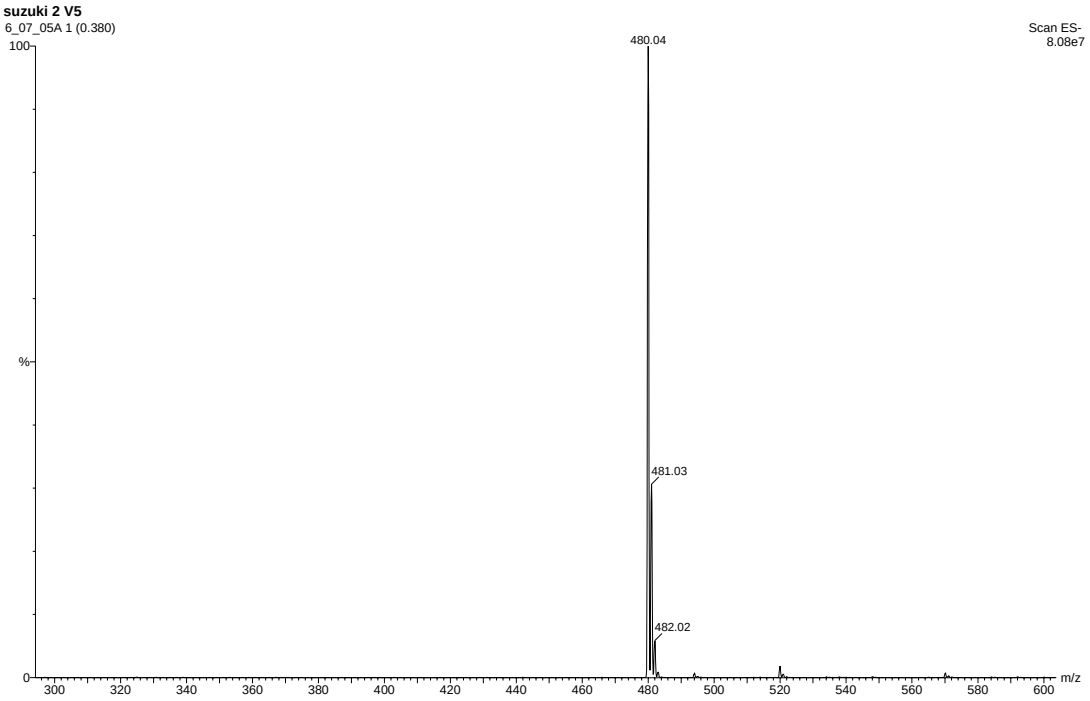
130
120
110
100
90
80
70
60
50
ppm

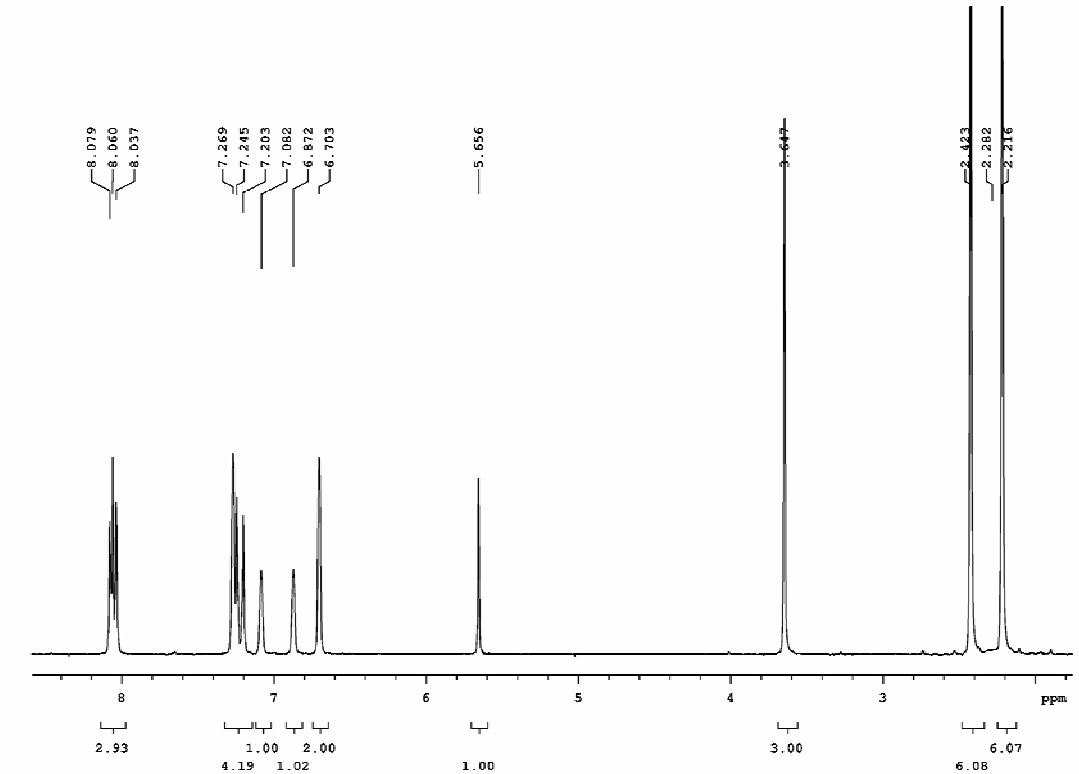


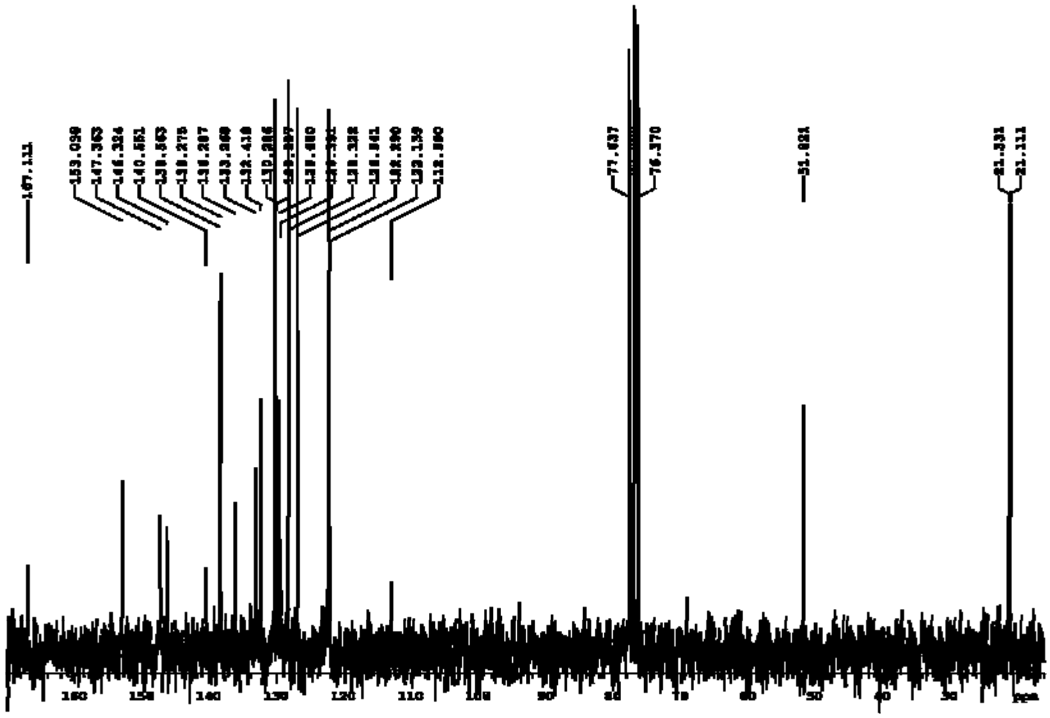
8

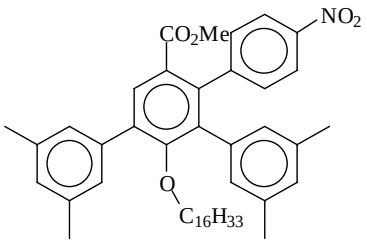
3,5-Bis(3',5'-dimethylphenyl)-4-hydroxy-2-(4'-nitrophenyl)benzoic acid methyl esther.

To a degassed mixture of dioxane (12 mL) and water (2 mL) were added, under Argon atmosphere, K_3PO_4 (0.888 g, 4.18 mmol), 3,5-dimethylphenylboronic acid (0.450 g, 3.00 mmol), tetrakis(triphenylphosphine)palladium (0.152 g, 0.132 mmol) and derivative **7** (0.431 g, 1.00 mmol). The mixture was heated to 100°C and left 15 hrs. under stirring. After cooling, the crude was diluted with water, the pH was adjusted to 4 with dil. HCl and the mixture was extracted with Et_2O (3x50 mL). The combined ethereal extracts were dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by chromatography over silica (eluant: petroleum ether/CH_2Cl_2, gradient from 3:2 to 1:1) affording **8** as a pale yellow solid in an 84% yield (0.404 g.). M.p. 209-211°C. HRMS (EI): Calcd. for $C_{30}H_{27}NO_5$: 481.1889, Found: 481.1888.


suzuki 2 V5
6_07_05A 1 (0.380)
Scan ES-
8.08e7
100
%
0
480.04
481.03
482.02
300
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
m/z


8.079
8.060
8.037
7.269
7.245
7.203
7.082
6.872
6.703
5.656
3.647
2.423
2.282
2.216
8
7
6
5
4
3
ppm
2.93
1.00
2.00
3.00
6.07
4.19
1.02
1.00
6.08

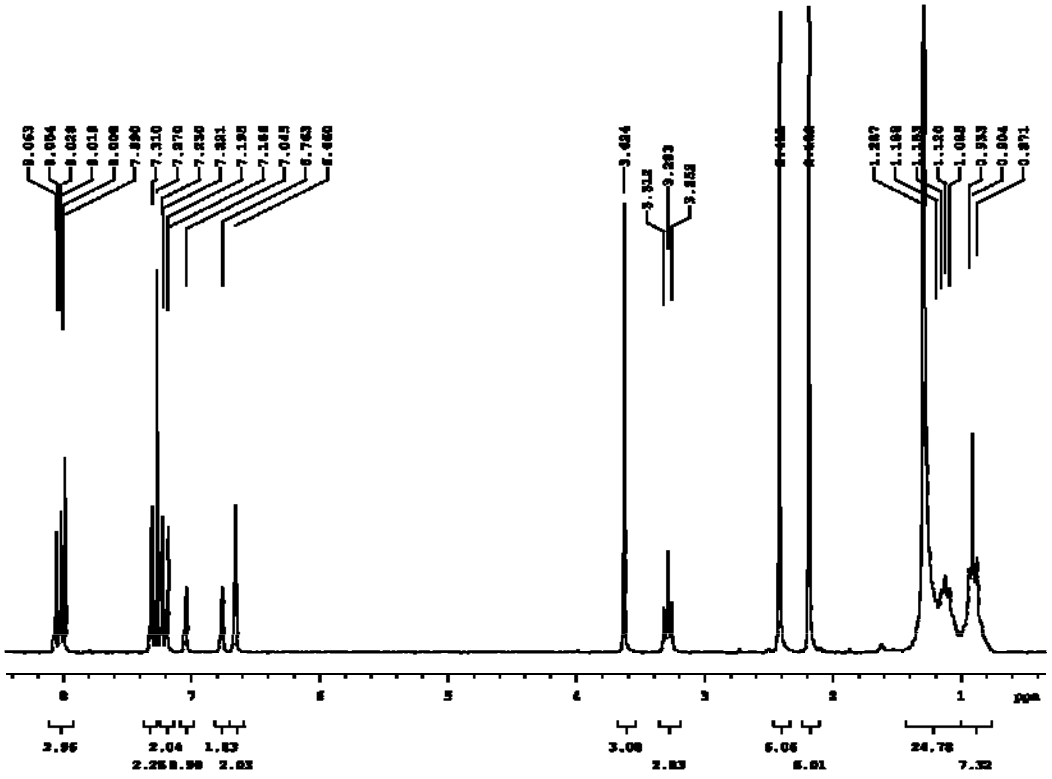


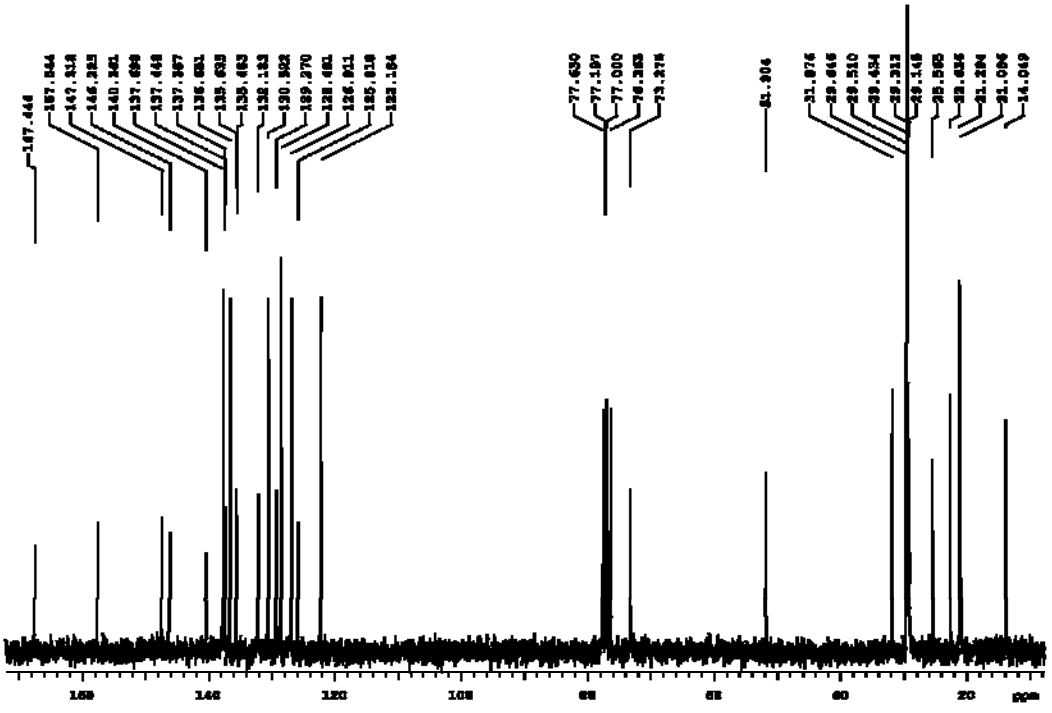


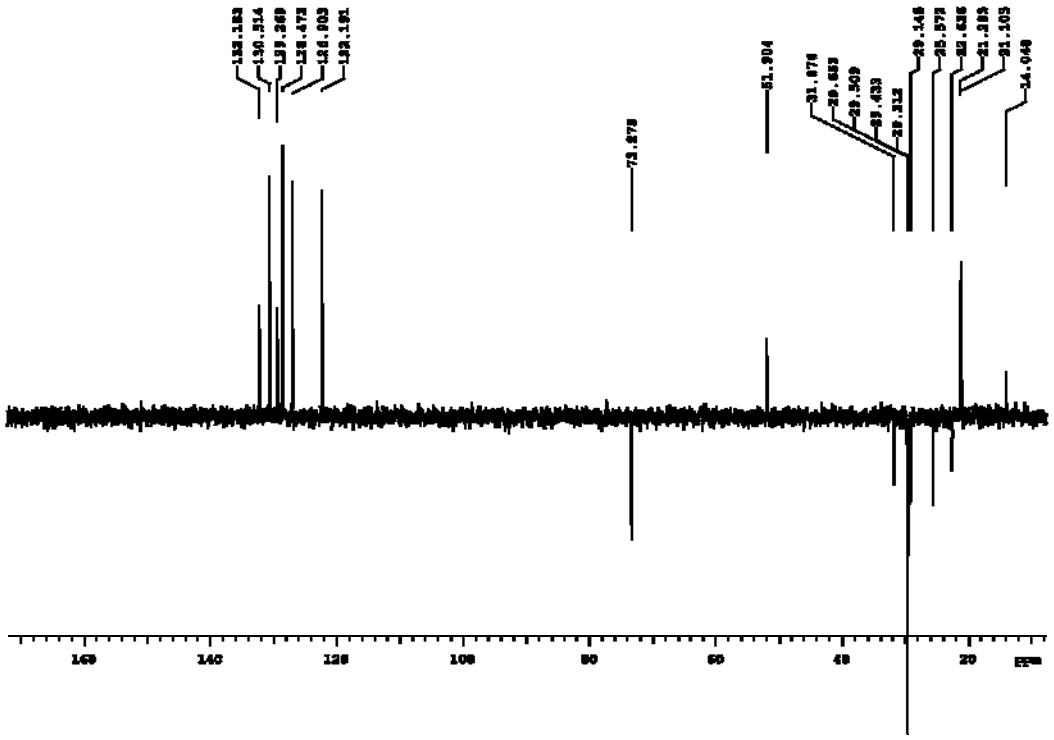
9

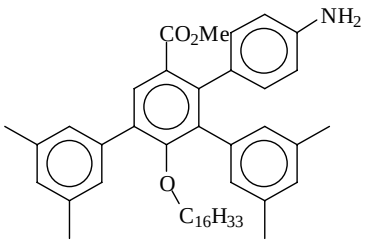
4-Hexadecyloxy-3,5-bis(3',5'-dimethylphenyl)-2-(4'-nitrophenyl)benzoic acid methyl esther.

A mixture containing phenol **8** (1.886 g, 3.92 mmol), Cs_2CO_3 (3.83 g, 11.8 mmol) and 1-iodohexadecane (1.85 mL, 5.88 mmol) in DMF was heated to 100°C under inert atmosphere for 19 h. After cooling to r.t., the mixture was partitioned between water (50 mL) and ethyl ether (50 mL). The aqueous layer was extracted with ether (3x50 mL) and the combined organic fractions were dried over $MgSO_4$. After removal of the solvents, the crude was purified by chromatography on silica (eluant petroleum ether/$CHCl_3$, gradient from 3:1 to 1:1). Compound 9 was obtained in a 97% yield (2.685 g.) as an oil, which solidified on standing. HRMS (EI): Calcd. for $C_{46}H_{59}NO_5$: 705.4393, Found: 705.4393.





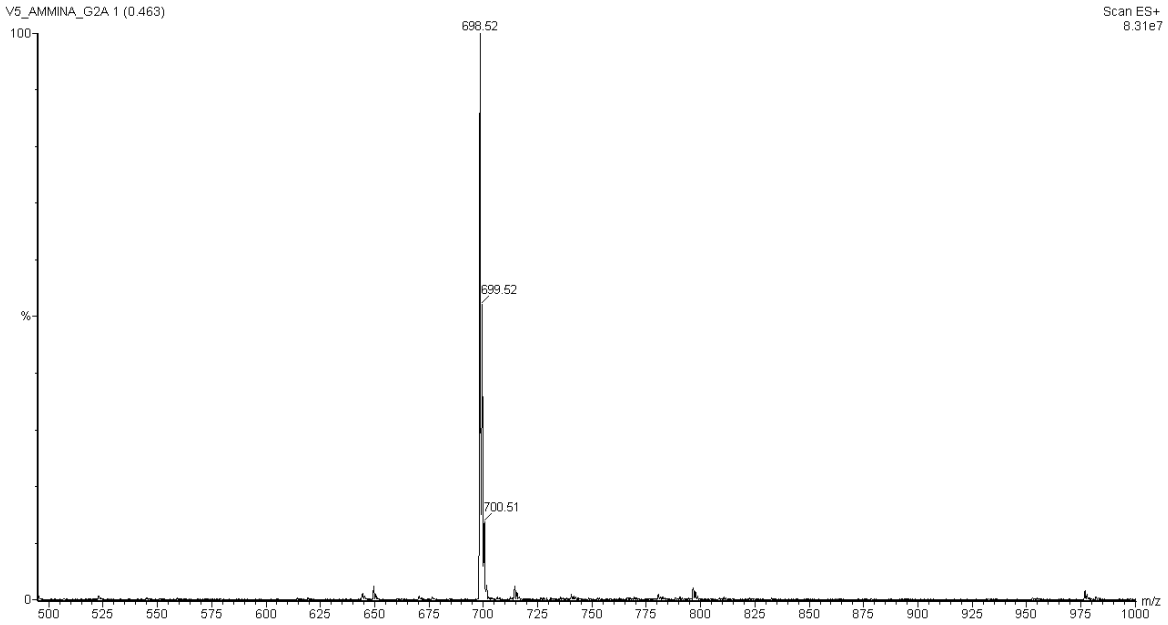

133.183
130.314
129.269
128.473
126.003
123.191
73.878
61.904
31.878
29.683
29.509
29.433
29.312
29.145
25.573
22.636
21.285
21.103
14.048
160
140
120
100
80
60
40
20
ppm

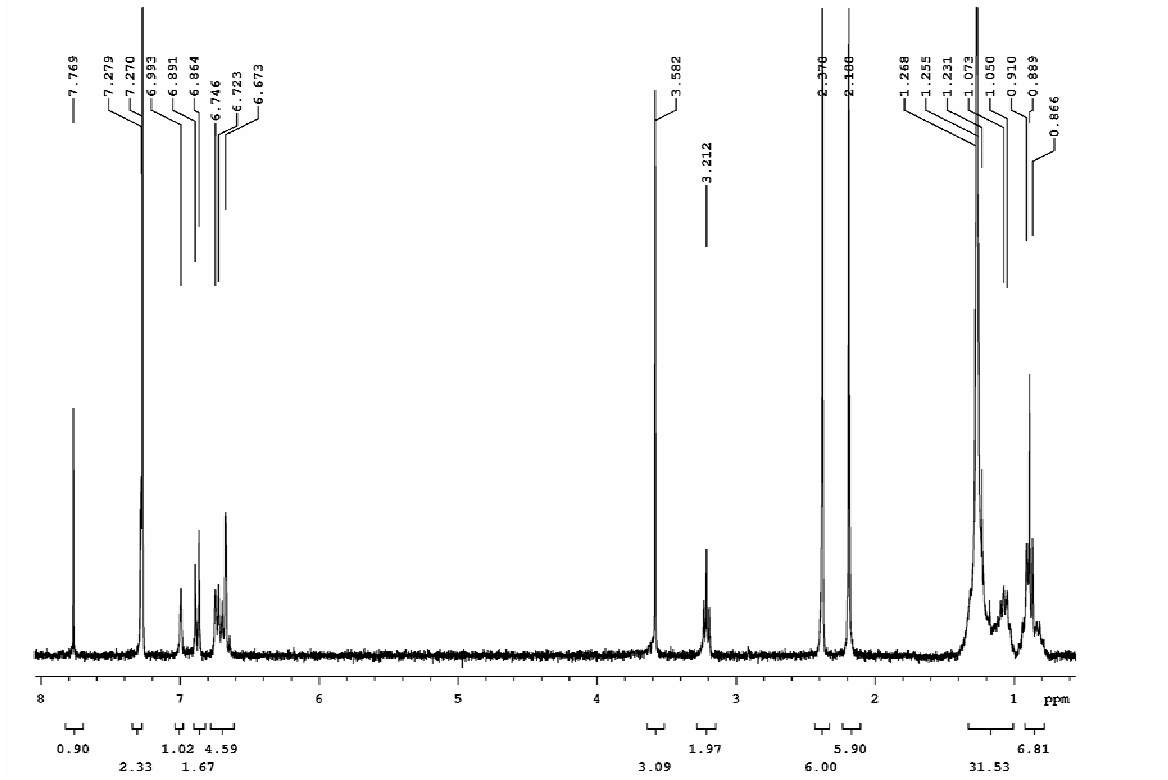


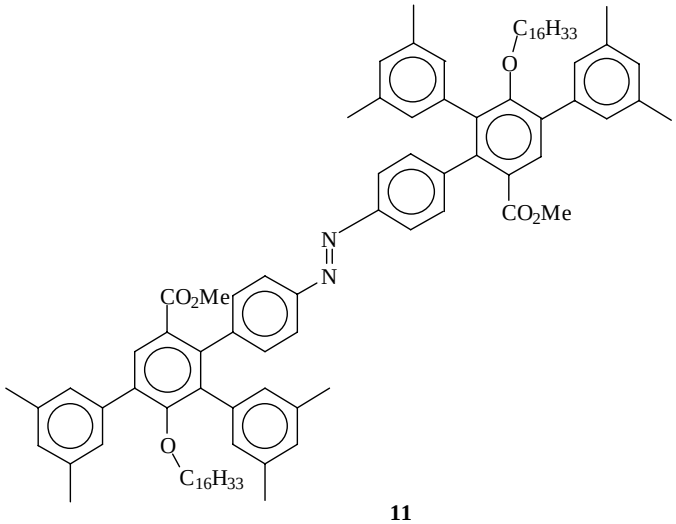
10

2-(4'-Aminophenyl)-4-hexadecyloxy-3,5-bis(3',5'-dimethylphenyl)benzoic acid methyl esther.

A mixture of compound **9** (2.684 g, 3.81 mmol) and $SnCl_2$ (3.61 g, 19.0 mmol) in ethanol (8 mL) was kept at 70°C for 1hr. and then cooled in an ice bath and diluted with cold water (50 mL). The pH of the reaction mixture was made slightly alkaline by the addition of 5% $NaHCO_3$ and the mixture was filtered. The precipitate was washed several times with water and ethyl acetate. The combined organic filtrates were washed with brine and dried over $MgSO_4$. Solvents were removed by distillation and the residue was purified by chromatography on silica (eluant petroleum ether/$CHCl_3$, gradient from 1:1 to pure $CHCl_3$). Aniline **10** was obtained in a 94% yield (2.417 g.) as a brownish-yellow oil. HRMS (EI): Calcd. for $C_{46}H_{61}NO_3$: 675.4651, Found: 675.4656.


V5_AMMINA_G2A 1 (0.463)
Scan ES+
8.31e7
100
%
0
698.52
699.52
700.51
500 525 550 575 600 625 650 675 700 725 750 775 800 825 850 875 900 925 950 975 1000
m/z

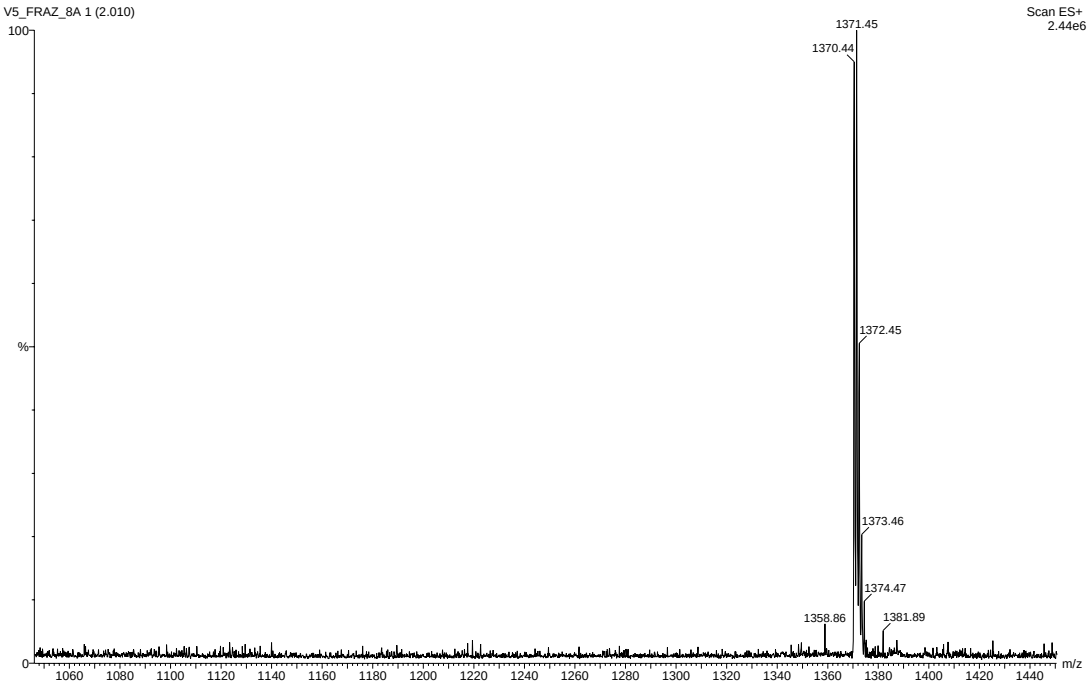

7.769
7.279
7.270
6.993
6.891
6.864
6.746
6.723
6.673
3.582
3.212
2.376
2.188
1.268
1.255
1.231
1.073
1.050
0.910
0.889
0.866
8 7 6 5 4 3 2 1 ppm
0.90
2.33
1.02
1.67
4.59
3.09
1.97
6.00
5.90
31.53
6.81

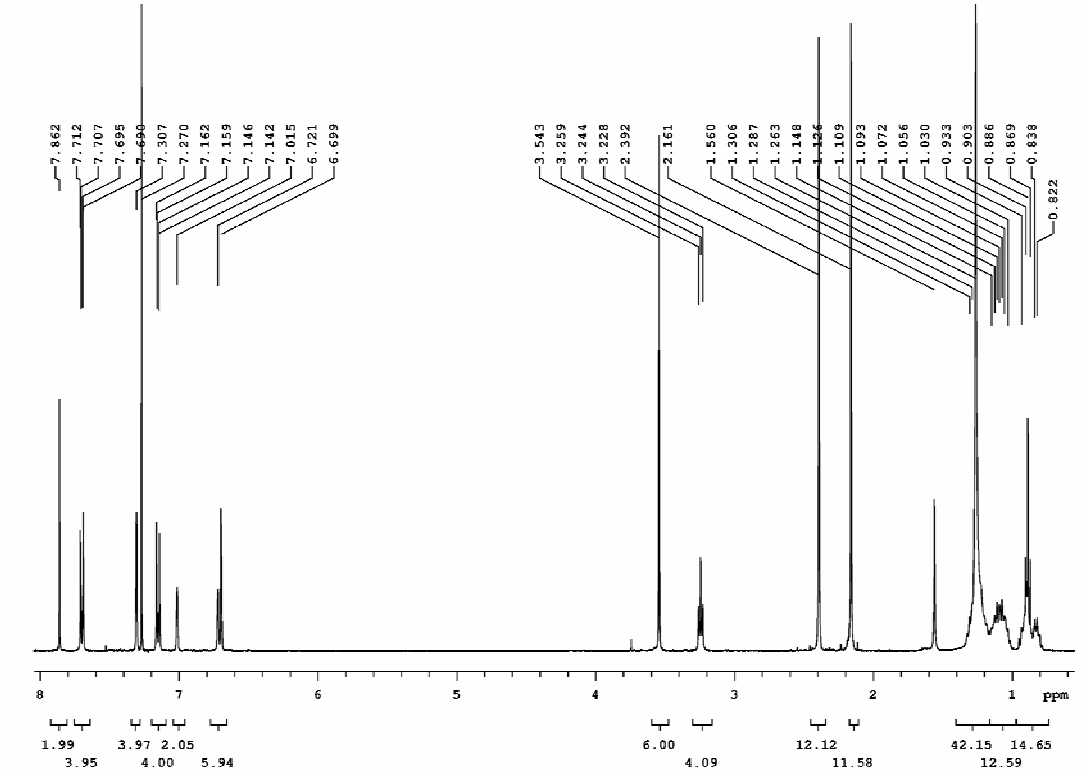


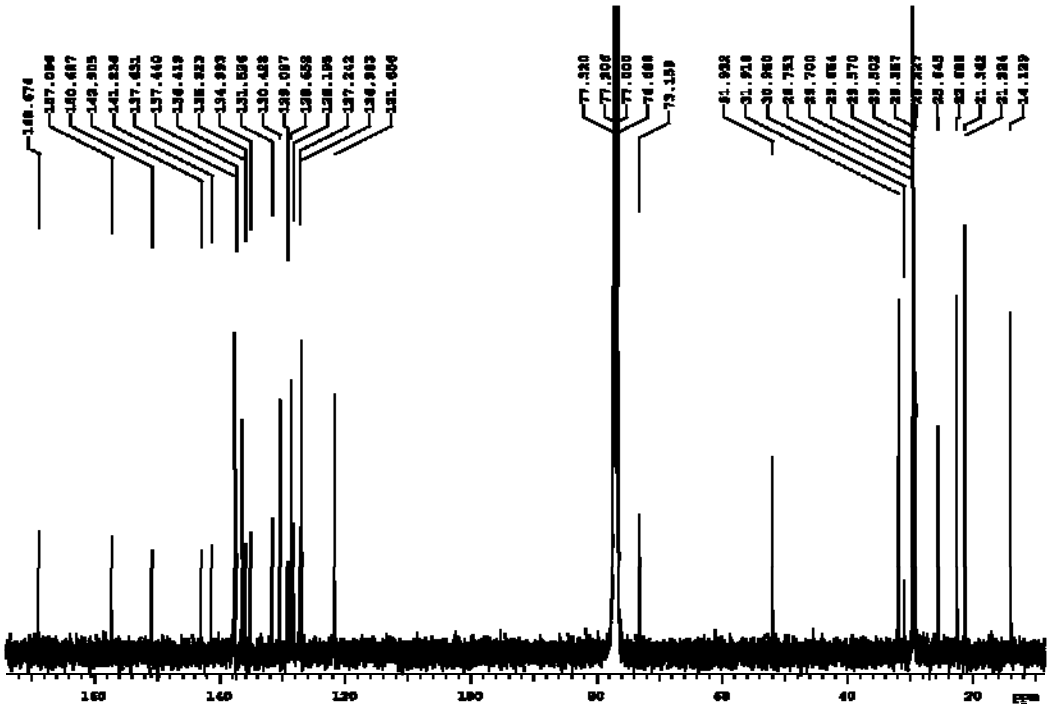
11

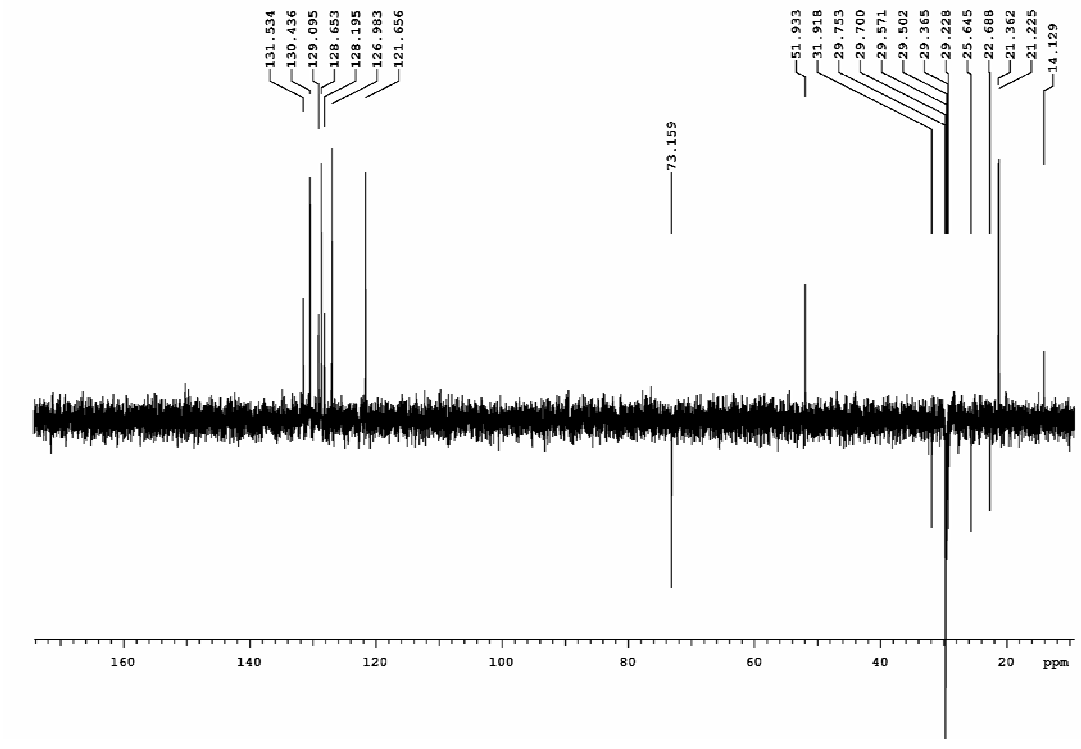
Bis{4-[6'-carboxymethyl-3'-hexadecyloxy-2',4'-bis(3",5"-dimethylphenyl)]phenyl} diazene.

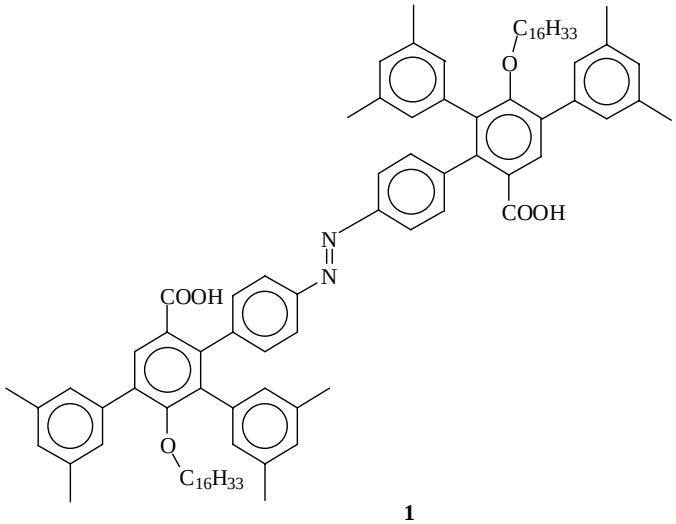
To a solution of amine **10** (2.413 g, 3.57 mmol) in CH_2Cl_2 (35 mL) were added 3.6 g of a finely ground mixture obtained by mixing equal weights of potassium permanganate and copper sulfate pentahydrate. The resulting suspension was stirred for 3 days at r.t. and filtered. The filtrate was concentrated in vacuo and the residue was chromatographed on silica (eluant: petroleum ether/CH_2Cl_2, gradient from 1:1 to 1:2). Azo-derivative **11** was obtained in a 27% yield (0.649 g.) as a glassy orange solid. M.p. 99-101°C. Elemental analysis: Calcd. (%) for $C_{92}H_{118}N_2O_6$: C 81.98, H 8.82, N 2.08; Found: C 81.65, H 9.04, N 2.12.


V5_FRAZ_8A 1 (2.010)
Scan ES+
2.44e6
100
%
0
1371.45
1370.44
1372.45
1373.46
1374.47
1358.86
1381.89
1060 1080 1100 1120 1140 1160 1180 1200 1220 1240 1260 1280 1300 1320 1340 1360 1380 1400 1420 1440
m/z


7.862
7.712
7.707
7.695
7.690
7.307
7.270
7.162
7.159
7.146
7.142
7.015
6.721
6.699
3.543
3.259
3.244
3.228
2.392
2.161
1.560
1.306
1.287
1.263
1.148
1.126
1.109
1.093
1.072
1.056
1.030
0.933
0.903
0.886
0.869
0.838
0.822
8 7 6 5 4 3 2 1 ppm
1.99 3.97 2.05
3.95 4.00 5.94
6.00
4.09
12.12
11.58
42.15 14.65
12.59



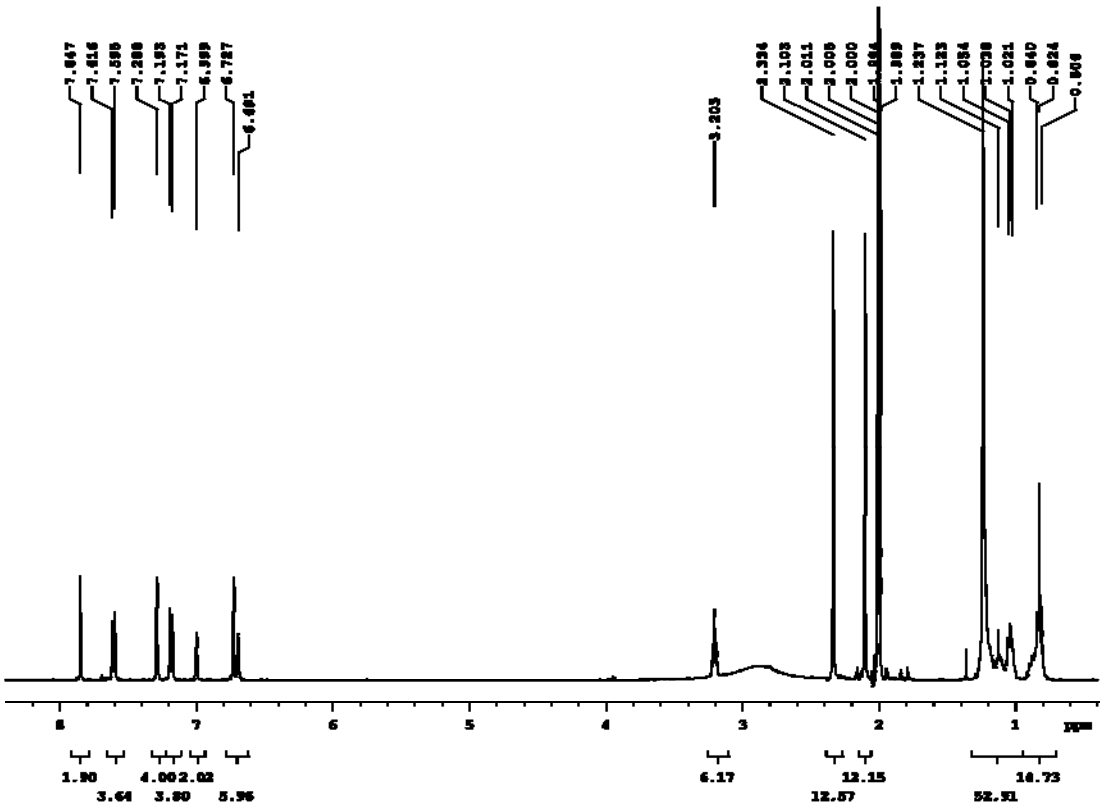

131.534
130.436
129.095
128.653
128.195
126.983
121.656
73.159
51.933
31.918
29.753
29.700
29.571
29.502
29.365
29.228
25.645
22.688
21.362
21.225
14.129
160
140
120
100
80
60
40
20
ppm

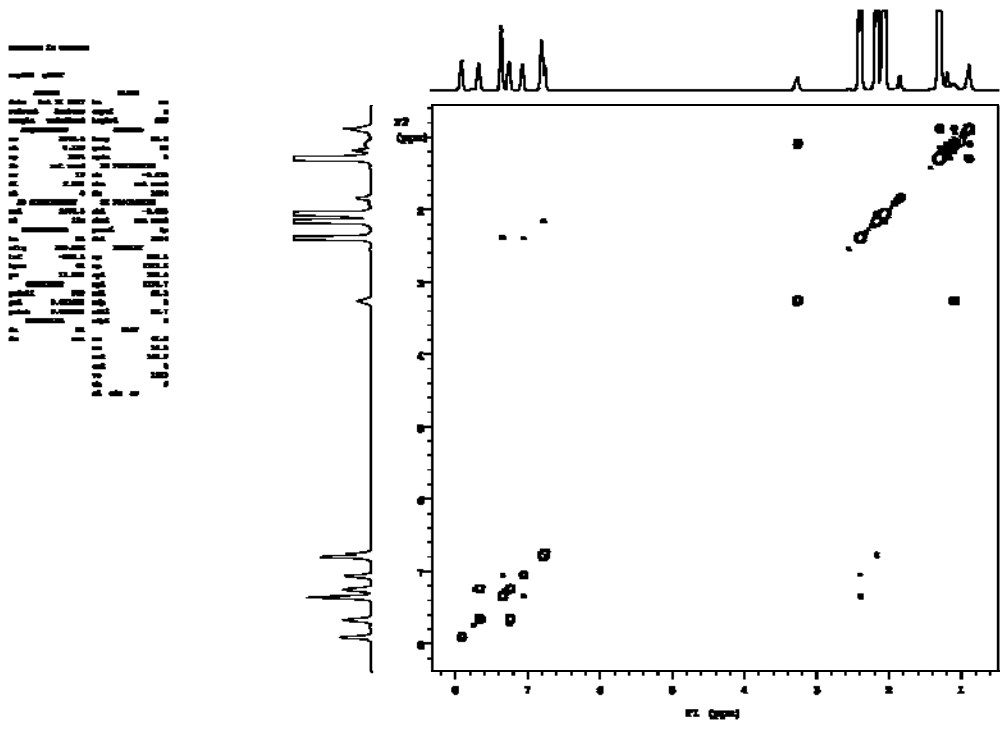


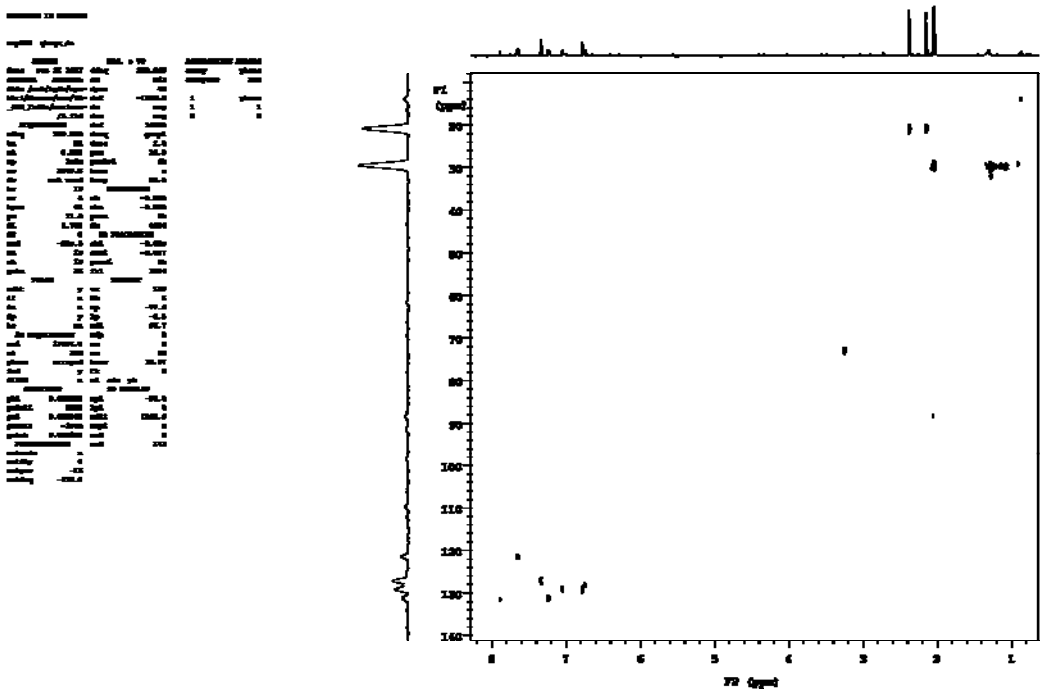
1

Bis{4-[6'-carboxy-3'-hexadecyloxy-2',4'-bis(3",5"-dimethylphenyl)]phenyl}diazene.

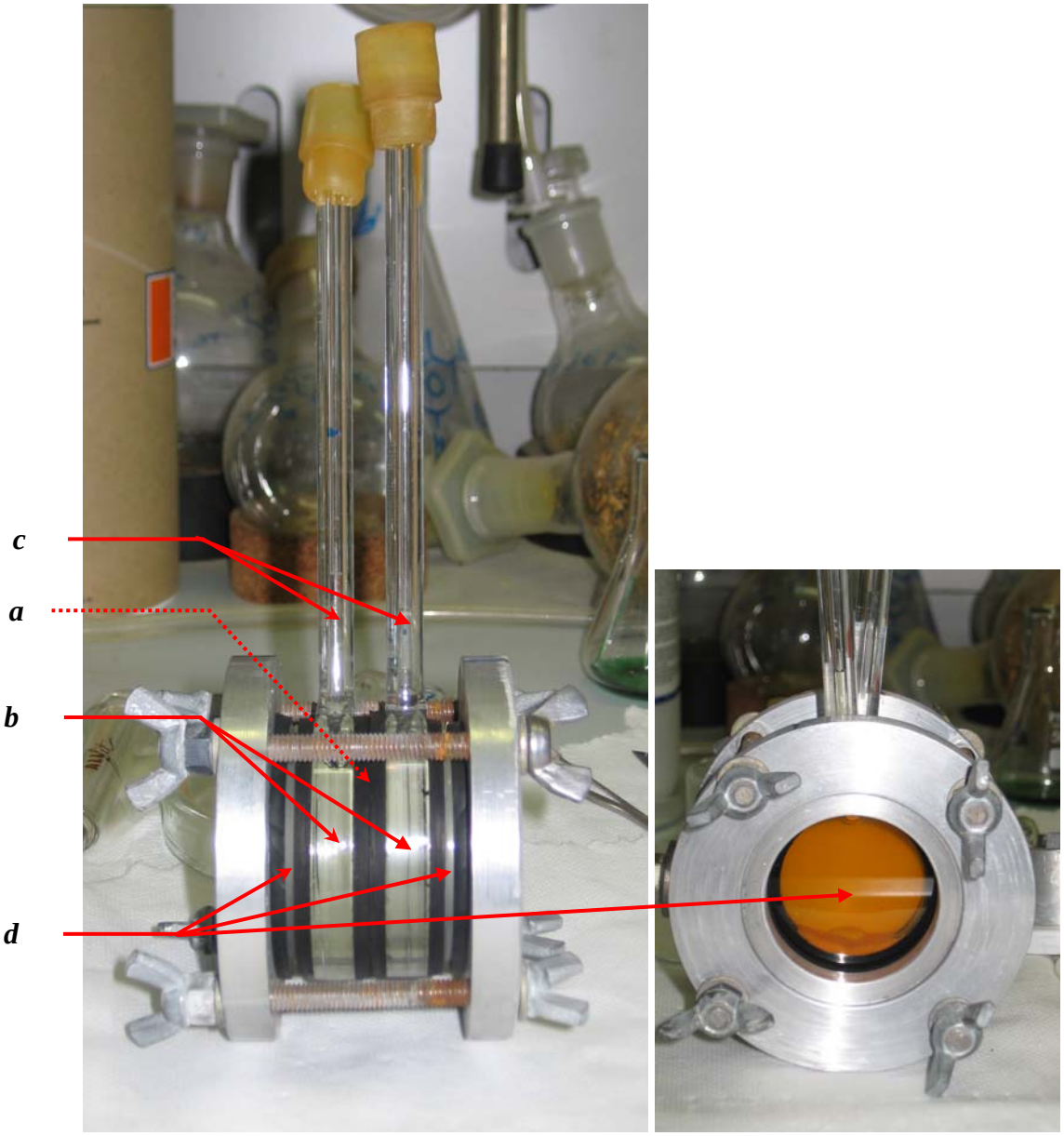
To a cold solution of **11** (0.639 g, 0.475 mmol) in dry ethyl ether (15 mL) were added in sequence 80 μL of water and 0.89 g (7.93 mmol) of potassium t-buthoxide. Stirring was continued overnight at r.t under inert atmosphere. The mixture was then diluted with cold water, pH was adjusted to 3 with HCl 1N and the mixture was extracted several times with ethyl ether. The combined organic fractions were concentrated under reduced pressure and the residue was crystallized from acetone. Target compound **1** was obtained in a 96% yield (0.603 g.) as an orange solid. M.p. 252-254°C. Elemental analysis: Calcd. (%) for $C_{90}H_{114}N_2O_6$: C 81.90, H 8.71, N 2.12; Found: C 82.42, H 8.48, N 2.15.







Osmotic cell construction details.



A membrane disk ***a*** (50 mm dia.) of Starmem 240 (mwco 400 Da) (MET, London, UK) was sandwiched between two custom-made pyrex rings ***b*** (38 mm i.d., 60 mm o.d., thickness 9 mm), each having a hole radially drilled and a calibrated pyrex pipe ***c*** (3 mm i.d, 150 mm long) soldered coaxially to the hole. Two circular fused silica windows ***d*** (50 mm dia. 2 mm thickness) (UQG Optics LTD, Cambridge, UK) were used as the external walls of the cell. An EPDM (peroxide cured) gasket (thickness 2 mm) of

appropriate diameter was placed between each couple of the above listed components. The device was assembled between two aluminum flanges (40 mm i.d., 85 mm o.d., thickness 10 mm) secured with four bolts. The resulting optical path was about 12 mm in each compartment. The outer face of each flange was shaped for housing the filters. During set-up, a magnetic stirrer was placed in each compartment.

Osmosis experiments and notes on movie S1.

Both sides of the osmotic cell (assembled as described above) were filled with acetone for membrane conditioning. The solvent was replaced several times over two days with fresh aliquots to remove membrane preservative. Care was taken to avoid drying of the membrane.

Two sonicated suspensions of *E*-**1** in acetone, each containing 100-160 mg of compound in 12 mL of solvent (corresponding to a 6-10 mM nominal concentration) were loaded into the two compartments by means of a syringe. The solvent was set at the same level in both sides. An immersion magnetic stirrer was mounted on the lower side of the cell and the two pipes were connected by means of silicone tubing and a three-way stopper (in this way, both sides were always in contact with each other and under the same pressure, but could either be insulated or be in contact with the environment) . Filters (50 mm diameter, 365 nm, bandpass 10 nm (Andover Co., USA) for UV and a pyrex disk or 50 mm diameter, 436 nm, bandpass 10 nm (Andover Co., USA) for Vis) were set on the two sides. The device was immersed in a thermostat set at 20°C and allowed to equilibrate.

Irradiation was then started: a Mercury 125W lamp was used as source of UV radiation and a low-consumption Osram 21W lamp was used for Vis.

Under these conditions, complete *E* to *Z* isomerisation required 6-8 hrs., while *Z* to *E* isomerisation occurred in 4-6 hrs. The osmotic flow for each step required 18-24 hrs. to complete.

To record movie S1, a digital camera was placed in front of the thermostated cell and pictures were taken at regular intervals. Movie S1 is the collage of these pictures.

References:

[1] a) M. Urbanovà, V. Setnicka, F. J. Devlin, P. J. Stephens, *J. Am. Chem .Soc*. **2005**, *127*, 6700; b) I. Wolfs, H. O. Desseyn, *Appl. Spectr*. **1996**, *50*, 1000; c) *SDBS database* (http://www.aist.go.jp/RIODB/SDBS/cgibin/cre_index.cgi? lang=eng), compounds No.: 1159 (*cfr*. J. L. Derissen, *Acta Crystallogr., Sec. B* **1974**, *B30*, 2764), 2912, (*cfr*. M. Bailey, C. J. Brown, *Acta Crystallog*. **1967**, *22*, 387), 19580.

[2] T.D.W. Claridge, *High-Resolution NMR Techniques in Organic Chemistry*, Pergamon-Elsevier, Oxford, **1999**, Ch. 8.

[3] F. Rakotondradany, M. A. Whitehead, A.M. Lebuis, H. F. Sleiman, *Chem. Eur. J.* **2003**, *9*, 4771.

[4] J. A. R. P. Sarma, A. Nagaraju, *J. Chem. Soc. Perkin Trans.* **2000**, *2*, 1113.

[5] M.F. Abdel-Wahab; M.Z. Barakat; *Monatsh. Chem*. **1957**, *88*, 692.

[6] K. Friedrich, H. Oester, *Chem. Ber*. **1961,** *94*, 834.