Supplementary Material (ESI) for Chemical Communications

Sulfonic acid funtionalized crystal-like mesoporous benzene-silica as a remarkable water-tolerant catalyst

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Supporting information

1) Chemicals: A31 and A70 cation exchange resins were kindly provided by Rohm et Hass. Industrial grade glycerin was kindly provided by Valagro and was collected from an industrial process of ethanolysis of vegetable oils. Chemicals were purchased to Acros and Sigma-Aldrich.

2) Apparatus: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 DPX. Chemical shift are expressed in ppm relative to Me_4Si. IR spectra were recorded on a FT-IR Perkin Elmer (spectrum one) using ATR technology. Mass spectrometry analyses were performed either on a GC/MS Varian 1200 Triple quadripole equipped with a column Factor Four VF5MS (30m x 0.25mm x 0.25 mm) or a HPLC Alliance (Waters) coupled to a quadripole 3100 (Waters) equipped with a ESI source. Specific areas of solid catalysts were determined on a TRISTAR 3000. Pore diameters were determined from the adsorption branch of the N_2 isotherm using the BJH method. XRD patterns were recorded on a Bruker diffractometer D5005. The microstructures were analyzed by transmission electron microscopy (HRTEM) with a 300 eV Hitachi H9000-NA instrument. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument with a program rate of 5 °C min^{-1} in air. ^{29}Si and ^{13}C solid-state NMR spectra were recorded at 79.49 and 100.62 MHz, respectively, on a (9.4T) Bruker Avance 400P spectrometer. ^{29}Si CP MAS NMR spectra were recorded with 4 μs ^{1}H 90° pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays. ^{13}C CP MAS NMR spectra were recorded with 4.5 μs ^{1}H 90° pulses, 2 ms contact time, a spinning rate of 7 kHz and 4 s recycle delays. Chemical shifts are quoted in ppm from TMS.

3) General procedure for the synthesis of HMS_1-SO_3H (inspired from ref 13 of the manuscript)

Typically, 3.2g (0.013mol) of *n*-hexadecylamine was dissolved at room temperature in aqueous ethanol (ethanol/water: 21/27). Then 8.3 g of tetraethoxysilane (TEOS, 0.039mol) and 1.97g of 3-mercaptopropyltrimethoxysilane (MPTMS, 0.01 mol) was simultaneously but separately added to the template mixture. The resulting solution was stirred for 20 h at room temperature and the white solid was recovered by filtration. Removal of the *n*-hexadecylamine was carried out by soxhlet extraction over boiling ethanol for 18h affording the hybrid organic-inorganic HMS-SH. Thiol groups were oxidized with 35% aqueous H_2O_2 (2g/g of solid) in a methanol/water mixture. The suspension was stirred for 24 hours at room temperature and then washed with ethanol and water. Finally, the resulting solid was suspended in 0.1M H_2SO_4 (1g of solid per 100mL of solution) and stirred for an additional 4h before filtration and extensive washing with H_2O. The recovered HMS-SO_3H was dried in an oven at 50°C (10^{-1} mmHg) for 18h. The XRD patterns of HMS-SO_3H was similar than those reported in the literature and was typical of a worm-like structure.

4) General procedure for the synthesis of SBA-15-SO_3H (inspired from ref 13 of the manuscript)

Pluronic 123 (4g) was dissolved in 125g of aqueous HCl (1.9M) and stirred at room temperature. The solution was then heated at 40°C before addition of 7.7 g (0.0369 mol) of TEOS. After stirring for 45mn, MPTMS (0.8 g, 0.0018 mol) and 0.0369 mol of 35% H_2O_2 was added. The solution was then stirred for 24h at 40°C and aged into a teflon autoclave for an additional 24h at 100°C. The resulting solid was finally collected by filtration and thoroughly washed with water. The recovered SBA-15-SO_3H was dried in an oven at 50°C (10^{-1} mmHg) for 18h. Then, thiol groups were oxidized with 35% aqueous H_2O_2 (2g/g of solid) in a methanol/water mixture. The suspension was stirred for 24 hours at room temperature and then washed with ethanol and water. Finally, the resulting solid was suspended in 0.1M H_2SO_4 (1g of solid per 100mL of solution) and stirred for an additional 4h before filtration and extensive washing with H_2O. The recovered SBA-SO_3H was dried in an oven at 50°C (10^{-1} mmHg) for 18h. The XRD patterns of SBA-SO_3H was similar than those previously reported in the literature.

5) General procedure for the synthesis of Ph-PMO-SO_3H

Sulfonic funtionalized crystal-like mesoporous benzene-silica was synthesized as follows: 1.12 g of octadecyltrimethylammonium bromide was dissolved in 30 ml of water in the presence of 0.8 ml of a 6 M NaOH solution. The mixture was stirred at 50 ^oC until a clear solution was obtained. After cooling to ambient temperature, a mixture of 1,4-bis(triethoxysilyl)benzene (BTEB) (0.4 g) and 3-mercaptopropyltrimethoxysilane (0.2 g MPTMS) in 50:50 molar ratio was slowly added. The resulting solution was stirred for 24 h at room temperature after which the mixture was aged under reflux at 90 ^oC for another 24 h. Finally, the white precipitate was filtered, washed with deionized water and dried at 60 ^oC overnight. The surfactant was removed by solvent extraction method using a HCl-ethanol solution. Typically 1g of as-synthesized material was suspended in a 200 ml ethanol - 3 g HCl (Panreac, 36%) solution mixture. After extraction of the surfactant, conversion to a sulfonic acid-derivatized mesoporous material was accomplished as follows: first 0.5 g of the extracted sample was wetted with 1 ml deionized water and after that with 20 wt% aqueous HNO_3 solution. Then, 10 g of concentrated HNO_3 (Panreac, 67 wt%) was carefully introduced very slowly. The resulting mixture was then stirred at ambient temperature for 24 h. Before centrifugation 10 ml deionized water was added. The obtained white powder was again washed with water and dried overnight at 60 ^oC.

6) Ph-PMO-SO_3H characterization

Mesostructure and porosity

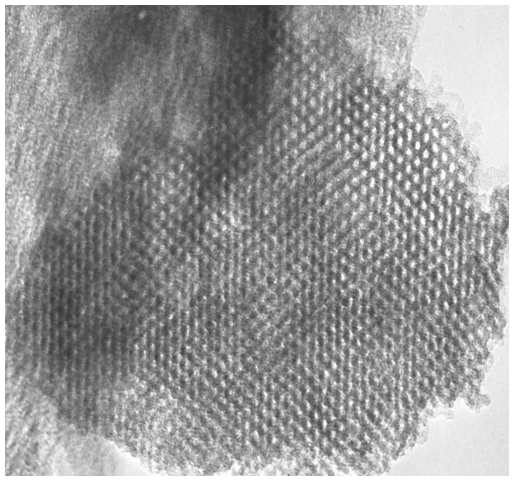


Figure S1. *High-resolution TEM image of Ph-PMO-SO_3H sample.*

In agreement with the existing literature, the image reported in figure S1 shows that Ph-PMO-SO_3H has an ordered region with a distinctly hexagonal arrangement of uniform channels.

Materials structure

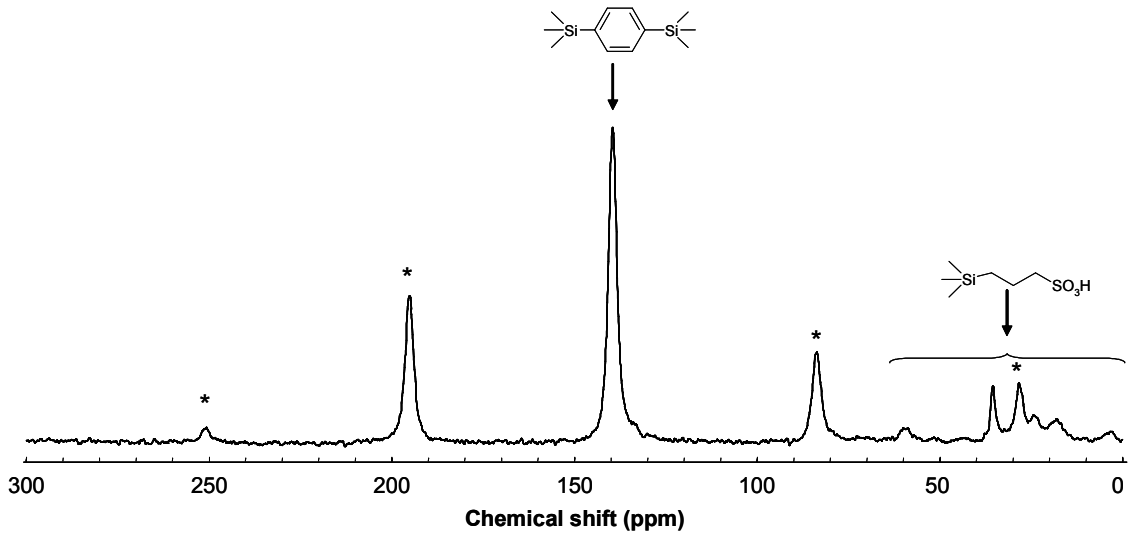


Figure S2 *^{13}C CP-MAS NMR spectra of Ph-PMO-SO_3H sample. (* refers to spinning sideband)*

In the ^{13}C CP-MAS NMR spectrum of Ph-PMO-SO_3H sample (Figure S2), the signal at 132.9 ppm was assigned to the carbon of the phenyl groups. The bands in the domain 60-0 ppm were characteristic of the three carbons of the propylsulfonic groups. In this range of chemical shifts, some bands due to remaining surfactant and a spinning sideband are also visible.

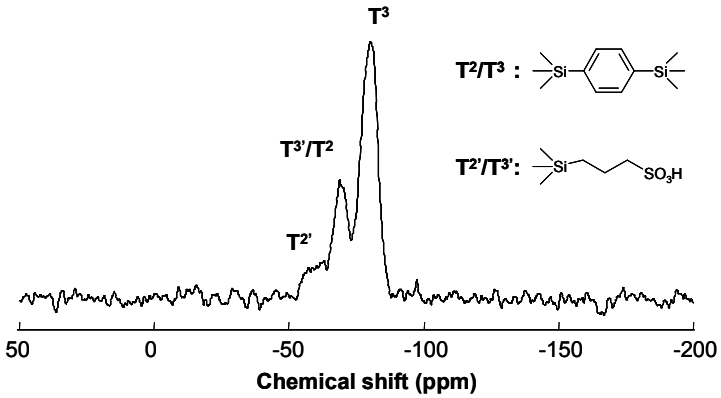


Figure S3 *^{29}Si CP-MAS NMR spectra of Ph-PMO-SO_3H sample*

The ^{29}Si CP MAS NMR spectrum of Ph-PMO-SO_3H sample showed three signals at -80.8, -70.1, and -58.9 ppm (Figure S3). They could be assigned as T^2/T^3 for Si attached with benzene (-70.1 and -80.8 ppm) and $T^{2'}$/ $T^{3'}$ for Si attached with propylsulfonic (-58.9 and -70.1 ppm). The broad signal at 70.1 ppm was a mixture of T^2 and $T^{3'}$ for silica connected with benzene and propylsulfonic groups, respectively. No resonances for Q_n sites were observed. This clearly indicates that the integrity of the Si-C bonds of the material remain under oxidation conditions.

Thermal properties and stability

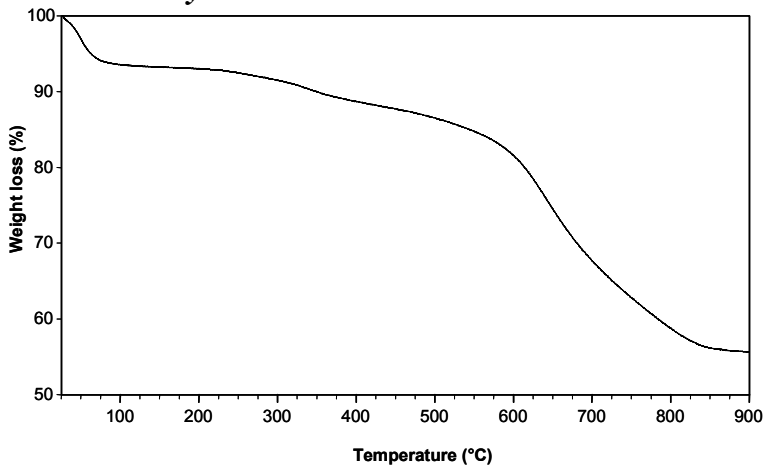


Figure S4 *Thermogravimetric weight loss curve for Ph-PMO-SO_3H sample under air atmosphere*

The TGA curve was performed from 25 ^{o}C to 900 ^{o}C under air atmosphere. The weight loss in the TGA curve below 100 ^{o}C was due to the removal of physisorbed water. A weight loss around 360^{o}C was assigned to the decomposition of propylsulfonic acid functionality. The last weight loss in the range from 550 to 800 ^{o}C is due to the decomposition of bridged benzene moiety.

SEM pictures were recorded to observe the morphology of the Ph-PMO-SO_3H sample. The image in the figure S5 shows randomly shaped particles of 1-3 μm. Similar shape and size of particles were observed with the recycled Ph-PMO-SO_3H sample.

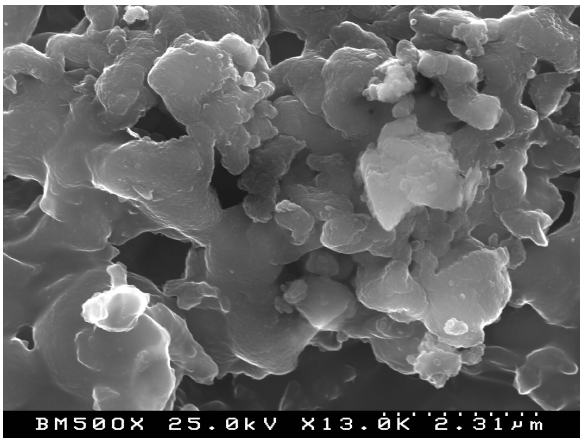


Figure S5 *SEM image of Ph-PMO-SO_3H sample*.

7) Determination of the H^+ exchange capacity of the tested solid acid catalysts

0.2 g of acid solid was suspended in 20mL of an aqueous solution of KCl (0.1mol/L) and stirred for 30 mn. Titration of the resulting solution was then carried out with a solution of KOH (0.02mol/L) and the pH evolution was monitored by a Metrohm pH meter. Note that for A31 and A70 cation exchange resins, H^+ exchange capacity was kindly provided by Rohm et Hass

8) General procedure for the synthesis of 3a-j (Table 2 of the manuscript)

In a typical procedure, indole (2 mmol), aldehyde (1 mmol) and 0.7 mol% of supported sulfonic sites were mixed in 2mL of H_2O and magnetically stirred at 60°C. After completion of the reaction, the reaction products were selectively extracted from water with ethyl acetate (3 x 2mL). Then, ethyl acetate was removed under reduced pressure and the products were purified by flash chromatography over silica gel (60Å, 40-63 µm, surface area: 550 m^2/g). For all products a mixture ethyl acetate/heptane 30/70 was used as eluting solvent. Full characterization of **3a-j** and copies of their ^1H and ^{13}C NMR spectra are provided below.

Note that no leaching of catalytic sites occurred. Indeed, when the acid solid catalyst was removed after 40% conversion, the reaction immediately stops.

9) Recycling experiments (Figure 1 of the manuscript)

Recycling experiments were performed starting from indole (2mmol), benzaldehyde (1mmol) and 0.7 mol% of -SO_3H supported over either Ph-PMO or SBA-15 or HMS. The

reaction was carried out in 2mL of H_2O and heated at 60°C for 20 min. After this period of time, **3a** was selectively extracted from the water phase with ethyl acetate. The solid catalyst remained in suspension in water and was not reactivated or purified. Then indole (2mmol) and benzaldehyde (1mmol) were directly reloaded to the suspension of solid catalyst in H_2O. This procedure was then repeated 5 times in the case of PMS-SO_3H and 6 times in the case of Ph-PMO-SO_3H.

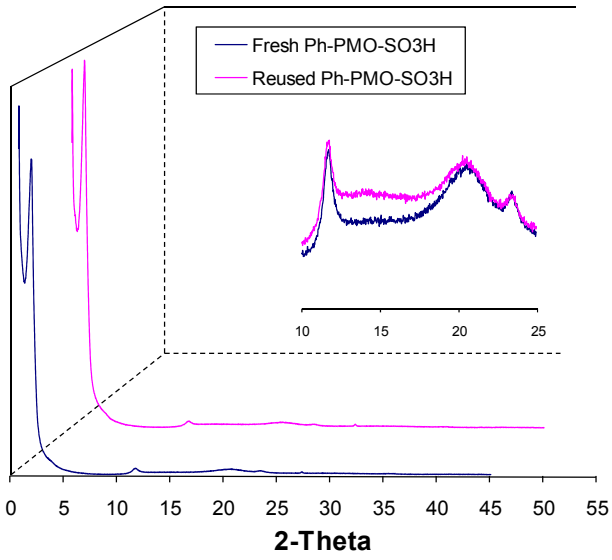


Figure S6: XRD of fresh and reused Ph-PMO-SO_3H

10) Etherification of glycerol with 1-phenyl-1-propanol (scheme 1 of the manuscript)

In a typical experiment, 4 mmol of glycerin (glycerol/H_2O: 80/20), 1 mmol of 1-phenyl-1-propanol were mixed and magnetically stirred at 100°C in the presence of 2 mol% of -SO_3H supported over either Ph-PMO or SBA-15. After 1h of reaction, the glycerol benzylethers were extracted from the glycerol phase with ethyl acetate (3 x 5 mL). After concentration of the organic phase, crude compounds were then purified by flash chromatography over silica gel (60Å, 40-63 µm, surface area: 550 m^2/g) using a mixture of ethyl acetate and heptane ($E/H_{v/v}$ = 5/1) as eluting solvent. The collected product was a mixture of two regioisomers: 1-phenyl-1-propyl α-glyceryl ether (**4a**) and 1-phenyl-1-propyl β-glyceryl ether (**4b**). The **4a**/**4b** molar ratio was determined by ^1H NMR and GC and was found to be equal to 9/1).

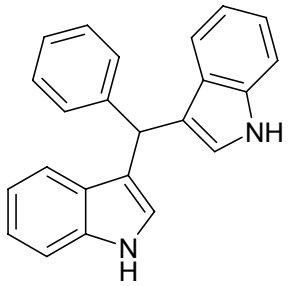
11) Recycling experiments (scheme 1 of the manuscript)

In a similar procedure than that described above, after extraction of the reaction products with ethyl acetate, the solid catalysts SBA-SO_3H and Ph-PMO-SO_3H remained in

suspension in glycerin. SBA-SO_3H and Ph-PMO-SO_3H were not reactivated or purified. Then, glycerin (1 mmol) and 1-phenyl-1-propanol (1mmol) were directly reloaded. This procedure was then repeated 5 times.

12) Full characterization of the reaction products

3a: 3,3'-(phenylmethylene)bis-1*H*-indole



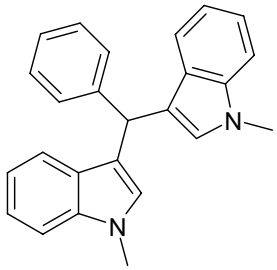
^{1}H-NMR (400MHz, $CDCl_3$) δ: 5.88 (s, 1H, -C*H*), 6.63 (d, 2H, *J*= 2.4 Hz, -NH-C*H*=), 7.00 (dd, 2H, *J* = 7.9 Hz, -C*H*=), 7.17 (dd, 2H, *J* = 7.9 Hz, -C*H*=), 7.21 (m, 1H, -C*H*=), 7.27 (m, 2H, -C*H*=), 7.33 (d, 4H, *J* = 8.0 Hz, -C*H*=), 7.38 (d, 2H, *J* = 8.0 Hz, -C*H*=), 7.87 (br s, 2H, -N*H*).

^{13}C-NMR ($CDCl_3$) δ: 40.2 (-*C*H-), 111.0 (-*C*H=), 119.3 (-*C*H=), 119.7 (-*C*=), 119.9 (-*C*H=), 121.9 (-*C*H=), 123.6 (-*C*H=), 126.2 (-*C*=), 127.1 (-*C*H=), 128.2 (-*C*H=), 128.7 (-*C*H=), 136.9 (-*C*=), 144.0 (-*C*=).

IR (neat) ν 740, 1011, 1092, 1224, 1330, 1455, 1599, 2852 (-CH-), 2928 (-CH-), 3022 (Ar-H), 3055 (Ar-H), 3410 (-NH-) cm^{-1}

MS (EI): m/z = 322 $[M]^+$, 246 [M-Ph].

3b: 3,3'-(phenylmethylene)bis(1-methyl-1*H*-indole)



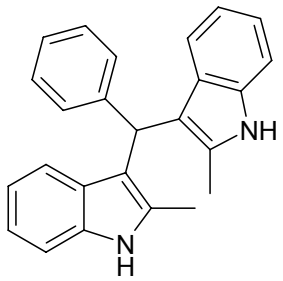
^{1}H-NMR (400MHz, $CDCl_3$) δ: 3.66 (s, 6H, -CH_3), 5.87 (s, 1H, -C*H*), 6.52 (s, 2H, -N-C*H*=), 6.98 (dd, 2H, *J* = 7.9 Hz, -C*H*=), 7.19 (dd, 3H, J = 7.9 Hz, -C*H*=), 7.29 (m, 4H, -C*H*=), 7.33 (d, 2H, *J* = 7.9 Hz, -C*H*=), 7.35 (d, 2H, *J* = 7.9 Hz, -C*H*=).

^{13}C-NMR ($CDCl_3$) δ: 32.7 (-*C*H_3), 40.1 (-*C*H-), 109.1 (-*C*H=), 118.3 (-*C*=), 118.7 (-*C*H=), 120.1 (-*C*H=), 121.4 (-*C*H=), 126.0 (-*C*H=), 127.5 (-*C*=), 128.2 (-*C*H=), 128.3 (-*C*H=), 128.7 (-*C*H=), 137.4 (-*C*=), 144.5 (-*C*=).

IR (neat) ν 739, 801, 1011, 1225, 1328, 1369, 1472, 1598, 2853 (-CH-), 2927 (-CH-), 3021 (Ar-H), 3054 cm^{-1}

MS (EI): m/z = 350 $[M]^+$, 274 $[M\text{-}Ph]^+$

3c: 3,3'-(phenylmethylene)bis(2-methyl-1*H*-indole)



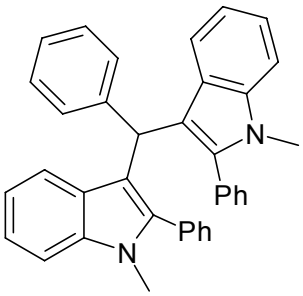
^{1}H-NMR (400MHz, $CDCl_3$) δ: 2.11 (s, 6H, -C*H*$_3$), 6.05 (s, 1H, -C*H*-), 6.71 (dd, 2H, *J* = 7.9 Hz, -C*H*=), 6.92 (m, 4H, -C*H*=), 7.26 (m 7H, -C*H*=), 9.85 (br s, 2H, -NH=).

^{13}C-NMR ($CDCl_3$) δ: 12.3 (-*C*H_3), 40.2 (-*C*H-), 111.1 (-*C*H=), 113.7 (-*C*=), 119.1 (-*C*H=), 119.8 (-*C*H=), 120.8 (-*C*H=), 126.6 (-*C*=), 128.8 (-*C*H=), 129.8 (-*C*H=), 129.9 (-*C*H=), 132.8 (-*C*=), 136.4 (-*C*=), 145.6 (-*C*=).

IR (neat) ν 719, 808, 833, 924, 1022, 1039, 1127, 1171, 1206, 1291, 1439, 1453, 1484, 1584, 1623, 2925 (-CH-), 2960 (-CH-), 3314, 3391 (-NH-) cm^{-1}

MS (EI): m/z = 350 $[M]^+$, 274 $[M\text{-}Ph]^+$

3d: 3,3'-(phenylmethylene)bis(1-methyl-2-phenyl-1*H*-indole)



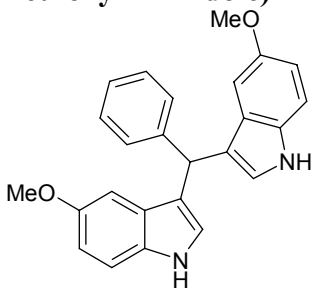
^{1}H-NMR (400MHz, $CDCl_3$) δ: 3.42 (s, 6H, -C*H*$_3$), 5.68 (s, 1H, -C*H*-CH=), 6.82 (dd, 6H, *J*= 6.9 Hz, -C*H*=), 6.89 (d, 2H, *J* = 7.6 Hz, -C*H*=), 7.11-7.25 (m, 15H, -C*H*=).

^{13}C-NMR ($CDCl_3$) δ: 30.7 (-N*C*H$_3$), 40.3 (-*C*H-), 109.0 (-*C*H=), 115.3 (-*C*=), 119.0 (-*C*H=), 120.9 (-*C*H=), 121.4 (-*C*=), 125.7-128.3 (-*C*H=), 127.8 (-*C*H=), 130.5 (-*C*H=), 132.0 (-*C*=), 137.1 (-*C*=), 138.6 (-*C*=), 145.2 (-*C*=).

IR (neat) ν 731, 761, 798, 882, 1006, 1091, 1196, 1314, 1333, 1411, 1442, 1562, 2923 (-CH-), 3108 (Ar-H) cm^{-1}

MS (EI): m/z = 502 $[M]^+$

3e: 3,3'-(phenylmethylene)bis(5-methoxy-1*H*-indole)



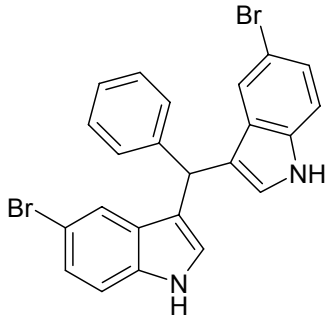
^{1}H-NMR (400MHz, $CDCl_3$) δ: 3.66 (s, 6H, -OC*H*$_3$), 5.76 (s, 1H, -C*H*-CH=), 6.66 (d, 2H, *J* = 1.7 Hz, -N-C*H*=), 6.65-6.85 (m, 4H, -C*H*=), 7.21-7.35 (m, 7H, -C*H*=), 7.81 (br s, 2H, NH).

^{13}C-NMR ($CDCl_3$) δ: 40.3 (-*C*H-), 55.9 (-O*C*H$_3$), 102.0 (-*C*H=), 111.7 (-*C*H=), 111.9 (-*C*H=), 119.3 (-*C*=), 124.4 (-*C*H=), 126.1 (-*C*H=), 127.5 (-*C*=), 128.2 (-*C*H=), 128.7 (-*C*H=), 131.8 (-*C*=), 143.9 (-*C*=), 153.7 (-O-*C*=).

IR (neat) ν 719, 808, 924, 1022, 1171, 1206, 1291, 1439, 1453, 1484, 1584, 1623, 2925 (-CH-), 2960 (-CH-), 3004 (Ar-H), 3314, 3391 (-NH-) cm^{-1}

MS (ESI): m/z = 383 $[MH]^+$

3f: 3,3'-(phenylmethylene)bis(5-bromo-1*H*-indole)



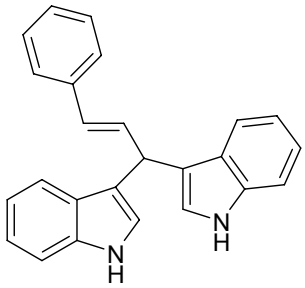
^{1}H-NMR (400MHz, CD_3COCD_3) δ: 5.96 (s, 1H, -C*H*-CH=), 6.90 (d, 2H, *J* = 2.4 Hz, -N-C*H*=), 7.22 (dd, 2H, *J* = 8.4 Hz, -C*H*=); 7.32 (m, 3H, -C*H*=), 7.41 (m, 4H, -C*H*=), 7.55 (d, 2H, *J* = 1.6 Hz, -C*H*=); 10.32 (br s, 2H, -N*H*-).

^{13}C-NMR ($CDCl_3$) δ: 40.6 (-*C*H-), 112.5 (-*C*=), 114.2 (-*C*H=), 119.4 (-*C*=), 122.7 (-*C*H=), 124.9 (-*C*H=); 126.3 (-*C*=), 127.1 (-*C*H=), 129.1 (-*C*H=), 129.4 (-*C*H=), 129.8 (-*C*=), 136.8 (-*C*=), 145.4 (-*C*=).

IR (neat) ν 700, 790, 882, 1094, 1211, 1318, 1416, 1451, 1565, 2851 (-CH-), 2924 (-CH-), 3025 (Ar-H), 3419 (-NH-) cm^{-1}

MS (ESI): m/z = 481 $[MH]^+$

3g: 3,3'-[(1*E*)-1-phenylbut-1-ene-4,4'-diyl]bis-1*H*-indole



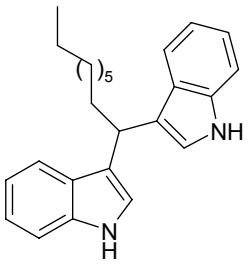
^{1}H-NMR (400MHz, $CDCl_3$) δ:5.23 (d, 1H, *J* = 7.2 Hz, -C*H*-), 6.45 (d, 1H, J_{trans} = 15.6 Hz, Ph-C*H*=CH-), 6.78 (d, 2H, *J* = 7.6 Hz, -C*H*=), 6.81 (d, 2H, *J* = 7.6 Hz, -C*H*=), 6.93 (dd, 2H, *J* = 7.2 Hz, -C*H*=), 7.00 (d, 2H, *J* = 2.0 Hz, -N-C*H*=), 7.04 (dd, 1H, J_{cis} = 7.2 Hz, J_{trans} = 15.6 Hz Ph-C*H*=CH-), 7.13 (dd, 2H, *J* = 7.6 Hz, -C*H*=), 7.28 (m, 3H, -C*H*=), 7.43 (d, 2H, *J* = 8.0 Hz, -C*H*=), 9.96 (br s, 2H, -N*H*-)

^{13}C-NMR ($CDCl_3$) δ: 38.7 (-CH-), 112.2 (-*C*H=), 118.7 (-*C*=), 119.3 (-*C*H=), 120.4 (-*C*H=), 122.0 (-*C*H=), 123.6 (-*C*H=), 127.0 (-*C*H=), 127.7 (-*C*=), 128.0 (-*C*H=), 129.4 (-*C*H=), 130.0 (-*C*H=), 134.1 (-*C*H=), 138.1 (-*C*=), 138.9 (-*C*=).

IR (neat) ν 738, 964, 1093, 1218, 1245, 1337, 1417, 1455, 1490, 1530, 1599, 2855 (-CH-), 2925 (-CH-), 3055 (Ar-H), 3407 (-NH-) cm^{-1}

MS (EI): m/z = 322 $[M-C_2H_4]^+$

3h: 3,3'-nonane-1,1-diylbis-1*H*-indole



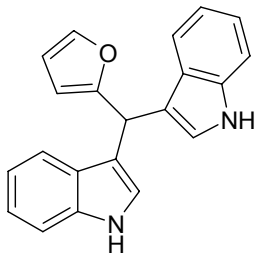
^{1}H-NMR (400MHz, $CDCl_3$) δ: 0.83 (t, 3H, *J* = 6.8 Hz, -C*H*$_3$), 1.22-1.37 (s, 12H, -C*H*$_2$), 2.18 (m, 2H, -C*H*$_2$-), 4.44 (t, 1H, *J* = 7.2 Hz, -C*H*-CH=), 6.89 (d, 2H, *J*= 2.0 Hz, -N-C*H*=), 7.02 (dd, 2H, *J*= 6.9 Hz, -C*H*=), 7.13 (dd, 2H, *J*= 7.0, C*H*=), 7.26 (d, 2H, *J* = 8.0 Hz, -C*H*=), 7.58 (d, 2H, *J* = 8.0 Hz, -C*H*=), 7.73 (br s, 2H, NH).

^{13}C-NMR ($CDCl_3$) δ: 14.2 (-*C*H$_3$), 22.7 (-*C*H$_2$), 28.4-29.9 (-*C*H$_2$), 31.9 (-*C*H$_2$), 34.1 (-*C*H$_2$), 35.9 (-*C*H-), 111.1 (-*C*H=), 119.0-121.7 (-*C*H=), 127.2 (-*C*=), 136.6 (-*C*=).

IR (neat) ν 738, 1011, 1095, 1334, 1455, 1485, 1618, 2853 (-CH-), 2924 (-CH-), 2953 (-CH-), 3057 (Ar-H), 3386 (-NH-) cm^{-1}

MS (ESI): m/z = 359 $[MH]^+$, 397 $[M+K]^+$

3i: **3,3'-(furylmethylene)bis-1*H*-indole**



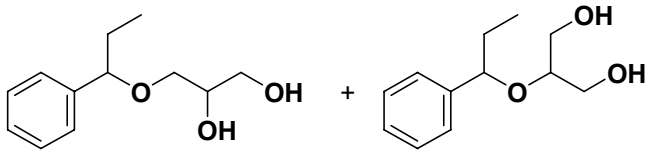
^{1}H-NMR (400MHz, CD_3COCD_3) δ: 5.97 (s, 1H, -C*H*-CH=), 6.07 (d, 1H, *J*= 3.2 Hz, -O-C*H*=), 6.31 (d, 2H, *J*= 1.9 Hz, -N-C*H*=), 6.92 (dd, 2H, *J* = 7.2 Hz, -C*H*=), 7.06 (m, 3H, -C*H*=), 7.38 (d, 2H, *J* = 8.0 Hz, -C*H*=), 7.42 (m, 1H, -C*H*=), 7.47 (d, 2H, *J*= 8.0 Hz, -CH=), 10.03 (br s, 2H, -NH-).

^{13}C-NMR (400MHz, CD_3COCD_3) δ: 35.0 (-*C*H-), 106.9 (-*C*H=), 110.9 (-*C*H=), 112.2 (-*C*H=), 112.3 (-*C*H=), 117.5 (-*C*H=), 117.6 (-*C*=), 119.5 (-*C*H=), 120.2 (-*C*H=), 122.1 (-*C*H=), 124.1 (-*C*H=), 124.2 (-*C*H=), 127.9 (-*C*=), 137.8 (-*C*H=), 137.9 (-*C*=), 141.9 (O-*C*H=), 158.9 (-O-*C*=).

IR (neat) ν 741, 927, 1009, 1239, 1416, 1456, 1615, 1693, 2920 (-CH-), 3055 (Ar-H), 3406 (-NH-) cm^{-1}

MS (ESI): m/z = 313 $[MH]^+$

4a/4b: 1-Phenyl-1-propyl α-glyceryl ether and 1-phenyl-1-propyl β-glyceryl ether (α/β = 90/10)

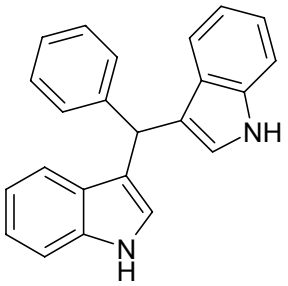


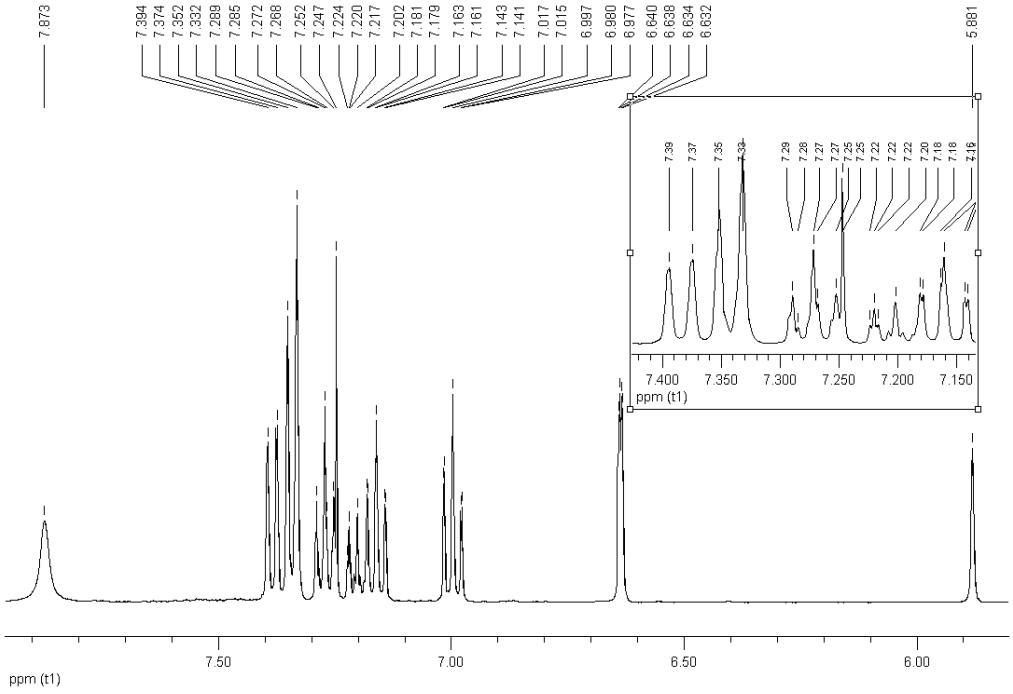
^{1}H NMR δ 0.85 (t, *J* = 7.4 Hz, 3H), 1.59-1.73 (m, 1H), 1.76-1.91 (m, 1H), 3.25-3.35 (m, 2H), 3.46-3.75 (m, 4H), 3.77-3.82 (m, 1H), 4.12 (t, *J* = 6.7 Hz, 0.9 H), 4.30 (t, *J* = 6.8 Hz, 0.1 H), 7.21-7.34 (m, 5H).

^{13}C NMR δ 10.2, 10.4, 30.8, 31.0, 61.1, 62.4, 64.0, 64.2, 70.1, 70.2, 70.9, 71.1, 82.8, 84.5, 84.6, 126.7, 126.8, 127.6, 127.8, 128.4, 128.5, 141.9, 142.4.

IR (neat) 3381, 2965, 2933, 2876, 1452, 1103, 1042, 727, 755, 700 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.35; H, 8.91.


NH
N
H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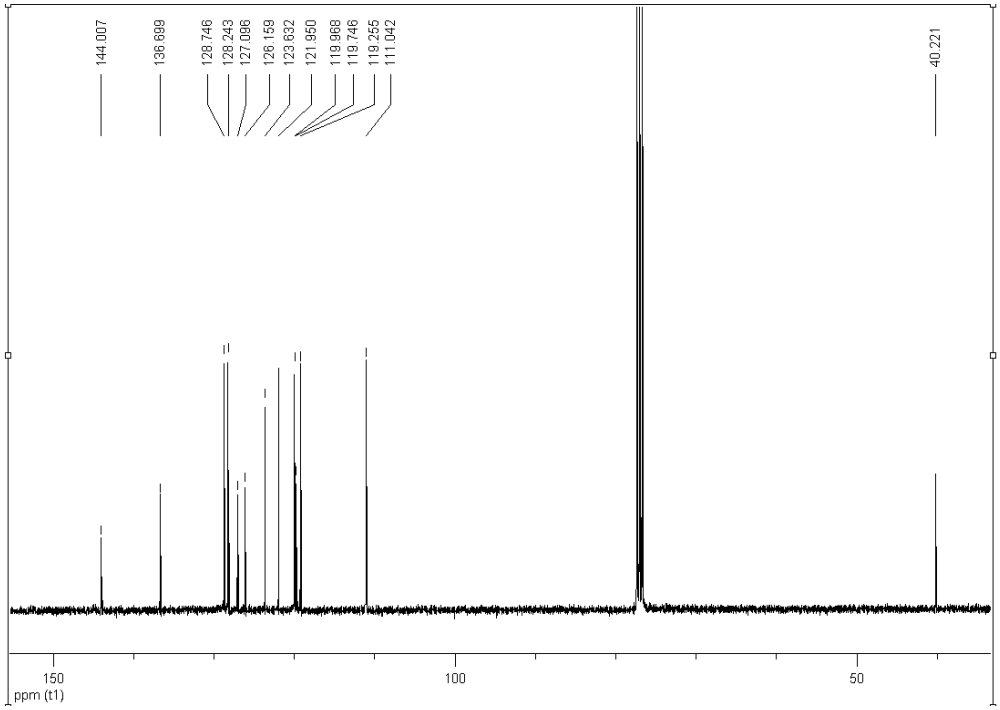
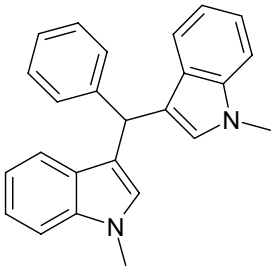
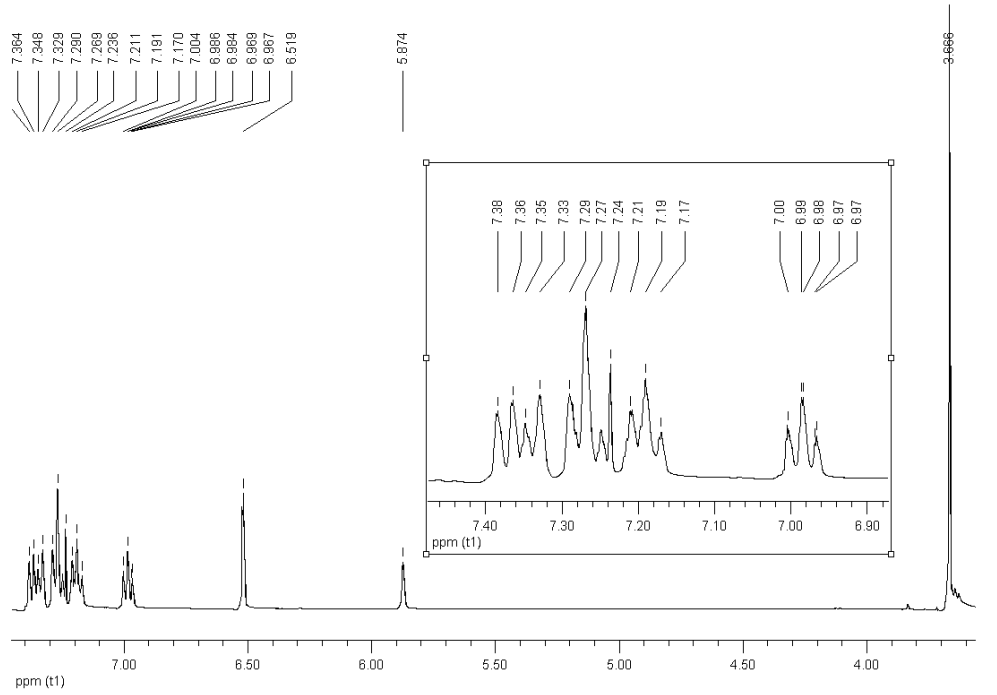
7.374
7.352
7.332
7.289
7.285
7.272
7.268
7.252
7.247
7.224
7.220
7.217
7.202
7.181
7.179
7.163
7.161
7.143
7.141
7.017
7.015
6.997
6.980
6.977
6.640
6.638
6.634
6.632
5.881
7.39
7.37
7.35
7.33
7.29
7.28
7.27
7.27
7.25
7.25
7.22
7.22
7.22
7.20
7.18
7.18
7.16
7.400
7.350
7.300
7.250
7.200
7.150
ppm (t1)
7.50
7.00
6.50
6.00
ppm (t1)


144.007
136.699
128.746
128.243
127.086
126.159
123.632
121.950
119.968
119.746
119.255
111.042
40.221
150
100
50
ppm (t1)


N
N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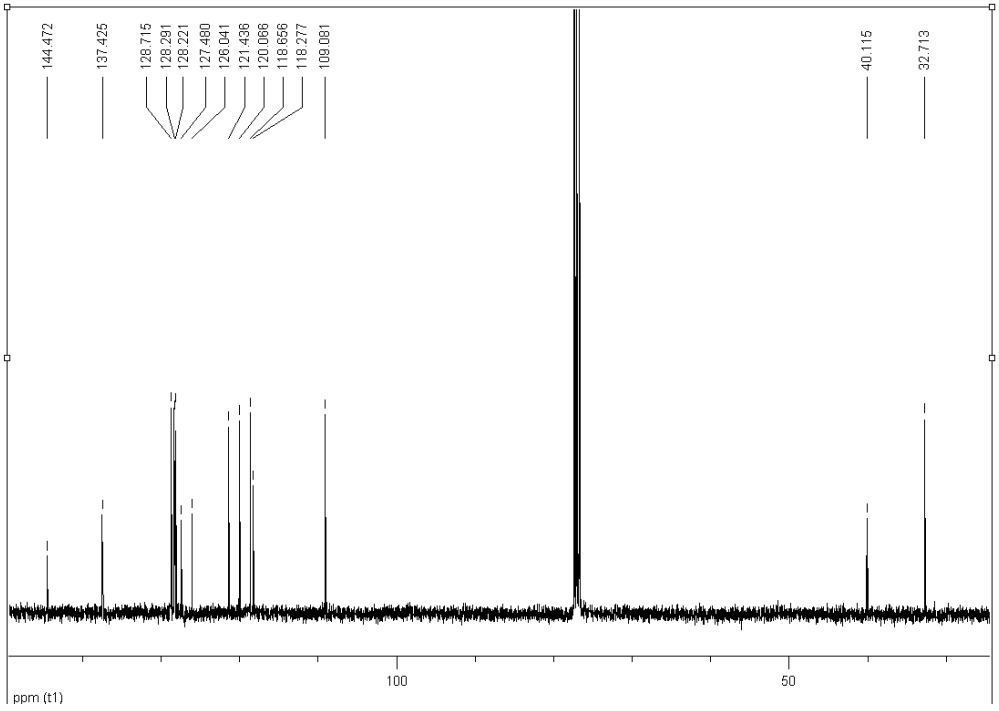
7.348
7.329
7.290
7.269
7.236
7.211
7.191
7.170
7.004
6.986
6.984
6.969
6.967
6.519
5.874
3.666
7.38
7.36
7.35
7.33
7.29
7.27
7.24
7.21
7.19
7.17
7.00
6.99
6.98
6.97
6.97
7.40
7.30
7.20
7.10
7.00
6.90
ppm (t1)
7.00
6.50
6.00
5.50
5.00
4.50
4.00
ppm (t1)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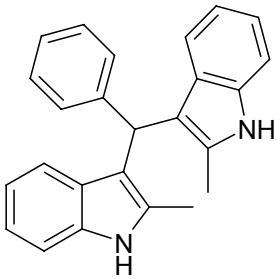
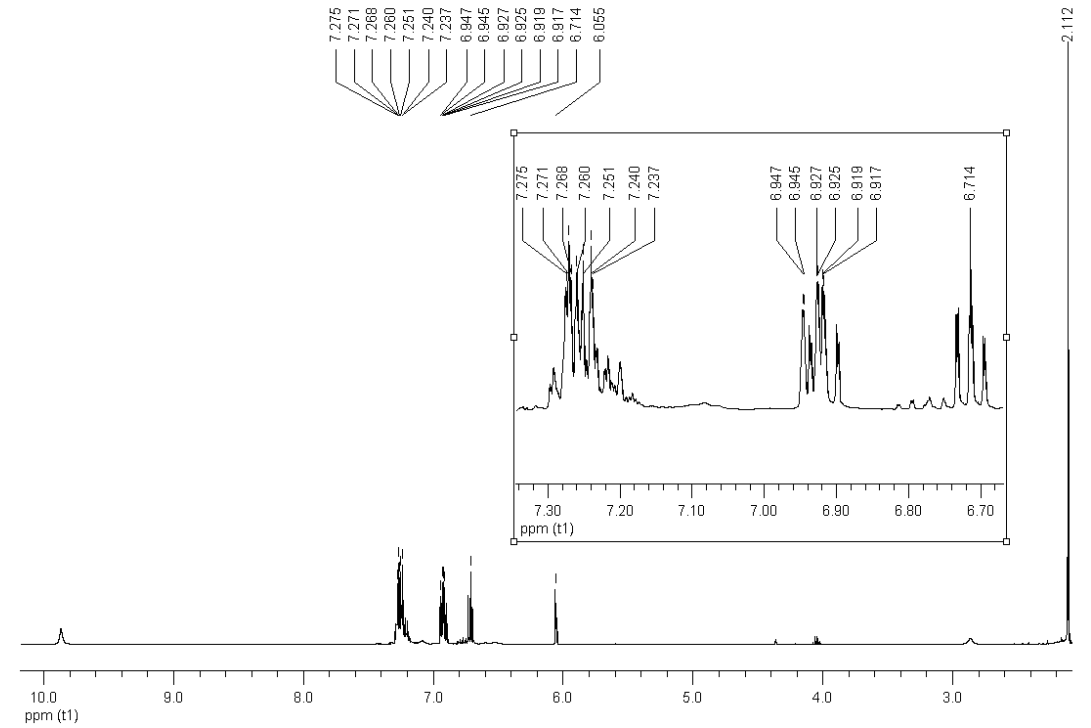
137.425
128.715
128.291
128.221
127.480
126.041
121.436
120.066
118.656
118.277
109.081
40.115
32.713
100
50
ppm (t1)


NH
N
H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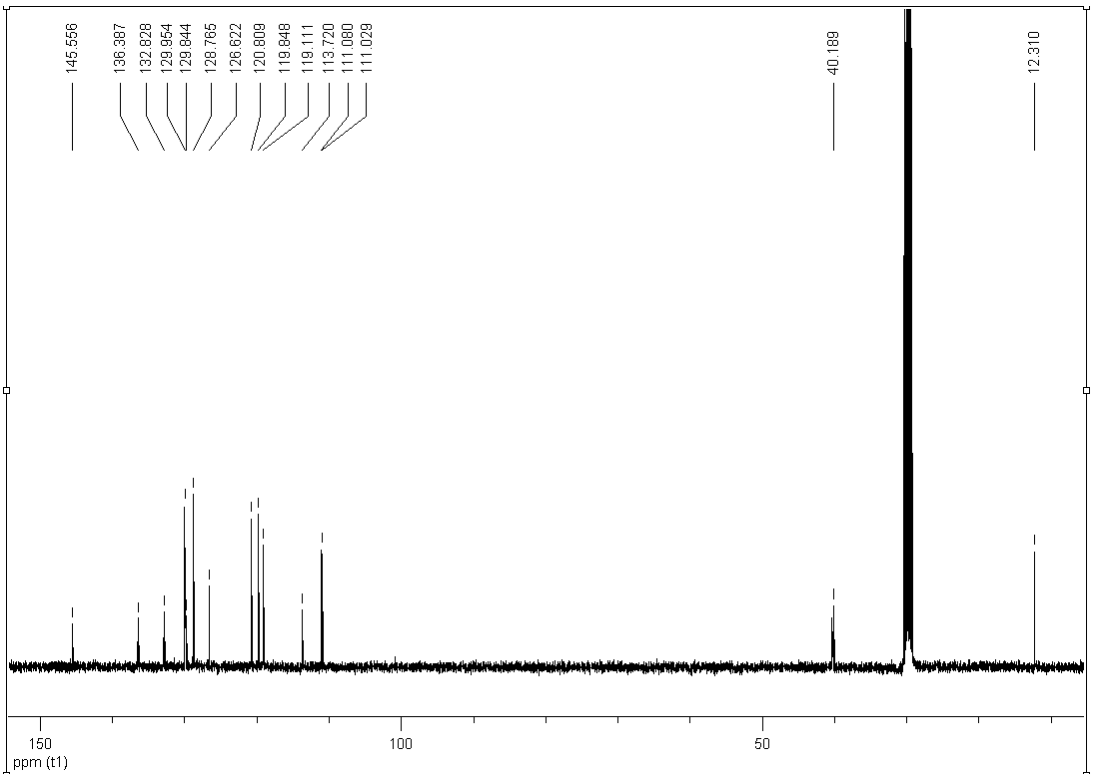
7.271
7.268
7.260
7.251
7.240
7.237
6.947
6.945
6.927
6.925
6.919
6.917
6.714
6.055
2.112
7.30
7.20
7.10
7.00
6.90
6.80
6.70
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)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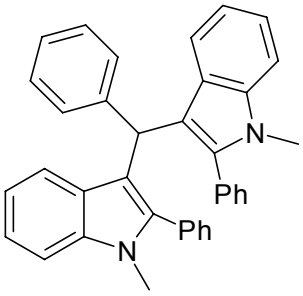
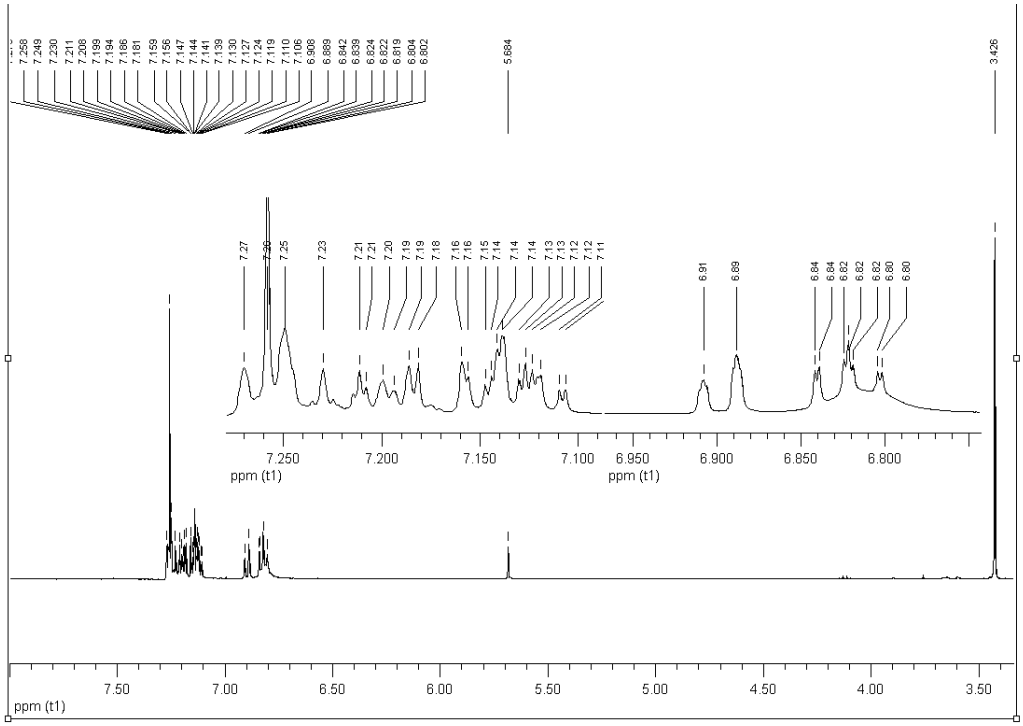
132.828
129.954
129.844
128.765
126.622
120.809
119.848
119.111
113.720
111.080
111.029
40.189
12.310
150
100
50
ppm (t1)


N
Ph
Ph
N


7.258
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7.211
7.208
7.199
7.194
7.186
7.181
7.159
7.156
7.147
7.144
7.141
7.139
7.130
7.127
7.124
7.119
7.110
7.106
6.906
6.889
6.842
6.839
6.824
6.822
6.819
6.804
6.802
5.684
3.426
7.27
7.26
7.25
7.23
7.21
7.21
7.20
7.19
7.19
7.18
7.16
7.16
7.15
7.14
7.14
7.14
7.13
7.13
7.12
7.12
7.11
6.91
6.89
6.84
6.84
6.82
6.82
6.82
6.80
6.80
7.250
7.200
7.150
7.100
6.950
6.900
6.850
6.800
ppm (t1)
ppm (t1)
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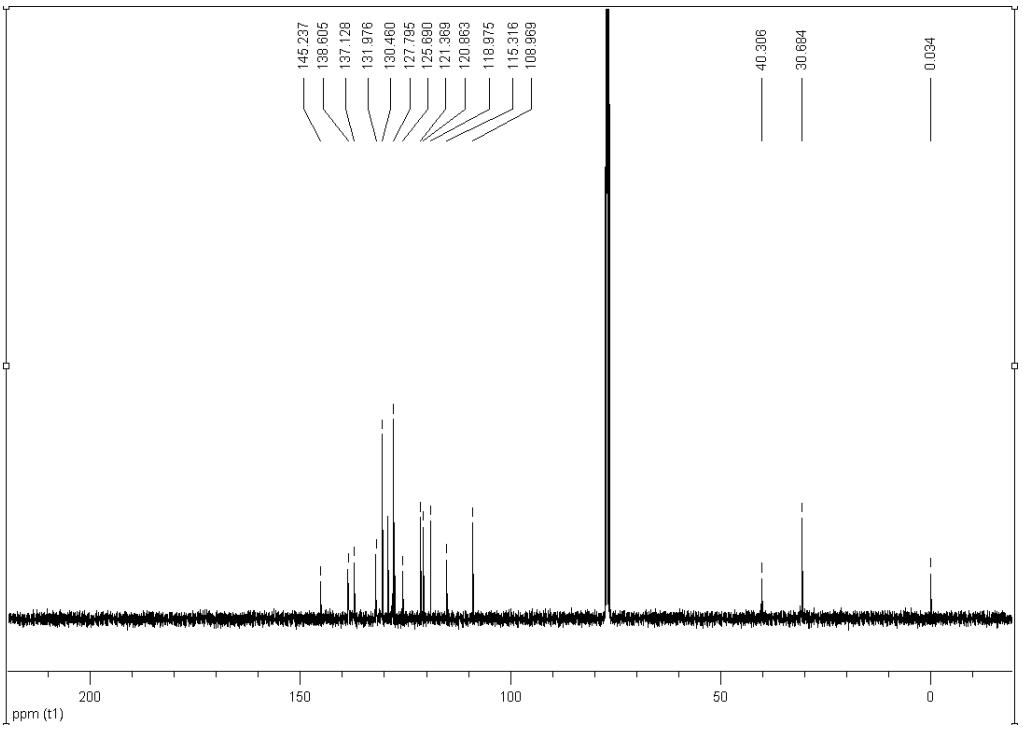
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
ppm (t1)


145.237
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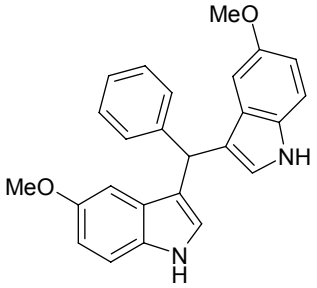
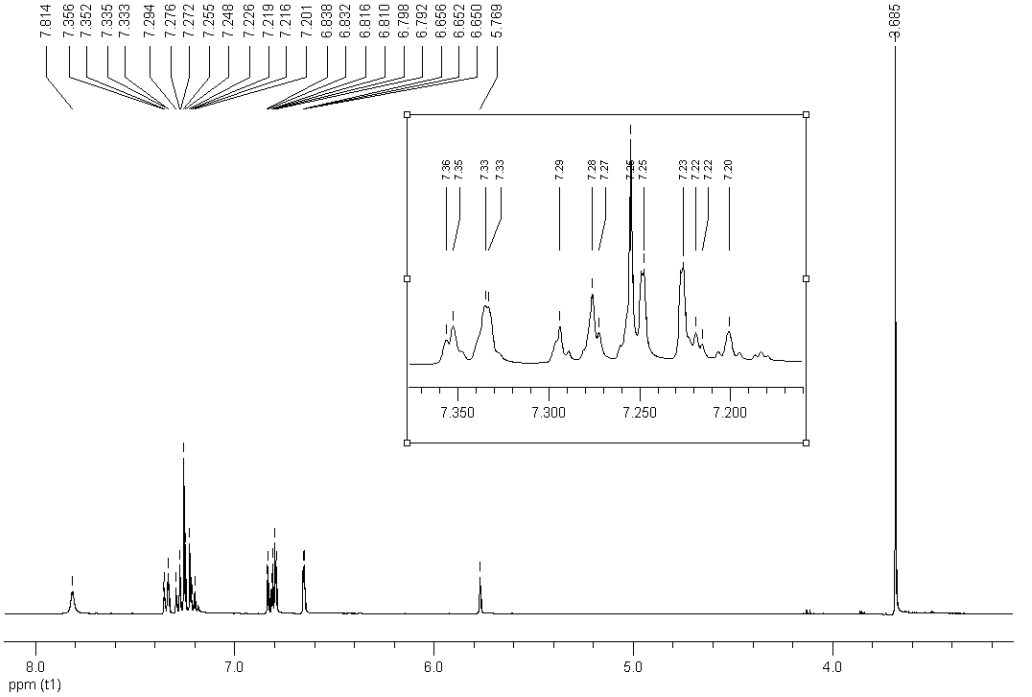
137.128
131.976
130.460
127.795
125.890
121.369
120.863
118.975
115.316
108.969
40.306
30.684
0.034
200
150
100
50
0
ppm (t1)


MeO
NH
MeO
N
H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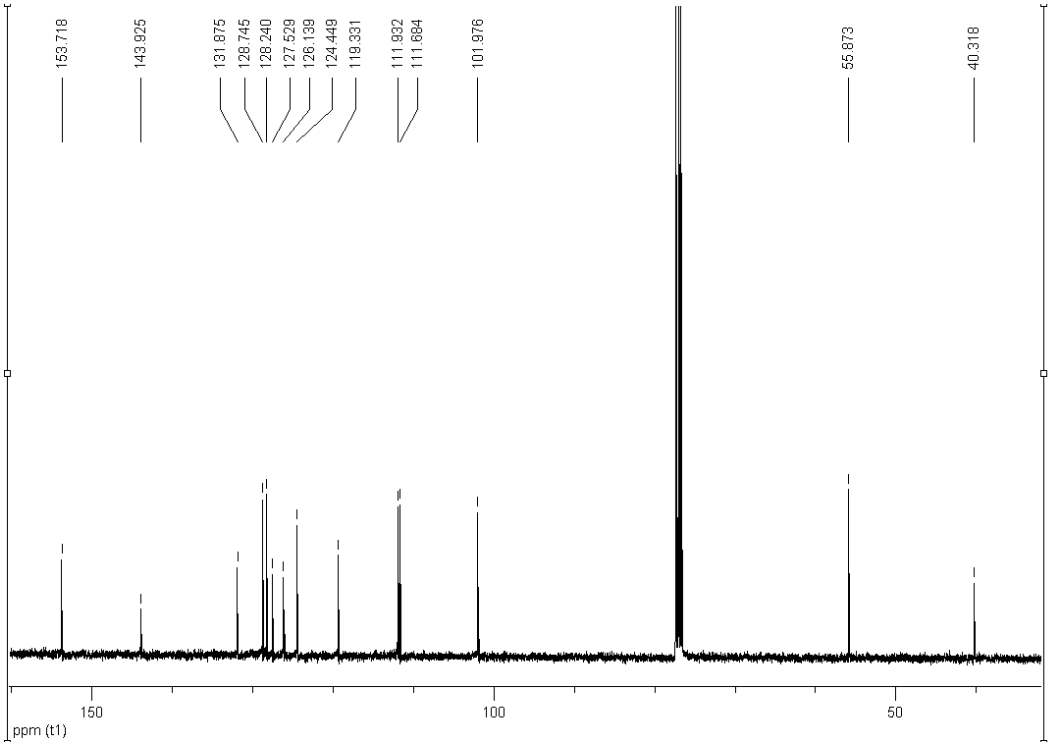
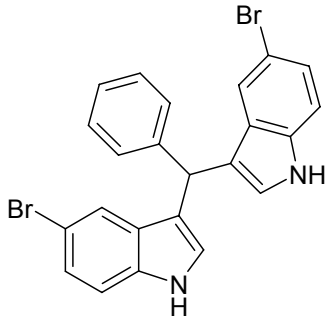
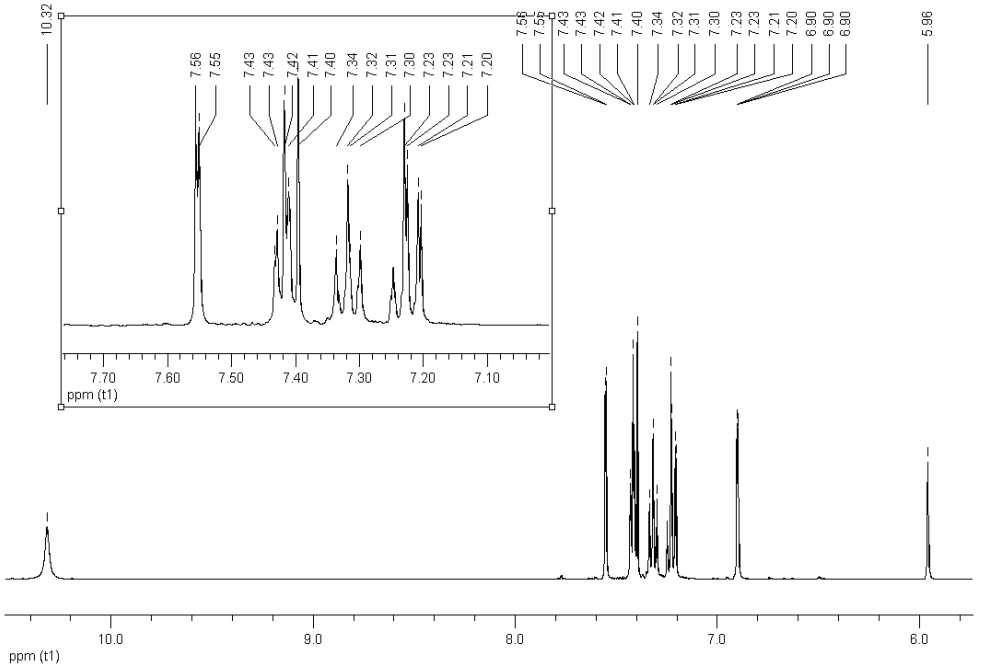
7.352
7.335
7.333
7.294
7.276
7.272
7.255
7.248
7.226
7.219
7.216
7.201
6.838
6.832
6.816
6.810
6.798
6.792
6.656
6.652
6.650
5.769
3.685
7.36
7.35
7.33
7.33
7.29
7.28
7.27
7.25
7.23
7.22
7.22
7.20
7.350
7.300
7.250
7.200
8.0
7.0
6.0
5.0
4.0
ppm (t1)


153.718
143.925
131.875
128.745
128.240
127.529
126.139
124.449
119.331
111.932
111.684
101.976
55.873
40.318
150
100
50
ppm (t1)


Br
NH
Br
N
H


10.32
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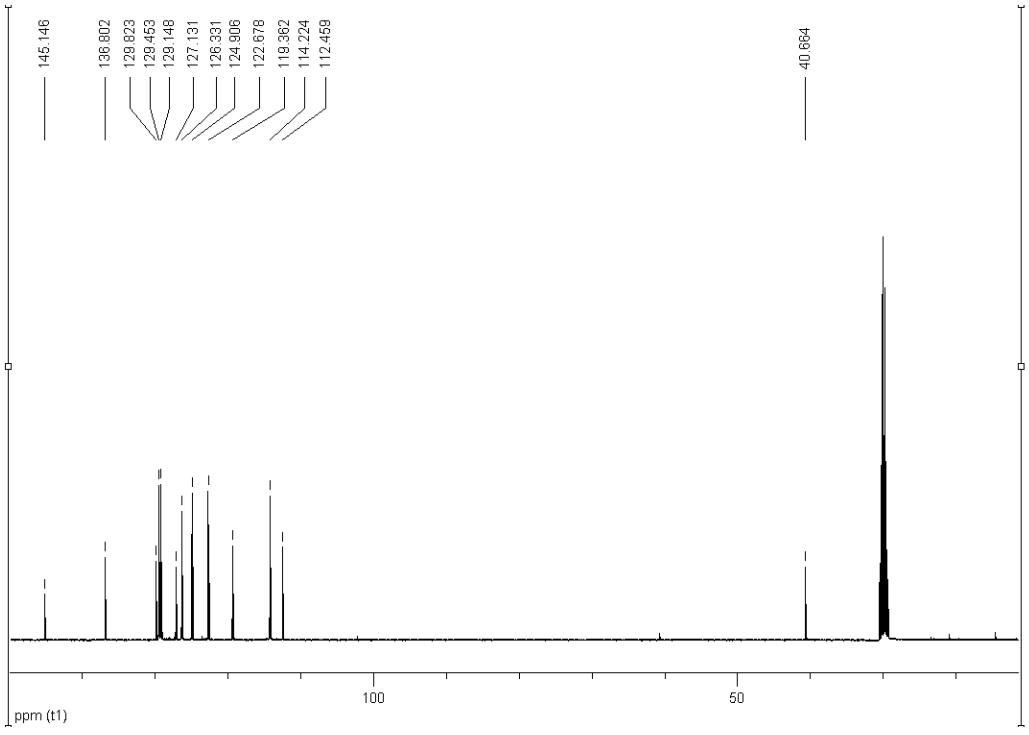
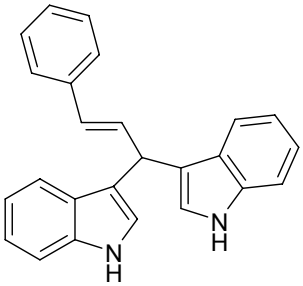
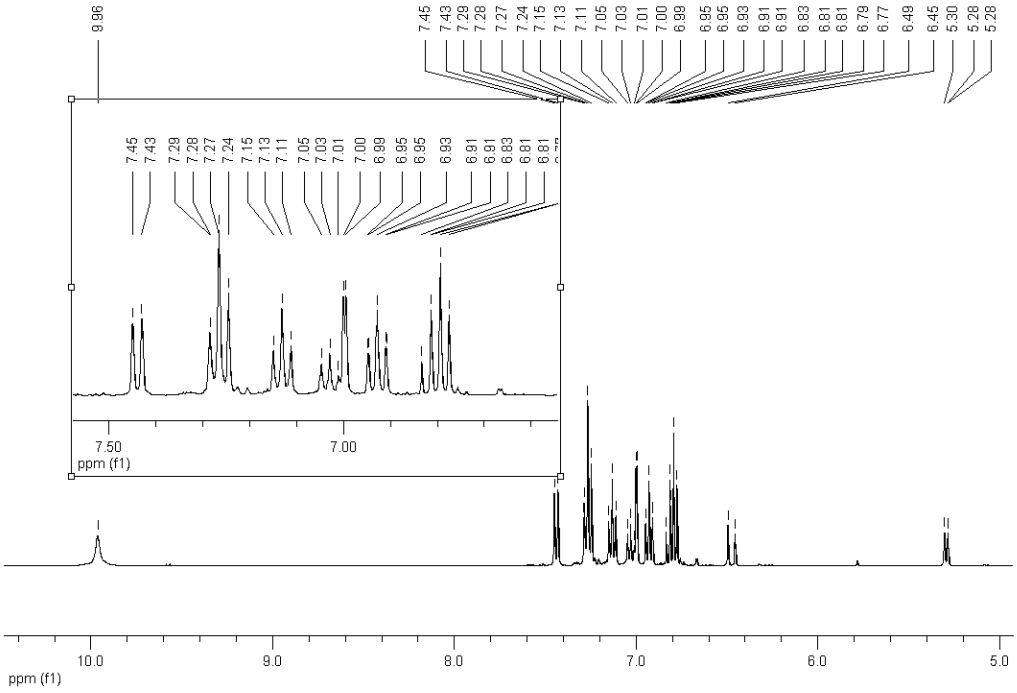
7.55
7.43
7.43
7.42
7.41
7.40
7.34
7.32
7.31
7.30
7.23
7.23
7.21
7.20
6.90
6.90
5.96
7.70
7.60
7.50
7.40
7.30
7.20
7.10
ppm (t1)
10.0
9.0
8.0
7.0
6.0
ppm (t1)


145.146
136.802
129.823
129.453
129.148
127.131
126.331
124.906
122.678
119.362
114.224
112.459
40.664
100
50
ppm (t1)


N
H
N
H


9.96
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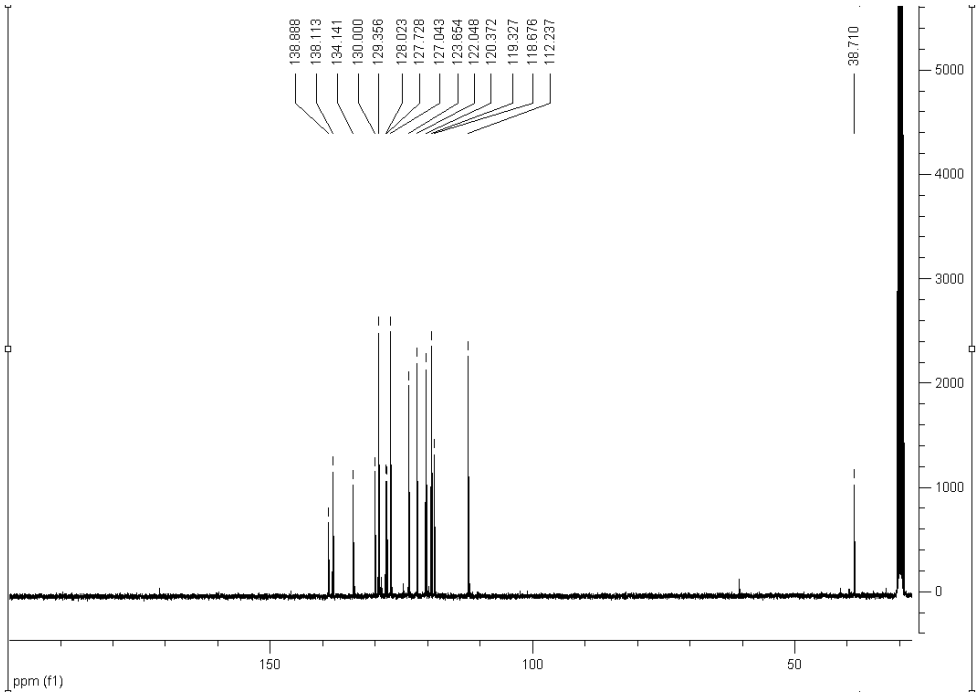
7.28
7.27
7.24
7.15
7.13
7.11
7.05
7.03
7.01
7.00
6.99
6.95
6.95
6.93
6.91
6.91
6.83
6.81
6.81
6.79
6.77
6.49
6.45
5.30
5.28
5.28
7.50
7.00
ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
ppm (f1)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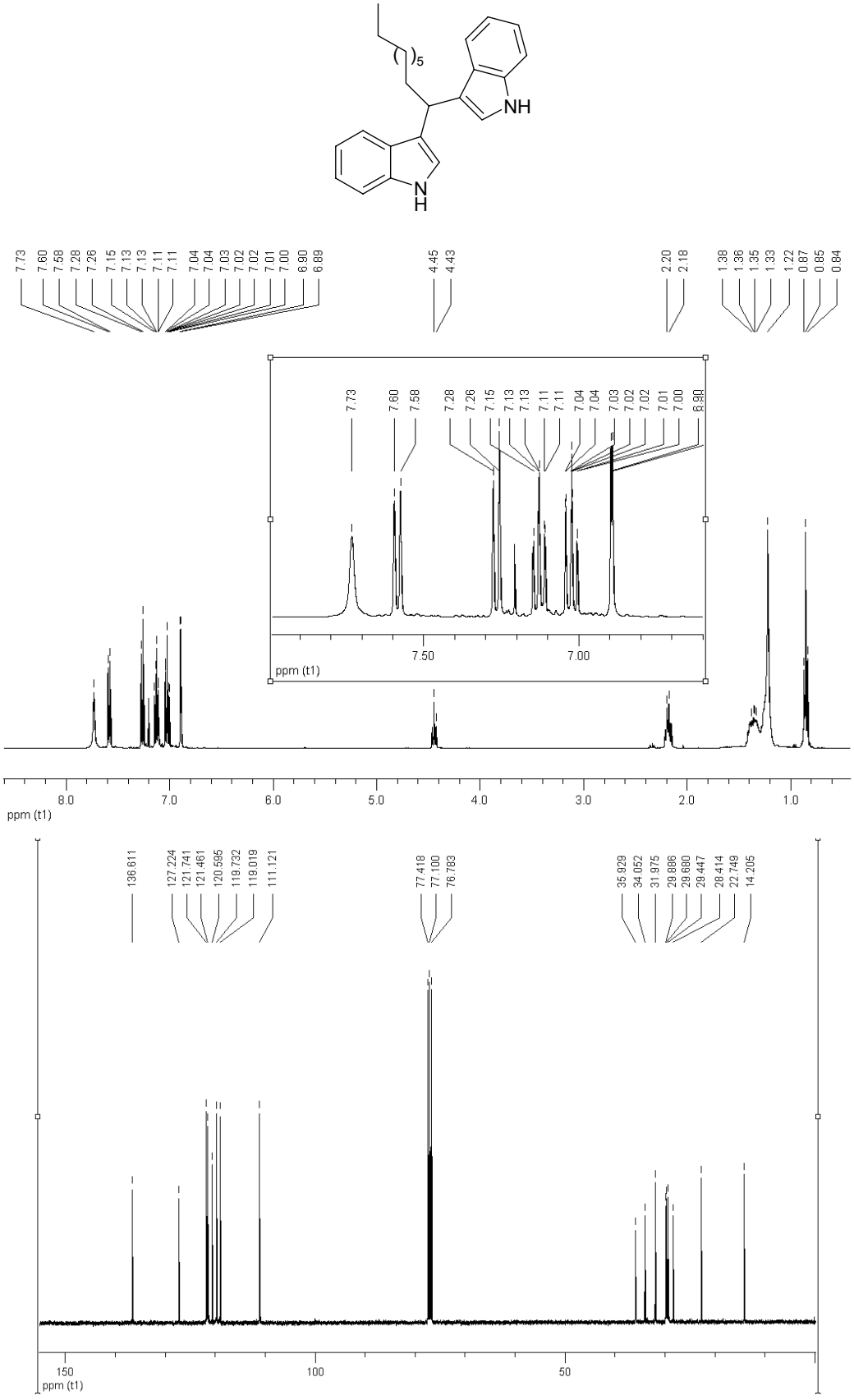
130.000
129.356
128.023
127.728
127.043
123.654
122.048
120.372
119.327
118.676
112.237
38.710
5000
4000
3000
2000
1000
0
150
100
50
ppm (f1)


NH
N
H
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7.26
7.15
7.13
7.13
7.11
7.11
7.04
7.04
7.03
7.02
7.02
7.01
7.00
6.90
6.89
4.45
4.43
2.20
2.18
1.38
1.36
1.35
1.33
1.22
0.87
0.85
0.84
7.50
7.00
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
136.611
127.224
121.741
121.461
120.595
119.732
119.019
111.121
77.418
77.100
76.783
35.929
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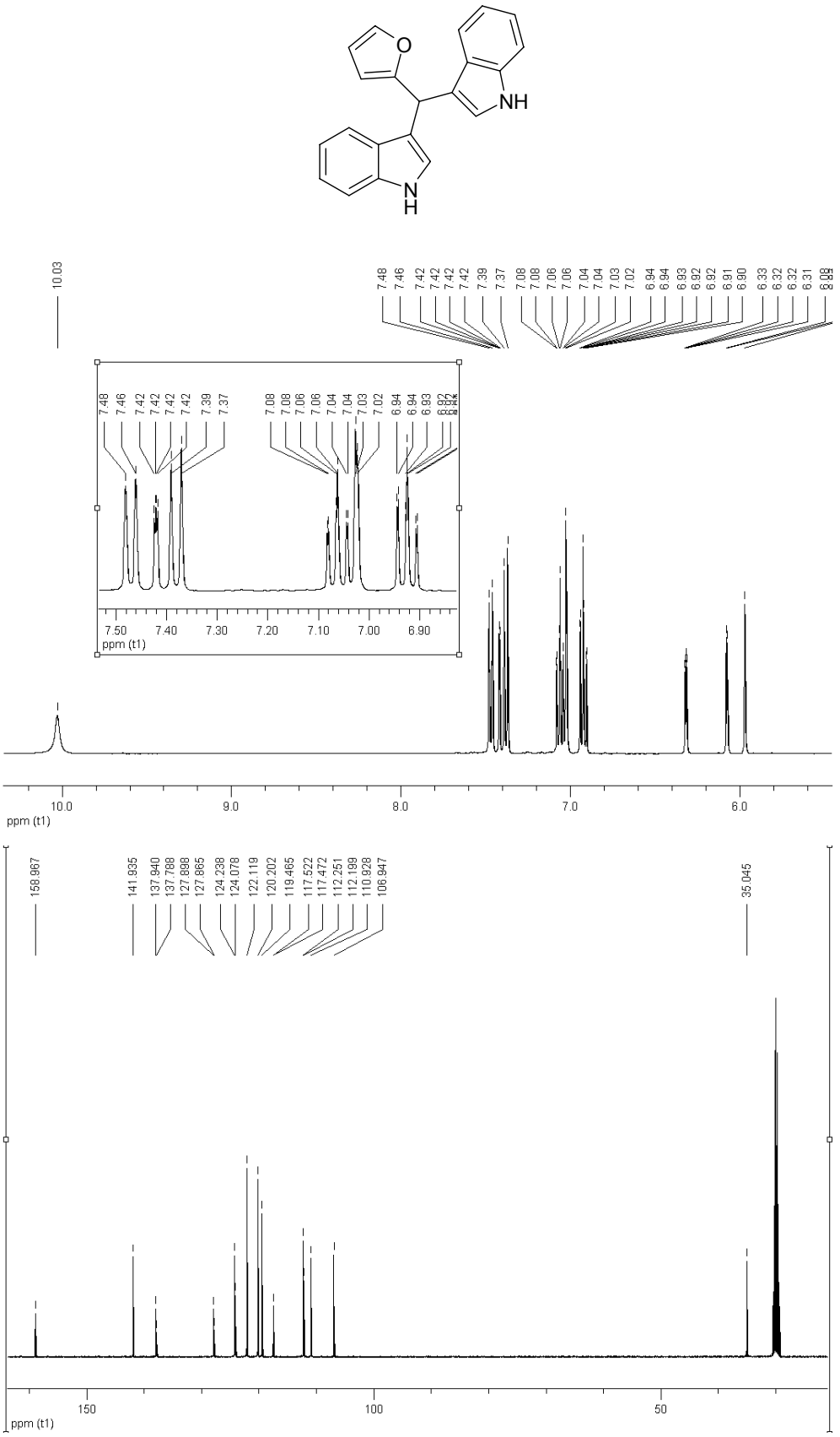
22.749
14.205
150
100
50
ppm (t1)


O
NH
N
H
10.03
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7.46
7.42
7.42
7.42
7.42
7.39
7.37
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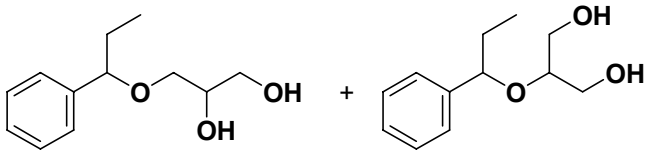
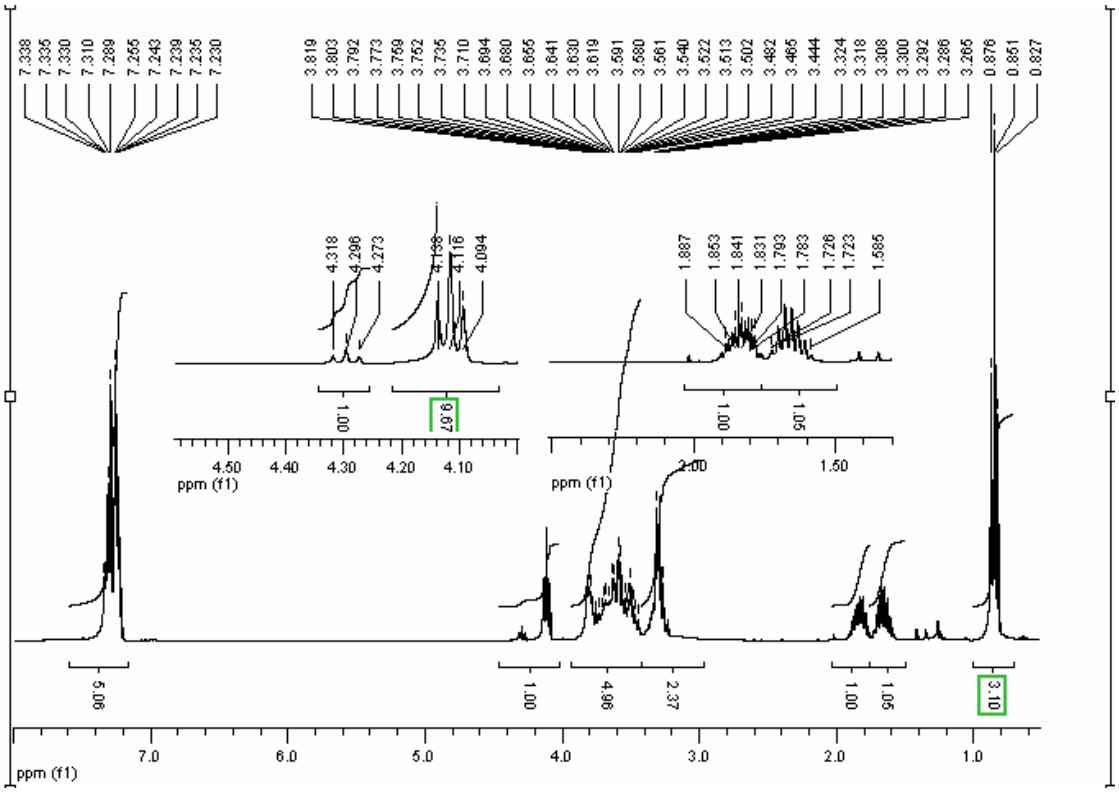
7.08
7.06
7.06
7.04
7.04
7.03
7.02
6.94
6.94
6.93
6.92
6.92
6.91
6.90
6.33
6.32
6.32
6.31
7.50
7.40
7.30
7.20
7.10
7.00
6.90
ppm (t1)
10.0
9.0
8.0
7.0
6.0
ppm (t1)
158.967
141.935
137.940
137.788
127.898
127.865
124.238
124.078
122.119
120.202
119.465
117.522
117.472
112.251
112.199
110.928
106.947
35.045
150
100
50
ppm (t1)


OH
O
OH
+
OH
O
OH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3.773
3.759
3.752
3.735
3.710
3.694
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3.655
3.641
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3.619
3.591
3.580
3.561
3.540
3.522
3.513
3.502
3.482
3.465
3.444
3.324
3.318
3.308
3.300
3.292
3.286
3.265
0.876
0.851
0.827
4.318
4.296
4.273
4.138
4.116
4.094
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1.853
1.841
1.831
1.793
1.783
1.726
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1.00
9.67
1.00
1.06
4.50
4.40
4.30
4.20
4.10
ppm (f1)
2.00
1.50
ppm (f1)
6.06
1.00
4.98
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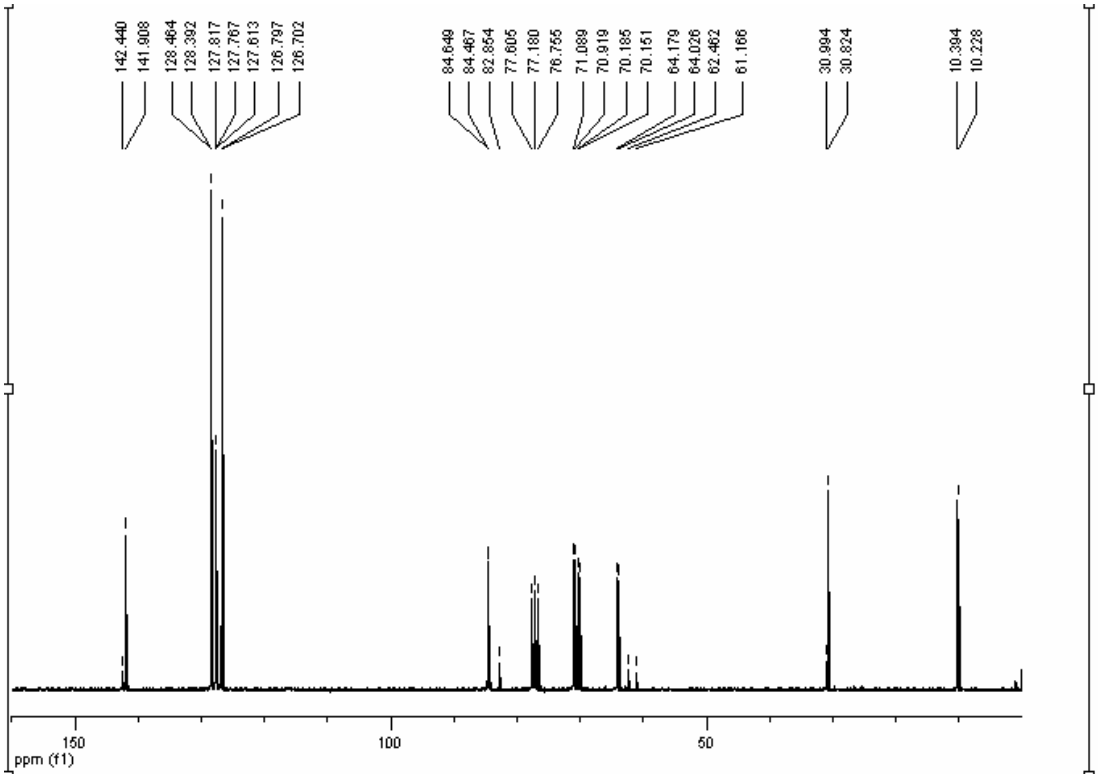
ppm (f1)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84.467
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77.605
77.180
76.755
71.089
70.919
70.185
70.151
64.179
64.026
62.462
61.166
30.994
30.824
10.394
10.228
150
100
50
ppm (f1)