Electronic Supplementary Material (ESI) for RSC Advances


# Synthesis of molecular photoswitches based on azobenzene with organosilane anchor

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# Supplementary Material

Spectra of synthesized chemical compounds: **$^{1}$H-NMR, $^{13}$C-NMR, GC-MS**, **IR**

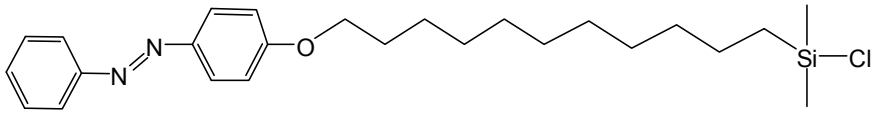
A. 4-Phenylazo-(4´-(11-dimethylchlorosilanyl-)undecyloxy)benzene

B. 4-(4´-Pentyl)phenylazo-(4´-(11-dimethylchlorosilanyl-)undecyloxy)benzene

C. 4-(4´-Pentyloxy)phenylazo-(4´-(11-dimethylchlorosilanyl-)undecyloxy)benzene

# A.

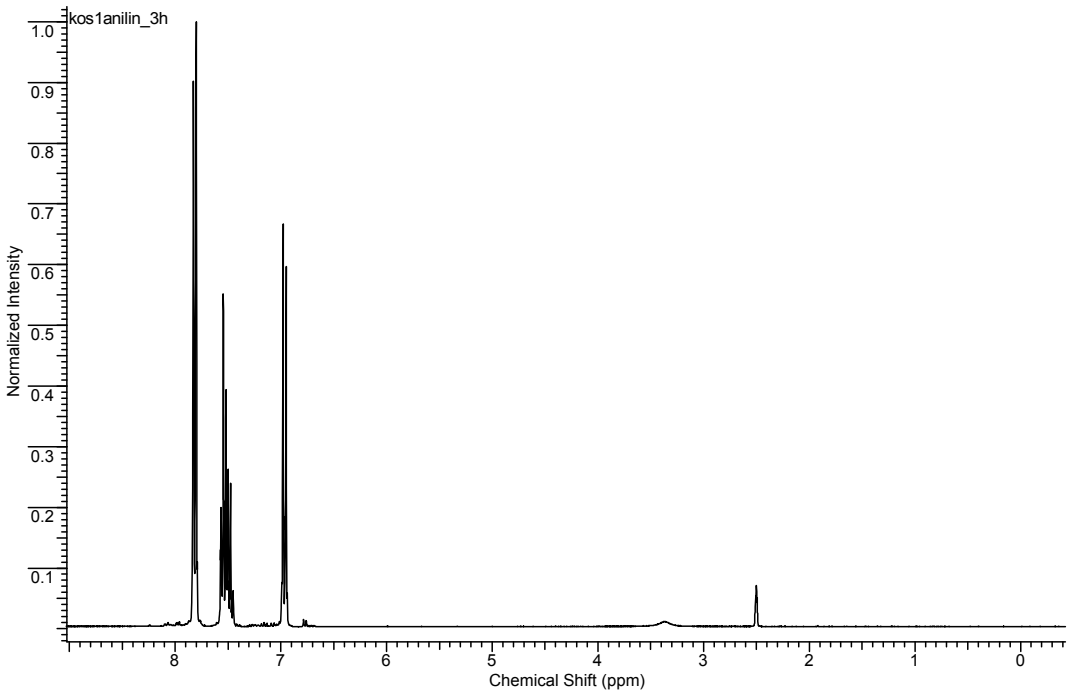
## 4-Phenylazo-(4′-(11-dimethylchlorosilanyl-)undecyloxy)benzene




PAP: 4-Phenylazophenol
PAPU: 11-(4-(Phenylazo-phenoxy)-undecene
PAS: 4-Phenylazo-(4′-(11-dimethylchlorosilanyl-)undecyloxy)benzene

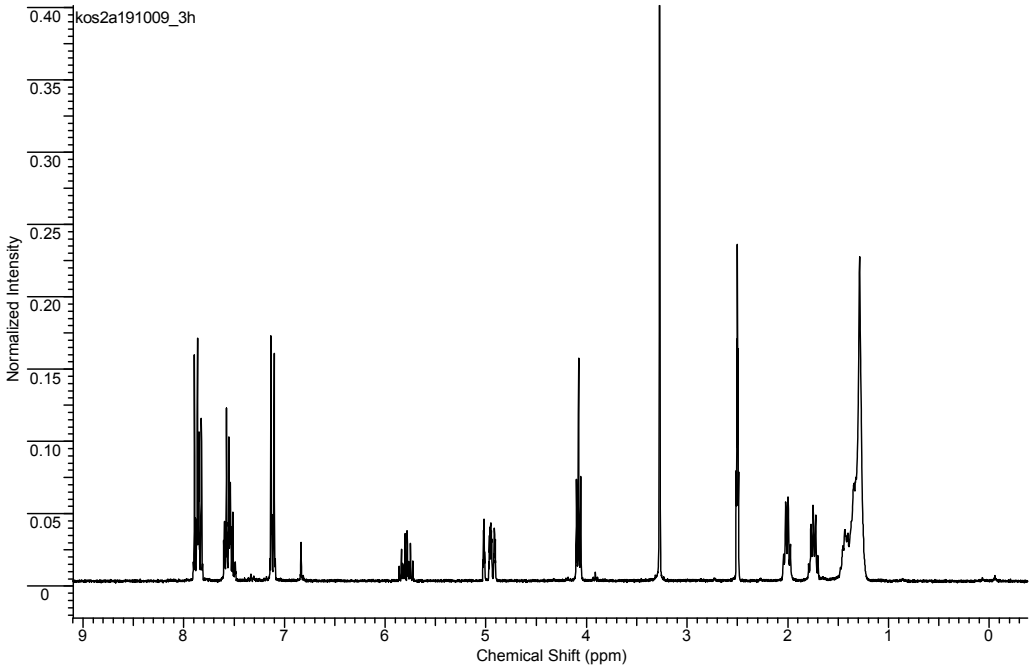
# $^1$H-NMR

## PAP



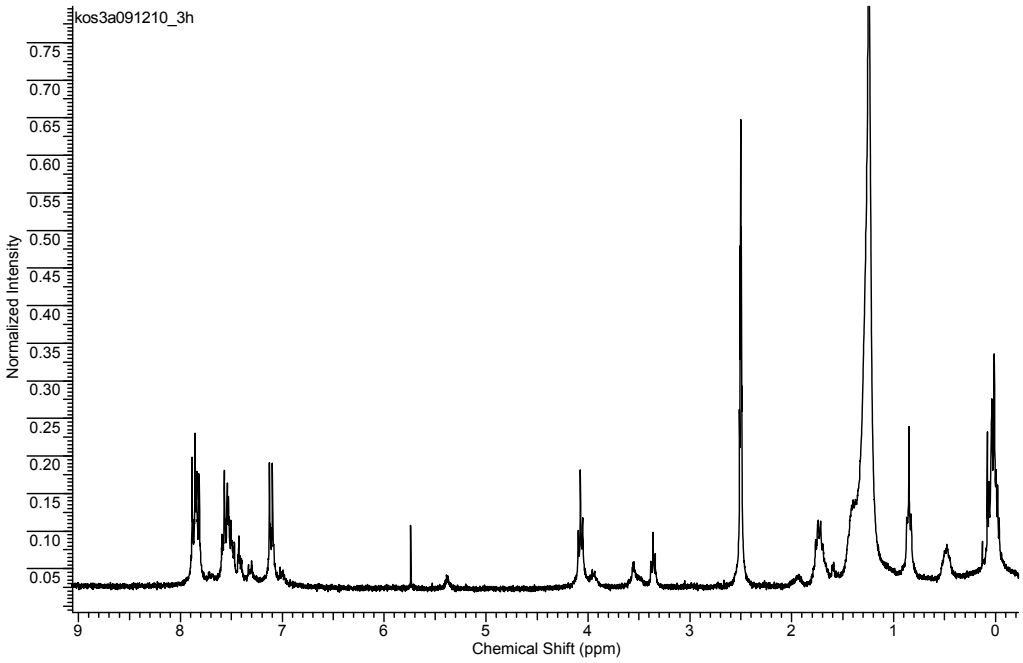

$^1$H NMR (300MHz, DMSO); δ[ppm]: 7.1 (d, 2H, Ph-H), 7.5 (m, 3H, Ph-H), 7.8 (2×d, 4H, Ph-H)

**PAPU**




$^1$H NMR (300MHz, DMSO); δ[ppm]: 1.1–1.5 (m, 12H, $CH_2$=$CHCH_2(CH_2)_6CH_2$), 1.7 (m, 2H, $CH_2CH_2CH_2O$), 2.0 (dt, 2H, $CH_2$=$CHCH_2CH_2$), 2.5 (DMSO), 3.3 (dicyclohexano-18-crown-6), 4.1 (t, 2H, $CH_2CH_2O$), 4.9–5.1 (m, 2H, $CH_2$=$CHCH_2$), 5.8 (m, 1H, $CH_2$=$CHCH_2$), 7.1 (d, 2H, Ph-H), 7.5 (m, 3H, Ph-H),7.8 (2×d, 4H, Ph-H)

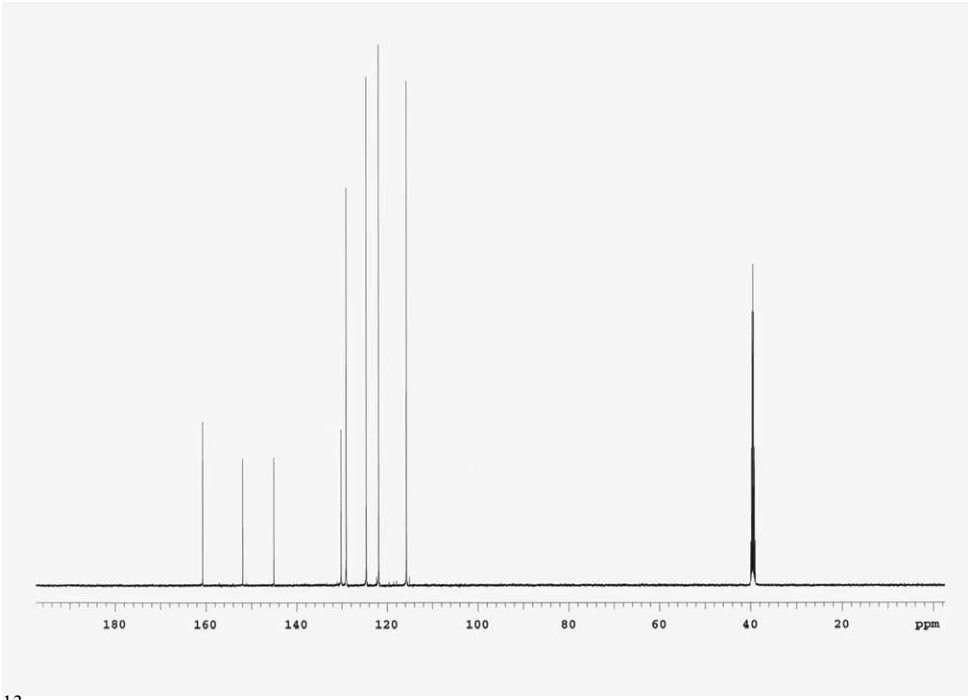
PAS




$^1$H NMR (300MHz, DMSO); δ [ppm]: 0 (silyl residues), 0.5 (s, 6H, $ClSi(CH_3)_2CH_2$), 0.8 (t, 2H, $ClSi(CH_3)_2CH_2CH_2$), 1.1–1.5 (m, 16H, $ClSi(CH_3)_2CH_2(CH_2)_8CH_2CH_2O$), 1.7 (m, 2H, $CH_2CH_2CH_2O$), 2.5 (DMSO), 3.3 (dicyclohexano-18-crown-6), 4.1 (t, 2H, $CH_2CH_2O$), 7.1 (d, 2H, Ph-H), 7.5 (m, 3H, Ph-H), 7.8 (2×d, 4H, Ph-H)

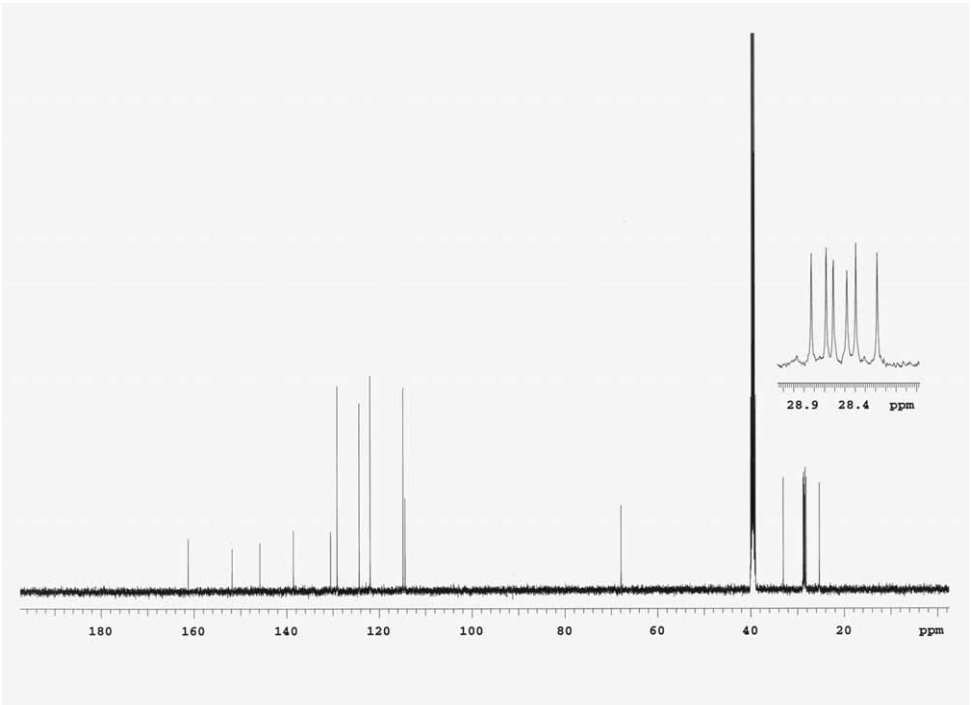
# $^{13}$C-NMR

## PAP



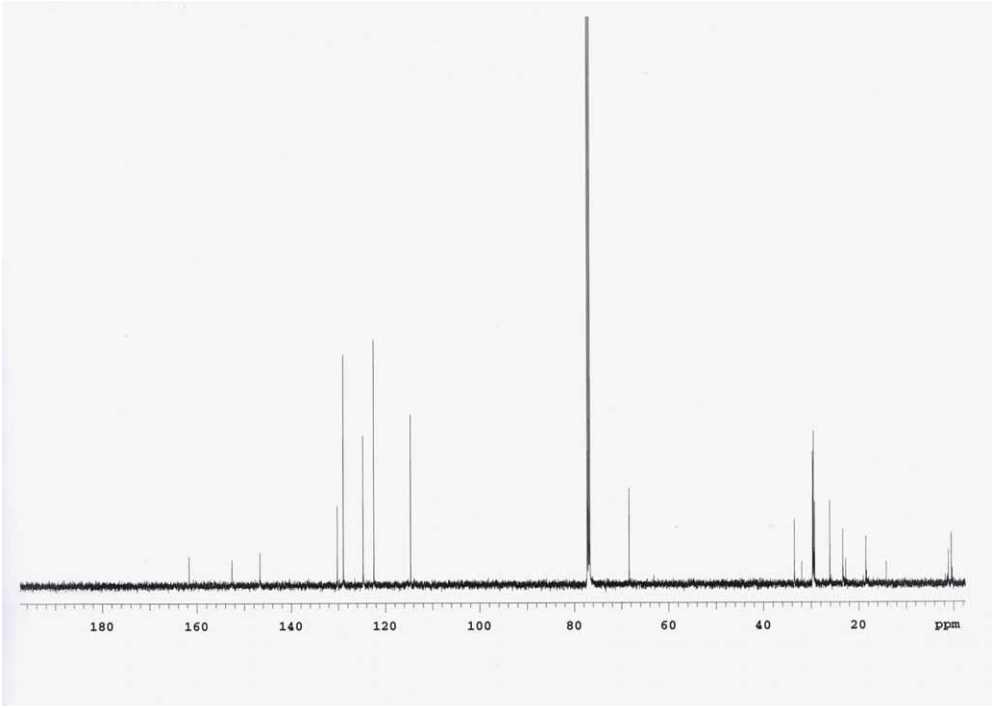

$^{13}$C-NMR (DMSO, 126MHz) 115.75 (2C, $C_{phenyl}$H), 121.89 (2C, $C_{phenyl}$H), 124.62 (2C, $C_{phenyl}$H), 129.11 (2C, $C_{phenyl}$H), 129.16 (Ph-*C*H), 130.18 (1C, terminal $C_{phenyl}$H), 145.05 (1C, $C_{phenyl}$N=N), 151.91 (1C, $C_{phenyl}$N=N), 160.72 (1C, $C_{phenyl}OCH_2$),

## PAPU




$^{13}$C NMR (126 MHz, DMSO) δ [ppm] 25.35 (1C, $CH_2$=CH$(CH_2)_4CH_2$), 28.18-28.94 six signals (6C, *C*$H_2$), 33.05 (1C, $CH_2$=CH*C*$H_2$), 39.5-39.83 (DMSO), 67.88 (1C, $C_{phenyl}OCH_2CH_2$), 114.37 (1C, *C*$H_2$=CHCH$_2$), 114.83 (2C, $C_{phenyl}$H), 121.98 (2C, $C_{phenyl}$H), 124.33 (2C, $C_{phenyl}$H), 129.11 (2C, $C_{phenyl}$H), 130.50 (1C, terminal $C_{phenyl}$H), 138.57 (1C, $CH_2$=*C*HCH$_2$), 145.82 (1C, $C_{phenyl}$N=N), 151.80 (1C, $C_{phenyl}$N=N), 161.24 (1C, $C_{phenyl}OCH_2$)

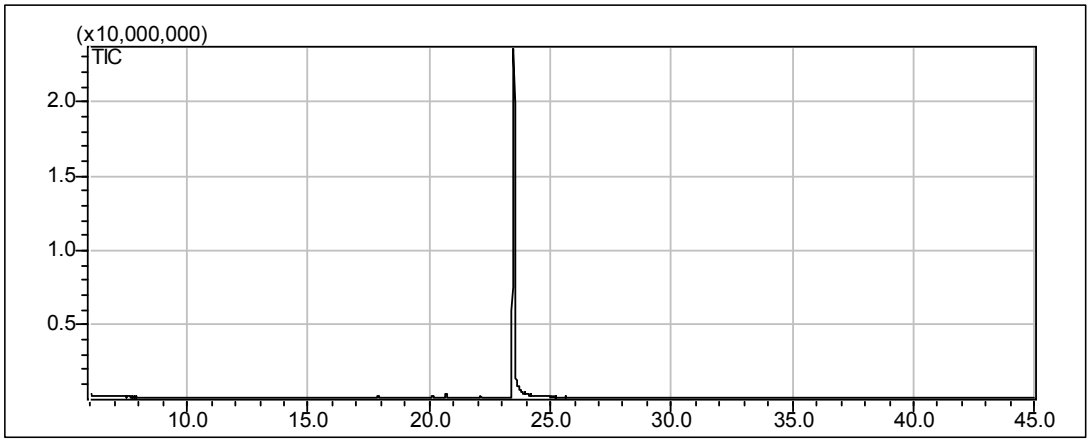
**PAS**

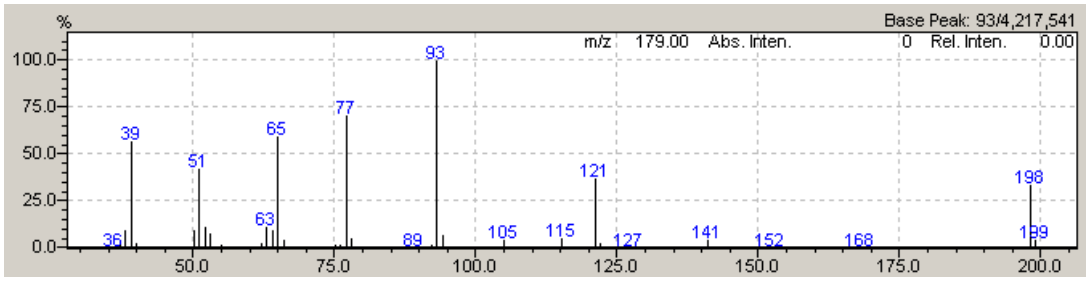



$^{13}$C NMR (126 MHz, $CDCl_3$) δ [ppm] 0.33 (silyl residues), 0.51 (2C, Si*C*$H_3$), 18.51 (1C, Si*C*$H_2$), 22.76-33.51 eight signals (9C, *C*$H_2$), 68.41 (1C, $C_{phenyl}OCH_2CH_2$), 77.00 ($CHCl_3$), 114.65 (2C, $C_{phenyl}H$), 122.46 (2C, $C_{phenyl}H$), 124.74 (2C ,$C_{phenyl}H$), 128.93 (2C, $C_{phenyl}H$), 130.21 (1C, terminal $C_{phenyl}H$), 146.68 (1C, $C_{phenyl}N{=}N$), 152.59 (1C, $C_{phenyl}N{=}N$), 161.66 (1C, $C_{phenyl}OCH_2$)

# GC-MS

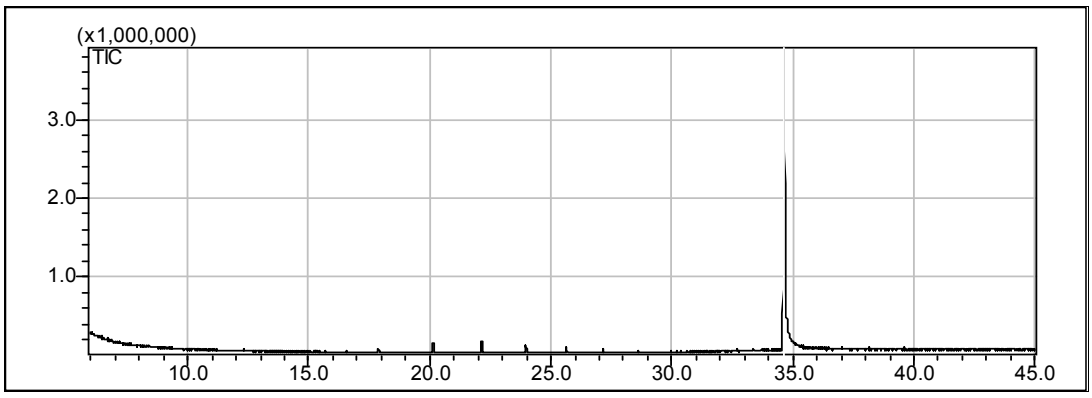
## PAP

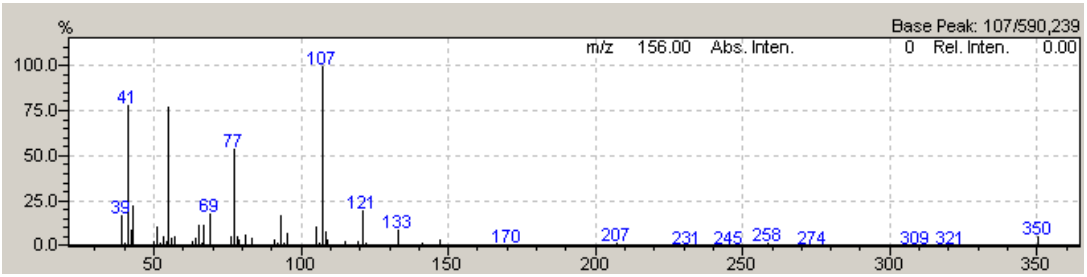



MS (70 eV): m/z (%): 198 (30) $[M–H]^+$, 121 (30) $[C_9H_{12}]^+$, 93 (100) $[CHN]^+$, 77 (56) $[C_6H_6]^+$, 41 (80) $[C_3H_5]^+$, 65 (60) $[CH_5H_5]^+$, 51(45) $[C_4H_3]^+$, 39 (60) $[C_3H_3]^+$

## PAPU

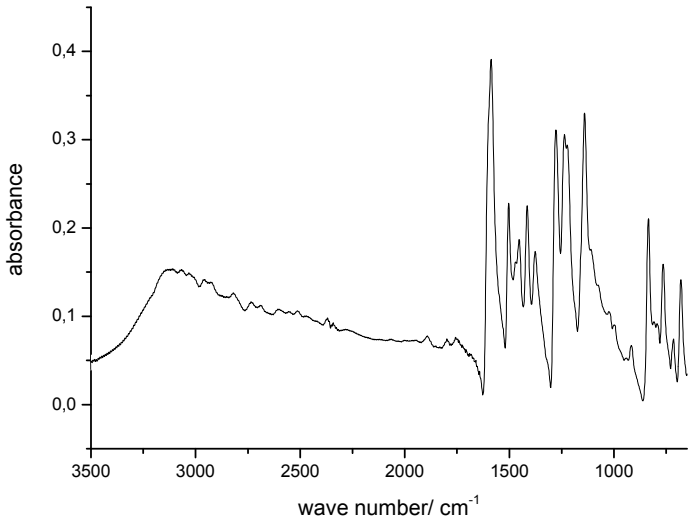





MS (70 eV): *m/z* (%): 350 (8) $[M–H]^+$, 121 (20) $[C_9H_{12}]^+$, 107 (100) $[C_6H_7N_2]^+$, 77 (56) $[C_6H_6]^+$, 41 (80) $[C_3H_5]^+$, 39 (16) $[C_3H_3]^+$

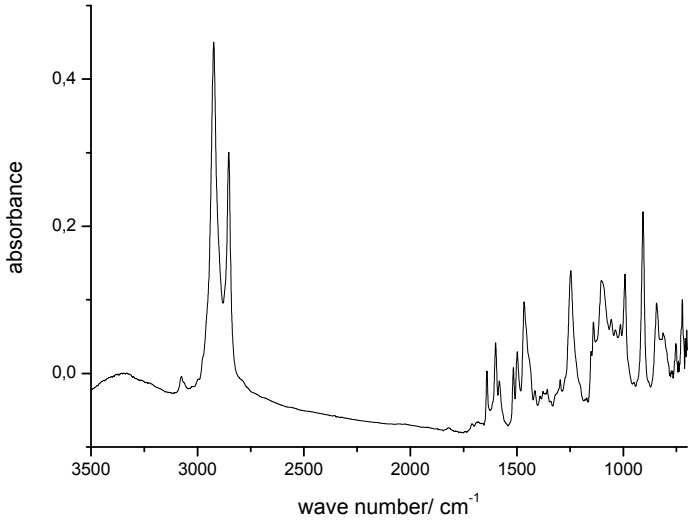
# IR

## PAP



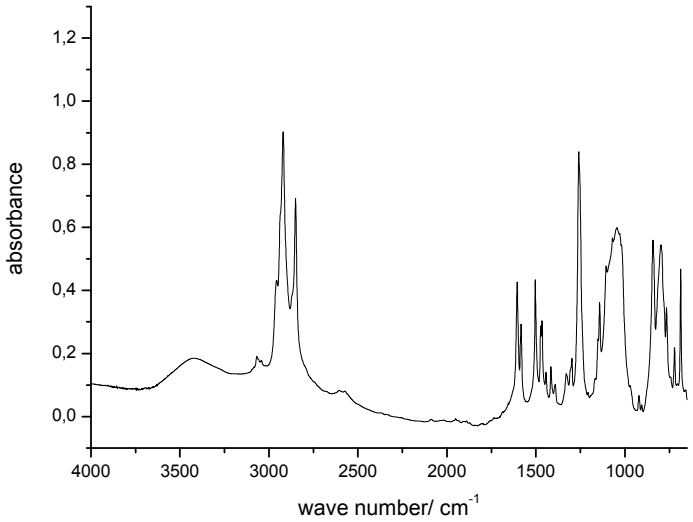

IR (KBr) [$cm^{-1}$]: 800-840 m, 1,4-disubstituted aromatic compound; 1143 s, ν(C-OH); 1415 m, δ($CH_2$), 1506-1585 m, ν(C=C), aromatic compound; 3069 w, ν(O-H), aromatic compound

**PAPU**




IR (KBr) [$cm^{-1}$]: 800-840 m, 1,4-disubstituted aromatic compound; 1250 s, ν(C-O) alkylaryl ether; 1460 m, δ($CH_2$), 1520-1680 m, ν(C=C), aromatic compound; 2851 s, $\nu_s(CH_2)$; 2926 s, $\nu_{as}(CH_2)$; 3069 w, ν(C-H), aromatic compound, and ν(C-H), double bond

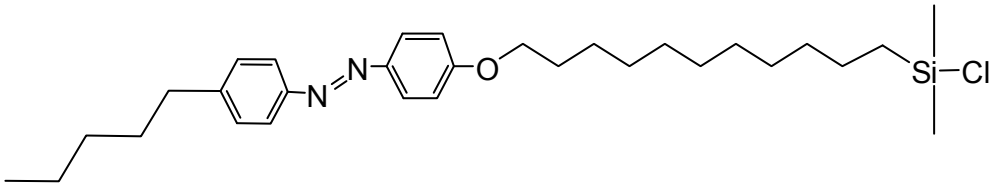
**PAS**




IR (KBr) [$cm^{-1}$]: 800-840 m, 1,4-disubstituted aromatic compound; 1100 s, ν(Si-O, due to hydrolysis of Si-Cl during KBr preparation); 1250 s, ν(C-O) alkylarylether; 1460 m, δ($CH_2$), 1520-1680 m, ν(C=C), aromatic compound; 2851 s, $\nu_s(CH_2)$; 2926 s, $\nu_{as}(CH_2)$; 2963 w, ν($CH_3$); 3069 w, ν(C-H), aromatic compound

## B.

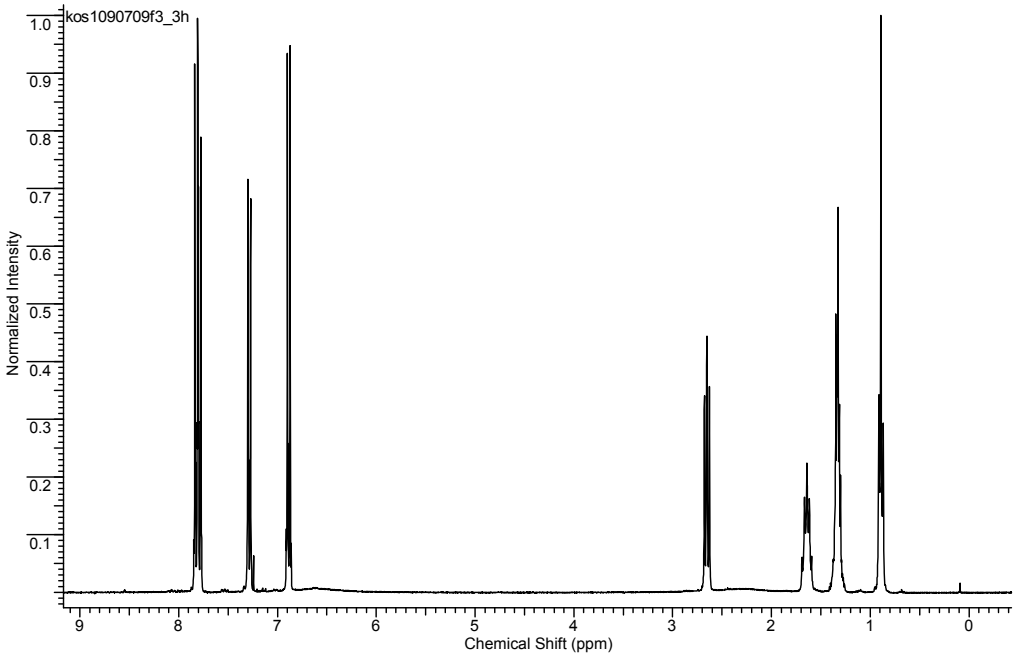
### 4-(4´-Pentyl)phenylazo-(4´-(11-dimethylchlorosilanyl-)undecyloxy)benzene




PPAP: 4-(4´-Pentyl)phenylazophenol
PPAPU: 11-(4-(4´-Pentyl)phenylazo-phenoxy)-undecene
PPAS: 4-(4´-Pentyl)phenylazo-(4´-(11-dimethylchlorosilanyl-)undecyloxy)benzene

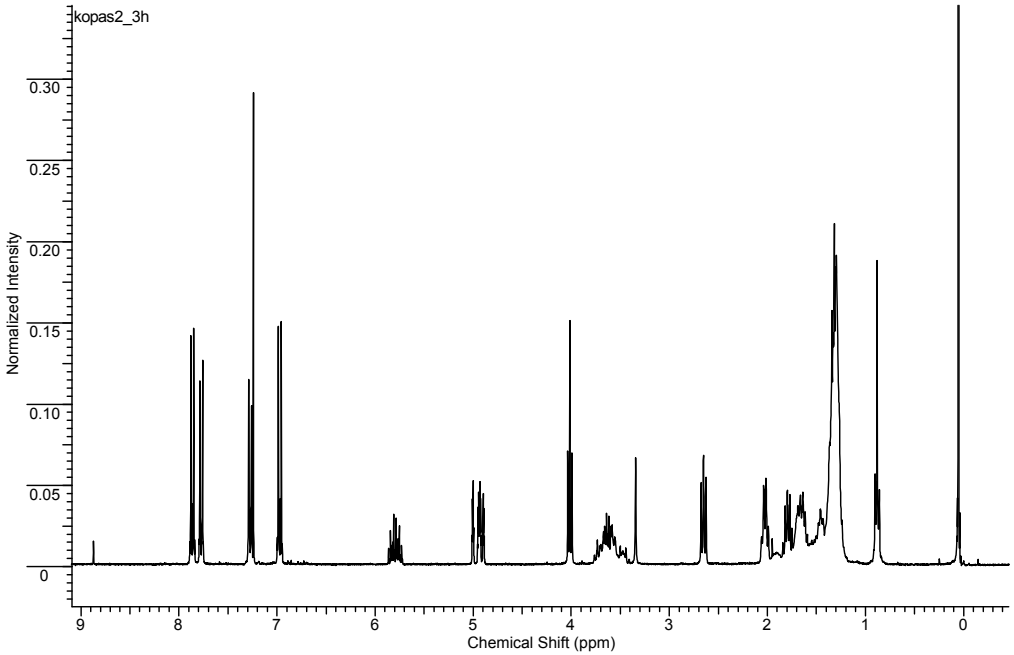
## $^1$H-NMR

### PPAP



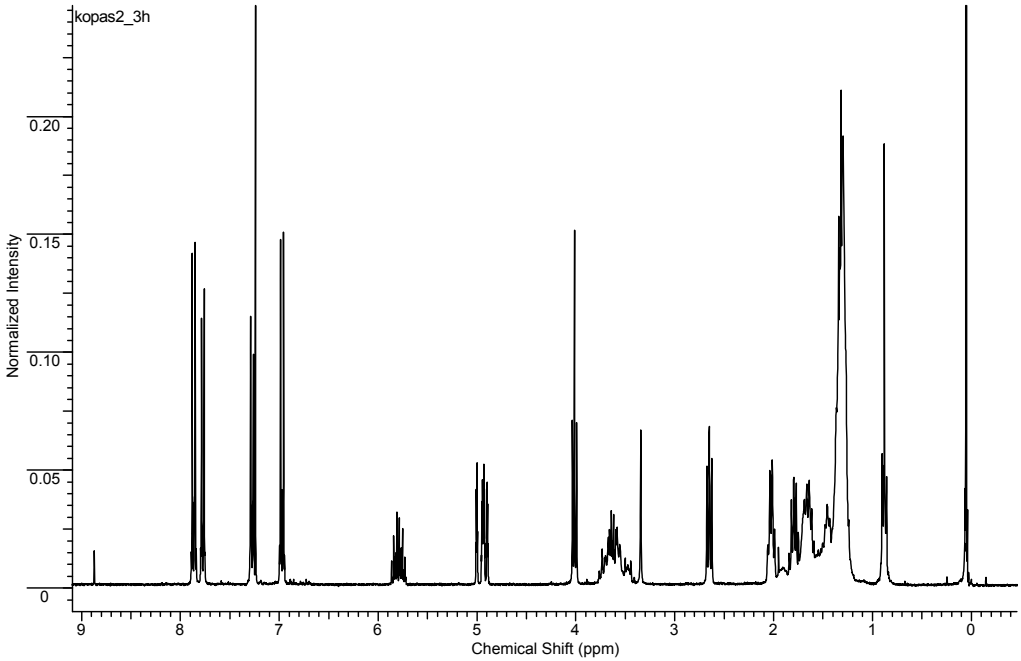

$^1$H NMR (300MHz, DMSO); δ[ppm]: 0.88 (t, 3H, C*H*$_3$CH$_2$CH$_2$), 1.35 (m, 4H, CH$_3$C*H*$_2$*CH*$_2$), 1.63 (t, 2H, PH-C*H*$_2$), 7.1 (d, 2H, Ph-H), 7.5 (m, 3H, Ph-H), 7.8 (2×d, 4H, Ph-H)

**PPAPU**




$^1$H-NMR ($CDCl_3$, 300MHz) 0.88 (3H, t, *$CH_3$*-$CH_2$-), 1.35 (16H, s, $CH_3$-*$CH_2$*-*$CH_2$*-), 1.6 (2H, t, Ph-$CH_2$-*$CH_2$*-), 1.7 (2H, m, O-$CH_2$-*$CH_2$*-), 2.0 (2H, m, *$CH_2$* -CH- $CH_2$) 2.6 (2H, t, Ph-C*$H_2$*-), 3.9 (2H, t, Ph-O-*$CH_2$*-), 4.9 (2H, t, $CH_2$-CH-*$CH_2$*), 5.8 (1H, m, $CH_2$-*CH*-$CH_2$-), 6.9 (2H, d, Ph-H), 7.3 (2H, d, Ph-H), 7.8 (2H, d, Ph-H), 7.9 (2H, d, Ph-H)

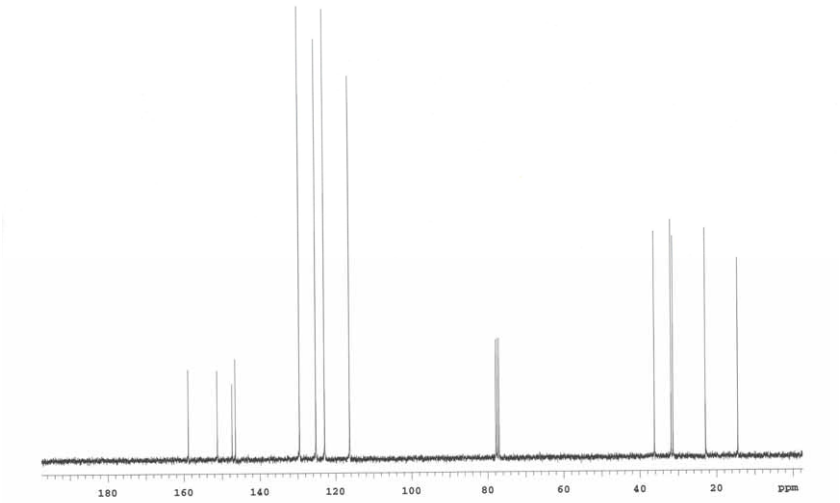
**PPAS**




$^1$H NMR (300MHz, DMSO); δ [ppm]: 0 (silyl residues), 0.5 (s, 6H, $ClSi(CH_3)_2CH_2$), 0.8 (t, 2H, $ClSi(CH_3)_2CH_2CH_2$), 1.1–1.5 (m, 16H, $ClSi(CH_3)_2CH_2(CH_2)_8CH_2CH_2O$), 1.7 (m, 2H, $CH_2CH_2CH_2O$), 2.5 (DMSO), 3.3 (dicyclohexano-18-crown-6), 4.1 (t, 2H, $CH_2CH_2O$), 7.1 (d, 2H, Ph-H), 7.5 (m, 3H, Ph-H), 7.8 (2×d, 4H, Ph-H)

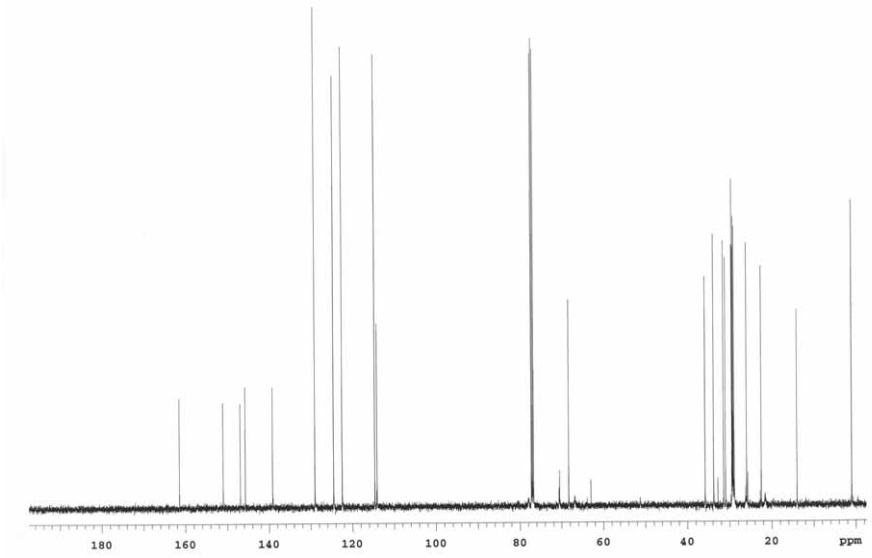
# $^{13}$C-NMR

## PPAP



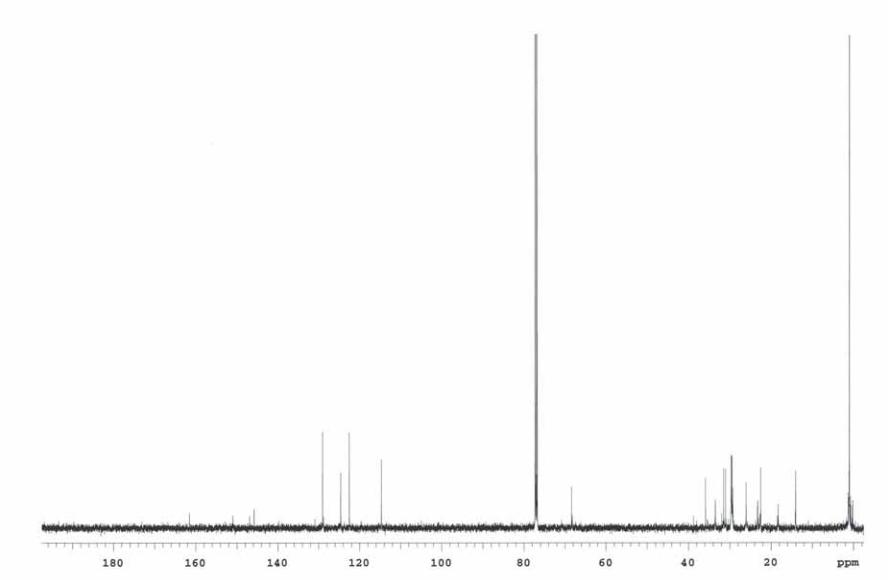

$^{13}$C-NMR ($CDCl_3$, 126 MHz) δ [ppm] 13.98 (1C, $CH_3CH_2$), 22.48 (1C, $CH_3CH_2CH_2$), 25.97 (1C, $CH_2$=CH$(CH_2)_4CH_2$) 28.88-29.46 six signals (6C, $CH_2$), 30.96 (1C, $CH_3CH_2CH_2$), 31.43 (1C, $C_{phenyl}CH_2CH_2$), 33.76 (1C, $CH_2$=$CHCH_2$), 35.78 (1C, $C_{phenyl}CH_2CH_2$), 68.30 (1C, $C_{phenyl}OCH_2CH_2$), 77.00 ($CHCl_3$), 114.63 (1C, $CH_2$=$CHCH_2$), 114.56 (2C, $C_{phenyl}H$), 122.47 (2C, $C_{phenyl}H$), 124.51 (2C, $C_{phenyl}H$), 128.98 (2C, $C_{phenyl}H$), 139.16 (1C, $CH_2$=$CHCH_2$), 145.72 1C, $C_{phenyl}CH_2$), 146.90 (1C, $C_{phenyl}N$=N), 151.01 (1C, $C_{phenyl}N$=N), 161.43 (1C, $C_{phenyl}OCH_2$)

## PPAPU




$^{13}$C NMR (126MHz, DMSO) δ[ppm] 13.87 (1C, $CH_3CH_2$), 22.48– 35.6 eleven signals (11C, $CH_2$), 68.01 (Ph-O-$CH_2$), 79 ($CDCl_3$); 114.29 ($CH_2$-CH), 115.5 (Ph-C), 122.22 (Ph-CH), 124.22 (Ph-CH), 128.61 (Ph-CH), 138.69 ($CH_2$-CH), 146.51 (1C, $C_{phenyl}N$=N), 145.29 (1C, $C_{phenyl}CH_2$), 150.63 (1C, $C_{phenyl}N$=N), 161.08 (1C, $C_{phenyl}OCH_2$)

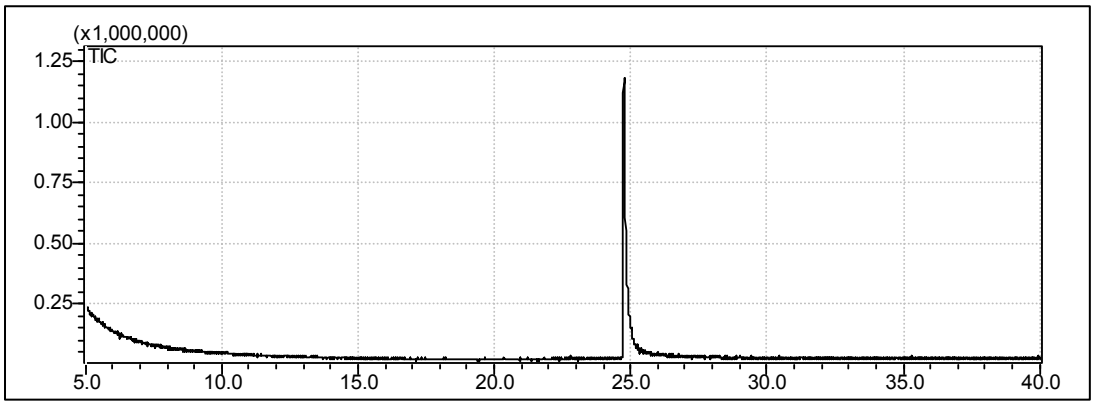
**PPAS**

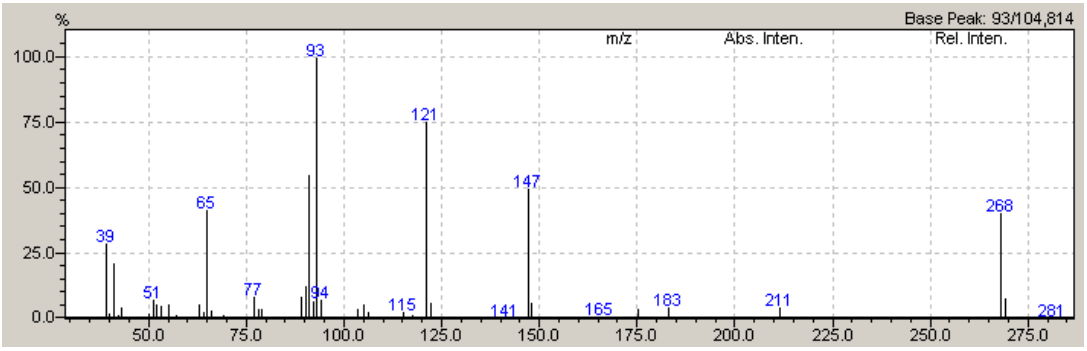



$^{13}$C-NMR ($CDCl_3$, 126 MHz) δ [ppm] 0.21 (silyl residues), 0.71-1.01 (2C, Si*C*$H_3$), 14.01 (1C, *C*$H_3CH_2$), 18.27 (1C, Si*C*$H_2$), 22.52 (1C, $CH_3$*C*$H_2CH_2$), 23.23-31.45 eleven signals (11C, *C*$H_2$), 35.82 (1C, $C_{phenyl}$*C*$H_2CH_2$), 68.37 (1C, $C_{phenyl}$O*C*$H_2CH_2$), 76.75-77.25 ($CHCl_3$), 114.68 (2C, *C*$_{phenyl}$H), 122.50 (2C, *C*$_{phenyl}$H), 124.60 (2C, *C*$_{phenyl}$H), 129.03 (2C, *C*$_{phenyl}$H), 145.79 (1C, *C*$_{phenyl}$$CH_2$), 146.88 (1C, *C*$_{phenyl}$N=N), 150.97 (1C, *C*$_{phenyl}$N=N), 161.53 (1C, *C*$_{phenyl}$$OCH_2$)

# GC-MS

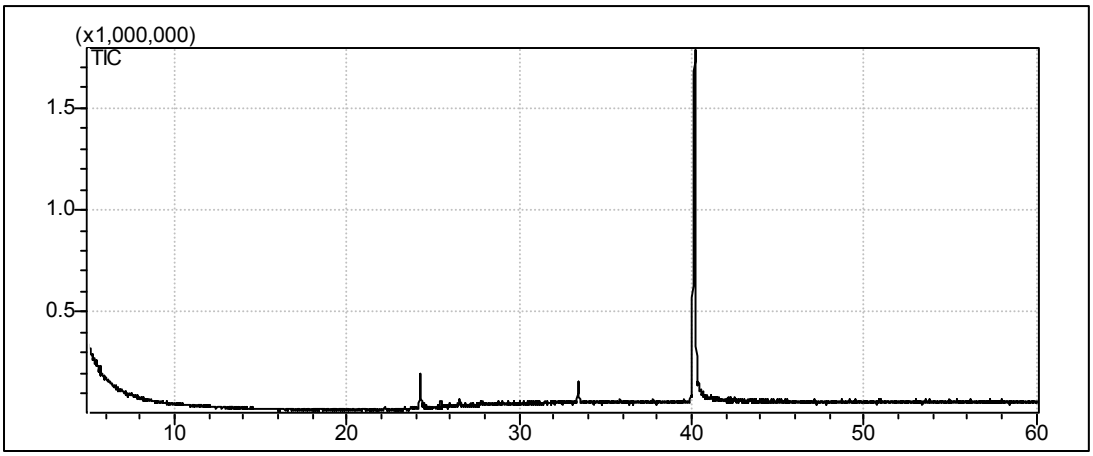
**PPAP**

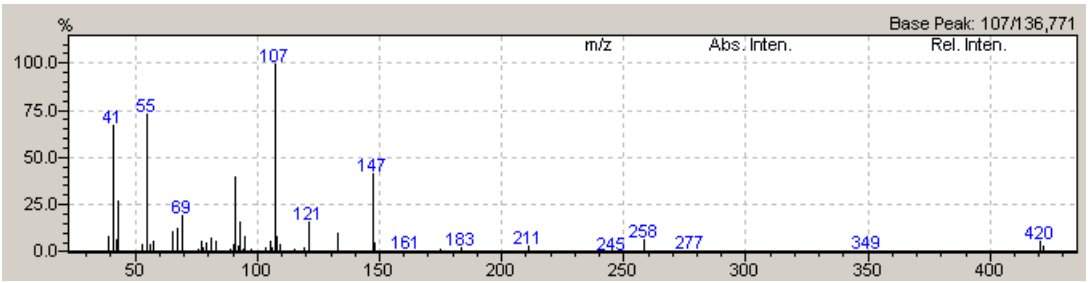





MS (70 eV): *m/z* (%): 268 (35) $[M–H]^+$, 147 (50) $[C_{11}H_{15}N_2]^+$, 121 (75) $[C_9H_{12}]^+$, 93 (100) $[C_8H_{10}]^+$, 65 (40) $[C_5H_5]^+$, 39 (30) $[C_3H_3]^+$

**PPAPU**

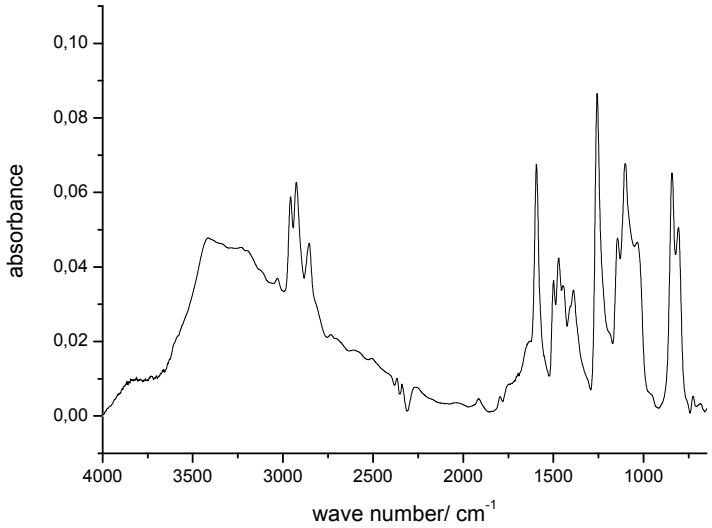



MS (70 eV): *m/z* (%): 420 (8) $[M–H]^+$, 147 (45) $[C_{10}H_{13}N]^+$, 121 (20) $[C_9H_{12}]^+$, 107 (100) $[C_6H_7N_2]^+$, 55 (75) $[C_3H_3O]^+$, 41 (70) $[C_3H_5]^+$

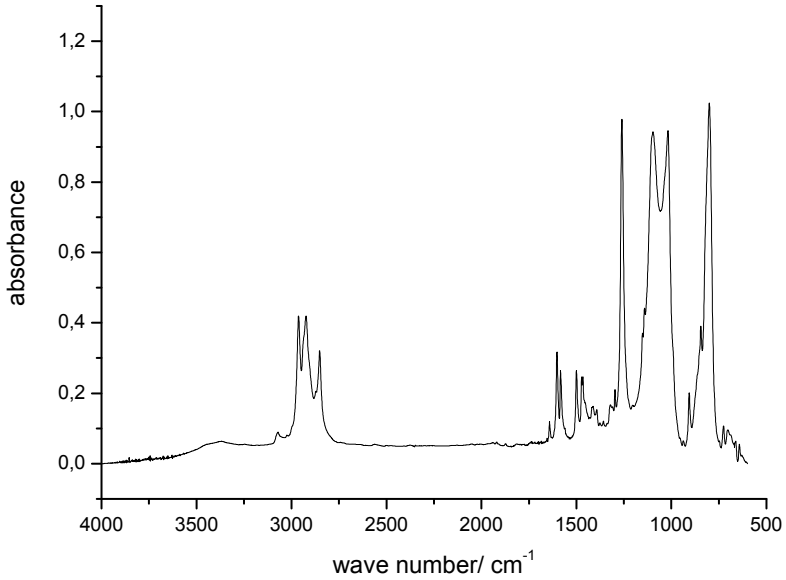
# IR

## PPAP



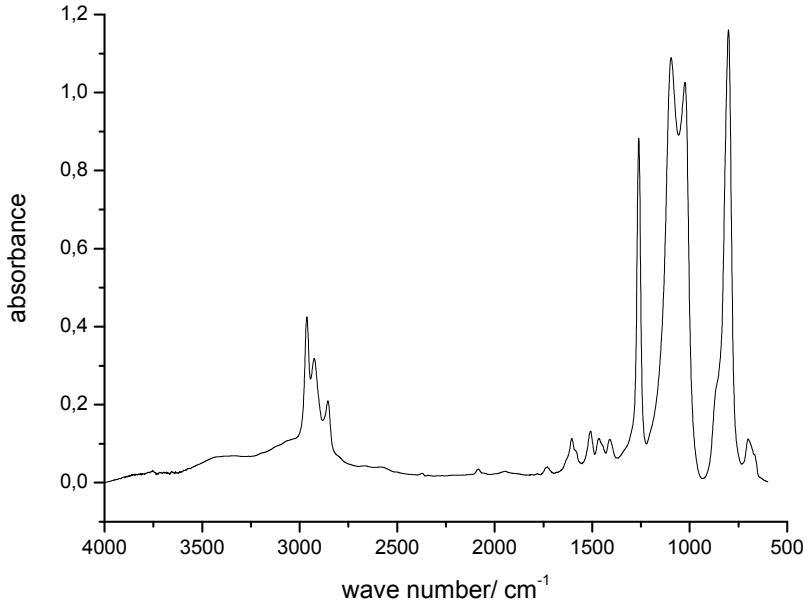

IR (KBr) [$cm^{-1}$]: 839 m, 1,4-disubstituted aromatic compound; 1238 s, ν(C-O) alkylaryl ether; 1389-1498 m, ν(C=C), aromatic compound; 2862 s, $\nu_s(CH_2)$; 2938 s, $\nu_{as}(CH_2)$; 2957 s, $\nu_s(CH_3)$; 3069 w, ν(C-H), aromatic compound, 3250 w, $\nu_s$ (O-H)

## PPAPU




IR (KBr) [$cm^{-1}$]: 800-840 m, 1,4-disubstituted aromatic compound; 1021 1103 s, ν(C-O-C) sometimes splitted, alkylaryl ether; 1250 s, ν(C-O) alkylaryl ether; 1460 m, $\delta(CH_2)$, 1520-1680 m, ν(C=C), aromatic compound; 2851 s, $\nu_s(CH_2)$; 2926 s, $\nu_{as}(CH_2)$; 2963 s, $\nu(CH_3)$; 3069 w, ν(C-H), aromatic compound, and ν(C-H), double bond

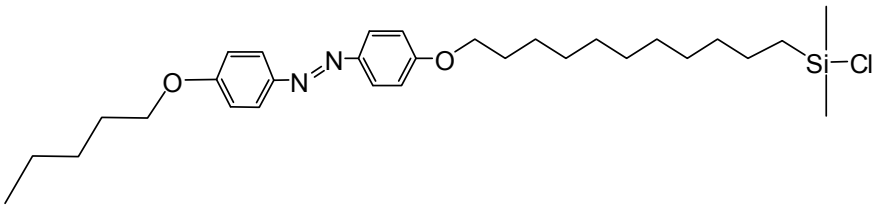
**PPAS**




IR (KBr) [$cm^{-1}$]: 802 m, 1,4-disubstituted aromatic compound; 1096 s, ν(Si-O, due to hydrolysis of Si-Cl during KBr preparation); 1024 s, ν(C-O-C); 1261s, ν(C-O) alkylaryl ether; 1466 m, δ($CH_2$), 1520-1608 m, ν(C=C), aromatic compound; 2855 s, $\nu_s(CH_2)$; 2925 s, $\nu_{as}(CH_2)$; 2963 s, ν($CH_3$); 3069 w, ν(C-H), aromatic compound

# C.

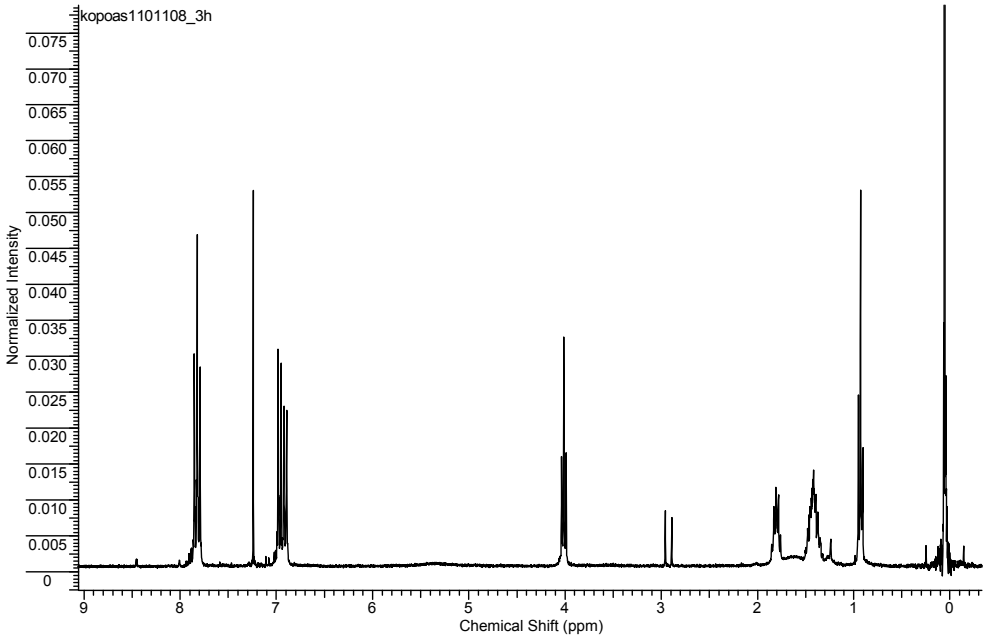
## 4-(4´-Pentyloxy)phenylazo-(4´-(11-dimethylchlorosilanyl-)undecyloxy)benzene




POPAP: 4-(4´-Pentyloxy)phenylazophenol
POPAPU: 11-(4-(4´-Pentyl)phenylazo-phenoxy)undecene
POPAS 4-(4´-Pentyloxy)phenylazo-(4´-(11-dimethylchlorosilanyl)undecyloxy)benzene

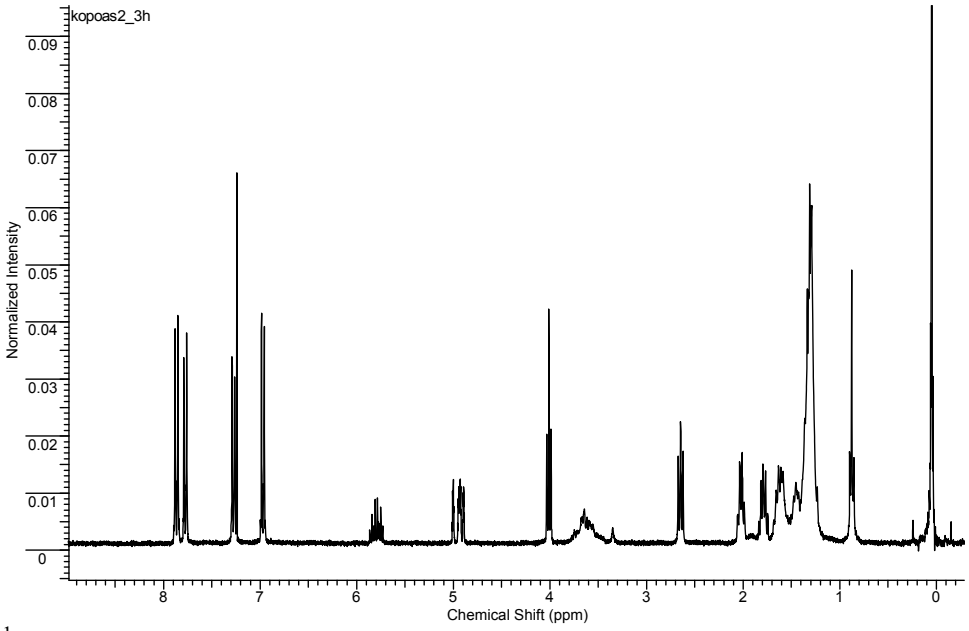
## $^1$H-NMR

### POPAP



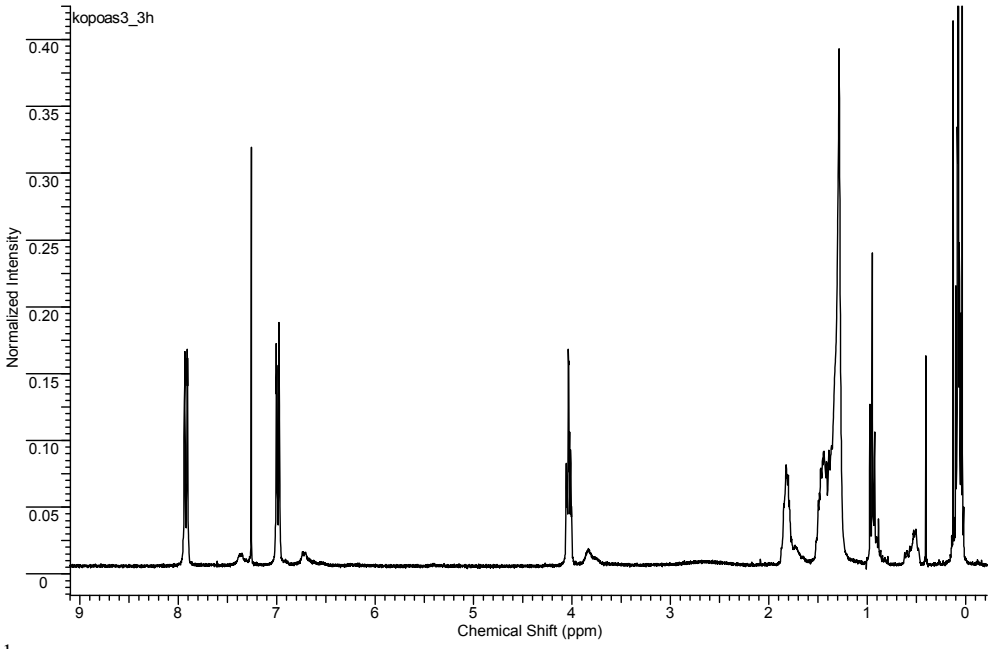

$^1$H-NMR ($CDCl_3$, 300MHz) 0.88 (3H, t, C*H*$_3$-$CH_2$-), 1.35 (4H, m, $CH_3$-C*H*$_2$-C*H*$_2$-), 1.8 (2H, t, Ph-$CH_2$-C*H*$_2$-), 4.0 (4H, t, O-C*H*$_2$), 6.9 (4H, dd, Ph-*H*), 7.81 (4H, dd, Ph-*H*)

**POPAPU**




$^1$H-NMR ($CDCl_3$, 300MHz) 0.92 (3H, t, C*H*$_3$-$CH_2$-), 1.33 (16H, s, $CH_3$-C*H*$_2$-C*H*$_2$-), 1.6 (2H, t, Ph-$CH_2$-C*H*$_2$-), 1.7 (2H,m, $CH_2$-C*H*$_2$-$CH_2$-), 2.0 (2H, m, O-$CH_2$-C*H*$_2$-), 2.6 (2H, t, Ph-C*H*$_2$-$CH_2$-), 4.0 (2H, t, Ph-O-C*H*$_2$-), 5.0 (2H, t, $CH_2$-CH=C*H*$_2$), 5.8 (1H, m, $CH_2$=C*H*-$CH_2$-), 6,9 (4H, d, Ph-*H*), 7.8 (4H, d, Ph-*H*)

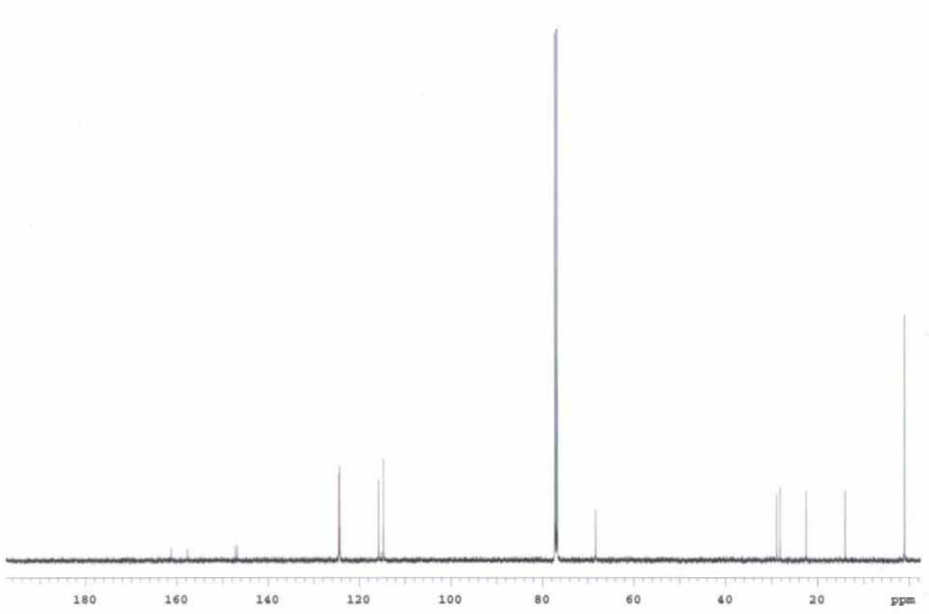
**POPAS**




$^1$H NMR (300 MHz, $CDCl_3$); δ [ppm]: 0.05 (silyl residues), 0.50 (s, 6H, ClSi(C*H*$_3$)$_2$$CH_2$), 0.95 (t, 2H, Si($CH_3$)$_2$C*H*$_2$$CH_2$) and (t, 3H, C*H*$_3$$CH_2$), 1.29 (m, 16H, ClSi($CH_3$)$_2$$CH_2$(C*H*$_2$)$_8$$CH_2$$CH_2$O and 4H, $CH_3$C*H*$_2$C*H*$_2$$CH_2$), 1.82 (m, 4H, $CH_2$C*H*$_2$$CH_2$O), 4.04 (t, 4H, $CH_2$C*H*$_2$O), 6.98 (d, 4H, Ph-H), 7.26 ($CHCl_3$), 7.93 (d, 4H, Ph-H)

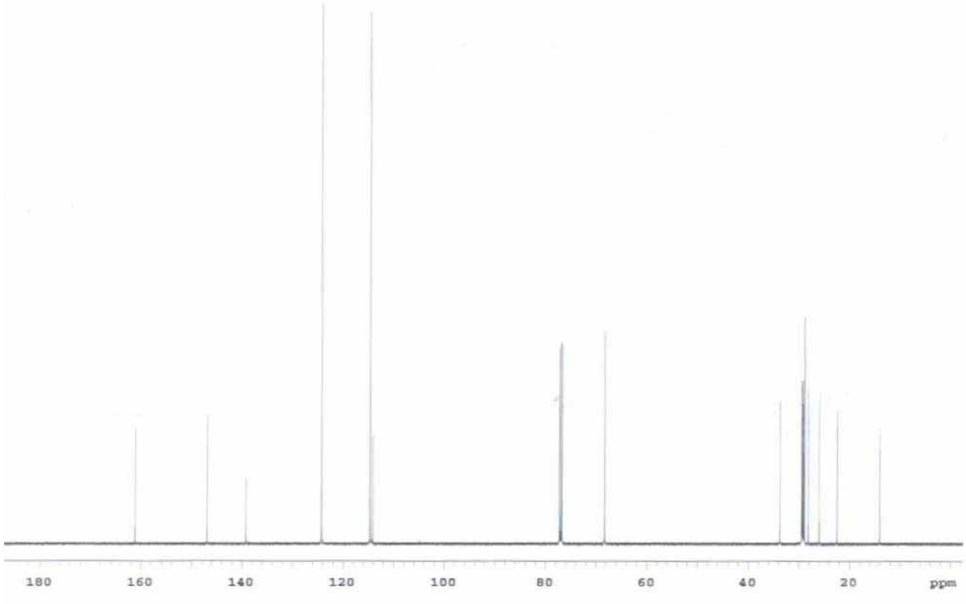
# $^{13}$C-NMR

## POPAP



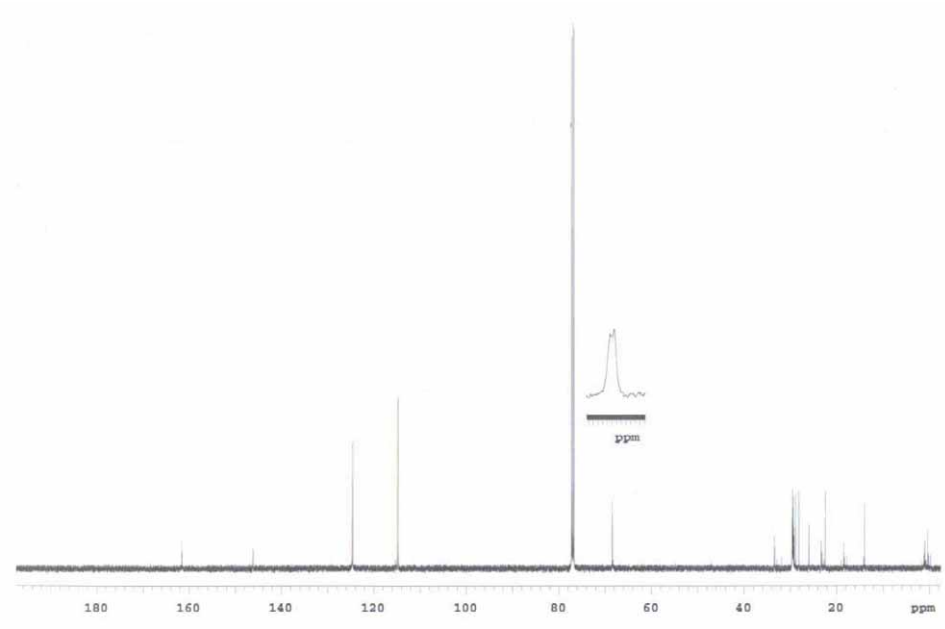

$^{13}$C-NMR ($CDCl_3$, 126 MHz) δ [ppm] 14.10 (1C, $CH_3CH_2$), 22.52 (1C, $CH_3CH_2CH_2$), 77.42 ($CHCl_3$), 115.68 (4C, $C_{phenyl}H$), 124.45 (4C, $C_{phenyl}H$), 146.71 (2C, $C_{phenyl}CH_2$), 157.51 (4C, $C_{phenyl}N{=}N$), 161.15 (1C, $C_{phenyl}OH$)

## POPAPU




$^{13}$C-NMR ($CDCl_3$, 126 MHz) δ [ppm] 14.00 (1C, $CH_3CH_2$), 22.44 (1C, $CH_3CH_2CH_2$), 26.00 (1C, $CH_2{=}CH(CH_2)_4CH_2$) 28.91-29.20 six signals (6C, $CH_2$), 33.79 (1C, $CH_3CH_2CH_2$), 33.79 (1C, $CH_2{=}CHCH_2$), 68.29 (1C, $C_{phenyl}OCH_2CH_2$), 77.00 ($CHCl_3$), 114.12 (1C, $CH_2{=}CHCH_2$), 114.64 (2C, $C_{phenyl}H$), 124.27 (4C, $C_{phenyl}H$), 139.18 (1C, $CH_2{=}CHCH_2$), 146.93 (2C, $C_{phenyl}N{=}N$), 161.15 (2C, $C_{phenyl}OCH_2$)

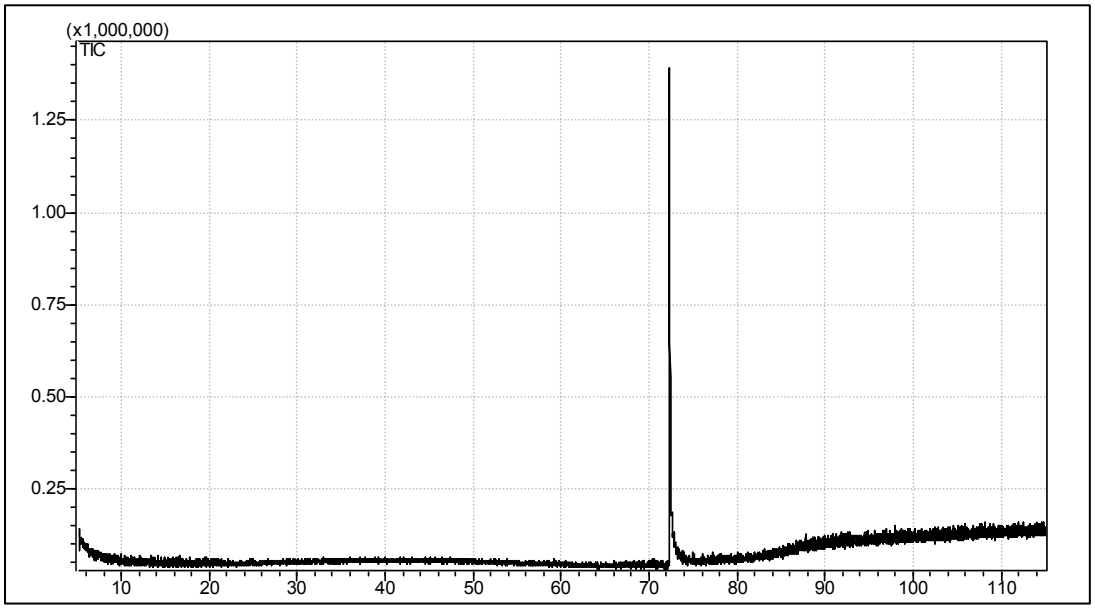
**POPAS**

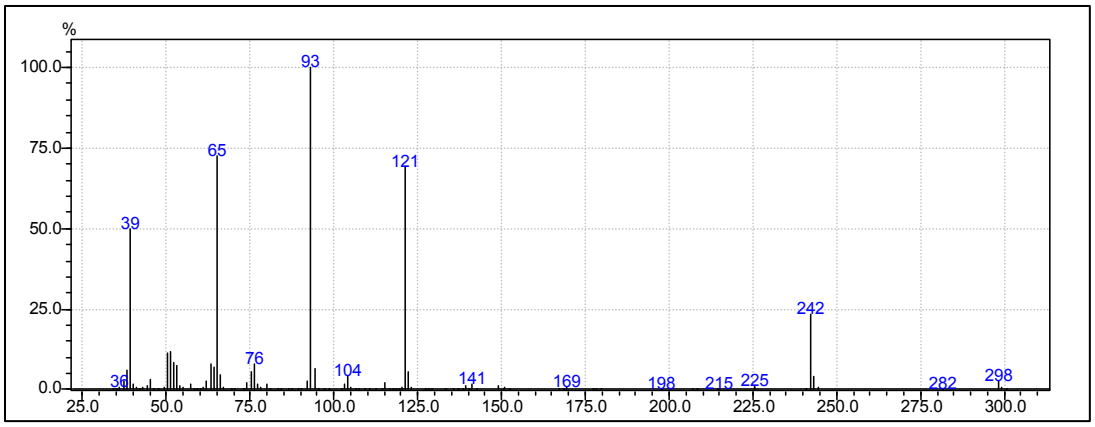



$^{13}$C-NMR ($CDCl_3$, 126 MHz) δ [ppm] 0.20-0.39 (silyl residues), 0.73-1.66 (2C, Si*C*$H_3$), 14.00 (1C, *C*$H_3$C$H_2$), 18.42 (1C, Si*C*$H_2$), 22.44 (1C, $CH_3$*C*$H_2$C$H_2$), 23.29-33.43 eleven signals (11C, *C*$H_2$), 68.39 (1C, $C_{phenyl}$O*C*$H_2$C$H_2$), 76.75-77.25 ($CHCl_3$), 114,78 (4C, *C*$_{phenyl}$H), 124.65 (4C, *C*$_{phenyl}$H), 146.17 (2C, *C*$_{phenyl}$N=N), 161.55 (2C, *C*$_{phenyl}$O$CH_2$)

# GC-MS

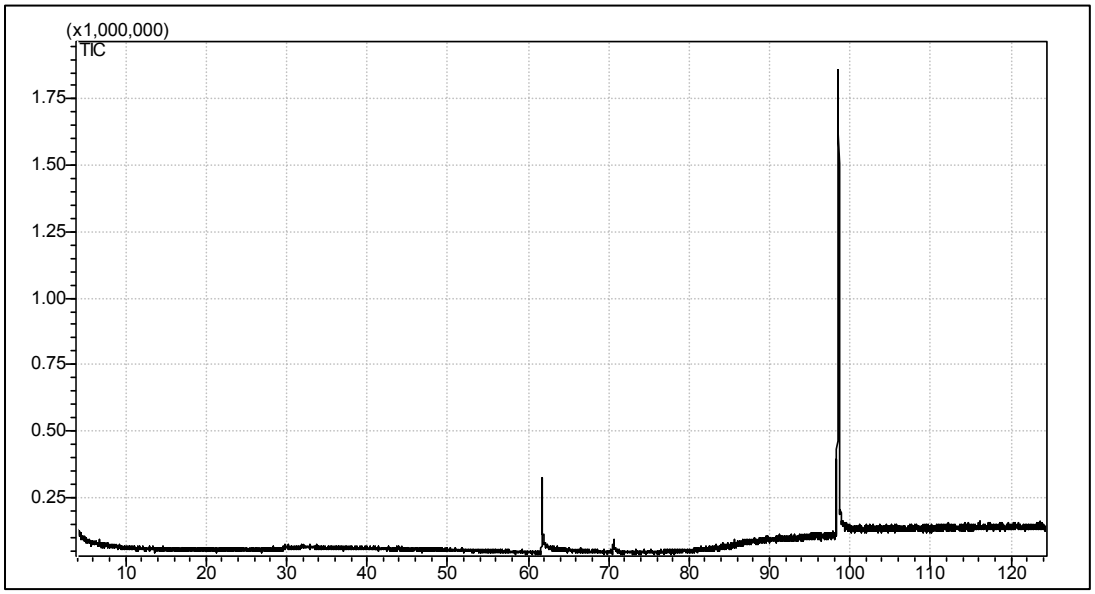
**POPAP**

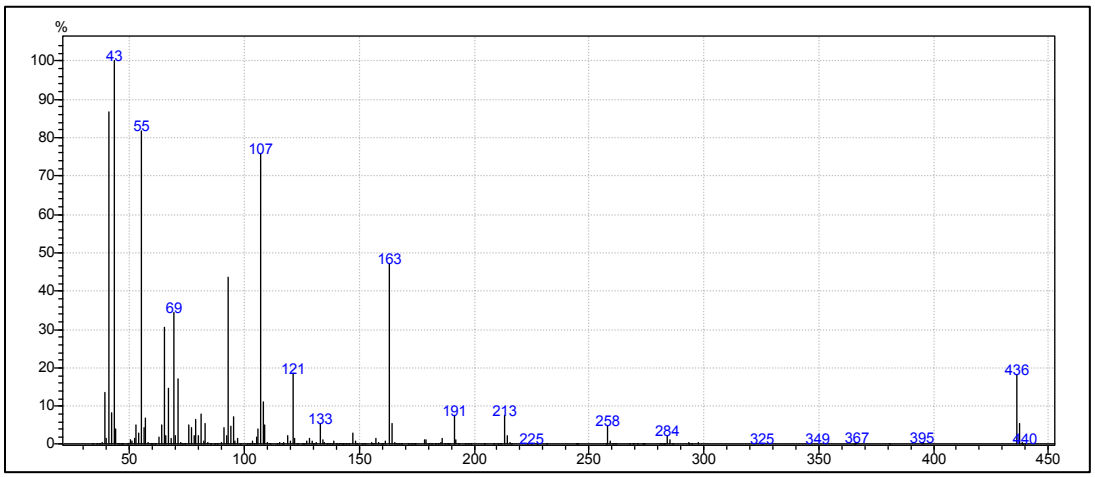





MS (70 eV): *m/z* (%): 298 (5) $[M–H]^+$, 242 (25) $[C_{15}H_{16}N_2O]^+$ 121 (70) $[C_9H_{12}]^+$, 93 (100) $[C_8H_{10}]^+$, 65 (75) $[C_5H_5]^+$, 39 (50) $[C_3H_3]^+$

**POPAPU**

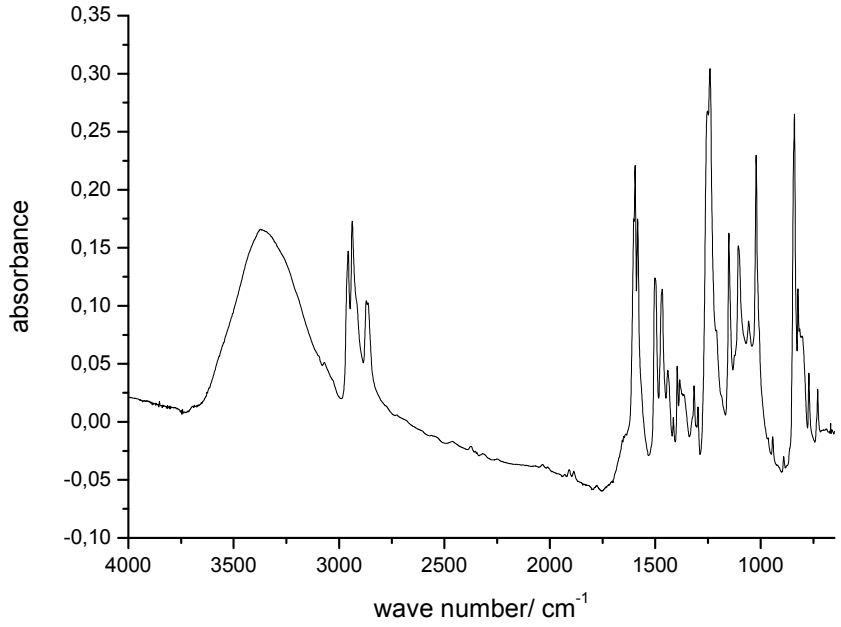



MS (70 eV): *m/z* (%): 436 (18) $[M–H]^+$, 163 (48) $[C_{11}H_{14}O]^+$, 121 (18) $[C_9H_{12}]^+$, 107 (76) $[C_6H_7N_2]^+$, 69 (36) $[C_4H_5O]^+$, 55 (84) $[C_3H_3O]^+$, 43 (100) $[C_3H_5]^+$

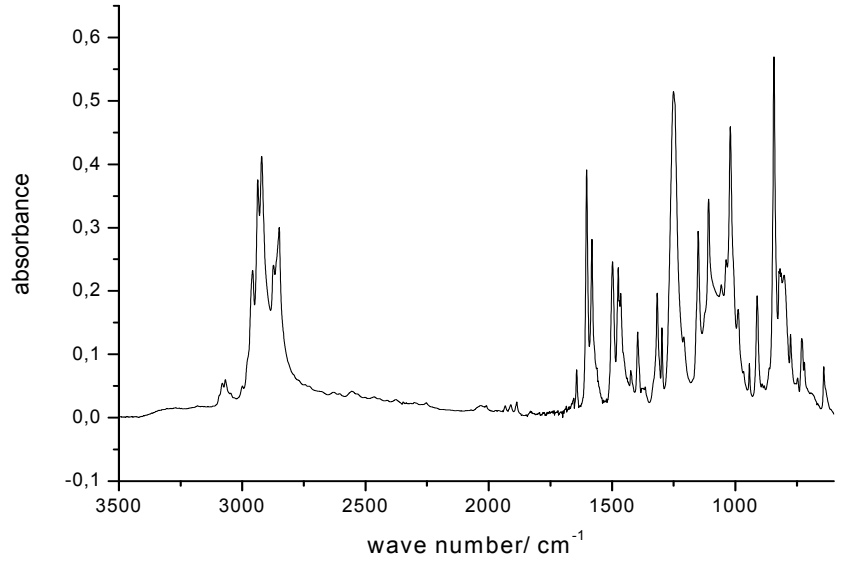
# IR

## POPAP




IR (KBr) [$cm^{-1}$]: 839 m, 1,4-disubstituted aromatic compound; 1238 s, ν(C-O) alkylaryl ether; 1389-1498 m, ν(C=C), aromatic compound; 2862 s, $\nu_s(CH_2)$; 2938 s, $\nu_{as}(CH_2)$; 2957 s, $\nu_s(CH_3)$; 3069 w, ν(C-H), aromatic compound, 3250 w, $\nu_s$ (O-H)

## POPAPU




IR (KBr) [$cm^{-1}$]: 841 m, 1,4-disubstituted aromatic compound; 1046 s, ν(C-O-C) sometimes splitted, alkylaryl ether; 1246 s, ν(C-O) alkylaryl ether; 1466 m, $\delta(CH_2)$, 1520-1642 m, ν(C=C), aromatic compound; 2852 s, $\nu_s(CH_2)$; 2924 s, $\nu_{as}(CH_2)$; 2963 s, $\nu(CH_3)$; 3069 s, ν(C-H), aromatic compound, and ν(C-H), double bond

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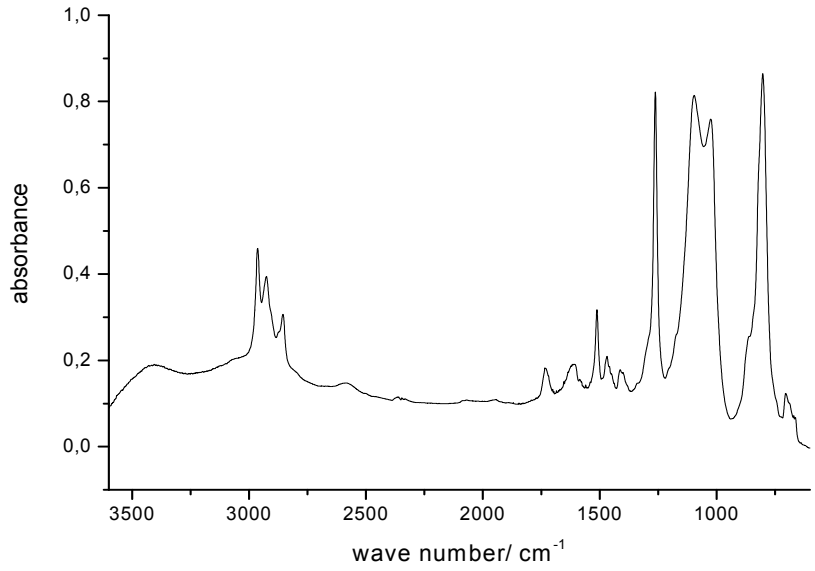


IR (KBr) [$cm^{-1}$]: 802 m, 1,4-disubstituted aromatic compound; 1095 s, ν(Si-O, due to hydrolysis of Si-Cl during KBr preparation); 1261s, ν(C-O) alkylaryl ether; 1466 m, δ($CH_2$), 1511-1729 m, ν(C=C), aromatic compound; 2854 s, $\nu_s(CH_2)$; 2925 s, $\nu_{as}(CH_2)$; 2963 s, ν($CH_3$); 3069 w, ν(C-H), aromatic compound