Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPLEMENTARY SECTION-1

First use of p-tert-butylcalix[4]arene-tetra-O-acetate as nanoreactor having tunable selectivity towards cross azo-compounds by trapping silver ion

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A. Experimental Section

1. General methods: ^{1}H and ^{13}C spectra were obtained on Bruker 300 MHz instrument at 300 MHz and 75 MHz respectively. DEPTQ-135 experiments were performed on Bruker 300 MHz instrument at 75 MHz. Chemical shifts are reported in parts per million (ppm) downfield from an internal TMS (tetramethylsilane) reference. Coupling constants (*J*) are reported in hertz (Hz), and spin multiplicities are represented by the symbols s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). IR spectra were recorded on a Perkin Elmer Spectrophotometer RX / FT- IR system. Band positions are reported in reciprocal centimeters (cm^{-1}). The CHN analyses were carried out on a 2400 Series II CHNS Analyzer, Perkin Elmer USA. Melting points were determined on an electrical melting point apparatus with an open capillary. The progress of the reaction was checked by TLC using 300-400 mesh silica gel. Column chromatography was performed using 60-120 mesh silica gel. All the available reagents were purchased from commercial sources and used without purification. All the solvents used during reactions were distilled for purity. Sizes of p-tert-butylcalix[8]arene particles in aqueous solution were determined by Beckman Coulter Delsa^{Tm} Nano C particle analyser instrument and the SEM images were taken by CARL ZEISS EVO18.

2. Synthesis of p-tert-butylcalix[4]arene:

p-tert-Butylcalix[4]arene was synthesized from the mixture of *p-tert*-butylphenol (2 g, 13.32 mmol), 37% formaldehyde solution (1.24 mL, 16.6 mmol of HCHO), and NaOH (240 mg, 0.6 mmol) according to our reported procedure [Ref].

3. Synthesis of p-tert-Butylcalix[4]arene-tetra-O-acetate:

p-tert-Butylcalix[4]arene (200mg, 0.3 mmol) was dissolved in 1 ml acetic anhydride and refluxed for 3 hours. After completion of the reaction the mixture was poured into crashed ice and the filtered followed by washing with cold water. Then the product was crystallized from $CHCl_3$. 235 mg, 95.92% was gained. mp. above 300 ºC; IR (KBr, υ cm^{-1}): 2972, 2863, 2368, 1676, 1498, 1356, 1206, 1107, 1044. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26-1.28 (m, 36H, -CH_3), 1.43 (s, 12H, -$COCH_3$), 3.67 (s, 8H, -CH_2), 7.06 (s, 36H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 31.6, 34.4, 38.3, 125.8, 132.4, 146.1, 147.5, 168.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{52}H_{64}O_8Na]$: 839.4493. Found 839.4490. Anal. calcd. for $C_{52}H_{64}O_8$; C: 76.44; H: 7.90. Found: C: 76.49; H: 7.92.

4. General procedure for the synthesis of cross azo-compounds (all entries of Scheme 3):

Equivalent amount (1 mmol) of two different amines were stirred with calix[4]acetate (16.3 mg, 2 mol%) in 2 ml water for 5 min. and $AgNO_3$ (8.5 mg, 5 mol%) was added in dark condition and stirred at 60 °C for 1 h. Then the organic part was separated by filtration and the crude was treated for column chromatography. We got the pure products using petroleum ether as eluent vand the pure cavitand at 5% ethyl acetate in petroleum ether.

5. General procedure for the synthesis of homo azo-compounds (all entries of Scheme 4):

Above procedure is fully applicable for the synthesis of the homo coupled product, just by starting with only one single amine.

Ref: P. Sarkar, S. Maiti, K. Ghosh, S. Sengupta (Bandyopadhyay), R. J. Butcher and C. Mukhopadhyay, *Tetrahedron Letters*, 2014, **55**, 996–1001;

6. Spectral and Analytical Data of the cross-products:

(E)-1-(4-Bromophenyl)-p-tolyldiazene (4a): Orange solid (88%), mp. 166 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2969, 2932, 2859, 2250, 1578, 1405, 1397, 1258, 1106, 1032, 965; ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, $-CH_3$), 7.24 (d, J = 7.8 Hz, 2H, Ar-H), 7.56-7.59 (m, 2H, Ar-H), 7.69-7.80 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 123.0, 124.2, 125.0, 129.8, 132.3, 142.0, 150.7, 151.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{13}H_{11}BrN_2Na]$: 297.0003. Found 297.0005. Anal. calcd. for $C_{13}H_{11}BrN_2$; C: 56.75; H: 4.03; N: 10.18. Found: C: 56.79; H: 4.01; N: 10.15.

(E)-1-(4-Chlorophenyl)-p-tolyldiazene (4b): Reddish yellow solid (87%), mp. 252 ºC ($CDCl_3$) ; IR (KBr, υ cm^{-1}): 2950, 2366, 1715, 1677, 1478, 1345, 1281, 992; ^1H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H, $-CH_3$), 7.34 (d, J = 8.1 Hz, 2H, Ar-H), 7.51 (d, J = 8.7 Hz, 2H, Ar-H), 7.84-7.91 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.1, 150.6,141.9, 136.6, 129.8, 129.3, 124.0, 122.9, 21.6; Anal. calcd. for $C_{13}H_{11}ClN_2$; C: 67.68; H: 4.81; N: 12.14. Found: C: 67.71; H: 4.79; N: 12.11.

1-(4-Nitrophenyl)-2-p-tolyldiazene (4c): Yellow solid (89%), mp. 174 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1604, 1590, 1527, 1342, 1299, 1129, 1099, 858; ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, $-CH_3$), 7.25 (d, J = 8.1 Hz, 2H, Ar-H), 7.78 (d, J = 8.1 Hz, 2H, Ar-H), 7.92 (d, J = 8.7 Hz, 2H, Ar-H), 8.28 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 123.1, 123.2, 124.5, 129.6, 143.1, 148.3, 150.4, 155.6; Anal. calcd. for $C_{13}H_{11}N_3O_2$; C: 64.72; H: 4.60; N: 17.42. Found: C: 64.79; H: 4.58; N: 17.40.

1-(3-Nitrophenyl)-2-p-tolyldiazene (4d): Orange solid (88%), mp. 112 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1610, 1580, 1499, 1352, 1155, 1076, 932; ^1H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H, $-CH_3$), 7.33 (d, J = 8.4 Hz, 2H, Ar-H), 7.69 (t, J = 8.1 Hz, 1H, Ar-H), 7.84 (d, J = 8.4 Hz, 2H, Ar-H), 8.21 (d, J = 8.1 Hz, 1H, Ar-H), 8.27 (d, J = 8.1 Hz, 1H, Ar-H), 8.70 (s, 1H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 116.9, 123.3, 129.0, 129.9, 129.9, 143.0, 149.0, 150.3, 153.1; Anal. calcd. for $C_{13}H_{11}N_3O_2$; C: 64.72; H: 4.60; N: 17.42. Found: C: 64.69; H: 4.59; N: 17.39.

Ethyl 4-(p-Tolyldiazenyl)benzoate (4e): Orange solid (86%), mp. 102 °C ($CDCl_3$); IR (KBr, υ cm^{-1}): 2928, 1723, 1596, 1244, 1095, 1085; ^1H NMR (300 MHz, $CDCl_3$): δ 1.32 (t, J = 7.0 Hz, 3H, $-CH_3$), 2.34 (s, 3H, $-CH_3$), 4.33 (q, J = 7.0 Hz, 2H, $-OCH_2$), 7.24 (d, J = 8.4 Hz, 2H, Ar-H), 7.76 (d, J = 8.4 Hz, 2H, Ar-H), 7.83 (d, J = 8.7 Hz, 2H, Ar-H), 8.11 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 21.6, 61.2, 122.4, 123.1, 129.7, 130.4, 131.7, 142.4, 150.6, 155.1, 165.9; Anal. calcd. for $C_{16}H_{16}N_2O_2$; C: 71.62; H: 6.01; N: 10.44. Found: C: 71.58; H: 6.03; N: 10.49.

1-(4-Acetylphenyl)-2-p-tolyldiazene (4f): red solid (85%), mp. 132 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1672, 1600, 1349, 1266, 1011, 974; ^1H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H, $-CH_3$), 2.48 (s, 3H, $-CH_3$), 7.25 (d, J = 8.4 Hz, 2H, Ar-H), 7.74 (d, J = 8.4 Hz, 2H, Ar-H), 7.89 (d, J = 8.7 Hz, 2H, Ar-H), 8.16 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 26.8, 122.7, 123.1, 129.3, 129.8, 138.2, 142.6, 150.7, 155.1, 197.5; Anal. calcd. for $C_{15}H_{14}N_2O$; C: 75.61; H: 5.92; N: 11.76. Found: C: 75.69; H: 5.95; N: 11.74.

1-(3-Chlorophenyl)-2-p-tolyldiazene (4g): Orange solid (84%), mp. 100-101 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2930, 1732, 1602, 1444, 1271, 1066; ^1H NMR (300 MHz,): δ 2.38 (s, 3H, $-CH_3$), 7.24−7.38 (m, 4H, Ar-H), 7.73−7.83 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 121.6, 122.3, 123.0, 129.8, 130.1, 130.4, 135.0, 142.2, 150.4, 153.5; Anal. calcd. for $C_{13}H_{11}ClN_2$; C: 67.68; H: 4.81; N: 12.14. Found: C: 67.63; H: 4.82; N: 12.17.

Ethyl 4-(o-tolyldiazenyl)benzoate (4h): Reddish yellow solid (83%), mp. 157 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2988, 1719, 1601, 1273, 1105; ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (t, J = 7.0 Hz, 3H, $-CH_3$), 2.75 (s, 3H, $-CH_3$), 4.43 (q, J = 7.1 Hz, 2H, $-OCH_2$), 7.24-7.30 (m, 1H, Ar-H), 7.34-7.42 (m, 2H, Ar-H), 7.65 (d, J = 8.4 Hz, 1H, Ar-H), 7.95 (d, J = 8.4 Hz, 2H, Ar-H), 8.18 (d, J = 8.4 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 155.4, 150.6, 138.9, 131.9, 131.7, 131.4, 130.6, 126.4, 122.7, 115.4, 61.2, 17.5, 14.3; Anal. calcd. for $C_{16}H_{16}N_2O_2$; C: 71.62; H: 6.01; N: 10.44. Found: C: 71.66; H: 6.00; N: 10.41.

Ethyl 4-(m-tolyldiazenyl)benzoate (4i): Red solid (84%), mp. 136 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2931, 1720, 1601, 1265, 1100; ^1H NMR (300 MHz, $CDCl_3$): δ 1.43 (t, J = 7.0 Hz, 3H, $-CH_3$), 2.46 (s, 3H, $-CH_3$), 4.42 (q, J = 7.0 Hz, 2H, $-OCH_2$), 7.34 (d, J = 7.5 Hz, 1H, Ar-H), 7.43 (t, J = 8.0 Hz, 1H, Ar-H), 7.77 (d, J = 5.7 Hz, 2H, Ar-H), 7.94 (d, J = 8.7 Hz, 2H, Ar-H), 8.20 (d, J = 8.4 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 155.1, 152.6, 139.1, 132.5, 132.1, 130.5, 129.0, 123.2, 122.5, 120.7, 61.2, 21.3, 14.3; Anal. calcd. for $C_{16}H_{16}N_2O_2$; C: 71.62; H: 6.01; N: 10.44. Found: C: 71.60; H: 6.03; N: 10.48.

(*E*)-2-(4-bromophenyl)-1-*m*-tolyldiazene (4j): Orange solid (84%), mp. 166 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2962, 2930, 2863, 2248, 1576, 1470, 1393, 1264, 1100, 1065, 914; ^1H NMR (300 MHz, $CDCl_3$): δ2.44 (s, 3H, $-CH_3$), 7.31 - 7.35 (m, 1H, Ar-H), 7.38 -7.43 (m, 1H, Ar-H), 7.62 (d, J = 8.7 Hz, 2H, Ar-H), 7.69 - 7.72 (m, 2H, Ar-H), 7.81 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 151.3, 139.1, 132.3, 131.7, 128.9, 125.5, 124.3, 123.1, 122.9, 120.5, 21.4; Anal. calcd. for $C_{13}H_{11}BrN_2$; C: 56.75; H: 4.03; N: 10.18. Found: C: 56.77; H: 4.01; N: 10.15.

(*E*)-1-(4-chlorophenyl)-2-*m*-tolyldiazene (4k): Orange solid (83%), mp. 98 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2965, 2930, 1633, 1385, 1257, 1075, 923; ^1H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H, $-CH_3$), 7.26 (d, J = 8.7 Hz, 1H, Ar-H), 7.37 (t, J = 8.7 Hz, 1H, Ar-H), 7.44 - 7.48 (m, 2H, Ar-H), 7.68 (d, J = 9.0 Hz, 2H, Ar-H), 7.83 (d, J = 8.7 Hz, 2H, Ar-H);^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 151.1, 139.1, 136.7, 132.1, 129.3, 129.0, 124.1, 123.1, 120.5, 21.4; Anal. calcd. for $C_{13}H_{11}ClN_2$; C: 67.68; H: 4.81; N: 12.14. Found: C: 67.71; H: 4.79; N: 12.11.

Ethyl 4-(phenyldiazenyl)benzoate (4l): Orange solid (89%), mp. 105 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2962, 1707, 1269, 1110, 932; ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (t, J = 7.0 Hz, 3H, $-CH_3$), 4.43 (q, J = 6.9 Hz, 2H, $-OCH_2$), 7.50-7.56 (m, 3H, Ar-H), 7.93-7.97 (m, 4H, Ar-H), 8.18 (d, J = 8.4 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 155.1, 152.5, 132.1, 131.6, 130.5, 129.2, 123.1, 122.6, 61.2, 14.3; Anal. calcd. for $C_{15}H_{14}N_2O_2$; C: 70.85; H: 5.55; N: 11.02. Found: C: 70.83; H: 5.54; N: 11.00.

(*E*)-2-(4-bromophenyl)-1-phenyldiazene (4m): Reddish yellow solid (83%), mp. 176 ºC ($CDCl_3$)**;** IR (KBr, υ cm^{-1}): 3061, 2963, 2927, 2859, 1573, 1477, 1395, 1392, 1291, 1103, 1021, 910; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38 - 7.46 (m, 3H, Ar-H), 7.57 - 7.61 (m, 2H, Ar-H), 7.72 - 7.76 (m, 2H, Ar-H), 7.83 - 7.88 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 151.5, 132.3, 131.4, 130.3, 129.0, 125.4, 124.5, 122.9; Anal. calcd. for $C_{12}H_9BrN_2$; C: 55.20; H: 3.47; N: 10.73. Found: C: 55.24; H: 3.44; N: 10.75.

(*E*)-2-(4-chlorophenyl)-1-phenyldiazene (4n): Reddish yellow solid (82%), mp. 65 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2968, 2933, 1629, 1384, 1265, 1088, 1034; ^1H NMR (300 MHz, $CDCl_3$): δ 7.39 - 7.44 (m, 5H, Ar-H), 7.78 - 7.84 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.4, 150.9, 136.8, 131.2, 129.3, 129.3, 129.2, 129.1, 124.1, 124.1, 122.9, 122.8; Anal. calcd. for $C_{12}H_9ClN_2$; C: 66.52; H: 4.19; N: 12.93. Found: C: 66.57; H: 4.21; N: 12.89.

(*E*)-1-(4-bromophenyl)-2-(4-methoxyphenyl)diazene (4o): Reddish yellow solid (85%), mp. 185 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2962, 2839, 1603, 1258, 1030, 913; ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H, $-OCH_3$), 6.90 (d, J = 8.7 Hz, 2H, Ar-H), 7.51 (d, J = 8.7 Hz, 2H, Ar-H), 7.65 - 7.69 (m, 2H, Ar-H), 7.78 -7.84 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.3, 151.5, 146.8, 132.2, 124.9, 124.5, 124.1, 114.2, 55.6; Anal. calcd. for $C_{13}H_{11}BrN_2O$; C: 53.63; H: 3.81; N: 9.62. Found: C: 53.67; H: 3.83; N: 9.60.

(*E*)-1-(4-Chlorophenyl)-2-(4-methoxyphenyl)diazene (4p): Orange solid (85%), mp. 164 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2965, 1708, 1642, 1464, 1192, 1015, 991; ^1H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H, $-OCH_3$), 7.00 (d, J = 9.0 Hz, 2H, Ar-H), 7.46 (d, J = 8.7 Hz, 2H, Ar-H), 7.81 (d, J = 8.7 Hz, 2H, Ar-H), 7.89 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 151.1, 146.8, 136.1, 129.3, 124.8, 123.8, 114.2, 55.6; Anal. calcd. for $C_{13}H_{11}ClN_2O$; C: 63.29; H: 4.49; N: 11.36. Found: C: 63.21; H: 4.44; N: 11.41.

(*E*)-1-(4-Methoxyphenyl)-2-(4-nitrophenyl)diazene (4q): Yellow solid (86%), mp. 189 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1623, 1501, 1203, 1100, 1015; ^1H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 3H, $-CH_3$), 7.00–7.05 (m, 2H, Ar-H), 7.93–8.01 (m, 4H, Ar-H), 8.45 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ 163.2, 156.0, 148.2, 147.0, 125.6, 124.7, 123.1, 114.4, 55.7; Anal. calcd. for $C_{13}H_{11}N_3O_3$; C: 60.70; H: 4.31; N: 16.33. Found: C: 60.77; H: 4.33; N: 16.27.

1-(4-Acetylphenyl)-2-(4-chlorophenyl)diazene (4r): Orange solid (76%), mp. 150 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1675, 1480, 1399, 1340, 1260, 1088, 1001, 863; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64 (s, 3H, -CH_3), 7.51 (d, J = 8.7 Hz, 2H, Ar-H), 7.89 (d, J = 8.7 Hz, 2H, Ar-H), 7.96 (d, J = 8.7 Hz, 2H, Ar-H), 8.10 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.8, 122.9, 124.4, 129.4, 129.5, 137.7, 138.5, 150.7, 154.8, 197.3; Anal. calcd. for $C_{14}H_{11}ClN_2O$; C: 65.00; H: 4.29; N: 10.83. Found: C: 65.01; H: 4.33; N: 10.80.

1-(4-Acetylphenyl)-2-(4-bromophenyl)diazene (4s): Orange solid (75%), mp. 168 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2925, 1666, 1348, 1268, 1062, 998; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 3H, -CH_3), 7.64 (d, J = 8.7 Hz, 2H, Ar-H), 7.81 (d, J = 8.7 Hz, 2H, Ar-H), 7.94 (d, J = 8.7 Hz, 2H, Ar-H), 8.07 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9, 123.0, 124.6, 126.3, 129.3, 132.4, 138.5, 151.2, 154.7, 197.4; Anal. calcd. for $C_{14}H_{11}BrN_2O$; C: 55.47; H: 3.66; N: 9.24. Found: C: 55.50; H: 3.68; N: 9.21.

1-(4-Acetylphenyl)-2-(4-nitrophenyl)diazene (4t): Red solid (73%), mp. 156 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1683, 1700, 1529, 1344, 1259, 1210, 1111; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.67 (s, 3H, -CH_3), 7.98−8.12 (m, 6H, Ar-H), 8.38 (d, J = 8.4 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.8, 123.4, 123.6, 124.7, 129.4, 139.3, 149.1, 154.4, 155.2, 197.1; Anal. calcd. for $C_{14}H_{11}N_3O_3$; C: 62.45; H: 4.12; N: 15.61. Found: C: 62.40; H: 4.15; N: 15.58.

Ethyl 4-((4-Nitrophenyl)diazenyl)benzoate (4u): Red solid (71%), mp. 164 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1705, 1523, 1351, 1266, 1098, 903; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (t, J = 7.0 Hz, 3H, -CH_3), 4.42 (q, J = 7.0 Hz, 2H, -OCH_2), 7.96 (d, J = 9.0 Hz, 2H, Ar-H), 8.04 (d, J = 8.7 Hz, 2H, Ar-H), 8.21 (d, J = 8.7 Hz, 2H, Ar-H), 8.36 (d, J = 9.0 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 61.4, 123.0, 123.5, 124.6, 130.5, 133.6, 148.9, 154.4, 155.2, 165.5; Anal. calcd. for $C_{15}H_{13}N_3O_4$; C: 60.20; H: 4.38; N: 14.04. Found: C: 60.15; H: 4.36; N: 14.07.

Ethyl 4-((4-bromophenyl)diazenyl)benzoate (4v): Orange solid (73%), mp. 188 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 3433, 1711, 1269, 1110, 998; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (t, J = 7.2 Hz, 3H, -CH_3), 4.44 (q, J = 7.1Hz, 2H, -OCH_2), 7.66 (d, J = 8.7 Hz, 2H, Ar-H), 7.83 (d, J = 8.4 Hz, 2H, Ar-H), 7.95 (d, J = 8.4 Hz, 2H, Ar-H), 8.21 (d, J = 8.4 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 154.8, 151.1, 132.4, 130.5, 126.2, 124.6, 122.8, 61.3, 14.3; Anal. calcd. for $C_{15}H_{13}BrN_2O_2$; C: 54.07; H: 3.93; N: 8.41. Found: C: 54.04; H: 3.95; N: 8.43.

1-(4-Acetylphenyl)-2-phenyldiazene (4w): Red solid (87%), mp. 100 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2930, 1671, 1361, 1263, 1010; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 3H, -CH_3), 7.51−7.57 (m, 3H, Ar-H), 7.91−7.98 (m, 4H, Ar-H), 8.11 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.7, 122.8, 123.0, 129.1, 129.3, 131.7, 138.3, 152.6, 155.1, 197.4; Anal. calcd. for $C_{14}H_{12}ClN_2O$; C: 74.98; H: 5.39; N: 12.49. Found: C: 74.93; H: 5.42; N: 12.46.

1-(4-Methoxyphenyl)-2-*p*-tolyldiazene (4x): Orange solid (70%), mp. 104 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 3428, 2930, 1600, 1503, 1256; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H, -CH_3), 3.80 (s, 3H, -OCH_3), 6.91-6.94 (m, 2H, Ar-H), 7.22 (d, J = 8.1 Hz, 2H, Ar-H), 7.71 (d, J = 8.4 Hz, 2H, Ar-H), 7.81-7.84 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 55.5, 114.1, 122.6, 124.6, 129.7, 140.8, 147.2, 150.9, 161.8; Anal. calcd. for $C_{14}H_{14}N_2O$; C: 74.31; H: 6.24; N: 12.38. Found: C: 74.27; H: 6.26; N: 12.35.

(*E*)-1-(Phenyl)-2-p-tolyldiazene (4y): Orange solid (68%), mp. 54 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 3005, 1709, 1622, 1315, 1032, 943; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H, -CH_3), 7.28 (d, J= 8.1 Hz, 2H, Ar-H), 7.42-7.51 (m, 3H, Ar-H), 7.81 (d, J = 8.4 Hz, 2H, Ar-H), 7.86-7.90 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 150.7, 141.6, 130.7, 129.7, 129.0, 122.8, 122.7, 21.6; Anal. calcd. for $C_{13}H_{12}N_2$; C, 79.56; H, 6.16; N, 14.27; Found: C: 79.50; H: 6.08; N: 14.22. Found: C: 64.31; H: 5.04; N: 4.61.

1-(4-Methoxyphenyl)-2-phenyldiazene (4z): Orange solid (66%), mp. 72 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}):

2919, 2856, 1598, 1254, 1033; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H, -CH_3), 7.02 (d, J = 8.4 Hz, 2H, Ar-H), 7.42-7.54 (m, 3H, Ar-H), 7.89 (d, J = 7.2 Hz, 2H, Ar-H), 7.94 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.1, 152.9, 147.2, 130.3, 129.1, 124.8, 122.6, 114.3, 55.6; Anal. calcd. for $C_{13}H_{12}N_2O$; C: 73.56; H: 5.70; N: 13.20. Found: C: 73.60; H: 5.71; N: 13.18.

1-(4-Bromophenyl)-2-(4-isopropylphenyl)-diazene (4a'): Reddish yellow solid (66%), mp. 208 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2993, 2209, 1535, 1415, 1146, 971; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18-1.29 (m, 6H, -CH_3), 2.92-2.99 (m, 1H, -CH), 7.34 (t, J = 8.1 Hz, 2H, Ar-H), 7.57-7.62 (m, 2H, Ar-H), 7.72-7.84 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.8, 34.2, 123.0, 124.2, 124.4, 124.9, 127.2, 132.2, 132.4, 150.9, 151.5, 152.8; Anal. calcd. for $C_{15}H_{15}BrN_2$; C: 59.42; H: 4.99; N: 9.24. Found: C: 59.50; H: 4.97; N: 9.20.

1-(4-Bromophenyl)-2-(4-tert-butylphenyl)-diazene (4b'): Orange solid (48%), mp. 216 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2980, 2210, 1553, 1413, 1201, 1021; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21-1.33 (m, 9H, -CH_3), 7.59-7.79 (m, 8H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.2, 34.1, 122.8, 124.2, 126.0, 132.2, 138.3, 151.5, 152.0, 155.0; Anal. calcd. for $C_{16}H_{17}BrN_2$; C: 60.58; H: 5.40; N: 8.83. Found: C: 60.64; H: 5.42; N: 8.79.

7. Spectral and Analytical Data of the homo-products:

(E)-1,2-Di-p-tolyldiazene (5a): Orange solid (96%), mp. 132 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2931, 1598, 1501, 1160, 1109, 945; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 6H, -CH_3), 7.23 (d, 4H, J = 8.1 Hz, Ar-H), 7.74 (d, 4H, J = 8.1 Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 122.4, 129.3, 140.8, 150.5; Anal. calcd. for $C_{14}H_{14}N_2$; C: 79.97; H: 6.71; N: 13.32. Found: C: 79.90; H: 6.74; N: 13.36.

(*E*)-1,2-Di-*m*-tolyldiazene (5b): Reddish yellow solid (94%), mp. 128 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2979, 1709, 1541, 1488, 1161, 931, 832; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 6H, -CH_3), 7.28 - 7.32 (m, 2H, Ar-H), 7.37 - 7.40 (m, 2H, Ar-H), 7.80 - 7.86 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.8, 139.1, 131.8, 129.1, 122.9, 120.6, 21.4; Anal. calcd. for $C_{14}H_{14}N_2$; C: 79.97; H: 6.71; N: 13.32. Found: C: 79.99; H: 6.70; N: 13.35.

(*E*)-1,2-Di-*o*-tolyldiazene (5c): Reddish yellow solid (94%), mp. 134 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2968, 1708, 1496, 1397, 1156, 935; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 6H, -CH_3), 7.15-7.26 (m, 6H, Ar-H), 7.53 (d, J = 7.8 Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.1, 138.0, 131.2, 130.6, 126.3, 115.8, 17.6; Anal. calcd. for $C_{14}H_{14}N_2$; C: 79.97; H: 6.71; N: 13.32. Found: C: 79.93; H: 6.73; N: 13.28.

(E)-1,2-Diphenyldiazene (5d): Reddish yellow solid (96%), mp. 65 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1582, 1501, 1456, 1308, 1067, 923; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42−7.51 (m, 6H, Ar-H), 7.88−7.93 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 122.7, 129.0, 130.8, 152.5; Anal. calcd. for $C_{12}H_{10}N_2$; C: 71.10; H: 5.53; N: 15.37. Found: C: 71.05; H: 5.55; N: 15.40.

(E)-1,2-Bis(4-methoxyphenyl)diazene (5e): Reddish yellow solid (93%), mp. 150 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2930, 1731, 1578, 1251, 1142, 1105, 1035, 956; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 6H, -OCH_3), 6.90 (d, 4H, J = 8.4 Hz, Ar-H), 7.79 (d, 4H, J = 8.4 Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 114.1, 124.3, 147.1, 161.6; Anal. calcd. for $C_{14}H_{14}N_2O_2$; C: 79.97; H: 6.71; N: 13.32. Found: C: 79.93; H: 6.69; N: 13.31.

(E)-1,2-Bis(4-bromophenyl)diazene (5f): Red solid (90%), mp. 196 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1729, 1572, 1463, 1401, 1271, 1058, 1008; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56-7.59 (m, 4H, Ar-H), 7.71-7.74 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.4, 125.8, 132.4, 151.2; Anal. calcd. for $C_{12}H_8Br_2N_2$;

C: 42.39; H: 2.37; N: 8.24. Found: C: 42.33; H: 2.41; N: 8.27.

(E)-1,2-Bis(4-chlorophenyl)diazene (5g): Orange solid (91%), mp. 183 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1569, 1483, 1112, 1085, 1010; ^1H NMR (300 MHz, $CDCl_3$): δ 7.40-7.43 (m, 4H, Ar-H), 7.78-7.80 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.1, 129.3, 137.1, 150.6; Anal. calcd. for $C_{12}H_8Cl_2N_2$; C: 57.40; H: 3.21; N: 11.16. Found: C: 57.34; H: 3.19; N: 11.14.

(E)-1,2-Bis(3-chlorophenyl)diazene (5h): Orange solid (88%), mp. 99 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1585, 1569, 1466, 1203, 1061; ^1H NMR (300 MHz, $CDCl_3$): δ 7.42−7.44 (m, 4H, Ar-H), 7.66−7.82 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.8, 122.5, 130.0, 131.0, 135.1, 152.9; Anal. calcd. for $C_{12}H_8Cl_2N_2$; C: 57.40; H: 3.21; N: 11.16. Found: C: 57.47; H: 3.21; N: 11.11.

(*E*)-1,2-Bis(2,4-dimethylphenyl)diazene (5i): Orange solid (92%), mp. 232 ºC (EtOAc); IR (KBr, υ cm^{-1}): 3004, 1713, 1622, 1444, 1249, 1135, 952, 743; ^1H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 6H, Ar-H), 2.25 (s, 6H, Ar-H), 7.16 (d, J = 7.8 Hz, 2H, Ar-H), 7.55-7.60 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.9, 120.8, 123.4, 130.2, 130.2, 137.4, 139.9, 151.2; Anal. calcd. for $C_{16}H_{18}N_2$; C: 80.63; H: 7.61; N: 11.75. Found: C: 80.69; H: 7.58; N: 11.71.

(*E*)-Diethyl 4,4'-(diazene-1,2-diyl)dibenzoate (5j): red solid (86%), mp. 162 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 3409, 1726, 1275, 1101; ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (t, J = 7.0 Hz, 6H, $-CH_3$), 4.44 (q, J = 7.1 Hz, 4H, $-OCH_2$), 7.98 (d, J = 8.4 Hz, 4H, Ar-H), 8.23 (d, J = 8.4 Hz, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 154.7, 132.6, 130.5, 122.8, 61.3, 14.4; Anal. calcd. for $C_{18}H_{18}N_2O_4$; C: 66.25; H: 5.56; N: 8.58. Found: C: 66.31; H: 5.57; N: 8.55.

(E)-1,2-Bis(4-acetylphenyl)diazene (5k): Red solid (88%), mp. 210 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1668, 1411, 1361, 1305, 1263, 1231, 1112, 1001, 972; ^1H NMR (300 MHz, $CDCl_3$): δ 2.69 (s, 6H, $-CH_3$), 8.03 (d, 4H, J = 8.4 Hz, Ar-H), 8.14 (d, 4H, J = 8.4 Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.1, 123.2, 129.3, 138.8, 154.6, 197.2; Anal. calcd. for $C_{16}H_{14}N_2O_2$; C: 72.16; H: 5.30; N: 10.52. Found: C: 72.11; H: 5.33; N: 10.55.

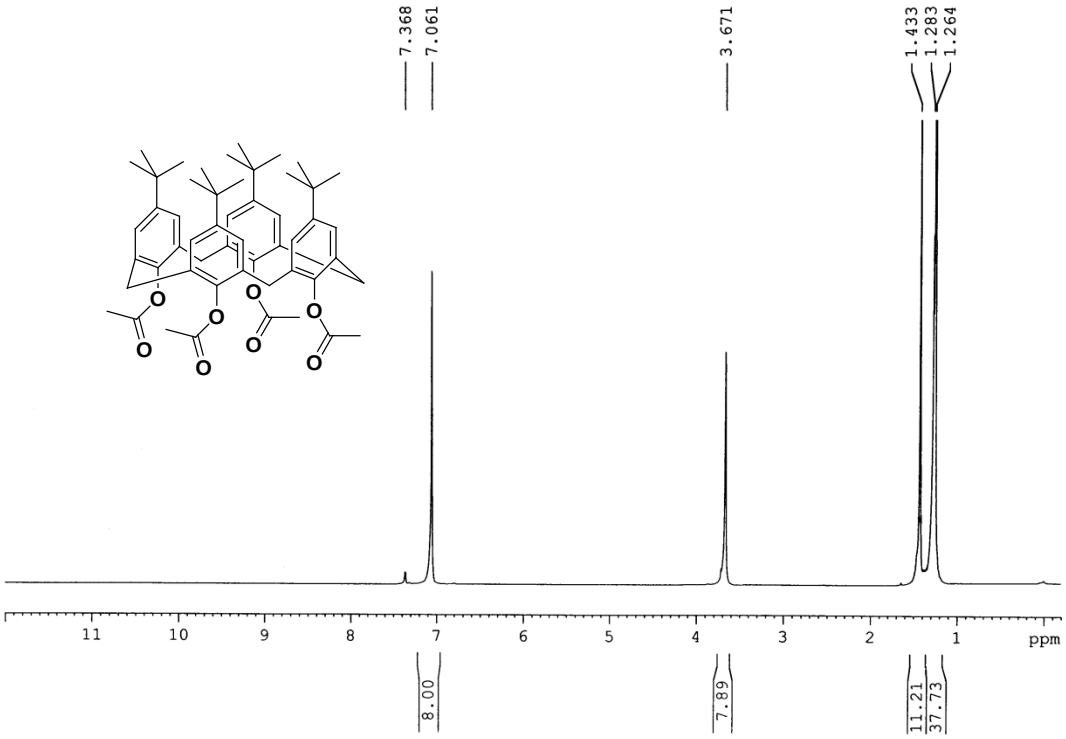
(E)-1,2-Bis(4-nitrophenyl)diazene (5l): Orange solid (83%), mp. 222 ºC (EtOAc); IR (KBr, υ cm^{-1}): 1608, 1533, 1344, 1319, 1209, 1105, 1002; ^1H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, 4H, J = 8.4 Hz, Ar-H), 8.45 (d, 4H, J = 8.4 Hz, Ar-H)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 123.8, 124.7, 149.2, 154.8; Anal. calcd. for $C_{12}H_8N_4O_4$; C: 52.95; H: 2.96; N: 20.58. Found: C: 53.02; H: 2.95; N: 20.61.

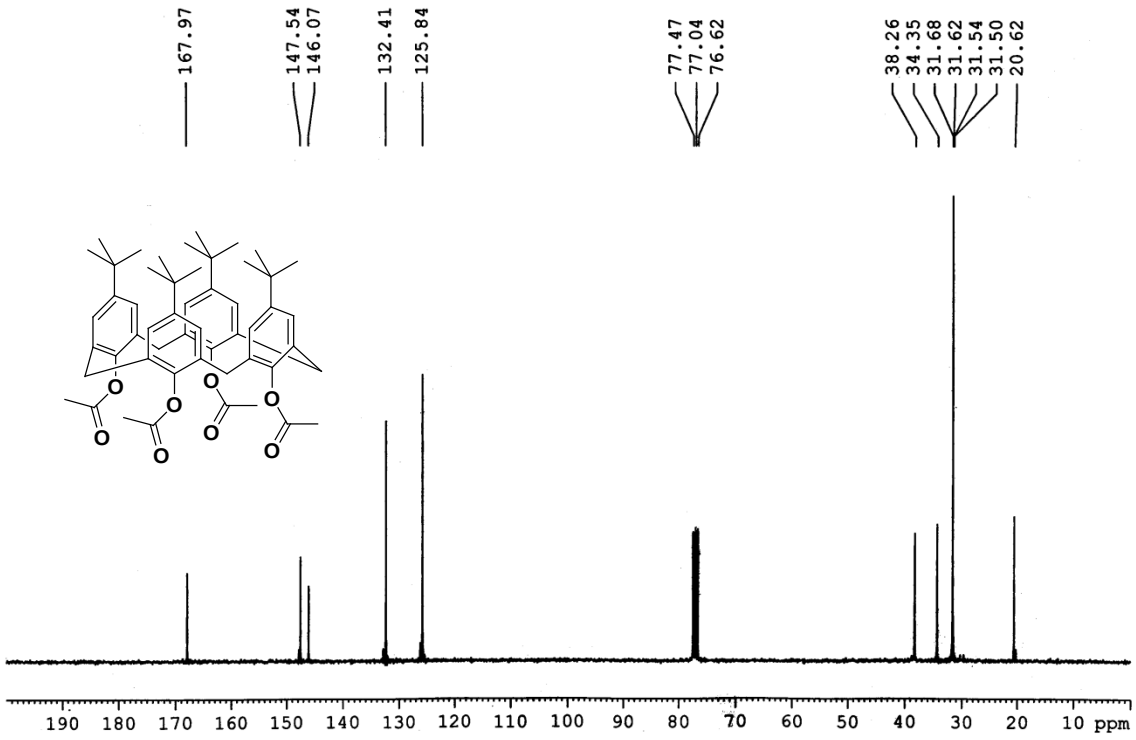
(E)-1,2-Bis(3-nitrophenyl)diazene (5m): Orange solid (85%), mp. 154 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 1530, 1352, 1317, 1077, 923; ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (t, 2H, J = 8.1, Ar-H), 8.34 (dd, 2H, J = 8.1, 1.2 Hz, Ar-H), 8.41 (dd, 2H, J = 8.1, 1.2 Hz, Ar-H), 8.78 (s, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 117.1, 125.8, 129.6, 130.2, 148.9, 152.2; Anal. calcd. for $C_{12}H_8N_4O_4$; C: 52.95; H: 2.96; N: 20.58. Found: C: 53.00; H: 2.97; N: 20.52.

(E)-1,2-Bis(4-isopropylphenyl)diazene (5n): Orange solid (86%), mp. 146 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2933, 1602, 1501, 1171, 1112, 958; ^1H NMR (300 MHz, $CDCl_3$): δ 1.19-1.22 (m, 12H, $-CH_3$), 2.84-2.93 (m, 2H, -CH), 7.26 (d, J = 8.4, 4H, Ar-H), 7.76 (d, J = 8.1, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.8, 34.1, 122.8, 127.0, 151.2, 152.0; Anal. calcd. for $C_{18}H_{22}N_2$; C: 81.16; H: 8.32; N: 10.52. Found: C: 81.21; H: 8.30; N: 10.49.

(E)-1,2-Bis(4-tert-butylphenyl)diazene (5o): Orange solid (84%), mp. 166 ºC ($CDCl_3$); IR (KBr, υ cm^{-1}): 2920, 1588, 1499, 1165, 1117, 946; ^1H NMR (300 MHz, $CDCl_3$): δ 1.40-1.65 (m, 18H, $-CH_3$), 7.56-7.68 (m, 4H, Ar-H), 7.82-7.90 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.2, 34.9, 122.7, 126.0, 150.8, 154.2; Anal. calcd. for $C_{20}H_{26}N_2$; C: 81.59; H: 8.90; N: 9.51. Found: C: 81.55; H: 8.88; N: 9.52.

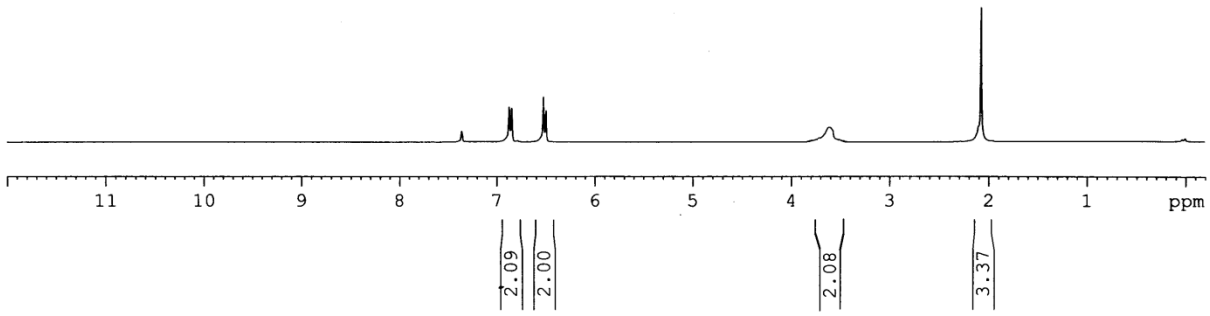
8. ^{1}H and ^{13}C -NMR spectra of the cavitand p-tert-Butylcalix[4]arene-tetra-O-acetate



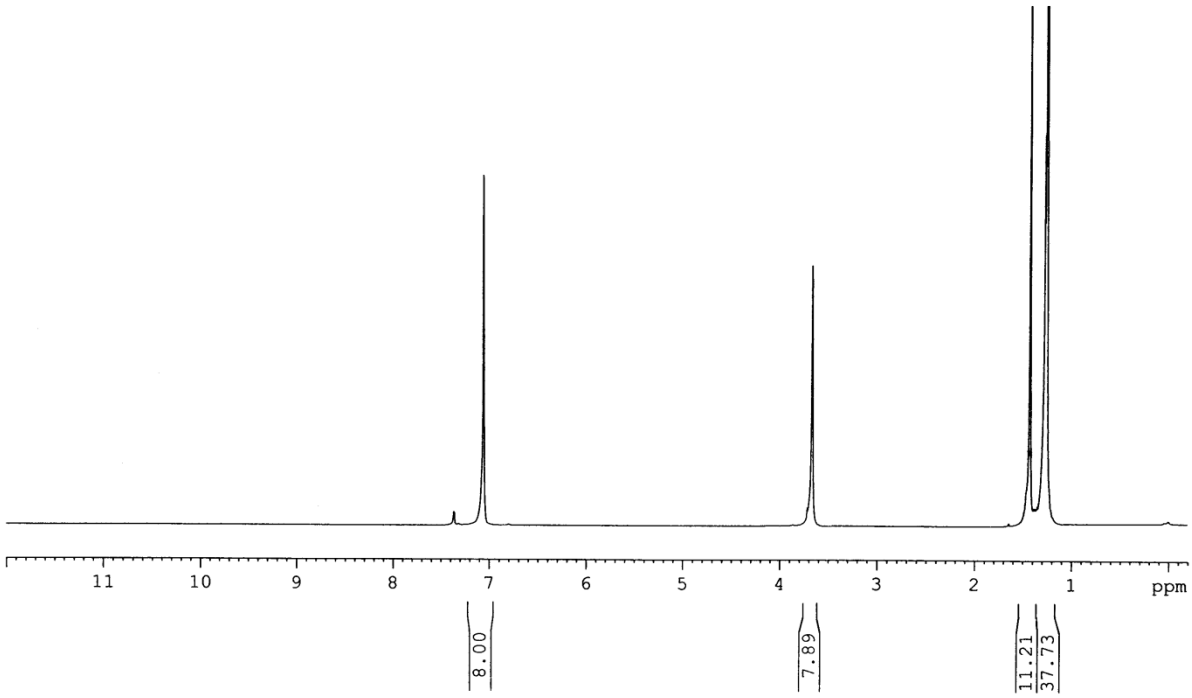


9. Corresponding 1H-NMRs of Fig. 1 (Manuscript) [Stacked 1H NMR spectra ($CDCl_3$, room temperature; 303 K) of the guest *p*-toluidine, the host calix[4]acetate, and silver ion with p-toluidine ⊂ calix[4]acetate]

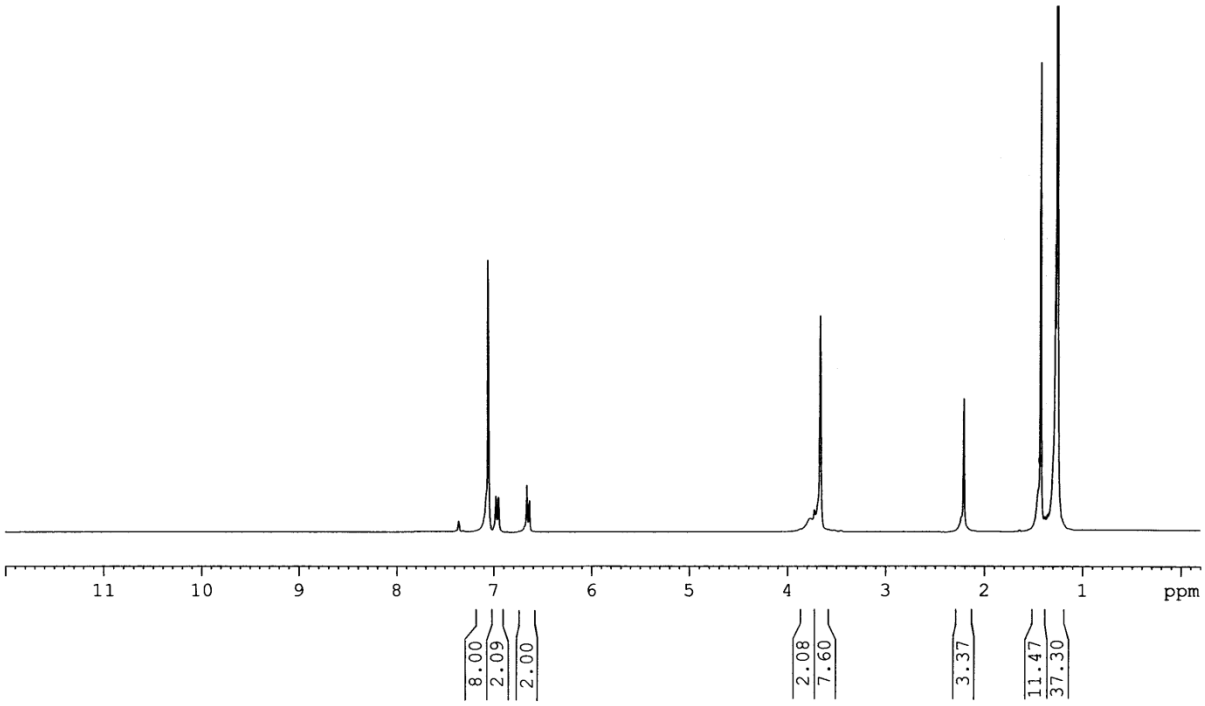
p-Toluidine



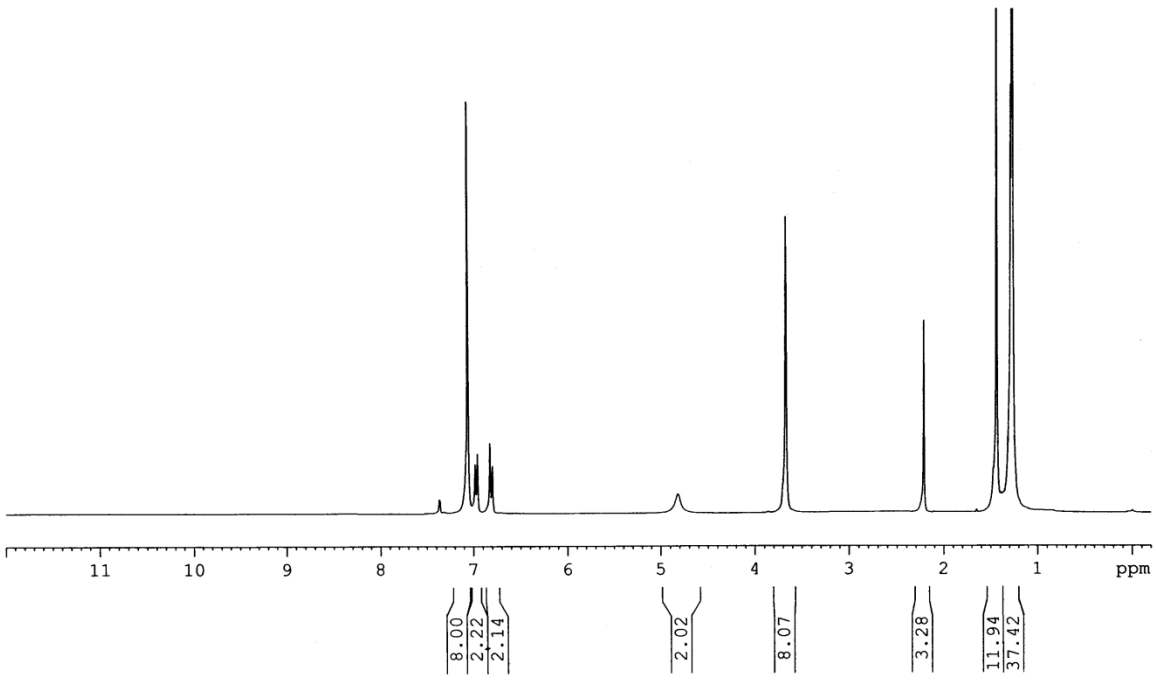
Calix[4]acetate



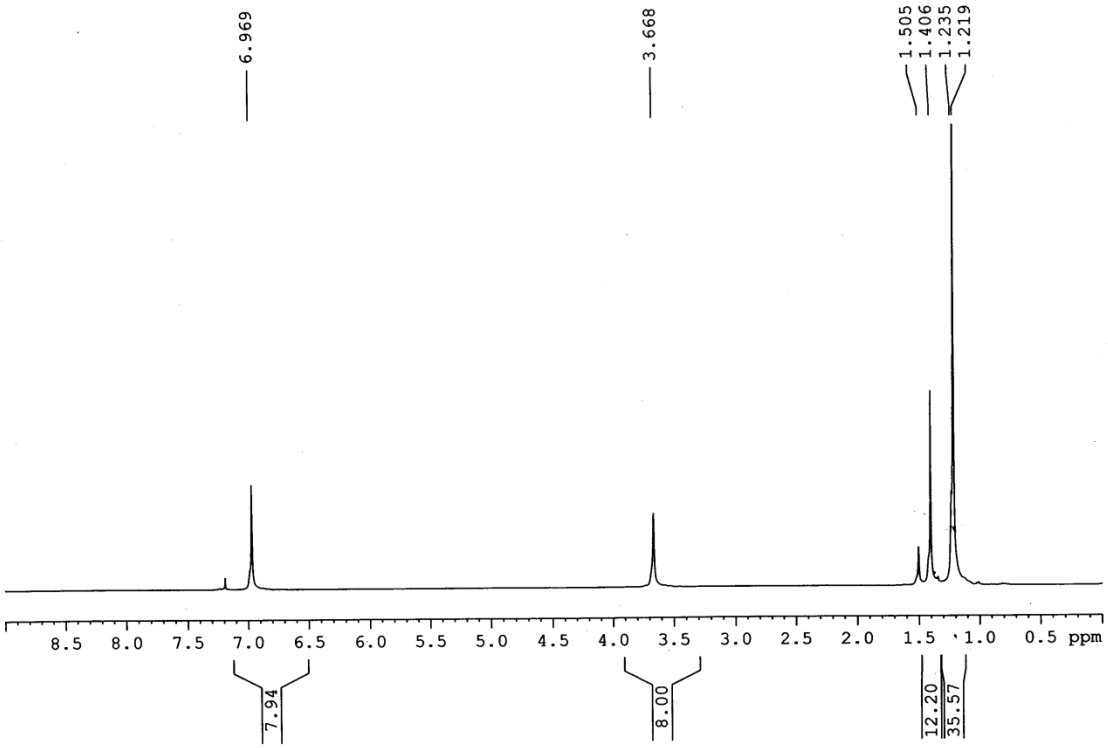
p-Toluidine ⊂Calix[4]acetate



Silver Ion with p-Toluidine ⊂Calix[4]acetate



10. ^{1}H , ^{13}C NMR and TEM of recovered catalyst after five times recycled:


6.969
3.668
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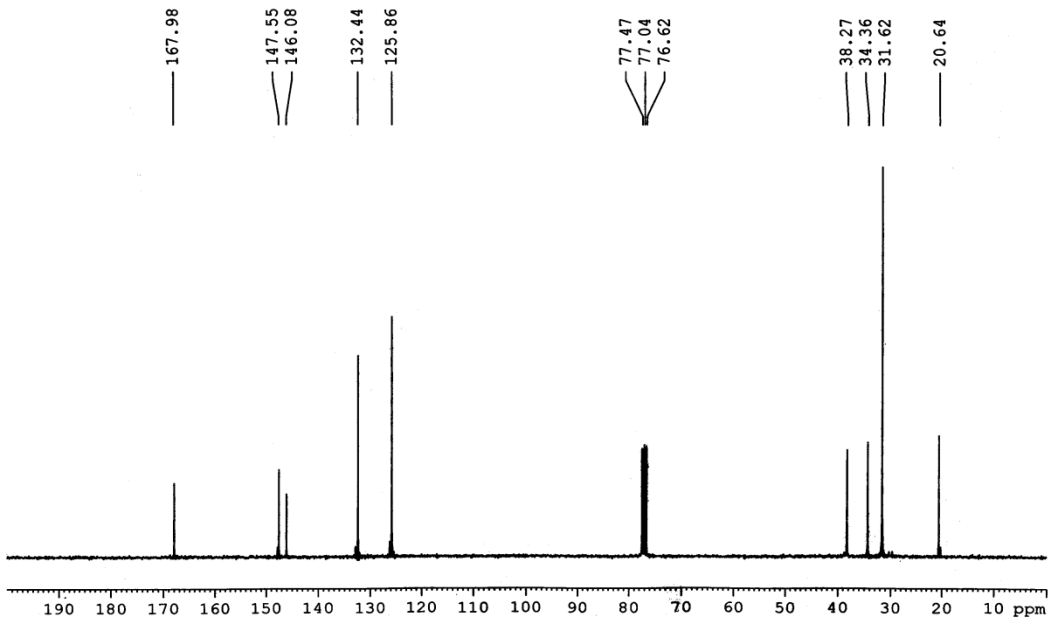
1.406
1.235
1.219
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
7.94
8.00
12.20
35.57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132.44
125.86
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77.04
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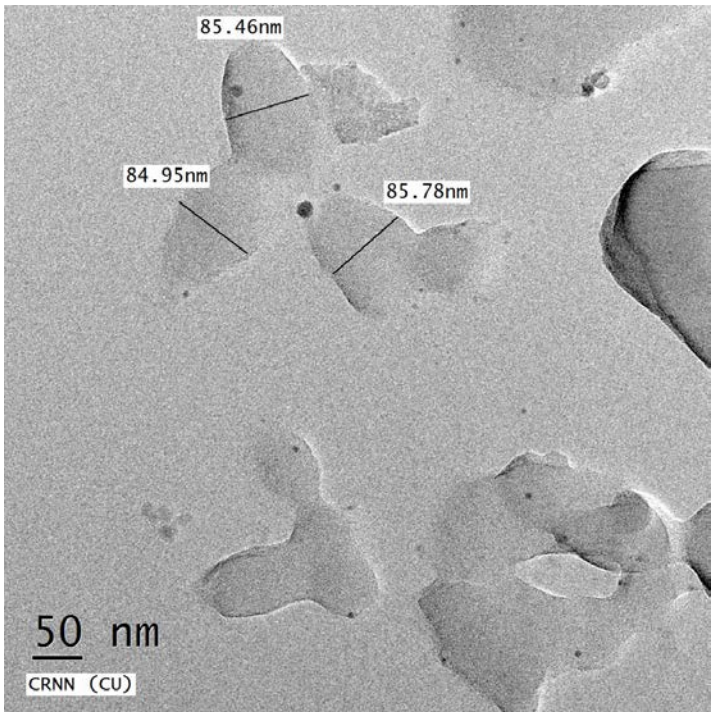
31.62
20.64
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

TEM Image


85.46nm
84.95nm
85.78nm
50 nm
CRNN (CU)