

Electronic Supplementary Information

for

Oxidative dimerization of anilines with heterogeneous sulfonic acids catalysts

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1. General remarks

Reagents were obtained from commercial sources and used as received. Anilines were distilled prior to use under N₂. H₂O₂ was degassed by bubbling Ar for 20 minutes prior to use to avoid contamination by traces of O₂.

Reactions were carried out under argon using standard Schlenk technique.

Flash column chromatography was performed on Merck Geduran SI 60 Å silica gel (0.040-0.063mm) and thin-layer chromatography on Merck 60F254 plates.

IR spectra were recorded with a ATR Nicolet 5700 FT-IR spectrometer.

Unless otherwise indicated, ¹H-NMR and ¹³C-NMR spectra were recorded in CDCl₃ at 298 K on a Bruker 400 AVANCE spectrometer fitted with a BBFO probe-head at 400.1 and 100.5 MHz respectively, using the solvent as internal standard (7.26 ppm for ¹H-NMR and 77.00 ppm for ¹³C-NMR). The terms m, s, d, t, q represent multiplet, singlet, doublet, triplet, quadruplet respectively, and the term br means a broad signal.

Mass analyses were measured on an Infusion Water Acquity Ultra Performance LC HO6UPS-823M instrument with SQ detector and ESI source.

2. Experimental Procedures

Synthesis of Aquivion @SiO₂

200 mL of a NaOH solution (1.6 g, 40 mmol), dimethyldioctadecylammonium bromide (3.15 g, 5 mmol) and aqueous Aquivion[®] dispersion (Aquivion[®] D66-20BS 20.1 w/w%, 2.39 g) were added to a 500 mL flask. The mixture was stirred for two hours at room temperature. 18 mL of TEOS (80 mmol) were then added dropwise by means of a dropping funnel and the resulting mixture was kept under magnetic stirring at room temperature for 16 hours. The resulting solid dispersion was filtered on a Büchner funnel, washed with water (100 mL) and dried overnight in an oven at 80°C. The resulting white powder was dispersed in a 1 M solution of H₂SO₄ in ethanol (100 mL of solution for 1.0 g of powder) and warmed at reflux overnight. The solid is recovered by filtration and dispersed in ethanol (100 mL for 1.0 g of powder). The mixture is then warmed at reflux for 12 hours. The resulting powder is filtered, washed with water (100 mL) and dried overnight in an oven at 80°C, eventually yielding 4.1 g of the desired material used for catalytic reactions.

General procedure for the synthesis of **2** (GP1)

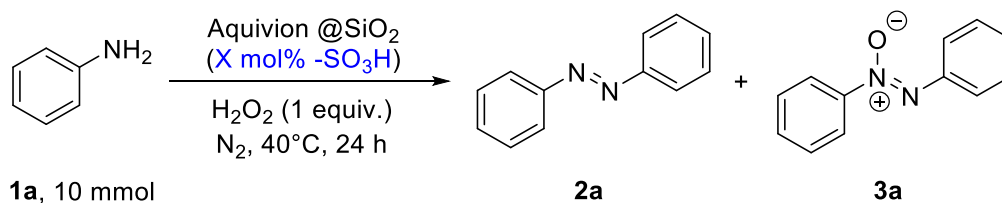
The desired aniline derivative (10 mmol, 1 eq.) and 35% hydrogen peroxide (10 mmol, 1 eq.) were added under argon to a Schlenk-type flask containing 50 mg of catalyst. The mixture was kept under vigorous stirring and warmed at 40°C for 24 hours. The mixture was diluted with hexane (30 mL) and the solid catalyst was recovered by filtration on a small celite pad. The biphasic mixture is then placed in a funnel and the organic layer was washed with 1 M HCl solution (3 x 10 mL) to recover unreacted aniline. The organic phase was then dried over anhydrous Na₂SO₄, filtered and the solvent was removed under vacuum to afford technically pure product **2** (see page 7). Traces of **3** were eventually removed by flash column chromatography on silica gel.

Synthesis of heteroazo compound **2p**

Aniline **1p** (5 mmol, 1 eq.), nitrosobenzene (**4a**, 5 mmol, 1 eq.) and water (1.2 mL) were sequentially added to a Schlenk-type flask containing 50 mg of catalyst under argon. The mixture was kept at 40°C under vigorous stirring for 6 hours. Following the same work-up described above, spectroscopically pure **2p** was eventually recovered upon flash column chromatography on silica gel.

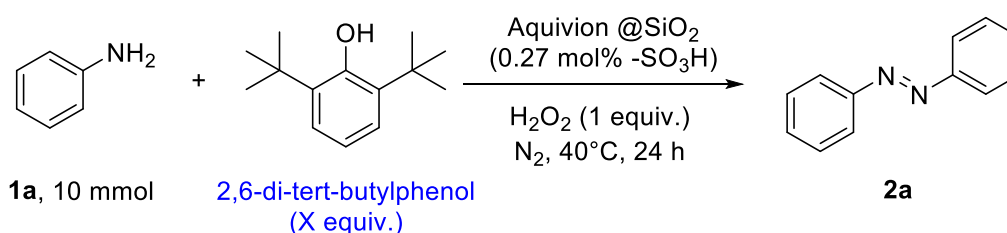
3. Additional experiments

Table S1 Effect of the amount of catalyst



Entry	mg cat. / mol% -SO ₃ H	1 Conv. (%)	2 Yield (%)	3 Yield (%)	2 Sel. (%)
1	250 mg / 1.325 %	98	72	18	73
2	500 mg / 2.65 %	98	64	22	65
3	100 mg / 0.53 %	98	81	15	83
4	50 mg / 0.265 %	96	89	4	93

Table S2 Reactions with 2,6-di-tert-butylphenol



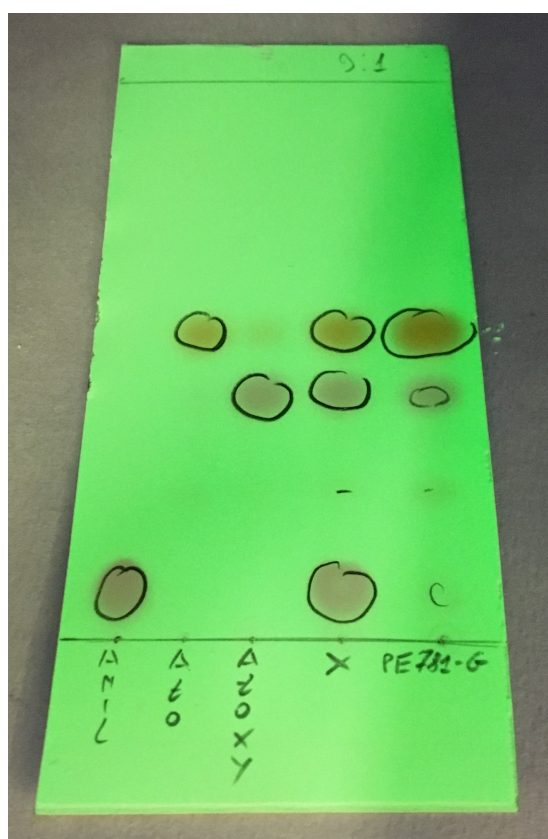
Entry	mmol phenol	1 Conv. (%)	2 Yield (%)	2 Sel. (%)
1	10	24	4	18
2	5	36	10	28
3	0.05	44	22	52
4	0.003	58	32	54

Procedure for catalyst recycle

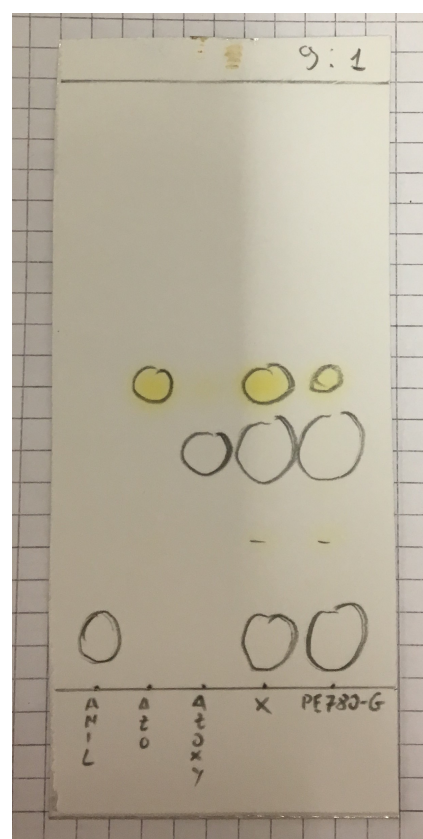
Upon the model experiments, the catalyst is recovered by filtration (49 mg, 98% recovery, brown powder). This material is no longer catalytically active. A 1 M HCl solution (15 mL) is then added to the resulting material and the mixture is put under stirring for 30 minutes. This enables to restore both the original white color of the solid material and, furthermore, its original Bronsted acidity. The mixture is then filtered and 47 mg of material are eventually recovered upon vacuum drying (3 hours). Repeating **GP1** with 9.8 mmol of **1a** (915 mg) led to the formation of **2a** in 88% isolated yield (788 mg).

Procedure for the separation of mixtures of 2a and 3a

Crudes of unselective reactions that yielded mixtures of **2** and **3** can be purified via chromatography on silica gel to afford the two spectroscopically pure products. The solid residue is charged on silica and elution with hexane yields in sequence **2a**, which absorbs in the visible, **3a** (UV) and eventually unreacted amine if present (Figure S1, right). Figure S1 shows the relative difference in polarity of these three molecules for two representative experiments. As shown in the next page (Figure S2), chromatographic purification is not necessary to recover technically pure product **2** under optimized conditions.



1a 2a 3a X Crude



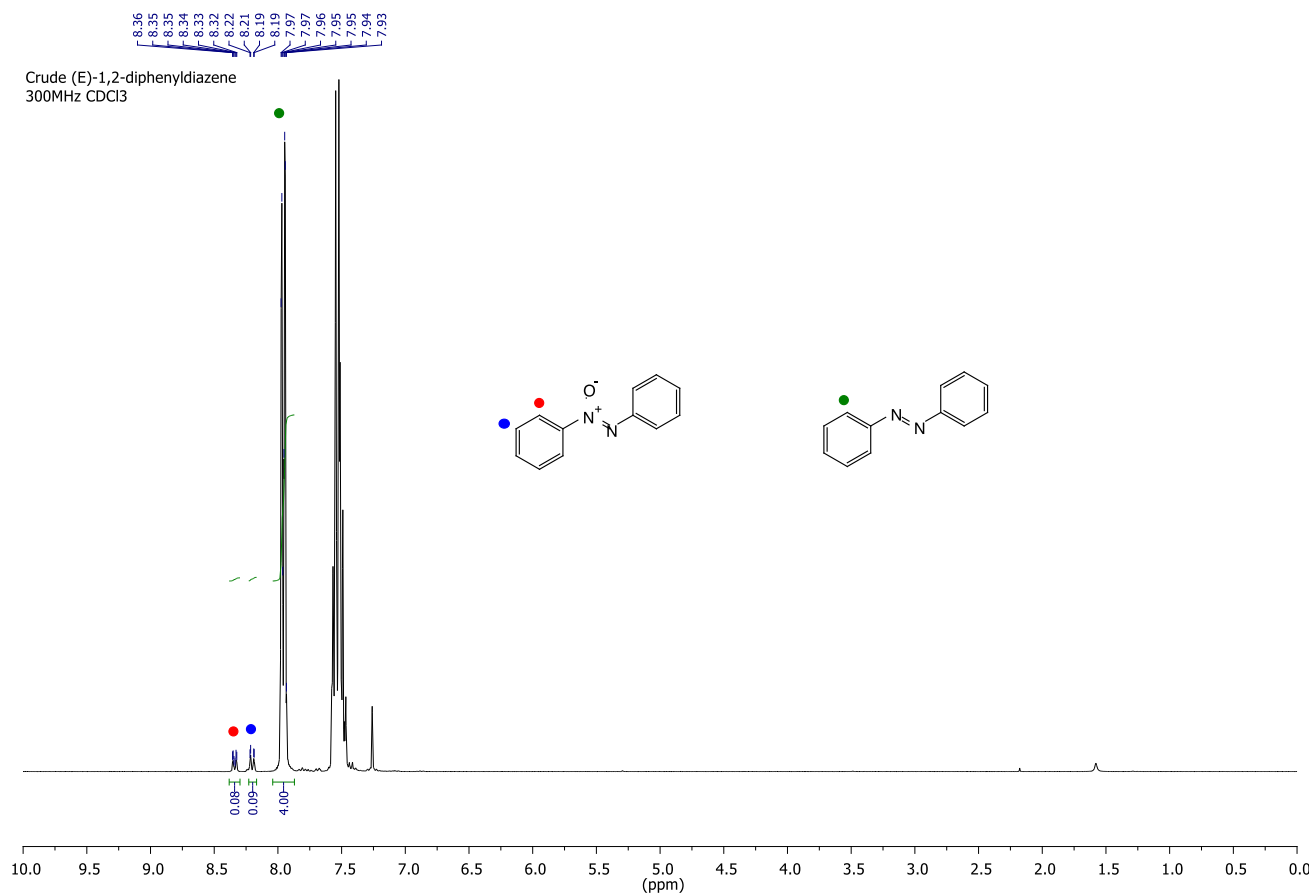
1a 2a 3a X Crude

Figure S1 Copies of crude TLC showing the separate spots of **2a** and **3a** (as Table 1, entry 13 the left, entry 14 on the right)

4. Crude NMR of 2a upon work-up

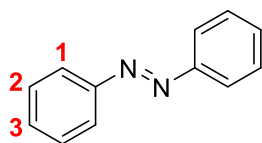
Figure S2 $^1\text{H-NMR}$ spectrum of the crude mixture upon acidic work-up.

The spectrum shows diphenyldiazene **2a** (96% pure) and traces of **3a** (red and blue dots).



5. Characterization of products

(E)-1,2-diphenyldiazene (**2a**)



$C_{12}H_{10}N_2$ MW = 182.23 g/mol

Synthesized following GP1 from aniline (931 mg, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as orange solid. Yield: 89% (811 mg, 4.45 mmol)

Eluent: hexane

1H -NMR: δ 8.05-8.01 (m, 4H, H1), 7.59-7.55 (m, 6H, H2-H3)

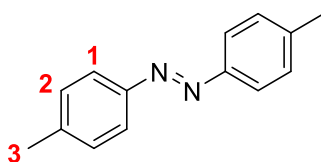
^{13}C -NMR: δ 152.6, 130.9, 129.1, 122.8

IR (ATR): ν = 3418, 1581, 1481, 1452, 775, 688 cm^{-1}

MS calcd. for $C_{12}H_{11}N_2$ ($[M-H]^+$) 183.09, found 183.13

Spectroscopic data correspond to the literature.¹

(E)-1,2-di-p-tolyldiazene (**2b**)



$C_{14}H_{14}N_2$ MW = 210.31 g/mol

Synthesized following GP1 from p-toluidine (1.071 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as orange solid. Yield: 80% (841 mg, 4 mmol)

Eluent: hexane

1H -NMR: δ 7.83 (d, J = 8.3 Hz, 4H, H1), 7.31 (d, J = 8.1 Hz, 4H, H2), 2.44 (s, 6H, H3)

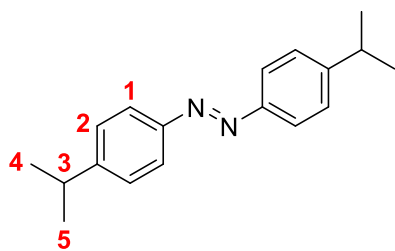
^{13}C -NMR: δ 150.8, 141.2, 129.7, 122.7, 21.5

IR (ATR): ν = 3419, 2920, 1598, 1499, 1152, 824 cm^{-1}

MS calcd. for $C_{14}H_{15}N_2$ ($[M-H]^+$) 211.12, found 211.12

Spectroscopic data correspond to the literature.¹

(E)-1,2-bis(4-isopropylphenyl)diazene (**2c**)



$C_{18}H_{22}N_2$ MW = 266.39 g/mol

Synthesized following GP1 from 4-isopropylaniline (1.352 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as red solid. Yield: 74% (986 mg, 3.7 mmol)

Eluent: hexane/dichloromethane 9:1

1H -NMR: δ 7.86 (d, J = 8.4 Hz, 4H, H1), 7.37 (d, J = 8.3 Hz, 4H, H2), 3.0 (dt, J = 6.9, 13.8 Hz, 2H, H3), 1.31 (d, J = 6.9 Hz, 12H, H4-H5)

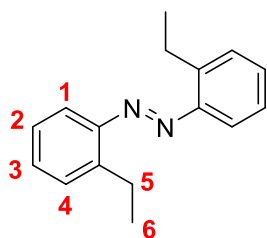
^{13}C -NMR: δ 152, 151.2, 127.1, 122.8, 34.1, 23.9

IR (ATR): ν = 3426, 2895, 1601, 1496, 1464, 1417 cm^{-1}

MS calcd. for $C_{18}H_{23}N_2$ ($[M-H]^+$) 267.18, found 267.18

Spectroscopic data correspond to the literature.²

(E)-1,2-bis(2-ethylphenyl)diazene (**2d**)



$C_{16}H_{18}N_2$ MW = 238.33 g/mol

Synthesized following GP1 from 2-ethylaniline (1.212 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as red solid. Yield: 76% (906 mg, 3.8 mmol)

Eluent: hexane/dichloromethane 9:1

1H -NMR: δ 7.64 (d, J = 7.8 Hz, 2H, H1), 7.41-7.37 (m, 4H, H2-H4), 7.32-7.27 (m, 2H, H3), 3.21 (q, J = 7.5 Hz, 4H, H5), 1.33 (t, J = 7.4 Hz, 6H, H6)

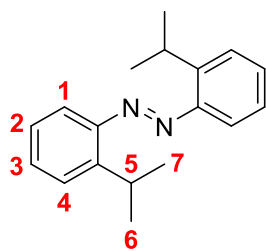
^{13}C -NMR: δ 150.5, 144.3, 130.9, 129.8, 126.4, 115.6, 24.7, 16.5

IR (ATR): ν = 2965, 2929, 1479, 1152, 747 cm^{-1}

MS calcd. for $C_{16}H_{19}N_2$ ($[M-H]^+$) 239.16, found 239.16

Spectroscopic data correspond to the literature.³

(E)-1,2-bis(2-isopropylphenyl)diazene (**2e**)



$C_{18}H_{22}N_2$ MW = 266.39 g/mol

Synthesized following GP1 from 2-isopropylaniline (1.352 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as orange solid. Yield: 51% (679 mg, 2.5 mmol)

Eluent: hexane/ethyl acetate 9:1

1H -NMR: δ 7.72 (dd, $J = 0.8, 8.1$ Hz, 2H, H1), 7.52 (m, 4H, H2-H4), 7.35 (ddd, $J = 1.9, 6.9, 8.5$ Hz, 2H, H4), 4.28 (hept, $J = 6.9$ Hz, 2H, H5), 1.46 (d, $J = 7$ Hz, 12H, H6-H7)

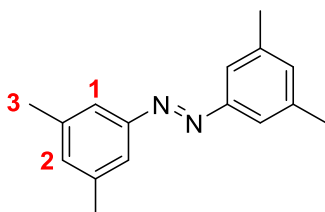
^{13}C -NMR: δ 150.0, 148.0, 131.0, 126.3, 126.2, 115.5, 27.7, 23.8

IR (ATR): $\nu = 2964, 1736, 1372, 1234, 1049, 988, 847, 607$ cm^{-1}

MS calcd. for $C_{18}H_{23}N_2$ ($[M-H]^+$) 267.18, found 267.18

Spectroscopic data correspond to the literature.⁴

(E)-1,2-bis(3,5-dimethylphenyl)diazene (**2f**)



$C_{16}H_{18}N_2$ MW = 238.33 g/mol

Synthesized following GP1 from 3,5-dimethylaniline (1.212 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as red solid. Yield: 78% (921 mg, 3.9 mmol).

Eluent: hexane/dichloromethane 9:1

1H -NMR: δ 7.54 (s, 4H, H1), 7.12 (s, 2H, H2), 2.42 (s, 12H, H3)

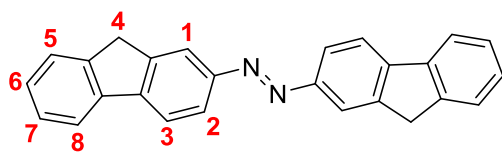
^{13}C -NMR: δ 152.9, 138.7, 132.5, 120.5, 21.2

IR (ATR): $\nu = 2914, 1608, 1442, 1292, 1038, 903, 853$ cm^{-1}

MS calcd. for $C_{16}H_{19}N_2$ ($[M-H]^+$) 239.16, found 239.16

Spectroscopic data correspond to the literature.⁵

(E)-1,2-di(9H-fluoren-2-yl)diazene (**2g**)



$C_{26}H_{18}N_2$ MW = 358.44 g/mol

Synthesized following GP1 from 2-aminofluorene (1.8123 g, 10 mmol) and hydrogen peroxide (0.972g of 35 w/w% solution, 10 mmol)

Isolated as orange/brown solid. Yield 60% (1.0753 g, 3 mmol)

Eluent: hexane/ethyl acetate 19:1

1H -NMR: δ 8.38 (s, 2H, H1), 8.28 (dd, J = 1.8, 8.4 Hz, 2H, H2), 7.86 (dd, J = 4.1, 8.4 Hz, 4H, H5+H8), 7.63-7.60 (m, 2H, H3), 7.44 (dd, J = 2.5, 6 Hz, 4H, H6-H7), 3.99 (s, 4H, H4)

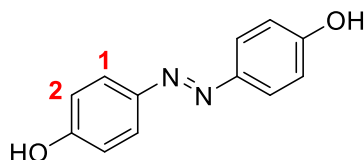
^{13}C -NMR: δ 148, 146.7, 144.8, 143.9, 139.4, 128.8, 127.4, 125.4, 123.1, 121.3, 120.4, 119.8, 36.9

IR (ATR): ν = 2961, 2923, 2848, 2363, 2328, 1720, 1604

MS calcd. for $C_{26}H_{19}N_2$ ($[M-H]^+$) 359.16, found 359.19

Spectroscopic data correspond to the literature.⁶

(E)-4,4'-(diazene-1,2-diyl)diphenol (**2h**)



$C_{12}H_{10}N_2O_2$ MW = 214.22 g/mol

Synthesized following GP1 from 4-aminophenol (1.091 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as dark brown solid. Yield: 70% (750 mg, 3.5 mmol).

Eluent: hexane/dichloromethane 9:1

1H -NMR (MeOD- d_4): δ 7.77 (d, J = 8.8 Hz, 4H, H1), 6.92 (d, J = 8.8 Hz, 4H, H2)

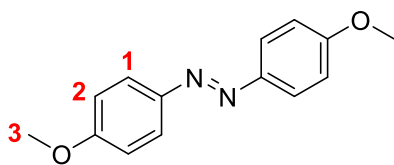
^{13}C -NMR (MeOD- d_4): δ 161.5, 147.8, 125.6, 116.9

IR (ATR): ν = 3377, 1589, 1500, 1425, 842, 766, 644 cm^{-1}

MS calcd. for $C_{12}H_{11}N_2O_2$ ($[M-H]^+$) 215.08, found 215.12

Spectroscopic data correspond to the literature.⁷

(E)-1,2-bis(4-methoxyphenyl)diazene (**2i**)



$C_{14}H_{14}N_2O_2$ MW = 242.28 g/mol

Synthesized following GP1 from p-anisidine (1.231 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as yellow solid. Yield: 77% (933 mg, 3.9 mmol)

Eluent: hexane/ethyl acetate 9:1

1H -NMR: δ 7.91-7.86 (m, 4H, H1), 7.03-6.98 (m, 4H, H2), 3.89 (s, 6H, H3)

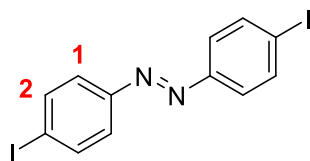
^{13}C -NMR: δ 161.6, 147, 124.4, 114.4, 55.6

IR (ATR): ν = 2920, 1728, 1575, 1240, 1139, 1101, 1022, 813 cm^{-1}

MS calcd. for $C_{14}H_{15}N_2O_2$ ($[M-H]^+$) 243.10, found 243.11

Spectroscopic data correspond to the literature.¹

(E)-1,2-bis(4-iodophenyl)diazene (**2j**)



$C_{12}H_8I_2N_2$ MW = 434.02 g/mol

Synthesized following GP1 from 4-iodoaniline (2.190 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as orange solid. Yield: 51% (1.107 g, 2.5 mmol).

Eluent: hexane/dichloromethane 9:1

1H -NMR: δ 7.89-7.84 (m, 4H, H1), 7.66-7.62 (m, 4H, H2)

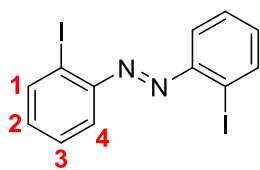
^{13}C -NMR: δ 151.7, 138.4, 124.5, 98.1

IR (ATR): ν = 1560, 1467, 1390, 1296, 1278, 1095, 1049, 1001, 810, 713 cm^{-1}

MS calcd. for $C_{12}H_9I_2N_2$ ($[M-H]^+$) 434.89, found 435.01

Spectroscopic data correspond to the literature.⁵

(E)-1,2-bis(2-iodophenyl)diazene (**2k**)



$C_{12}H_8I_2N_2$ MW = 434.02 g/mol

Synthesized following GP1 from 2-iodoaniline (2.1902 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as yellow solid. Yield: 46% (998 mg, 2.3 mmol)

Eluent: hexane/dichlorometane 9:1

1H -NMR: δ 8.03 (d, J = 7.8 Hz, 2H, H4), 7.76 (d, J = 7.8 Hz, 2H, H1), 7.45 (t, J = 7.3 Hz, 2H, H3), 7.18 (t, J = 7 Hz, 2H, H2)

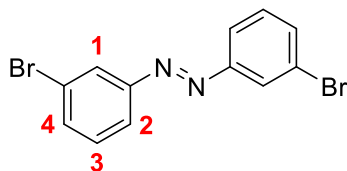
^{13}C -NMR: δ 150.7, 139.9, 132.7, 129, 118.2, 103.3

IR (ATR): 1561, 1455, 1245, 1037, 1014, 766 cm^{-1}

MS calcd. for $C_{12}H_9I_2N_2$ ($[M^+]$) 434.89, found 435.00

Spectroscopic data correspond to the literature.⁹

(E)-1,2-bis(3-bromophenyl)diazene (**2l**)



$C_{12}H_8Br_2N_2$ MW = 340.02 g/mol

Synthesized following GP1 from 3-bromoaniline (1.720 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as yellow solid. Yield: 50% (850 mg, 2.5 mmol).

Eluent: hexane/dichloromethane 9:1

1H -NMR: δ 8.06 (s, 2H, H2), 7.90-7.87 (m, 2H, H1), 7.62 (ddd, J = 1, 1.8, 7.9 Hz, 2H, H4), 7.44-7.39 (m, 2H, H3)

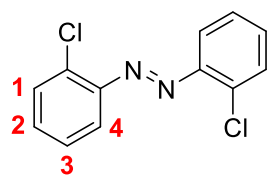
^{13}C -NMR: δ 153.1, 134.1, 130.5, 124.7, 124.5, 123.2

IR (ATR): ν = 3080, 1596, 1467, 1410, 1192, 887, 676 cm^{-1}

MS calcd. for $C_{12}H_9Br_2N_2$ ($[M(^{79}Br)-H]^+$) 338.91, found 338.93

Spectroscopic data correspond to the literature.⁸

(E)-1,2-bis(2-chlorophenyl)diazene (**2m**)



$C_{12}H_8Cl_2N_2$ MW = 251.11 g/mol

Synthesized following GP1 from 2-chloroaniline (1.276 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as yellow solid. Yield: 49% (615 mg, 2.4 mmol).

Eluent: hexane/dichloromethane 9:1

1H -NMR: δ 7.78 (dd, J = 1.8, 7.8 Hz, 2H, H1), 7.57 (dd, J = 1.5, 7.8 Hz, 2H, H2), 7.39 (td, J = 2.9, 6.3 Hz, 4H, H3-H4)

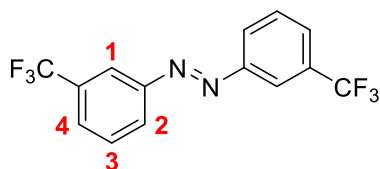
^{13}C -NMR: δ 148.7, 135.8, 132.2, 130.7, 127.4, 118.1

IR (ATR): ν = 1584, 1566, 1462, 1198, 1067, 885, 790 cm^{-1}

MS calcd. for $C_{12}H_8Cl_2N_2$ ($[M-H]^+$) 251.02, found 251.09

Spectroscopic data correspond to the literature.¹⁰

(E)-1,2-bis(3-(trifluoromethyl)phenyl)diazene (**2n**)



$C_{14}H_8F_6N_2$ MW = 318.22 g/mol

Synthesized following GP1 from 3-(trifluoromethyl)aniline (1.611 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as yellowish red solid. Yield: 69% (1.097 g, 3.4 mmol).

Eluent: hexane/ethyl acetate 95:5

1H -NMR: δ 8.22 (s, 2H, H1), 8.14 (d, J = 7.9 Hz, 2H, H2), 7.78 (d, J = 7.8 Hz, 2H, H3), 7.67 (7, J = 15.6, 7.8 Hz, 2H, H4)

^{13}C -NMR: δ 152.2, 131.8 (q, J = 33.0 Hz), 129.9, 127.9 (q, J = 3.7 Hz), 125.5, 123.75 (q, J = 272.5 Hz, -CF₃), 119.7 (q, J = 4.0 Hz)

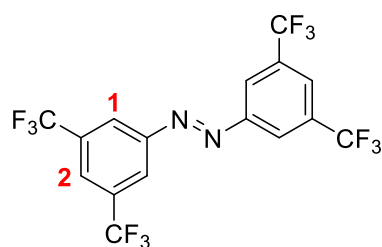
^{19}F -NMR: δ -62.8

IR (ATR): ν = 2962, 1581, 1492, 1309, 1251, 1197, 1099, 892, 825 cm^{-1}

MS calcd. for $C_{14}H_8F_6N_2$ ($[M-H]^+$) 319.07, found 319.16

Spectroscopic data correspond to the literature.⁸

(E)-1,2-bis(3,5-bis(trifluoromethyl)phenyl)diazene (**2o**)



$C_{16}H_6F_{12}N_2$ MW = 454.22 g/mol

Synthesized following GP1 from 3,5-bis(trifluoromethyl)aniline (2.291 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as yellow solid. Yield: 63% (1.430 g, 3.1 mmol).

Eluent: hexane

1H -NMR: δ 8.45 (s, 4H, H1), 8.07 (s, 2H, H2)

^{13}C -NMR: δ 152.1, 133.1 (q, $J = 34.1$ Hz, $-CCF_3$), 125.3-125.0 (m), 123.6-123.2 (m), 122.9 (q, $J = 272.73$ Hz, $-CF_3$)

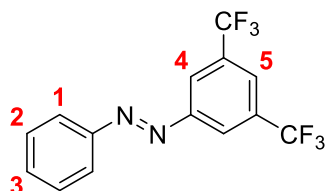
^{19}F -NMR: δ -58.2

IR (ATR): $\nu = 1373, 1277, 1262, 1165, 1105, 1055, 935, 907, 847, 729$ cm^{-1}

MS calcd. for $C_{16}H_7F_6N_2$ ($[M-H]^+$) 455.04, found 455.09

Spectroscopic data correspond to the literature.⁵

(E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenyldiazene (**2p**)



$C_{14}H_8F_6N_2$ MW = 318.22

Synthesized from nitrosobenzene (5 mmol) and 3,5-bis(trifluoromethyl)aniline (5 mmol).

Isolated as orange solid. Yield: 77% (1.226 g, 3.8 mmol)

Eluent: hexane/ethyl acetate 9:1

1H -NMR: δ 8.37 (s, 2H, H4), 8.01-7.95 (m, 3H, H1-H5), 7.59-7.54 (m, 3H, H2-H3)

^{13}C -NMR: δ 152.8, 152.0, 132.7 (q, $J=33.8$, $-CCF_3$), 132.5, 129.3, 123.9-123.5 (m), 123.4, 123.2-122.8 (m), 123.1 (q, $J = 272.9$ Hz, $-CF_3$)

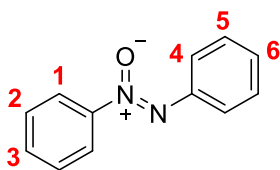
^{19}F -NMR: δ -63.0

IR (ATR): $\nu = 1367, 1274, 1164, 1119, 1104, 897, 842, 772$ cm^{-1}

MS calcd. for $C_{14}H_9N_2F_6$ ($[M-H]^+$) 319.07, found 319.04

Spectroscopic data correspond to the literature.¹¹

(E)-1,2-diphenyldiazene 1-oxide (**3a**)



C₁₂H₁₀N₂O MW = 198.23

Isolated from the reaction of Table 1, entry 2 from aniline (0.9313 g, 10 mmol) and hydrogen peroxide (0.972 g of 35 w/w% solution, 10 mmol)

Isolated as a yellow solid. Yield: 74% (1.46 g, 7.4 mmol)

Eluent: hexane

¹H-NMR: δ 8.35-8.31 (m, 2H, H1), 8.21-8.18 (m, 2H, H2), 7.53 (dddd, J = 1.3, 5.4, 7.9, 9.9 Hz, 5H, H4-H5-H6), 7.43-7.38 (m, 1H, H3)

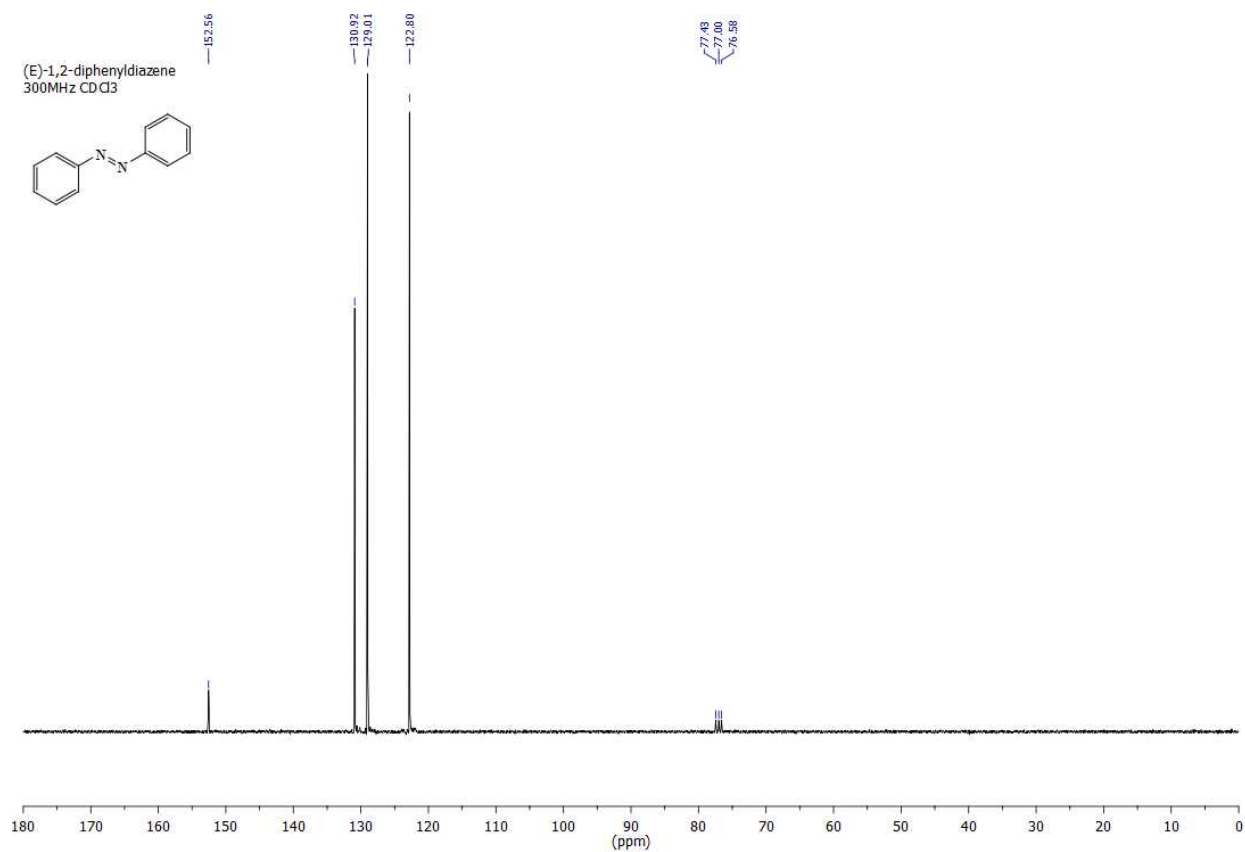
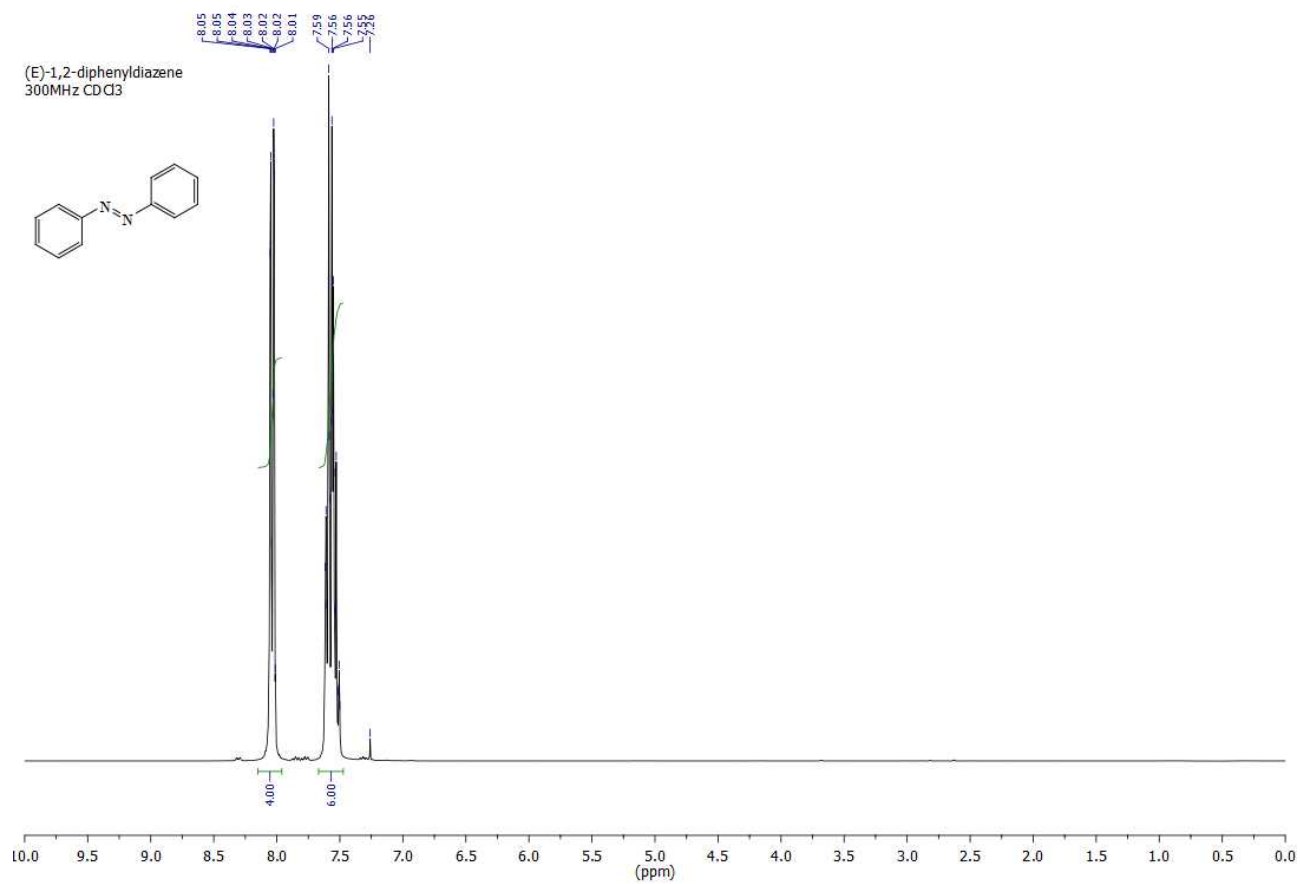
¹³C-NMR: δ 144, 131.5, 129.6, 128.7, 128.6, 125.5, 122.3

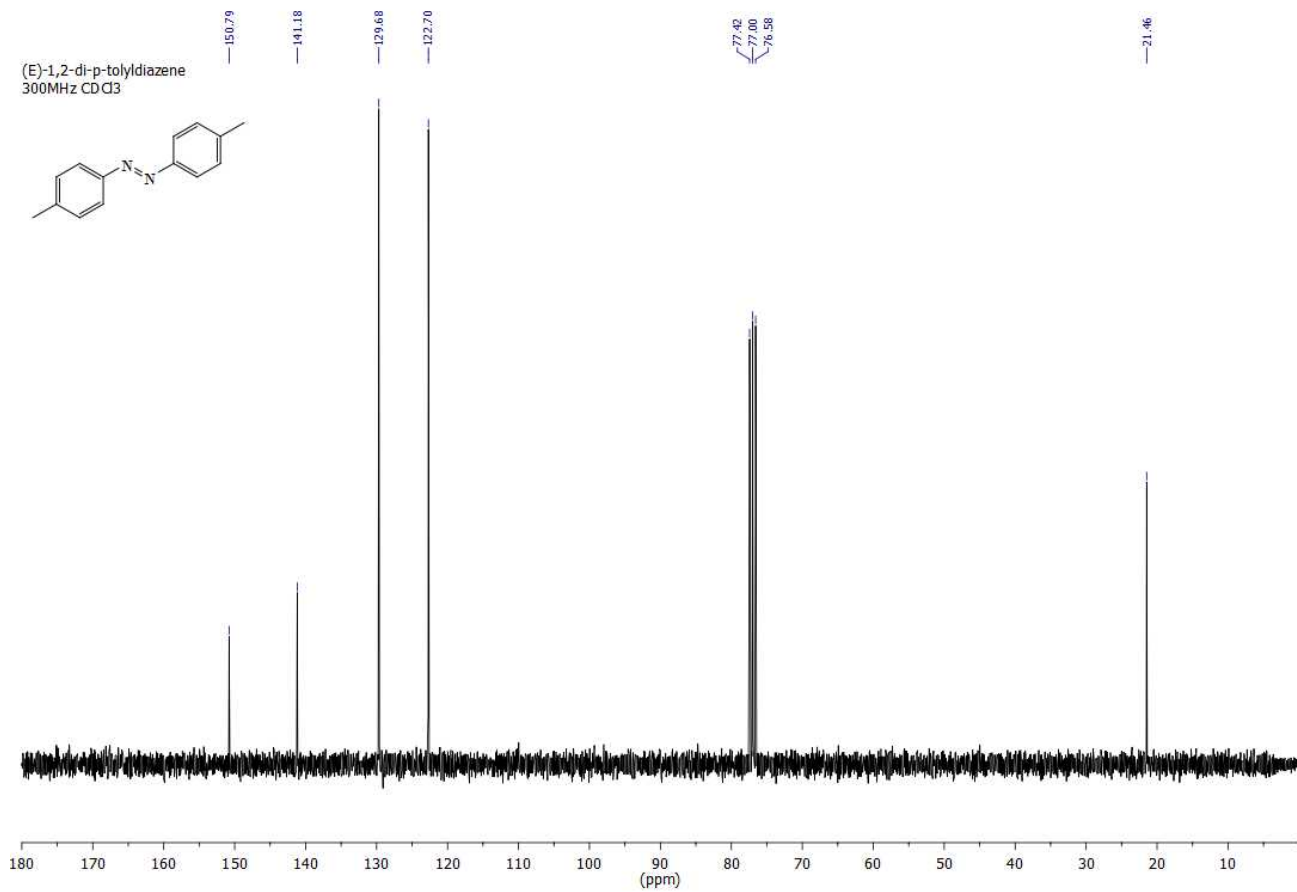
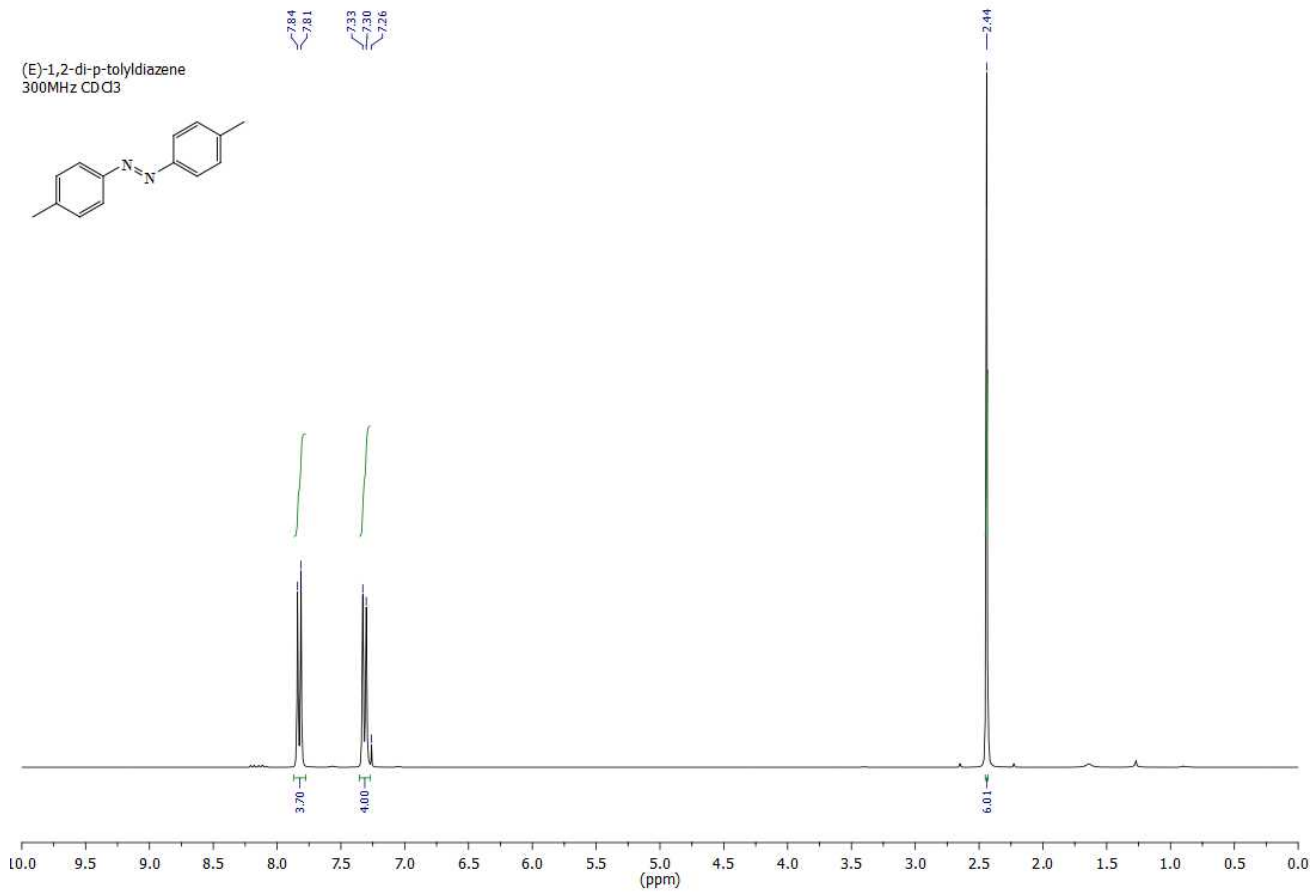
IR (ATR): ν = 1478, 1437, 1296, 1162, 1071, 1024, 917, 762, 683, 521

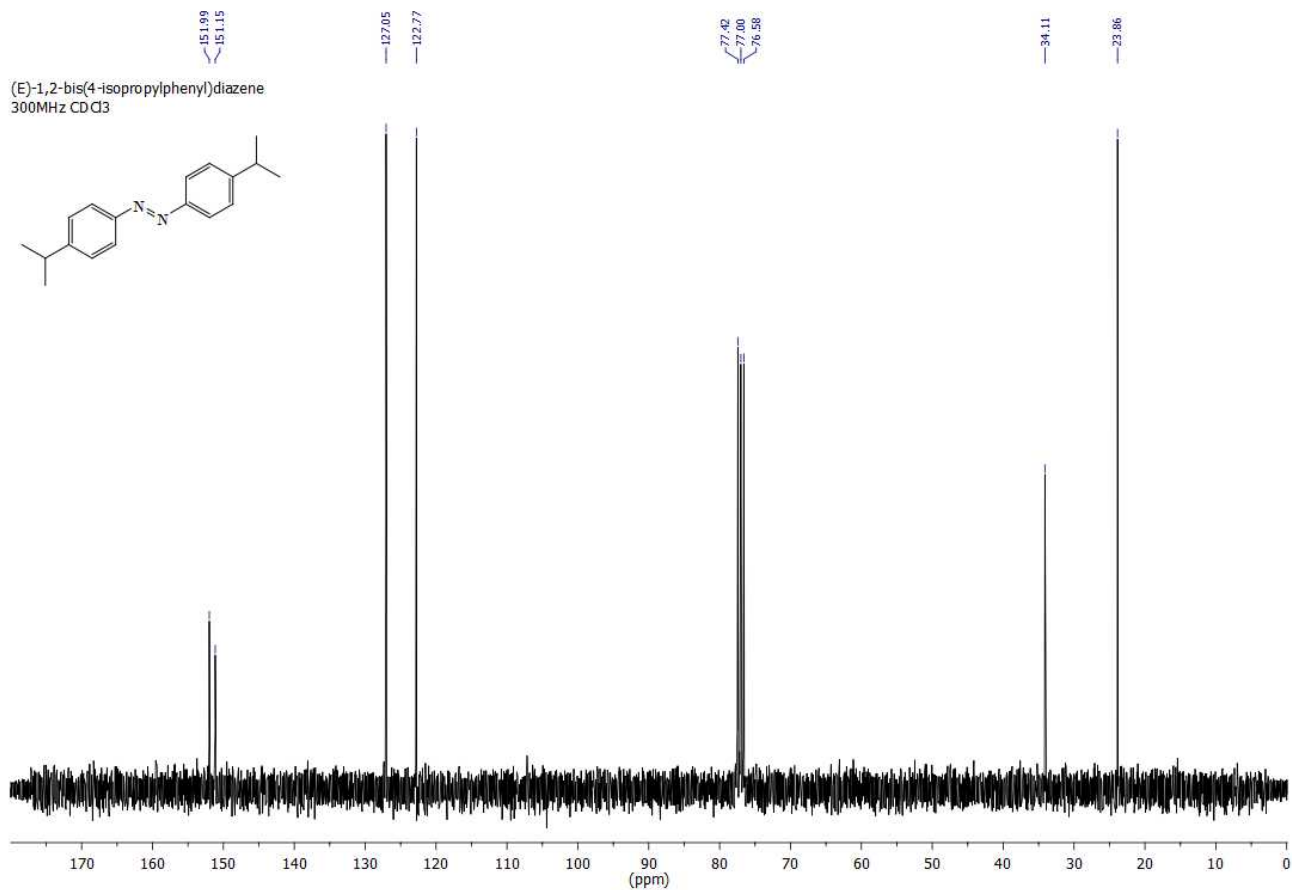
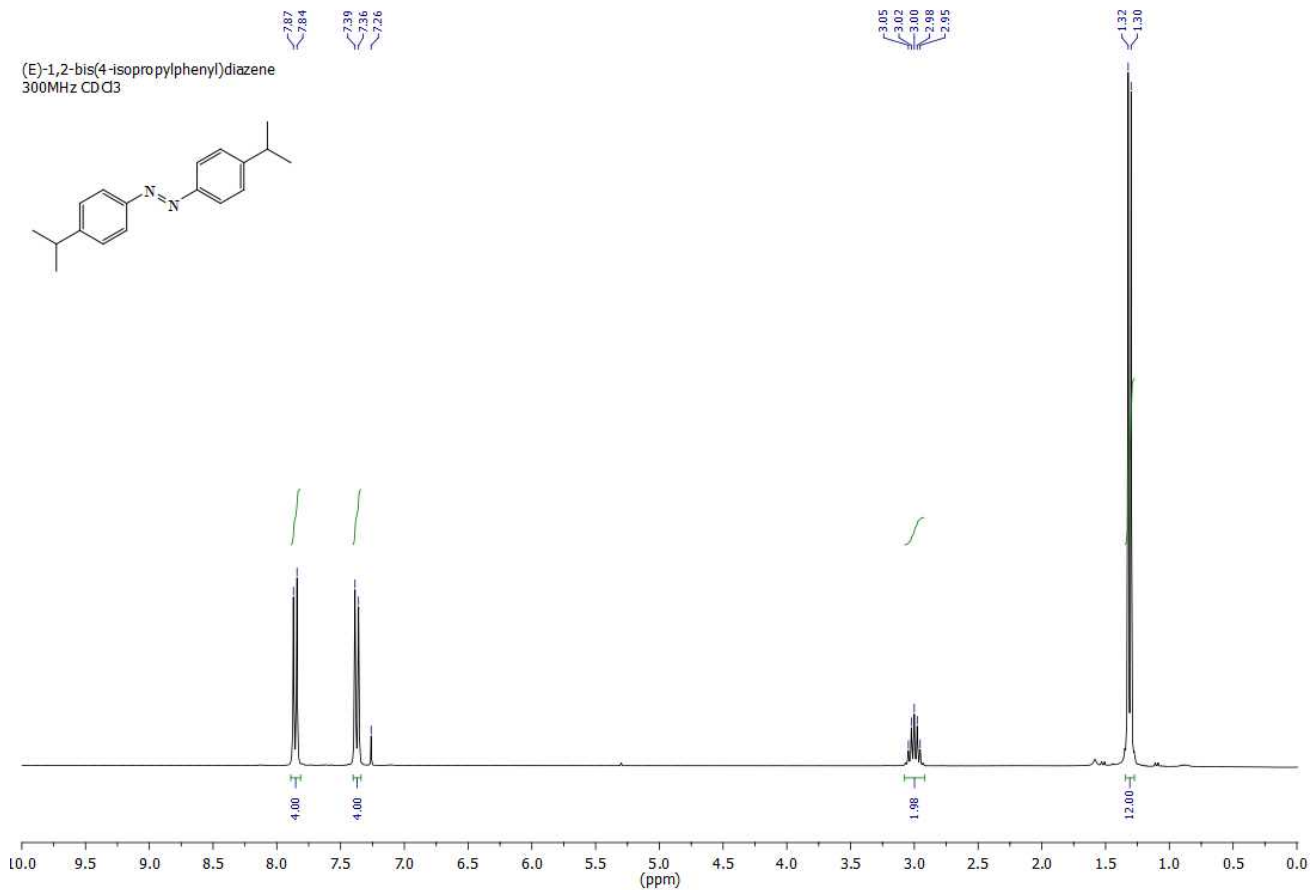
MS calcd. for C₁₂H₁₁N₂O ([M-H]⁺) 199.09, found 199.12

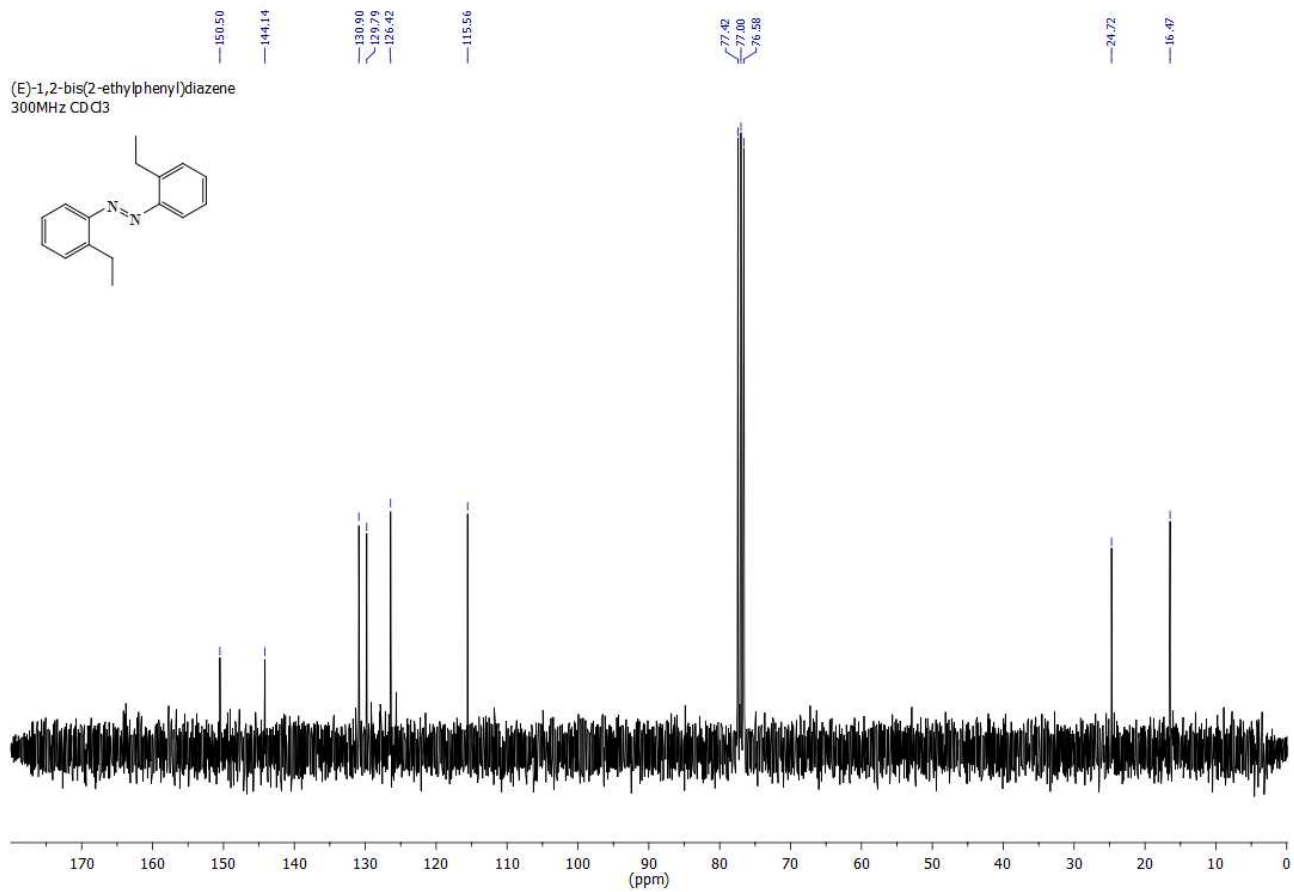
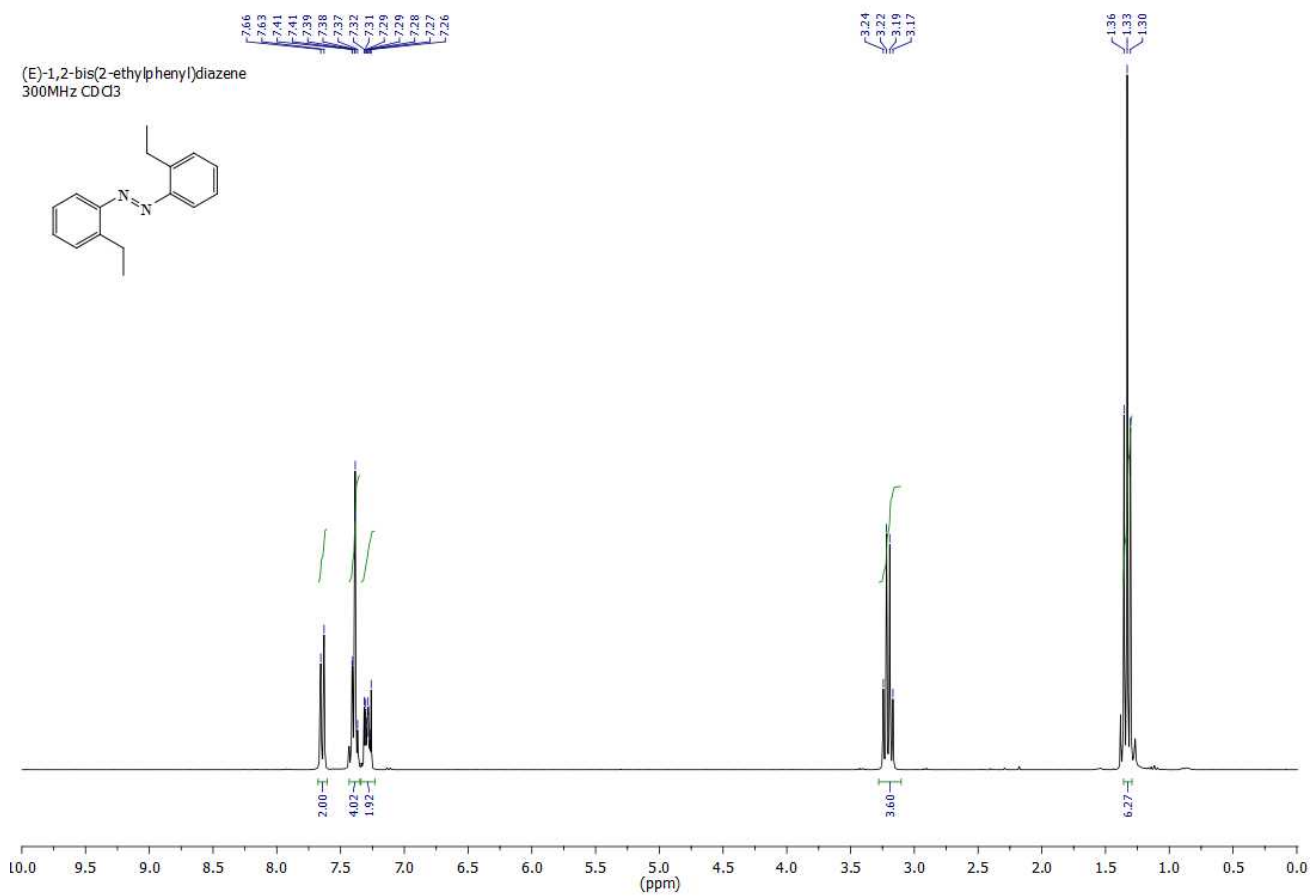
Spectroscopic data correspond to the literature.¹²

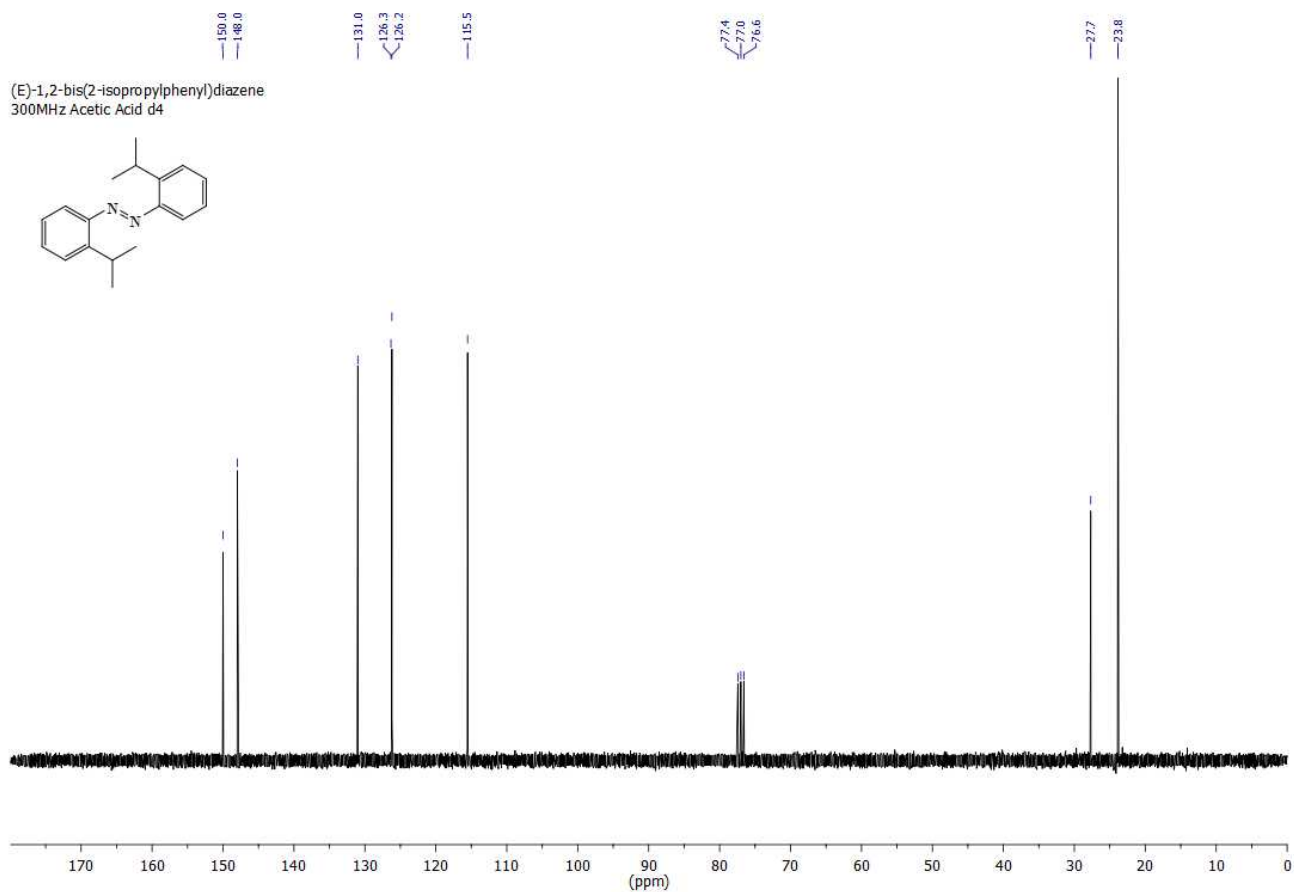
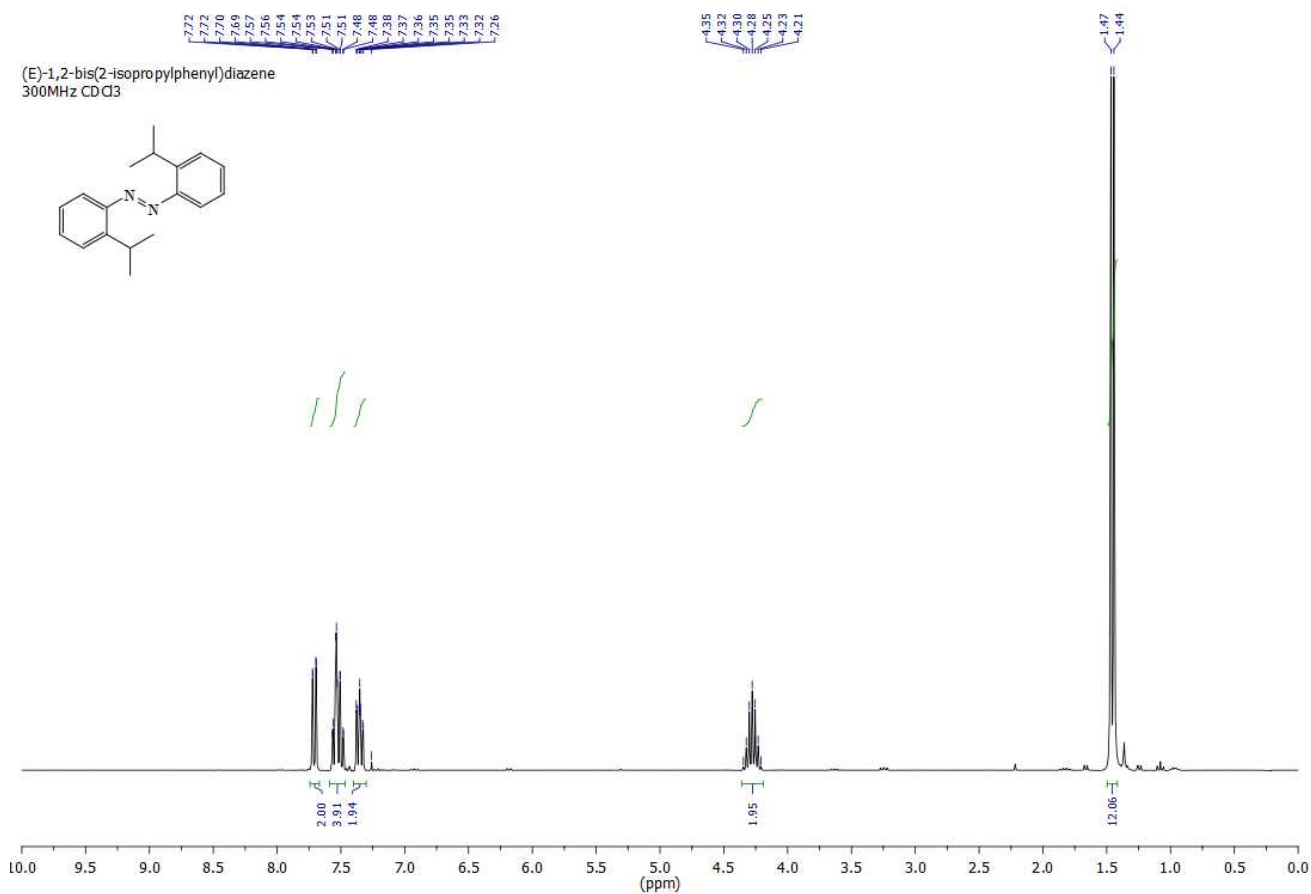
6. Copies of NMR spectra



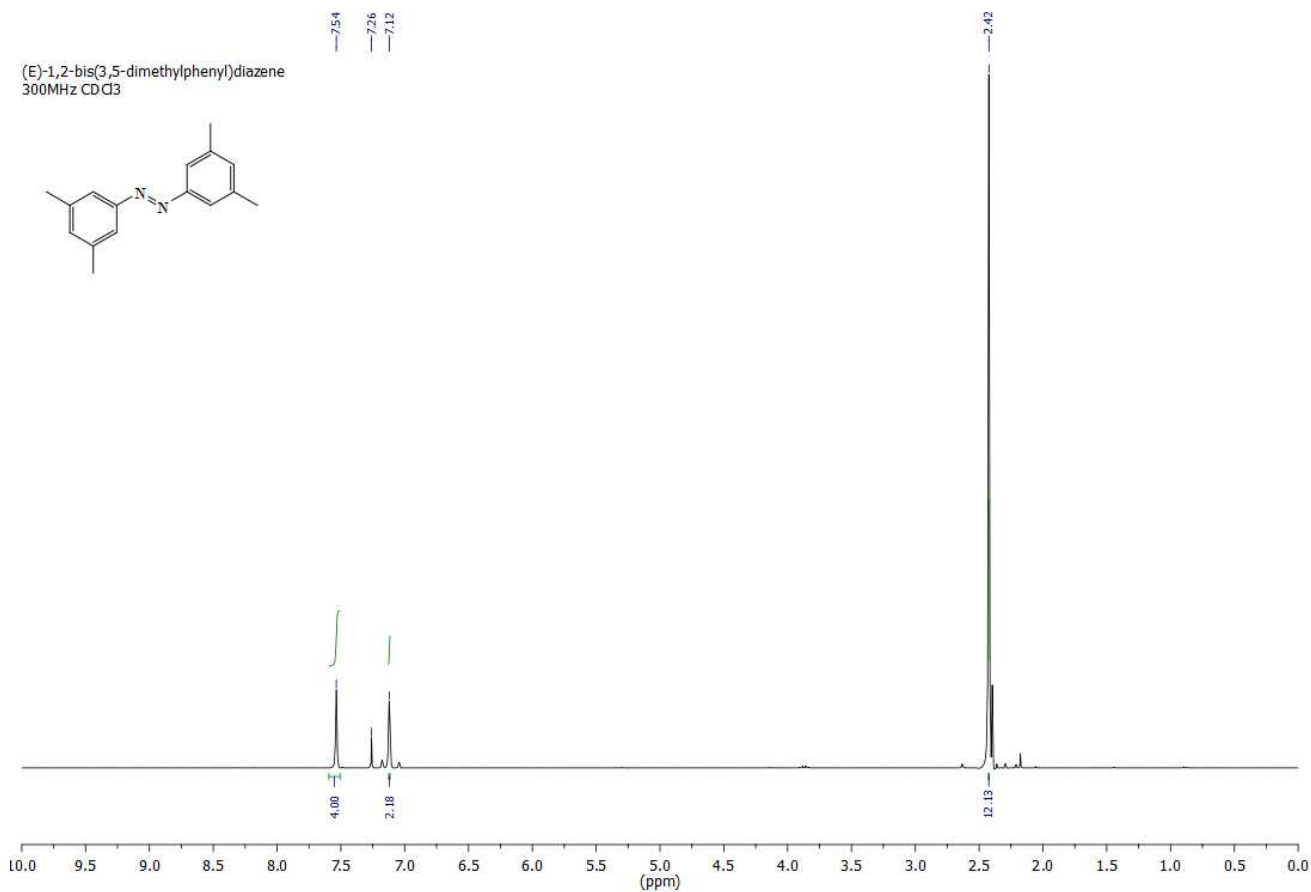
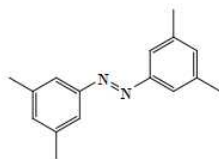




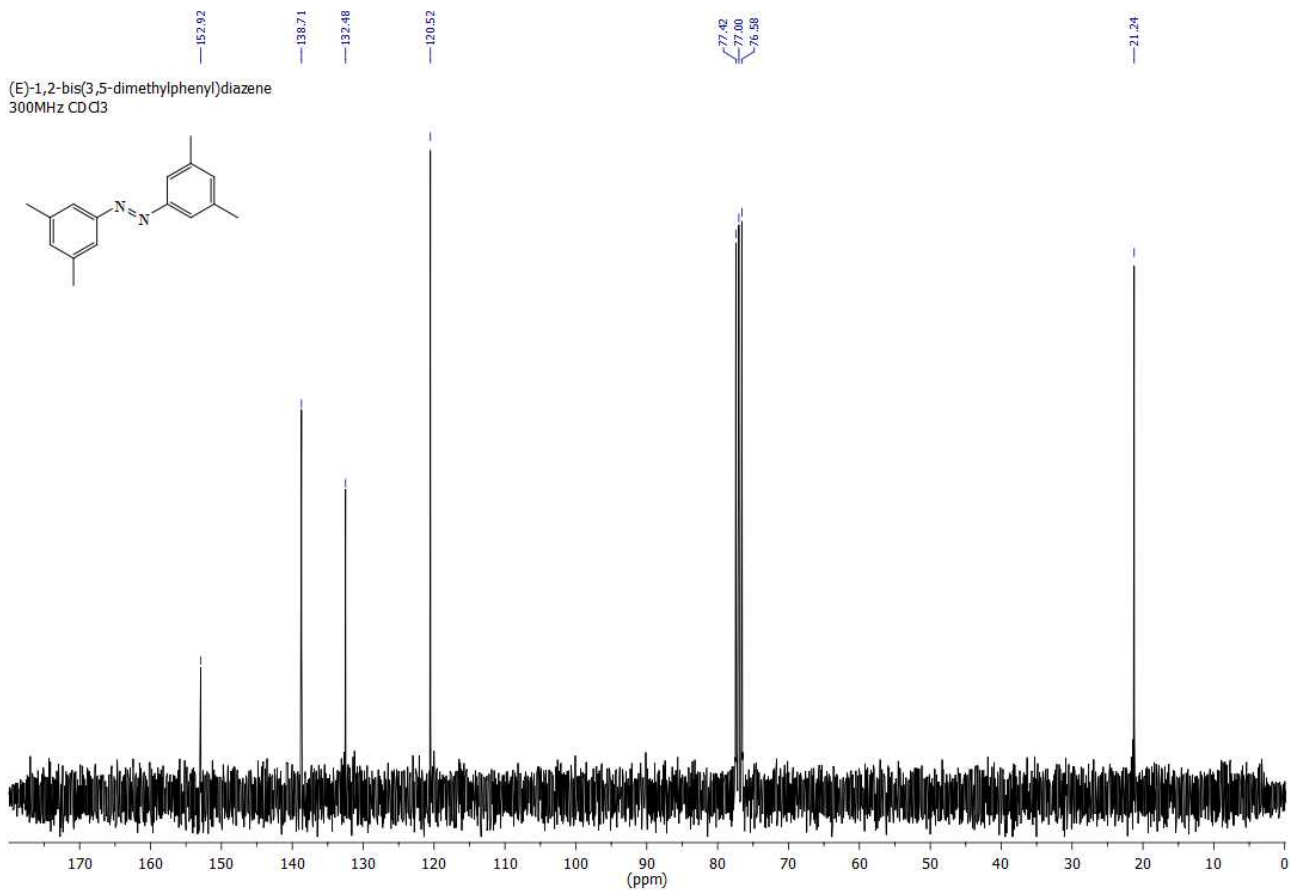
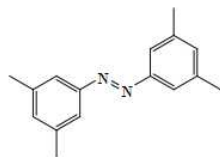


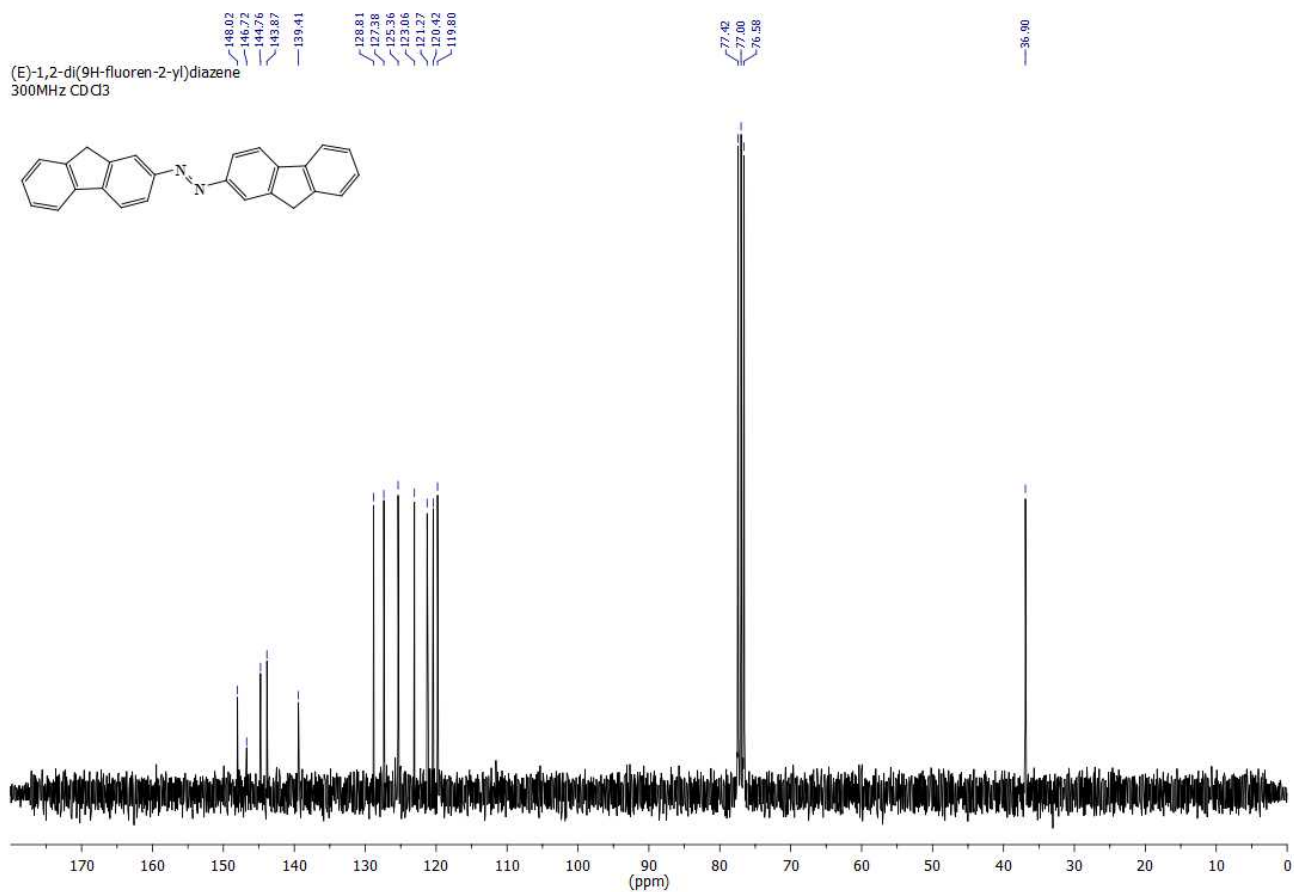
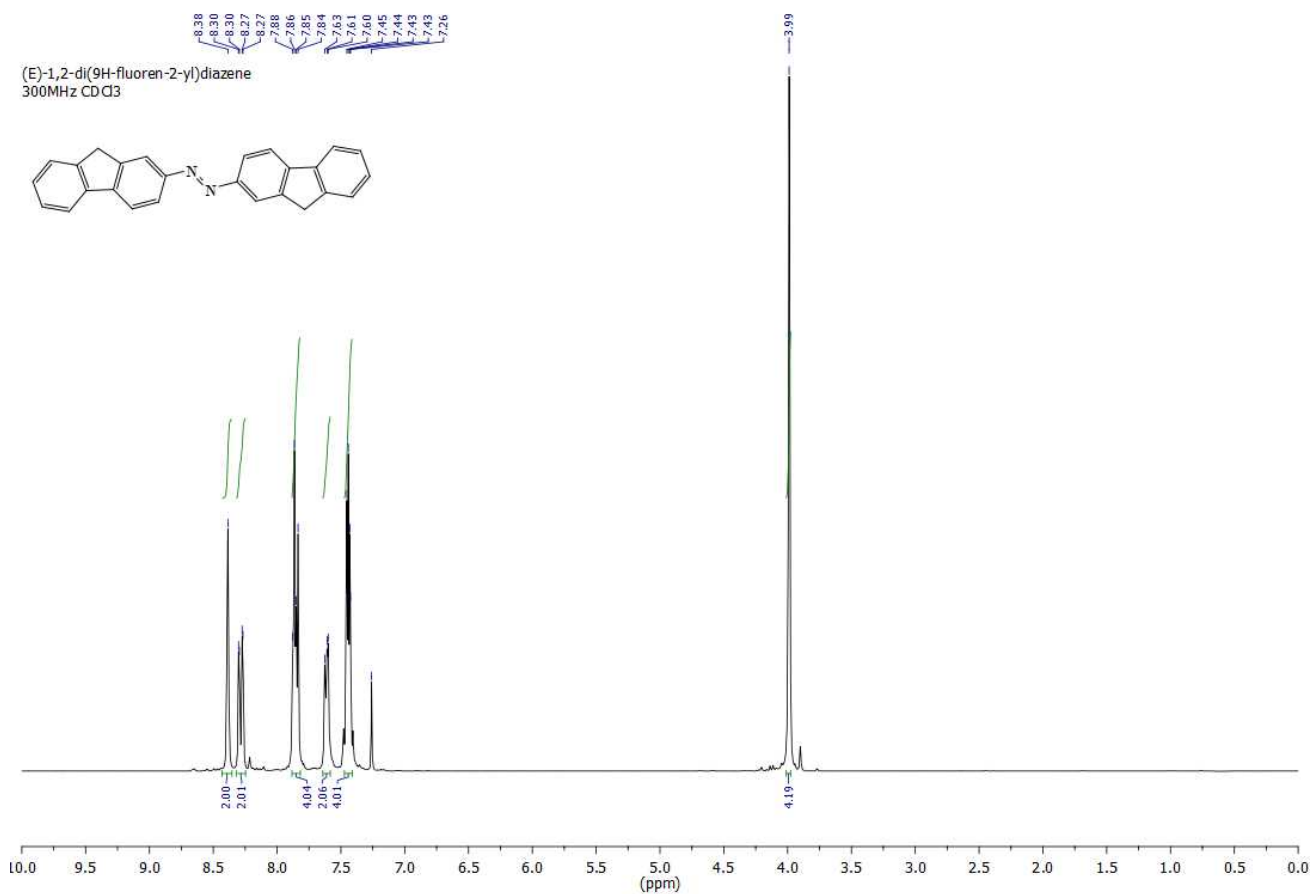


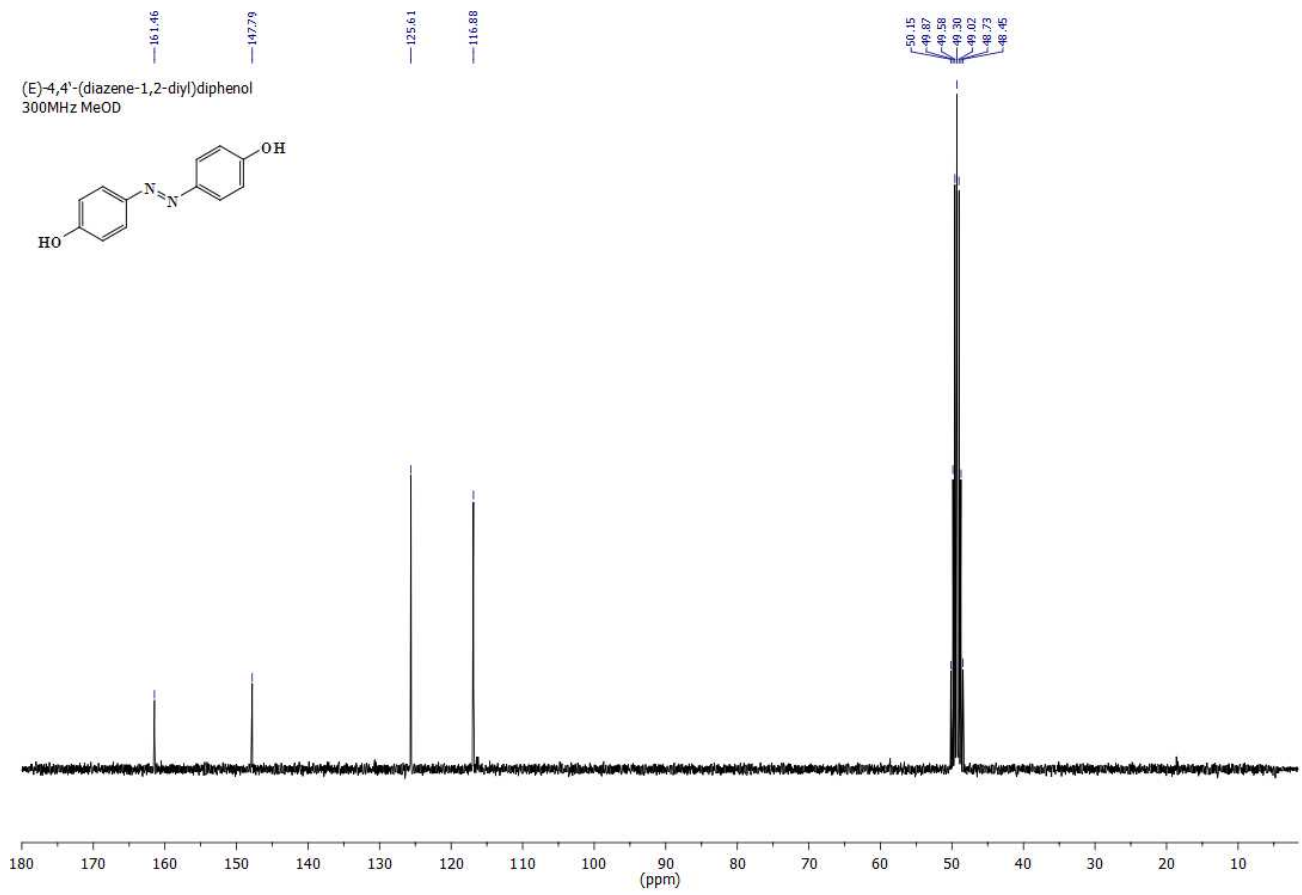
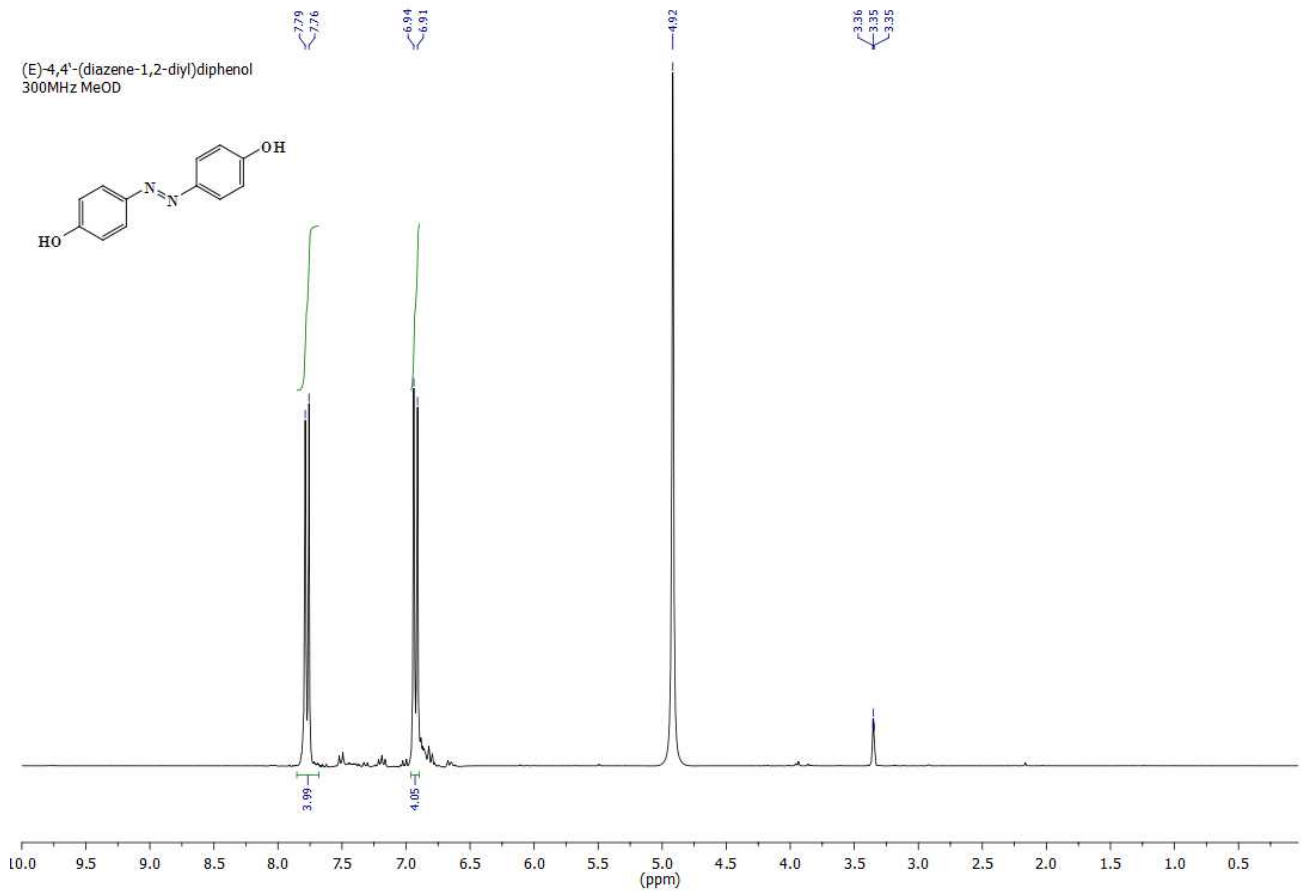
(E)-1,2-bis(3,5-dimethylphenyl)diazene
300MHz CDCl₃

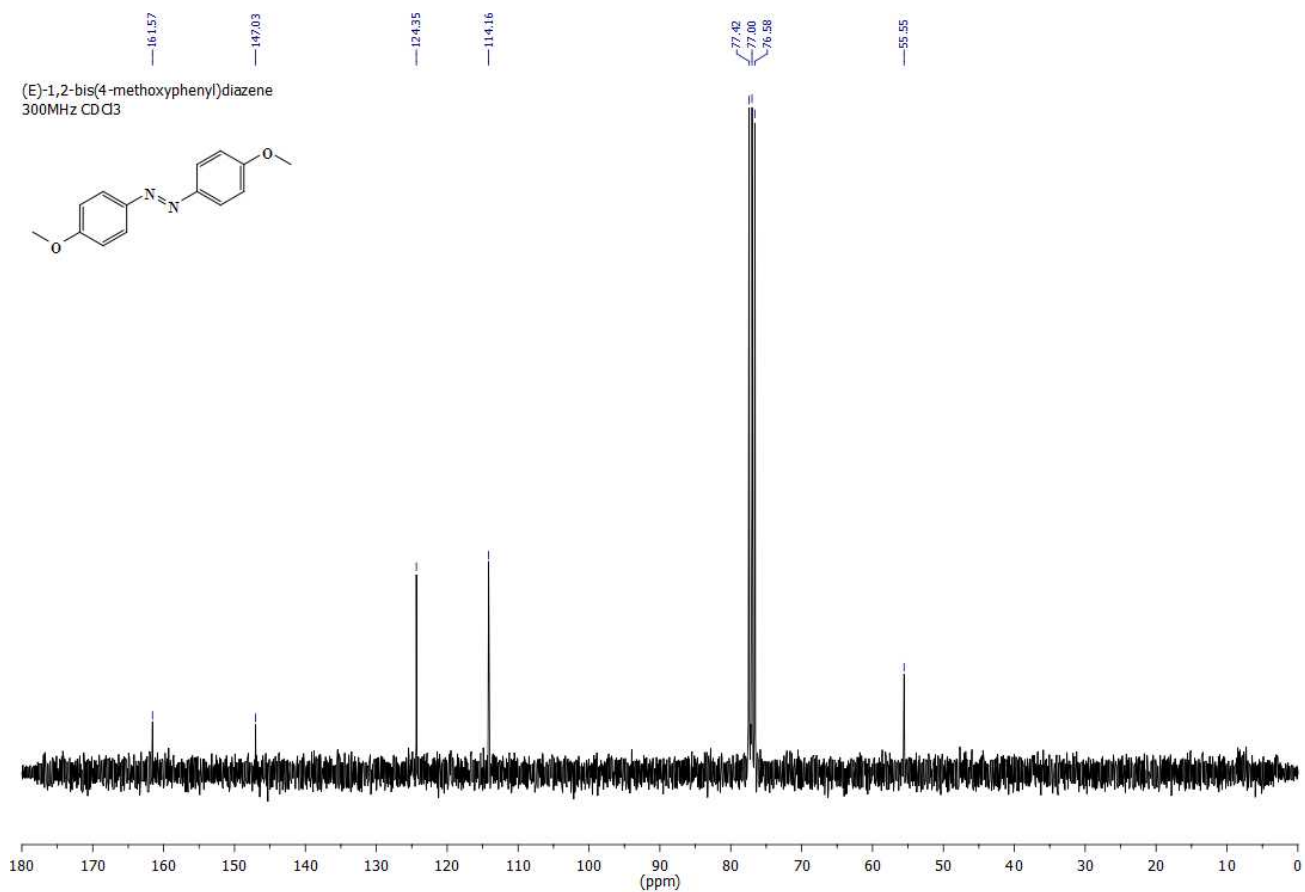
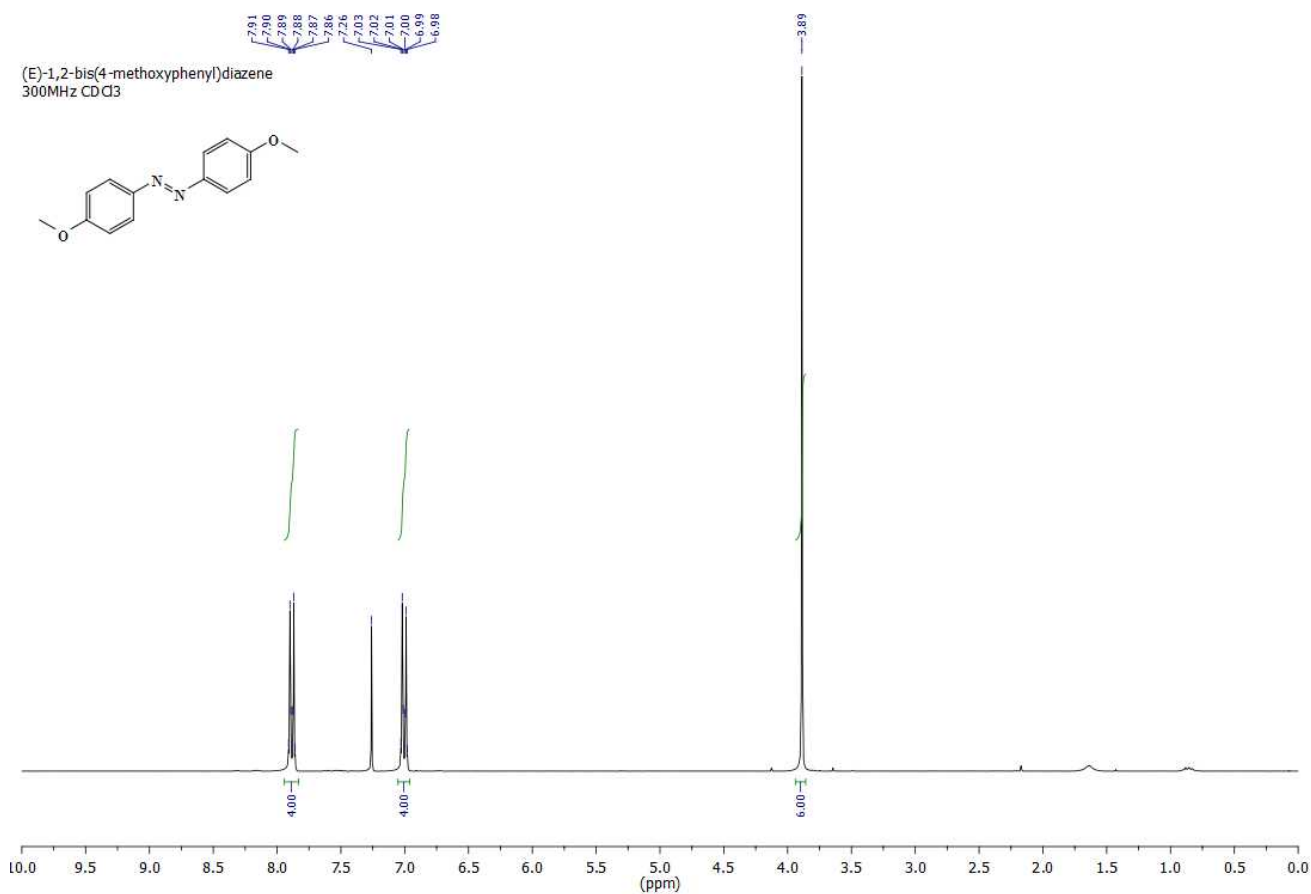


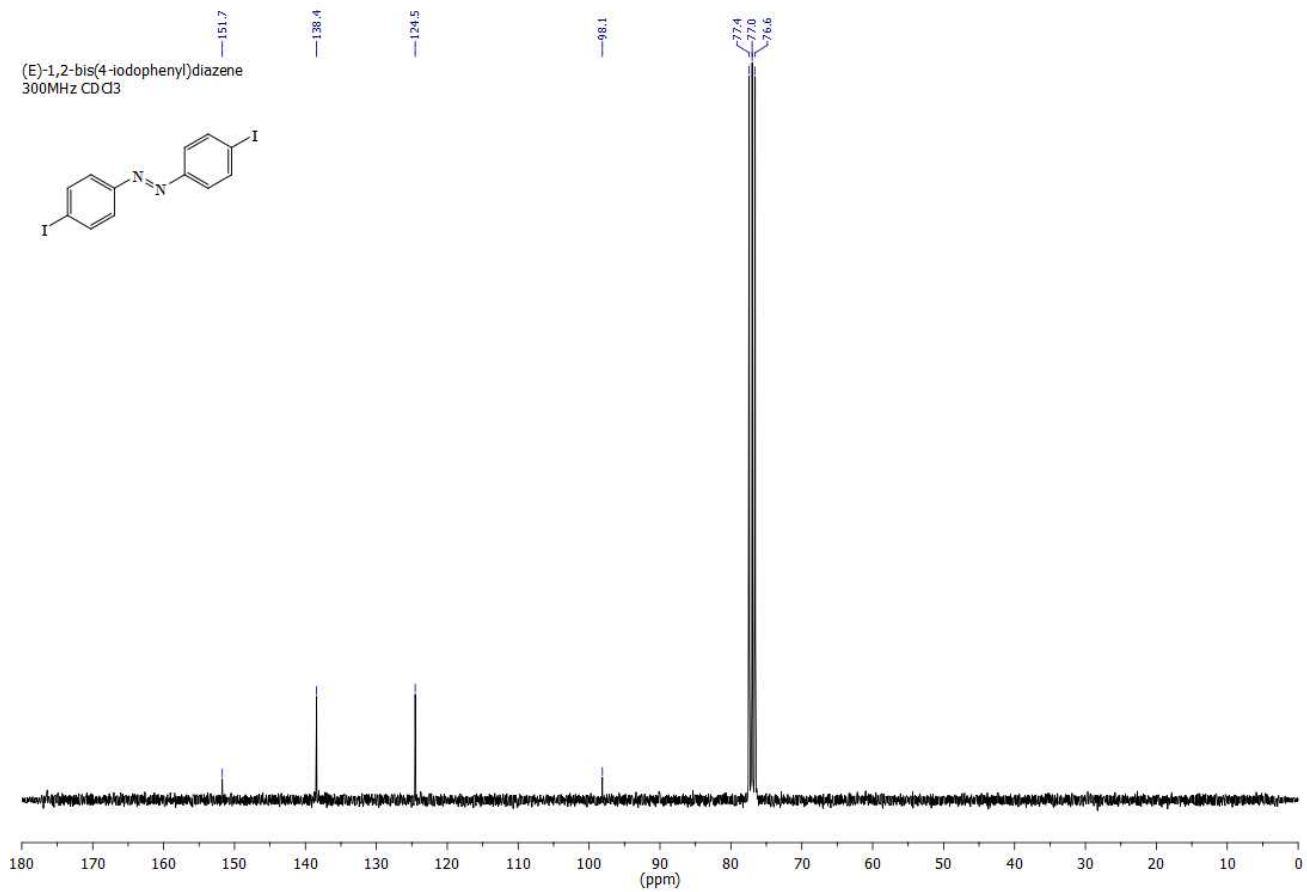
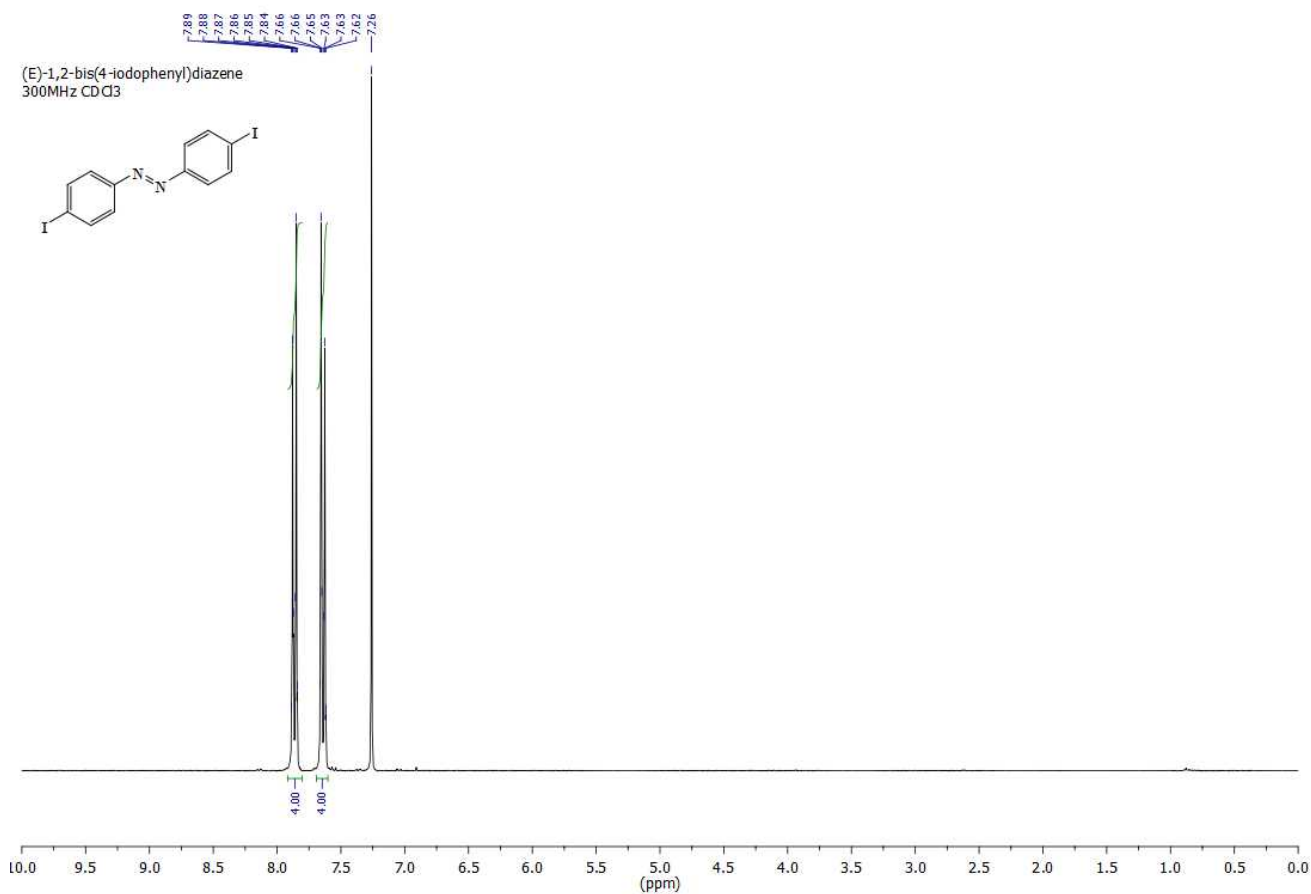
(E)-1,2-bis(3,5-dimethylphenyl)diazene
300MHz CDCl₃



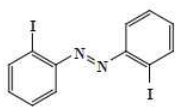




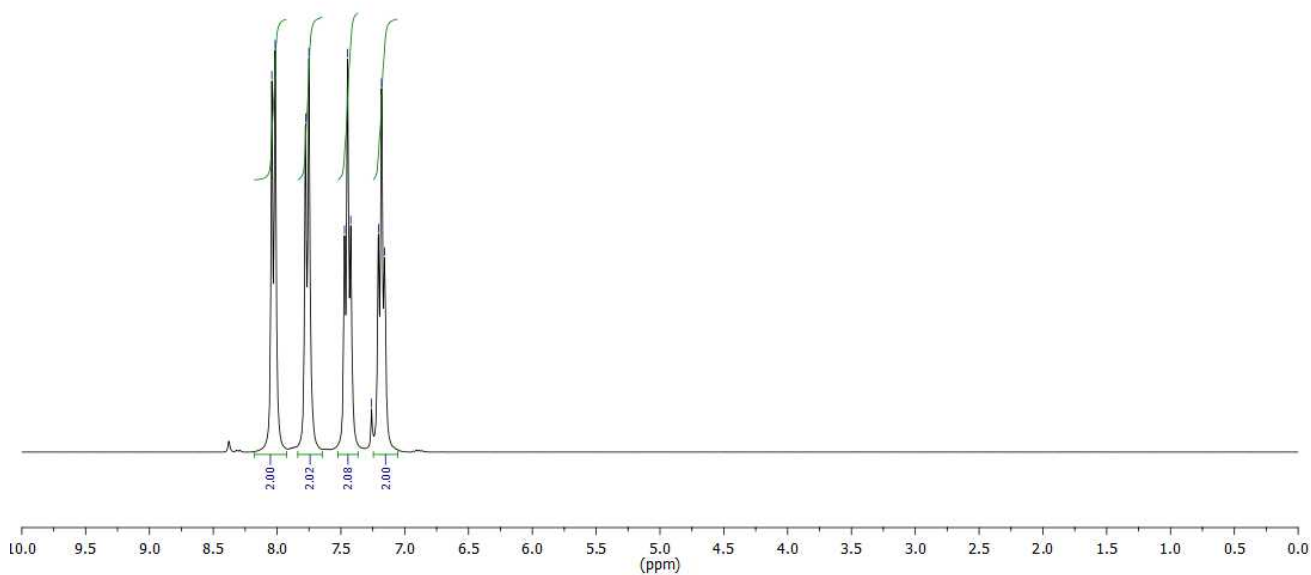




(E)-1,2-bis(2-iodophenyl)diazene
300MHz CDCl₃

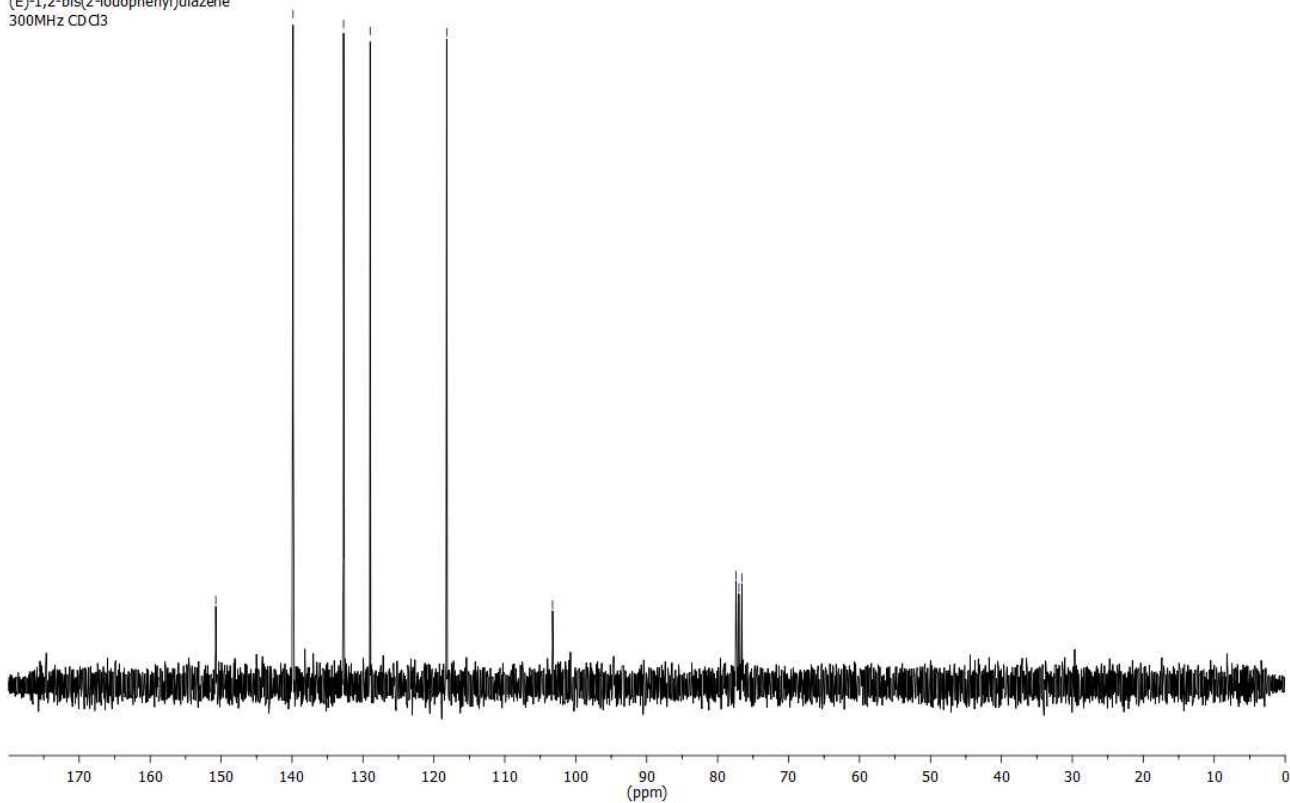


8.04
8.02
7.78
7.75
7.47
7.45
7.36
7.30
7.18
7.16

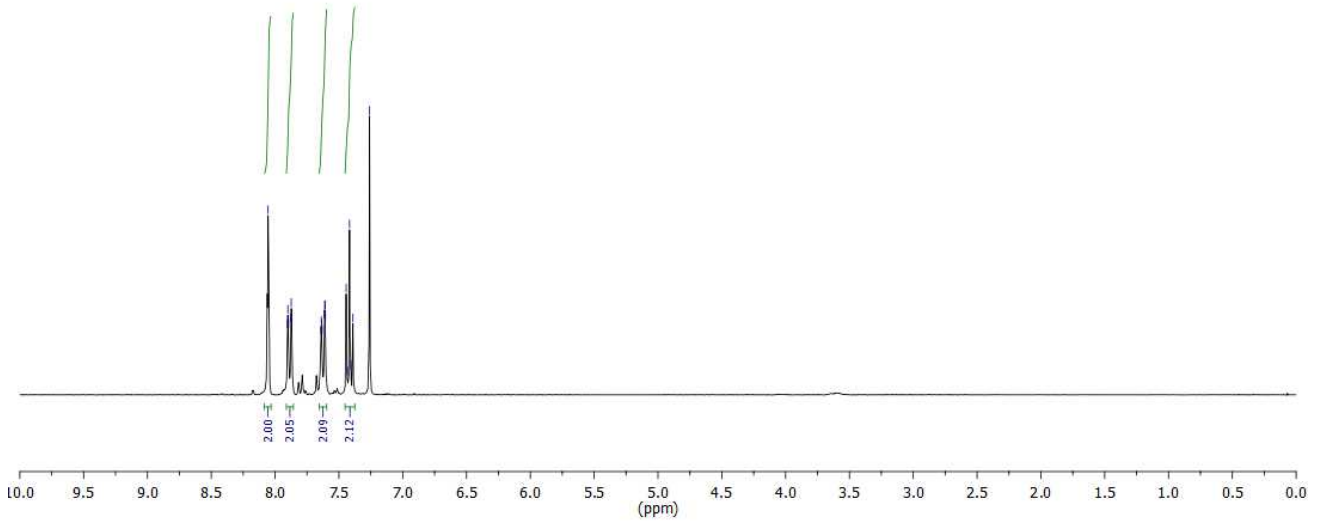
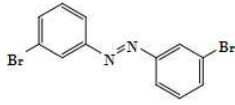


(E)-1,2-bis(2-iodophenyl)diazene
300MHz CDCl₃

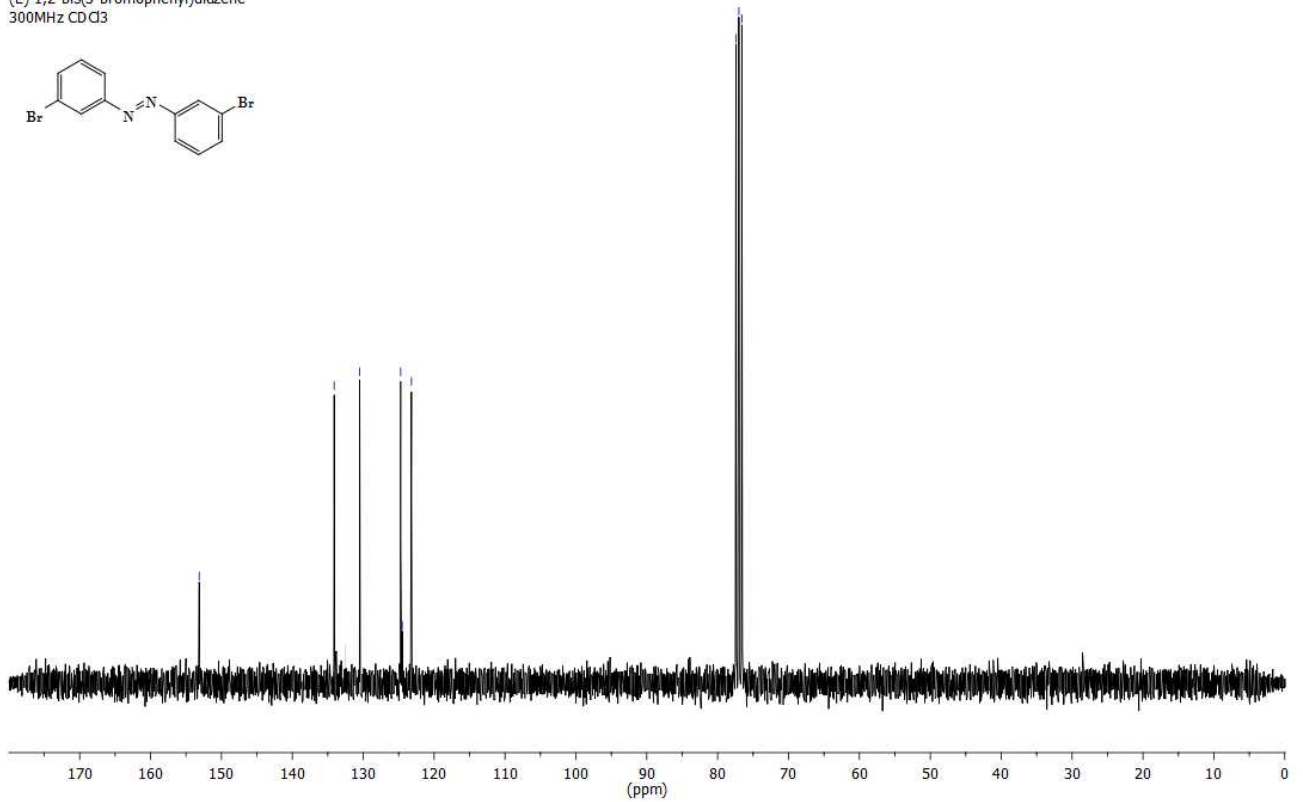
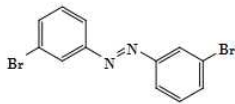
150.74
139.85
132.74
128.99
118.20
103.27
77.42
77.00
76.58

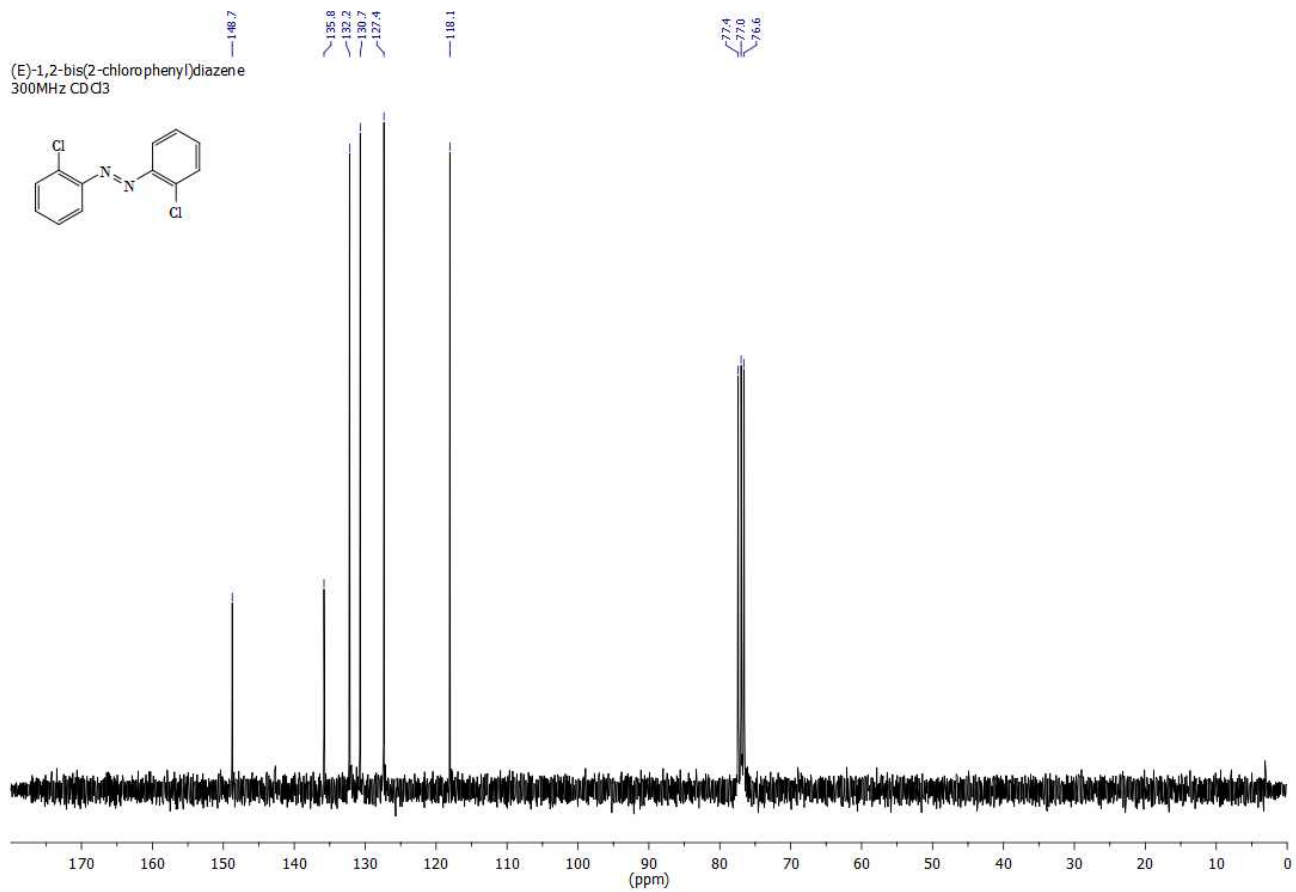
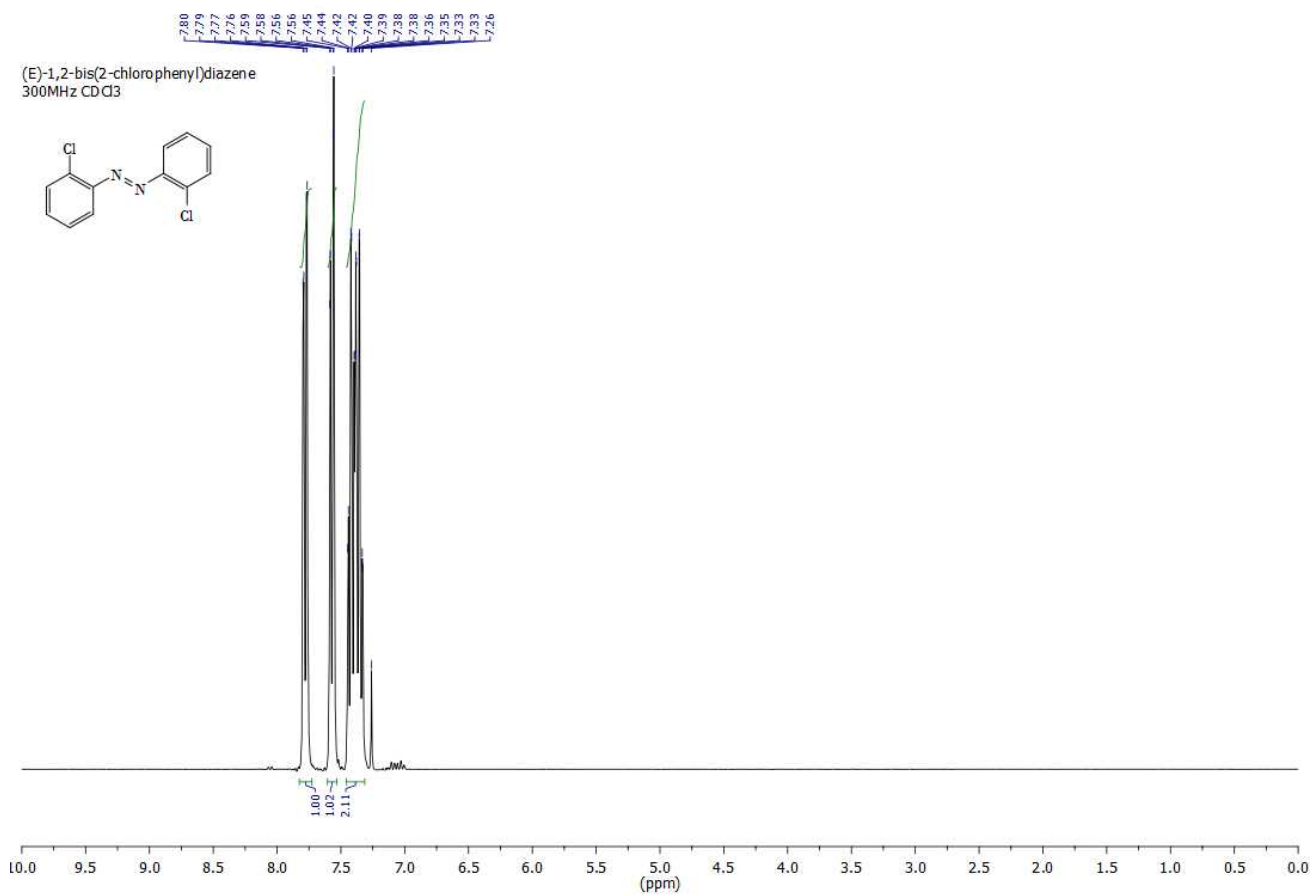


(E)-1,2-bis(3-bromophenyl)diazene
300MHz CDCl₃

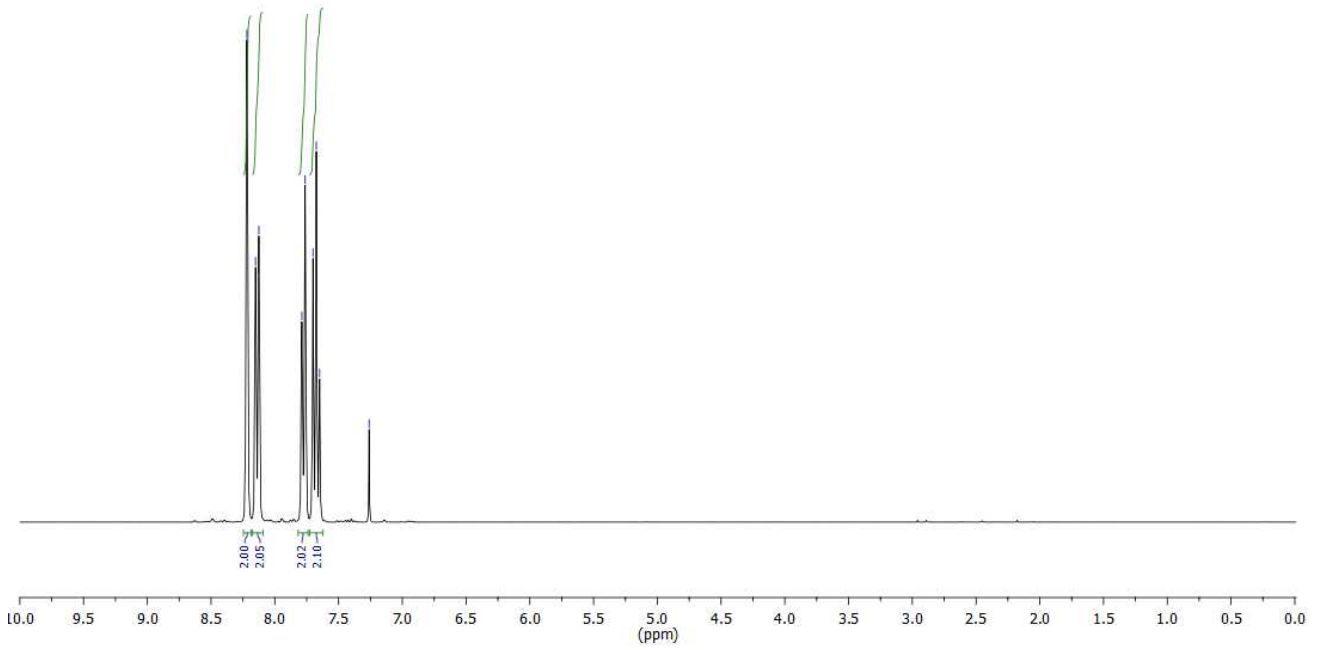
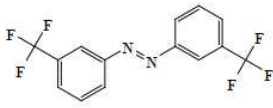


(E)-1,2-bis(3-bromophenyl)diazene
300MHz CDCl₃

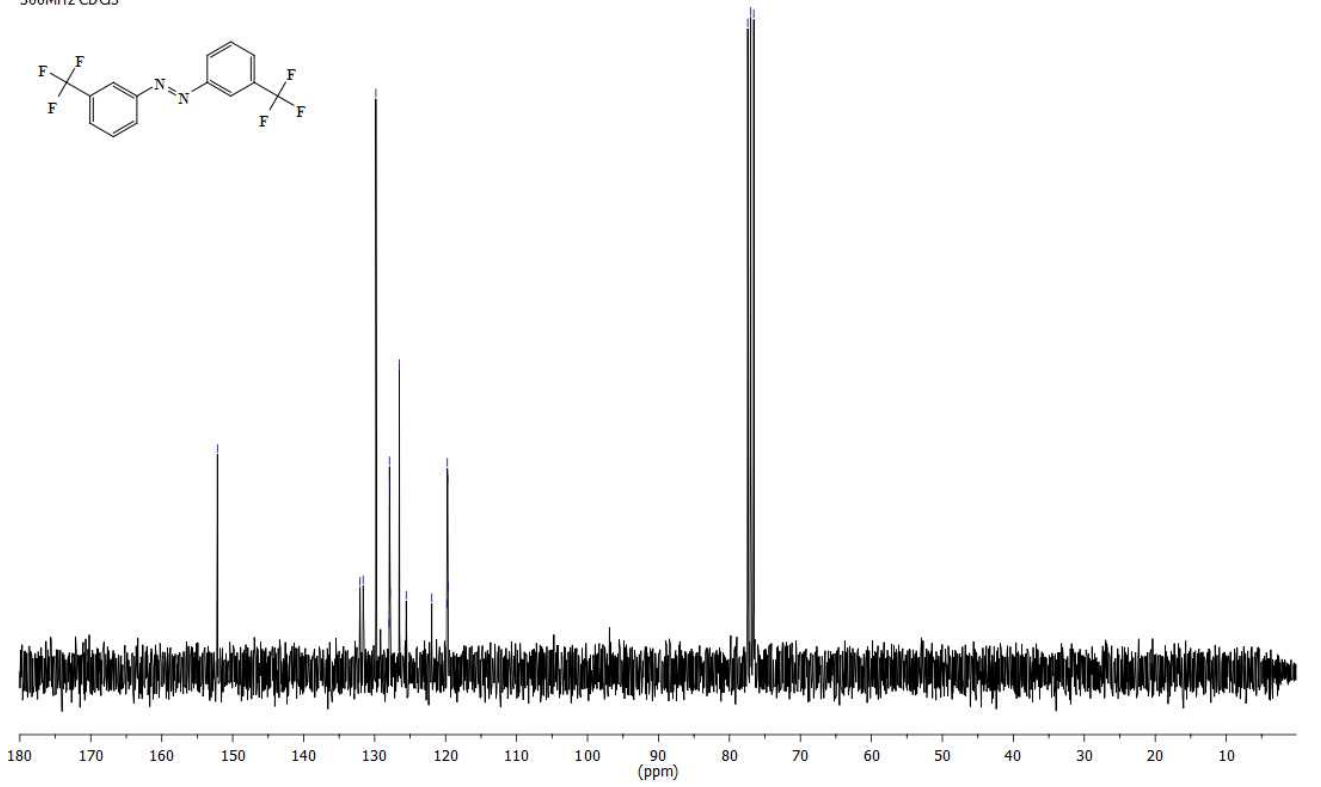
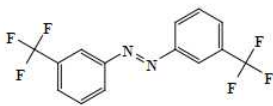




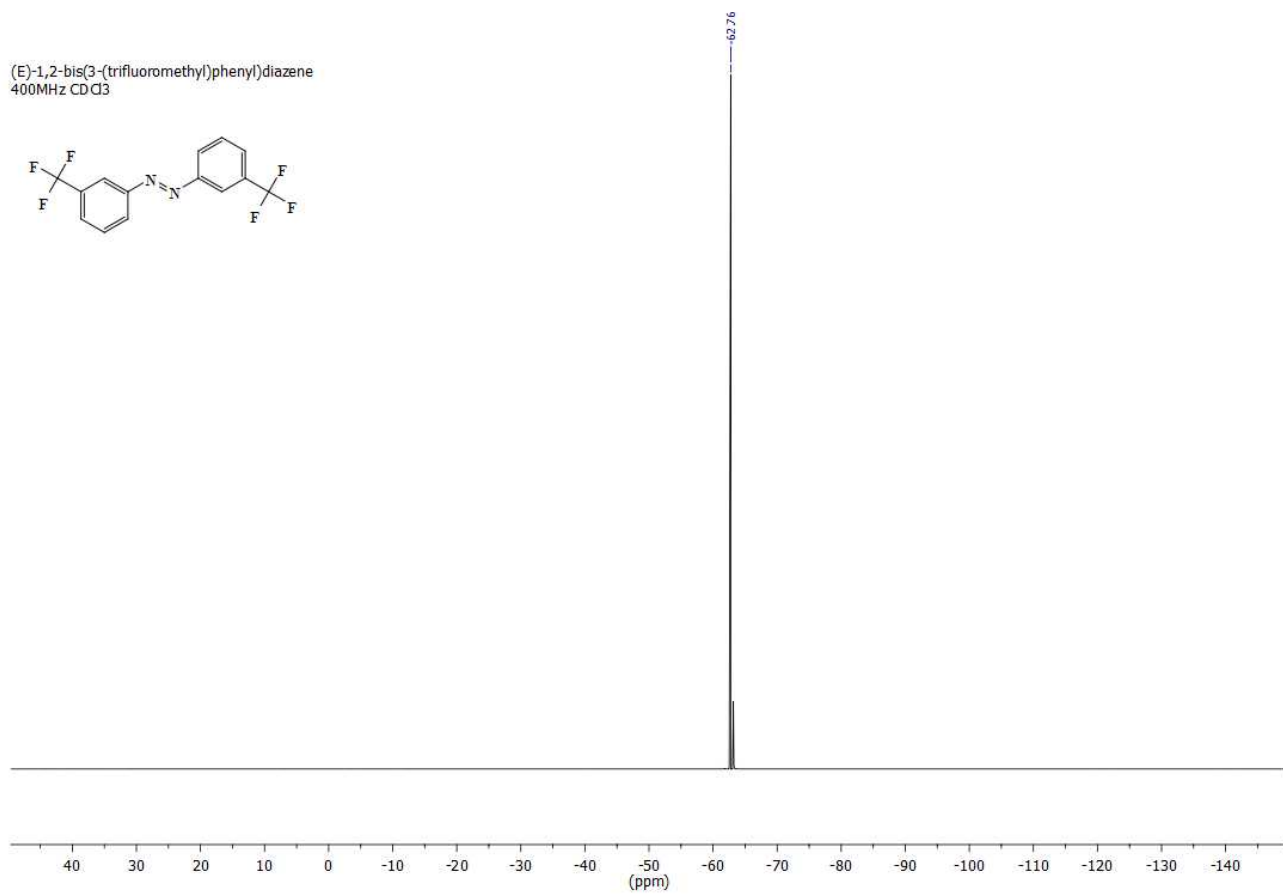
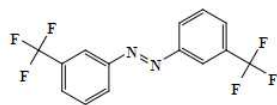
(E)-1,2-bis(3-(trifluoromethyl)phenyl)diazene
300MHz CDCl₃

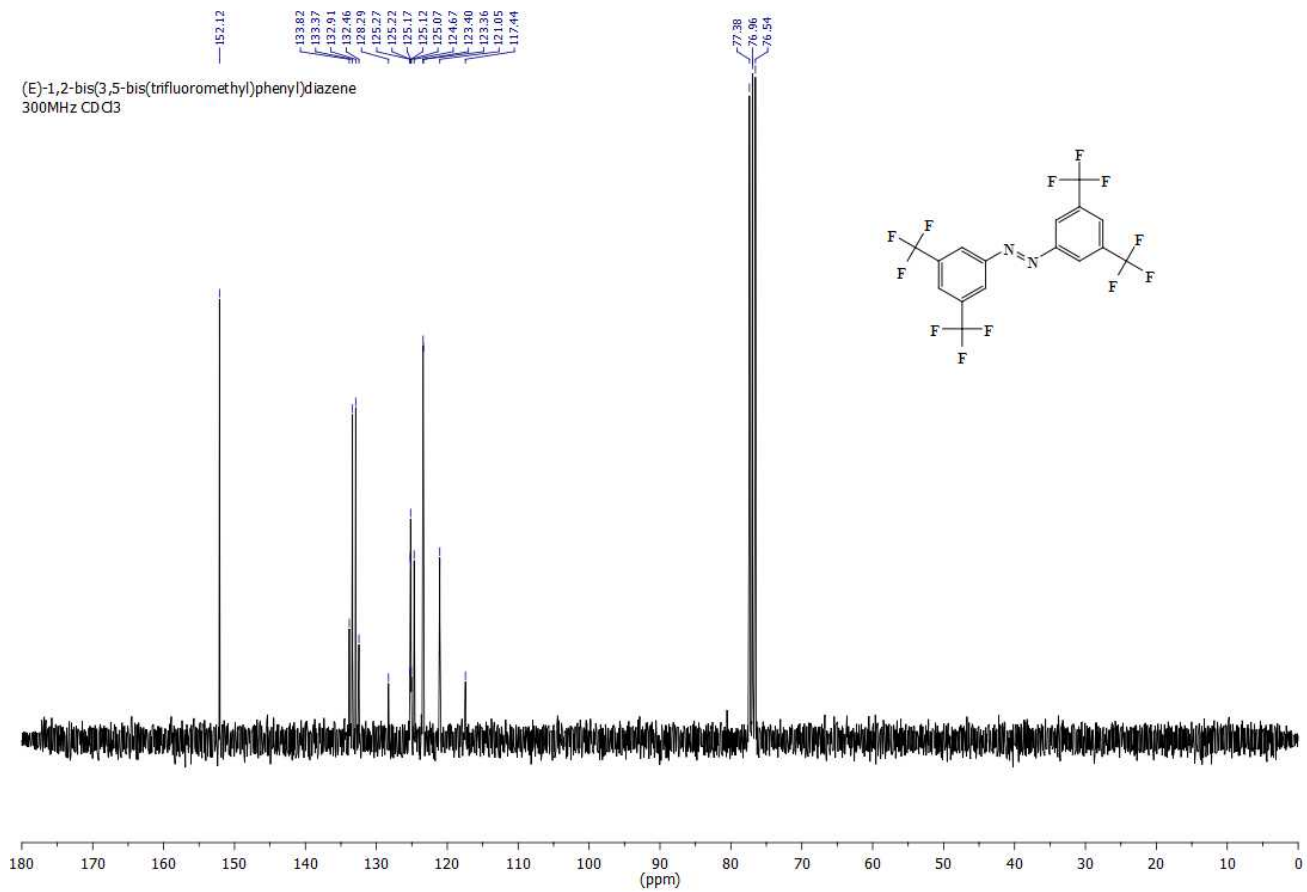
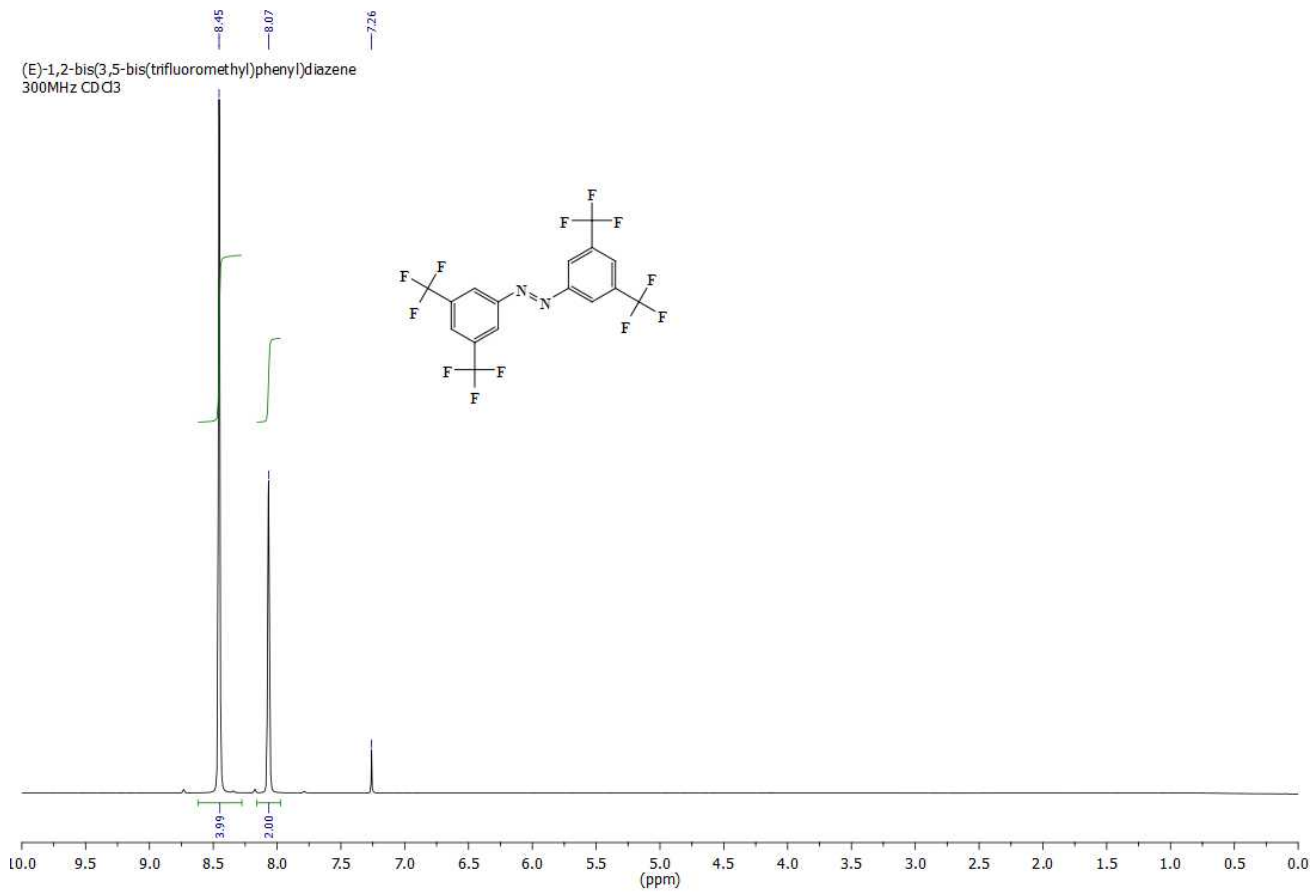


(E)-1,2-bis(3-(trifluoromethyl)phenyl)diazene
300MHz CDCl₃

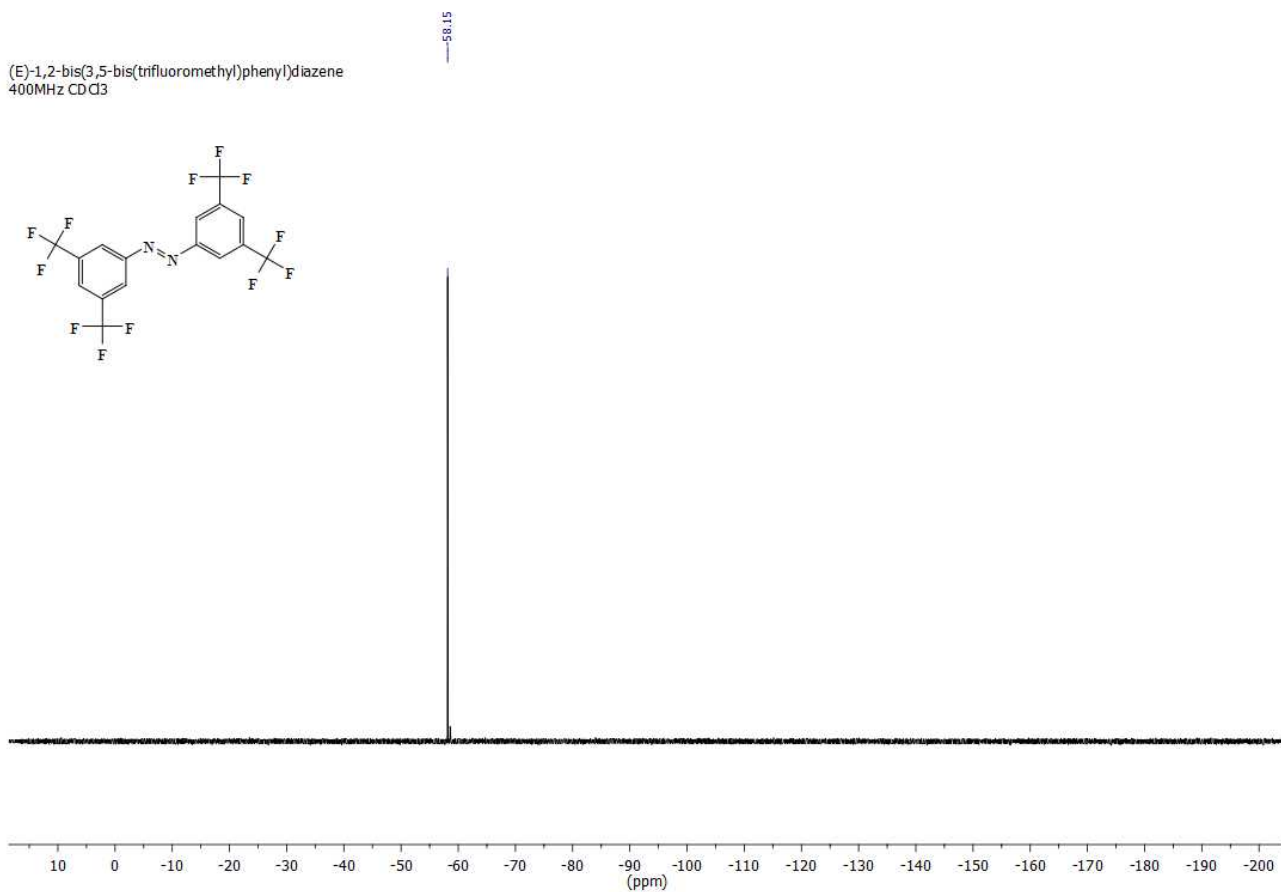
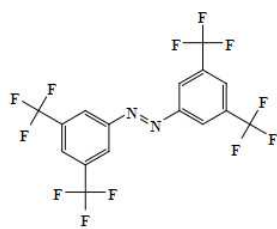


(E)-1,2-bis(3-(trifluoromethyl)phenyl)diazene
400MHz CDCl₃

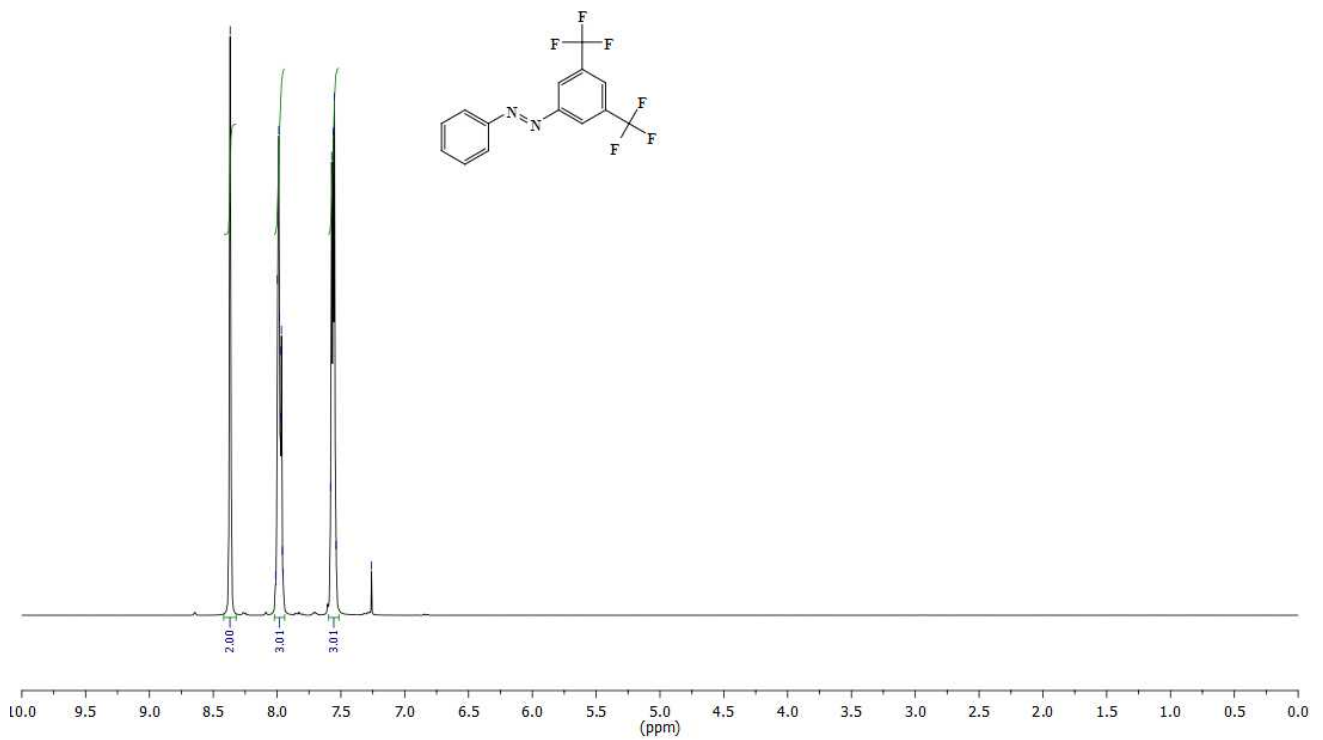




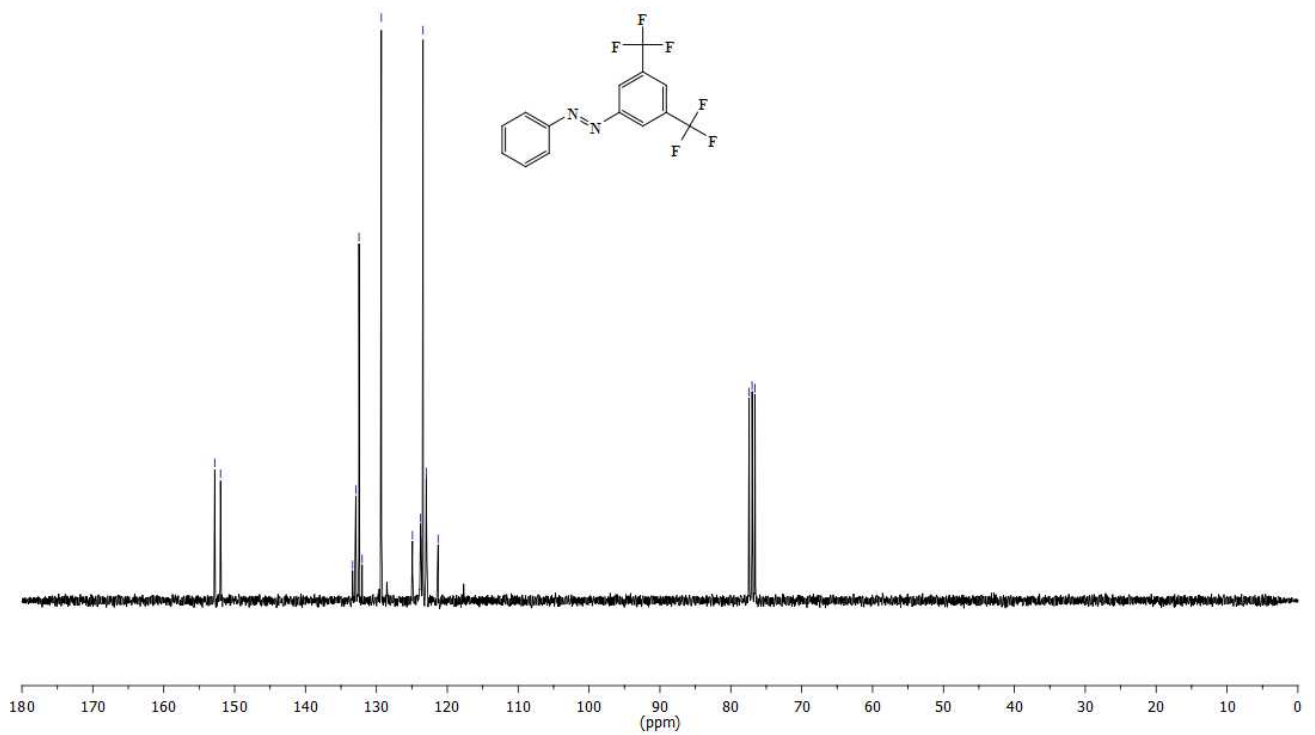
(E)-1,2-bis(3,5-bis(trifluoromethyl)phenyl)diazene
400MHz CDCl₃



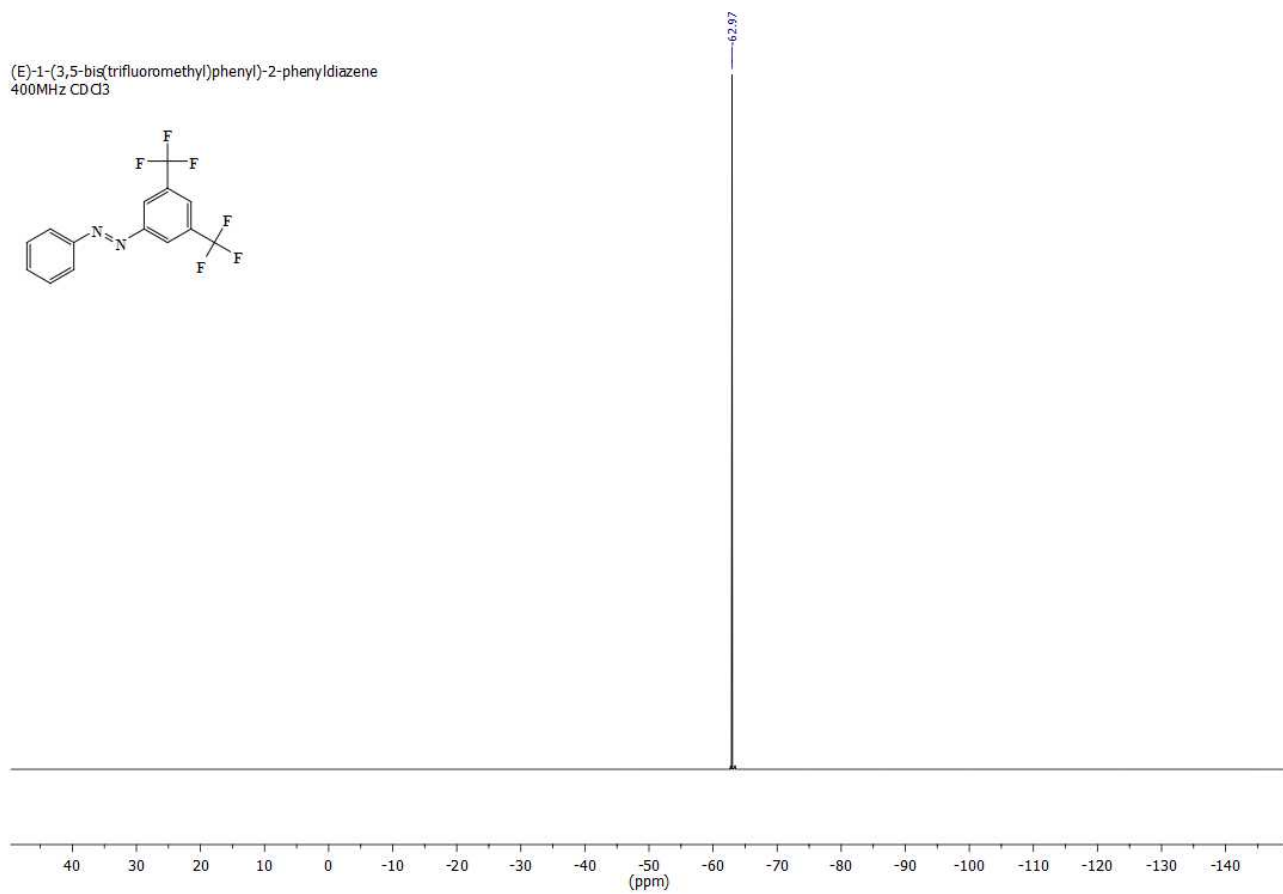
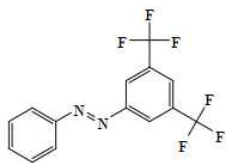
(E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenyldiazene
300MHz CDCl₃

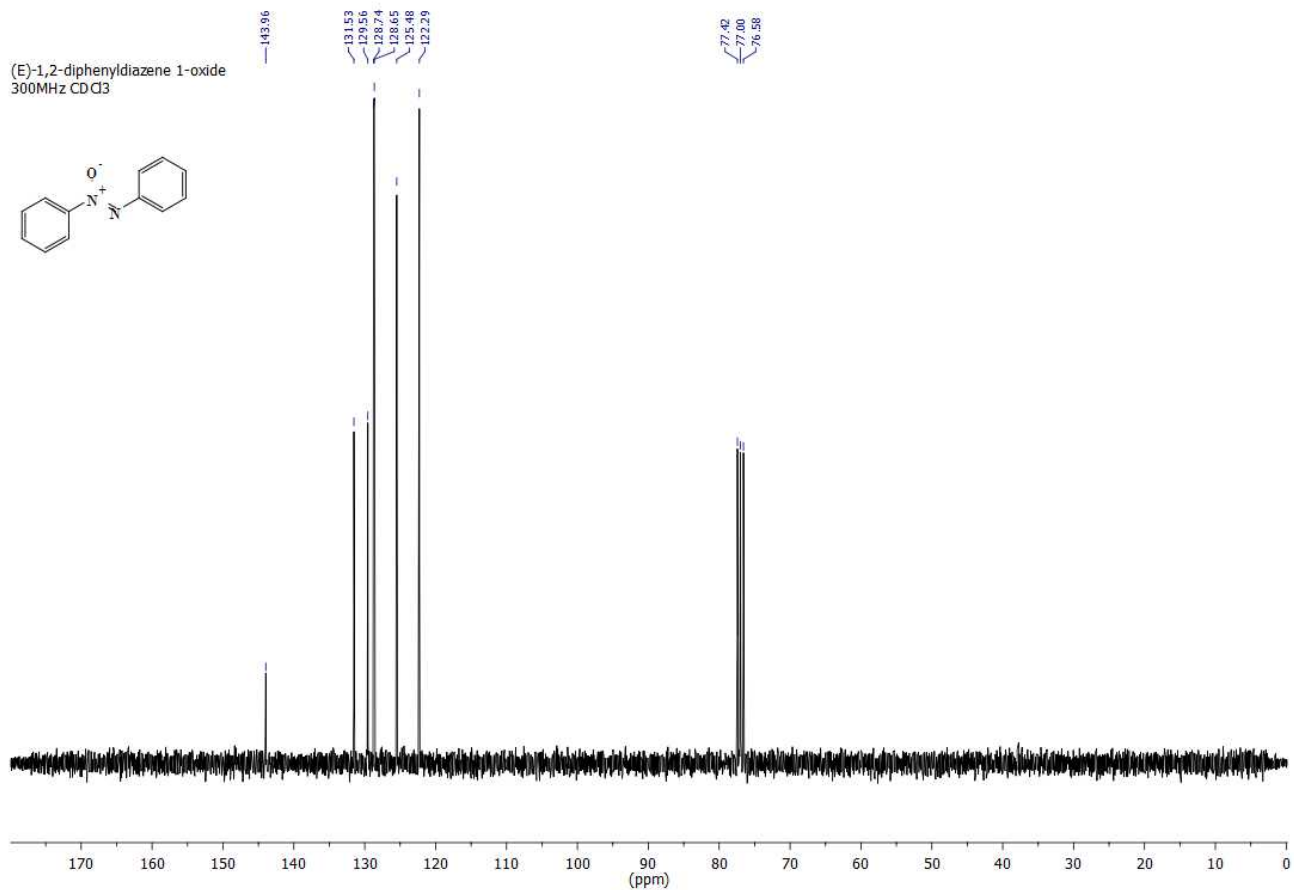
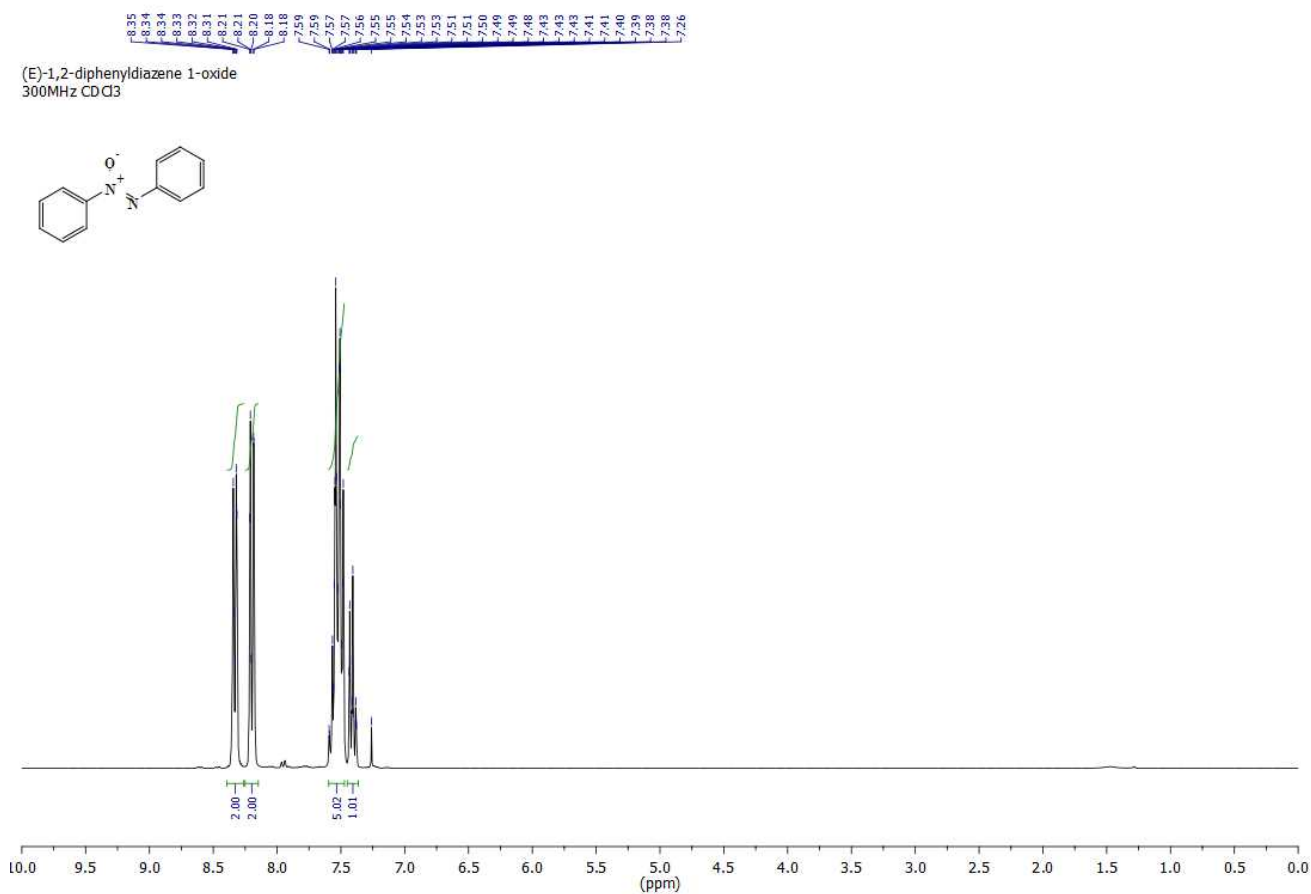


(E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenyldiazene
300MHz CDCl₃



(E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenyldiazene
400MHz CDCl₃





7. Copies of key GC chromatograms

Table 1, entry 2

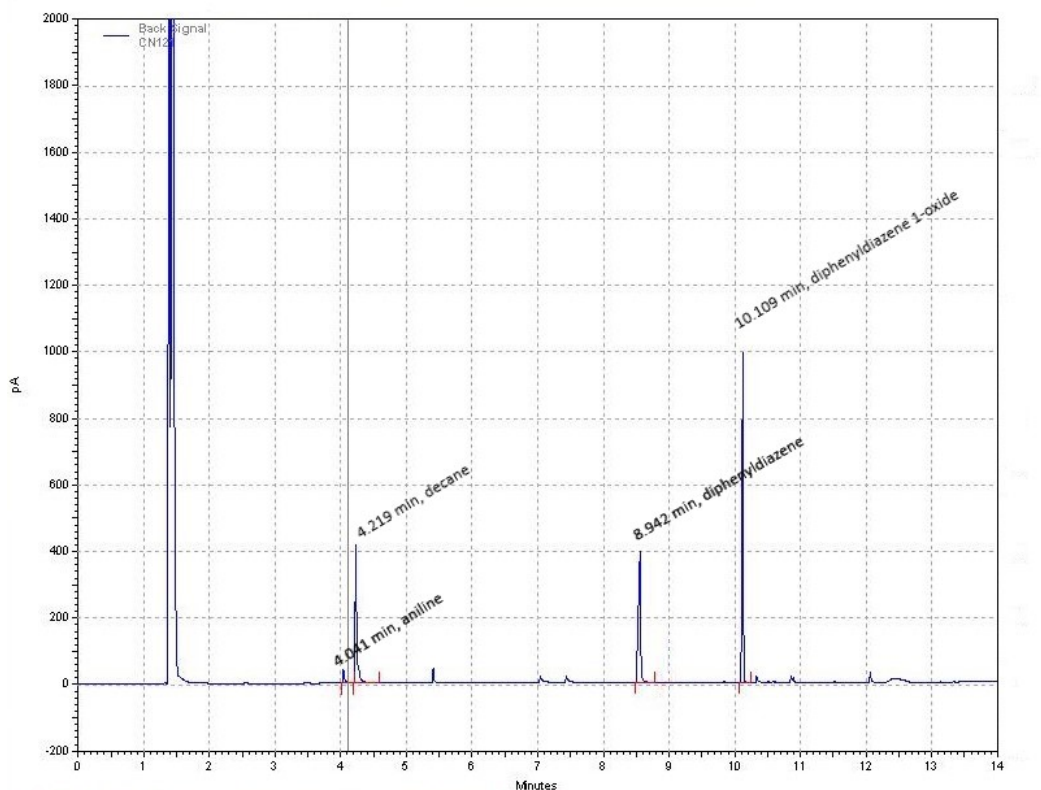


Table 1, entry 14 (freeze-thaw technique)

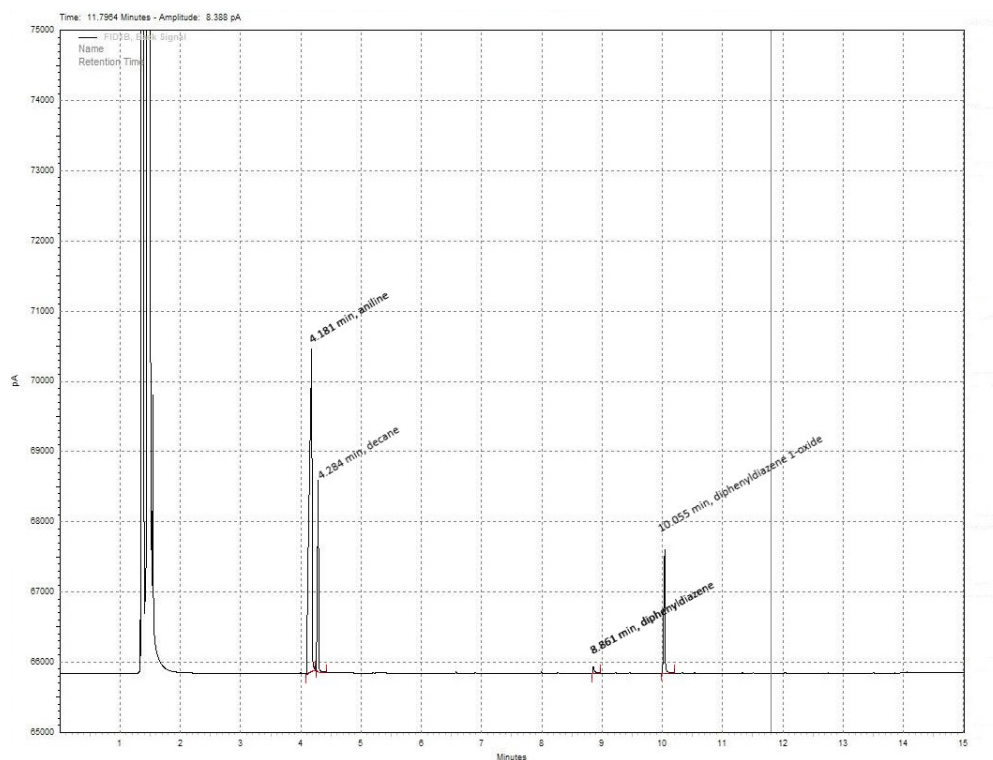
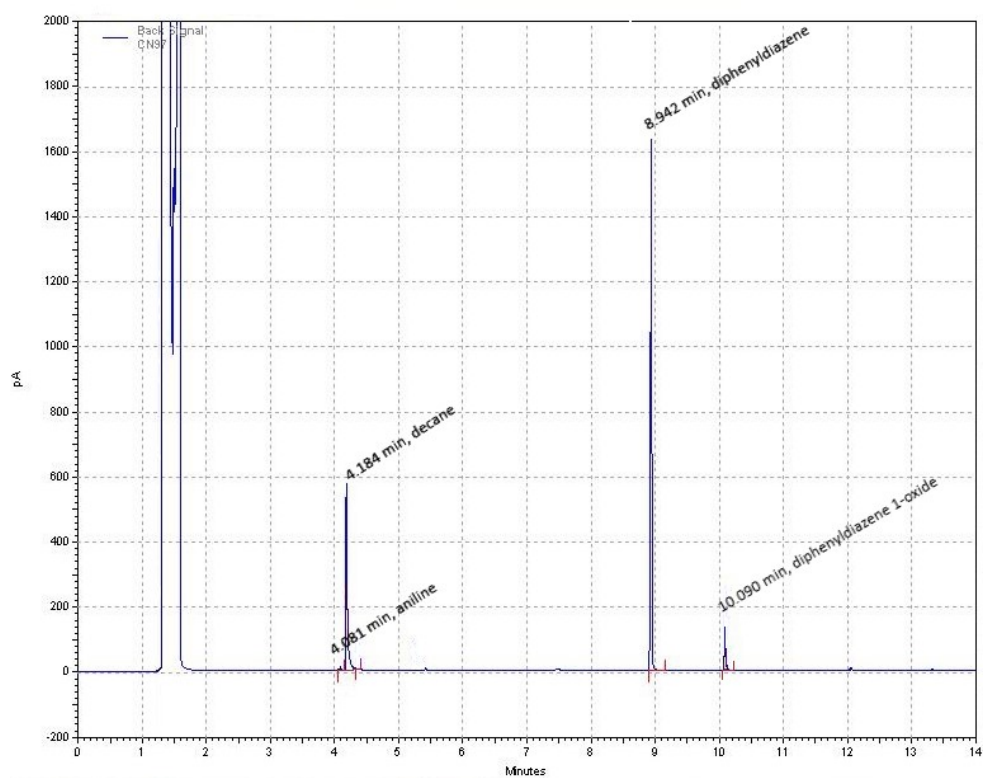


Table 1, entry 13 (optimized conditions for 2a)



8. References

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