Organocatalytic reduction of aromatic nitro compounds - Part II.
The use of solid-supported phenyl(2-quinolyl)methanol
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Experimental data

General information. Chemicals were purchased from commercial suppliers and used as received. Silica gel plates (Merck F254) and silica gel 60 (Merck, 230-400 mesh) were used for TLC and flash chromatographies (FC), respectively; petroleum ether (PE) employed for crystallization and chromatographic workup refers to the fraction of bp 30-50 and 40-70 °C, respectively. IR spectra were recorded with a Shimadzu FT-IR 8400S spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded with Varian Mercuryplus 400 and Varian Inova instruments, operating at 400 and 100 MHz, respectively. Unless otherwise stated, the reported NMR spectra were recorded in CDCl$_3$. Elemental analyses were performed with a Thermoscientific FlashSmart Elemental Analyzer CHNS/O.

Reduction of nitroarenes with (2-quinolyl)(4-tolyl)methanol (QTM, 1)

Scheme S1.

General procedure
In a screw-cap Pyrex tube, alcohol 1 (1.55-2.05 mmol), the nitroarene (0.5 mmol), and AcOH (0.006 g, 0.006 mL, 0.1 mmol) were mixed in toluene (1 mL), degassed by several vacuum-nitrogen cycles to reduce the air oxidation of alcohol 1 to ketone 2, and heated at 110 °C for the reported time. Removal of the solvent and purification by FC allowed isolating the reaction product and ketone 2. The excess alcohol 1 was recovered and recycled.

Reduction of 2-chloro-3-nitropyridine
The reaction crude obtained by heating 2-chloro-3-nitropyridine (0.079 g, 0.5 mmol) and alcohol 1 (0.386 g, 1.55 mmol) for 18 hours was resolved by FC (PE/EtOAc 5:1) leading to ketone 2 ($R_f = 0.52$, 0.370 g, 96%) and 3-amino-2-chloropyridine ($R_f = 0.11$, 0.050 g, 78%). This compound is commercially available, and its identity was confirmed by comparison with an authentic sample.
Reduction of 1-chloro-2-nitrobenzene (7d)

FC (PE/CH₂Cl₂ 1:1) resolution of the reaction crude obtained by heating 1-chloro-2-nitrobenzene (7d) (0.079 g, 0.5 mmol) and alcohol 1 (0.386 g, 1.55 mmol) for 24 hours allowed to isolate 2-chloroaniline (8d) (R₉ = 0.52, 0.048 g, 75%) and ketone 2 (R₉ = 0.26, 0.371 g, 97%). Compound 8d is commercially available, and its identity was confirmed by comparison with an authentic sample.

Reduction of nitrobenzene (7h)
The reaction mixture obtained by heating alcohol 1 (0.511 g, 2.05 mmol) and nitrobenzene (7h) (0.062 g, 0.5 mmol) for 120 hours was subjected to FC with CH₂Cl₂/PE 1:3. The fastest moving band led to N-[(4-tolyl)(2-quinolyl)methyl]aniline (12h) (Rₙ = 0.59, 0.073 g, 45%) as white needles, mp: 57-58 °C (from PE/Et₂O 5:1). IR, νₘₐₓ (KBr): 3296, 3026, 2918, 2858, 1661, 1610, 1315, 1167, 924, 768 cm⁻¹. ¹H NMR (CDCl₃) δ: 8.21 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.81-7.71 (m, 2H), 7.48-7.41 (m, 3H), 7.19-7.10 (m, 4H), 6.73 (d, J = 7.6 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.30-5.90 (vbr s, 1H), 5.74 (s, 1H), 2.30 (s, 3H). ¹³C NMR (CDCl₃) δ: 160.7 (s), 147.0 (s), 139.3 (s), 137.3 (d), 137.0 (s), 129.7 (s), 129.6 (d), 129.1 (d), 129.0 (s), 127.5 (d, 2x), 127.4 (d), 127.3 (d), 126.4 (d), 120.0 (d), 117.3 (d), 113.6 (d), 63.0 (d), 21.1 (q). Anal. Calcd for C₂₃H₂₀N₂: C, 85.15; H, 6.21; N, 8.63. Found: C, 84.91; H, 6.42; N, 8.34.

Ketone 2 (R₉ = 0.24, 0.352 g, 95%) was recovered from the slowest fractions.

Reduction of 4-nitrotoluene (7f)
The reaction mixture obtained by heating alcohol 1 (0.511 g, 2.05 mmol) and 4-nitrotoluene (7f) (0.068 g, 0.5 mmol) for 48 hours was resolved by FC (toluene/CH₂Cl₂ 1:3 v/v). The first moving band led to 4-methyl-N-[(4-tolyl)(2-quinolyl)methyl]aniline (12f) (R₉ = 0.58, 0.125 g, 74%) as a sticky solid. IR, νₘₐₓ (KBr): 3363, 3060, 2919, 2850, 1657, 1606, 1319, 1159, 924, 769 cm⁻¹. ¹H NMR (CDCl₃) δ: 8.17 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.79-7.69 (m, 2H), 7.52 (t, J = 8.1 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 5.87 (vbr s, 1H), 5.70 (s, 1H), 2.30 (s, 3H), 2.21 (s, 3H). ¹³C NMR (CDCl₃) δ: 161.0 (s), 147.1 (s), 144.8 (s), 139.5 (s), 137.2 (d), 136.9 (s), 129.8 (d), 129.6 (d), 129.5 (d), 129.1 (d), 127.5 (s), 127.4 (d), 127.2 (d), 126.3 (d), 123.5 (s), 119.9 (d), 113.7 (d), 63.4 (d), 21.1 (q), 20.4 (q). Anal. Calcd for C₂₃H₂₂N₂: C, 85.15; H, 6.55; N, 8.28. Found: C, 84.94; H, 6.72; N, 8.04.

The following moving bands led to ketone 2 (R₉ = 0.35, 0.367 g, 99%) and unreacted alcohol 1 (R₉ = 0.10, 0.010 g).

Reduction of 4-nitroanisole (7e)
The reaction crude obtained by heating alcohol 1 (0.511 g, 2.05 mmol) and 4-nitroanisole (7e) (0.077 g, 0.5 mmol) for 72 hours was subjected to FC (PE/EtOAc 10:1). Ketone 2 (R₉ = 0.49, 0.360 g, 97%) was recovered from the first moving band while the second one led to 4-methoxy-N-[(4-tolyl)(2-
quinolyl)methyl]aniline (12e) ($R_f = 0.37, 0.117 \text{ g}, 66\%$) as white needles, mp: 127-128 °C (from PE/Et$_2$O 5:1). IR, $\nu_{\text{max}}$ (KBr): 3373, 3024, 2951, 2922, 2826, 1614, 1601, 1510, 1240, 1036, 812, 771 cm$^{-1}$. $^1$H NMR (CD$_3$OD) $\delta$: 8.22 (d, $J = 8.6$ Hz, 1H), 8.06 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.0$, 1H), 7.75 (d, $J = 7.7$ Hz, 1H), 7.65 (d, $J = 8.6$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 6.65 (s, 4H), 5.70 (s, 1H), 3.63 (s, 3H), 2.27 (s, 3H).

$^{13}$C NMR (CD$_3$OD) $\delta$: 164.5 (s), 153.7 (s), 148.4 (s), 142.9 (s), 138.7 (d), 138.4 (s), 131.0 (d), 130.3 (s), 129.0 (d), 128.9 (d), 128.8 (s), 127.7 (d), 121.1 (d), 116.4 (d), 115.6 (d), 66.0 (d), 56.0 (q), 21.1 (q). Anal. Calcld for C$_{24}$H$_{22}$N$_2$O: C, 81.33; H, 6.26; N, 7.90. Found: C, 81.04; H, 6.52; N, 8.20.

The slowest moving band afforded unreacted 1 ($R_f = 0.17, 0.008 \text{ g}$).

**General procedure for the synthesis of Merrifield-QTK (3)**

In a dried three necked flask equipped with a condenser and two dropping funnels, diisopropylamine or 2,2,6,6-tetramethylpiperidine was dissolved in dry THF (8 mL) and cooled at -78 °C. Then a solution 1.6 M of $n$-BuLi in hexane and, after 20 minutes, a solution of ketone 2 (0.494 g, 2 mmol) in dry THF (10 mL) were added dropwise. The reaction mixture was kept at -78 °C under stirring and after 30 minutes the solid Merrifield resin (4.3 mmol/g) (0.465 g, 2 mmol) was added portionwise. After the end of the addition, the crude was stirred at -78 °C for 2 hours, then warmed to room temperature and kept under stirring overnight. The reaction was quenched with aq. NH$_4$Cl (10 mL) and the partially functionalized resin was recovered by filtration, washed with water and then with Et$_2$O, dried, and analysed via FT-IR and elemental analysis. Evaporation of the organic phase afforded unreacted ketone 2 (or alcohol 1).

A quantitative evaluation of the grafting of 2 on the resin support was performed via elemental analyses.

**Commercial Merrifield resin (4.3 mmol/g).** Elemental analysis: C, 77.46; H, 6.53 corresponding to the minimal formula C$_{14}$H$_{14}$Cl. IR, $\nu_{\text{max}}$ (KBr): 3020, 2914, 2851, 1605, 1504, 1446, 1419, 1258, 816, 752, 661, 532 cm$^{-1}$.

The resin loading was estimated from the ratio of the percentage of nitrogen determined via elemental analysis in the functionalized resin and the calculated percentage of nitrogen for the totally functionalized resin Merrifield-QTK (3) (minimal formula: C$_{31}$H$_{26}$NO; elemental analysis: C, 86.88; H, 6.17; N 3.27).

a) **Reaction with LDA**

$n$-BuLi 1.6 M (2.5 mL, 4 mmol), ketone 2 and the Merrifield resin were added to a solution of diisopropylamine (0.404 g, 0.560 mL, 4 mmol). Evaporation of the organic phase allowed to recover alcohol 1 (0.328 g, 66%) while the solid-supported ketone 3 (0.539 g) was isolated by filtration. IR,
\[ \nu_{\text{max}} (\text{KBr}): 3030, 2921, 2850, 1656, 1601, 1413, 1261, 816, 696, 685, 524 \text{ cm}^{-1}. \]

Anal. Calcd for C\textsubscript{31}H\textsubscript{26}NO: C, 86.88; H, 6.17; N 3.27. Found: C, 75.08; H, 6.11, N 1.36. The ratio between the experimental and theoretical nitrogen percentages for Merrifield-QTK (3) allowed estimating a 42\% resin loading.

b) Reaction with 2,2,6,6-tetramethylpiperidine and n-BuLi

n-BuLi 1.6 M (2.5 mL, 4 mmol), ketone 2, and the Merrifield resin were added to a solution of 2,2,6,6-tetramethylpiperidine (565 g, 0.678 mL, 4 mmol). Evaporation of the organic phase led to unreacted ketone 2 (0.440 g, 89\%) and the solid-supported ketone 3 (0.436 g) was recovered by filtration. Anal. Calcd for C\textsubscript{31}H\textsubscript{26}NO: C, 86.88; H, 6.17; N 3.27. Found: C, 78.29; H, 6.45, N 0.76 (indicating a 23\% resin loading).

c) Reaction with t-BuOK, 2,2,6,6-tetramethylpiperidine, and n-BuLi

To a suspension of t-BuOK (0.269 g, 2.4 mmol) in THF (6 mL) were added a solution of 2,2,6,6-tetramethylpiperidine (0.339 g, 0.405 mL, 2.4 mmol) in THF (2 mL), n-BuLi 1.6 M (1.5 mL, 2.4 mmol), ketone 2 and the Merrifield resin. Unreacted ketone 2 (0.355 g, 72\%) was recovered by evaporation of the organic phase and the solid-supported ketone 3 (0.396 mg) was collected by filtration. Anal. Calcd for C\textsubscript{31}H\textsubscript{26}NO: C, 86.88; H, 6.17; N 3.27. Found: C, 76.06; H, 6.87, N 1.00 (assessing a 30\% loading).

Reduction of methyl 4-nitrobenzoate (7a) with phenyl(2-quinolyl)methanol (PQM)

a) In the presence of AcOH

In a screw-cap Pyrex tube, a solution of methyl 4-nitrobenzoate (7a) (0.045 g, 0.25 mmol), PQM (0.183 g, 0.78 mmol, 3.1 equiv), and AcOH (0.003 g, 0.003 mL, 0.05 mmol) in toluene (0.5 mL) was degassed by several vacuum-nitrogen cycles to reduce the air oxidation of PQM to phenyl (2-quinolyl) ketone (PQK), and heated at 110 °C for 18 hours. Removal of the solvent and purification by FC (PE/EtOAc 4:1 v/v) allowed to recover PQK (\( R_f = 0.75, 0.169 \text{ g}, 96\% \)) and methyl 4-aminobenzoate (8a) (\( R_f = 0.19, 0.027 \text{ g}, 71\% \)), which structure was confirmed by comparison with an authentic sample.

b) Without AcOH

Operating as above, the solution of methyl 4-nitrobenzoate (7a) (0.045 g, 0.25 mmol) and PQM (0.183 g, 0.78 mmol, 3.1 equiv) in toluene (0.5 mL) was degassed and heated at 110 °C for 18 hours. FC resolution allowed to isolate PQK (\( R_f = 0.75, 0.176 \text{ g}, 97\% \)) and methyl 4-aminobenzoate (8a) (\( R_f = 0.19, 0.035 \text{ g}, 93\% \)).
Reductions of nitroarenes 7 with NaBH₄: synthesis of azoxy derivatives 9.

Table S1.

| entry | R      | time (h) | Conversion (%)<sup>a</sup> | yields (%)<sup>b</sup> |
|-------|--------|----------|----------------------------|------------------------|
| 1     | 7f (R = 4-Me) | 96       | 100                        | 9f 94                  |
| 2     | 7h (R = H)   | 96       | 100                        | 9h 92                  |
| 3     | 7i (R = 3-Cl) | 24       | 100                        | 9i 97                  |
| 4     | 7j (R = 4-Cl) | 96       | 100                        | 9j 96                  |
| 5     | 7n (R = 3-COMe) | 18   | 100                        | 9n 96 [R = CH(OH)Me]<sup>c</sup> |
| 6     | 7o (R = 4-COMe) | 8 (18, 24, 96) | 100                       | 9o 96 [R = CH(OH)Me] |
| 7     | 7p (R = 3-CHO) | 14<sup>d</sup> | 100                        | 9p 94 (R = CH₂OH)<sup>c</sup> |

<sup>a</sup>Determined via ¹H NMR analysis. <sup>b</sup>Isolated yields. <sup>c</sup>Small traces of the corresponding azo compound were observed via ¹H NMR. <sup>d</sup>Reaction performed first at room temperature for 18 hours and then at 110 °C for 14 hours.

General procedure

In a screw-cap Pyrex tube, a mixture of nitroarene 7 (0.5 mmol) and NaBH₄ (0.038 g, 1 mmol) in toluene (0.5 mL) and THF (0.5 mL) was heated at 110 °C for the given time. The reaction crude was quenched by addition of water (0.5 mL) and extracted with EtOAc (3x1 mL). The organic phase was washed with water and brine, dried on anhydrous Na₂SO₄, and evaporated under reduced pressure to give compounds 9.

Reduction of 4-nitrotoluene (7f): synthesis of 1,2-bis(p-tolyl)diazene oxide (9f)

Starting from 4-nitrotoluene (7f) (0.069 g), after 96 hours heating diazene oxide 9f was isolated (0.053 g, 94%) and its structure confirmed by comparison with literature data.<sup>1</sup>
Reduction of nitrobenzene (7h): synthesis of azoxybenzene (9h)
Starting from nitrobenzene (7h) (0.062 g, 0.051 mL), compound 9h was isolated (0.045 g, 92%) after 96 hours heating and its structure confirmed by comparison with literature data.\(^1\)

Reduction of 1-chloro-3-nitrobenzene (7i): synthesis of 1,2-bis(3-chlorophenyl)diazene oxide (9i)
1-Chloro-3-nitrobenzene (7i) (0.079 g), after 18 hours heating, was converted into 9i (0.065 g, 97%), which structure was confirmed by comparison with literature data.\(^1\)

Reduction of 1-chloro-4-nitrobenzene (7j): synthesis of 1,2-bis(4-chlorophenyl)diazene oxide (9j)
By heating 1-chloro-4-nitrobenzene (7j) (0.079 g) for 72 hours, diazene oxide 9j was isolated (0.064 g, 96%) and its structure confirmed by comparison with literature data.\(^1\)

Reduction of 3-nitroacetophenone (7n): synthesis of 1,2-bis[3-(1-hydroxyethyl)phenyl]diazene oxide (9n)
Starting from 3-nitroacetophenone (7n) (0.083 g), diazene oxide 9n was isolated (0.069 g, 96%) after 18 hours heating and its structure confirmed by comparison with literature data.\(^2\)

Reduction of 4-nitroacetophenone (7o): synthesis of 1,2-bis[4-(1-hydroxyethyl)phenyl]diazene oxide (9o)
After 18 hours heating, 4-nitroacetophenone (7o) (0.083 g) was converted into 9o (0.069 g, 96%).\(^3\)

\(^{1}H\) NMR (CDCl\(_3\)) \(\delta\): 8.27 (d, \(J = 8.7\) Hz, 2H), 8.17 (d, \(J = 8.5\) Hz, 2H), 7.56-7.44 (m, 4H), 5.11-4.88 (m, 2H), 2.85-2.20 (vbr s, 2H), 1.53 (d, \(J = 6.5\) Hz, 6H). \(^{13}C\) NMR (CDCl\(_3\)) \(\delta\): 149.6 (s), 147.5 (s), 147.4 (s), 143.2 (s), 125.8 (d), 125.7 (d), 125.6 (d), 122.5 (d), 70.1 (d), 69.7 (d), 25.4 (q), 25.2 (q).

Reduction of 3-nitrobenzaldehyde (7p): synthesis of 1,2-bis(3-hydroxymethylphenyl)diazene oxide (9p)
Diazene oxide 9p (0.061 g, 94%) was isolated from 3-nitrobenzaldehyde (7p) (0.076 g), after 15 hours stirring at room temperature and 8 hours heating at 110 °C.\(^4\) \(^{1}H\) NMR (CDCl\(_3\)) \(\delta\): 8.31 (s, 1H), 8.21 (d, \(J = 8.1\) Hz, 1H), 8.16 (s, 1H), 8.07 (d, \(J = 8.0\) Hz, 1H), 7.60-7.39 (m, 4H), 4.82 (s, 2H), 4.77 (s, 2H).

Calculation of the formula and equivalent weights of Wang-QTK (5) and Wang-QTM (6)
Applying Equation (1), where \(MW(\text{Reagent})\) and \(FW(\text{Resin})\) are the residual molecular weight and molecular formula of the reagent and resin, respectively, after reacting groups removal, while \(FW(\text{ResinY})\) is the formula weight of the unreacted resin:
the following results were obtained for Wang-QTK (5) and Wang-QTM (6), on the basis of 90% and 88% loading, respectively.

\[
FW_{\text{Wang-QTK (5)}} = (246.29 + 394.2) \cdot 0.9 + 395.2 \cdot 0.1 = 616.0 \text{ g/mol}
\]

\[
FW_{\text{Wang-QTM (6)}} = (246.29 + 394.2) \cdot 0.88 + 395.2 \cdot 0.12 = 612.8 \text{ g/mol}
\]

From the experimental viewpoint, considering the loading, the Equivalent Weight \((EW_{FR})\) of the functionalized resin has been calculated by Equation (2) to evaluate the amount of functionalized resin corresponding to 1 equivalent of supported Reagent to apply in the reaction:

\[
EW_{FR} = \frac{FW_{FR}}{L} \quad (2)
\]

\[
EW_{\text{Wang-QTK (5)}} = \frac{616.0}{0.9} = 684.4 \text{ g/equiv}
\]

\[
EW_{\text{Wang-QTM (6)}} = \frac{612.8}{0.88} = 696.4 \text{ g/equiv}
\]

**Figure S1.** IR spectra of: a) Wang resin (2.53 mmol/g); b) Wang-QTK (5); c) Wang-QTM (6).
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$^1$H NMR spectrum of QTM (1)

$^1$H NMR spectrum of QTK (2)
$^{1}H$ NMR spectrum of QTK-Br (4)

$^{13}C$ NMR spectrum of QTK-Br (4)
$^1$H NMR spectrum of the mixture of QTK-Br (4) and QTK-Br$_2$

$^1$H NMR spectrum of methyl-4-aminobenzoate (8a)
$^1$H NMR spectrum of $p$-phenylenediamine (8b)

$^1$H NMR spectrum of $o$-phenylenediamine (8c)
$^1$H NMR spectrum of 2-chloroaniline (8d)

$^1$H NMR spectrum of 4-aminoanisole (8e)
$^1$H NMR spectrum of hydrazobenzene (11h)

$^1$H NMR spectrum of 1,2-bis-(3-chlorophenyl)hydrazine (11i)
\(^1\)H NMR spectrum of 1,2-bis-(4-chlorophenyl)hydrazine (11j)

\(^1\)H NMR spectrum of 2,2’-(hydrazine-1,2-diyl)dibenzamide (11k)
$^{13}$C NMR spectrum of 2,2'-(hydrazine-1,2-diyl)dibenzamide (11k)

$^1$H NMR spectrum of 3,3'-(hydrazine-1,2-diyl)dibenzonitrile (11l)
$^1$H NMR spectrum of 3,3’-(hydrazine-1,2-diyl)dibenzonitrile (11l) in CD$_2$OD

$^{13}$C NMR spectrum of 3,3’-(hydrazine-1,2-diyl)dibenzonitrile (11l) in CD$_2$OD
$^1$H NMR spectrum of 4,4'-((hydrazine-1,2-diyl)dibenzonitrile (11m)

$^1$H NMR spectrum of the mixture 3.5:1 of 10n and 11n
$^1\text{H NMR spectrum of the mixture 1:1 of 10n and 11n}$

$^1\text{H NMR spectrum of the mixture 1:10 of 10n and 11n}$
$^{13}$C NMR spectrum of the mixture 1:10 of 10n and 11n

$^1$H NMR spectrum of 1,2-bis[4-(1-hydroxyethyl)phenyl]diazene (10o)
$^1$H NMR spectrum of the mixture 3:1 of 10o and 11o

$^1$H NMR spectrum of the mixture 1:5 of 10p and 11p
$^1$H NMR spectrum of the mixture 1:2 of 10q and 11q

$^1$H NMR spectrum of azobenzene (10h)
$^1$H NMR spectrum of 1,2-bis-(3-chlorophenyl)diazene (10i)

$^1$H NMR spectrum of 1,2-bis-(4-chlorophenyl)diazene (10j)
$^1$H NMR spectrum of 3,3'-(diazene-1,2-diyl)dibenzonitrile (10l)

$^1$H NMR spectrum of 1,2-bis[3-(1-hydroxyethyl)phenyl]diazene (10n)
$^{13}$C NMR spectrum of 1,2-bis[3-(1-hydroxyethyl)phenyl]diazene (10n)

$^{1}$H NMR spectrum of 1,2-bis(3-hydroxymethylphenyl)diazene (10p)
$^1$H NMR spectrum of 1,2-bis(4-hydroxymethylphenyl)diazene (10q) in CD$_3$OD

$^{13}$C NMR spectrum of 1,2-bis(4-hydroxymethylphenyl)diazene (10q) in CD$_3$OD
$^1$H NMR spectrum of 2-chloro-3-aminopyridine

$^1$H NMR spectrum of N-[(4-tolyl)(2-quinolyl)methyl]aniline (12h)
$^{13}$C NMR spectrum of $N$-[(4-tolyl)(2-quinolyl)methyl]aniline (12h)

$^1$H NMR spectrum of 4-methyl-$N$-[(4-tolyl)(2-quinolyl)methyl]aniline (12f)
$^{13}$C NMR spectrum of 4-methyl-N-[(4-tolyl)(2-quinolyl)methyl]aniline (12f)

$^{1}$H NMR spectrum of 4-methoxy-N-[(4-tolyl)(2-quinolyl)methyl]aniline (12e) in CD$_3$OD
$^{13}$C NMR spectrum of 4-methoxy-$N$-[(4-toly$l(2$-quinolyl)methyl]aniline (12e) in CD$_3$OD

$^1$H NMR spectrum of 1,2-bis($p$-tolyl)diazene oxide (9f)
$^1$H NMR spectrum of azoxybenzene (9h)

$^1$H NMR spectrum of 1,2-bis(3-chlorophenyl)diazene oxide (9i)
$^1$H NMR spectrum of 1,2-bis(4-chlorophenyl)diazene oxide (9j)

$^1$H NMR spectrum of 1,2-bis[3-(1-hydroxyethyl)phenyl]diazene oxide (9n)
$^1$H NMR spectrum of 1,2-bis[4-(1-hydroxyethyl)phenyl]diazene oxide (9o)

$^{13}$C NMR spectrum of 1,2-bis[4-(1-hydroxyethyl)phenyl]diazene oxide (9o)
$^1$H NMR spectrum of 1,2-bis(3-hydroxymethylphenyl)diazene oxide (9p)