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Electronic Supporting Information

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General remarks

All reagents were obtained from commercial sources and used as received. Pluronic F-127 (Mw = 12,600, EO106PO70EO106) was supplied by Sigma-Aldrich Co. LLC. Technical grade petroleum ether (40-60°C bp.) and ethyl acetate were used for chromatography column.

The images of surface morphologies and the energy-dispersive spectrometry (EDS) spectra were acquired by scanning electron microscope (SEM) with FEI Quanta 400 FEG. The structure and crystallinity of the as-synthesized catalysts was tested by powder X-ray diffraction (XRD) analysis on a D8 Advance diffractometer (Bruker, Germany). X-ray photoelectron spectra (XPS) was analyzed on the Thermo ESCALAB 250XI instrument.

¹H NMR spectra were recorded in CDCl₃ at ambient temperature on Bruker AVANCE I 300 or 400 spectrometers at 300.1 or 400.1 MHz, using the solvent as internal standard (7.26 ppm). ¹³C NMR spectra were obtained at 75 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm). Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad.

GC analyses were performed with GC-14C (Shimadzu) equipped with a 30-m capillary column (Supelco, SPB-5, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with N₂/air as vector gas. GCMS were measured by GCMS-7890A-5975C (Agilent) with GC-7890A equipped with a 30-m capillary column (HP-5ms, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with helium as vector gas.

The following GC conditions were used: initial temperature 80 °C, for 2 minutes, then rate 20 °C/min. until 260 °C and 260°C for 20 minutes.

Preparation of the Ru-OMC catalyst

During the fabrication process of catalysts, 9.45 g Pluronic F127 was firstly dissolved in ethanol solution under stirred conditions to form a transparent solution A. Then, 16.5 g resorcinol was completely dissolved in water and obtained solution was slowly added in the solution A and continuously stirred to obtain solution B. Subsequently, 13.5 g formaldehyde (37 wt%) was added to solution B slowly. After stirring for 30 min, 2.3 ml HCl was added slowly as a catalyst to solution presents two separated phases, the upper transparent phase was discarded, while the lower yellow phase was considered as polymer-rich resorcinol formaldehyde resin precursor. The RuCl₃ was then added to this precursor with 5 wt% Ru contents. Finally, the precursors with different Ru contents were dried in an oven at 90 °C for 12 h. The resulted polymers were then carbonized at 1000 °C for 2 h with a heating rate 2 °C/min under a N₂ atmosphere with the flow rate of 80 mL/min. Finally, the Ru-OMC catalysts were obtained after cooling down the materials to room temperature. The obtained catalysts were denoted as Ru-OMC.

Characterization of Ru-OMC catalysts

The images of surface morphologies and the energy-dispersive spectrometry (EDS) spectra were acquired by scanning electron microscope (SEM) with FEI Quanta 400 FEG. The structure and crystallinity of the as-synthesized catalysts was tested by powder X-ray diffraction (XRD) analysis on a D8 Advance diffractometer (Bruker, Germany) in the 20 range of 10° ~80°. Small-angle XRD was also performed at 20 from 0.5° to 5°. X-ray photoelectron spectra (XPS) was analyzed on the Thermo ESCALAB 250XI instrument using Al Ka (hv = 1486.6 eV) from an X-ray source operating at 15 kV and 10 mA. The C(1s) line at 284.6 eV was used as the binding energy reference.

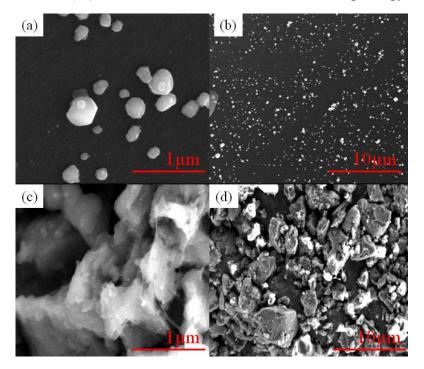
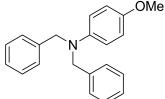


Fig. S1. The SEM micrographs of (a), (b) as-synthesized Ru-OMC catalyst and (c), (d) reused for 14 times.

<u>General procedure for Ru-OMC catalyzed selective reductive aminations of</u> <u>aldehydes with imines</u>

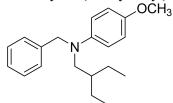
Ru-OMC (5 wt%, 1 mol%, 20 mg), imine (0.5 mmol), aldehyde (0.75 mmol), PhSiH₃ (0.75 mmol, 90 μ L) and MeOH (2 mL) were introduced in a tube under air, equipped with magnetic stirring bar and was stirred at 40 °C. After 16 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

N-benzyl-4-methoxy-*N*-benzylaniline¹ (3a)



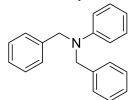
Light green solid, yield = 82%, 124 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.41-7.28 (m, 10H), 6.85-6.76 (m, 4H), 4.64 (s, 4H), 3.79 (s, 3H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ = 151.8, 143.9, 139.1, 128.7, 127.1, 127.0, 114.8, 114.6, 55.8, 55.3. MS (EI): m/z: 303 (70, M⁺), 212 (70), 91 (100), 65 (20).

N-benzyl-*N*-(2-ethylbutyl)-4-methoxyaniline (3b)



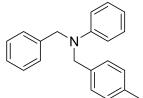
Colorless solid, yield = 85%, 126 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.35-7.22 (m, 5H), 6.81 (d, 2H, *J* = 9.3 Hz), 6.70 (d, 2H, *J* = 9.0 Hz), 4.53 (s, 2H), 3.77 (s, 3H), 3.24 (d, 2H, *J* = 7.2 Hz), 1.75-1.73 (m, 1H), 1.49-1.30 (m, 4H), 0.91 (t, 6H, *J* = 7.5 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 151.4, 143.9, 139.5, 128.6, 127.1, 126.7, 114.8, 114.7, 56.6, 56.3, 55.9, 39.4, 23.7, 10.9.

N,*N*-dibenzylaniline² (3c)



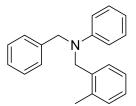
Colorless solid, yield = 86%, 117 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.42-7.21 (m, 12H), 6.82-6.75 (m, 3H), 4.72 (s, 4H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 149.3, 138.7, 129.4, 128.8, 127.0, 126.8, 116.9, 112.6, 54.3. MS (EI): m/z: 273 (30, M⁺), 196 (25), 182 (25), 91 (100), 65 (10).

N-benzyl-*N*-(4-methylbenzyl)aniline¹ (3d)



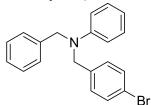
Orange solid, yield = 58%, 83 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.39-7.19 (m, 11H), 6.81-6.75(m, 3H), 4.69 (s, 4H), 2.412 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 149.3, 138.7, 136.5, 135.5, 129.4, 129.3, 128.7, 126.9, 126.7, 124.5, 116.8, 112.6, 54.2, 54.0, 21.1. MS (EI): m/z: 287 (40, M⁺), 196 (10), 105 (100), 91 (55), 77 (35).

N-benzyl-*N*-(2-methylbenzyl)aniline¹ (3e)



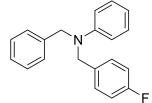
White solid, yield = 45%, 65 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.37-7.22 (m, 11H), 6.74-6.72(m, 3H), 4.72 (s, 2H), 4.62 (s, 2H), 2.32 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 149.2, 138.7, 135.7, 130.5, 129.4, 128.8, 127.0, 126.9, 126.8, 126.3, 126.1, 116.8, 116.6, 112.4, 54.3, 52.5, 19.1. MS (EI): m/z: 287 (45, M⁺), 183 (90), 105 (100), 91 (80), 77 (50).

N-benzyl-*N*-(4-bromobenzyl)aniline¹ (3f)



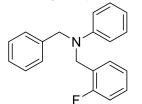
Green solid, yield = 62%, 109 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.51-7.17 (m, 11H), 6.80-6.77 (m, 3H), 4.69 (s, 2H), 4.64 (s, 2H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 149.0, 138.4, 137.8, 131.9, 129.4, 128.8, 128.6, 127.2, 126.9, 120.8, 117.3, 112.8, 54.5, 53.9. MS (EI): m/z: 351 (30, M⁺), 207 (10), 169 (35), 91 (100), 77 (55).

N-benzyl-*N*-(4-fluorobenzyl)aniline¹ (3g)



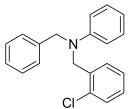
Light yellow solid, yield = 83%, 121 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.38-7.21 (m, 9H), 7.09-7.03 (m, 2H), 6.81-6.78 (m, 3H), 4.69 (s, 2H), 4.66 (s, 2H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 163.7 (d, *J*_{CF} = 243.1Hz), 149.2, 138.6, 134.3, 129.4, 128.8, 128.5 (d, *J*_{CF} = 7.9Hz), 127.1, 126.9, 117.2, 115.8 (d, *J*_{CF} = 21.3Hz), 112.8, 54.4, 53.8. MS (EI): m/z: 291 (50, M⁺), 200 (10), 109 (100), 91 (80), 77 (25).

N-benzyl-*N*-(2-fluorobenzyl)aniline¹ (3h)



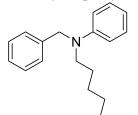
White solid, yield = 78%, 113 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.41-7.10 (m, 11H), 6.79-6.76 (m, 3H), 4.77 (s, 2H), 4.73 (s, 2H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 162.59 (d, J_{CF} = 243.75Hz), 148.7, 138.4, 139.3, 128.7, 128.5, 128.4, 127.0, 126.7, 125.4 (d, J_{CF} = 13.5Hz), 124.2 (d, J_{CF} = 3.75Hz), 117.0, 115.5 (d, J_{CF} = 21.0Hz), 112.5, 54.5, 48.5. MS (EI): m/z: 291 (45, M⁺), 200 (35),109 (55), 91 (100), 77 (35).

N-benzyl-*N*-(2-chlorobenzyl)aniline¹ (3i)



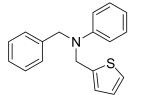
White solid, yield = 51%, 78 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.45-7.19 (m, 11H), 6.79-6.70 (m, 3H), 4.75 (s, 2H), 4.74 (s, 2H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ = 148.7, 138.4, 135.5, 133.2, 129.8, 129.4, 128.9, 128.3, 127.9, 127.2, 127.1, 126.8, 117.2, 112.5, 54.7, 52.8. MS (EI): m/z: 307 (50, M⁺), 180 (15), 125 (55), 91 (100), 77 (50).

N-benzyl-N-pentylaniline³ (3j)



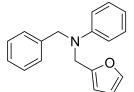
Light yellow oil, yield = 72%, 91 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.40-7.22 (m, 7H), 6.76-6.70 (m, 3H), 4.61 (s, 2H), 3.45 (t, 2H, *J* = 7.5 Hz), 1.79-1.69 (m, 2H), 1.47-1.34 (m, 4H), 0.98 (t, 3H, *J* = 6.6 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 148.7, 139.3, 129.3, 128.7, 126.9, 126.7, 116.0, 112.2, 54.6, 51.5, 29.5, 27.0, 22.8, 14.3. MS (EI): m/z: 253 (20, M⁺), 196 (65), 91 (100), 77 (15).

N-benzyl-*N*-(thiophen-2-ylmethyl)aniline¹ (3k)



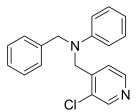
Light yellow oil, yield = 68%, 95 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.43-7.25 (m, 8H), 7.04-6.80 (m, 5H), 4.82 (s, 2H), 4.69 (s, 2H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ = 148.8, 142.6, 138.6, 129.4, 128.8, 127.1, 127.0, 126.9, 125.2, 124.5, 117.6, 113.5, 54.2, 50.0. MS (EI): m/z: 279 (50, M⁺), 97 (100), 77 (20), 51 (10).

N-benzyl-*N*-(furan-2-ylmethyl)aniline (3l)



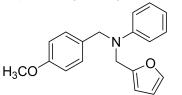
Light yellow oil, yield = 71%, 93 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.42-7.27 (m, 8H), 6.92-6.80 (m, 3H), 6.42-6.31 (m, 1H), 6.28-6.19 (m, 1H), 4.68 (s, 2H), 4.60 (s, 2H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 152.4, 149.0, 142.1, 138.8, 129.3, 128.8, 127.1, 126.9, 117.3, 113.1, 110.4, 107.6, 54.4, 47.8. MS (EI): m/z: 263 (75, M⁺), 220 (15), 91 (50), 81 (100).

N-benzyl-N-((3-chloropyridin-4-yl)methyl)aniline (3m)



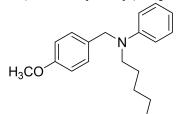
Light yellow solid, yield = 55%, 85 mg, ¹H NMR (300 MHz, CDCl₃): δ = 8.34-8.35 (m, 1H), 7.58 (d, 1H, *J* = 7.6 Hz), 7.20-7.41 (m, 8H), 6.68-6.81 (m, 3H), 4.72 (s, 2H), 4.70 (s, 2H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 150.3, 148.3, 148.1, 138.0, 136.8, 132.4, 129.6, 129.0, 127.3, 126.7, 122.8, 117.6, 112.4, 54.8, 52.2. MS (EI): m/z: 308 (60, M⁺), 231 (20), 126 (25), 91 (100), 65 (10).

N-(furan-2-ylmethyl)-N-(4-methoxybenzyl)aniline (3n)



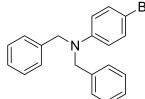
Light yellow oil, yield = 69%, 101 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.42-7.41 (m, 1H), 7.29-7.22 (m, 4H), 6.94-6.89 (m, 4H), 6.79 (t, 1H, *J* = 7.2 Hz), 6.37-6.35 (m, 1H), 6.22-6.21 (m, 1H), 4.60 (s, 2H), 4.56 (s, 2H), 3.85 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 158.8, 152.5, 149.0, 142.0, 130.6, 129.3, 128.1, 117.3, 114.1, 113.2, 110.4, 107.6, 55.4, 53.8, 47.6. MS (EI): m/z: 293 (35, M⁺), 121 (100), 81 (10).

N-(4-methoxybenzyl)-N-pentylaniline (30)



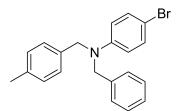
Light yellow oil, yield = 77%, 109 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.28-7.20 (m, 4H), 6.94-6.90 (m, 2H), 6.77-6.71 (m, 3H), 4.55 (s, 2H), 3.85 (s, 3H), 1.78-1.68 (m, 2H), 1.47-1.36 (m, 4H), 0.99 (t, 3H, J = 6.6 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 158.6, 148.8, 131.1, 129.3, 127.8, 116.0, 114.1, 112.3, 55.4, 54.0, 51.3, 29.5, 26.9, 22.7, 14.3. MS (EI): m/z: 283 (20, M⁺), 226 (10), 121 (100), 77 (15).

N,*N*-dibenzyl-4-bromoaniline⁴ (3p)



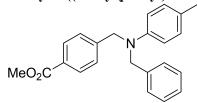
Brown solid, yield = 33%, 58 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.44-7.29 (m, 12H), 6.69 (d, 2H, *J* = 8.7 Hz), 4.71 (s, 4H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 148.2, 138.1, 132.0, 128.9, 127.2, 126.7, 114.4, 108.8, 54.6. MS (EI): m/z: 351 (20, M⁺), 260 (5), 91 (100), 65 (20).

N-benzyl-4-bromo-*N*-(4-methylbenzyl)aniline¹ (3q)



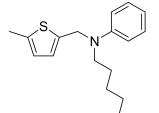
Light yellow solid, yield = 50%, 92 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.46-7.20 (m, 11H), 6.70 (d, 2H, *J* = 8.7 Hz), 4.72 (s, 2H), 4.70 (s, 2H), 2.45 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 148.2, 138.2, 136.8, 134.9, 131.9, 129.6, 128.9, 127.2, 126.7, 114.3, 108.7, 54.5, 54.3, 21.2. MS (EI): m/z: 365 (20, M⁺), 207 (5), 105 (100), 91, (45), 77 (20).

Methyl 4-((benzyl(p-tolyl)amino)methyl)benzoate¹ (3r)



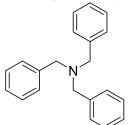
White solid, yield = 66%, 114 mg, ¹H NMR (300 MHz, CDCl₃): δ = 8.01 (d, 2H, *J* = 7.8 Hz), 7.36-7.29 (m, 7H), 7.01 (d, 2H, *J* = 8.1 Hz), 6.67 (d, 2H, *J* = 8.7 Hz), 4.67 (s, 2H), 4.65 (s, 2H), 3.93 (s, 3H), 2.26 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 167.1, 146.9, 144.7, 138.7, 130.1, 129.9, 129.0, 128.8, 127.1, 126.9, 126.8, 126.5, 113.0, 54.9, 54.6, 52.2, 20.4. MS (EI): m/z: 345 (45, M⁺), 253 (10), 195 (25), 91 (100), 65 (25).

N-((5-methylthiophen-2-yl)methyl)-N-pentylaniline (3s)



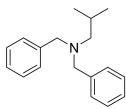
Light yellow oil, yield = 74%, 106 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.29-7.25 (m, 2H), 6.83-6.62 (m, 5H), 4.63 (s, 2H), 3.39 (t, 2H, *J* = 7.6 Hz), 2.47 (s, 3H), 1.70-1.68 (m, 2H), 1.43-1.39 (m, 4H), 0.98 (t, 3H, *J* = 7.2 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 148.4, 140.6, 138.7, 129.3, 124.8, 124.5, 116.6, 112.8, 51.0, 50.3, 29.5, 27.1, 22.8, 15.5, 14.3. MS (EI): m/z: 273 (25, M⁺), 216 (10), 111 (100), 77 (15).

Tribenzylamine⁵ (3t)



Light yellow solid, yield = 64%, 92 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.51-7.29 (m, 15H), 3.65 (s, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 139.8, 128.9, 128.4, 127.0, 58.1. MS (EI): m/z: 287 (30, M⁺), 210 (35), 91 (100), 65 (15).

N,*N*-dibenzyl-2-methylpropan-1-amine⁶ (3u)

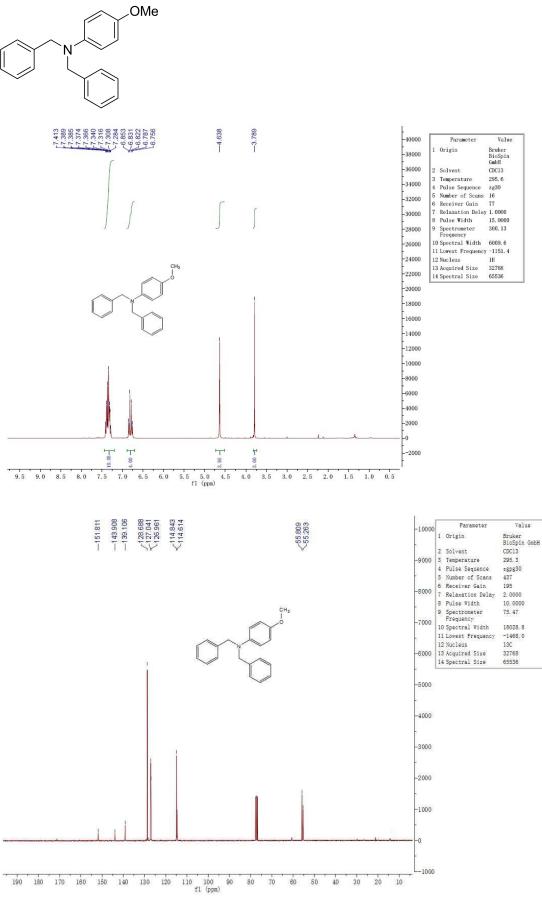


Light yellow solid, yield = 80%, 101 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.53-7.32 (m, 10H), 3.65 (s, 4H), 2.29 (d, 2H, *J* = 7.5 Hz), 2.05-1.96 (m, 1H), 1.02-0.99 (m, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 140.2, 129.0, 128.3, 126.9, 62.4, 59.0, 26.3, 21.0. MS (EI): m/z: 253 (5, M⁺), 210 (60), 91 (100), 65 (15).

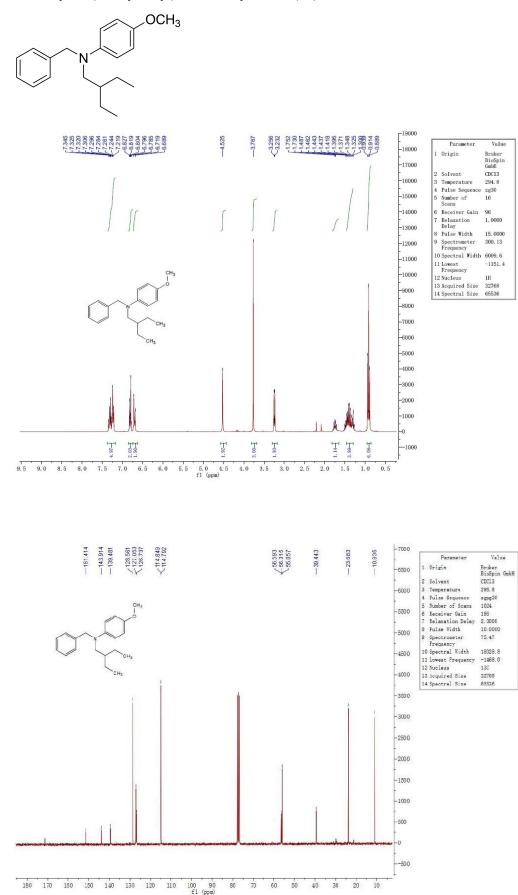
References

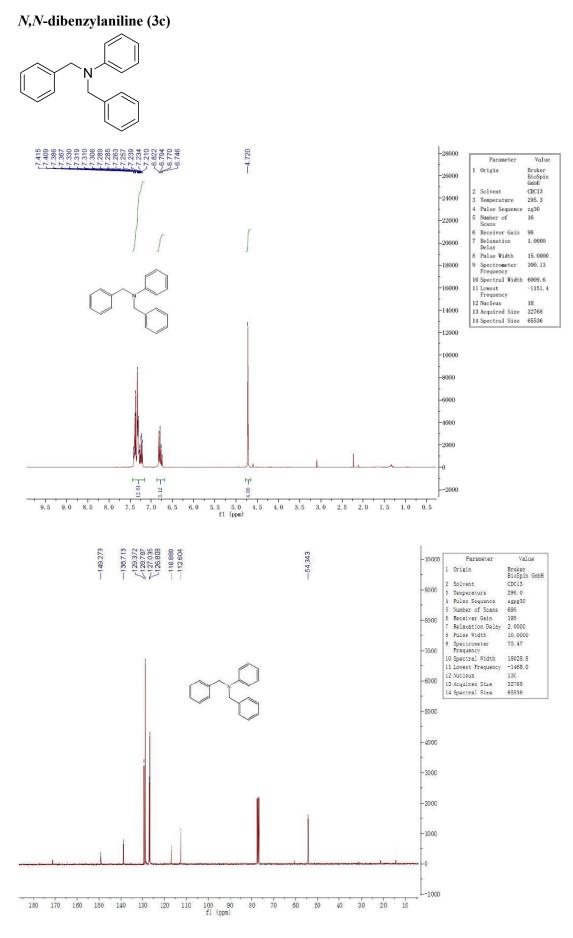
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N-benzyl-4-methoxy-N-benzylaniline (3a)

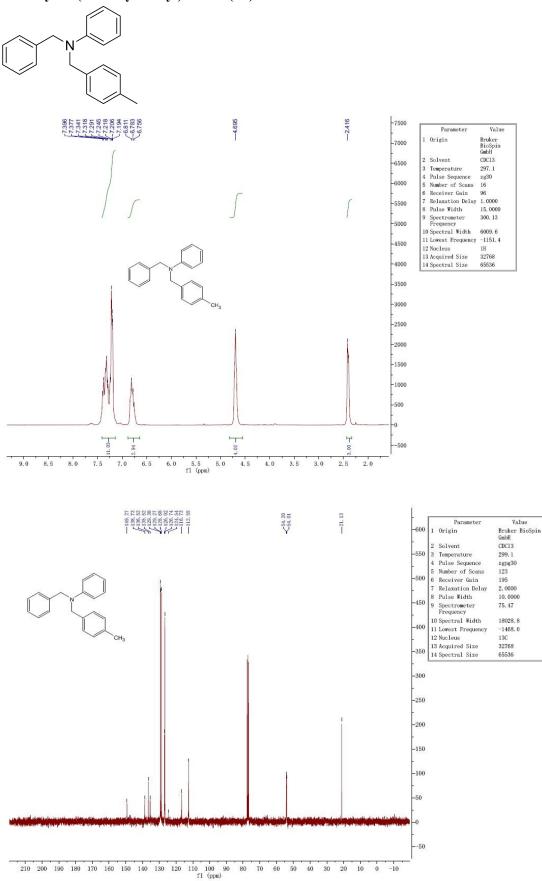


N-benzyl-N-(2-ethylbutyl)-4-methoxyaniline (3b)

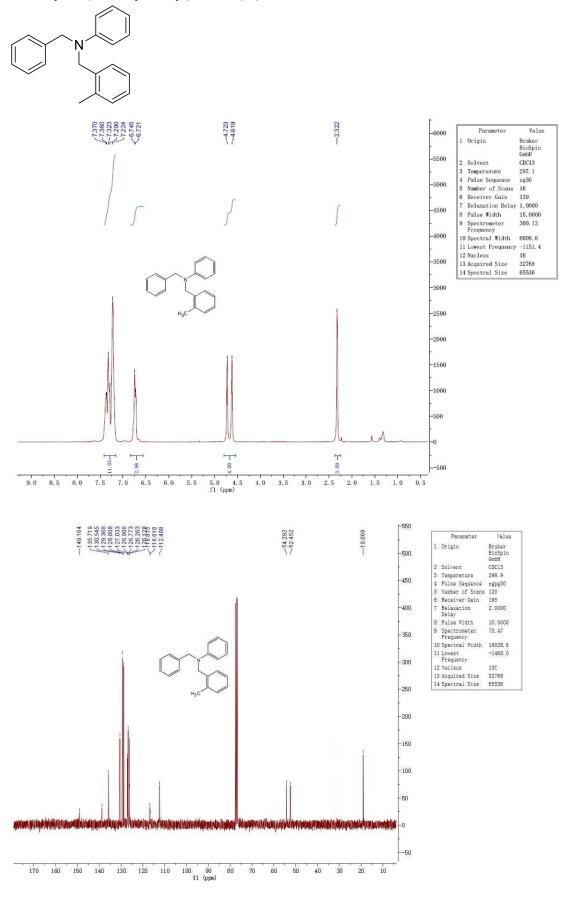




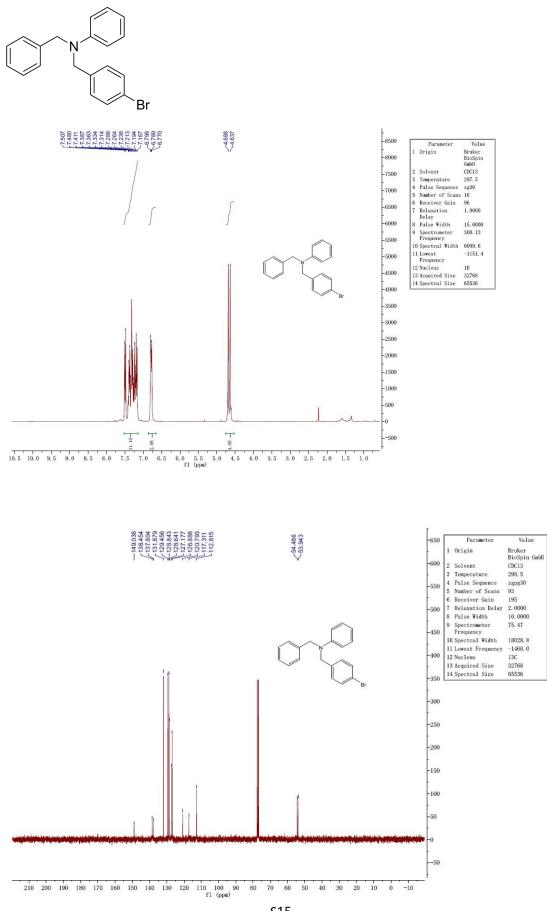
N-benzyl-N-(4-methylbenzyl)aniline (3d)



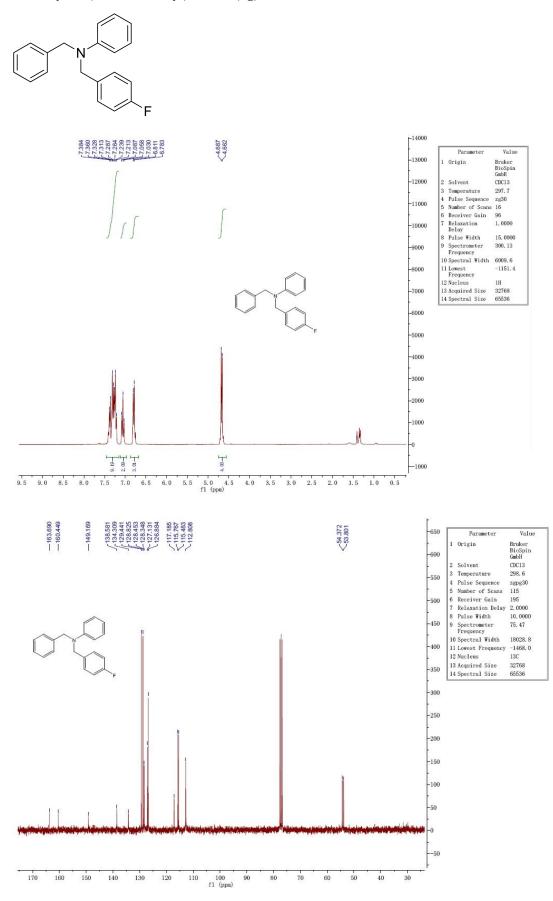
N-benzyl-N-(2-methylbenzyl)aniline (3e)



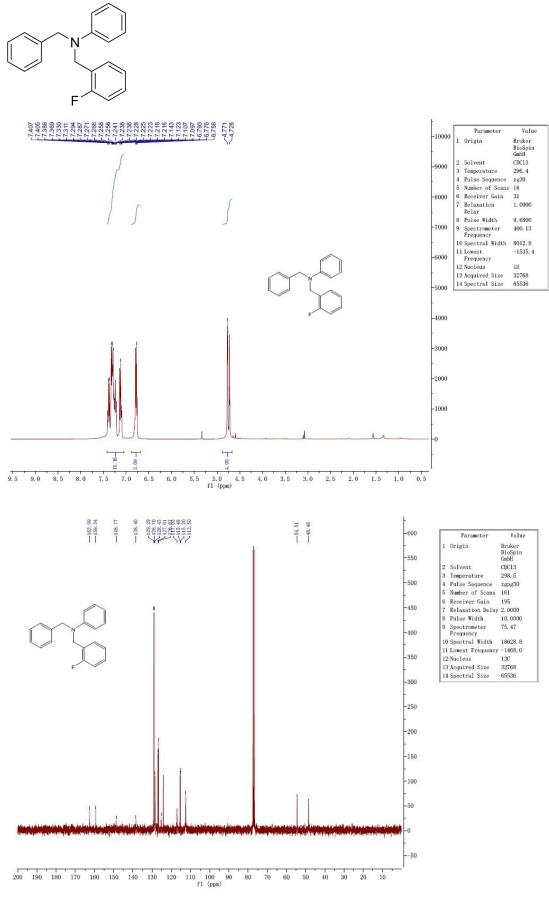
N-benzyl-N-(4-bromobenzyl)aniline (3f)



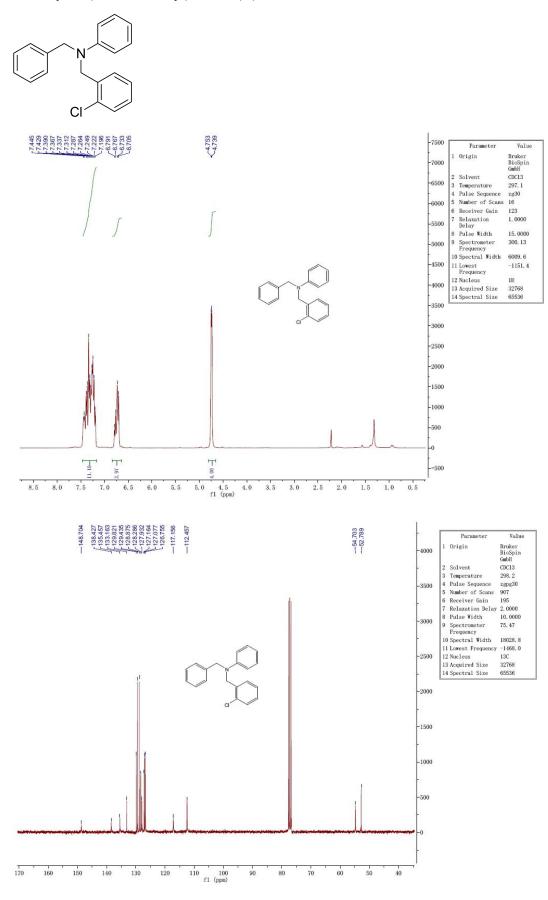
N-benzyl-N-(4-fluorobenzyl)aniline (3g)



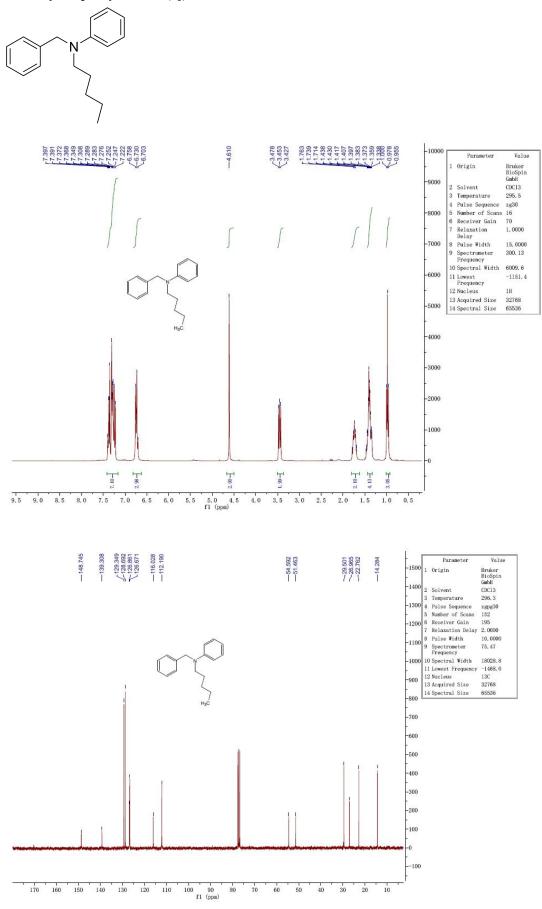
N-benzyl-N-(2-fluorobenzyl)aniline (3h)

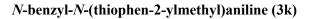


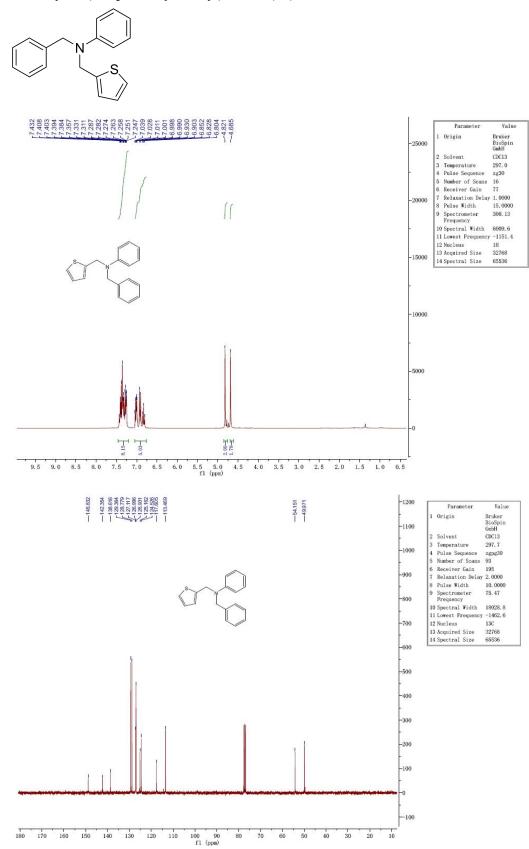
N-benzyl-N-(2-chlorobenzyl)aniline (3i)



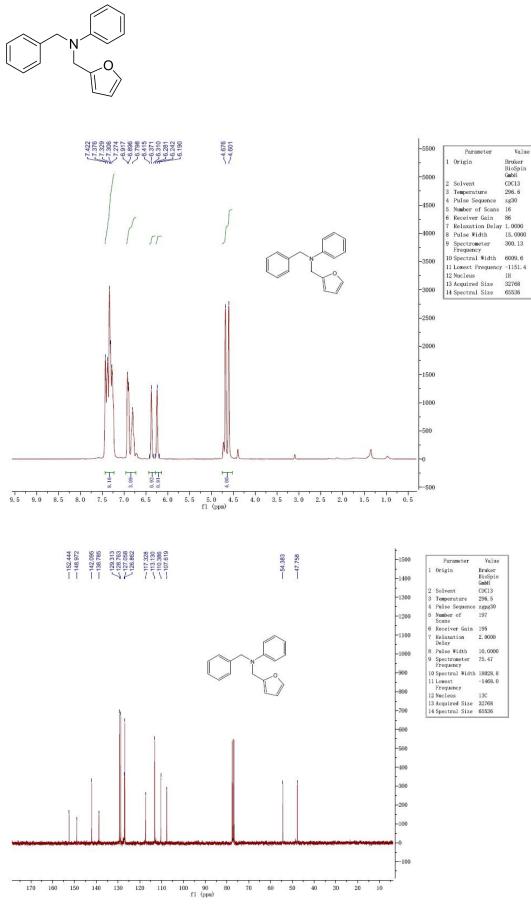
N-benzyl-N-pentylaniline (3j)

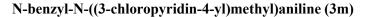


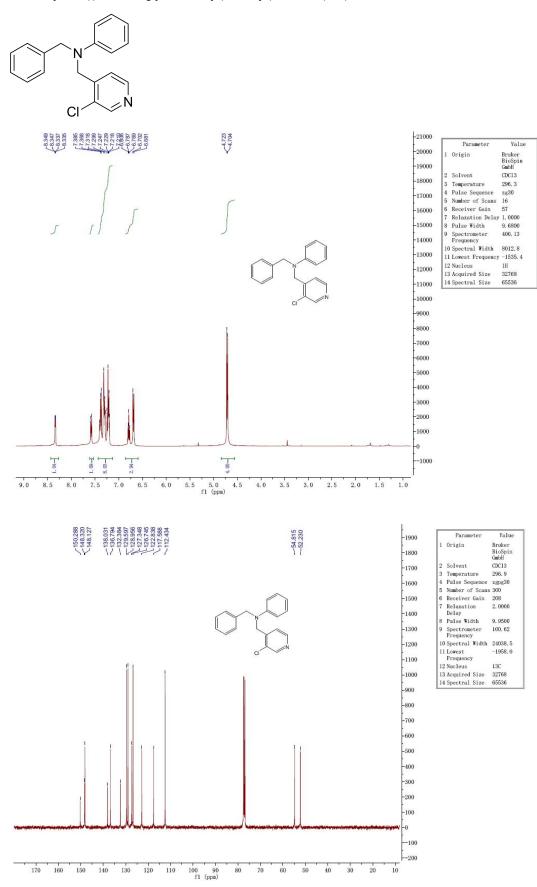


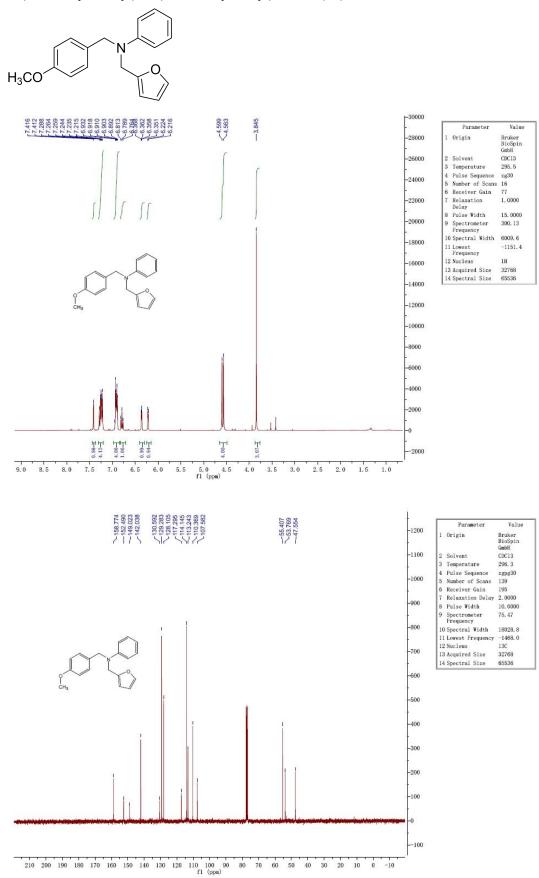


N-benzyl-N-(furan-2-ylmethyl)aniline (3l)

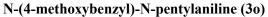


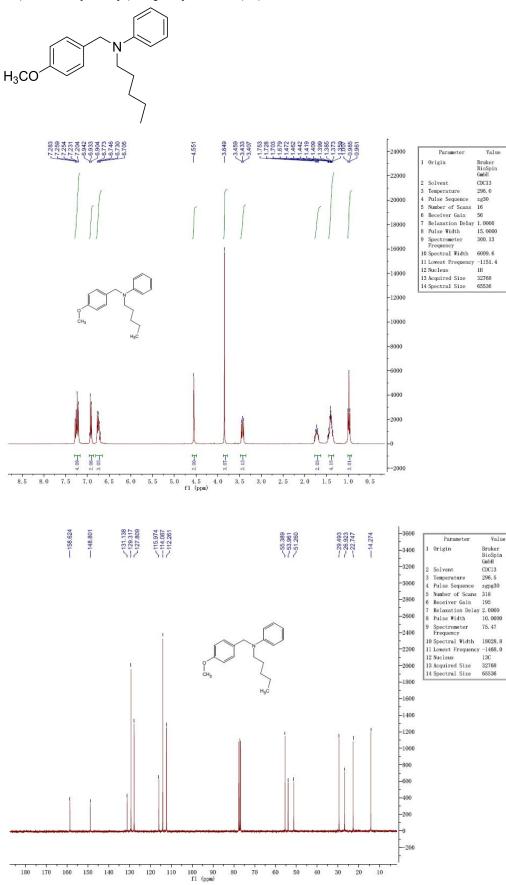






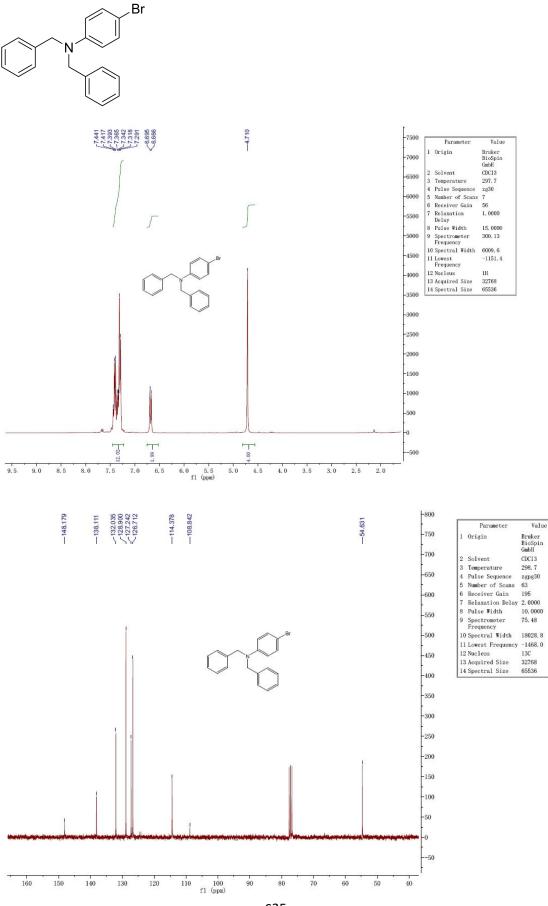
N-(furan-2-ylmethyl)-N-(4-methoxybenzyl)aniline (3n)



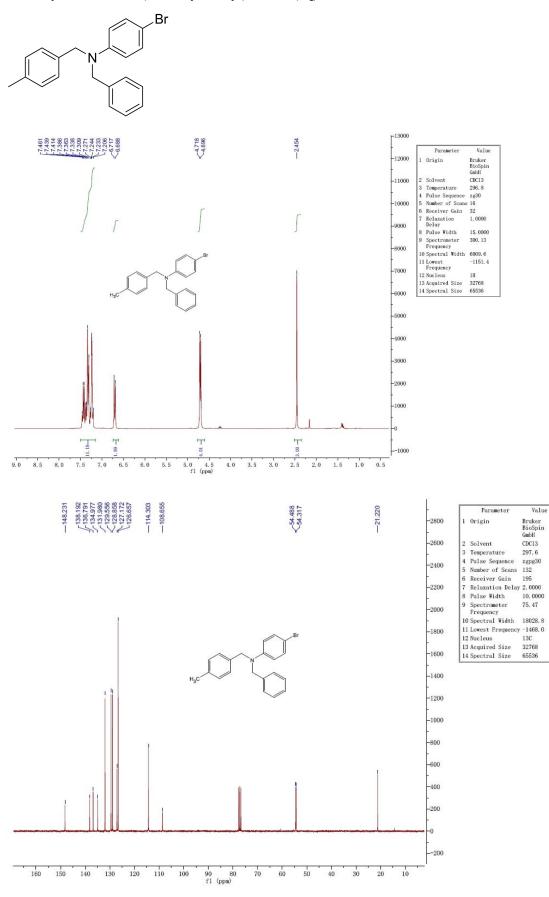




N,N-dibenzyl-4-bromoaniline (3p)



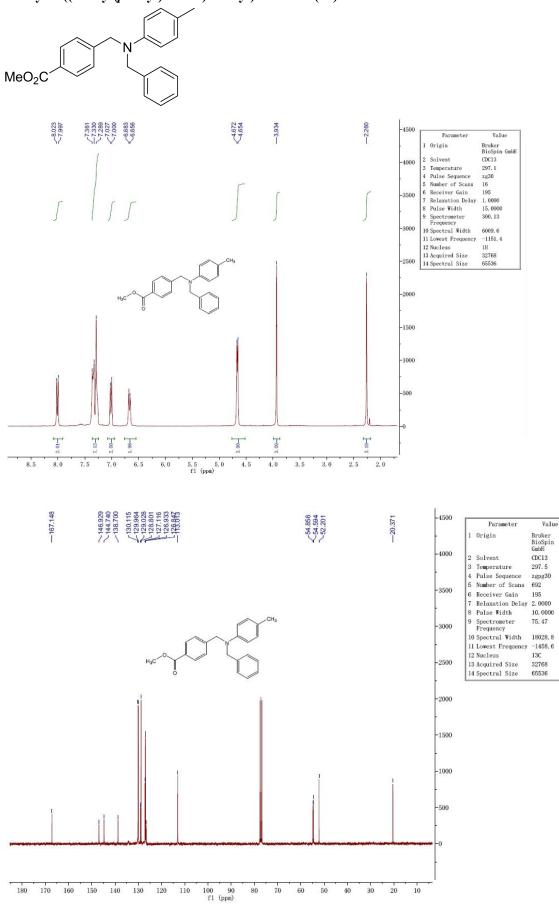
N-benzyl-4-bromo-N-(4-methylbenzyl)aniline (3q)



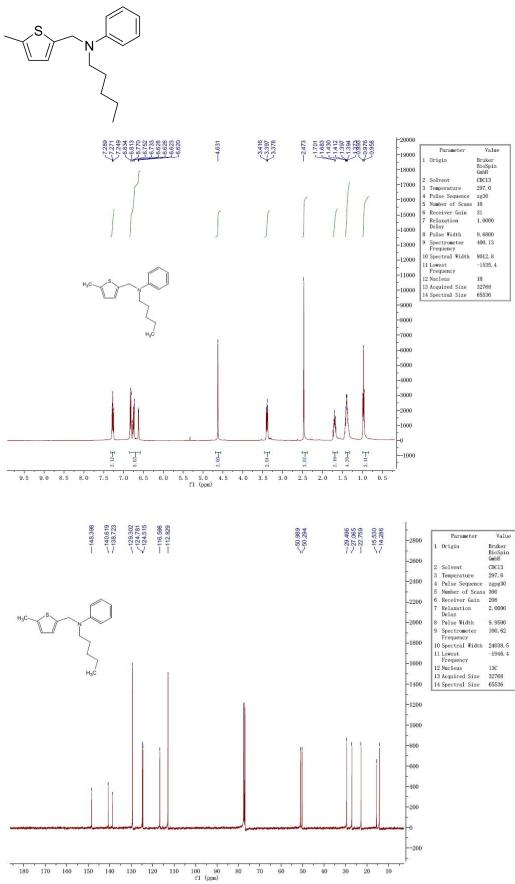
Value

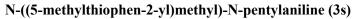
Bruker BioSpin GmbH





Methyl 4-((benzyl(p-tolyl)amino)methyl)benzoate (3r)





Tribenzylamine (3t)

