Electronic Supporting Information

Imidazolium-Based Ionic Liquids Catalyzed Hydrosilylation of Imines and Reductive Amination of Aldehydes Using Hydrosilane as the Reductant

Bin Li[a]*, Shilin Zhang[a], Weizhen Wu[a], Lecheng Liang[ab], Shaohua Jiang[a], Lu Chen[a]* and Yibiao Li[a]
[a]*School of Chemical & Environmental Engineering, Wuyi University, Jiangmen 529020, Guangdong Province, P.R. China*
[b]*Guangdong Wamo New Material Technology Co., Ltd, Jiangmen 529020, Guangdong Province, P.R. China*

Table of Contents

General remarks

All reagents were obtained from commercial sources and used as received. Ethanol (anhydrous) were used as received. Technical grade petroleum ether (40-60°C bp.) and ethyl acetate were used for chromatography column.

^{1}H NMR spectra were recorded in $CDCl_3$ at ambient temperature on Bruker AVANCE I 300 spectrometers at 300.1 MHz, using the solvent as internal standard (7.26 ppm). ^{13}C 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-2010 (Shimadzu) equipped with a 30-m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with N_2/air as vector gas. The following GC conditions were used: initial temperature 80 °C, for 2 minutes, then rate 10 °C/min. until 260 °C and 260°C for 10 minutes.

Method A: General procedure for [BMIm][$FeCl_4$] catalyzed hydrosilylation of imines

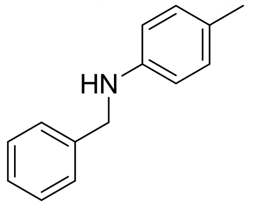
[BMIm][$FeCl_4$] (0.1 mmol, 33.6 mg), imine (0.5 mmol), Ph_2SiH_2 (0.75 mmol, 139 µL), and ethanol (2 mL) were introduced in Schlenck tube under air, equipped with magnetic stirring bar and was stirred at 80 °C. After 16 h, the conversion of the reaction was analyzed by gas chromatography. The solvent 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.

Method B: General procedure for [BMIm][$FeCl_4$] catalyzed reductive amination of aldhydes and anilines

[BMIm][$FeCl_4$] (0.1 mmol, 33.6 mg), aldhydes (0.6 mmol), aniline (0.5 mmol), Ph_2SiH_2 (0.75 mmol, 139 µL), 4 Å molecular sieves (200 mg) and ethanol (2 mL) were introduced in Schlenck tube under air, equipped with magnetic stirring bar and was stirred at 80 °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.

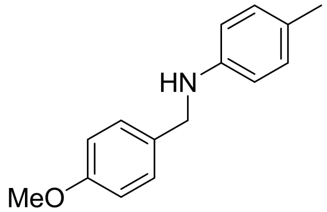
Characterization data of substrates

4-Methyl-*N*-(benzyl)aniline[1] (4a)



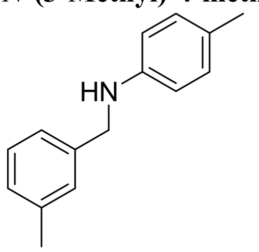
Light yellow oil, Method A: yield = 85%, 84 mg; Method B: yield = 80%, 79 mg.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33-7.45 (m, 5H), 7.04-7.07 (m, 2H), 6.62-6.65 (m, 2H), 4.37 (s, 2H), 3.96 (brs, 1H), 2.31 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.1, 139.8, 129.9, 128.7, 127.6, 127.3, 126.9, 113.1, 48.8, 20.6.

***N*-(4-Methoxybenzyl)-4-methylaniline[1] (4b)**



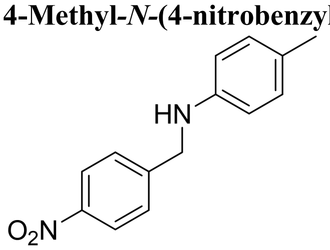
Light yellow powder, Melting Point: 79 - 81 °C, Method A: yield = 84%, 89 mg.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, 2H, *J* = 8.4 Hz), 7.06 (d, 2H, *J* = 8.1 Hz), 6.94 (d, 2H, *J* = 8.1 Hz), 6.63 (d, 2H, *J* = 8.1 Hz), 4.29 (s, 2H), 3.86 (s+brs, 4H), 2.31 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 146.1, 131.7, 129.8, 128.8, 126.7, 114.0, 113.1, 55.3, 48.2, 20.5.

***N*-(3-Methyl)-4-methylaniline[2] (4c)**



Light yellow oil, Method A: yield = 88%, 93 mg; Method B: yield = 85%, 90 mg.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17-7.33 (m, 4H), 7.08 (d, 2H, *J* = 7.8 Hz), 6.67 (d, 2H, *J* = 7.8 Hz), 4.35 (s, 2H), 3.97 (brs, 1H), 2.45 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.1, 139.7, 138.4, 129.9, 128.7, 128.5, 128.1, 127.0, 124.8, 113.3, 48.9, 21.6, 20.6.

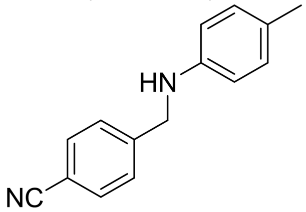
4-Methyl-*N*-(4-nitrobenzyl)aniline[1] (4d)



Red oil, Method A: yield = 36%, 44 mg; Method B: yield = 48%, 58 mg.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, 2H, *J* = 9.0 Hz), 7.55 (d, 2H, *J* = 9.0 Hz), 7.02 (d, 2H, *J* = 7.8 Hz), 6.54 (d, 2H, *J* = 8.4 Hz), 4.48 (s, 2H), 4.18 (brs, 1H), 2.27 (s, 3H).

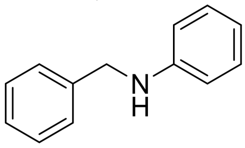
^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.0, 147.2, 145.2, 130.0, 127.8, 127.5, 123.9, 113.2, 48.0, 20.5.

***N*-(4-Cyanobenzyl)-4-methylaniline[1] (4e)**



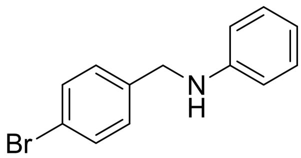
Orange powder, Melting Point: 88 - 90 ºC, Method A: yield = 52%, 58 mg; Method B: yield = 55%, 61 mg.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.64 (m, 2H), 7.49 (d, 2H, *J* = 7.8 Hz), 7.00-7.02 (m, 2H), 6.50-6.54 (m, 2H), 4.42 (s, 2H), 4.12 (brs, 1H), 2.26 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.7, 145.2, 132.4, 129.9, 127.7, 127.3, 118.9, 113.0, 110.8, 48.1, 20.4.

***N*-Benzylaniline[3] (4f)**



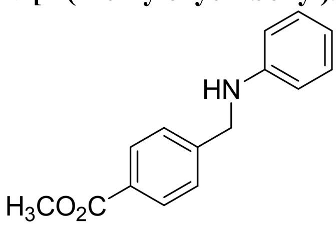
Light yellow oil, Method A: yield = 94%, 86 mg;
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44-7.32 (m, 5H), 7.25-7.20 (m, 2H), 6.79-6.74 (m, 1H), 6.70-6.67 (m, 2H), 4.38 (s, 2H), 4.11 (brs, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.3, 139.6, 129.4, 128.8, 127.7, 127.4, 117.8, 113.0, 48.5.

***N*-(4-bromobenzyl)aniline[4] (4g)**



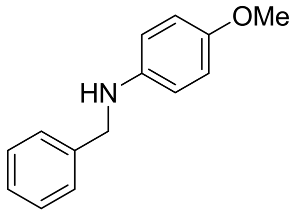
Light yellow oil, Method A: yield = 70%, 91 mg.
^{1}H NMR (300 MHz, CDCl3): δ = 7.43-7.30 (m, 7H), 6.57-6.54 (m, 2H), 4.34 (s, 2H), 4.04 (brs, 1H).
^{13}C NMR (75 MHz, CDCl3): δ = 147.1, 139.0, 132.0, 128.8, 127.5, 127.4, 114.6, 109.2, 48.3.

***N*-[4-(Methyloxycarbonyl)benzyl]aniline[2] (4h)**



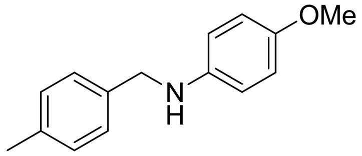
White powder, Melting Point: 46 - 48 ºC, Method A: yield = 75%, 90 mg.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, 2H, *J* = 7.8 Hz), 7.47 (d, 2H, *J* = 7.8 Hz), 7.20-7.18 (m, 2H), 6.77 (t, 1H, *J* = 7.5 Hz), 6.65 (d, 2H, *J* = 7.8 Hz), 4.44 (s, 2H), 4.34 (brs, 1H), 3.94 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 147.8, 145.1, 129.8, 129.2, 128.9, 127.0, 117.6, 112.8, 51.9, 47.7.

4-Methoxy-*N*-benzylaniline[1] (4i)



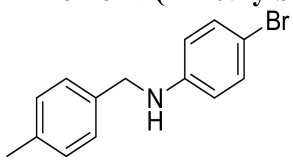
Light yellow cuboids, Melting Point: 47 - 49 ^{o}C, Method A: yield = 86%, 92 mg.
Method B: yield = 78%, 86 mg. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46-7.32 (m, 5H), 6.84-6.80 (m, 2H), 6.67-6.64 (m, 2H), 4.33 (s, 3H), 3.78 (s+brs, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.1, 55.8, 49.3.

4-methoxy-*N*-(4-methylbenzyl)aniline[5] (4j)



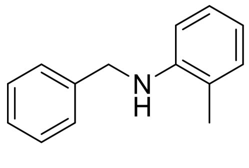
Light yellow oil, Method A: yield = 90%, 102 mg.
^{1}H NMR (300 MHz, CDCl3): δ = 7.31 (d, 2H, J = 8.1 Hz), 7.19 (d, 2H, J = 7.8 Hz), 6.83 (d, 2H, J = 9.0 Hz), 6.65 (d, 1H, J = 9.0 Hz), 4.28 (s, 2H), 3.78 (s, 3H), 2.39 (s, 3H).
^{13}C NMR (75 MHz, CDCl3): δ = 152.3, 142.7, 136.8, 134.5, 129.4, 127.7, 115.1, 114.3, 55.9, 49.2, 21.2.

4-Bromo-*N*-(4-methylbenzyl)aniline[6] (4l)



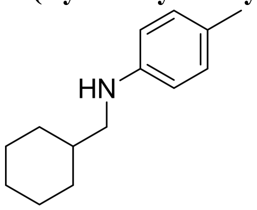
Light yellow oil, Method A: yield = 72%, 99 mg.
1H NMR (300 MHz, CDCl3): δ = 7.23-7.33 (m, 6H), 6.54-6.57 (m, 2H), 4.31 (s, 2H), 3.98 (brs, 1H), 2.44 (s, 3H).
13C NMR (75 MHz, CDCl3): δ = 147.2, 137.1, 135.9, 132.0, 129.5, 127.5, 114.5, 109.1, 48.1, 21.2.

***N*-benzyl-2-methylaniline[1] (4m)**



White powder, Melting Point : 58 - 60 ^{o}C, Method A: yield = 77%, 76 mg.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38-7.50 (m, 5H), 7.17-7.21 (m, 2H), 6.71-6.81 (m, 2H), 4.47 (s, 2H), 3.95 (brs, 1H), 2.27 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ =146.2, 139.6, 130.2, 128.8, 127.6, 127.4, 127.3, 122.0, 117.3, 110.1, 48.4, 17.7.

N-(Cyclohexylmethyl)-4-methylaniline[7] (4n)

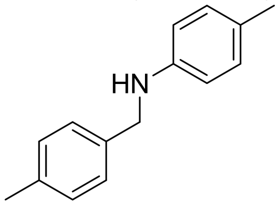


Light yellow oil, Method A: yield = 75%, 76 mg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07 (d, 2H, *J* = 7.8 Hz), 6.62 (d, 2H, *J* = 7.8 Hz), 3.63 (brs, 1H), 3.03 (d, 2H, *J* = 6.6 Hz), 2.34 (s, 3H), 1.93-1.65 (m, 5H), 1.40-1.15 (m, 4H), 1.09-1.03 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.5, 129.9, 126.3, 113.0, 51.2, 37.7, 31.5, 26.7, 26.1, 20.5.

N-(4-Methyl)-4-methylaniline[1] (4o)

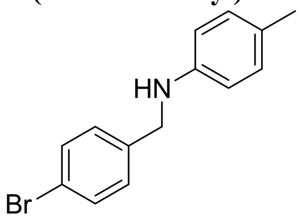


White powder, Melting Point: 54 - 56 °C, Method B: yield = 86%, 91 mg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, 2H, *J* = 7.8 Hz), 7.21 (d, 2H, *J* = 7.8 Hz), 7.05 (d, 2H, *J* = 8.4 Hz), 6.61-6.64 (m, 2H), 4.32 (s, 2H), 3.90 (brs, 1H), 2.40 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 136.7, 136.6, 129.7, 129.2, 127.5, 126.6, 112.9, 48.4, 21.1, 20.4.

N-(4-Bromobenzyl)-4-methylaniline[1] (4p)

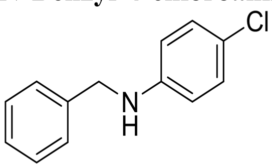


Light yellow powder, Melting Point: 89.5 - 91 °C, Method B: yield = 82%, 113 mg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, 2H, *J* = 8.4 Hz), 7.26 (d, 2H, *J* = 8.4 Hz), 7.01 (d, 2H, *J* = 8.1 Hz), 6.56 (d, 2H, *J* = 8.4 Hz), 4.29 (s, 2H), 3.95 (brs, 1H), 2.27 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 138.8, 131.7, 129.8, 129.1, 127.0, 120.9, 113.1, 48.0, 20.4.

N-Benzyl-4-chloroaniline[8] (4q)

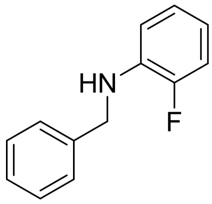


Light yellow oil, Method B: yield = 75%, 81 mg,

1H NMR (300 MHz, CDCl3): δ = 7.36-7.42 (m, 5H), 7.18 (d, 2H, *J* = 9.0 Hz), 6.60 (d, 2H, *J* = 9.0 Hz), 4.35 (s, 2H), 4.01 (brs, 1H).

13C NMR (75 MHz, CDCl3): δ = 146.7, 139.0, 129.2, 128.8, 127.5, 127.4, 122.2, 114.1, 48.4.

2-Fluoro-N-benzylaniline[9] (4r)

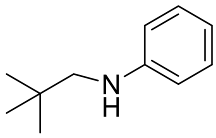


Colorless oil, Method B: yield = 88%, 78 mg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34-7.47 (m, 5H), 7.01-7.09 (m, 2H), 6.60-6.78 (m, 2H), 4.43 (s, 2H), 4.21 (brs, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1 (d, J_{CF} = 236.9Hz), 139.1, 134.5, 128.8, 128.0, 127.5, 124.7 (d, J_{CF} = 3.45Hz), 116.9 (d, J_{CF} = 6.9Hz), 114.4 (d, J_{CF} = 18.3Hz), 112.5 (d, J_{CF} = 3.3Hz), 48.0.

***N*-neopentylaniline[10] (4s)**

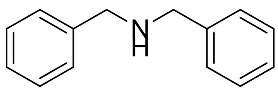


Light yellow oil, Method B: yield = 80%, 65 mg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24-7.20 (m, 2H), 6.67-6.75 (m, 3H), 4.80 (brs, 1H), 2.96 (s, 2H), 1.06 (s, 9H).

^{13}C NMR (75 MHz, CDCl3): δ = 149.1, 129.2, 117.0, 112.7, 55.9, 31.9, 27.7.

Dibenzylamine[3] (4t)



Colorless oil, Method B: yield = 76%, 75 mg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38-7.27 (m, 10H), 3.85 (s, 4H), 1.87 (brs, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3, 128.4, 128.2, 127.0, 53.2.

References

[1] Li, B.; Sortais, J.-B.; Darcel, C.; Dixneuf, P. H. *ChemSusChem*, **2012**, *5*, 396.

[2] Cui, X.; Zhang, Y.; Shi, F.; Deng, Y. *Chem. Eur. J.*, **2011**, *17*, 2581.

[3] Zheng, J.; Roisnel, T.; Darcel, C.; Sortais, J.-B. *ChemCatChem*, **2013**, *5*, 2729.

[4] Liu, P.; Liang, R.; Lu, L.; Yu, Z.; Li, F. *J. Org. Chem.* **2017**, *82*, 1943.

[5] Kolesnikov, P. N.; Yagafarov, N. Z.; Usanov, D. L.; Maleev, V. I.; Chusov, D. *Org. Lett.* **2015**, *17*, 173.

[6] Motoyama, Y.; Taguchi, M.; Desmira, N.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *Chem-Asian J.* **2014**, *9*, 71.

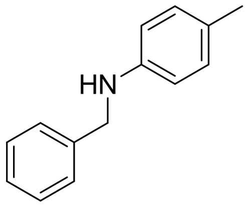
[7] Zhou, W.; Fan, M.; Yin, J.; Jiang, Y.; Ma, D. *J. Am. Chem. Soc.*, **2015**, *137*, 11942.

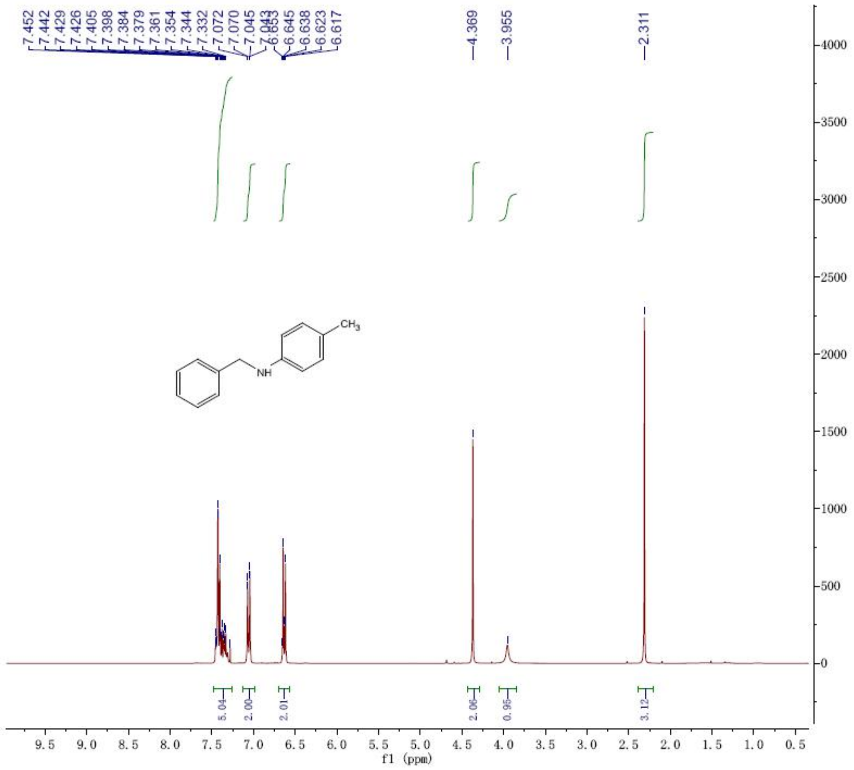
[8] Zhan, L.-W.; Han, L.; Xing, P.; Jiang, B. *Org. Lett.* **2015**, *17*, 5990.

[9] Zhao, Y.; Foo, S. W.; Saito, S. *Angew. Chem., Int. Ed.*, **2011**, *50*, 3006.

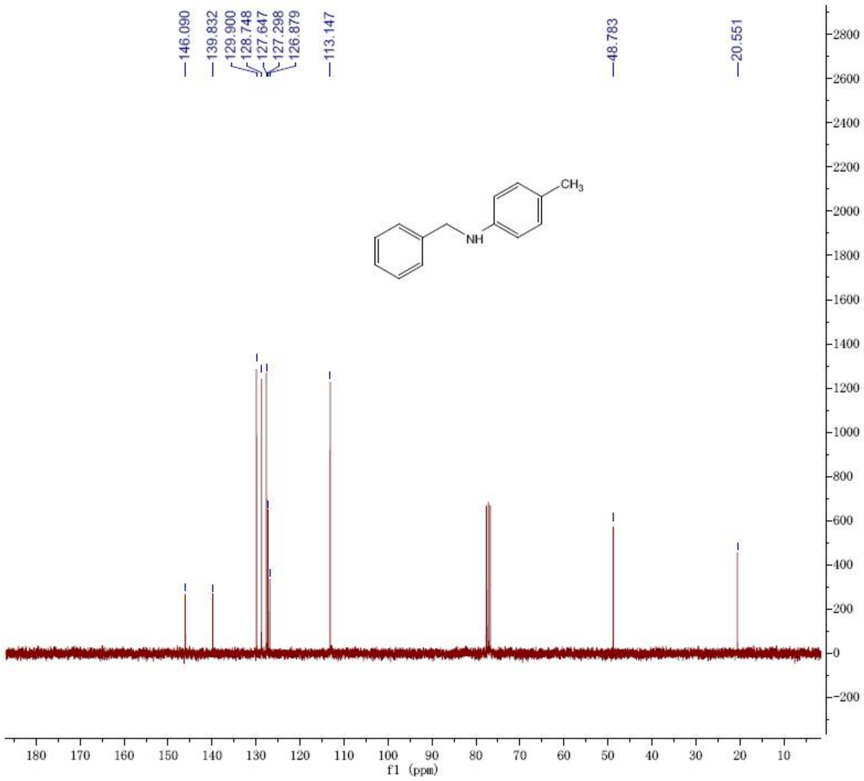
[10] Sorribes, I.; Junge, K.; Beller, M. *J. Am. Chem. Soc.*, **2014**, *136*, 14314.

4-Methyl-*N*-(benzyl)aniline (4a)



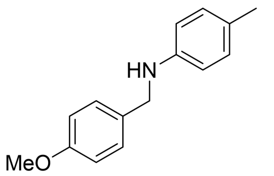


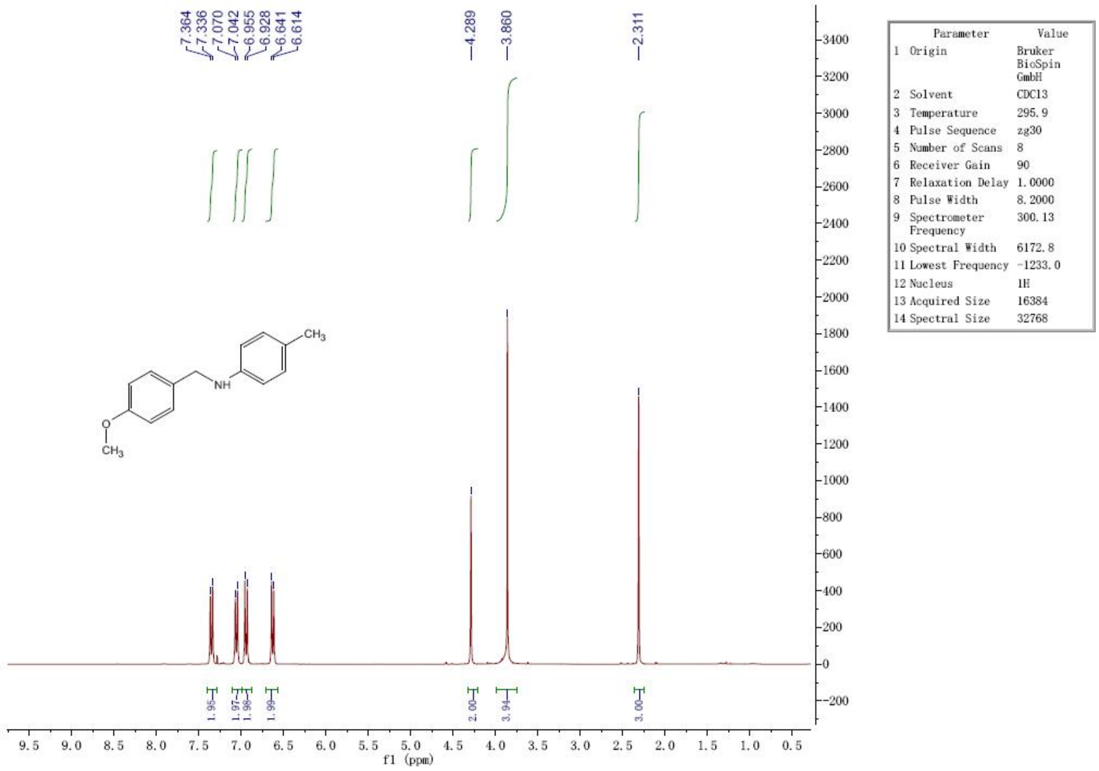
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.6
4 Pulse Sequence	zg30
5 Number of Scans	8
6 Receiver Gain	128
7 Relaxation Delay	1.0000
8 Pulse Width	8.2000
9 Spectrometer Frequency	300.13
10 Spectral Width	6172.8
11 Lowest Frequency	-1233.0
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768

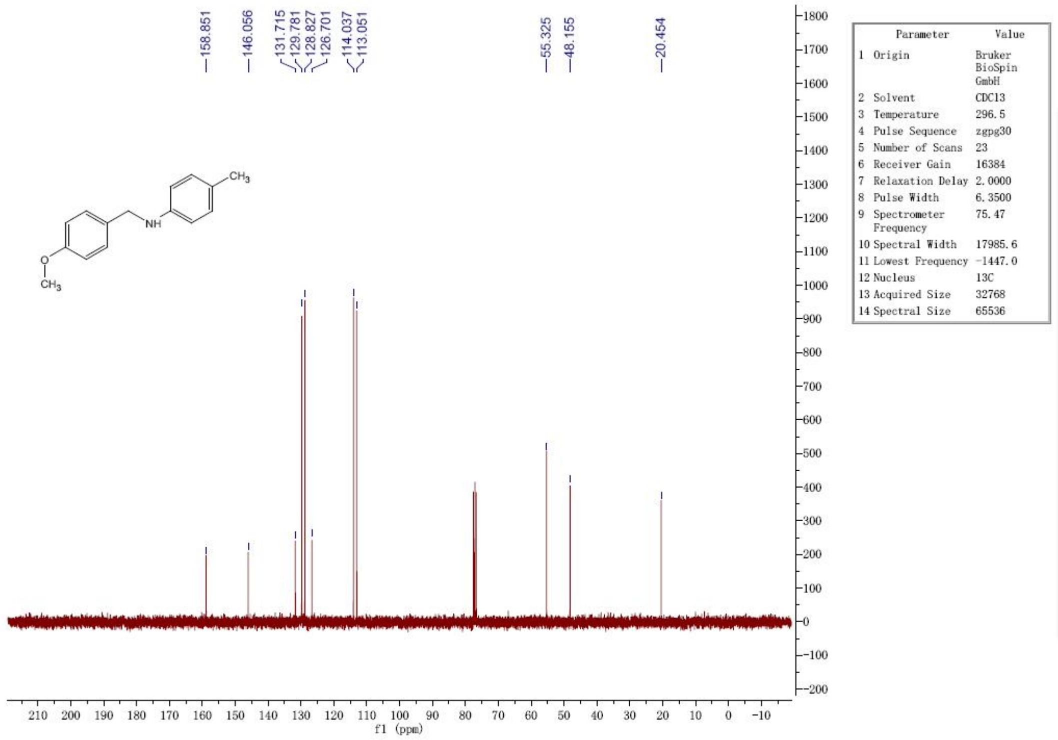


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.9
4 Pulse Sequence	zgpg30
5 Number of Scans	41
6 Receiver Gain	16384
7 Relaxation Delay	2.0000
8 Pulse Width	6.3500
9 Spectrometer Frequency	75.47
10 Spectral Width	17985.6
11 Lowest Frequency	-1447.0
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

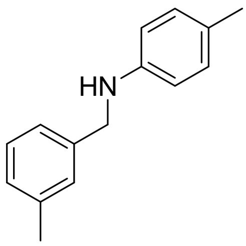
N-(4-Methoxybenzyl)-4-methylaniline (4b)

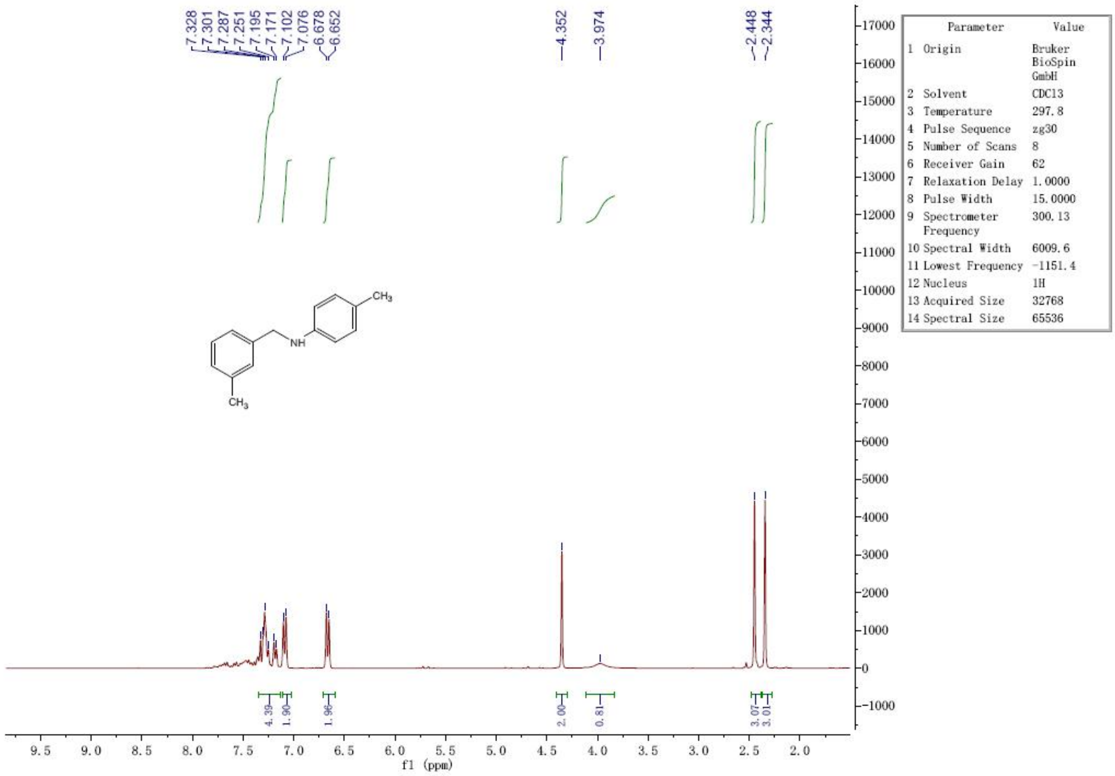


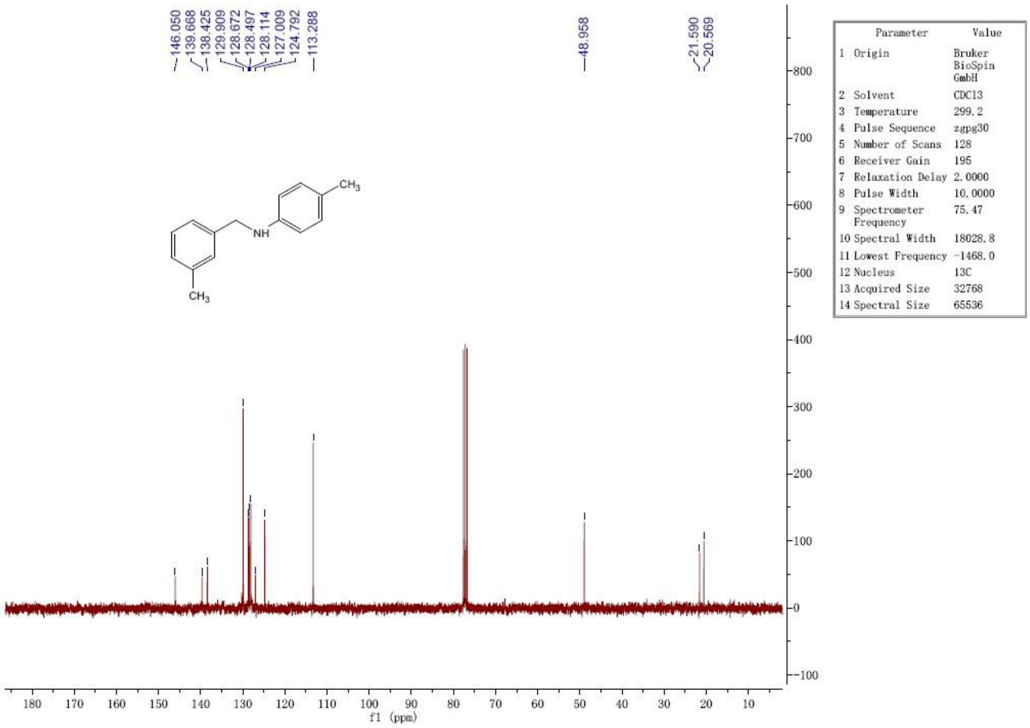




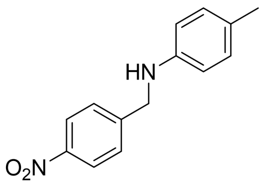
***N*-(3-Methyl)-4-methylaniline (4c)**

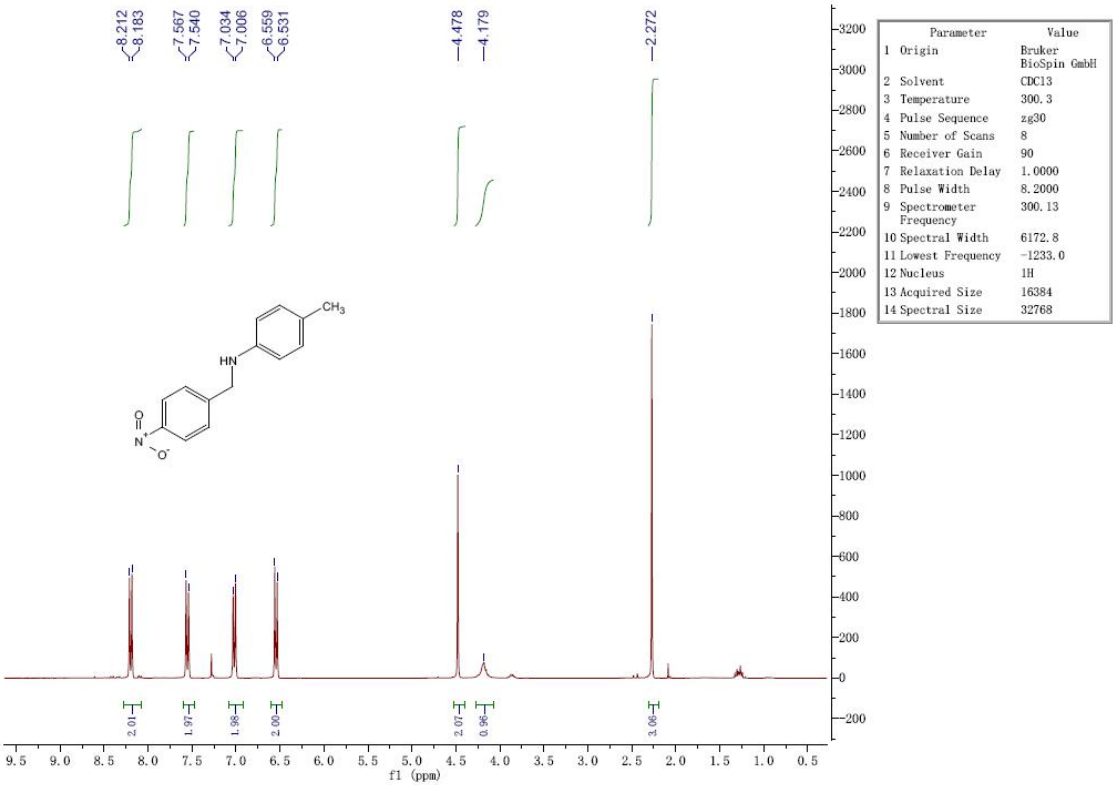


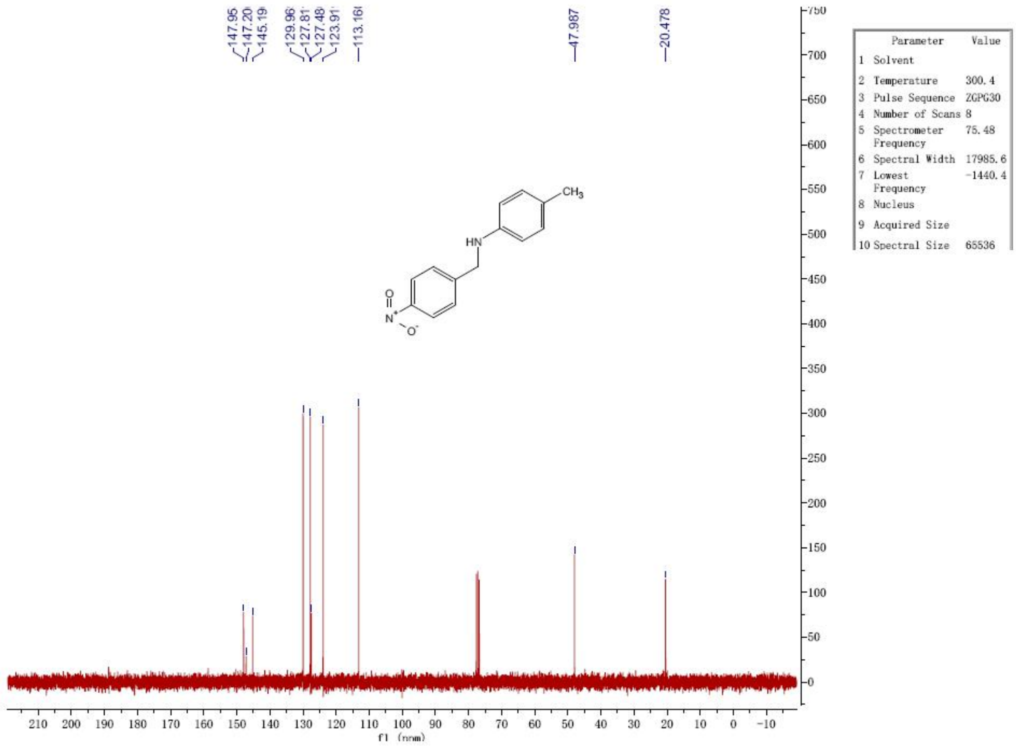




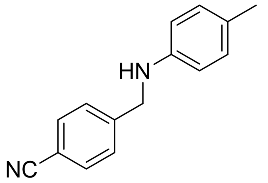
4-Methyl-*N*-(4-nitrobenzyl)aniline (4d)

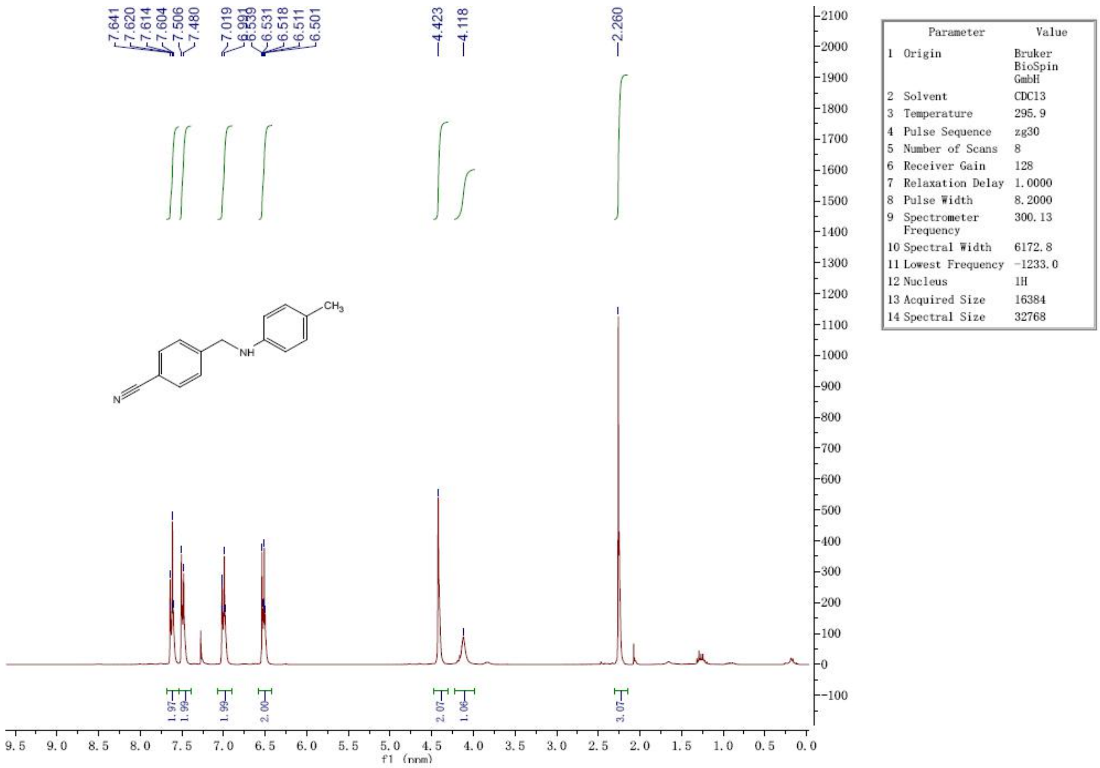


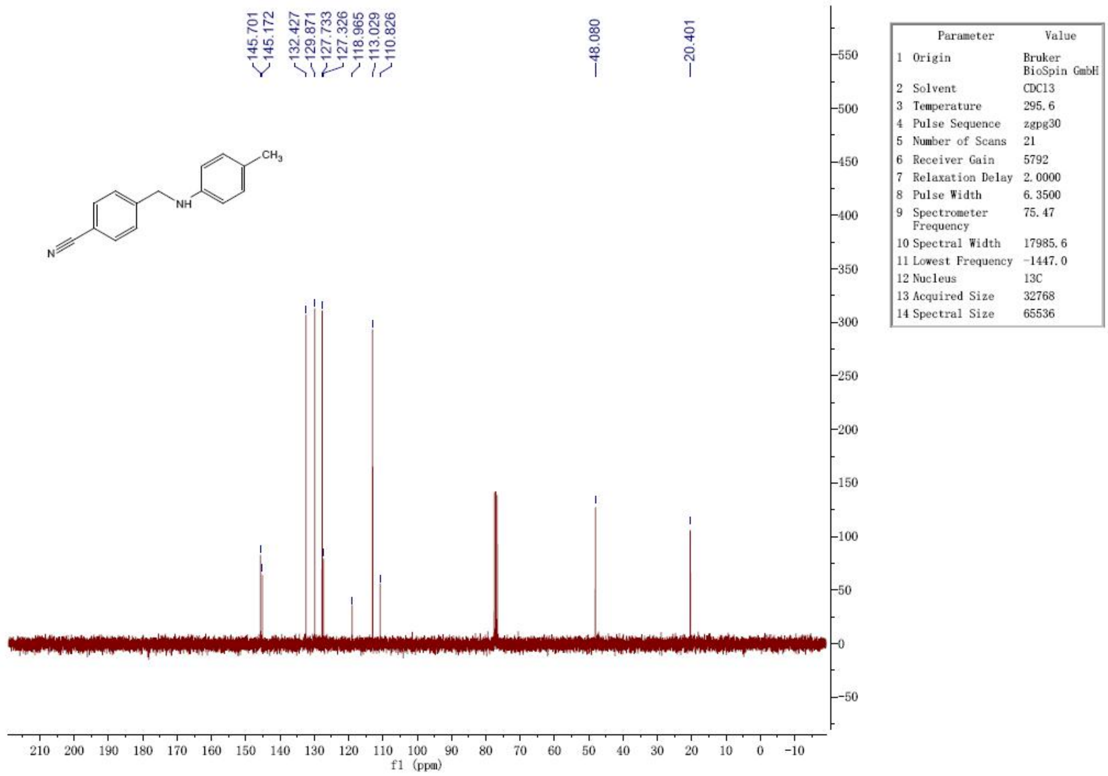




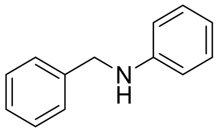
***N*-(4-Cyanobenzyl)-4-methylaniline (4e)**

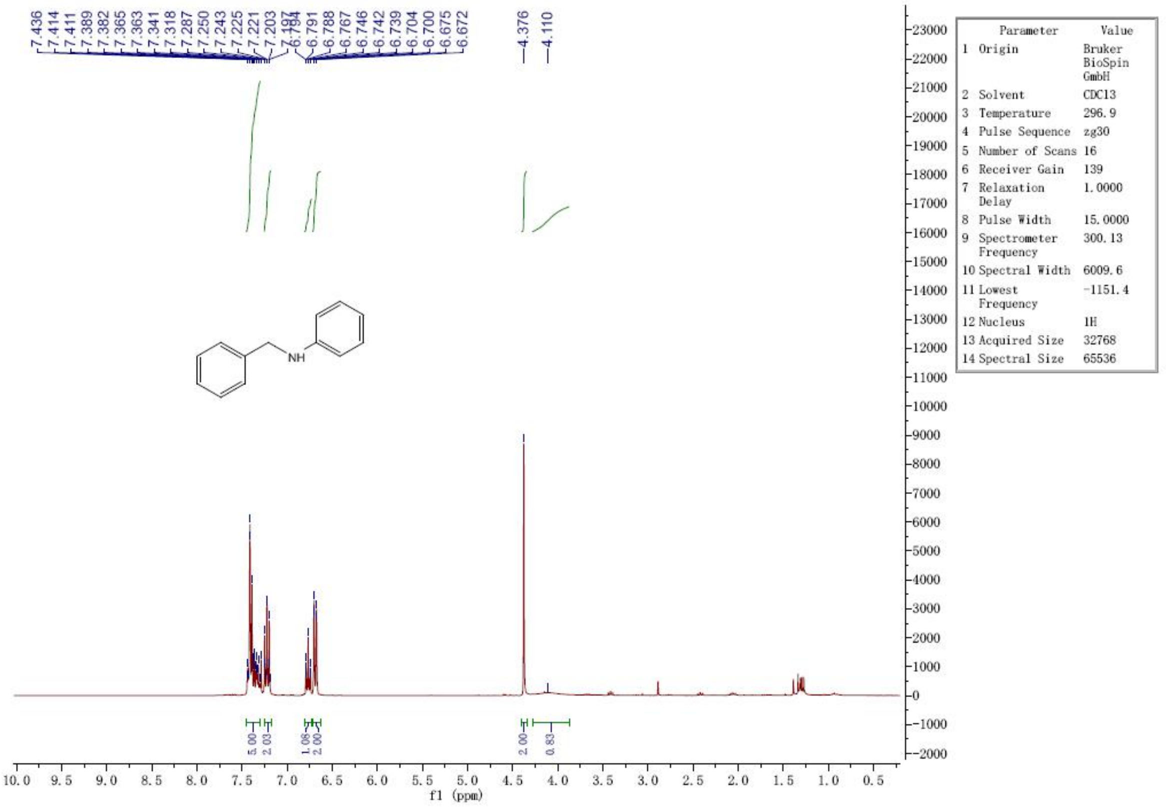


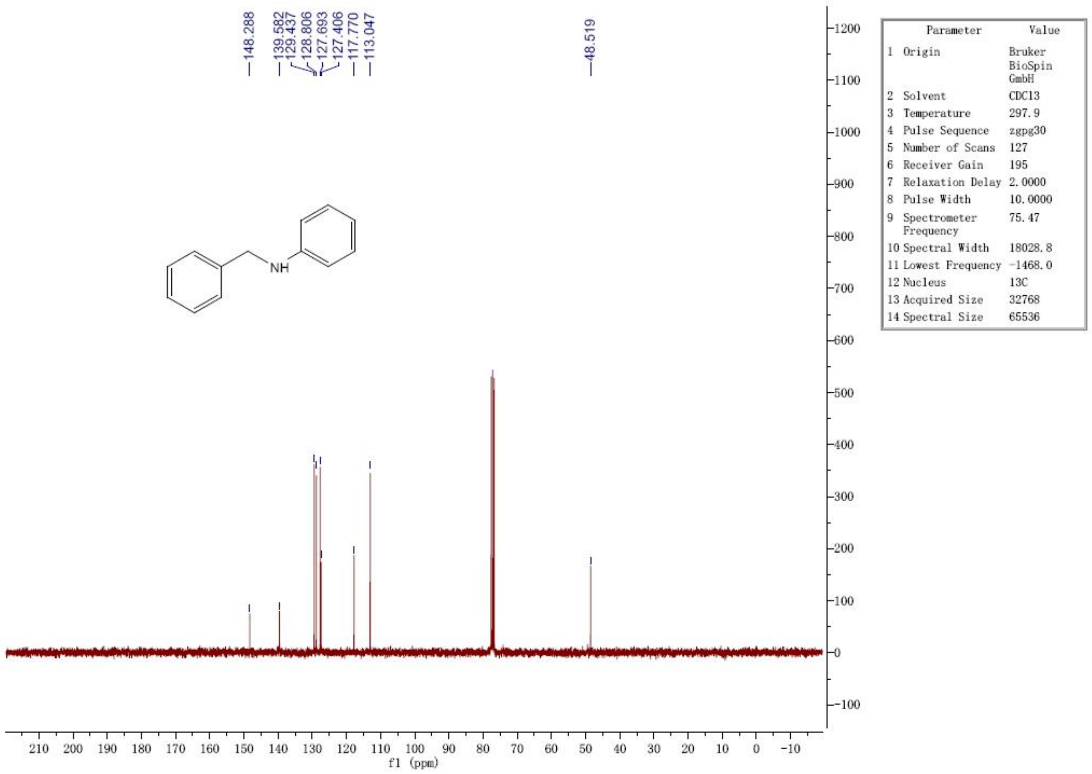




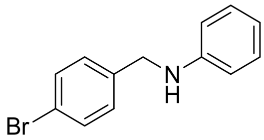
N-Benzylaniline (4f)

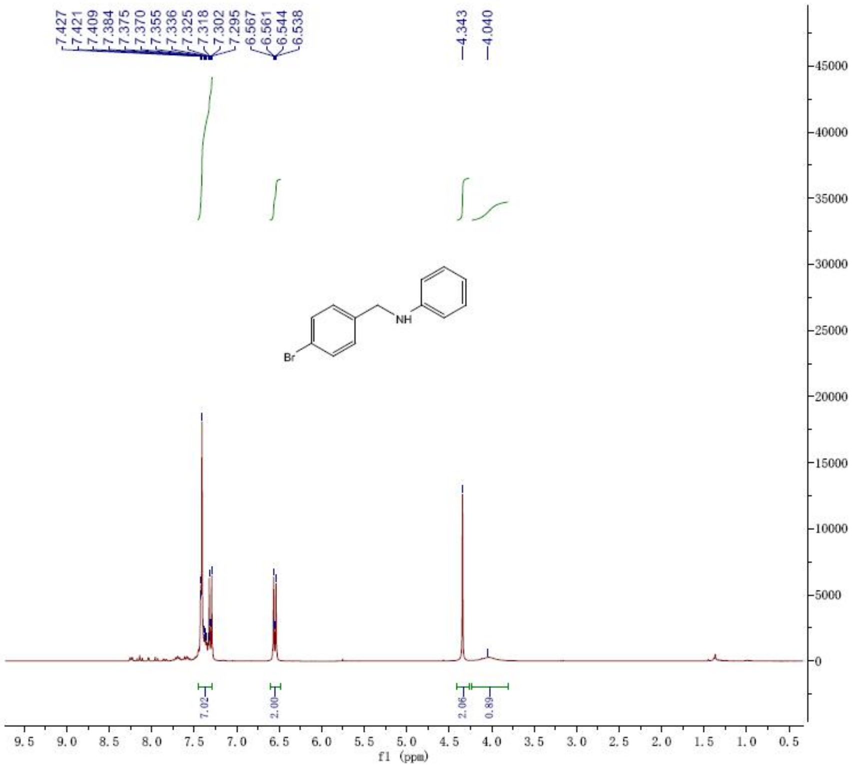




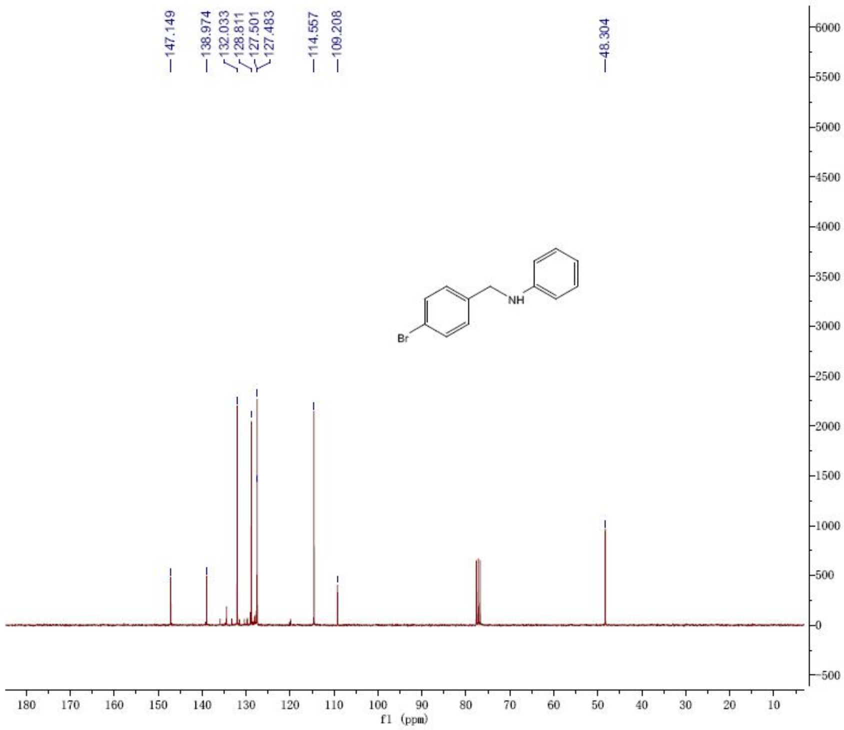


***N*-(4-bromobenzyl)aniline (4g)**



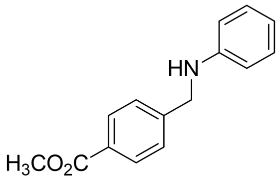


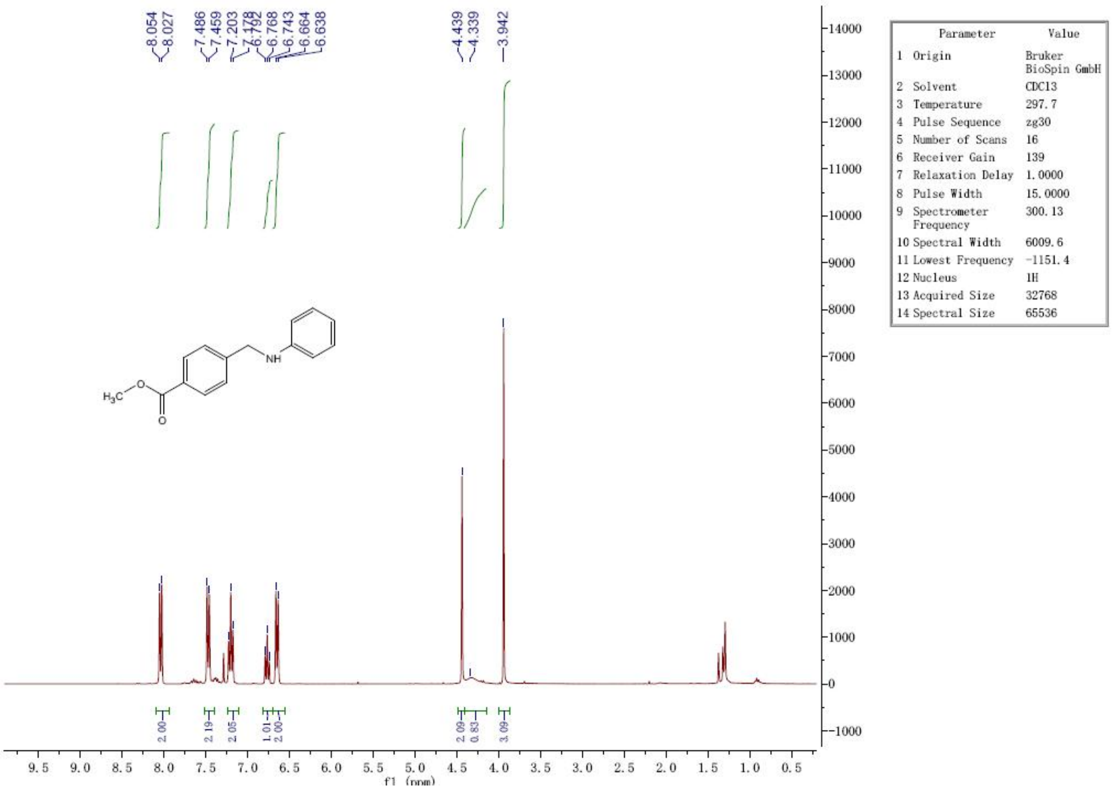
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.3
4 Pulse Sequence	zg30
5 Number of Scans	16
6 Receiver Gain	56
7 Relaxation Delay	1.0000
8 Pulse Width	15.0000
9 Spectrometer Frequency	300.13
10 Spectral Width	6009.6
11 Lowest Frequency	-1151.4
12 Nucleus	1H
13 Acquired Size	32768
14 Spectral Size	65536

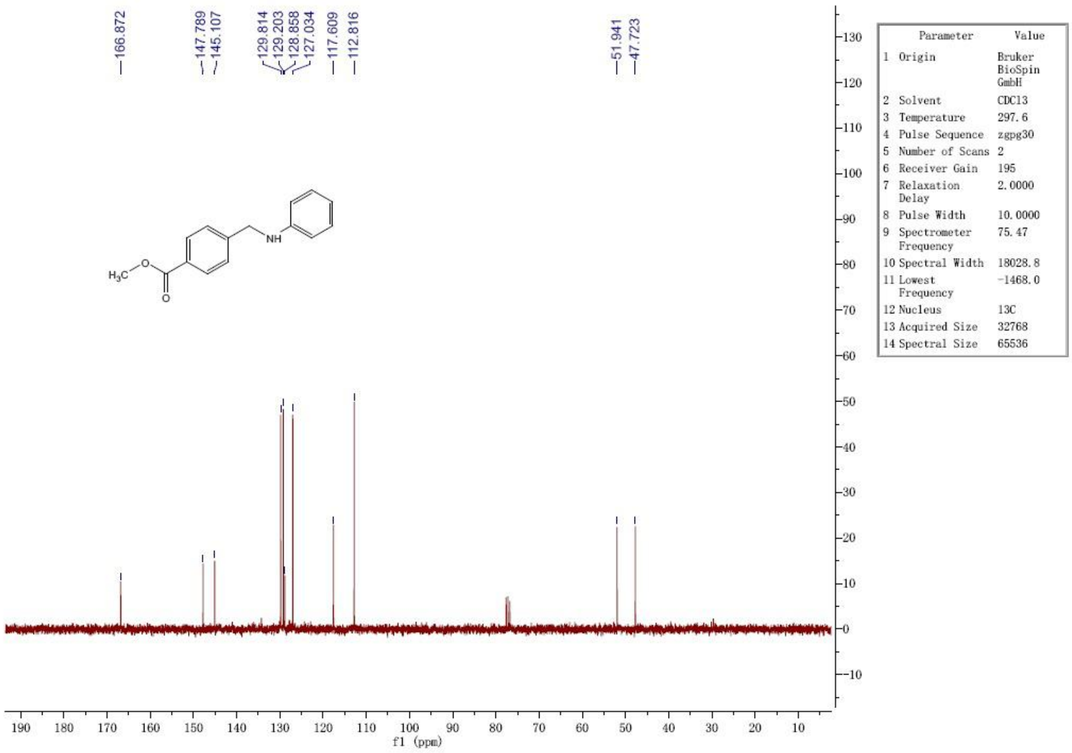


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.9
4 Pulse Sequence	zgpg30
5 Number of Scans	170
6 Receiver Gain	195
7 Relaxation Delay	2.0000
8 Pulse Width	10.0000
9 Spectrometer Frequency	75.47
10 Spectral Width	18028.8
11 Lowest Frequency	-1468.0
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

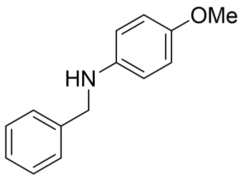
N-[4-(Methyloxycarbonyl)benzyl]aniline (4h)

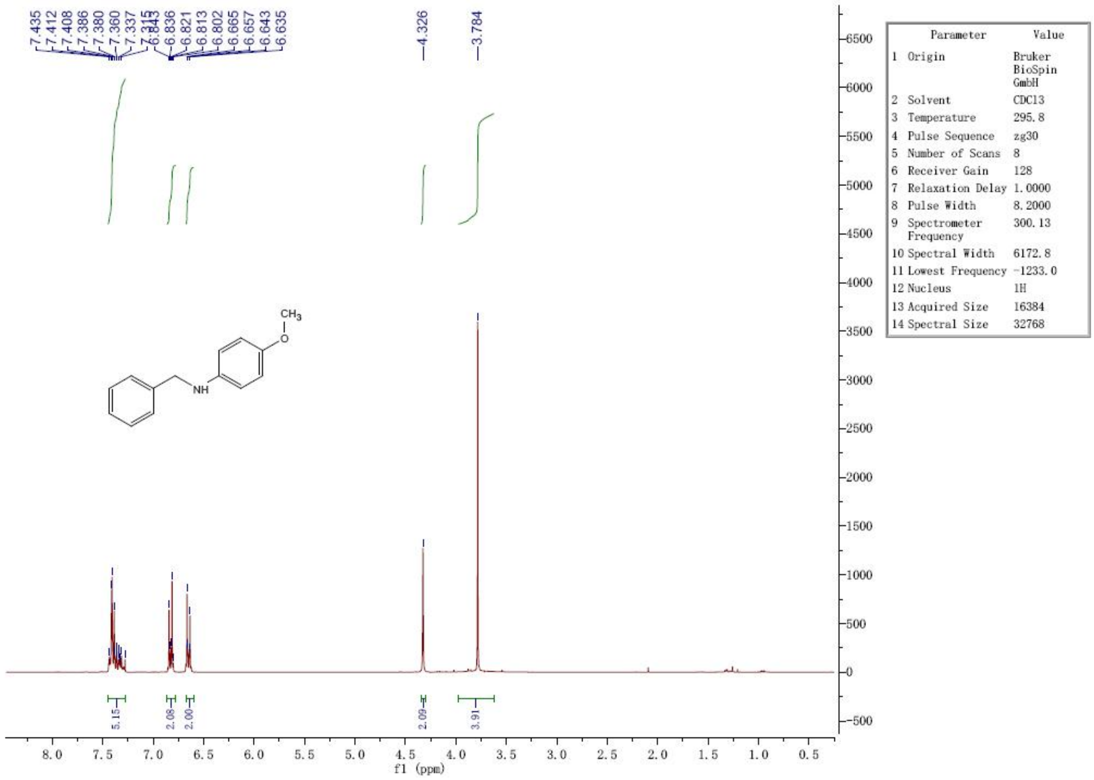


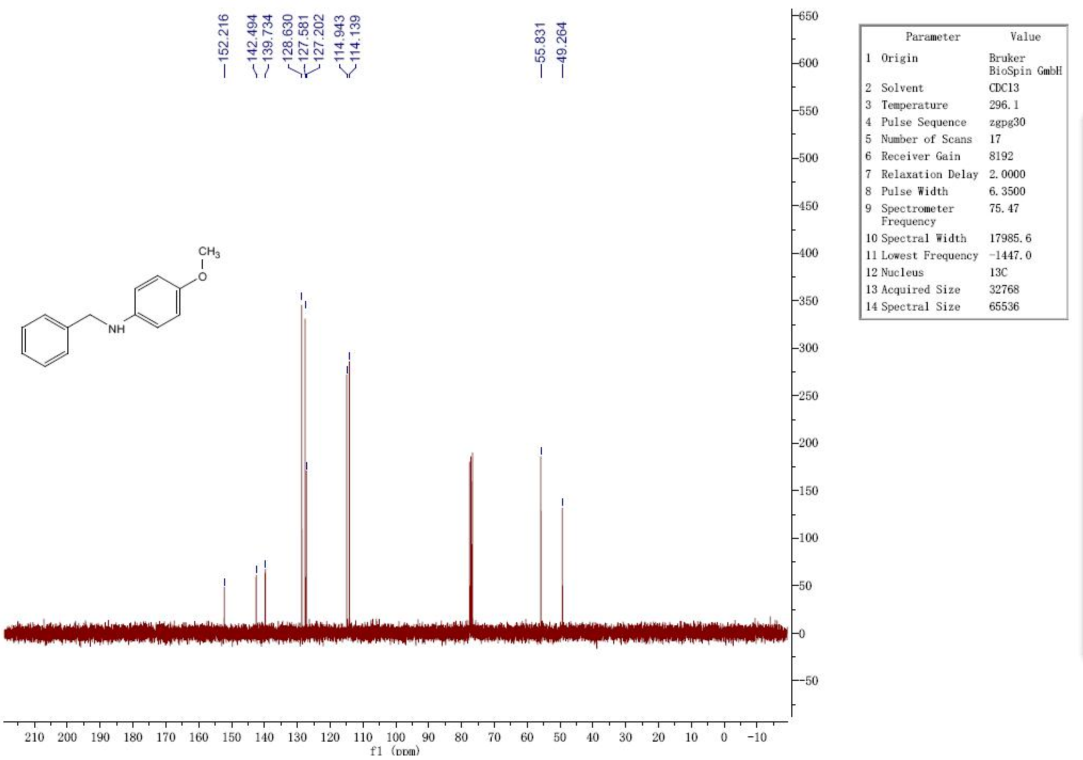




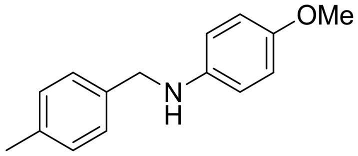
4-Methoxy-*N*-benzylaniline (4i)

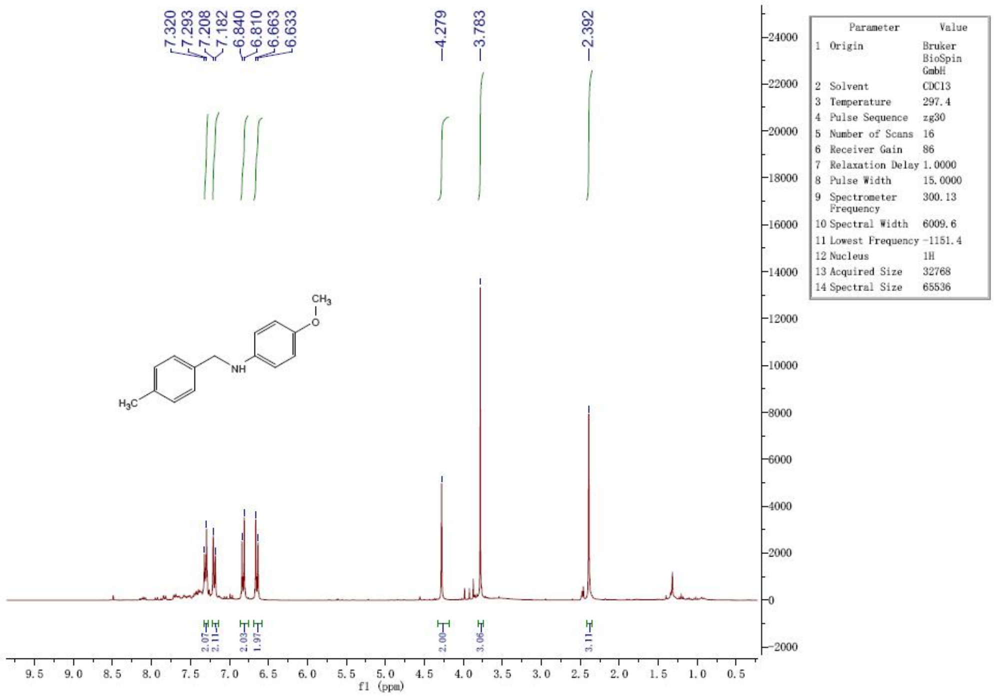


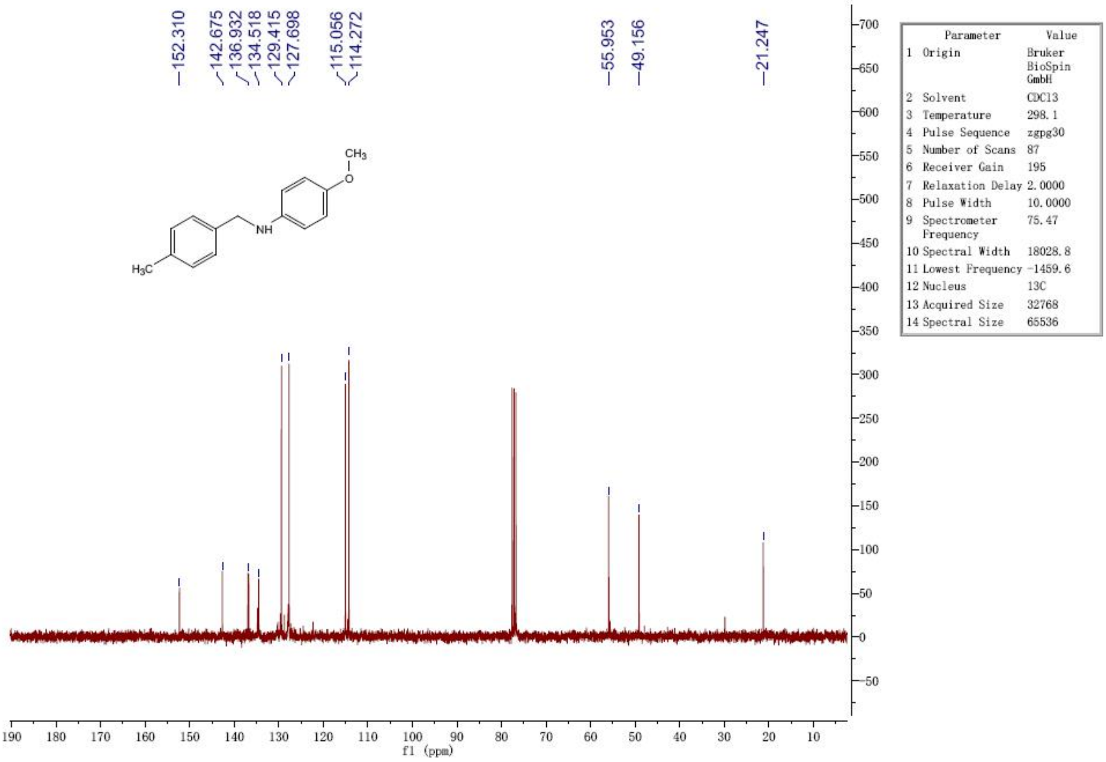




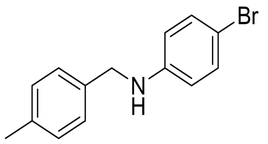
***4*-methoxy-N-(4-methylbenzyl)aniline (4j)**

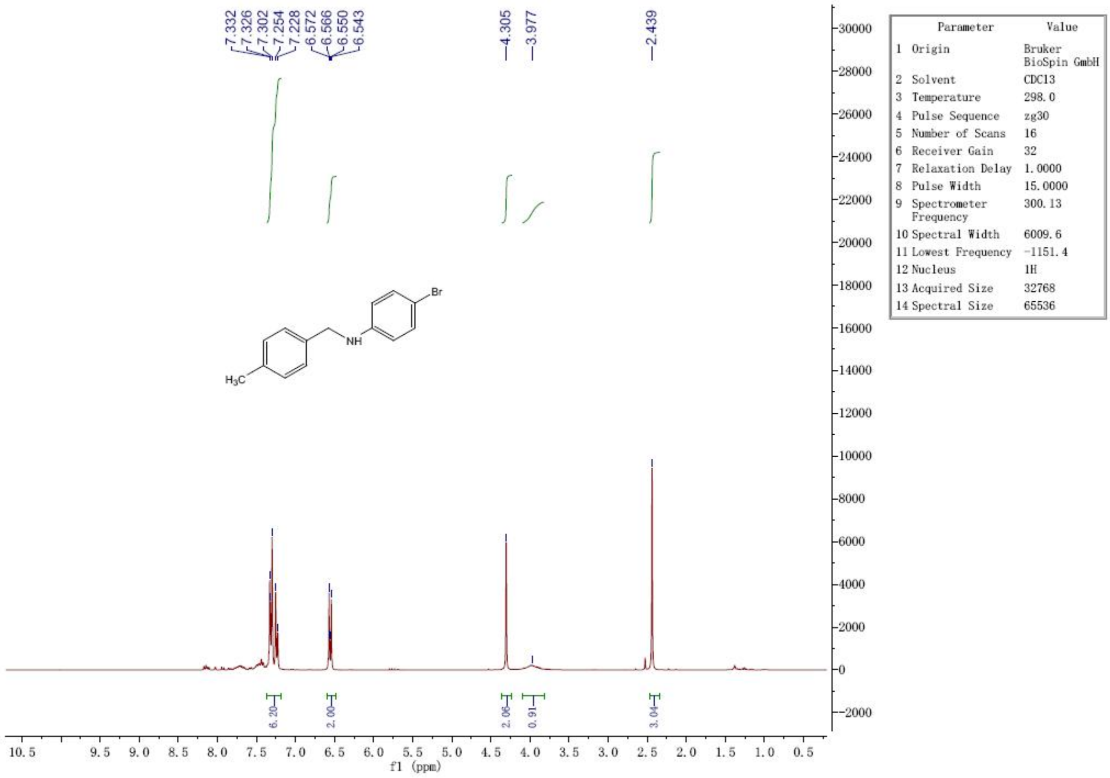


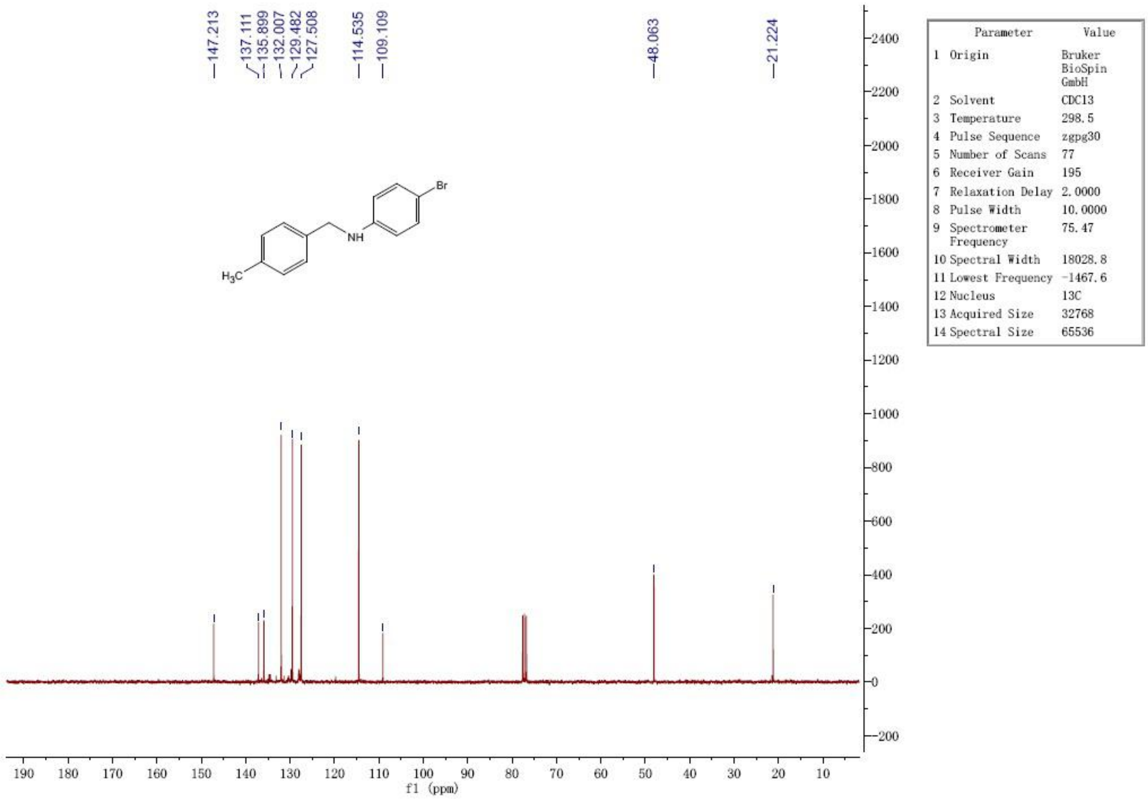




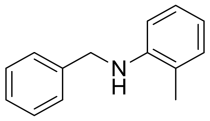
4-Bromo-*N*-(4-methylbenzyl)aniline (4l)

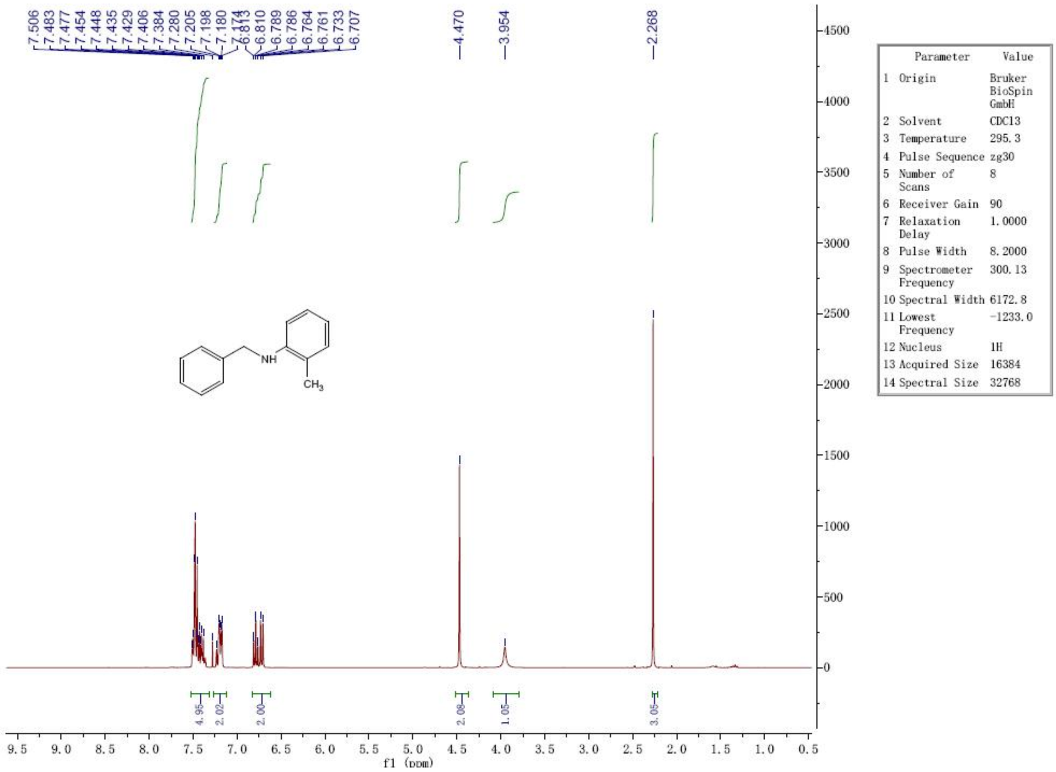


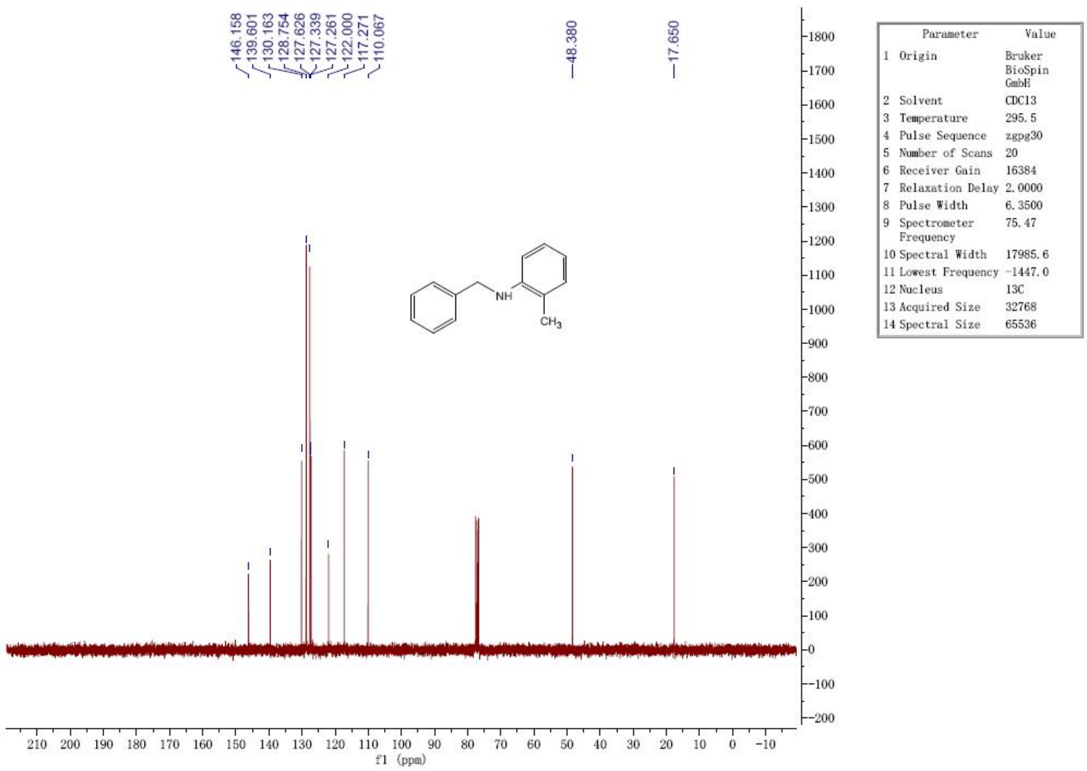




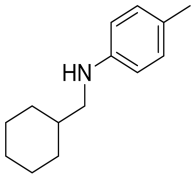
***N*-benzyl-2-methylaniline (4m)**

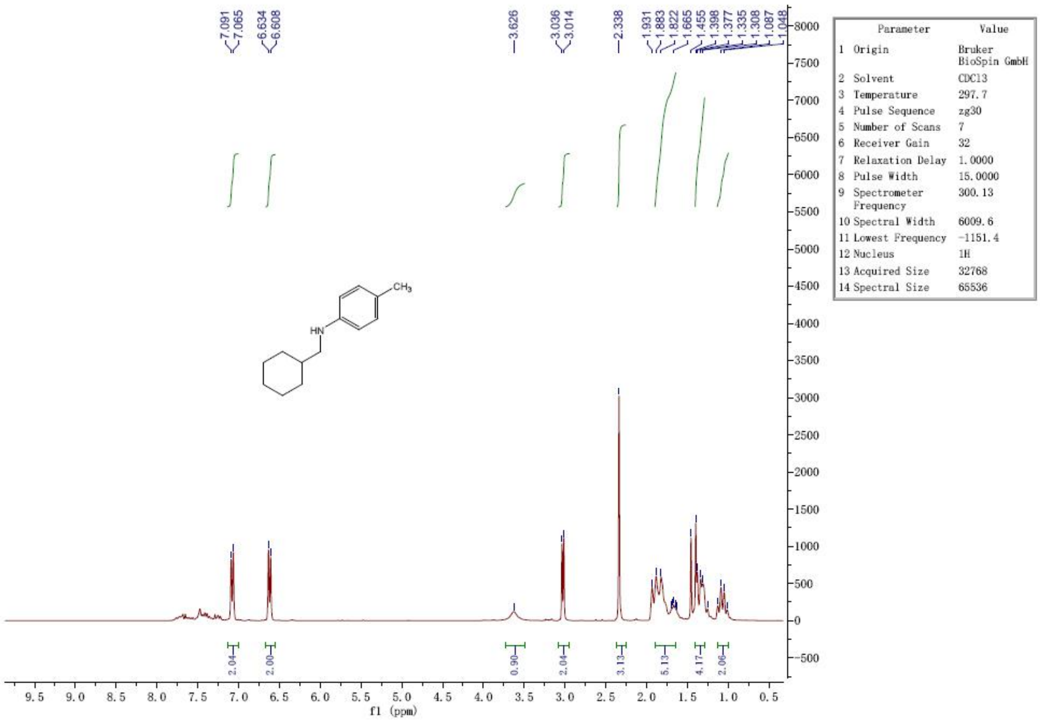


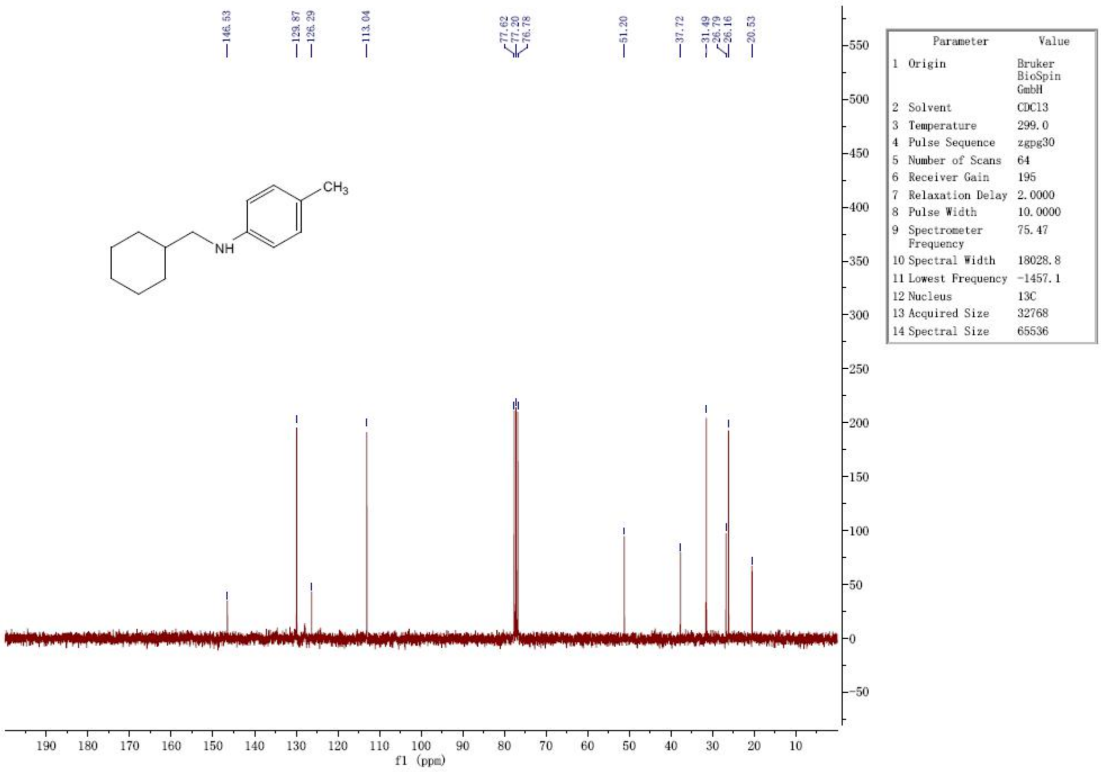




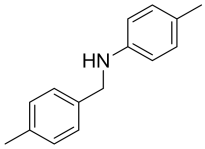
***N*-(Cyclohexylmethyl)-4-methylaniline (4n)**

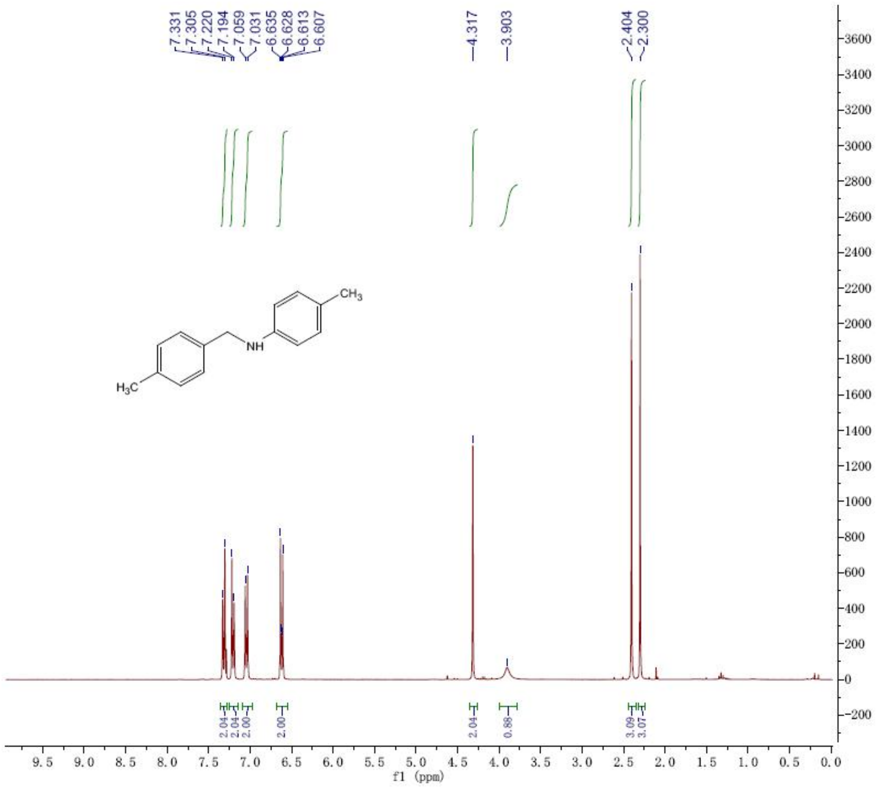




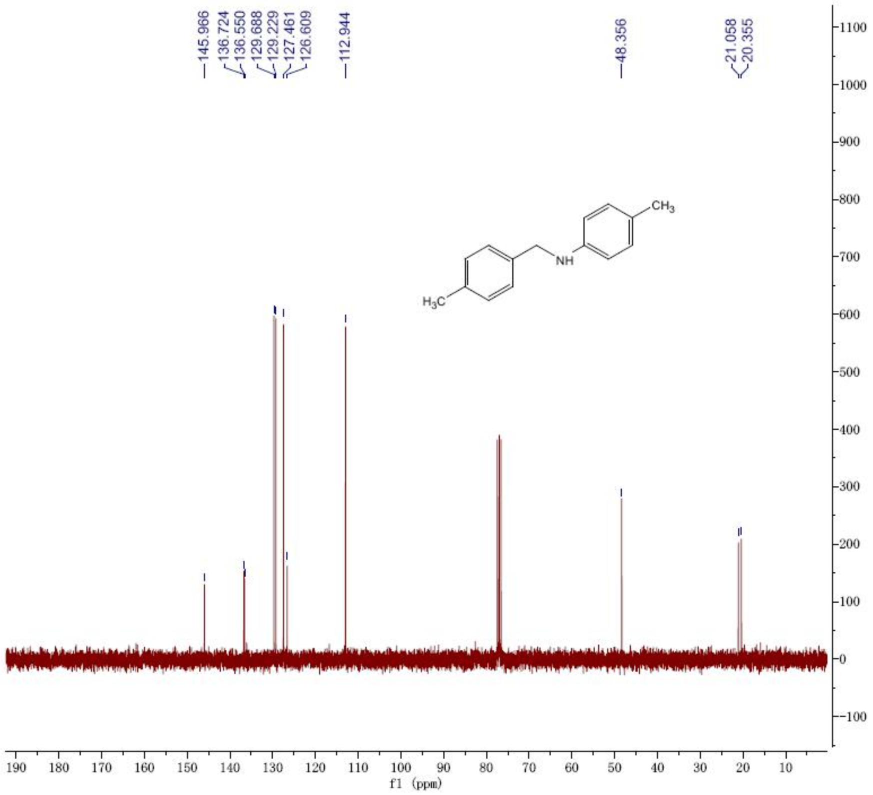


N-(4-Methyl)-4-methylaniline (4o)



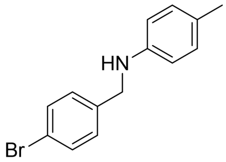


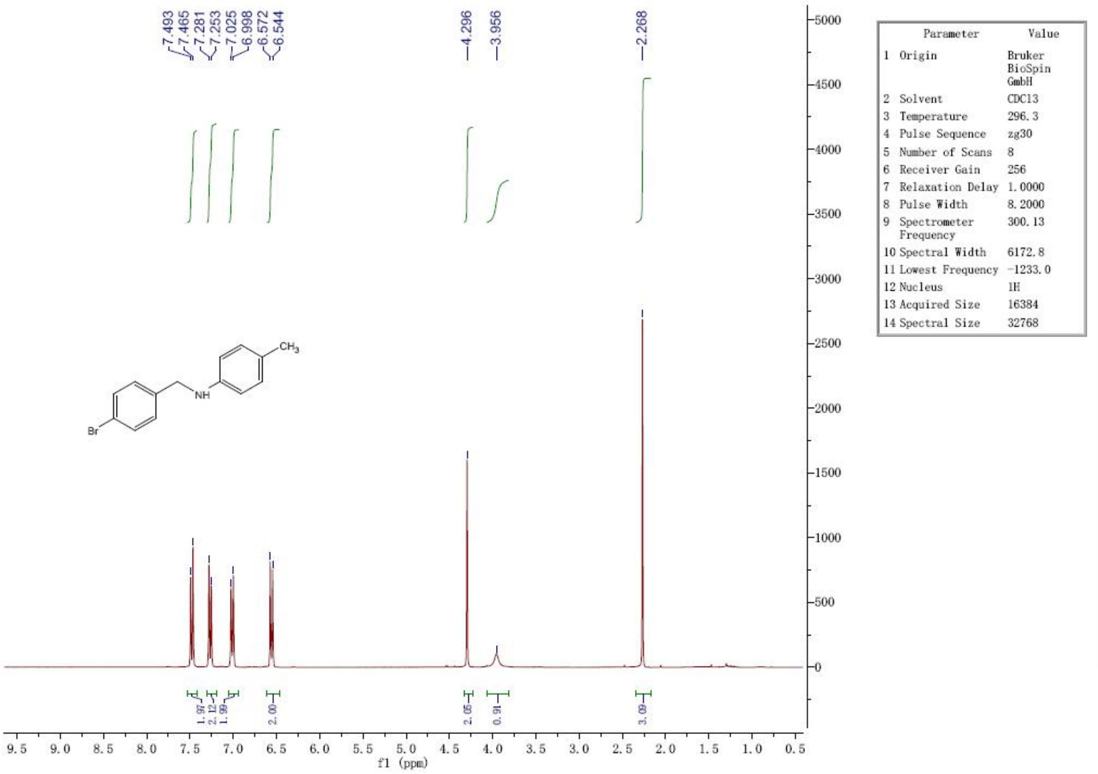
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.3
4 Pulse Sequence	zg30
5 Number of Scans	8
6 Receiver Gain	181
7 Relaxation Delay	1.0000
8 Pulse Width	8.2000
9 Spectrometer Frequency	300.13
10 Spectral Width	6172.8
11 Lowest Frequency	-1233.0
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768

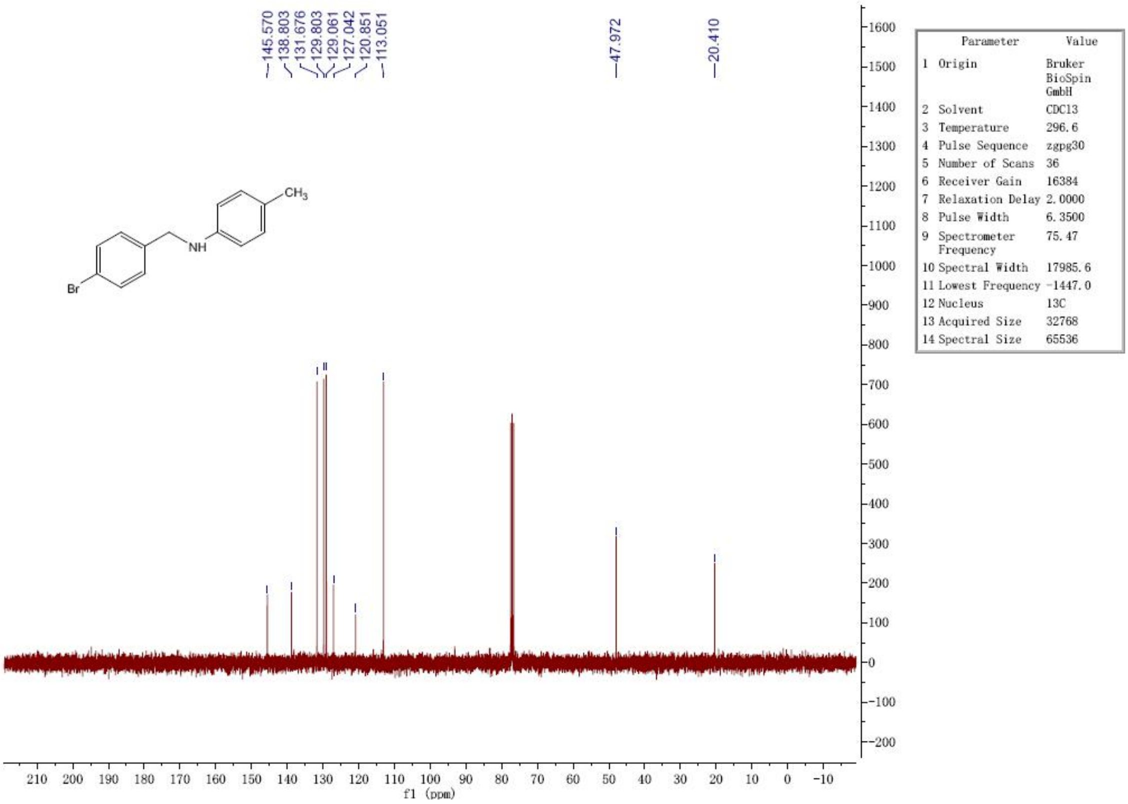


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.6
4 Pulse Sequence	zgpg30
5 Number of Scans	21
6 Receiver Gain	16384
7 Relaxation Delay	2.0000
8 Pulse Width	6.3500
9 Spectrometer Frequency	75.47
10 Spectral Width	17985.6
11 Lowest Frequency	-1447.0
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

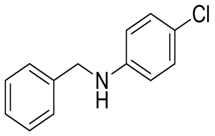
N-(4-Bromobenzyl)-4-methylaniline (4p)

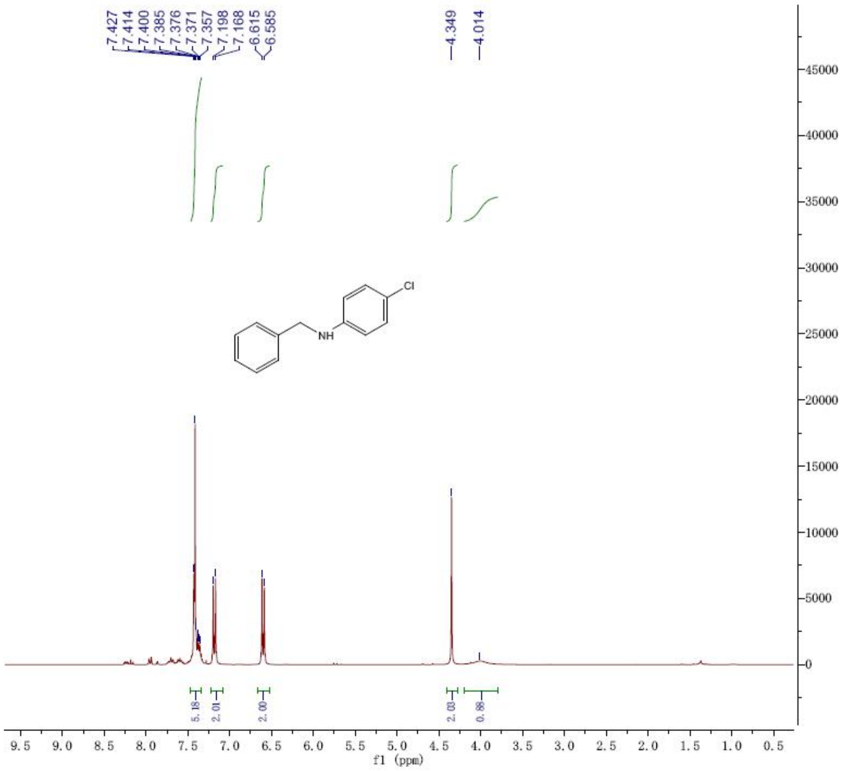




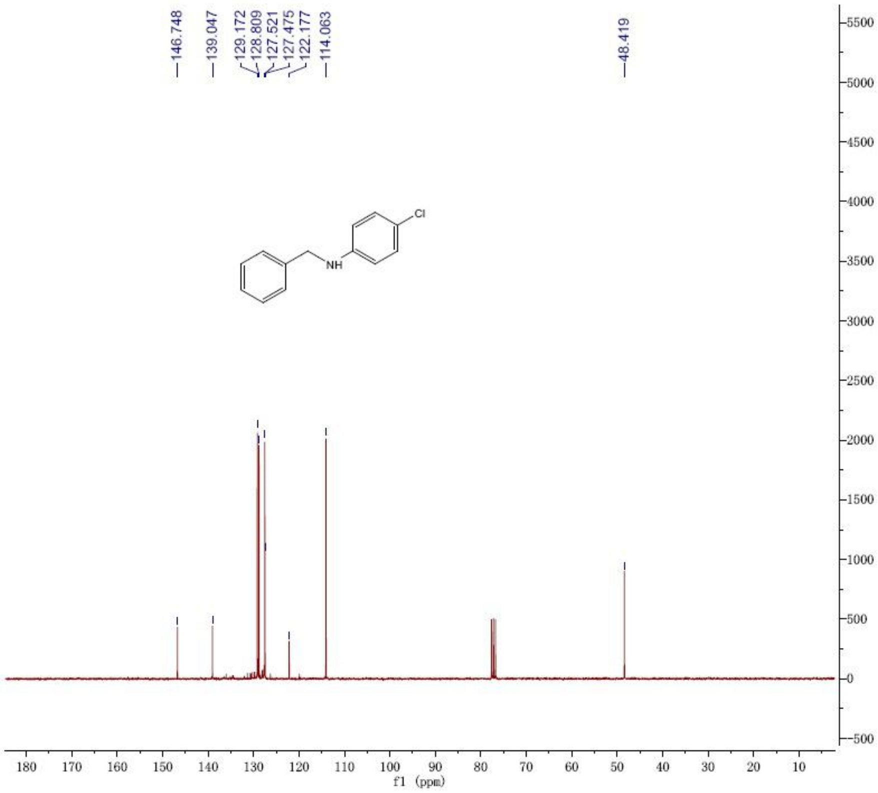


_N_-Benzyl-4-chloroaniline (4q)



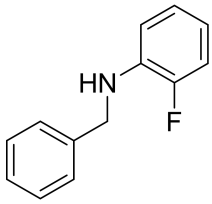


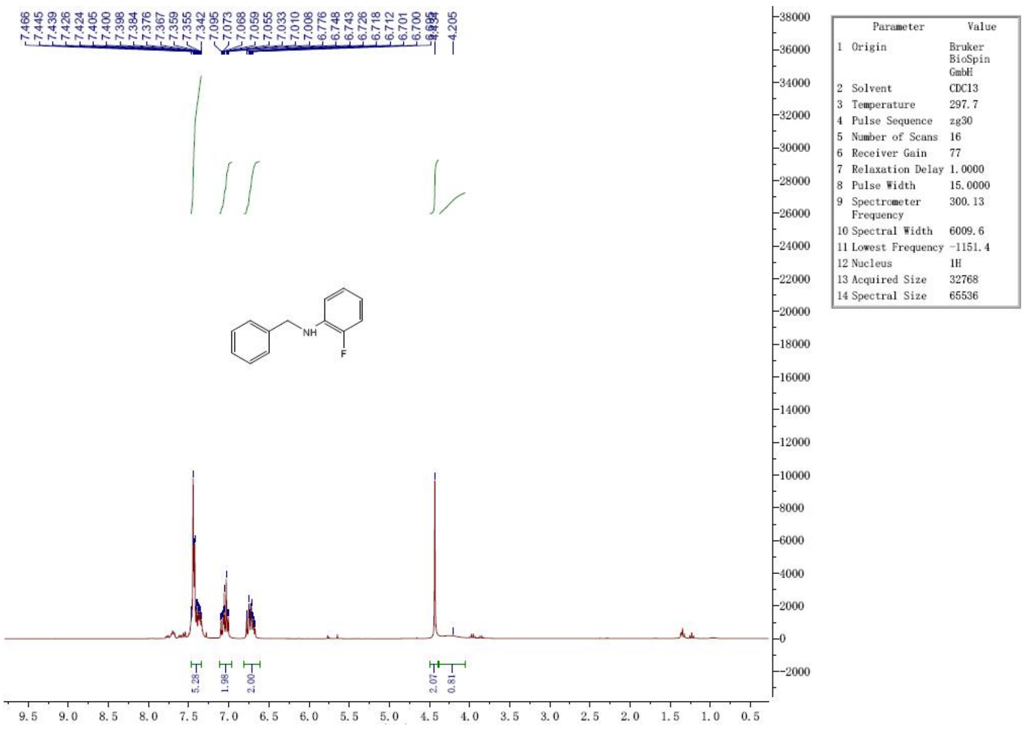
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.9
4 Pulse Sequence	zg30
5 Number of Scans	16
6 Receiver Gain	56
7 Relaxation Delay	1.0000
8 Pulse Width	15.0000
9 Spectrometer Frequency	300.13
10 Spectral Width	6009.6
11 Lowest Frequency	-1151.4
12 Nucleus	1H
13 Acquired Size	32768
14 Spectral Size	65536

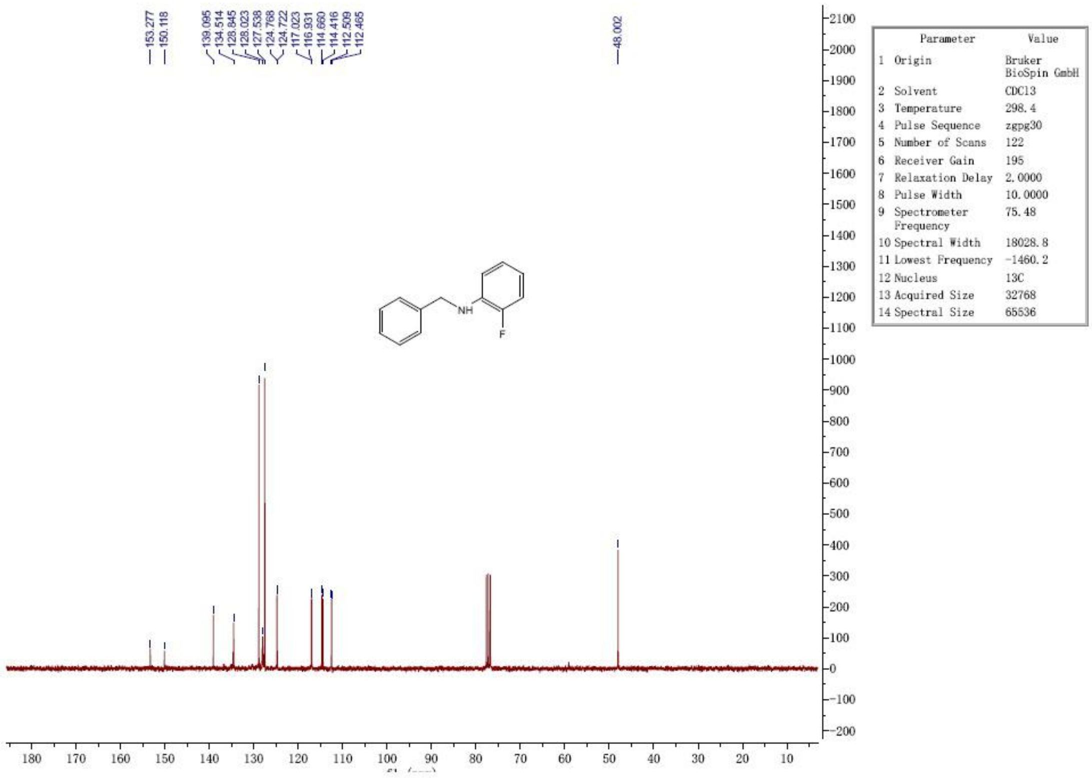


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.7
4 Pulse Sequence	zgpg30
5 Number of Scans	174
6 Receiver Gain	195
7 Relaxation Delay	2.0000
8 Pulse Width	10.0000
9 Spectrometer Frequency	75.47
10 Spectral Width	18028.8
11 Lowest Frequency	-1466.1
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

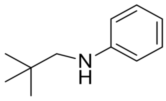
2-Fluoro-*N*-benzylaniline (4r)

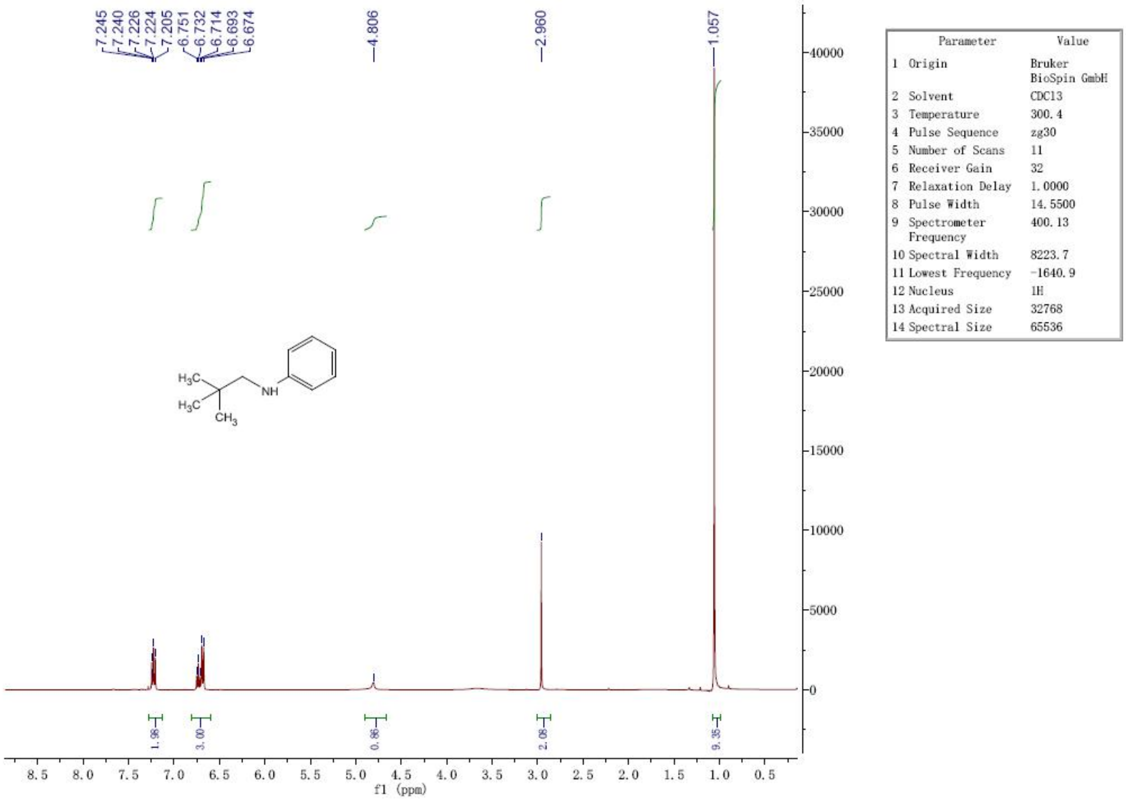


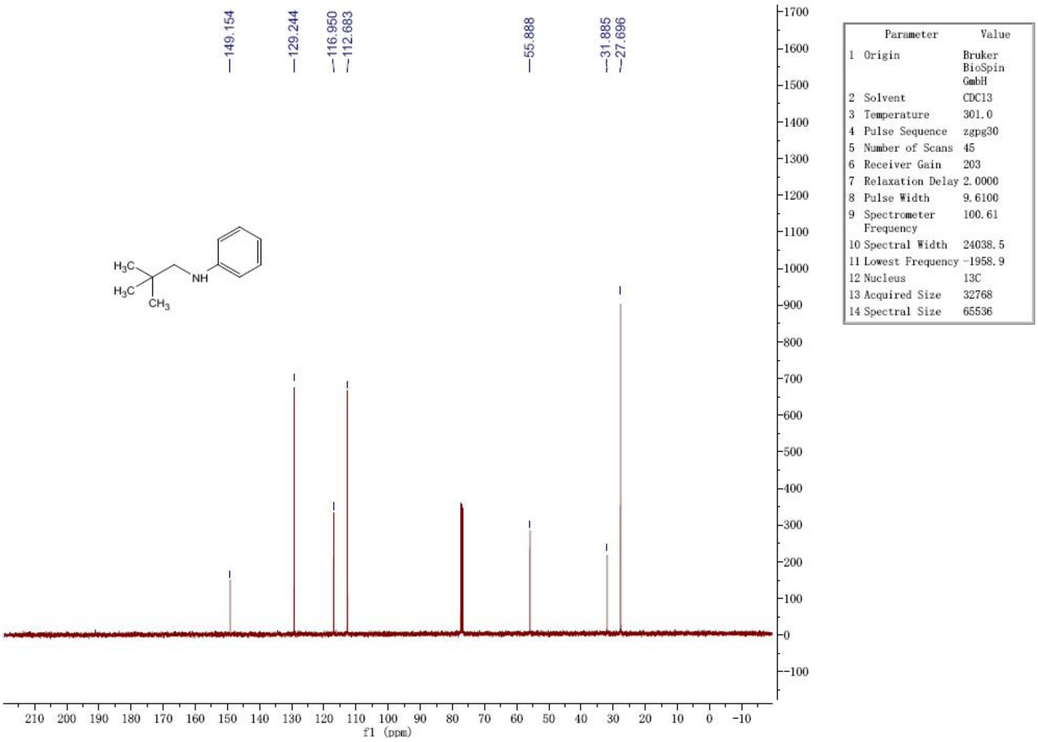




N-neopentylaniline (4s)







Dibenzylamine (4t)