Supporting Information for

Highly active and regioselective hydroaminomethylation of olefins catalyzed by Rh/sulfoxantphos with ZSM-5

Xiaoshuang Yuan,‡[a] Xueqing Zhang,‡[a] Shuxiang Dong[b], Shuhui Sun[c] and Xiaofei Jia*[a]

[a]Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China.
[b]Liaoning Sino More New Material Co., Ltd., Panjin, 124000, P. R. China.
[c]Xianhe Oil Production Plant, SINOPEC, Dongying, 257000, P. R. China.

1. General methods

Unless otherwise noted, all manipulations involving air or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. ^{1}H NMR spectra were recorded on 400 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^{1}H NMR), CDCl$_3$ (^{13}C NMR). GC analyses were measured on an Agilent 7820A system using an FID detector. HRMS analyses were measured on Waters Synapt G2Si HDMS.

2. General procedure for hydroaminomethylation of olefins.

In a glove box, an autoclave with a magnetic stirring bar was charged with Rh(acac)(CO)$_2$ (0.083 mg, 3.2×10^{-4} mmol), sulfoxantphos (0.96 mg, 1.3×10^{-3} mmol) and toluene/EtOH (1:1, 2.0 mL). The mixture was stirred for 5 min. Then olefin (1.6 mmol), amine (1.6 mmol) and ZSM-5 (75 mg) were added to the autoclave. The mixture was purged with hydrogen for three times and subsequently charged with CO (10 bar) and H$_2$ (15 bar). The autoclave was then heated to 120 °C (oil bath) and was kept at this temperature for 10 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The mixture subsequently was analyzed by gas chromatography (GC). Then the mixture was purified by flash column chromatography on silica gel to afford the product amine.

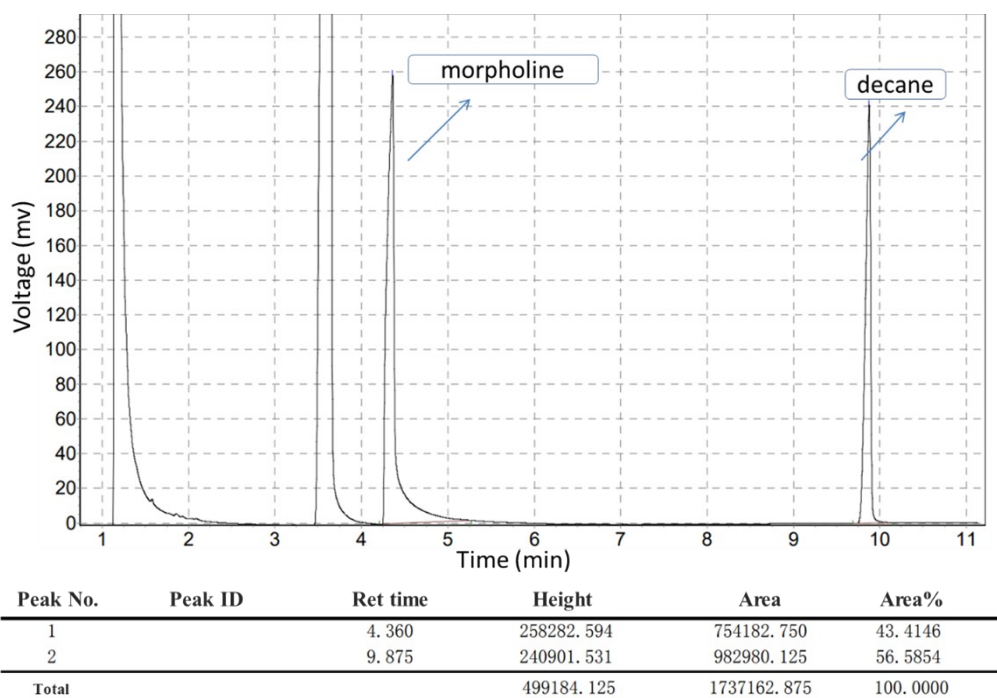# 3. Adsorption experiment of morpholine and ZSM-5

Peak No.	Peak ID	Ret time	Height	Area	Area%
1		4. 360	258282. 594	754182. 750	43. 4146
2		9. 875	240901. 531	982980. 125	56. 5854
Total			499184. 125	1737162. 875	100. 0000

Fig. S1. The GC spectrum of morpholine (90 µL), decane (20 µL) in toluene and EtOH

Peak No.	Peak ID	Ret time	Height	Area	Area%
1		4. 427	395518. 688	1311504. 500	37. 6120
2		9. 882	434490. 531	2175425. 000	62. 3880
Total			830009. 219	3486929. 500	100. 0000
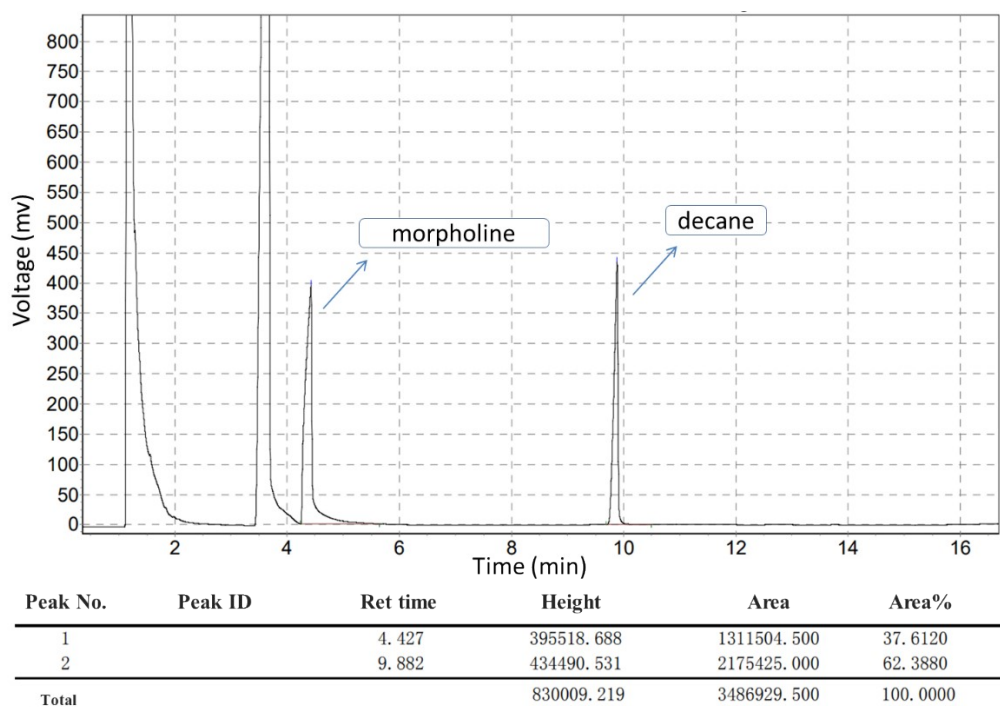
Fig. S2. The GC spectrum of morpholine (90 µL), decane (20 µL) and ZSM-5 (75 mg) in toluene and EtOH (the mixture was detected after stirring for 30 minutes at room temperature)

# 4. The preparation and characterization of [Rh] species

In a glove box, a glass vial with a magnetic stirring bar was charged with

sulfoxantphos (5.9 mg, 0.008 mmol) and Rh(acac)(CO)$_2$ (2.1 mg, 0.008 mmol) in toluene (1.0 mL) and MeOH (0.2 mL). The mixture was transferred to an autoclave, which was purged with nitrogen three times and subsequently charged with CO (10 bar) and H$_2$ (10 bar). The autoclave was then heated to 40 °C (oil bath) for 10 h. The autoclave was cooled to room temperature, and the gas was carefully released in a well-ventilated hood. The reaction mixture was immediately analyzed by HRMS. HRMS (ESI) m/z: Calcd. For C$_{43}$H$_{38}$O$_9$P$_2$RhS$_2$$^+$: 927.0482, Found: 927.4387 (M+H$^+$).

5. The GC spectrum for hydroaminomethylation reaction of 1-hexene and morpholine
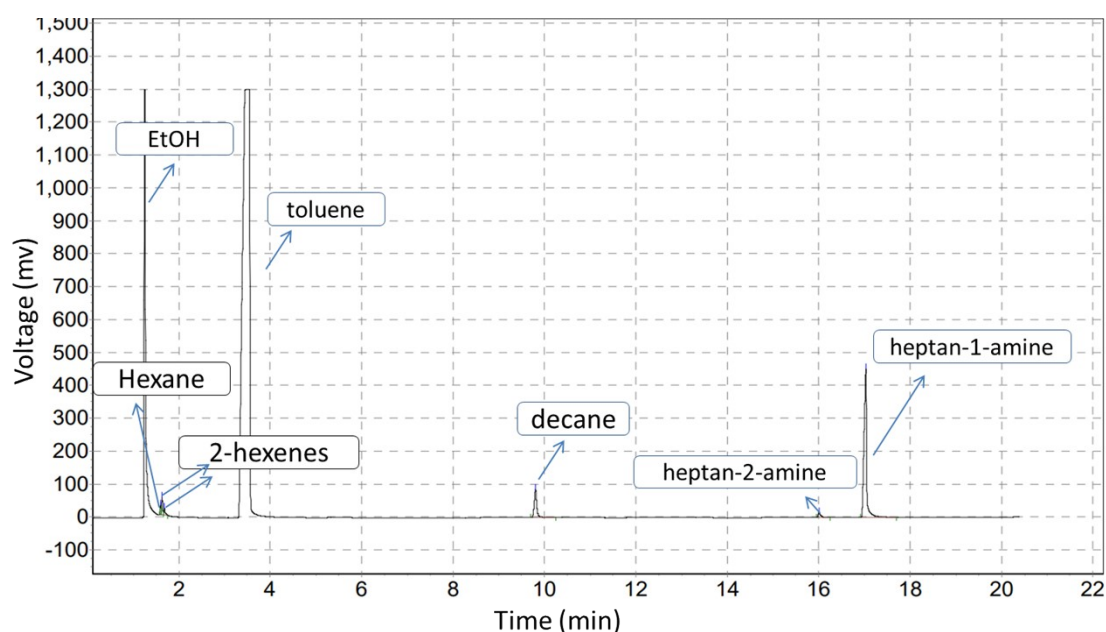
## 6. Characterization data for the products
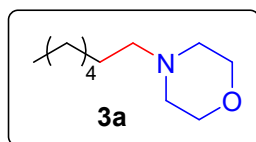
4-Heptylmorpholine (3a)[1]: colorless liquid, 266.4 mg, 90% yield. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 3.61 (t, J = 4.8 Hz, 4H), 2.32 (t, J = 4.8 Hz, 4H), 2.23-2.19 (m, 2H), 1.40-1.36 (m, 2H), 1.22-1.67 (m, 8H), 0.78 (t, J = 7.2 Hz, 3H) ppm.
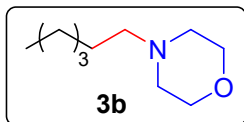
4-Hexylmorpholine (3b)[2]: colorless liquid, 259.9 mg, 95% yield. **¹H NMR** (400 MHz, CDCl₃): δ 3.66 (t, J = 4.4 Hz, 4H), 2.38 (s, 4H), 2.26 (t, J = 7.6 Hz, 2H), 1.44-1.39 (m, 2H), 1.26-1.24 (m, 6H), 0.83 (t, J = 6.0 Hz, 3H) ppm.
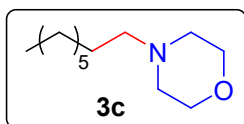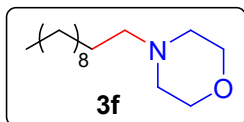

4-Octylmorpholine (3c)[3]: colorless liquid, 290 mg, 91% yield. **¹H NMR** (400 MHz, CDCl₃): δ 3.63 (t, J = 4.4 Hz, 4H), 2.36-2.33 (m, 4H), 2.25-2.21 (m, 2H), 1.42-1.38 (m, 2H), 1.21-1.78 (m, 10H), 0.80 (t, J = 6.0 Hz, 3H) ppm.
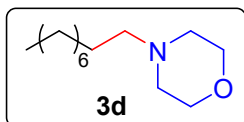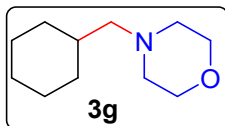

4-Nonylmorpholine (3d)[4]: colorless liquid, 299.9 mg, 88% yield. **¹H NMR** (400 MHz, CDCl₃): δ 3.68 (t, J = 4.4 Hz, 4H), 2.40-2.38 (m, 4H), 2.73 (t, J = 7.6 Hz, 2H), 1.46-1.42 (m, 2H), 1.24-1.22 (m, 12H), 0.84 (t, J = 6.0 Hz, 3H) ppm.
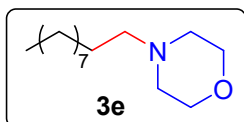

4-Decylmorpholine (3e)[5]: colorless liquid, 312.4 mg, 86% yield. **¹H NMR** (400 MHz, CDCl₃): δ 3.68 (t, J = 4.4 Hz, 4H), 2.40-2.38 (m, 4H), 2.29-2.26 (m, 2H), 1.46-1.43 (m, 2H), 1.25-1.22 (m, 14H), 0.84 (t, J = 5.6 Hz, 3H) ppm.


4-Undecylmorpholine (3f)[6]: colorless liquid, 354.8 mg, 92% yield. **¹H NMR** (400 MHz, CDCl₃): δ 3.59 (t, J = 4.8 Hz, 4H), 2.32-2.30 (m, 4H), 2.20 (t, J = 7.6 Hz, 2H), 1.38-1.35 (m, 2H), 1.17-1.15 (m, 16H), 0.76 (t, J = 6.4 Hz, 3H) ppm.

4-(Cyclohexylmethyl)morpholine (3g)[7]: colorless liquid, 222.5 mg, 76% yield. **¹H NMR** (400 MHz, CDCl₃): δ 3.70 (t, J = 4.8 Hz, 4H), 2.39-2.37 (m, 4H), 2.11 (d, J = 7.2 Hz, 2H), 1.77-1.67 (m, 4H), 1.50-1.47 (m, 1H), 1.26-1.16 (m, 4H), 0.88-0.84 (m, 2H) ppm.
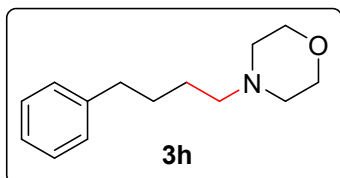

4-(4-Phenylbutyl)morpholine (3h)[8]: colorless oil, 318.9 mg, 91% yield. **¹H NMR** (400 MHz, CDCl₃): δ 7.28-7.25 (m, 2H), 7.17-7.16 (m, 3H), 3.70 (t, J = 3.6 Hz, 4H), 2.62 (t, J = 6.0 Hz, 2H), 2.41-2.39 (m, 4H), 2.34 (t, J = 6.0 Hz, 2H), 1.65-1.62 (m, 2H), 1.53-1.50 (m, 2H) ppm.
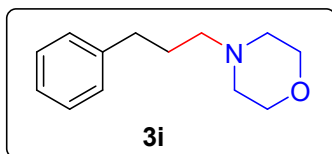

4-(3-Phenylpropyl)morpholine (3i)[7]: colorless oil, 233.1 mg, 71% yield. **¹H NMR** (400 MHz, CDCl₃): δ 7.29-7.26 (m, 2H), 7.19-7.18 (m, 3H), 3.71 (t, J = 4.0 Hz, 4H), 2.64 (t, J = 4.0 Hz, 2H), 2.44-2.42 (m, 4H), 2.36 (t, J = 6.0 Hz, 2H), 1.85-1.79 (m, 2H), ppm.
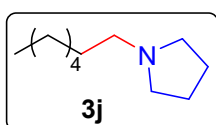

1-Heptylpyrrolidine (3j)[9]: colorless liquid, 219.0 mg, 81% yield. **¹H NMR** (400 MHz, CDCl₃): δ 2.46 (m, 4H), 2.38 (t, J = 8.0 Hz, 2H), 1.74-1.73 (m, 4H), 1.49-1.45 (m, 2H), 1.25-1.23 (m, 8H), 0.83 (t, J = 5.2 Hz, 3H) ppm.
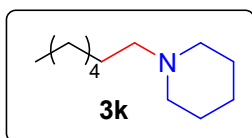

1-Heptylpiperidine (3k)[1]: colorless oil, 228.4 mg, 78% yield. **¹H NMR** (400 MHz, CDCl₃): δ 2.46 (m, 4H), 2.38 (t, J = 8.0 Hz, 2H), 1.74-1.73 (m, 4H), 1.49-1.45 (m, 2H), 1.25-1.23 (m, 8H), 0.83 (t, J = 5.2 Hz, 3H) ppm.
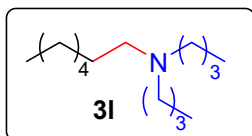
N,N-dibutylheptan-1-amine (3l)[10]: colorless liquid, 261.5 mg, 72% yield. **¹H NMR** (400 MHz, CDCl₃): δ 2.39-2.34 (m, 6H), 1.41-1.37 (m, 6H), 1.30-1.24 (m, 12H), 0.91-0.86 (m, 9H) ppm.
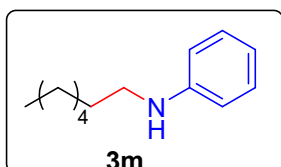

N-heptylaniline (3m)[11]: colorless oil, 271.9 mg, 89% yield. **¹H NMR** (400 MHz, CDCl₃): δ 7.14 (t, *J* = 8.0 Hz, 2H), 6.68-6.55 (m, 3H), 3.50 (s, br, 1H), 3.05 (t, *J* = 6.8 Hz, 2H), 1.58-1.55 (m, 2H), 1.33-1.29 (m, 8H), 0.89 (t, *J* = 6.0 Hz, 3H) ppm.
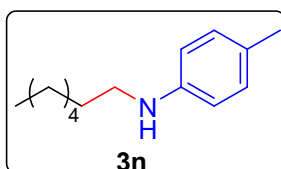
N-heptyl-4-methylaniline (3n)[12]: colorless oil, 285.4 mg, 87% yield. **¹H NMR** (400 MHz, CDCl₃): δ 7.01 (d, *J* = 6.4 Hz, 2H), 6.55 (d, *J* = 6.4 Hz, 2H), 3.47 (s, br, 1H), 3.09 (t, *J* = 5.6 Hz, 2H), 2.26 (s, 3H), 1.64-1.59 (m, 2H), 1.37-1.30 (m, 8H), 0.92 (t, *J* = 5.6 Hz, 3H) ppm.
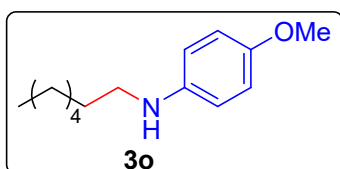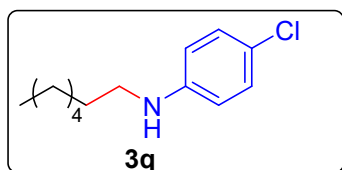

N-heptyl-4-methoxyaniline (3o)[13]: colorless oil, 297.0 mg, 84% yield. **¹H NMR** (400 MHz, CDCl₃): δ 6.79 (d, *J* = 7.2 Hz, 2H), 6.58 (d, *J* = 7.2 Hz, 2H), 3.76 (s, br, 1H), 3.75 (s, 3H), 3.06 (t, *J* = 5.6 Hz, 2H), 1.62-1.59 (m, 2H), 1.41-1.30 (m, 8H), 0.90 (t, *J* = 5.6 Hz, 3H) ppm.
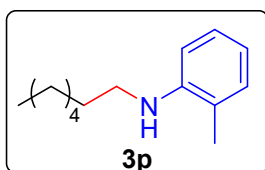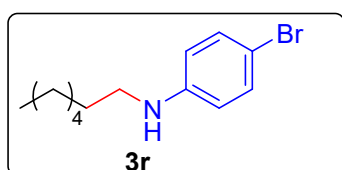

N-heptyl-2-methylaniline (3p)[14]: red brown oil, 272.2 mg, 83% yield. **¹H NMR** 400 MHz, CDCl₃): δ 7.16-7.13 (m, 1H), 7.07-7.06 (m, 1H), 6.68-6.62 (m, 2H), 3.49 (s, br,

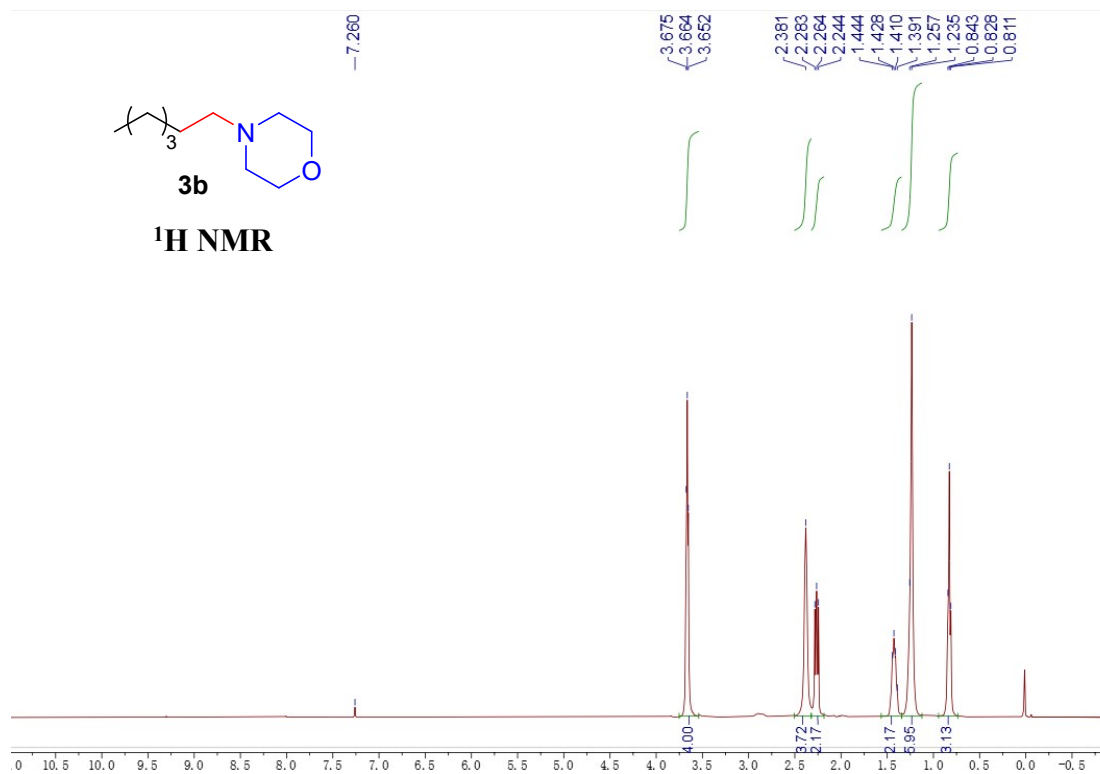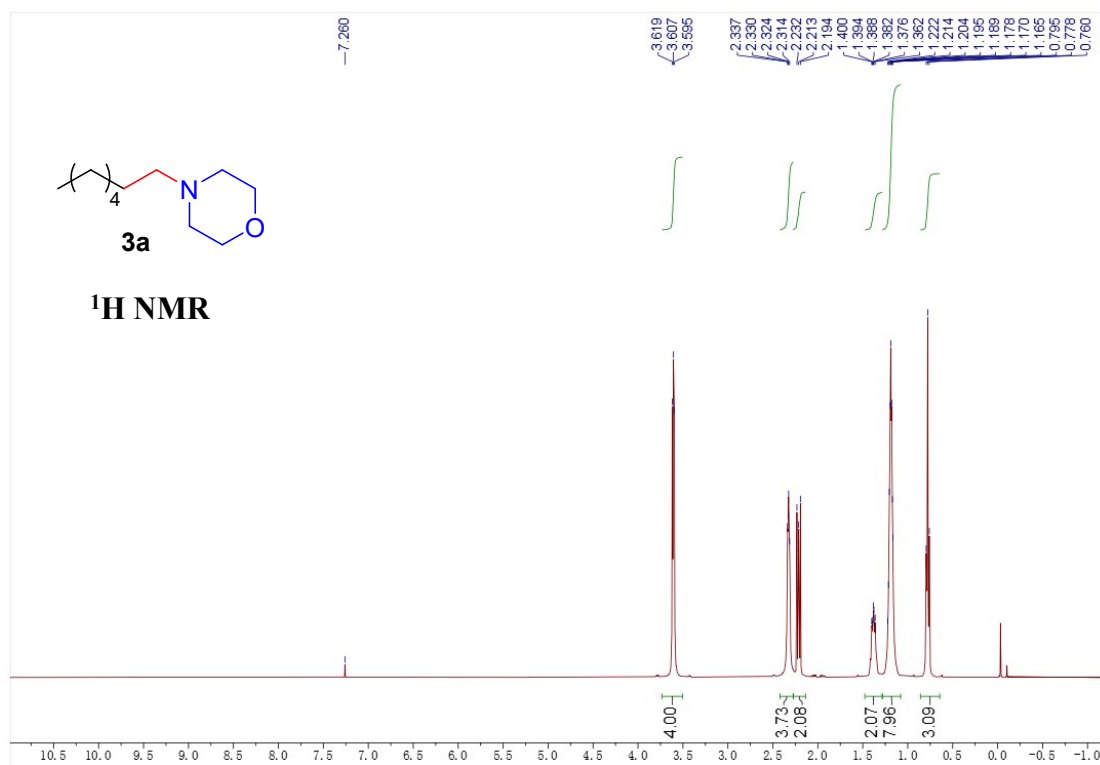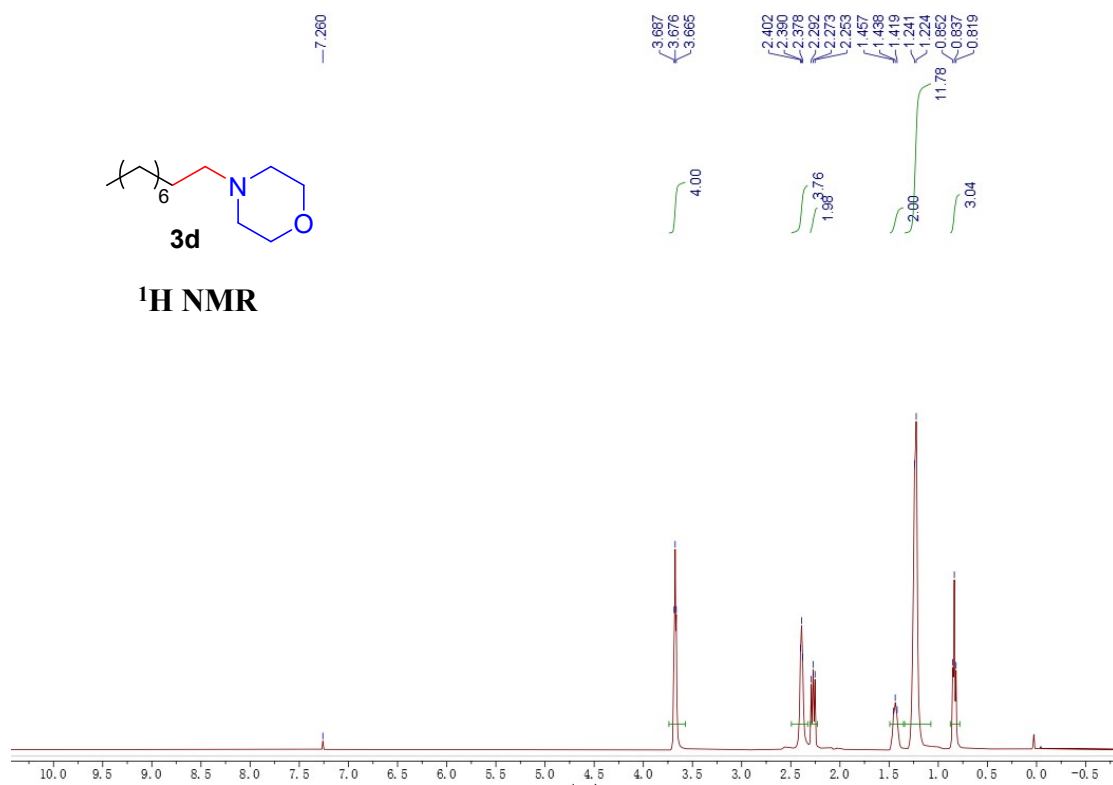1H), 3.16 (t, J = 5.6 Hz, 2H), 2.15 (s, 3H), 1.70-1.67 (m, 2H), 1.44-1.32 (m, 8H), 0.92 (t, J = 5.2 Hz, 3H) ppm.
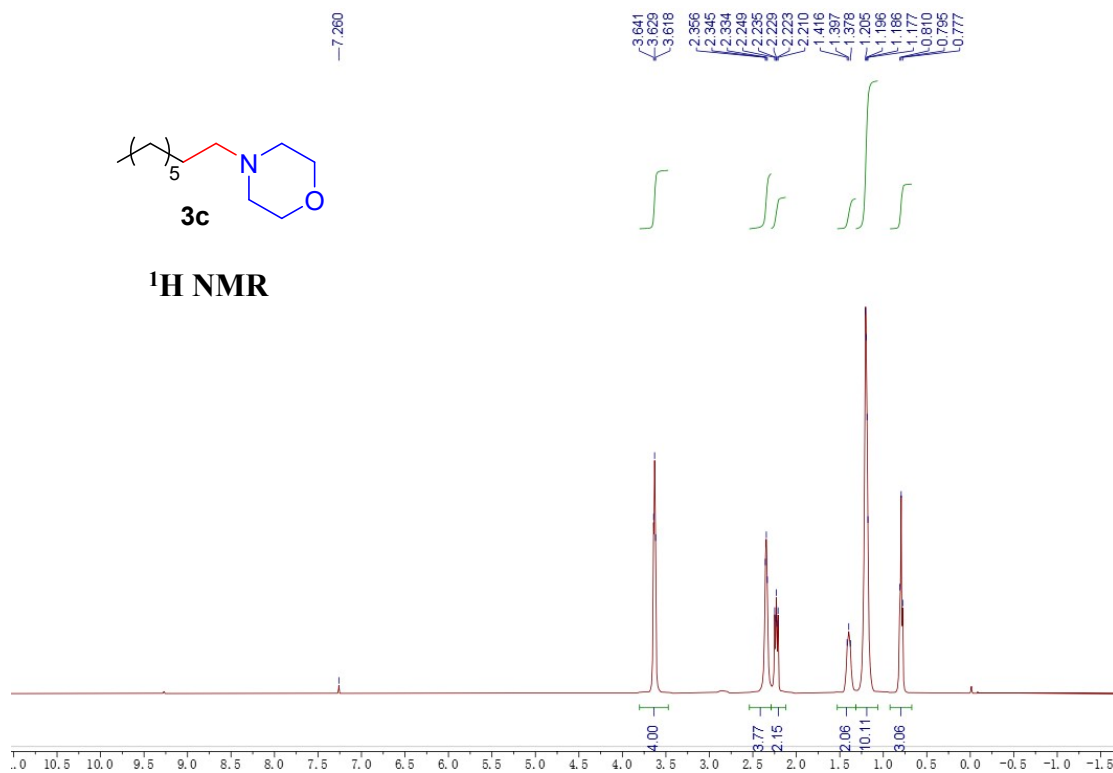

4-Chloro-N-heptylaniline (3q)[14]: pale yellow oil, 320.4 mg, 89% yield. **¹H NMR** (400 MHz, CDCl$_3$): δ 7.12 (d, J = 6.8 Hz, 2H), 6.52 (d, J = 6.8 Hz, 2H), 3.55 (s, br, 1H), 3.07 (t, J = 6.0 Hz, 2H), 1.63-1.58 (m, 2H), 1.38-1.31 (m, 8H), 0.93-0.91 (m, 3H) ppm.
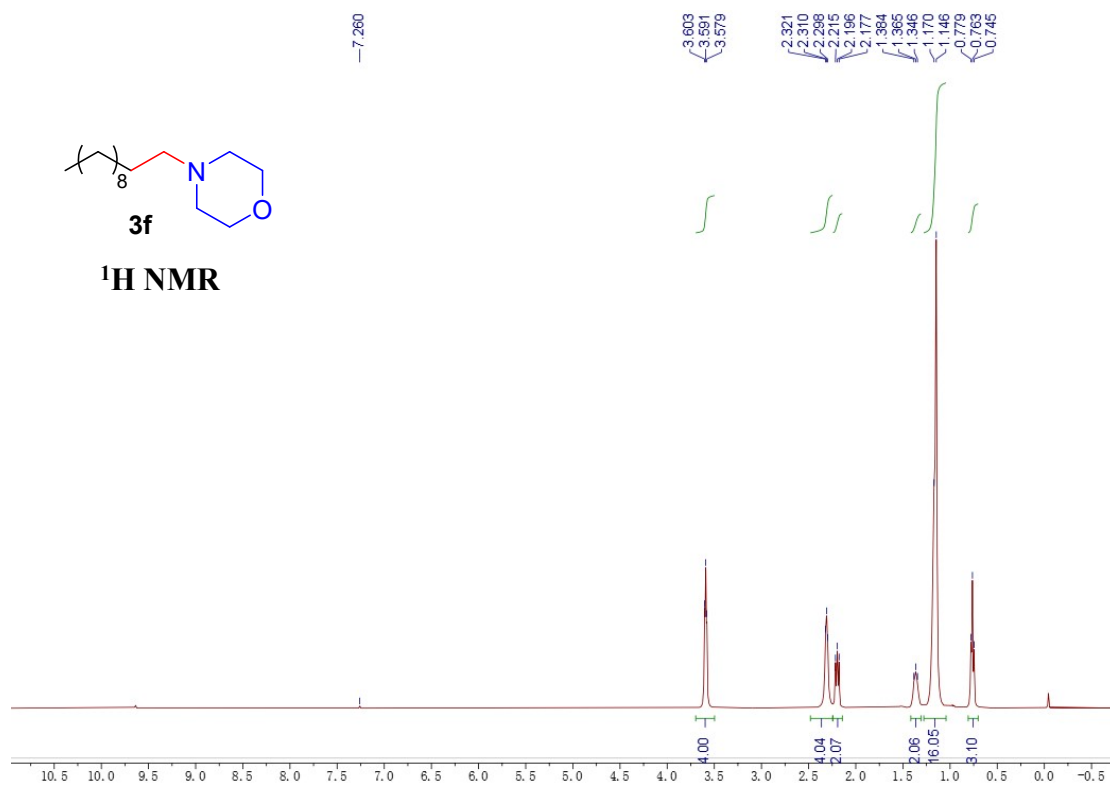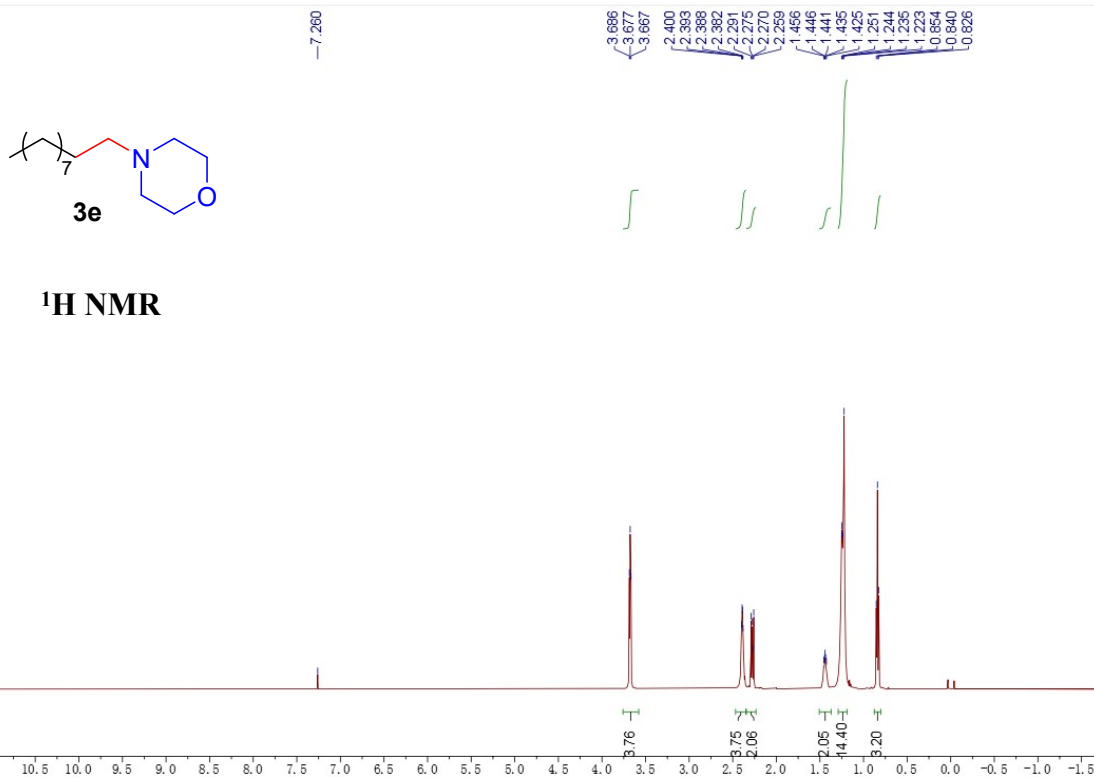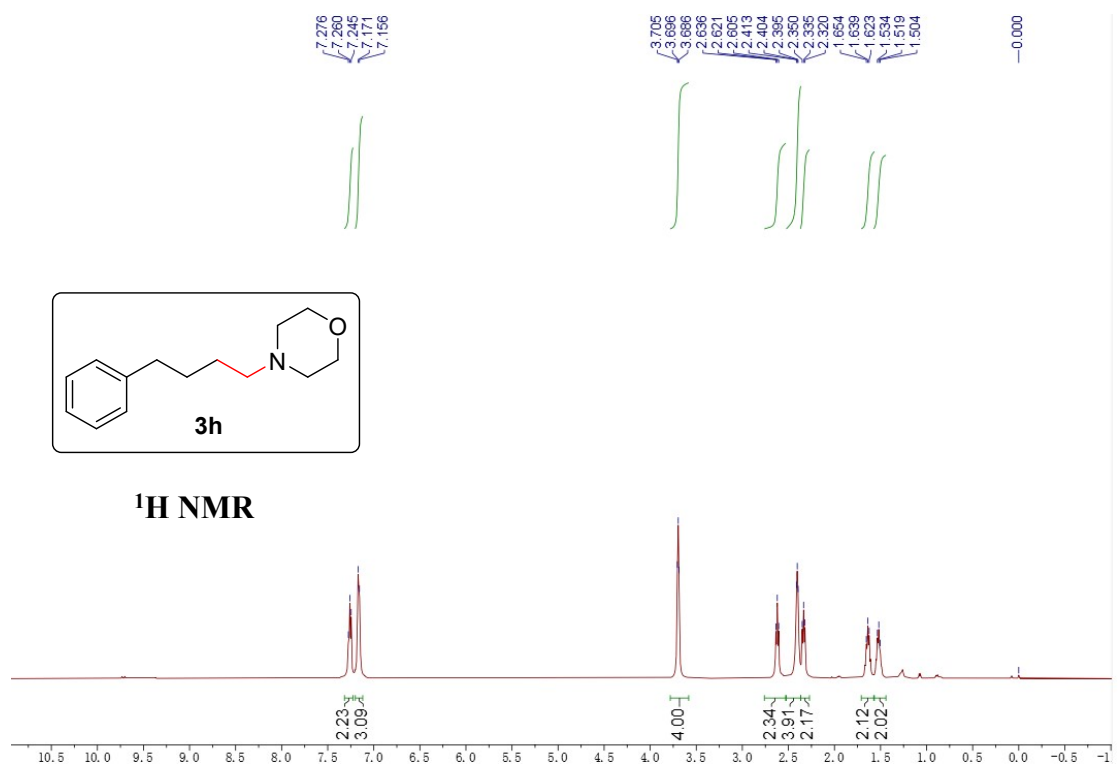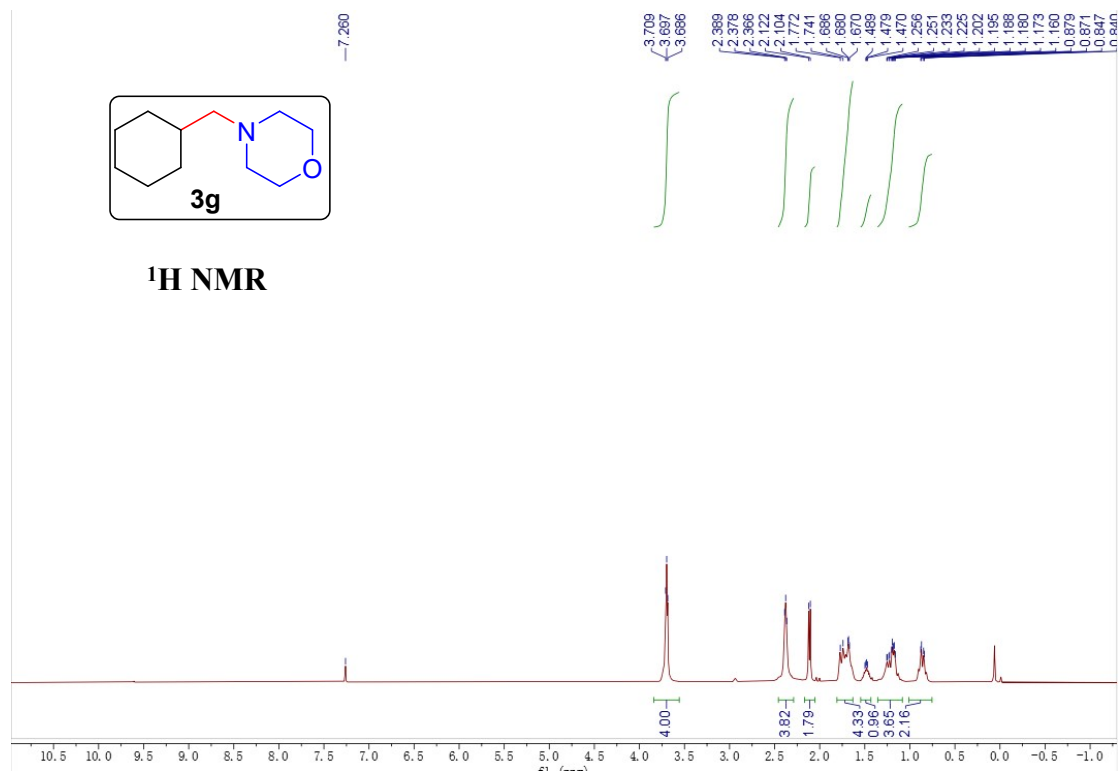

4-Bromo-N-heptylaniline (3r)[14]: pale yellow oil, 374.4 mg, 87% yield. **¹H NMR** (400 MHz, CDCl$_3$): δ 7.22 (d, J = 6.8 Hz, 2H), 6.45 (d, J = 6.8 Hz, 2H), 3.59 (s, br, 1H), 3.05 (t, J = 5.6 Hz, 2H), 1.60-1.57 (m, 2H), 1.32-1.26 (m, 8H), 0.90-0.87 (m, 3H) ppm.
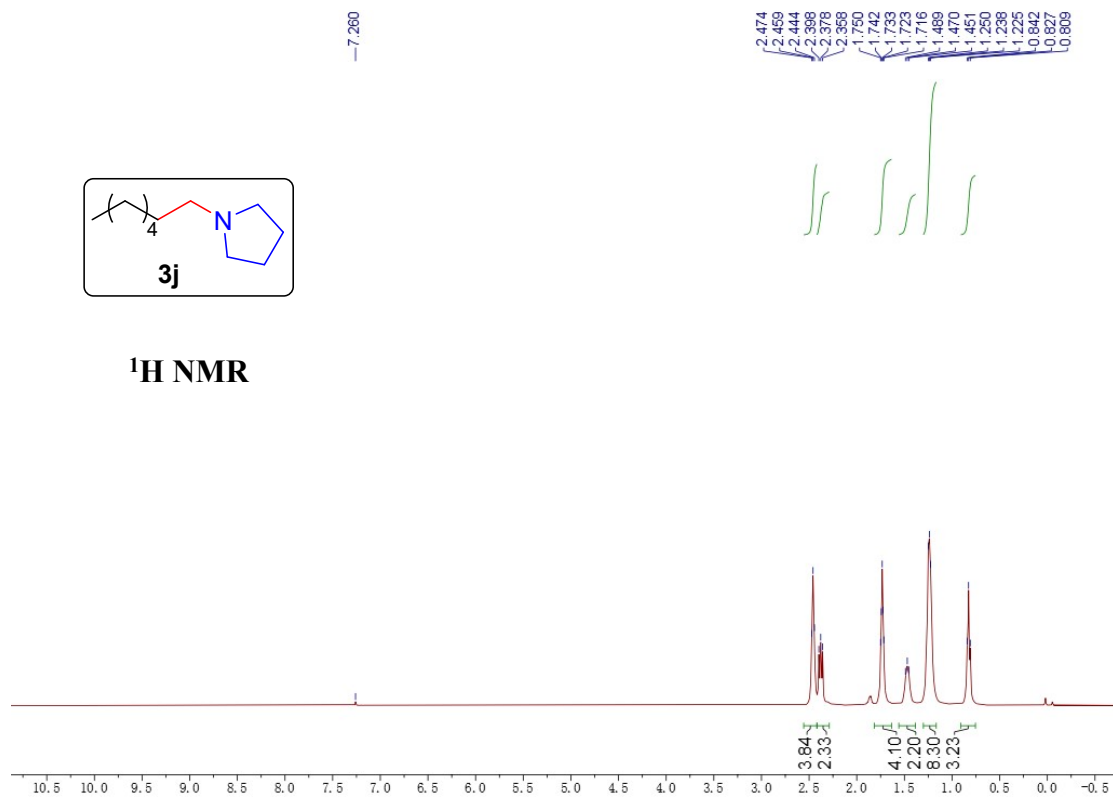
7. NMR spectra of products

3a

^{1}H NMR

7.260

3.619, 3.607, 3.595

2.337, 2.330, 2.324, 2.314, 2.232, 2.213, 2.194

1.400, 1.394, 1.388, 1.382, 1.376, 1.362, 1.222, 1.214, 1.204, 1.195, 1.189, 1.178, 1.170, 1.165, 0.795, 0.778, 0.760

4.00 3.73 2.08 2.07 7.96 3.09

3b

^{1}H NMR

7.260

3.675, 3.664, 3.652

2.381, 2.283, 2.264, 2.244

1.444, 1.428, 1.410, 1.391, 1.257, 1.235, 0.843, 0.828, 0.811

4.00 3.72 2.17 2.17 5.95 3.13

3c

¹H NMR

3d

¹H NMR

3e

¹H NMR

7.260

3.686, 3.677, 3.667
2.400, 2.393, 2.388, 2.382, 2.291, 2.275, 2.270, 2.259
1.456, 1.446, 1.441, 1.435, 1.425, 1.251, 1.244, 1.235, 1.223, 0.854, 0.840, 0.826

3.76   3.75 2.06   2.05 14.40   3.20

3f

¹H NMR

7.260

3.603, 3.591, 3.579
2.321, 2.310, 2.298, 2.215, 2.196, 2.177
1.384, 1.365, 1.346, 1.170, 1.146, 0.779, 0.763, 0.745

4.00   4.04 2.07   2.06 16.05 3.10

3g

¹H NMR

3h

¹H NMR

3i

^{1}H NMR

3j

^{1}H NMR

^{1}H NMR

^{1}H NMR

¹H NMR

¹H NMR

3o

^{1}H NMR

7.260, 6.798, 6.780, 6.594, 6.576

3.760, 3.752

3.076, 3.062, 3.048

1.621, 1.607, 1.592, 1.398, 1.394, 1.314, 1.308, 1.304, 1.300, 0.916, 0.902, 0.901, 0.888

1.95, 1.89

0.21, 2.88

1.88

1.93, 8.40, 3.20

3p

^{1}H NMR

7.260, 7.161, 7.158, 7.146, 7.143, 7.131, 7.127, 7.072, 7.059, 7.056, 6.675, 6.663, 6.661, 6.648, 6.646, 6.640, 6.637, 6.623, 6.621

3.485, 3.178, 3.164, 3.150

2.151, 1.700, 1.685, 1.671, 1.441, 1.425, 1.335, 1.330, 1.324, 0.932, 0.919, 0.905

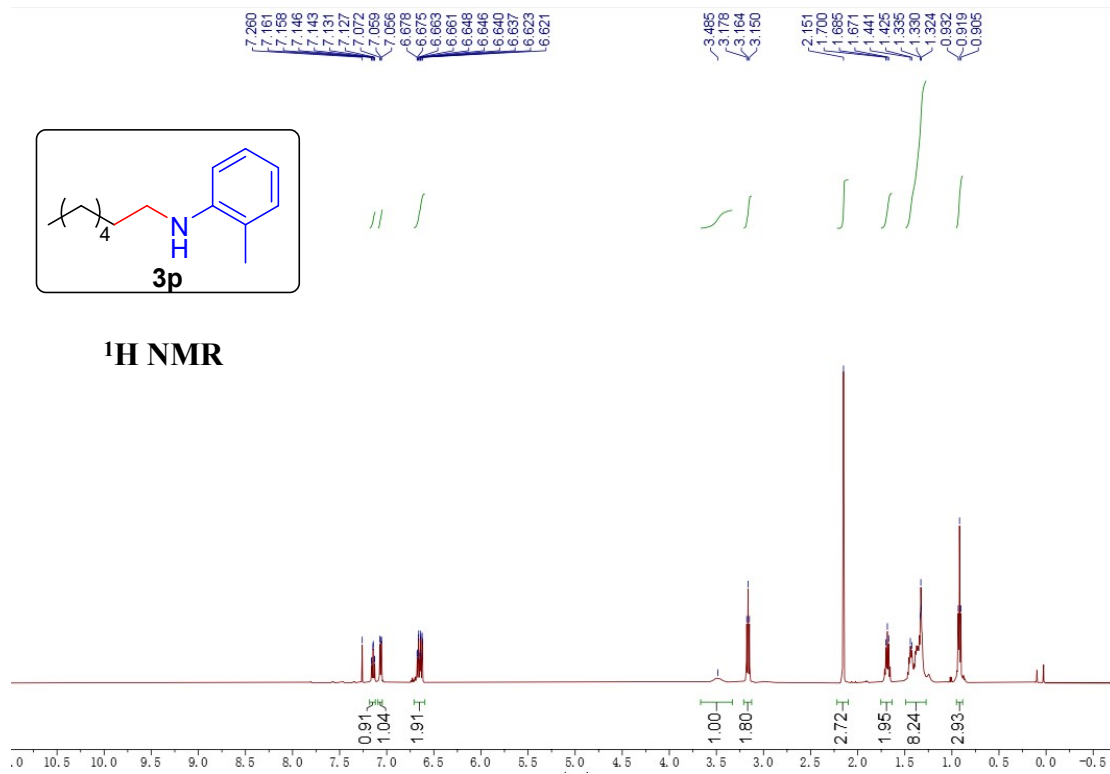0.91, 1.04, 1.91

1.00, 1.80, 2.72, 1.95, 8.24, 2.93

3q

¹H NMR

3r

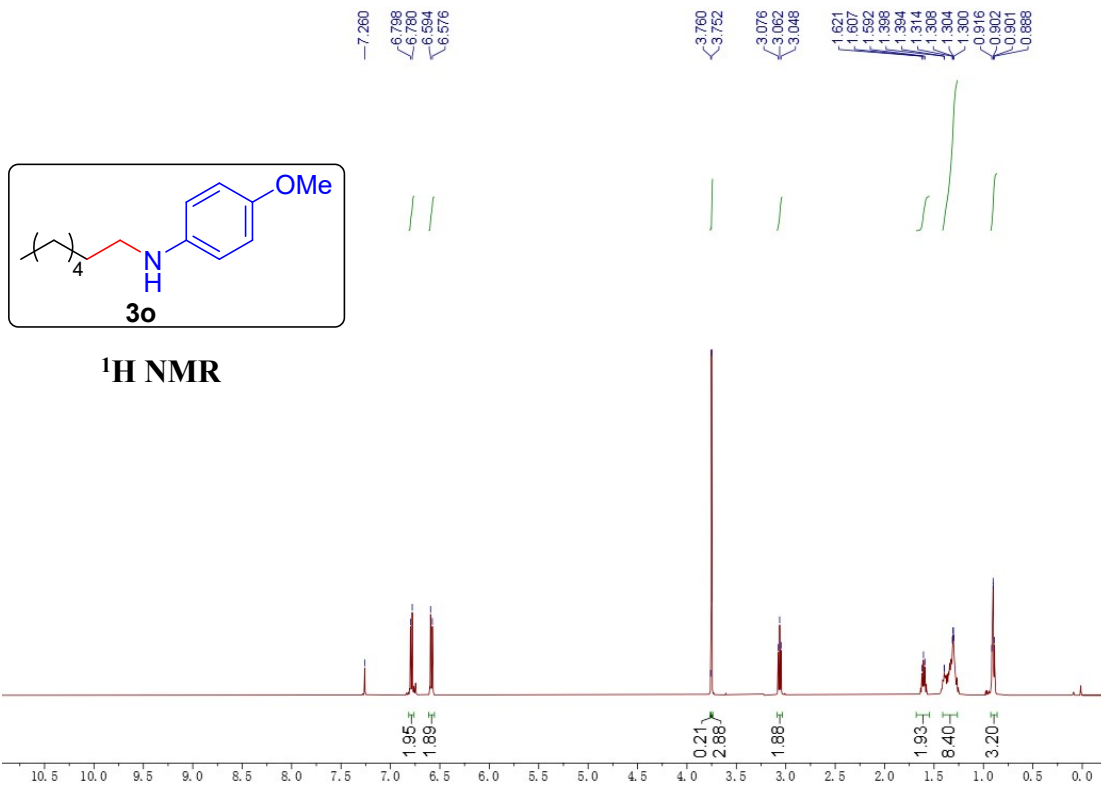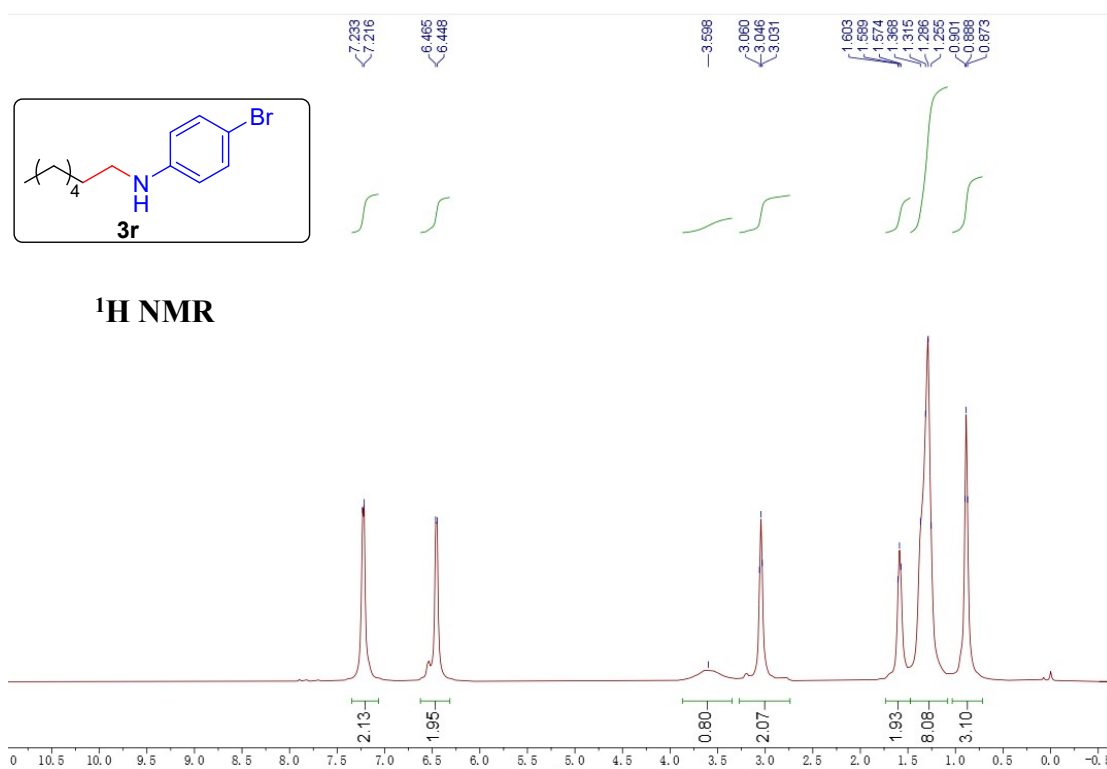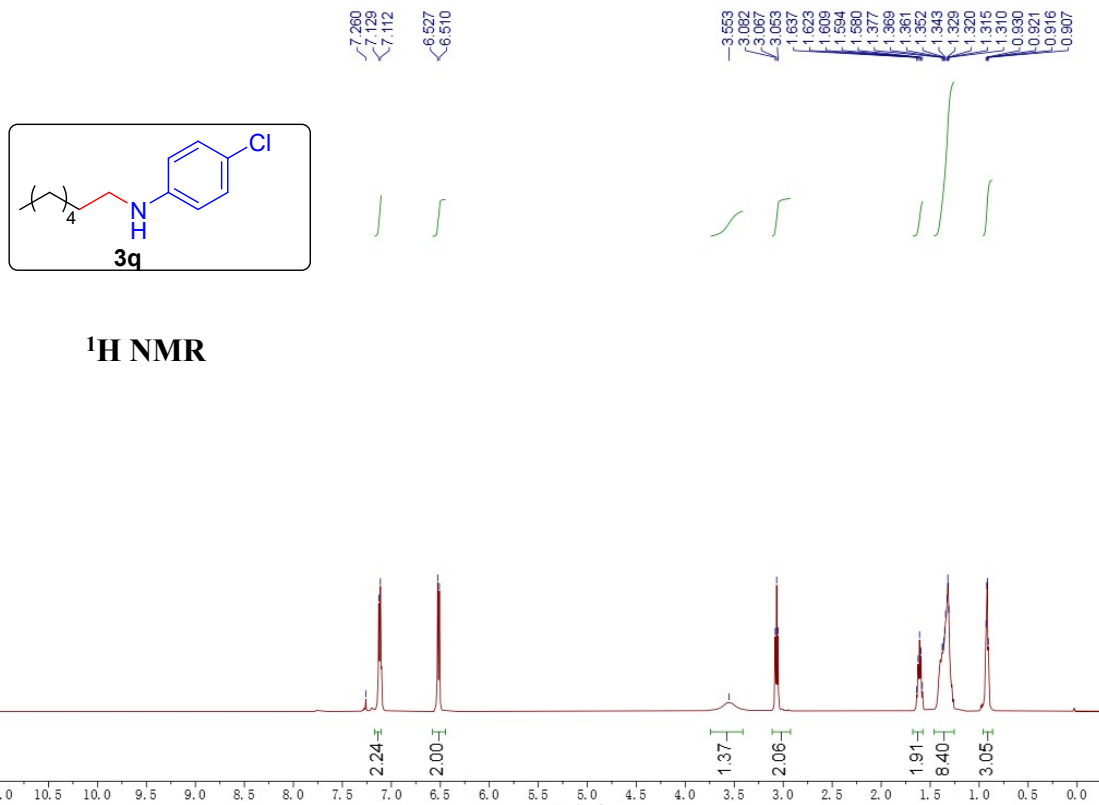**¹H NMR**

References:

[1] G. Liu, K. Huang, C. Cai, B. Cao, M. Chang, W. Wu and X. Zhang, *Chem.–Eur. J.*, 2011, **17**,

14559–14563.

[2] A. Wetzel, S. Wöckel, M. Schelwies, M. K. Brinks, F. Rominger, P. Hofmann and M. Limbach, *Org. Lett.* 2013, **15**, 266–269.

[3] X. Cui, X. Dai, Y. Deng and F. Shi, *Chem.–Eur. J.*, 2013, **19**, 3776-3776.

[4] A. R. Sawkar, W.-C. Cheng, E. Beutler, C.-H. Wong, W. E. Balch and J. W. Kelly, *PNAS*, 2002, **99**, 15428–15433.

[5] W. Li, W. Liu, D. K. Leonard, J. Rabeah, K. Junge, A. Brückner and M. Beller, *Angew. Chem. Int. Ed.* 2019, **58**, 10693-10697.

[6] J. Bianga, N. Kopplin, J. Hülsmann, D. Vogt and T. Seidensticker, *Adv. Synth. Catal.* 2020, **362**, 4415– 4424.

[7] M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, H. C. Maytum, A. C. Maxwell, A. J. A. Watson and J. M. J. Williams, *J. Am. Chem. Soc.* 2009, **131**, 1766–1774.

[8] R. P. Rucker, A. M. Whittaker, H. Dang and G. Lalic, *J. Am. Chem. Soc.* 2012, **134**, 6571−6574.

[9] S. Hwang, H. Park, Y. Kwon and S. Kim, *RSC Adv.* 2014, **4**, 60017–60024.

[10] H. Egged and C. Djerassih, *J. Am. Chem. Soc.*1973, **95**, 3710-3718.

[11] M. Vellakkaran, K. Singh and D. Banerjee, *ACS Catal.* 2017, **7**, 8152−8158.

[12] E. A. Artiukha, A. L. Nuzhdin, G. A. Bukhtiyarova, S. Yu. Zaytsev, P. E. Plyusnin, Y. V. Shubin and V. I. Bukhtiyarov *Catal. Sci. Technol.*, 2015, **5**, 4741–4745.

[13] S. Semwal and J. Choudhury, *ACS Catal.* 2016, **6**, 2424–2428.

[14] A. L. Nuzhdin, E. A. Artiukha, G. A. Bukhtiyarova, E. A. Derevyannikova, V. I. Bukhtiyarov, *Cat. Commun.* 2017, **102**, 108–113.