Electronic Supplementary Information

for

An Expedient and Novel Strategy for Reductive Amination by Employing H_2O as Both Hydrogen Source and Solvent via $B_2(OH)_4/H_2O$ Systems

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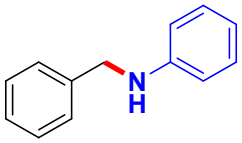
I. General Methods

Unless otherwise noted, otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. ^{1}H, ^{13}C spectra were recorded in $CDCl_3$ on a Bruker AVIII-500M spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Column chromatography was performed using silica gel (200-300 mesh).

General Procedure for Ru-catalyzed reductive amination reactions via $B_2(OH)_4/H_2O$ or $B_2(OH)_4/D_2O$ systems.

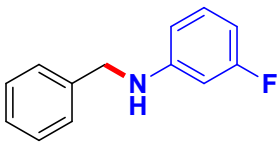
To a reaction tube equipped with a stir bar, 67.2 mg of $B_2(OH)_4$ (0.75 mmol), 12.4 mg $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol) were added. Next, 0.5 mmol of aldehyde, 0.5 mmol of amine and H_2O or D_2O (1ml) were added via syringe, then sealed the reaction tube. The mixture was stired at room temperature under air for about 4-10h. After the reaction was finished, the mixture was extracted with ethyl acetate, repeat three times. The combined organic layer was evaporated under reduced pressure, and the product was purified by column chromatography.

II. Analytic Data



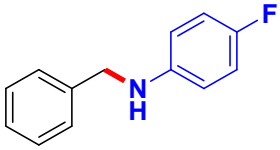
N-benzylaniline (4): colorless oil (83%, 76 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 15.0, 7.4 Hz, 4H), 7.38 (d, *J* = 6.8 Hz, 1H), 7.30 – 7.24 (m, 2H), 6.82 (td, *J* = 7.3, 0.6 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 2H), 4.41 (s, 2H), 4.10 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 139.5, 129.4, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4.

Pedrajas, E.; Sorribes, I.; Junge, K.; Beller, M.; and Llusar, R. *Green Chem.*, **2017**, *19*, 3764-3768.



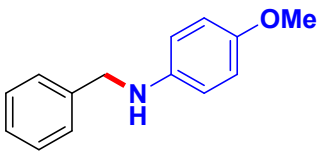
N-benzyl-3-fluoroaniline (5): bluish oil (81%, 81.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 4.2 Hz, 4H), 7.35 – 7.30 (m, 1H), 7.12 (td, *J* = 8.1, 6.9 Hz, 1H), 6.42 (ddd, *J* = 10.5, 5.2, 2.5 Hz, 2H), 6.34 (dt, *J* = 11.6, 2.3 Hz, 1H), 4.35 (d, *J* = 10.9 Hz, 2H), 4.20 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1 (d, *J* = 242.8 Hz), 149.8, 138.8, 130.3 (d, *J* = 10.2 Hz), 128.7, 127.5, 108.7 (d, *J* = 2.3 Hz), 104.0 (d, *J* = 21.6 Hz), 99.5 (d, *J* = 25.4 Hz).

Yang, C.; Fu, Y.; Huang, Y.; Yi, J.; Guo, Q.; Liu, L.*Angew. Chem. Int. Ed.* **2009**, *48*, 7398-7401.



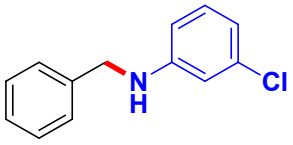
N-benzyl-4-fluoroaniline (6): greenish oil (82%, 82.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 4H), 7.36 – 7.29 (m, 1H), 6.97 – 6.87 (m, 2H), 6.66 – 6.55 (m, 2H), 4.32 (s, 2H), 3.97 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9 (d, *J* = 235.0 Hz), 144.5, 139.2, 128.7, 127.5, 127.3, 115.7 (d, *J* = 22.4 Hz), 113.7 (d, *J* = 7.4 Hz), 48.9.

Wong, C. M.; McBurney, R. T.; Binding, S. C.; Peterson, M. B.; Gonçales, V. R.; Gooding, J. J.; and Messerle, B. A. *Green Chem.*, **2017**, *19*, 3142-3151.



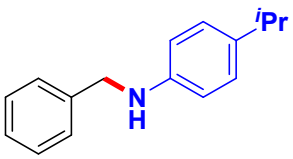
N-benzyl-4-methoxyaniline (7): yellowish oil (87%, 92.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 4H), 7.31 (t, *J* = 7.1 Hz, 1H), 6.86 – 6.78 (m, 2H), 6.67 – 6.62 (m, 2H), 4.32 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.2, 55.8, 49.3.

Wong, C. M.; McBurney, R. T.; Binding, S. C.; Peterson, M. B.; Gonçales, V. R.; Gooding, J. J.; and Messerle, B. A. *Green Chem.*, **2017**, *19*, 3142-3151.



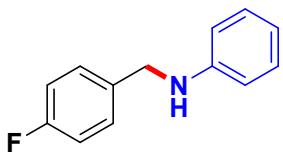
N-benzyl-3-chloroaniline (8): yellowish oil (73%, 79.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.5 Hz, 4H), 7.36 – 7.30 (m, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.73 – 6.69 (m, 1H), 6.65 (t, *J* = 2.0 Hz, 1H), 6.52 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.34 (d, *J* = 5.4 Hz, 2H), 4.14 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 138.8, 135.0, 130.2, 128.8, 127.5, 127.5, 117.4, 112.5, 111.1, 48.1.

Yang, C.; Fu, Y.; Huang, Y.; Yi, J.; Guo, Q.; Liu, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 7398-7401.



N-benzyl-4-isopropylaniline (9): yellowish oil (84%, 94.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (ddd, *J* = 12.8, 8.0, 3.8 Hz, 4H), 7.37 – 7.30 (m, 1H), 7.17 – 7.08 (m, 2H), 6.71 – 6.62 (m, 2H), 4.36 (s, 2H), 3.97 (s, 1H), 2.86 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 139.7, 138.1, 128.6, 127.6, 127.2, 127.2, 112.9, 48.7, 33.2, 24.3.

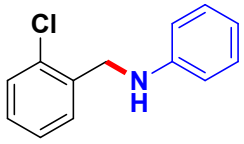
Mamidala, R.; Mukundam, V.; Dhanunjayarao, K.; Venkatasubbaiah, K.*Tetrahedron*, **2017**, *73*, 2225-2233.



N-(4-fluorobenzyl)aniline (10): yellowish oil (85%, 85.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.28 – 7.21 (m, 2H), 7.13 – 7.05 (m, 2H), 6.80 (tt, *J* = 7.4, 1.0 Hz,

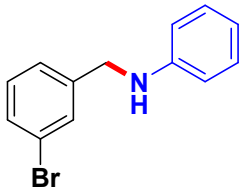
1H), 6.72 – 6.65 (m, 2H), 4.35 (s, 2H), 4.07 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, J = 244.9 Hz), 148.0, 135.2 (d, J = 3.1 Hz), 129.4, 129.1 (d, J = 8.0 Hz), 117.8, 115.5 (d, J = 21.4 Hz), 112.9, 47.6.

Yang, C.; Fu, Y.; Huang, Y.; Yi, J.; Guo, Q.; Liu, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 7398-7401.



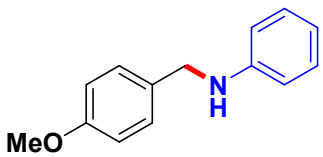
N-(2-chlorobenzyl)aniline (11): yellowish oil (79%, 85.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 1H), 7.44 – 7.41 (m, 1H), 7.27 – 7.19 (m, 4H), 6.79 – 6.74 (m, 1H), 6.66 (dd, J = 8.6, 0.9 Hz, 2H), 4.48 (s, 2H), 4.20 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 136.7, 133.2, 129.6, 129.3, 129.0, 128.4, 127.0, 117.8, 113.0, 45.9.

Yang, C.; Fu, Y.; Huang, Y.; Yi, J.; Guo, Q.; Liu, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 7398-7401.



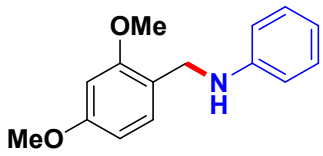
N-(3-bromobenzyl)aniline (12): yellowish oil (80%, 104.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 7.7 Hz, 1H), 7.27 – 7.19 (m, 3H), 6.79 (dd, J = 10.5, 4.1 Hz, 1H), 6.65 (dd, J = 8.6, 0.9 Hz, 2H), 4.35 (s, 2H), 4.11 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 142.1, 130.4, 130.3, 130.2, 129.4, 125.9, 122.8, 117.9, 112.9, 47.8.

Zhao,Y.; Foo, S.; and Saito, S. *Angew. Chem. Int. Ed.* **2011**, *50*, 3006-3009.



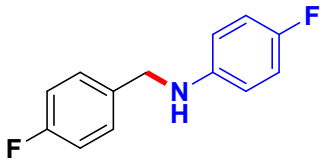
N-(4-methoxybenzyl)aniline (13): yellowish oil (81%, 86.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.7 Hz, 2H), 7.27 – 7.21 (m, 2H), 6.98 – 6.91 (m, 2H), 6.81 – 6.73 (m, 1H), 6.69 (dd, J = 8.6, 1.0 Hz, 2H), 4.30 (s, 2H), 4.00 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 148.3, 131.5, 129.3, 128.9, 117.5, 114.1, 112.9, 55.3, 47.8.

Pedrajas, E.; Sorribes, I.; Junge, K.; Beller, M.; and Llusar, R.*Green Chem.*, **2017**,*19*, 3764-3768.



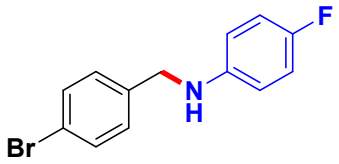
N-(2,4-dimethoxybenzyl)aniline (14): colorless oil (77%, 93.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 3H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.74 – 6.69 (m, 2H), 6.54 (d, *J* = 2.4 Hz, 1H), 6.50 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.32 (s, 2H), 4.12 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 158.5, 148.6, 129.7, 129.2, 119.8, 117.3, 113.1, 103.9, 98.6, 55.4, 55.4, 43.2.

Mamidala, R.; Mukundam, V.; Dhanunjayarao, K.; Venkatasubbaiah, K. Tetrahedron, 2017, 73, 2225-2233.



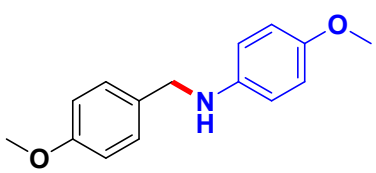
4-fluoro-N-(4-fluorobenzyl)aniline (15): off-white solid (85%, 93.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 6.62 – 6.54 (m, 2H), 4.29 (s, 2H), 3.94 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.2 Hz), 156.0 (d, *J* = 235.2 Hz), 144.3 (d, *J* = 1.8 Hz), 134.9 (d, *J* = 3.1 Hz), 129.0 (d, *J* = 8.0 Hz), 115.6 (dd, *J* = 27.5, 21.9 Hz), 115.6 (d, *J* = 5.6 Hz), 113.7 (d, *J* = 7.5 Hz), 48.3.

Shao, Z.; Fu, S.; Wei, M.; Zhou, S.; and Liu, Q. *Angew. Chem. Int. Ed.*, **2016**, *55*, 14653-14657.



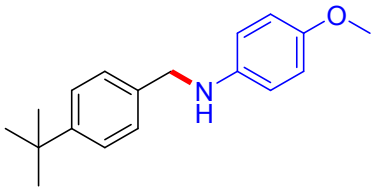
N-(4-bromobenzyl)-4-fluoroaniline (16): yellow solid (78%, 108.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.90 (t, *J* = 8.7 Hz, 2H), 6.59 – 6.53 (m, 2H), 4.28 (s, 2H), 3.98 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.99 (d, *J* = 235.5 Hz), 144.1, 138.3, 131.75 (s), 129.0, 121.0, 115.7 (d, *J* = 22.4 Hz), 113.7 (d, *J* = 7.5 Hz), 48.3.

Shao, Z.; Fu, S.; Wei, M.; Zhou, S.; and Liu, Q. *Angew. Chem. Int. Ed.*, **2016**, *55*, 14653-14657.



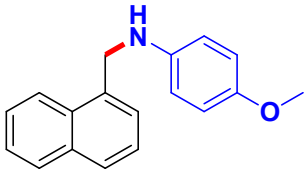
4-methoxy-N-(4-methoxybenzyl)aniline (17): off-white solid (87%, 105.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 4.23 (s, 2H), 3.83 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 152.2, 142.5, 131.7, 128.8, 114.9, 114.1, 114.0, 55.8, 55.3, 48.8.

Zhao,Y.; Foo, S.; and Saito, S. *Angew. Chem. Int. Ed.* **2011**, *50*, 3006-3009.



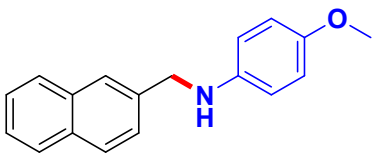
N-(4-(tert-butyl)benzyl)-4-methoxyaniline (18): yellowish oil (79%, 106.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.26 (d, *J* = 9.7 Hz, 1H), 3.78 (d, *J* = 5.6 Hz, 3H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 150.2, 142.7, 136.6, 127.4, 125.5, 114.9, 114.1, 55.9, 49.0, 34.5, 31.4.

Mamidala, R.; Mukundam, V.; Dhanunjayarao, K.; Venkatasubbaiah, K. *Tetrahedron*, **2017**, *73*, 2225-2233.



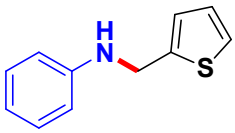
4-methoxy-N-(naphthalen-1-ylmethyl)aniline (19): yellowish oil (81%, 106.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.06 (m, 1H), 7.92 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.55 (ddd, *J* = 6.7, 5.4, 3.1 Hz, 3H), 7.50 – 7.42 (m, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.69 (d, *J* = 8.9 Hz, 2H), 4.73 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 142.6, 134.7, 133.9, 131.6, 128.8, 128.1, 126.3, 126.0, 125.8, 125.6, 123.6, 115.0, 114.0, 55.9, 47.3.

Wong, C. M.; McBurney, R. T.; Binding, S. C.; Peterson, M. B.; Gonçales, V. R.; Gooding, J. J.; and Messerle, B. A. *Green Chem.*, **2017**, *19*, 3142-3151.



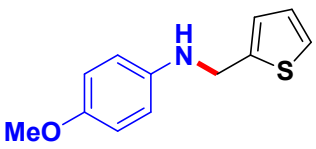
4-methoxy-N-(naphthalen-2-ylmethyl)aniline (20): off-white solid (75%, 98.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 13.6, 5.8 Hz, 4H), 7.50 (ddd, *J* = 11.1, 10.7, 7.0 Hz, 3H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 4.48 (s, 2H), 3.92 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 142.5, 137.2, 133.5, 132.8, 128.3, 127.8, 127.7, 126.1, 125.9, 125.8, 125.7, 114.9, 114.2, 55.8, 49.5.

Wong, C. M.; McBurney, R. T.; Binding, S. C.; Peterson, M. B.; Gonçales, V. R.; Gooding, J. J.; and Messerle, B. A. *Green Chem.*, **2017**, *19*, 3142-3151.



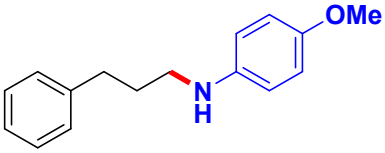
N-(thiophen-2-ylmethyl)aniline (21): colorless oil (80%, 75.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 3H), 7.09 – 7.03 (m, 1H), 7.01 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.80 (dd, *J* = 10.5, 4.1 Hz, 1H), 6.72 (dd, *J* = 8.5, 0.9 Hz, 2H), 4.55 (s, 2H), 4.08 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 143.0, 129.3, 126.9, 125.1, 124.6, 118.1, 113.2, 43.5.

Li, Q.; Xiao, Z.; Yao,C.; Zheng, H.; and Kang, Y. *Org. Lett.* **2015**, *17*, 5328-5331.



4-methoxy-N-(thiophen-2-ylmethyl)aniline (22): yellow solid (83%, 90.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 5.0 Hz, 1H), 7.03 (d, *J* = 3.2 Hz, 1H), 7.00 (dd, *J* = 4.8, 3.7 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 4.50 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 143.3, 141.8, 126.8, 124.9, 124.5, 114.9, 114.6, 55.8, 44.5.

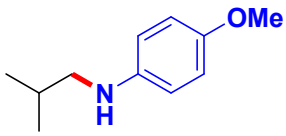
Li, Q.; Xiao, Z.; Yao,C.; Zheng, H.; and Kang, Y. *Org. Lett.* **2015**, *17*, 5328-5331.



4-methoxy-N-(3-phenylpropyl)aniline (23): yellow solid (81%, 97.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.24 (dd, *J* = 5.2, 2.6 Hz, 3H), 6.87 – 6.77 (m, 2H), 6.64 – 6.56 (m, 2H), 3.78 (s, 3H),

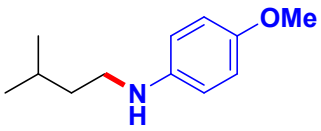
3.14 (t, J = 7.0 Hz, 2H), 2.80 – 2.74 (m, 2H), 1.97 (td, J = 14.4, 7.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 142.7, 141.8, 128.4, 128.4, 125.9, 114.9, 114.1, 55.9, 44.5, 33.5, 31.2.

Shao, Z.; Fu, S.; Wei, M.; Zhou, S.; and Liu, Q. *Angew. Chem. Int. Ed.*, **2016**, *55*, 14653-14657.



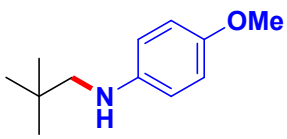
N-isobutyl-4-methoxyaniline (24): yellow solid (86%, 77.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 – 6.78 (m, 2H), 6.64 – 6.58 (m, 2H), 3.78 (s, 3H), 3.47 (s, 1H), 2.92 (d, J = 6.8 Hz, 2H), 1.90 (dp, J = 13.3, 6.7 Hz, 1H), 1.01 (d, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 142.9, 114.9, 114.0, 55.9, 52.9, 28.1, 20.5.

Mamidala, R.; Mukundam, V.; Dhanunjayarao, K.; Venkatasubbaiah, K.*Tetrahedron*, **2017**, *73*, 2225-2233.



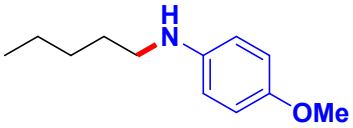
N-isopentyl-4-methoxyaniline (25): yellow solid (82%, 79.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 – 6.79 (m, 2H), 6.64 – 6.59 (m, 2H), 3.78 (s, 3H), 3.30 (s, 1H), 3.13 – 3.07 (m, 2H), 1.75 (dp, J = 13.3, 6.7 Hz, 1H), 1.53 (dd, J = 14.6, 7.1 Hz, 2H), 0.98 (d, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 142.9, 114.9, 114.0, 55.9, 43.2, 38.8, 26.1, 22.7.

Mamidala, R.; Mukundam, V.; Dhanunjayarao, K.; Venkatasubbaiah, K.*Tetrahedron*, **2017**, *73*, 2225-2233.



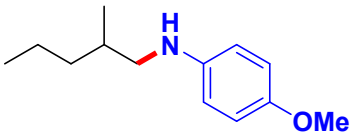
4-methoxy-N-neopentylaniline (26): yellow solid (79%, 76.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 – 6.79 (m, 2H), 6.65 – 6.60 (m, 2H), 3.78 (s, 3H), 3.40 (s, 1H), 2.88 (s, 2H), 1.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 143.5, 114.9, 113.9, 57.1, 55.9, 31.8, 27.7.

Shao, Z.; Fu, S.; Wei, M.; Zhou, S.; and Liu, Q. *Angew. Chem. Int. Ed.*, **2016**, *55*, 14653-14657.



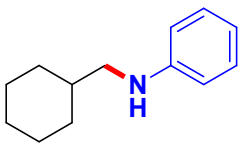
4-methoxy-N-pentylaniline (27): yellow solid (81%, 78.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 – 6.78 (m, 2H), 6.64 – 6.57 (m, 2H), 3.78 (s, 3H), 3.36 (s, 1H), 3.09 (t, *J* = 7.2 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.39 (dt, *J* = 12.8, 6.3 Hz, 4H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0 142.9, 114.9, 114.0, 55.9, 45.0, 29.4, 22.6, 14.1.

Wong, C. M.; McBurney, R. T.; Binding, S. C.; Peterson, M. B.; Gonçales, V. R.; Gooding, J. J.; and Messerle, B. A. *Green Chem.*, **2017**, *19*, 3142-3151.



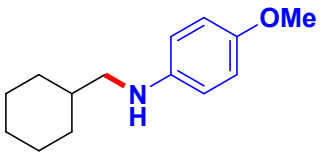
4-methoxy-N-(2-methylpentyl)aniline (28): yellow solid (83%, 85.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 – 6.80 (m, 2H), 6.66 – 6.59 (m, 2H), 3.79 (s, 3H), 3.46 (s, 1H), 3.05 (dd, *J* = 12.0, 5.8 Hz, 1H), 2.88 (dd, *J* = 12.0, 7.3 Hz, 1H), 1.78 (td, *J* = 13.2, 6.9 Hz, 1H), 1.50 – 1.42 (m, 2H), 1.37 (ddd, *J* = 14.5, 7.7, 4.7 Hz, 1H), 1.22 (ddd, *J* = 16.2, 10.4, 5.7 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 143.0, 114.9, 113.9, 55.9, 51.4, 37.2, 32.8, 20.1, 18.1, 14.4.

Mamidala, R.; Mukundam, V.; Dhanunjayarao, K.; Venkatasubbaiah, K. *Tetrahedron*, **2017**, *73*, 2225-2233.



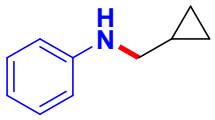
N-(cyclohexylmethyl)aniline (29): yellow solid (86%, 81.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.67 – 6.61 (m, 2H), 3.74 (s, 1H), 3.00 (d, *J* = 6.7 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.76 (dddd, *J* = 6.3, 4.9, 4.2, 2.4 Hz, 3H), 1.67 – 1.59 (m, 1H), 1.34 – 1.22 (m, 3H), 1.03 (qd, *J* = 12.3, 3.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 129.2, 116.9, 112.6, 50.6, 37.6, 31.4, 26.6, 26.0.

Wong, C. M.; McBurney, R. T.; Binding, S. C.; Peterson, M. B.; Gonçales, V. R.; Gooding, J. J.; and Messerle, B. A. *Green Chem.*, **2017**, *19*, 3142-3151.



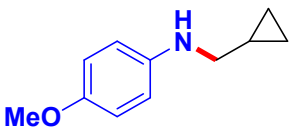
N-(cyclohexylmethyl)-4-methoxyaniline (30): yellow solid (87%, 95.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 – 6.78 (m, 2H), 6.64 – 6.58 (m, 2H), 3.78 (s, 3H), 3.49 (s, 1H), 2.95 (d, *J* = 6.7 Hz, 2H), 1.85 (dd, *J* = 13.2, 1.6 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.73 (dd, *J* = 8.5, 2.6 Hz, 1H), 1.64 – 1.55 (m, 1H), 1.34 – 1.20 (m, 3H), 1.02 (tt, *J* = 12.2, 6.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 143.0, 114.9, 113.9, 55.9, 51.7, 37.6, 31.4, 26.7, 26.0.

Mamidala, R.; Mukundam, V.; Dhanunjayarao, K.; Venkatasubbaiah, K. *Tetrahedron*, **2017**, *73*, 2225-2233.



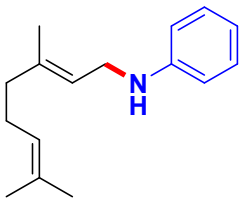
N-(cyclopropylmethyl)aniline (31): yellow solid (90%, 66.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 2H), 6.81 – 6.73 (m, 1H), 6.67 (dd, *J* = 8.6, 0.9 Hz, 2H), 3.84 (s, 1H), 3.01 (d, *J* = 6.9 Hz, 2H), 1.20 – 1.11 (m, 1H), 0.65 – 0.57 (m, 2H), 0.30 (dt, *J* = 9.6, 4.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 129.3, 117.3, 112.8, 49.1, 11.0, 3.5.

Wong, C. M.; McBurney, R. T.; Binding, S. C.; Peterson, M. B.; Gonçales, V. R.; Gooding, J. J.; and Messerle, B. A. *Green Chem.*, **2017**, *19*, 3142-3151.



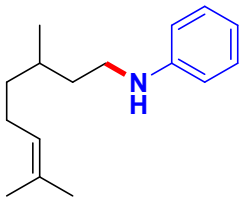
N-(cyclopropylmethyl)-4-methoxyaniline (32): yellow solid (92%, 81.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 – 6.79 (m, 2H), 6.67 – 6.60 (m, 2H), 3.78 (s, 3H), 3.56 (s, 1H), 2.94 (d, *J* = 6.9 Hz, 2H), 1.19 – 1.07 (m, 1H), 0.63 – 0.54 (m, 2H), 0.26 (q, *J* = 4.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 142.9, 114.9, 114.2, 55.8, 50.2, 11.0, 3.5.

Yang, C.; Fu, Y.; Huang, Y.; Yi, J.; Guo, Q.; Liu, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 7398-7401.



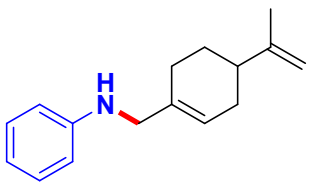
N-(3,7-dimethylocta-2,6-dien-1-yl)aniline (33): yellow solid (83%, 95.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 2H), 6.77 (td, *J* = 7.3, 1.1 Hz, 1H), 6.68 (ddd, *J* = 8.5, 3.9, 0.9 Hz, 2H), 5.41 (ddd, *J* = 8.8, 7.8, 4.1 Hz, 1H), 5.23 – 5.13 (m, 1H), 3.76 (dd, *J* = 10.9, 6.8 Hz, 2H), 3.63 (s, 1H), 2.22 – 2.09 (m, 4H), 1.83 – 1.75 (m, 6H), 1.69 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 139.0, 131.7, 129.2, 124.0 121.6, 117.3, 113.0, 42.0, 39.6, 26.5, 25.8, 17.8, 17.7.

Zhao,Y.; Foo, S.; and Saito, S. *Angew. Chem. Int. Ed.* **2011**, *50*, 3006-3009.



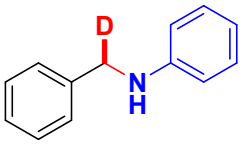
N-(3,7-dimethyloct-6-en-1-yl)aniline (34): yellow solid (83%, 95.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 5.14 (t, *J* = 7.1 Hz, 1H), 3.60 (s, 1H), 3.21 – 3.11 (m, 2H), 2.12 – 1.96 (m, 2H), 1.94 – 1.81 (m, 1H), 1.73 (s, 3H), 1.70 – 1.60 (m, 5H), 1.51 – 1.39 (m, 2H), 0.98 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 129.2, 124.7, 117.1, 112.7, 42.0, 37.1 36.7, 30.5, 25.7, 25.5, 19.6, 17.7.

Li, Q.; Xiao, Z.; Yao,C.; Zheng, H.; and Kang, Y. *Org. Lett.* **2015**, *17*, 5328−5331.



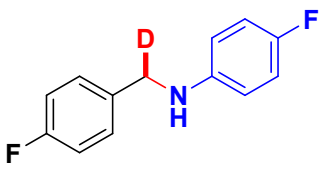
N-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)aniline (34): yellow solid (79%, 89.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 6.73 (dd, *J* = 10.5, 4.1 Hz, 1H), 6.64 (dd, *J* = 8.5, 0.9 Hz, 2H), 5.74 (s, 1H), 4.76 (dd, *J* = 6.1, 1.1 Hz, 2H), 3.80 (s, 1H), 3.67 (s, 2H), 2.22 – 2.11 (m, 4H), 2.03 – 1.95 (m, 1H), 1.89 (ddd, *J* = 7.9, 5.4, 3.4 Hz, 1H), 1.78 (s, 3H), 1.57 – 1.50 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 148.6, 134.9, 129.2, 122.4, 117.2, 112.8, 108.7, 50.0, 41.2, 30.5, 27.6, 27.2, 20.8.

Maya, R. J.; Poulose, S.; John, J.; and Varma, R. *Adv. Synth. Catal., **2017, 359,*** 1177-1184.

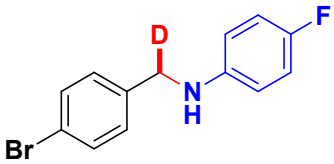


N-(phenylmethyl-d)aniline (d-4): colorless oil (83%, 76.4 mg);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 4H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 2H), 4.39 (d, *J* = 9.5 Hz, 1H), 4.09 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 139.5, 129.4, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4.

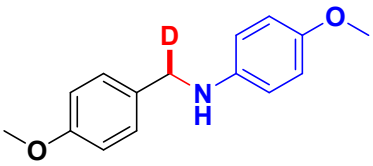
Wong, C. M.; McBurney, R. T.; Binding, S. C.; Peterson, M. B.; Gonçales, V. R.; Gooding, J. J.; and Messerle, B. A. *Green Chem.*, **2017**, *19*, 3142-3151.



4-fluoro-N-((4-fluorophenyl)methyl-d)aniline (d-15): off-white solid (85%, 93.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 6.63 – 6.55 (m, 2H), 4.28 (d, *J* = 9.4 Hz, 1H), 3.94 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.2 Hz), 156.0 (d, *J* = 235.2 Hz), 144.3 (d, *J* = 1.8 Hz), 134.9 (d, *J* = 3.1 Hz), 129.0 (d, *J* = 8.0 Hz), 115.6 (dd, *J* = 27.5, 21.9 Hz), 115.6 (d, *J* = 5.6 Hz), 113.7 (d, *J* = 7.5 Hz), 48.3. HRMS-(DART) for: $^{12}C_{13}$ $^{1}H_{10}$ ^{2}D $^{19}F_2$ ^{14}N $[M+H]^+$: calculated: 221.0995, found: 221.0993.

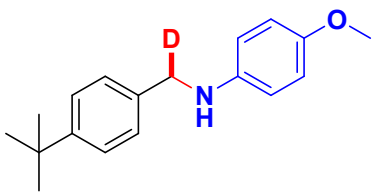


N-((4-bromophenyl)methyl-d)-4-fluoroaniline (d-16): yellow solid (78%, 109.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 6.90 (t, *J* = 8.7 Hz, 2H), 6.60 – 6.53 (m, 2H), 4.27 (d, *J* = 9.6 Hz, 1H), 3.98 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.99 (d, *J* = 235.5 Hz), 144.1, 138.3, 131.75 (s), 129.0, 121.0, 115.7 (d, *J* = 22.4 Hz), 113.7 (d, *J* = 7.5 Hz), 48.3. HRMS-(DART) for: $^{12}C_{13}$ $^{1}H_{10}$ ^{2}D $^{80}Br^{19}F$ ^{14}N $[M+H]^+$: calculated: 281.0194, found: 281.0191.

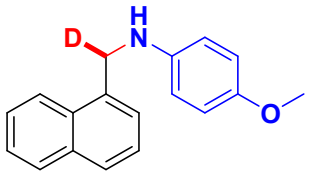


4-methoxy-N-((4-methoxyphenyl)methyl-d)aniline (d-17): off-white solid (87%, 106.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 4.23 (d, *J* = 9.7 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 152.2, 142.5,

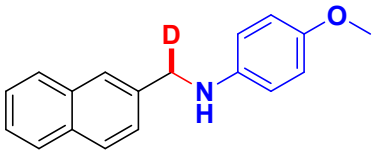
131.7, 128.8, 114.9, 114.1, 114.0, 55.8, 55.3, 48.8. HRMS-(DART) for:$^{12}C_{15}$ $^{1}H_{16}$ ^{2}D ^{14}N $^{16}O_2[M+H]^+$: calculated: 245.1395, found: 245.1387.



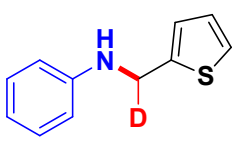
N-((4-(tert-butyl)phenyl)methyl-d)-4-methoxyaniline (d-18): yellowish oil (79%, 106.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.26 (d, *J* = 9.7 Hz, 1H), 3.78 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 150.2, 142.7, 136.6, 127.4, 125.5, 114.9, 114.1, 55.9, 49.0, 34.5, 31.4. HRMS-(DART) for:$^{12}C_{18}$ $^{1}H_{22}$ ^{2}D ^{14}N $^{16}O[M+H]^+$: calculated: 271.1915, found: 271.1910.



4-methoxy-N-(naphthalen-1-ylmethyl-d)aniline (d-19): yellowish oil (81%, 107.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 1H), 7.96 – 7.89 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.49 – 7.44 (m, 1H), 6.90 – 6.81 (m, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.72 (d, *J* = 9.6 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 142.6, 134.7, 133.9, 131.6, 128.8, 128.1, 126.3, 126.0, 125.8, 125.6, 123.6, 115.0, 114.0, 55.9, 47.3. HRMS-(DART) for:$^{12}C_{18}$ $^{1}H_{16}$ ^{2}D ^{14}N $^{16}O[M+H]^+$: calculated: 265.1446, found: 265.1441.

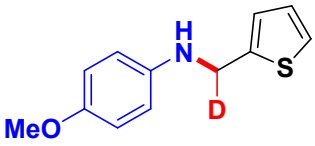


4-methoxy-N-(naphthalen-2-ylmethyl-d)aniline (d-20): off-white solid (75%, 99.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 13.7, 5.8 Hz, 4H), 7.55 – 7.47 (m, 3H), 6.83 – 6.78 (m, 2H), 6.70 – 6.65 (m, 2H), 4.47 (d, *J* = 9.9 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 142.5, 137.2, 133.5, 132.8, 128.3, 127.8, 127.7, 126.1, 125.9, 125.8, 125.7, 114.9, 114.2, 55.8, 49.5. HRMS-(DART) for:$^{12}C_{18}$ $^{1}H_{16}$ ^{2}D ^{14}N $^{16}O[M+H]^+$: calculated: 265.1446, found: 265.1443.

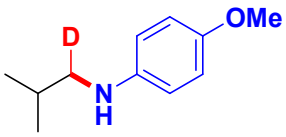


N-(thiophen-2-ylmethyl-d)aniline (d-21): colorless oil (80%, 76.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dt, *J* = 13.9, 7.5

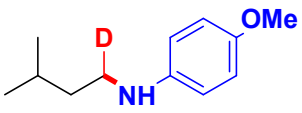
Hz, 3H), 7.06 (d, J = 2.6 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.80 (td, J = 7.3, 0.7 Hz, 1H), 6.73 (d, J = 8.4 Hz, 2H), 4.55 (d, J = 8.7 Hz, 1H), 4.08 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 143.0, 129.3, 126.9, 125.1, 124.6, 118.1, 113.2, 43.5. HRMS-(DART) for:$^{12}C_{11}$ $^{1}H_{10}$ ^{2}D ^{14}N $^{32}S[M+H]^+$: calculated: 191.0748, found: 191.0742.



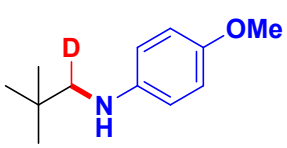
4-methoxy-N-(thiophen-2-ylmethyl-d)aniline (d-22): yellow solid (83%, 91.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 5.0 Hz, 1H), 7.03 (d, J = 3.0 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 4.49 (d, J = 8.7 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 143.3, 141.8, 126.8, 124.9, 124.5, 114.9, 114.6, 55.8, 44.5. HRMS-(DART) for:$^{12}C_{12}$ $^{1}H_{12}$ ^{2}D ^{14}N $^{16}O^{32}S[M+H]^+$: calculated: 221.0853, found: 221.0855.



4-methoxy-N-(2-methylpropyl-1-d)aniline (d-24): yellow solid (86%, 77.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 – 6.74 (m, 2H), 6.65 – 6.56 (m, 2H), 3.78 (s, 3H), 2.93 – 2.88 (m, 1H), 1.90 (dq, J = 13.3, 6.6 Hz, 1H), 1.01 (d, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 142.9, 114.9, 114.0, 55.9, 52.9, 28.1, 20.5. HRMS-(DART) for:$^{12}C_{11}$ $^{1}H_{16}$ ^{2}D ^{14}N $^{16}O[M+H]^+$: calculated: 181.1446, found: 181.1445.

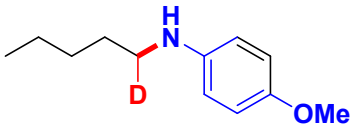


4-methoxy-N-(3-methylbutyl-1-d)aniline (d-25): yellow solid (82%, 79.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (d, J = 8.8 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 3.09 (t, J = 7.4 Hz, 1H), 1.75 (dp, J = 13.3, 6.7 Hz, 1H), 1.53 (t, J = 7.1 Hz, 2H), 0.98 (d, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 142.9, 114.9, 114.0, 55.9, 43.2, 38.8, 26.1, 22.7. HRMS-(DART) for:$^{12}C_{12}$ $^{1}H_{18}$ ^{2}D ^{14}N $^{16}O[M+H]^+$: calculated: 195.1602, found: 195.1601.

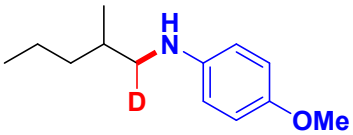


N-(2,2-dimethylpropyl-1-d)-4-methoxyaniline (d-26): yellow solid (79%, 76.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 – 6.76 (m, 2H), 6.66 –6.59 (m, 2H), 3.77 (s, 3H), 2.86 (d, J = 10.2 Hz,

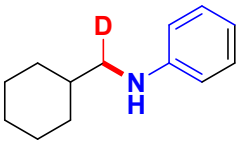
1H), 1.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 143.5, 114.9, 113.9, 57.1, 55.9, 31.8, 27.7. HRMS-(DART) for:$^{12}C_{12}$ $^{1}H_{18}$ ^{2}D ^{14}N $^{16}O[M+H]^+$: calculated: 195.1602, found: 195.1602.



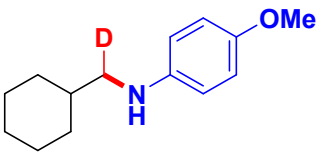
4-methoxy-N-(pentyl-1-d)aniline (d-27): yellow solid (81%, 78.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 – 6.77 (m, 2H), 6.63 – 6.57 (m, 2H), 3.77 (s, 3H), 3.06 (t, *J* = 7.1 Hz, 1H), 1.67 – 1.59 (m, 2H), 1.38 (dt, *J* = 13.7, 6.9 Hz, 4H), 0.94 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0 142.9, 114.9, 114.0, 55.9, 45.0, 29.4, 22.6, 14.1. HRMS-(DART) for:$^{12}C_{12}$ $^{1}H_{18}$ ^{2}D ^{14}N $^{16}O[M+H]^+$: calculated: 195.1602, found: 195.1604.



4-methoxy-N-2-methylpentyl-1-d)aniline (d-28): yellow solid (83%, 86.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 – 6.77 (m, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.04 – 2.84 (m, 1H), 1.83 – 1.72 (m, 1H), 1.50 – 1.41 (m, 2H), 1.40 – 1.31 (m, 1H), 1.22 (dd, *J* = 13.2, 5.6 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.96 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 143.0, 114.9, 113.9, 55.9, 51.4, 37.2, 32.8, 20.1, 18.1, 14.4. HRMS-(DART) for:$^{12}C_{13}$ $^{1}H_{20}$$^{2}D$ ^{14}N $^{16}O[M+H]^+$: calculated: 209.1759, found: 209.1757.

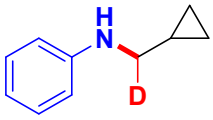


N-(cyclohexylmethyl-d)aniline (d-29): yellow solid (86%, 82.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.8 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 2H), 3.73 (s, 1H), 3.02 – 2.96 (m, 1H), 1.90 – 1.70 (m, 5H), 1.66 – 1.58 (m, 1H), 1.28 (qdd, *J* = 12.3, 9.3, 3.2 Hz, 3H), 1.03 (qd, *J* = 12.3, 2.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 129.2, 116.9, 112.6, 50.6, 37.6, 31.4, 26.6, 26.0. HRMS-(DART) for:$^{12}C_{13}$$^{1}H_{18}$$^{2}D$$^{14}N[M+H]^+$: calculated: 191.1653, found: 191.1654.

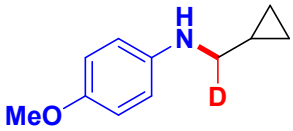


N-(cyclohexylmethyl-d)-4-methoxyaniline (d-30): yellow solid (87%, 95.7 mg); ^{1}H NMR (500 MHz,

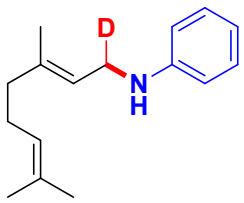
$CDCl_3$) δ 6.82 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.59 – 3.22 (m, 1H), 2.97 – 2.90 (m, 1H), 1.90 – 1.69 (m, 5H), 1.64 – 1.55 (m, 1H), 1.34 – 1.23 (m, 3H), 1.02 (qd, *J* = 12.3, 2.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 143.0, 114.9, 113.9, 55.9, 51.7, 37.6, 31.4, 26.7, 26.0. HRMS-(DART) for:$^{12}C_{14}{}^{1}H_{20}{}^{2}D^{14}N^{16}O[M+H]^+$:calculated:221.1759, found: 221.1757.



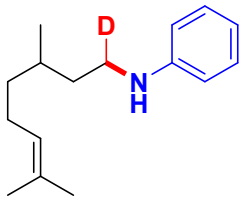
N-(cyclopropylmethyl-d)aniline (d-31): yellow solid (90%, 66.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.16 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 3.81 (s, 1H), 3.03 – 2.94 (m, 1H), 1.20 – 1.08 (m, 1H), 0.65 – 0.53 (m, 2H), 0.27 (q, *J* = 4.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 129.3, 117.3, 112.8, 49.1, 11.0, 3.5. HRMS-(DART) for:$^{12}C_{10}{}^{1}H_{12}{}^{2}D{}^{14}N$ $[M+H]^+$: calculated: 149.1184, found: 149.1181.



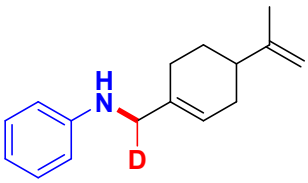
N-(cyclopropylmethyl-d)-4-methoxyaniline (d-32): yellow solid (92%, 81.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 – 6.78 (m, 2H), 6.66 – 6.59 (m, 2H), 3.77 (s, 3H), 2.93 (dd, *J* = 13.0, 6.9 Hz, 1H), 1.16 – 1.06 (m, 1H), 0.61 – 0.53 (m, 2H), 0.25 (q, *J* = 4.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 142.9, 114.9, 114.2, 55.8, 50.2, 11.0, 3.5. HRMS-(DART) for:$^{12}C_{11}{}^{1}H_{14}{}^{2}D^{14}N$ $^{16}O[M+H]^+$: calculated: 179.1289, found: 179.1287.



N-(3,7-dimethylocta-2,6-dien-1-yl-1-d)aniline (d-33):yellow solid (84%, 96.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 2H), 6.75 (td, *J* = 7.3, 1.0 Hz, 1H), 6.68 – 6.62 (m, 2H), 5.39 (t, *J* = 7.9 Hz, 1H), 5.19 – 5.11 (m, 1H), 3.72 (dd, *J* = 17.5, 10.6 Hz, 1H), 3.60 (s, 1H), 2.18 – 2.06 (m, 4H), 1.76 (t, *J* = 15.9 Hz, 6H), 1.66 (d, *J* = 2.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 139.0, 131.7, 129.2, 124.0 121.6, 117.3, 113.0, 42.0, 39.6, 26.5, 25.8, 17.8, 17.7. HRMS-(DART) for:$^{12}C_{16}$ $^{1}H_{22}$ ^{2}D $^{14}N[M+H]^+$: calculated: 231.1966, found: 231.1963.



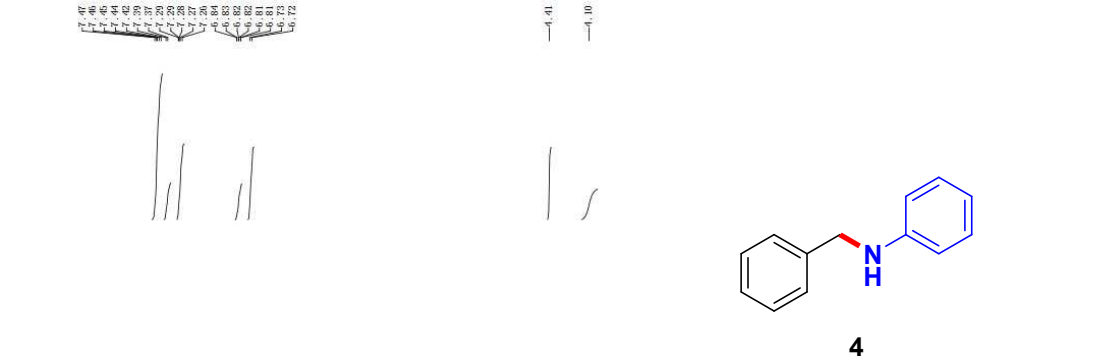
N-(3,7-dimethyloct-6-en-1-yl-1-d)aniline (d-34): yellow solid (81%, 94.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.75 – 6.69 (m, 1H), 6.64 (dt, *J* = 6.6, 1.5 Hz, 2H), 5.19 – 5.07 (m, 1H), 3.59 (s, 1H), 3.17 – 3.09 (m, 1H), 2.03 (pd, *J* = 14.5, 7.1 Hz, 2H), 1.94 – 1.80 (m, 1H), 1.72 (d, *J* = 1.0 Hz, 3H), 1.68 – 1.58 (m, 5H), 1.43 (dddd, *J* = 9.8, 8.9, 7.2, 5.6 Hz, 2H), 0.98 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 129.2, 124.7, 117.1, 112.7, 42.0, 37.1 36.7, 30.5, 25.7, 25.5, 19.6, 17.7. HRMS-(DART) for:$^{12}C_{16}$ $^{1}H_{24}$ ^{2}D $^{14}N[M+H]^+$: calculated: 233.2123, found: 233.2130.



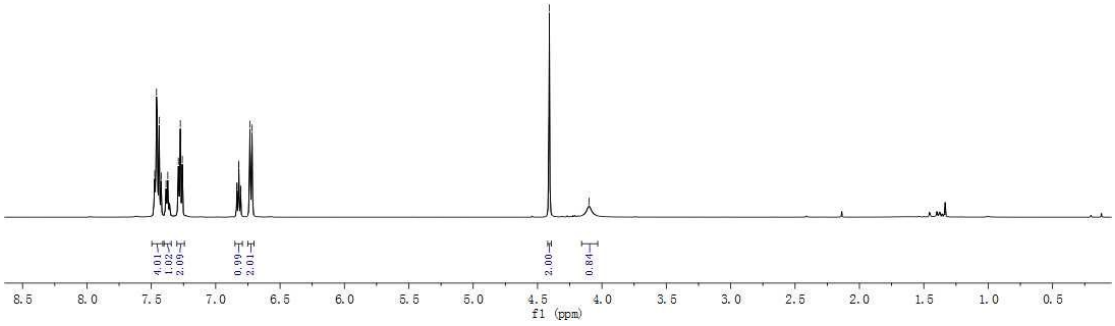
N-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl-d)aniline (d-35): yellow solid (78%, 89.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 2H), 6.73 (tt, *J* = 7.4, 1.0 Hz, 1H), 6.64 (dd, *J* = 8.6, 1.0 Hz, 2H), 5.73 (d, *J* = 2.4 Hz, 1H), 4.78 – 4.73 (m, 2H), 3.80 (s, 1H), 3.66 (d, *J* = 9.5 Hz, 1H), 2.21 – 2.11 (m, 4H), 2.04 – 1.94 (m, 1H), 1.89 (dtd, *J* = 12.6, 4.4, 2.5 Hz, 1H), 1.78 (s, 3H), 1.56 – 1.50 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 148.6, 134.9, 129.2, 122.4, 117.2, 112.8, 108.7, 50.0, 41.2, 30.5, 27.6, 27.2, 20.8. HRMS-(DART) for:$^{12}C_{16}$ $^{1}H_{20}$ ^{2}D $^{14}N[M+H]^+$: calculated: 229.1810, found: 229.1812.

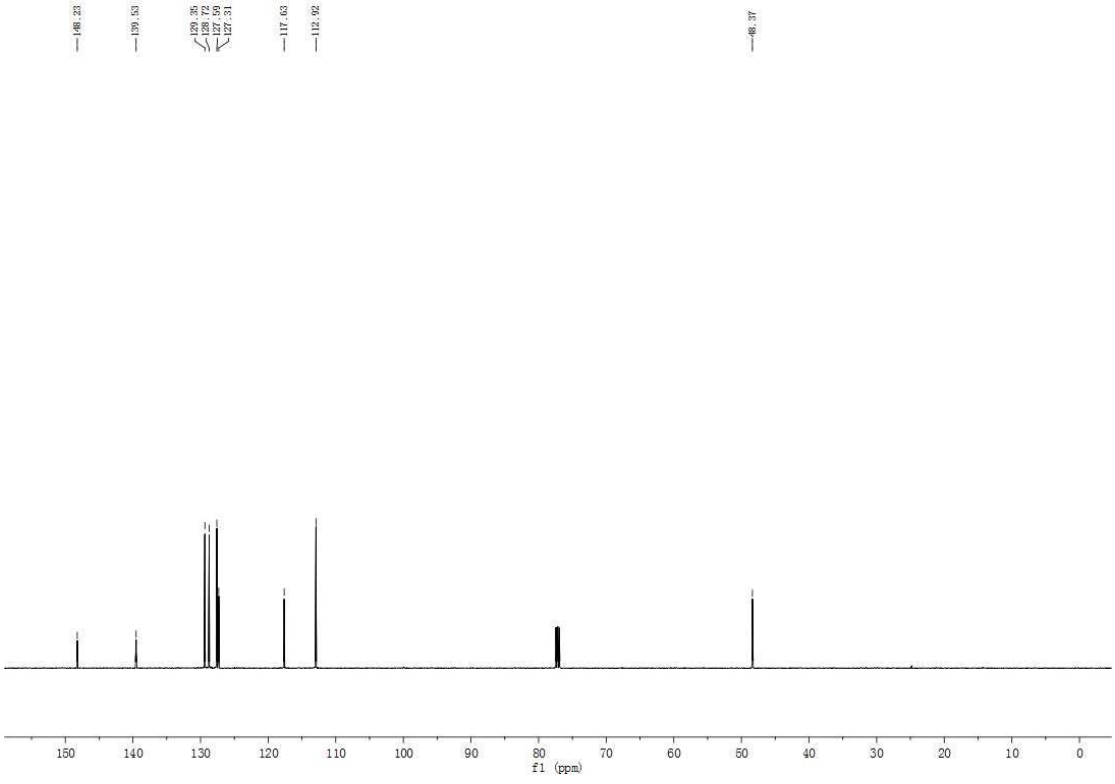
III ^{1}H and ^{13}C NMR Spectrum of Products

NMR Spectrum of Compound **4**

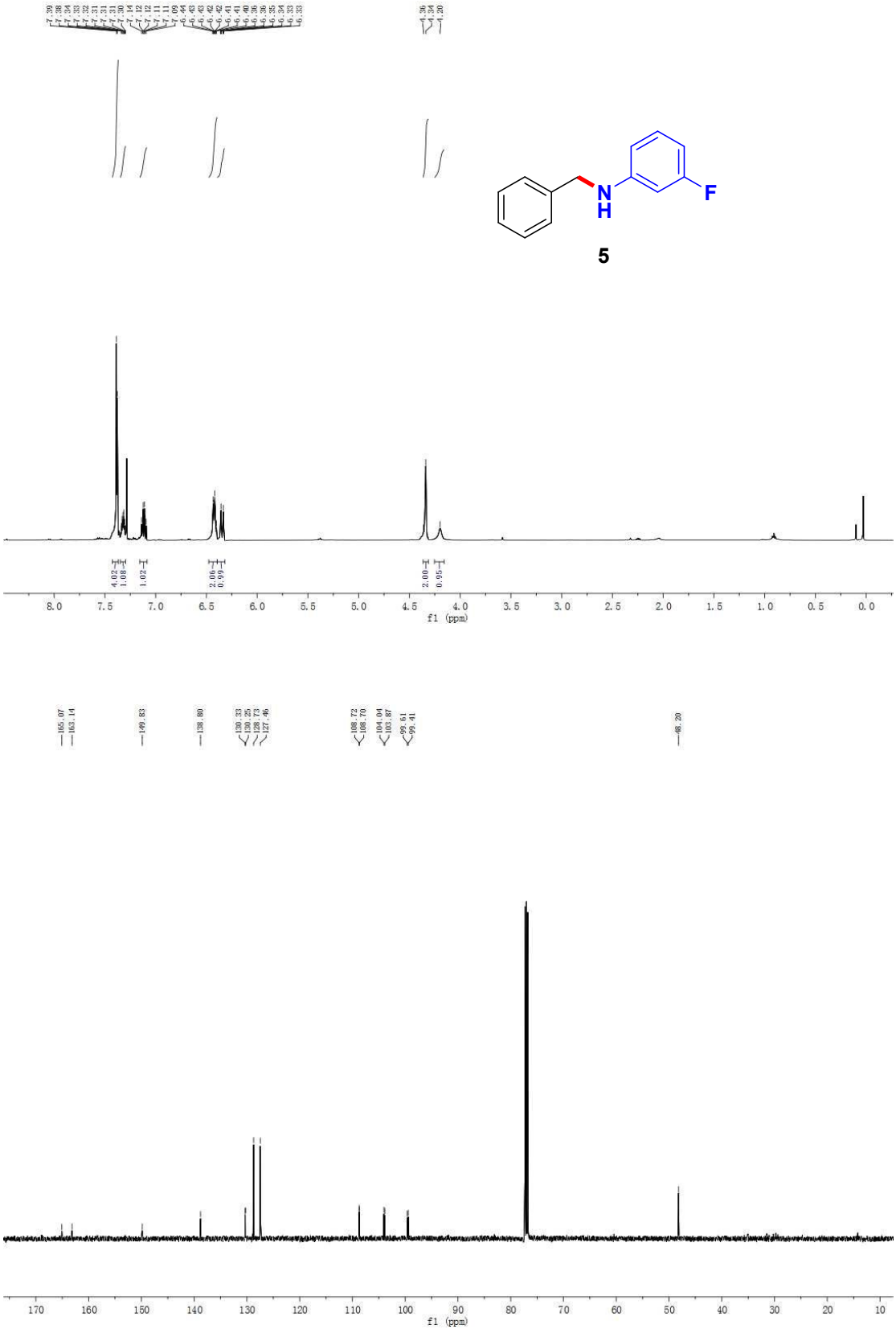


4

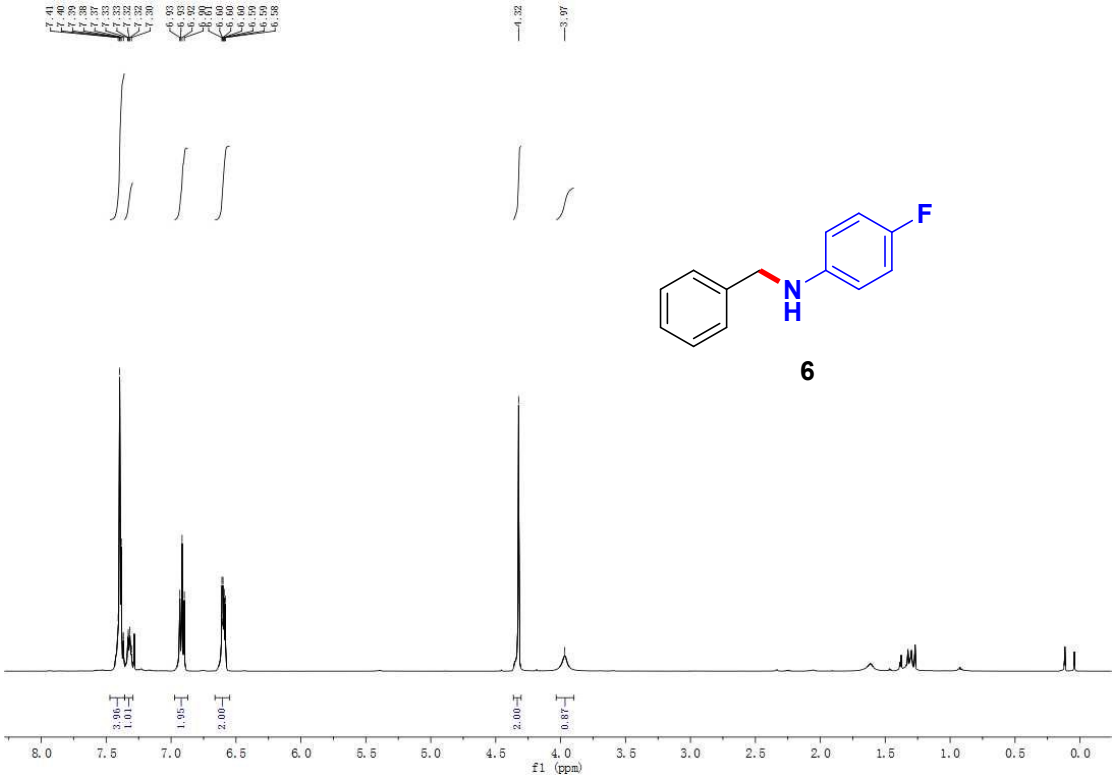


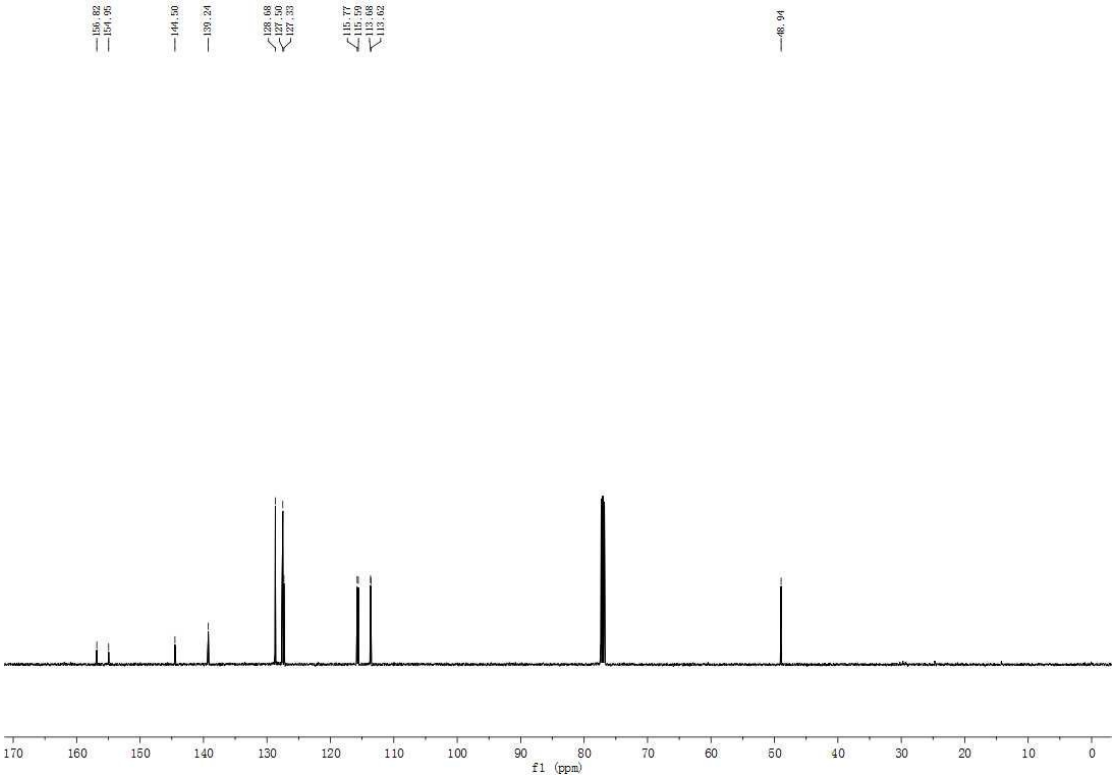


NMR Spectrum of Compound **5**

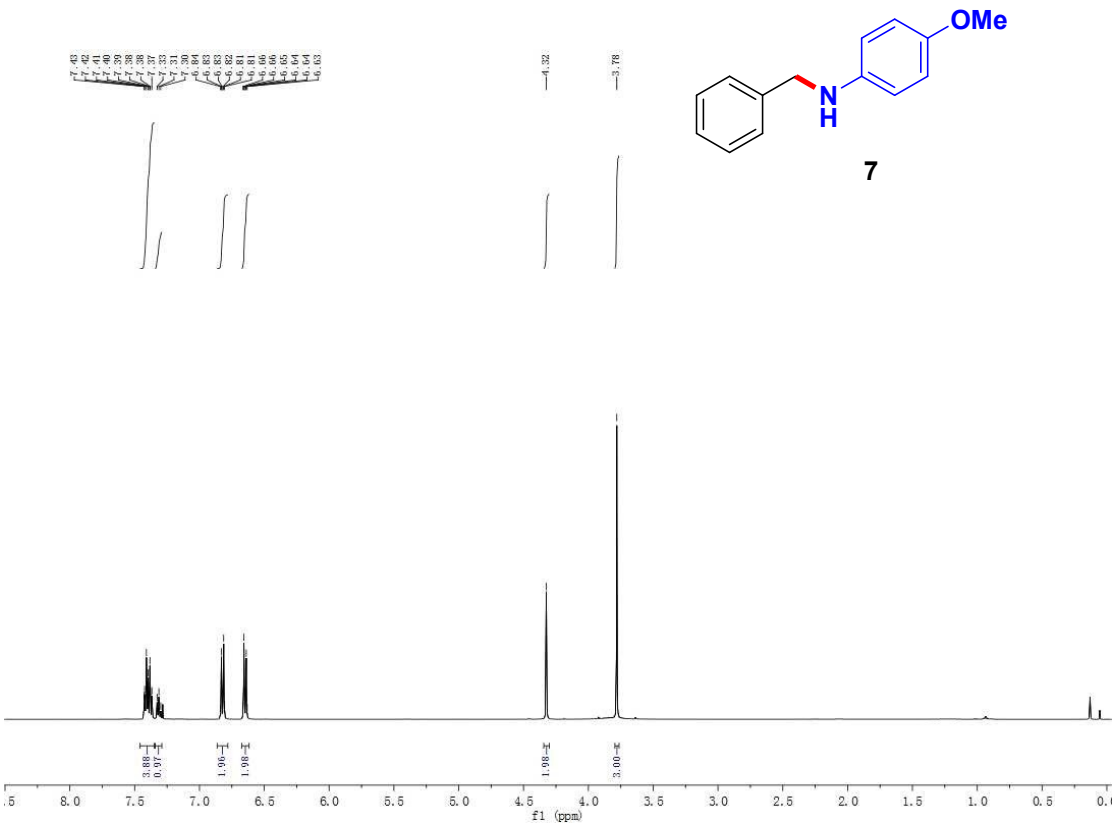


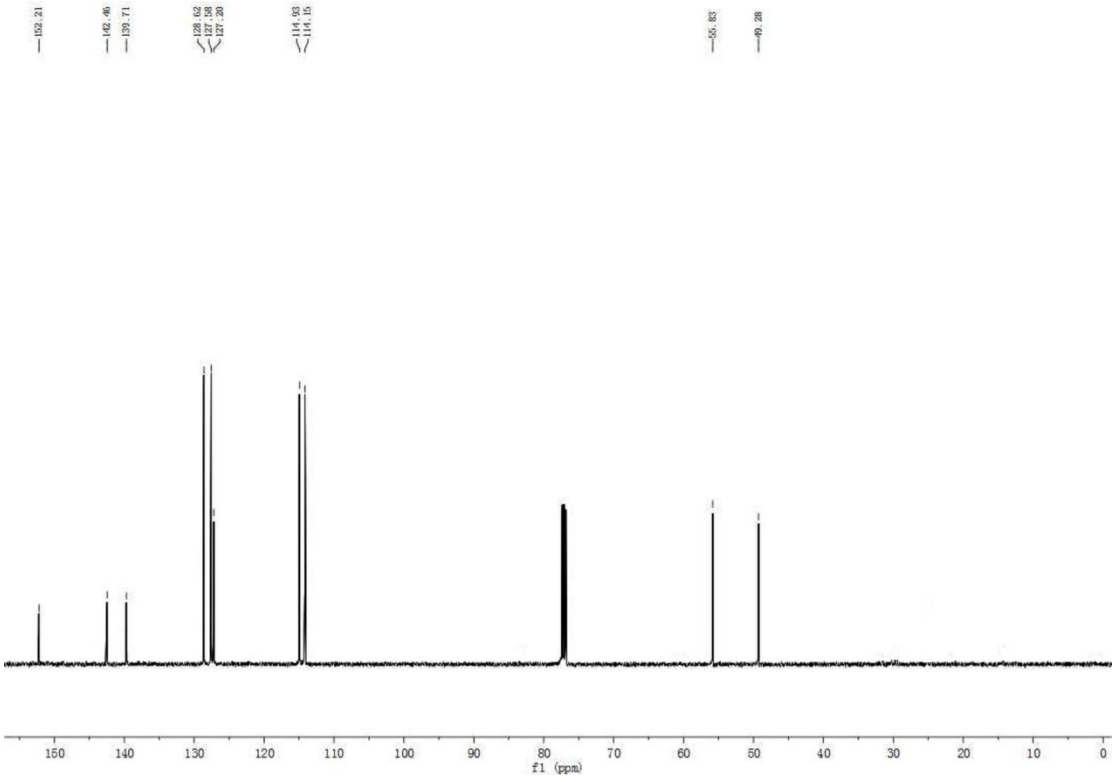
NMR Spectrum of Compound **6**



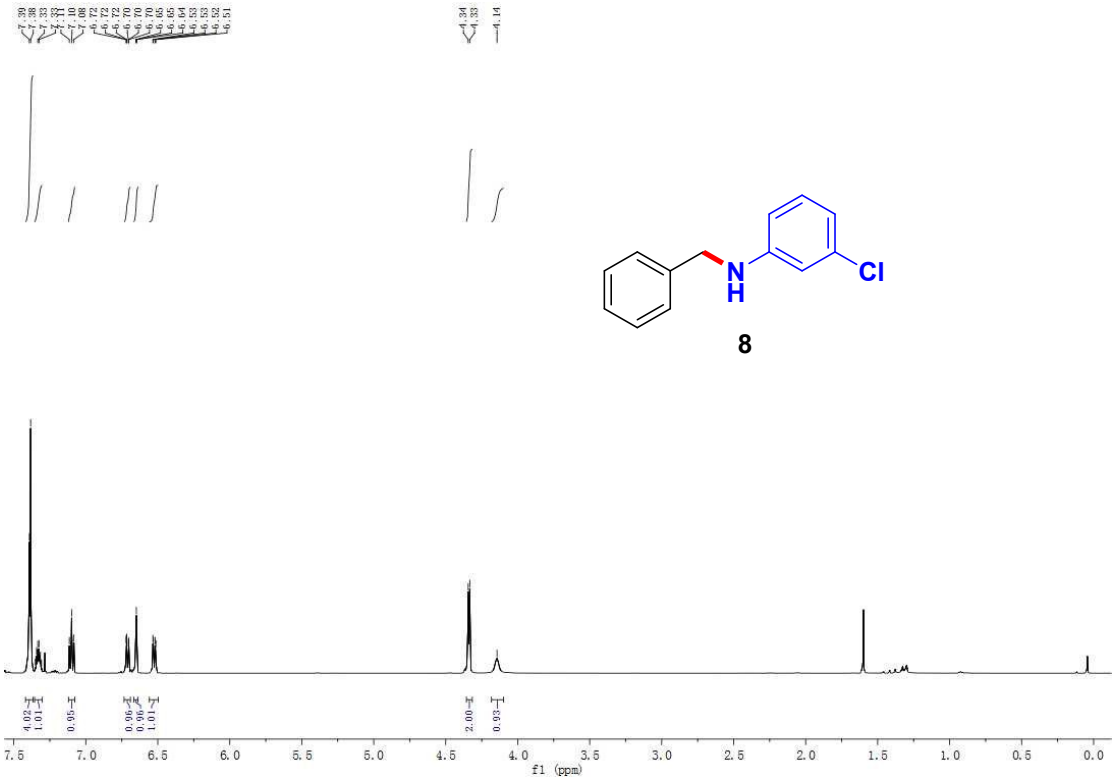


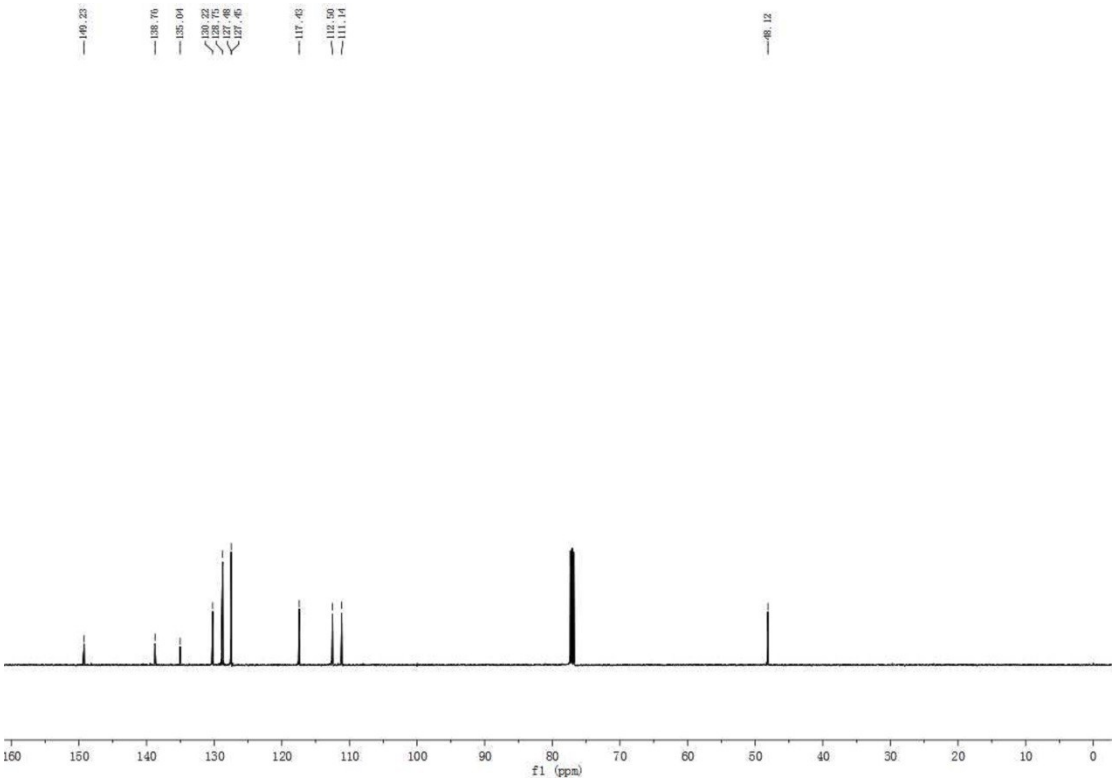
NMR Spectrum of Compound **7**



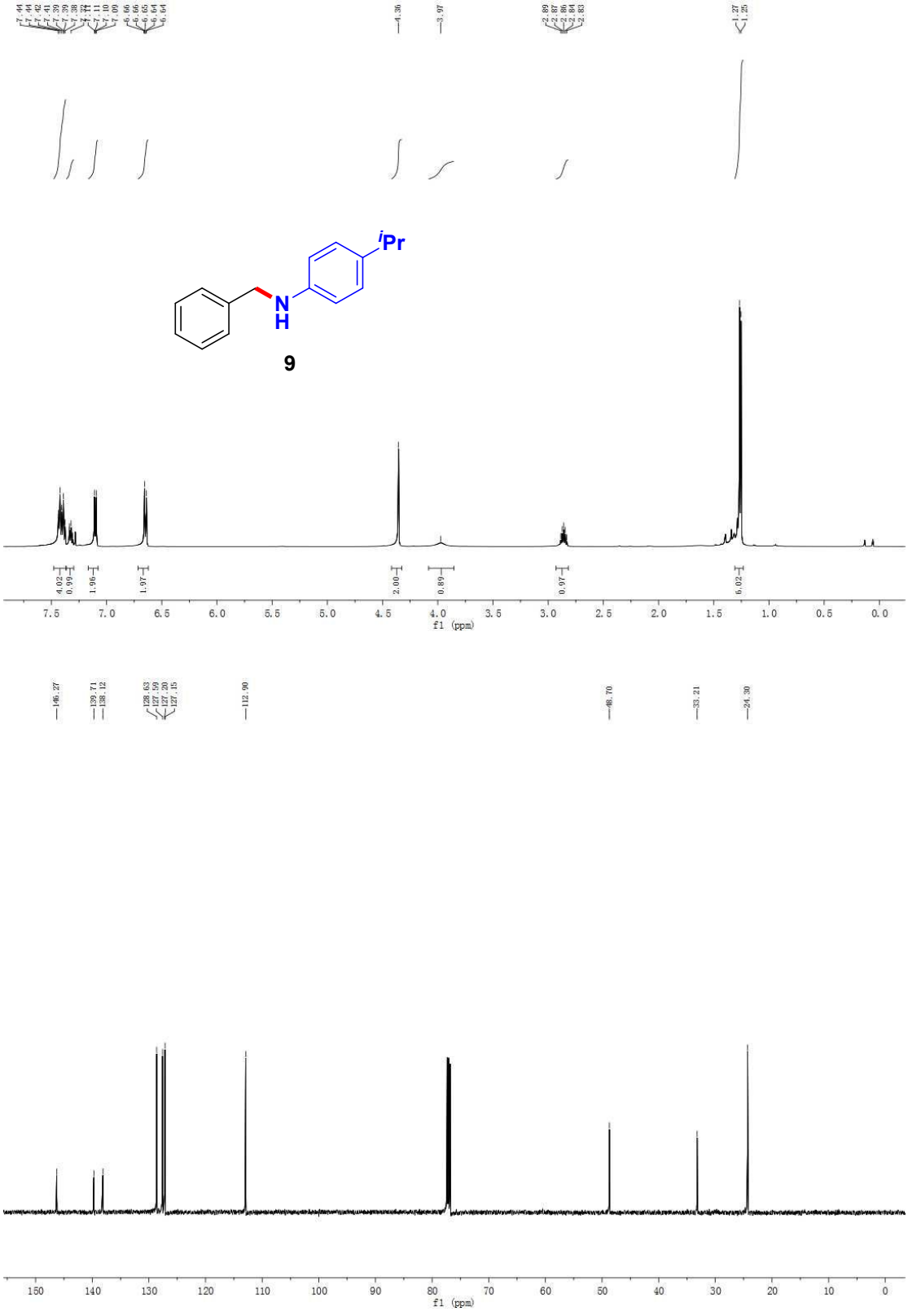


NMR Spectrum of Compound **8**

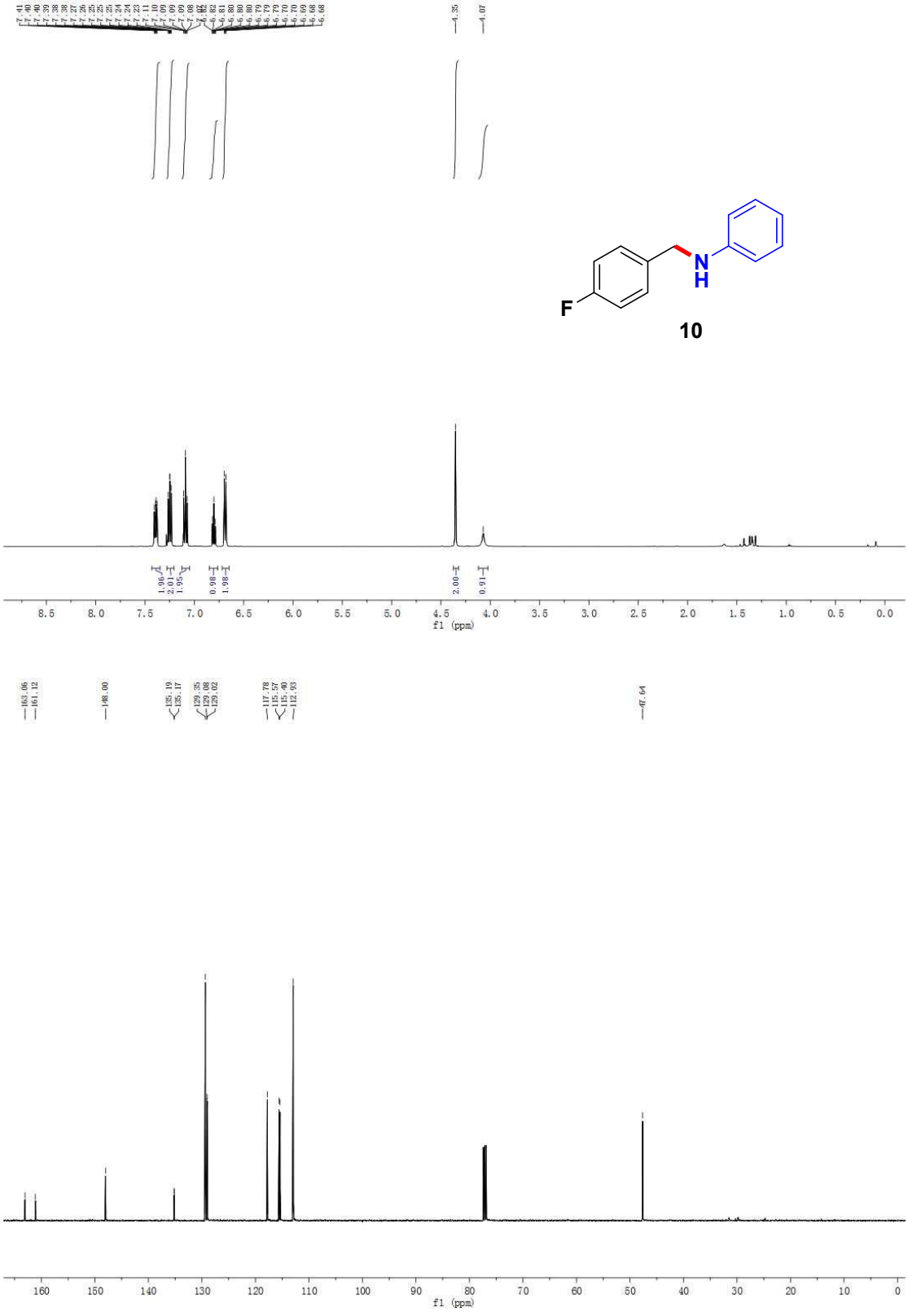




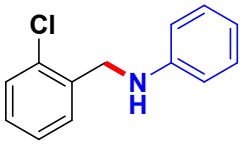
NMR Spectrum of Compound **9**



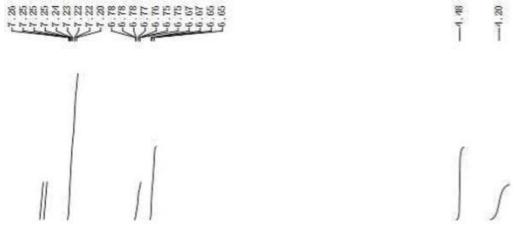
NMR Spectrum of Compound **10**

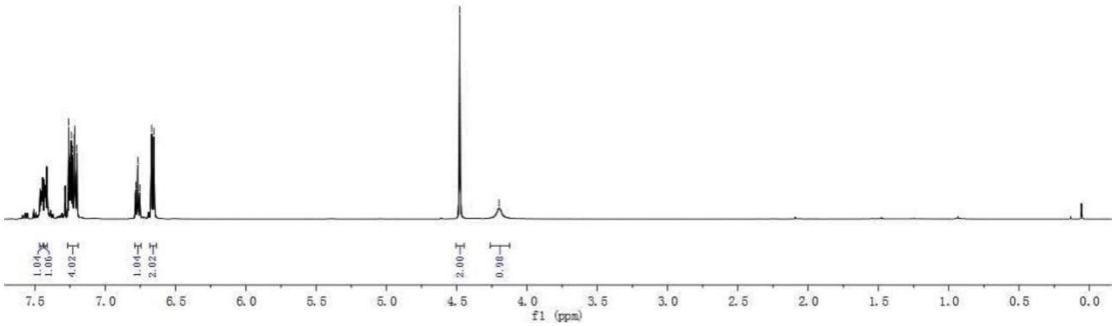


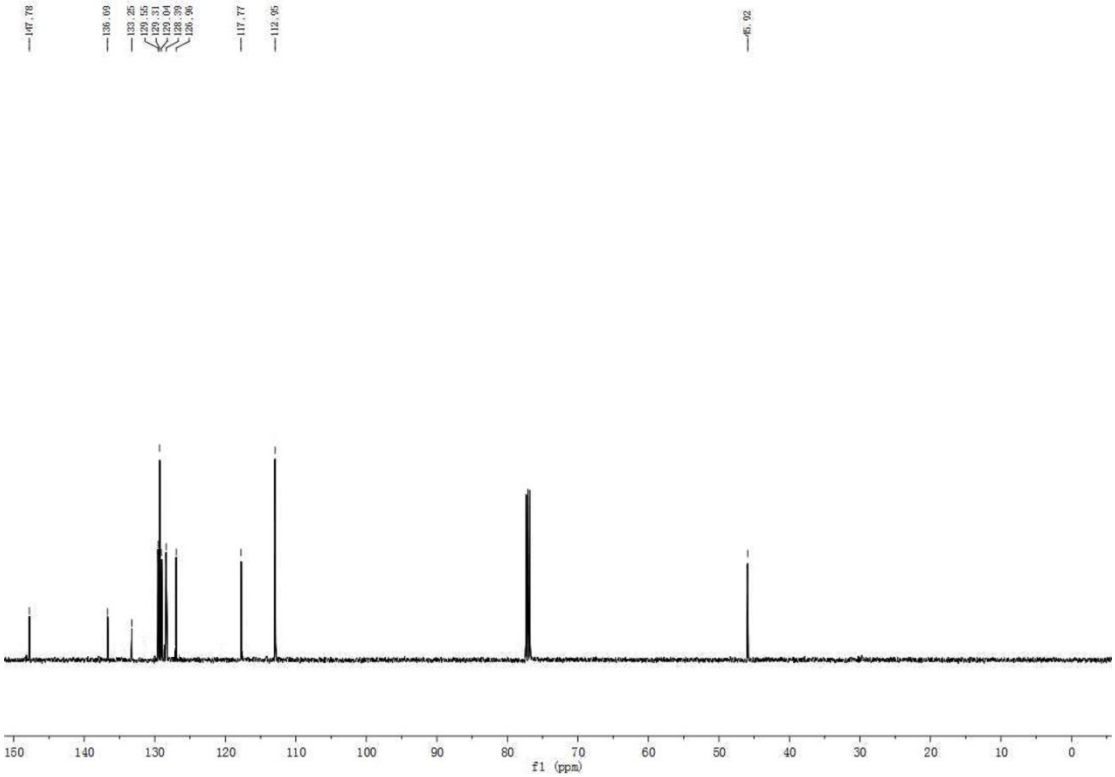
NMR Spectrum of Compound **11**



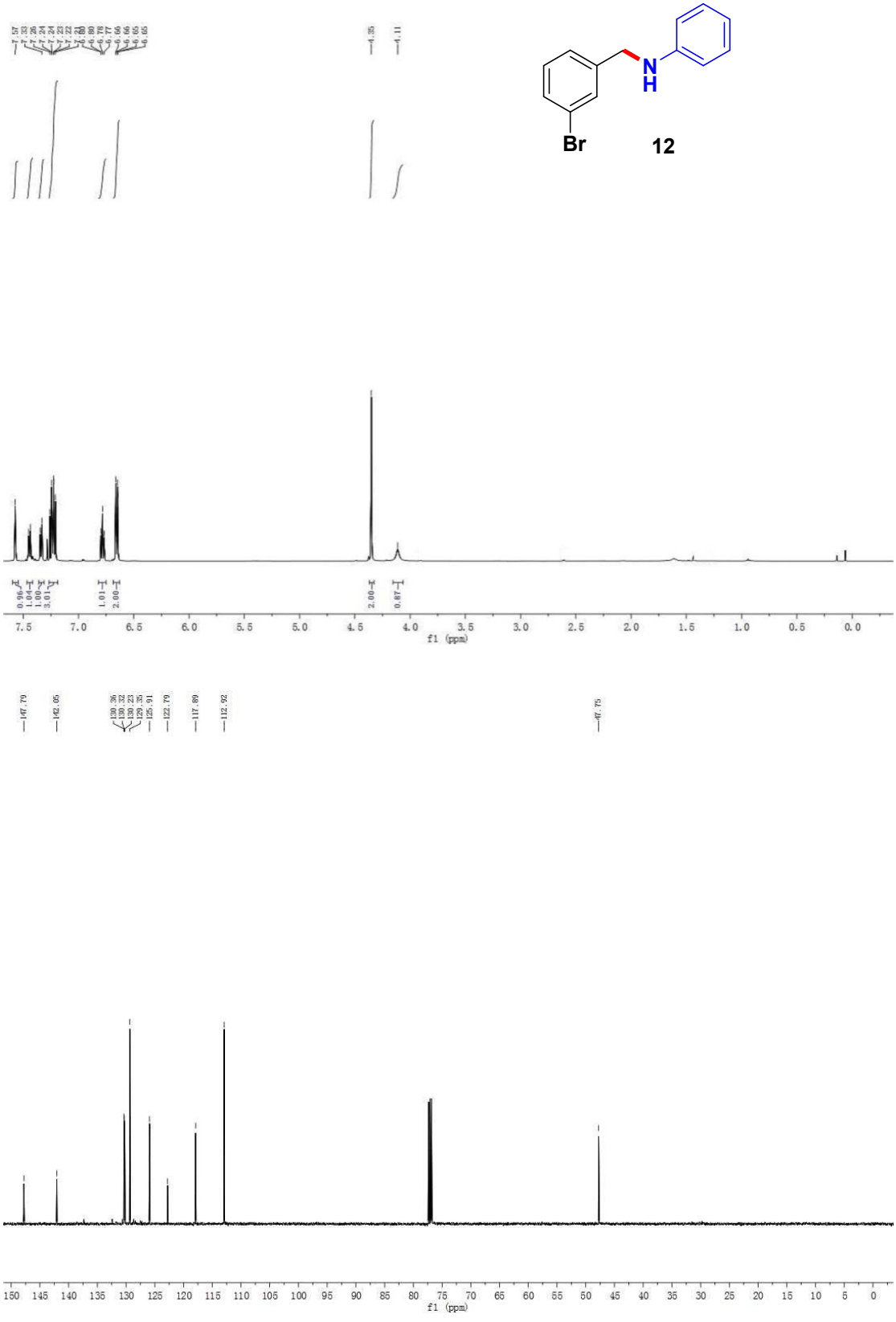
11



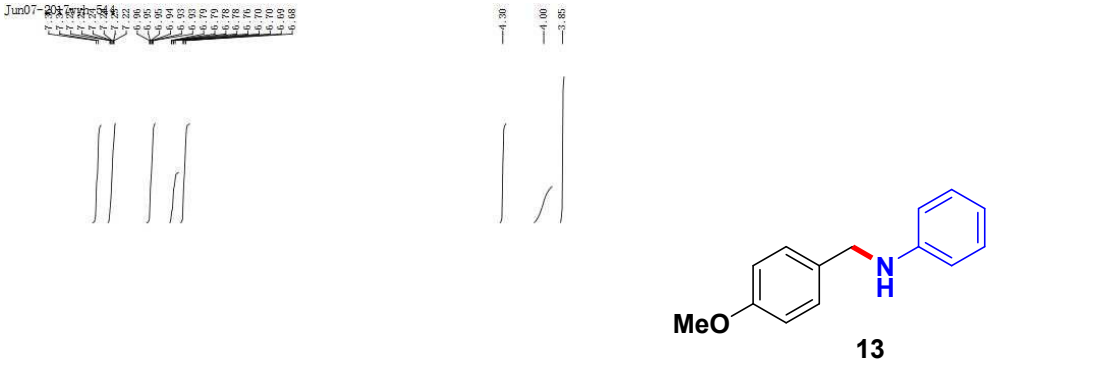




NMR Spectrum of Compound **12**



NMR Spectrum of Compound **13**



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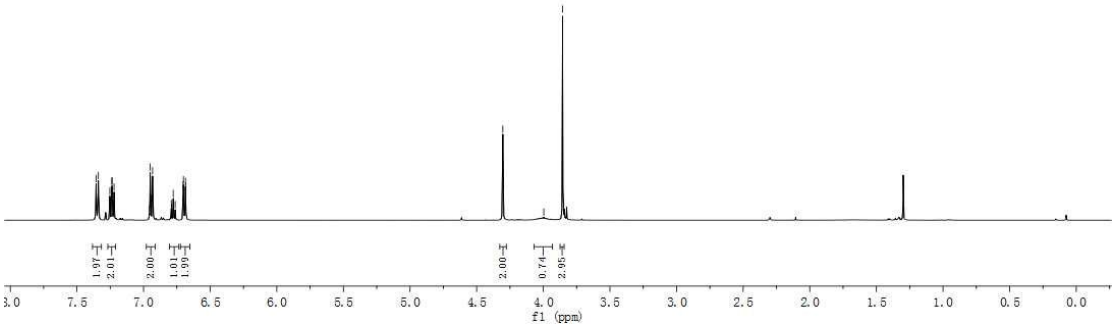
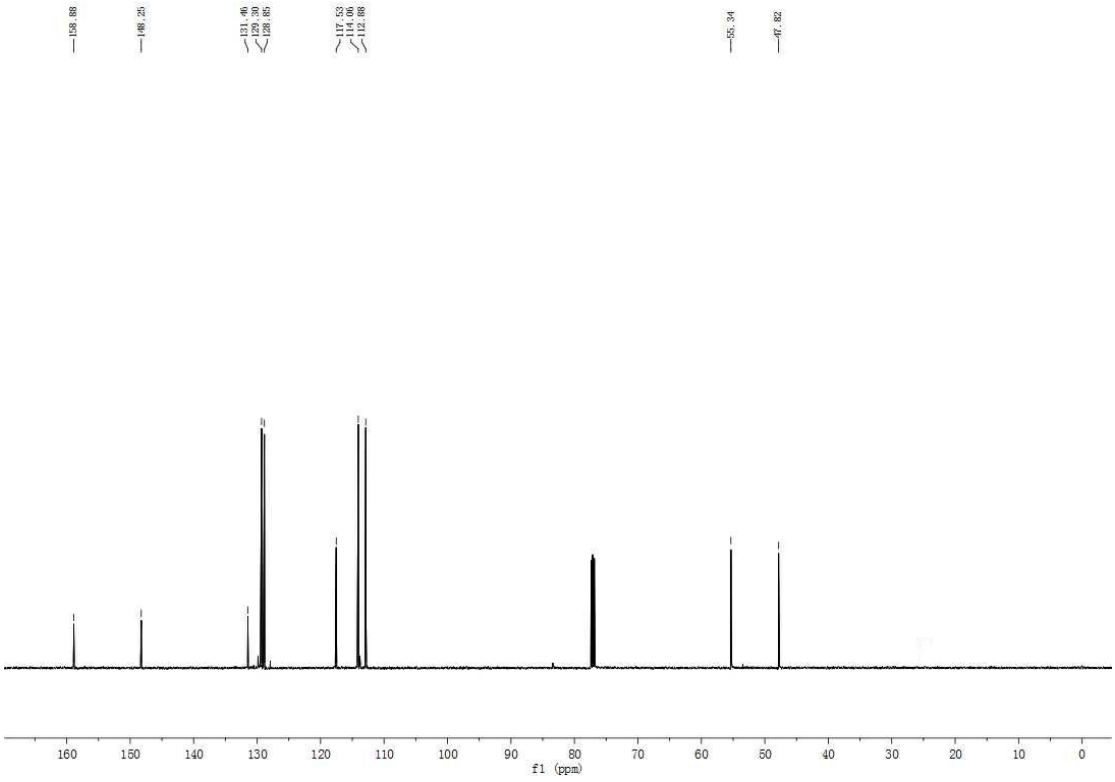
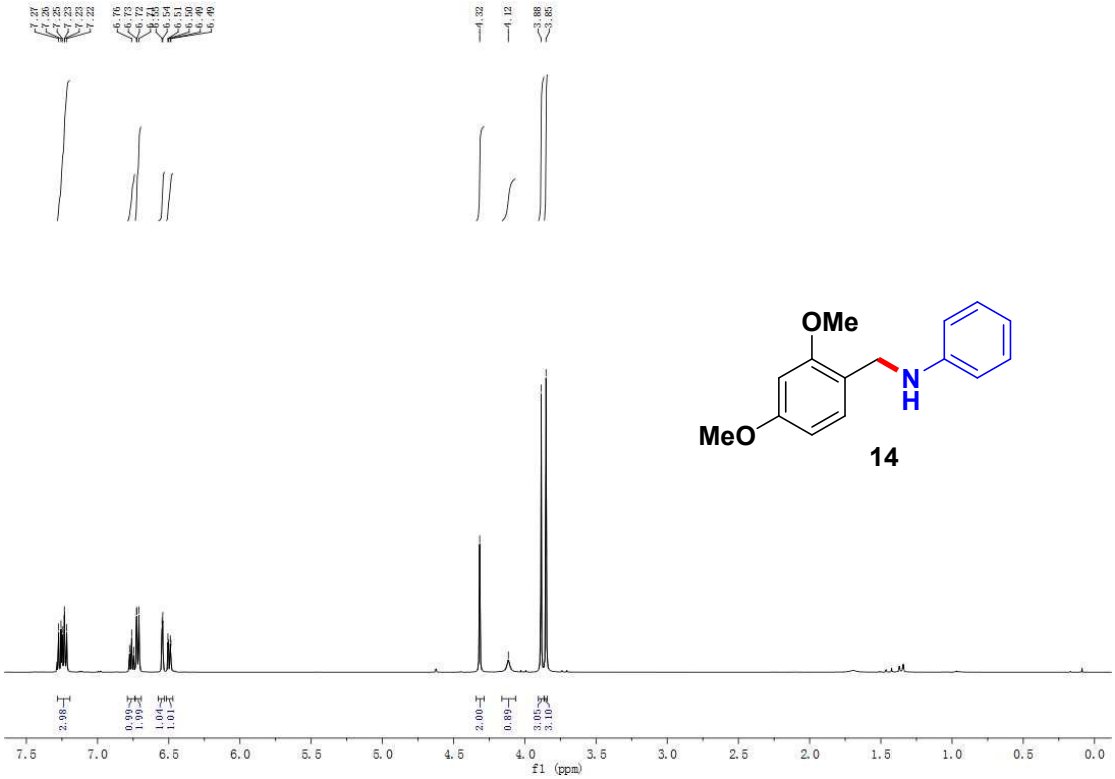
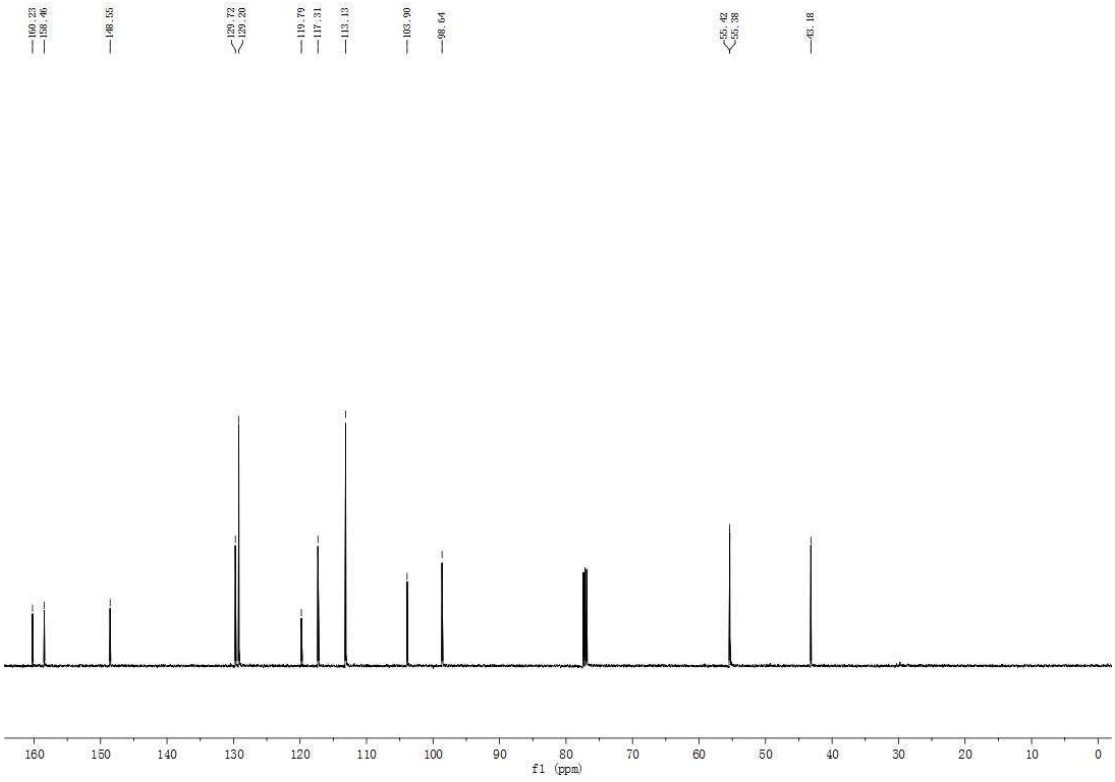


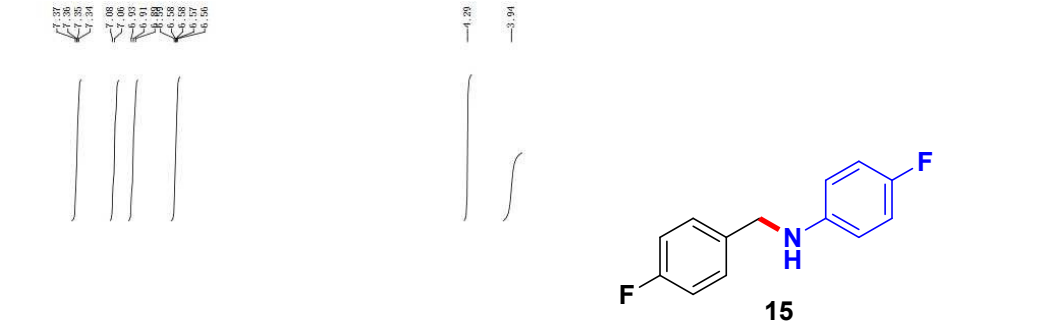


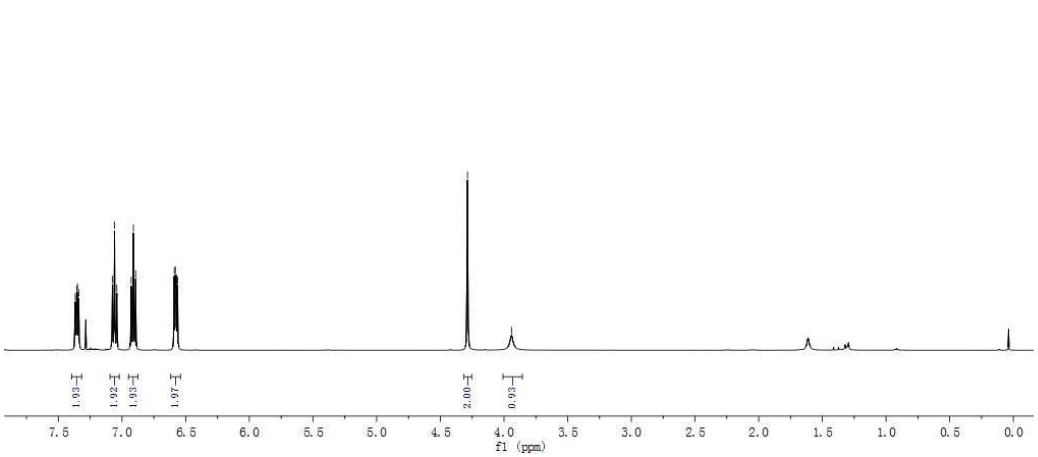
NMR Spectrum of Compound **14**

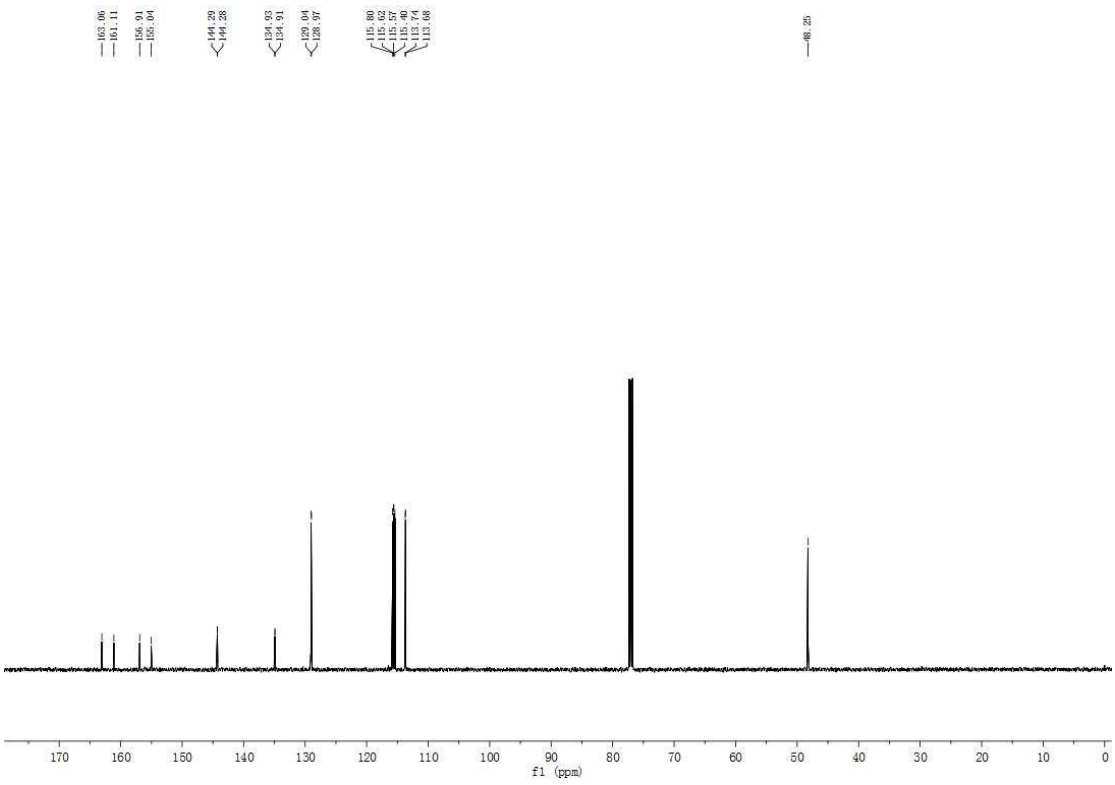




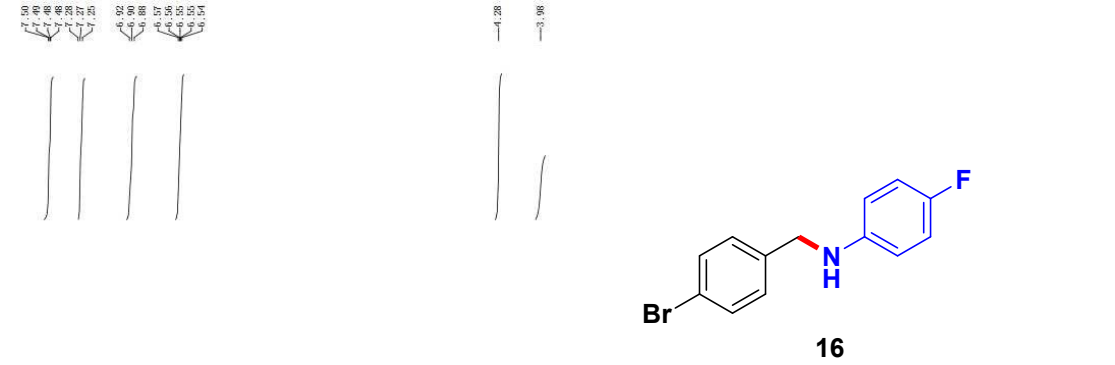
NMR Spectrum of Compound **15**



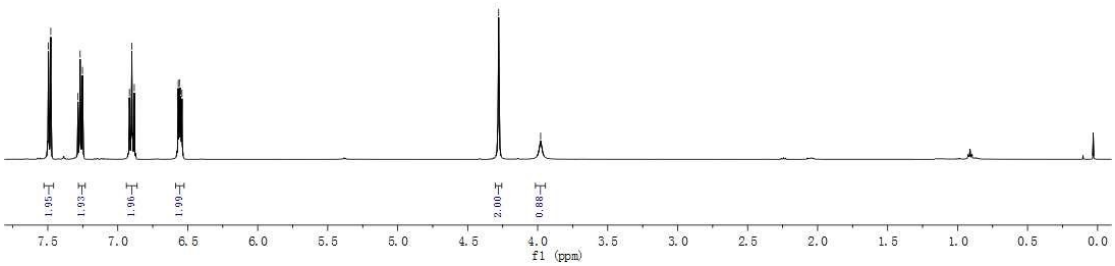


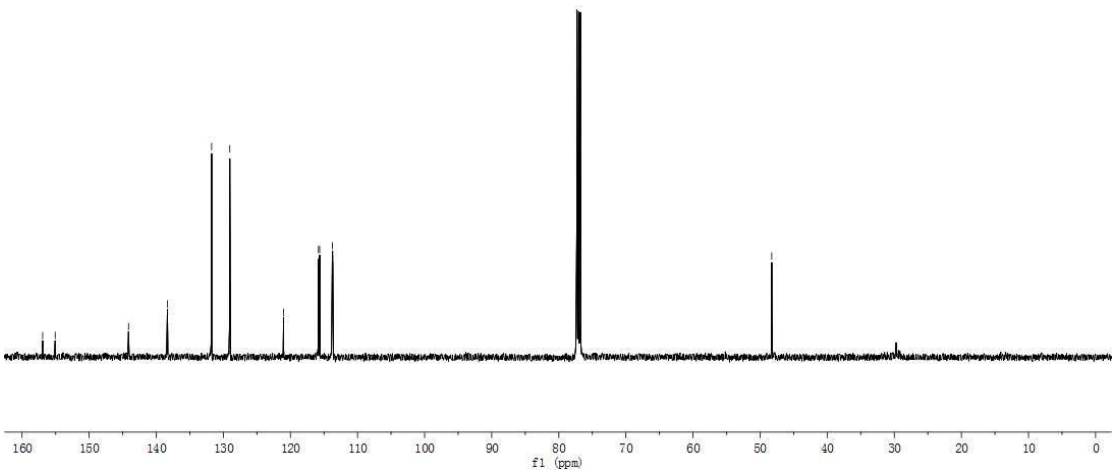


NMR Spectrum of Compound **16**

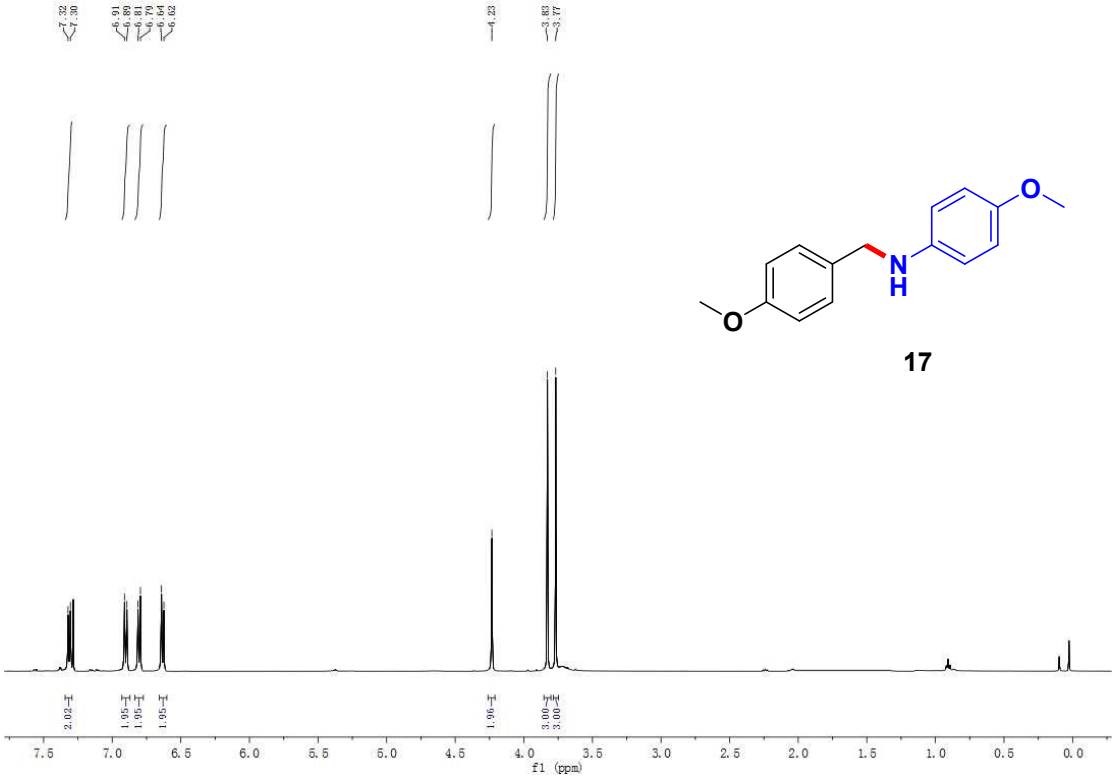


16





NMR Spectrum of Compound **17**



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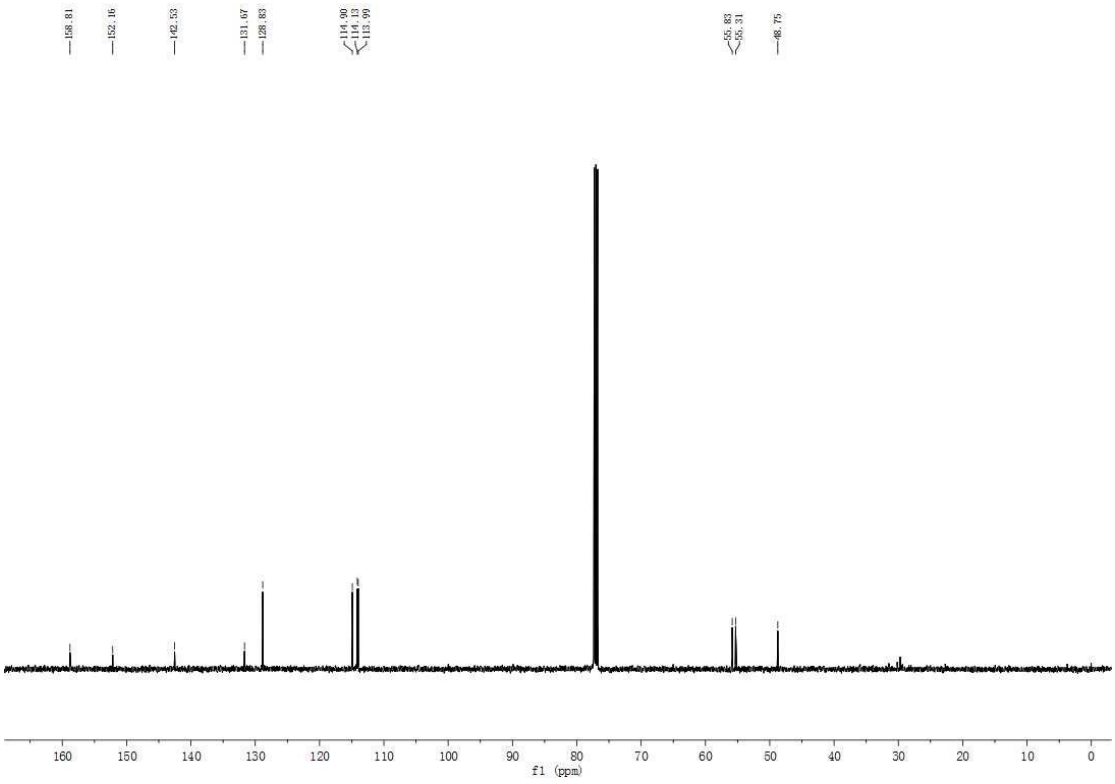
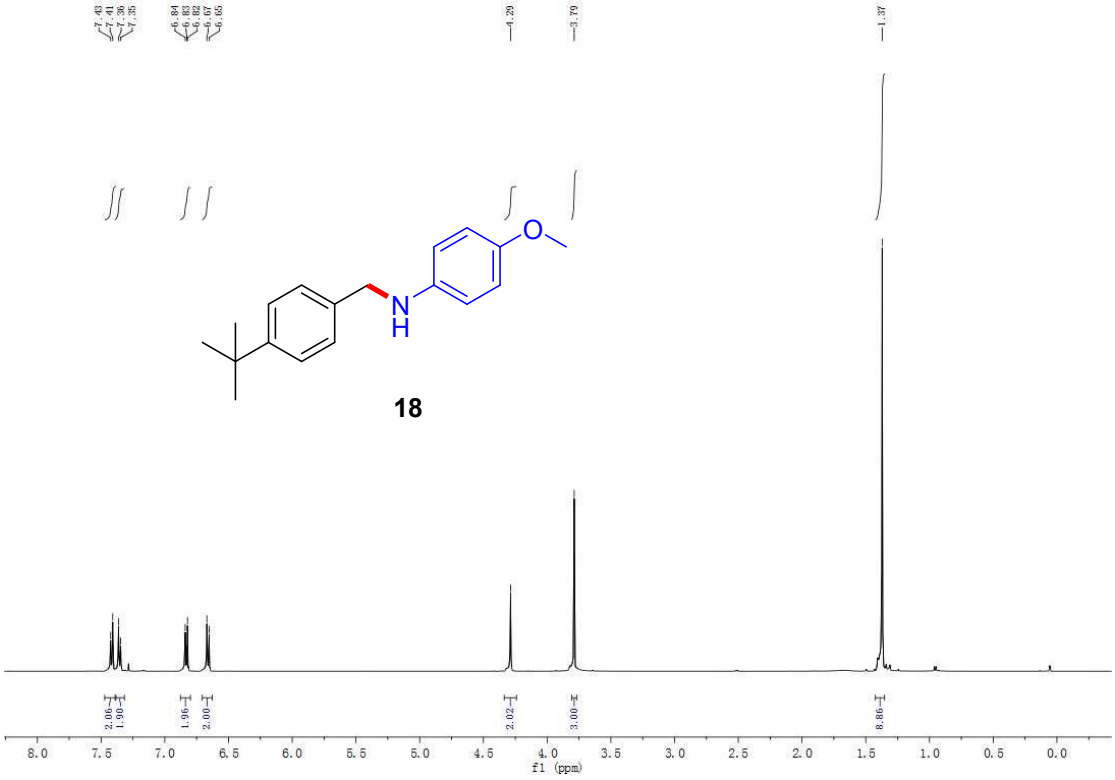


NMR Spectrum of Compound **18**



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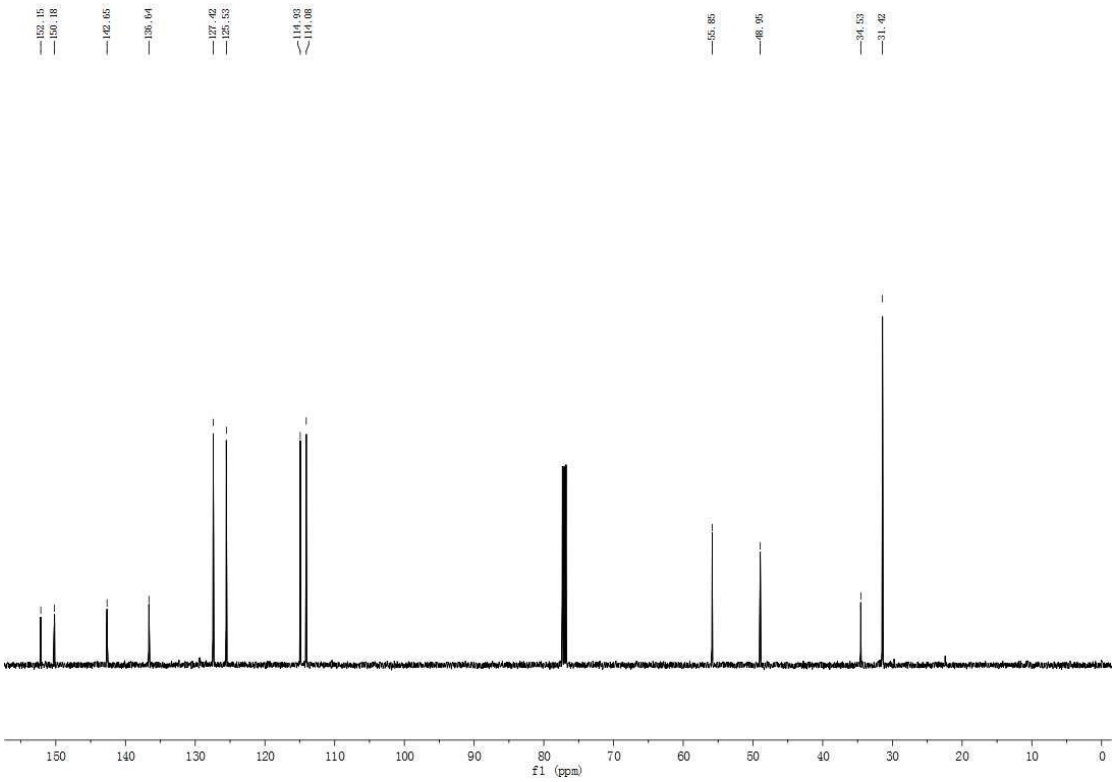
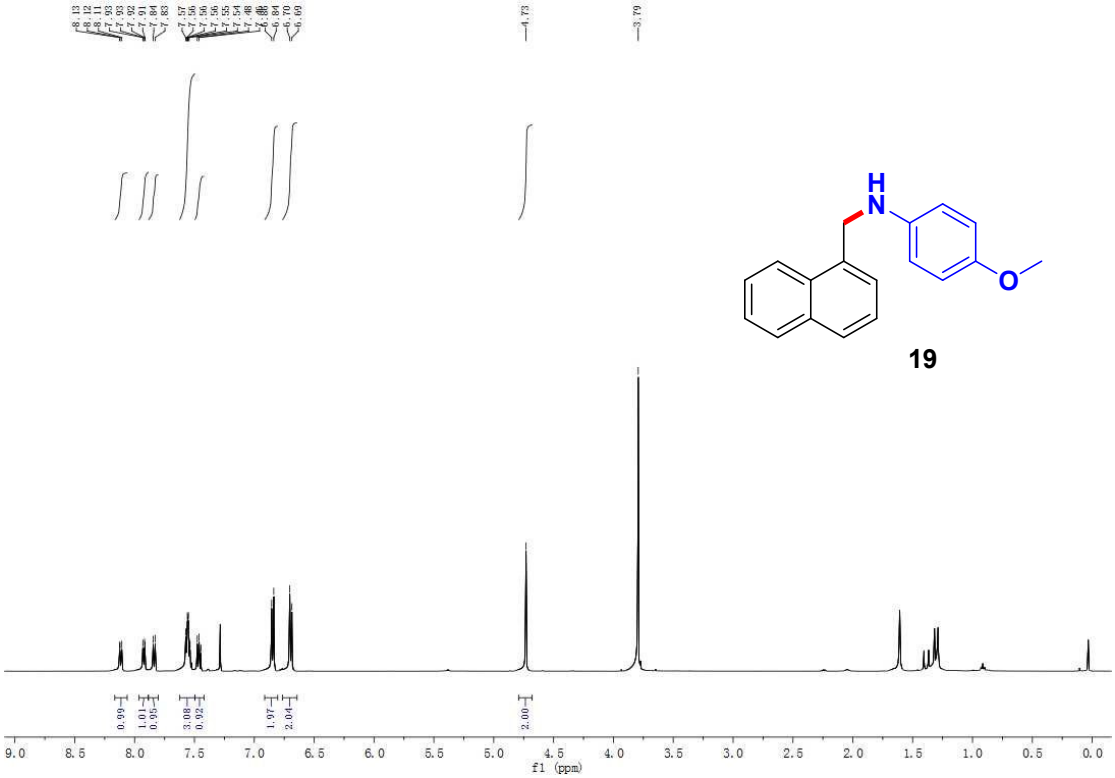
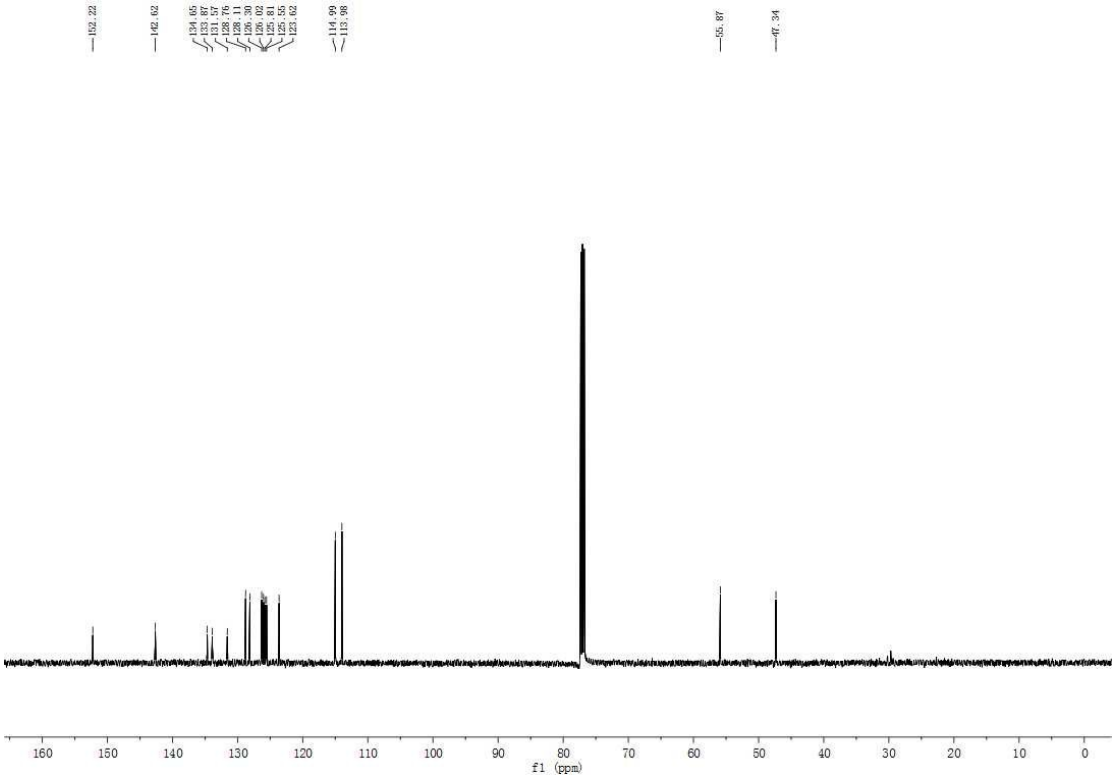
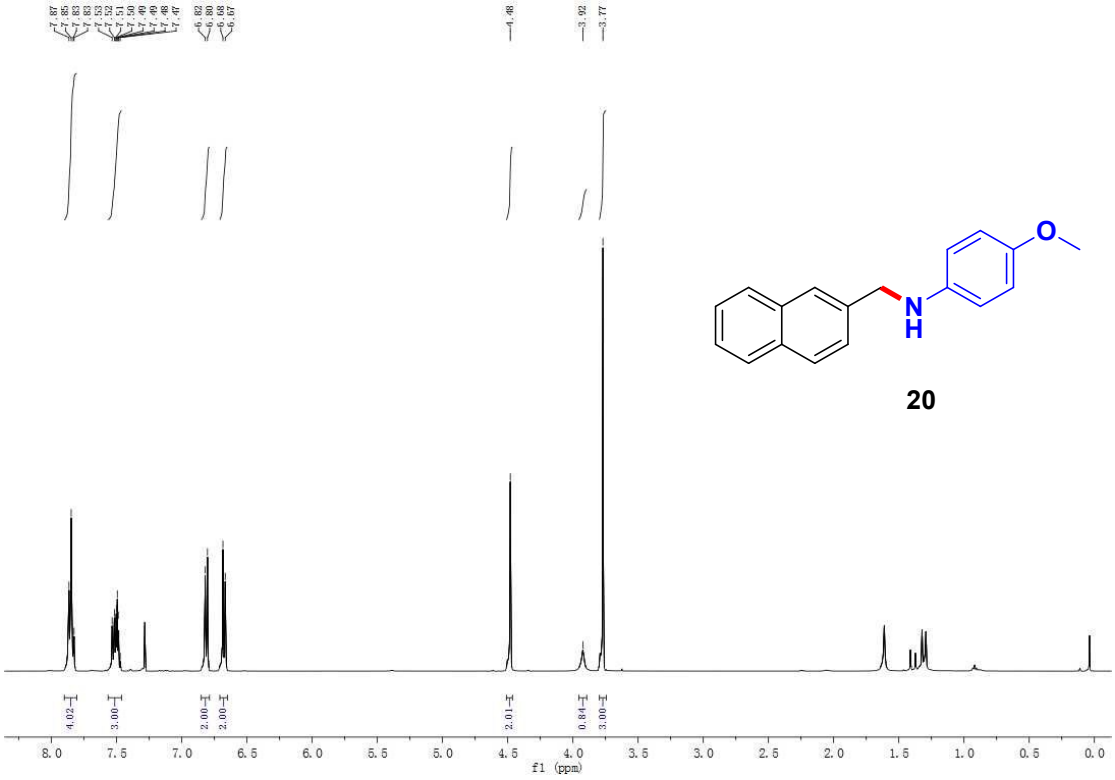


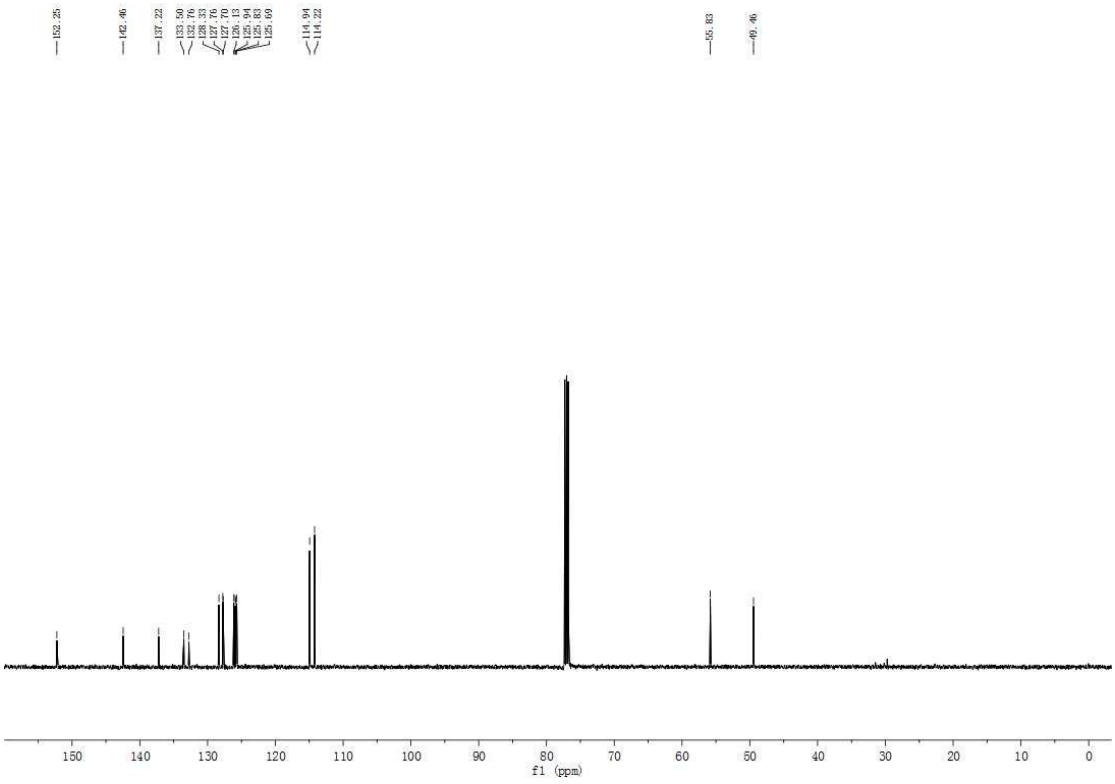
NMR Spectrum of Compound **19**



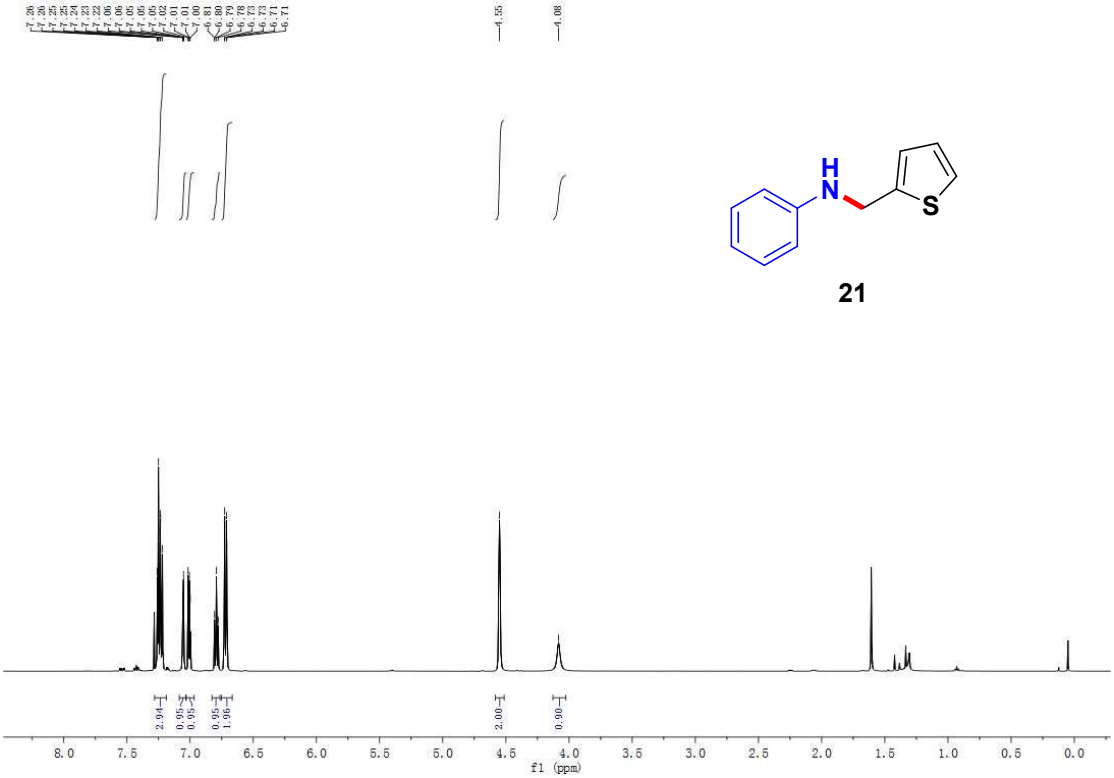


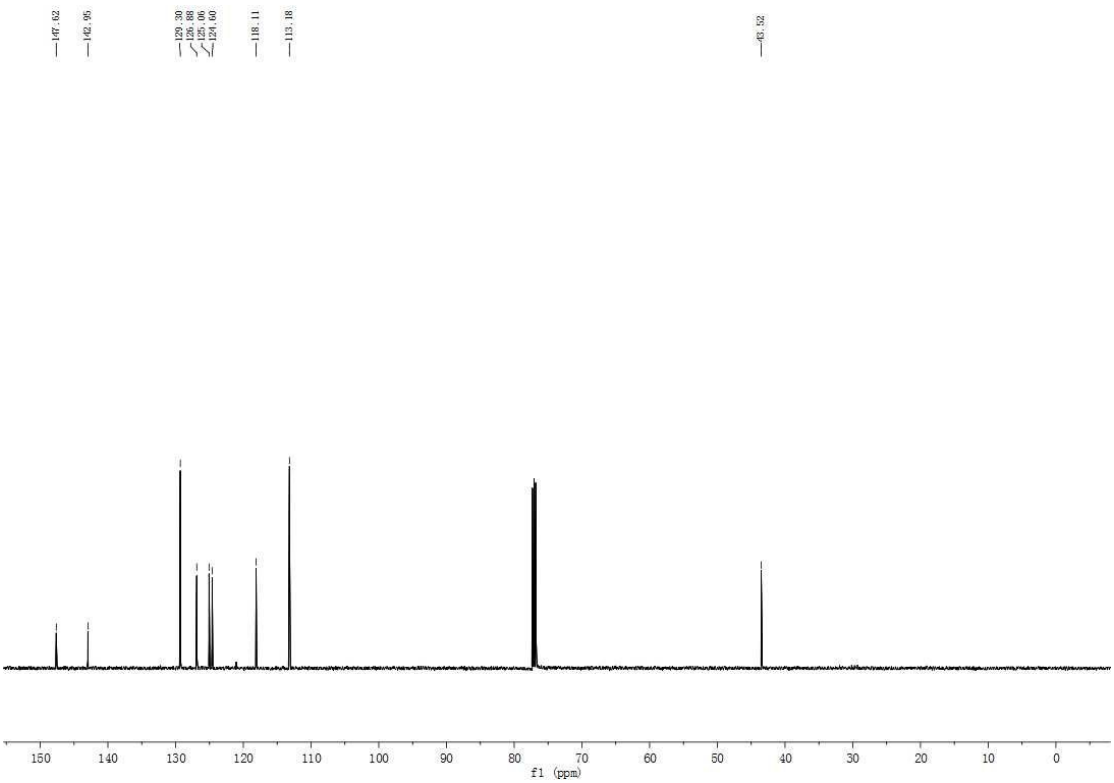
NMR Spectrum of Compound **20**



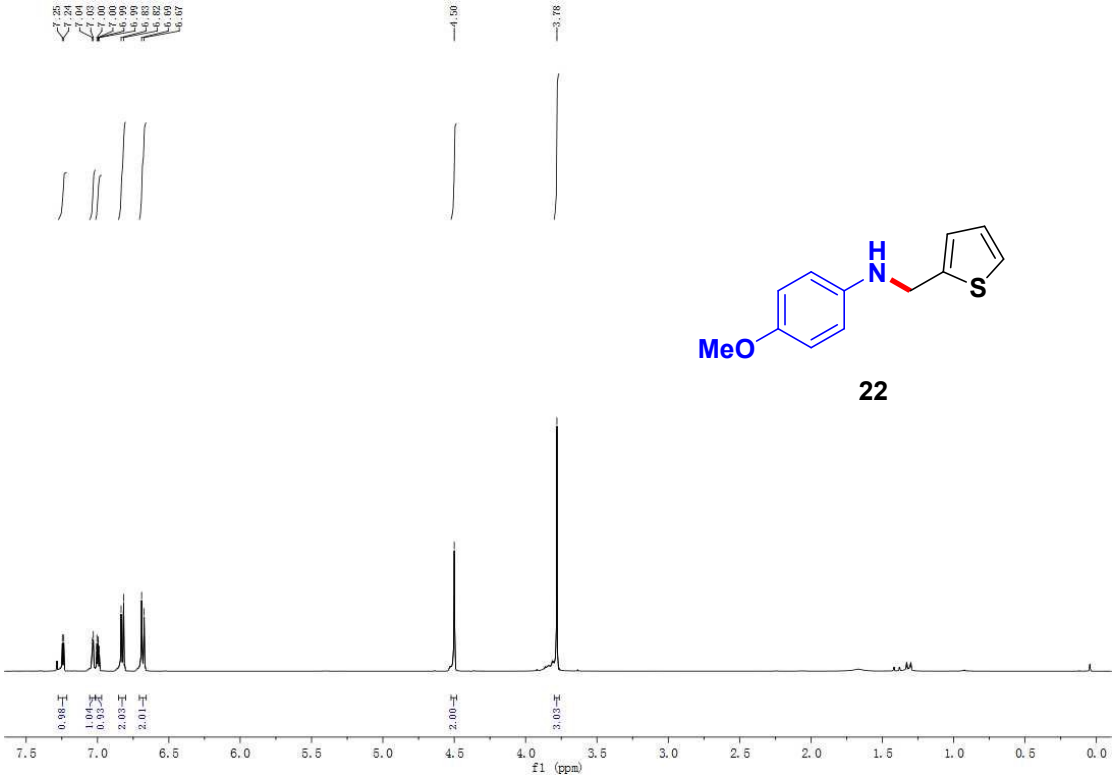


NMR Spectrum of Compound **21**

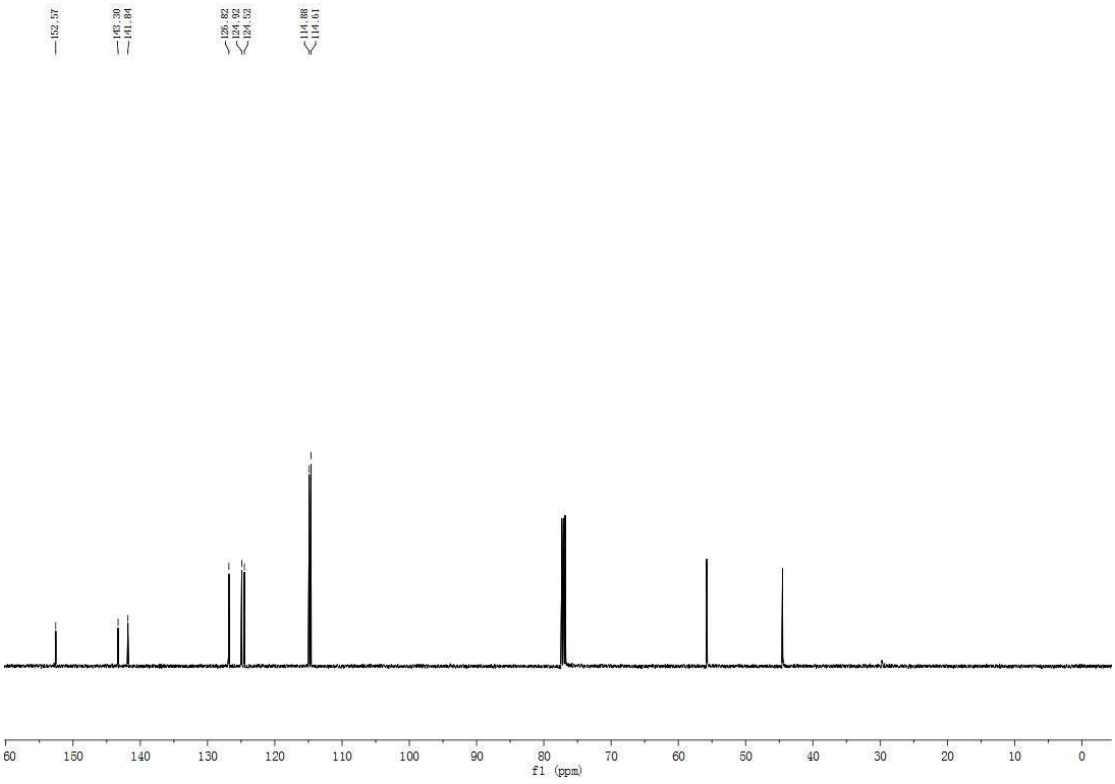




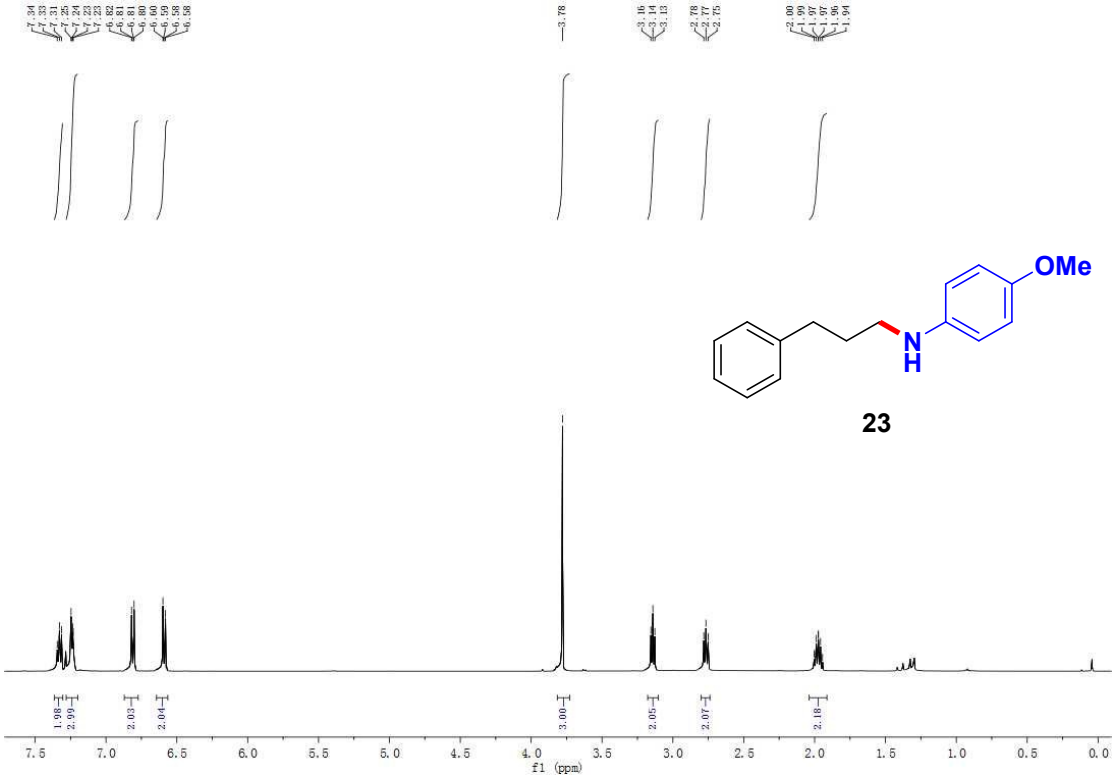
NMR Spectrum of Compound **22**

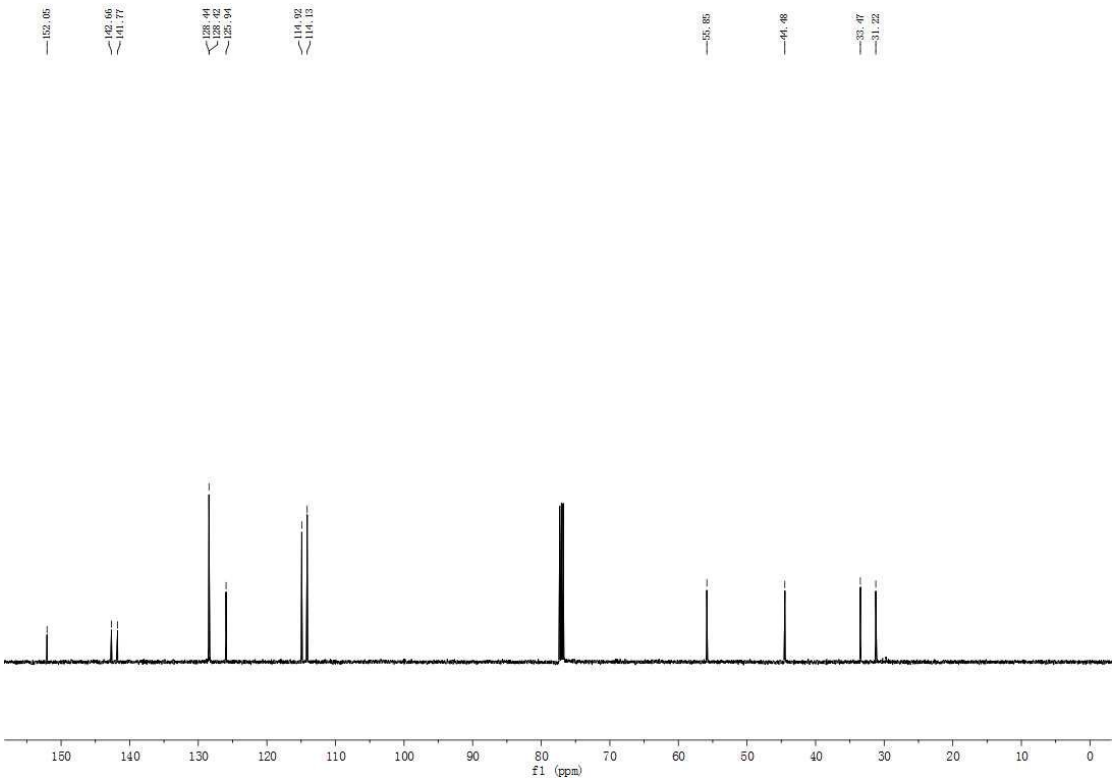


22

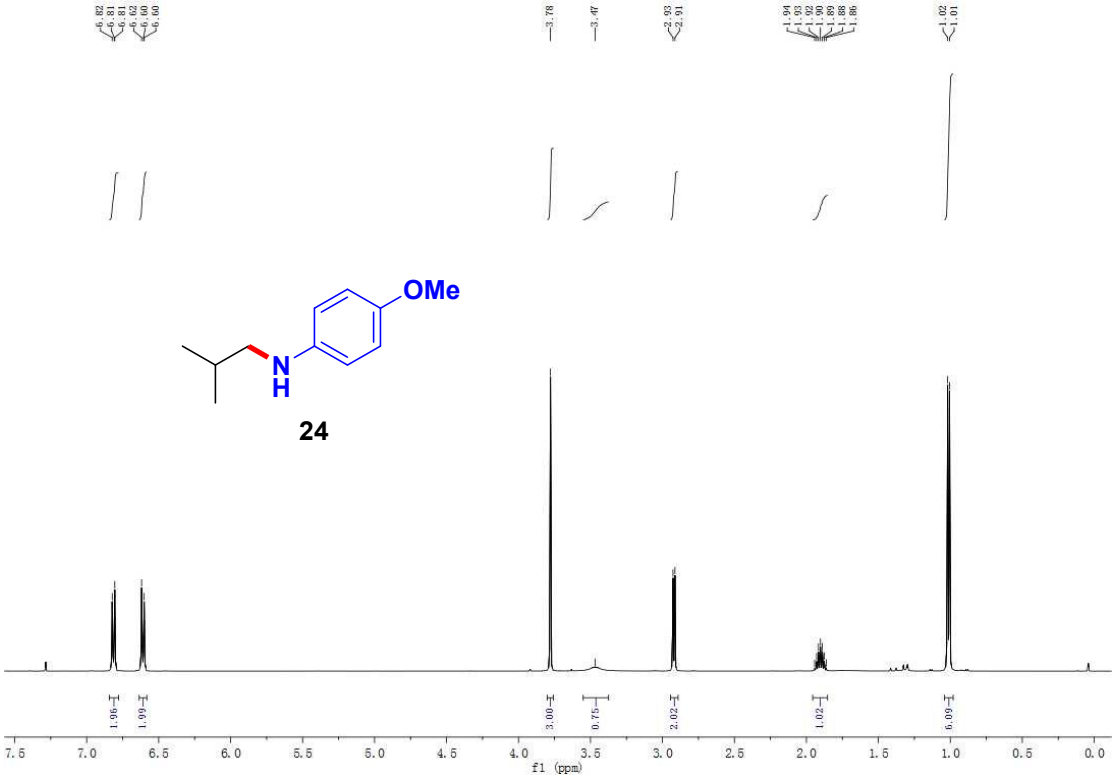


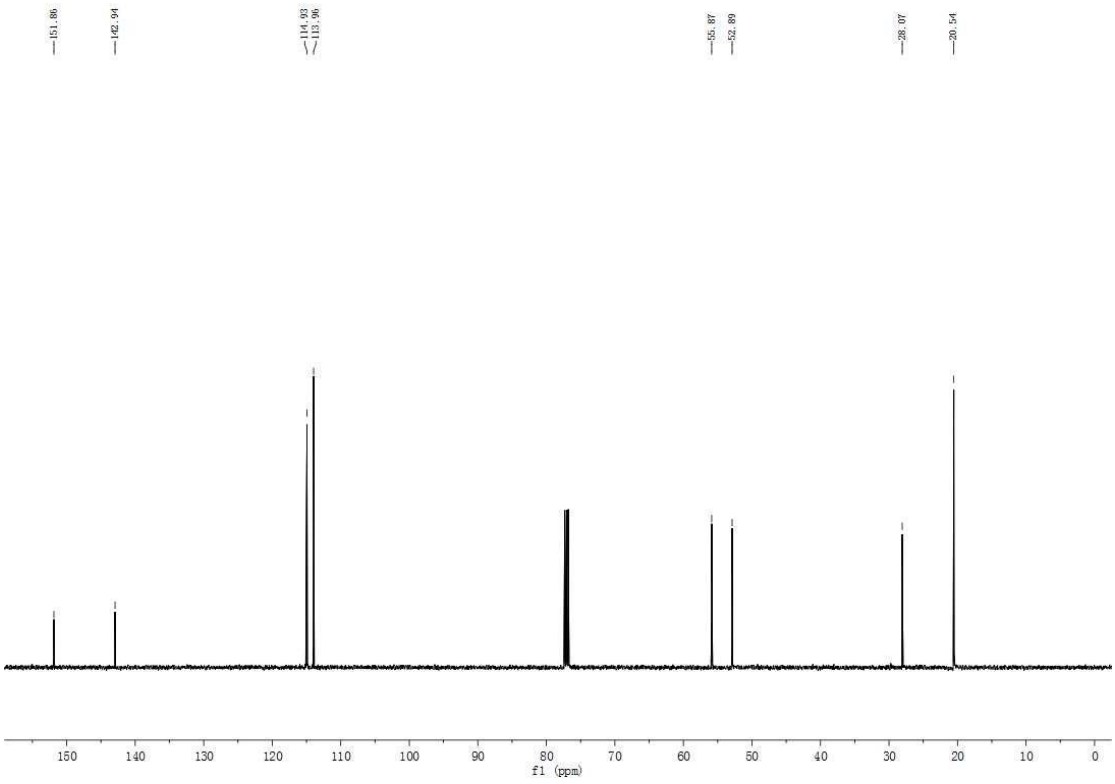
NMR Spectrum of Compound **23**



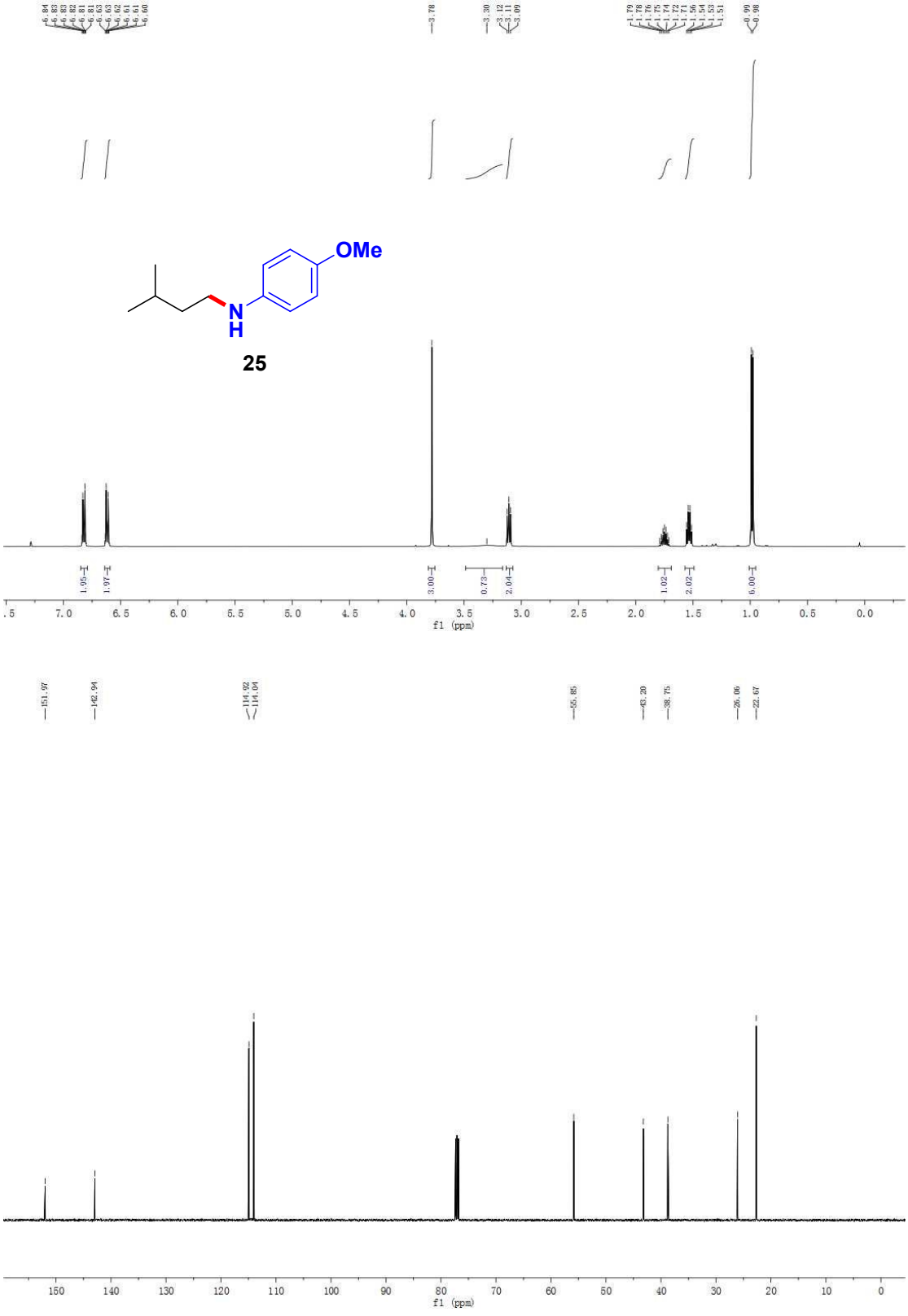


NMR Spectrum of Compound **24**

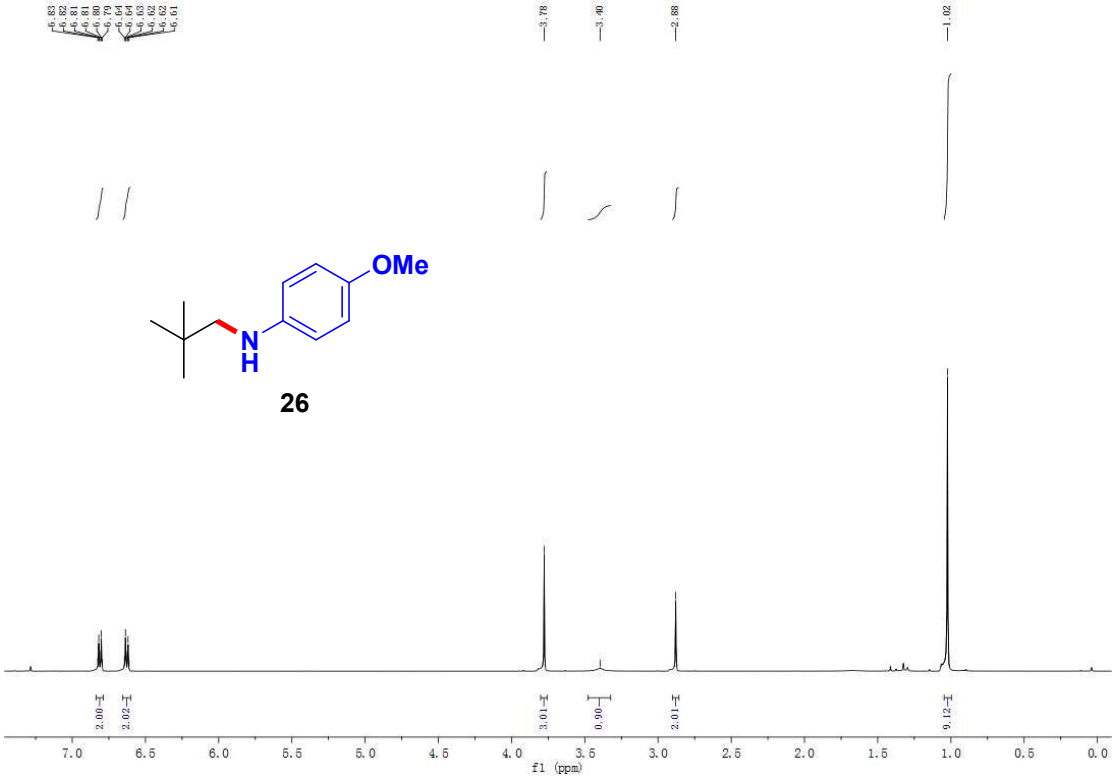


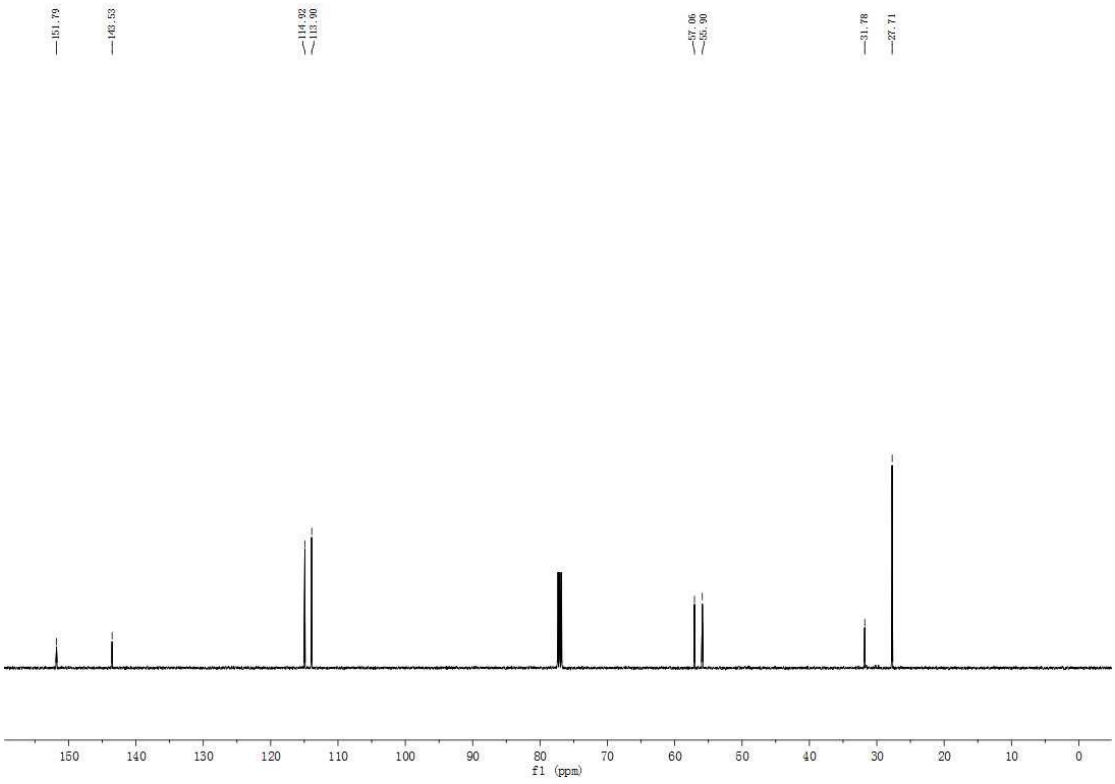


NMR Spectrum of Compound **25**

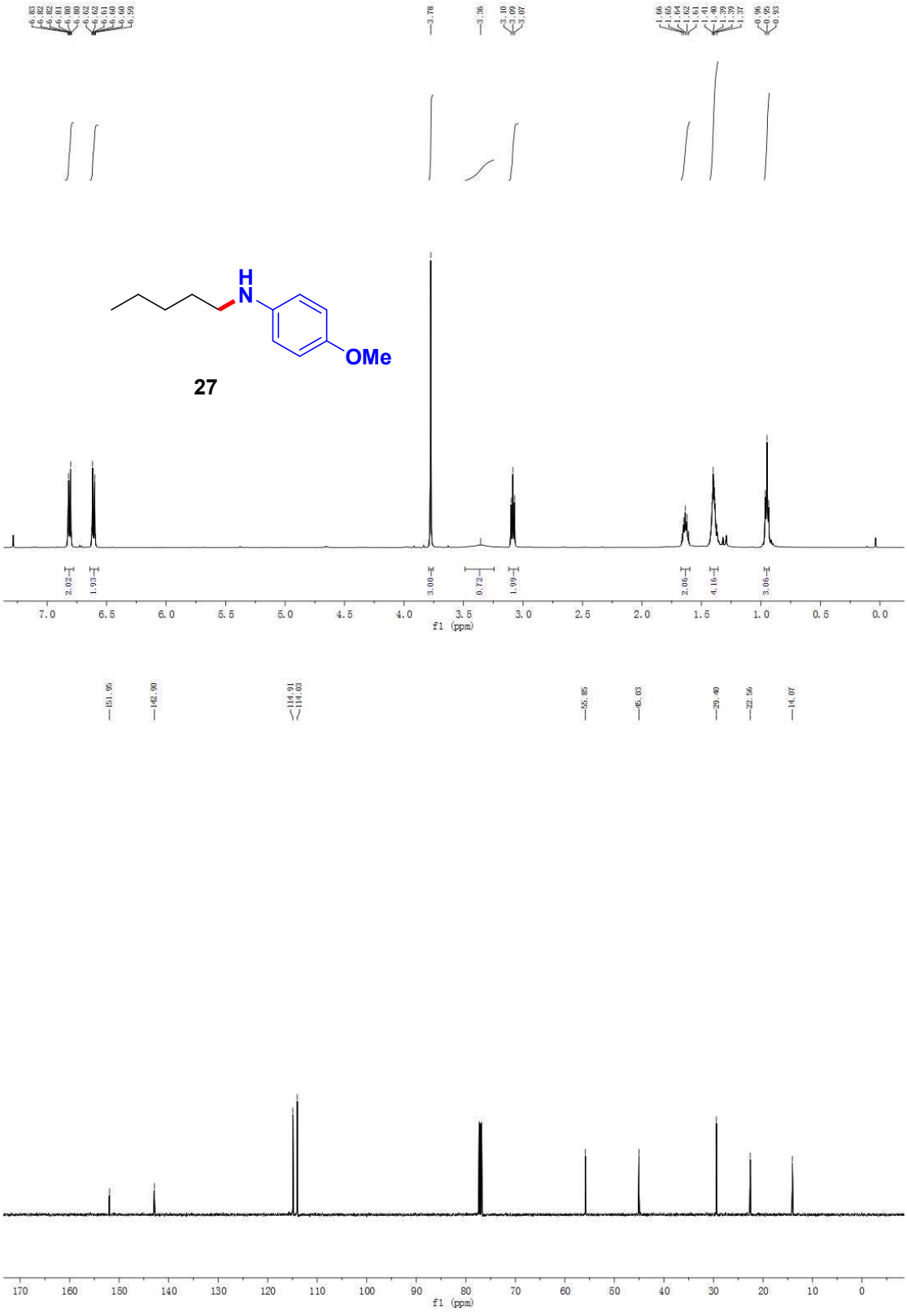


NMR Spectrum of Compound **26**

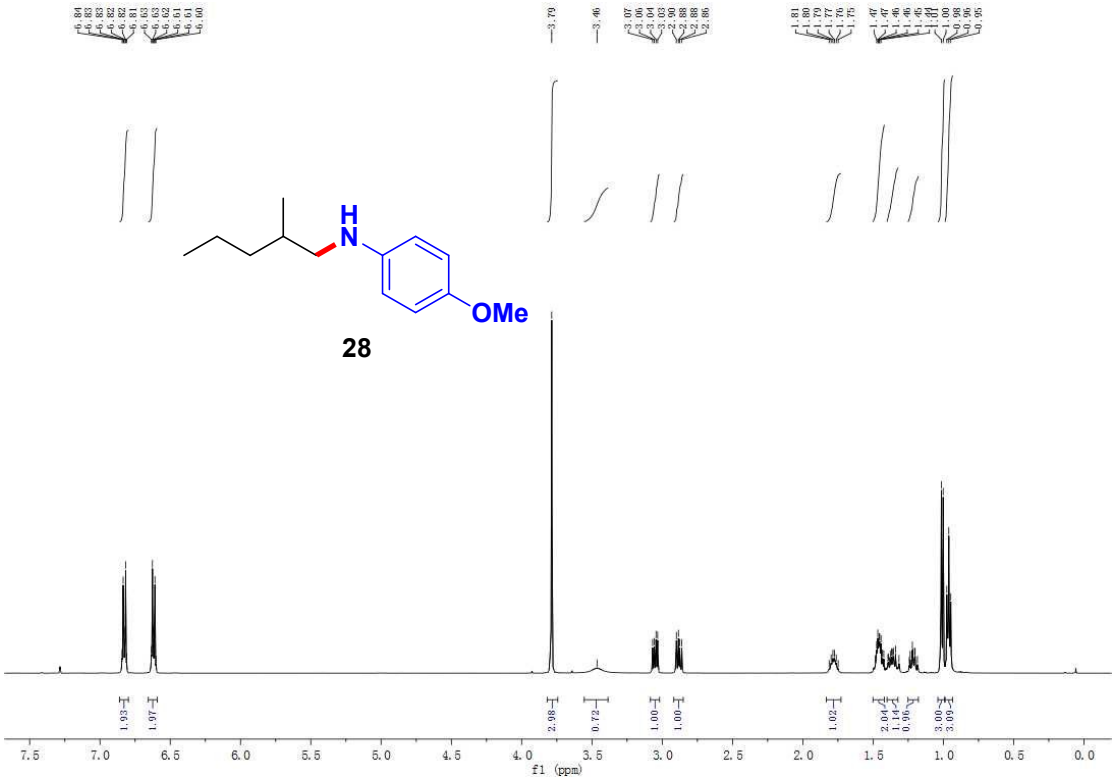


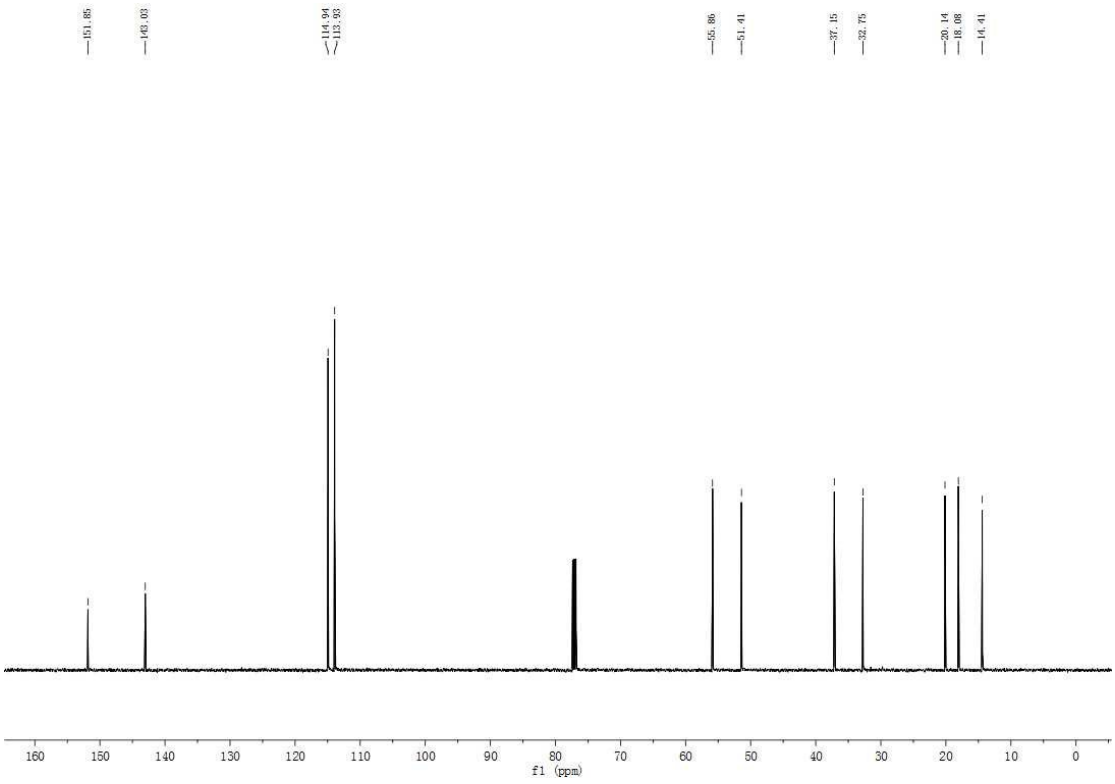


NMR Spectrum of Compound **27**

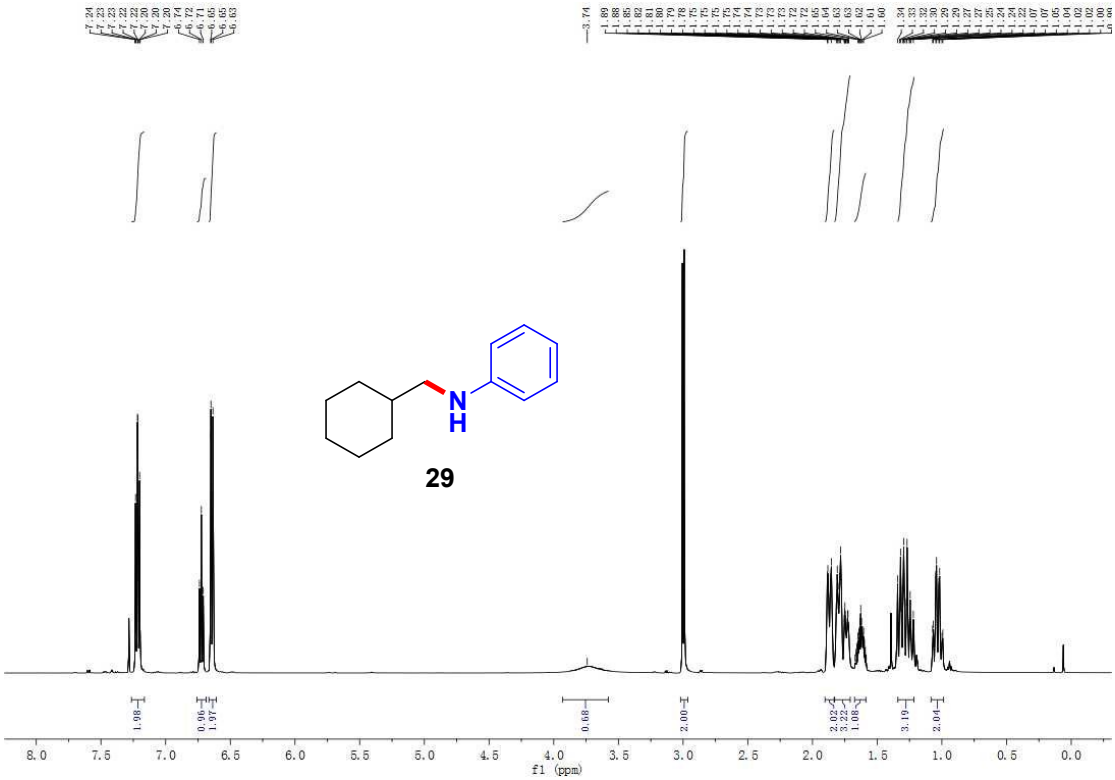


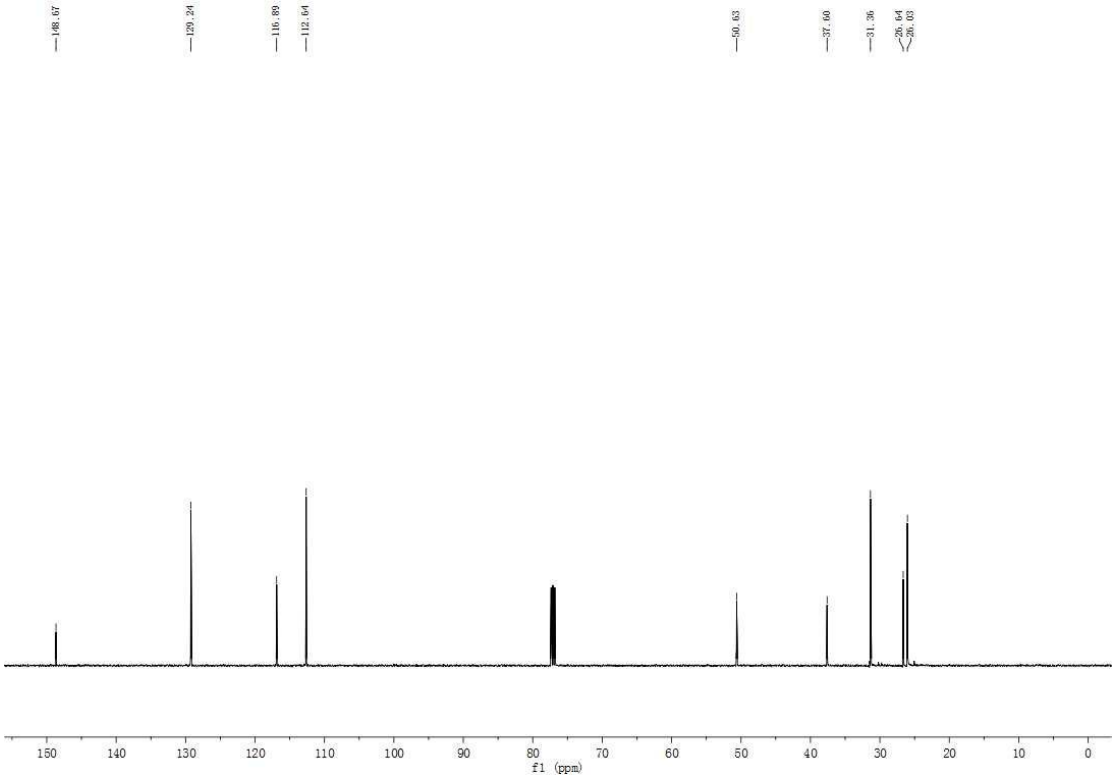
NMR Spectrum of Compound **28**



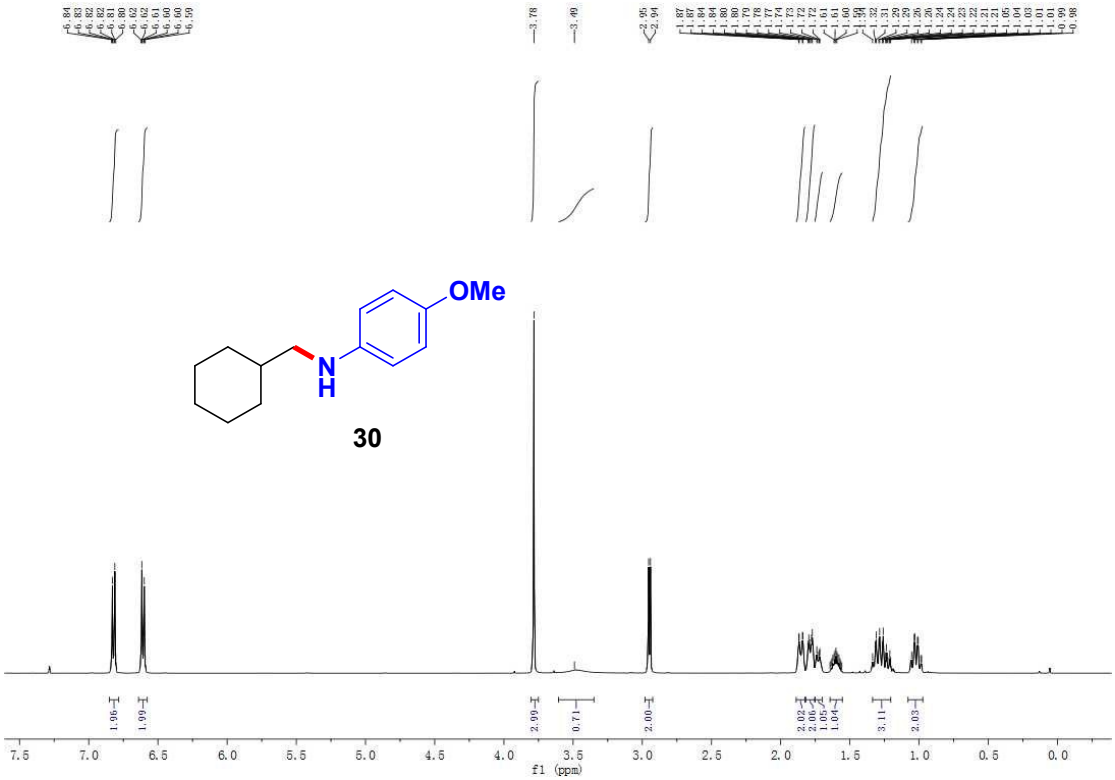


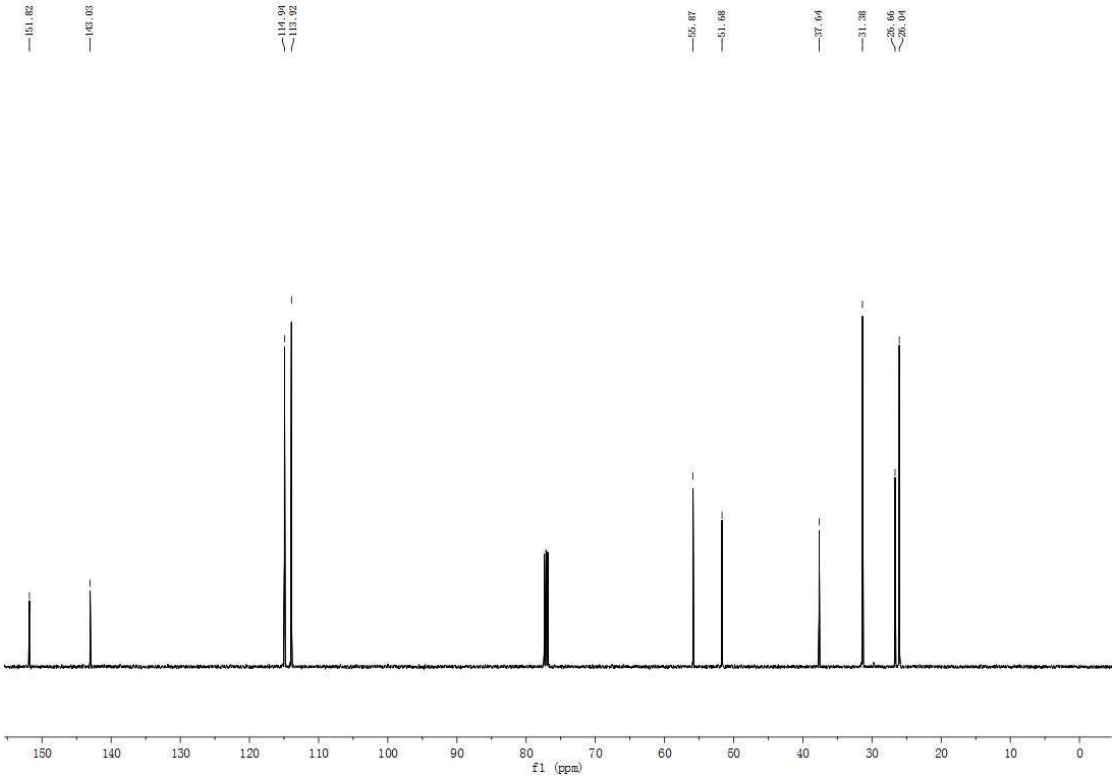
NMR Spectrum of Compound **29**



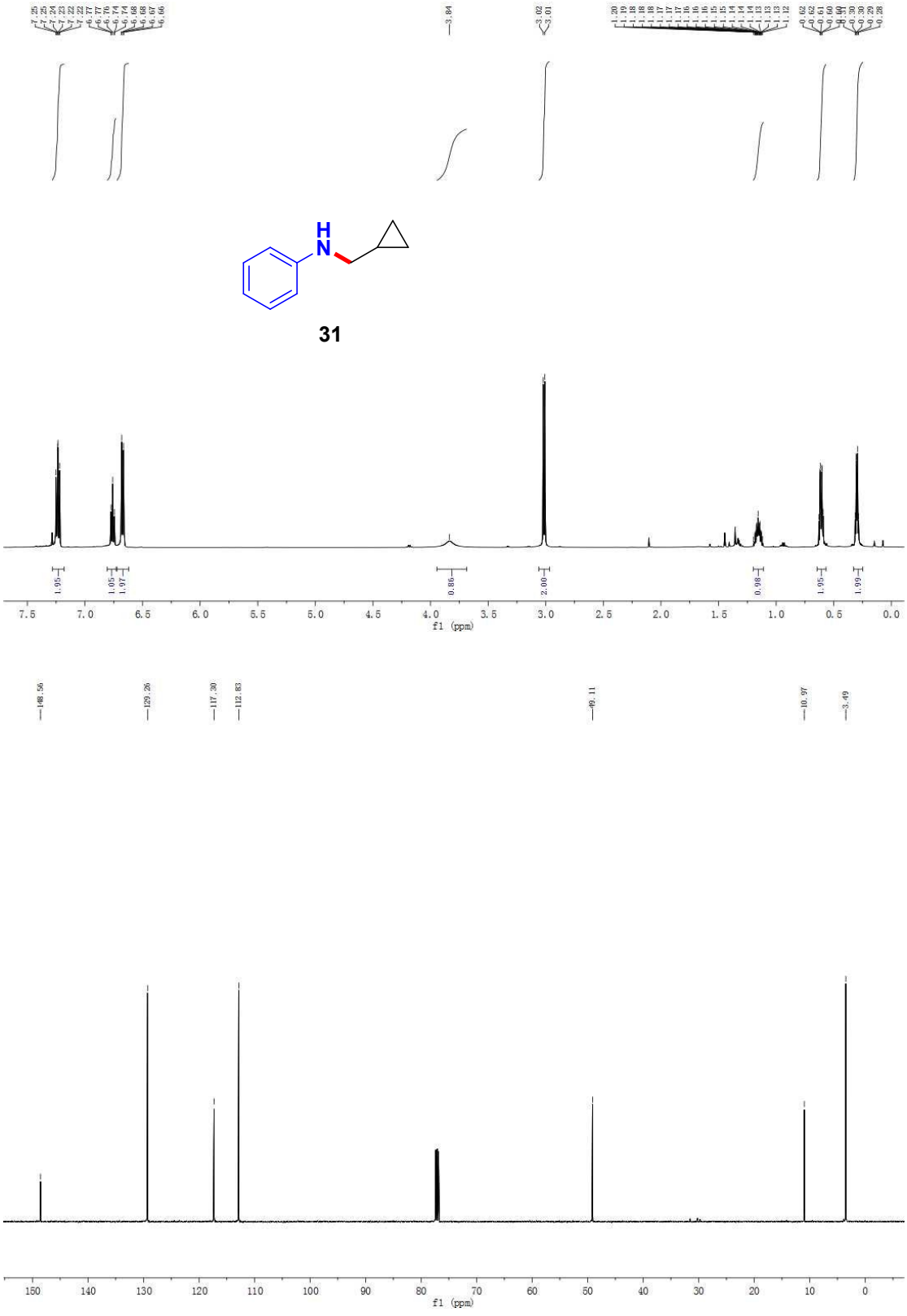


NMR Spectrum of Compound **30**

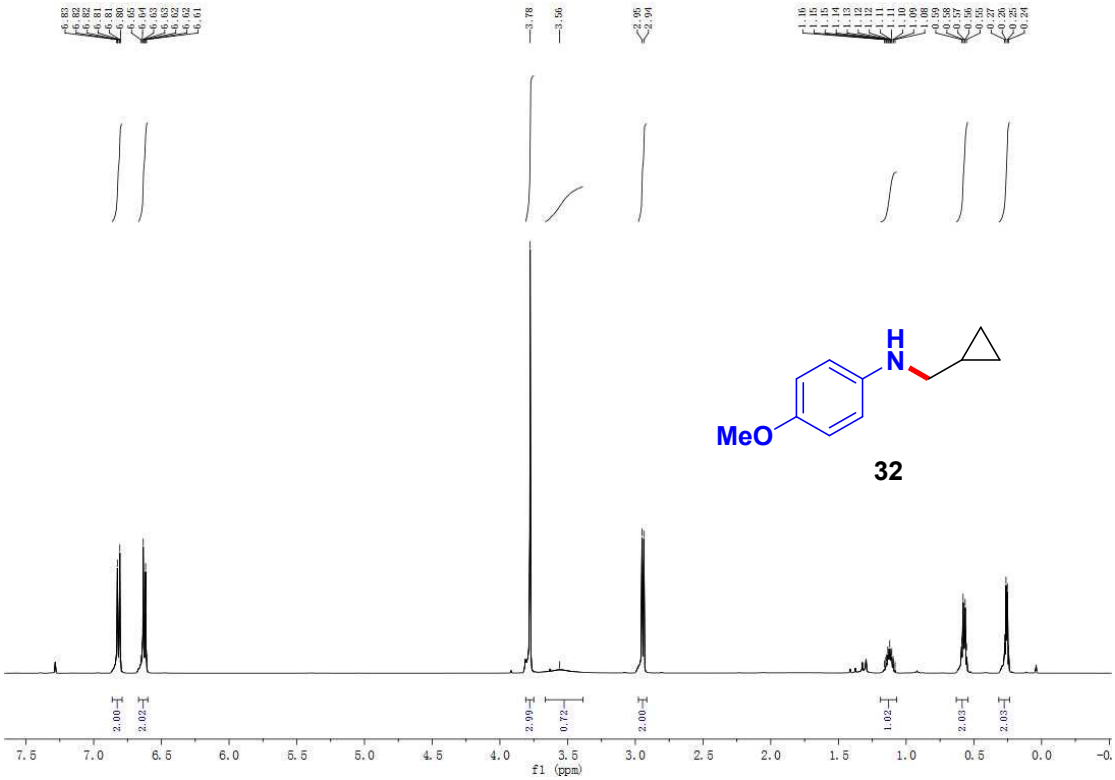


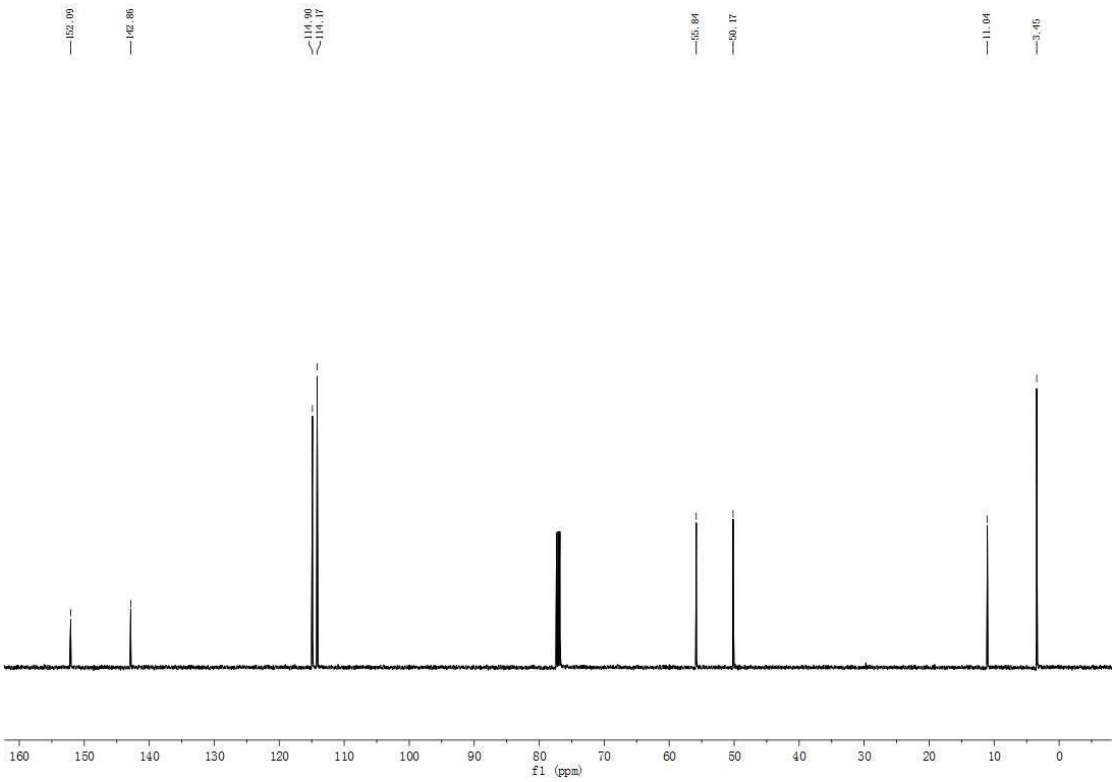


NMR Spectrum of Compound **31**

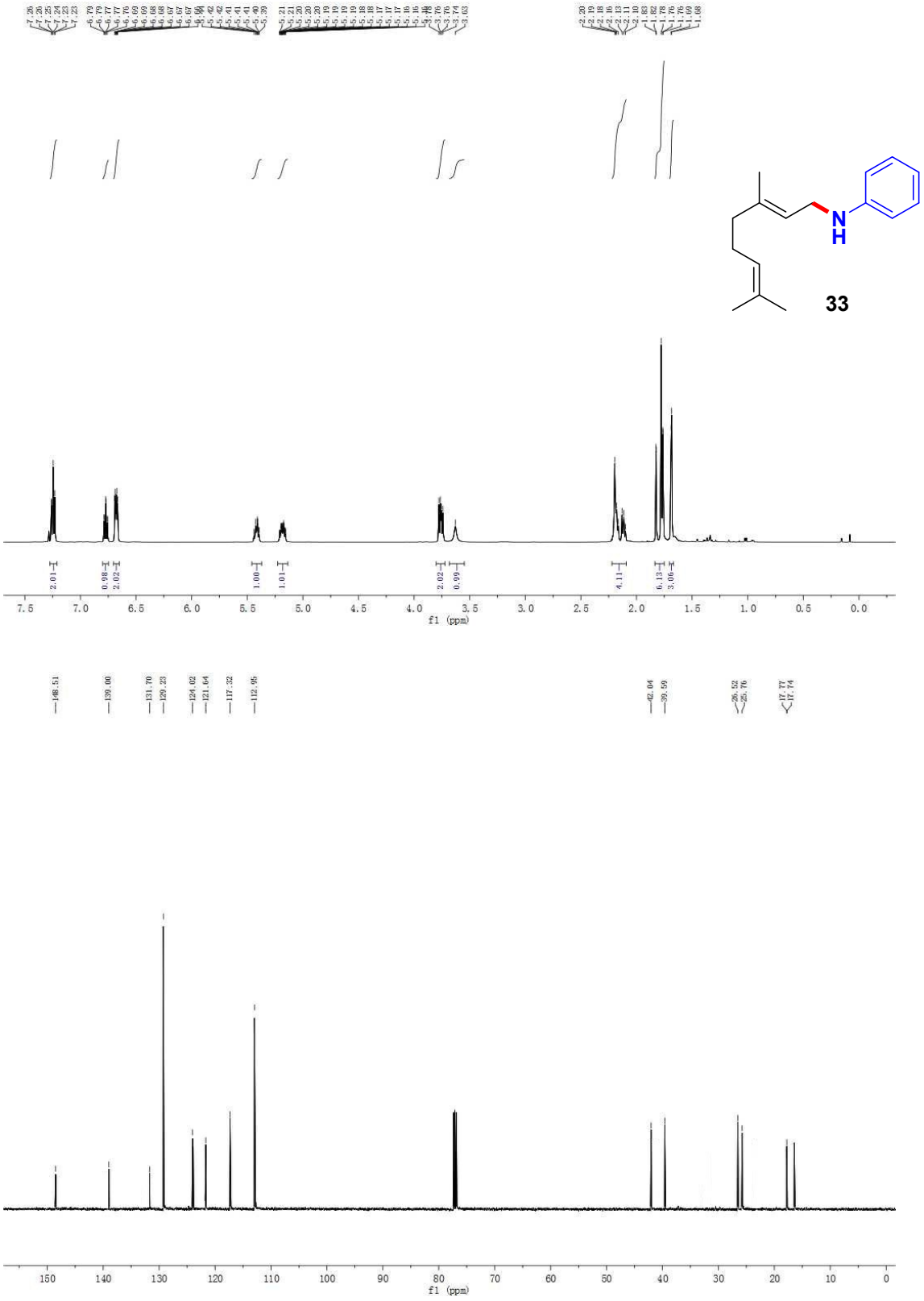


NMR Spectrum of Compound **32**

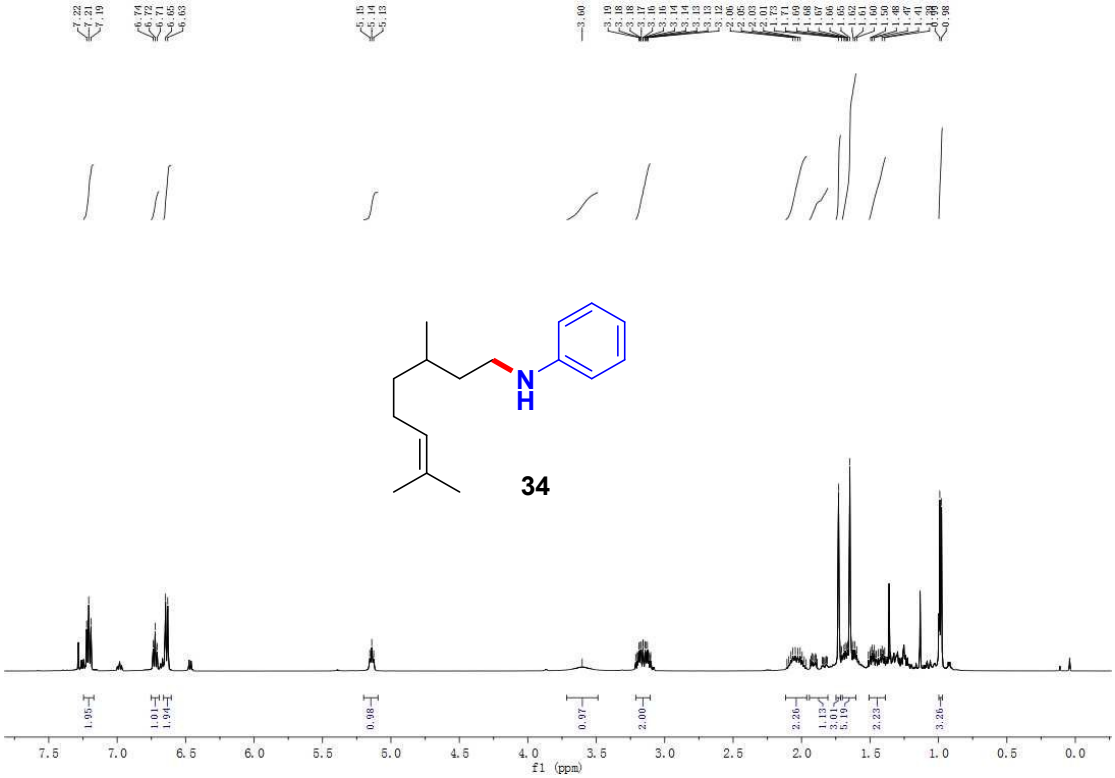


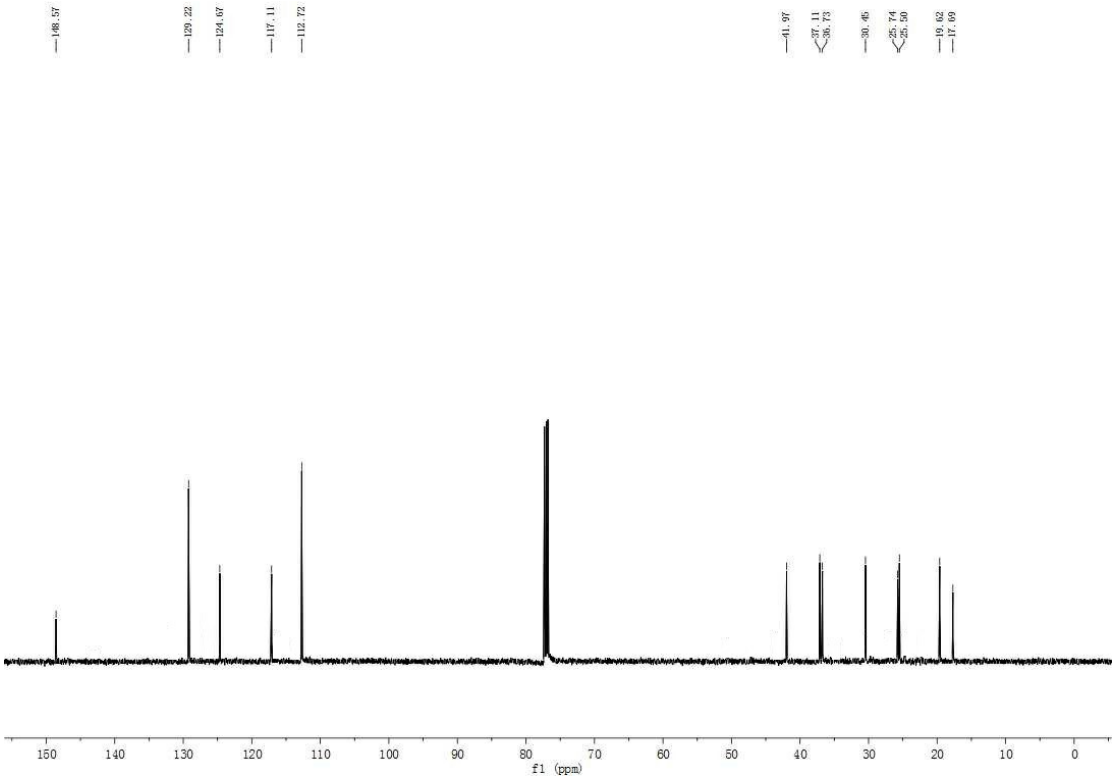


NMR Spectrum of Compound **33**

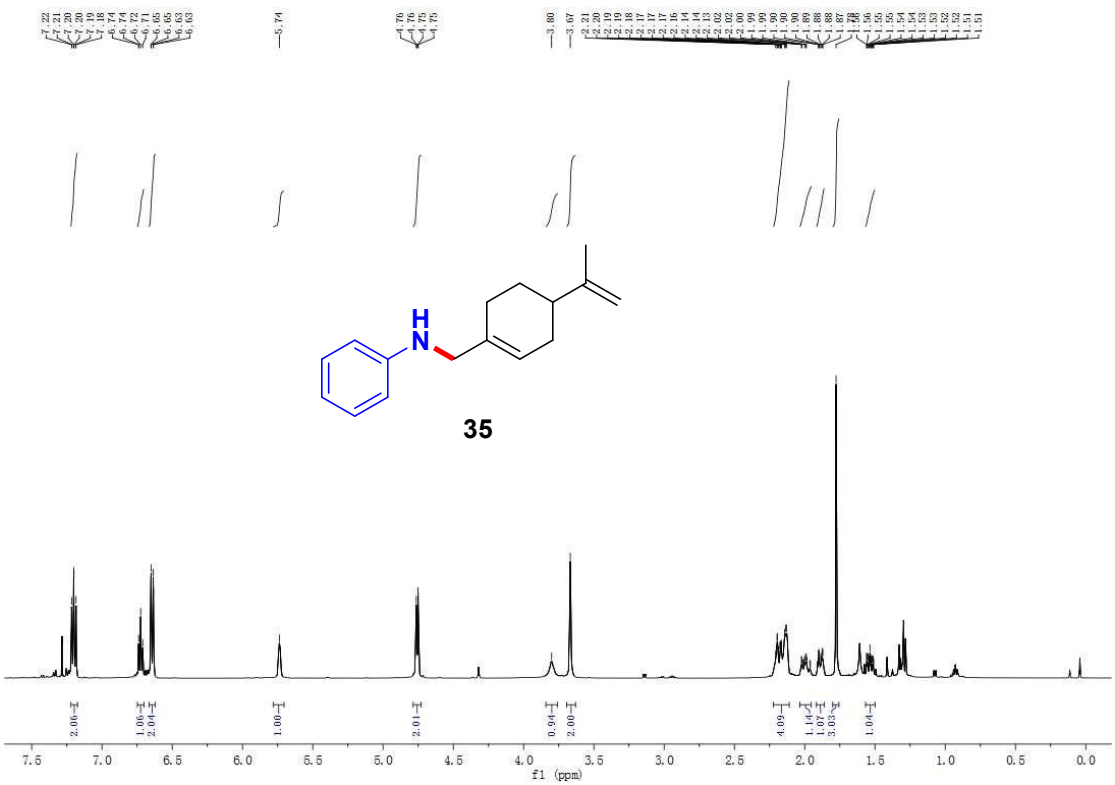


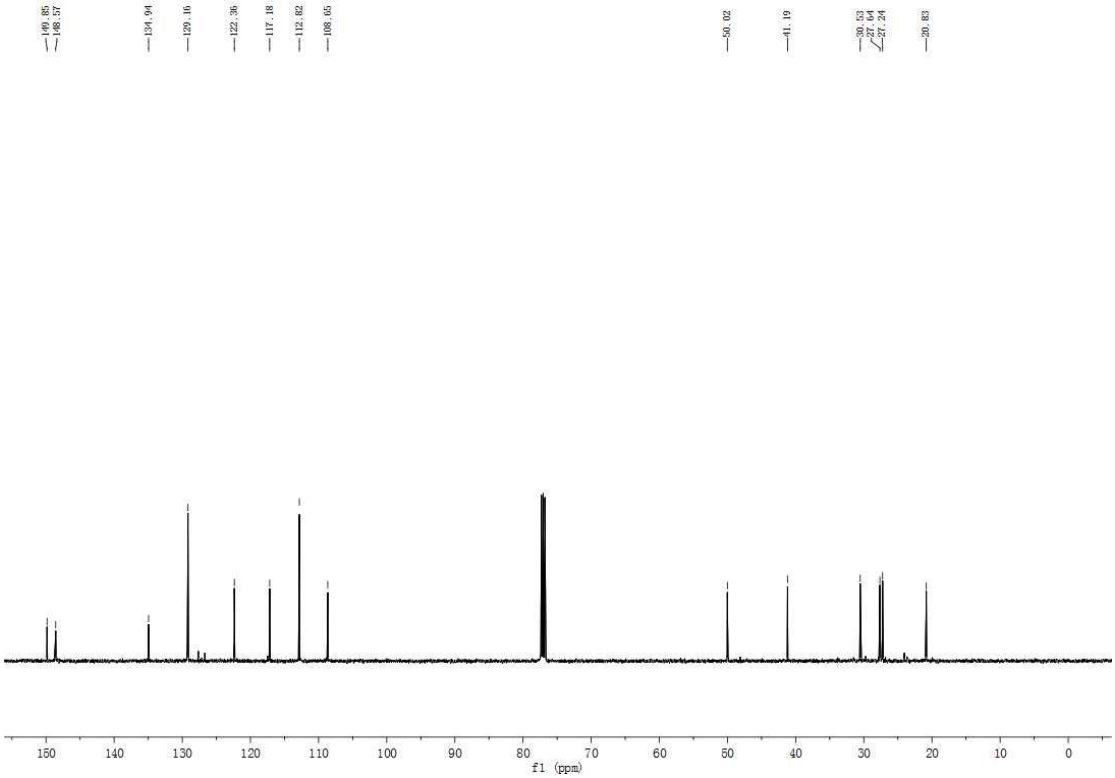
NMR Spectrum of Compound **34**



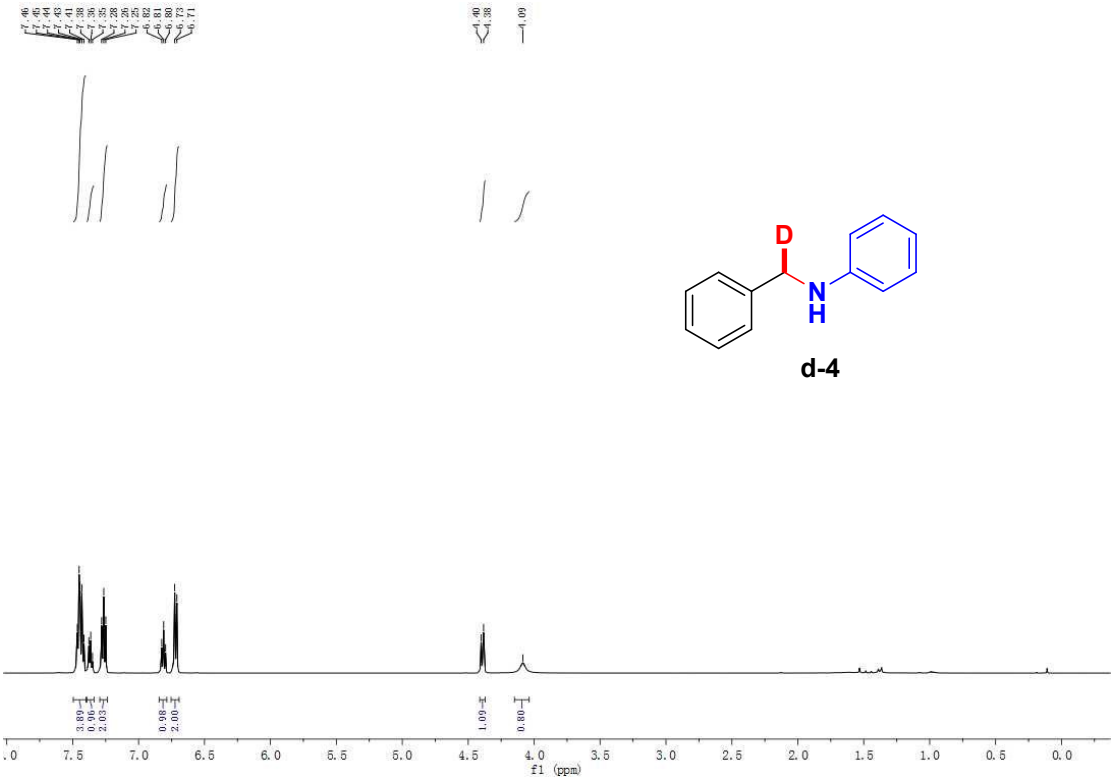


NMR Spectrum of Compound **35**

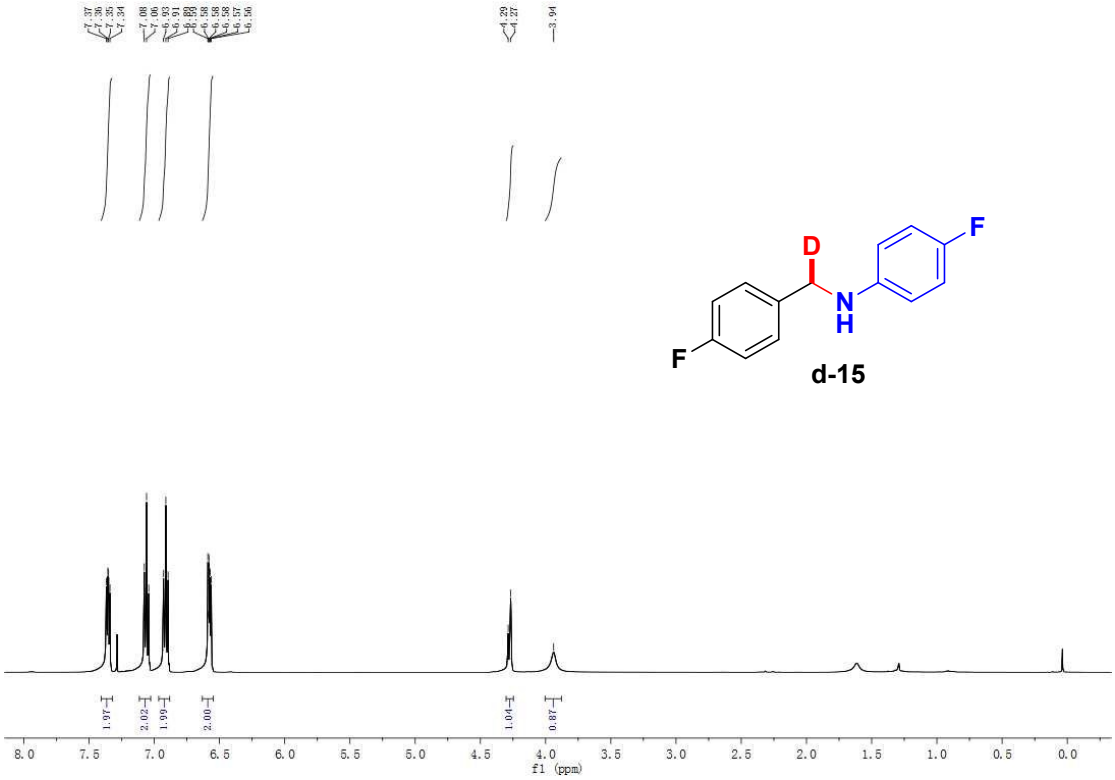




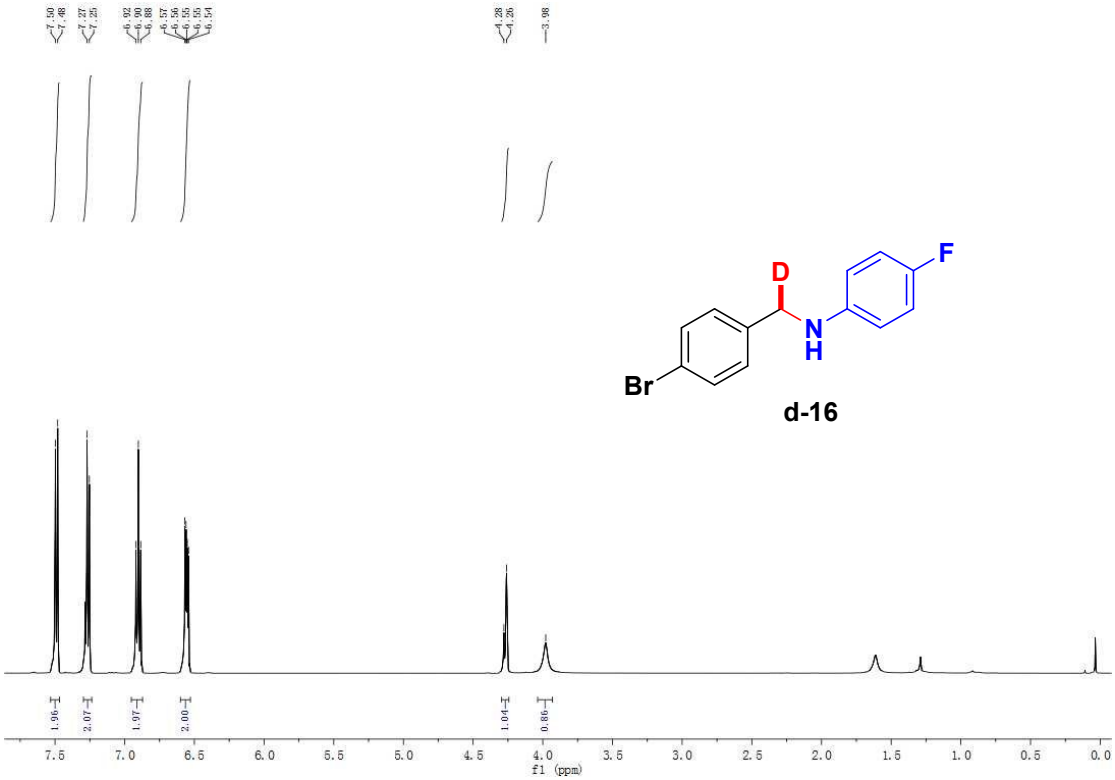
NMR Spectrum of Compound d-**4**



NMR Spectrum of Compound d-**15**

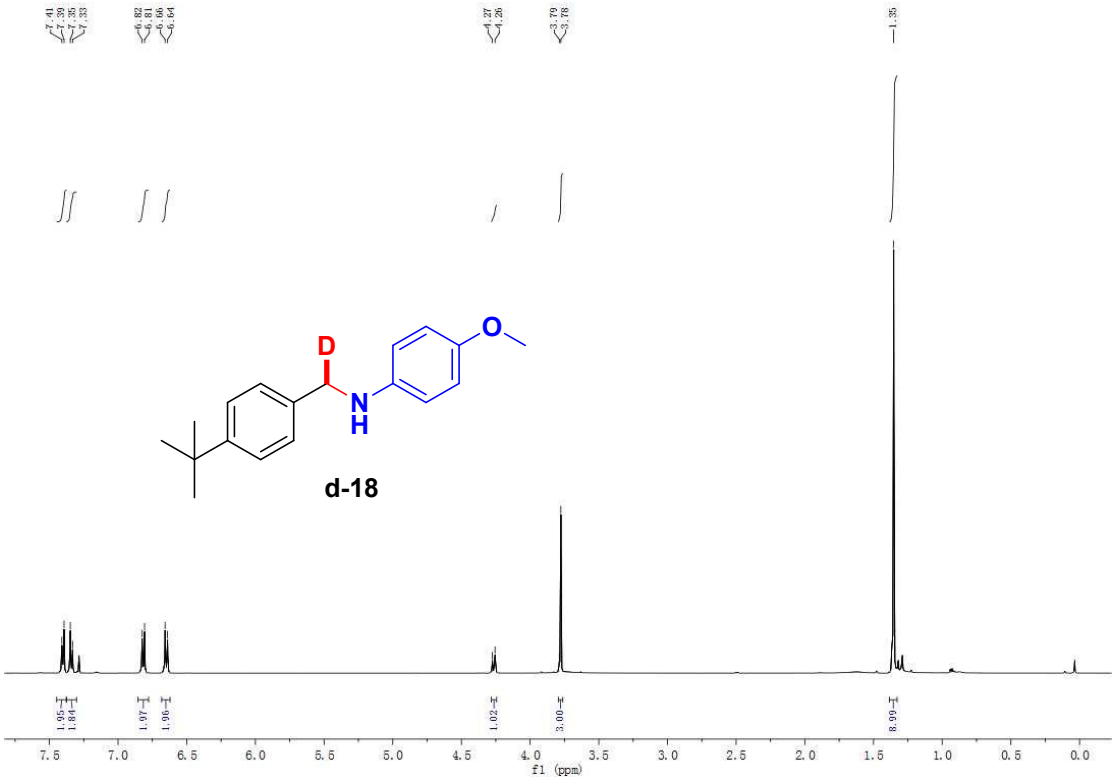


NMR Spectrum of Compound d-**16**

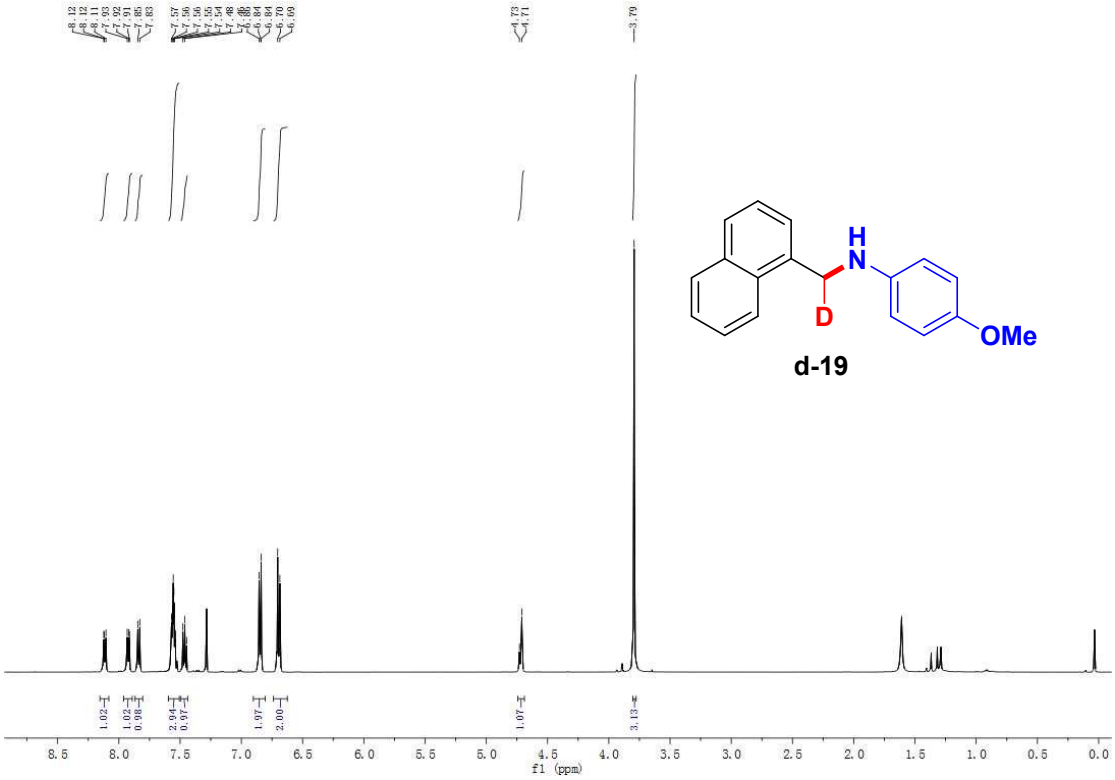


NMR Spectrum of Compound d-**17**

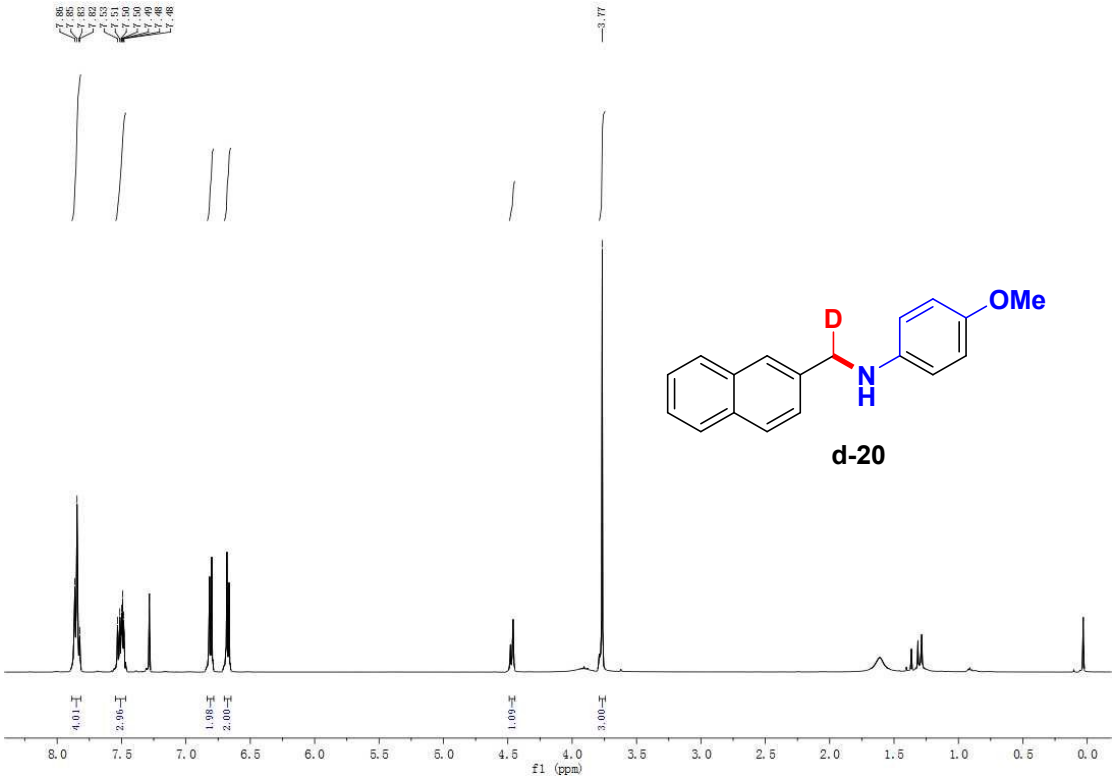
NMR Spectrum of Compound d-**18**



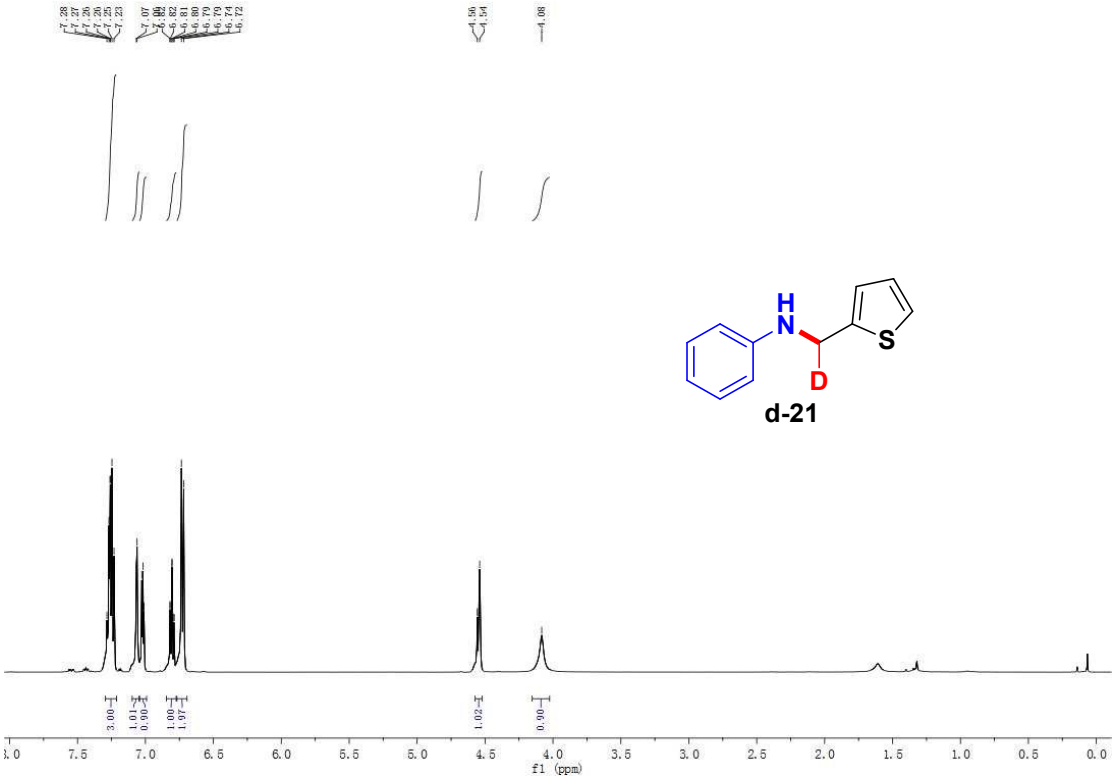
NMR Spectrum of Compound d-**19**



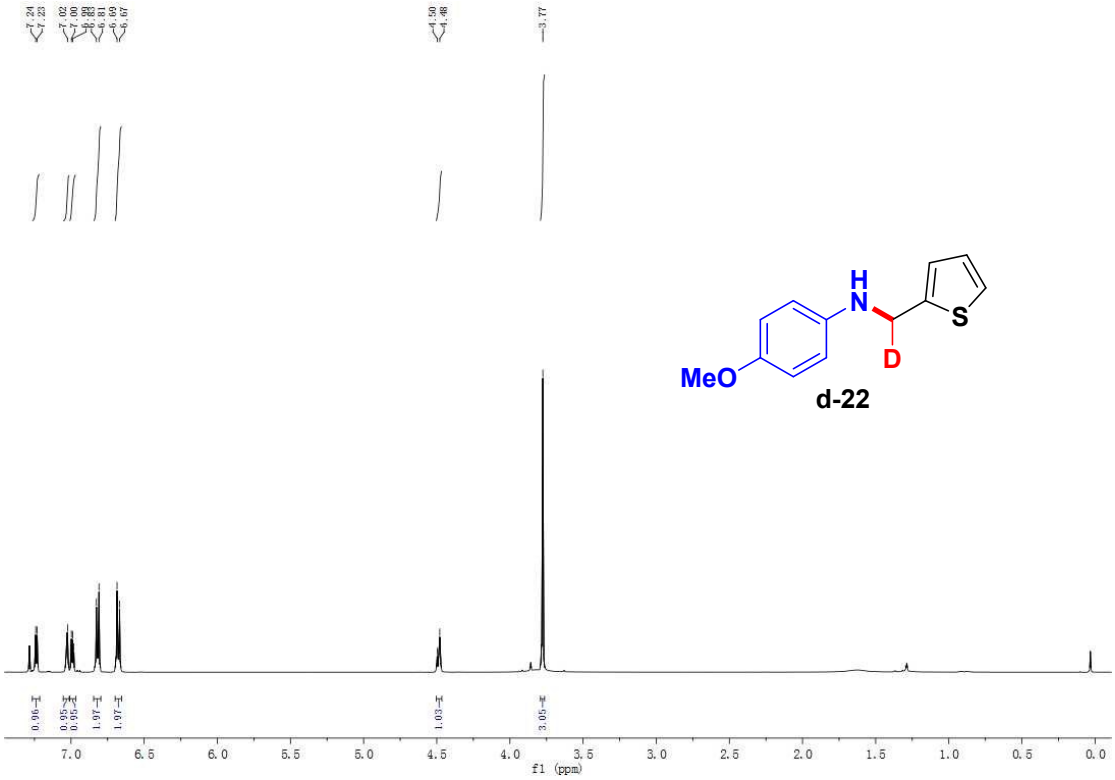
NMR Spectrum of Compound d-**20**



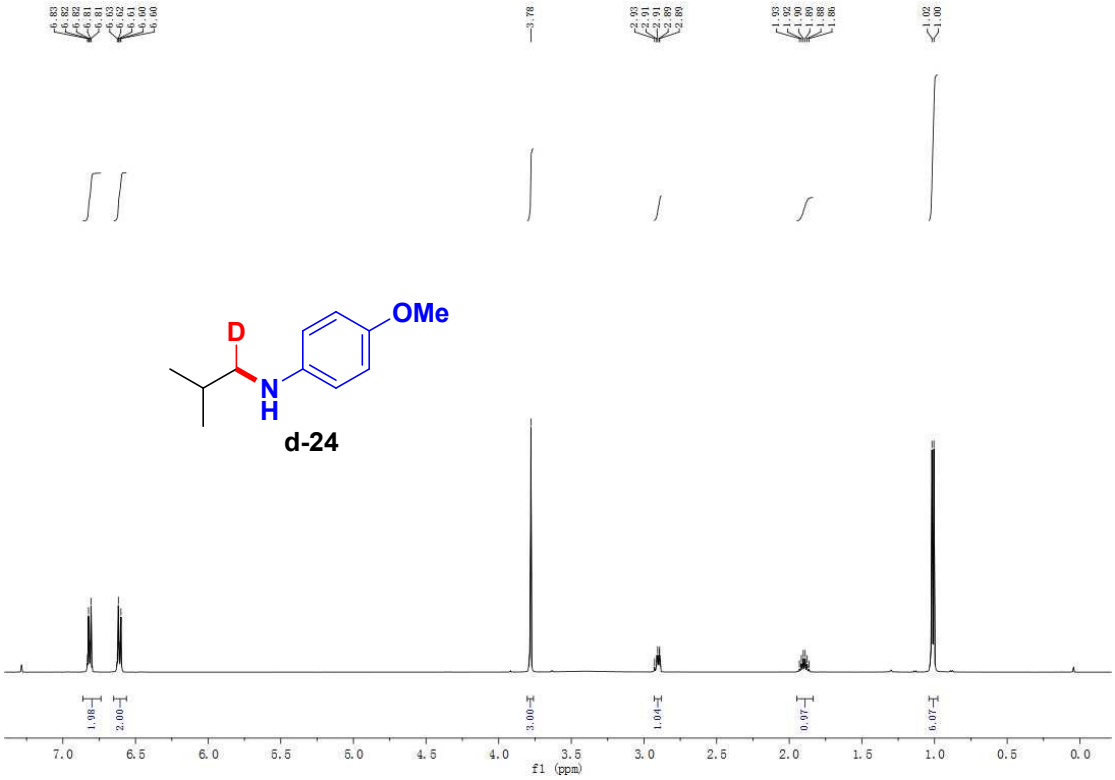
NMR Spectrum of Compound d-**21**



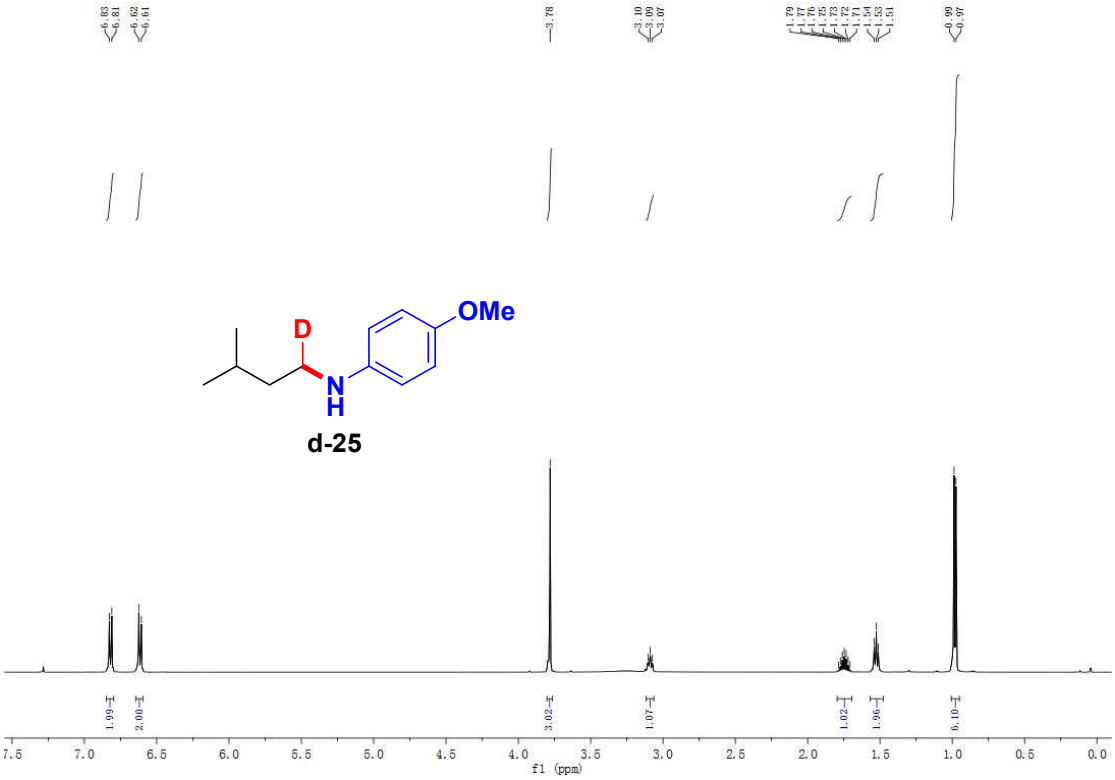
NMR Spectrum of Compound d-**22**



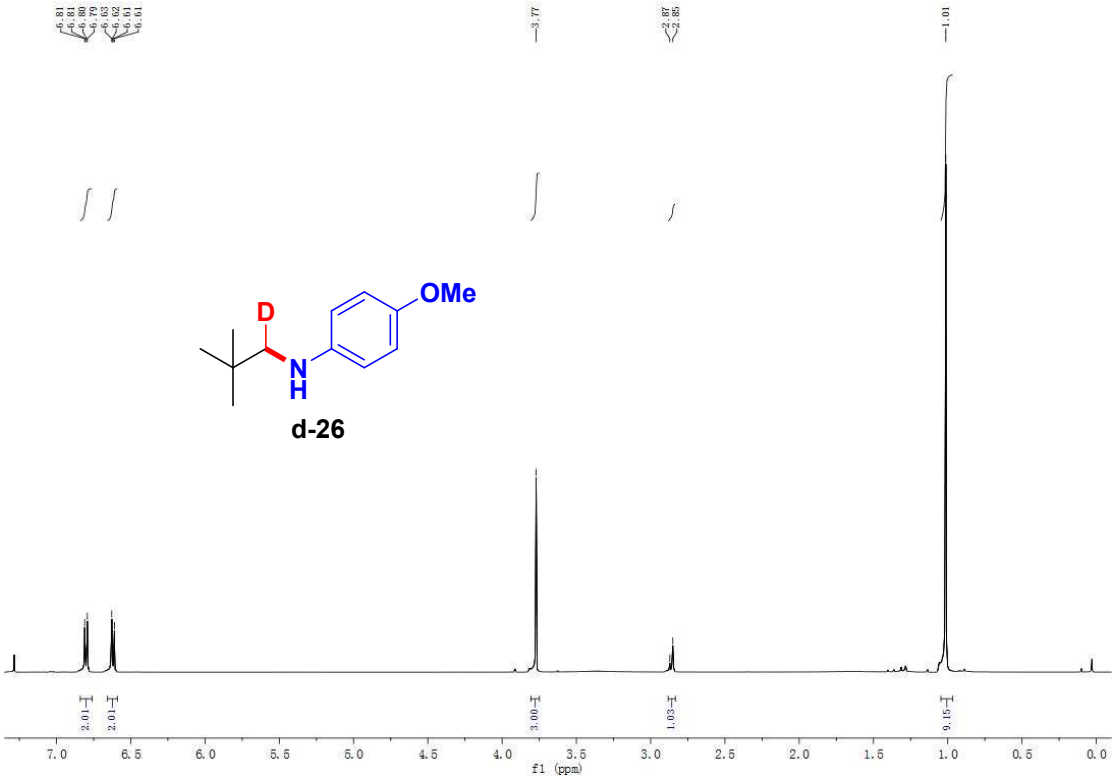
NMR Spectrum of Compound d-**24**



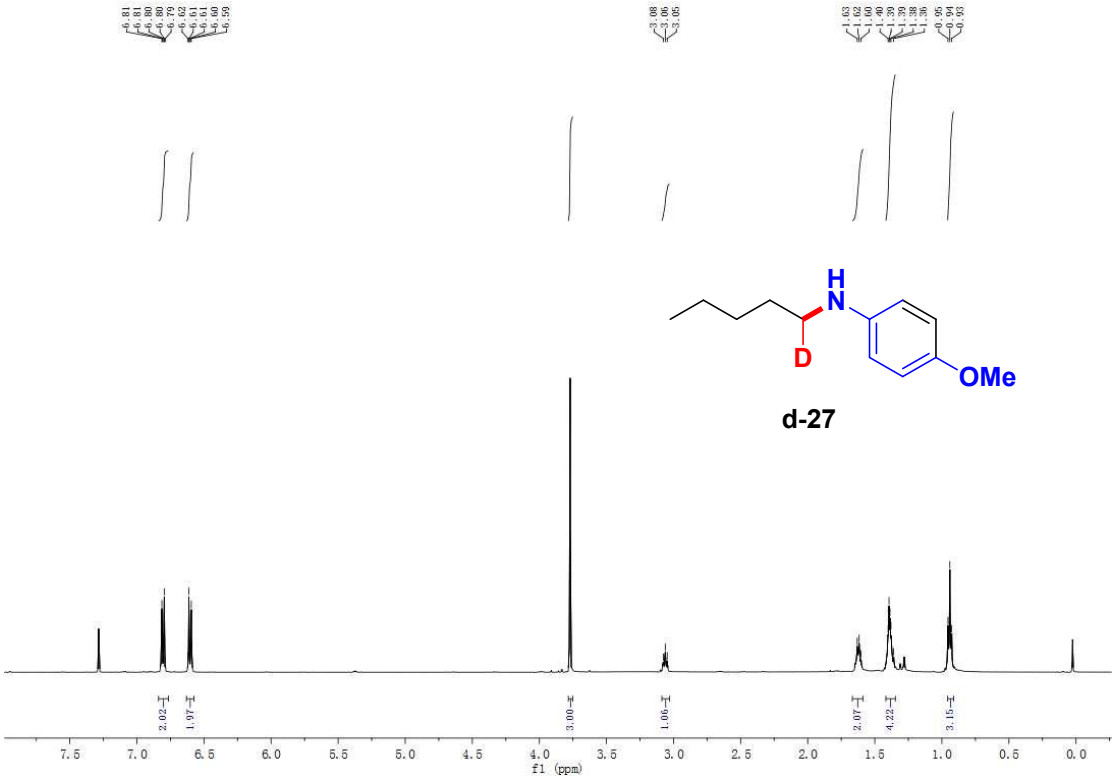
NMR Spectrum of Compound d-**25**



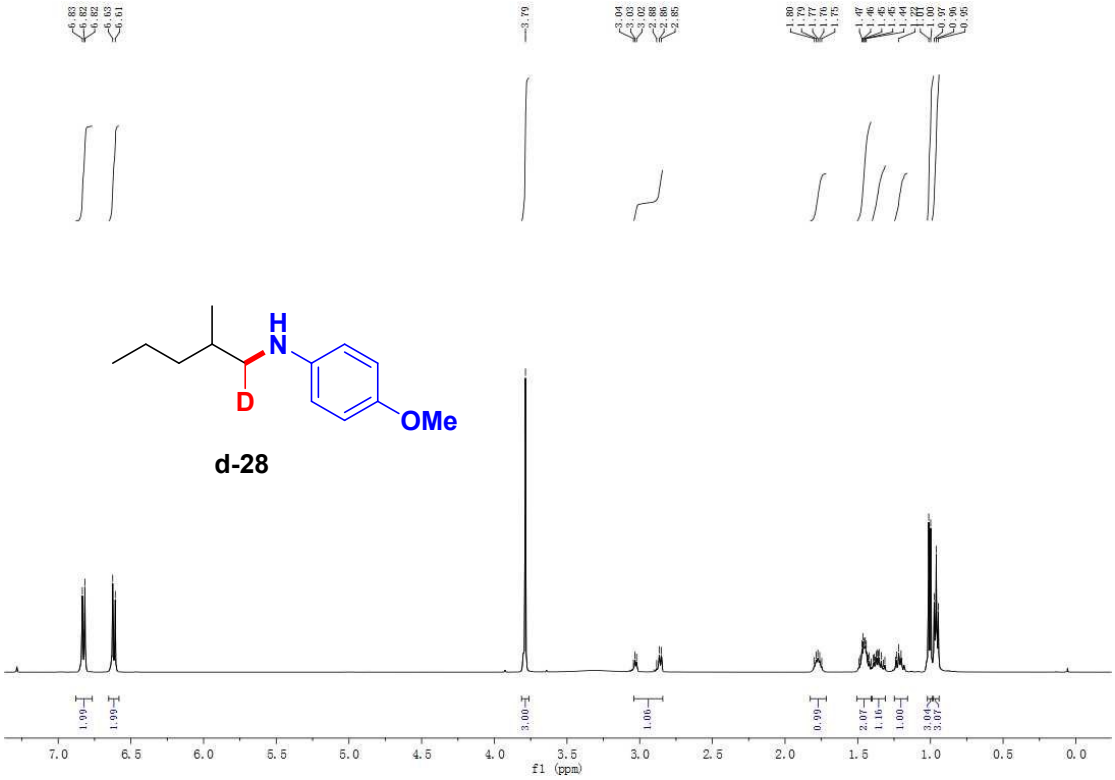
NMR Spectrum of Compound d-**26**



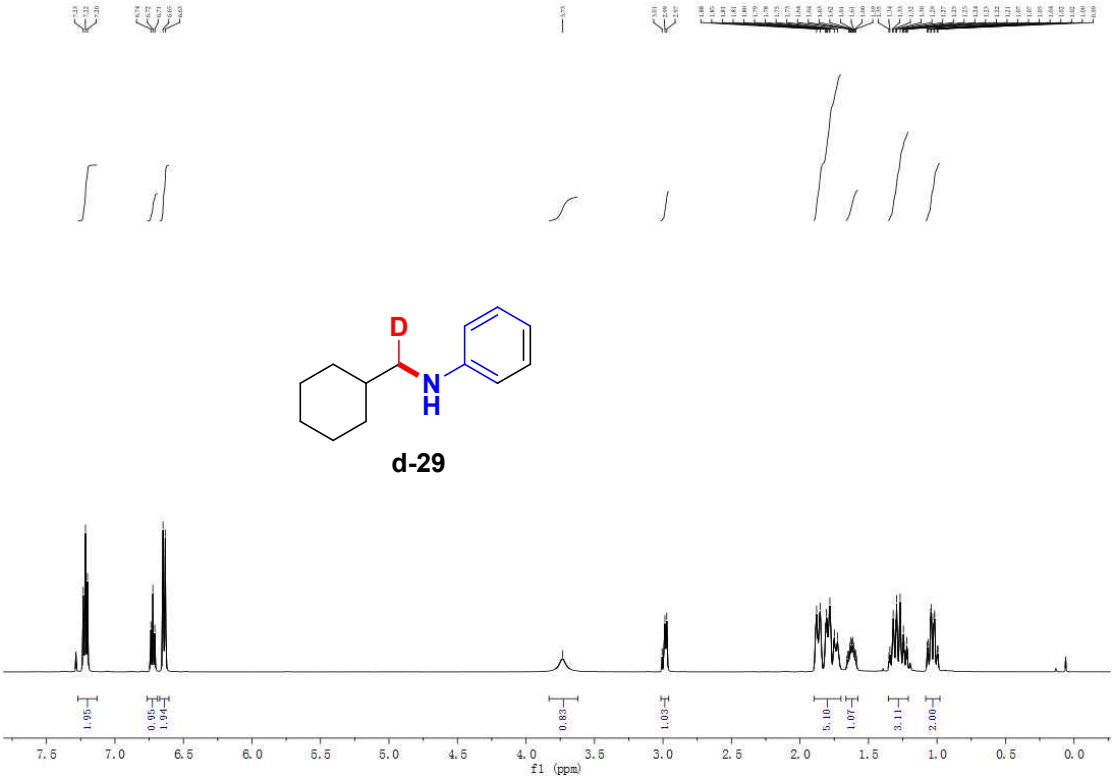
NMR Spectrum of Compound d-**27**



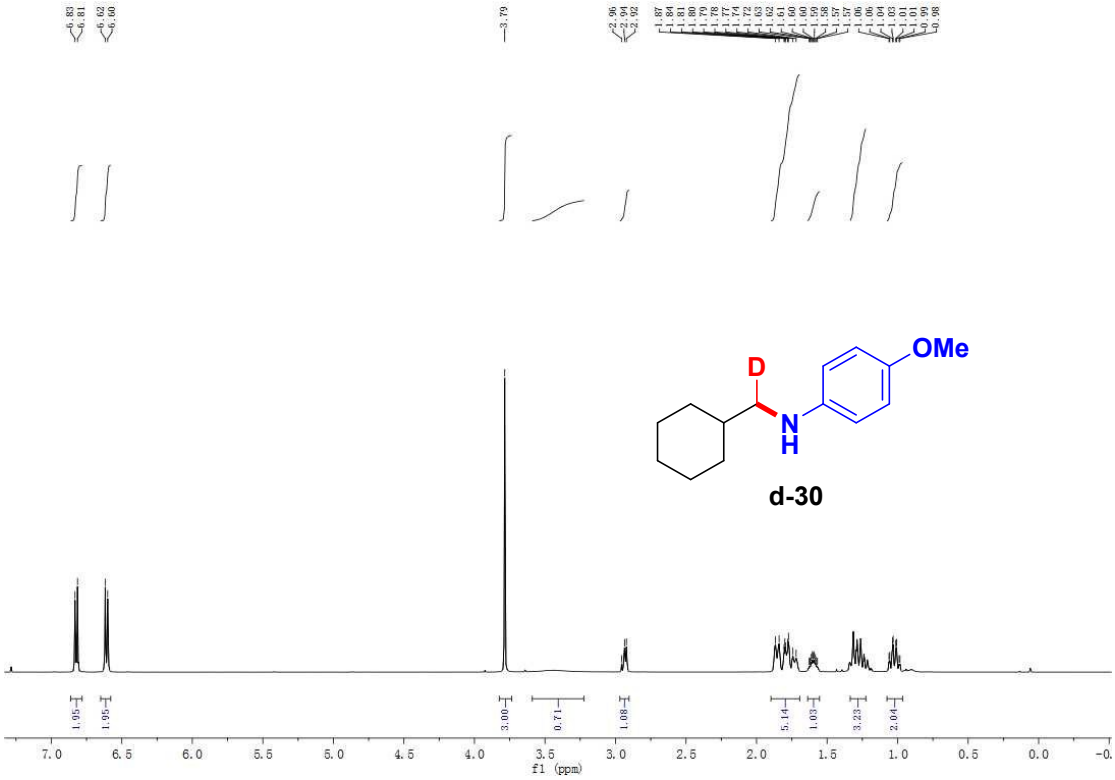
NMR Spectrum of Compound d-**28**



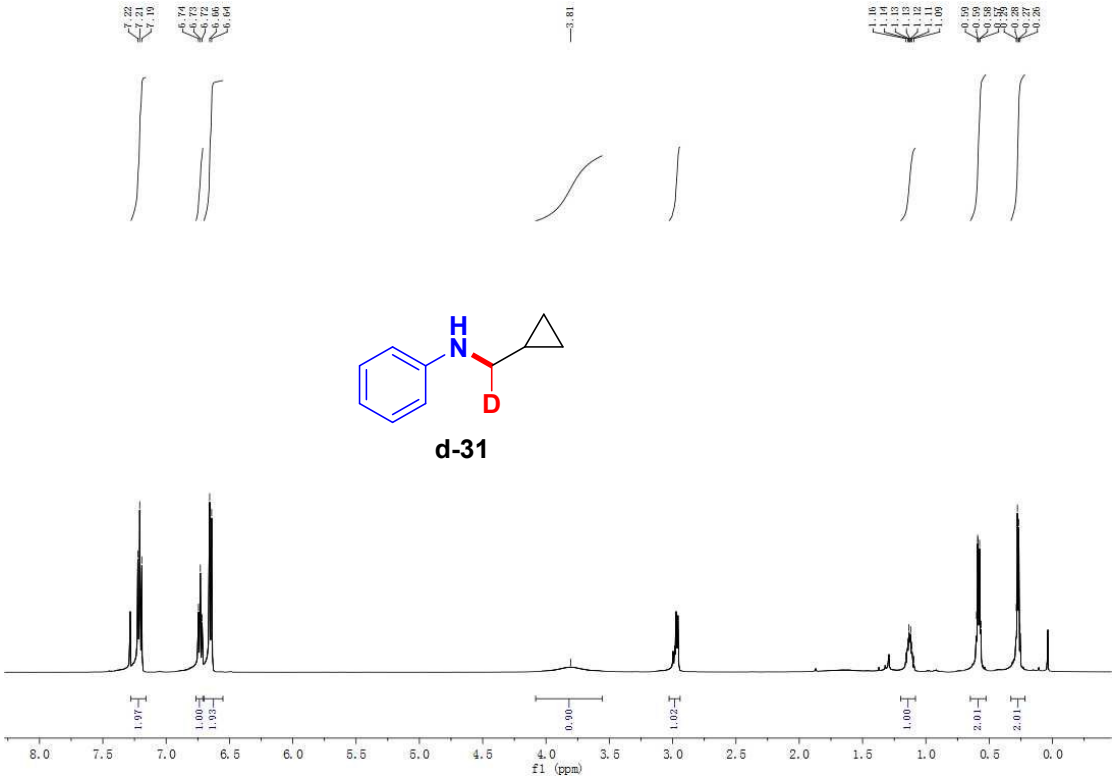
NMR Spectrum of Compound d-**29**



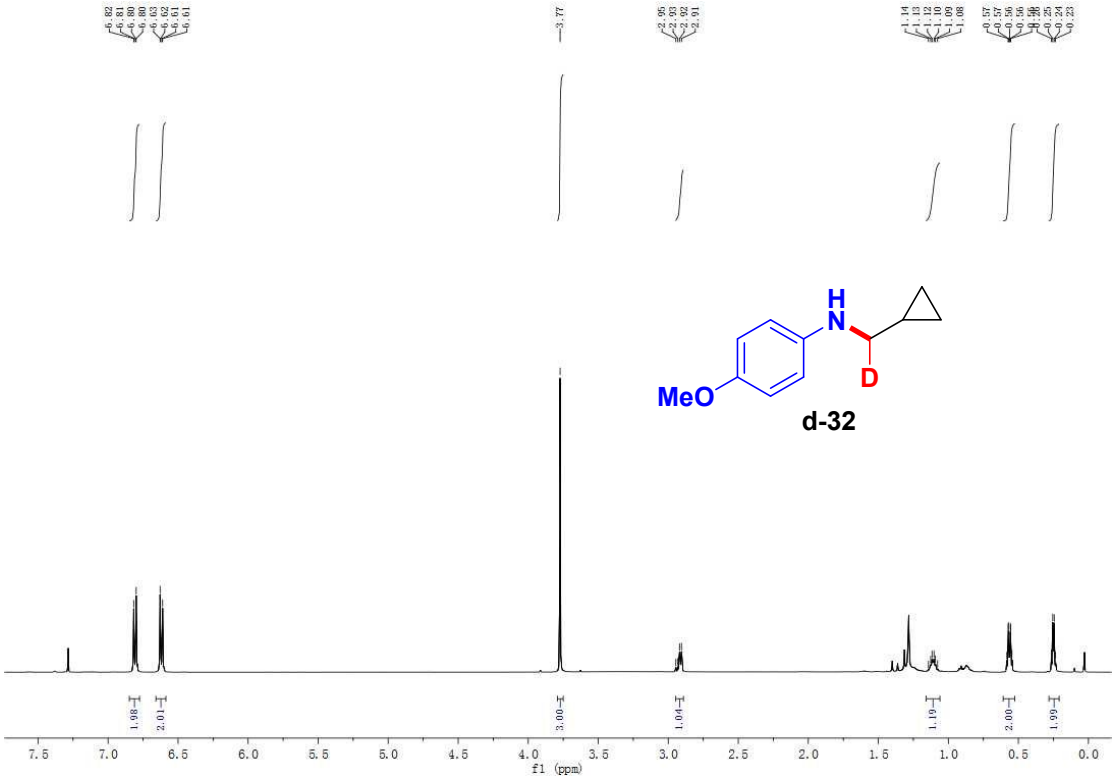
NMR Spectrum of Compound d-**30**



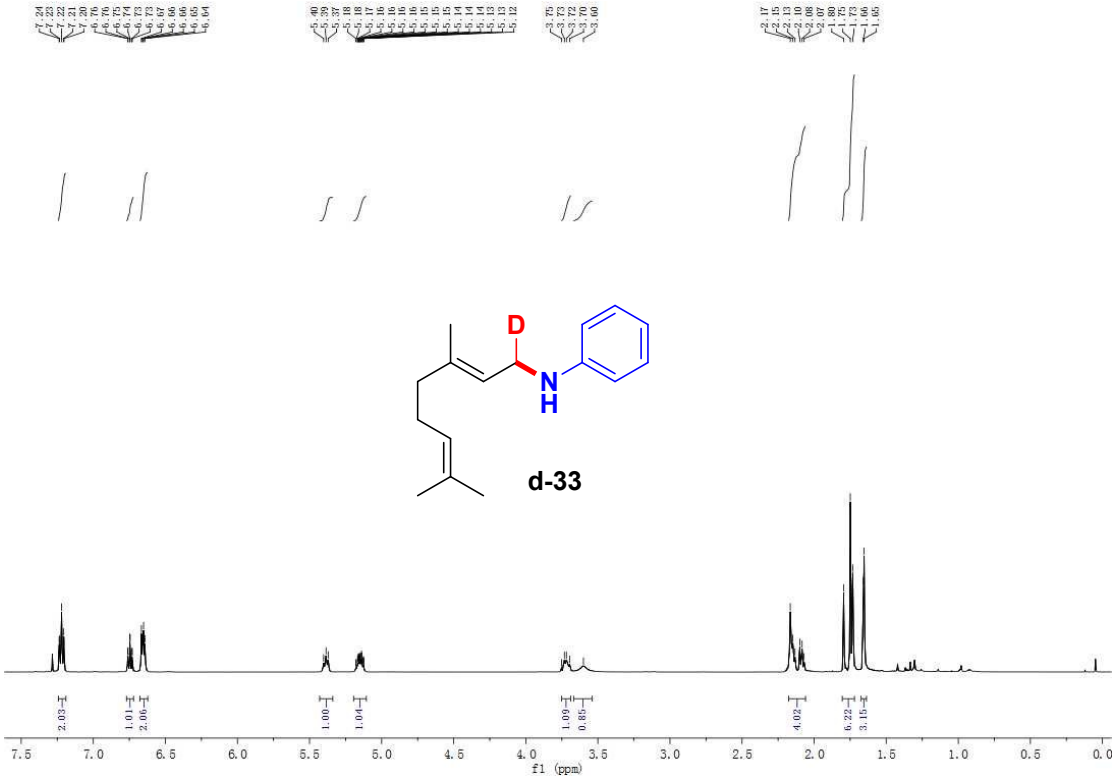
NMR Spectrum of Compound d-**31**



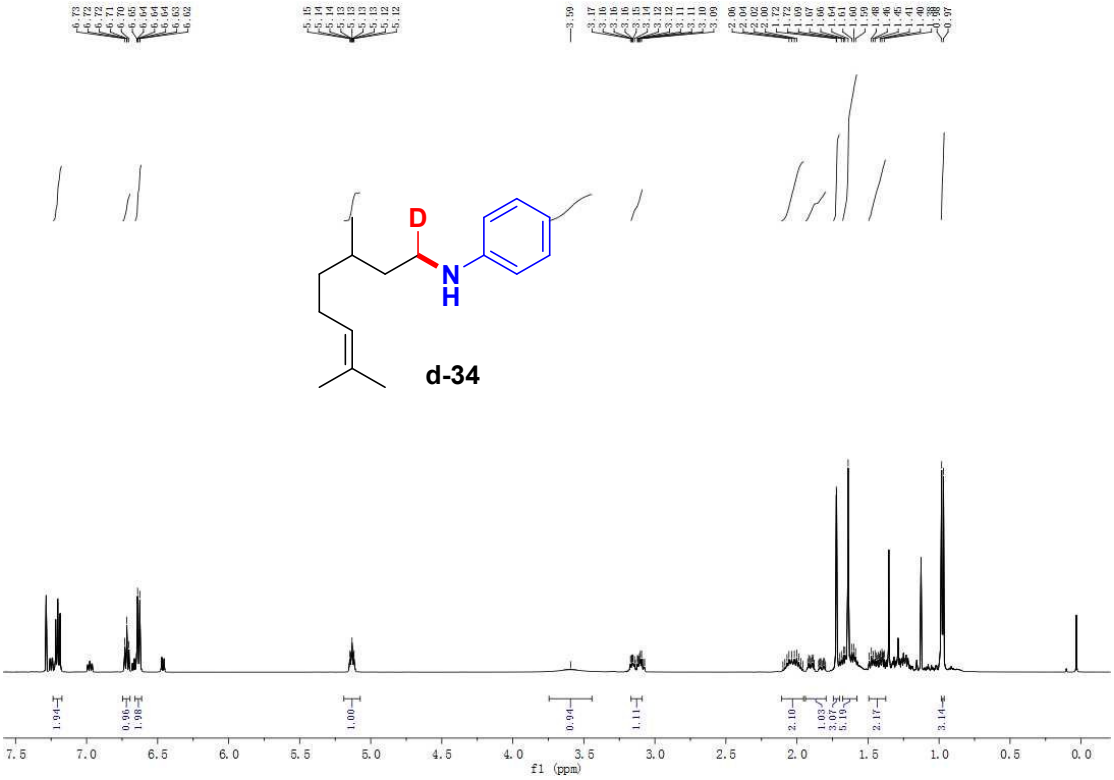
NMR Spectrum of Compound d-**32**



NMR Spectrum of Compound d-**33**



NMR Spectrum of Compound d-**34**



NMR Spectrum of Compound d-**35**