Electronic Supplementary Material (ESI) for Green Chemistry.

Conversion of furfural to tetrahydrofuran-derived secondary amines under mild conditions

Shi Jiang,[a,b] Eric Muller,[c] François Jérôme,[a] Marc Pera-Titus,[b]* and Karine De Oliveira Vigier[a]*

[a] *IC2MP UMR CNRS_Université de Poitiers 7285, ENSIP 1 rue Marcel Doré, TSA 41195, 86073 Poitiers Cedex 9, France*

[b] *Eco-Efficient Products and Processes Laboratory (E2P2L), UMI 3464 CNRS – Solvay, 3966 Jin Du Road, Xin Zhuang Ind. Zone, 201108 Shanghai, China*

[c] *SOLVAY-Advanced Organic Chemistry & Molecule Design Laboratory, 85 Avenue des Frères Perret, 69192 Saint Fons, France*

Corresponding author: marc.pera-titus-ext@solvay.com, karine.vigier@univ-poitiers.fr

Experimental Section

Chemicals

Furfural (99%), 1-butylamine (99.5%), 1-octylamine (99%), 1-dodecylamine (98%), cyclohexylamine (99%), ethanolamine (99%, Sigma-Aldrich), 3-amino-1-propanol (99%), amino-2-propanol (93%), 3-amino-1,2-propanediol (97%), aniline (99%), benzylamine (99%), *p*-toluidine (99%, Sigma-Aldrich), *p*-anisidine (99%), ehylenediamine (99%), 3,4-dimethoxyphenethylamine (97%), N,N-dimethylethylenediamine (95%), 3-(dimethylamino)-1-propylamine (99%), 3-(diethylamino) propylamine (99%) and acetonitrile (99.8%), all supplied by Sigma-Aldrich, were used as reagents. Ethanol (99.8%), tetrahydrofuran (99.9%) and toluene (99.8%), all supplied by Sigma-Aldrich, were used as solvents for the catalytic tests. Chloroform-d (99.8 atom% D) and dimethyl sulfoxide-D6 (99.8 atom% D), also supplied by Sigma-Aldrich, were used as deuterated solvents for NMR analysis. Finally, Pt(5%)/C, Pt(5%)/Al_2O_3, Pd(5%)/C, Pd(5%)/Al_2O_3, all provided by Johnson Matthey, were used as catalysts,.

General procedure for synthesis of secondary amines

The reactions were carried in a 20-mL round bottom flask equipped with a H_2 balloon. In a typical experiment, the reactor was charged with 1 mmol of furfural, 1 mmol of the given amine, 5 g of ethanol and 9.6 mg of the catalyst. The reactor was sealed and flushed with H_2 three times. Then a H_2 balloon (0.1 MPa H_2) was introduced into the reactor and the reaction was started. After the reaction, the products were analyzed and quantified on a BRUKER SCION 455-GC equipped with a HP-5MS capillary column with 5 wt% phenyl groups, a FID detector, and a split/splitless injection. N-dodecane was used as internal standard. ^1H and 1^3C NMR and HRMS analyses were also performed.

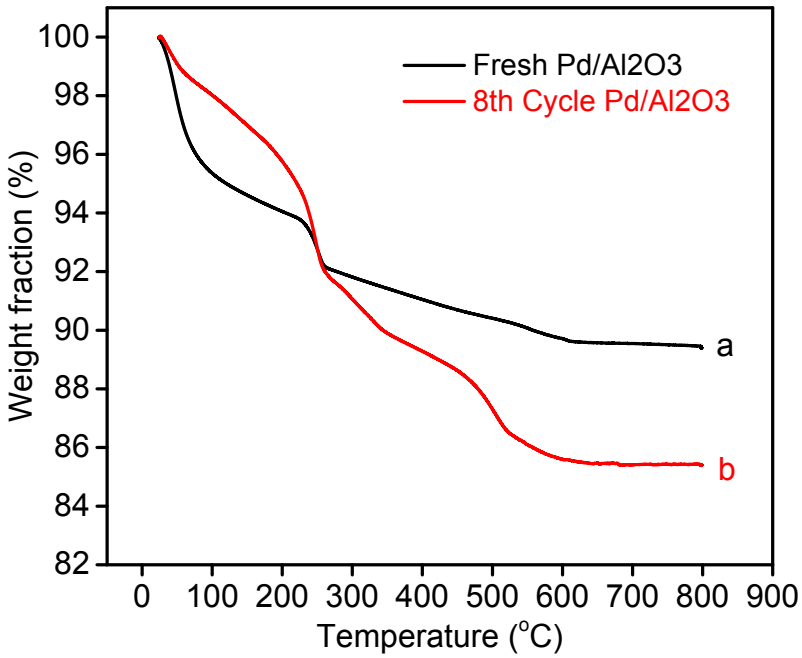


Fig. S1 TG profiles of Pd/Al_2O_3 under air: (a) fresh and (b) spent catalyst.

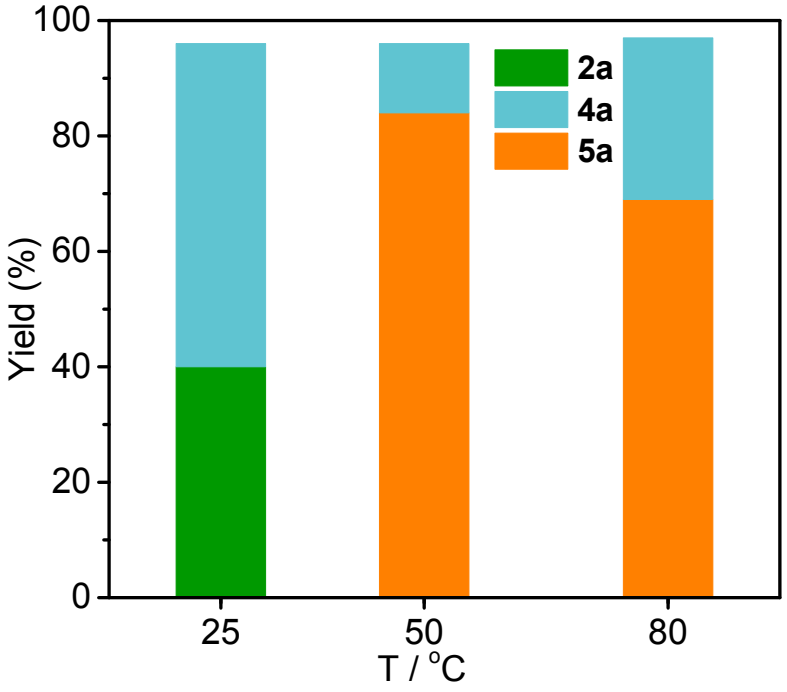
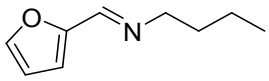


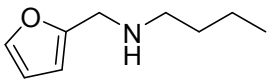
Fig. S2 Effect of reaction temperature; Reaction conditions: FF (1 mmol), $BuNH_2$ (1 mmol), EtOH (5 g), Pd/Al_2O_3 (10 mg), H_2 (1 MPa).

Characterization of products



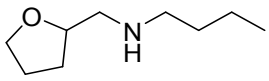
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.49 (d, J = 1.7 Hz, 1H), 6.70 (d, J = 3.4 Hz, 1H), 6.45 (dd, J = 3.4, 1.8 Hz, 1H), 3.56 (td, J = 7.0, 1.3 Hz, 2H), 1.76 – 1.60 (m, 2H), 1.44 – 1.26 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.61, 149.35, 144.52, 113.55, 111.49, 61.59, 32.90, 20.42, 13.87.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, J = 1.8, 0.8 Hz, 1H), 6.30 (dd, J = 3.1, 1.9 Hz, 1H), 6.16 (d, J = 3.1 Hz, 1H), 3.77 (s, 2H), 2.66 – 2.51 (m, 2H), 1.66 – 1.41 (m, 3H), 1.38 – 1.29 (m, 2H), 0.89 (d, J = 7.3 Hz, 3H).

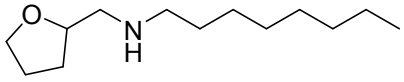
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.07, 141.70, 110.05, 106.73, 48.88, 46.29, 32.11, 20.45, 14.00.



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.98 (qd, J = 7.4, 4.0 Hz, 1H), 3.82 (dt, J = 8.2, 6.7 Hz, 1H), 3.77 – 3.67 (m, 1H), 2.69 – 2.53 (m, 4H), 2.00 – 1.90 (m, 1H), 1.90 – 1.77 (m, 2H), 1.57 – 1.40 (m, 4H), 1.38 – 1.25 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.36, 67.88, 54.63, 49.93, 32.27, 29.35, 25.77, 20.50, 14.05.

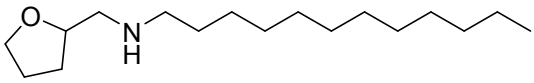
HRMS (ESI-TOF, m/z): Calcd for $C_9H_{20}NO$ [M+H]+ 158.1539; found 158.1540



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (qd, J = 7.4, 4.1 Hz, 1H), 3.83 (dt, J = 8.2, 6.7 Hz, 1H), 3.78 – 3.68 (m, 1H), 2.74 – 2.51 (m, 4H), 2.05 – 1.77 (m, 3H), 1.61 – 1.38 (m, 4H), 1.36 – 1.16 (d, J = 6.2 Hz, 10H), 0.96 – 0.75 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.37, 67.87, 54.62, 50.27, 31.83, 30.15, 29.55, 29.36, 29.26, 27.38, 25.77, 22.66, 14.09.

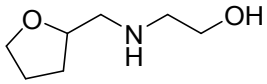
HRMS (ESI-TOF, m/z): Calcd for $C_{13}H_{28}NO$ [M+H]+ 214.2165; found 214.2169



^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00 (qd, J = 7.4, 4.1 Hz, 1H), 3.84 (dt, J = 8.3, 6.7 Hz, 1H), 3.78 – 3.69 (m, 1H), 2.75 – 2.53 (m, 4H), 2.02 – 1.92 (m, 1H), 1.92 – 1.80 (m, 2H), 1.64 (brs, 1H), 1.58 – 1.41 (m, 3H), 1.35 – 1.17 (m, 18H), 0.93 – 0.80 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.32, 67.89, 54.58, 50.25, 31.92, 30.11, 29.67, 29.64, 29.62, 29.61, 29.59, 29.37, 29.35, 27.38, 25.77, 22.69, 14.12.

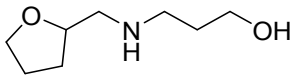
HRMS (ESI-TOF, m/z): Calcd for $C_{17}H_{36}NO$ [M+H]+ 270.2791; found 270.2805



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (qd, J = 7.3, 3.8 Hz, 1H), 3.84 (dt, J = 8.2, 6.6 Hz, 1H), 3.78 – 3.70 (m, 1H), 3.62 (t, J = 5.2 Hz, 2H), 2.79 (td, J = 4.9, 1.5 Hz, 2H), 2.75 – 2.59 (m, 2H), 2.39 (brs, 2H), 2.02 – 1.81 (m, 3H), 1.62 – 1.45 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.30, 67.96, 60.82, 53.76, 51.14, 29.22, 25.80.

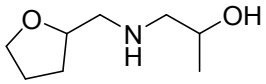
HRMS (ESI-TOF, m/z): Calcd for $C_7H_{16}NO_2$ [M+H]+ 146.1176; found 146.1184



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.98 (qd, J = 7.2, 3.7 Hz, 1H), 3.88 – 3.77 (m, 3H), 3.72 (dt, J = 8.2, 6.7 Hz, 1H), 3.14 (brs, 2H), 2.89 (t, J = 5.6 Hz, 2H), 2.74 (dd, J = 12.0, 3.7 Hz, 1H), 2.61 (dd, J = 12.0, 7.3 Hz, 1H), 2.01 – 1.80 (m, 3H), 1.75 – 1.61 (m, 2H), 1.61 – 1.47 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 77.90, 68.01, 64.34, 53.97, 49.97, 30.55, 29.14, 25.87.

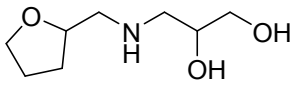
HRMS (ESI-TOF, m/z): Calcd for $C_8H_{18}NO_2$ [M+H]+ 160.1332; found 160.1336



^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 – 3.93 (m, 1H), 3.90 – 3.80 (m, 1H), 3.80 – 3.66 (m, 2H), 2.76 – 2.66 (m, 2H), 2.5 (brs, 2H), 2.61 (dd, J = 12.1, 7.8 Hz, 1H), 2.40 (ddd, J = 12.1, 9.5, 5.8 Hz, 1H), 2.01 – 1.78 (m, 3H), 1.64 – 1.47 (m, 1H), 1.13 (d, J = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.31, 78.30, 68.03, 67.97, 65.52, 65.34, 56.88, 56.87, 53.95, 53.87, 29.18, 29.14, 25.86, 25.83, 20.35, 20.31.

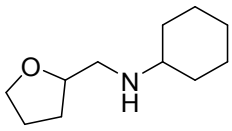
HRMS (ESI-TOF, m/z): Calcd for $C_8H_{18}NO_2$ [M+H]+ 160.1332; found 160.1337



^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00 (qt, J = 7.1, 3.4 Hz, 1H), 3.89 – 3.80 (m, 1H), 3.80 – 3.64 (m, 3H), 3.58 (ddd, J = 11.3, 7.8, 5.0 Hz, 1H), 3.01 (brs, 3H), 2.86 – 2.57 (m, 4H), 2.03 – 1.80 (m, 3H), 1.60 – 1.45 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.15, 78.10, 69.76, 69.74, 68.01, 68.00, 65.65, 65.58, 54.22, 52.45, 52.30, 29.23, 29.21, 25.80.

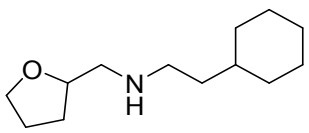
HRMS (ESI-TOF, m/z): Calcd for $C_8H_{18}NO_3$ [M+H]+ 176.1281; found 176.1287



^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 – 3.92 (m, 1H), 3.84 (dt, J = 8.2, 6.7 Hz, 1H), 3.78 – 3.68 (m, 1H), 2.72 (dd, J = 11.8, 3.8 Hz, 1H), 2.62 (dd, J = 11.8, 8.1 Hz, 1H), 2.41 (tt, J = 10.5, 3.8 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.92 – 1.80 (m, 4H), 1.76 – 1.66 (m, 2H), 1.65 – 1.45 (m, 3H), 1.31 – 0.98 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.61, 67.84, 56.96, 51.65, 33.55, 33.47, 29.43, 26.18, 25.73, 25.07, 25.05.

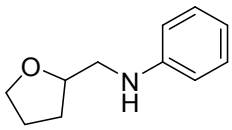
HRMS (ESI-TOF, m/z): Calcd for $C_{11}H_{22}NO$ [M+H]+ 184.1696; found 184.1704



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (qd, J = 7.4, 4.1 Hz, 1H), 3.90 – 3.79 (m, 1H), 3.79 – 3.68 (m, 1H), 2.78 – 2.51 (m, 4H), 2.04 – 1.78 (m, 3H), 1.73 – 1.58 (m, 5H), 1.57 – 1.42 (m, 2H), 1.37 (dt, J = 8.5, 6.2 Hz, 2H), 1.33 – 1.06 (m, 4H), 0.96 – 0.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.38, 67.89, 54.72, 47.91, 37.85, 35.78, 33.49, 33.43, 29.37, 26.62, 26.33, 25.78.

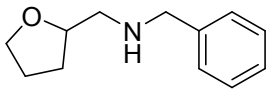
HRMS (ESI-TOF, m/z): Calcd for $C_{13}H_{26}NO$ [M+H]+ 212.2009; found 212.2007



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.11 (m, 2H), 6.74 – 6.67 (m, 1H), 6.67 – 6.59 (m, 2H), 4.14 (qd, J = 7.1, 3.8 Hz, 1H), 4.00 (brs, 1H), 3.89 (dt, J = 8.4, 6.6 Hz, 1H), 3.79 (dt, J = 8.3, 6.8 Hz, 1H), 3.26 (dd, J = 12.3, 3.8 Hz, 1H), 3.08 (dd, J = 12.3, 7.5 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.97 – 1.86 (m, 2H), 1.72 – 1.60 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.40, 129.21, 117.48, 113.04, 77.58, 68.06, 48.19, 29.12, 25.82.

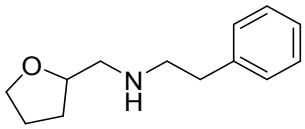
HRMS (ESI-TOF, m/z): Calcd for $C_{11}H_{16}NO$ [M+H]+ 178.1226; found 178.1228



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 4H), 7.27 – 7.21 (m, 1H), 4.04 (qd, J = 7.3, 3.8 Hz, 1H), 3.89 – 3.79 (m, 3H), 3.74 (dt, J = 8.2, 6.7 Hz, 1H), 2.77 – 2.57 (m, 2H), 2.01 – 1.92 (m, 2H), 1.91 – 1.80 (m, 2H), 1.64 – 1.47 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.18, 128.36, 128.15, 126.90, 78.30, 67.95, 53.95, 53.64, 29.28, 25.80.

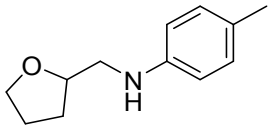
HRMS (ESI-TOF, m/z): Calcd for $C_{12}H_{18}NO$ [M+H]+ 192.1383; found 192.1384



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 2H), 7.24 – 7.15 (m, 3H), 3.99 (qd, J = 7.3, 4.1 Hz, 1H), 3.83 (dt, J = 8.3, 6.7 Hz, 1H), 3.73 (dt, J = 8.3, 6.7 Hz, 1H), 2.95 – 2.87 (m, 2H), 2.85 – 2.77 (m, 2H), 2.75 – 2.61 (m, 2H), 2.01 – 1.80 (m, 3H), 1.63 (brs, 1H), 1.57 – 1.44 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.11, 128.71, 128.42, 126.08, 78.33, 67.93, 54.41, 51.60, 36.53, 29.37, 25.78.

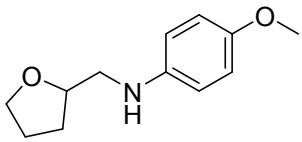
HRMS (ESI-TOF, m/z): Calcd for $C_{13}H_{20}NO$ [M+H]+ 206.1539; found 206.1549



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 – 6.92 (m, 2H), 6.63 – 6.50 (m, 2H), 4.13 (qd, J = 7.1, 3.8 Hz, 1H), 3.90 (brs, 1H), 3.89 (dt, J = 8.3, 6.7 Hz, 1H), 3.79 (dt, J = 8.2, 6.8 Hz, 1H), 3.24 (dd, J = 12.3, 3.8 Hz, 1H), 3.06 (dd, J = 12.3, 7.5 Hz, 1H), 2.24 (s, 3H), 2.10 – 1.98 (m, 1H), 1.98 – 1.85 (m, 2H), 1.71 – 1.58 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.16, 129.70, 126.70, 113.25, 77.63, 68.04, 48.63, 29.13, 25.83, 20.41.

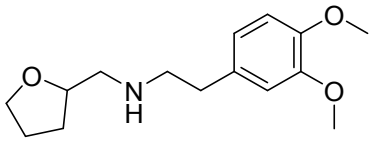
HRMS (ESI-TOF, m/z): Calcd for $C_{12}H_{18}NO$ [M+H]+ 192.1383; found 192.1388



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 – 6.70 (m, 2H), 6.69 – 6.52 (m, 2H), 4.12 (qd, J = 7.2, 3.7 Hz, 1H), 4.01 – 3.59 (m, 6H), 3.21 (dd, J = 12.1, 3.7 Hz, 1H), 3.03 (dd, J = 12.1, 7.7 Hz, 1H), 2.08 – 1.98 (m, 1H), 1.96 – 1.86 (m, 2H), 1.71 – 1.59 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.19, 142.66, 114.84, 114.40, 77.63, 68.04, 55.81, 49.33, 29.14, 25.83.

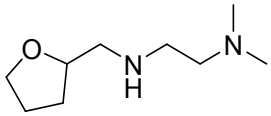
HRMS (ESI-TOF, m/z): Calcd for $C_{12}H_{18}NO_2$ [M+H]+ 208.1332; found 208.1337



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 – 6.61 (m, 3H), 3.98 (qd, J = 7.3, 4.0 Hz, 1H), 3.90 – 3.77 (m, 7H), 3.72 (dt, J = 8.2, 6.7 Hz, 1H), 2.95 – 2.81 (m, 2H), 2.80 – 2.60 (m, 4H), 2.00 – 1.90 (m, 1H), 1.90 – 1.81 (m, 2H), 1.75 (brs, 1H), 1.58 – 1.44 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.82, 147.34, 132.65, 120.53, 111.95, 111.24, 78.26, 67.93, 55.90, 55.80, 54.40, 51.67, 35.99, 29.37, 25.76.

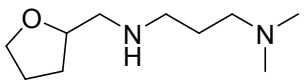
HRMS (ESI-TOF, m/z): Calcd for $C_{15}H_{24}NO_3$ [M+H]+ 266.1751; found 266.1753



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (qd, J = 7.1, 4.6 Hz, 1H), 3.84 (dt, J = 8.3, 6.7 Hz, 1H), 3.77 – 3.67 (m, 1H), 2.77 – 2.61 (m, 4H), 2.45 – 2.36 (m, 2H), 2.21 (s, 6H), 2.03 – 1.76 (m, 4H), 1.61 – 1.44 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.37, 67.88, 59.22, 54.63, 47.68, 45.64, 29.42, 25.72.

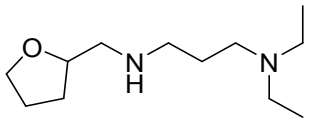
HRMS (ESI-TOF, m/z): Calcd for $C_9H_{21}N_2O$ [M+H]+ 173.1648; found 173.1653



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (qd, J = 7.4, 4.0 Hz, 1H), 3.83 (dt, J = 8.3, 6.7 Hz, 1H), 3.78 – 3.69 (m, 1H), 2.76 – 2.56 (m, 4H), 2.34 – 2.26 (m, 2H), 2.20 (s, 6H), 2.09 – 1.73 (m, 4H), 1.71 – 1.61 (m, 2H), 1.58 – 1.46 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.24, 67.91, 58.01, 54.56, 48.55, 45.55, 29.34, 28.08, 25.78.

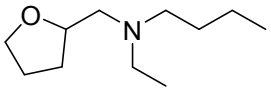
HRMS (ESI-TOF, m/z): Calcd for $C_{10}H_{23}N_2O$ [M+H]+ 187.1805; found 187.1809



^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00 (qd, J = 7.3, 4.0 Hz, 1H), 3.83 (dt, J = 8.3, 6.7 Hz, 1H), 3.78 – 3.69 (m, 1H), 2.73 – 2.58 (m, 4H), 2.55 – 2.43 (m, 6H), 2.14 – 1.78 (m, 4H), 1.72 – 1.59 (m, 2H), 1.58 – 1.46 (m, 1H), 1.00 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.26, 67.89, 54.57, 51.11, 48.92, 46.85, 29.36, 27.23, 25.79, 11.66.

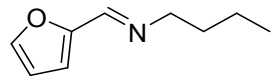
HRMS (ESI-TOF, m/z): Calcd for $C_{12}H_{27}N_2O$ [M+H]+ 215.2118; found 215.2127

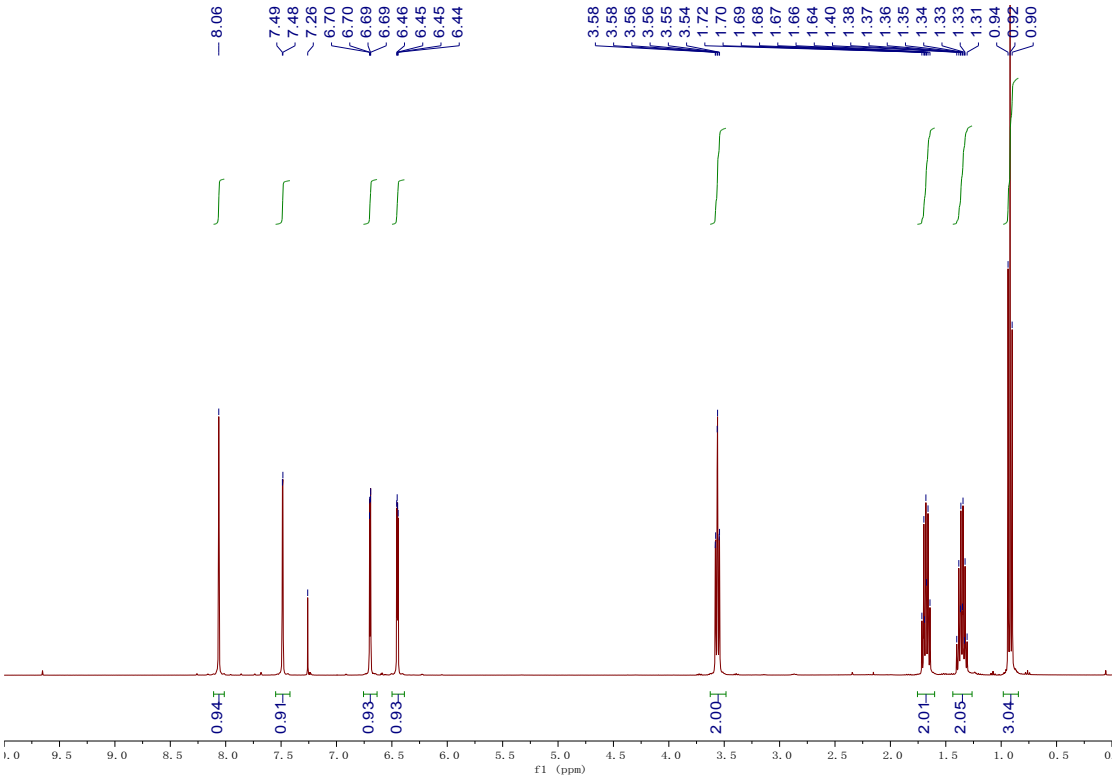


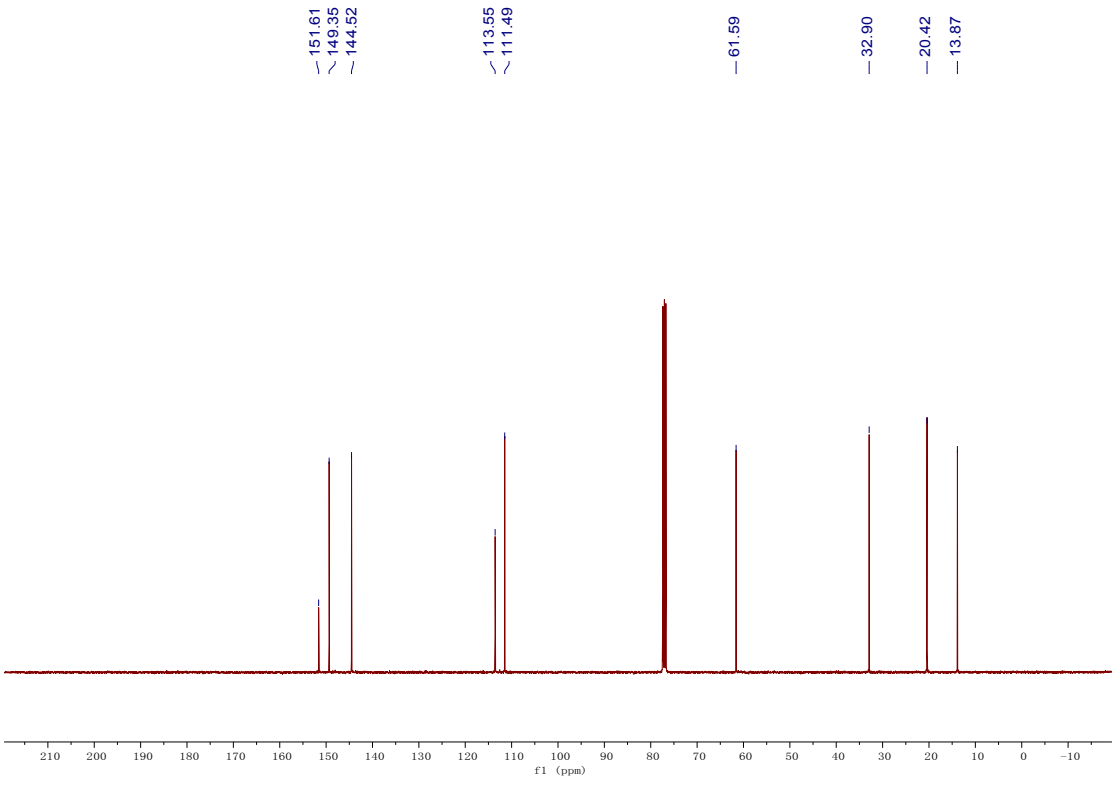
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 – 3.90 (m, 1H), 3.90 – 3.80 (m, 1H), 3.75 – 3.67 (m, 1H), 2.63 – 2.40 (m, 6H), 2.01 – 1.90 (m, 1H), 1.90 – 1.76 (m, 2H), 1.57 – 1.47 (m, 1H), 1.47 – 1.36 (m, 2H), 1.34 – 1,22 (m, 2H), 1.00 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H).

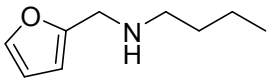
^{13}C NMR (101 MHz, $CDCl_3$): δ 77.66, 67.90, 58.27, 53.90, 48.18, 30.29, 29.07, 25.42, 20.73, 14.12, 11.59.

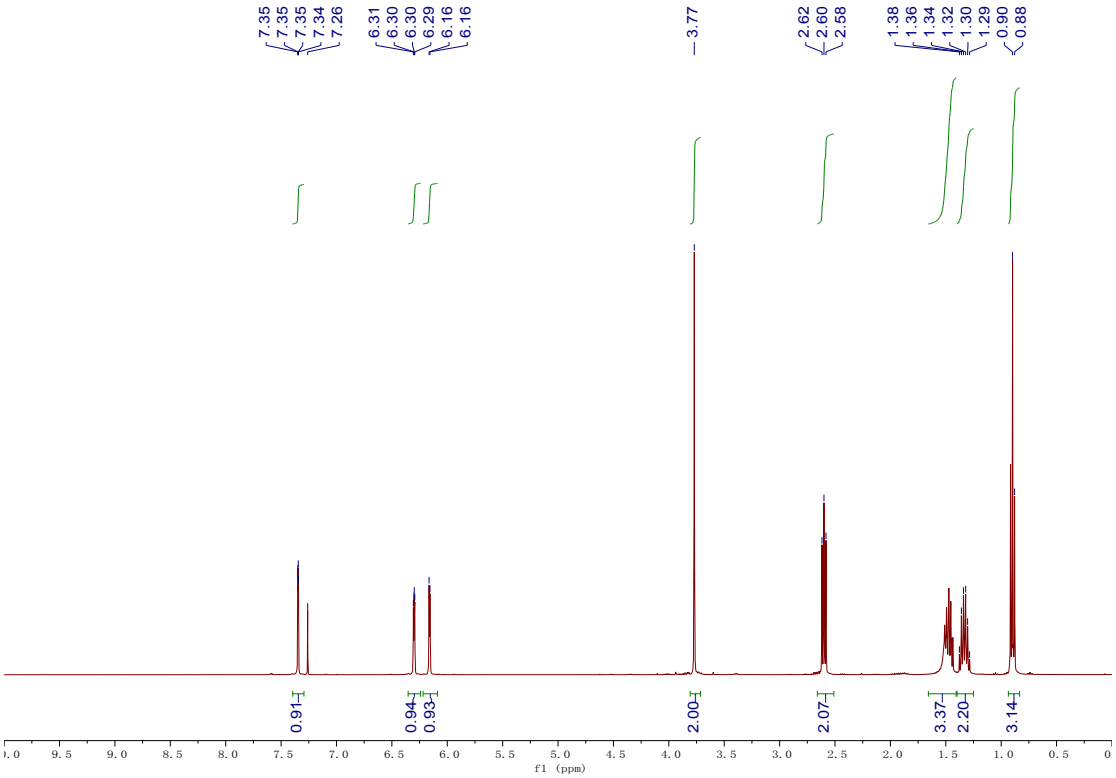
HRMS (ESI-TOF, m/z): Calcd for $C_{11}H_{24}NO$ [M+H]+ 186.1852; found 186.1860

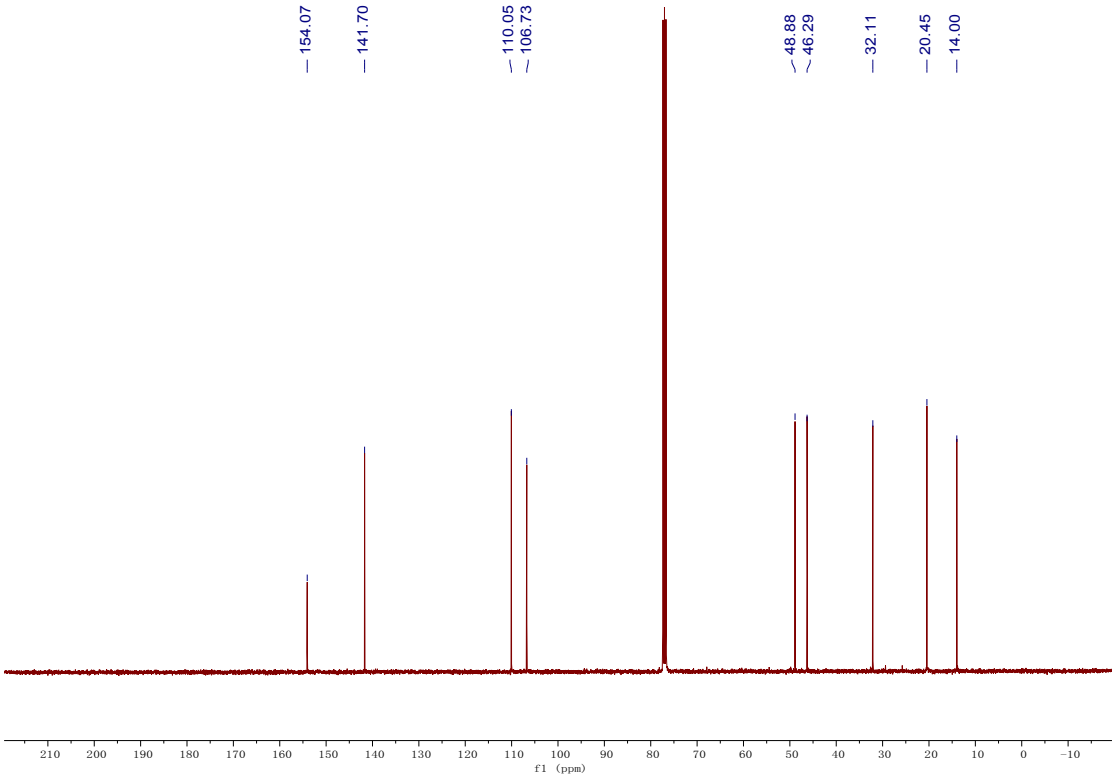

O
N

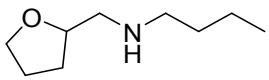

8.06
7.49
7.48
7.26
6.70
6.70
6.69
6.69
6.46
6.45
6.45
6.44
3.58
3.58
3.56
3.56
3.55
3.54
1.72
1.70
1.69
1.68
1.67
1.66
1.64
1.40
1.38
1.37
1.36
1.35
1.34
1.33
1.33
1.31
0.94
0.92
0.90
0.94
0.91
0.93
0.93
2.00
2.01
2.05
3.04
f1 (ppm)

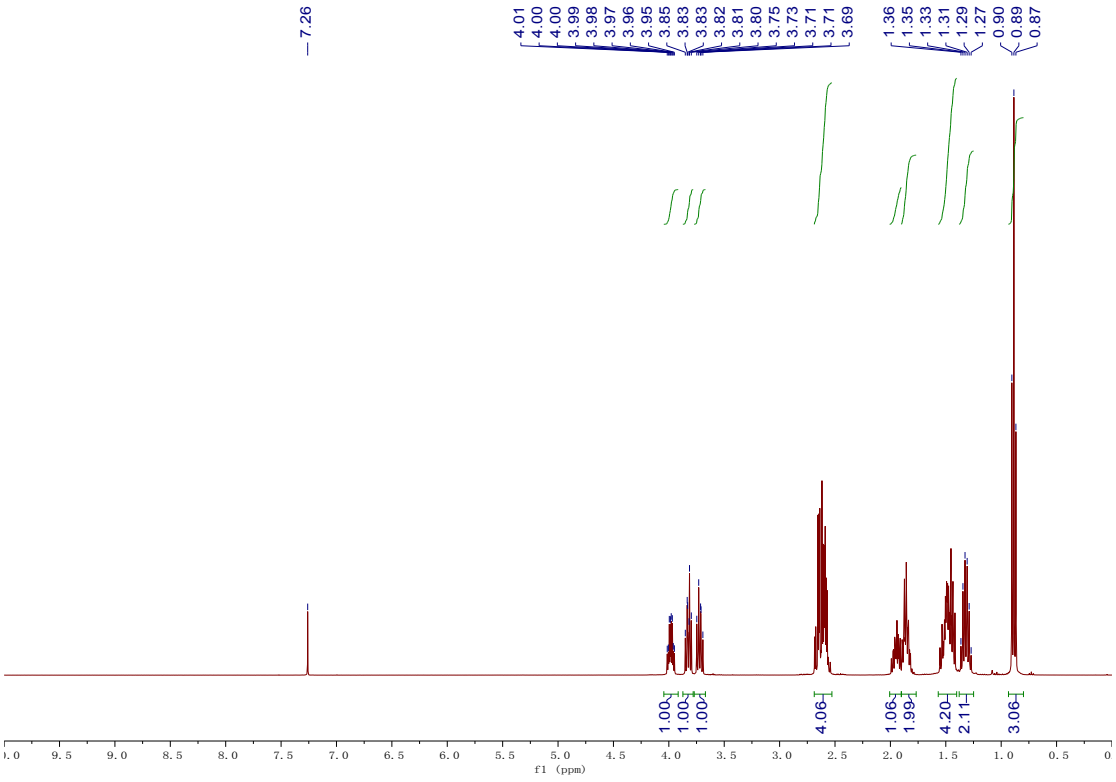

151.61
149.35
144.52
113.55
111.49
61.59
32.90
20.42
13.87
f1 (ppm)

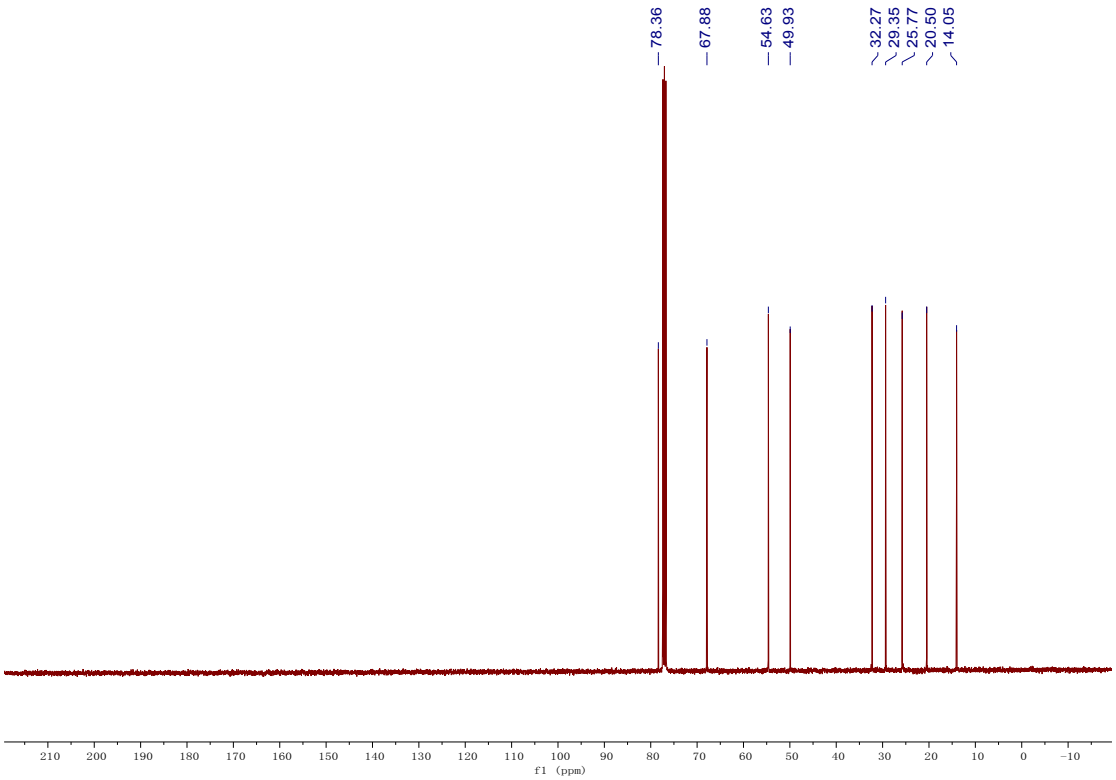

O
N
H

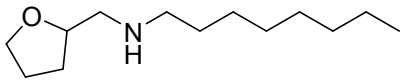

7.35
7.35
7.35
7.34
7.26
6.31
6.30
6.30
6.29
6.16
6.16
3.77
2.62
2.60
2.58
1.38
1.36
1.34
1.32
1.30
1.29
0.90
0.88
0.91
0.94
0.93
2.00
2.07
3.37
2.20
3.14
f1 (ppm)

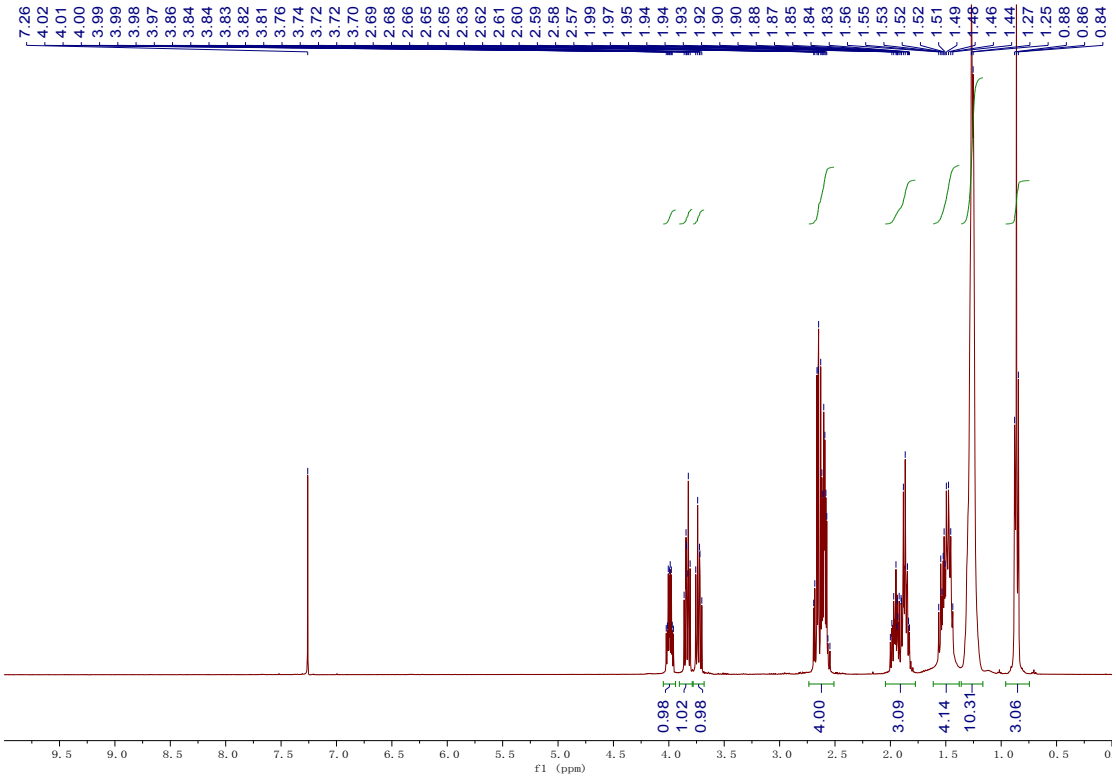

154.07
141.70
110.05
106.73
48.88
46.29
32.11
20.45
14.00
f1 (ppm)

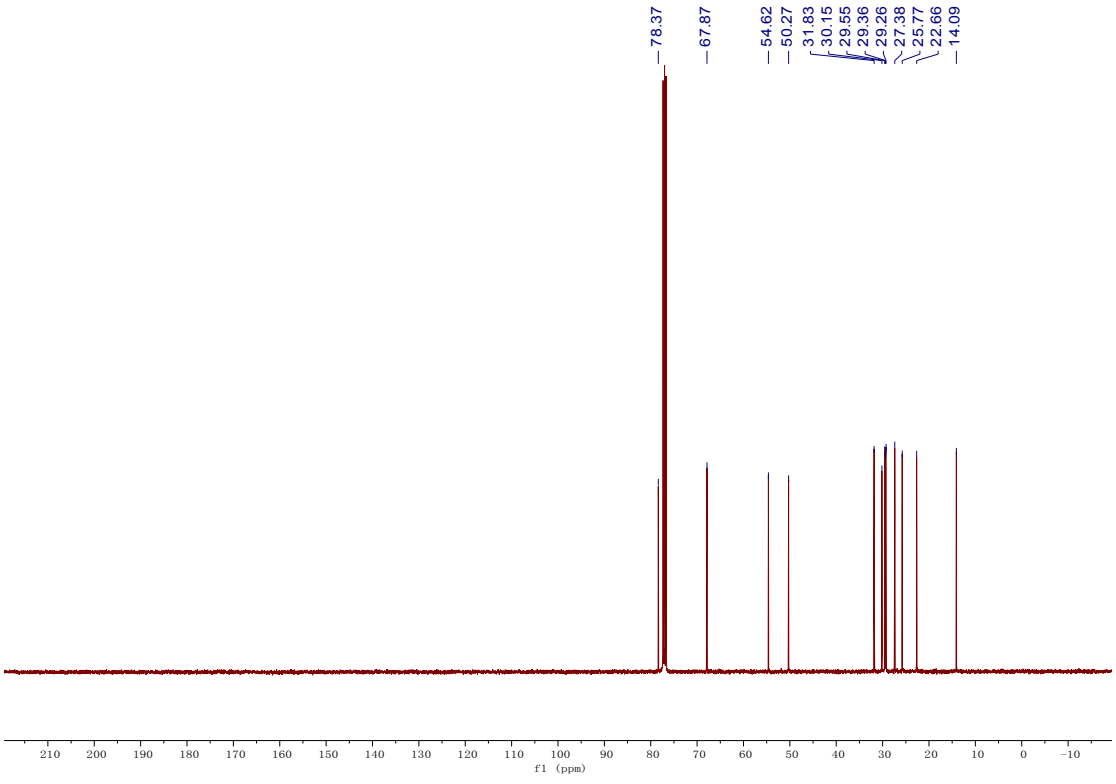

O
N
H

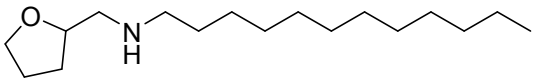

7.26
4.01
4.00
4.00
3.99
3.98
3.97
3.96
3.95
3.85
3.83
3.83
3.82
3.81
3.80
3.75
3.73
3.71
3.71
3.69
1.36
1.35
1.33
1.31
1.29
1.27
0.90
0.89
0.87
1.00
1.00
1.00
4.06
1.06
1.99
4.20
2.11
3.06
f1 (ppm)

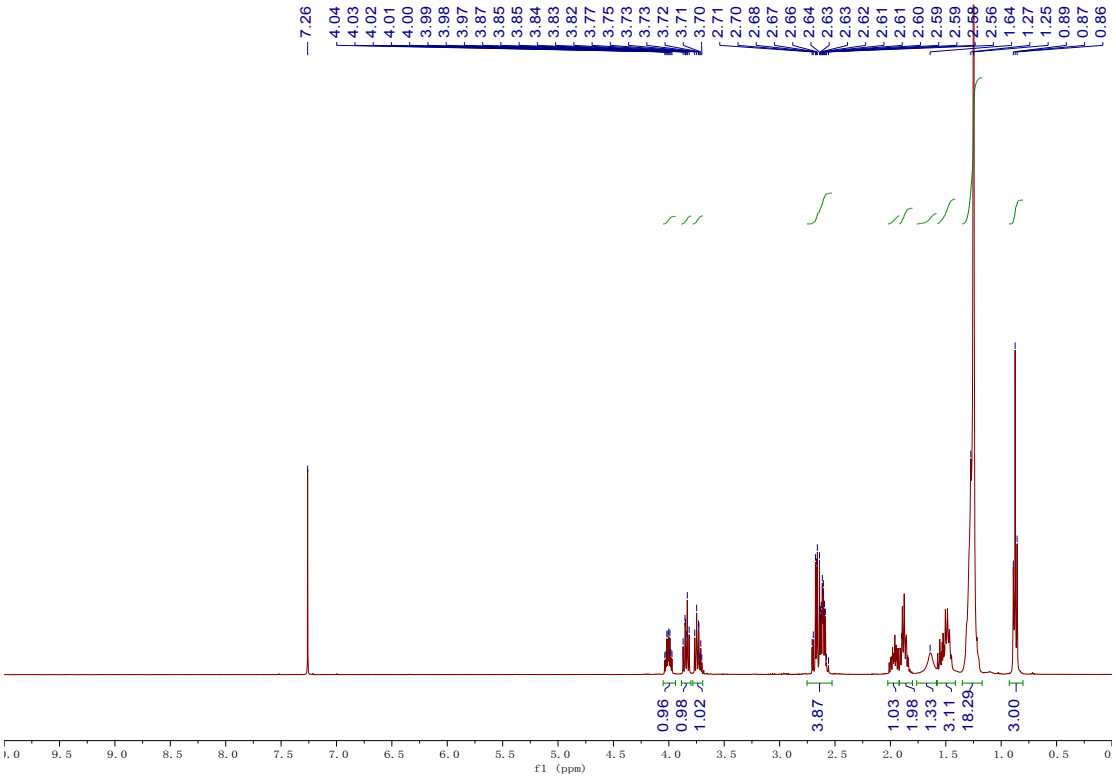

78.36
67.88
54.63
49.93
32.27
29.35
25.77
20.50
14.05
f1 (ppm)

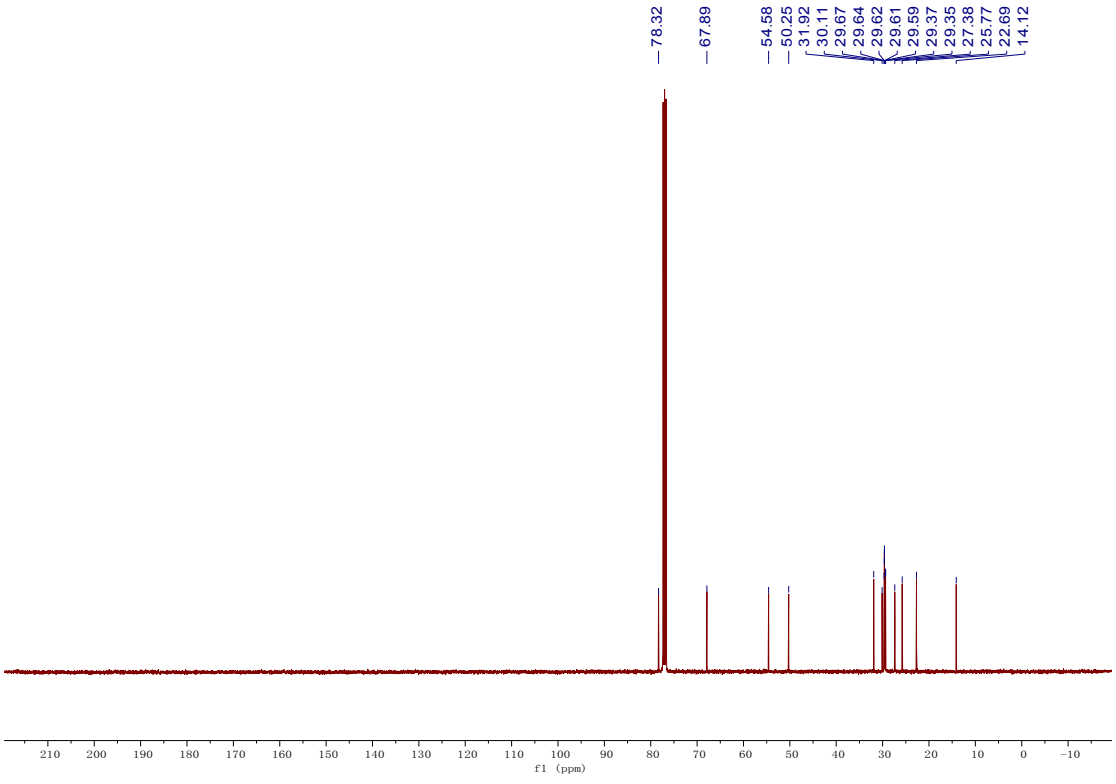

O
N
H

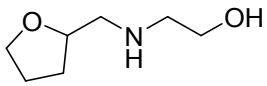

7.26
4.02
4.01
4.00
3.99
3.99
3.98
3.97
3.86
3.84
3.84
3.83
3.82
3.81
3.76
3.74
3.72
3.72
3.70
2.69
2.68
2.66
2.65
2.65
2.63
2.62
2.61
2.60
2.59
2.58
2.57
1.99
1.97
1.95
1.94
1.94
1.93
1.92
1.90
1.90
1.88
1.87
1.85
1.84
1.83
1.56
1.55
1.53
1.52
1.52
1.51
1.49
1.48
1.46
1.44
1.27
1.25
0.88
0.86
0.84
0.98
1.02
0.98
4.00
3.09
4.14
10.31
3.06
f1 (ppm)

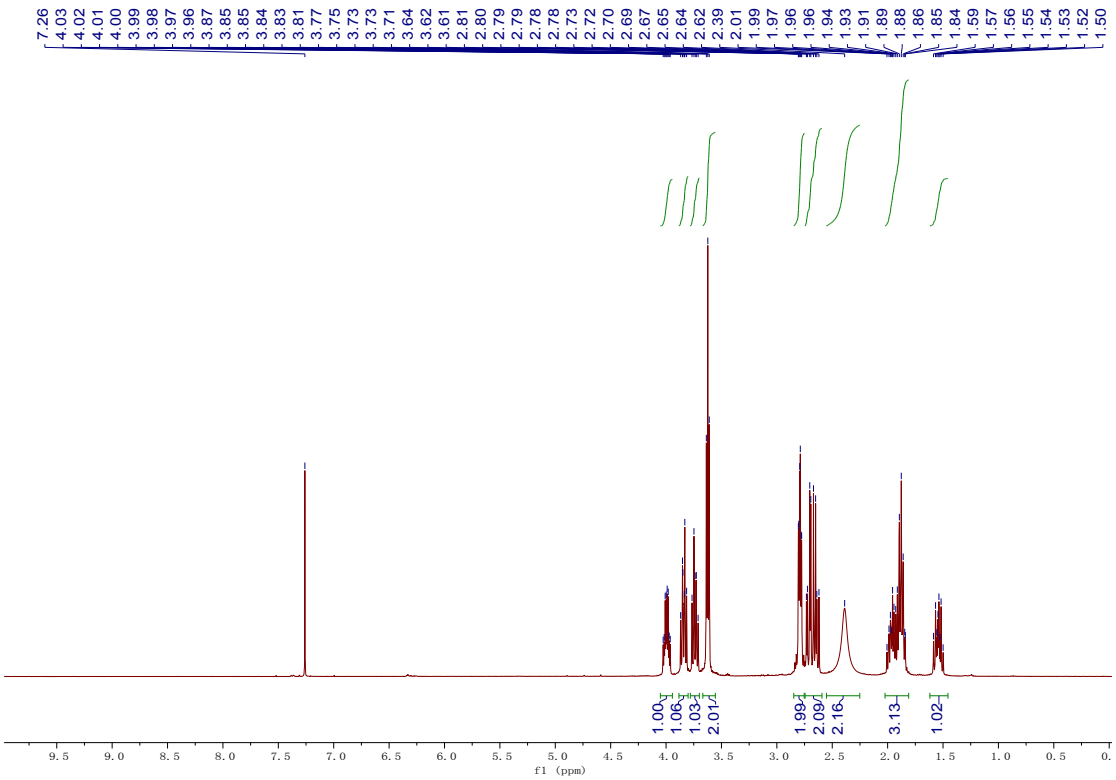

78.37
67.87
54.62
50.27
31.83
30.15
29.55
29.36
29.26
27.38
25.77
22.66
14.09
f1 (ppm)

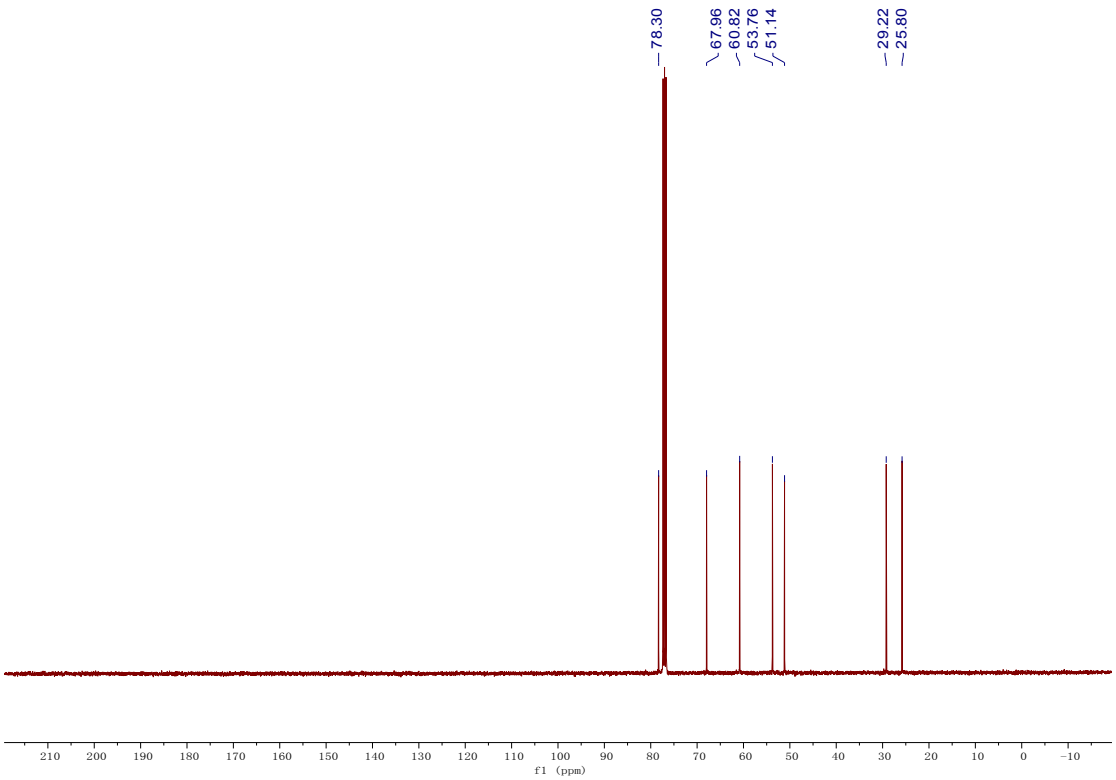

O
N
H

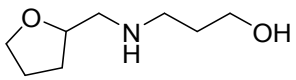

7.26
4.04
4.03
4.02
4.01
4.00
3.99
3.98
3.97
3.87
3.85
3.85
3.84
3.83
3.82
3.77
3.75
3.73
3.73
3.72
3.71
3.70
2.71
2.70
2.68
2.67
2.66
2.64
2.63
2.63
2.62
2.61
2.61
2.60
2.59
2.59
2.58
2.56
1.64
1.27
1.25
0.89
0.87
0.86
0.96
0.98
1.02
3.87
1.03
1.98
1.33
3.11
18.29
3.00
f1 (ppm)

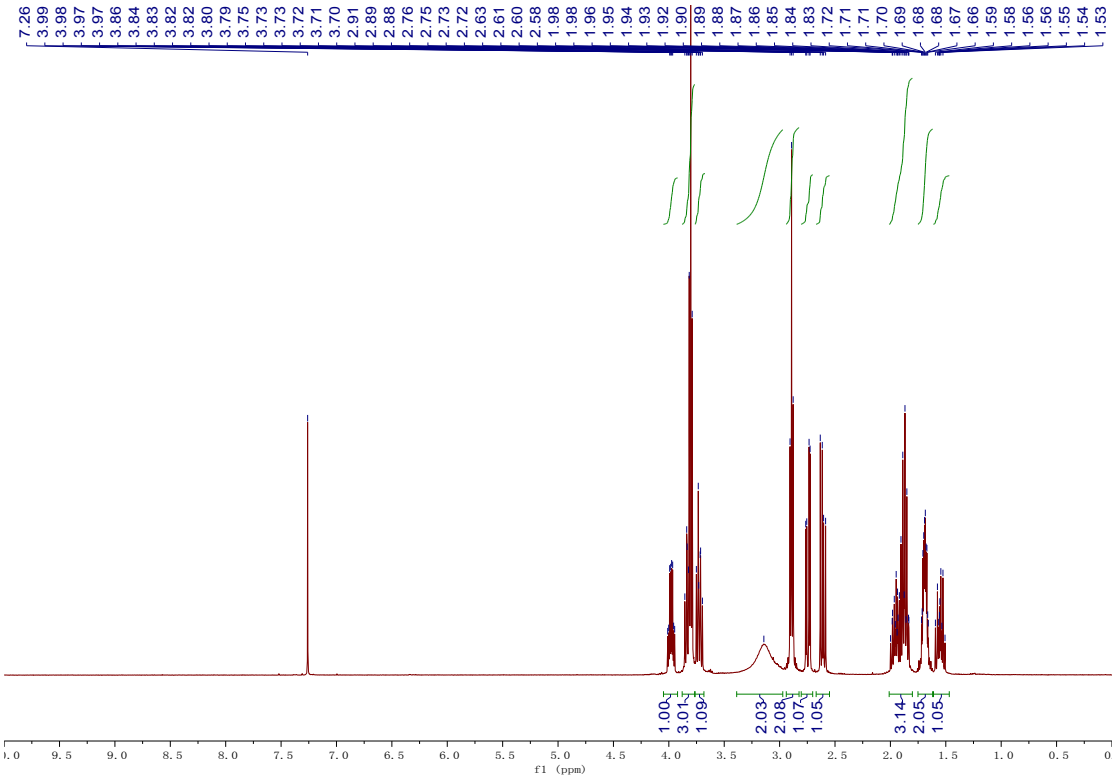

78.32
67.89
54.58
50.25
31.92
30.11
29.67
29.64
29.62
29.61
29.59
29.37
29.35
27.38
25.77
22.69
14.12
f1 (ppm)

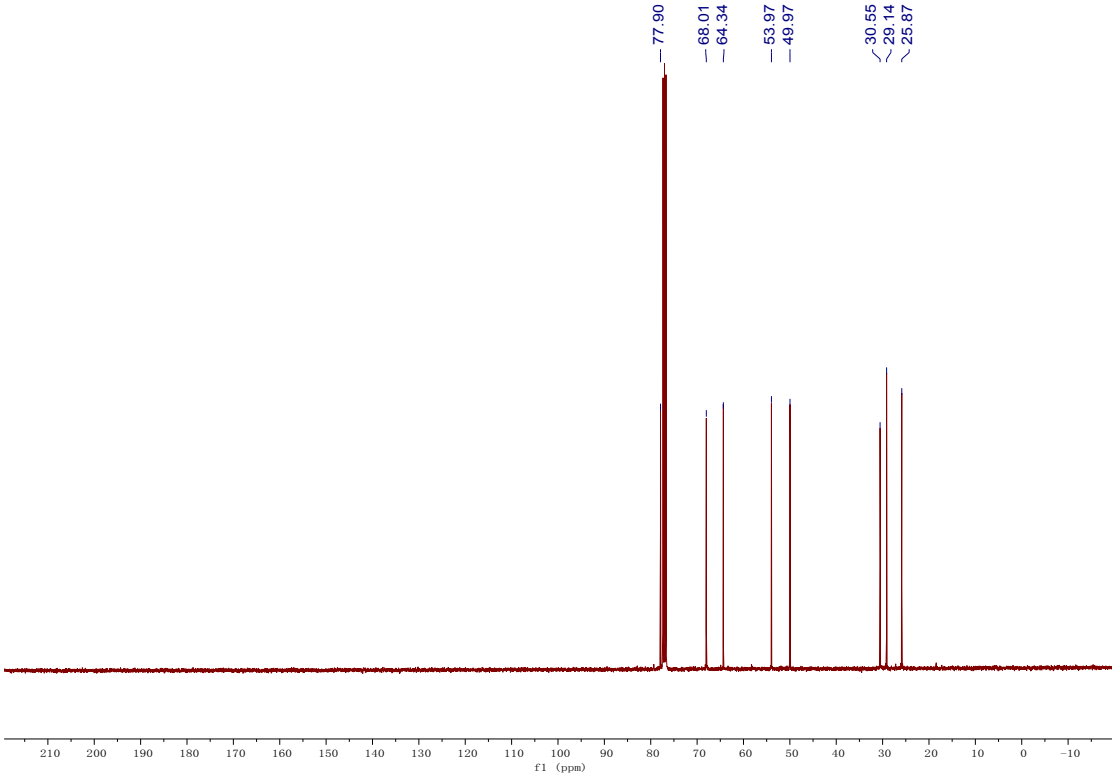

O
N
H
OH

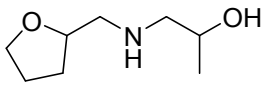

7.26
4.03
4.02
4.01
4.00
3.99
3.98
3.97
3.96
3.87
3.85
3.85
3.84
3.83
3.81
3.77
3.75
3.73
3.73
3.71
3.64
3.62
3.61
2.81
2.80
2.79
2.79
2.78
2.78
2.73
2.72
2.70
2.69
2.67
2.65
2.64
2.62
2.39
2.01
1.99
1.97
1.96
1.96
1.94
1.93
1.91
1.89
1.88
1.86
1.85
1.84
1.59
1.57
1.56
1.55
1.54
1.53
1.52
1.50
1.00
1.06
1.03
2.01
1.99
2.09
2.16
3.13
1.02
f1 (ppm)

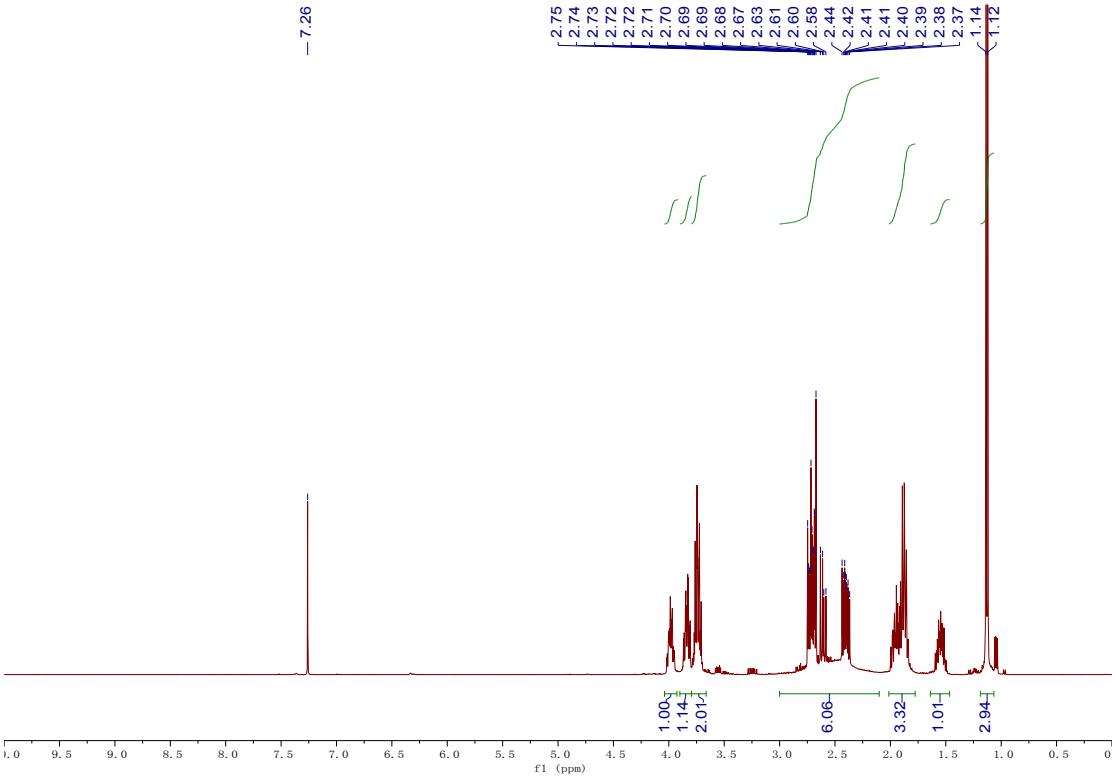

78.30
67.96
60.82
53.76
51.14
29.22
25.80
f1 (ppm)

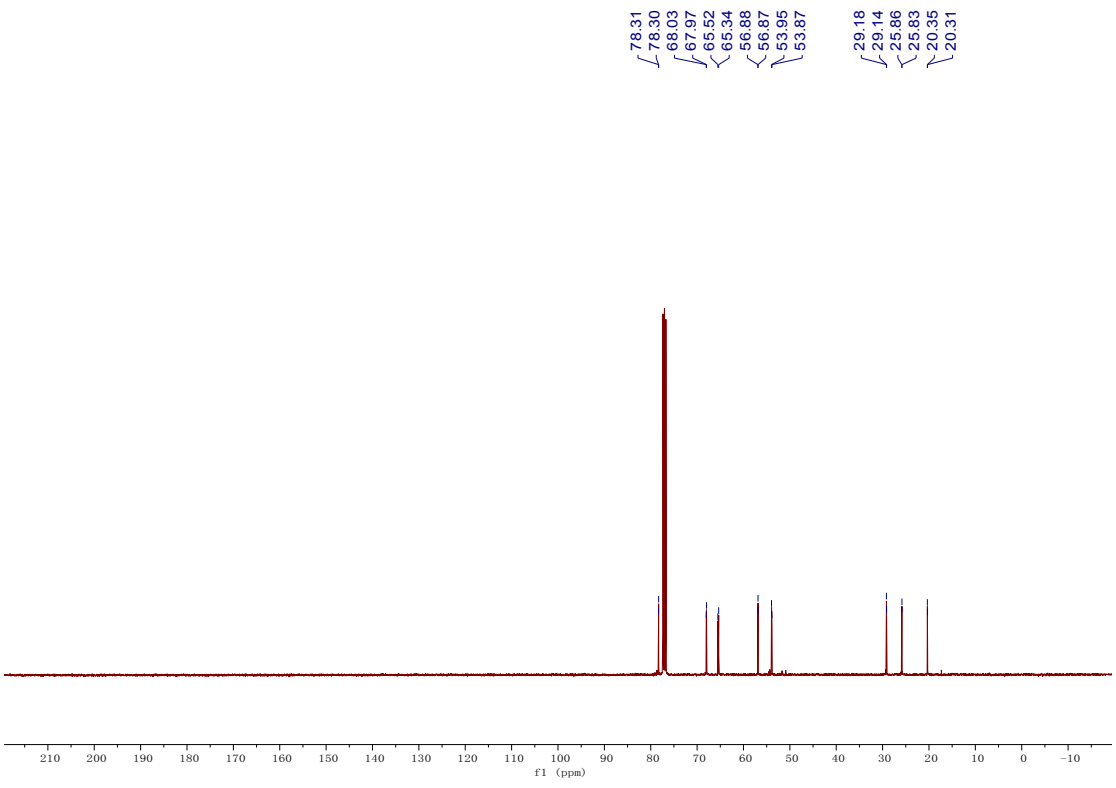

O
N
H
OH

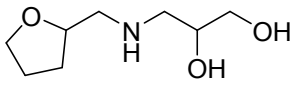

7.26
3.99
3.98
3.97
3.97
3.86
3.84
3.83
3.82
3.82
3.80
3.79
3.75
3.73
3.73
3.72
3.71
3.70
2.91
2.89
2.88
2.76
2.75
2.73
2.72
2.63
2.61
2.60
2.58
1.98
1.98
1.96
1.95
1.94
1.93
1.92
1.90
1.89
1.88
1.87
1.86
1.85
1.84
1.83
1.72
1.71
1.71
1.70
1.69
1.68
1.68
1.67
1.66
1.59
1.58
1.56
1.56
1.55
1.54
1.53
1.00
3.01
1.09
2.03
2.08
1.07
1.05
3.14
2.05
1.05
f1 (ppm)

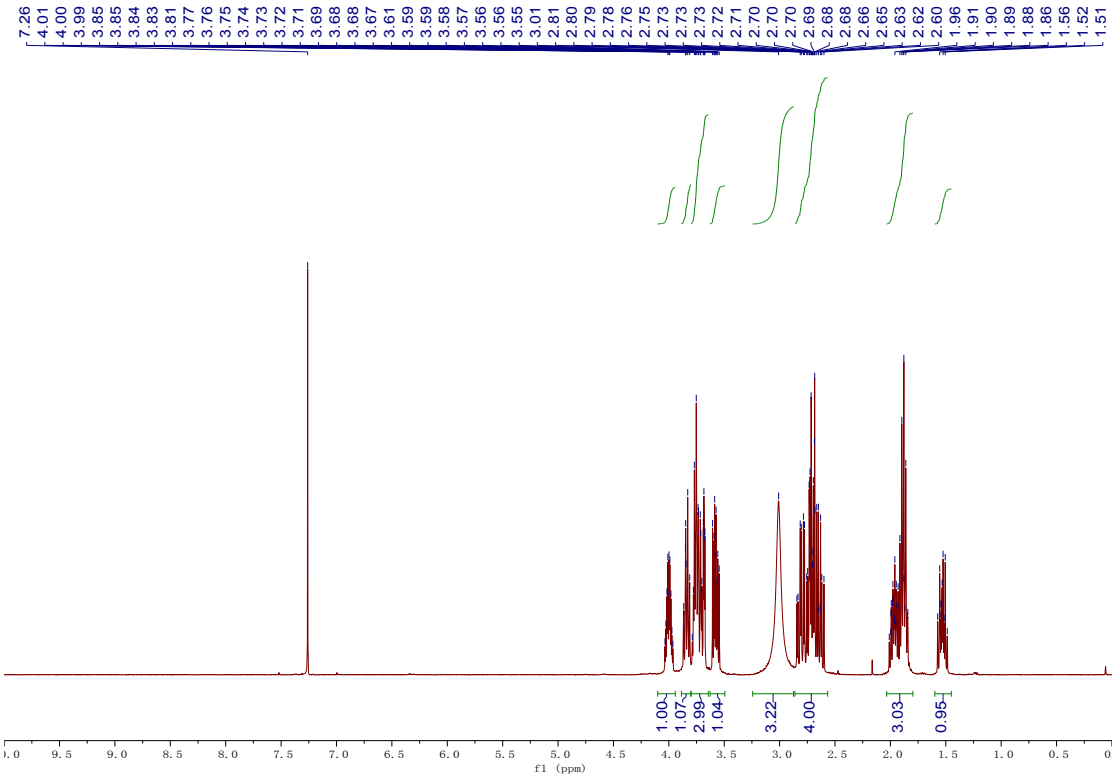

77.90
68.01
64.34
53.97
49.97
30.55
29.14
25.87
f1 (ppm)

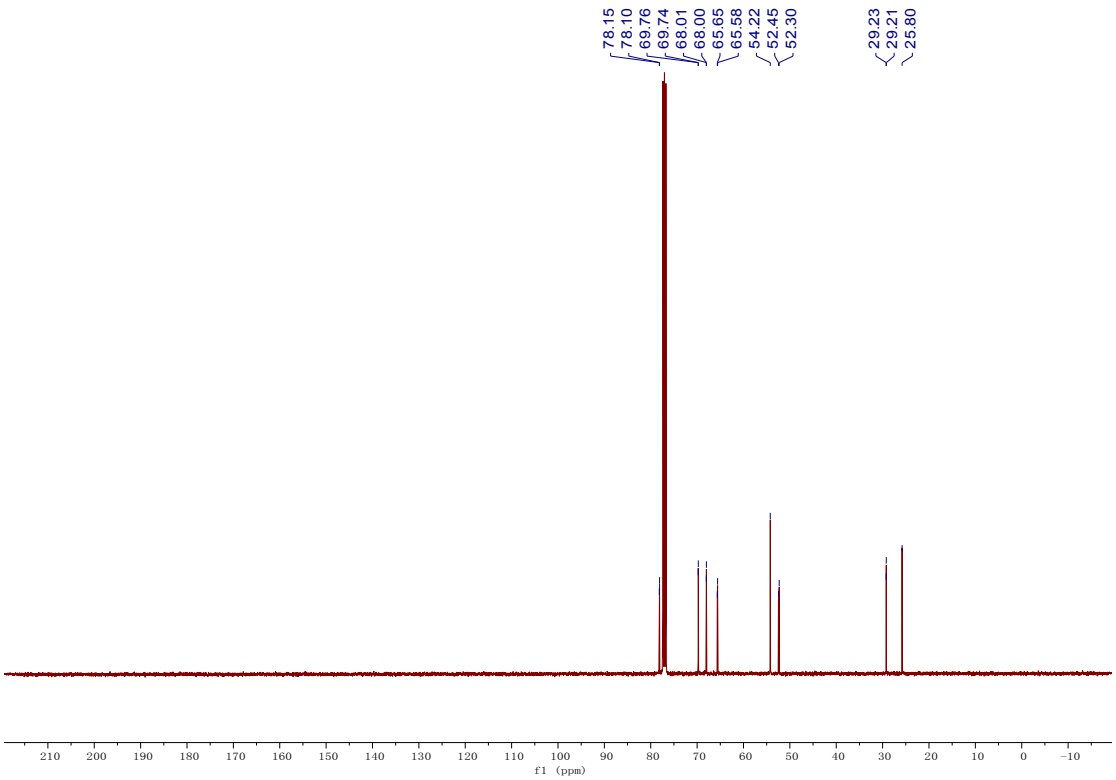

O
N
H
OH

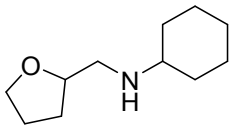

7.26
2.75
2.74
2.73
2.72
2.72
2.71
2.70
2.69
2.69
2.68
2.67
2.63
2.61
2.60
2.58
2.44
2.42
2.41
2.41
2.40
2.39
2.38
2.37
1.14
1.12
1.00
1.14
2.01
6.06
3.32
1.01
2.94
f1 (ppm)

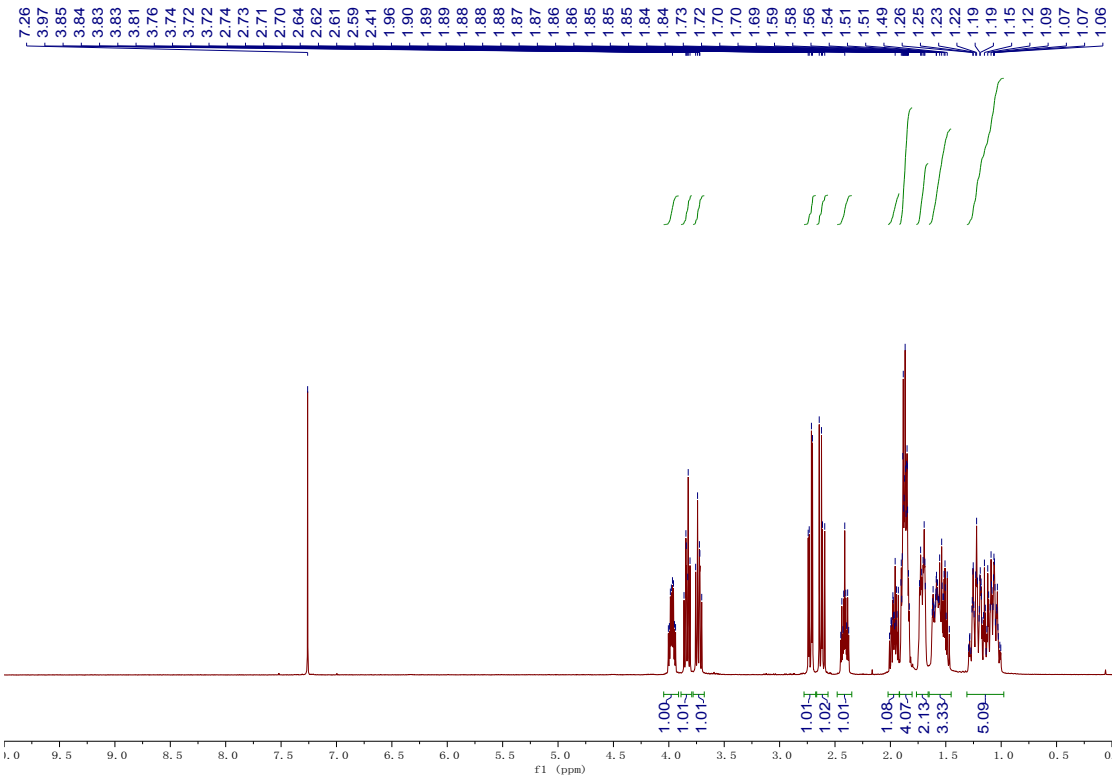

78.31
78.30
68.03
67.97
65.52
65.34
56.88
56.87
53.95
53.87
29.18
29.14
25.86
25.83
20.35
20.31
f1 (ppm)

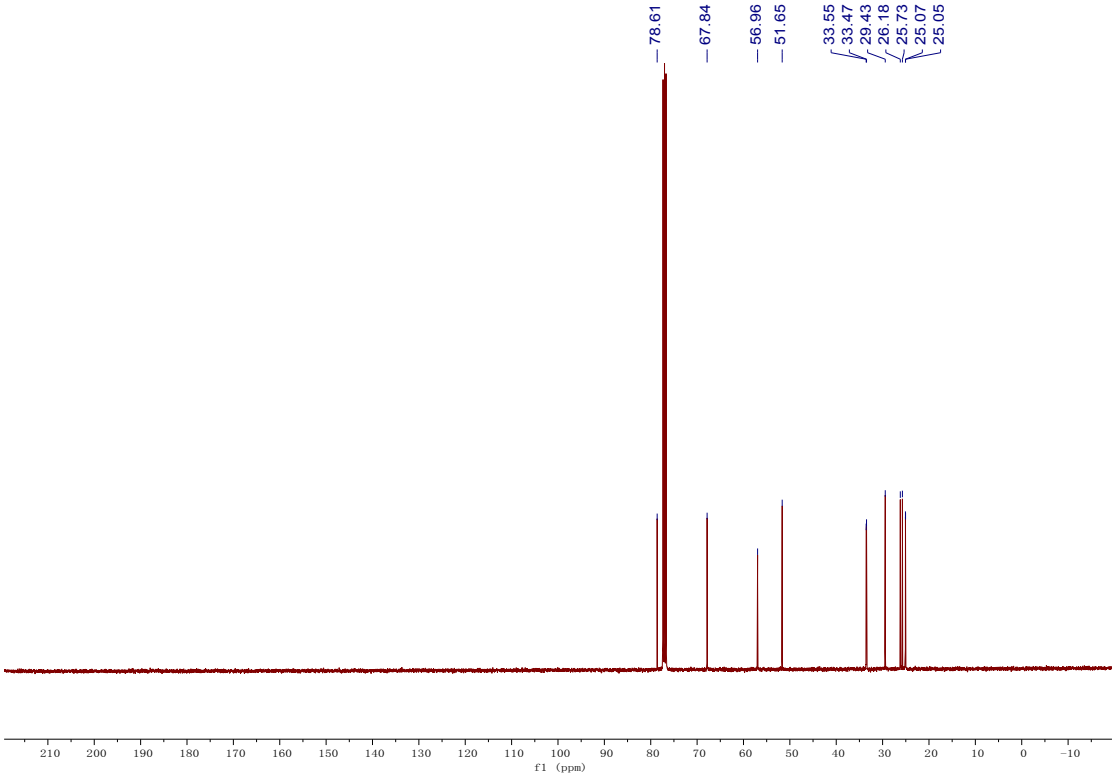

O
N
H
OH
OH

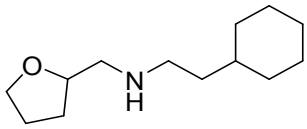

7.26
4.01
4.00
3.99
3.85
3.85
3.84
3.83
3.81
3.77
3.76
3.75
3.74
3.73
3.72
3.71
3.69
3.68
3.68
3.67
3.61
3.59
3.59
3.58
3.57
3.56
3.56
3.55
3.01
2.81
2.80
2.79
2.78
2.76
2.75
2.73
2.73
2.73
2.72
2.71
2.70
2.70
2.70
2.69
2.68
2.68
2.66
2.65
2.63
2.62
2.60
1.96
1.91
1.90
1.89
1.88
1.86
1.56
1.52
1.51
1.00
1.07
2.99
1.04
3.22
4.00
3.03
0.95
f1 (ppm)

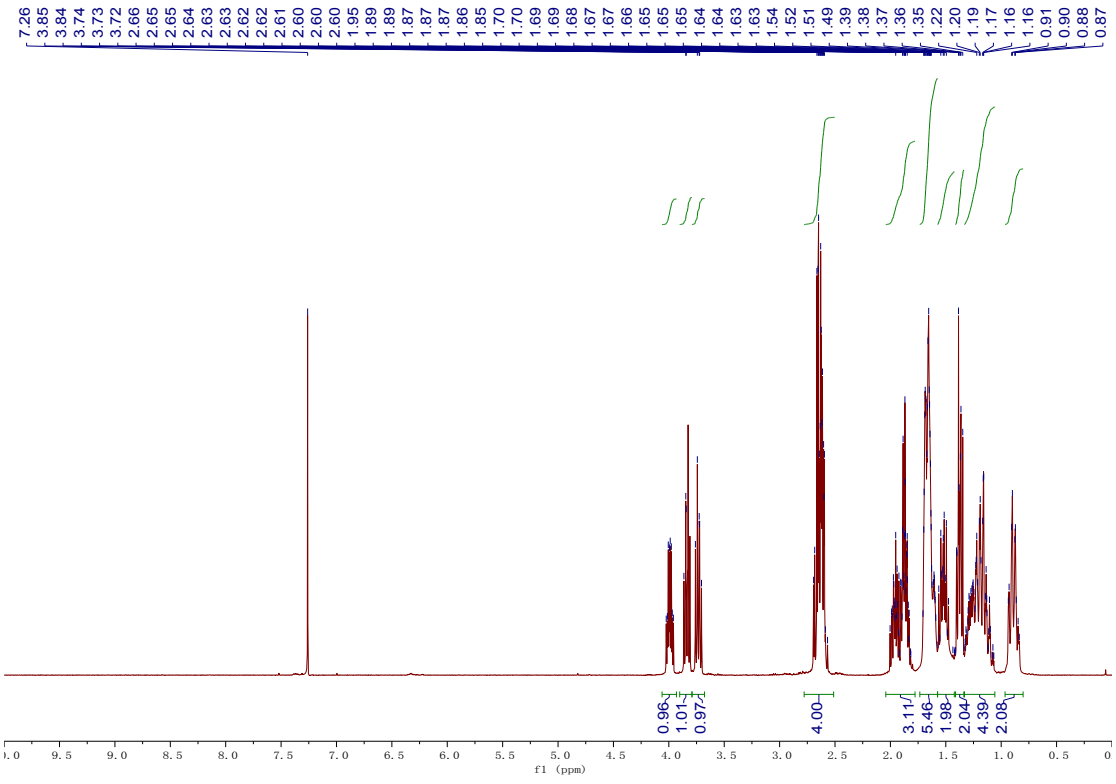

78.15
78.10
69.76
69.74
68.01
68.00
65.65
65.58
54.22
52.45
52.30
29.23
29.21
25.80
f1 (ppm)

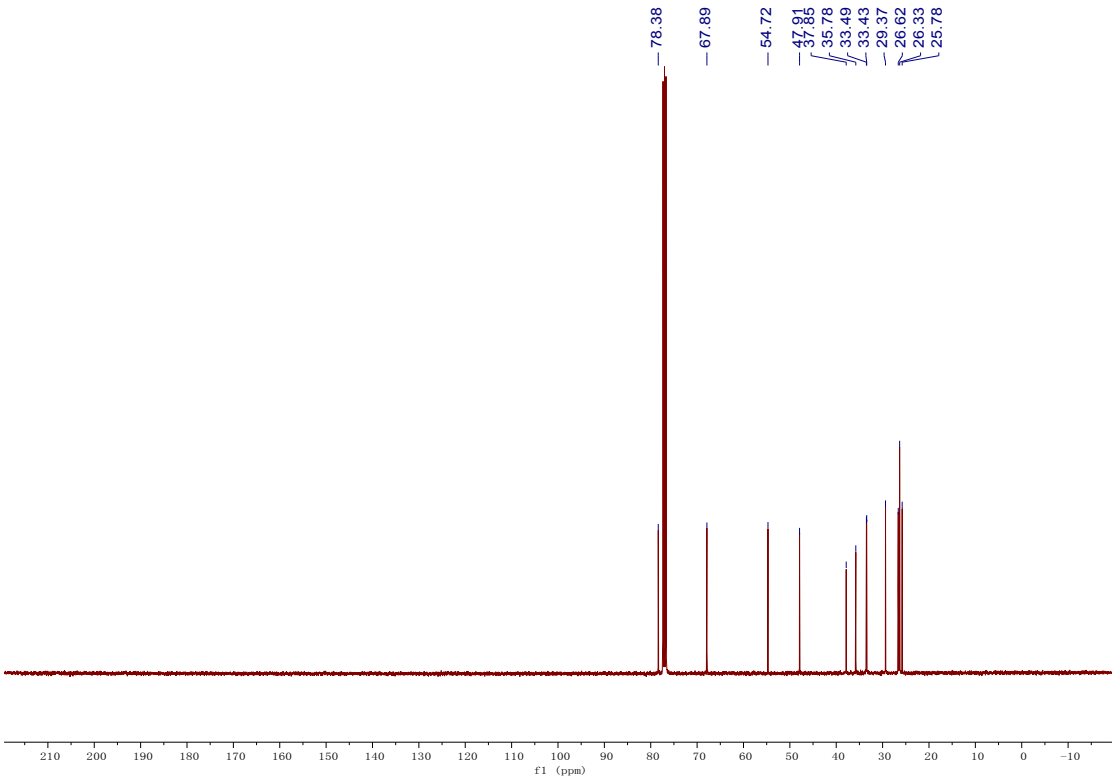

O
N
H

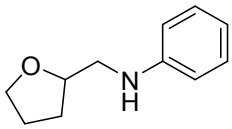

7.26
3.97
3.85
3.84
3.83
3.83
3.81
3.76
3.74
3.72
3.72
2.74
2.73
2.71
2.70
2.64
2.62
2.61
2.59
2.41
1.96
1.90
1.89
1.89
1.88
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.85
1.85
1.84
1.84
1.73
1.72
1.70
1.70
1.69
1.59
1.58
1.56
1.54
1.51
1.51
1.49
1.26
1.25
1.23
1.22
1.19
1.19
1.15
1.12
1.09
1.07
1.07
1.06
1.00
1.01
1.01
1.01
1.02
1.01
1.08
4.07
2.13
3.33
5.09
f1 (ppm)

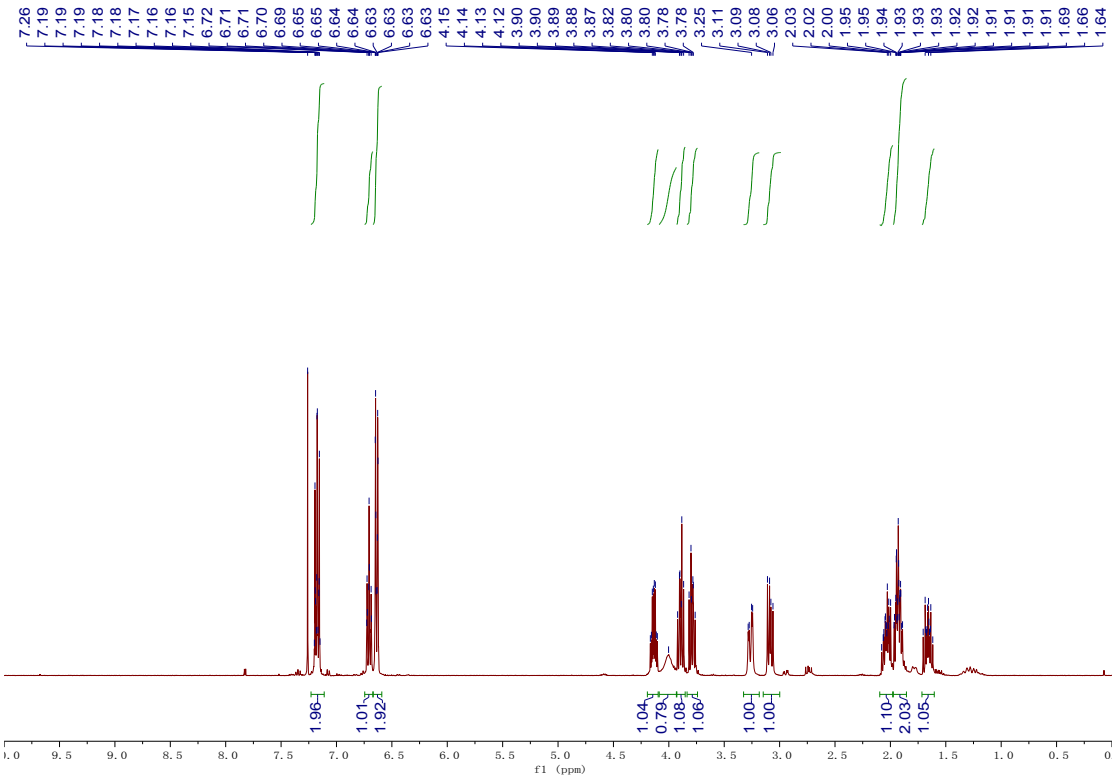

78.61
67.84
56.96
51.65
33.55
33.47
29.43
26.18
25.73
25.07
25.05
f1 (ppm)

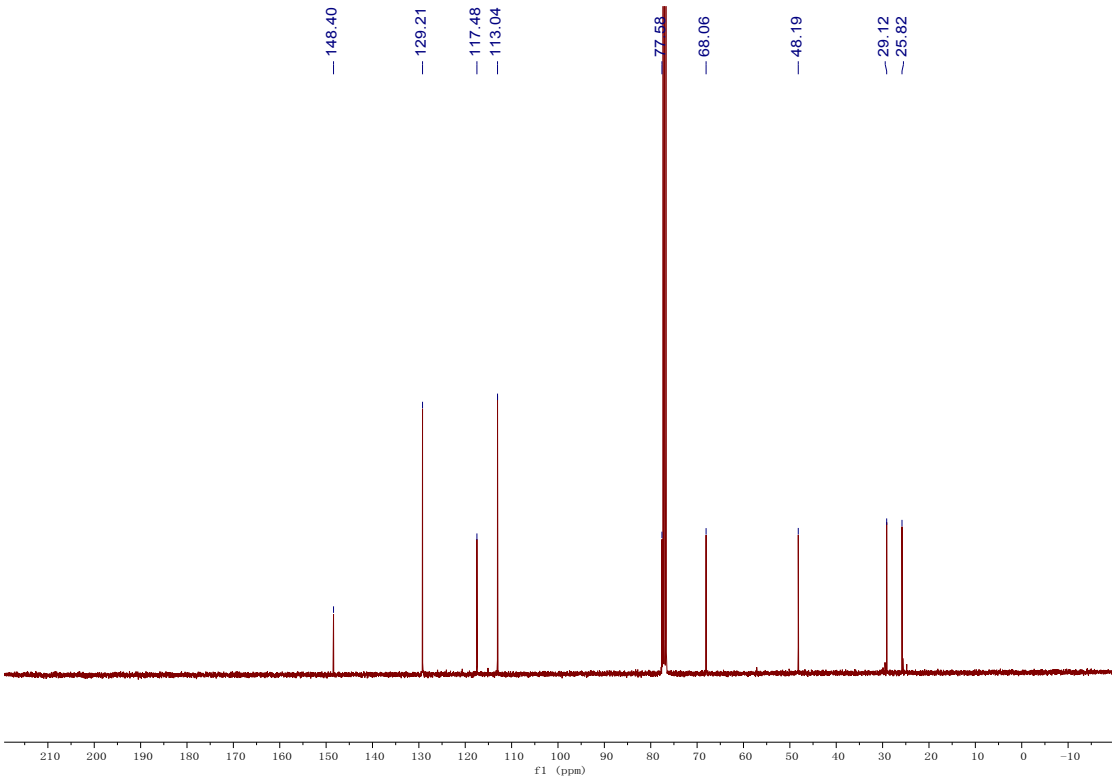

O
N
H

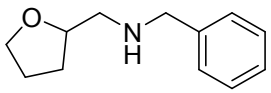

7.26
3.85
3.84
3.74
3.73
3.72
2.66
2.65
2.65
2.64
2.63
2.63
2.62
2.62
2.61
2.60
2.60
2.60
1.95
1.89
1.89
1.87
1.87
1.87
1.86
1.85
1.70
1.70
1.69
1.69
1.68
1.67
1.67
1.66
1.65
1.65
1.65
1.64
1.64
1.63
1.63
1.54
1.52
1.51
1.49
1.39
1.38
1.37
1.36
1.35
1.22
1.20
1.19
1.17
1.16
1.16
0.91
0.90
0.88
0.87
0.96
1.01
0.97
4.00
3.11
5.46
1.98
2.04
4.39
2.08
f1 (ppm)

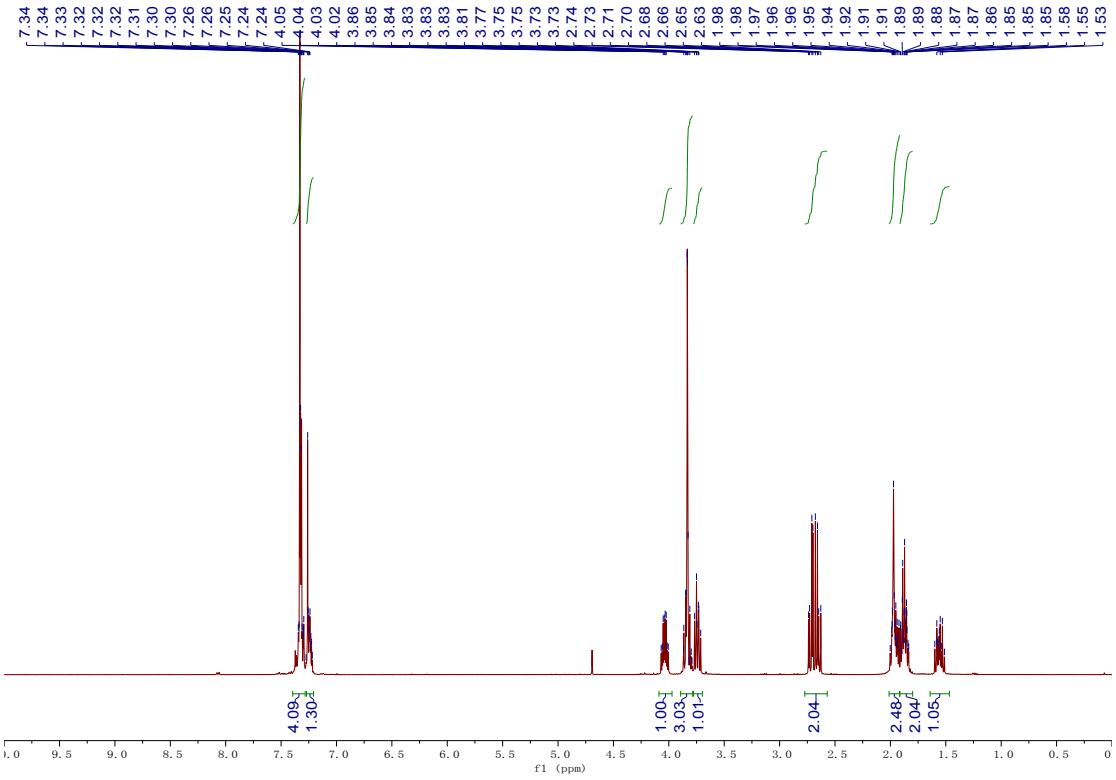

78.38
67.89
54.72
47.91
37.85
35.78
33.49
33.43
29.37
26.62
26.33
25.78
f1 (ppm)

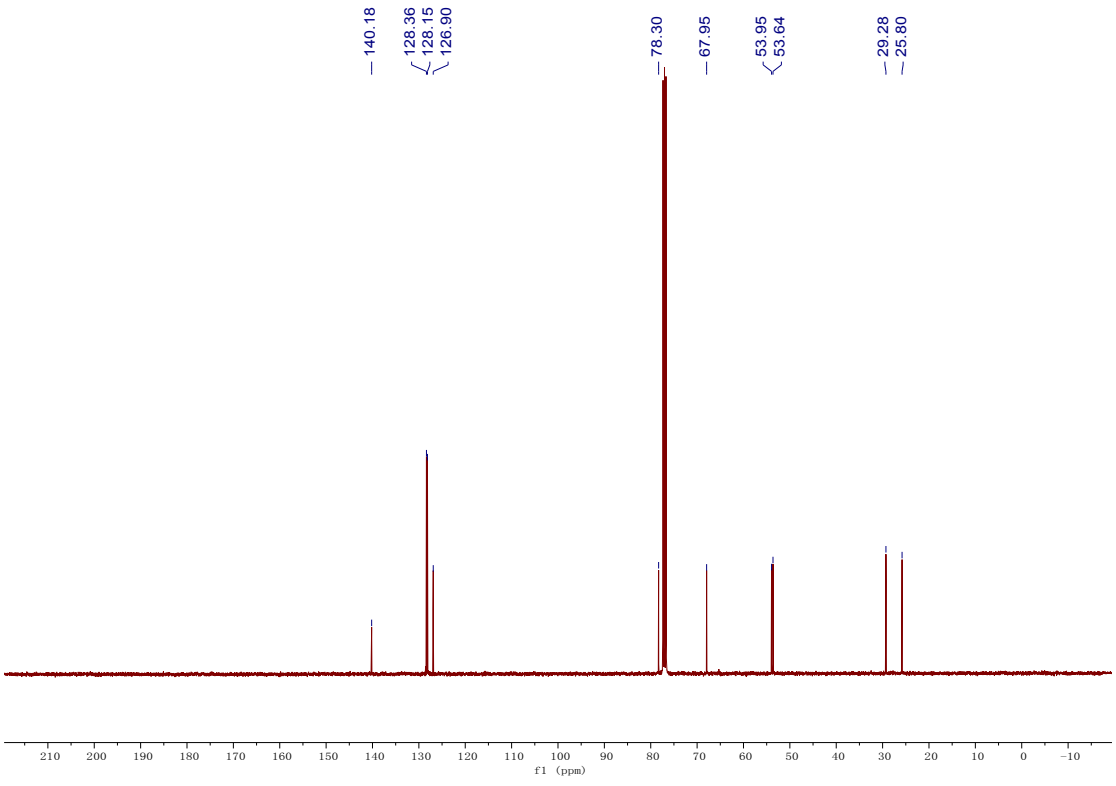

O
N
H

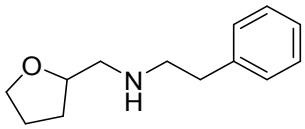

7.26
7.19
7.19
7.19
7.18
7.18
7.17
7.16
7.16
7.15
6.72
6.71
6.71
6.70
6.69
6.65
6.65
6.64
6.64
6.63
6.63
6.63
6.63
4.15
4.14
4.13
4.12
3.90
3.90
3.89
3.88
3.87
3.82
3.80
3.80
3.78
3.78
3.25
3.11
3.09
3.08
3.06
2.03
2.02
2.00
1.95
1.95
1.94
1.93
1.93
1.93
1.92
1.92
1.91
1.91
1.91
1.91
1.69
1.66
1.64
1.96
1.01
1.92
1.04
0.79
1.08
1.06
1.00
1.00
1.10
2.03
1.05
f1 (ppm)

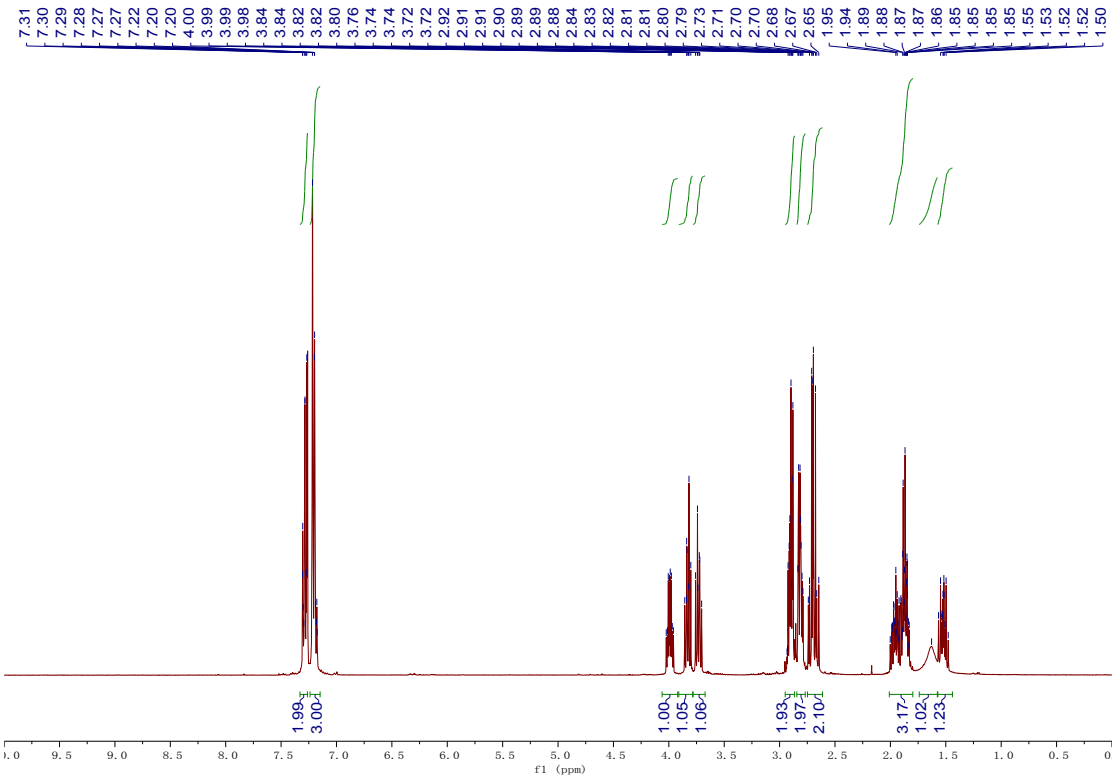

148.40
129.21
117.48
113.04
77.58
68.06
48.19
29.12
25.82
f1 (ppm)

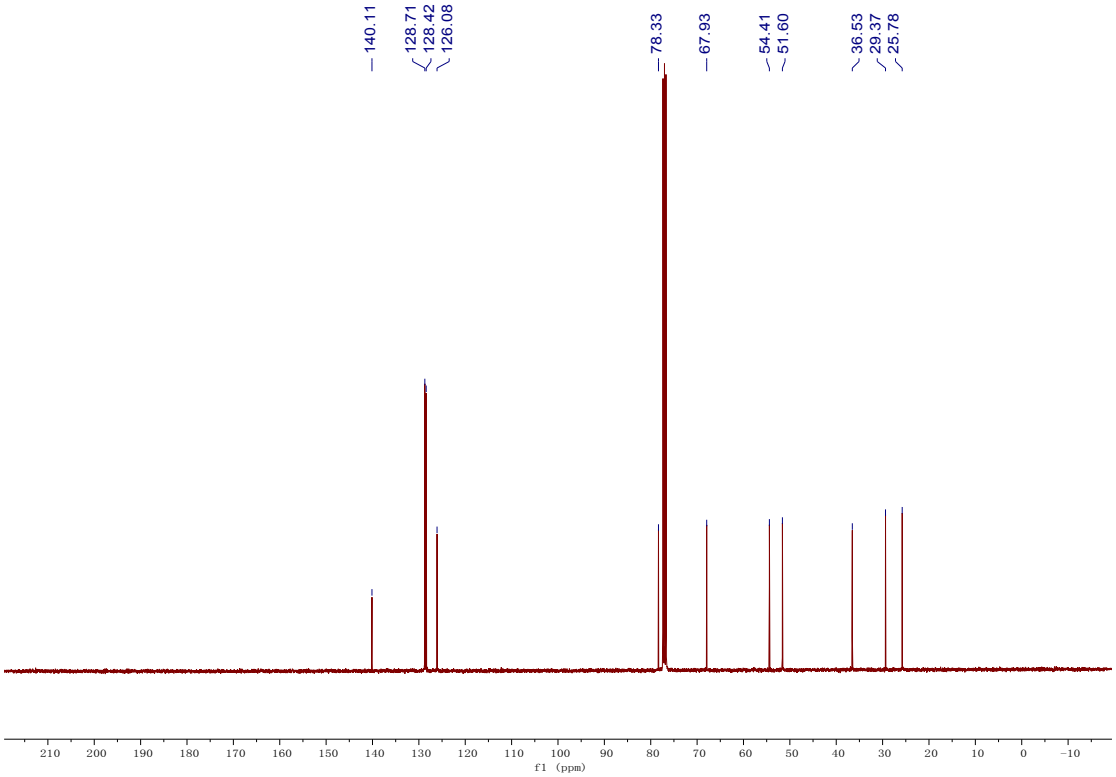

O
N
H

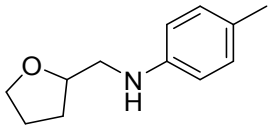

7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.26
7.26
7.25
7.24
7.24
4.05
4.04
4.03
4.02
3.86
3.85
3.84
3.83
3.83
3.83
3.81
3.77
3.75
3.75
3.73
3.73
2.74
2.73
2.71
2.70
2.68
2.66
2.65
2.63
1.98
1.97
1.96
1.96
1.95
1.94
1.92
1.91
1.91
1.89
1.89
1.88
1.87
1.87
1.86
1.85
1.85
1.85
1.58
1.55
1.53
4.09
1.30
1.00
3.03
1.01
2.04
2.48
2.04
1.05
f1 (ppm)

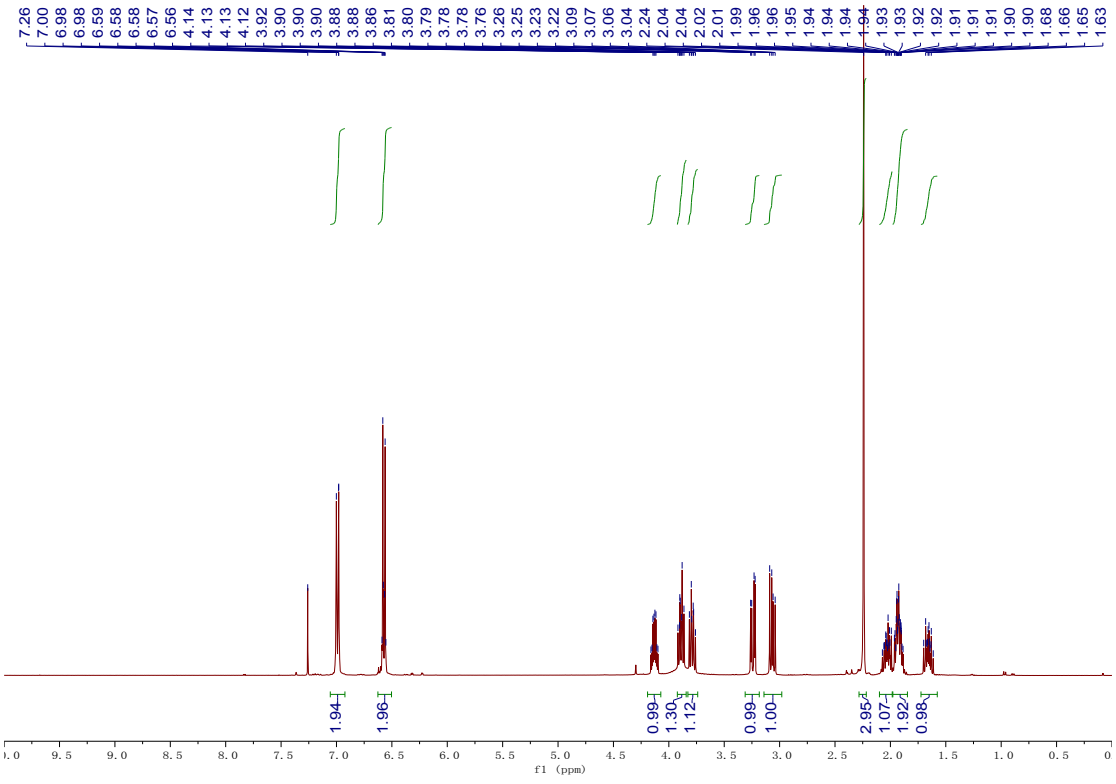

140.18
128.36
128.15
126.90
78.30
67.95
53.95
53.64
29.28
25.80
f1 (ppm)

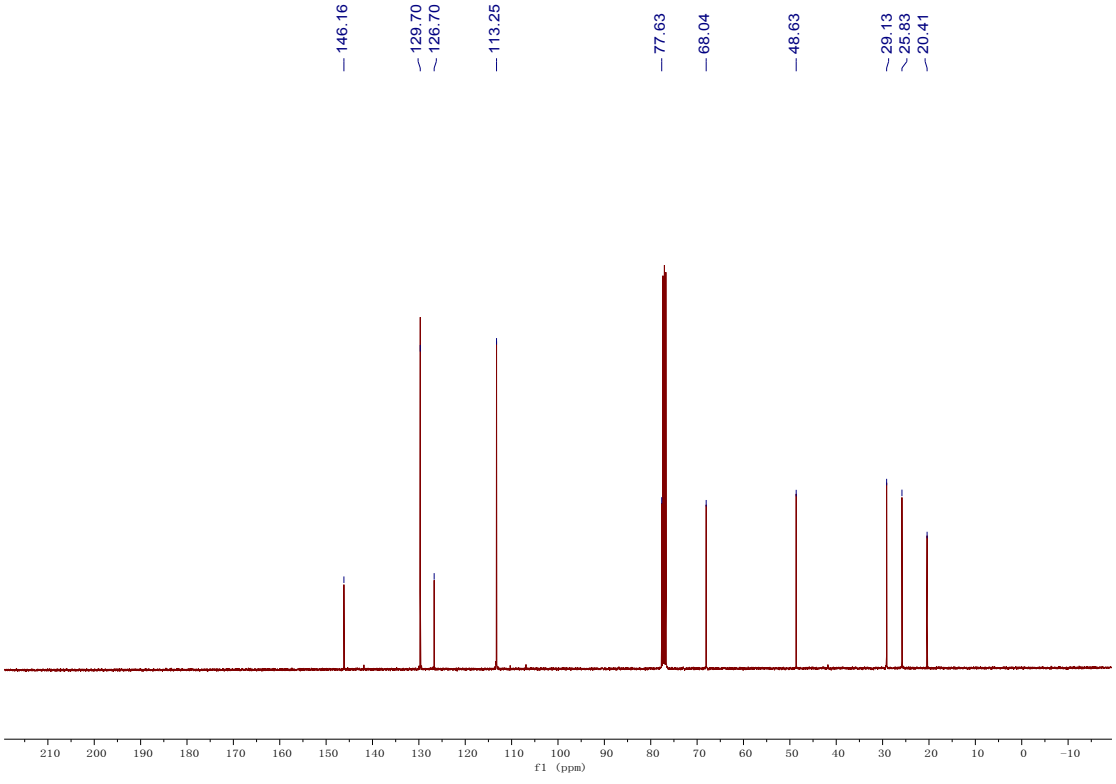

O
N
H

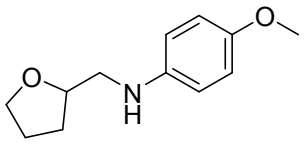

7.31
7.30
7.29
7.28
7.27
7.27
7.22
7.20
7.20
4.00
3.99
3.99
3.98
3.84
3.84
3.82
3.82
3.80
3.76
3.74
3.74
3.72
3.72
2.92
2.91
2.91
2.90
2.89
2.89
2.88
2.84
2.83
2.82
2.81
2.81
2.80
2.79
2.73
2.71
2.70
2.70
2.68
2.67
2.65
1.95
1.94
1.89
1.88
1.87
1.87
1.86
1.85
1.85
1.85
1.85
1.55
1.53
1.52
1.52
1.50
1.99
3.00
1.00
1.05
1.06
1.93
1.97
2.10
3.17
1.02
1.23
f1 (ppm)

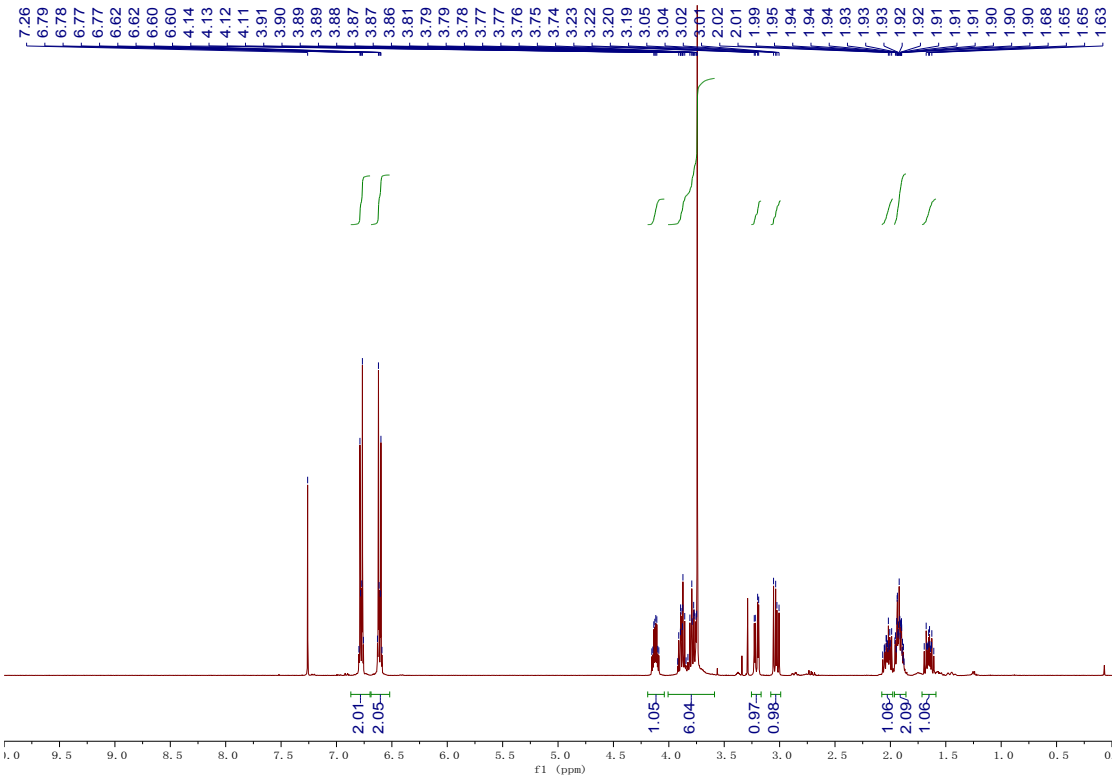

140.11
128.71
128.42
126.08
78.33
67.93
54.41
51.60
36.53
29.37
25.78
f1 (ppm)

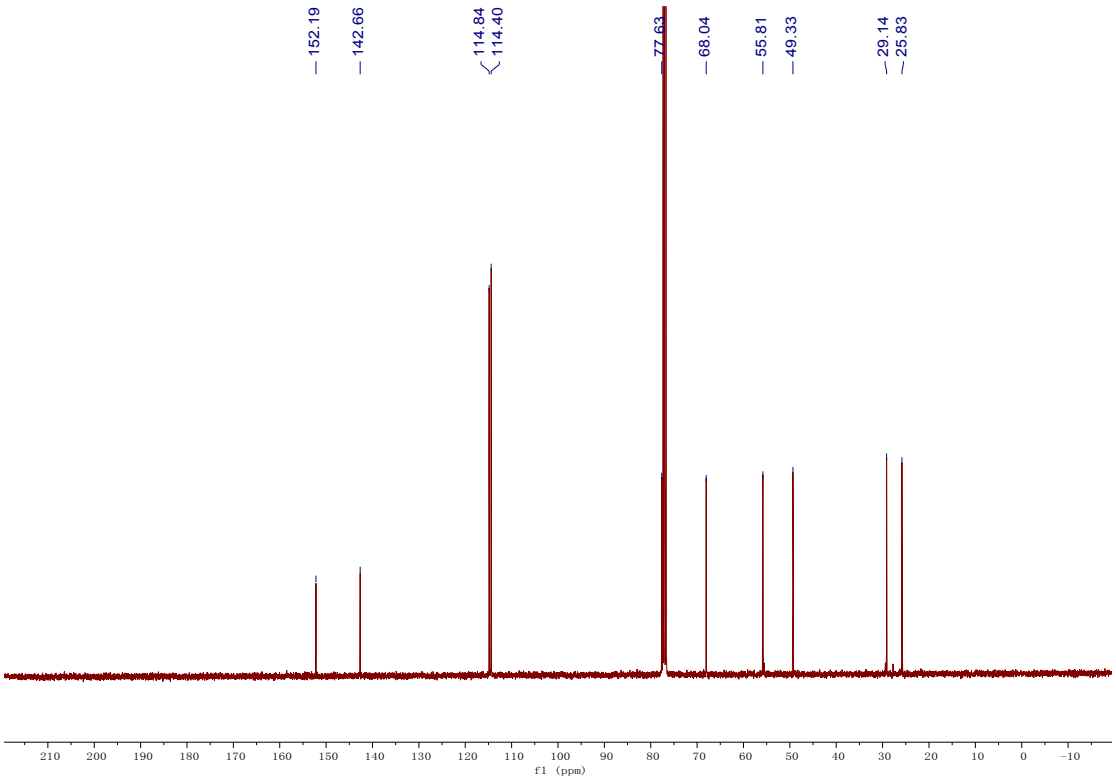

O
N
H

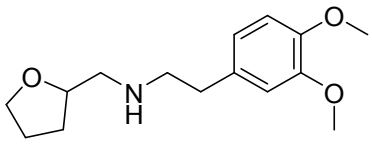

7.26
7.00
6.98
6.98
6.59
6.58
6.58
6.57
6.56
4.14
4.13
4.13
4.12
3.92
3.90
3.90
3.90
3.88
3.88
3.86
3.81
3.80
3.79
3.78
3.78
3.76
3.26
3.25
3.23
3.22
3.09
3.07
3.06
3.04
2.24
2.04
2.04
2.02
2.01
1.99
1.96
1.96
1.95
1.94
1.94
1.94
1.94
1.93
1.93
1.92
1.91
1.91
1.91
1.90
1.90
1.68
1.66
1.65
1.63
1.94
1.96
0.99
1.30
1.12
0.99
1.00
2.95
1.07
1.92
0.98
f1 (ppm)

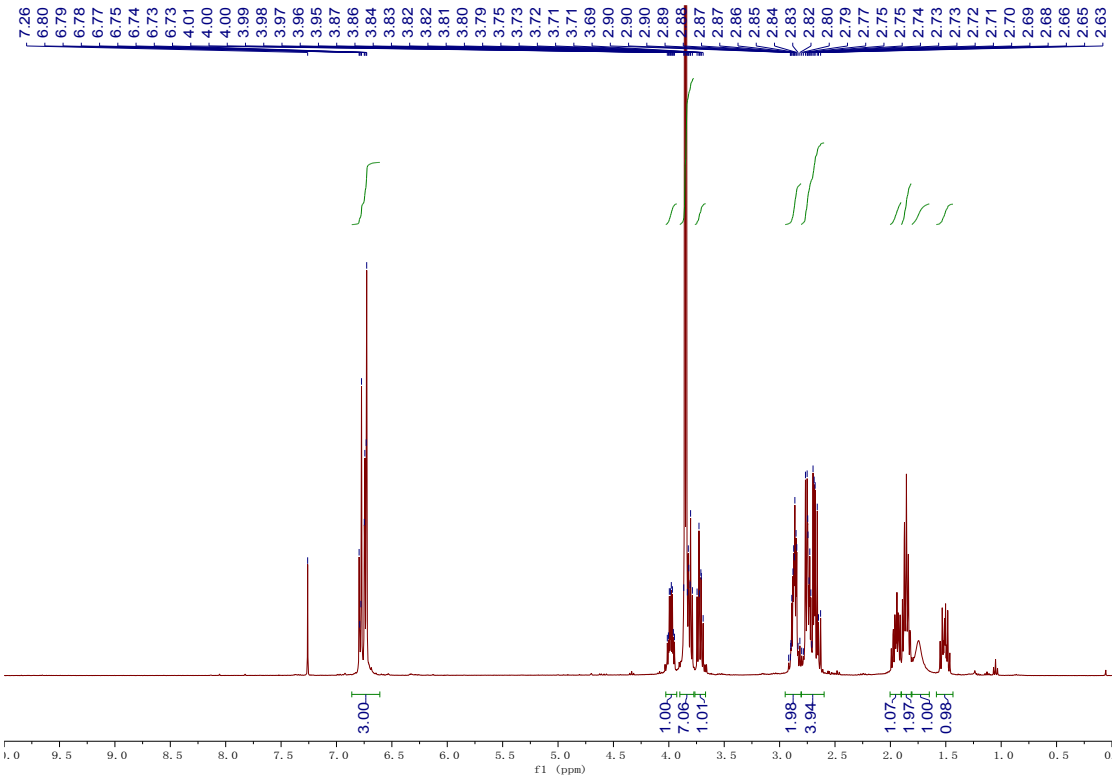

146.16
129.70
126.70
113.25
77.63
68.04
48.63
29.13
25.83
20.41
f1 (ppm)

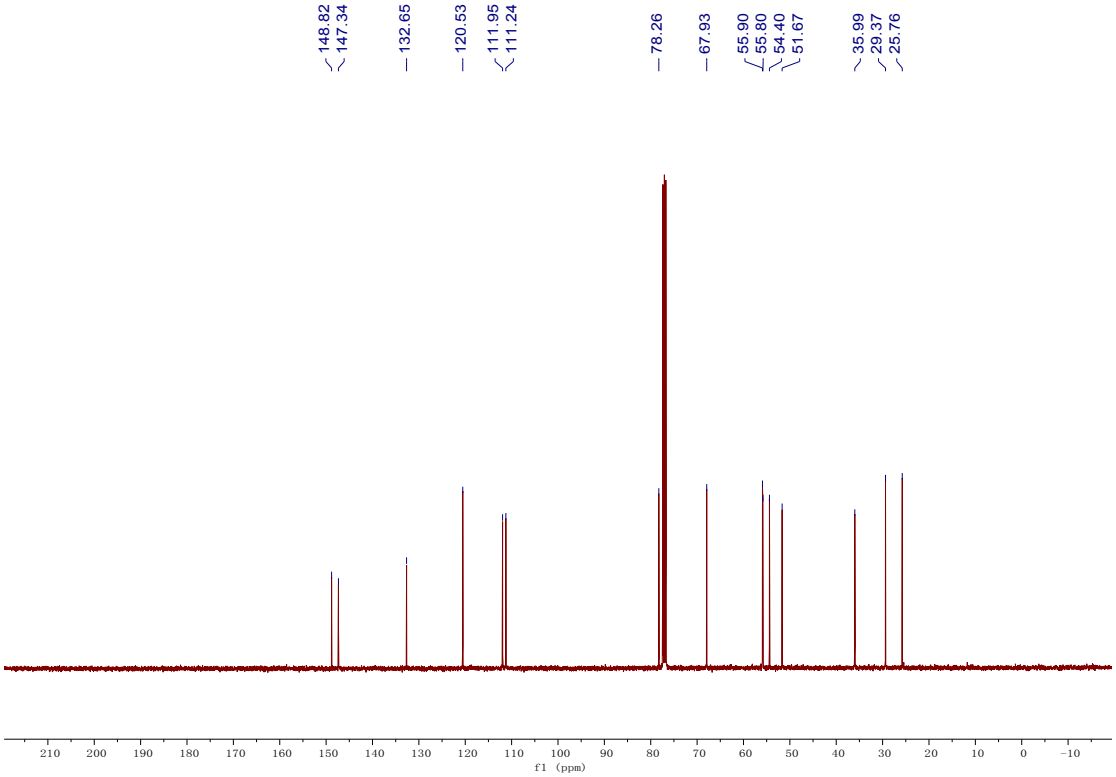

O
N
H
O

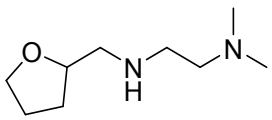

7.26
6.79
6.78
6.77
6.77
6.62
6.62
6.60
6.60
4.14
4.13
4.12
4.11
3.91
3.90
3.89
3.89
3.88
3.87
3.87
3.86
3.81
3.79
3.79
3.78
3.77
3.77
3.76
3.75
3.74
3.23
3.22
3.20
3.19
3.05
3.04
3.02
3.01
2.02
2.01
1.99
1.95
1.94
1.94
1.94
1.93
1.93
1.93
1.92
1.92
1.91
1.91
1.91
1.90
1.90
1.90
1.68
1.65
1.65
1.63
2.01
2.05
1.05
6.04
0.97
0.98
1.06
2.09
1.06
f1 (ppm)

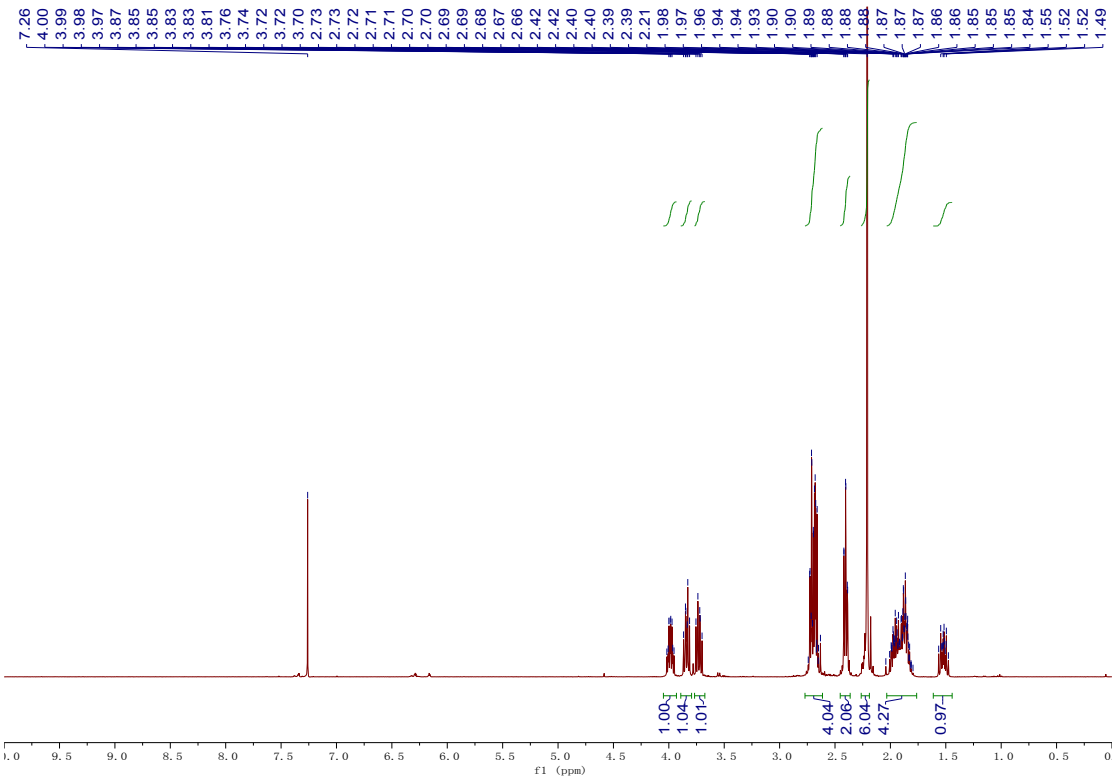

152.19
142.66
114.84
114.40
77.63
68.04
55.81
49.33
29.14
25.83
f1 (ppm)

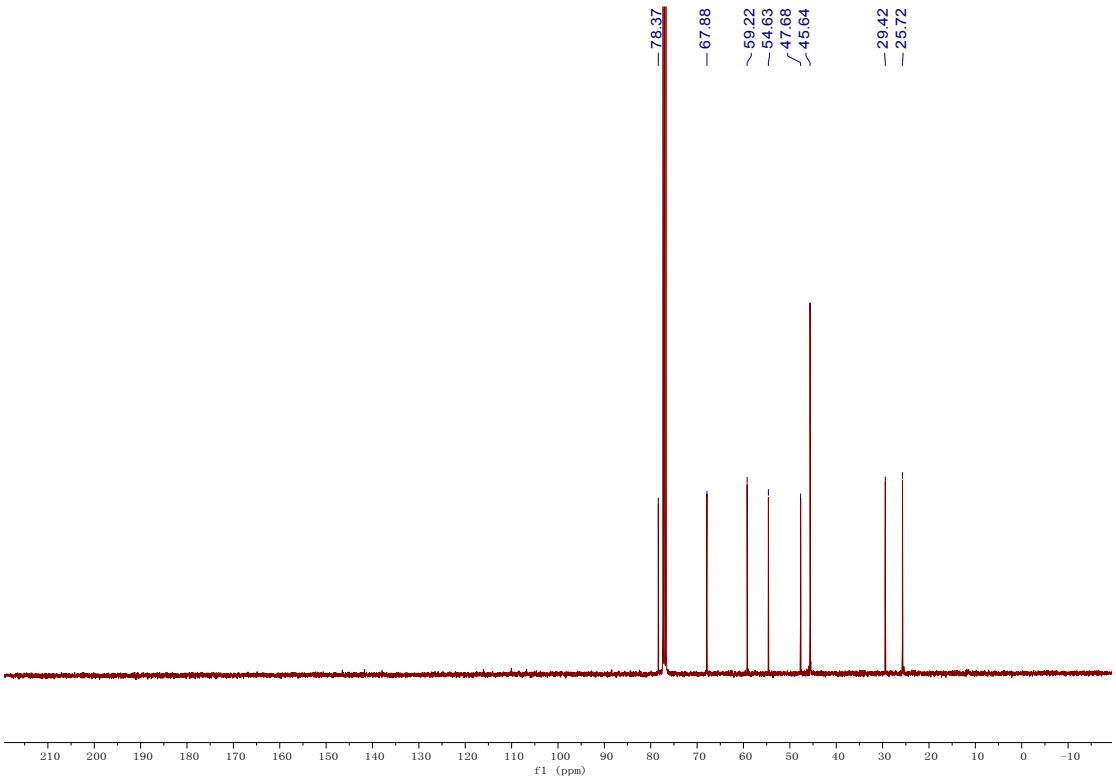

O
N
H
O
O

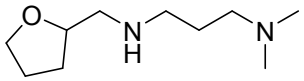

7.26
6.80
6.79
6.78
6.77
6.75
6.74
6.73
6.73
4.01
4.00
4.00
3.99
3.98
3.97
3.96
3.95
3.87
3.86
3.84
3.83
3.82
3.82
3.81
3.80
3.79
3.75
3.73
3.72
3.71
3.71
3.69
2.90
2.90
2.89
2.88
2.87
2.86
2.85
2.84
2.83
2.82
2.80
2.79
2.77
2.75
2.75
2.74
2.73
2.73
2.72
2.71
2.70
2.69
2.68
2.66
2.65
2.63
3.00
1.00
7.06
1.01
1.98
3.94
1.07
1.97
1.00
0.98
f1 (ppm)

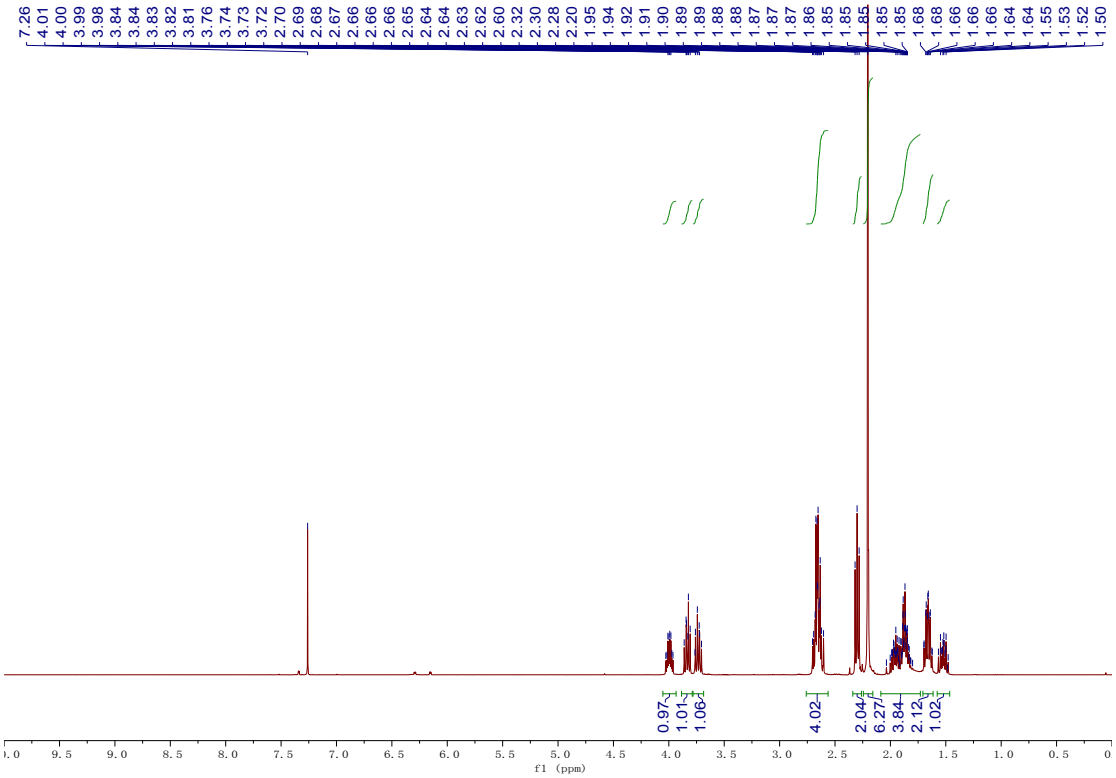

148.82
147.34
132.65
120.53
111.95
111.24
78.26
67.93
55.90
55.80
54.40
51.67
35.99
29.37
25.76
f1 (ppm)

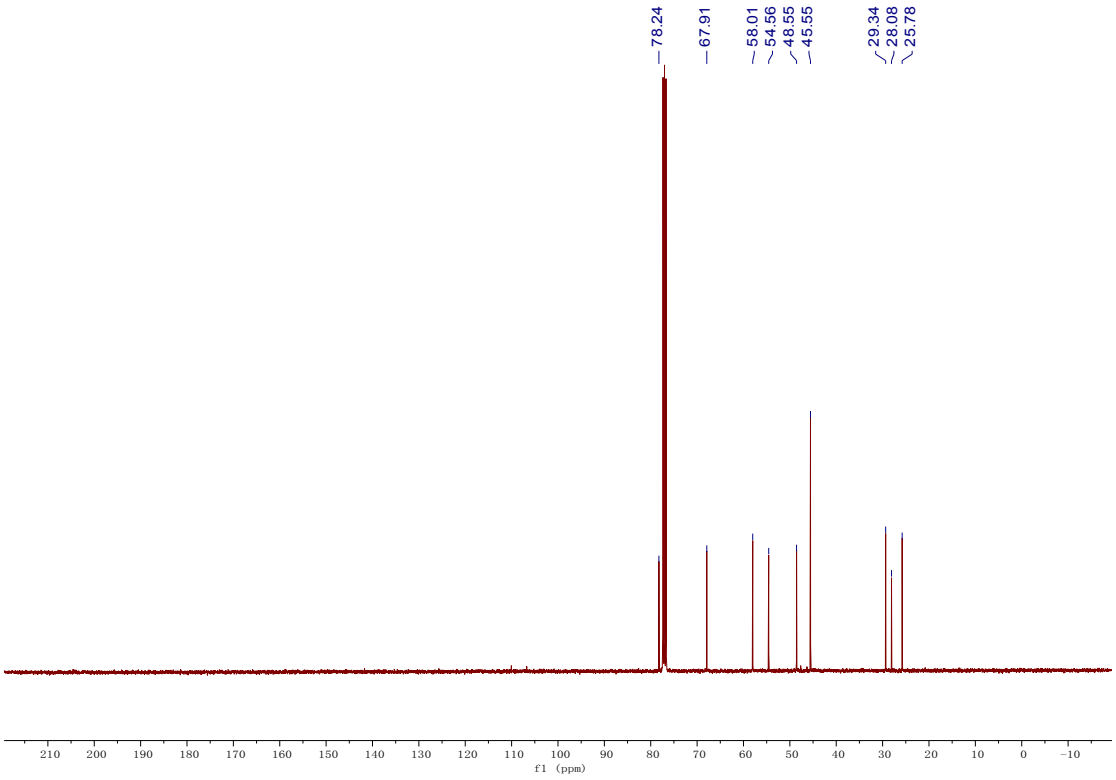

O
N
H
N

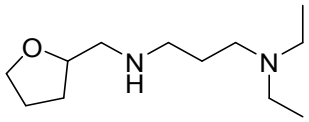

7.26
4.00
3.99
3.98
3.97
3.87
3.85
3.85
3.83
3.83
3.81
3.76
3.74
3.72
3.72
3.70
2.73
2.73
2.72
2.71
2.71
2.70
2.70
2.69
2.69
2.68
2.67
2.66
2.42
2.42
2.40
2.40
2.39
2.39
2.21
1.98
1.97
1.96
1.94
1.94
1.93
1.90
1.90
1.89
1.88
1.88
1.88
1.87
1.87
1.87
1.86
1.86
1.85
1.85
1.85
1.84
1.55
1.52
1.52
1.49
1.00
1.04
1.01
4.04
2.06
6.04
4.27
0.97
f1 (ppm)

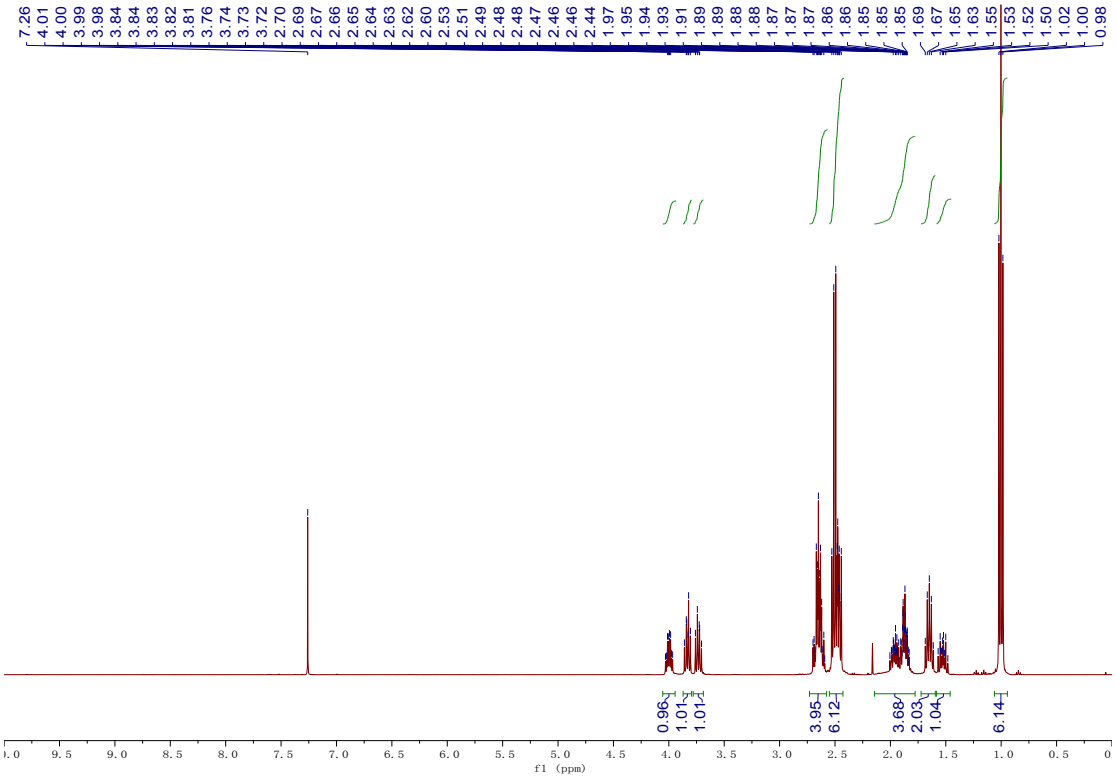

78.37
67.88
59.22
54.63
47.68
45.64
29.42
25.72
f1 (ppm)

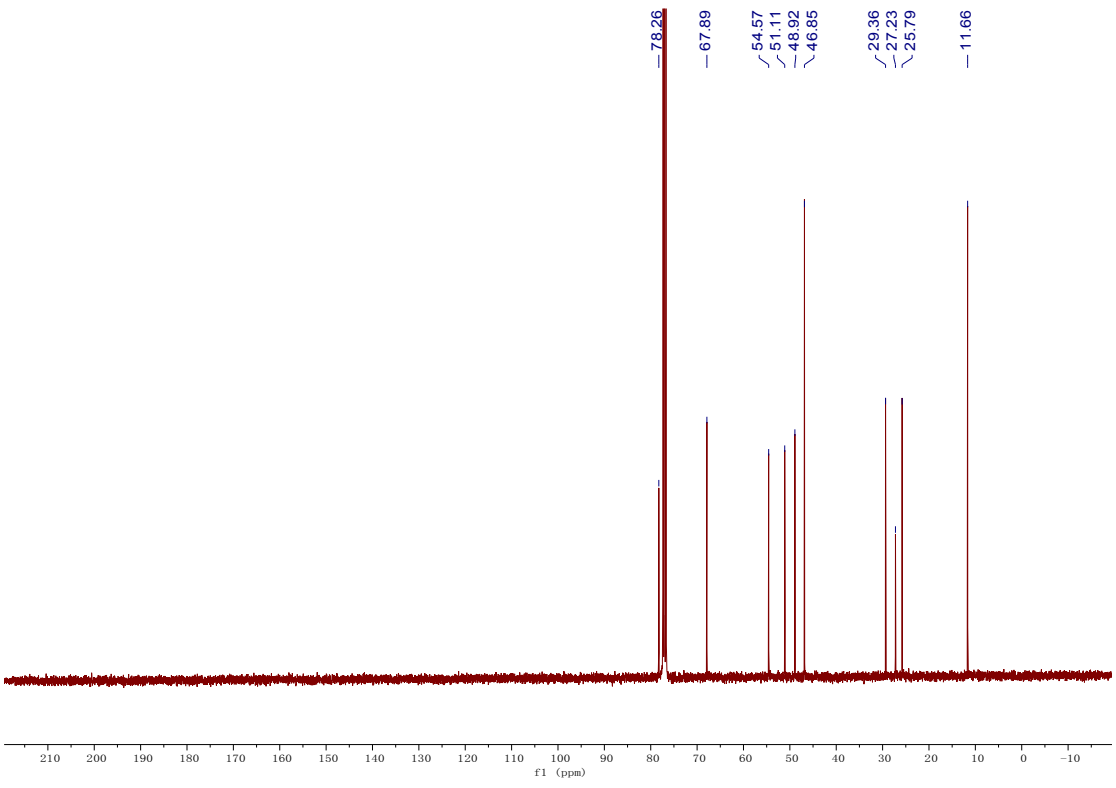

O
N
H
N

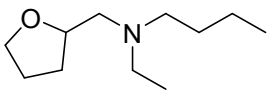

7.26
4.01
4.00
3.99
3.98
3.84
3.84
3.83
3.82
3.81
3.76
3.74
3.73
3.72
2.70
2.69
2.68
2.67
2.66
2.66
2.66
2.65
2.64
2.64
2.63
2.62
2.60
2.32
2.30
2.28
2.20
1.95
1.94
1.92
1.91
1.90
1.89
1.89
1.88
1.88
1.87
1.87
1.87
1.86
1.85
1.85
1.85
1.85
1.85
1.68
1.68
1.66
1.66
1.66
1.64
1.64
1.55
1.53
1.52
1.50
0.97
1.01
1.06
4.02
2.04
6.27
3.84
2.12
1.02
f1 (ppm)

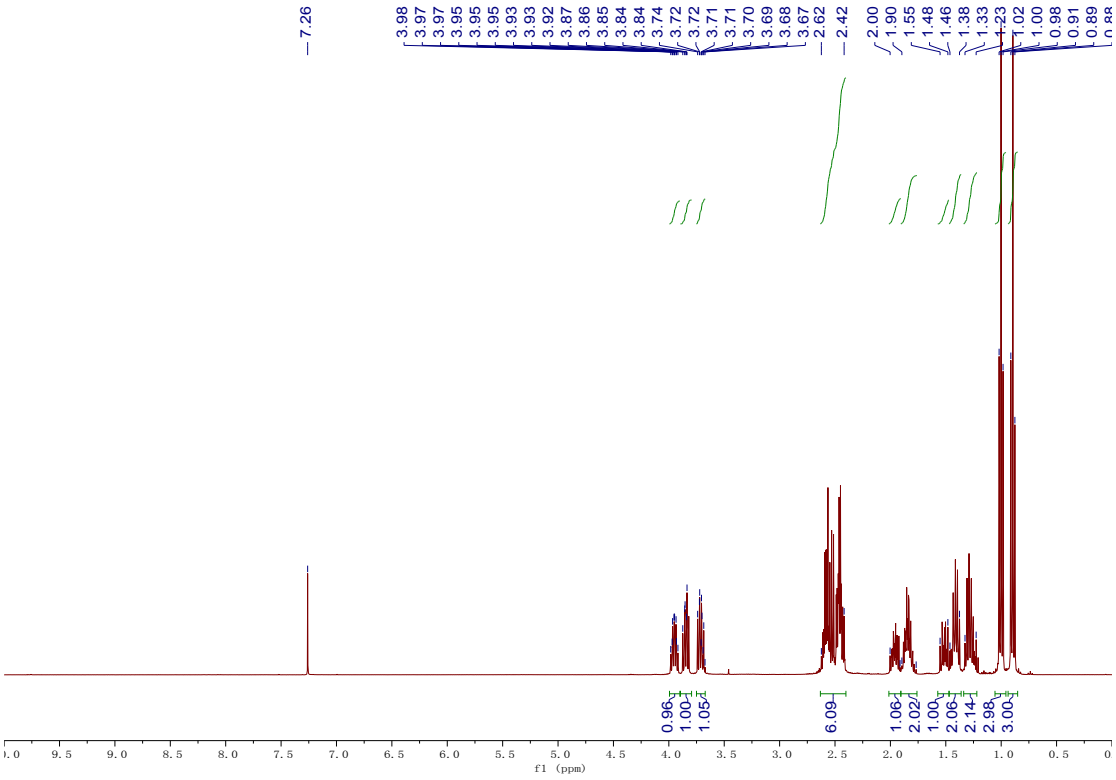

78.24
67.91
58.01
54.56
48.55
45.55
29.34
28.08
25.78
f1 (ppm)

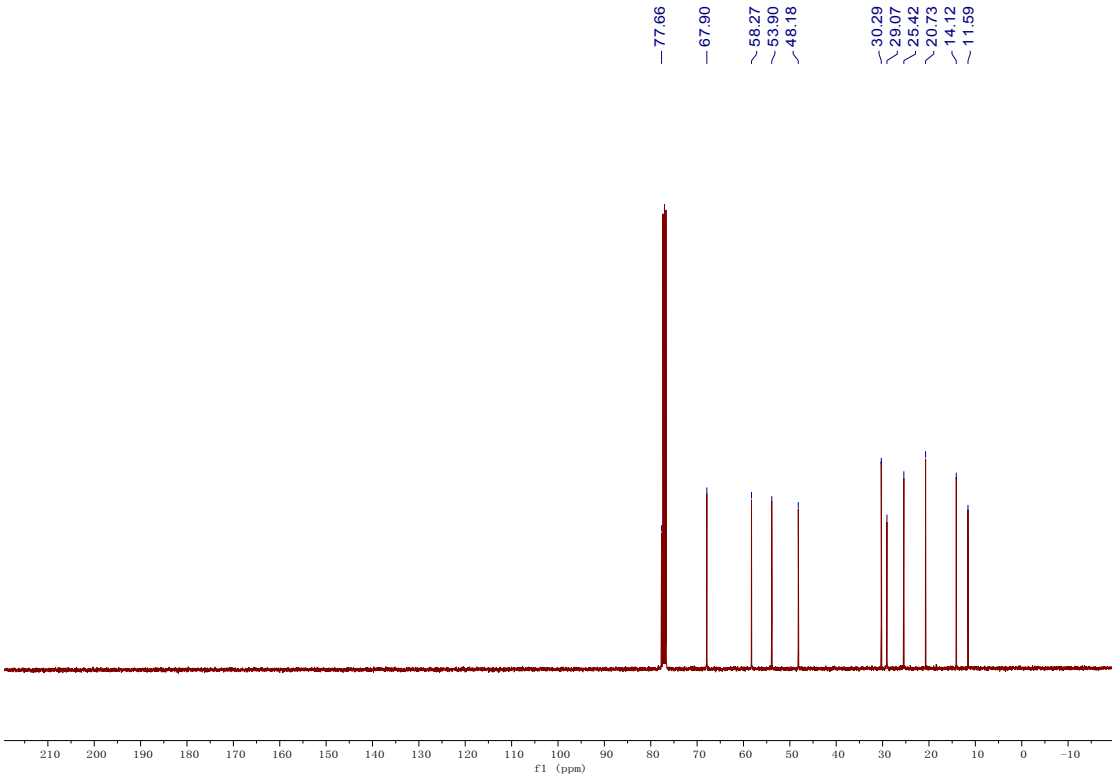

O
N
H
N


7.26
4.01
4.00
3.99
3.98
3.84
3.84
3.83
3.82
3.81
3.76
3.74
3.73
3.72
2.70
2.69
2.67
2.66
2.65
2.64
2.63
2.62
2.60
2.53
2.51
2.49
2.48
2.48
2.47
2.46
2.46
2.44
1.97
1.95
1.94
1.93
1.91
1.89
1.89
1.88
1.88
1.87
1.87
1.87
1.86
1.86
1.85
1.85
1.69
1.67
1.65
1.63
1.55
1.53
1.52
1.50
1.02
1.00
0.98
0.96
1.01
1.01
3.95
6.12
3.68
2.03
1.04
6.14
f1 (ppm)


78.26
67.89
54.57
51.11
48.92
46.85
29.36
27.23
25.79
11.66
f1 (ppm)


O
N


7.26
3.98
3.97
3.97
3.95
3.95
3.95
3.93
3.93
3.92
3.87
3.86
3.85
3.84
3.84
3.74
3.72
3.72
3.71
3.71
3.70
3.69
3.68
3.67
2.62
2.42
2.00
1.90
1.55
1.48
1.46
1.38
1.33
1.23
1.02
1.00
0.98
0.91
0.89
0.96
1.00
1.05
6.09
1.06
2.02
1.00
2.06
2.14
2.98
3.00
f1 (ppm)


77.66
67.90
58.27
53.90
48.18
30.29
29.07
25.42
20.73
14.12
11.59
f1 (ppm)