Supporting Information

Carboxylate-promoted reductive functionalization of CO_2 with amine and hydrosilane under mild conditions

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Table of Contents

1. General Experimental Section S2

2. Cesium Formate-Catalyzed Hydrosilation of CO_2 in the Absence of Amines ……………………………………………………………...S3

3. Experimental procedure for reductive functionalization of CO_2 with aniline to *N*-methylaniline and *N,N*-methylaniline…………………… S4

4. Characterization Data for the Products and Aminal Intermediate……………………………………………………………..S5

5. NMR Spectral Copies of the Products and Aminal Intermediate...S9

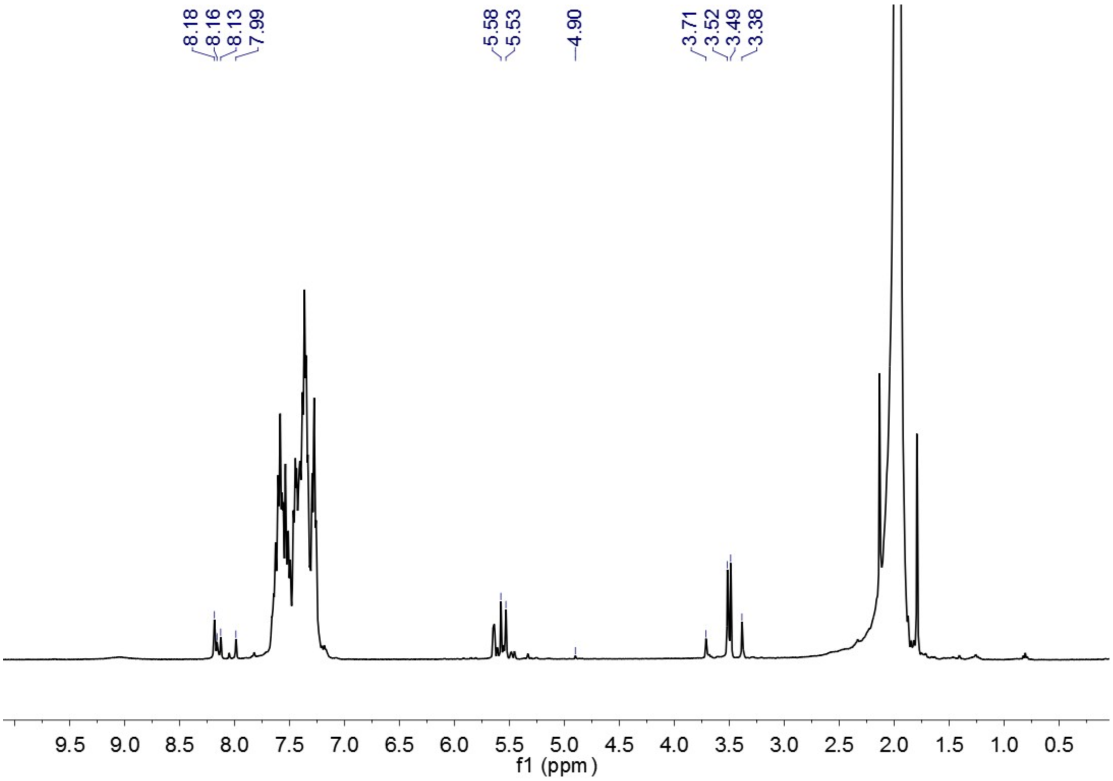
1. General Experimental Section

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 ^oC) and ethyl acetate. All compounds were characterized by ^1H NMR, ^{13}C NMR and mass spectroscopy, which are consistent with those reported in the literature. NMR spectra were determined on Bruker 400 in $CDCl_3$ or C_6D_6. ^1H NMR spectra was recorded on 400 MHz spectrometers using $CDCl_3$ as solvent referenced to tetramethylsilane (TMS, 0 ppm). The ^{13}C NMR chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (central peak is 77.0 ppm). ^1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, *J*, are reported in Hertz (Hz). GC-MS data were performed on Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-17 30 m × 0.25 μm) using a flame ionization detector.

2. Cesium formate-catalyzed hydrosilation of CO_2 in the absence of amines

$$CO_2 + Ph_2SiH_2 \xrightarrow[CH_3CN,\ 50\ ^{o}C]{HCOOCs} HCOO[Si] + [Si]OCH_2O[Si] + CH_3O[Si]$$

Under inert atmosphere (Ar), a 10 mL Schlenk flask was charged with cesium formate (2.3 mg), diphenylsilane (186 μL, 1 mmol) and CH_3CN (2 mL) successfully. The reaction mixture was stirred at 50 °C under an atmosphere of CO_2 (99.999%, balloon). Samples were taken for the desired time (6 h) to be analyzed through ^1H NMR. It was found that diphenylsilane (4.90 ppm) was consumed in 6 h, giving rise to peaks at ~ 8.1, ~ 5.5 and ~ 3.5 ppm, indicative of CO_2 reduction to silyl formates, silyl acetals and silyl methoxides.[1]

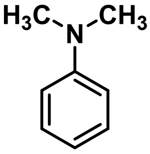


1. (a) S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem. Int. Ed.*, 2009, **48**, 3322-3325. (b) M.-A. Courtemanche, M.-A. Legare, E. Rochette and F.-G. Fontaine, *Chem. Commun.*, 2015, **51**, 6858-6861.

3. Experimental procedure for reductive functionalization of CO_2 with aniline to *N*-methylaniline and *N,N*-methylaniline

Under inert atmosphere (Ar), a 50 mL Schlenk flask was charged successively with cesium formate (9.2 mg, 5 mol% relative to amine), aniline (1 mmol), diphenylsilane (744 µL, 4 mmol) and CH_3CN (8 mL). The reaction mixture was stirred at 50 ^{o}C for 6 h under an atmosphere of CO_2 (99.999%, balloon). After the reaction, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether-EtOAc). *N*-methylaniline was obtained with 21% isolated yield, and *N,N*-methylaniline were with 28% yield. The spectrum of *N*-methylaniline are as below: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.8 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 8.2 Hz, 2H), 3.63 (s, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.25, 129.14, 117.18, 112.36, 30.66.

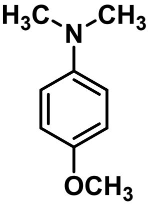
4. Characterization Data for the Products



1c (10c)

N,N-Dimethylaniline

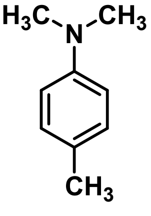
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ 7.24 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.85 – 6.62 (m, 3H), 2.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 150.58, 129.03, 116.60, 112.62, 40.61. GC-MS (EI, 70 eV) m/z (%) 121.15 (81.29), 120.15 (100.00), 77.05 (29.56).



2c (11c)

4-Methoxy-N,N-dimethylaniline

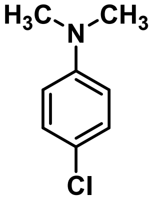
White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ 6.88 – 6.81 (m, 2H), 6.79 – 6.72 (m, 2H), 3.76 (s, 3H), 2.86 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 152.12, 145.52, 115.04, 114.60, 55.72, 41.92. GC-MS (EI, 70 eV) m/z (%) 151.25 (59.49), 136.20 (100.00).



3c (12c)

N,N-Dimethyl-p-toluidine

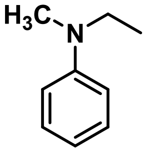
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ 7.05 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 8.2 Hz, 2H), 2.89 (s, 6H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 148.77, 129.54, 126.09, 113.19, 41.05, 20.22. GC-MS (EI, 70 eV) m/z (%) 35.20 (77.14), 134.15 (100.00), 91.10 (22.96).



4c (13c)

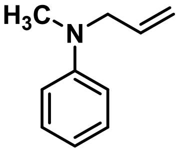
4-Chloro-N,N-dimethylaniline

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ 7.17 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 149.10, 128.75, 121.36, 113.59, 40.64. GC-MS (EI, 70 eV) m/z (%) 157.10 (25.27), 156.10 (39.00), 155.10 (82.99), 154.10 (100.00).



5c

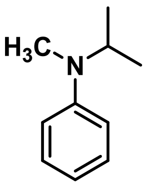
Yellow liquid ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.7 Hz, 2H), 6.84 – 6.52 (m, 3H), 3.39 (q, *J* = 7.0 Hz, 2H), 2.89 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.05, 129.11, 115.97, 112.33, 46.75, 37.38, 11.13.



6c

N-allyl-N-methylaniline

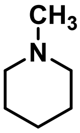
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ7.25 – 7.20 (m, 2H), 6.74 – 6.68 (m, 3H), 5.89 – 5.80 (m, 1H), 5.18 – 5.13 (m, 2H), 3.92 (d, *J* = 4.9 Hz, 2H), 2.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 149.43, 133.75, 129.07, 116.36, 116.12, 112.40, 55.23, 37.97. HRMS (ESI, m/z) calcd. For $C_{10}H_{13}N$ $[M+H]^+$: 148.1126, found: 148.1122.



7c

N-isopropyl-N-methylaniline

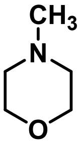
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 4.18 – 3.96 (m, 1H), 2.72 (s, 3H), 1.15 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.10, 129.07, 116.38, 113.28, 48.87, 29.75, 19.26.



8c

1-Methylpiperidine

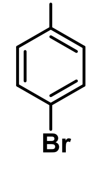
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ 2.33 (s, 4H), 2.24 (s, 3H), 1.68 – 1.51 (m, 4H), 1.41 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 56.46, 46.86, 25.95, 23.70. GC-MS (EI, 70 eV) m/z (%) 99.15 (42.36), 98.15 (100.00), 71.10 (22.54).



9c

4-methylmorpholine

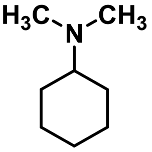
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ 3.80 – 3.61 (m, 4H), 2.41 (s, 4H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 66.67, 55.20, 46.23. GC-MS (EI, 70 eV) m/z (%) 101.15 (100.00), 100.15 (36.36), 71.10 (60.10).



14c

4-Bromo-N,N-dimethylaniline

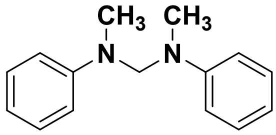
White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ 7.30 (d, *J* = 9.1 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 56.46, 46.86, 25.95, 23.70. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.46, 131.64, 114.06, 108.45, 40.53. GC-MS (EI, 70 eV) m/z (%) 201.00 (93.41), 200.00 (100.00), 199.00 (99.32), 198.00 (97.76), 118.15 (45.22), 77.10 (20.98).



15c

N,N-dimethylcyclohexanamine

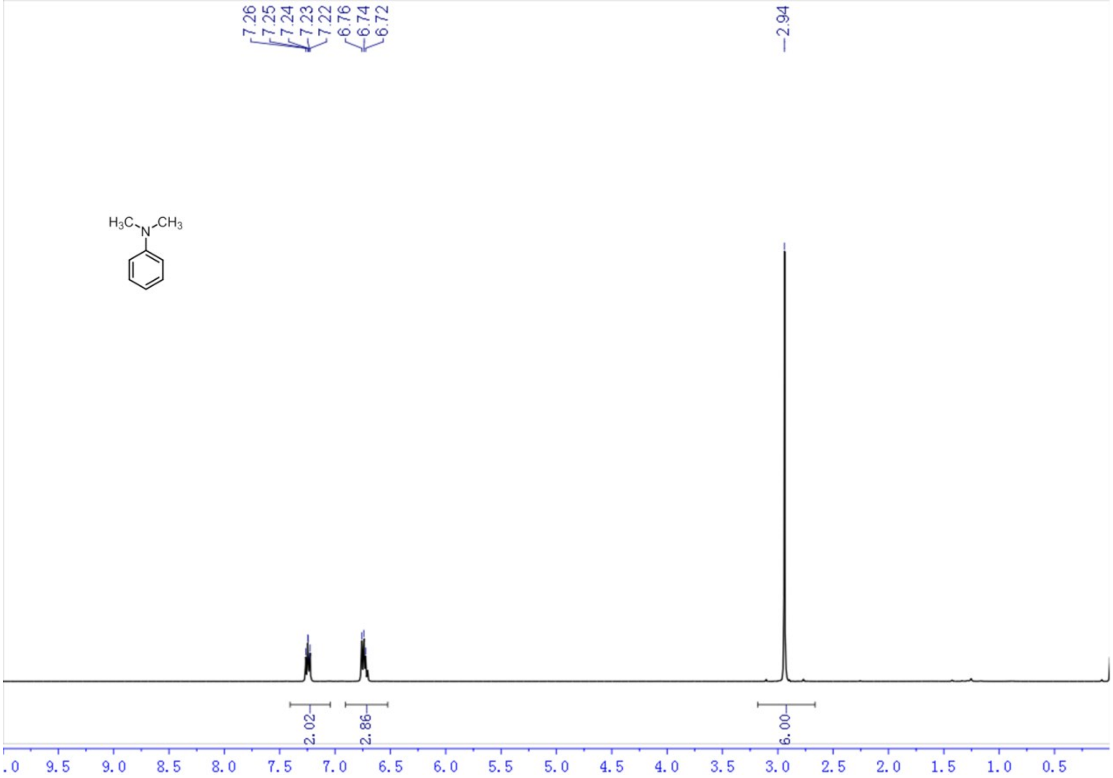
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS) δ 2.27 (s, 6H), 2.14 – 2.10 (m, 1H), 1.86 – 1.76 (m, 4H), 1.68 – 1.55 (m, 1H), 1.26 – 1.09 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$, 25℃, TMS) δ 63.60, 41.43, 28.82, 26.14, 25.60. GC-MS (EI, 70 eV) 127.20 (26.01), 84.15 (100.00), 71.10 (21.41).

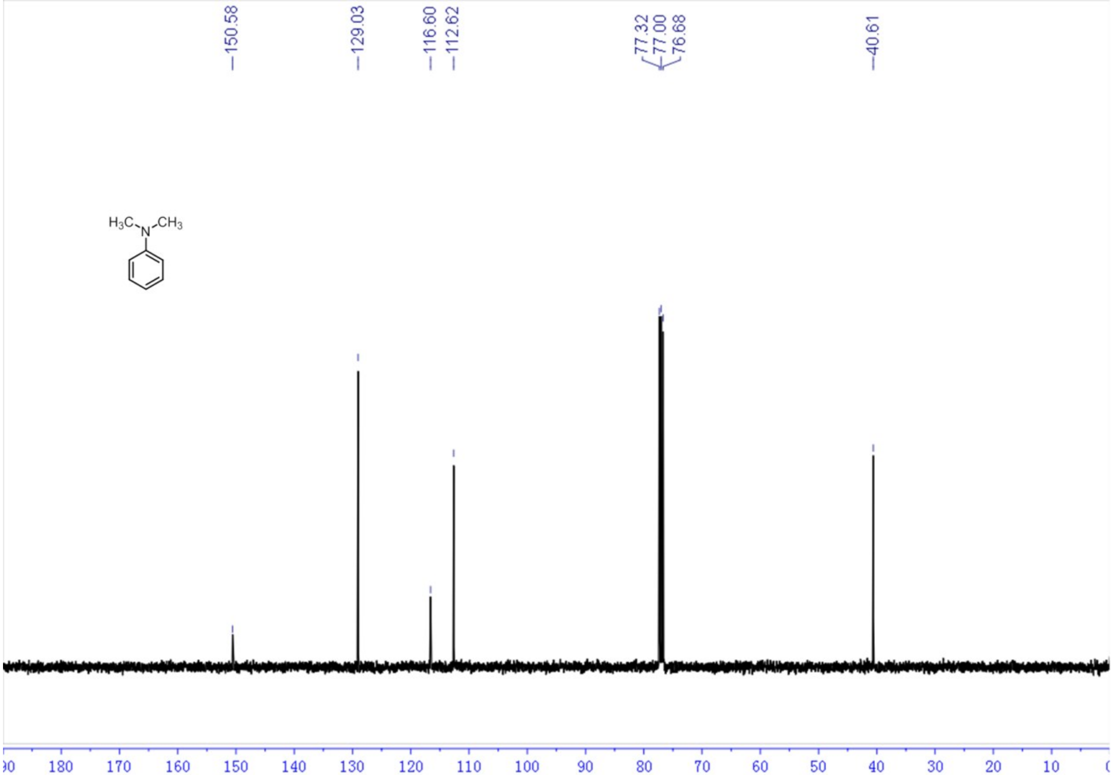


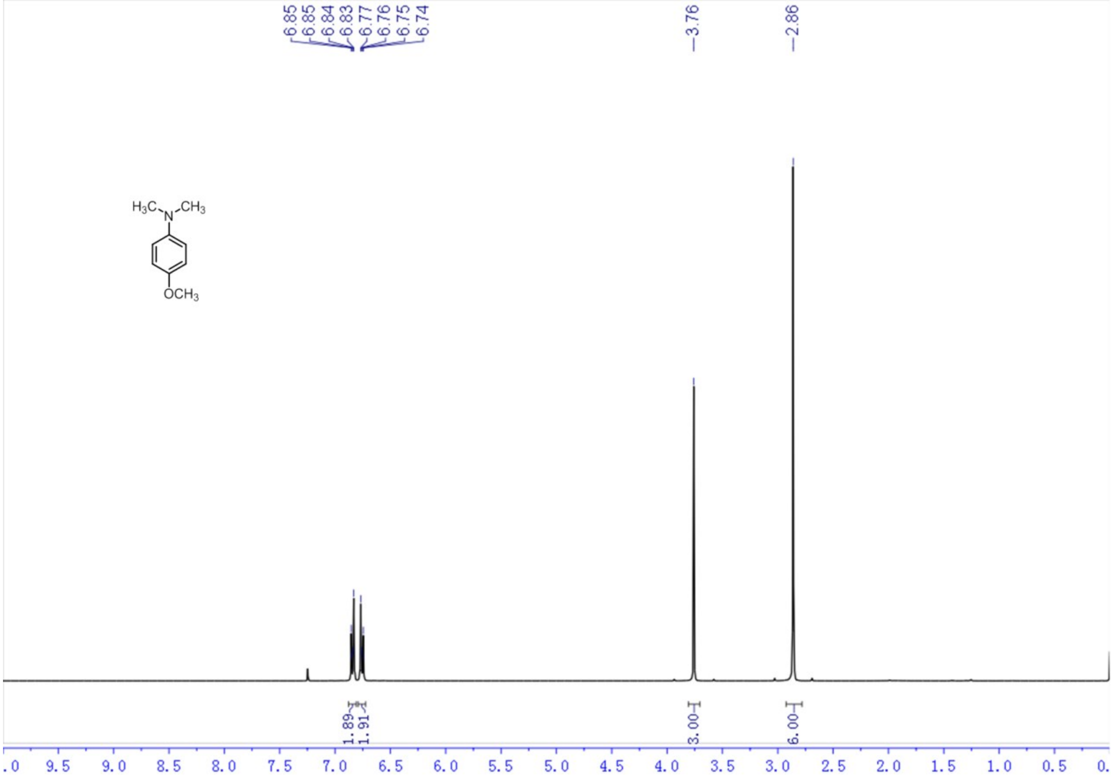
N,N’-dimethyl-N,N’-diphenylmethanediamine

Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.6, 7.4 Hz, 4H), 6.84 (d, *J* = 8.1 Hz, 4H), 6.78 (t, *J* = 7.3 Hz, 2H), 4.76 (s, 2H), 2.87 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.31, 129.27, 117.86, 113.76, 70.44, 36.31. GC-MS (EI, 70 eV) m/z (%) 226.20 (2.83), 121.15 (16.02), 120.15 (100.00), 107.15 (61.88), 106.15 (71.81), 79.10 (21.17), 77.10 (39.67).

4. NMR Spectral Copies of the Products



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1.91
3.00
6.00
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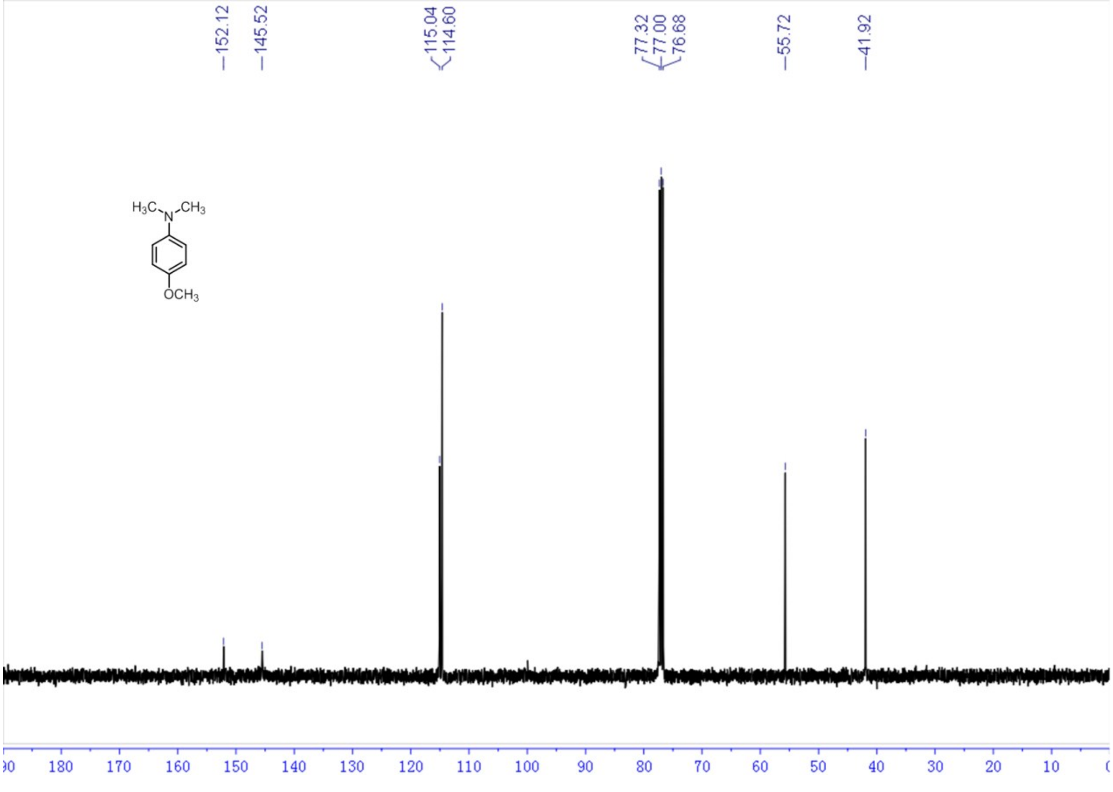
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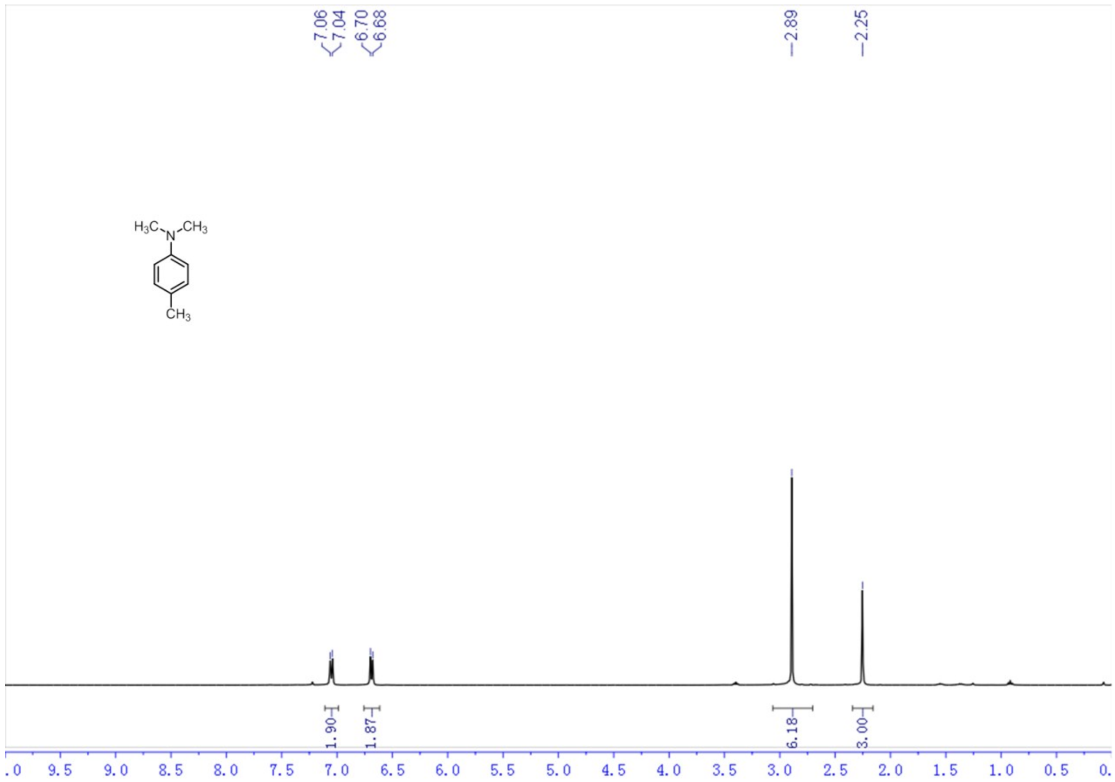
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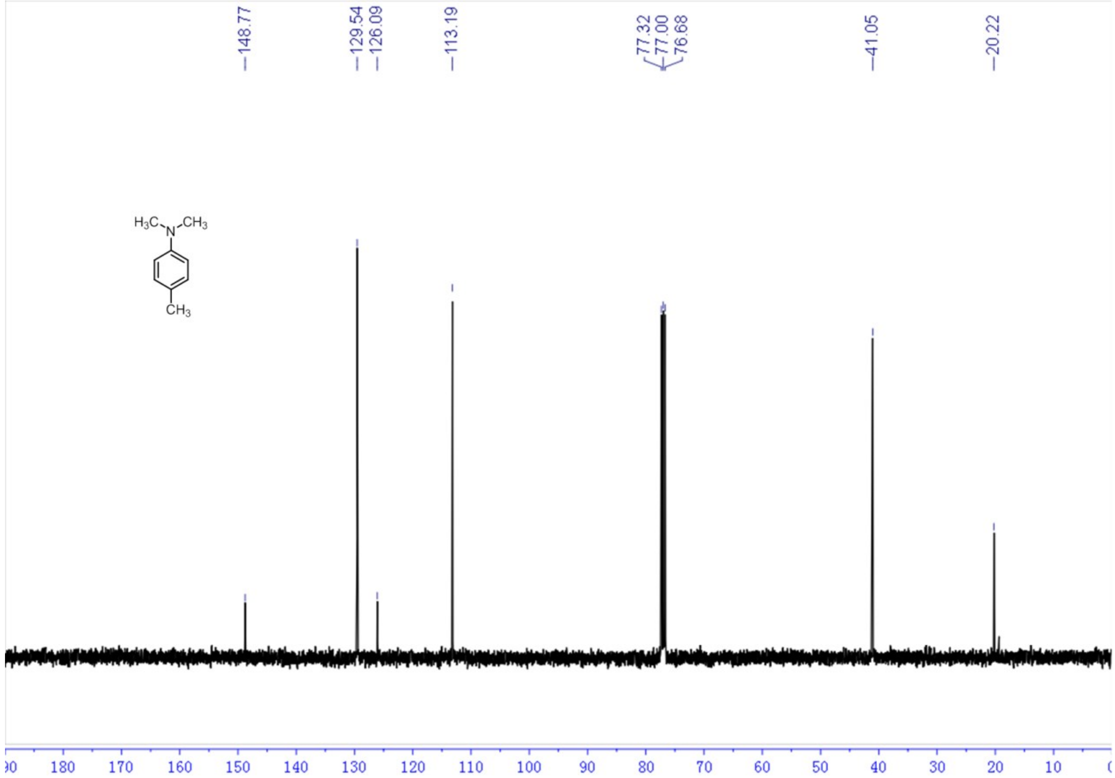
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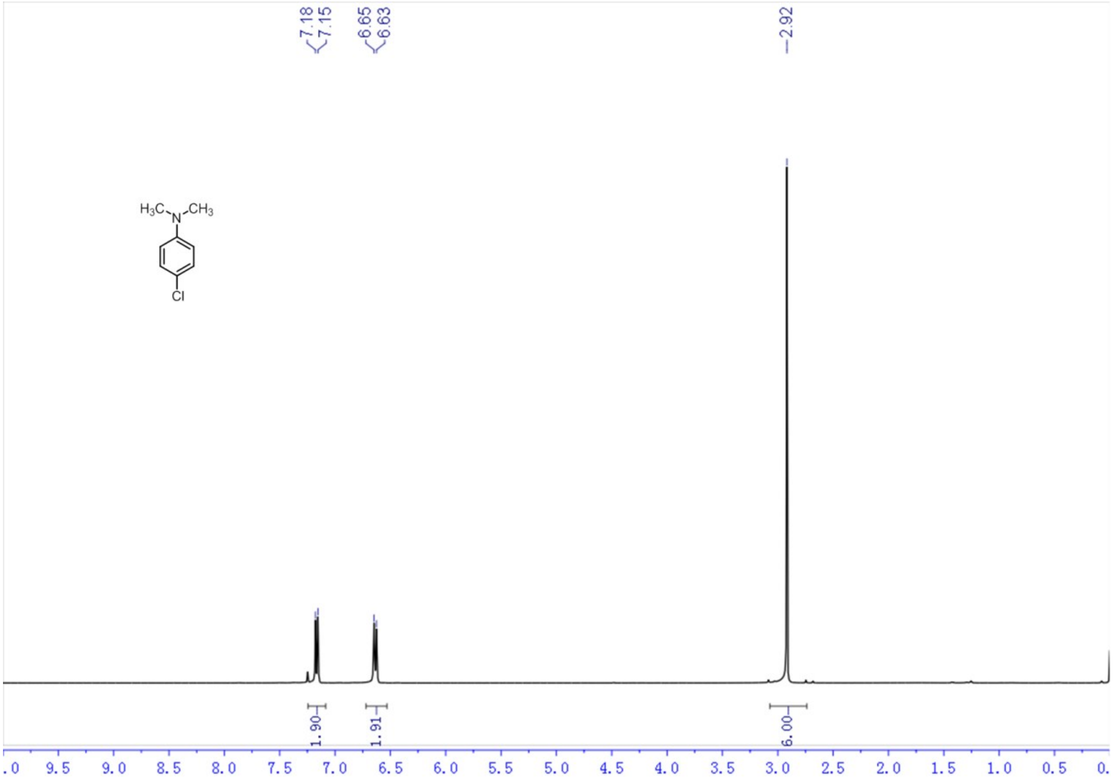
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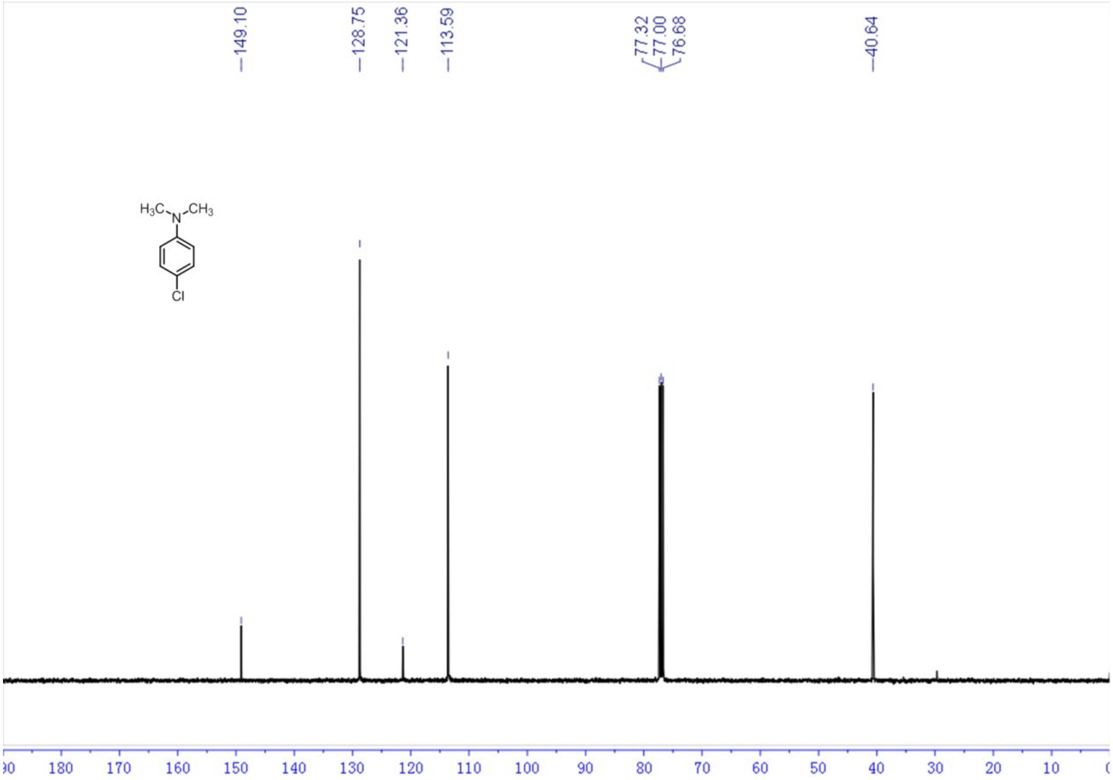
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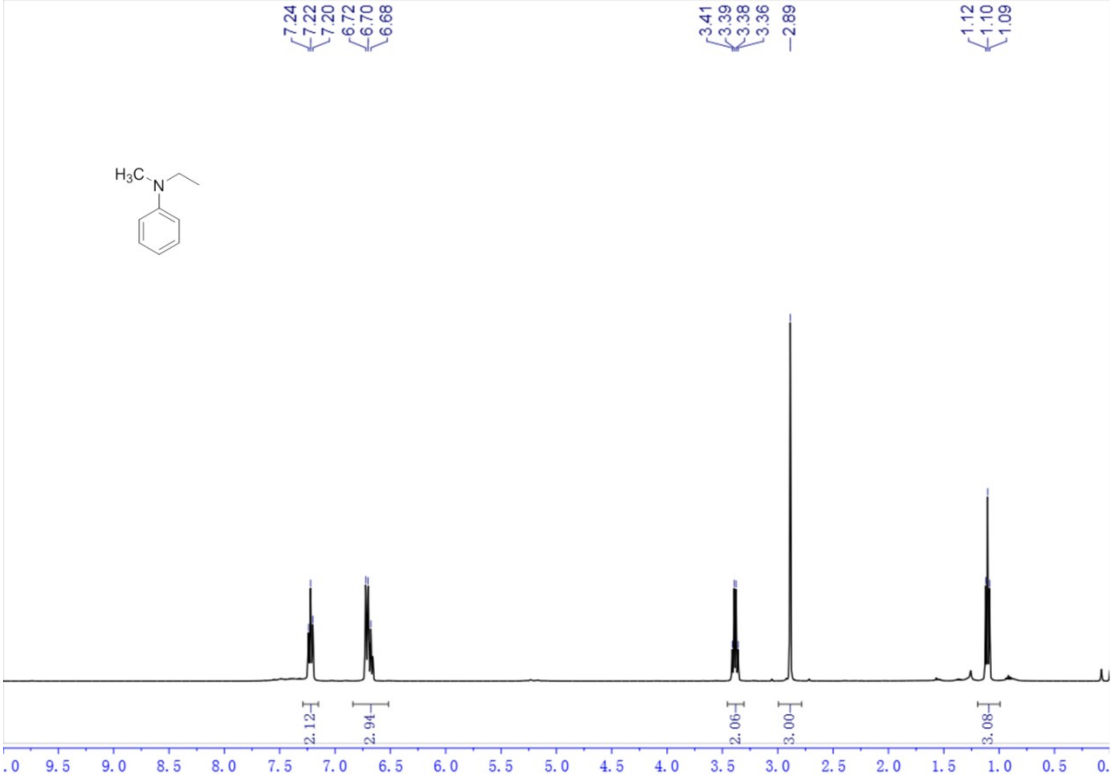
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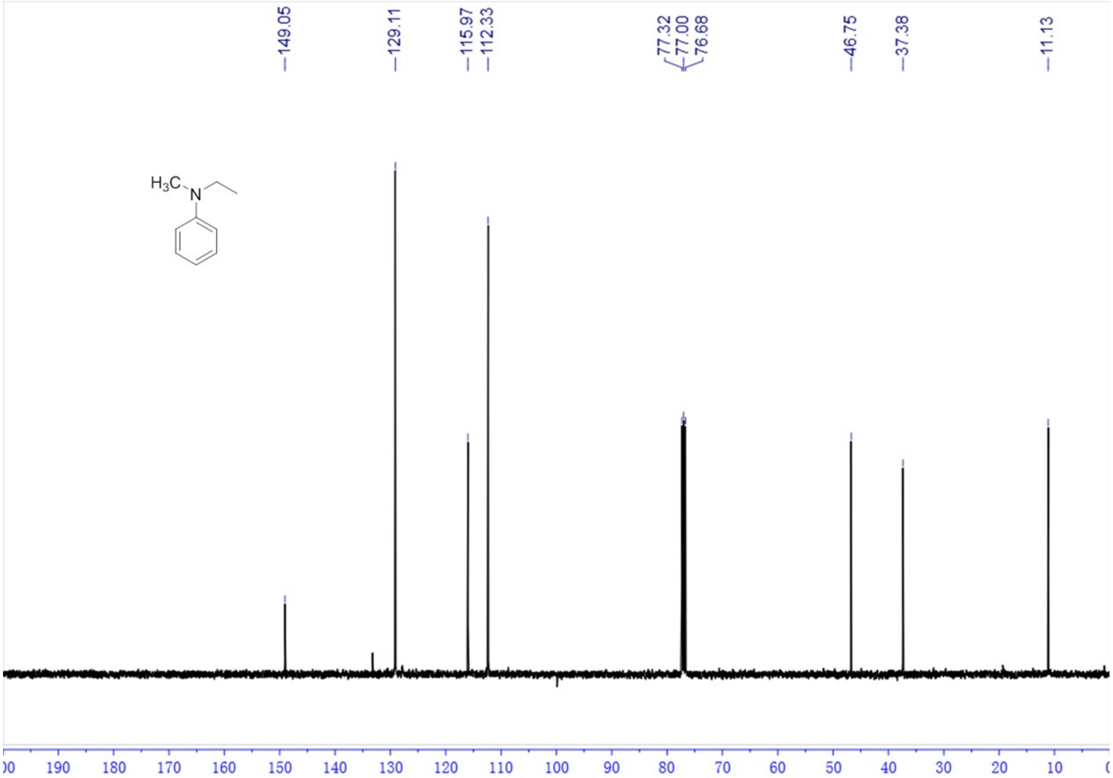
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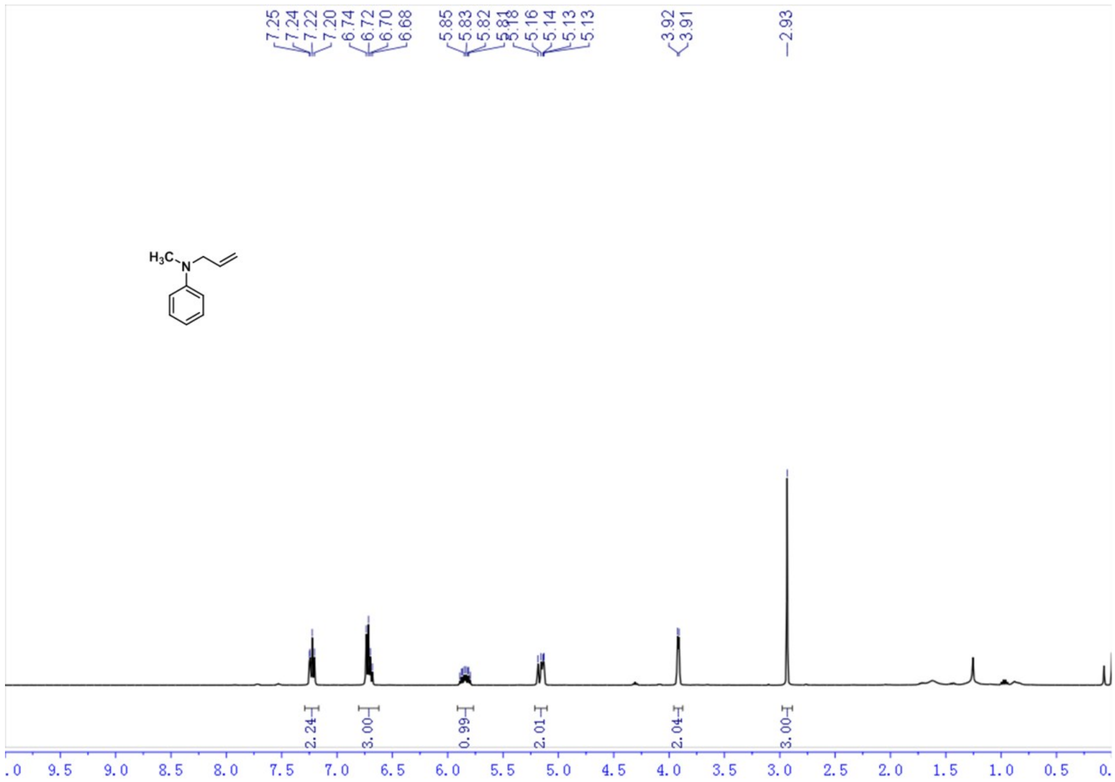
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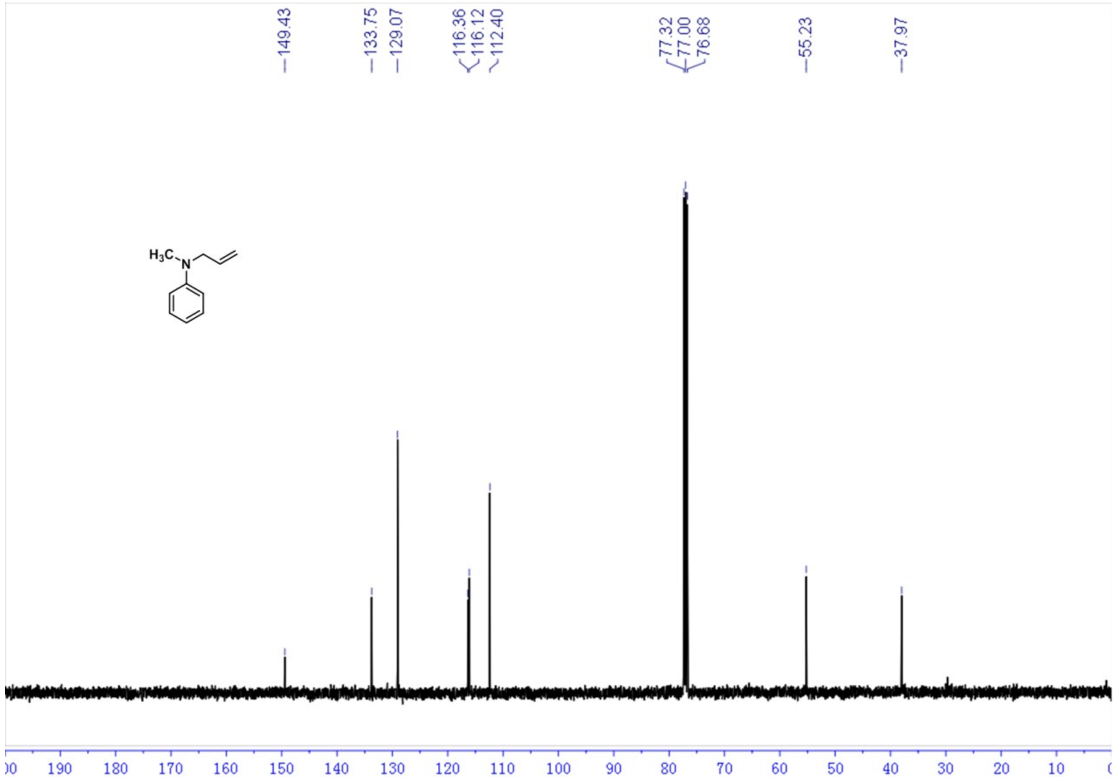
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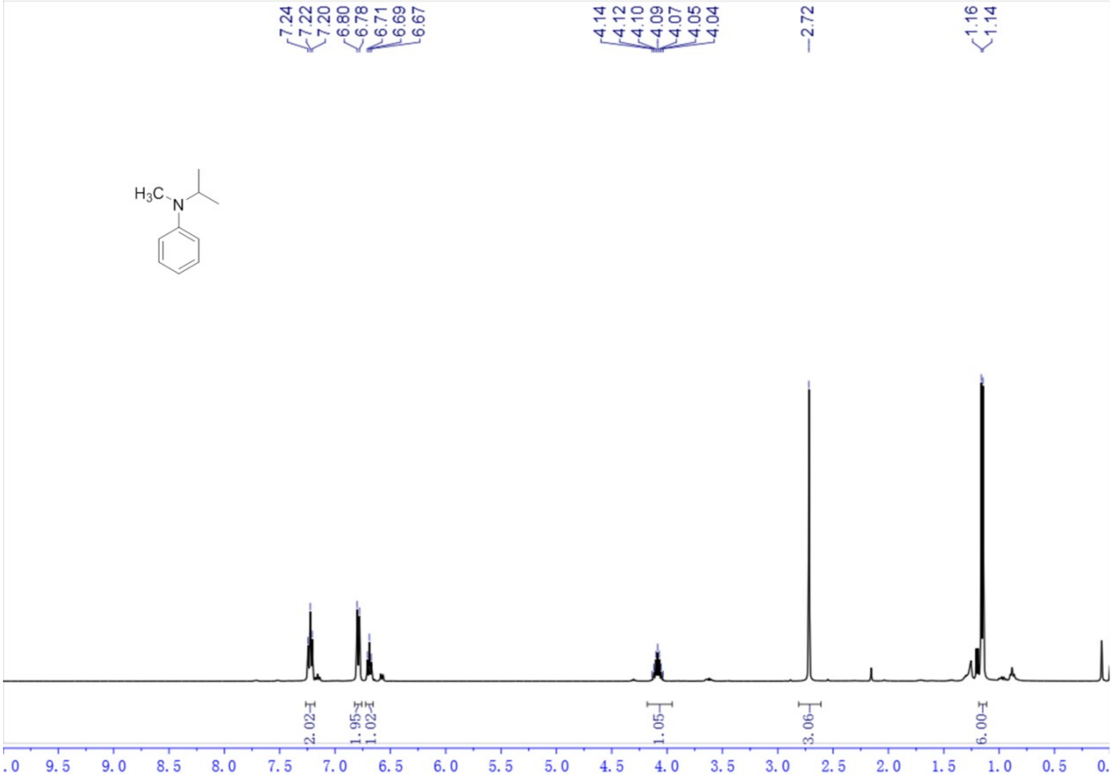
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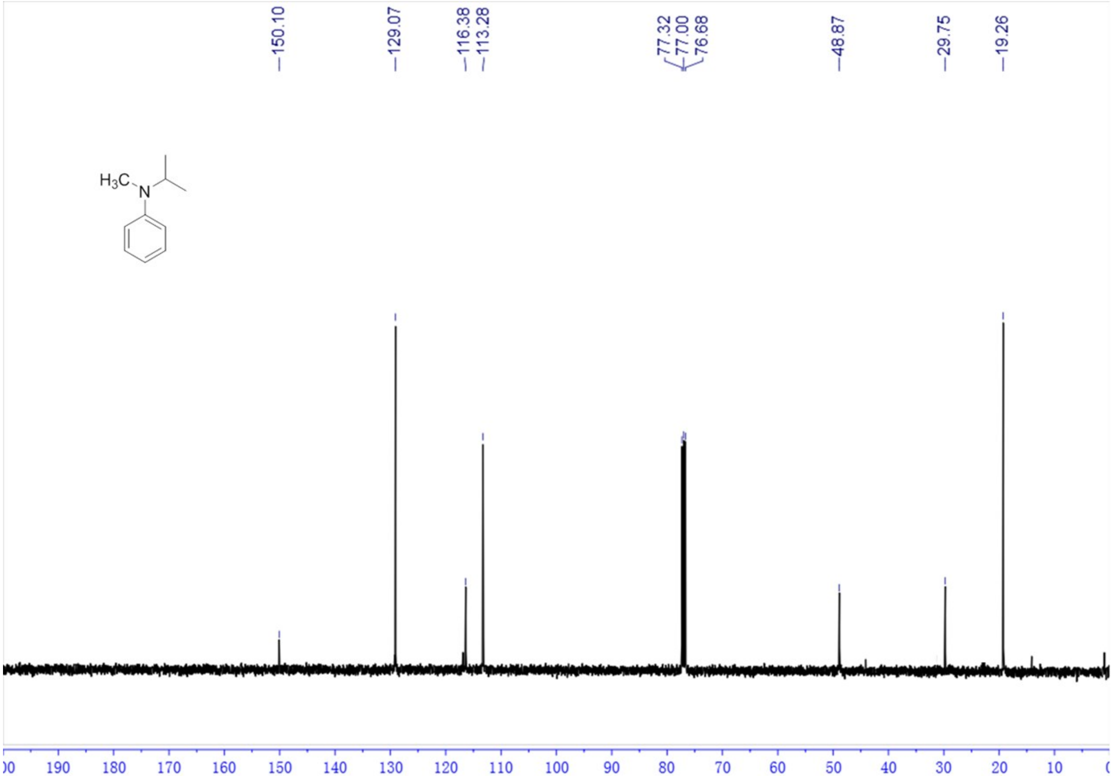
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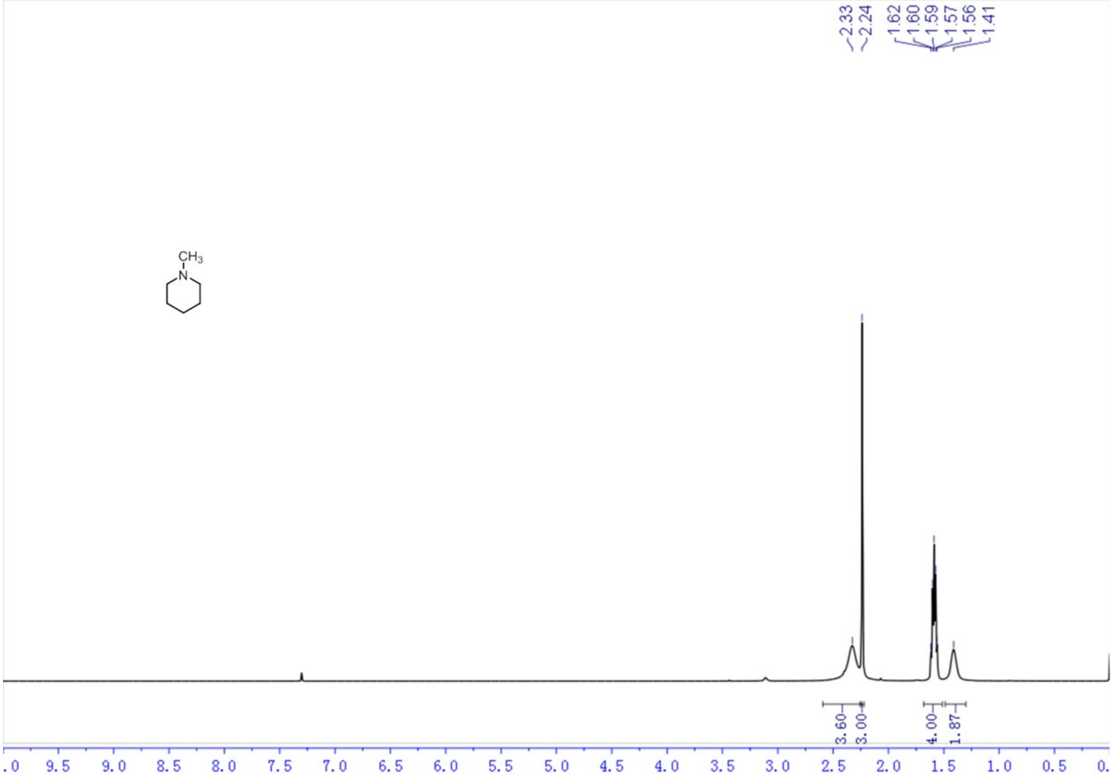
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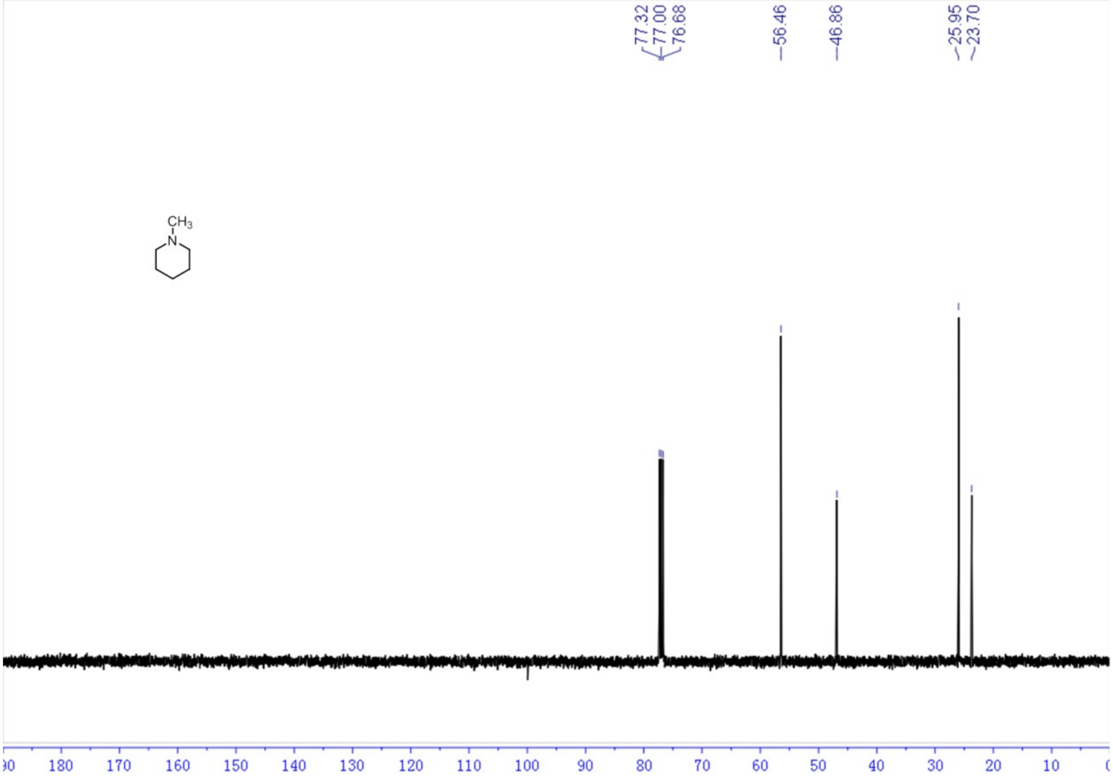
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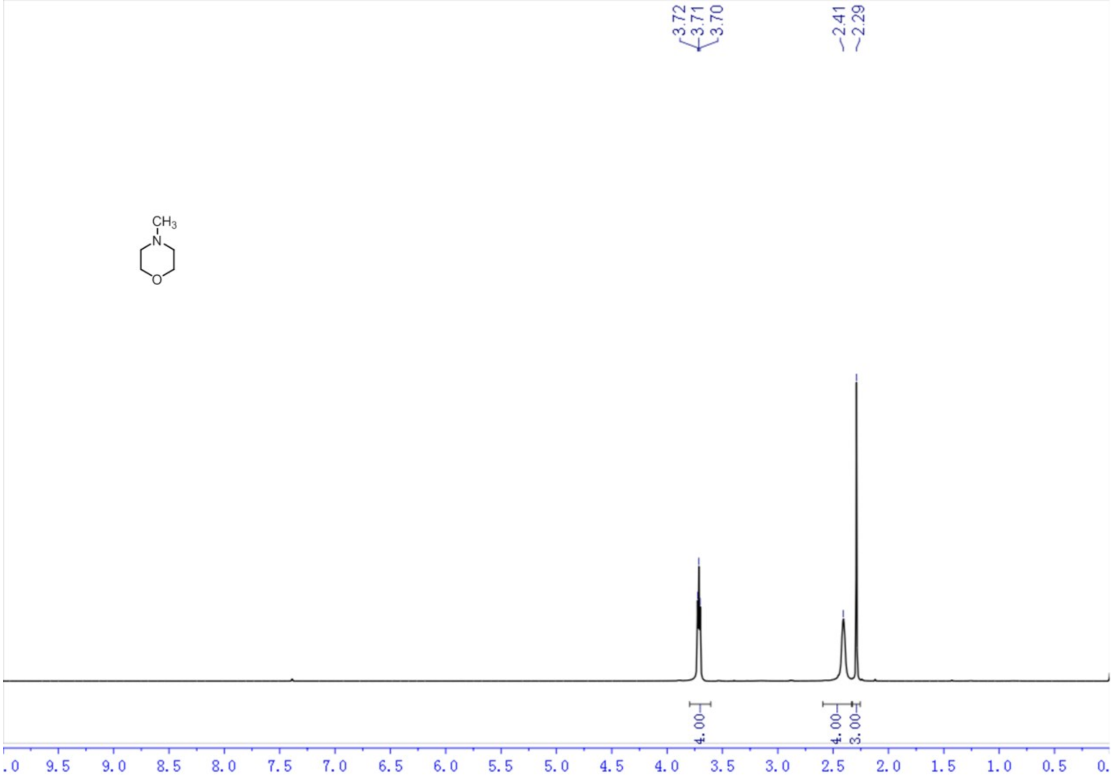
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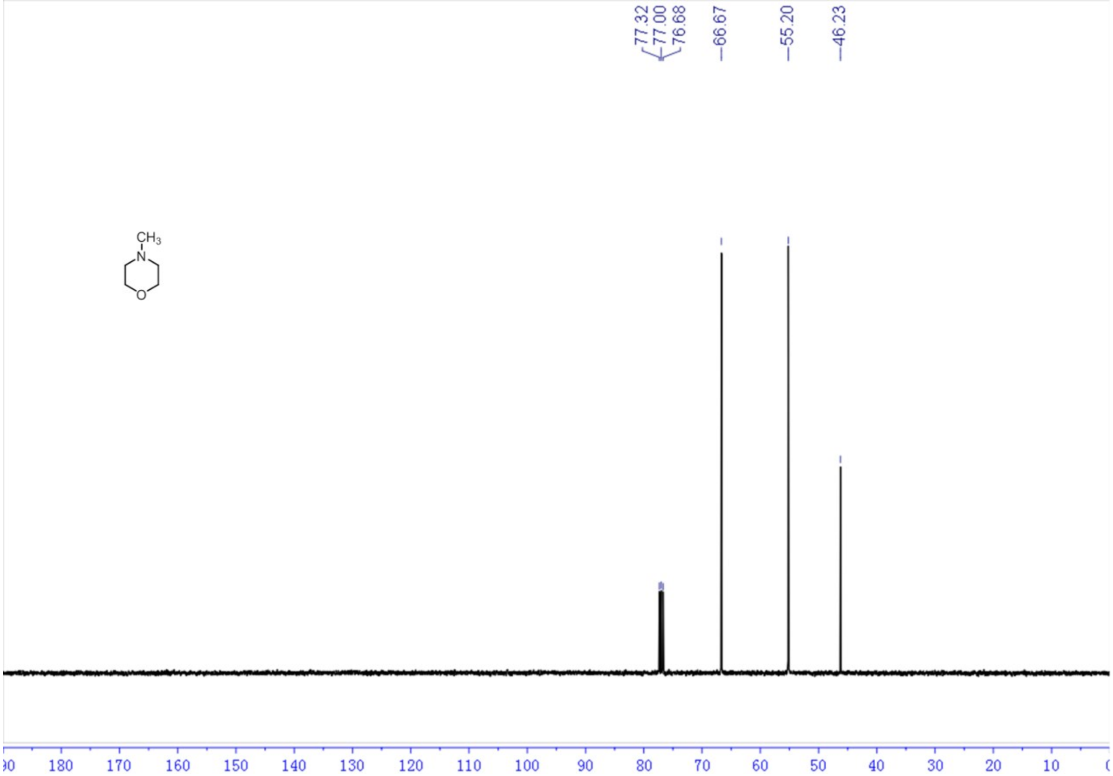
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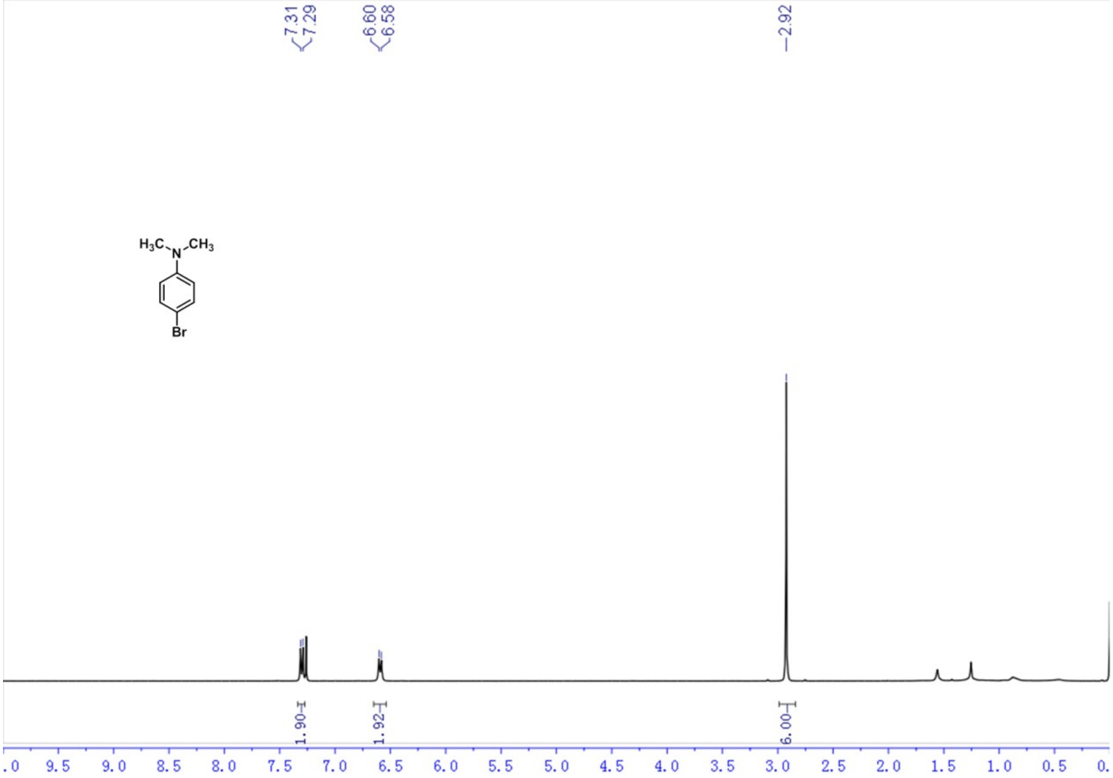
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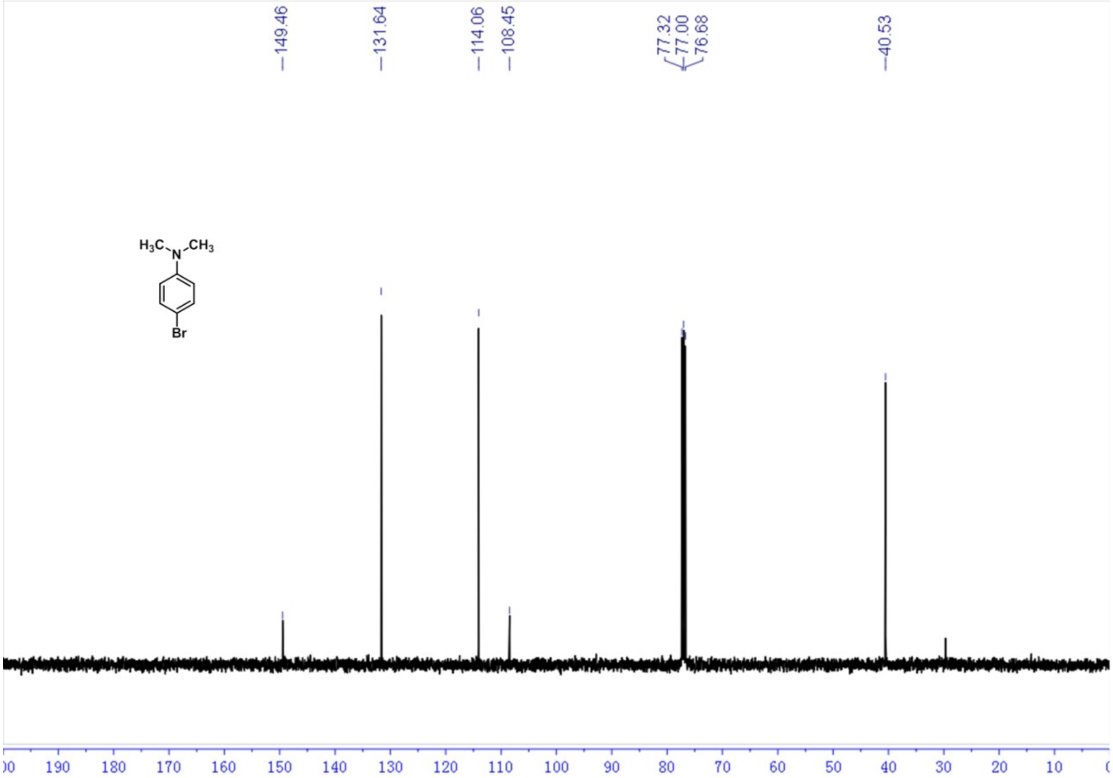
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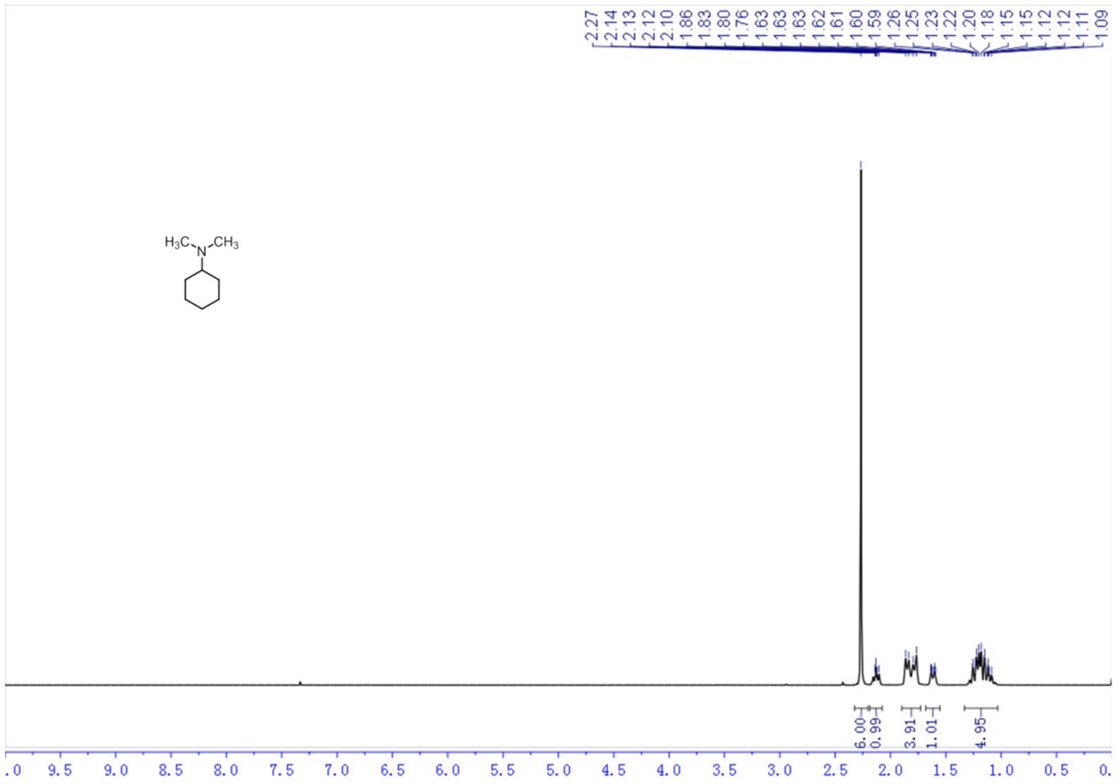
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1.26
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1.18
1.15
1.15
1.12
1.12
1.11
1.09
H_3C
N
CH_3
6.00
0.99
3.91
1.01
4.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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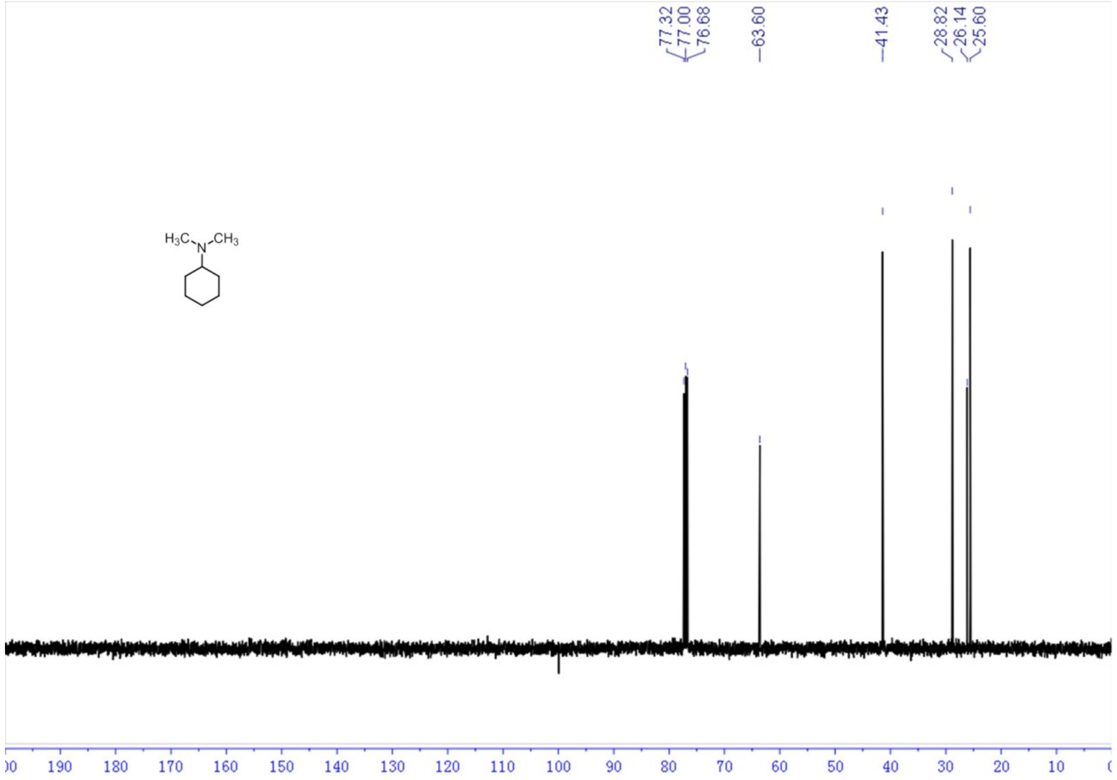
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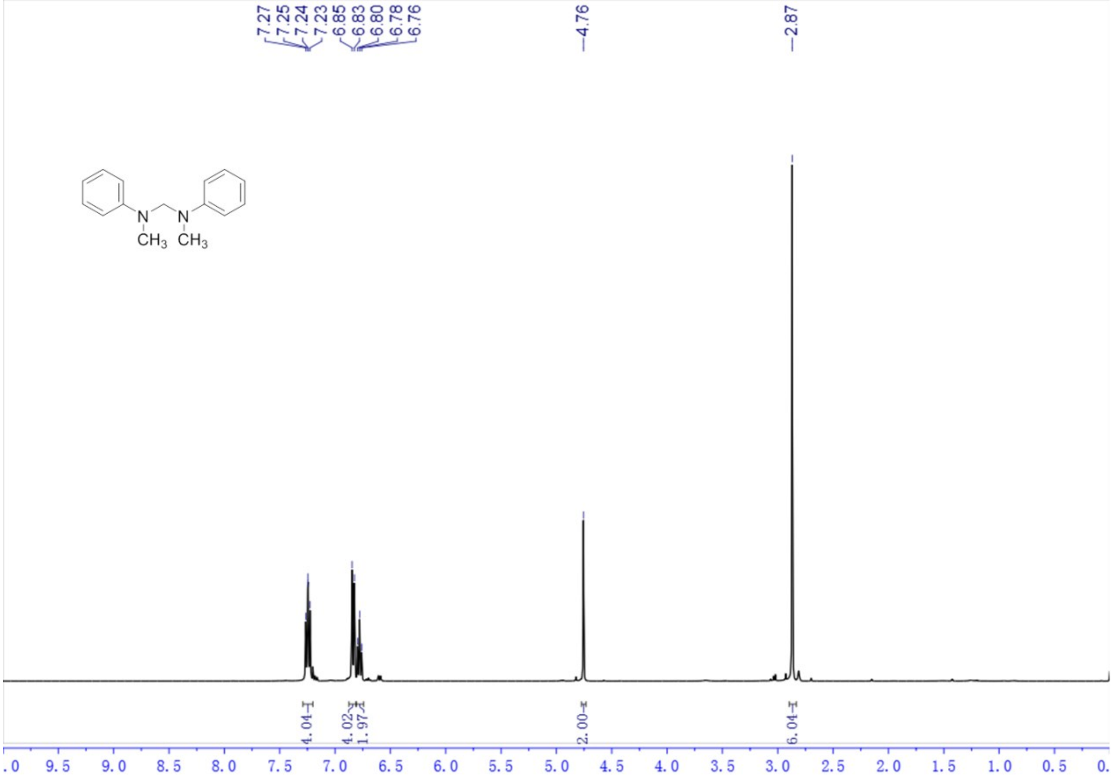
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N
CH3
CH3
4.04
4.02
1.97
2.00
6.04
.0
9.5
9.0
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7.0
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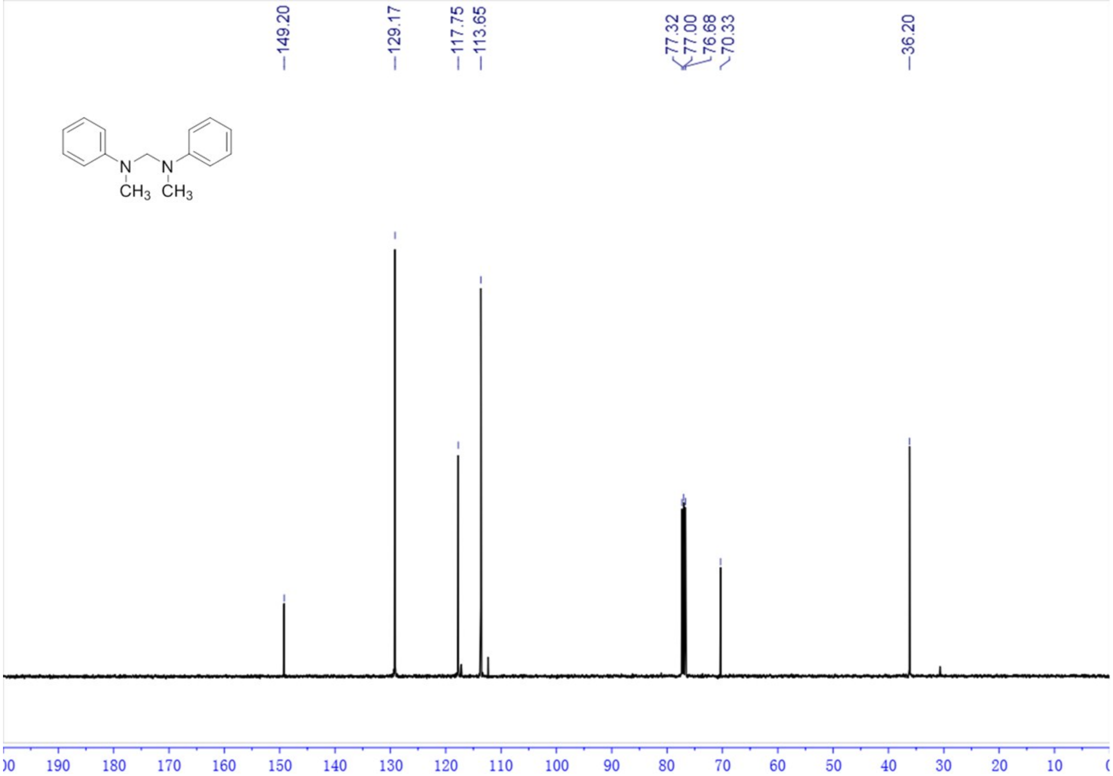
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CH3
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140
130
120
110
100
90
80
70
60
50
40
30
20
10