Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Pd-catalyzed hydroaminocarbonylation of alkynes with aliphatic amines and its mechanism study

Experimental Section

1. Reagents and analysis

All the reagents used in this work were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd., and Acros China, and were used as received. NMR spectra were recorded on Bruker Avance 500 spectrometer. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. Gas chromatography (GC) was performed on a SHIMADZU- 2014 equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μm).

2. General procedure for aminocarbonylation of alkynes

A mixture of alkyne (2.0 mmol), amine (2.5 mmol), $Pd(OAc)_2$ (1.0 mol%), Dppp (1.0 mol%) and CH_3CN (2 mL) was added to a stainless-steel autoclave lined with Teflon. The autoclave was flushed three times with CO and then pressurized to appointed pressure of CO. The mixture was stirred with a mechanical stirrer at the appointed conditions. The reactor was cooled to room temperature and degassed carefully. Upon completion, the autoclave was cooled down to room temperature and slowly depressurized. The reaction solution was analyzed by GC to determine the conversions (*n*-dodecane as internal standard) and the selectivities (normalization method). Then the solvent was removed under vacuum and the obtained residue was purified by flash column chromatography on a silica gel (eluted with ethyl acetate/petroleum ether = 1/10-1/1) to furnish the desired products.

3. Synthesis of S1 and the reaction procedures of S1 with phenylacetylene

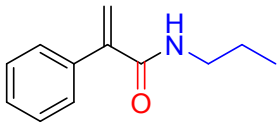
The synthesis of complex **S1** was carried out according to the protocol described in Ref. 35 in the text. The spectral data of these compounds were in accordance with the reported values.

The reaction procedures for the control experiments of S1 with phenylacetylene

In N_2 atmosphere, a solution of **S1** (0.1 mmol) and phenylacetylene (0.1 mmol) in 1 mL CH_3CN was treated with Et_3N, propylamine or aniline respectively. The obtained mixture was heated at 120 °C for 2 h under vigorous stirring. Upon completion, the reaction solution was analyzed by GC (SHIMADZU- 2014) equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μm).

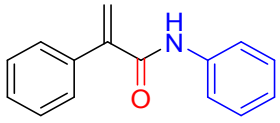
4. ^{1}H and ^{13}C NMR spectroscopic data of the products

2-Phenyl-N-propylacrylamide



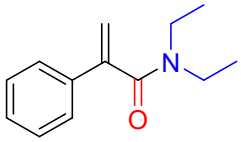
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.40-7.36 (m, 5H), 6.14-6.13 (m, 1H), 5.79 (br, 1H), 5.61 (s, 1H),3.31 (d, *J*=6.9 Hz, 2H), 1.54 (q, *J*=7.3 Hz, 2H), 0.92 (t, *J*=7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 167.3, 144.9, 137.2, 128.7, 128.5, 128.1, 121.9, 41.6, 22.8, 11.4.

N,2-diphenylacrylamide



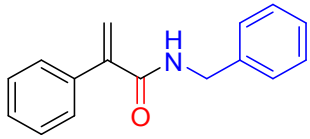
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.58 – 7.38 (m, 7H), 7.32 (m, 2H), 7.12 (t, *J*=7.4 Hz, 1H), 6.29 (s, 1H), 5.73 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 165.2, 145.1, 137.6, 136.7,129.0, 129.0, 128.9, 128.3, 124.6, 123.4, 119.9.

***N*, *N*-diethyl-α-methylene**



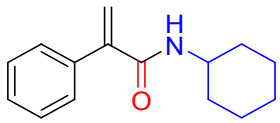
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.53 – 7.27 (m, 5H), 5.70 (s, 1H), 5.33 (s, 1H), 3.51 (q, *J*=7.1 Hz, 2H), 3.24 (q, *J*=7.1 Hz, 2H), 1.23 (t, *J*=7.1 Hz, 3H), 1.01 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 170.2, 145.5, 135.7, 128.8, 128.5, 128.5, 125.6, 113.0, 42.8, 38.8, 14.0, 12.8.

α-Methylene-N-(phenylmethyl)benzeneacetamide



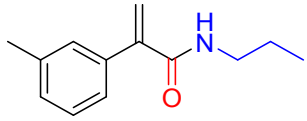
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.43 – 7.21 (m, 10H), 6.24 – 6.12 (m, 1H), 6.04 (br, 1H), 5.63 (d, *J*=1.3 Hz, 1H), 4.53 (d, *J*=5.8 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 167.2, 144.6, 138.1, 137.0, 128.8, 128.7, 128.6, 128.2, 127.7, 127.5, 122.7, 43.9.

α-Methylene-N-(cyclohexyl)benzeneacetamide



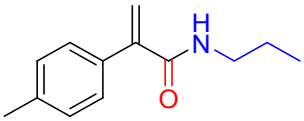
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.45 – 7.35 (m, 1H), 6.12 (d, *J*=1.3 Hz, 1H), 5.62 (d, *J*=1.3 Hz, 1H), 5.57 (br, 1H), 1.96 (dd, *J*=12.6 Hz, 4.1 Hz, 2H), 1.73 – 1.56 (m, 3H), 1.47 – 1.32 (m, 2H), 1.21 – 1.07 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 166.4, 145.1, 137.2, 128.7, 128.5, 128.1, 121.8, 48.5, 33.0, 25.5, 24.8.

2-*m*-tolyl-N-propylacrylamide



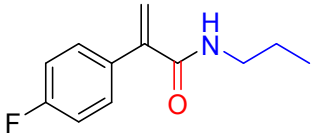
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.36 – 7.09 (m, 4H), 6.10 (s, 1H), 5.85 (br, 1H), 5.57 (s, 1H), 3.29 (d, *J*=6.5 Hz, 2H), 2.37 (s, 3H), 1.54 (q, *J*=7.3 Hz, 2H), 0.91 (t, *J*=7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 167.4, 145.0, 138.4, 137.1, 129.2, 128.8, 128.5, 125.1, 121.7, 41.5, 22.7, 21.4, 11.4.

2-*p*-tolyl-N-propylacrylamide



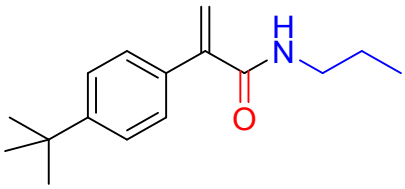
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.42 – 7.04 (m, 4H), 6.05 (s, 1H), 5.88 (br, 1H), 5.55 (s, 1H), 3.28 (d, *J*=6.9 Hz, 2H), 2.36 (s, 3H), 1.52 (d, *J*=7.2 Hz, 2H), 0.90 (t, *J*=7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 167.5, 144.8, 138.4, 134.2, 129.3, 128.0, 121.1, 41.5, 22.7, 21.2, 11.4.

2-(4-fluorophenyl)-N-propylacrylamide



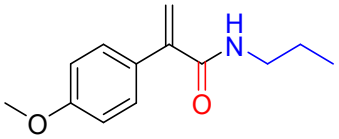
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.43 – 7.28 (m, 2H), 7.09-6.96 (m, 2H), 6.00 – 5.95 (m, 1H), 5.93 (br, 1H), 5.66 – 5.46 (m, 1H), 3.53 – 2.96 (m, 2H), 1.53 (q, *J*=8.4 Hz, 7.3 Hz, 2H), 1.03 – 0.71 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 167.5, 163.8, 161.8, 144.2, 133.0, 129.7, 120.9, 115.6, 41.5, 22.7, 11.3.

2-(4-tert-butylphenyl)-N-propylacrylamide



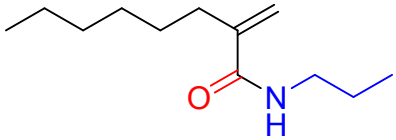
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.42 (d, *J*=8.3 Hz, 2H), 7.33 (d, *J*=8.4 Hz, 2H), 6.12 (s, 1H), 5.78 (s, 1H), 5.60 (s, 1H), 3.40 – 3.25 (m, 2H), 1.62 – 1.52 (m, 2H), 1.36 (s, 9H), 0.93 (t, *J*=7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 167.4, 159.9, 151.6, 144.7, 134.2, 127.9, 125.6, 121.6, 41.4, 34.7, 31.3, 22.8, 11.4.

2-(4-methoxybutylphenyl)-N-propylacrylamide



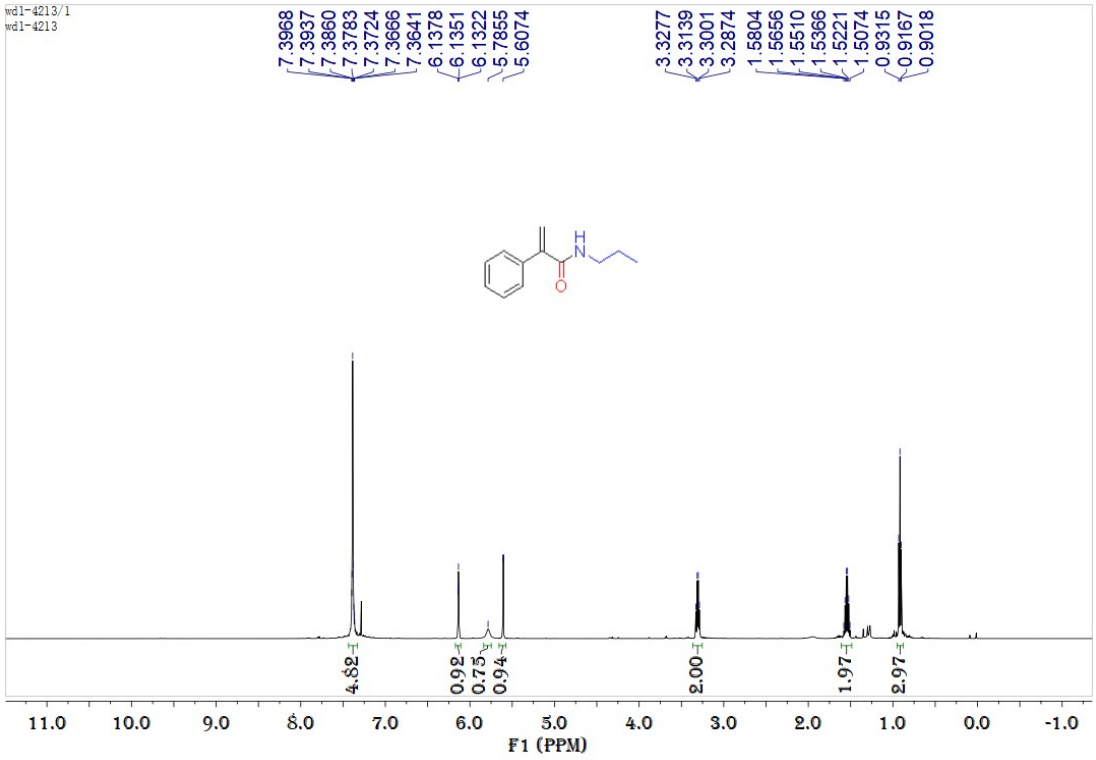
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.33 (d, *J*=8.7 Hz, 2H), 6.92 (d, *J*=8.7 Hz, 2H), 6.05 (s, 1H), 5.75 (br, 1H), 5.55 (s, 1H), 3.85 (s, 3H), 3.32 (q, *J*=6.8 Hz, 2H), 1.56 (q, *J*=7.3 Hz, 2H), 0.93 (t, *J*=7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 167.7, 159.8, 144.4, 129.5, 195.5, 120.6, 114.1, 55.3, 41.5, 22.8, 11.4.

2-Methylene-N-propyloctanamide



^{1}H NMR (500 MHz, Chloroform-*d*) δ = 6.12 (s, 1H), 5.52 (d, *J*=4.8 Hz, 1H), 5.27 – 5.13 (m, 1H), 3.31 – 3.15 (m, 2H), 2.26 (t, *J*=7.6 Hz, 2H), 1.52 (q, *J*=7.3 Hz, 2H), 1.44 – 1.36 (m, 2H), 1.25 (q, *J*=7.0 Hz, 6.5 Hz, 6H), 0.94 – 0.80 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 169.1, 146.0, 116.6, 41.2, 32.4, 31.6, 28.9, 28.0, 22.8, 22.5, 14.0, 11.3.

5. Copies for ^{1}H NMR and ^{13}C NMR of the amides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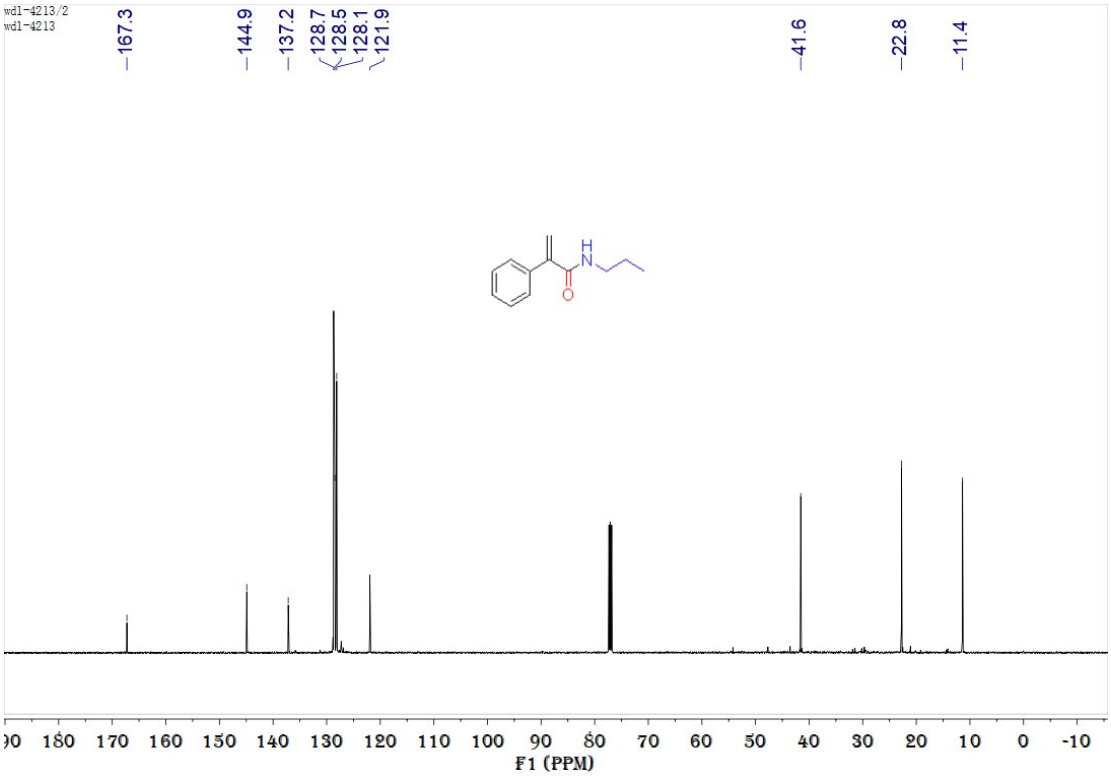
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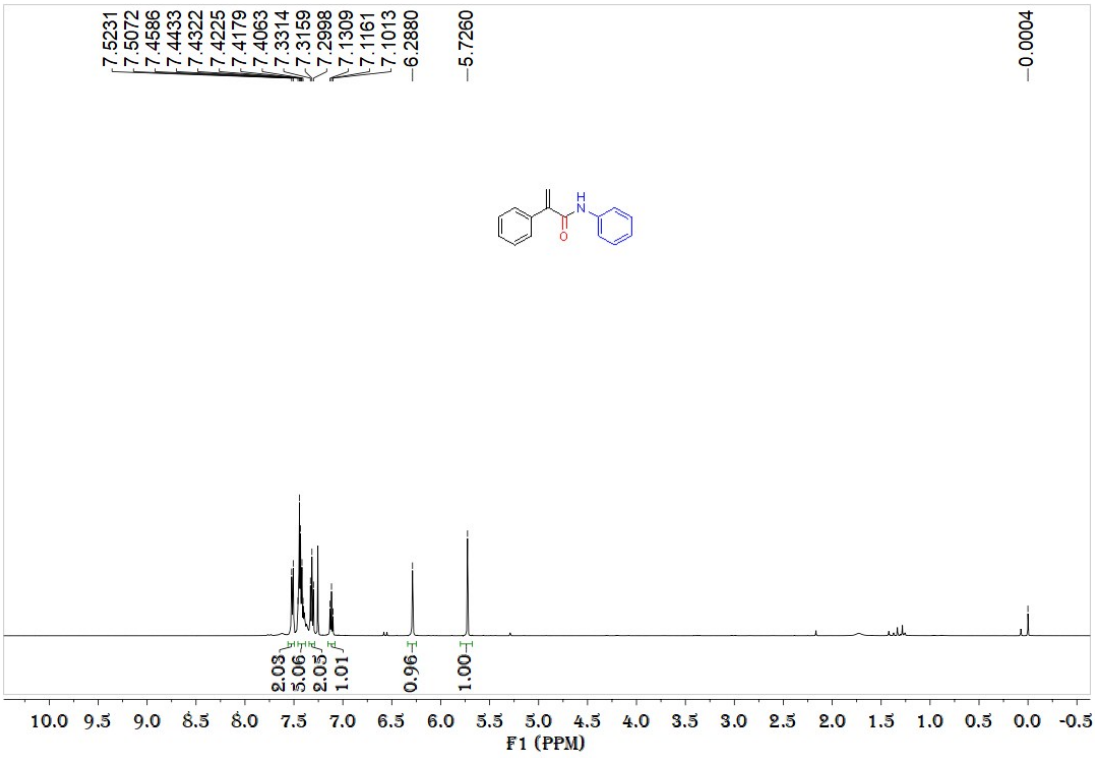
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1.00
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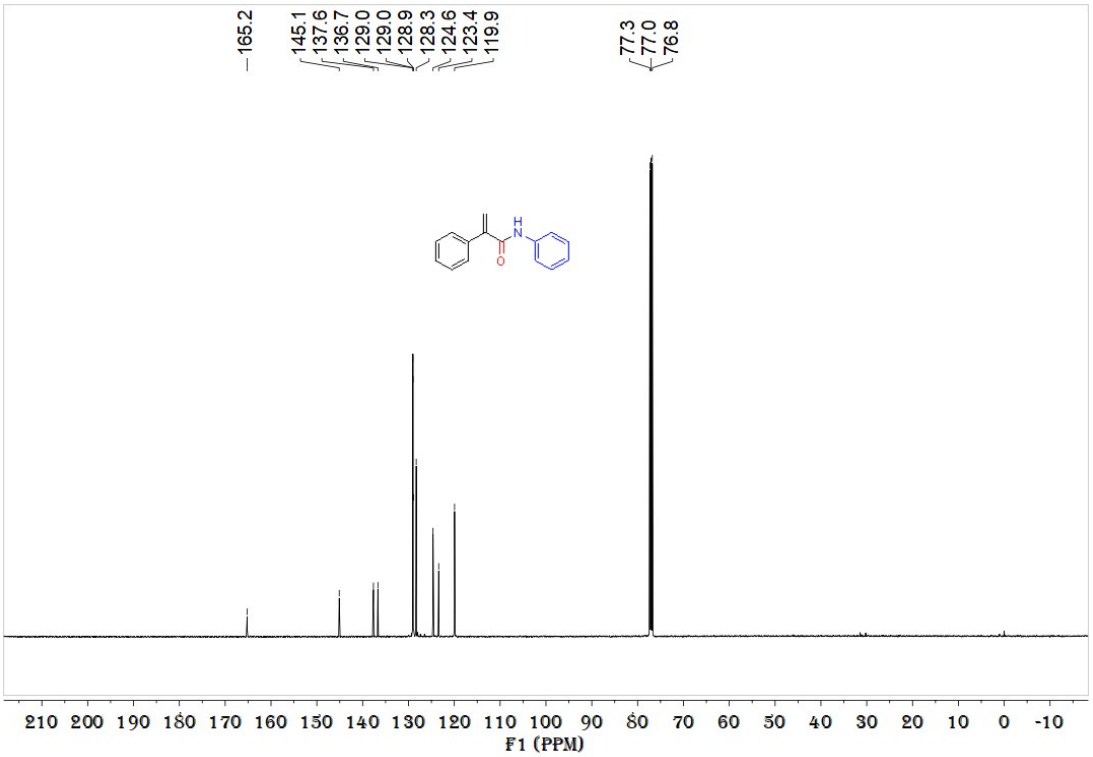
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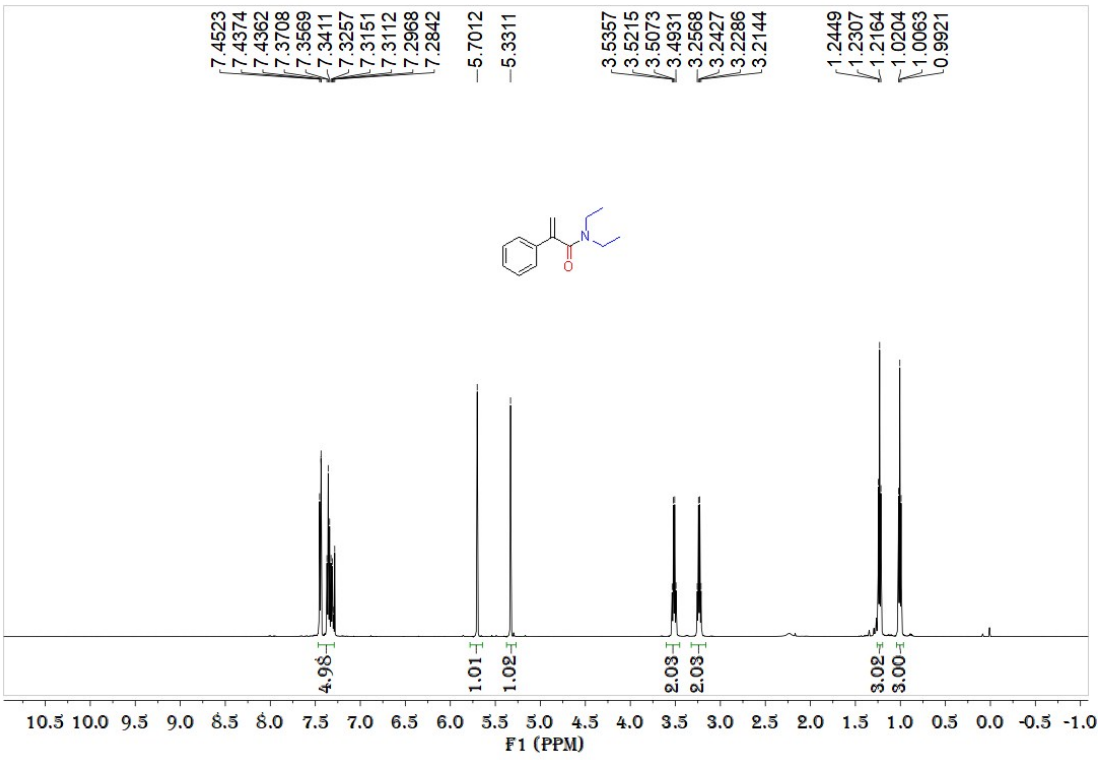
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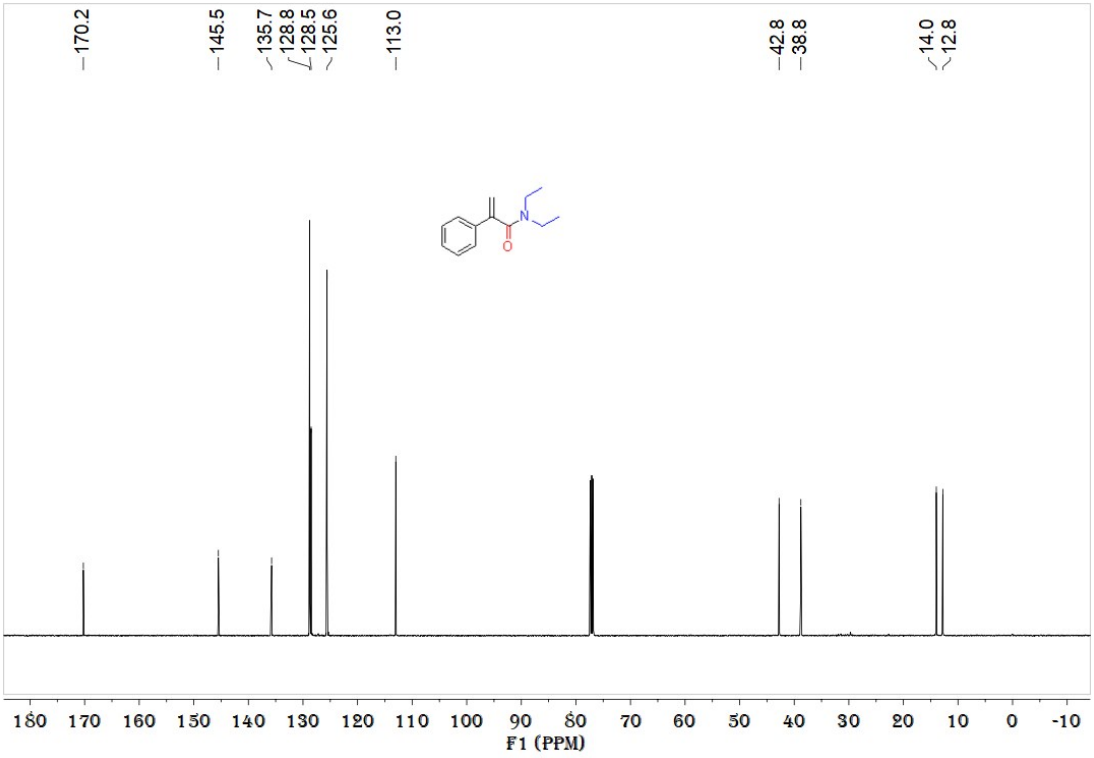
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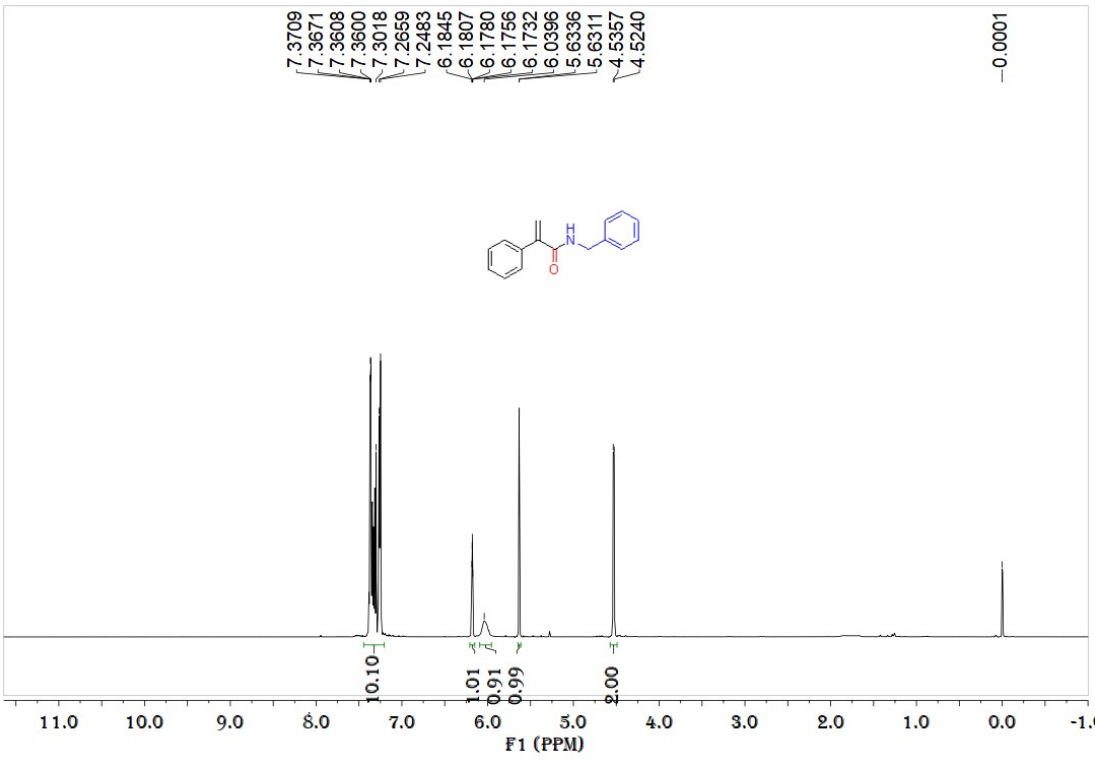
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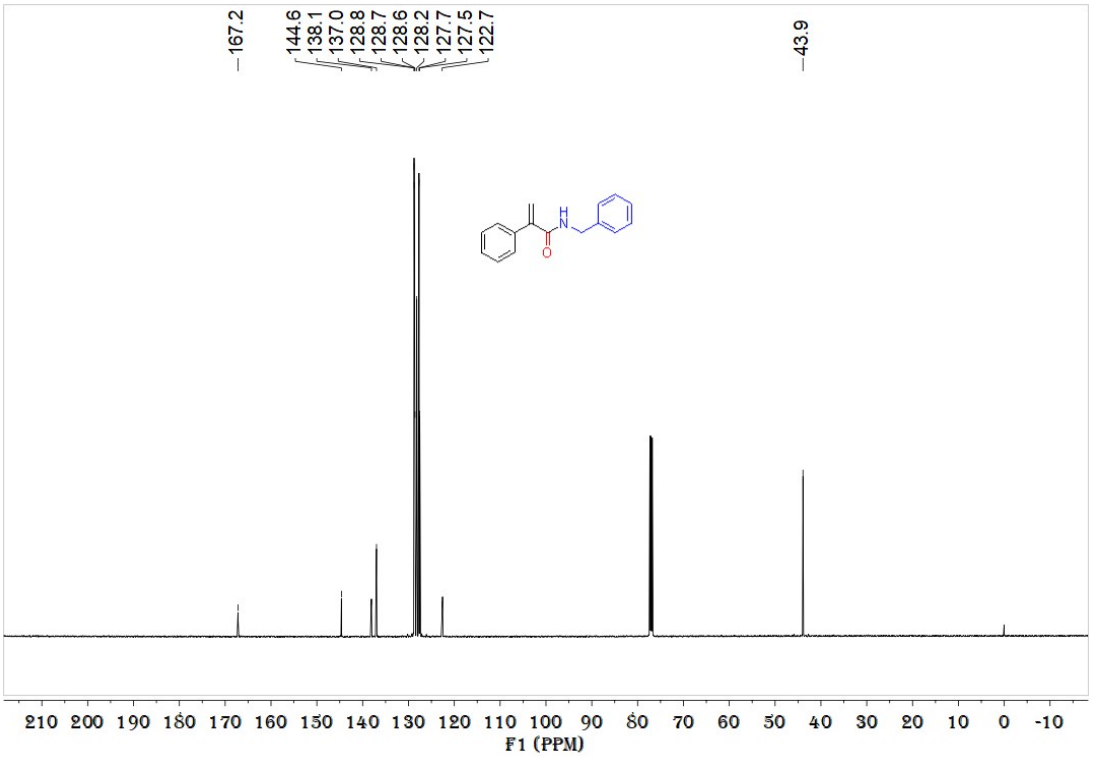
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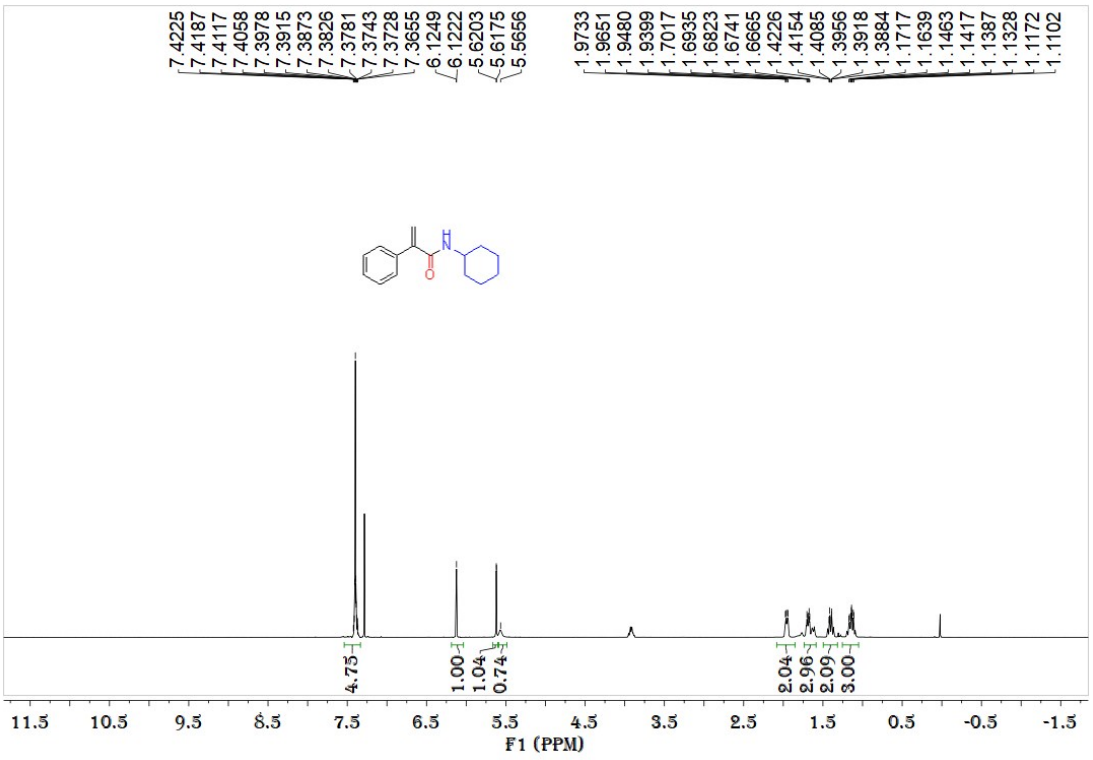
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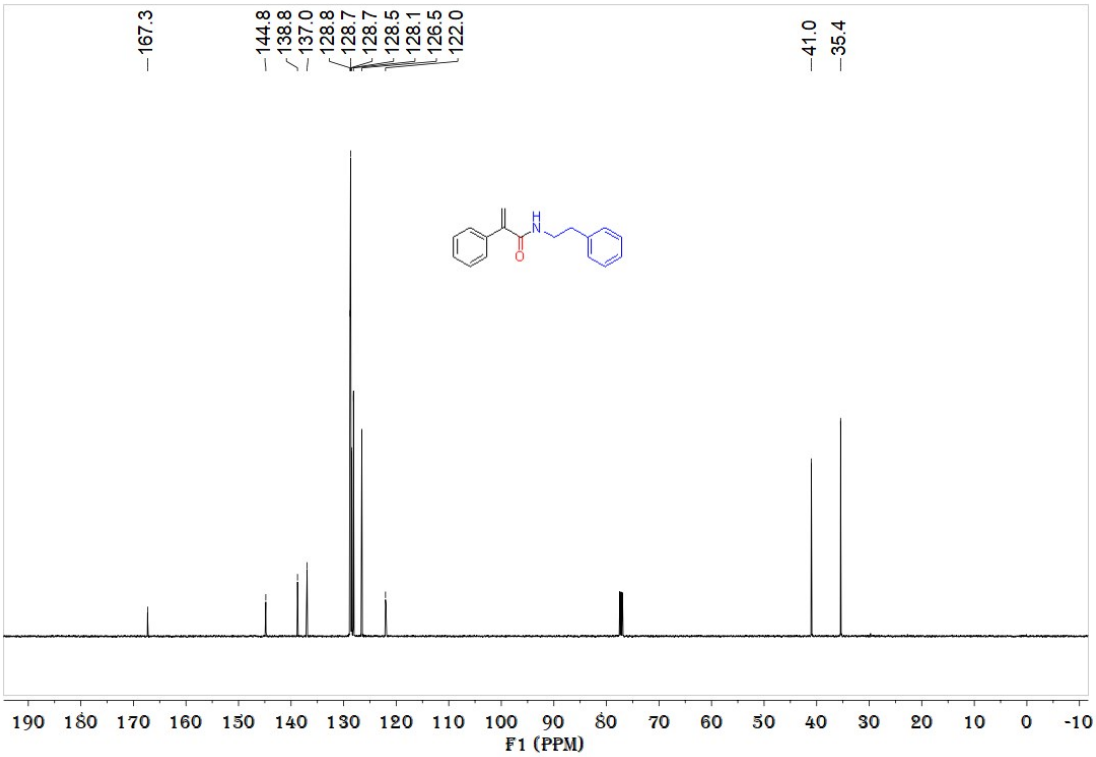
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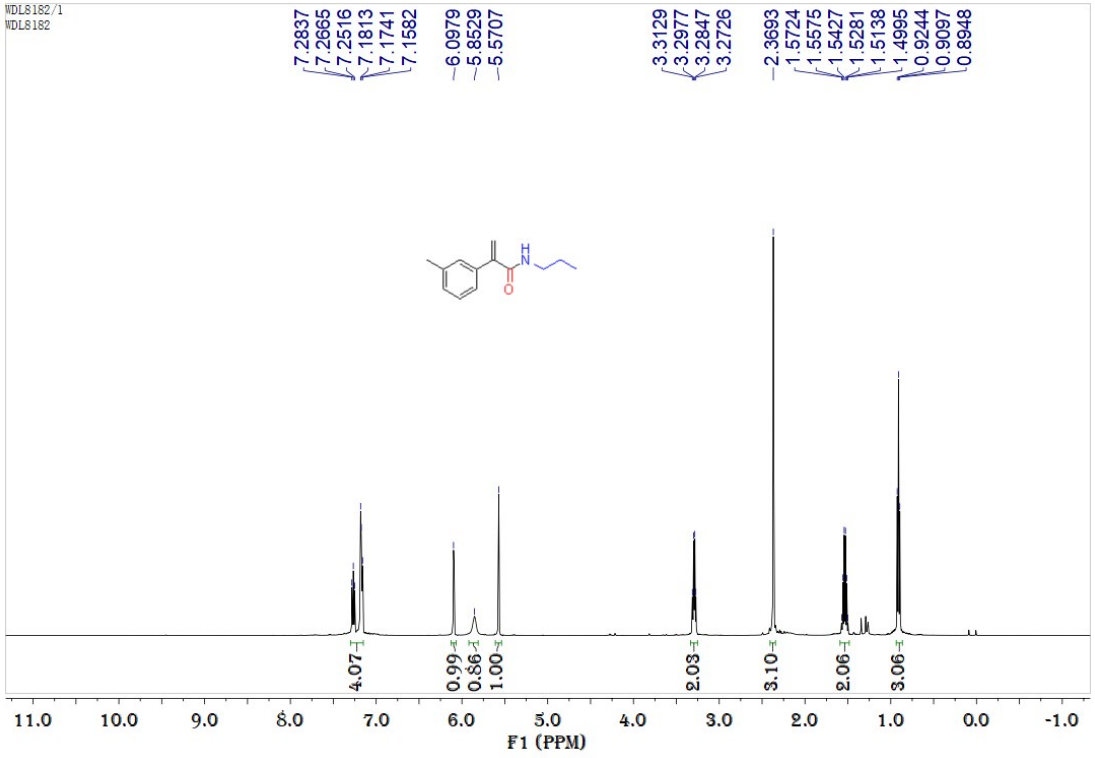
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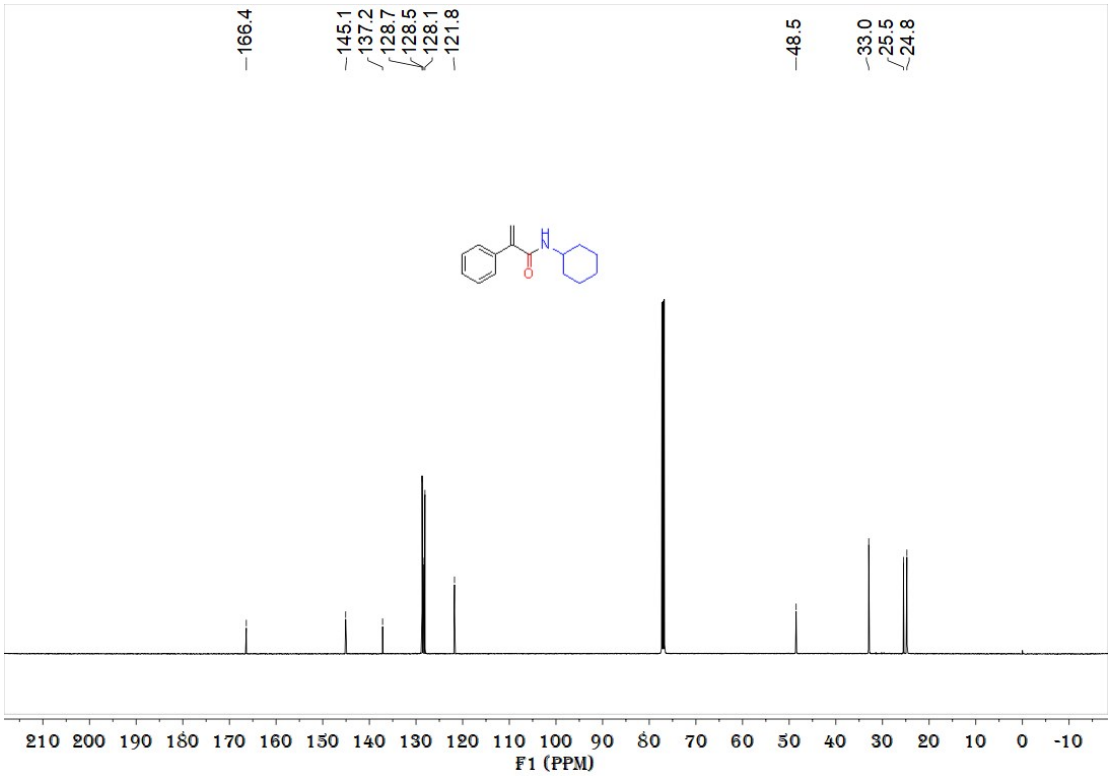
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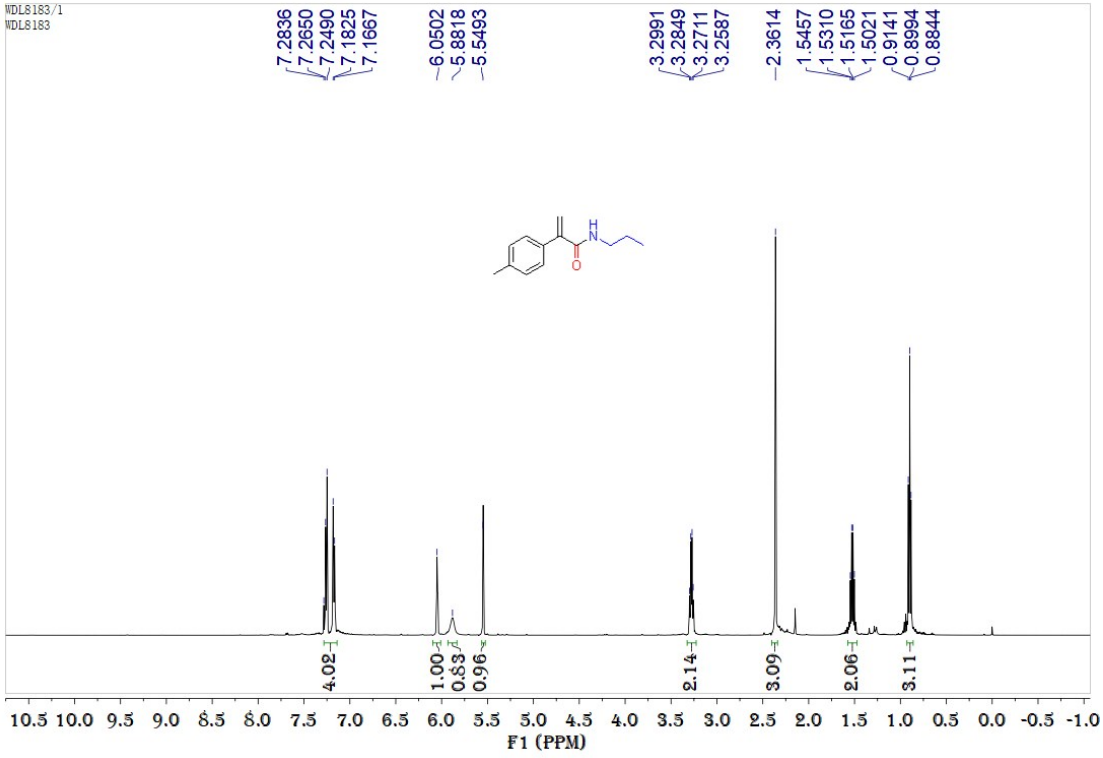
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2.14
3.09
2.06
3.11
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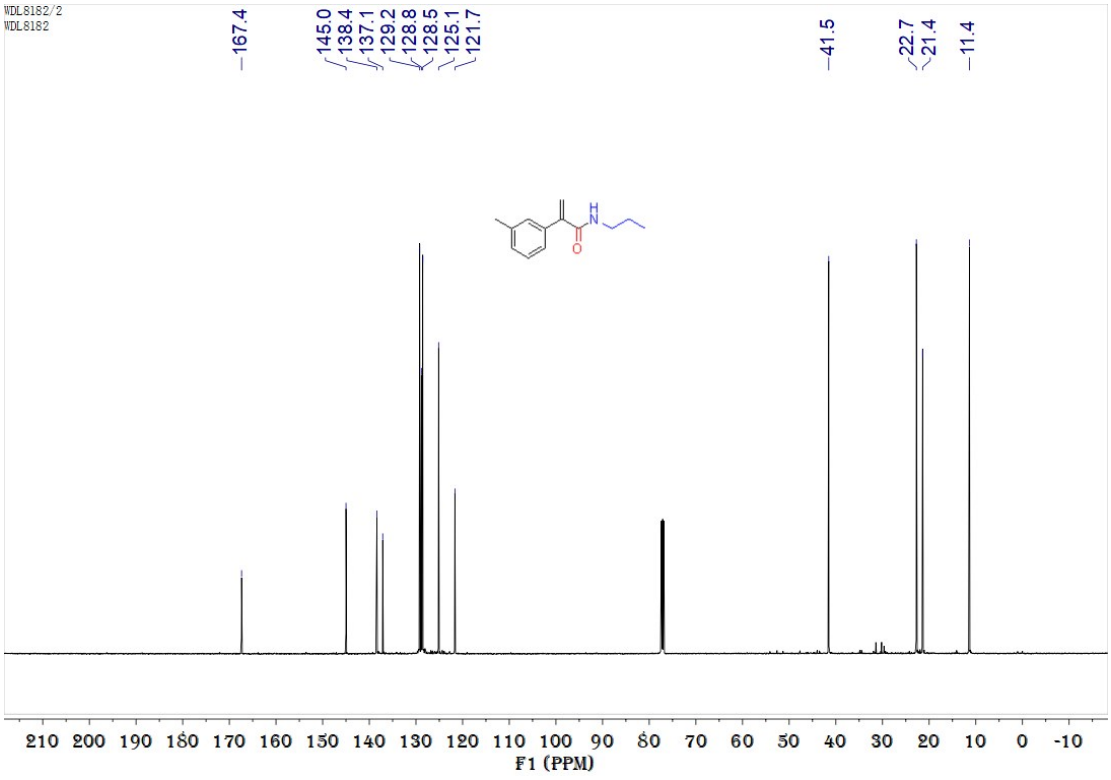
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125.1
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22.7
21.4
11.4
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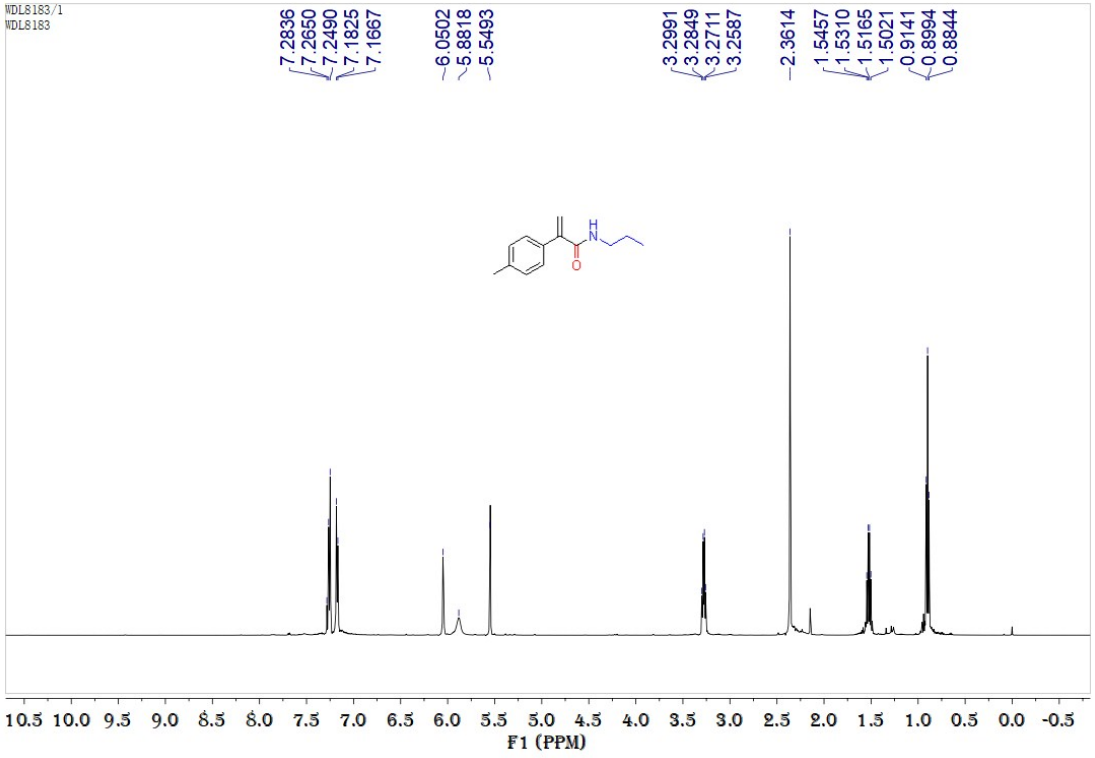
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3.2849
3.2711
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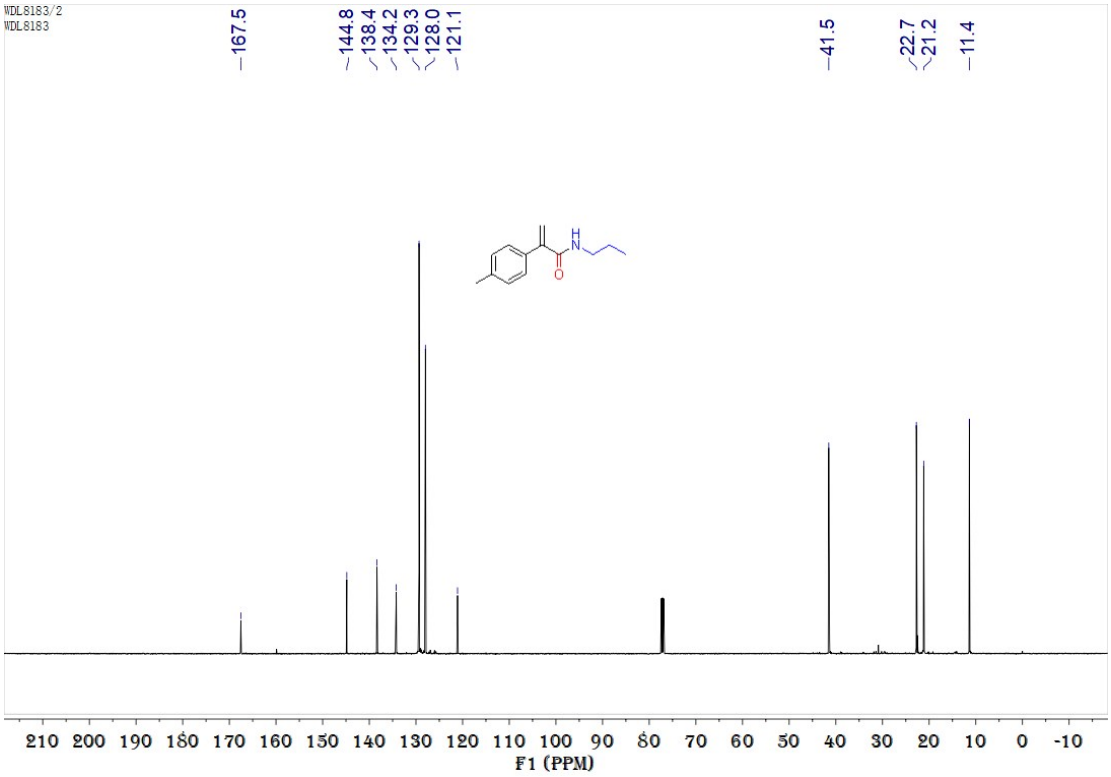
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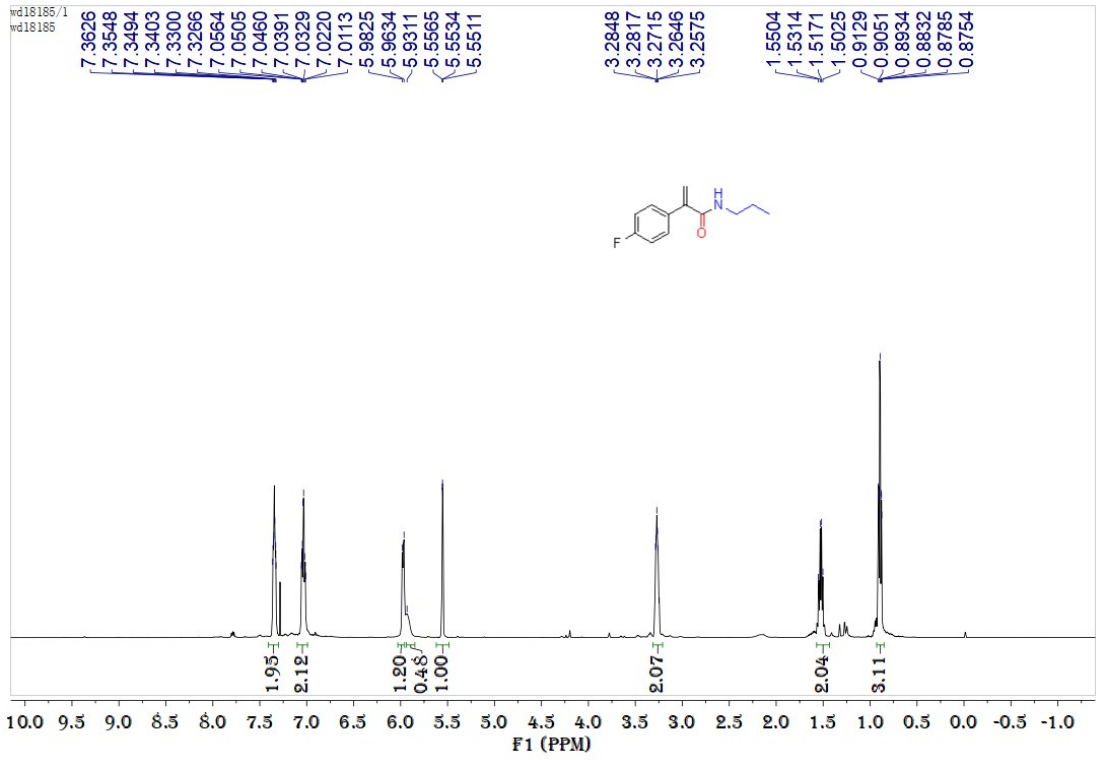
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5.5534
5.5511
3.2848
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3.2715
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3.2575
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1.5314
1.5171
1.5025
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0.9051
0.8934
0.8832
0.8785
0.8754
F
H
N
O
1.95
2.12
1.20
0.48
1.00
2.07
2.04
3.11
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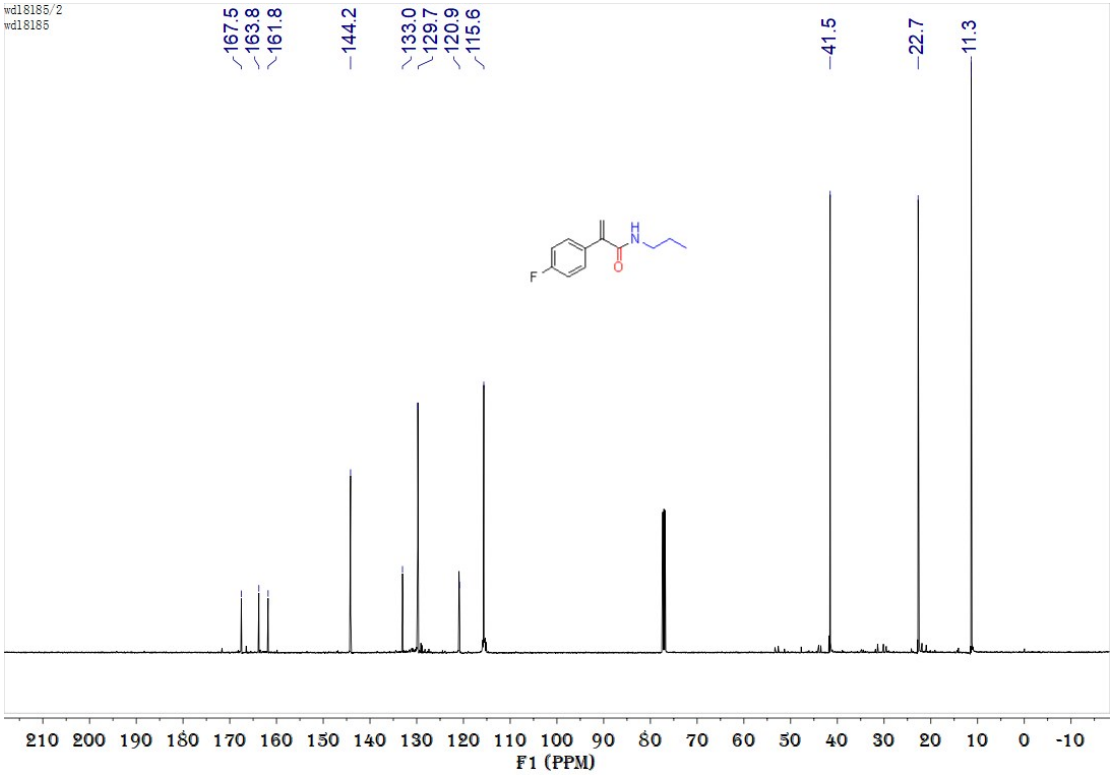
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11.3
F
H
N
O
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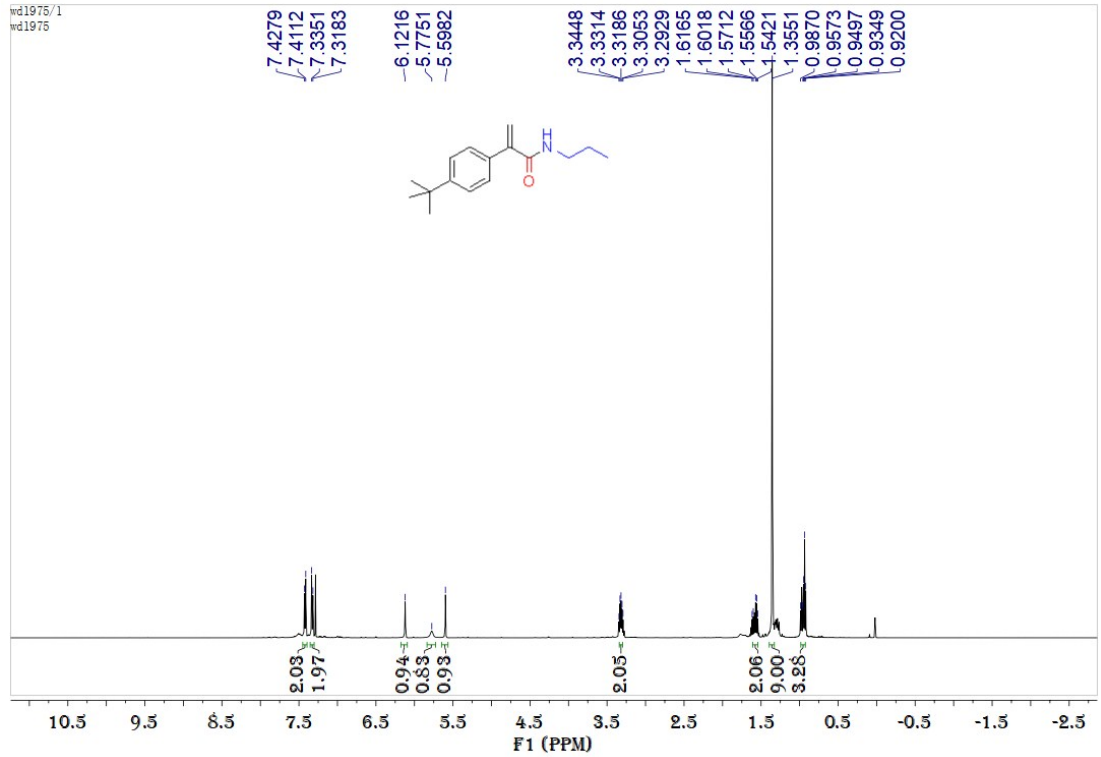
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3.2929
1.6165
1.6018
1.5712
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1.5421
1.3551
0.9870
0.9573
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0.9200
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1.97
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0.83
0.93
2.05
2.06
9.00
3.28
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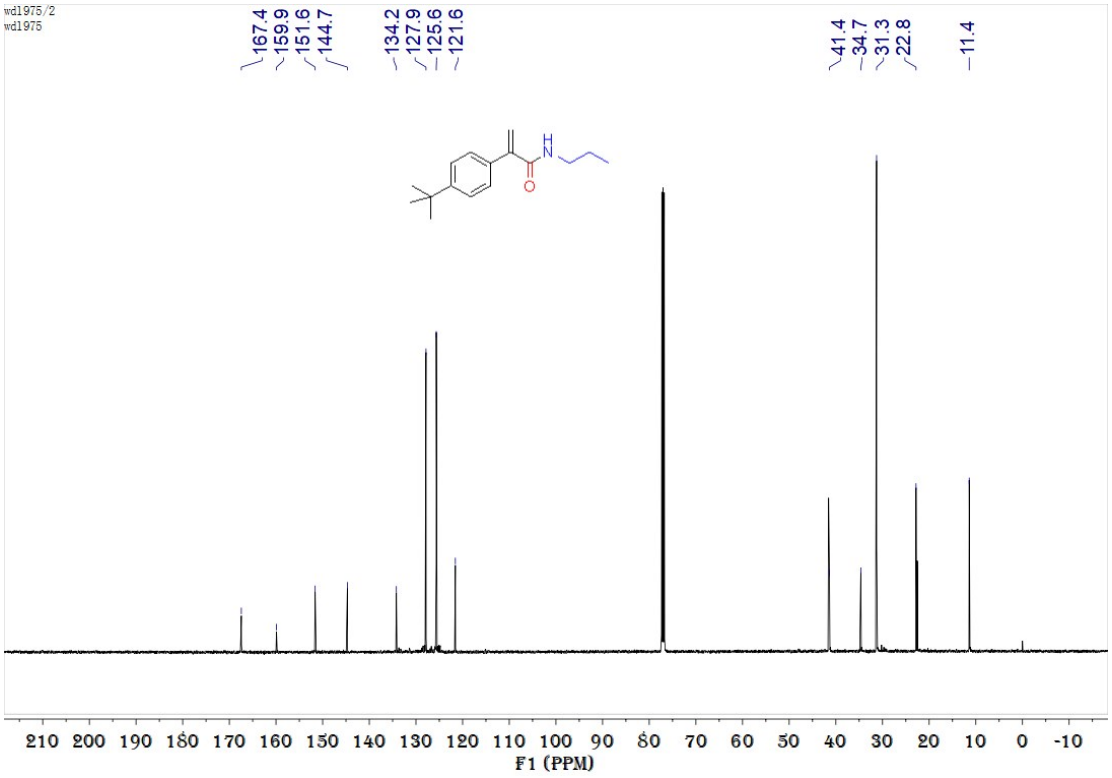
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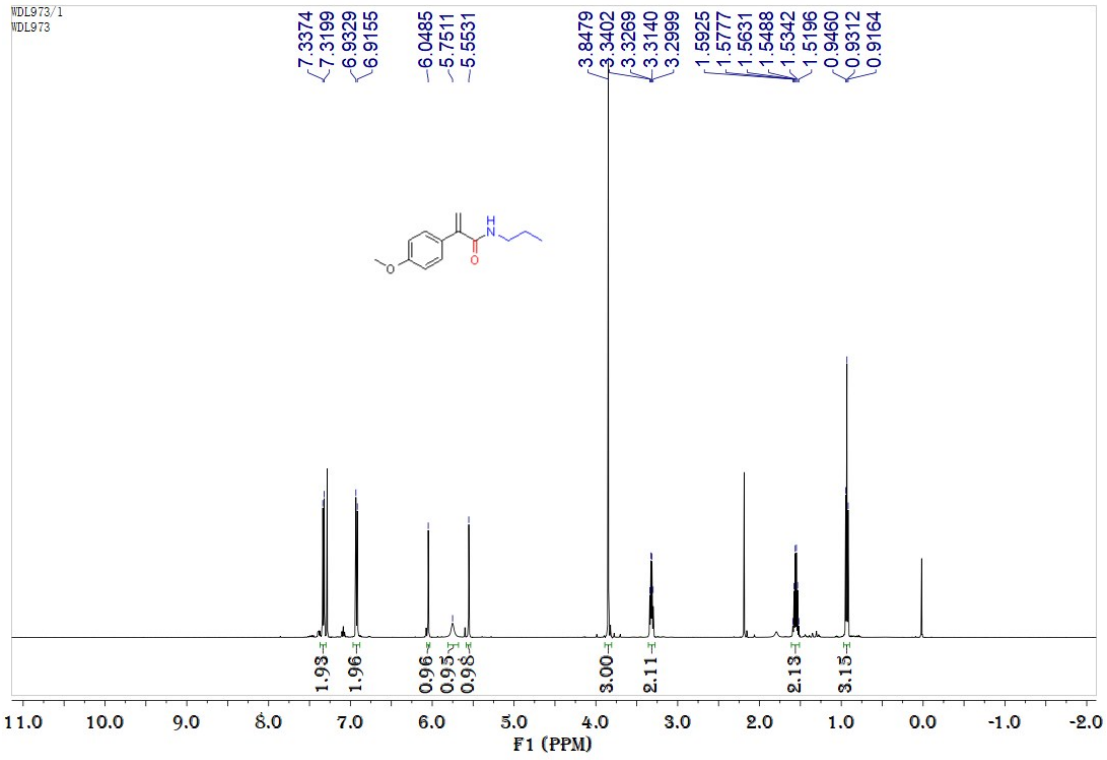
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3.3140
3.2999
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1.5777
1.5631
1.5488
1.5342
1.5196
0.9460
0.9312
0.9164
1.93
1.96
0.96
0.95
0.98
3.00
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2.13
3.15
11.0
10.0
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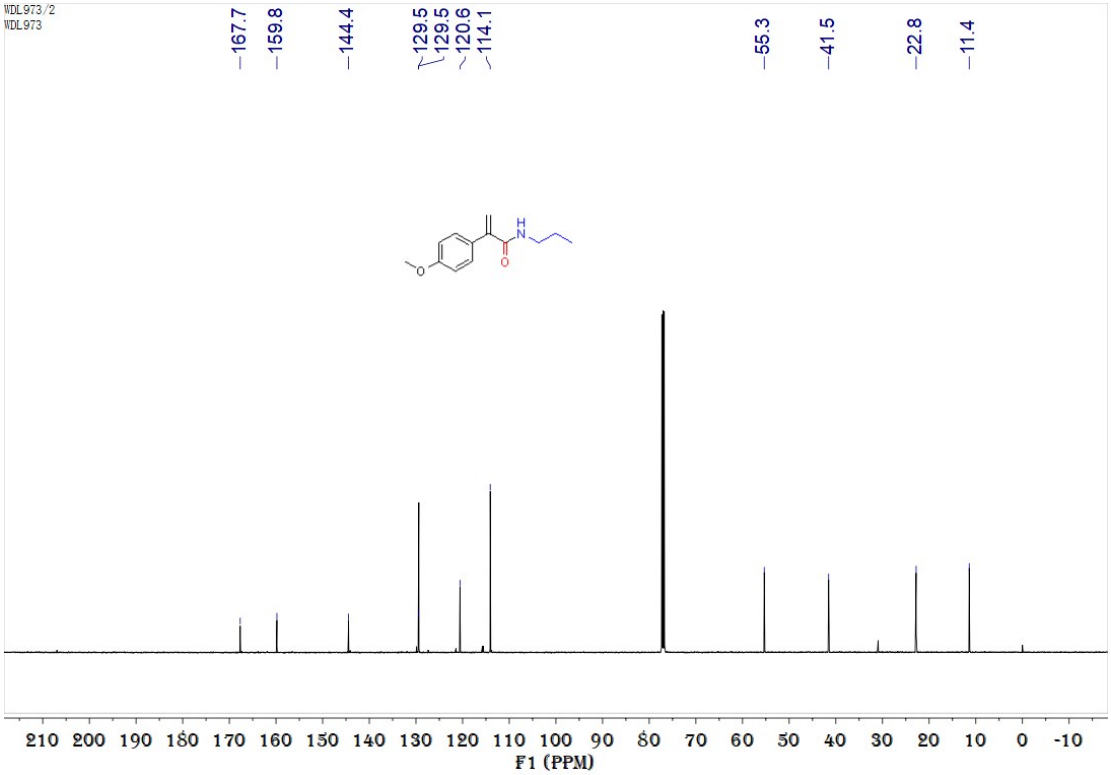
F1 (PPM)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22.8
11.4
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200
190
180
170
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110
100
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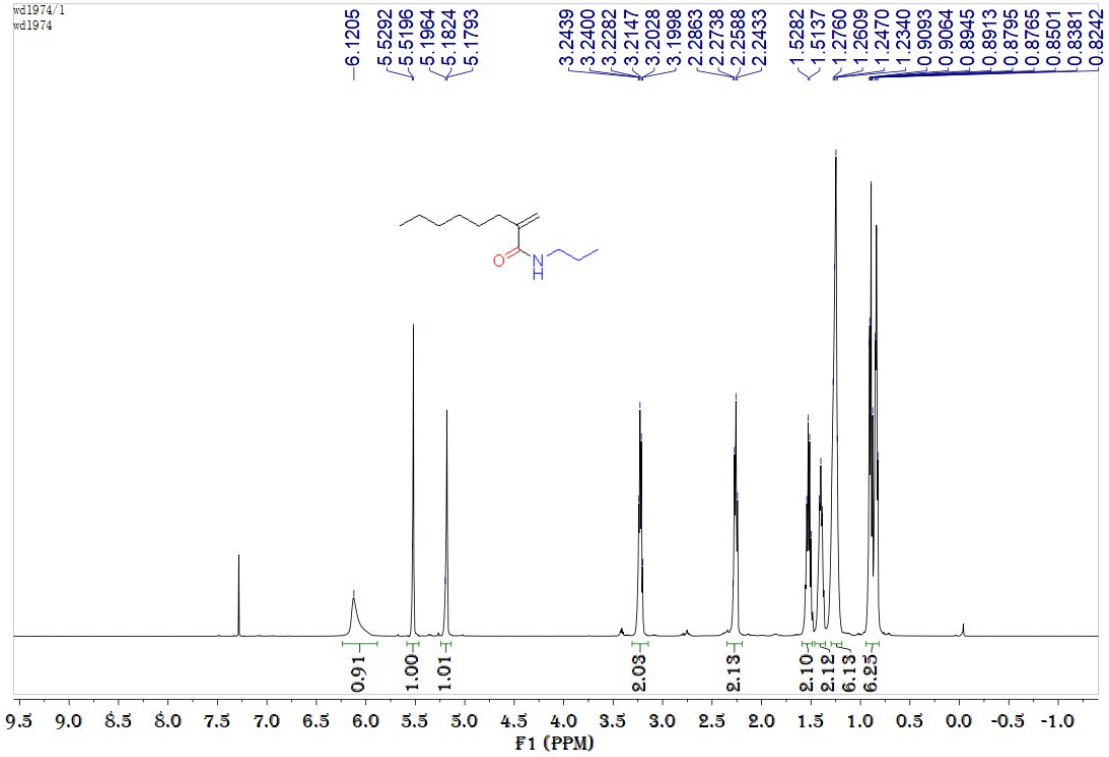
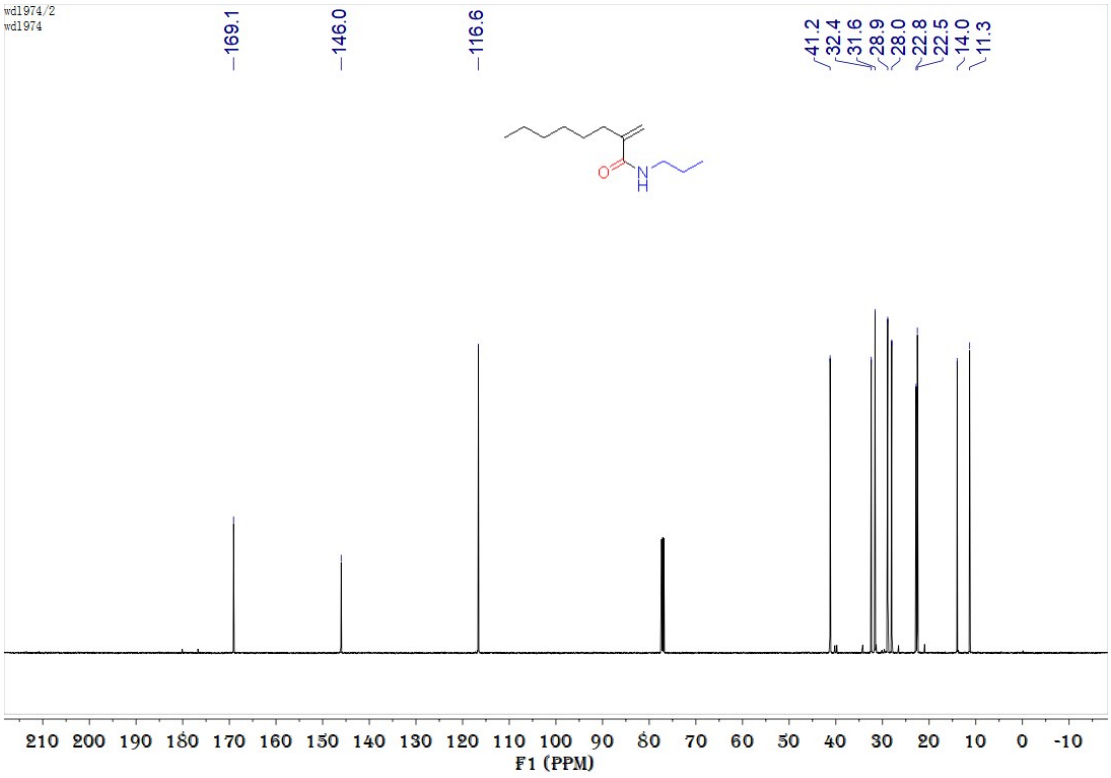
F1 (PPM)





6. References

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