Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Metal free access to amide compounds *via* peroxide-mediated N=N double bond cleavage of azobenzenes

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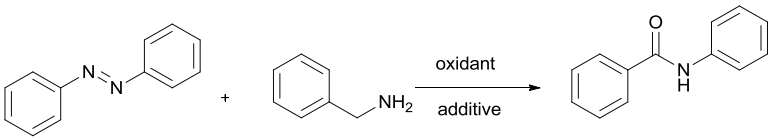
1. General experimental details

^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. High Resolution Mass spectra (HRMS) were performed on an ESI-TOF spectrometer**.** All reagents were obtained from commercial sources and used without further purification except as indicated below: DCE and benzaldehyde were purified according to the Purification of Laboratory Chemicals book, and azobenzenes were prepared according to the literature procedure.[1]

1.1 Optimization study for the reaction of azobenzene with benzyl amine[a]



1a **3a** **4a**

Entry	Oxidant	Additive (equiv)	Solvent	T (^{o}C)	Yield (%)[b]
1	TBHP	KOH (1.0)	DCE	120	34
2	TBHP	K_2CO_3 (1.0)	DCE	120	23
3	TBHP	^{t}BuOK (1.0)	DCE	120	57
4	TBHP	KI (1.0)	DCE	120	N.P.
5	TBHP	NBS (1.0)	DCE	120	17
6	TBHP	TBAB (1.0)	DCE	120	70
7	TBHP	TBAI (0.2)	DCE	120	N.P.
8	TBHP	CuBr (0.2)	DCE	120	N.P.
9	TBHP	/	DCE	120	72
10	DTBP	/	DCE	120	N.P.
11	$K_2S_2O_8$	/	DCE	120	N.P.
12	TBPB	/	DCE	120	44
13	TBHP	/	CH_3CN	120	54
14	TBHP	/	Dioxane	120	57
15	TBHP	/	DMF	120	N.P.
16	TBHP	/	DMSO	120	N.P.
17	TBHP		DCE	80	17
18	TBHP		DCE	rt	N.P.

[a]Reaction conditions: **1a** (0.25 mmol), **3a** (0.5 mmol), oxidant (4.0 equiv), additive, solvent (1.0 mL), 24 h, air. [b]Isolated yield.

1.2 General procedure for preparation of azobenzenes: Arylamine (1.0 mmol), CuBr (4.2 mg. 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), and toluene (4 mL) were added together. The mixture was stirred at 60 ^{o}C under air for 20 h, then cooled down to room temperature. The mixture was evaporated under vacuum. The corresponding azobenzene was isolated by silica gel column chromatography with a petroleum ether/ethyl acetate mixture as eluent.

1.3 Typical procedure for TBHP-mediated reaction of aldehydes or benzyl amines with azobenzenes: The mixture of azobenzenes **1** (0.25 mmol), aldehydes **2** (0.25 mmol) (or benzyl amines **3** (0.5 mmol)), TBHP (1.0 mmol) and DCE (1 mL) were added into a sealed tube. After being stirred vigorously at 120 ^{o}C for 24 h, the mixture was evaporated under vacuum. The corresponding product was isolated by silica gel column chromatography with a petroleum ether/ethyl acetate mixture as eluent.

1.4 The GC-MS and HRMS spectra about the reaction mixture.

The mixture of azobenzene **1a** (0.25 mmol), benzaldehyde **2a** (0.25 mmol), TBHP (1.0 mmol) and DCE (1 mL) were added into a sealed tube. After being stirred vigorously at 120 ^{o}C for 24 h, part of the mixture was analyzed by GC-MS and HRMS, respectively.

The by-product azoxybenzene was detected by HRMS spectrum of reaction mixture:

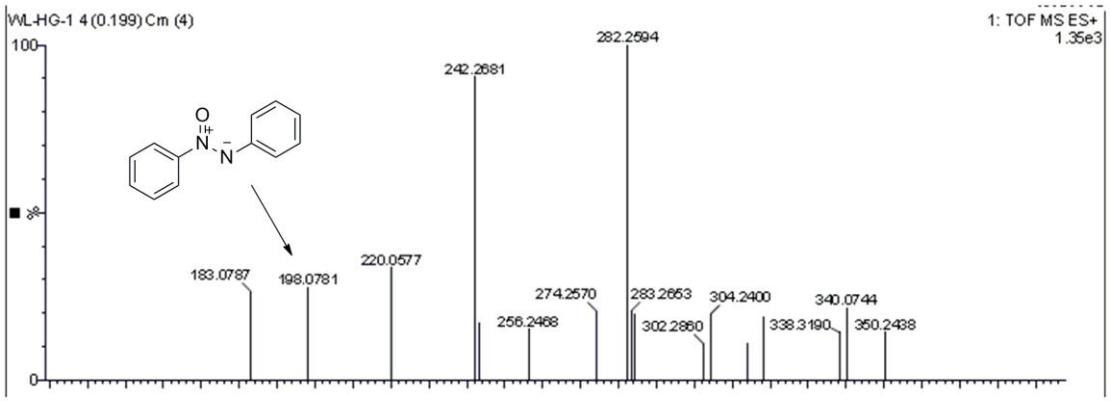


Figure S1. The HRMS spectrum of the reaction mixture

The corresponding GC-MS spectra about the by-product nitrobenzene was shown in Figure 2 and Figure 3.

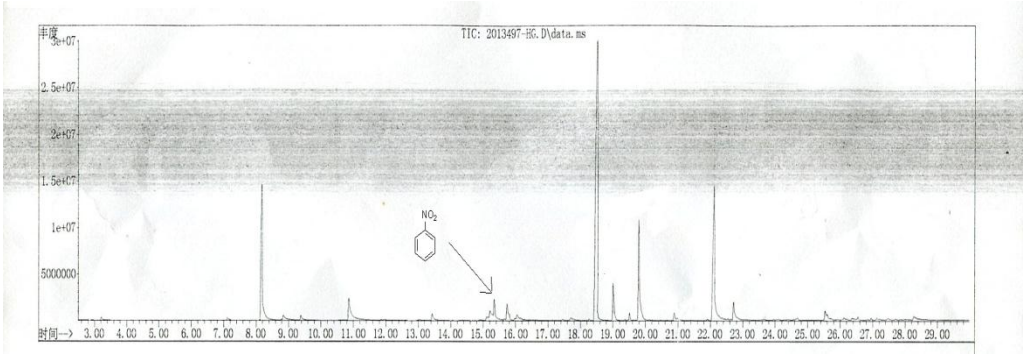


Figure S2. The GC-MS spectra from the reaction mixture which was carried out for 24 h

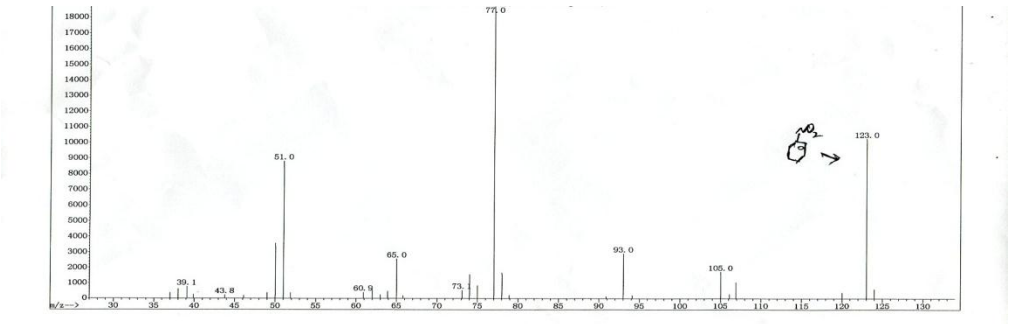
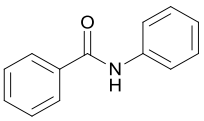


Figure S3. The GC-MS spectra of nitrobenzene

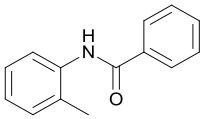
2. Experimental characterization data for products

***N*-phenylbenzamide (4a)[2]**



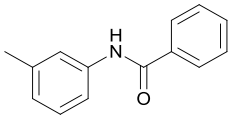
White soild. 40 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.80 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.59-7.47 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 137.9, 135.0, 131.9, 129.1, 128.8, 127.0, 124.6, 120.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}NO$ 198.0919; Found 198.0930

***N*-(*o*-tolyl)benzamide (4b)[2]**



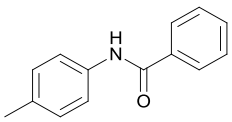
White soild. 25 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.78 (s, 1H), 7.67-7.55 (m, 3H), 7.37-7.30 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 134.7, 134.0, 132.6, 130.8, 129.5, 127.8, 126.0, 125.9, 124.4, 122.0, 16.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO$ 212.1075; Found 212.1066

***N*-(*m*-tolyl)benzamide (4c)[2]**



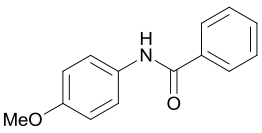
White soild. 37 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 6.8 Hz, 1H), 7.93 (s, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.63-7.39 (m, 4H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 139.0, 137.8, 135.0, 133.7, 131.8, 130.2, 128.5, 127.1, 125.4, 121.0, 117.4, 21.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO$ 212.1075; Found 212.1067

***N*-(*p*-tolyl)benzamide (4d)[2]**



White soild. 38 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 6.8 Hz, 2H), 7.80 (s, 1H), 7.54-7.45 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 135.4, 135.1, 134.2, 131.7, 129.6, 128.7, 127.0, 120.4, 20.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO$ 212.1075; Found 212.1078

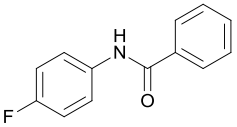
***N*-(4-methoxyphenyl)benzamide (4e)[2]**



Pale yellow solid. 24 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.56-7.51 (m,

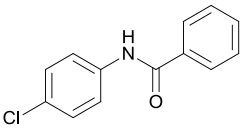
3H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 135.6, 135.0, 131.7, 131.0, 128.7, 128.4, 127.0, 122.1, 114.2, 55.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1025; Found 228.1024

***N*-(4-fluorophenyl)benzamide (4f)[2]**



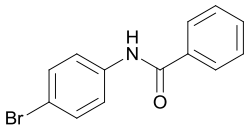
Pale yellow soild. 34 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.84 (s, 1H), 7.52-7.47 (m, 4H), 7.07 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 160.8, 158.3, 134.7, 133.6, 131.9, 130.2, 128.8, 128.5, 127.0, 122.1 (*J* = 7.7 Hz), 115.9, 115.7. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{13}H_9FNO$ 214.0668; Found 214.0661

***N*-(4-chlorophenyl)benzamide (4g)[2]**



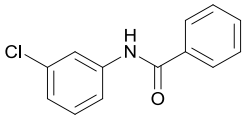
Pale yellow soild. 43 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.83 (bs, 1H), 7.53-7.46 (m, 4H), 7.34 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 136.5, 134.6, 132.1, 130.2, 129.6, 129.1, 128.9, 127.0, 121.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}ClNO$ 232.0529; Found 232.0513

***N*-(4-bromophenyl)benzamide (4h)[3]**



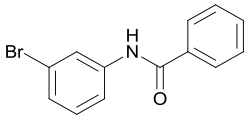
Pale yellow soild. 62 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.82 (s, 1H), 7.58-7.47 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 134.6, 133.7, 132.1, 132.0, 128.9, 127.0, 121.7. 117.2. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{13}H_9BrNO$ 273.9868; Found 273.9833

***N*-(3-chlorophenyl)benzamide (4i)[2]**



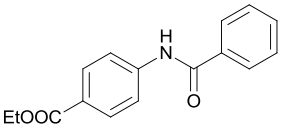
Pale yellow soild. 33 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.2 Hz, 1H), 8.04 (s, 1H), 7.77-7.75 (m, 1H), 7.50-7.42 (m, 5H), 7.28-7.23 (m, 1H), 7.13-7.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 139.1, 134.7, 134.5, 132.1, 130.0, 128.8, 127.1, 124.6, 120.4, 118.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}ClNO$ 232.0529; Found 232.0523

***N*-(3-bromophenyl)benzamide (4j)[2]**



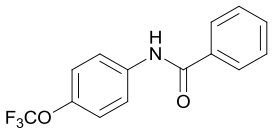
White soild. 40 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.91-7.82 (m, 3H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.28-7.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 139.2, 134.5, 132.1, 130.3, 128.5, 127.6, 127.1, 123.2, 122.7, 118.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}BrNO$ 276.0024; Found 276.0021

ethyl 4-benzamidobenzoate (4k)[4]



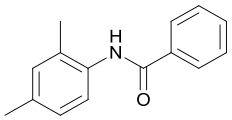
White soild. 55 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.57-7.53 (m, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 166.0, 142.2, 134.5, 132.2, 130.8, 128.8, 127.1, 126.1, 119.3, 60.9, 14.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_3$ 270.1130; Found 270.1129

***N*-(4-(trifluoromethoxy)phenyl)benzamide (4l)**



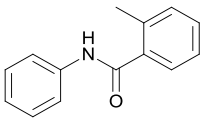
White soild. 49 mg, 70% yield. mp: 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 6.8 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.61-7.46 (m, 4H), 7.23 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 136.5, 134.5, 133.7, 132.1, 130.2, 128.9, 128.5, 127.0, 121.9, 121.3. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{14}H_9F_3NO_2$ 280.0585; Found 280.0573

***N*-(2,4-dimethylphenyl)benzamide (4m)[3]**



Pale yellow soild. 16 mg, 29% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 6.8 Hz, 1H), 7.63-7.46 (m, 5H), 7.12-7.02 (m, 1H), 2.32 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 139.1, 133.8, 131.8, 131.3, 130.2, 129.4, 128.8, 128.5, 127.4, 127.3, 20.9, 17.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NO$ 226.1232; Found 226.1226

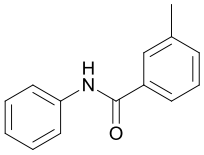
2-methyl-*N*-phenylbenzamide (4n)[2]



White soild. 30 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.46-7.32 (m, 4H), 7.27-7.22 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 138.0, 136.4, 131.3, 130.3, 129.1, 126.6, 125.9, 124.6, 119.9, 19.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO$

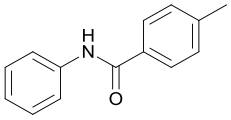
212.1075; Found 212.1081

3-methyl-*N*-phenylbenzamide (4o)[2]



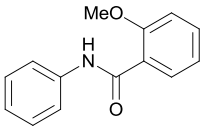
Pale yellow soild. 38 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (bs, 1H), 7.69-7.63 (m, 3H), 7.39-7.35 (m, 5H), 7.15 (t, *J* = 7.2 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 138.7, 138.3, 135.0, 132.6, 129.1, 128.7, 127.8, 124.5, 123.9, 120.2, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO$ 212.1075; Found 212.1079

4-methyl-*N*-phenylbenzamide (4p)[2]



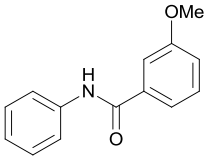
White soild. 36 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 142.4, 138.0, 132.1, 129.4, 129.1, 127.0, 124.4, 120.2, 21.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{13}NNaO$ 234.0895; Found 234.0893

2-methoxy-*N*-phenylbenzamide (4q)[5]



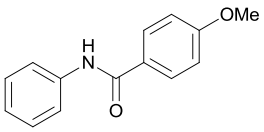
White soild. 26 mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.31-8.27 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.50-7.47 (m, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.16-7.12 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 157.2, 138.4, 133.3, 132.5, 129.0, 124.2, 121.7, 120.4, 111.5, 56.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1025; Found 228.1022

3-methoxy-*N*-phenylbenzamide (4r)[2]



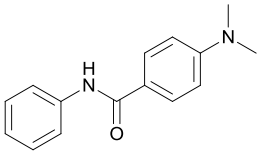
White soild. 36 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 1H), 7.40-7.35 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.09-7.07 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 159.9, 137.9, 136.5, 129.8, 129.1, 124.6, 120.2, 118.7, 118.0, 112.5, 55.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1025; Found 228.1022

4-methoxy-*N*-phenylbenzamide (4s)[2]



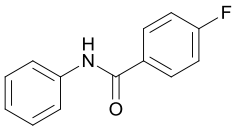
White soild. 38 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.8 Hz, 2H), 7.80 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 162.5, 138.1, 129.1 129.0, 127.1, 124.3, 120.1, 114.0, 55.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1025; Found 228.1029

4-(dimethylamino)-*N*-phenylbenzamide (4t)[5]



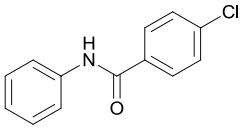
White soild. 25 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.73 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.25-7.23 (m, 2H), 7.13-7.08 (m, 1H), 3.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 153.8, 138.5, 132.0, 131.4, 129.0, 128.6, 124.5, 123.9, 111.2, 40.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}N_2O$ 241.1341; Found 241.1346

4-fluoro-*N*-phenylbenzamide (4u)[3]



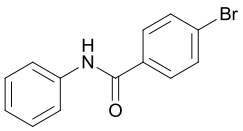
Pale yellow soild. 22 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.87 (m, 2H), 7.77 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 164.7, 163.7, 137.7, 131.2, 130.5 (*J* = 2.1 Hz), 129.4 (*J* = 8.9 Hz), 129.2, 124.7, 120.2, 115.9 (*J* = 21.8 Hz). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}FNO$ 216.0825; Found 216.0819

4-chloro-*N*-phenylbenzamide (4v)[2]



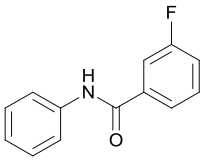
White soild. 31 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 138.2, 137.6, 133.3, 129.2, 129.1, 128.5, 124.8, 120.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}ClNO$ 232.0529; Found 232.0531

4-bromo-*N*-phenylbenzamide (4w)[2]



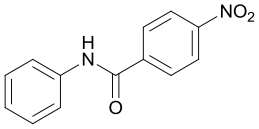
White soild. 27 mg, 39% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.65-7.61 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 136.6, 132.8, 131.0, 128.1, 127.6, 125.6, 123.8, 119.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{10}BrNNaO$ 297.9843; Found 297.9829

3-fluoro-*N*-phenylbenzamide (4x)[2]



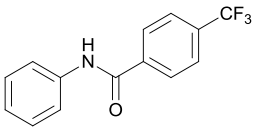
White soild. 42 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (bs, 1H), 7.65-7.57 (m, 4H), 7.49-7.43 (m, 1H), 7.40-7.35 (m, 2H), 7.28-7.22 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 164.1, 161.6, 137.6, 137.2 (*J* = 6.8 Hz), 130.5 (*J* = 7.9 Hz), 129.2, 124.9, 122.4, 120.3, 118.9 (*J* = 21.1 Hz), 114.6 (*J* = 22.9 Hz). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}FNO$ 216.0825; Found 216.0831

4-nitro-*N*-phenylbenzamide (4y)[5]



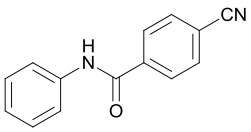
White soild. 24 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 149.3, 140.7, 137.4, 129.2, 127.5, 125.9, 125.1, 120.3. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{13}H_9N_2O_3$ 241.0613; Found 241.0591

***N*-phenyl-4-(trifluoromethyl)benzamide (4z)[6]**



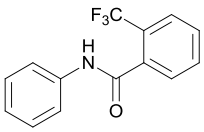
White soild. 28 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.82 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 139.2, 133.5, 131.5, 128.3, 127.2, 124.3, 123.7, 123.0, 120.5. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{14}H_9F_3NO$ 264.0636; Found 264.0615

4-cyano-*N*-phenylbenzamide (4aa)[7]



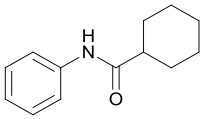
White soild. 21 mg, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.91 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 138.9, 137.3, 132.6, 129.2, 127.8, 125.3, 120.4, 117.9, 115.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}N_2O$ 223.0871; Found 223.0876

***N*-phenyl-2-(trifluoromethyl)benzamide (4ab)[2]**



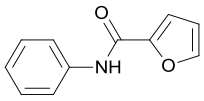
White soild. 28 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.67-7.56 (m, 5H), 7.51 (s, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 137.4, 135.8, 132.2, 130.9, 130.2, 129.2, 128.6, 126.5 (*J* = 4.9 Hz), 125.1, 120.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{10}F_3NNaO$ 288.0612; Found 288.0605

***N*-phenylcyclohexanecarboxamide (4ac)[8]**



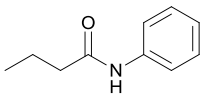
White soild. 17 mg, 34% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 2.27-2.20 (m, 1H), 1.85-1.65 (m, 5H), 1.57-1.43 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 138.1, 128.9, 124.1, 119.8, 46.6, 29.7, 25.7, 25.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}NO$ 204.1388; Found 204.1386

***N*-phenylfuran-2-carboxamide (4ad)[9]**



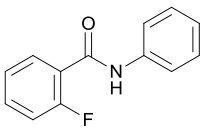
Brown soild. 18 mg, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.52 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.26-7.24 (m, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.58-6.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 146.8, 143.1, 136.3, 128.1, 123.5, 118.9, 114.3, 111.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}NO_2$ 188.0712; Found 188.0719

***N*-phenylbutyramide (4ae)[9]**



White soild. 19 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.79-1.72 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 137.9, 128.9, 124.2, 119.9, 39.7, 19.1, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_{14}NO$ 164.1075; Found 164.1083

2-fluoro-*N*-phenylbenzamide (4af)[2]



White soild. 31 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (bs, 1H), 8.20-8.15 (m, 1H), 7.66 (d, *J* =

7.6 Hz, 2H), 7.54-7.51 (m, 1H), 7.40-7.29 (m, 3H), 7.21-7.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 161.3, 159.2, 137.7, 133.8 (*J* = 9.4 Hz), 132.3, 129.1, 125.1, 124.8, 121.3 (*J* = 11.2 Hz), 120.5, 116.1 (*J* = 24.9 Hz). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}FNO$ 216.0825; Found 216.0818

3. References

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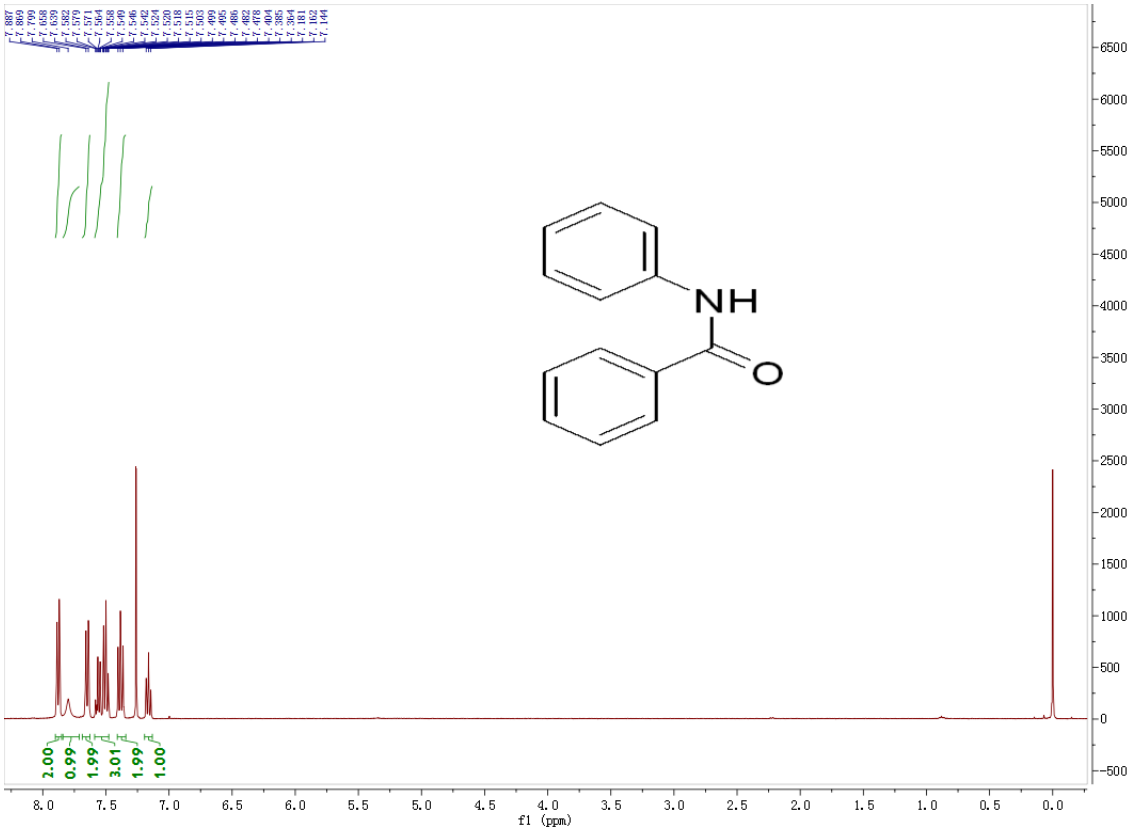
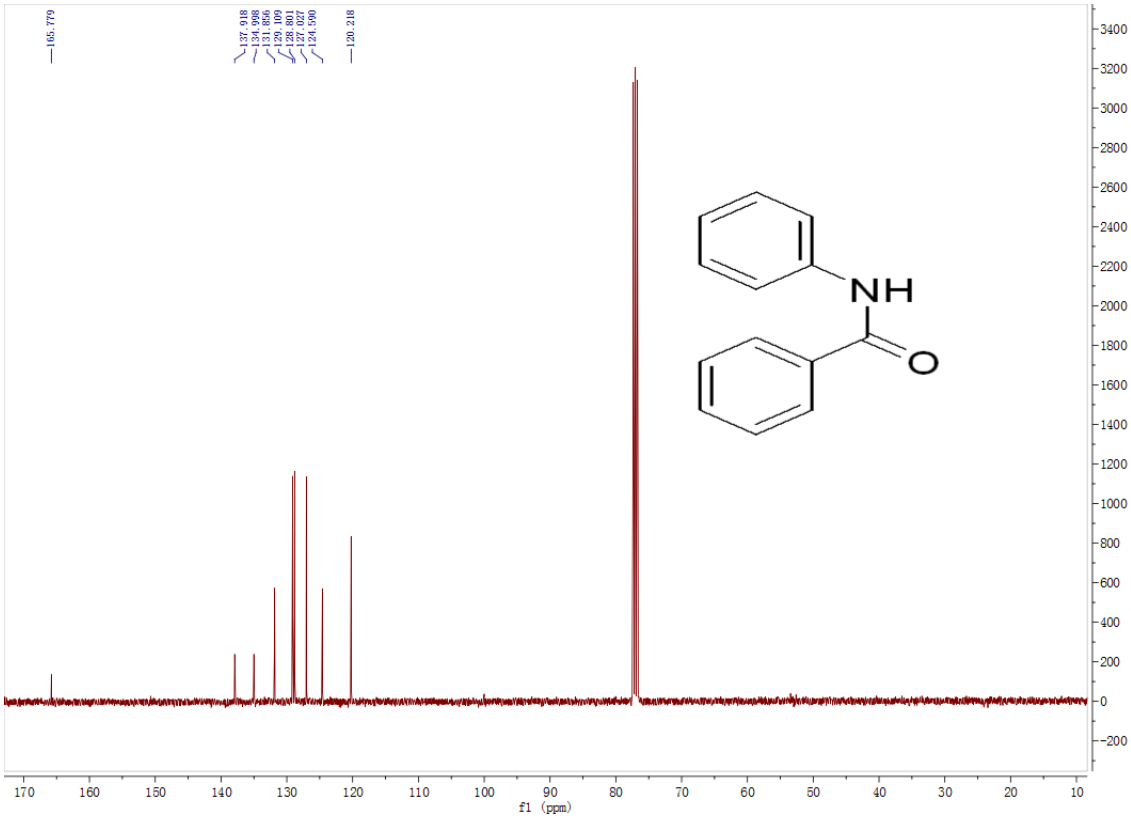
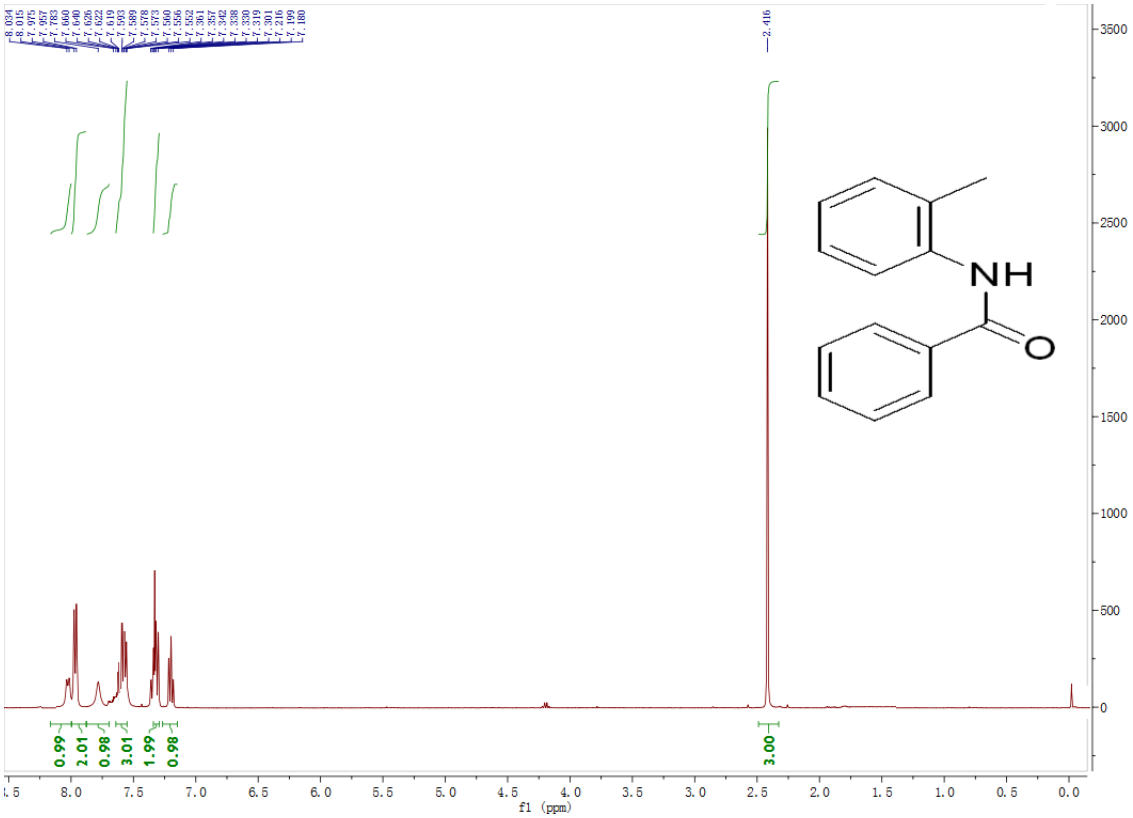
4. NMR spectra

4a





4b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7.573
7.560
7.556
7.552
7.361
7.352
7.342
7.338
7.330
7.319
7.301
7.216
7.199
7.180
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NH
O
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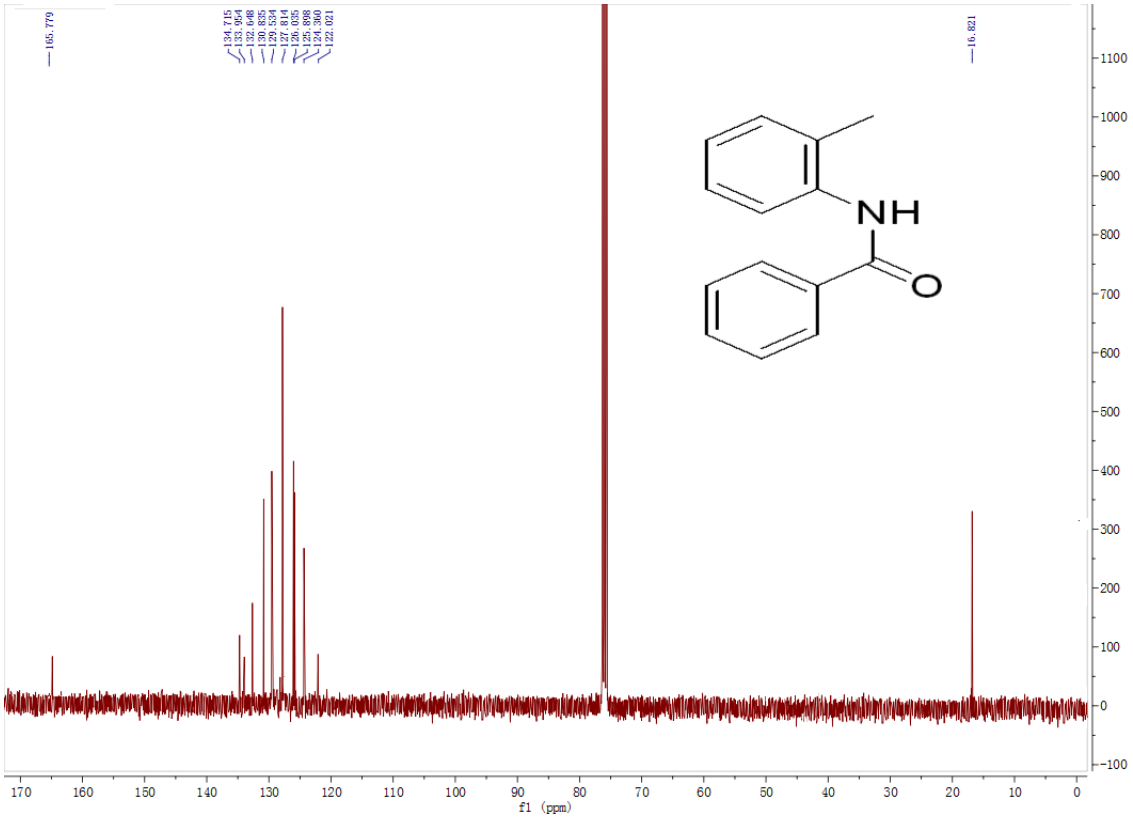
2.01
0.98
3.01
1.99
0.98
3.00
f1 (ppm)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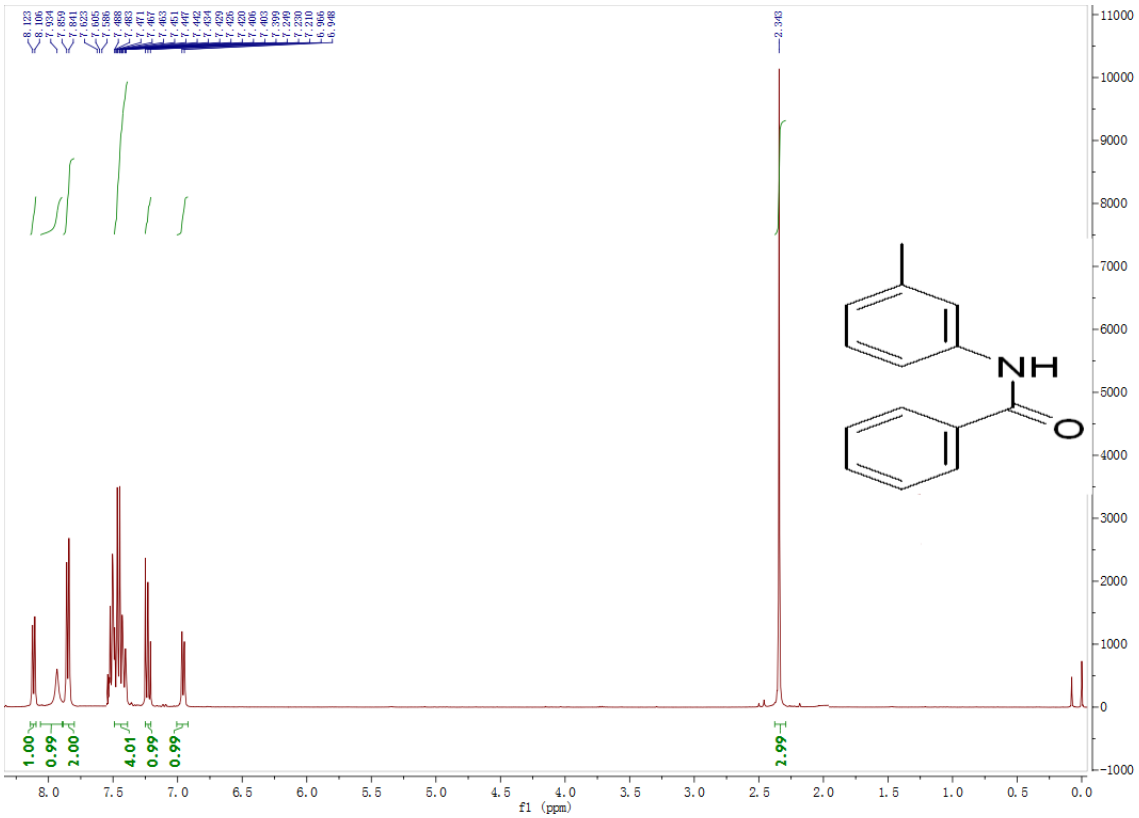
O
f1 (ppm)

4c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7.403
7.399
7.249
7.230
7.210
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0.99
2.00
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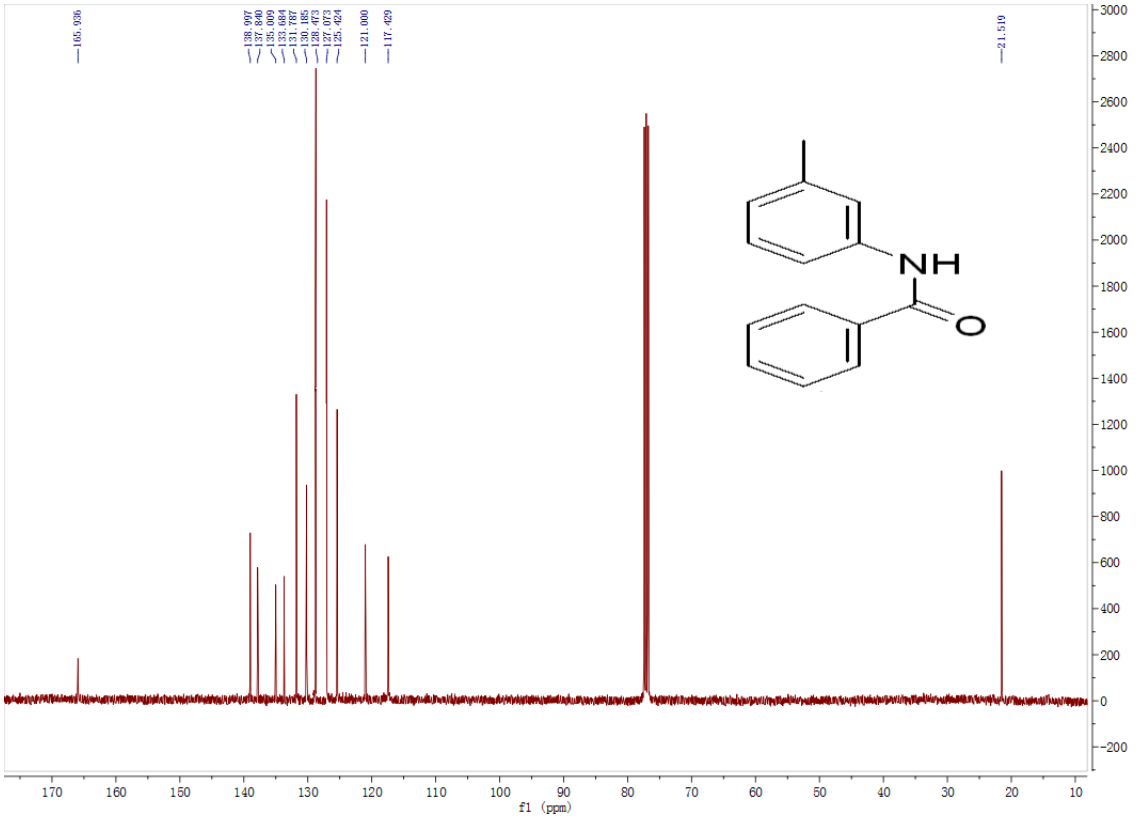
NH
O
f1 (ppm)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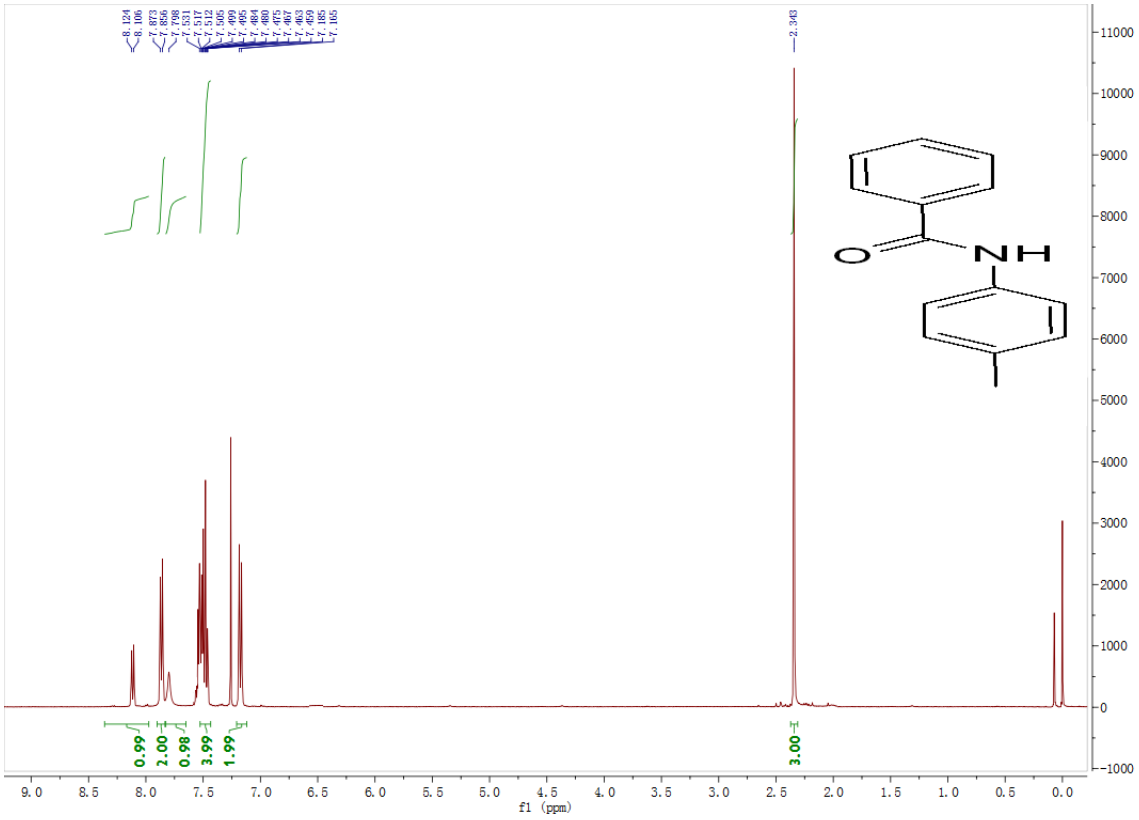
O
f1 (ppm)

4d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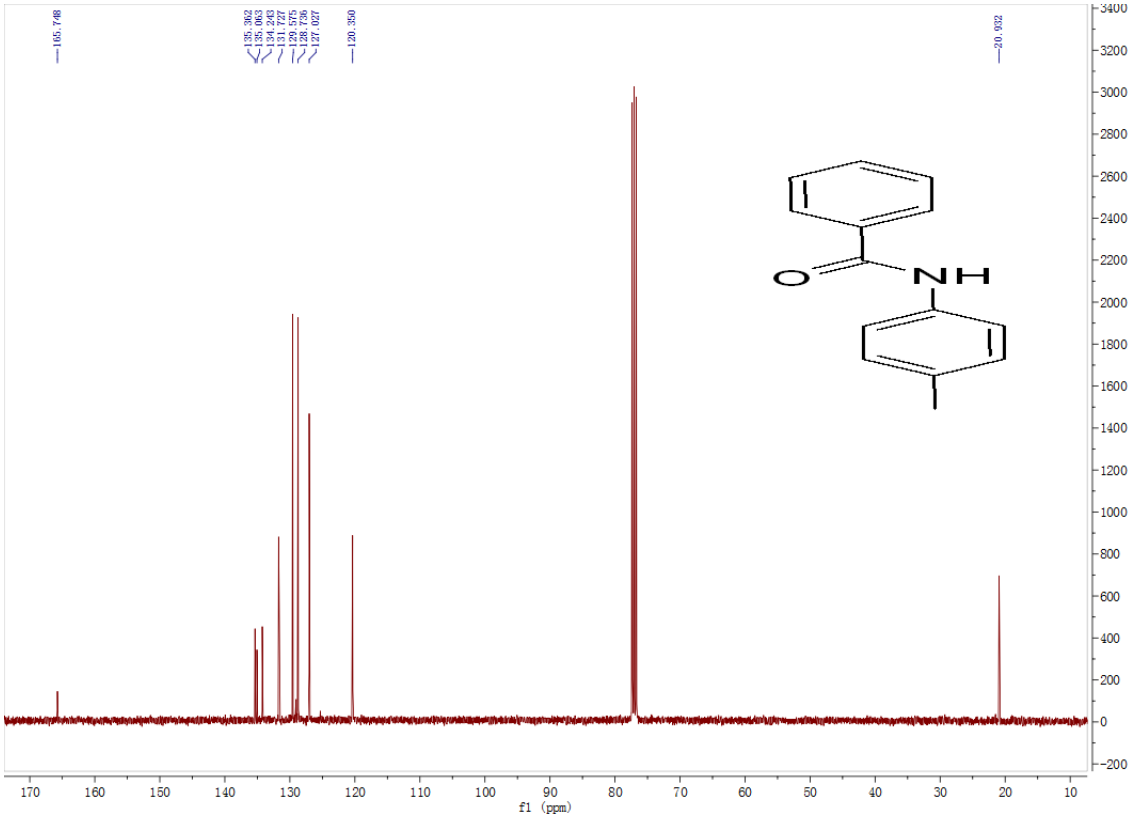
O
f1 (ppm)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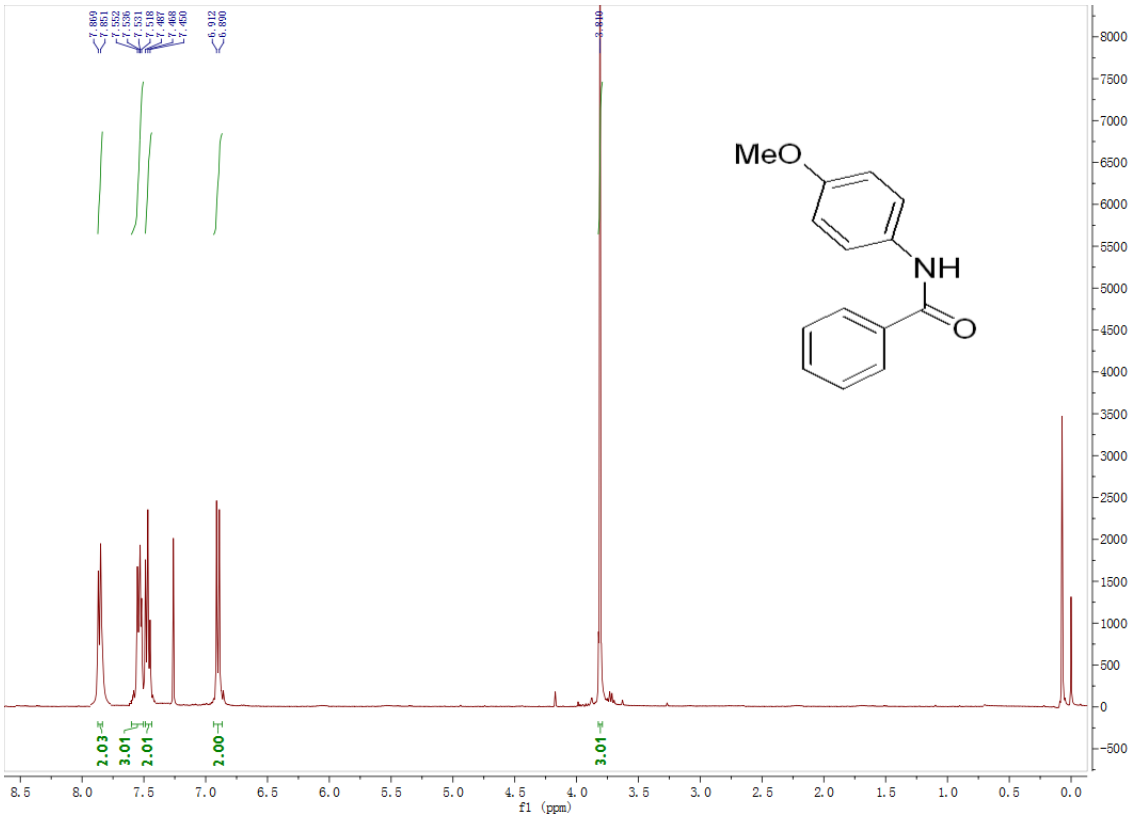
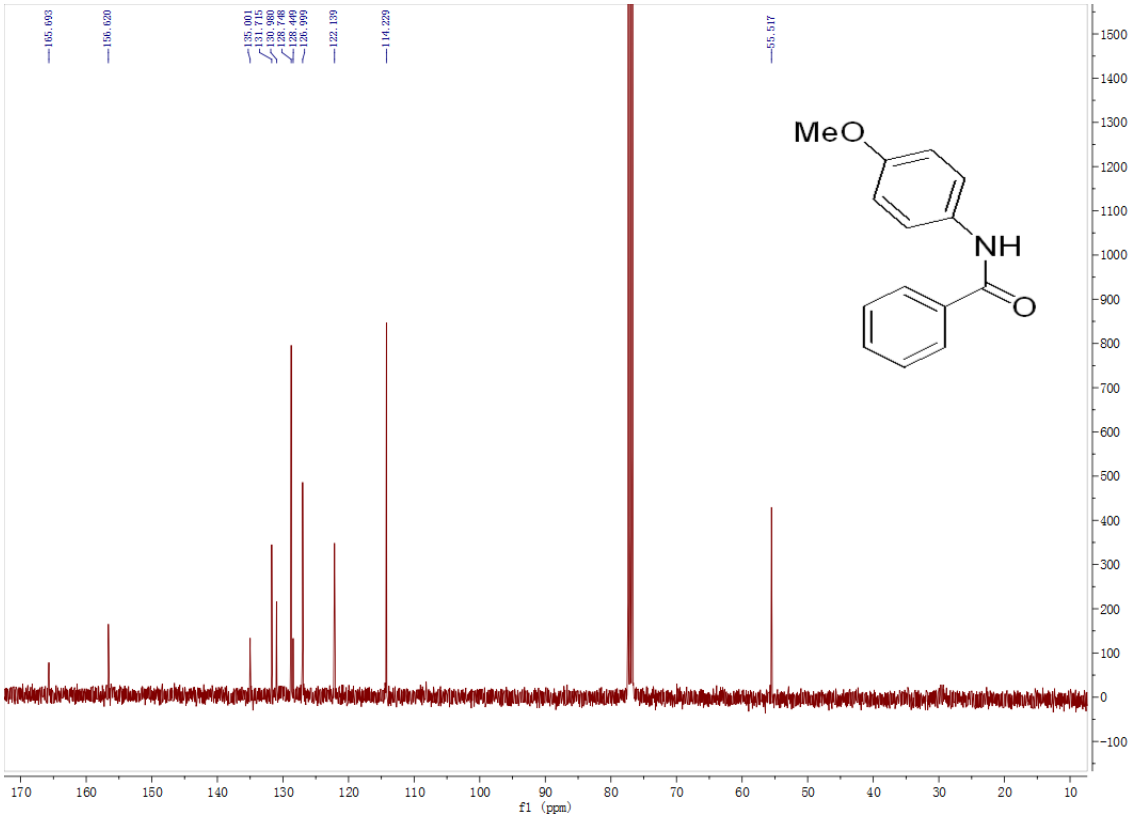
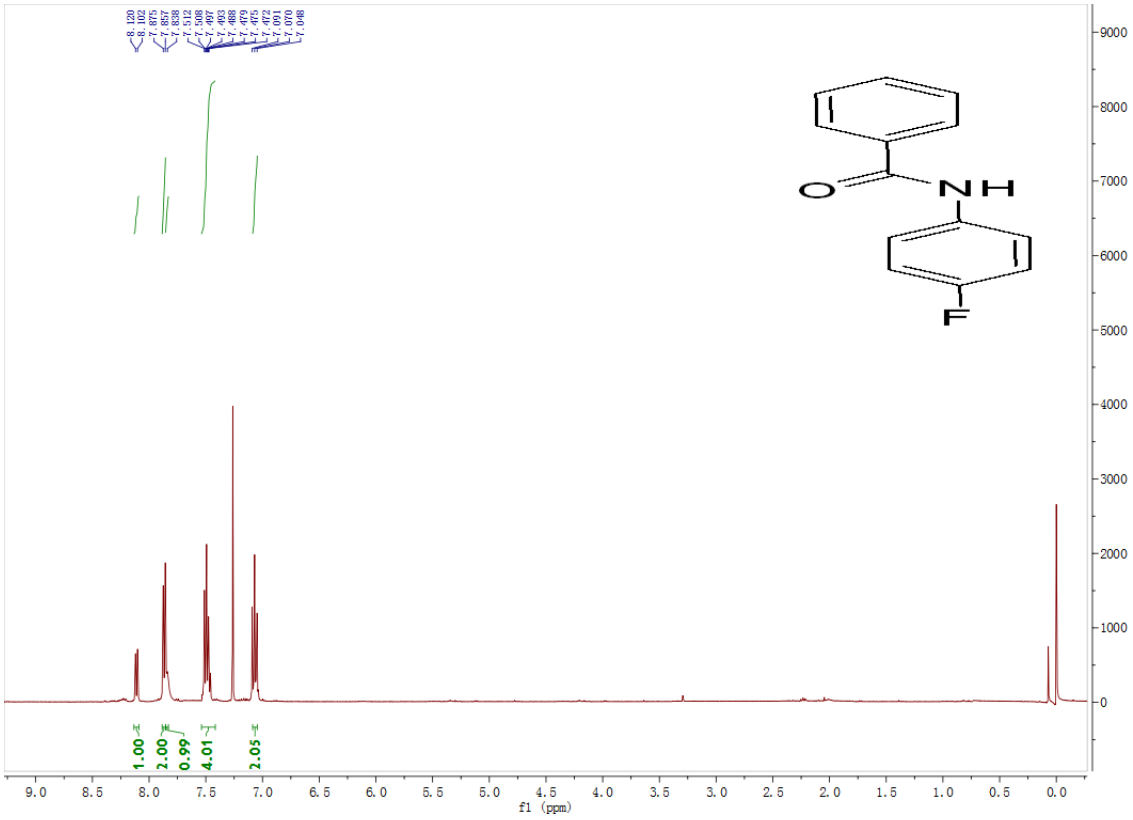
NH
O
f1 (ppm)

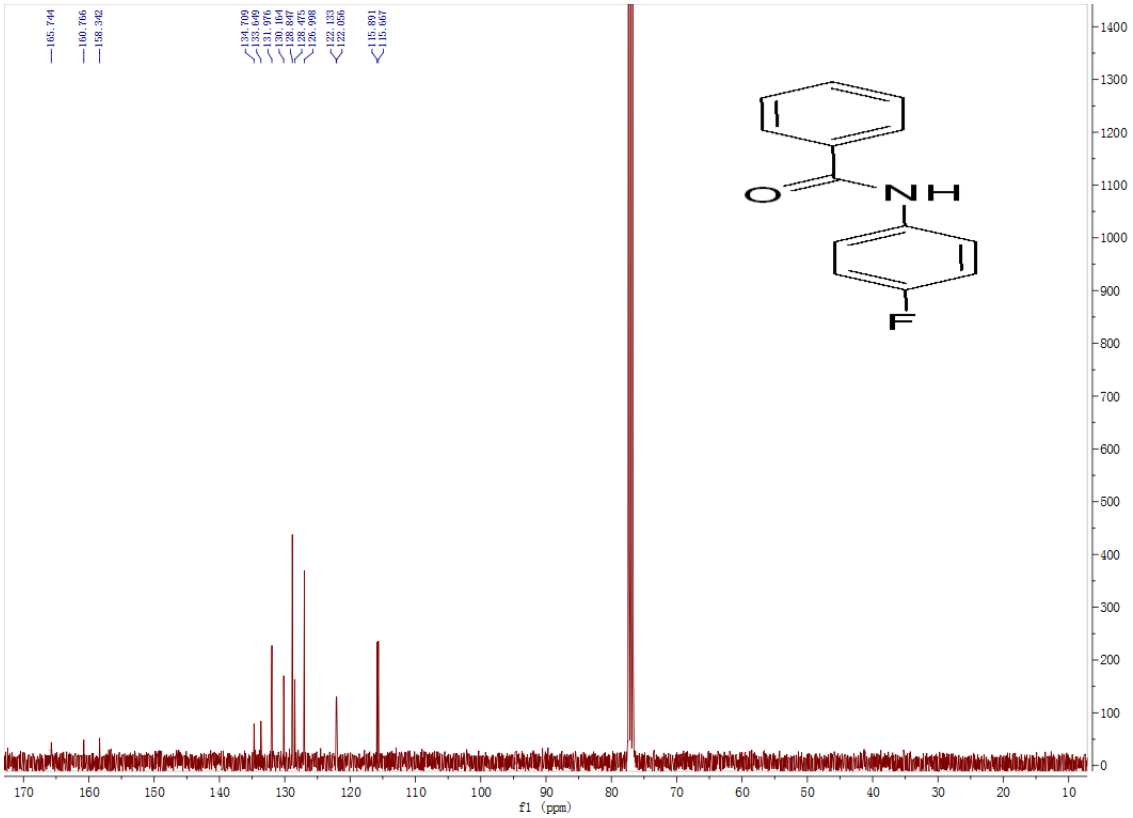
4e


7.869
7.851
7.552
7.536
7.531
7.518
7.487
7.468
7.460
6.912
6.899
3.810
MeO
NH
O
2.03
3.01
2.01
2.00
3.01
f1 (ppm)

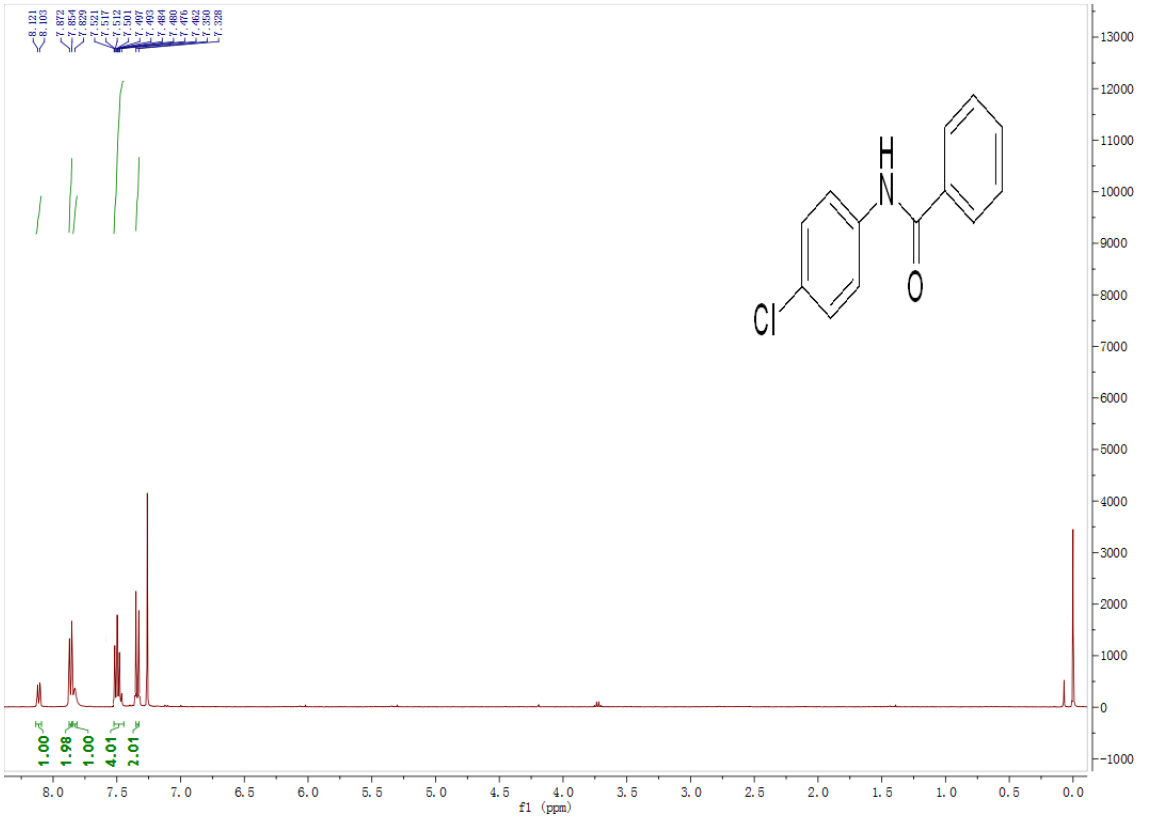

165.693
156.620
135.001
131.715
130.980
129.748
128.449
126.999
122.139
114.229
55.517
MeO
NH
O
f1 (ppm)

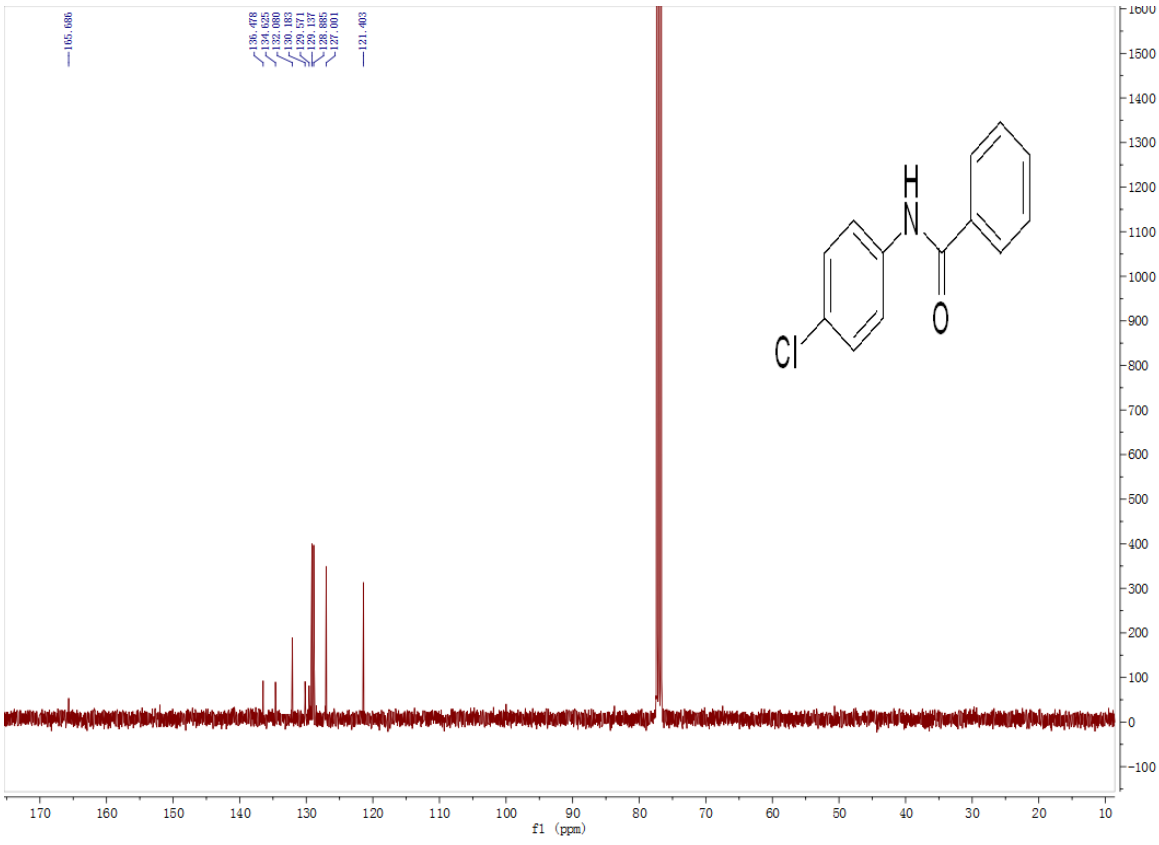
4f


8.120
8.102
7.875
7.857
7.838
7.512
7.498
7.496
7.493
7.488
7.479
7.475
7.472
7.091
7.070
7.048
1.00
2.00
0.99
4.01
2.05
f1 (ppm)
O
NH
F

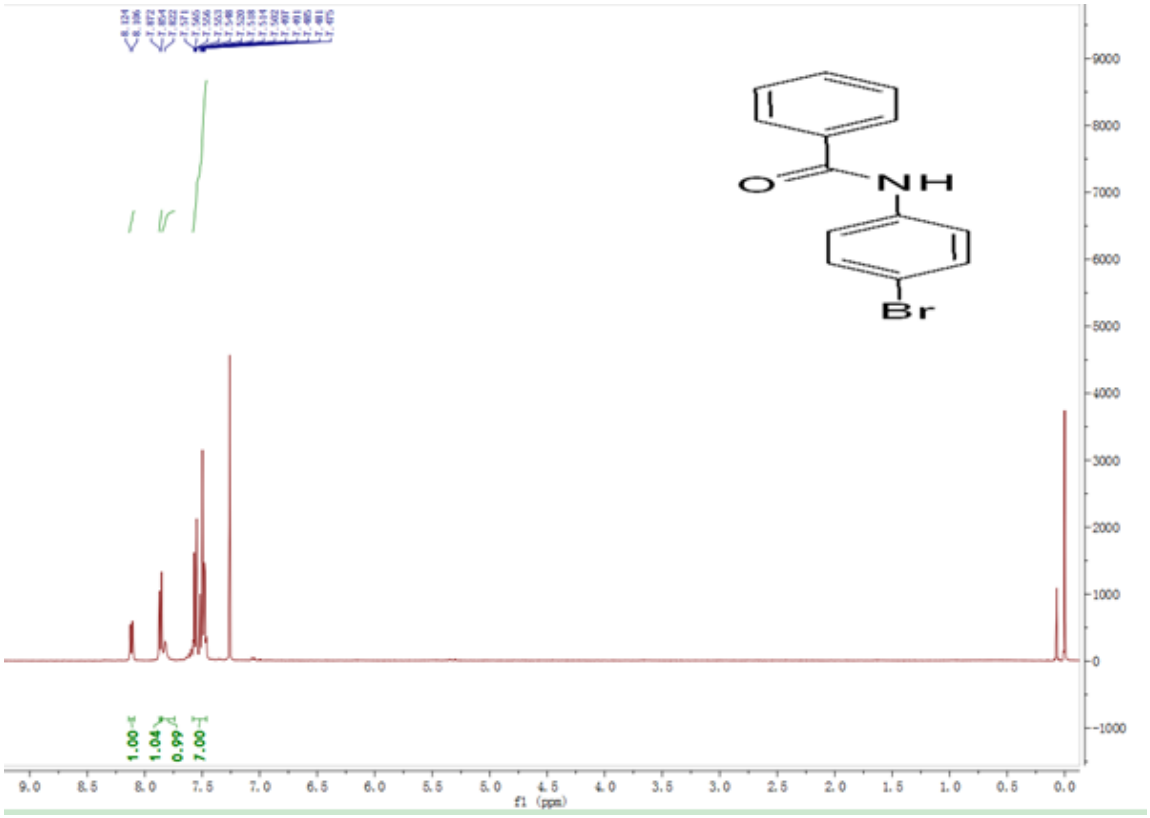

165.744
160.766
158.342
134.709
133.649
131.096
130.164
128.847
128.475
126.998
122.133
122.056
115.891
115.667
f1 (ppm)
O
NH
F

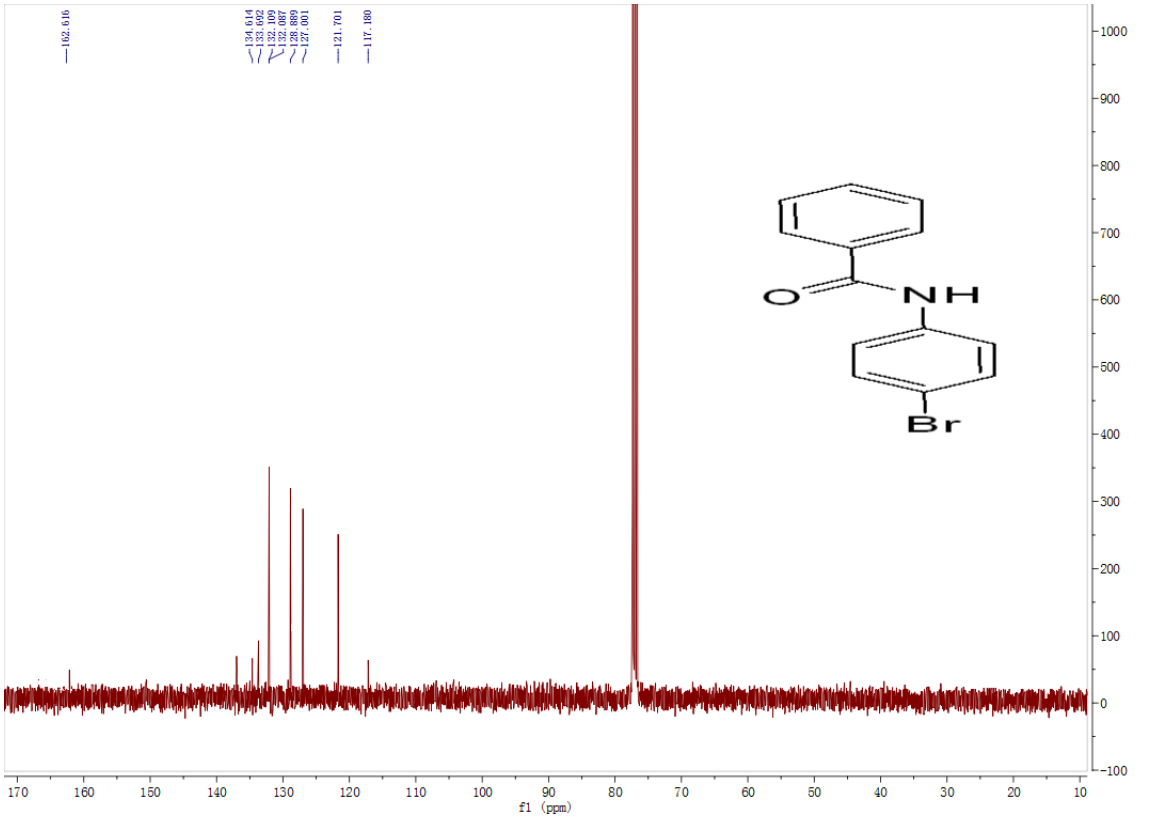
4g


8.121
8.103
7.872
7.856
7.829
7.521
7.517
7.512
7.501
7.497
7.493
7.484
7.480
7.476
7.462
7.356
7.328
1.00
1.98
1.00
4.01
2.01
f1 (ppm)

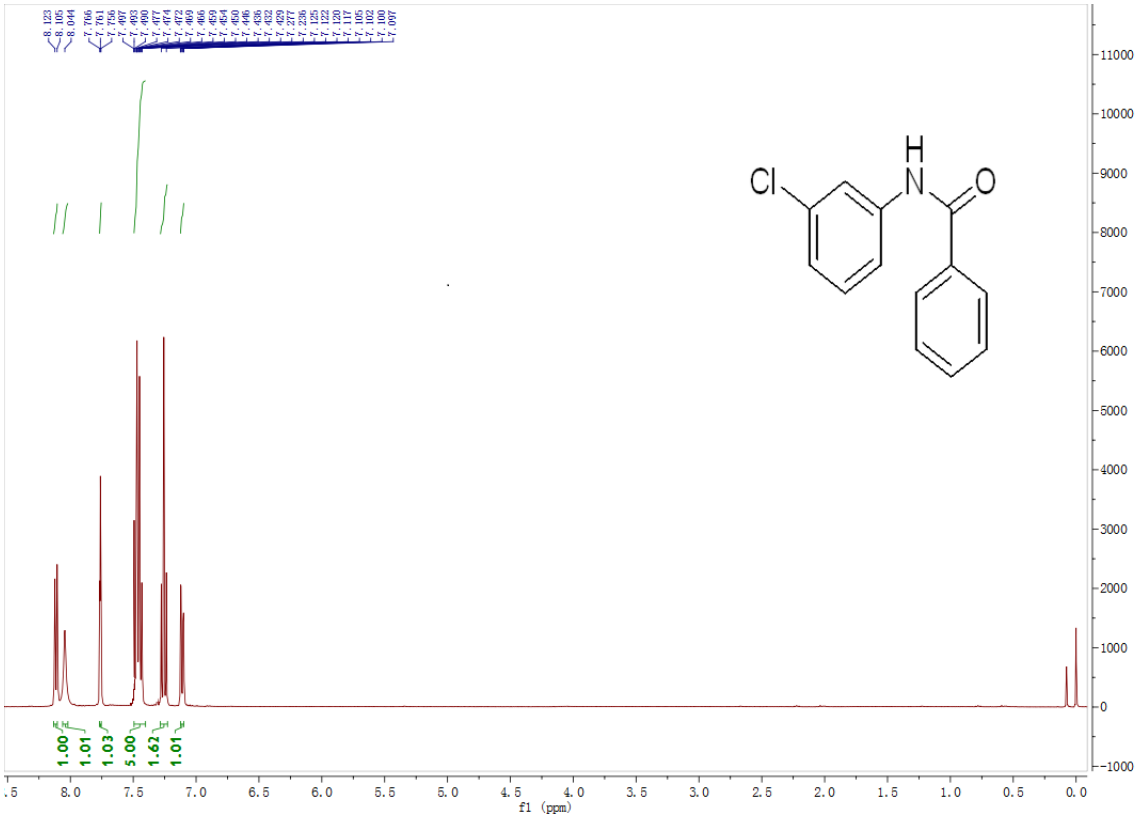

165.686
136.478
134.625
132.080
130.183
129.571
129.137
128.865
127.001
121.403
f1 (ppm)

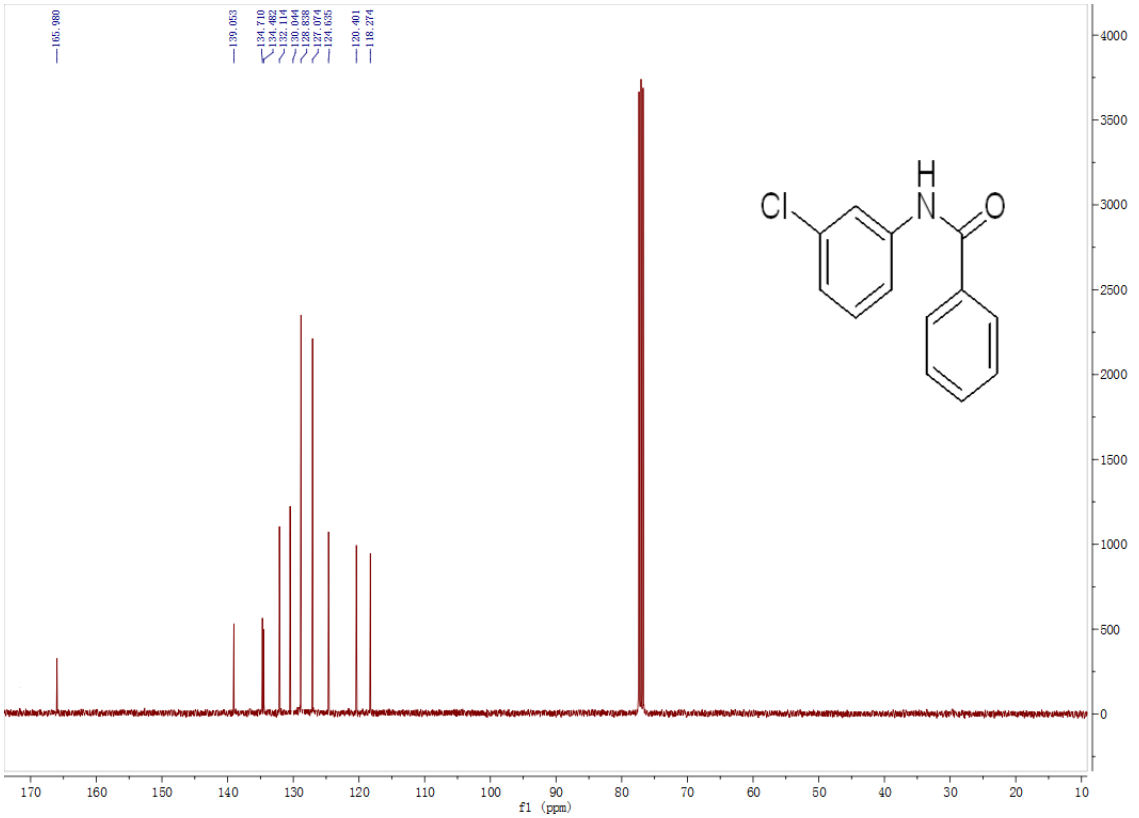
4h


O
NH
Br
1.00
1.04
0.99
7.00
f1 (ppm)

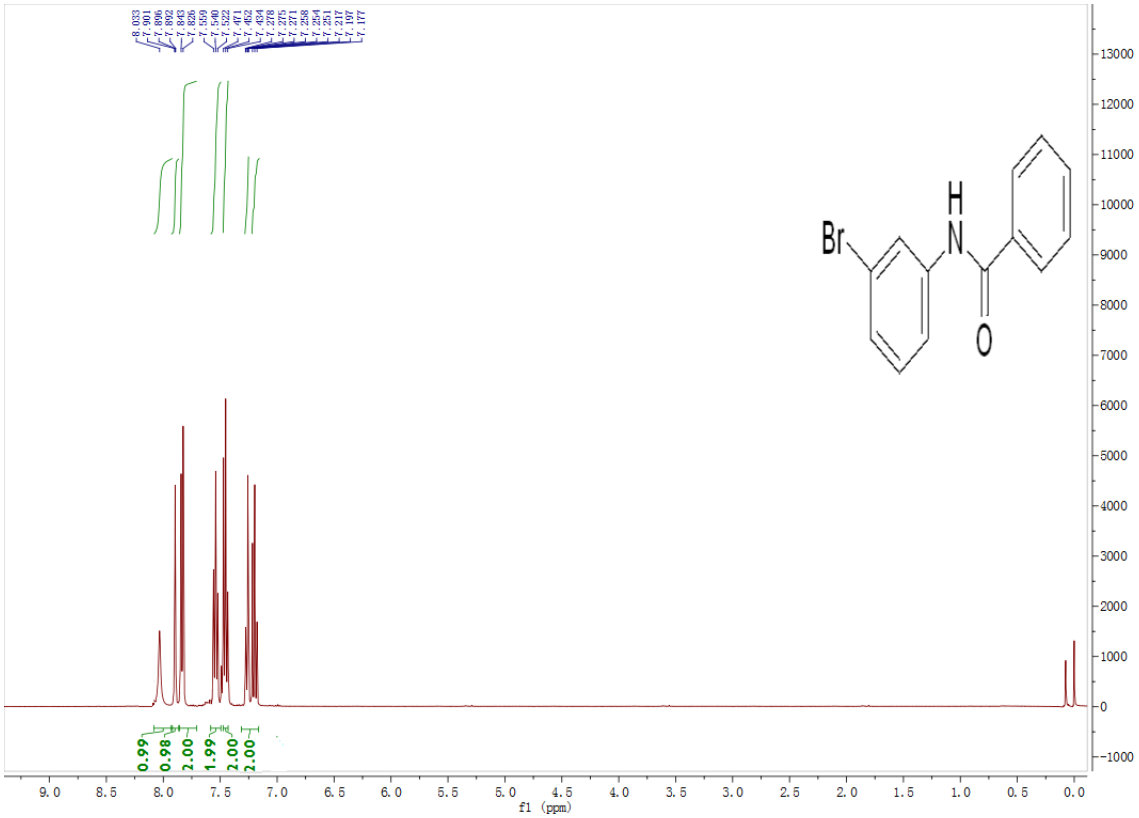

162.616
134.614
133.692
132.109
132.097
128.889
127.001
121.701
117.180
O
NH
Br
f1 (ppm)

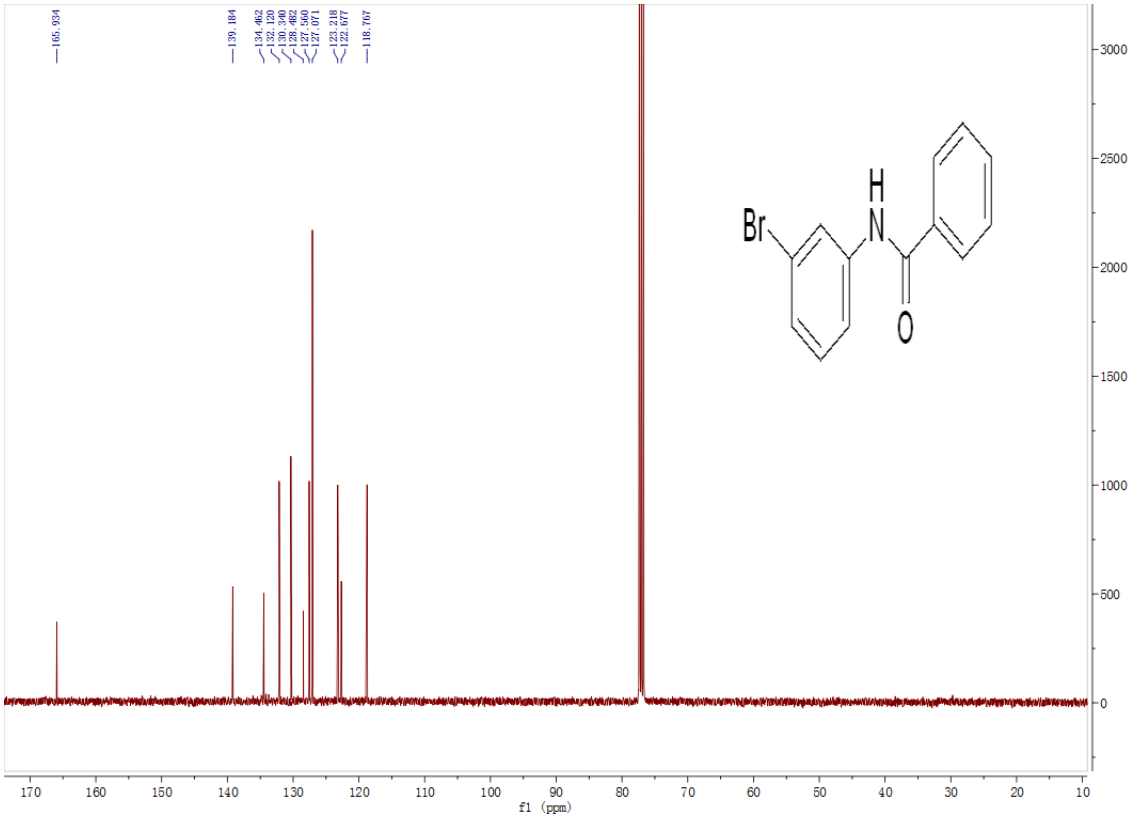
4i


8.123
8.105
8.044
7.766
7.751
7.736
7.497
7.493
7.490
7.477
7.474
7.472
7.469
7.466
7.459
7.454
7.450
7.446
7.436
7.432
7.429
7.277
7.236
7.125
7.122
7.120
7.117
7.105
7.102
7.100
7.097
1.00
1.01
1.03
5.00
1.62
1.01
Cl
H
N
O
f1 (ppm)

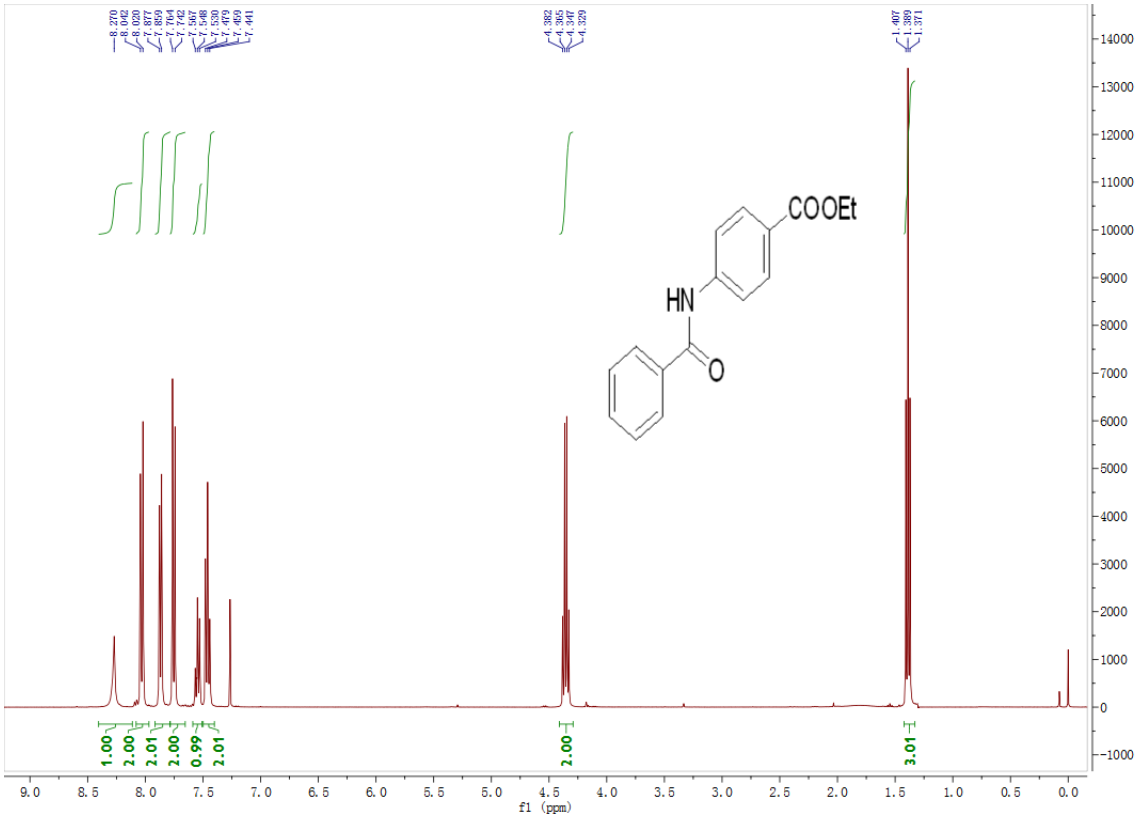

165.980
139.053
134.710
134.482
132.114
130.044
128.838
127.074
124.635
120.401
118.274
Cl
H
N
O
f1 (ppm)

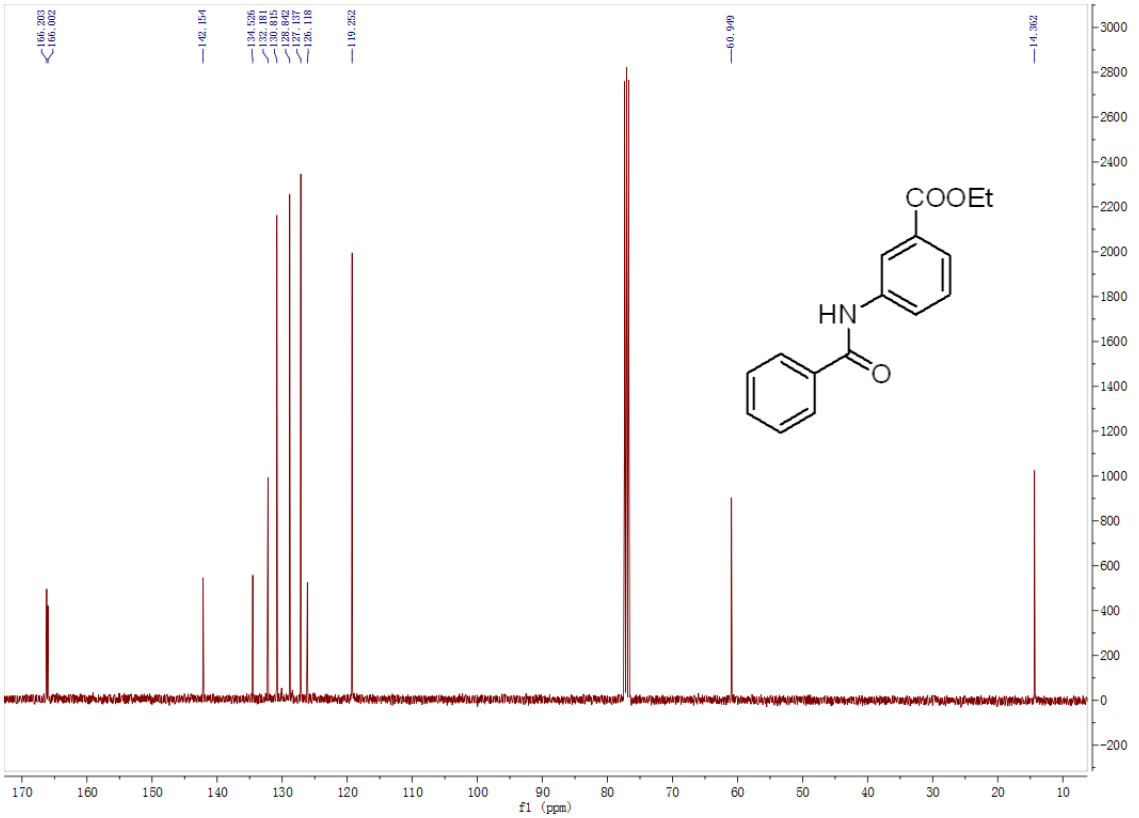
4j


8.033
7.901
7.896
7.892
7.843
7.826
7.559
7.540
7.522
7.471
7.462
7.434
7.278
7.275
7.271
7.258
7.254
7.251
7.197
7.197
7.195
7.177
Br
H
N
O
0.99
0.98
2.00
1.99
2.00
2.00
f1 (ppm)

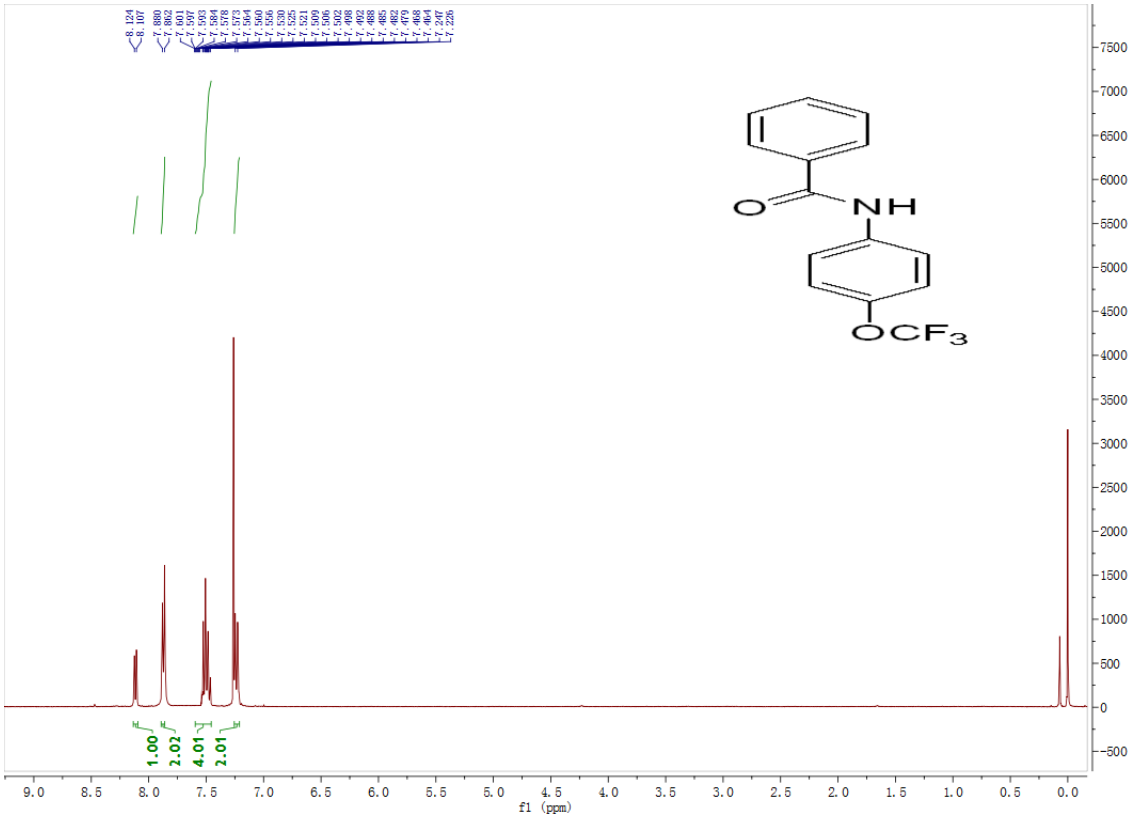

165.934
139.184
134.462
132.120
130.340
128.482
127.560
127.071
123.218
122.677
118.767
Br
H
N
O
f1 (ppm)

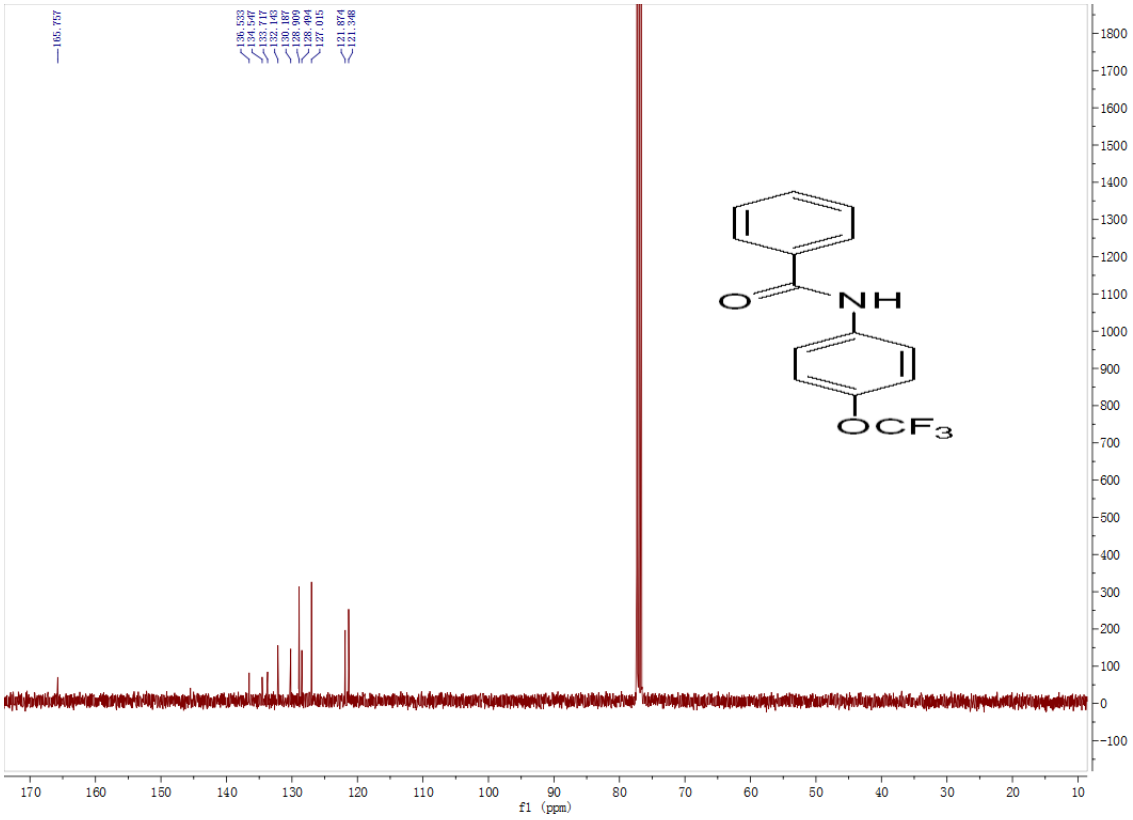
4k


8.270
8.042
8.020
7.877
7.859
7.764
7.742
7.567
7.548
7.530
7.470
7.469
7.441
4.382
4.365
4.347
4.329
1.407
1.389
1.371
COOEt
HN
O
1.00
2.00
2.01
2.00
0.99
2.01
2.00
3.01
f1 (ppm)

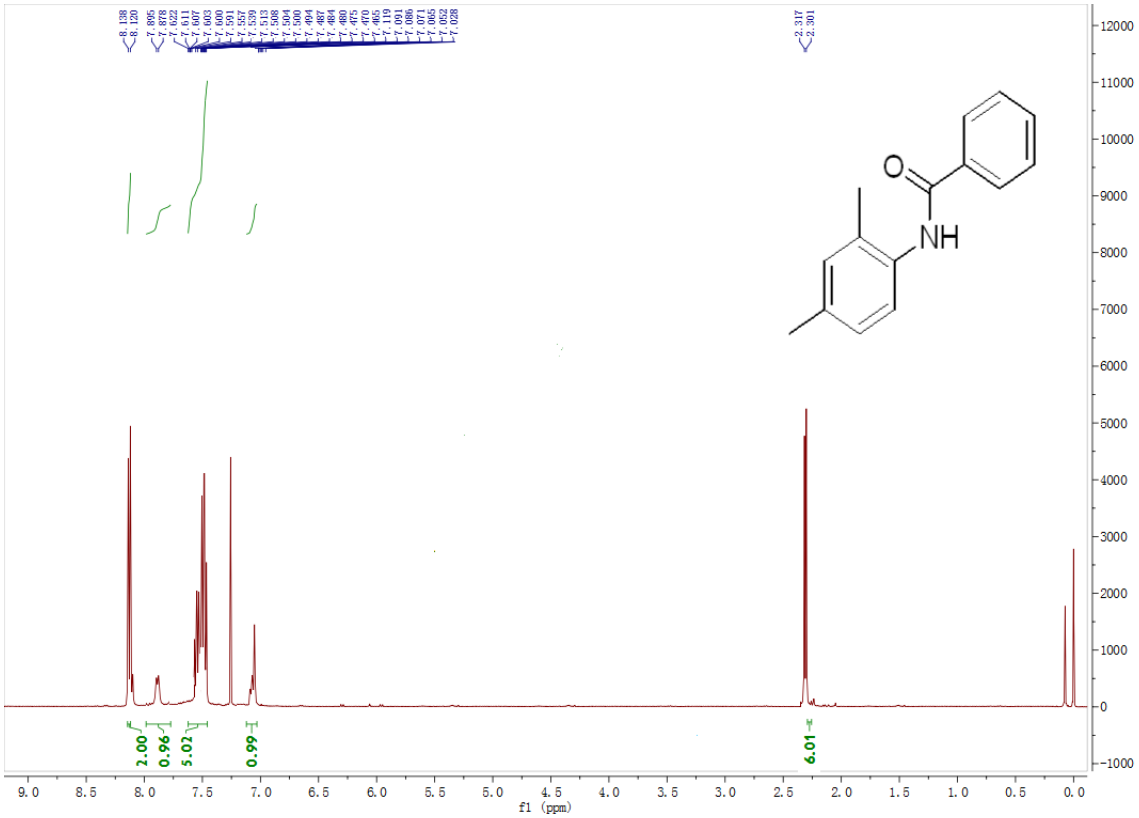

166.203
166.002
142.154
134.526
132.181
130.815
128.842
127.137
126.118
119.252
60.949
14.362
COOEt
HN
O
f1 (ppm)

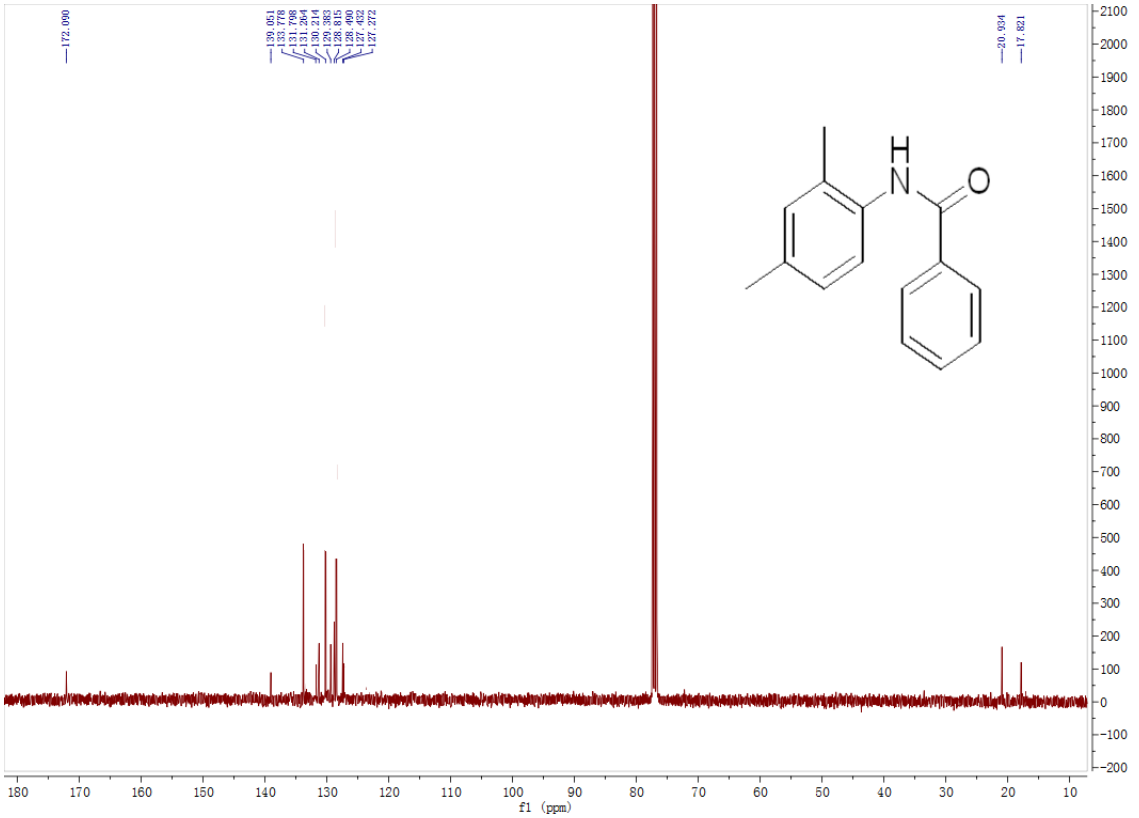
4l


8.124
8.107
7.880
7.862
7.601
7.597
7.593
7.584
7.578
7.573
7.564
7.560
7.556
7.530
7.525
7.521
7.509
7.506
7.502
7.498
7.492
7.488
7.485
7.482
7.479
7.468
7.464
7.247
7.226
1.00
2.02
4.01
2.01
NH
OCF3
f1 (ppm)

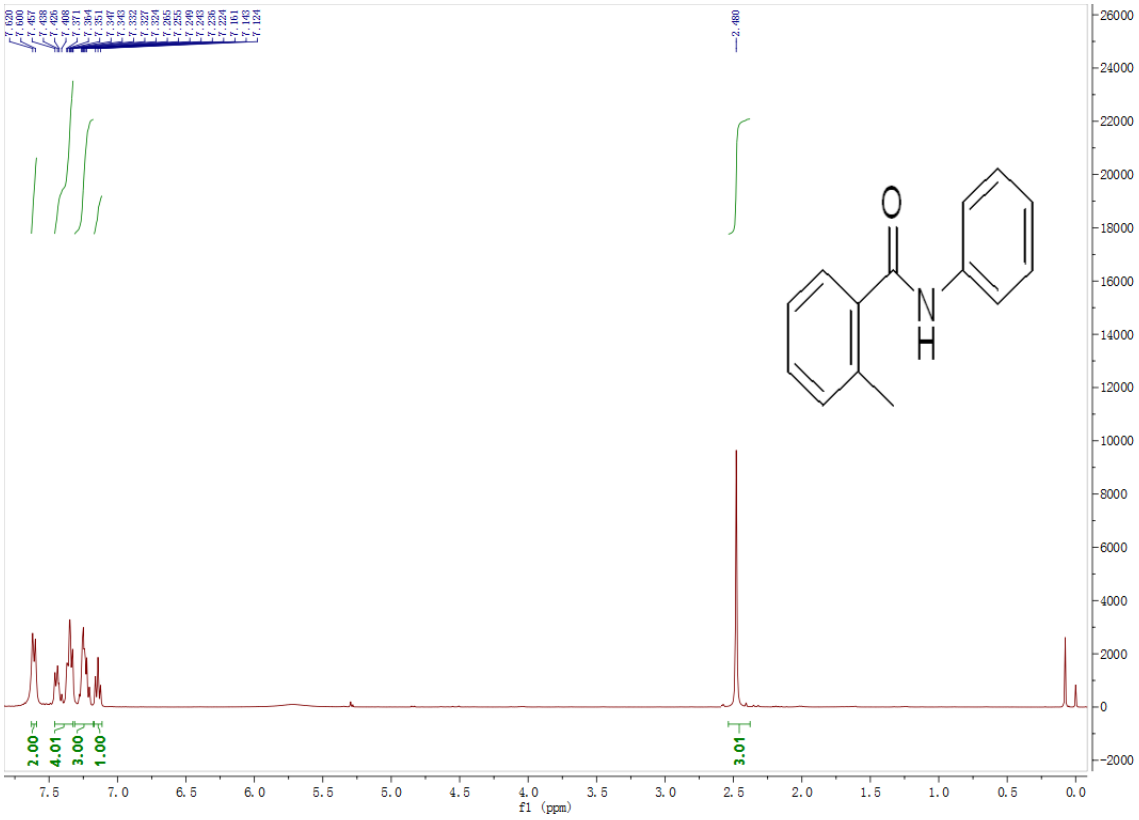

165.757
136.533
134.547
133.717
132.143
130.187
129.999
128.494
127.015
121.874
121.598
NH
OCF3
f1 (ppm)

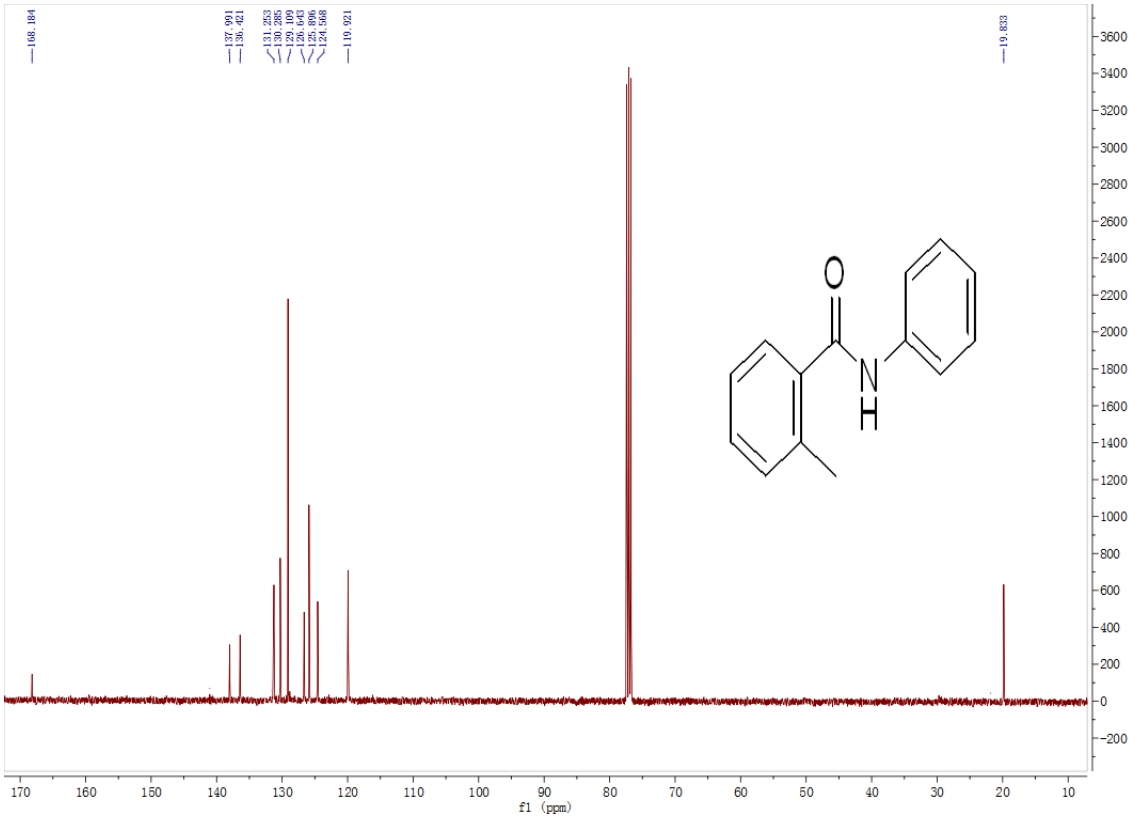
4m


8.138
8.120
7.895
7.878
7.622
7.611
7.608
7.603
7.600
7.591
7.557
7.550
7.513
7.508
7.504
7.500
7.490
7.487
7.484
7.480
7.475
7.470
7.465
7.119
7.091
7.086
7.071
7.065
7.052
7.028
2.317
2.301
O
NH
2.00
0.96
5.07
0.99
6.01
f1 (ppm)

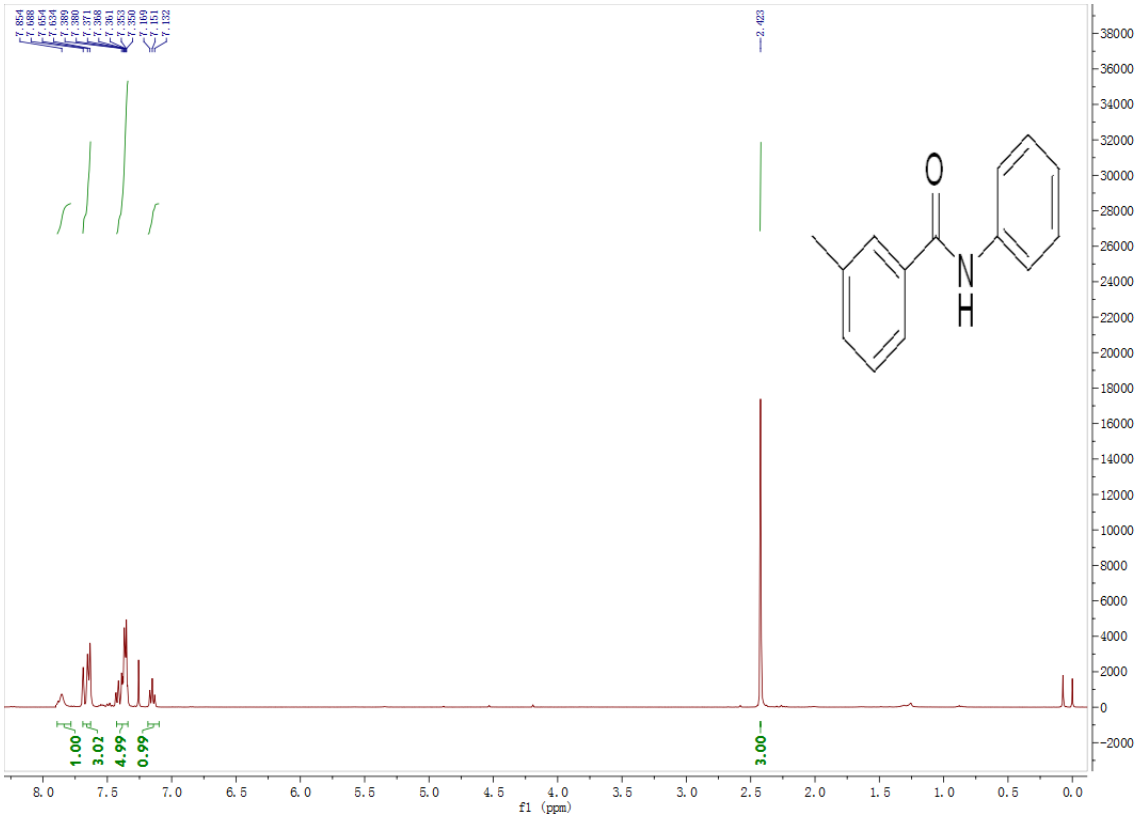

172.090
139.051
133.798
131.798
131.264
130.214
129.383
128.815
128.490
127.432
127.272
20.934
17.821
H
N
O
f1 (ppm)

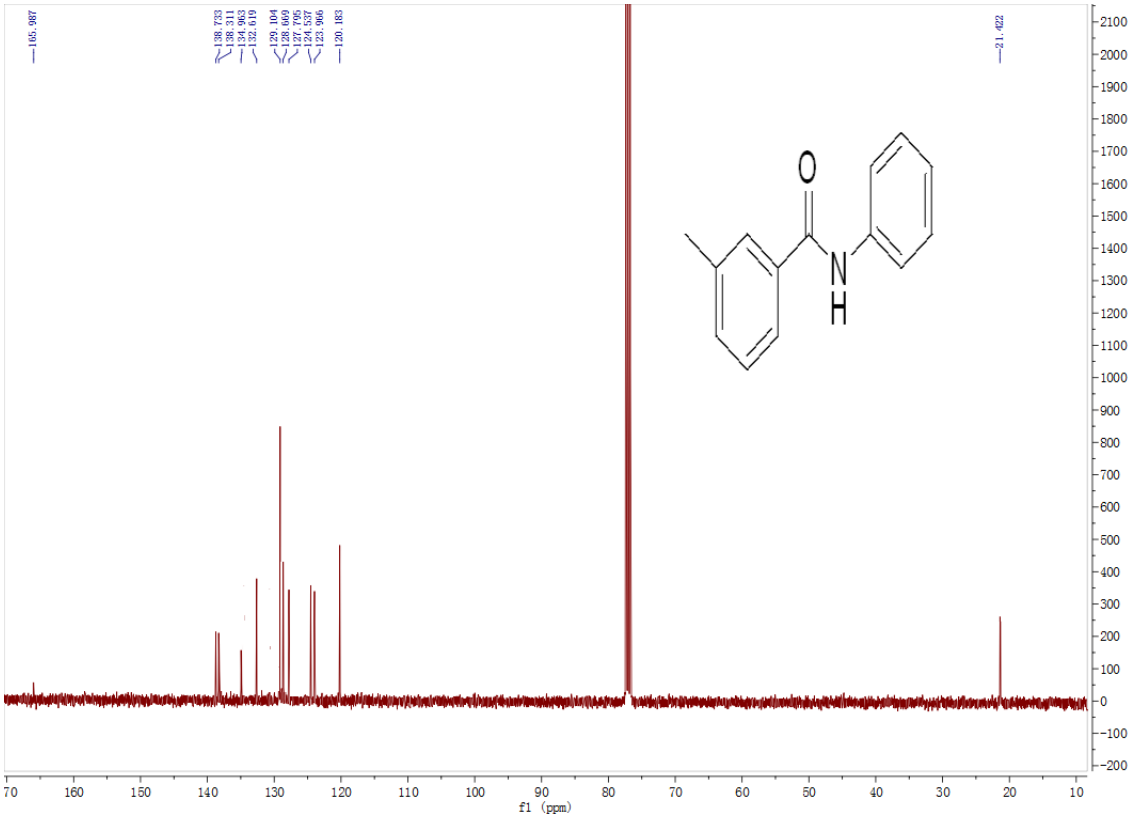
4n


7.620
7.600
7.497
7.488
7.426
7.408
7.371
7.364
7.351
7.347
7.343
7.332
7.327
7.324
7.265
7.255
7.249
7.243
7.236
7.224
7.161
7.143
7.124
2.480
2.00
4.01
3.00
1.00
3.01
f1 (ppm)

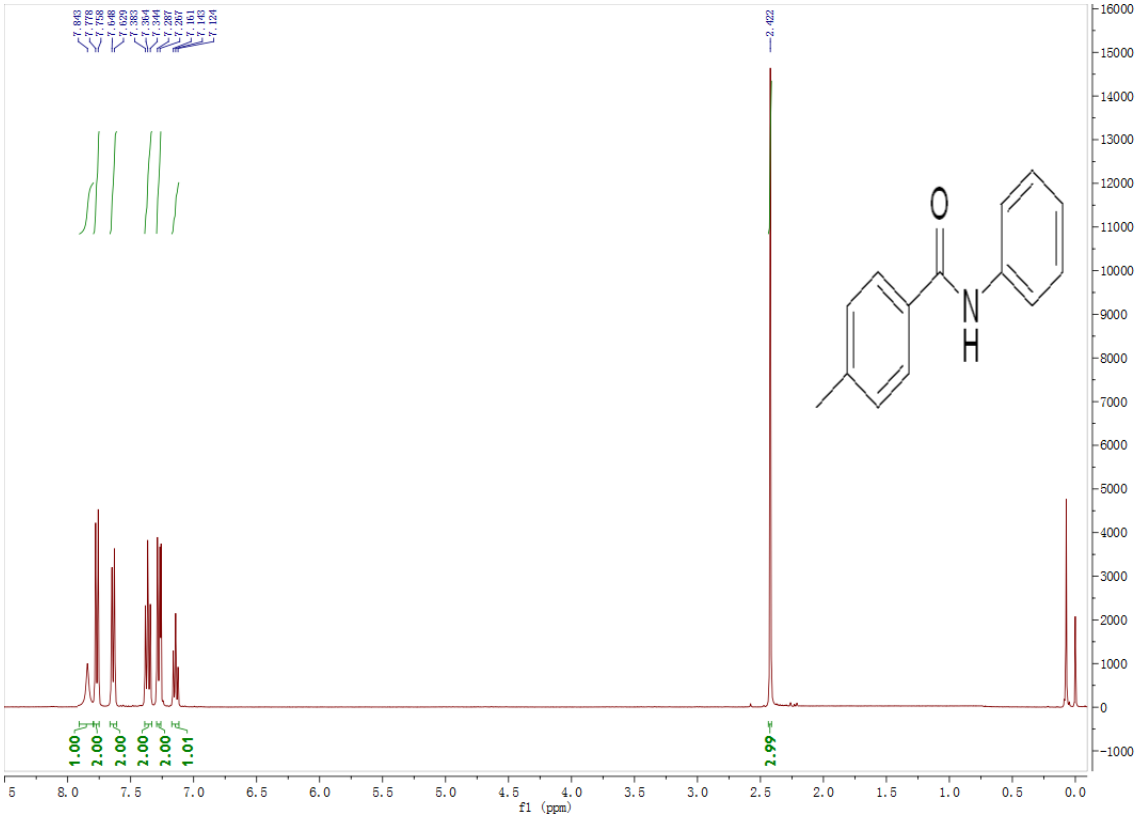

168.184
137.991
136.421
131.253
130.285
129.109
126.643
125.896
124.568
119.921
19.833
f1 (ppm)

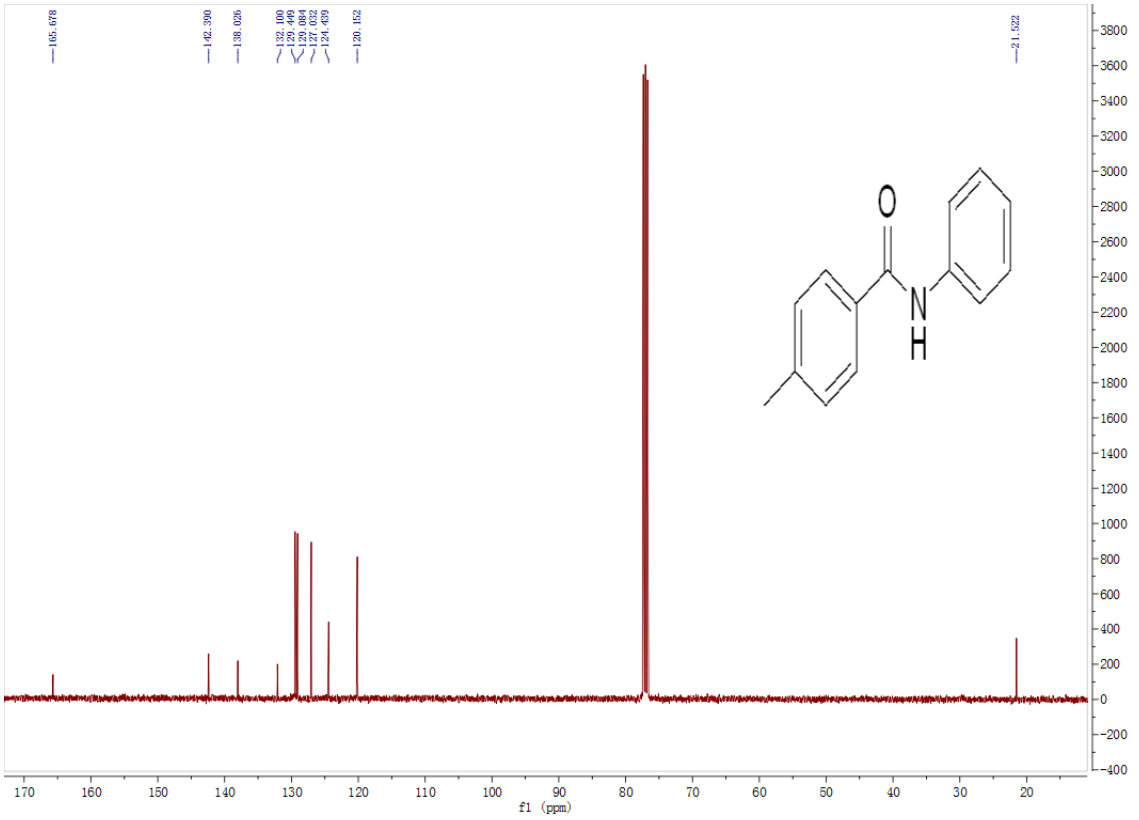
4o


7.854
7.698
7.696
7.654
7.634
7.389
7.380
7.371
7.368
7.361
7.353
7.350
7.169
7.111
7.132
2.423
1.00
3.01
4.99
0.99
3.00
f1 (ppm)

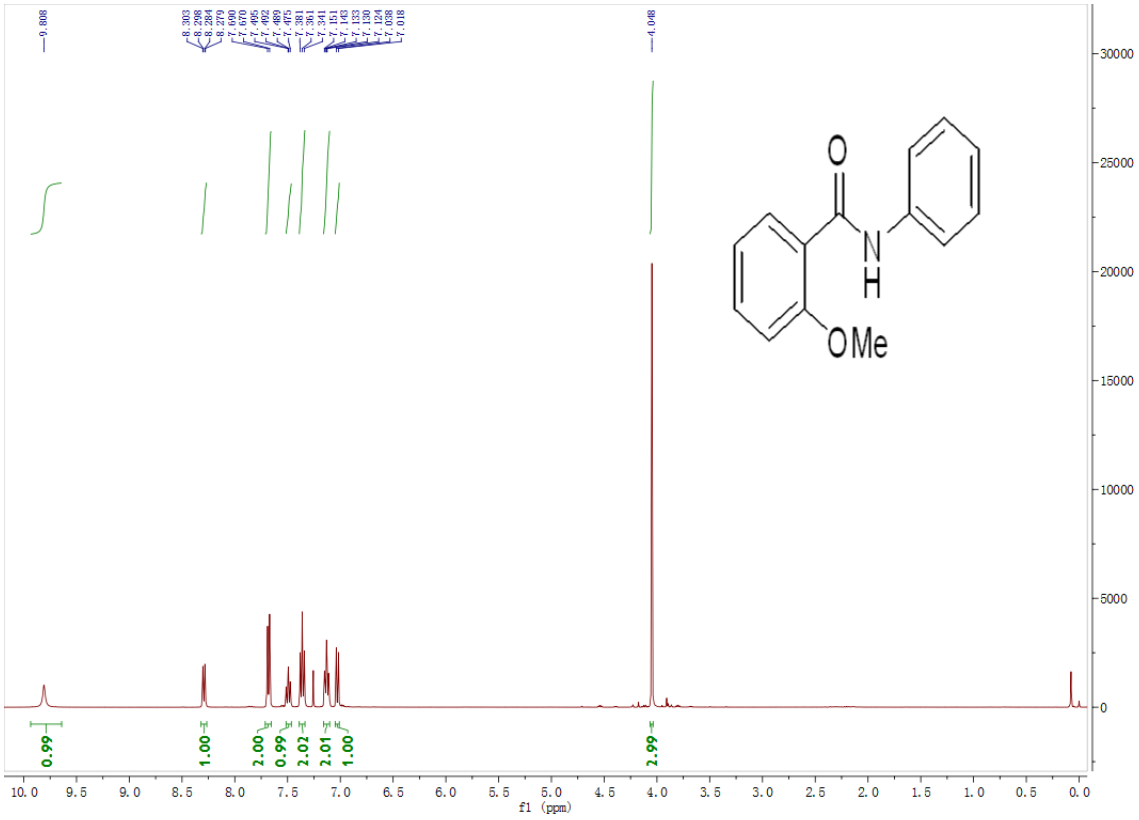

165.987
138.733
138.311
134.963
132.619
129.104
128.669
127.795
124.557
123.966
120.183
21.422
f1 (ppm)

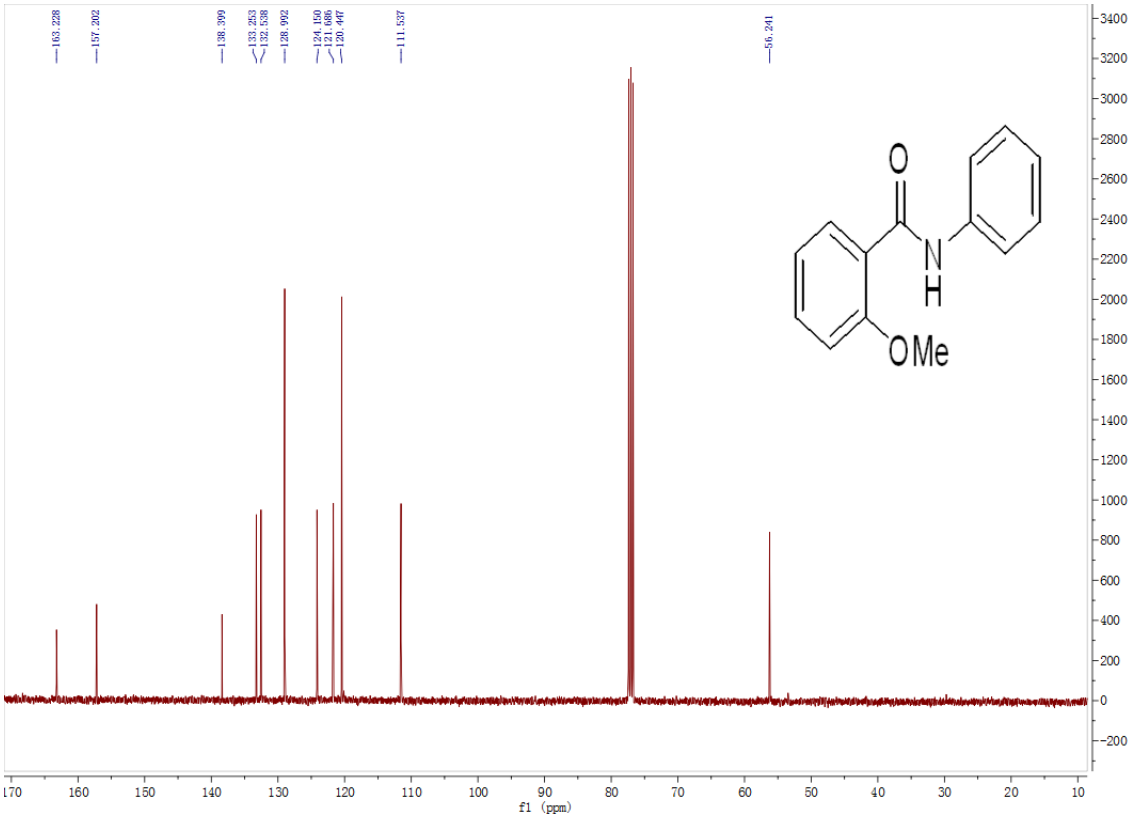
4p


7.843
7.778
7.758
7.648
7.629
7.383
7.364
7.344
7.287
7.267
7.161
7.143
7.124
2.422
1.00
2.00
2.00
2.00
2.00
1.01
2.99
f1 (ppm)

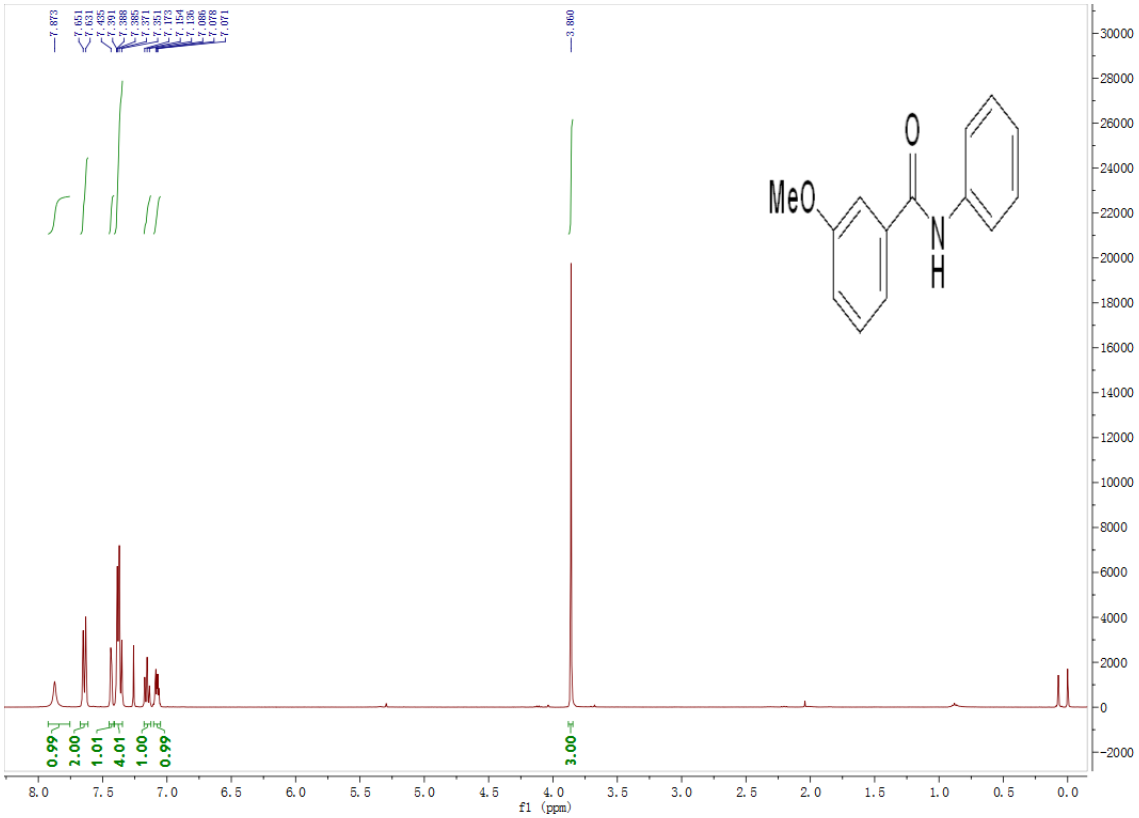

165.678
142.390
138.026
132.100
129.449
129.084
127.032
124.439
120.152
21.522
f1 (ppm)

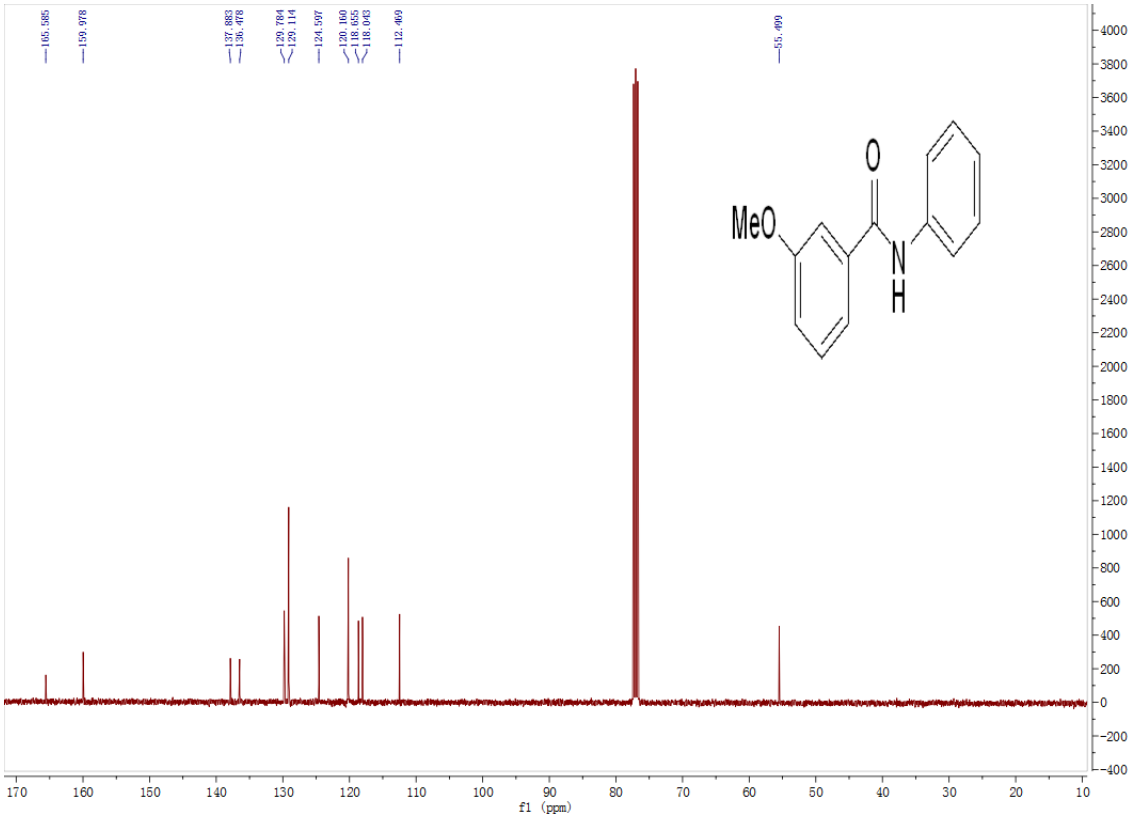
4q


9.808
8.303
8.298
8.284
8.279
7.690
7.670
7.495
7.492
7.489
7.475
7.381
7.361
7.341
7.151
7.145
7.133
7.130
7.124
7.038
7.018
4.048
O
N
H
OMe
0.99
1.00
2.00
0.99
2.02
2.01
1.00
2.99
f1 (ppm)

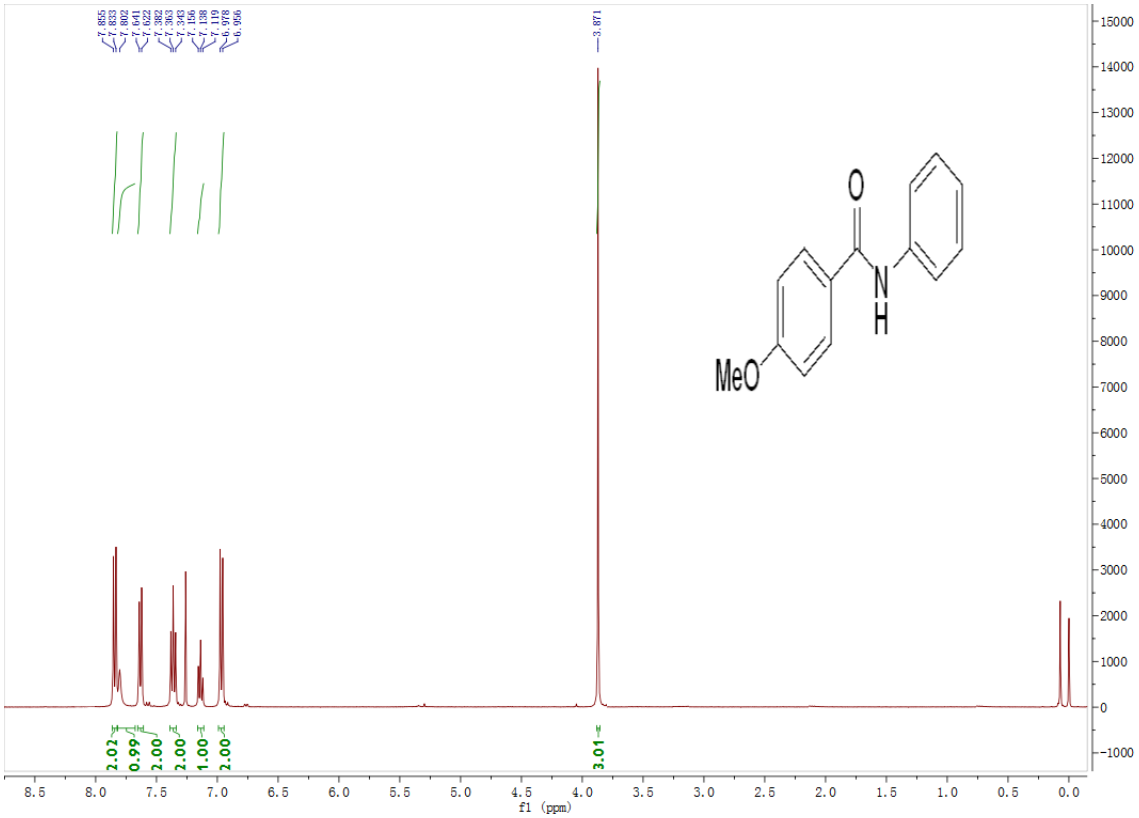

163.228
157.202
138.399
133.253
132.538
128.902
124.150
121.686
120.447
111.537
56.241
O
N
H
OMe
f1 (ppm)

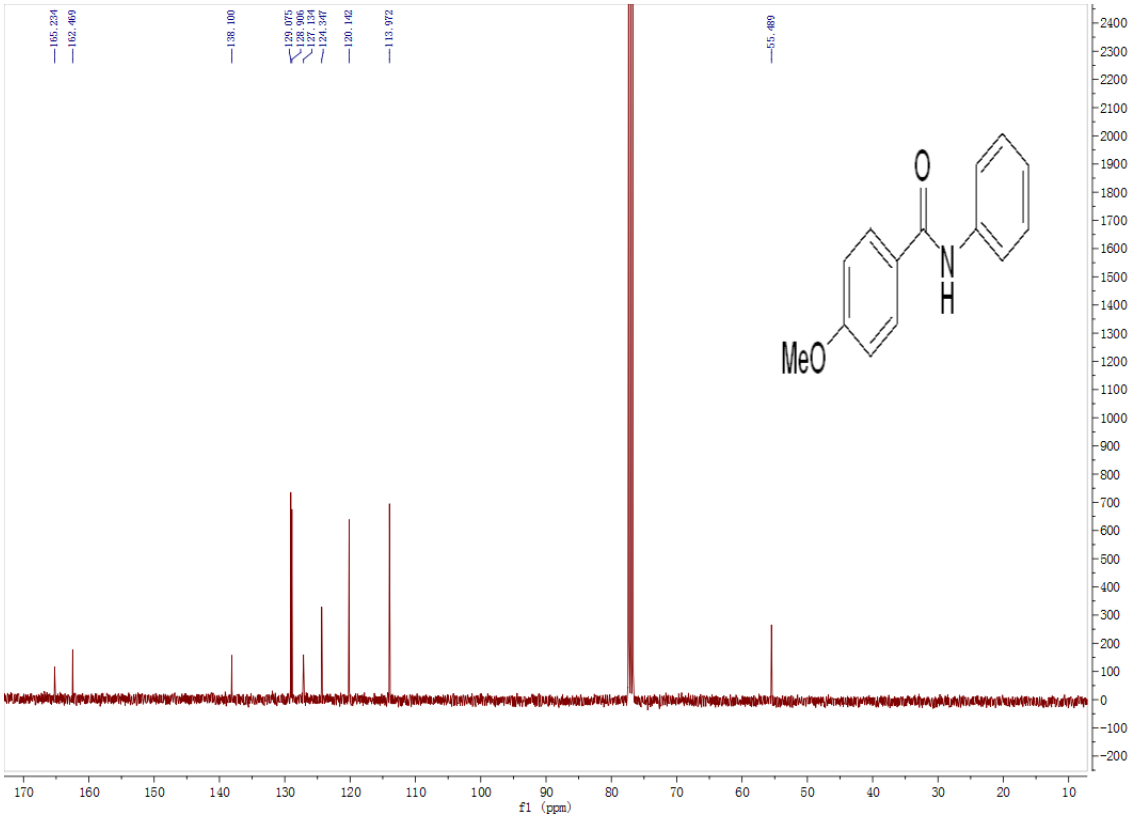
4r


7.873
7.651
7.631
7.395
7.391
7.388
7.385
7.371
7.371
7.154
7.136
7.086
7.078
7.071
3.860
MeO
O
N
H
0.99
2.00
1.01
4.01
1.00
0.99
3.00
f1 (ppm)

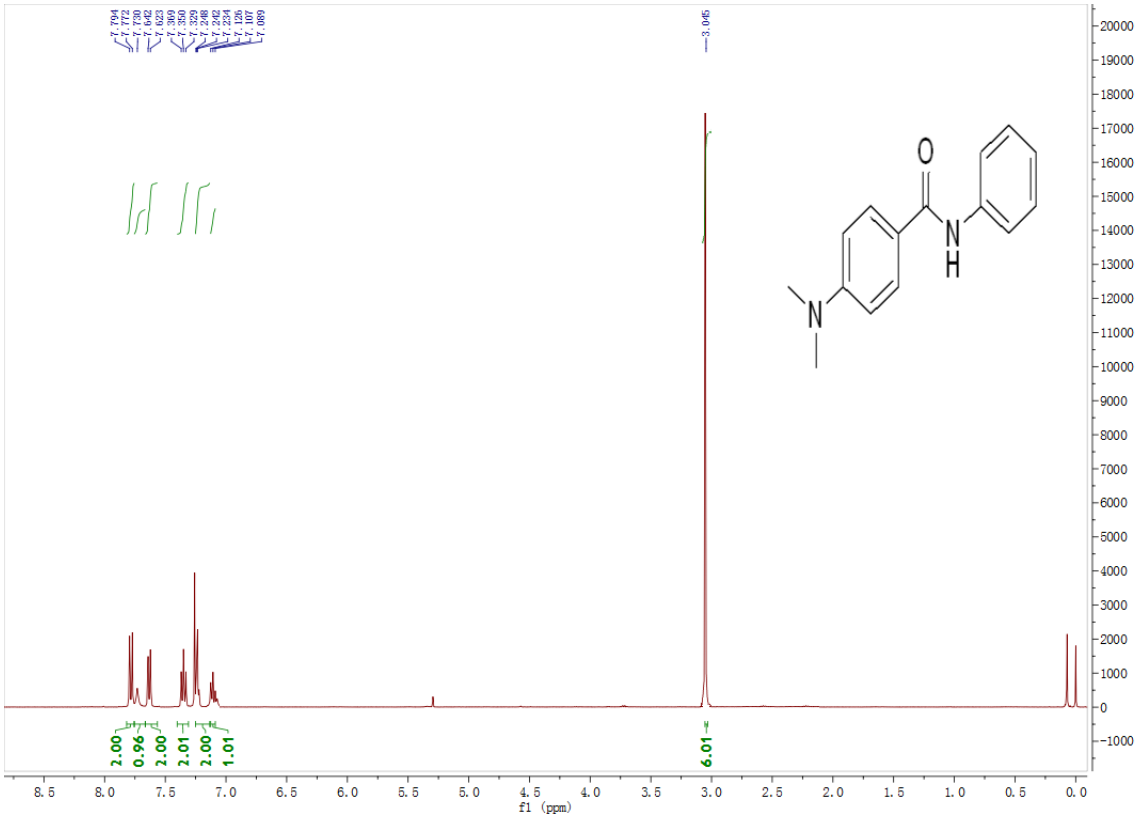

165.585
159.978
137.883
136.478
129.784
129.114
124.597
120.160
118.655
118.043
112.469
55.499
MeO
O
N
H
f1 (ppm)

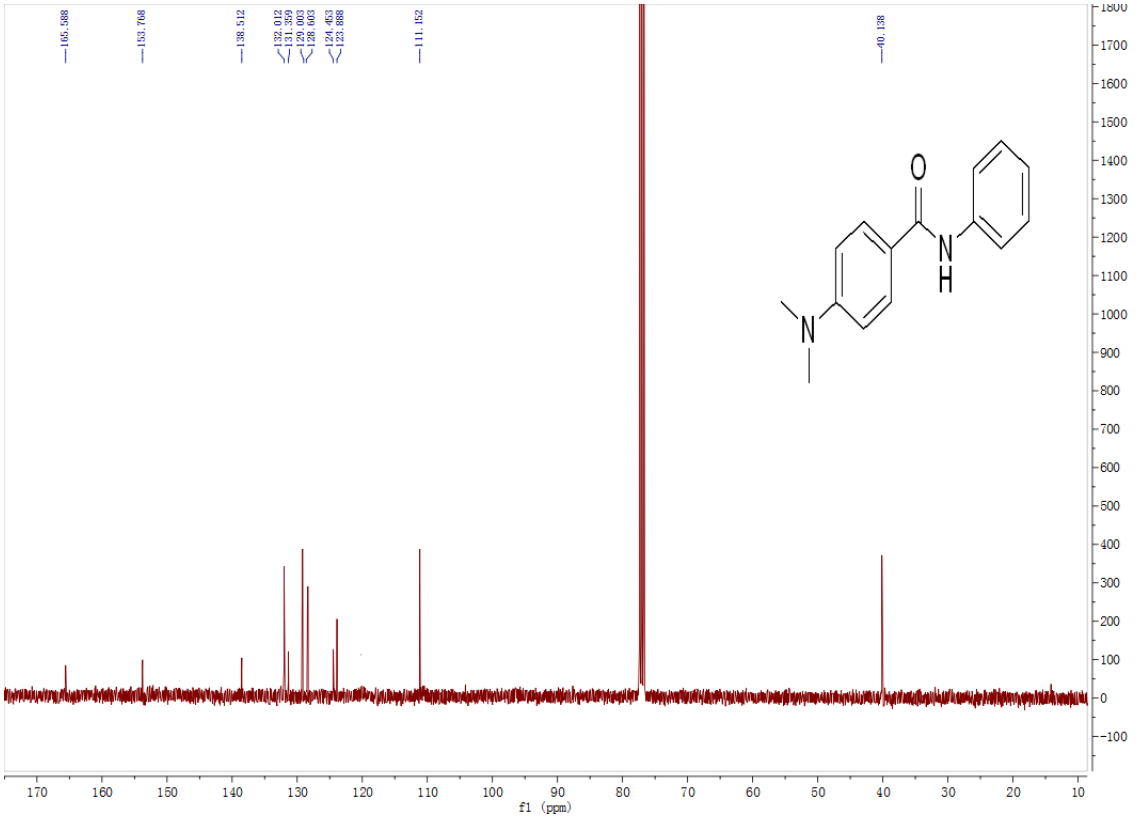
4s


7.855
7.853
7.802
7.641
7.622
7.382
7.363
7.343
7.156
7.138
7.119
6.998
6.966
3.871
2.01
0.99
2.00
2.00
1.00
2.00
3.01
O
N
H
MeO
f1 (ppm)

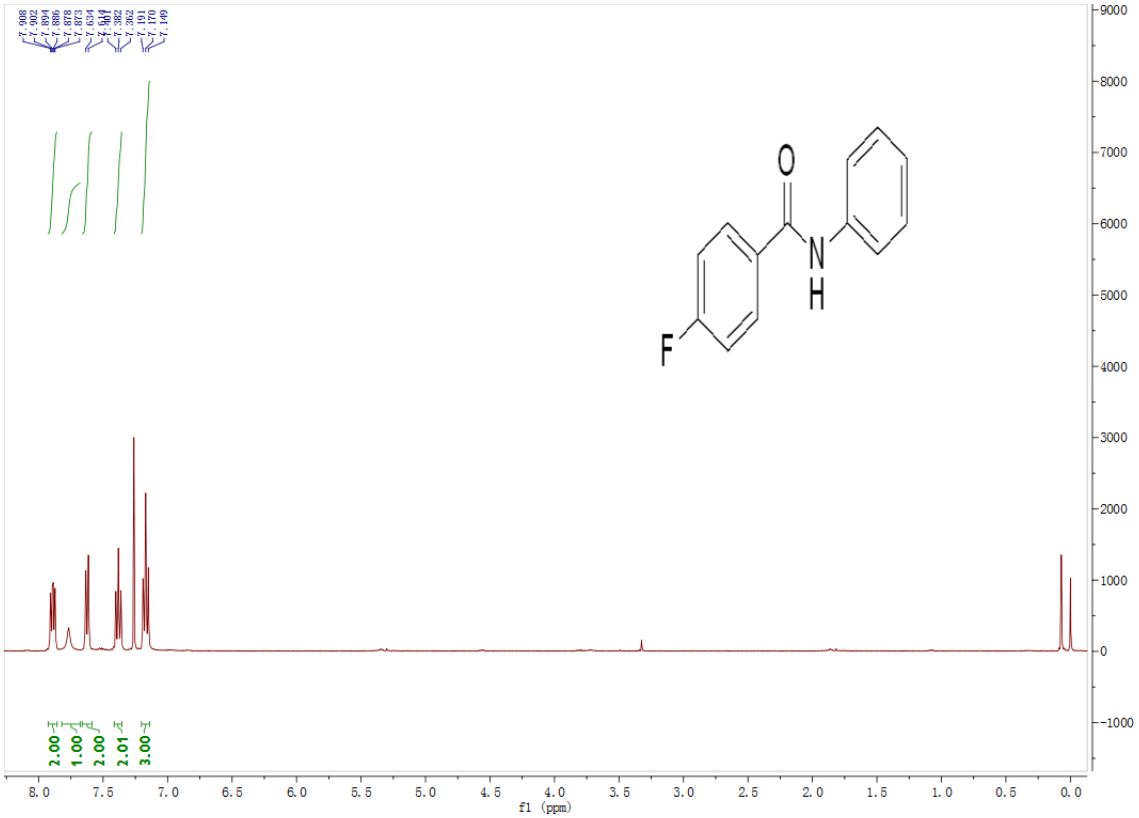

165.234
162.469
138.100
129.075
128.906
127.134
124.547
120.142
113.972
55.489
O
N
H
MeO
f1 (ppm)

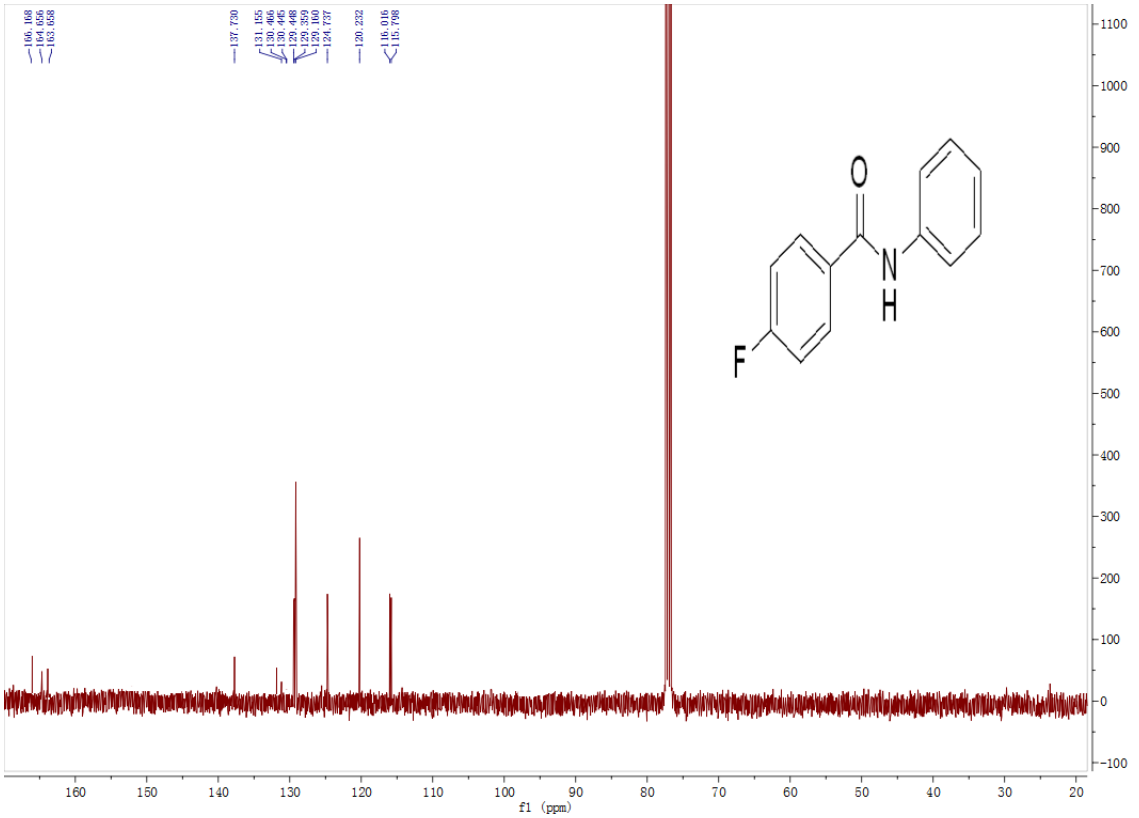
4t


7.794
7.772
7.730
7.642
7.623
7.369
7.360
7.329
7.248
7.242
7.234
7.197
7.107
7.089
3.045
2.00
0.96
2.00
2.01
2.00
1.01
6.01
O
N
H
N
f1 (ppm)

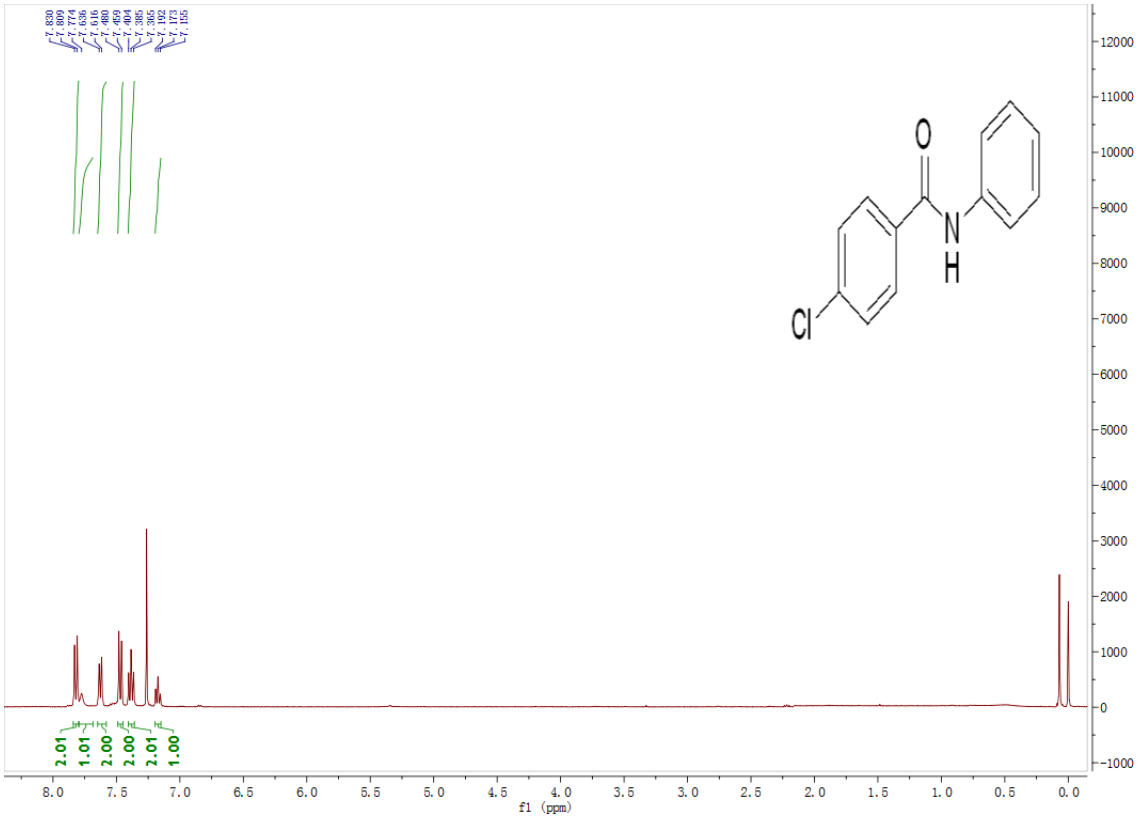

165.588
153.768
138.512
132.012
131.359
129.003
126.603
124.453
123.888
111.152
40.138
O
N
H
N
f1 (ppm)

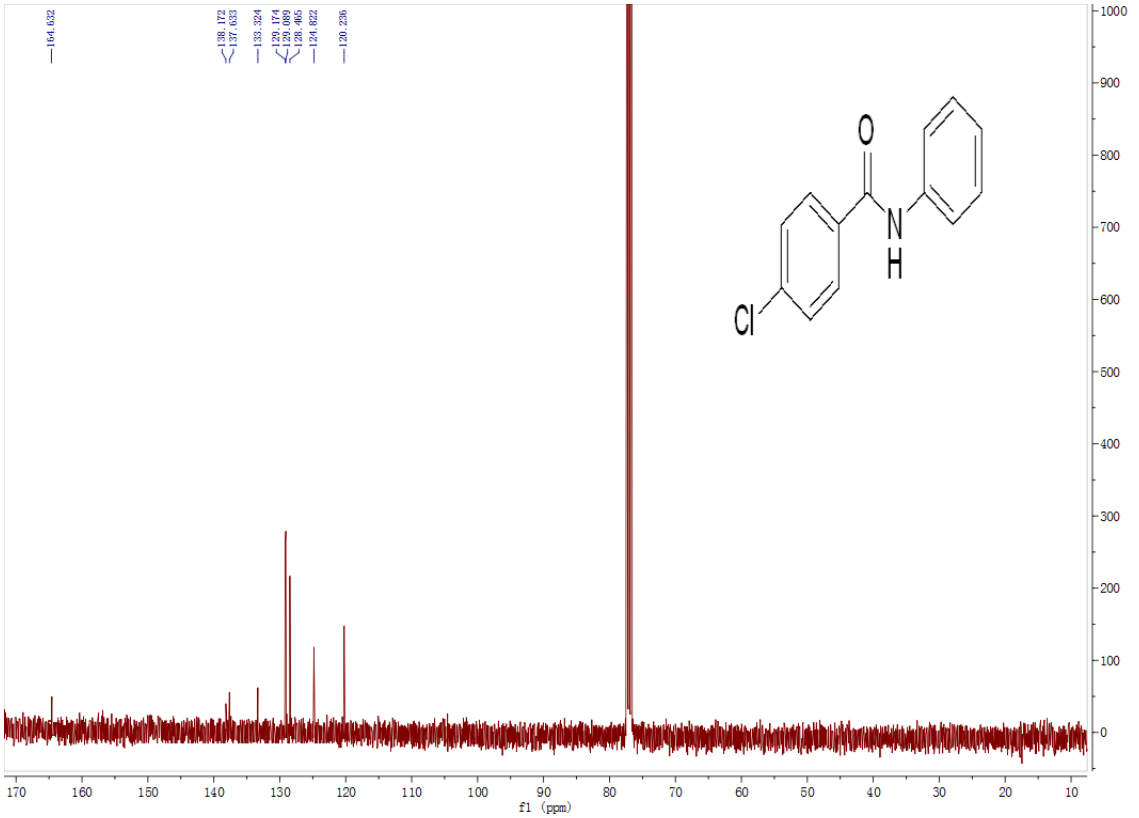
4u


7.908
7.902
7.894
7.886
7.878
7.873
7.634
7.627
7.382
7.362
7.311
7.170
7.149
2.00
1.00
2.00
2.01
3.00
f1 (ppm)

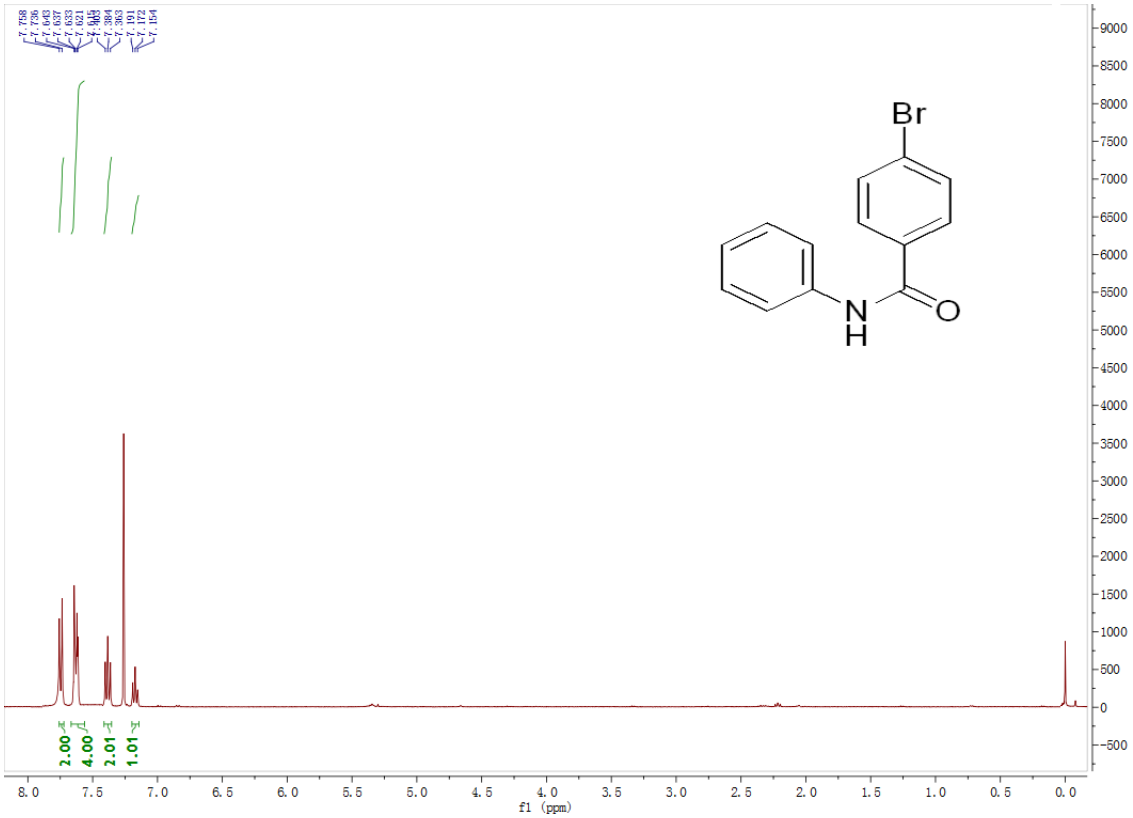

166.168
164.656
163.658
137.730
131.155
130.466
130.446
129.448
129.359
129.160
124.737
120.232
116.016
115.798
f1 (ppm)

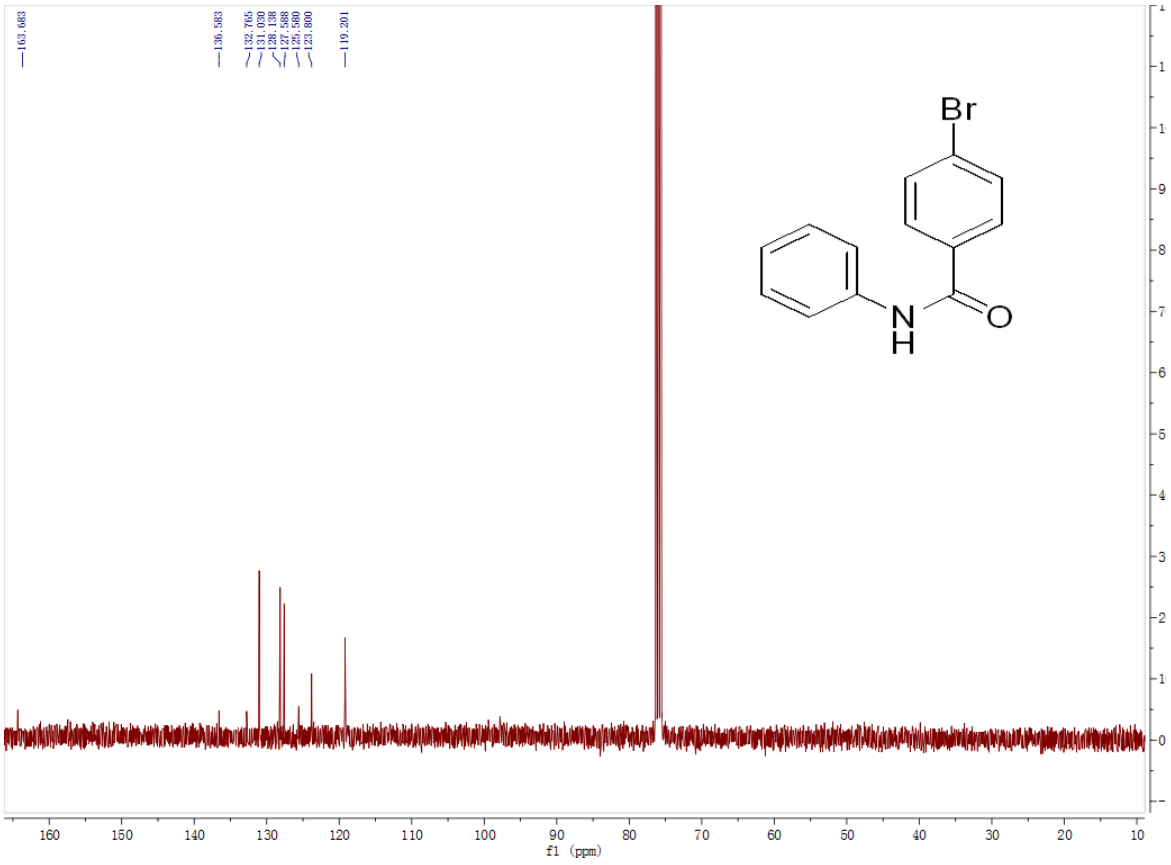
4v


7.830
7.809
7.774
7.638
7.616
7.480
7.459
7.406
7.385
7.365
7.192
7.173
7.155
2.01
1.01
2.00
2.00
2.01
1.00
f1 (ppm)

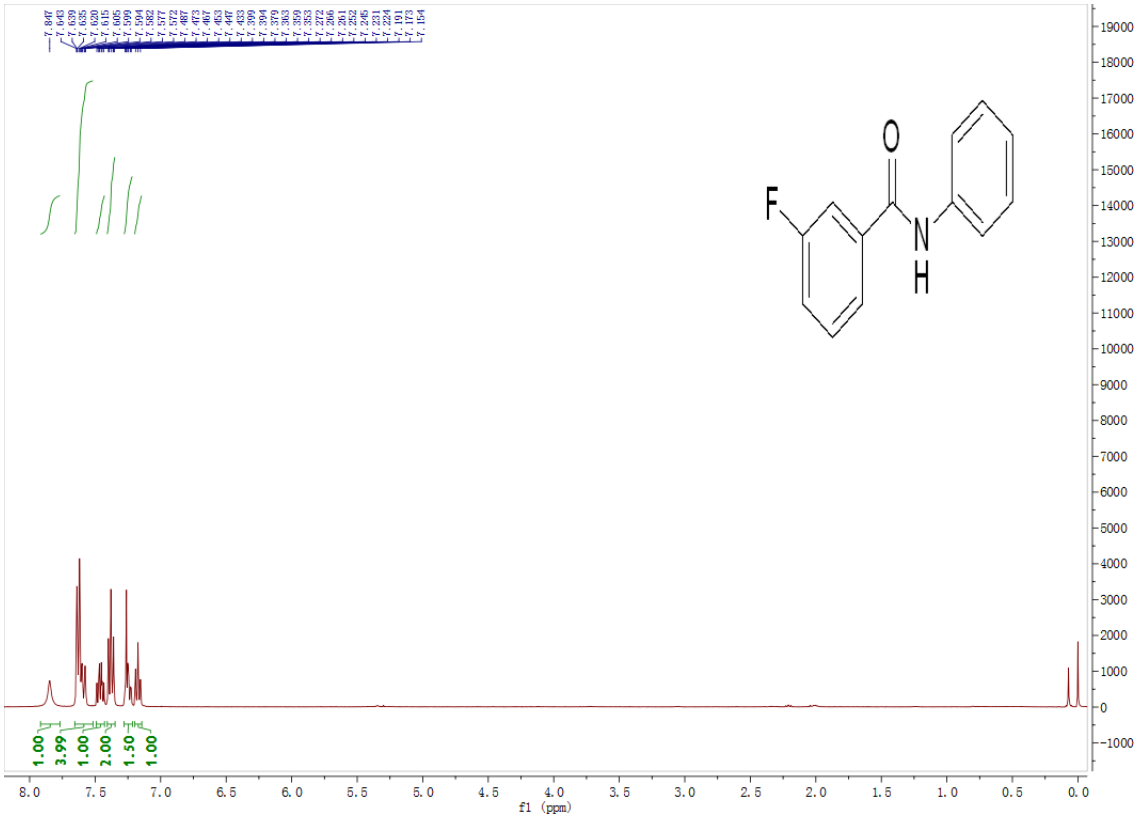

164.632
138.172
137.633
133.324
129.174
129.089
126.465
124.822
120.236
f1 (ppm)

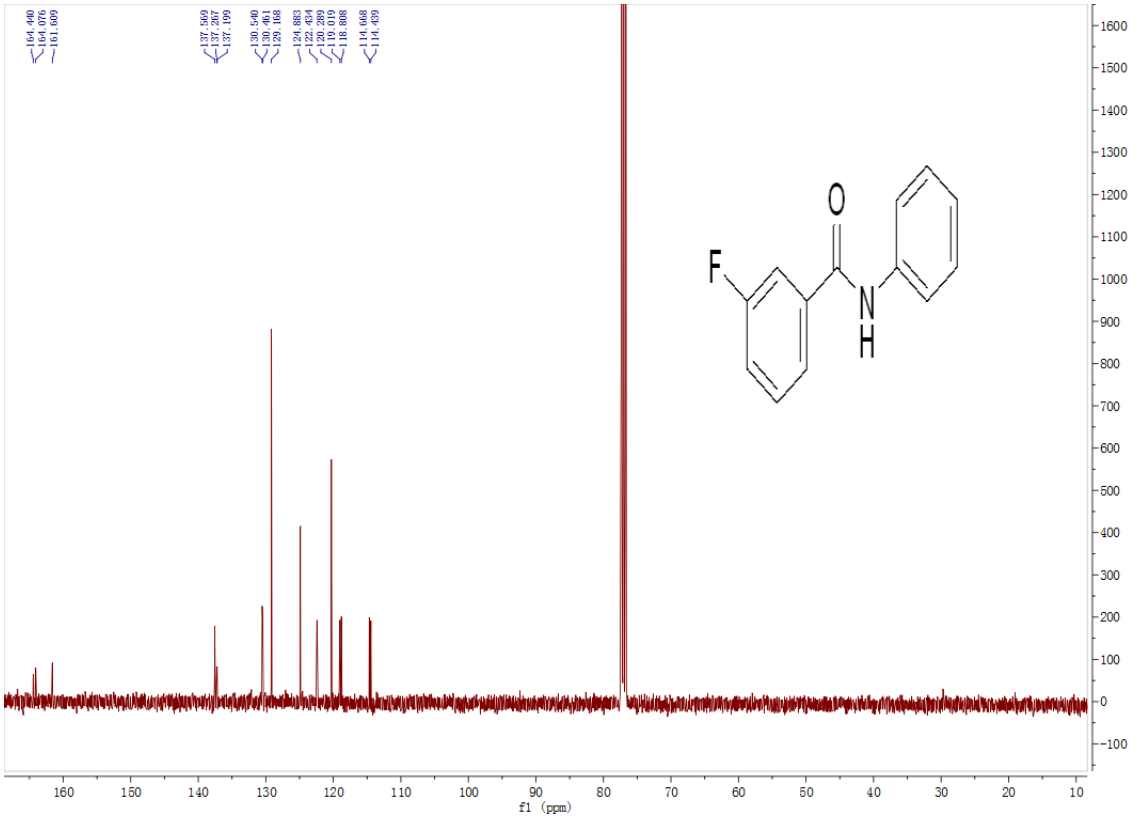
4w


7.758
7.736
7.643
7.637
7.633
7.621
7.384
7.363
7.191
7.172
7.154
Br
N
H
O
2.00
4.00
2.01
1.01
f1 (ppm)

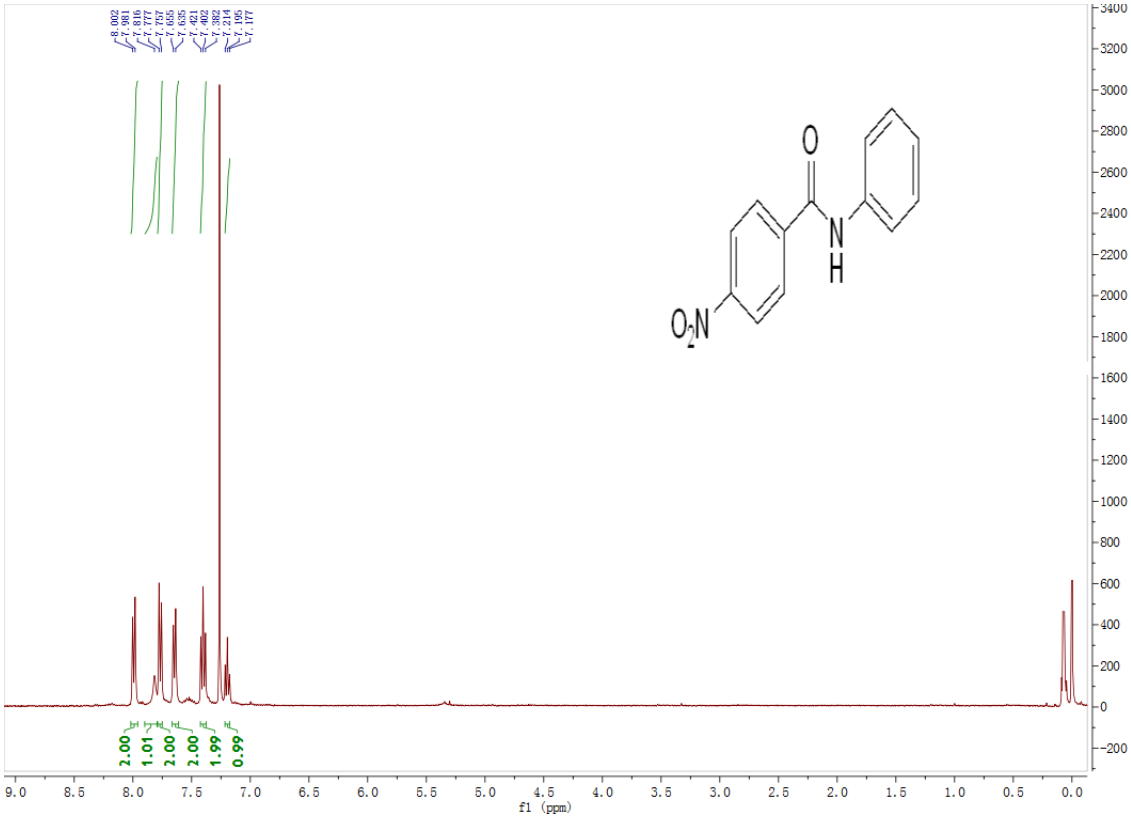

163.683
136.583
132.765
131.030
128.138
127.588
125.580
123.800
119.201
Br
N
H
O
f1 (ppm)

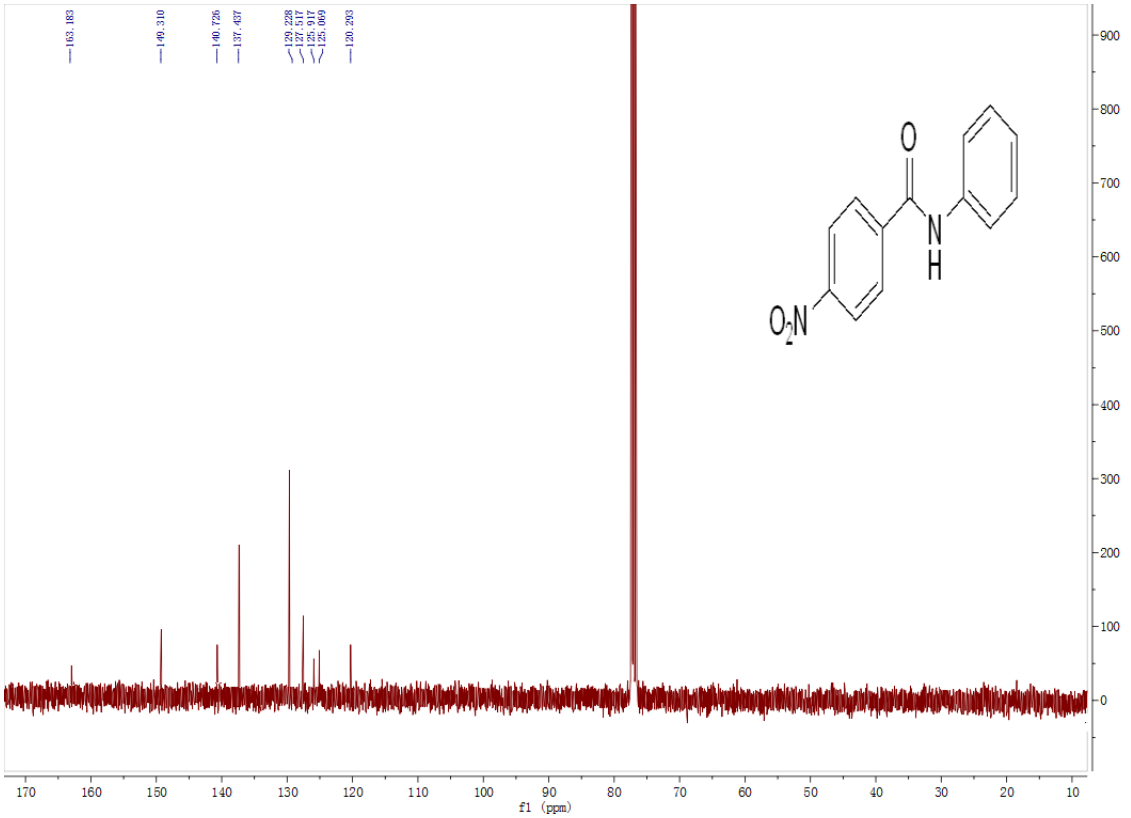
4x


7.847
7.645
7.639
7.635
7.620
7.615
7.605
7.599
7.594
7.582
7.577
7.572
7.498
7.495
7.467
7.463
7.447
7.433
7.398
7.394
7.379
7.363
7.359
7.355
7.272
7.266
7.261
7.252
7.236
7.231
7.224
7.191
7.173
7.154
O
F
N
H
1.00
3.99
1.00
2.00
1.50
1.00
f1 (ppm)

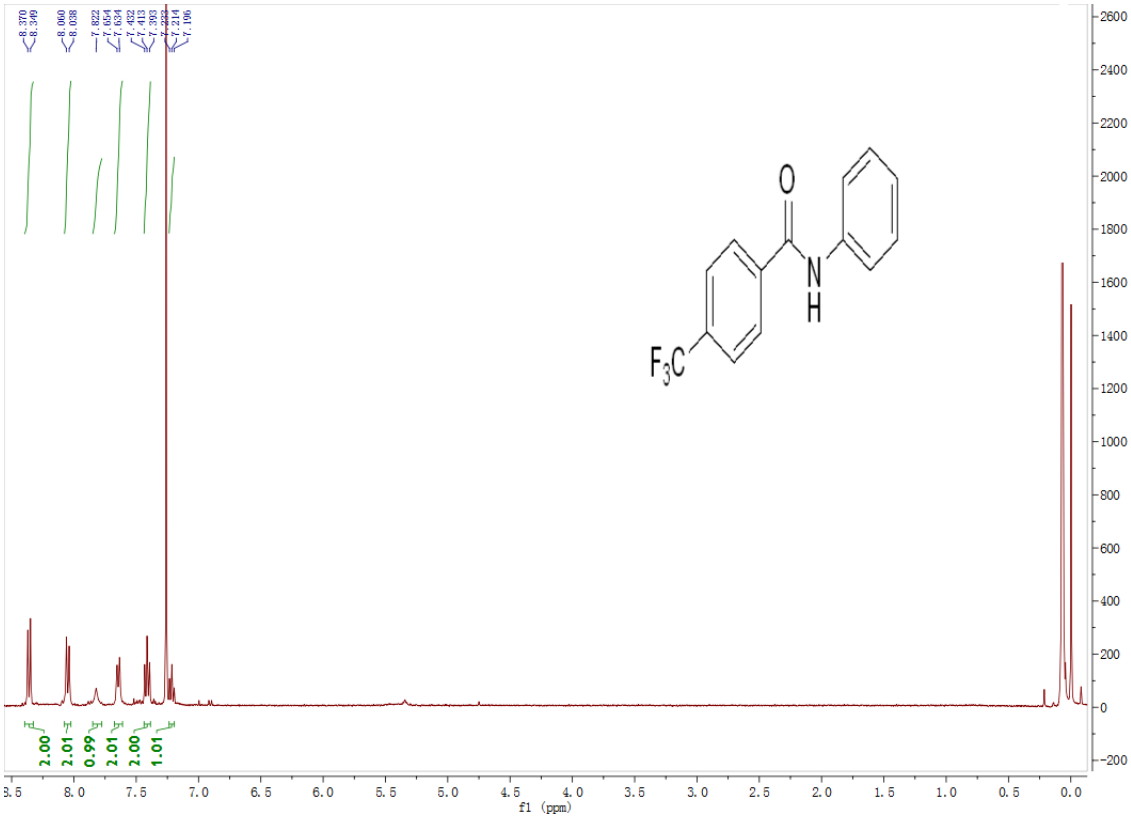

164.440
164.076
161.609
137.569
137.267
137.199
130.540
130.461
129.168
124.883
122.454
120.289
119.019
118.808
114.668
114.439
O
F
N
H
f1 (ppm)

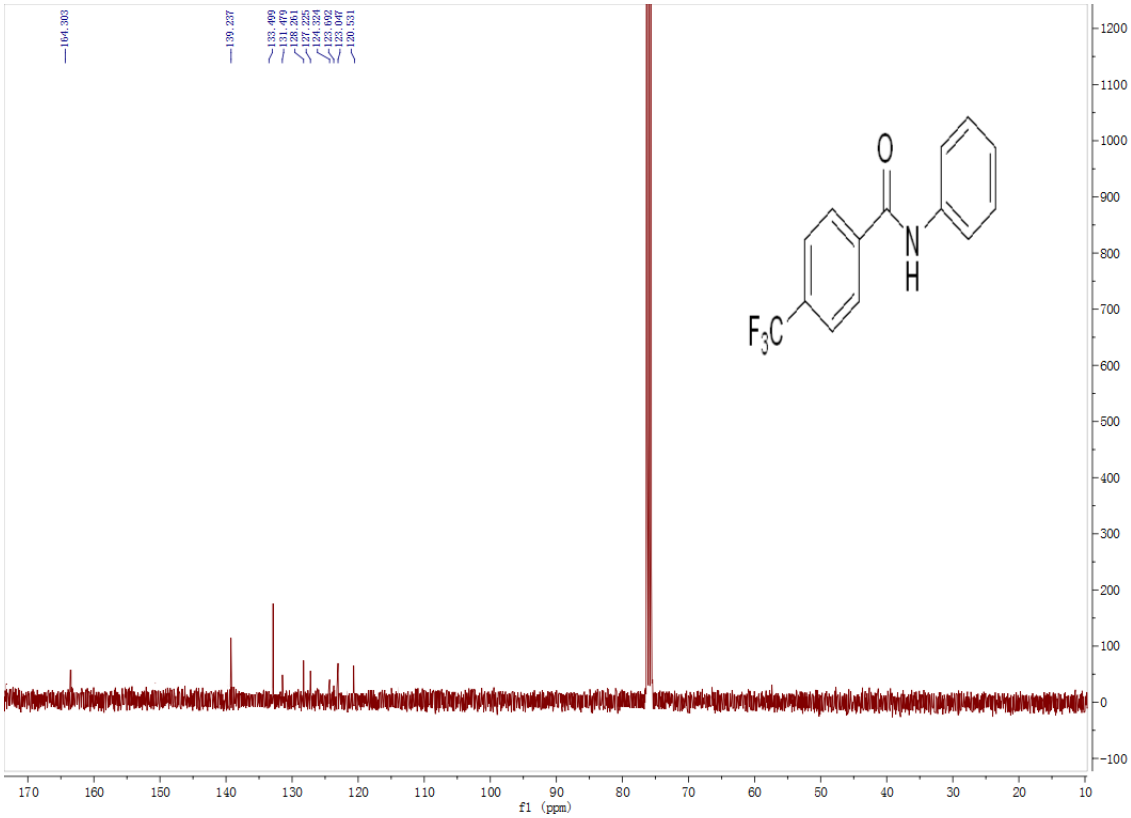
4y


8.002
7.981
7.816
7.777
7.757
7.655
7.635
7.421
7.402
7.382
7.214
7.195
7.177
2.00
1.01
2.00
2.00
1.99
0.99
O
N
H
O2N
f1 (ppm)

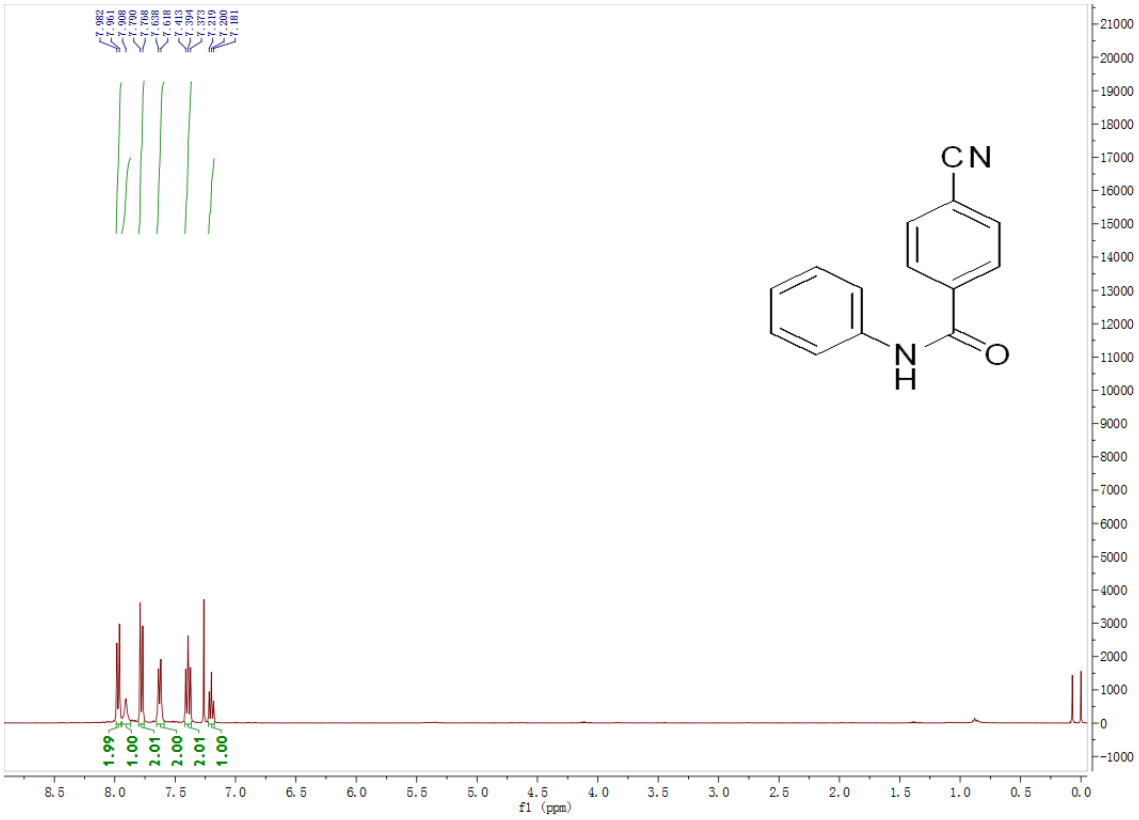

163.183
149.310
140.726
137.437
129.228
127.517
125.917
125.069
120.293
O
N
H
O2N
f1 (ppm)

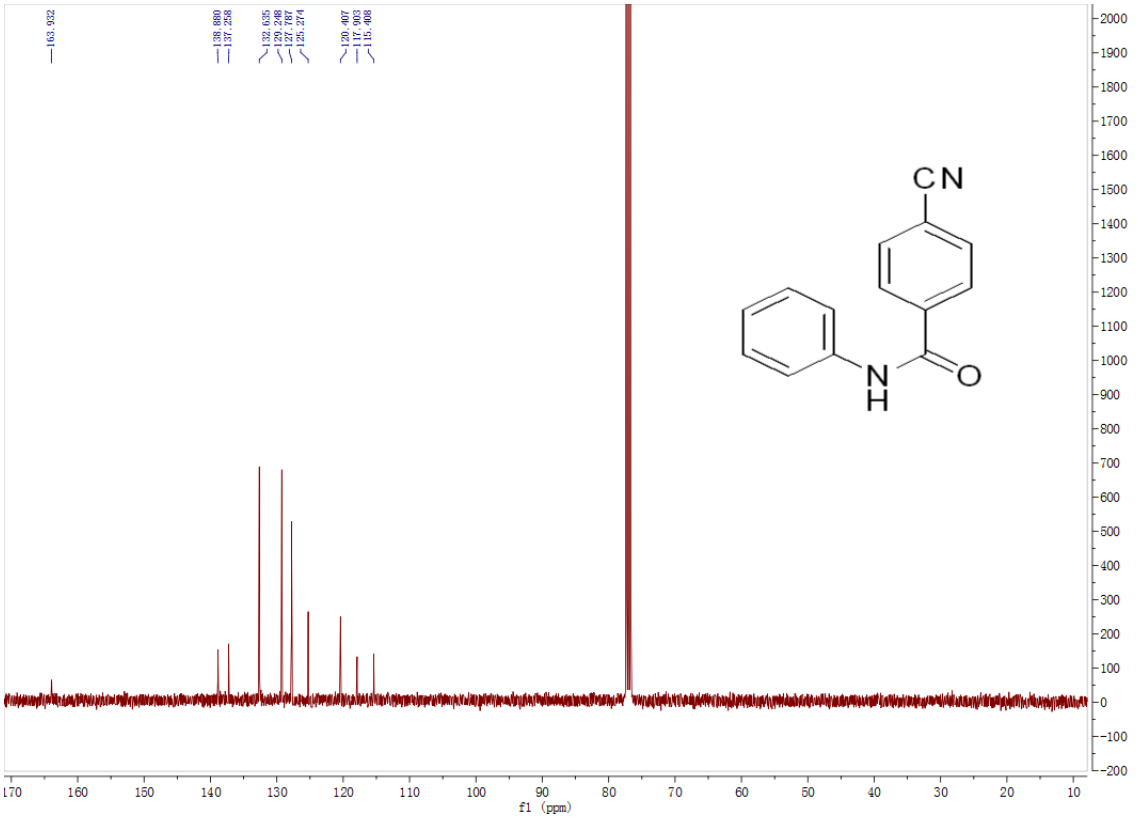
4z


8.370
8.349
8.060
8.038
7.822
7.654
7.634
7.432
7.413
7.393
7.225
7.214
7.196
2.00
2.01
0.99
2.01
2.00
1.01
O
N
H
F3C
f1 (ppm)

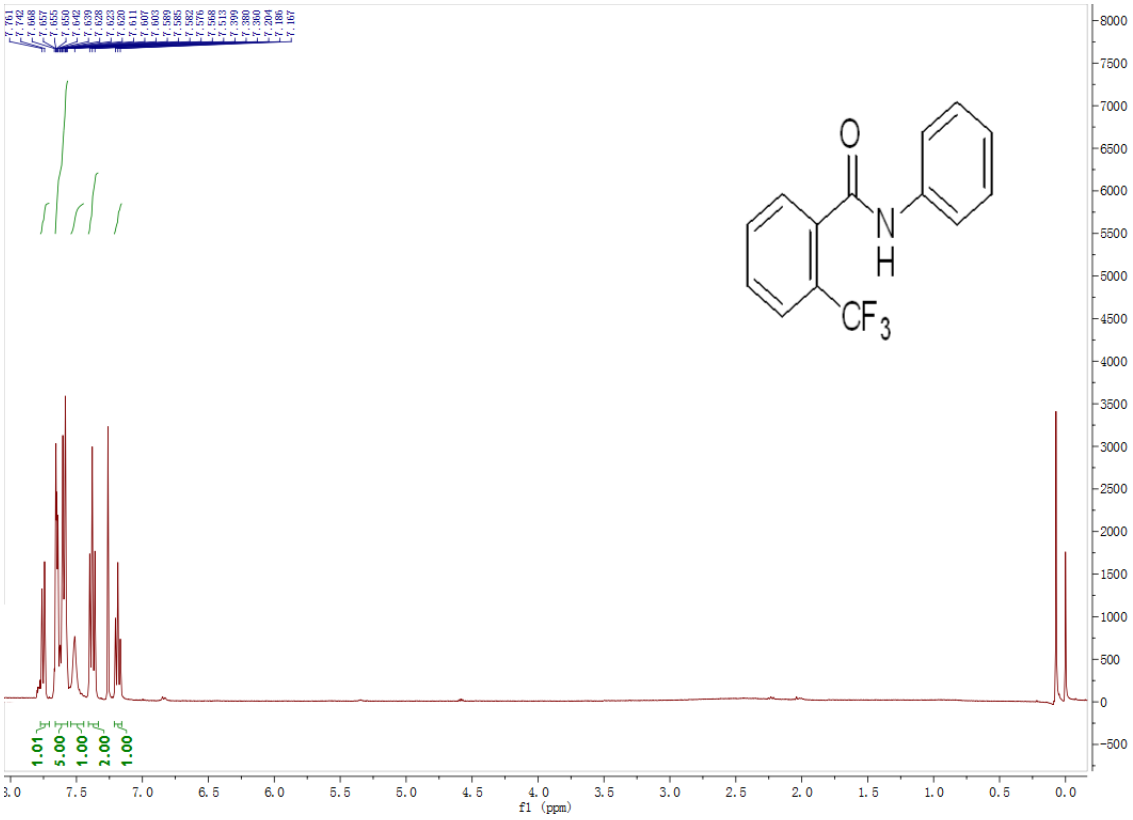

164.303
139.237
133.499
131.979
131.701
127.225
124.324
123.692
122.047
120.531
O
N
H
F3C
f1 (ppm)

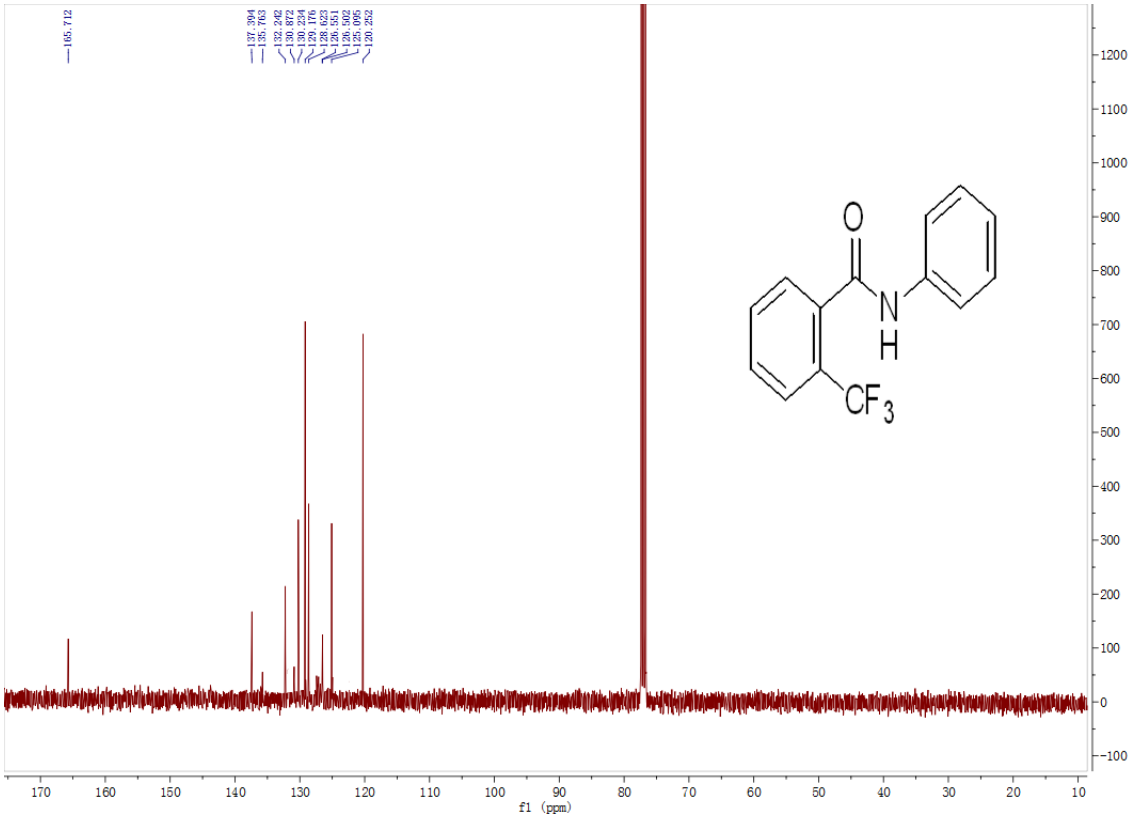
4aa


7.982
7.961
7.908
7.790
7.768
7.698
7.618
7.413
7.394
7.373
7.219
7.200
7.181
1.99
1.00
2.01
2.00
2.01
1.00
CN
N
H
O
f1 (ppm)

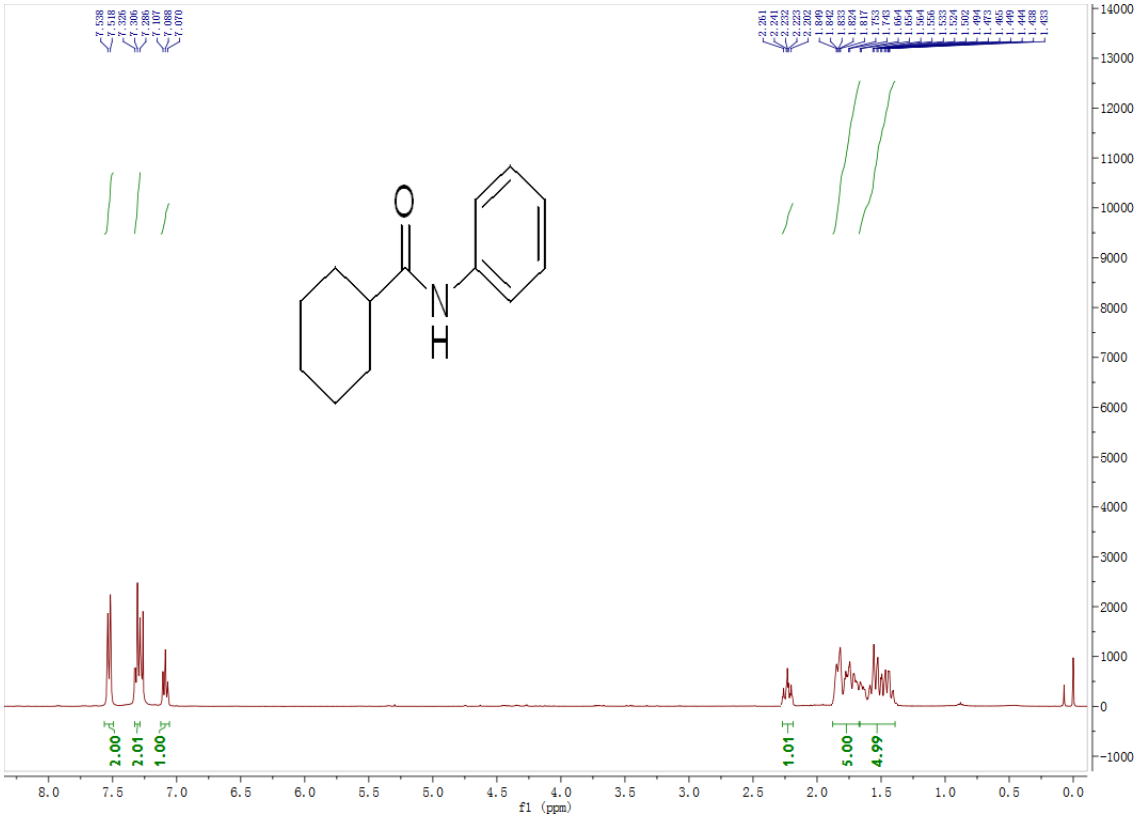

163.932
138.880
137.258
132.635
129.248
127.787
125.274
120.407
117.903
115.408
CN
N
H
O
f1 (ppm)

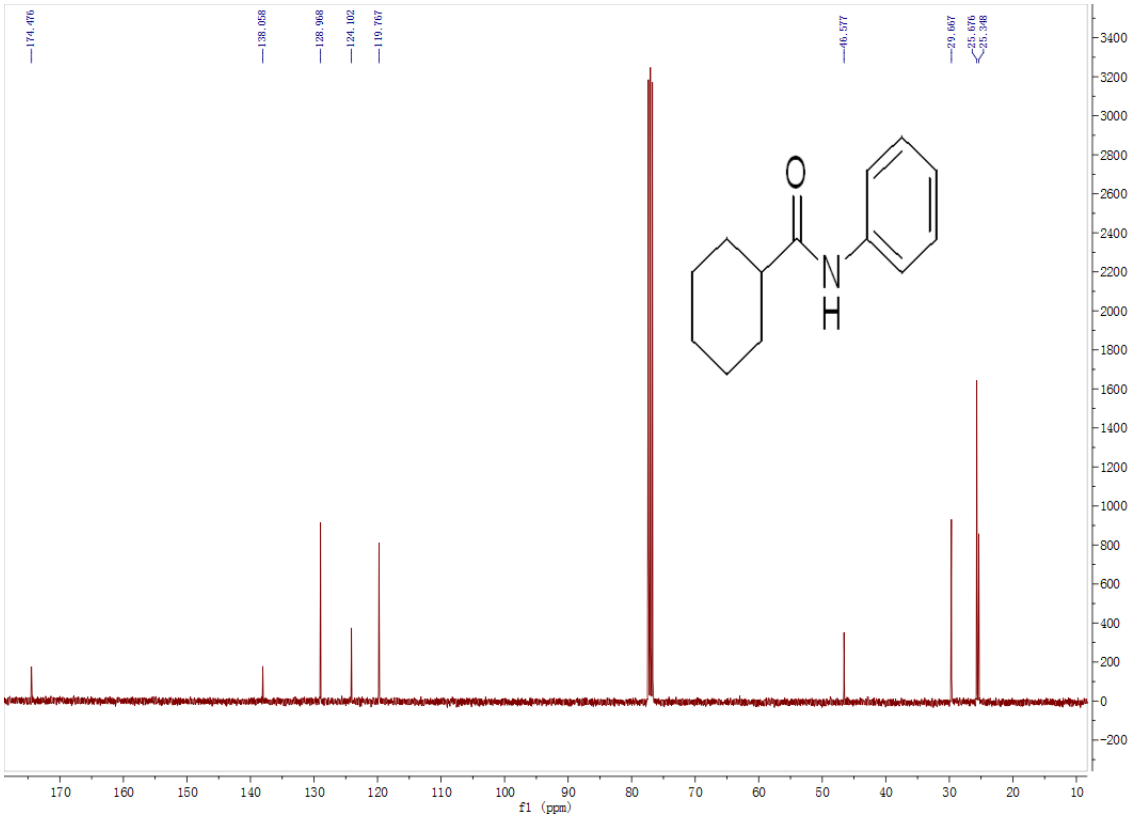
4ab


7.761
7.742
7.668
7.657
7.655
7.650
7.642
7.639
7.628
7.623
7.620
7.611
7.607
7.603
7.589
7.585
7.582
7.576
7.568
7.513
7.399
7.380
7.360
7.304
7.186
7.167
1.01
5.00
1.00
2.00
1.00
O
N
H
CF3
f1 (ppm)

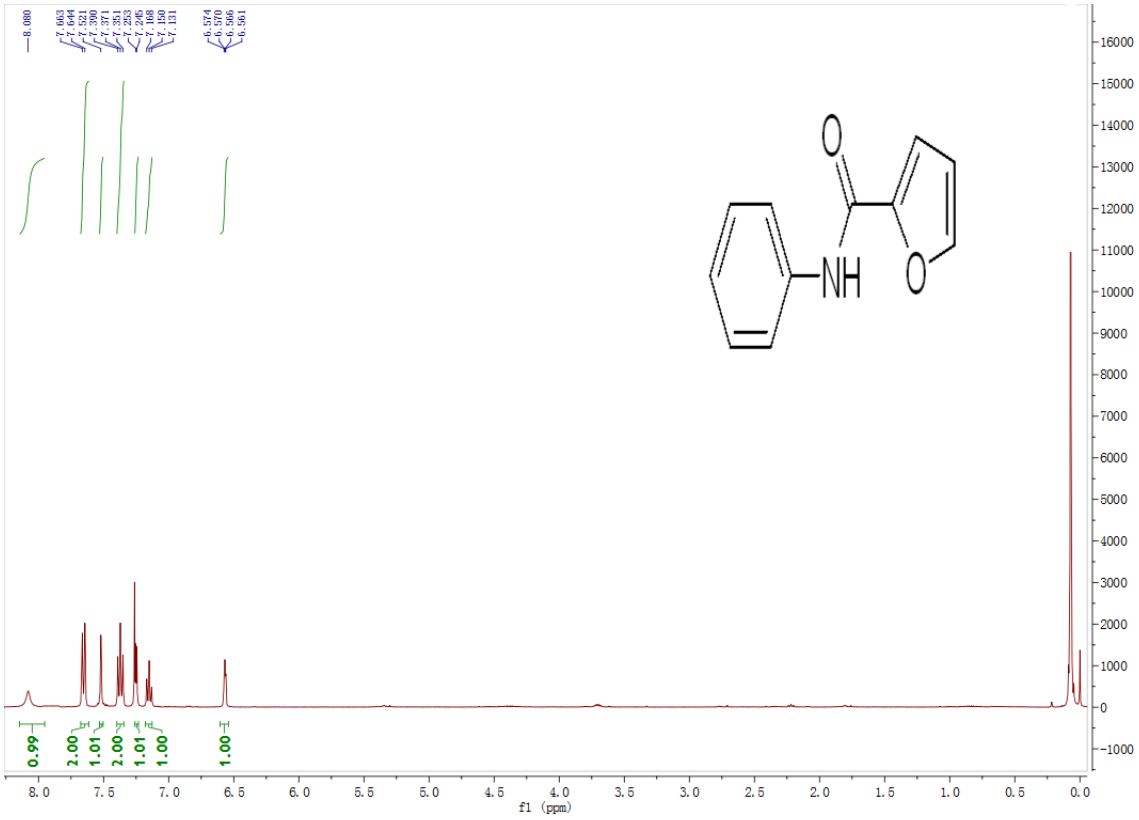

165.712
137.394
135.763
132.242
130.872
130.234
129.176
128.623
126.551
126.502
125.095
120.252
O
N
H
CF3
f1 (ppm)

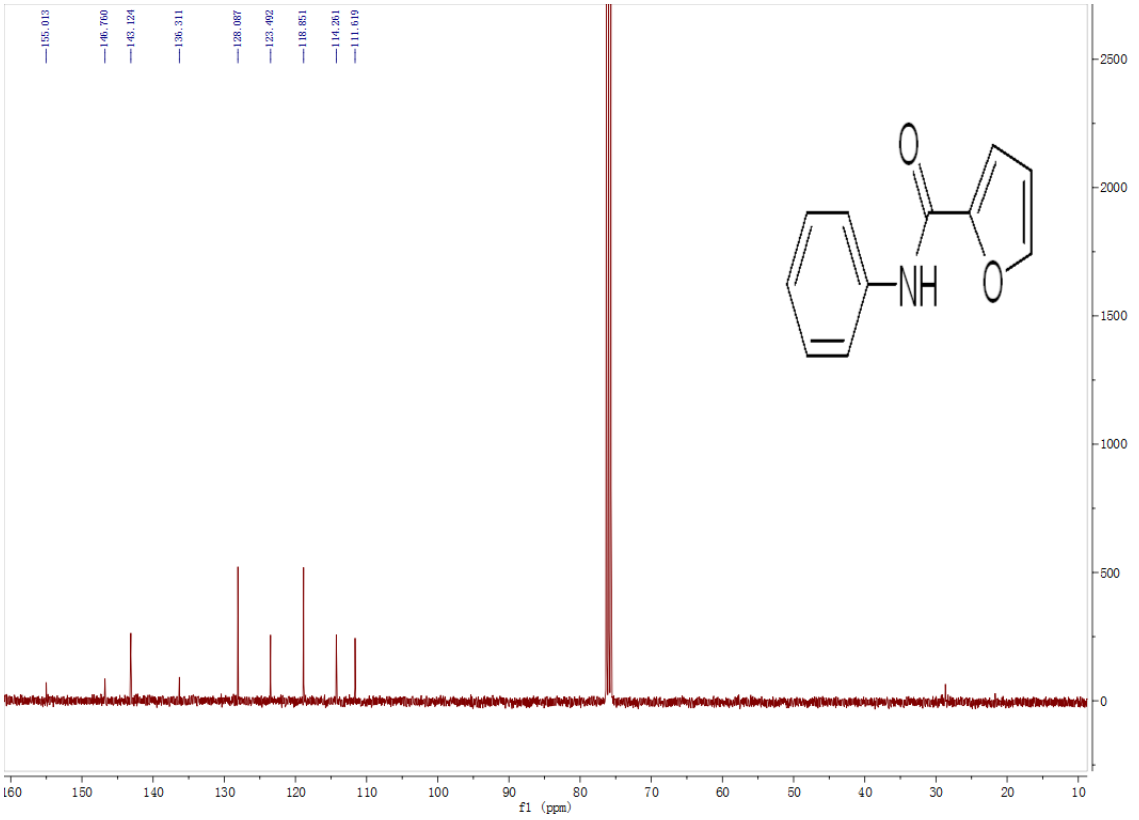
4ac


7.538
7.518
7.326
7.306
7.286
7.107
7.088
7.070
2.261
2.241
2.222
2.202
1.849
1.842
1.835
1.824
1.817
1.753
1.743
1.664
1.654
1.564
1.556
1.533
1.524
1.505
1.494
1.473
1.465
1.449
1.444
1.438
1.433
2.00
2.01
1.00
1.01
5.00
4.99
f1 (ppm)

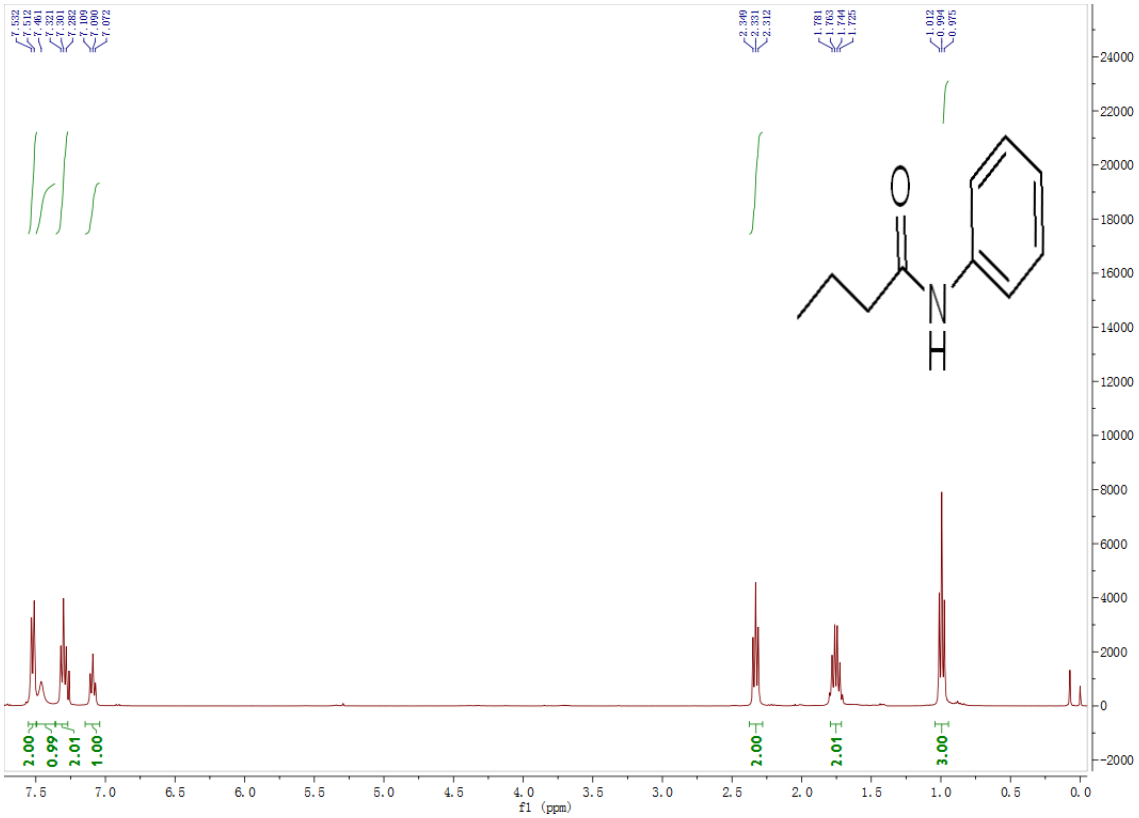

174.476
138.058
128.968
124.102
119.767
46.577
29.667
25.676
25.348
f1 (ppm)

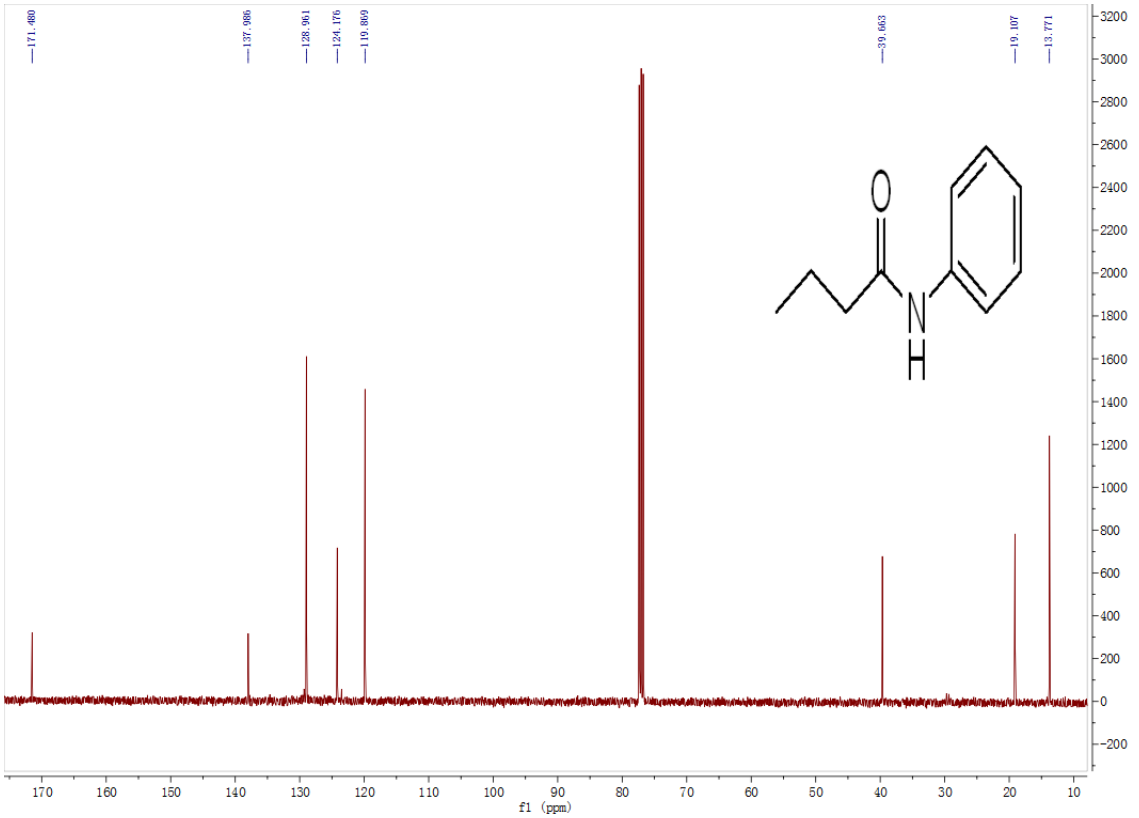
4ad


8.080
7.663
7.644
7.521
7.390
7.371
7.351
7.295
7.246
7.168
7.150
7.131
6.574
6.570
6.566
6.561
NH
O
0.99
2.00
1.01
2.00
1.01
1.00
1.00
f1 (ppm)

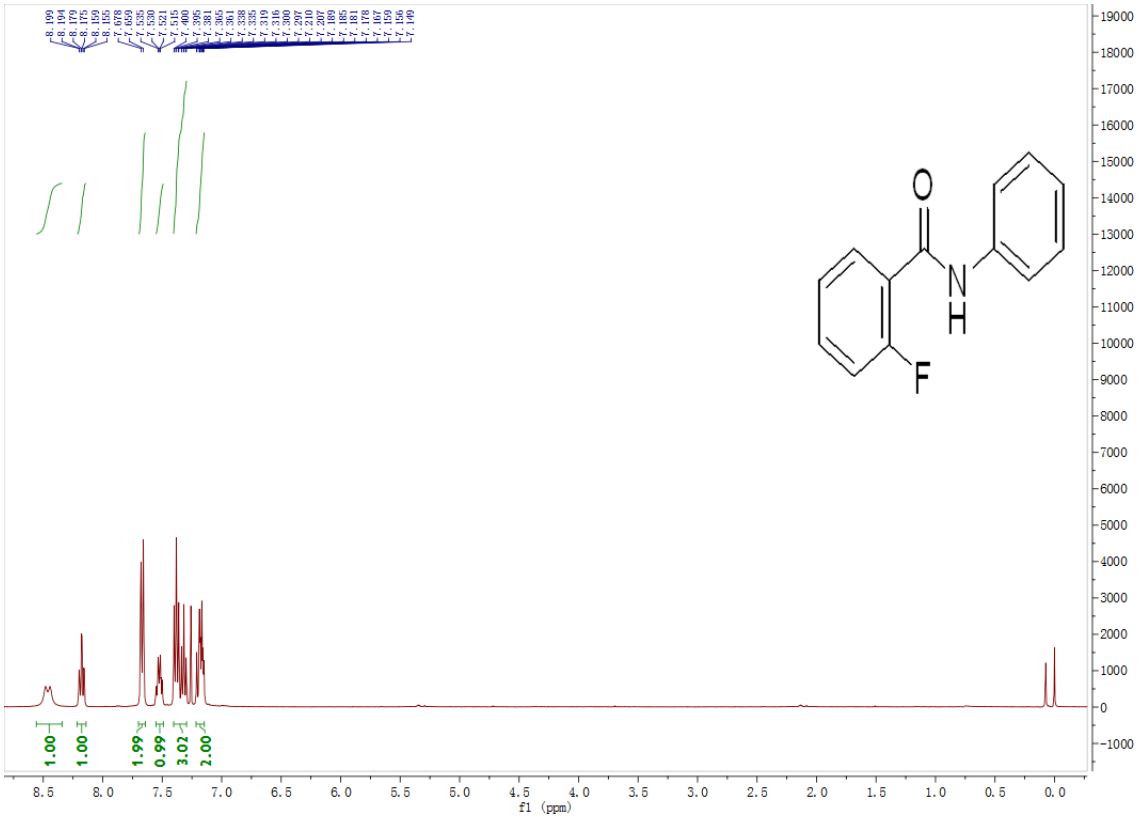

155.013
146.760
145.124
136.311
128.087
123.492
118.851
114.261
111.619
NH
O
f1 (ppm)

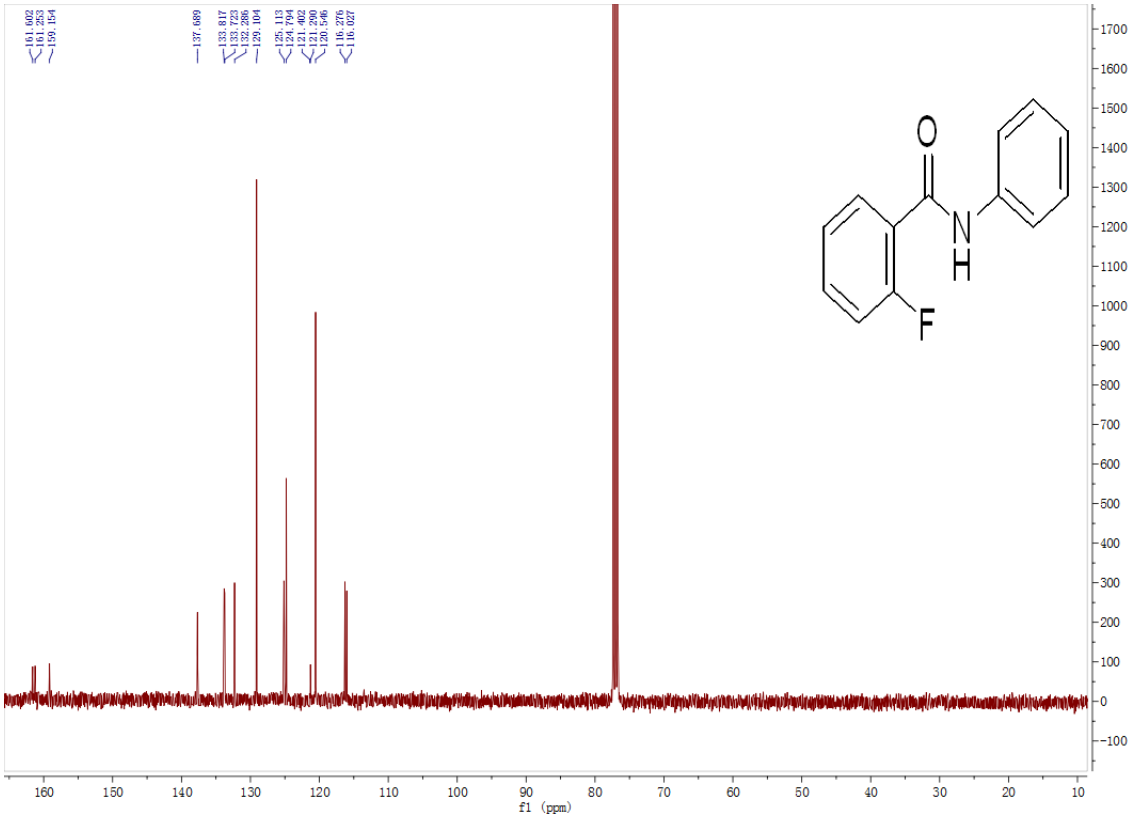
4ae


7.532
7.512
7.461
7.321
7.301
7.282
7.109
7.090
7.072
2.349
2.331
2.312
1.781
1.763
1.744
1.725
1.012
0.994
0.975
2.00
0.99
2.01
1.00
2.00
2.01
3.00
f1 (ppm)


171.480
137.986
128.961
124.176
119.869
39.663
19.107
13.771
f1 (ppm)

4af


8.199
8.194
8.179
8.175
8.159
8.155
7.678
7.659
7.555
7.530
7.521
7.515
7.400
7.395
7.381
7.365
7.361
7.338
7.325
7.319
7.316
7.300
7.297
7.210
7.207
7.189
7.185
7.181
7.179
7.167
7.159
7.156
7.149
1.00
1.00
1.99
0.99
3.01
2.00
f1 (ppm)


161.602
161.253
159.154
137.689
133.817
133.723
132.286
129.104
125.113
124.794
121.402
121.290
120.546
116.276
116.027
f1 (ppm)