

Visible-light-promoted and chlorophyll-catalyzed aerobic desulfurization of thioamides to amides

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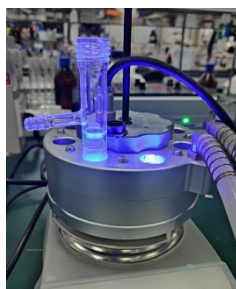
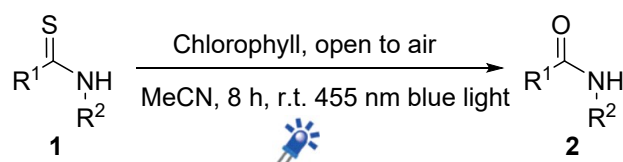
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1. General information

Column chromatography silica gel (200-300 mesh) and TLC plate were purchased from Qingdao Meijin Chemical Inc (Qingdao; China); HRMS data were obtained in the ESI mode on an Agilent 6530 Q-TOF/MS system. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer and chemical shifts were given in δ with TMS as an internal reference.

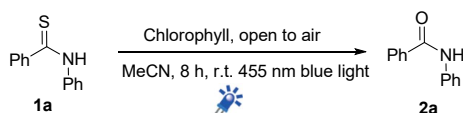
2. General procedure for the synthesis compounds 2



Scheme 1s.

A Schlenk tube equipped with a magnetic stir bar was charged with a mixture of thioamide **1** (0.3mmol) and 15 mg of chlorophyll a powder (5 mol%) and 3 mL MeCN. The tube was set on a RLH-18 photo reactor (Beijing Rogertech Ltd.) and irradiated by 10 W blue LED open to air. After irradiation at room temperature for 8 h, the LED light was removed, and the solvent was poured to 30 mL water and extracted with 30mL EtOAc for three times. The organic layer was then washed with 20mL water for three times and evaporated giving crude product, which was purified on silica gel chromatography and eluted with PE/EtOAc to give target compounds.

3. GC-MS analysis of model reaction



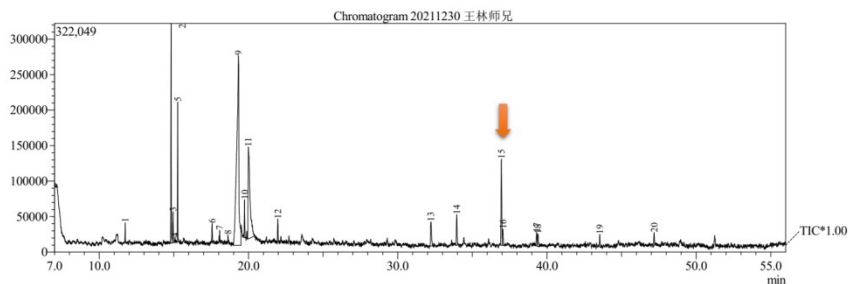
Method

==== Analytical Line 1 =====

Column Oven Temp. :35.0 °C
 Injection Temp. :250.00 °C
 Injection Mode :Splitless
 Column Flow :2.02 mL/min
 Split Ratio :-1.0
 Oven Temp. Program

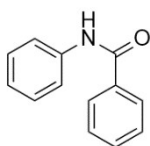
Rate	Temperature(°C)	Hold Time(min)
-	35.0	6.00
10.00	130.0	2.00
5.00	150.0	5.00
4.00	230.0	10.00

[GCMS-QP2010]
 IonSourceTemp :230.00 °C
 Interface Temp. :250.00 °C
 质核比扫描范围: 45~500m/z



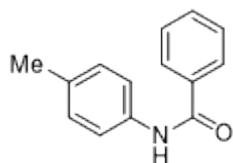
Peak#	R.Time	Area	Area%	Height	Height%	A/H Name
1	11.740	39609	0.63	26951	1.91	1.47 Furfural
2	14.814	492973	7.87	309493	21.89	1.59 Benzaldehyde
3	14.948	124063	1.98	43998	3.11	2.82 Cyclotetrasiloxane, octamethyl-
4	15.079	15187	0.24	7093	0.50	2.14 1-Octen-3-ol
5	15.255	318576	5.09	196928	13.93	1.62 Benzonitrile
6	17.563	56252	0.90	25760	1.82	2.18 Benzoic acid, methyl ester
7	18.071	25659	0.41	16044	1.13	1.60 Cyclopentasiloxane, decamethyl-
8	18.626	20735	0.33	11114	0.79	1.87 Cyclotrisiloxane, hexamethyl-
9	19.325	2802754	44.74	267408	18.91	10.48 Benzoic acid
10	19.736	115550	1.84	53355	3.77	2.17 Octanoic acid, ethyl ester
11	19.996	1150384	18.36	129163	9.14	8.91 Ethanone, 2,2-dihydroxy-1-phenyl-
12	21.969	74260	1.19	32422	2.29	2.29 Cyclotetrasiloxane, octamethyl-
13	32.227	151355	2.42	34057	2.41	4.44 3H-1,2-Benzodithiol-3-one
14	33.957	144270	2.30	43216	3.06	3.34 Asarone
Peak#	R.Time	Area	Area%	Height	Height%	A/H Name
15	36.948	400517	6.39	121571	8.60	3.29 Sulfurous acid
16	37.047	79150	1.26	23086	1.63	3.43 Hexadecane
17	39.314	67652	1.08	19052	1.35	3.55 Benzoxazole, 2-phenyl-
18	39.395	73216	1.17	17625	1.25	4.15 Cyclononasiloxane, octadecamethyl-
19	43.540	51788	0.83	17483	1.24	2.96 Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,1
20	47.184	60205	0.96	18068	1.28	3.33 Cyclononasiloxane, octadecamethyl-
		6264155	100.00	1413887	100.00	

4. Spectra data of compounds 2

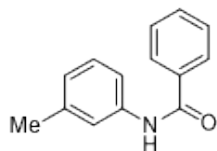


Compound **2a**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 7.99 (s, 1H), 7.89-7.88 (m, 2H), 7.67 (d, $J=8\text{Hz}$, 2H), 7.58-7.54 (m, 1H), 7.51-7.46 (m, 2H), 7.40-7.36 (m, 2H), 7.19-7.12 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.8, 137.9, 135.0, 131.8, 129.1($\times 2$), 128.8($\times 2$), 127.1($\times 2$), 124.6, 120.3($\times 2$). HRMS (ESI $^+$): calcd 198.0913 for

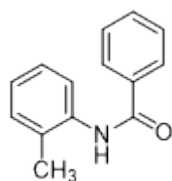
$C_{13}H_{12}NO^+$ $[M+H]^+$; Found, 198.0913. Data were consistent with those previously reported¹.



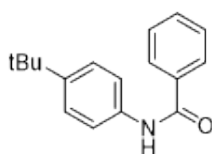
Compound **2b**, obtained as white solid, 1H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.86-7.84 (m, 2H), 7.56-7.49 (m, 3H), 7.44-7.39 (m, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.02, 135.49, 135.47, 135.05, 134.16, 131.62, 129.49($\times 2$), 128.64, 128.62, 127.14, 127.12, 120.62, 120.58, 20.94. HRMS (ESI⁺): calcd 212.1070 for $C_{14}H_{14}NO^+[M+H]^+$; Found, 212.1070. Data were consistent with those previously reported².



Compound **2c**, obtained as white solid, 1H NMR (400 MHz, $CDCl_3$): δ 7.91-7.86 (m, 4H), 7.59-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.23 (s, 1H), 7.17-7.13 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.82, 135.79, 134.94, 131.81, 130.58, 129.87, 128.78($\times 2$), 127.14($\times 2$), 126.81, 125.51, 123.56, 17.78. HRMS (ESI⁺): calcd 212.1070 for $C_{14}H_{14}NO^+[M+H]^+$; Found, 212.1070. Data were consistent with those previously reported¹.

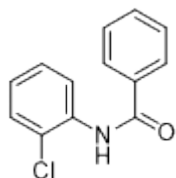


Compound **2d**, obtained as white solid, 1H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.86-7.85 (m, 2H), 7.54-7.46 (m, 3H), 7.42-7.38 (m, 2H), 7.22 (t, $J = 8$ Hz, 2H), 6.97 (d, $J = 7.6$ Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.21, 138.85, 138.01, 135.02, 131.67, 128.78, 128.61($\times 2$), 127.20($\times 2$), 125.36, 121.28, 117.73, 21.47. HRMS (ESI⁺): calcd 212.1070 for $C_{14}H_{14}NO^+[M+H]^+$; Found, 212.1070. Data were consistent with those previously reported¹.

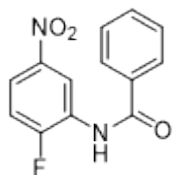


Compound **2e**, obtained as white solid, 1H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.85-7.82 (m, 2H), 7.71 (d, $J = 7.2$ Hz, 2H), 7.43-7.40 (m, 2H), 7.35-7.31 (m, 2H), 7.17-7.12 (m, 1H), 1.36 (s, 9H).

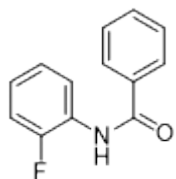
^{13}C NMR (100 MHz, CDCl_3): δ 166.21, 155.21, 138.27, 132.05, 128.95($\times 2$), 127.14($\times 2$), 125.63($\times 2$), 124.38, 120.62($\times 2$), 34.96, 31.20($\times 3$). HRMS (ESI $^+$): calcd 254.1539 for $\text{C}_{17}\text{H}_{20}\text{NO}^+[\text{M}+\text{H}]^+$; Found, 254.1542.



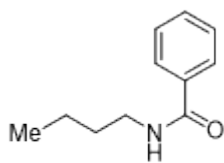
Compound **2f**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 8.68 (d, $J = 22$ Hz, 1H), 7.82-7.76 (m, 3H), 7.51-7.46 (m, 2H), 7.38-7.34 (m, 2H), 7.22-7.18 (m, 1H), 7.12-7.08 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.60, 139.21, 134.51, 134.42, 131.99, 129.91, 128.65, 127.23, 127.21, 124.59, 120.85, 120.81, 118.81, 118.76. HRMS (ESI $^+$): calcd 232.0524 for $\text{C}_{13}\text{H}_{11}\text{ClNO}^+[\text{M}+\text{H}]^+$; Found, 232.0520.



Compound **2g**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 9.50, 9.49 (dd, $J = 2.8\text{Hz}$, $J = 6.8\text{Hz}$, 1H), 8.19 (d, $J = 2.4\text{Hz}$, 1H), 8.07-8.03 (m, 1H), 7.94-7.92 (m, 2H), 7.67-7.62 (m, 1H), 7.58-7.54 (m, 2H), 7.34-7.28 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.41, 155.61(d, $^1J_{\text{F-C}} = 51.9\text{Hz}$), 144.63, 133.55, 132.76, 129.08($\times 2$), 127.46(d, $^2J_{\text{F-C}} = 11.5\text{Hz}$), 127.16($\times 2$), 119.96(d, $^3J_{\text{F-C}} = 9.2\text{Hz}$), 117.42(d, $^4J_{\text{F-C}} = 3.2\text{Hz}$), 115.38(d, $^2J_{\text{F-C}} = 22\text{Hz}$). HRMS (ESI $^+$): calcd 261.0670 for $\text{C}_{13}\text{H}_{10}\text{FN}_2\text{O}_3^+[\text{M}+\text{H}]^+$; Found, 261.0679.

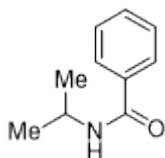


Compound **2h**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 8.46-8.42 (m, 1H), 8.18 (s, 1H), 7.91-7.89 (m, 2H), 7.59-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.20-7.09 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.54, 152.89(d, $^1J_{\text{F-C}} = 241.6\text{Hz}$), 134.51, 132.09, 128.83($\times 2$), 127.13($\times 2$), 126.49(d, $^2J_{\text{F-C}} = 10$ Hz), 124.66, 124.56(d, $^2J_{\text{F-C}} = 3.7\text{Hz}$), 122.10, 114.87(d, $^3J_{\text{F-C}} = 9.8\text{Hz}$). HRMS (ESI $^+$): calcd 216.0819 for $\text{C}_{13}\text{H}_{11}\text{FNO}^+[\text{M}+\text{H}]^+$; Found, 216.0819.

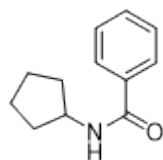


Compound **2i**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 7.78-7.76 (m, 2H), 7.42-7.38 (m, 1H), 7.33-7.29 (m, 2H), 7.12 (t, $J = 6\text{Hz}$, 1H), 3.38-3.33 (m, 2H), 1.57-1.49 (m, 2H),

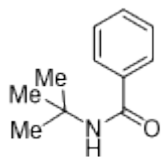
1.37-1.27 (m, 2H), 0.88 (t, 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.83, 134.80, 131.12, 128.32($\times 2$), 127.01($\times 2$), 39.85, 31.65, 20.14, 13.75. HRMS (ESI^+): calcd 178.1226 for $\text{C}_{11}\text{H}_{16}\text{NO}^+[\text{M}+\text{H}]^+$; Found, 178.1225. Data were consistent with those previously reported¹.



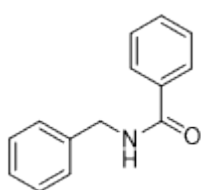
Compound **2j**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 7.77-7.75 (m, 2H), 7.43-7.39 (m, 1H), 7.33 (t, $J = 8\text{Hz}$, 2H), 6.58 (d, $J = 9.2\text{Hz}$, 1H), 4.28-4.20 (m, 1H), 1.22(s, 3H), 1.20 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.82, 134.96, 131.10, 128.33($\times 2$), 126.96($\times 2$), 41.83, 22.67($\times 2$). HRMS (ESI^+): calcd 164.1070 for $\text{C}_{10}\text{H}_{14}\text{NO}^+[\text{M}+\text{H}]^+$; Found, 164.1071.



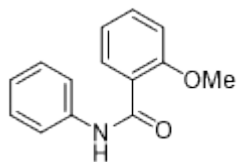
Compound **2k**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 7.76-7.74 (m, 2H), 7.45-7.42 (m, 1H), 7.37-7.33 (m, 2H), 6.56 (d, $J = 7.6\text{Hz}$, 1H), 4.39-4.31 (m, 1H), 2.01-1.98 (m, 2H), 1.73-1.65 (m, 2H), 1.61-1.56 (m, 2H), 1.53-1.44 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.3, 134.9, 131.2, 128.4($\times 2$), 127.0($\times 2$), 51.7, 33.0($\times 2$), 23.8($\times 2$). HRMS (ESI^+): calcd 190.1226 for $\text{C}_{12}\text{H}_{16}\text{NO}^+[\text{M}+\text{H}]^+$; Found, 190.1225.



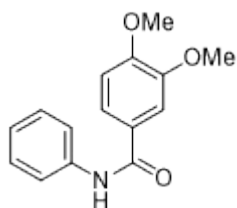
Compound **2l**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 7.67-7.63 (m, 2H), 7.35-7.22 (m, 2H), 6.31 (d, $J = 16.4\text{Hz}$, 1H), 1.40-1.38 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 135.9, 130.9, 128.3($\times 2$), 126.8($\times 2$), 51.5, 28.8($\times 3$). HRMS (ESI^+): calcd 178.1226 for $\text{C}_{11}\text{H}_{16}\text{NO}^+[\text{M}+\text{H}]^+$; Found, 178.1221.



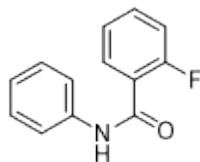
Compound **2m**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 7.84-7.82 (m, 2H), 7.50-7.46 (m, 1H), 7.39-7.27 (m, 7H), 4.57 (d, $J = 6\text{Hz}$, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.70, 138.50, 134.41, 131.46, 128.65($\times 2$), 128.49($\times 2$), 127.74($\times 2$), 127.38, 127.19($\times 2$), 43.94. HRMS (ESI^+): calcd 212.1070 for $\text{C}_{14}\text{H}_{14}\text{NO}^+[\text{M}+\text{H}]^+$; Found, 212.1070. Data were consistent with those previously reported³.



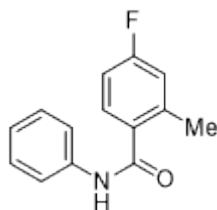
Compound **2n**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 8.61-8.58 (m, 2H), 7.94-7.91 (m, 2H), 7.57-7.47 (m, 3H), 7.12-7.02 (m, 2H), 6.94-6.90 (m, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.22, 148.26, 135.27, 131.73, 128.77($\times 2$), 127.81, 127.05($\times 2$), 123.96, 121.11, 119.88, 110.03, 55.82. HRMS (ESI $^+$): calcd 228.1019 for $\text{C}_{14}\text{H}_{14}\text{NO}_2^+[\text{M}+\text{H}]^+$; Found, 228.1021.



Compound **2o**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 8.28 (s, 1H), 7.68-7.64 (m, 2H), 7.47 (d, $J = 2.0$ Hz, 1H), 7.47, 7.42 (dd, $J_1 = 2\text{Hz}$, $J_2 = 8.4$ Hz, 1H), 7.35-7.31 (m, 2H), 7.15-7.11 (m, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.58, 151.97, 149.04, 138.22, 128.97($\times 2$), 127.48, 124.34, 120.38($\times 2$), 119.75, 110.75, 110.31, 55.99, 55.91. HRMS (ESI $^+$): calcd 258.1125 for $\text{C}_{15}\text{H}_{16}\text{NO}_3^+[\text{M}+\text{H}]^+$; Found, 258.1125.

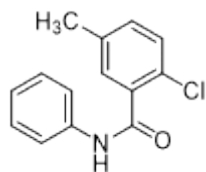


Compound **2p**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 8.58 (d, $J = 14$ Hz, 1H), 8.08 (td, $J = 7.6$ Hz, $J = 1.6\text{Hz}$, 1H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.50-7.45 (m, 1H), 7.39-7.35 (m, 2H), 7.25 (td, $J = 1.2$ Hz, $J = 8$ Hz, 1H), 7.19-7.10 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.53, 159.03, 137.80, 133.61(d, $^3J_{\text{F-C}} = 2.1\text{Hz}$), 131.95(d, $^4J_{\text{F-C}} = 2.1$ Hz), 129.04($\times 2$), 124.97(d, $^3J_{\text{F-C}} = 3.2$ Hz), 124.74, 121.67(d, $^2J_{\text{F-C}} = 11.4$ Hz), 120.57($\times 2$), 116.23(d, $^1J_{\text{F-C}} = 24.6$ Hz). HRMS (ESI $^+$): calcd 216.0819 for $\text{C}_{13}\text{H}_{11}\text{FNO}^+[\text{M}+\text{H}]^+$; Found, 216.0819.

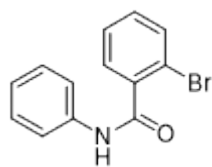


Compound **2q**, obtained as white solid, ^1H NMR (400 MHz, CDCl_3): δ 7.88 (s, 1H), 7.61 (d, $J = 8$ Hz, 2H), 7.43-7.34 (m, 3H), 7.19-7.15 (m, 1H), 6.95-6.86 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.37, 163.36(d, $^1J_{\text{F-C}} = 248.3$ Hz), 139.68(d, $^3J_{\text{F-C}} = 8.4$ Hz), 137.91, 132.55, 129.07($\times 3$), 128.79(d, $^3J_{\text{F-C}} = 8.9$ Hz), 124.67, 120.06, 117.95(d, $^2J_{\text{F-C}} = 21.2$ Hz), 112.67(d, $^2J_{\text{F-C}} = 21.4$ Hz), 19.93(d, $^4J = 1.5$ Hz). HRMS

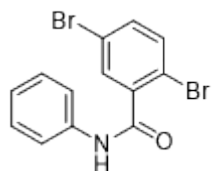
(ESI⁺): calcd 230.0976 for C₁₄H₁₃FNO⁺[M+H]⁺; Found, 230.0976.



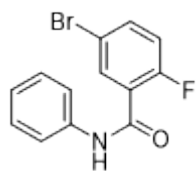
Compound **2r**, obtained as white solid, ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 1.2 Hz, 1H), 7.67-7.65 (m, 2H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.40-7.36 (m, 2H), 7.31 (d, *J* = 8Hz, 1H), 7.21-7.16 (m, 2H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 164.74, 137.67, 137.37, 134.75, 132.40, 130.81, 130.06, 129.08(×2), 127.46, 124.76, 120.16(×2), 20.75. HRMS (ESI⁺): calcd 353.9100 for C₁₃H₁₀Br₂NO⁺[M+H]⁺; Found, 355.9103. HRMS (ESI⁺): calcd 246.0680 for C₁₄H₁₃ClNO⁺[M+H]⁺; Found, 246.0678.



Compound **2s**, obtained as white solid, ¹H NMR (400 MHz, CDCl₃): δ 8.31 (s, 1H), 7.64-7.61 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.2Hz, 1H), 7.36-7.30 (m, 3H), 7.27-7.22 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 165.97, 137.81, 137.72, 133.37, 131.44, 129.43, 129.02(×2), 127.56, 124.77, 120.29(×2), 119.41. HRMS (ESI⁺): calcd 276.0019 for C₁₃H₁₁BrNO⁺[M+H]⁺; Found, 276.0019.

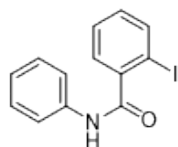


Compound **2t**, obtained as white solid, ¹H NMR (400 MHz, CDCl₃): δ 8.00 (s, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.63-7.61 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.42-7.36 (m, 3H), 7.22-7.18 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 164.19, 139.31, 137.24, 134.85, 134.49, 132.45, 129.15(×2), 125.14, 121.64, 120.27(×2), 118.01. HRMS (ESI⁺): calcd 353.9124 for C₁₃H₁₀Br₂NO⁺[M+H]⁺; Found, 353.9124.

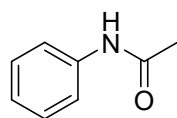


Compound **2u**, obtained as white solid, ¹H NMR (400 MHz, CDCl₃): δ 8.42 (d, *J* = 14.8 Hz, 1H), 8.30, 8.29 (dd, *J* = 2.4Hz, *J* = 6.8Hz, 1H), 7.67-7.61 (m, 3H), 7.43-7.38 (m, 2H), 7.22-7.18 (m, 1H), 7.11, 7.11 (dd, *J* = 8.4 Hz, *J* = 11.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 160.50, 159.83(d, ¹*J*_{F-C} = 3.8 Hz), 158.05, 137.35, 136.44(d, ³*J*_{F-C} = 10 Hz), 134.90(d, ³*J*_{F-C} = 2.3 Hz), 129.15(×2), 125.09, 123.14(d, ²*J*_{F-C} = 12.8 Hz), 120.60, 118.18(d, ²*J*_{F-C} = 27

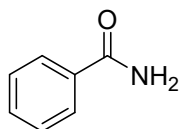
Hz). HRMS (ESI⁺): calcd 293.9924 for C₁₃H₁₀BrFNO⁺[M+H]⁺; Found, 293.9924.



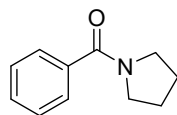
Compound **2v**, obtained as white solid, ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, *J*=8.0 Hz, 2H), 7.64 (d, *J*= 7.6 Hz, 2H), 7.47-7.45 (m, 1H), 7.39-7.35 (m, 3H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.14-7.10 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 167.40, 142.03, 139.97, 137.62, 131.42, 129.08(×2), 128.48, 128.28, 124.86, 120.23(×2), 92.49. HRMS (ESI⁺): calcd 323.9880 for C₁₃H₁₁I⁺[M+H]⁺; Found, 323.9884.



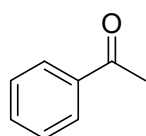
Compound **2w**, obtained as white solid, ¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, *J* = 8Hz, 2H), 7.30 (t, *J* = 8Hz, 2H), 7.11 (t, *J* = 8Hz, 1H), 2.16 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 169.2, 138.1, 128.8(×2), 124.3, 120.3(×2), 24.4. HRMS (ESI⁺): calcd 136.0757 for C₈H₁₀NO⁺ [M+H]⁺; Found, 136.0757. Data were consistent with those previously reported¹.



Compound **2x**, Obtained as white solid, ¹H NMR (400MHz, CDCl₃): δ 7.84(d, *J* = 8.5 Hz, 2H), 7.54(t, *J* = 8.5 Hz, 1H), 7.46(t, *J* = 8.6 Hz, 2H), 6.34(s, 2H), ¹³C NMR (100MHz, CDCl₃): δ 169.8, 133.3, 132.0, 128.6(2), 127.4(2). HRMS (ESI⁺): calcd 122.0600 for C₇H₈NO⁺ [M+H]⁺; found, 122.0601.

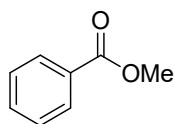


Compound **2y**, Obtained as colorless oil, ¹H NMR (400MHz, CDCl₃): δ 7.34(dd, *J* = 8.6 Hz, 2H), 7.20(dd, *J* = 8.5 Hz, 3H), 3.45(t, *J* = 8.6 Hz, 2H), 3.22(t, *J* = 8.6 Hz, 2H), 1.77-1.71(m, 2H), 1.67-1.61(m, 2H), ¹³C NMR (100MHz, CDCl₃): δ 169.4, 137.1, 129.6, 128.0(×2), 126.9(×2), 49.4, 46.0, 26.2, 24.3. HRMS (ESI⁺): calcd 176.1070 for C₁₁H₁₄NO [M+H]⁺; found, 176.1072



Compound **5**, Obtain as the yellow oil, ¹H NMR (400 MHz, CDCl₃): δ 7.99-7.97 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H), 2.62 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 198.2, 137.1, 133.1, 128.6($\times 2$), 128.3($\times 2$), 26.6.
HRMS (ESI $^+$): calcd 121.0648 for $\text{C}_8\text{H}_9\text{O}^+$ [M+H] $^+$; Found, 121.0648.



Compound **6**, Obtain as the yellow oil, ^1H NMR (400 MHz, CDCl_3): δ 8.06-8.03 (m, 2H), 7.56-7.51 (m, 1H), 7.44-7.40 (m, 2H), 3.40 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 132.9, 130.2, 129.5($\times 2$), 128.3($\times 2$), 52.0. HRMS (ESI $^+$): calcd 159.0417 for $\text{C}_8\text{H}_8\text{NaO}_2^+$ [M+Na] $^+$; Found, 159.0420.

5. X-ray crystal data for compound **2a** (CCDC deposition number: 2160655).

$\text{C}_{13}\text{H}_{11}\text{NO}$, $M = 197.23$, $a = 5.3315(6)$ Å, $b = 7.7796(8)$ Å, $c = 12.4238(14)$ Å, $\alpha = 72.694(6)^\circ$, $\beta = 78.711(5)^\circ$, $\gamma = 89.961(5)^\circ$, $V = 481.54(9)$ Å 3 , $T = 100.(2)$ K, space group $P-1$, $Z = 2$, $\mu(\text{Cu K}\alpha) = 0.687$ mm $^{-1}$, 5689 reflections measured, 1857 independent reflections ($R_{int} = 0.0652$). The final R_I values were 0.1139 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.3700 ($I > 2\sigma(I)$). The final R_I values were 0.1245 (all data). The final $wR(F^2)$ values were 0.3950 (all data). The goodness of fit on F^2 was 1.833.

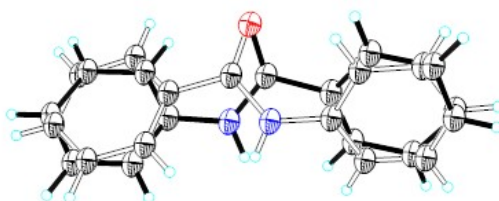


Figure 1s. View of the molecules in an asymmetric unit.
Displacement ellipsoids are drawn at the 30% probability level.

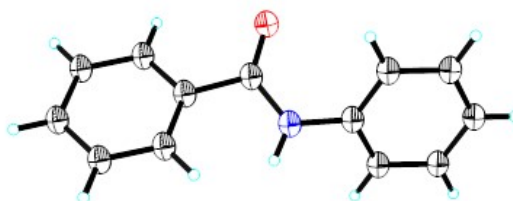


Figure 2s. View of a molecule of cp2 with the atom-labelling scheme.
Displacement ellipsoids are drawn at the 30% probability level.

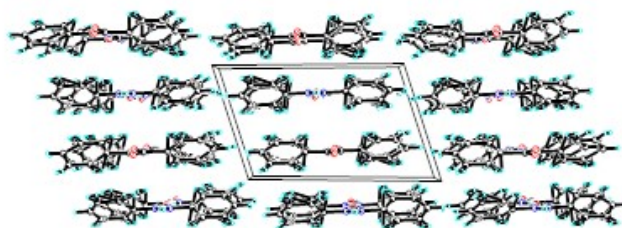
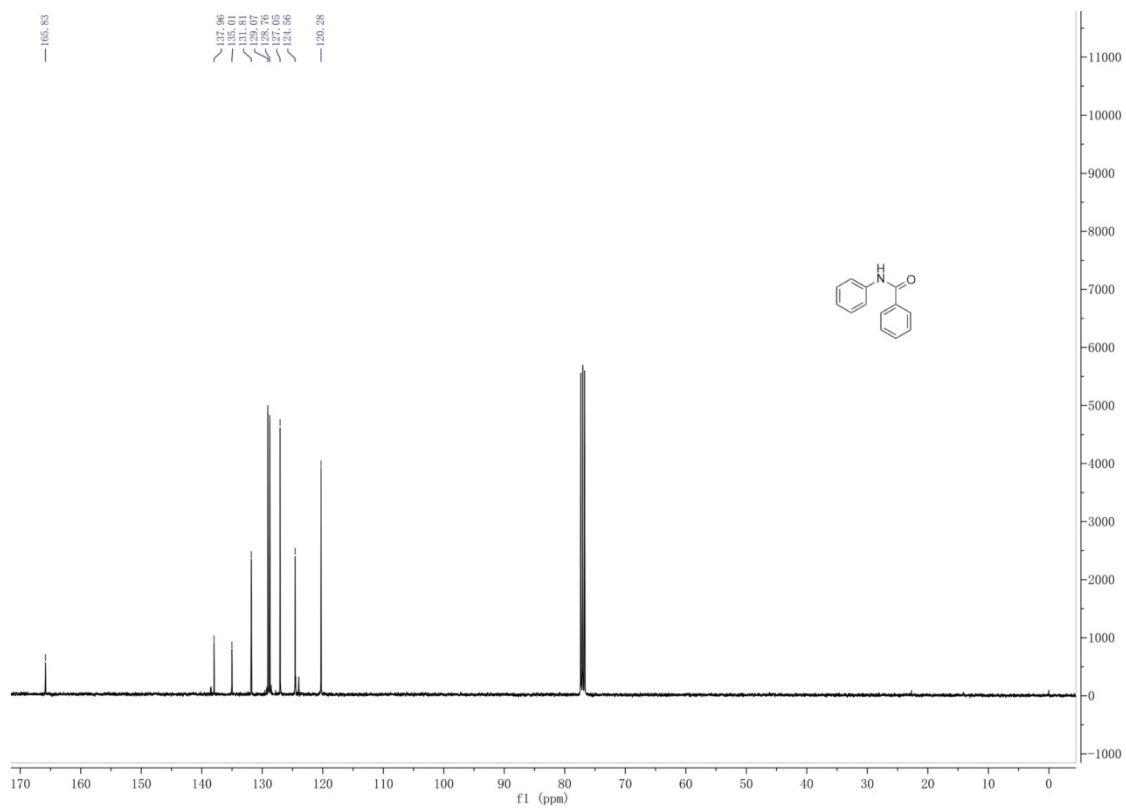
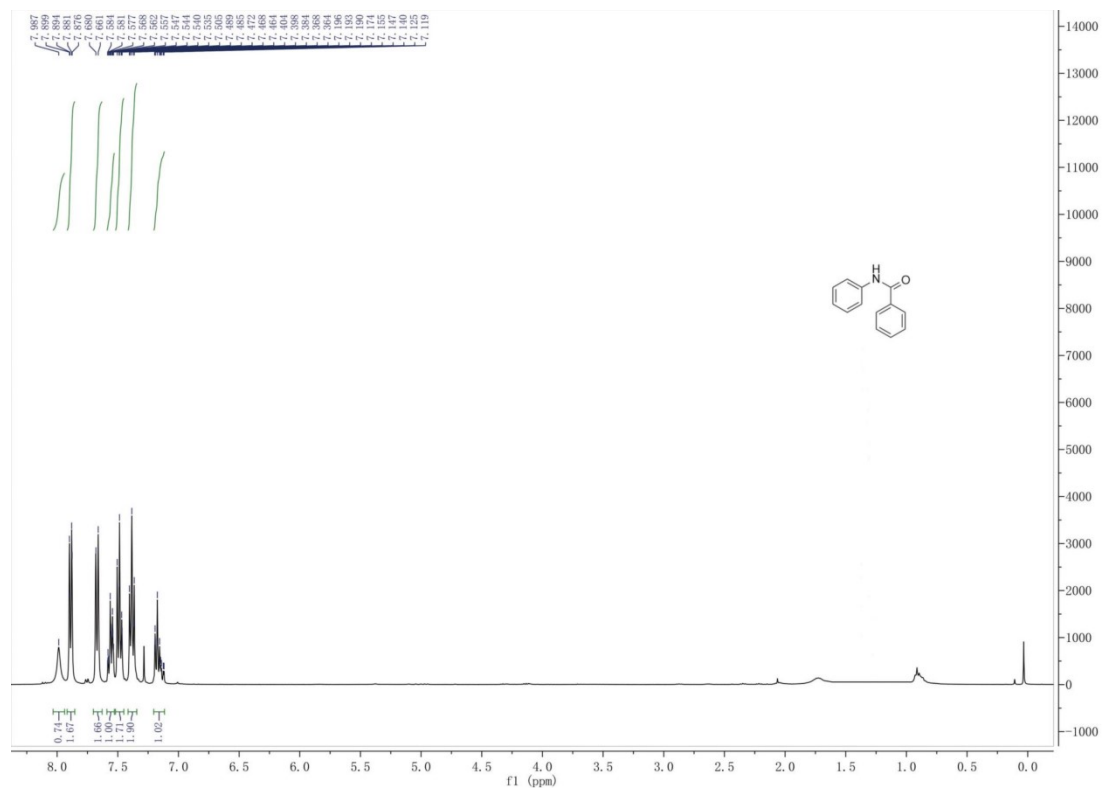


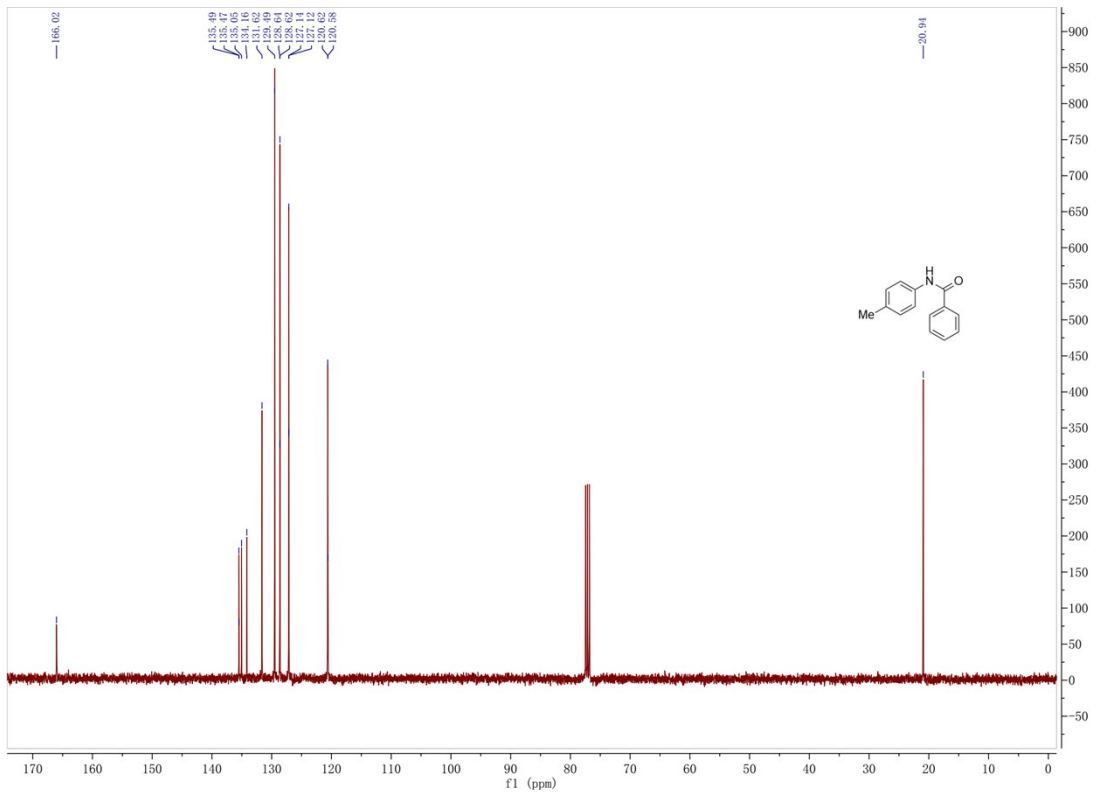
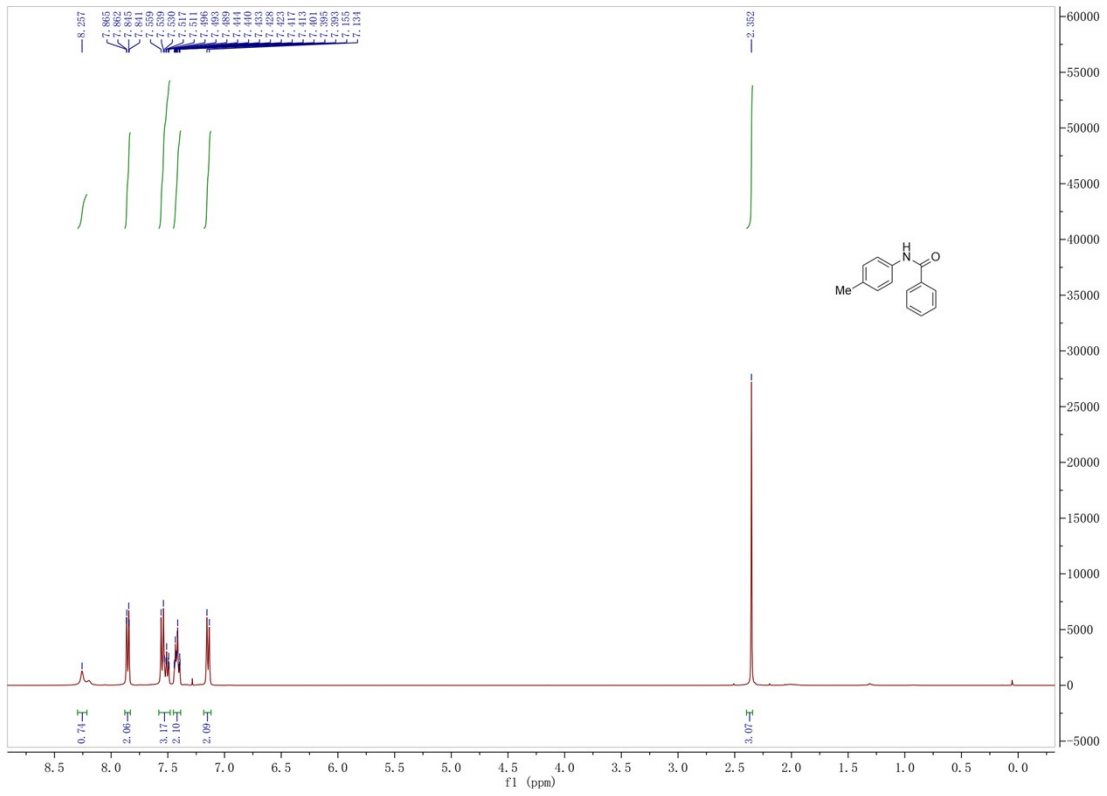
Figure 3s. View of the pack drawing of compound **2a**. Hydrogen-bonds are shown as dashed lines.

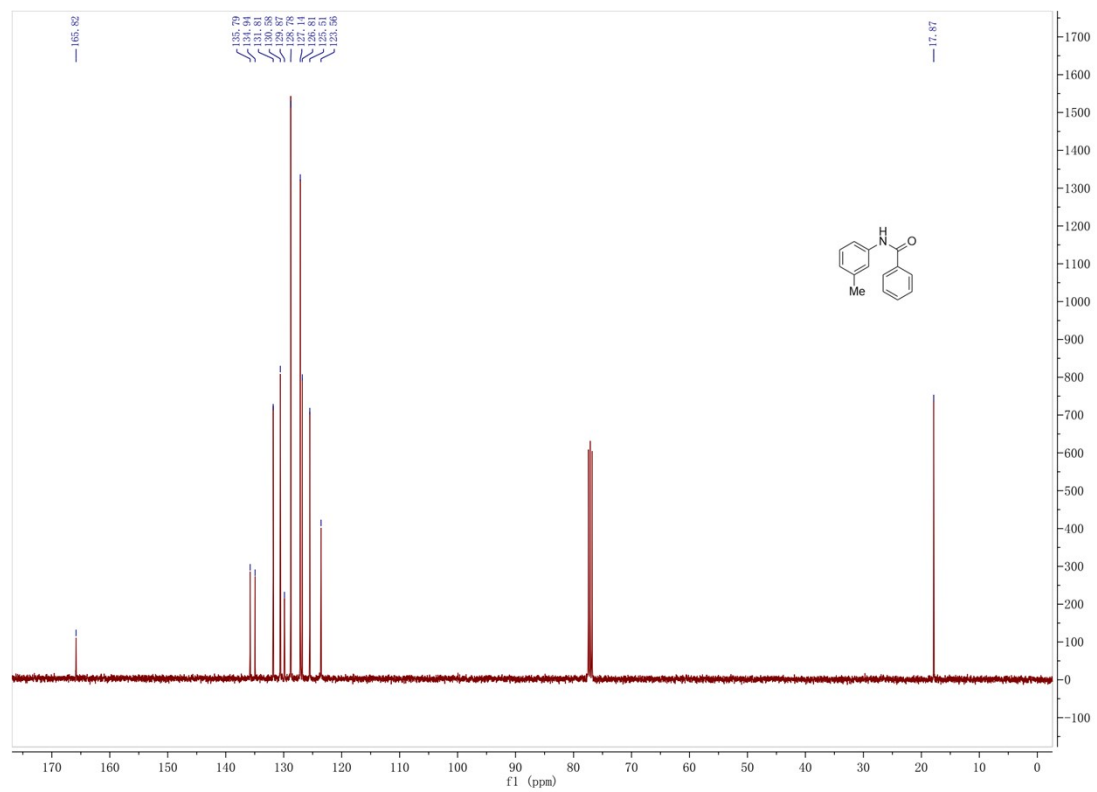
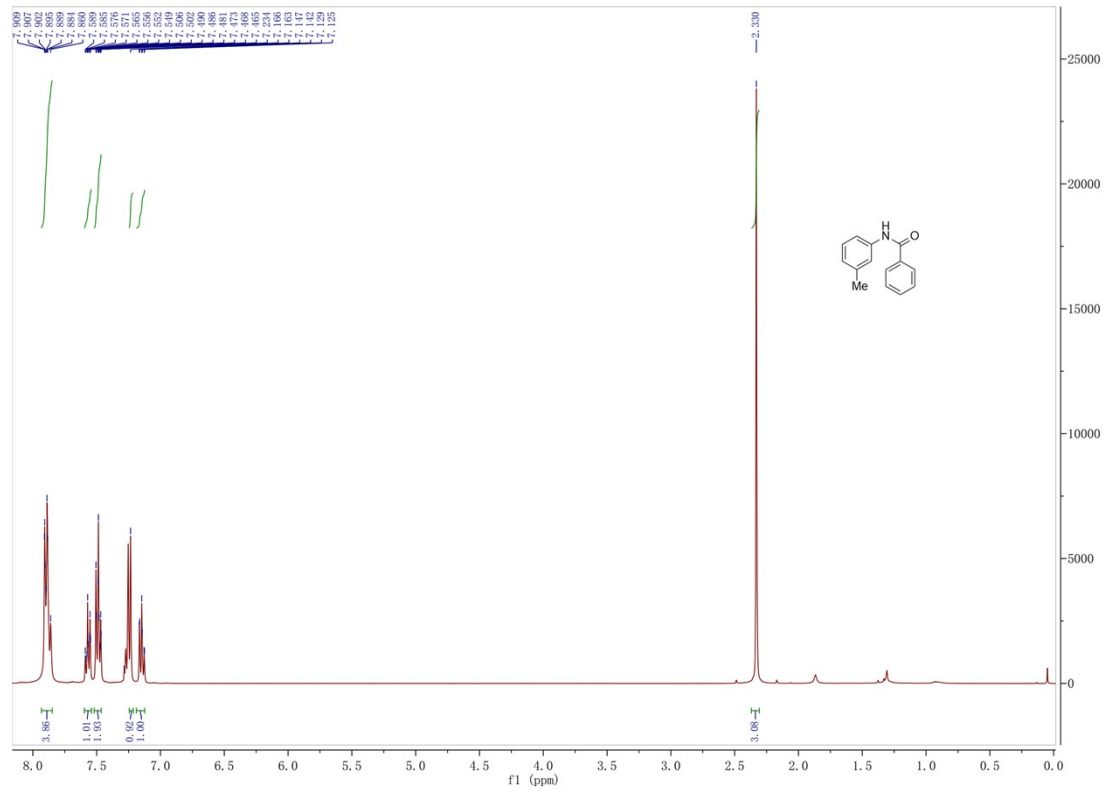
Table 1s. Crystal data and structure refinement for compound **2a**

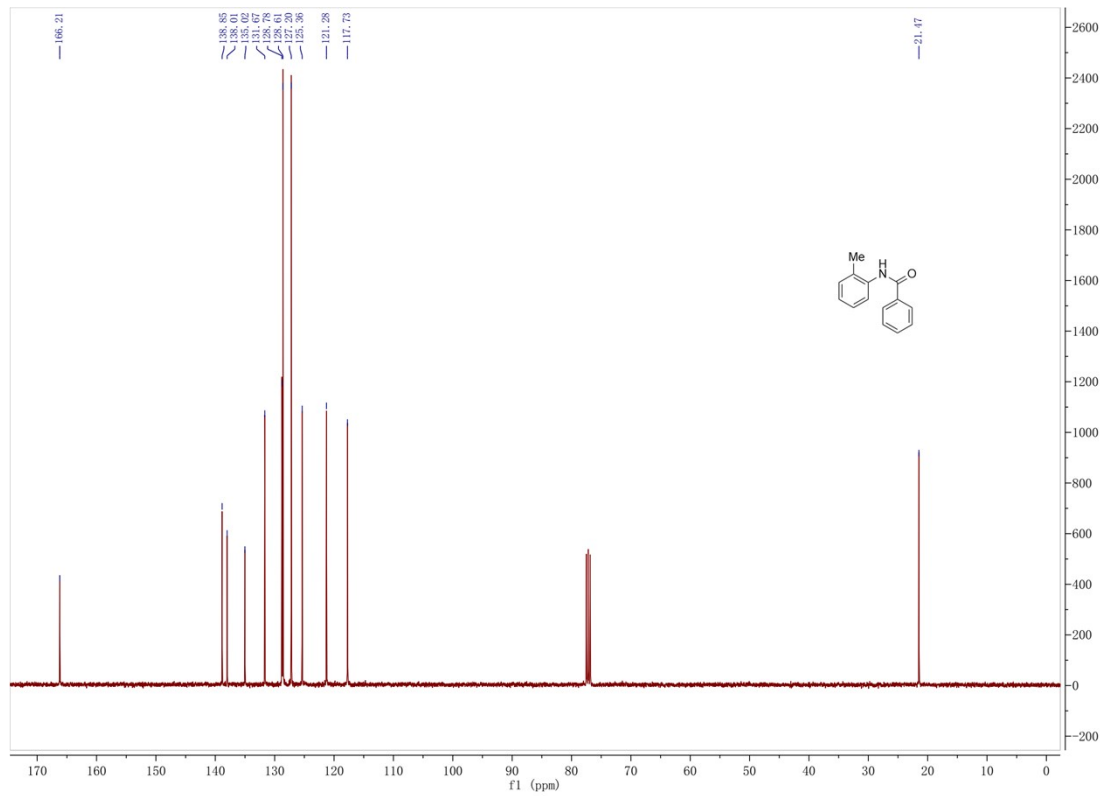
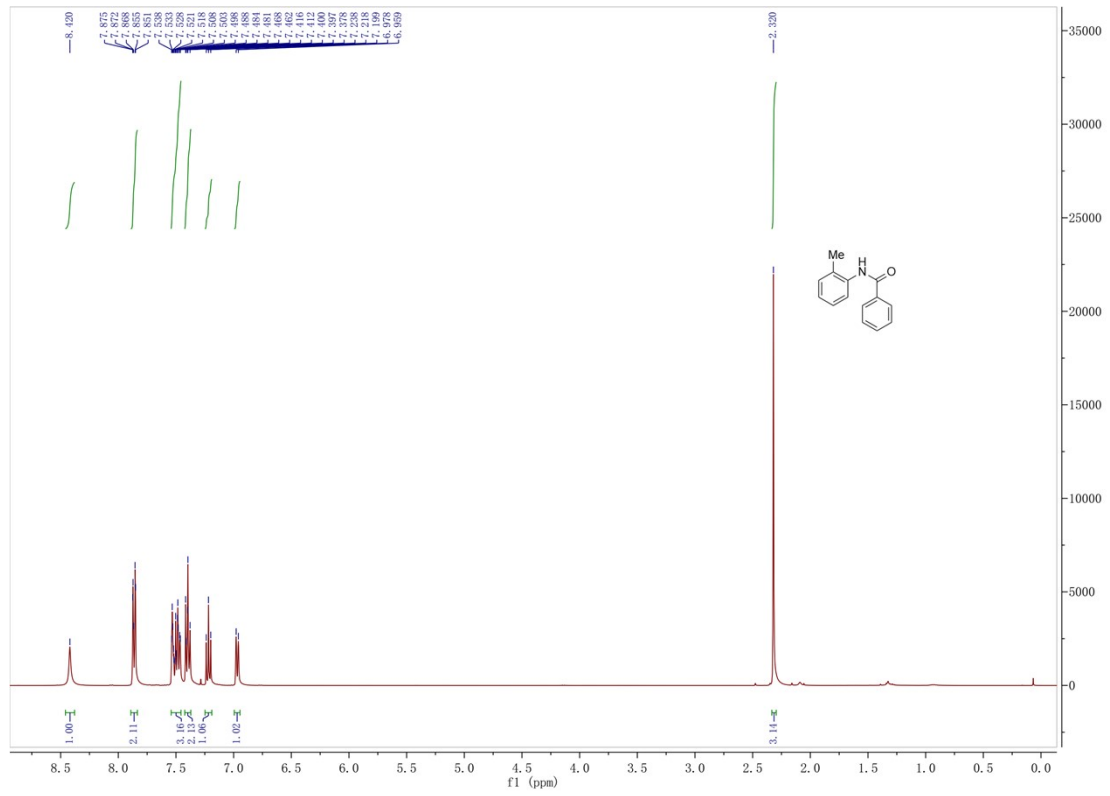
Identification code	global
Empirical formula	C ₁₃ H ₁₁ N O
Formula weight	197.23
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 5.3315(6) Å α = 72.694(6)°.
	b = 7.7796(8) Å β = 78.711(5)°.
	c = 12.4238(14) Å γ = 89.961(5)°.
Volume	481.54(9) Å ³
Z	2
Density (calculated)	1.360 Mg/m ³
Absorption coefficient	0.687 mm ⁻¹
F(000)	208
Crystal size	0.700 x 0.400 x 0.150 mm ³
Theta range for data collection	3.81 to 74.94°.
Index ranges	-6 ≤ h ≤ 6, -7 ≤ k ≤ 9, -15 ≤ l ≤ 15
Reflections collected	5689
Independent reflections	1857 [R(int) = 0.0652]
Completeness to theta = 74.94°	93.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.90 and 0.52
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1857 / 716 / 272
Goodness-of-fit on F ²	1.833
Final R indices [I > 2σ(I)]	R1 = 0.1139, wR2 = 0.3700
R indices (all data)	R1 = 0.1245, wR2 = 0.3950
Largest diff. peak and hole	0.436 and -0.381 e.Å ⁻³

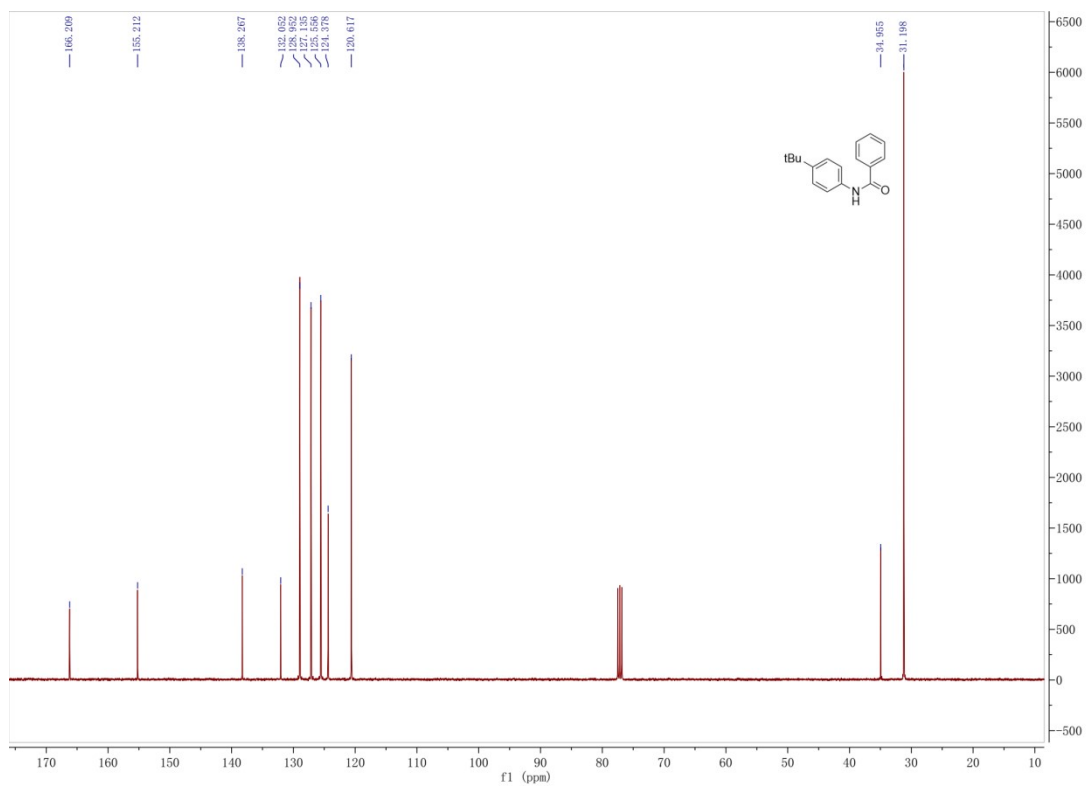
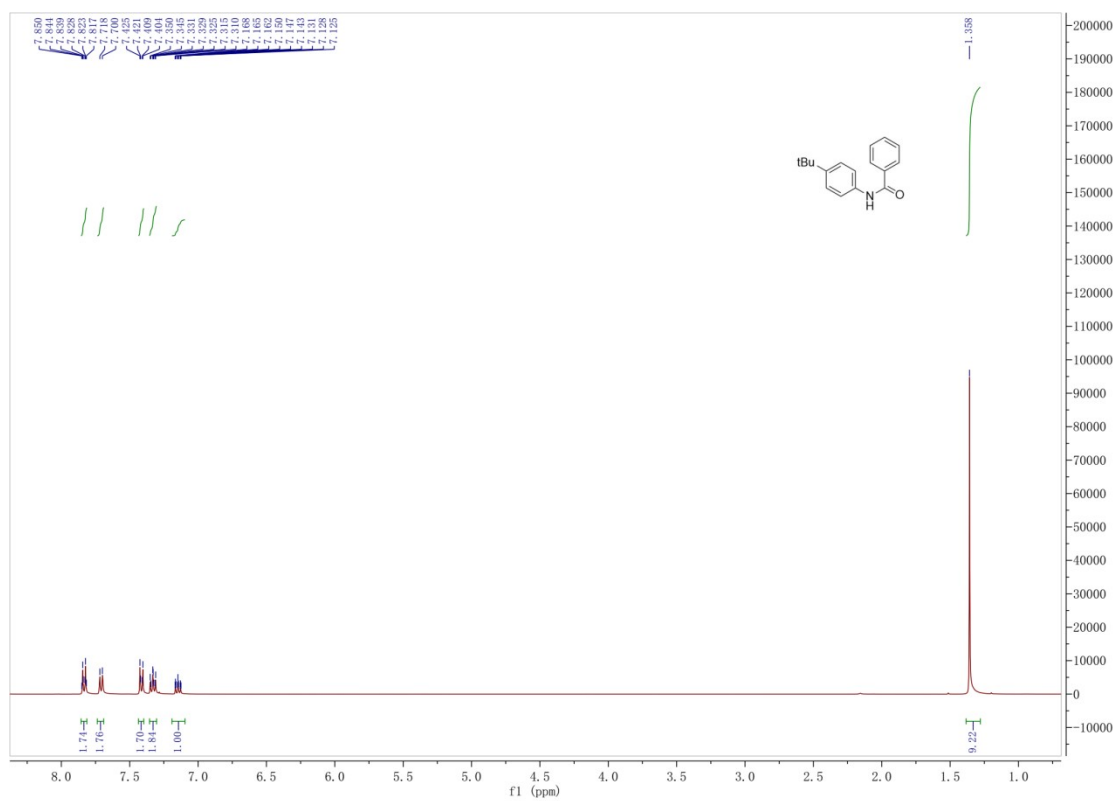
6. NMR Spectra data of compounds 2

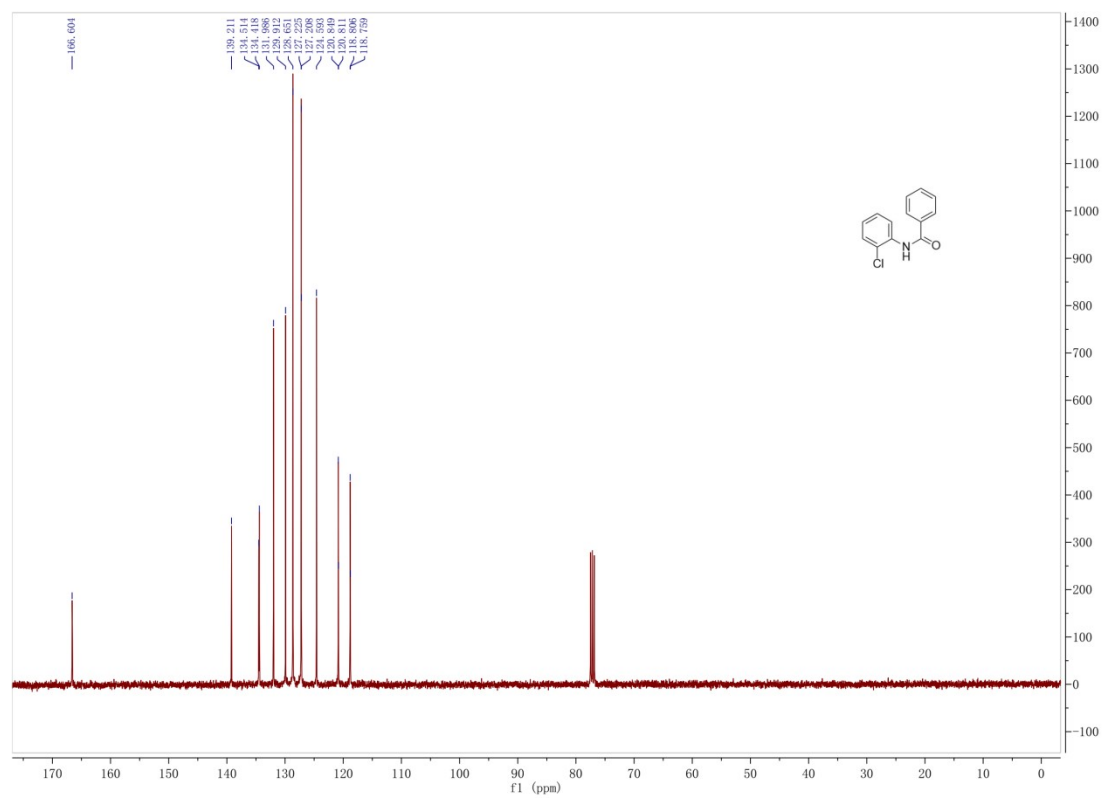
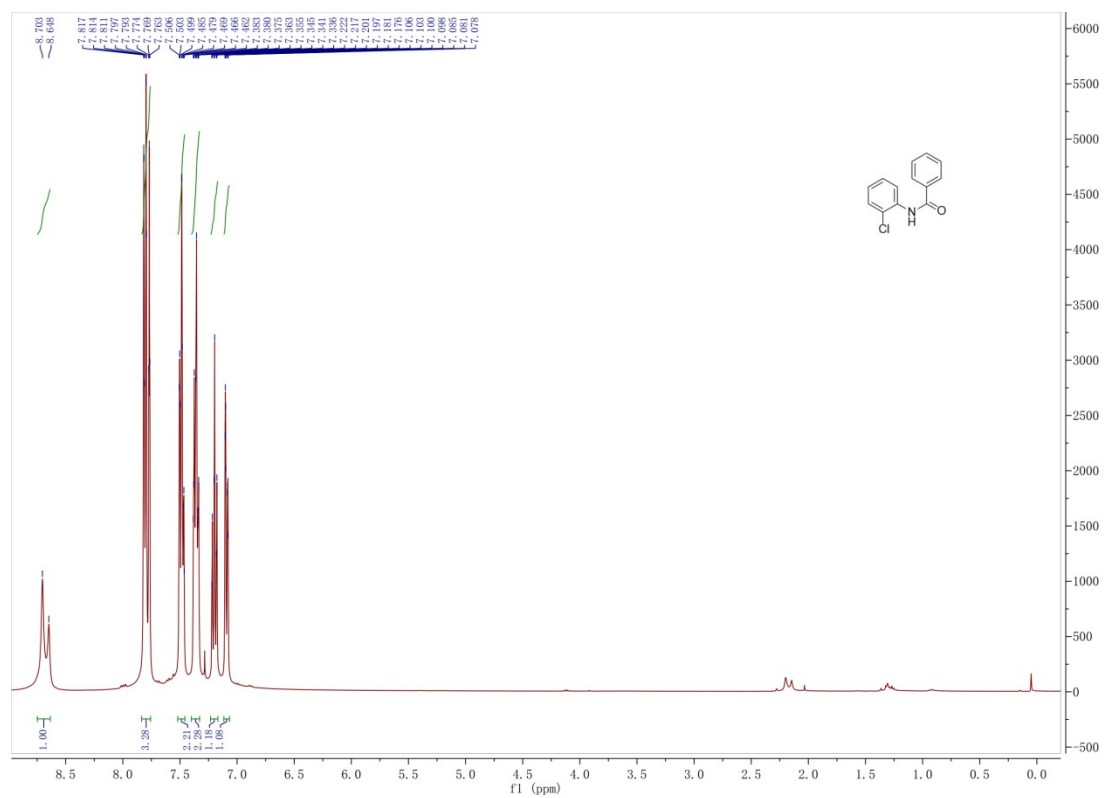


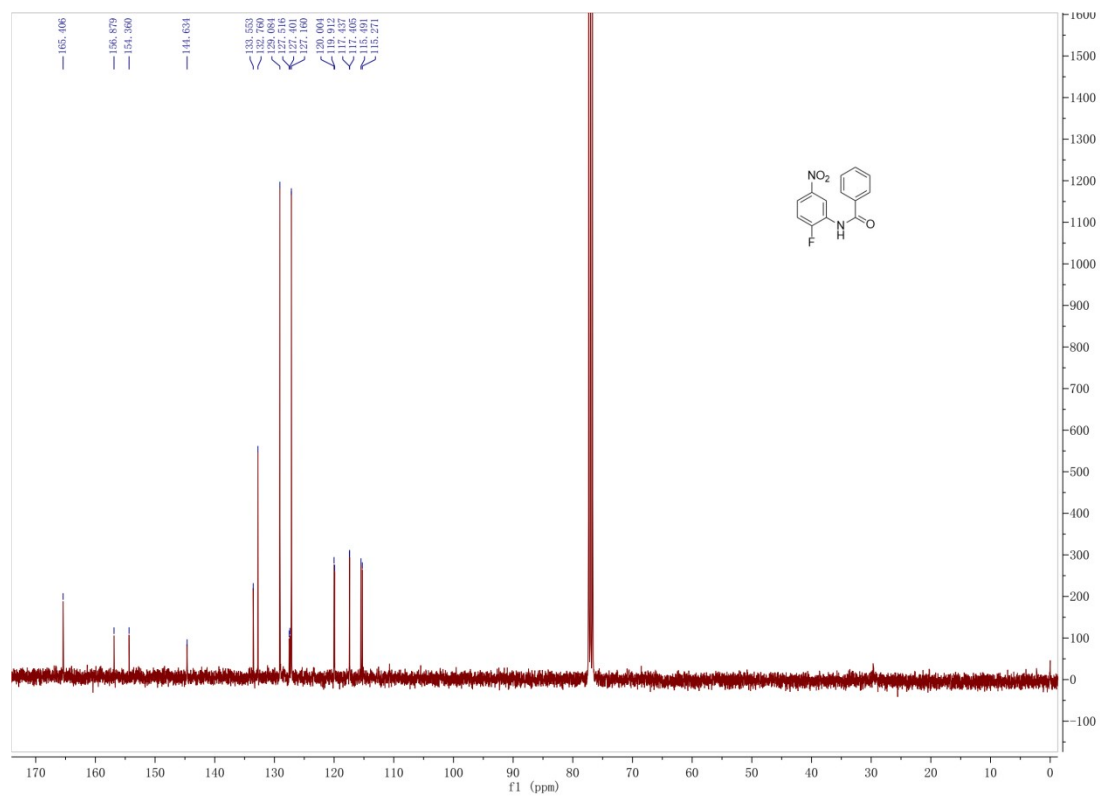
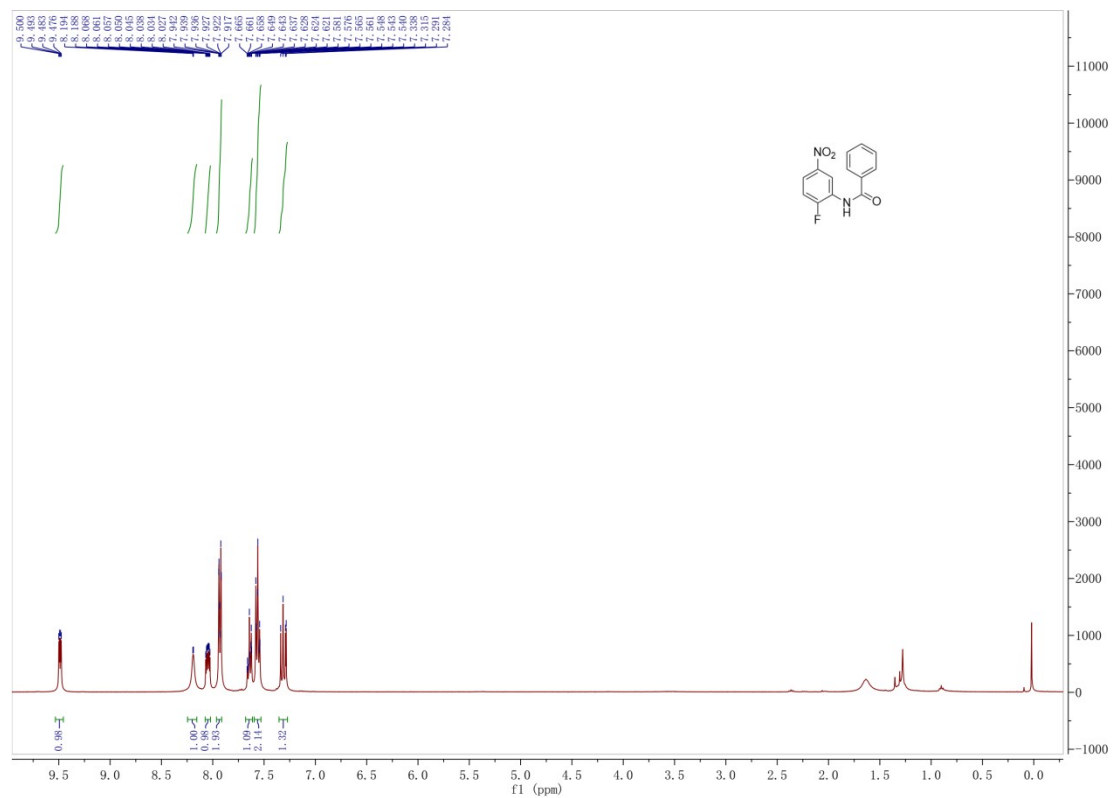


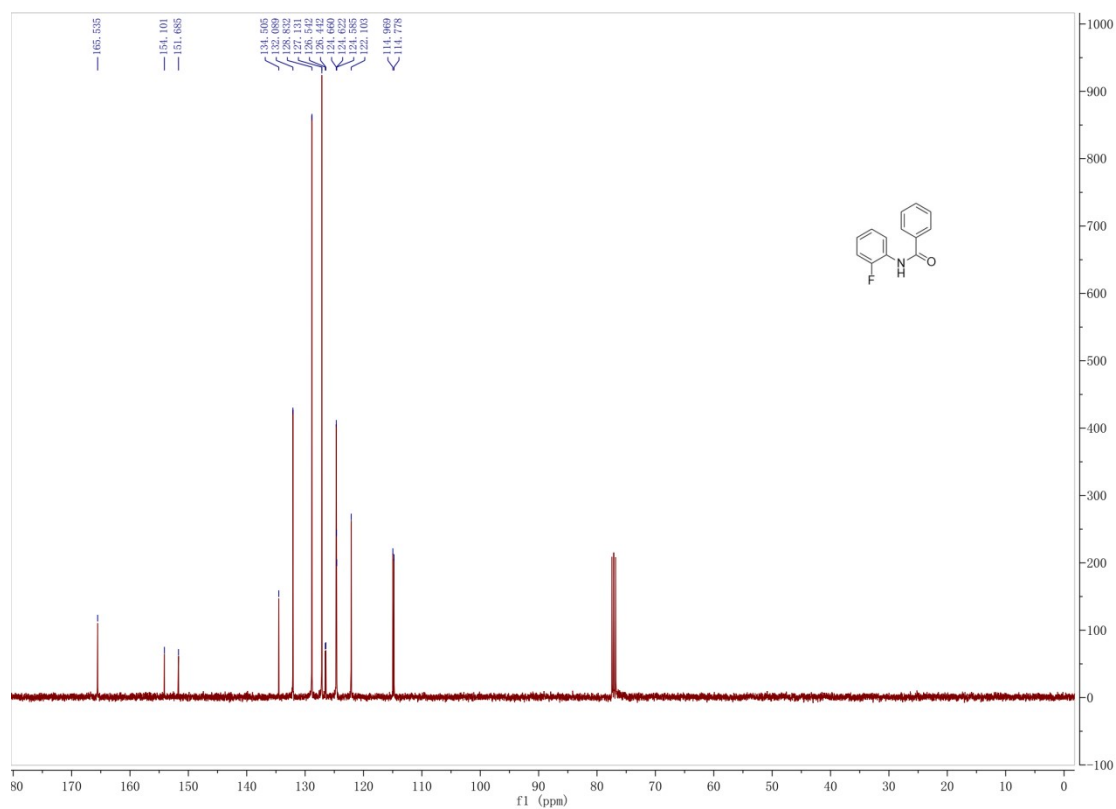
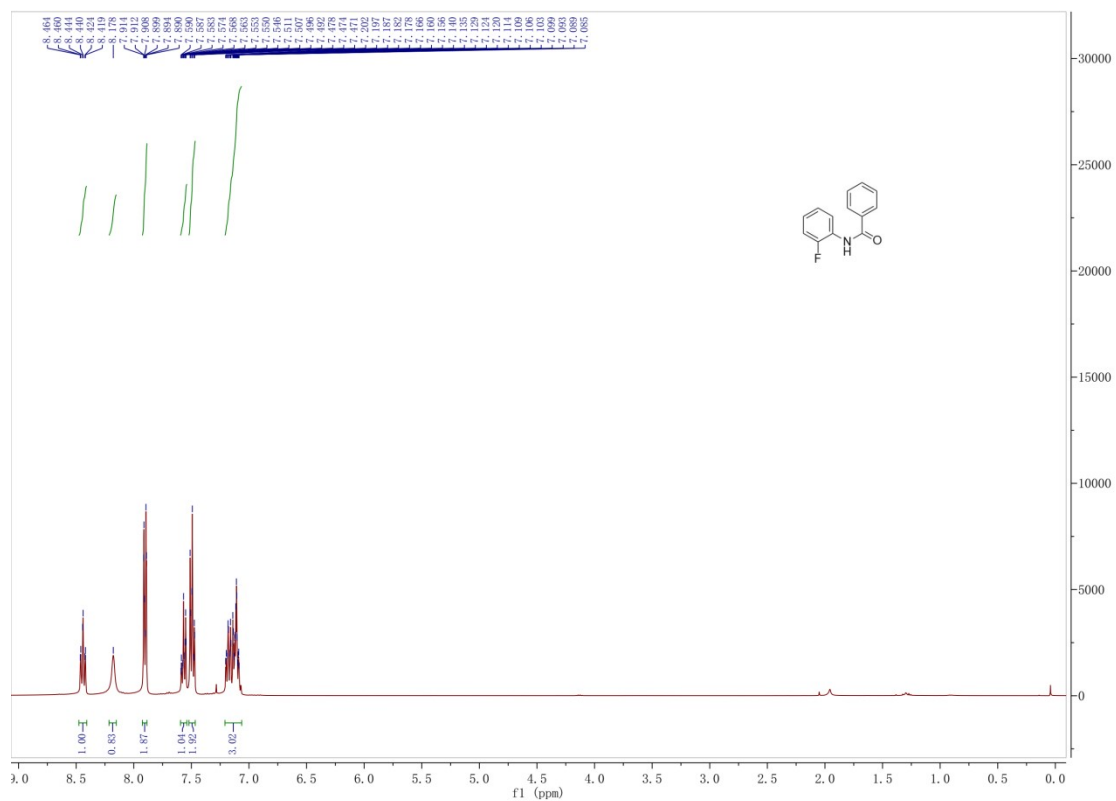


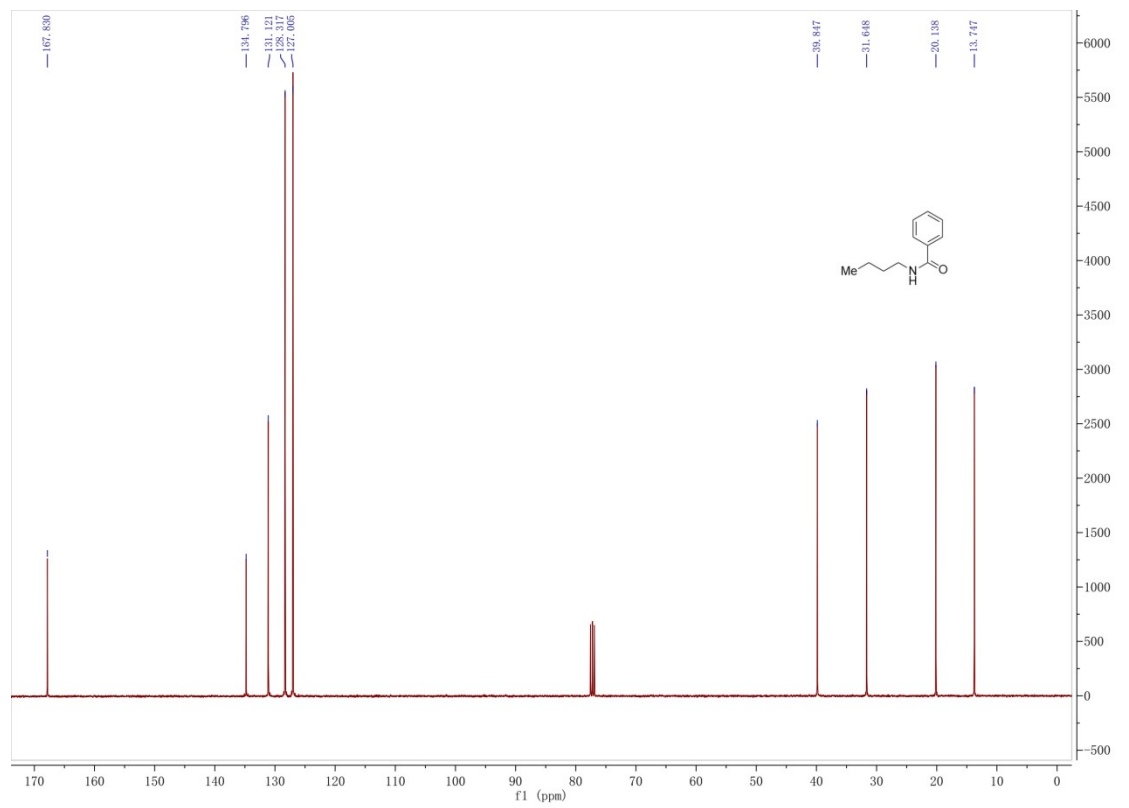
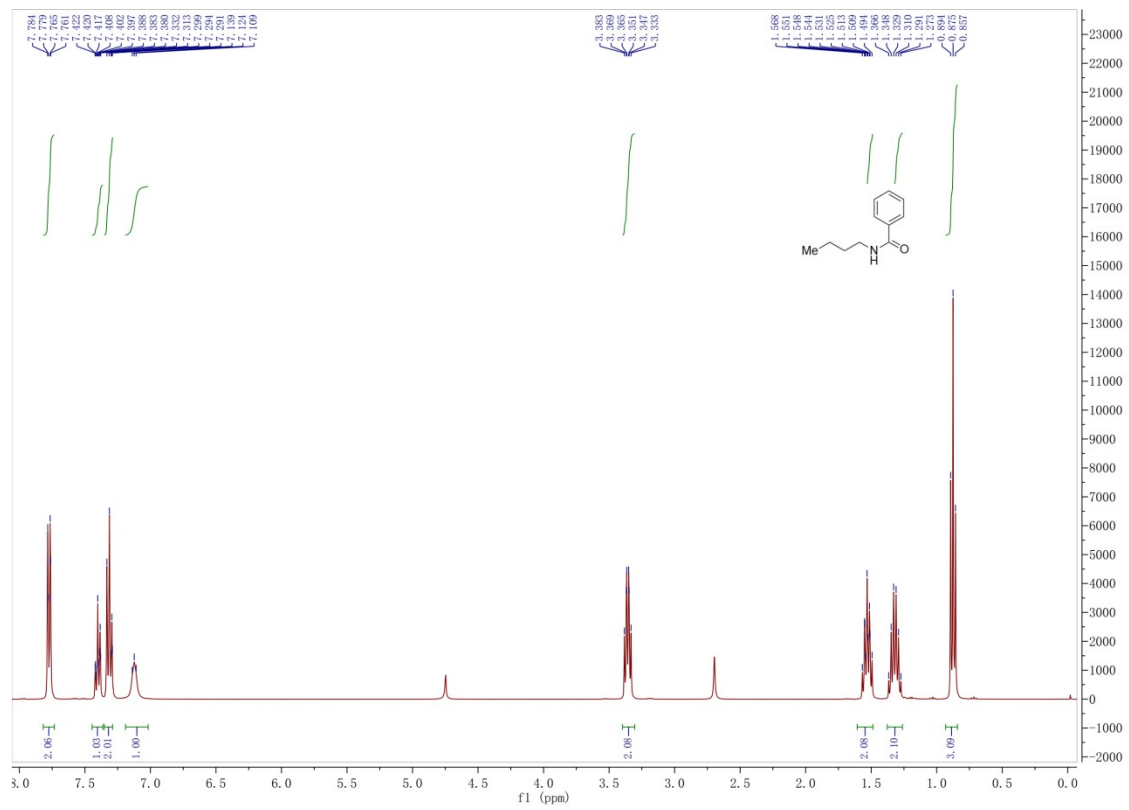


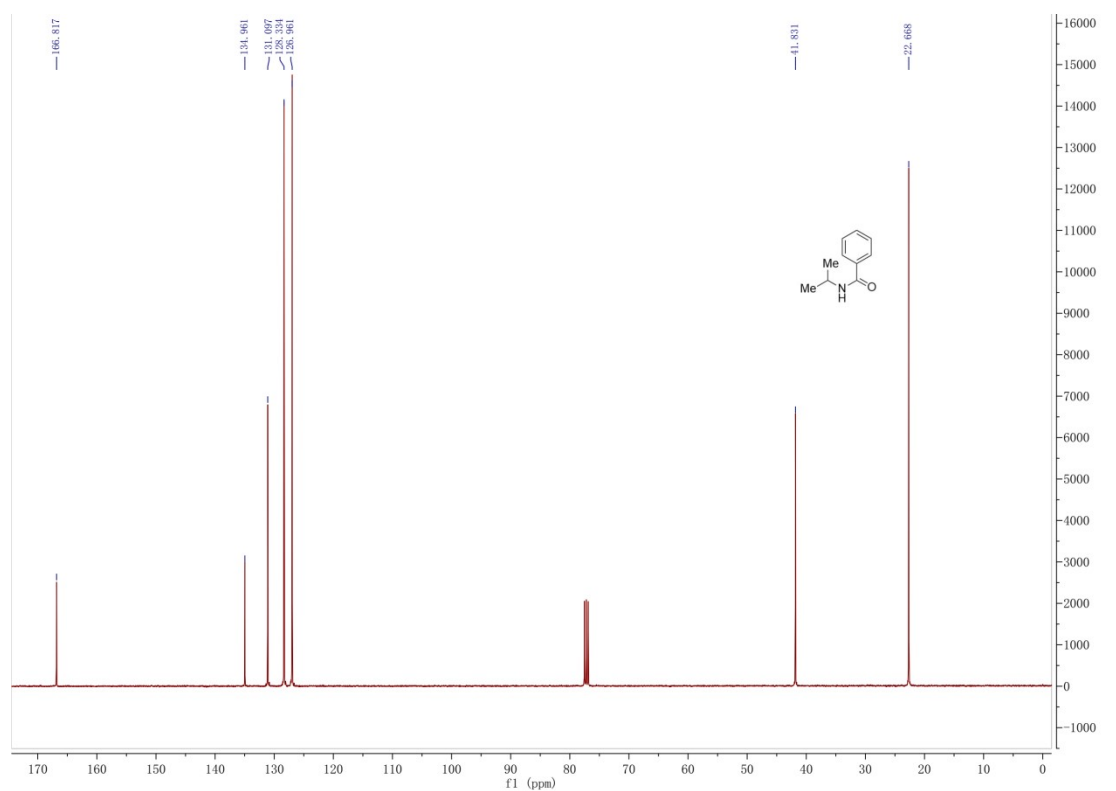
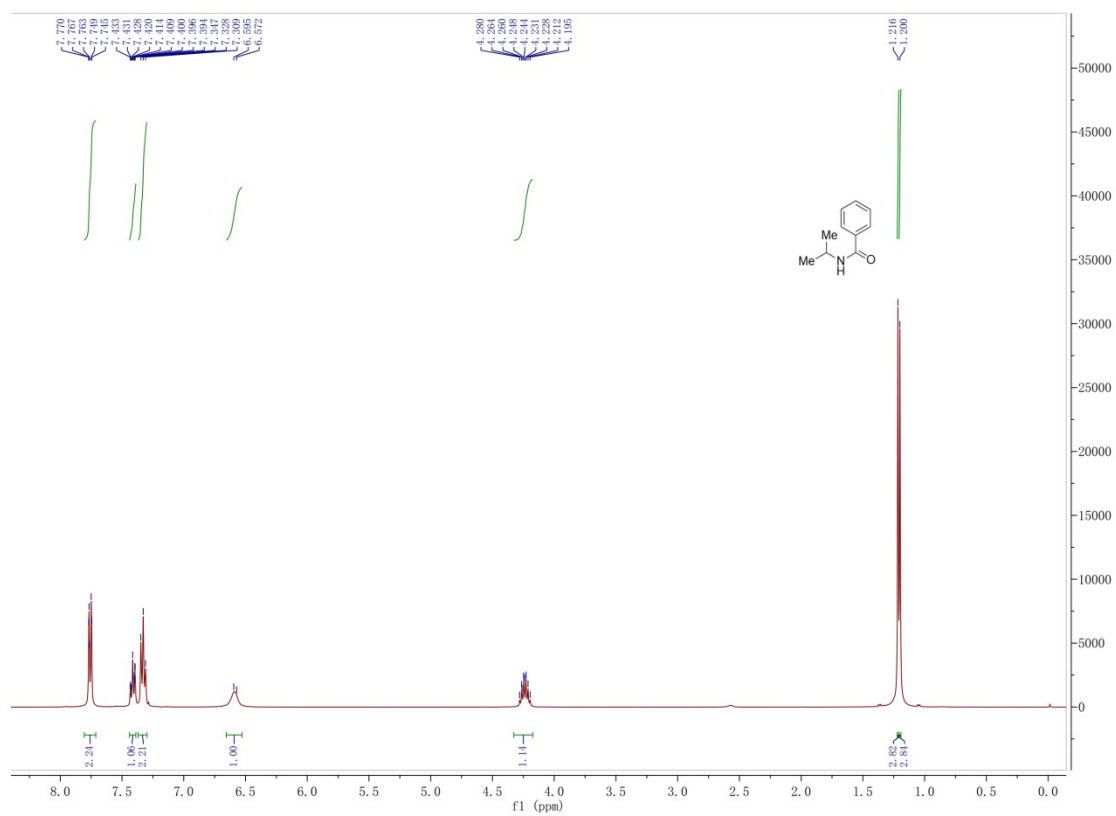


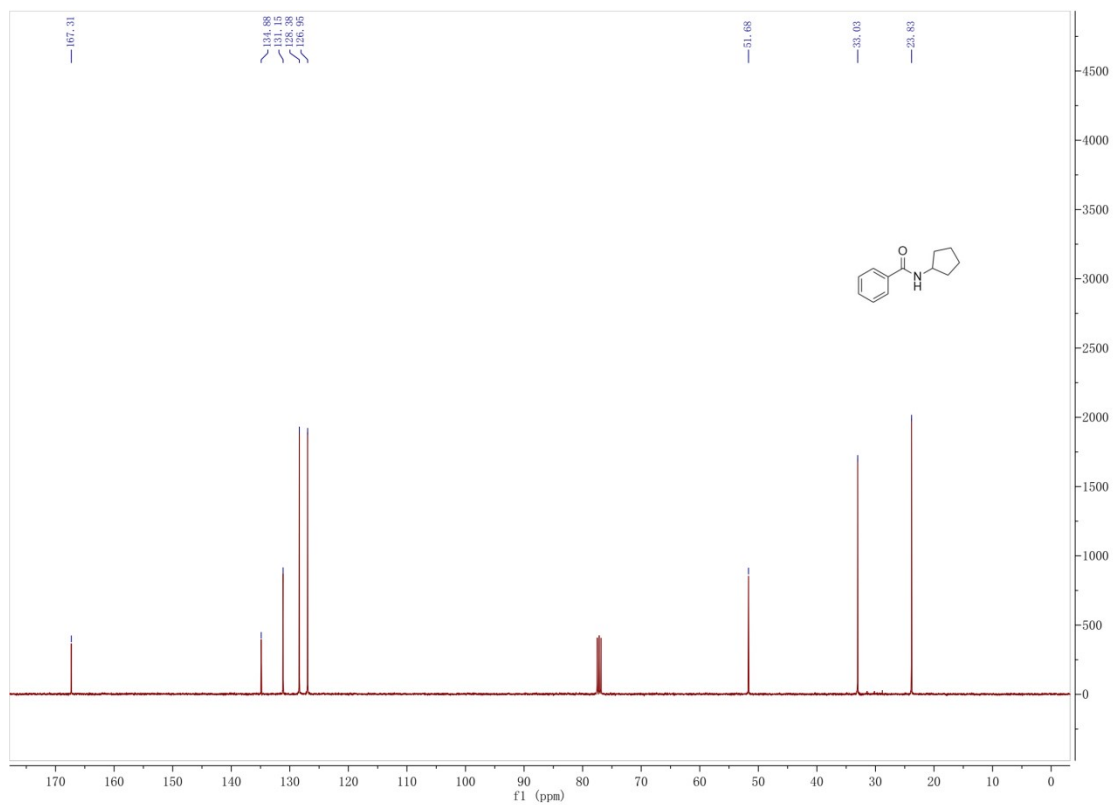
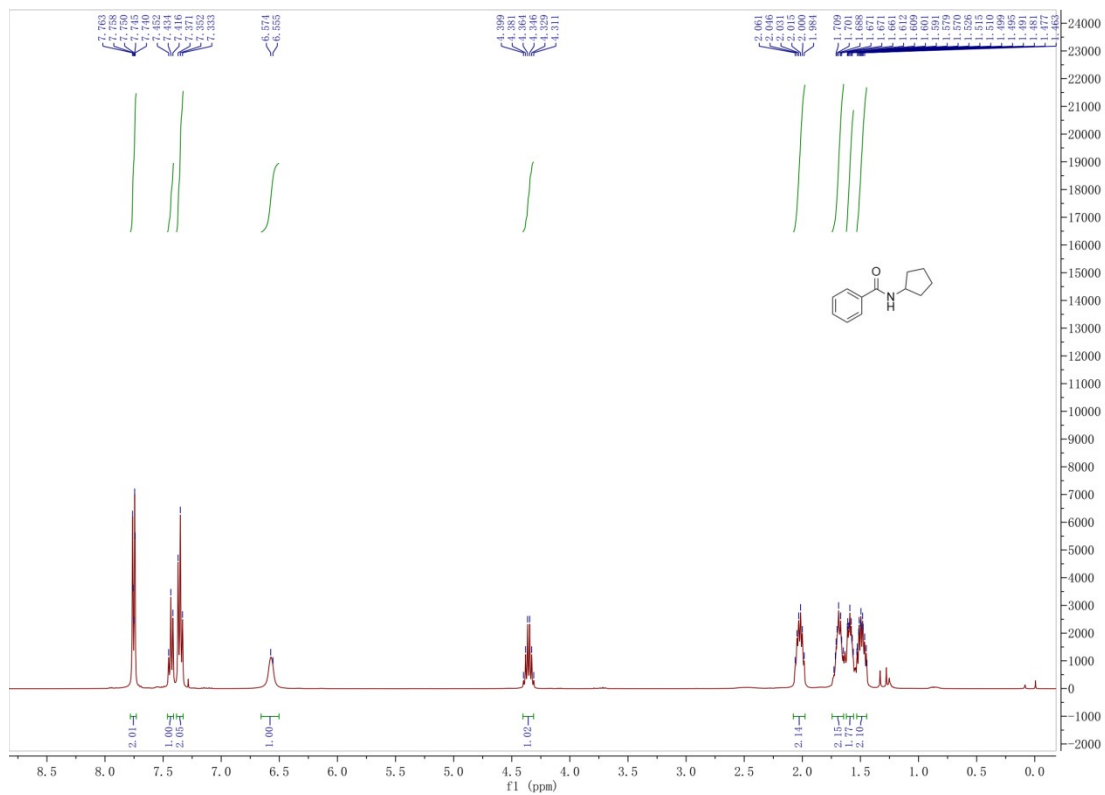


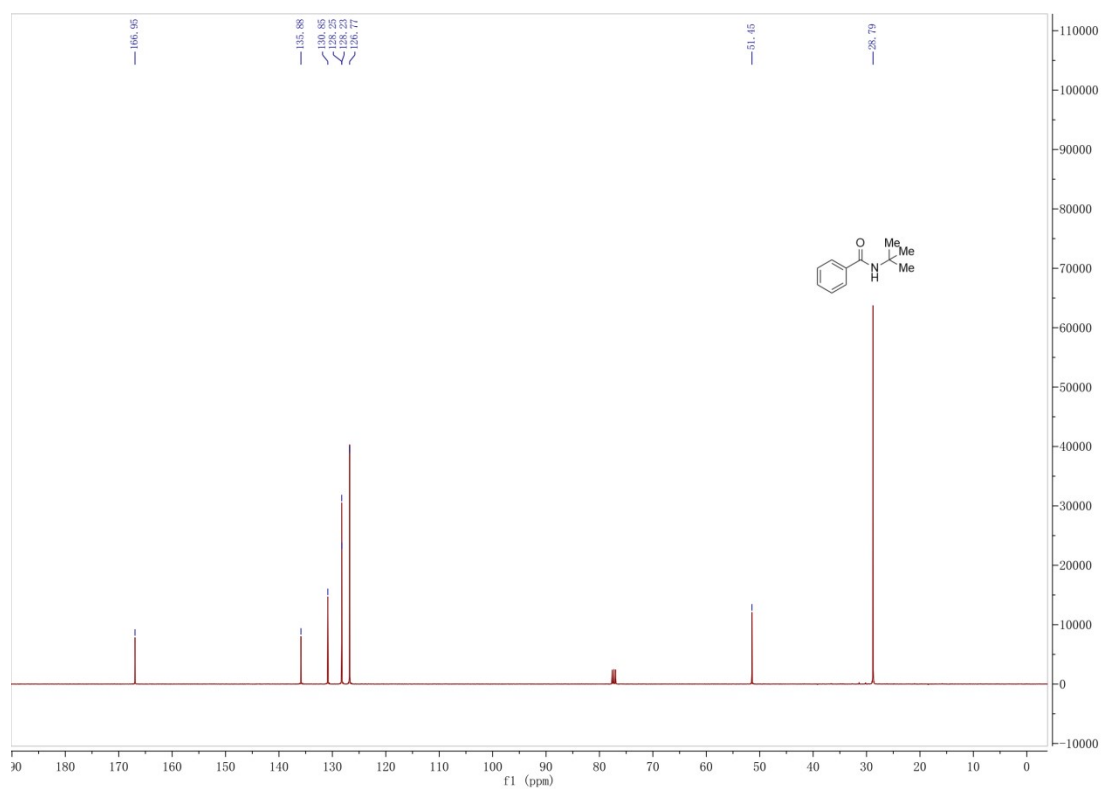
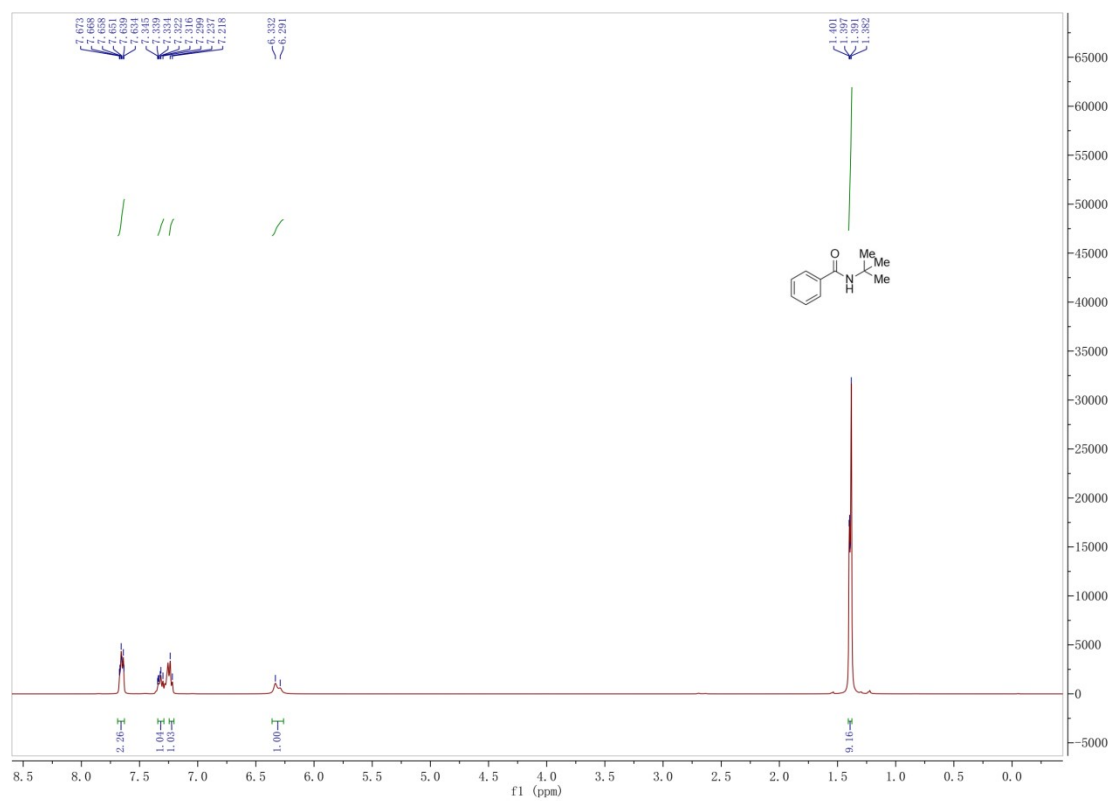


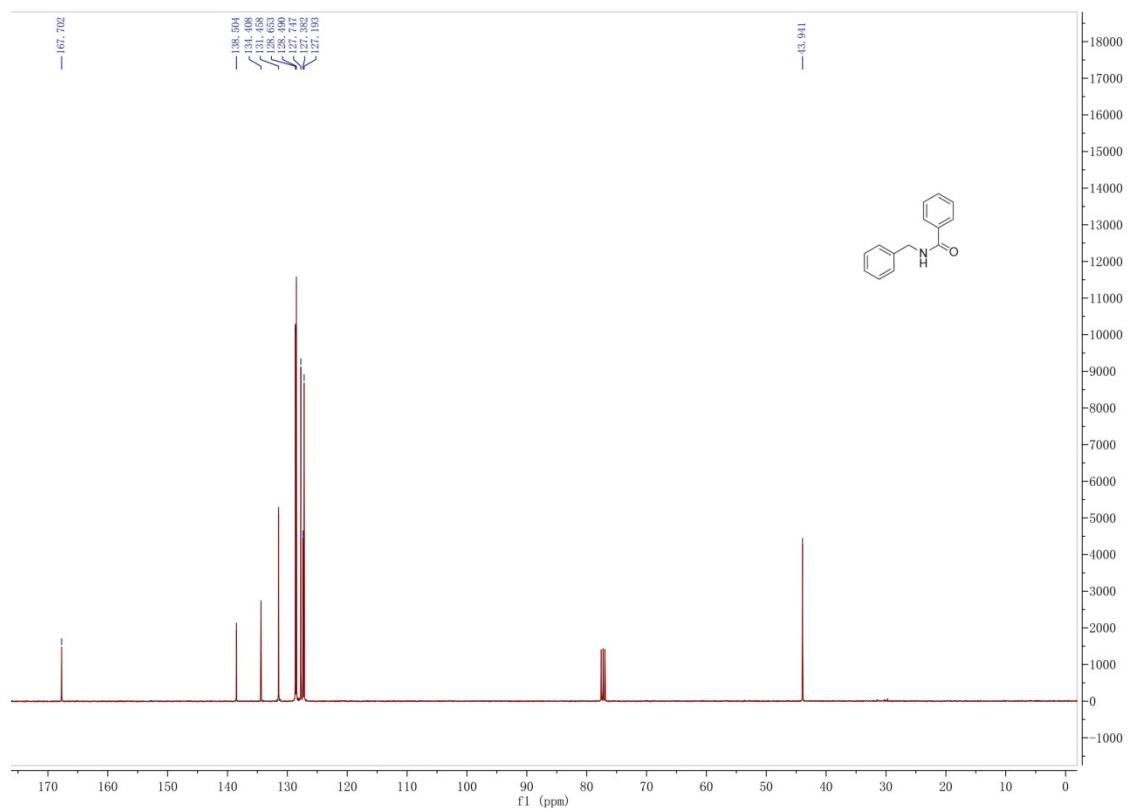
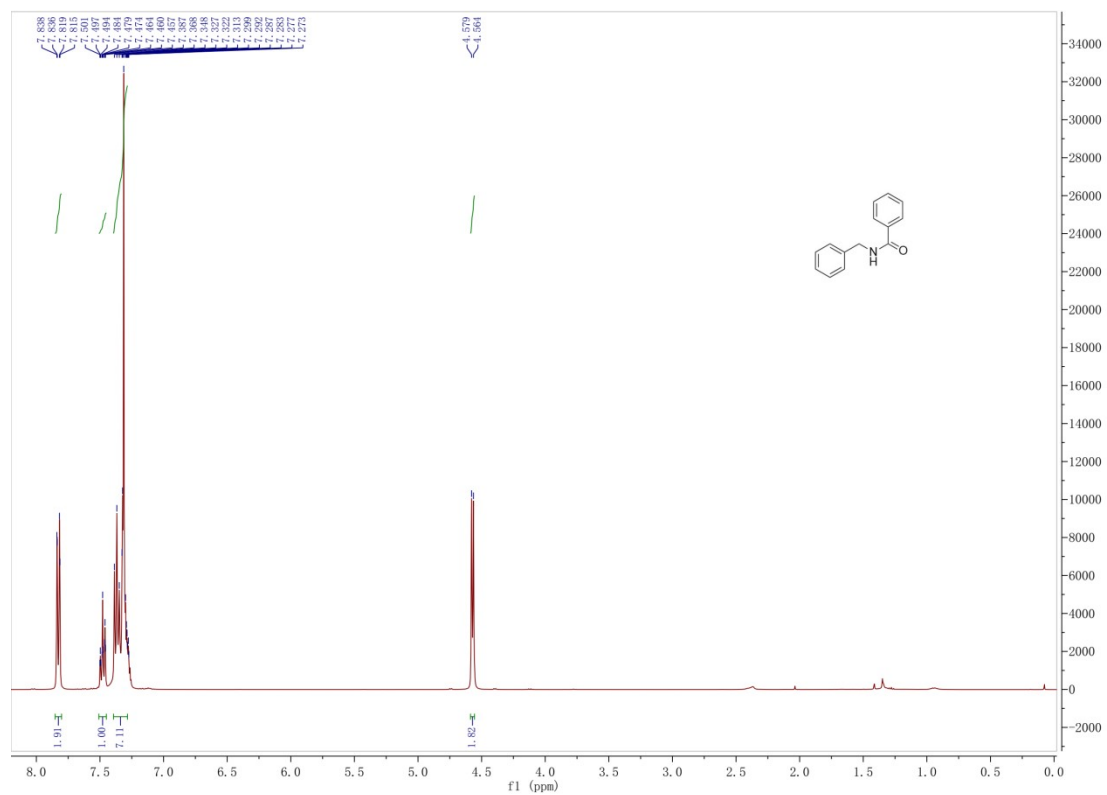


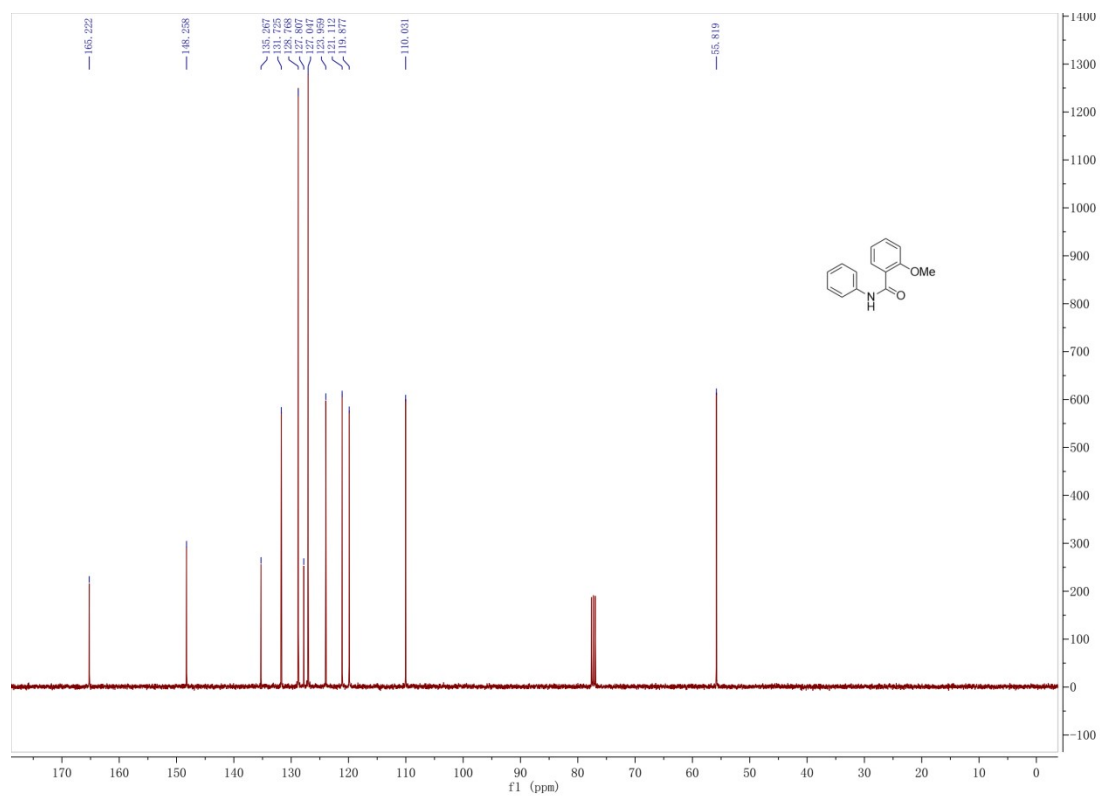
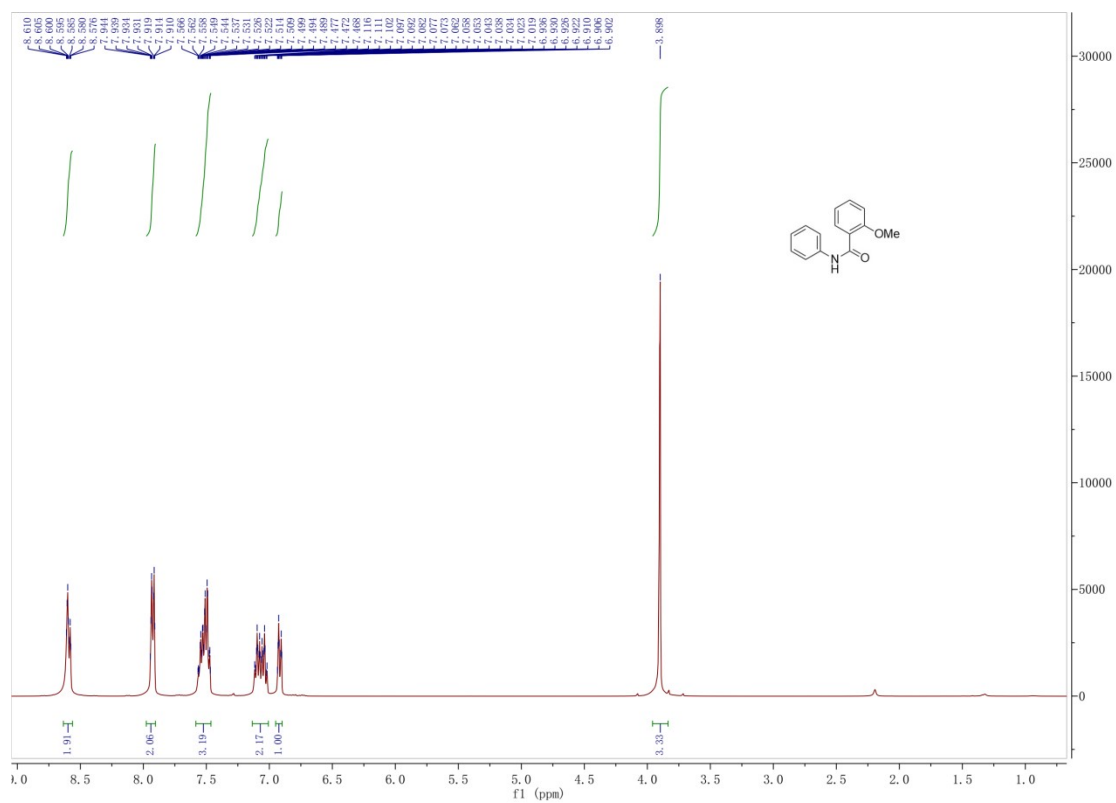


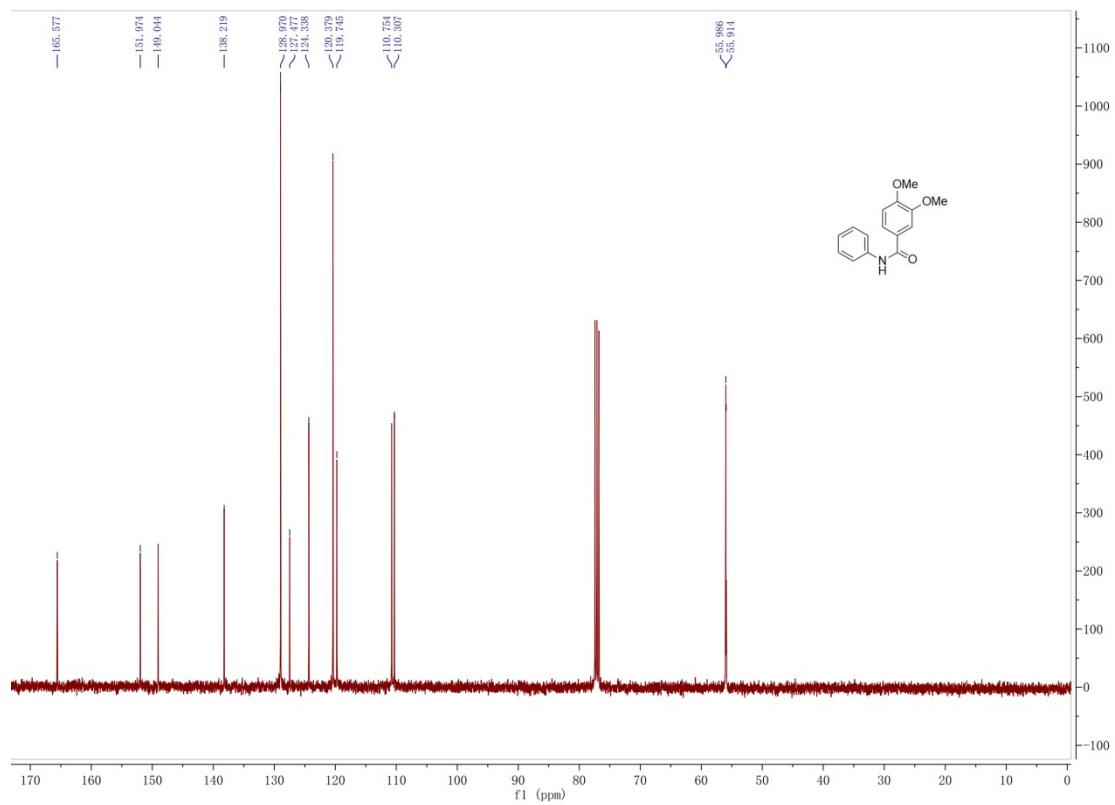
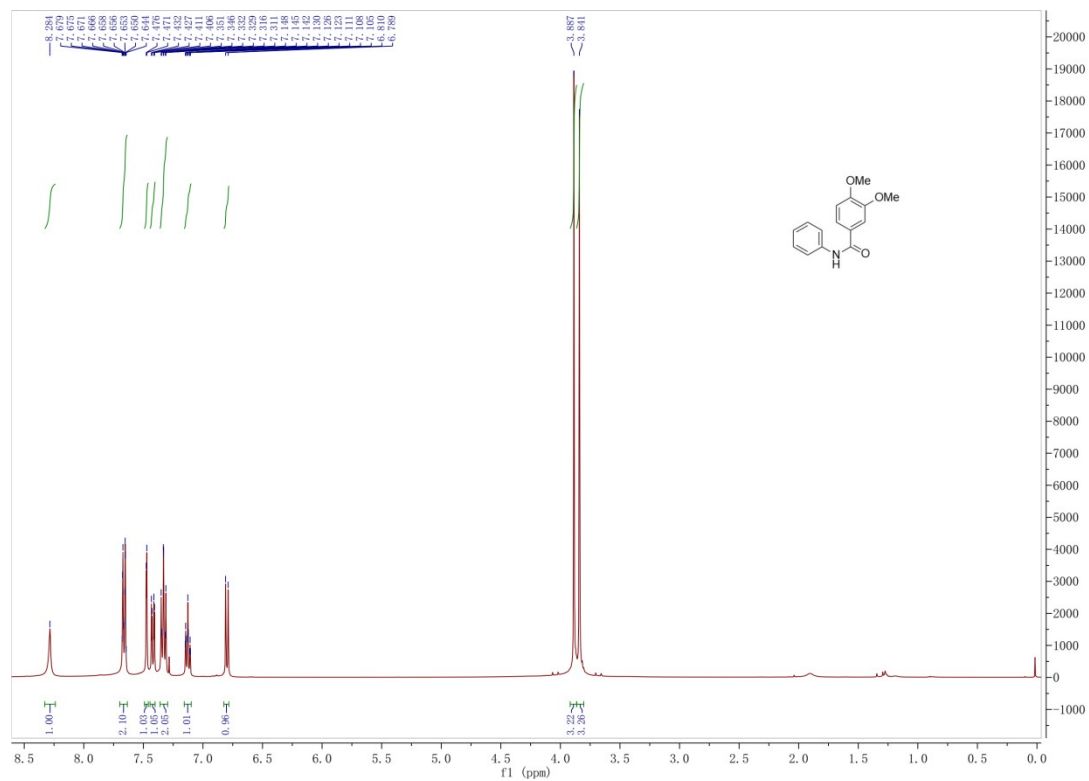


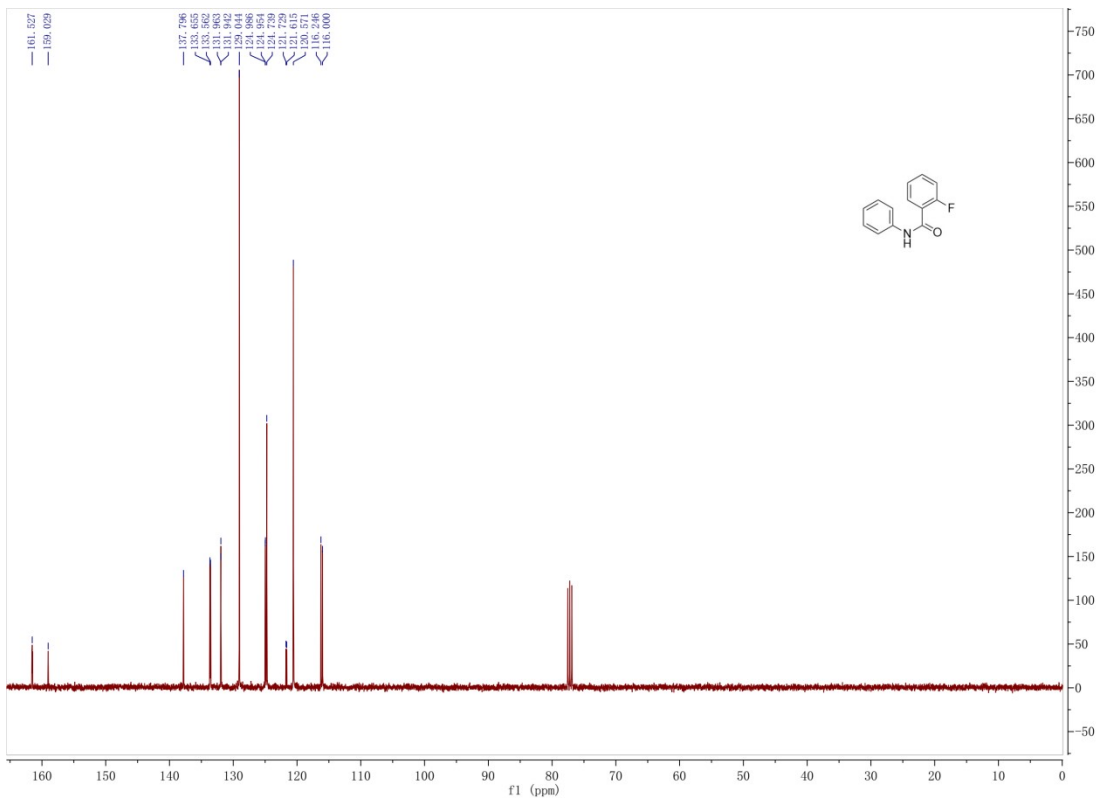
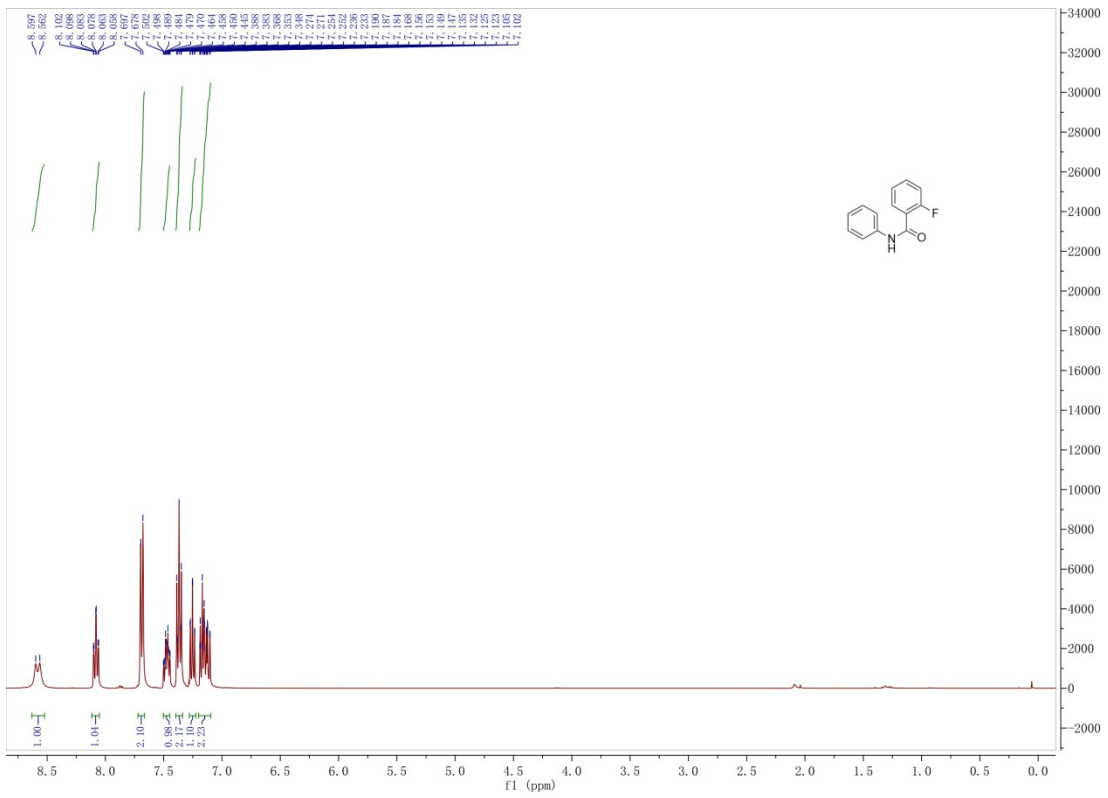


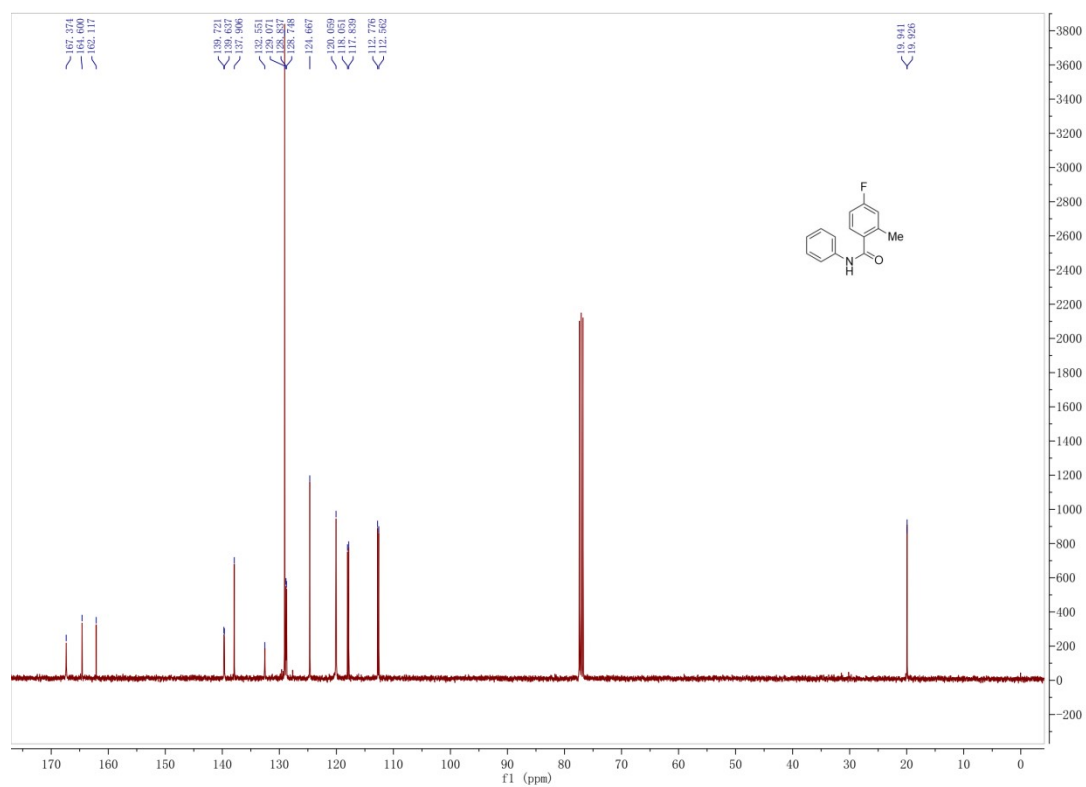
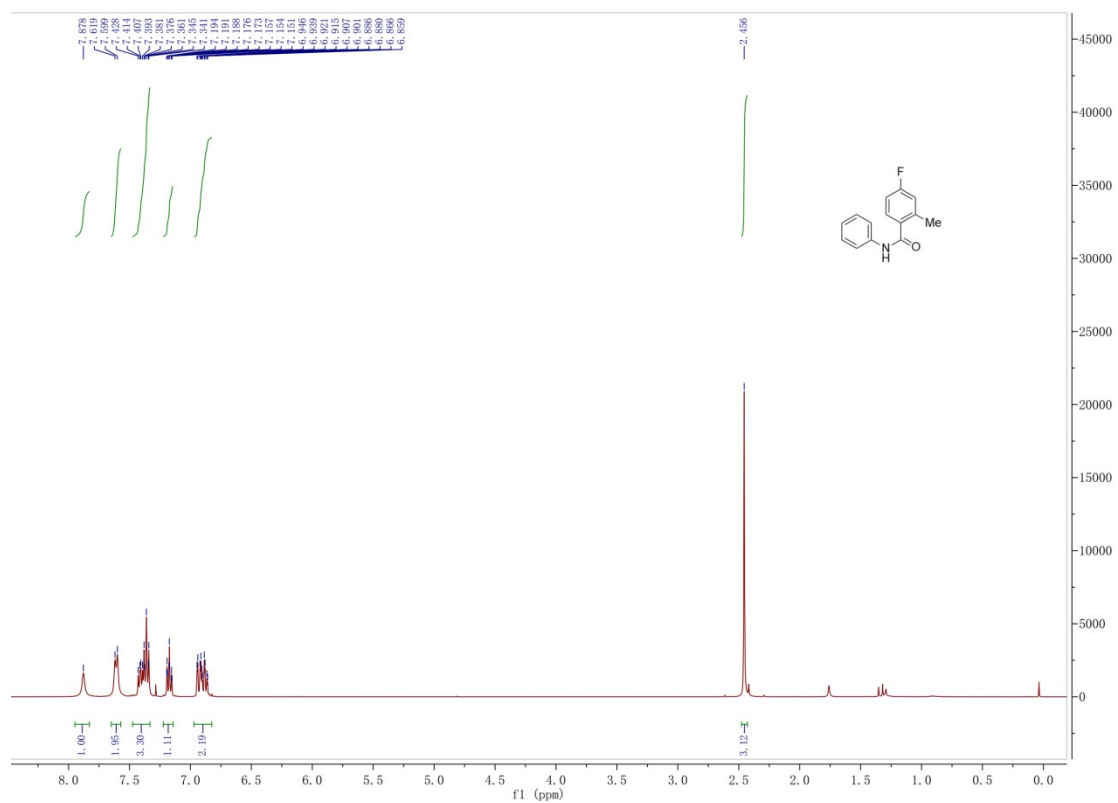


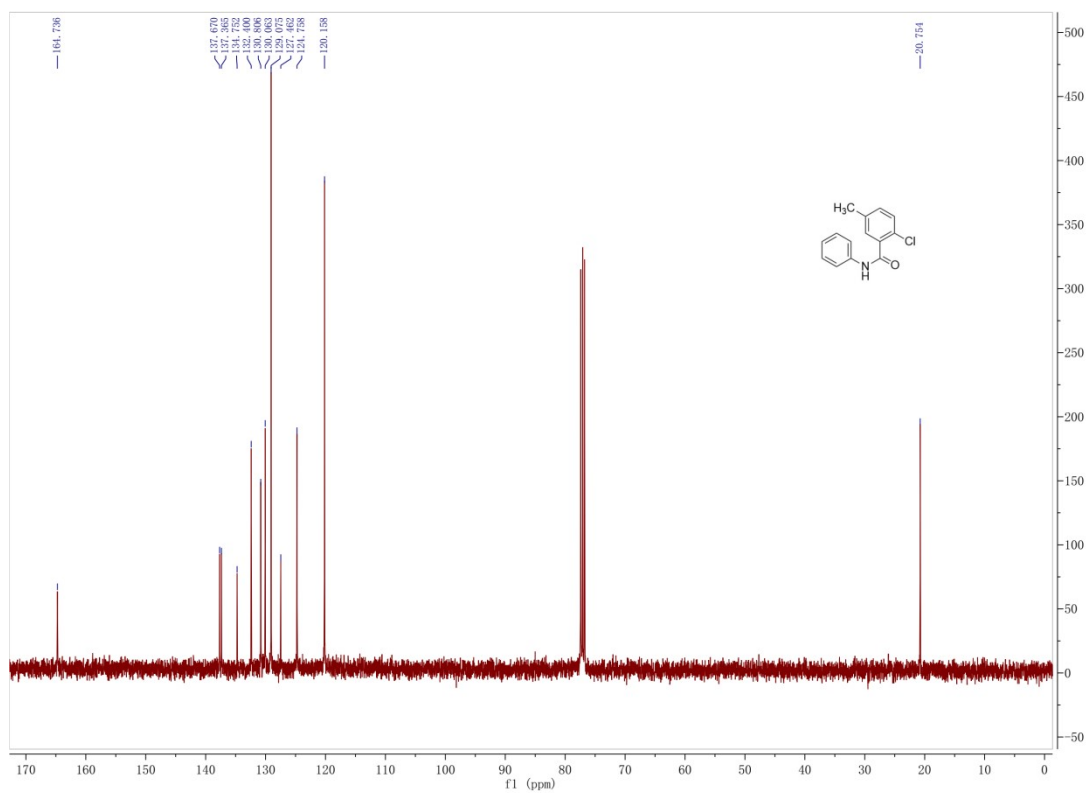
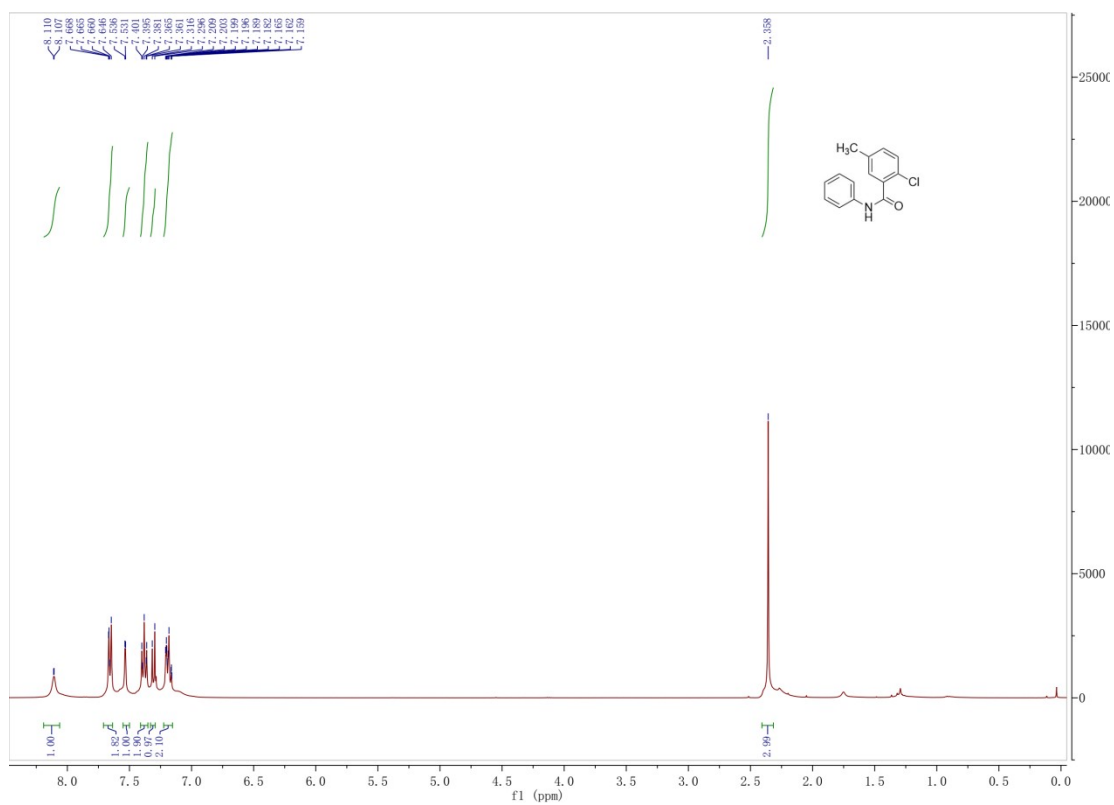


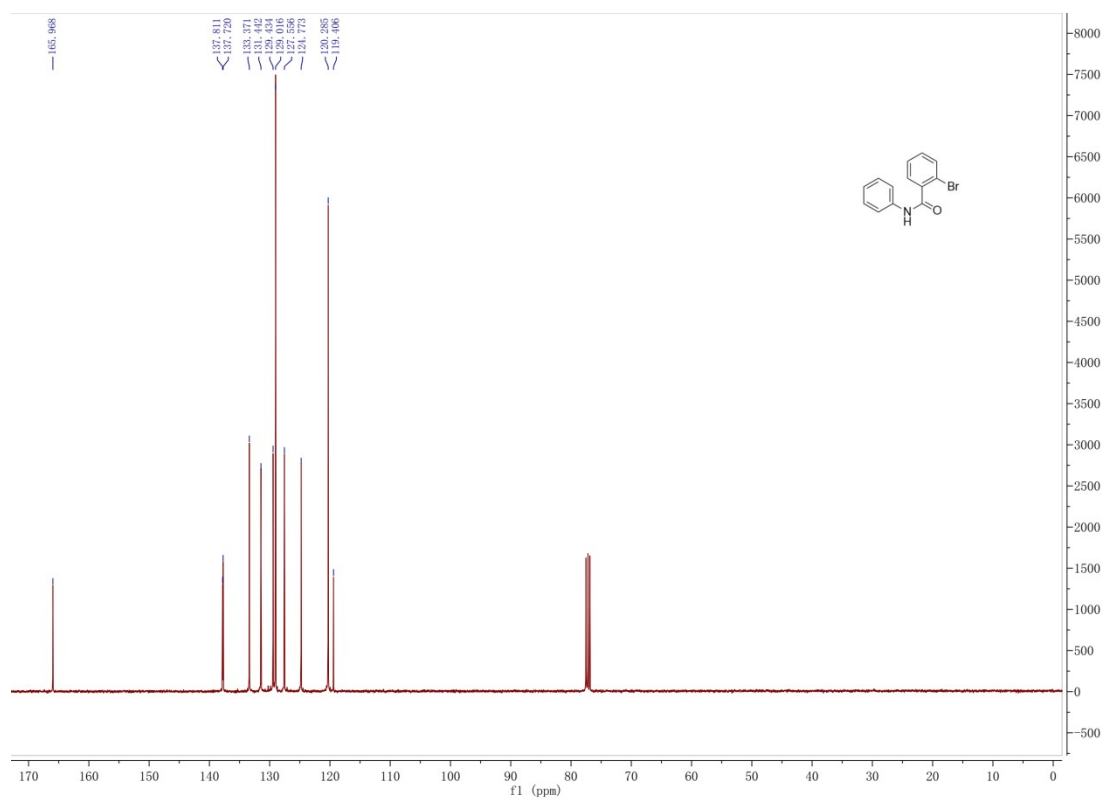
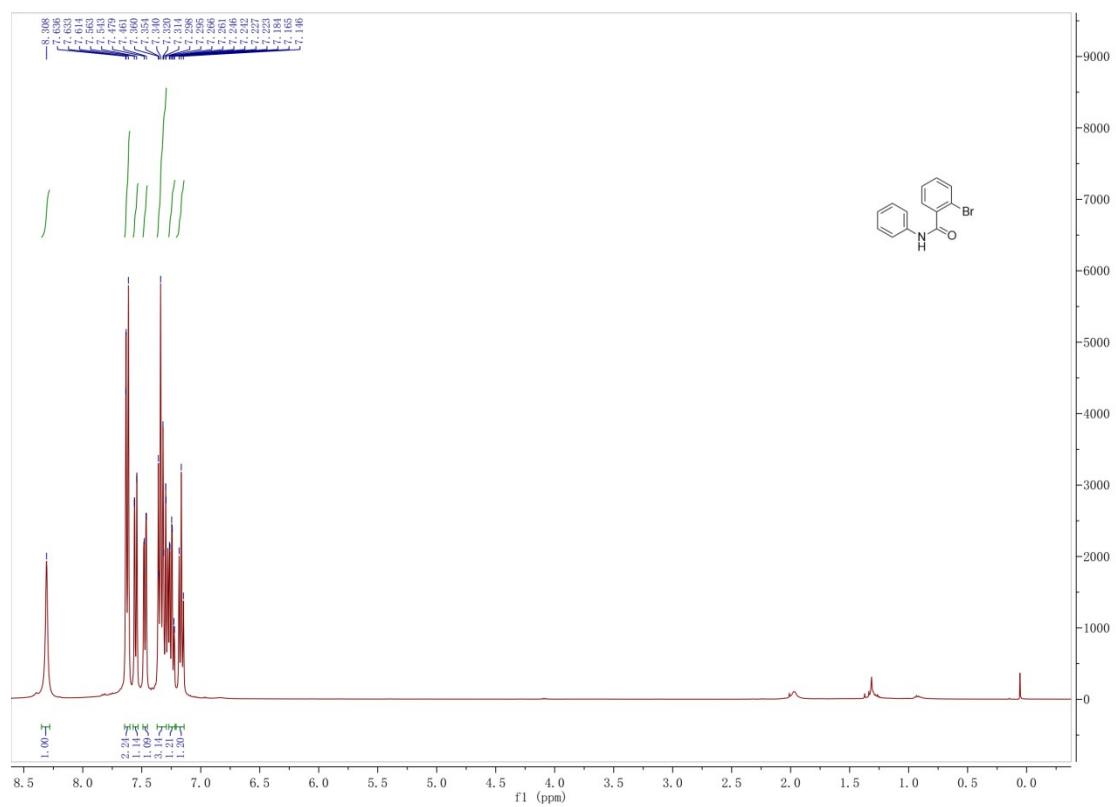


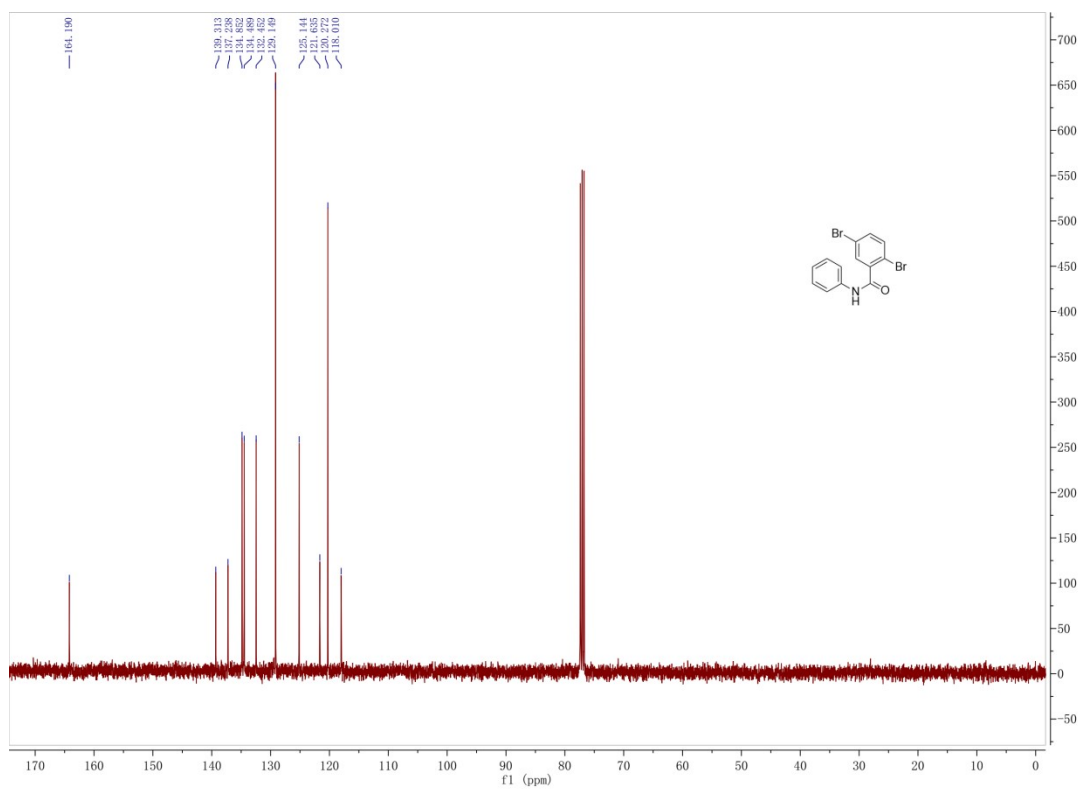
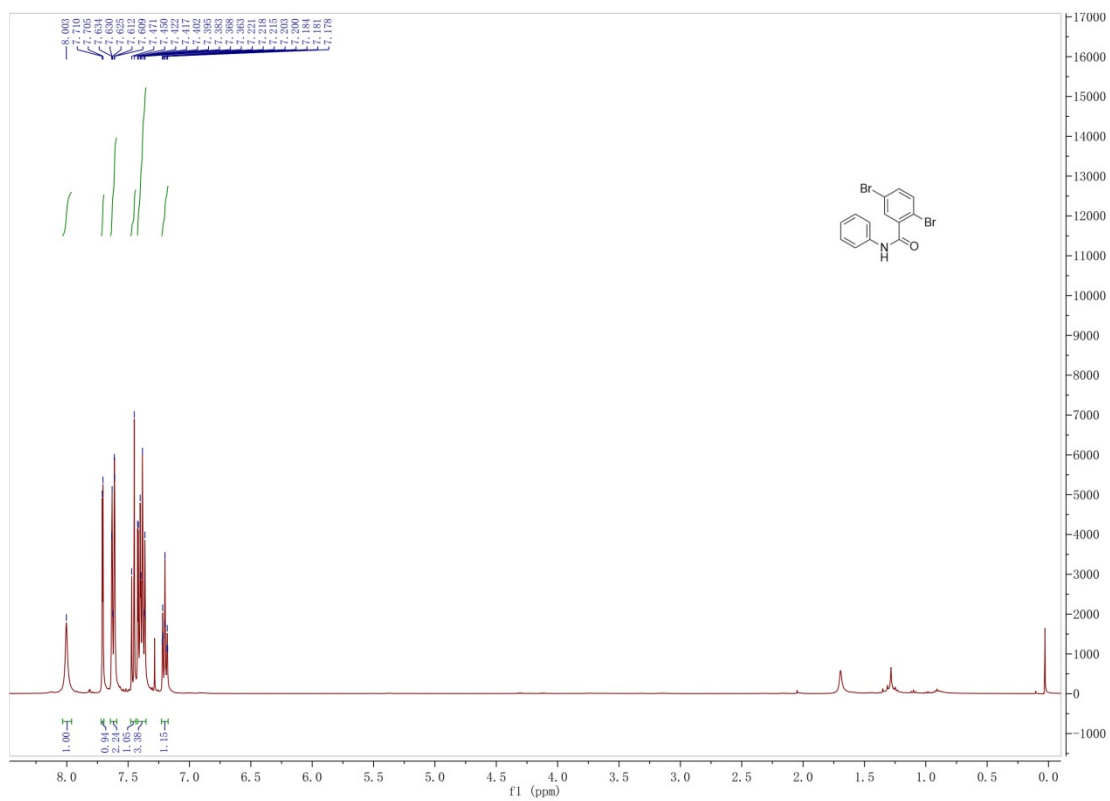


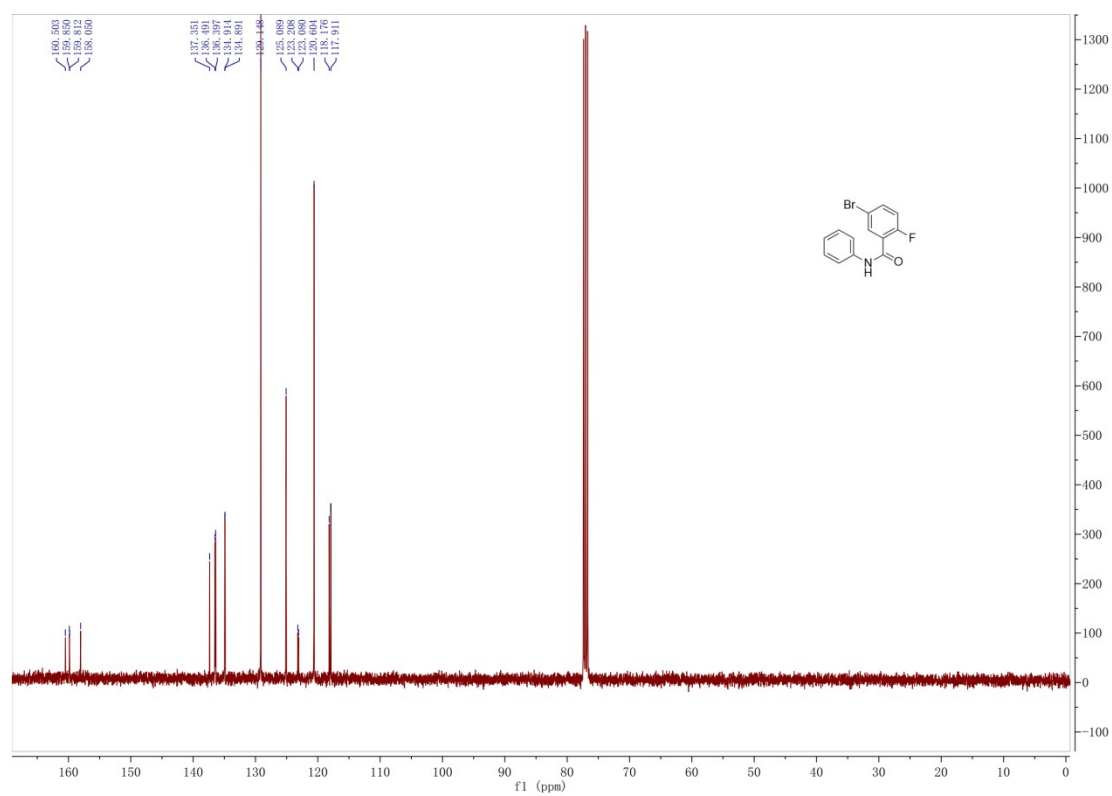
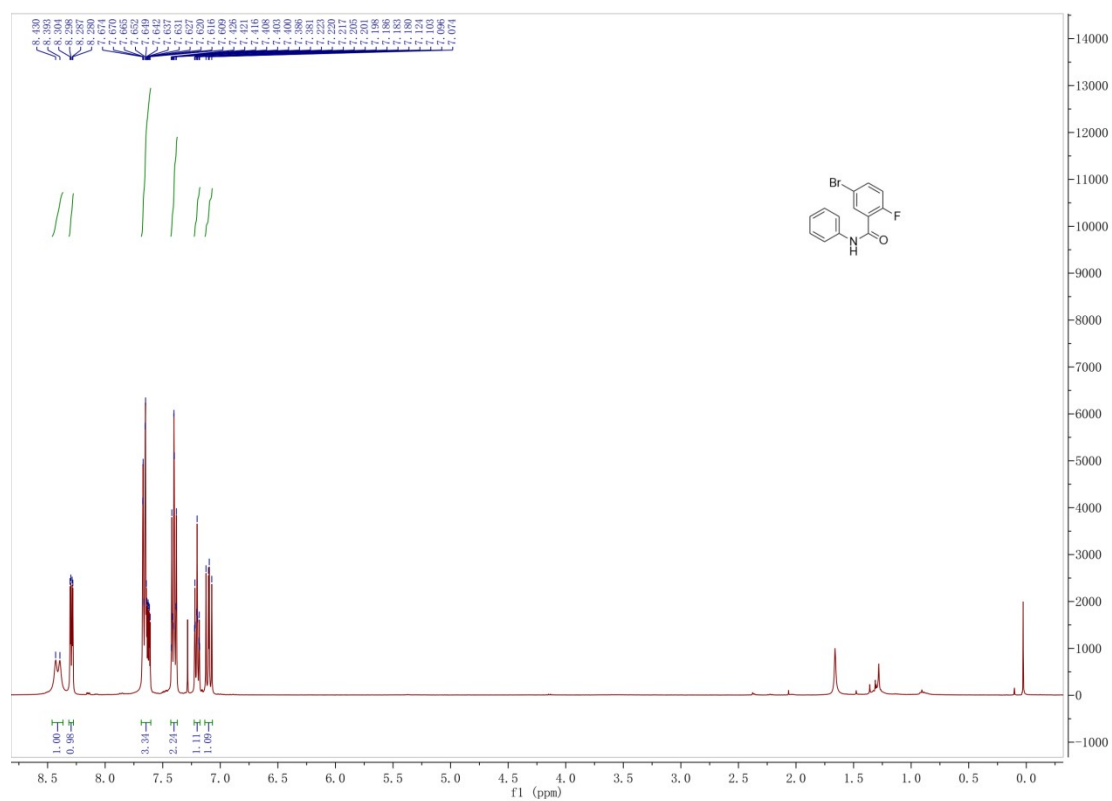


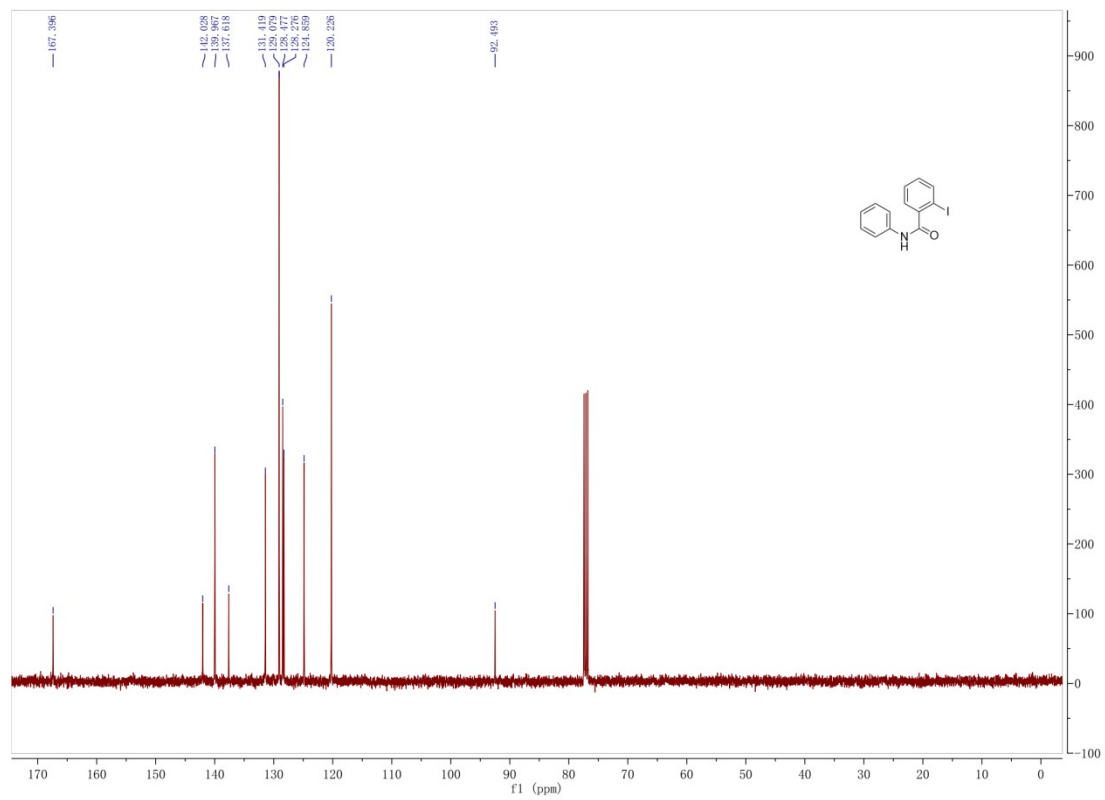
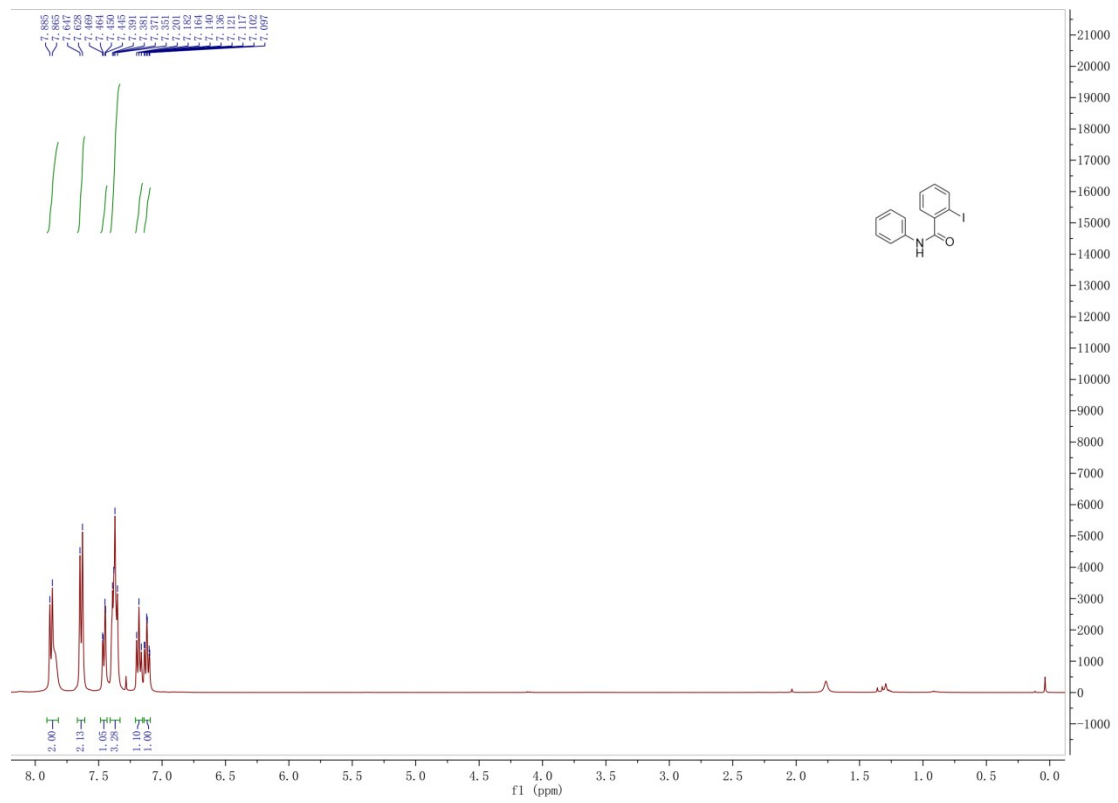


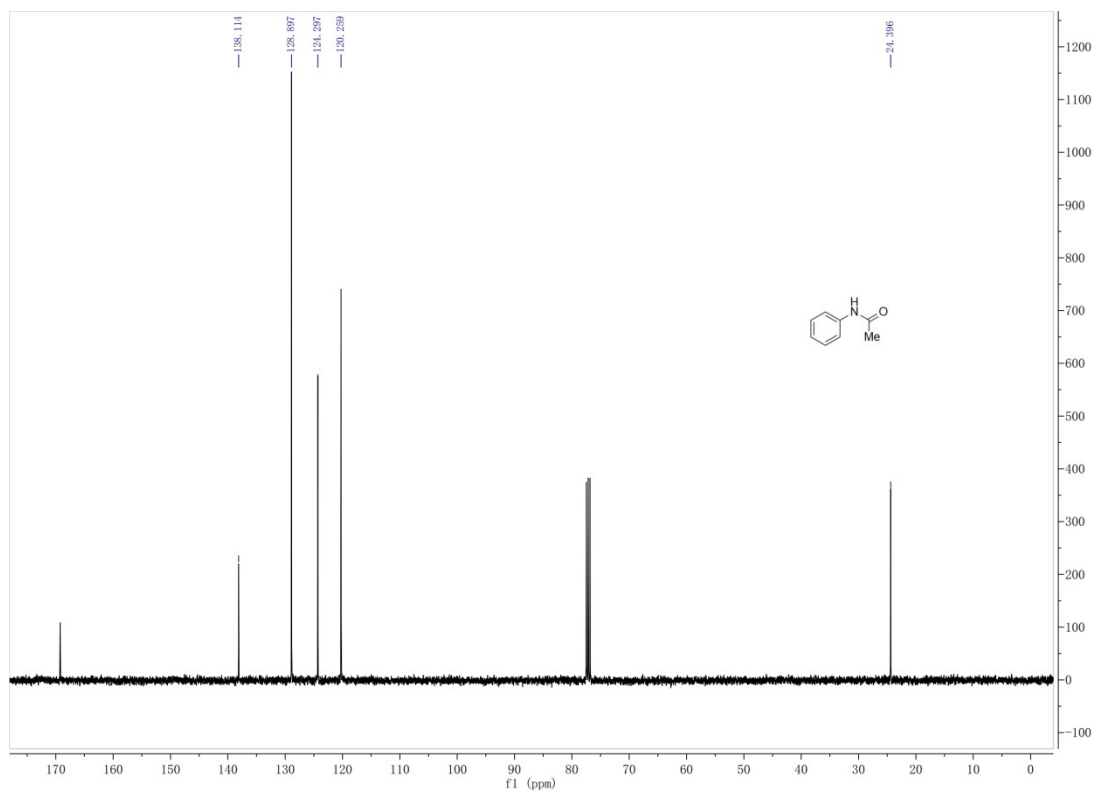
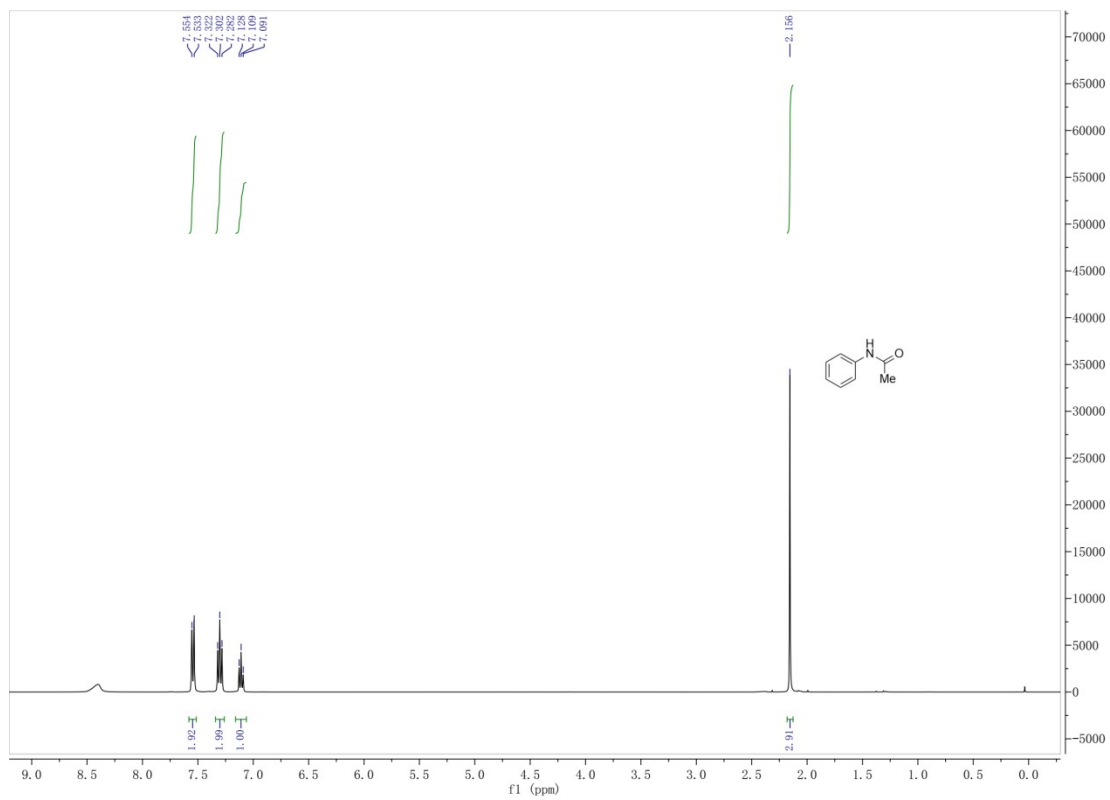


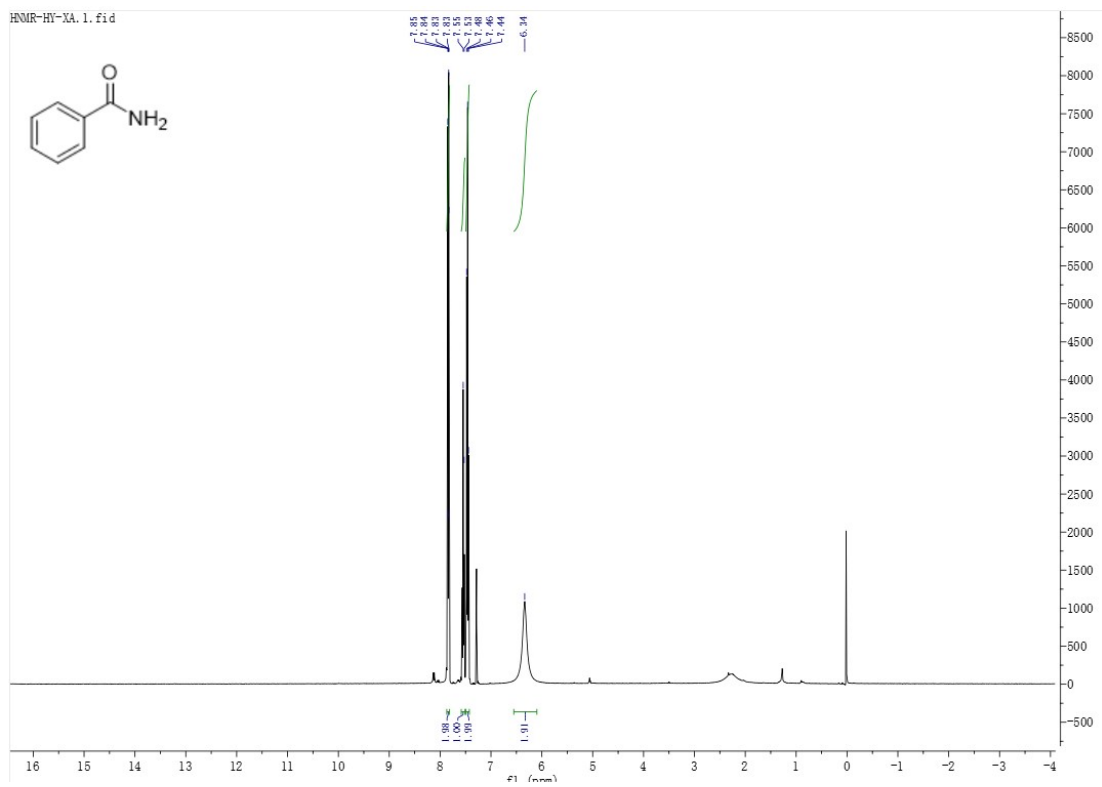
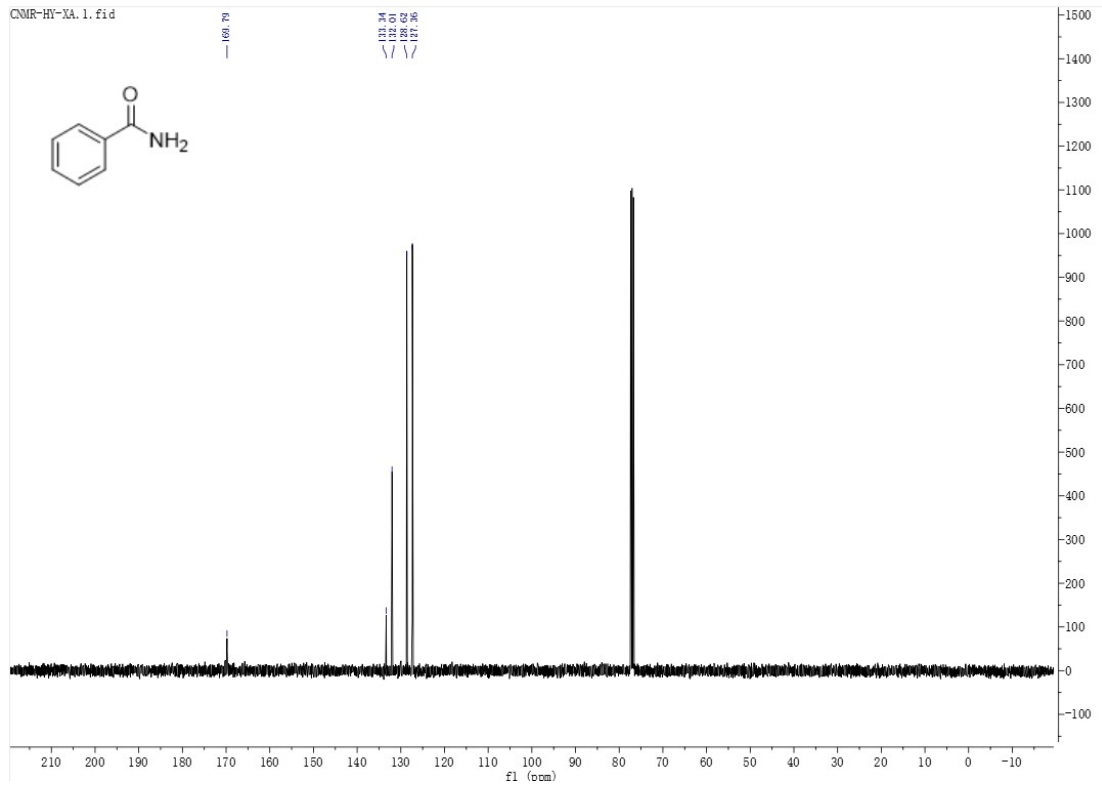


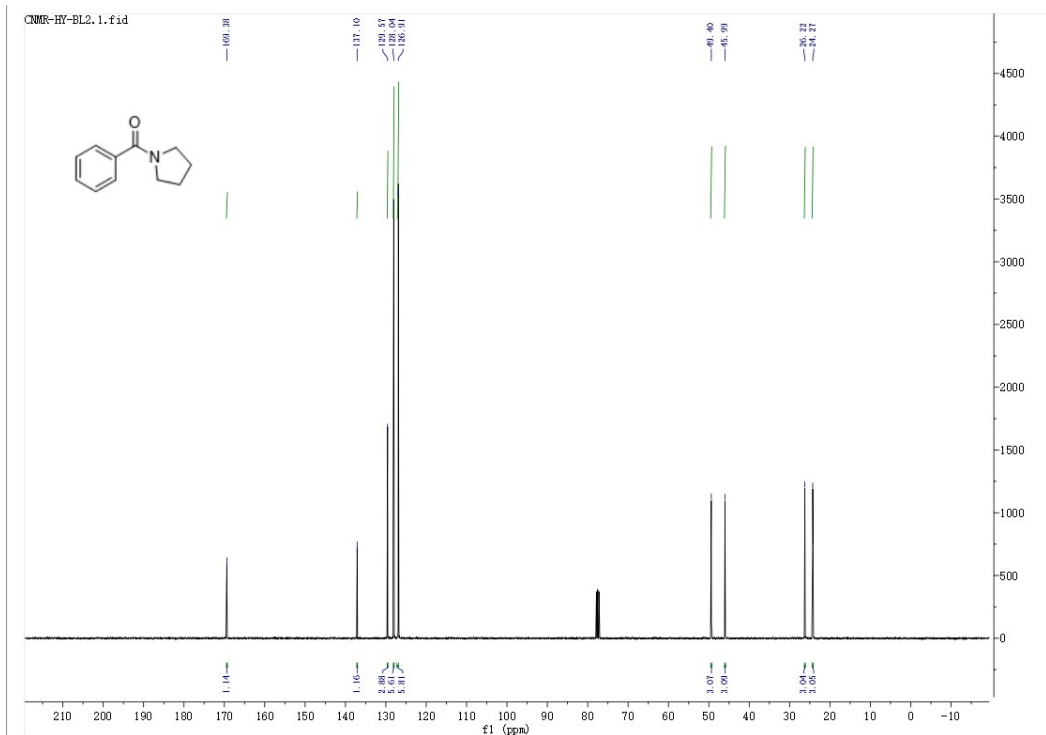
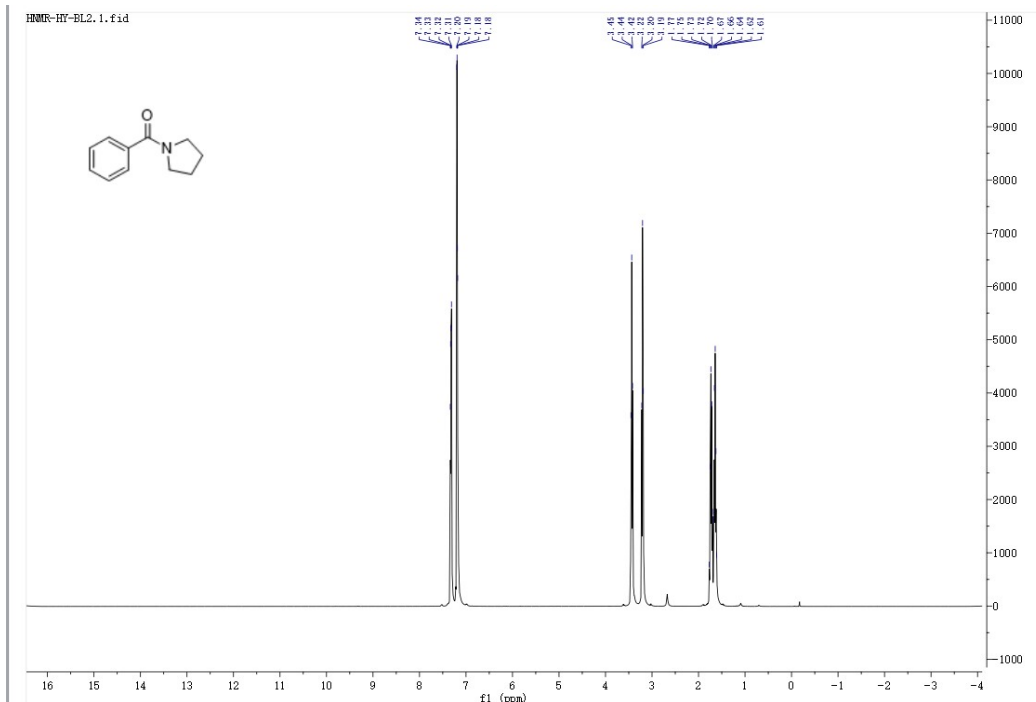


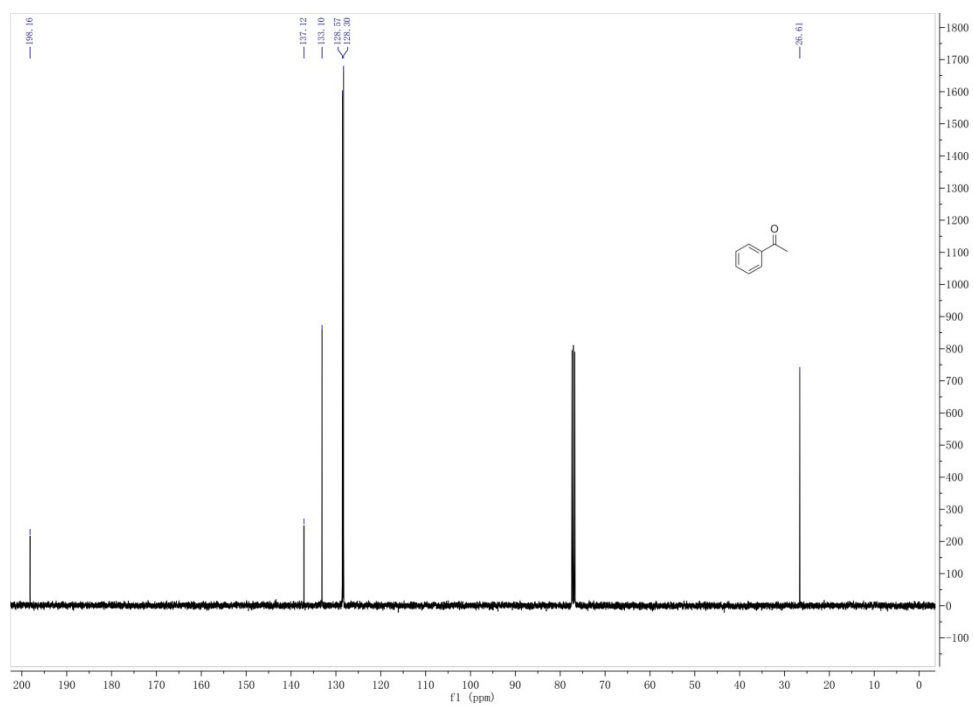
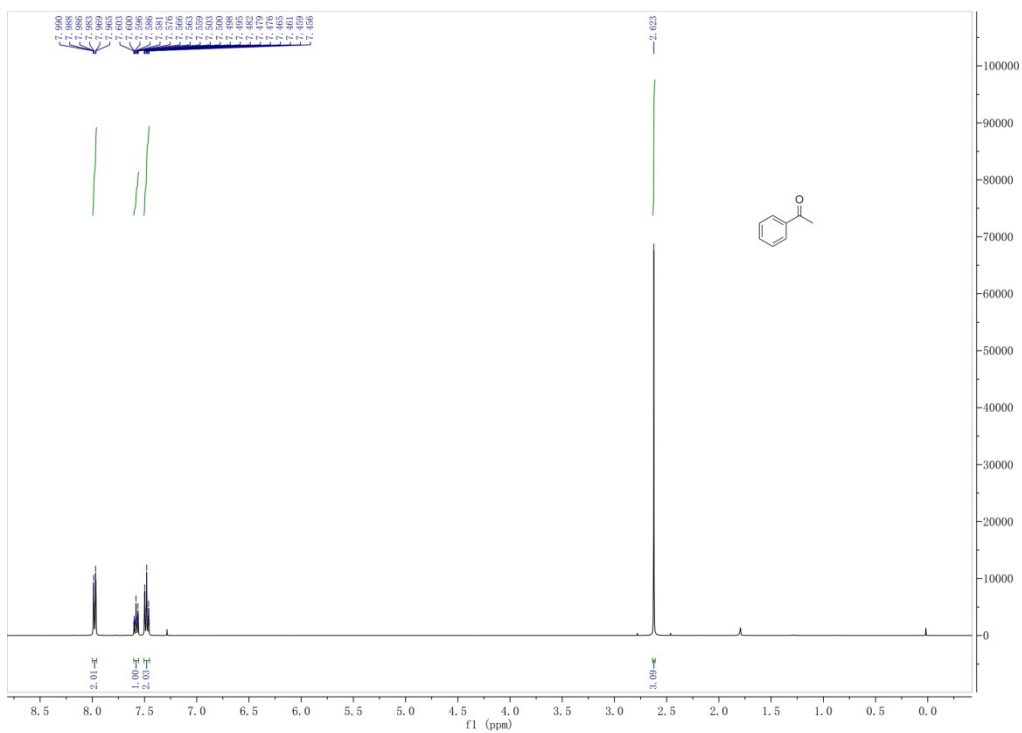


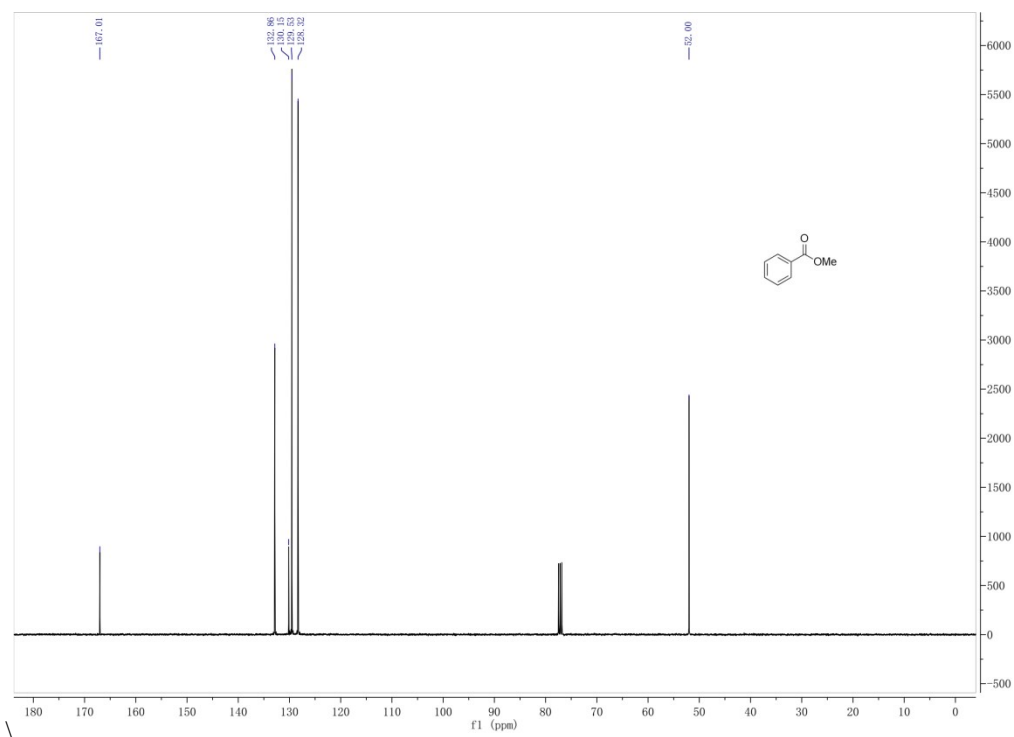
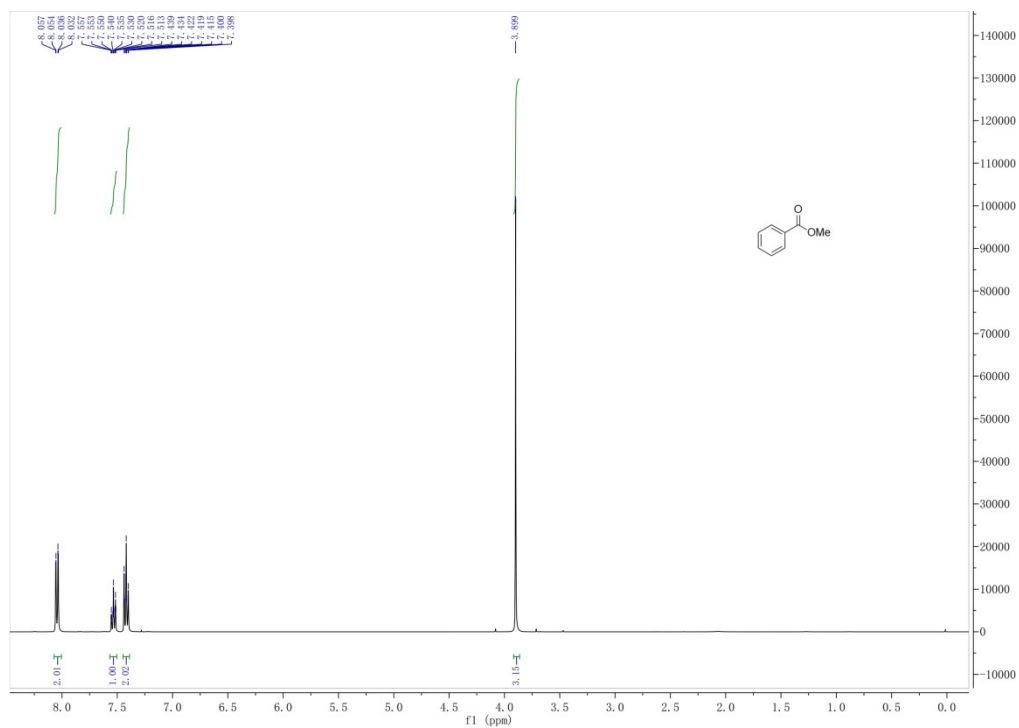












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