

Supporting Information for

***N*-Heterocyclic Carbenes-Catalyzed [3+3] Annulation
of Bromoenals with 2-Aminochromones to Access
Chromeno[2,3-*b*]pyridinones**

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I	General information
II	a) Condition optimization (Table S1) b) General procedure for the reactions of 1 with enlas 2 to synthesize product 3 c) Synthetic transformations d) Stereochemistry determination 3a via X-ray crystallographic analysis
III	a) Characterizations of substrates b) Characterizations of products c) References
IV	¹ H, ¹³ C and ¹⁹ F NMR spectra of the substrates and products

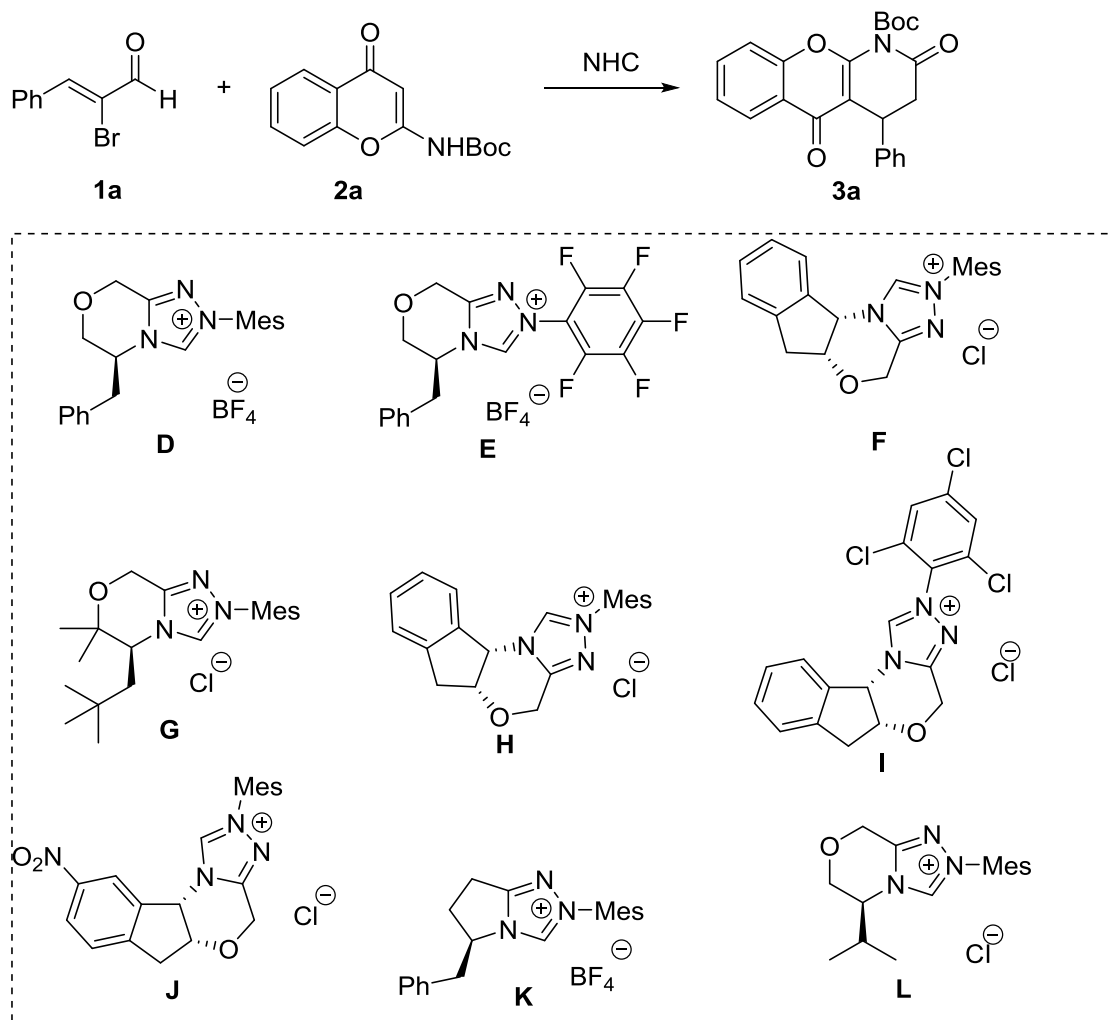
I: General Information

Commercially available materials purchased from Alfa Aesar or Sigma-Aldrich was used as received. Toluene and DCM was dried over Pure Solv solvent purification system. THF was distilled over sodium. Other solvents were dried over 4Å molecular sieve prior use. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on a Waters Q-TOF Premier Spectrometer. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or potassium permanganate stain.

II. General procedure

a) Condition Optimization

Table S1. Screening of various reaction conditions for the reaction of **3**



Entry ^[a]	Base	NHC	Solvent	Yield [%] ^[b]	ee ^[c]
1	Cs ₂ CO ₃	D	THF	69	32
2	Cs ₂ CO ₃	E	THF	71	35
3	Cs ₂ CO ₃	F	THF	69	38
4	Cs ₂ CO ₃	G	THF	73	40
6	Cs ₂ CO ₃	H	THF	75	50
7	Cs ₂ CO ₃	I	THF	72	48
8	Cs ₂ CO ₃	J	THF	74	49
9	Cs ₂ CO ₃	K	THF	72	42
10	Cs ₂ CO ₃	L	THF	70	40
11	Cs ₂ CO ₃	H	CH ₃ CN	75	38
12	Cs ₂ CO ₃	H	toluene	80	28
13	Cs ₂ CO ₃	H	1,4-dioxane	79	34

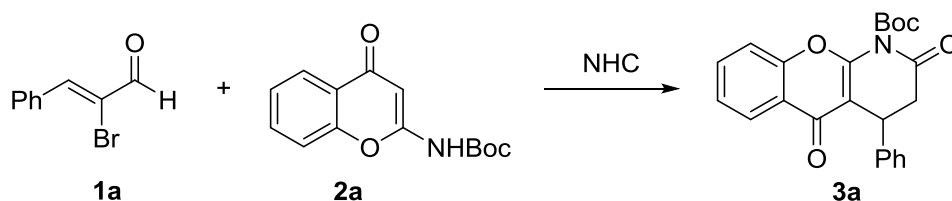
14	Cs ₂ CO ₃	H	DCM	66	42
15	Cs ₂ CO ₃	H	chlorobenzene	86	31
16	K ₂ CO ₃	H	THF	80	47
17	DBU	H	THF	78	42
18	Et ₃ N	H	THF	76	45
19	AcONa	H	THF	74	39
20	DABCO	H	THF	86	48
21	DIPEA	H	THF	84	51
22 ^[d]	DIPEA	H	THF	80	52

^[a] Standard condition: **2a** (0.1 mmol), **1a** (1.5 equiv), base (2.5 equiv.), NHC precursor (20 mol%), solvent (1.0 ml), 30°C, 12 h. ^[b] Yield (after SiO₂ chromatography purification) were based on **2a**, ^[c] Determined by HPLC. ^[d] 0°C.

b) General procedure for the reactions of 1 with 2 to synthesize product 3 (3a as an example):

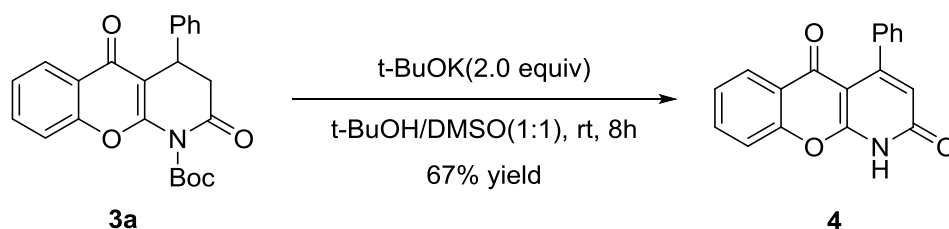
α -Bromocinnamaldehyde **1** was synthesized according to the literature.^[1]

Tert-butyl (4-oxo-4H-chromen-2-yl)carbamate **2** were synthesized according to the literature.^[2]



The reaction was operated in a glove box. To a flame-dried screw-capped tube equipped with a magnetic stir bar α -Bromocinnamaldehyde (31.6 mg, 0.15 mmol), tert-butyl (4-oxo-4H-chromen-2-yl)carbamate **2a** (26.3 mg, 0.10 mmol), DABCO (28.0 mg, 2.5 equiv.), NHC A (5.3 mg, 20 mol%), anhydrous 4 Å MS (100 mg) and PhCl (2.0 mL) were added. The reaction mixture was stirred at 30°C until tert-butyl (4-oxo-4H-chromen-2-yl)carbamate **2a** disappeared (detected by TLC), and then directly applied to silica gel column chromatography (25% v/v ethyl acetate in hexane) to afford **3a** as a white solid in 88% yield.

c) Synthetic transformations

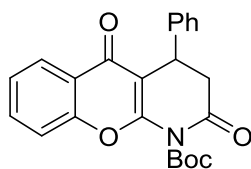


The reaction was operated in a glove box. To a flame-dried screw-capped tube equipped with a magnetic stir bar **3a** (39.1 mg, 0.1 mmol), t-BuOK (22.4 mg, 2.0 equiv), the mixture of solvents (t-BuOH: DMSO = 1:1, 2.0 mL) was added. The reaction mixture was stirred at room temperature. After the completion of reaction, the solvent was concentrated under reduced pressure, and the crude residue was

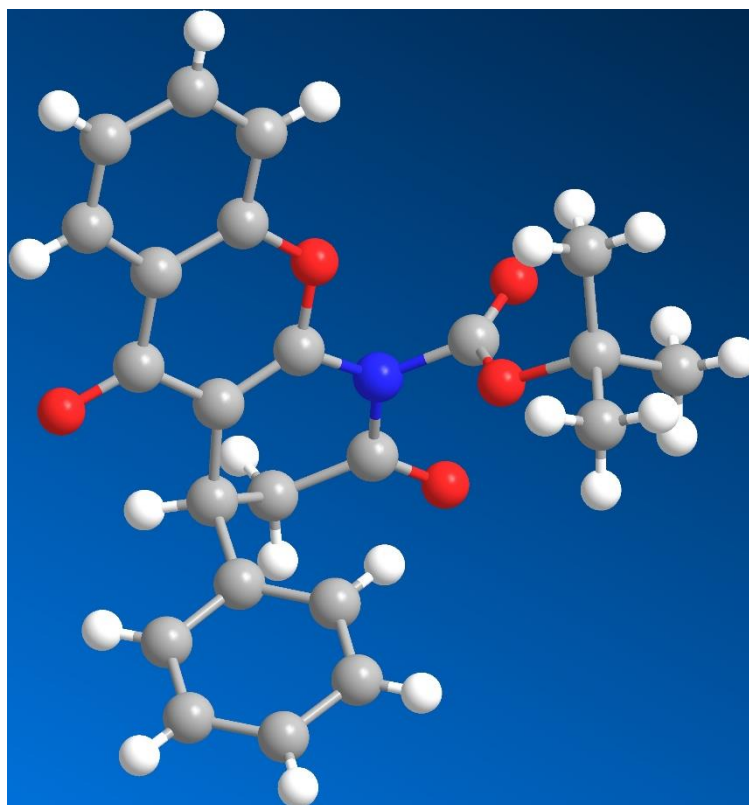
purified by flash chromatography (5% v/v methanol in DCM) to afford **4** as a white solid in 67% yield.

d) Stereochemistry determination 3a via X-ray crystallographic analysis

Product **3a** was crystallized as a colorless crystal *via* vaporization of a hexane/ethyl acetate solution, and its relative configuration was determined by x-ray structure analysis. CCDC 2081889 contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

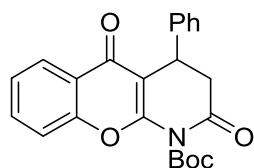


3a



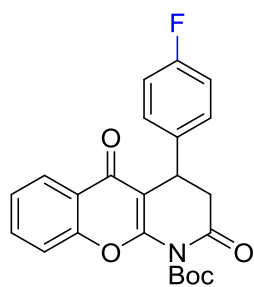
III. Characterizations of products, reference

a) Characterizations of Products



3a

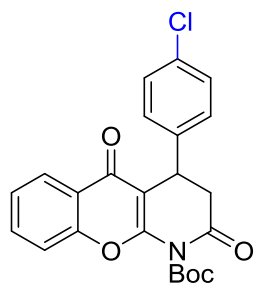
Tert-butyl 2,5-dioxo-4-phenyl-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate (3a): white solid; mp 110.4-111.8°C; ^1H NMR (400 MHz, CDCl_3) δ = 8.18 (dd, J = 8.0, 2.0 Hz, 1H), 7.68-7.63(m, 1H), 7.44-7.40 (m, 1H), 7.35 (dd, J = 8.4, 2.4Hz, 1H), 7.31-7.20(m, 4H), 6.95 (t, J = 8.8Hz, 1H), 4.64 (t, J = 7.2, 1H), 3.12-3.06 (m, 1H), 2.98-2.90 (m, 1H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.5, 167.4, 165.9, 153.9, 153.1, 146.7, 139.4, 135.8, 133.8, 133.7, 129.1, 128.5, 128.4, 127.6, 126.8, 126.3, 126.0, 125.90, 123.2, 117.4, 117.3, 116.1, 115.8, 87.3, 87.1, 38.7, 38.7, 32.8, 32.2, 23.9; FTIR (cm^{-1} : KBr): 2910, 2837, 1658, 1523, 1436, 1395, 1330, 1290, 1229, 1006, 958, 849, 772; HRMS(ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_5^+(\text{M}+\text{H})^+$: 392.1492, Found: 392.1494. 52 *ee* as determined by HPLC (Chiralcel ADH, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), t_r (major) = 18.9 min, t_r (minor) = 32.0 min.



3b

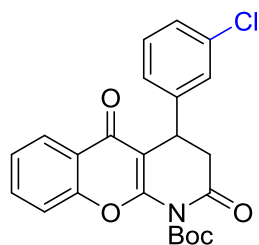
Tert-butyl 4-(4-fluorophenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate (3b) : white solid; mp 124.4-125.8°C; ^1H NMR (400 MHz, CDCl_3) δ = 8.19 (dd, J = 8.0, 2.0 Hz, 1H), 7.69-7.65 (m, 1H, 7.46-7.42(m, 1H), 7.37(d, J = 8.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.00-6.94 (m, 2H), 4.65 (dd, J = 7.6, 1.6 Hz, 1H), 3.11(dd, J = 16.0, 7.6 Hz, 1H), 2.94 (dd, J = 16.0, 1.6 Hz, 1H), 1.66 (s, 9H);

^{13}C NMR (100 MHz, CDCl_3) δ = 174.7, 167.2, 163.4, 160.9, 153.9, 153.7, 147.4, 136.2, 136.2, 133.7, 128.5, 128.4, 126.3, 125.9, 122.7, 117.3, 116.0, 115.8, 103.8, 87.3, 38.7, 32.2, 27.6; ^{19}F NMR (376 MHz, CDCl_3) δ = -115.06; FTIR (cm^{-1} : KBr): 2359, 2341, 2057, 1785, 1720, 1636, 1509, 1465, 1409, 1245, 1139, 760; HRMS(ESI) calcd for $\text{C}_{23}\text{H}_{21}\text{FNO}_5^+(\text{M}+\text{H})^+$: 410.1398, Found: 410.1396.



3c

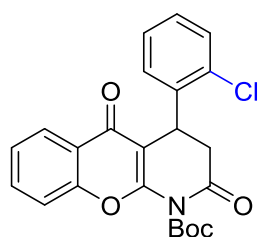
Tert-butyl 4-(4-chlorophenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b]pyridine -1(5H)-carboxylate (3c): white solid; mp 136.8-137.9°C; ^1H NMR (400 MHz, CDCl_3) δ = 8.18 (dd, J = 7.6, 1.6 Hz, 1H), 7.68-7.64 (m, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.35 (dd, J = 8.4, 1.2 Hz, 1H), 7.23 (s, 4H), 4.62 (dd, J = 7.6, 1.6 Hz, 1H), 3.14 (dd, J = 16.0, 4.0 Hz, 1H), 2.92 (dd, J = 16.0, 1.6 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ = 173.4, 163.6, 153.9, 148.6, 138.9, 132.8, 132.6, 130.8, 129.2, 128.2, 126.3, 126.0, 123.1, 121.8, 117.3, 104.6, 85.3, 39.1, 30.9, 25.9; FTIR (cm^{-1} : KBr): 2980, 2924, 2853, 1785, 1723, 1635, 1574, 1465, 1420, 1245, 1140, 840, 759; HRMS(ESI) calcd for $\text{C}_{23}\text{H}_{21}\text{ClNO}_5^+(\text{M}+\text{H})^+$: 426.1103, Found: 426.1100.



3d

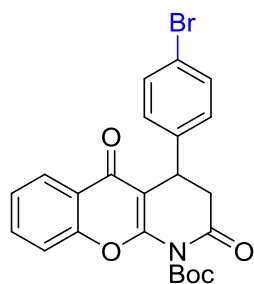
Tert-butyl 4-(3-chlorophenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b]pyridine -1(5H)-carboxylate (3d): white solid; mp 216.1-216.4°C; ^1H NMR (400

MHz, CDCl₃) δ = 8.18 (dd, J = 8.0, 2.0 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.37(d, J = 9.6 Hz 1H), 7.26 (t, J = 2.0 Hz, 1H), 7.22-7.18 (m, 3H), 4.62 (dd, J = 7.6, 1.6 Hz, 1H), 3.09 (dd, J = 16.0, 7.6 Hz, 1H), 2.92 (dd, J = 16.0, 2.0 Hz, 1H), 1.64 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 174.6, 166.8, 153.9, 146.7, 142.3, 136.1, 133.9, 130.4, 129.1, 127.9, 126.9, 126.3, 126.0, 125.2, 123.1, 102.8, 87.4, 37.9, 31.9, 27.7; FTIR (cm⁻¹: KBr): 2773, 2050, 1785, 1632, 1497, 1464, 1412, 1253, 1141, 758; HRMS(ESI) calcd for C₂₃H₂₁ClNO₅⁺(M+H)⁺: 426.1103, Found: 426.1111.



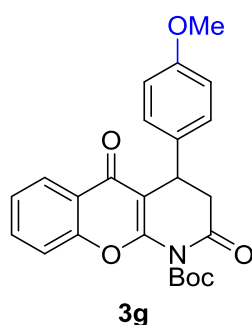
3e

Tert-butyl 4-(2-chlorophenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b]pyridine -1(5H)-carboxylate (3e): white solid; mp 144.1-150.5°C; ¹H NMR (400 MHz, CDCl₃) δ = 8.16 (dd, J = 8.0, 1.6 Hz, 1H), 7.70-7.66 (m, 1H), 7.58 (dd, J = 8.0, 1.6 Hz, 1H), 7.42 (dd, J = 14.0, 7.6 Hz, 2H), 7.15 (t, J = 6.4 Hz, 1H), 7.08 (dd, J = 8.0, 2.0 Hz, 1H), 7.06-7.03 (m, 1H), 5.04 (dd, J = 7.6, 2.0 Hz, 1H), 3.06 (dd, J = 16.0, 7.6 Hz, 1H), 2.97 (dd, J = 16.0, 2.0 Hz, 1H), 1.66 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 174.5, 167.2, 156.2, 154.1, 147.5, 138.6, 133.9, 129.2, 128.1, 127.0, 126.3, 125.5, 124.3, 123.1, 117.4, 104.2, 85.6, 37.8, 31.8, 27.7; FTIR (cm⁻¹: KBr): 2982, 2927, 2049, 1786, 1720, 1636, 1465, 1414, 1331, 1245, 1138, 756; HRMS(ESI) calcd for C₂₃H₂₁ClNO₅⁺(M+H)⁺: 426.1103, Found: 426.1108.

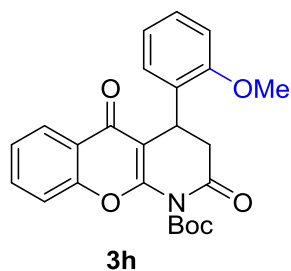


3f

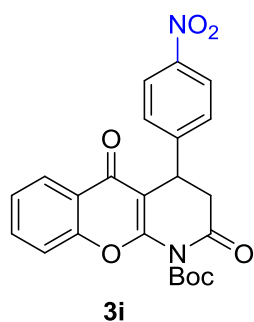
Tert-butyl 4-(4-bromophenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate (3f): white solid; mp 171.3-172.5 °C; ¹H NMR (400 MHz, CDCl₃) δ = 8.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68-7.64 (m, 1H), 7.45-7.34 (m, 4H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.19 (dd, *J* = 16.4, 8.0 Hz, 1H), 2.92 (dd, *J* = 16.0, 2.0 Hz, 1H), 1.64 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 175.3, 166.4, 153.9, 153.5, 146.5, 139.5, 134.2, 132.2, 128.6, 126.3, 124.9, 123.1, 119.9, 117.4, 102.1, 88.3, 85.2, 38.4, 32.4, 27.6; FTIR (cm⁻¹: KBr): 2931, 2858, 1734, 1560, 1491, 1255, 1149, 1008, 881, 765; HRMS(ESI) calcd for C₂₃H₂₁BrNO₅⁺ (M+H)⁺: 470.0598, Found: 470.0601.



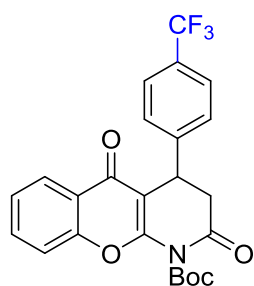
Tert-butyl 4-(4-methoxyphenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b] pyridine-1(5H)-carboxylate (3g): white solid; mp 141.5-142.2 °C; ¹H NMR (400 MHz, CDCl₃) δ = 8.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.42 (t, *J* = 1.2 Hz, 1H), 7.35 (d, *J* = 14.0 Hz, 1H), 7.20 (s, 1H), 6.98 (s, 1H), 6.79 (m, 2H), 4.60 (d, *J* = 9.2 Hz, 1H), 3.73 (s, 3H), 3.06 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.92 (dd, *J* = 16.0, 2.0 Hz, 1H), 1.64 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 174.1, 167.0, 159.5, 152.9, 134.6, 132.2, 129.8, 129.2, 127.2, 126.3, 125.9, 122.5, 116.9, 114.0, 104.2, 54.8, 37.9, 32.1, 28.5; FTIR (cm⁻¹: KBr): 2981, 2933, 2837, 1785, 1720, 1636, 1574, 1512, 1465, 1411, 1371, 1247, 1140, 1031, 840, 760; HRMS(ESI) calcd for C₂₄H₂₄NO₆⁺ (M+H)⁺: 422.1598, Found: 422.1593.



Tert-butyl 4-(2-methoxyphenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate (3h): white solid; mp 160.6-160.9°C; ¹H NMR (400 MHz, CDCl₃) δ = 8.12 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.64-7.59 (m, 1H), 7.39 (t, *J* = 4.2 Hz, 1H), 7.33-7.30 (m, 2H), 7.20-7.16 (m, 1H), 6.87-6.80 (m, 2H), 4.70 (d, *J* = 9.2 Hz, 1H), 3.78 (s, 3H), 3.04 (dd, *J* = 16.4, 9.2 Hz, 1H), 2.87 (dd, *J* = 16.8, 1.6 Hz, 1H), 1.67 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 175.6, 167.5, 156.4, 153.2, 148.1, 132.9, 129.7, 128.7, 128.3, 126.2, 125.6, 122.8, 120.5, 117.3, 110.6, 101.4, 86.7, 54.7, 35.8, 29.7, 27.7; FTIR (cm⁻¹: KBr): 2980, 2937, 2838, 1781, 1721, 1634, 1574, 1465, 1414, 1331, 1244, 1140, 1030, 841, 753; HRMS(ESI) calcd for C₂₄H₂₄NO₆⁺(M+H)⁺: 422.1598, Found: 422.1590.

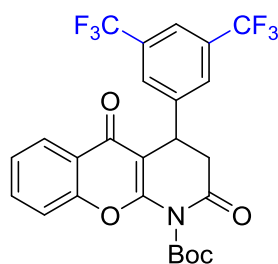


Tert-butyl 4-(4-nitrophenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate (3i): white solid; mp 173.5-175.2°C; ¹H NMR(400 MHz, CDCl₃) δ = 8.16(m, 3H), 7.68 (m, 1H), 7.47 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 4.74 (d, *J* = 8.0 Hz, 1H), 3.16 (dd, *J* = 16.4, 8.0 Hz, 1H), 2.97 (dd, *J* = 16.4, 2.0 Hz, 1H), 1.65 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 185.8, 173.4, 166.7, 153.3, 148.3, 137.9, 134.0, 132.8, 127.5, 126.3, 126.0, 125.3, 124.4, 117.4, 116.9, 101.9, 94.3, 87.7, 37.9, 32.4, 28.1, 27.6; FTIR (cm⁻¹: KBr): 2052, 1636, 1527, 1246, 1138, 513; HRMS(ESI) calcd for C₂₃H₂₁N₂O₇⁺(M+H)⁺: 437.1343, Found: 437.1349.



3j

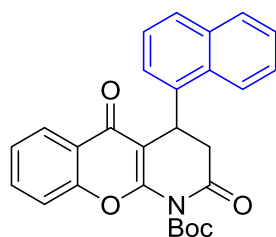
Tert-butyl 2,5-dioxo-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate(3j): white solid; mp 132.6-133.9°C; ¹H NMR(400 MHz, CDCl₃) δ = 8.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70-7.65(m, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.45-7.42 (m, 3H), 7.37 (d, *J* = 7.6 Hz, 1H), 4.71 (d, *J* = 9.2 Hz, 1H), 3.14 (dd, *J* = 16.4, 8.0 Hz, 1H), 2.95 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.65 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 175.3, 166.8, 153.9, 153.9, 147.3, 144.5, 133.9, 127.3, 126.3, 126.1, 126.1, 124.9, 122.3, 117.4, 103.1, 87.4, 38.3, 32.8, 28.4; ¹⁹F NMR (376 MHz, CDCl₃) δ = -62.53; FTIR (cm⁻¹: KBr): 2983, 2930., 2854, 1787, 1724, 1635, 1574, 1466, 1412, 1372, 1326 1246, 1139, 1068, 1016, 840, 760; HRMS(ESI) calcd for C₂₄H₂₀NNaO₅⁺(M+Na)⁺: 482.1186, Found: 482.1194.



3k

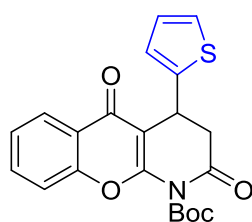
Tert-butyl 4-(3,5-bis(trifluoromethyl)phenyl)-2,5-dioxo-3,4-dihydro-2H-chromeno [2,3-b]pyridine-1(5H)-carboxylate(3k): yellow solid; mp 152.5-154.8°C; ¹H NMR (400 MHz, CDCl₃) δ = 8.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75-7.68 (m, 4H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 4.4 Hz, 1H), 4.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.17 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.92 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.64 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 174.3, 166.0, 154.3, 154.0, 146.7, 142.9, 134.1, 132.6, 131.9,

127.2, 126.3, 126.3, 123.0, 121.3, 118.0, 102.6, 87.8, 37.6, 31.8, 27.5; ^{19}F NMR (376 MHz, CDCl_3) $\delta = -62.72$; FTIR (cm^{-1} : KBr): 2985, 2914, 1792, 1726, 1636, 1574, 1466, 1416, 1373, 1279, 1134, 896, 839, 760; HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{F}_7\text{NO}_5^+(\text{M}+\text{Na})^+$: 550.1060, Found: 550.1069.



3l

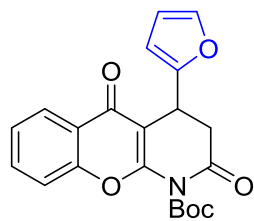
Tert-butyl 4-(naphthalen-1-yl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b] pyridine-1(5H)-carboxylate (3l): white solid; mp 142.1-143.8°C; ^1H NMR (400 MHz, CDCl_3) $\delta = 8.20$ (dd, $J = 8.0, 1.6$ Hz, 1H), 7.78-7.73 (m, 3H), 7.70-7.66 (m, 2H), 7.47 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.44-7.38 (m, 4H), 4.83 (dd, $J = 7.6, 2.0$ Hz, 1H), 3.17 (dd, $J = 16.0, 7.6$ Hz, 1H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 174.8, 167.3, 157.5, 147.1, 138.2, 133.7, 133.5, 132.8, 129.1, 128.0, 127.6, 126.3, 126.3, 126.0, 125.9, 125.4, 125.1, 123.2, 116.8, 103.3, 85.6, 37.9, 32.9, 27.7, 23.7$; FTIR (cm^{-1} : KBr): 2979, 2915, 2848, 1786, 1722, 1635, 1573, 1465 1414, 1246, 1138, 840, 759; HRMS(ESI) calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_5^+(\text{M}+\text{H})^+$: 442.1649, Found: 442.1655.



3m

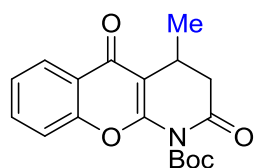
Tert-butyl 2,5-dioxo-4-(thiophen-2-yl)-3,4-dihydro-2H-chromeno[2,3-b] pyridine-1(5H)-carboxylate (3m): white solid; mp 281.2-283.0°C; ^1H NMR (400 MHz, CDCl_3) $\delta = 8.21$ (dd, $J = 8.0, 2.0$ Hz, 1H), 7.67-7.63 (m, 1H), 7.43 (m, 1H), 7.45-7.41 (m, 1H), 7.34 (d, $J = 9.2$ Hz, 1H), 7.28 (dd, $J = 1.6, 0.8$ Hz, 1H), 6.22 (dd, $J = 3.6,$

2.0 Hz, 1H), 6.13 (d, $J = 3.2$ Hz, 1H), 4.71 (dd, $J = 7.6, 1.6$ Hz, 1H), 3.06 (dd, $J = 16.0, 2.0$ Hz, 1H), 2.96 (dd, $J = 16.0, 6.8$ Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 175.0, 165.8, 153.9, 152.0, 147.8, 142.5, 135.6, 127.9, 124.8, 122.3, 116.5, 110.4, 105.6, 100.3, 88.8, 37.3, 28.4, 27.1$; FTIR (cm^{-1} : KBr): 2979, 2914, 2847, 1781, 1723, 1635, 1571, 1465, 1417, 1331, 1266, 1141, 1007, 840, 759; HRMS(ESI) calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$: 398.1057, Found: 398.1064.



3n

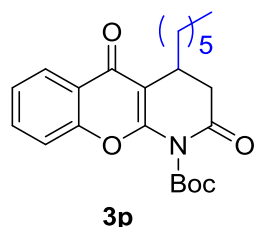
Tert-butyl 4-(furan-2-yl)-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b] pyridine-1(5H)-carboxylate(3n): white solid; mp 120.5-122.1 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) $\delta = 8.21$ (dd, $J = 8.0, 2.0$ Hz, 1H), 7.65 (m, 1H), 7.43 (m, 1H), 7.34 (d, $J = 8.4$ Hz, 1H), 7.29 (dd, $J = 2.0, 0.8$ Hz, 1H), 6.22 (dd, $J = 3.2, 2.0$ Hz, 1H), 6.13 (m, 1H), 4.71 (dd, $J = 7.2, 2.0$ Hz, 1H), 3.07 (dd, $J = 16.0, 4.0$ Hz, 1H), 2.96 (dd, $J = 16.0, 6.8$ Hz, 1H), 1.64(s, 9H); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 175.1, 166.2, 154.3, 152.7, 142.5, 133.0, 126.3, 125.3, 117.3, 110.4, 105.6, 86.4, 36.2, 27.7, 27.1$; FTIR (cm^{-1} : KBr): 2982, 2927, 1783, 1725, 1636, 1573, 1465, 1417, 1371, 1330, 1247, 1141, 1011, 886, 759; HRMS(ESI) calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_6^+$ ($\text{M}+\text{H}$) $^+$: 382.1285, Found: 382.1288.



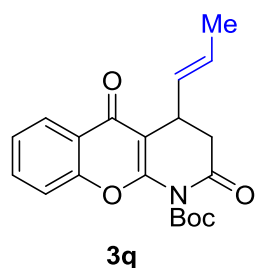
3o

Tert-butyl 4-methyl-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b] pyridine-1(5H)-carboxylate (3o): white solid; mp 101.2-103.8 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) $\delta = 8.21$ (dd, $J = 8.0, 2.0$ Hz, 1H), 7.64 (t, $J = 6.8$ Hz, 1H), 7.42(t, $J = 6.8$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 3.51 (t, $J = 7.2$ Hz, 1H), 2.80 (dd, $J = 15.6, 6.8$ Hz, 1H), 2.59 (dd, $J = 15.6, 6.8$ Hz, 1H), 1.63 (s, 9H), 1.19 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz,

CDCl₃) δ = 175.0, 167.5, 153.8, 151.6, 146.8, 133.5, 126.9, 125.2, 123.2, 116.8, 104.7, 89.3, 37.2, 28.4, 22.0, 17.6; FTIR (cm⁻¹: KBr): 2930, 2029, 1781, 1635, 1465, 1415, 1270, 1250, 1140, 758; HRMS(ESI) calcd for C₁₈H₂₀NO₅⁺(M+H)⁺: 330.1336, Found: 330.1333.

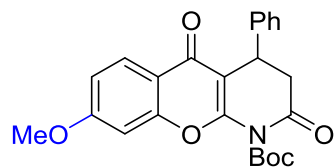


Tert-butyl 4-hexyl-2,5-dioxo-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate(3p): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ = 8.20 (dd, J = 8.0, 2.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.45-7.41 (m, 1H), 7.33 (dd, J = 8.4, 0.8 Hz, 1H), 3.42-3.36 (m, 1H), 2.72(d, J = 4.4 Hz, 2H), 1.63 (s, 9H), 1.29-1.23 (m, 10H), 0.84 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 175.6, 168.2, 154.1, 153.0, 133.5, 126.2, 125.7, 123.2, 117.3, 105.4, 86.8, 36.3, 33.1, 31.8, 29.9, 29.3, 28.1, 27.6, 26.4, 22.7, 14.2; FTIR (cm⁻¹: KBr): 2051, 1636, 1413. 1245, 1141, 759; HRMS(ESI) calcd for C₁₈H₂₀NO₅⁺(M+H): 330.1336, Found: 330.1333.



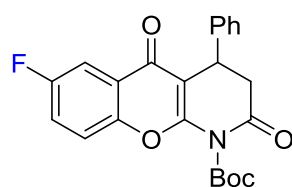
Tert-butyl (Z)-2,5-dioxo-4-(prop-1-en-1-yl)-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate(3q): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ = 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 7.68-7.64 (m, 1H), 7.46-7.42 (m, 1H), 7.35 (dd, J = 8.4, 1.2 Hz, 1H), 5.65-5.56 (m, 1H), 5.50-5.43 (m, 1H), 4.04-4.00 (m, 1H), 2.85-2.75 (m, 2H), 1.64-1.63 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ = 175.3, 167.7, 153.9, 152.9, 147.6, 133.5, 127.9, 126.9, 126.2, 125.8, 123.2, 117.3, 103.6, 86.8, 37.1, 29.8, 27.7, 17.9; FTIR (cm⁻¹: KBr): 2979, 2917, 2854, 1784, 1724, 1635, 1573, 1465, 1416, 1371,

1327, 1245, 1140, 959, 842, 759; HRMS(ESI) calcd for $C_{20}H_{22}NO_5^+(M+H)$: 356.1492, Found: 356.1490.



3r

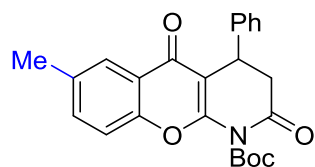
Tert-butyl 7-methoxy-2,5-dioxo-4-phenyl-3,4-dihydro-2H-chromeno[2,3-b] pyridine-1(5H)-carboxylate (3r): white solid; mp 103.1-116.8°C; 1H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, J = 8.8 Hz, 1H), 7.33-7.28 (m, 4H), 7.23-7.20 (m, 1H), 6.98 (dd, J = 8.8, 2.4 Hz, 1H), 6.74 (d, J = 2.4 Hz, 1H), 4.64 (d, J = 6.8 Hz, 1H), 3.91 (s, 3H), 3.09 (dd, J = 16.0, 7.6 Hz, 1H), 2.96 (d, J = 11.6 Hz, 1H), 1.65 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 174.70, 167.10, 157.33, 154.47, 148.08, 133.37, 130.36, 128.76, 128.32, 126.19, 125.66, 123.70, 120.52, 117.21, 111.49, 102.93, 86.71, 57.79, 36.97, 31.72, 29.21; FTIR (cm^{-1} : KBr): 2922, 2851, 1785, 1560, 1409, 1273, 1241, 1136, 930; HRMS(ESI) calcd for $C_{24}H_{24}NO_6 (M+H)^+$: 422.1598, Found: 422.1595.



3s

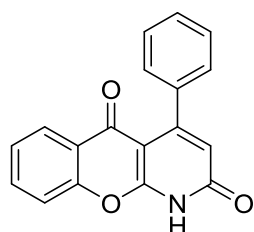
Tert-butyl 7-fluoro-2,5-dioxo-4-phenyl-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate(3s): white solid; mp 193.5-195.4°C; 1H NMR (400 MHz, $CDCl_3$) δ = 7.84-7.81 (m, 1H), 7.38-7.36 (m, 1H), 7.31-7.28 (m, 4H), 7.24-7.20 (m, 1H), 4.65 (dd, J = 7.6, 1.6 Hz, 1H), 3.11 (dd, J = 16.0, 7.6 Hz, 1H), 2.97 (dd, J = 16.0, 1.6 Hz, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.7, 166.6, 161.2, 157.1, 153.4, 149.0, 146.0, 139.0, 129.2, 127.7, 126.8, 124.6, 124.5, 122.2, 121.5, 119.4, 119.3, 112.4, 111.4, 101.7, 86.5, 37.7, 32.9, 27.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.03; FTIR (cm^{-1} : KBr): 2981, 2916, 1788, 1725, 1633, 1583, 1478, 1456, 1406, 1372,

1248, 1197, 1139, 1019, 822, 785; HRMS(ESI) calcd for $C_{23}H_{21}FNO_5^+(M+H)$: 410.1398, Found: 410.1395.



3t

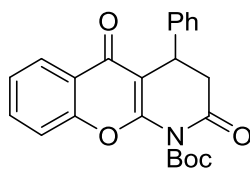
Tert-butyl 7-methoxy-2,5-dioxo-4-phenyl-3,4-dihydro-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate(3t) : white solid; mp 102.1-118.6°C; 1H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, J = 2.8 Hz, 1H), 7.45 (dd, J = 8.4, 2.0 Hz, 1H), 7.31-7.20 (m, 3H), 7.25-7.23 (m, 2H), 7.22-7.18 (m, 1H), 4.64 (dd, J = 7.6, 1.6 Hz, 1H), 3.09 (dd, J = 16.0, 7.6 Hz, 1H), 2.97 (dd, J = 16.0, 2.0 Hz, 1H), 2.43 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.3, 166.4, 154.7, 151.1, 146.3, 140.5, 136.4, 134.7, 129.0, 127.5, 126.7, 125.3, 121.8, 116.6, 103.4, 85.3, 38.6, 32.4, 27.0, 21.0; FTIR (cm^{-1} : KBr): 2921, 2849, 1786, 1724, 1635, 1398, 1247, 1139, 961, 780; HRMS(ESI) calcd for $C_{24}H_{24}NO_6 (M+H)^+$: 422.1598, Found: 422.1590.



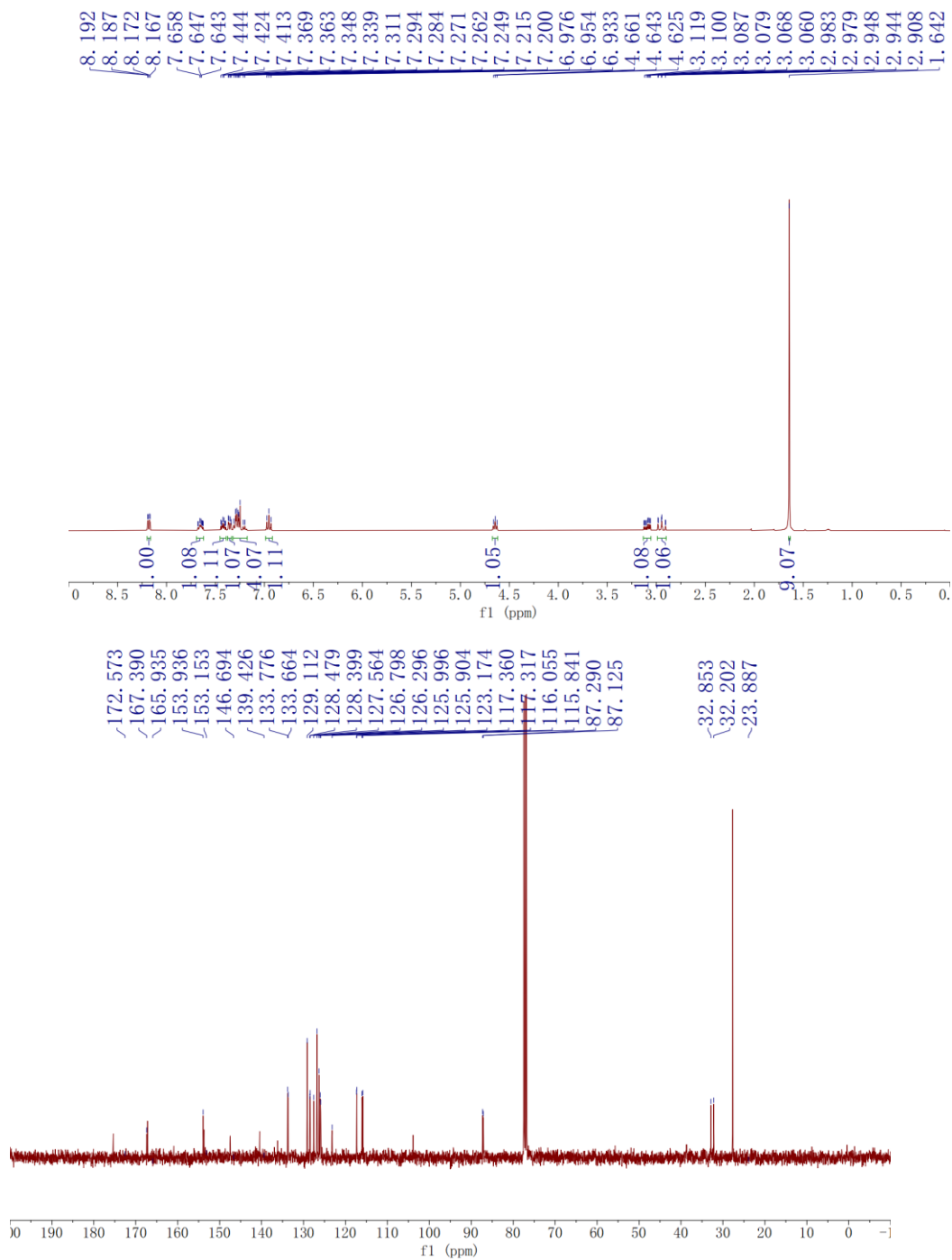
4

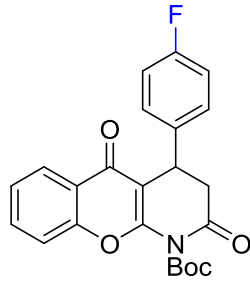
Tert-butyl 2,5-dioxo-4-phenyl-2H-chromeno[2,3-b]pyridine-1(5H)-carboxylate (4) : white solid; mp 330.3-335.8°C; 1H NMR (400 MHz, $CDCl_3$) δ = 9.94 (s, 1H), 8.22 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.82-7.77 (m, 2H), 7.47 (s, 3H), 7.31 (s, 1H), 6.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.2, 170.3, 154.6, 153.7, 141.4, 133.4, 129.0, 127.4, 126.7, 126.3, 125.7, 123.3, 117.3, 102.3; FTIR (cm^{-1} : KBr): 2918, 2849, 1643, 1517, 1467, 1390, 1328, 1296, 1248, 1006, 924, 880, 764; HRMS(ESI) calcd for $C_{24}H_{24}NO_6 (M+H)^+$: 422.1598, Found: 422.1590.

IV: ^1H , ^{13}C NMR and HPLC dates of products

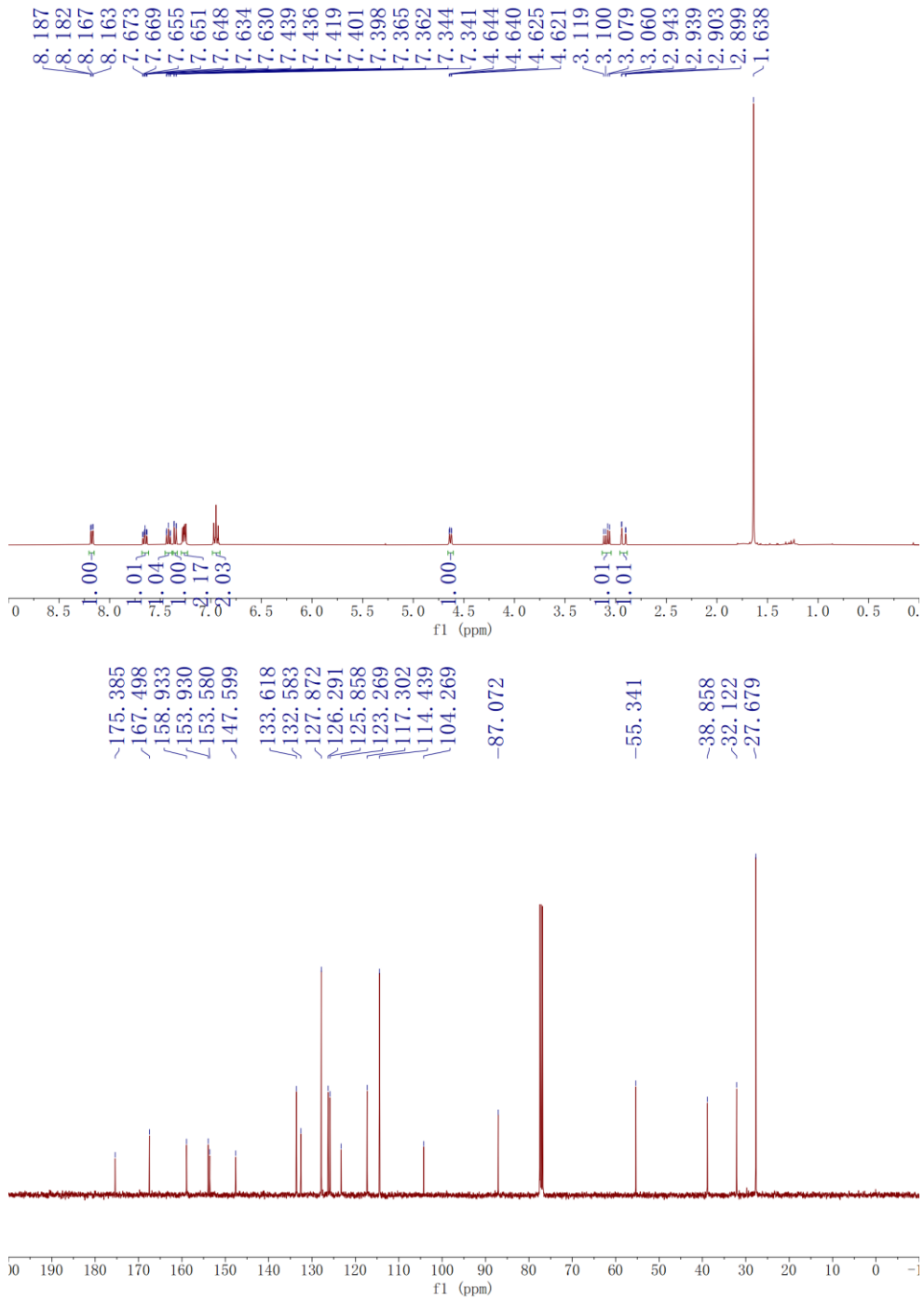


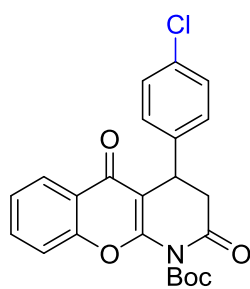
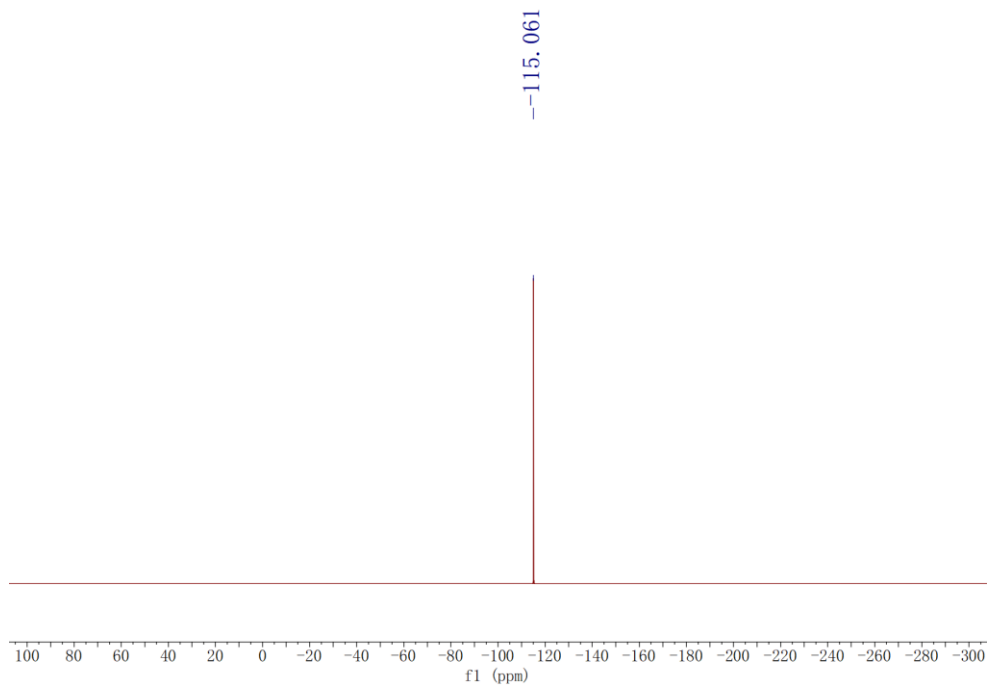
3a



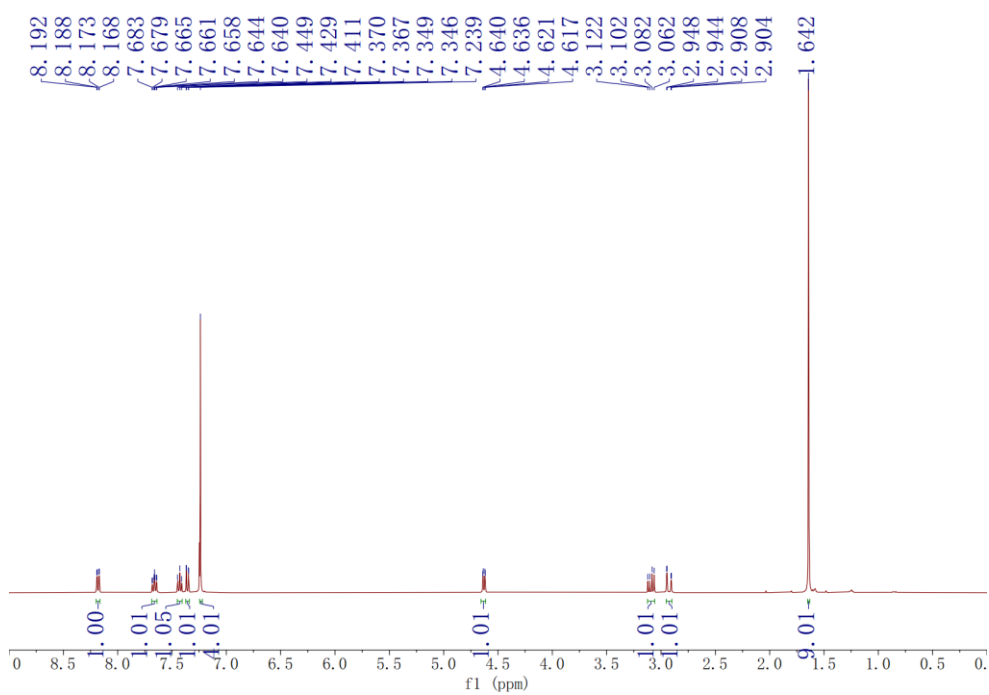


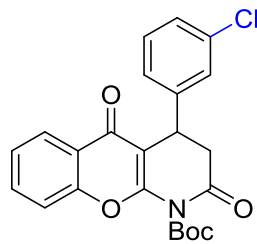
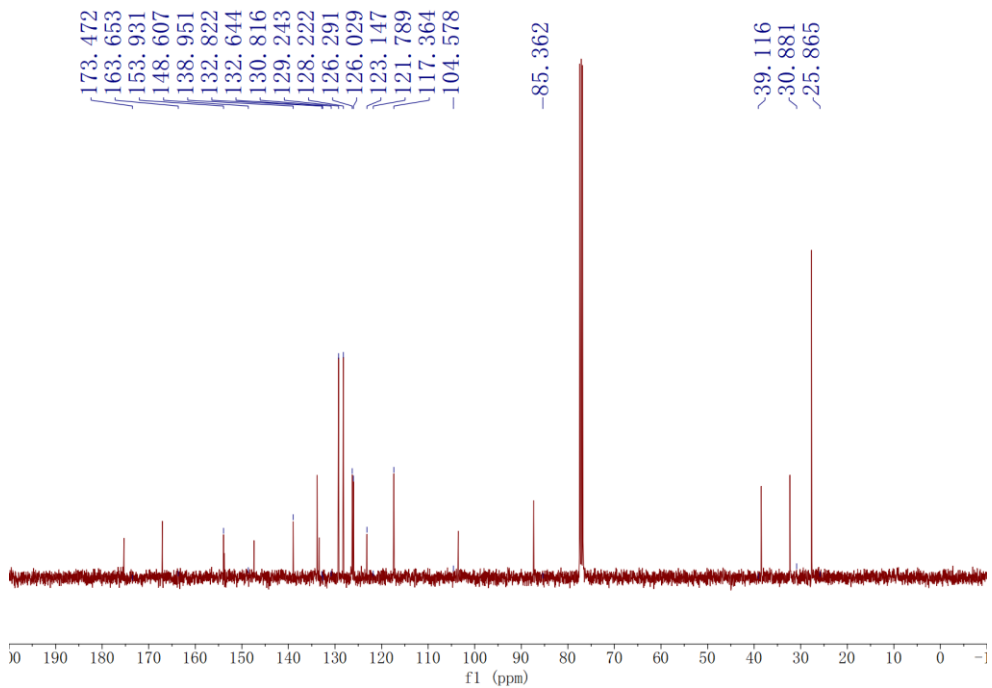
3b



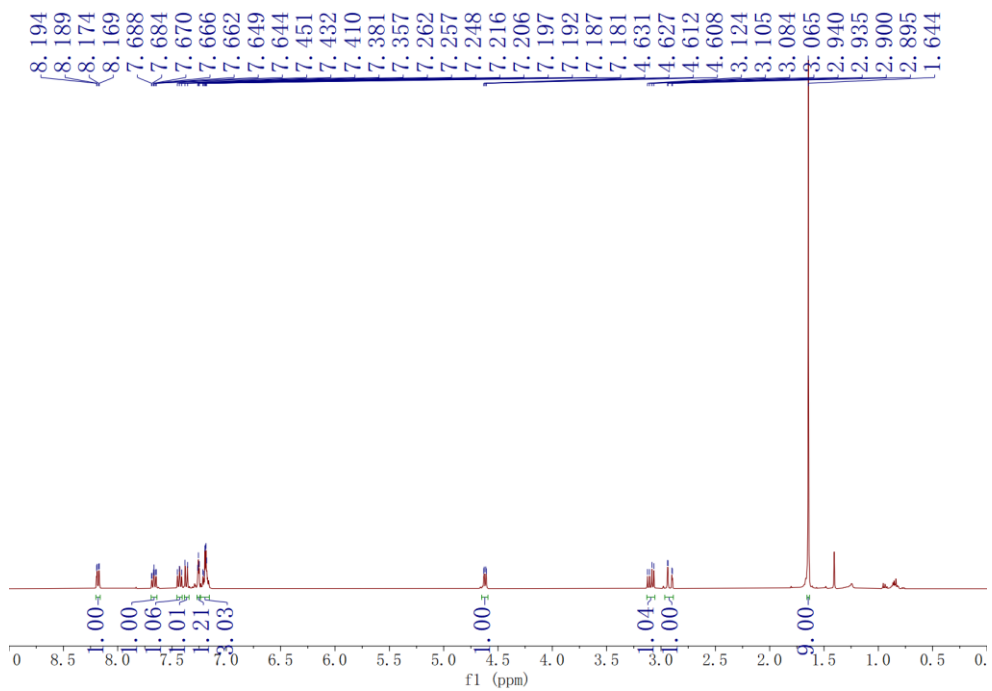


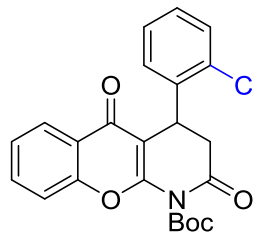
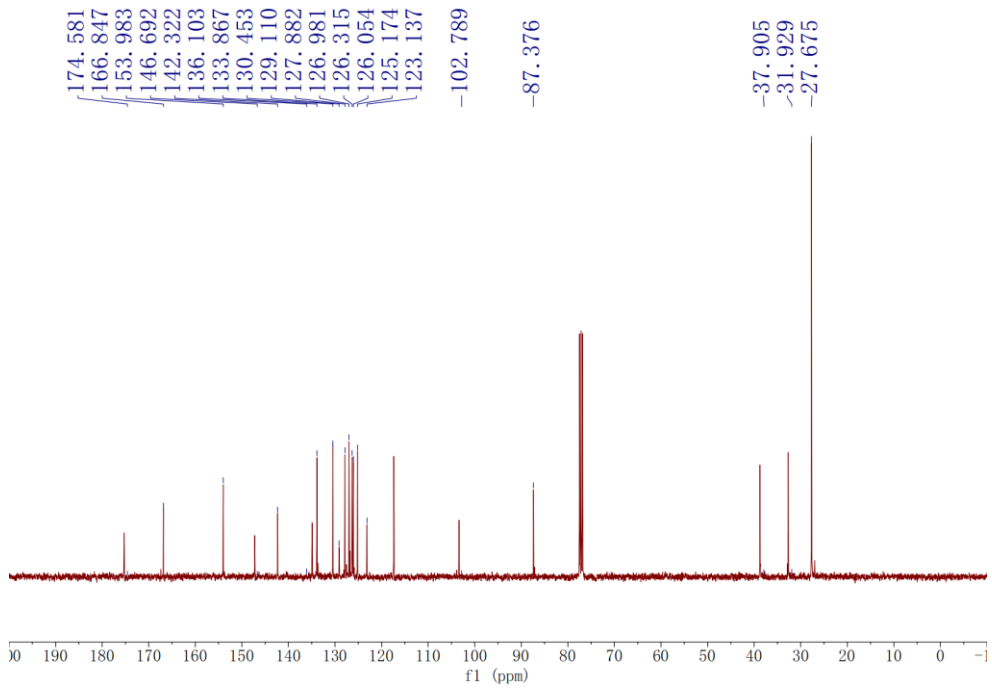
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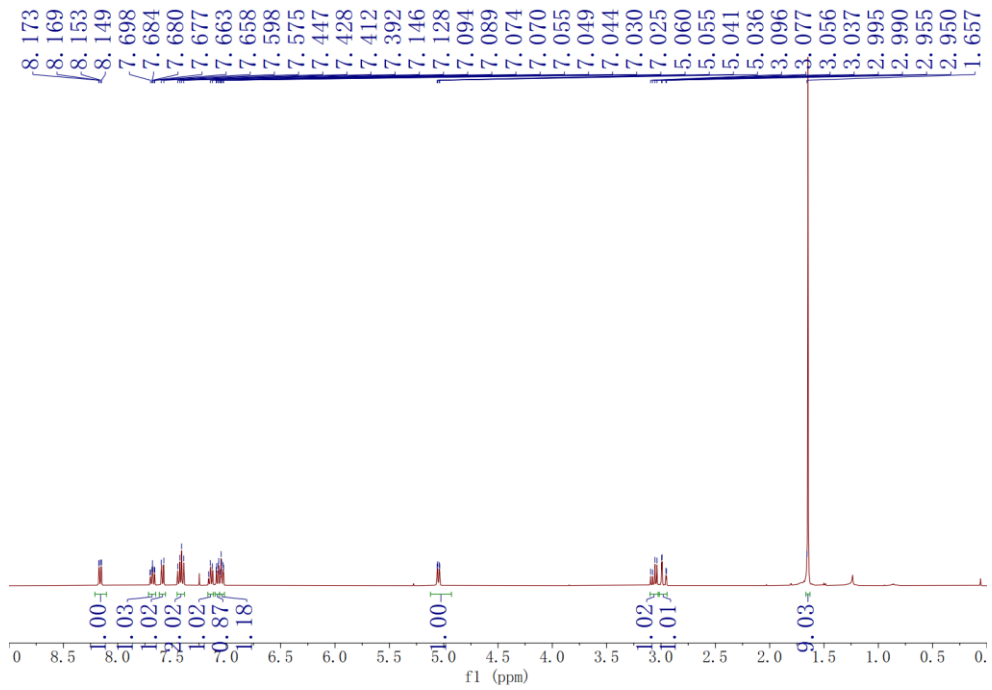


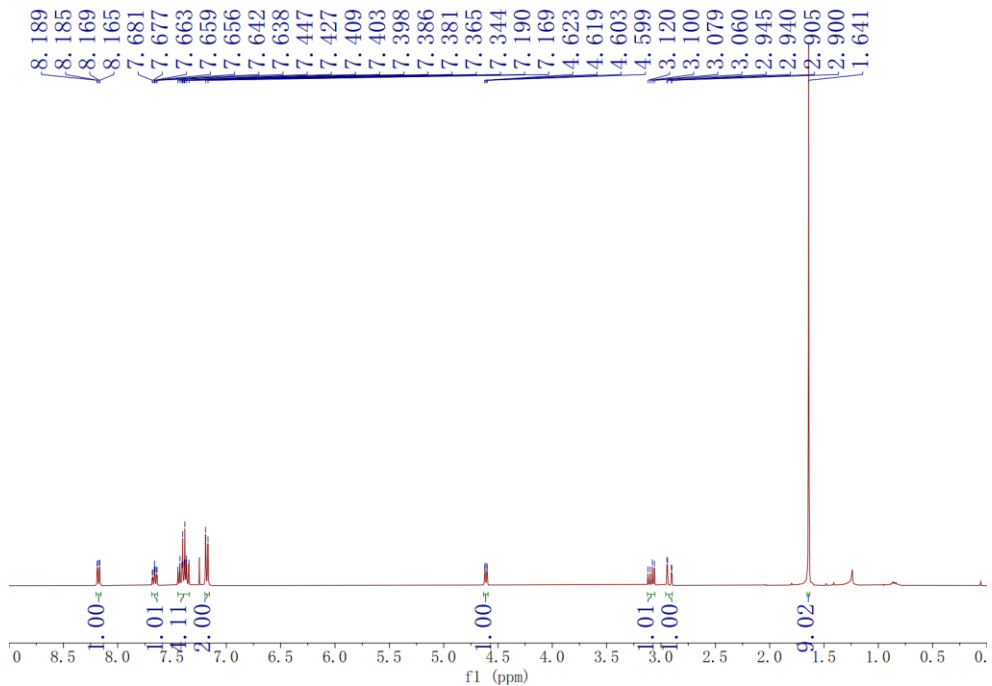
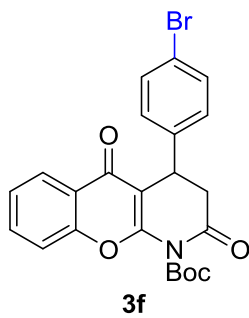
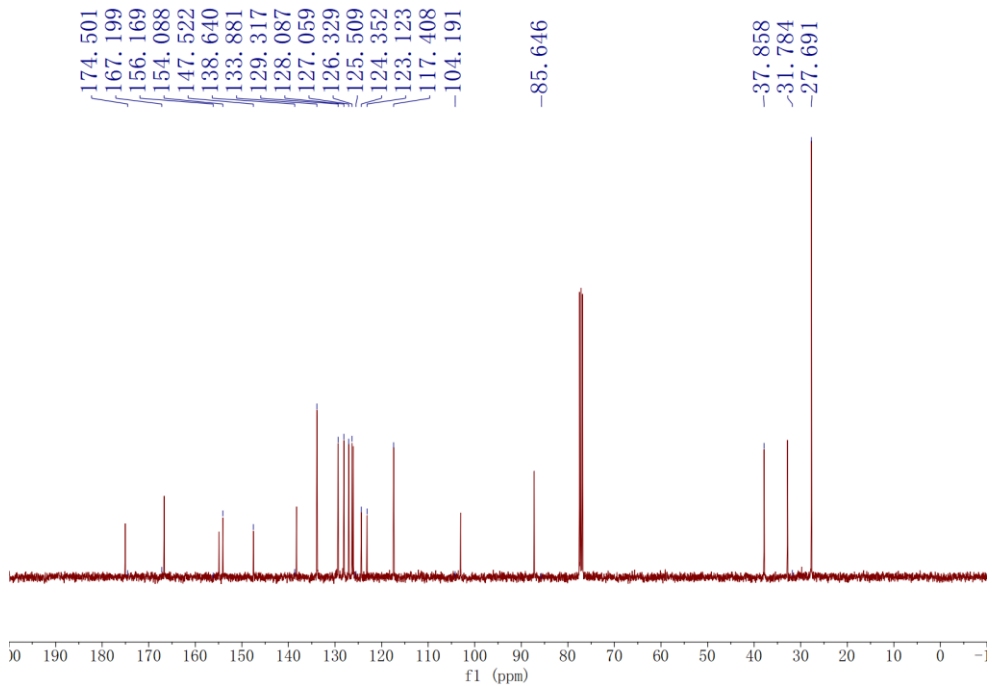
3d

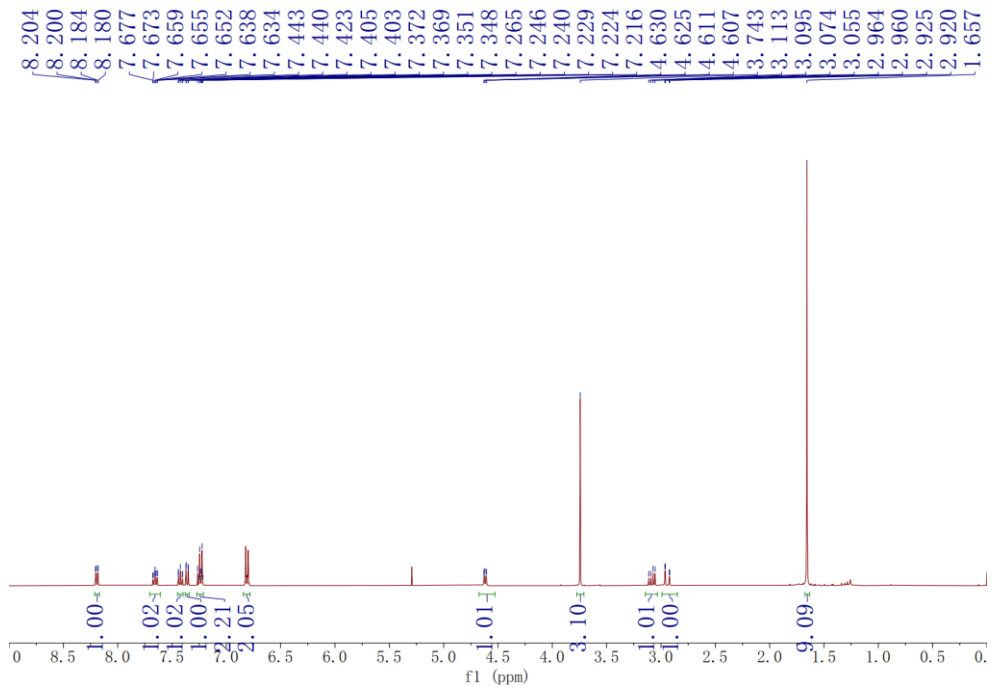
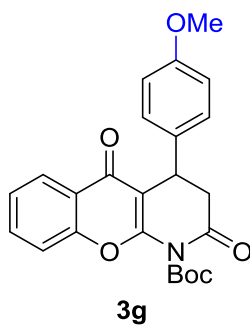
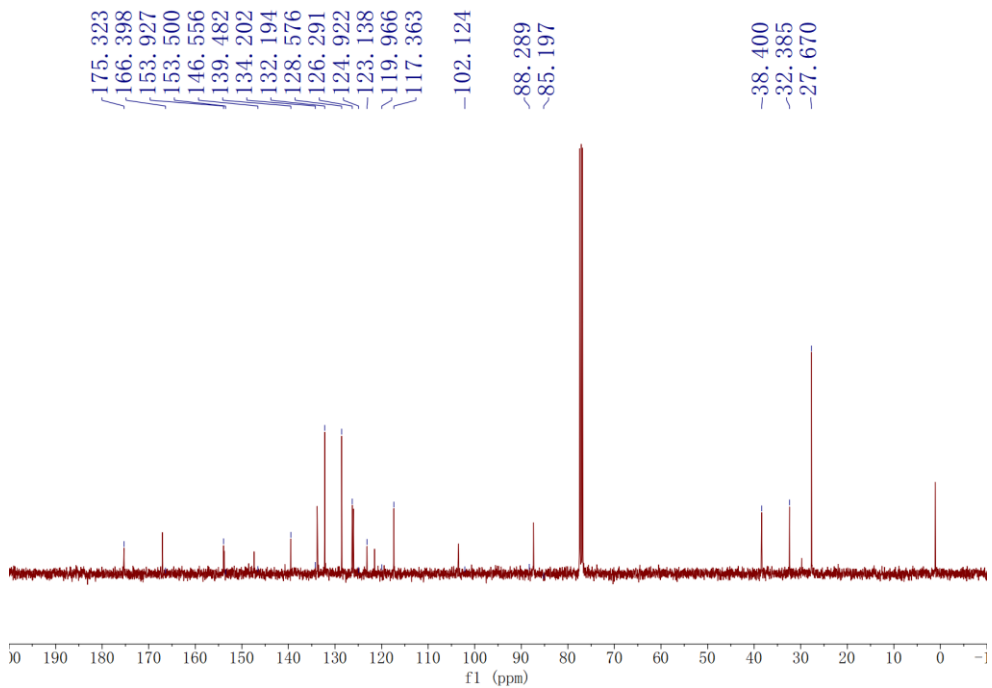


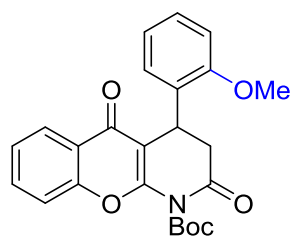
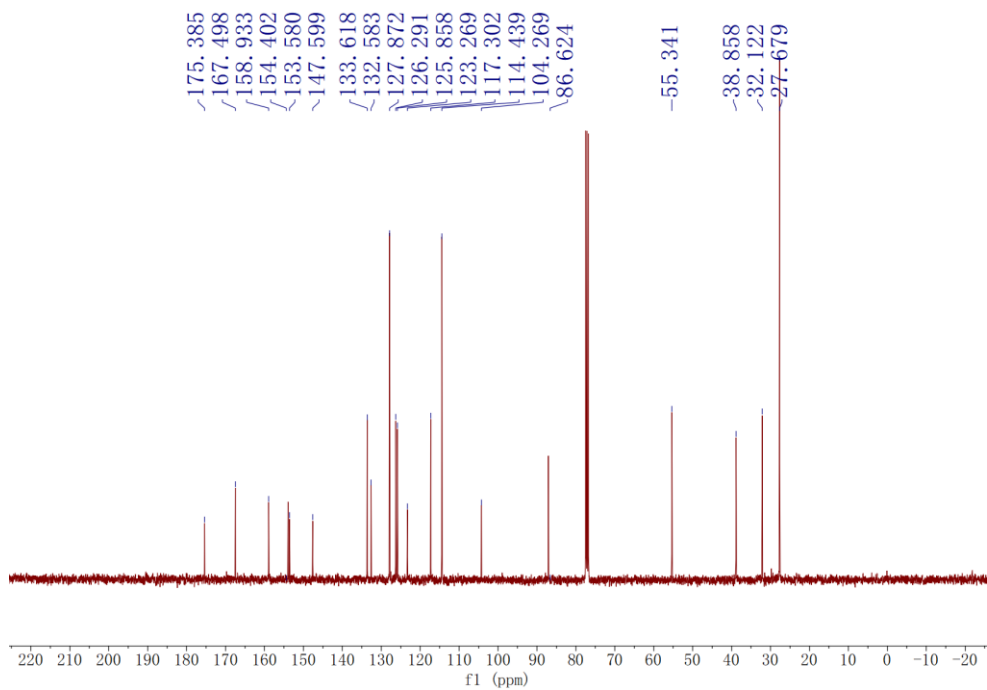


3e

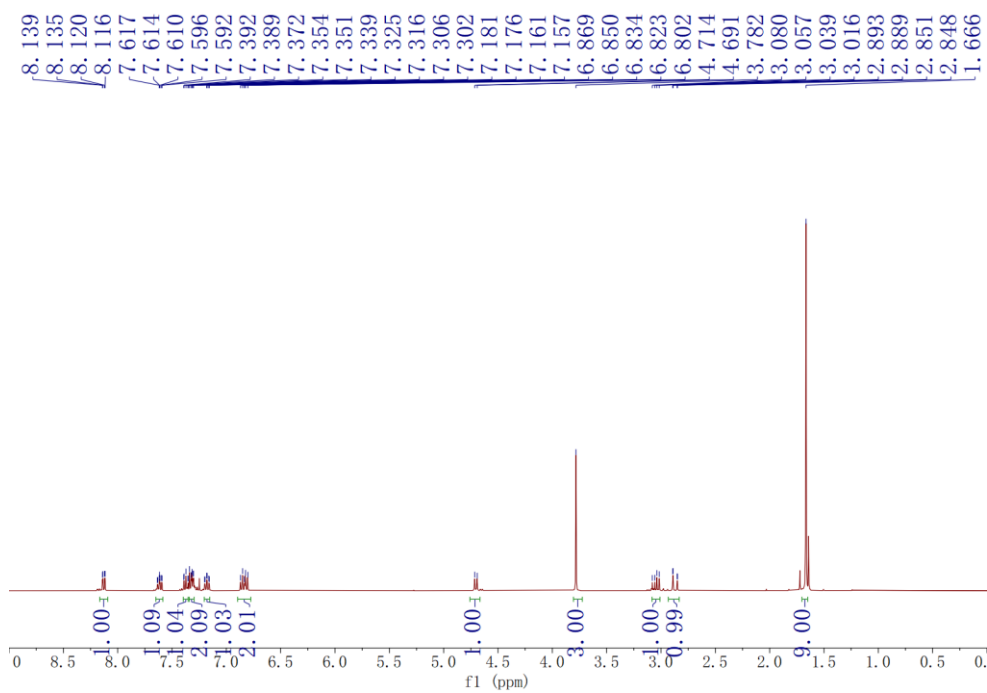


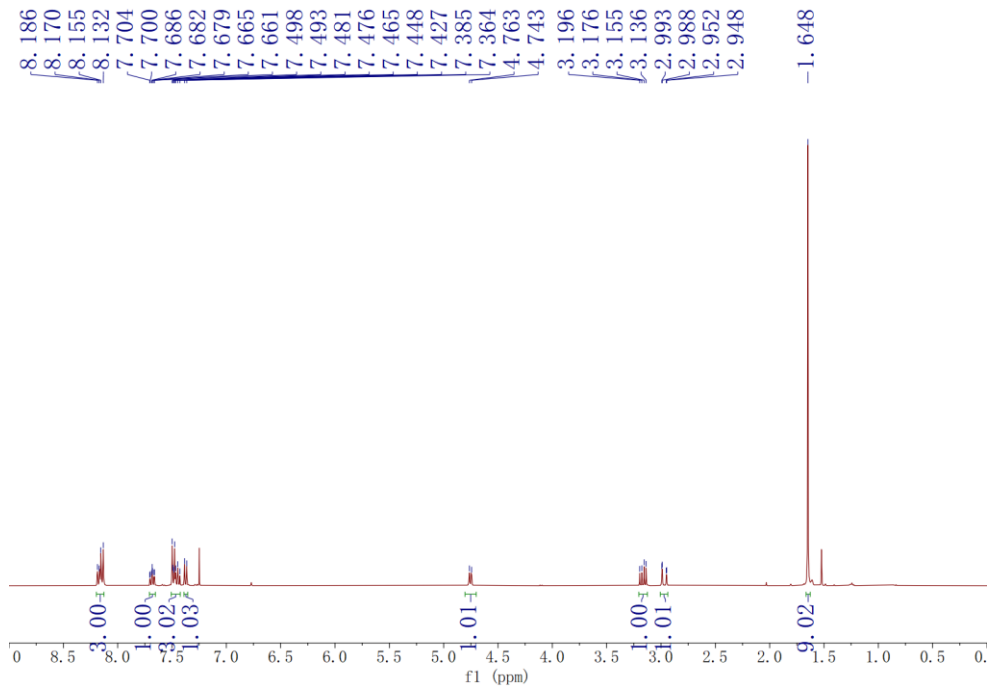
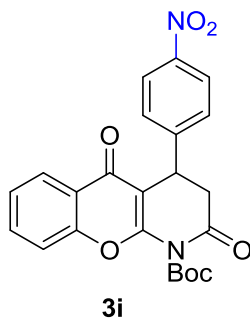
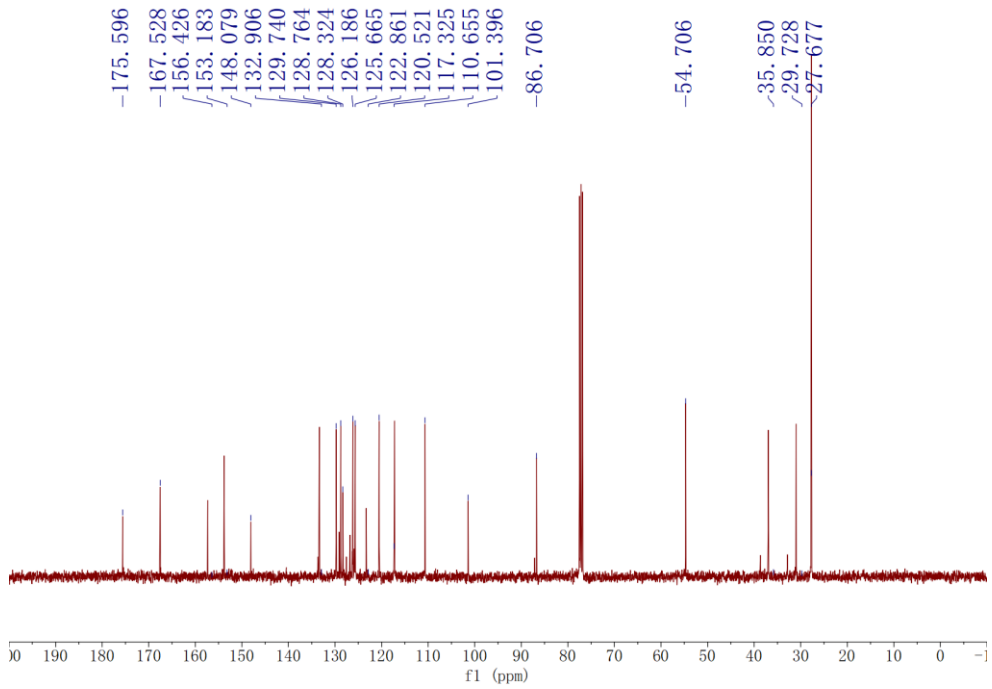


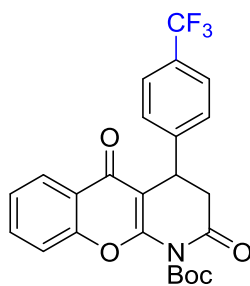
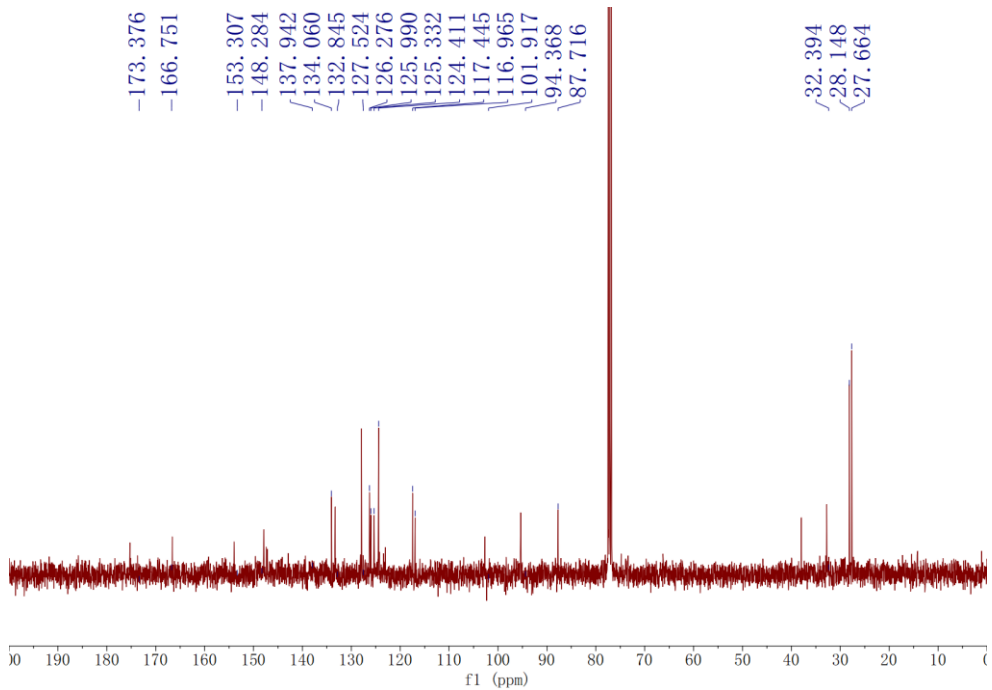




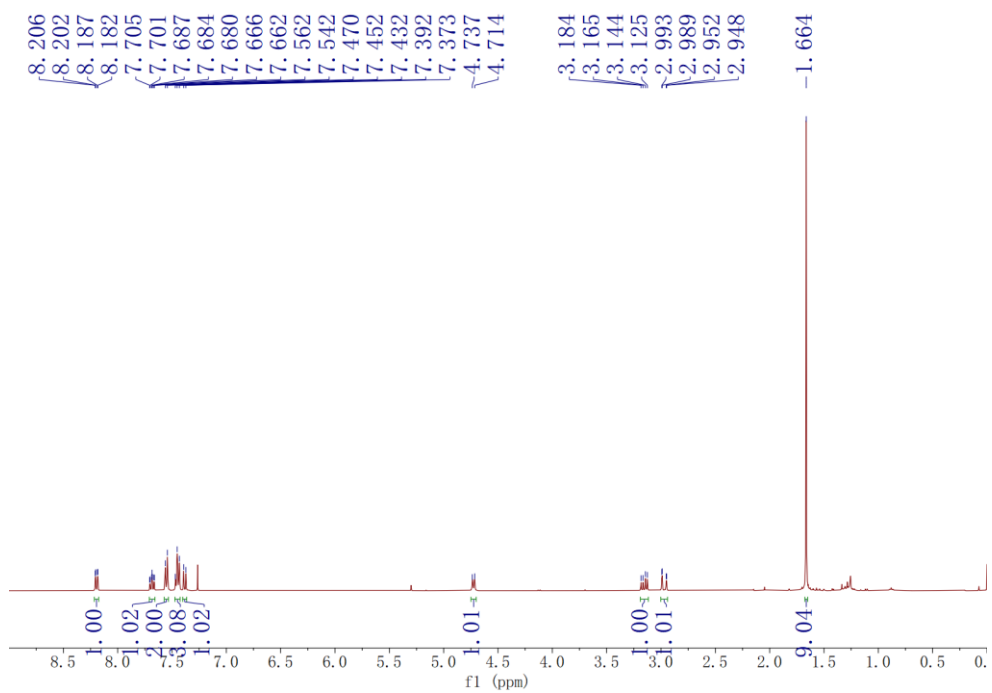
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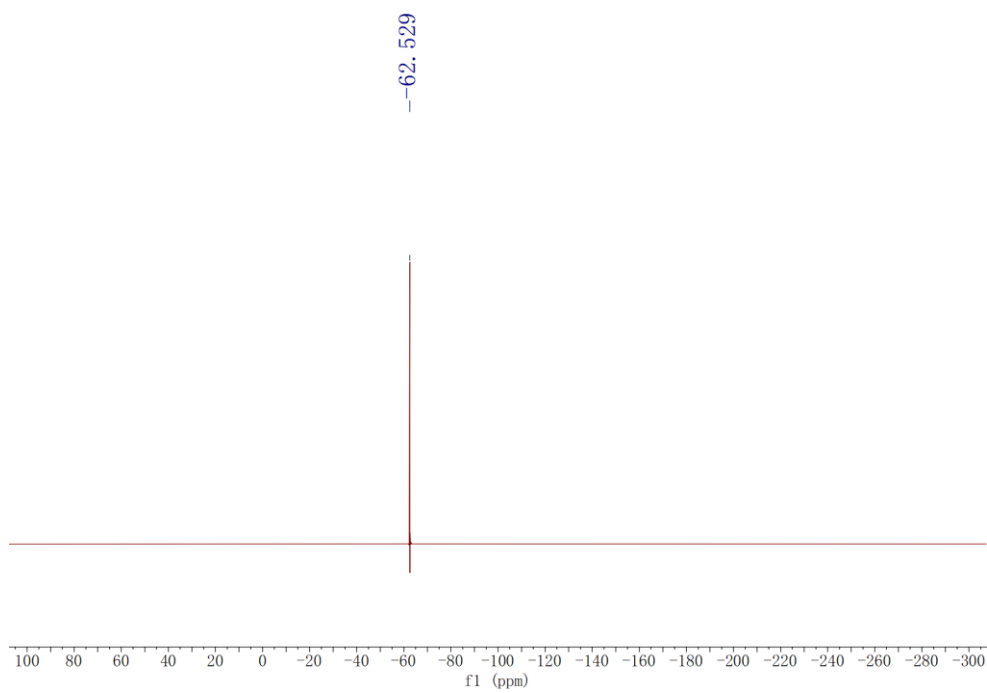
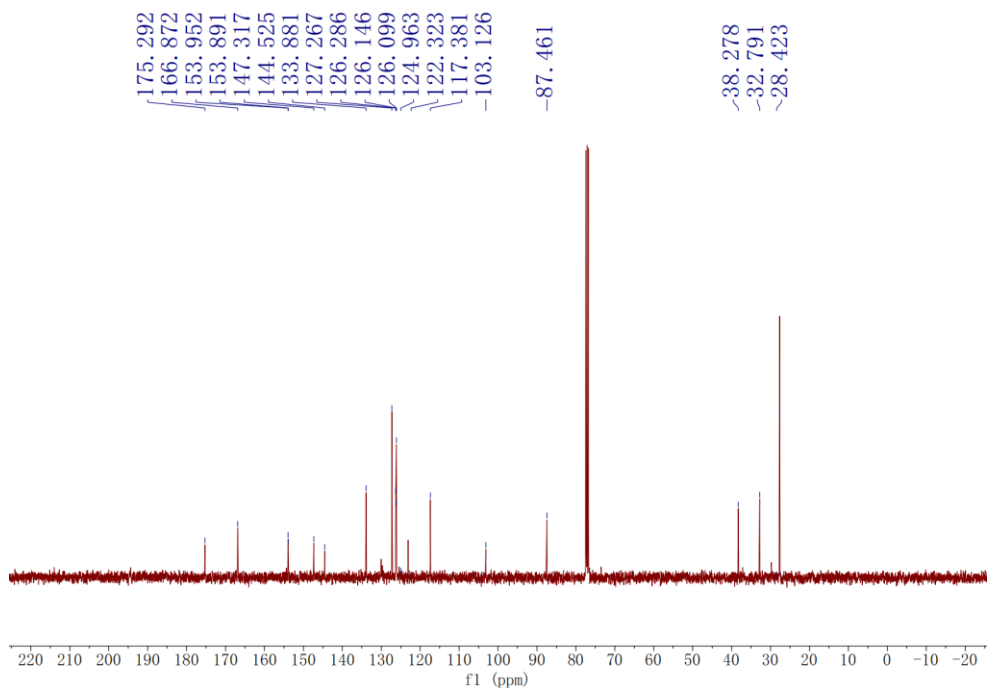


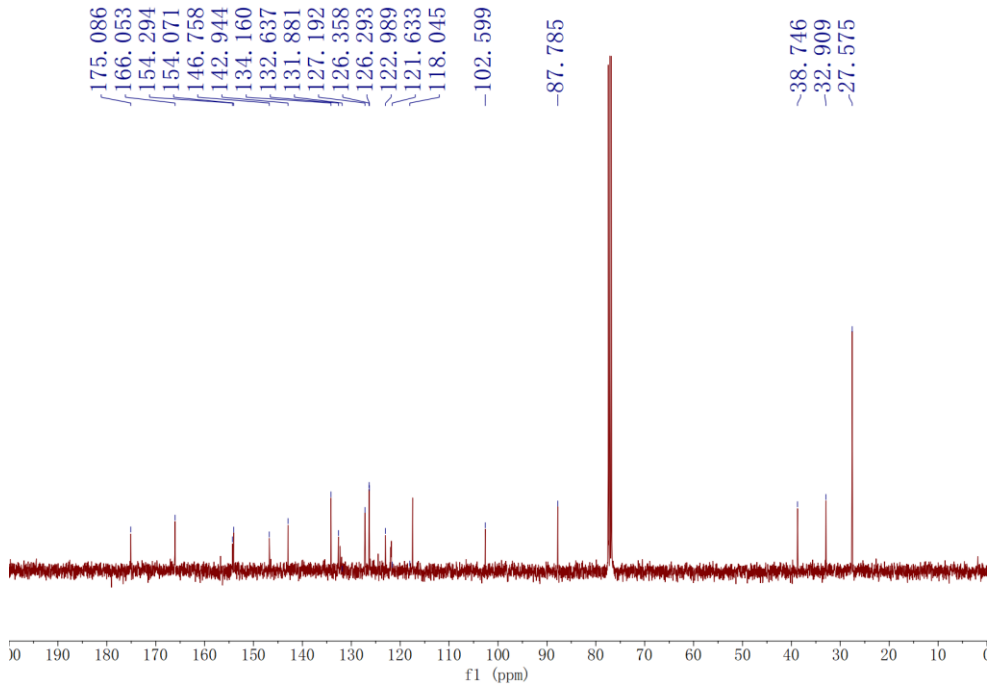
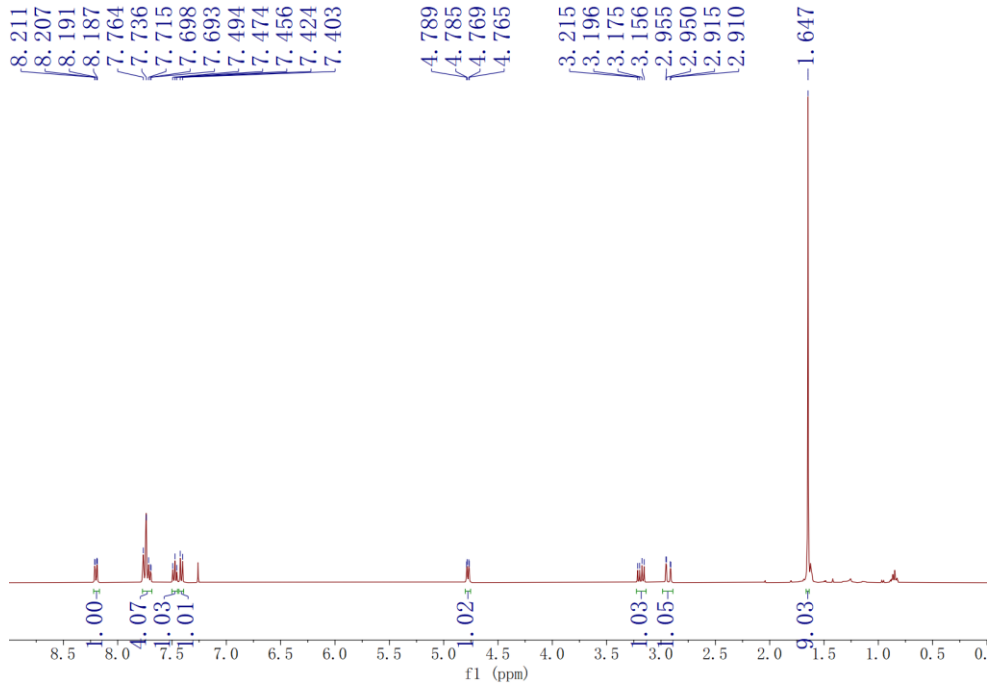
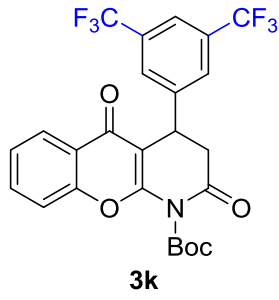


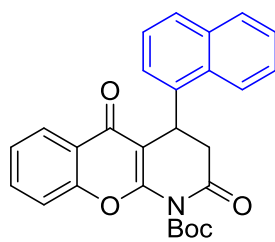
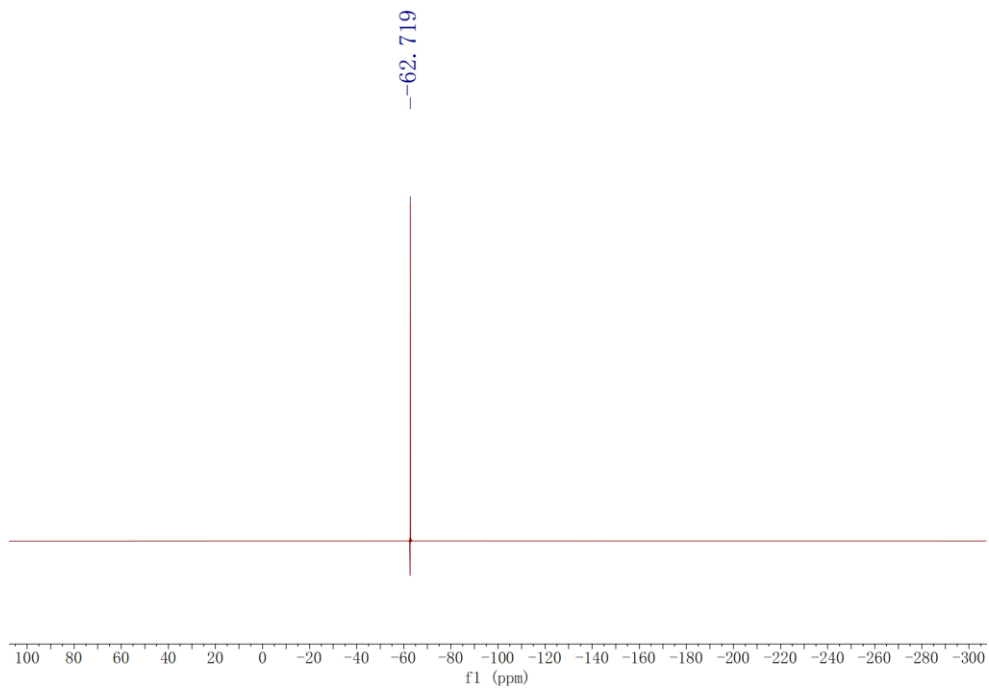


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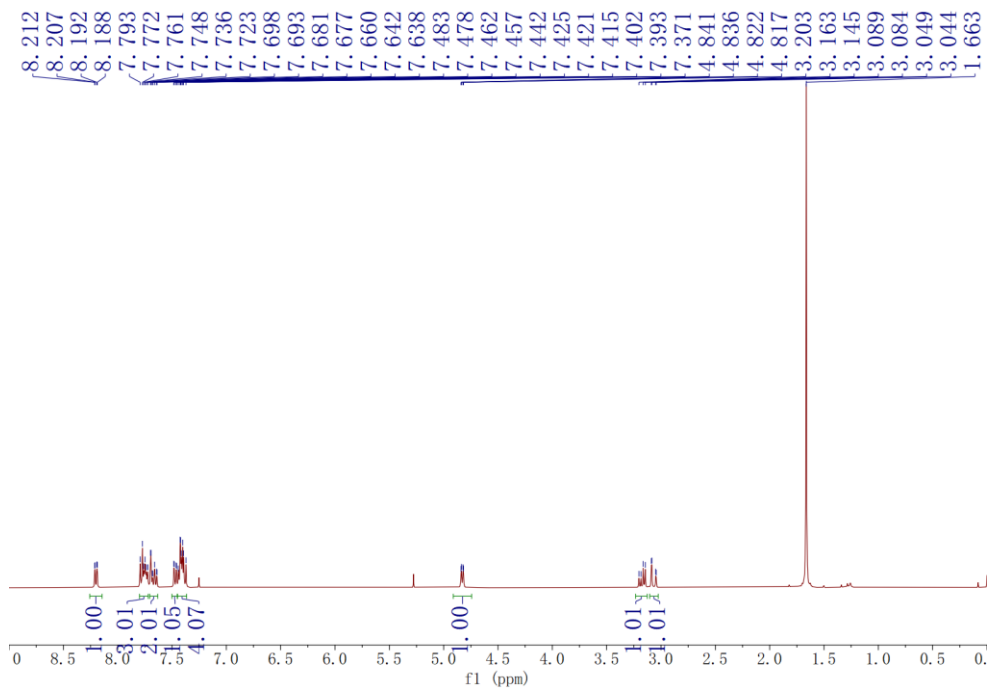


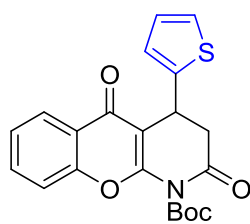
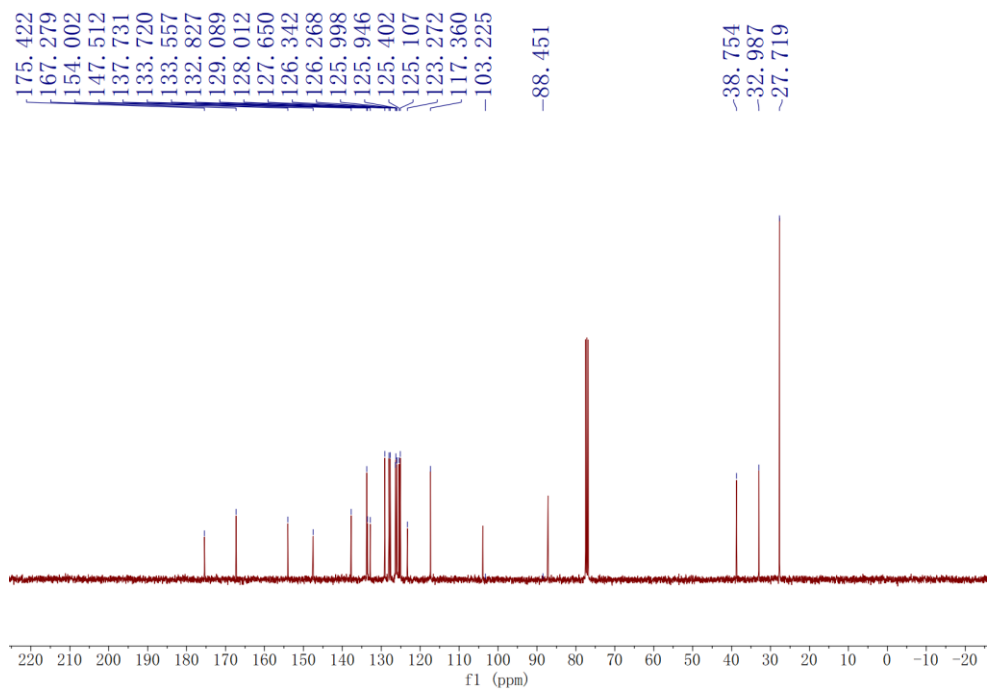




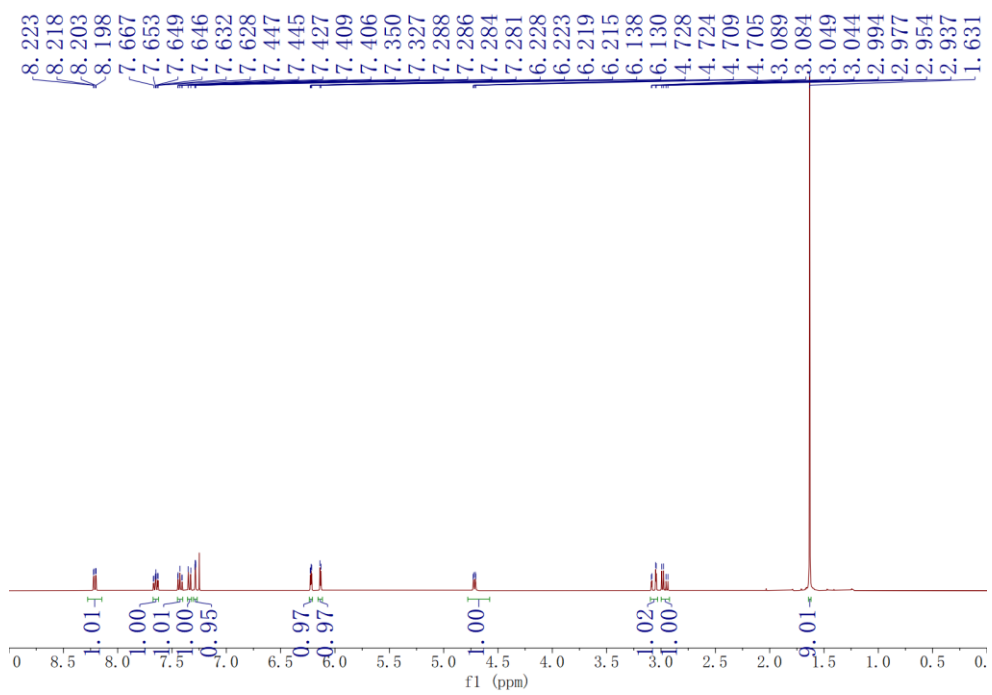


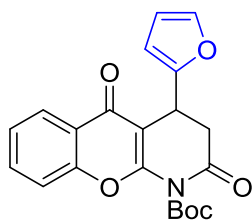
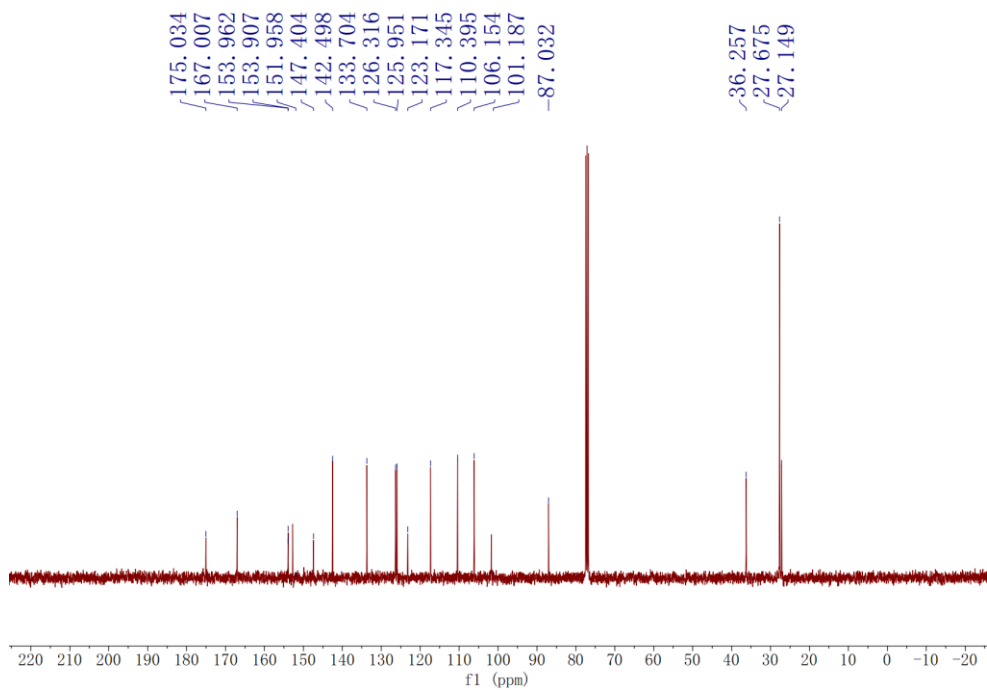
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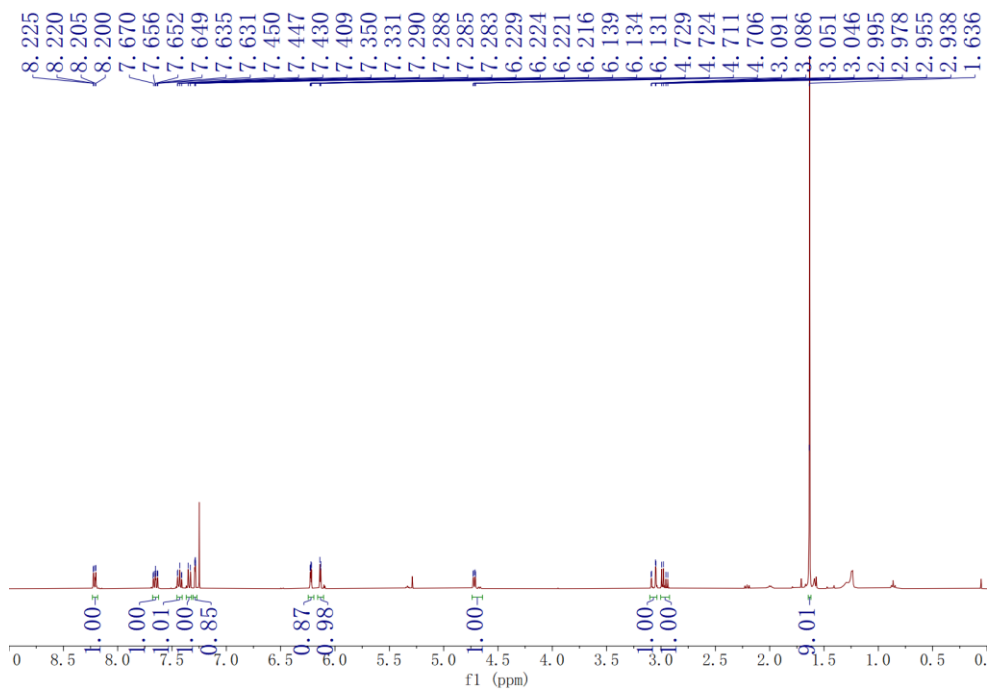


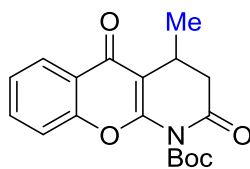
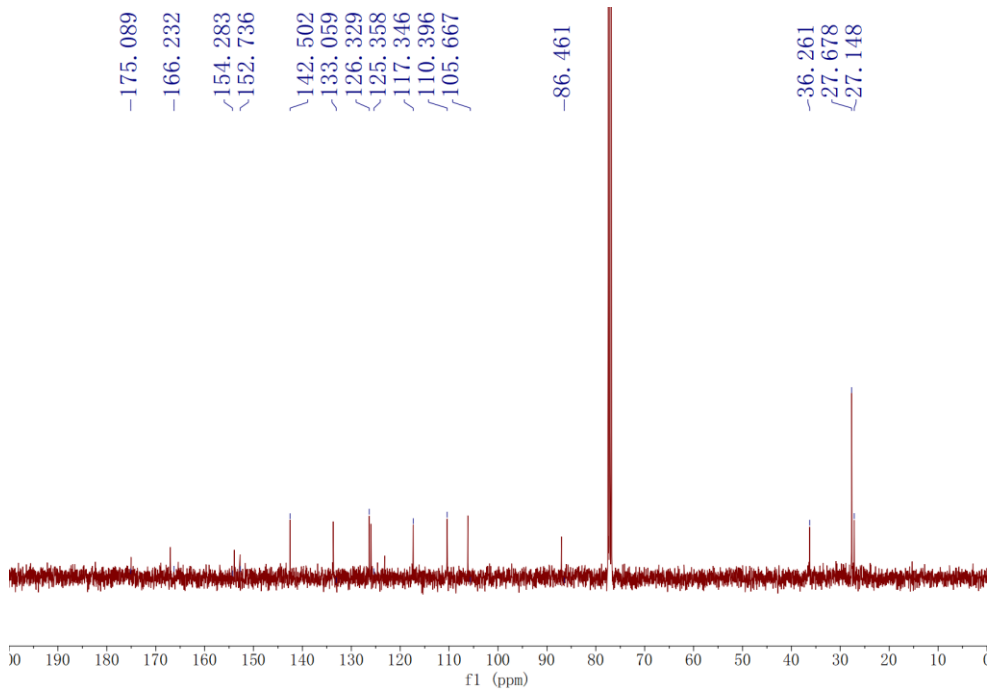
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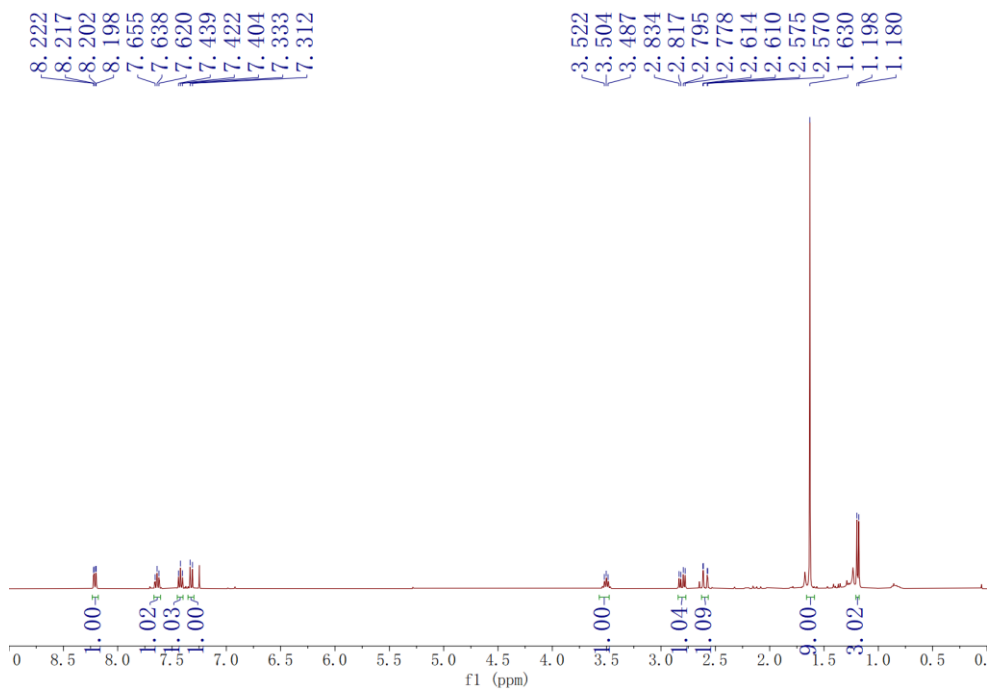


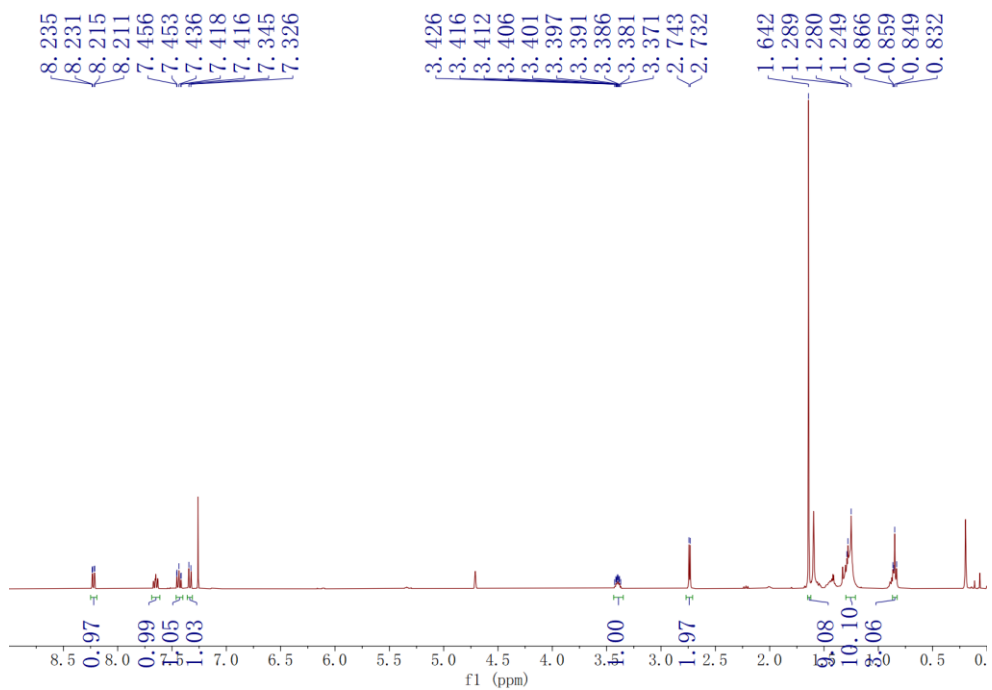
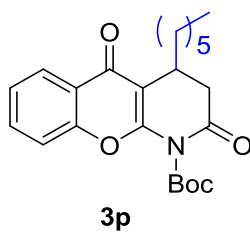
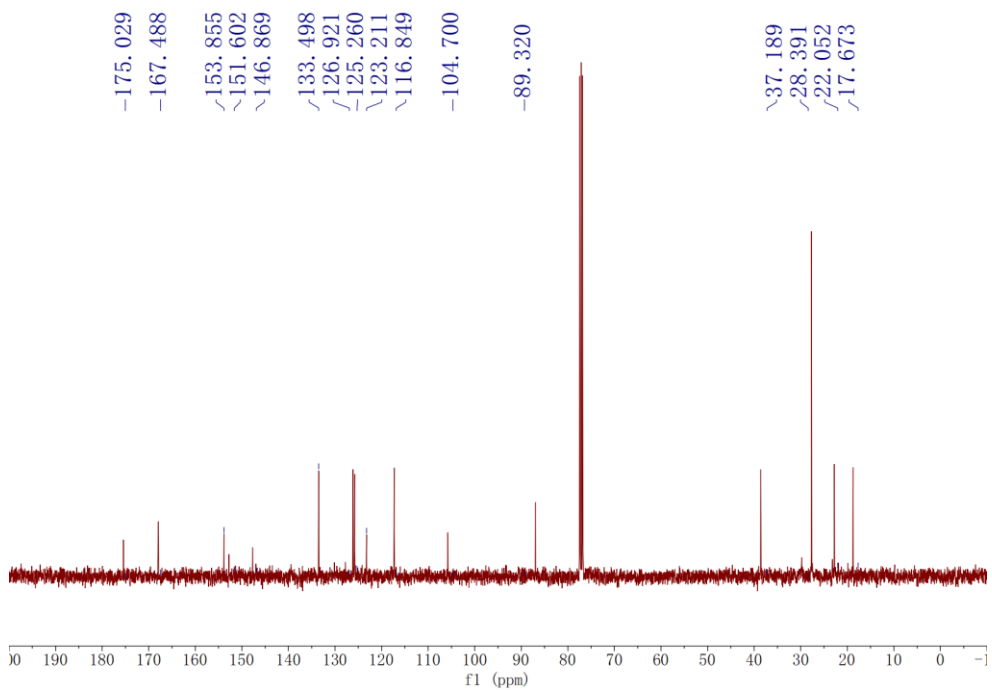
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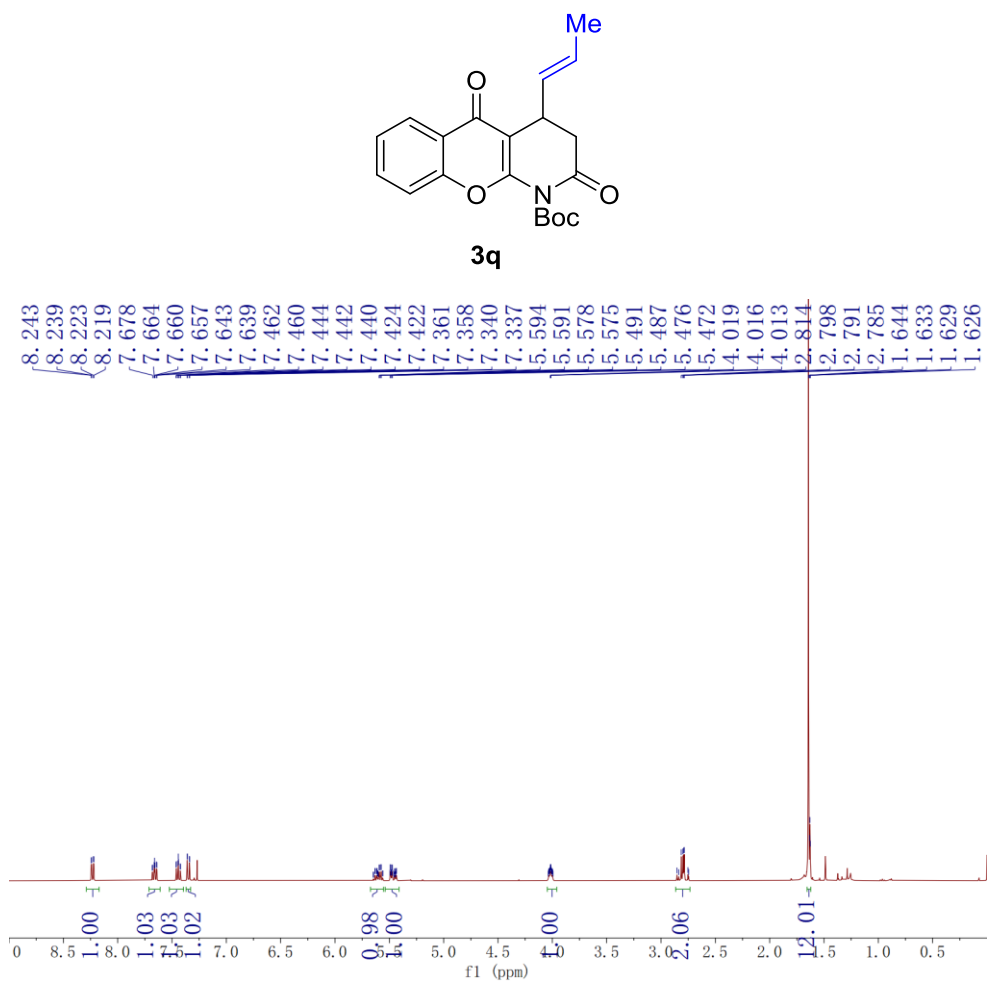
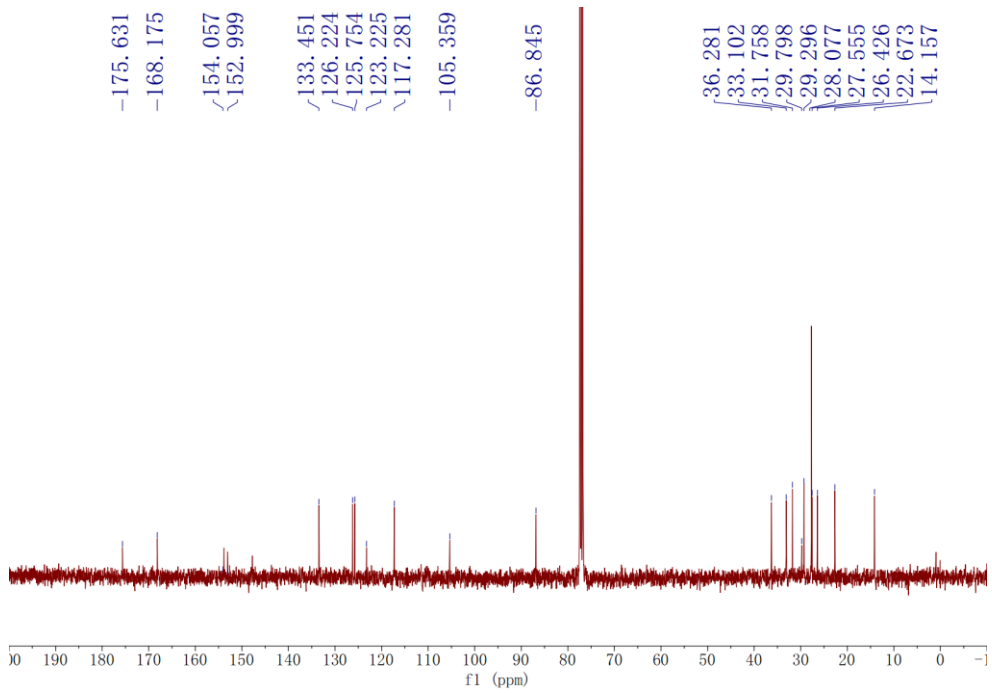


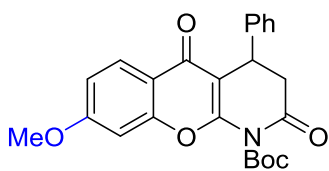
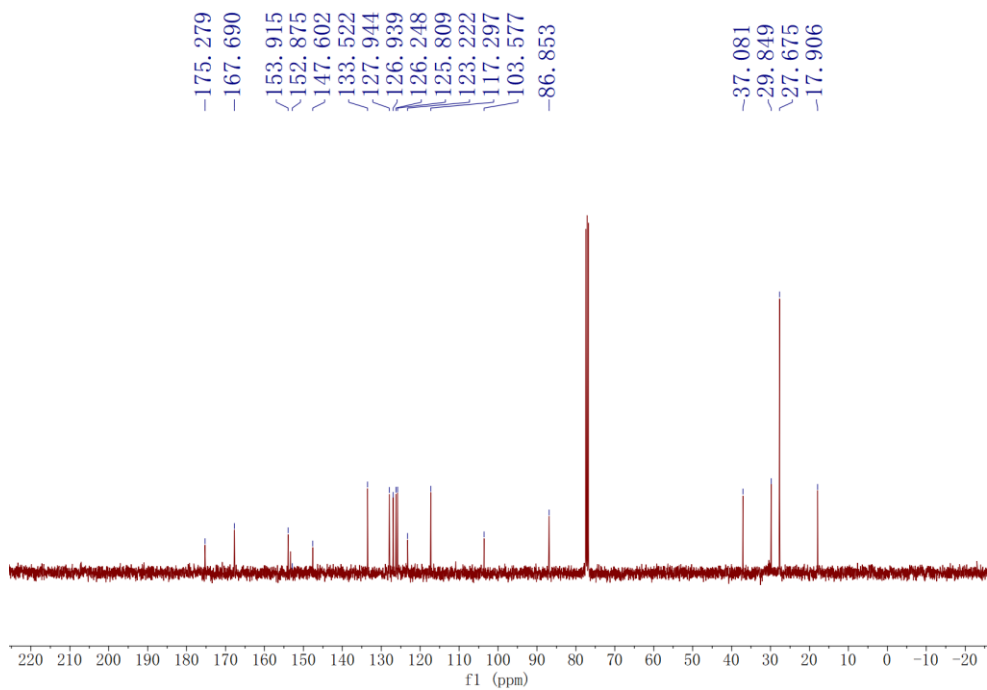


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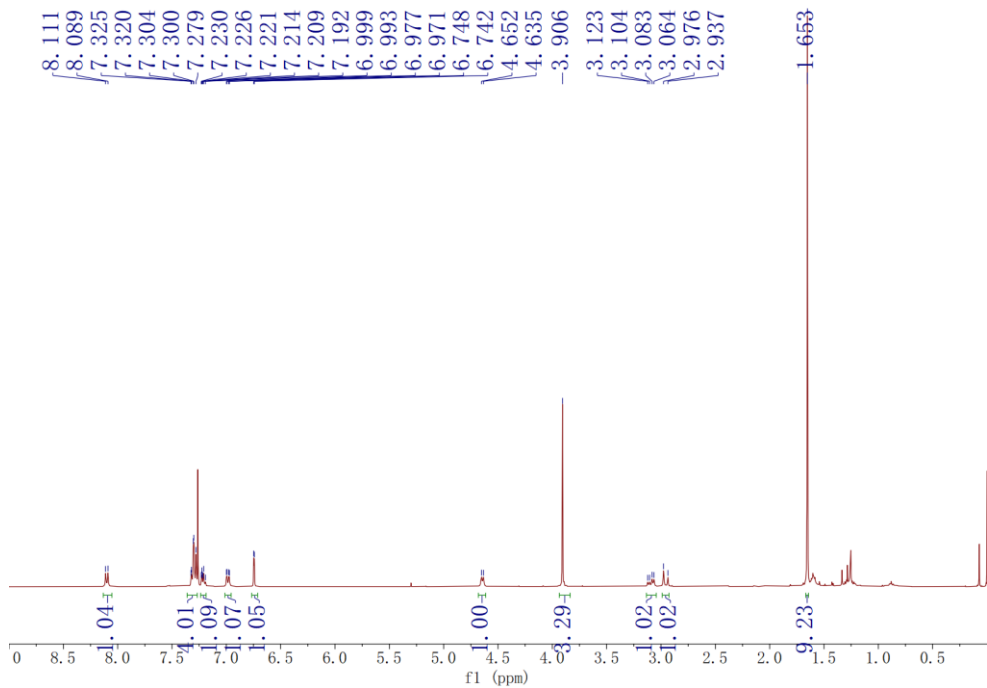


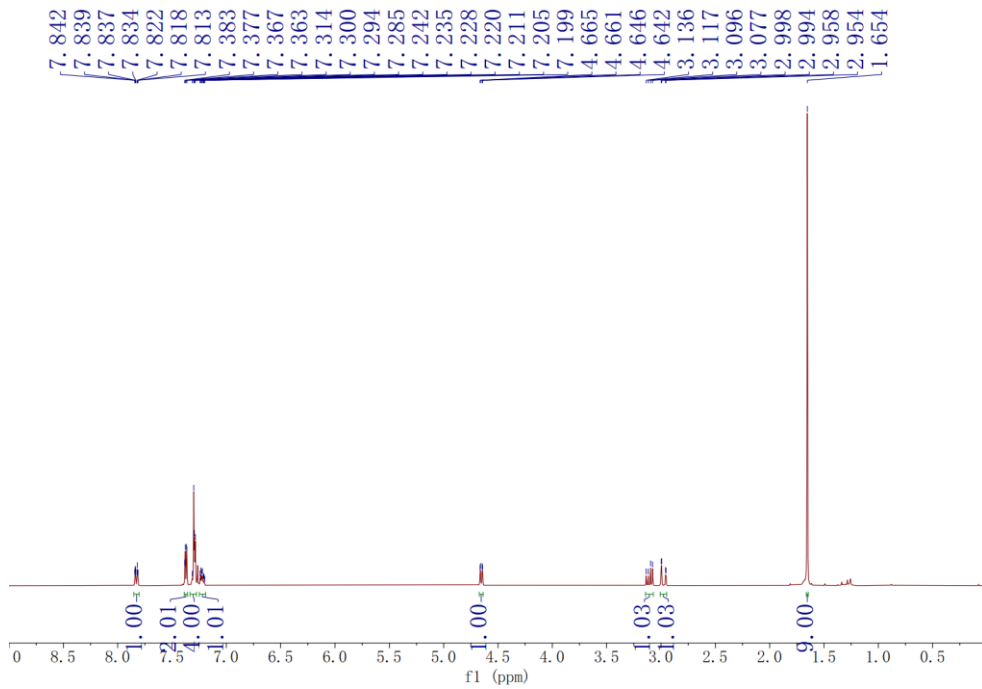
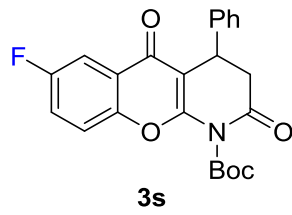
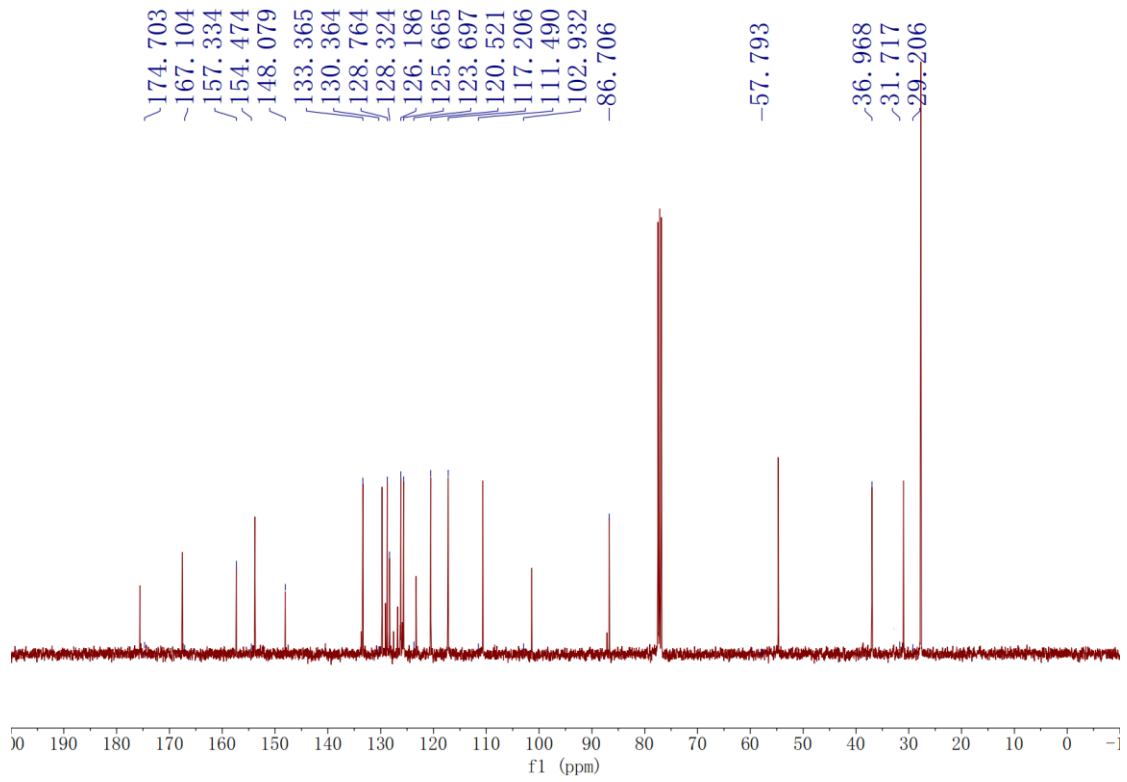


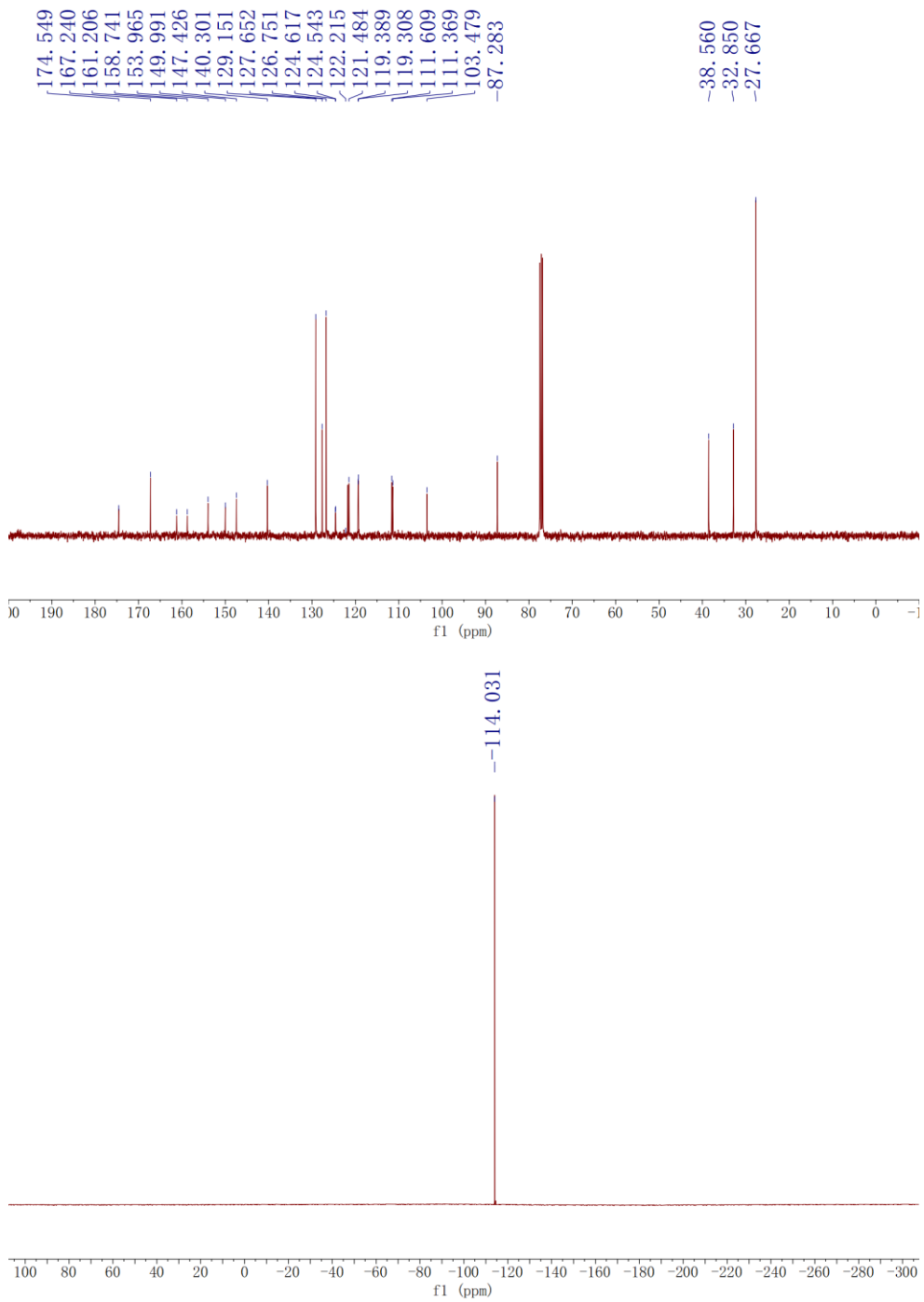


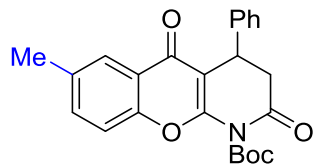


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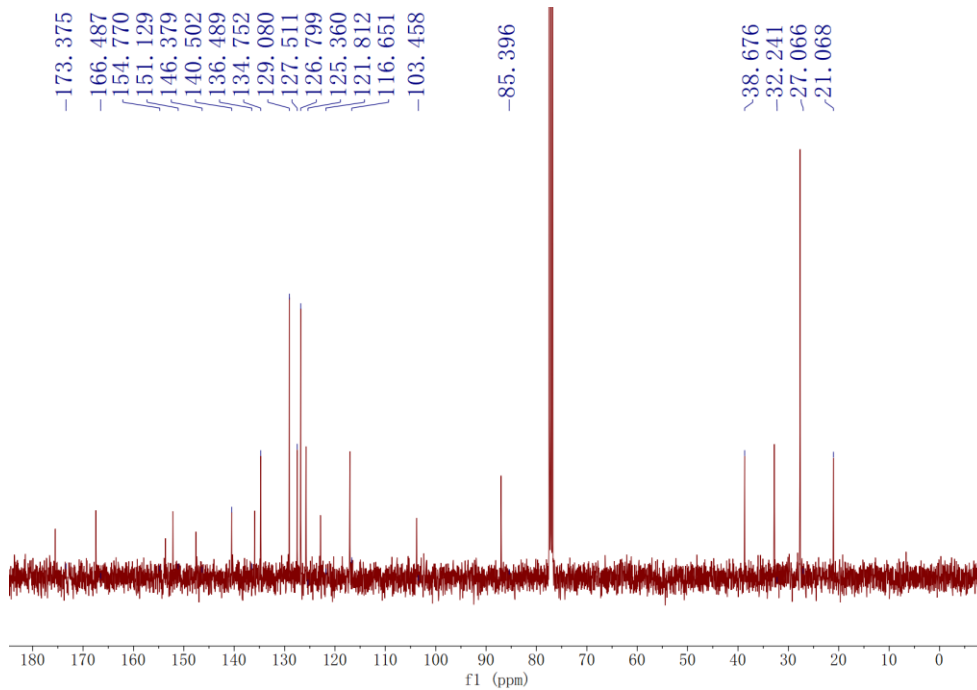
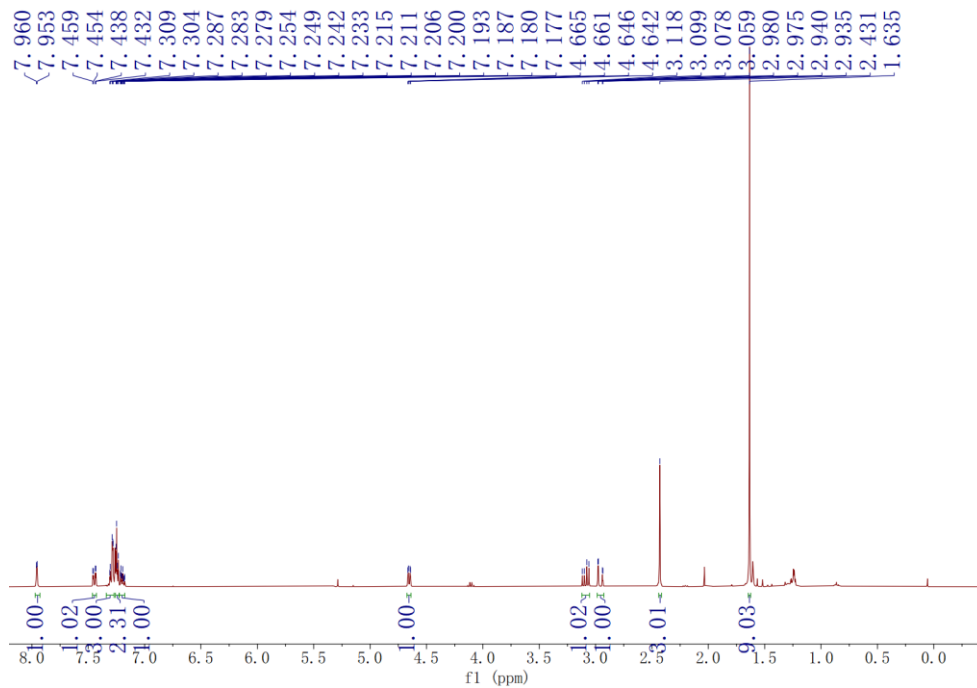


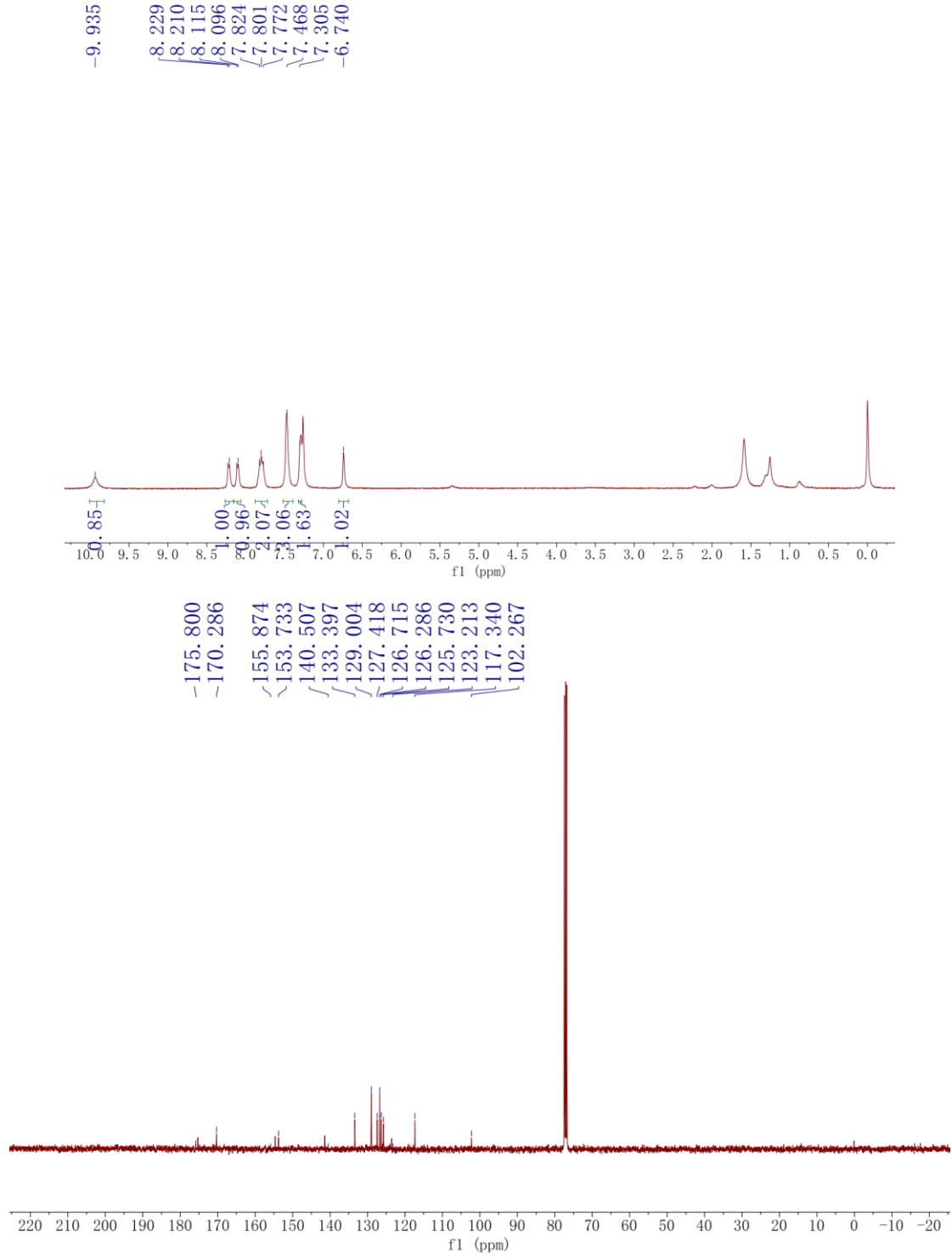
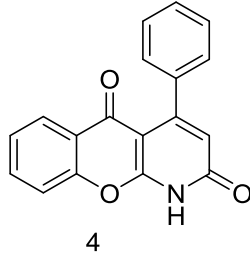


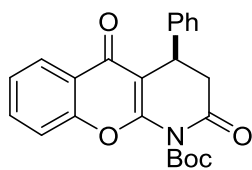




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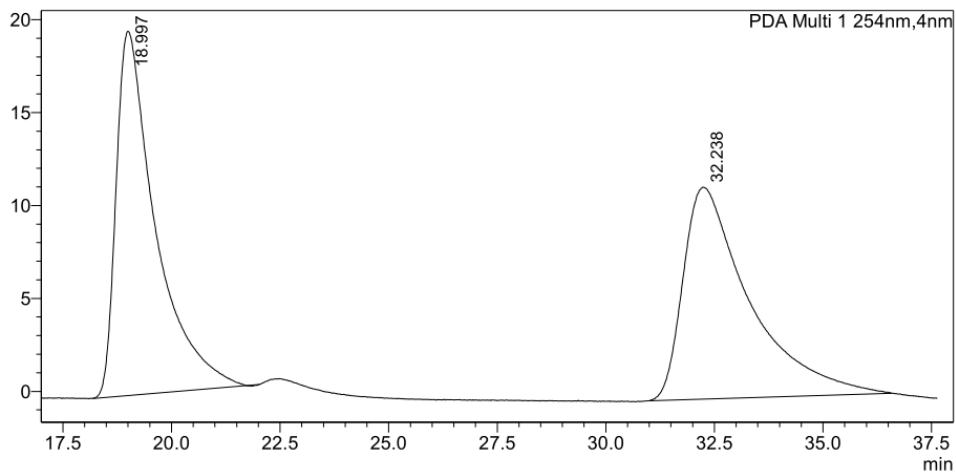






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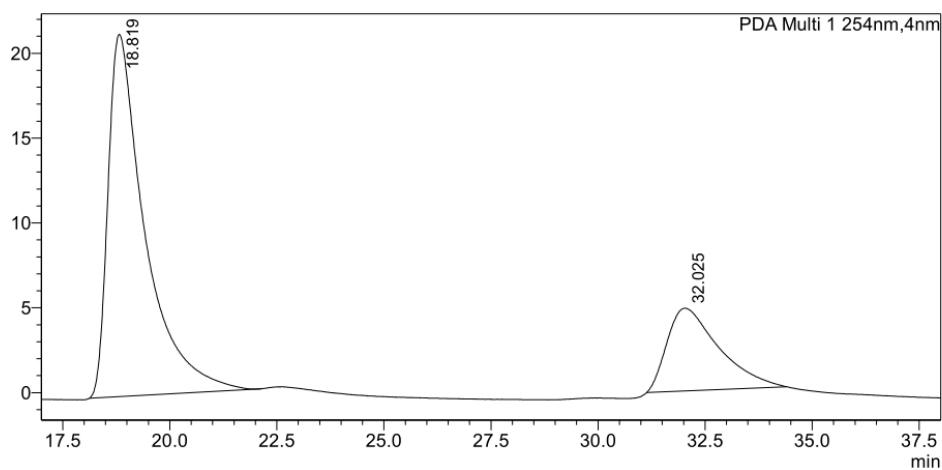
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	18.997	1235028	50.502	19596
2	32.238	1210498	49.498	11405
Total		2445527	100.000	31000

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	18.819	1278886	75.774	21349
2	32.025	408883	24.226	4873
Total		1687769	100.000	26222

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- (1) (a) C. B. Gilley, M. J. Buller, Y. Kobayashi, *Org. Lett.* **2007**, *18*, 3631; (b) Y. Liu, J. Chen, Z. Zhang, J. Qin, M. Zhao, W. Zhang, *Org. Biomol. Chem.*, **2016**, *14*, 7099; (c) S. Yuan, G. Gao, L. Wang, C. Liu, L. Wan, H. Huang, H. Geng, M. Chang. *Nat Comm.*, **2020**, *11*, 621.
- (2) (a) K. S. Levchenko, K. A. Chudov, E. V. Zinoviev, K. A. Lyssenko, D. U. Demin, N. O. Poroshin, P. S. Shmelin, E. P. Grebennikov, K. S. Levchenko *Tetrahedron Lett.* **2018**, *59*, 2788; (b) P. Tong, Z. Sun, S. Wang, Y. Zhang, Y. Li, *J. Org. Chem.* **2019**, *84*, 13967; (c) X. X. Xu, G. T. Wang, X. Zhao, X. K. Jiang, and Z. T. Li, *Soft Matter*, **2010**, *6*, 1246; (d) H. M. Sheldrake, S. Travica, L. Johansson, P. M. Loadman, M. Sutherland, L. Elsalem, N. Illingworth, A. J. Cresswell, T. Reuillon, S. D. Shnyder, S. Mkrtchian, M. Searcey, M. L. Sundberg, L. H. Patterson, and K. Pors, *J. Med. Chem.*, **2013**, *56*, 6273–6277.