Electronic Supplementary Material (ESI) for RSC Advances.

Metal-free synthesis of 1,N^6-ethenoadenine from N^6-propargyl-adenine *via* NIS mediated radical cascade reaction

Ruchun Yang,[a,b] Si Deng,[b] Xiangyou Dong,[b] Xian-Rong Song,[b] Hu Cai[a,*] Jiang Bai,[b] Qiang Xiao[b,*]

[a] Institute of Chemistry, Nanchang University, Jiangxi Province, Nanchang 330031, China. E-mail: caihu@ncu.edu.cn

[b] Institute of Organic Chemistry, Jiangxi Science & Technology Normal University, Key Laboratory of Organic Chemistry, Jiangxi Province, Nanchang 330013, China. E-mail: xiaoqiang@tsinghua.org.cn

Table of Contents

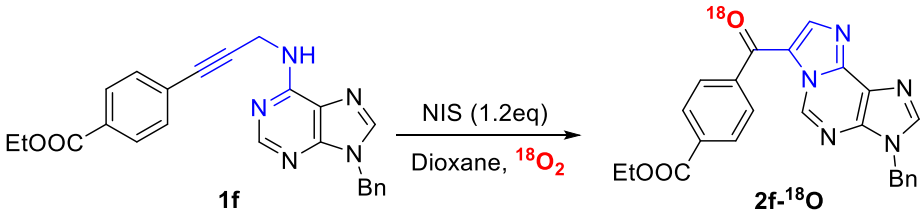
General Considerations

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. Other materials were prepared according to the literature [1]. Dioxane were dried over CaH_2, distilled under reduced pressure, and stored under an argon atmosphere over activated 4 Å molecular sieves in Teflon screwed Schlenk flasks before using them. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometers or Bruker 500 MHz spectrometers, chemical shifts are given in parts per million (ppm) relative to standard tetramethylsilane (0.00 ppm for ^{1} H NMR) or residual solvent peaks for ^{13} C NMR. HRMS was obtained using a Q-TOF instrument equipped with ESI source. Fluorescence spectra were measured with a Hitachi F-4600 fluorescence spectrophotometer. UV-vis absorption spectra were recorded on an Agilent 8453 UV/Vis spectrophotometer equipped with an MUΛ-165 UV lamp and MVL-210 visible lamp for photoirradiation. Standard column chromatography was performed on 200-300 mesh silica gel. using flash column chromatography techniques.

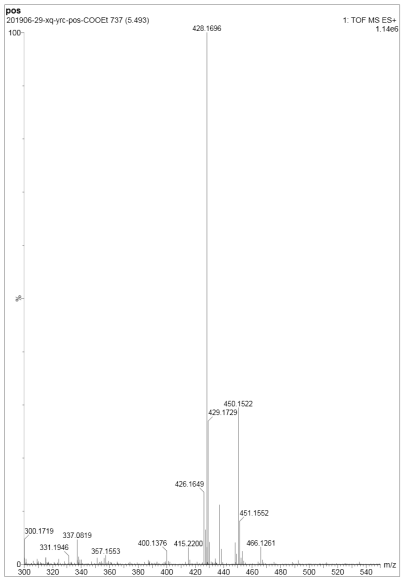
General procedure for cascade cyclization-oxidation reaction

NIS (27.0 mg, 0.12 mmol) was added to a stirred solution of **1a-1w** (0.1 mmol) in dioxane (2 mL). The resulting mixture was stirred at room temperature in the air and the progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction, the reaction mixture was quenched by slow addition of saturated sodium thiosulfate and extracted with EtOAc (3×5mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the corresponding product **2a–2w**.

$^{18}O_2$ experiment

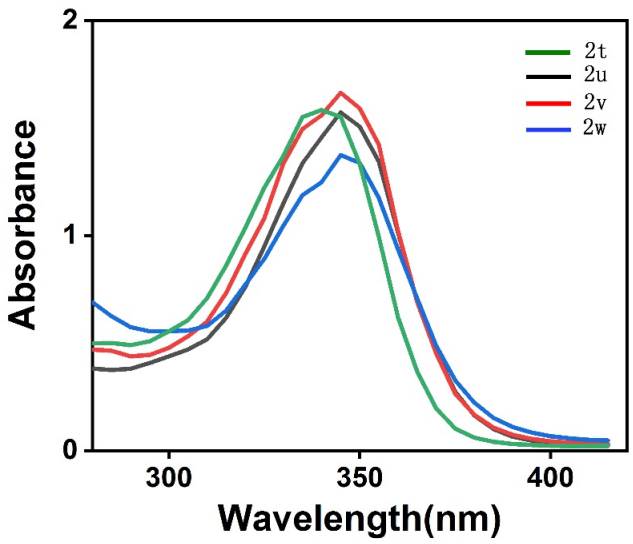


The product was detected by HRMS. HRMS (ESI, m/z): calcd for $C_{24}H_{20}N_5O_2{}^{18}O$: $[M+H]^+$ =428.1603; found: 428.1696.

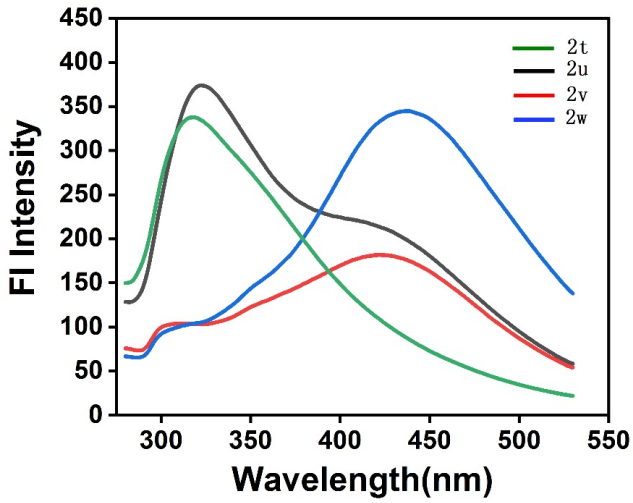


Ultraviolet spectrum and fluorescence emission spectrum of compound 2t-2w

Ultraviolet spectrum（$1*10^{-4}$mol/L in Methanol）



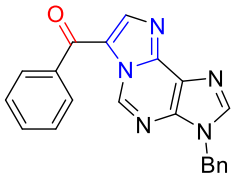
Fluorescence emission spectrum（$2*10^{-5}$mol/L in Methanol）



Excitation wavelength: 270nm
Emission wavelength: **2t**: 318nm, **2u**: 322nm, **2v**: 422nm, **2w**: 437nm

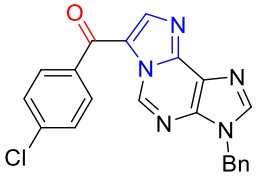
Characterization Data for Isolated Products

(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (phenyl)methanone (2a):



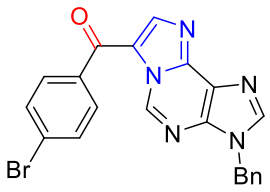
The resultant residue was purified by flash silica gel column chromatography to afford **2a** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.24 (s, 1H), 8.09 (s, 1H), 7.91 (d, *J* = 5.4 Hz, 2H), 7.66-7.56 (m, 3H), 7.40-7.34 (m, 5H), 5.56 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.9, 146.3, 145.3, 142.1, 141.9, 138.8, 137.8, 136.1, 132.6, 129.2, 128.9, 128.8, 128.7, 127.8, 123.6, 123.2, 48.1. HRMS (ESI, m/z): calcd for $C_{21}H_{16}N_5O$: $[M+H]^+$= 354.1349; found: 354.1347.

(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (4-chlorophenyl) methanone (2b):



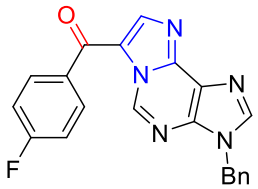
The resultant residue was purified by flash silica gel column chromatography to afford **2b** as a white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.14 (s, 1H), 8.70 (s, 1H), 8.34 (s, 1H), 8.00 – 7.87 (m, 2H), 7.75 – 7.62 (m, 2H), 7.42 – 7.10 (m, 6H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 182.9, 146.3, 145.1, 144.2, 142.1, 137.7*2, 137.4, 137.0, 131.3, 129.4, 129.3, 128.4, 127.9, 123.6, 123.0, 47.5. HRMS (ESI, m/z): calcd for $C_{21}H_{15}ClN_5O$: $[M+H]^+$= 388.0960; found: 388.0964

(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (4-bromophenyl) methanone (2c):



The resultant residue was purified by flash silica gel column chromatography to afford **2c** as a white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.13 (s, 1H), 8.70 (s, 1H), 8.33 (s, 1H), 7.94 – 7.76 (m, 4H), 7.63 – 7.28 (m, 5H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 183.1, 146.4, 145.4, 144.1, 142.0, 137.8, 137.7, 132.3, 131.4, 129.2, 128.4, 128.0, 126.8, 123.5, 123.0, 47.5. HRMS (ESI, m/z): calcd for $C_{21}H_{15}BrN_5O$: $[M+H]^+$ = 432.0454; found: 432.0458

(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (4-fluorophenyl) methanone (2d):

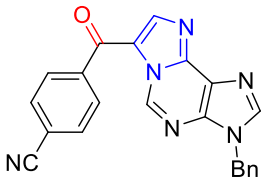


The resultant residue was purified by flash silica gel column chromatography to afford **2d** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.22 (s, 1H), 8.10 (s, 1H), 7.95 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.42 – 7.33 (m, 5H), 7.29 – 7.22 (m, 2H), 5.56 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.3, 165.4 (d, *J* = 254.0 Hz), 146.1, 145.5, 142.2, 141.9, 137.7, 136.0, 135.0, 134.9, 131.4 (d, *J* = 9.1 Hz), 129.8, 128.7, 127.9, 123.4 (d, *J* = 16.0 Hz), 116.0 (d, *J* = 22.0 Hz), 48.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -105.84.

HRMS (ESI, m/z): calcd for $C_{21}H_{15}FN_5O$: $[M+H]^+$= 32.1255; found: 372.1257

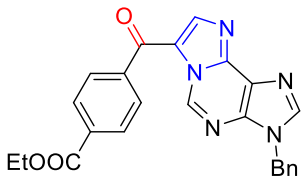
4-(3-benzyl-3H-imidazo[2,1-i] purine-7-carbonyl) benzonitrile (2e):



The resultant residue was purified by flash silica gel column chromatography to afford **2e** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 8.21 (s, 1H), 8.12 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.34-7.38 (m, 5H), 5.57 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 182.6, 146.8, 145.9, 142.5, 142.3*2, 137.7, 134.9, 132.7, 129.3, 129.2, 128.8, 127.9, 123.3, 123.2, 117.9, 115.8, 48.2.

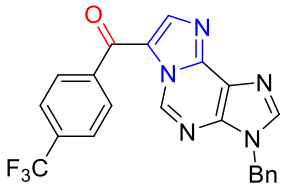
HRMS (ESI, m/z): calcd for C $C_{22}H_{15}N_6O$: $[M+H]^+$= 379.1302; found: 379.1308

ethyl 4-(3-benzyl-3H-imidazo[2,1-i] purine-7-carbonyl) benzoate (2f):



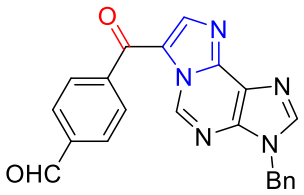
The resultant residue was purified by flash silica gel column chromatography to afford **2f** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.22-8.24 (m, 3H), 8.12 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.31 (m, 5H), 5.57 (s, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.9, 165.7, 146.7, 145.6, 142.3, 142.2, 142.1, 137.6, 135.0, 133.8, 129.9, 129.2, 128.8, 127.9, 123.5, 123.3, 61.5, 48.2, 14.3. HRMS (ESI, m/z): calcd for $C_{24}H_{19}N_5O_3$: $[M+H]^+$ = 426.1561; found: 426.1562

(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (4-(trifluoromethyl) phenyl) methanone (2g):



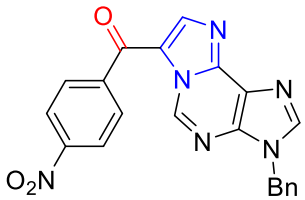
The resultant residue was purified by flash silica gel column chromatography to afford **2g** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.22 (s, 1H), 8.12 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.35-7.38 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.4, 146.8, 145.7, 142.4, 142.2, 141.8, 137.7, 134.9, 133.9 (q, *J* = 32.8 Hz), 129.3, 129.2, 128.8, 127.9, 125.8 (q, *J* = 2.52 Hz), 123.6 (q, *J* = 273.4 Hz), 123.4, 123.3, 48.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.95. HRMS (ESI, m/z): calcd for $C_{22}H_{15}F_3N_5O$: $[M+H]^+$= 422.1223; found: 422.1227

4-(3-benzyl-3H-imidazo[2,1-i] purine-7-carbonyl) benzaldehyde (2h):



The resultant residue was purified by flash silica gel column chromatography to afford **2h** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 10.17 (s, 1H), 8.23 (s, 1H), 8.12 (s, 1H), 8.07 (dd, *J* = 18.1, 7.9 Hz, 4H), 7.41 – 7.33 (m, 5H), 5.57 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 183.7, 146.9, 145.7, 143.6, 142.4, 142.2, 138.6, 137.7, 134.9, 130.0, 129.4, 129.2, 128.8, 127.9, 123.4, 123.3, 48.2. HRMS (ESI, m/z): calcd for $C_{22}H_{16}N_5O_2$: $[M+H]^+$= 382.1299; found: 382.1294

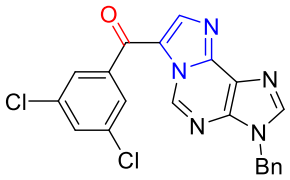
(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (4-nitrophenyl) methanone (2i):



The resultant residue was purified by flash silica gel column chromatography to afford **2i** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.43 (d, *J* = 8.2 Hz, 2H), 8.22 (s, 1H), 8.13 (s, 1H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.36-7.39 (m, 5H), 5.58 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.3, 150.0, 147.1,

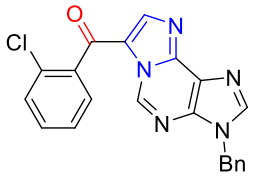
146.0, 143.9, 142.7, 142.3, 137.6, 134.9, 129.8, 129.3, 128.8, 127.9, 124.0, 123.4, 123.2, 47.9. HRMS (ESI, m/z): calcd for $C_{21}H_{15}N_6O_3$: $[M+H]^+$= 399.1200; found: 399.1197

3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (3,5-dichlorophenyl) methanone (2j):



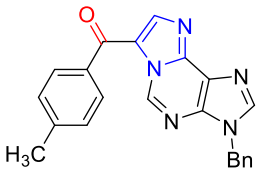
The resultant residue was purified by flash silica gel column chromatography to afford **2j** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 8.25 (s, 1H), 8.11 (s, 1H), 7.75 (s, 2H), 7.61 (s, 1H), 7.40 – 7.34 (m, 4H), 5.56 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.5, 146.8, 145.9, 142.5, 142.2, 141.2, 137.7, 136.7, 134.9, 132.2, 129.2, 128.8, 127.9, 127.2, 123.3, 123.0, 48.0. HRMS (ESI, m/z): calcd for $C_{21}H_{14}Cl_2N_5O$: $[M+H]^+$= 422.0570; found: 422.0566

(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (2-chlorophenyl) methanone (2k):



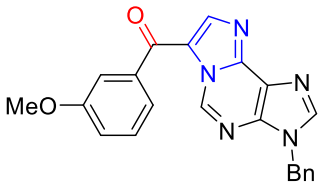
The resultant residue was purified by flash silica gel column chromatography to afford **2k** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 8.11 (s, 1H), 7.94 (s, 1H), 7.57 – 7.46 (m, 3H), 7.45 – 7.32 (m, 6H), 5.57 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.1, 147.7, 145.8, 142.4, 142.2, 137.9, 137.7, 135.0, 131.7, 131.6, 130.6, 129.2*2, 128.8, 127.9, 126.8, 123. 9, 123.3, 48.2. HRMS (ESI, m/z): calcd for $C_{21}H_{15}ClN_5O$: $[M+H]^+$=388.0960; found: 388.0961

(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (p-tolyl) methanone (2l):



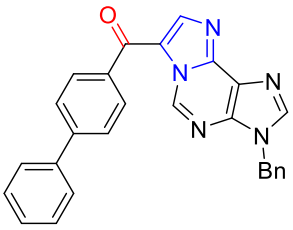
The resultant residue was purified by flash silica gel column chromatography to afford **2l** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.22 (s, 1H), 8.07 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.31 (m, 7H), 5.55 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 145.9, 145.2, 143.3, 142.0, 141.8, 137.8, 136.1, 135.1, 129.4, 129.2, 129.1, 128.7, 127.9, 123.7, 123.3, 48.1, 21.7. HRMS (ESI, m/z): calcd for $C_{22}H_{18}N_5O$: $[M+H]^+$= 368.1506; found: 368.1503

3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (3-methoxyphenyl) methanone (2n):



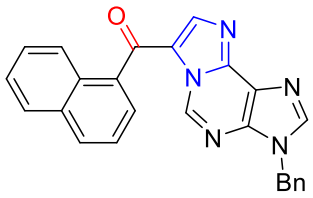
The resultant residue was purified by flash silica gel column chromatography to afford **2n** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 8.26 (s, 1H), 8.08 (s, 1H), 7.49 – 7.32 (m, 8H), 7.21 – 7.16 (m, 1H), 5.56 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 184.6, 159.8, 146.3, 145.4, 142.1, 141.9, 140.1, 137.8, 136.1, 129.7, 129.2, 128.7, 127.9, 123.6, 123.3, 121.4, 118.8, 113.6, 55.6, 48.1. HRMS (ESI, m/z): calcd for $C_{22}H_{19}N_5O_2$: $[M+H]^+$= 384.1455; found: 384.1459

[1,1'-biphenyl]-4-yl(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) methanone (2p):



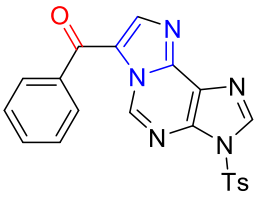
The resultant residue was purified by flash silica gel column chromatography to afford **2p** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.31 (s, 1H), 8.10 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.33 (m, 6H), 5.57 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 146.2, 145.4, 145.3, 142.1, 141.8, 139.8, 137.8, 137.4, 136.0, 129.6, 129.2, 129.0, 128.7, 128.2, 127.8, 127.4, 127.3, 123. 7, 123.3, 48.1. HRMS (ESI, m/z): calcd for $C_{27}H_{20}N_5O$: $[M+H]^+$= 430.1662; found: 430.1657

(3-benzyl-3H-imidazo[2,1-i] purin-7-yl) (naphthalen-1-yl) methanone (2q):



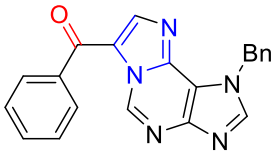
The resultant residue was purified by flash silica gel column chromatography to afford **2q** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.26 – 8.21 (m, 1H), 8.10 (s, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.01 (s, 1H), 7.98 – 7.89 (m, 1H), 7.80 (d, *J* = 7.0 Hz, 1H), 7.57-7.60 (m, 3H), 7.40 – 7.34 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.0, 147.3, 145.7, 142.2, 142.1, 137.9, 136.2, 136.1, 133.9, 131.7, 130.7, 129.2, 128.8, 128.6, 127.9, 127.5, 127.4, 126.7, 125.2, 125.1, 124.4, 123.4, 48.2. HRMS (ESI, m/z): calcd for $C_{25}H_{18}N_5O$: $[M+H]^+$ = 404.1506; found: 404.1513

phenyl(3-tosyl-3H-imidazo[2,1-i] purin-7-yl) methanone (2r):



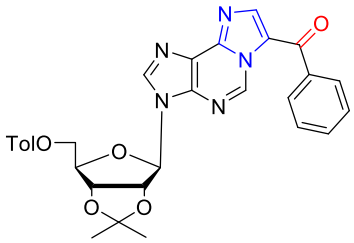
The resultant residue was purified by flash silica gel column chromatography to afford **2r** as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.39 (s, 1H), 8.58 (s, 1H), 8.24 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 2.44 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.8, 147.2, 146.0, 144.3, 140.1, 139.6, 138.9, 138.3, 133.7, 132.8, 130.3, 128.9, 128.8*2, 124.7, 123.8, 21.8. HRMS (ESI, m/z): calcd for $C_{21}H_{16}N_5O_3S$: $[M+H]^+$= 418.0968; found: 418.0966

(1-benzyl-1H-imidazo[2,1-i] purin-7-yl) (phenyl) methanone (2s):



The resultant residue was purified by flash silica gel column chromatography to afford **2s** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 10.34 (s, 1H), 8.17 (s, 1H), 8.10 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.51 – 7.24 (m, 5H), 5.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 150.6, 145.2, 143.0, 141.5, 138.7, 137.3, 135.1, 132.6, 129.2, 128.9, 128.8, 128.7, 128.1, 123.8, 114.4, 51.2. HRMS (ESI, m/z): calcd for $C_{21}H_{16}N_5O$: $[M+H]^+$= 354.1349; found: 354.1354

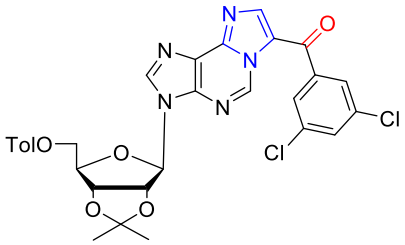
((3aR,4R,6R,6aR)-6-(7-benzoyl-3H-imidazo[2,1-i] purin-3-yl)-2,2-dimethyltetrahydrofuro[3,4-d] [1,3] dioxol-4-yl) methyl 4-methylbenzoate (2t):



The resultant residue was purified by flash silica gel column chromatography to afford **2t** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.21 (d, *J* = 9.2 Hz, 2H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.69-7.57 (m, 3H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.27 (d, *J* = 2.2 Hz, 1H), 5.58 (dd, *J* = 6.2 Hz, 2.2 Hz, 1H), 5.22 (dd, *J* = 6.3, 3.0 Hz, 1H), 4.68 – 4.65 (m, 2H), 4.51 (dd, *J* = 13.1, 5.8 Hz, 1H), 2.31 (s, 3H), 1.71 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 166.0, 146.1, 145.1, 144.1, 141.5, 140.5, 138.7, 137.8, 132.6, 129.6, 129.1, 128.9, 128.8, 126.5, 124.4, 123.6, 115.0, 91.7, 85.1, 84.5,

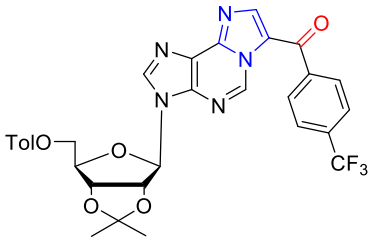
81.5, 63.8, 27.3, 25.5, 21.6. HRMS (ESI, m/z): calcd for $C_{30}H_{28}N_5O_6$: $[M+H]^+$= 554.2034; found: 554.2032

((3aR,4R,6R,6aR)-6-(7-(3,5-dichlorobenzoyl)-3H-imidazo[2,1-i] purin-3-yl)-2,2-dimethyltetrahydrofuro[3,4-d] [1,3] dioxol-4-yl) methyl 4-methylbenzoate (2u):



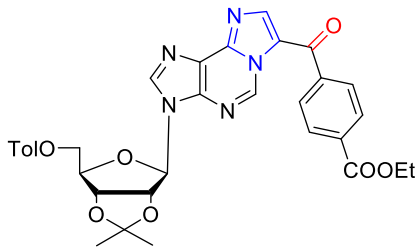
The resultant residue was purified by flash silica gel column chromatography to afford **2u** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.23 (d, *J* = 7.8 Hz, 2H), 7.76-7.79 (m, 4H), 7.62-7.64 (m, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.27 (d, *J* = 2.2 Hz, 1H), 5.57 (dd, *J* = 6.2, 2.2 Hz, 1H), 5.22 (dd, *J* = 6.2, 3.0 Hz, 1H), 4.66-4.69 (m, 2H), 4.54 – 4.48 (m, 1H), 2.33 (s, 3H), 1.68 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 166.0, 146.6, 145.6, 144.1, 141.8, 141.2, 141.0, 137.6, 135.8, 132.3, 129.6, 129.1, 127.2, 126.6, 124.5, 123.0, 115.1, 91.7, 85.1, 84.5, 81.5, 63.8, 27.3, 25.5, 21.7. HRMS (ESI, m/z): calcd for $C_{30}H_{26}Cl_2N_5O_6$: $[M+H]^+$=622.1255; found: 622.1255

((3aR,4R,6R,6aR)-2,2-dimethyl-6-(7-(4-(trifluoromethyl) benzoyl)-3H-imidazo[2,1-i] purin-3-yl) tetrahydrof uro[3,4-d] [1,3] dioxol-4-yl) methyl 4-methylbenzoate (2v):



The resultant residue was purified by flash silica gel column chromatography to afford **2v** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.21 (d, *J* = 6.9 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.28 (d, *J* = 2.2 Hz, 1H), 5.58 (dd, *J* = 6.3, 2.2 Hz, 1H), 5.22 (dd, *J* = 6.3, 3.1 Hz, 1H), 4.669-4.66 (m, 2H), 4.54 – 4.47 (m, 1H), 2.32 (s, 3H), 1.68 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 166.0, 146.6, 145.4, 144.1, 141.8*2, 140.9, 137.6, 134.1 (q, *J* = 32.8 Hz), 129.6, 129.2, 129.1, 126.6, 125.9, 124.5, 123.6 (q, *J* = 273.0 Hz), 123.4, 115.1, 91.7, 85.1, 84.5, 81.5, 63.8, 27.3, 25.5, 14.1. HRMS (ESI, m/z): calcd for $C_{31}H_{27}F_3N_5O_6$: $[M+H]^+$= 622.1908; found: 622.1908

((3aR,4R,6R,6aR)-6-(7-(4-(ethoxycarbonyl) benzoyl)-3H-imidazo[2,1-i] purin-3-yl)-2,2-dimethyltetrahydrofuro[3,4-d] [1,3] dioxol-4-yl) methyl 4-methylbenzoate (2w):

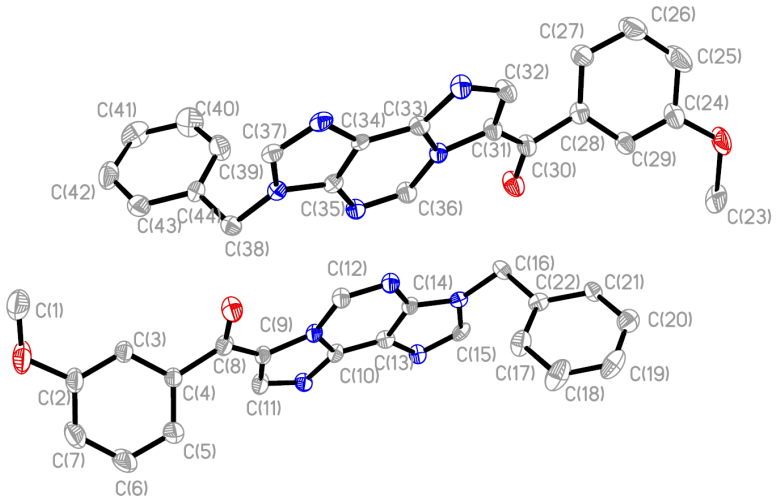


The resultant residue was purified by flash silica gel column chromatography to afford **2w** as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.25 – 8.23 (m, 4H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.28 (d, *J* = 2.1 Hz, 1H), 5.58 (dd, *J* = 6.2, 2.1 Hz, 1H), 5.23 (dd, *J* = 6.2, 3.2 Hz, 1H), 4.70 – 4.62 (m, 2H), 4.55 – 4.39 (m, 4H), 2.32 (s, 3H), 1.69 (s, 3H), 1.47-1.43 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.8, 166.0, 165.7, 146.5, 145.2, 144.1, 142.2, 141.7, 140.7, 137.6, 133.8, 129.9, 129.5, 129.0, 128.7, 126.4, 124.4, 123.5, 115.0, 91.7, 85.0, 84.5, 81.4, 63.8, 61.5, 27.3, 25.5, 21.7, 14.3. HRMS (ESI, m/z): calcd for $C_{33}H_{32}N_5O_8$: $[M+H]^+$= 626.2245; found: 626.2247

Notes and references

1. Li, R. L.; Liang, L.; Xie, M. S.; Qu, G. R.; Niu, H. Y.; Guo, H. M., *The Journal of organic chemistry* **2014,** *79*, 3665-70.

Crystal preparation and X-ray diffraction analysis of compound 2n



Crystal structure of compoud **2n**

Datablock: Y

Bond precision: C-C = 0.0112 A Wavelength=0.71073

Cell: a=20.554(2) b=7.7056(8) c=23.283(3)
alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	3687.6(7)	3687.6(7)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	C22 H17 N5 O2	?
Sum formula	C22 H17 N5 O2	C44 H34 N10 O4
Mr	383.41	766.81
Dx,g cm-3	1.381	1.381
Z	8	4
Mu (mm-1)	0.093	0.093
F000	1600.0	1600.0
F000'	1600.62	
h,k,lmax	24,9,27	24,9,27
Nref	6475[3325]	6451
Tmin,Tmax	0.977,0.980	
Tmin'	0.977	

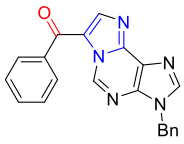
Correction method= Not given

Data completeness= 1.94/1.00 Theta(max)= 24.996

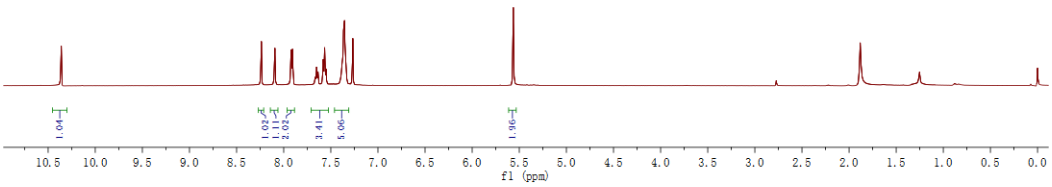
R(reflections)= 0.0671(4559) wR2(reflections)= 0.1730(6451)

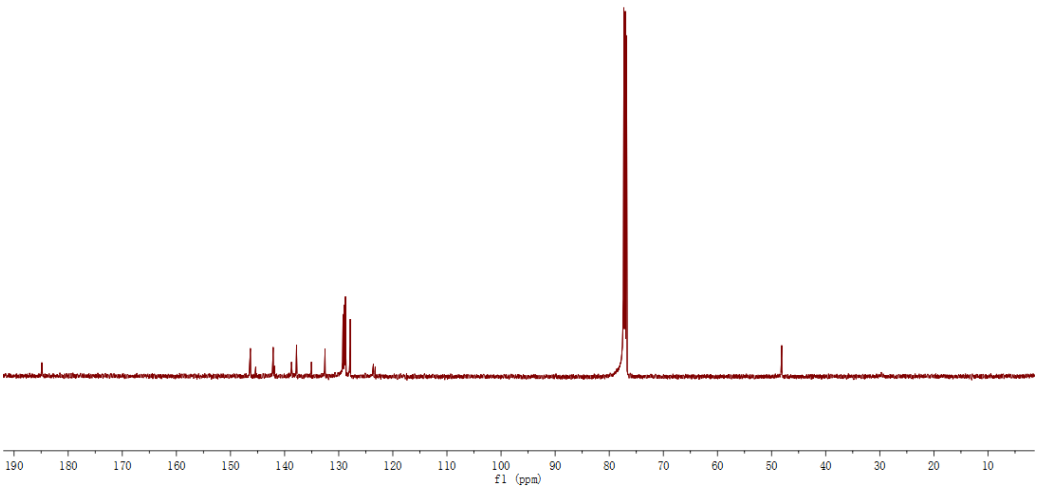
S = 1.096 Npar= 523

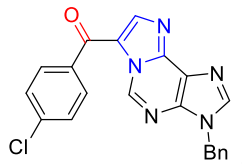
^{1}H and ^{13}C NMR Data



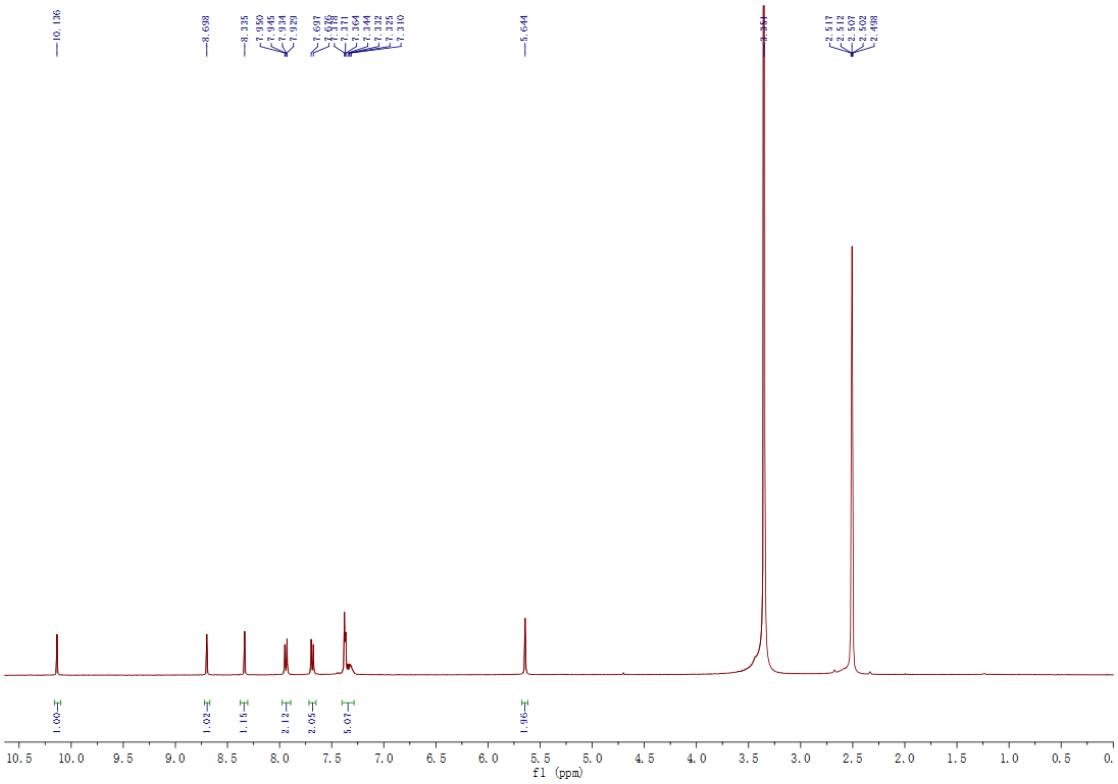
2a

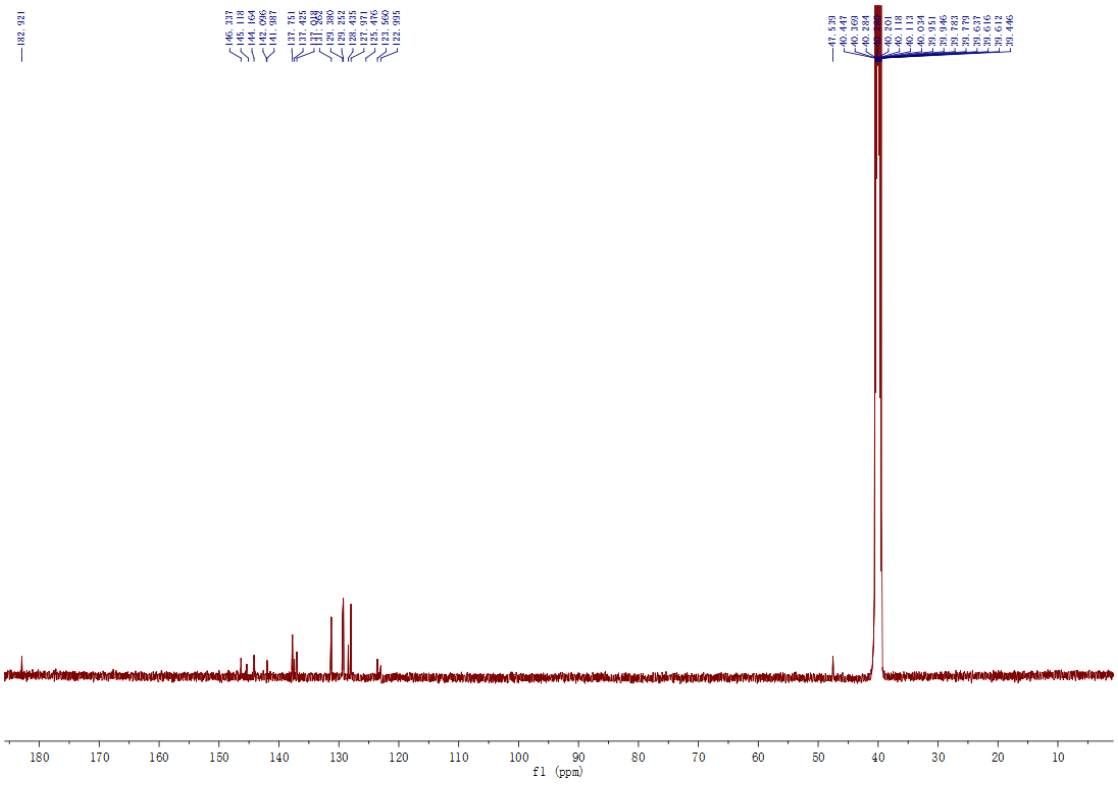


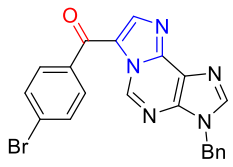



O
N
N
N
N
N
Cl
Bn

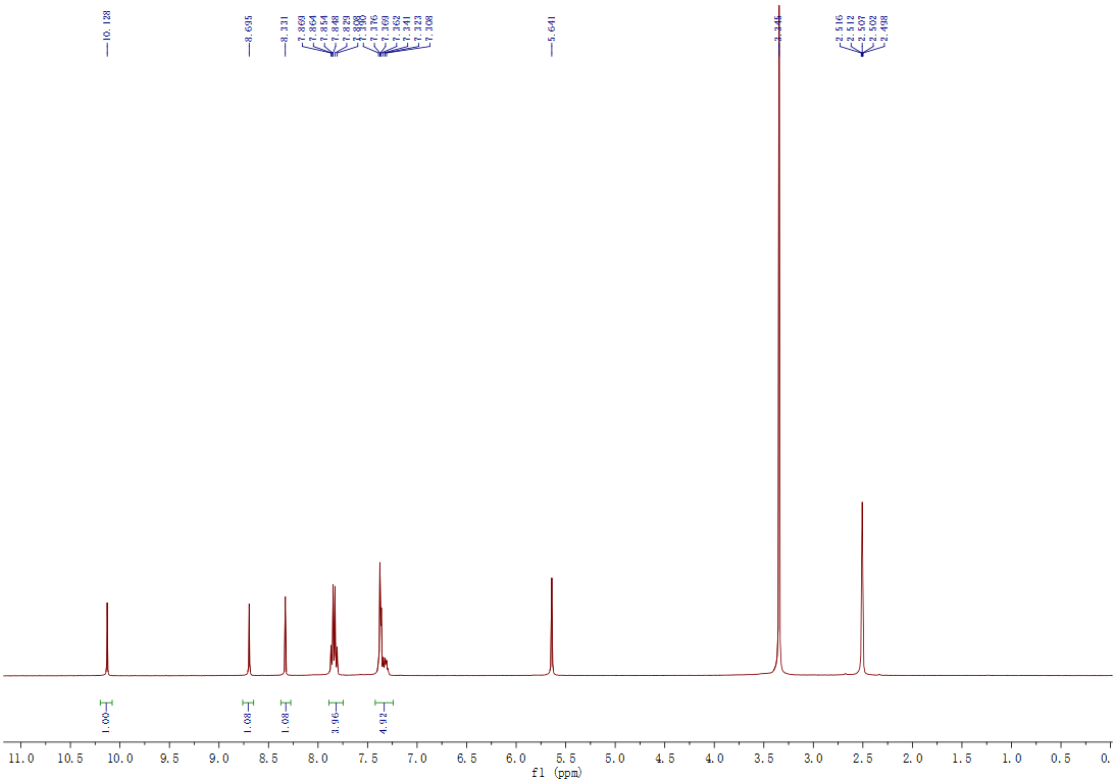
2b

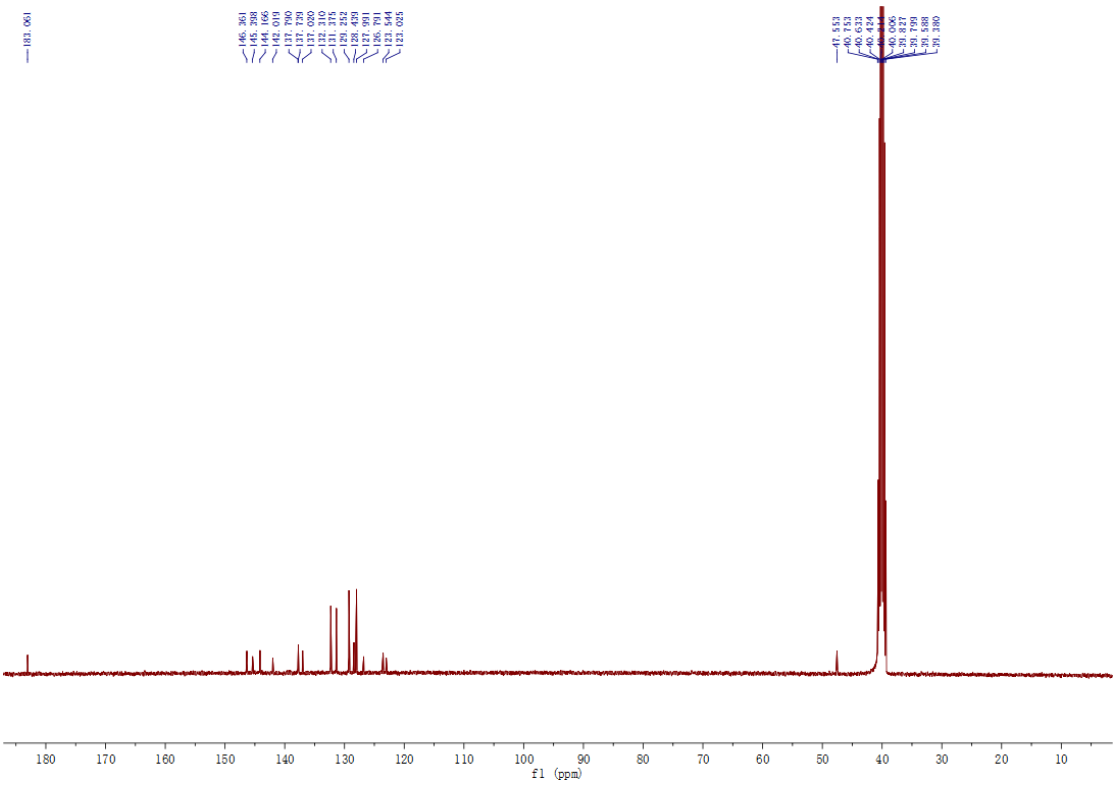

10.136
8.698
8.335
7.950
7.946
7.934
7.929
7.697
7.371
7.364
7.344
7.332
7.325
7.310
5.644
3.961
2.517
2.513
2.507
2.502
2.498
1.00
1.02
1.15
2.12
2.05
5.07
1.96
f1 (ppm)

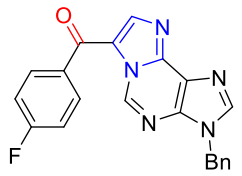

182.921
146.337
145.118
144.654
142.096
141.987
137.751
137.425
129.380
129.252
128.435
127.971
125.476
123.560
122.995
47.539
40.447
40.201
40.118
40.034
39.951
39.946
39.783
39.779
39.637
39.616
39.612
39.446
f1 (ppm)


O
N
N
N
N
N
Br
Bn

2c

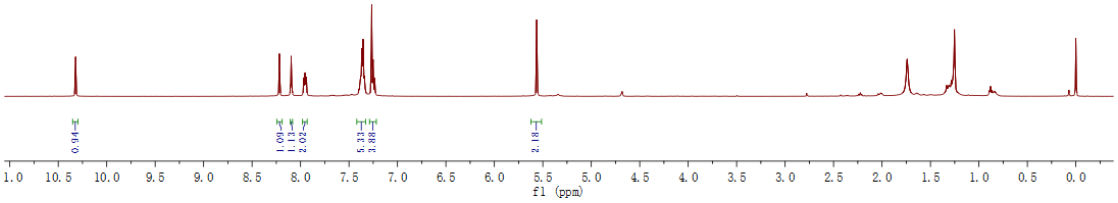

10.128
8.695
8.331
7.869
7.864
7.854
7.848
7.838
7.820
7.376
7.369
7.362
7.341
7.333
7.308
5.641
3.346
2.516
2.512
2.507
2.502
2.498
1.00
1.08
1.08
3.96
4.92
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

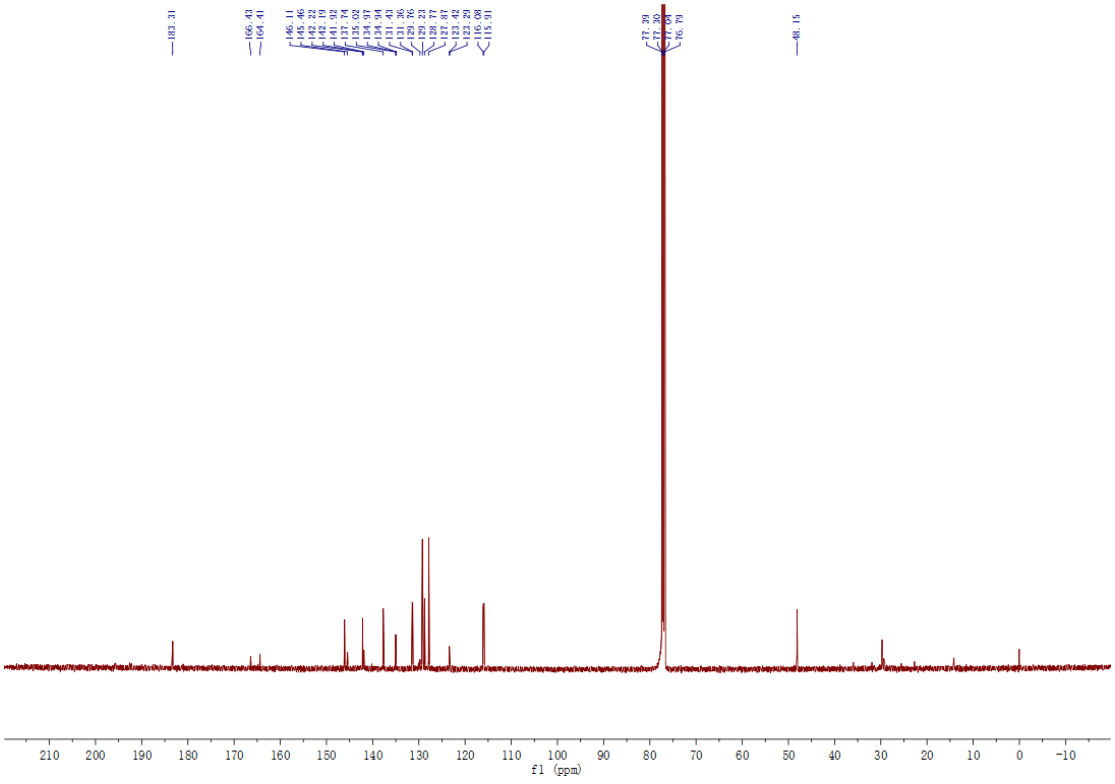

183.061
146.361
145.258
144.166
142.010
137.790
137.739
137.020
132.319
131.315
129.252
128.439
127.991
126.791
125.544
123.025
47.553
40.753
40.633
40.424
40.006
39.827
39.799
39.588
39.380
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

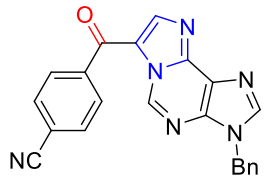

O
N
N
N
N
F
Bn

2d

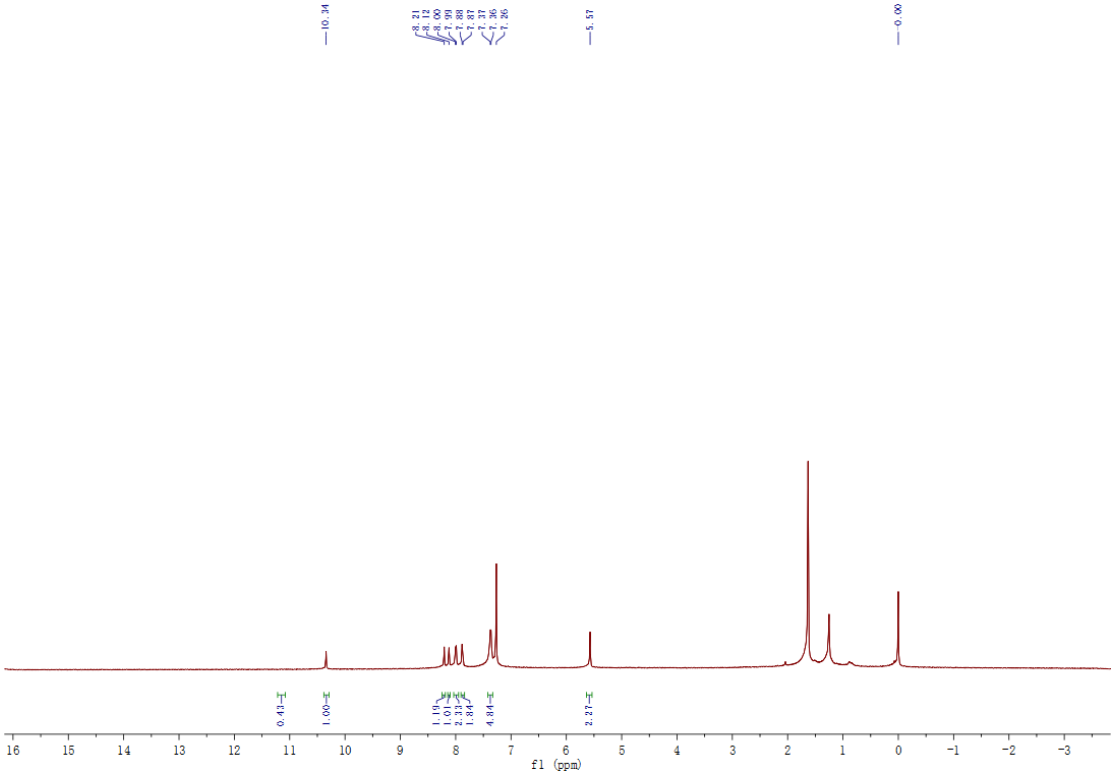

10.321
8.219
8.097
7.967
7.957
7.951
7.940
7.380
7.369
7.355
7.340
7.256
7.252
7.235
5.563

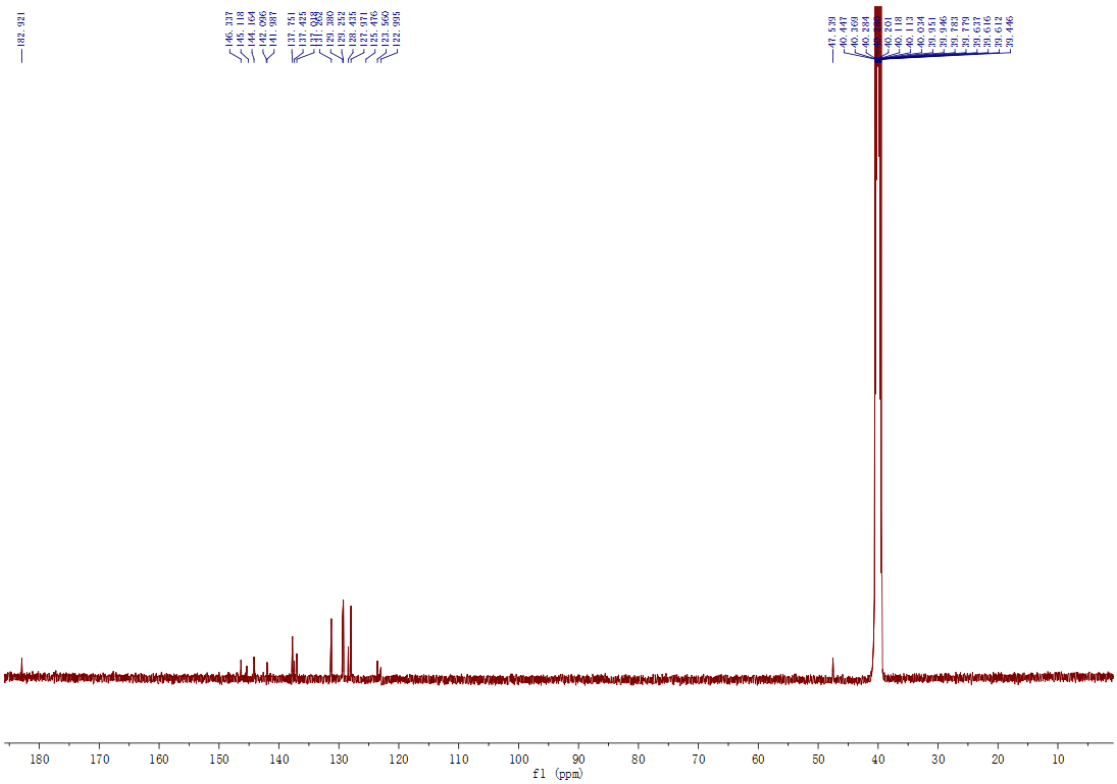

0.94
1.09
1.13
2.02
5.33
3.88
2.18
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

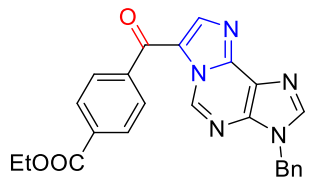

183.31
166.43
164.41
146.11
145.46
142.22
142.10
141.92
137.74
135.02
134.97
134.84
134.43
131.36
129.76
129.23
128.97
127.87
123.42
123.29
116.08
115.91
77.39
77.20
77.00
76.79
68.15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
N
N
N
N
NC
Bn

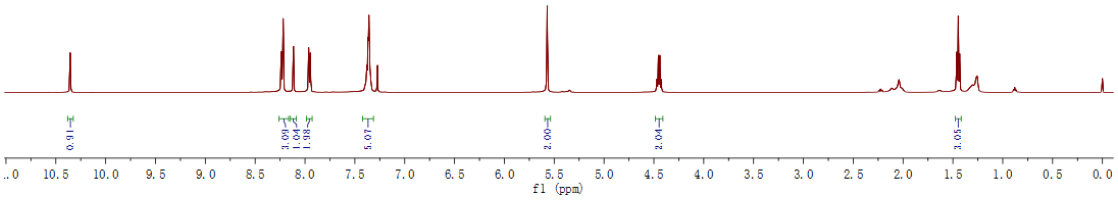
2e

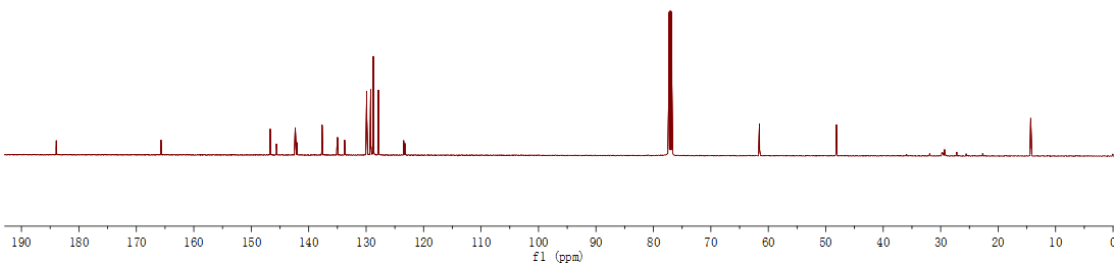

10.34
8.21
8.12
8.00
7.99
7.88
7.87
7.37
7.36
7.35
5.57
0.00
0.43
1.00
1.19
1.03
2.33
1.84
4.04
2.27
f1 (ppm)

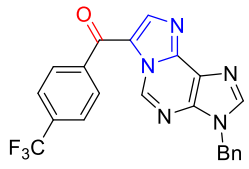

182.921
146.337
145.118
144.164
142.096
141.987
137.751
137.425
131.948
131.564
129.380
129.252
128.435
127.571
125.476
123.560
122.995
47.539
40.447
40.359
40.284
40.201
40.118
40.111
40.034
39.951
39.946
39.783
39.779
39.637
39.616
39.612
39.446
f1 (ppm)



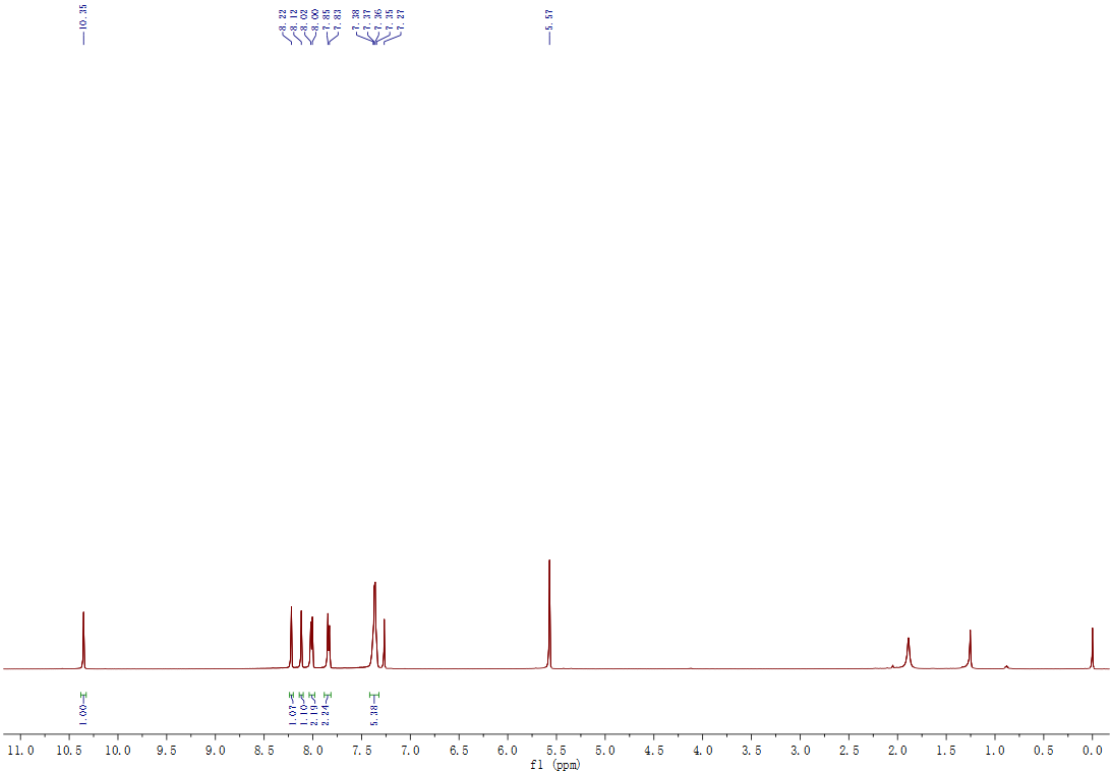
2f

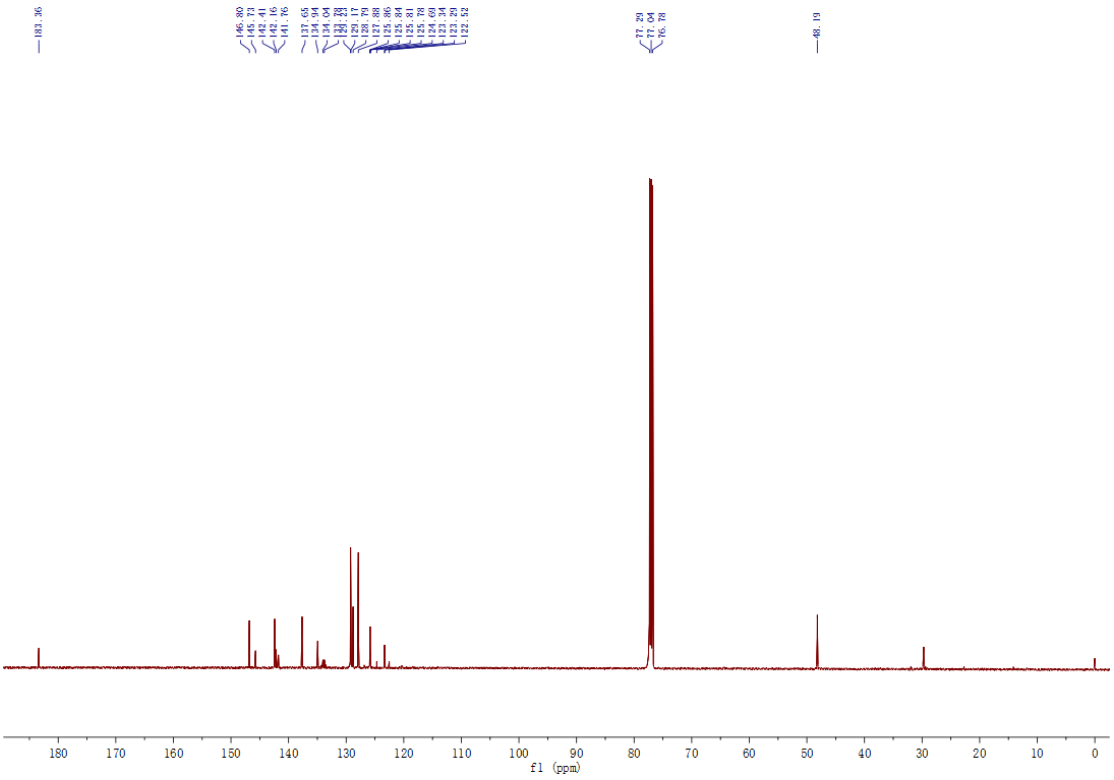


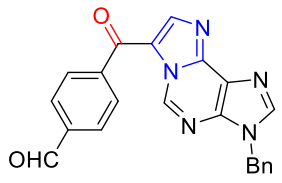



O
N
N
N
N
N
Bn
F3C

2g

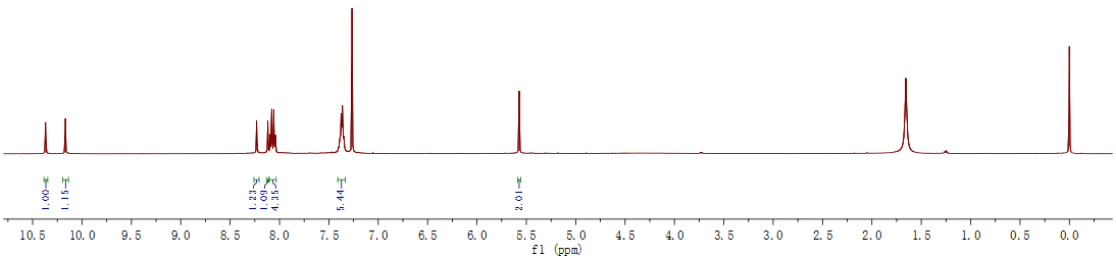

10.35
8.22
8.12
8.02
8.00
7.85
7.83
7.38
7.37
7.36
7.35
7.27
5.57
1.00
1.07
1.10
2.19
2.24
5.38
f1 (ppm)

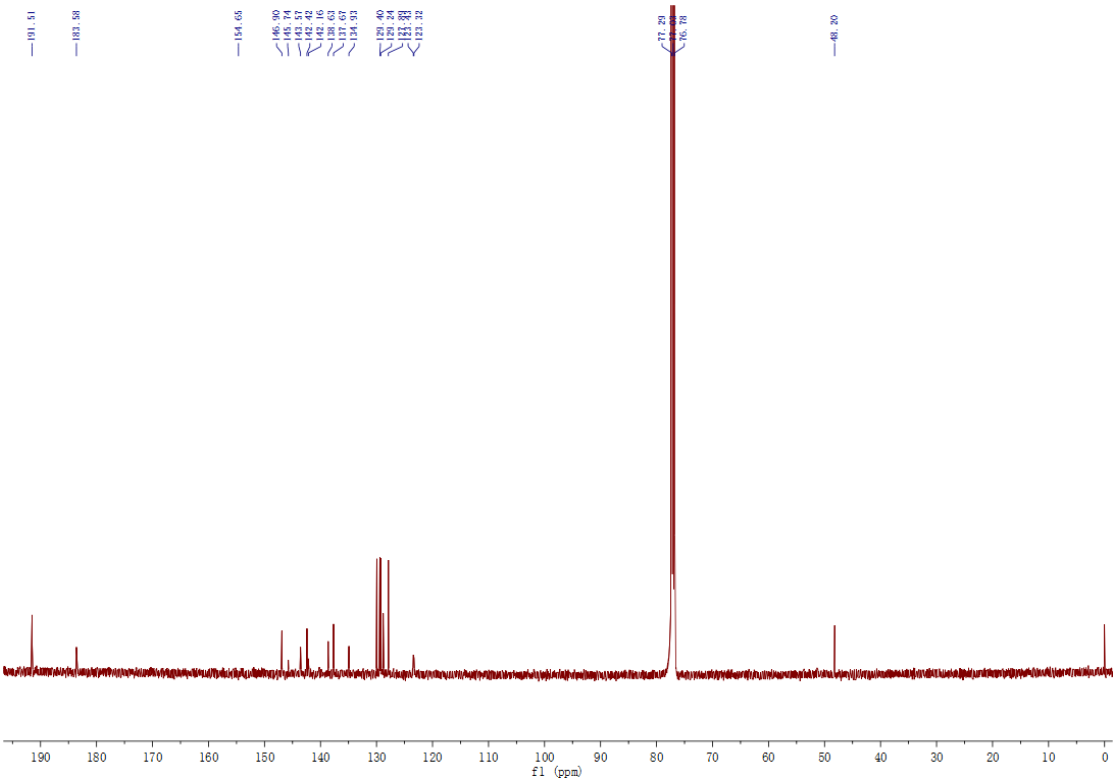

183.36
146.80
145.73
145.41
142.16
141.76
137.65
134.94
134.04
129.17
128.79
128.66
125.86
125.84
125.81
125.78
124.60
123.94
123.29
122.52
77.29
77.04
76.78
48.19
f1 (ppm)

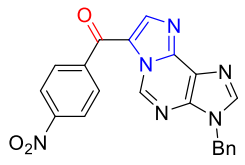

O
N
N
N
N
OHC
Bn

2h

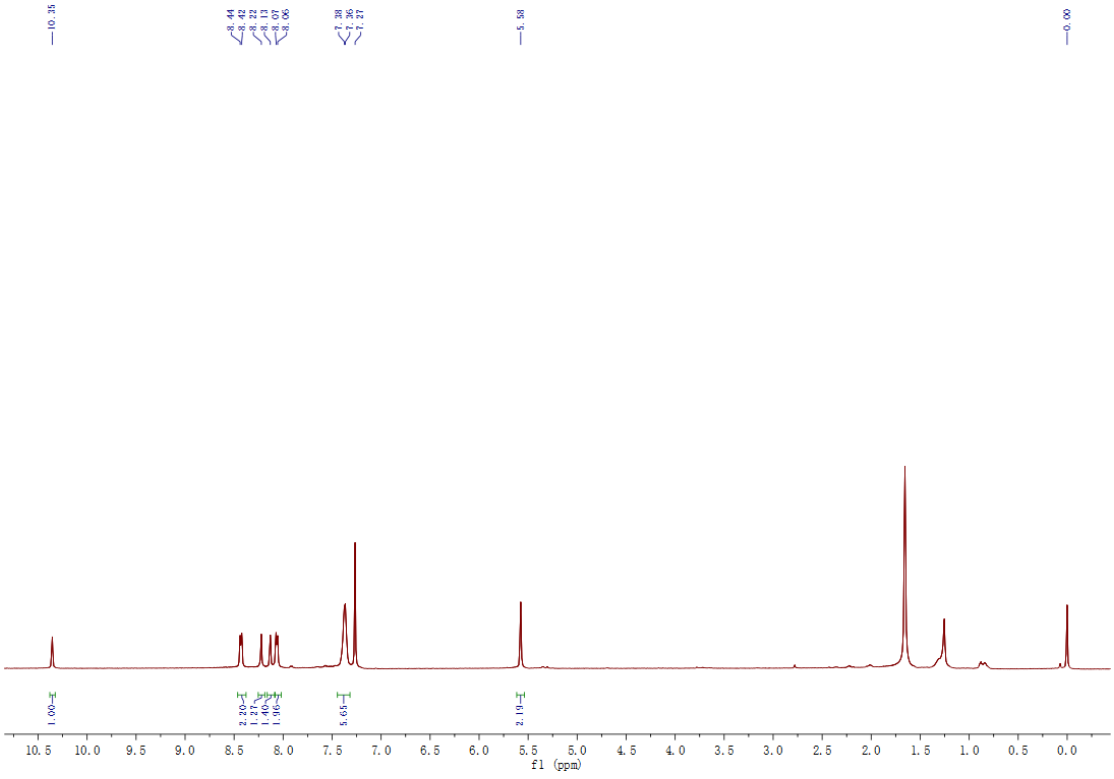

10.37
10.17
8.23
8.12
8.09
8.08
8.06
8.04
7.39
7.38
7.36
7.35
7.26
5.57
1.66
0.00

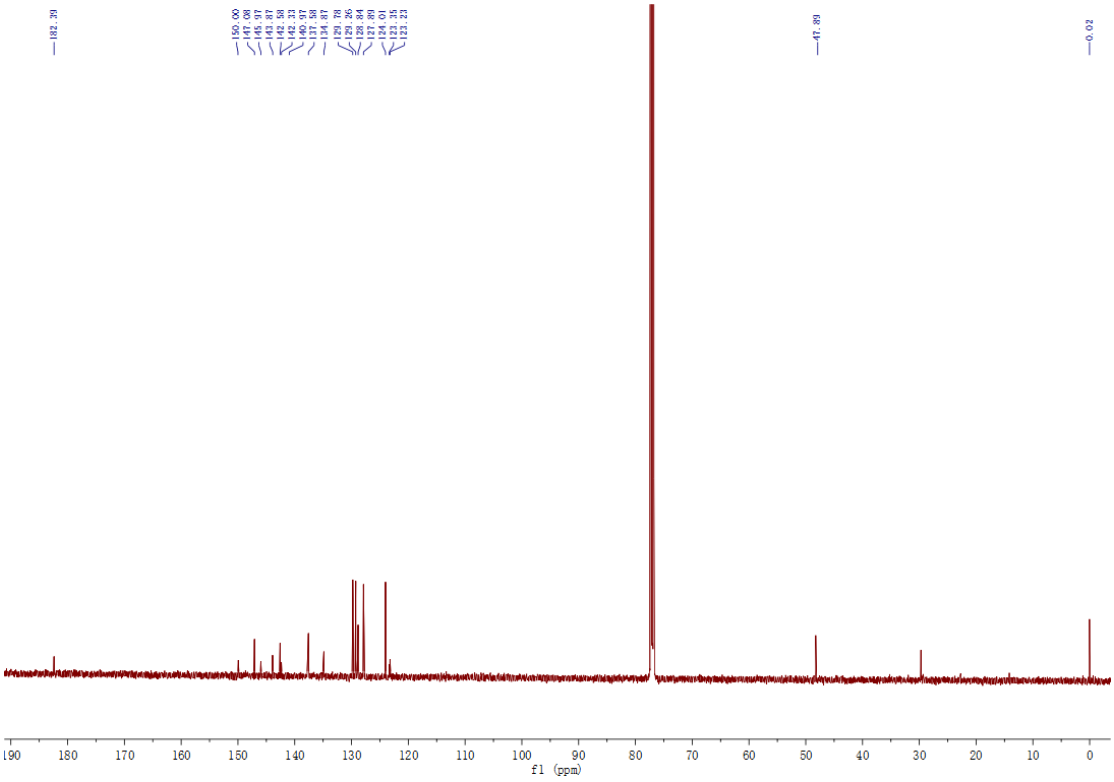

1.00
1.15
1.23
1.00
4.35
5.44
2.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

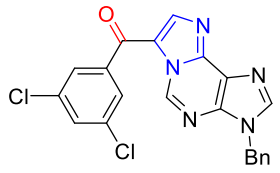

191.51
183.58
154.65
146.90
145.74
143.57
142.42
140.16
138.63
137.67
134.93
129.40
127.24
125.80
123.83
123.32
77.29
77.04
76.78
48.20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N
N
N
N
O_2N
Bn

2i

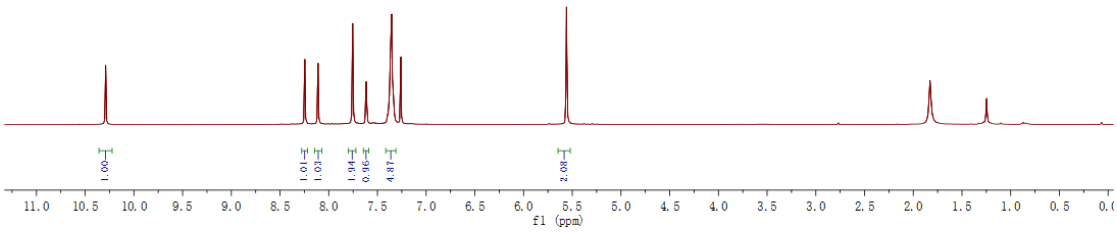

10.35
8.44
8.42
8.22
8.13
8.07
8.06
7.38
7.36
7.27
5.58
0.00
1.00
2.20
1.17
1.40
1.96
5.65
2.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


182.39
150.00
147.08
145.97
143.87
142.58
142.33
140.97
137.58
134.87
129.78
129.36
128.84
127.89
124.01
123.35
123.23
47.89
0.02
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

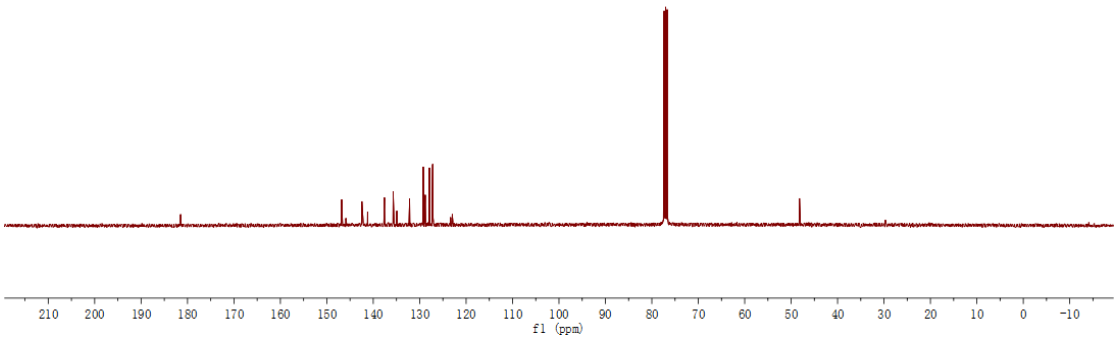

O
N
N
N
N
N
Cl
Cl
Bn

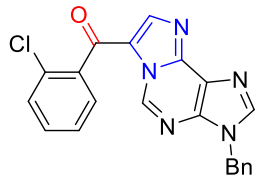
2j


10.290
8.246
8.110
7.754
7.615
7.363
7.354
7.260
6.996
5.559

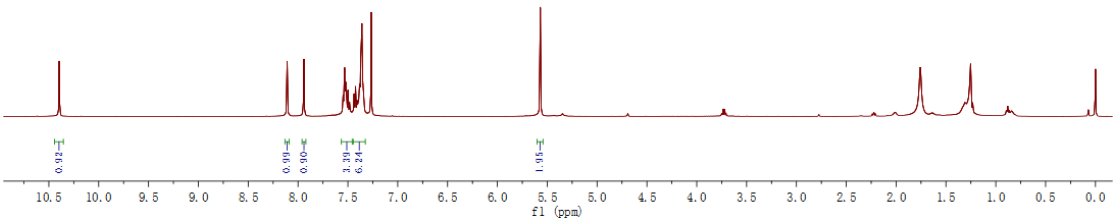

1.00
1.01
1.03
1.94
0.96
4.87
2.08
f1 (ppm)

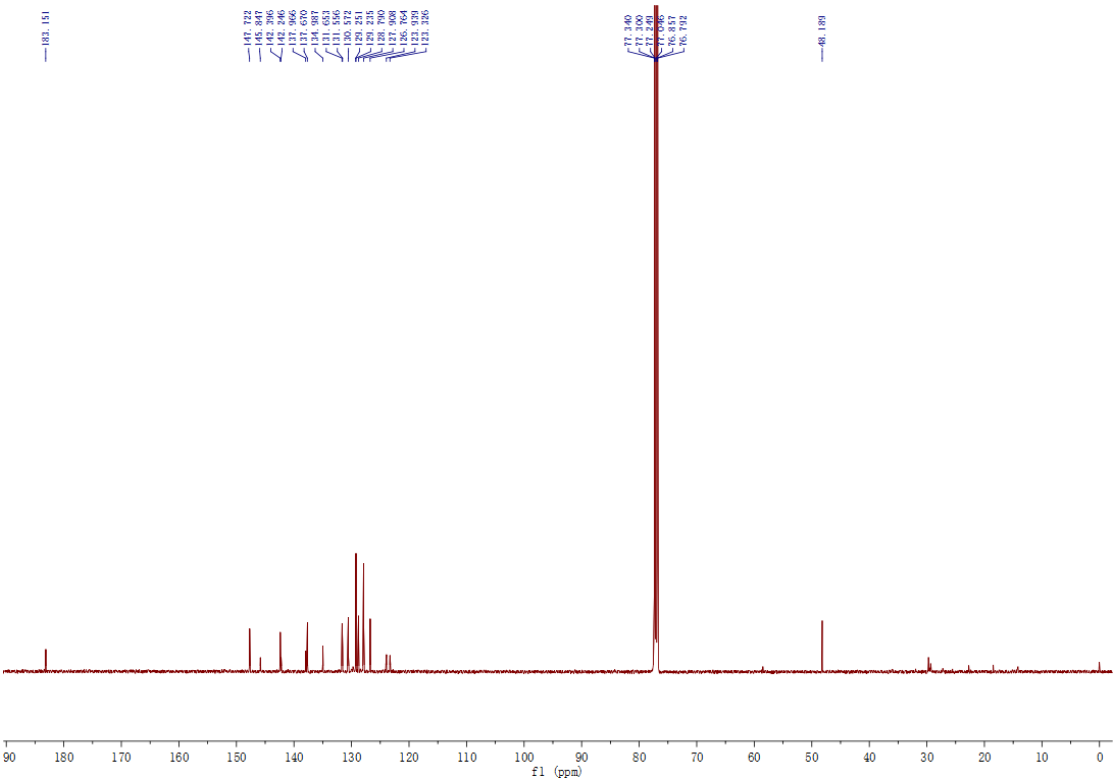

181.483
146.798
145.891
142.459
142.252
141.230
137.593
135.711
134.918
132.168
129.241
128.808
127.900
127.192
123.338
122.982
77.347
77.233
77.029
76.712
48.208

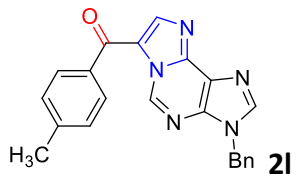

f1 (ppm)



2k

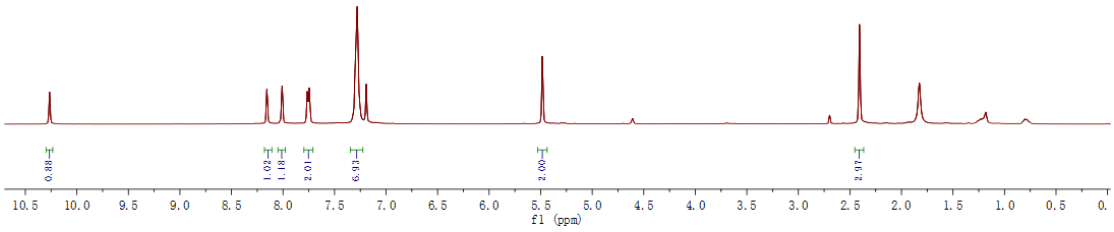




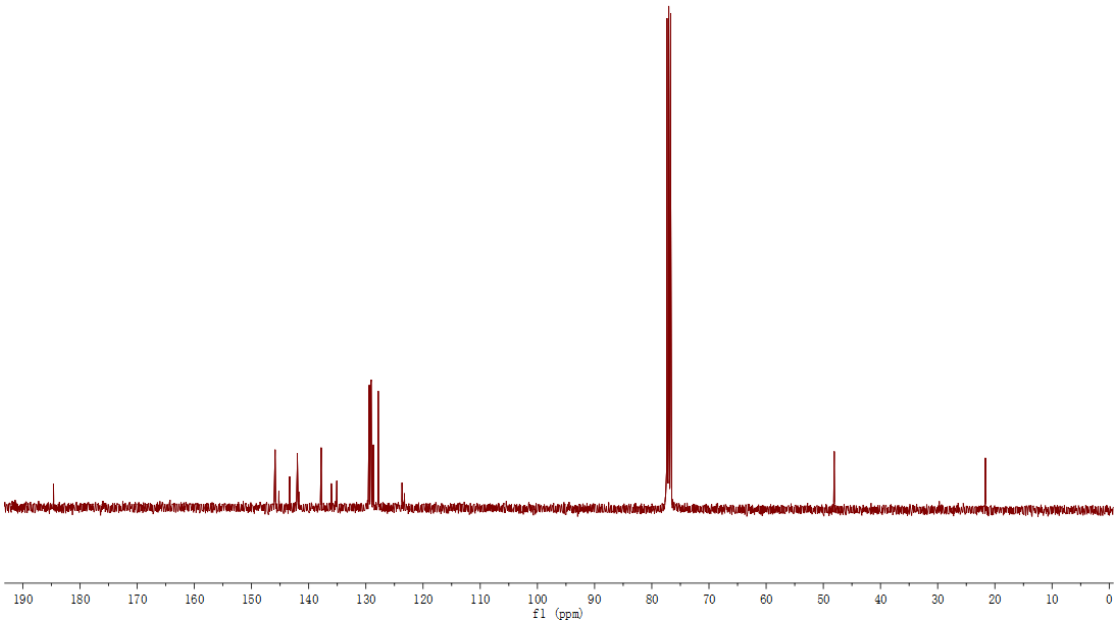

O
N
N
N
N
N
H3C
Bn

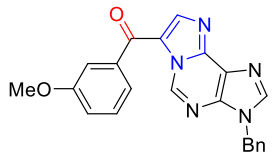
2l


10.265
8.157
8.009
7.765
7.746
7.280
7.193
5.484
2.407

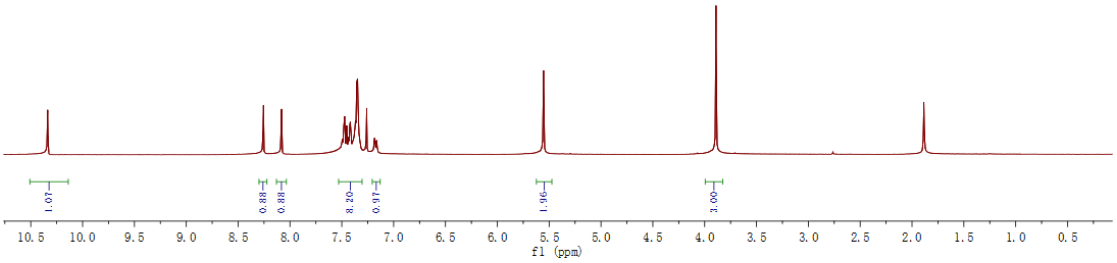

0.88
1.02
1.18
2.01
6.93
2.00
2.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

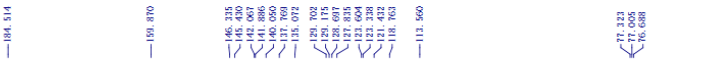

184.646
145.895
145.236
143.342
142.999
141.770
137.834
136.063
135.096
129.429
129.196
129.068
123.273
77.352
77.236
77.034
76.716
48.103
21.662

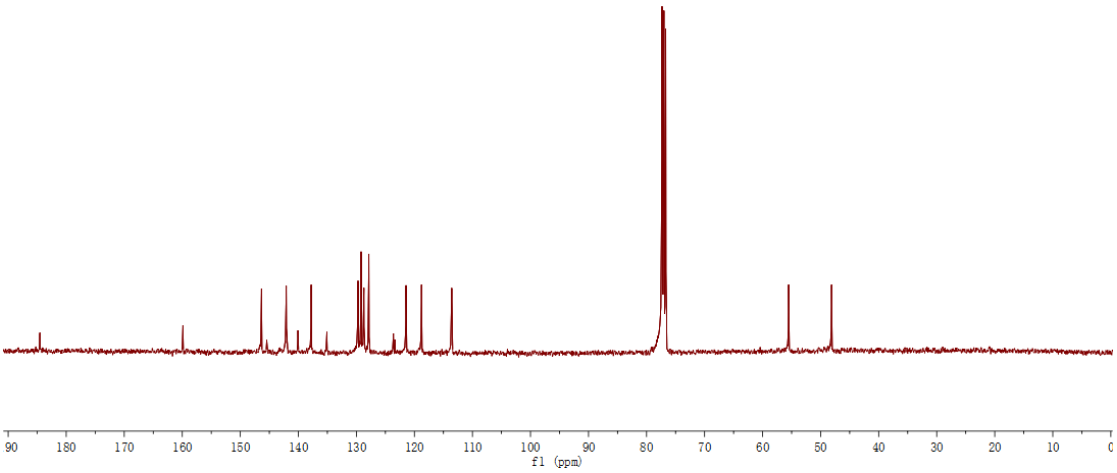

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

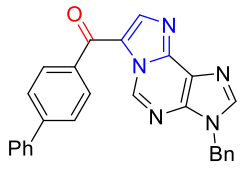

O
N
N
N
N
N
MeO
Bn

2n

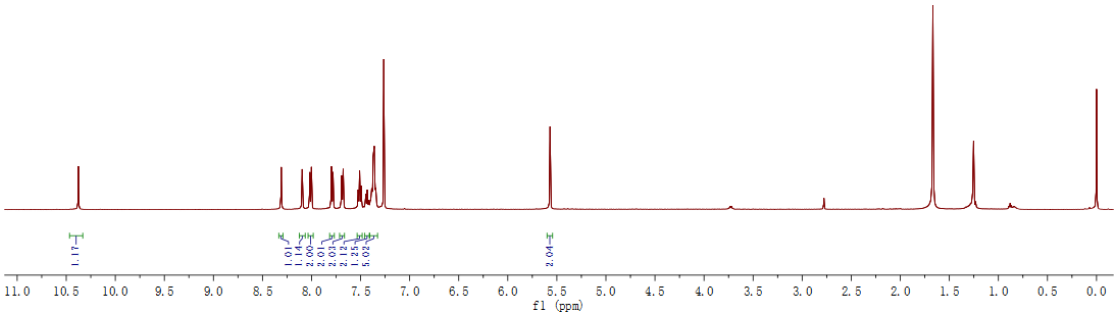

1.07
0.88
0.88
8.20
0.97
1.96
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

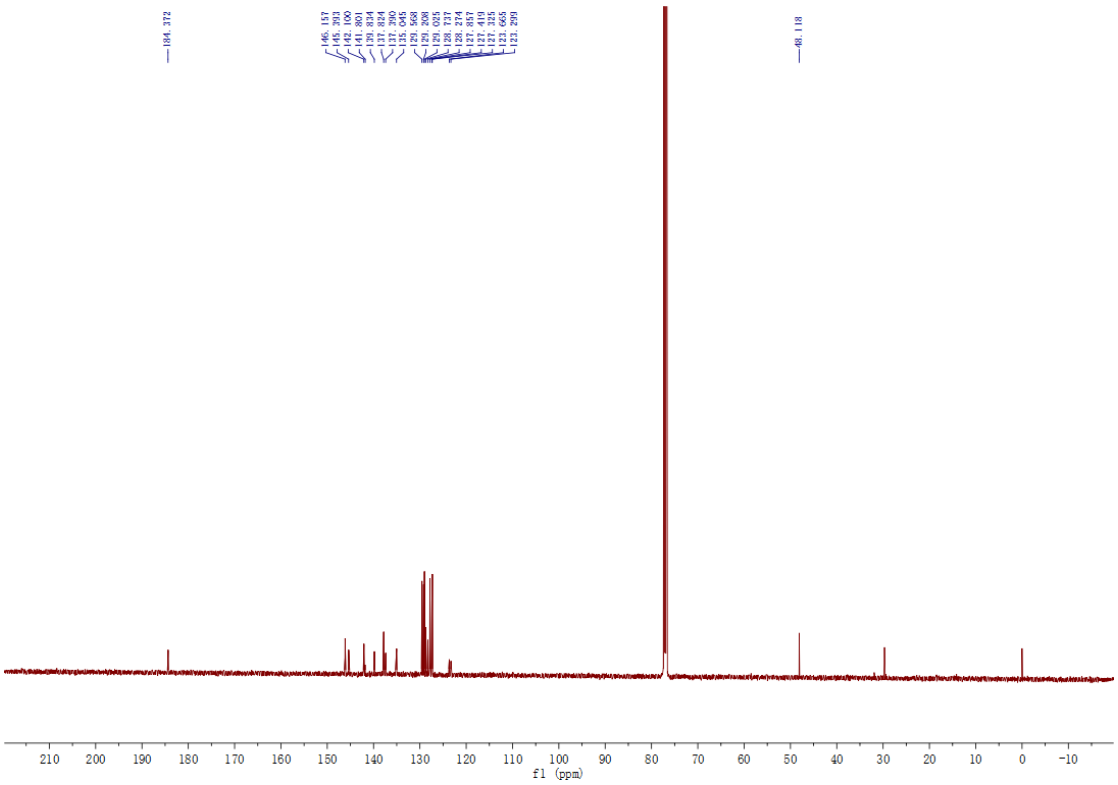


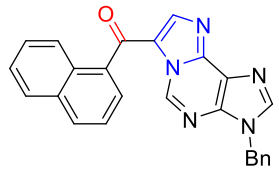

90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



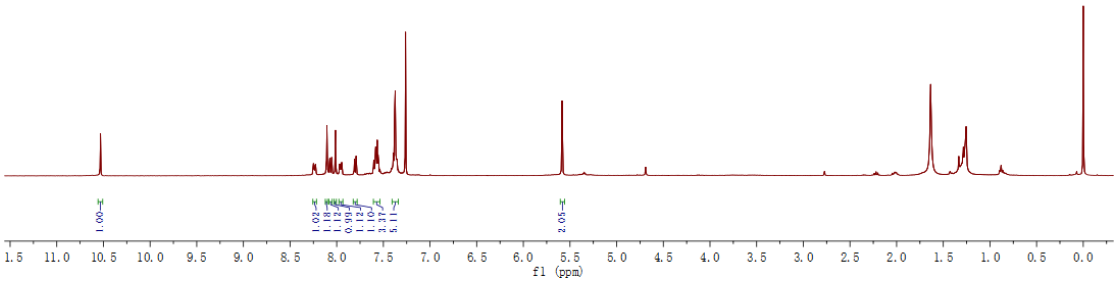
2p

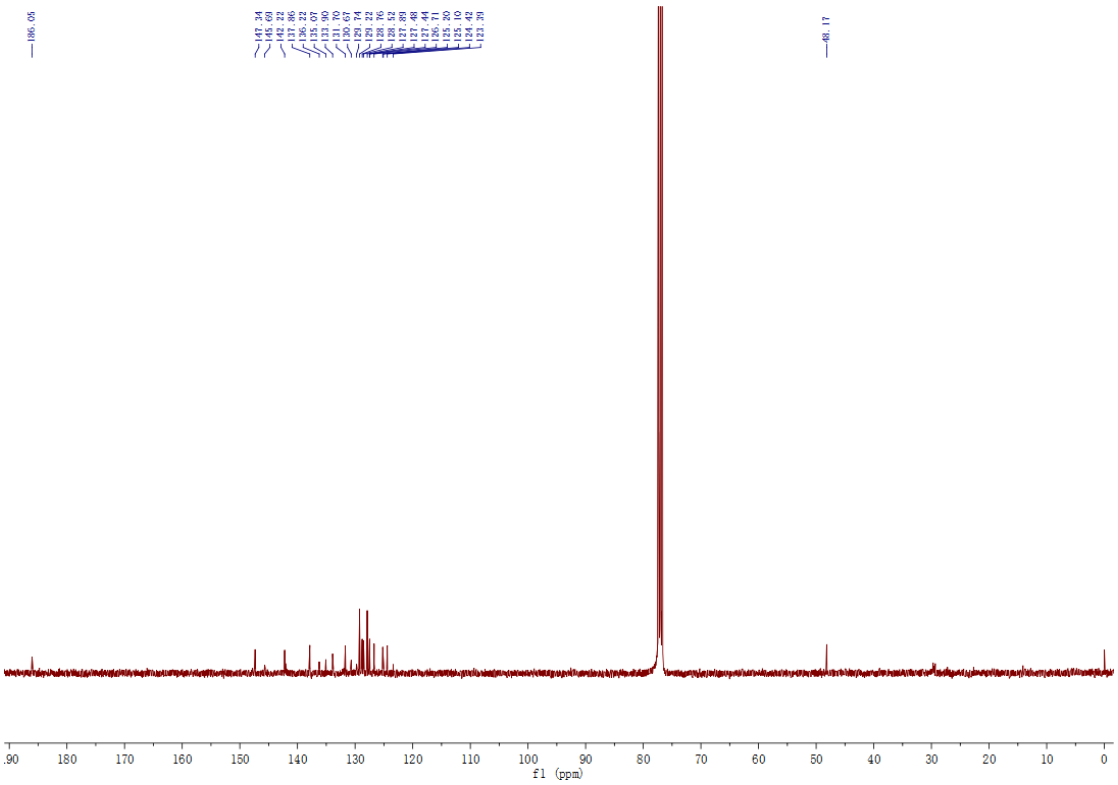


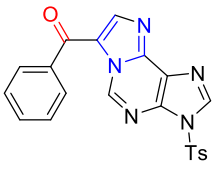




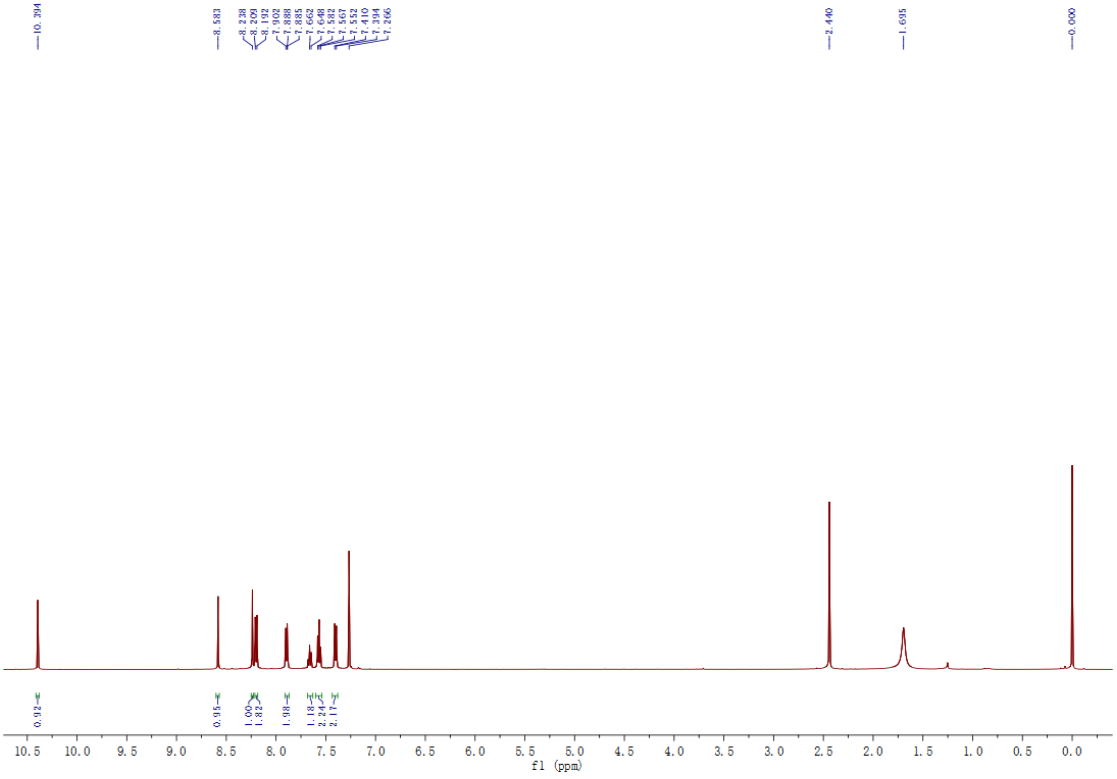
2q

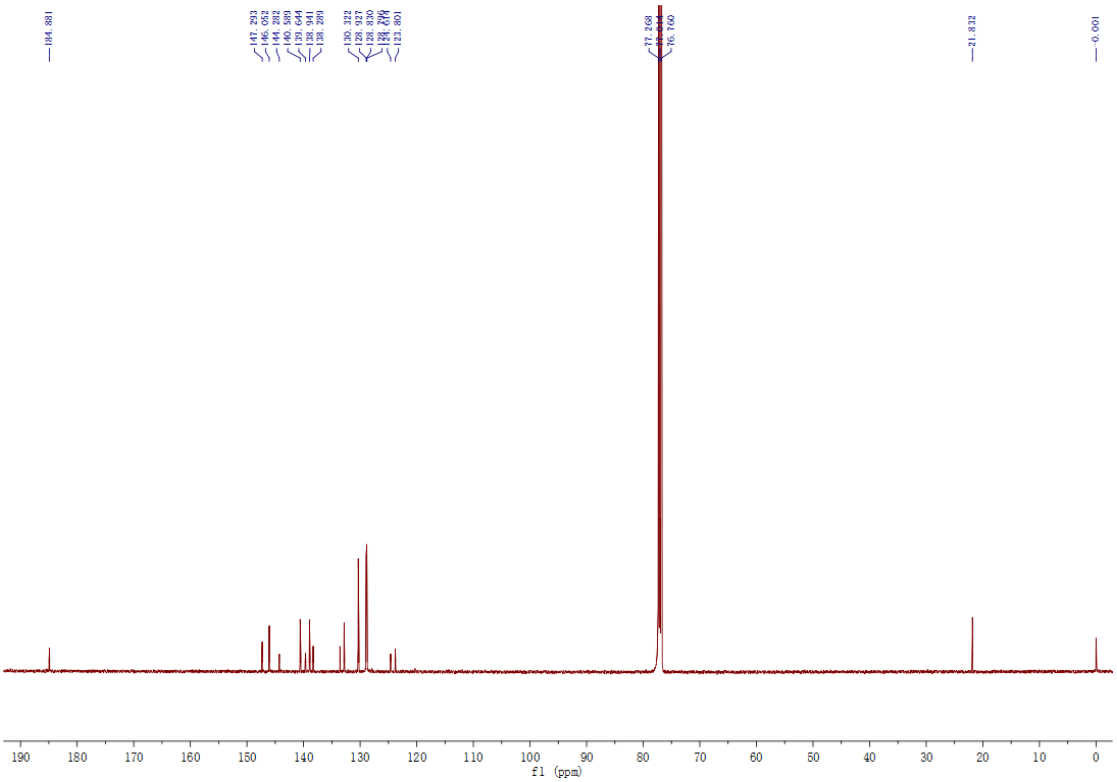


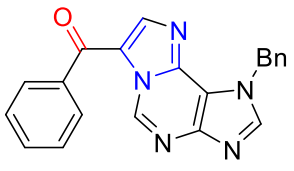



O
N
N
N
N
N
Ts

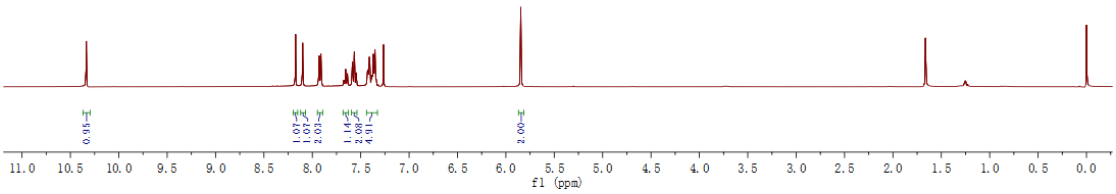
2r

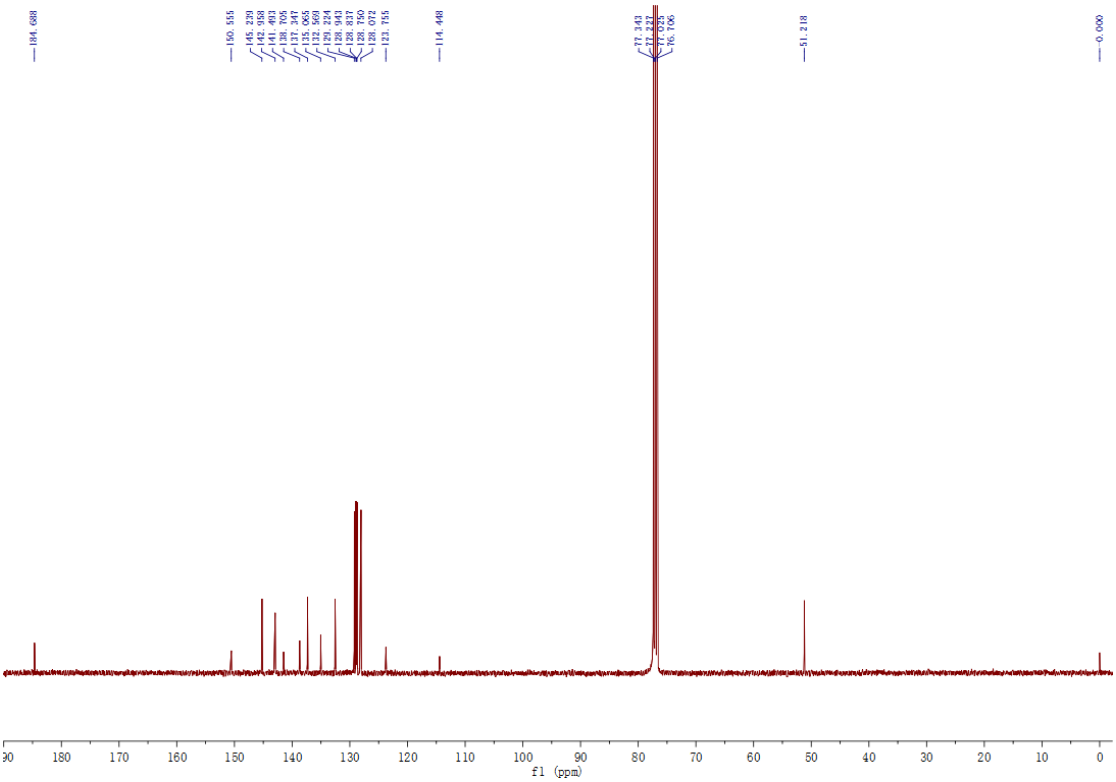

10.394
8.583
8.238
8.229
8.193
7.902
7.888
7.885
7.662
7.660
7.582
7.567
7.552
7.410
7.394
7.266
2.440
1.695
0.000
0.92
0.95
1.00
1.82
1.98
1.18
2.24
2.17
f1 (ppm)

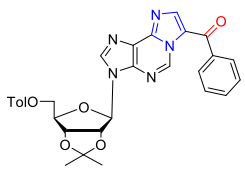

184.881
147.293
146.952
144.282
140.589
139.644
138.941
138.269
130.322
128.927
128.830
123.801
77.268
77.144
76.760
21.832
0.001
f1 (ppm)



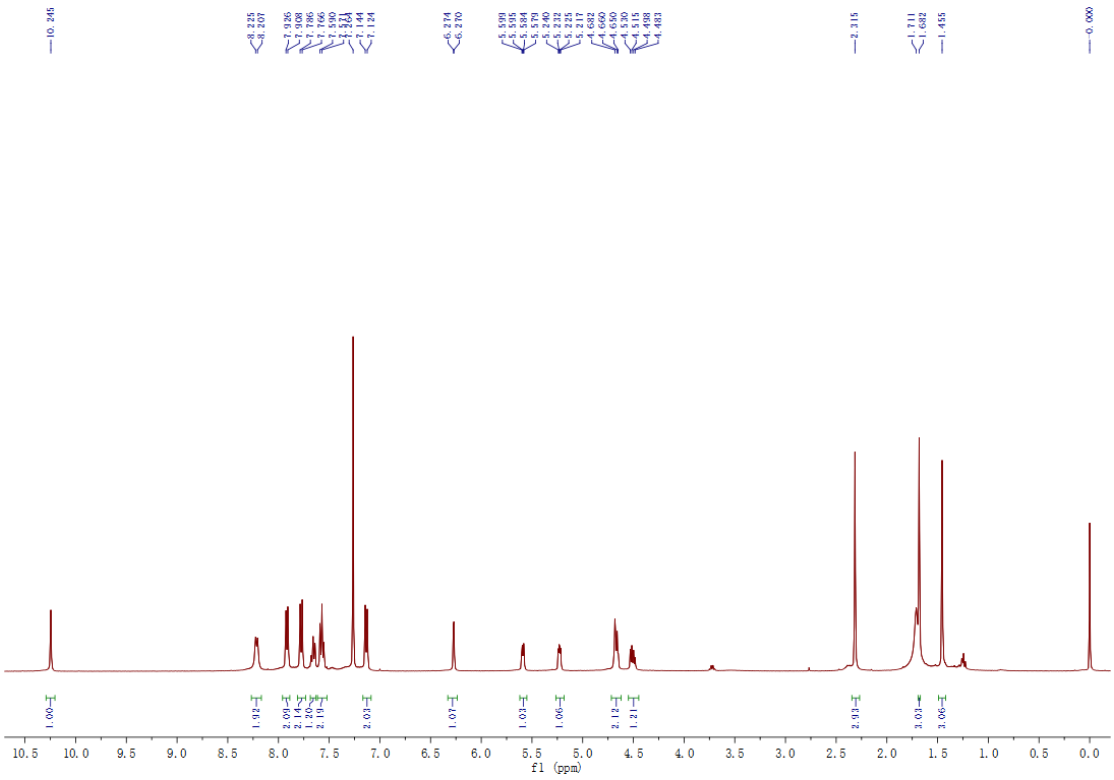
2s

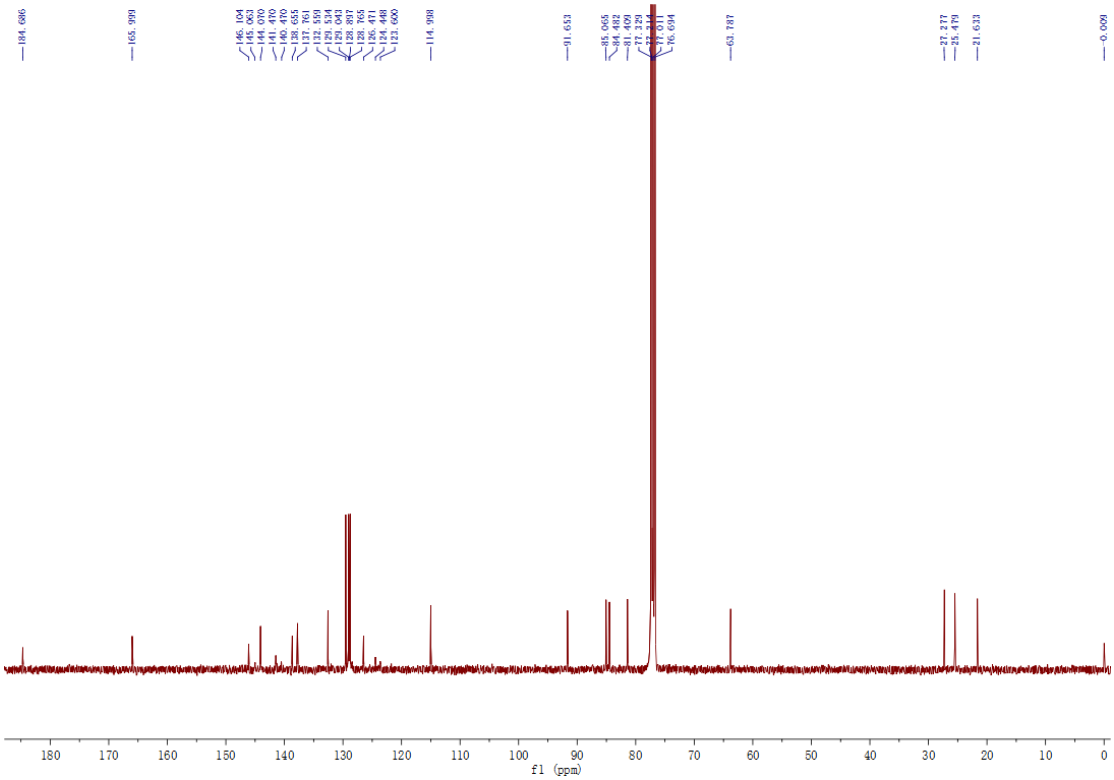


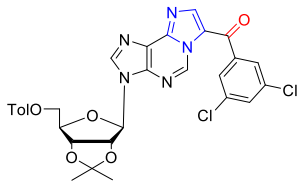



TolO
O
O
O
N
N
N
N
O

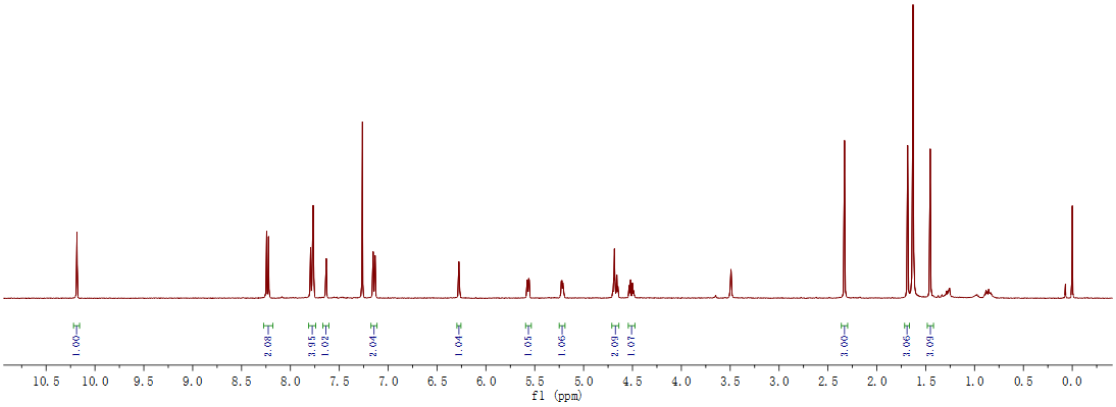
2t

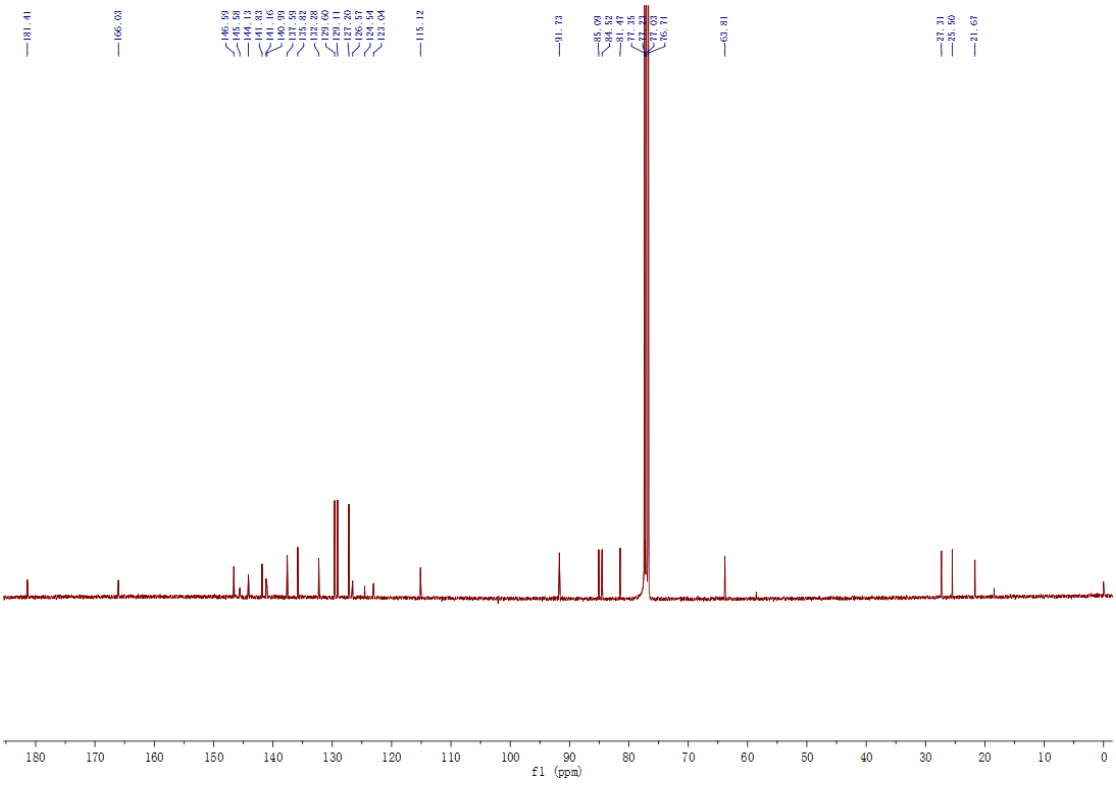

10.245
8.225
8.207
7.926
7.908
7.785
7.766
7.590
7.574
7.564
7.144
7.124
6.274
6.270
5.599
5.595
5.584
5.579
5.240
5.230
5.225
5.217
4.682
4.666
4.650
4.530
4.515
4.498
4.483
2.315
1.711
1.682
1.455
0.000
1.00
1.92
2.09
2.14
1.03
2.19
2.03
1.07
1.03
1.06
2.12
1.21
2.93
3.03
3.06
f1 (ppm)

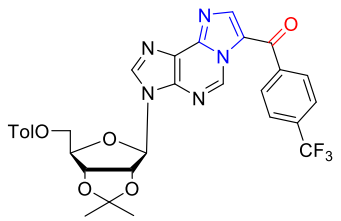

184.686
165.999
146.104
145.063
144.070
141.470
140.470
138.655
137.701
132.559
129.534
129.043
128.892
128.765
126.471
124.448
123.660
114.998
91.653
85.066
84.482
81.409
77.329
77.011
76.694
63.787
27.277
25.479
21.633
0.000
f1 (ppm)



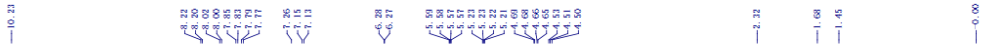
2u

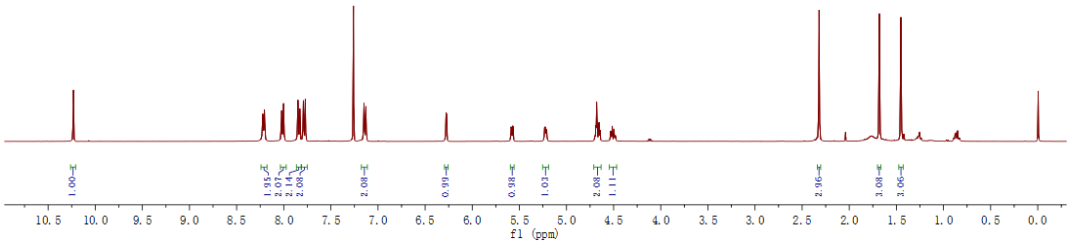


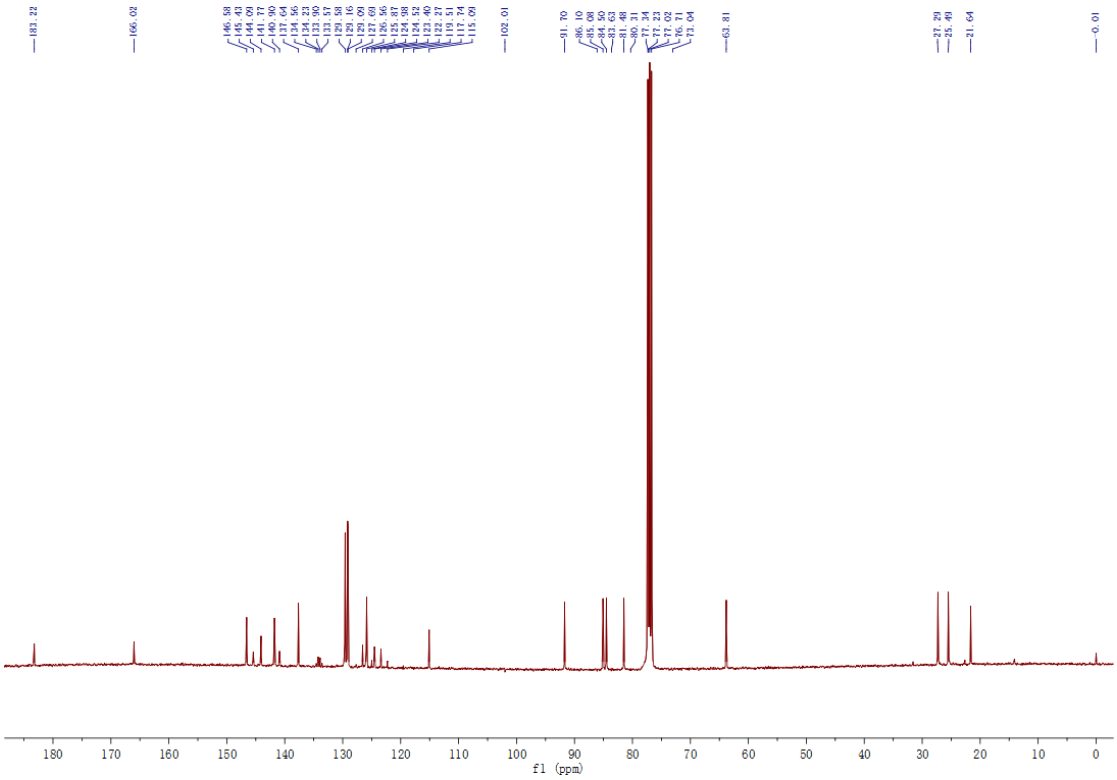


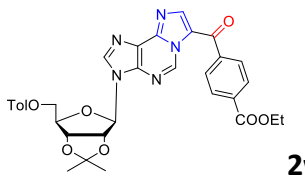


2v









2w