Electronic Supplementary Material (ESI) for ChemComm.

Copper-Catalyzed *ortho*−Halogenation of Arenes and Heteroarenes Directed by a Removable Auxiliary

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Supporting Information

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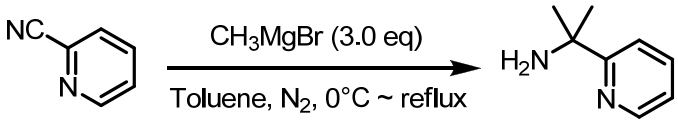
1. General Information:

1,2-dichloroethane was dried by calcium hydride，distilled and stored under nitrogen. Toluene was dried by sodium and freshly distilled. CuX (X= Br, Cl and I) was obtained from Aladdin® and NXS (X= Br, Cl and I) from Energy®. The other materials and solvents were purchased from Adamas-beta® or other commercial suppliers and used without additional purification. NMR spectra were recorded on a Bruke Advance operating for ^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, using TMS as internal standard. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument using EI ionization or ESI ionization.

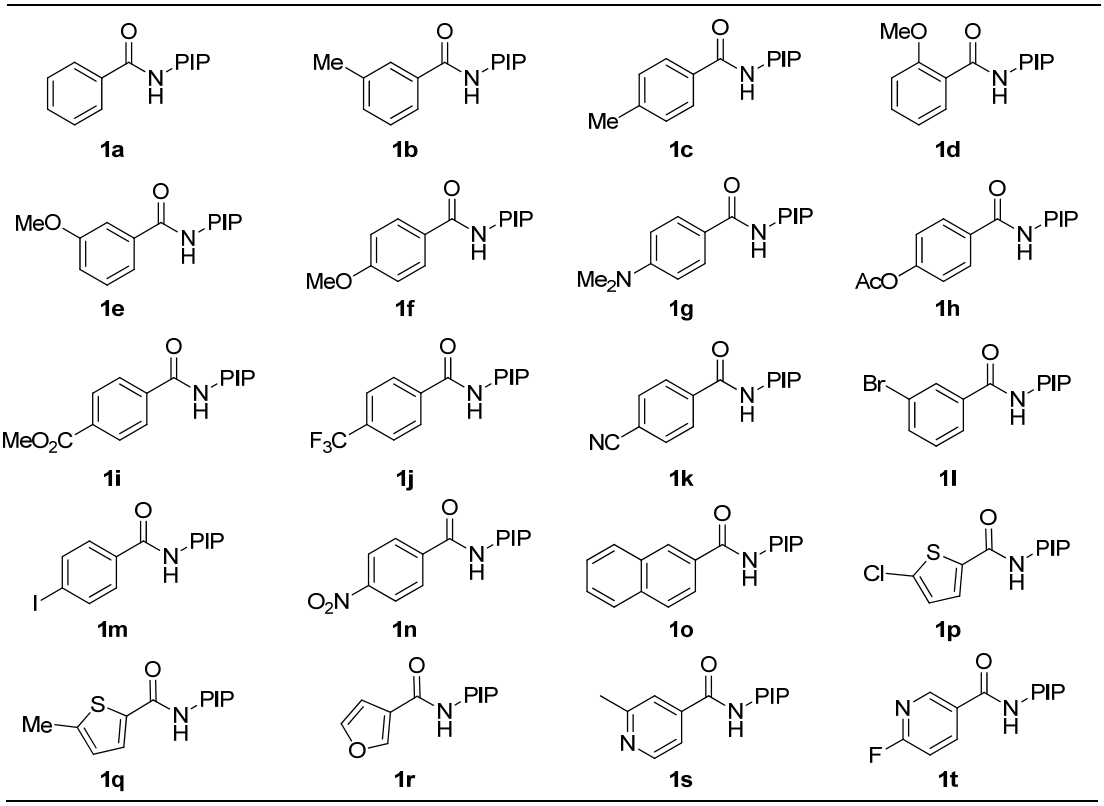
2. Experimental Section

2.1 Preparation of 2-(Pyridin-2-yl)isopropyl (PIP) Amine

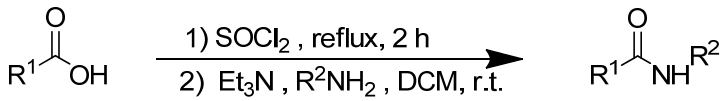


An analogous procedure to the literature[1] was used: To a solution of 2-cyanopyridine (33.0 g, 0.32 mol) in 500 mL of toluene was added CH_3MgBr (3.2M in 2-methyl tetrahydrofuran, 300 mL, 0.96 mol) dropwise at 0 ^{o}C under nitrogen atmosphere by vigorous magnetometric stirring. Upon completion of addition, the mixture was heated to reflux overnight. The reaction was quenched by adding saturated aqueous NH_4Cl dropwise at 0 ^{o}C until the dark mixture changed to yellow. The suspension was filtrated through a pad of celite® and the filtration was acidified by aqueous HCl (6 M, 10 mL). The resulting water phase combined with the filter residue was basified by saturated aqueous NaOH until the yellow colored mixture turned dark brown with slurry sticky to the bottom. The mixture was washed with dichloromethane (500 mL×4) carefully and the supernatant was combined and concentrated using a rotary evaporator. The crude product was further purified by distillation under reduced pressure. The target product was obtained as a light yellow liquid (>98% purity. 24 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 4.4 Hz, 1 H), 7.63 (td, J = 7.6, 1.6 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.12 (ddd, J = 7.2, 4.8, 0.8 Hz, 1 H), 1.87 (s, 2 H), 1.50 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 148.8, 136.6, 121.4, 118.5, 54.1, 31.4.

2.2 General Procedure for the Preparation of Starting Materials

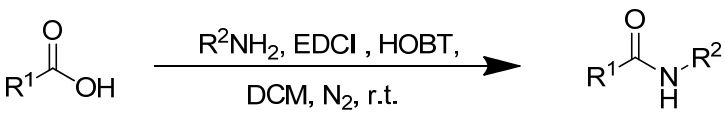


General Procedure for the Preparation of Starting Materials (Method A):



A solution of an acid (5 mmol) was refluxed in 10 mL $SOCl_2$ for 2 h and cooled to room temperature. The excess of $SOCl_2$ was removed under vacuum to give corresponding acid choloride. The acid choloride was then re-dissolved in 5 mL dry CH_2Cl_2 and added dropwise to a 20 mL dry CH_2Cl_2 solution containing amine (5 mmol) and Et_3N (10 mmol) at 0 ^oC. After stirring for 6h at ambient temperature, the resulting mixture was washed with sat. $NaHCO_3$ followed by brine and dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

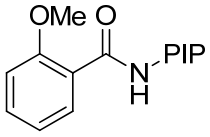
General Procedure for the Preparation of Starting Materials (Method B):



A mixture of amine (5 mmol), acid (5 mmol), EDCI (5.5 mmol) and HOBT (5.5 mmol) in anhydrous DCM (20 mL) was stirred at room temperature overnight. Water was added and the mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

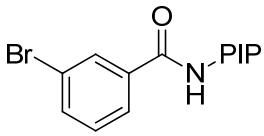
Compounds **1a, 1b, 1c, 1e, 1f, 1h, 1i, 1j, 1k, 1m, 1n, 1q, 1s** and **1t** were known compounds and were prepared according to literature[1,2]. **1d, 1l,** and **1o** were prepared according to the general procedure (Method **A**). **1p,** and **1r** were prepared according to the general procedure (Method **B**).

2-methoxy-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (1d)



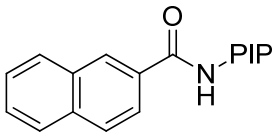
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (brs, 1H), 8.58 (d, *J* = 4.8, 1H), 8.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70 (td, *J* = 8.0, 1.6 Hz, 1H), 7.50 – 7.37 (m, 2H), 7.21 – 7.13 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H), 1.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.2, 157.8, 148.1, 136.9, 132.5, 132.1, 122.9, 121.8, 121.2, 119.7, 111.4, 57.5, 56.1, 28.0. HRMS (EI-TOF) calcd for $C_{16}H_{18}N_2O_2$ (M^+): 270.1368, found: 270.1367.

3-bromo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (1l)



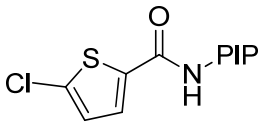
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (brs, 1H), 8.56 (d, *J* = 4.4 Hz, 1H), 8.04 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.76 (td, *J* = 8.4, 1.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.21 (m, 1H), 1.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 164.5, 147.7, 138.2, 137.5, 134.1, 130.5, 130.1, 125.6, 122.8, 122.2, 119.7, 56.9, 27.5. HRMS (EI-TOF) calcd for $C_{15}H_{15}BrN_2O_2$ (M^+): 318.0368, found: 318.0367.

***N*-(2-(pyridin-2-yl)propan-2-yl)-2-naphthamide (1o)**



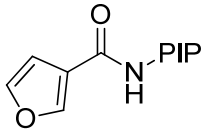
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (brs, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 8.43 (s, 1H), 8.0 – 7.84 (m, 4H), 7.77 (td, *J* = 8.0, 1.6 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.21 (m, 1H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.9, 147.8, 137.4, 134.8, 133.4, 132.9, 129.2, 128.4, 127.8, 127.5 (2 x C), 126.6, 123.9, 122.1, 119.7, 56.9, 27.7. HRMS (EI-TOF) calcd for $C_{19}H_{18}N_2O$ (M^+): 290.1419, found: 290.1420.

5-chloro-*N*-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide (1p)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (brs, 1H), 8.54 (d, *J* = 4.0 Hz, 1H), 7.76 (td, *J* = 8.0, 1.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 3.6 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 1.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 160.1, 147.6, 139.9, 137.5, 134.6, 126.9, 126.8, 122.2, 119.6, 56.9, 27.6. HRMS (EI-TOF) calcd for $C_{13}H_{13}ClN_2OS$ (M^+): 280.0437, found: 280.0435.

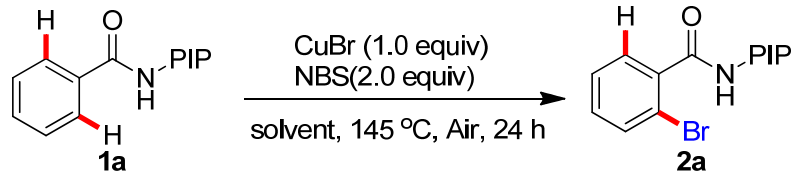
***N*-(2-(pyridin-2-yl)propan-2-yl)furan-3-carboxamide (1r)**



The title compound **1q** was prepared according to the general procedure (Method **B**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 8.46 (brs, 1H), 7.97 (s, 1H), 7.77 – 7.73 (m, 1H), 7.45 (d, *J* = 9.6 Hz, 2H), 7.23 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.73 (s, 1H), 1.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 161.9, 147.7, 144.6, 143.6, 137.4, 124.3, 122.1, 119.7, 108.7, 56.6, 27.7. HRMS (EI-TOF) calcd for $C_{13}H_{14}N_2O_2$ (M^+): 230.1055, found: 230.1051.

2.3 Optimization of Reaction Conditions

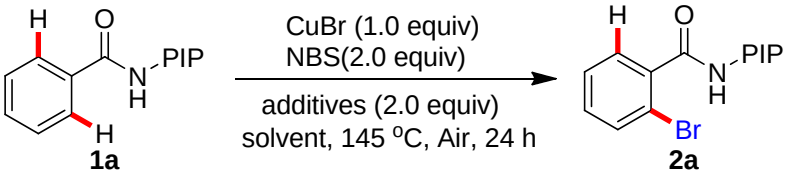
Screening of solvents[a]



Entry	solvent	**2a (%)**
1	CH_3CN	trace
2	DCE	20[b]
3	toluene	0
4	THF	0
5	dioxane	0

[a] Reaction conditions: **1a** (0.2 mmol), CuBr (0.2 mmol), and NBS (0.4 mmol) in solvent (2.0 mL) at 145 °C for 24 h. [b] Isolated yields.

Screening of additives[a]

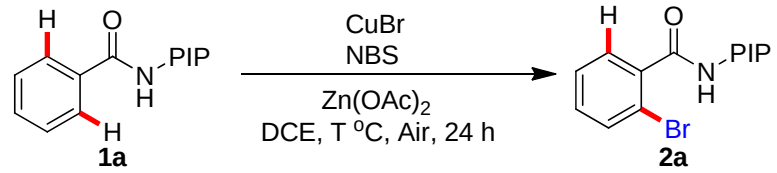


Entry	additives	**2a (%)**[b]
1	$Zn(OAc)_2$	95 (1.4:1)
2	Na_2CO_3	25
3	Ag_2CO_3	0
4	$K_2S_2O_8$	10
5	HOAc	27[c]
6	TBAB	0
7	NaOAc	37

[a] Reaction conditions: **1a** (0.2 mmol), CuBr (0.2 mmol), and NBS (0.4 mmol) in solvent (2.0 mL) at 145 °C for 24 h. [b] Yields and conversions are based on **1a**,

determined by ^{1}H-NMR using CH_2Br_2 as the internal standard. Data in the paratheses were the ratio of mono- to dihalogenated products. [c] Isolated yields.

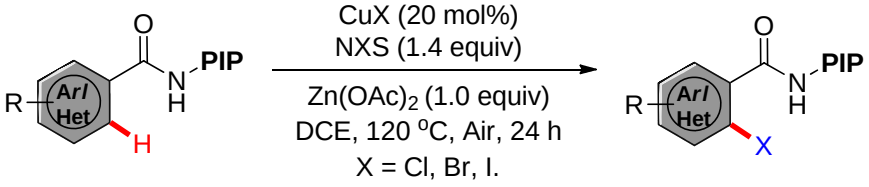
Screening of Quantity of CuBr, NBS, additives and temperature[a]



Entry	CuBr (equiv)	NBS (equiv)	$Zn(OAc)_2$ (equiv)	T / °C	**2a** (%)[b]
1	1.0	2.0	2.0	100	62
2	1.0	2.0	2.0	145	95 (1.4:1)[c]
3	1.0	1.4	2.0	145	92 (2.4:1)[c]
4	1.0	2.0	2.0	120	96 (4.3:1)
5	0.5	1.4	1.0	120	88 (10:1)
6	**0.2**	**1.4**	**1.0**	**120**	**87 (5.7:1)**
7	0	1.4	1.0	120	0

[a] Reaction were conducted on a 0.2 mmol scale for 24 h. [b] Isolated yields. [c] Yields and conversions are based on **1a**, determined by ^{1}H-NMR using CH_2Br_2 as the internal standard. Data in the paratheses were the ratio of mono- to dihalogenated products.

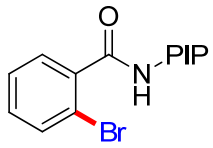
2.4 General Procedure for the Halogenation Process



To a 50 mL sealed tube was added substrate (0.2 mmol), CuX (0.04 mmol), NXS (0.28 mmol), $Zn(OAc)_2$ (36.7 mg, 0.2 mmol) and 1,2-dichloroethane (2.0 mL). The mixture was stirred at room temperature for 10 mins, then put into pre-heated 120℃oil bath for 24 hours. The reaction mixture was cooled to room temperature, diluted with ethyl acetate and quenched with saturated ammonia solution. The aqueous phase was extracted with ethyl acetate (10 mL× 3). The combined organic

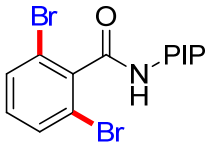
phase was dried with anhydrous magnesium sulfate. After concentration, the resulting residue was purified by flash chromatography to afford the product.

2-Bromo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2a)



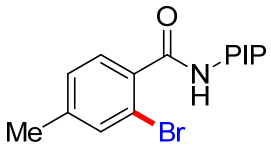
The title compound **2a** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **2a** was obtained as a white solid (47.2 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.0, 0.8 Hz, 1H), 8.24 (brs, 1H), 7.77 – 7.69 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.29 – 7.23 (m, 1H), 7.23 – 7.15 (m, 1H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ 167.0, 164.3, 147.7, 139.5, 137.3, 133.4, 130.8, 129.3, 127.5, 122.0, 119.6, 57.6, 27.6. The analytical datas above were matched with literature.[2]

2,6-dibromo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2a')



The title compound **2a'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **2a'** was obtained as a white solid (10.5 mg, 13%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.4 Hz, 1H), 8.28 (brs, 1H), 7.77 – 7.71 (m, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.22 – 7.14(m, 1H), 7.09 (t, *J* = 8.4 Hz, 1H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.0, 147.5, 140.8, 137.4, 131.9, 130.9, 122.1, 120.7, 119.7, 57.7, 27.3. HRMS (EI-TOF) calcd for $C_{15}H_{14}Br_2N_2O$ (M^+): 395.9473, found: 395.9479.

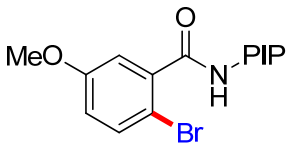
2-bromo-4-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2c)



The title compound **2c** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **2c** was

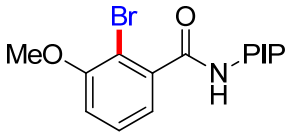
obtained as a white solid (41.3 mg, 62%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.45 (m, 1H), 8.20 (brs, 1H), 7.73 (td, *J* = 7.6, 1.2 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.22 – 7.12 (m, 2H), 2.34 (s, 3H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 164.4, 147.7, 141.3, 137.2 136.5, 133.8, 129.3, 128.3, 122.0, 119.6, 119.4, 57.5, 27.6, 21.1. HRMS (EI-TOF) calcd for $C_{16}H_{17}BrN_2O$ (M^+): 332.0524, found: 332.0526.

2-bromo-5-methoxy-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2e)



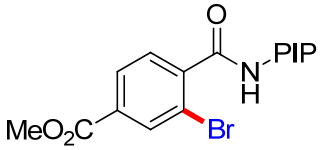
The title compound **2e** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **2e** was obtained as a white solid (32.3 mg, 46%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.0 Hz, 1H), 8.26 (brs, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.24 – 7.17 (m, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.81 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.2, 159.0, 147.7, 140.1, 137.3, 134.2, 122.1, 119.6, 117.4, 114.5, 109.8, 57.6, 55.8, 27.6. HRMS (EI-TOF) calcd for $C_{16}H_{17}BrN_2O_2$ (M^+): 348.0473, found: 348.0475.

2-bromo-3-methoxy-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2e')



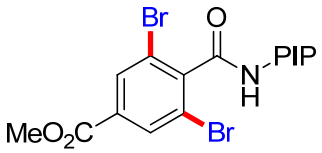
The title compound **2e'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **2e'** was obtained as a white solid (12.0 mg, 17%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.4 Hz, 1H), 8.19 (brs, 1H), 7.73 (t, *J* = 6.8 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 164.3 156.2, 147.7, 141.5, 137.3, 128.6, 122.1, 120.9, 119.6, 112.6, 109.4, 57.6, 56.7, 27.6. HRMS (EI-TOF) calcd for $C_{16}H_{17}BrN_2O_2$ (M^+): 348.0473, found: 348.0476.

methyl 3-bromo-4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)benzoate (2i)



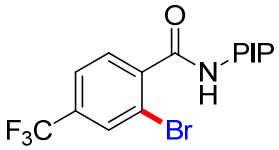
The title compound **2i** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **2i** was obtained as a white solid (60.5 mg, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.4 Hz, 1H), 8.39 (brs, 1H), 8.27 (d, *J* = 1.2 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75 (td, *J* = 8.0, 1.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 6.8, 5.2 Hz, 1H), 3.94 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.4, 164.0, 147.6, 143.3, 137.4, 134.5, 132.4, 129.2, 128.7, 122.2, 119.7, 119.6, 57.7, 52.7, 27.5. HRMS (EI-TOF) calcd for $C_{17}H_{17}BrN_2O_3$ (M^+): 376.0423, found: 376.0428.

methyl 3,5-dibromo-4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)benzoate (2i')



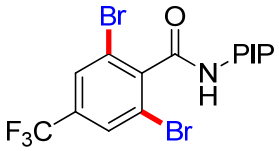
The title compound **2i'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **2i'** was obtained as a white solid (12.1 mg, 10%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 3.6 Hz, 1H), 8.41 (brs, 1H), 8.19 (s, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.16 (m, 1H), 3.94 (s, 3H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.3, 163.8, 147.5, 144.3, 137.5 133.0, 132.7, 122.2, 120.8, 119.6, 57.8, 52.9, 27.3. HRMS (EI-TOF) calcd for $C_{17}H_{16}Br_2N_2O_3$ (M^+): 453.9528, found: 453.9523.

2-bromo-*N*-(2-(pyridin-2-yl)propan-2-yl)-4-(trifluoromethyl)benzamide (2j)



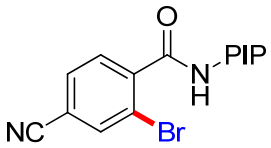
The title compound **2j** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **2j** was obtained as a white solid (45.1 mg, 58%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.40 (m, 2H), 7.86 (s, 1H), 7.76 (td, *J* = 8.0, 1.6 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.24 –7.19 (m, 1H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.9, 147.6, 142.8, 137.6, 132.8 (d, $J_{C\text{-}F}$ = 33 Hz), 130.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 129.6, 124.5 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.0 (q, $J_{C\text{-}F}$ = 272 Hz), 122.3, 120.0, 119.7, 57.6, 27.5. HRMS (ESI-TOF) calcd for $C_{16}H_{15}BrF_3N_2O$ $[M+H]^+$: 387.0314, found: 387.0306.

2,6-dibromo-*N*-(2-(pyridin-2-yl)propan-2-yl)-4-(trifluoromethyl)benzamide (2j')



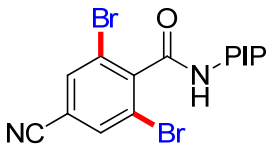
The title compound **2j'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 6 : 1). **2j'** was obtained as a white solid (9.2 mg, 10%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (brs, 1H), 8.47 – 8.43 (m, 1H), 7.80 (s, 2H), 7.76 (td, J = 8.0, 1.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.24 – 7.09 (m, 1H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.7, 147.4, 143.9, 137.6, 133.1 (q, $J_{C\text{-}F}$ = 34 Hz), 129.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 122.3, 122.2 (q, $J_{C\text{-}F}$ = 273 Hz), 121.3, 119.6, 57.8, 27.3. HRMS (EI-TOF) calcd for $C_{16}H_{13}Br_2F_3N_2O$ (M^+): 463.9347, found: 463.9349.

2-bromo-4-cyano-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2k)



The title compound **2k** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **2k** was obtained as a white solid (49.2 mg, 71%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (brs, 1H), 8.46 (d, J = 4.0 Hz, 1H), 7.89 (s, 1H), 7.79 – 7.73 (m, 1H), 7.67 – 7.58 (m, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.22 (dd, J = 7.6, 5.0 Hz, 1H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 163.7, 147.6, 143.6, 137.6, 136.7, 131.2, 129.7, 122.3, 120.3, 119.6, 117.0, 114.6, 57.7, 27.4. HRMS (EI-TOF) calcd for $C_{16}H_{14}BrN_3O$ (M^+): 343.0320, found: 343.0320.

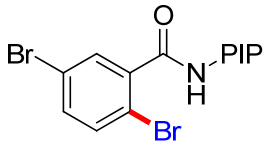
2,6-dibromo-4-cyano-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2k')



The title compound **2k'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **2k'** was obtained as a white solid (16.1 mg, 19%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (brs, 1H), 8.44 (d, J = 4.8 Hz, 1H), 7.83 (s, 2H), 7.76 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.25 – 7.19 (m, 1H), 1.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6,

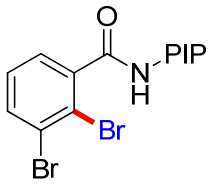
163.5, 147.4, 144.8, 137.6, 135.1, 122.4, 121.5, 119.6, 115.7, 115.1, 57.8, 27.2. HRMS (EI-TOF) calcd for $C_{16}H_{13}Br_2N_3O$ (M^+): 420.9425, found: 420.9424.

2,5-dibromo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2l)



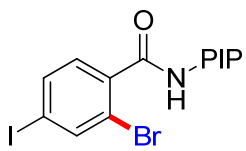
The title compound **2l** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **2l** was obtained as a white solid (40.1 mg, 50%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.0 Hz, 1H), 8.36 (brs, 1H), 7.79 – 7.72 (m, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.46 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.38 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.24 – 7.18 (m, 1H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.9, 147.7, 141.1, 137.4, 134.8 133.8 132.2, 122.2, 121.5, 119.6, 118.3, 57.6, 27.5. HRMS (EI-TOF) calcd for $C_{15}H_{14}Br_2N_2O$ (M^+): 395.9473, found: 395.9468.

2,3-dibromo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide(2l')



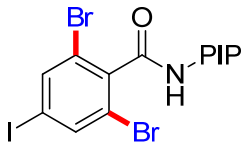
The title compound **2l'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **2l'** was obtained as a white solid (34.1 mg, 43%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.43 (m, 1H), 8.29 (brs, 1H), 7.74 (td, *J* = 7.6, 1.6 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.24 – 7.18 (m, 2H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7 164.0, 147.6, 142.3, 137.4, 134.4, 128.7, 127.3, 126.6, 122.2, 119.6, 57.5, 27.5. HRMS (EI-TOF) calcd for $C_{15}H_{14}Br_2N_2O$ (M^+): 395.9473, found: 395.9470.

2-bromo-4-iodo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2m)



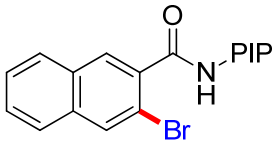
The title compound **2m** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **2m** was obtained as a white solid (60.1 mg, 67%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.4 Hz, 1H), 8.36 (brs, 1H), 7.96 (s, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.16 (m, 1H), 1.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 164.0, 147.6, 141.3, 138.9, 137.4, 136.7, 130.5, 122.2, 120.4, 119.6, 95.5, 57.6, 27.5. HRMS (ESI-TOF) calcd for $C_{15}H_{15}BrIN_2O$ $[M+Na]^+$: 466.9226, found: 466.9222.

2,6-dibromo-4-iodo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (2m')



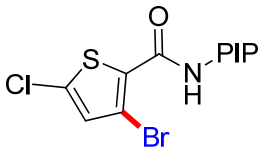
The title compound **2m'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **2m'** was obtained as a white solid (18.2 mg, 17%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.4 Hz, 1H), 8.36 (brs, 1H), 7.89 (s, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.17 (m, 1H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 163.8, 147.5, 140.4, 139.9, 137.5, 122.2, 121.2, 119.6, 94.3, 57.7, 27.3. HRMS (ESI-TOF) calcd for $C_{15}H_{14}Br_2IN_2O$ $[M+H]^+$: 522.8512, found: 522.8525.

3-bromo-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-naphthamide (2o)



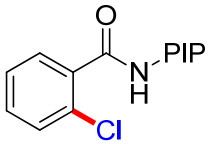
The title compound **2o** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **2o** was obtained as a white solid (45.2 mg, 61%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.4 Hz, 1H), 8.34 (brs, 1H), 8.10 (s, 1H), 8.03 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.57 – 7.45 (m, 3H), 7.23 – 7.17 (m, 1H), 1.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 164.3, 147.6, 137.4, 136.8, 134.5, 132.1, 131.8, 128.7, 128.4, 127.9, 127.1, 126.9, 122.1, 119.7, 116.7, 57.6, 27.6. HRMS (EI-TOF) calcd for $C_{19}H_{17}BrN_2O$ (M^+): 368.0524, found: 368.0522.

3-bromo-5-chloro-*N*-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide (2p)



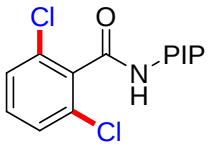
The title compound **2p** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **2p** was obtained as a white solid (56.0 mg, 78%).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (brs, 1H), 8.54 (d, *J* = 4.4 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.17 (m, 1H), 6.88 (d, *J* = 0.8 Hz, 1H), 1.85 (d, *J* = 0.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.9, 147.8, 137.3, 136.1, 135.1, 131.0, 122.2, 119.5, 107.1, 58.3, 27.7. HRMS (EI-TOF) calcd for $C_{13}H_{12}BrClN_2OS$ (M^+): 357.9542, found: 357.9545.

2-chloro-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3a)



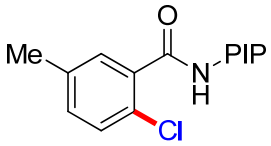
The title compound **3a** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **3a** was obtained as a white solid (45.2 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.1 Hz, 1H), 8.36 (s, 1H), 7.73 (td, *J* = 7.8, 1.8 Hz, 1H), 7.63 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.41 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.19 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 1.90 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.3, 147.7, 137.2, 130.9, 130.2, 129.8, 127.0, 122.0, 119.6, 57.6, 27.6. The analytical datas above were matched with literature.[3]

2,6-dichloro-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3a')



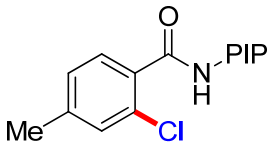
The title compound **3a'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **3a'** was obtained as a white solid (9.4 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.4 Hz, 1H), 8.25 (brs, 1H), 7.77 – 7.69 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.24 – 7.16 (m, 2H), 1.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 163.4, 147.5, 137.4,137.1, 132.5, 130.2, 128.2, 122.1, 119.6, 57.7, 27.4. HRMS (EI-TOF) calcd for $C_{15}H_{14}Cl_2N_2O$ (M^+): 308.0483, found: 308.0483.

2-chloro-5-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3b)



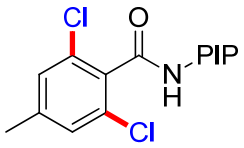
The title compound **3b** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 8 : 1). **3b** was obtained as a white solid (49.8 mg, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.29 (brs, 1H), 7.73 (t, *J* = 6.8 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.28 (s, 1H), 7.23 – 7.10 (m, 2H), 2.34 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 164.4, 147.8, 137.2, 137.1, 136.6, 131.6, 130.4, 130.0, 127.8, 122.0, 119.6, 57.6, 27.7, 20.9. HRMS (EI-TOF) calcd for $C_{16}H_{17}ClN_2O$ (M^+): 288.1029, found: 288.1026.

2-chloro-4-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3c)



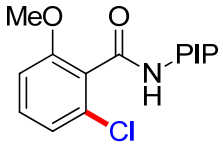
The title compound **3c** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **3c** was obtained as a white solid (40.1 mg, 69%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.0 Hz, 1H), 8.33 (brs, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 7.21 – 7.16 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 2.35 (s, 3H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.5, 147.8, 141.4, 137.2, 133.9, 130.7, 130.6, 129.9, 127.8, 122.0, 119.6, 57.6, 27.7, 21.1. HRMS (EI-TOF) calcd for $C_{16}H_{17}ClN_2O$ (M^+): 288.1029, found: 288.1032.

2,6-dichloro-4-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3c')



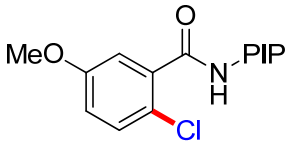
The title compound **3c'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **3c'** was obtained as a white solid (9.6 mg, 15%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.4 Hz, 1H), 8.19 (brs, 1H), 7.73 (t, *J* = 6.8 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.14 (s, 2H), 2.33 (s, 3H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.6, 147.6, 140.9, 137.3, 134.4, 132.0, 128.7, 122.1, 119.6, 57.7, 27.5, 21.0. HRMS (EI-TOF) calcd for $C_{16}H_{16}Cl_2N_2O$ (M^+): 322.0640, found: 322.0641.

2-chloro-6-methoxy-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3d)



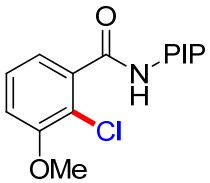
The title compound **3d** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **3d** was obtained as a white solid (41.1 mg, 67%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.0 Hz, 1H), 7.88 (brs, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.20 – 7.14 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.2, 157.5, 147.7, 137.2, 132.1, 130.2, 127.9, 121.9, 121.8, 119.7, 109.7, 57.7, 56.4, 27.7. HRMS (EI-TOF) calcd for $C_{16}H_{17}ClN_2O_2$ (M^+): 304.0979, found: 304.0980.

2-chloro-5-methoxy-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3e)



The title compound **3e** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **3e** was obtained as a white solid (39.8 mg, 50%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.0 Hz, 1H), 8.40 (brs, 1H), 7.73 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.22 – 7.16 (m, 2H), 6.89 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.82 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 164.3, 158.5, 147.8, 137.4, 137.3, 131.1, 122.1, 122.0, 119.6, 117.5, 114.5, 57.7, 55.9, 27.7. HRMS (EI-TOF) calcd for $C_{16}H_{17}ClN_2O_2$ (M^+): 304.0979, found: 304.0979.

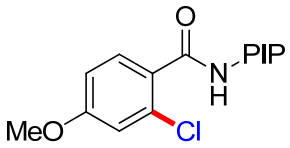
2-chloro-3-methoxy-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3e')



The title compound **3e'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **3e'** was obtained as a white solid (20.8 mg, 34%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.8 Hz, 1H), 8.29 (brs, 1H), 7.73 (td, *J* = 8.4, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H),

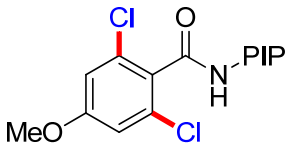
7.30 – 7.25 (m, 1H), 7.21 – 7.15 (m, 2H), 6.97 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 164.3, 155.4 147.7, 138.9, 137.3, 127.7, 122.1, 121.0, 119.6, 112.9, 57.6, 56.6, 27.6. HRMS (EI-TOF) calcd for $C_{16}H_{17}ClN_2O_2$ (M^+): 304.0979, found: 304.0979.

2-chloro-4-methoxy-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3f)



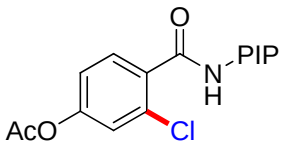
The title compound **3f** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **3f** was obtained as a white solid (42.5 mg, 70%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 2.4 Hz, 1H), 8.36 (brs, 1H), 7.72 (t, J = 6.8 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.23 – 7.15 (m, 1H), 6.92 (s, 1H), 6.84 (d, J = 7.2 Hz, 1H), 3.82 (s, 3H), 1.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 164.5, 161.2, 147.8, 137.2, 132.0, 131.5, 129.0, 122.0, 119.6, 115.5, 113.0, 57.6, 55.8, 27.7. HRMS (EI-TOF) calcd for $C_{16}H_{17}ClN_2O_2$ (M^+): 304.0979, found: 304.0981.

2,6-dichloro-4-methoxy-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3f')



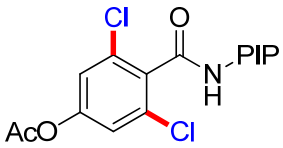
The title compound **3f'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **3f'** was obtained as a white solid (15.7 mg, 23%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 3.2 Hz, 1H), 8.17 (brs, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.22 – 7.15 (m, 1H), 6.86 (s, 2H), 3.81 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.5, 160.1, 147.6, 137.3, 133.1, 130.0, 122.1, 119.7, 114.1, 57.6, 56.0, 27.4. HRMS (EI-TOF) calcd for $C_{16}H_{16}Cl_2N_2O_2$ (M^+): 338.0589, found: 338.0590.

3-chloro-4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)phenyl acetate (3h)



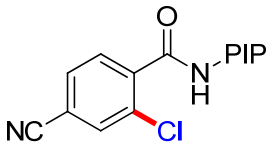
The title compound **3h** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 2 : 1). **3h** was obtained as a white solid (43.5 mg, 65%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.37 (m, 2H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.15 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 2.31 (s, 3H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.2, 164.2, 151.7, 147.7, 137.3, 134.7, 131.7, 130.6, 123.6, 122.1, 120.5, 119.6, 57.7, 27.6, 21.2. HRMS (EI-TOF) calcd for $C_{17}H_{17}ClN_2O_3$ (M^+): 332.0928, found: 332.0928.

3,5-dichloro-4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)phenyl acetate (3h')



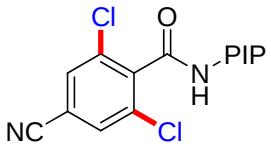
The title compound **3h'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **3h'** was obtained as a white solid (18.5 mg, 25%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.4 Hz, 1H), 8.34 (brs, 1H), 7.74 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 6.8, 5.2 Hz, 1H), 7.13 (s, 2H), 2.32 (s, 3H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 163.9, 162.9, 150.7, 147.6, 137.4, 134.9, 132.9, 122.2, 121.9, 119.6, 57.7, 27.4, 21.1. HRMS (EI-TOF) calcd for $C_{16}H_{16}Cl_2N_2O_3$ (M^+): 366.0538, found: 366.0535.

2-chloro-4-cyano-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3k)



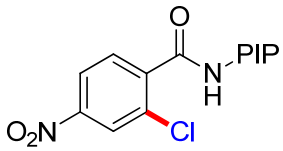
The title compound **3k** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **3k** was obtained as a white solid (43.7 mg, 73%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (brs, 1H), 8.46 (d, *J* = 3.6 Hz, 1H), 7.80 – 7.67 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.18 (m, 1H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 163.8, 147.6, 141.3, 137.6, 133.6, 132.1, 130.7, 130.3, 122.3, 119.6, 117.1, 114.7, 57.8, 27.5. HRMS (EI-TOF) calcd for $C_{16}H_{14}ClN_3O$ (M^+): 299.0825, found: 299.0827.

2,6-dichloro-4-cyano-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3k')



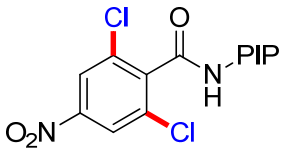
The title compound **3k'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **3k'** was obtained as a white solid (17.0 mg, 24%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (brs, 1H), 8.44 (d, *J* = 4.0 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.63 (s, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.19 (m, 1H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.6, 147.4, 141.2, 137.6, 133.8, 131.5, 122.4, 119.6, 116.1, 114.6, 57.9, 27.4. HRMS (EI-TOF) calcd for $C_{16}H_{13}Cl_2N_3O$ (M^+): 333.0436, found: 333.0440.

2-chloro-4-nitro-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3n)



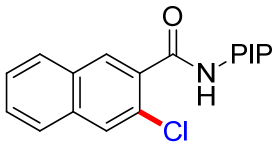
The title compound **3n** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **3n** was obtained as a white solid (31.0 mg, 48%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (brs, 1H), 8.46 (d, *J* = 4.4 Hz, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 8.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J* = 7.0, 5.2 Hz, 1H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 163.7, 148.6, 147.6, 142.7, 137.6, 132.4, 130.4, 125.5, 122.4, 122.1, 119.6, 57.8, 27.5. HRMS (ESI-TOF) calcd for $C_{15}H_{15}ClN_3O_3$ $[M+H]^+$: 320.0796, found: 320.0781.

2,6-dichloro-4-nitro-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3n')



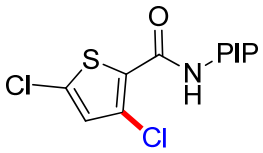
The title compound **3n'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **3n'** was obtained as a white solid (18.1 mg, 25%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (brs, 1H), 8.44 (d, *J* = 4.4 Hz, 1H), 8.21 (s, 2H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.19 (m, 1H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.6, 148.0, 147.4, 142.3, 137.7, 133.8, 123.5, 122.4, 119.6, 57.9, 27.4. HRMS (EI-TOF) calcd for $C_{15}H_{13}Cl_2N_3O_3$ (M^+): 353.0334, found: 353.0330.

3-chloro-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-naphthamide (3o)



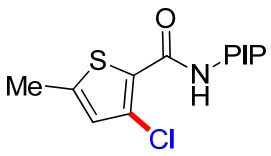
The title compound **3o** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **3o** was obtained as a white solid (50.1 mg, 77%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.40 (m, 2H), 8.12 (s, 1H), 7.90 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.58 – 7.46 (m, 3H), 7.20 (dd, *J* = 6.8, 5.2 Hz, 1H), 1.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 164.3, 147.8, 137.3, 134.9, 134.2, 131.5, 129.4, 128.6, 128.4, 128.2, 128.0, 127.0, 126.9, 122.1, 119.6, 57.7, 27.7. HRMS (EI-TOF) calcd for $C_{19}H_{17}ClN_2O$ (M^+): 324.1029, found: 324.1030.

3,5-dichloro-*N*-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide (3p)



The title compound **3p** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **3p** was obtained as a white solid (53.0 mg, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (brs, 1H), 8.54 (d, *J* = 4.4 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.18 (m, 1H), 6.83 (s, 1H), 1.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.7, 147.8, 137.3, 134.4, 134.3, 128.5, 122.2, 121.8, 119.5, 58.2, 27.7. HRMS (EI-TOF) calcd for $C_{13}H_{12}Cl_2N_2OS$ (M^+): 314.0047, found: 314.0048.

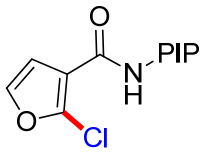
3-chloro-5-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide (3q)



The title compound **3q** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **3q** was obtained as a white solid (52.2 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (brs, 1H), 8.54 (d, *J* = 4.0 Hz, 1H), 7.71 (td, *J* = 8.0, 1.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 6.8, 5.2 Hz, 1H), 6.66 (s, 1H), 2.44 (s, 3H), 1.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 159.7, 147.9, 143.5, 137.1, 132.3, 127.7, 122.3, 122.0, 119.5,

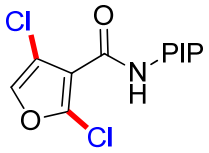
58.0 , 27.8, 15.9. HRMS (EI-TOF) calcd for $C_{14}H_{15}ClN_2OS$ (M^+): 294.0594, found: 294.0594.

4-chloro-*N*-(2-(pyridin-2-yl)propan-2-yl)furan-3-carboxamide (3r)



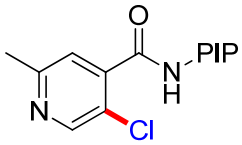
The title compound **3r** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). **3r** was obtained as a white solid (17.8 mg, 34%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (brs, 1H), 8.54 (d, *J* = 4.0 Hz, 1H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.84 (d, *J* = 1.6 Hz, 1H), 1.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 160.2, 147.7, 141.6, 137.3, 136.4, 122.1, 119.6, 117.9, 112.7, 57.3, 27.7. HRMS (EI-TOF) calcd for $C_{13}H_{13}ClN_2O_2$ (M^+): 264.0666, found: 264.0665.

2,4-dichloro-*N*-(2-(pyridin-2-yl)propan-2-yl)furan-3-carboxamide (3r')



The title compound **3r'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 8 : 1). **3r'** was obtained as a white solid (6.5 mg, 13%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (brs, 1H), 8.52 (d, *J* = 3.6 Hz, 1H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.24 – 7.17 (m, 1H), 1.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 158.6, 147.7, 139.9, 138.4, 137.4, 122.1, 119.6, 116.0, 115.9, 57.7, 27.7. HRMS (EI-TOF) calcd for $C_{13}H_{12}Cl_2N_2O_2$ (M^+): 298.0276, found: 298.0278.

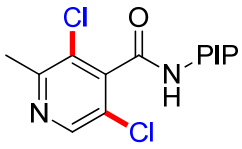
5-chloro-2-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)isonicotinamide (3s)



The title compound **3s** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 2 : 1). **3s** was obtained as a white solid (26.2 mg, 45%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (brs,

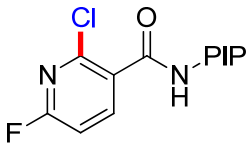
1H), 8.52 (s, 1H), 8.48 (d, J = 4.0 Hz, 1H), 7.75 (td, J = 8.0, 1.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.38 (s, 1H), 7.24 – 7.17 (m, 1H), 2.56 (s, 3H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 163.7, 157.6, 149.6, 147.6, 143.4, 137.5, 125.2, 122.9, 122.3, 119.6, 57.8, 27.5, 23.9. HRMS (EI-TOF) calcd for $C_{15}H_{16}ClN_3O$ (M^+): 289.0982, found: 289.0984.

3,5-dichloro-2-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)isonicotinamide (3s')



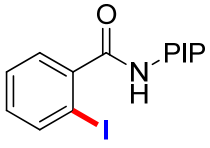
The title compound **3s'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **3s'** was obtained as a white solid (9.1 mg, 14%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.40 (m, 3H), 7.76 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.25 – 7.17 (m, 1H), 2.63 (s, 3H), 1.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.7, 155.6, 147.5, 146.7, 143.3, 137.6, 128.4, 126.6, 122.3, 119.6, 57.9, 27.4, 22.8. HRMS (EI-TOF) calcd for $C_{15}H_{15}Cl_2N_3O$ (M^+): 323.0592, found: 323.0594.

4-chloro-6-fluoro-*N*-(2-(pyridin-2-yl)propan-2-yl)nicotinamide (3t)



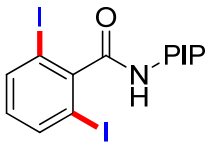
The title compound **3t** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 2 : 1). **3t** was obtained as a white solid (28.2 mg, 48%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (brs, 1H), 8.49 (d, J = 4.0 Hz, 1H), 8.17 (t, J = 8.0 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.95 (dd, J = 8.0, 2.4 Hz, 1H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 163.1, 162.0 (d, J_{C-F} = 247 Hz), 147.7, 145.4 (d, J_{C-F} = 14.6 Hz), 144.3 (d, J_{C-F} = 8.0 Hz), 137.5, 130.9 (d, J_{C-F} = 5.3 Hz), 122.3, 119.6, 108.7, 108.3, 57.8, 27.5. HRMS (EI-TOF) calcd for $C_{14}H_{13}ClFN_3O$ (M^+): 293.0731, found: 293.0734.

2-iodo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (4a)



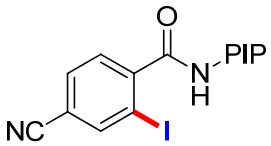
The title compound **4a** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **4a** was obtained as a white solid (41.2 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 1H), 8.18 (brs, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.74 (td, *J* = 7.8, 1.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.08 (td, *J* = 7.6, 1.6 Hz, 1H), 1.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 164.3, 147.7, 143.6, 140.0, 137.3, 130.8, 128.3, 128.2, 122.1, 119.7, 92.8, 57.5, 27.5; The analytical datas above were matched with literature.[2]

2,6-diiodo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (4a')



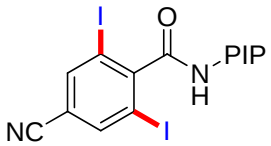
The title compound **4a'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **4a'** was obtained as a white solid (9.2 mg, 9%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 3.6 Hz, 1H), 8.31 (brs, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.16 (m, 1H), 6.72 (t, *J* = 8.0 Hz, 1H), 1.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 164.0, 147.8, 147.5, 139.2, 137.4, 131.4, 122.2, 119.7, 92.6, 57.6, 27.2. HRMS (EI-TOF) calcd for $C_{15}H_{14}I_2N_2O$ (M^+): 491.9195, found: 491.9199.

4-cyano-2-iodo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (4k)



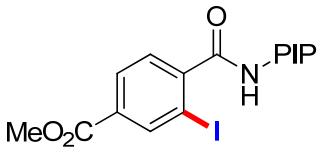
The title compound **4k** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **4k** was obtained as a white solid (54.2 mg, 69%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 2.4 Hz, 2H), 8.15 (s, 1H), 7.77 (t, *J* = 6.4 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.18 (m, 1H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 163.7, 147.6, 147.5, 143.0, 137.6, 131.9, 128.4, 122.4, 119.6, 116.8, 114.6, 92.8, 57.6, 27.4. HRMS (EI-TOF) calcd for $C_{16}H_{14}IN_3O$ (M^+): 391.0182, found: 391.0183.

4-cyano-2,6-diiodo-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (4k')



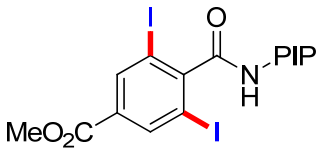
The title compound **4k'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **4k'** was obtained as a white solid (16.1 mg, 15%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (brs, 1H), 8.46 (d, *J* = 4.0 Hz, 1H), 8.08 (s, 2H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 1H), 1.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 163.5, 151.8, 147.4, 142.1, 137.6, 122.4, 119.7, 115.3, 115.2, 92.3, 57.7, 27.1. HRMS (EI-TOF) calcd for $C_{16}H_{13}I_2N_3O$ (M^+): 516.9148, found: 516.9146.

methyl 3-iodo-4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)benzoate (4i)



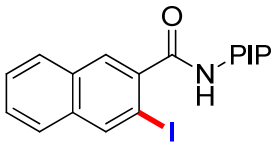
The title compound **4i** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **4i** was obtained as a white solid (60.1 mg, 71%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.46 (d, *J* = 4.0 Hz, 1H), 8.33 (brs, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.48 (dd, *J* = 14.4, 8.0 Hz, 2H), 7.23 – 7.18 (m, 1H), 3.93 (s, 3H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 165.2, 164.0, 147.6, 147.3, 141.0, 137.4, 132.1, 129.4, 128.0, 122.2, 119.6, 92.3, 57.5, 52.7, 27.5. HRMS (EI-TOF) calcd for $C_{17}H_{17}IN_2O_3$ (M^+): 424.0284, found: 424.0287.

methyl 3,5-diiodo-4-((2-(pyridin-2-yl)propan-2-yl)carbamoyl)benzoate (4i')



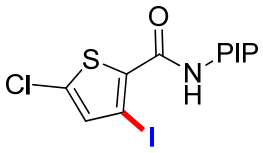
The title compound **4i'** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 3 : 1). **4i'** was obtained as a white solid (17.1 mg, 15%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.37 (m, 4H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.22 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.93 (s, 3H), 1.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 163.9, 163.8, 151.3, 147.4, 140.2, 137.5, 132.7, 122.3, 119.7, 92.0, 57.6, 52.9, 27.2. HRMS (EI-TOF) calcd for $C_{17}H_{16}I_2N_2O_3$ (M^+): 549.9250, found: 549.9252.

3-iodo-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-naphthamide (4o)



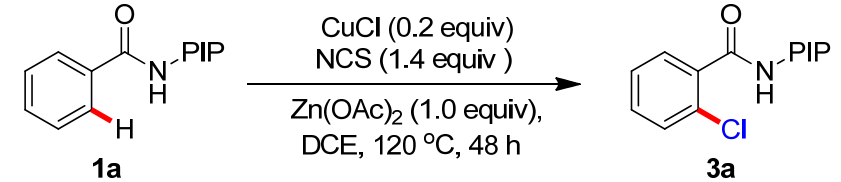
The title compound **4o** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 4 : 1). **4o** was obtained as a white solid (50.2 mg, 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.0 Hz, 1H), 8.39 (s, 1H), 8.31 (brs, 1H), 7.93 (s, 1H), 7.86 – 7.79 (m, 1H), 7.78 – 7.66 (m, 2H), 7.56 – 7.47 (m, 3H), 7.23 – 7.16 (m, 1H), 1.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 164.2, 147.7, 140.0, 139.4, 137.3, 134.9, 132.2, 128.3, 127.7, 127.2, 126.7, 122.1, 119.7, 89.4, 57.5, 27.6. HRMS (EI-TOF) calcd for $C_{19}H_{17}IN_2O$ (M^+): 416.0386, found: 416.0385.

5-chloro-3-iodo-*N*-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide (4p)



The title compound **4p** was prepared according to the general procedure and was purified by flash chromatography (petroleum ether : ethyl acetate = 2 : 1). **4p** was obtained as a white solid (73.2 mg, 90%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (brs, 1H), 8.54 (d, *J* = 4.0 Hz, 1H), 7.78 – 7.67 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 6.8, 5.2 Hz, 1H), 6.97 (s, 1H), 1.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 159.2, 147.7, 139.1, 137.3, 136.3, 135.6, 122.2, 119.5, 76.5, 58.1, 27.7. HRMS (EI-TOF) calcd for $C_{13}H_{12}ClIN_2OS$ (M^+): 405.9404, found: 405.9400.

2.5 Gram Scale Halogenation of Benzamide 1a



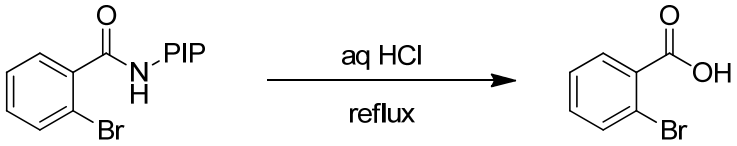
1a
5.0 mmol, 1.20 g

3a
Yield: 90%, m/d = 3.5:1

To a 100 mL Schlenk tube was added substrate **1a** (1.20 g, 5.0 mmol), CuCl (99.0 mg, 1.0 mmol), NCS (943.7 mg, 7.0 mmol), $Zn(OAc)_2$ (917.0 mg, 5.0 mmol) and 1,2-dichloroethane (20 mL). The mixture was stirred at room temperature for 10 mins,

then put into pre-heated 120℃oil bath for 48 hours. The reaction mixture was cooled to room temperature, diluted with ethyl acetate and quenched with saturated ammonia solution. The aqueous phase was extracted with ethyl acetate (20 mL× 3). The combined organic phase was dried with anhydrous magnesium sulfate. After concentration, the resulting residue was purified by flash chromatography to afford the desired product.

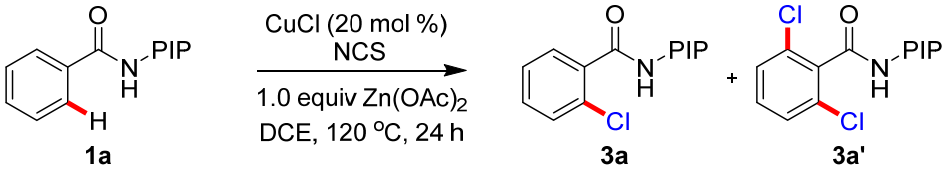
2.6 Removal of the Directing Group



2a **5**

To a 50 mL Schlenk tube was added **2a** (0.2 mmol, 63.84 mg) and conc. HCl (3 mL). The mixture was then heated at 145 ^{o}C for 48 hours. After cooling down to room temperature, aqueous NaOH (1 M) was added and the aqueous phase was extracted with DCM (10 mL x 2). Then, conc. HCl was added slowly into the aqueous phase (pH = 2) and the aqueous phase was as extracted with DCM (10 mL x 3). The combined organic phase was dried with anhydrous sodium sulfate. After concentration, the desired product **5** was obtained as a white solid (32 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.29 (brs, 1H), 8.02 (d, J = 5.2 Hz, 1H), 7.72 (d, J = 6.8 Hz, 1H), 7.48 – 7.32 (m, 2H).

2.7 Tuning the ratio of Mono- and Dihalogenated Products



1a **3a** **3a'**

Entry	NCS (equiv)	T (°C)	yield %[a]	
			3a	**3a'**
1	**1.0**	**120**	**70**	**10**
2	1.2	120	75	15
3[b]	1.2	120	74	16
4[c]	2.0	120	60	30
5	4.0	120	60	30
6	2.2	145	45	48
7[c]	3.0	145	48	43
8	4.0	145	25	44
9	3.0	160	20	50
10	**4.0**	**160**	**18**	**48**

Reaction were conducted on a 0.2 mmol scale for 24 h under air. [a]^{1}H-NMR Yields and conversions are based on **1a**, determined by using CH_2Br_2 as the internal standard. [b]O_2. [c]48h.

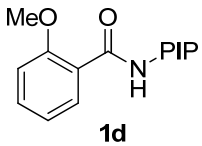
3. References

1. X. Li, Y.-H. Liu, W.-J. Gu, B. Li, F.-J. Chen, B.-F. Shi, *Org. Lett.* 2014, **16**, 3904.

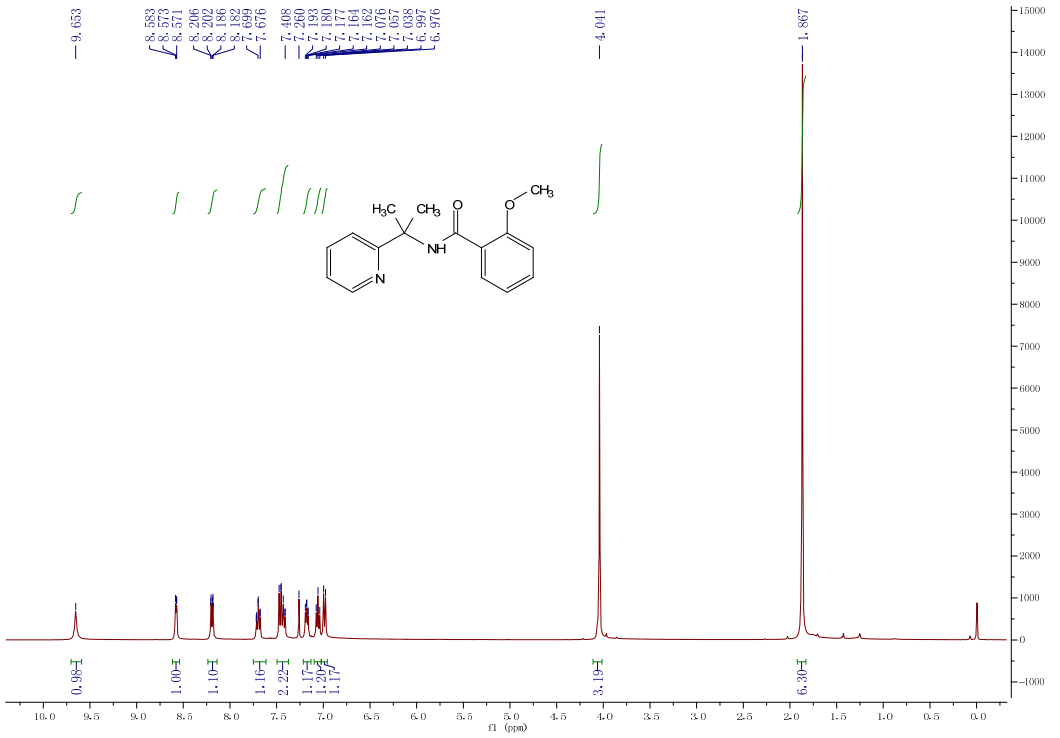
2. F.-J. Chen, G. Liao, X. Li, J. Wu, B.-F. Shi, *Org. Lett.* 2014, **16**, 5644.

3.Y.-J. Liu, Y.-H. Liu, X.-S. Yin, W.-J. Gu, B.-F. Shi, *Chem. Eur. J.* 2015, **21**, 205.

4. Spectra


MeO
O
N
H
PIP

1d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8.571
8.206
8.202
8.186
8.182
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7.408
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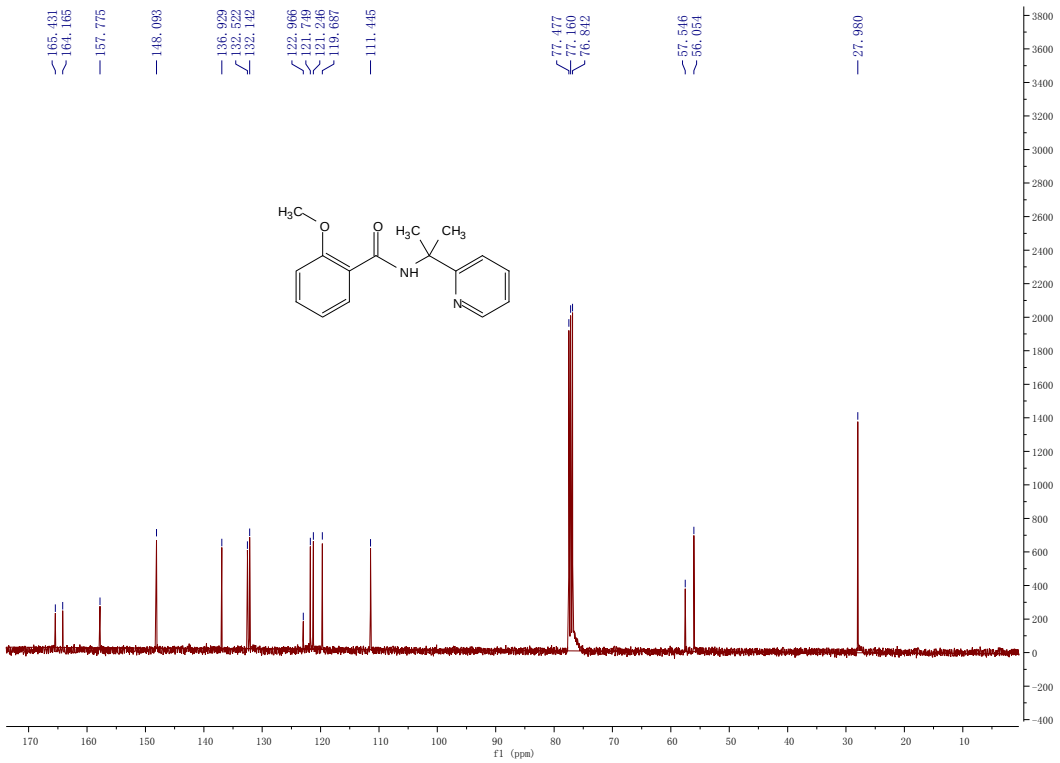
7.193
7.180
7.177
7.164
7.162
7.076
7.057
7.038
6.997
6.976
4.041
1.867
0.98
1.00
1.10
1.16
2.22
1.17
1.20
1.17
3.19
6.30
f1 (ppm)


165.431
164.165
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148.093
136.929
132.522
132.142
122.966
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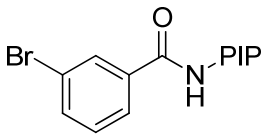
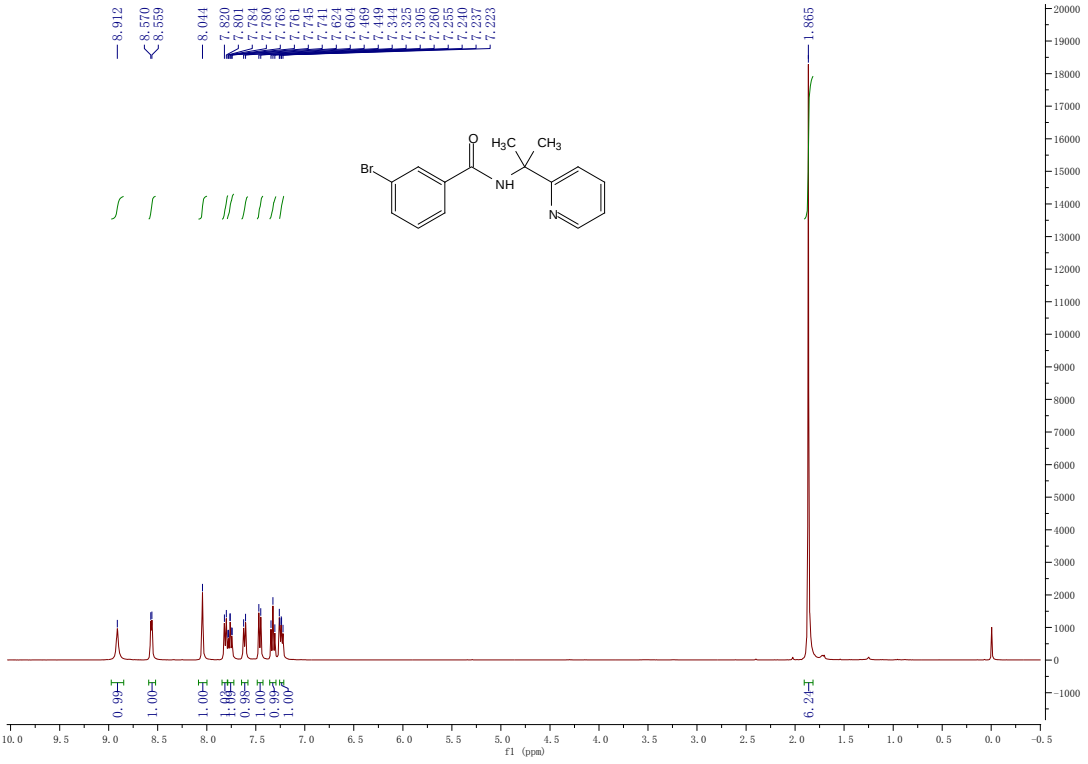
77.160
76.842
57.546
56.054
27.980
f1 (ppm)


O
Br
N
H
PIP

1l


8.912
8.570
8.559
8.044
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7.801
7.784
7.780
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7.761
7.745
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7.624
7.604
7.469
7.449
7.344
7.325
7.305
7.260
7.255
7.240
7.237
7.223
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0.99
1.00
1.00
0.98
1.00
0.99
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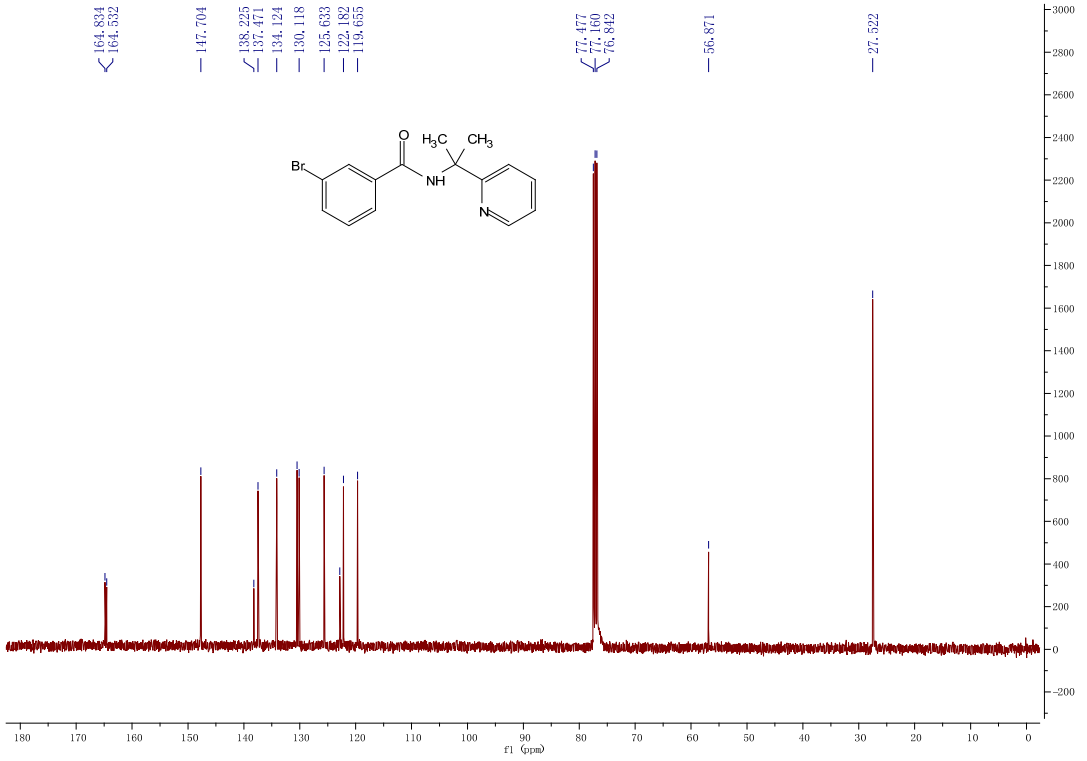
6.24
f1 (ppm)


164.834
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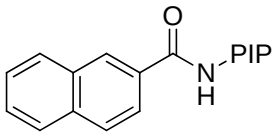
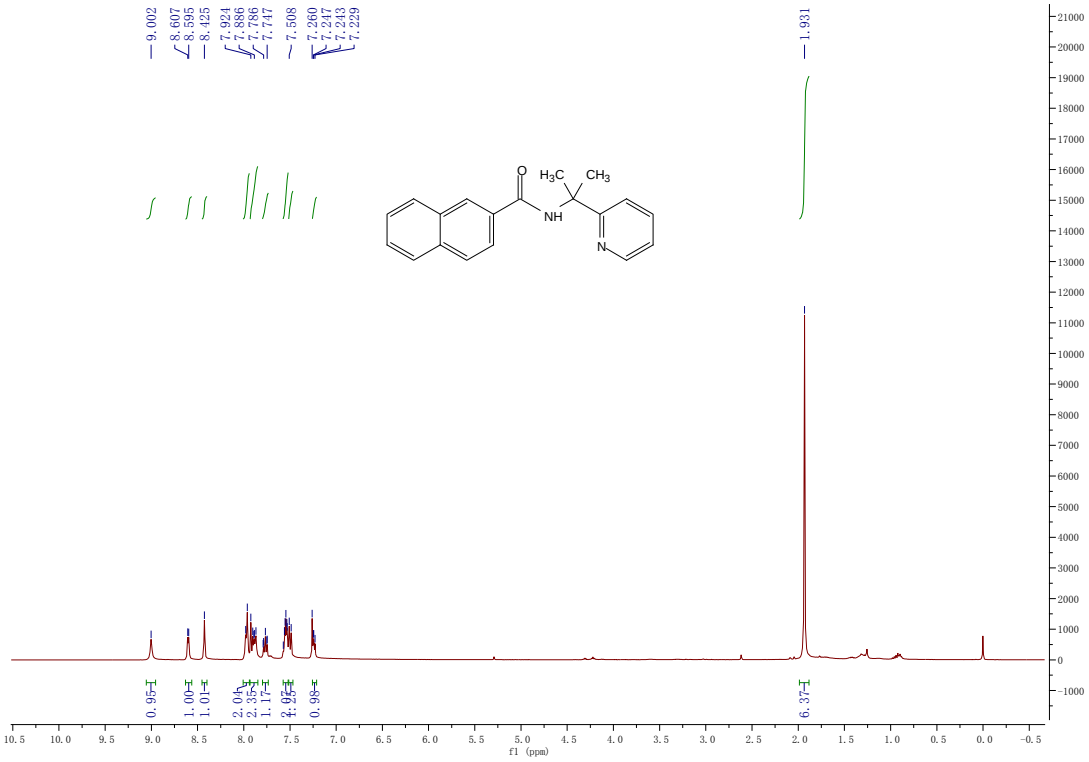
56.871
27.522
f1 (ppm)


O
N
H
PIP

1o


9.002
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7.747
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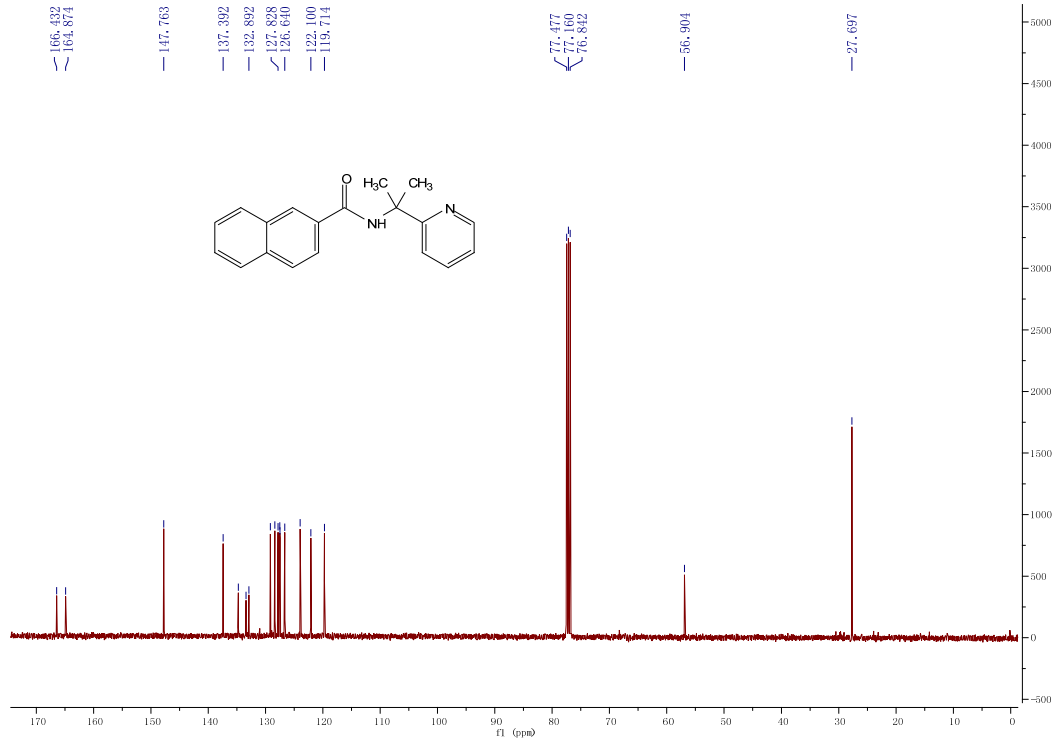
7.260
7.247
7.243
7.229
1.931
O
H3C
CH3
NH
N
0.95
1.00
1.01
2.04
2.35
1.17
2.25
0.98
6.37
f1 (ppm)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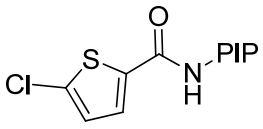
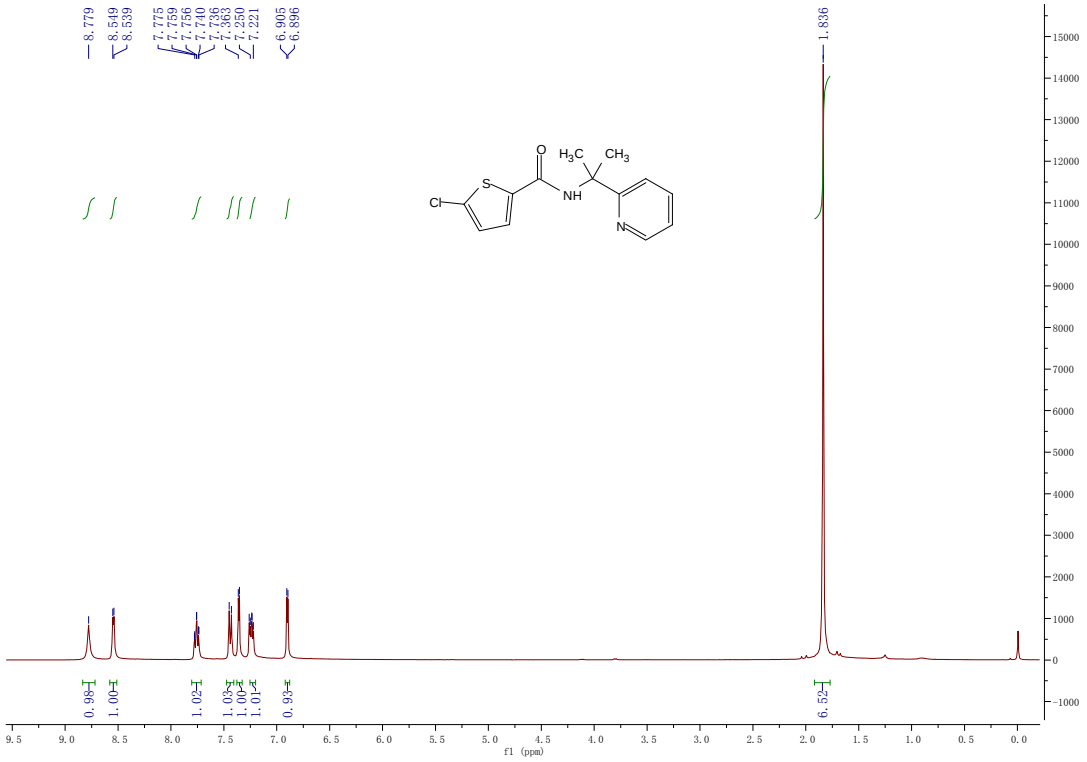
164.874
147.763
137.392
132.892
127.828
126.640
122.100
119.714
77.477
77.160
76.842
56.904
27.697
O
H3C
CH3
NH
N
f1 (ppm)


O
S
N
H
PIP
Cl

1p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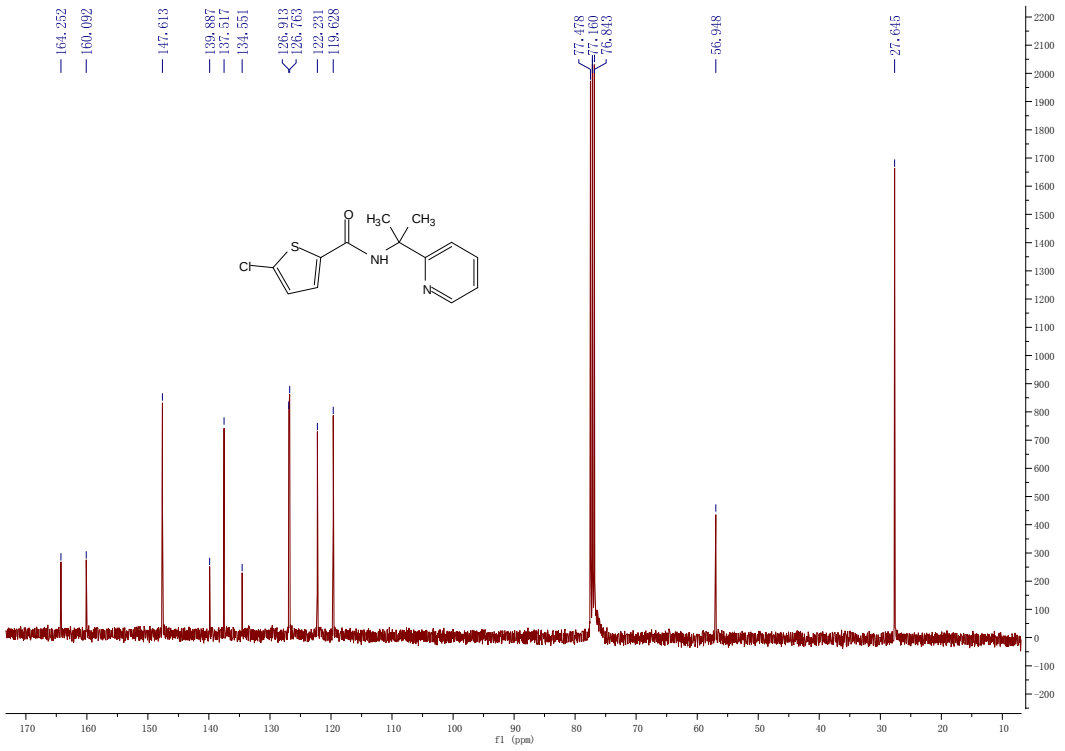
8.549
8.539
7.775
7.759
7.756
7.740
7.736
7.363
7.250
7.221
6.905
6.896
1.836
0.98
1.00
1.02
1.03
1.00
1.01
0.93
6.52
f1 (ppm)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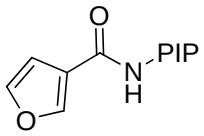
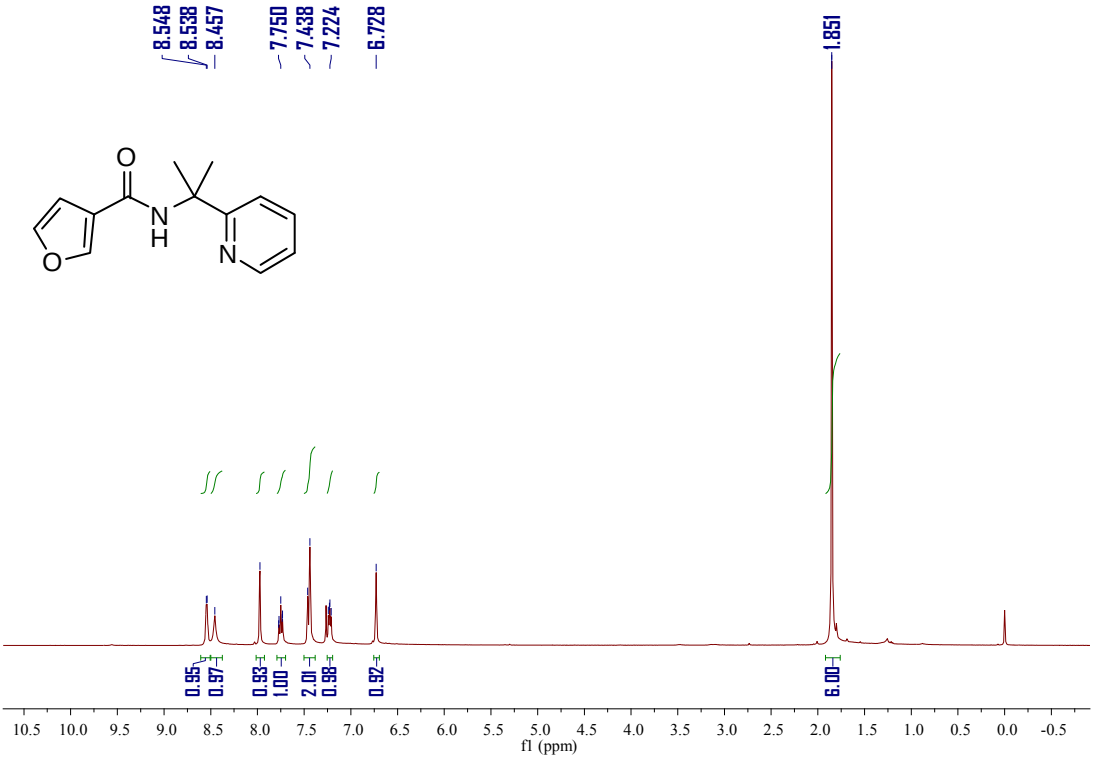
160.092
147.613
139.887
137.517
134.551
126.913
126.763
122.231
119.628
77.478
77.160
76.843
56.948
27.645
f1 (ppm)


O
N
H
PIP
O

1r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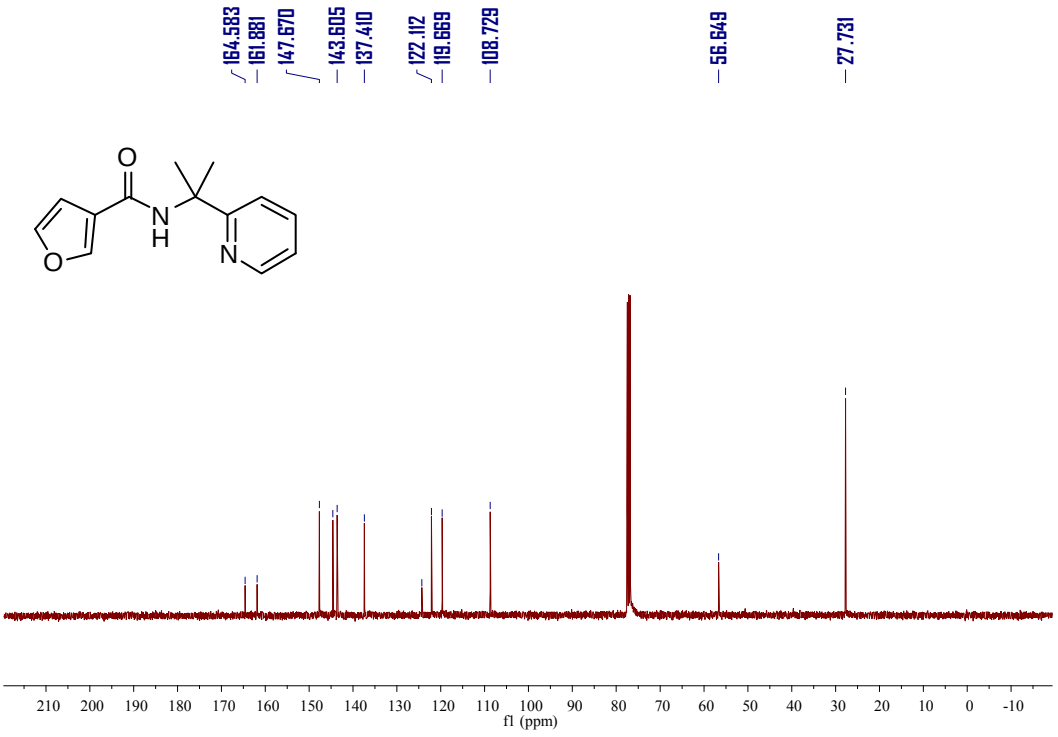
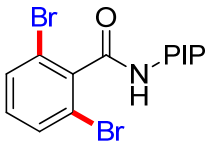
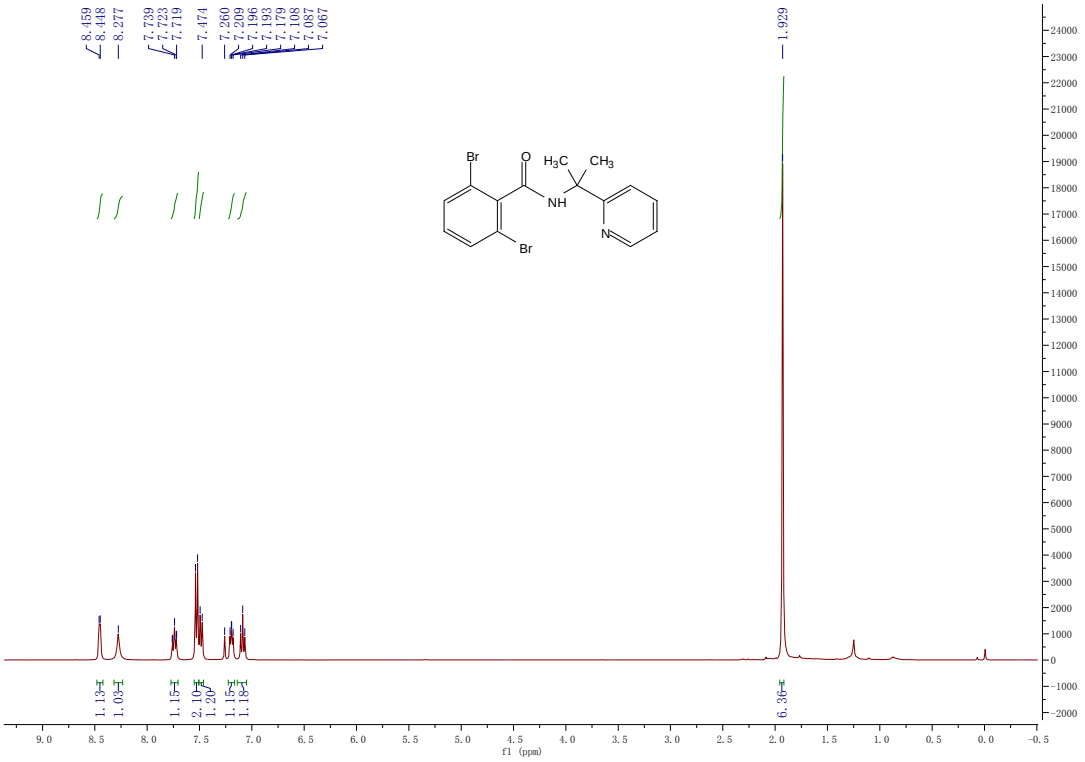
8.538
8.457
7.750
7.438
7.224
6.728
1.851
O
N
H
O
N
0.95
0.97
0.93
1.00
2.01
0.98
0.92
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.583
161.881
147.670
143.605
137.410
122.112
119.669
108.729
56.649
27.731
O
N
H
O
N
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)


Br
O
N
H
PIP
Br

2a'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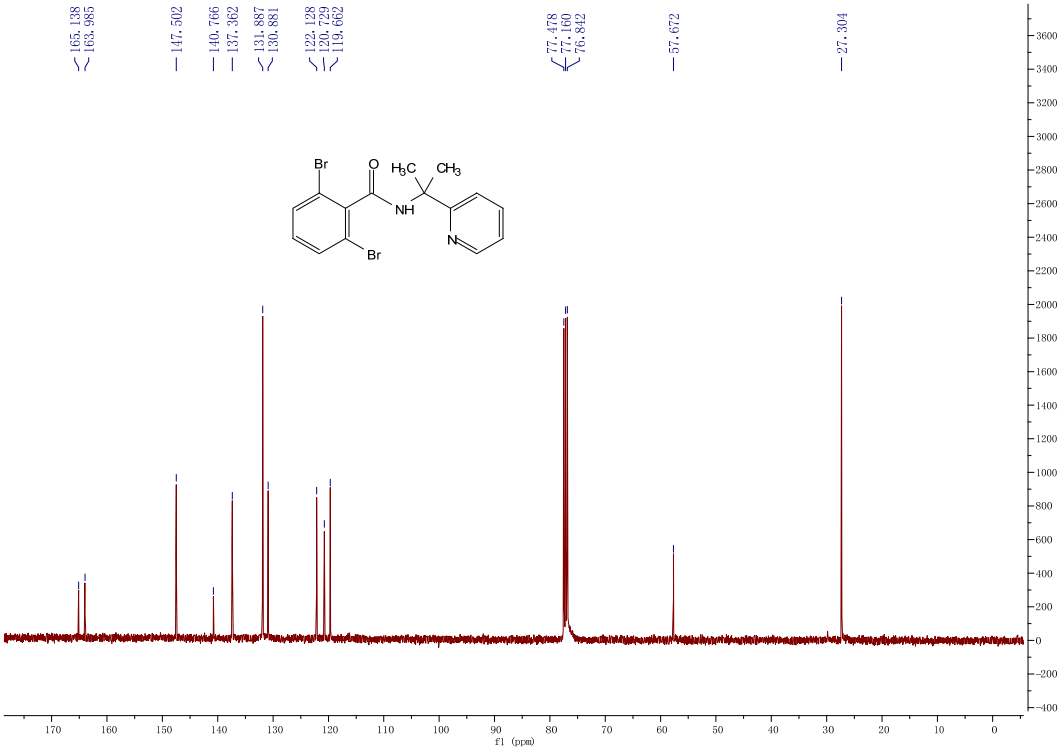
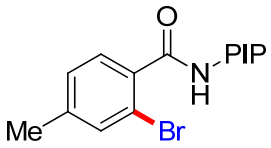
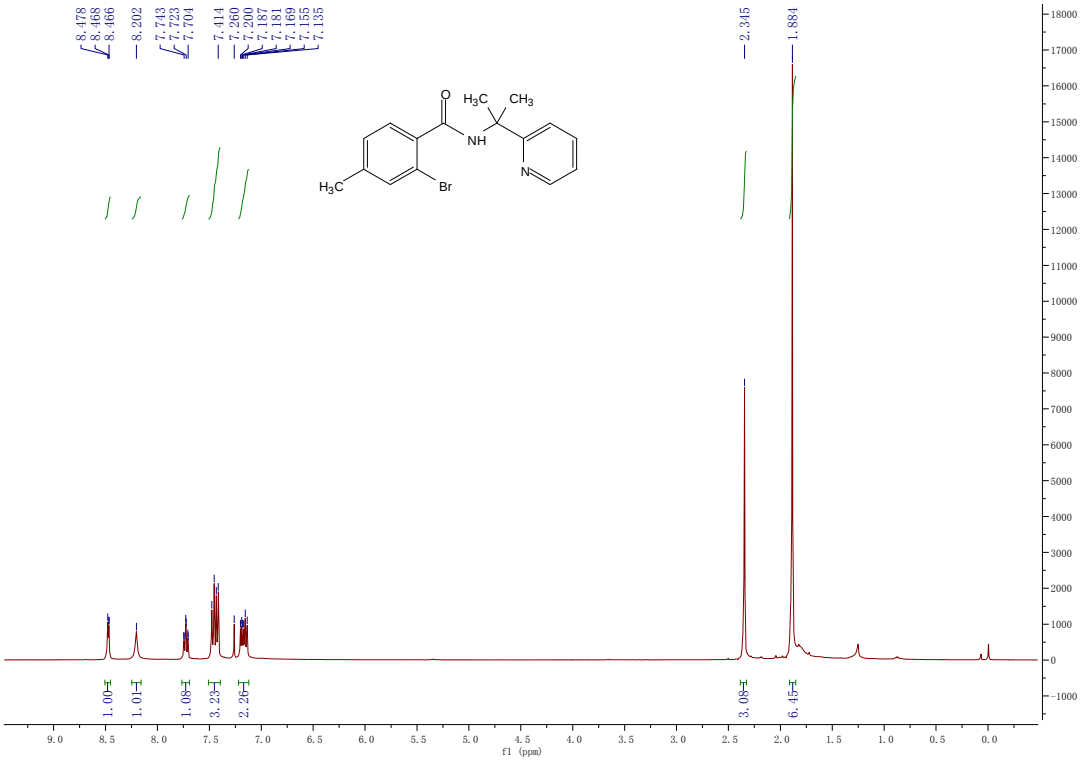
8.277
7.739
7.723
7.719
7.474
7.260
7.209
7.196
7.193
7.179
7.108
7.087
7.067
1.929
Br
O
H3C
CH3
NH
N
Br
1.13
1.03
1.15
2.10
1.20
1.15
1.18
6.36
f1 (ppm)


165.138
163.985
147.502
140.766
137.362
131.887
130.881
122.128
120.729
119.662
77.478
77.160
76.842
57.672
27.304
Br
O
H3C
CH3
NH
N
Br
f1 (ppm)


O
N
H
PIP
Me
Br

2c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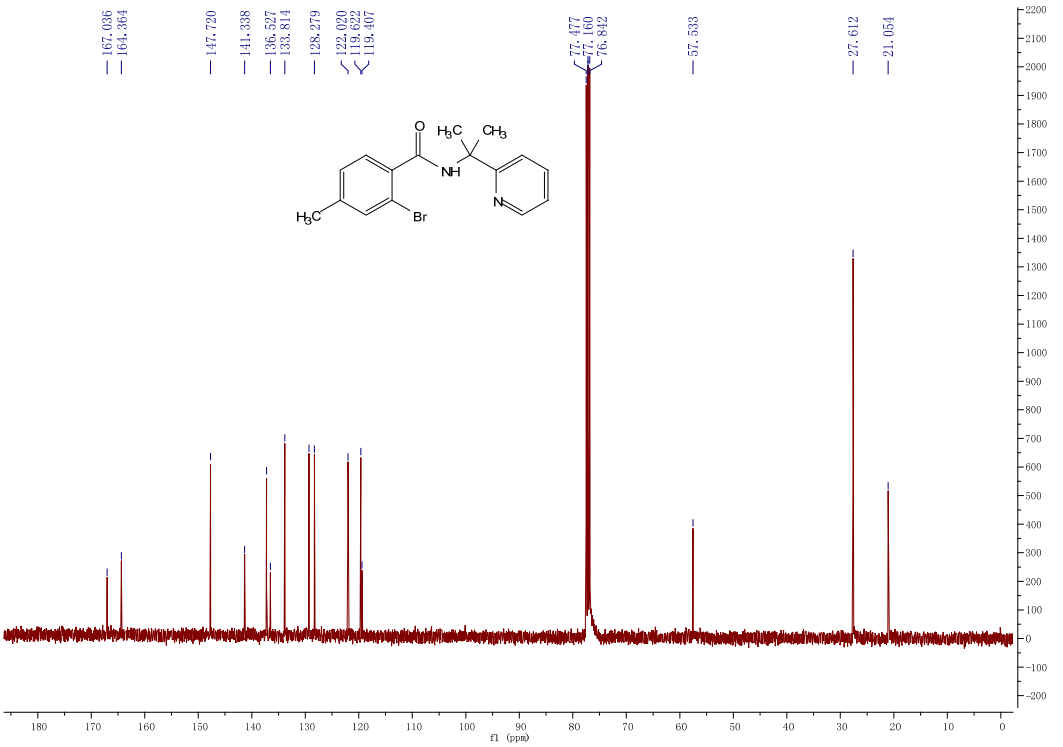
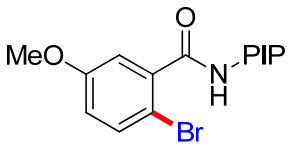
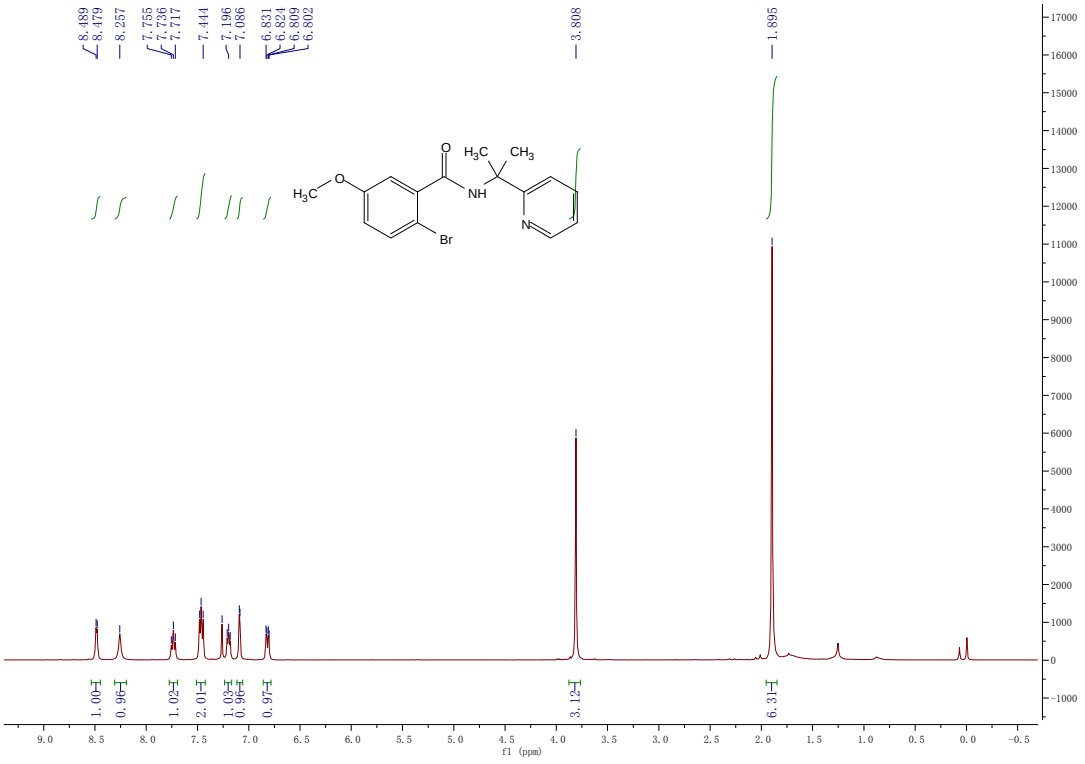
8.468
8.466
8.202
7.743
7.723
7.704
7.414
7.260
7.200
7.187
7.181
7.169
7.155
7.135
2.345
1.884
1.00
1.01
1.08
3.23
2.26
3.08
6.45
f1 (ppm)


167.036
164.364
147.720
141.338
136.527
133.814
128.279
122.020
119.622
119.407
77.477
77.160
76.842
57.533
27.612
21.054
f1 (ppm)


MeO
O
N
H
PIP
Br

2e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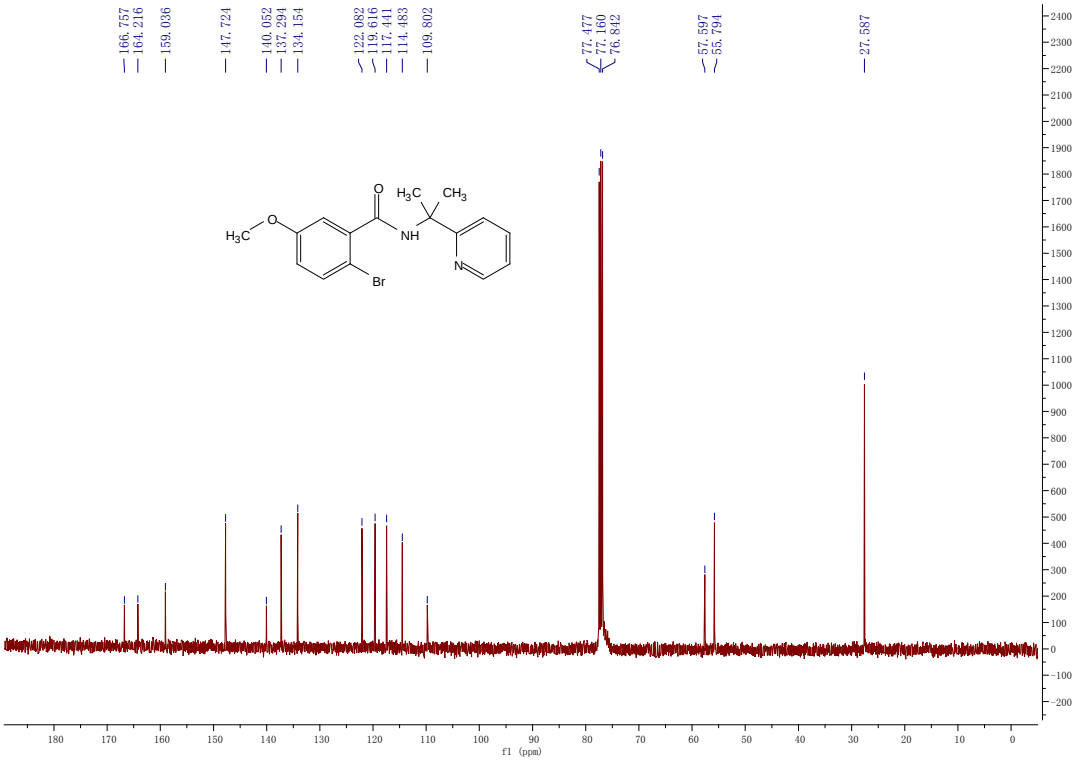
8.479
8.257
7.755
7.736
7.717
7.444
7.196
7.086
6.831
6.824
6.809
6.802
3.808
1.895
1.00
0.96
1.02
2.01
1.03
0.96
0.97
3.12
6.31
f1 (ppm)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164.216
159.036
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140.052
137.294
134.154
122.082
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117.441
114.483
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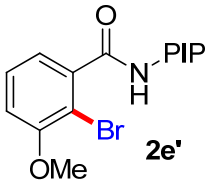
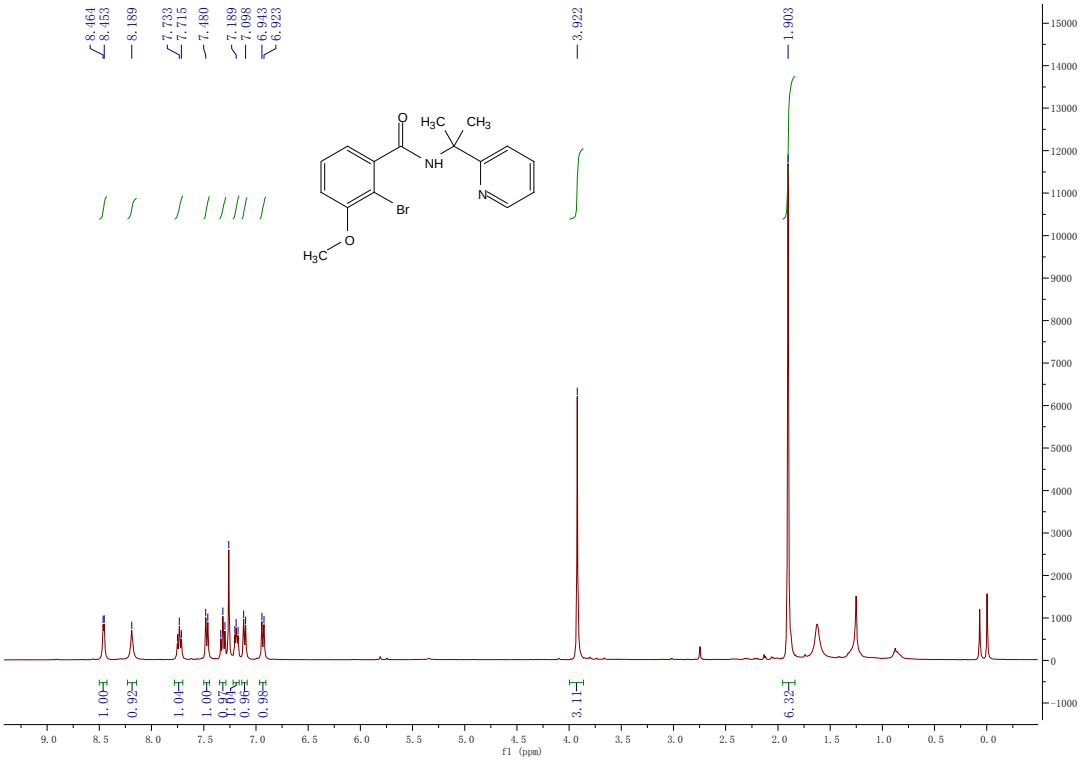
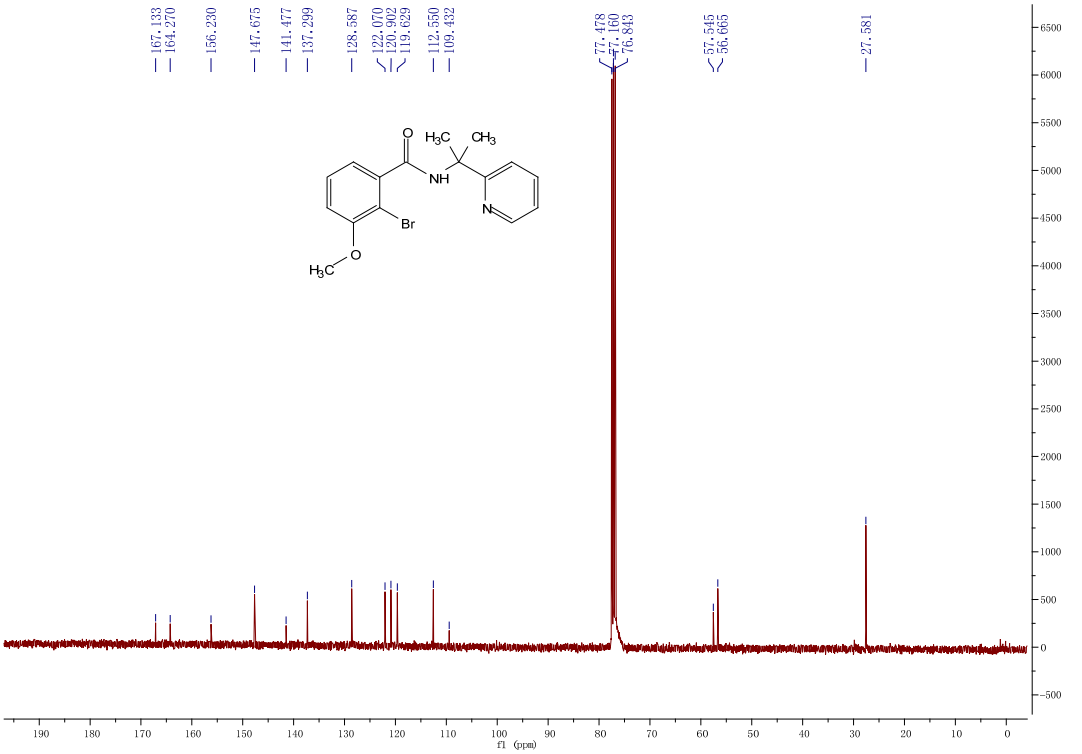
77.477
77.160
76.842
57.597
55.794
27.587
f1 (ppm)


O
N
H
PIP
Br
OMe

2e'


8.464
8.453
8.189
7.733
7.715
7.480
7.189
7.098
6.943
6.923
3.922
1.903
1.00
0.92
1.04
1.00
0.97
1.05
0.96
0.98
3.11
6.32
f1 (ppm)


167.133
164.270
156.230
147.675
141.477
137.299
128.587
122.070
120.902
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112.550
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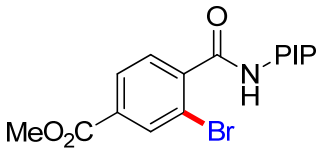
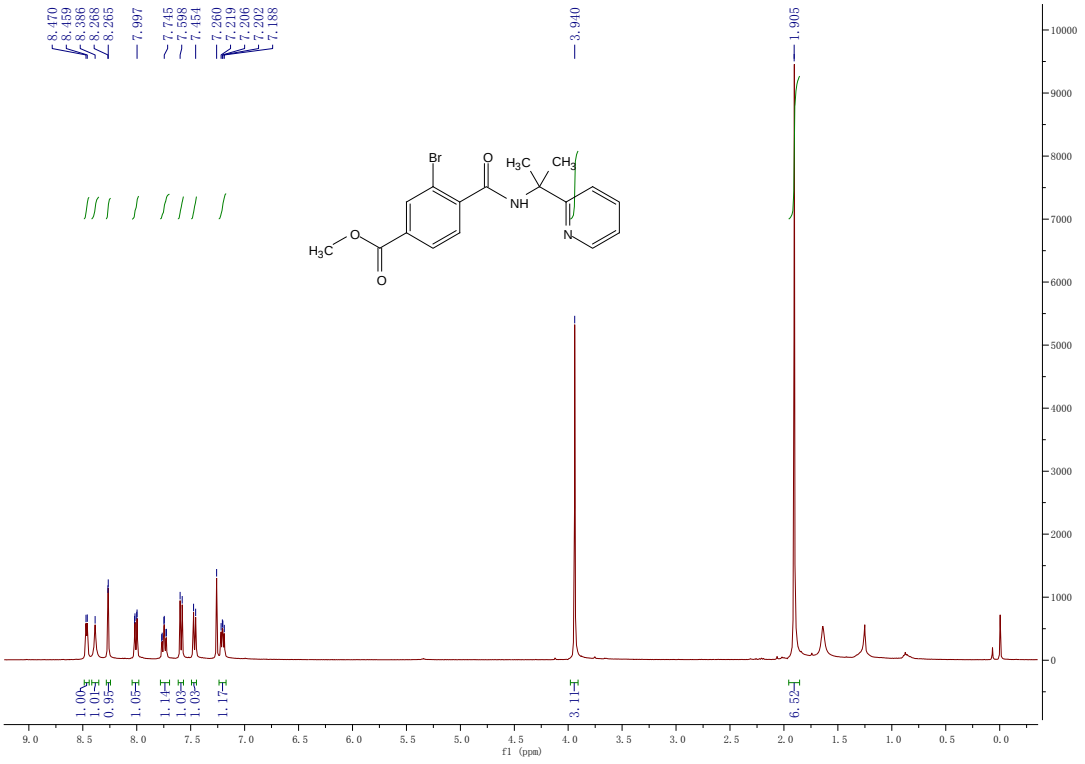
76.843
57.545
56.665
27.581
f1 (ppm)


O
N
PIP
H
MeO2C
Br

2i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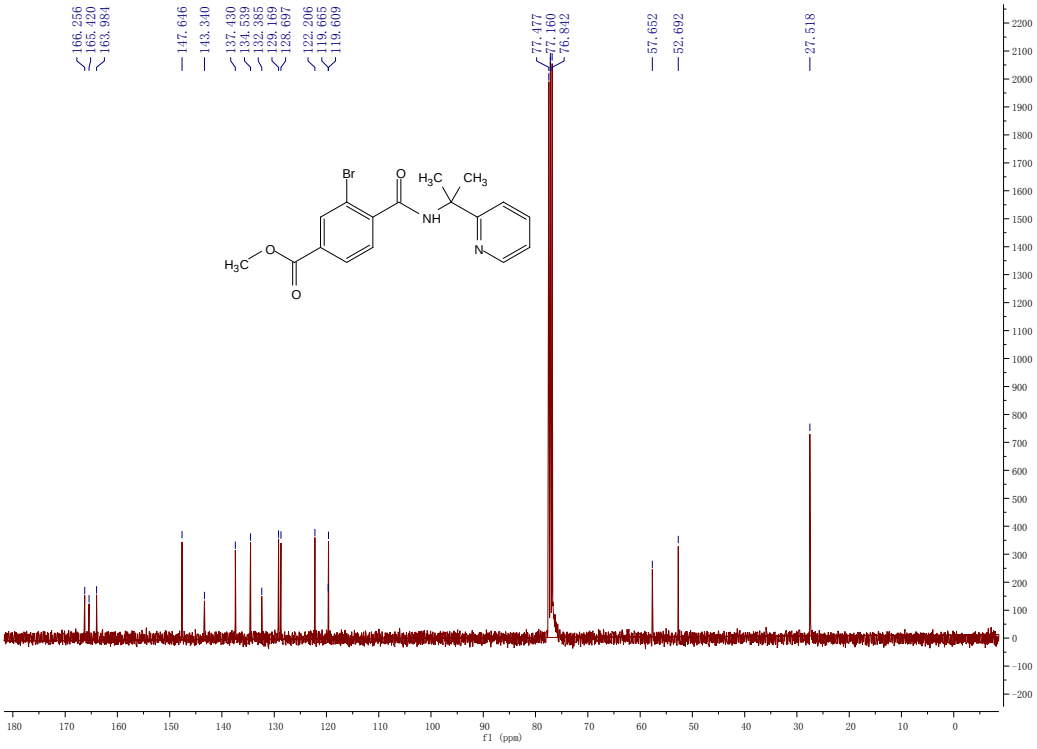
8.386
8.268
8.265
7.997
7.745
7.598
7.454
7.260
7.219
7.206
7.202
7.188
3.940
1.905
Br
O
H3C
CH3
NH
N
H3C
O
O
1.00
1.01
0.95
1.05
1.14
1.03
1.03
1.17
3.11
6.52
f1 (ppm)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163.984
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143.340
137.430
134.539
132.385
128.169
128.697
122.206
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119.609
77.477
77.160
76.842
57.652
52.692
27.518
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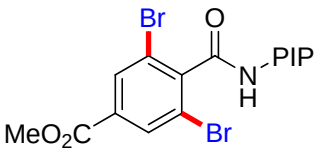
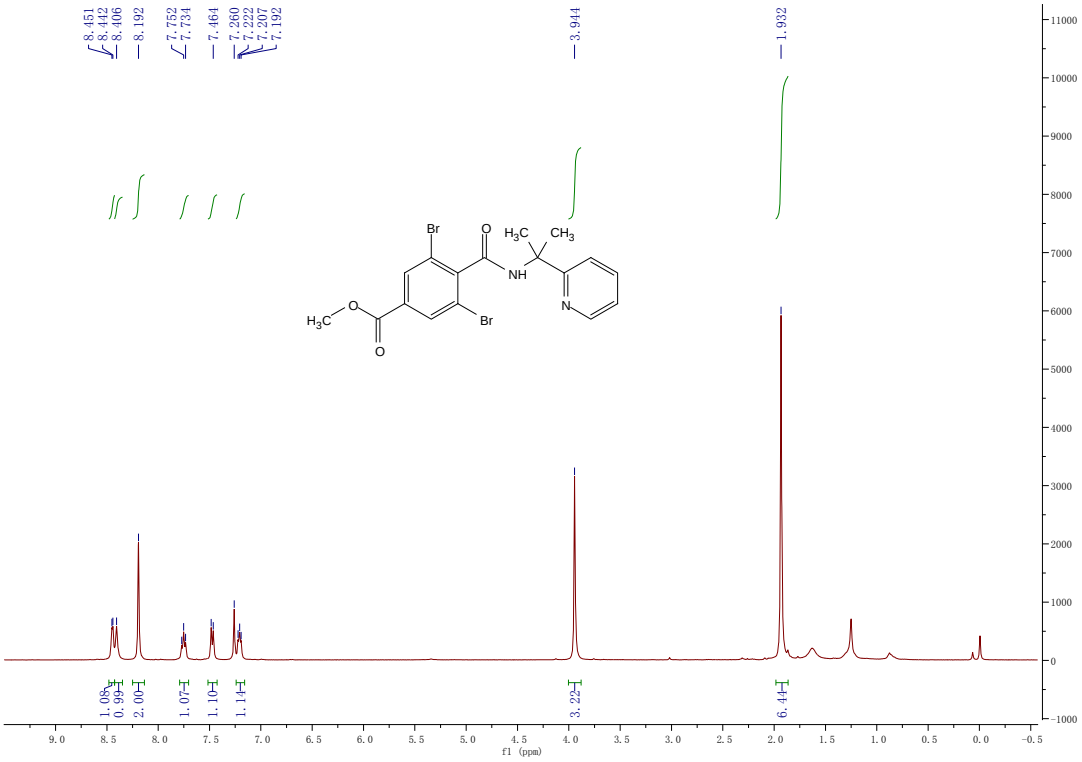
O
H3C
CH3
NH
N
H3C
O
O
f1 (ppm)


Br
O
N
H
PIP
MeO2C
Br

2i'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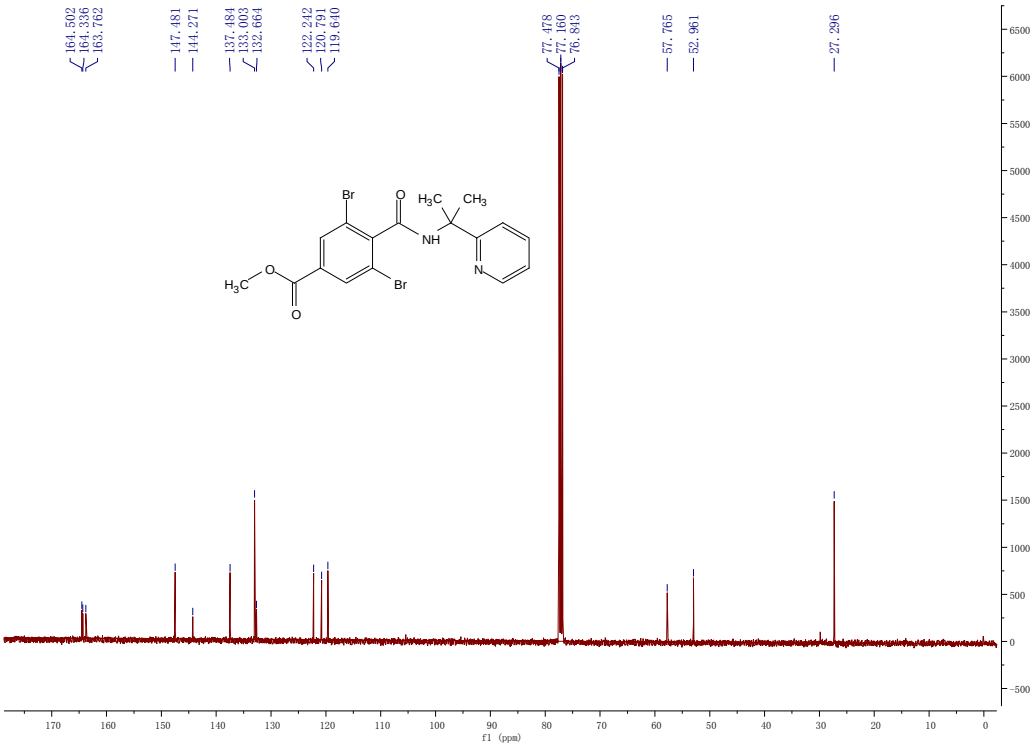
8.406
8.192
7.752
7.734
7.464
7.260
7.222
7.207
7.192
3.944
1.932
1.08
0.99
2.00
1.07
1.10
1.14
3.22
6.44
f1 (ppm)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144.271
137.484
133.003
132.664
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119.640
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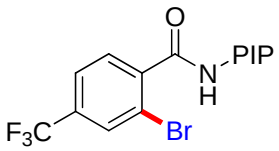
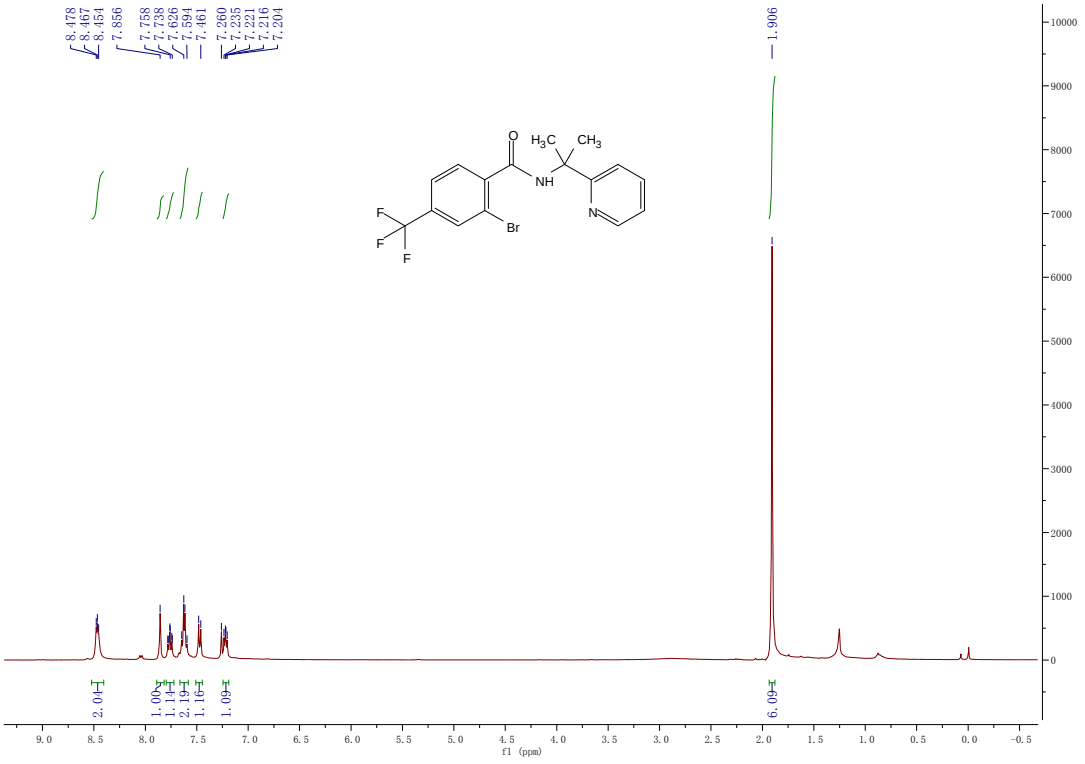
77.160
76.843
57.765
52.961
27.296
f1 (ppm)


O
N
H
PIP
F3C
Br

2j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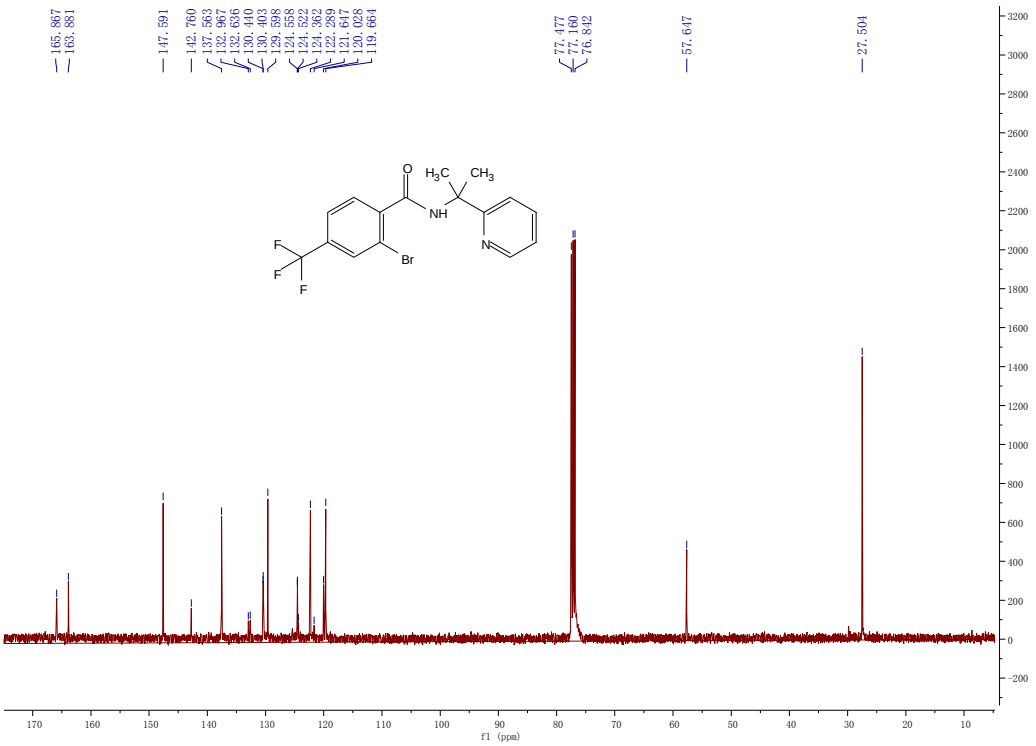
7.856
7.758
7.738
7.626
7.594
7.461
7.260
7.235
7.221
7.216
7.204
1.906
2.04
1.00
1.14
2.19
1.16
1.09
6.09
f1 (ppm)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130.440
130.403
129.598
124.558
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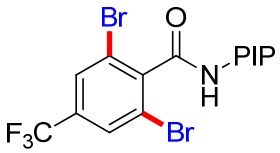
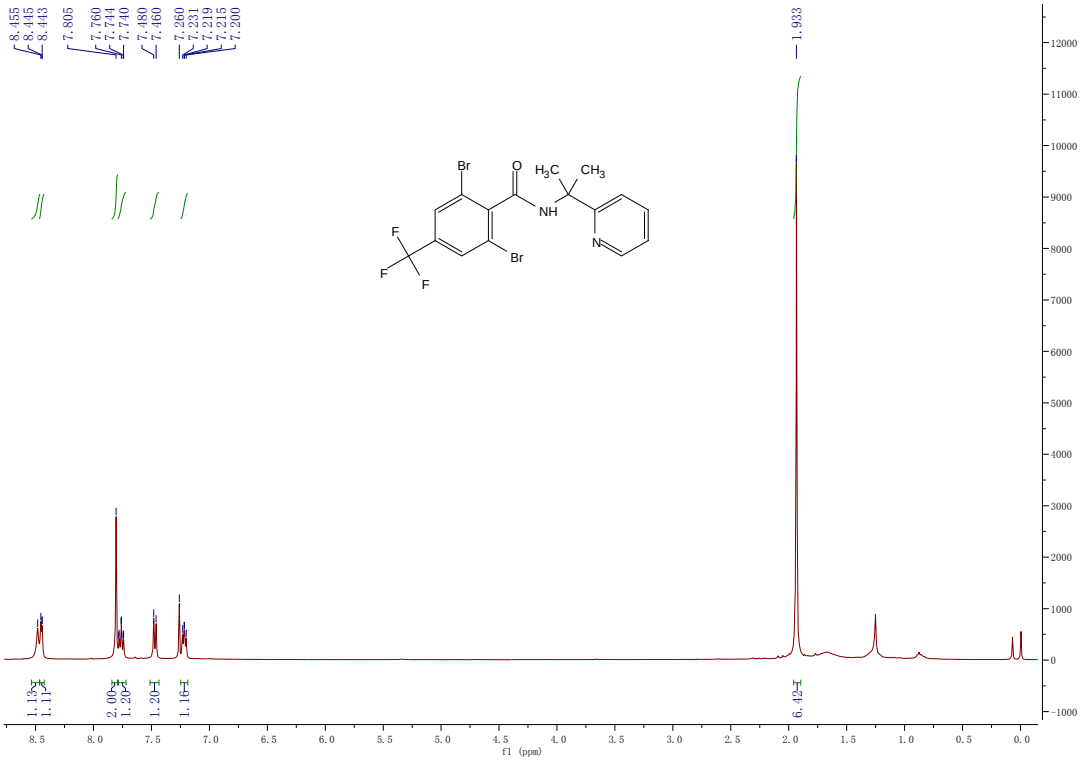
124.362
122.289
121.647
120.028
119.664
77.477
77.160
76.842
57.647
27.504
f1 (ppm)


Br
O
N
H
PIP
F3C
Br

2j'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7.744
7.740
7.480
7.460
7.260
7.231
7.219
7.215
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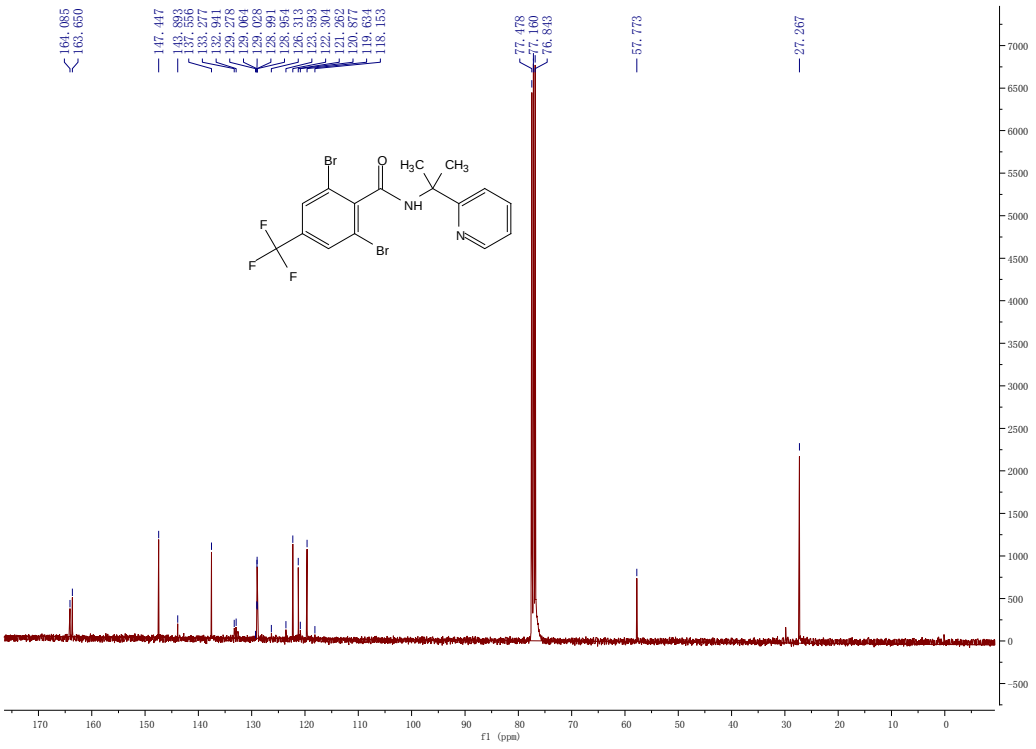
1.933
1.13
1.11
2.00
1.20
1.20
1.16
6.42
f1 (ppm)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129.278
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122.304
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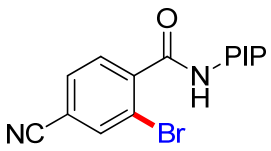
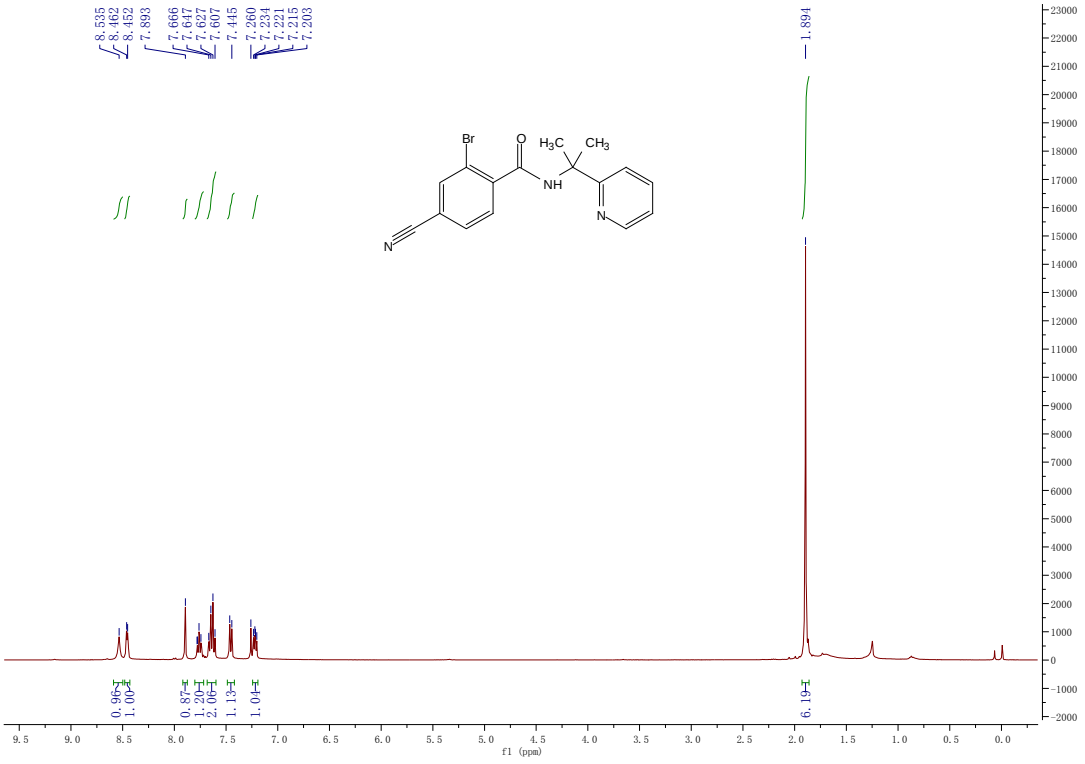
77.478
77.160
76.843
57.773
27.267
f1 (ppm)


O
N
H
PIP
NC
Br

2k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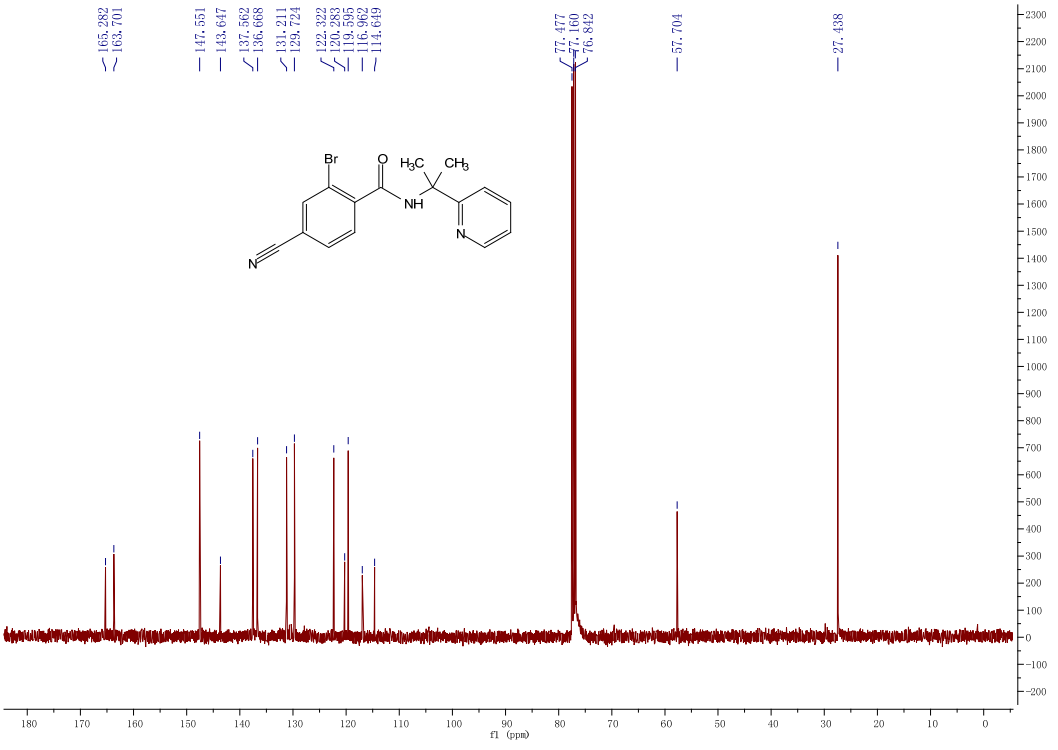
8.452
7.893
7.666
7.647
7.627
7.607
7.445
7.260
7.234
7.221
7.215
7.203
1.894
Br
O
H3C
CH3
NH
N
N
0.96
1.00
0.87
1.20
2.06
1.13
1.04
6.19
f1 (ppm)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129.724
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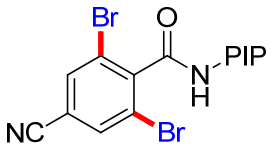
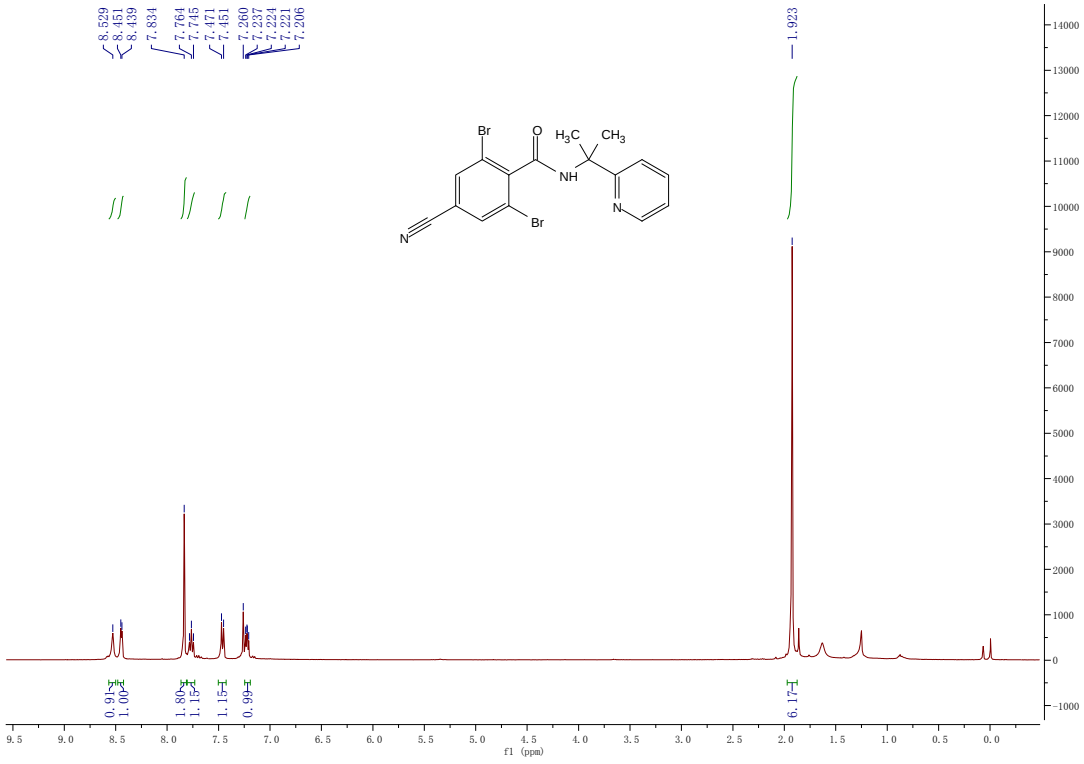
119.595
116.962
114.649
77.477
77.160
76.842
57.704
27.438
Br
O
H3C
CH3
NH
N
N
f1 (ppm)


Br
O
N
PIP
H
NC
Br

2k'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8.451
8.439
7.834
7.764
7.745
7.471
7.451
7.260
7.237
7.224
7.221
7.206
1.923
Br
O
H3C
CH3
NH
N
Br
N
0.91
1.00
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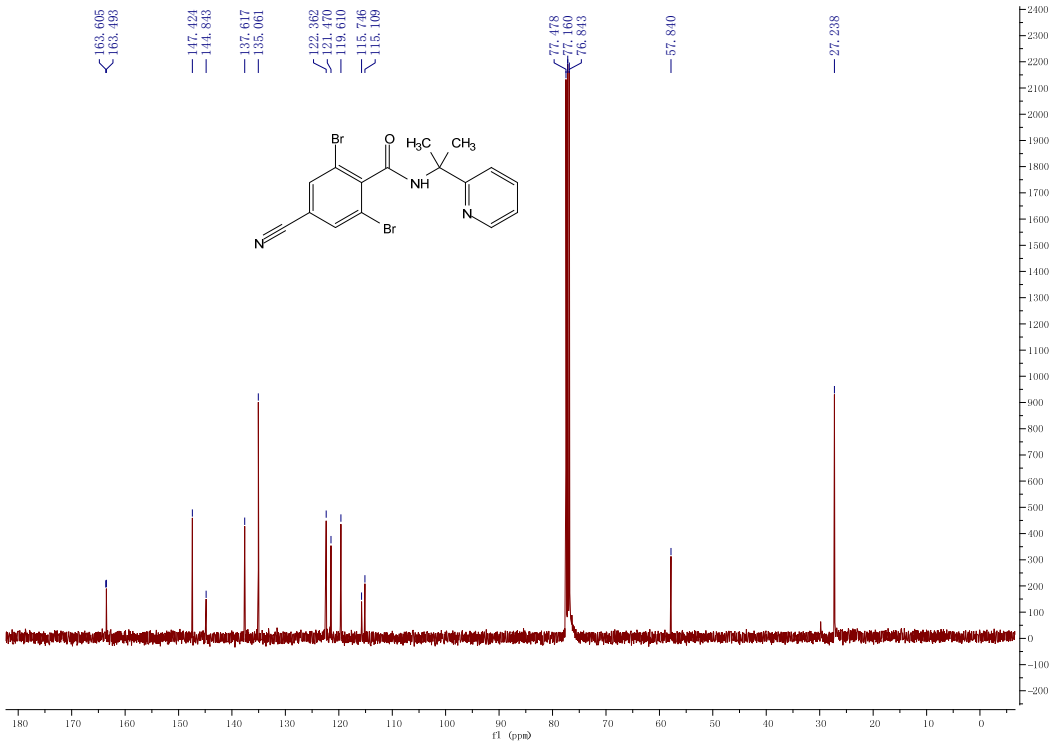
1.15
1.15
0.99
6.17
f1 (ppm)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137.617
135.061
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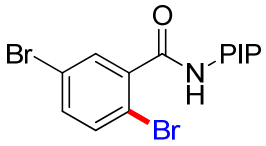
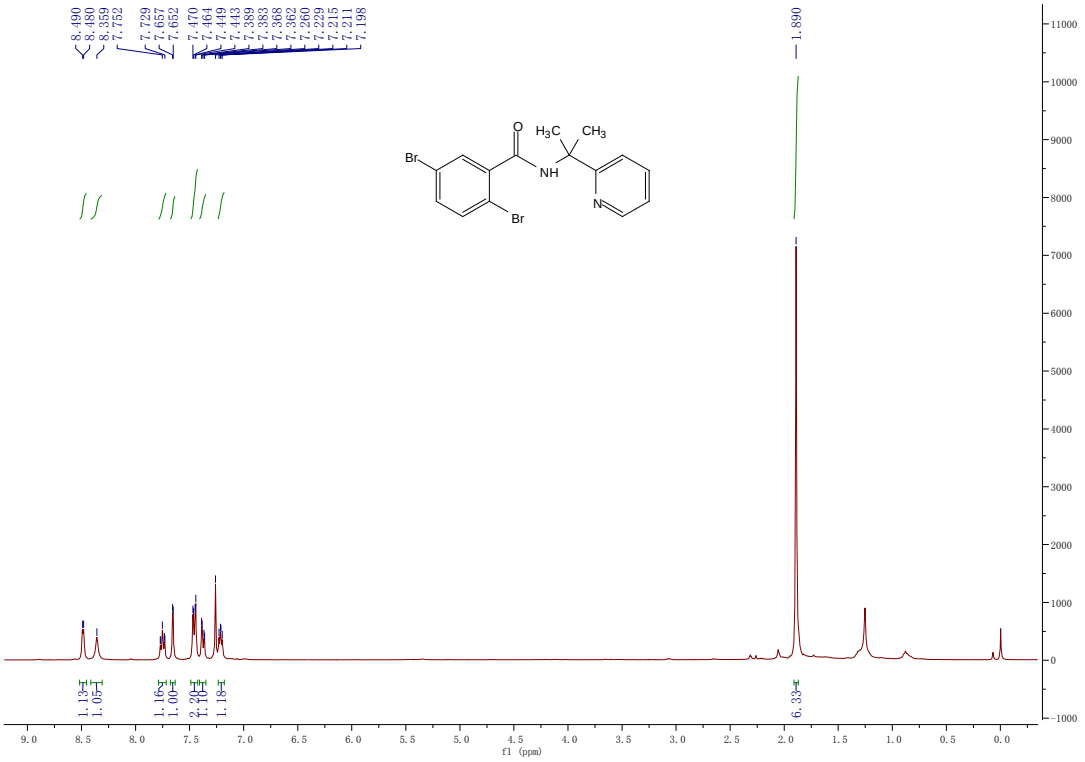
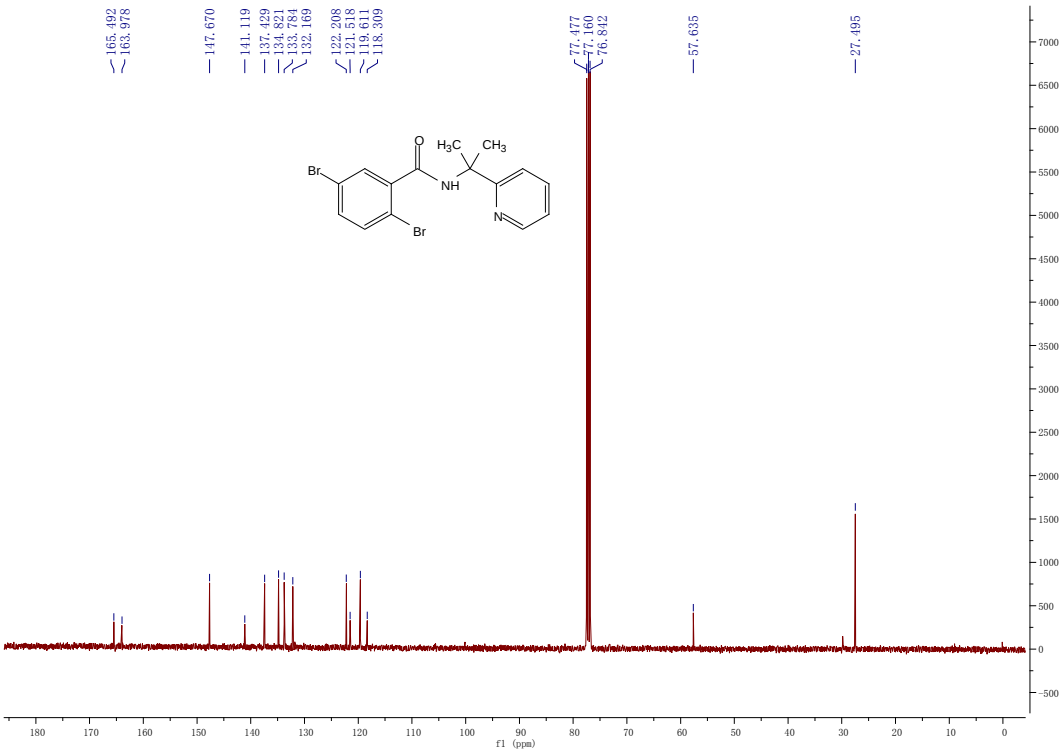
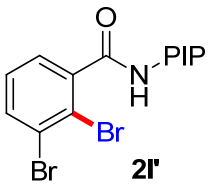
121.470
119.610
115.746
115.109
77.478
77.160
76.843
57.840
27.238
Br
O
H3C
CH3
NH
N
Br
N
f1 (ppm)


O
Br
N
PIP
H
Br

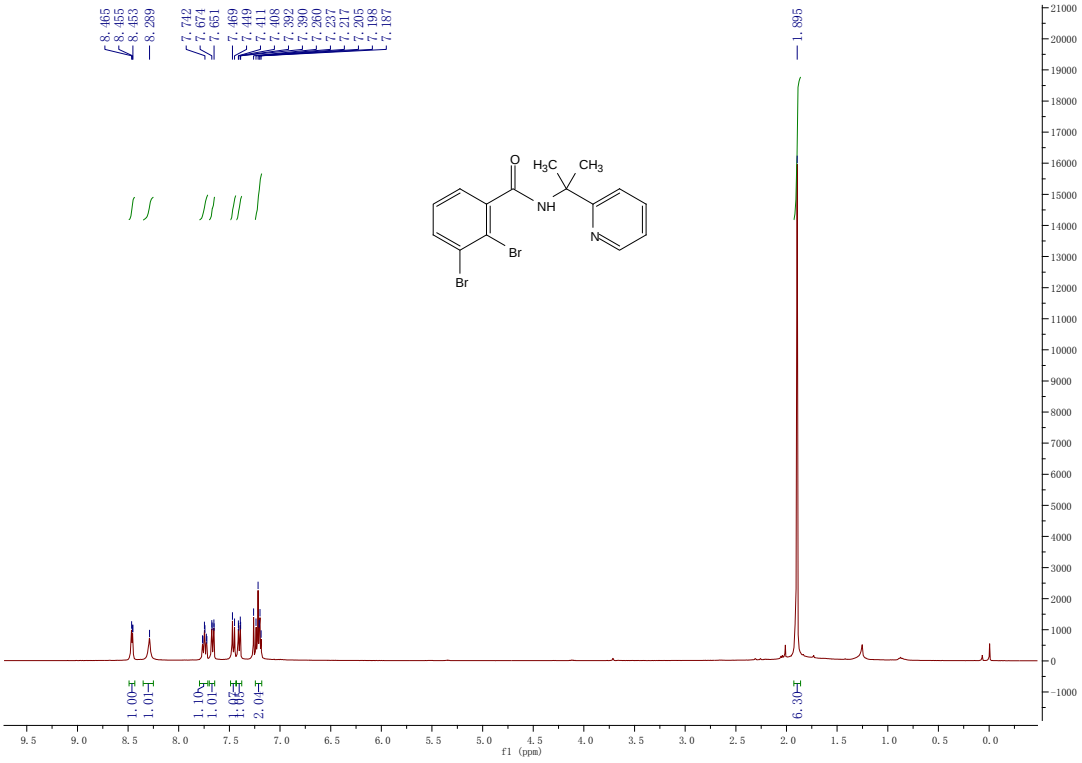
2l

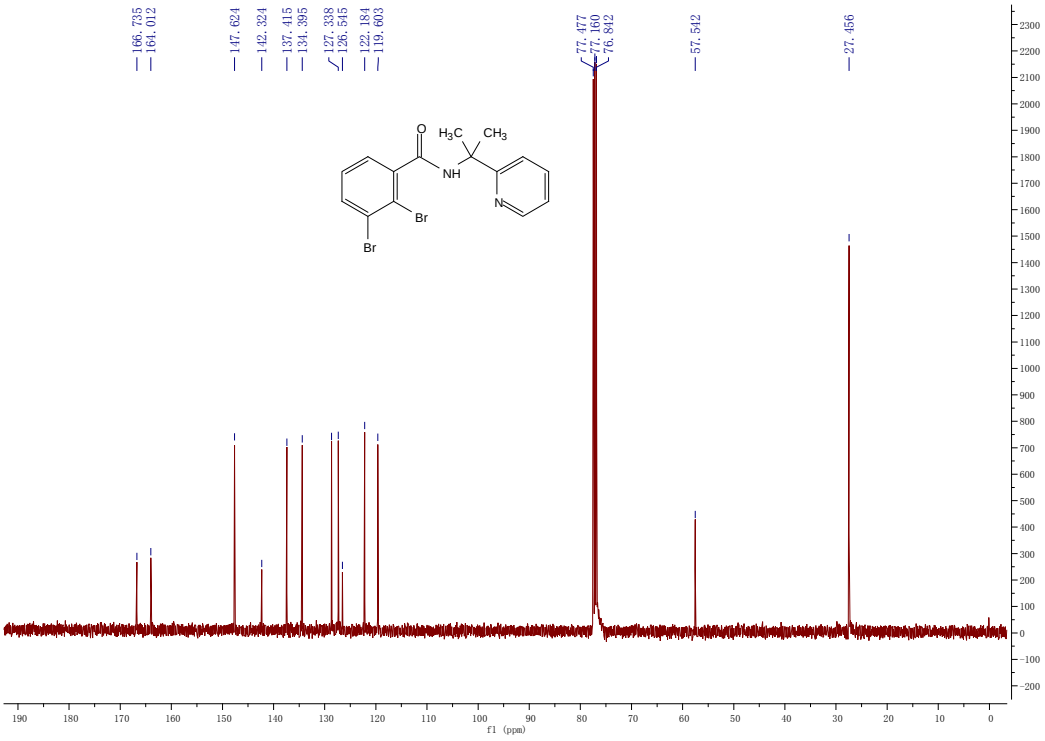

8.490
8.480
8.359
7.752
7.729
7.657
7.652
7.470
7.464
7.449
7.443
7.389
7.383
7.368
7.362
7.260
7.229
7.215
7.211
7.198
1.890
O
H3C
CH3
Br
NH
N
Br
1.13
1.05
1.16
1.00
2.20
1.10
1.18
6.33
f1 (ppm)

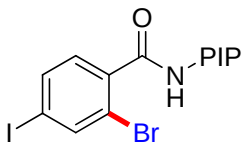

165.492
163.978
147.670
141.119
137.429
134.821
133.784
132.169
122.208
121.518
119.611
118.309
77.477
77.160
76.842
57.635
27.495
O
H3C
CH3
Br
NH
N
Br
f1 (ppm)


O
N
PIP
H
Br
Br

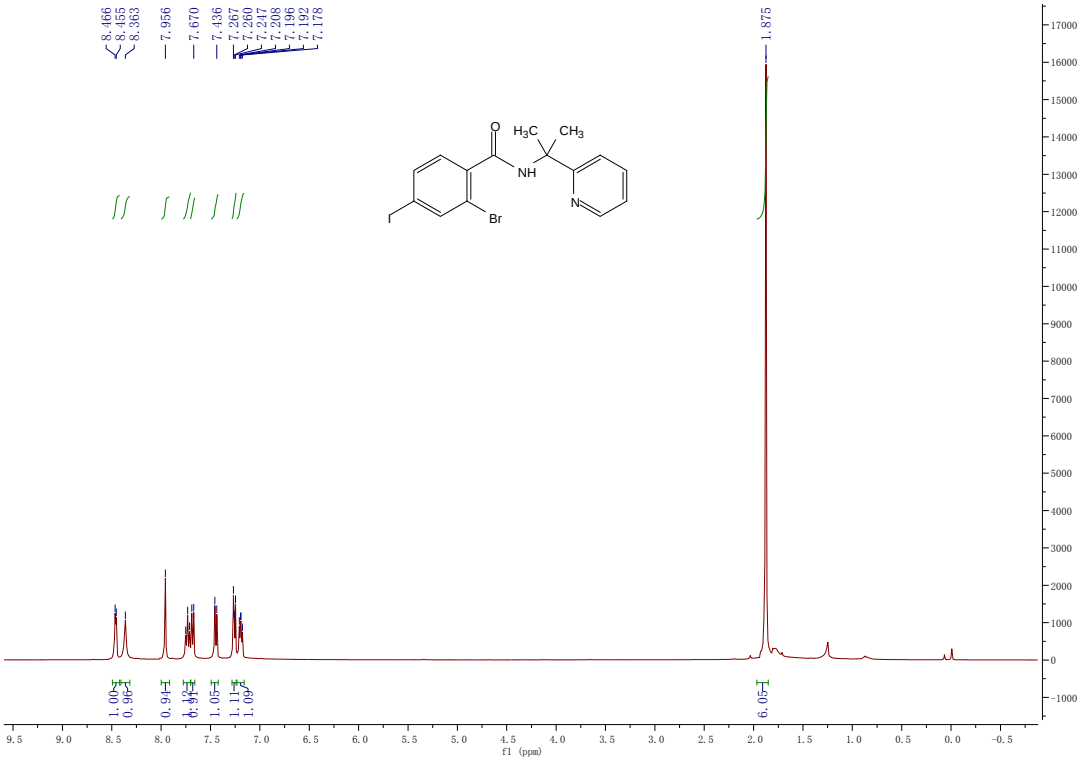
2l'

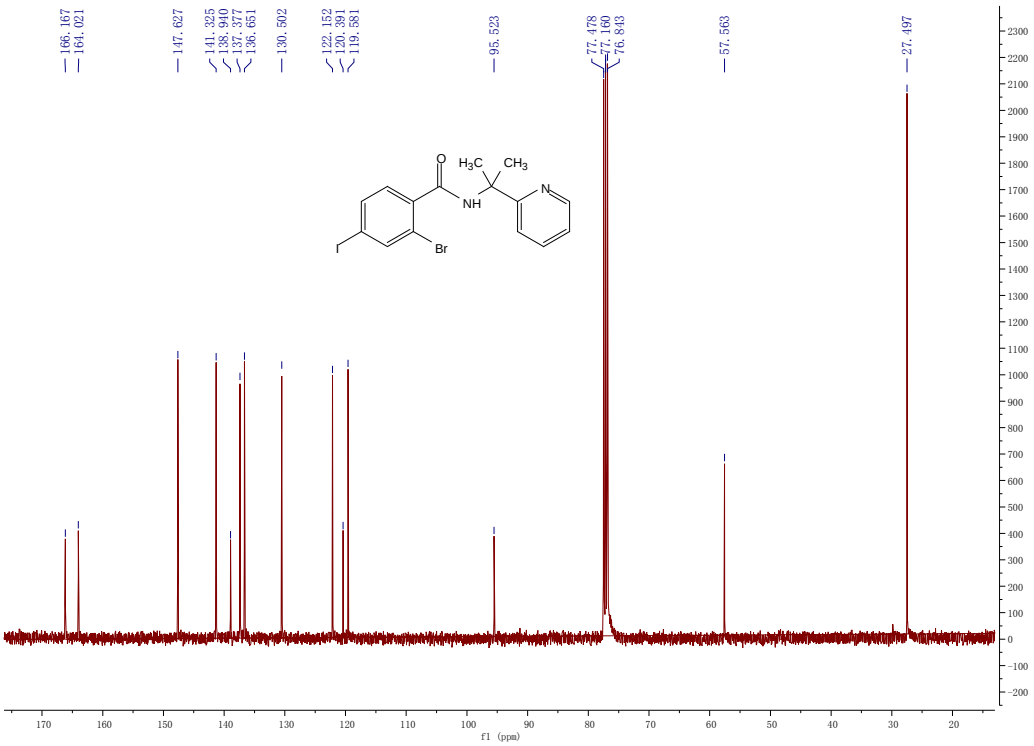

8.465
8.455
8.453
8.289
7.742
7.674
7.651
7.469
7.449
7.411
7.408
7.392
7.390
7.260
7.237
7.217
7.205
7.198
7.187
1.895
O
H3C
CH3
NH
N
Br
Br
1.00
1.01
1.10
1.01
1.05
2.04
6.30
f1 (ppm)


166.735
164.012
147.624
142.324
137.415
134.395
127.338
126.545
122.184
119.603
77.477
77.160
76.842
57.542
27.456
O
H3C
CH3
NH
N
Br
Br
f1 (ppm)


O
N
H
PIP
I
Br

2m


8.466
8.455
8.363
7.956
7.670
7.436
7.267
7.260
7.247
7.208
7.196
7.192
7.178
1.875
O
H3C
CH3
NH
N
I
Br
1.00
0.96
0.94
1.12
0.97
1.05
1.11
1.09
6.05
f1 (ppm)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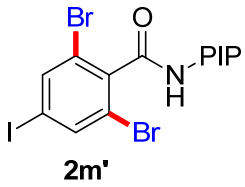
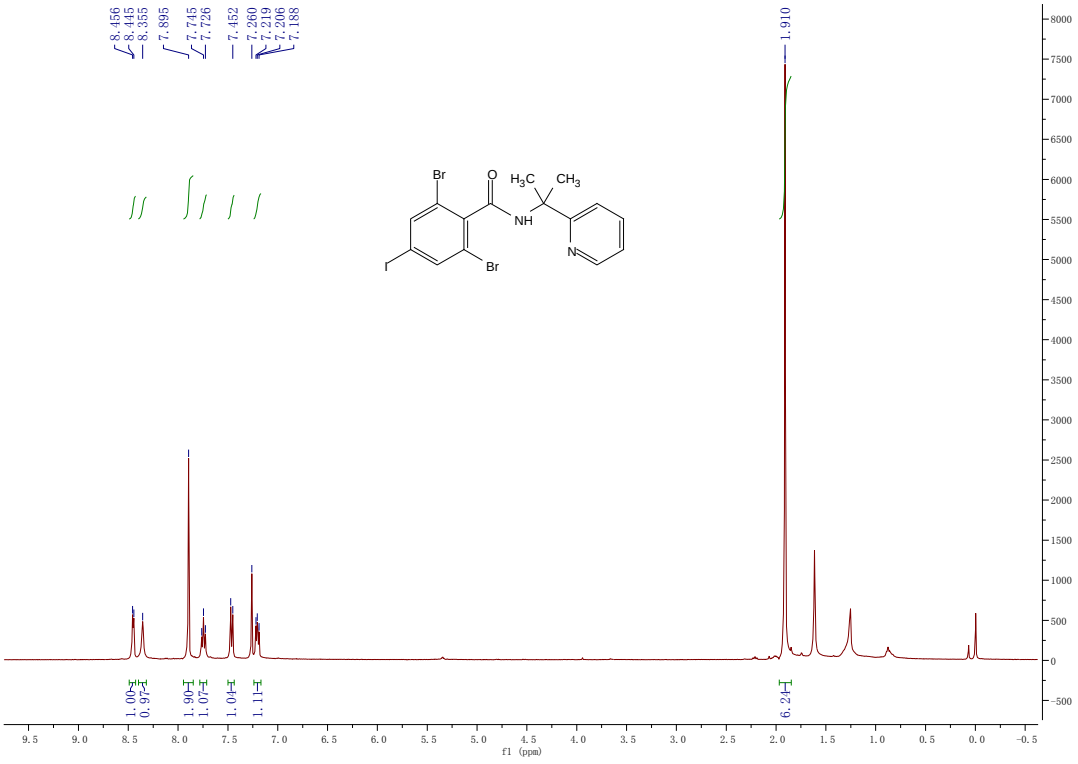
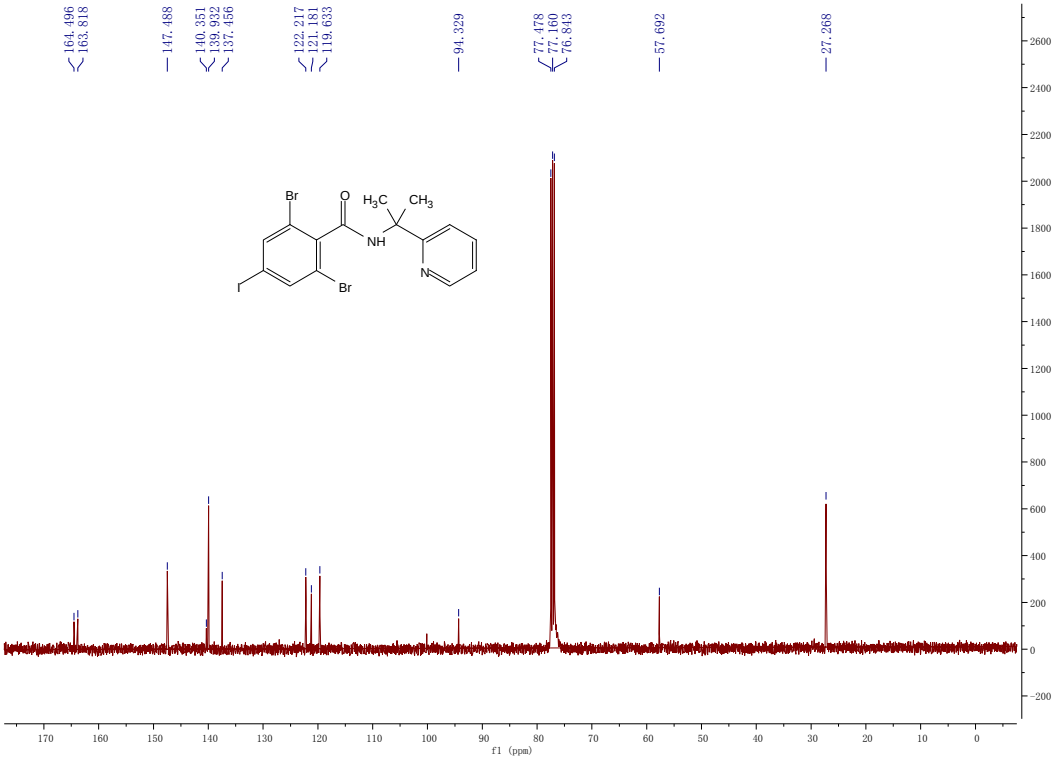
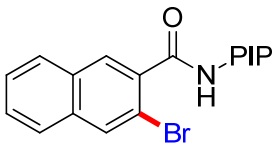
164.021
147.627
141.325
138.940
137.377
136.651
130.502
122.152
120.391
119.581
95.523
77.478
77.160
76.843
57.563
27.497
O
H3C
CH3
NH
N
I
Br
f1 (ppm)


Br
O
N
H
PIP
I
Br

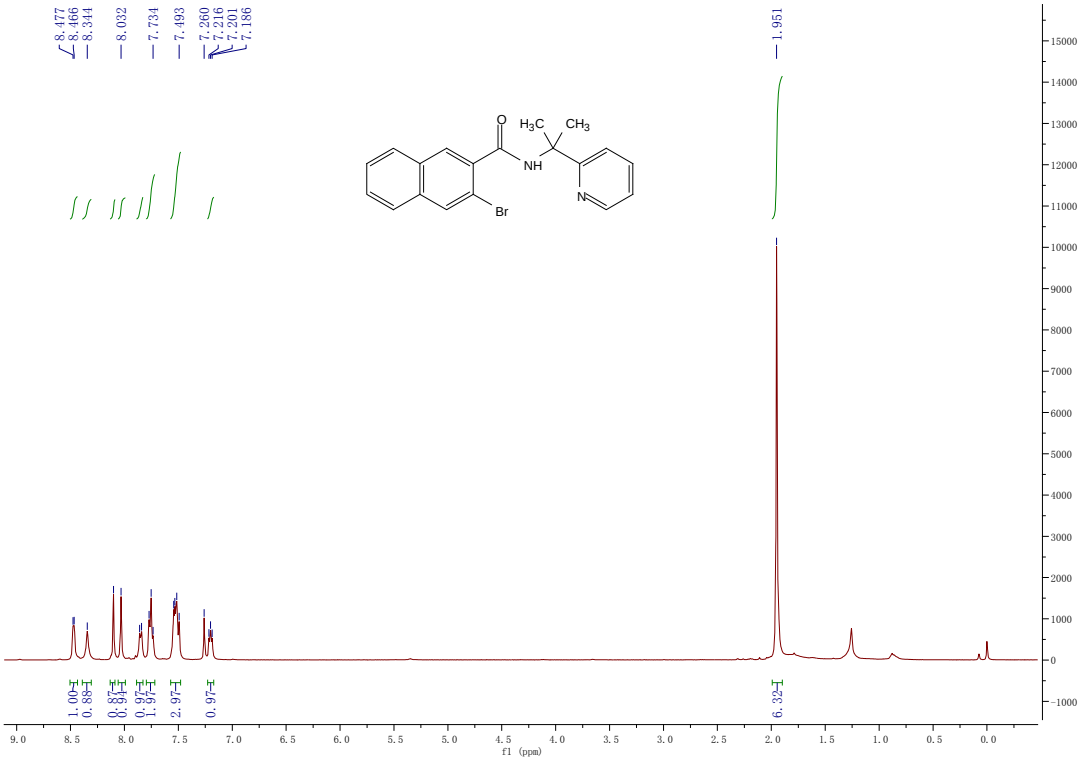
2m'

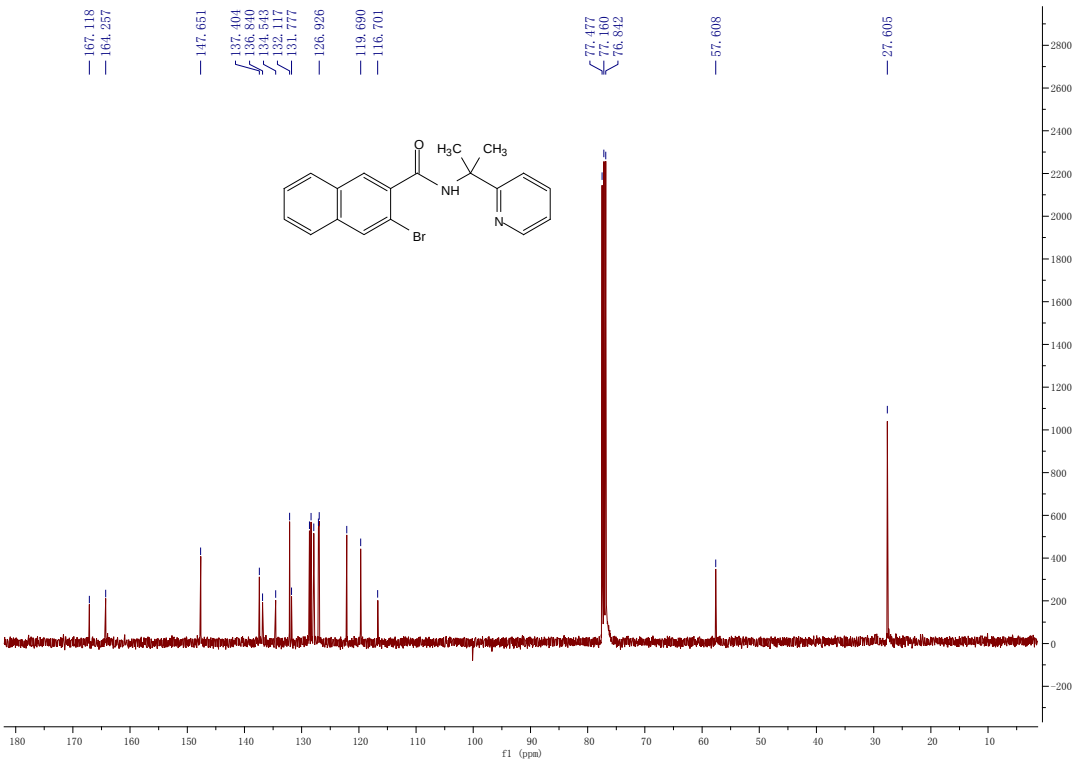

8.456
8.445
8.355
7.895
7.745
7.726
7.452
7.260
7.219
7.206
7.188
1.910
Br
O
H3C
CH3
NH
N
I
Br
1.00
0.97
1.90
1.07
1.04
1.11
6.24
f1 (ppm)

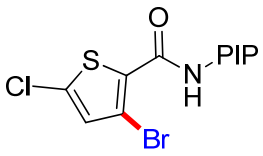

164.496
163.818
147.488
140.351
139.932
137.456
122.217
121.181
119.633
94.329
77.478
77.160
76.843
57.692
27.268
Br
O
H3C
CH3
NH
N
I
Br
f1 (ppm)


O
N
H
PIP
Br

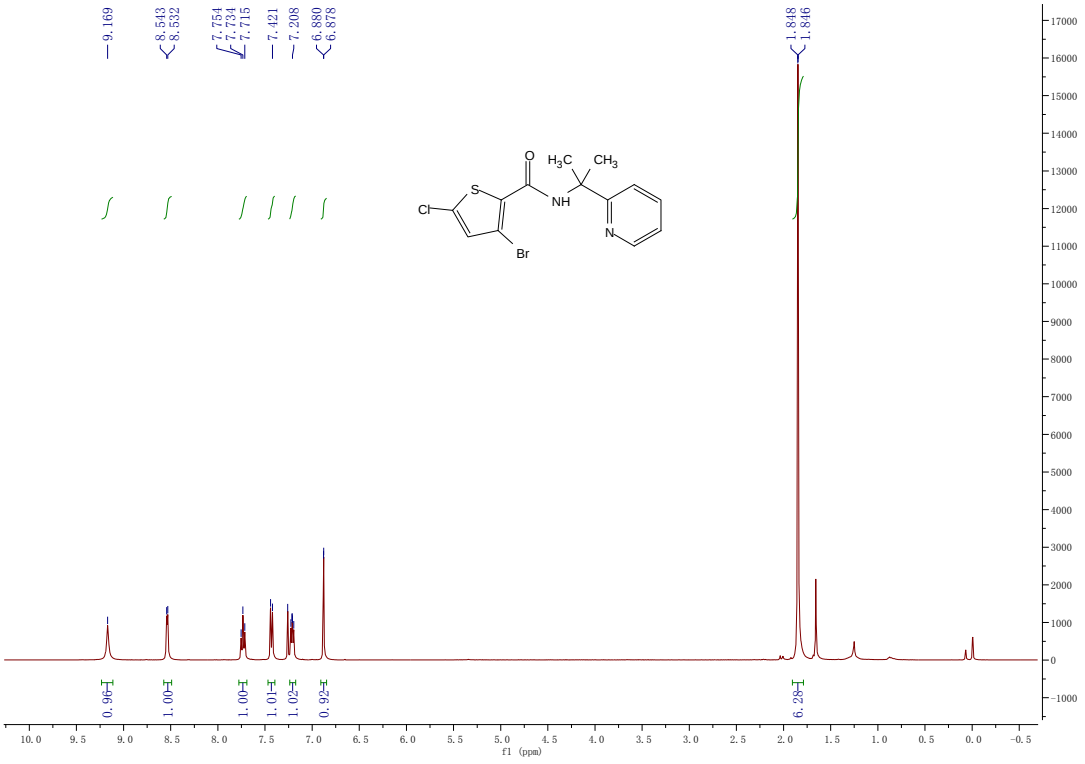
2o

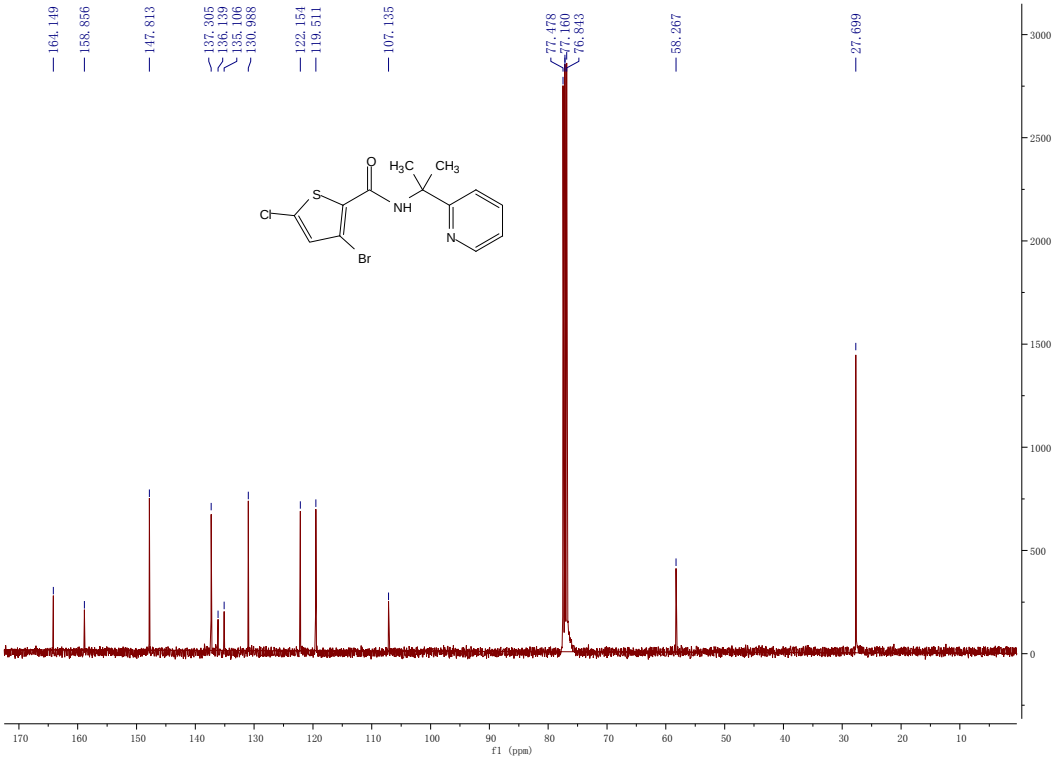

8.477
8.466
8.344
8.032
7.734
7.493
7.260
7.216
7.201
7.186
1.951
O
H3C
CH3
NH
N
Br
1.00
0.88
0.87
0.91
0.97
1.97
2.97
0.97
6.32
f1 (ppm)

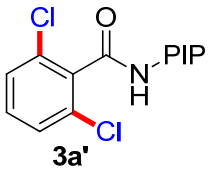

167.118
164.257
147.651
137.404
136.840
134.543
132.117
131.777
126.926
119.690
116.701
77.477
77.160
76.842
57.608
27.605
O
H3C
CH3
NH
N
Br
f1 (ppm)


O
S
N
PIP
H
Cl
Br

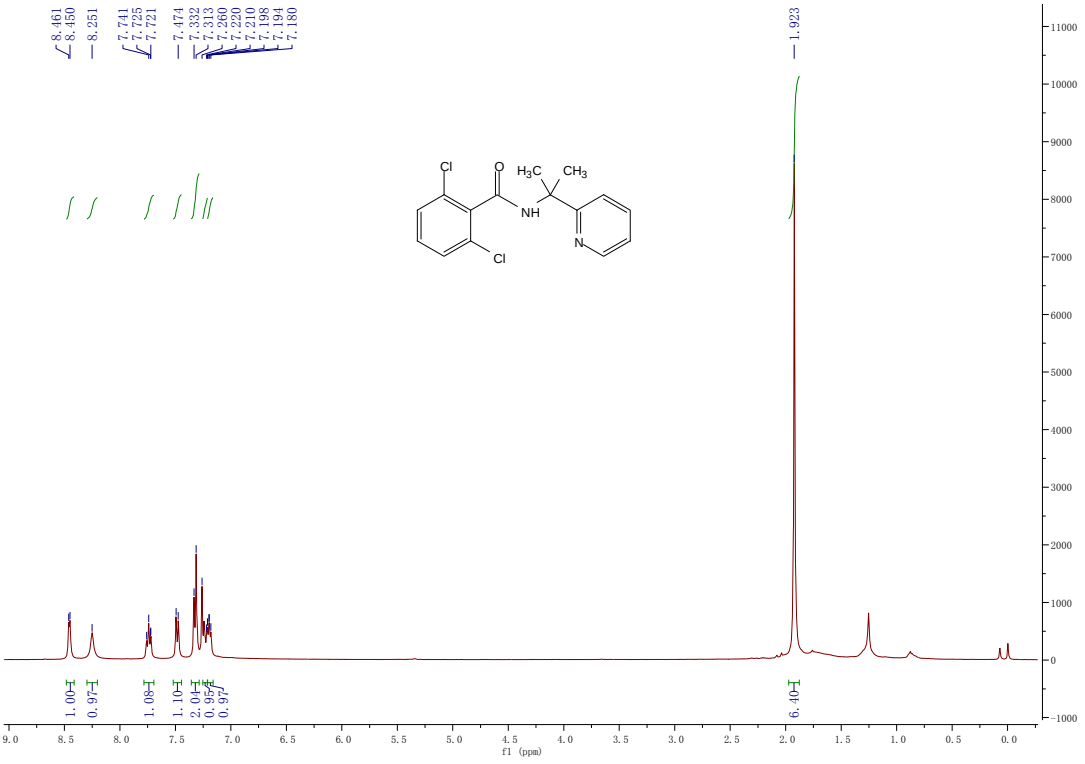
2p

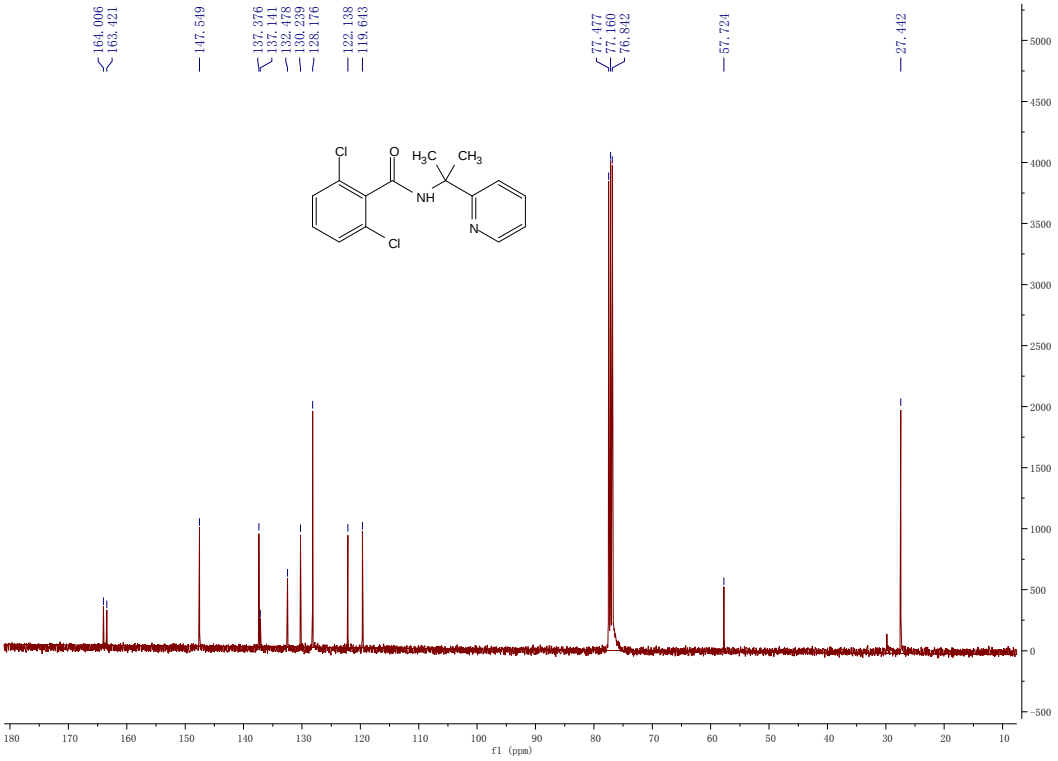

9.169
8.543
8.532
7.754
7.734
7.715
7.421
7.208
6.880
6.878
1.848
1.846
0.96
1.00
1.00
1.01
1.02
0.92
6.28
f1 (ppm)

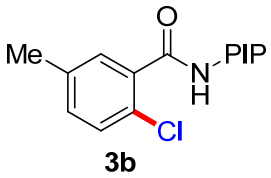

164.149
158.856
147.813
137.305
136.139
135.106
130.988
122.154
119.511
107.135
77.478
77.160
76.843
58.267
27.699
f1 (ppm)


Cl
O
PIP
N
H
Cl

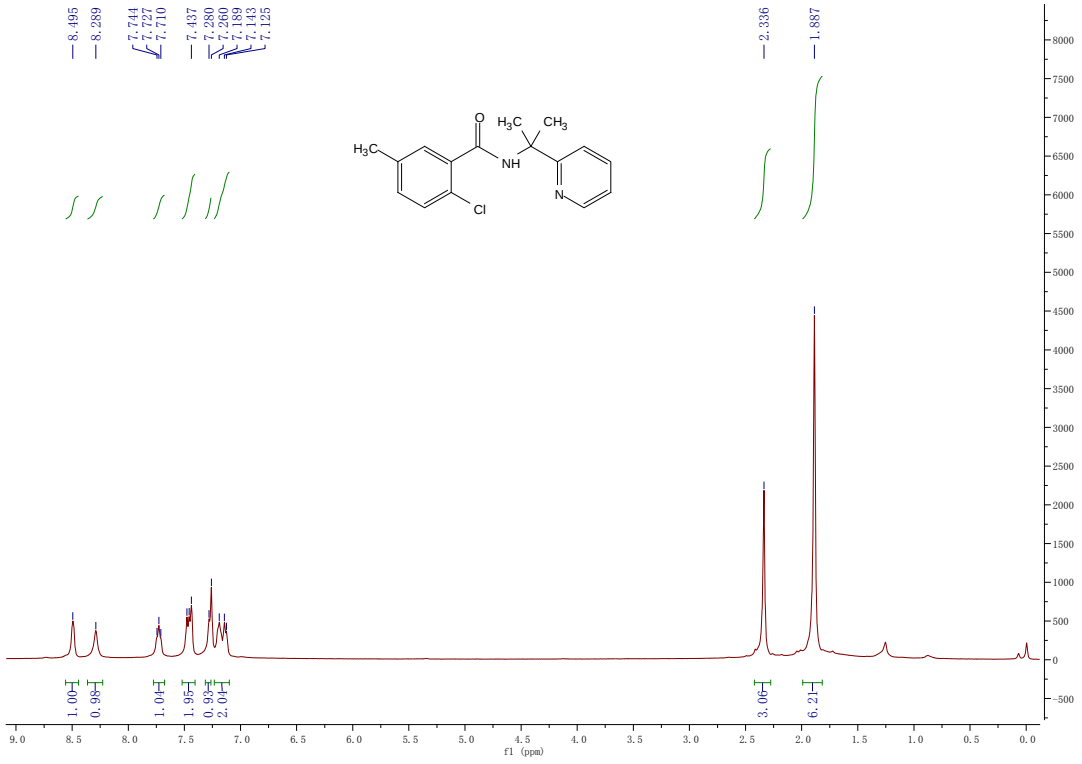
3a'

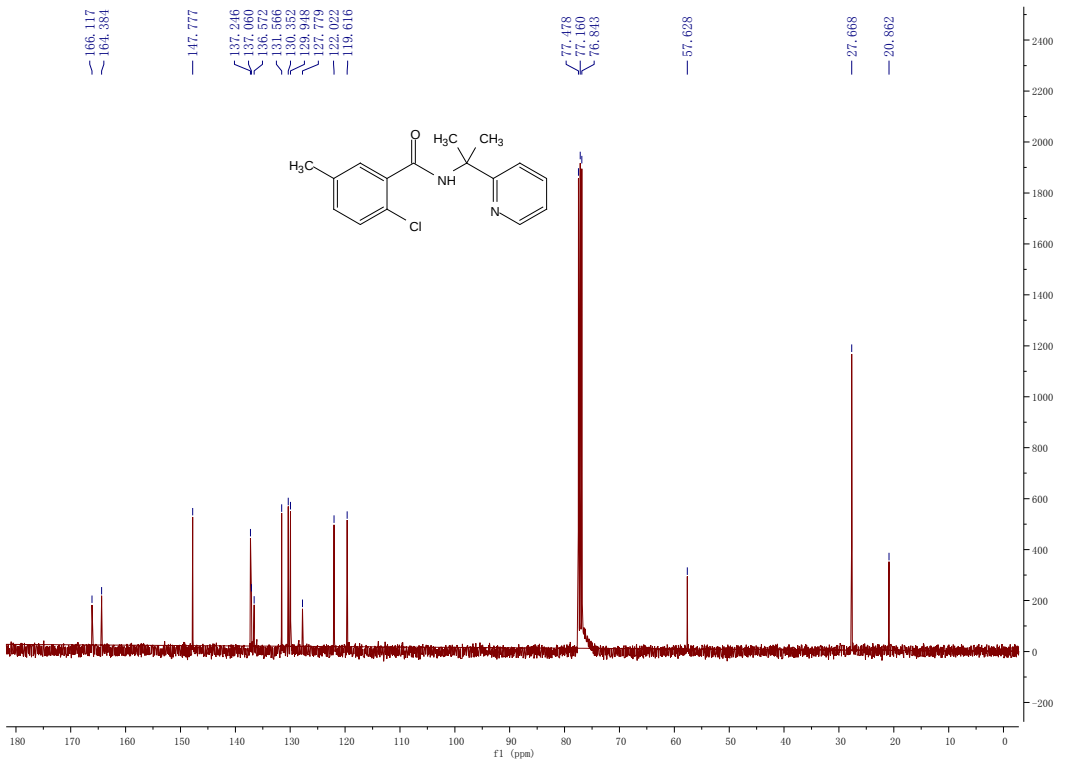

8.461
8.450
8.251
7.741
7.725
7.721
7.474
7.332
7.313
7.260
7.220
7.210
7.198
7.194
7.180
1.923
Cl
O
H3C
CH3
NH
N
Cl
1.00
0.97
1.08
1.10
2.04
0.95
0.97
6.40
f1 (ppm)

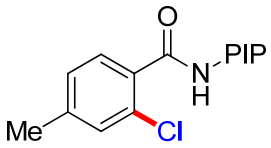

164.006
163.421
147.549
137.376
137.141
132.478
130.239
128.176
122.138
119.643
77.477
77.160
76.842
57.724
27.442
Cl
O
H3C
CH3
NH
N
Cl
f1 (ppm)


Me
O
N
H
PIP
Cl

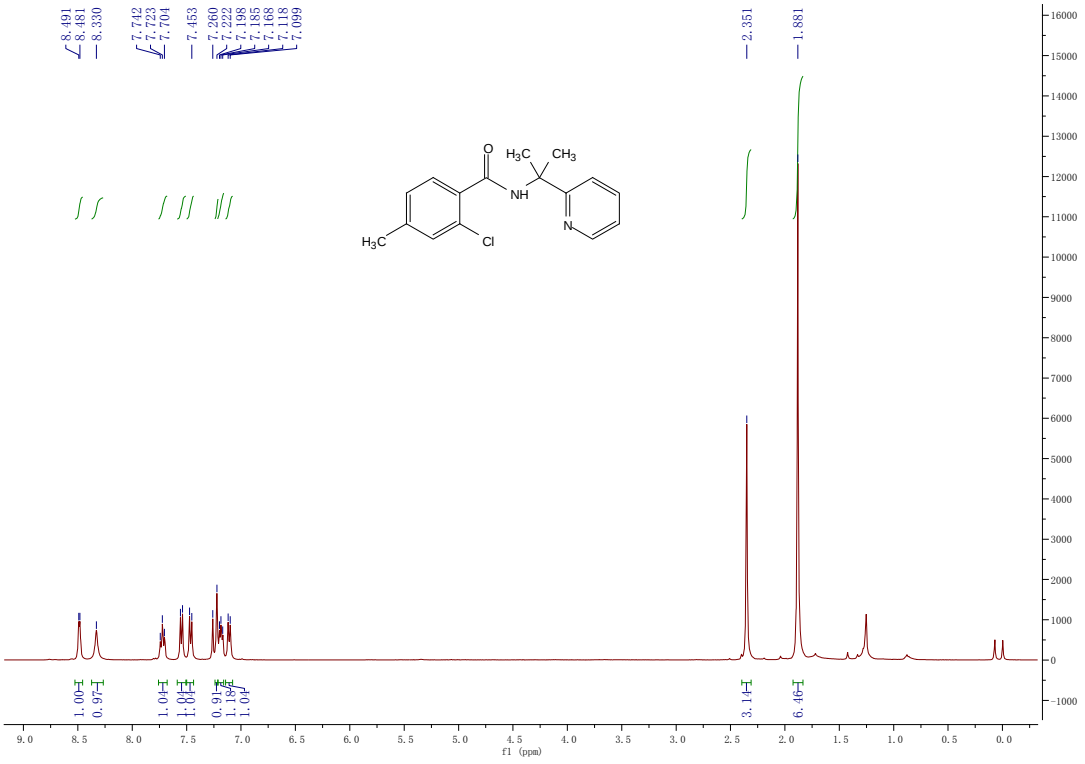
3b

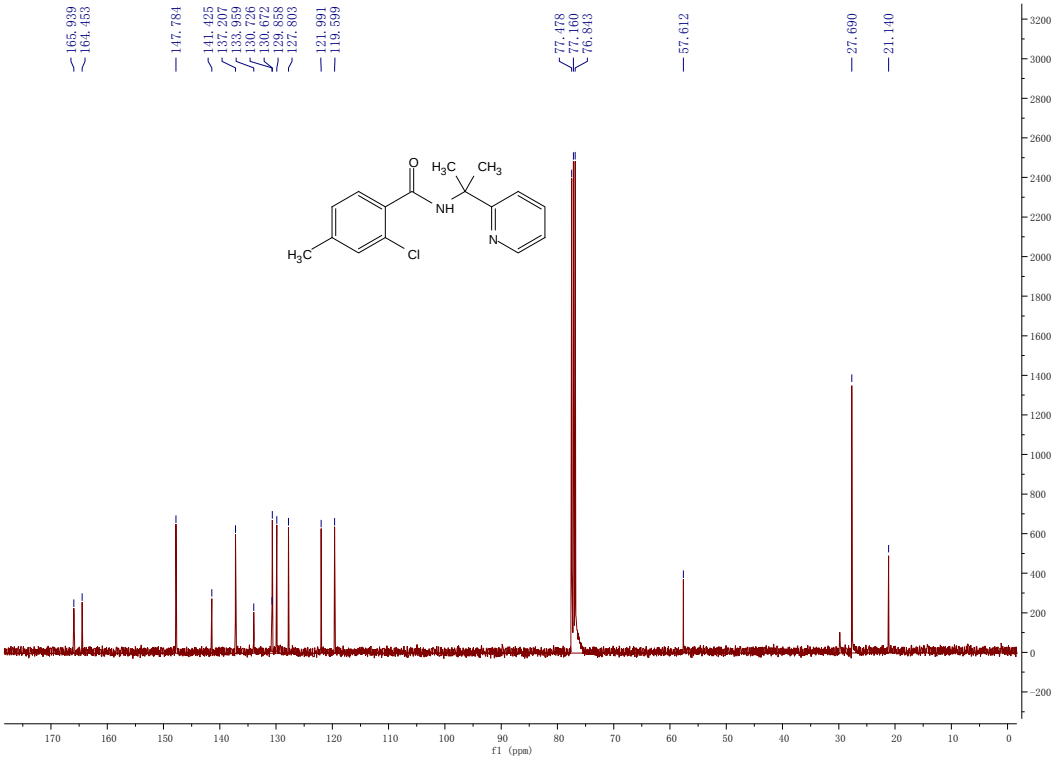

8.495
8.289
7.744
7.727
7.710
7.437
7.280
7.260
7.189
7.143
7.125
2.336
1.887
1.00
0.98
1.04
1.95
0.93
2.04
3.06
6.21
f1 (ppm)

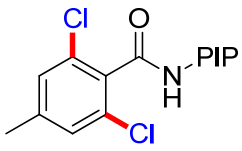

166.117
164.384
147.777
137.246
137.060
136.572
131.566
130.352
129.948
127.779
122.022
119.616
77.478
77.160
76.843
57.628
27.668
20.862
f1 (ppm)


O
N
H
PIP
Me
Cl

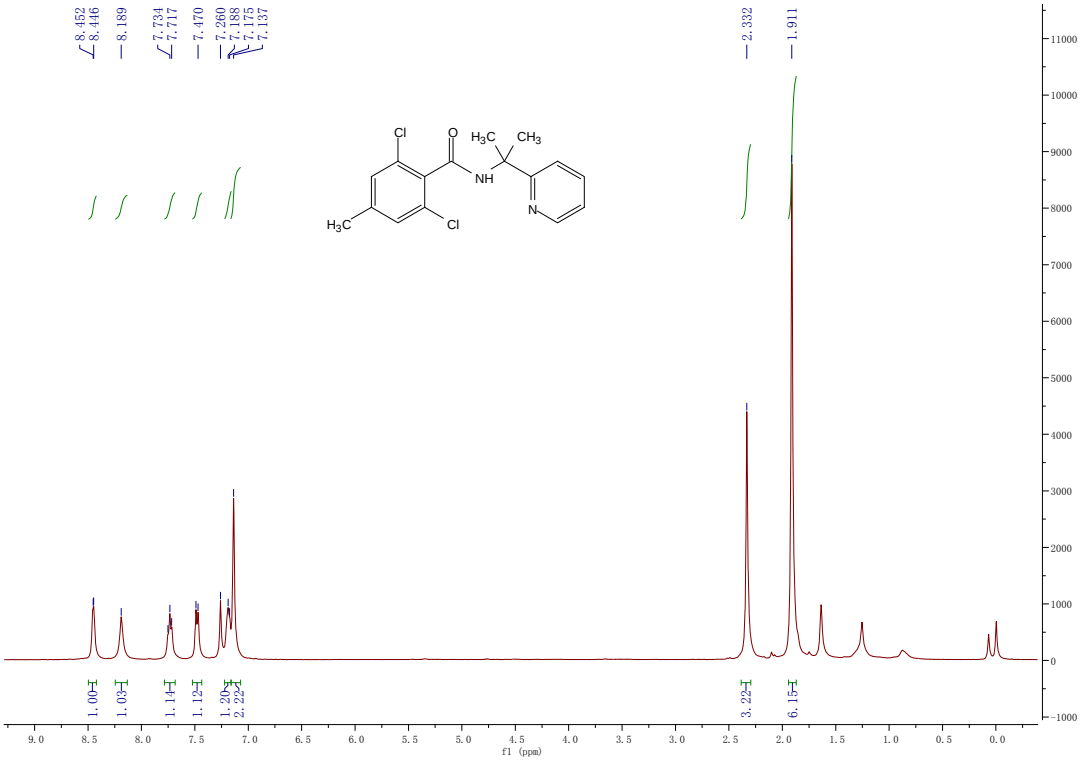
3c

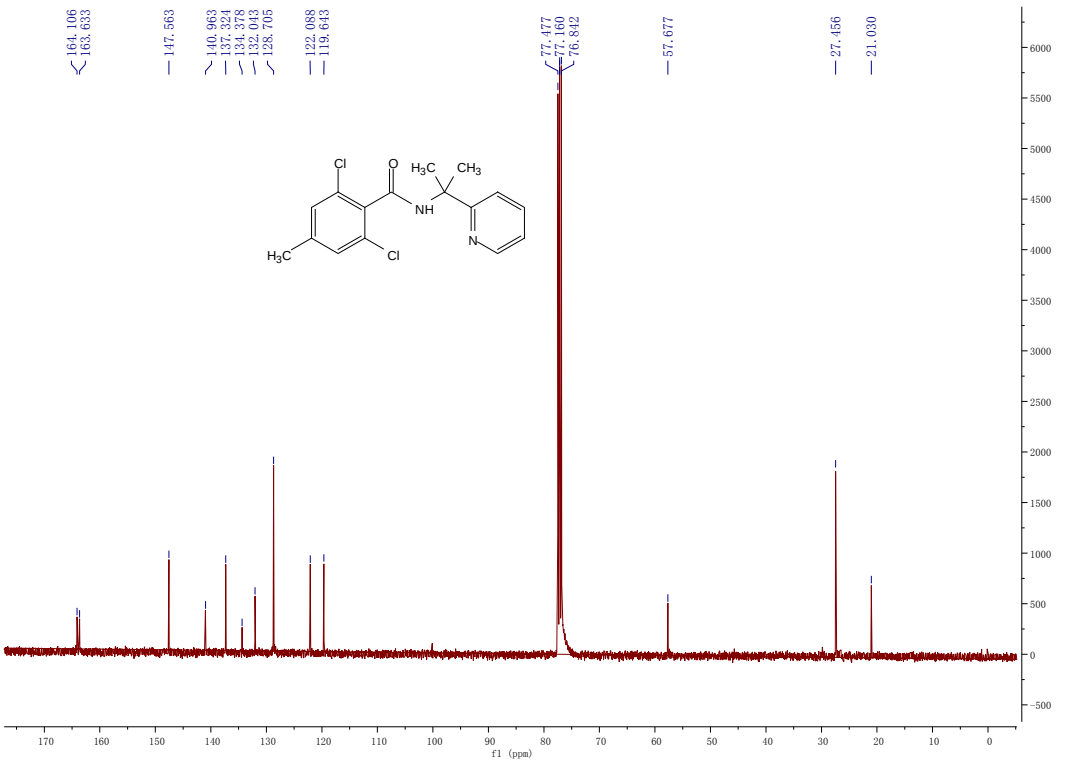

8.491
8.481
8.330
7.742
7.723
7.704
7.453
7.260
7.222
7.198
7.185
7.168
7.118
7.099
2.351
1.881
1.00
0.97
1.04
1.01
1.01
0.91
1.18
1.04
3.14
6.46
f1 (ppm)

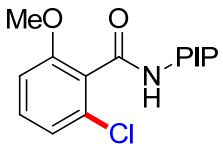

165.939
164.453
147.784
141.425
137.207
133.959
130.726
130.672
129.858
127.803
121.991
119.599
77.478
77.160
76.843
57.612
27.690
21.140
f1 (ppm)


Cl
O
N
H
PIP
Cl

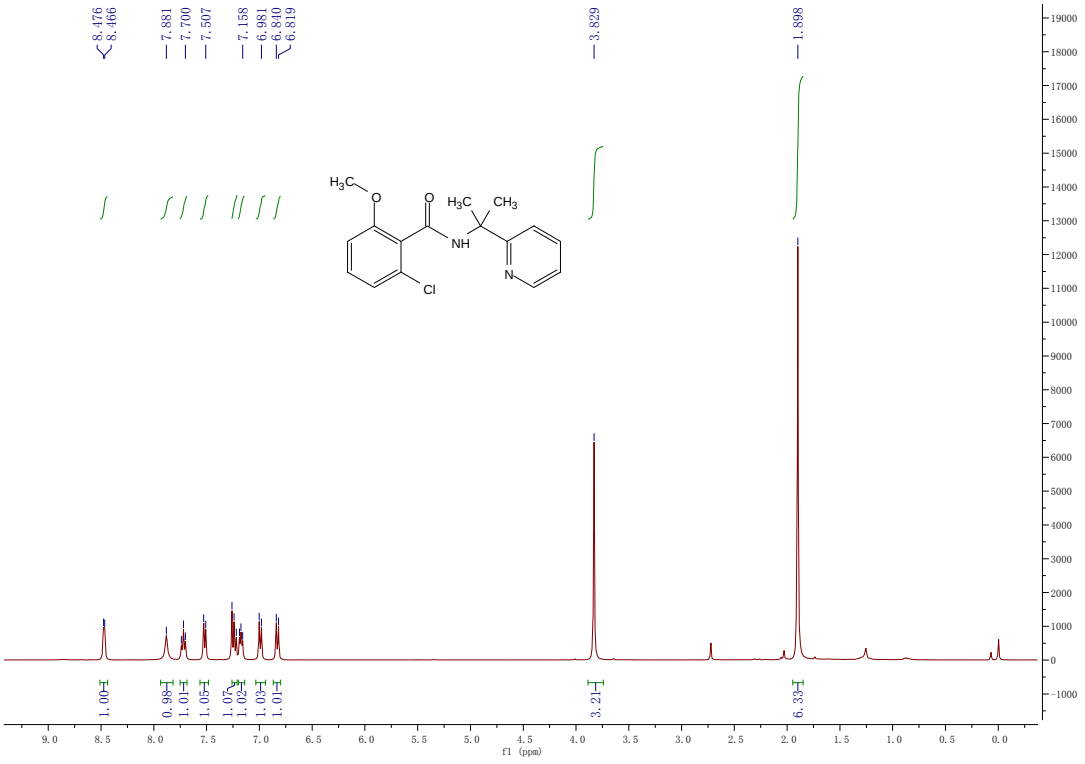
3c'

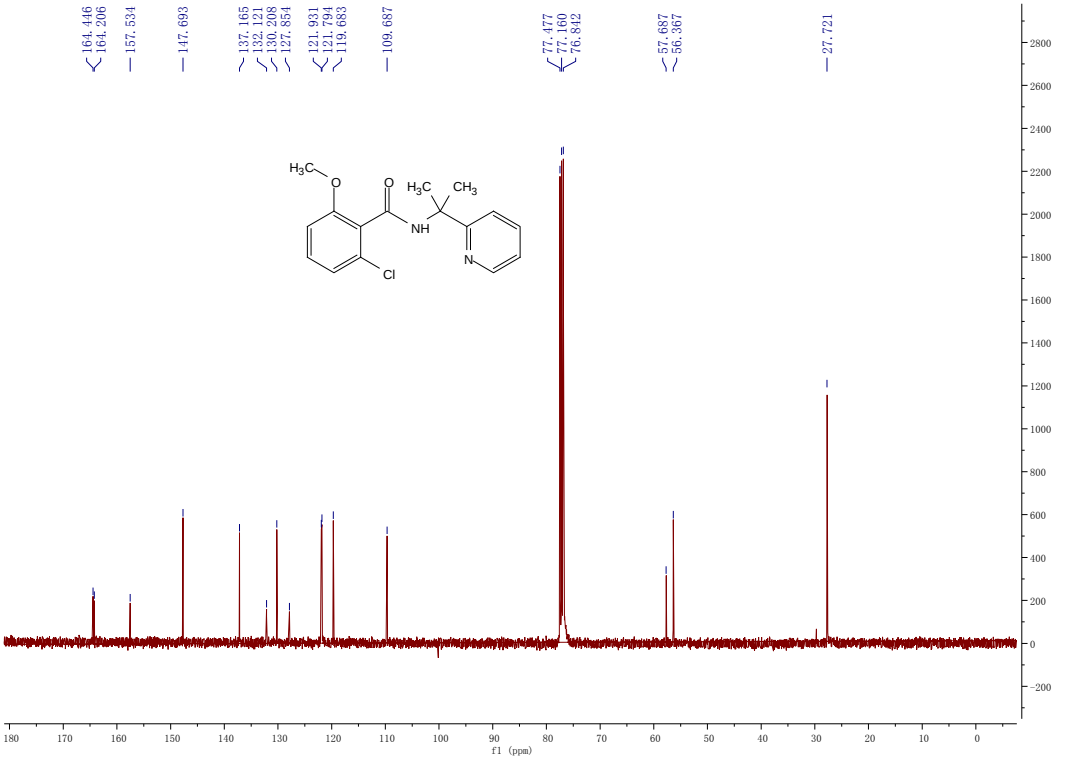

8.452
8.446
8.189
7.734
7.717
7.470
7.260
7.188
7.175
7.137
2.332
1.911
1.00
1.03
1.14
1.12
1.20
2.22
3.22
6.15
f1 (ppm)

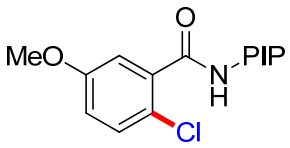

164.106
163.633
147.563
140.963
137.324
134.378
132.043
128.705
122.088
119.643
77.477
77.160
76.842
57.677
27.456
21.030
f1 (ppm)


MeO
O
N
H
PIP
Cl

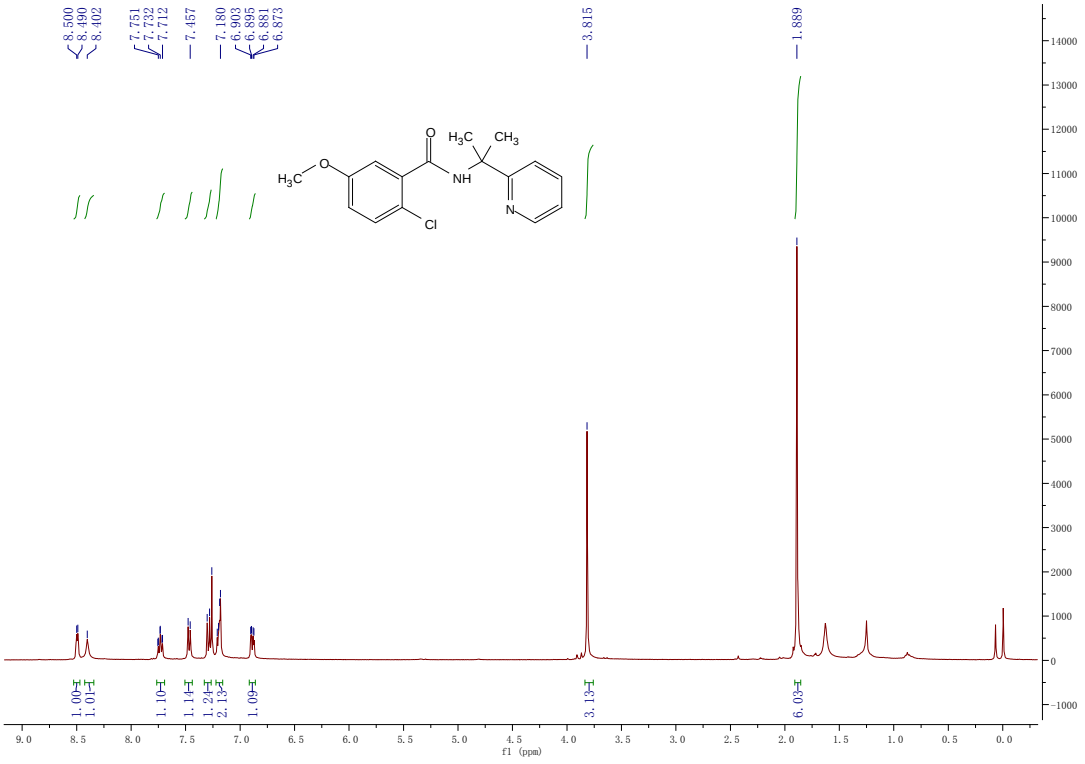
3d


8.476
8.466
7.881
7.700
7.507
7.158
6.981
6.840
6.819
3.829
1.898
1.00
0.98
1.01
1.05
1.07
1.02
1.03
1.01
3.21
6.33
f1 (ppm)


164.446
164.206
157.534
147.693
137.165
132.121
130.208
127.854
121.931
121.794
119.683
109.687
77.477
77.160
76.842
57.687
56.367
27.721
f1 (ppm)


MeO
O
N
H
PIP
Cl

3e


8.500
8.490
8.402
7.751
7.732
7.712
7.457
7.180
6.903
6.895
6.881
6.873
3.815
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1.10
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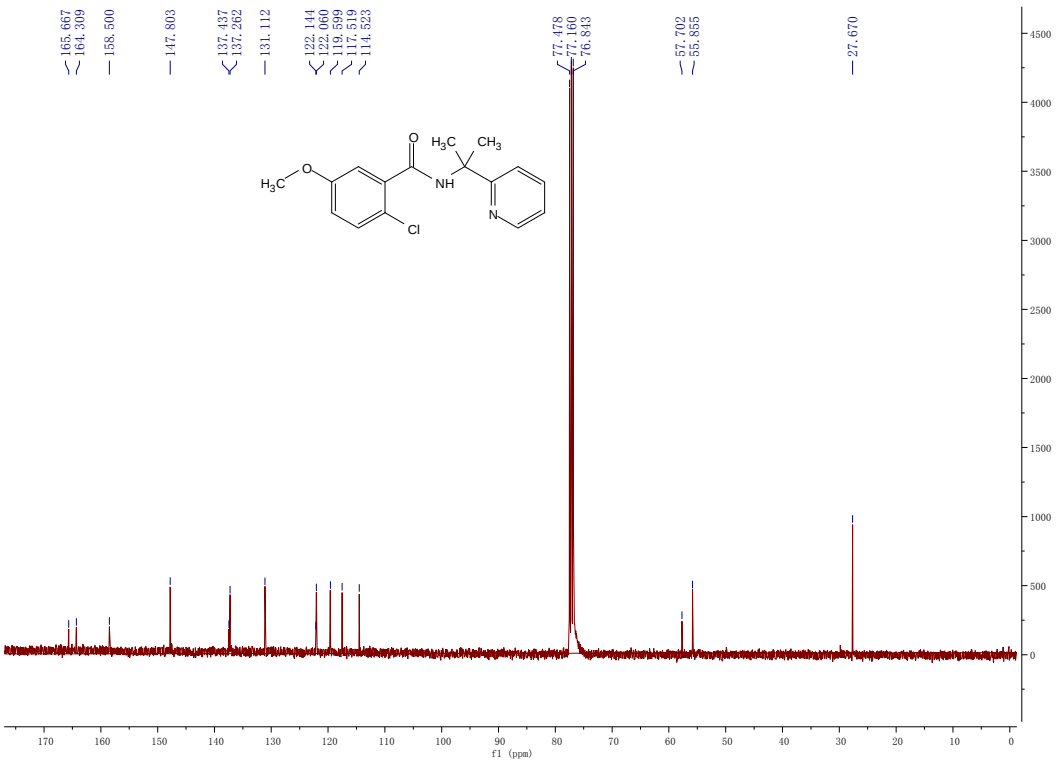
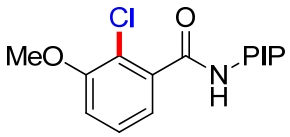
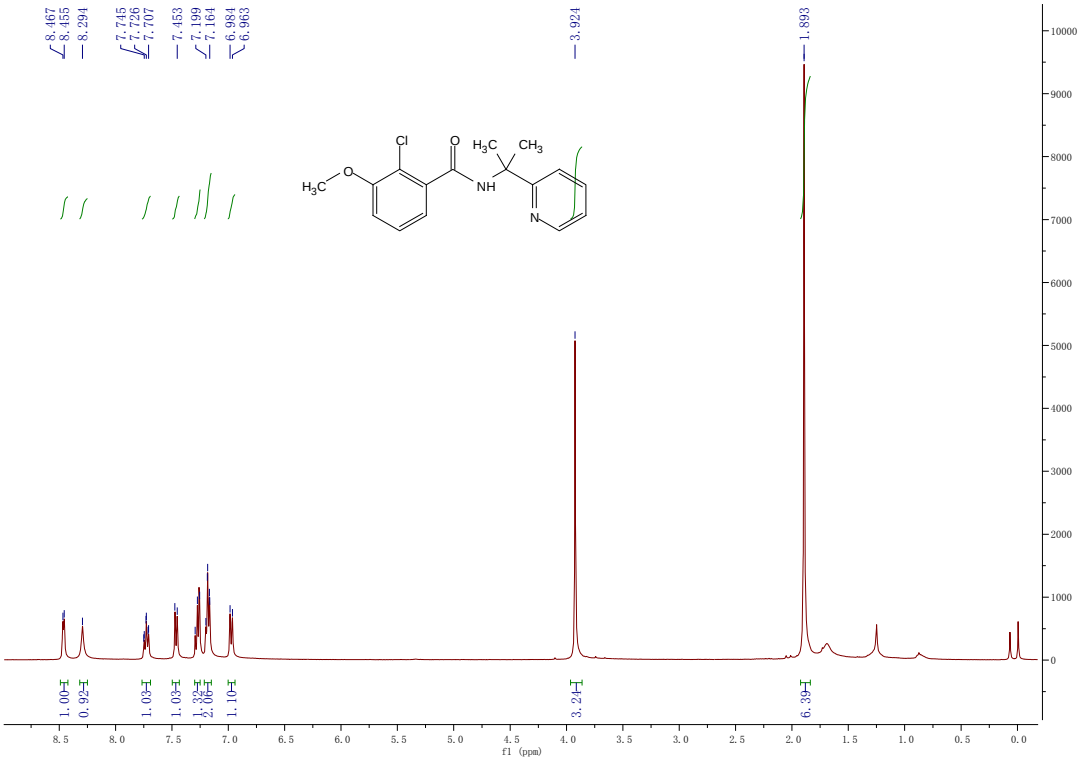
1.24
2.13
1.09
3.13
6.03
f1 (ppm)


165.667
164.309
158.500
147.803
137.437
137.262
131.112
122.144
122.060
119.599
117.519
114.523
77.478
77.160
76.843
57.702
55.855
27.670
f1 (ppm)


Cl
O
MeO
N
H
PIP

3e'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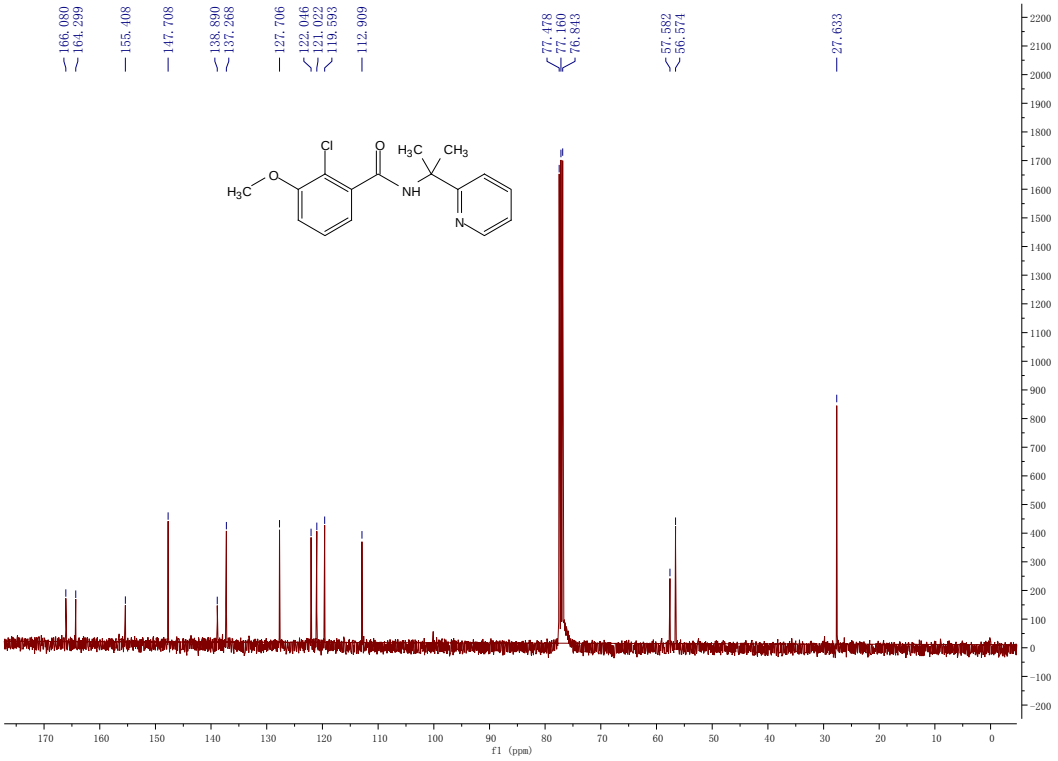
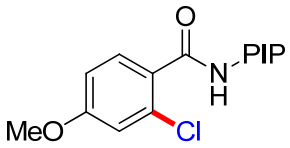
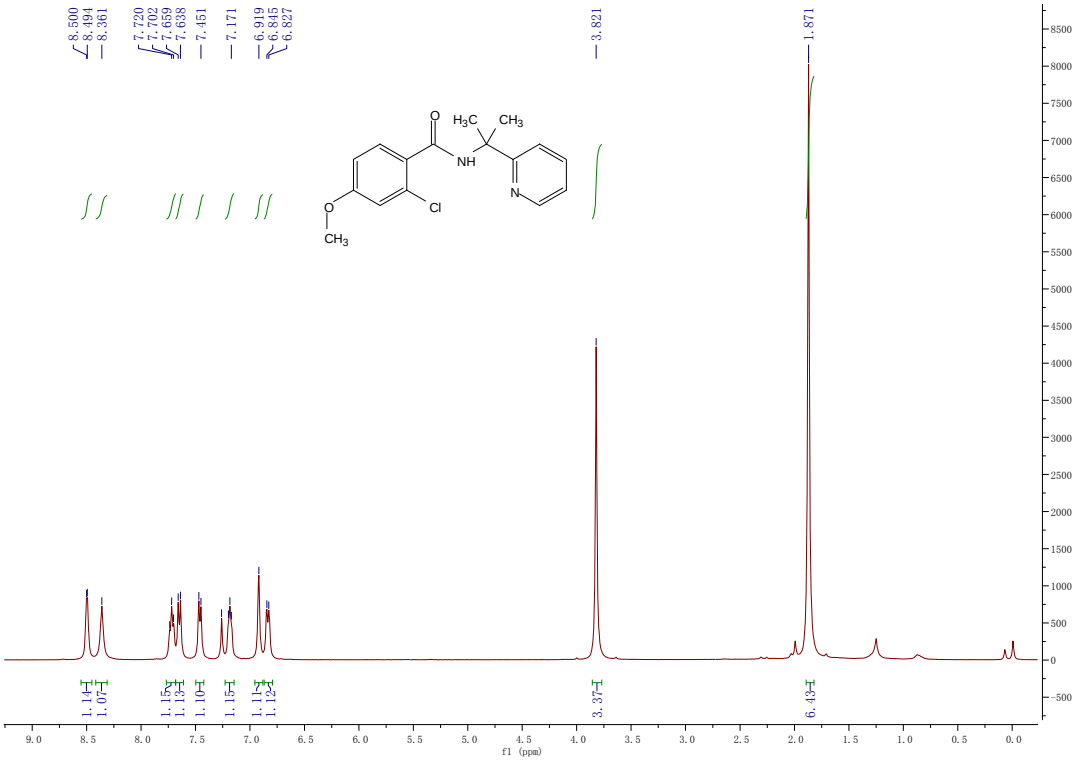
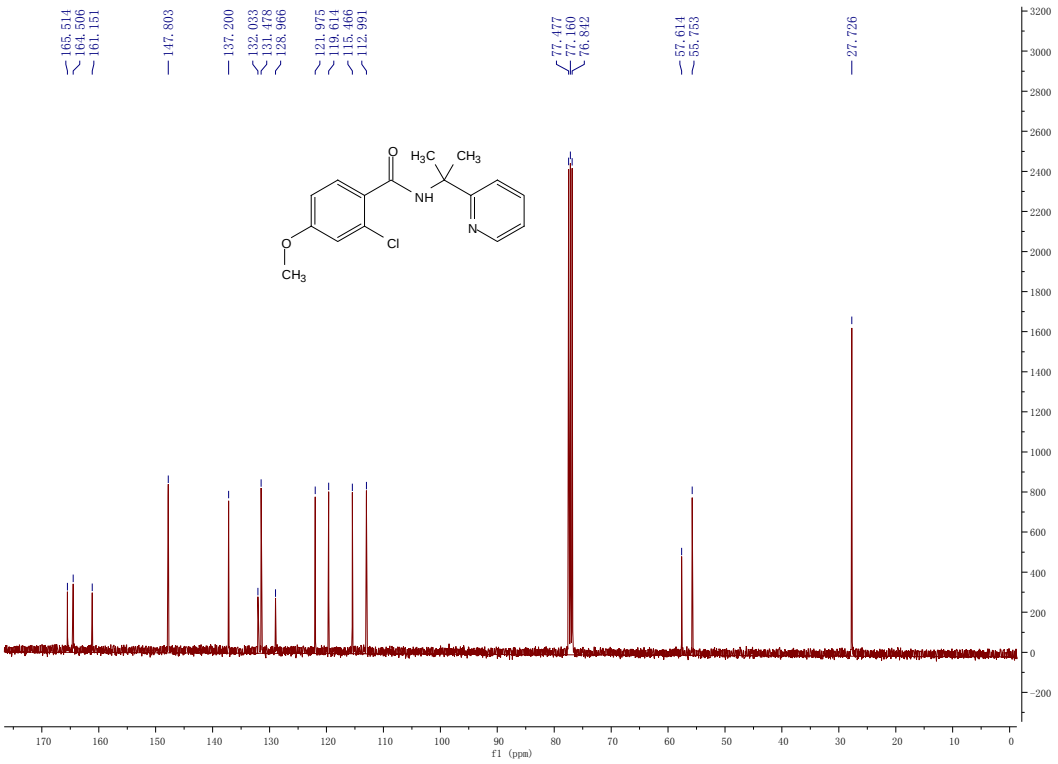
8.455
8.294
7.745
7.726
7.707
7.453
7.199
7.164
6.984
6.963
3.924
1.893
1.00
0.92
1.03
1.03
1.32
2.06
1.10
3.24
6.39
f1 (ppm)


166.080
164.299
155.408
147.708
138.890
137.268
127.706
122.046
121.022
119.593
112.909
77.478
77.160
76.843
57.582
56.574
27.633
f1 (ppm)


O
N
H
PIP
MeO
Cl

3f


8.500
8.494
8.361
7.720
7.702
7.659
7.638
7.451
7.171
6.919
6.845
6.827
3.821
1.871
1.14
1.07
1.15
1.13
1.10
1.15
1.11
1.12
3.37
6.43
f1 (ppm)


165.514
164.506
161.151
147.803
137.200
132.033
131.478
128.966
121.975
119.614
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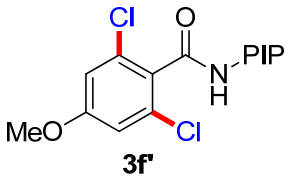
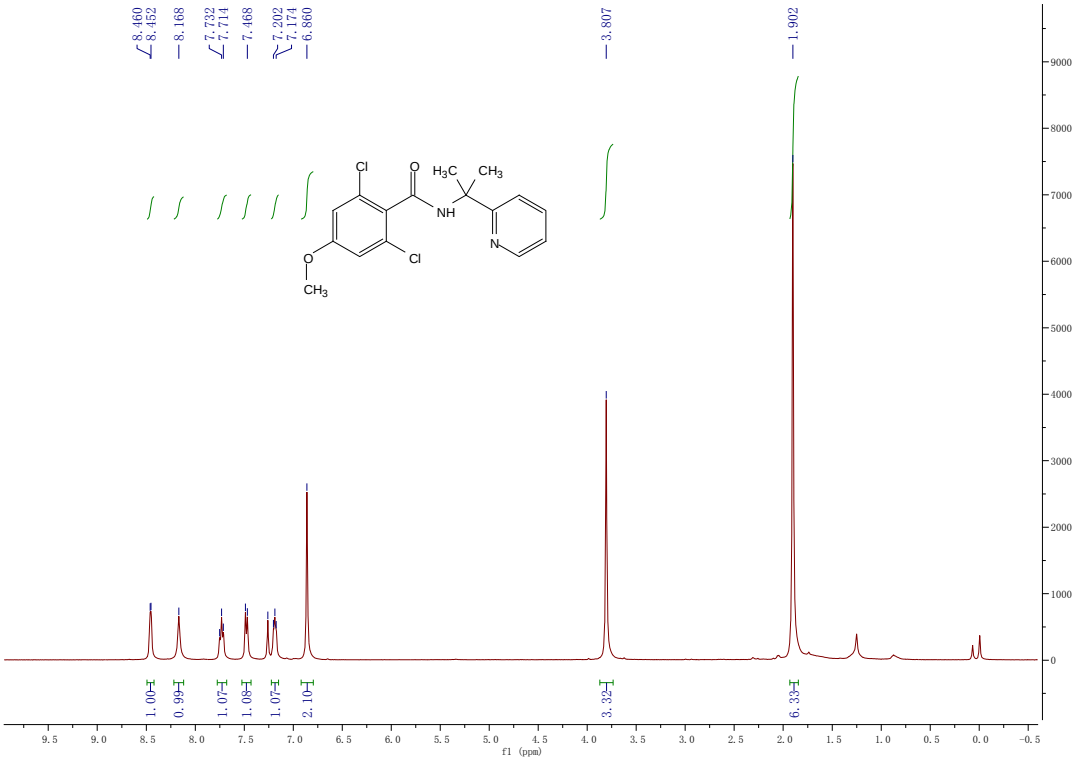
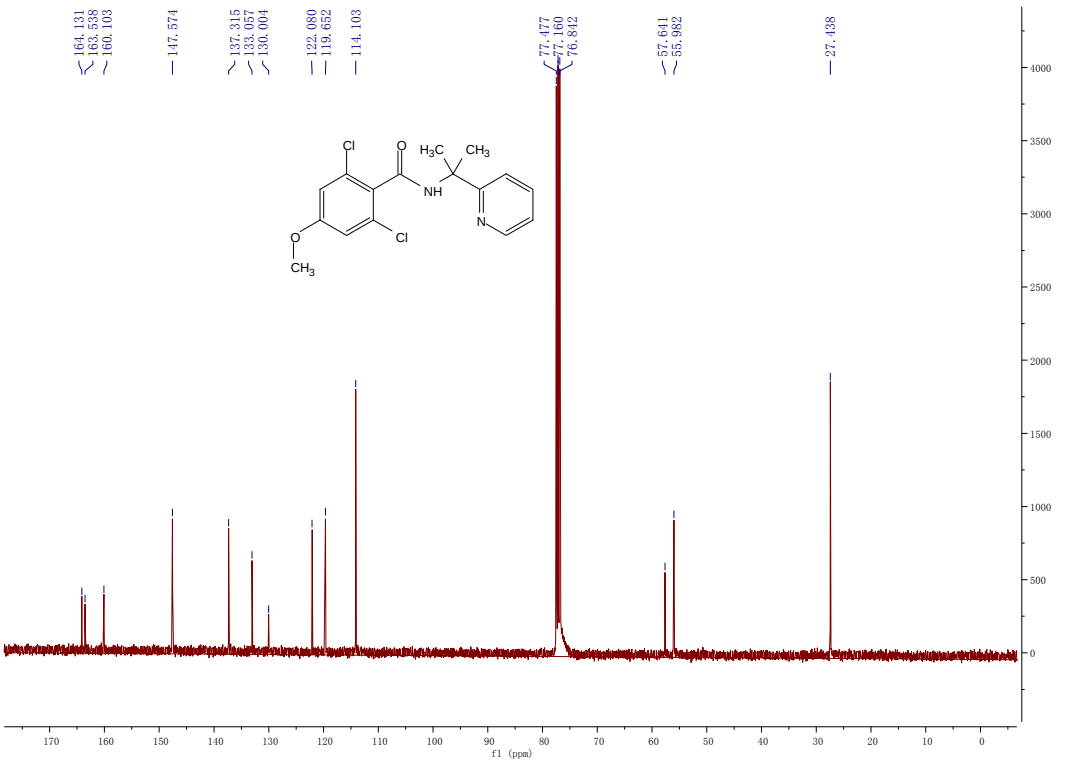
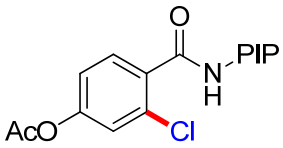
112.991
77.477
77.160
76.842
57.614
55.753
27.726
f1 (ppm)


Cl
O
N
PIP
H
MeO
Cl

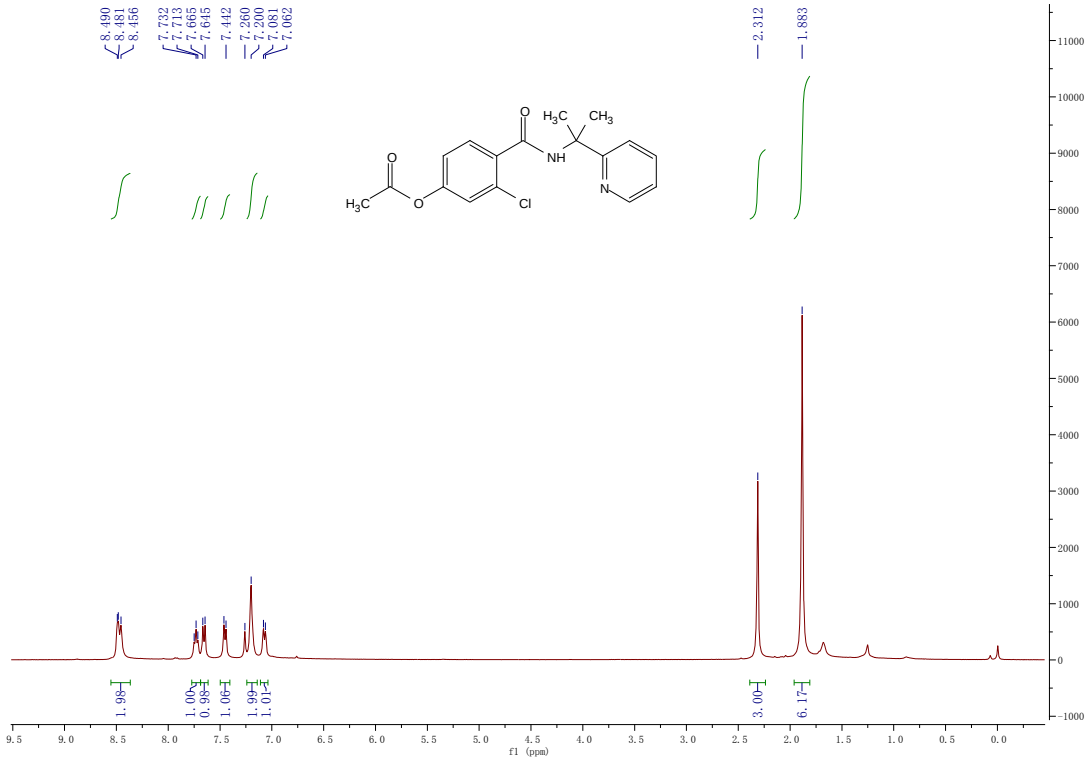
3f'

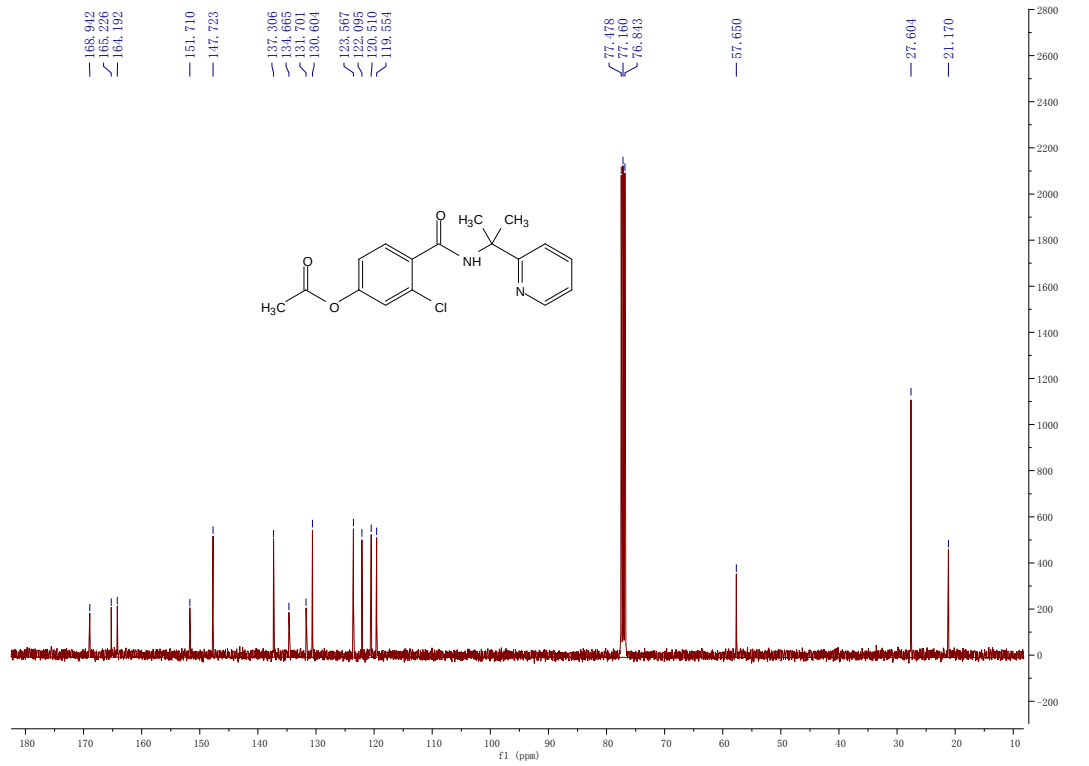

8.460
8.452
8.168
7.732
7.714
7.468
7.202
7.174
6.860
3.807
1.902
1.00
0.99
1.07
1.08
1.07
2.10
3.32
6.33
f1 (ppm)

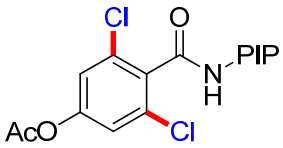

164.131
163.538
160.103
147.574
137.315
133.057
130.004
122.080
119.652
114.103
77.477
77.160
76.842
57.641
55.982
27.438
f1 (ppm)


O
N
H
PIP
AcO
Cl

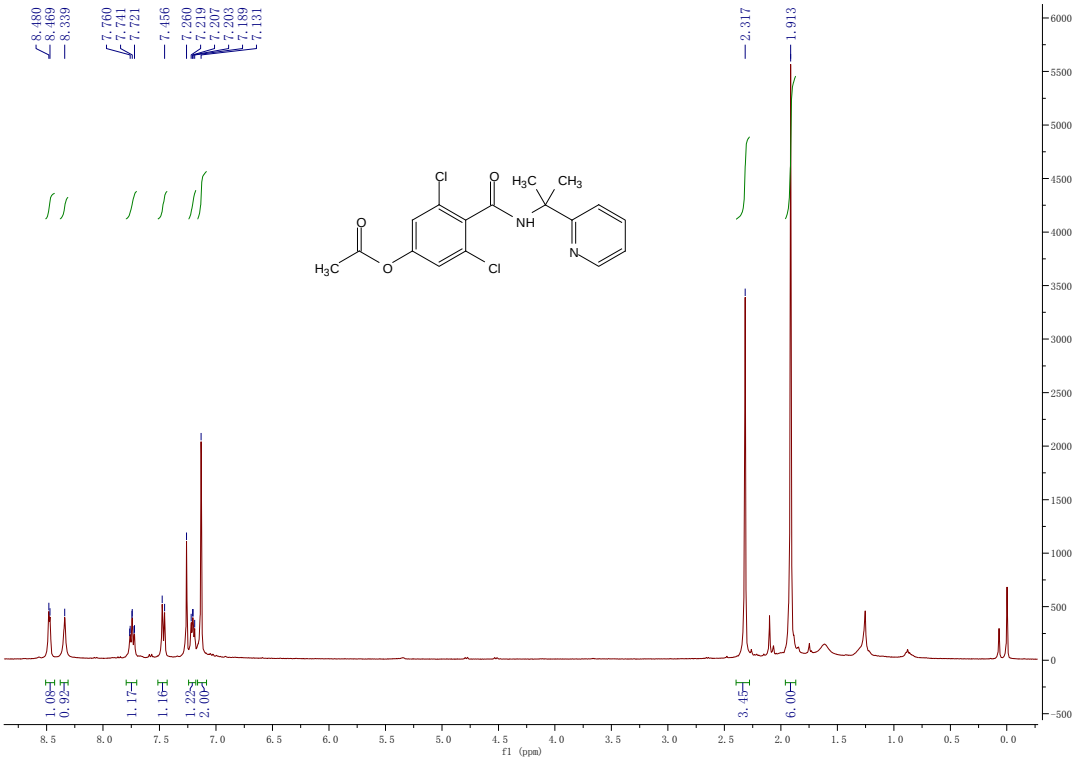
3h

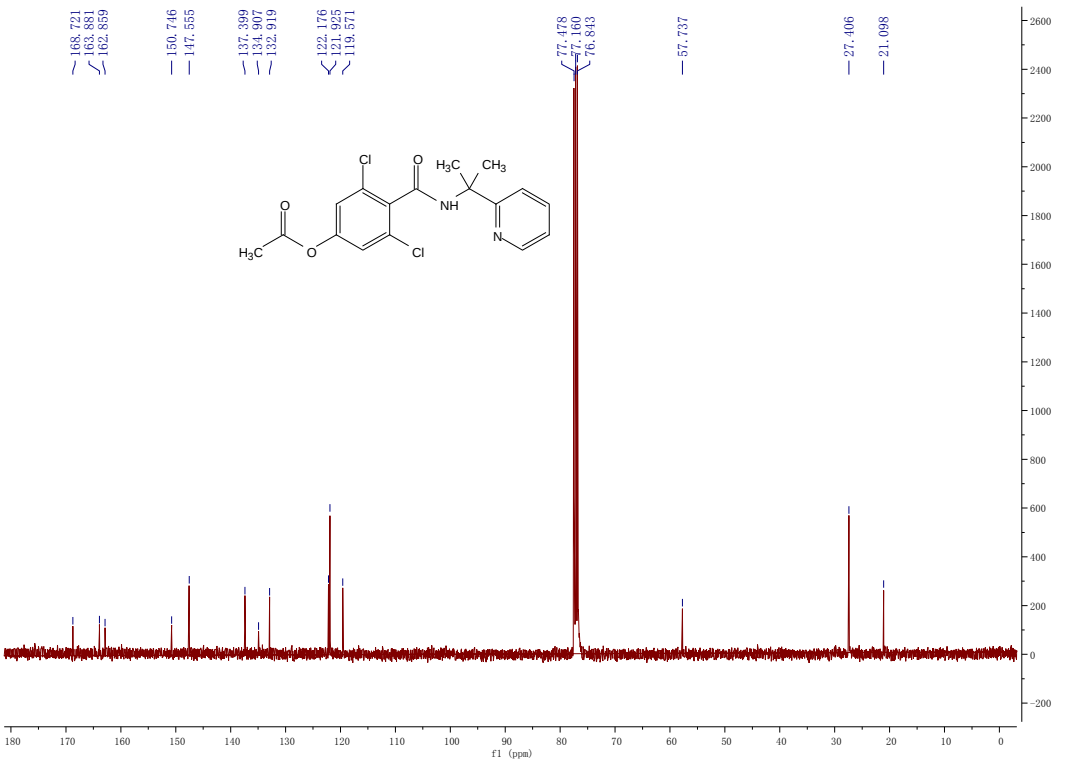

8.490
8.481
8.456
7.732
7.713
7.665
7.645
7.442
7.260
7.200
7.081
7.062
2.312
1.883
1.98
1.00
0.98
1.06
1.99
1.01
3.00
6.17
f1 (ppm)


168.942
165.226
164.192
151.710
147.723
137.306
134.665
131.701
130.604
123.567
122.095
120.510
119.554
77.478
77.160
76.843
57.650
27.604
21.170
f1 (ppm)


Cl
O
N
PIP
H
AcO
Cl

3h'


8.480
8.469
8.339
7.760
7.741
7.721
7.456
7.260
7.219
7.207
7.203
7.189
7.131
2.317
1.913
1.09
0.92
1.17
1.16
1.22
2.00
3.45
6.00
f1 (ppm)


168.721
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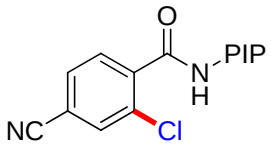
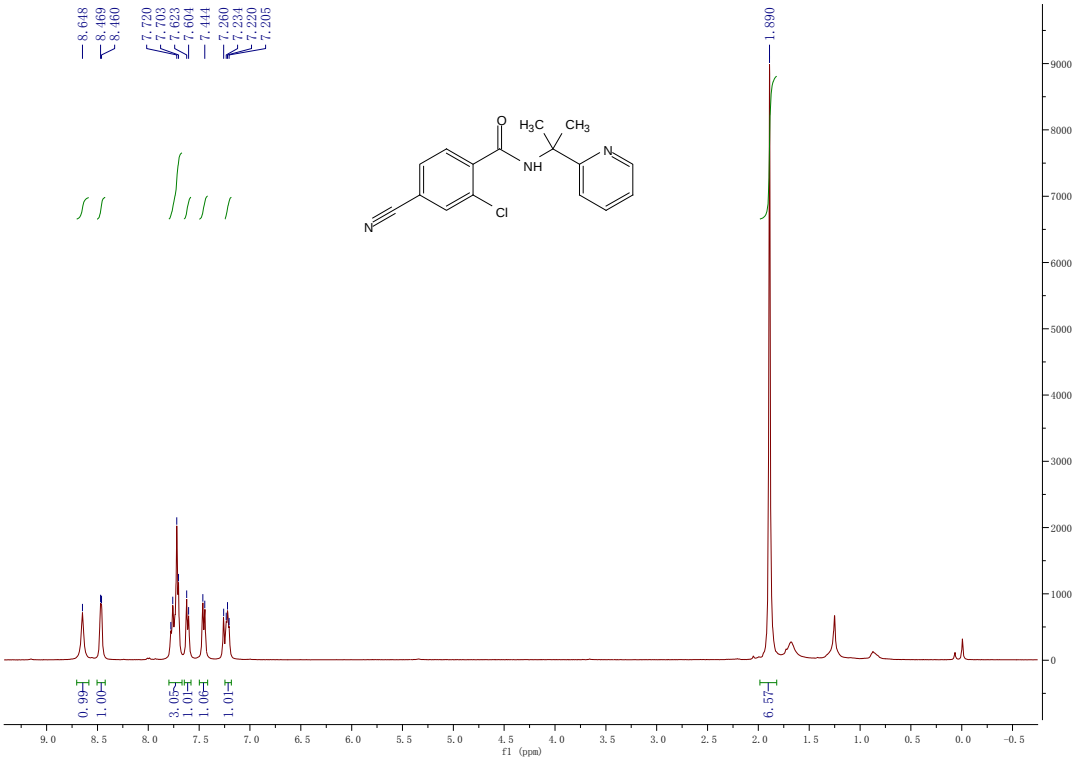
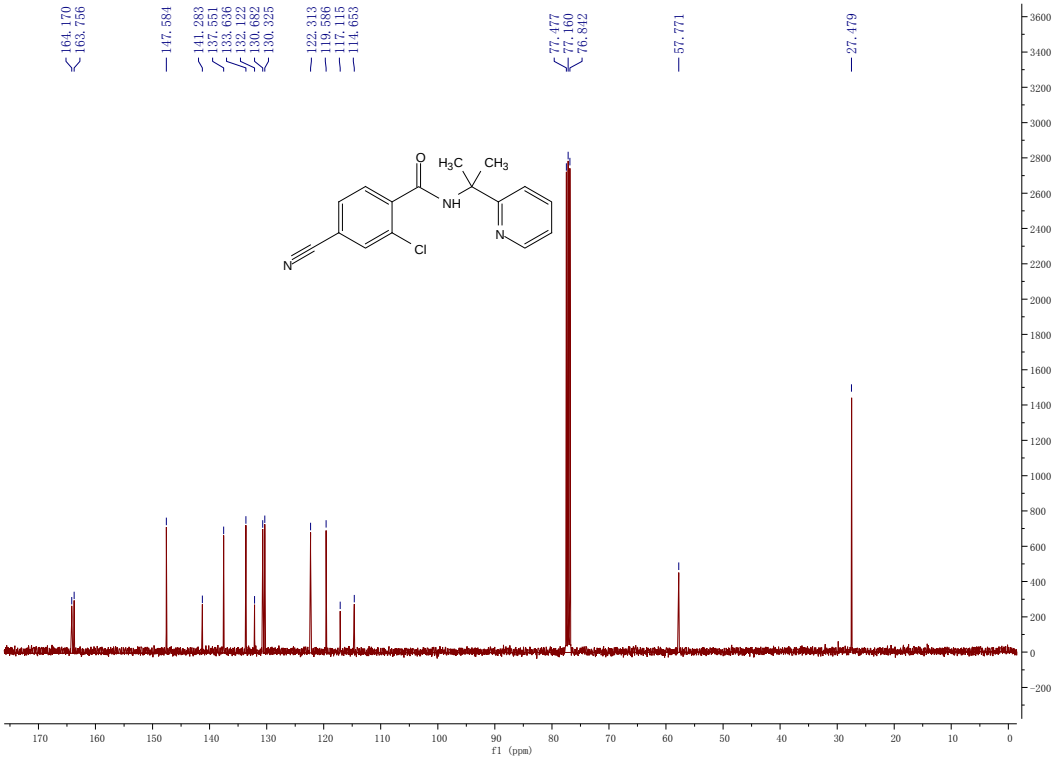
162.859
150.746
147.555
137.399
134.907
132.919
122.176
121.925
119.571
77.478
77.160
76.843
57.737
27.406
21.098
f1 (ppm)


O
N
PIP
H
NC
Cl

3k


8.648
8.469
8.460
7.720
7.703
7.623
7.604
7.444
7.260
7.234
7.220
7.205
1.890
O
H3C
CH3
NH
N
Cl
N
0.99
1.00
3.05
1.01
1.06
1.01
6.57
f1 (ppm)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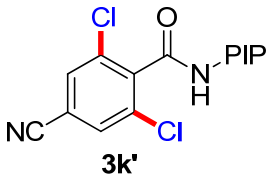
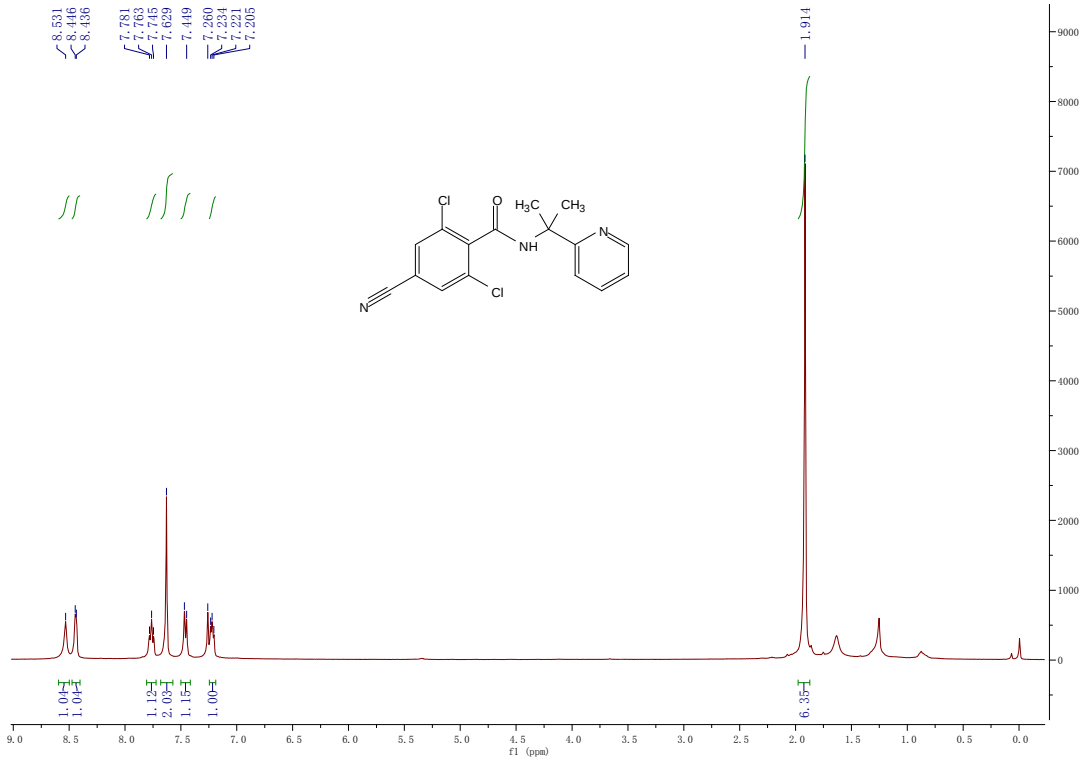
147.584
141.283
137.551
133.636
132.122
130.682
130.325
122.313
119.586
117.115
114.653
77.477
77.160
76.842
57.771
27.479
O
H3C
CH3
NH
N
Cl
N
f1 (ppm)


Cl
O
N
PIP
H
NC
Cl

3k'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8.446
8.436
7.781
7.763
7.745
7.629
7.449
7.260
7.234
7.221
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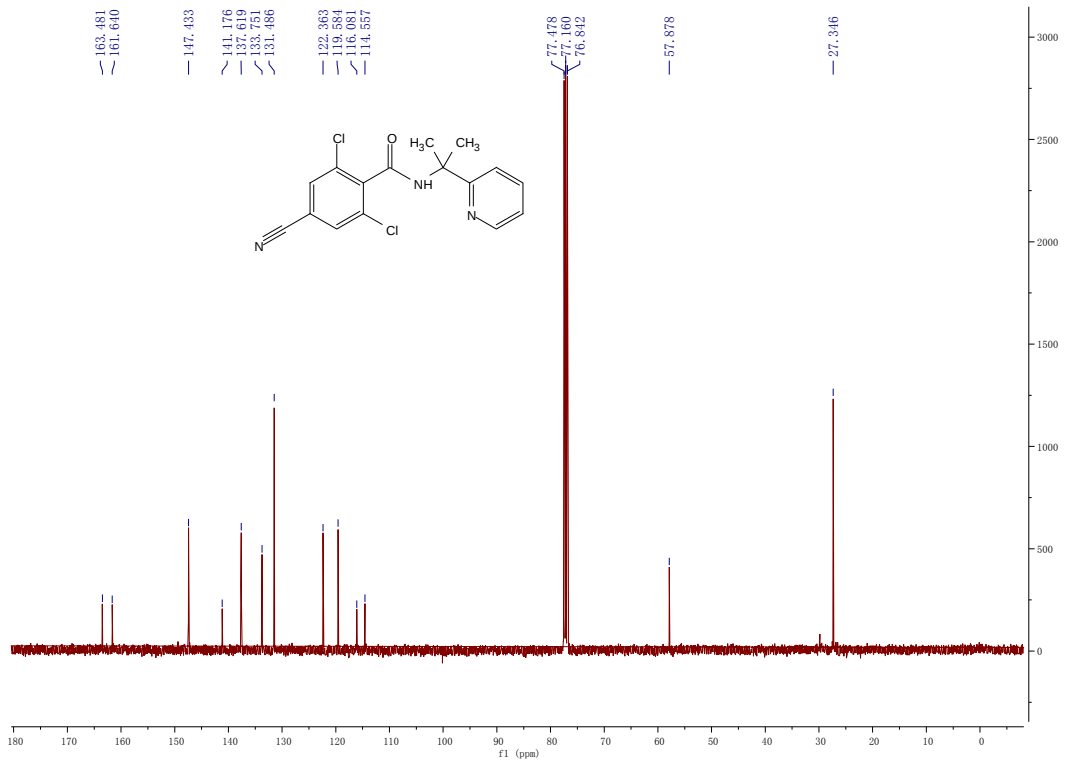
2.03
1.15
1.00
6.35
f1 (ppm)


163.481
161.640
147.433
141.176
137.619
133.751
131.486
122.363
119.584
116.081
114.557
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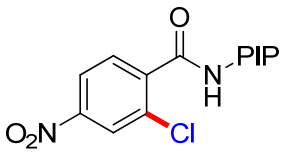
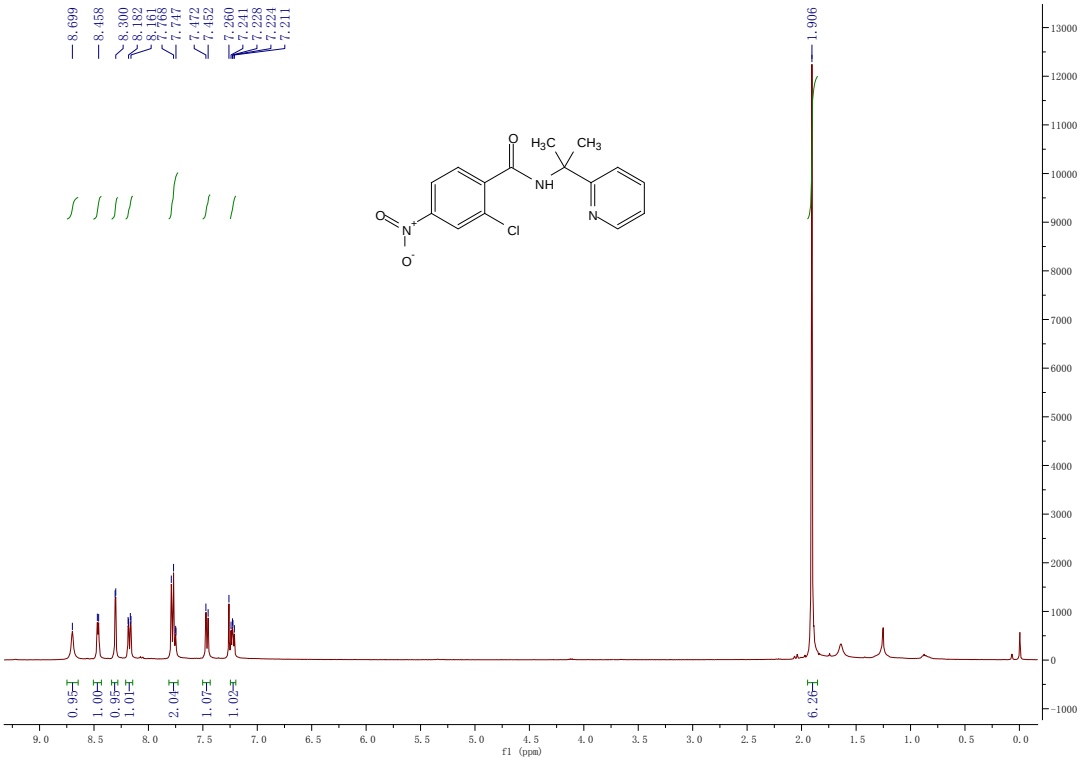
77.160
76.842
57.878
27.346
f1 (ppm)


O
N
PIP
H
O_2N
Cl

3n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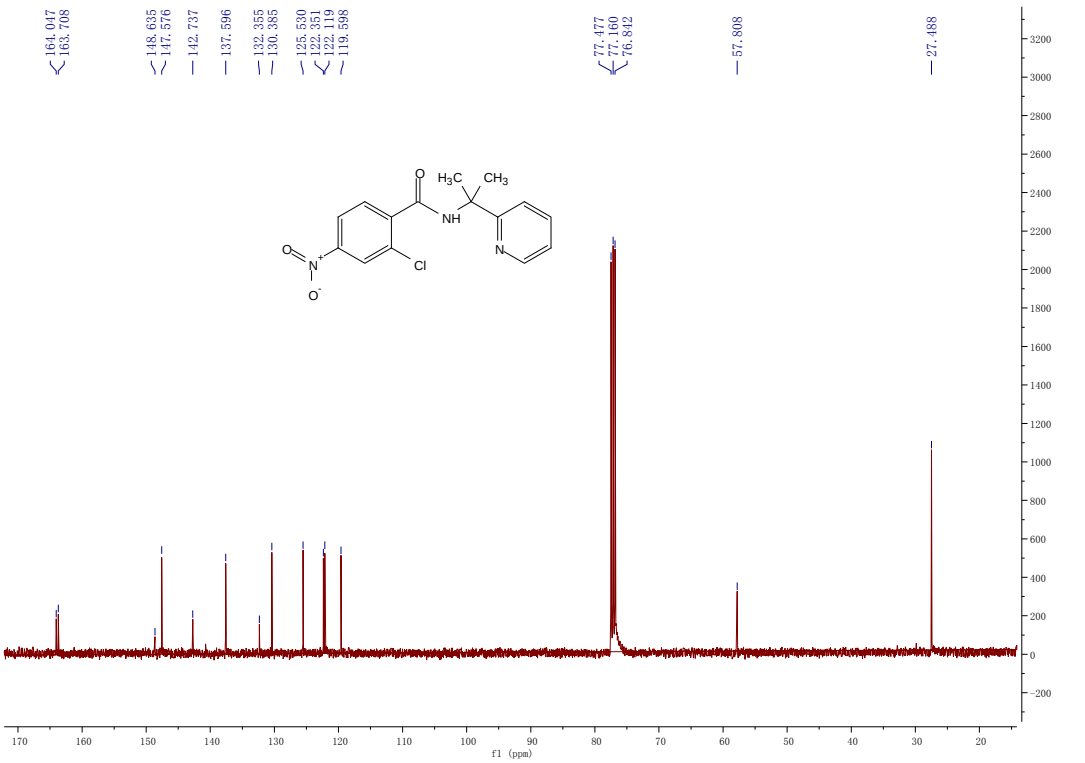
8.458
8.300
8.182
8.161
7.768
7.747
7.472
7.452
7.260
7.241
7.228
7.224
7.211
1.906
H_3C
CH_3
NH
N
Cl
O
N^+
O^-
0.95
1.00
0.95
1.01
2.04
1.07
1.02
6.26
f1 (ppm)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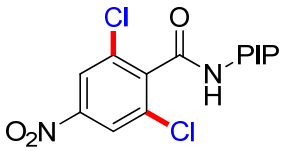
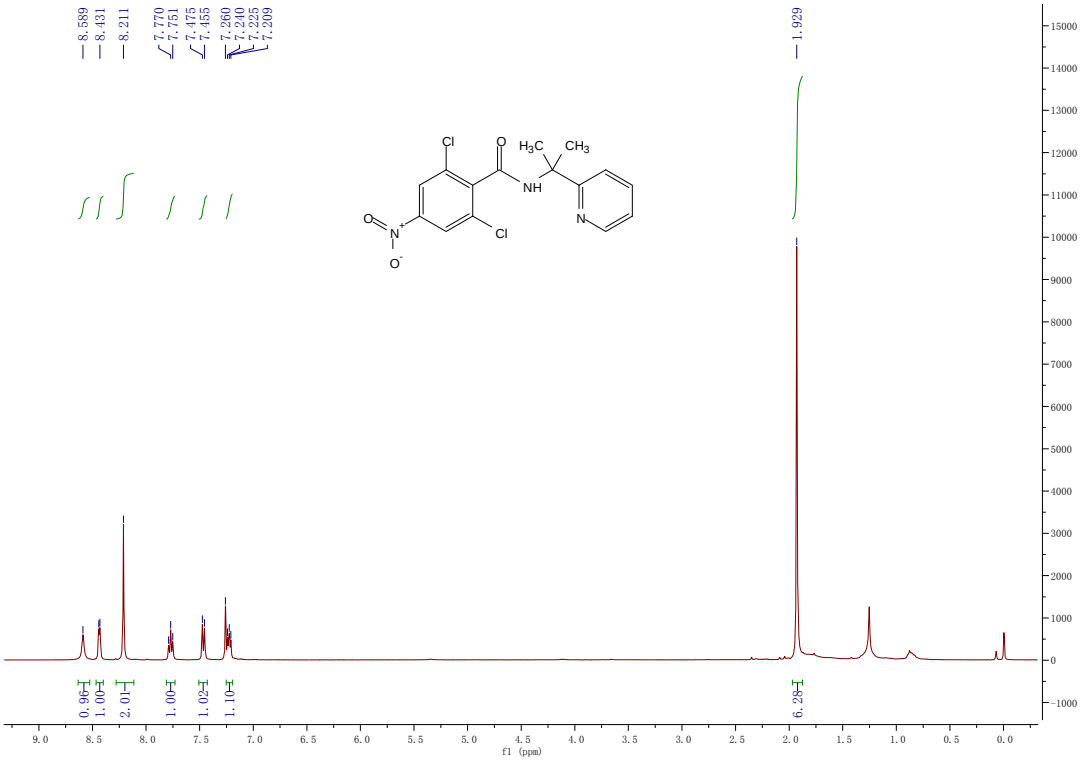
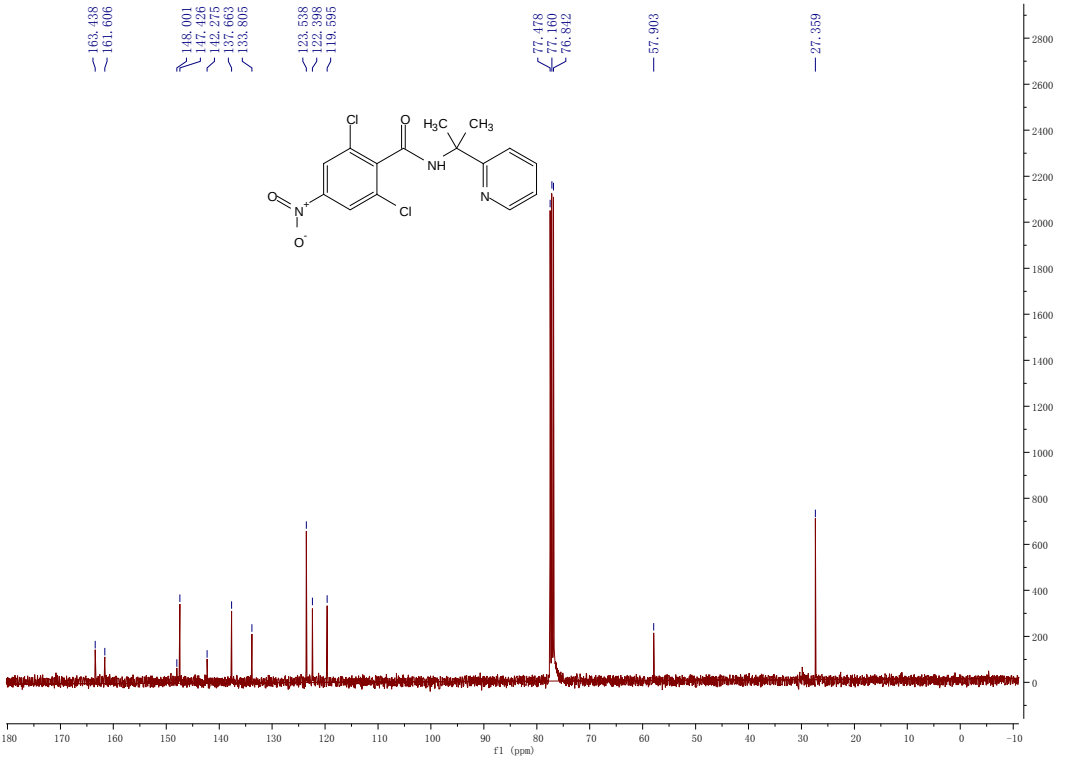
163.708
148.635
147.576
142.737
137.596
132.355
130.385
125.530
122.351
122.119
119.598
77.477
77.160
76.842
57.808
27.488
H_3C
CH_3
NH
N
Cl
O
N^+
O^-
f1 (ppm)


Cl
O
N
PIP
H
O_2N
Cl

3n'


8.589
8.431
8.211
7.770
7.751
7.475
7.455
7.260
7.240
7.225
7.209
1.929
0.96
1.00
2.01
1.00
1.02
1.10
6.28
f1 (ppm)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148.001
147.426
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123.538
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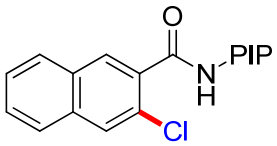
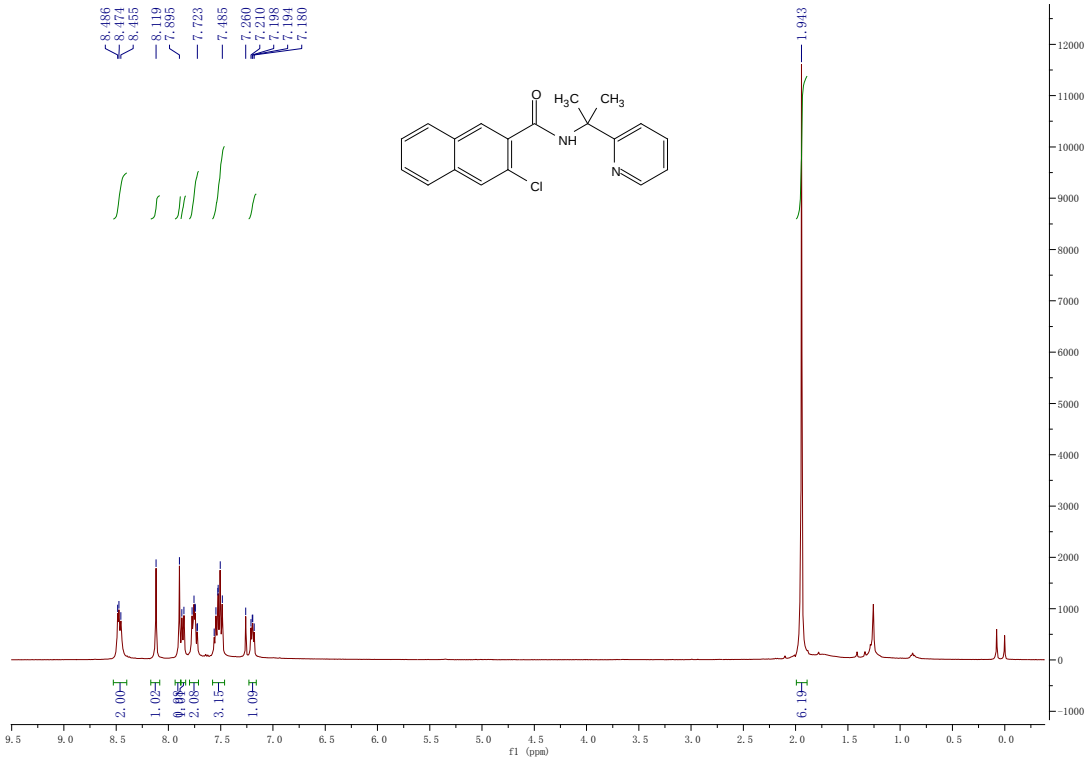
119.595
77.478
77.160
76.842
57.903
27.359
f1 (ppm)


O
N
H
PIP
Cl

3o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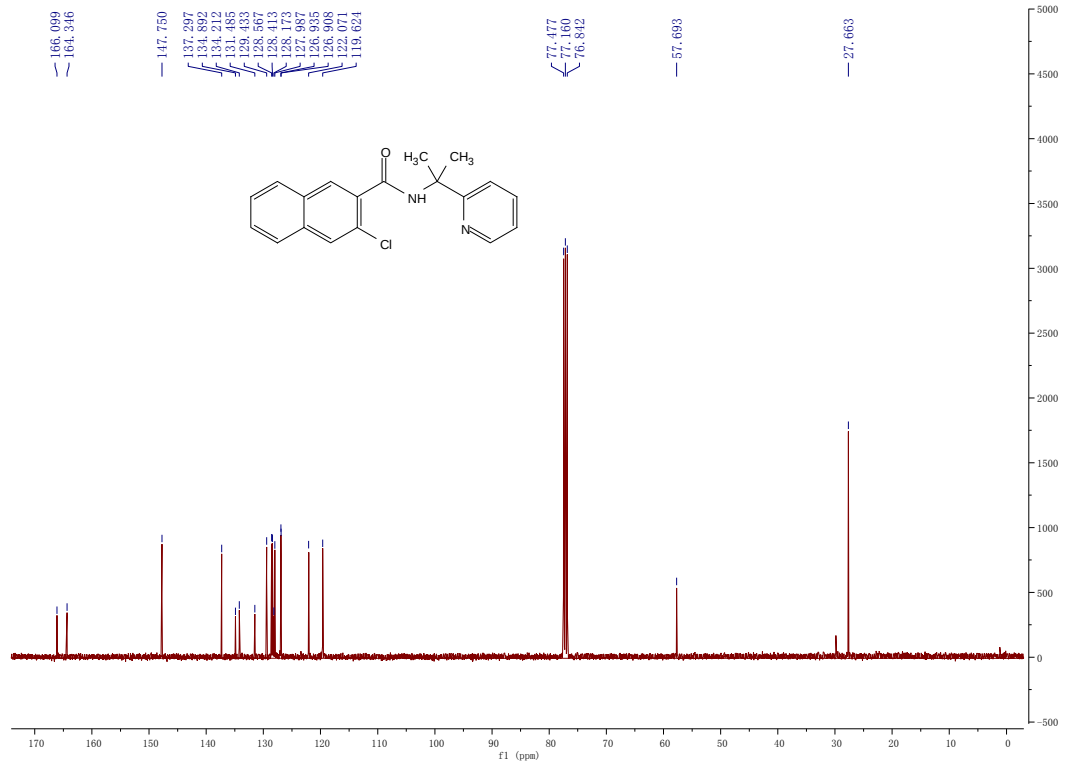
8.474
8.455
8.119
7.895
7.723
7.485
7.260
7.210
7.198
7.194
7.180
1.943
O
H3C
CH3
NH
N
Cl
2.00
1.02
2.08
3.15
1.09
6.19
f1 (ppm)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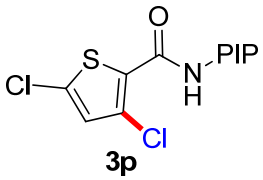
131.485
129.433
128.567
128.413
128.173
127.987
126.935
126.908
122.071
119.624
77.477
77.160
76.842
57.693
27.663
O
H3C
CH3
NH
N
Cl
f1 (ppm)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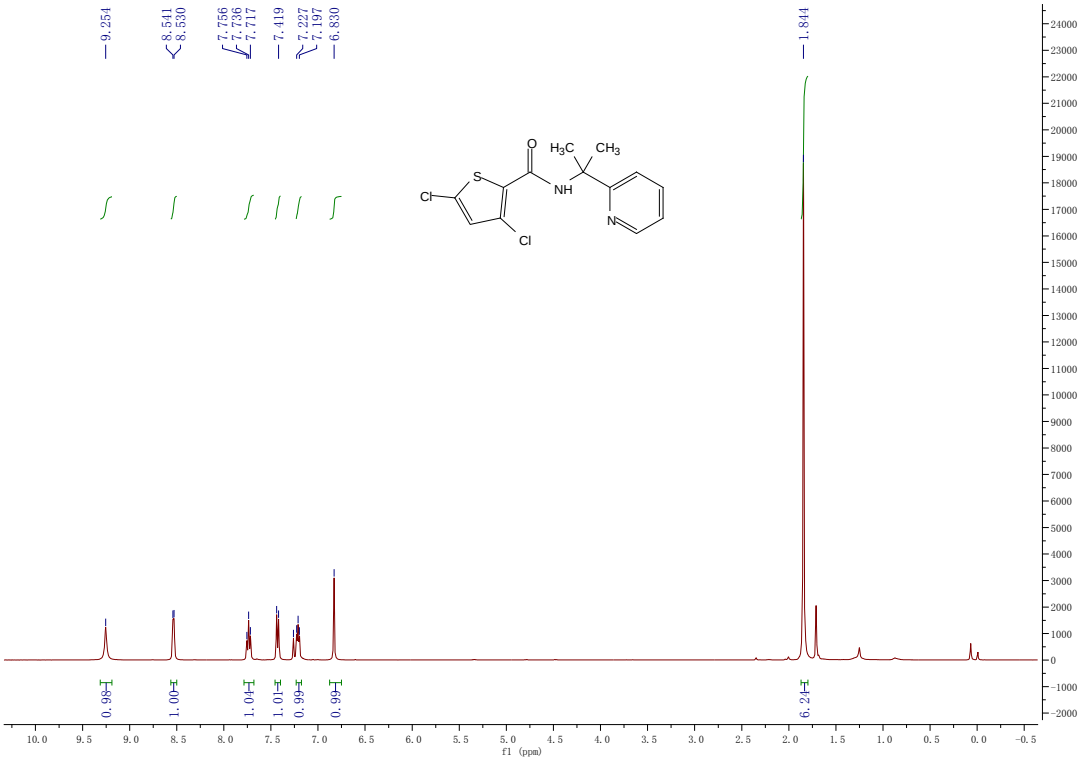
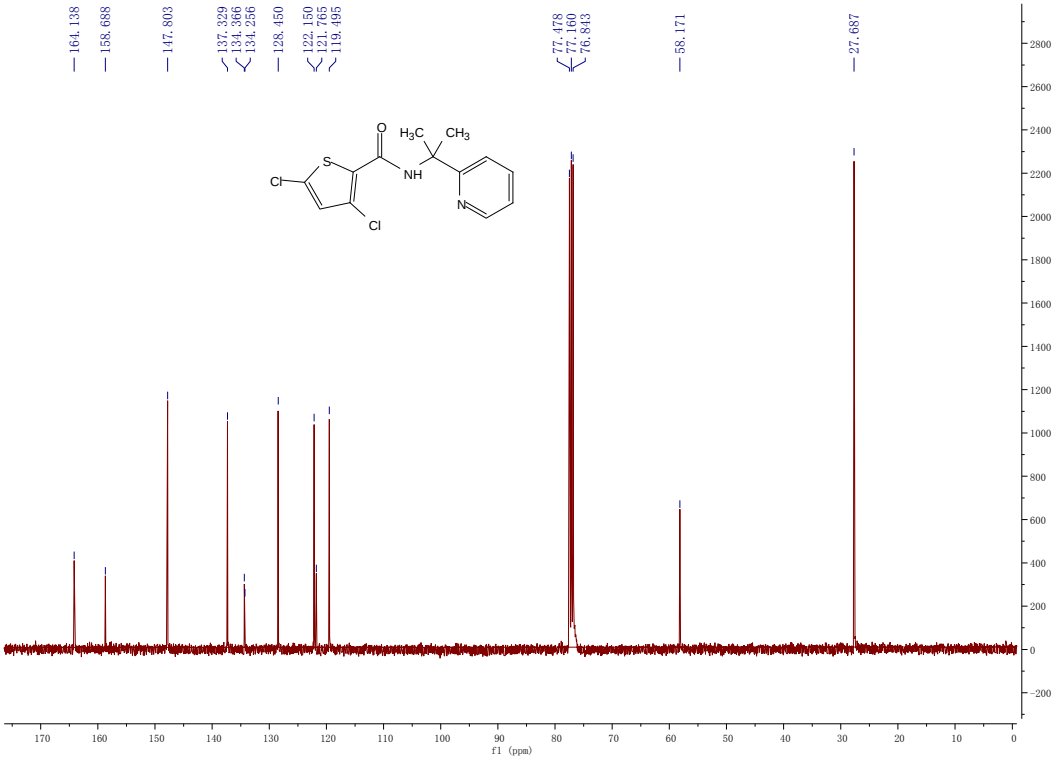
S
N
H
PIP
Cl
Cl

3p


9.254
8.541
8.530
7.756
7.736
7.717
7.419
7.227
7.197
6.830
1.844
0.99
1.00
1.04
1.01
0.99
0.99
6.24
f1 (ppm)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137.329
134.366
134.256
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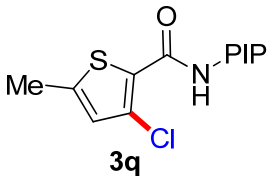
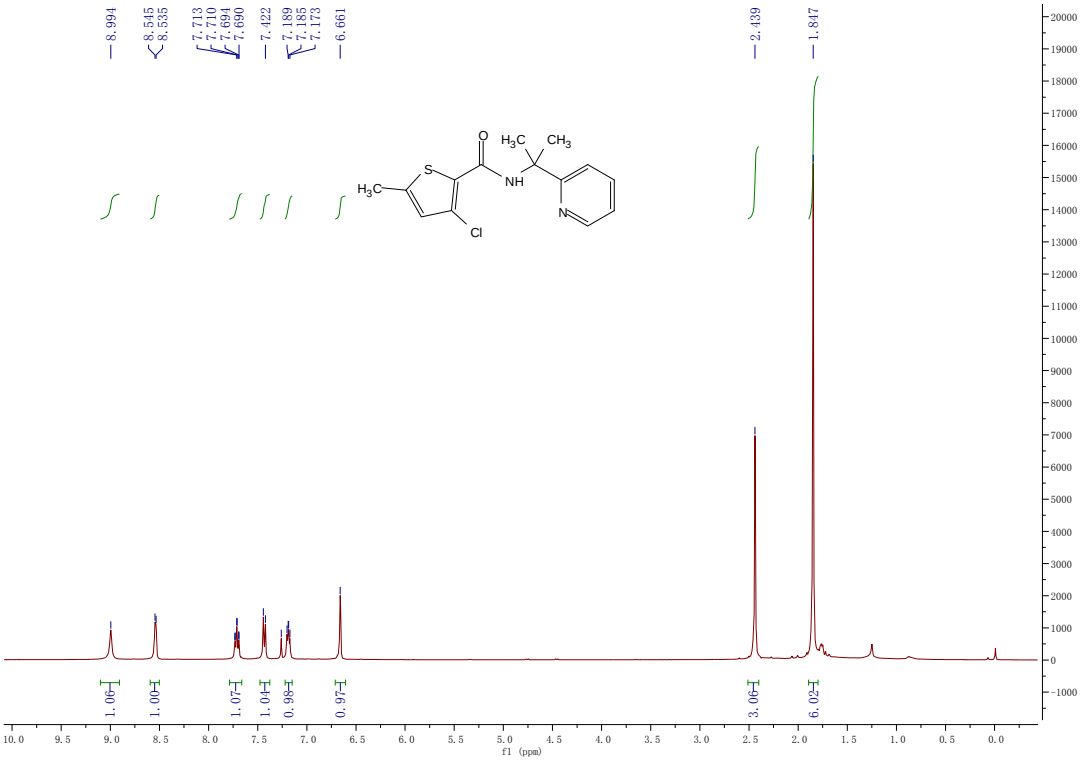
122.150
121.765
119.495
77.478
77.160
76.843
58.171
27.687
f1 (ppm)


O
S
N
PIP
H
Me
Cl

3q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7.710
7.694
7.690
7.422
7.189
7.185
7.173
6.661
2.439
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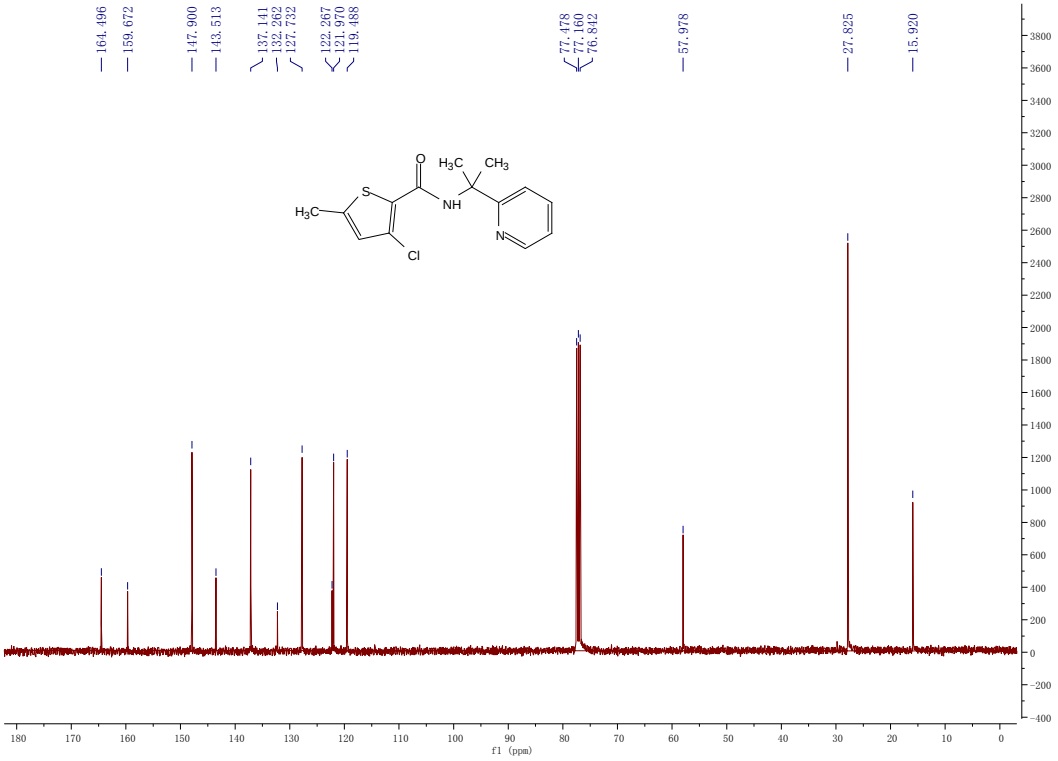
1.06
1.00
1.07
1.04
0.98
0.97
3.06
6.02
f1 (ppm)


164.496
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143.513
137.141
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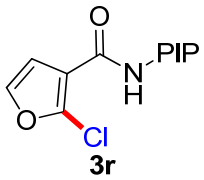
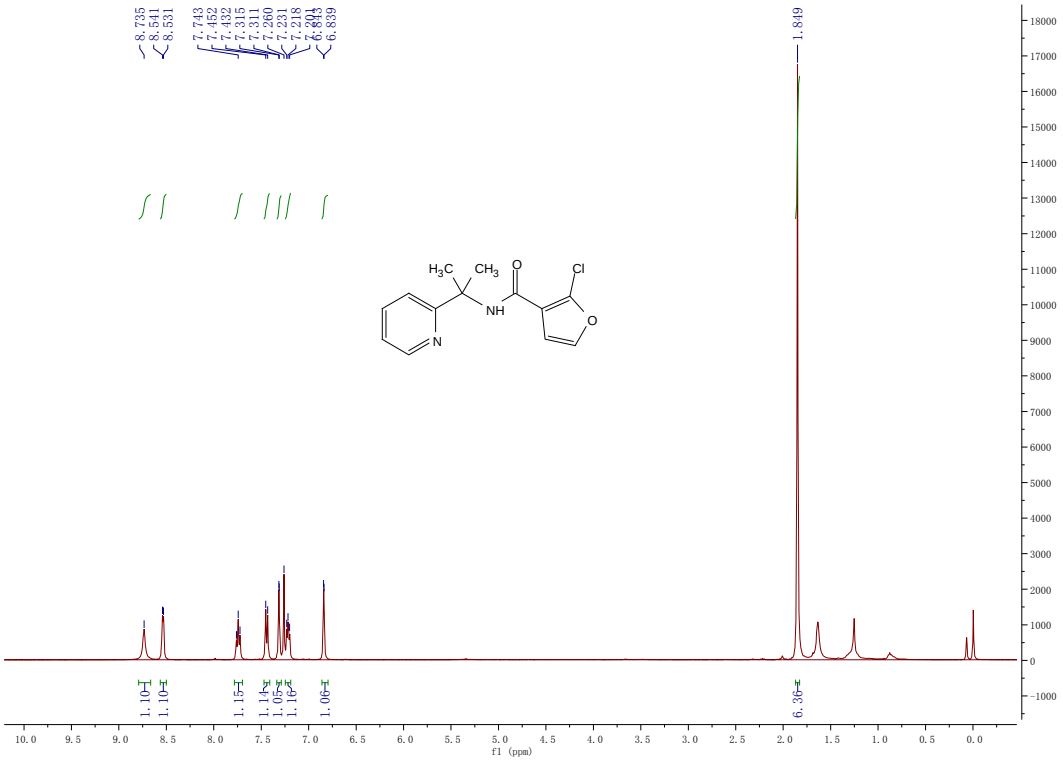
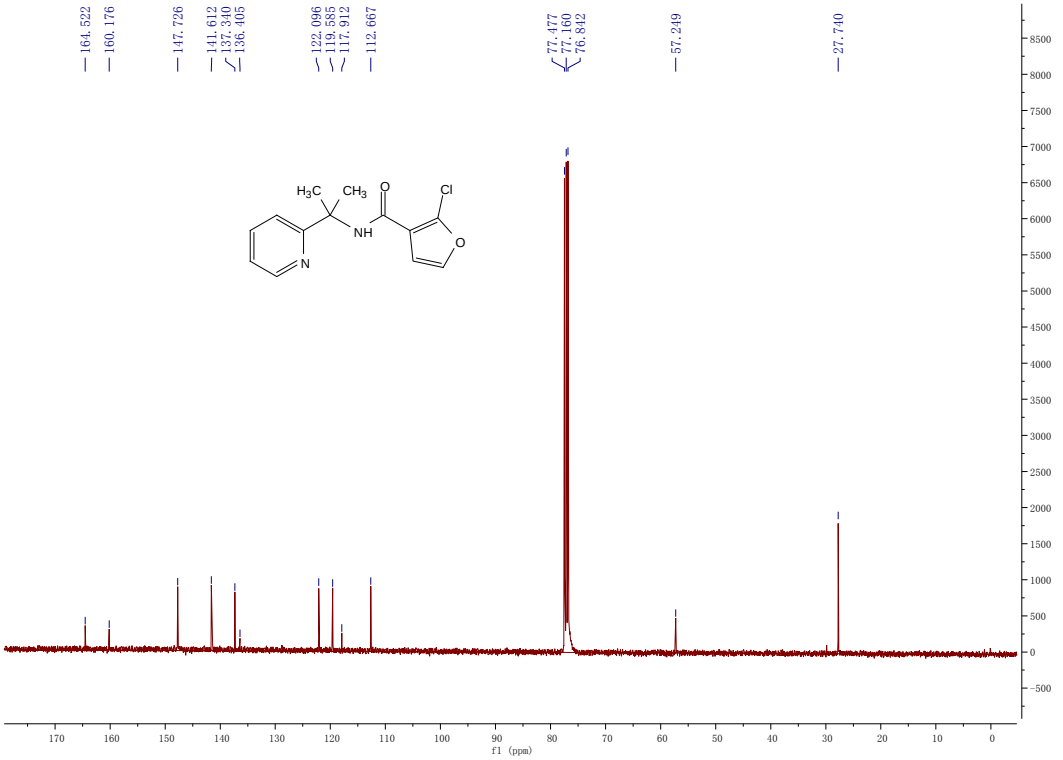
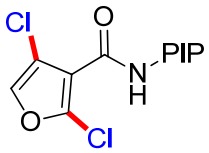
127.732
122.267
121.970
119.488
77.478
77.160
76.842
57.978
27.825
15.920
f1 (ppm)


O
N
PIP
H
O
Cl

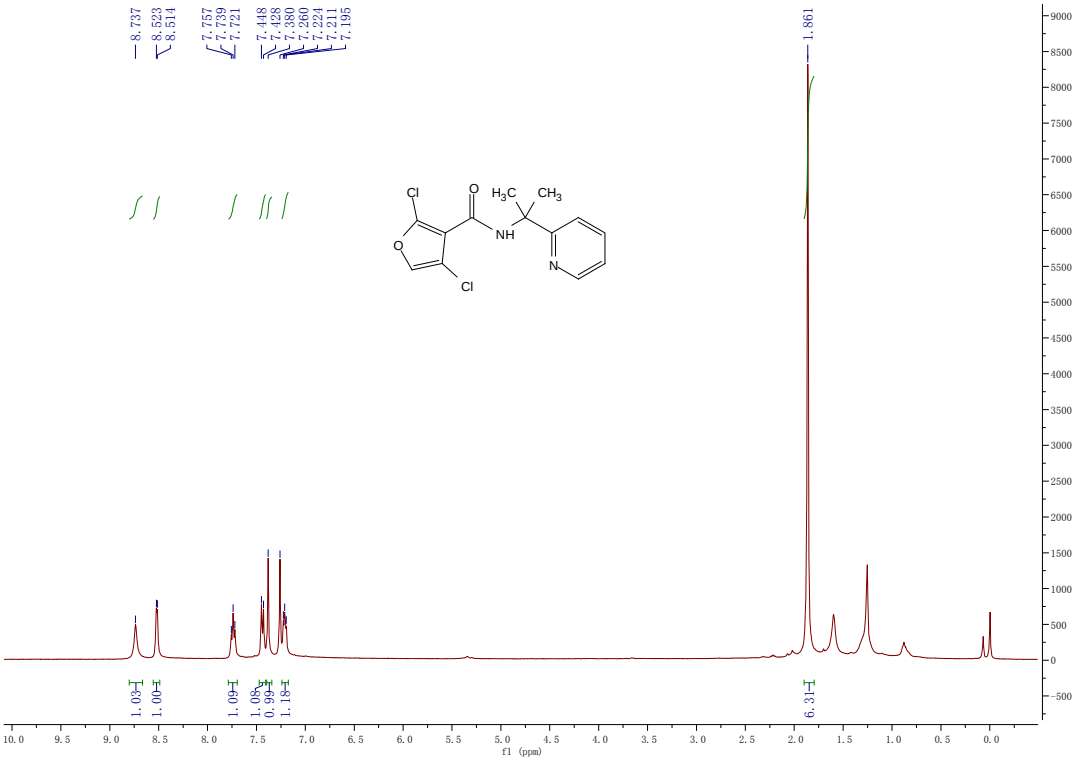
3r

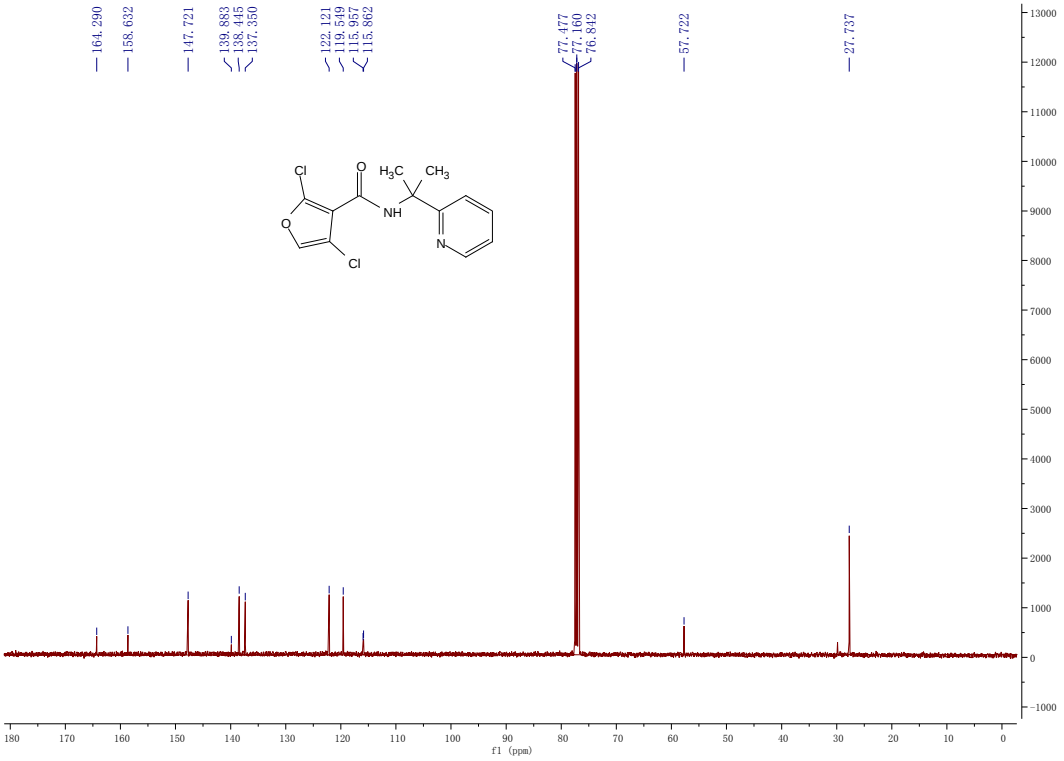

8.735
8.541
8.531
7.743
7.452
7.432
7.315
7.311
7.260
7.231
7.218
7.201
6.843
6.839
1.849
H3C
CH3
O
Cl
NH
N
O
1.10
1.10
1.15
1.14
1.05
1.16
1.06
6.36
f1 (ppm)


164.522
160.176
147.726
141.612
137.340
136.405
122.096
119.585
117.912
112.667
77.477
77.160
76.842
57.249
27.740
H3C
CH3
O
Cl
NH
N
O
f1 (ppm)


Cl
O
N
H
PIP
O
Cl

3r'


8.737
8.523
8.514
7.757
7.739
7.721
7.448
7.428
7.380
7.260
7.224
7.211
7.195
1.861
1.03
1.00
1.09
1.08
0.99
1.18
6.31
f1 (ppm)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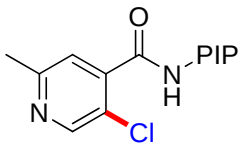
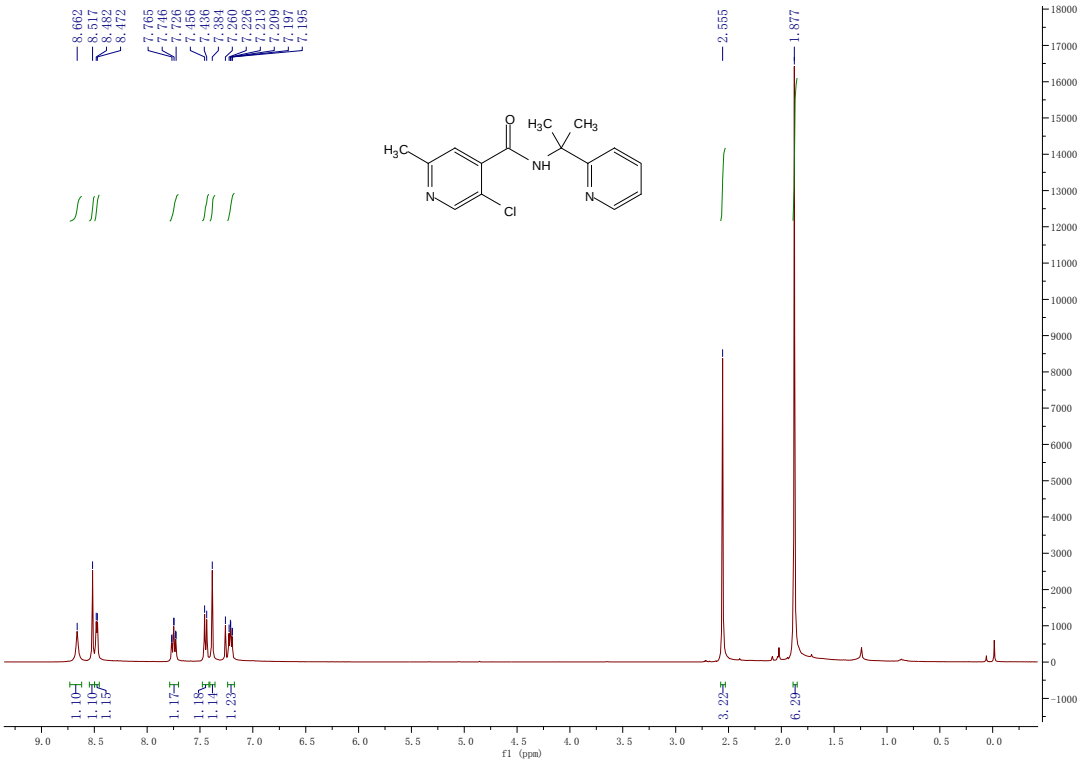
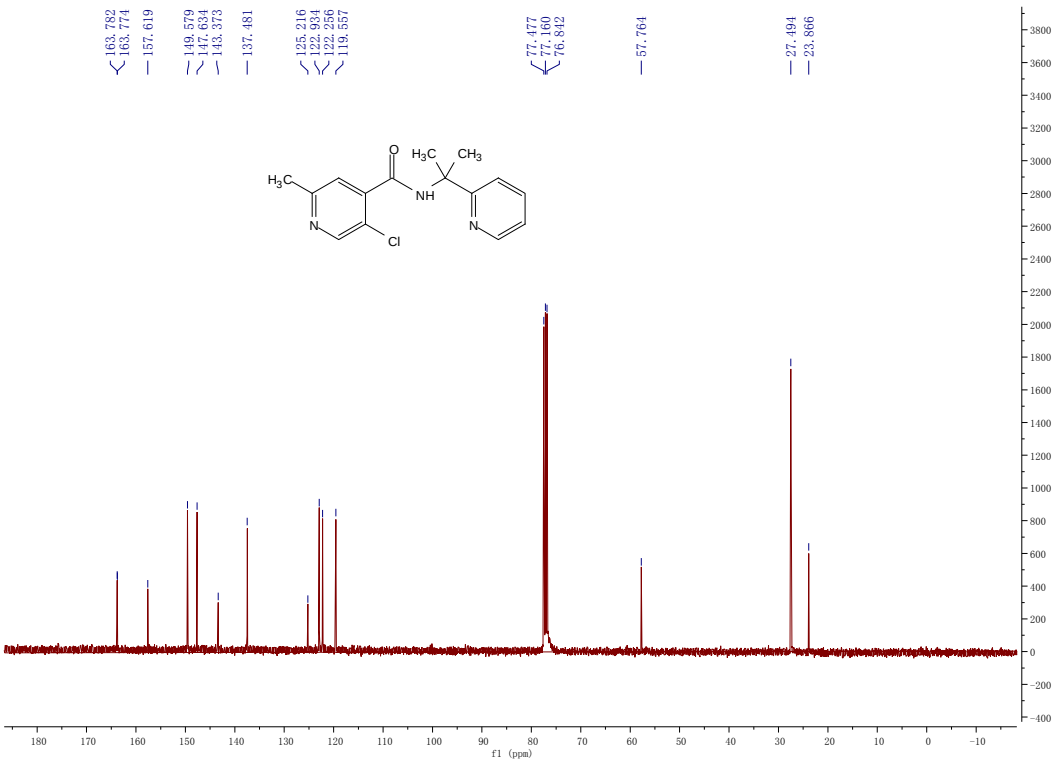
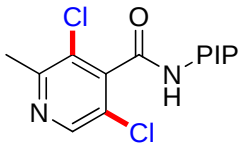
158.632
147.721
139.883
138.445
137.350
122.121
119.549
115.957
115.862
77.477
77.160
76.842
57.722
27.737
f1 (ppm)


O
N
H
PIP
N
Cl

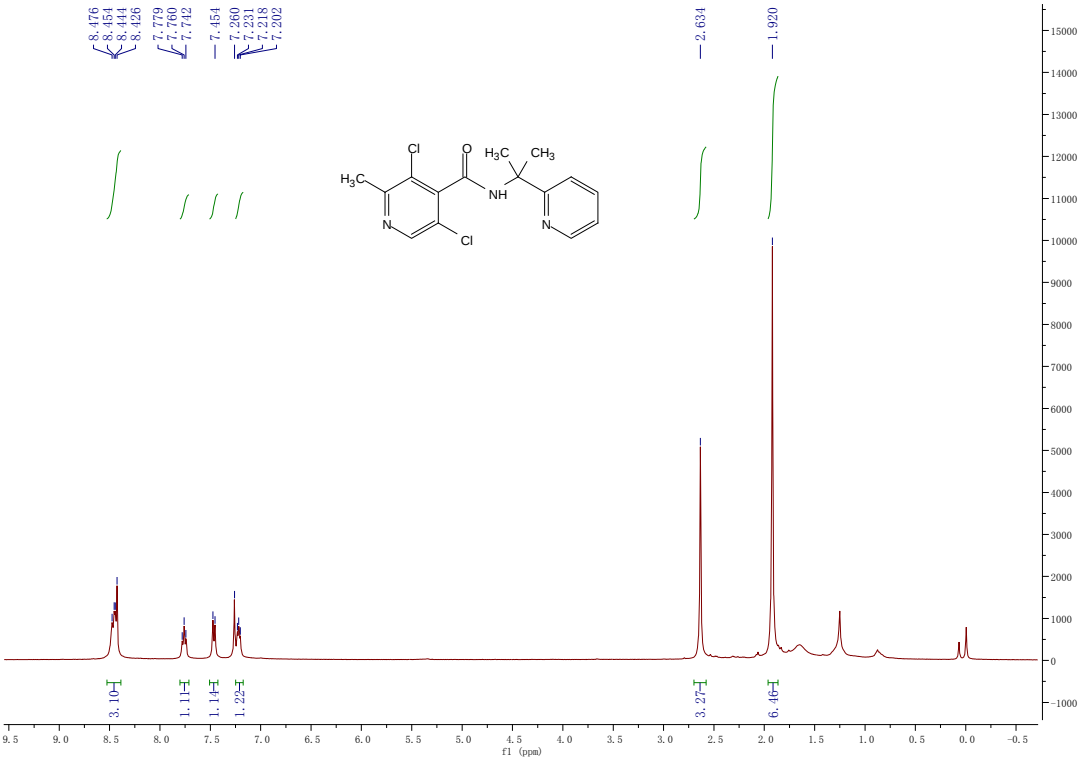
3s

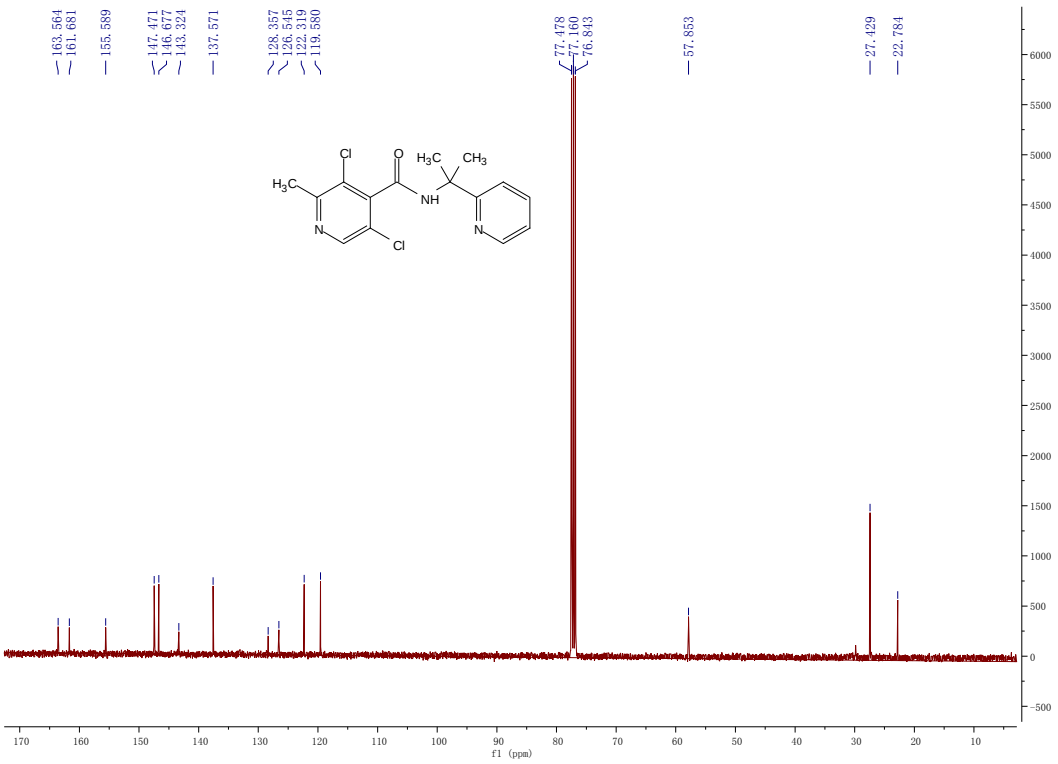

8.662
8.517
8.482
8.472
7.765
7.746
7.726
7.456
7.436
7.384
7.260
7.226
7.213
7.209
7.197
7.195
2.555
1.877
1.10
1.10
1.15
1.17
1.18
1.14
1.23
3.22
6.29
f1 (ppm)

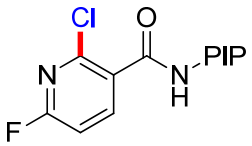

163.782
163.774
157.619
149.579
147.634
143.373
137.481
125.216
122.994
122.256
119.557
77.477
77.160
76.842
57.764
27.494
23.866
f1 (ppm)


Cl
O
PIP
N
H
N
Cl

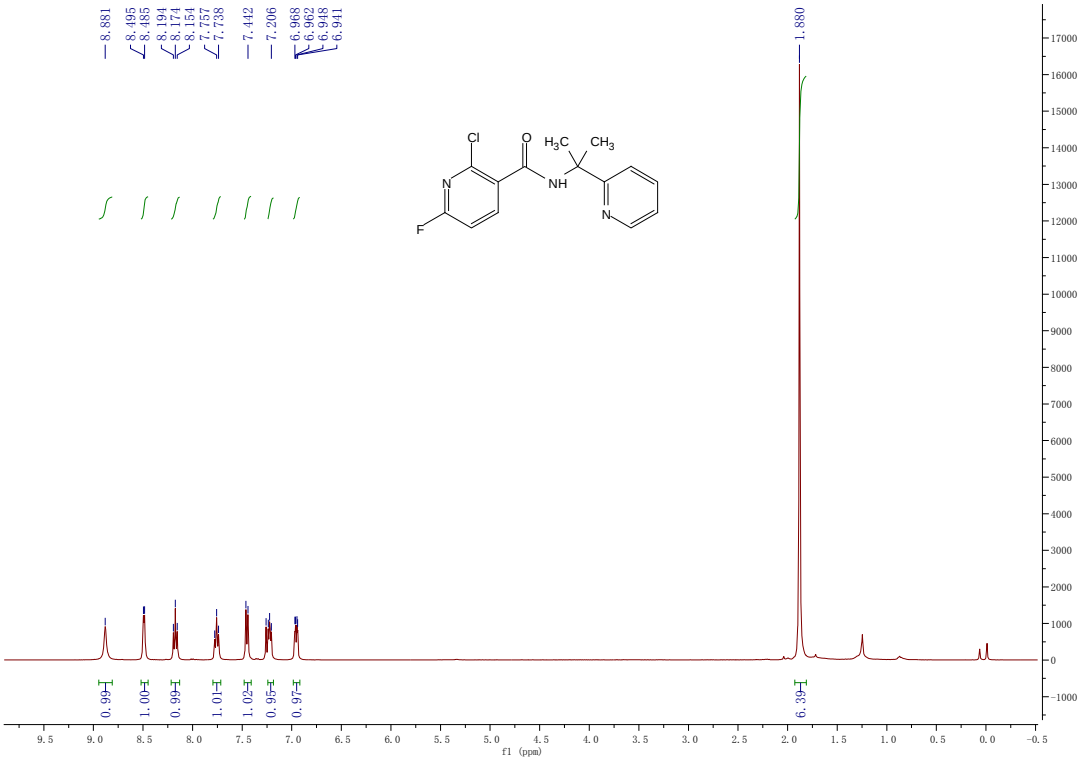
3s'

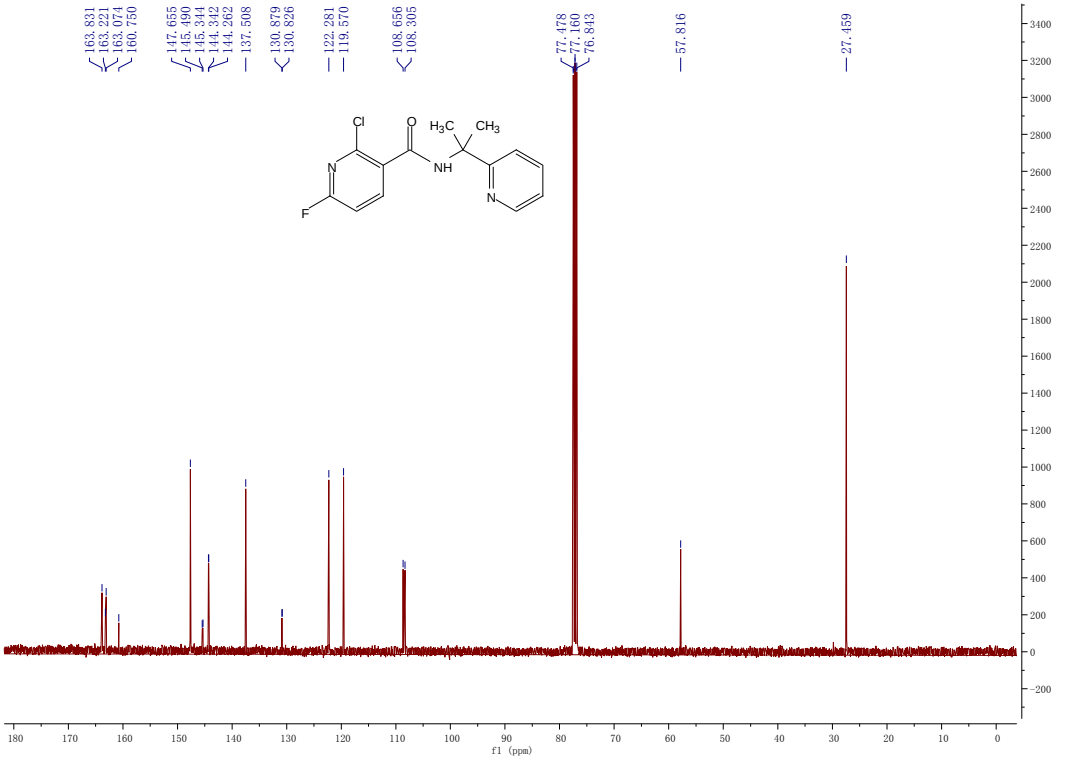

8.476
8.454
8.444
8.426
7.779
7.760
7.742
7.454
7.260
7.231
7.218
7.202
2.634
1.920
3.10
1.11
1.14
1.22
3.27
6.46
f1 (ppm)

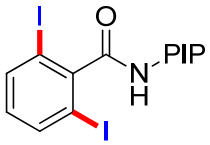

163.564
161.681
155.589
147.471
146.677
143.324
137.571
128.357
126.545
122.319
119.580
77.478
77.160
76.843
57.853
27.429
22.784
f1 (ppm)


Cl
O
N
PIP
N
H
F

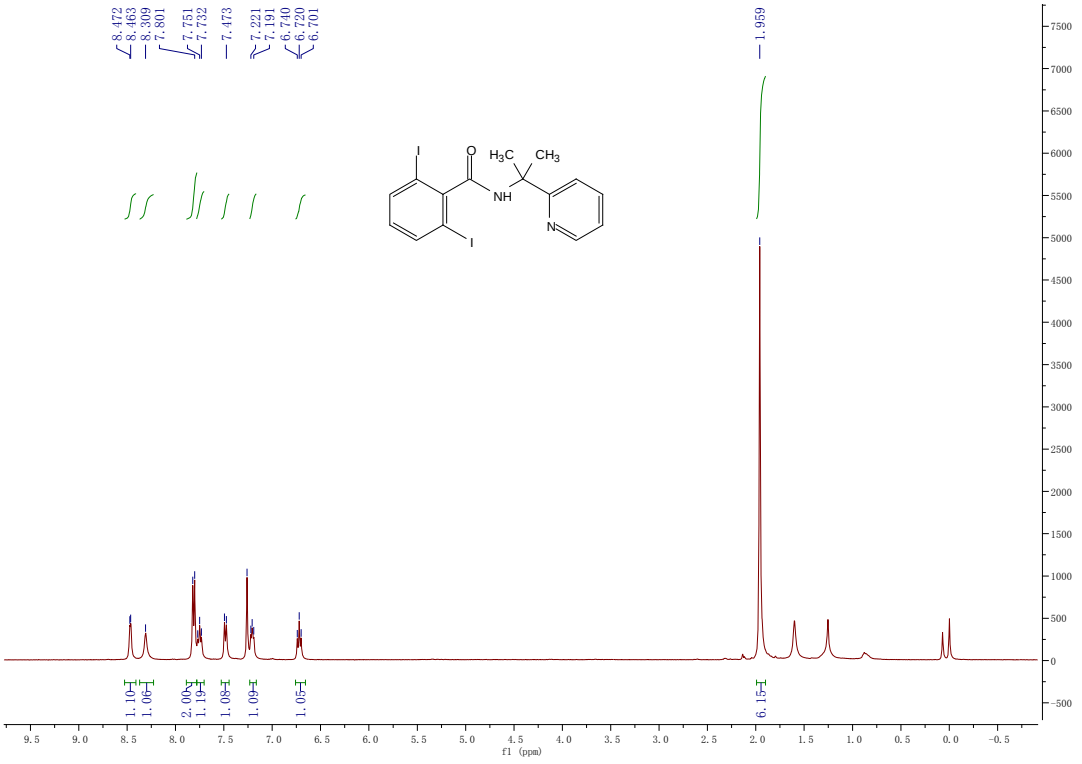
3t

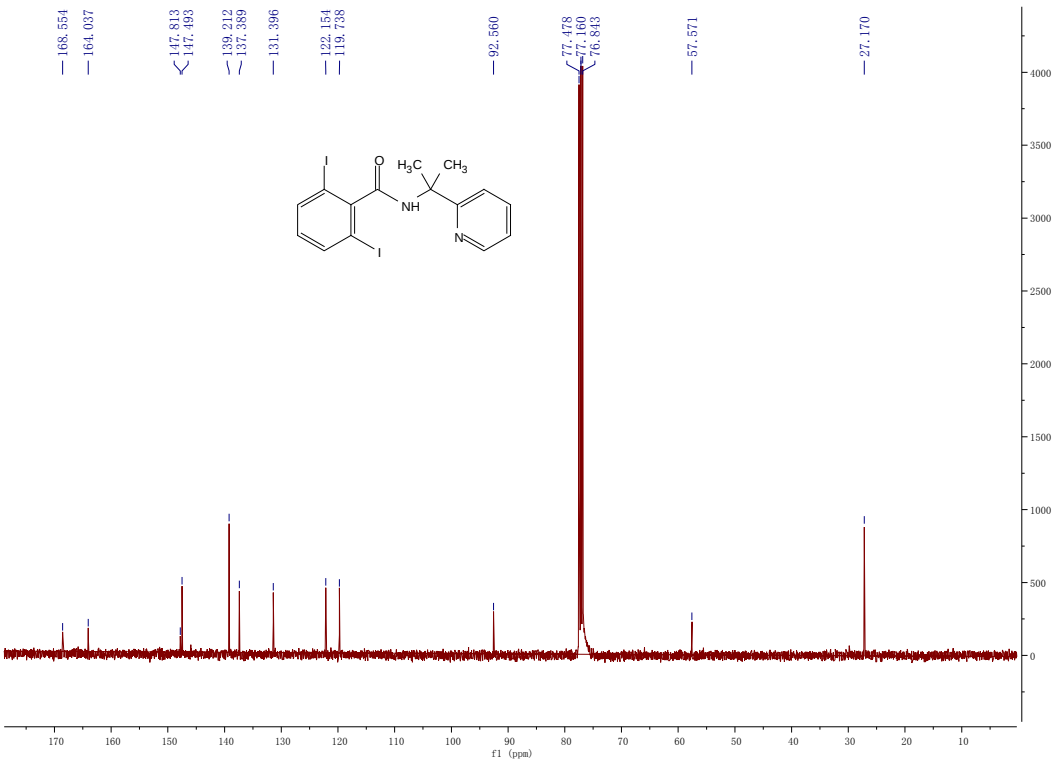

8.881
8.495
8.485
8.194
8.174
8.154
7.757
7.738
7.442
7.206
6.968
6.962
6.948
6.941
1.880
0.99
1.00
0.99
1.01
1.02
0.95
0.97
6.39
f1 (ppm)

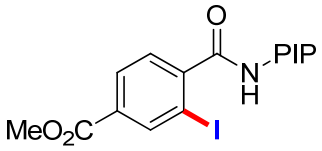

163.831
163.221
163.074
160.750
147.655
145.490
145.344
144.342
144.262
137.508
130.879
130.826
122.281
119.570
108.656
108.305
77.478
77.160
76.843
57.816
27.459
f1 (ppm)


I
O
N
H
PIP
I

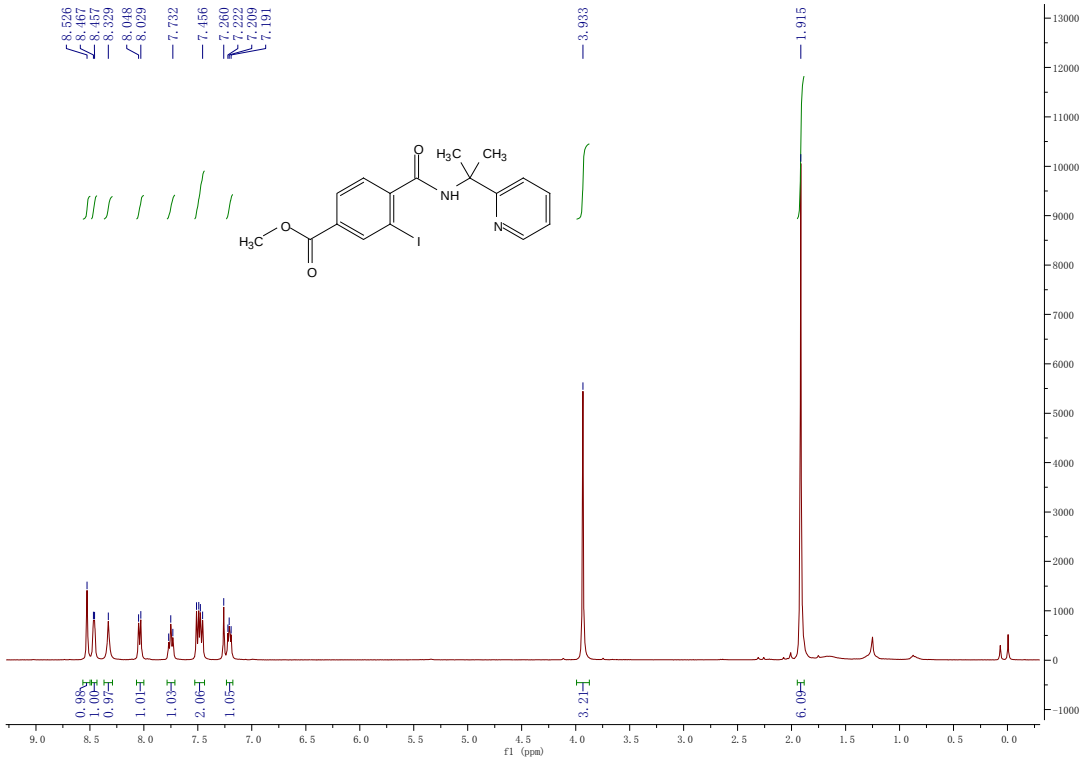
4a'

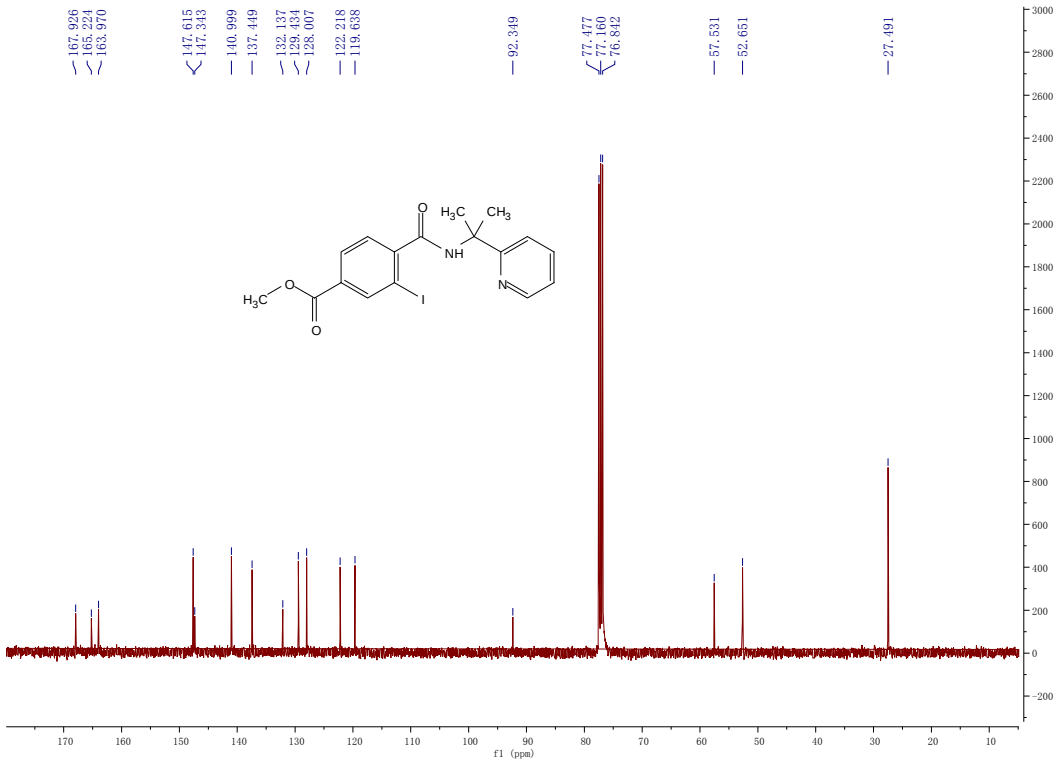

8.472
8.463
8.309
7.801
7.751
7.732
7.473
7.221
7.191
6.740
6.720
6.701
1.959
1.10
1.06
2.00
1.19
1.08
1.09
1.05
6.15
f1 (ppm)

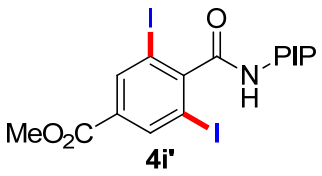

168.554
164.037
147.813
147.493
139.212
137.389
131.396
122.154
119.738
92.560
77.478
77.160
76.843
57.571
27.170
f1 (ppm)


O
N
PIP
H
MeO2C
I

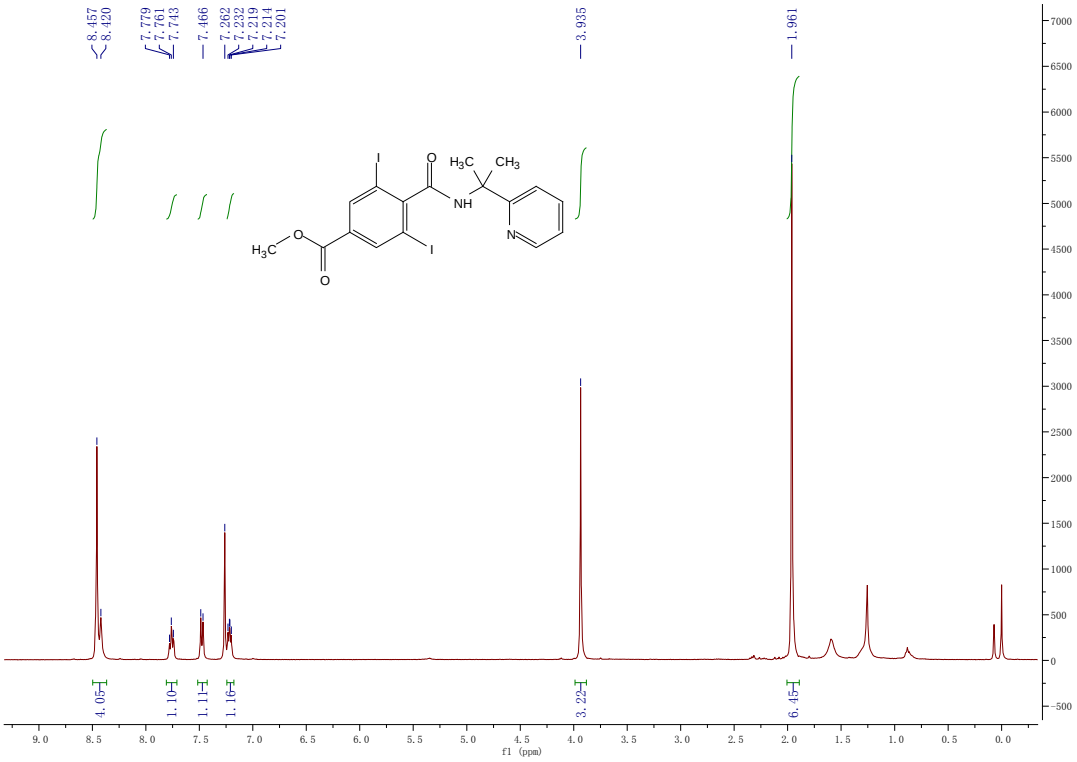
4i


8.526
8.467
8.457
8.329
8.048
8.029
7.732
7.456
7.260
7.222
7.209
7.191
3.933
1.915
H3C
CH3
NH
N
O
I
0.98
1.00
0.97
1.01
1.03
2.06
1.05
3.21
6.09
f1 (ppm)


167.926
165.224
163.970
147.615
147.343
140.999
137.449
132.137
129.434
128.007
122.218
119.638
92.349
77.477
77.160
76.842
57.531
52.651
27.491
H3C
CH3
NH
N
O
I
f1 (ppm)


I
O
N
H
PIP
MeO2C
I

4i'


8.457
8.420
7.779
7.761
7.743
7.466
7.262
7.232
7.219
7.214
7.201
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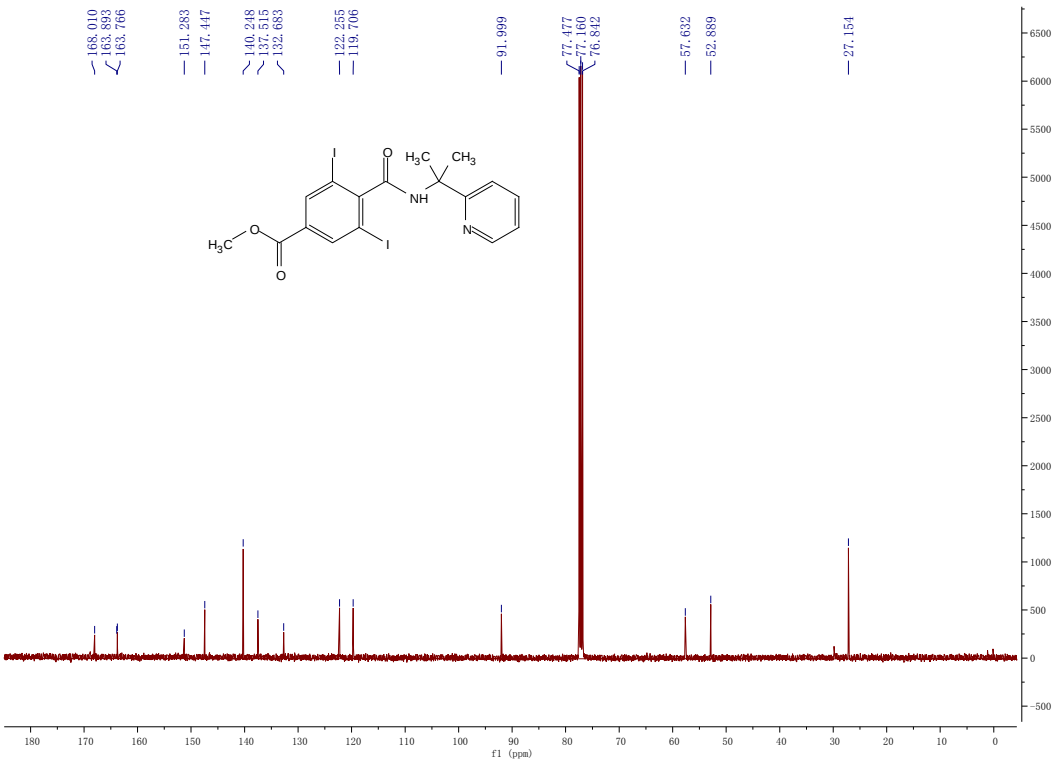
1.961
4.05
1.10
1.11
1.16
3.22
6.45
f1 (ppm)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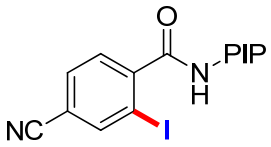
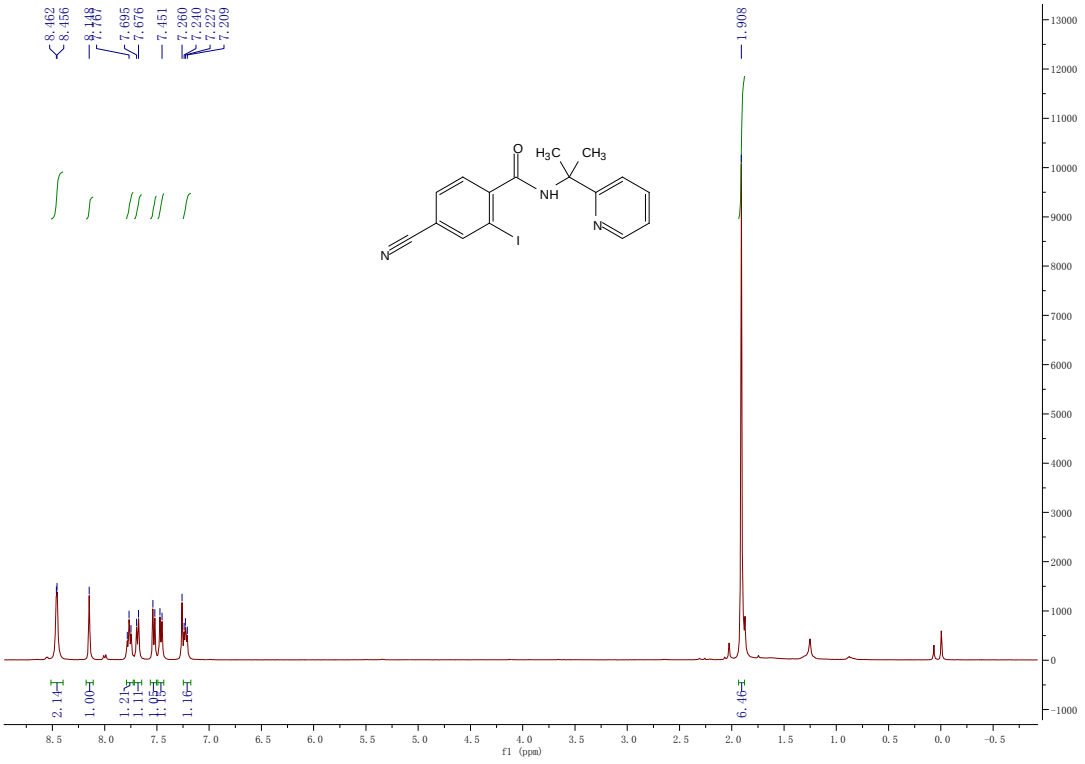
163.893
163.766
151.283
147.447
140.248
137.515
132.683
122.255
119.706
91.999
77.477
77.160
76.842
57.632
52.889
27.154
f1 (ppm)


O
N
PIP
H
NC
I

4k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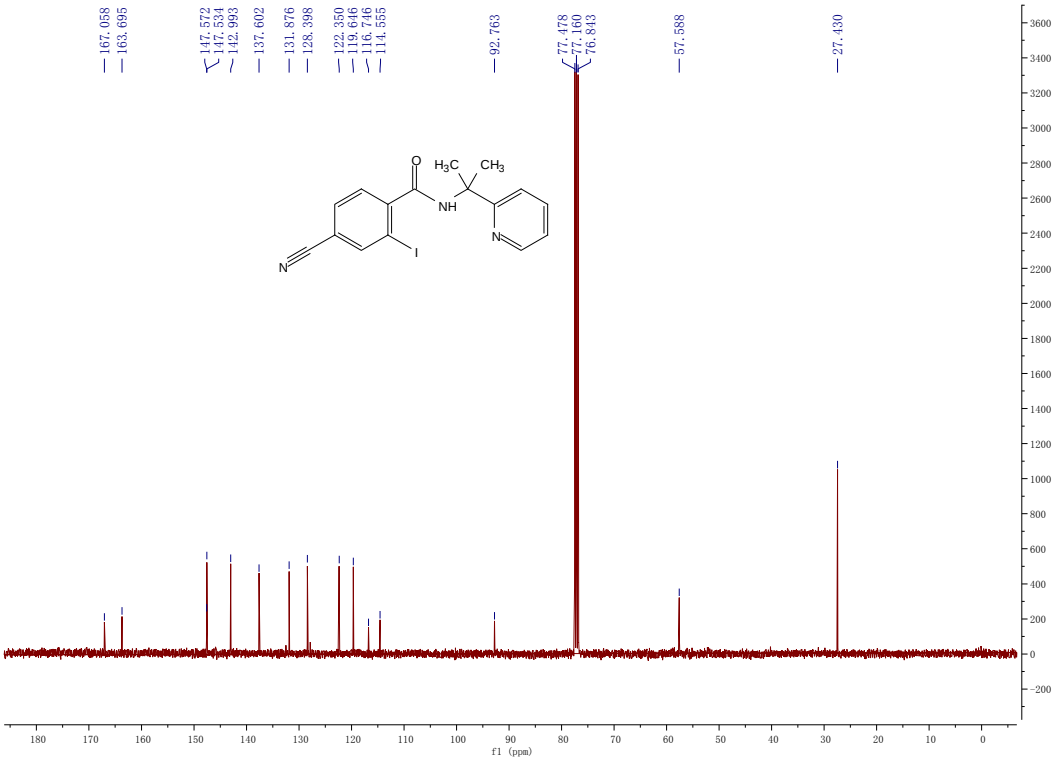
8.456
8.148
8.147
7.695
7.676
7.451
7.260
7.240
7.227
7.209
1.908
O
H3C
CH3
NH
N
N
I
2.14
1.00
1.21
1.11
1.05
1.19
1.16
6.46
f1 (ppm)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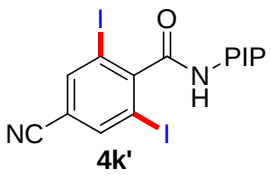
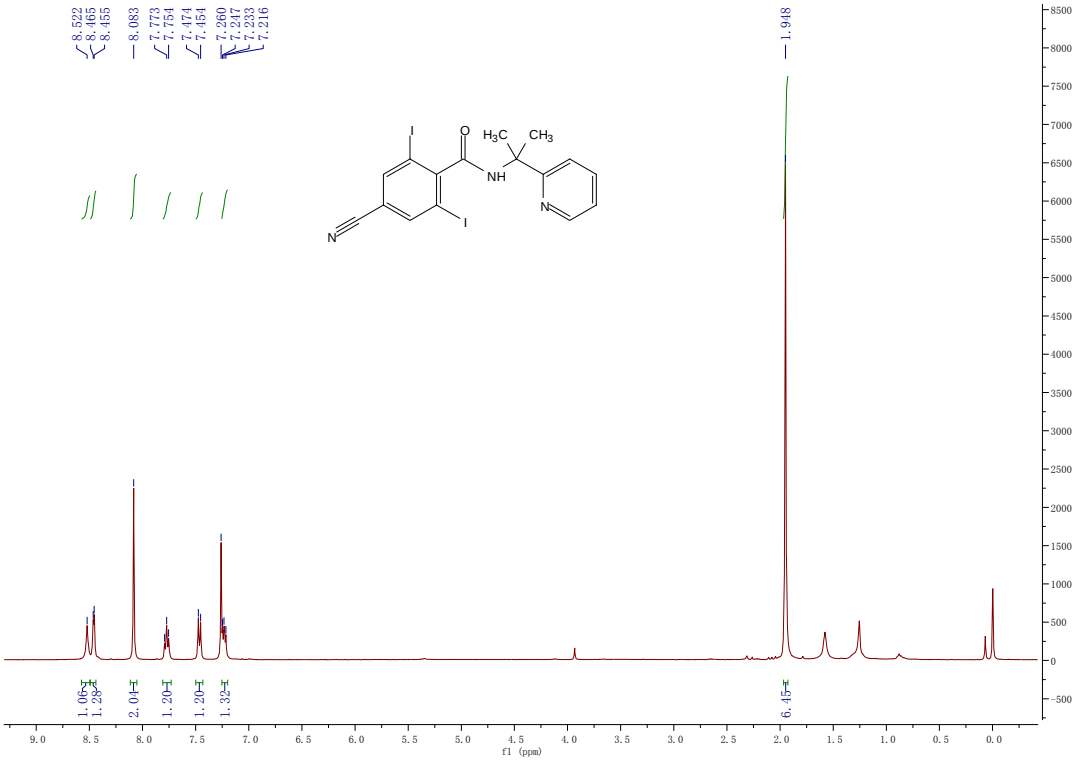
147.572
147.534
142.993
137.602
131.876
128.398
122.350
119.646
116.746
114.555
92.763
77.478
77.160
76.843
57.588
27.430
O
H3C
CH3
NH
N
N
I
f1 (ppm)


I
O
N
H
PIP
NC
I

4k'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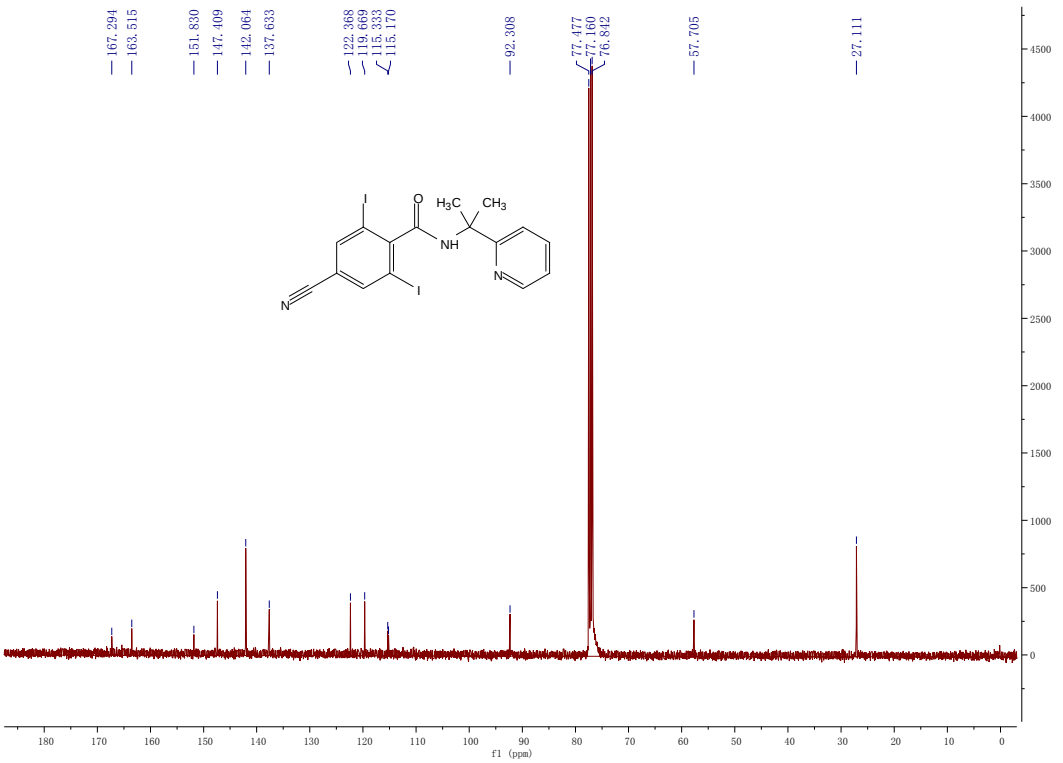
8.465
8.455
8.083
7.773
7.754
7.474
7.454
7.260
7.247
7.233
7.216
1.948
1.06
1.28
2.04
1.20
1.20
1.32
6.45
f1 (ppm)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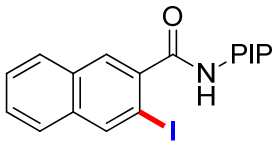
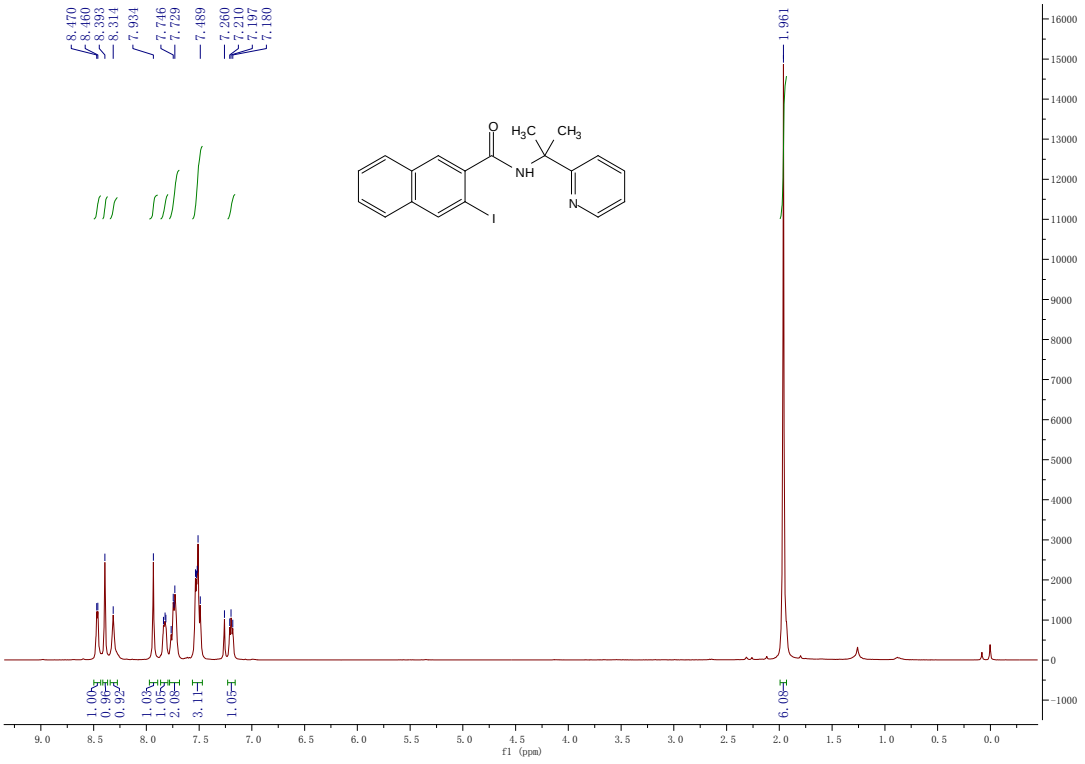
163.515
151.830
147.409
142.064
137.633
122.368
119.669
115.333
115.170
92.308
77.477
77.160
76.842
57.705
27.111
f1 (ppm)


O
N
H
PIP
I

4o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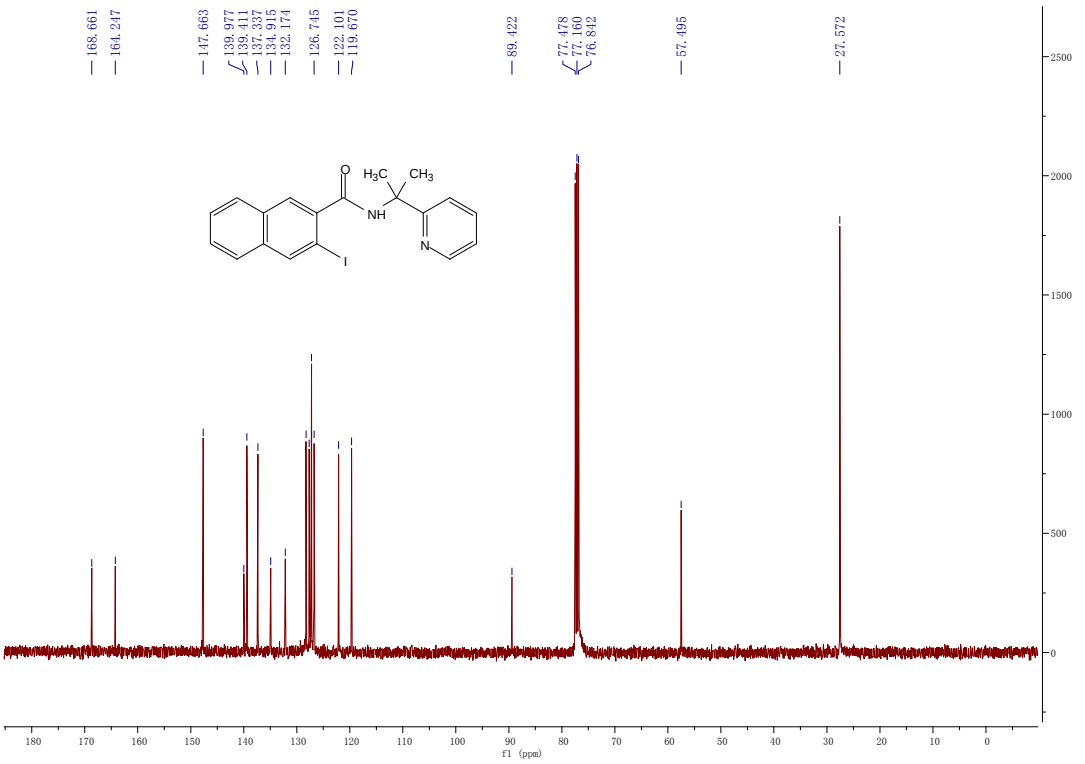
8.460
8.393
8.314
7.934
7.746
7.729
7.489
7.260
7.210
7.197
7.180
1.961
O
H3C
CH3
NH
N
I
1.00
0.96
0.92
1.03
1.05
2.08
3.11
1.05
6.08
f1 (ppm)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164.247
147.663
139.977
139.411
137.337
134.915
132.174
126.745
122.101
119.670
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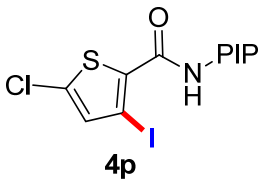
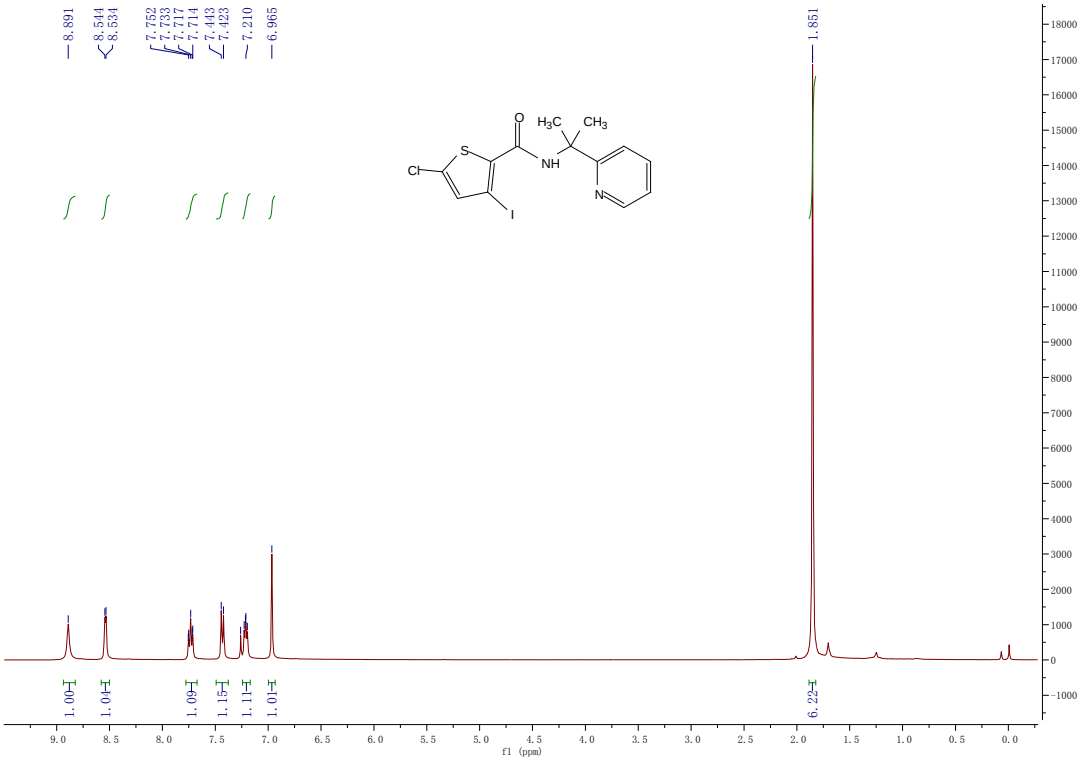
77.478
77.160
76.842
57.495
27.572
O
H3C
CH3
NH
N
I
f1 (ppm)


O
S
N
H
PIP
Cl
I

4p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7.752
7.733
7.717
7.714
7.443
7.423
7.210
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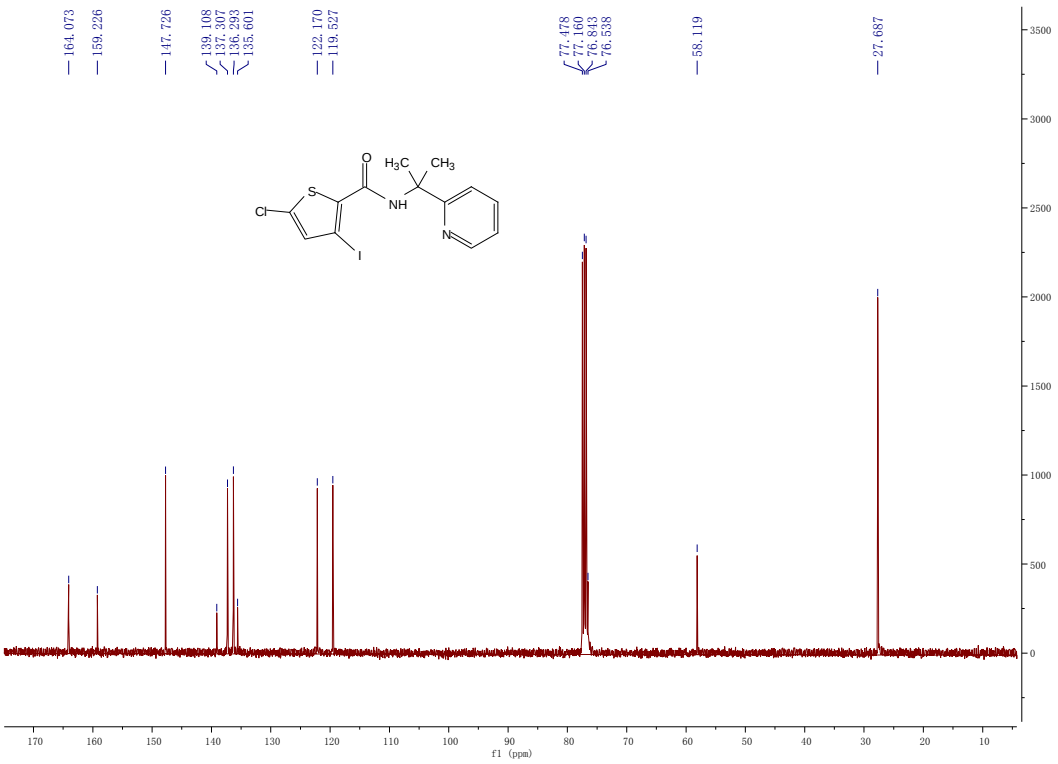
1.15
1.11
1.01
6.22
f1 (ppm)


164.073
159.226
147.726
139.108
137.307
136.293
135.601
122.170
119.527
77.478
77.160
76.843
76.538
58.119
27.687
f1 (ppm)