

Supporting Information

Ruthenium-Catalysed Direct C–H Amidation of 4-Aryl-pyrrolo[2,3-*d*]pyrimidines with Acyl/Phosphoryl Azides

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1. General Information

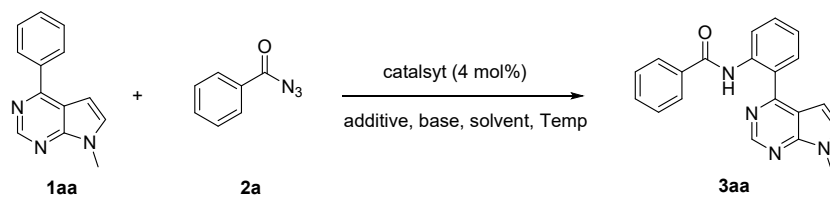
All reagents were purchased from commercial suppliers and used without further purification. The starting material 4-Chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine is commercially available. A series of substrates **1** were prepared according to the literature procedure¹⁻². NMR spectra were obtained on a Bruker ADNANCE III 400 and 500MHz with TMS as the internal standard using CDCl₃ as the solvent. Chemical shifts are given in parts per million (ppm) and coupling constants in Hz. In the ¹H and ¹³C spectra, chemical shifts are reported in ppm relative to CDCl₃ with 7.28 for ¹H and 77.04 for ¹³C. The following abbreviations were used for ¹H NMR to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), m (multiplet). Melting points were measured on a BUCHI B-540 and uncorrected. Analytical thin-layer chromatography was carried out using commercial aluminum sheets precoated (0.2 mm layer thickness) with silica gel GF254, and visualization was effected with short wavelength UV light (254 nm). Product purification by flash chromatography was performed using 200-400 mesh silica gel. HRMS (ESI) was recorded using Agilent 6520 accurate-Mass Q-TOF LC/MS system.

Reference:

1. M. Klečka, R. Pohl, B. Klepetářov, M. Hocek, Direct C–H Borylation and C–H Arylation of Pyrrolo[2,3-*d*]pyrimidines: Synthesis of 6,8-Disubstituted 7-Deazapurines, *Org. Biomol. Chem.*, 2009, **7**, 866-868.
2. J. Zhou, Z. Mao, H. Pan, X. Zhang, Pd-Catalyzed Highly Selective and Direct *Ortho* C–H Arylation of Pyrrolo[2,3-*d*]pyrimidine Derivatives, *Org. Chem. Front.*, 2020, **7**, 324-328.

2. Condition optimization

Table S1. Condition optimization^a



Entry	Catalyst	Additive(mol%)	Base(mol%)	Temp. (°C)	Solvent	Yield (%) ^b
1	[RuCl ₂ (<i>p</i> -cymene)] ₂	-	NaOAc (20)	85	DCE ^c	NR ^d
2	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgBF ₄ (16)	NaOAc(20)	85	DCE	NR
3	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgOAc(16)	NaOAc(20)	85	DCE	NR
4	[RuCl ₂ (<i>p</i> -cymene)] ₂	Ag ₂ CO ₃ (16)	NaOAc(20)	85	DCE	61
5	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgSbF ₆ (16)	NaOAc(20)	85	DCE	36
6	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgOTf(16)	NaOAc(20)	85	DCE	43
7	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	88
8	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	KOAc(20)	85	DCE	87
9	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	K ₂ CO ₃ (20)	85	DCE	50
10	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaHCO ₃ (20)	85	DCE	25
11	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	-	85	DCE	20
12	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	r.t.	DCE	NR
13	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	50	DCE	76
14	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	110	DCE	37
15	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	85	THF	trace
16	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	85	1,4-dioxane	trace
17	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	85	MeCN	NR
18	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	85	Toluene	73
19	PdCl ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
20	Pd(PPh ₃) ₄	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
21	Pd(MeCN) ₂ Cl ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
22	Pd(OAc) ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
23	Cu(OAc) ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
24	Co(OAc) ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
25	Cp*Co(CO)I ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
26	-	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
27	[IrCp*Cl ₂] ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	71
28	[RuI ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	62
29	[(C ₆ H ₅) ₃ P] ₃ RuCl ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
30	[Ru(COD)Cl ₂] _n	AgNTf ₂ (16)	NaOAc(20)	85	DCE	NR
31 ^e	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(20)	85	DCE	69

Entry	Catalyst	Additive	Base	Temp. (°C)	Solvent	Yield (%) ^b
32	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (4)	NaOAc(20)	85	DCE	17
33	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (8)	NaOAc(20)	85	DCE	35
34	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (12)	NaOAc(20)	85	DCE	59
35	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (20)	NaOAc(20)	85	DCE	75
36	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(4)	85	DCE	32
37	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(8)	85	DCE	56
38	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(12)	85	DCE	69
39	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(16)	85	DCE	82
40	[RuCl ₂ (<i>p</i> -cymene)] ₂	AgNTf ₂ (16)	NaOAc(24)	85	DCE	86

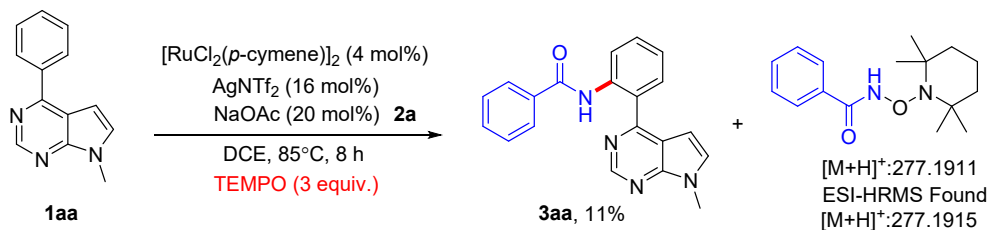
^a General conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), [RuCl₂(*p*-cymene)]₂ (4 mol%), additive (x mol%), base (x mol%) in solvent (3 mL), under air, 8 h. ^b Isolated yield. ^c DCE:1,2-dichloroethane. ^d NR: no reaction. ^e **2a** (0.30 mmol).

3. General Procedure

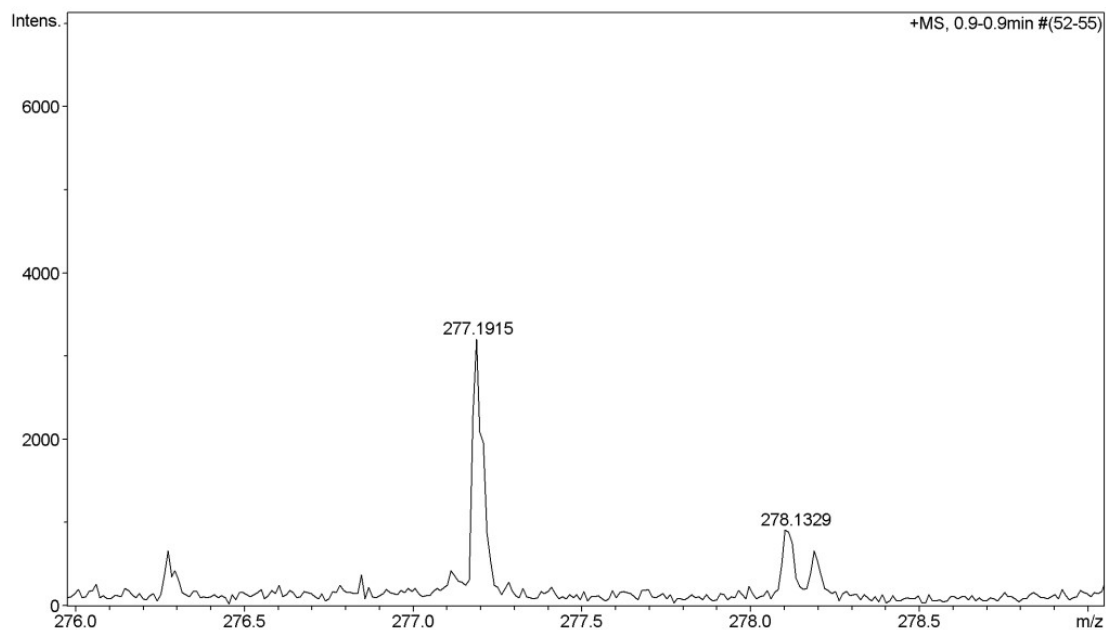
3.1 General Procedures for the synthesis of 3aa-3o: A 15 mL pressure vessel equipped with a magnetic stirrer was charged with **1** (1.0 eq.), **2a** (2.0 eq.), [RuCl₂(*p*-cymene)]₂ (4 mol%), AgNTf₂ (16 mol%), NaOAc (20 mol%) and DCE (3.0 mL) as solvent. The reaction mixture was then stirred at 85 °C in oil bath. After completion of the reaction, it was then cooled to room temperature. The solvent was then removed in vacuo and the residue was purified by column chromatography on silica gel to provide the desired product **3**.

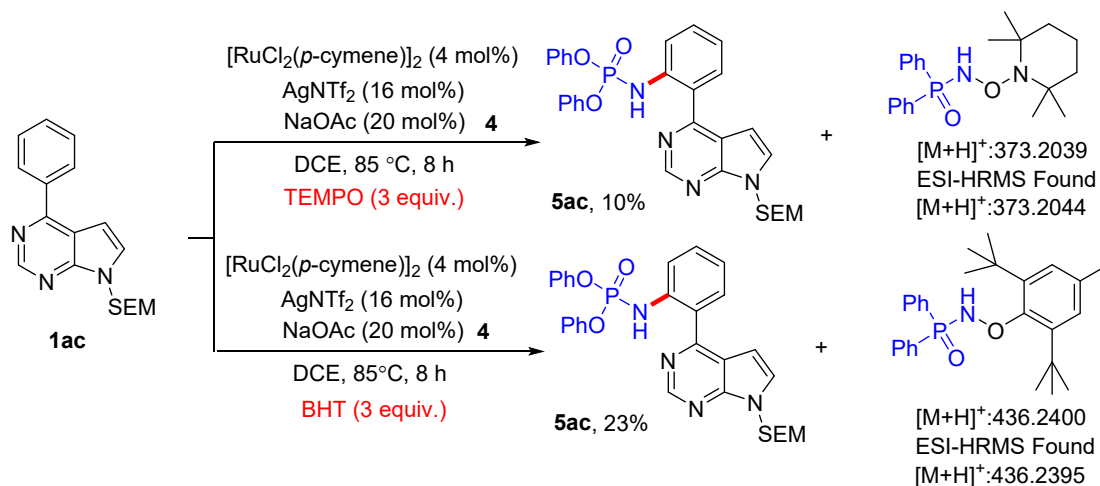
3.2 General Procedures for the synthesis of 5aa-5bd: A 15 mL pressure vessel equipped with a magnetic stirrer was charged with starting material (1.0 eq.), **4** (2.0 eq.), [RuCl₂(*p*-cymene)]₂ (4 mol%), AgNTf₂ (16 mol%), NaOAc (20 mol%) and DCE (3.0 mL) as solvent. After the reaction mixture was stirred at 85 °C in oil bath. After completion of the reaction, it was then cooled to room temperature. The solvent was then removed in vacuo and the residue was purified by column chromatography on silica gel to provide the desired product **5**.

4. Mechanism studies

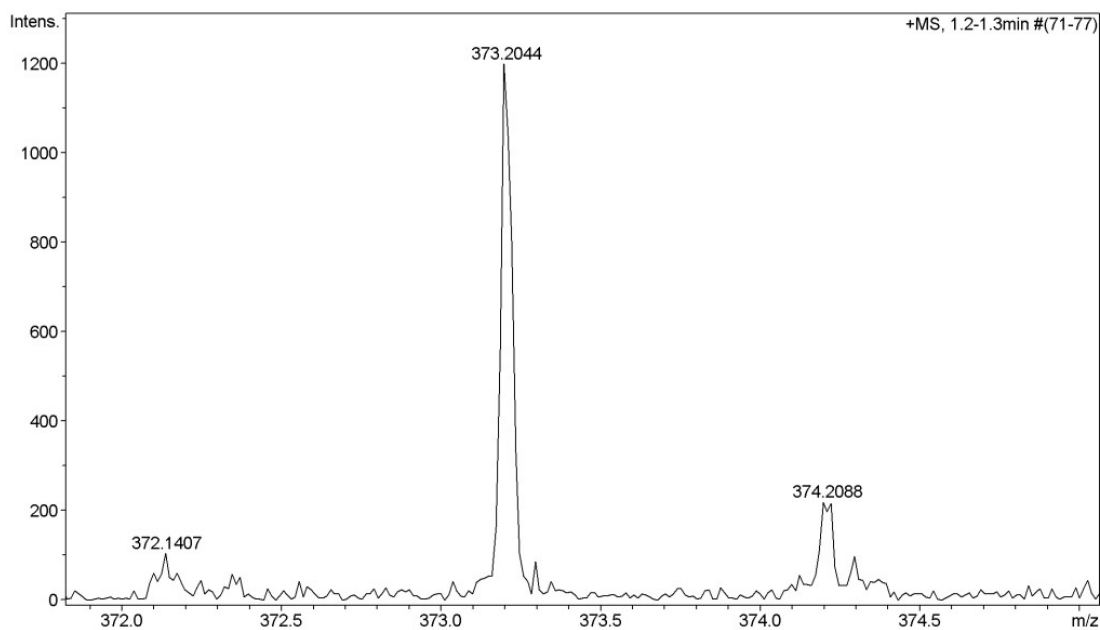


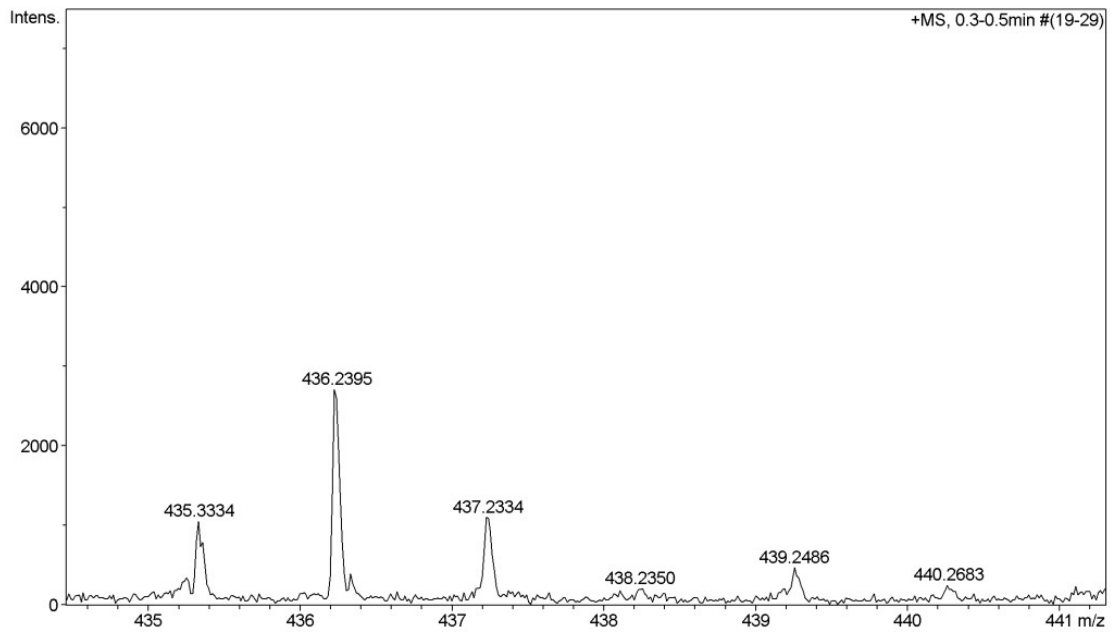
To 15 mL pressure vessel equipped with a magnetic stirrer was charged with **1aa** (0.2 mmol), **2a** (0.4 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (5.0 mg, 4 mol%), AgNTf_2 (12 mg, 16 mol%), NaOAc (3 mg, 20 mol%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (94 mg, 0.6 mmol) and DCE (3.0 mL) were added. The reaction mixture was then stirred at 85 °C in oil bath for 8 h. A lower yield of the amidated products was observed and the reaction of TEMPO was detected by ESI-HRMS analysis.





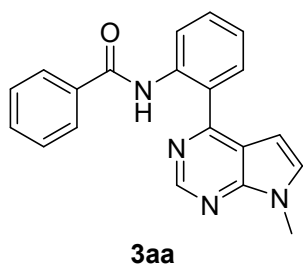
To 15 mL pressure vessel equipped with a magnetic stirrer was charged with with **1ac** (0.2 mmol), **4a** (0.4 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (5.0 mg, 4 mol%), AgNTf_2 (12 mg, 16 mol%), NaOAc (3 mg, 20 mol%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (94 mg, 0.6 mmol) or 2,6-di-tert-butyl-4-methylphenol (BHT) (132 mg, 0.6 mmol) and DCE (3.0 mL) were added, respectively. The reaction mixture was then stirred at 85 °C in oil bath for 8 h. Both lower yields of the phosphoramidated products were observed and the reaction of TEMPO and BHT were detected by ESI-HRMS analysis.





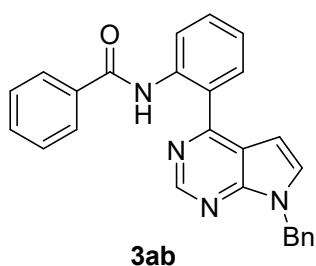
5. Characterization of Compounds

N-(2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (**3aa**)



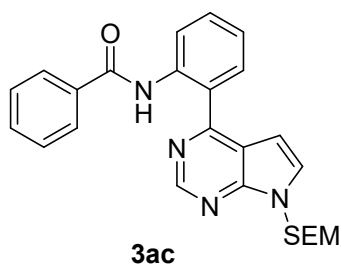
The reaction of 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (130 mg, 0.45 mmol), benzoyl azide (0.90 mmol), [RuCl₂(*p*-cymene)]₂ (11 mg, 4 mol%), AgNTf₂ (28 mg, 16 mol%) and NaOAc (7 mg, 20 mol%) in DCE (7 mL) at 85 °C for 8 h, affords 130 mg (88%) of **3aa** (PE/EA = 4:1) as a yellow solid. Mp: 191-193 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.98 (s, 1H), 8.98 (s, 1H), 8.82 (d, *J* = 8.3 Hz, 1H), 8.03-7.98 (m, 3H), 7.59-7.47 (m, 4H), 7.27-7.24 (m, 2H), 6.77-6.75 (m, 1H), 3.88 (d, *J* = 5.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.42, 157.33, 152.00, 149.53, 138.21, 135.39, 131.66, 131.00, 130.66, 128.65, 127.30, 124.71, 123.33, 122.18, 116.39, 101.02, 31.27. HRMS *m/z* (ESI) calcd for C₂₀H₁₆N₄O [M+H]⁺: 351.1216, found: 351.1217.

N-(2-(7-benzyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (**3ab**)



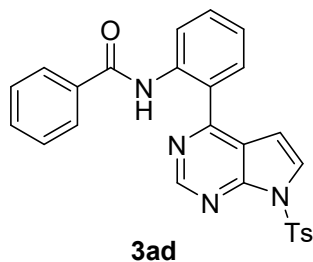
The reaction of 7-benzyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (140 mg, 0.49 mmol), benzoyl azide (0.98 mmol), [RuCl₂(*p*-cymene)]₂ (12 mg, 4 mol%), AgNTf₂ (30 mg, 16 mol%) and NaOAc (8 mg, 20 mol%) in DCE (7 mL) at 85 °C for 9 h, affords 156 mg (78%) of **3ab** (PE/EA = 4:1) as a white solid. Mp: 122-124 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.62 (s, 1H), 9.08 (s, 1H), 8.58-8.53 (m, 1H), 8.08-8.04 (m, 1H), 7.95-7.90 (m, 2H), 7.86 (d, *J* = 3.6 Hz, 1H), 7.62-7.55 (m, 4H), 7.40-7.35 (m, 1H), 7.33-7.24 (m, 5H), 6.87 (d, *J* = 3.7 Hz, 1H), 5.54 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 164.92, 156.74, 151.69, 150.25, 137.93, 135.01, 132.37, 131.81, 131.42, 131.21, 129.38, 129.13, 128.11, 127.93, 127.51, 125.86, 124.50, 122.63, 116.17, 101.13, 47.85. HRMS *m/z* (ESI) calcd for C₂₆H₂₀N₄O [M+H]⁺: 405.1710, found: 405.1713.

***N*-(2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (**3ac**)**



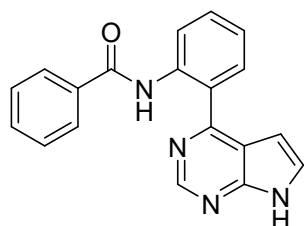
The reaction of 4-phenyl-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (85 mg, 0.26 mmol), benzoyl azide (0.52 mmol), [RuCl₂(*p*-cymene)]₂ (6 mg, 4 mol%), AgNTf₂ (16 mg, 16 mol%) and NaOAc (4 mg, 20 mol%) in DCE (4 mL) at 85 °C for 8 h, affords 73 mg (63%) of **3ac** (PE/EA = 4:1) as a yellow solid. Mp: 151-153 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.89 (s, 1H), 9.02 (s, 1H), 8.81 (d, *J* = 8.3 Hz, 1H), 8.06-8.01 (m, 2H), 7.64-7.45 (m, 4H), 7.36-7.27 (m, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 6.96-6.84 (m, 2H), 5.70 (d, *J* = 23.3 Hz, 2H), 3.64-3.52 (m, 2H), 1.01-0.92 (m, 2H), -0.03 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 165.59, 157.75, 152.58, 149.96, 138.09, 135.28, 131.75, 131.19, 130.76, 128.70, 127.32, 124.67, 123.50, 122.36, 116.60, 115.41, 102.35, 72.98, 66.75, 17.72, -1.44. HRMS *m/z* (ESI) calcd for C₂₅H₂₈N₄O₂Si [M+H]⁺: 467.1874, found: 467.1874.

***N*-(2-(7-tosyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (**3ad**)**



The reaction of 4-phenyl-7-tosyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (192 mg, 0.55 mmol), benzoyl azide (1.10 mmol), [RuCl₂(*p*-cymene)]₂ (13 mg, 4 mol%), AgNTf₂ (34 mg, 16 mol%) and NaOAc (9 mg, 20 mol%) in DCE (8 mL) at 85 °C for 9 h, affords 174 mg (68%) of **3ad** (PE/EA = 4:1) as a white solid. Mp: 219-220 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.43 (s, 1H), 9.10 (s, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.00-7.96 (m, 2H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.84-7.80 (m, 1H), 7.60-7.49 (m, 4H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.31-7.26 (m, 1H), 6.92 (d, *J* = 4.1 Hz, 1H), 2.41 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 160.62, 154.09, 147.40, 146.58, 141.44, 133.31, 130.36, 129.84, 127.11, 126.98, 125.99, 125.27, 124.00, 123.71, 122.65, 122.48, 119.11, 118.86, 117.88, 113.79, 100.05, 17.00. HRMS *m/z* (ESI) calcd for C₂₆H₂₀N₄O₃S [M+H]⁺: 469.1329, found: 469.1329.

N-(2-(7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (**3ae**)

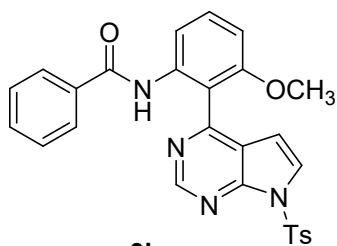


3ae

The reaction of 4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (148 mg, 0.76 mmol), benzoyl azide (1.52 mmol), [RuCl₂(*p*-cymene)]₂ (19 mg, 4 mol%), AgNTf₂ (53 mg, 16 mol%) and NaOAc (12 mg, 20 mol%) in DCE (11 mL) at 85 °C for 10 h, affords 12 mg (5%) of **3ae** (PE/EA = 2:1) as a white solid.

Mp: 258-260 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.81 (s, 1H), 12.46 (s, 1H), 9.03 (s, 1H), 8.60-6.58 (m, 1H), 8.10-8.07 (m, 1H), 7.96-7.94 (m, 2H), 7.73-7.71 (m, 1H), 7.63-7.56 (m, 4H), 7.39-7.35 (m, 1H), 6.83-6.81 (m, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 164.87, 156.32, 153.14, 149.98, 137.97, 135.04, 132.39, 131.37, 131.09, 129.43, 128.84, 127.48, 125.75, 124.40, 122.39, 115.86, 101.11. HRMS *m/z* (ESI) calcd for C₁₉H₁₄N₄O [M+H]⁺: 315.1240, found: 315.1230.

N-(3-methoxy-2-(7-tosyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (**3b**)

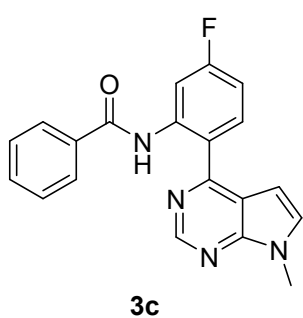


3b

The reaction of 4-(2-methoxyphenyl)-7-tosyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (53 mg, 0.14 mmol), benzoyl azide (0.28 mmol), [RuCl₂(*p*-cymene)]₂ (3 mg, 4 mol%), AgNTf₂ (9 mg, 16 mol%) and NaOAc (2 mg, 20 mol%) in DCE (2 mL) at 85 °C for 8 h, affords 59 mg (82%) of

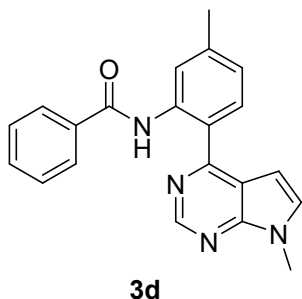
3b (PE/EA = 4:1) as a white solid. Mp: 175-176 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.21 (s, 1H), 9.05 (s, 1H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 4.0 Hz, 1H), 7.61-7.57 (m, 3H), 7.56-7.50 (m, 2H), 7.47-7.40 (m, 4H), 7.09-7.07 (m, 1H), 6.58 (d, *J* = 4.0 Hz, 1H), 3.72 (s, 3H), 2.35 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 165.41, 157.55, 156.42, 152.60, 151.26, 146.64, 137.64, 134.91, 134.67, 132.01, 131.57, 130.73, 128.88, 128.27, 127.61, 127.31, 121.29, 118.54, 117.68, 108.90, 106.23, 56.11, 21.60. HRMS *m/z* (ESI) calcd for C₂₇H₂₂N₄O₄S [M+Na]⁺: 521.1254, found: 521.1253.

***N*-(5-fluoro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (3c)**



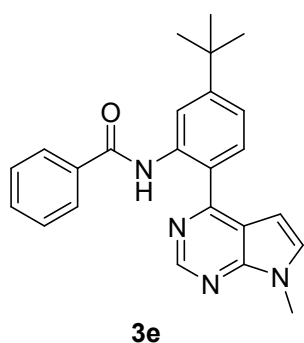
The reaction of 4-(2-fluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (188 mg, 0.83 mmol), benzoyl azide (1.66 mmol), [RuCl₂(*p*-cymene)]₂ (20 mg, 4 mol%), AgNTf₂ (51 mg, 16 mol%) and NaOAc (14 mg, 20 mol%) in DCE (12 mL) at 85 °C for 8 h, affords 220 mg (77%) of **3c** (PE/EA = 4:1) as a white solid. Mp: 195-197 °C. ¹H NMR (400 MHz, CDCl₃) δ 13.31 (s, 1H), 8.94 (s, 1H), 8.69-8.66 (m, 1H), 8.02-7.97 (m, 3H), 7.59-7.46 (m, 3H), 7.27 (d, *J* = 3.5 Hz, 1H), 6.97-6.91 (m, 1H), 6.74 (d, *J* = 3.5 Hz, 1H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.63, 163.92 (d, *J*_{C-F} = 250.5 Hz), 156.52, 151.89, 149.35, 140.38 (d, *J*_{C-F} = 12.1 Hz), 134.98, 132.31 (d, *J*_{C-F} = 10.1 Hz), 131.92, 130.77, 128.71, 127.31, 120.40 (d, *J*_{C-F} = 3.1 Hz), 116.04, 110.25 (d, *J*_{C-F} = 22.2 Hz), 109.00 (d, *J*_{C-F} = 27.3 Hz), 100.77, 31.30. HRMS *m/z* (ESI) calcd for C₂₀H₁₅FN₄O [M+H]⁺: 369.1122, found: 369.1125.

***N*-(5-methyl-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (3d)**



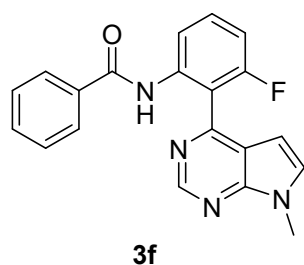
The reaction of 7-methyl-4-(*p*-tolyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (125 mg, 0.56 mmol), benzoyl azide (1.12 mmol), [RuCl₂(*p*-cymene)]₂ (14 mg, 4 mol%), AgNTf₂ (35 mg, 16 mol%) and NaOAc (9 mg, 20 mol%) in DCE (8 mL) at 85 °C for 8 h, affords 162 mg (85%) of **3d** (PE/EA = 4:1) as a yellow solid. Mp: 169-170 °C. ¹H NMR (400 MHz, CDCl₃) δ 13.09 (s, 1H), 8.94 (s, 1H), 8.68 (s, 1H), 8.04-8.02 (m, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.56-7.46 (m, 3H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.07-7.05 (m, 1H), 6.74 (d, *J* = 3.6 Hz, 1H), 3.86 (s, 3H), 2.48 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.37, 157.36, 151.83, 149.40, 141.59, 138.19, 135.43, 131.63, 130.68, 130.35, 128.63, 127.30, 124.24, 122.46, 121.91, 116.07, 101.03, 31.22, 21.92. HRMS *m/z* (ESI) calcd for C₂₁H₁₈N₄O [M+H]⁺: 365.1373, found: 365.1371.

***N*-(5-(*tert*-butyl)-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (3e)**



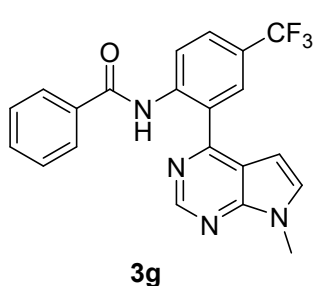
The reaction of 4-(4-(*tert*-butyl)phenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (101 mg, 0.38 mmol), benzoyl azide (0.76 mmol), [RuCl₂(*p*-cymene)]₂ (9 mg, 4 mol%), AgNTf₂ (24 mg, 16 mol%) and NaOAc (6 mg, 20 mol%) in DCE (6 mL) at 85 °C for 8 h, affords 66 mg (45%) of **3e** (PE/EA = 4:1) as a yellow solid. Mp: 188-189 °C. ¹H NMR (400 MHz, CDCl₃) δ 13.10 (s, 1H), 9.08-8.83 (m, 2H), 8.13-7.92 (m, 3H), 7.61-7.46 (m, 3H), 7.33-7.31 (m, 1H), 7.27 (d, *J* = 3.6 Hz, 1H), 6.83 (d, *J* = 3.6 Hz, 1H), 3.92 (s, 3H), 1.46 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 165.52, 157.41, 154.74, 151.93, 149.54, 138.20, 135.55, 131.61, 130.49, 130.30, 128.65, 127.31, 121.99, 120.51, 119.35, 116.17, 101.15, 35.25, 31.22. HRMS *m/z* (ESI) calcd for C₂₄H₂₅N₄O [M+H]⁺: 385.2023, found: 385.2022.

***N*-(3-fluoro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (3f)**



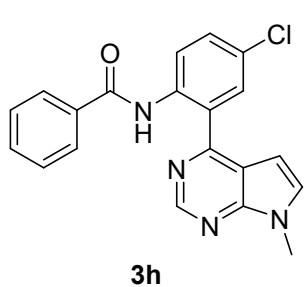
The reaction of 4-(2-fluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (86 mg, 0.38 mmol), benzoyl azide (0.76 mmol), [RuCl₂(*p*-cymene)]₂ (9 mg, 4 mol%), AgNTf₂ (24 mg, 16 mol%) and NaOAc (6 mg, 20 mol%) in DCE (6 mL) at 85 °C for 8 h, affords 120 mg (92%) of **3f** (PE/EA = 4:1) as a black solid. Mp: 176-177 °C. ¹H NMR (400 MHz, CDCl₃) δ 11.76 (s, 1H), 9.07 (s, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 7.92-7.87 (m, 2H), 7.56-7.44 (m, 4H), 7.26 (d, *J* = 3.6 Hz, 1H), 7.07-7.02 (m, 1H), 6.56-6.54 (m, 1H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.24, 161.52, 159.03, 151.88 (d, *J*_{C-F} = 54.5 Hz), 150.00, 138.50 (d, *J*_{C-F} = 20.1 Hz), 134.72, 131.95, 131.83 (d, *J*_{C-F} = 40.6 Hz), 130.57 (d, *J*_{C-F} = 7.8 Hz), 128.75, 127.15, 118.69 (d, *J*_{C-F} = 10.5 Hz), 118.04 (d, *J*_{C-F} = 12.7 Hz), 111.37, 111.14, 101.62 (d, *J*_{C-F} = 39.5 Hz), 31.21. HRMS *m/z* (ESI) calcd for C₂₀H₁₅FN₄O [M+H]⁺: 347.1303, found: 347.1311.

***N*-(2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-4-(trifluoromethyl)phenyl)benzamide (**3g**)**



The reaction of 7-methyl-4-(3-(trifluoromethyl)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (25 mg, 0.09 mmol), benzoyl azide (0.18 mmol), [RuCl₂(*p*-cymene)]₂ (2 mg, 4 mol%), AgNTf₂ (6 mg, 16 mol%) and NaOAc (1 mg, 20 mol%) in DCE (1 mL) at 85 °C for 8 h, affords 21 mg (57%) of **3g** (PE/EA = 4:1) as a yellow solid. Mp: 183-184 °C. ¹H NMR (400 MHz, CDCl₃) δ 13.23 (s, 1H), 9.01 (d, *J* = 8.9 Hz, 2H), 8.31 (d, *J* = 1.5 Hz, 1H), 8.10-7.95 (m, 2H), 7.81-7.79 (m, 1H), 7.65-7.47 (m, 3H), 7.36 (d, *J* = 3.6 Hz, 1H), 6.81 (d, *J* = 3.6 Hz, 1H), 3.96 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.73, 155.86, 152.15, 149.44, 141.34, 134.86, 132.07, 131.34, 128.77, 127.87 (d, *J*_{C-F} = 162.6 Hz), 127.71 (d, *J*_{C-F} = 2.0 Hz), 127.39, 125.04 (d, *J*_{C-F} = 33.3 Hz), 124.30, 124.10 (d, *J*_{C-F} = 272.7 Hz), 122.00, 116.31, 100.58, 31.37. HRMS *m/z* (ESI) calcd for C₂₁H₁₅F₃N₄O [M+H]⁺: 419.1090, found: 419.1095.

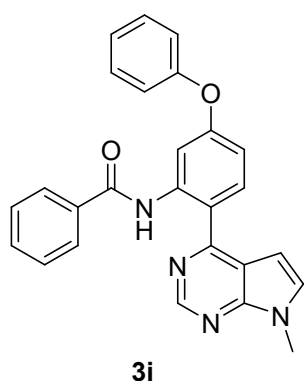
***N*-(4-chloro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)benzamide (**3h**)**



The reaction of 4-(3-chlorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (85 mg, 0.35 mmol), benzoyl azide (0.70 mmol), [RuCl₂(*p*-cymene)]₂ (9 mg, 4 mol%), AgNTf₂ (22 mg, 16 mol%) and NaOAc (6 mg, 20 mol%) in DCE (5 mL) at 85 °C for 8 h, affords 76 mg (60%) of **3h** (PE/EA = 4:1) as a yellow solid. Mp: 191-192 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.92 (s, 1H), 8.99 (s, 1H), 8.80 (d, *J* = 8.9 Hz, 1H), 8.07-7.92 (m, 3H), 7.56-7.48 (m, 4H), 7.32 (d, *J* = 3.6 Hz, 1H), 6.81 (d, *J* = 3.6 Hz, 1H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.40, 155.77, 152.09, 149.48, 136.89, 135.06, 131.83, 131.11, 130.69, 130.19, 128.70, 128.30, 127.28, 125.95, 123.48, 116.25, 100.68, 31.33. HRMS *m/z* (ESI) calcd for C₂₀H₁₅ClN₄O [M+H]⁺: 385.0827, found: 385.0830.

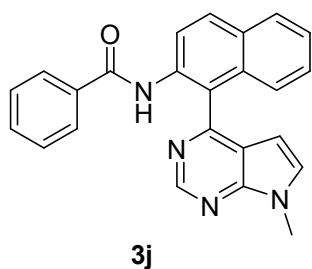
N-(2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-5-phenoxyphenyl)benzamide

(3i)



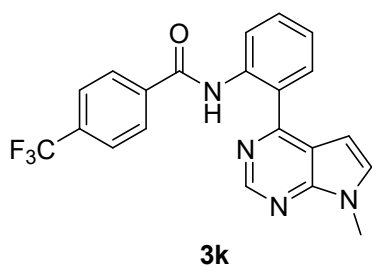
The reaction of 7-methyl-4-(4-phenoxyphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (96 mg, 0.32 mmol), benzoyl azide (0.64 mmol), [RuCl₂(*p*-cymene)]₂ (8 mg, 4 mol%), AgNTf₂ (20 mg, 16 mol%) and NaOAc (5 mg, 20 mol%) in DCE (5 mL) at 85 °C for 8 h, affords 93 mg (70%) of **3i** (PE/EA = 4:1) as a brown solid. Mp: 138-141 °C. ¹H NMR (400 MHz, CDCl₃) δ 13.29 (s, 1H), 8.97 (s, 1H), 8.59 (s, 1H), 8.02 (t, *J* = 7.4 Hz, 3H), 7.57-7.49 (m, 3H), 7.46-7.38 (m, 2H), 7.28 (d, *J* = 3.0 Hz, 1H), 7.23-7.16 (m, 3H), 6.91-6.85 (m, 1H), 6.81 (t, *J* = 3.0 Hz, 1H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.57, 159.84, 157.07, 156.09, 151.89, 149.48, 140.20, 135.29, 132.18, 131.77, 130.43, 129.95, 128.68, 127.36, 124.16, 119.89, 119.23, 115.94, 112.81, 111.46, 100.99, 31.32. HRMS *m/z* (ESI) calcd for C₂₆H₂₀N₄O₂ [M+Na]⁺: 443.1478, found: 443.1468.

N-(1-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)naphthalen-2-yl)benzamide (3j)



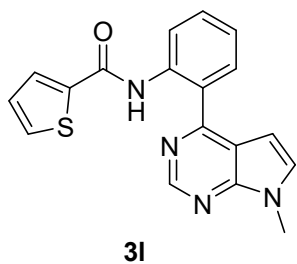
The reaction of 7-methyl-4-(naphthalen-1-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (65 mg, 0.25 mmol), benzoyl azide (0.50 mmol), [RuCl₂(*p*-cymene)]₂ (6 mg, 4 mol%), AgNTf₂ (15 mg, 16 mol%) and NaOAc (4 mg, 20 mol%) in DCE (4 mL) at 85 °C for 8 h, affords 71 mg (76%) of **3j** (PE/EA = 4:1) as a brown solid. Mp: 182-183 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.10 (s, 1H), 8.72 (t, *J* = 5.6 Hz, 1H), 7.98-7.91 (m, 2H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.58-7.53 (m, 1H), 7.43-7.38 (m, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.30-7.26 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.12 (d, *J* = 3.6 Hz, 1H), 3.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.89, 157.36, 151.06, 137.88, 134.24, 133.85, 132.59, 131.13, 130.79, 129.70, 129.68, 128.80, 128.31, 127.32, 127.17, 126.46, 125.43, 124.25, 119.75, 119.71, 100.21, 31.19. HRMS *m/z* (ESI) calcd for C₂₄H₁₈N₄O [M+H]⁺: 379.1553, found: 379.1546.

***N*-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)-4-(trifluoromethyl)benzamide (**3k**)**



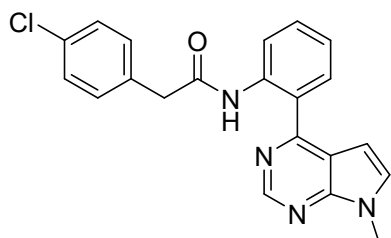
The reaction of 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (84 mg, 0.40 mmol), 4-(trifluoromethyl)benzoyl azide (0.80 mmol), [RuCl₂(*p*-cymene)]₂ (10 mg, 4 mol%), AgNTf₂ (25 mg, 16 mol%) and NaOAc (7 mg, 20 mol%) in DCE (8 mL) at 85 °C for 8 h, affords 125 mg (79%) of **3k** (PE/EA = 3:1) as a white solid. Mp: 110-112 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.86 (s, 1H), 9.03 (s, 1H), 8.55-8.53 (m, 1H), 8.05-7.98 (m, 3H), 7.68 (d, *J* = 3.6 Hz, 1H), 7.57-7.52 (m, 3H), 7.34-7.30 (m, 1H), 6.76 (d, *J* = 3.6 Hz, 1H), 3.83 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 163.51, 156.22, 151.83, 151.12 (d, *J*_{C-F} = 7.04 Hz), 149.87, 137.84, 133.96, 132.60, 131.29, 131.08, 129.82, 125.62, 124.47, 122.39, 121.43, 115.93, 100.35, 31.36. HRMS *m/z* (ESI) calcd for C₂₁H₁₅F₃N₄O [M+H]⁺: 397.1271, found: 397.1280.

***N*-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)thiophene-2-carboxamide (**3l**)**



The reaction of 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (188 mg, 0.90 mmol), thiophene-2-carbonyl azide (1.80 mmol), [RuCl₂(*p*-cymene)]₂ (22 mg, 4 mol%), AgNTf₂ (56 mg, 16 mol%) and NaOAc (15 mg, 20 mol%) in DCE (13 mL) at 85 °C for 8 h, affords 262 mg (87%) of **3l** (PE/EA = 3:1) as a white solid. Mp: 155-156 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.79 (s, 1H), 9.07 (s, 1H), 8.48-8.46 (m, 1H), 8.05-8.02 (m, 1H), 7.88-7.87 (m, 1H), 7.78-7.77 (m, 1H), 7.73 (d, *J* = 3.5 Hz, 1H), 7.59-7.55 (m, 1H), 7.36-7.32 (m, 1H), 7.25-7.23 (m, 1H), 6.81 (d, *J* = 3.6 Hz, 1H), 3.87 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 159.69, 156.23, 151.87, 149.87, 140.19, 137.68, 132.76, 132.41, 131.35, 131.19, 129.30, 128.99, 125.30, 124.41, 122.34, 115.98, 100.39, 31.47. HRMS *m/z* (ESI) calcd for C₁₈H₁₄N₄OS [M+H]⁺: 335.0961, found: 335.0956.

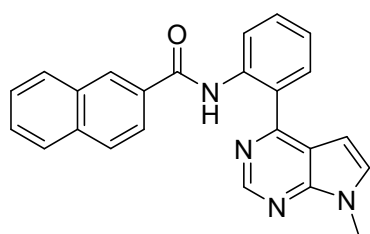
2-(4-chlorophenyl)-N-(2-(7-methyl-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)acetamide (3m)



3m

The reaction of 7-methyl-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (42 mg, 0.20 mmol), 2-(4-chlorophenyl)acetyl azide (0.40 mmol), [RuCl₂(*p*-cymene)]₂ (5 mg, 4 mol%), AgNTf₂ (12 mg, 16 mol%) and NaOAc (3 mg, 20 mol%) in DCE (3 mL) at 85 °C for 8 h, affords 38 mg (50%) of **3m** (PE/EA = 4:1) as a white solid. Mp: 169-170 °C. ¹H NMR (400 MHz, CDCl₃) δ 11.45 (s, 1H), 8.51 (d, *J* = 9.1 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 7.28-7.19 (m, 5H), 6.68 (d, *J* = 3.5 Hz, 1H), 3.91 (s, 3H), 3.69 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 169.39, 156.93, 151.77, 149.59, 137.20, 133.36, 132.93, 131.17, 130.72, 130.61, 130.49, 129.03, 125.14, 123.68, 122.51, 116.27, 100.81, 44.72, 31.36. HRMS *m/z* (ESI) calcd for C₂₁H₁₇ClN₄O [M+H]⁺: 377.1164, found: 377.1168.

N-(2-(7-methyl-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)-2-naphthamide(3n)

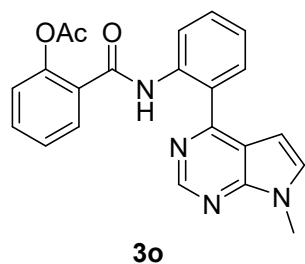


3n

The reaction of 7-methyl-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (67 mg, 0.32 mmol), 2-naphthoyl azide (0.64 mmol), [RuCl₂(*p*-cymene)]₂ (8 mg, 4 mol%), AgNTf₂ (20 mg, 16 mol%) and NaOAc (5 mg, 20 mol%) in DCE (5 mL) at 85 °C for 10 h, affords 56 mg (47%) of **3n** (PE/EA = 2:1) as a yellow solid. Mp: 189-191 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.92 (s, 1H), 8.74 (s, 1H), 8.44 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 8.01-7.95 (m, 2H), 7.75-7.69 (m, 2H), 7.64-7.52 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 3.3 Hz, 1H), 3.85 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.08, 156.67, 151.73, 150.09, 137.43, 134.60, 133.78, 132.38, 131.30, 131.19, 130.90, 130.13, 128.80, 127.72, 127.38, 126.88, 125.90, 125.66, 125.56, 125.03, 123.64, 116.27, 100.30, 31.41. HRMS *m/z* (ESI) calcd for C₂₄H₁₈N₄O [M+H]⁺: 379.1553, found: 379.1552.

2-((2-(7-methyl-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)carbamoyl)phenyl

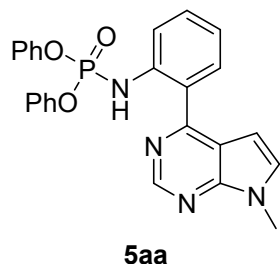
acetate (3o)



The reaction of 7-methyl-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (42 mg, 0.20 mmol), 2-(azidocarbonyl)phenyl acetate (0.40 mmol), [RuCl₂(*p*-cymene)]₂ (5 mg, 4 mol%), AgNTf₂ (12 mg, 16 mol%) and NaOAc (3 mg, 20 mol%) in DCE (3 mL) at 85 °C for 8 h, affords 48 mg (62%) of **3o** (PE/EA = 2:1) as a black solid. Mp: 187-188 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.14 (s, 1H), 8.87 (s, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.75-7.71 (m, 2H), 7.62-7.57 (m, 2H), 7.44-7.35 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 3.6 Hz, 1H), 3.87 (s, 3H), 2.07 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.35, 163.63, 156.27, 151.85, 149.94, 148.46, 137.35, 132.70, 131.29, 131.03, 129.51, 129.29, 126.81, 126.28, 124.73, 124.18, 122.80, 116.11, 100.25, 31.45, 20.94. HRMS *m/z* (ESI) calcd for C₂₂H₁₈N₄O₃ [M+H]⁺: 387.1452, found: 387.1446.

diphenyl (2-(7-methyl-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate

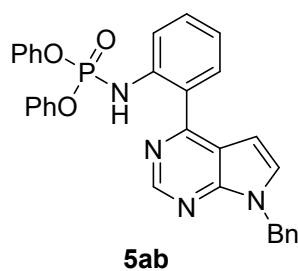
(5aa)



The reaction of 7-methyl-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (142 mg, 0.68 mmol), diphenyl phosphorazidate (1.36 mmol), [RuCl₂(*p*-cymene)]₂ (17 mg, 4 mol%), AgNTf₂ (42 mg, 16 mol%) and NaOAc (11 mg, 20 mol%) in DCE (10 mL) at 85 °C for 8 h, affords 234 mg (76%) of **5aa** (PE/EA = 4:1) as a yellow oil. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.12 (d, *J* = 11.5 Hz, 1H), 8.83 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 3.6 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.59-7.54 (m, 1H), 7.36-7.31 (m, 4H), 7.27-7.20 (m, 5H), 7.20-7.15 (m, 2H), 6.82 (d, *J* = 3.6 Hz, 1H), 3.36 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 155.97, 151.72, 150.43 (d, *J*_{C-P} = 2.8 Hz), 149.35, 139.37, 132.75, 131.78, 131.59, 130.47, 125.89, 123.58, 123.48, 122.81, 120.53 (d, *J*_{C-P} = 1.9 Hz), 119.78, 115.51, 100.55, 31.48. ³¹P NMR (162 MHz, DMSO-*d*₆) δ -7.85 (s, 1P). HRMS *m/z* (ESI): calcd for C₂₅H₂₁N₄O₃P [M+Na]⁺: 479.1243, found: 479.1250.

diphenyl (2-(7-benzyl-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate

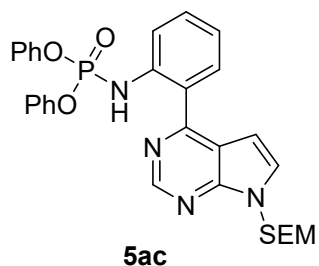
(5ab)



The reaction of 7-benzyl-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (143 mg, 0.50 mmol), diphenyl phosphorazidate (1.00 mmol), [RuCl₂(*p*-cymene)]₂ (12 mg, 4 mol%), AgNTf₂ (31 mg, 16 mol%) and NaOAc (8 mg, 20 mol%) in DCE (8 mL) at 85 °C for 9 h, affords 200 mg (75%) of **5ab** (PE/EA = 4:1) as a yellow oil. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.98 (d, *J* = 11.3 Hz, 1H), 8.85 (d, *J* = 4.4 Hz, 1H), 8.02 (t, *J* = 6.5 Hz, 1H), 7.88 (d, *J* = 4.4 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.57 (t, *J* = 6.9 Hz, 1H), 7.40-7.25 (m, 10H), 7.15-7.05 (m, 5H), 7.11 (t, *J* = 6.7 Hz, 2H), 6.85 (d, *J* = 4.8 Hz, 1H), 5.55 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 156.24, 151.52, 150.41 (d, *J*_{C-P} = 2.8 Hz), 149.64, 139.30, 137.93, 131.82 (d, *J*_{C-P} = 1.3 Hz), 131.61, 130.41, 129.14, 128.17, 128.03, 125.84, 123.75, 123.66, 122.90, 120.53 (d, *J*_{C-P} = 1.9 Hz), 119.95, 115.68, 101.24, 47.89. ³¹P NMR (162 MHz,

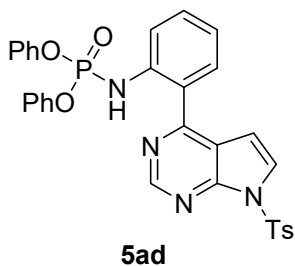
DMSO-*d*₆) δ -7.77 (s, 1P). HRMS *m/z* (ESI): calcd for C₃₁H₂₅N₄O₃P [M+H]⁺: 533.1737, found: 533.1746.

diphenyl (2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)phosphoramidate (5ac)



The reaction of 4-phenyl-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (192 mg, 0.59 mmol), diphenyl phosphorazidate (1.18 mmol), [RuCl₂(*p*-cymene)]₂ (14 mg, 4 mol%), AgNTf₂ (37 mg, 16 mol%) and NaOAc (10 mg, 20 mol%) in DCE (9 mL) at 85 °C for 8 h, affords 277 mg (82%) of **5ac** (PE/EA = 4:1) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 10.95 (d, *J* = 11.3 Hz, 1H), 8.87 (s, 1H), 8.03-8.00(m, 1H), 7.88 (d, *J* = 3.7 Hz, 1H), 7.73-7.71 (m, 1H), 7.59-7.55 m,1H), 7.33 (d, *J* = 7.9 Hz, 3H), 7.24-7.19 (m, 5H), 7.18-7.13 (m, 2H), 6.87 (d, *J* = 3.7 Hz, 1H), 5.69 (s, 2H), 3.59-3.54 (m, 2H), 2.53-2.48 (m, 2H), 0.87-0.83 (m, 2H), -0.09 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 161.17, 157.09, 155.18 (d, *J*_{C-P} = 2.8 Hz), 144.07, 136.63 (d, *J*_{C-P} = 2.6 Hz), 136.37, 135.16, 130.60, 128.38, 128.28, 127.64, 125.29 (d, *J*_{C-P} = 1.9 Hz), 124.68, 120.56, 106.49, 77.74, 71.05, 22.37, 3.79. ³¹P NMR (162 MHz, CDCl₃) δ -7.82 (s, 1P). HRMS *m/z* (ESI): calcd for C₃₀H₃₃N₄O₄PSi [M+H]⁺: 573.2081, found: 573.2072.

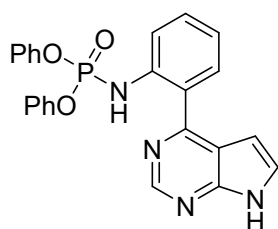
diphenyl (2-(7-tosyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)phosphoramidate (5ad)



The reaction of 4-phenyl-7-tosyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (84 mg, 0.24 mmol), diphenyl phosphorazidate (0.48 mmol), [RuCl₂(*p*-cymene)]₂ (6 mg, 4 mol%), AgNTf₂ (15 mg, 16 mol%) and NaOAc (4 mg, 20 mol%) in DCE (4 mL) at 85 °C for 9 h, affords 120 mg (83%) of **5ad** (PE/EA = 2:1) as a white solid. Mp: 148-150 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.78 (t, *J* = 9.1 Hz, 1H), 9.01-8.93 (m, 1H), 8.13 (d, *J* = 8.5 Hz, 2H), 8.07-8.01 (m, 1H), 7.77-7.62 (m, 2H), 7.59-7.45 (m, 3H), 7.26-7.11 (m, 9H), 7.03 (t, *J* = 7.5 Hz, 2H), 6.88-

6.79 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 157.96, 151.88, 151.73, 150.34 (d, $J_{\text{C-P}} = 2.7$ Hz), 146.85, 138.65, 134.52, 132.15, 131.79, 130.75, 130.30, 128.47, 128.22, 125.75, 124.34 (d, $J_{\text{C-P}} = 4.1$ Hz), 123.29, 120.61, 120.47 (d, $J_{\text{C-P}} = 1.9$ Hz), 118.30, 105.45, 21.61. ^{31}P NMR (162 MHz, DMSO- d_6) δ -7.55 (s, 1P). HRMS m/z (ESI): calcd for $\text{C}_{31}\text{H}_{25}\text{N}_4\text{O}_5\text{PS}$ $[\text{M}+\text{H}]^+$: 597.1356, found: 597.1370.

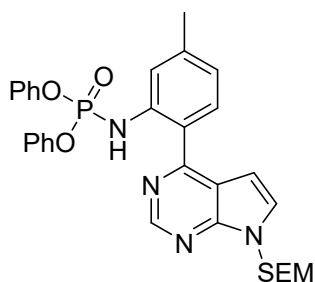
diphenyl (2-(7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate (**5ae**)



5ae

The reaction of 4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (42 mg, 0.20 mmol), diphenyl phosphorazidate (0.40 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (5 mg, 4 mol%), AgNTf_2 (12 mg, 16 mol%) and NaOAc (3 mg, 20 mol%) in DCE (3 mL) at 85 °C for 9 h, affords 22 mg (25%) of **5ae** (PE/EA = 2:1) as a white solid. Mp: 171-172 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 12.46 (s, 1H), 11.16 (d, $J = 11.6$ Hz, 1H), 8.79 (s, 1H), 8.07-8.03 (m, 1H), 7.73-7.71 (m, 1H), 7.58-7.54 (m, 1H), 7.36-7.31 (m, 5H), 7.25-7.20 (m, 5H), 7.19-7.15 (m, 2H), 6.82-6.80 (m, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 155.91, 152.97, 150.42, 150.35, 149.43, 139.33, 131.70 (d, $J_{\text{C-P}} = 17.1$ Hz), 130.46, 128.84, 125.90, 123.70 (d, $J_{\text{C-P}} = 16.0$ Hz), 122.79, 120.55 (d, $J_{\text{C-P}} = 7.7$ Hz), 119.72, 115.30, 101.23. ^{31}P NMR (162 MHz, DMSO- d_6) δ -7.83 (s, 1P). HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{N}_4\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 443.1268, found: 443.1257.

diphenyl (5-methyl-2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate (**5bc**)

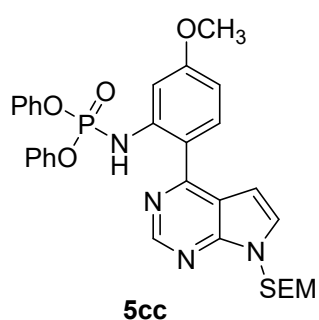


5bc

The reaction of 4-(*p*-tolyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidine (64 mg, 0.19 mmol), diphenyl phosphorazidate (0.38 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (5 mg, 4 mol%), AgNTf_2 (12 mg, 16 mol%) and NaOAc (3 mg, 20 mol%) in DCE (3 mL) at 85 °C for 8 h, affords 96 mg (86%) of **5bc** (PE/EA = 4:1) as a yellow solid. Mp: 82-83 °C. ^1H NMR (400 MHz, CDCl_3) δ 11.17 (d,

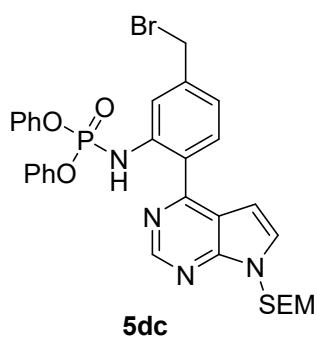
$J = 11.8$ Hz, 1H), 8.78 (s, 1H), 7.92-7.88 (m, 1H), 7.66 (s, 1H), 7.44 (d, $J = 3.7$ Hz, 1H), 7.27 (d, $J = 3.5$ Hz, 8H), 7.15-7.09 (m, 2H), 7.02-6.98 (m, 1H), 6.84 (d, $J = 3.7$ Hz, 1H), 5.70 (s, 2H), 3.62-3.56 (m, 2H), 2.47 (s, 3H), 1.00-0.94 (m, 2H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.36, 152.31, 150.60 (d, $J_{\text{C-P}} = 11.2$ Hz), 149.82, 141.91, 139.78, 130.97, 129.70, 128.86, 125.19, 125.17, 122.84, 120.77, 120.68, 120.45 (d, $J_{\text{C-P}} = 7.7$ Hz), 115.55, 102.37, 72.90, 66.68, 21.87, 17.78, -1.37. ^{31}P NMR (162 MHz, CDCl_3) δ -7.67 (s, 1P). HRMS m/z (ESI) calcd for $\text{C}_{31}\text{H}_{35}\text{N}_4\text{O}_4\text{PSi}$ $[\text{M}+\text{H}]^+$: 587.2238, found: 587.2246.

diphenyl (5-methoxy-2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate (5cc)



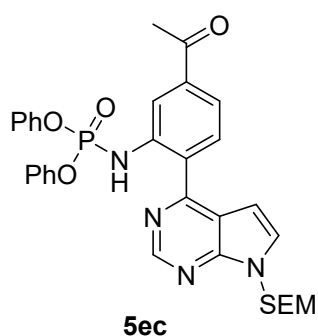
The reaction of 4-(4-methoxyphenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidine (71 mg, 0.20 mmol), diphenyl phosphorazidate (0.40 mmol), $[\text{RuCl}_2(p\text{-cymene})_2]$ (5 mg, 4 mol%), AgNTf_2 (12 mg, 16 mol%) and NaOAc (3 mg, 20 mol%) in DCE (3 mL) at 85 °C for 8 h, affords 98 mg (81%) of **5cc** (PE/EA = 4:1) as a yellow solid. Mp: 59-62 °C. ^1H NMR (400 MHz, CDCl_3) δ 11.59 (d, $J = 11.9$ Hz, 1H), 8.75 (s, 1H), 7.99-7.96 (m, 1H), 7.43 (d, $J = 3.7$ Hz, 1H), 7.39 (d, $J = 2.5$ Hz, 1H), 7.28 (d, $J = 4.3$ Hz, 8H), 7.15-7.10 (m, 2H), 6.85 (d, $J = 3.8$ Hz, 1H), 6.75-6.72 (m, 1H), 5.70 (s, 2H), 3.91 (s, 3H), 3.61-3.56 (m, 2H), 0.99-0.93 (m, 2H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.91, 157.27, 152.19, 150.55 (d, $J_{\text{C-P}} = 11.3$ Hz), 149.74, 141.94, 132.40, 129.72, 128.62, 125.23 (d, $J_{\text{C-P}} = 2.2$ Hz), 120.46 (d, $J_{\text{C-P}} = 7.5$ Hz), 116.15 (d, $J_{\text{C-P}} = 15.9$ Hz), 115.04, 108.24, 104.72 (d, $J_{\text{C-P}} = 4.1$ Hz), 102.37, 72.88, 66.67, 55.46, 17.77, -1.39. ^{31}P NMR (162 MHz, CDCl_3) δ -7.90 (s, 1P). HRMS m/z (ESI) calcd for $\text{C}_{31}\text{H}_{35}\text{N}_4\text{O}_5\text{PSi}$ $[\text{M}+\text{H}]^+$: 603.2187, found: 603.2187.

diphenyl (5-(bromomethyl)-2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate (5dc)



The reaction of 4-(4-(bromomethyl)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (83 mg, 0.20 mmol), diphenyl phosphoramidate (0.40 mmol), [RuCl₂(*p*-cymene)]₂ (5 mg, 4 mol%), AgNTf₂ (12 mg, 16 mol%) and NaOAc (3 mg, 20 mol%) in DCE (3 mL) at 85 °C for 8 h, affords 98 mg (74%) of **5dc** (PE/EA = 4:1) as a white solid. Mp: 114-116 °C. ¹H NMR (400 MHz, CDCl₃) δ 11.14 (d, *J* = 11.8 Hz, 1H), 8.77 (s, 1H), 7.96-7.94 (m, 1H), 7.80 (s, 1H), 7.43 (d, *J* = 3.7 Hz, 1H), 7.24 (d, *J* = 4.4 Hz, 8H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.10 (q, *J* = 4.1 Hz, 2H), 6.81 (d, *J* = 3.7 Hz, 1H), 5.69 (s, 2H), 4.76 (s, 2H), 3.61-3.57 (m, 2H), 0.98-0.94 (m, 2H), -0.02 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 157.09 (d, *J*_{C-P} = 2.4 Hz), 152.32, 150.50 (d, *J*_{C-P} = 11.4 Hz), 149.79, 144.97, 139.83, 131.19, 129.71, 129.06, 125.24 (d, *J*_{C-P} = 2.3 Hz), 122.29 (d, *J*_{C-P} = 10.6 Hz), 120.44 (d, *J*_{C-P} = 7.5 Hz), 120.03, 117.87 (d, *J*_{C-P} = 3.5 Hz), 115.71, 102.32, 72.92, 66.74, 64.52 (d, *J*_{C-P} = 5.9 Hz), 17.77, -1.39. ³¹P NMR (162 MHz, CDCl₃) δ -7.65 (s, 1P). HRMS *m/z* (ESI) calcd for C₃₁H₃₄BrN₄O₄PSi [M+H]⁺: 665.1343, found: 665.1331.

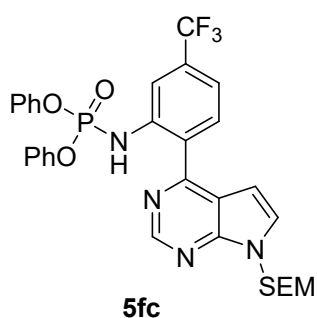
diphenyl (5-acetyl-2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)phosphoramidate (5ec)



The reaction of 1-(4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)ethan-1-one (40 mg, 0.11 mmol), diphenyl phosphoramidate (0.22 mmol), [RuCl₂(*p*-cymene)]₂ (3 mg, 4 mol%), AgNTf₂ (7 mg, 16 mol%) and NaOAc (2 mg, 20 mol%) in DCE (2 mL) at 85 °C for 8 h, affords 44 mg (66%) of **5ec** (PE/EA = 4:1) as a yellow solid. Mp: 89-90 °C. ¹H NMR (400 MHz, CDCl₃) δ 11.01 (d, *J* = 11.6 Hz, 1H), 8.87 (s, 1H), 8.42 (d, *J* = 1.6 Hz, 1H), 8.09-8.06 (m, 1H), 7.77-7.74 (m, 1H), 7.51 (d, *J* = 3.7 Hz, 1H), 7.28-7.27 (m, 3H), 7.27 (s, 5H), 7.18-7.09 (m, 2H), 6.84 (d, *J* = 3.7 Hz, 1H), 5.73 (s, 2H), 3.63-3.58 (m, 2H), 2.68 (s, 3H), 0.99-0.94 (m, 2H), -0.01 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 197.40, 155.97, 152.57, 150.43 (d, *J*_{C-P} = 11.3

Hz), 149.94, 140.10, 138.72, 131.21, 129.81 (d, $J_{C-P} = 6.1$ Hz), 127.23, 127.14, 125.34 (d, $J_{C-P} = 2.2$ Hz), 121.17, 120.40 (d, $J_{C-P} = 7.7$ Hz), 119.83 (d, $J_{C-P} = 3.3$ Hz), 116.14, 101.97, 72.99, 66.83, 26.83, 17.77, -1.39. ^{31}P NMR (162 MHz, CDCl_3) δ -8.20 (s, 1P). HRMS m/z (ESI) calcd for $\text{C}_{32}\text{H}_{35}\text{N}_4\text{O}_5\text{PSi}$ $[\text{M}+\text{H}]^+$: 615.2187, found: 615.2190.

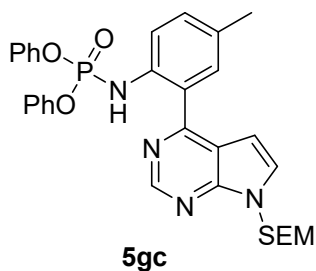
diphenyl (5-(trifluoromethyl)-2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate (5fc)



The reaction of 4-(4-(trifluoromethyl)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidine (67 mg, 0.17 mmol), diphenyl phosphorazidate (0.34 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (4 mg, 4 mol%), AgNTf_2 (11 mg, 16 mol%) and NaOAc (3 mg, 20 mol%) in DCE (3 mL) at 85 °C for 9 h, affords 50 mg (45%) of **5fc** (PE/EA = 4:1) as a yellow solid. Mp: 96-97 °C. ^1H NMR (400 MHz, CDCl_3) δ 11.10 (d, $J = 11.6$ Hz, 1H), 8.89 (s, 1H), 8.10 (q, $J = 3.7, 3.2$ Hz, 2H), 7.52 (d, $J = 3.7$ Hz, 1H), 7.44-7.42 (m, 1H), 7.31-7.29 (m, 2H), 7.27 (d, $J = 5.2$ Hz, 5H), 7.24 (d, $J = 1.4$ Hz, 1H), 7.17-7.12 (m, 2H), 6.83 (d, $J = 3.7$ Hz, 1H), 5.73 (s, 2H), 3.63-3.58 (m, 2H), 0.99-0.94 (m, 2H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.74, 152.59, 150.37 (d, $J_{C-P} = 11.2$ Hz), 149.97, 140.33, 132.91, 132.58, 131.41, 129.86, 129.80, 125.39 (d, $J_{C-F} = 4.9$ Hz), 120.29 (d, $J_{C-P} = 7.7$ Hz), 118.18 (d, $J_{C-F} = 14.3$ Hz), 116.65, 116.05, 101.83, 73.01, 66.87, 17.78, -1.41. ^{31}P NMR (162 MHz, CDCl_3) δ -8.68 (s, 1P). HRMS m/z (ESI) calcd for $\text{C}_{31}\text{H}_{32}\text{F}_3\text{N}_4\text{O}_4\text{PSi}$ $[\text{M}+\text{H}]^+$: 641.1955, found: 641.1944.

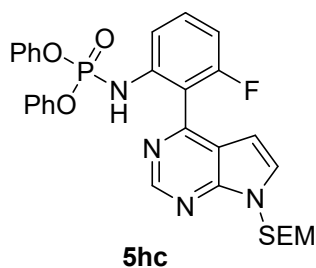
diphenyl (4-methyl-2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate (5gc)

The reaction of 4-(*m*-tolyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidine (61 mg, 0.18 mmol), diphenyl phosphorazidate (0.36 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (4 mg, 4 mol%), AgNTf_2 (11 mg, 16 mol%) and NaOAc (3 mg, 20 mol%)



in DCE (3 mL) at 85 °C for 9 h, affords 73 mg (71%) of **5gc** (PE/EA = 4:1) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 10.72 (d, *J* = 12.1 Hz, 1H), 8.82 (s, 1H), 7.79 (d, *J* = 2.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.33-7.30 (m, 1H), 7.26 (d, *J* = 3.9 Hz, 4H), 7.25 (s, 4H), 7.14-7.09 (m, 2H), 6.84 (d, *J* = 3.7 Hz, 1H), 5.71 (s, 2H), 3.62-3.57 (m, 2H), 2.43 (s, 3H), 0.99-0.94 (m, 2H), -0.01 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 157.36, 152.42, 150.53, 150.04, 137.02, 131.96, 131.41, 131.22, 129.66, 128.94, 125.12, 120.43 (d, *J*_{C-P} = 7.9 Hz), 119.93, 115.80, 102.36, 72.90, 66.72, 20.85, 17.78, -1.40. ³¹P NMR (162 MHz, CDCl₃) δ -7.50 (s, 1P). HRMS *m/z* (ESI) calcd for C₃₁H₃₅F₃N₄O₄PSi [M+H]⁺: 587.2238, found: 587.2230.

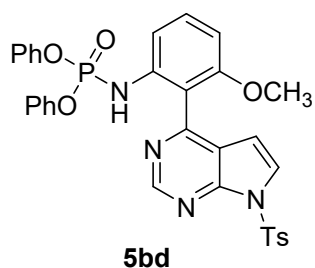
diphenyl (3-fluoro-2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)phosphoramidate (5hc**)**



The reaction of 4-(2-fluorophenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-*d*]pyrimidine (93 mg, 0.27 mmol), diphenyl phosphoramidate (0.54 mmol), [RuCl₂(*p*-cymene)]₂ (7 mg, 4 mol%), AgNTf₂ (17 mg, 16 mol%) and NaOAc (4 mg, 20 mol%) in DCE (4 mL) at 85 °C for 13 h, affords 76 mg (48%) of **5hc** (PE/EA = 4:1) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 9.38 (d, *J* = 11.5 Hz, 1H), 8.89 (s, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.49-7.44 (m, 1H), 7.42 (d, *J* = 3.8 Hz, 1H), 7.26-7.22 (m, 4H), 7.20-7.16 (m, 4H), 7.14-7.09 (m, 2H), 6.98-6.92 (m, 1H), 6.54-6.51 (m, 1H), 5.71 (s, 2H), 3.64-3.59 (m, 2H), 1.00-0.95 (m, 2H), -0.01 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 161.96, 159.46, 152.24, 151.92, 150.57, 150.29 (d, *J*_{C-P} = 11.1 Hz), 140.07, 131.90 (d, *J*_{C-P} = 17.1 Hz), 129.72, 128.92 (d, *J*_{C-F} = 8.0 Hz), 125.33 (d, *J*_{C-F}

= 5.2 Hz), 120.30 (d, $J_{C-F} = 17.8$ Hz), 118.33 (d, $J_{C-P} = 3.8$ Hz), 115.50, 109.98 (d, $J_{C-F} = 85.8$ Hz), 102.83 (d, $J_{C-F} = 40.0$ Hz), 72.93, 66.78, 17.78, -1.40. ^{31}P NMR (162 MHz, CDCl_3) δ -8.28 (s, 1P). HRMS m/z (ESI) calcd for $\text{C}_{30}\text{H}_{32}\text{FN}_4\text{O}_4\text{PSi}$ $[\text{M}+\text{H}]^+$: 591.1987, found: 591.1978.

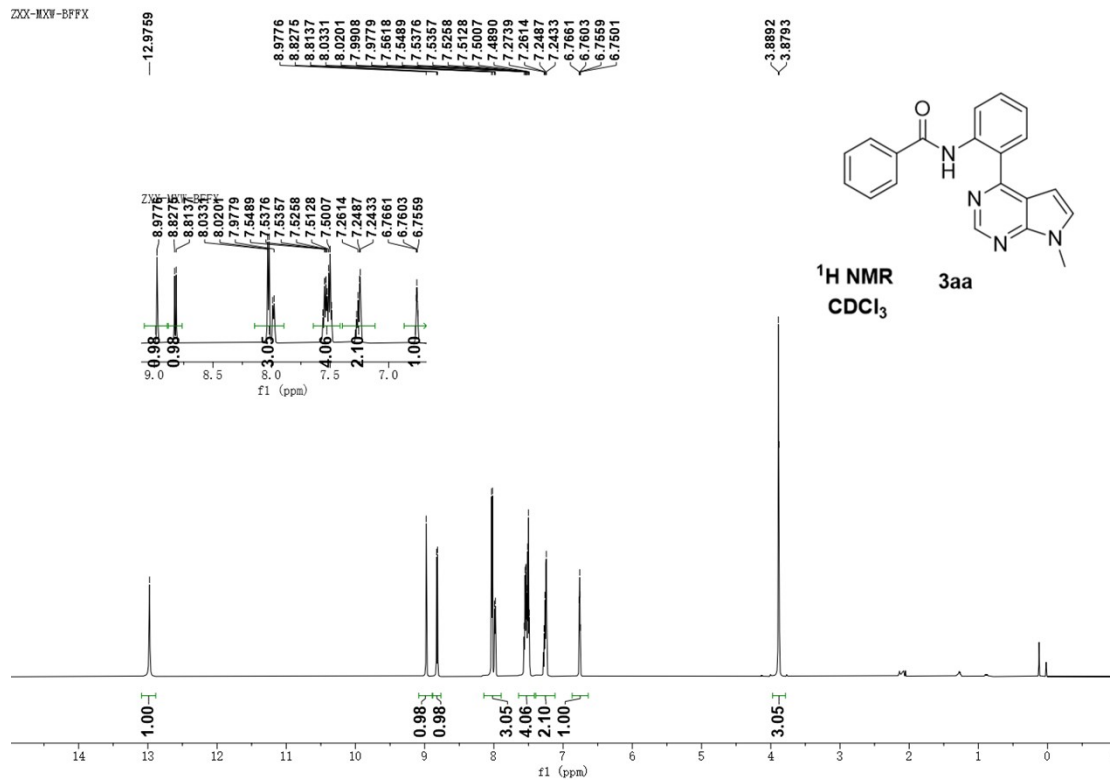
diphenyl (3-methoxy-2-(7-tosyl-7H-pyrrolo[2,3-d]pyrimidin-4-yl)phenyl)phosphoramidate (5bd)



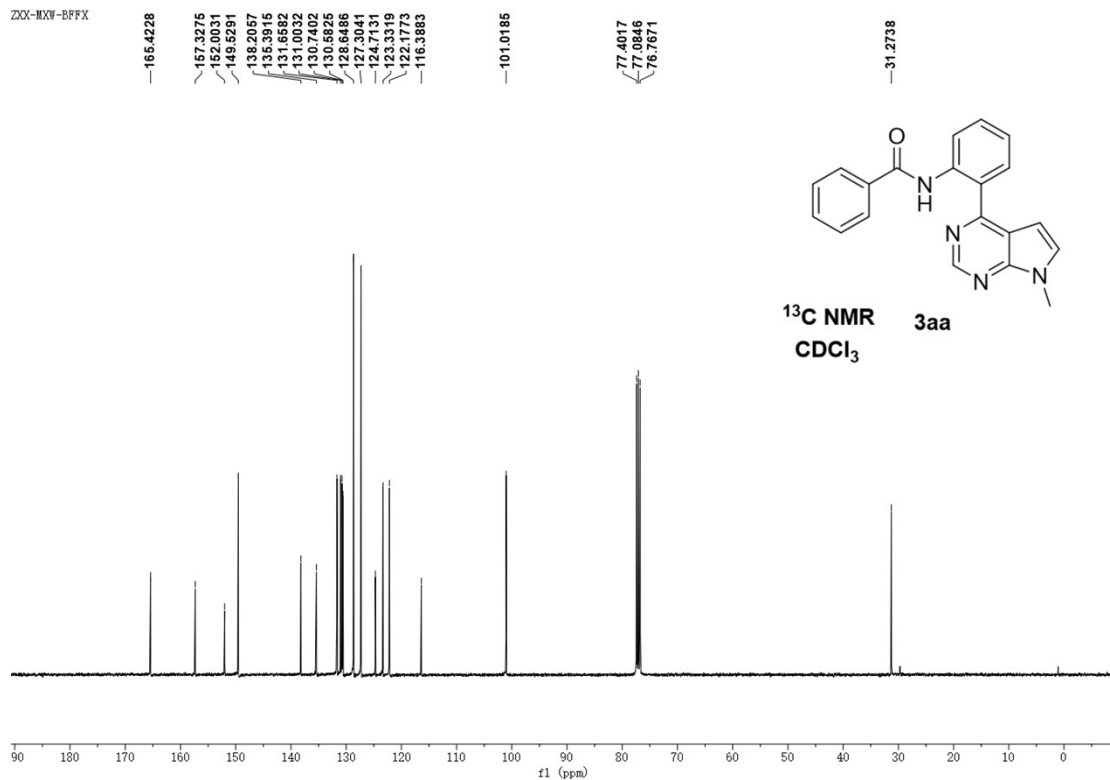
The reaction of 4-(2-methoxyphenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7H-pyrrolo[2,3-d]pyrimidine (99 mg, 0.28 mmol), diphenyl phosphoramidate (0.56 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (7 mg, 4 mol%), AgNTf_2 (17 mg, 16 mol%) and NaOAc (5 mg, 20 mol%) in DCE (4 mL) at 85 °C for 9 h, affords 111 mg (63%) of **5bd** (PE/EA = 2:1) as a yellow oil. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 9.00 (s, 1H), 8.18-8.12 (m, 3H), 7.90 (d, $J = 4.0$ Hz, 1H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.48 (t, $J = 8.4$ Hz, 1H), 7.28-7.21 (m, 5H), 7.13-7.08 (m, 6H), 6.89 (d, $J = 8.4$ Hz, 1H), 6.35 (d, $J = 4.1$ Hz, 1H), 3.64 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 157.88, 155.78, 152.75, 151.24, 150.38 (d, $J_{C-P} = 10.5$ Hz), 146.78, 138.69 (d, $J_{C-P} = 3.9$ Hz), 134.71, 132.04, 130.78, 130.27, 128.50, 127.17, 125.68, 121.25, 120.44 (d, $J_{C-P} = 7.6$ Hz), 115.59 (d, $J_{C-P} = 18.8$ Hz), 113.01, 106.59, 105.68, 56.01, 21.62. ^{31}P NMR (162 MHz, $\text{DMSO-}d_6$) δ -7.07 (s, 1P). HRMS m/z (ESI) calcd for $\text{C}_{32}\text{H}_{27}\text{N}_4\text{O}_6\text{PS}$ $[\text{M}+\text{H}]^+$: 627.1462, found: 627.1472.

^1H , ^{13}C , ^{31}P NMR Spectra for the compounds

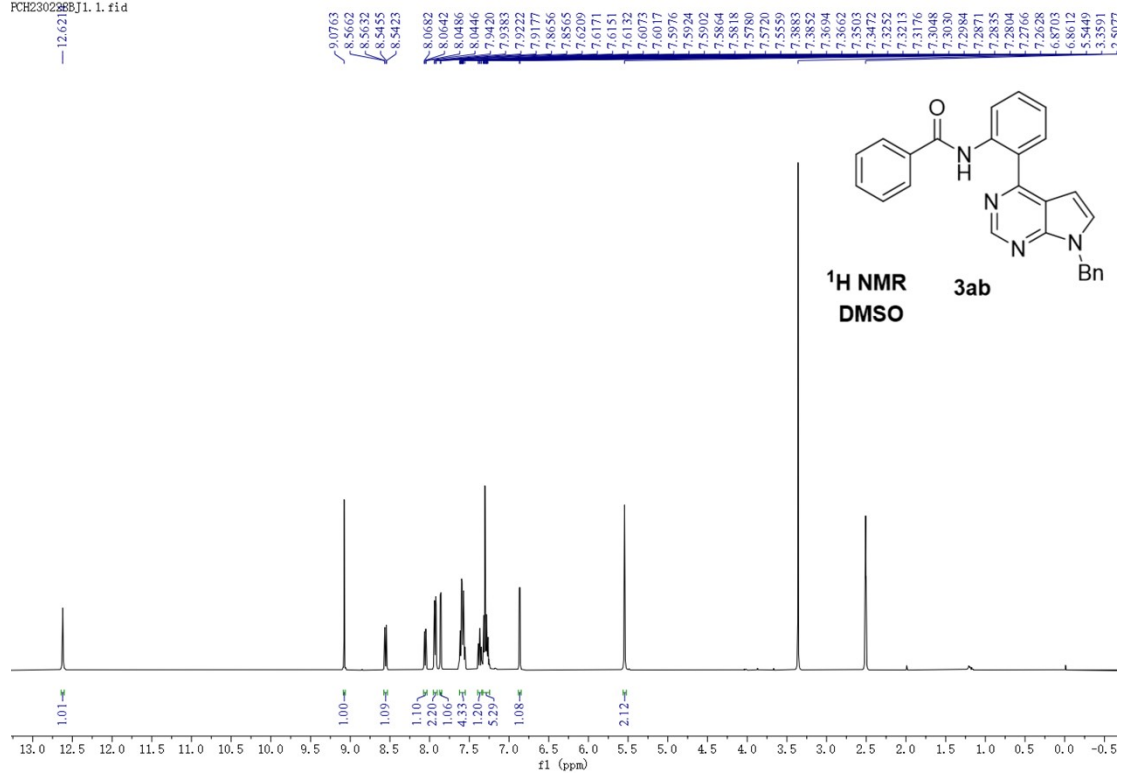
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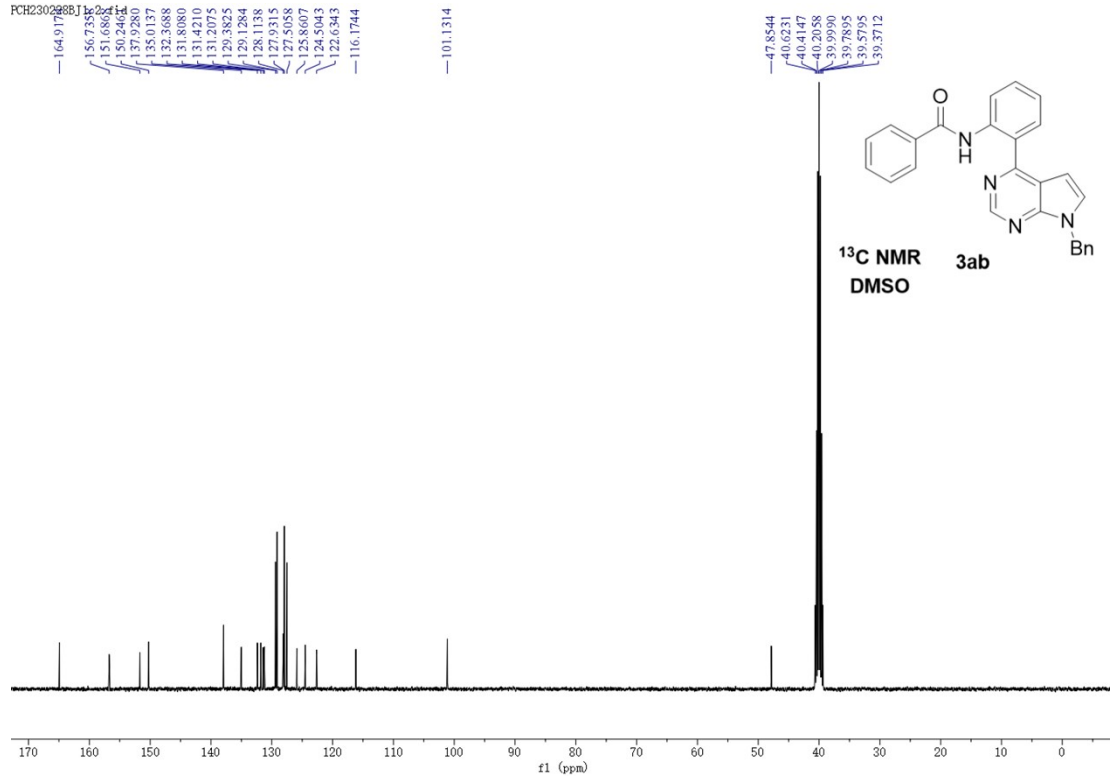
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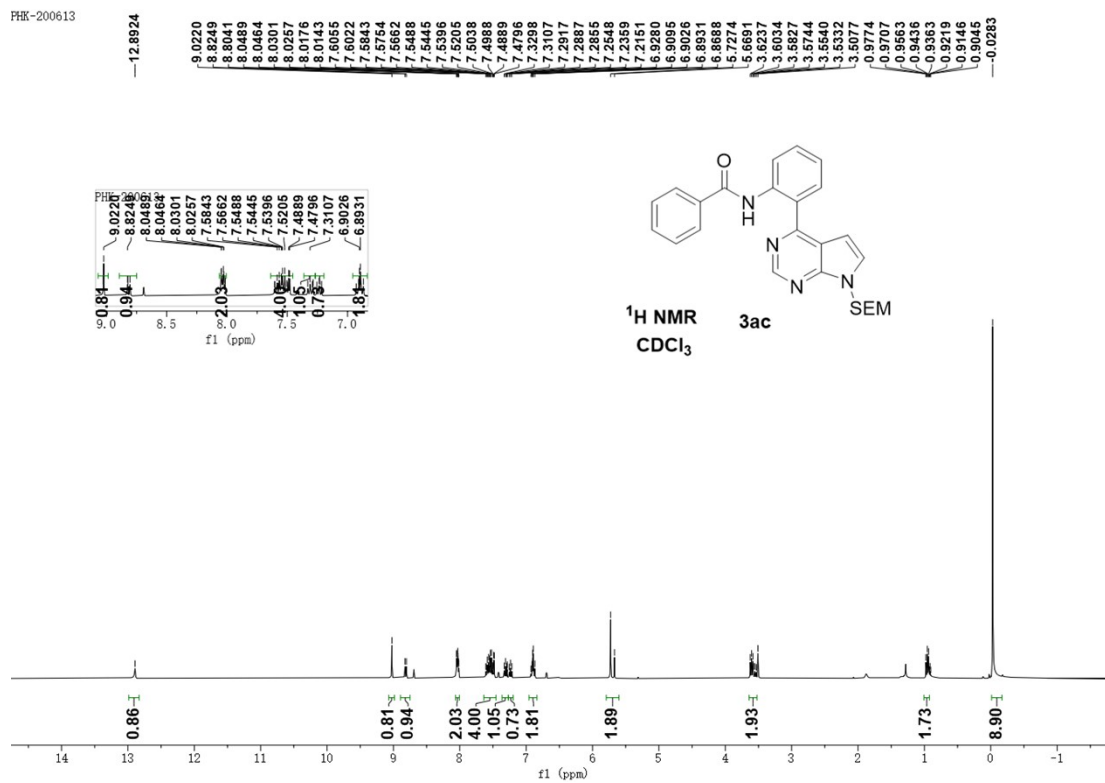
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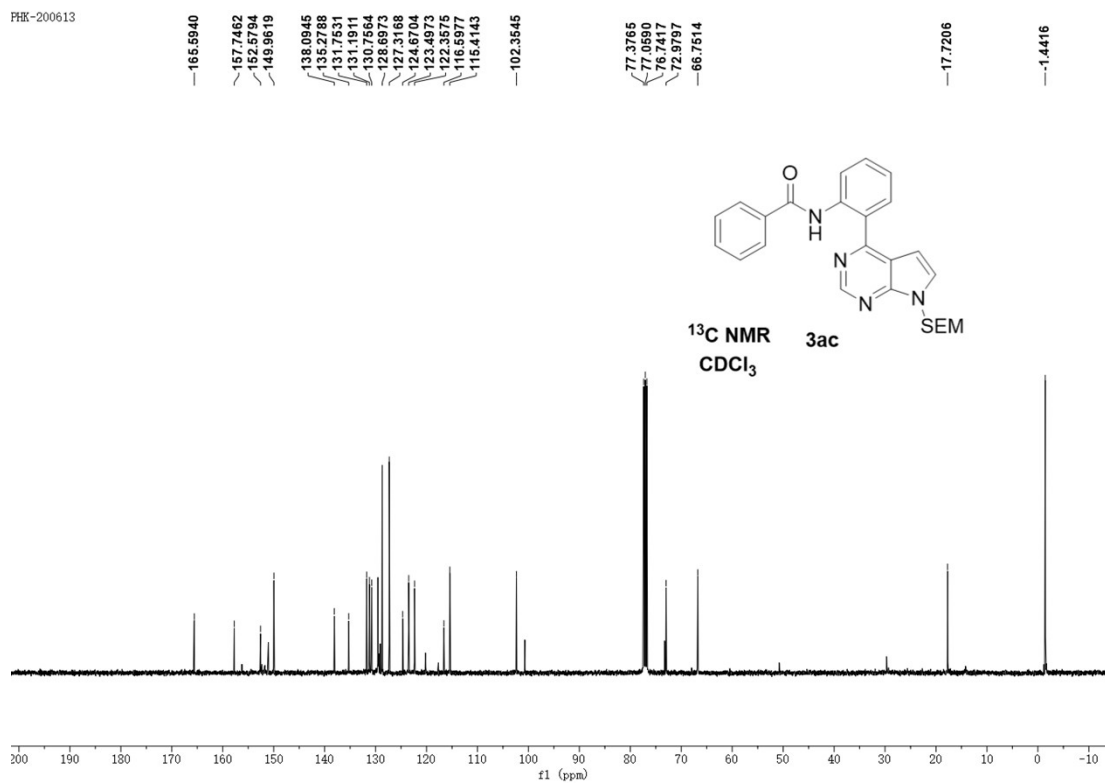
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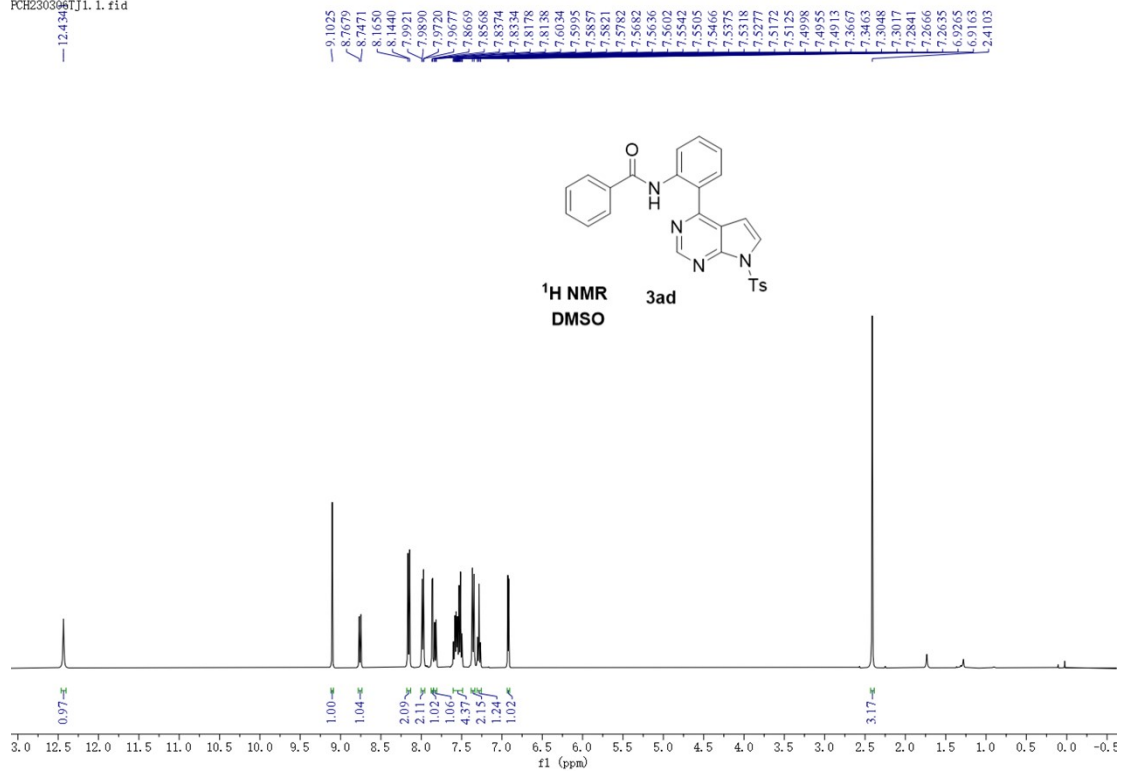
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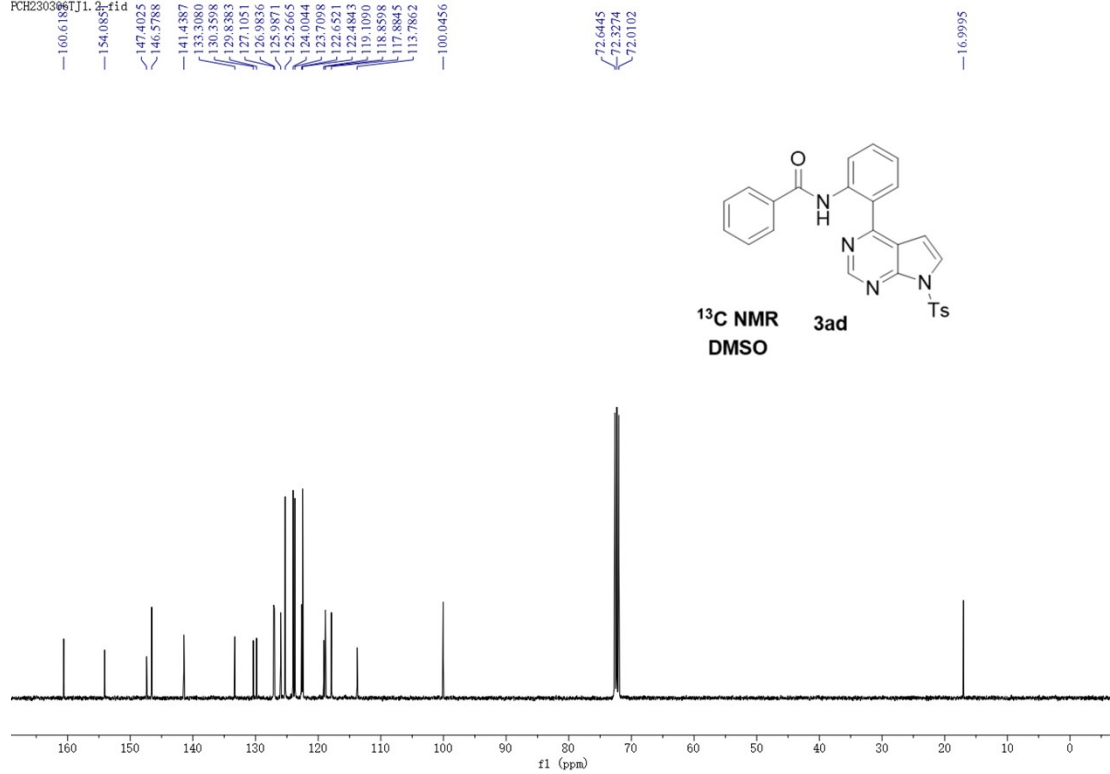
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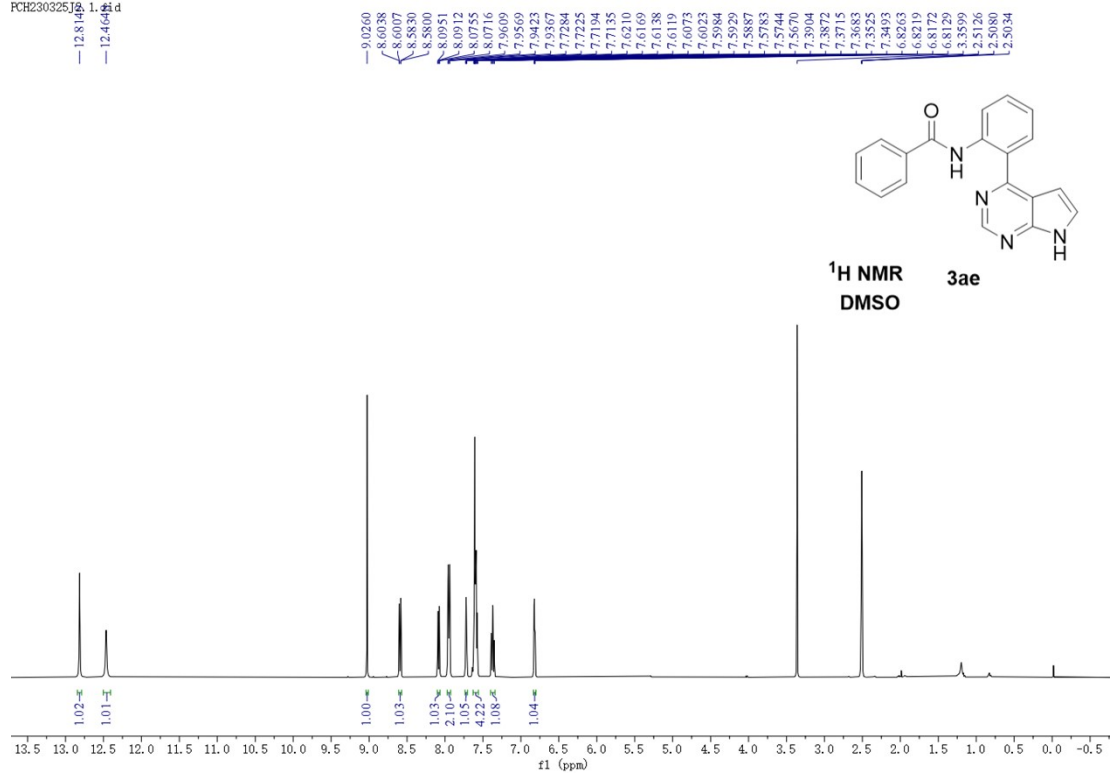
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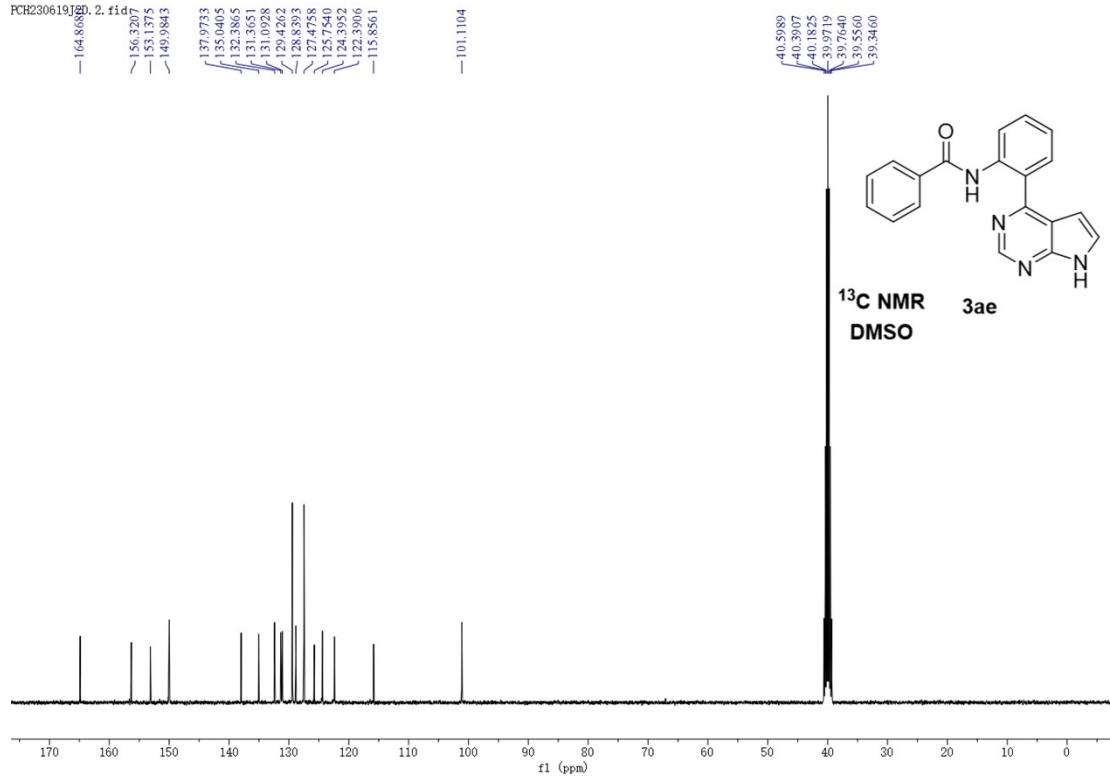
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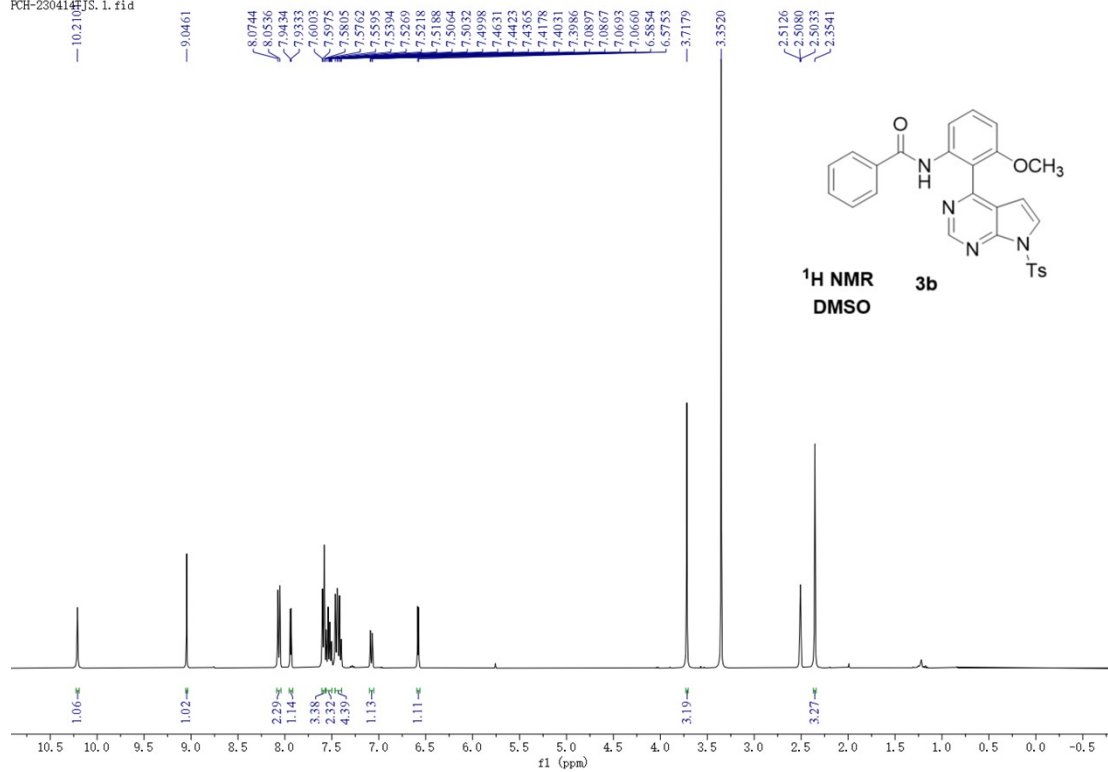
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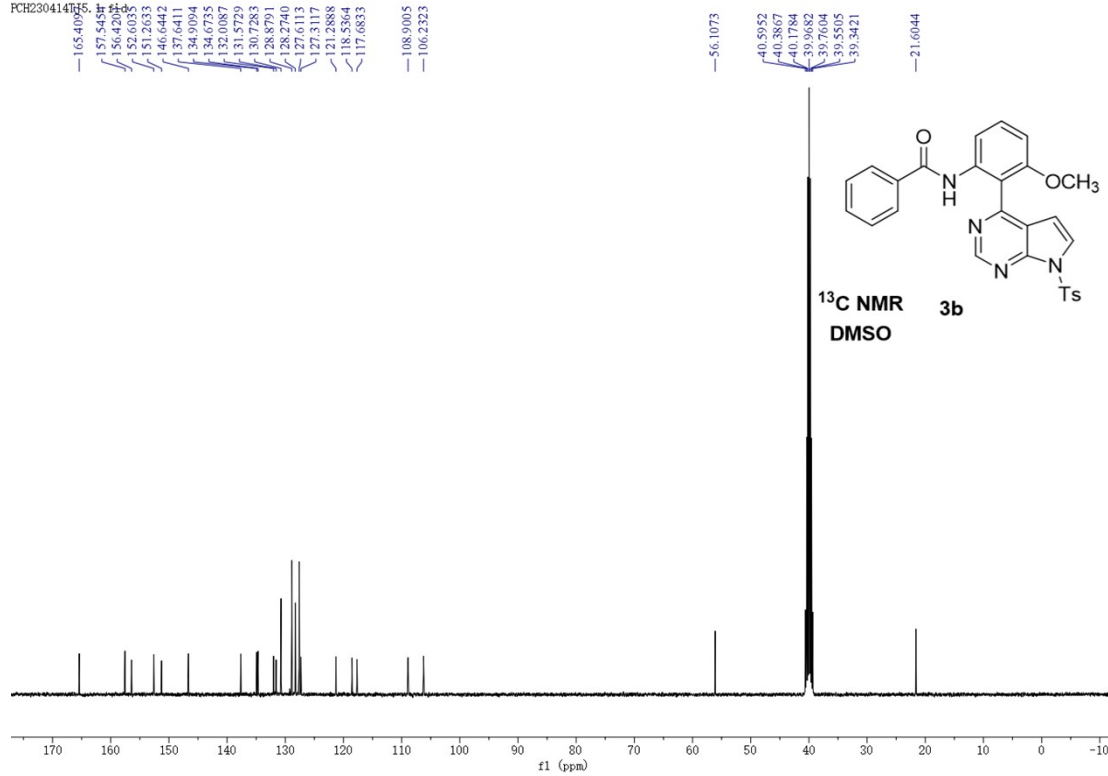
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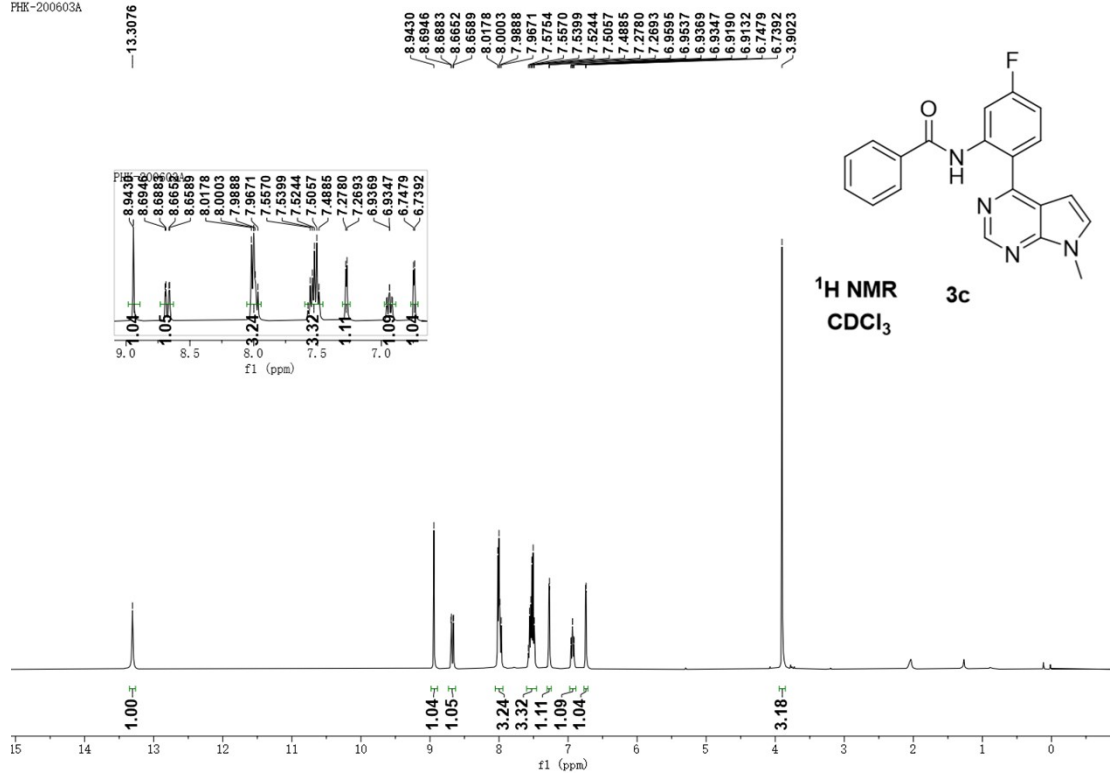


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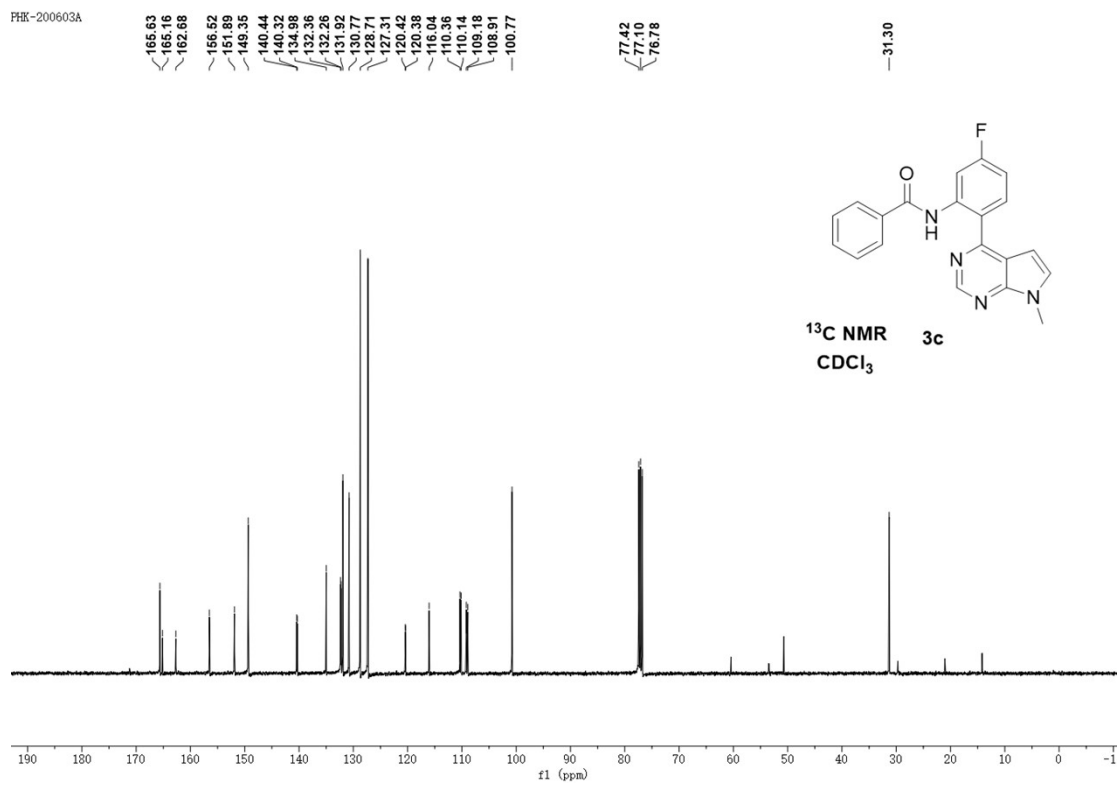


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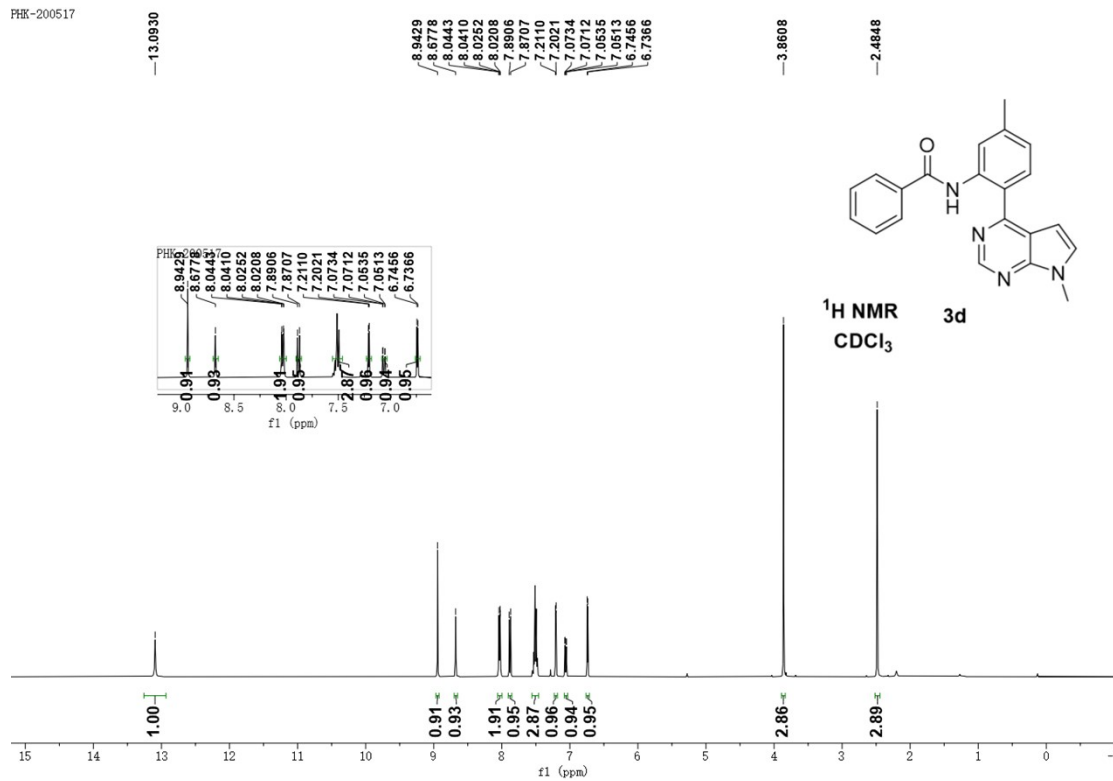
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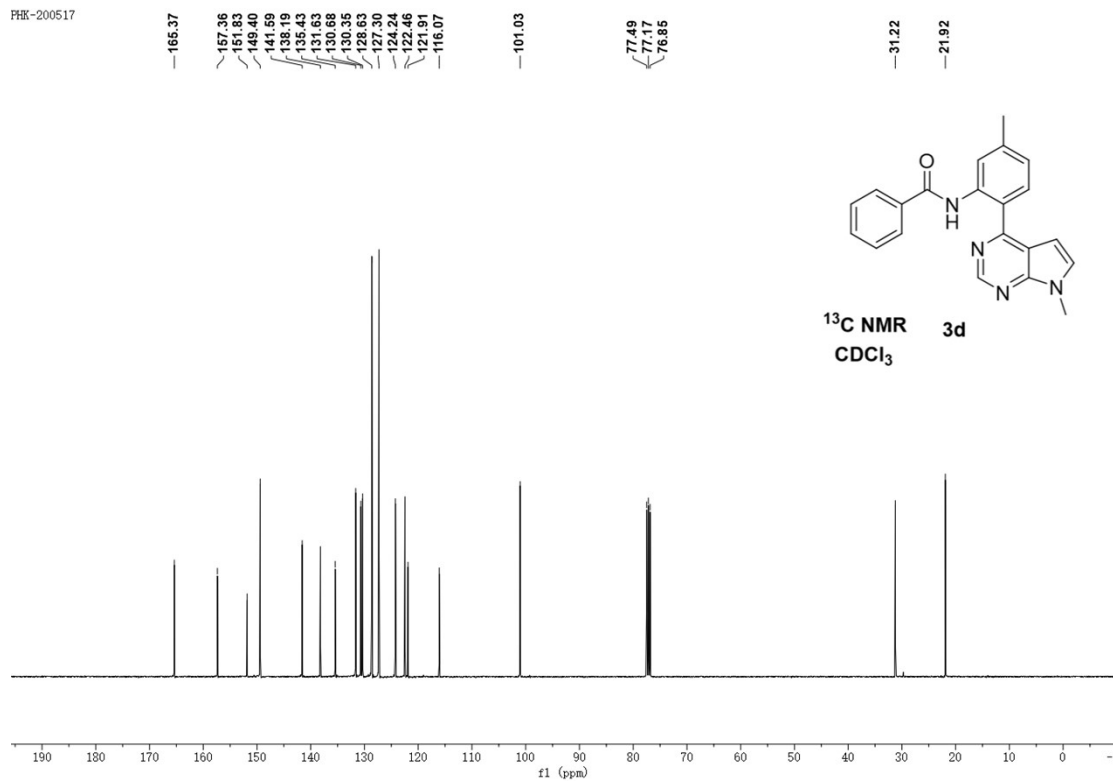
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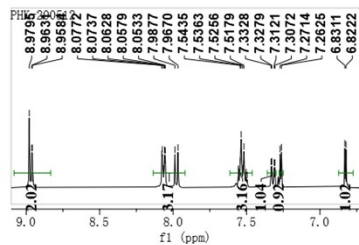


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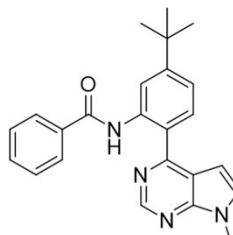
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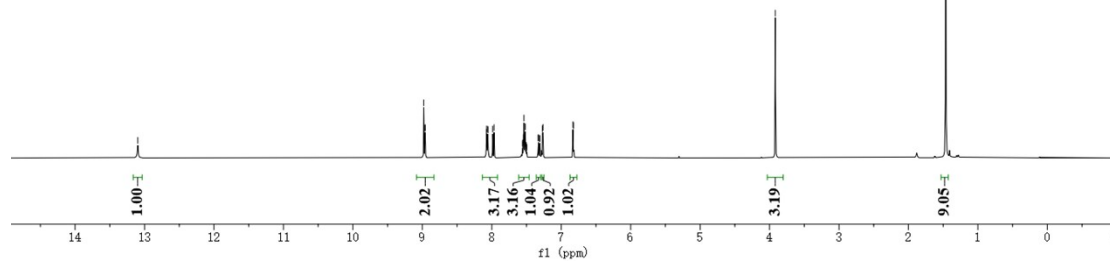
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¹H NMR
CDCl₃

3e



PHK-200512

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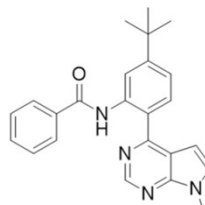
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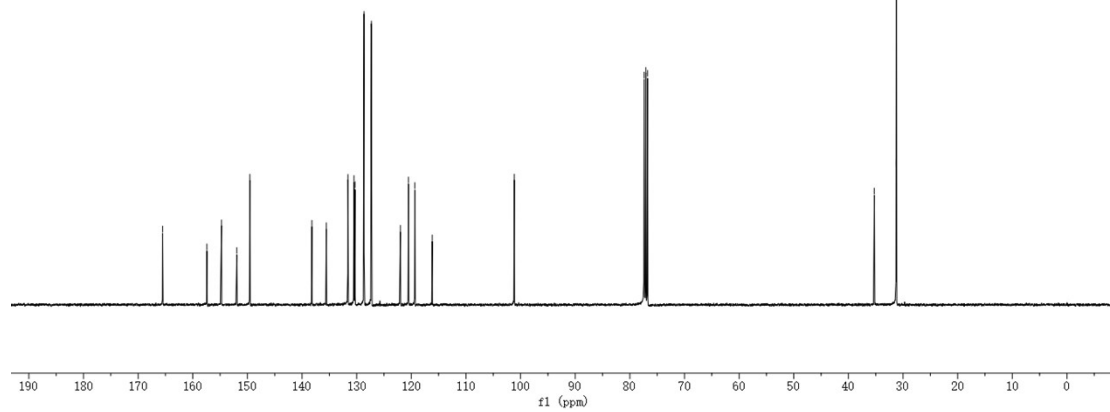
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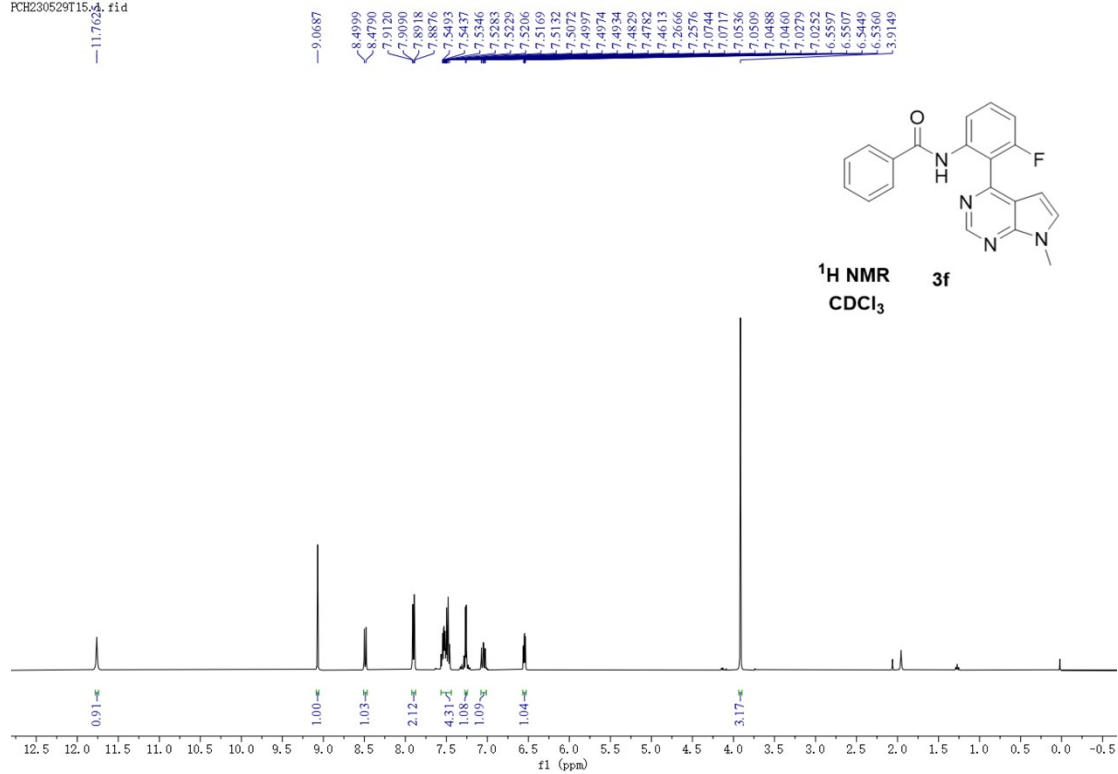


¹³C NMR
CDCl₃

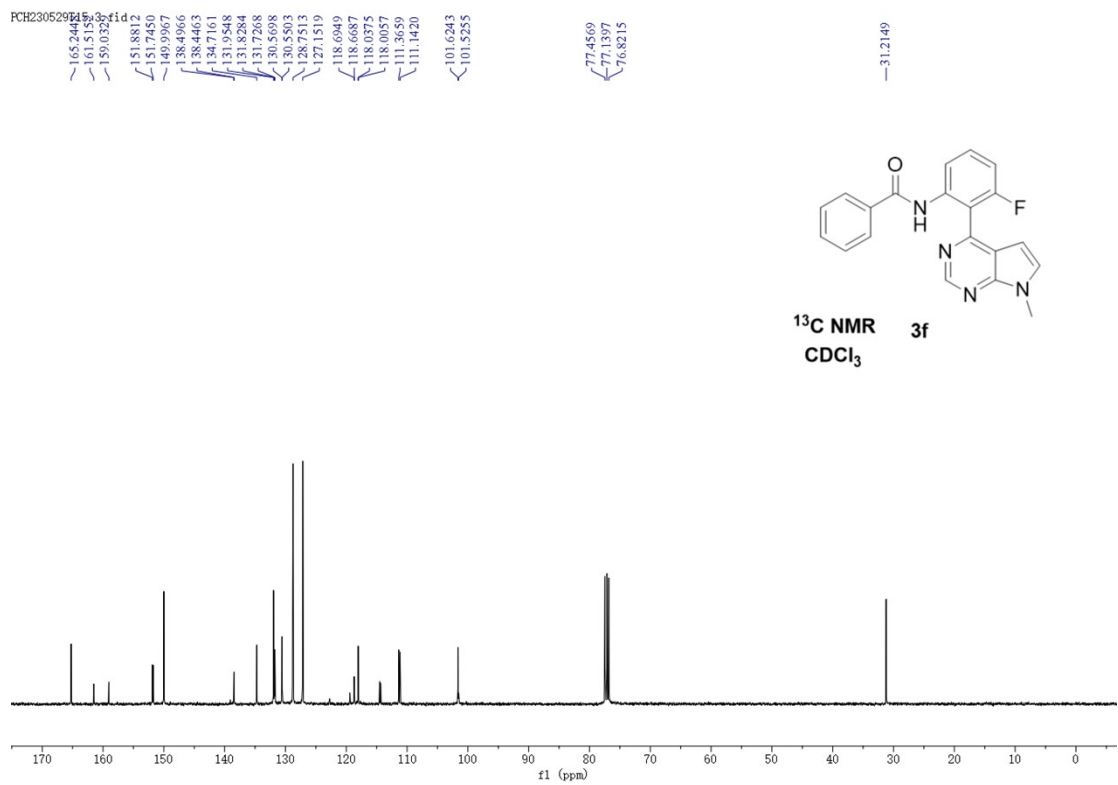
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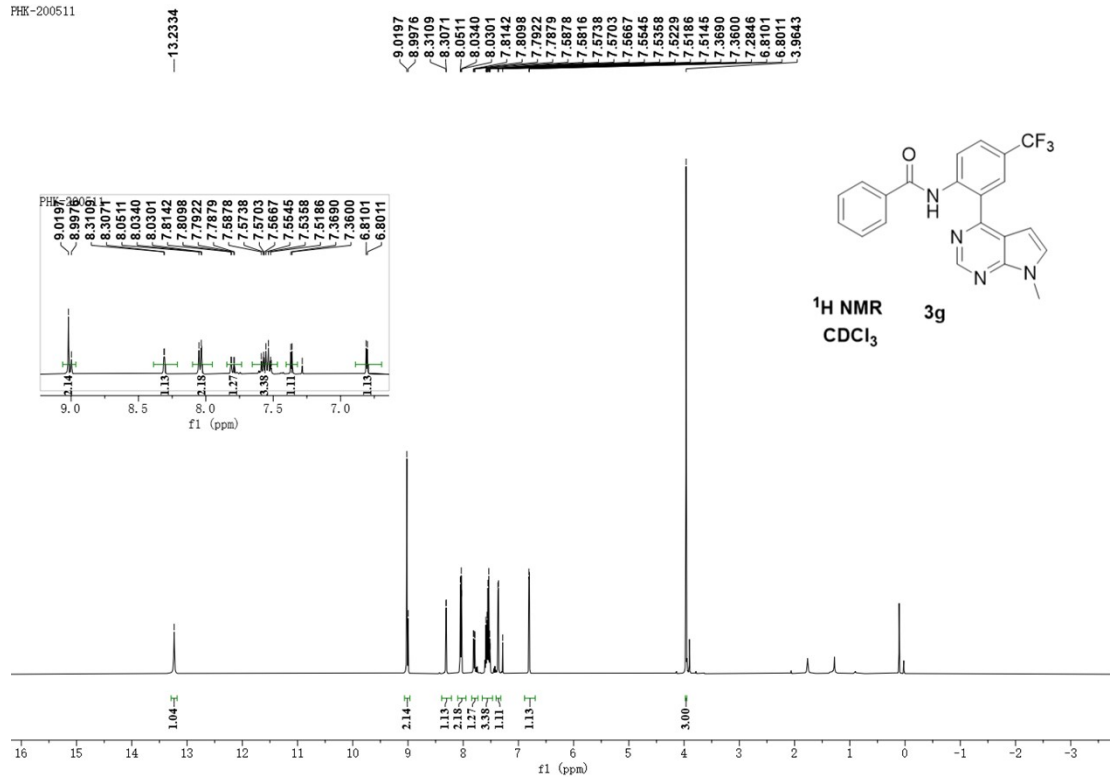
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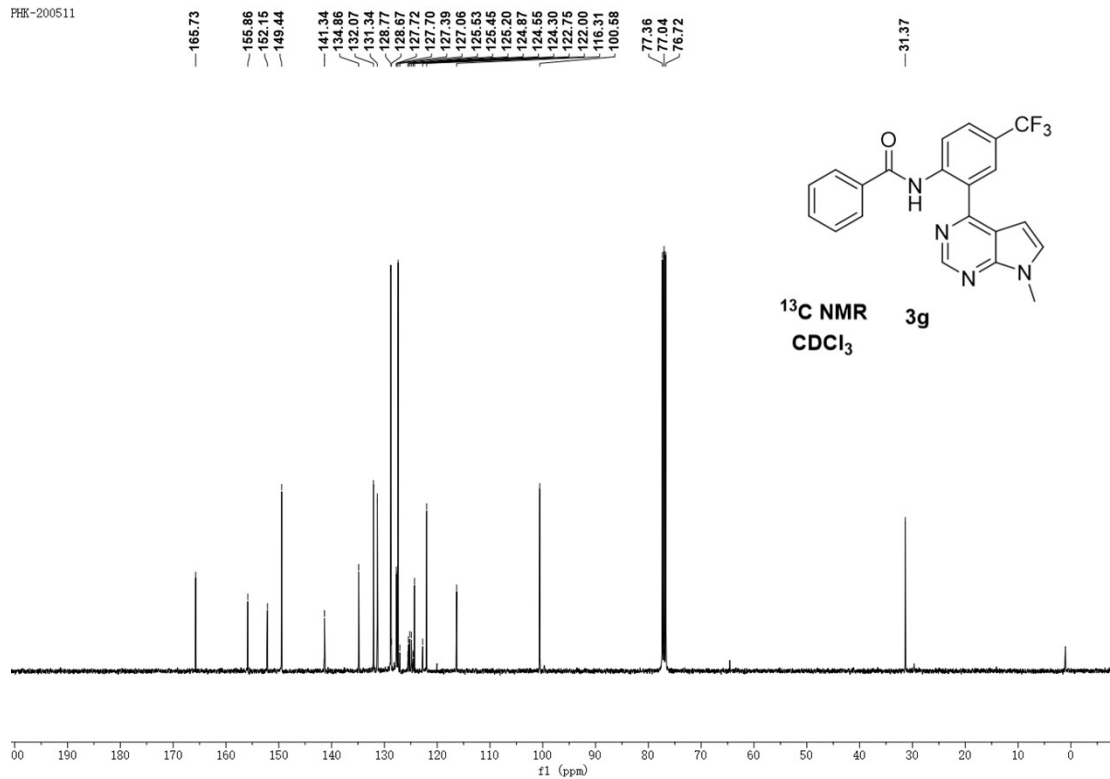
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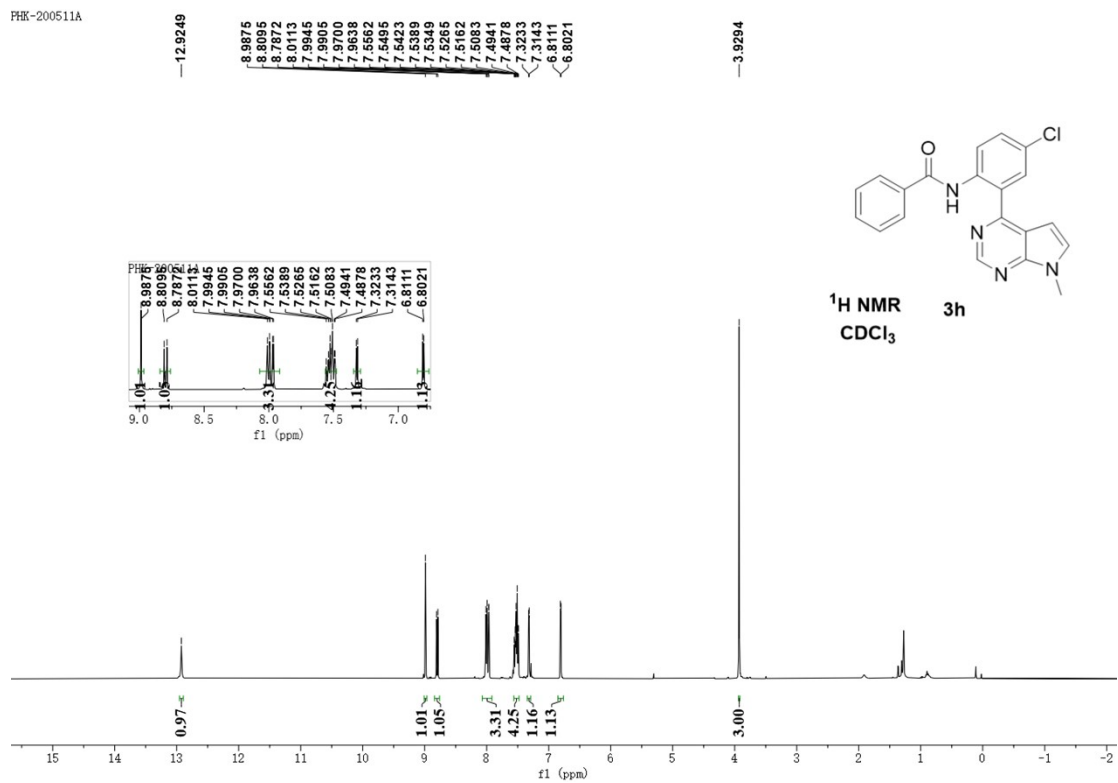
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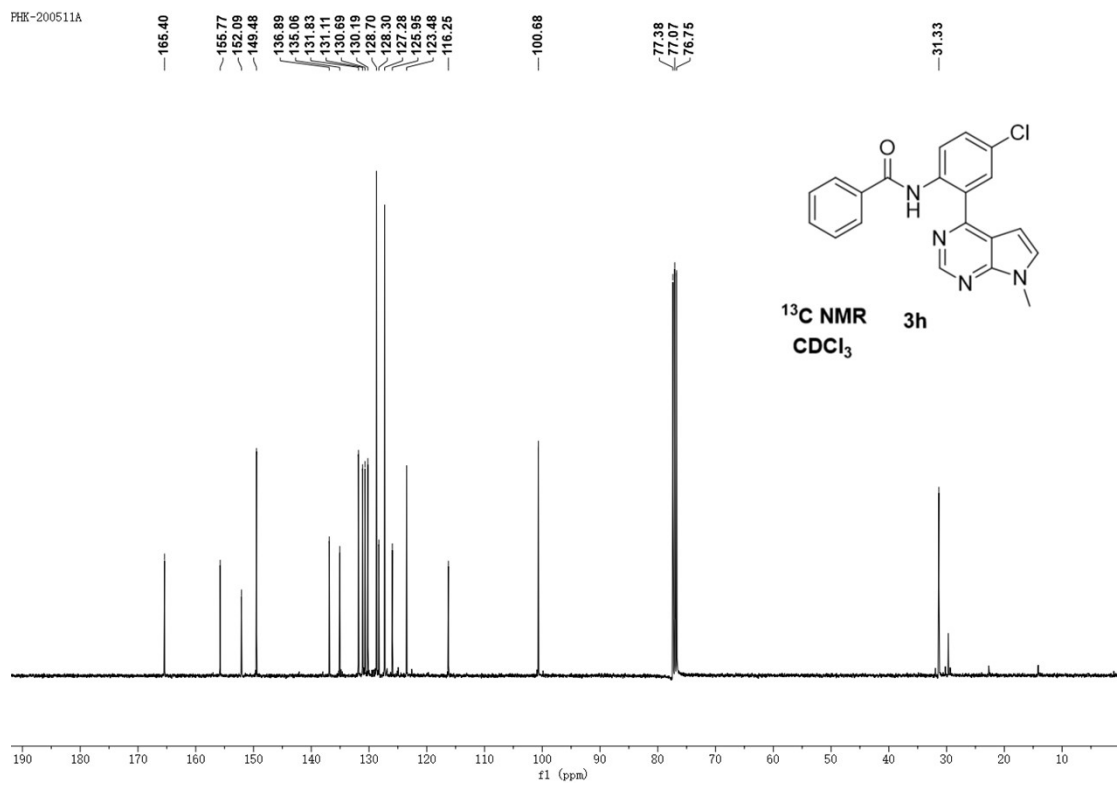
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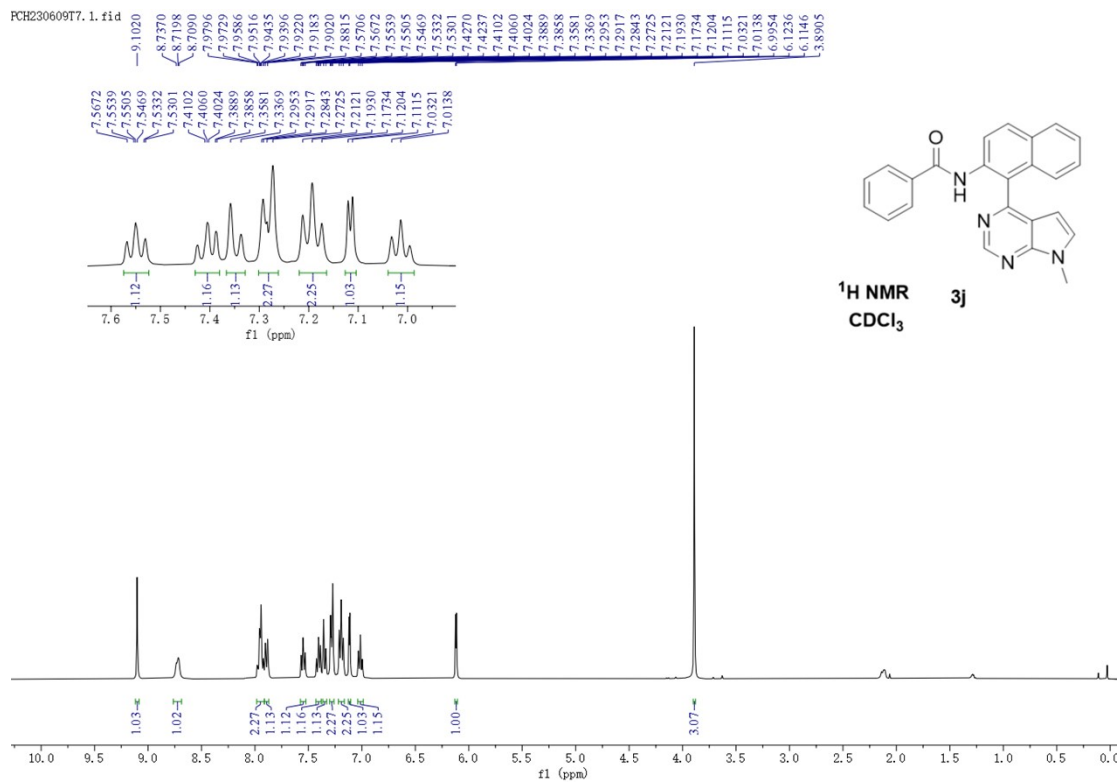
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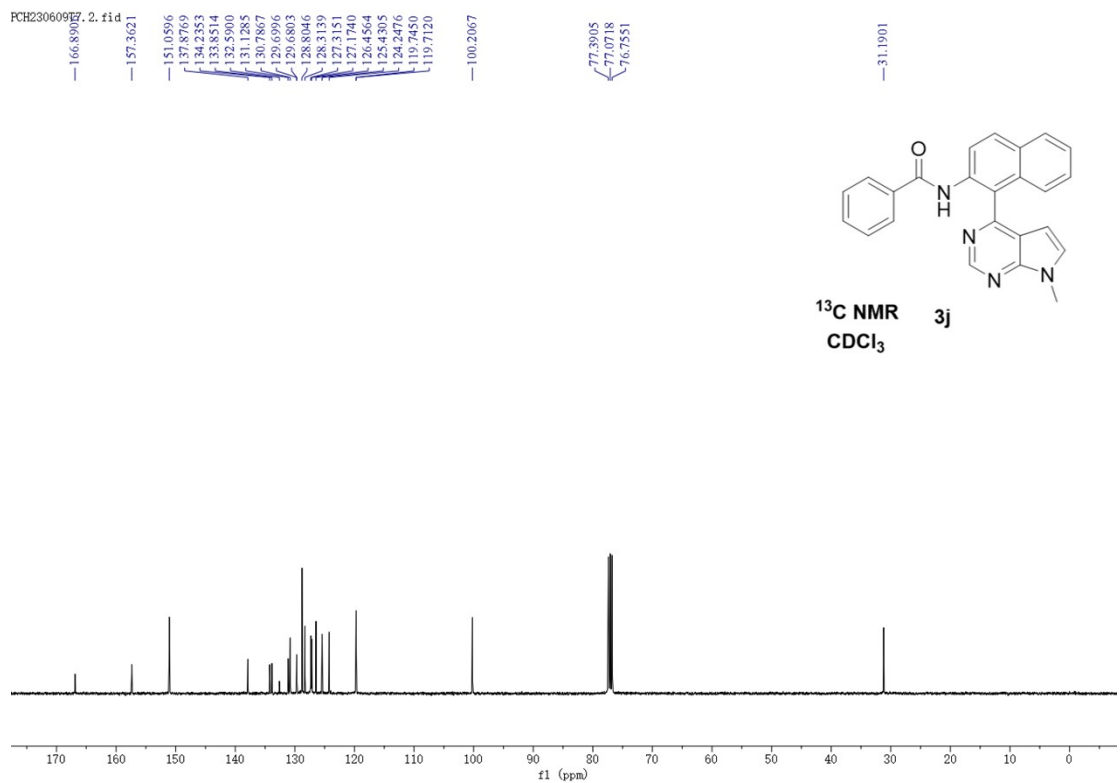
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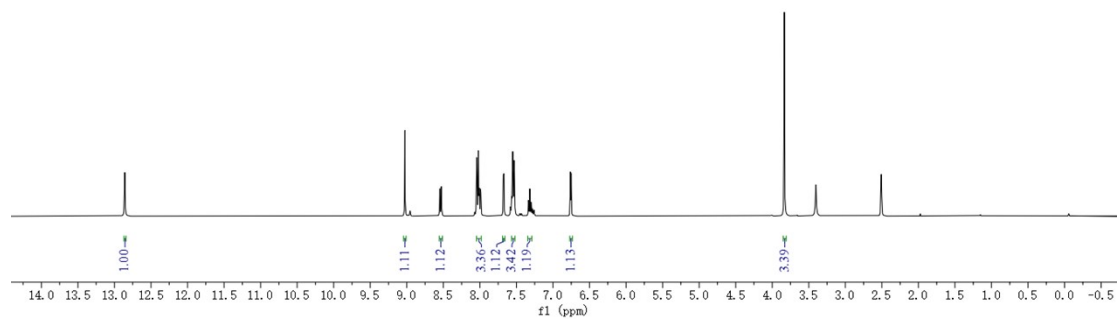
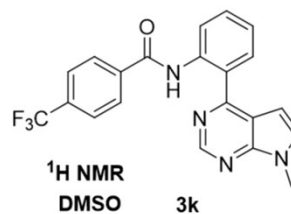
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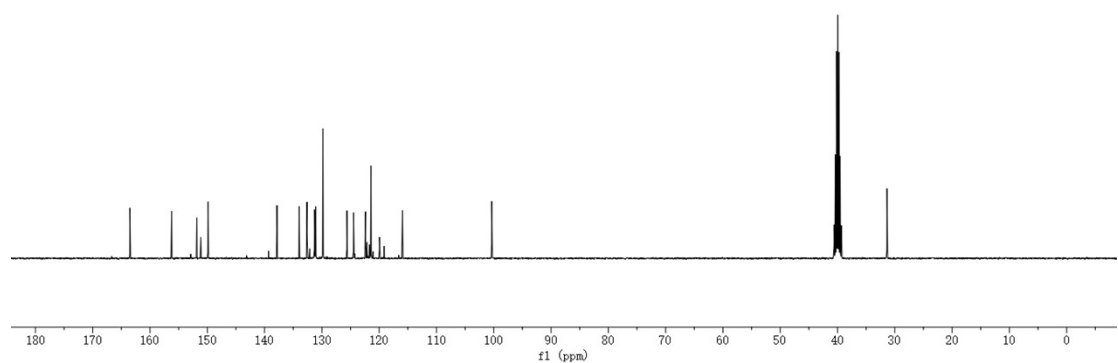
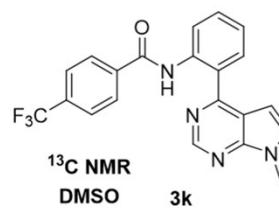
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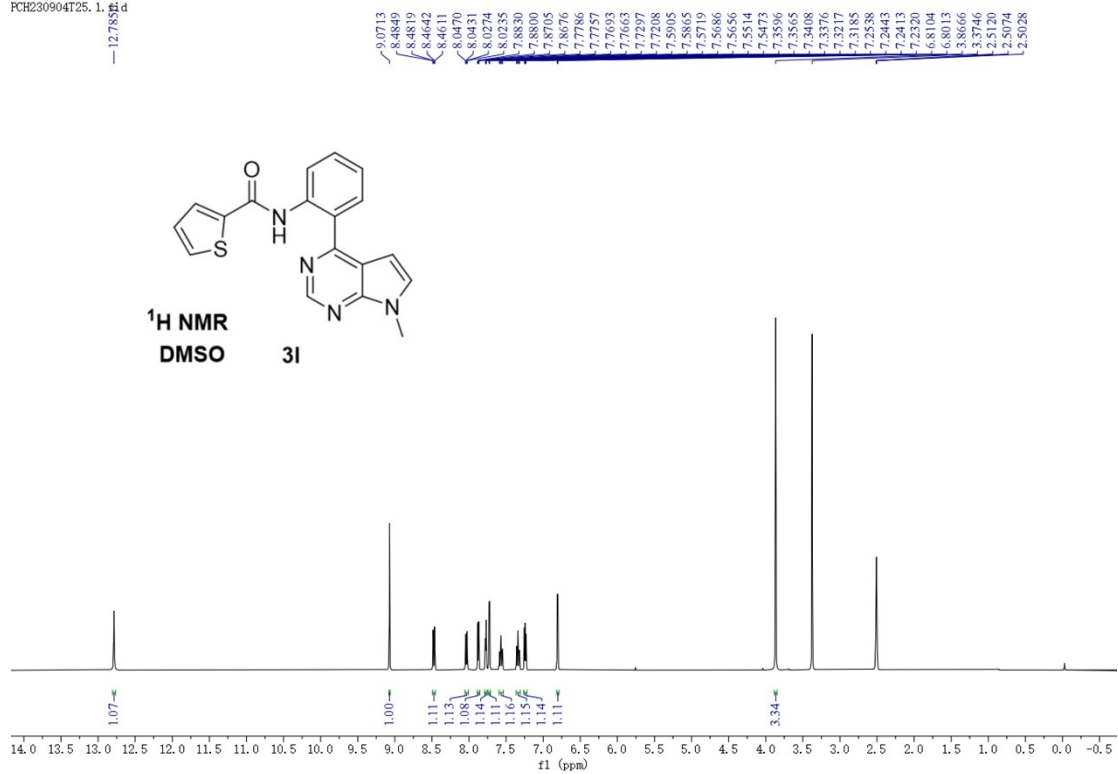
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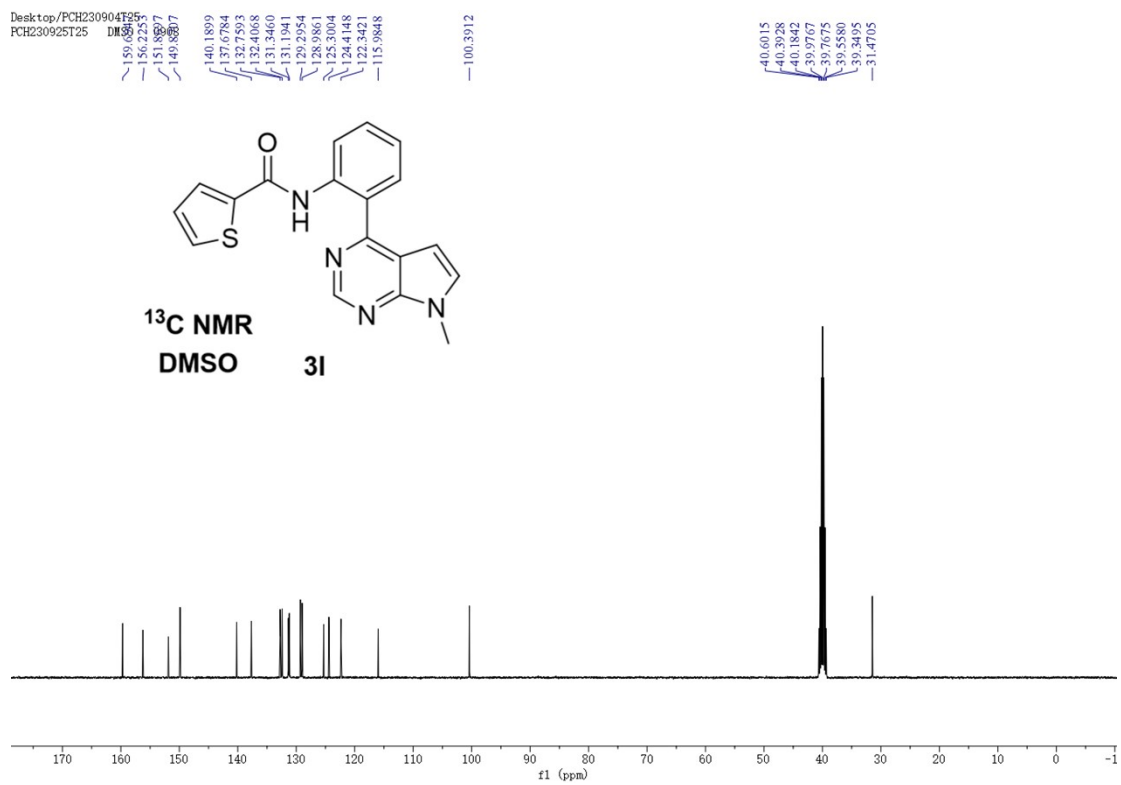
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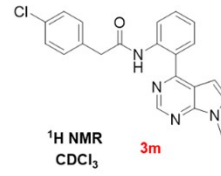
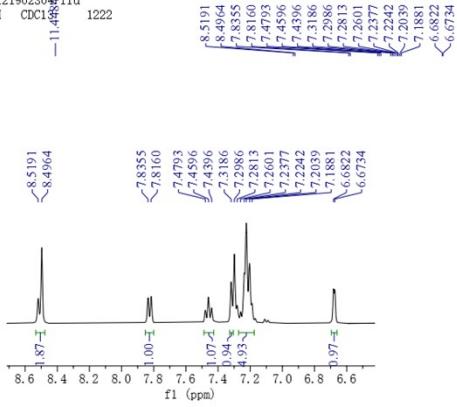
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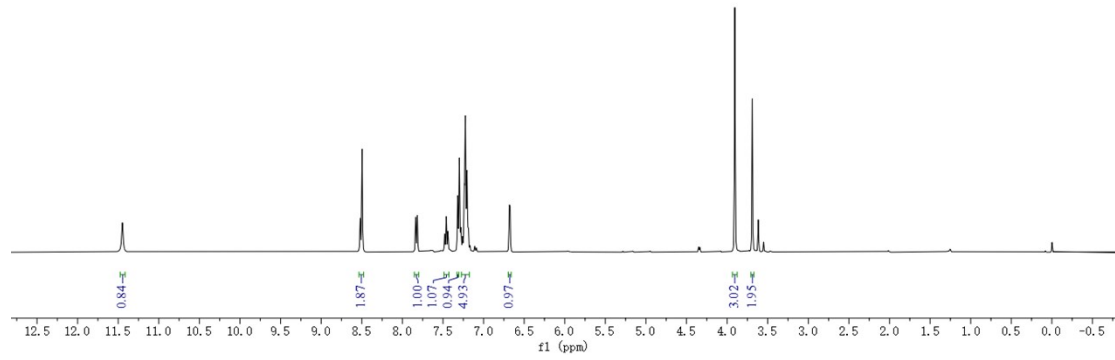
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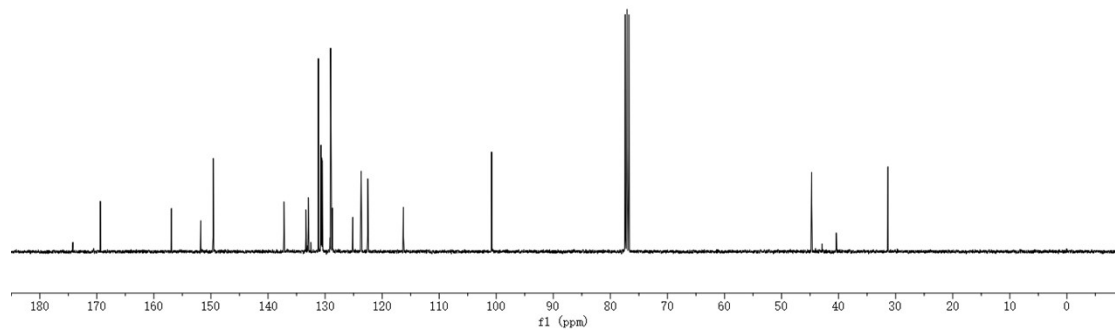


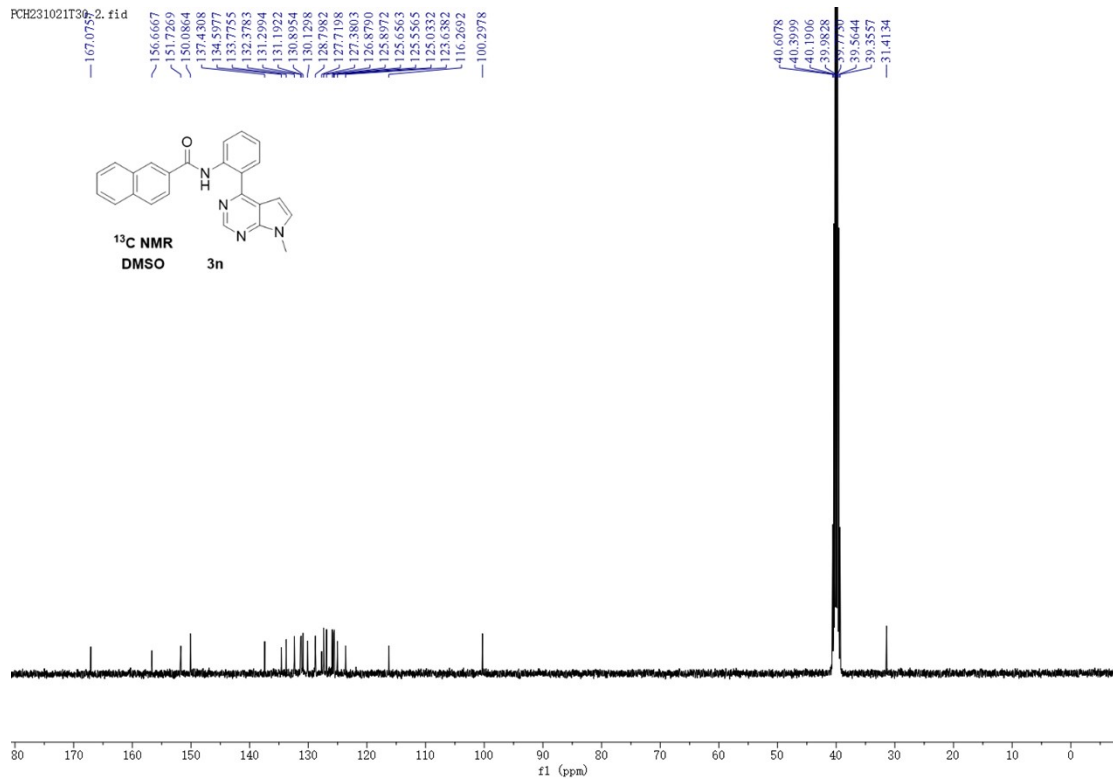
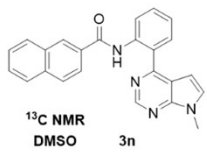
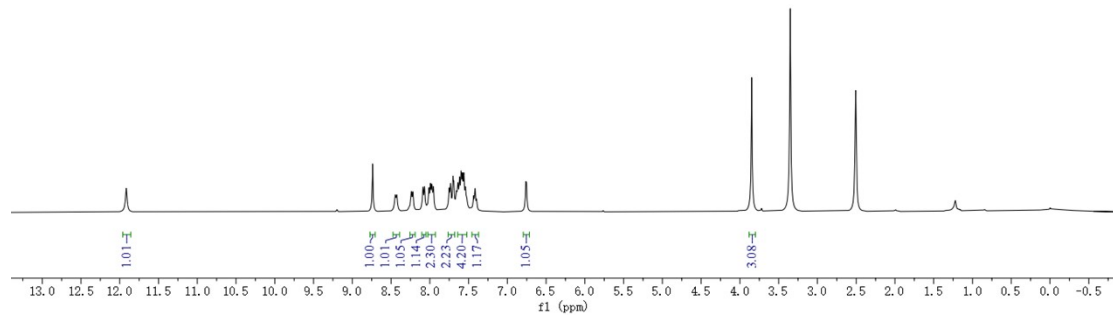
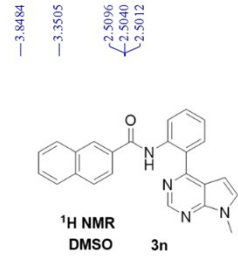
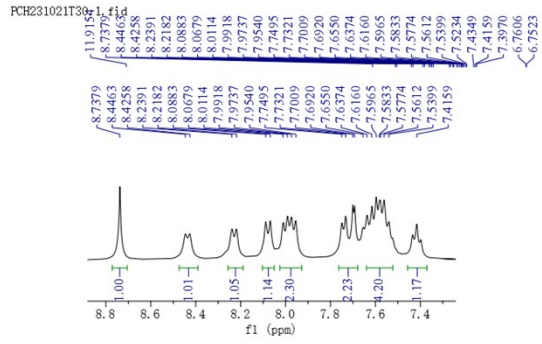
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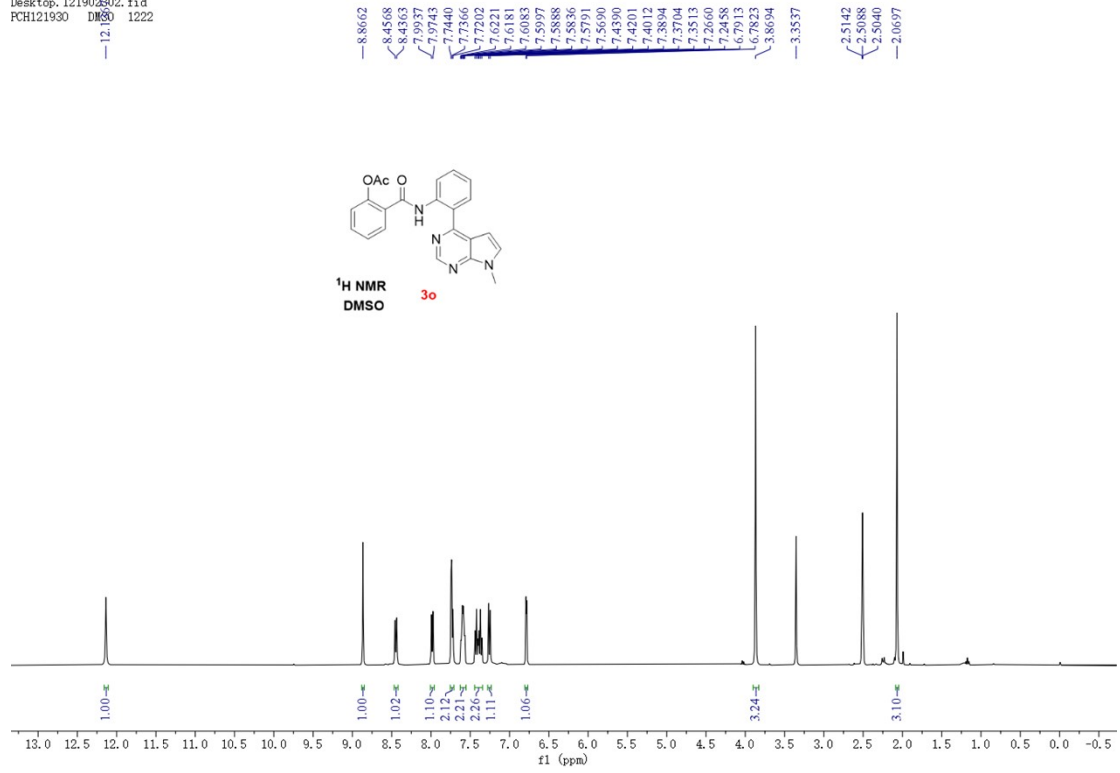
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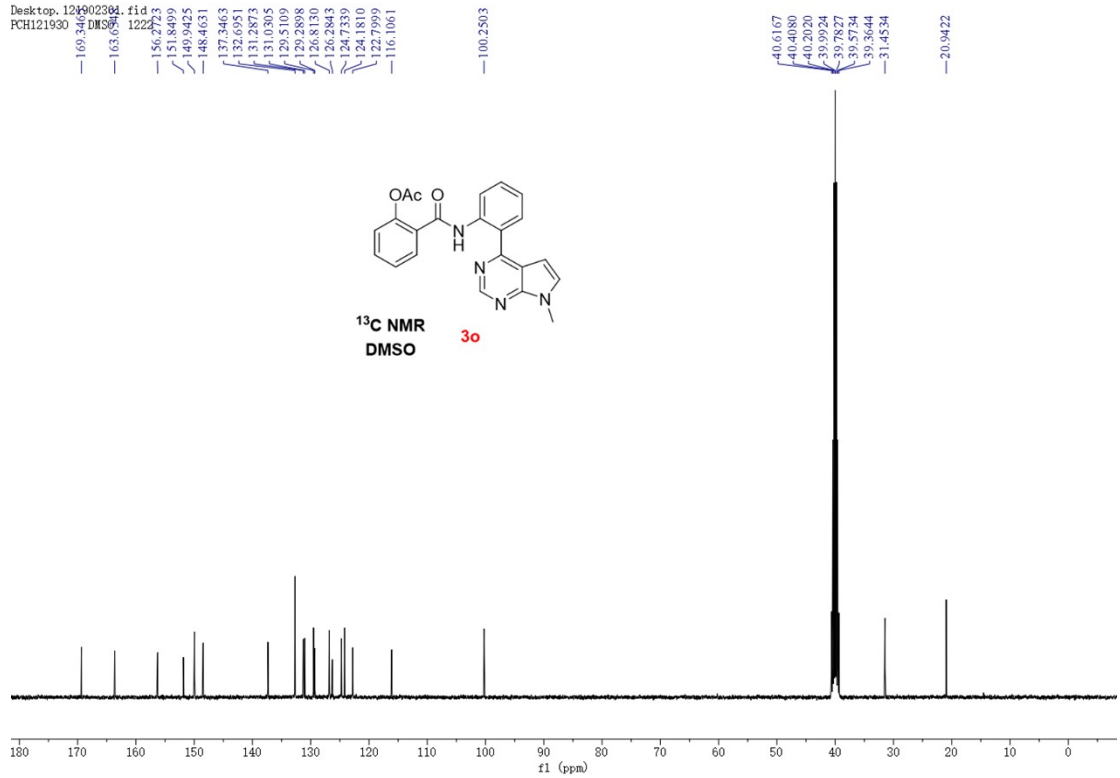




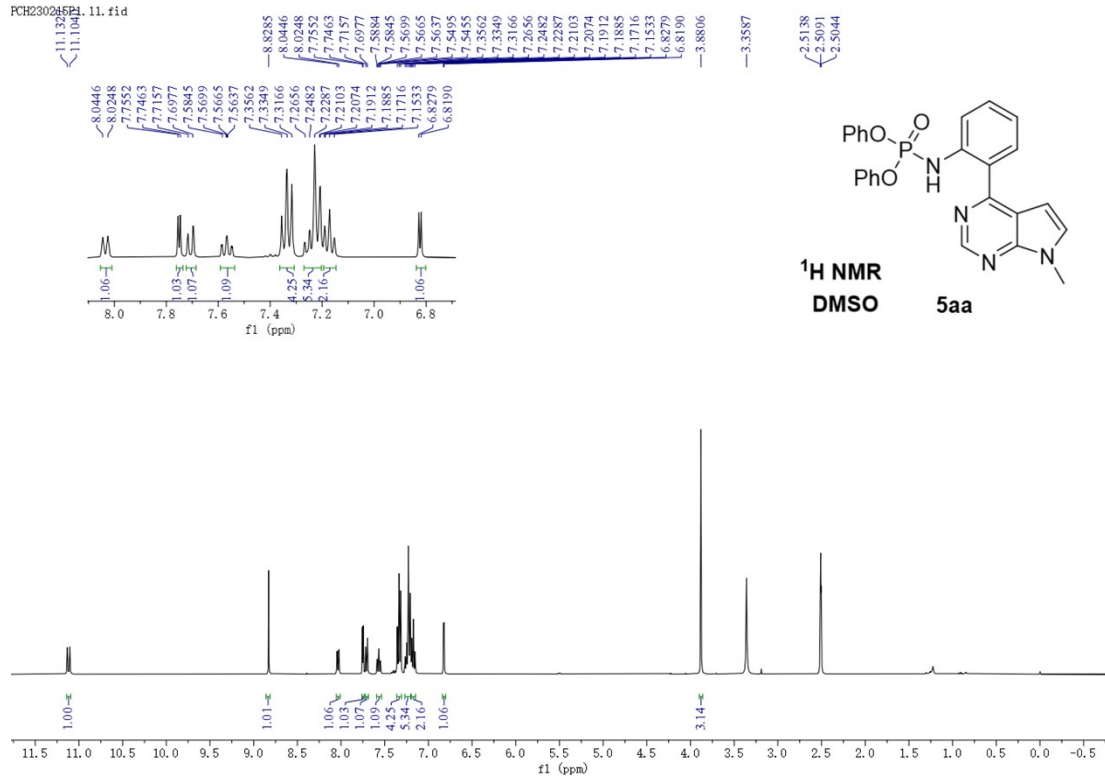
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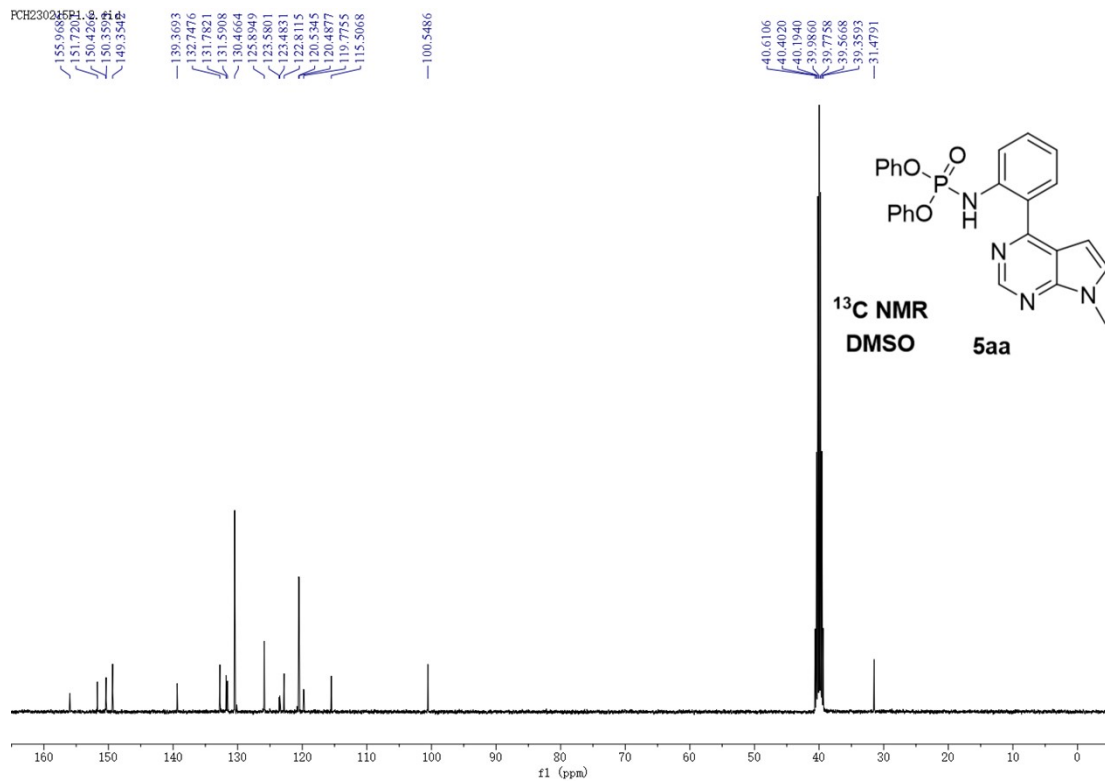
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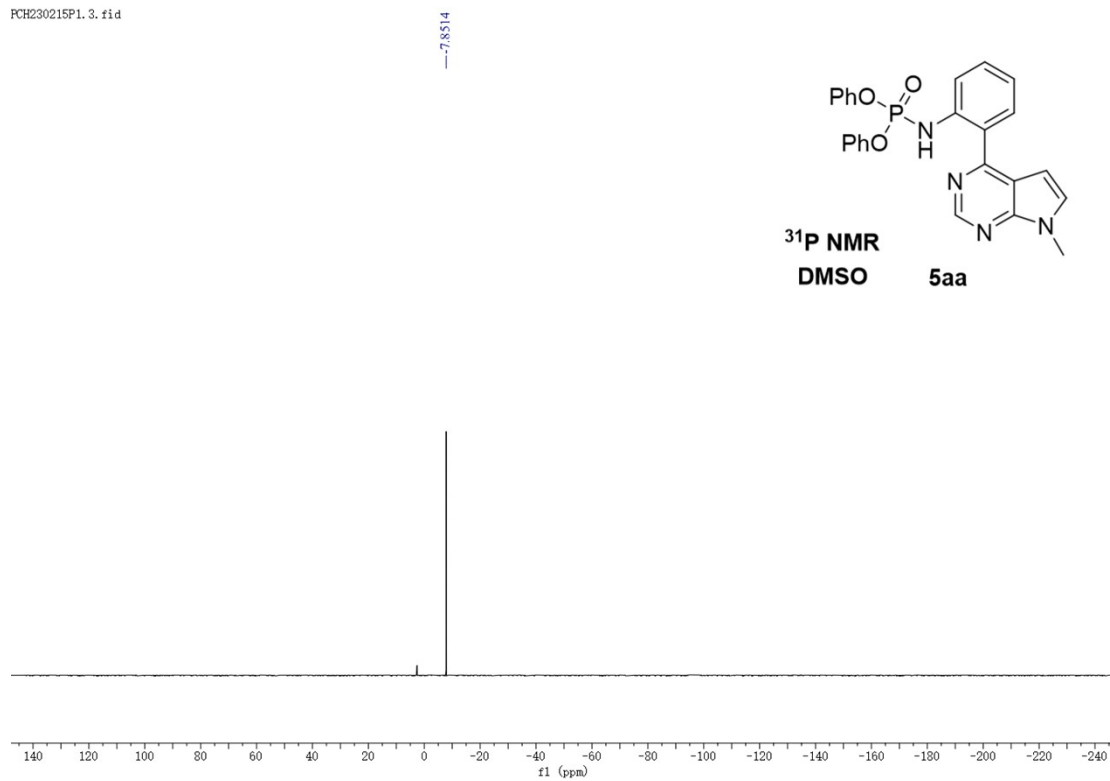
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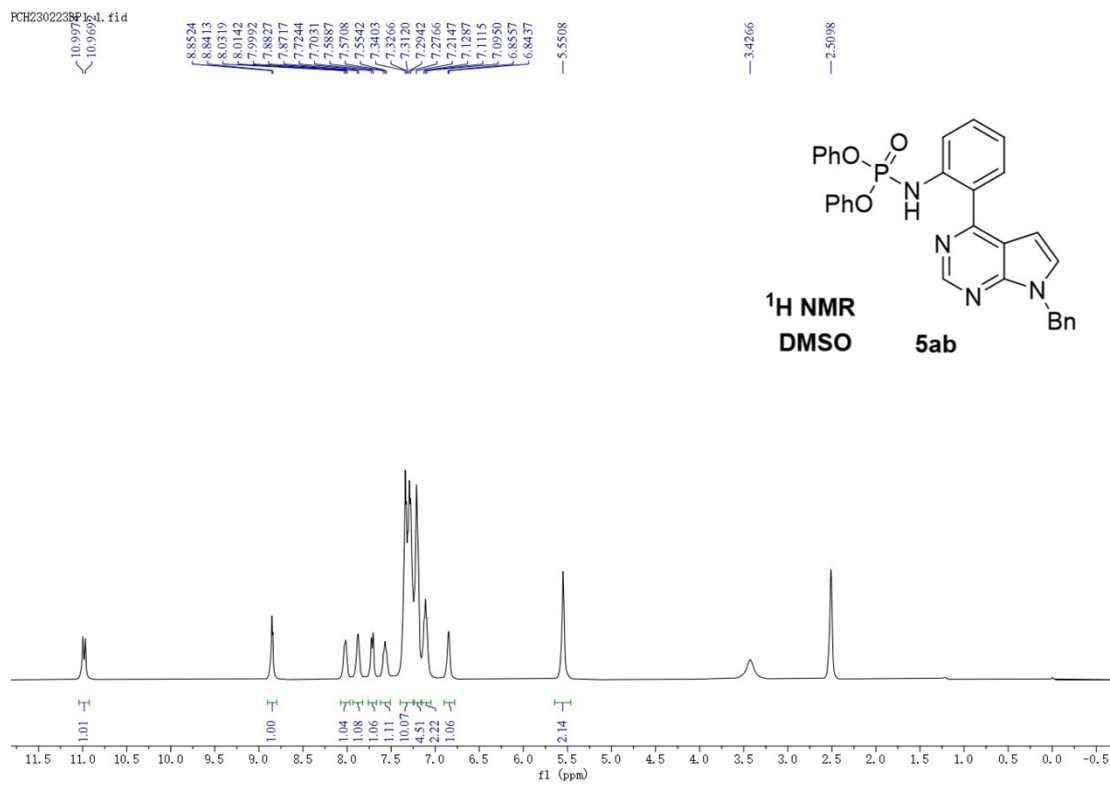
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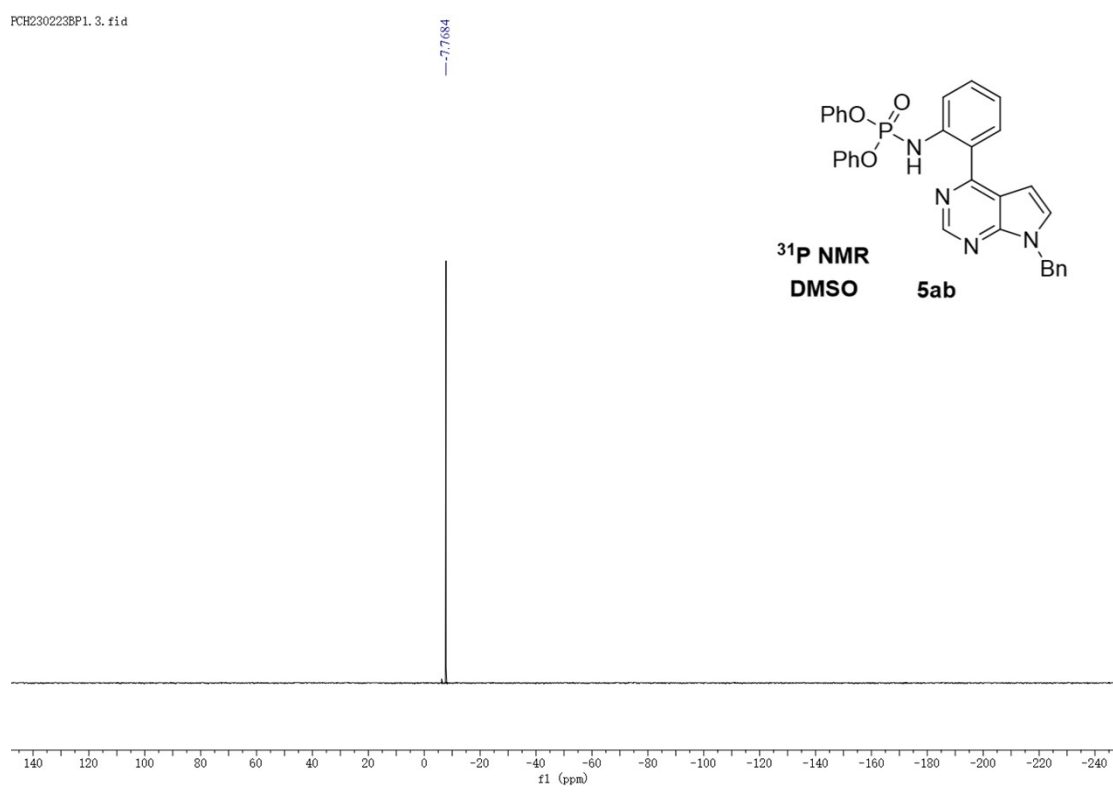
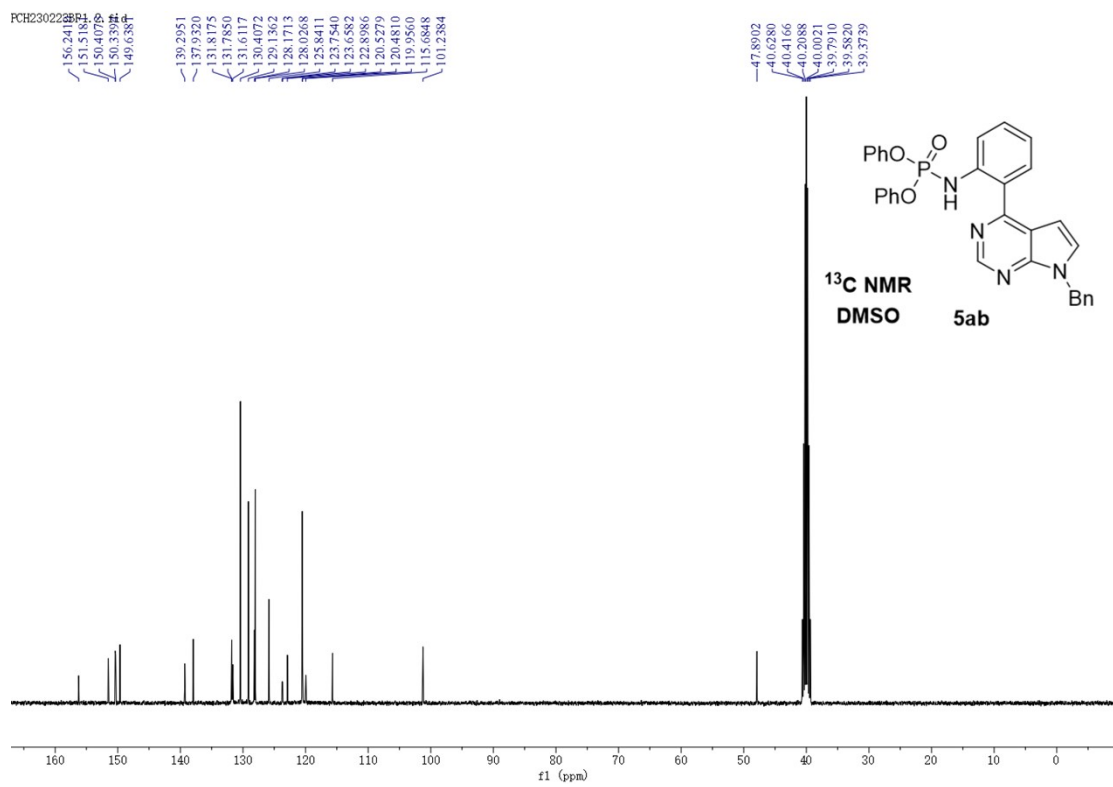


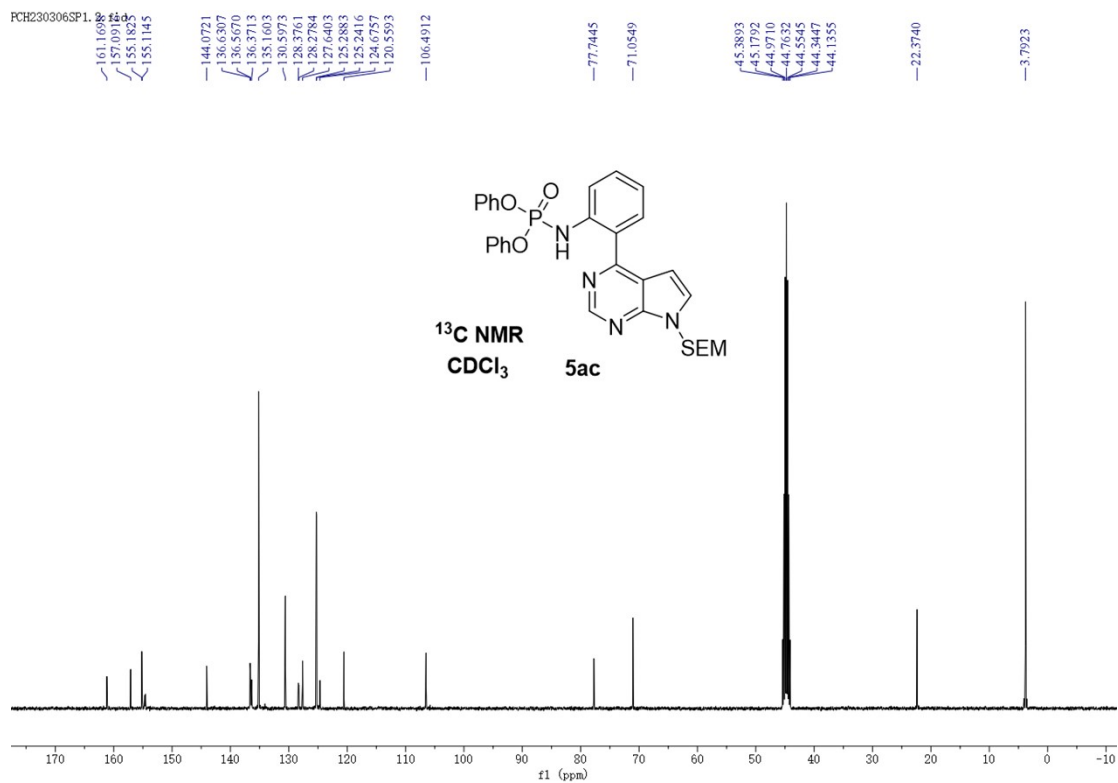
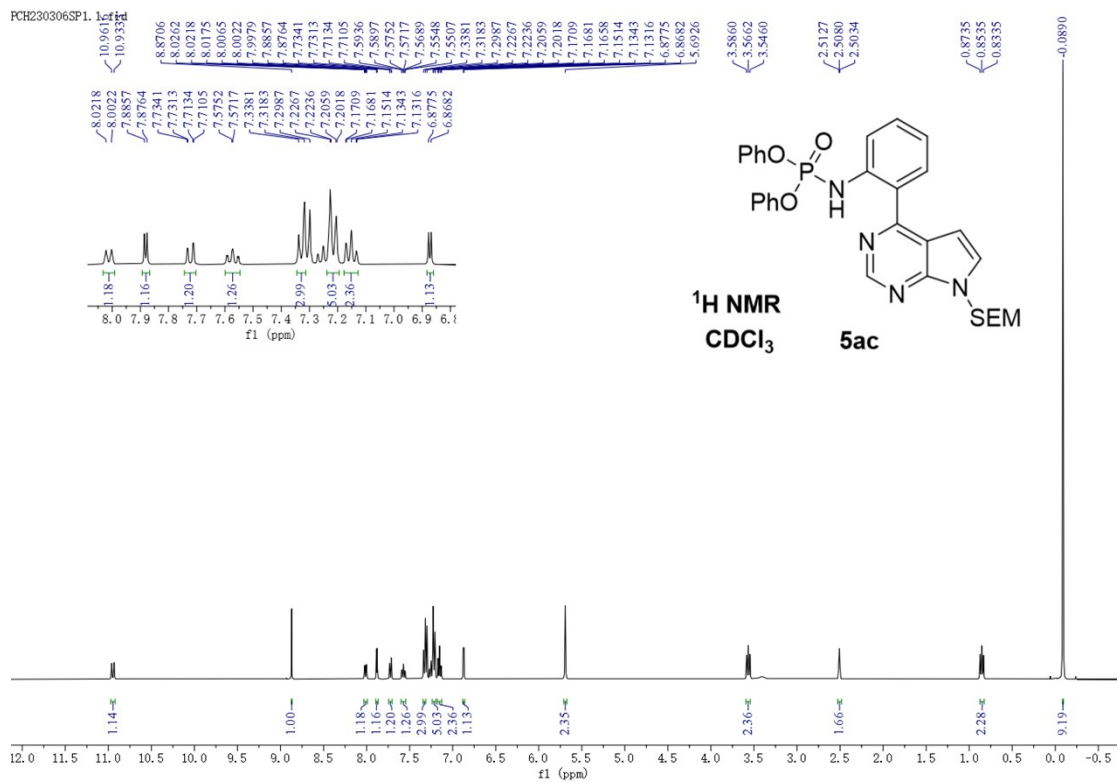
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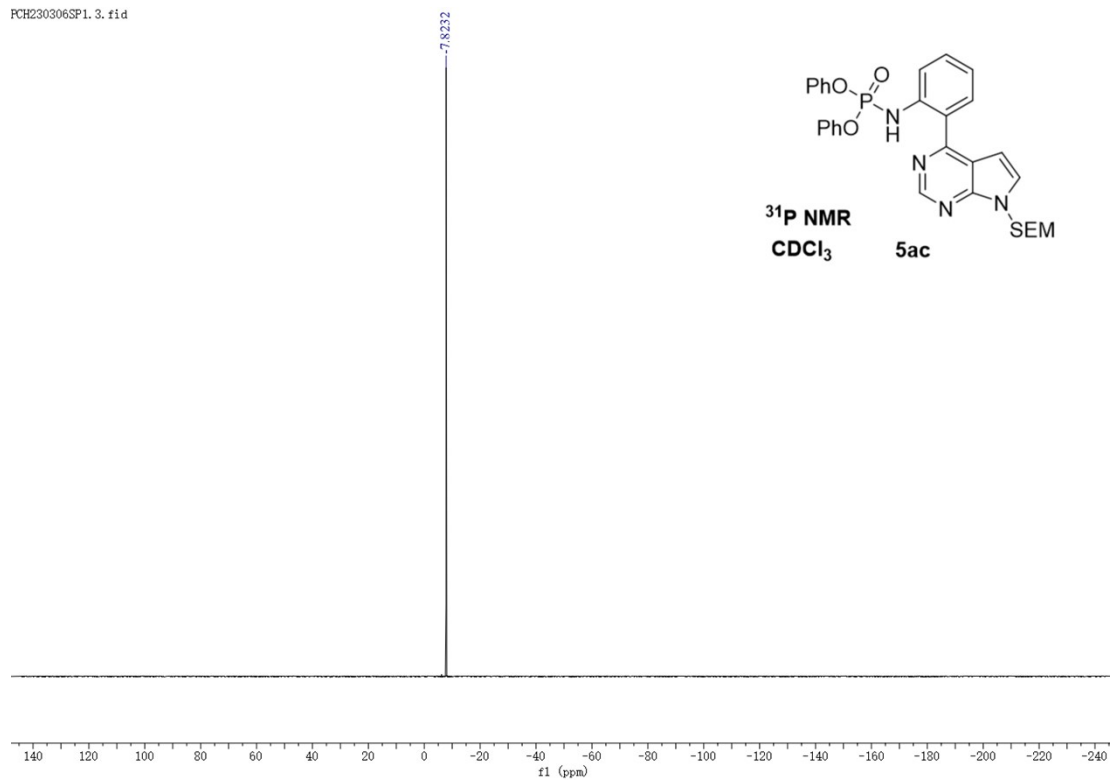
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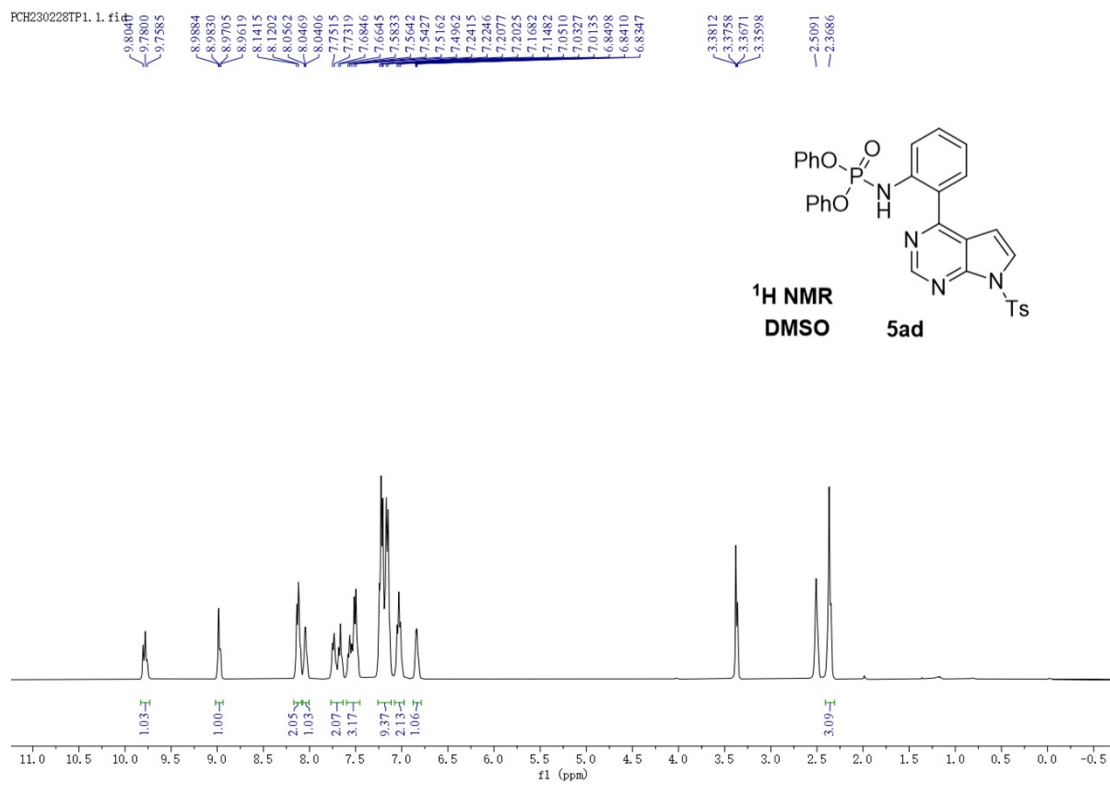


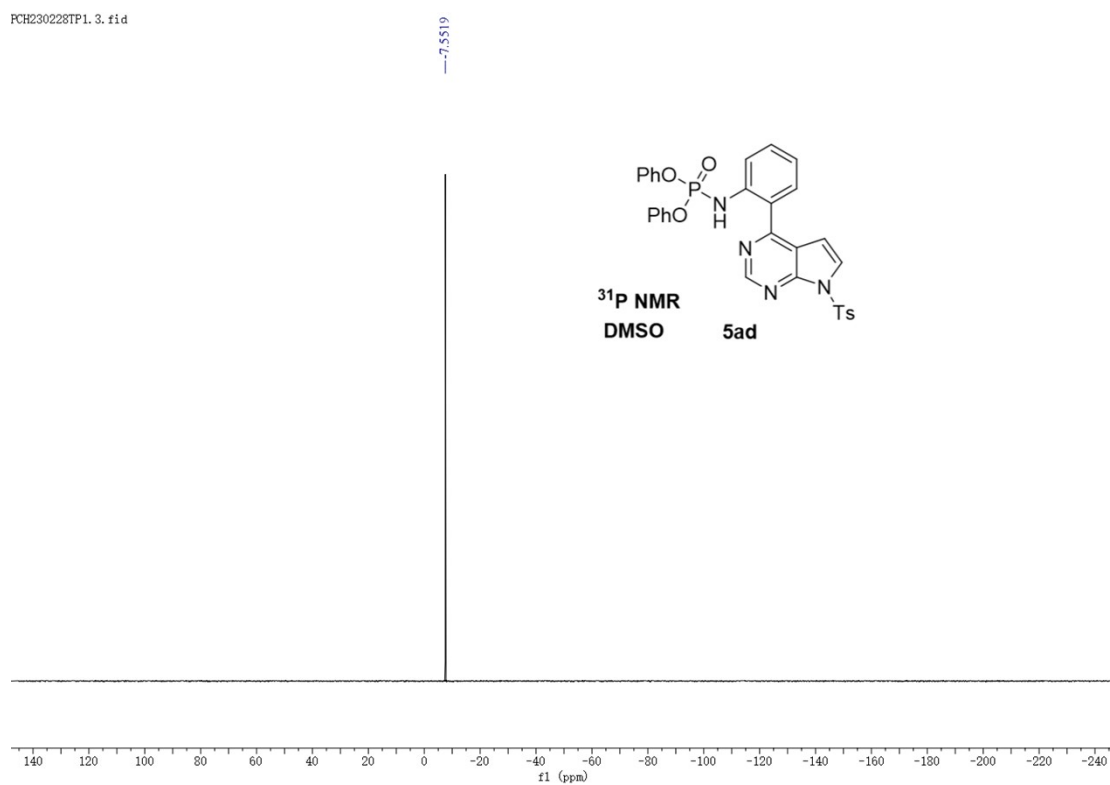
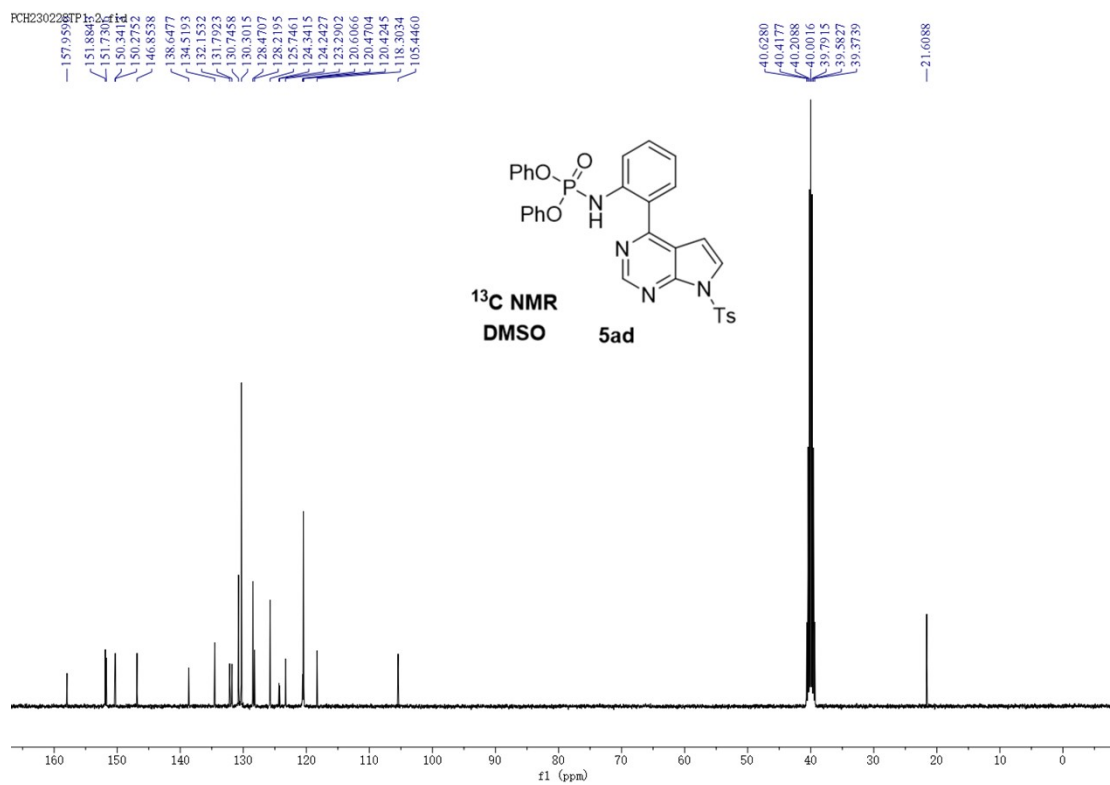


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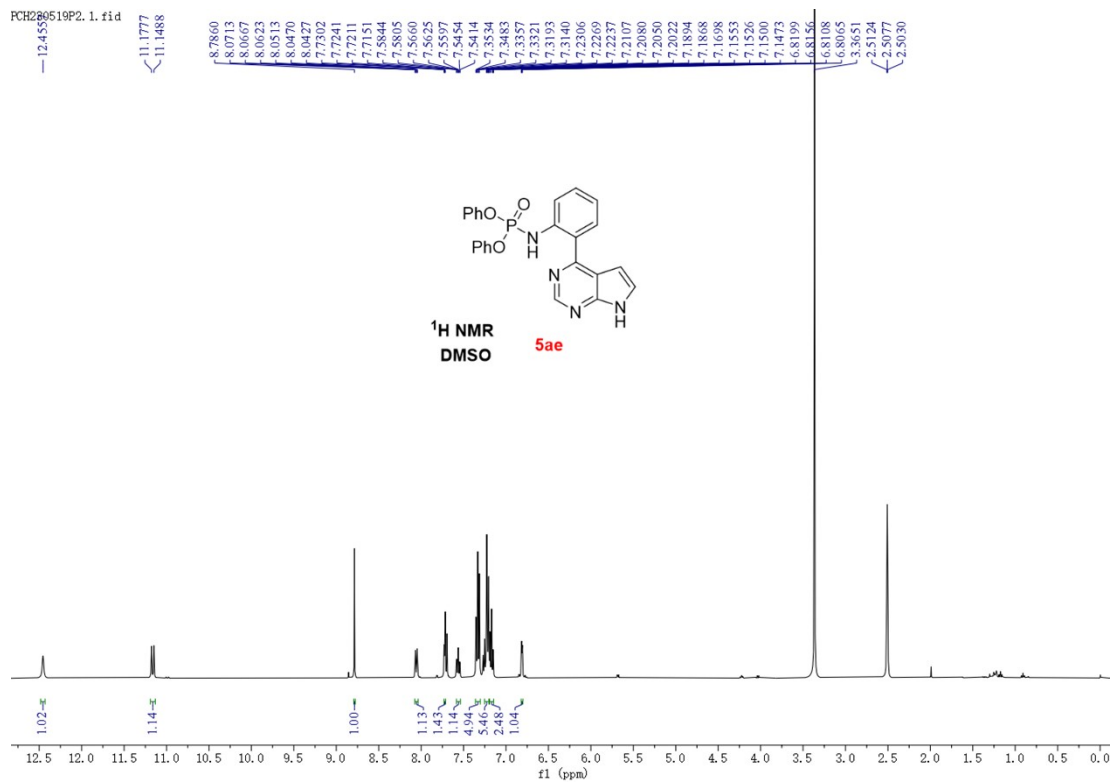


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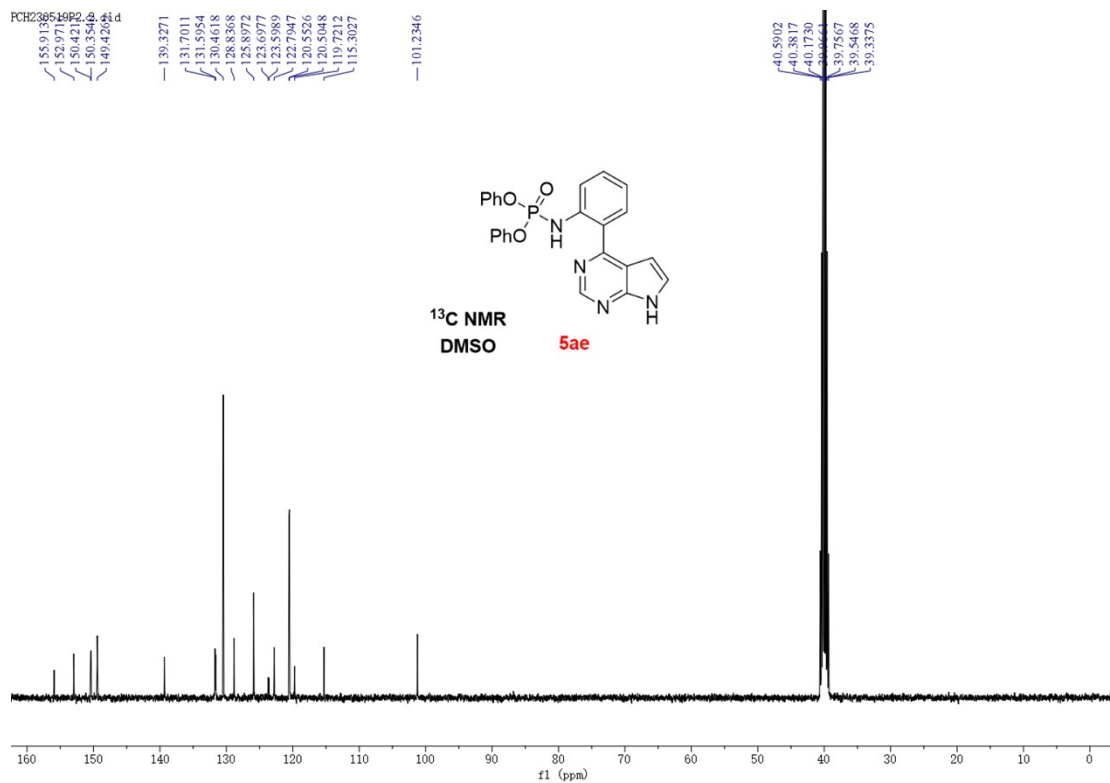




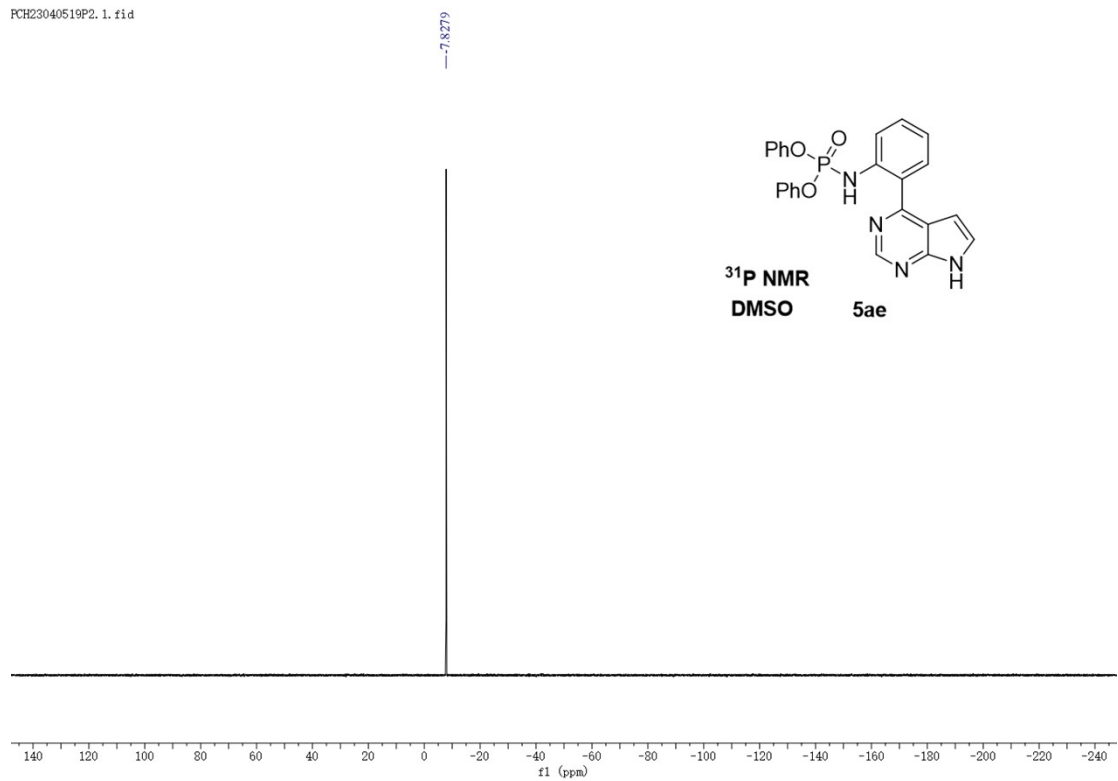
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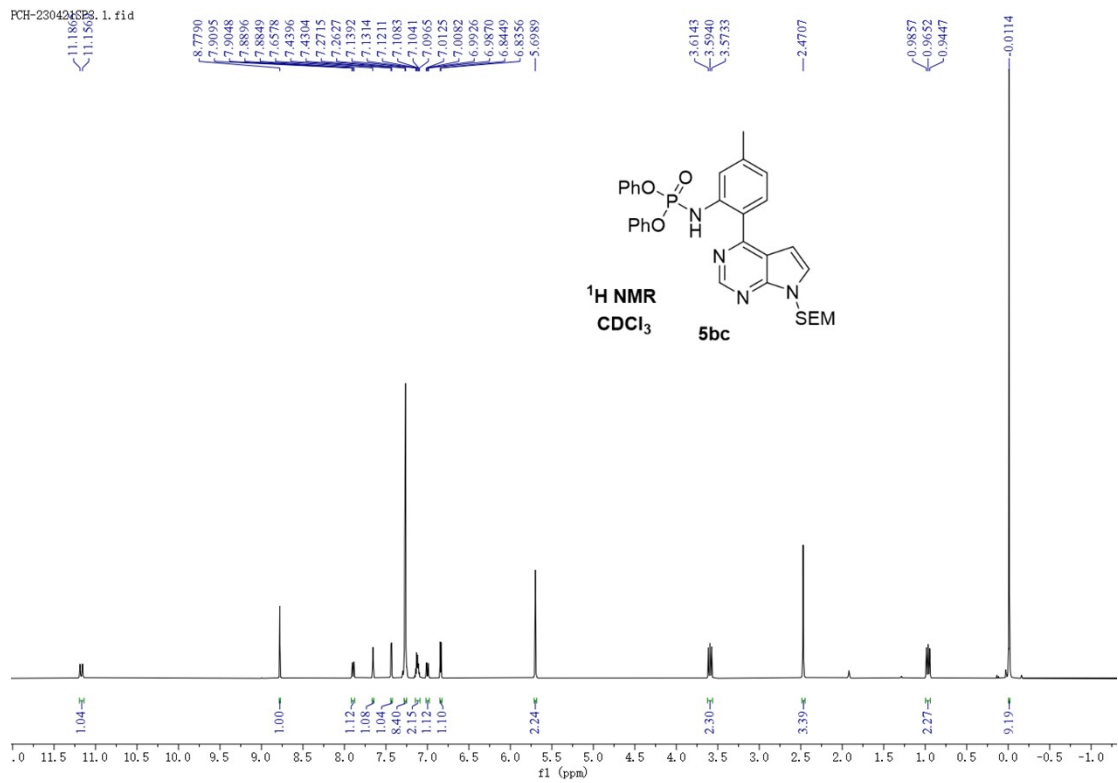
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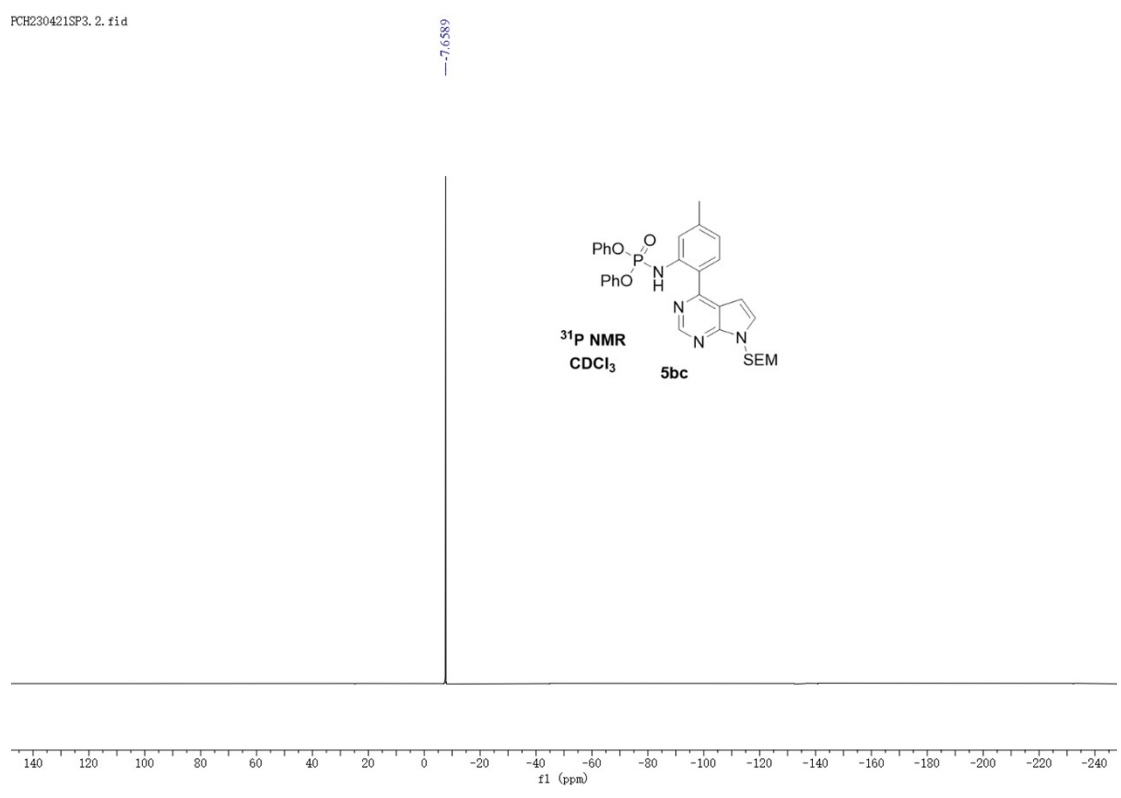
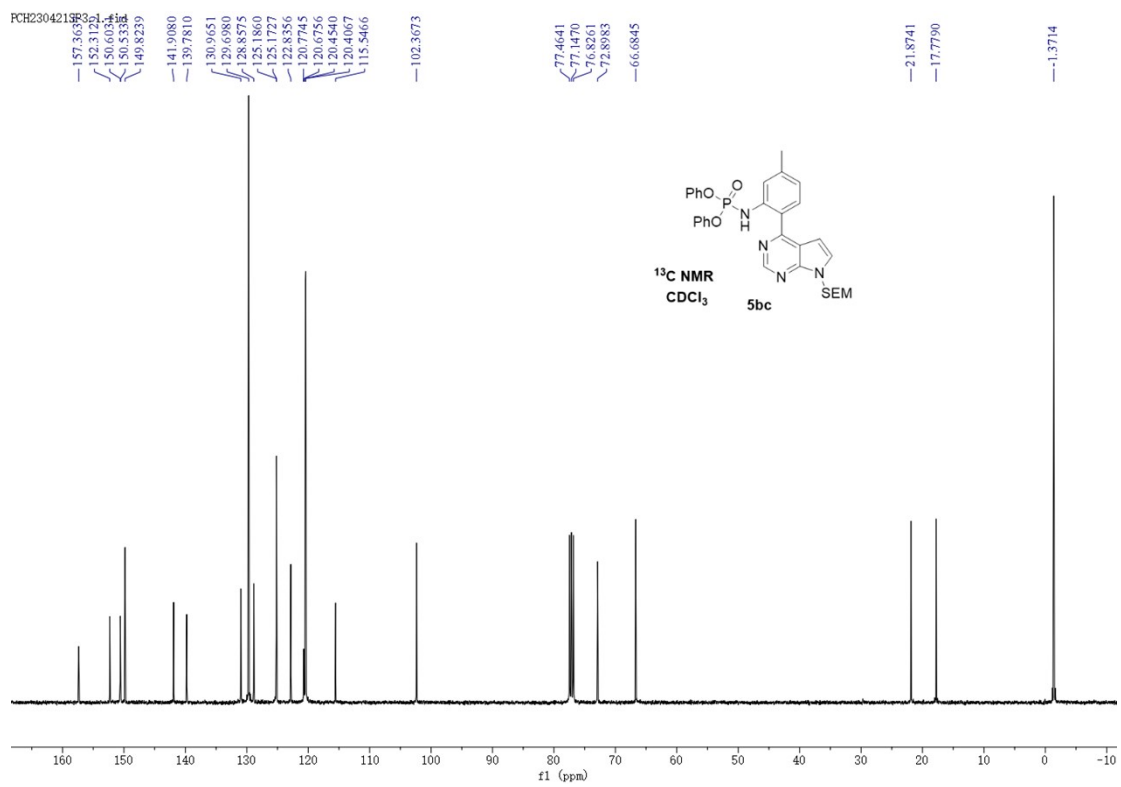


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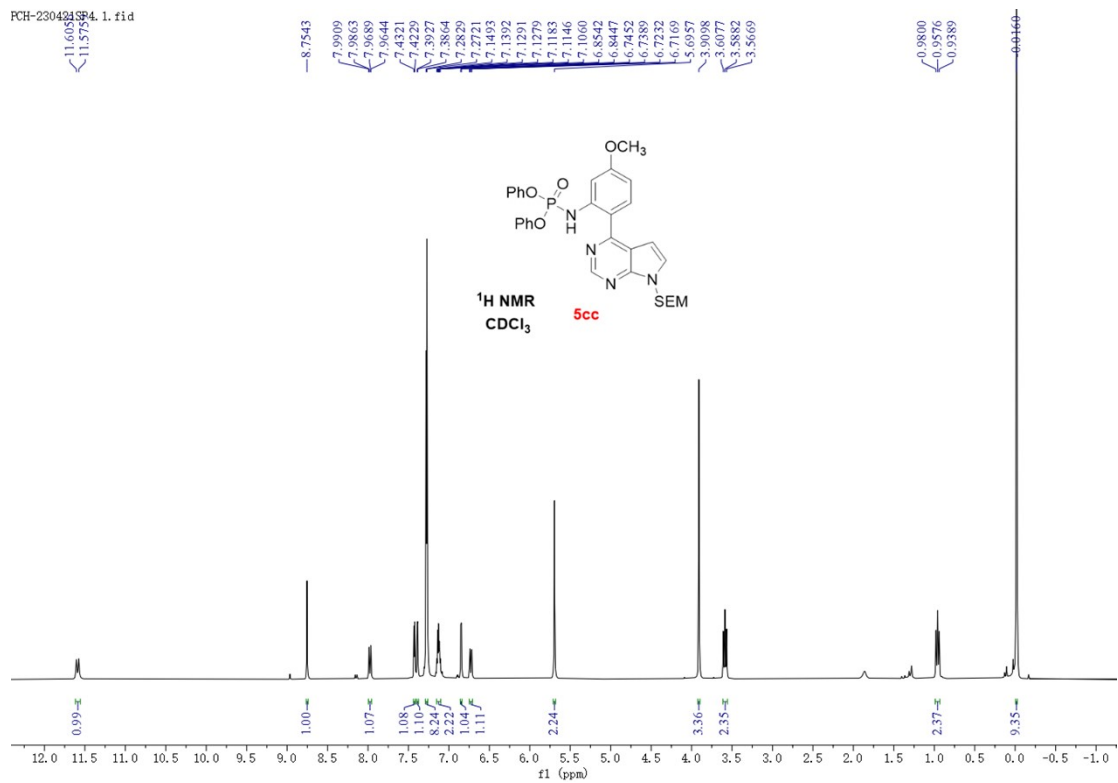


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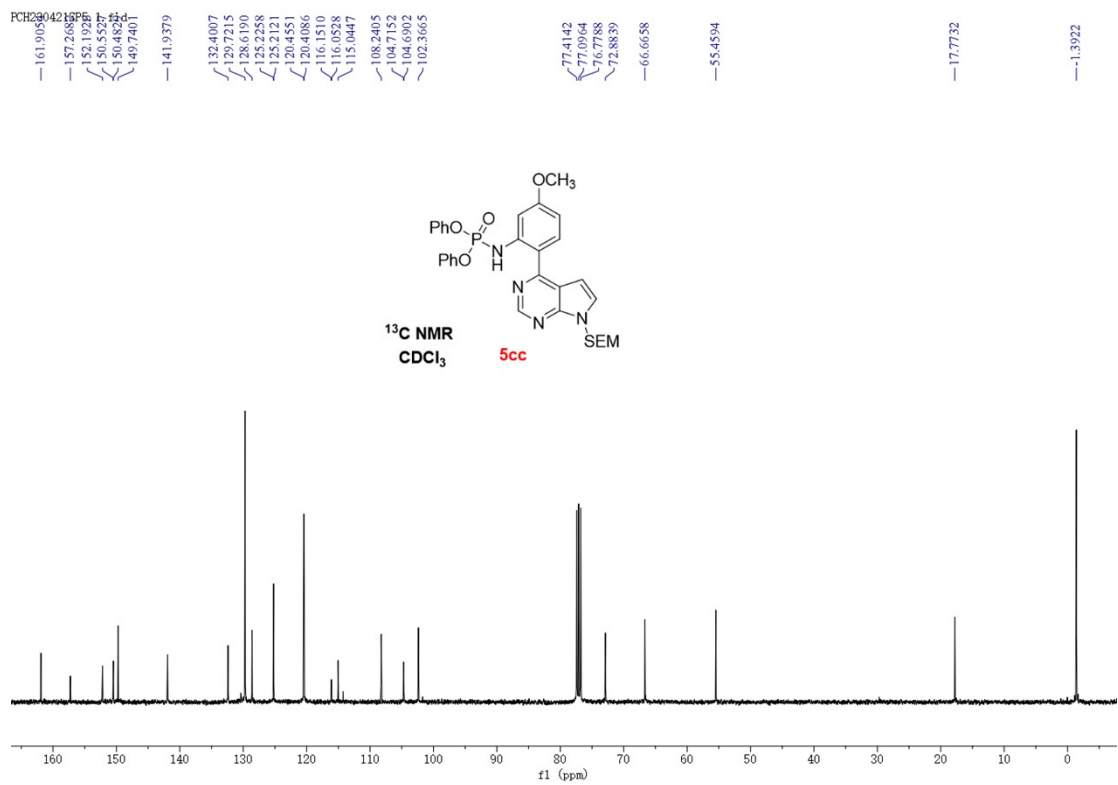




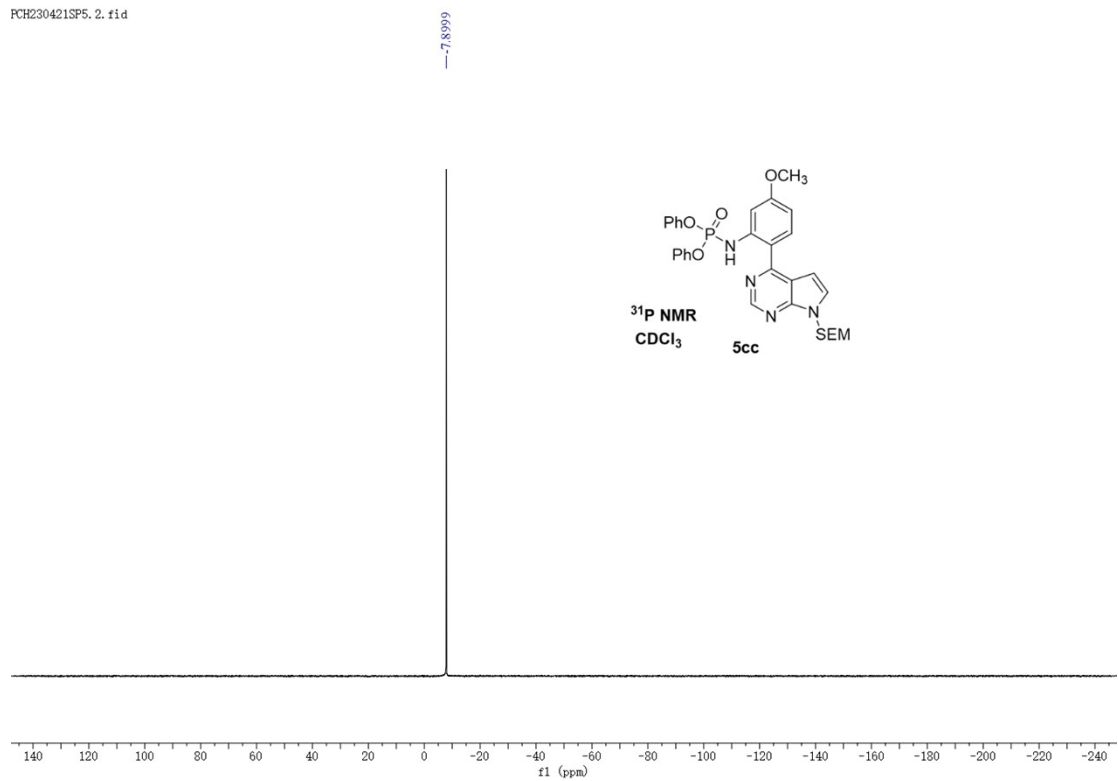
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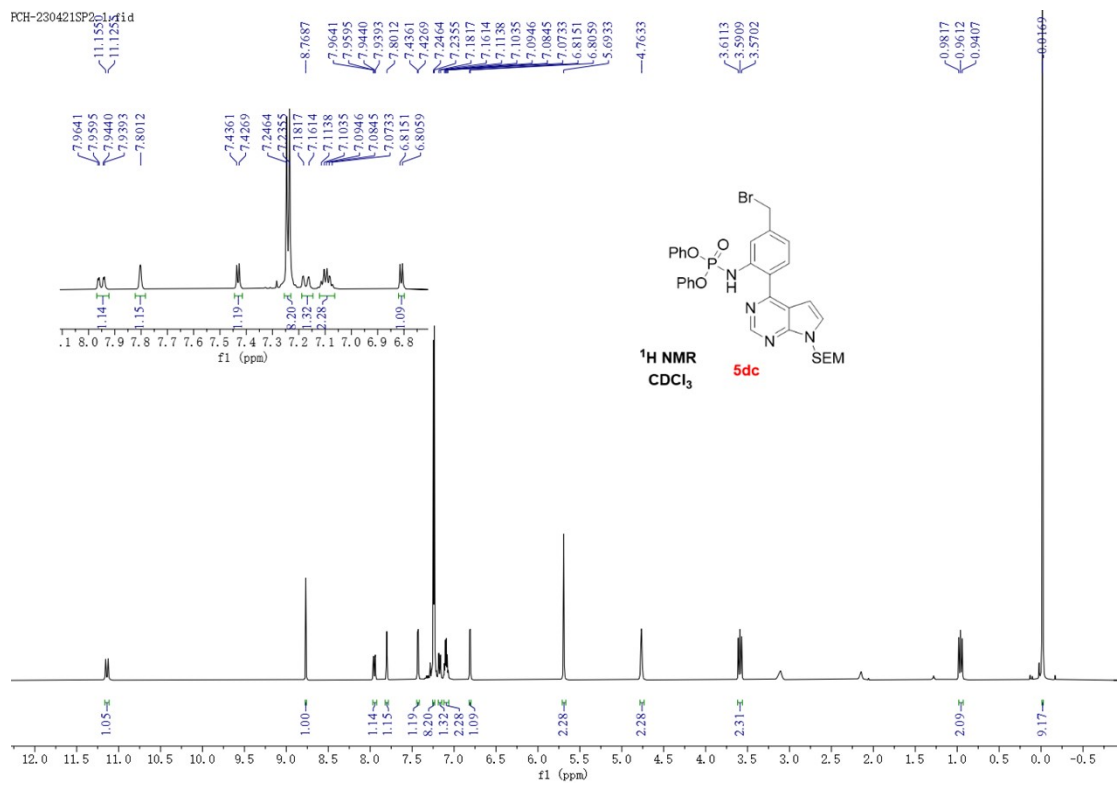
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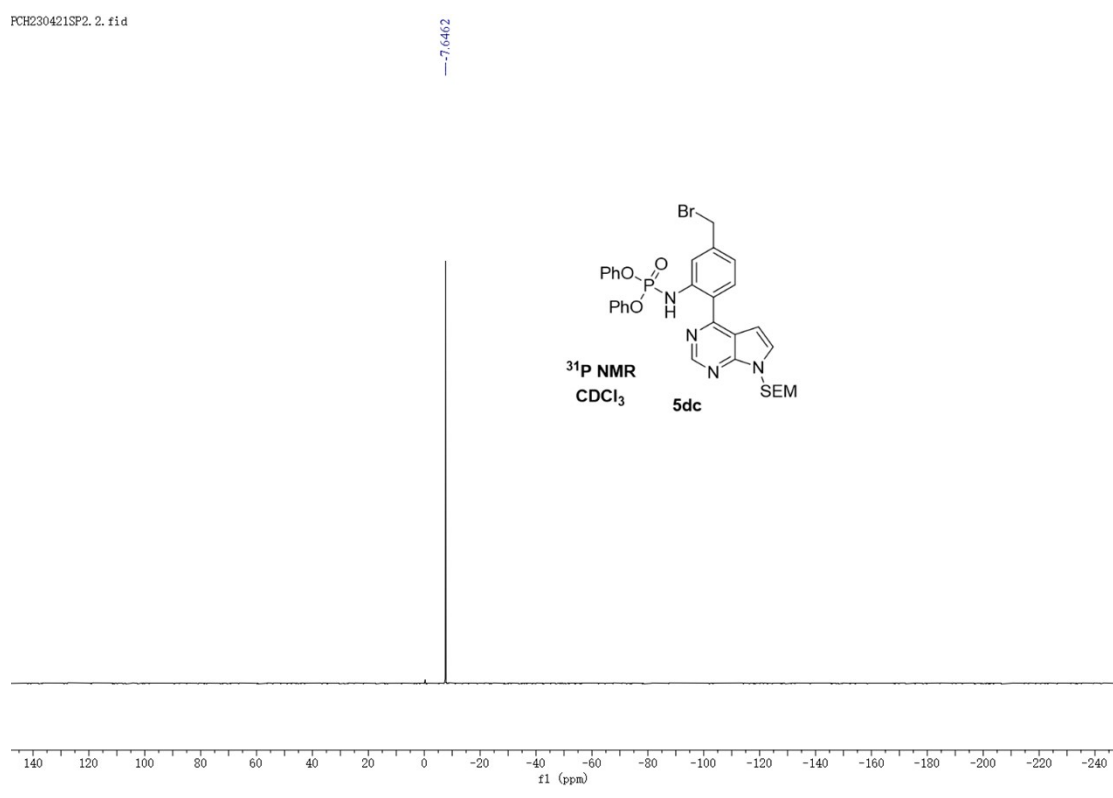
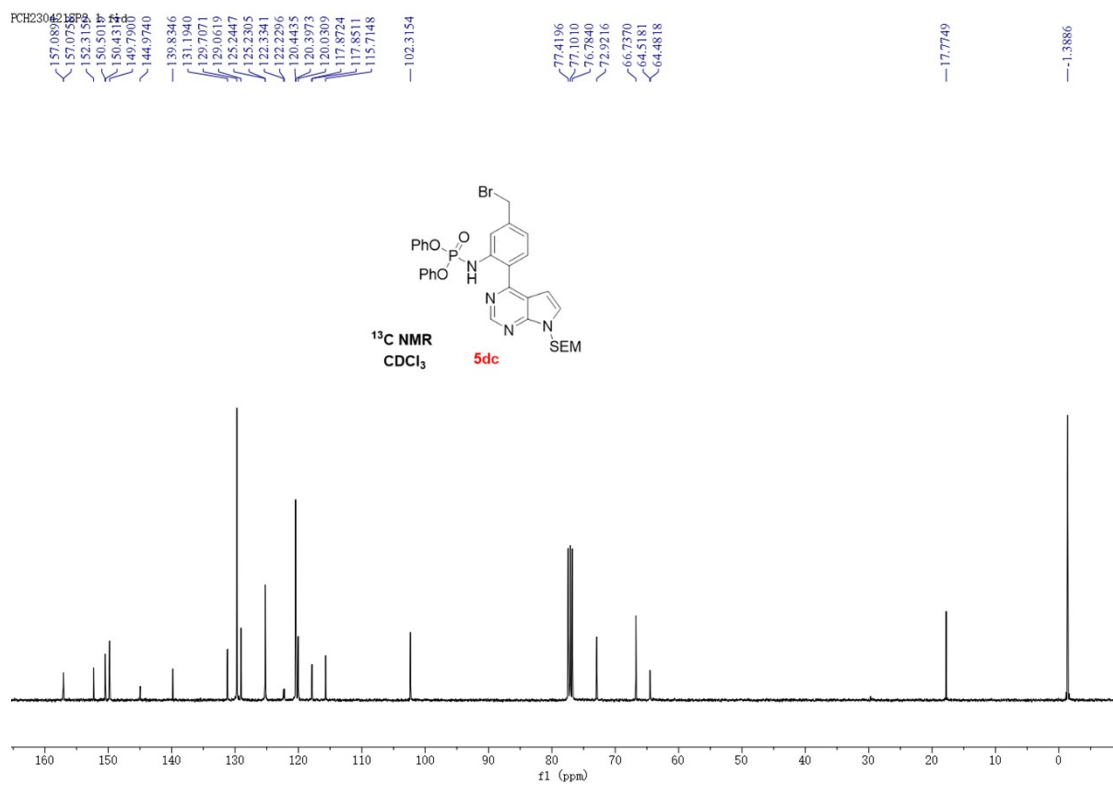


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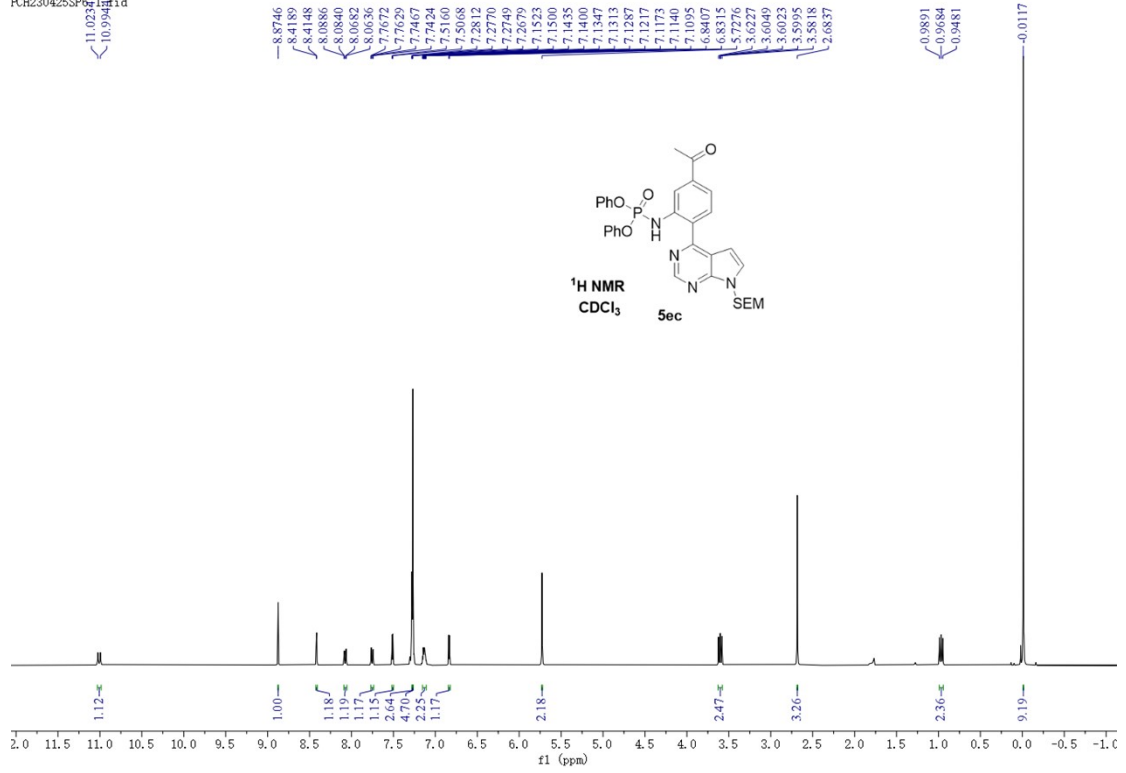


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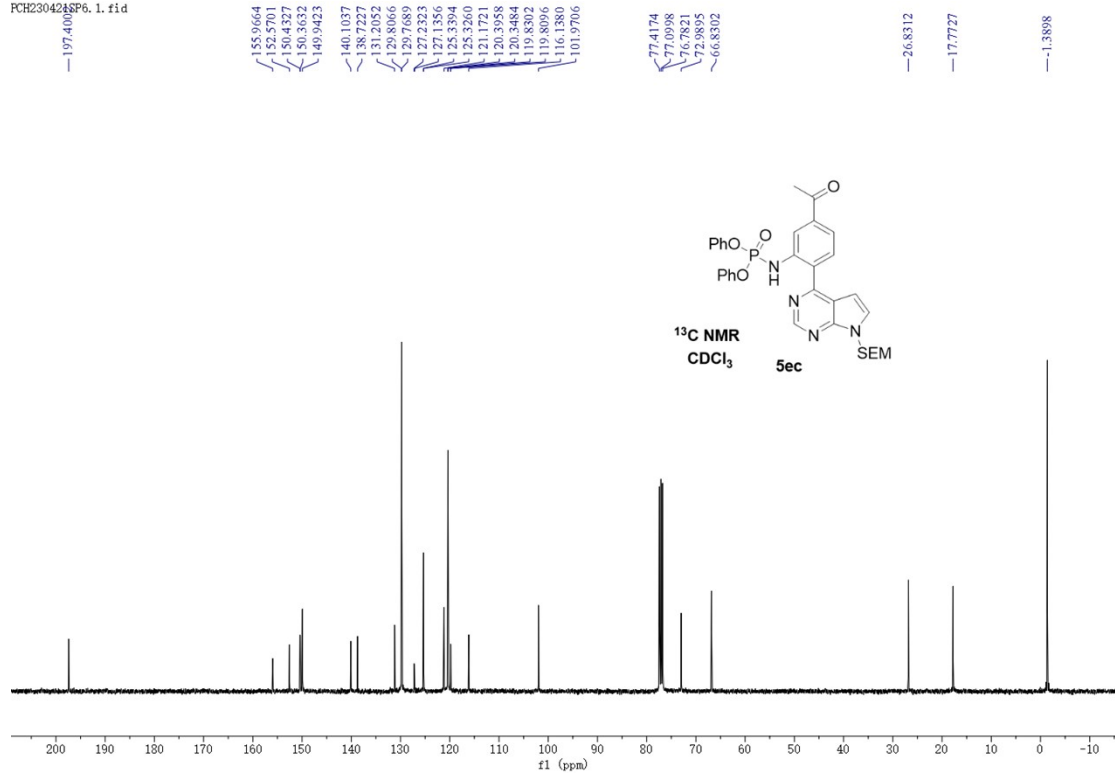




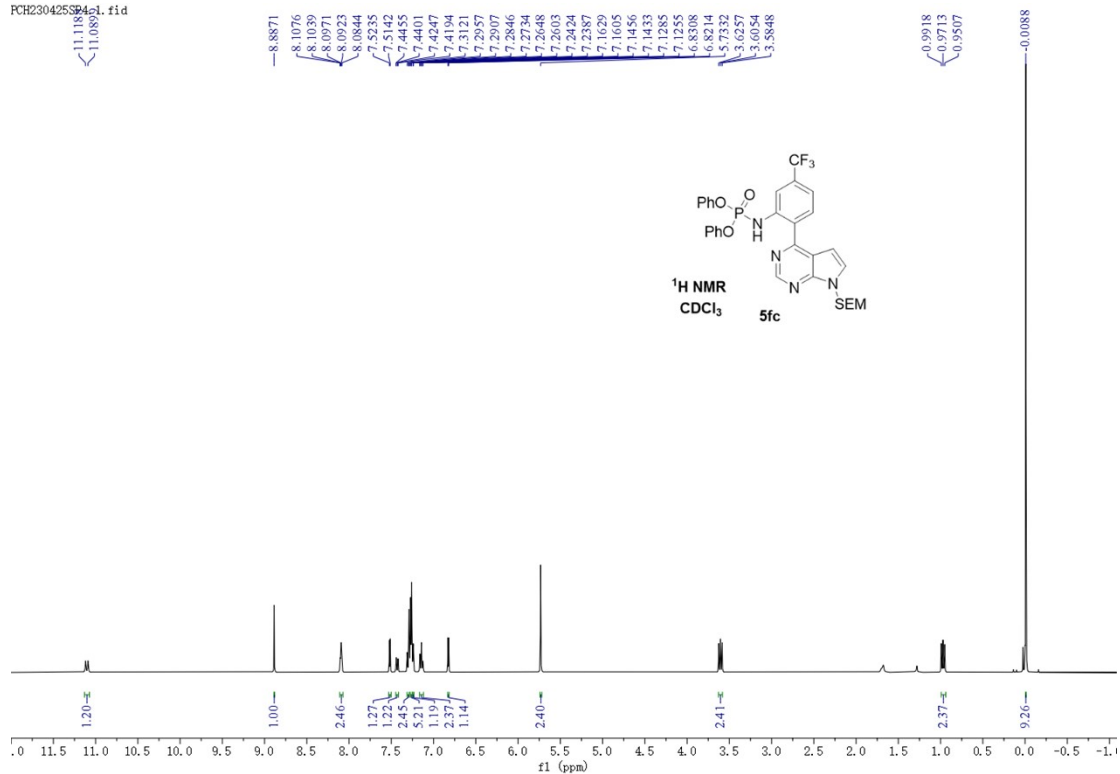
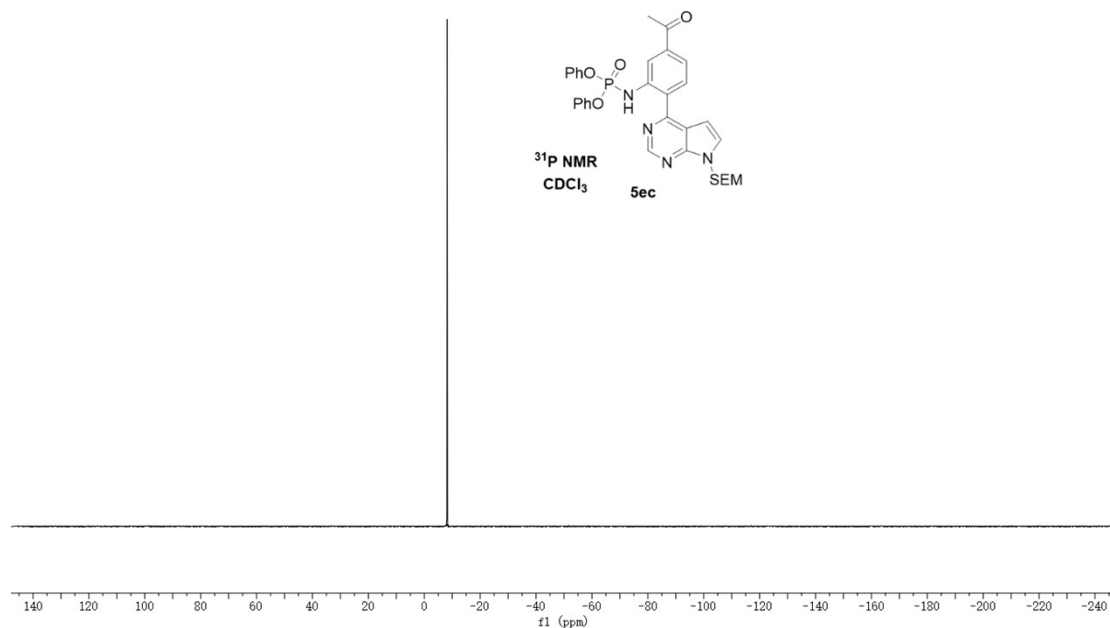
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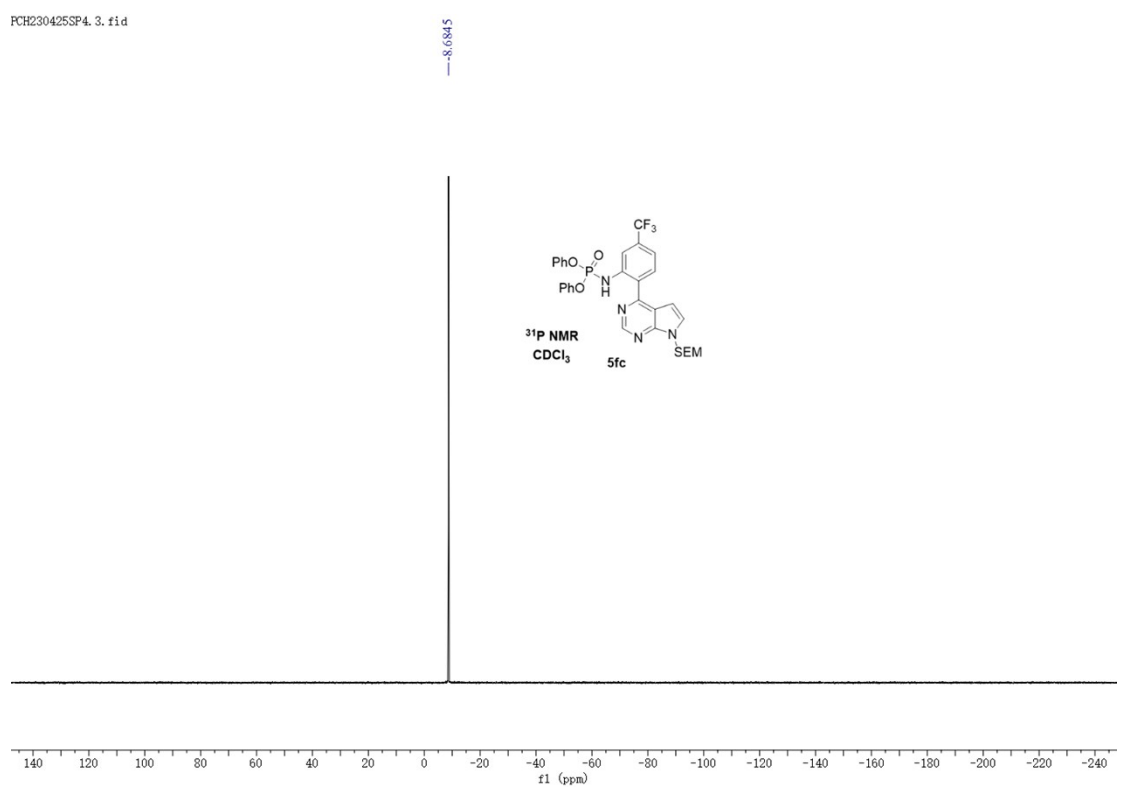
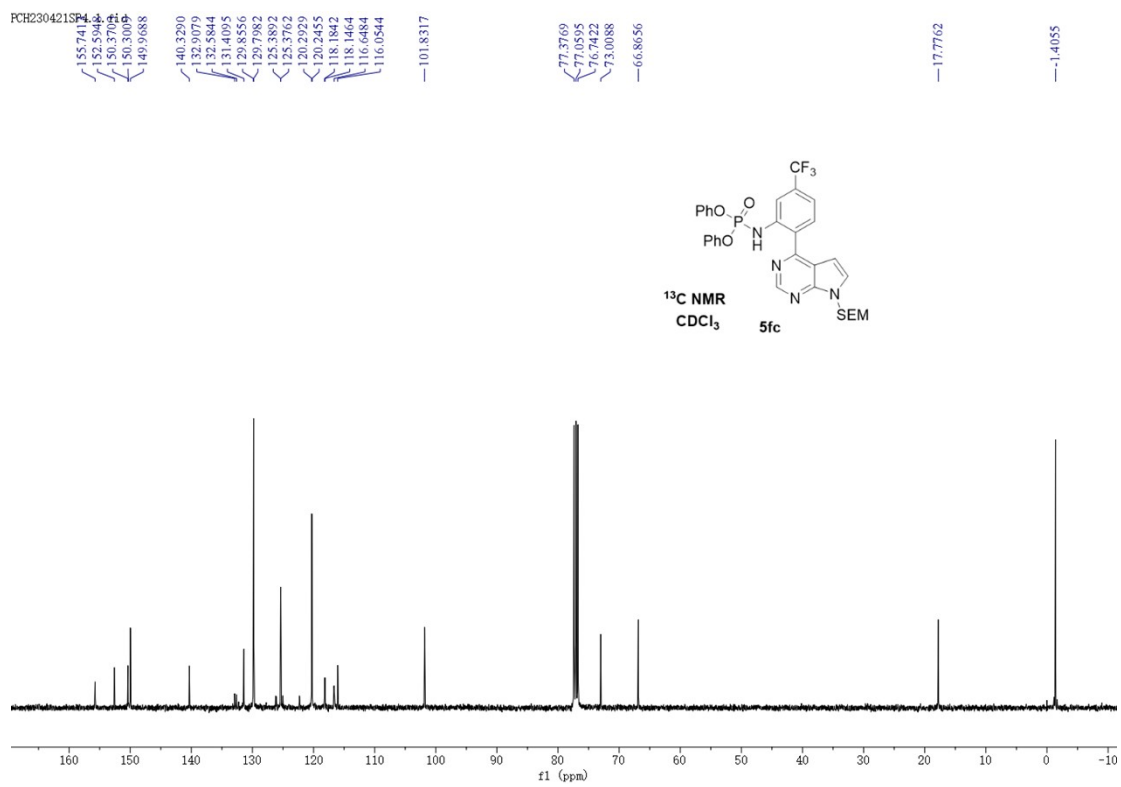


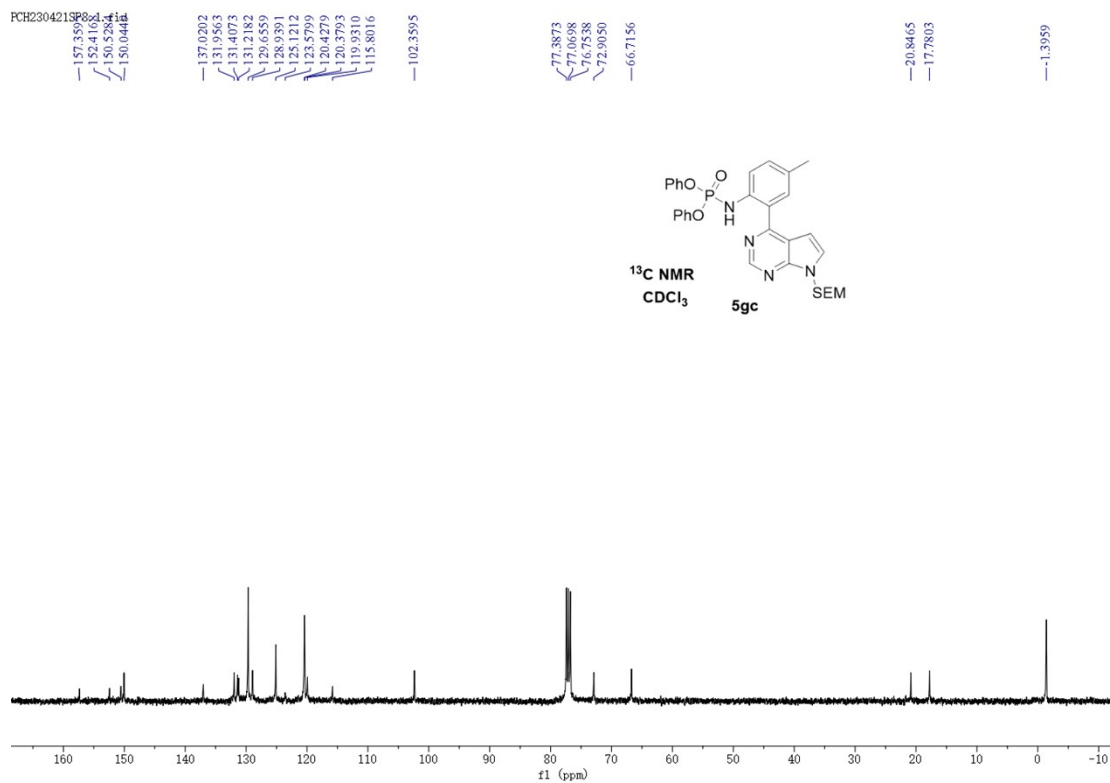
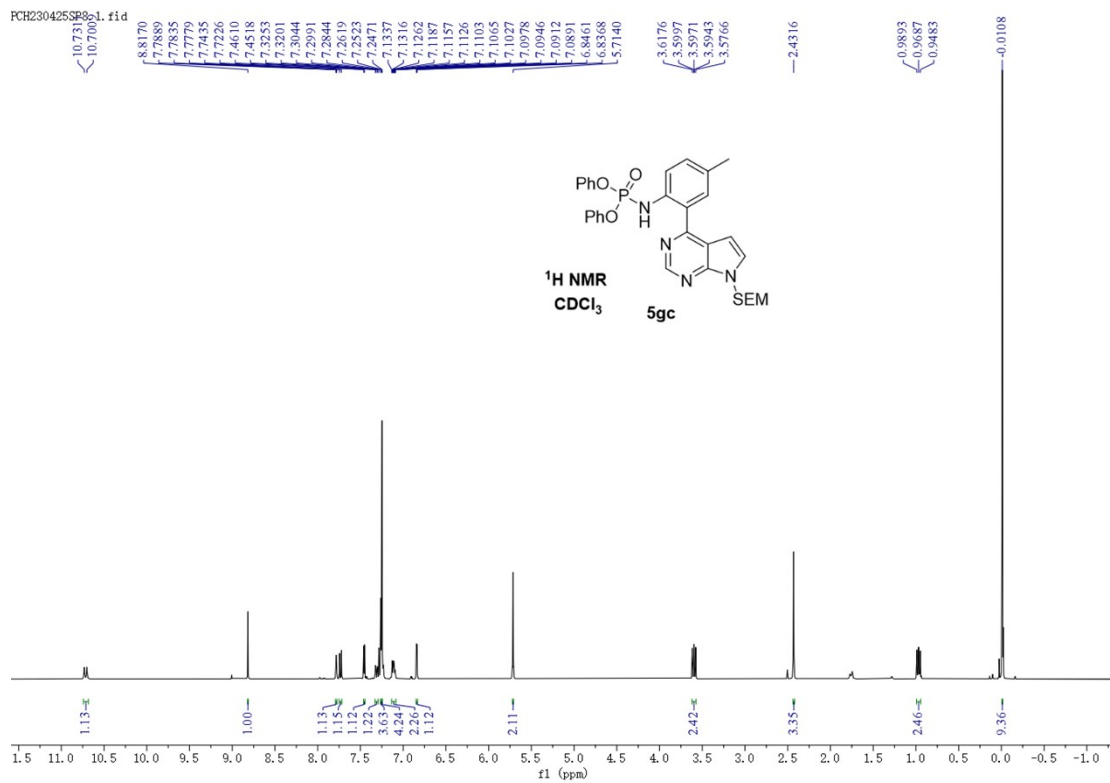
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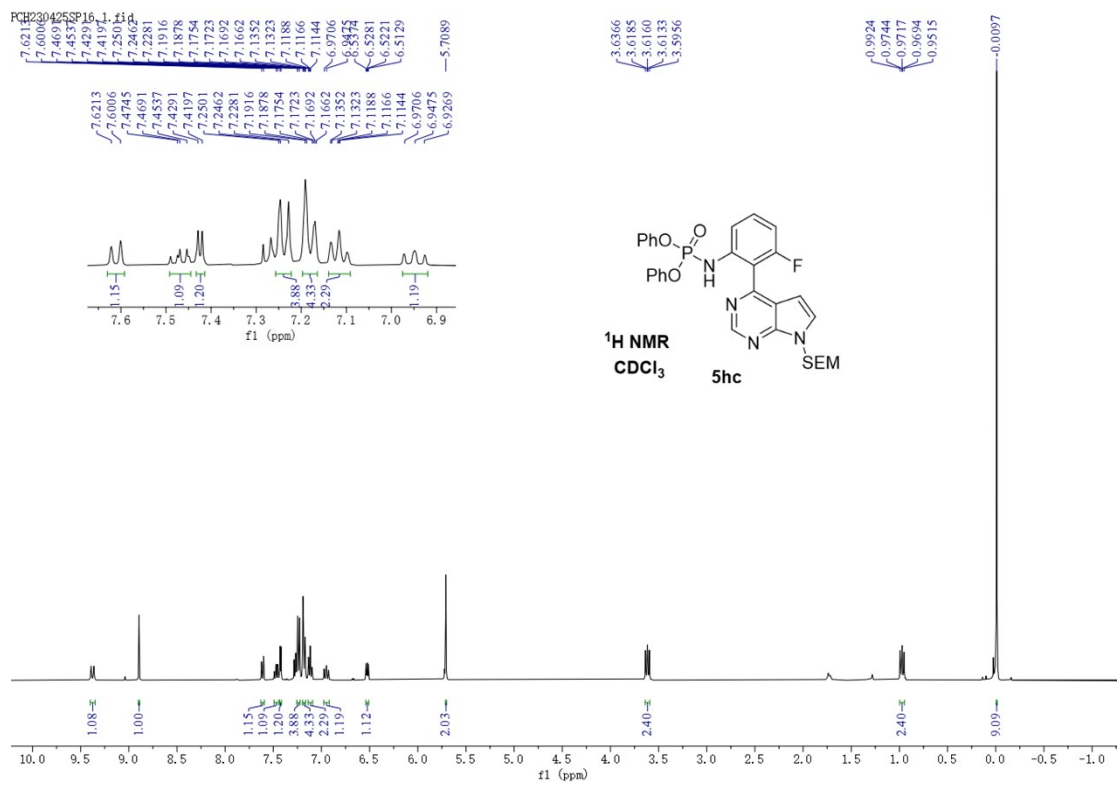
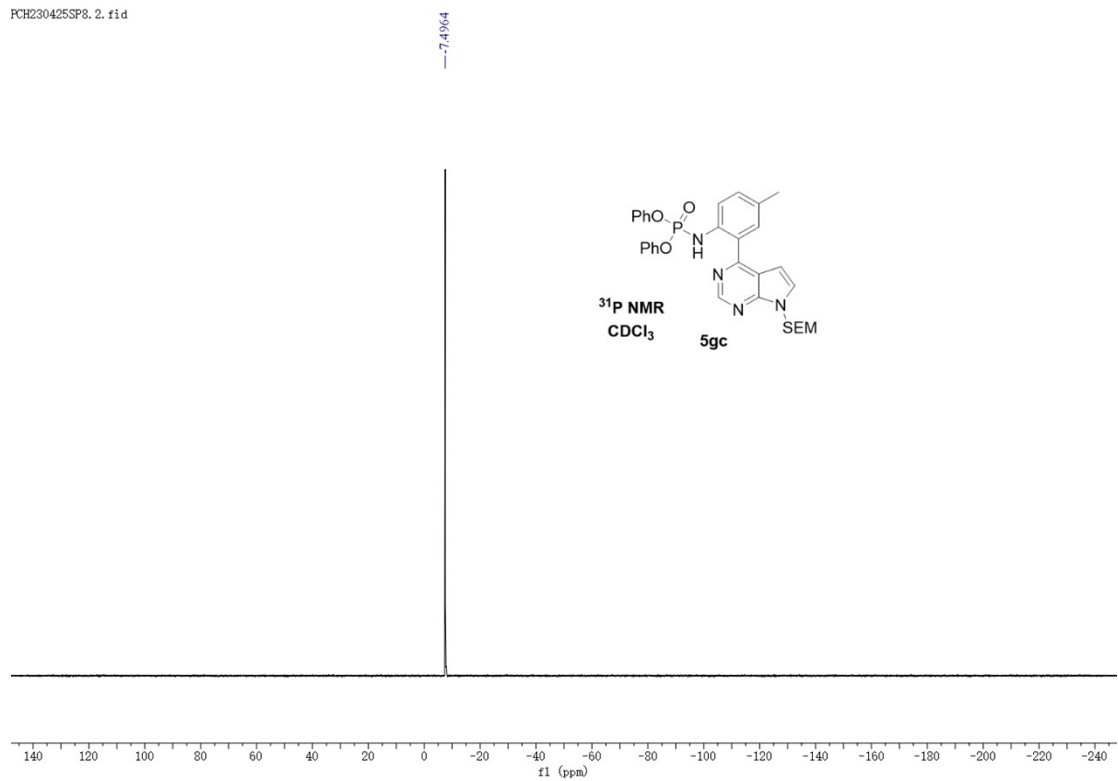


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PCH230421SP16

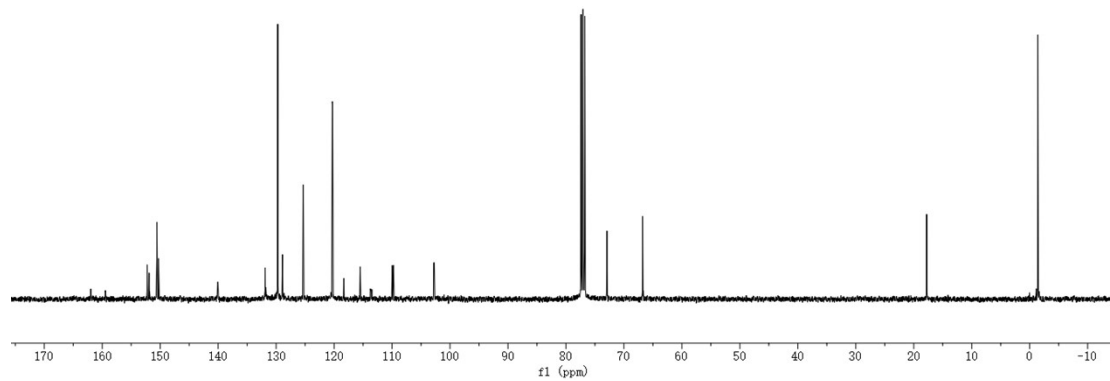
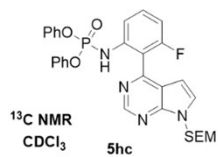
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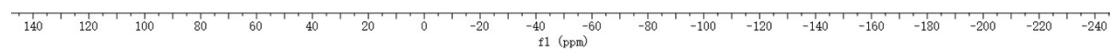
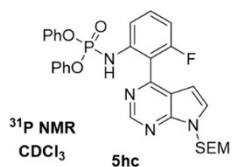
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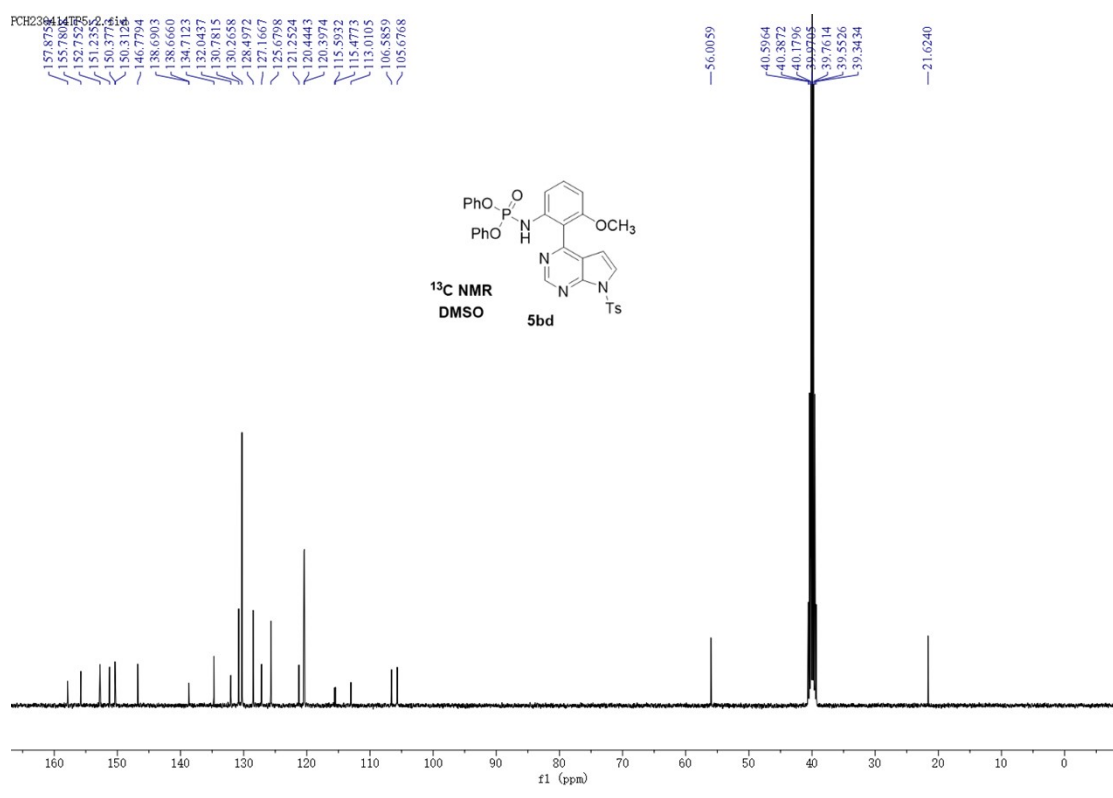
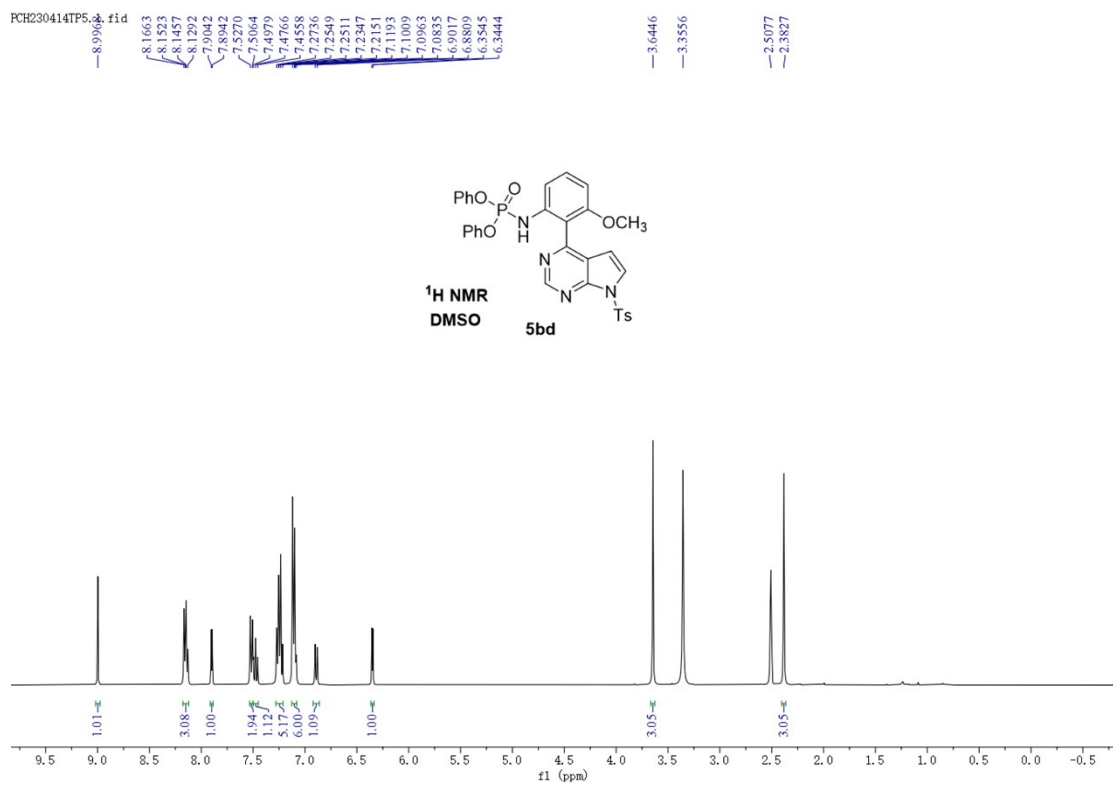
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-7.0732

