Supporting Information

Palladium-Catalysed Site-Selective Arene *Ortho* C-H Fluoroalkoxylation of 4-Aryl-pyrrolo[2,3-*d*]pyrimidines

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1. General Information

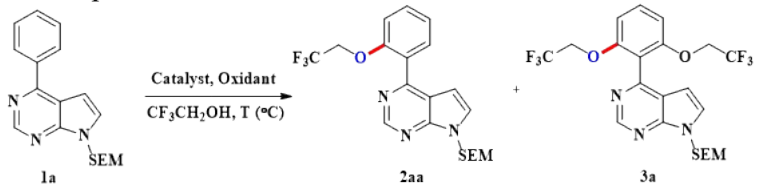
All reagents were purchased from commercial suppliers and used without further purfication. The starting material 4-Chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine is commercially available. A series of substrates **1** were prepared according to the literature procedure.[1-2] NMR spectra were obtained on a Bruker ADNANCE III 400 or 500 and 377 MHz (^{19}F NMR) with TMS as the internal standard using $CDCl_3$ as the solvent. Chemical shifts are given in parts per million (ppm) and coupling constants in Hz. In the ^{1}H and ^{13}C spectra, chemical shifts are reported in ppm relative to $CDCl_3$ with 7.28 for ^{1}H, 77.04 for ^{13}C and -73.50 for ^{19}F. The following abbreviations were used for ^{1}H 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, *Org. Biomol. Chem.,* 2009, **7** 866-868.
2. J. Zhou, Z. Mao, H. Pan, X. Zhang, *Org. Chem. Front.,* 2020, **7**, 324-328.

2. Condition optimization

Table S1. Condition optimization[a]



1a 2aa 3a

entry	Catalyst	oxidant	T (°C)	Time (h)	Yield (%)[b]	
					2aa	3a
1	$Pd(TFA)_2$(20)	$PhI(OAc)_2$(2)	95	2	35	44
2	/	$PhI(OAc)_2$(2)	95	12	NR[c]	-
3	$Pd(TFA)_2$(20)	/	95	12	NR	-
4	$Pd(OAc)_2$(20)	$PhI(OAc)_2$(2)	95	5	27	43
5	$Pd(MeCN)_2Cl_2$(20)	$PhI(OAc)_2$(2)	95	12	20	-
6	$PdCl_2$(20)	$PhI(OAc)_2$(2)	95	12	NR	-
7	$Pd(PPh_3)Cl_2$(20)	$PhI(OAc)_2$(2)	95	12	NR	-
8	$Pd_2(dba)_3$(20)	$PhI(OAc)_2$(2)	95	12	NR	-
9	$Pd(PPh_3)_4$(20)	$PhI(OAc)_2$(2)	95	12	NR	-
10	$Pd(TFA)_2$(20)	$K_2S_2O_8$(2)	95	24	NR	-
11	$Pd(TFA)_2$(20)	$Cu(OAc)_2$(2)	95	24	NR	-
12	$Pd(TFA)_2$(20)	TBHP(2)	95	24	NR	-
13	$Pd(TFA)_2$(20)	O_2(1 atm)	95	24	NR	-
14	$Pd(TFA)_2$(20)	Ag_2CO_3(2)	95	24	NR	-
15	$Pd(TFA)_2$(20)	$AgSbF_6$(2)	95	24	NR	-
16	$Pd(TFA)_2$(20)	AgNTf(2)	95	24	NR	-
17	$Pd(TFA)_2$(20)	AgOTf(2)	95	24	NR	-
18[d]	$Pd(TFA)_2$(20)	$PhI(OAc)_2$(2)	95	5	26	32
19[e]	$Pd(TFA)_2$(20)	$PhI(OAc)_2$(2)	95	5	30	40
20	$Pd(TFA)_2$(10)	$PhI(OAc)_2$(2)	95	2	43	26
21	$Pd(TFA)_2$(5)	$PhI(OAc)_2$(2)	95	2	46	15
22	$Pd(TFA)_2$(5)	$PhI(OAc)_2$(1.5)	60	8	73	trace
23[f]	$Pd(TFA)_2$(5)	$PhI(OAc)_2$(1.5)	60	8	82	-
24	$Pd(TFA)_2$(5)	$PhI(OAc)_2$(3)	60	8	33	28
25	$Pd(TFA)_2$(5)	$PhI(OAc)_2$(3)	80	8	31	37
26	$Pd(TFA)_2$(10)	$PhI(OAc)_2$(3)	80	8	32	46
27[g]	$Pd(TFA)_2$(10)	$PhI(OAc)_2$(3)	100	8	-	78

[a]General conditions: **1a** (0.15 mmol), catalyst (x mol%), oxidant (x equiv.) in CF_3CH_2OH (0.5 mL), 2-12 h. [b]Isolated yield. [c]NR: no reaction. [d]Add 2.0 equiv. of TFA. [e]Add 2.0 equiv. of CH_3COOH. [f]2.0 mL of CF_3CH_2OH. [g]3.0 mL of CF_3CH_2OH.

3. **General Procedure**

3.1 General Procedures for the synthesis of 2aa-2e: A 15 mL pressure vessel equipped with a magnetic stirrer was charged with **1** (0.3 mmol), $Pd(TFA)_2$ (5.0 mg, 5 mol%), $PhI(OAc)_2$ (145.0 mg, 1.5 equiv.) and CF_3CH_2OH (4.0 mL) as solvent. The reaction mixture was then stirred at 60 °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 **2**.

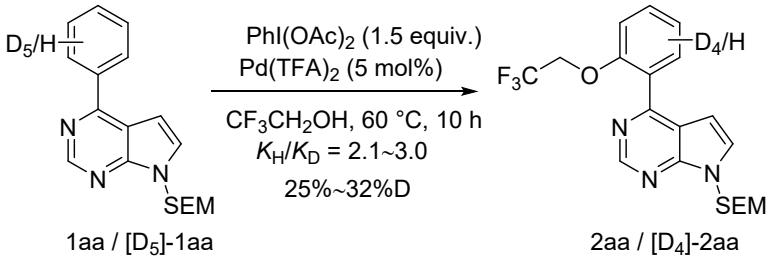
3.2 General Procedures for the synthesis of 3a-3p: A 15 mL pressure vessel equipped with a magnetic stirrer was charged with starting material (0.3 mmol), $Pd(TFA)_2$ (10 mg, 10 mol%), $PhI(OAc)_2$ (290.0 mg, 3.0 equiv.) and CF_3CH_2OH (6.0 mL) as solvent. After the reaction mixture was stirred at 100 °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**.

3.3 General Procedures for the synthesis of 4a-4m: A 15 mL pressure vessel equipped with a magnetic stirrer was charged with starting material (0.3 mmol), $Pd(TFA)_2$ (5.0 mg, 5 mol%), $PhI(OAc)_2$ (145 mg, 1.5 equiv.) and $R_FCH(R)OH$ (4.0 mL) as solvent. After the reaction mixture was stirred at 100 °C in oil bath. After completion of the reaction, it was then cooled to room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the desired product **4.**

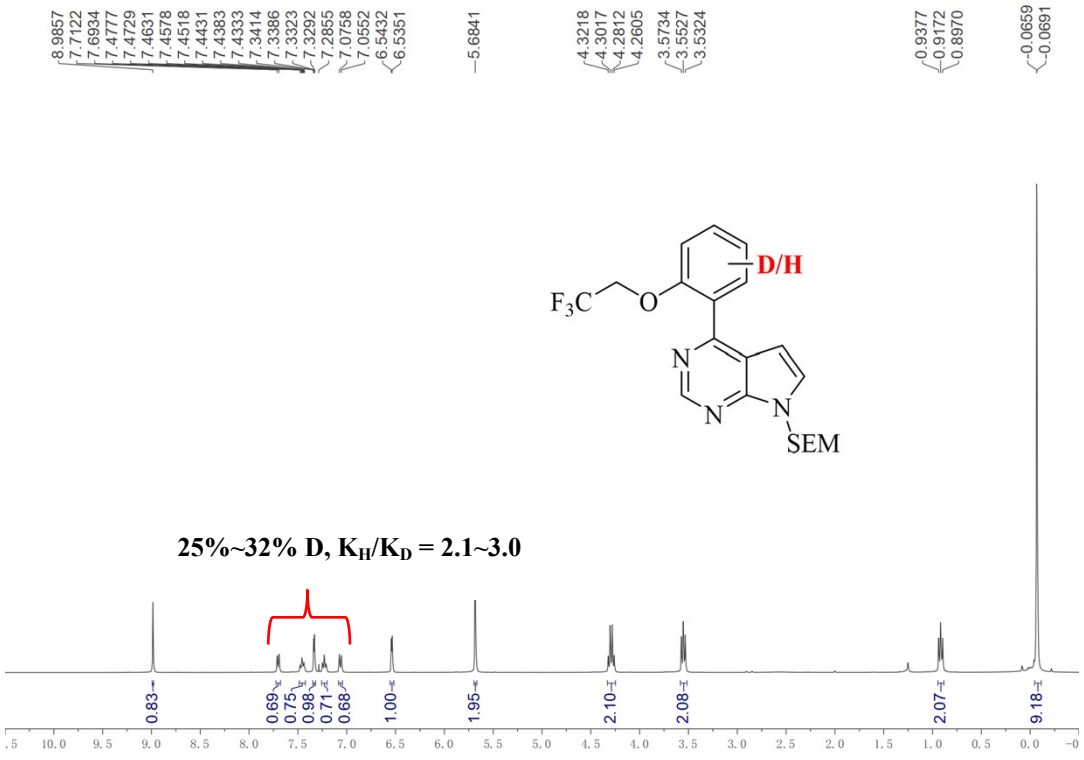
3.4 The procedure for the synthesis of 5: A 15 mL pressure vessel equipped with a magnetic stirrer was charged with starting material (0.3 mmol), $Pd(TFA)_2$ (5.0 mg, 5 mol%), $PhI(OAc)_2$ (145 mg, 1.5 equiv.) and MeOH (4.0 mL) as solvent. After the reaction mixture was stirred at 100 °C in oil bath. After completion of the reaction, it was then cooled to room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the desired product **5.**

4. Mechanism studies

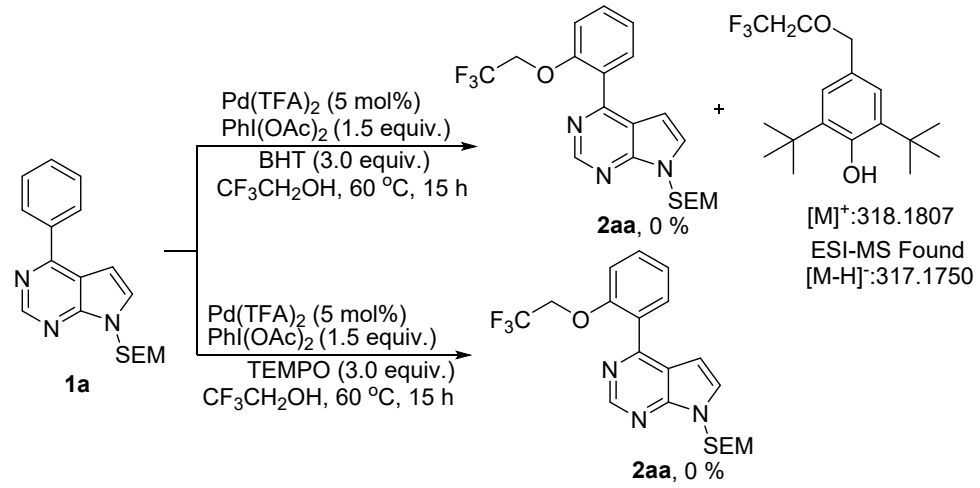
4.1 Kinetic isotope effect



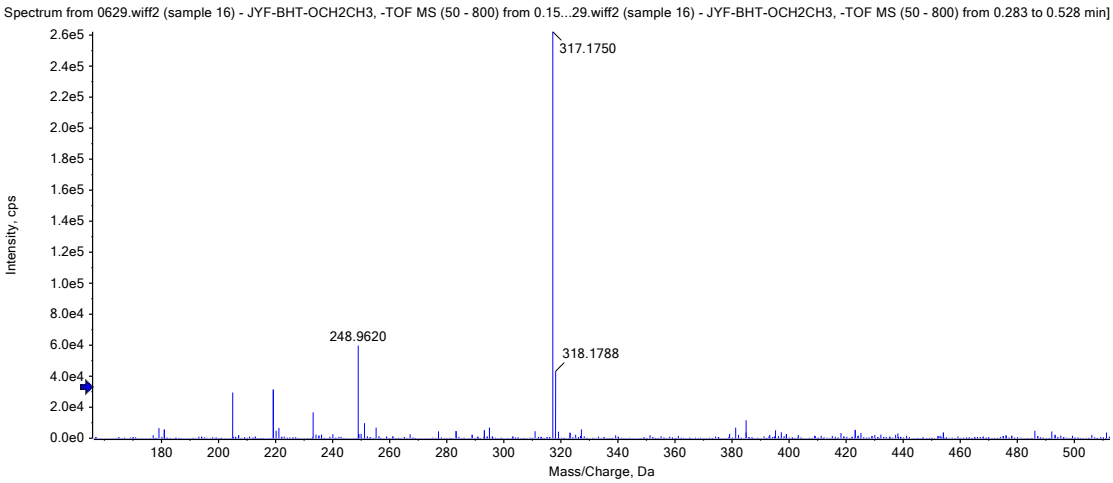
A 15 mL pressure vessel equipped with a magnetic stirrer was charged with **1aa** (0.3 mmol), $Pd(TFA)_2$ (5.0 mg, 5 mol%), $PhI(OAc)_2$ (145.0 mg, 1.5 equiv.), D_5-**1aa** (0.3 mmol), and CF_3CH_2OH (4.0 mL) as solvent. After the reaction mixture was stirred at 60 °C in oil bath for 10 h before it was cooled to r.t. and the solvent was then removed in vacuo and the residue was purified by column chromatography on silica gel to provide the desired mixture **2aa**/[D_4]-**2aa.**



4.2 The effects of radical scavengers of this reaction

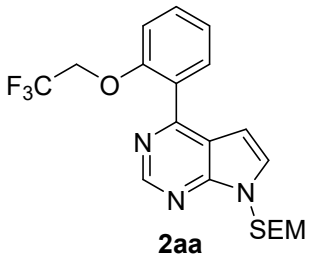


Two 15 mL pressure vessel equipped with a magnetic stirrer was charged with **1a** (0.3 mmol), $Pd(TFA)_2$ (5.0 mg, 5 mol%), $PhI(OAc)_2$ (145.0 mg, 1.5 equiv.) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (72 mg, 0.46 mmol) or 2,6-di-tert-butyl-4-methylphenol (BHT) (102 mg, 0.46 mmol) was added, respectively, followed by addition of CF_3CH_2OH (4.0 mL) as solvent. The reaction mixture was then stirred at 60 °C in oil bath for 15 h before it was cooled to room temperature. Both no products were observed and the reaction of BHT was detected by ESI-MS analysis.



5. Characterization of Compounds

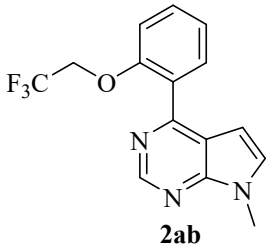
4-(2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2aa*)



2aa

Product **2aa** was purified by PE/EtOAc (6/1); brown oil (104 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.70 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.48-7.44 (m, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.23 (td, *J* = 7.8, 1.0 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 5.69 (s, 2H), 4.29 (q, *J* = 8.2 Hz, 2H), 3.55 (t, *J* = 8.2 Hz, 2H), 0.92 (t, *J* = 8.3 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 155.0, 151.8, 151.7, 132.0, 131.0, 128.8, 128.1, 123.4, 123.1 (q, $J_{C\text{-}F}$ = 279.0 Hz), 118.0, 114.7, 102.5, 72.8, 67.2 (q, $J_{C\text{-}F}$ = 35.7 Hz), 66.5, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.67 (s, 3F). HRMS m/z (ESI) calcd for $C_{20}H_{25}F_3N_3O_2Si$ $[M+H]^+$: 424.1663, found: 424.1644.

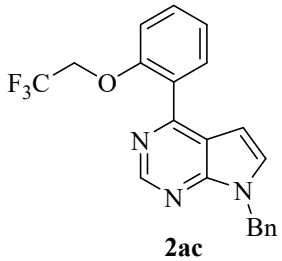
7-methyl-4-(2-(2,2,2-trifluoroethoxy)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2ab*)



2ab

Product **2ab** was purified by PE/EtOAc (4/1); yellow oil (51 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.70 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.48 (m, 1H), 7.25 (td, *J* = 7.5, 1.1 Hz, 1H), 7.18 (d, *J* = 3.6 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.50 (d, *J* = 3.6 Hz, 1H), 4.30 (q, *J* = 8.2 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 155.1, 151.3, 151.1, 132.0, 130.9, 129.4, 128.9, 123.4, 123.2 (q, $J_{C\text{-}F}$ = 279.6 Hz), 117.9, 114.7, 101.1, 67.2 (q, $J_{C\text{-}F}$ = 35.8 Hz), 31.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.66 (s, 3F). HRMS m/z (ESI) calcd for $C_{15}H_{13}F_3N_3O$ $[M+H]^+$: 308.1005, found: 308.1001.

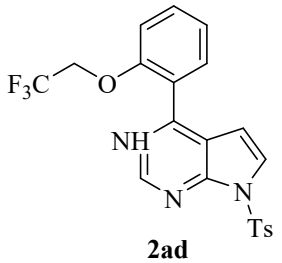
7-benzyl-4-(2-(2,2,2-trifluoroethoxy)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2ac*)



2ac

Product **2ac** was purified by PE/EtOAc (4/1); brown oil (49 mg, 43% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.73 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.49 (td, *J* = 8.3, 1.8 Hz, 1H), 7.36-7.33 (m, 2H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.25 -7.23 (m, 2H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.10 (d, *J* = 8.3, 1H), 6.53 (d, *J* = 3.6 Hz, 1H), 5.52 (s, 2H), 4.32 (q, *J* = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 155.1, 151.5, 151.2, 136.9, 132.0, 131.0, 128.9, 128.8, 128.4, 128.0, 127.5, 123.4, 123.2 (q, $J_{C\text{-}F}$ = 279.6 Hz), 117.9, 114.7, 101.8, 67.2 (q, $J_{C\text{-}F}$ = 35.7 Hz), 47.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.59 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{17}F_3N_3O$ $[M+H]^+$: 384.1318, found: 384.1299.

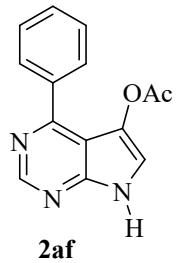
7-tosyl-4-(2-(2,2,2-trifluoroethoxy)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2ad*)



2ad

Product **2ad** was purified by PE/EtOAc (4/1); white solid (70 mg, 52% yield). mp: 127.7-128.4 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.51-7.47 (m, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 4.0 Hz, 1H), 4.31 (q, *J* = 8.1 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 154.7, 153.1, 151.4, 145.8, 134.9, 132.0, 131.6, 129.9, 128.2, 127.6, 126.2, 123.4, 123.0 (q, $J_{C\text{-}F}$ = 279.0 Hz), 120.0, 114.0, 105.5, 66.8 (q, $J_{C\text{-}F}$ = 36.0 Hz), 21.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.51 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{17}F_3N_3O_3S$ $[M+H]^+$: 448.0937, found: 448.0924.

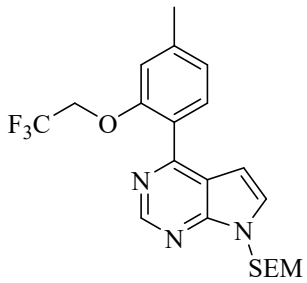
4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (*2af*)



2af

Product **2af** was purified by PE/EtOAc (2/1); white solid (46 mg, 61% yield). mp: 99.6-101.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 1H), 9.02 (s, 1H), 7.89 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.55 (s, 1H), 7.54 (d, *J* = 2.4 Hz, 2H), 7.43 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 159.0, 151.4, 149.1, 137.4, 130.0, 129.5, 128.3, 127.6, 115.7, 109.0, 20.6. HRMS m/z (ESI) calcd for $C_{14}H_{12}N_3O_2$ $[M+H]^+$: 254.0924, found: 254.0919.

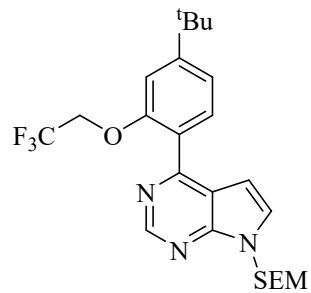
4-(4-methyl-2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2ba*)



2ba

Product **2ba** was purified by PE/EtOAc (4/1); brown oil (97 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 3.7 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 1.4 Hz, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 5.68 (s, 2H), 4.28 (q, *J* = 8.2 Hz, 2H), 3.55 (t, *J* = 7.8 Hz, 2H), 2.43 (s, 3H), 0.92 (t, *J* = 8.3 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 154.9, 151.7, 151.7, 141.6, 131.8, 127.9, 125.9, 124.1, 123.2 (q, $J_{C\text{-}F}$ = 279.5 Hz), 117.9, 115.4, 102.6, 72.8, 67.2 (q, $J_{C\text{-}F}$ = 35.8 Hz), 66.4, 21.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.70 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{27}F_3N_3O_2Si$ $[M+H]^+$: 438.1819, found: 438.1796.

4-(4-(tert-butyl)-2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2bb*)

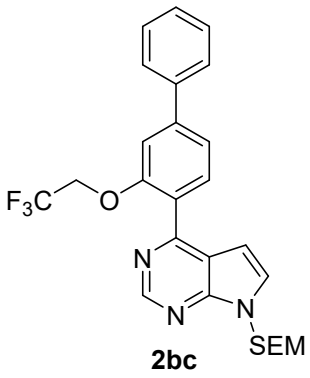


2bb

Product **2bb** was purified by PE/EtOAc (4/1); yellowish solid (98 mg, 68% yield). mp: 41.5-42.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 3.7 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 1.7 Hz, 1H), 6.61 (d, *J* = 3.6 Hz, 1H), 5.71 (s, 2H), 4.29 (q, *J* = 8.3 Hz, 2H), 3.57 (t, *J* = 7.7 Hz, 2H), 1.39 (s, 9H), 0.94 (t, *J* = 7.8 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 155.1, 155.0,

151.8, 151.7, 131.6, 127.9, 126.1, 123.2 (q, $J_{C\text{-}F}$ = 279.6 Hz), 120.8, 117.8, 112.7, 102.7, 72.8, 67.6 (q, $J_{C\text{-}F}$ = 35.6 Hz), 66.4, 35.1, 31.2 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ-73.73 (s, 3F). HRMS m/z (ESI) calcd for $C_{24}H_{33}F_3N_3O_2Si$ $[M+H]^+$: 480.2289, found: 480.2269.

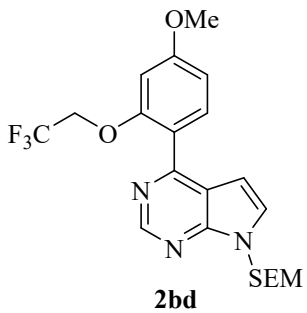
4-(3-(2,2,2-trifluoroethoxy)-[1,1'-biphenyl]-4-yl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2bc*)



2bc

Product **2bc** was purified by PE/EtOAc (10/1); yellowish oil (73 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.53 (d, *J* = 5.1 Hz, 1H), 7.52-7.49 (m, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 3.7 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 6.64 (d, *J* = 3.7 Hz, 1H), 5.73 (s, 2H), 4.39 (q, *J* = 8.2 Hz, 2H), 3.59 (t, *J* = 8.2 Hz, 2H), 0.96 (t, *J* = 8.2 Hz, 2H), -0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 155.4, 151.8, 151.7, 144.4, 140.0, 132.5, 129.0, 128.2, 128.2, 127.6, 127.2, 123.1 (q, $J_{C\text{-}F}$ = 279.2 Hz), 122.3, 118.0, 113.6, 102.6, 72.9, 67.3 (q, $J_{C\text{-}F}$ = 36.0 Hz), 66.5, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.57(s, 3F). HRMS m/z (ESI) calcd for $C_{26}H_{29}F_3N_3O_2Si$ $[M+H]^+$: 500.1976, found: 500.1962.

4-(4-methoxy-2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2bd*)

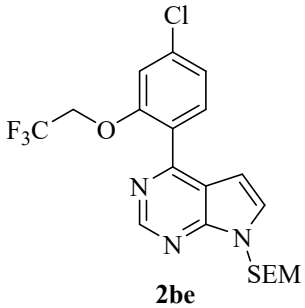


2bd

Product **2bd** was purified by PE/EtOAc (5/1); brown oil (99 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 3.8 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.62 (d, *J* = 2.3 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 5.69 (s, 2H), 4.28 (q, *J* = 8.2 Hz, 2H), 3.88 (s, 3H), 3.56 (t, *J* = 8.1 Hz, 2H), 0.92 (t, *J* = 7.8 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 156.2, 155.7, 151.7, 151.6, 133.1, 127.8, 123.1 (q, $J_{C\text{-}F}$ = 279.4 Hz), 121.3, 117.7, 107.9, 102.7, 101.7, 72.8, 67.1 (q, $J_{C\text{-}F}$ = 36.0 Hz), 66.4, 55.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.56 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{27}F_3N_3O_3Si$ $[M+H]^+$:

454.1768, found: 454.1749.

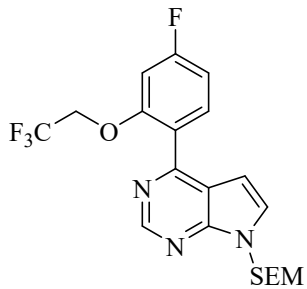
4-(4-chloro-2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2be*)



2be

Product **2be** was purified by PE/EtOAc (5/1); brown oil (86 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 3.7 Hz, 1H), 7.23 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.07 (d, *J* = 1.9 Hz, 1H), 6.51 (d, *J* = 3.7 Hz, 1H), 5.69 (s, 2H), 4.31 (q, *J* = 8.1 Hz, 2H), 3.54 (t, *J* = 8.2 Hz, 2H), 0.91 (t, *J* = 8.3 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 154.6, 151.8, 151.6, 136.4, 133.0, 128.4, 127.2, 123.5, 122.8 (q, $J_{C\text{-}F}$ = 279.4 Hz), 117.8, 114.9, 102.2, 72.8, 67.0 (q, $J_{C\text{-}F}$ = 36.1 Hz), 66.5, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.55 (s, 3F). HRMS m/z (ESI) calcd for $C_{20}H_{24}ClF_3N_3O_2Si$ $[M+H]^+$: 458.1273, found: 458.1269.

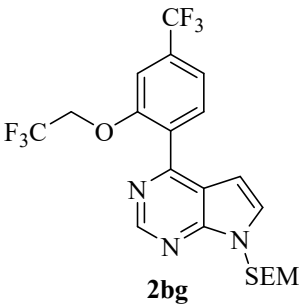
4-(4-fluoro-2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2bf*)



2bf

Product **2bf** was purified by PE/EtOAc (6/1); brown oil (71 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.72 (dd, *J* = 8.5, 6.6 Hz, 1H), 7.36 (d, *J* = 3.6 Hz, 1H), 6.97 (td, *J* = 8.2, 2.2 Hz, 1H), 6.81 (dd, *J* = 10.1, 2.3 Hz, 1H), 6.53 (d, *J* = 3.7 Hz, 1H), 5.70 (s, 2H), 4.31 (q, *J* = 8.0 Hz, 2H), 3.56 (t, *J* = 7.8 Hz, 2H), 0.93 (t, *J* = 7.9 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 162.9, 156.0 (d, $J_{C\text{-}F}$ = 10.1 Hz), 154.9, 151.8, 151.7, 133.4 (d, $J_{C\text{-}F}$ = 10.0 Hz), 128.2, 124.8, 122.8 (q, $J_{C\text{-}F}$ = 227.2 Hz), 117.9, 110.2 (d, $J_{C\text{-}F}$ = 21.3 Hz), 102.3 (t, $J_{C\text{-}F}$ = 13.3 Hz), 72.8, 67.0 (q, $J_{C\text{-}F}$ = 36.2 Hz), 66.4, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.50(s, 3F), -108.03(s, 1F). HRMS m/z (ESI) calcd for $C_{20}H_{24}F_4N_3O_2Si$ $[M+H]^+$: 442.1568, found: 442.1562.

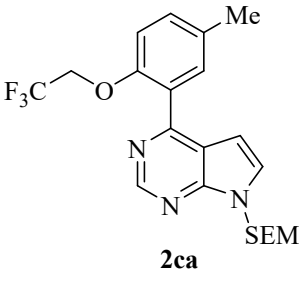
4-(2-(2,2,2-trifluoroethoxy)-4-(trifluoromethyl)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2bg*)



2bg

Product **2bg** was purified by PE/EtOAc (4/1); yellowish solid (106 mg, 72% yield). mp: 42.0-42.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.40 (d, J = 3.6 Hz, 1H), 7.32 (s, 1H), 6.53 (d, J = 3.7 Hz, 1H), 5.72 (s, 2H), 4.38 (q, J = 8.0 Hz, 2H), 3.57 (t, J = 8.2 Hz, 2H), 0.94 (t, J = 8.2 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 154.2, 151.8, 151.7, 133.4 (q, $J_{C\text{-}F}$ = 32.9 Hz), 132.7, 132.2, 128.7, 123.5 (q, $J_{C\text{-}F}$ = 273.6 Hz), 122.8 (q, $J_{C\text{-}F}$ = 279.3 Hz), 120.1 (q, $J_{C\text{-}F}$ = 3.5 Hz), 118.0, 111.2 (q, $J_{C\text{-}F}$ = 3.5 Hz), 102.0, 72.9, 67.1 (q, $J_{C\text{-}F}$ = 36.3 Hz), 66.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.76 (s, 3F), -73.58 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{24}F_6N_3O_2Si$ $[M+H]^+$: 492.1536, found: 492.1523.

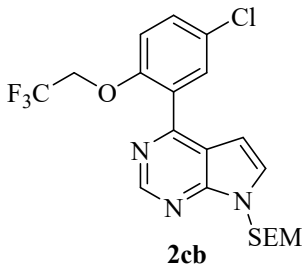
4-(5-methyl-2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2ca*)



2ca

Product **2ca** was purified by PE/EtOAc (5/1); white solid (93 mg, 71% yield). mp: 52.4-53.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.50 (s, 1H), 7.31 (s, 1H), 7.23 (d, J = 8.5 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.53 (s, 1H), 5.67 (s, 2H), 4.21 (q, J = 8.1 Hz, 2H), 3.53 (t, J = 7.8 Hz, 2H), 2.35 (s, 3H), 0.90 (t, J = 7.8 Hz, 2H), -0.08 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 152.9, 151.6, 151.5, 132.8, 132.2, 131.3, 128.3, 127.9, 123.0 (q, $J_{C\text{-}F}$ = 279.5 Hz), 117.8, 114.7, 102.5, 72.6, 67.2 (q, $J_{C\text{-}F}$ = 35.6 Hz), 66.3, 20.4, 17.5, -1.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.52 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{27}F_3N_3O_2Si$ $[M+H]^+$: 438.1819, found: 438.1811.

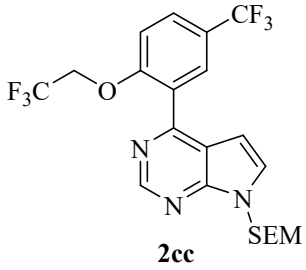
4-(5-chloro-2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2cb*)



2cb

Product **2cb** was Purified by PE/EtOAc (10/1); yellowish oil (71 mg, 52% yield). 1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.70 (d, *J* = 2.6 Hz, 1H), 7.43 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.38 (d, *J* = 3.6 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 5.70 (s, 2H), 4.27 (q, *J* = 8.1 Hz, 2H), 3.55 (t, *J* = 8.2 Hz, 2H), 0.93 (t, *J* = 8.2 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 153.6, 151.8, 151.6, 131.8, 130.7, 130.3, 128.6, 128.6, 122.9 (q, J_{C-F} = 279.5 Hz), 117.8, 116.1, 102.2, 72.9, 67.4 (q, J_{C-F} = 35.9 Hz), 66.5, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.66 (s, 3F). HRMS m/z (ESI) calcd for $C_{20}H_{24}ClF_3N_3O_2Si$ $[M+H]^+$: 458.1273, found: 458.1262.

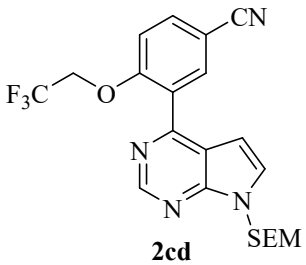
4-(2-(2,2,2-trifluoroethoxy)-5-(trifluoromethyl)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2cc*)



2cc

Product **2cc** was Purified by PE/EtOAc (10/1); yellowish oil (94 mg, 64% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.02 (s, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 3.8 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 6.52 (d, *J* = 3.7 Hz, 1H), 5.72 (s, 2H), 4.40 (q, *J* = 8.0 Hz, 2H), 3.57 (t, *J* = 8.1 Hz, 2H), 0.94 (t, *J* = 8.3 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 154.1, 151.8, 151.7, 129.5 (q, J_{C-F} = 3.6 Hz), 129.0, 128.6, 128.1 (q, J_{C-F} = 3.6 Hz), 125.6 (q, J_{C-F} = 33.4 Hz), 123.8 (q, J_{C-F} = 272.8 Hz), 122.8 (q, J_{C-F} = 279.4 Hz), 118.0, 113.7, 102.1, 72.9, 66.7 (q, J_{C-F} = 28.4 Hz), 66.6, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.87 (s, 3F), -73.44 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{24}F_6N_3O_2Si$ $[M+H]^+$: 492.1536, found: 492.1535.

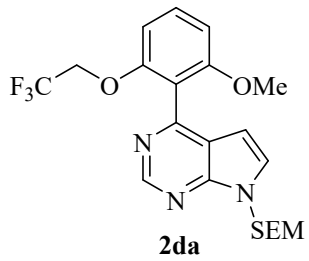
4-(2,2,2-trifluoroethoxy)-3-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)benzonitrile (*2cd*)



2cd

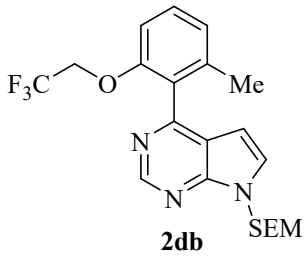
Product **2cd** was Purified by PE/EtOAc (10/1); yellowish solid (58 mg, 43% yield). mp: 72.8-73.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.06 (s, 1H), 7.82 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.42 (d, *J* = 3.8 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.50 (d, *J* = 3.7 Hz, 1H), 5.73 (s, 2H), 4.43 (q, *J* = 7.9 Hz, 2H), 3.57 (t, *J* = 8.2 Hz, 2H), 0.94 (t, *J* = 8.4 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.69, 153.20, 151.90, 151.71, 136.22, 135.0, 129.8, 128.9, 122.6 (q, $J_{C\text{-}F}$ = 279.4 Hz), 118.0, 117.9, 113.9, 107.1, 101.8, 72.9, 66.4 (q, $J_{C\text{-}F}$ = 36.4 Hz), 66.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.25 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{24}F_3N_4O_2Si$ $[M+H]^+$: 449.1615, found: 449.1612.

4-(2-methoxy-6-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2da*)



2da

Product **2da** was Purified by PE/EtOAc (4/1); brown oil (96 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.39 (t, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 3.8 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.31 (d, *J* = 3.6 Hz, 1H), 5.68 (q, *J* = 10.7 Hz, 2H), 4.27-4.20 (m, 2H), 3.71 (s, 3H), 3.56 (t, *J* = 8.0 Hz, 2H), 0.92 (td, *J* = 7.9, 3.1 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 156.1, 154.2, 151.6, 151.5, 130.8, 128.1, 123.0 (q, $J_{C\text{-}F}$ = 279.6 Hz), 119.4, 117.4, 106.8, 106.3, 101.6, 72.7, 67.2 (q, $J_{C\text{-}F}$ = 35.7 Hz), 66.4, 56.0, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.09 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{27}F_3N_3O_3Si$ $[M+H]^+$: 454.1768, found: 454.1729.

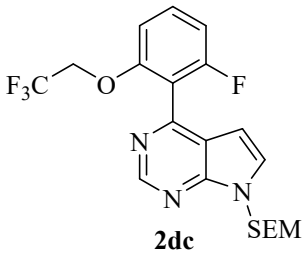


2db

4-(2-methyl-6-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2db*)

Product **2db** was Purified by PE/EtOAc (4/1); orange-yellow oil (81 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$)δ 9.01 (s, 1H), 7.36 (d, *J* = 2.9 Hz, 1H), 7.34 (d, *J* = 1.4 Hz, 1H), 7.08 (d, *J* =

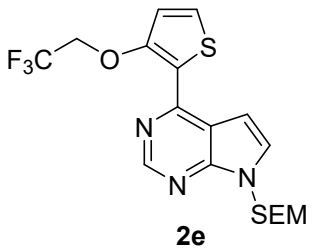
7.6 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.33 (d, *J* = 3.6 Hz, 1H), 5.72 (q, *J* = 10.8 Hz, 2H), 4.29-4.15 (m, 2H), 3.57 (dd, *J* = 9.1, 7.4 Hz, 2H), 2.13 (s, 3H), 0.94 (dd, *J* = 9.2, 7.3 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 155.1, 151.6, 151.5, 138.8, 129.9, 128.6, 127.6, 125.1, 123.0 (q, $J_{C\text{-}F}$ = 279.3 Hz), 118.8, 111.4, 101.5, 72.8, 67.0 (q, $J_{C\text{-}F}$ = 35.7 Hz), 66.5, 19.7, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.12 (s, 3F). HRMS m/z (ESI) calcd for $C_{21}H_{27}F_3N_3O_2Si$ [M H]$^+$: 438.1819, found: 438.1804.



2dc

4-(2-fluoro-6-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2dc*)

Product **2dc** was Purified by PE/EtOAc (4/1); brown oil (86 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.42 (q, *J* = 7.9, 7.4 Hz, 1H), 7.36 (d, *J* = 3.8 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 3.7 Hz, 1H), 5.70 (s, 2H), 4.31 (q, *J* = 8.1 Hz, 2H), 3.56 (t, *J* = 8.2 Hz, 2H), 0.92 (t, *J* = 8.3 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (d, $J_{C\text{-}F}$ = 251.3 Hz), 156.2 (d, $J_{C\text{-}F}$ = 6.6 Hz), 151.7, 151.4, 151.1, 131.1 (d, $J_{C\text{-}F}$ = 10.5 Hz), 128.8, 123.4 (q, $J_{C\text{-}F}$ = 279.4 Hz), 119.1, 117.0 (d, $J_{C\text{-}F}$ = 18.2 Hz), 110.8 (d, $J_{C\text{-}F}$ = 22.3 Hz), 109.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 101.4, 72.8, 67.2 (q, $J_{C\text{-}F}$ = 36.1 Hz), 66.5, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.91 (s, 3F), -112.70 (s, 1F). HRMS m/z (ESI) calcd for $C_{20}H_{24}F_4N_3O_2Si$ [M+H]$^+$: 442.1568, found: 442.1560.



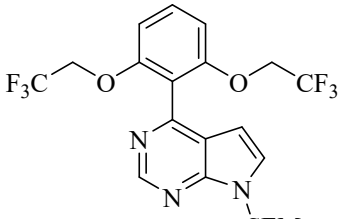
2e

4-(3-(2,2,2-trifluoroethoxy)thiophen-2-yl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*2e*)

Product **2e** was purified by PE/EtOAc (10/1); yellowish oil (99 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.46 (dd, *J* = 5.5, 2.0 Hz, 1H), 7.35 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.02 (d, *J* = 3.5 Hz, 1H), 6.90 (dd, *J* = 5.5, 1.9 Hz, 1H), 5.65 (s, 2H), 4.44 (q, *J* = 8.2 Hz, 2H), 3.54 (t, *J* = 8.5 Hz, 2H), 0.91 (t, *J* = 8.3 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 152.5, 151.2, 150.2, 129.2, 127.7, 123.6, 123.0 (q, $J_{C\text{-}F}$ = 279.5 Hz),

118.2, 114.8, 103.2, 72.8, 68.9 (q, $J_{C\text{-}F}$ = 35.6 Hz), 66.5, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.68 (s, 3F). HRMS m/z (ESI) calcd for $C_{18}H_{23}F_3N_3O_2SSi$ $[M+H]^+$: 430.1227, found: 430.1214.

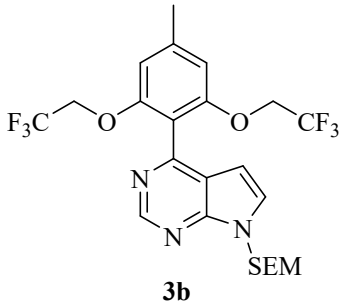
4-(2,6-bis(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3a*)



3a

Product **3a** was purified by PE/EtOAc (5/1); orange-yellow oil (122 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.42 (t, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 3.7 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.33 (d, *J* = 3.6 Hz, 1H), 5.70 (s, 2H), 4.30-4.23 (m, 4H), 3.52 (t, *J* = 8.2 Hz, 2H), 0.92 (t, *J* = 8.3 Hz, 2H)), -0.08 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 152.9, 151.6, 151.3, 130.9, 128.3, 122.9 (q, $J_{C\text{-}F}$ = 279.0 Hz), 119.4, 119.2, 109.1, 101.4, 72.7, 67.2 (q, $J_{C\text{-}F}$ = 35.9 Hz), 66.3, 17.6, -1.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.04 (s, 3F). HRMS m/z (ESI) calcd for $C_{22}H_{26}F_6N_3O_3Si$ $[M+H]^+$: 522.1642, found: 522.1629.

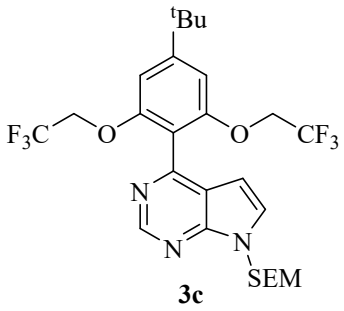
4-(4-methyl-2,6-bis(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3b*)



3b

Product **3b** was purified by PE/EtOAc (5/1); yellowish solid (116 mg, 72% yield). mp:107.8-108.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.32 (t, *J* = 3.1 Hz, 1H), 6.64 (s, 2H), 6.34 (t, *J* = 3.0 Hz, 1H), 5.71 (s, 2H), 4.27 (q, *J* = 7.8 Hz, 4H), 3.53 (t, *J* = 8.2 Hz, 2H), 2.45 (s, 3H), 0.93 (t, *J* = 7.9 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 148.4, 146.6, 146.6, 137.0, 123.5, 118.2 (q, $J_{C\text{-}F}$ = 279.5 Hz), 114.6, 111.8, 105.2, 96.9, 68.0, 62.5 (q, $J_{C\text{-}F}$ = 35.9 Hz), 61.6, 17.3, 12.9, -6.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.05 (s, 3F). HRMS m/z (ESI) calcd for $C_{23}H_{28}F_6N_3O_3Si$ $[M+H]^+$: 536.1799, found: 536.1776.

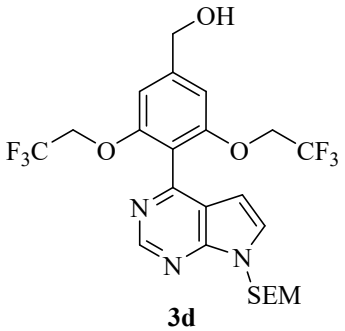
4-(4-(tert-butyl)-2,6-bis(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3c*)



3c

Product **3c** was purified by PE/EtOAc (6/1); yellowish solid (132 mg, 76% yield). mp: 38.7-38.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.34 (d, *J* = 3.7 Hz, 1H), 6.85 (s, 2H), 6.39 (d, *J* = 3.7 Hz, 1H), 5.72 (s, 2H), 4.31-4.24 (m, 4H), 3.57 (t, *J* = 8.2 Hz, 2H), 1.39 (s, 9H), 0.94 (t, *J* = 8.2 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 155.4, 153.2, 151.6, 151.3, 128.2, 123.0 (q, J_{C-F} = 279.6 Hz), 119.3, 117.1, 107.3, 101.7, 72.7, 67.6 (q, J_{C-F} = 35.8 Hz), 66.3, 35.4, 31.2, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.04 (s, 3F). HRMS m/z (ESI) calcd for $C_{26}H_{34}F_6N_3O_3Si$ $[M+H]^+$: 578.2268, found: 578.2252.

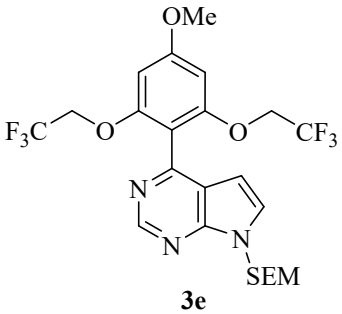
(3,5-bis(2,2,2-trifluoroethoxy)-4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)methanol (*3d*)



3d

Product **3d** was purified by PE/EtOAc (2/1); yellow oil (117 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.35 (d, *J* = 3.7 Hz, 1H), 6.66 (s, 2H), 6.29 (d, *J* = 3.7 Hz, 1H), 5.73 (s, 2H), 4.73 (s, 2H), 4.21 (q, *J* = 8.1 Hz, 4H), 3.54 (t, *J* = 8.2 Hz, 2H), 0.94 (t, *J* = 8.4 Hz, 2H), -0.06 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 152.8, 151.6, 151.0, 147.0, 128.7, 122.8 (q, J_{C-F} = 279.5 Hz), 119.2, 116.0, 105.1, 101.5, 72.8, 66.7 (q, J_{C-F} = 35.8 Hz), 66.4, 63.1, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.02 (s, 3F). HRMS m/z (ESI) calcd for $C_{23}H_{28}F_6N_3O_4Si$ $[M+H]^+$: 552.1748, found: 552.1730.

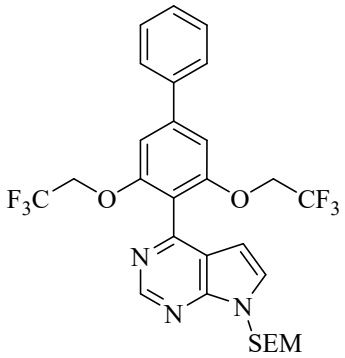
4-(4-methoxy-2,6-bis(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3e*)



3e

Product **3e** was purified by PE/EtOAc (5/1); yellow oil (124 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.31 (d, *J* = 3.7 Hz, 1H), 6.35 (s, 2H), 6.34 (d, *J* = 3.6 Hz, 1H), 5.69 (s, 2H), 4.28-4.21 (m, 4H), 3.86 (s, 3H), 3.52 (t, *J* = 8.2 Hz, 2H), 0.91 (t, *J* = 8.3 Hz, 2H), -0.08 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 157.2, 152.9, 151.6, 151.2, 128.2, 122.9 (q, $J_{C\text{-}F}$ = 279.6 Hz), 119.4, 112.1, 101.7, 95.9, 72.7, 67.3 (q, $J_{C\text{-}F}$ = 35.9 Hz), 66.3, 55.7, 17.6, -17. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.99 (s, 3F). HRMS m/z (ESI) calcd for $C_{23}H_{28}F_6N_3O_4Si$ $[M+H]^+$: 552.1748, found: 552.1727.

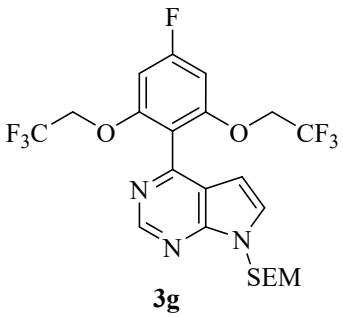
4-(3,5-bis(2,2,2-trifluoroethoxy)-[1,1'-biphenyl]-4-yl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3f*)



3f

Product **3f** was purified by PE/EtOAc (8/1); yellowish oil (131 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.62 (d, *J* = 6.8 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 3.7 Hz, 1H), 7.02 (s, 2H), 6.47 (d, *J* = 3.6 Hz, 1H), 5.75 (s, 2H), 4.41 (q, *J* = 8.1 Hz, 4H), 3.56 (t, *J* = 8.2 Hz, 2H), 0.95 (t, *J* = 8.3 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 151.7, 145.4, 139.8, 129.1, 128.6, 127.21, 122.9 (q, $J_{C\text{-}F}$ = 279.5 Hz), 119.2, 108.0, 102.1, 72.9, 67.3 (q, $J_{C\text{-}F}$ = 35.9 Hz), 66.5, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.83 (s, 3F). HRMS m/z (ESI) calcd for $C_{28}H_{30}F_6N_3O_3Si$ $[M+H]^+$: 598.1955, found: 598.1935.

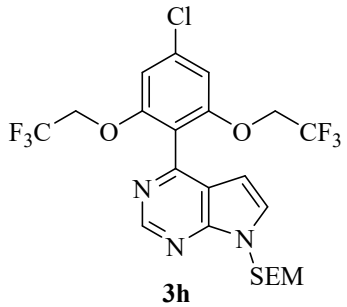
4-(4-fluoro-2,6-bis(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3g*)



3g

Product **3g** was purified by PE/EtOAc (5/1); brown oil (110 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.37 (d, J = 3.7 Hz, 1H), 7.06 (s, 2H), 6.32 (d, J = 3.7 Hz, 1H), 5.72 (s, 2H), 4.37-4.31 (m, 4H), 3.54 (t, J = 8.3 Hz, 2H), 0.93 (t, J = 8.3 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 151.6 (d, J_{C-F} = 35.1 Hz), 151.4, 133.2 (q, J_{C-F} = 33.6 Hz), 128.9, 123.2 (q, J_{C-F} = 273.9 Hz), 122.6 (q, J_{C-F} = 279.5 Hz), 122.4, 118.9, 105.9 (d, J_{C-F} = 3.8 Hz), 101.0, 72.8, 67.2 (q, J_{C-F} = 36.3 Hz), 66.4, 17.6, -1.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.01 (s, 1F), -73.99 (s, 3F). HRMS m/z (ESI) calcd for $C_{22}H_{25}F_7N_3O_3Si$ $[M+H]^+$: 540.1548, found: 540.1545.

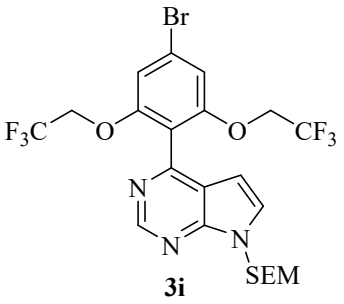
4-(4-chloro-2,6-bis(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3h*)



3h

Product **3h** was purified by PE/EtOAc (5/1); yellow oil (120 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.35 (d, J = 3.7 Hz, 1H), 6.83 (s, 2H), 6.32 (d, J = 3.6 Hz, 1H), 5.71 (s, 2H), 4.31-4.25 (m, 4H), 3.53 (t, J = 8.2 Hz, 2H), 0.92 (t, J = 8.2 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 151.8, 151.7, 151.3, 136.4, 128.7, 122.6 (q, J_{C-F} = 279.6 Hz), 119.1, 117.6, 109.7, 101.2, 72.8, 67.2 (q, J_{C-F} = 36.2 Hz), 66.4, 17.6, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.94 (s, 3F). HRMS m/z (ESI) calcd for $C_{22}H_{25}ClF_6N_3O_3Si$ $[M+H]^+$: 556.1252, found: 556.1229.

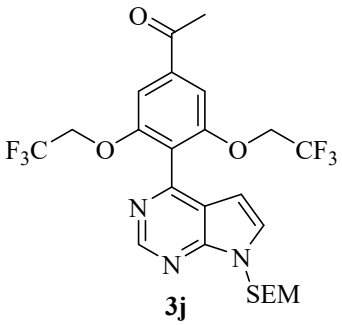
4-(4-bromo-2,6-bis(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3i*)



3i

Product **3i** was purified by PE/EtOAc (10/1); yellow oil (120 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.35 (d, J = 3.7 Hz, 1H), 6.99 (s, 2H), 6.32 (d, J = 3.7 Hz, 1H), 5.72 (s, 2H), 4.31-4.25 (m, 4H), 3.53 (t, J = 8.2 Hz, 2H), 0.93 (t, J = 8.2 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 151.9, 151.7, 151.4, 128.6, 123.8, 122.6 (q, $J_{C\text{-}F}$ = 279.4 Hz), 119.1, 118.3, 112.7, 101.2, 72.8, 67.3 (q, $J_{C\text{-}F}$ = 36.3 Hz), 66.4, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.95 (s, 3F). HRMS m/z (ESI) calcd for $C_{22}H_{25}BrF_6N_3O_3Si$ $[M+H]^+$: 600.0747, found: 600.0729.

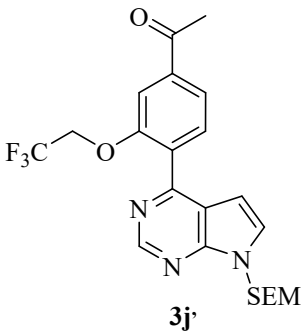
1-(3,5-bis(2,2,2-trifluoroethoxy)-4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)ethan-1-one (*3j*)



3j

Product **3j** was purified by PE/EtOAc (5/1); yellow oil (101 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.40 (s, 2H), 7.36 (d, J = 3.6 Hz, 1H), 6.30 (d, J = 3.7 Hz, 1H), 5.72 (s, 2H), 4.40-4.32 (m, 4H), 3.53 (t, J = 8.2 Hz, 2H), 2.67 (s, 3H), 0.93 (t, J = 8.2 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 156.5, 151.8, 151.7, 151.3, 139.4, 128.8, 123.6, 122.7 (q, $J_{C\text{-}F}$ = 279.6 Hz), 118.9, 108.8, 101.1, 72.8, 67.2 (q, $J_{C\text{-}F}$ = 36.1 Hz), 66.4, 26.7, 17.6, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.93 (s, 3F). HRMS m/z (ESI) calcd for $C_{24}H_{28}F_6N_3O_4Si$ $[M+H]^+$: 564.1748, found: 564.1734.

1-(3-(2,2,2-trifluoroethoxy)-4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl)ethan-1-one (*3j'*)

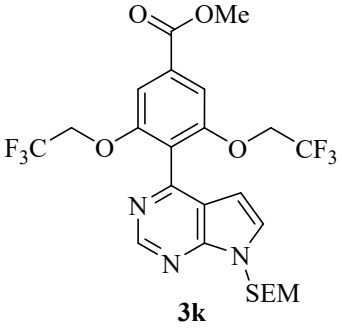


3j'

Product **3j'** was purified by PE/EtOAc (8/1); yellowish oil (10 mg, 7% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.81 (dd, *J* = 7.6, 19.9 Hz, 2H), 7.68 (s, 1H), 7.38 (d, *J* = 3.8 Hz, 1H), 6.51 (d, *J* = 3.8 Hz, 1H), 5.71 (s, 2H), 4.41 (q, *J* = 8.0 Hz, 2H), 3.56 (t, *J* = 8.2 Hz, 2H), 2.67 (s, 3H), 0.92 (t, *J* = 8.2 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 155.1, 154.5, 151.8, 151.6, 139.2, 133.0, 132.4, 128.6, 123.5, 122.9 (q, $J_{C\text{-}F}$ = 279.4 Hz), 118.0, 112.6, 102.2, 72.9, 66.7 (q, $J_{C\text{-}F}$ = 36.2 Hz), 66.5, 26.7, 17.7, -1.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.52. HRMS (ESI) calcd for $C_{22}H_{27}F_3N_3O_3Si$ $[M+H]^+$: 466.1768, found: 466.1779.

methyl 3,5-bis(2,2,2-trifluoroethoxy)-4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)benzoate (*3k*)

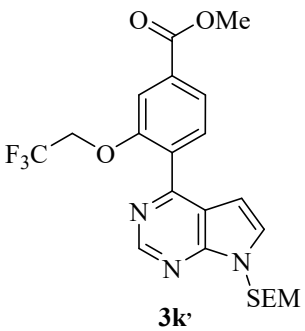
Product **3k** was purified by PE/EtOAc (5/1); yellow oil (123 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.48 (s, 2H), 7.35 (d, *J* = 3.5 Hz, 1H), 6.30 (d, *J* = 3.7 Hz, 1H), 5.71 (s, 2H), 4.40-4.31 (m, 4H), 3.97 (d, *J* = 1.8 Hz, 3H), 3.52 (t, *J* = 8.2 Hz, 2H), 0.91 (t, *J* = 8.3 Hz, 2H), -0.08 (d, *J* = 1.1 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 156.2, 151.9, 151.7, 151.2, 132.8, 128.8, 122.9, 122.7 (q, $J_{C\text{-}F}$ = 279.5 Hz), 118.9, 109.4, 101.1, 72.7, 66.9 (q, $J_{C\text{-}F}$ = 36.3 Hz), 66.4, 52.7, 17.6, -1.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.96 (s, 3F). HRMS (ESI) calcd for $C_{24}H_{28}F_6N_3O_5Si$ $[M+H]^+$: 580.1697, found: 580.1680.



3k

methyl 3-(2,2,2-trifluoroethoxy)-4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)benzoate (*3k'*)

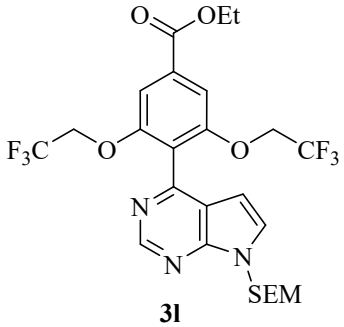
Product **3k'** was purified by PE/EtOAc (8/1); yellowish oil (13 mg, 9% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.75 (s, 1H), 7.38 (d, *J* = 3.7 Hz, 1H), 6.52 (d, *J* = 3.7 Hz, 1H), 5.71 (s, 2H), 4.41 (q, *J* = 8.0 Hz, 2H), 3.97 (s, 3H), 3.56 (t, *J* = 8.2 Hz, 2H), 0.93 (t, *J* = 8.2 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 154.7, 154.7, 151.8, 151.6, 132.8, 132.5, 132.2, 128.6, 124.2, 122.9 (q, J_{C-F} = 279.4 Hz), 118.0, 114.7, 102.2, 72.9, 66.8 (q, J_{C-F} = 36.1 Hz), 66.52, 52.51, 17.70, -1.55. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.55. HRMS (ESI) calcd for $C_{22}H_{27}F_3N_3O_4Si$ $[M+H]^+$: 482.1717, found: 482.1708.



3k'

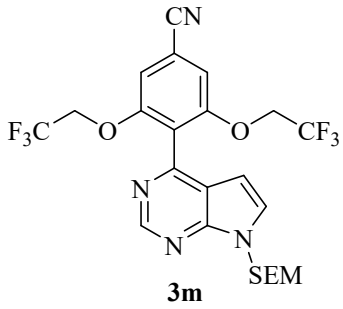
ethyl 3,5-bis(2,2,2-trifluoroethoxy)-4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)benzoate (*3l*)

Product **3l** was purified by PE/EtOAc (5/1); yellow oil (103 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.48 (s, 2H), 7.34 (d, *J* = 3.0 Hz, 1H), 6.29 (d, *J* = 3.6 Hz, 1H), 5.70 (s, 2H), 4.46-4.40 (m, 3H), 4.38-4.30 (m, 4H), 3.52 (t, *J* = 8.2 Hz, 2H), 1.42 (dd, *J* = 4.9, 2.3 Hz, 2H), 0.91 (t, *J* = 8.2 Hz, 2H), -0.09 (d, *J* = 1.4 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 156.1, 151.9, 151.7, 151.3, 133.2, 128.7, 122.9, 122.7 (q, J_{C-F} = 279.5 Hz), 118.9, 109.5, 101.1, 72.7, 67.0 (q, J_{C-F} = 36.1 Hz), 66.3, 61.8, 17.6, 14.3, -1.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.99 (d, *J* = 3.5 Hz, 3F). HRMS (ESI) calcd for $C_{25}H_{30}F_6N_3O_5Si$ $[M+H]^+$: 594.1853, found: 594.1830.



3l

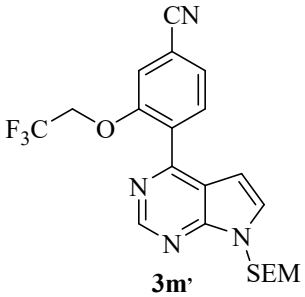
3,5-bis(2,2,2-trifluoroethoxy)-4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)benzonitrile (*3m*)



3m

Product **3m** was purified by PE/EtOAc (10/1); yellow oil (79 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.39 (d, *J* = 3.7 Hz, 1H), 7.11 (s, 2H), 6.30 (d, *J* = 3.7 Hz, 1H), 5.73 (s, 2H), 4.36-4.30 (m, 4H), 3.55 (t, *J* = 8.2 Hz, 2H), 0.94 (t, *J* = 8.2 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 151.8, 151.4, 150.7, 129.1, 123.9, 122.5 (q, $J_{C\text{-}F}$ =279.8 Hz), 118.8, 117.4, 114.5, 112.4, 100.8, 72.8, 67.2 (q, $J_{C\text{-}F}$ = 36.7 Hz), 66.5, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.82 (s, 3F). HRMS m/z (ESI) calcd for $C_{23}H_{25}F_6N_4O_3Si$ $[M+H]^+$: 547.1595, found: 547.1580.

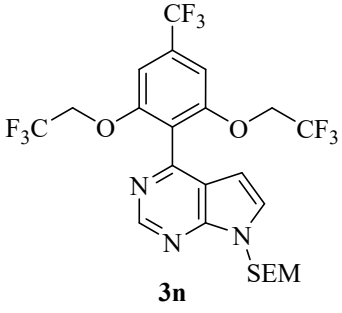
3-(2,2,2-trifluoroethoxy)-4-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)benzonitrile (*3m'*)



3m'

Product **3m'** was purified by PE/EtOAc (6/1); yellow oil (50 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.42 (d, *J* = 3.8 Hz, 1H), 7.37 (d, *J* = 1.4 Hz, 1H), 6.51 (d, *J* = 3.7 Hz, 1H), 5.72 (s, 2H), 4.36 (q, *J* = 7.9 Hz, 2H), 3.58 (t, *J* = 8.2 Hz, 2H), 0.94 (t, *J* = 8.3 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 153.6, 151.9, 151.7, 133.5, 133.1, 129.0, 127.0, 122.7 (q, $J_{C\text{-}F}$ = 279.4 Hz), 117.9, 117.9, 117.5, 114.4, 101.9, 72.9, 67.1 (q, $J_{C\text{-}F}$ = 36.5 Hz), 66.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.44 (s, 3F). HRMS (ESI) calcd for $C_{21}H_{24}F_3N_4O_2Si$ $[M+H]^+$: 449.1615, found: 449.1610.

4-(2,6-bis(2,2,2-trifluoroethoxy)-4-(trifluoromethyl)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3n*)

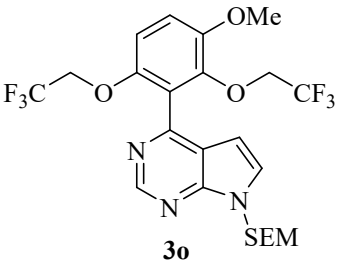


3n

Product **3n** was purified by PE/EtOAc (5/1); yellow oil (85 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.32 (d, *J* = 3.8 Hz, 1H), 6.53 (d, *J* = 9.9 Hz, 2H), 6.30 (d, *J* = 3.7 Hz, 1H), 5.68 (s, 2H), 4.24 (q, *J* = 7.9 Hz, 4H), 3.51 (t, *J* = 8.2 Hz, 2H), 0.90 (t, *J* = 8.6 Hz, 2H), -0.09 (s, 9H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 165.2, 162.8, 157.0 (d, $J_{C\text{-}F}$ = 12.7 Hz), 152.0, 151.7, 151.3, 128.5, 122.6 (q, $J_{C\text{-}F}$ = 279.5 Hz), 119.2, 115.0 (d, $J_{C\text{-}F}$ = 3.9 Hz), 101.2, 96.9 (d, $J_{C\text{-}F}$ = 25.8 Hz), 72.7, 67.0 (q, $J_{C\text{-}F}$ = 36.4 Hz), 66.3, 17.6, -1.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.97 (s, 3F), -106.49 (s, 3F). HRMS (ESI) calcd for $C_{23}H_{25}F_9N_3O_3Si$ $[M+H]^+$: 590.1516, found: 590.1502.

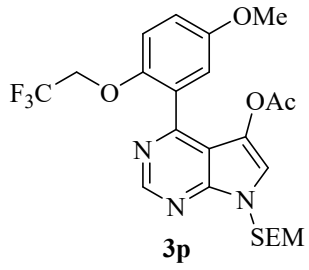
4-(3-methoxy-2,6-bis(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*3o*)



3o

Product **3o** was purified by PE/EtOAc (5/1); brown oil (86 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.34 (s, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.36 (s, 1H), 5.72 (q, *J* = 10.8 Hz, 2H), 4.44-4.18 (m, 4H), 3.91 (s, 3H), 3.52 (t, *J* = 8.4 Hz, 2H), 0.93 (t, *J* = 8.1 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 151.6, 151.2, 149.3, 148.5, 145.1, 128.5, 124.4, 122.9 (q, $J_{C\text{-}F}$ = 287.7 Hz), 122.9 (q, $J_{C\text{-}F}$ = 271.6 Hz), 119.1, 113.4, 111.8, 101.6, 72.7, 69.6 (q, $J_{C\text{-}F}$ = 35.2 Hz), 68.2 (q, $J_{C\text{-}F}$ = 35.5 Hz), 66.3, 56.4, 17.6, -1.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.90 (s, 3F), -79.82 (s, 3F). HRMS (ESI) calcd for $C_{23}H_{28}F_6N_3O_4Si$ $[M+H]^+$: 552.1748, found: 552.1736.

4-(5-methoxy-2-(2,2,2-trifluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (*3p*)

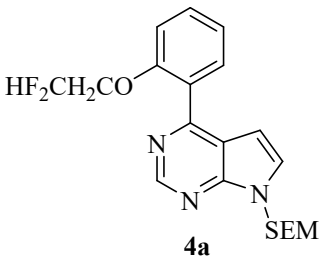


3p

Product **3p** was purified by PE/EtOAc (5/1); yellowish solid (52 mg, 34% yield). mp : 79.5-80.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.34 (t, *J* = 3.3 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.41 (t, *J* = 3.3 Hz, 1H), 5.70 (q, *J* = 9.5 Hz, 2H), 4.22-4.14 (m, 2H), 3.87 (s, 3H), 3.55 (t, *J* = 8.0 Hz, 2H), 1.98 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 152.4, 151.7, 151.4, 149.25, 148.0, 138.7, 128.7, 123.9, 122.3 (q, $J_{C\text{-}F}$ = 279.7 Hz), 118.9, 113.5, 113.2, 101.6, 72.8, 68.2 (q, $J_{C\text{-}F}$ = 35.5 Hz), 66.4, 56.5, 20.3, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.16 (s, 3F). HRMS

(ESI) calcd for $C_{23}H_{29}F_3N_3O_5Si$ [M+H]$^+$: 512.1823, found: 512.1819.

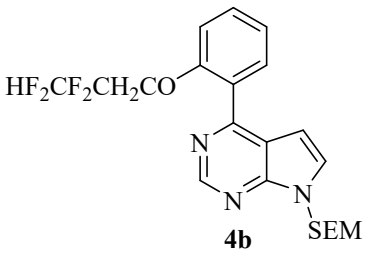
4-(2-(2,2-difluoroethoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4a*)



4a

Product **4a** was purified by PE/EtOAc (5/1); yellowish oil (101 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.50-7.45 (m, 1H), 7.34 (d, *J* = 3.7 Hz, 1H), 7.24-7.18 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 6.00-5.71 (m, 1H), 5.70 (s, 2H), 4.23-4.14 (m, 2H), 3.59 (td, *J* = 8.1, 1.0 Hz, 2H), 0.94 (t, *J* = 8.4 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 155.2, 151.7 (2C), 131.9, 131.0, 128.1, 128.0, 122.5, 118.0, 113.5 (t, $J_{C\text{-}F}$ = 242.2 Hz), 113.3, 102.6, 72.8, 68.3 (t, $J_{C\text{-}F}$ = 30.2 Hz), 66.5, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -124.72 (s, 2F). HRMS (ESI) calcd for $C_{20}H_{26}F_2N_3O_2Si$ [M+H]$^+$: 406.1757, found: 406.1740.

4-(2-(2,2,3,3-tetrafluoropropoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4b*)

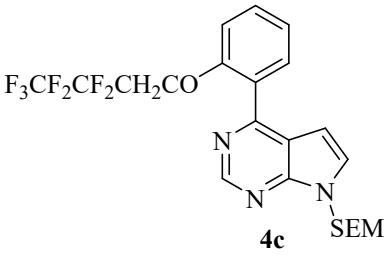


4b

Product **4b** was purified by PE/EtOAc (8/1); yellow oil (105 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.70 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.53-7.49 (m, 1H), 7.39 (d, *J* = 3.7 Hz, 1H), 7.26 (td, *J* = 7.6, 1.1 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 5.72 (s, 2H), 5.65 (tt, *J* = 53.0, 5.4 Hz, 1H), 4.35 (tt, *J* = 11.6, 1.6 Hz, 2H), 3.59 (t, J = 8.2 Hz, 2H), 0.95 (t, J = 8.2 Hz, 2H), -0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 154.7, 151.8, 131.9, 131.1, 128.3, 128.1, 123.0, 117.8, 114.3 (tt, $^1J_{C\text{-}F}$ = 251.2, $^2J_{C\text{-}F}$ = 26.5 Hz), 113.5, 109.4, 108.7 (tt, $^1J_{C\text{-}F}$ = 250.6, $^2J_{C\text{-}F}$ = 33.3 Hz), 102.1, 72.9, 66.6, 66.5 (t, $J_{C\text{-}F}$ = 31.2 Hz), 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -125.59 (t, *J* = 5.5 Hz, 2F), -140.45 (t, *J* = 5.5 Hz, 2F). HRMS (ESI) calcd for $C_{21}H_{26}F_4N_3O_2Si$ [M+H]$^+$: 456.1725, found: 456.1706.

4-(2-(2,2,3,3,4,4,4-heptafluorobutoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-

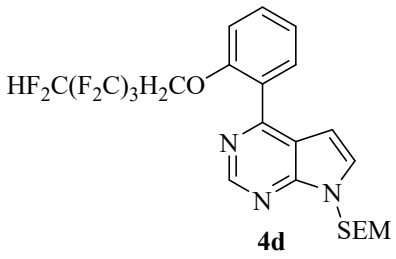
7*H*-pyrrolo[2,3-*d*]pyrimidine (*4c*)



4c

Product **4c** was purified by PE/EtOAc (10/1); yellowish oil (122 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.69 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.51-7.47 (m, 1H), 7.35 (d, *J* = 3.7 Hz, 1H), 7.26 (td, *J* = 7.5, 1.0 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 3.7 Hz, 1H), 5.70 (s, 2H), 4.41 (tt, *J* = 13.3, 1.5 Hz, 2H), 3.57 (t, J = 8.2 Hz, 2H), 0.94 (t, J = 8.2 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 155.1, 151.7, 151.6, 131.8, 131.0, 128.9, 128.1, 123.4, 119.2-108.4 (m, 3C-F), 118.0, 114.6, 102.3, 72.7, 66.5 (t, $J_{C\text{-}F}$ = 26.8 Hz), 66.4, 17.6, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.05 (t, *J* = 9.2 Hz, 3F), -120.22--120.31 (m, 2F), -127.66 (s, 2F). HRMS (ESI) calcd for $C_{22}H_{25}F_7N_3O_2Si$ $[M+H]^+$: 524.1599, found: 524.1580.

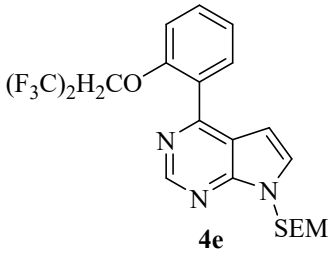
4-(2-((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-d]pyrimidine (*4d*)



4d

Product **4d** was purified by PE/EtOAc (5/1); yellow oil (133 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.70 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.52-7.48 (m, 1H), 7.35 (d, *J* = 3.7 Hz, 1H), 7.26 (td, *J* = 7.6, 1.1 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 5.93 (tt, *J* = 51.9, 5.5 Hz, 1H), 5.71 (s, 2H), 4.43 (tt, *J* = 13.5, 1.5 Hz, 2H), 3.58 (t, *J* = 8.1 Hz, 2H), 0.95 (t, *J* = 8.2 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 155.2, 151.7, 151.6, 131.8, 131.0, 128.8, 128.2, 123.4, 118.0, 117.6-104.6 (m, 4C-F), 114.6, 102.3, 72.8, 66.6 (t, $J_{C\text{-}F}$ = 26.4 Hz), 66.4, 17.7, -1.6. ^{19}F NMR (377 MHz, C*D*Cl_3) δ -119.49 (td, *J* = 10.4, 2.8 Hz, 2F), -125.59 (t, *J* = 8.4 Hz, 2F), -130.31--130.40 (m, 2F), -137.32--137.42 (m, 2F). HRMS (ESI) calcd for $C_{23}H_{26}F_8N_3O_2Si$ $[M+H]^+$: 556.1661, found: 556.1632.

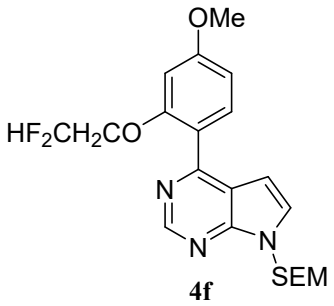
4-(2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4e*)



4e

Product **4e** was purified by PE/EtOAc (10/1); yellowish oil (49 mg, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.38-7.35 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 3.7 Hz, 1H), 5.72 (s, 2H), 4.94-4.85 (m, 1H), 3.54 (t, *J* = 7.8 Hz, 2H), 0.93 (t, *J* = 8.3 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 154.7, 151.8, 151.6, 132.1, 131.2, 130.2, 129.5, 128.3, 125.2, 120.8 (q, $J_{C\text{-}F}$ = 285.3 Hz), 118.2, 116.5, 102.4, 72.8, 66.4, 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.36 (s, 6F). HRMS (ESI) calcd for $C_{21}H_{24}F_6N_3O_2Si$ $[M+H]^+$: 492.1536, found: 492.1517.

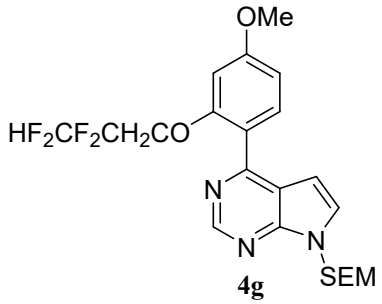
4-(2-(2,2-difluoroethoxy)-4-methoxyphenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4f*)



4f

Product **4f** was purified by PE/EtOAc (5/1); yellow oil (103 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 6.75 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.60 (d, *J* = 2.2 Hz, 1H), 6.56 (d, *J* = 3.7 Hz, 1H), 5.88 (tt, *J* = 55.2, 4.1 Hz, 1H), 5.69 (s, 2H), 4.17 (td, *J* = 13.0, 4.1 Hz, 2H), 3.89 (s, 3H), 3.59 (t, *J* = 8.2 Hz, 2H), 0.94 (t, *J* = 8.6 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 156.4, 156.0, 151.7, 151.6, 133.0, 127.7, 120.8, 117.8, 113.4 (t, $J_{C\text{-}F}$ = 242.2 Hz), 106.9, 102.8, 100.6, 72.8, 68.2 (t, $J_{C\text{-}F}$ = 30.3 Hz), 66.5, 55.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -124.64 (s, 2F). HRMS (ESI) calcd for $C_{21}H_{28}F_2N_3O_3Si$ $[M+H]^+$: 436.1863, found: 436.1885.

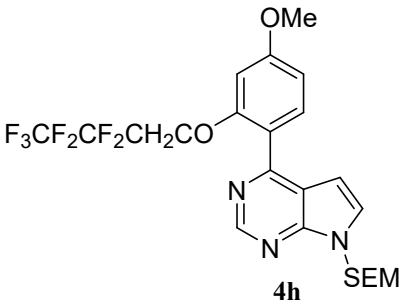
4-(4-methoxy-2-(2,2,3,3-tetrafluoropropoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4g*)



4g

Product **4g** was purified by PE/EtOAc (8/1); yellowish oil (128 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 3.7 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 6.61 (s, 1H), 6.55 (d, *J* = 3.6 Hz, 1H), 5.71 (s, 2H), 5.68 (tt, *J* = 53.1, 5.5 Hz, 1H), 4.33 (t, *J* = 11.5 Hz, 2H), 3.91 (s, 3H), 3.58 (t, *J* = 8.2 Hz, 2H), 0.95 (t, *J* = 8.2 Hz, 2H), -0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 156.0, 155.9, 151.8, 133.0, 128.0, 120.8, 117.5, 114.3 (tt, $^{1}J_{C\text{-}F}$ = 251.4, $^{2}J_{C\text{-}F}$ = 26.8 Hz), 108.7 (tt, $^{1}J_{C\text{-}F}$ = 250.5, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 107.4, 102.3, 101.4, 100.8, 72.8, 66.5, 66.5 (t, $J_{C\text{-}F}$ = 30.9 Hz), 55.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -125.49 (t, *J* = 5.7 Hz, 2F), -140.45 (t, *J* = 5.6 Hz, 2F). HRMS (ESI) calcd for $C_{22}H_{28}F_4N_3O_3Si$ $[M+H]^+$: 486.1831, found: 486.1819.

4-(2-(2,2,3,3,4,4,4-heptafluorobutoxy)-4-methoxyphenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4h*)

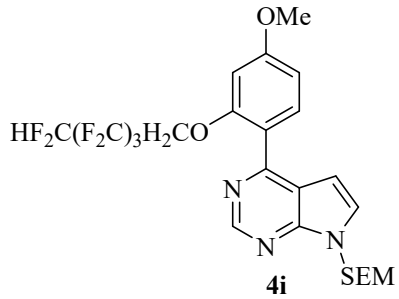


4h

Product **4h** was purified by PE/EtOAc (5/1); yellow oil (126 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 6.81-6.78 (m, 1H), 6.64 (d, *J* = 2.2 Hz, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 5.69 (s, 2H), 4.38 (t, *J* = 13.3 Hz, 2H), 3.89 (s, 3H), 3.56 (t, J = 8.1 Hz, 2H), 0.93 (t, *J* = 9.2 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 156.3, 155.7, 151.7, 151.6, 132.9, 127.80, 121.5, 119.4-111.5 (m, 3C-F), 117.7, 108.0, 102.5, 101.9, 72.7, 66.5 (t, $J_{C\text{-}F}$ = 26.6 Hz), 66.3, 55.6, 17.6, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.04 (t, *J* = 4.4 Hz, 3F), -120.14--120.22 (m, *2F*), -127.62 (s, *2F*). HRMS (ESI) calcd for $C_{23}H_{27}F_7N_3O_3Si$ $[M+H]^+$: 554.1704, found: 554.1685.

4-(4-methoxy-2-((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)phenyl)-7-((2-

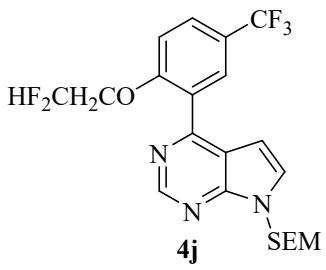
(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4i*)



4i

Product **4i** was purified by PE/EtOAc (5/1); yellow oil (147 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 3.7 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.64 (s, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 5.93 (tt, *J* = 57.4, 5.5 Hz, 1H), 5.69 (s, 2H), 4.39 (t, *J* = 13.5 Hz, 2H), 3.88 (s, 3H), 3.57 (t, *J* = 8.2 Hz, 2H), 0.93 (t, *J* = 8.2 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 156.3, 155.8, 151.7, 151.6, 132.9, 127.84, 121.5, 117.6, 117.5-104.6 (m, 4C-F), 107.9, 102.5, 101.9, 72.8, 66.6 (t, J_{C-F} = 26.2 Hz), 66.4, 55.6, 17.6, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.41 (t, *J* = 11.0 Hz, 2F), -125.57 (t, *J* = 8.5 Hz, 2F), -130.32--130.39 (m, 2F), -137.42 (s, 2F). HRMS (ESI) calcd for $C_{24}H_{28}F_8N_3O_3Si$ $[M+H]^+$: 586.1767, found: 586.1740.

4-(2-(2,2-difluoroethoxy)-5-(trifluoromethyl)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4j*)

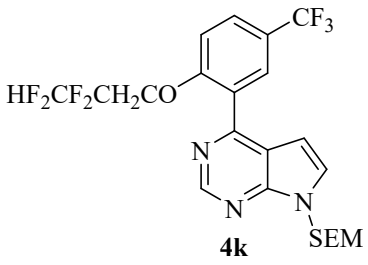


4j

Product **4j** was purified by PE/EtOAc (8/1); yellow oil (86 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.00 (d, *J* = 2.1 Hz, 1H), 7.76 (ddd, *J* = 8.7, 2.5, 0.8 Hz, 1H), 7.39 (d, *J* = 3.7 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 6.51 (d, *J* = 3.7 Hz, 1H), 5.90 (tt, *J* = 55.0, 4.0 Hz, 1H), 5.72 (s, 2H), 4.27 (td, *J* = 12.8, 4.1 Hz, 2H), 3.60 (t, *J* = 8.1 Hz, 2H), 0.95 (t, *J* = 8.2 Hz, 2H), -0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 154.5, 151.9, 151.8, 129.4 (q, J_{C-F} = 3.3 Hz), 128.5, 128.5, 128.1 (q, J_{C-F} = 3.6 Hz), 124.9 (q, J_{C-F} = 33.3 Hz), 124.0 (q, J_{C-F} = 272.7 Hz), 118.0, 113.1 (t, J_{C-F} = 242.6 Hz), 112.8, 102.1, 72.9, 68.1 (t, J_{C-F} = 30.6 Hz), 66.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.77(s, 3F), -124.67(s, 2F). HRMS (ESI) calcd for $C_{21}H_{25}F_5N_3O_2Si$ $[M+H]^+$: 474.1631, found: 474.1622.

4-(2-(2,2,3,3-tetrafluoropropoxy)-5-(trifluoromethyl)phenyl)-7-((2-

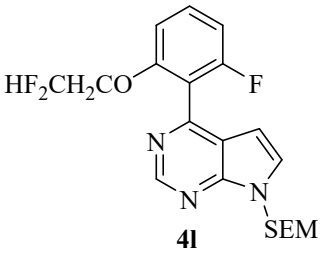
(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4k*)



4k

Product **4k** was purified by PE/EtOAc (15/1); yellowish oil (110 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.99 (d, J = 2.4 Hz, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.43 (d, J = 3.7 Hz, 1H), 7.16 (d, J = 8.7 Hz, 1H), 6.51 (d, J = 3.7 Hz, 1H), 5.73 (s, 2H), 5.65 (tt, J = 53.0, 5.1 Hz, 1H), 4.42 (tt, J = 11.6, 1.5 Hz, 2H), 3.59 (t, J = 8.0 Hz, 2H), 0.96 (t, J = 8.0 Hz, 2H), -0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 154.4, 151.9, 151.8, 129.4 (q, $J_{C\text{-}F}$ = 3.6 Hz), 128.8, 128.5, 128.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.4 (q, $J_{C\text{-}F}$ = 33.5 Hz), 117.7, 115.8, 114.1 (tt, $^{1}J_{C\text{-}F}$ = 251.4, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 113.1, 108.6 (tt, $^{1}J_{C\text{-}F}$ = 250.9, $^{2}J_{C\text{-}F}$ = 33.4 Hz), 101.6, 72.9, 66.6, 66.2 (t, $J_{C\text{-}F}$ =31.0 Hz), 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.88 (s, *3F*), -124.98 (t, J = 4.9 Hz, 2F), -139.88 (t, J = 4.9 Hz, 2F). HRMS (ESI) calcd for $C_{22}H_{25}F_7N_3O_2Si$ $[M+H]^+$: 524.1599, found: 524.1592.

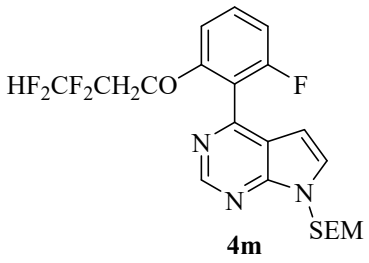
4-(2-(2,2-difluoroethoxy)-6-fluorophenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4l*)



4l

Product **4l** was purified by PE/EtOAc (6/1); yellowish oil (72 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.46-7.40 (m, 1H), 7.36 (d, J = 3.7 Hz, 1H), 6.95 (t, J = 8.7 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 3.7 Hz, 1H), 5.80 (tt, J = 59.2, 4.2 Hz, 1H), 5.70 (s, 2H), 4.17 (td, J = 12.9, 4.2 Hz, 2H), 3.60 (t, J = 8.1 Hz, 2H), 0.94 (t, J = 8.3 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (d, $J_{C\text{-}F}$ = 250.8 Hz), 156.5 (d, $J_{C\text{-}F}$ = 6.6 Hz), 151.7, 151.4, 151.4, 131.1 (d, $J_{C\text{-}F}$ = 10.5 Hz), 128.7, 119.2, 116.3 (d, $J_{C\text{-}F}$ = 17.9 Hz), 113.5 (t, $J_{C\text{-}F}$ =242.2 Hz), 110.1 (d, $J_{C\text{-}F}$ = 22.4 Hz), 108.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 101.5, 72.9, 68.6 (t, $J_{C\text{-}F}$ = 30.4 Hz), 66.6, 17.7, -1.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.36 (s, 1F), -124.82--125.46 (m, 2F). HRMS (ESI) calcd for $C_{20}H_{25}F_3N_3O_2Si$ $[M+H]^+$: 424.1663, found: 424.1648.

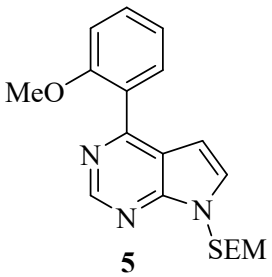
4-(2-fluoro-6-(2,2,3,3-tetrafluoropropoxy)phenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*4m*)



4m

Product **4m** was purified by PE/EtOAc (6/1); yellowish oil (79 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.49-7.43 (m, 1H), 7.39 (d, *J* = 3.7 Hz, 1H), 6.99 (td, *J* = 9.1, 0.9 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.41 (dd, *J* = 3.7, 1.3 Hz, 1H), 5.72 (s, 2H), 5.59 (tt, *J* = 53.0, 6.4 Hz, 1H), 4.33 (tt, *J* = 11.5, 1.6 Hz, 2H), 3.59 (t, *J* = 8.1 Hz, 2H), 0.95 (t, *J* = 8.2 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (d, $J_{C\text{-}F}$ = 251.4 Hz), 155.9 (d, $J_{C\text{-}F}$ = 6.8 Hz), 151.8, 151.5, 151.2, 131.3 (d, $J_{C\text{-}F}$ = 10.5 Hz), 128.9, 119.0, 116.4 (d, $J_{C\text{-}F}$ = 18.3 Hz), 114.1 (tt, $^{1}J_{C\text{-}F}$ = 251.4, $^{2}J_{C\text{-}F}$ = 26.8 Hz), 110.6 (d, $J_{C\text{-}F}$ = 22.5 Hz), 108.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 108.6 (tt, $^{1}J_{C\text{-}F}$ = 250.8, $^{2}J_{C\text{-}F}$ = 29.5 Hz), 101.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 72.8, 66.6, 66.6 (t, $J_{C\text{-}F}$ = 31.2 Hz), 17.7, -1.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.53 (s, 1F), -125.69 (d, *J* = 160.0 Hz, 2F), -140.38 (d, *J* = 187.2 Hz, 2F). HRMS (ESI) calcd for $C_{20}H_{25}F_3N_3O_2Si$ $[M+H]^+$: 474.1631, found: 474.1612.

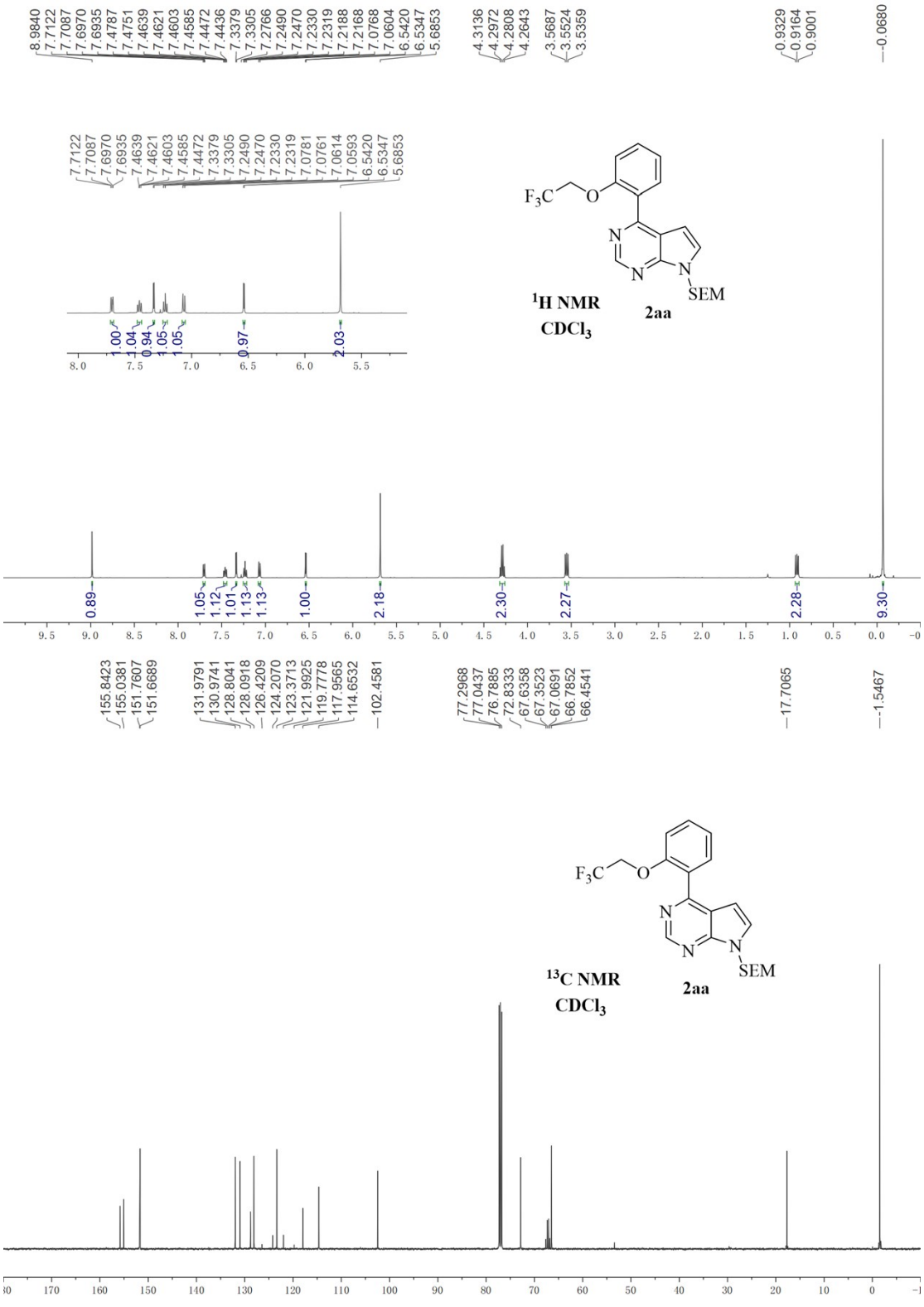
4-(2-methoxyphenyl)-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (*5*)

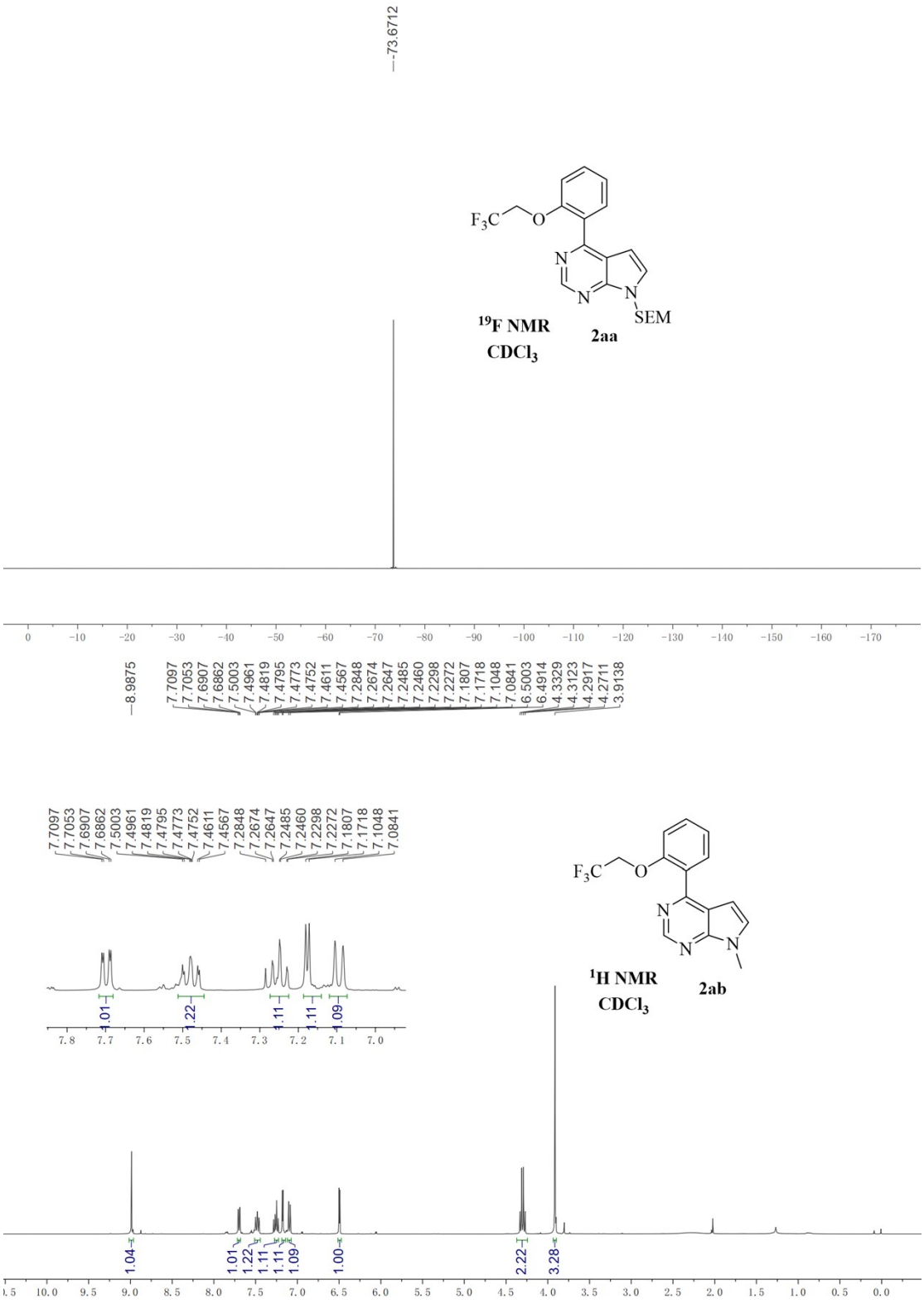


5

Product **5** was purified by PE/EtOAc (4/1); colorless oil (96 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.65 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.13 (td, *J* = 7.5, 1.1 Hz, 1H), 7.07 (d, *J* = 1.0 Hz, 1H), 6.52 (d, *J* = 3.7 Hz, 1H), 5.69 (s, 2H), 3.84 (s, 3H), 3.60 (t, *J* = 8.2 Hz, 2H), 0.94 (t, *J* = 8.3 Hz, 2H), -0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.04, 156.99, 151.74, 131.56, 130.99, 127.87, 127.05, 120.91, 118.04, 111.39, 102.72, 72.85, 66.58, 55.48, 29.72, 17.78, -1.40. HRMS (ESI) calcd for $C_{19}H_{26}N_3O_2Si$ $[M+H]^+$: 356.1789, found: 356.1781.

6. ^{1}H, ^{13}C, ^{19}F NMR Spectra for the compounds

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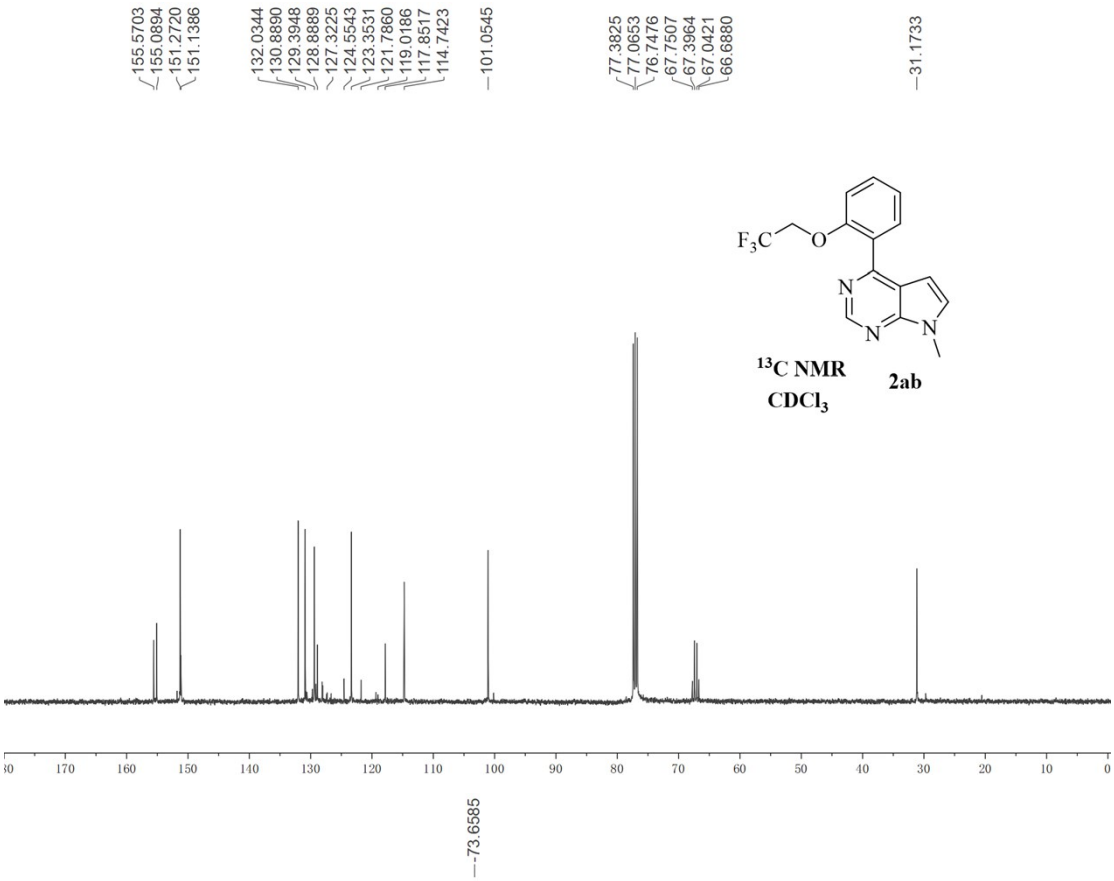
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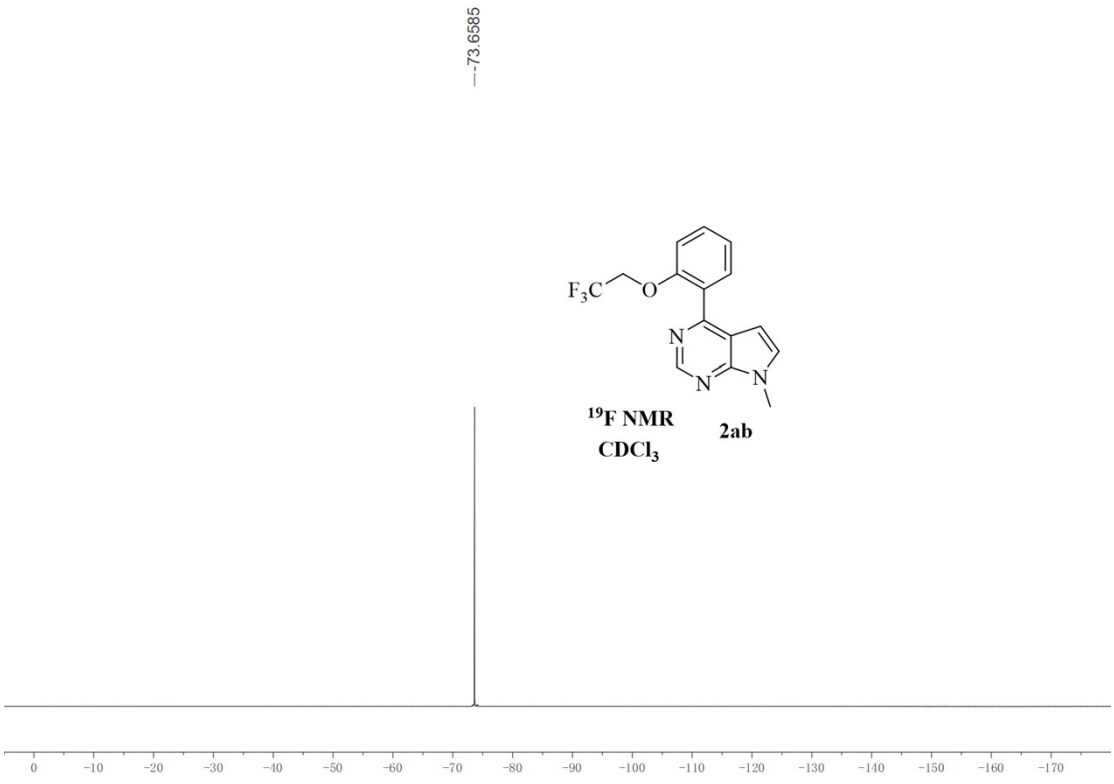
CDCl$_3$
2ab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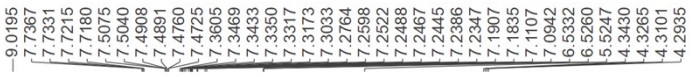
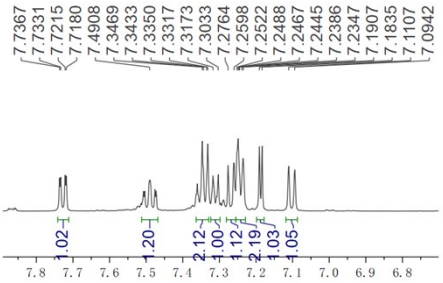
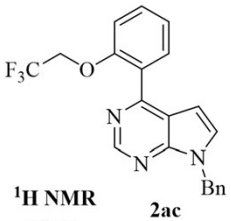
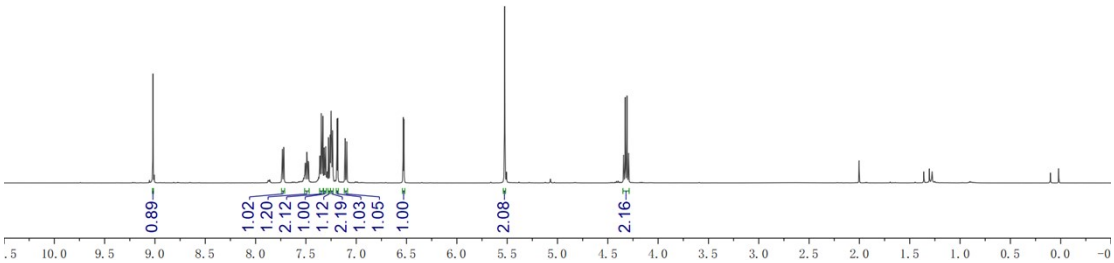
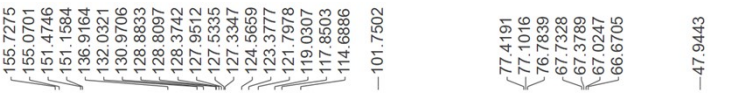


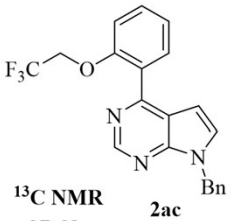




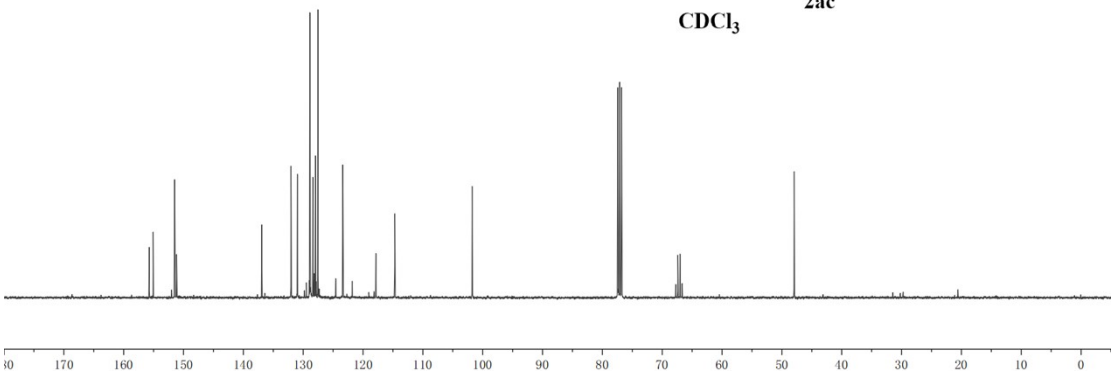
^{1}H NMR
$CDCl_3$
2ac

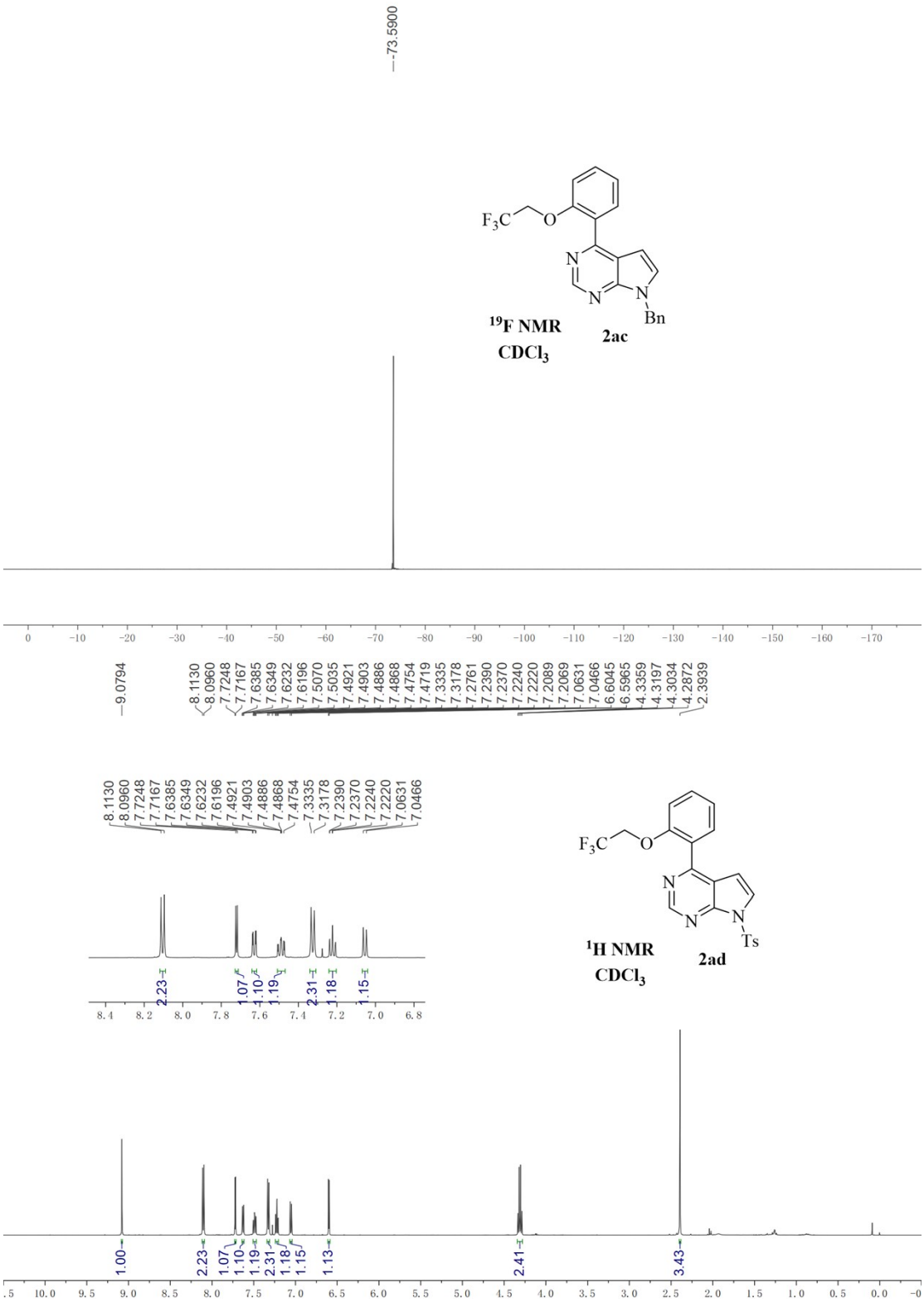






^{13}C NMR
$CDCl_3$
2ac

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N
N
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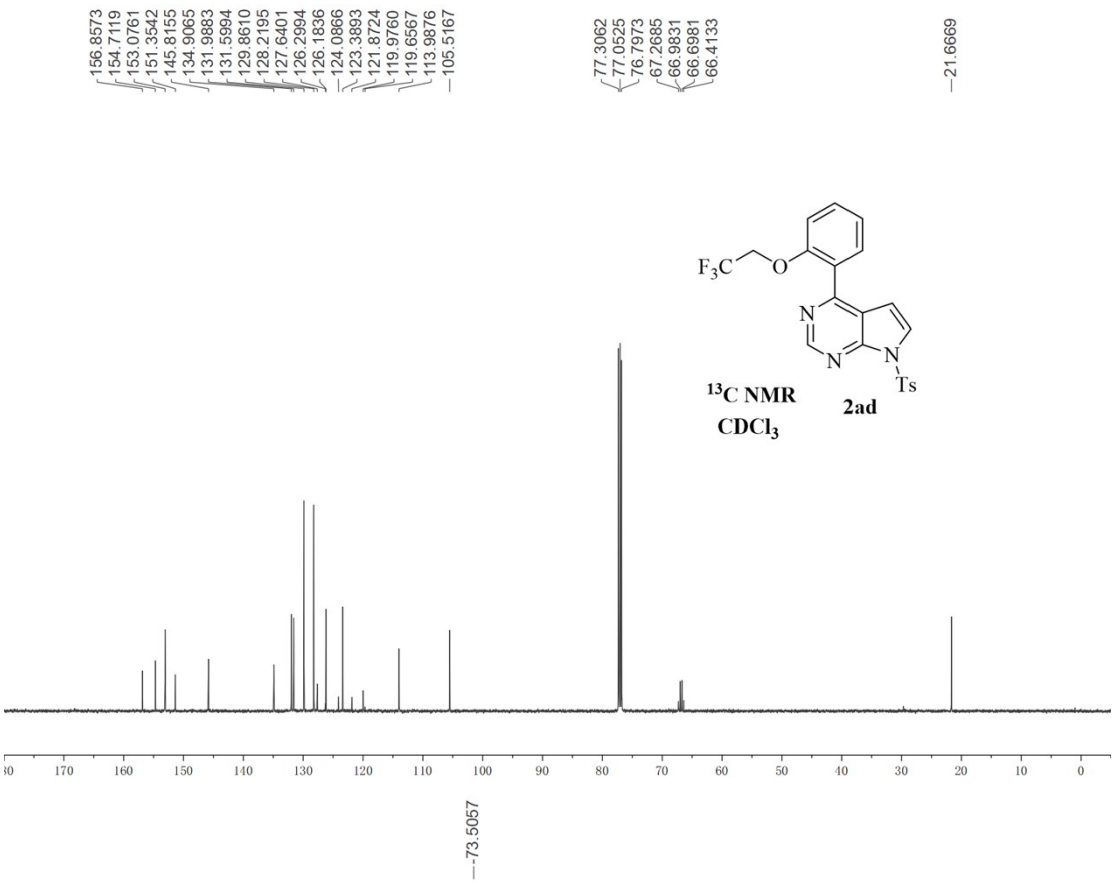
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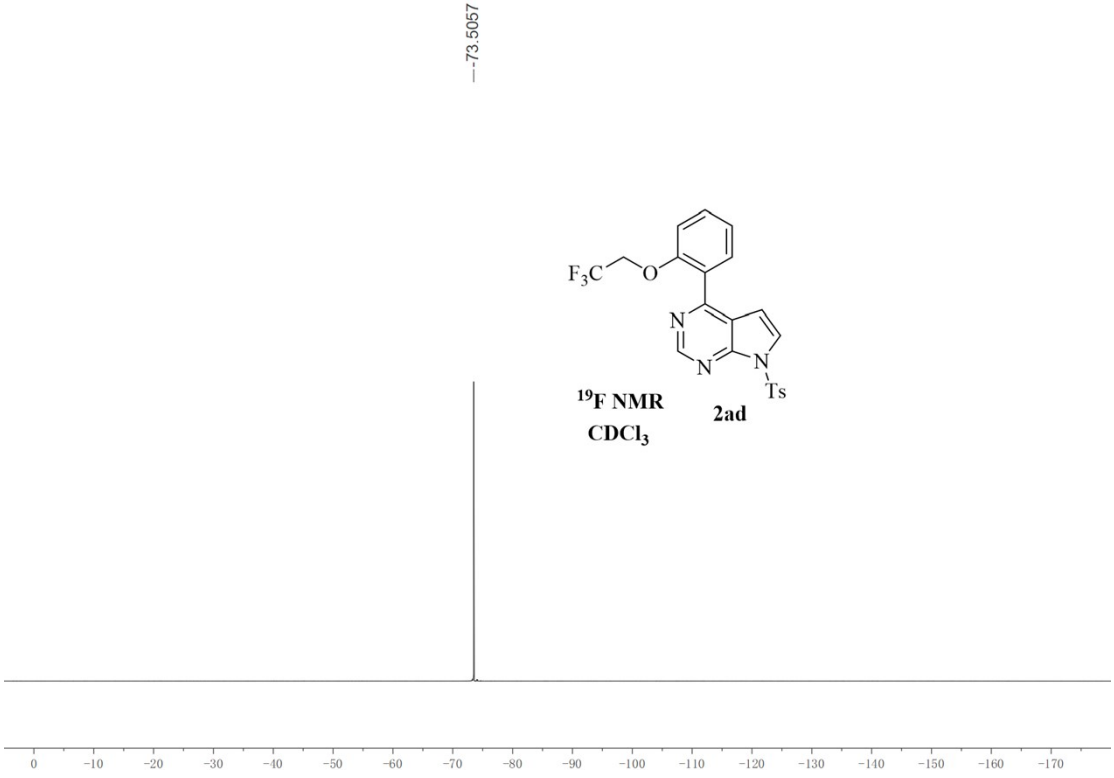
Ts
13C NMR
CDCl3
2ad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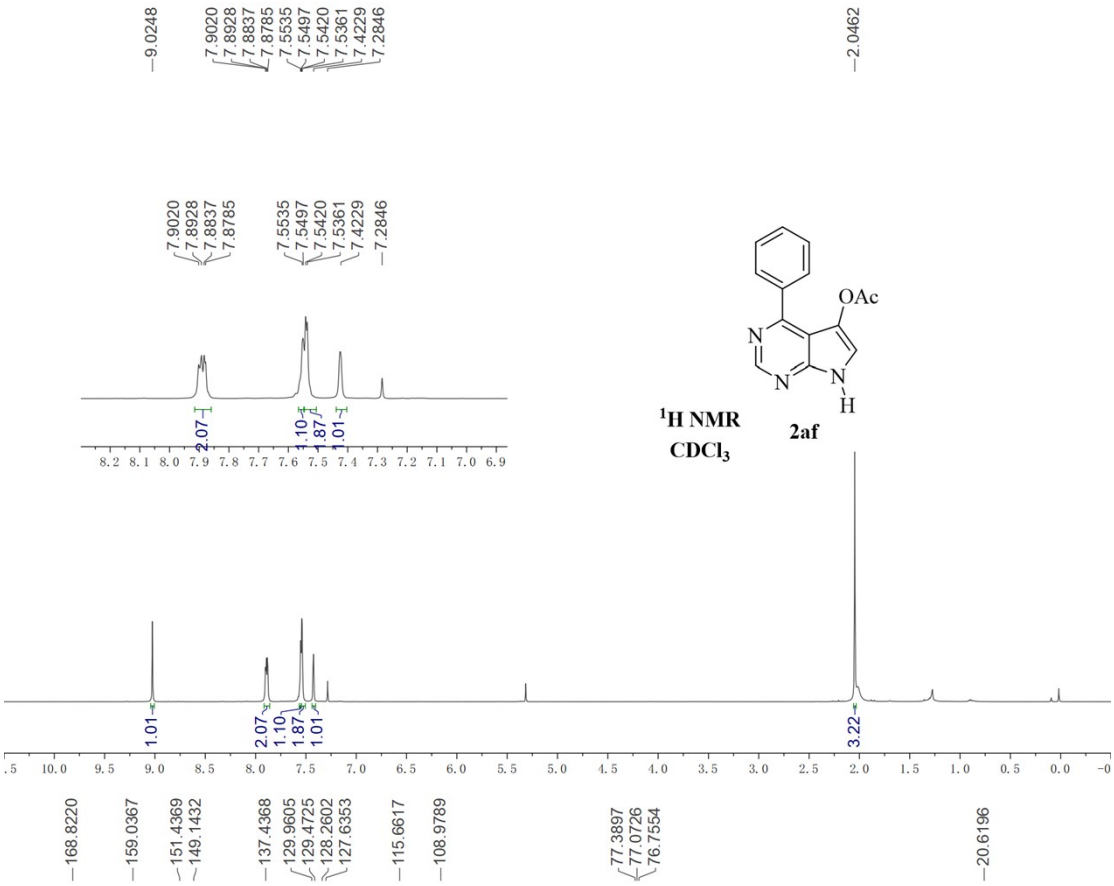
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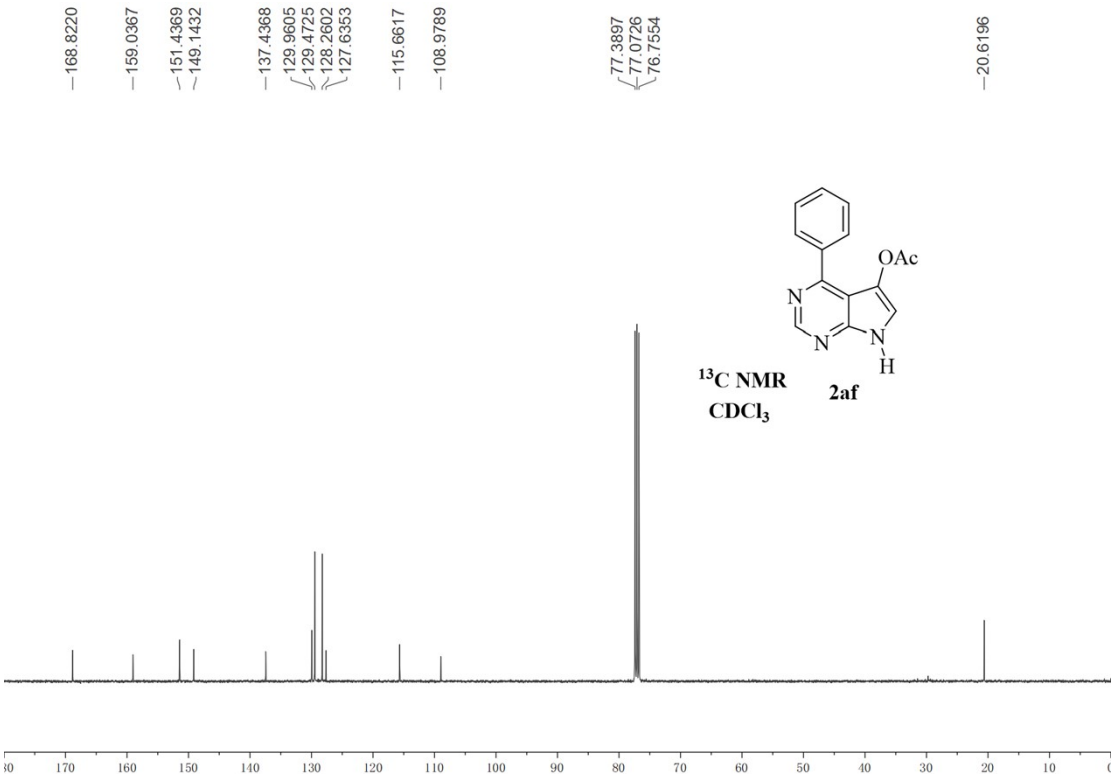
3.22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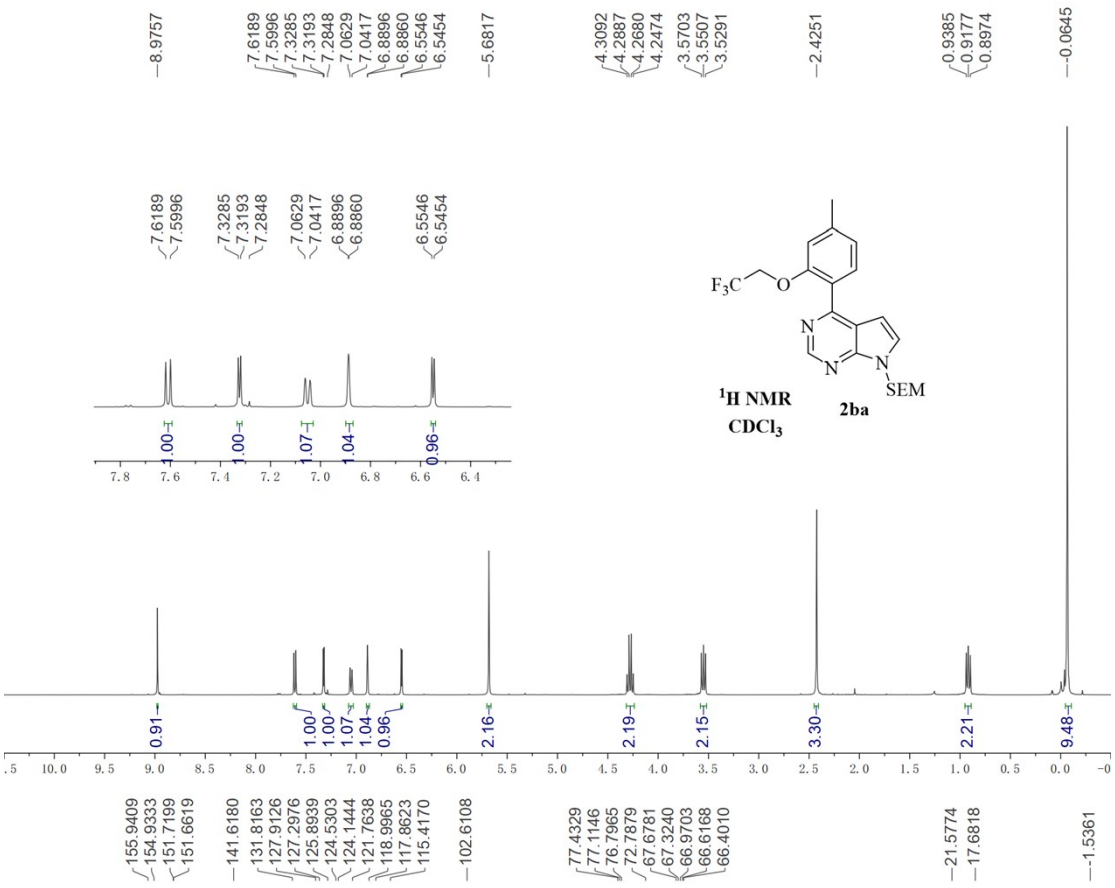
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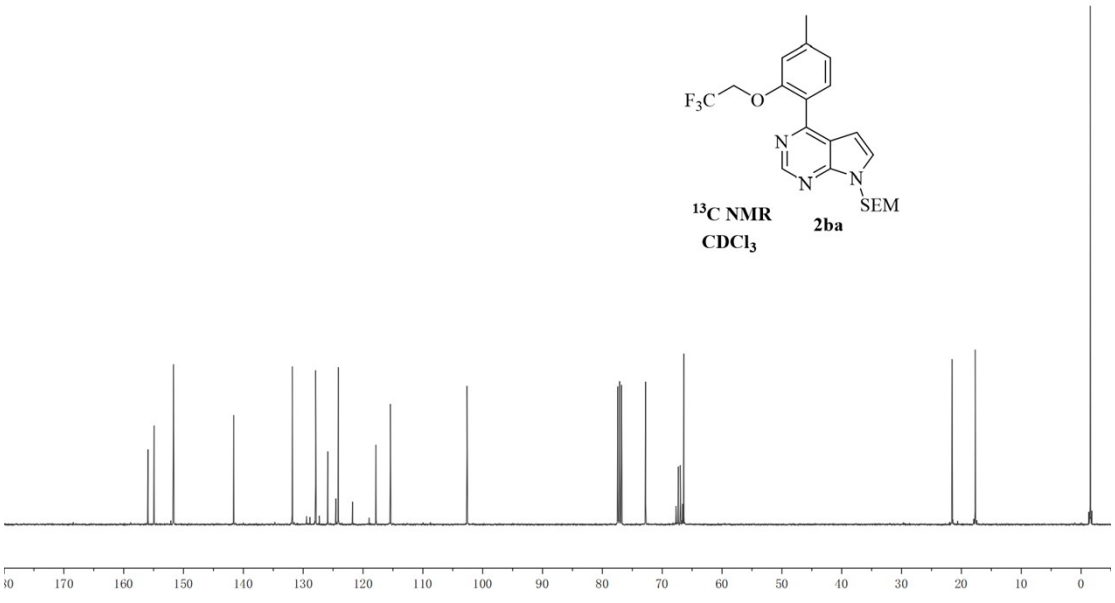
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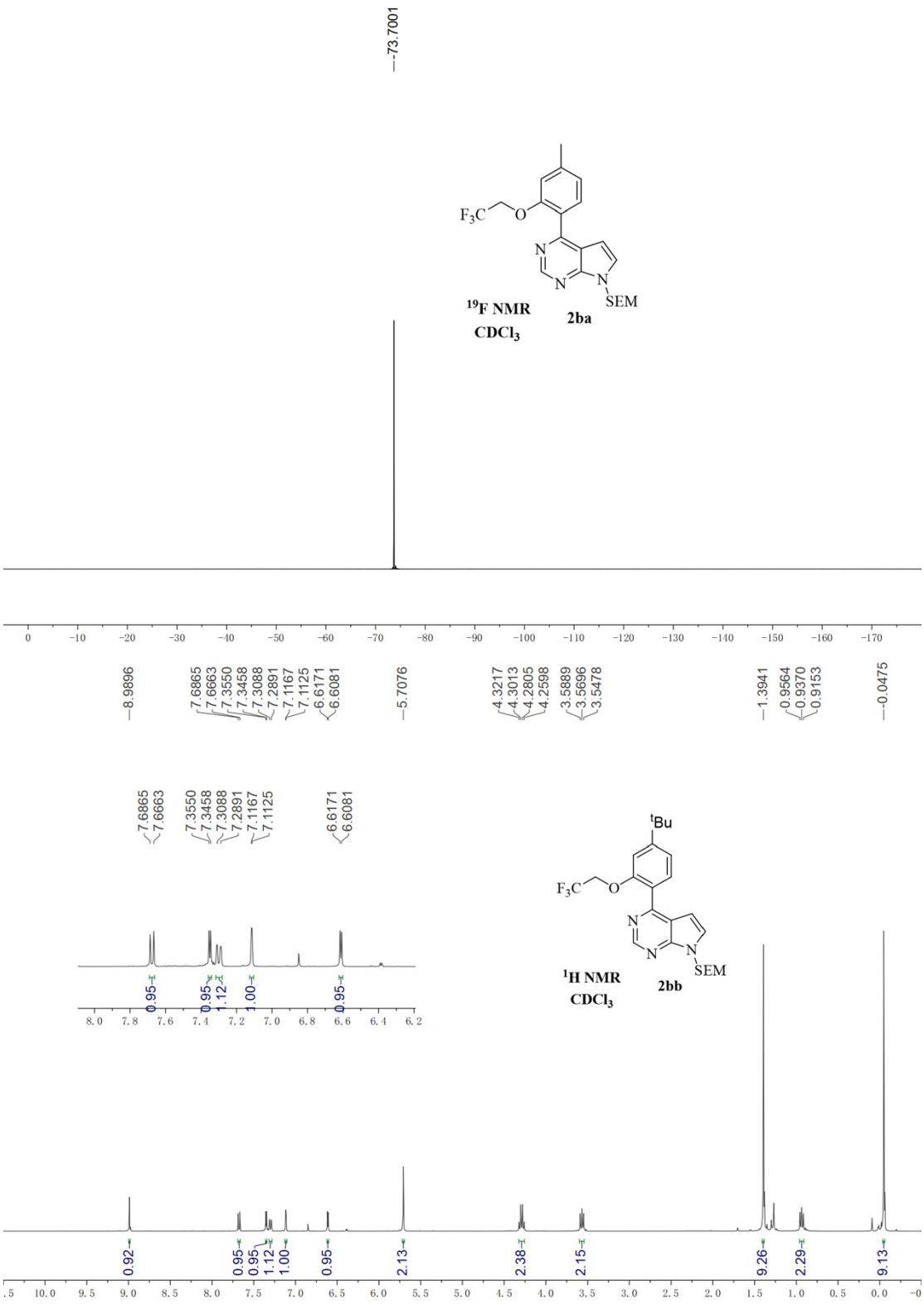
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7.0
6.8
6.6
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N
SEM
1H NMR
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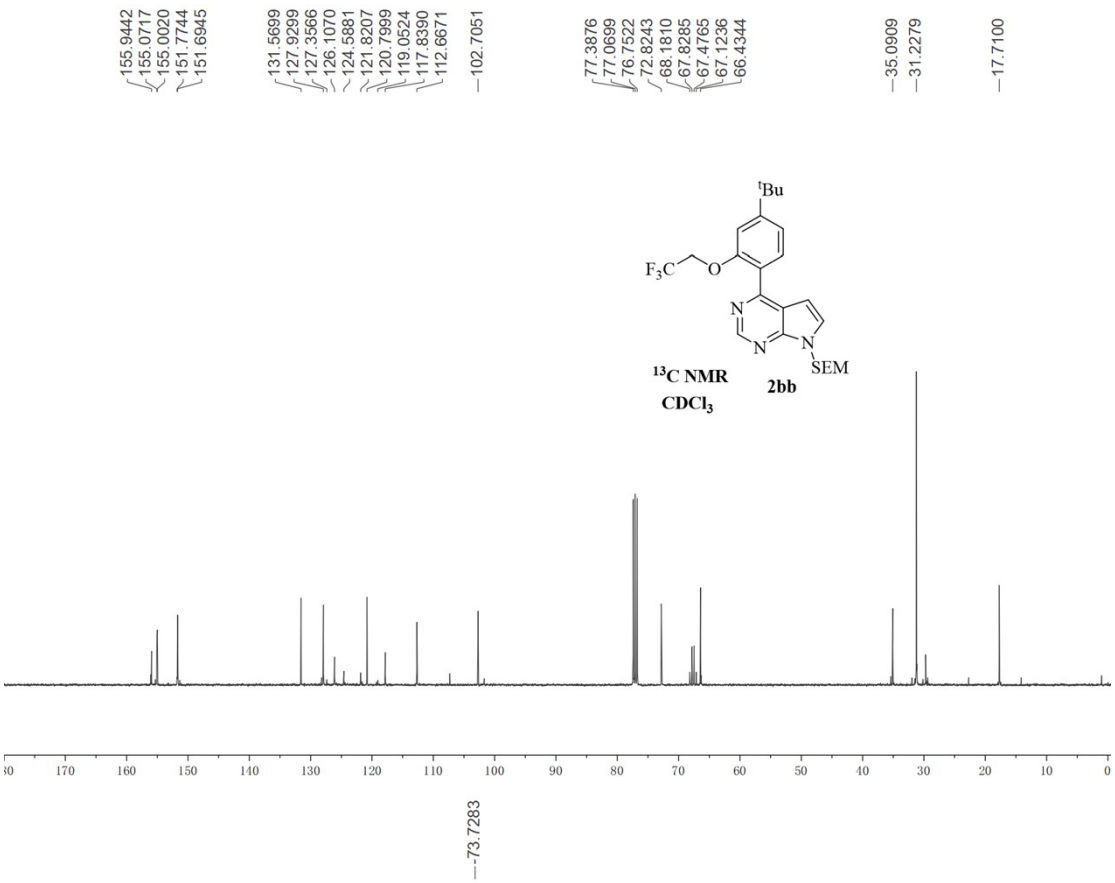
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F3C
O
N
N
N
SEM
13C NMR
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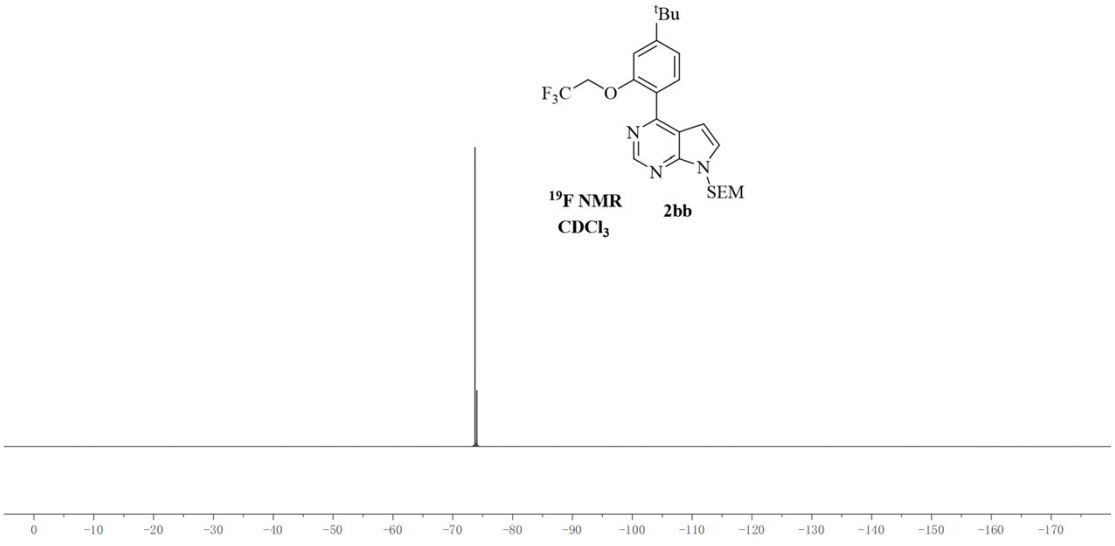
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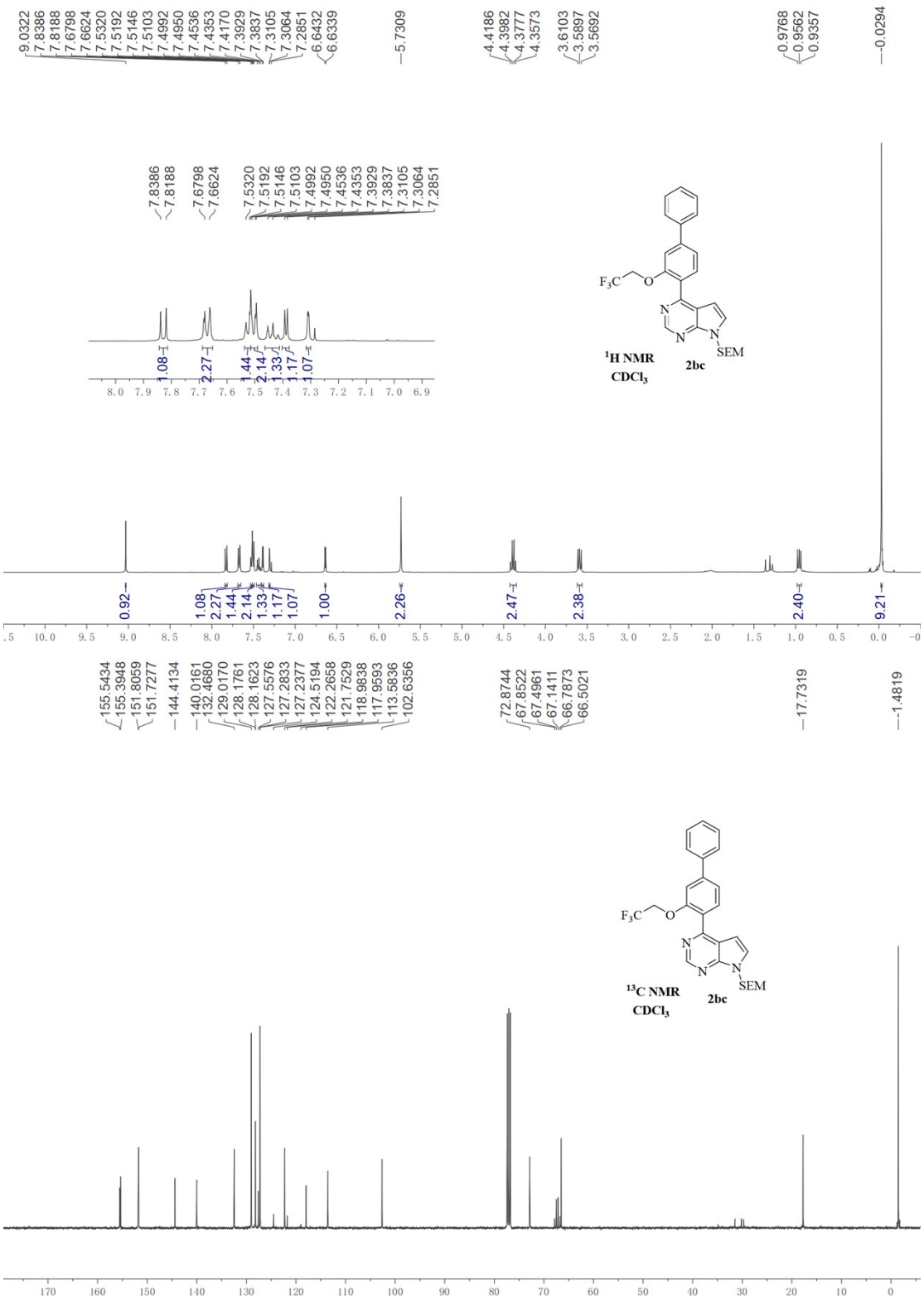
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2bc
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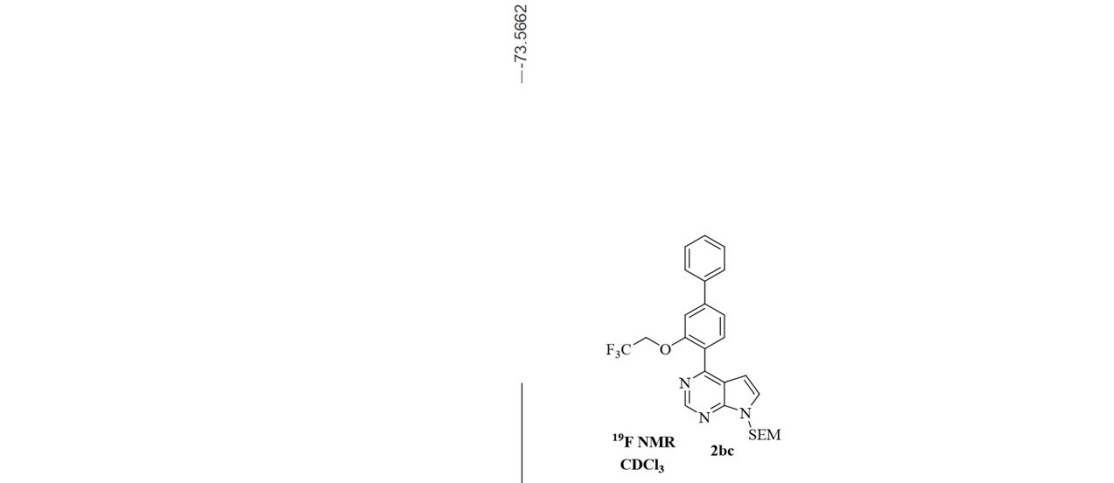
2bc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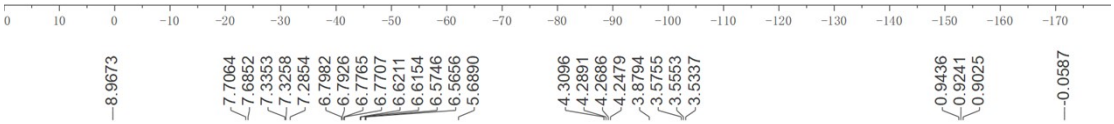
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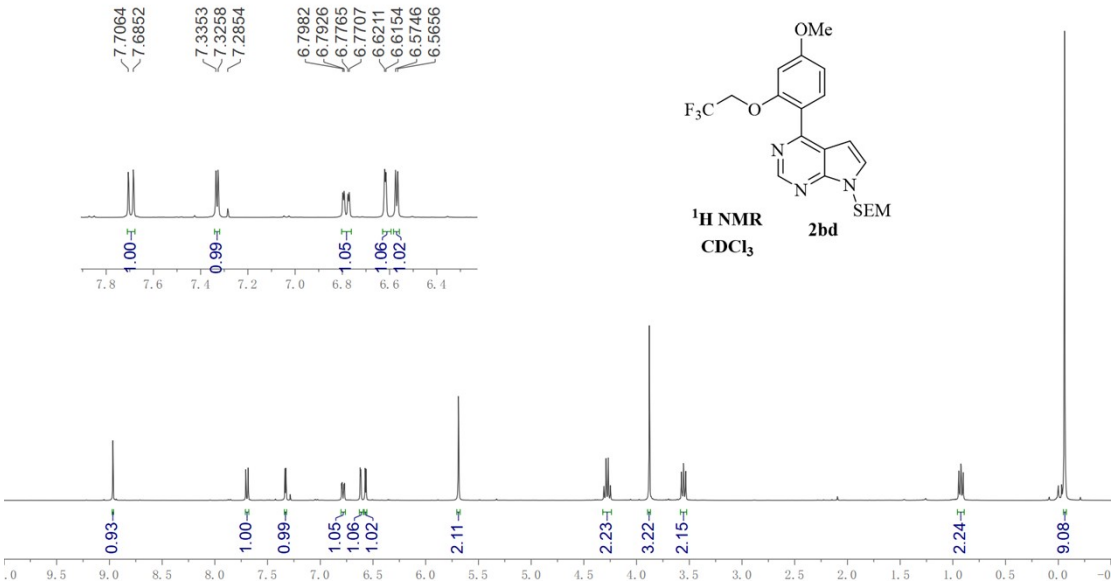
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SEM
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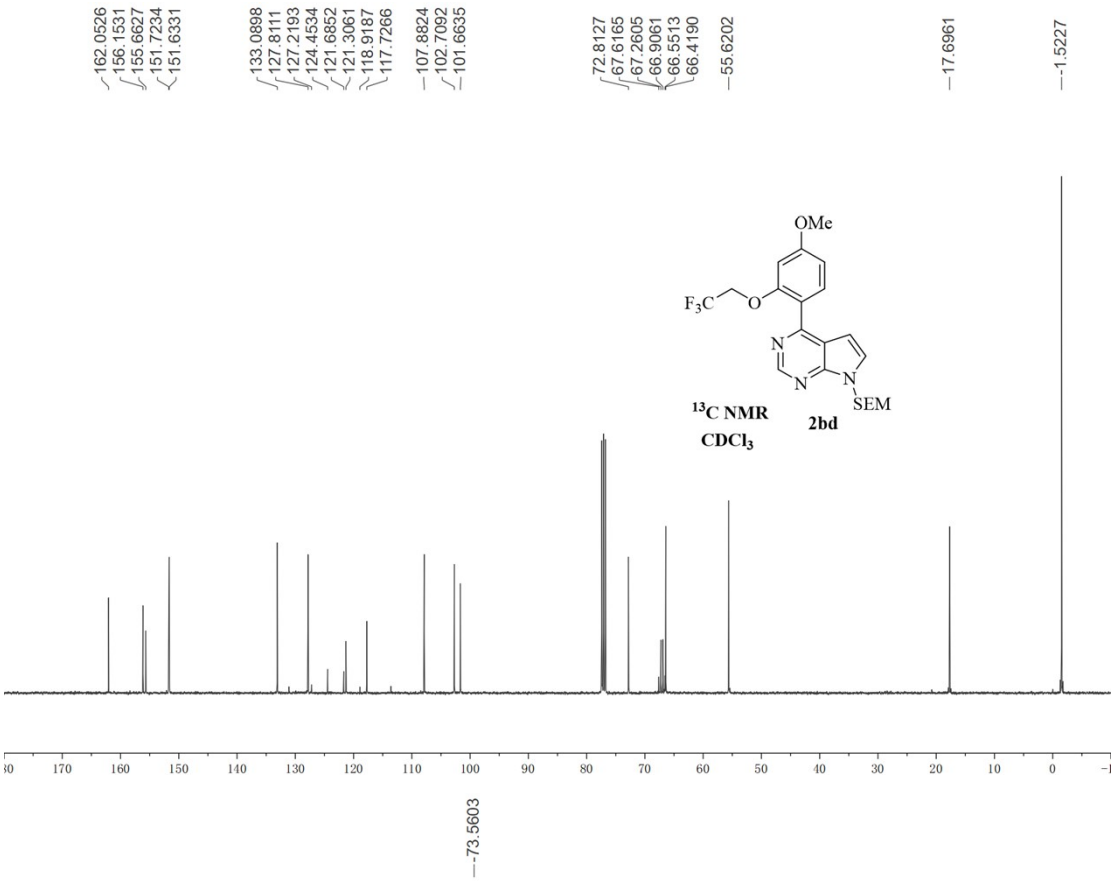
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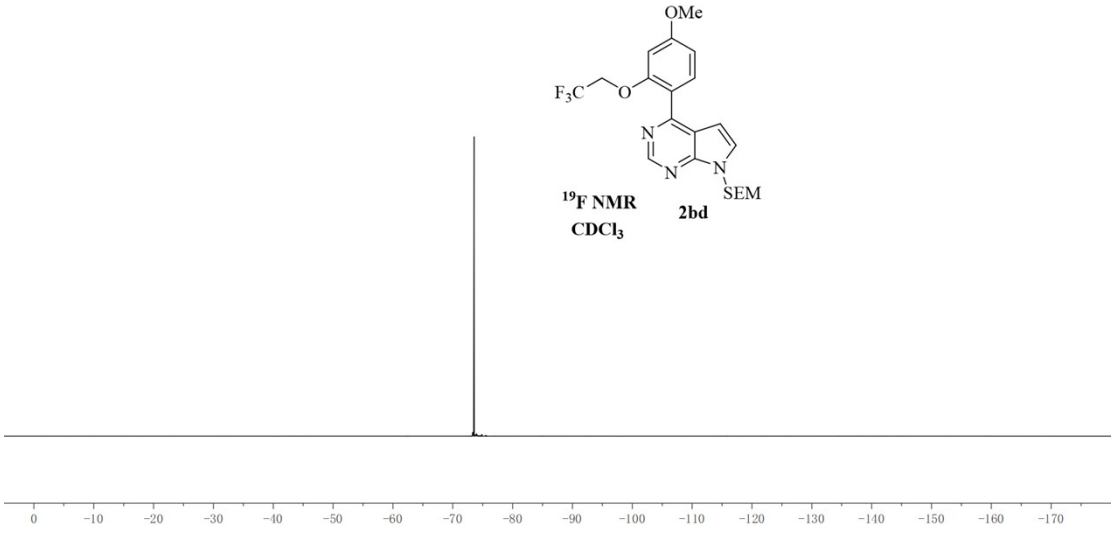
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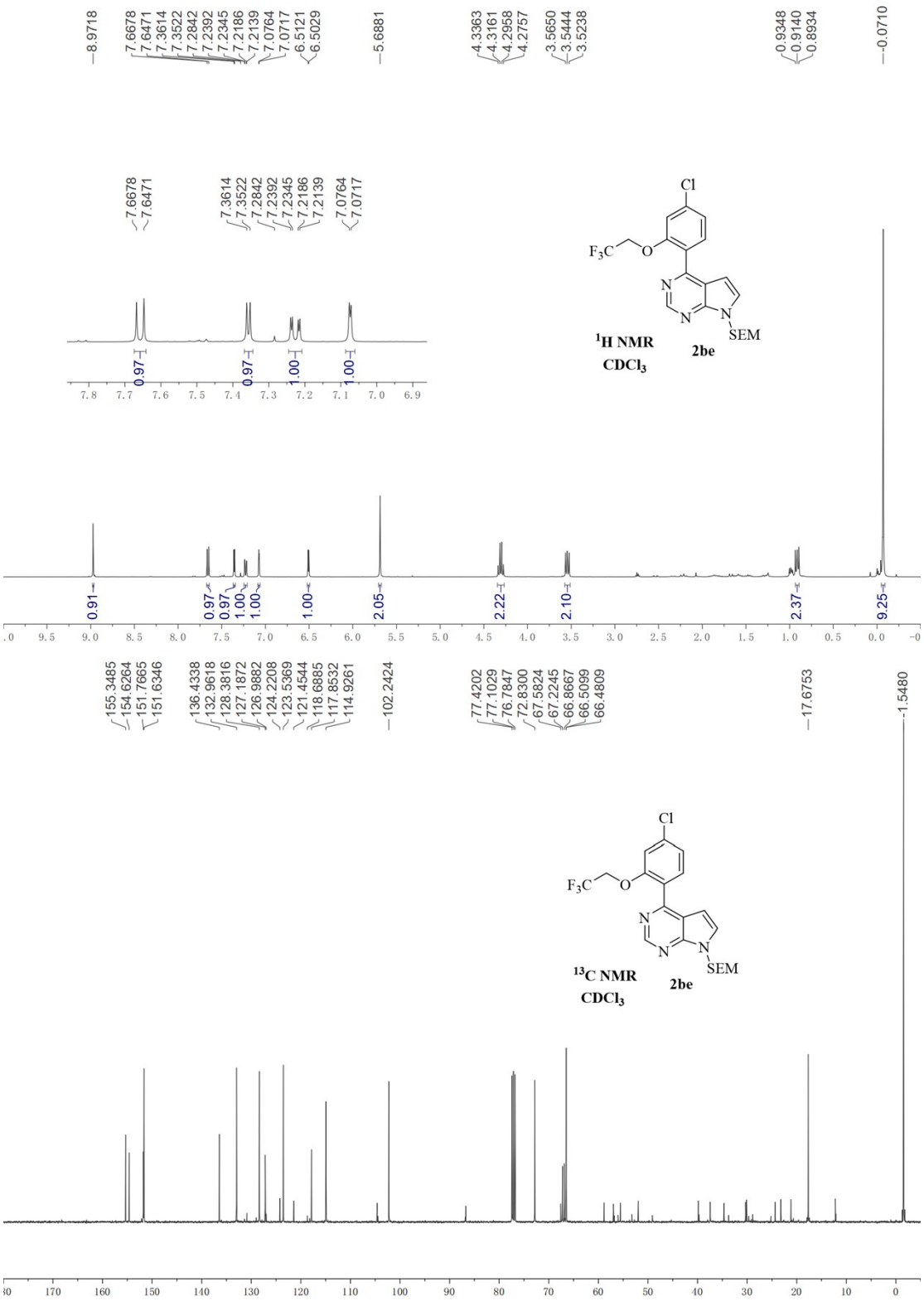
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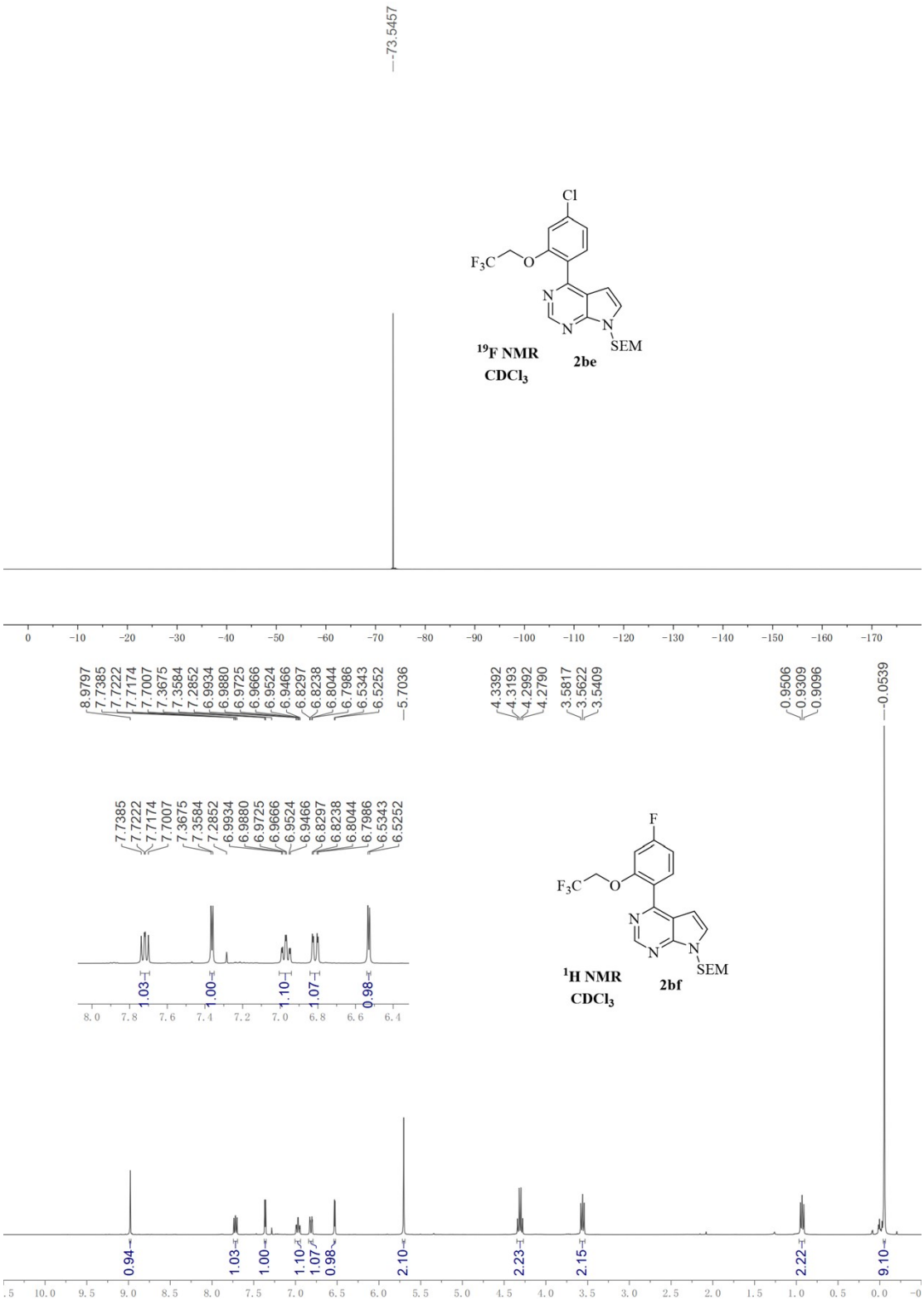
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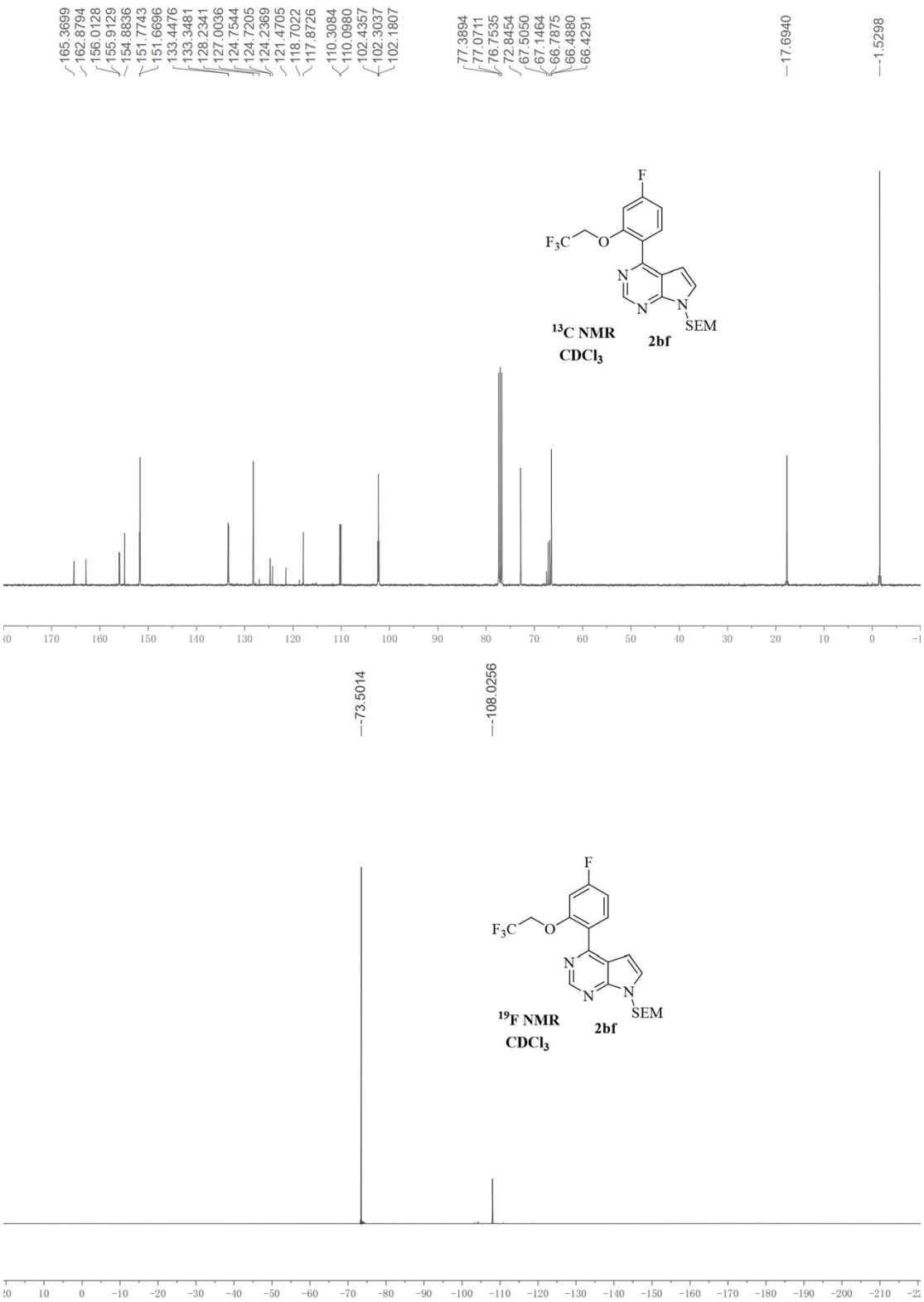
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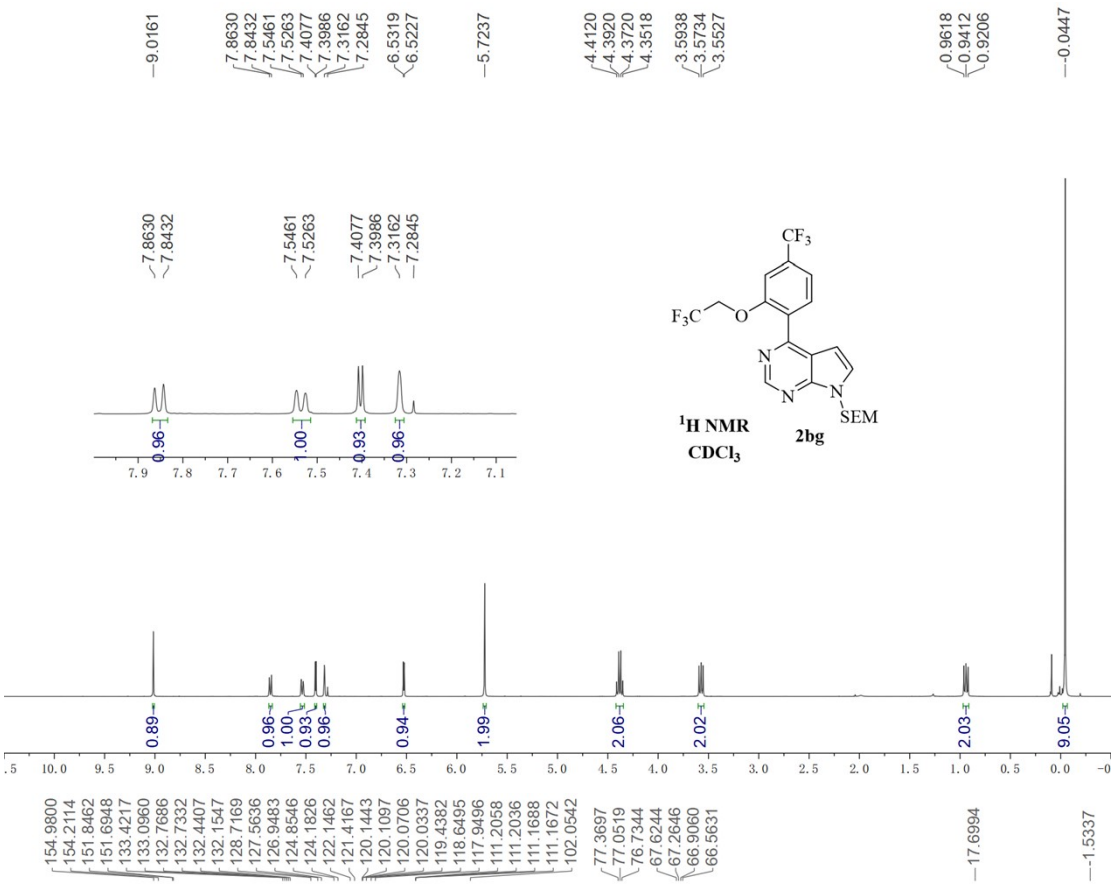
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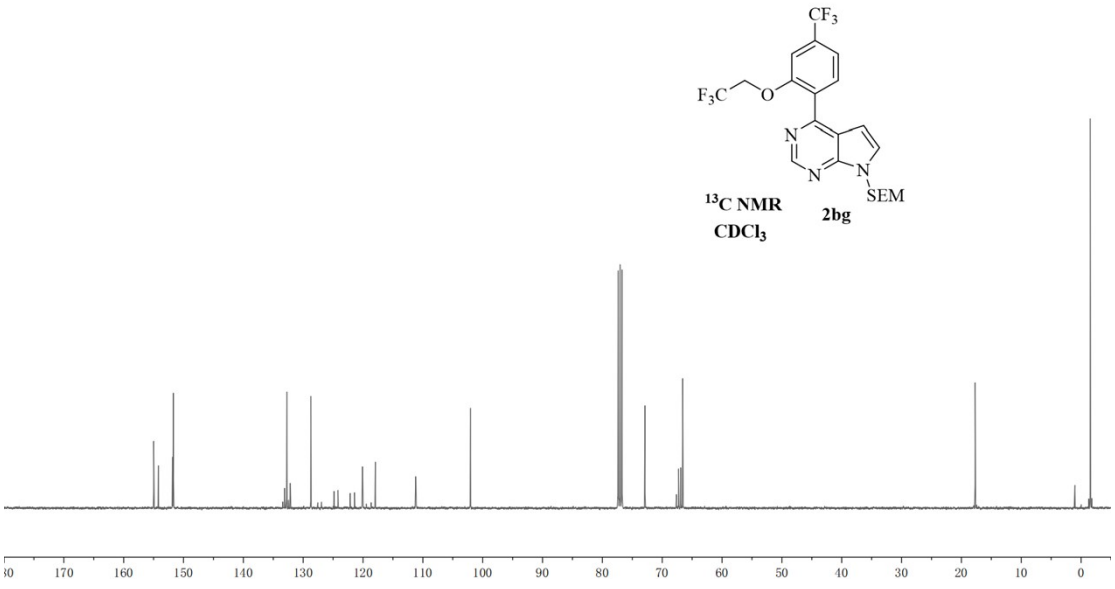
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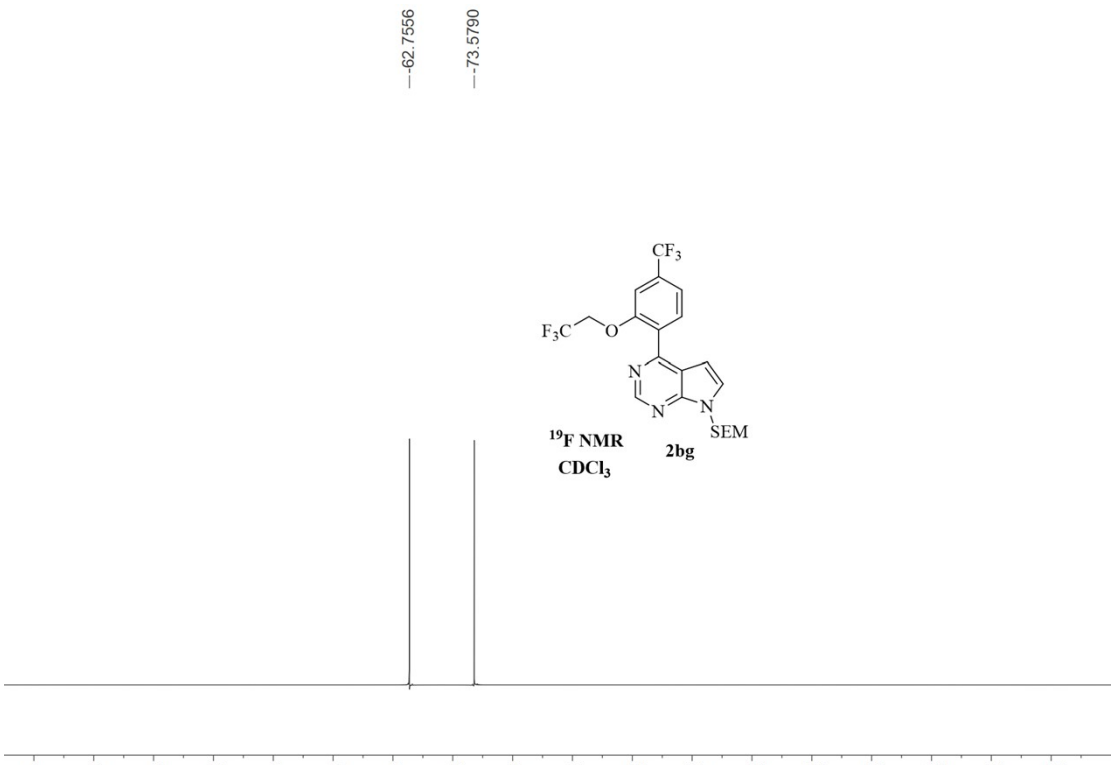
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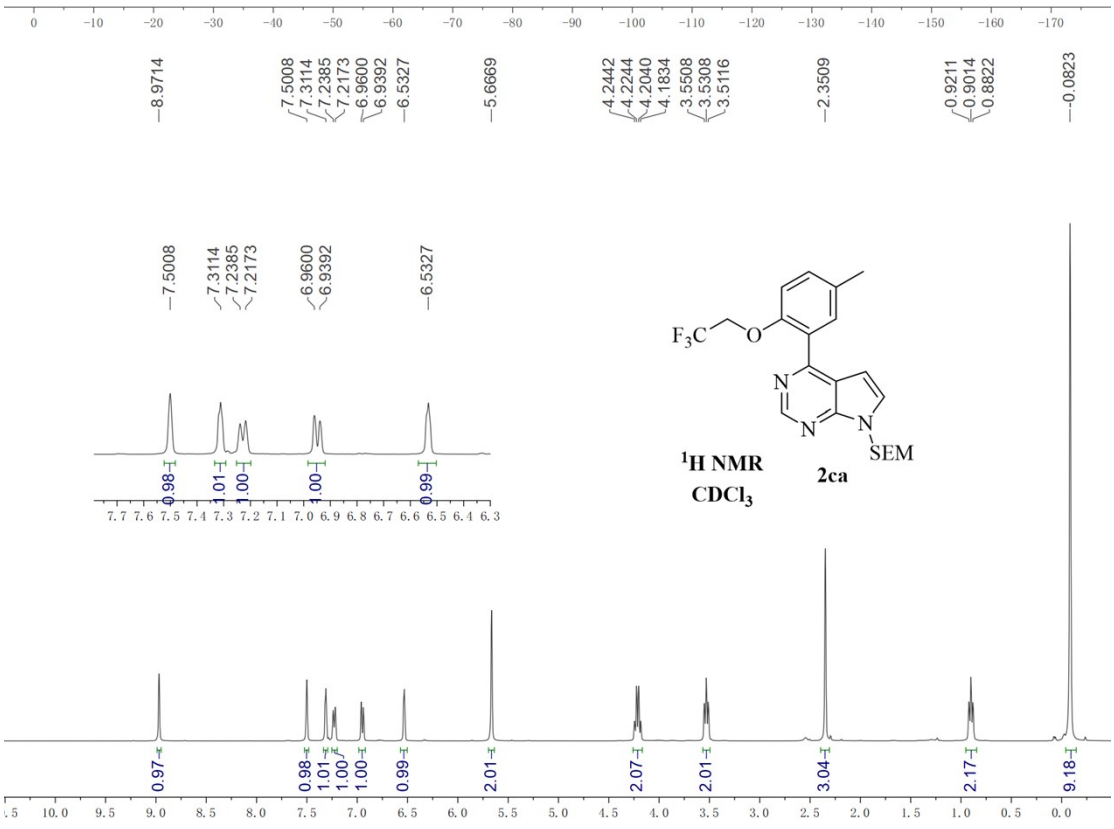
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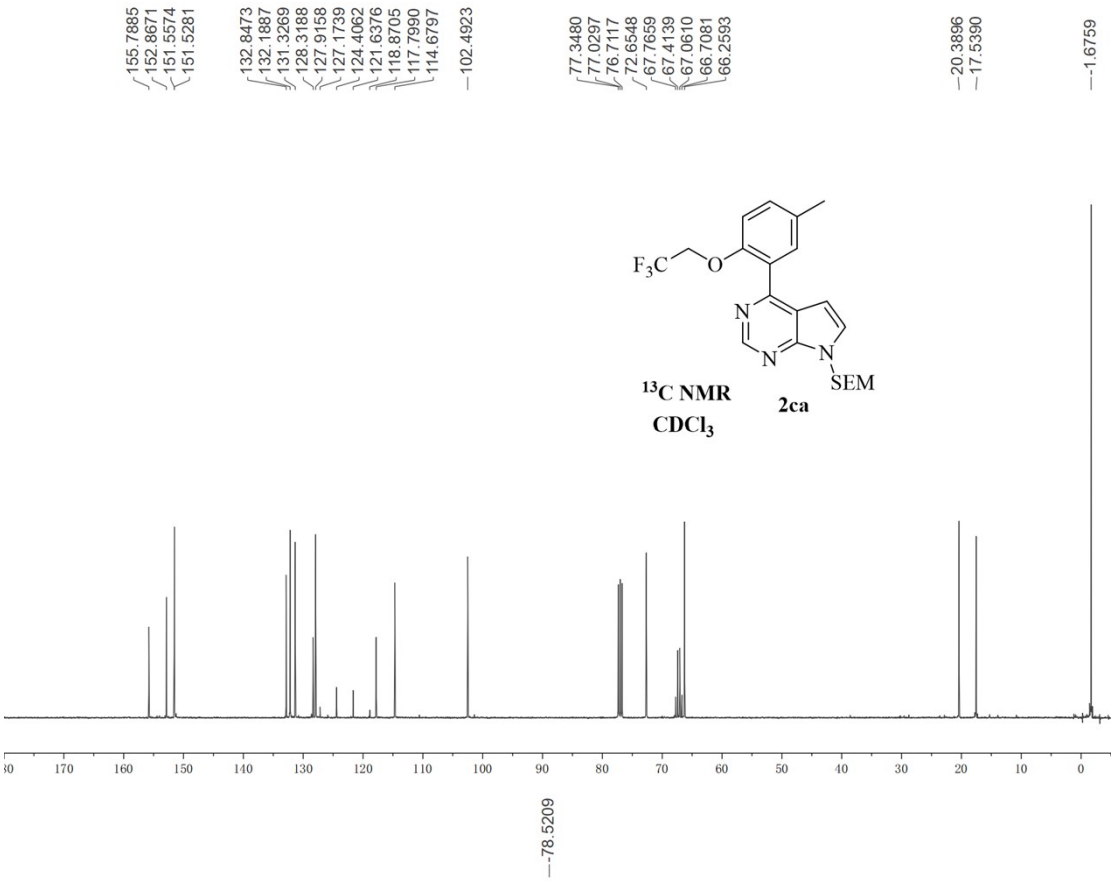
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SEM
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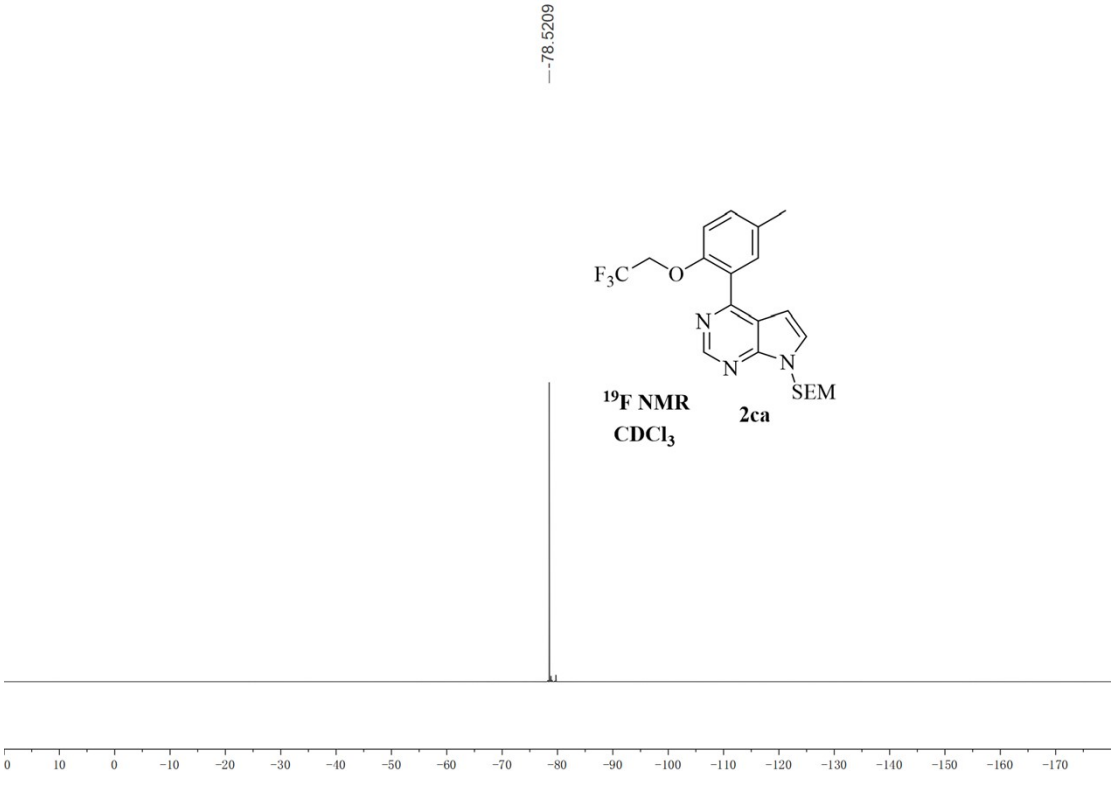
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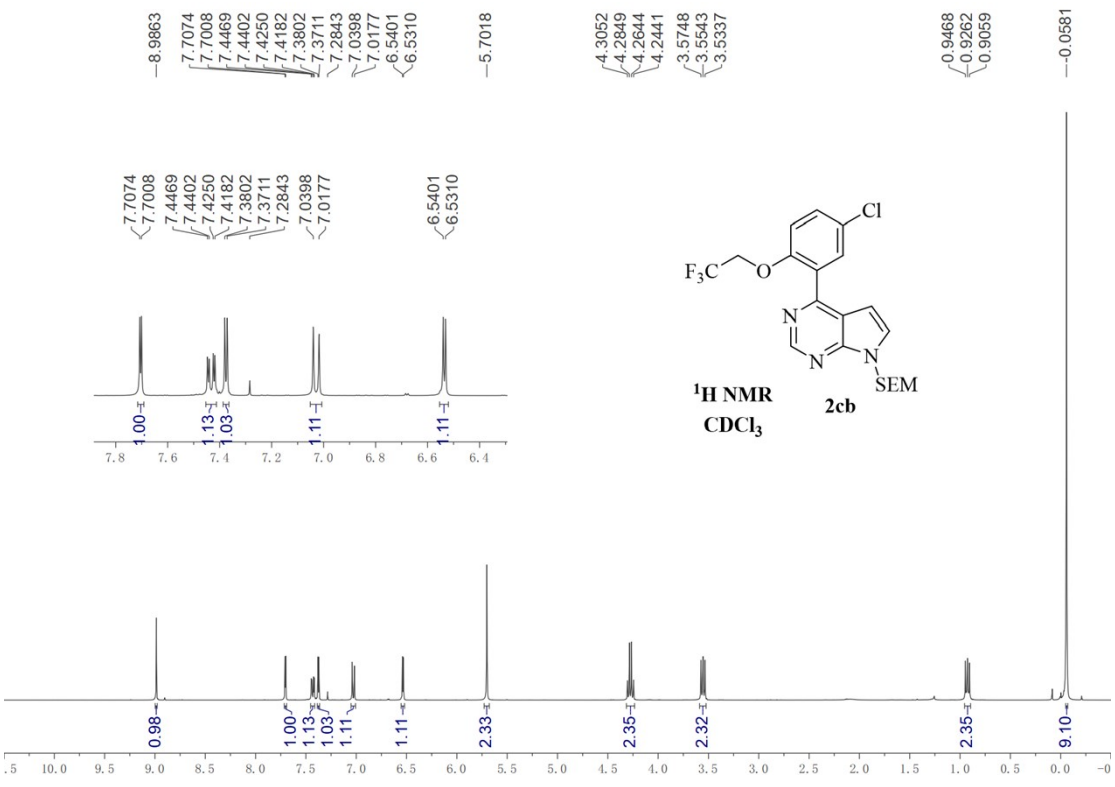
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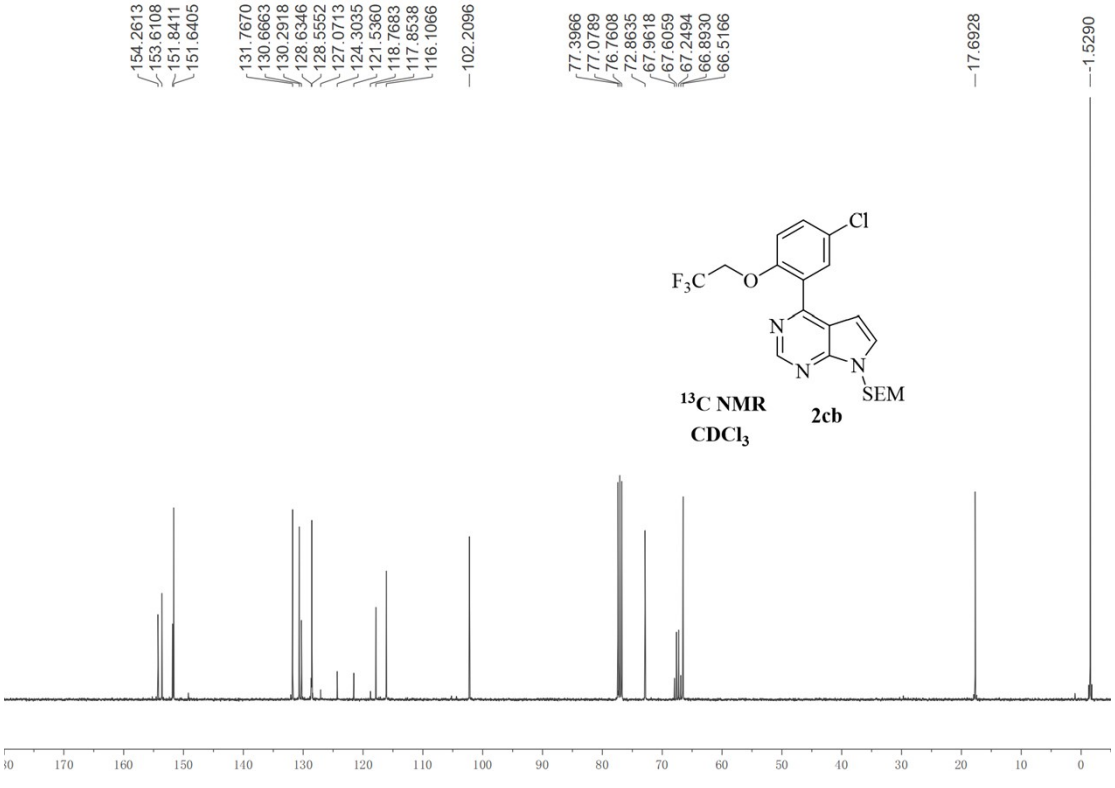
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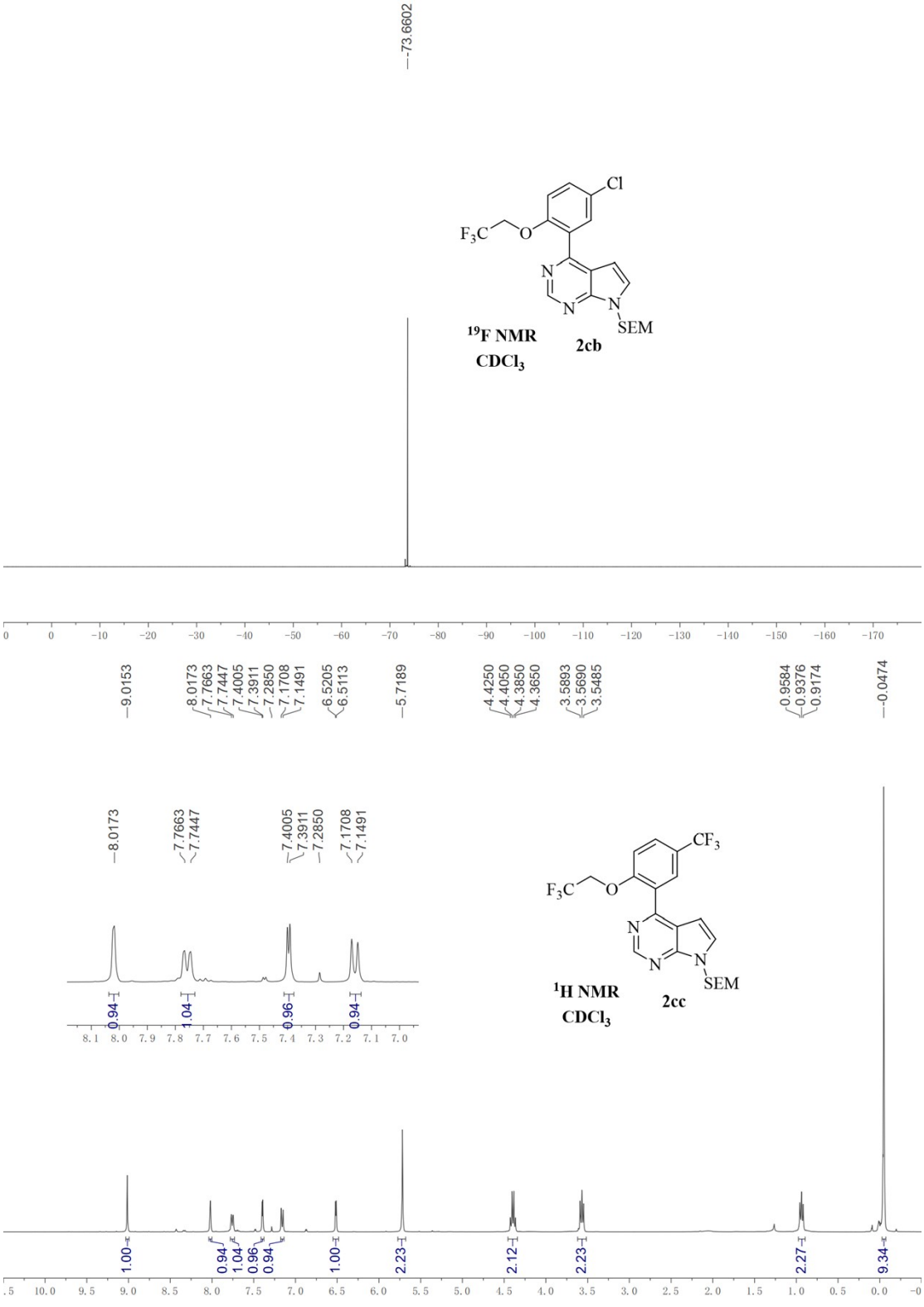
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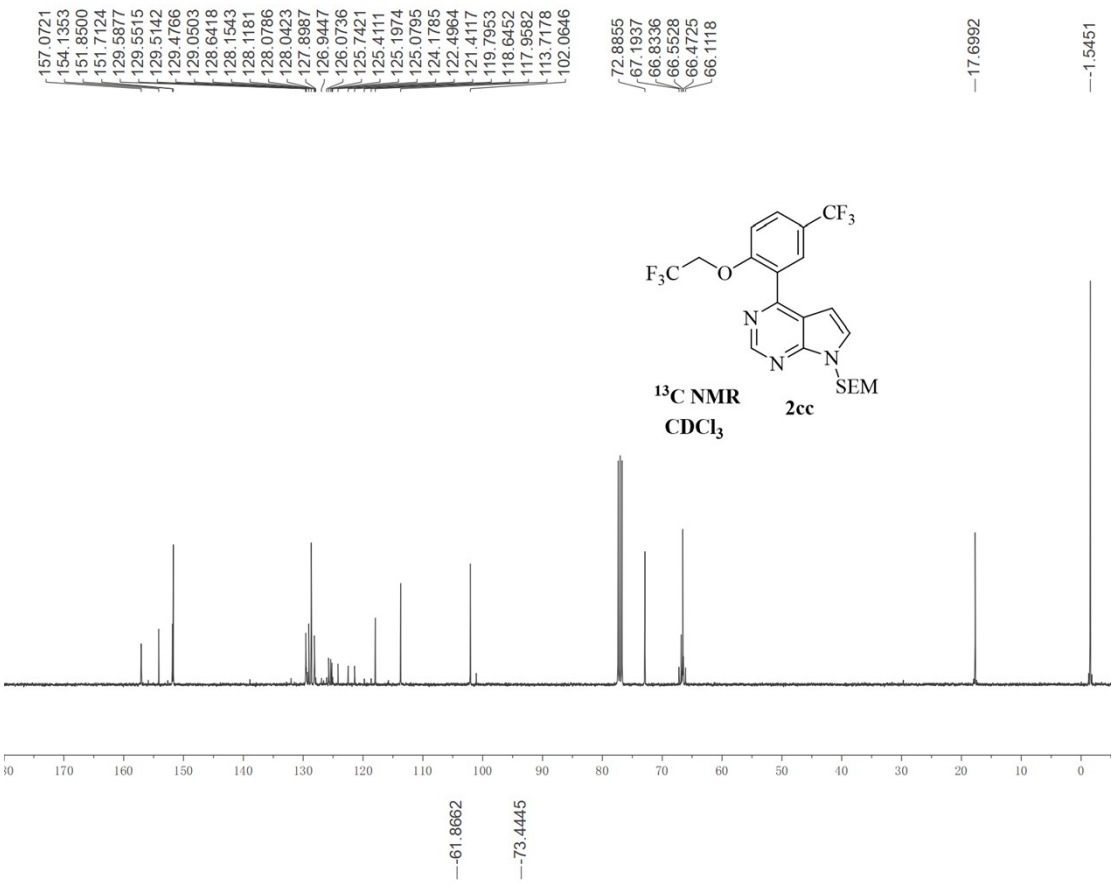
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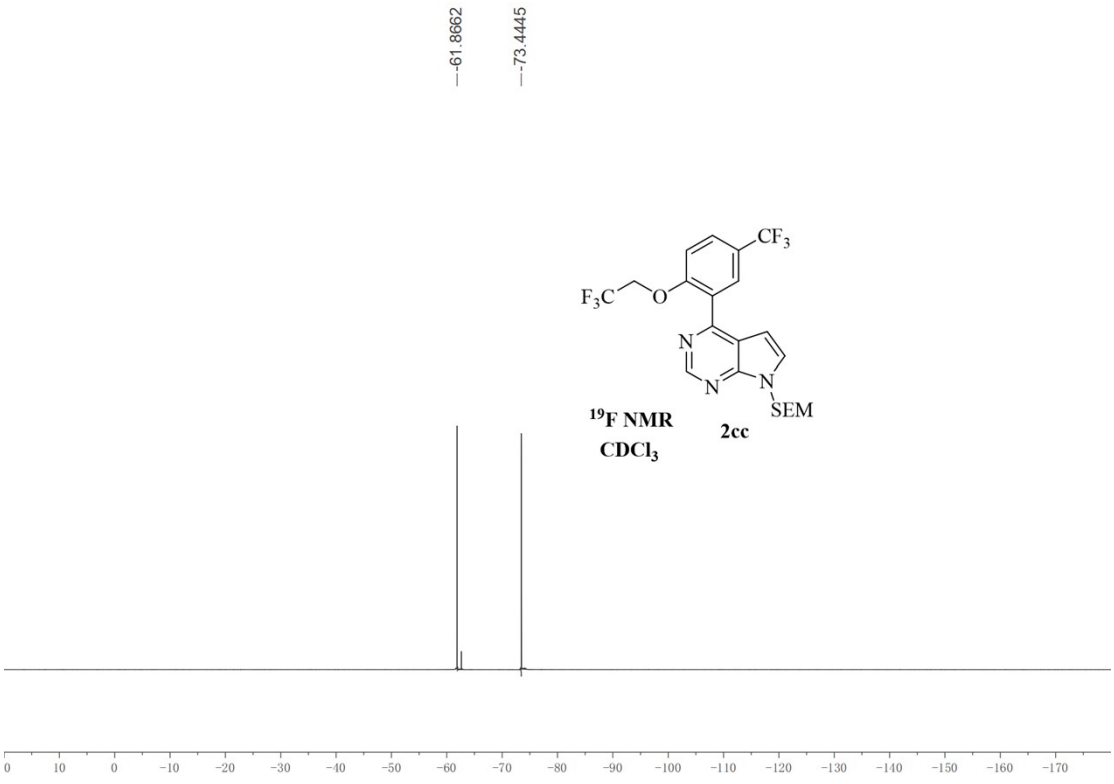
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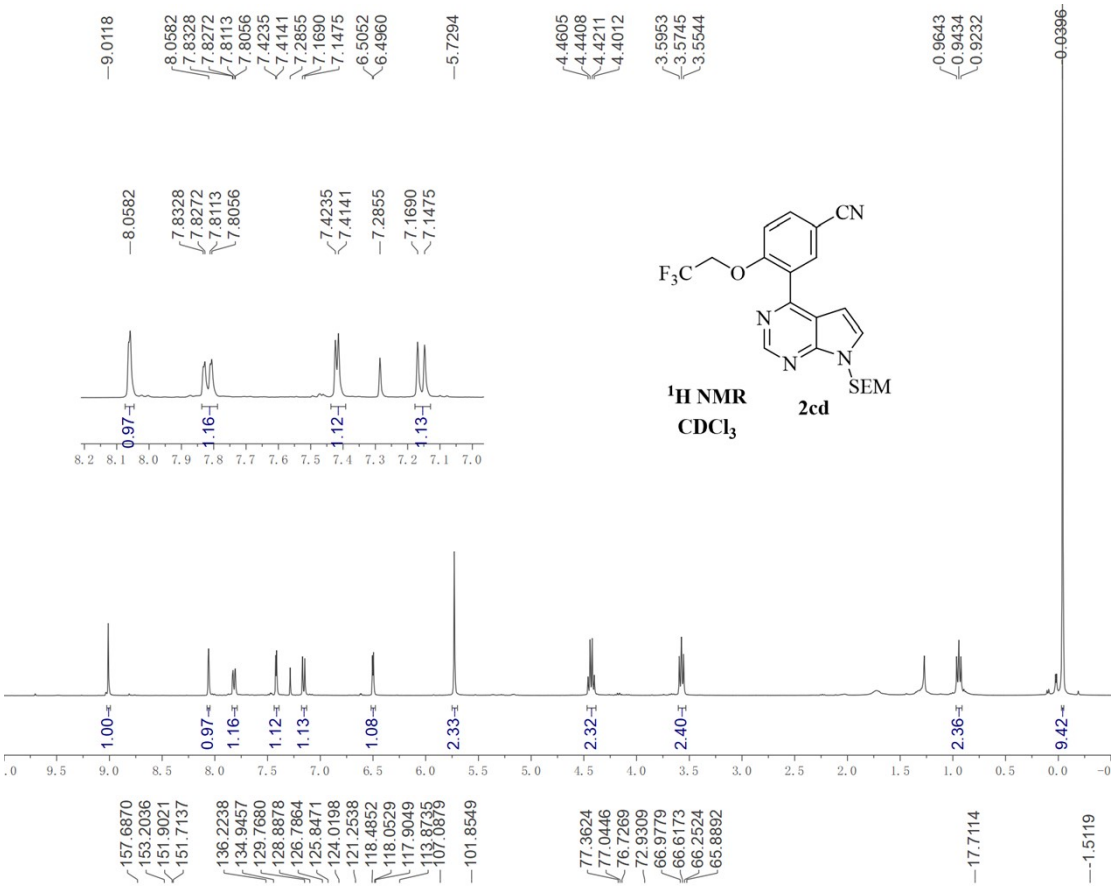
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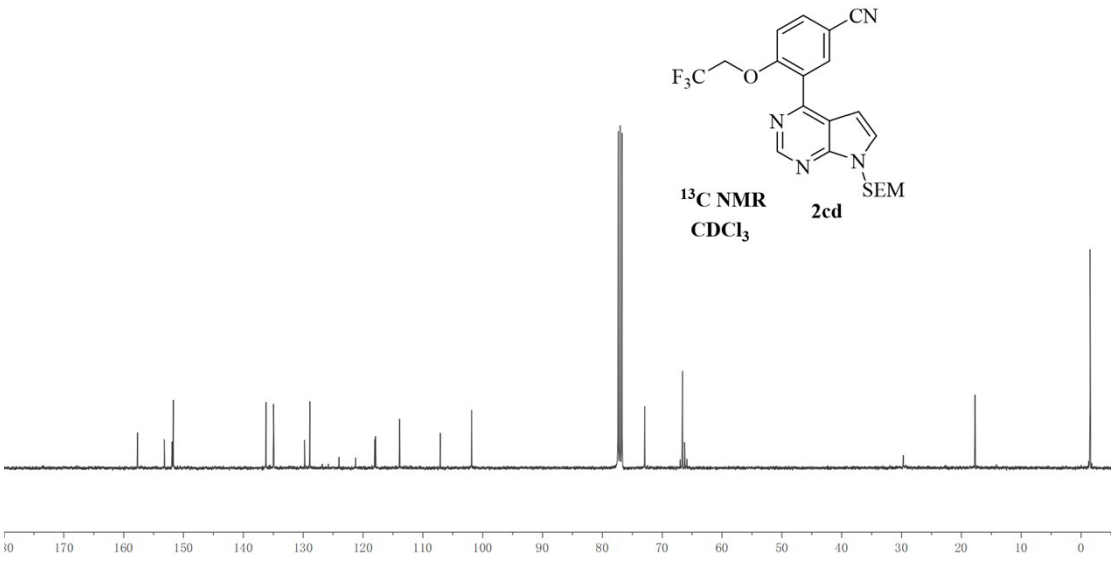
2cd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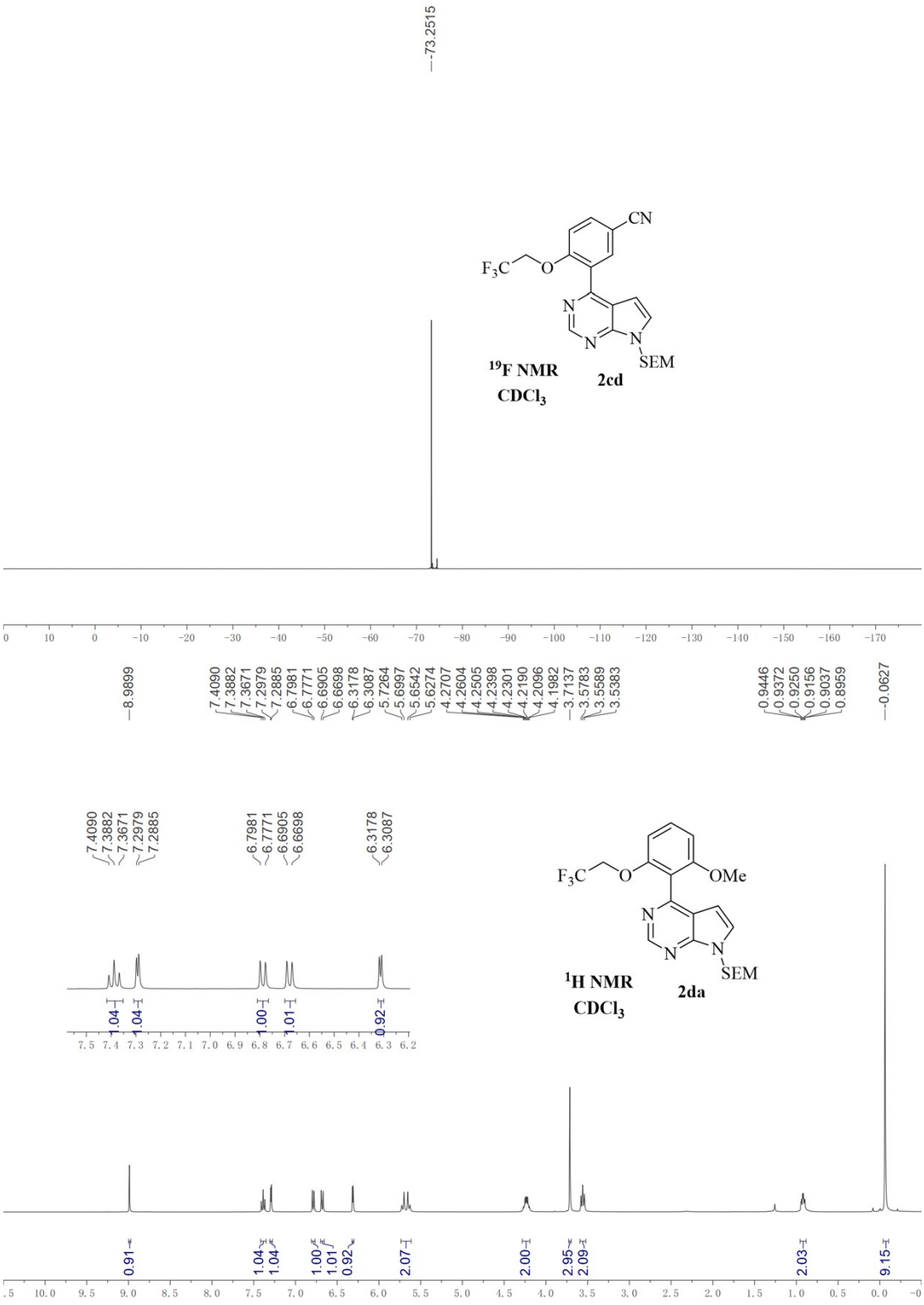
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N
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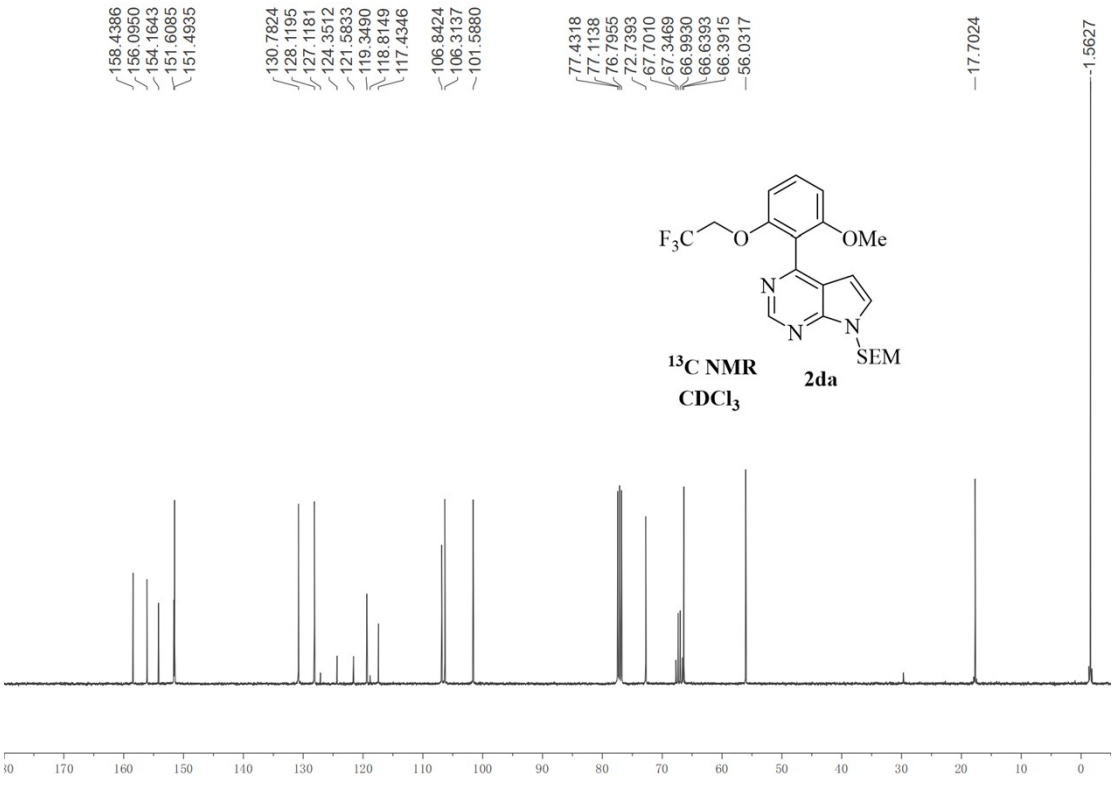
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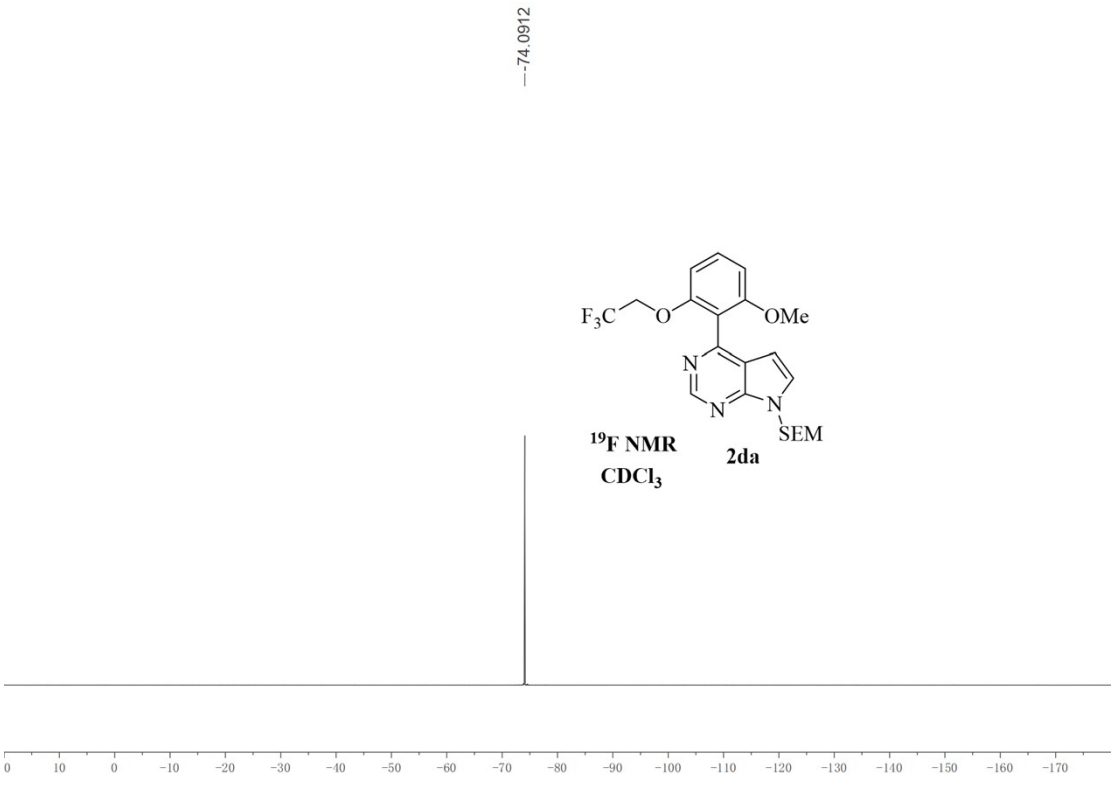
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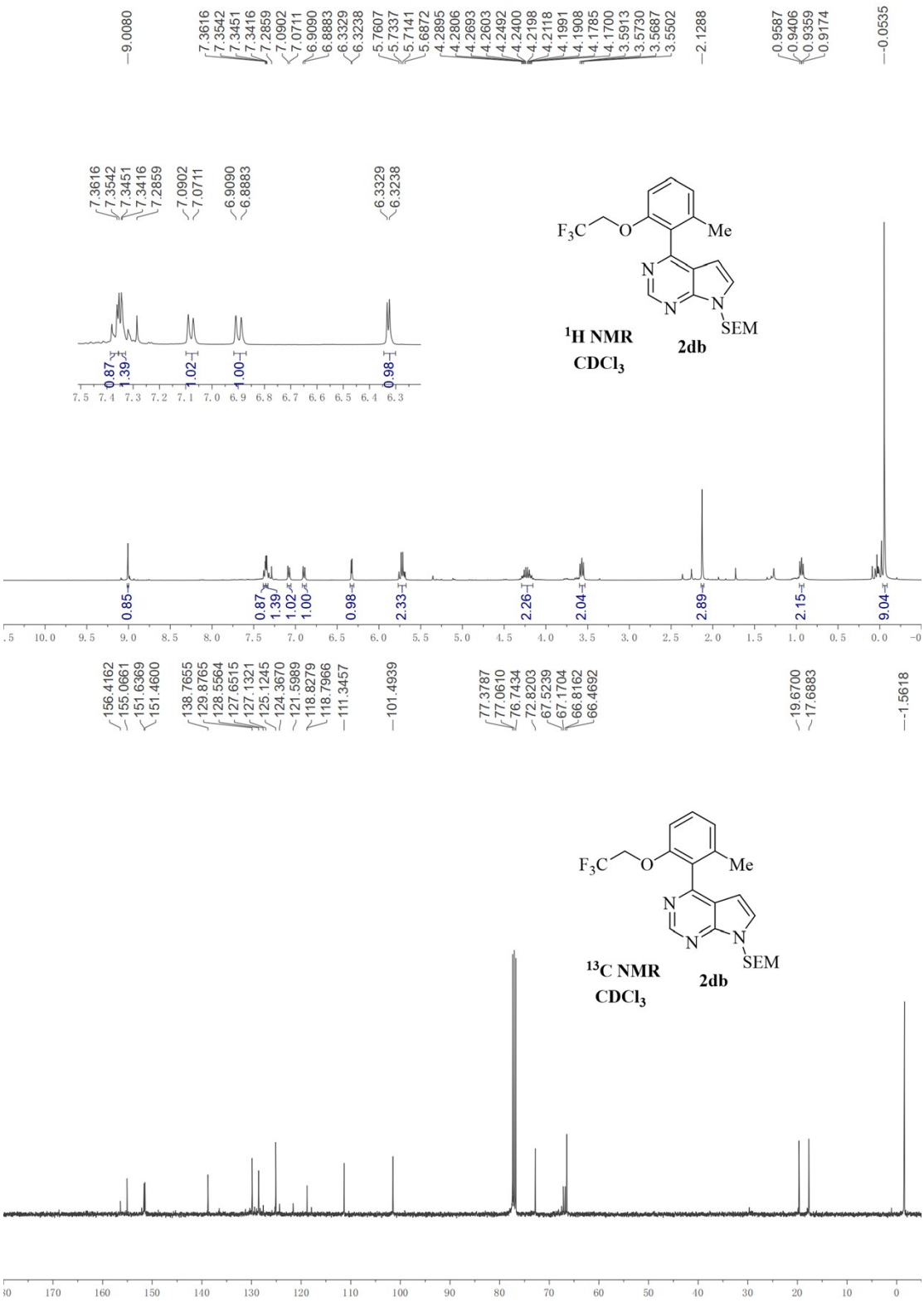
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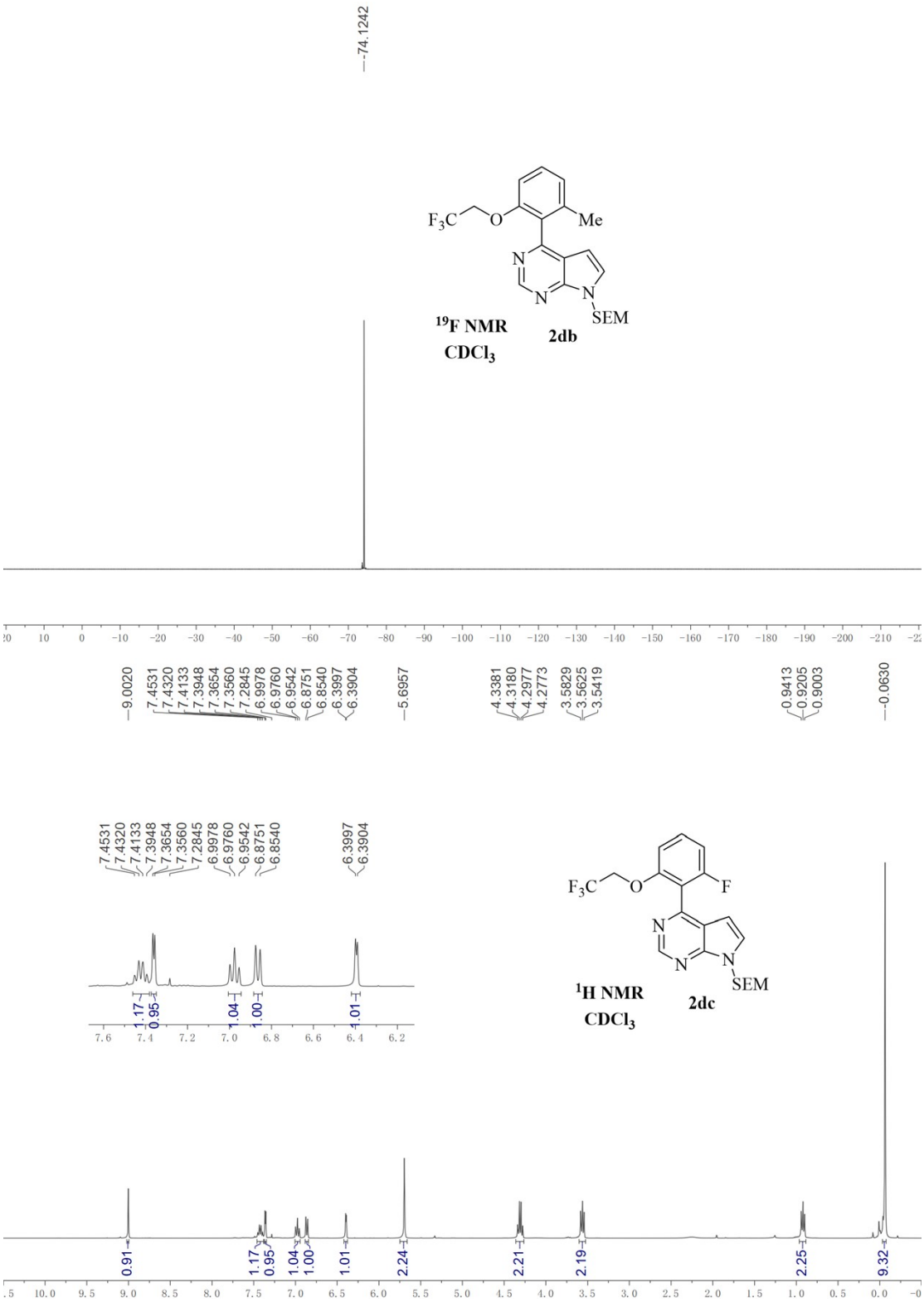
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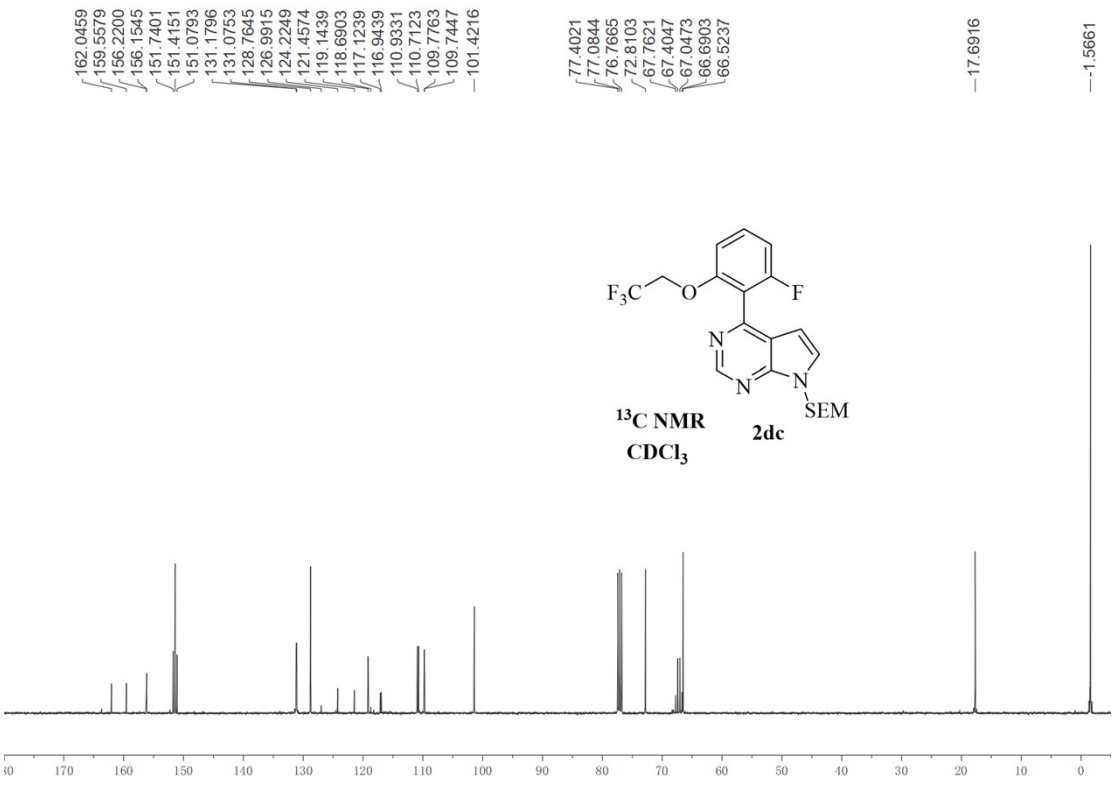
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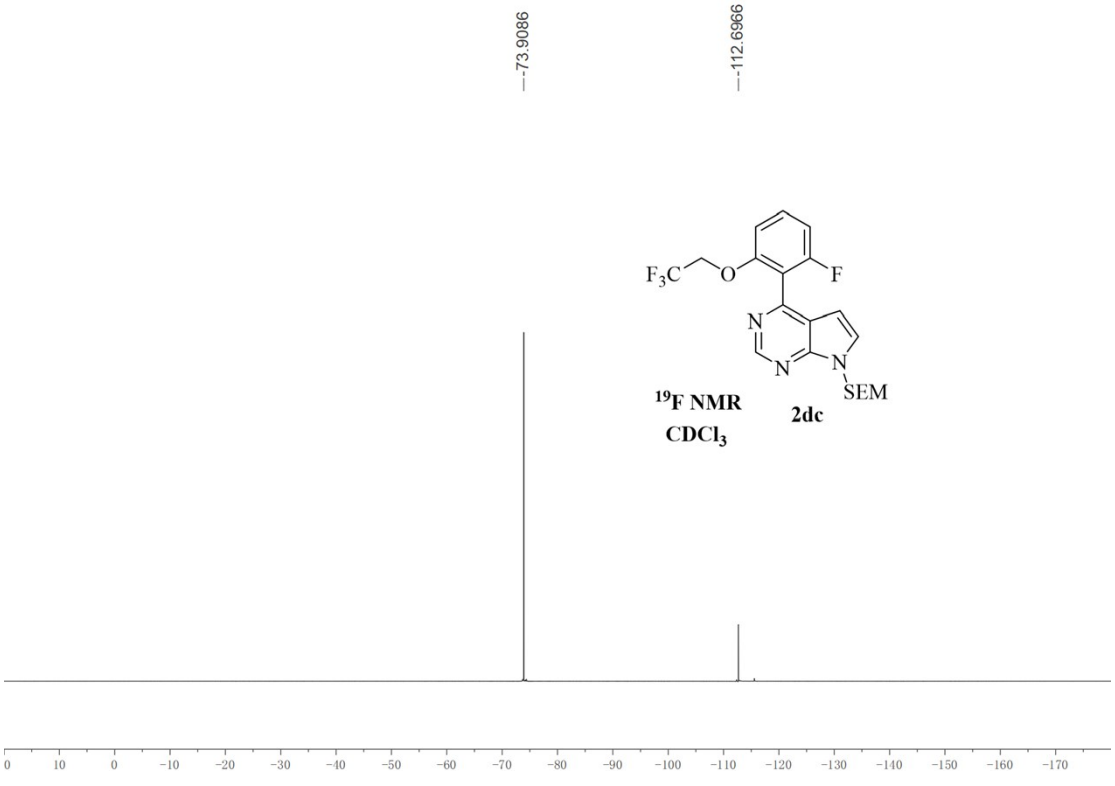
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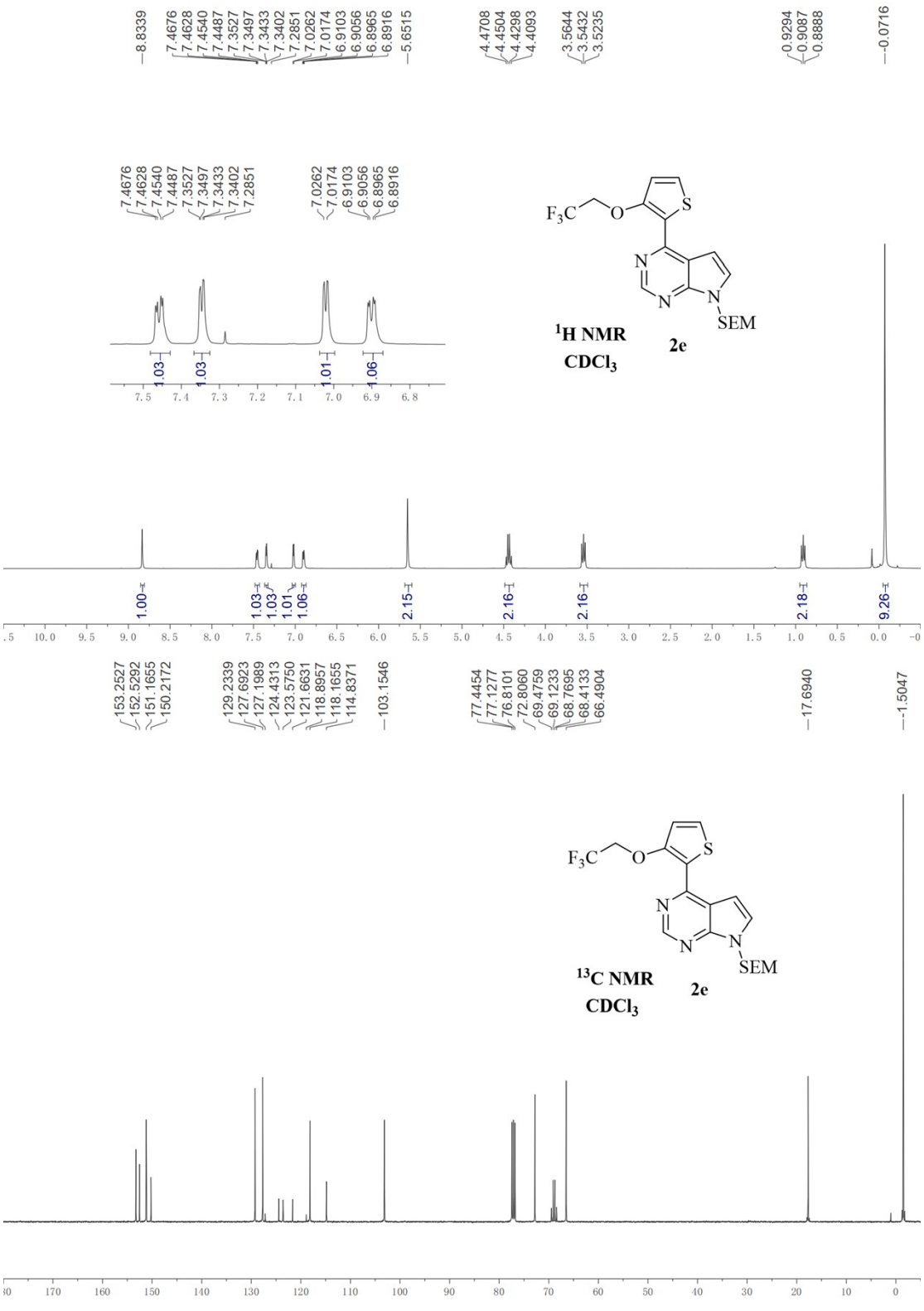
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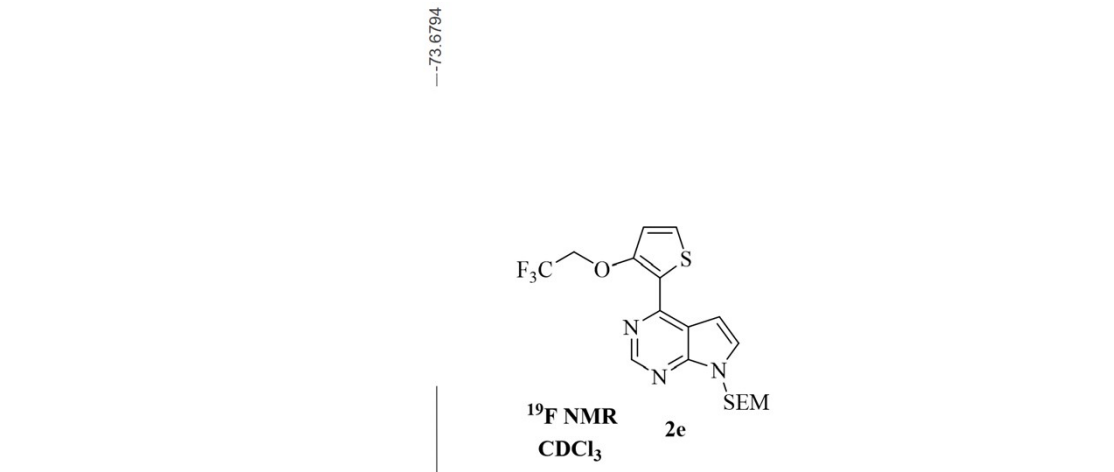
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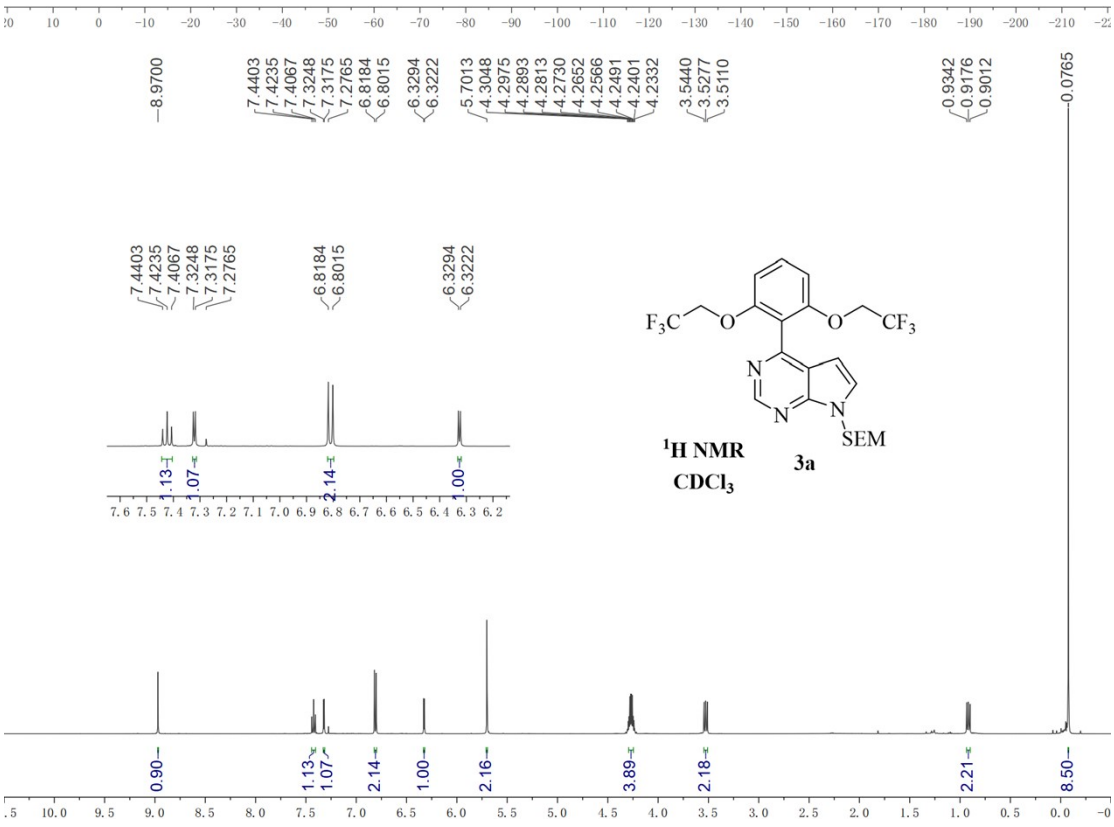
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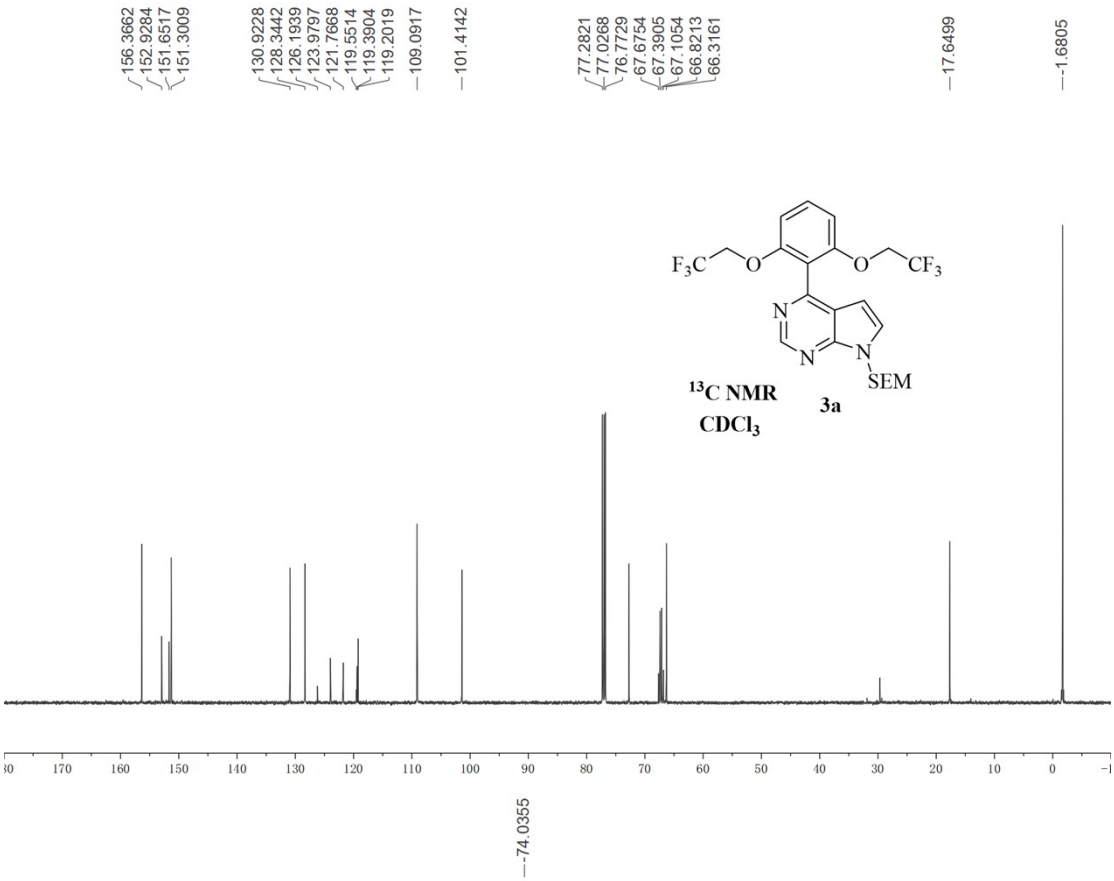
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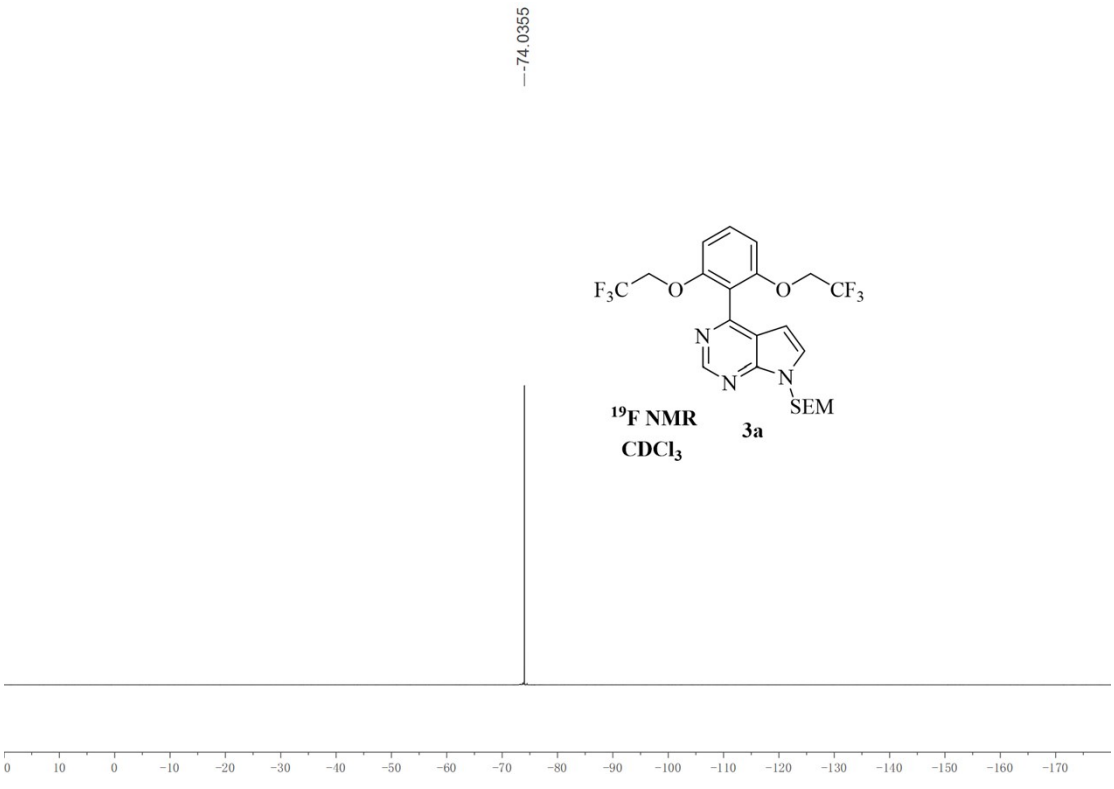
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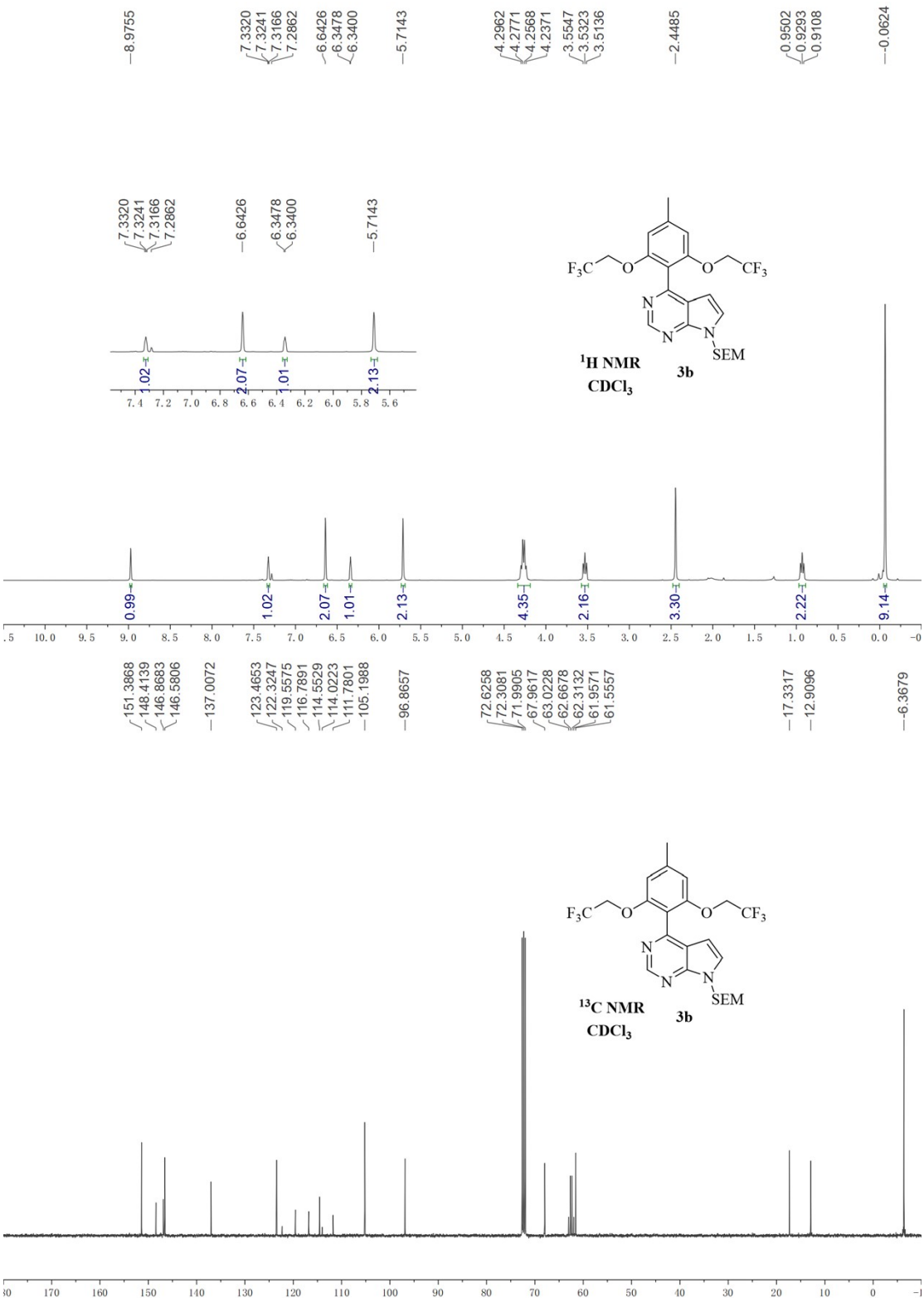
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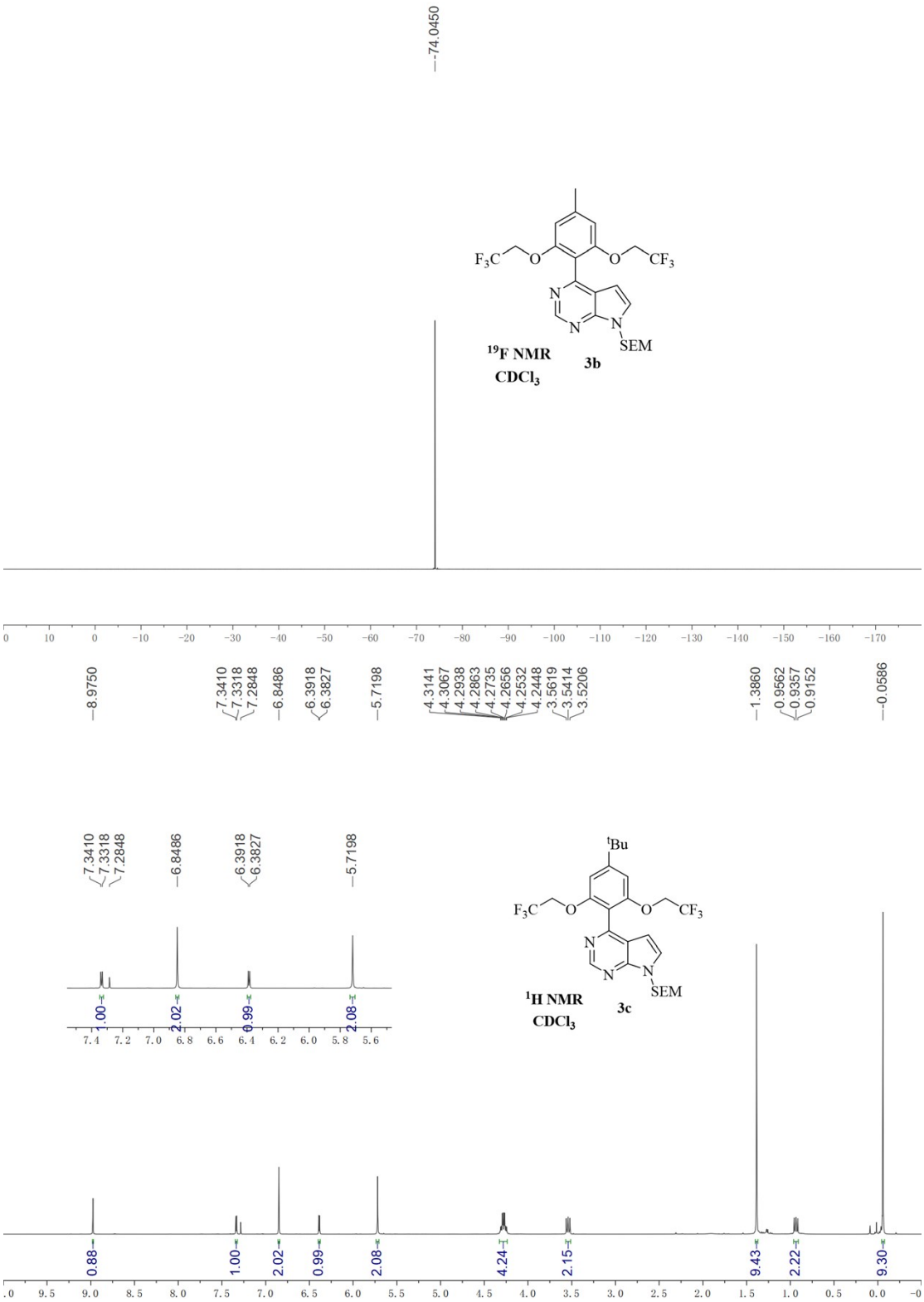
3b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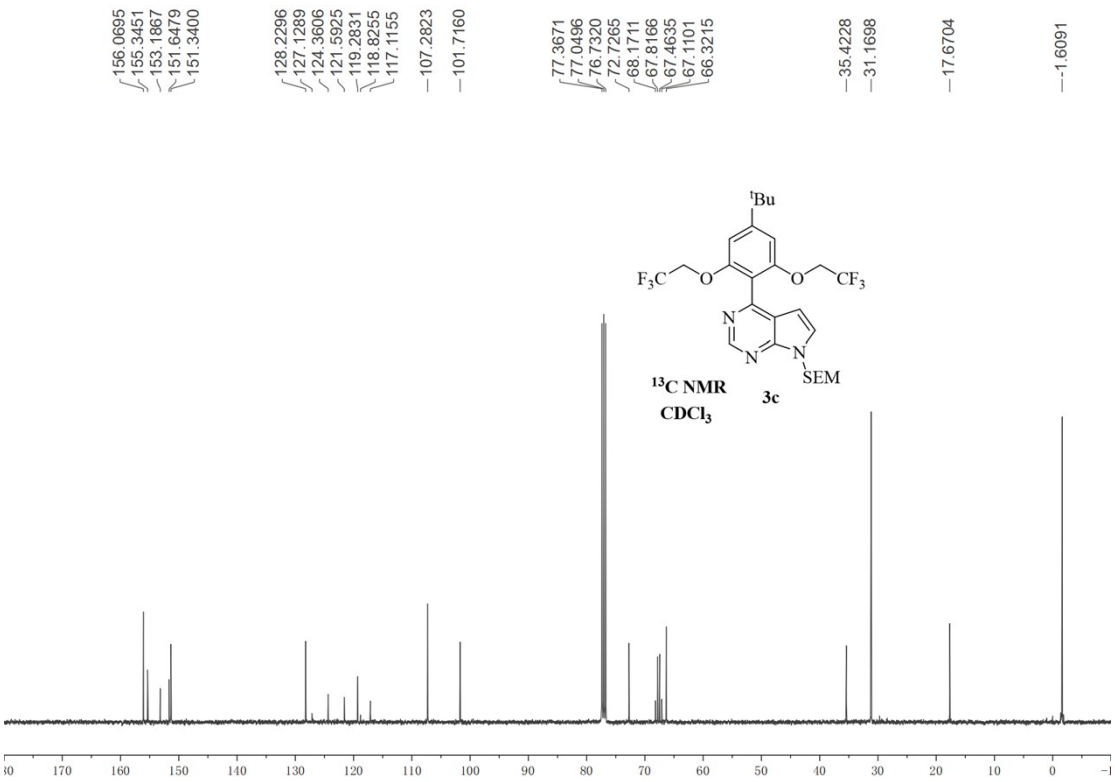
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CDCl3
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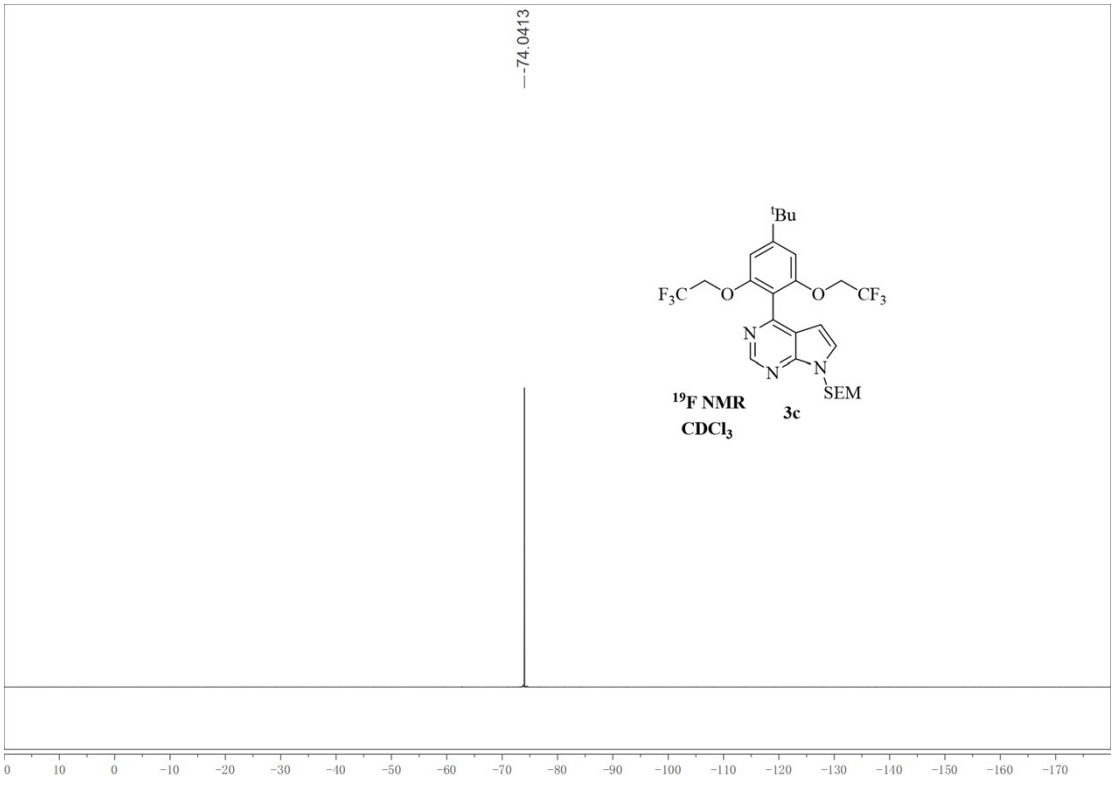
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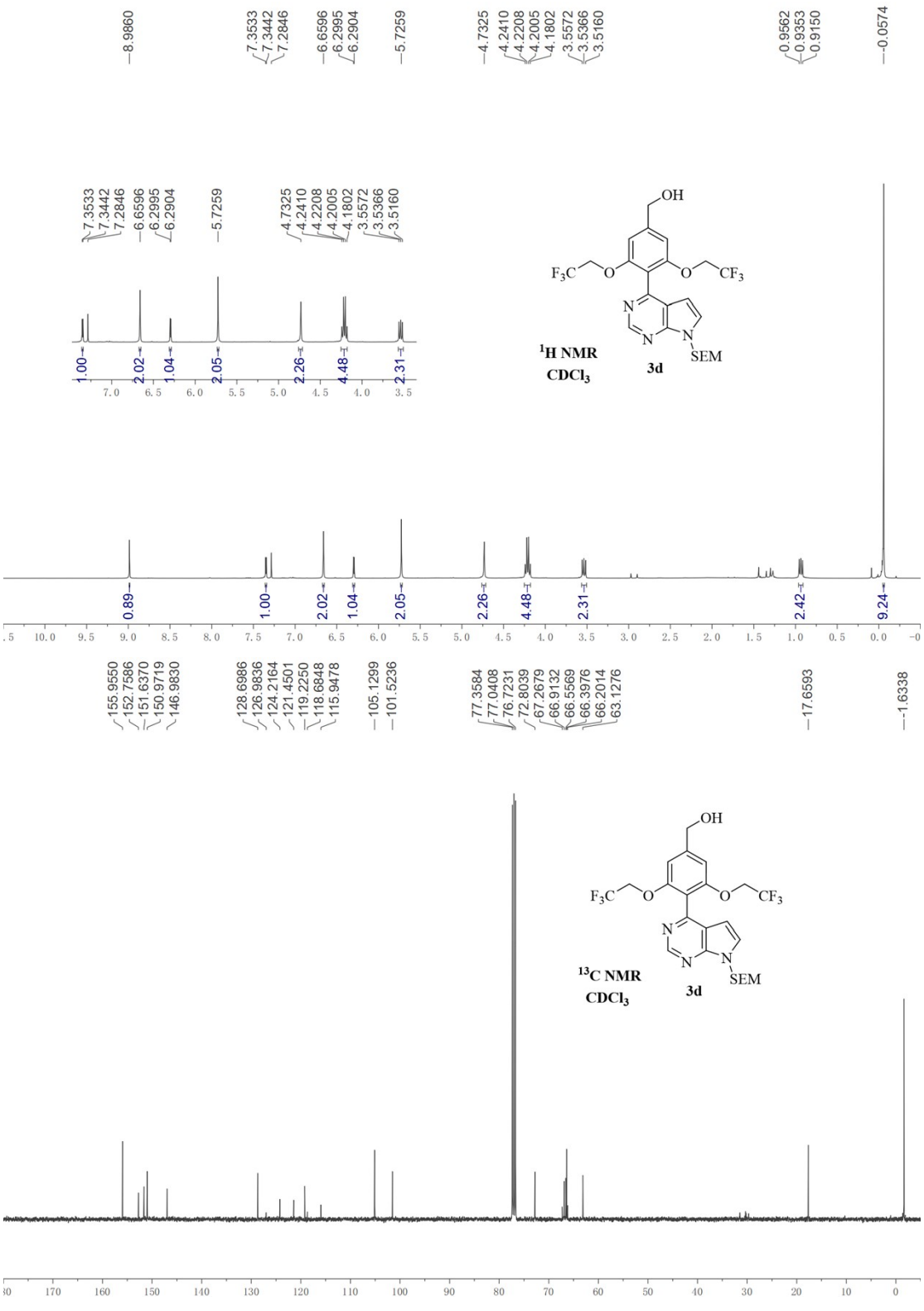
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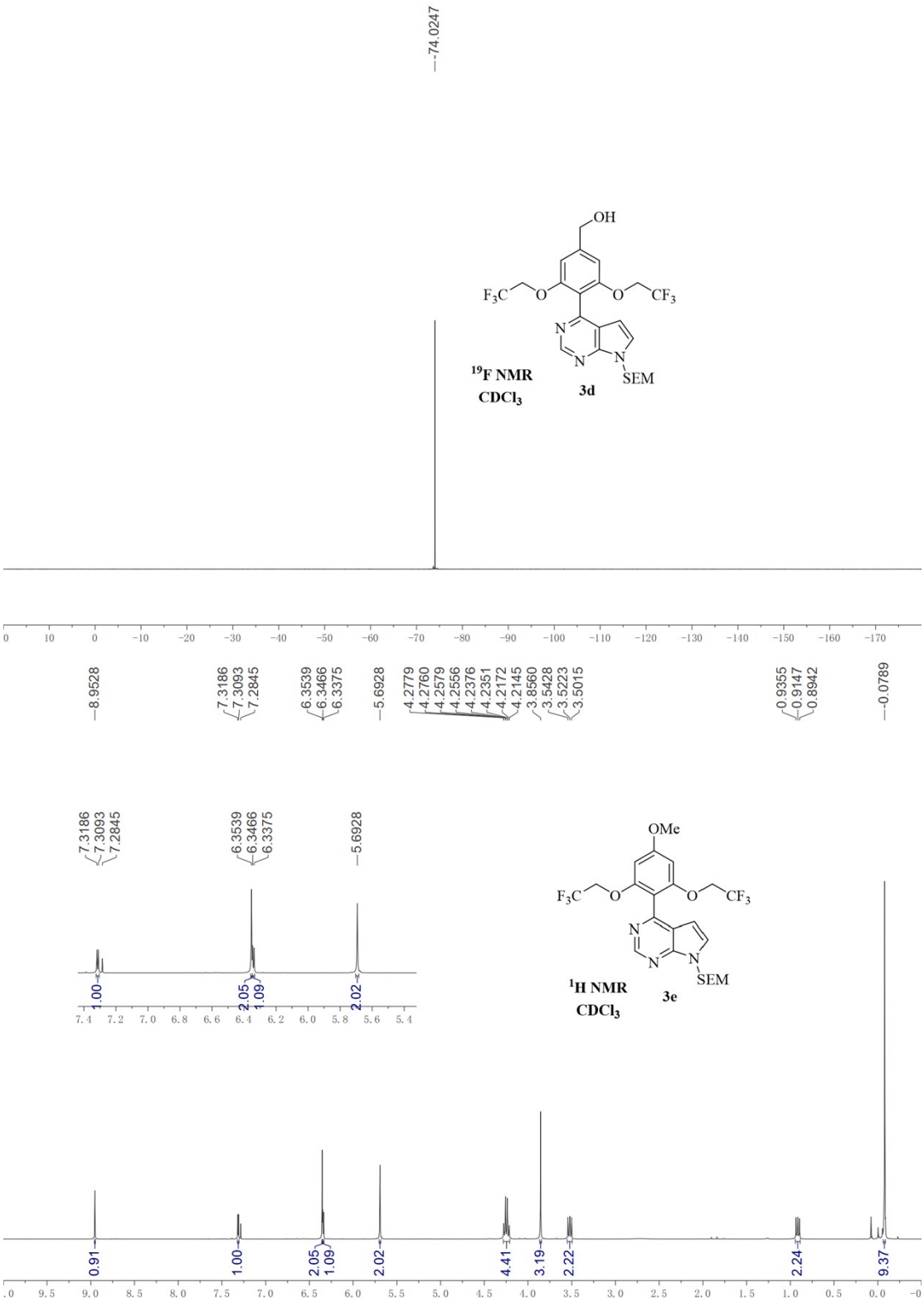
3d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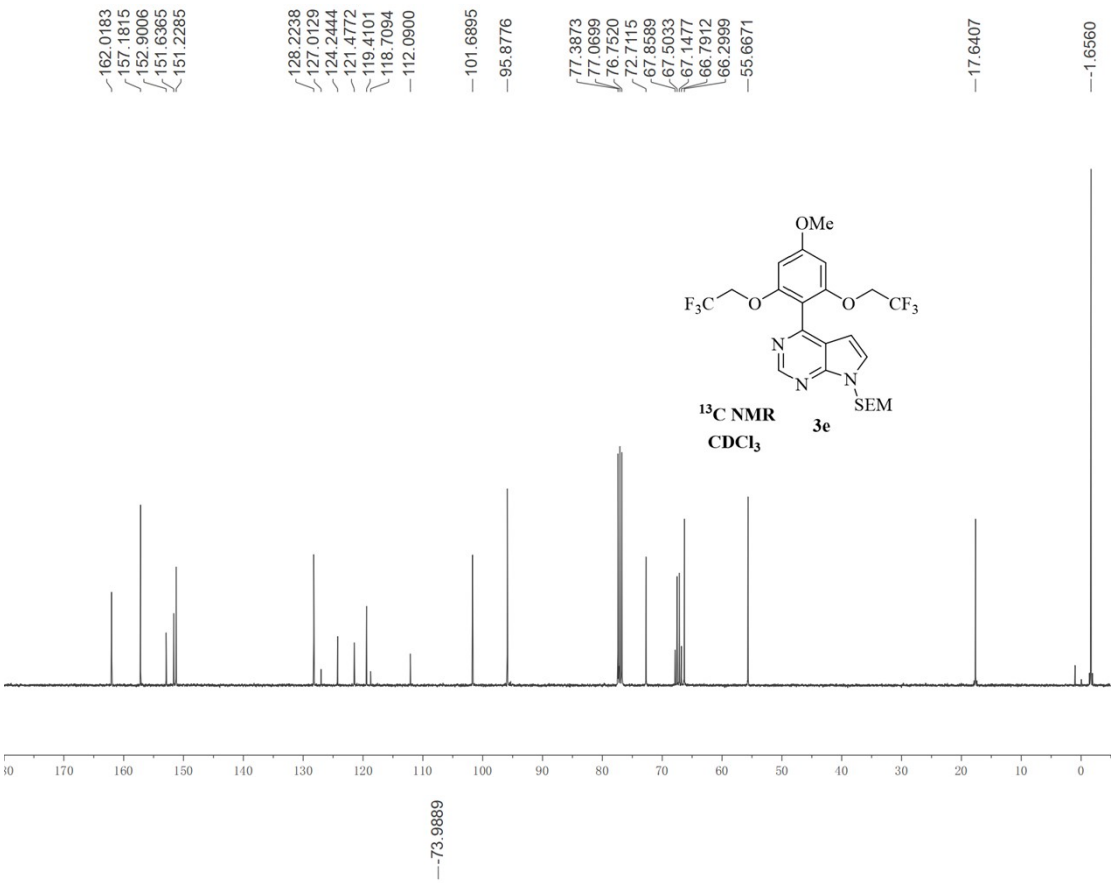
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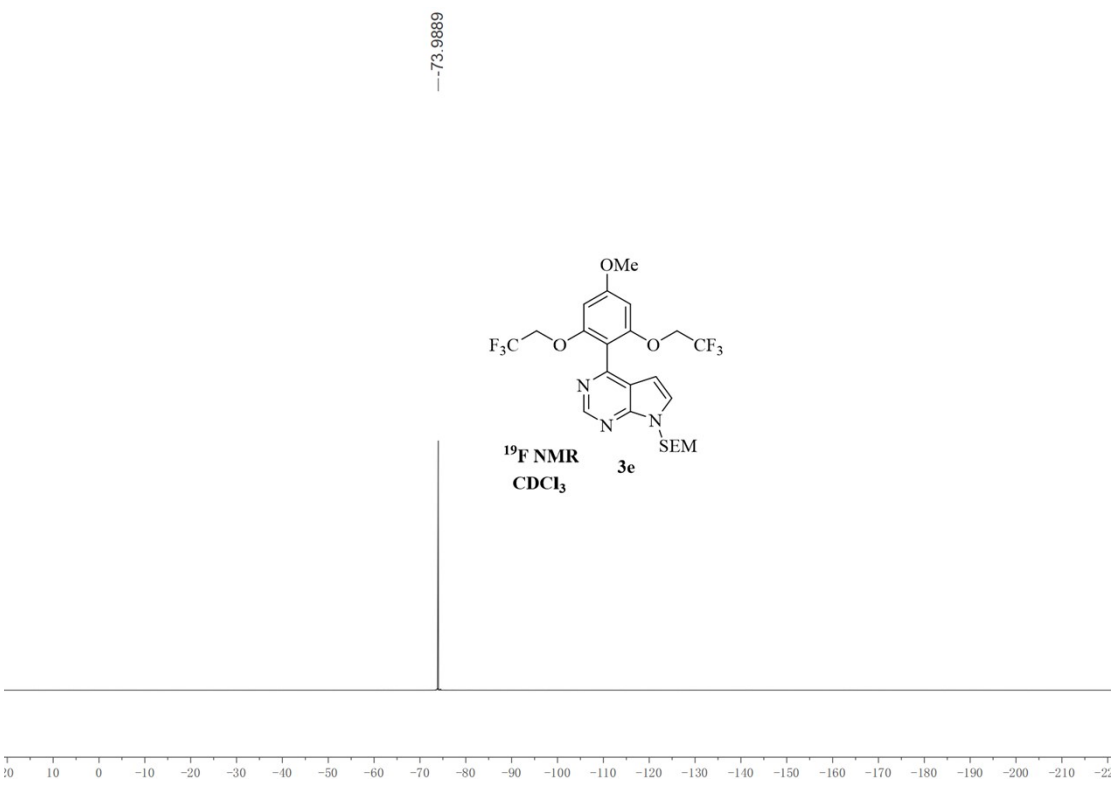
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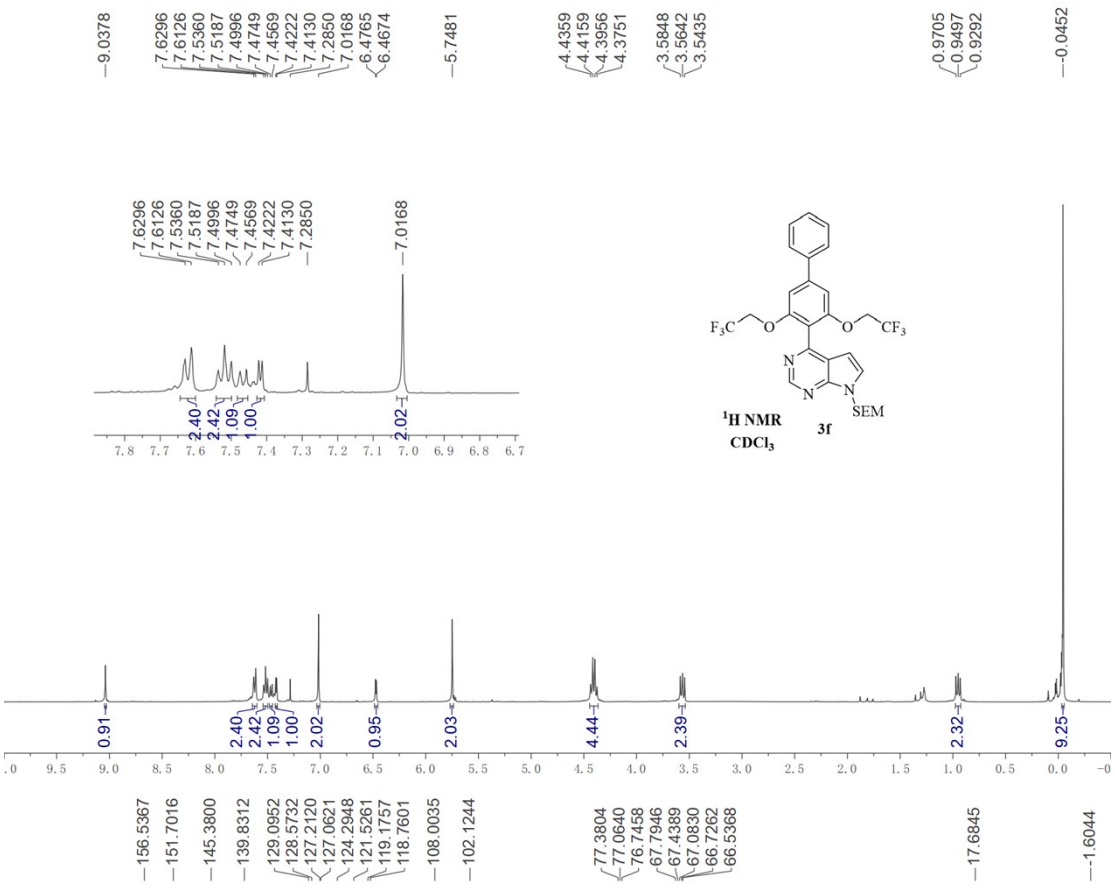
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2.42
1.09
1.00
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2.40
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2.02
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1H NMR
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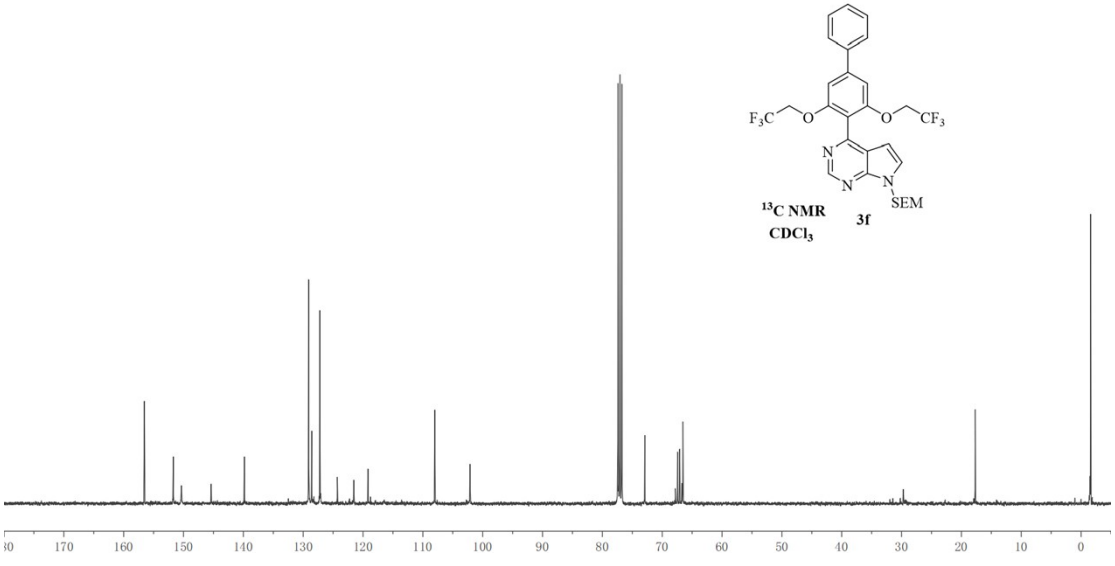
3f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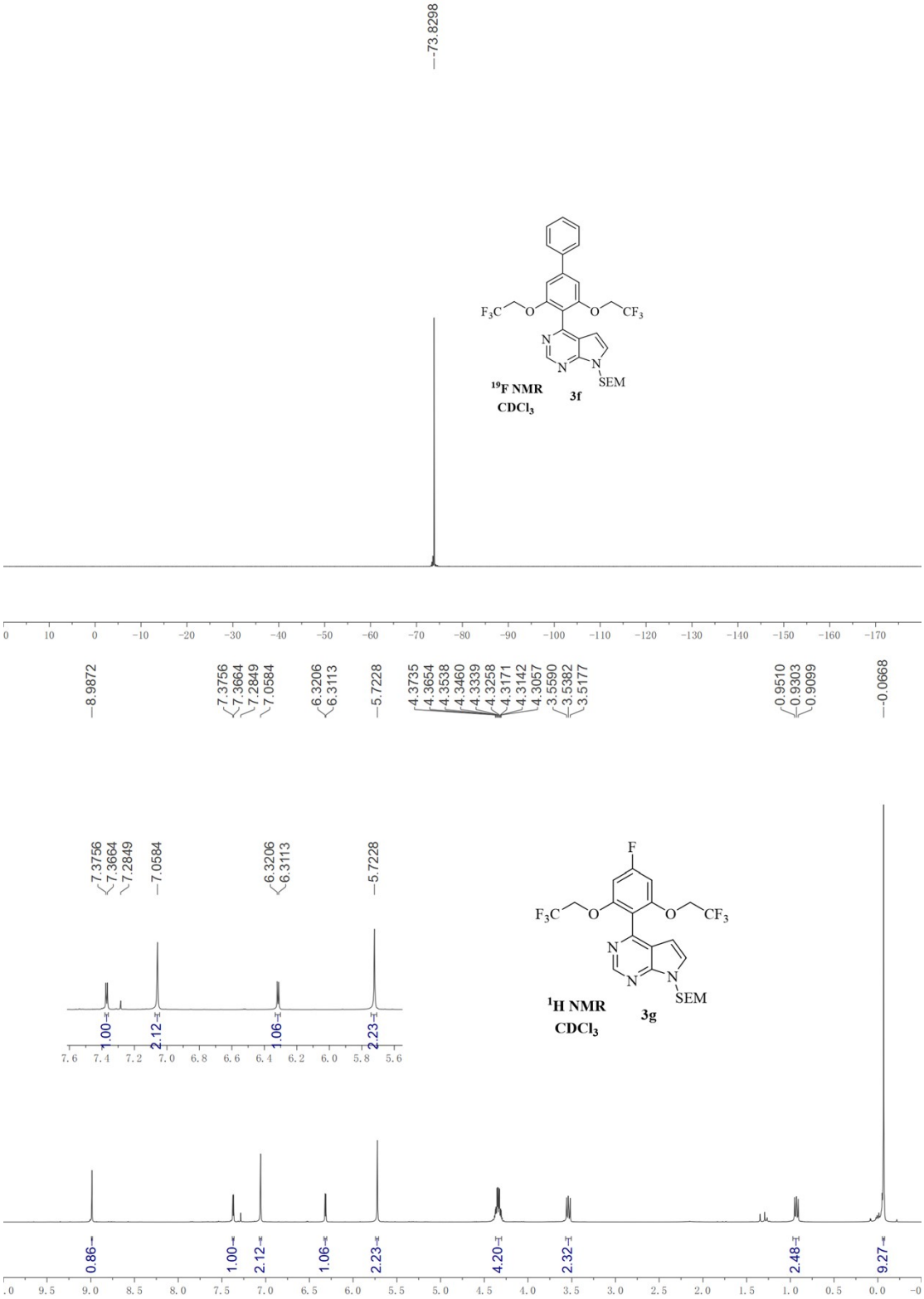
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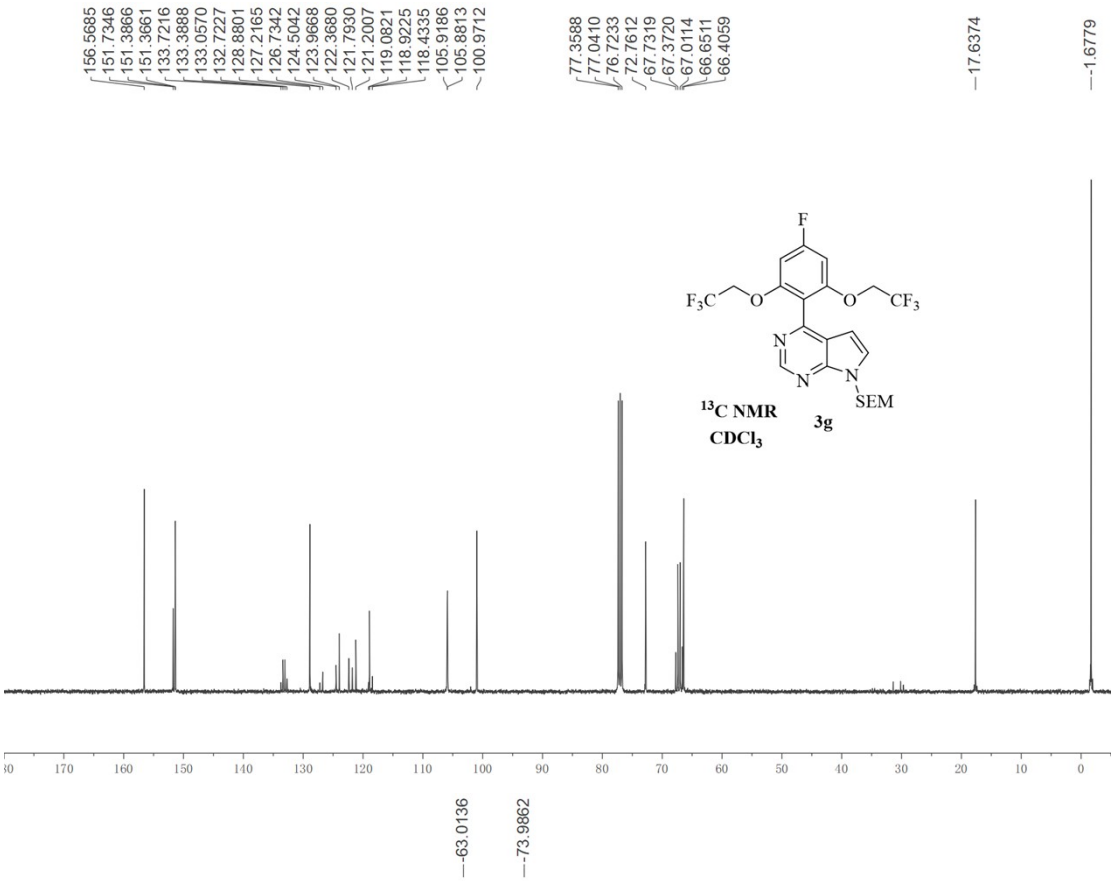
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13C NMR
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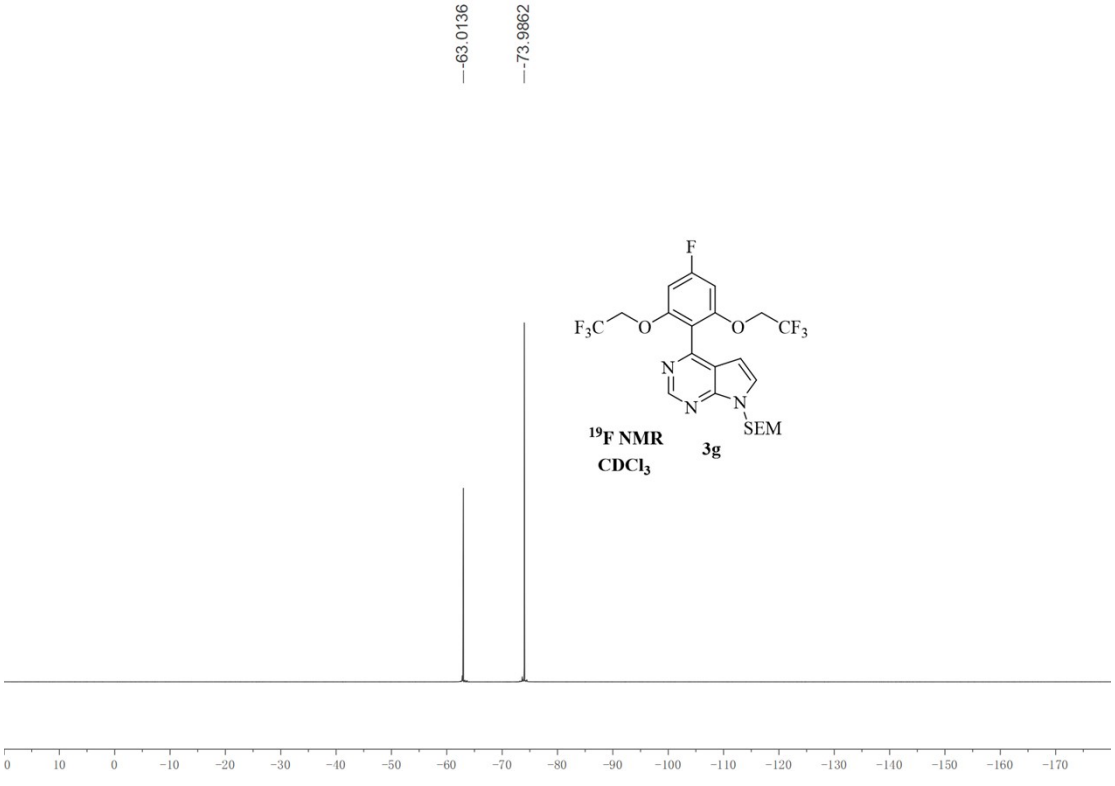
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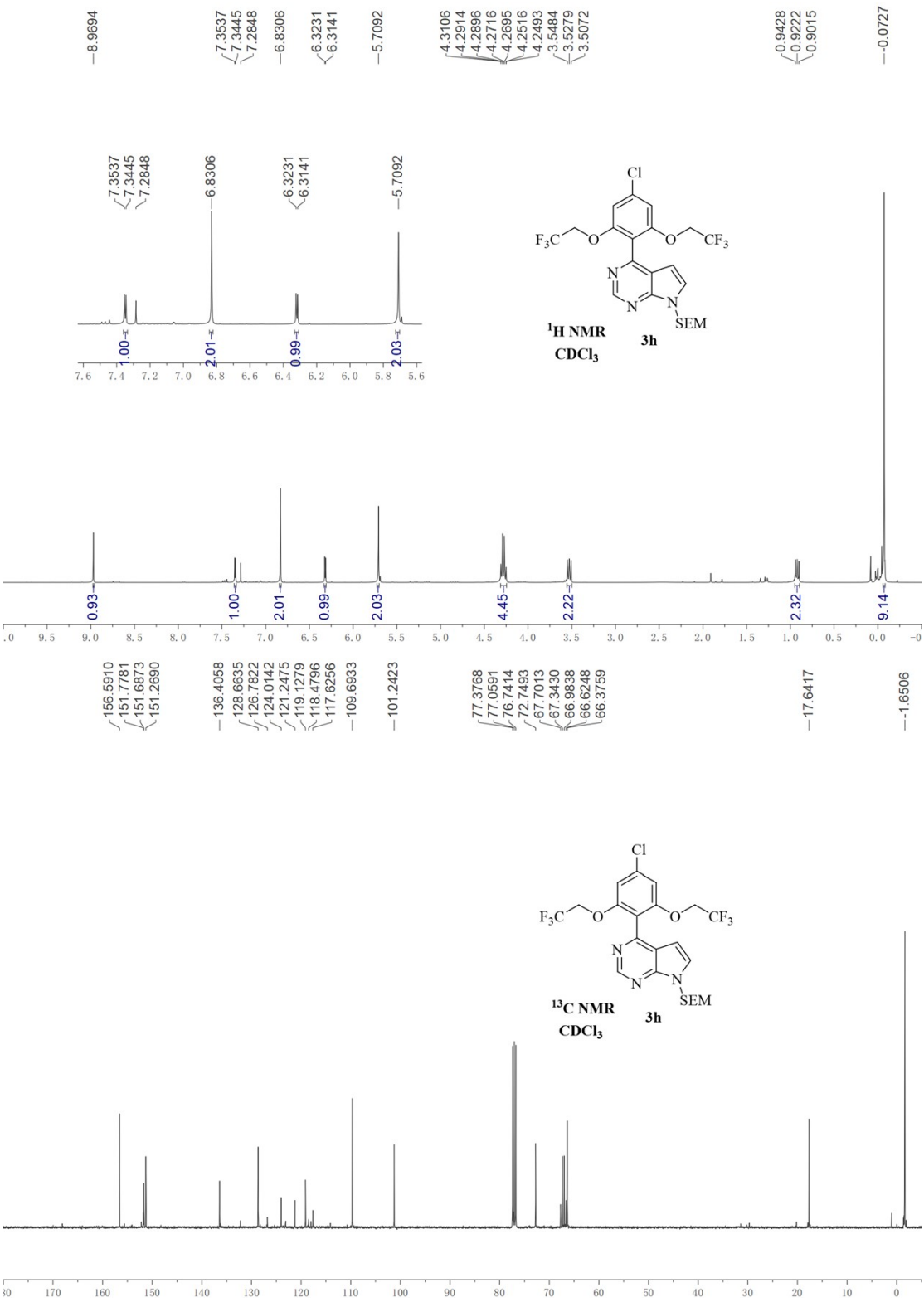
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CF3
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N
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CDCl3
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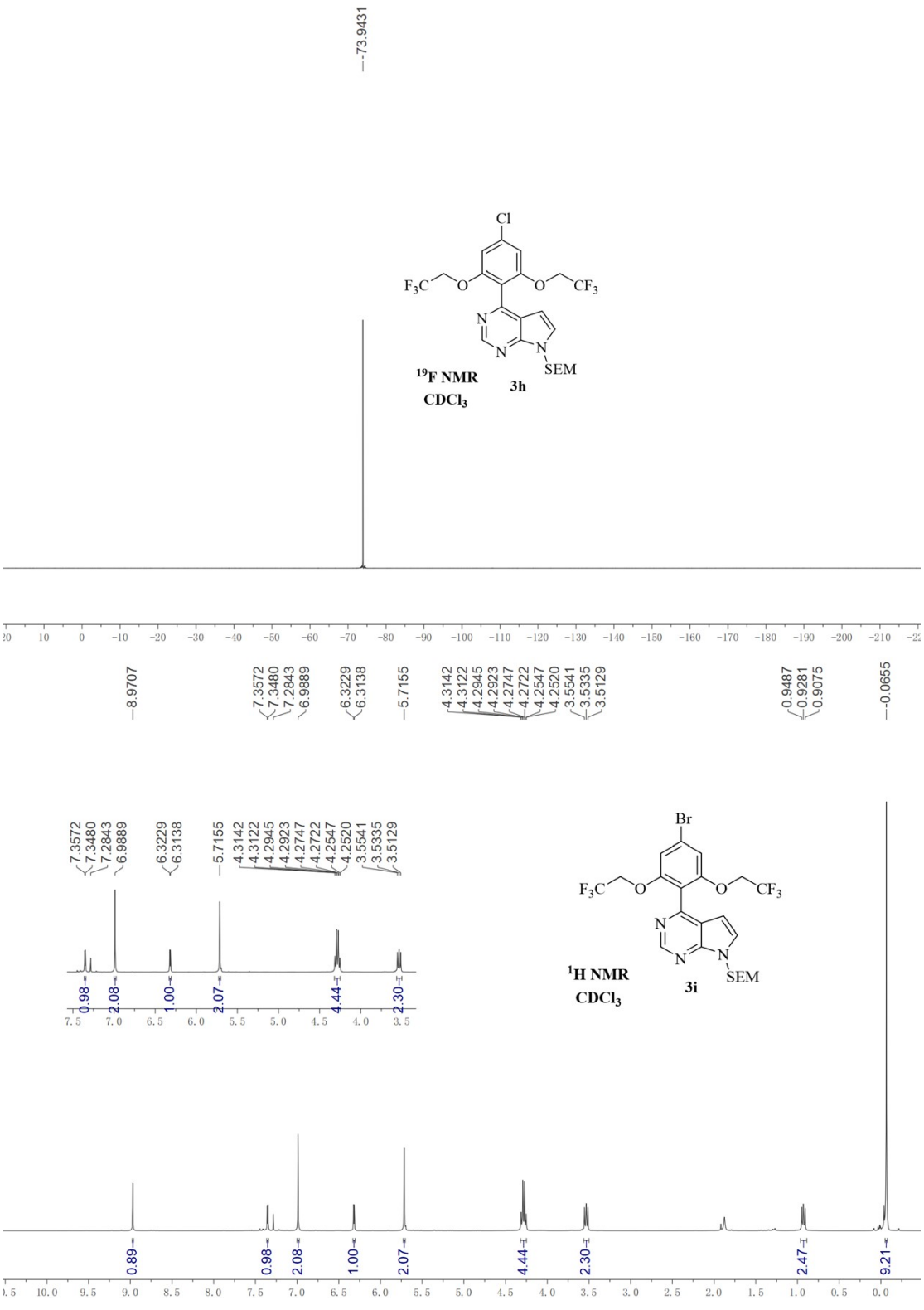
3h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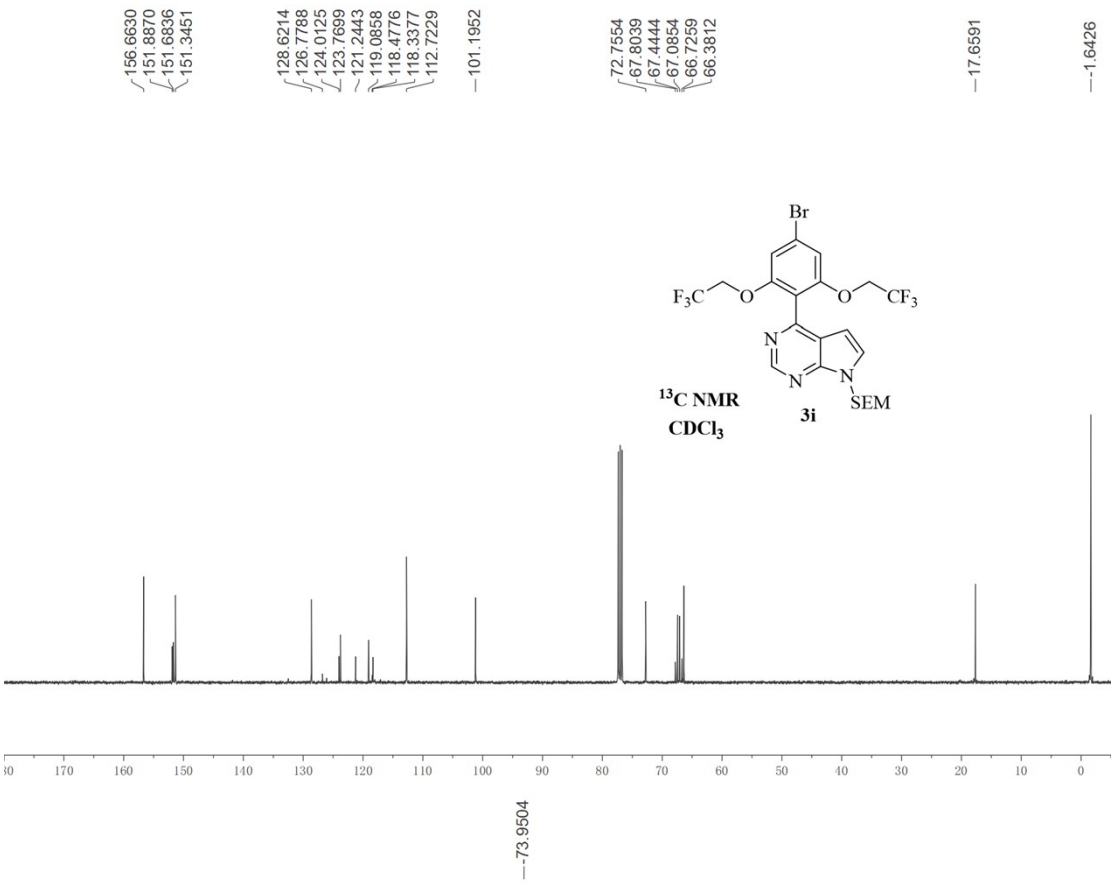
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CF3
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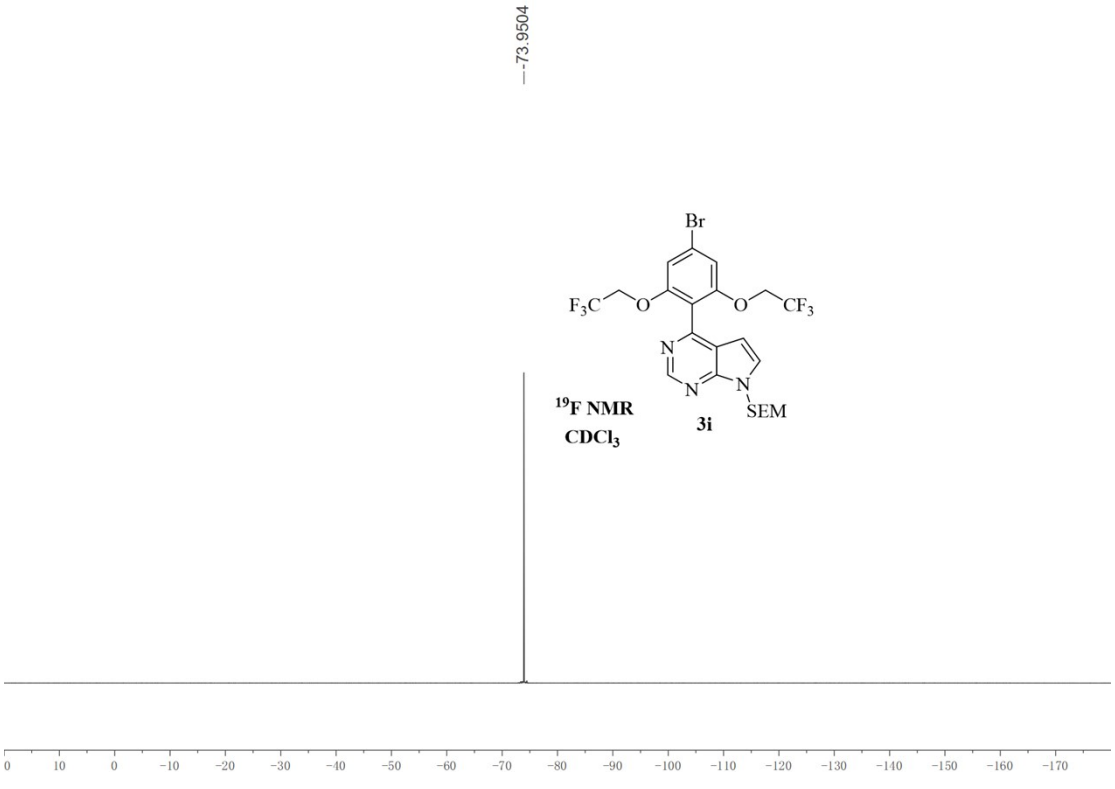
3i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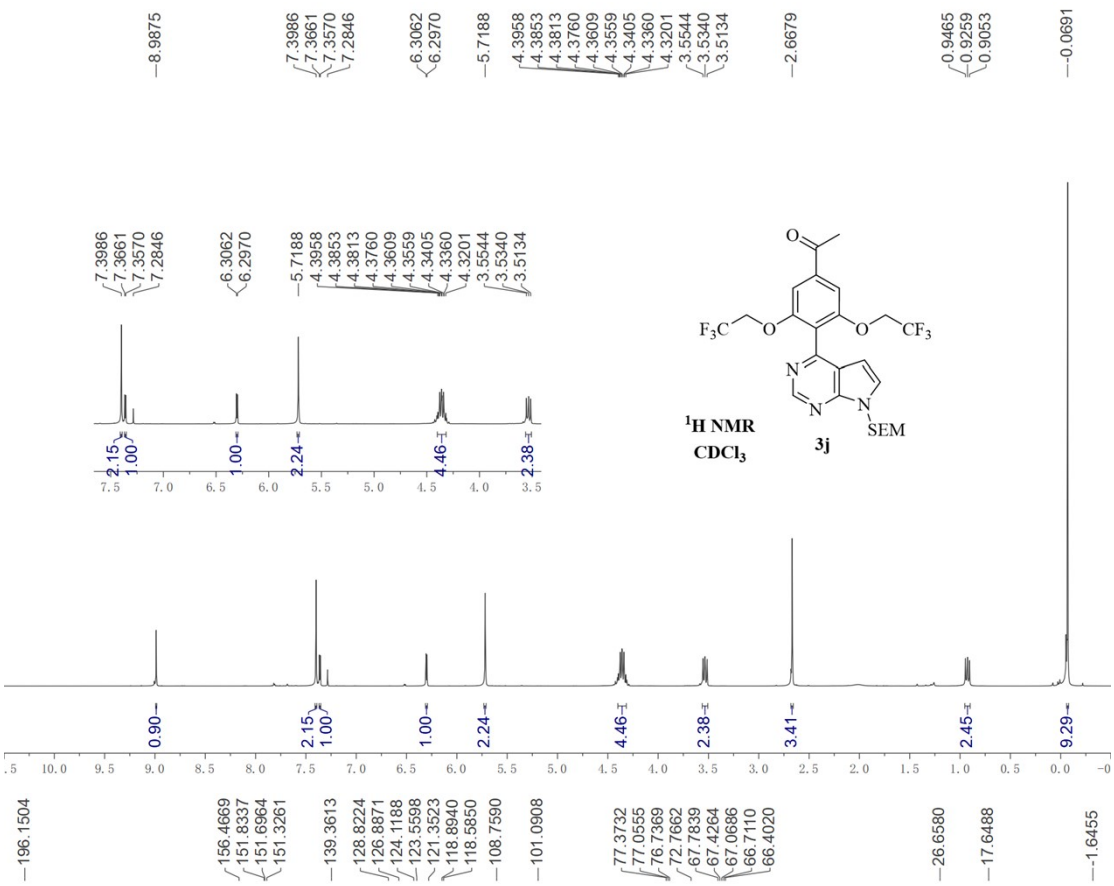
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CDCl$_3$
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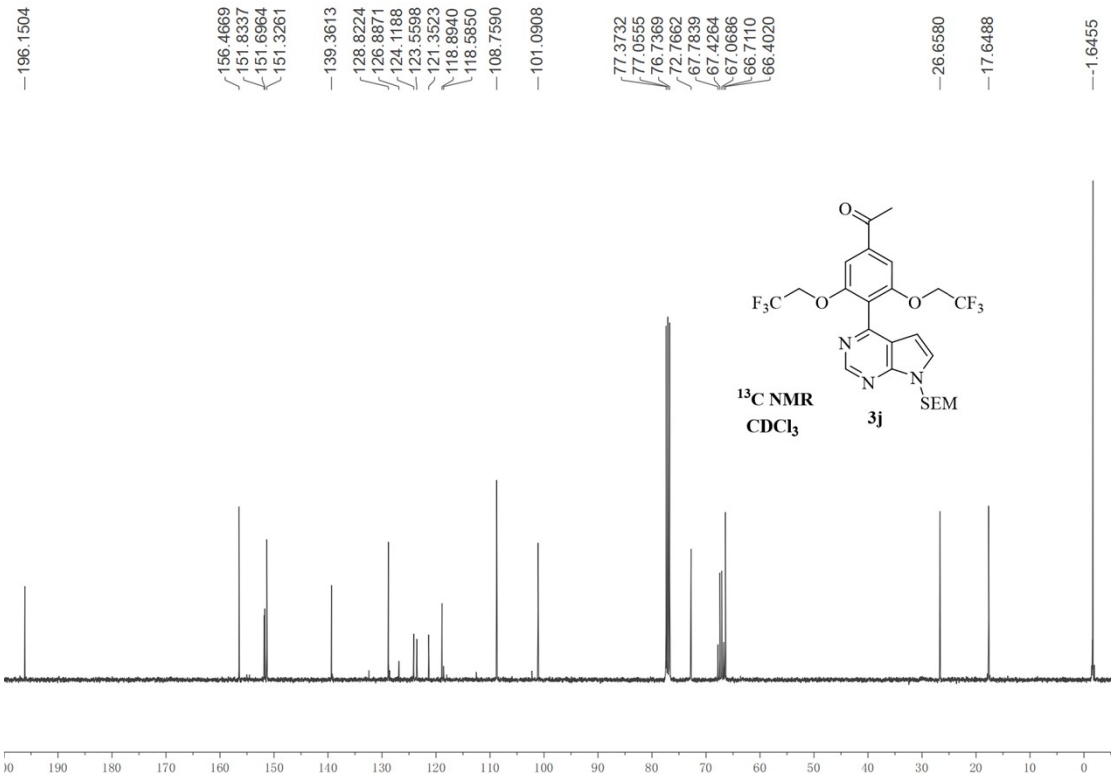
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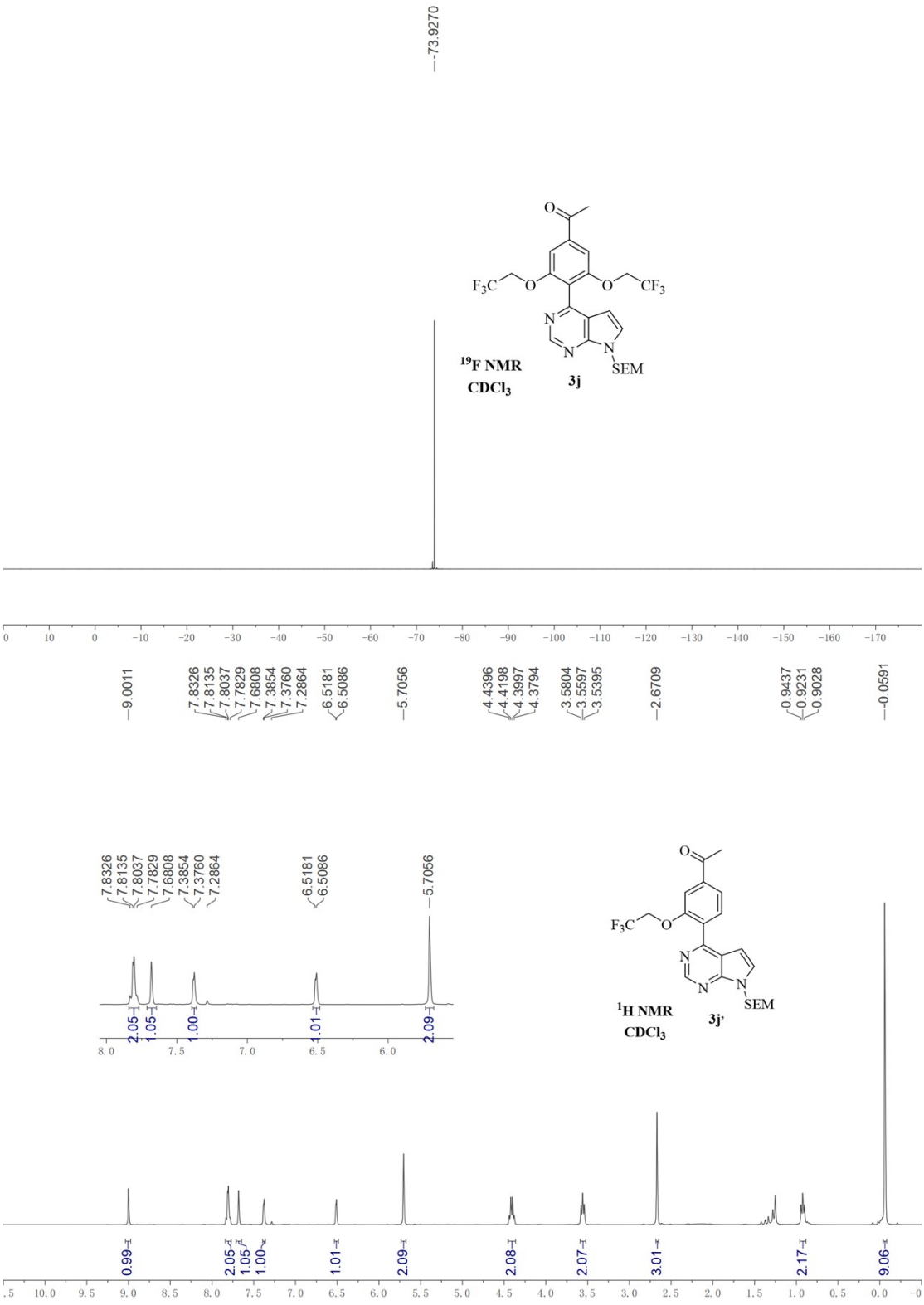
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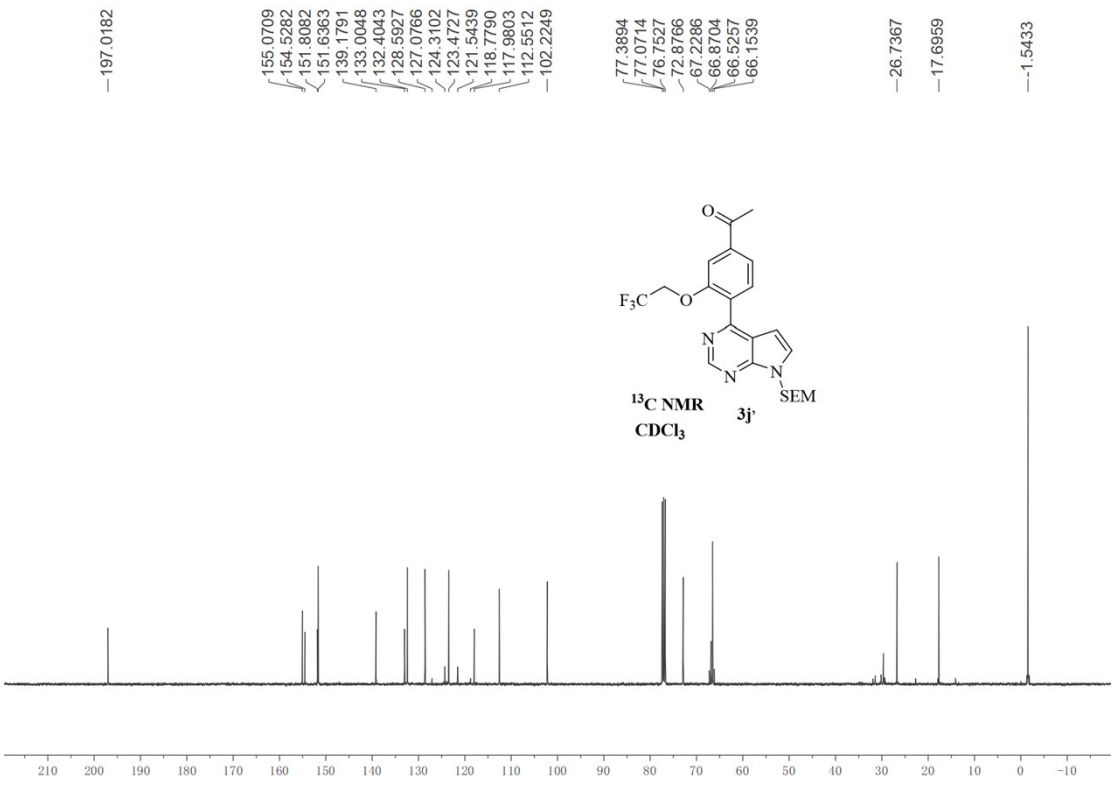
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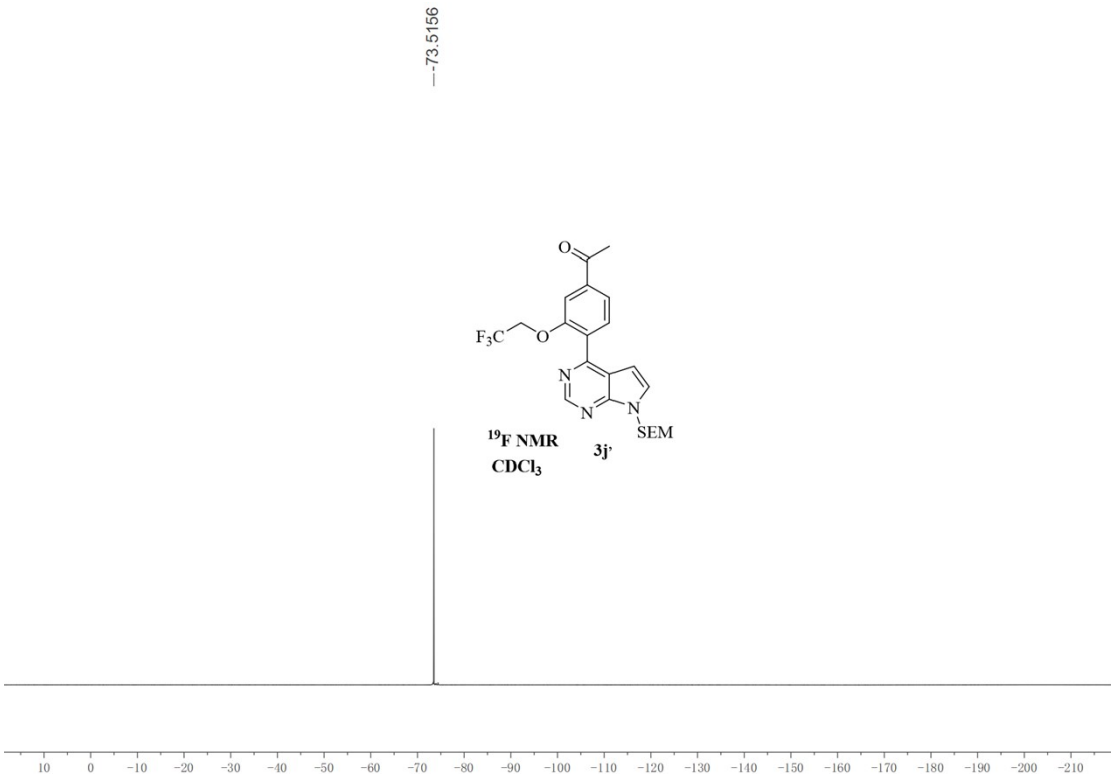
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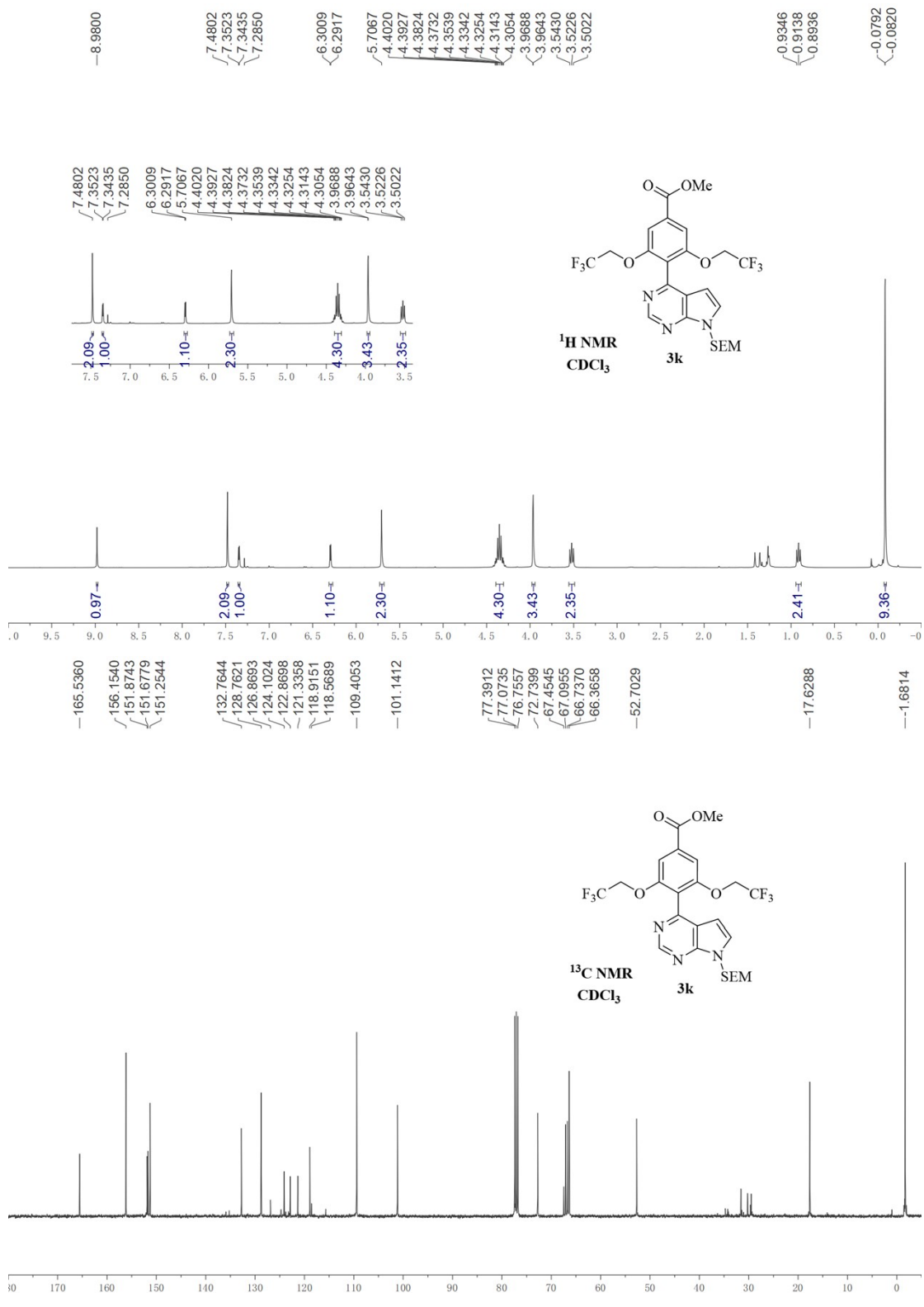
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0.8936
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4.30
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2.35
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CF3
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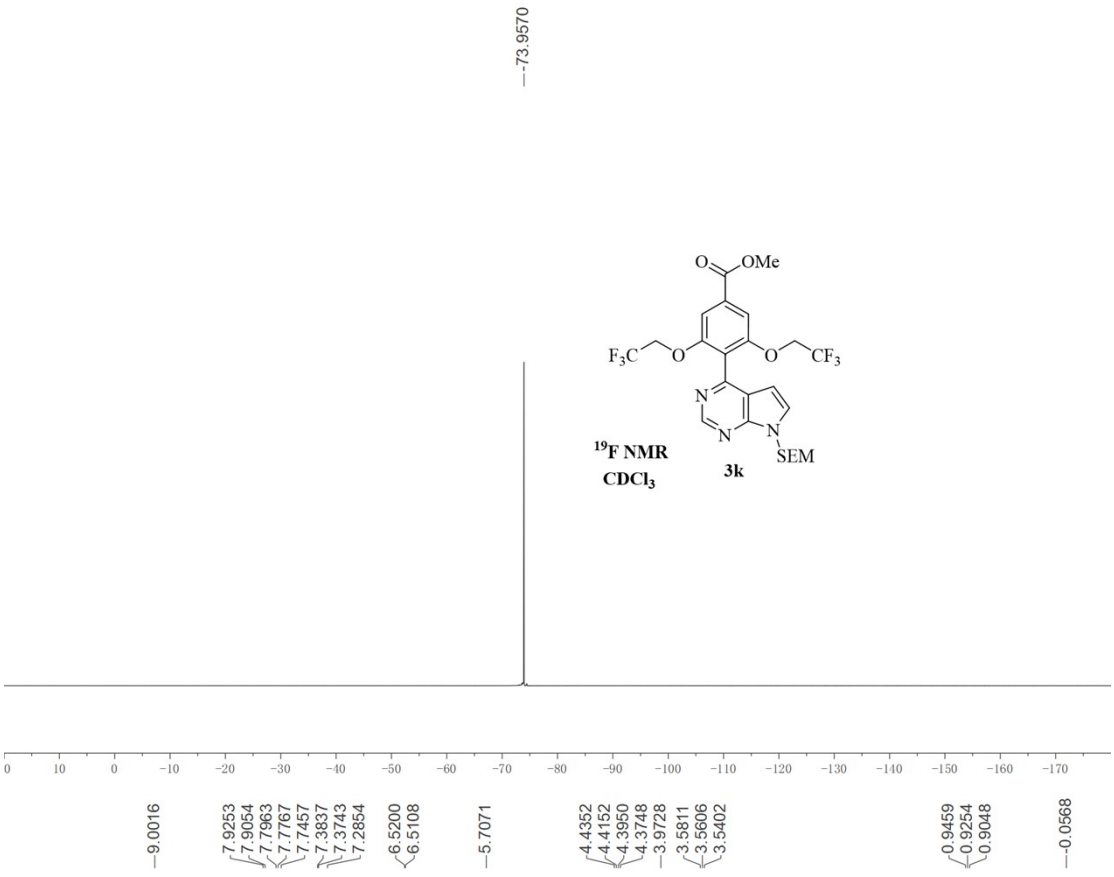
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7.7457
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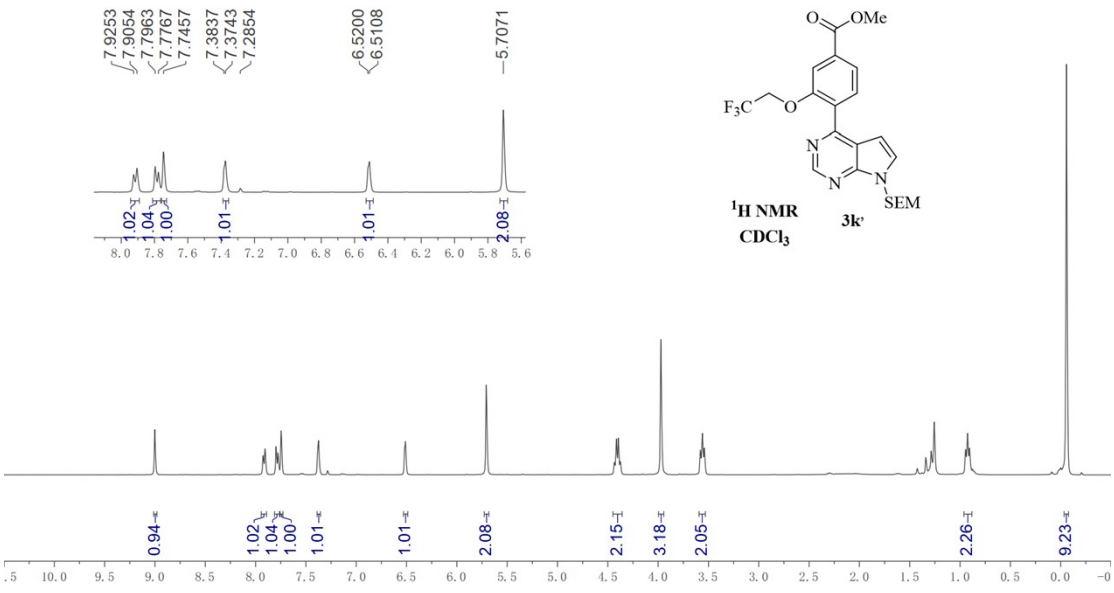
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7.4
7.2
7.0
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6.6
6.4
6.2
6.0
5.8
5.6
OMe
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O
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N
N
SEM
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1.01
1.01
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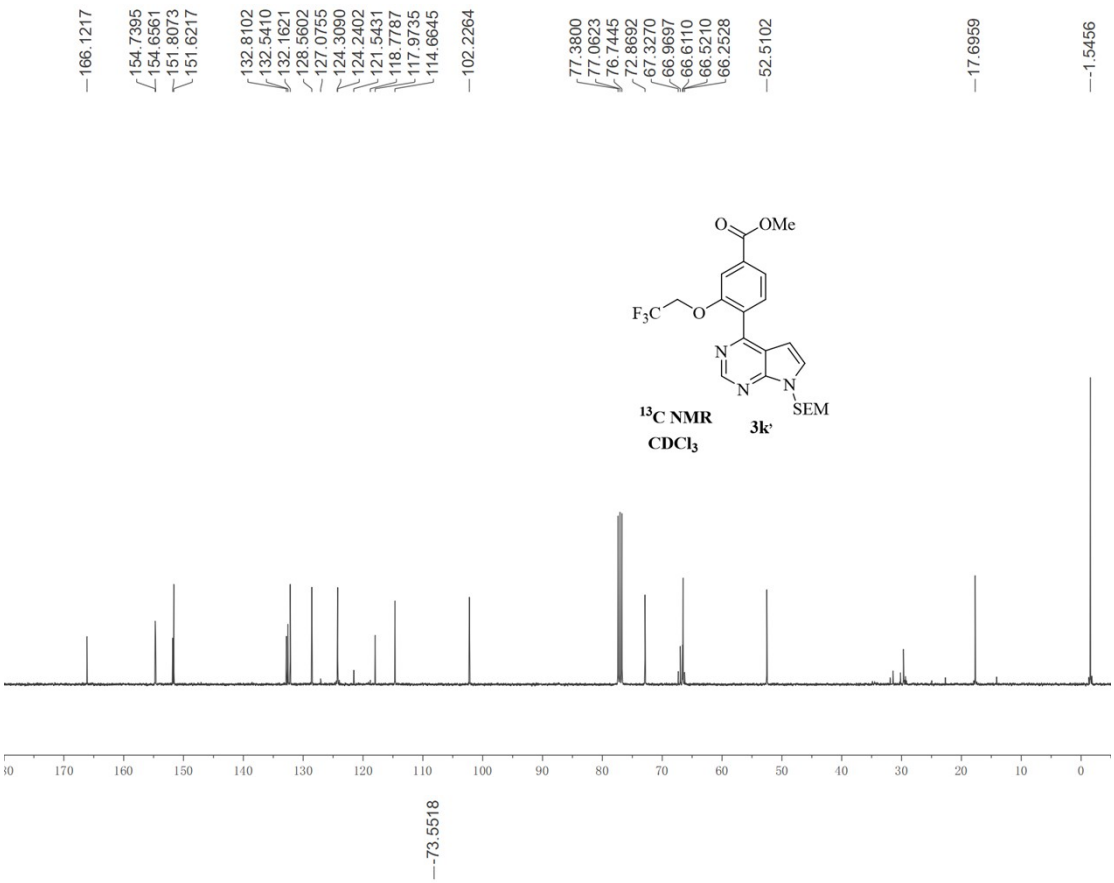
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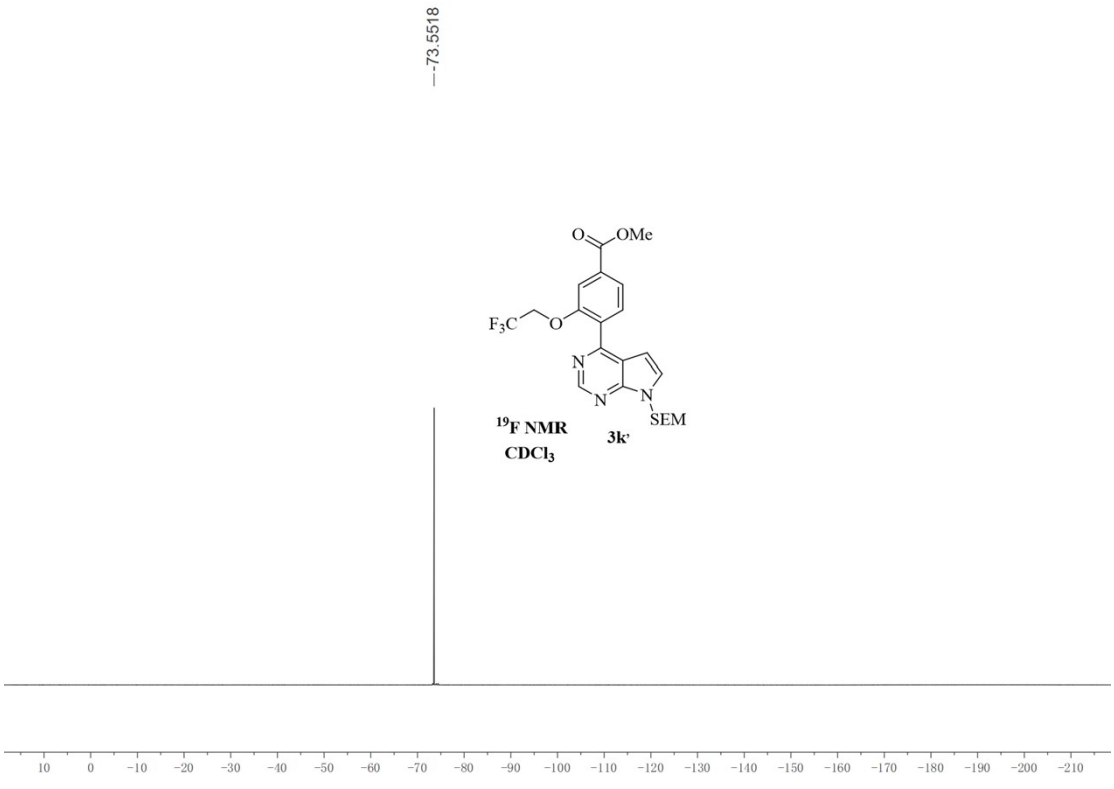
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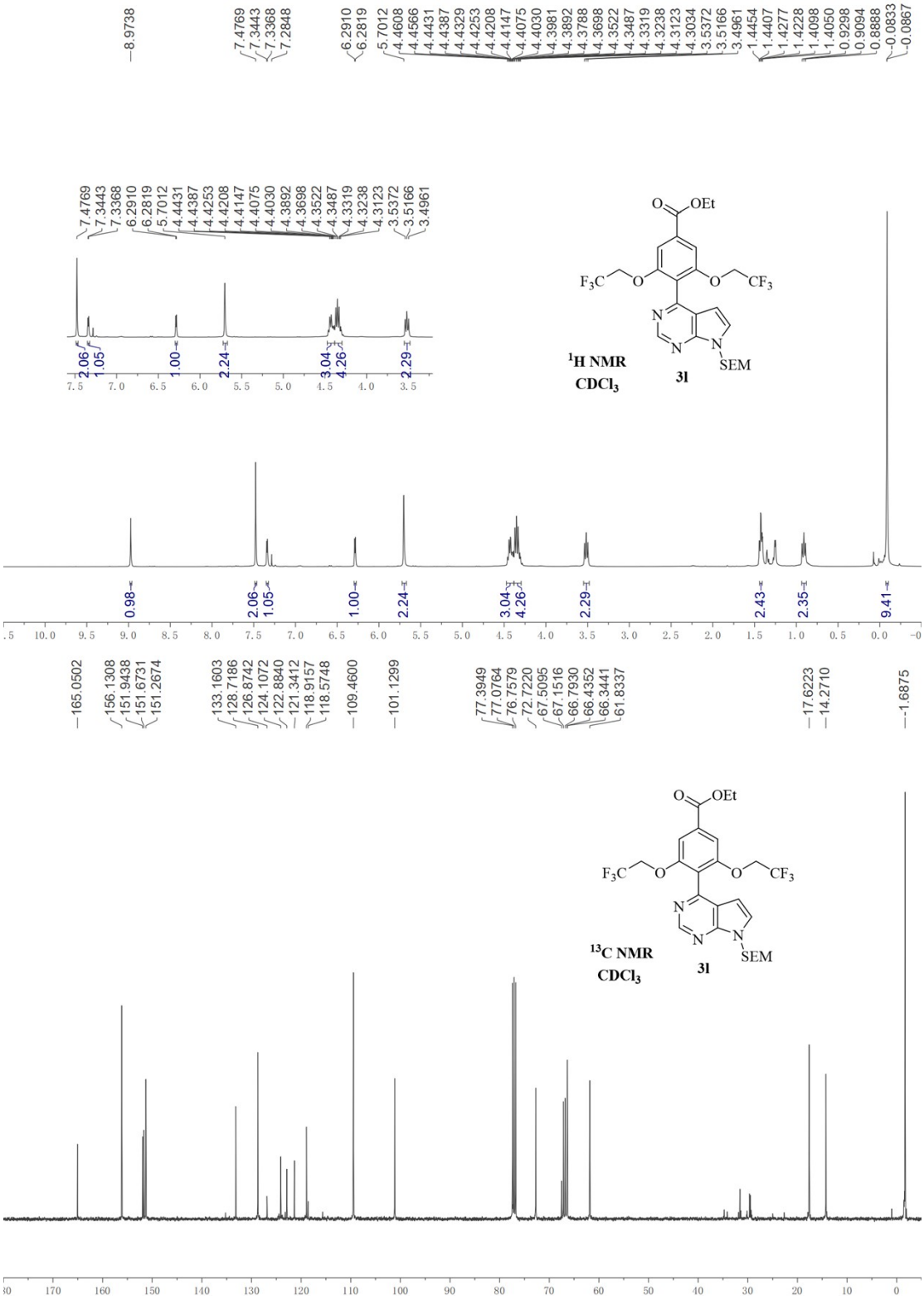
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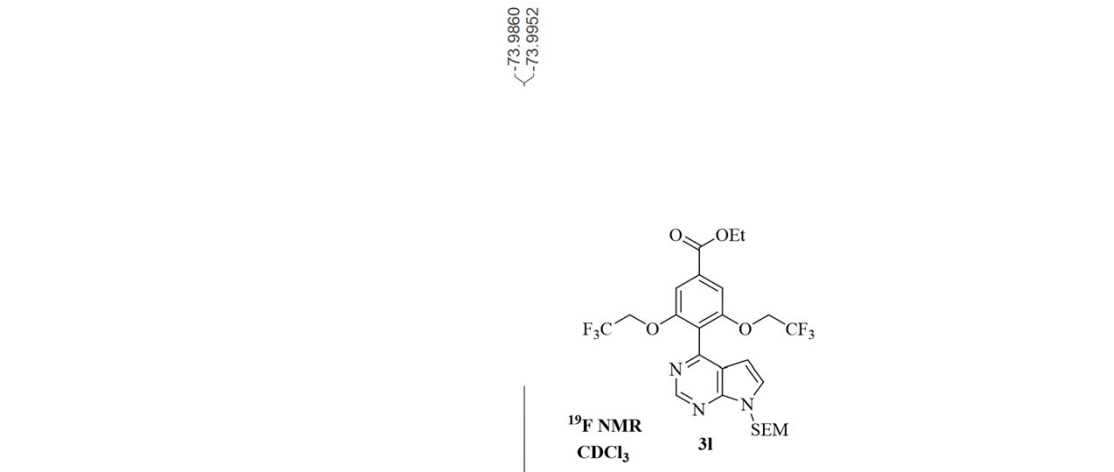

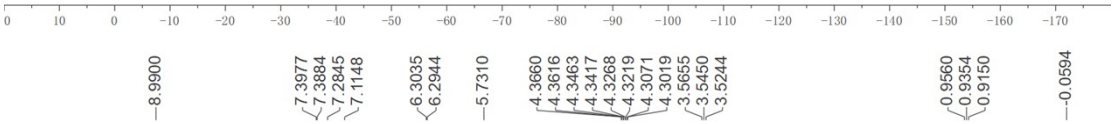

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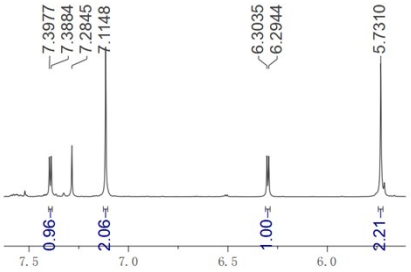

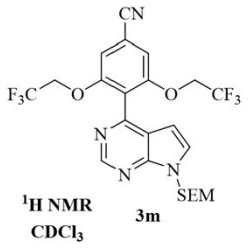

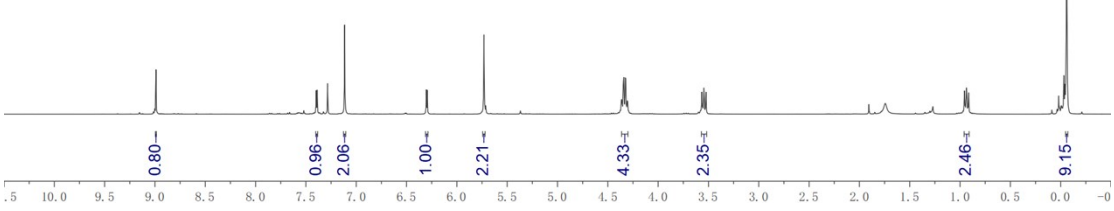

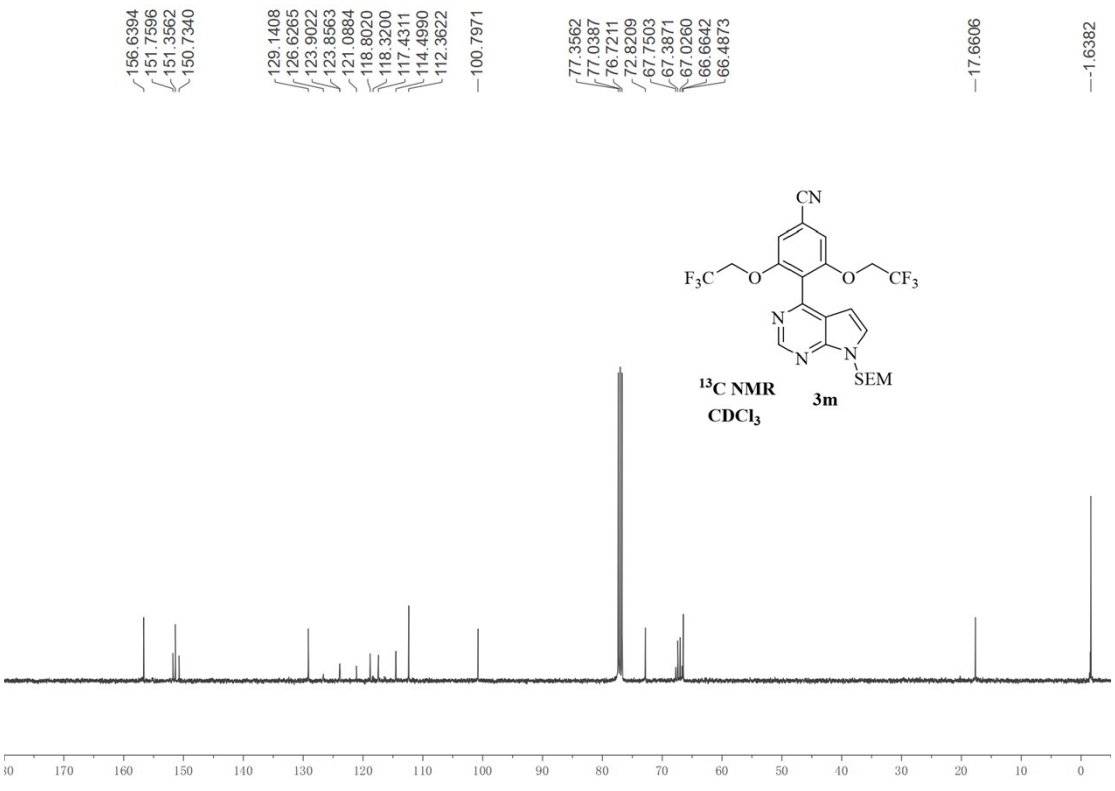
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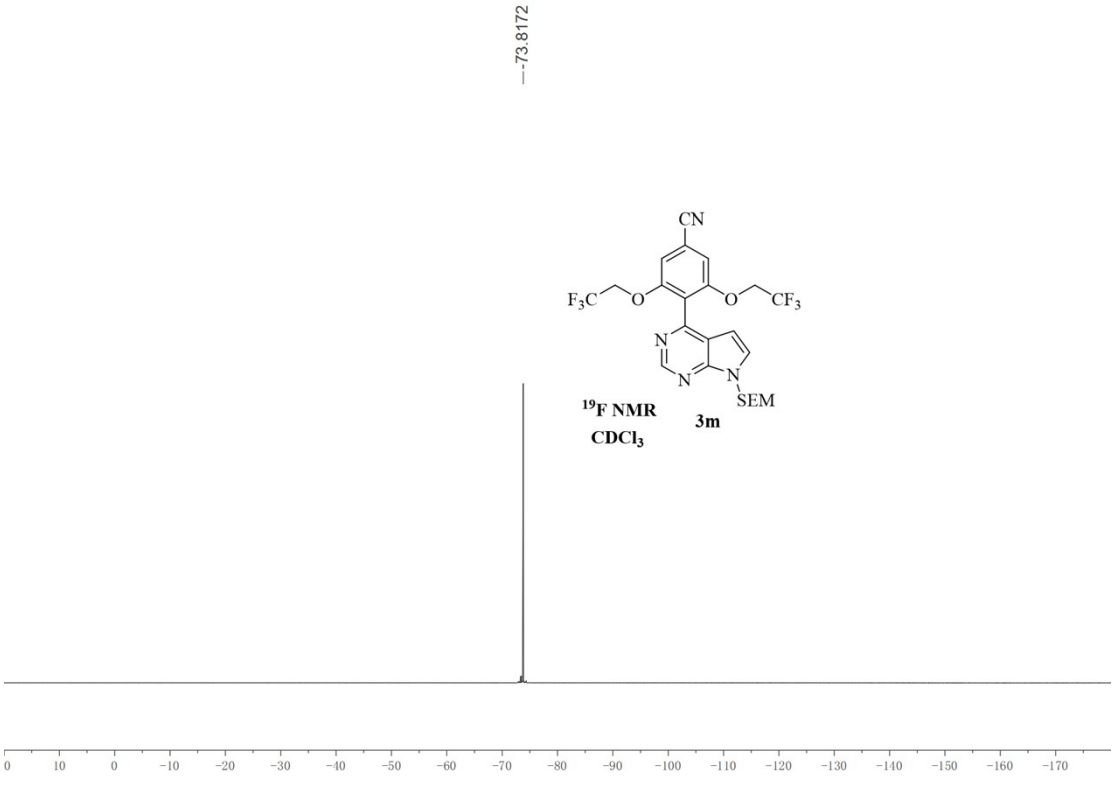
13C NMR
CDCl3
3m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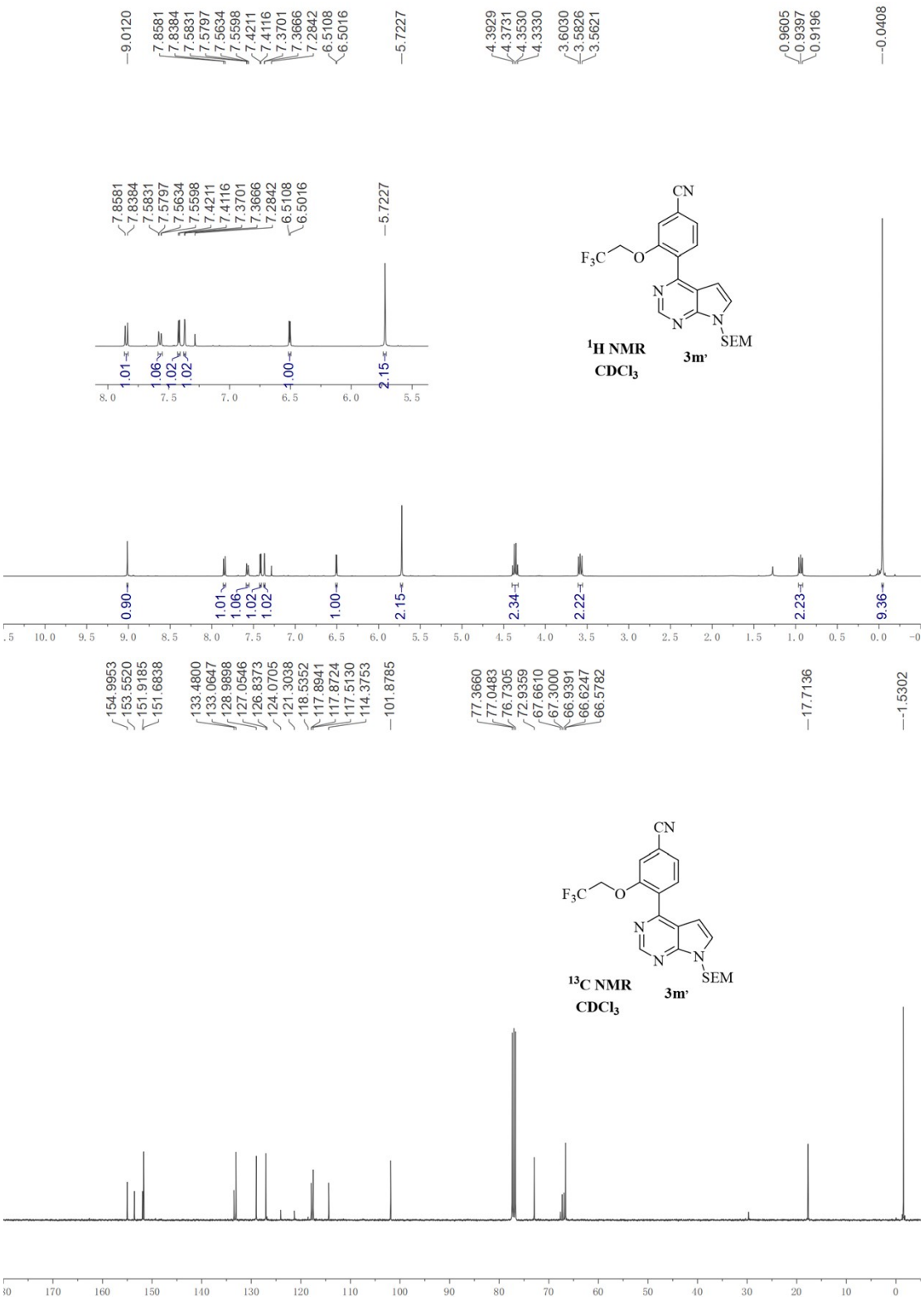
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SEM
1H NMR
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3m'
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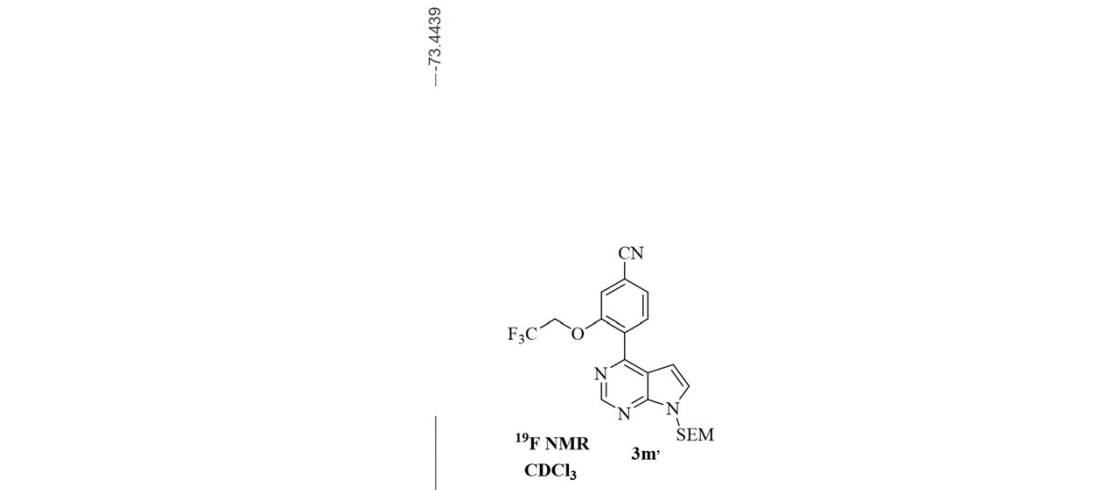
CDCl3
3m'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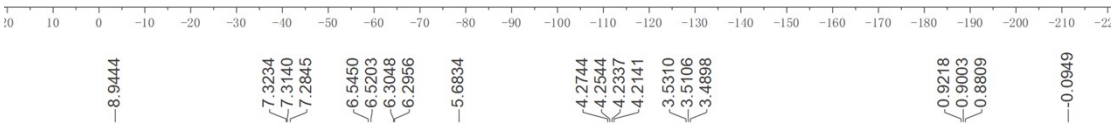
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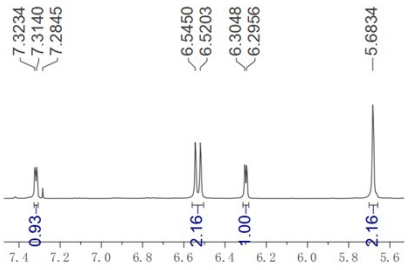
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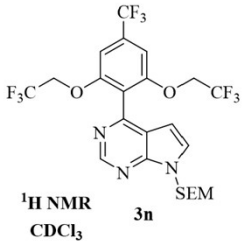
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SEM
1H NMR
CDCl3
3n

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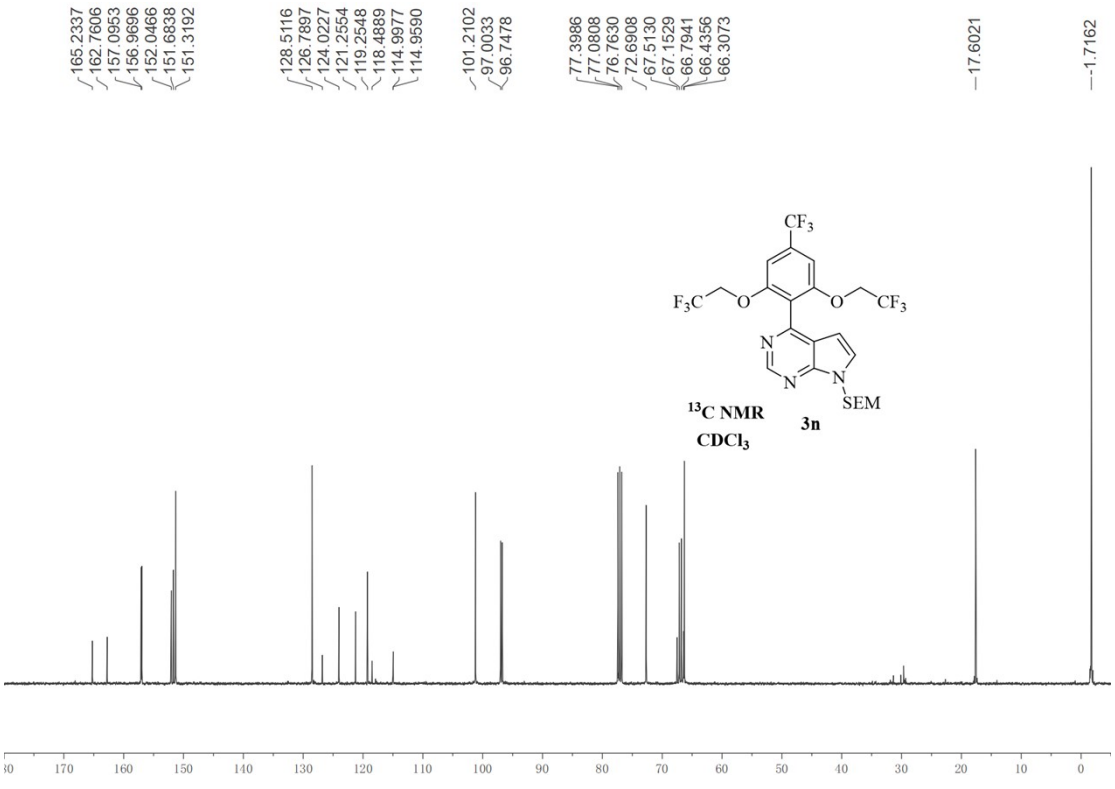
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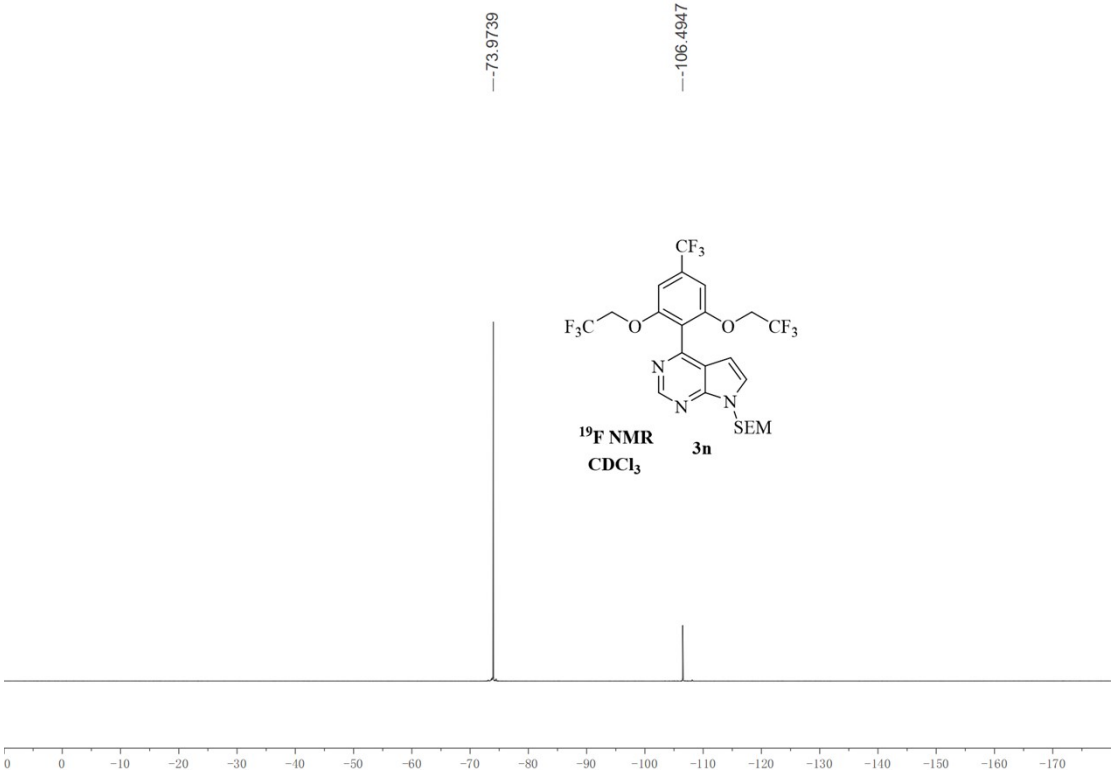
CDCl$_3$
3n
SEM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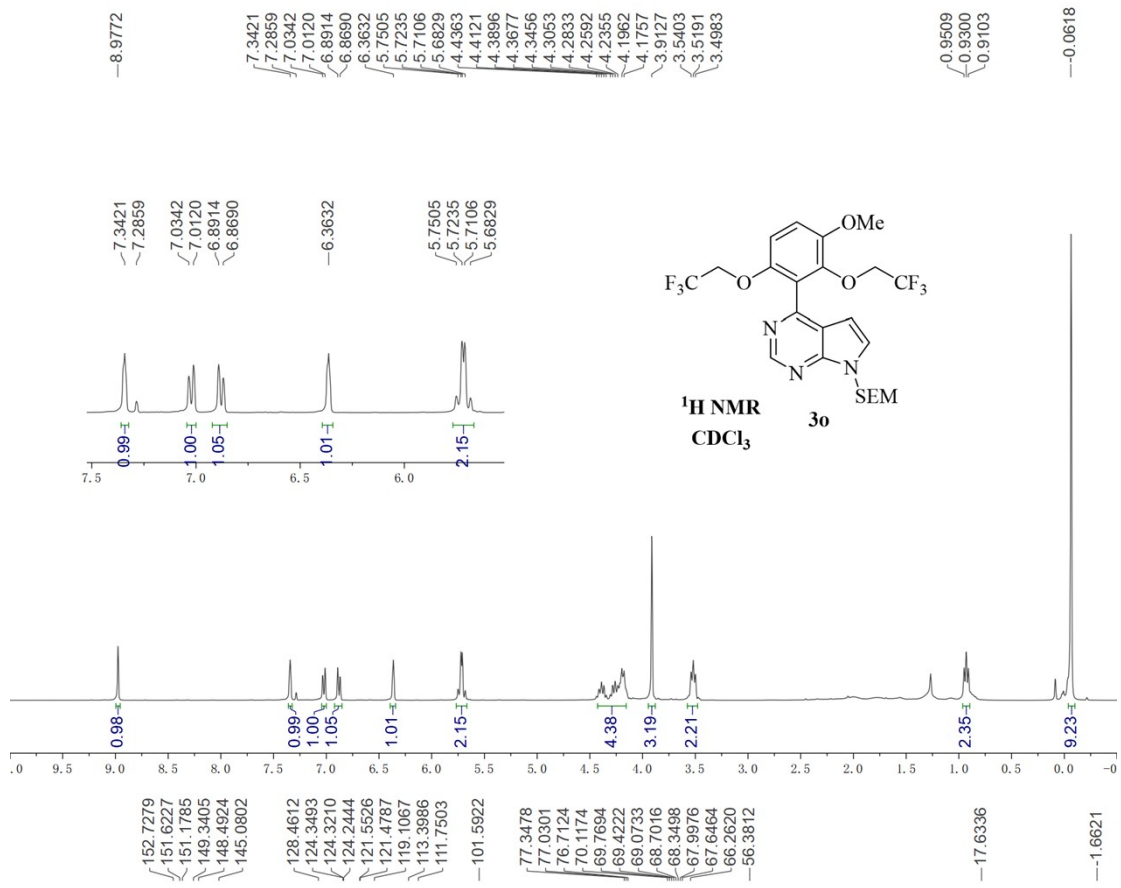
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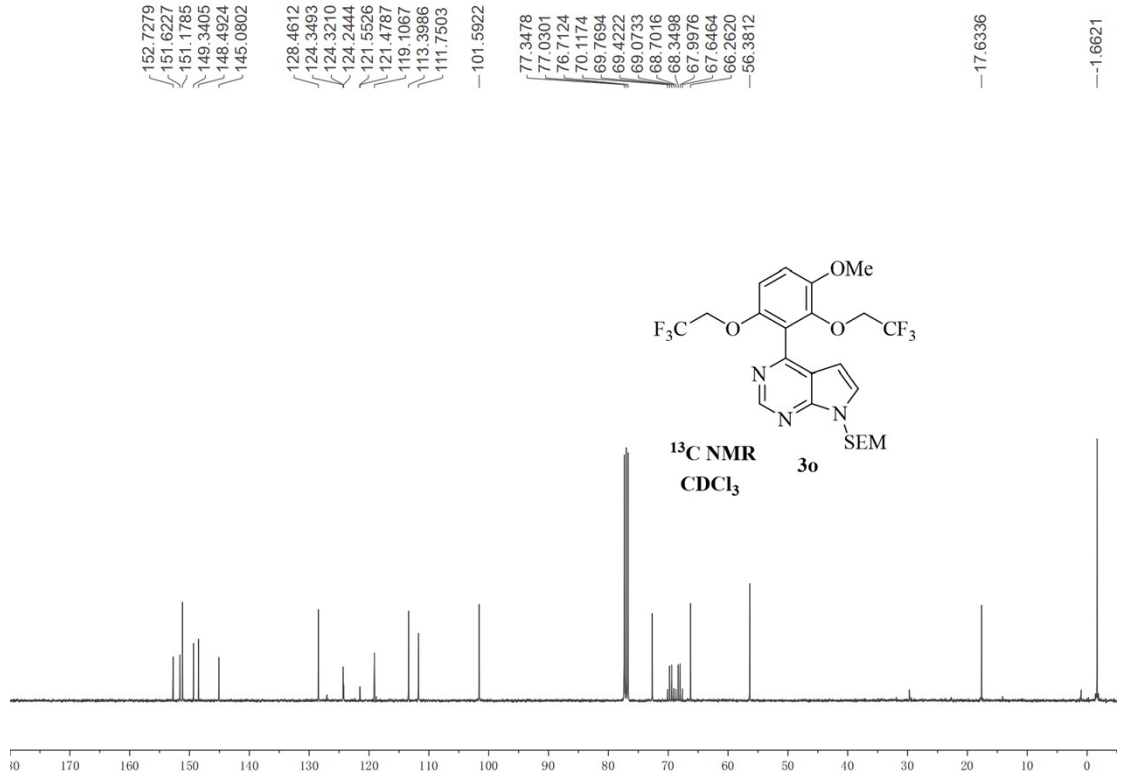
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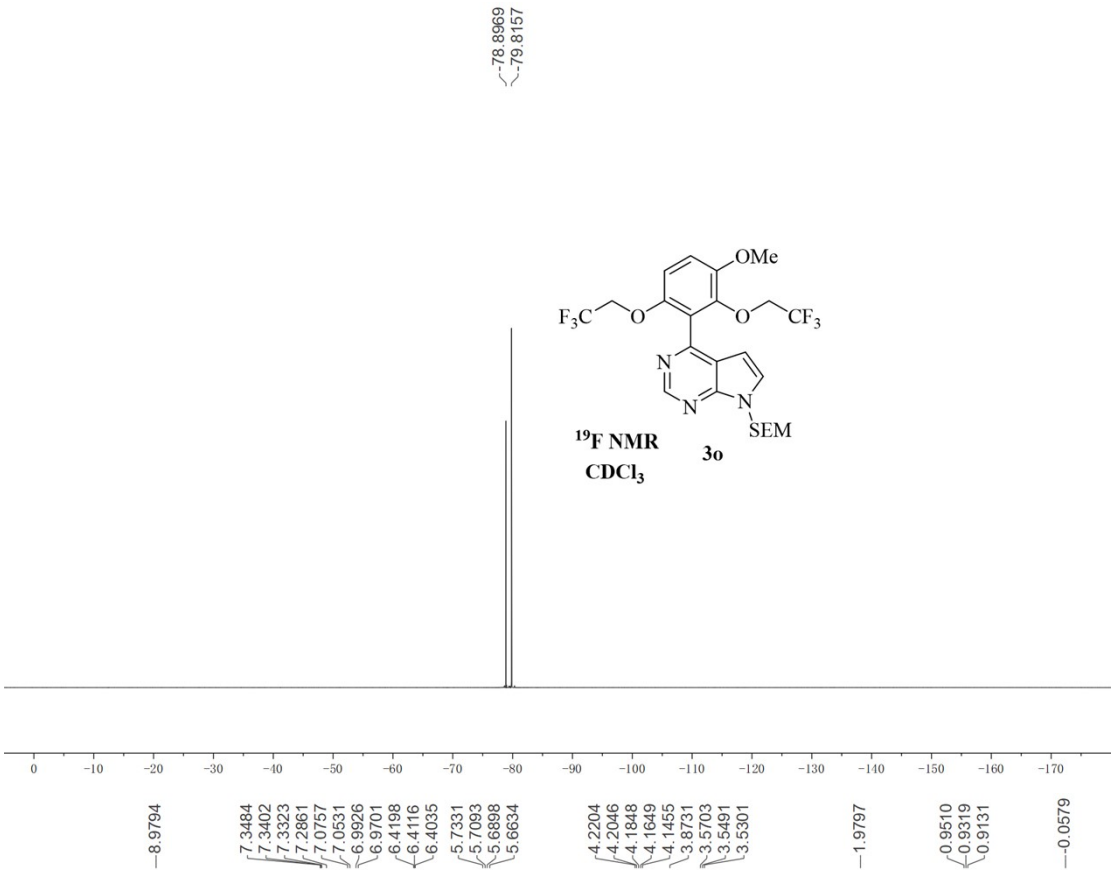
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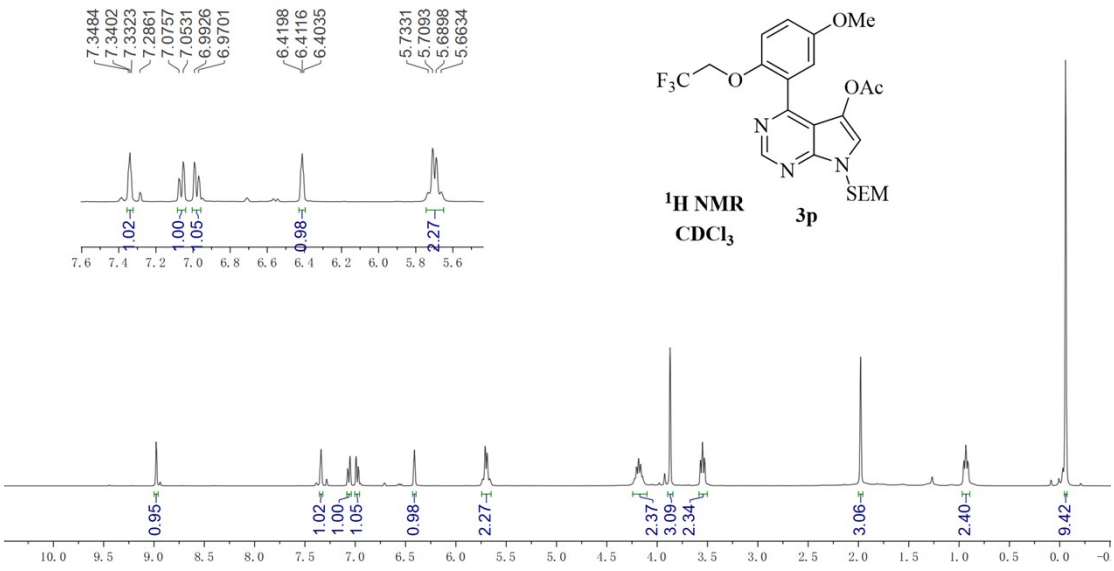
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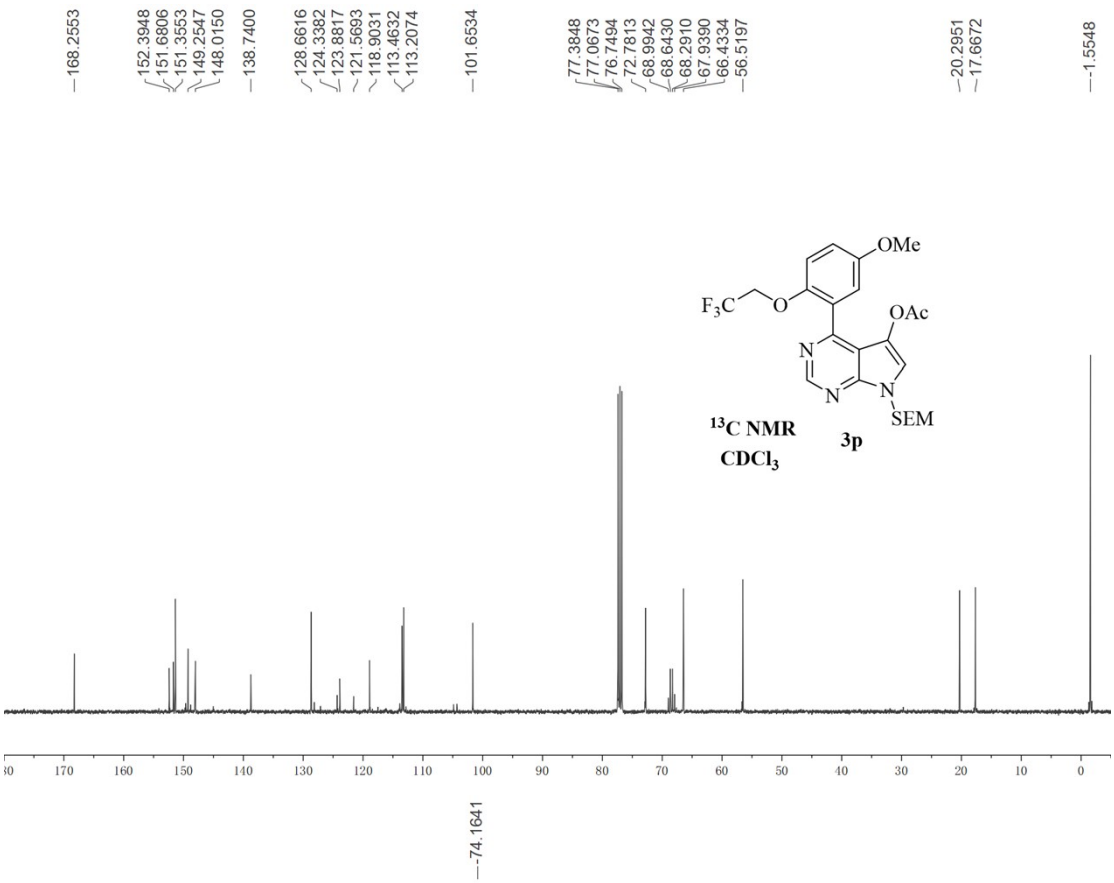
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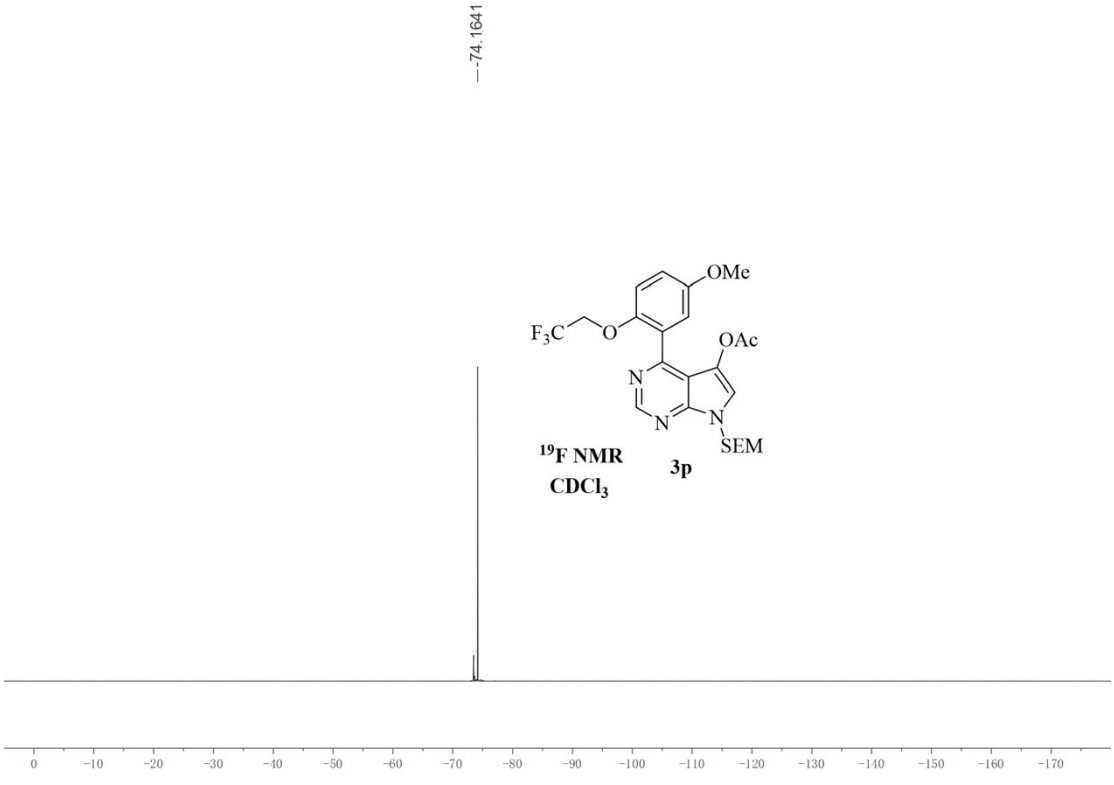
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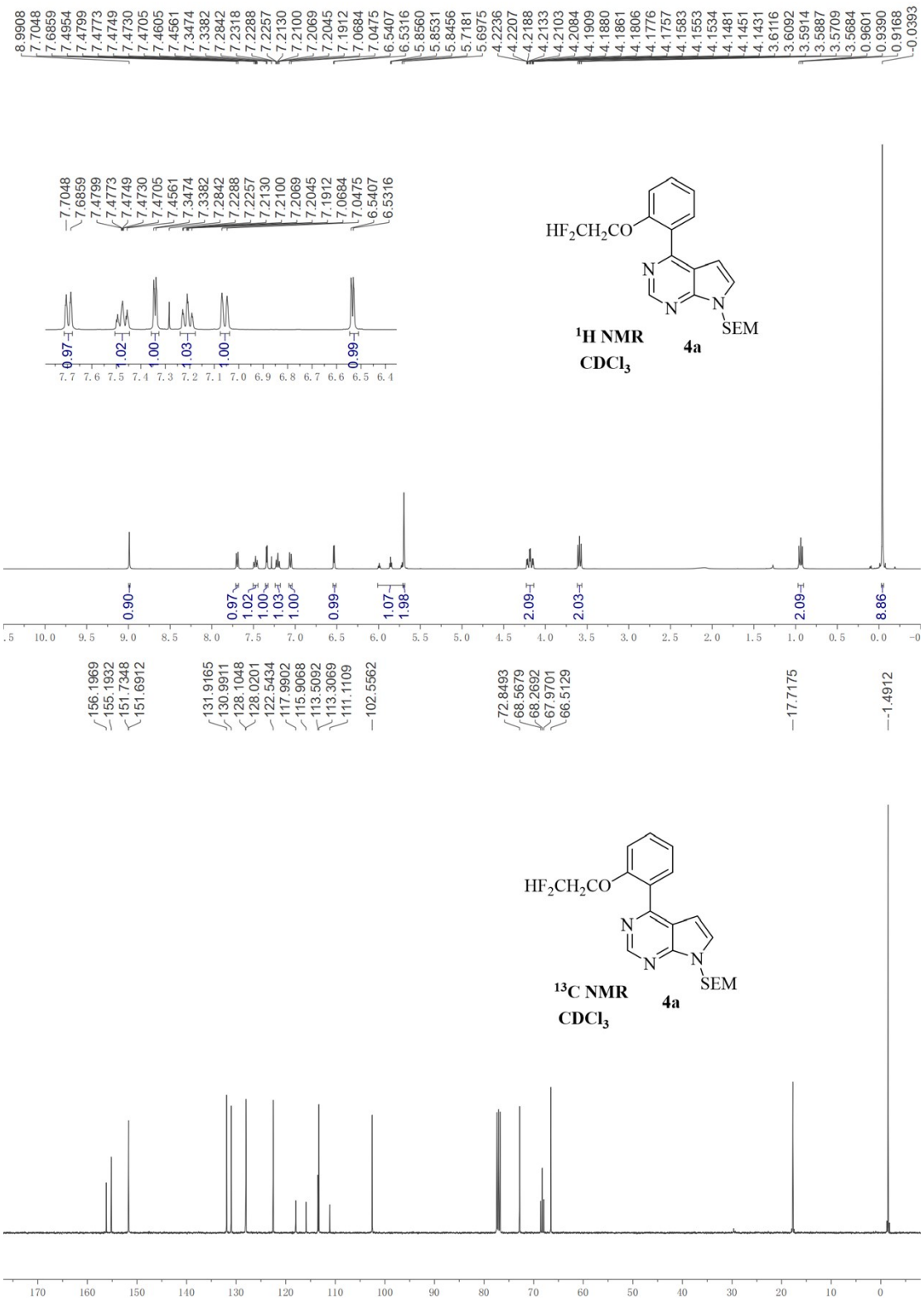
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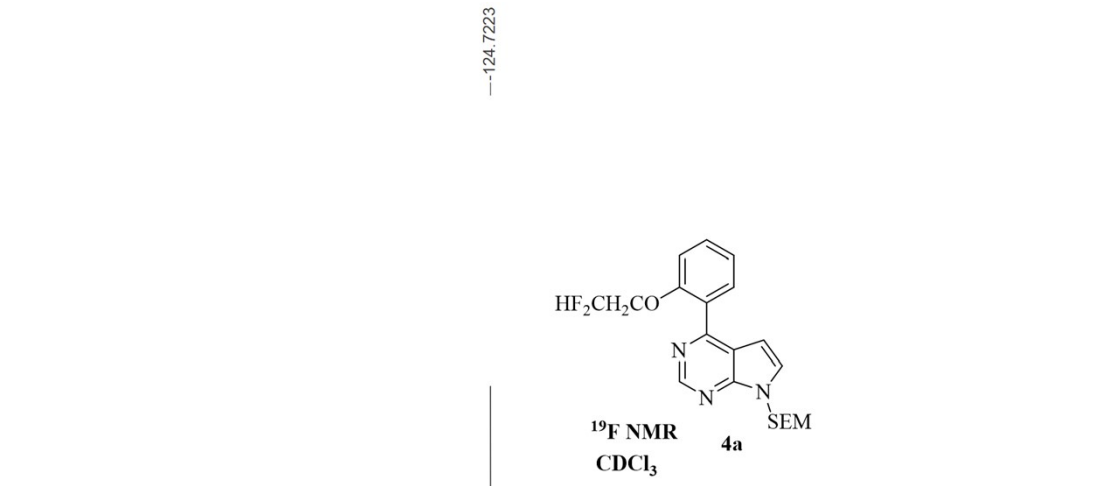

^{19}F NMR **4a**

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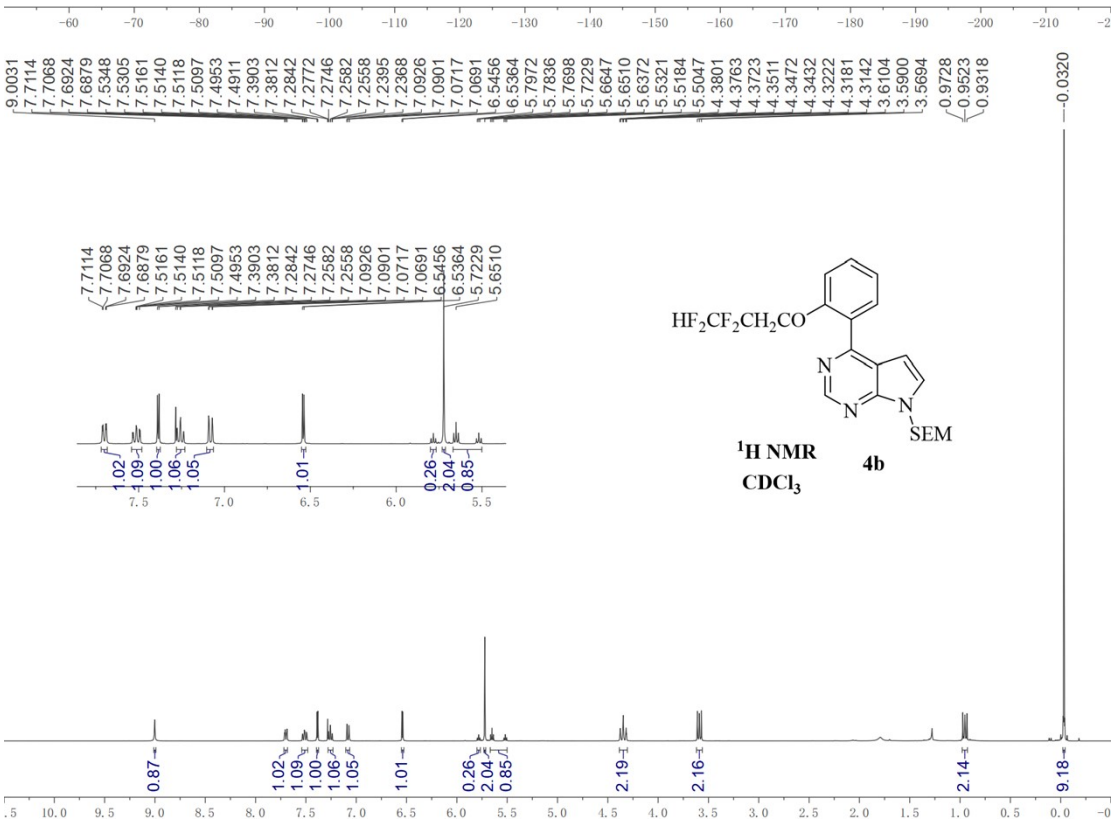
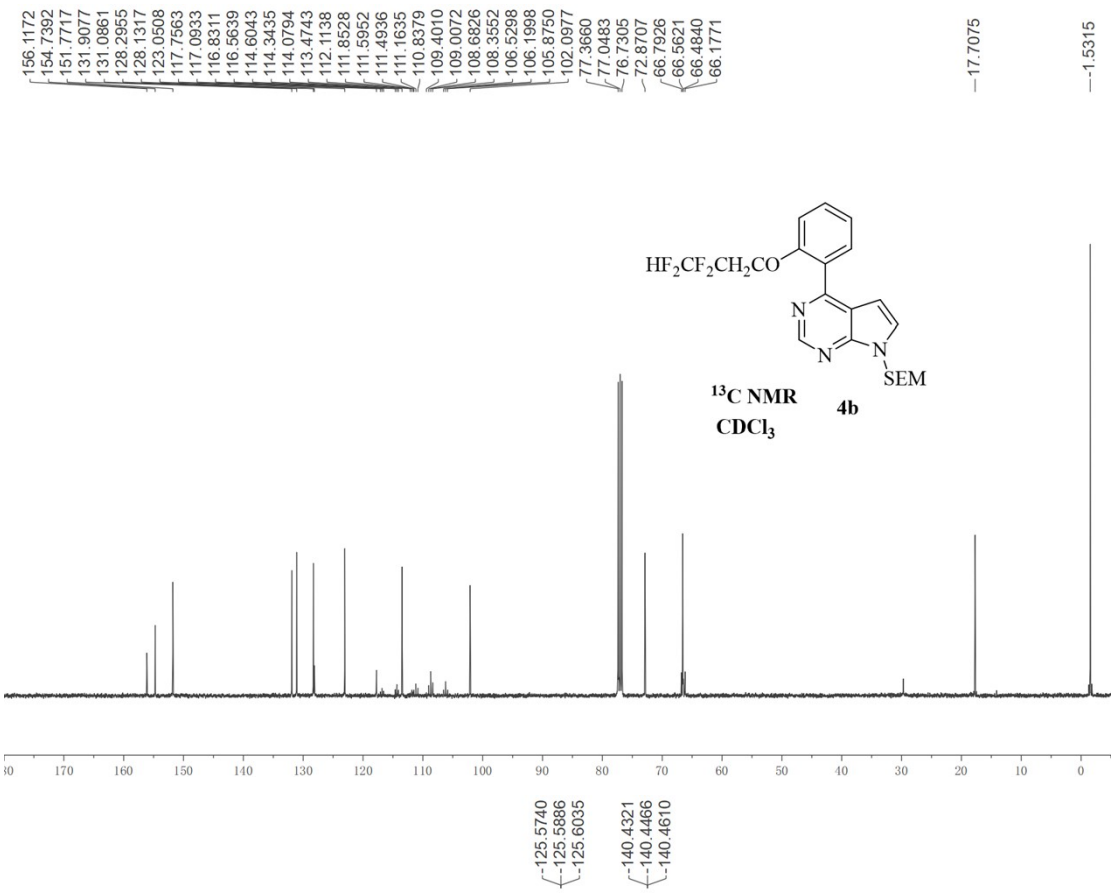


^{1}H NMR **4b**

$CDCl_3$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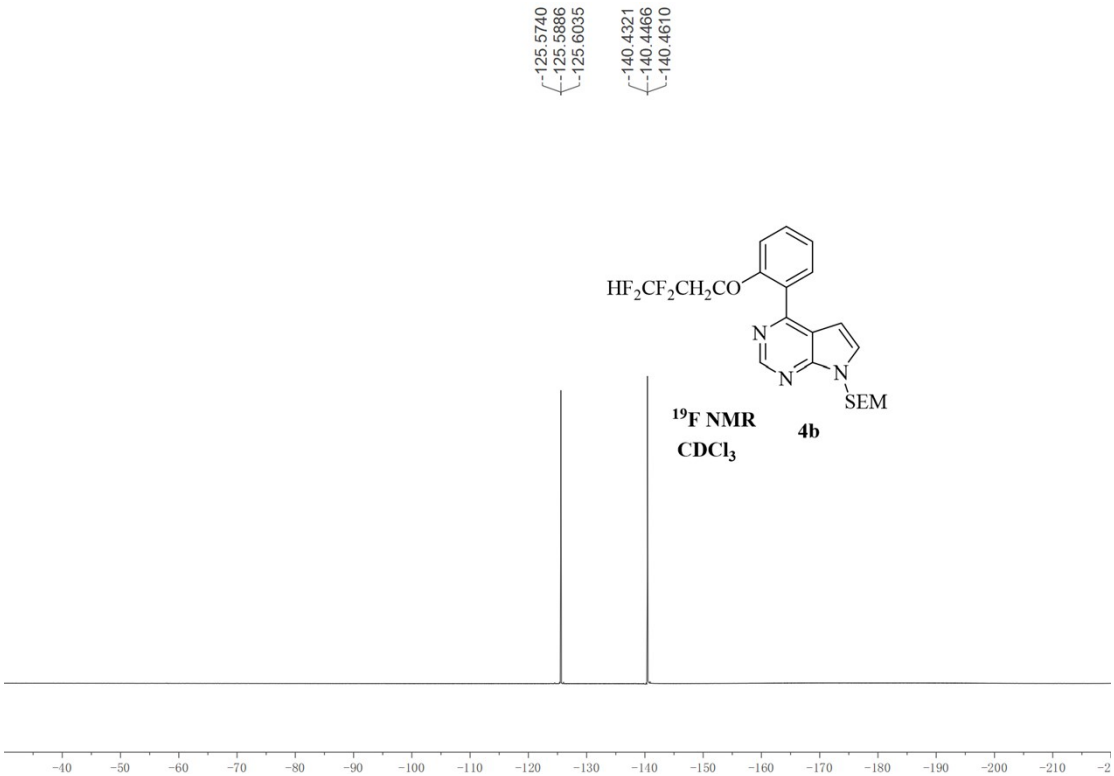
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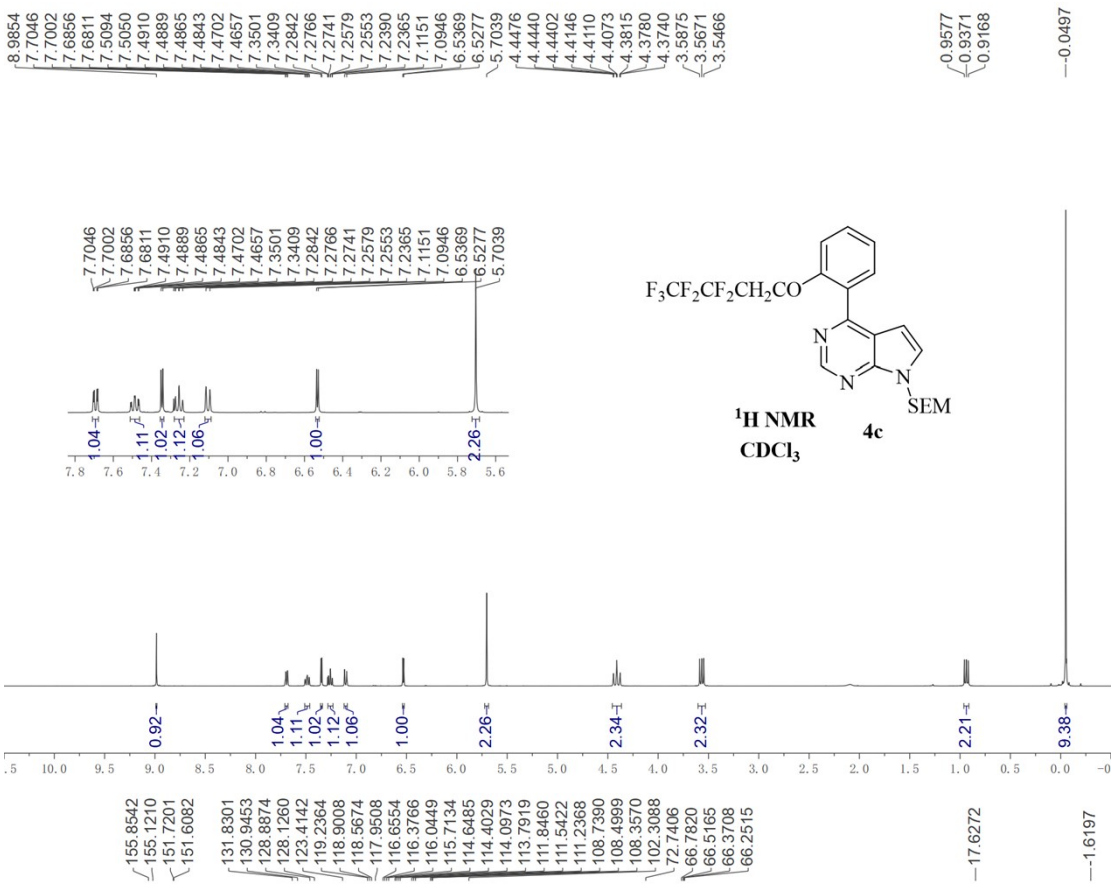
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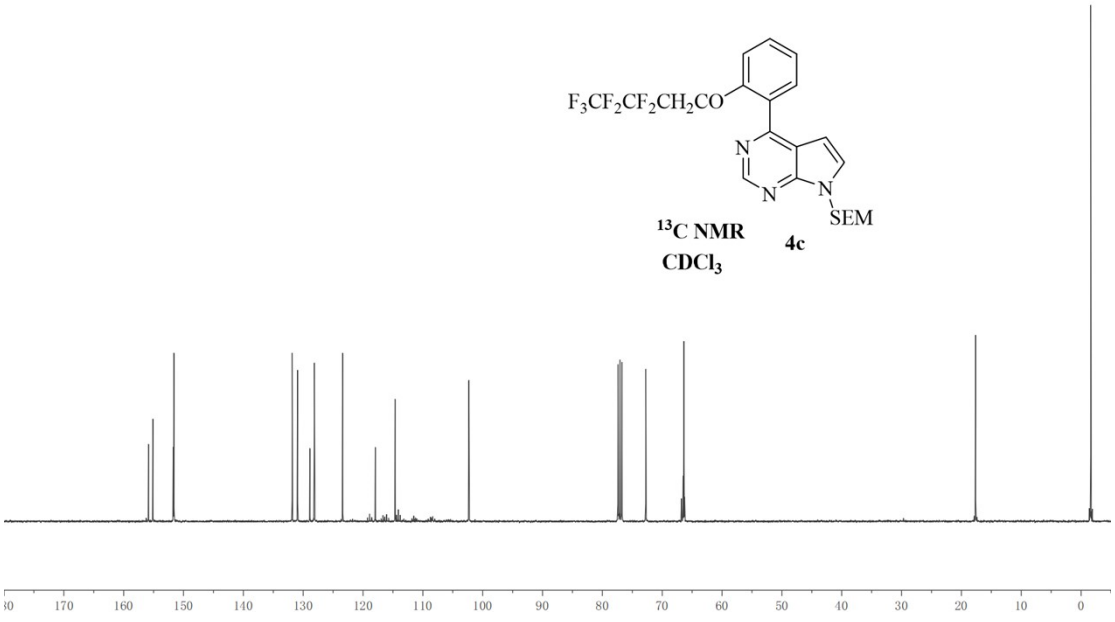
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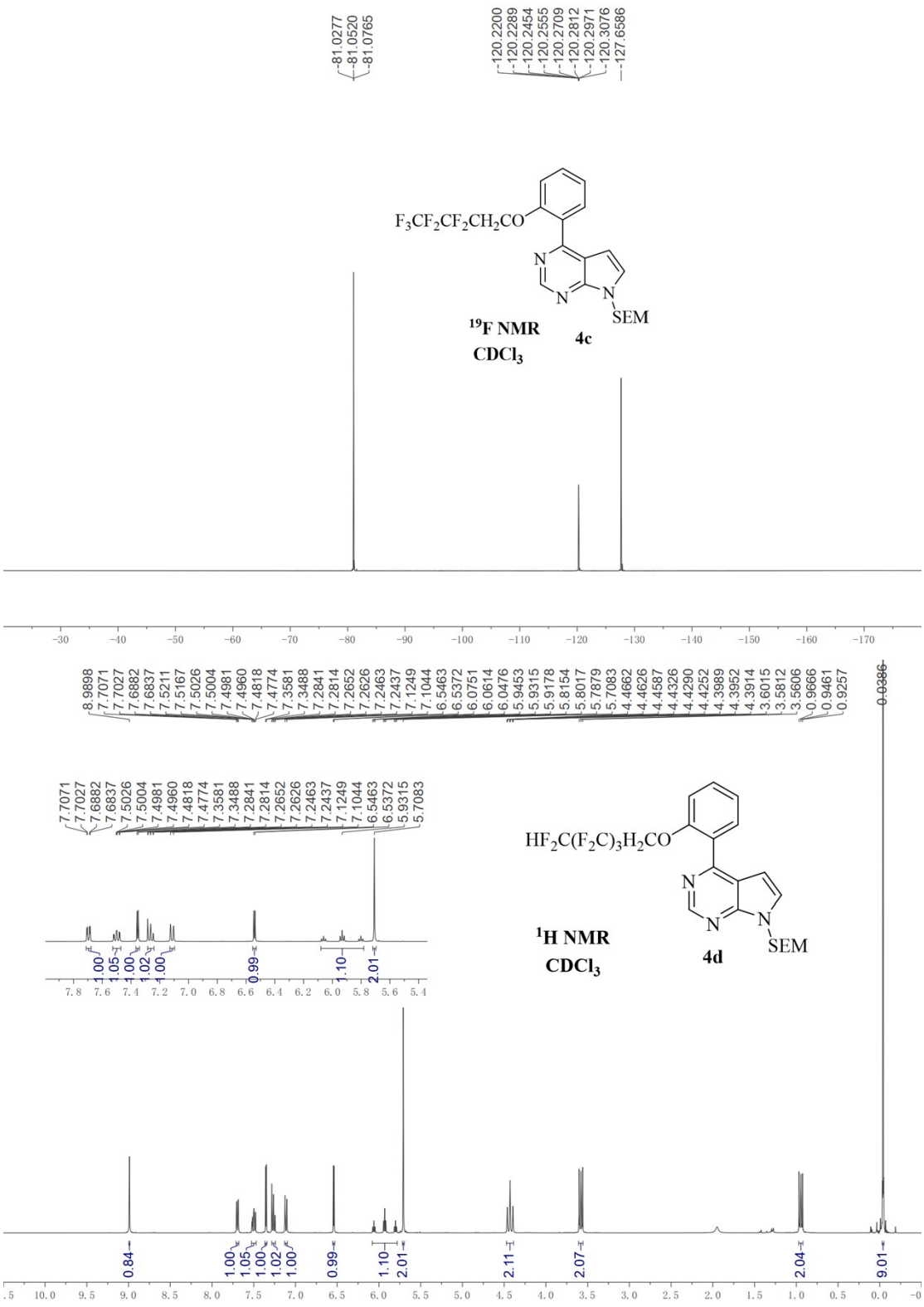
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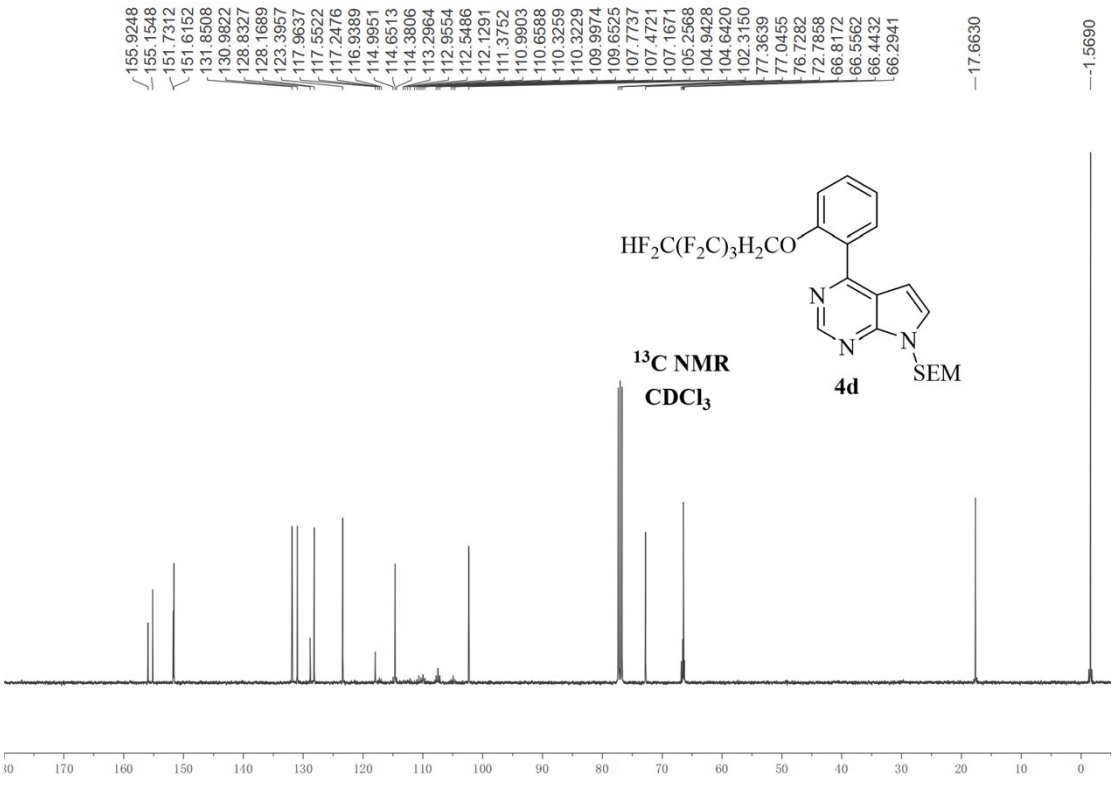
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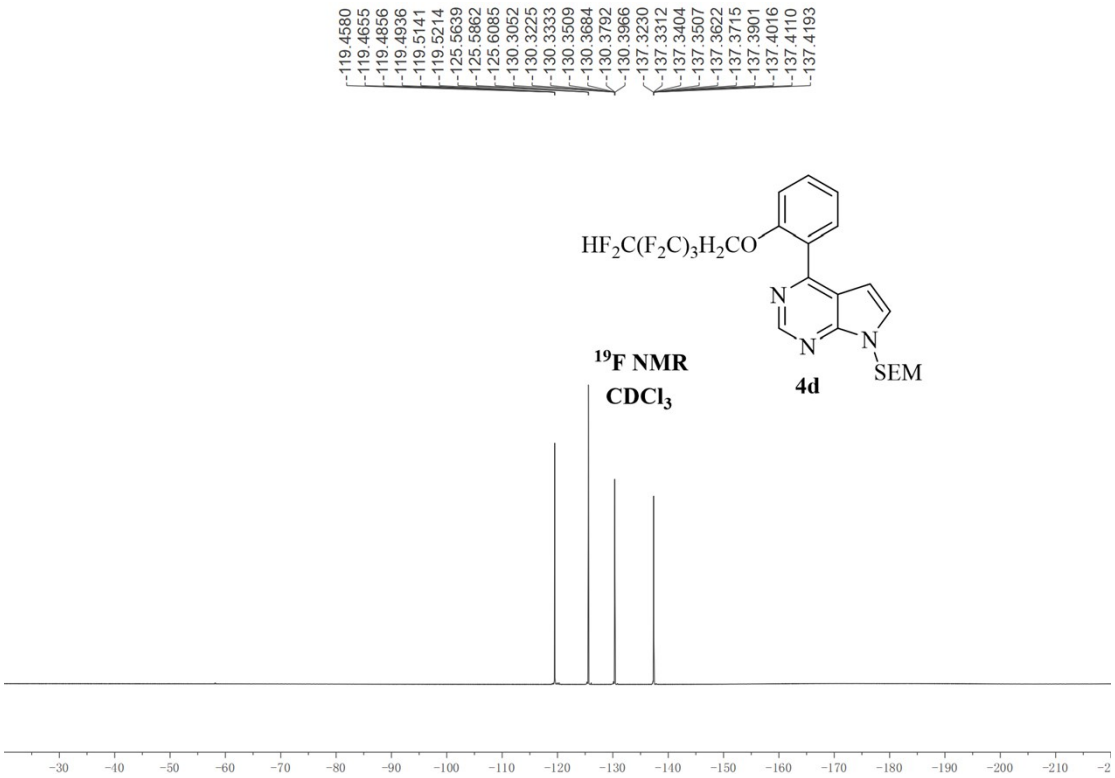
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SEM
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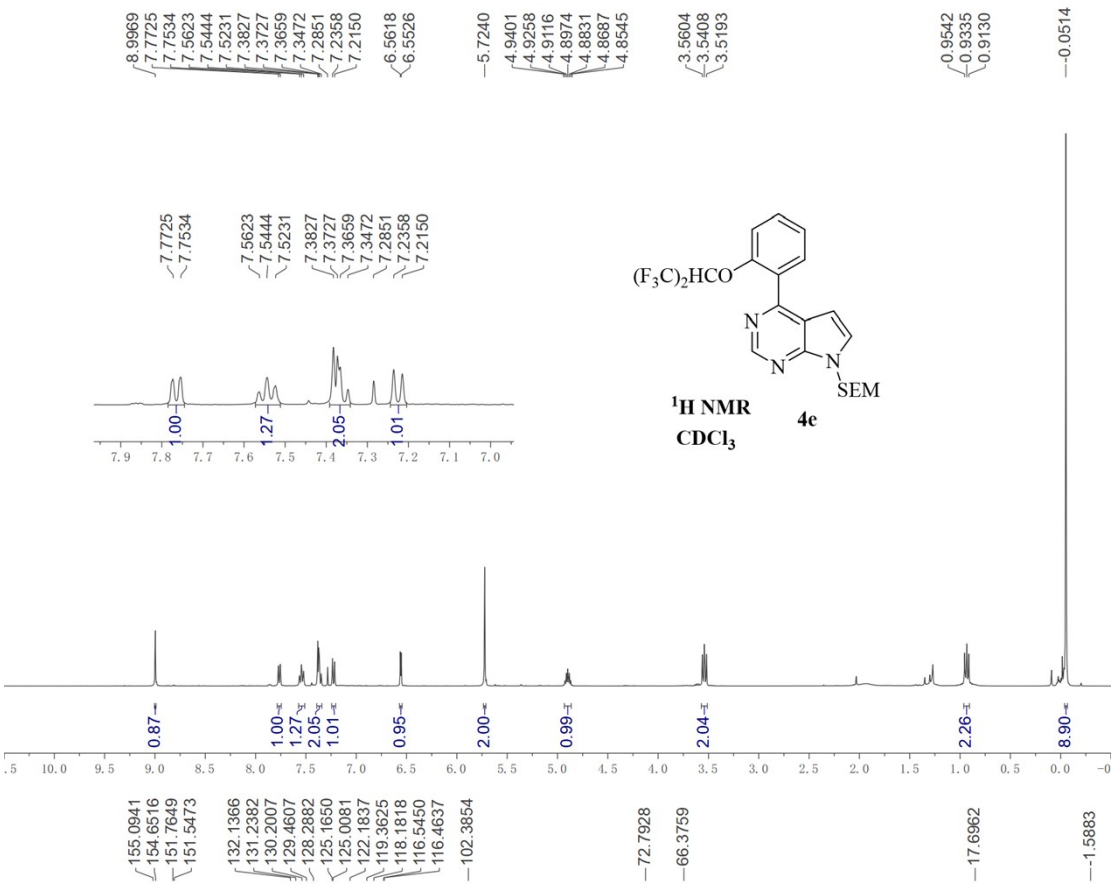
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1H NMR
CDCl3
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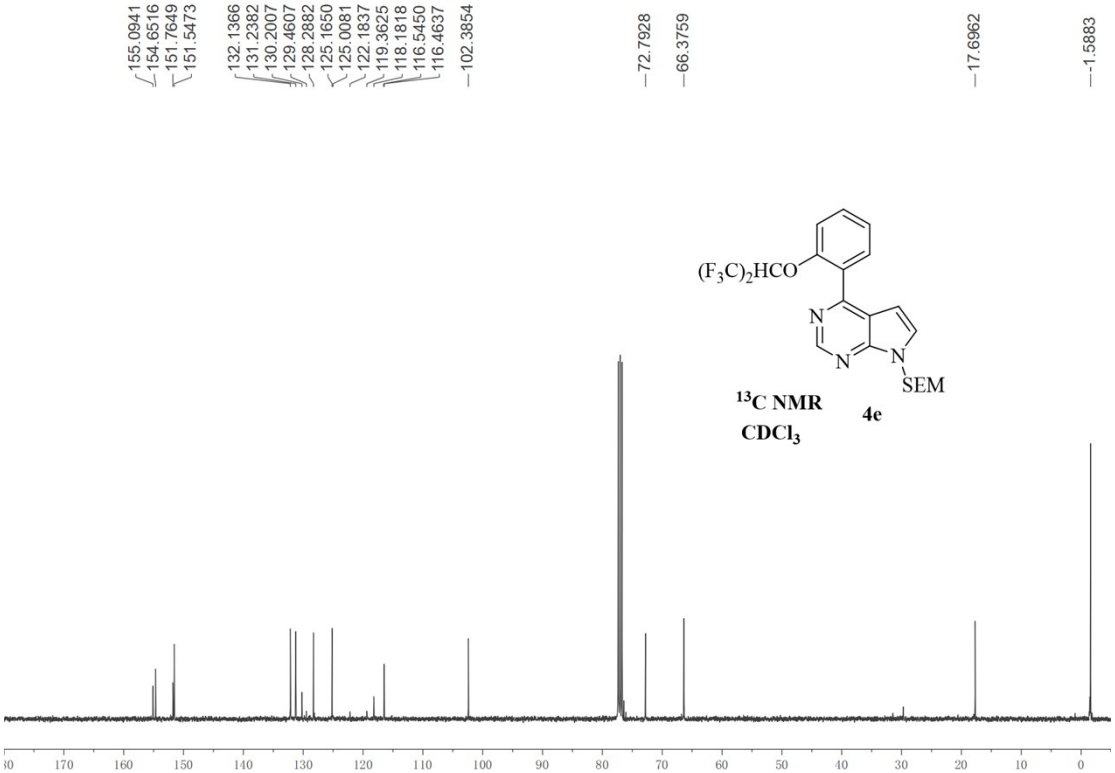
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(F3C)2HCO
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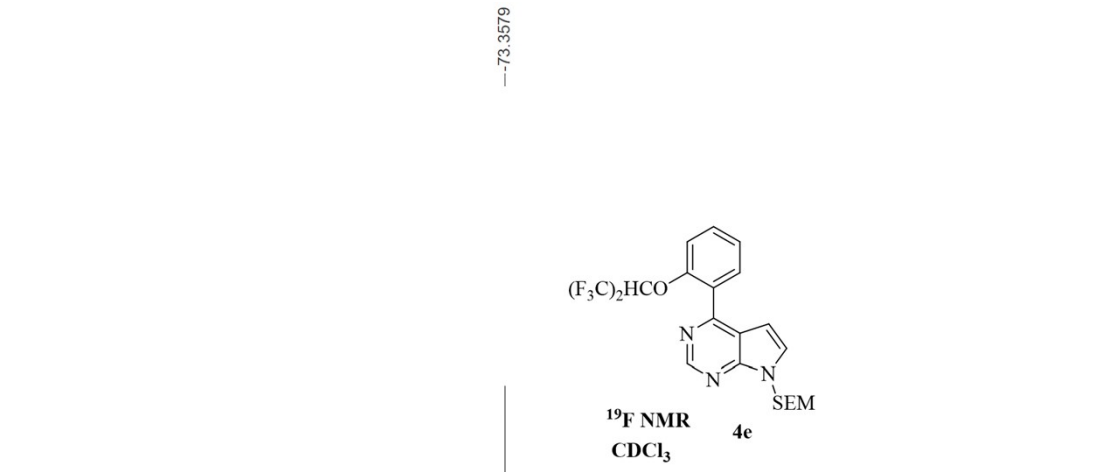
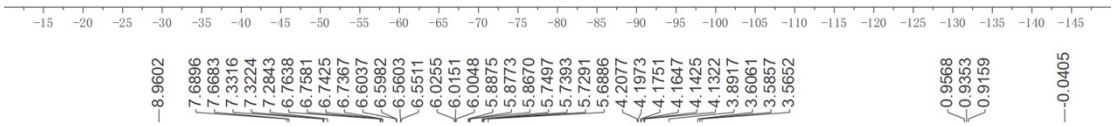
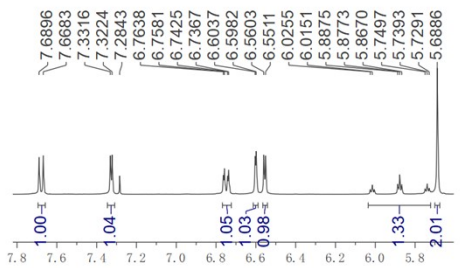
13C NMR
CDCl3
4e

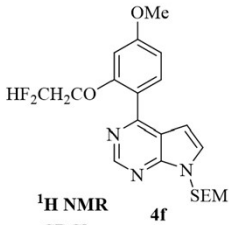


^{19}F NMR **4e**

$CDCl_3$

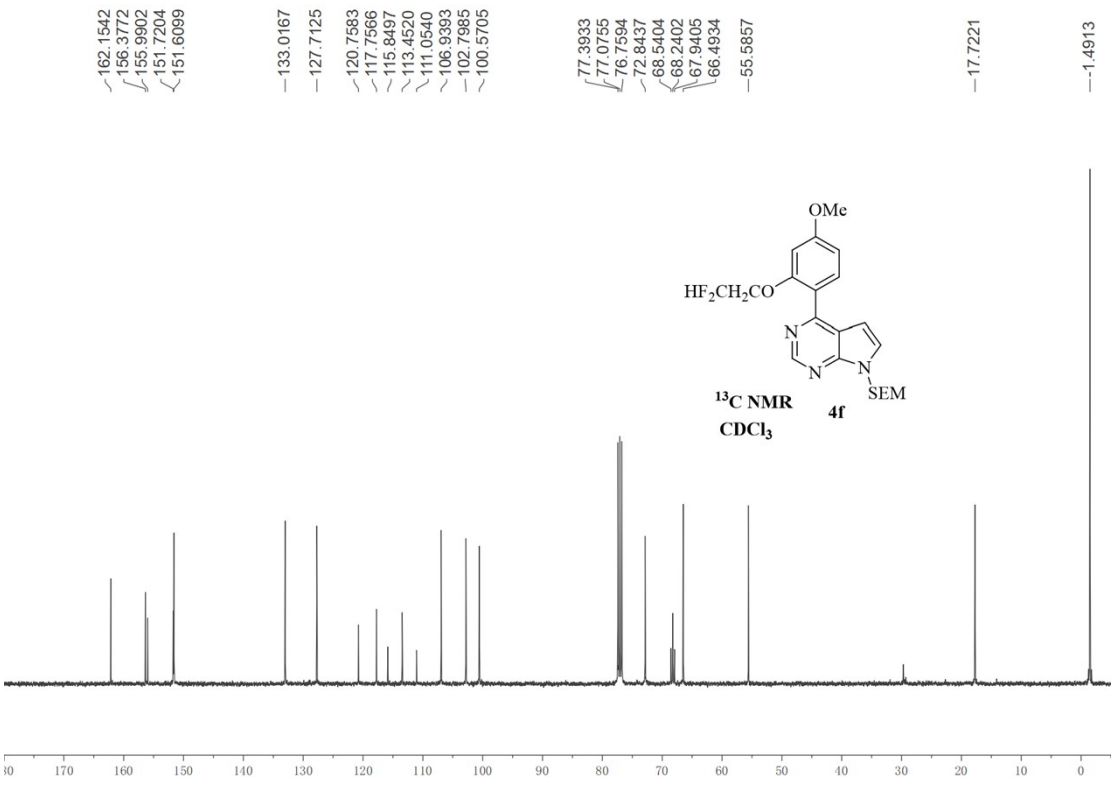






^{1}H NMR **4f**

$CDCl_3$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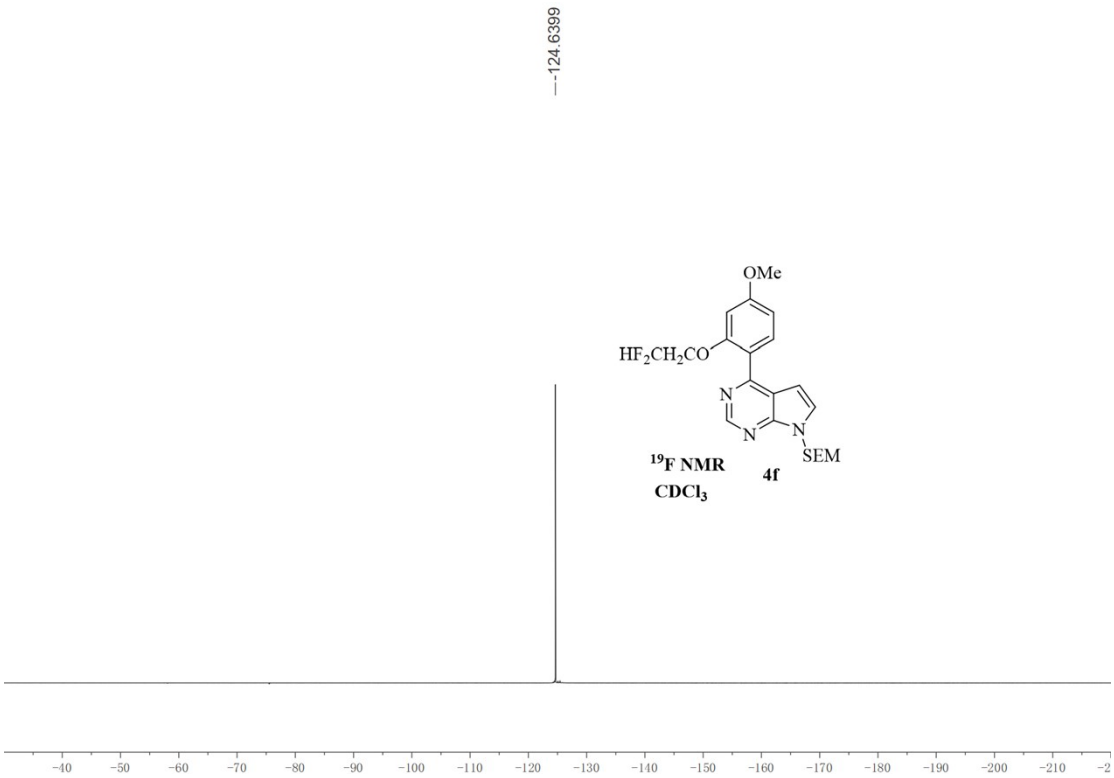
SEM
13C NMR
CDCl3
4f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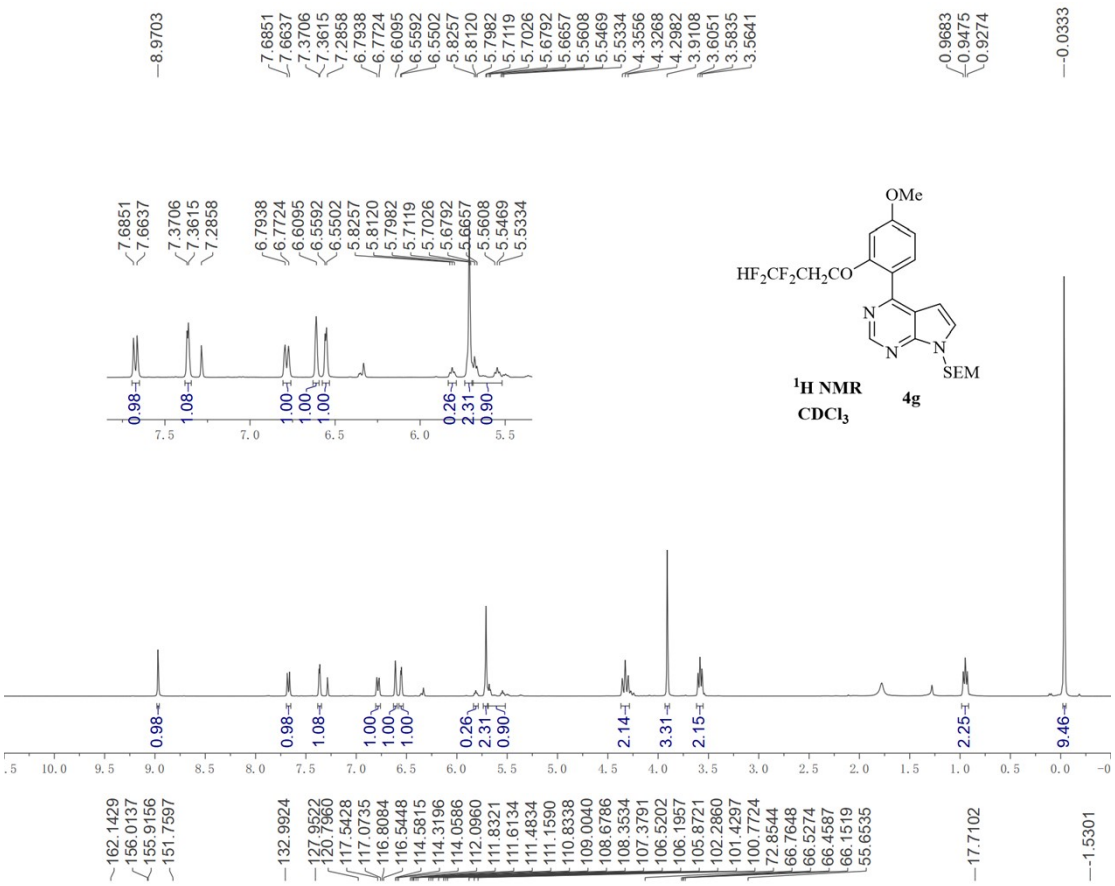
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N
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SEM
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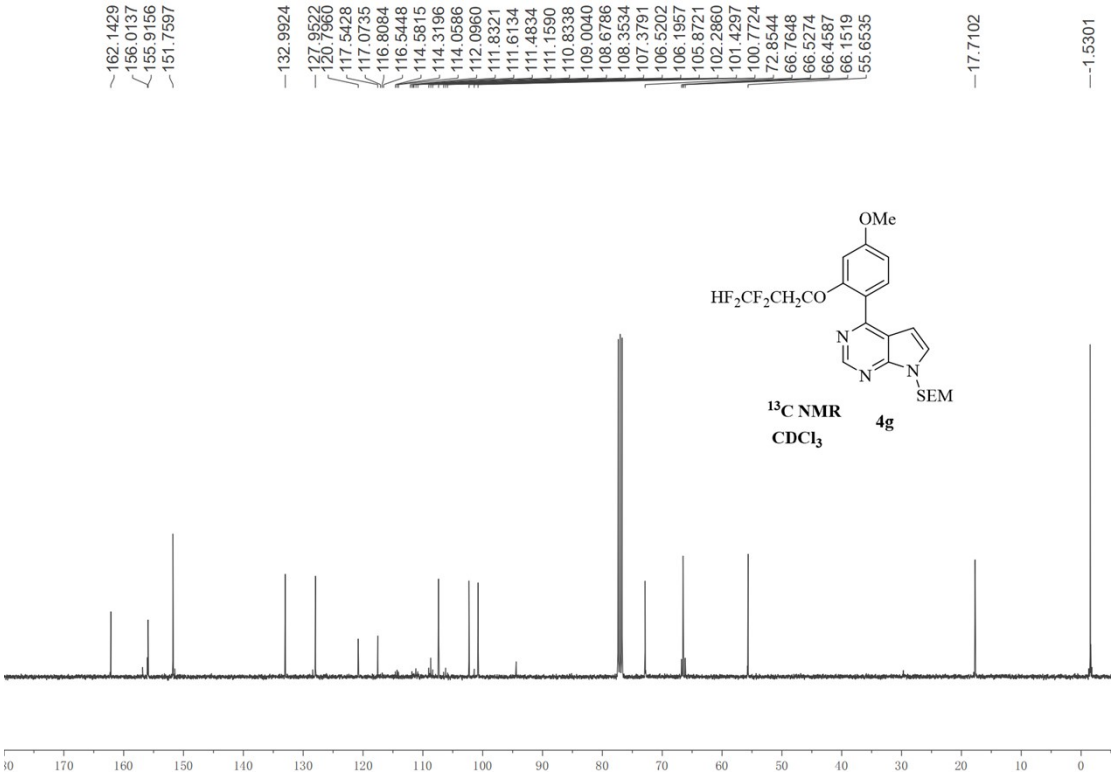
CDCl3
4g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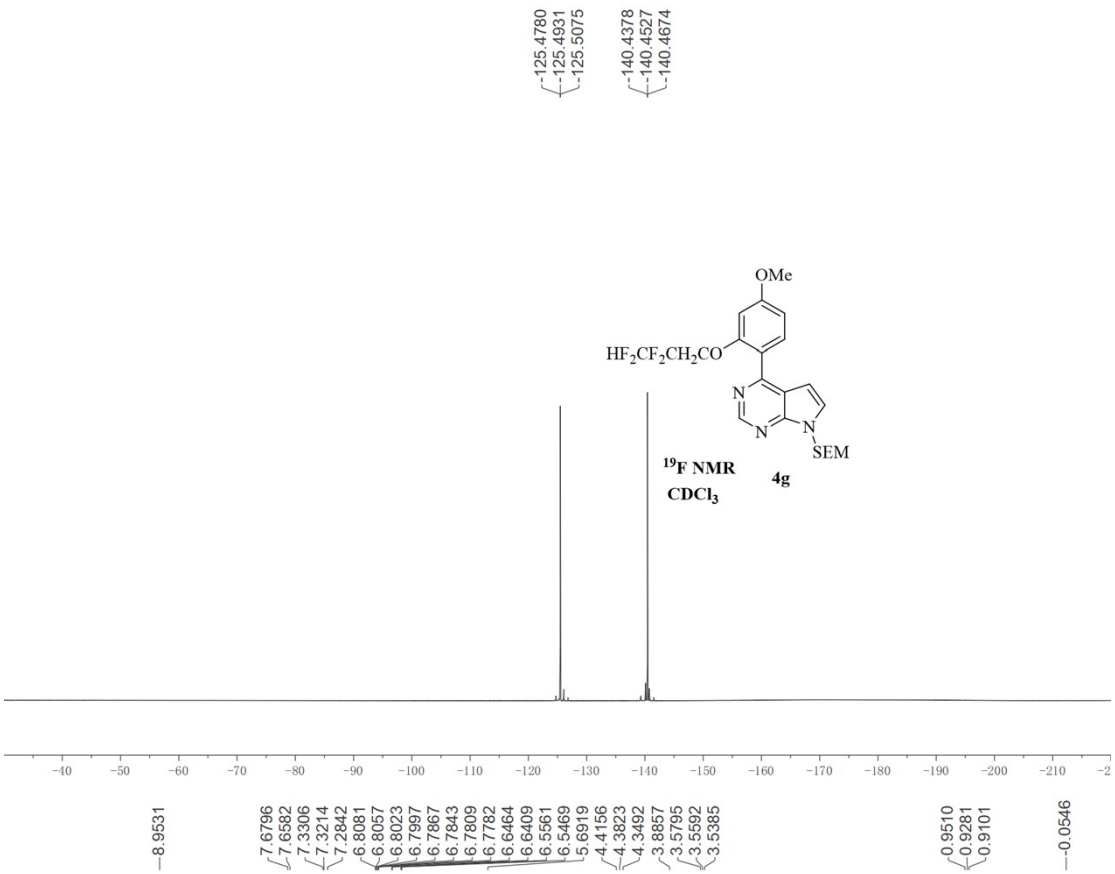
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19F NMR
CDCl3
4g
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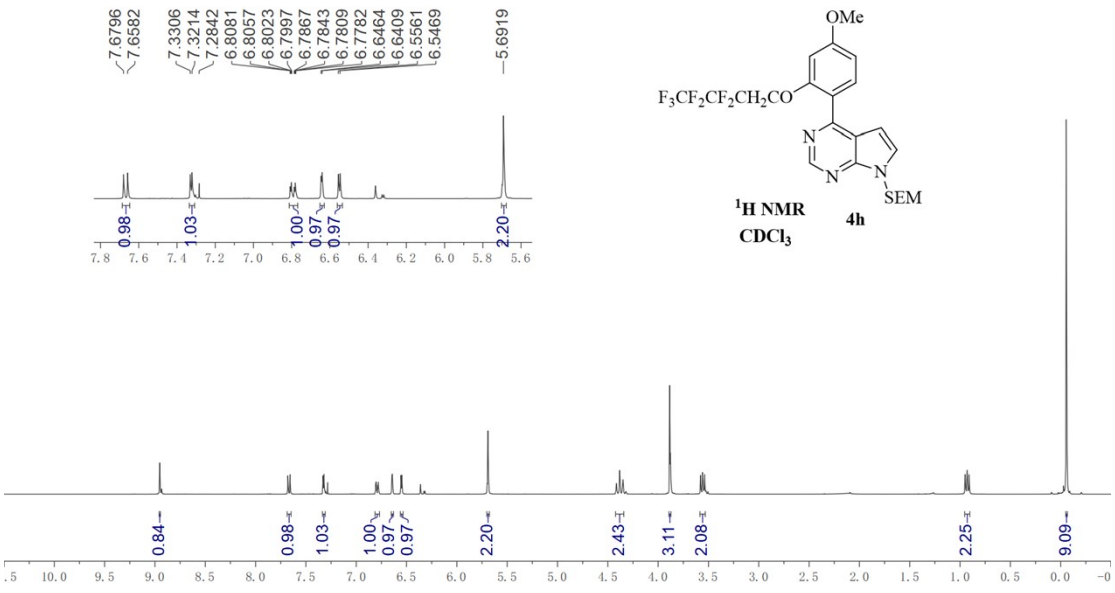
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N
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CDCl3
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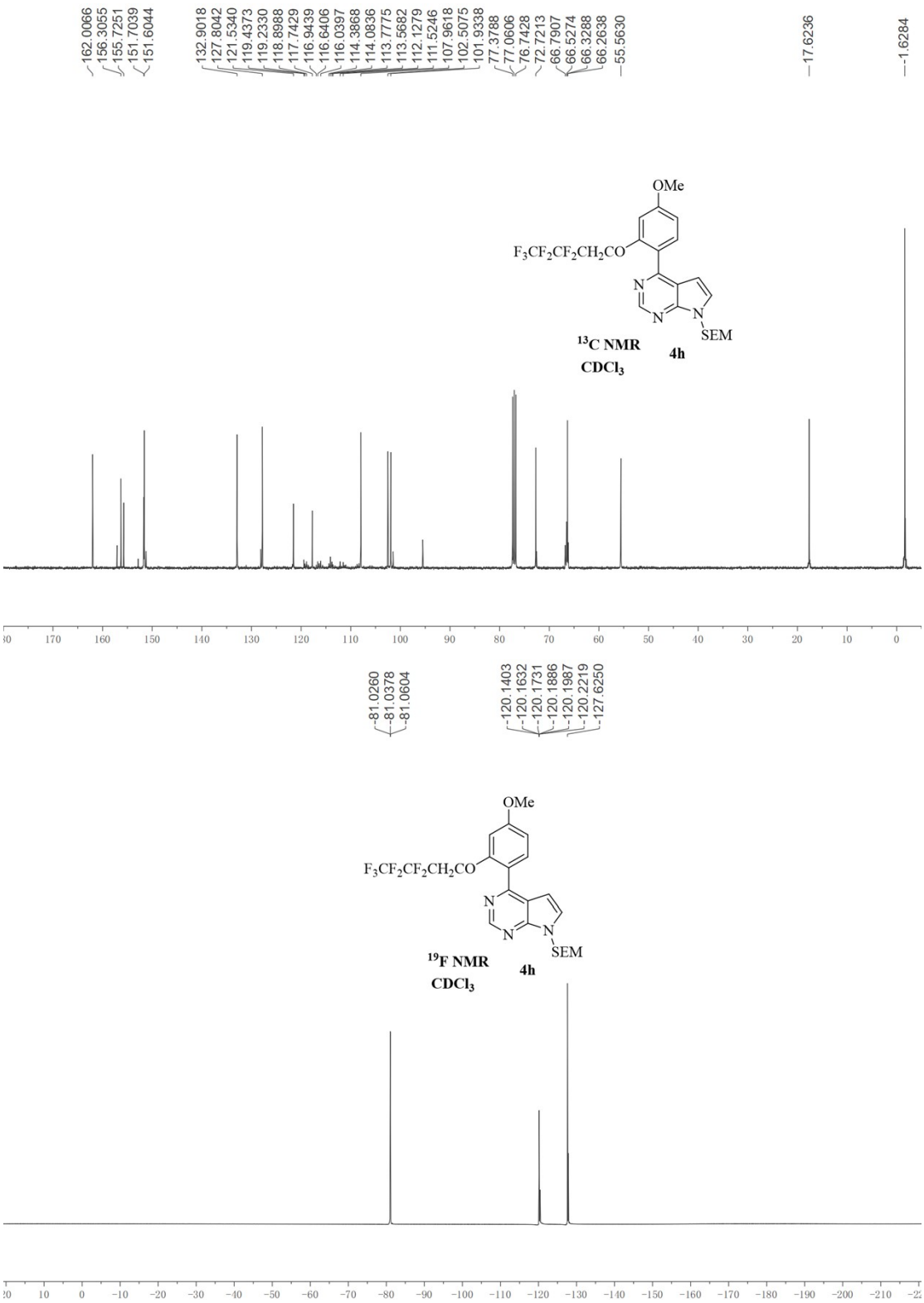
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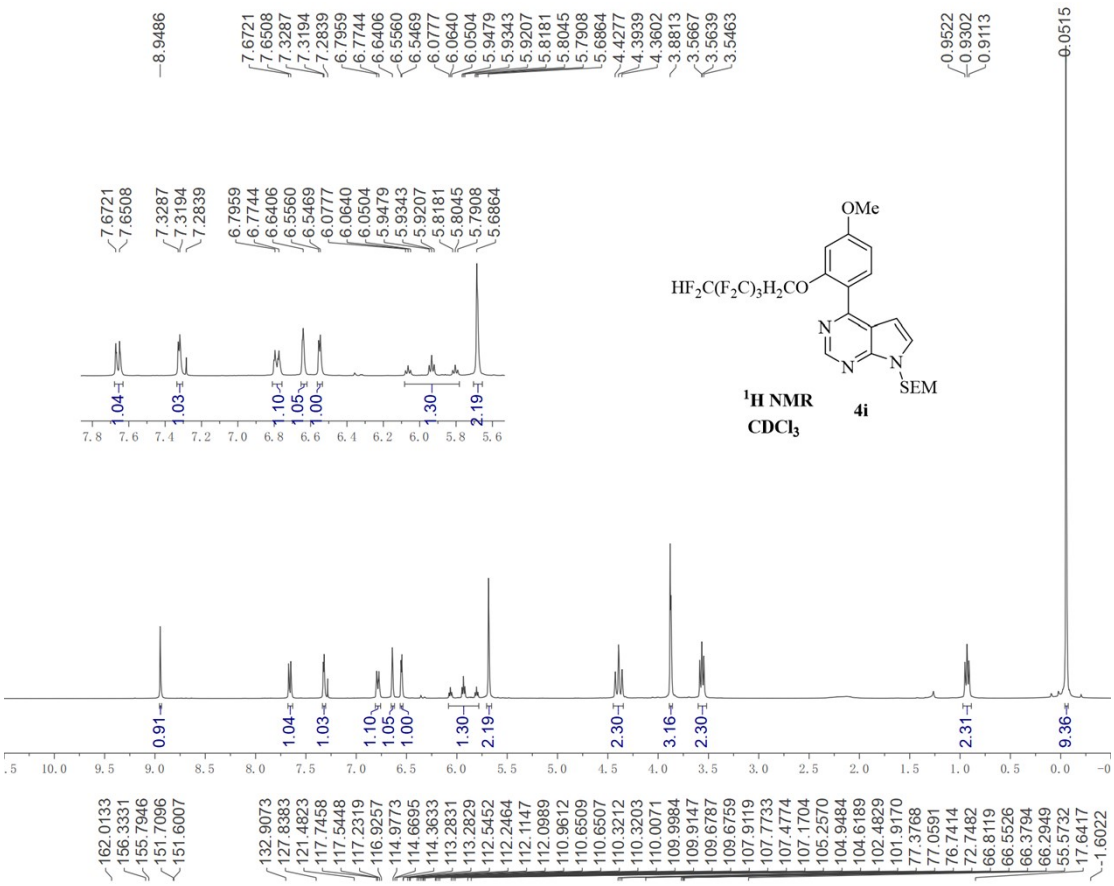
4h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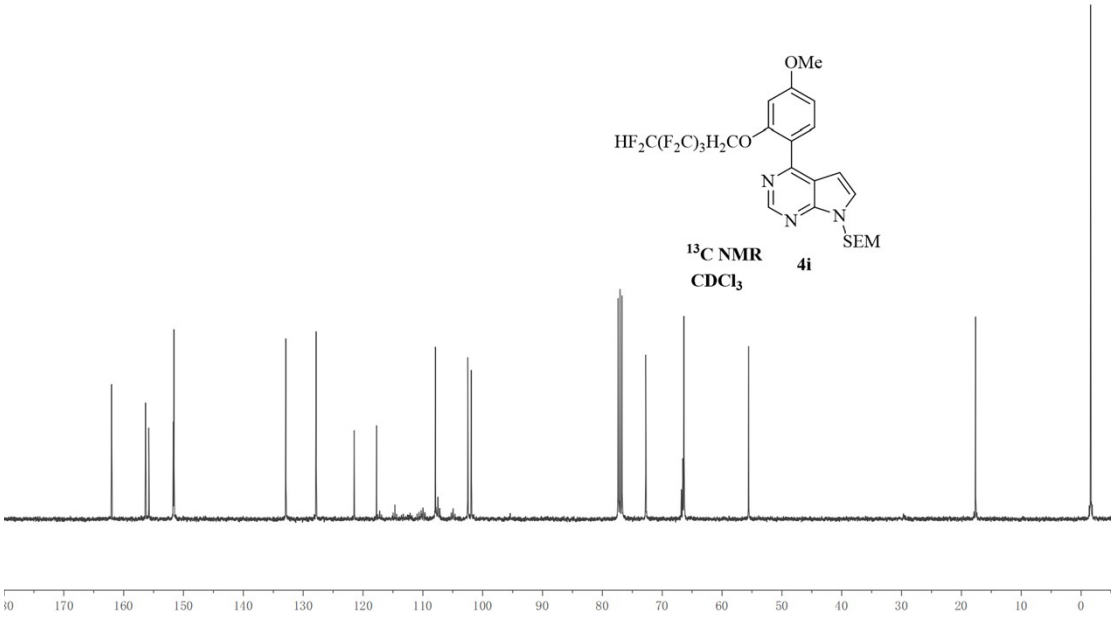
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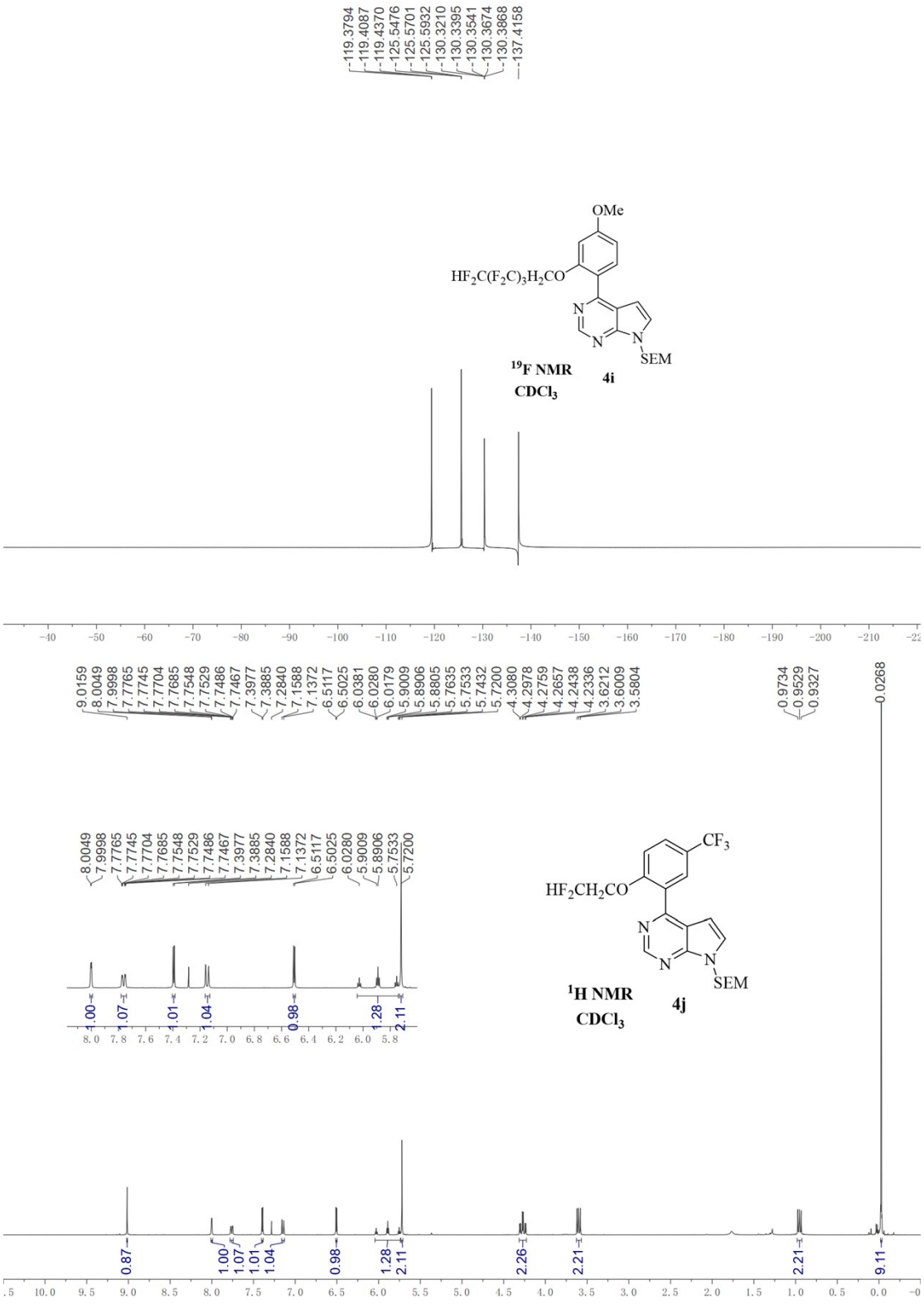
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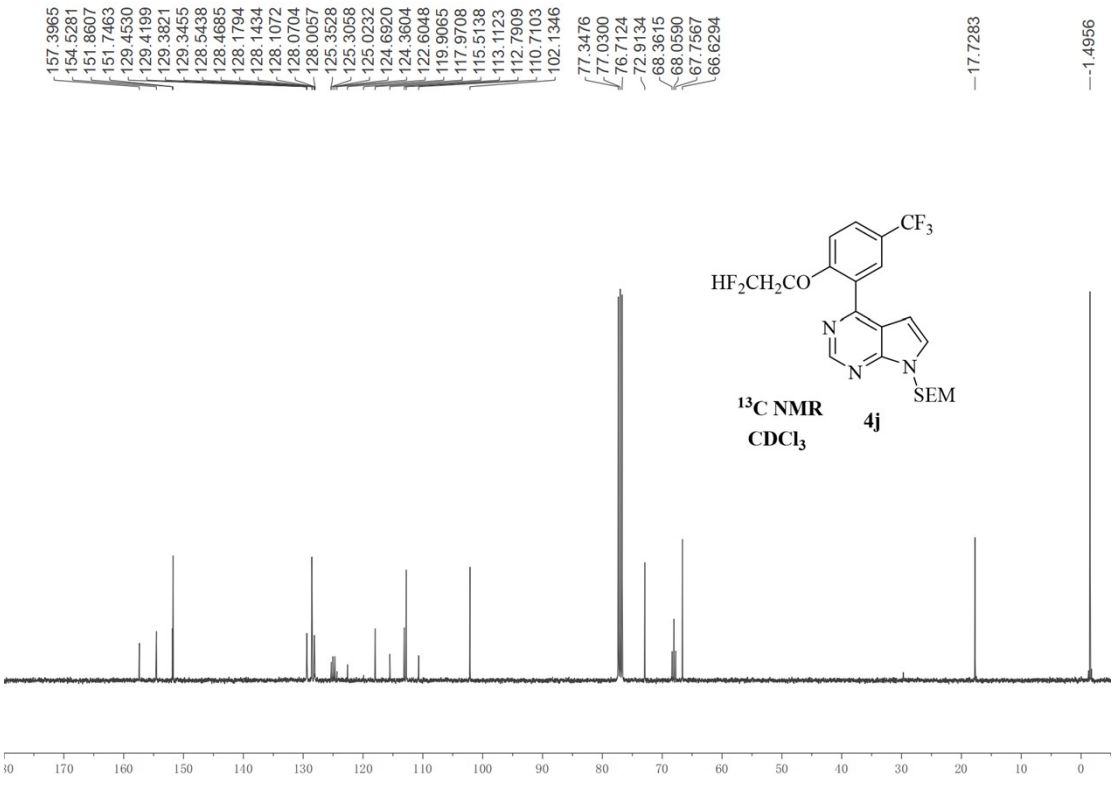
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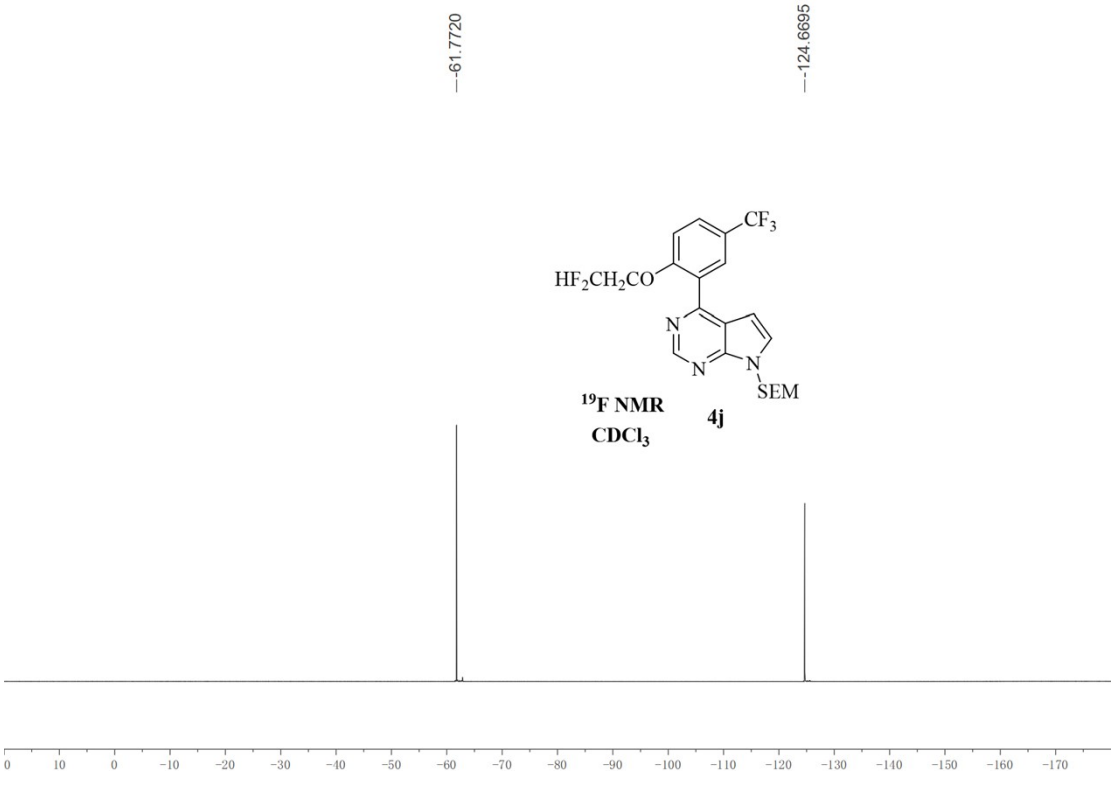
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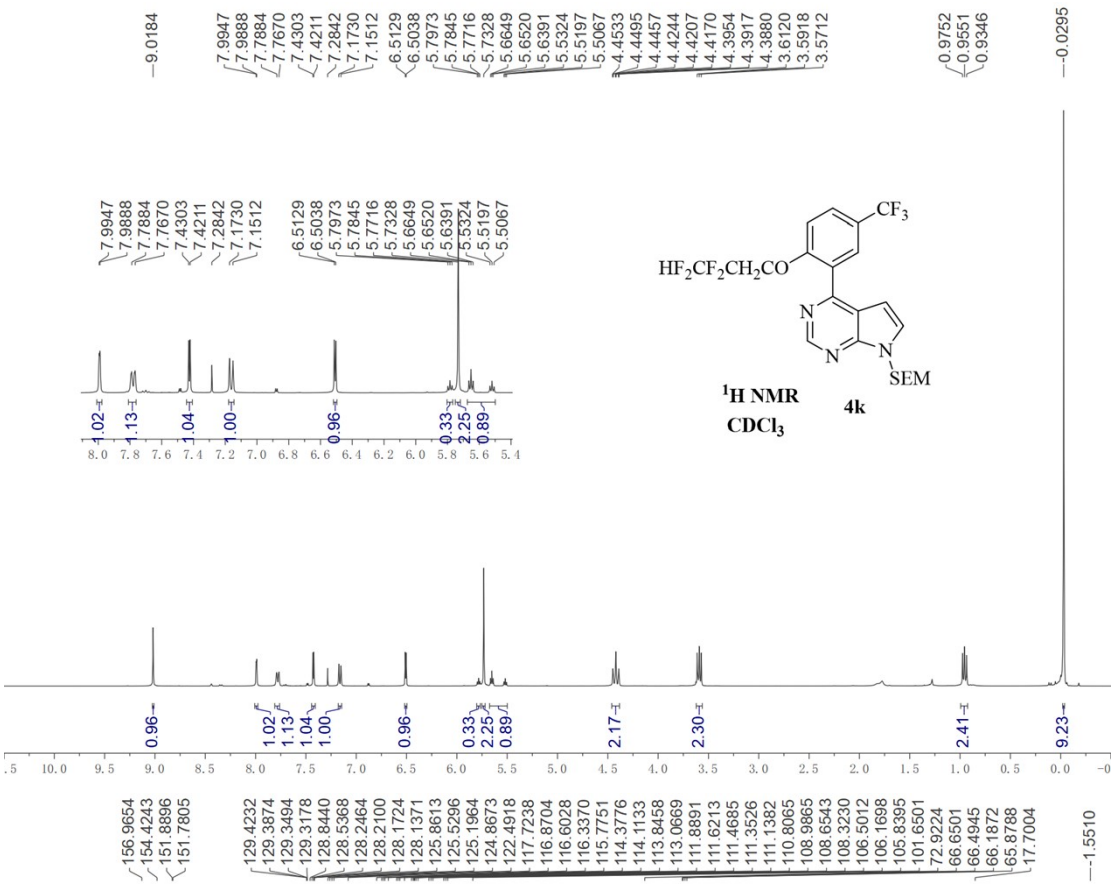
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SEM
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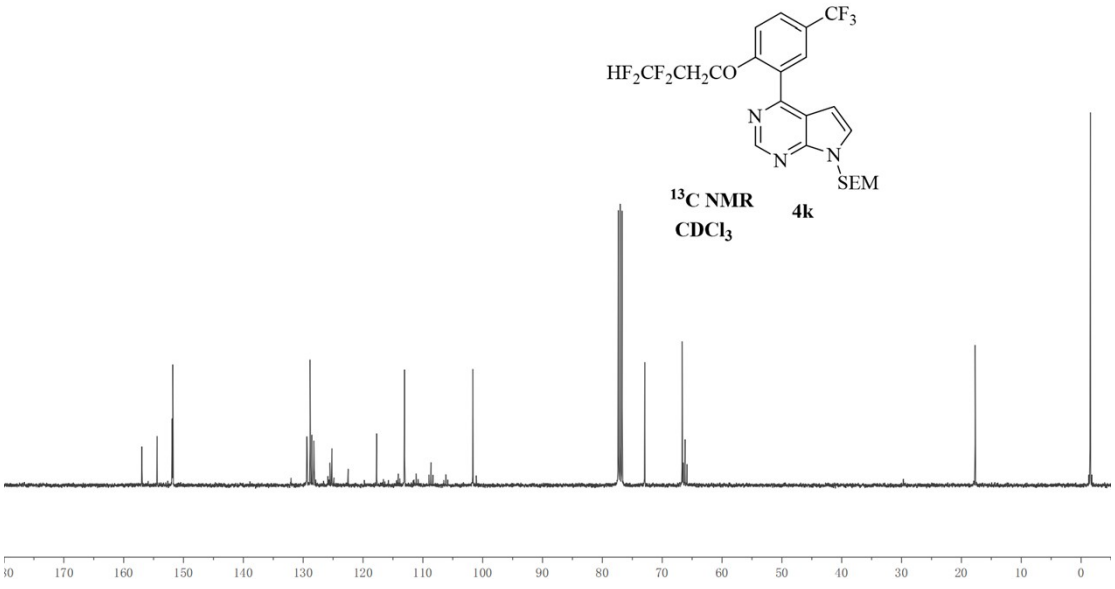
4k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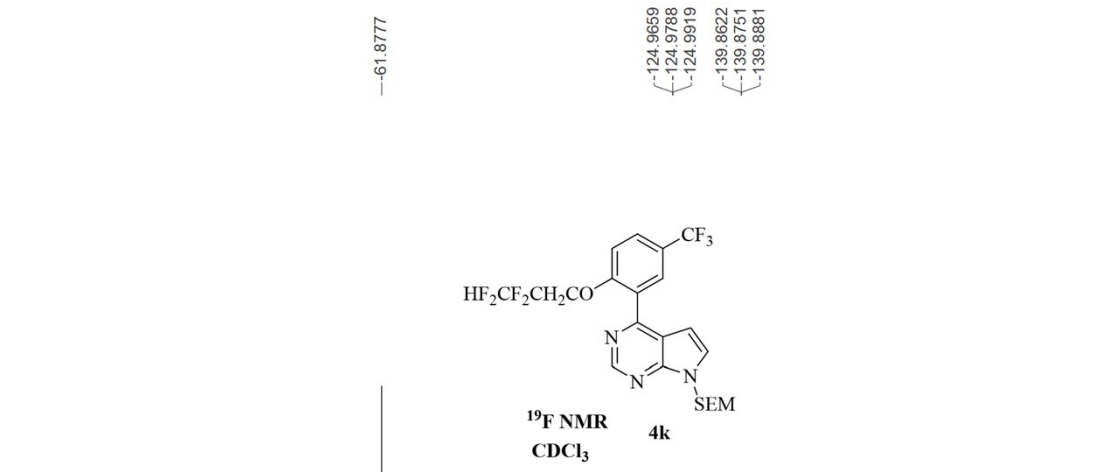
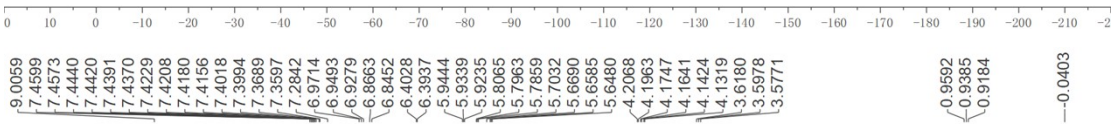
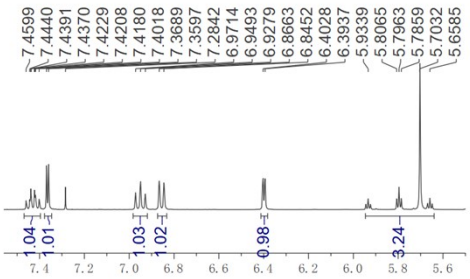
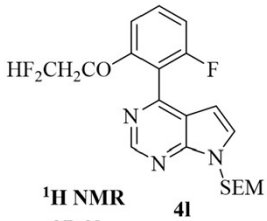


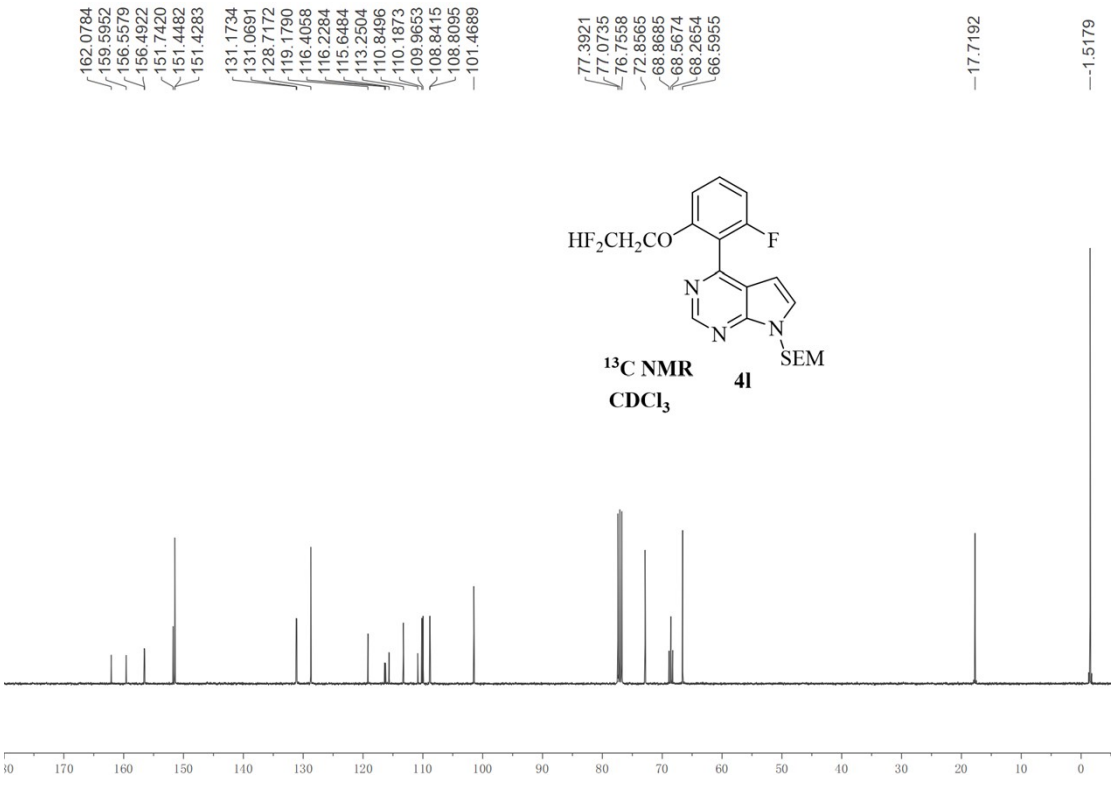
^{19}F NMR
$CDCl_3$
4k







^{1}H NMR
$CDCl_3$
4l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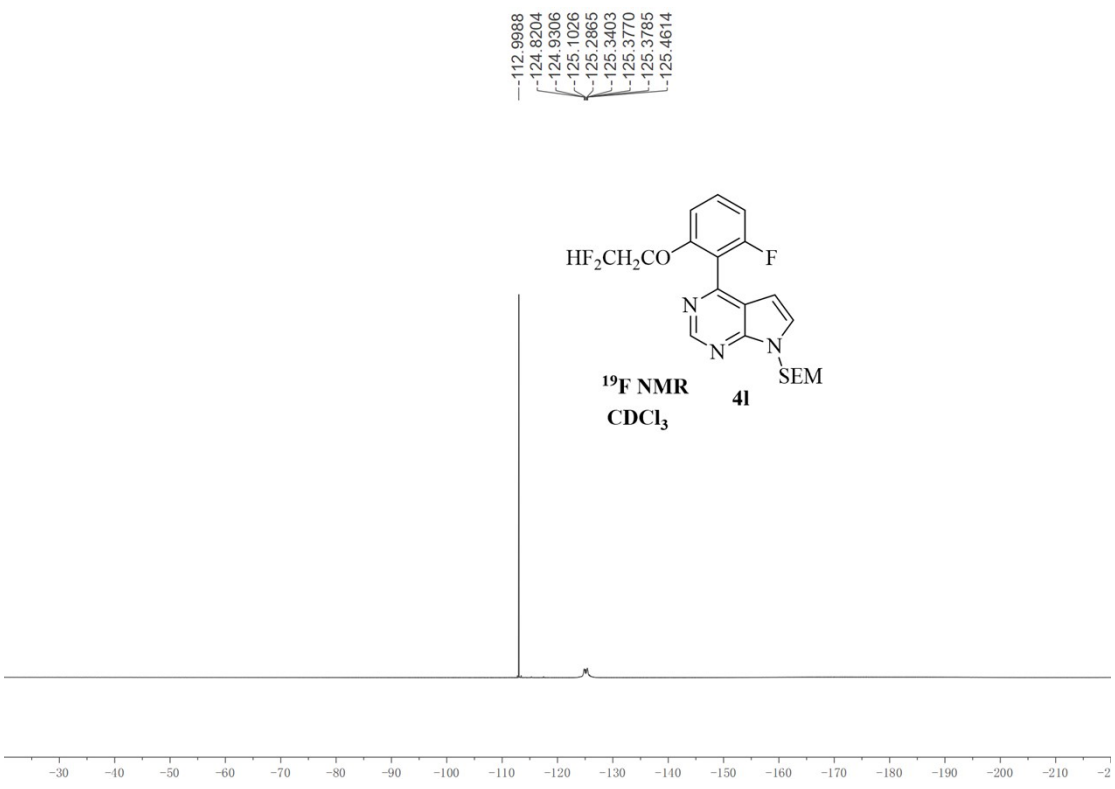
131.0691
128.7172
119.1790
116.4058
116.2284
115.6484
113.2504
110.8496
110.1873
109.9653
108.8415
108.8095
101.4689
77.3921
77.0735
76.7558
72.8565
68.8685
68.5674
68.2654
66.5955
17.7192
-1.5179
HF2CH2CO
F
N
N
N
SEM
13C NMR
CDCl3
4l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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124.9306
125.1026
125.2865
125.3403
125.3770
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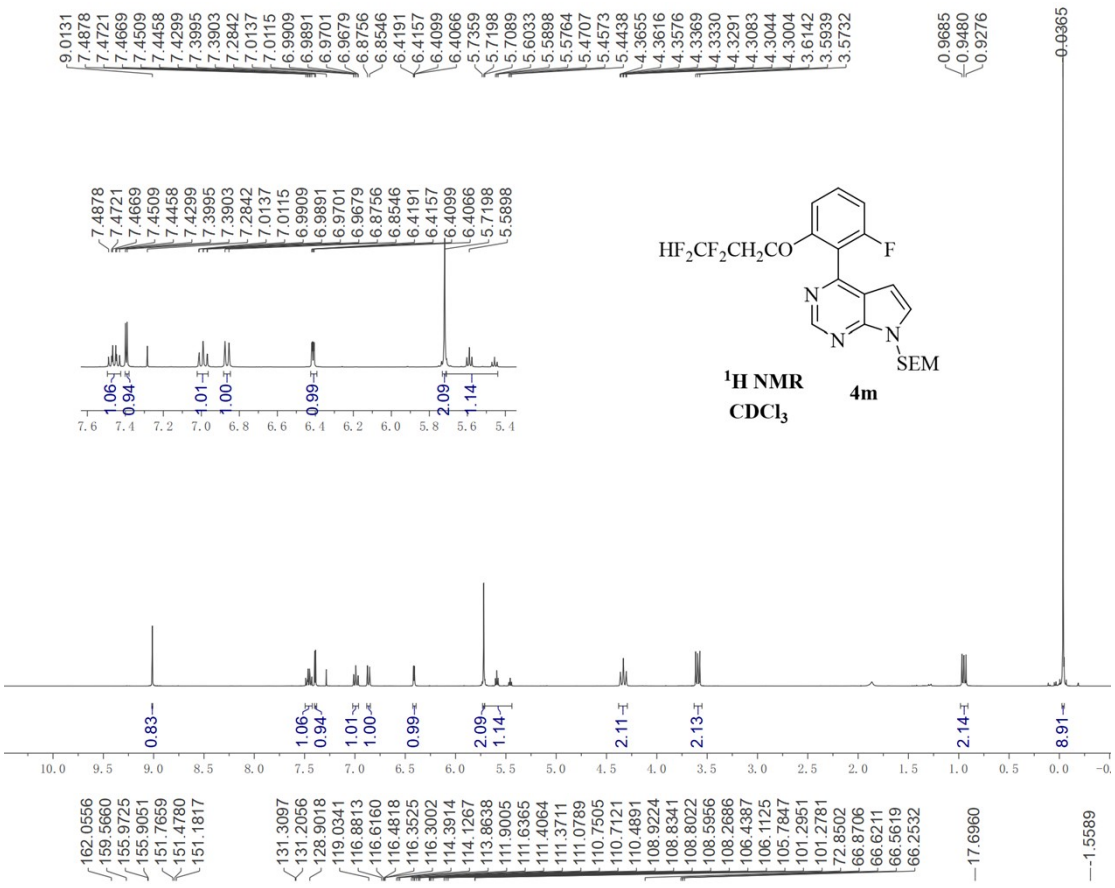
125.4614
HF2CH2CO
F
N
N
N
SEM
19F NMR
CDCl3
4l
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210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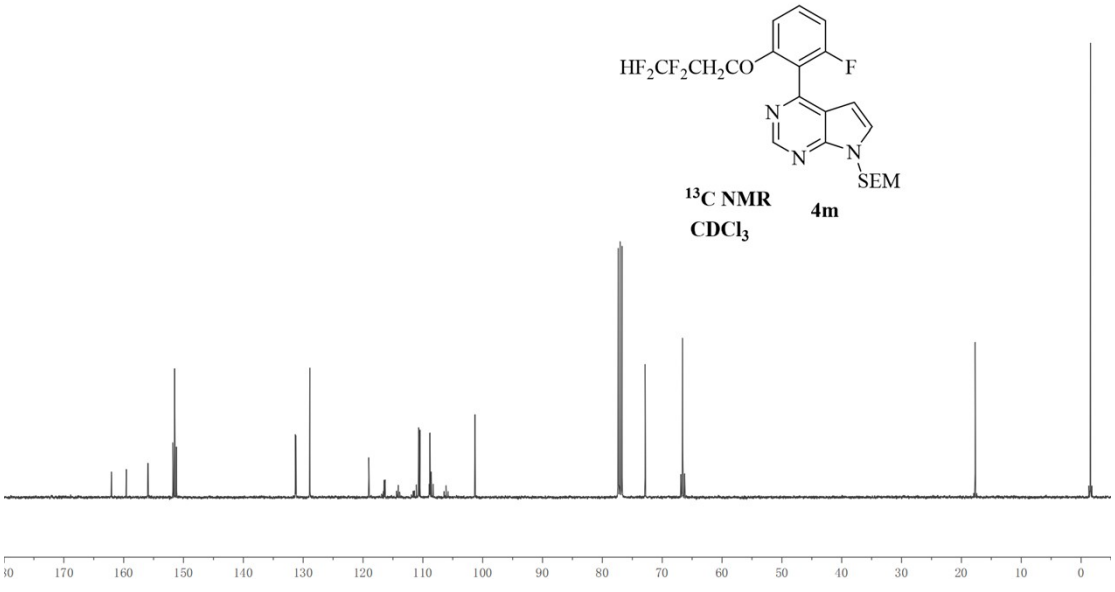
F
N
N
N
SEM
1H NMR
CDCl3
4m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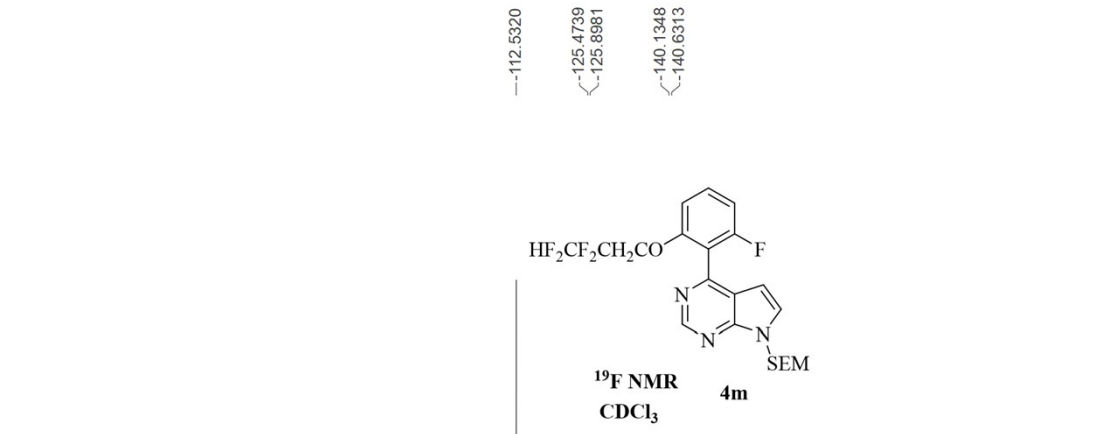
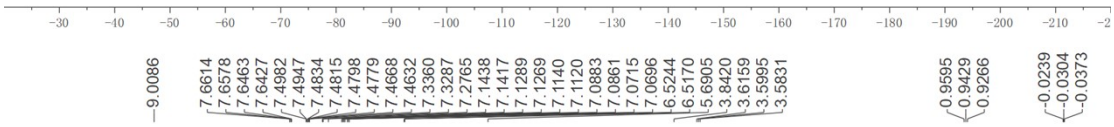
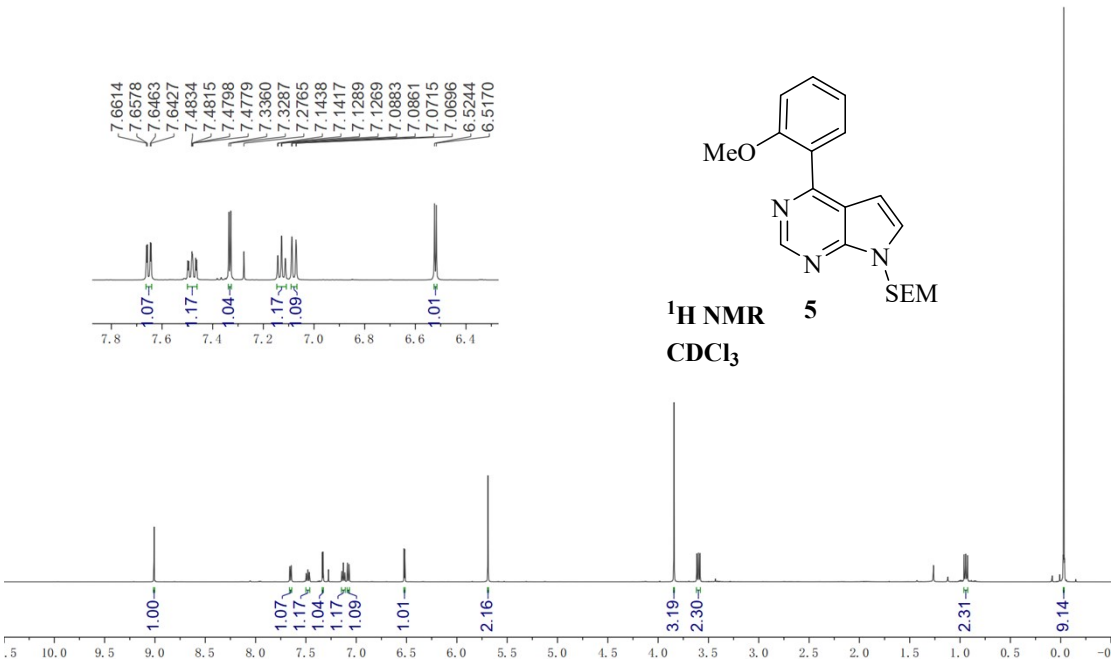
F
N
N
N
SEM
13C NMR
CDCl3
4m



^{19}F NMR **4m**

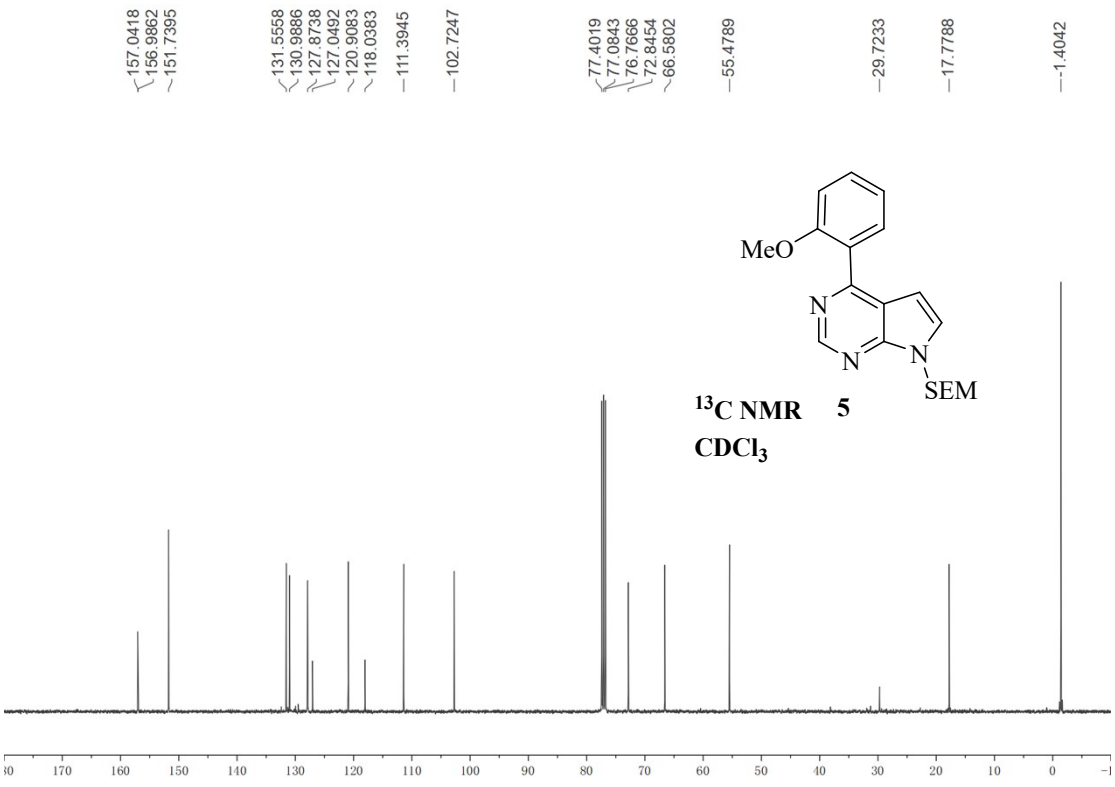
$CDCl_3$





^{1}H NMR **5**

$CDCl_3$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102.7247
77.4019
77.0843
76.7666
72.8454
66.5802
55.4789
29.7233
17.7788
-1.4042
MeO
N
N
N
SEM
13C NMR 5
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0