Supporting Information

Transition Metal-Promoted Switchable Cascade Processes: Diverse Synthesis of *N*-Containing Compounds through a Remote Trifluoromethylazidation/1, n-Acyl Migration Sequence

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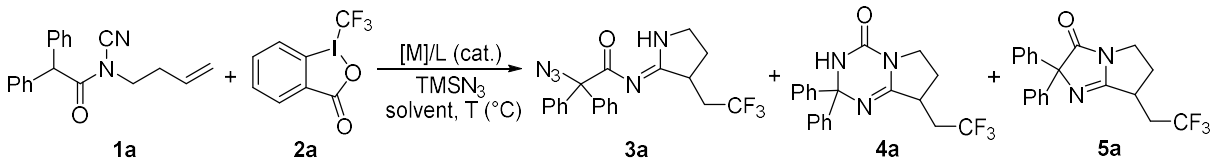
I. General Information

All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), $KMnO_4$, *p*-anisaldehyde stain, and phosphomolybdic acid (PMA) stain; column chromatography purifications were carried out using silica gel. For reactions that require heating, heating mantle was used. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a 300, 400 or 500 MHz spectrometer in $CDCl_3$ or DMSO, fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a 376 or 470 MHz spectrometer in $CDCl_3$ or DMSO, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 125 or 100 MHz spectrometer in $CDCl_3$ or DMSO unless otherwise noted. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 ppm, DMSO = δ 2.50 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm, DMSO = δ 39.52 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Mass spectra were recorded on the Bruker MicrOTOF Q II.

II. Reaction Conditions Screening

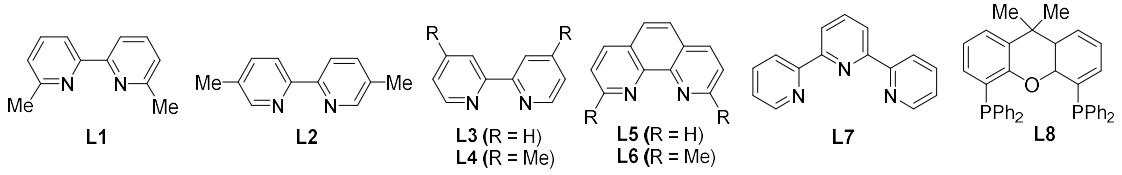
Table S1. Selected optimization of reaction conditions [a]



1a 2a 3a 4a 5a

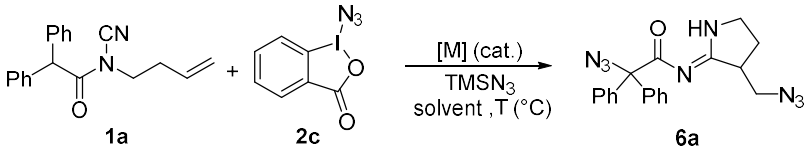
Entry	[M]	L	Solvent	*T* (°C)	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]	Yield of **5a** (%)[b]
1	$NiCl_2$·DME	L1	EtOAc	60	56	13	nd
2	$NiBr_2$·DME	L1	EtOAc	60	43	15	nd
3	$NiCl_2(PPh_3)_2$	L1	EtOAc	60	48	10	nd
4	$NiCl_2$(dppe)	L1	EtOAc	60	40	7	nd
5	$Ni(OTf)_2$	L1	EtOAc	60	15	36	nd
6	$Ni(COD)_2$	L1	EtOAc	60	42	trace	nd
7	$NiCl_2$·DME	-	EtOAc	60	12	29	nd
8	$NiCl_2$·DME	L2/L3/L4	EtOAc	60	44/32/45	18/21/19	nd
9	$NiCl_2$·DME	L5/L6/L7/L8	EtOAc	60	29/44/45/33	18/17/19/12	nd
10	$NiCl_2$·DME	L1	EtOAc	50	59	nd	nd
11[c]	$NiCl_2$·DME	L1	EtOAc	50	53	5	nd
12	$NiCl_2$·DME	-	EtOAc	80	nd	54	nd
13	$NiCl_2$·DME	L1	DCM/THF/Acetone	50	24/nd/16	14/nd/5	nd
14	$NiCl_2$·DME	-	DCM/THF/Acetone	80	nd/nd/nd	52/nd/52	nd
15[d]	$NiCl_2$·DME	L1/-	EtOAc	50/80	63 (62)/nd	nd/62 (63)	nd
16	CuCl	L1/-	EtOAc	50/80	31/trace	13/33	19/22
17	$Cu(OAc)_2$	L1/-	EtOAc	50/80	21/nd	27/27	23/43
18	$FeCl_2$	L1/-	EtOAc	50/80	25/nd	nd/nd	25/34
19	$Fe(acac)_3$	L1/-	EtOAc	50/80	52/nd	nd/nd	nd/33
20	-	-	EtOAc	50/80	nd/nd	nd/nd	nd/nd

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (Togni II, 0.24 mmol), catalyst (10 mol %), ligand (10 mol %), and $TMSN_3$ (0.6 mmol) in solvent (2 mL), 12 h, N_2. [b] ^1H NMR yield using mesitylene as the internal standard. Isolated yield in parentheses. [c] Togni I (**2b**). [d] **2a** (0.3 mmol).



L1 L2 L3 (R = H) L4 (R = Me) L5 (R = H) L6 (R = Me) L7 L8

Table S2. Optimized reaction conditions for preparation product 6a [a]

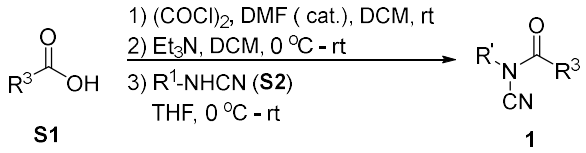


Entry	Cat.	solvent	T (°C)	*t* (h)	L	Conv of **1a** (%)	Yield of **6a** (%)
1	$NiCl_2$·DME	EtOAc	50	12	L1	67	nd
2	$NiCl_2$·DME	EtOAc	30	12	L1	64	26
3	$Cu(MeCN)_4PF_6$	EtOAc	30	12	L1	79	13
4	$Cu(MeCN)_4PF_6$	EtOAc	30	12	L2	81	26
5	$Cu(MeCN)_4PF_6$	EtOAc	30	12	L3	82	31
6	$Cu(OAc)_2$	EtOAc	30	12	L3	61	24
7	$Cu(MeCN)_4PF_6$	DCM	30	12	L3	79	34
8	$Cu(MeCN)_4PF_6$	DCE	30	12	L3	79	35
9	$Cu(MeCN)_4PF_6$	THF	30	12	L3	9	nd
10	$Cu(MeCN)_4PF_6$	MeCN	30	12	L3	88	30
11	$Cu(MeCN)_4PF_6$	DCE	30	6	L3	79	41
12	$Cu(MeCN)_4PF_6$	DCE	30	1	L3	72	49

[a] Reaction conditions: **1a** (0.2 mmol), **2c** (0.3 mmol), catalyst (10 mol %) and $TMSN_3$ (0.6 mmol) in solvent (2 mL), 12 h, N_2. Isolated yield.

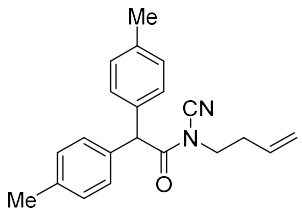
III. Preparation of Substrates

Substrates were prepared according to the known literature, [1] and NMR spectra data of substrates **1a**, **1e-1q**, **1s-1w** were in accordance with the reported data. [1]



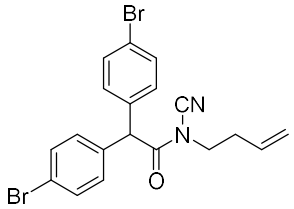
To a suspension of acid **S1** (1.2 mmol, 1.2 equiv.) in DCM (1 ml, 1.2 *M*) was added DMF (2 drops), followed by dropwise addition of $(COCl)_2$ (1.2 mmol, 1.2 equiv.) under nitrogen atmosphere at 0 °C. The mixture was stirred for 1 hour, whereupon gas evolution ceased and all acid dissolved. The reaction flask was cooled to -12 °C and a solution of Et_3N (2.4 equiv.) in DCM (3.0 *M*) was dropwise added. Thereafter, a solution of cyanamide **S2** (1.0 mmol, 1 equiv.) in CH_2Cl_2/THF (3/1, 0.8 ml, 1.2 *M*) was slowly added at the same temperature. The resulting mixture was allowed to warm up to room temperature and stirred for 20–24 h. Upon completion, the reaction mixture was quenched with H_2O and the aqueous phase was extracted with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to give the desired substrates.

Spectral data for *N*-(but-3-en-1-yl)-*N*-cyano-2,2-di-p-tolylacetamide (1b)



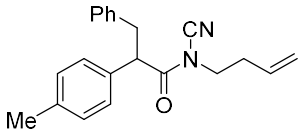
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (95% yield, 302 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 8H), δ 5.68 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.51 (s, 1H), 5.12 – 5.03 (m, 2H), 3.67 (t, *J* = 6.9 Hz, 2H), 2.44 – 2.37 (m, 2H), 2.32 (s, 6H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 171.9, 137.7, 134.2, 132.8, 129.6, 128.7, 119.0, 110.6, 55.4, 46.1, 32.0, 21.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}N_2O$ 319.1805; found: 319.1793.

Spectral data for 2,2-bis(4-bromophenyl)-*N*-(but-3-en-1-yl)-*N*-cyanoacetamide (1c)



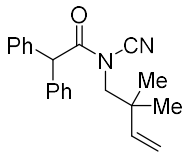
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (72% yield, 323 mg) as yellowish solid, mp: 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 4H), 7.17 – 7.11 (m, 4H), 5.67 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.49 (s, 1H), 5.12 – 5.02 (m, 2H), 3.69 (t, *J* = 6.9 Hz, 2H), 2.49 – 2.29 (m, 2H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 170.8, 135.4, 132.6, 132.3, 130.5, 122.5, 119.2, 110.2, 54.8, 46.2, 32.0. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}Br_2N_2O$ 446.9702; found: 446.9689.

Spectral data for *N*-(but-3-en-1-yl)-*N*-cyano-3-phenyl-2-(p-tolyl)propenamide (1d)



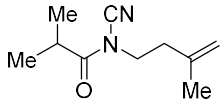
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/100) to afford the title compound (72% yield, 229 mg) as white solid, mp: 65-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 5H), 7.18 – 7.09 (m, 4H), 5.50 (ddt, *J* = 17.2, 10.4, 6.9 Hz, 1H), 4.97 – 4.79 (m, 2H), 4.40 (dd, *J* = 9.2, 5.9 Hz, 1H), 3.61 – 3.37 (m, 3H), 3.01 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.33 (s, 3H), 2.26 – 2.17 (m, 2H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 172.4, 138.4, 138.0, 133.8, 132.6, 129.8, 129.2, 128.6, 128.2, 126.8, 118.8, 110.5, 52.5, 45.8, 40.3, 31.9, 21.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}N_2O$ 319.1805; found: 319.1814.

Spectral data for *N*-cyano-*N*-(2,2-dimethylbut-3-en-1-yl)-2,2-diphenylacetamide (1r)



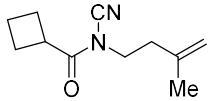
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (89% yield, 283 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 10H), 5.76 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.66 (s, 1H), 5.05 – 4.92 (m, 2H), 3.53 (s, 2H), 1.04 (s, 6H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 171.9, 143.8, 137.0, 129.0, 128.9, 128.0, 114.1, 111.8, 56.2, 55.8, 39.6, 24.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}N_2O$ 319.1805; found: 319.1789.

Spectral data for *N*-cyano-*N*-(3-methylbut-3-en-1-yl) isobutyramide (1x)



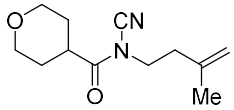
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (89% yield, 160 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (t, *J* = 1.7 Hz, 1H), 4.80 – 4.77 (m, 1H), 3.71 (t, *J* = 7.0 Hz, 2H), 3.13 (hept, *J* = 6.8 Hz, 1H), 2.38 (t, *J* = 7.0 Hz, 2H), 1.77 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 6H). ^{13}C{H^{1}} NMR (125 MHz, $CDCl_3$) δ 176.5, 140.6, 113.9, 110.7, 44.2, 35.8, 33.6, 22.0, 19.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{17}N_2O$ 181.1335; found: 181.1333.

Spectral data for *N*-cyano-*N*-(3-methylbut-3-en-1-yl)cyclobutanecarboxamide (1y)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (78% yield, 150 mg) as colorless oil. **1**H NMR (500 MHz, $CDCl_3$) δ 4.86 (t, *J* = 1.6 Hz, 1H), 4.80 – 4.76 (m, 1H), 3.69 (t, *J* = 7.1 Hz, 2H), 3.64 – 3.56 (m, 1H), 2.41 – 2.28 (m, 6H), 2.11 – 1.99 (m, 1H), 1.97 – 1.87 (m, 1H), 1.77 (s, 3H). ^{13}C{H^{1}} NMR (125 MHz, $CDCl_3$) δ 174.2, 140.6, 113.8, 110.5, 44.0, 38.4, 35.8, 25.1, 22.1, 18.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}N_2O$ 193.1335; found: 193.1342.

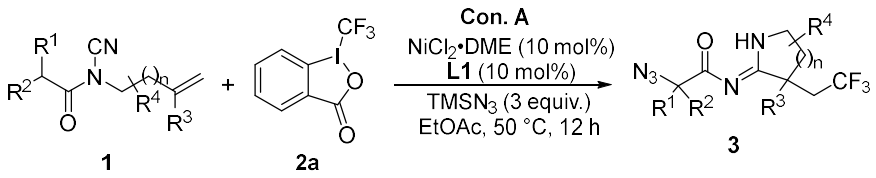
Spectral data for *N*-cyano-*N*-(3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-4-carboxamide (1z)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (87% yield, 193 mg) as colorless oil. **1**H NMR (500 MHz, $CDCl_3$) δ 4.86 (t, *J* = 1.7 Hz, 1H), 4.78 (s, 1H), 4.05 – 3.97 (m, 2H), 3.72 (t, *J* = 6.9 Hz, 2H), 3.52 – 3.43 (m, 2H), 3.15 – 3.04 (m, 1H), 2.38 (t, *J* = 7.0 Hz, 2H), 1.90 – 1.78 (m, 4H), 1.77 (s, 3H). ^{13}C{H^{1}} NMR (100 MHz, $CDCl_3$) δ 173.7, 140.5, 114.1, 110.5, 66.7, 44.1, 40.2, 35.8, 28.5, 22.0. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{19}N_2O_2$ 223.1441; found: 223.1437.

IV. General Procedure and Experimental Details

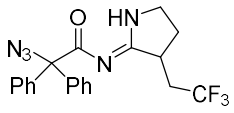
1. General procedure for preparation of products 3



1 2a 3

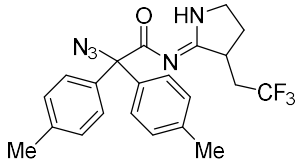
To a flame-dried sealed tube equipped with a magnetic stir bar were added **1** (0.2 mmol, 1 equiv.), Togni's reagent **2a** (0.3 mmol, 1.5 equiv.), $NiCl_2$·DME (10 mol%, 0.02 mmol) and L1 (10 mol%, 0.02 mmol). The tube was evacuated and backfilled with nitrogen for three times. Then ethyl acetate (2.0 mL) and $TMSN_3$ (0.6 mmol, 3 equiv.) were added *via* syringe. The tube was stirred at 50 °C for 12 h. After completion, the mixture was cooled to room temperature, and sat. aq. soln. of $NaHCO_3$ was added. Then the aqueous phase was extracted with DCM, washed with brine, dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the crude was purified by flash chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to give the desired compounds.

Spectral data for (*Z*)-2-azido-2,2-diphenyl-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene) acetamide (3a)



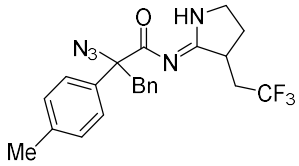
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (62% yield, 51 mg) as white solid, mp: 133-135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.40 – 7.25 (m, 10H), 3.61 – 3.45 (m, 2H), 3.07 – 2.85 (m, 2H), 2.43 – 2.30 (m, 1H), 2.05 – 1.89 (m, 1H), 1.86 – 1.72 (m, 1H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 184.8, 174.9, 140.8, 140.7, 128.5, 128.1, 128.0, 127.9, 126.8 (q, *J* = 276.5 Hz), 78.9, 45.6, 39.5, 35.5 (q, *J* = 28.7 Hz), 27.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.60 (t, *J* = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}F_3N_5O$ 402.1536; found: 402.1521.

Spectral data for (*Z*)-2-azido-2,2-di-p-tolyl-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene) acetamide (3b)



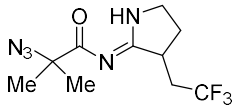
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (63% yield, 54 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.28 – 7.18 (m, 4H), 7.17 – 7.09 (m, 4H), 3.70 – 3.51 (m, 2H), 3.10 – 2.86 (m, 2H), 2.49 – 2.37 (m, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.07 – 1.92 (m, 1H), 1.91 – 1.74 (m, 1H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 185.2, 174.9, 138.0, 137.9, 137.7, 137.6, 128.8, 128.7, 128.4, 128.3, 126.9 (q, *J* = 276.7 Hz), 78.6, 45.6, 39.4 (q, *J* = 2.7 Hz), 35.6 (q, *J* = 29.0 Hz), 27.2, 21.2, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.62 (t, *J* = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}F_3N_5O$ 430.1849; found: 430.1843.

Spectral data for (*Z*)-2-azido-3-phenyl-2-(p-tolyl)-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene) propenamide (3d)



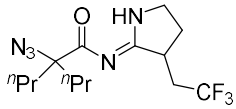
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (an inseparable mixture, 19% yield, 17 mg, dr = 1.1/1) as yellowish oil. The mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 2H), 7.32 – 7.27 (m, 4H), 7.21 – 7.15 (m, 6H), 7.15 – 7.07 (m, 8H), 3.68 – 3.53 (m, 6H), 3.30 (d, *J* = 5.5 Hz, 1H), 3.27 (d, *J* = 5.4 Hz, 1H), 3.10 – 2.93 (m, 4H), 2.49 – 2.35 (m, 2H), 2.33 (s, 3H), 2.33 (s, 3H), 2.08 – 1.91 (m, 2H), 1.90 – 1.76 (m, 2H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 185.1, 185.0, 174.9, 174.6, 137.7, 137.6, 136.9, 136.7, 136.6, 130.9, 130.8, 129.2, 129.1, 127.9, 127.8, 126.9 (q, *J* = 274.3 Hz), 126.7, 126.6, 126.4, 126.3, 75.8, 75.7, 45.6, 45.5, 44.7, 44.5, 39.4 (q, *J* = 3.0 Hz), 39.3 (q, *J* = 3.0 Hz), 35.7 (q, *J* = 28.8 Hz), 35.6 (q, *J* = 29.0 Hz), 27.2, 27.1, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.64 (t, *J* = 11.0 Hz, 6F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}F_3N_5O$ 430.1849; found: 430.1846.

Spectral data for (*Z*)-2-azido-2-methyl-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene) propenamide (3e)



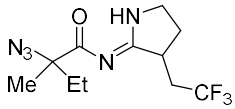
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (48% yield, 27 mg) as white solid, mp: 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 3.75 – 3.56 (m, 2H), 3.17 – 2.98 (m, 2H), 2.52 – 2.40 (m, 1H), 2.18 – 1.97 (m, 1H), 1.93 – 1.79 (m, 1H), 1.46 (s, 3H), 1.45 (s, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 187.9, 175.0, 126.9 (q, *J* = 276.3 Hz), 76.8, 45.5, 39.4 (q, *J* = 2.4 Hz), 35.8 (q, *J* = 29.0 Hz), 27.3, 25.0, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.72 (t, *J* = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}F_3N_5O$ 278.1223; found: 278.1228.

Spectral data for (*Z*)-2-azido-2-propyl-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene) pentanamide (3f)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (42% yield, 28 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 3.76 – 3.48 (m, 2H), 3.15 – 2.93 (m, 2H), 2.51 – 2.38 (m, 1H), 2.16 – 1.97 (m, 1H), 1.93 – 1.77 (m, 3H), 1.75 – 1.63 (m, 2H), 1.49 – 1.33 (m, 2H), 1.31 – 1.12 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 187.3, 174.4, 126.9 (q, *J* = 276.7 Hz), 72.9, 45.5, 39.4 (q, *J* = 3.1 Hz), 39.3, 39.2, 35.8 (q, *J* = 29.1 Hz), 27.2, 17.7, 17.6, 14.5, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.61 (t, *J* = 10.9 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{23}F_3N_5O$ 334.1849; found: 334.1843.

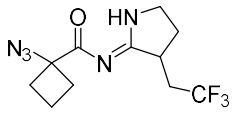
Spectral data for (*Z*)-2-azido-2-methyl-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene) butanamide (3g)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (an inseparable mixture, 35% yield, 20 mg, dr = 1/1) as colorless oil. The mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 2H), 3.72 – 3.55 (m, 4H), 3.15 – 2.95 (m, 4H), 2.53 – 2.38 (m, 2H), 2.16 – 1.99 (m, 2H), 1.89 (q, *J* = 7.4 Hz,

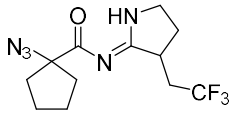
4H), 1.80 – 1.63 (m, 2H), 1.43 (s, 6H), 0.90 (t, J = 7.4 Hz, 6H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 187.6, 174.7, 126.9 (q, J = 276.6 Hz), 69.7, 45.5, 39.4 (q, J = 3.0 Hz), 35.8 (q, J = 28.8 Hz), 31.3, 31.2, 27.3, 22.4, 22.3, 8.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.68 (t, J = 11.1 Hz, 3F), -64.70 (t, J = 11.0 Hz, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}F_3N_5O$ 292.1380; found: 292.1383.

Spectral data for (*Z*)-1-azido-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)cyclobutane-1- carboxamide (3h)



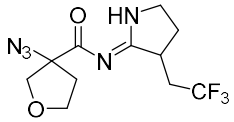
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (44% yield, 25 mg) as yellowish solid, mp: 69-71 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 3.75 – 3.56 (m, 2H), 3.18 – 3.01 (m, 2H), 2.67 – 2.55 (m, 2H), 2.52 – 2.41 (m, 1H), 2.28 – 2.16 (m, 2H), 2.14 – 1.81 (m, 4H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 186.3, 175.0, 126.9 (q, J = 276.6 Hz), 68.2, 45.5, 39.4 (q, J = 2.9 Hz), 35.8 (q, J = 28.9 Hz), 31.4, 31.2, 27.3, 14.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.71 (t, J = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{15}F_3N_5O$ 290.1223; found: 290.1214.

Spectral data for (*Z*)-1-azido-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)cyclopentane-1- carboxamide (3i)



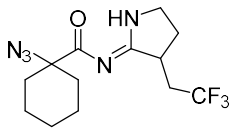
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (41% yield, 25 mg) as yellowish oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 3.74 – 3.55 (m, 2H), 3.17 – 2.97 (m, 2H), 2.52 – 2.38 (m, 1H), 2.23 – 1.99 (m, 3H), 1.94 – 1.75 (m, 7H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 187.7, 174.6, 126.9 (q, J = 276.7 Hz), 77.0, 45.5, 39.4 (q, J = 2.9 Hz), 36.8, 36.6, 35.8 (q, J = 28.9 Hz), 27.3, 24.8, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.72 (t, J = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{17}F_3N_5O$ 304.1380; found: 304.1370.

Spectral data for (*Z*)-3-azido-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)tetrahydrofuran-3-carboxamide (3j)



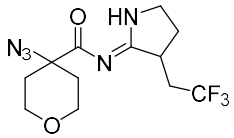
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (an inseparable mixture, 60% yield, 37 mg, dr = 1/1) as purple solid. The mixture: ^1H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 2H), 4.21 – 3.98 (m, 6H), 3.99 – 3.87 (m, 2H), 3.78 – 3.56 (m, 4H), 3.16 – 2.94 (m, 4H), 2.65 – 2.52 (m, 2H), 2.52 – 2.40 (m, 2H), 2.21 – 2.00 (m, 4H), 1.96 – 1.79 (m, 2H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 184.3, 184.2, 175.2, 126.8 (q, J = 276.5 Hz), 76.0, 75.7, 75.6, 68.5, 68.4, 45.6, 39.5 (q, J = 3.4 Hz), 37.1, 37.0, 35.7 (q, J = 29.1 Hz), 27.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.73 (q, J = 9.8 Hz, 3F), -64.75 (q, J = 10.2 Hz, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{15}F_3N_5O$ 306.1172; found: 306.1177.

Spectral data for (*Z*)-1-azido-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)cyclohexane-1- carboxamide (3k)



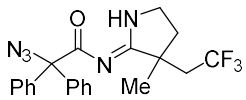
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (46% yield, 29 mg) as white solid, mp: 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 3.74 – 3.54 (m, 2H), 3.19 – 2.98 (m, 2H), 2.52 – 2.40 (m, 1H), 2.16 – 1.99 (m, 1H), 1.94 – 1.70 (m, 5H), 1.69 – 1.64 (m, 1H), 1.64 – 1.51 (m, 5H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 187.8, 175.0, 127.0 (q, J = 276.6 Hz), 68.9, 45.5, 39.4 (q, J = 2.9 Hz), 35.9 (q, J = 28.9 Hz), 32.3, 32.2, 27.4, 25.3, 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.71 (t, J = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{19}F_3N_5O$ 318.1536; found: 318.1539.

Spectral data for (*Z*)-4-azido-*N*-(3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)tetrahydro-2H-pyran-4-carboxamide (3l)



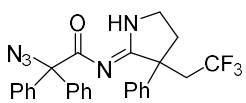
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (46% yield, 30 mg) as white solid, mp: 113-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 3.82 – 3.49 (m, 6H), 3.09 – 2.89 (m, 2H), 2.47 – 2.34 (m, 1H), 2.18 – 2.05 (m, 2H), 2.05 – 1.94 (m, 1H), 1.89 – 1.75 (m, 1H), 1.73 – 1.57 (m, 2H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 185.9, 175.4, 126.9 (q, J = 276.6 Hz), 66.0, 64.1 64.0, 45.6, 39.5 (q, J = 3.0 Hz), 35.8 (q, J = 29.0 Hz), 32.4, 32.3, 27.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.74 (t, J = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{17}F_3N_5O_2$ 320.1329; found: 320.1322.

Spectral data for (*Z*)-2-azido-*N*-(3-methyl-3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)-2,2-diphenylacetamide (3m)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (56% yield, 47 mg) as white solid, mp: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.38 – 7.28 (m, 10H), 3.68 – 3.59 (m, 2H), 2.58 – 2.42 (m, 1H), 2.41 – 2.29 (m, 1H), 2.29 – 2.17 (m, 1H), 2.04 – 1.95 (m, 1H), 1.24 (s, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 185.3, 178.3, 140.8, 140.7, 128.4, 127.9, 127.8, 127.7, 127.6, 126.4 (q, J = 278.3 Hz), 78.8, 44.5 (q, J = 1.9 Hz), 44.2, 40.7 (q, J = 27.5 Hz), 31.9, 23.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.38 (t, J = 11.4 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}F_3N_5O$ 416.1693; found: 416.1703.

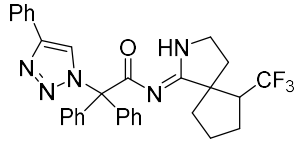
Spectral data for (*Z*)-2-azido-2,2-diphenyl-*N*-(3-phenyl-3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)acetamide (3n)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (18% yield, 17 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.30 (m, 10H), 7.28 – 7.22 (m, 3H), 3.69 – 3.60 (m, 1H), 3.59 – 3.48 (m, 1H), 3.03 – 2.79 (m, 2H), 2.69 – 2.50 (m, 1H), 2.46

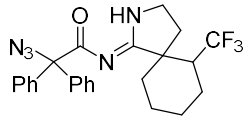
– 2.32 (m, 1H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 184.9, 176.0, 140.8, 140.4, 137.4, 128.8, 128.7, 128.2, 128.1, 128.0, 127.9, 127.8, 126.5, 126.1 (q, *J* = 278.4 Hz), 79.3, 51.0 (q, *J* = 2.3 Hz), 44.3, 42.6 (q, *J* = 27.1 Hz), 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.25 (t, *J* = 10.9 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{23}F_3N_5O$ 478.1849; found: 478.1828.

Spectral data for (*Z*)-2,2-diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-*N*-(6-(trifluoromethyl)-2-azaspiro[4.4]nonan-1-ylidene)acetamide (3o)



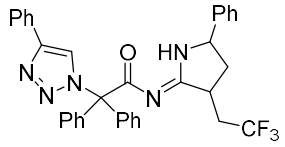
According to the general procedure, upon completion, the mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered with a pad of silica gel, the filtrate was concentrated under reduced pressure. Then the residue and CuI (20 mol%, 0.04 mmol) were added in a 25 mL oven-dried sealed tube. The tube was evacuated and backfilled with N_2 for three times, after that, phenylacetylene (0.6 mmol, 3.0 equiv.) and THF (2.0 mL) were then added via syringe under N_2. The tube was sealed with a Teflon lined cap and moved into a preheated oil bath at 60 ^oC for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and filtered through a pad of Celite. The filtrate was concentrated, and the residue was then purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (35% yield, 38 mg, dr > 19/1) as yellowish oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.93 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.27 (m, 13H), 3.67 – 3.49 (m, 2H), 2.93 – 2.75 (m, 1H), 2.42 – 2.25 (m, 1H), 1.90 – 1.77 (m, 2H), 1.76 – 1.53 (m, 5H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 183.0, 178.0, 140.3, 131.2, 129.7, 128.8, 128.3, 128.2, 128.0, 127.9, 127.4 (q, *J* = 278.5 Hz), 125.8, 80.5, 55.1, 48.3 (q, *J* = 26.4 Hz), 44.6, 39.0, 28.9, 25.4 (q, *J* = 2.2 Hz), 22.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.45 (d, *J* = 9.8 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{29}F_3N_5O$ 544.2319; found: 544.2306.

Spectral data for (*Z*)-2-azido-2,2-diphenyl-*N*-(6-(trifluoromethyl)-2-azaspiro[4.5]decan-1- ylidene)acetamide (3p)



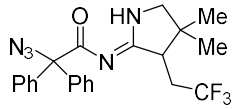
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (56% yield, 51 mg, dr > 19/1) as yellowish oil. ^1H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.43 – 7.30 (m, 10H), 3.71 – 3.53 (m, 2H), 2.74 – 2.61 (m, 1H), 2.35 – 2.24 (m, 1H), 1.98 – 1.89 (m, 2H), 1.87 – 1.78 (m, 1H), 1.77 – 1.63 (m, 2H), 1.56 – 1.47 (m, 1H), 1.47 – 1.22 (m, 3H). $^{13}C\{H^1\}$ NMR (125 MHz, $CDCl_3$) δ 185.3, 179.1, 141.1, 141.0, 128.7, 128.6, 127.9, 127.8, 127.7, 127.6, 127.3 (q, *J* = 281.6 Hz), 78.9, 49.2, 45.4 (q, *J* = 24.2 Hz), 44.4, 36.4, 25.2, 24.3, 22.7, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.74 (d, *J* = 9.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}F_3N_5O$ 456.2006; found: 456.1997.

Spectral data for (*Z*)-2,2-diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-*N*-(5-phenyl-3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)acetamide (3q)



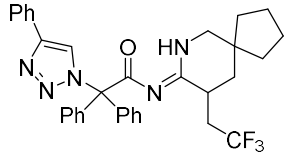
According to the general procedure, upon completion, the mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered with a pad of silica gel, the filtrate was concentrated under reduced pressure. Then the residue and CuI (20 mol%, 0.04 mmol) were added in a 25 mL oven-dried sealed tube. The tube was evacuated and backfilled with N_2 for three times, after that, phenylacetylene (0.6 mmol, 3.0 equiv.) and THF (2.0 mL) were then added via syringe under N_2. The tube was sealed with a Teflon lined cap and moved into a preheated oil bath at 60 °C for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and filtered through a pad of Celite. The filtrate was concentrated, and the residue was then purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (an inseparable mixture, 39% yield, 45 mg, dr = 1.8/1) as yellowish solid. The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.85 – 7.77 (m, 3H), 7.43 – 7.22 (m, 17H), 7.20 – 7.15 (m, 1H), 4.89 (dd, *J* = 9.9, 6.4 Hz, 1H), 3.17 – 3.01 (m, 1H), 2.80 – 2.71 (m, 1H), 2.35 – 2.26 (m, 1H), 2.02 – 1.85 (m, 1H), 1.75 – 1.63 (m, 1H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.85 – 7.77 (m, 3H), 7.43 – 7.22 (m, 17H), 7.20 – 7.15 (m, 1H), 4.98 (dd, *J* = 7.9, 3.5 Hz, 1H), 3.17 – 3.01 (m, 1H), 2.71 – 2.61 (m, 1H), 2.59 – 2.50 (m, 1H), 2.02 – 1.85 (m, 1H), 1.75 – 1.63 (m, 1H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 182.6, 174.0, 173.6, 145.9, 140.0, 139.9, 139.2, 131.0, 129.9, 129.7, 129.3, 128.9, 128.8, 128.6, 128.5, 128.1, 128.0, 126.6 (q, *J* = 278.4 Hz), 126.2, 125.8, 125.6, 123.0, 80.5, 62.1, 61.2, 40.2, 38.1, 37.9, 35.6 (q, *J* = 28.7 Hz), 35.5 (q, *J* = 28.8 Hz), 29.8. The major isomer: ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.67 (t, *J* = 10.9 Hz). The minor isomer: ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.57 (t, *J* = 10.9 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{29}F_3N_5O$ 580.2319; found: 580.2325.

Spectral data for (*Z*)-2-azido-*N*-(4,4-dimethyl-3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)-2,2-diphenylacetamide (3r)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (61% yield, 52 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.38 – 7.26 (m, 10H), 3.37 (d, *J* = 10.8 Hz, 1H), 3.21 (d, *J* = 11.0 Hz, 1H), 2.98 – 2.82 (m, 1H), 2.79 – 2.71 (m, 1H), 2.14 – 1.97 (m, 1H), 1.23 (s, 3H), 1.00 (s, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 184.8, 174.6, 140.9, 140.8, 128.1, 128.0, 127.9, 127.8, 126.8 (q, *J* = 276.0 Hz), 78.9, 59.0, 49.0 (q, *J* = 2.7 Hz), 39.4, 29.5 (q, *J* = 30.0 Hz), 25.0 (q, *J* = 1.9 Hz), 22.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.72 (t, *J* = 11.5 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}F_3N_5O$ 430.1849; found: 430.1862.

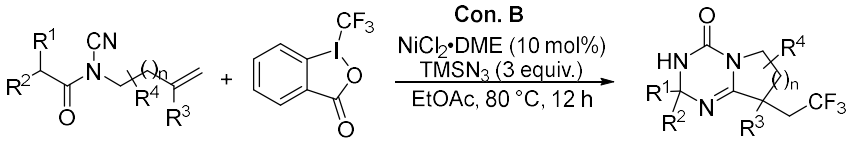
Spectral data for (*Z*)-2,2-diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-*N*-(9-(2,2,2-trifluoroethyl)-7-azaspiro[4.5]decan-8-ylidene)acetamide (3s)



According to the general procedure, upon completion, the mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered with a pad of silica gel, the filtrate was concentrated under reduced pressure. Then the residue and CuI (20 mol%, 0.04 mmol) were added in a 25 mL oven-dried sealed tube. The tube was evacuated and backfilled with N_2 for three times, after that, phenylacetylene (0.6 mmol, 3.0 equiv.) and THF (2.0 mL) were then added via syringe under N_2. The tube was sealed with a Teflon lined cap and moved into a preheated oil bath at 60 °C for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and filtered

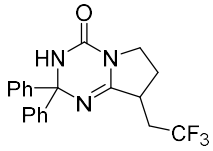
through a pad of Celite. The filtrate was concentrated, and the residue was then purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (8% yield, 10 mg) as yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.77 (s, 1H), 7.40 – 7.27 (m, 13H), 3.24 – 3.08 (m, 2H), 2.76 – 2.62 (m, 2H), 1.99 – 1.85 (m, 2H), 1.80 – 1.72 (m, 1H), 1.70 – 1.58 (m, 5H), 1.53 – 1.40 (m, 3H). ^{13}C{H^{1}} NMR (125 MHz, $CDCl_3$) δ 182.1, 171.2, 145.8, 140.4, 140.3, 131.1, 130.0, 129.7, 128.8, 128.3, 128.0, 127.9, 126.8 (q, *J* = 276.6 Hz), 125.8, 123.0, 80.6, 51.9, 40.4, 38.5, 37.8, 35.9 (q, *J* = 28.1 Hz), 35.0, 34.0, 24.8, 24.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.25 (t, *J* = 11.3 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{33}F_3N_5O$ 572.2632; found: 572.2622.

2. General procedure for preparation of products 4



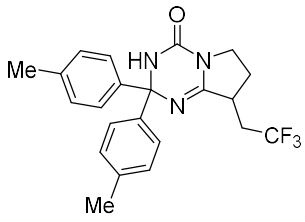
To a flame-dried sealed tube equipped with a magnetic stir bar were added **1** (0.2 mmol, 1 equiv.), Togni's reagent **2a** (0.3 mmol, 1.5 equiv.) and $NiCl_2$·DME (10 mol %, 0.02 mmol). The tube was evacuated and backfilled with nitrogen for three times. Then ethyl acetate (2.0 mL) and $TMSN_3$ (0.6 mmol, 3 equiv.) were added *via* syringe. The tube was stirred at 80 °C for 12 h. After completion, the mixture was cooled to room temperature, and sat. aq. soln. of $NaHCO_3$ was added. Then the aqueous phase was extracted with DCM, washed with brine, dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the crude was purified by flash chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to give the desired compounds **4**.

Spectral data for 2,2-diphenyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5] triazine-4(3H)-one (4a)



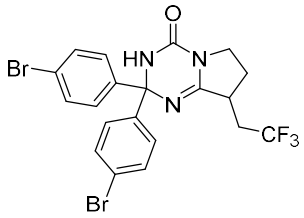
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (63% yield, 48 mg) as white solid, mp: 205-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.23 (m, 10H), 5.85 (brs, 1H), 3.83 (t, *J* = 9.7 Hz, 1H), 3.59 – 3.44 (m, 1H), 3.15 – 2.96 (m, 2H), 2.47 – 2.34 (m, 1H), 2.19 – 1.99 (m, 1H), 1.82 – 1.65 (m, 1H). ^{13}C{H^{1}} NMR (100 MHz, $CDCl_3$) δ 157.4, 151.1, 145.4, 145.3, 128.5, 128.4, 126.8 (q, *J* = 276.7 Hz), 126.4, 126.1, 79.4, 43.3, 36.8 (q, *J* = 2.9 Hz), 35.9 (q, *J* = 29.1 Hz), 27.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.67 (t, *J* = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}F_3N_3O$ 374.1475; found: 374.1482.

Spectral data for 2,2-di-p-tolyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5] triazin-4(3H)-one (4b)



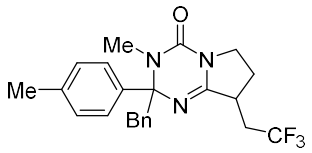
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (51% yield, 41 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 4H), 7.15 – 7.09 (m, 4H), 5.67 (brs, 1H), 3.89 – 3.76 (m, 1H), 3.59 – 3.45 (m, 1H), 3.13 – 2.96 (m, 2H), 2.49 – 2.37 (m, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 2.16 – 2.01 (m, 1H), 1.81 – 1.68 (m, 1H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 157.1, 151.1, 142.7, 142.5, 137.8, 137.6, 129.2, 129.1, 126.8 (q, *J* = 276.6 Hz), 126.3, 126.0, 79.2, 43.3, 36.7 (q, *J* = 3.1 Hz), 35.9 (q, *J* = 29.2 Hz), 27.4, 21.2, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.69 (t, *J* = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}F_3N_3O$ 402.1788; found: 402.1775.

Spectral data for 2,2-bis(4-bromophenyl)-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo [1,2-a][1,3,5]triazin-4(3H)-one (4c)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (57% yield, 61 mg) as yellowish solid, mp: 208-210 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 4H), 7.31 – 7.20 (m, 4H), 5.88 (brs, 1H), 3.96 – 3.74 (m, 1H), 3.64 – 3.47 (m, 1H), 3.23 – 2.88 (m, 2H), 2.63 – 2.35 (m, 1H), 2.19 – 1.97 (m, 1H), 1.91 – 1.70 (m, 1H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 157.9, 151.3, 144.1, 144.0, 131.7, 131.6, 128.2, 127.9, 126.6 (q, *J* = 276.6 Hz), 122.4, 122.2, 78.7, 43.4, 36.8 (q, *J* = 3.0 Hz), 35.8 (q, *J* = 29.2 Hz), 27.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.67 (t, *J* = 10.8 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}Br_2F_3N_3O$ 529.9685; found: 529.9682.

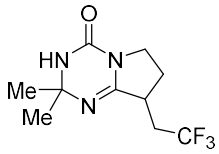
Spectral data for 2-benzyl-3-methyl-2-(p-tolyl)-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo [1,2-a][1,3,5]triazin-4(3H)-one (4d)



According to the general procedure, upon completion, the mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered with a pad of silica gel, the filtrate was concentrated under reduced pressure. Then to a solution of residue in THF (0.8 mL) was added NaH (2.0 equiv) and MeI (1.2 equiv) at 0 °C. The resulting mixture was warmed to room temperature for 20 h. After completion, the solvent was evaporated and the residue was dissolved in EtOAc, washed with H_2O and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (an inseparable mixture, 30% yield, 25 mg, dr = 1.1/1) as yellowish oil. The mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.32 – 7.27 (m, 5H), 7.25 – 7.11 (m, 9H), 3.64 – 3.53 (m, 3H), 3.27 (d, *J* = 7.0 Hz, 1H), 3.25 (d, *J* = 7.0 Hz, 1H), 3.23 – 3.17 (m, 1H), 3.14 – 3.08 (m, 1H), 2.94 – 2.85 (m, 1H), 2.84 – 2.77 (m, 2H), 2.75 (s, 6H), 2.72 – 2.65 (m, 1H), 2.64 – 2.56 (m, 1H), 2.37 (s, 6H), 2.15 – 2.07 (m, 1H), 2.07 – 1.96 (m, 2H), 1.95 – 1.83 (m, 1H), 1.61 – 1.53 (m, 1H), 1.12 – 0.99 (m, 1H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 155.9, 155.3, 151.1, 150.8, 141.1, 138.1, 138.0, 136.0, 135.9, 131.0, 130.8, 129.3, 129.2, 127.7, 127.6, 127.1, 127.0, 126.7 (q, *J* = 276.7 Hz), 126.5, 126.4, 82.9, 82.8, 42.8, 42.7, 41.7, 41.3, 36.6 (q, *J* = 2.9 Hz), 36.5 (q, *J* = 3.0 Hz), 35.6 (q, *J* = 28.9 Hz), 35.3 (q, *J* = 28.9 Hz), 30.2, 30.1, 27.0, 26.8, 21.1. ^{19}F NMR (470

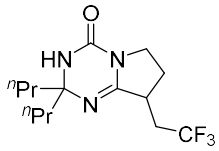
MHz, $CDCl_3$) δ -64.81 (t, J = 11.0 Hz), -64.92 (t, J = 11.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{25}F_3N_3O$ 416.1944; found: 416.1964.

Spectral data for 2,2-dimethyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5] triazin-4(3H)-one (4e)



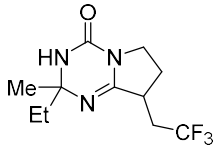
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (47% yield, 24 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (brs, 1H), 3.90 – 3.81 (m, 1H), 3.57 – 3.46 (m, 1H), 3.02 – 2.92 (m, 1H), 2.92 – 2.81 (m, 1H), 2.48 – 2.36 (m, 1H), 2.15 – 1.99 (m, 1H), 1.87 – 1.71 (m, 1H), 1.44 (s, 3H), 1.39 (s, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 156.5, 151.8, 126.8 (q, J = 276.7 Hz), 72.4, 43.0, 36.4 (q, J = 2.9 Hz), 35.9 (q, J = 29.0 Hz), 31.1, 30.6, 27.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.68 (t, J = 10.8 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}F_3N_3O$ 250.1162; found: 250.1169.

Spectral data for 2,2-dipropyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5] triazin-4(3H)-one (4f)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (45% yield, 28 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (brs, 1H), 3.84 – 3.71 (m, 1H), 3.44 – 3.34 (m, 1H), 2.99 – 2.72 (m, 2H), 2.39 – 2.26 (m, 1H), 2.07 – 1.91 (m, 1H), 1.77 – 1.63 (m, 1H), 1.61 – 1.49 (m, 2H), 1.46 – 1.35 (m, 2H), 1.34 – 1.23 (m, 2H), 1.21 – 1.12 (m, 2H), 0.84 (t, J = 7.2 Hz, 3H), δ 0.83 (t, J = 7.3 Hz, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 156.1, 151.9, 126.8 (q, J = 276.7 Hz), 77.8, 45.2, 45.0, 42.7, 36.5 (q, J = 2.8 Hz), 36.0 (q, J = 28.9 Hz), 27.4, 16.7, 16.6, 14.3, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.69 (t, J = 10.9 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{23}F_3N_3O$ 306.1788; found: 306.1783.

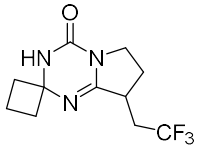
Spectral data for 2-ethyl-2-methyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5] triazin-4(3H)-one (4g)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (an inseparable mixture, 53% yield, 28 mg, dr = 1.2/1) as yellowish oil. The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (brs, 1H), 3.92 – 3.78 (m, 1H), 3.56 – 3.43 (m, 1H), 3.05 – 2.77 (m, 2H), 2.46 – 2.34 (m, 1H), 2.16 – 1.97 (m, 1H), 1.85 – 1.74 (m, 1H), 1.73 – 1.53 (m, 2H), 1.39 (s, 3H), 0.88 (t, J = 7.5 Hz, 3H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (brs, 1H), 3.92 – 3.78 (m, 1H), 3.56 – 3.43 (m, 1H), 3.05 – 2.77 (m, 2H), 2.46 – 2.34 (m, 1H), 2.16 – 1.97 (m, 1H), 1.85 – 1.74 (m, 1H), 1.73 – 1.53 (m, 2H), 1.34 (s, 3H), 0.88 (t, J = 7.5 Hz, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 156.5, 156.4, 152.1, 151.9, 126.8 (q, J = 276.7 Hz), 126.7 (q, J = 276.7 Hz), 75.3, 75.1, 42.9, 36.6 (q, J = 2.9 Hz), 36.4 (q, J = 2.7 Hz), 36.3, 36.2, 36.0 (q, J = 28.9 Hz), 35.9 (q, J = 28.9 Hz), 29.7, 29.4,

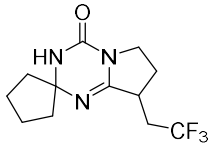
27.4, 27.3, 8.0, 7.9. The mixture: ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.69 (t, J = 10.9 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}F_3N_3O$ 264.1318; found: 264.1328.

Spectral data for 8'-(2,2,2-trifluoroethyl)-7',8'-dihydro-6'H-spiro[cyclobutane-1,2'-pyrrolo[1,2-a][1,3,5]triazin]-4'(3'H)-one (4h)



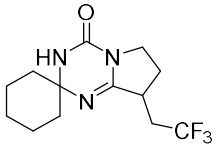
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (52% yield, 27 mg) as yellowish oil. ^1H NMR (500 MHz, $CDCl_3$) δ 5.42 (brs, 1H), 3.92 – 3.75 (m, 1H), 3.55 – 3.41 (m, 1H), 3.04 – 2.86 (m, 2H), 2.49 – 2.32 (m, 2H), 2.30 – 2.15 (m, 3H), 2.14 – 2.03 (m, 1H), 2.03 – 1.89 (m, 1H), 1.86 – 1.67 (m, 2H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 156.2, 151.5, 126.8 (q, J = 276.7 Hz), 75.1, 42.9, 40.9, 40.1, 36.4 (q, J = 2.9 Hz), 35.9 (q, J = 28.8 Hz), 27.4, 12.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.68 (t, J = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{15}F_3N_3O$ 262.1162; found: 262.1155.

Spectral data for 8'-(2,2,2-trifluoroethyl)-7',8'-dihydro-6'H-spiro[cyclopentane-1,2'-pyrrolo[1,2-a][1,3,5]triazin]-4'(3'H)-one (4i)



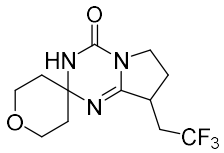
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (63% yield, 35 mg) as white solid, mp: 140-142 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (brs, 1H), 3.88 – 3.80 (m, 1H), 3.54 – 3.45 (m, 1H), 3.02 – 2.79 (m, 2H), 2.47 – 2.34 (m, 1H), 2.17 – 1.99 (m, 1H), 1.96 – 1.88 (m, 1H), 1.87 – 1.63 (m, 8H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 156.3, 152.2, 126.8 (q, J = 276.7 Hz), 82.1, 43.0, 42.1, 41.9, 36.3 (q, J = 3.1 Hz), 35.9 (q, J = 28.8 Hz), 27.4, 22.9, 22.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.67 (t, J = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{17}F_3N_3O$ 276.1318; found: 276.1327.

Spectral data for 8'-(2,2,2-trifluoroethyl)-7',8'-dihydro-6'H-spiro[cyclohexane-1,2'-pyrrolo[1,2-a][1,3,5]triazin]-4'(3'H)-one (4k)



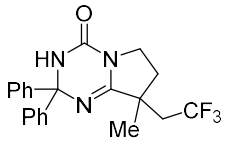
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (49% yield, 28 mg) as yellowish solid, mp: 154-156 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 5.29 (brs, 1H), 3.91 – 3.77 (m, 1H), 3.56 – 3.43 (m, 1H), 3.04 – 2.81 (m, 2H), 2.50 – 2.34 (m, 1H), 2.19 – 1.96 (m, 1H), 1.86 – 1.62 (m, 5H), 1.63 – 1.41 (m, 6H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 156.1, 151.8, 126.8 (q, J = 276.7 Hz), 73.6, 43.0, 39.5, 39.1, 36.4 (q, J = 2.8 Hz), 36.0 (q, J = 28.9 Hz), 27.5, 25.2, 21.9, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.64 (t, J = 10.9 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{19}F_3N_3O$ 290.1475; found: 290.1484.

Spectral data for 8'-(2,2,2-trifluoroethyl)-2,3,5,6,7',8'-hexahydro-6'H-spiro[pyran-4,2'-pyrrolo[1,2-a][1,3,5]triazin]-4'(3'H)-one (4l)



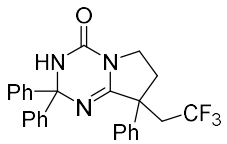
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 2/1) to afford the title compound (49% yield, 29 mg) as yellowish solid, mp: 169-171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (brs, 1H), 3.99 – 3.90 (m, 1H), 3.89 – 3.83 (m, 1H), 3.83 – 3.70 (m, 3H), 3.57 – 3.45 (m, 1H), 3.04 – 2.83 (m, 2H), 2.50 – 2.39 (m, 1H), 2.17 – 2.03 (m, 1H), 1.87 – 1.76 (m, 3H), 1.76 – 1.68 (m, 2H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 156.6, 151.6, 126.7 (q, J = 276.6 Hz), 71.2, 64.1, 64.0, 43.1, 40.4, 40.2, 36.6 (q, J = 2.9 Hz), 35.9 (q, J = 29.0 Hz), 27.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.61 (t, J = 10.8 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{17}F_3N_3O_2$ 292.1267; found: 292.1273.

Spectral data for 8-methyl-2,2-diphenyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5]triazin-4(3H)-one (4m)



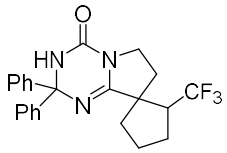
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (55% yield, 43 mg) as white solid, mp: 159-161 °C; and 12% yield of **7b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 10H), 5.67 (brs, 1H), 3.74 – 3.64 (m, 1H), 3.56 – 3.43 (m, 1H), 2.76 – 2.58 (m, 1H), 2.34 – 2.17 (m, 1H), 2.07 – 1.86 (m, 2H), 1.27 (s, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 160.1, 150.1, 144.2, 143.9, 127.3, 127.2, 126.8, 126.7, 125.5 (q, J = 277.7 Hz), 125.2, 125.1, 78.0, 41.0, 40.8, 40.2 (q, J = 27.7 Hz), 31.6, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.31 (t, J = 11.4 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}F_3N_3O$ 388.1631; found: 388.1648.

Spectral data for 2,2,8-triphenyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5]triazin-4(3H)-one (4n)



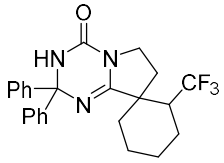
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (15% yield, 14 mg) as yellowish oil; and 10% yield of **7c**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.23 (m, 15H), 5.62 (brs, 1H), 3.90 – 3.79 (m, 1H), 3.41 – 3.30 (m, 1H), 3.18 – 3.01 (m, 1H), 2.92 – 2.66 (m, 2H), 2.33 – 2.17 (m, 1H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 159.3, 151.0, 145.1, 144.9, 137.9, 128.9, 128.5, 128.1, 128.0, 127.6 (q, J = 277.9 Hz), 126.6, 126.3, 79.7, 49.2 (q, J = 2.3 Hz), 42.9 (q, J = 27.4 Hz), 41.9, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.20 (t, J = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{23}F_3N_3O$ 450.1779; found: 450.1788.

Spectral data for 2',2'-diphenyl-2-(trifluoromethyl)-2',3',6',7'-tetrahydro-4'H-spiro[cyclopentane-1,8'-pyrrolo[1,2-a][1,3,5]triazin]-4'-one (4o)



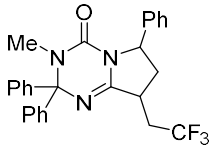
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (30% yield, 25 mg, dr > 19/1) as yellowish oil; and 11% yield of **7d** (dr >19/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.20 (m, 10H), 5.62 (brs, 1H), 3.85 – 3.73 (m, 1H), 3.59 – 3.46 (m, 1H), 3.37 – 3.23 (m, 1H), 2.33 – 2.15 (m, 2H), 2.02 – 1.70 (m, 6H). ^{13}C{H^{1}} NMR (100 MHz, $CDCl_3$) δ 161.1, 151.2, 145.4, 145.0, 128.4, 128.3, 128.0, 127.9, 127.5 (q, *J* = 278.9 Hz), 126.4, 126.3, 79.2, 52.7, 48.4 (q, *J* = 26.2 Hz), 42.4, 39.4, 29.4, 26.0 (q, *J* = 2.5 Hz), 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.69 (d, *J* = 10.4 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}F_3N_3O$ 414.1788; found: 414.1794.

Spectral data for 2',2'-diphenyl-2-(trifluoromethyl)-2',3',6',7'-tetrahydro-4'H-spiro[cyclohexane-1,8'-pyrrolo[1,2-a][1,3,5]triazin]-4'-one (4p)



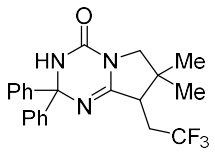
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (42% yield, 36 mg, dr > 19/1) as yellowish oil and 18% yield of **7e** (dr = 3.3/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.26 (m, 8H), 5.52 (brs, 1H), 3.76 – 3.57 (m, 2H), 2.85 – 2.67 (m, 1H), 2.31 – 2.19 (m, 1H), 2.03 – 1.95 (m, 1H), 1.90 – 1.68 (m, 4H), 1.63 – 1.54 (m, 1H), 1.52 – 1.32 (m, 3H). ^{13}C{H^{1}} NMR (100 MHz, $CDCl_3$) δ 161.8, 151.3, 145.5, 145.0, 128.3, 128.2, 127.9, 127.8, 127.3 (q, *J* = 281.7 Hz), 126.7, 126.5, 79.3, 46.4 (q, *J* = 24.7 Hz), 46.3, 42.3, 37.8, 25.8, 24.4, 22.8 (q, *J* = 2.8 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.69 (d, *J* = 9.3 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}F_3N_3O$ 428.1944; found: 428.1952.

Spectral data for 3-methyl-2,2,6-triphenyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5]triazin-4(3H)-one (4q)



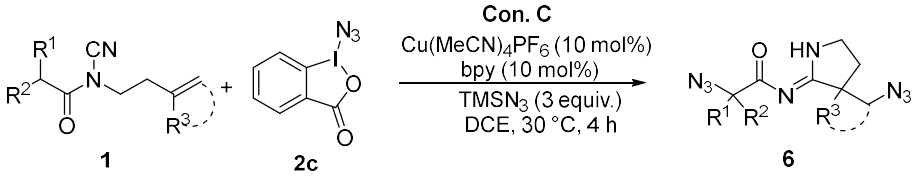
According to the general procedure, upon completion, the mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered with a pad of silica gel, the filtrate was concentrated under reduced pressure. Then to a solution of residue in THF (0.8 mL) was added NaH (2.0 equiv) and MeI (1.2 equiv) at 0 °C. The resulting mixture was warmed to room temperature for 20 h. After completion, the solvent was evaporated and the residue was dissolved in EtOAc, washed with H_2O and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (an inseparable mixture, 56% yield, 52 mg, dr = 1/1) as white solid. The mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 6H), 7.38 – 7.29 (m, 12H), 7.29 – 7.26 (m, 2H), 7.23 – 7.19 (m, 6H), 6.89 – 6.83 (m, 4H), 5.46 (dd, *J* = 7.9, 2.5 Hz, 1H), 5.04 (dd, *J* = 9.7, 6.8 Hz, 1H), 3.24 – 3.13 (m, 1H), 3.06 – 2.91 (m, 3H), 2.84 – 2.75 (m, 1H), 2.69 (s, 3H), 2.62 (s, 3H), 2.37 – 2.25 (m, 2H), 2.23 – 2.12 (m, 1H), 2.01 – 1.88 (m, 1H), 1.52 – 1.41 (m, 1H). ^{13}C{H^{1}} NMR (125 MHz, $CDCl_3$) δ 159.1, 157.9, 152.2, 151.4, 143.2, 142.9, 142.6, 142.3, 141.6, 140.9, 129.2, 128.9, 128.8, 128.5, 128.4, 128.2, 127.8, 127.6, 127.5, 127.2, 126.8 (q, *J* = 276.5 Hz), 125.5, 125.1, 84.1, 83.4, 60.4, 58.5, 38.4, 37.4, 36.0 (q, *J* = 28.3 Hz), 35.7, 35.5 (q, *J* = 29.1 Hz), 34.9, 32.0, 31.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.57 (t, *J* = 11.0 Hz, 3F), -64.76 (t, *J* = 10.9 Hz, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{25}F_3N_3O$ 464.1944; found: 464.1949.

Spectral data for 7,7-dimethyl-2,2-diphenyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo [1,2-a][1,3,5]triazin-4(3H)-one (4r)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (60% yield, 48 mg) as yellowish solid, mp: 174-176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 4H), 7.34 – 7.23 (m, 6H), 6.02 (brs, 1H), 3.53 (d, *J* = 10.5 Hz, 1H), 3.26 (d, *J* = 10.5 Hz, 1H), 2.99 – 2.83 (m, 1H), 2.79 – 2.72 (m, 1H), 2.23 – 2.09 (m, 1H), 1.20 (s, 3H), 0.74 (s, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 157.7, 151.4, 145.4, 145.2, 128.5, 128.3, 127.9, 127.8, 126.8 (q, *J* = 276.7 Hz), 126.4, 126.0, 79.1, 56.3, 46.4, 38.6, 30.2 (q, *J* = 30.0 Hz), 24.3, 21.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.72 (t, *J* = 11.5 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}F_3N_3O$ 402.1788; found: 402.1780.

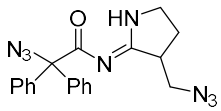
3. General procedure for preparation of products 6



1 2c 6

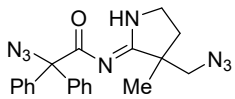
To a flame-dried sealed tube equipped with a magnetic stir bar were added **1** (0.2 mmol, 1 equiv.), **2c** (0.4 mmol, 2.0 equiv.), $Cu(MeCN)_4PF_6$ (10 mol%), bpy (10 mol%, 0.02 mmol). The tube was evacuated and backfilled with nitrogen for three times. Then DCE (2.0 mL) and $TMSN_3$ (0.6 mmol, 3 equiv.) were added *via* syringe. The tube was stirred at 30 °C for 4 h. After completion, the mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered with a pad of silica gel, the filtrate was concentrated under reduced pressure. The residue was then purified by flash column chromatography to give the triazoles **6**.

Spectral data for (*Z*)-2-azido-N-(3-(azidomethyl)pyrrolidin-2-ylidene)-2,2-diphenylacetamide (6a)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (49% yield, 37 mg) as white solid, mp: 135-137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.43 – 7.26 (m, 10H), 3.73 – 3.62 (m, 2H), 3.62 – 3.53 (m, 2H), 3.08 – 2.87 (m, 1H), 2.30 – 2.15 (m, 1H), 2.05 – 1.91 (m, 1H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 184.9, 174.8, 140.9, 140.8, 128.6, 128.5, 128.1, 128.0, 127.9, 78.8, 52.0, 45.8, 44.9, 23.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}N_8O$ 375.1676; found: 375.1680.

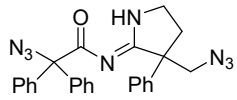
Spectral data for (*Z*)-2-azido-*N*-(3-(azidomethyl)-3-methylpyrrolidin-2-ylidene)-2,2- diphenylacetamide (6b)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (68% yield, 53 mg) as white solid, mp: 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.40 – 7.26 (m, 10H), 3.68 – 3.55 (m, 2H), 3.62 (d, *J* = 11.9 Hz, 1H), 3.25 (d, *J* = 11.9 Hz, 1H), 2.29 – 2.16 (m, 1H), 1.86 – 1.75 (m, 1H),

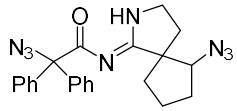
1.15 (s, 3H). $^{13}C\{H^1\}$ NMR (125 MHz, $CDCl_3$) δ 185.4, 177.8, 141.1, 141.0, 128.6, 128.5, 128.0, 127.8, 78.9, 58.0, 48.7, 44.4, 30.1, 22.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}N_8O$ 389.1833; found: 389.1824.

Spectral data for (*Z*)-2-azido-N-(3-(azidomethyl)-3-phenylpyrrolidin-2-ylidene)-2,2- diphenylacetamide (6c)



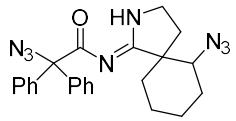
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (25% yield, 23 mg) as yellowish oil. ^1H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.29 (m, 8H), 7.29 – 7.20 (m, 5H), 3.90 (d, *J* = 12.0 Hz, 1H), 3.68 – 3.62 (m, 1H), 3.56 (d, *J* = 12.1 Hz, 1H), 3.54 – 3.47 (m, 1H), 2.59 – 2.45 (m, 2H). $^{13}C\{H^1\}$ NMR (125 MHz, $CDCl_3$) δ 185.0, 175.5, 140.8, 140.5, 138.3, 128.9, 128.7, 128.2, 128.1, 128.0, 127.8, 126.7, 79.2, 57.9, 56.0, 44.3, 30.0. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}N_8O$ 451.1989; found: 451.1993.

Spectral data for (*Z*)-2-azido-N-(6-azido-2-azaspiro[4.4]nonan-1-ylidene)-2,2-diphenylacetamide (6d)



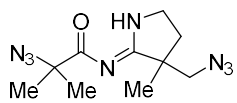
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (67% yield, dr > 19/1, 56 mg) as white solid, mp: 141-143 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.41 – 7.26 (m, 10H), 4.10 (dd, *J* = 9.3, 7.7 Hz, 1H), 3.69 – 3.61 (m, 1H), 3.59 – 3.51 (m, 1H), 2.39 – 2.28 (m, 1H), 2.19 – 2.06 (m, 1H), 2.01 – 1.88 (m, 1H), 1.78 – 1.68 (m, 3H), 1.67 – 1.56 (m, 2H). $^{13}C\{H^1\}$ NMR (125 MHz, $CDCl_3$) δ 185.2, 178.1, 141.1, 140.9, 128.6, 128.5, 128.0, 127.8, 79.0, 67.6, 57.8, 44.8, 35.5, 30.1, 27.8, 20.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}N_8O$ 415.1989; found: 415.1998.

Spectral data for (*Z*)-2-azido-N-(6-azido-2-azaspiro[4.5]decan-1-ylidene)-2,2-diphenylacetamide (6e)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (71% yield, dr > 19/1, 61 mg) as white solid, mp: 179-181 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.41 – 7.25 (m, 10H), 3.86 – 3.76 (m, 1H), 3.67 – 3.47 (m, 2H), 2.22 – 2.08 (m, 1H), 2.02 – 1.89 (m, 1H), 1.85 – 1.72 (m, 2H), 1.67 – 1.57 (m, 2H), 1.55 – 1.43 (m, 1H), 1.40 – 1.10 (m, 3H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 185.4, 178.3, 141.2, 141.0, 128.6, 128.5, 128.1, 128.0, 127.8, 127.7, 78.9, 64.3, 53.3, 44.9, 33.6, 28.1, 24.7, 24.2, 21.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{25}N_8O$ 429.2146; found: 429.2129.

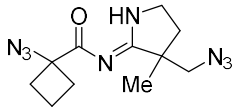
Spectral data for (*Z*)-2-azido-N-(3-(azidomethyl)-3-methylpyrrolidin-2-ylidene)-2-methylpropanamide (6f)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (57% yield, 30 mg) as colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 3.86 – 3.70 (m, 1H), 3.70 – 3.56 (m, 2H), 3.30 (d, *J* = 12.0 Hz, 1H), 2.33 – 2.16 (m, 1H), 1.88 – 1.78 (m, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 1.24 (s, 3H). $^{13}C\{H^1\}$ NMR (125 MHz, $CDCl_3$) δ 188.3, 177.8, 65.9, 57.9, 48.8, 44.2, 30.1, 24.9, 24.8, 22.3. HRMS (ESI) m/z: $[M+H]^+$

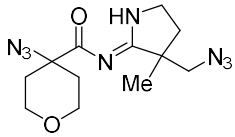
calcd for $C_{10}H_{17}N_8O$ 265.1520; found: 265.1525.

Spectral data for (*Z*)-1-azido-N-(3-(azidomethyl)-3-methylpyrrolidin-2-ylidene)cyclobutane-1-carboxamide (6g)



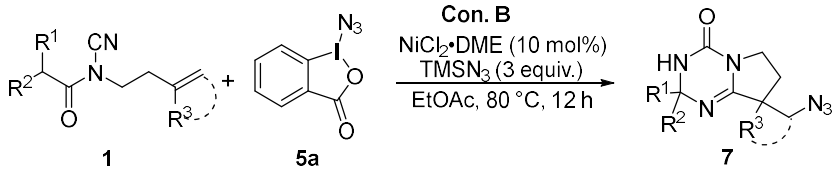
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (45% yield, 25 mg) as yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 3.76 (d, *J* = 12.0 Hz, 1H), 3.71 – 3.58 (m, 2H), 3.31 (d, *J* = 12.0 Hz, 1H), 2.68 – 2.55 (m, 2H), 2.32 – 2.15 (m, 3H), 2.08 – 1.90 (m, 2H), 1.88 – 1.78 (m, 1H), 1.24 (s, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 187.1, 177.6, 68.1, 57.9, 48.9, 44.3, 31.5, 31.2, 30.2, 22.3, 14.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}N_8O$ 277.1520; found: 277.1508.

Spectral data for (*Z*)-4-azido- N-(3-(azidomethyl) -3-methylpyrrolidin -2-ylidene) tetrahydro-2H -pyran-4-carboxamide (6h)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (52% yield, 32 mg) as white solid, mp: 97-99 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 3.84 – 3.77 (m, 2H), 3.77 – 3.70 (m, 3H), 3.70 – 3.59 (m, 2H), 3.29 (d, *J* = 12.0 Hz, 1H), 2.29 – 2.23 (m, 1H), 2.23 – 2.14 (m, 2H), 1.87 – 1.80 (m, 1H), 1.79 – 1.67 (m, 2H), 1.23 (s, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 186.4, 178.2, 65.9, 64.1, 64.0, 58.0, 48.8, 44.3, 32.4, 32.3, 30.1, 22.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{19}N_8O_2$ 307.1625; found: 307.1632.

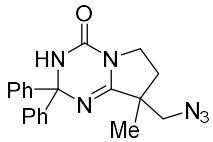
4. General procedure for preparation of products 7



1 **5a** **7**

The general procedure is the same as that of preparation **4** (Con. B).

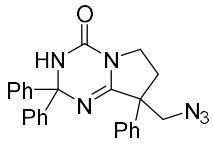
Spectral data for 8-(azidomethyl)-8-methyl-2,2-diphenyl-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5] triazin-4(3H)-one (7b)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (65% yield, 47 mg) as yellowish solid, mp: 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 4H), 7.35 – 7.22 (m, 6H), 5.90 (brs, 1H), 3.76 – 3.67 (m, 1H), 3.64 – 3.53 (m, 1H), 3.61 (d, *J* = 12.0 Hz, 1H), 3.45 (d, *J* = 12.0 Hz, 1H), 2.17 – 2.03 (m, 1H), 1.84 – 1.67 (m, 1H), 1.26 (s, 3H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 160.3, 151.2, 145.5, 145.2, 128.4, 128.3, 127.9, 126.4, 126.3, 79.2, 58.3, 46.2, 41.9, 30.8, 22.4. HRMS (ESI) m/z: $[M+H]^+$ calcd

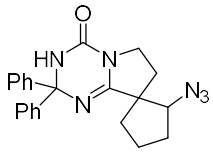
for $C_{20}H_{21}N_6O$ 361.1771; found: 361.1779.

Spectral data for 8-(azidomethyl)-2,2,8-triphenyl-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5]triazine -4(3H)-one (7c)



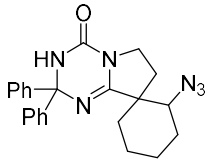
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (36% yield, 31 mg) as yellowish solid, mp: 179-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.21 (m, 15H), 5.91 (brs, 1H), 3.95 (d, *J* = 12.3 Hz, 1H), 3.87 – 3.76 (m, 1H), 3.81 (d, *J* = 12.4 Hz, 1H), 3.41 – 3.27 (m, 1H), 2.48 – 2.31 (m, 2H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 158.4, 151.1, 145.1, 145.0, 138.8, 128.9, 128.5, 128.4, 128.0, 127.9, 126.7, 126.6, 126.5, 79.6, 58.1, 54.0, 41.7, 30.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}N_6O$ 423.1936; found: 423.1928.

Spectral data for 2-azido-2',2'-diphenyl-2',3',6',7'-tetrahydro-4'H-spiro[cyclopentane-1,8'- pyrrolo [1,2-a][1,3,5]triazin]-4'-one (7d)



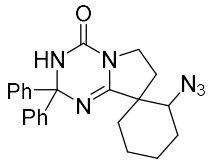
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (50% yield, 39 mg, dr > 19/1) as white solid, mp: 183-185 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.34 – 7.29 (m, 4H), 7.28 – 7.23 (m, 2H), 5.80 (brs, 1H), 4.19 (t, *J* = 7.6 Hz, 1H), 3.77 – 3.69 (m, 1H), 3.60 – 3.52 (m, 1H), 2.35 – 2.28 (m, 1H), 2.28 – 2.20 (m, 1H), 2.06 – 1.98 (m, 1H), 1.94 – 1.80 (m, 2H), 1.80 – 1.67 (m, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 160.7, 151.2, 145.5, 145.3, 128.4, 127.9, 126.4, 126.3, 79.1, 67.9, 55.6, 42.5, 35.7, 30.2, 28.0, 20.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}N_6O$ 387.1928; found: 387.1939.

Spectral data for 2-azido-2',2'-diphenyl-2',3',6',7'-tetrahydro-4'H-spiro[cyclohexane-1,8'-pyrrolo [1,2-a][1,3,5]triazin]-4'-one (7e)



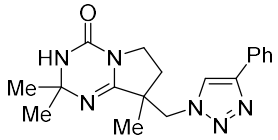
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (an inseparable mixture, 52% yield, 42 mg, dr = 3.1/1) as yellowish solid. The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.35 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 5.84 (brs, 1H), 3.97 – 3.89 (m, 1H), 3.78 – 3.66 (m, 1H), 3.60 – 3.50 (m, 1H), 2.21 – 2.02 (m, 2H), 1.99 – 1.87 (m, 1H), 1.86 – 1.74 (m, 2H), 1.74 – 1.59 (m, 3H), 1.51 – 1.35 (m, 2H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.35 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 5.83 (brs, 1H), 3.78 – 3.66 (m, 1H), 3.60 – 3.50 (m, 1H), 3.44 – 3.36 (m, 1H), 2.68 – 2.58 (m, 1H), 2.21 – 2.02 (m, 2H), 1.99 – 1.87 (m, 1H), 1.86 – 1.74 (m, 2H), 1.74 – 1.59 (m, 3H), 1.51 – 1.35 (m, 1H). The mixture: ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 161.3, 158.6, 151.6, 151.3, 145.6, 145.5, 145.3, 128.3, 127.9, 127.7, 126.5, 126.3, 79.2, 66.1, 65.2, 50.4, 48.2, 42.5, 42.0, 35.4, 34.3, 33.8, 28.3, 26.3, 24.9, 24.5, 24.2, 21.3, 20.7. The major isomer: HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{25}N_6O$ 401.2084; found: 401.2095. The minor isomer: HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{25}N_6O$ 401.2084; found: 401.2092.

Spectral data for 2-azido-2',2'-diphenyl-2',3',6',7'-tetrahydro-4'H-spiro[cyclohexane-1,8'-pyrrolo [1,2-a][1,3,5]triazin]-4'-one (7e-major)



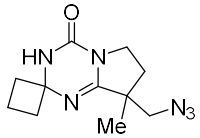
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 4H), 7.36 – 7.30 (m, 4H), 7.30 – 7.27 (m, 2H), 5.61 (brs, 1H), 3.97 – 3.89 (m, 1H), 3.77 – 3.69 (m, 1H), 3.62 – 3.52 (m, 1H), 2.17 – 2.01 (m, 2H), 1.86 – 1.74 (m, 2H), 1.74 – 1.60 (m, 4H), 1.48 – 1.39 (m, 2H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 161.4, 151.1, 145.6, 145.3, 128.4, 127.9, 126.5, 79.3, 65.2, 50.4, 42.5, 34.3, 28.3, 25.0, 24.3, 21.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{25}N_6O$ 401.2084; found: 401.2099.

Spectral data for 2,2,8- trimethyl- 8-((4-phenyl-1H-1,2,3-triazol-1-yl) methyl) -2,6,7,8- tetrahydropyrrolo [1,2-a][1,3,5]triazin-4(3H)-one (7f)



According to the general procedure, upon completion, the mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered with a pad of silica gel, the filtrate was concentrated under reduced pressure.Then the residue and CuI (20 mol%, 0.04 mmol) were added in a 25 mL oven-dried sealed tube. The tube was evacuated and backfilled with N_2 for three times, after that, phenylacetylene (0.6 mmol, 3.0 equiv.) and THF (2.0 mL) were then added via syringe under N_2. The tube was sealed with a Teflon lined cap and moved into a preheated oil bath at 60 ^{o}C for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and filtered through a pad of Celite. The filtrate was concentrated, and the residue was then purified by column chromatography (silica gel, EtOAc/Petroleum ether: 5/1) to afford the title compound (46% yield, 31 mg) as yellowish solid, mp: 219-221 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 5.59 (brs, 1H), 4.65 (d, J = 14.1 Hz, 1H), 4.57 (d, J = 14.0 Hz, 1H), 3.54 (dd, J = 8.8, 5.2 Hz, 2H), 2.22 – 2.12 (m, 1H), 1.93 – 1.85 (m, 1H), 1.49 (s, 3H), 1.48 (s, 3H), 1.33 (s, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 159.1, 151.6, 130.5, 129.0, 128.4, 125.7, 121.4, 72.4, 55.4, 46.1, 41.3, 31.1, 30.9, 30.3, 22.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{23}N_6O$ 339.1928; found: 339.1936.

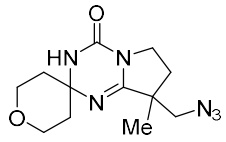
Spectral data for 8' -(azidomethyl) -8'- methyl- 7',8'- dihydro -6'H- spiro [cyclobutane-1,2'-pyrrolo[1,2-a] [1,3,5]triazin]-4'(3'H)-one (7g)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 2/1) to afford the title compound (61% yield, 30 mg) as yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (brs, 1H), 3.75 – 3.68 (m, 1H), 3.63 (d, J = 12.1 Hz, 1H), 3.60 – 3.51 (m, 1H), 3.31 (d, J = 12.2 Hz, 1H), 2.41 – 2.28 (m, 2H), 2.28 – 2.19 (m, 2H), 2.19 – 2.11 (m, 1H), 2.04 – 1.90 (m, 1H), 1.82 – 1.68 (m, 2H), 1.23 (s, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 159.1, 151.8, 75.0,

57.8, 46.0, 41.4, 40.5, 40.1, 30.7, 22.3, 12.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}N_6O$ 249.1458; found: 249.1448.

Spectral data for 8'- (azidomethyl) -8'-methyl -2,3,5,6,7',8' -hexahydro-6' H-spiro [pyran-4,2'-pyrrolo[1,2-a] [1,3,5]triazin]-4'(3'H)-one (7h)

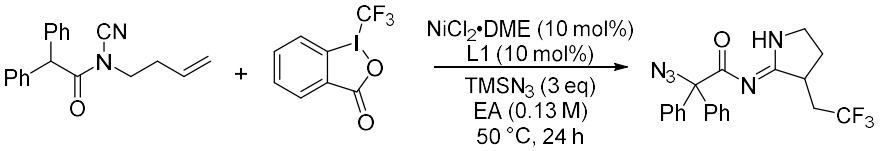


Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 2/1) to afford the title compound (54% yield, 31 mg) as white solid, mp: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (brs, 1H), 3.97 – 3.83 (m, 2H), 3.82 – 3.71 (m, 3H), 3.66 – 3.53 (m, 2H), 3.31 (d, J = 12.1 Hz, 1H), 2.25 – 2.11 (m, 1H), 1.93 – 1.68 (m, 5H), 1.22 (s, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 159.4, 151.9, 71.2, 64.1, 64.0, 58.0, 46.1, 41.6, 40.4, 40.1, 30.6, 22.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{19}N_6O_2$ 279.1564; found: 279.1556.

V. Scale-up Reaction and Synthetic Transformations

1. Scale-up Reaction

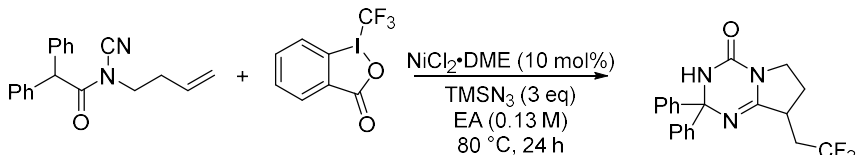
1) Scale-up reaction for preparation of product 3a



1a **2a** (1.5 eq) **3a**

To a flame-dried sealed tube equipped with a magnetic stir bar were added **1a** (2 mmol, 1 equiv.), Togni's reagent **2a** (3 mmol, 1.5 equiv.), $NiCl_2$·DME (10 mol%, 0.2 mmol) and **L1** (10 mol%, 0.2 mmol). The tube was evacuated and backfilled with nitrogen for three times. Then ethyl acetate (15 mL) and $TMSN_3$ (6 mmol, 3 equiv.) were added *via* syringe. The tube was stirred at 50 °C for 24 h. After completion, the mixture was cooled to room temperature, and sat. aq. soln. of $NaHCO_3$ was added. Then the aqueous phase was extracted with DCM, washed with brine, dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the crude was purified by flash chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to give the desired compounds **3a** (442 mg, 55%).

2) Scale-up reaction for preparation of product 4a

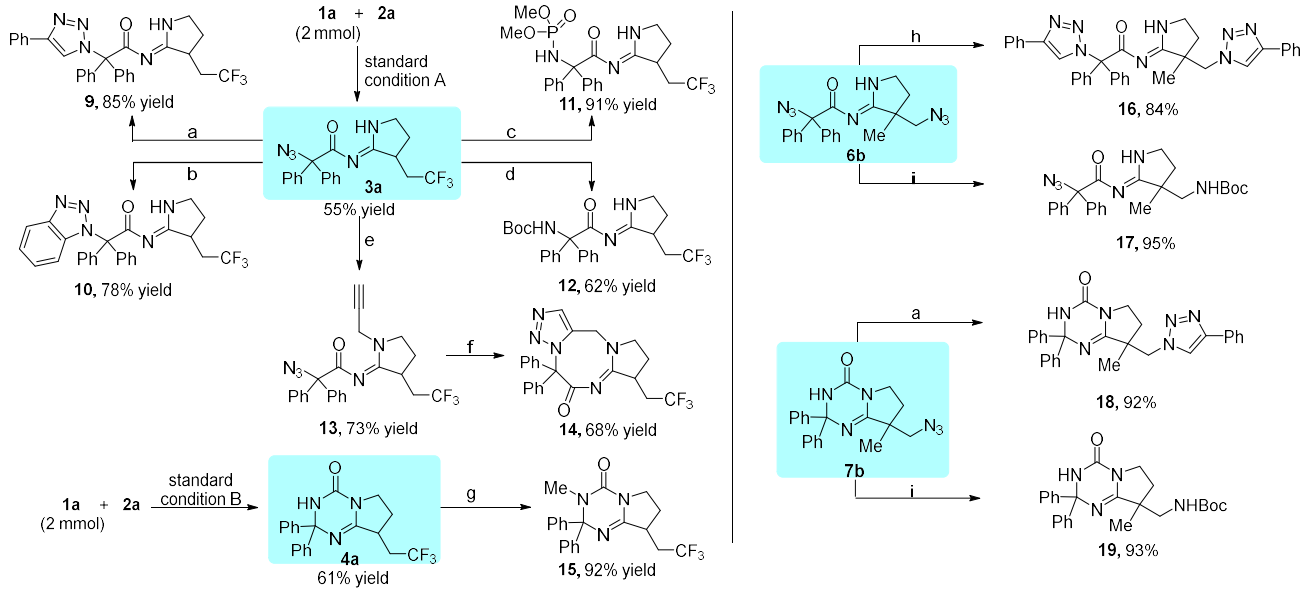


1a **2a** (1.5 eq) **4a**

To a flame-dried sealed tube equipped with a magnetic stir bar were added **1a** (2 mmol, 1 equiv.), Togni's reagent **2a** (3 mmol, 1.5 equiv.) and $NiCl_2$·DME (10 mol%, 0.2 mmol). The tube was evacuated and backfilled with nitrogen for three times. Then ethyl acetate (15 mL) and $TMSN_3$ (6 mmol, 3 equiv.) were added *via* syringe. The tube was stirred at 80 °C for 24 h. After completion, the mixture was cooled to room temperature, and sat. aq. soln. of $NaHCO_3$ was added. Then the aqueous phase was extracted with DCM, washed with brine, dried over Na_2SO_4.

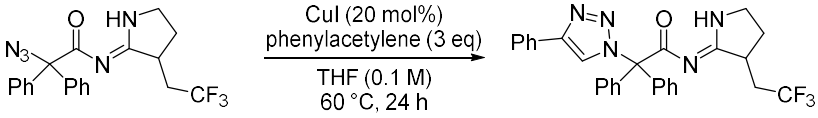
The filtrate was concentrated under reduced pressure and the crude was purified by flash chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to give the desired compounds **4a** (456 mg, 61%).

2. Synthetic Transformations



a Reaction conditions: a) CuI (20 mol %), phenylacetylene (3 equiv.), THF (0.1 M), 60 °C, 24 h. b) CsF (2 equiv.), MeCN (0.1 M), 70 °C, 24 h. c) $P(OMe)_3$ (1.5 equiv.), toulene (0.2 M), 80 °C, 12 h. d) $P(Me)_3$ (2 equiv.), THF/H2O = 4/1 (0.05 M), rt, 4 h, then, Boc_2O (1.2 equiv.), Et_3N (1.2 equiv.), DCM (0.2 M), 0 °C to rt, overnight. e) K_2CO_3 (2 equiv.), 3-Bromopropyne (1.1 equiv.), MeCN (0.25 M), 60 °C, 24 h. f) CuI (20 mol %), THF (0.1 M), 60 °C, 24 h. g) NaH (1.2 equiv.), MeI (1.2 equiv.), THF (0.2 M), 0 °C to rt, 20 h. h) CuI (20 mol%), phenylacetylene (6 equiv.), THF (0.1 M), 60 °C, 24 h. i) PPh_3 (2 equiv.), THF/H_2O = 50/1 (0.1 M), rt, 4 h, then, Boc_2O (1.2 equiv.), Et_3N (1.2 equiv.), DCM (0.2 M), 0 °C to rt, overnight.

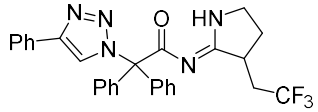
Preparation of product 9 [2]



3a **9**

CuI (0.02 mmol, 20 mol%) and **3a** (0.1 mmol, 1 equiv.) were added in an oven-dried sealed tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), after that, phenylacetylene (0.3 mmol, 3.0 equiv.) and THF (1.0 mL) were then added via syringe under N_2. The tube was sealed with a Teflon lined cap and moved into a preheated oil bath at 60 ºC for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and filtered through a pad of celite. The filtrate was concentrated, and the residue was then purified by flash column chromatography to afford the corresponding product.

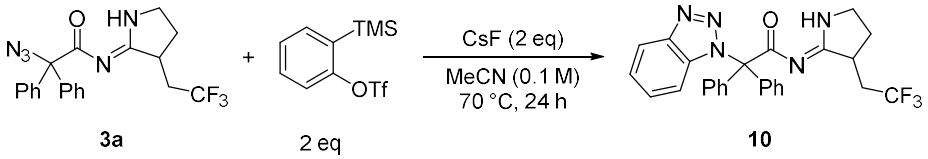
Spectral data for (*Z*)-2,2-diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-*N*-(3-(2,2,2-trifluoroethyl) pyrrolidin-2-ylidene)acetamide (9)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (85% yield, 43 mg) as yellowish solid, (mp: 135-137 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.83 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.27 (m, 13H), 3.71 – 3.53 (m, 2H), 3.04 – 2.90 (m, 1H), 2.67 – 2.50 (m, 1H), 2.45 –

2.32 (m, 1H), 1.95 – 1.74 (m, 2H). $^{13}C\{H^1\}$ NMR (125 MHz, $CDCl_3$) δ 182.4, 174.5, 145.8, 140.1, 140.0, 131.0, 129.8, 129.7, 128.8, 128.5, 128.4, 128.0, 126.7 (q, J = 276.2 Hz), 125.8, 123.1, 80.5, 45.6, 39.4, 35.5 (q, J = 28.9 Hz), 27.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.72 (t, J = 11.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{25}F_3N_5O$ 504.2006; found: 504.2014.

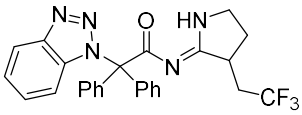
Preparation of product 10 [3]



3a 2 eq **10**

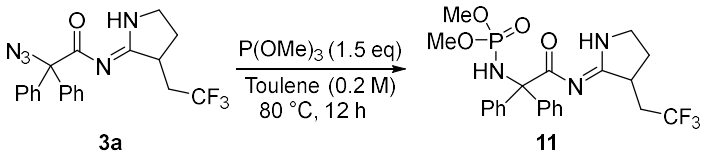
To a stirred solution of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 2.0 equiv.) in CH_3CN (1 mL) were added **3a** (0.1 mmol, 1.0 equiv.) and CsF (0.2 mmol, 2.0 equiv.). The mixture was stirred at 70 °C for 24 h. After completion, the reaction mixture was diluted with DCM and washed with brine. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product.

Spectral data for (*Z*)-2-(1H-benzo[d][1,2,3]triazol-1-yl)-2,2-diphenyl-*N*-(3-(2,2,2-trifluoroethyl) pyrrolidin-2-ylidene)acetamide (10)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (78% yield, 37 mg) as yellowish solid, (mp: 131-134 °C). ^1H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.42 – 7.28 (m, 10H), 7.23 (t, J = 7.9 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.61 (d, J = 8.4 Hz, 1H), 3.59 – 3.43 (m, 2H), 2.85 – 2.72 (m, 1H), 2.35 – 2.24 (m, 1H), 2.13 – 1.98 (m, 1H), 1.76 – 1.64 (m, 1H), 1.58 – 1.43 (m, 1H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 182.8, 174.5, 146.4, 139.2, 138.8, 135.0, 130.2, 129.9, 128.4, 128.3, 128.0, 127.9, 126.5 (q, J = 277.6 Hz), 126.2, 123.3, 119.9, 113.8, 80.3, 45.5, 39.3 (q, J = 2.9 Hz), 35.0 (q, J = 28.9 Hz), 26.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.84 (t, J = 10.9 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{23}F_3N_5O$ 478.1849; found: 478.1862.

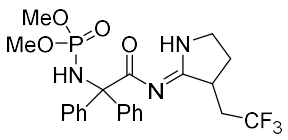
Preparation of product 11 [3]



3a **11**

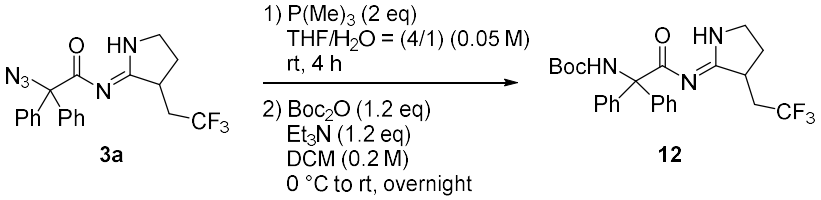
The mixture solution of azide **3a** (0.1 mmol, 1.0 equiv.) and $P(OMe)_3$ (0.15 mmol, 1.5 equiv.) in toluene (0.5 mL) was heated at 80 °C for 12 h. After completion, the organic solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the corresponding product.

Spectral data for dimethyl (*Z*)-(2-oxo-1,1-diphenyl-2-((3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)amino)ethyl) phosphoramidate (11)



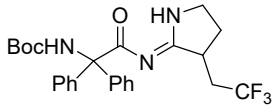
Purified by column chromatography (silica gel, EtOAc) to afford the title compound (91% yield, 44 mg) as yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.54 – 7.46 (m, 4H), 7.33 – 7.21 (m, 6H), 5.72 (d, *J* = 12.0 Hz, 1H), 3.65 – 3.47 (m, 2H), 3.32 (d, *J* = 2.8 Hz, 3H), 3.29 (d, *J* = 2.7 Hz, 3H), 3.05 – 2.90 (m, 1H), 2.90 – 2.67 (m, 1H), 2.43 – 2.29 (m, 1H), 2.02 – 1.70 (m, 2H). ^{13}C{H^{1}} NMR (100 MHz, $CDCl_3$) δ 186.0 (d, *J* = 11.9 Hz), 174.6, 141.8, 141.7, 129.9, 129.7, 127.3, 127.2, 127.0, 126.6 (q, *J* = 277.0 Hz), 71.8, 52.8, 52.7, 45.3, 39.3, 35.4 (q, *J* = 28.7 Hz), 26.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.52 (t, *J* = 11.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 7.14. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{26}F_3N_3O_4P$ 484.1608; found: 484.1592.

Preparation of product 12 [4]



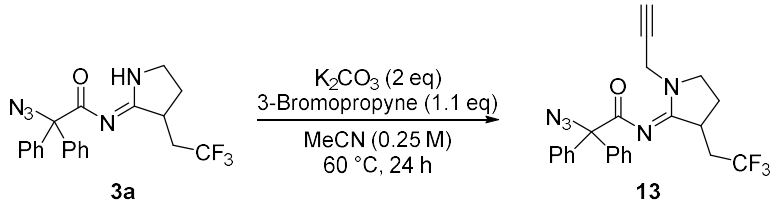
To a solution of the azido **3a** (0.1 mmol, 1 equiv.) in 2 mL of THF/H_2O (4/1), was added $P(Me)_3$ (0.2 mmol, 2 equiv.) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 4 h. The mixture was washed with water and the aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo affording amine without any further purification. To a suspension of amine (0.1 mmol, 1.0 equiv.) in DCM (0.5 ml) was added Et_3N (0.12 mmol, 1.2 equiv.) and Boc_2O (0.12 mmol, 1.2 equiv.) under nitrogen atmosphere at 0 °C. The resulting mixture was allowed to warm up to room temperature and stirred overnight. Upon completion, the reaction mixture was quenched with H_2O and the aqueous phase was extracted with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography to give the desired product.

Spectral data for tert-butyl (*Z*)-(2-oxo-1,1-diphenyl-2-((3-(2,2,2-trifluoroethyl)pyrrolidin-2-ylidene)amino)ethyl) carbamate (12)



Purified by column chromatography (silica gel, EtOAc) to afford the title compound (62% yield, 30 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.55 – 7.39 (m, 4H), 7.35 – 7.22 (m, 6H), 4.86 (s, 1H), 3.35 – 3.19 (m, 1H), 3.14 – 2.87 (m, 3H), 2.51 – 2.27 (m, 1H), 1.98 – 1.83 (m, 2H), 1.42 (s, 9H). ^{13}C{H^{1}} NMR (100 MHz, $CDCl_3$) δ 183.9, 163.8, 157.4, 140.2, 140.0, 128.5, 128.4, 127.7, 127.4 (q, *J* = 278.9 Hz), 127.1, 127.0, 80.6, 37.8, 36.1 (q, *J* = 29.6 Hz), 35.6, 31.6, 28.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.38. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{29}F_3N_3O_3$ 476.2156; found: 476.2160.

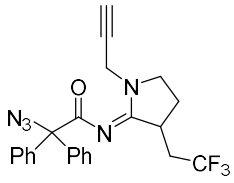
Preparation of product 13 [3]



To a solution of compound **3a** (0.1 mmol, 1.0 equiv.) in CH_3CN (0.4 mL) at 0 °C was added K_2CO_3 (0.2 mmol, 2.0 equiv.) and 3-Bromopropyne (0.11 mmol, 1.1 equiv.). The resulting mixture was heated at 60 °C for

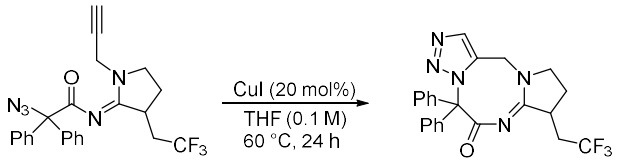
24 h. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in EtOAc, washed with H_2O and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product.

Spectral data for (*Z*)-2-azido-2,2-diphenyl-*N*-(1-(prop-2-yn-1-yl)-3-(2,2,2-trifluoroethyl) pyrrolidin-2-ylidene)acetamide (13)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (73% yield, 32 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.37 – 7.27 (m, 6H), 4.22 (dd, *J* = 2.6 Hz, 2.5 Hz, 2H), 3.83 – 3.71 (m, 1H), 3.64 – 3.48 (m, 2H), 2.37 – 2.29 (m, 1H), 2.28 (t, *J* = 2.6 Hz, 1H), 2.23 – 2.09 (m, 1H), 2.07 – 1.96 (m, 1H), 1.83 – 1.66 (m, 1H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 179.6, 171.1, 140.6, 140.5, 128.7, 128.6, 128.1, 128.0, 126.2 (q, *J* = 277.4 Hz), 79.3, 76.3, 73.6, 47.1, 36.5 (q, *J* = 2.8 Hz), 34.8, 34.0 (q, *J* = 28.9 Hz), 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.94 (t, *J* = 10.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}F_3N_5O$ 440.1693; found: 440.1684.

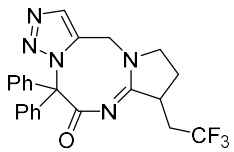
Preparation of product 14 [2]



13 14

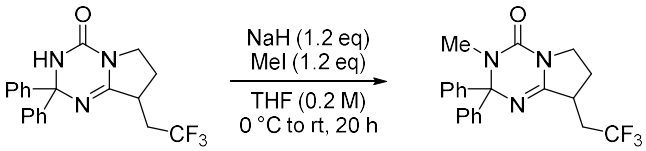
CuI (20 mol%, 0.02 mmol) and **13** (0.1 mmol, 1 equiv.) were added in an oven-dried sealed tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), after that, THF (1.0 mL) were then added via syringe under N_2. The tube was sealed with a Teflon lined cap and moved into a preheated oil bath at 60 °C for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and filtered through a pad of celite. The filtrate was concentrated, and the residue was then purified by flash column chromatography to afford the corresponding product.

Spectral data for (*Z*)-5,5-diphenyl-8-(2,2,2-trifluoroethyl)-9,10-dihydro-5H,12H-pyrrolo [1,2-a][1,2,3]triazolo[1,5-f][1,3,6]triazocin-6(8H)-one (14)



Purified by column chromatography (silica gel, MeOH/DCM : 1/10) to afford the title compound (65% yield, 29 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.26 – 7.11 (m, 10H), 4.44 (d, *J* = 15.1 Hz, 1H), 4.37 (d, *J* = 17.8 Hz, 1H), 3.83 (t, *J* = 10.6 Hz, 1H), 3.54 – 3.33 (m, 2H), 2.45 – 2.09 (m, 2H), 2.05 – 1.74 (m, 2H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 177.1, 172.2, 140.6, 140.0, 139.5, 129.6, 129.5, 129.4, 128.3, 128.2, 127.9, 126.4 (q, *J* = 277.7 Hz), 125.9, 80.8, 47.9, 40.5, 36.8, 33.9 (q, *J* = 28.4 Hz), 24.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.78 (d, *J* = 11.3 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}F_3N_5O$ 440.1693; found: 440.1702.

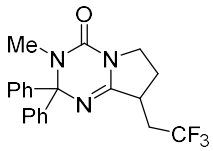
Preparation of product 15



4a **15**

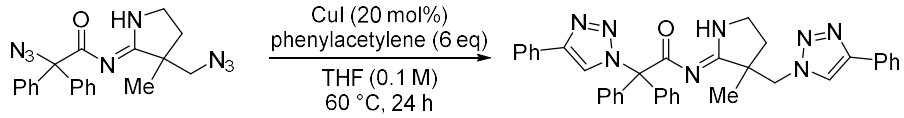
To a flame-dried Schlenk tube equipped with a magnetic stir bar were added **4a** (0.1 mmol, 1 equiv.), THF (0.5 mL), and NaH (1.2 equiv.) at 0 °C under N_2 atmosphere. After that MeI (1.2 equiv.) were then added via syringe. The resulting mixture was warmed to room temperature for 20 h. After completion, the solvent was evaporated and the residue was dissolved in DCM, washed with H_2O and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product.

Spectral data for 3-methyl-2,2-diphenyl-8-(2,2,2-trifluoroethyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5]triazin-4(3H)-one (15)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (92% yield, 36 mg) as yellowish solid, mp: 99-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 6H), 7.21 – 7.11 (m, 4H), 3.82 – 3.71 (m, 1H), 3.56 – 3.44 (m, 1H), 3.04 – 2.92 (m, 1H), 2.92 – 2.74 (m, 1H), 2.60 (s, 3H), 2.35 – 2.24 (m, 1H), 2.01 – 1.81 (m, 1H), 1.73 – 1.58 (m, 1H). ^{13}C{H^1} NMR (100 MHz, $CDCl_3$) δ 157.4, 152.1, 143.0, 142.4, 128.5, 128.2, 128.1, 128.0, 127.6, 126.7 (q, J = 276.8 Hz), 84.1, 44.2, 36.7 (q, J = 2.9 Hz), 35.7 (q, J = 28.9 Hz), 32.0, 27.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.71 (t, J = 11.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}F_3N_3O$ 388.1637; found: 388.1631.

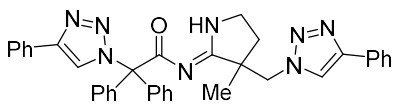
Preparation of product 16 [2]



6b **16**

CuI (0.02 mmol) and **6b** (0.1 mmol, 1 equiv.) were added in an oven-dried sealed tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), after that, phenylacetylene (0.6 mmol, 6.0 equiv.) and THF (1.0 mL) were then added via syringe under N_2. The tube was sealed with a Teflon lined cap and moved into a preheated oil bath at 60 °C for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (10 mL) and filtered through a pad of celite. The filtrate was concentrated, and the residue was then purified by flash column chromatography to afford the corresponding product.

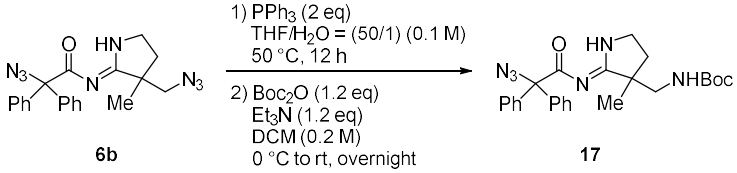
Spectral data for (*Z*)-N-(3-methyl-3-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)pyrrolidin-2-ylidene)-2,2-diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)acetamide (16)



Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (84% yield, 50 mg) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.76 – 7.63 (m, 5H), 7.49 (s, 1H), 7.41 –

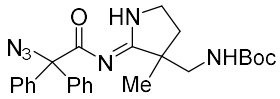
7.19 (m, 15H), 7.17 (s, 1H), 4.24 (d, J = 13.8 Hz, 1H), 4.16 (d, J = 13.8 Hz, 1H), 3.47 – 3.29 (m, 1H), 3.07 – 2.89 (m, 1H), 2.27 – 2.10 (m, 1H), 1.85 – 1.72 (m, 1H), 1.13 (s, 3H). $^{13}C\{H^1\}$ NMR (100 MHz, $CDCl_3$) δ 182.9, 176.7, 147.9, 145.9, 140.2, 140.0, 130.9, 130.4, 129.9, 129.7, 128.9, 128.8, 128.7, 128.4, 128.2, 128.1, 128.0, 127.9, 125.9, 125.7, 122.7, 121.5, 80.3, 55.6, 49.5, 44.1, 29.2, 22.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{36}H_{33}N_8O$ 593.2772; found: 593.2756.

Preparation of product 17 [5]



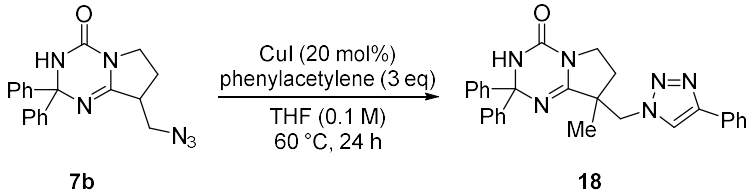
To a flame-dried Schlenk tube were added azide product **6b** (0.1 mmol, 1 equiv.), THF (1.0 mL) and H_2O (20.0 μL) under the atmosphere of nitrogen, a solution of PPh_3 (0.2 mmol, 2 equiv.) in THF (0.5 mL) was added drop-wise at 0 °C. The mixture was warmed up to 50 °C and stirred for 12 h. The mixture was then concentrated in vacuo and the residue was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and concentrated in vacuo affording amine without any further purification. To a suspension of amine (0.1 mmol, 1.0 equiv.) in DCM (0.5 mL) was added Et_3N (0.12 mmol, 1.2 equiv.) and Boc_2O (0.12 mmol, 1.2 equiv.) under nitrogen atmosphere at 0 °C. The resulting mixture was allowed to warm up to room temperature and stirred overnight. Upon completion, the reaction mixture was quenched with H_2O and the aqueous phase was extracted with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography to give the desired product.

Spectral data for Tert-butyl (*Z*)-((2-((2-azido-2,2-diphenylacetyl)imino)-3-methylpyrrolidin-3-yl) methyl)carbamate (17)



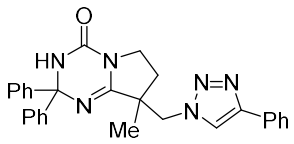
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (95% yield, 44 mg) as yellowish oil. ^1H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.45 – 7.40 (m, 2H), 7.38 – 7.28 (m, 8H), 5.01 (t, J = 6.6 Hz, 1H), 3.65 – 3.44 (m, 2H), 3.26 – 3.07 (m, 2H), 2.08 – 1.96 (m, 1H), 1.85 – 1.72 (m, 1H), 1.40 (s, 9H), 1.11 (s, 3H). $^{13}C\{H^1\}$ NMR (125 MHz, $CDCl_3$) δ 184.8, 178.8, 156.6, 141.0, 140.5, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 79.2, 48.2, 46.5, 44.2, 30.7, 28.4, 21.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{31}N_6O_3$ 463.2452; found: 463.2447.

Preparation of product 18



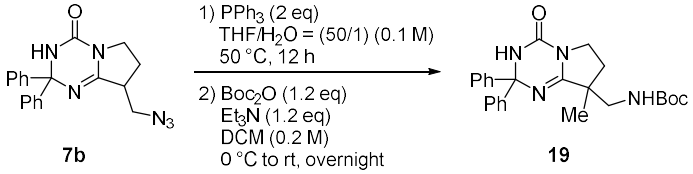
Product **18** was prepared from **7b** (0.1 mmol) by the same procedure as product **9**.

Spectral data for 8-methyl-2,2-diphenyl-8-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-2,6,7,8-tetrahydropyrrolo[1,2-a][1,3,5]triazin-4(3H)-one (18)



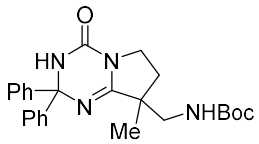
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (92% yield, 43 mg) as yellowish solid, mp: 114-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 4H), 7.41 – 7.26 (m, 11H), 7.05 (s, 1H), 6.04 (brs, 1H), 4.68 (d, *J* = 14.0 Hz, 1H), 4.60 (d, *J* = 14.0 Hz, 1H), 3.61 – 3.47 (m, 1H), 3.38 – 3.26 (m, 1H), 1.97 – 1.78 (m, 2H), 1.45 (s, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 159.8, 150.6, 148.0, 145.9, 145.1, 130.2, 128.8, 128.6, 128.5, 128.2, 128.1, 128.0, 126.3, 126.2, 126.0, 120.4, 79.7, 55.8, 46.9, 41.6, 29.7, 23.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_6O$ 463.2241; found: 463.2236.

Preparation of product 19



Product **19** was prepared from **7b** (0.1 mmol) according to the same method for the preparation of product **17**.

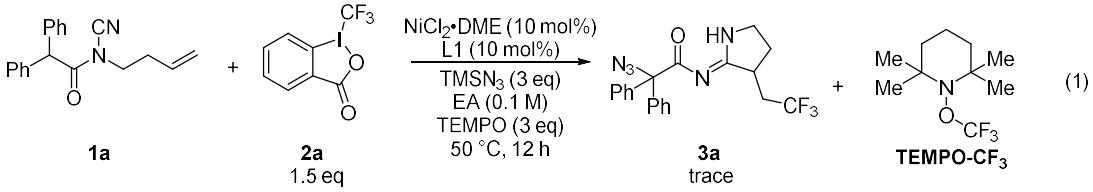
Spectral data for Tert-butyl ((8-methyl-4-oxo-2,2-diphenyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-a] [1,3,5]triazin-8-yl)methyl)carbamate (19)



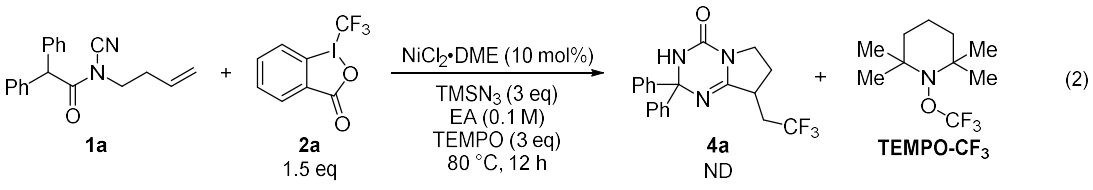
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (93% yield, 40 mg) as yellowish solid, mp: 83-85 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 10H), 5.99 (brs, 1H), 4.83 (t, *J* = 6.3 Hz, 1H), 3.71 – 3.53 (m, 2H), 3.36 – 3.21 (m, 2H), 2.01 – 1.91 (m, 1H), 1.79 – 1.68 (m, 1H), 1.39 (s, 9H), 1.26 (s, 3H). ^{13}C{H^1} NMR (125 MHz, $CDCl_3$) δ 161.6, 156.4, 151.3, 145.3, 128.5, 128.4, 127.9, 127.8, 126.4, 125.9, 79.3, 79.0, 46.9, 46.0, 41.9, 30.7, 28.4, 21.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{31}N_4O_3$ 435.2391; found: 435.2409.

VI. Control Experiments

1. Radical Trapping Experiment

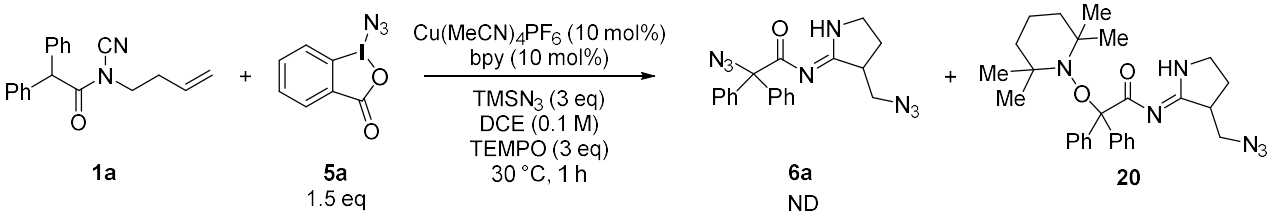


3a: trace, < 5% conv (1a);
TEMPO-CF_3: 78% (based on ^{19}F NMR using $PhCF_3$ as the internal standard)



4a: ND
TEMPO-CF_3: 40% (based on ^{19}F NMR using $PhCF_3$ as the internal standard)

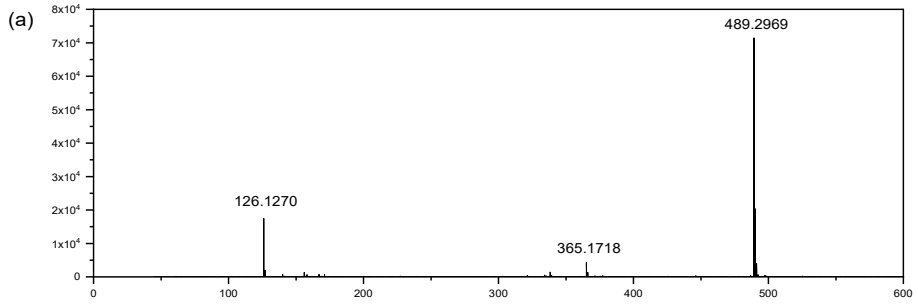
TEMPO-CF_3: ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.71. HRMS m/z (ESI) calcd for $C_{10}H_{19}F_3NO$ $[M+H]^+$ 226.1413, found 226.1416. The ^{19}F NMR spectra data were in accordance with the reported data of the known literatures. [6]



6a: ND, < 5% conv (1a);
20 was detected by LC-HRMS

Characterization of TEMPO-1a-N_3 additive product S-1 by mass spectrometry

Reaction mixture was analyzed on a LC/MS (Agilent 1290 Infinity LC System connected to the Bruker micrOTOF-QII MS instrument). The high-resolution mass spectrometry was performed to confirm the elemental compositions of TEMPO-**1a**-N_3 additive product **20**. **20**: HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{37}N_6O_2$ 489.2973; found: 489.2969 (Figure S2, a). The major product ions were observed in the fragmentation of protonated TEMPO additive product by CID mass spectra with argon as collision gas after isolation of the target precursor ion (Figure S2, b). The possible chemical structure of TEMPO additive product **20** and the major product ions observed in the fragmentation of its $[M+H]^+$ ion were given in Scheme S1.



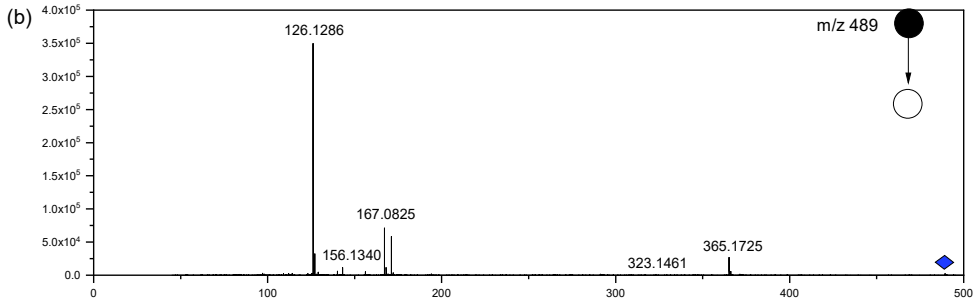
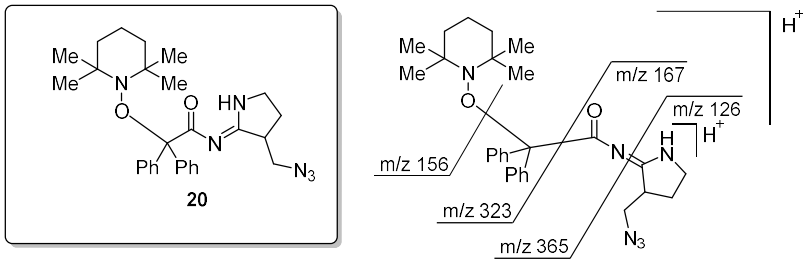


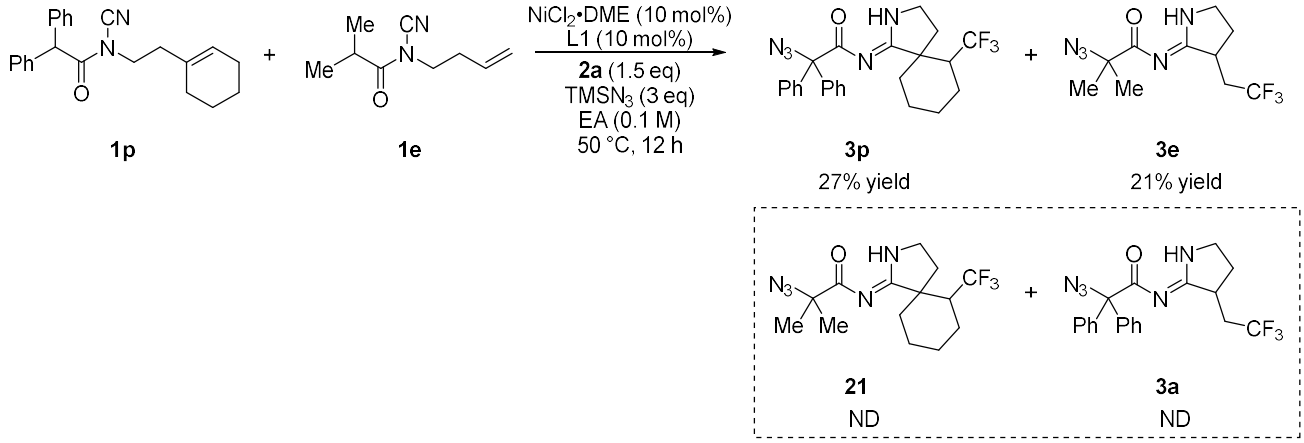
Figure S2. (a) High resolution mass spectra of TEMPO additive product **20** from reaction mixture by LC/MS. (b) MS^2 mass spectra of protonated TEMPO additive product **20**.



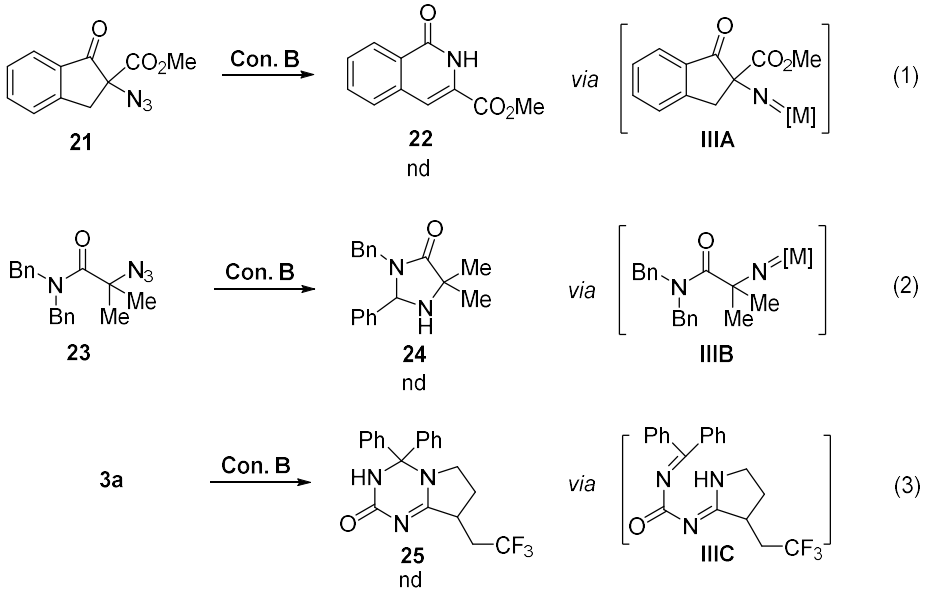
20: HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{37}N_6O_2$ 489.2973; found: 489.2969.

Scheme S1. The possible chemical structure of TEMPO additive product **20** and the major product ions observed in the fragmentation of its $[M+H]^+$ ion.

2. Intermolecular cross-over reaction



3. Nitrene intermediates verification experiment



Con. B: $NiCl_2$•DME (10 mol%), EtOAc (0.1 M), 80 °C, 12 h

Under our reaction condition B, the substrates in the literature that generate products through nitrene intermediates are unable to generate target products. These experiments show that under our reaction condition, there may be no nitrene intermediates produced. [7, 8] Notably, compound **3a** cannot underwent a similar 1,2-acylmigration to give cyclic compound **25**, presumably due to the attenuated reactivity of carbonyl group of **3a**.

VII. References

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2. Bian, K.-J.; Li, Y.; Zhang, K.-F.; He, Y.; Wu, T.-R.; Wang, C.-Y.; Wang, X.-S. *Chem. Sci.* **2020**, *11*, 10437-10443.
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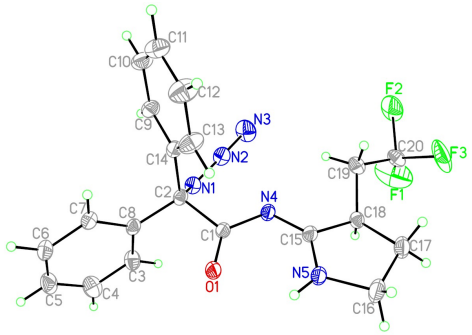
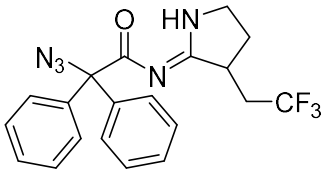
7. Yang, T.; Fan, X.; Zhao, X.; Yu, W. *Org. Lett.* **2018**, *20*, 1875-1879.
8. Zhao, X.; Liang, S.; Fan, X.; Yang, T.; Yu, W. *Org. Lett.* **2019**, *21*, 1559-1563.

VIII. Crystal Data and Structure Refinement for Compounds

1)





3a

X-ray crystal structure of compound **3a**. Single crystal of **3a** was obtained by slow evaporation of Petroleum ether /EtOAc solution. Crystal measurement of **3a** was measured on R-Axis RAPID of Rigaku Corporation plus 291.2 k. Thermal ellipsoids are set at 30% probability.

CCDC number: 2341706

Table S-crystal1-1. Crystal data and structure refinement for 3a.

Identification code	Y	
Empirical formula	C20 H18 F3 N5 O	
Formula weight	401.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.4542(7) Å	α= 90°.
	b = 19.2551(10) Å	β= 104.380(2)°.
	c = 7.9463(4) Å	γ = 90°.
Volume	1994.09(18) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	
F(000)	832	
Crystal size	0.210 x 0.200 x 0.180 mm^3	
Theta range for data collection	2.630 to 25.649°.	
Index ranges	-16<=h<=16, -23<=k<=23, -9<=l<=9	
Reflections collected	35677	
Independent reflections	3771 [R(int) = 0.0393]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9812 and 0.9782	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3771 / 0 / 317
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1180
R indices (all data)	R1 = 0.0635, wR2 = 0.1309
Extinction coefficient	n/a
Largest diff. peak and hole	0.199 and -0.230 e.Å^{-3}

Table S-crystal1-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Y. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8758(1)	30(1)	8712(2)	61(1)
N(1)	6756(1)	17(1)	4898(2)	54(1)
N(2)	6793(1)	483(1)	3843(2)	61(1)
N(3)	6772(2)	859(1)	2748(2)	91(1)
N(4)	8680(1)	603(1)	6122(2)	48(1)
N(5)	10379(1)	626(1)	7936(2)	55(1)
C(1)	8286(1)	268(1)	7311(2)	42(1)
C(2)	7094(1)	222(1)	6783(2)	42(1)
C(3)	6894(2)	-1051(1)	7346(3)	64(1)
C(4)	6589(2)	-1598(1)	8236(3)	79(1)
C(5)	6118(2)	-1470(1)	9550(3)	74(1)
C(6)	5961(2)	-802(1)	9984(3)	71(1)
C(7)	6262(1)	-252(1)	9095(3)	58(1)
C(8)	6730(1)	-372(1)	7758(2)	46(1)
C(9)	5636(1)	1088(1)	6278(3)	57(1)
C(10)	5216(2)	1716(1)	6585(3)	69(1)
C(11)	5780(2)	2187(1)	7701(3)	75(1)
C(12)	6772(2)	2032(1)	8542(4)	86(1)
C(13)	7202(2)	1404(1)	8238(3)	70(1)
C(14)	6645(1)	925(1)	7099(2)	45(1)
C(15)	9665(1)	759(1)	6532(2)	46(1)
C(16)	11390(2)	899(2)	7951(3)	89(1)
C(17)	11226(2)	1251(1)	6233(3)	66(1)
C(18)	10150(5)	1020(4)	5126(8)	45(1)
C(19)	9426(4)	1541(3)	4007(7)	61(2)

C(20)	9870(20)	1686(10)	2360(30)	60(3)
F(1)	9949(8)	1296(5)	1497(10)	202(4)
F(2)	9116(4)	2206(4)	1489(11)	136(3)
F(3)	10665(11)	2177(7)	3113(16)	155(5)
C(18')	10124(4)	1304(3)	5491(8)	44(1)
C(19')	9723(4)	1174(3)	3558(5)	55(1)
C(20')	9850(20)	1863(9)	2600(30)	70(4)
F(1')	9633(4)	1633(4)	811(5)	110(2)
F(2')	9418(6)	2340(3)	2720(9)	129(2)
F(3')	10837(8)	1933(6)	2690(13)	110(3)

Table S-crystal1-3. Bond lengths [Å] and angles [°] for Y.

O(1)-C(1)	1.225(2)
N(1)-N(2)	1.238(2)
N(1)-C(2)	1.506(2)
N(2)-N(3)	1.126(2)
N(4)-C(15)	1.318(2)
N(4)-C(1)	1.357(2)
N(5)-C(15)	1.304(2)
N(5)-C(16)	1.455(2)
N(5)-H(5N)	0.8495
C(1)-C(2)	1.555(2)
C(2)-C(8)	1.529(2)
C(2)-C(14)	1.529(2)
C(3)-C(8)	1.379(3)
C(3)-C(4)	1.386(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.372(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.362(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.387(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.383(3)
C(7)-H(7)	0.9300
C(9)-C(10)	1.381(3)

C(9)-C(14)	1.387(2)
C(9)-H(9)	0.9300
C(10)-C(11)	1.360(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.370(3)
C(11)-H(11)	0.9300
C(12)-C(13)	1.386(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.376(3)
C(13)-H(13)	0.9300
C(15)-C(18)	1.513(6)
C(15)-C(18')	1.556(6)
C(16)-C(17)	1.491(3)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-C(18')	1.457(6)
C(17)-C(18)	1.561(7)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-C(19)	1.521(9)
C(18)-H(18)	0.9800
C(19)-C(20)	1.59(3)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-F(1)	1.041(19)
C(20)-F(3)	1.44(2)
C(20)-F(2)	1.47(3)
C(18')-C(19')	1.517(8)
C(18')-H(18')	0.9801
C(19')-C(20')	1.56(2)
C(19')-H(19C)	0.9700
C(19')-H(19D)	0.9700
C(20')-F(2')	1.11(2)
C(20')-F(3')	1.32(3)
C(20')-F(1')	1.45(2)

N(2)-N(1)-C(2)	115.46(15)
N(3)-N(2)-N(1)	172.4(2)

C(15)-N(4)-C(1)	118.65(14)
C(15)-N(5)-C(16)	115.11(16)
C(15)-N(5)-H(5N)	125.5
C(16)-N(5)-H(5N)	119.3
O(1)-C(1)-N(4)	127.29(15)
O(1)-C(1)-C(2)	119.45(14)
N(4)-C(1)-C(2)	113.21(14)
N(1)-C(2)-C(8)	104.59(13)
N(1)-C(2)-C(14)	111.20(13)
C(8)-C(2)-C(14)	112.90(13)
N(1)-C(2)-C(1)	108.68(13)
C(8)-C(2)-C(1)	110.14(13)
C(14)-C(2)-C(1)	109.20(13)
C(8)-C(3)-C(4)	121.0(2)
C(8)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	120.2(2)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	119.5(2)
C(6)-C(5)-H(5)	120.3
C(4)-C(5)-H(5)	120.3
C(5)-C(6)-C(7)	120.6(2)
C(5)-C(6)-H(6)	119.7
C(7)-C(6)-H(6)	119.7
C(8)-C(7)-C(6)	120.6(2)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(3)-C(8)-C(7)	118.09(18)
C(3)-C(8)-C(2)	119.94(16)
C(7)-C(8)-C(2)	121.94(17)
C(10)-C(9)-C(14)	120.69(19)
C(10)-C(9)-H(9)	119.7
C(14)-C(9)-H(9)	119.7
C(11)-C(10)-C(9)	120.8(2)
C(11)-C(10)-H(10)	119.6
C(9)-C(10)-H(10)	119.6
C(10)-C(11)-C(12)	119.4(2)

C(10)-C(11)-H(11)	120.3
C(12)-C(11)-H(11)	120.3
C(11)-C(12)-C(13)	120.2(2)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
C(14)-C(13)-C(12)	121.0(2)
C(14)-C(13)-H(13)	119.5
C(12)-C(13)-H(13)	119.5
C(13)-C(14)-C(9)	117.85(17)
C(13)-C(14)-C(2)	121.87(16)
C(9)-C(14)-C(2)	120.25(16)
N(5)-C(15)-N(4)	130.41(16)
N(5)-C(15)-C(18)	109.7(3)
N(4)-C(15)-C(18)	118.9(3)
N(5)-C(15)-C(18')	106.4(3)
N(4)-C(15)-C(18')	122.0(2)
N(5)-C(16)-C(17)	103.39(16)
N(5)-C(16)-H(16A)	111.1
C(17)-C(16)-H(16A)	111.1
N(5)-C(16)-H(16B)	111.1
C(17)-C(16)-H(16B)	111.1
H(16A)-C(16)-H(16B)	109.0
C(18')-C(17)-C(16)	107.8(3)
C(16)-C(17)-C(18)	107.0(3)
C(16)-C(17)-H(17A)	110.3
C(18)-C(17)-H(17A)	110.3
C(16)-C(17)-H(17B)	110.3
C(18)-C(17)-H(17B)	110.3
H(17A)-C(17)-H(17B)	108.6
C(15)-C(18)-C(19)	108.7(5)
C(15)-C(18)-C(17)	100.8(4)
C(19)-C(18)-C(17)	120.7(5)
C(15)-C(18)-H(18)	108.7
C(19)-C(18)-H(18)	108.6
C(17)-C(18)-H(18)	108.7
C(18)-C(19)-C(20)	106.1(10)
C(18)-C(19)-H(19A)	110.5
C(20)-C(19)-H(19A)	110.5

C(18)-C(19)-H(19B)	110.5
C(20)-C(19)-H(19B)	110.5
H(19A)-C(19)-H(19B)	108.7
F(1)-C(20)-F(3)	124(2)
F(1)-C(20)-F(2)	110.4(19)
F(3)-C(20)-F(2)	95.9(14)
F(1)-C(20)-C(19)	122.2(19)
F(3)-C(20)-C(19)	99.6(14)
F(2)-C(20)-C(19)	98.5(15)
C(17)-C(18')-C(19')	117.9(5)
C(17)-C(18')-C(15)	103.6(4)
C(19')-C(18')-C(15)	109.8(4)
C(17)-C(18')-H(18')	108.4
C(19')-C(18')-H(18')	108.4
C(15)-C(18')-H(18')	108.3
C(18')-C(19')-C(20')	107.3(9)
C(18')-C(19')-H(19C)	110.2
C(20')-C(19')-H(19C)	110.2
C(18')-C(19')-H(19D)	110.2
C(20')-C(19')-H(19D)	110.2
H(19C)-C(19')-H(19D)	108.5
F(2')-C(20')-F(3')	117.2(17)
F(2')-C(20')-F(1')	110.7(18)
F(3')-C(20')-F(1')	92.4(16)
F(2')-C(20')-C(19')	123(2)
F(3')-C(20')-C(19')	107.1(16)
F(1')-C(20')-C(19')	101.4(11)

Symmetry transformations used to generate equivalent atoms:

Table S-crystal1-4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Y. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	38(1)	88(1)	56(1)	29(1)	6(1)	-5(1)
N(1)	51(1)	67(1)	42(1)	-5(1)	7(1)	-5(1)
N(2)	55(1)	84(1)	39(1)	-3(1)	6(1)	-2(1)

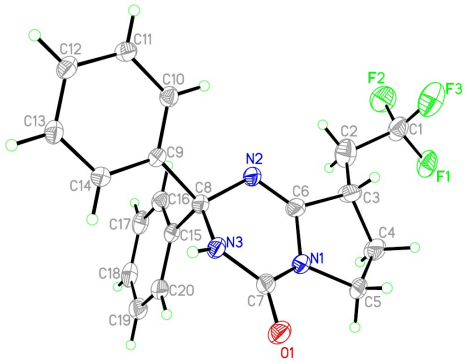
N(3)	101(2)	120(2)	45(1)	16(1)	7(1)	-7(1)
N(4)	36(1)	64(1)	42(1)	9(1)	11(1)	-1(1)
N(5)	38(1)	77(1)	49(1)	19(1)	8(1)	-7(1)
C(1)	36(1)	50(1)	41(1)	4(1)	10(1)	1(1)
C(2)	34(1)	56(1)	37(1)	-2(1)	7(1)	-1(1)
C(3)	69(1)	61(1)	66(1)	-9(1)	27(1)	-12(1)
C(4)	90(2)	59(1)	86(2)	-6(1)	22(1)	-24(1)
C(5)	60(1)	82(2)	81(2)	14(1)	17(1)	-26(1)
C(6)	51(1)	93(2)	74(1)	18(1)	29(1)	0(1)
C(7)	46(1)	70(1)	61(1)	9(1)	21(1)	8(1)
C(8)	31(1)	57(1)	48(1)	-1(1)	7(1)	-6(1)
C(9)	42(1)	66(1)	58(1)	1(1)	6(1)	4(1)
C(10)	56(1)	75(1)	74(1)	9(1)	11(1)	20(1)
C(11)	78(2)	67(1)	82(2)	-3(1)	21(1)	21(1)
C(12)	78(2)	75(2)	99(2)	-33(1)	7(1)	6(1)
C(13)	50(1)	77(1)	74(1)	-21(1)	-1(1)	8(1)
C(14)	39(1)	56(1)	40(1)	2(1)	10(1)	1(1)
C(15)	40(1)	56(1)	43(1)	7(1)	13(1)	2(1)
C(16)	42(1)	137(2)	84(2)	41(2)	7(1)	-21(1)
C(17)	52(1)	80(1)	68(1)	10(1)	20(1)	-15(1)
C(18)	47(2)	46(3)	48(3)	-1(3)	22(2)	-2(3)
C(19)	68(3)	57(3)	60(3)	15(2)	22(2)	0(2)
C(20)	82(5)	44(8)	53(6)	-3(5)	13(4)	-6(5)
F(1)	368(11)	185(7)	81(4)	22(4)	109(5)	67(7)
F(2)	122(3)	163(5)	111(4)	90(4)	6(3)	-17(4)
F(3)	170(10)	152(8)	125(7)	74(6)	4(5)	-91(7)
C(18')	48(2)	44(3)	44(3)	0(2)	18(2)	-2(2)
C(19')	63(3)	59(3)	46(2)	-1(2)	18(2)	-12(2)
C(20')	108(6)	47(9)	56(7)	9(6)	24(5)	-8(7)
F(1')	121(3)	156(5)	52(2)	14(2)	20(2)	-36(3)
F(2')	194(6)	100(3)	114(4)	45(3)	77(4)	52(3)
F(3')	87(3)	160(7)	89(4)	34(4)	33(3)	-39(4)

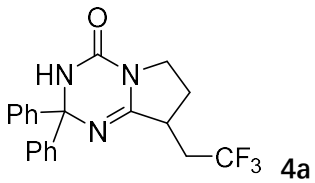
Table S-crystal1-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Y.

	x	y	z	U(eq)

H(5N)	10287	424	8836	66
H(3)	7214	-1144	6459	76
H(4)	6704	-2053	7941	94
H(5)	5907	-1837	10141	89
H(6)	5650	-713	10884	85
H(7)	6147	202	9401	69
H(9)	5239	772	5513	68
H(10)	4540	1818	6021	83
H(11)	5494	2610	7892	90
H(12)	7159	2348	9319	104
H(13)	7878	1305	8813	84
H(16A)	11889	528	8063	107
H(16B)	11620	1226	8896	107
H(17A)	11756	1116	5663	79
H(17B)	11248	1751	6380	79
H(18)	10239	626	4395	54
H(19A)	9403	1966	4648	73
H(19B)	8738	1351	3646	73
H(18')	9899	1767	5755	53
H(19C)	9006	1041	3295	66
H(19D)	10109	803	3188	66

2)





4a

X-ray crystal structure of compound **4a**. Single crystal of **4a** was obtained by slow evaporation of Petroleum ether /EtOAc solution. Crystal measurement of **4a** was measured on R-Axis RAPID of Rigaku Corporation plus 291.2 k. Thermal ellipsoids are set at 40% probability.

CCDC number: 2341707

Table S-crystal2-1. Crystal data and structure refinement for 4a.

Identification code	Y	
Empirical formula	C20 H18 F3 N3 O	
Formula weight	373.37	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 8.3452(5) Å	α= 90°.
	b = 16.1586(8) Å	β= 90°.
	c = 26.0208(15) Å	γ = 90°.
Volume	3508.8(3) $Å^3$	
Z	8	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	0.111 mm^{-1}	
F(000)	1552	
Crystal size	0.180 x 0.170 x 0.150 mm^3	
Theta range for data collection	2.521 to 25.095°.	
Index ranges	-9<=h<=9, -19<=k<=19, -31<=l<=31	
Reflections collected	62306	
Independent reflections	3086 [R(int) = 0.1087]	
Completeness to theta = 25.095°	98.8 %	
Max. and min. transmission	0.9835 and 0.9803	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3086 / 0 / 215	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0978, wR2 = 0.2472	
R indices (all data)	R1 = 0.1276, wR2 = 0.2955	
Extinction coefficient	0.0027(13)	
Largest diff. peak and hole	1.732 and -0.744 e.$Å^{-3}$	

Table S-crystal2-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Y. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3108(4)	5456(2)	-79(1)	43(1)
F(1)	-2613(4)	6586(2)	1848(1)	64(1)

F(2)	-1770(7)	6062(3)	2536(2)	100(2)
F(3)	-568(5)	7088(3)	2220(2)	88(1)
N(1)	1454(5)	5346(2)	619(1)	38(1)
N(2)	2381(5)	4821(3)	1413(1)	40(1)
N(3)	3919(5)	4736(2)	631(1)	34(1)
C(1)	-1294(8)	6386(4)	2102(2)	62(2)
C(2)	-398(9)	5673(5)	1838(3)	72(2)
C(3)	173(9)	5848(5)	1349(2)	84(3)
C(4)	-896(8)	5974(5)	875(2)	67(2)
C(5)	253(6)	5938(3)	431(2)	44(1)
C(6)	1443(6)	5273(3)	1153(2)	45(1)
C(7)	2871(5)	5186(3)	357(2)	36(1)
C(8)	3475(5)	4304(3)	1105(2)	34(1)
C(9)	5014(2)	4115(1)	1403(1)	32(1)
C(10)	5207(2)	4358(1)	1912(1)	34(1)
C(11)	6597(2)	4150(2)	2176(1)	37(1)
C(12)	7793(2)	3699(1)	1932(1)	39(1)
C(13)	7601(2)	3456(1)	1424(1)	38(1)
C(14)	6211(2)	3664(1)	1159(1)	38(1)
C(15)	2587(2)	3484(1)	995(1)	34(1)
C(16)	1998(2)	3020(1)	1409(1)	42(1)
C(17)	1184(2)	2302(1)	1334(1)	48(1)
C(18)	892(2)	1999(1)	829(1)	53(1)
C(19)	1481(2)	2451(2)	411(1)	52(1)
C(20)	2342(2)	3195(1)	495(1)	43(1)

Table S-crystal2-3. Bond lengths [Å] and angles [°] for Y.

O(1)-C(7)	1.231(6)
F(1)-C(1)	1.324(7)
F(2)-C(1)	1.307(7)
F(3)-C(1)	1.322(8)
N(1)-C(7)	1.389(6)
N(1)-C(6)	1.395(6)
N(1)-C(5)	1.469(6)
N(2)-C(6)	1.266(6)
N(2)-C(8)	1.474(6)

N(3)-C(7)	1.343(6)
N(3)-C(8)	1.464(6)
N(3)-H(3N)	0.8600
C(1)-C(2)	1.535(9)
C(2)-C(3)	1.388(9)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(6)	1.499(7)
C(3)-C(4)	1.535(7)
C(3)-H(3)	0.9800
C(4)-C(5)	1.503(8)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(8)-C(9)	1.532(4)
C(8)-C(15)	1.545(5)
C(9)-C(10)	1.3900
C(9)-C(14)	1.3900
C(10)-C(11)	1.3900
C(10)-H(10)	0.9300
C(11)-C(12)	1.3900
C(11)-H(11)	0.9300
C(12)-C(13)	1.3900
C(12)-H(12)	0.9300
C(13)-C(14)	1.3900
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-C(20)	1.3970
C(15)-C(16)	1.4028
C(16)-C(17)	1.3600
C(16)-H(16)	0.9300
C(17)-C(18)	1.4244
C(17)-H(17)	0.9300
C(18)-C(19)	1.3987
C(18)-H(18)	0.9300
C(19)-C(20)	1.4175
C(19)-H(19)	0.9300

C(20)-H(20)	0.9300
C(7)-N(1)-C(6)	118.6(4)
C(7)-N(1)-C(5)	122.6(4)
C(6)-N(1)-C(5)	112.4(4)
C(6)-N(2)-C(8)	114.7(4)
C(7)-N(3)-C(8)	122.7(4)
C(7)-N(3)-H(3N)	118.6
C(8)-N(3)-H(3N)	118.6
F(2)-C(1)-F(3)	106.5(5)
F(2)-C(1)-F(1)	106.0(5)
F(3)-C(1)-F(1)	106.7(5)
F(2)-C(1)-C(2)	103.6(5)
F(3)-C(1)-C(2)	121.6(6)
F(1)-C(1)-C(2)	111.4(6)
C(3)-C(2)-C(1)	115.2(6)
C(3)-C(2)-H(2A)	108.5
C(1)-C(2)-H(2A)	108.5
C(3)-C(2)-H(2B)	108.5
C(1)-C(2)-H(2B)	108.5
H(2A)-C(2)-H(2B)	107.5
C(2)-C(3)-C(6)	115.4(6)
C(2)-C(3)-C(4)	124.3(7)
C(6)-C(3)-C(4)	102.7(4)
C(2)-C(3)-H(3)	104.1
C(6)-C(3)-H(3)	104.1
C(4)-C(3)-H(3)	104.1
C(5)-C(4)-C(3)	104.0(5)
C(5)-C(4)-H(4A)	111.0
C(3)-C(4)-H(4A)	111.0
C(5)-C(4)-H(4B)	111.0
C(3)-C(4)-H(4B)	111.0
H(4A)-C(4)-H(4B)	109.0
N(1)-C(5)-C(4)	101.9(4)
N(1)-C(5)-H(5A)	111.4
C(4)-C(5)-H(5A)	111.4
N(1)-C(5)-H(5B)	111.4
C(4)-C(5)-H(5B)	111.4

H(5A)-C(5)-H(5B)	109.3
N(2)-C(6)-N(1)	125.3(4)
N(2)-C(6)-C(3)	127.8(5)
N(1)-C(6)-C(3)	106.9(4)
O(1)-C(7)-N(3)	125.2(4)
O(1)-C(7)-N(1)	121.5(4)
N(3)-C(7)-N(1)	113.2(4)
N(3)-C(8)-N(2)	110.2(3)
N(3)-C(8)-C(9)	108.0(3)
N(2)-C(8)-C(9)	110.9(3)
N(3)-C(8)-C(15)	111.9(3)
N(2)-C(8)-C(15)	106.8(3)
C(9)-C(8)-C(15)	108.9(3)
C(10)-C(9)-C(14)	120.0
C(10)-C(9)-C(8)	121.54(18)
C(14)-C(9)-C(8)	118.43(18)
C(9)-C(10)-C(11)	120.0
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	120.0
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	120.0
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-H(12)	120.0
C(14)-C(13)-C(12)	120.0
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(9)	120.0
C(13)-C(14)-H(14)	120.0
C(9)-C(14)-H(14)	120.0
C(20)-C(15)-C(16)	119.1
C(20)-C(15)-C(8)	121.99(18)
C(16)-C(15)-C(8)	118.93(18)
C(17)-C(16)-C(15)	121.4
C(17)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(16)-C(17)-C(18)	120.8

C(16)-C(17)-H(17)	119.6
C(18)-C(17)-H(17)	119.6
C(19)-C(18)-C(17)	118.5
C(19)-C(18)-H(18)	120.8
C(17)-C(18)-H(18)	120.8
C(18)-C(19)-C(20)	120.2
C(18)-C(19)-H(19)	119.9
C(20)-C(19)-H(19)	119.9
C(15)-C(20)-C(19)	120.1
C(15)-C(20)-H(20)	120.0
C(19)-C(20)-H(20)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S-crystal2-4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Y. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

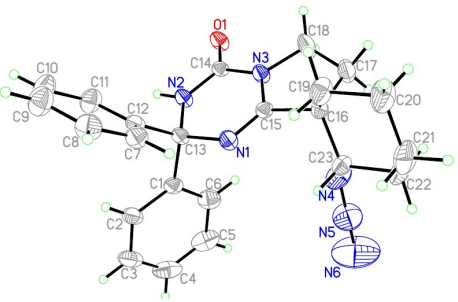
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	40(2)	48(2)	40(2)	6(2)	-6(1)	7(2)
F(1)	50(2)	70(2)	71(2)	14(2)	17(2)	27(2)
F(2)	160(4)	71(2)	69(2)	24(2)	-11(3)	-4(3)
F(3)	61(2)	84(3)	119(3)	35(3)	0(2)	4(2)
N(1)	35(2)	42(2)	36(2)	-1(2)	-6(2)	11(2)
N(2)	38(2)	50(2)	33(2)	-3(2)	-1(2)	18(2)
N(3)	32(2)	36(2)	36(2)	4(2)	-3(2)	7(2)
C(1)	68(4)	71(4)	47(3)	10(3)	13(3)	32(3)
C(2)	63(4)	67(4)	87(5)	6(3)	6(3)	17(3)
C(3)	89(5)	124(6)	38(3)	-28(3)	-18(3)	79(5)
C(4)	63(4)	88(5)	50(3)	-5(3)	-10(3)	46(3)
C(5)	39(3)	43(3)	49(3)	-2(2)	-15(2)	17(2)
C(6)	43(3)	56(3)	36(2)	-6(2)	-7(2)	17(2)
C(7)	36(2)	34(2)	39(2)	-4(2)	-9(2)	5(2)
C(8)	34(2)	38(2)	31(2)	-1(2)	-1(2)	10(2)
C(9)	30(2)	33(2)	33(2)	1(2)	-5(2)	5(2)
C(10)	31(2)	37(2)	35(2)	1(2)	2(2)	4(2)
C(11)	35(2)	41(2)	34(2)	-1(2)	-4(2)	-1(2)
C(12)	32(2)	39(2)	46(3)	3(2)	-8(2)	2(2)

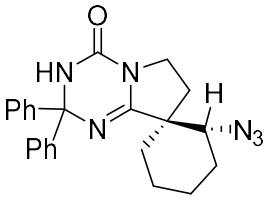
C(13)	32(2)	39(2)	43(2)	0(2)	1(2)	9(2)
C(14)	39(2)	43(3)	31(2)	-4(2)	-3(2)	10(2)
C(15)	26(2)	36(2)	39(2)	1(2)	-4(2)	8(2)
C(16)	31(2)	48(3)	47(3)	3(2)	2(2)	6(2)
C(17)	28(2)	49(3)	67(3)	9(2)	3(2)	8(2)
C(18)	39(3)	37(3)	83(4)	1(3)	-9(3)	7(2)
C(19)	57(3)	40(3)	59(3)	-10(2)	-16(3)	9(2)
C(20)	51(3)	34(2)	45(3)	-3(2)	-8(2)	9(2)

Table S-crystal2-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Y.

	x	y	z	U(eq)
H(3N)	4891	4700	524	41
H(2A)	501	5515	2053	87
H(2B)	-1111	5201	1817	87
H(3)	728	6378	1389	101
H(4A)	-1695	5540	850	80
H(4B)	-1434	6506	889	80
H(5A)	-268	5739	122	52
H(5B)	727	6476	364	52
H(10)	4406	4660	2075	41
H(11)	6726	4312	2517	44
H(12)	8723	3560	2109	47
H(13)	8401	3154	1260	46
H(14)	6082	3501	819	45
H(16)	2169	3208	1743	50
H(17)	813	2004	1616	57
H(18)	321	1511	777	64
H(19)	1308	2263	78	63
H(20)	2745	3491	217	52

3)





7e (major)

X-ray crystal structure of compound **7e** (major). Single crystal of **7e** was obtained by slow evaporation of Petroleum ether /EtOAc solution. Crystal measurement of **7e** was measured on R-Axis RAPID of Rigaku Corporation plus 291.2 k. Thermal ellipsoids are set at 30% probability.

CCDC number: 2341708

Table S-crystal3-1. Crystal data and structure refinement for 7e.

Identification code	YY	
Empirical formula	C23 H24 N6 O	
Formula weight	400.48	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 12.6779(12) Å	α= 90°.
	b = 15.4791(12) Å	β= 96.233(5)°.
	c = 21.483(2) Å	γ = 90°.
Volume	4190.9(6) $Å^3$	
Z	8	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	1696	
Crystal size	0.200 x 0.180 x 0.170 mm^3	
Theta range for data collection	2.632 to 27.562°.	
Index ranges	-16<=h<=16, -20<=k<=20, -27<=l<=27	
Reflections collected	89621	
Independent reflections	4839 [R(int) = 0.0583]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9862 and 0.9838	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4839 / 0 / 241	
Goodness-of-fit on F^2	1.049	

Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1525
R indices (all data)	R1 = 0.0792, wR2 = 0.1658
Extinction coefficient	n/a
Largest diff. peak and hole	0.221 and -0.220 e.Å^{-3}

Table S-crystal3-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for YY. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5443(1)	3315(1)	5502(1)	42(1)
C(2)	5905(1)	3978(1)	5189(1)	52(1)
C(3)	6202(1)	4741(1)	5501(1)	69(1)
C(4)	6037(1)	4841(1)	6126(1)	77(1)
C(5)	5575(1)	4179(1)	6439(1)	77(1)
C(6)	5278(1)	3416(1)	6127(1)	61(1)
C(7)	5446(1)	2399(1)	4514(1)	41(1)
C(8)	6417(1)	2073(1)	4388(1)	50(1)
C(9)	6704(1)	2072(1)	3785(1)	62(1)
C(10)	6009(1)	2373(1)	3295(1)	71(1)
C(11)	5041(1)	2706(1)	3408(1)	75(1)
C(12)	4749(1)	2718(1)	4024(1)	58(1)
C(13)	5159(1)	2434(1)	5188(1)	38(1)
C(14)	3544(1)	1640(1)	5471(1)	36(1)
C(15)	5321(1)	1186(1)	5812(1)	35(1)
C(16)	5879(1)	474(1)	6207(1)	39(1)
C(17)	4956(2)	-10(2)	6464(1)	64(1)
C(18)	3938(2)	305(2)	6120(1)	66(1)
C(19)	6516(2)	-95(2)	5797(1)	63(1)
C(20)	7192(2)	-765(2)	6181(1)	79(1)
C(21)	7929(2)	-333(2)	6687(1)	78(1)
C(22)	7315(2)	221(2)	7108(1)	65(1)
C(23)	6653(2)	886(1)	6717(1)	45(1)
N(1)	5788(1)	1783(1)	5556(1)	44(1)
N(2)	3999(1)	2293(1)	5199(1)	45(1)
N(3)	4241(1)	1065(1)	5779(1)	44(1)
N(4)	6014(2)	1433(2)	7101(1)	77(1)
N(5)	6491(3)	1890(2)	7482(1)	100(1)

N(6)	6845(5)	2330(3)	7863(2)	201(2)
O(1)	2579(1)	1546(1)	5457(1)	51(1)

Table S-crystal3-3. Bond lengths [Å] and angles [°] for YY.

C(1)-C(2)	1.3900
C(1)-C(6)	1.3900
C(1)-C(13)	1.546(2)
C(2)-C(3)	1.3900
C(3)-C(4)	1.3900
C(4)-C(5)	1.3900
C(5)-C(6)	1.3900
C(7)-C(8)	1.3845
C(7)-C(12)	1.3895
C(7)-C(13)	1.532(2)
C(8)-C(9)	1.3829
C(9)-C(10)	1.3779
C(10)-C(11)	1.3765
C(11)-C(12)	1.4137
C(13)-N(1)	1.463(2)
C(13)-N(2)	1.489(2)
C(14)-O(1)	1.229(2)
C(14)-N(2)	1.330(2)
C(14)-N(3)	1.373(2)
C(15)-N(1)	1.256(2)
C(15)-N(3)	1.377(2)
C(15)-C(16)	1.517(2)
C(16)-C(23)	1.529(3)
C(16)-C(19)	1.535(3)
C(16)-C(17)	1.542(3)
C(17)-C(18)	1.497(3)
C(18)-N(3)	1.459(2)
C(19)-C(20)	1.529(3)
C(20)-C(21)	1.509(4)
C(21)-C(22)	1.520(4)
C(22)-C(23)	1.521(3)
C(23)-N(4)	1.482(3)

N(4)-N(5)	1.196(3)
N(5)-N(6)	1.120(4)

C(2)-C(1)-C(6)	120.0
C(2)-C(1)-C(13)	122.04(7)
C(6)-C(1)-C(13)	117.86(7)
C(1)-C(2)-C(3)	120.0
C(2)-C(3)-C(4)	120.0
C(5)-C(4)-C(3)	120.0
C(4)-C(5)-C(6)	120.0
C(5)-C(6)-C(1)	120.0
C(8)-C(7)-C(12)	119.2
C(8)-C(7)-C(13)	120.37(7)
C(12)-C(7)-C(13)	120.44(7)
C(9)-C(8)-C(7)	120.9
C(10)-C(9)-C(8)	120.3
C(11)-C(10)-C(9)	120.0
C(10)-C(11)-C(12)	119.9
C(7)-C(12)-C(11)	119.7
N(1)-C(13)-N(2)	111.82(13)
N(1)-C(13)-C(7)	108.33(13)
N(2)-C(13)-C(7)	110.26(13)
N(1)-C(13)-C(1)	106.58(13)
N(2)-C(13)-C(1)	107.79(13)
C(7)-C(13)-C(1)	112.03(11)
O(1)-C(14)-N(2)	123.86(16)
O(1)-C(14)-N(3)	121.46(16)
N(2)-C(14)-N(3)	114.67(14)
N(1)-C(15)-N(3)	126.25(15)
N(1)-C(15)-C(16)	124.43(15)
N(3)-C(15)-C(16)	109.32(14)
C(15)-C(16)-C(23)	108.79(14)
C(15)-C(16)-C(19)	109.78(15)
C(23)-C(16)-C(19)	108.28(16)
C(15)-C(16)-C(17)	103.12(14)
C(23)-C(16)-C(17)	113.46(17)
C(19)-C(16)-C(17)	113.23(19)
C(18)-C(17)-C(16)	108.18(17)

N(3)-C(18)-C(17)	104.52(16)
C(20)-C(19)-C(16)	112.25(18)
C(21)-C(20)-C(19)	110.7(2)
C(20)-C(21)-C(22)	111.2(2)
C(21)-C(22)-C(23)	109.91(18)
N(4)-C(23)-C(22)	112.46(18)
N(4)-C(23)-C(16)	106.86(16)
C(22)-C(23)-C(16)	112.67(17)
C(15)-N(1)-C(13)	119.22(14)
C(14)-N(2)-C(13)	126.50(14)
C(14)-N(3)-C(15)	121.39(14)
C(14)-N(3)-C(18)	125.09(15)
C(15)-N(3)-C(18)	113.48(15)
N(5)-N(4)-C(23)	117.0(2)
N(6)-N(5)-N(4)	173.2(4)

Symmetry transformations used to generate equivalent atoms:

Table S-crystal3-4. Anisotropic displacement parameters ($Å^2$x 10^3) for YY. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	24(1)	43(1)	58(1)	4(1)	-4(1)	1(1)
C(2)	42(1)	42(1)	71(1)	7(1)	-6(1)	-8(1)
C(3)	51(1)	45(1)	105(2)	2(1)	-14(1)	-10(1)
C(4)	46(1)	61(2)	119(2)	-31(2)	-12(1)	5(1)
C(5)	54(1)	95(2)	82(2)	-33(2)	3(1)	8(1)
C(6)	47(1)	70(2)	68(1)	-7(1)	11(1)	-4(1)
C(7)	33(1)	32(1)	55(1)	4(1)	-1(1)	-3(1)
C(8)	35(1)	53(1)	60(1)	7(1)	1(1)	0(1)
C(9)	46(1)	73(2)	68(1)	2(1)	13(1)	2(1)
C(10)	66(2)	92(2)	55(1)	2(1)	11(1)	4(1)
C(11)	67(2)	101(2)	54(1)	11(1)	-5(1)	18(1)
C(12)	46(1)	68(1)	58(1)	7(1)	-2(1)	12(1)
C(13)	23(1)	36(1)	55(1)	10(1)	-1(1)	-1(1)
C(14)	27(1)	32(1)	47(1)	1(1)	0(1)	-1(1)
C(15)	28(1)	34(1)	40(1)	0(1)	-2(1)	1(1)

C(16)	36(1)	36(1)	42(1)	4(1)	-2(1)	2(1)
C(17)	46(1)	60(1)	83(2)	34(1)	-7(1)	-9(1)
C(18)	42(1)	57(1)	100(2)	39(1)	4(1)	-4(1)
C(19)	79(2)	54(1)	52(1)	-4(1)	-3(1)	29(1)
C(20)	95(2)	65(2)	76(2)	0(1)	0(1)	45(2)
C(21)	58(1)	87(2)	85(2)	21(2)	-1(1)	35(1)
C(22)	58(1)	79(2)	52(1)	8(1)	-14(1)	12(1)
C(23)	41(1)	49(1)	43(1)	-1(1)	-2(1)	5(1)
N(1)	26(1)	44(1)	62(1)	15(1)	-1(1)	2(1)
N(2)	23(1)	41(1)	68(1)	19(1)	-2(1)	-1(1)
N(3)	29(1)	39(1)	63(1)	15(1)	-1(1)	-2(1)
N(4)	83(2)	92(2)	56(1)	-22(1)	1(1)	22(1)
N(5)	137(2)	85(2)	77(2)	-33(2)	15(2)	-2(2)
N(6)	234(5)	190(5)	178(4)	-133(4)	28(4)	-40(4)
O(1)	26(1)	46(1)	81(1)	17(1)	2(1)	-2(1)

Table S-crystal3-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for YY.

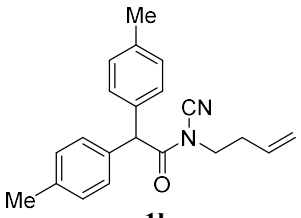
	x	y	z	U(eq)
H(2)	6015	3911	4771	63
H(3)	6511	5184	5292	82
H(4)	6236	5352	6335	92
H(5)	5464	4246	6857	93
H(6)	4968	2972	6336	73
H(8)	6883	1852	4713	60
H(9)	7368	1868	3710	74
H(10)	6194	2350	2888	85
H(11)	4580	2923	3079	90
H(12)	4093	2937	4101	70
H(17A)	5029	-627	6404	77
H(17B)	4962	101	6909	77
H(18A)	3627	-133	5834	80
H(18B)	3432	456	6410	80
H(19A)	6031	-389	5488	75
H(19B)	6975	269	5576	75

H(20A)	6733	-1166	6371	95
H(20B)	7605	-1091	5908	95
H(21A)	8431	26	6495	93
H(21B)	8326	-770	6937	93
H(22A)	7805	512	7416	77
H(22B)	6854	-143	7328	77
H(23)	7136	1262	6515	54
H(2N)	3516	2693	4983	54

IX. NMR Spectral Copies

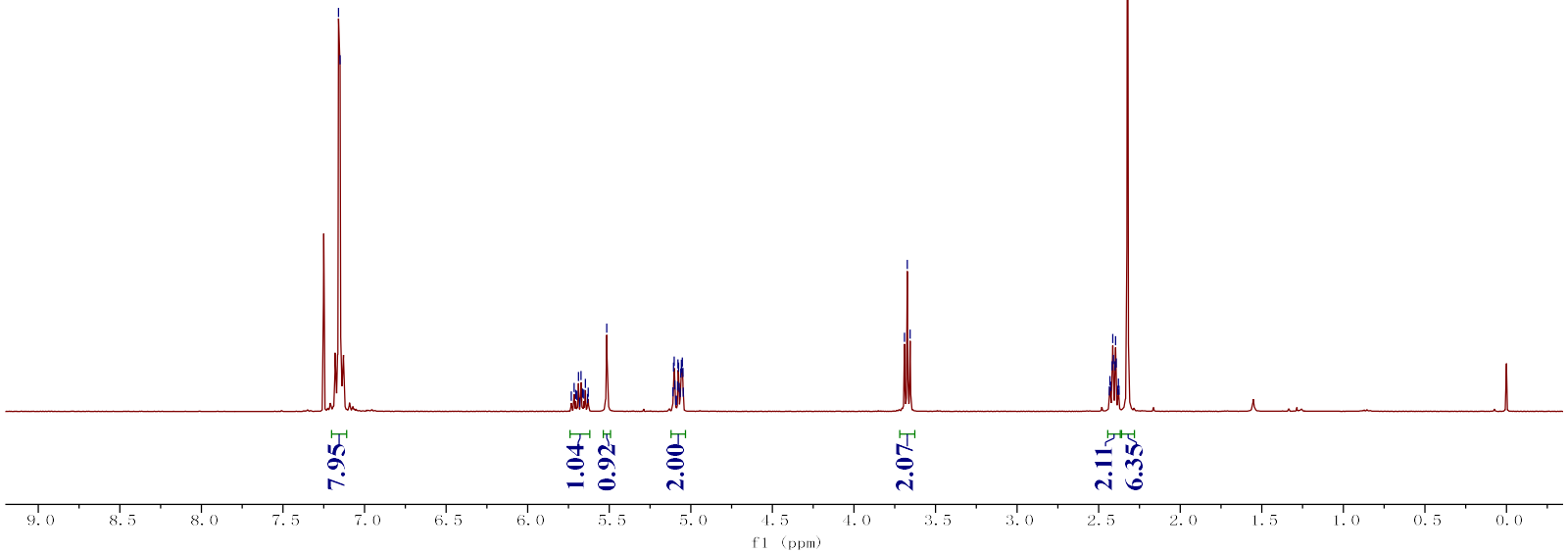
9xjm54cw.1.fid

7.16 7.15 5.73 5.71 5.71 5.70 5.69 5.68 5.67 5.66 5.65 5.65 5.63 5.63 5.51 5.11 5.10 5.10 5.10 5.08 5.08 5.07 5.07 5.06 5.06 5.05 5.05 5.05 5.05 3.69 3.67 3.65 2.43 2.43 2.43 2.42 2.41 2.41 2.40 2.40 2.39 2.38 2.38 2.38



1b

^{1}H NMR (400 MHz, $CDCl_3$)



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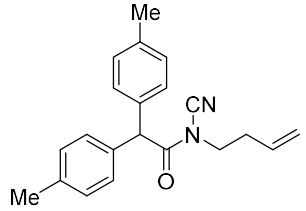
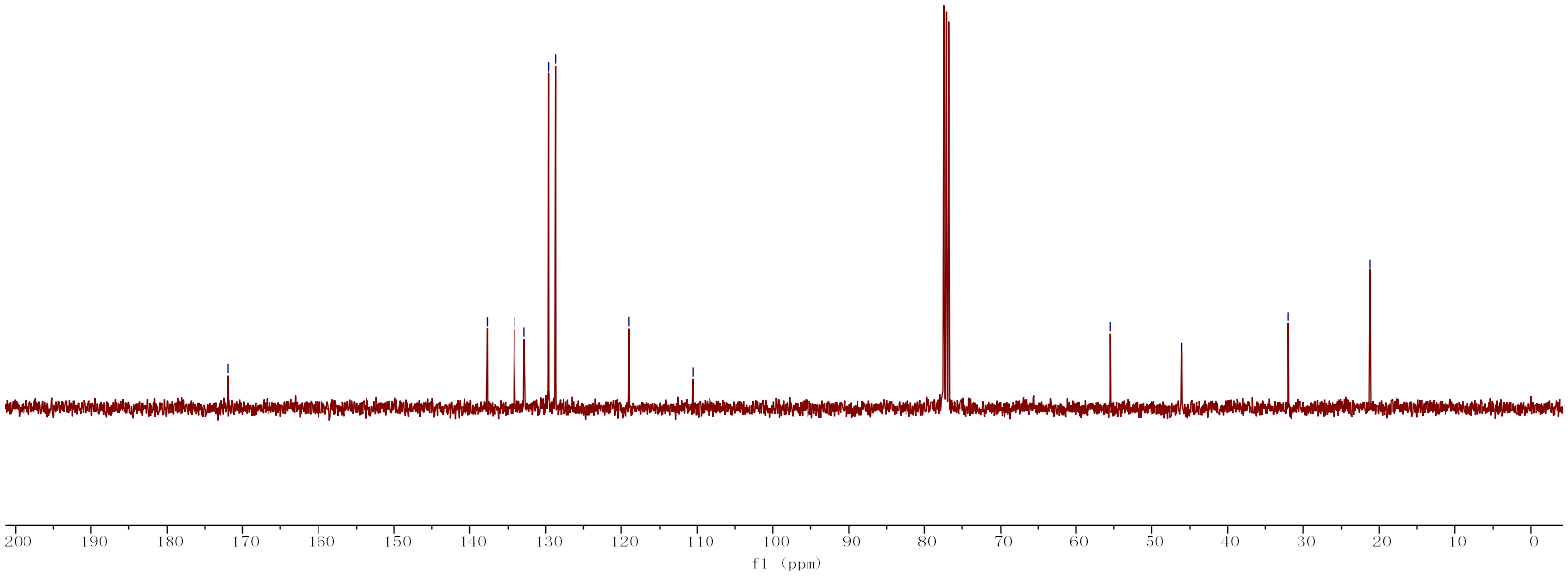
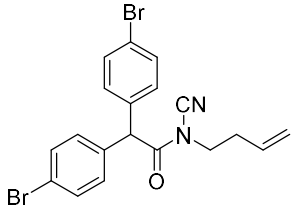
171.90
137.69
134.15
132.81
129.64
128.73
118.99
110.57
55.43
46.09
32.04
21.21



1b

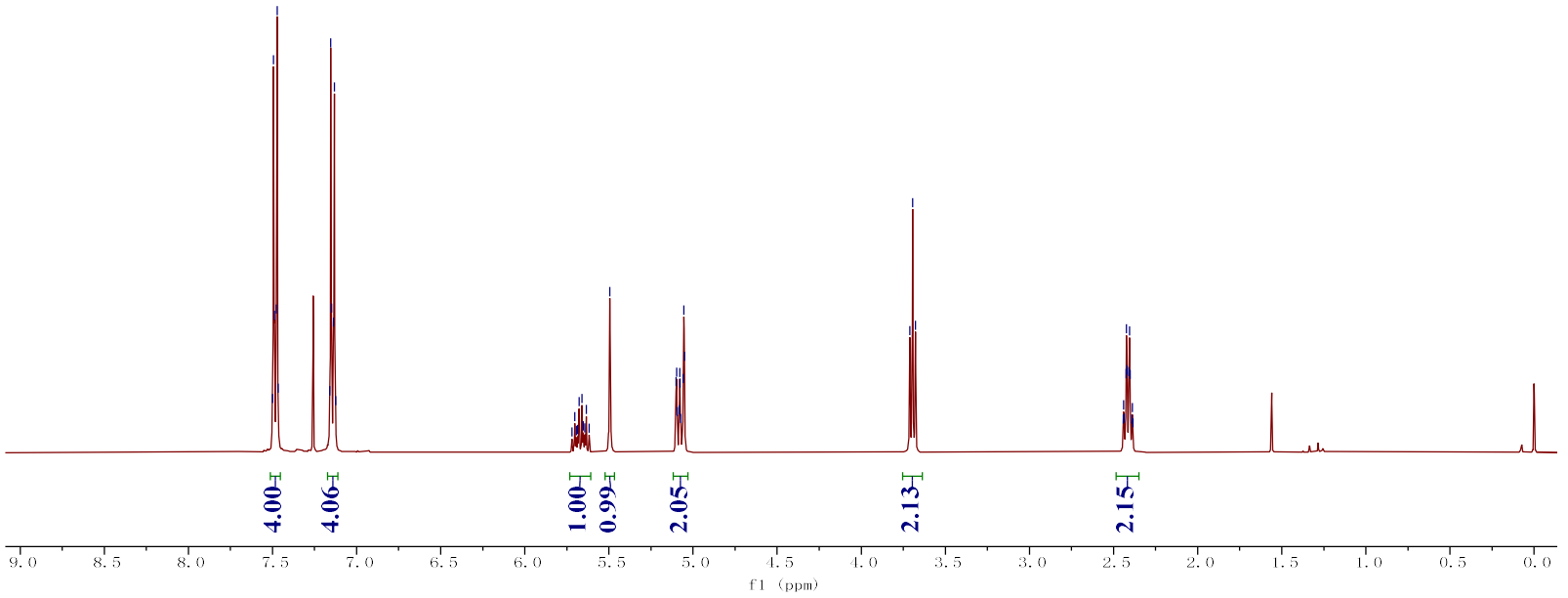
^{13}C NMR (100 MHz, $CDCl_3$)





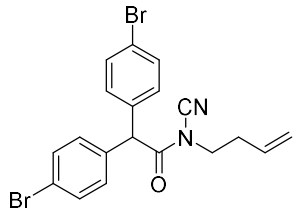
1c

^{1}H NMR (400 MHz, $CDCl_3$)



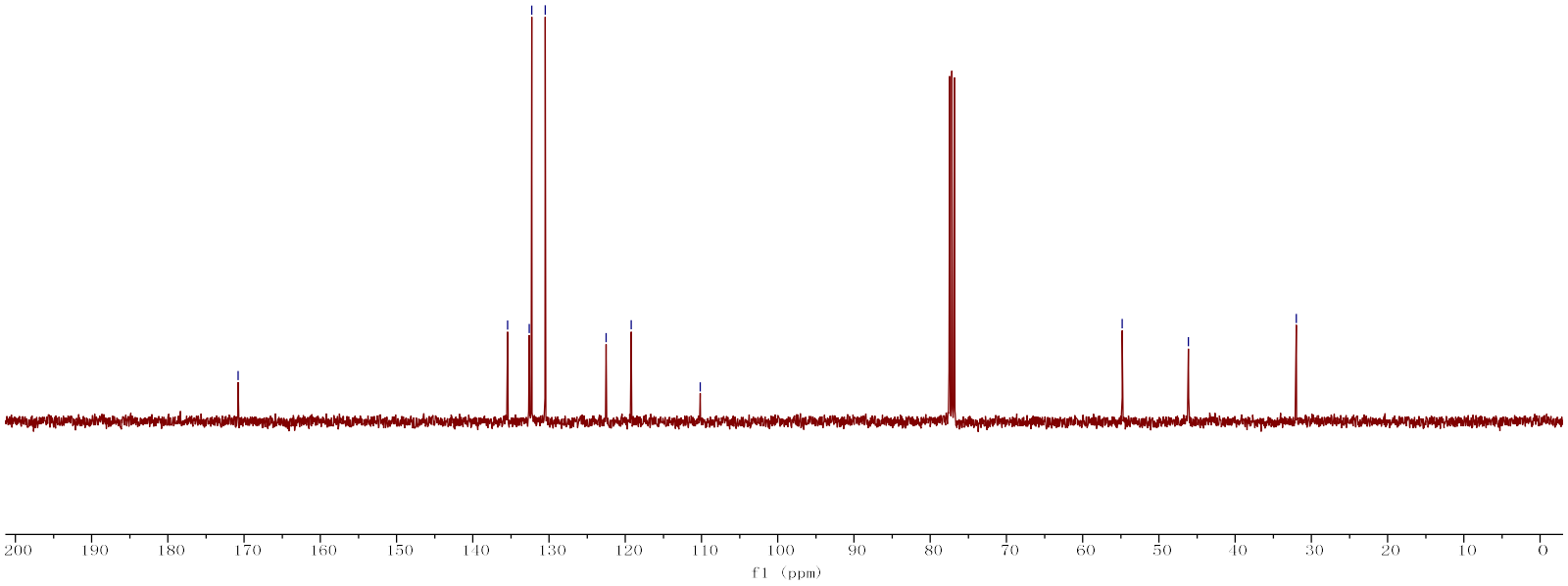
9xjm55a-c.3.fid

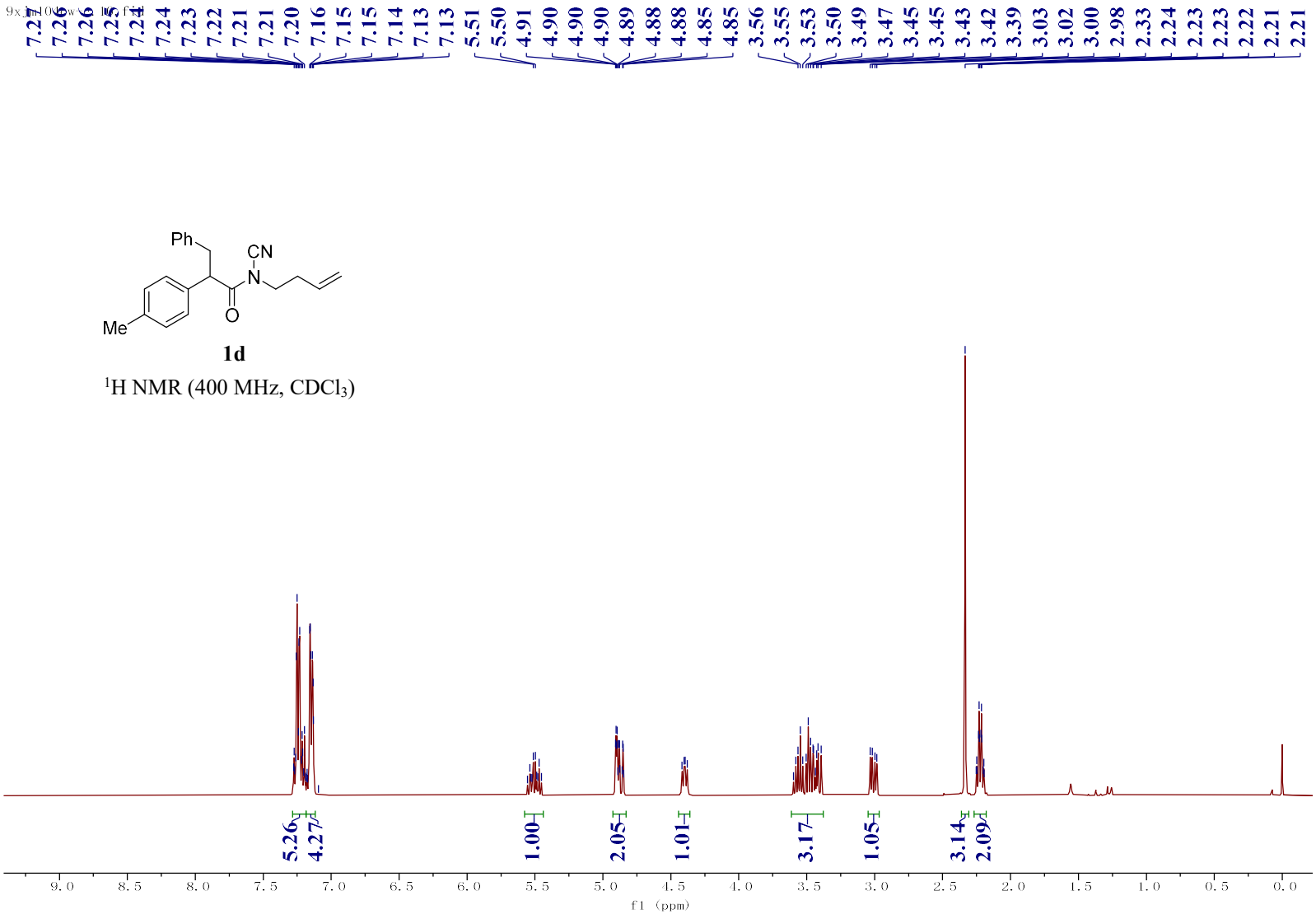
170.79
135.44
132.61
132.27
130.50
122.51
119.23
110.18
54.81
46.15
32.00



1c

^{13}C NMR (100 MHz, $CDCl_3$)



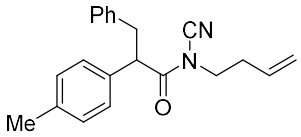


1d

^{1}H NMR (400 MHz, $CDCl_3$)

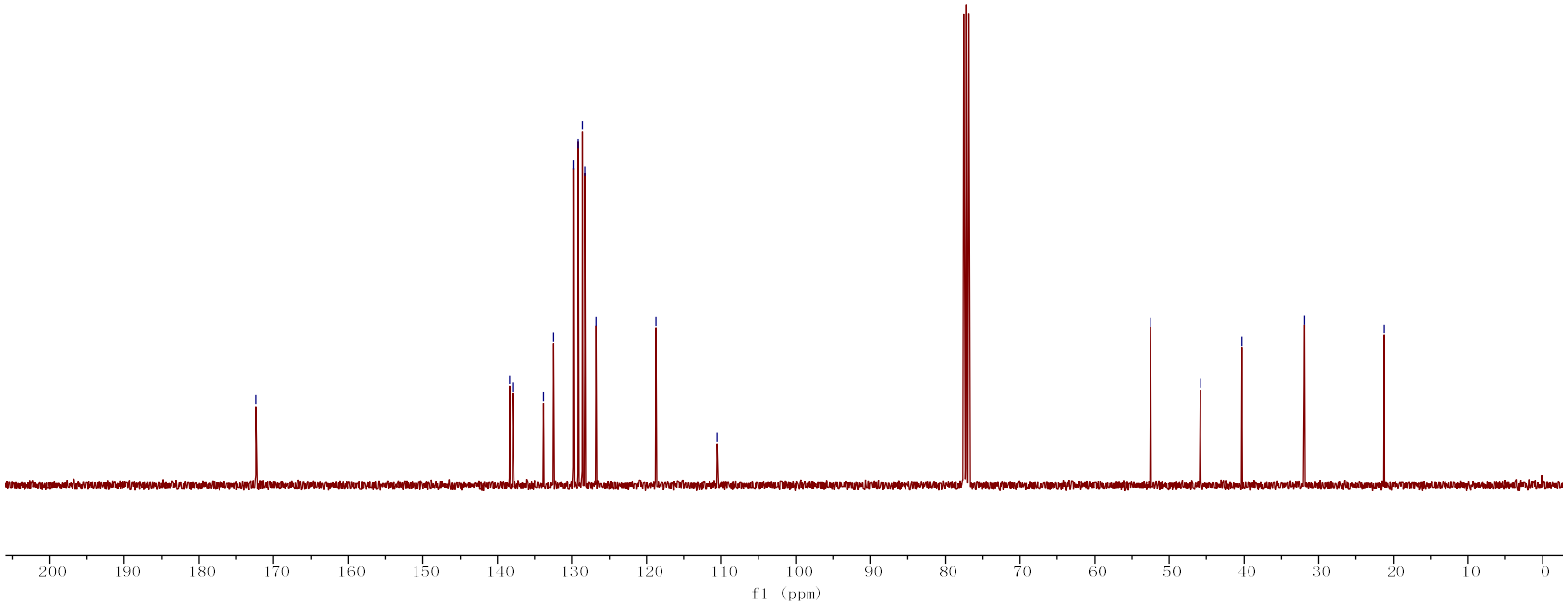
9xjm104cw-c.11.fid

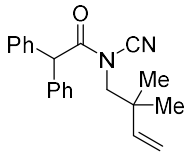
172.37
138.41
137.96
133.83
132.55
129.76
129.17
128.61
128.25
126.80
118.79
110.51
52.48
45.84
40.34
31.86
21.24



1d

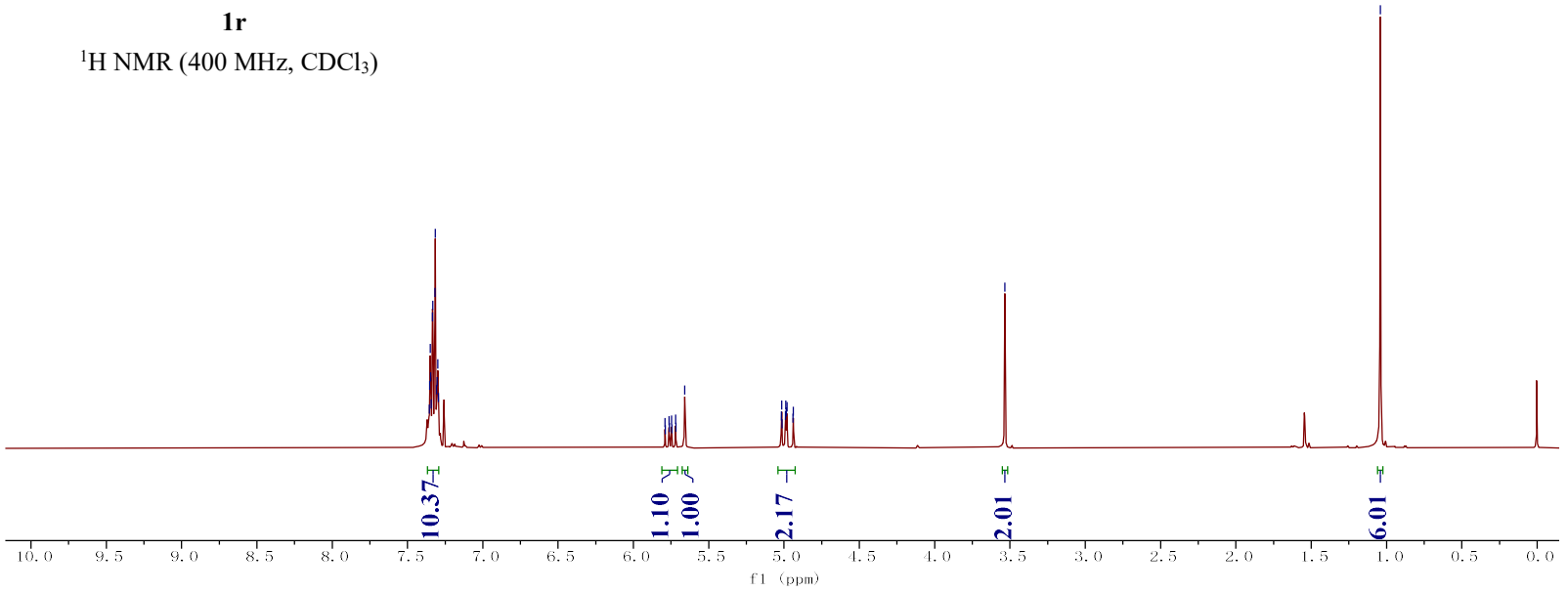
^{13}C NMR (100 MHz, $CDCl_3$)

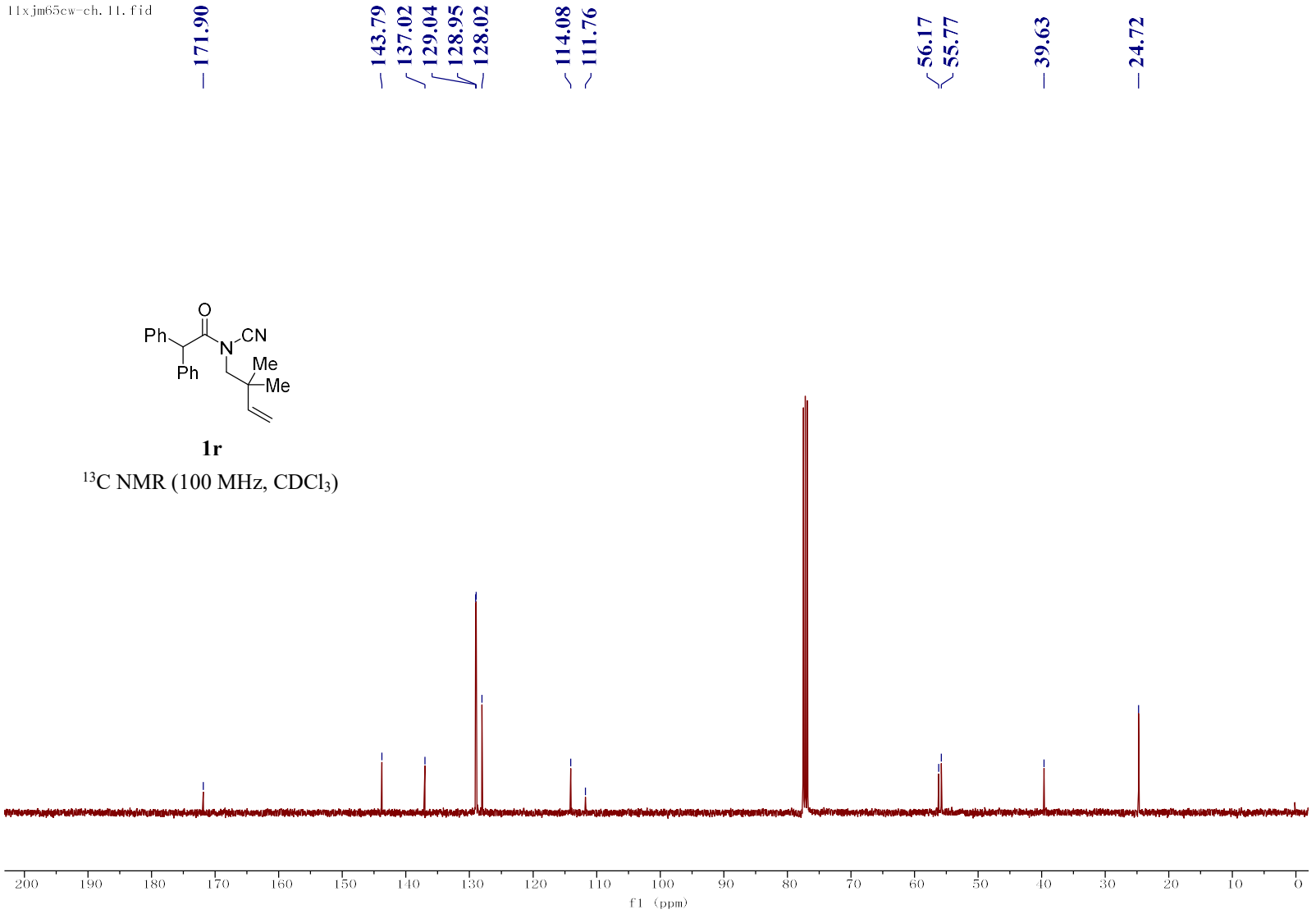




1r

^{1}H NMR (400 MHz, $CDCl_3$)

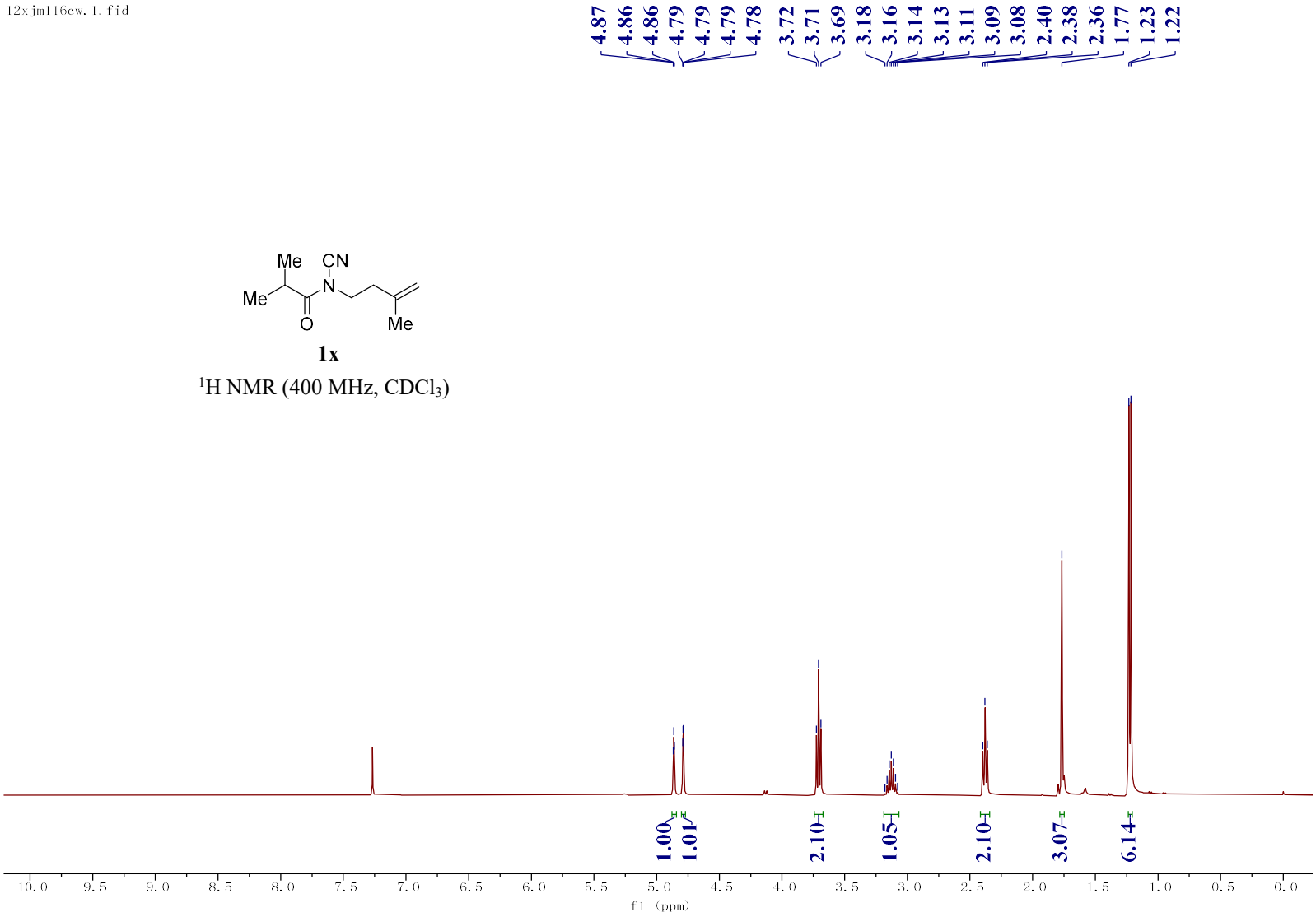




1r

^{13}C NMR (100 MHz, $CDCl_3$)

12xjm116cw.1.fid

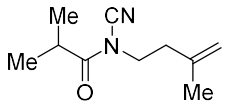


1x

^{1}H NMR (400 MHz, $CDCl_3$)

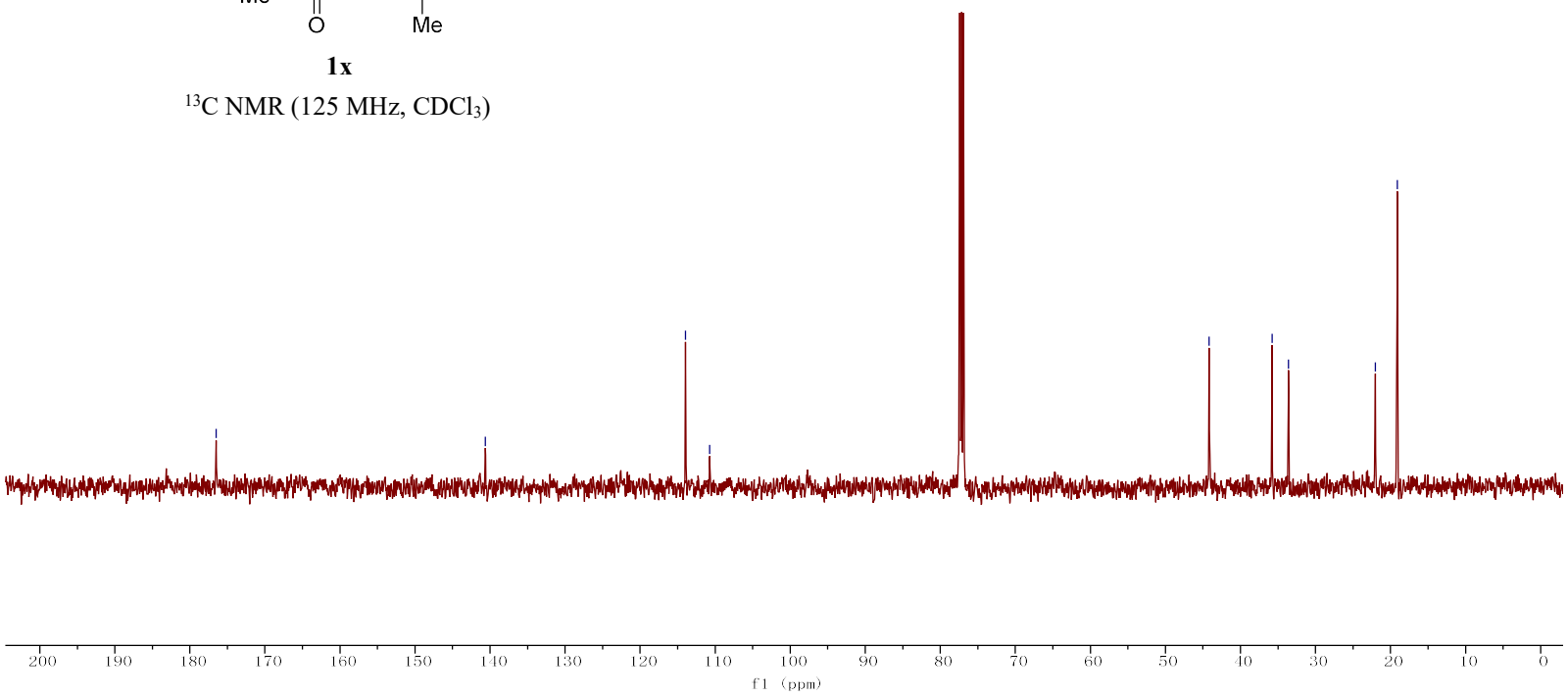
12xjm116cw-c.21.fid

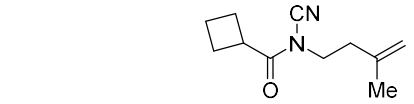
176.51
140.62
113.95
110.72
44.17
35.80
33.60
22.03
19.09



1x

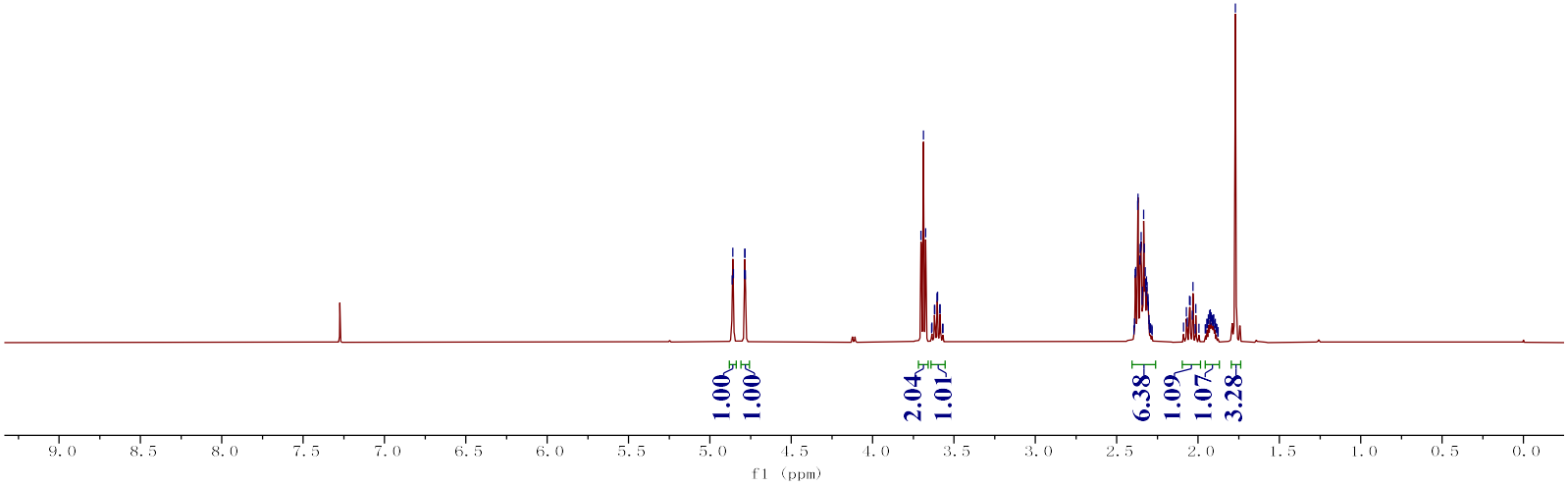
^{13}C NMR (125 MHz, $CDCl_3$)





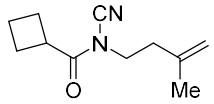
1y

^{1}H NMR (500 MHz, $CDCl_3$)



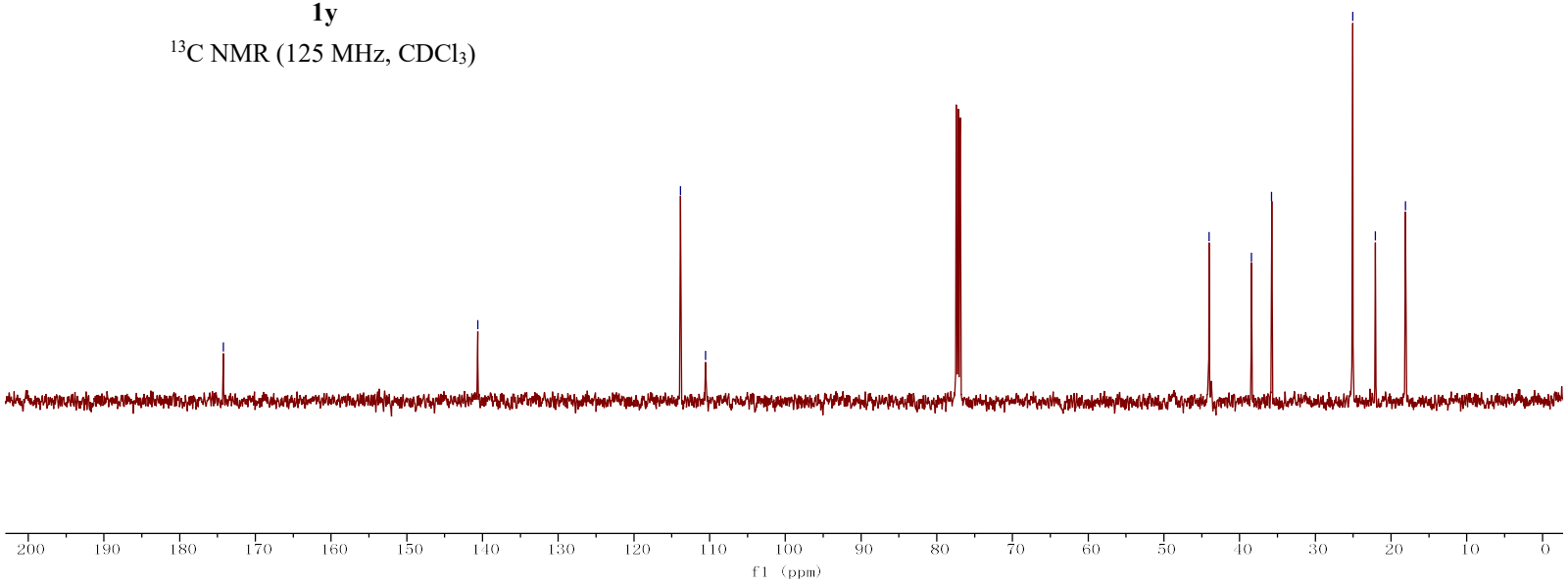
13xjm2cw.37.fid

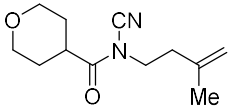
174.23
140.62
113.84
110.52
44.03
38.44
35.77
25.07
22.06
18.08



1y

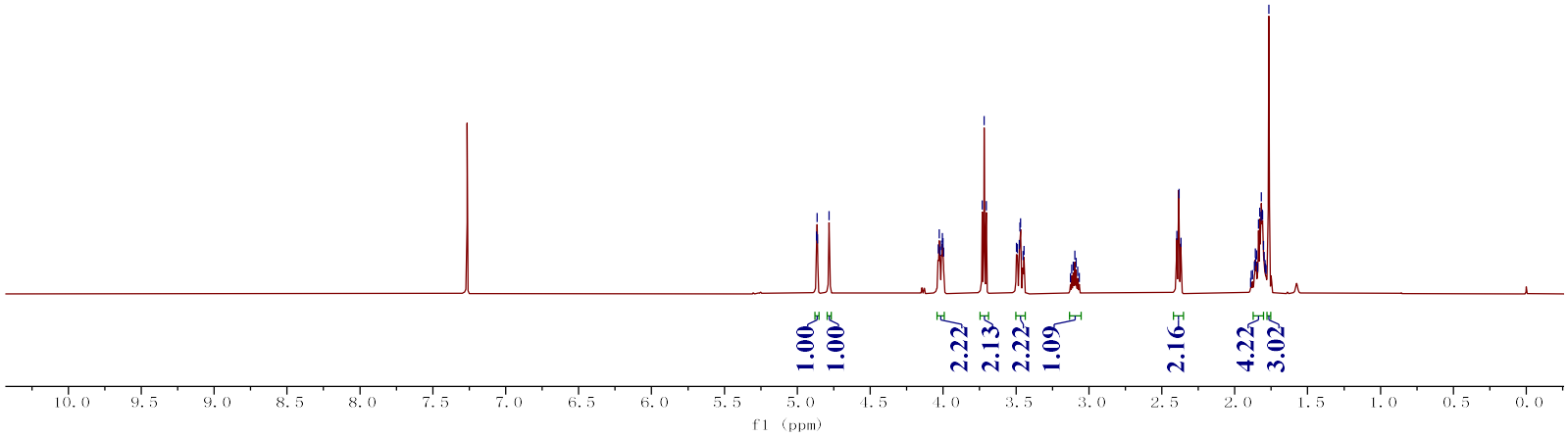
^{13}C NMR (125 MHz, $CDCl_3$)

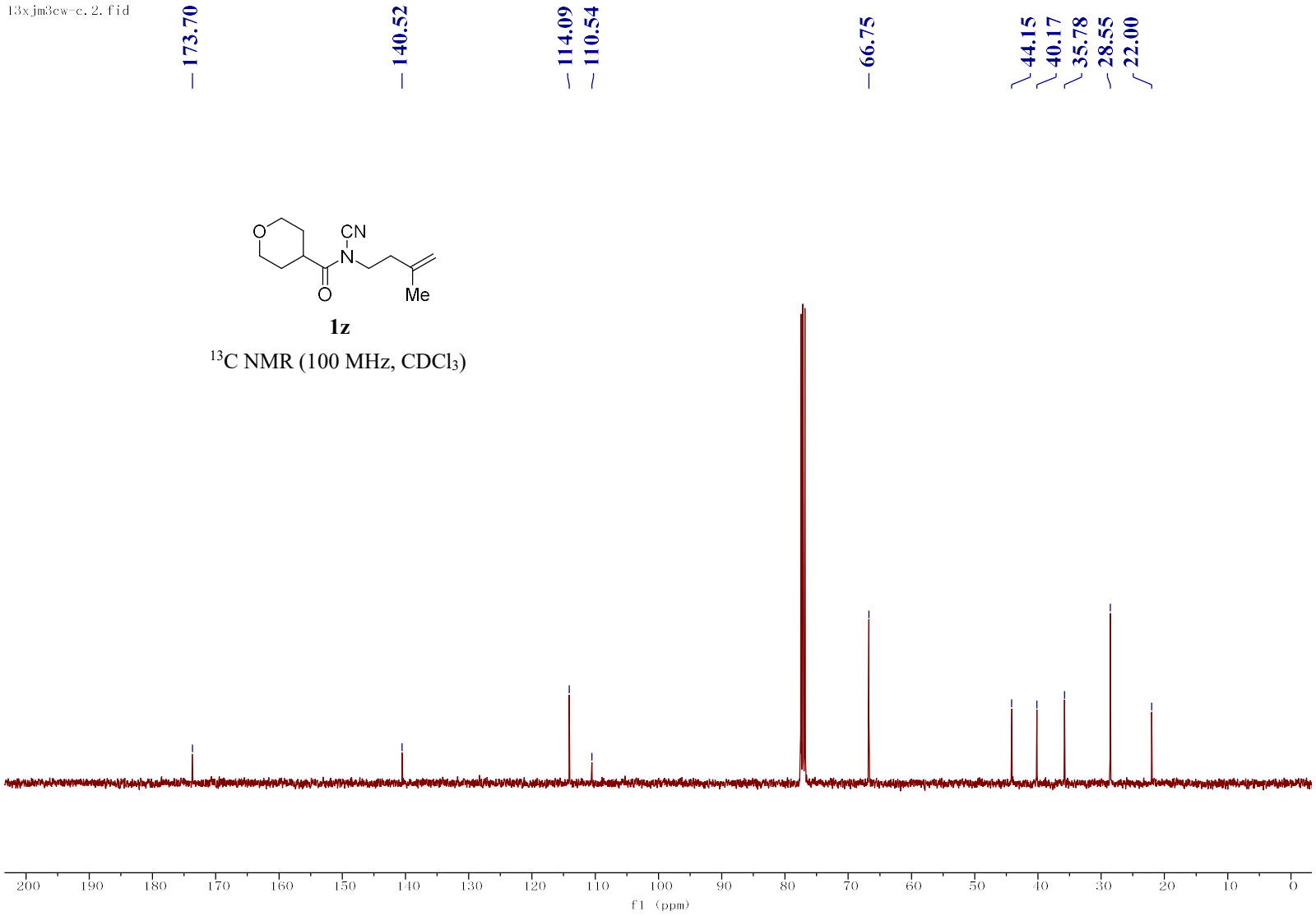




1z

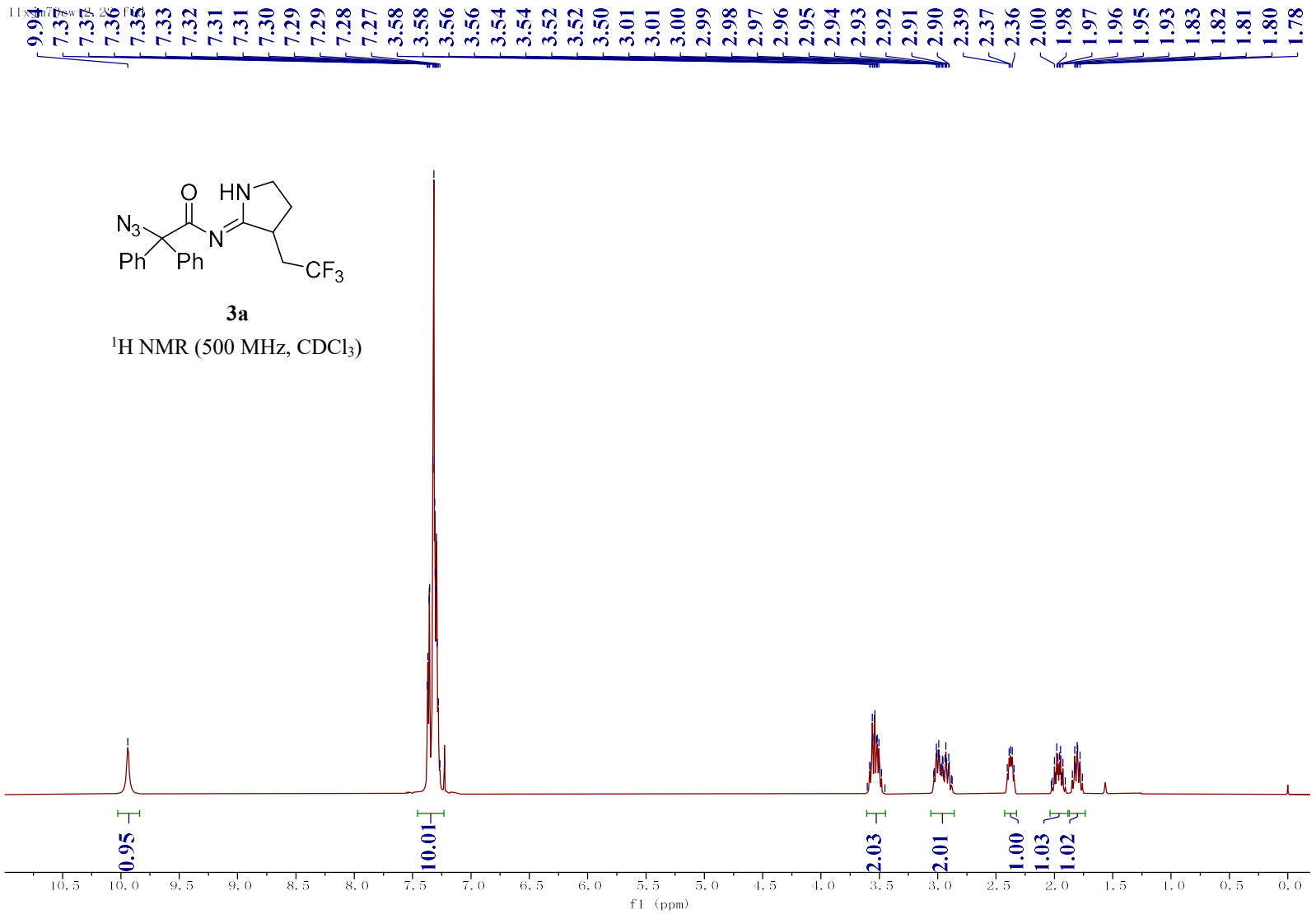
^{1}H NMR (500 MHz, $CDCl_3$)





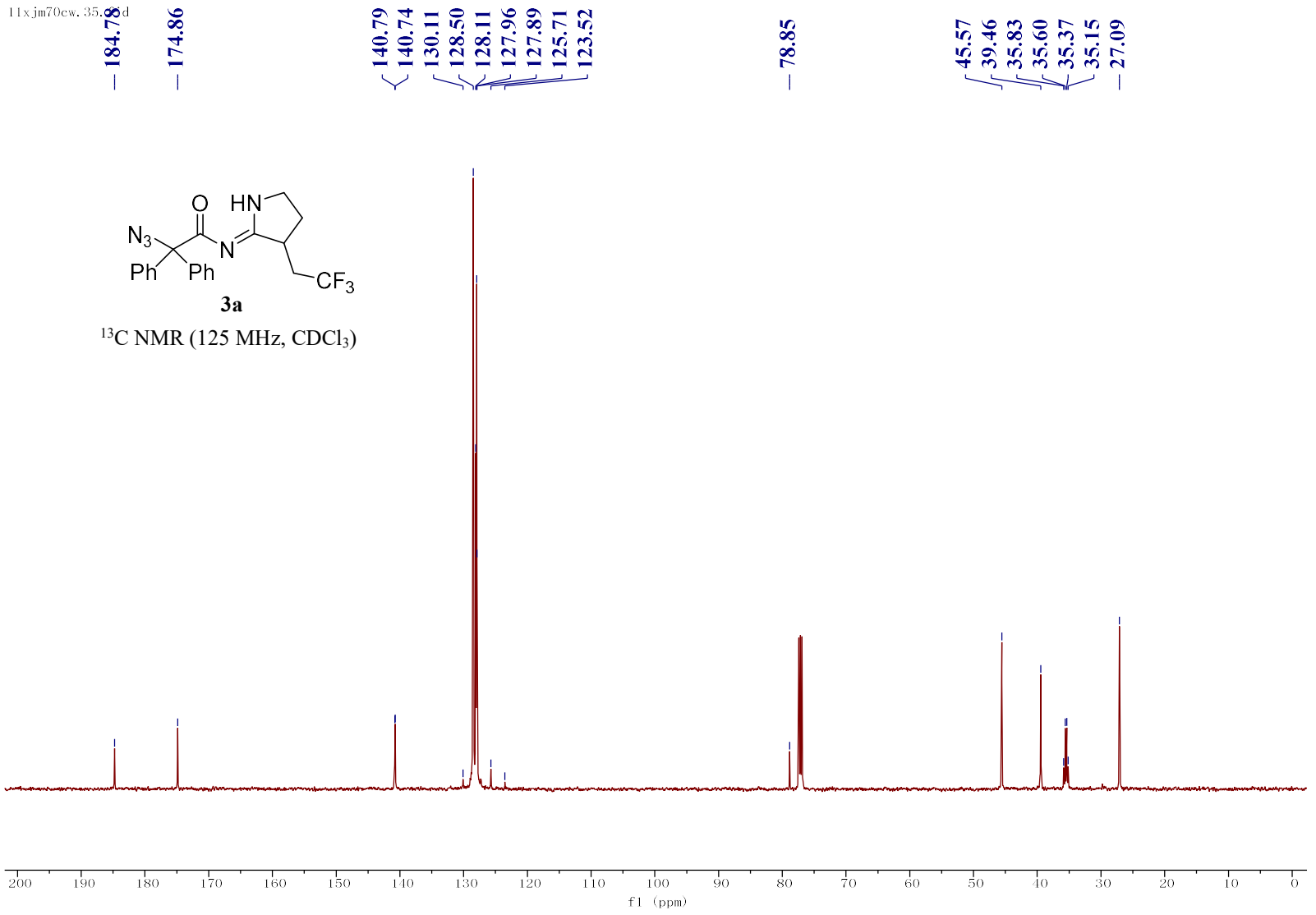
1z

^{13}C NMR (100 MHz, $CDCl_3$)



3a

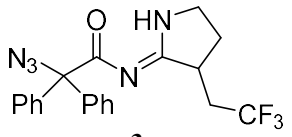
^{1}H NMR (500 MHz, $CDCl_3$)



3a

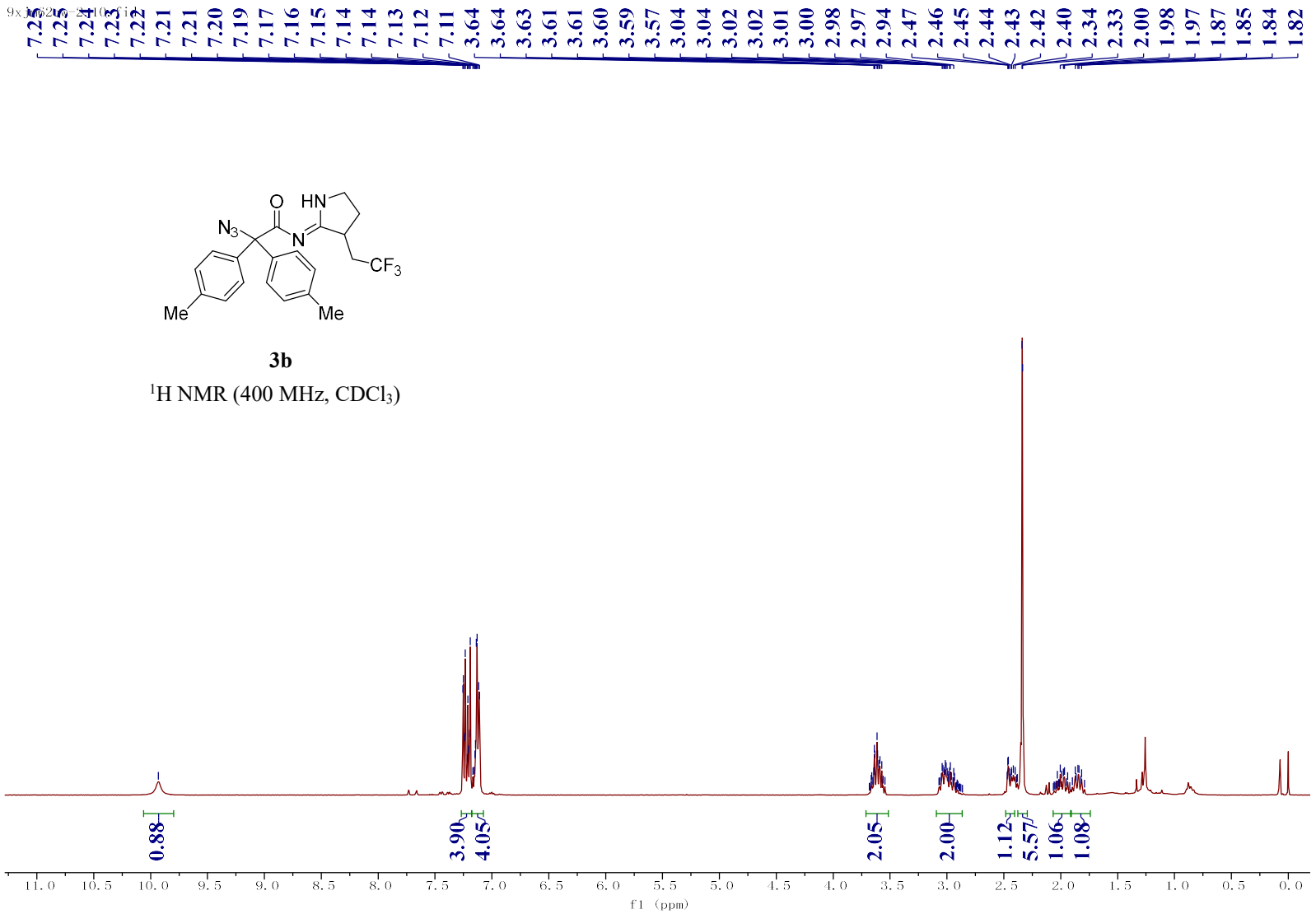
^{13}C NMR (125 MHz, $CDCl_3$)

11xjm70cw-2-f.23.fid



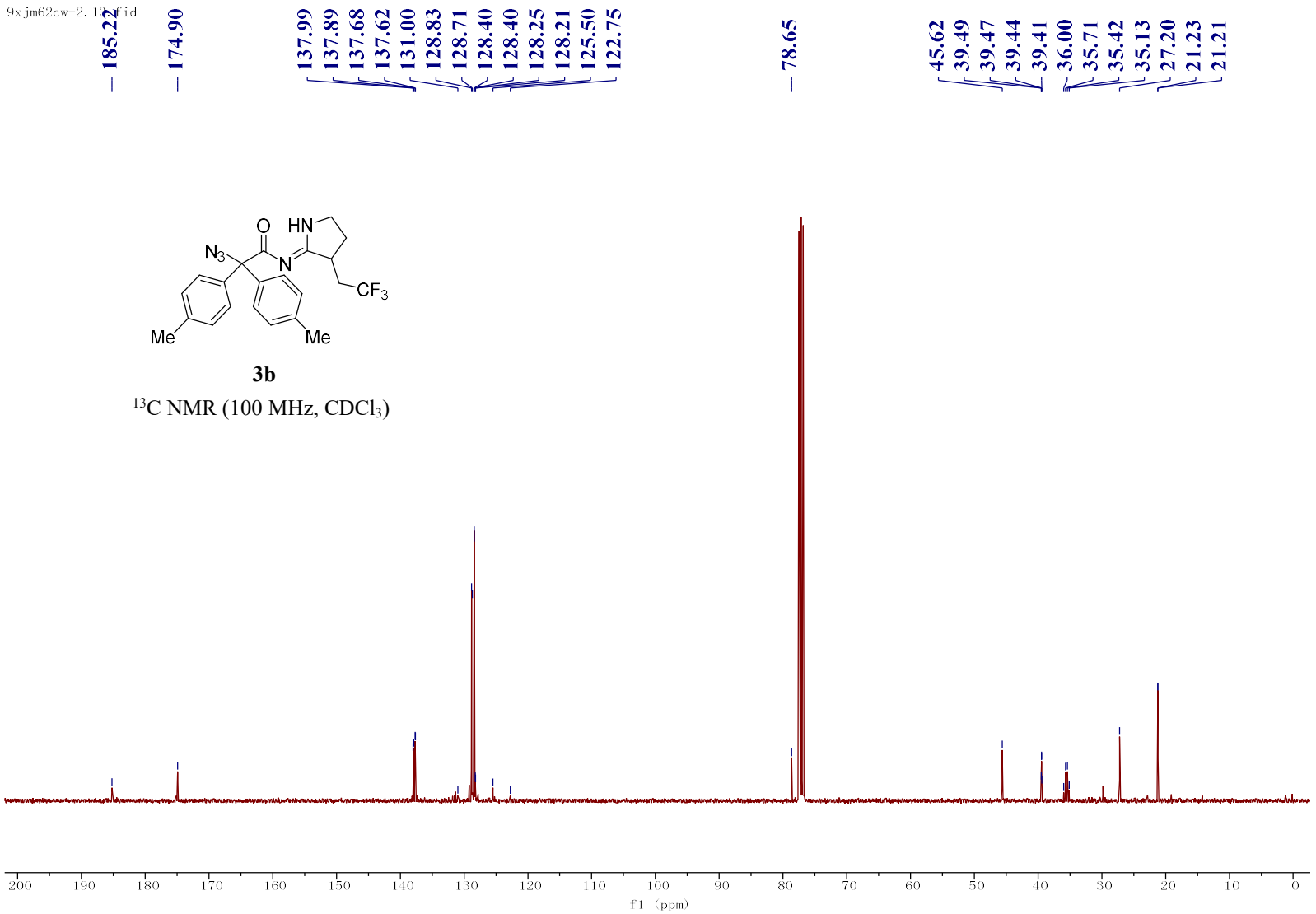
3a

^{19}F NMR (470 MHz, $CDCl_3$)



3b

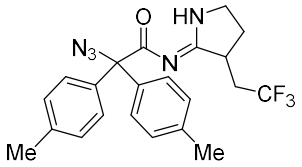
^{1}H NMR (400 MHz, $CDCl_3$)



3b

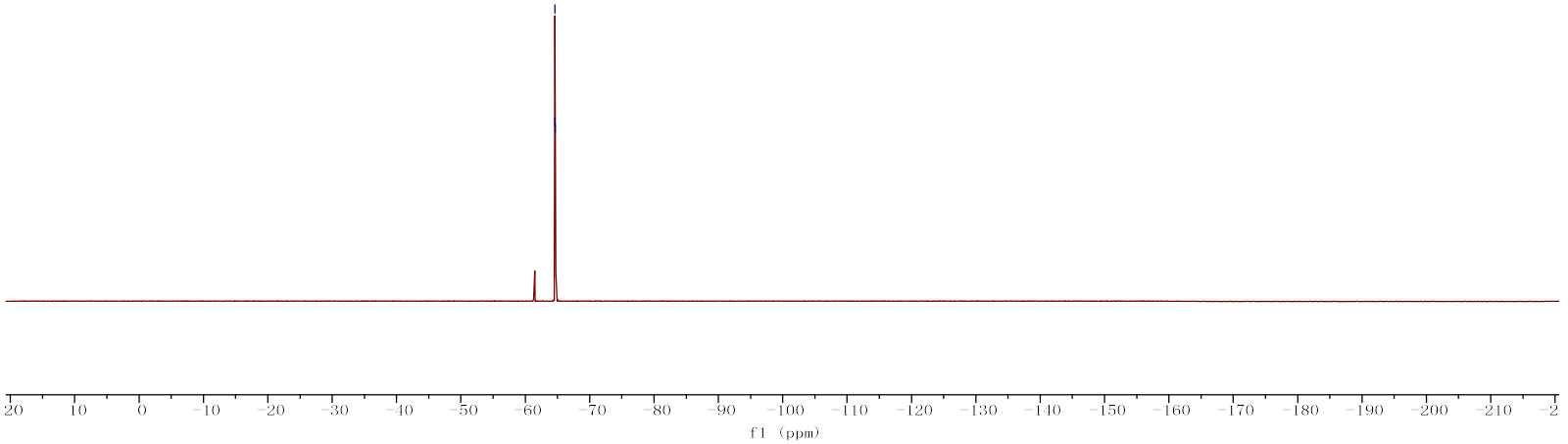
^{13}C NMR (100 MHz, $CDCl_3$)

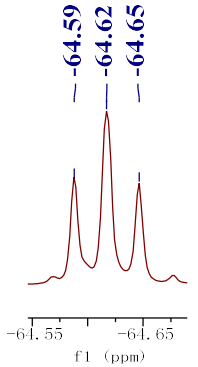
9xjm62cw-2.11.fid

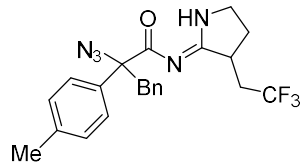


3b

^{19}F NMR (376 MHz, $CDCl_3$)

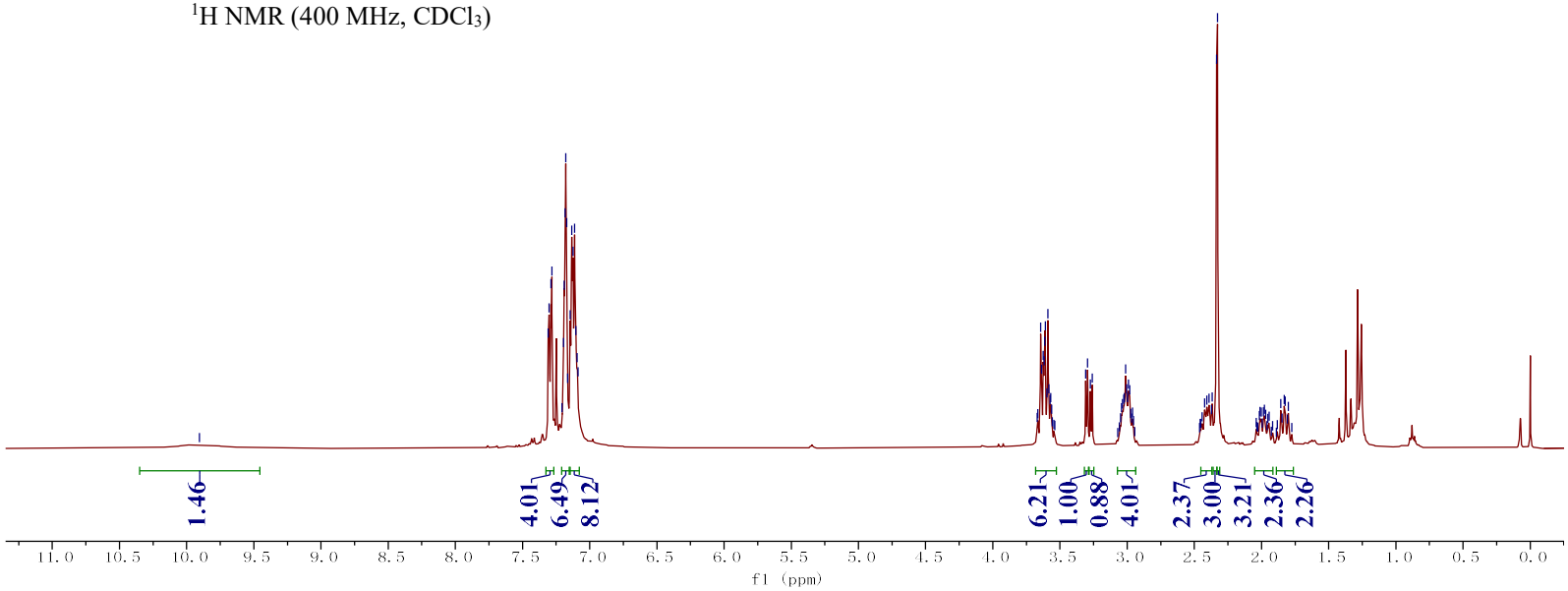


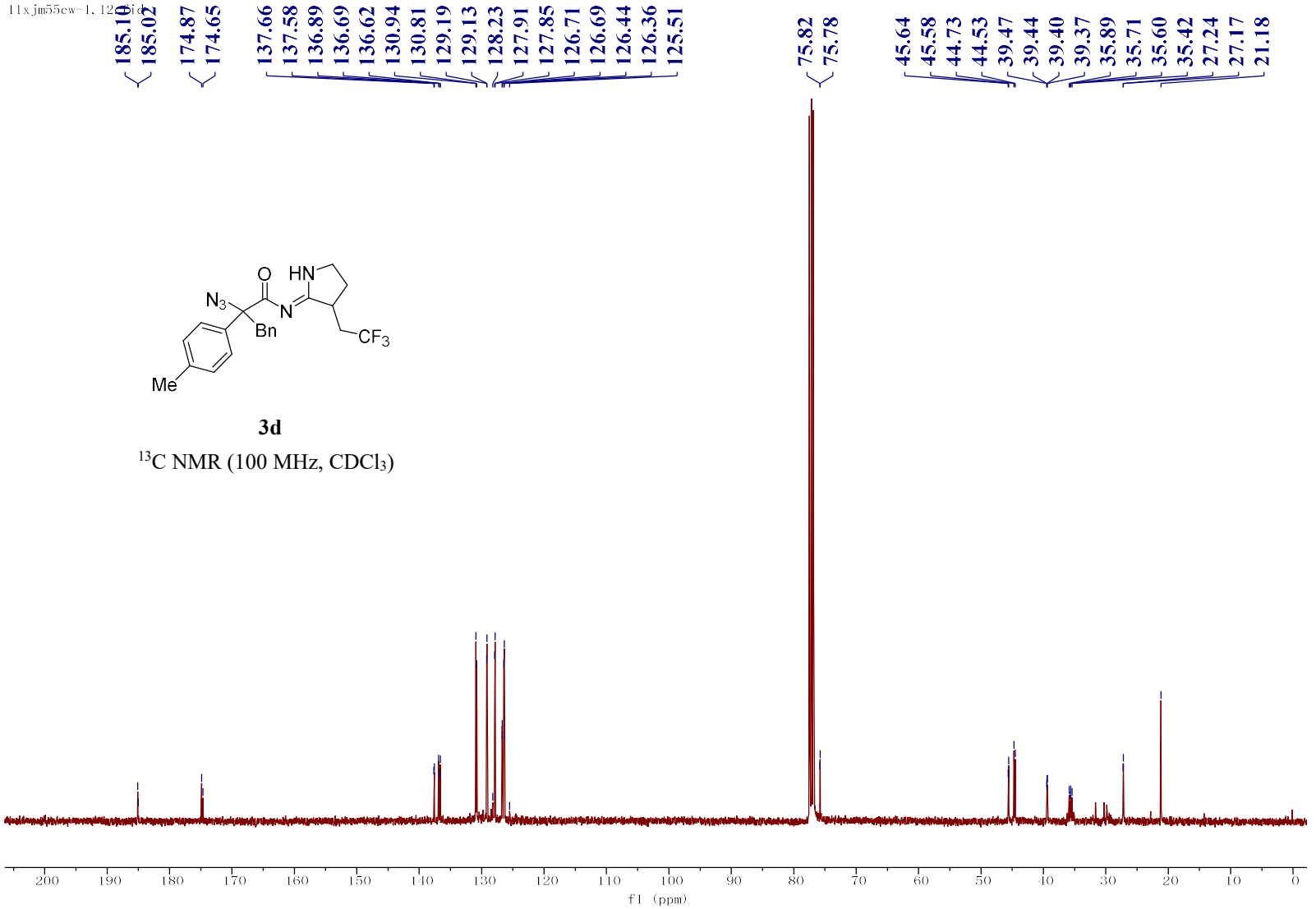




3d

^{1}H NMR (400 MHz, $CDCl_3$)

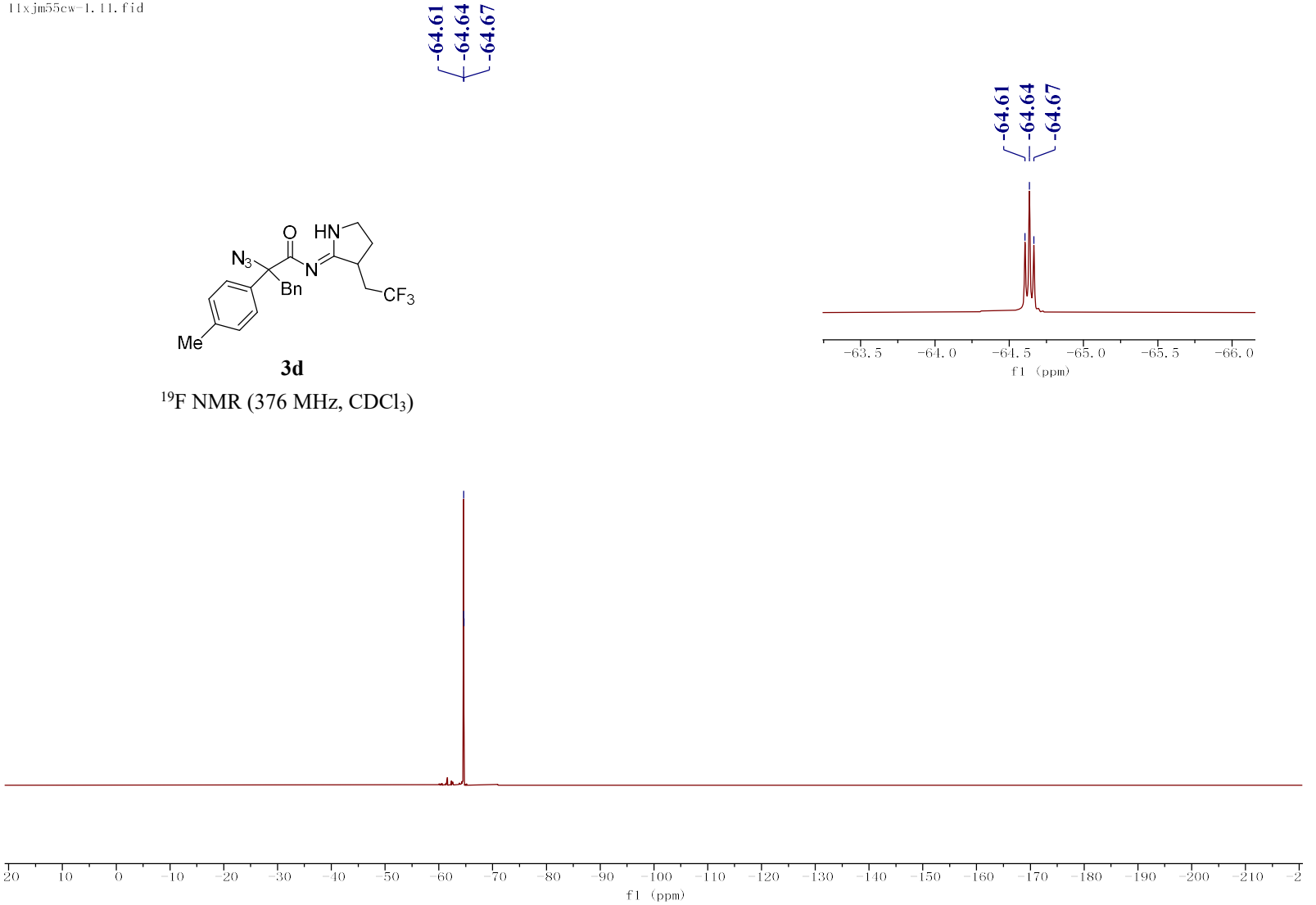




3d

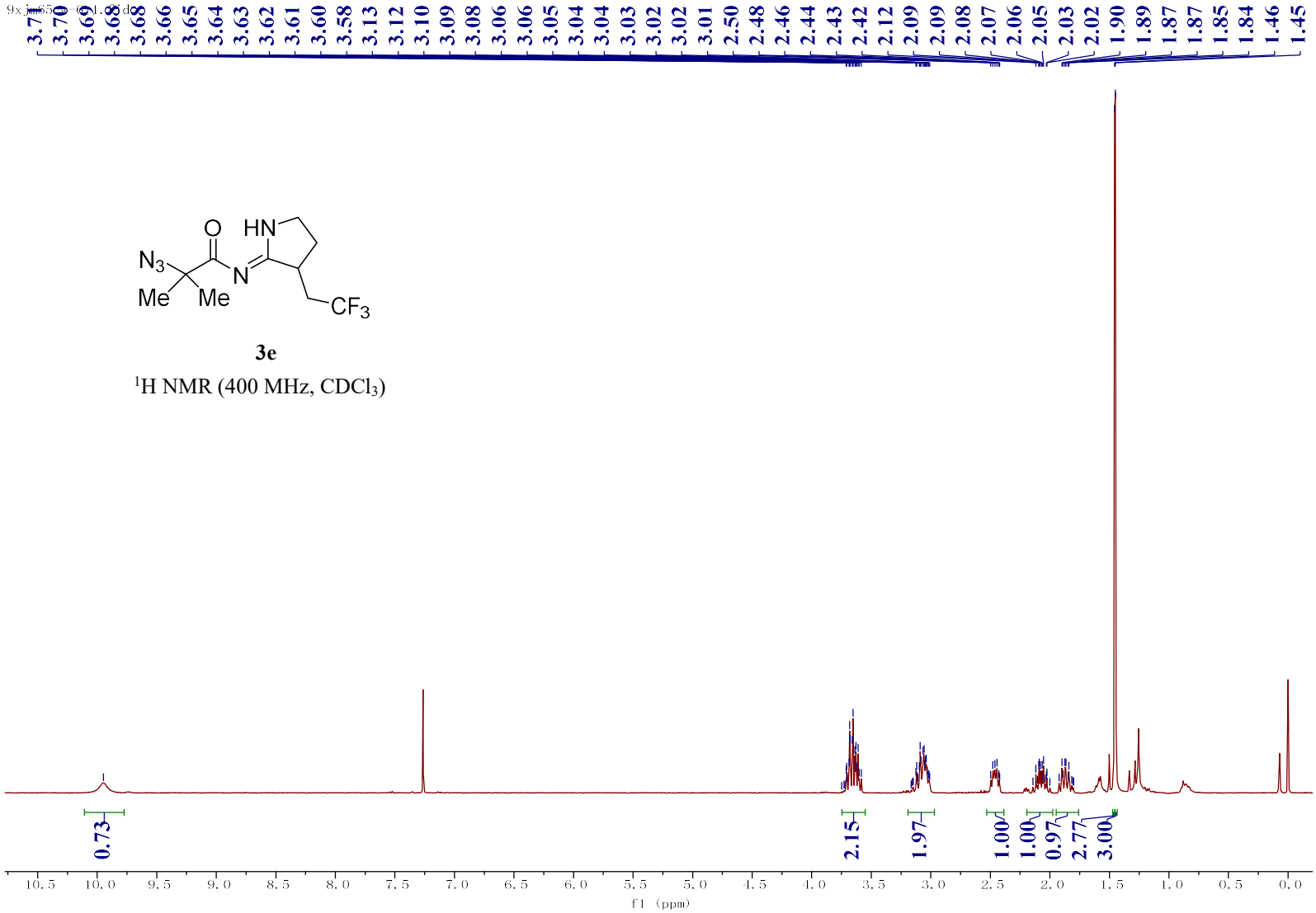
^{13}C NMR (100 MHz, $CDCl_3$)

11xjm55cw-1.11.fid



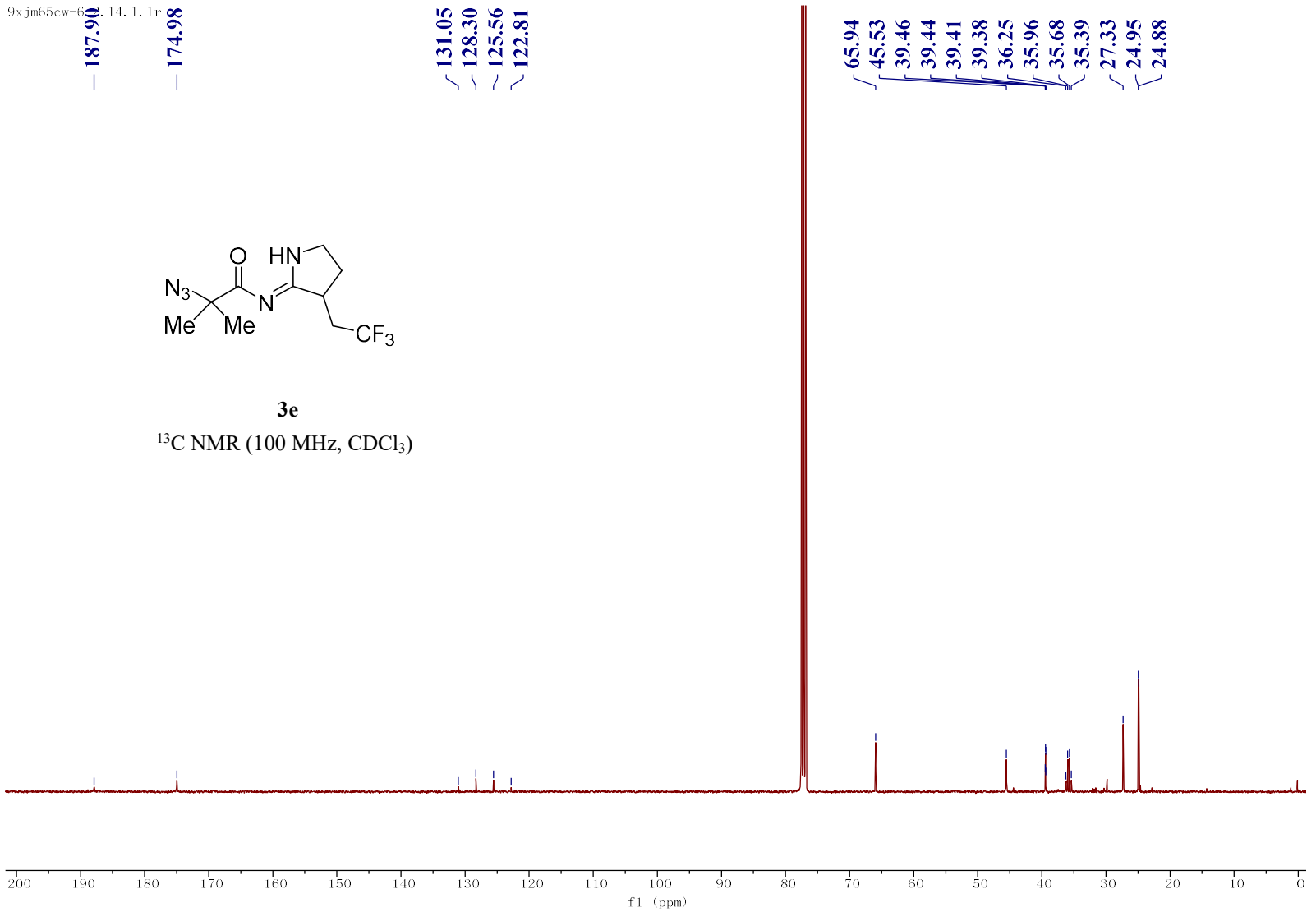
3d

^{19}F NMR (376 MHz, $CDCl_3$)



3e

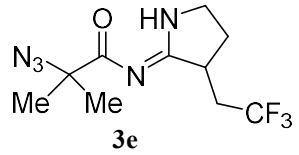
^{1}H NMR (400 MHz, $CDCl_3$)



3e

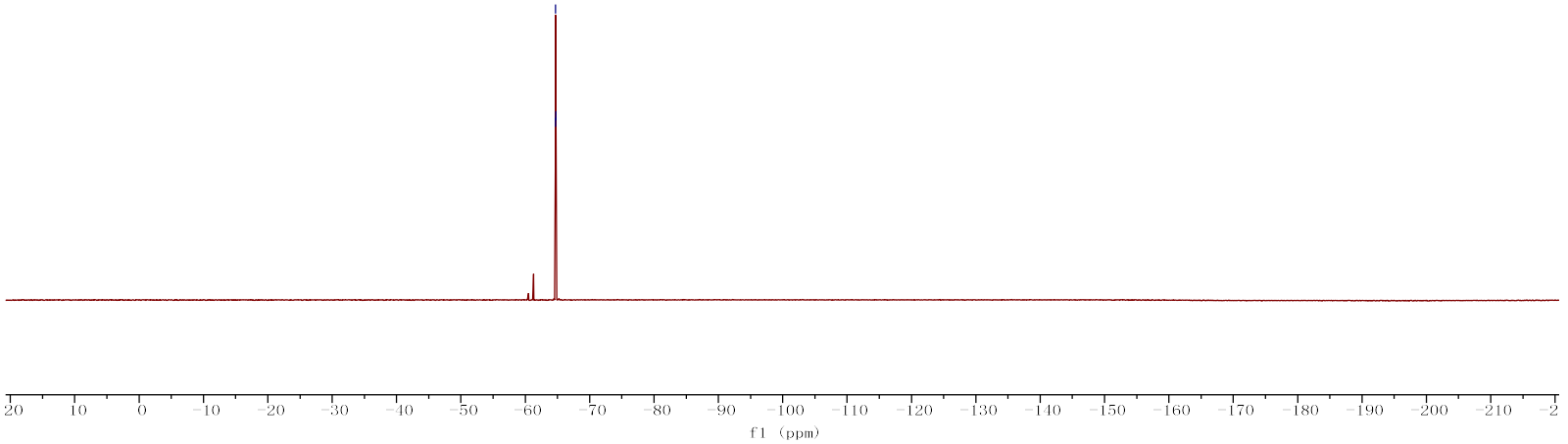
^{13}C NMR (100 MHz, $CDCl_3$)

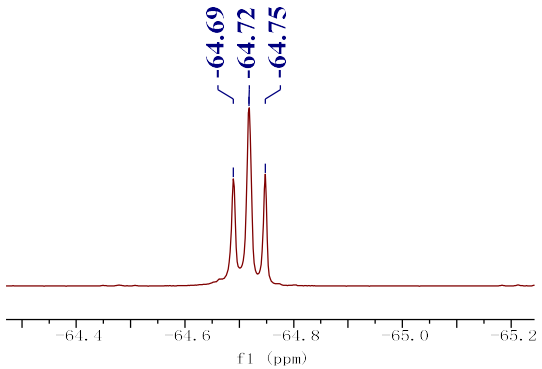
9xjm65cw-6.12.fid

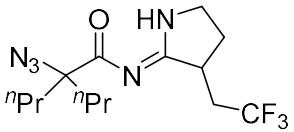


3e

^{19}F NMR (376 MHz, $CDCl_3$)





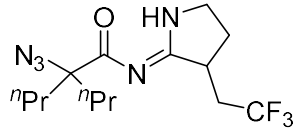


3f

^{1}H NMR (400 MHz, $CDCl_3$)

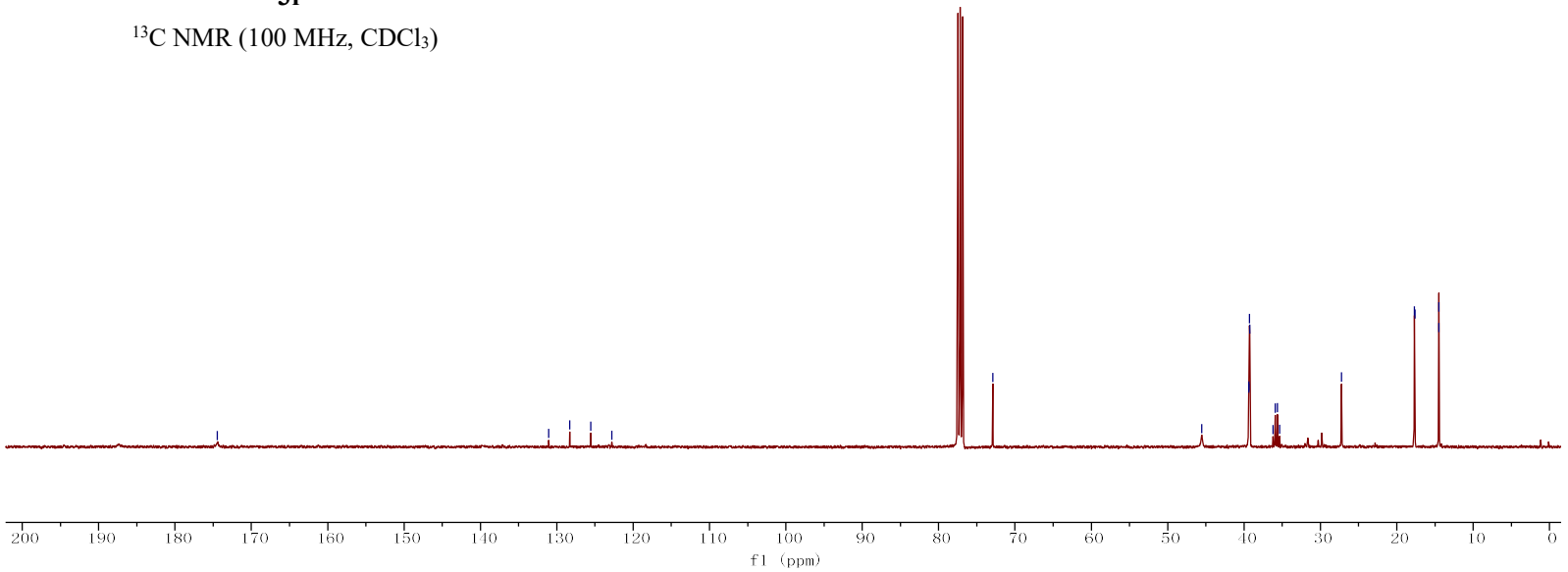
9xjm112cw.11.fid

174.45
131.05
128.30
125.55
122.80
72.90
45.54
39.39
39.36
39.30
39.24
36.19
35.90
35.62
35.33
27.23
17.69
17.62
14.48
14.48

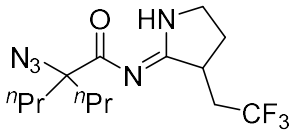


3f

^{13}C NMR (100 MHz, $CDCl_3$)

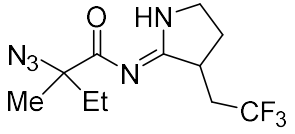


9XJM112CW-3.12.fid



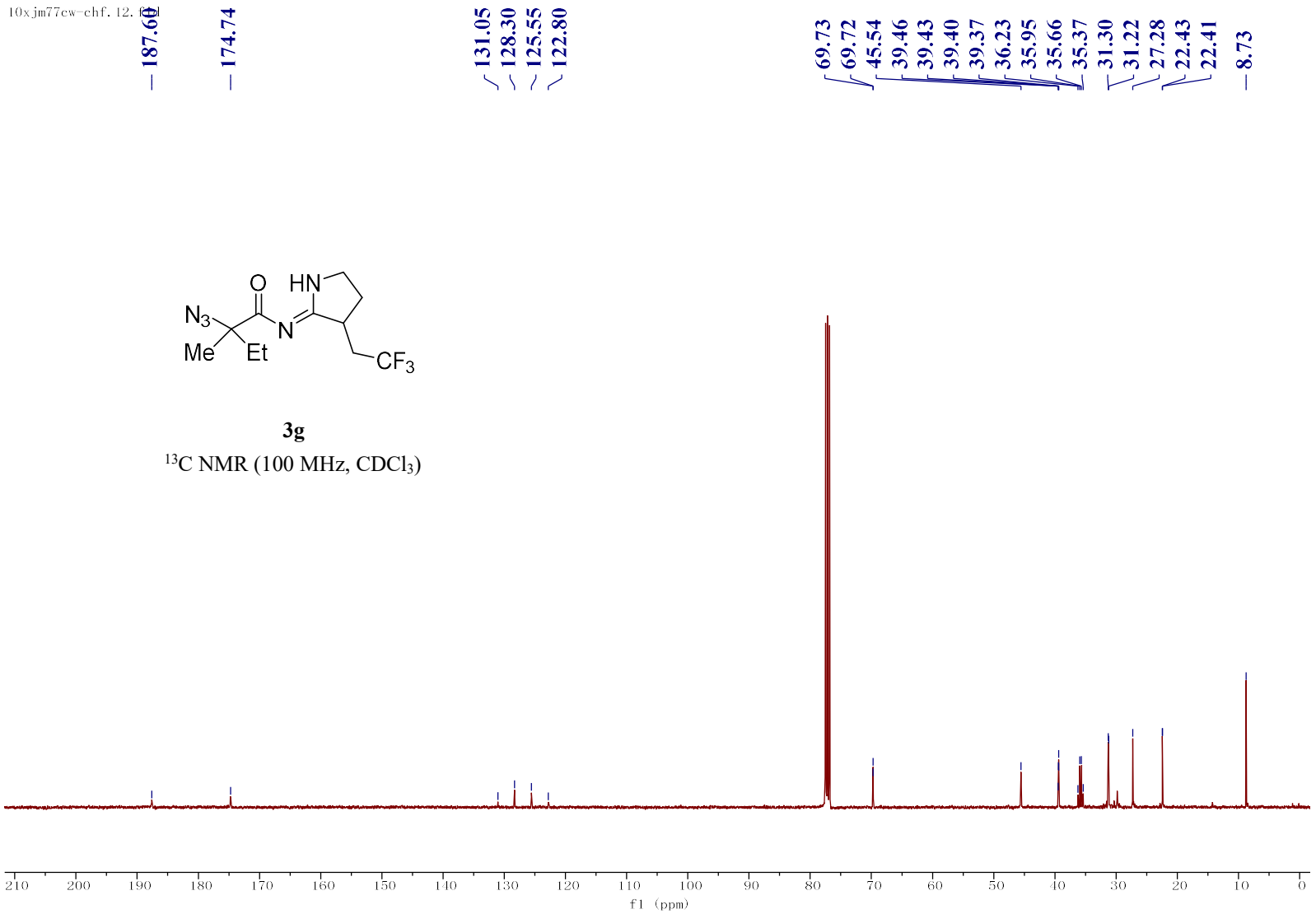
3f

^{19}F NMR (376 MHz, $CDCl_3$)



3g

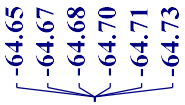
^{1}H NMR (400 MHz, $CDCl_3$)

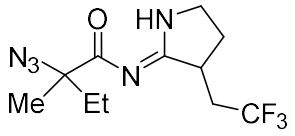


3g

^{13}C NMR (100 MHz, $CDCl_3$)

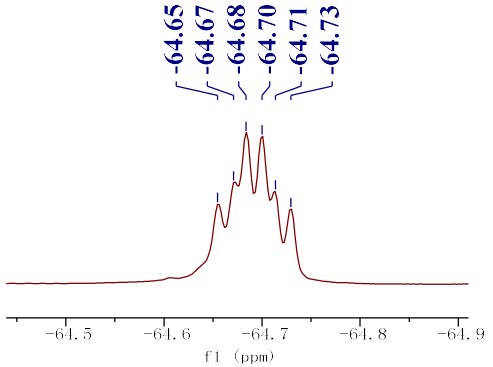
10xjm77cw-chf.11.fid

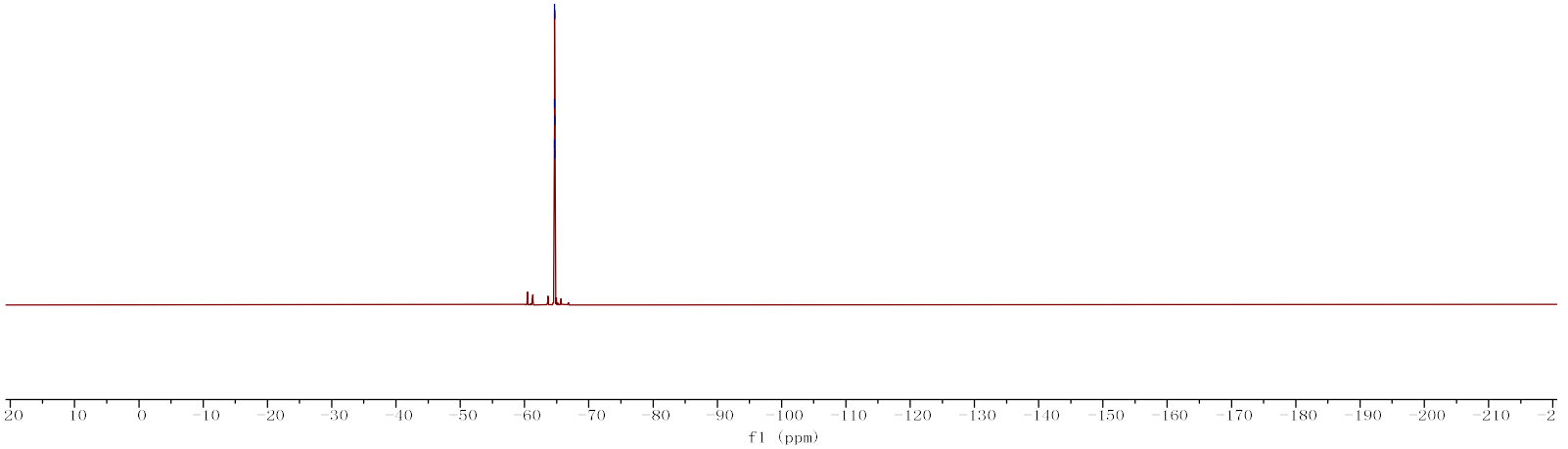


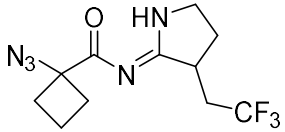


3g

^{19}F NMR (376 MHz, $CDCl_3$)

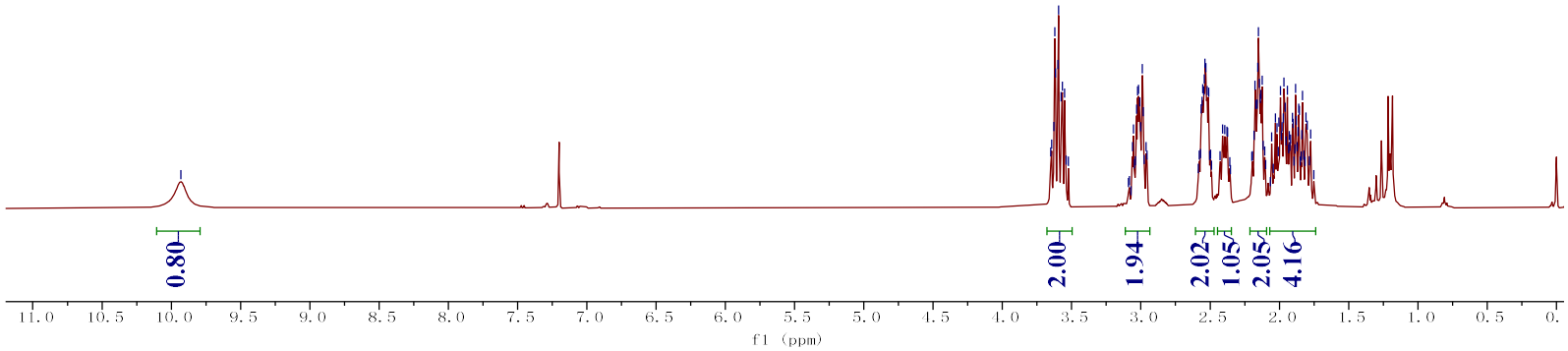


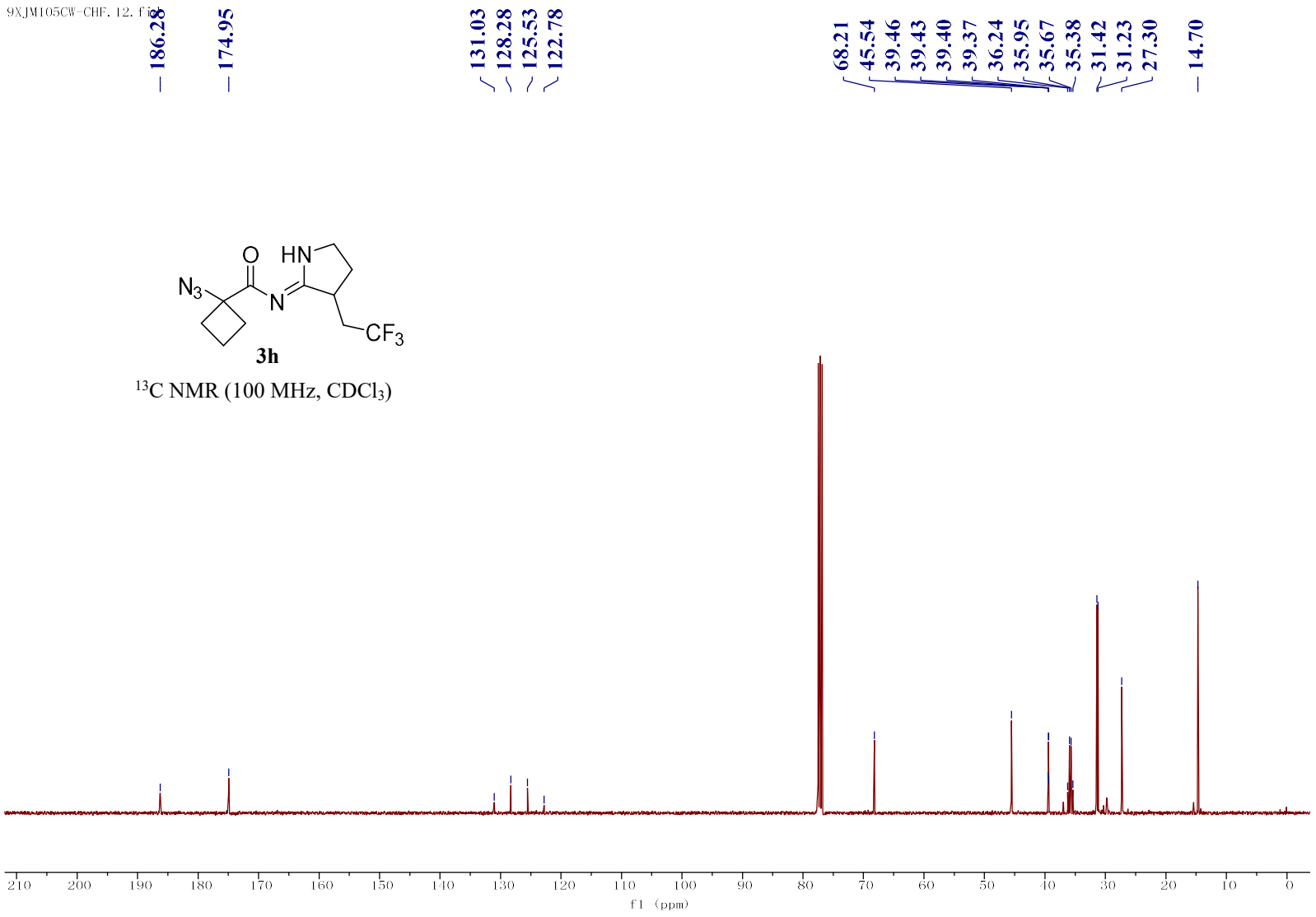




3h

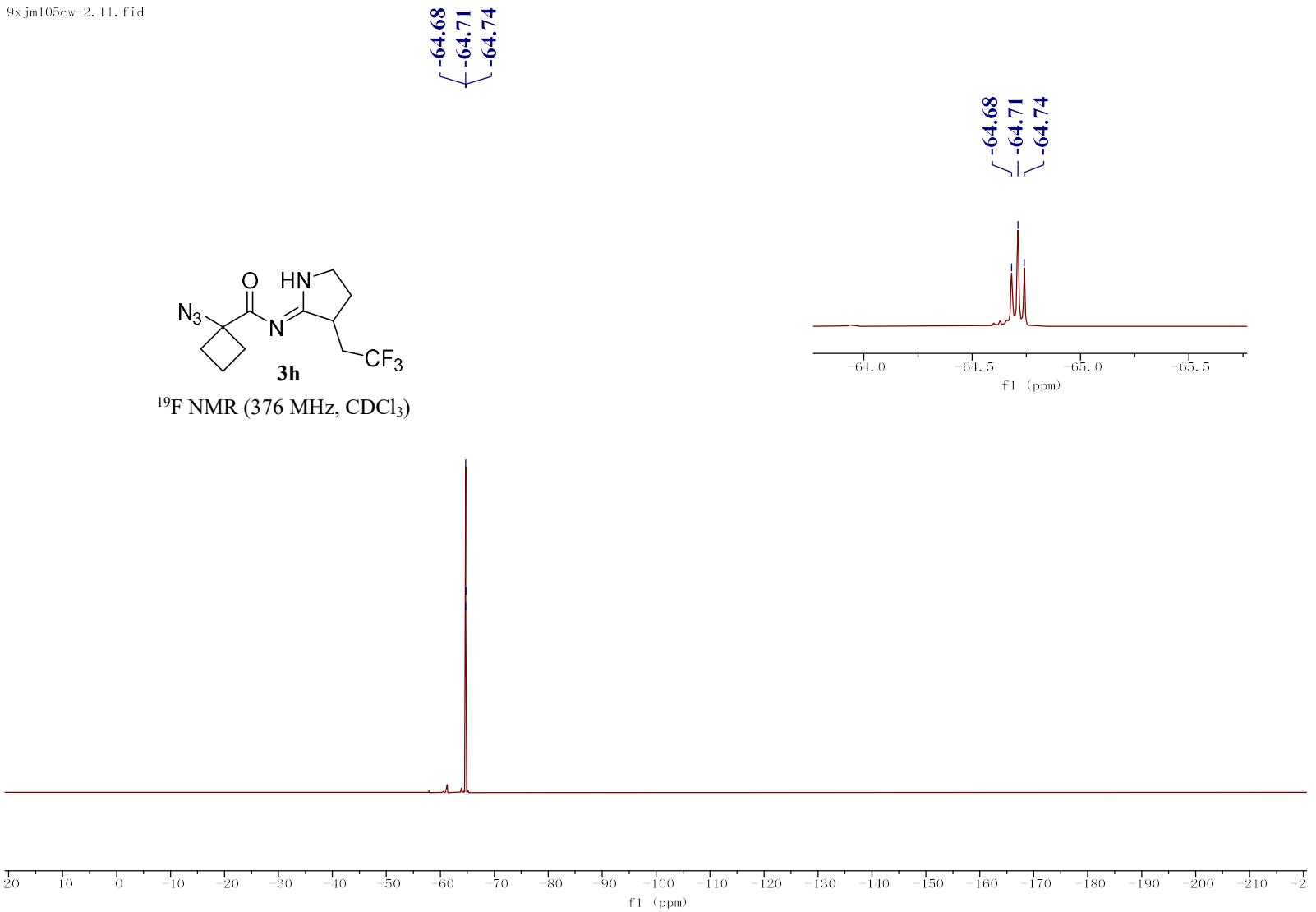
^{1}H NMR (400 MHz, $CDCl_3$)





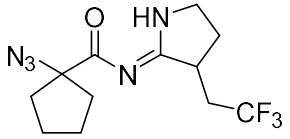
3h

^{13}C NMR (100 MHz, $CDCl_3$)



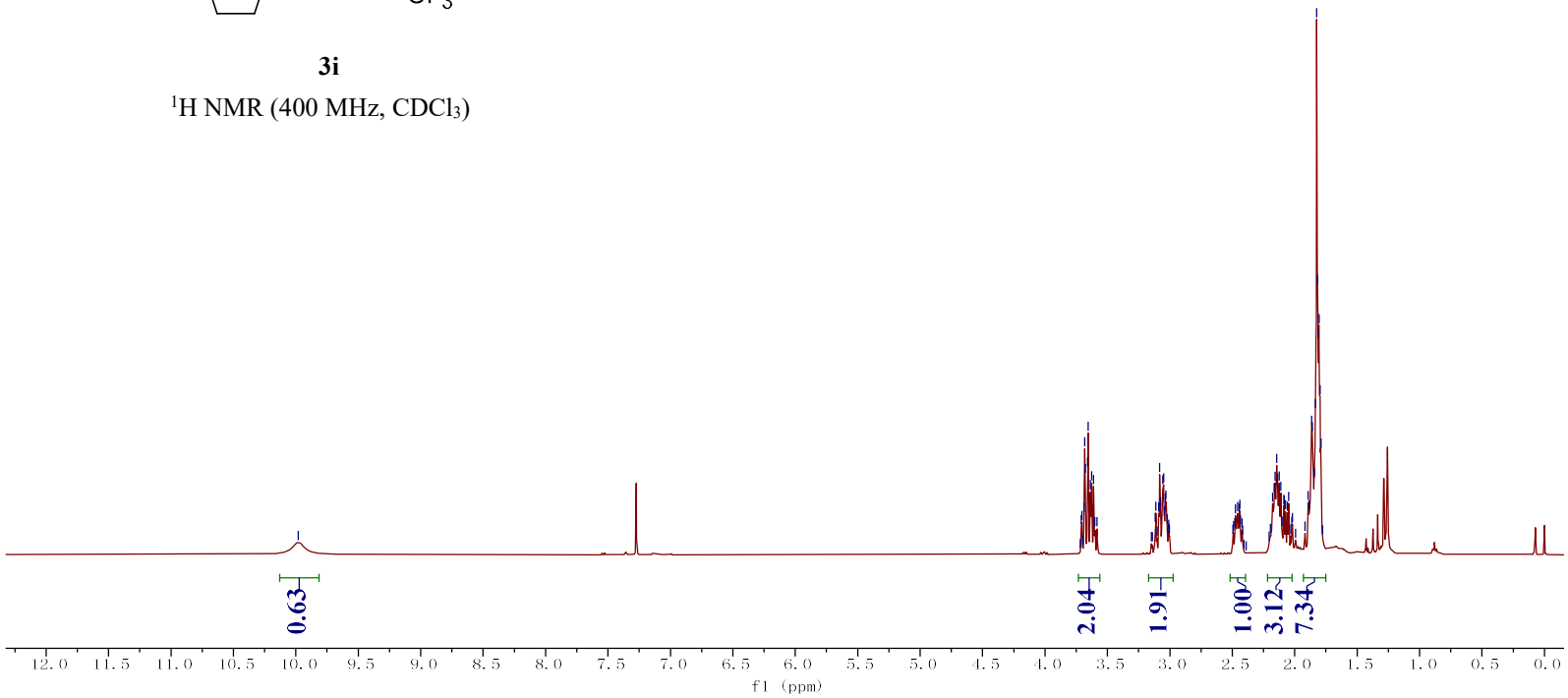
3h

^{19}F NMR (376 MHz, $CDCl_3$)



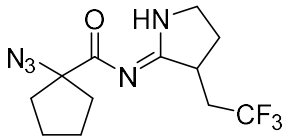
3i

^{1}H NMR (400 MHz, $CDCl_3$)



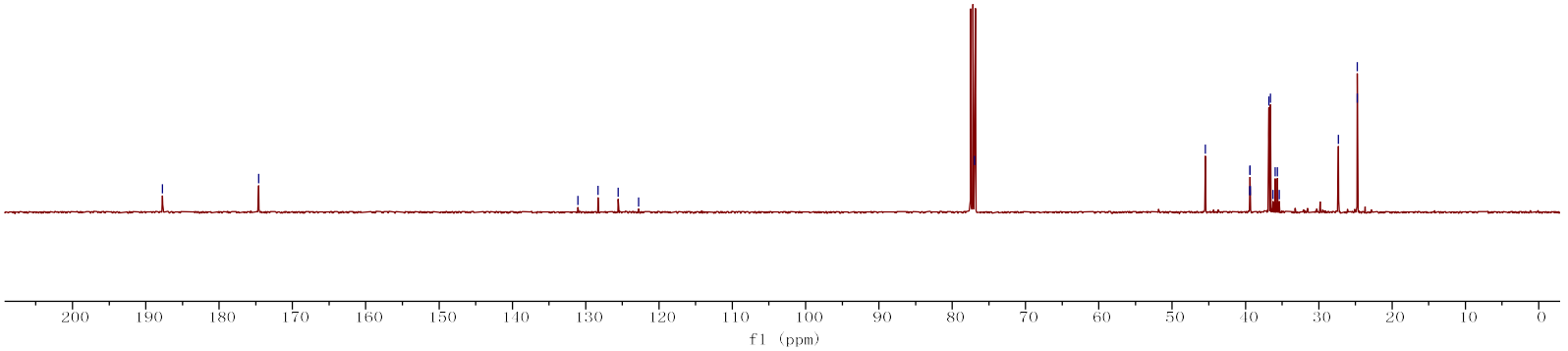
10xjm75cw-chf.13.fid

187.71
174.62
131.05
128.30
125.55
122.80
76.97
45.48
39.43
39.40
39.37
39.34
36.81
36.60
36.23
35.95
35.66
35.37
27.31
24.74
24.74

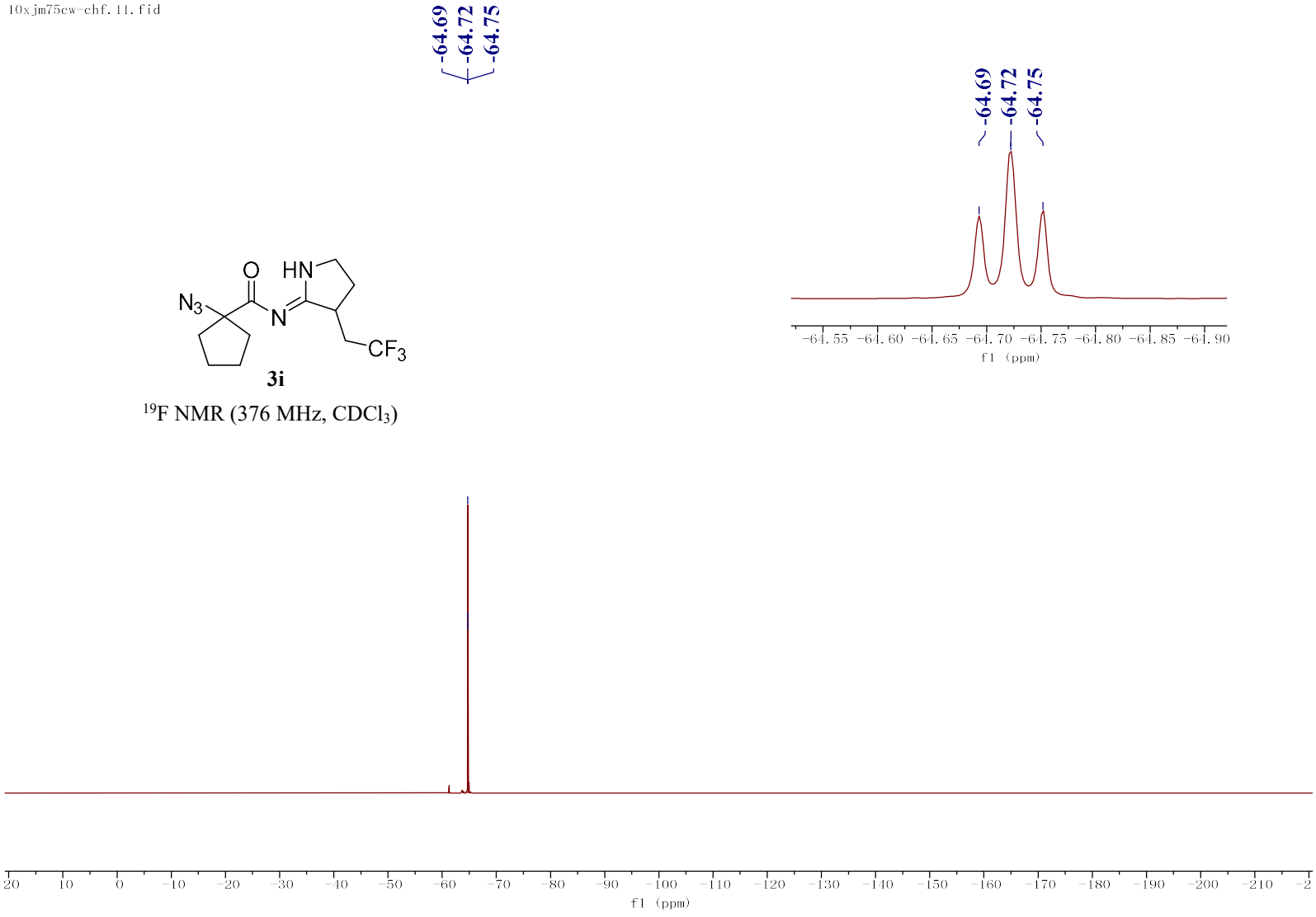


3i

^{13}C NMR (100 MHz, $CDCl_3$)

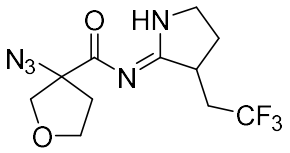


10xjm75cw-chf.11.fid



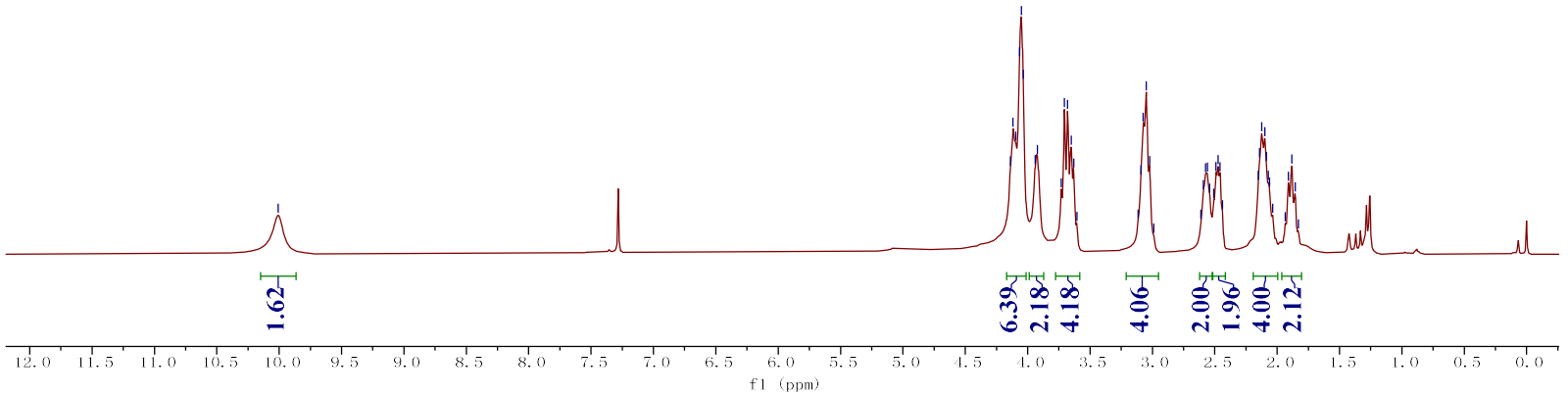
3i

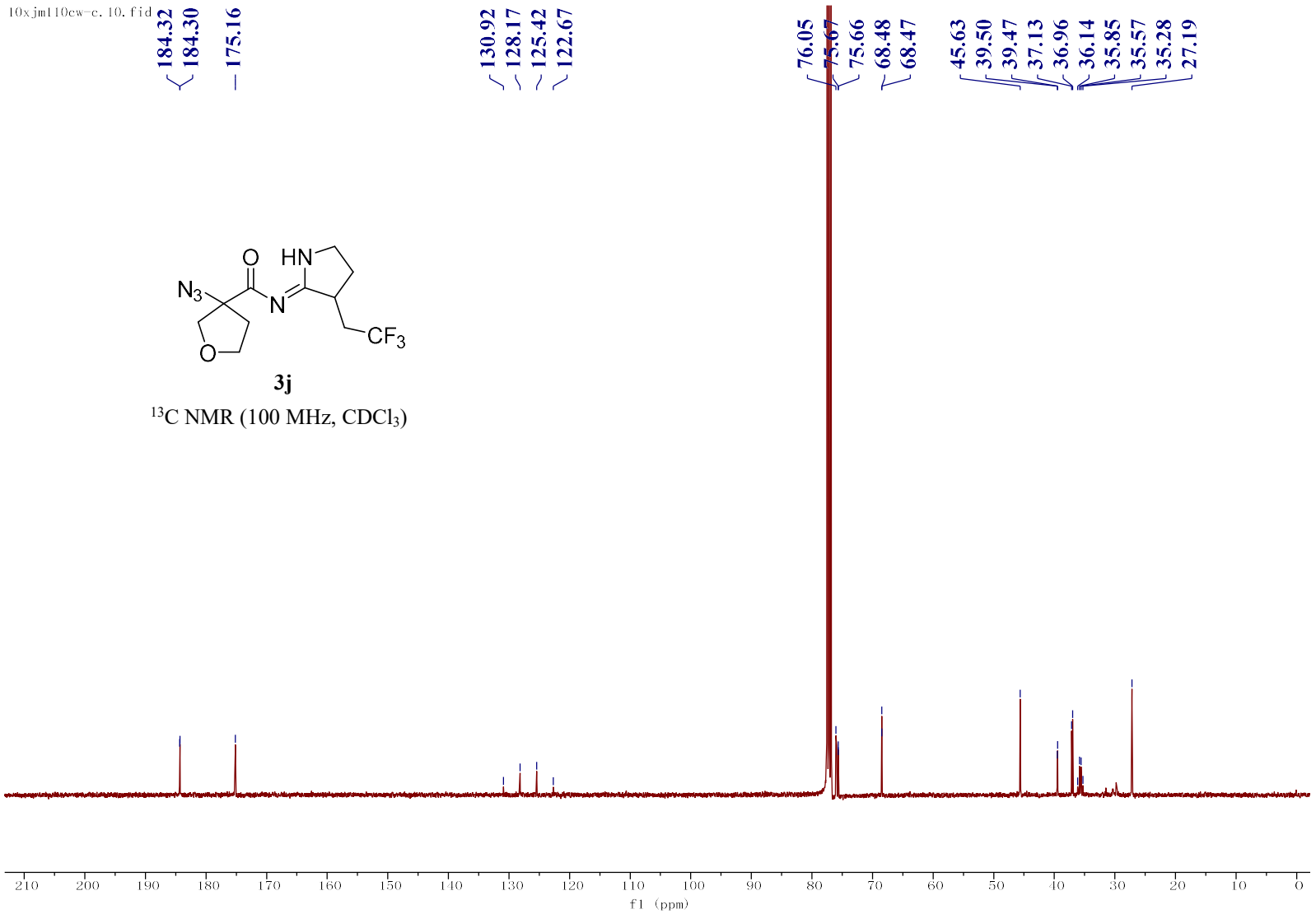
^{19}F NMR (376 MHz, $CDCl_3$)



3j

^{1}H NMR (400 MHz, $CDCl_3$)

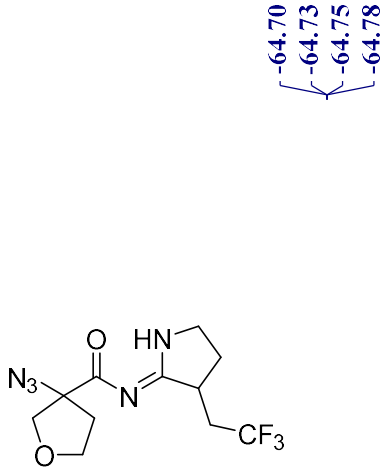


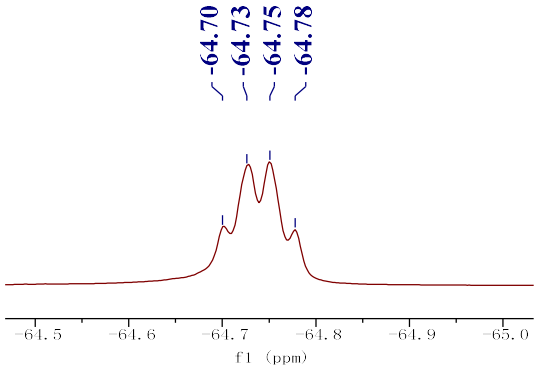


3j

^{13}C NMR (100 MHz, $CDCl_3$)

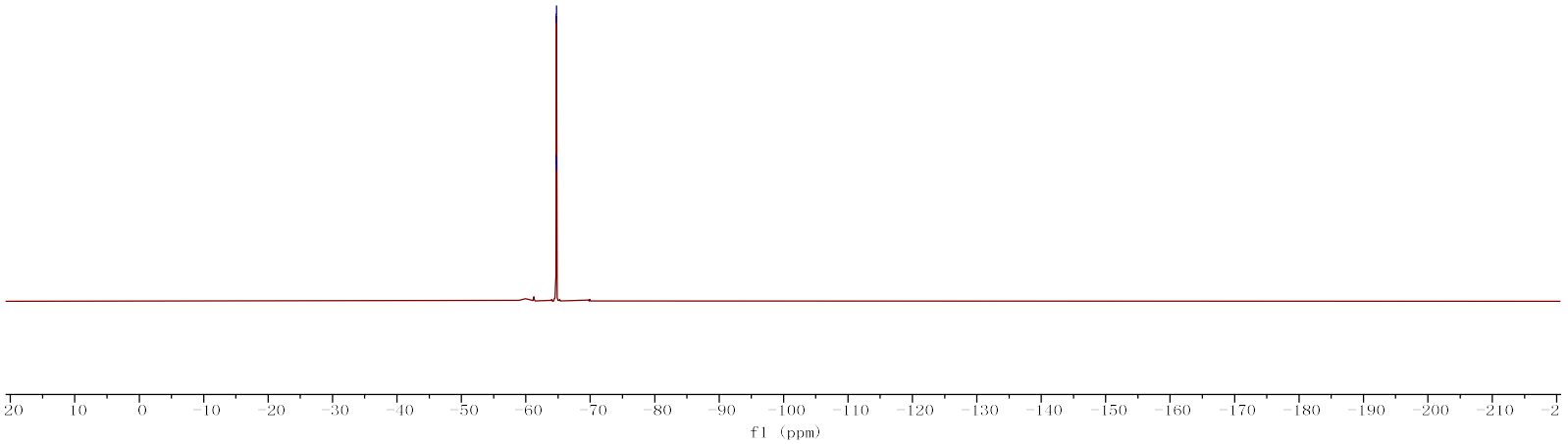
10xjm110cw.11.fid

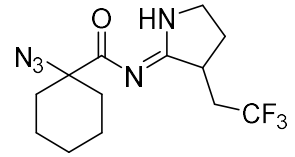




3j

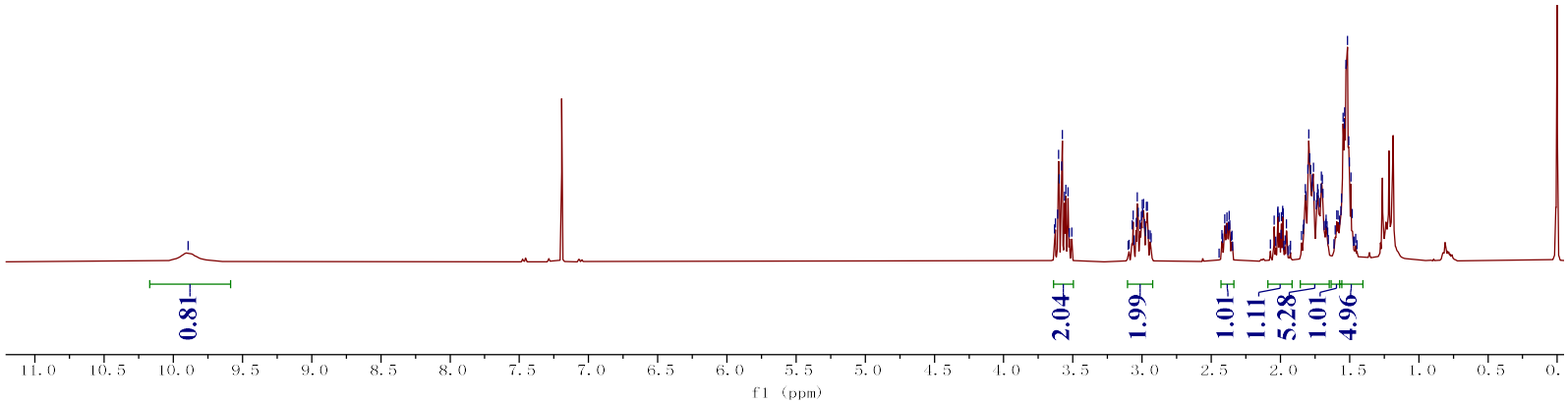
^{19}F NMR (376 MHz, $CDCl_3$)

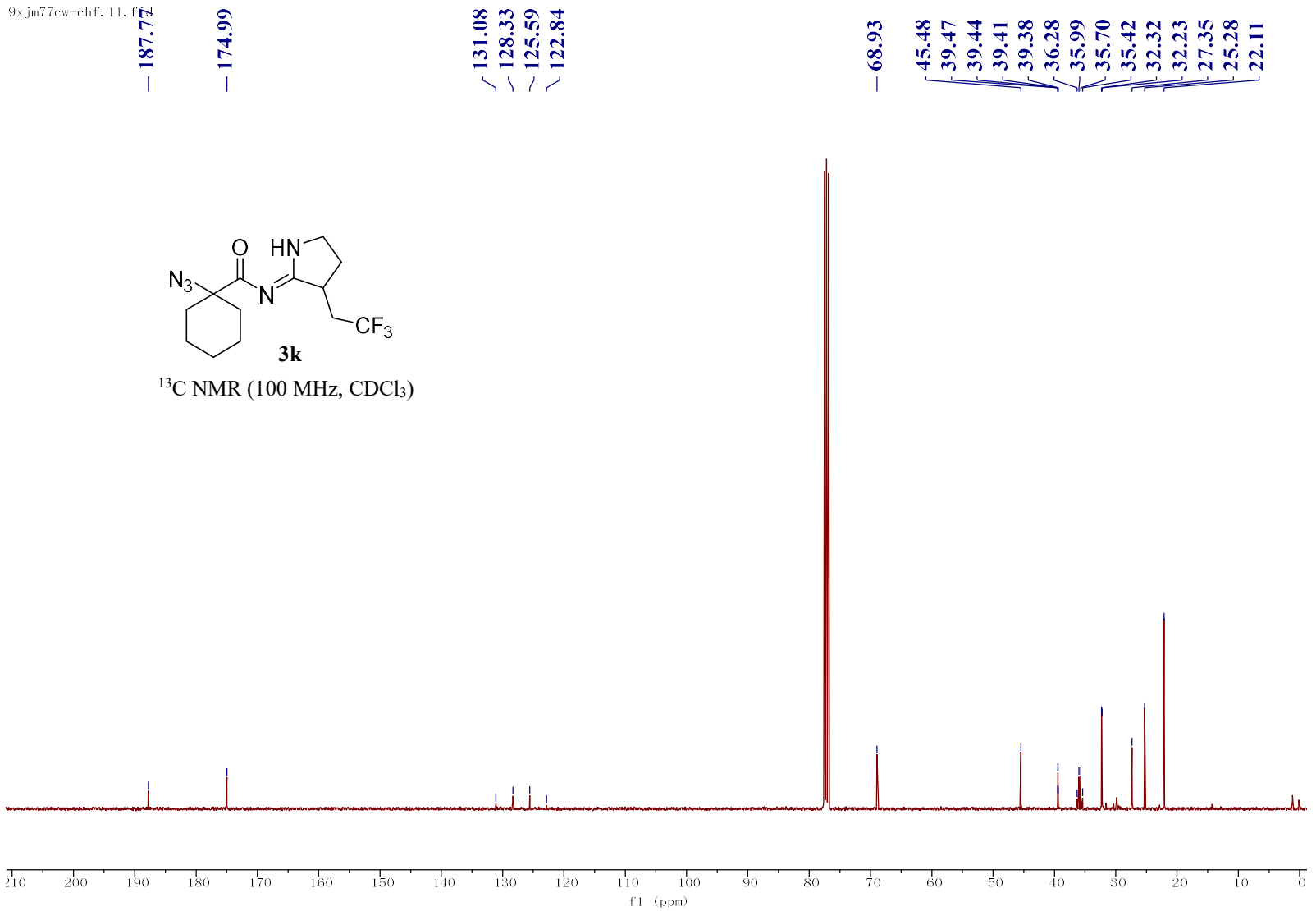




3k

^{1}H NMR (400 MHz, $CDCl_3$)

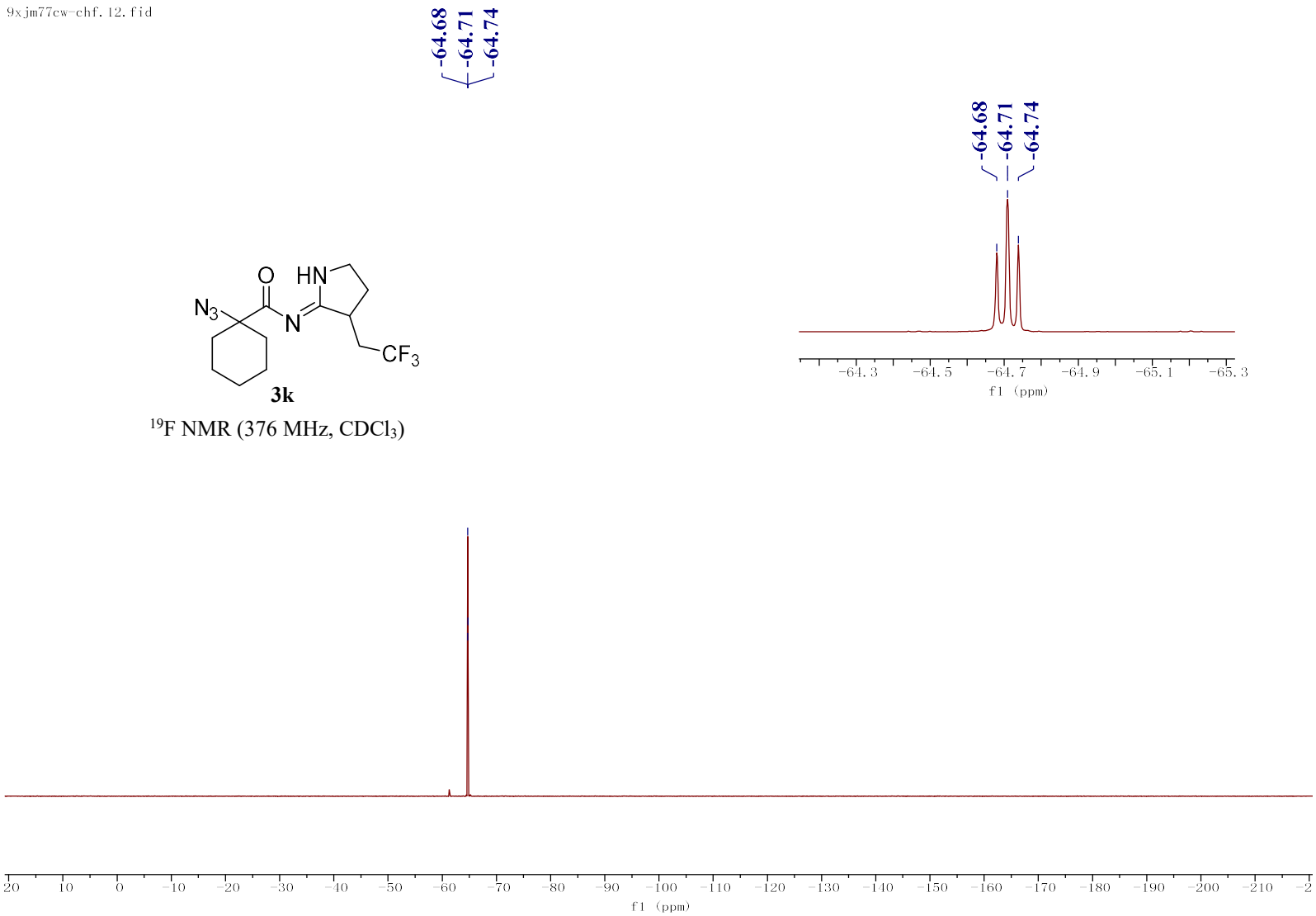




3k

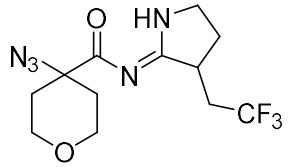
^{13}C NMR (100 MHz, $CDCl_3$)

9xjm77cw-chf.12.fid



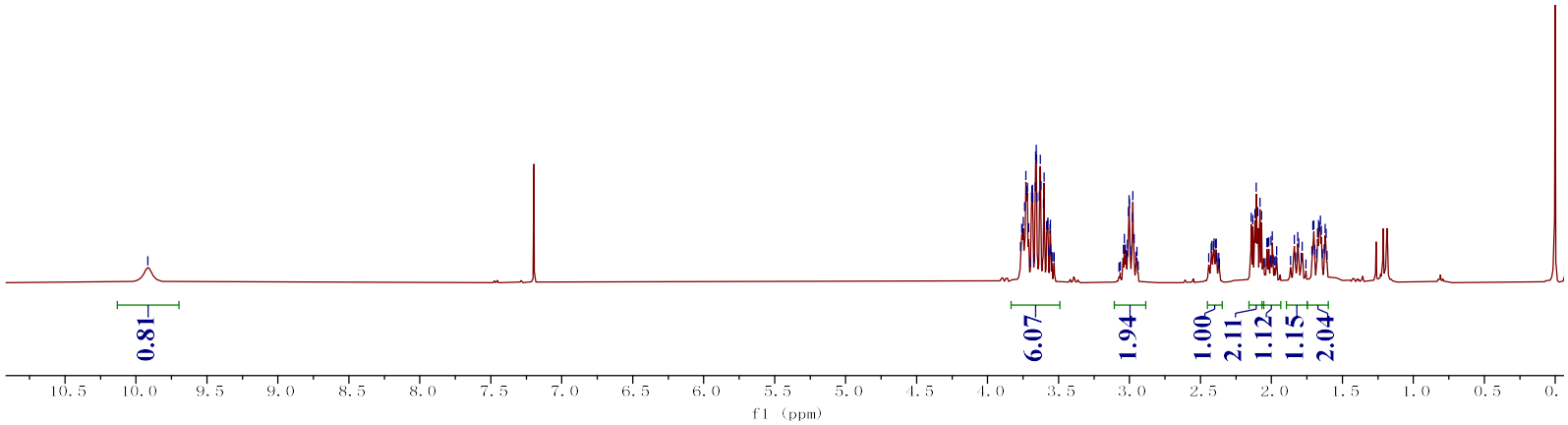
3k

^{19}F NMR (376 MHz, $CDCl_3$)



3l

^{1}H NMR (400 MHz, $CDCl_3$)



9xjm103cw.22.fid

185.89
175.40
130.99
128.24
125.49
122.74
65.95
64.07
64.05
45.58
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39.51
39.48
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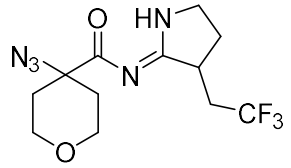
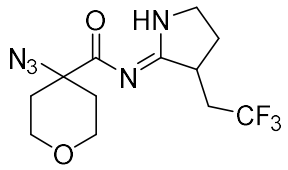
35.95
35.67
35.38
32.40
32.32
27.31



3l

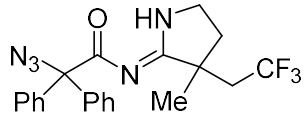
^{13}C NMR (100 MHz, $CDCl_3$)

9xjm103cw.21.fid



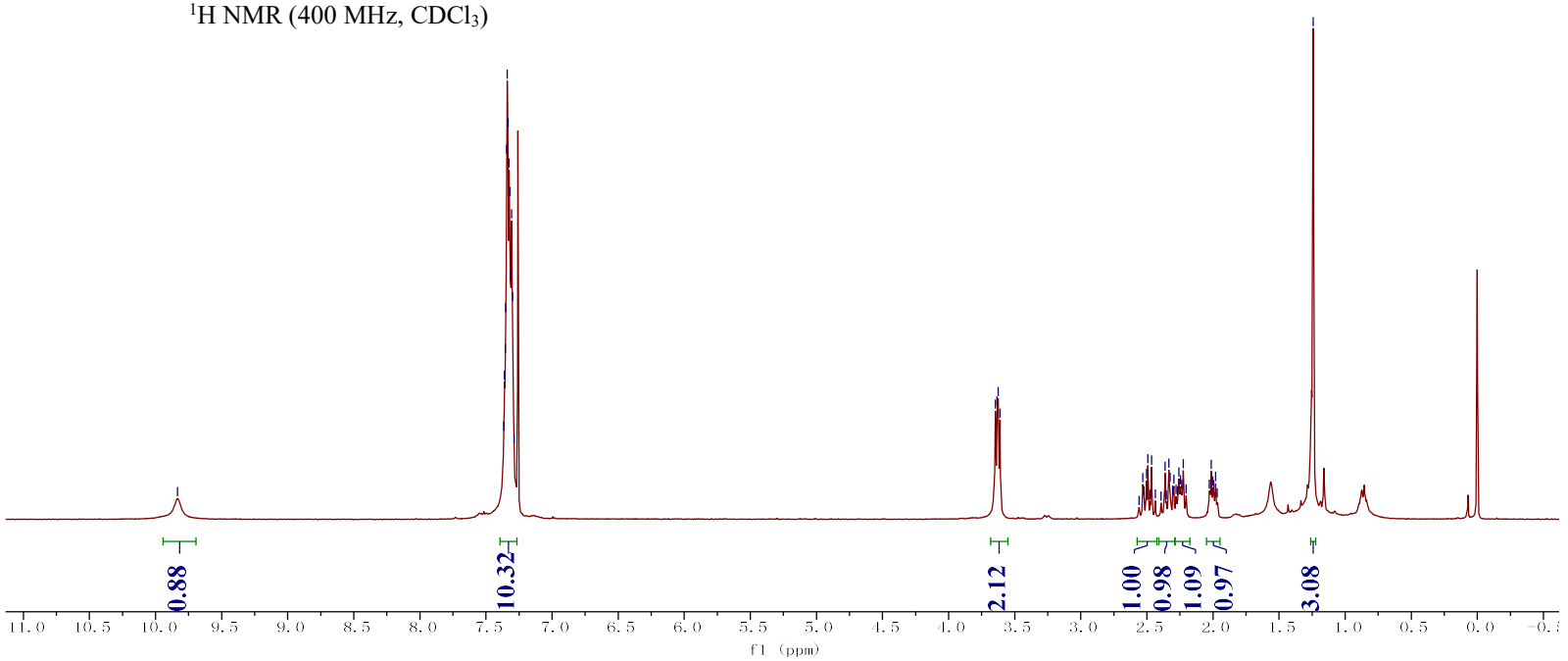
3l

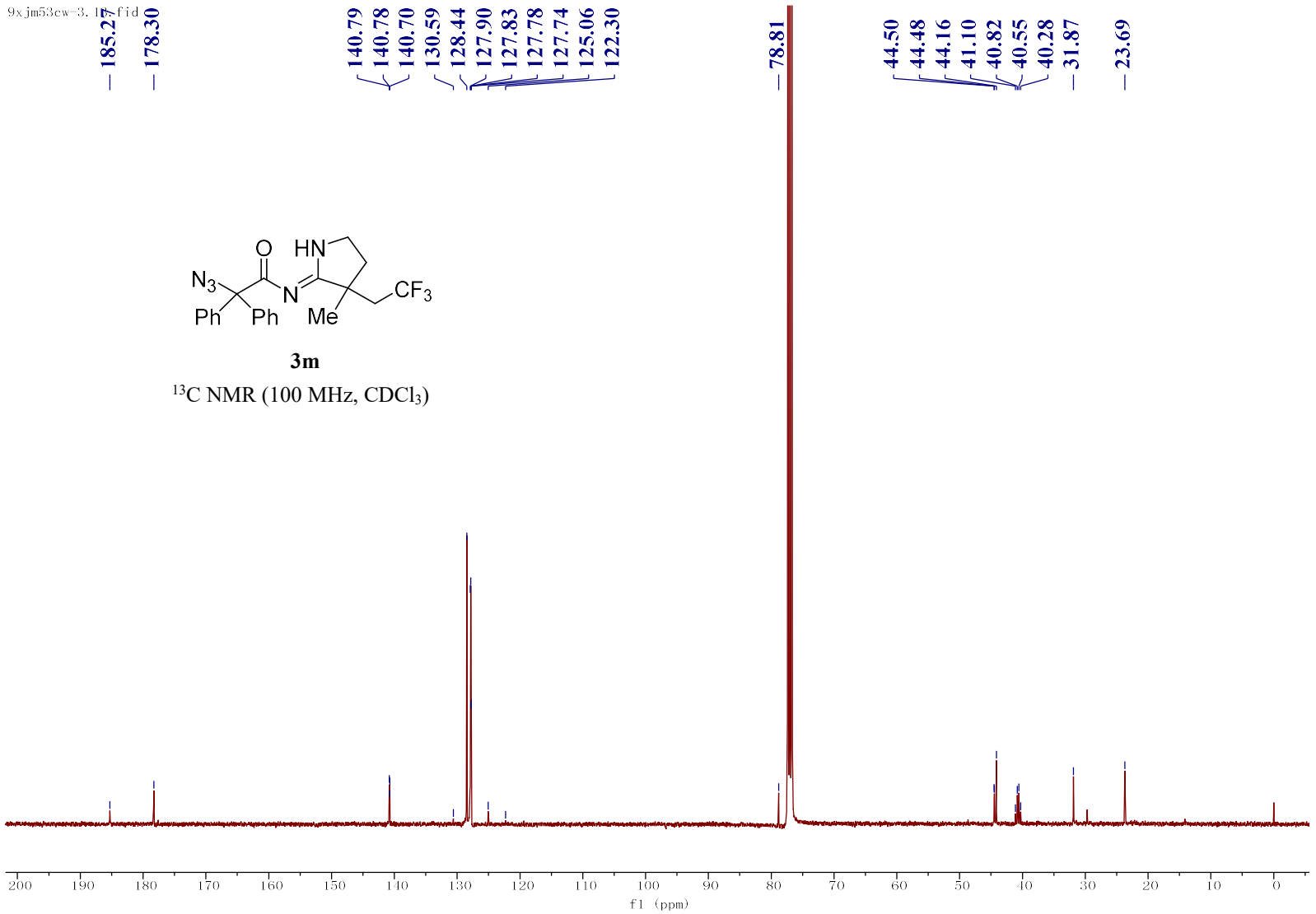
^{19}F NMR (376 MHz, $CDCl_3$)



3m

^{1}H NMR (400 MHz, $CDCl_3$)

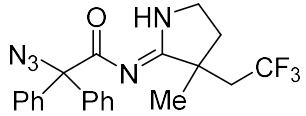




3m

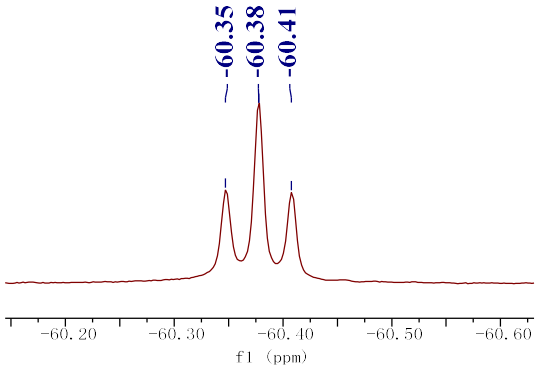
^{13}C NMR (100 MHz, $CDCl_3$)

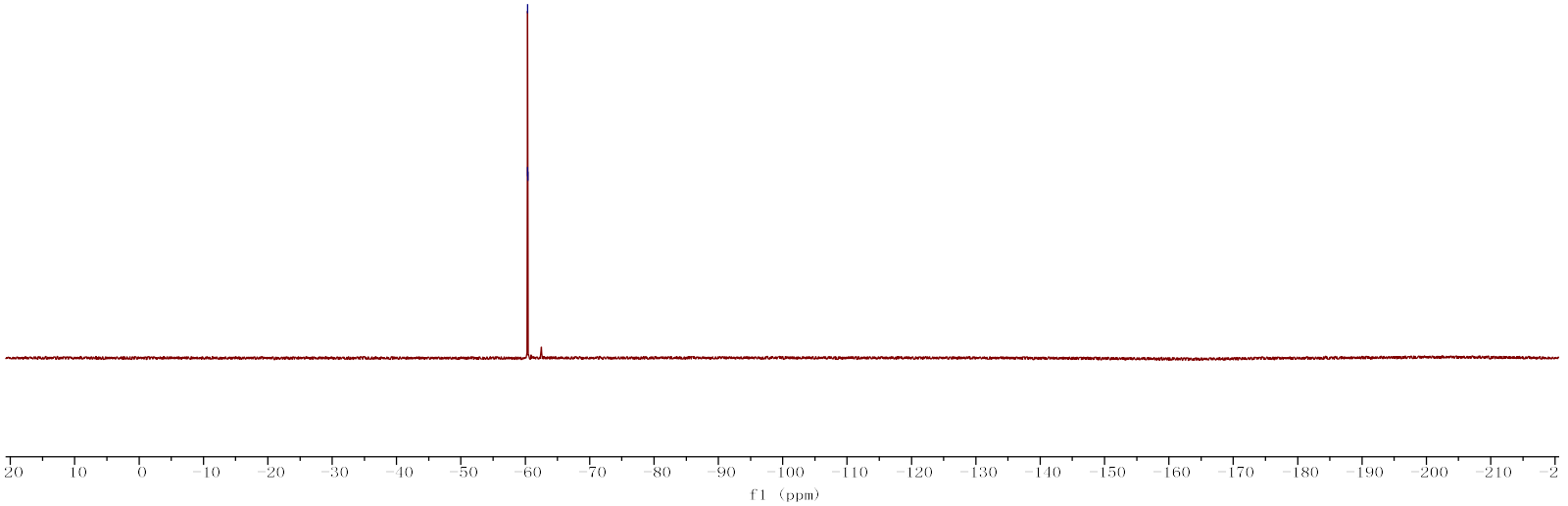
9xjm53cw-3.12.fid

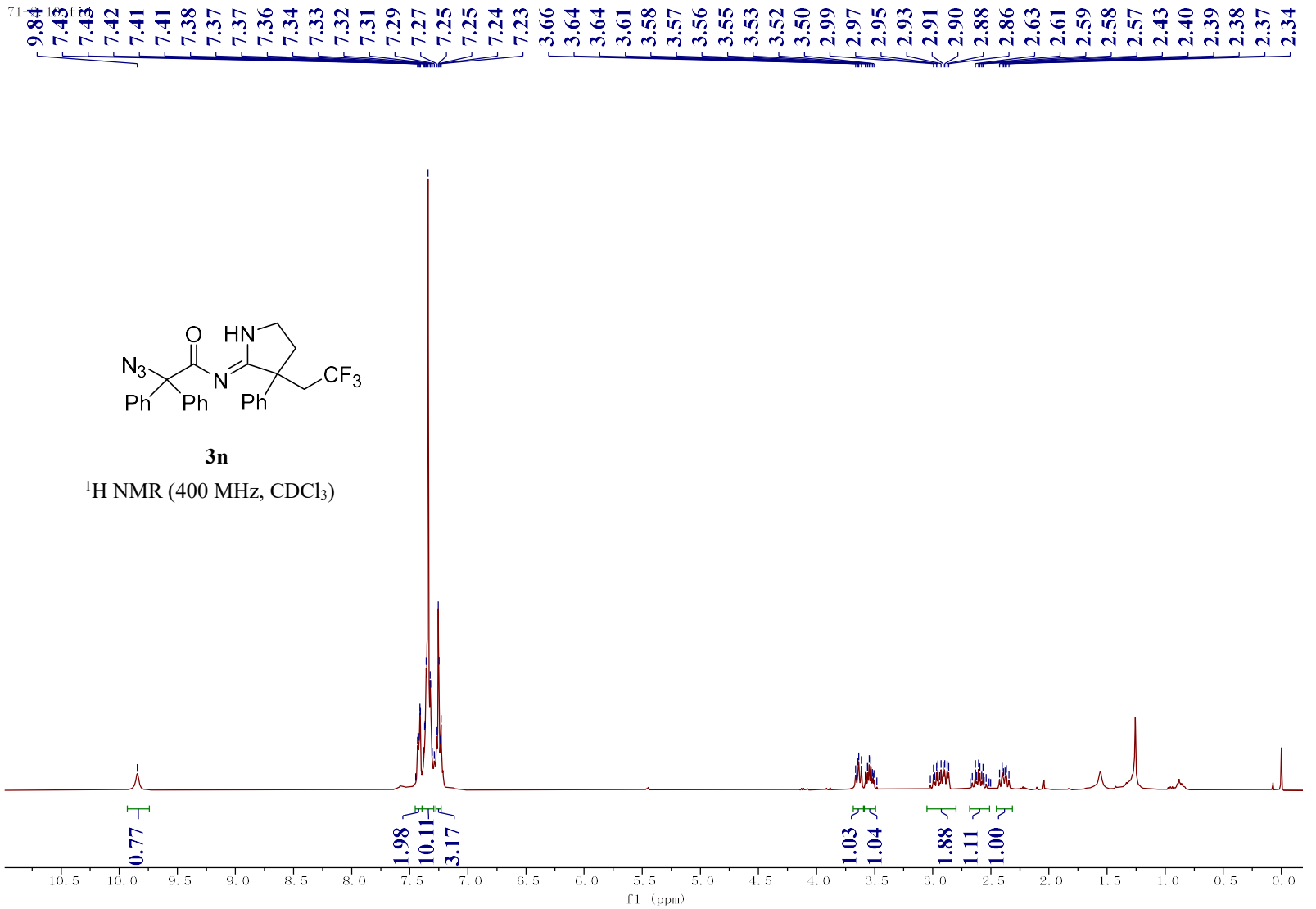


3m

^{19}F NMR (376 MHz, $CDCl_3$)






9.84
7.43
7.43
7.42
7.41
7.41
7.38
7.37
7.37
7.36
7.34
7.33
7.32
7.31
7.29
7.27
7.25
7.25
7.24
7.23
3.66
3.64
3.64
3.61
3.58
3.57
3.56
3.55
3.53
3.52
3.50
2.99
2.97
2.95
2.93
2.91
2.90
2.88
2.86
2.63
2.61
2.59
2.58
2.57
2.43
2.40
2.39
2.38
2.37
2.34
O
HN
N3
N
CF3
Ph
Ph
Ph
3n
1H NMR (400 MHz, CDCl3)
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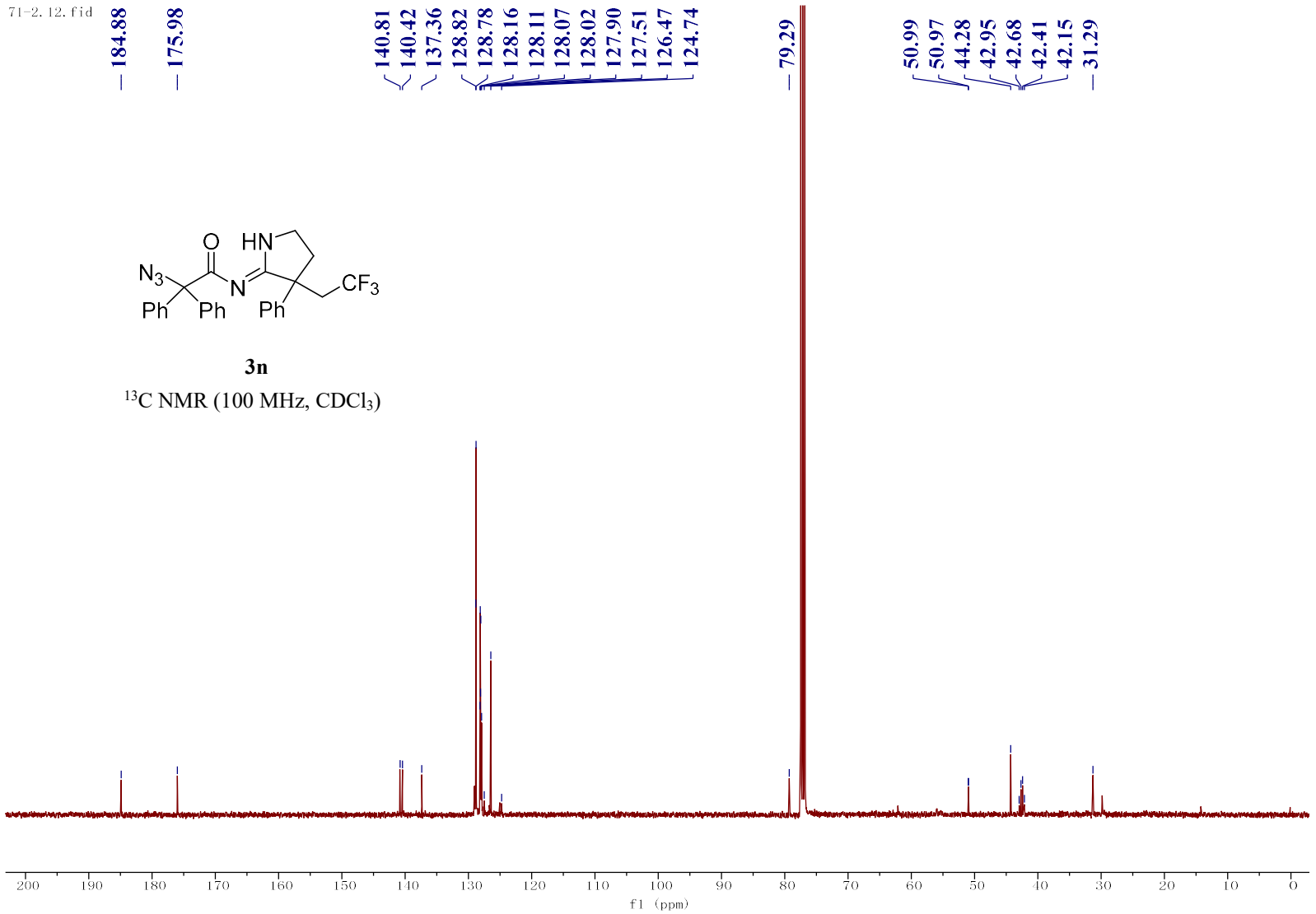
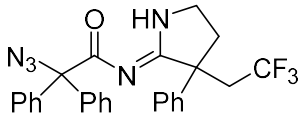
1.98
10.11
3.17
1.03
1.04
1.88
1.11
1.00
f1 (ppm)



3n

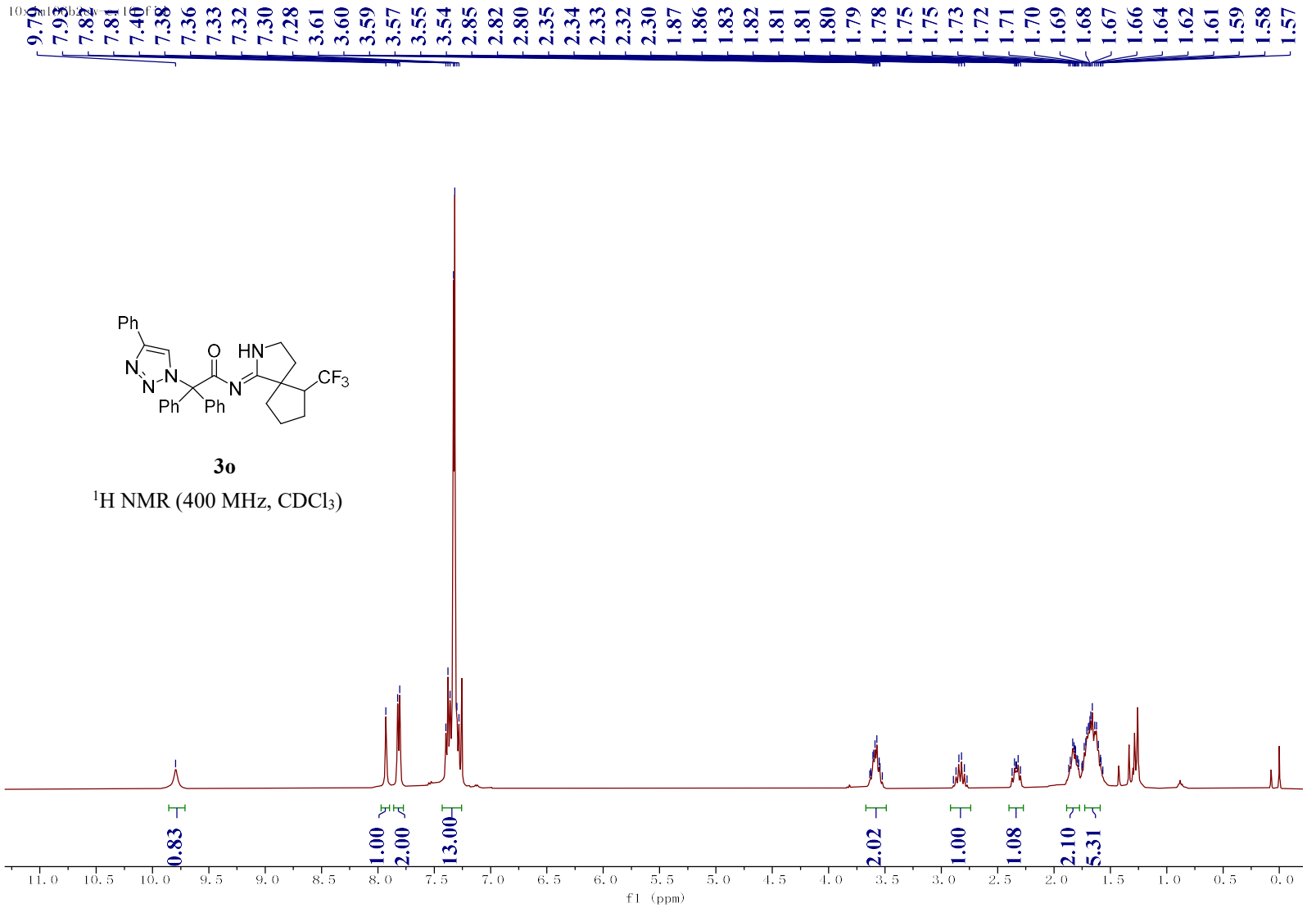
^{13}C NMR (100 MHz, $CDCl_3$)

71-2.11.fid



3n

^{19}F NMR (376 MHz, $CDCl_3$)

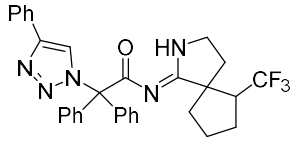


3o

^{1}H NMR (400 MHz, $CDCl_3$)

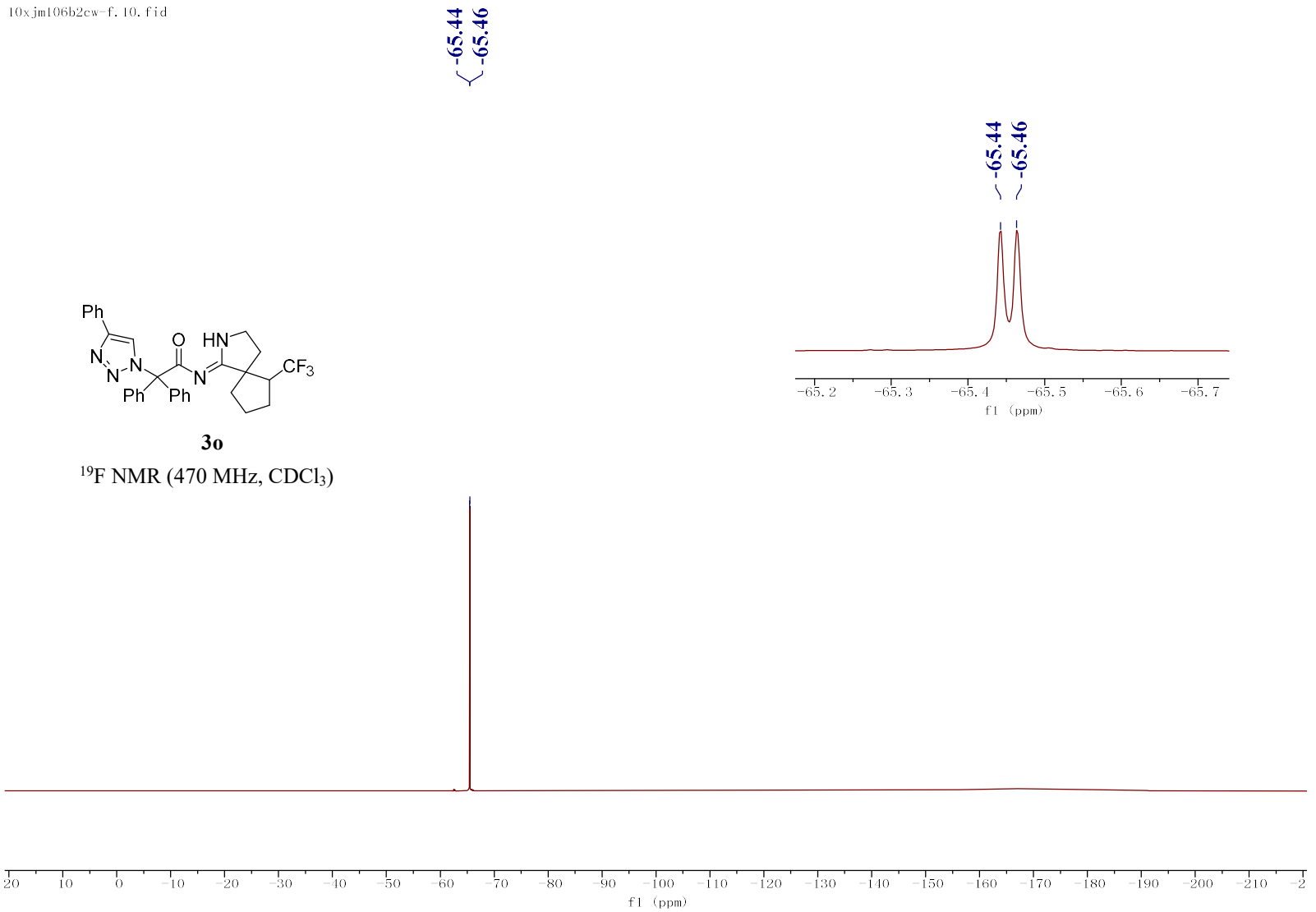
10xjm106b2cw-c.11.fid

182.97
178.02
140.27
131.19
129.69
128.80
128.32
128.20
128.01
127.88
126.00
125.75
80.53
55.05
48.72
48.45
48.19
47.93
44.58
39.00
28.88
25.42
25.40
22.65



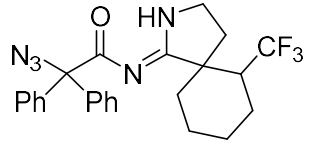
3o

^{13}C NMR (100 MHz, $CDCl_3$)



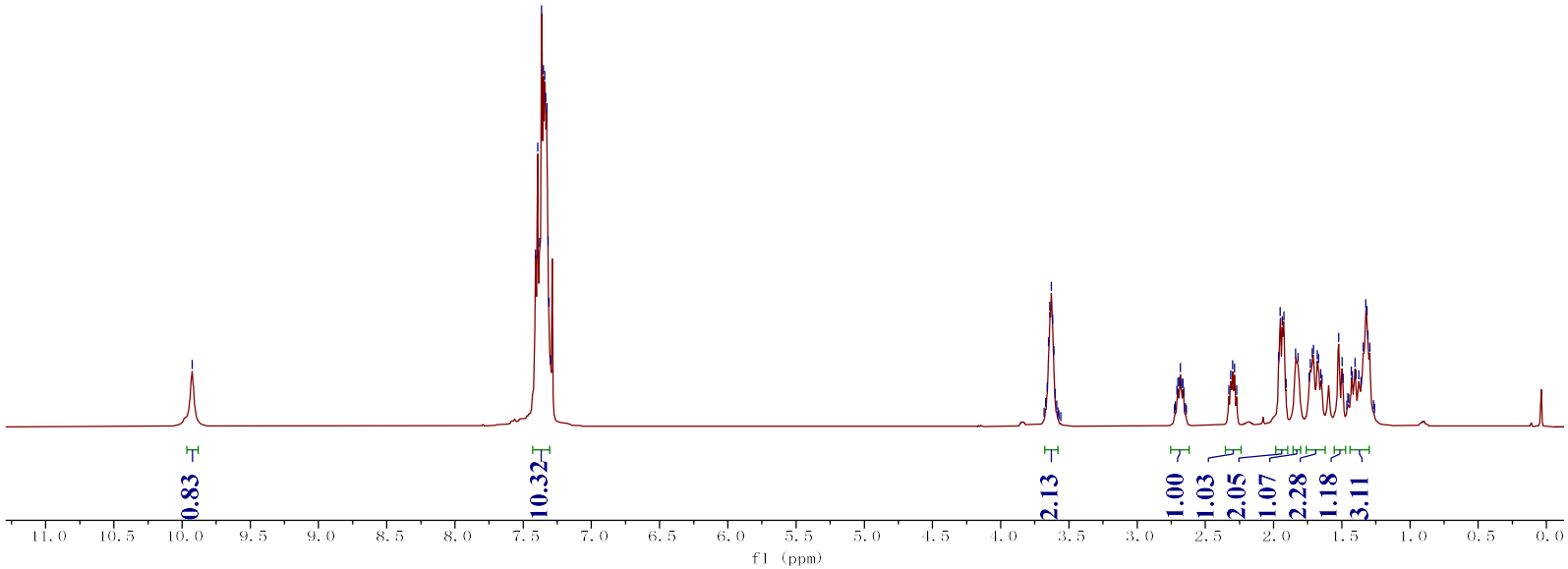
3o

^{19}F NMR (470 MHz, $CDCl_3$)



3p

^{1}H NMR (500 MHz, $CDCl_3$)



10xjm100cw-c.23.fid

185.25
179.10
141.14
141.05
128.65
128.57
127.93
127.88
127.77
127.70
126.30
78.88
49.15
45.65
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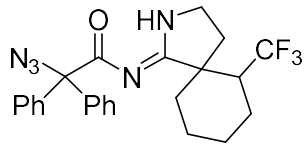
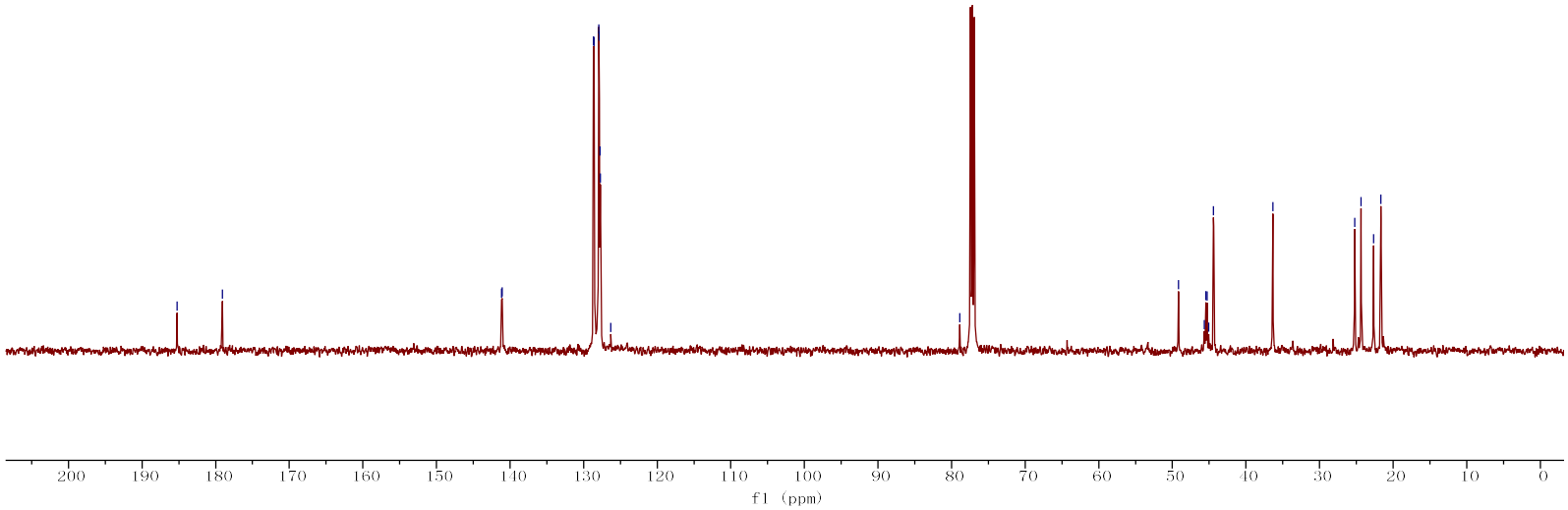
44.40
36.35
25.20
24.34
22.66
21.66

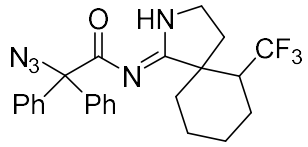


3p

^{13}C NMR (125 MHz, $CDCl_3$)

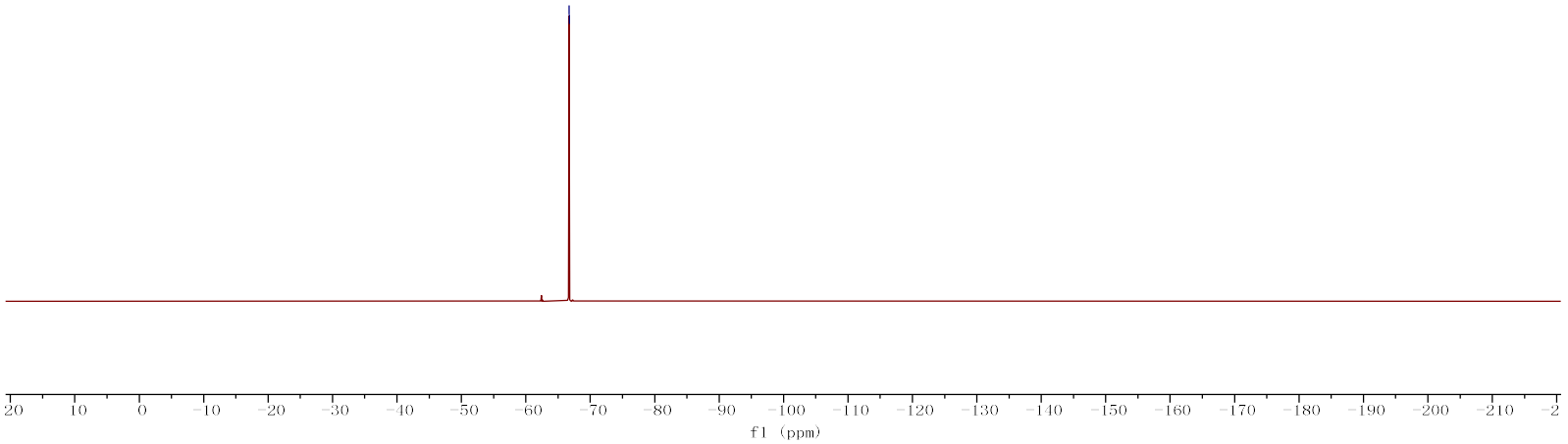


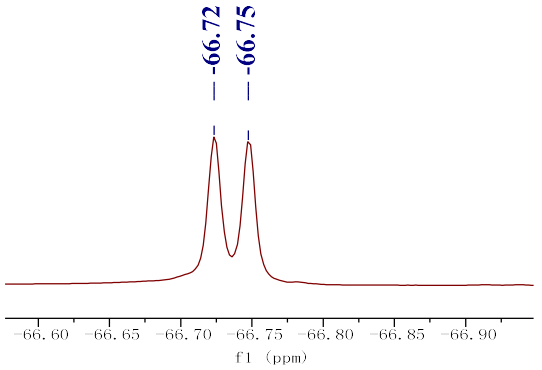
10xjm100cw-chf.11.fid

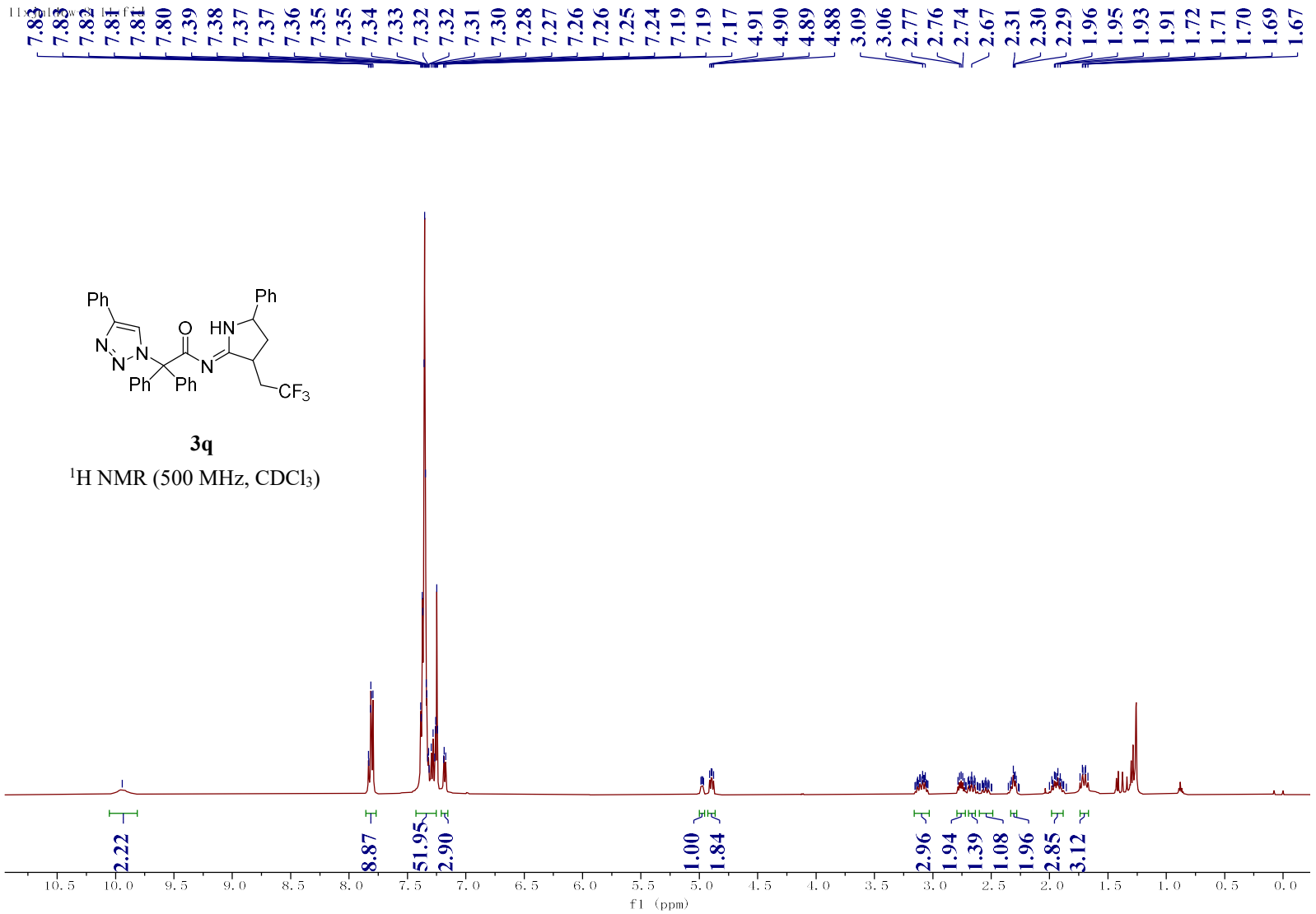


3p

^{19}F NMR (376 MHz, $CDCl_3$)

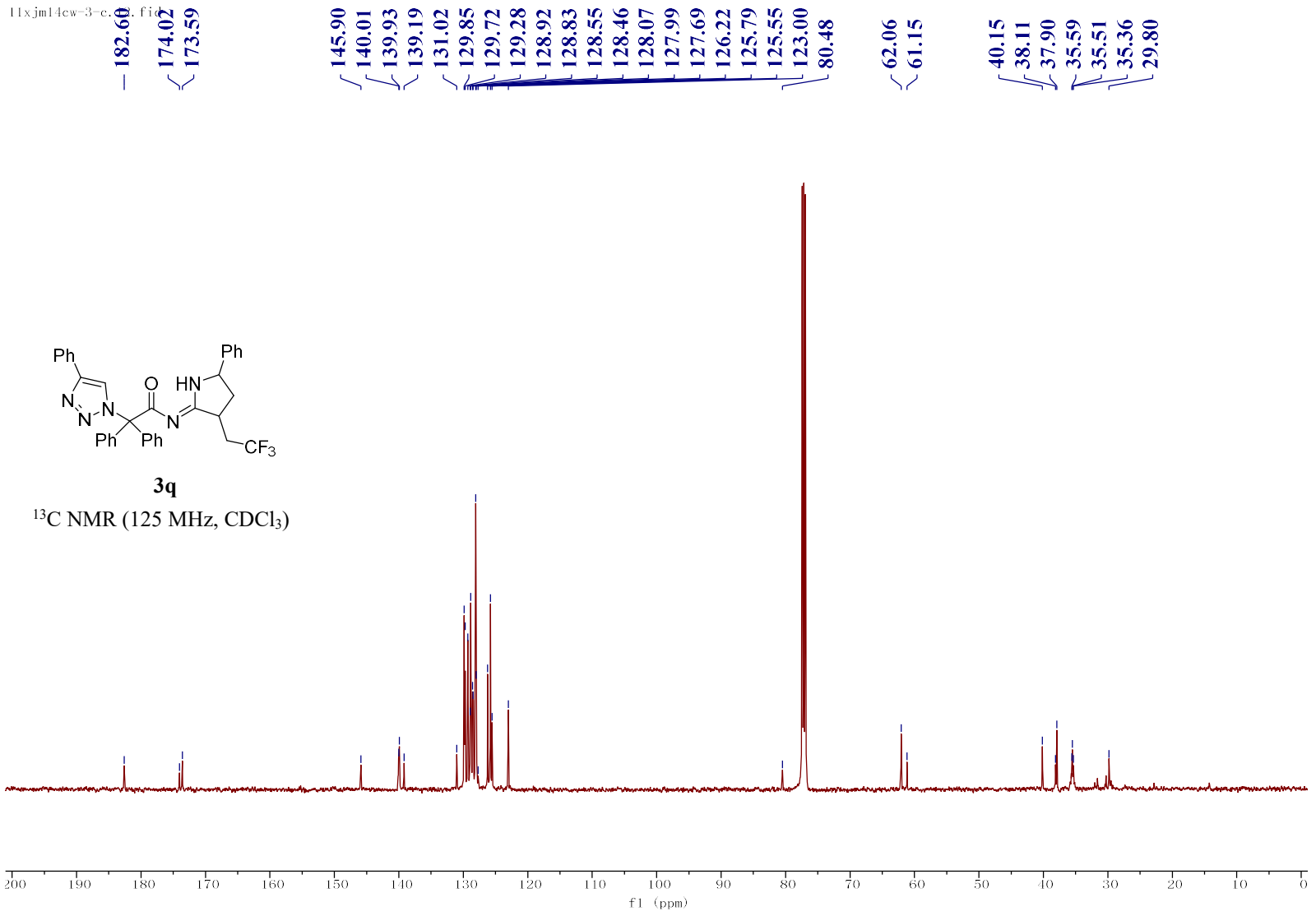






3q

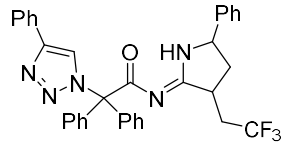
^{1}H NMR (500 MHz, $CDCl_3$)



3q

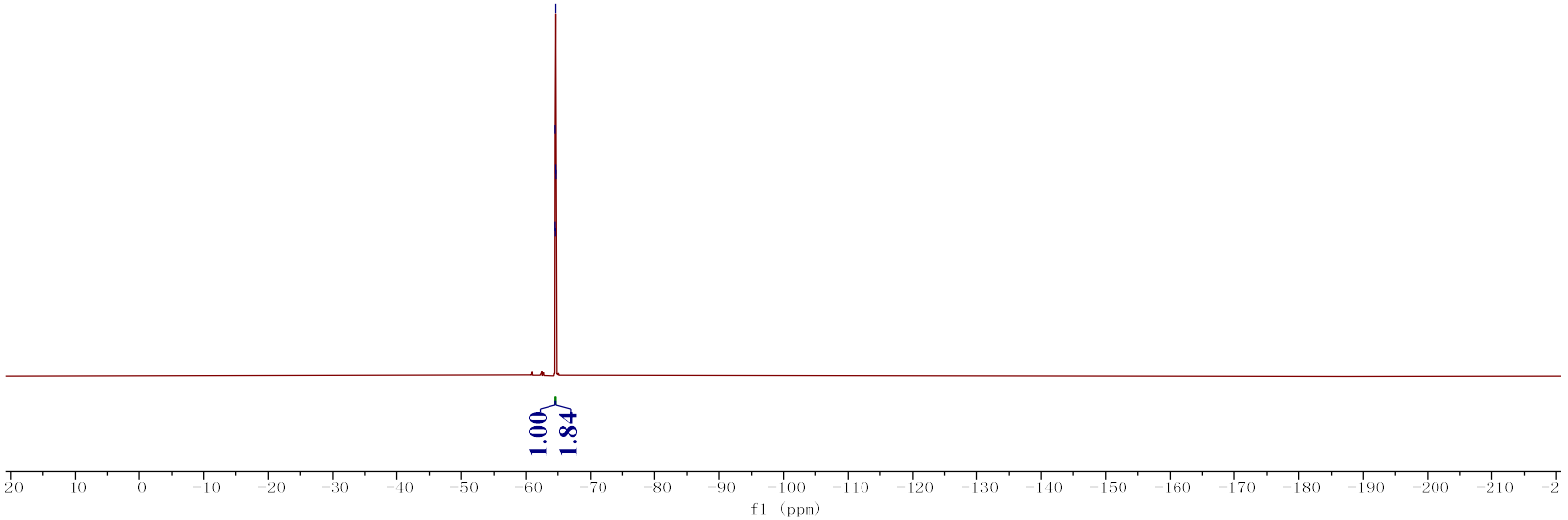
^{13}C NMR (125 MHz, $CDCl_3$)

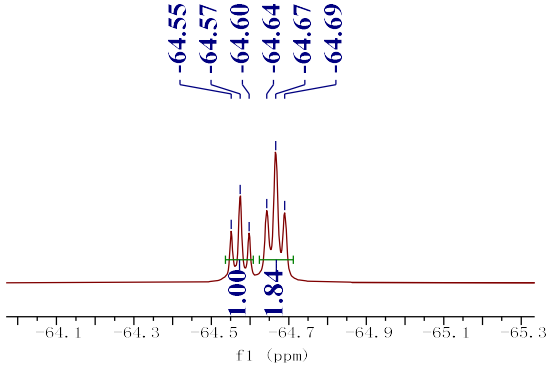
11xjm14cw-3-f.12.fid

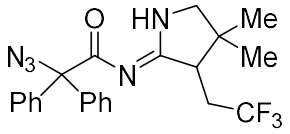


3q

^{19}F NMR (470 MHz, $CDCl_3$)

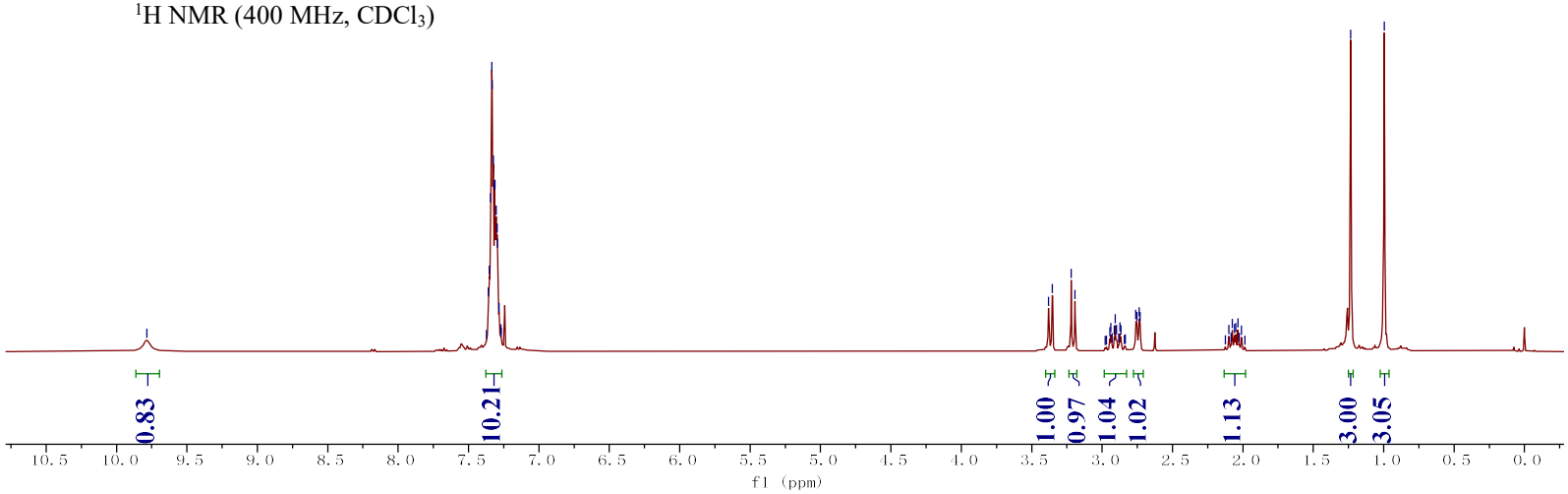






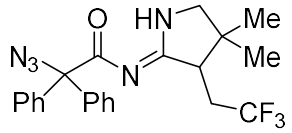
3r

^{1}H NMR (400 MHz, $CDCl_3$)



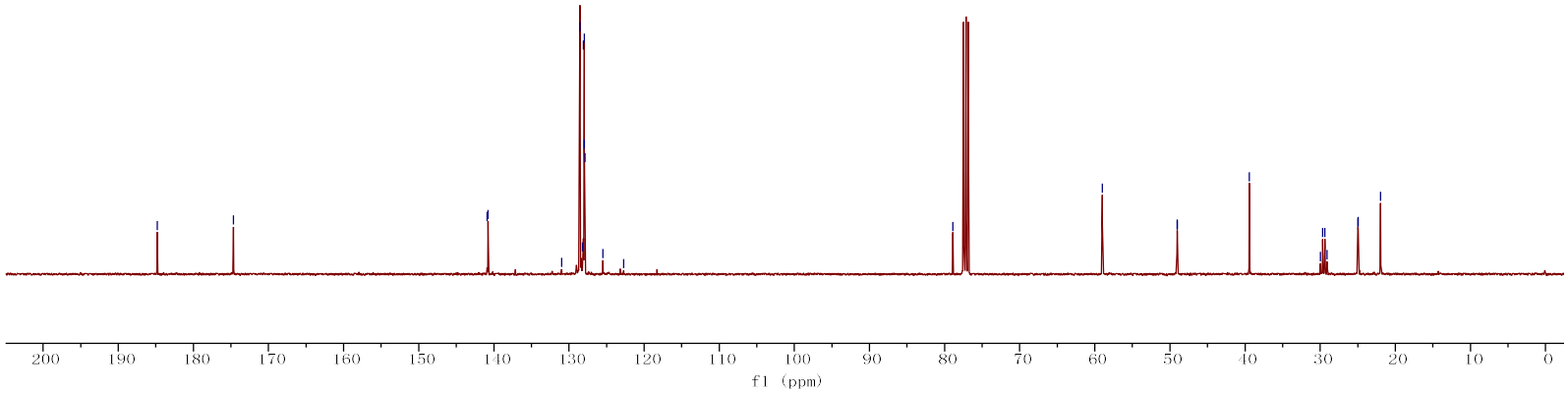
11xjm67cw.12.fid

184.81
174.65
140.89
140.76
130.96
128.55
128.22
128.07
127.96
127.94
127.88
125.48
122.73
78.89
58.99
49.04
49.02
39.42
29.98
29.68
29.38
29.09
24.98
24.96
21.95

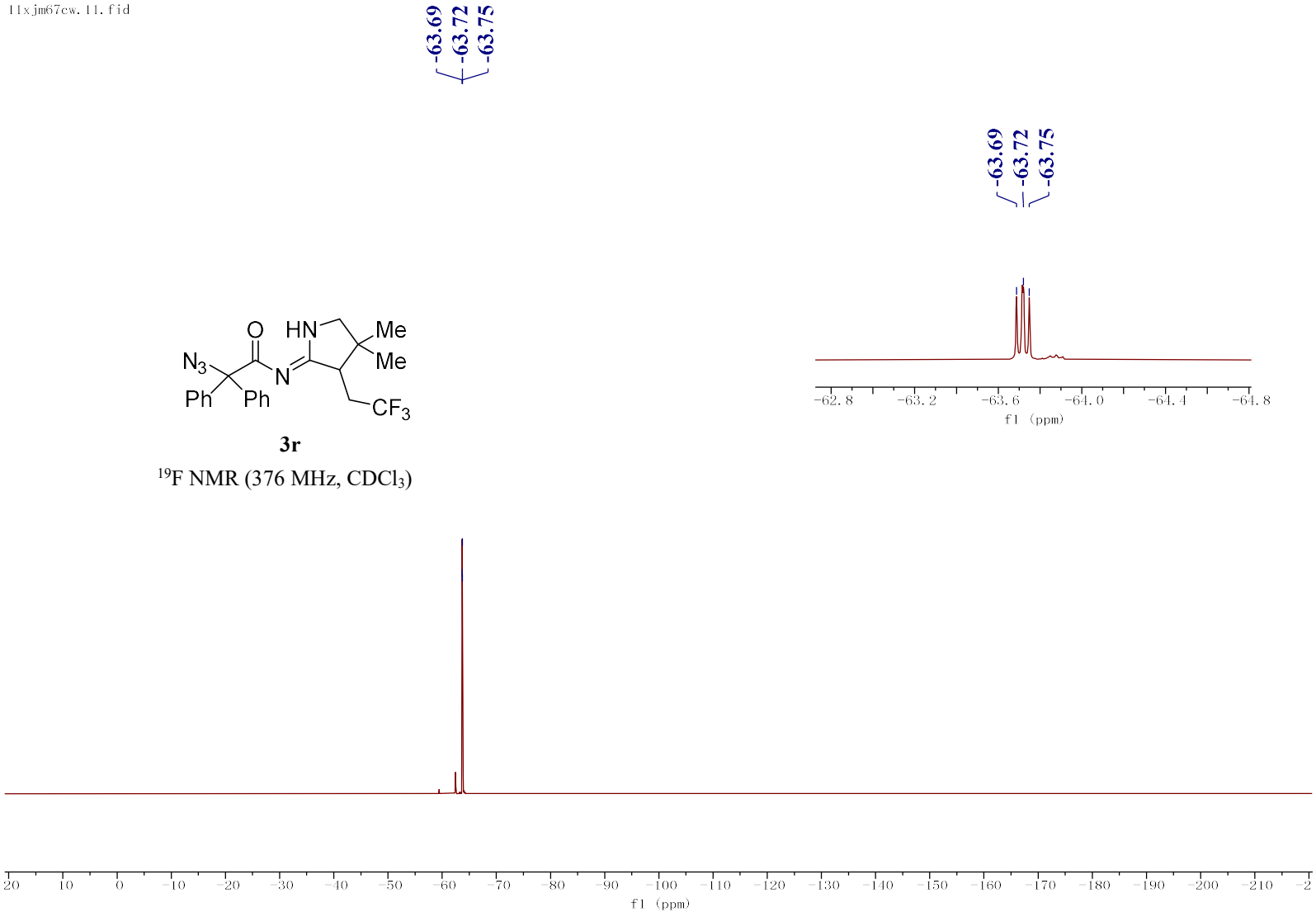


3r

^{13}C NMR (100 MHz, $CDCl_3$)

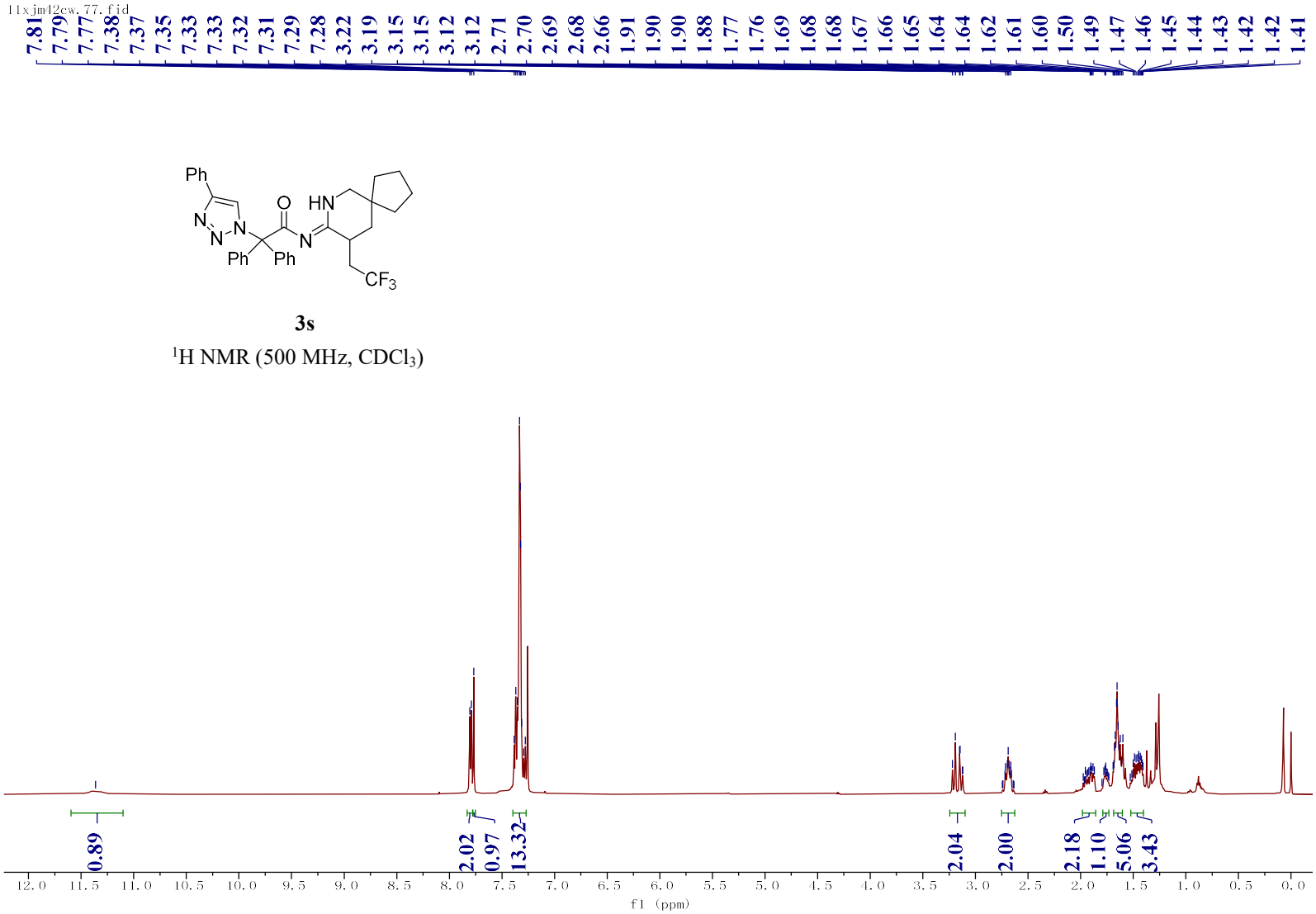


11xjm67cw.11.fid



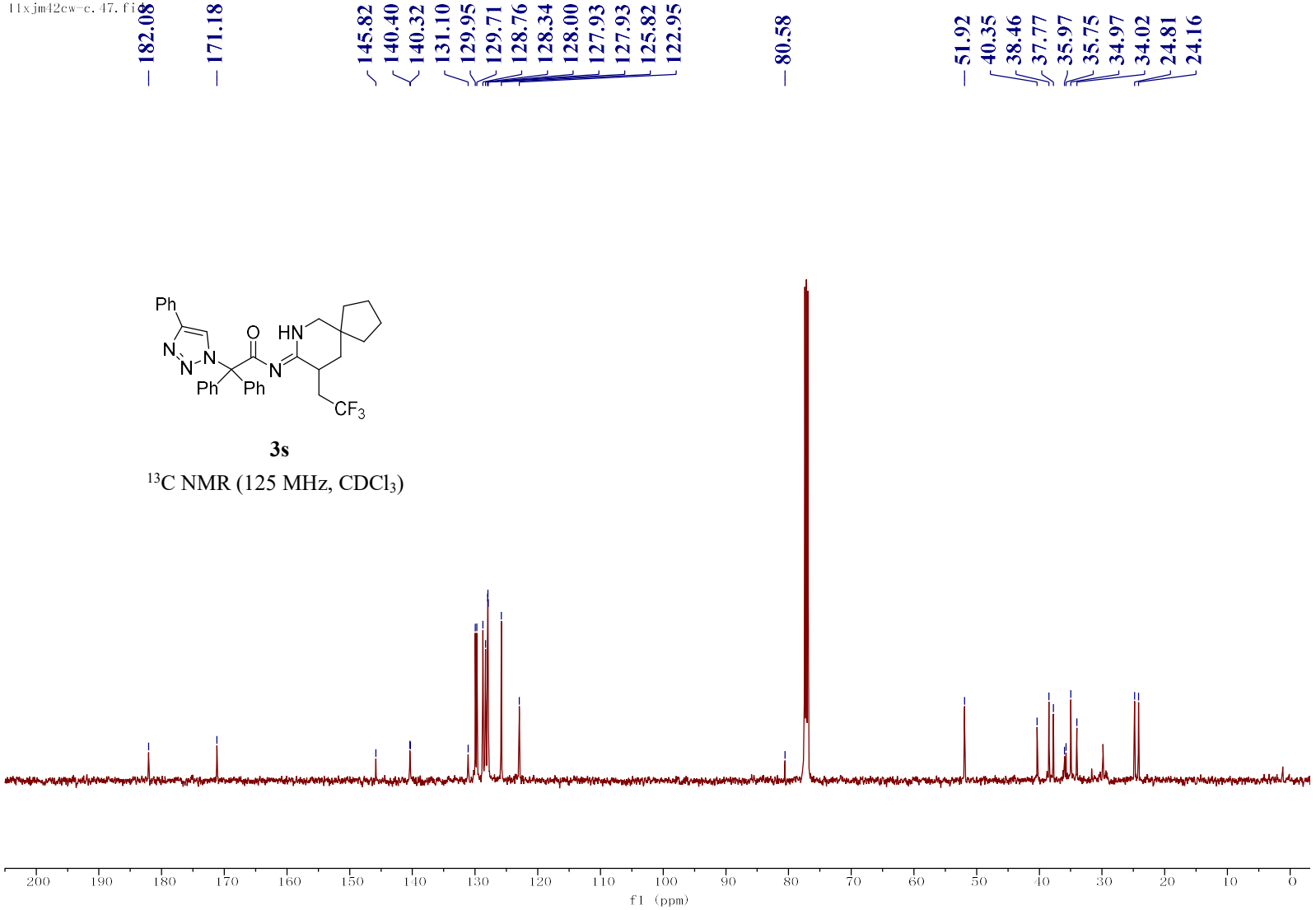
3r

^{19}F NMR (376 MHz, $CDCl_3$)



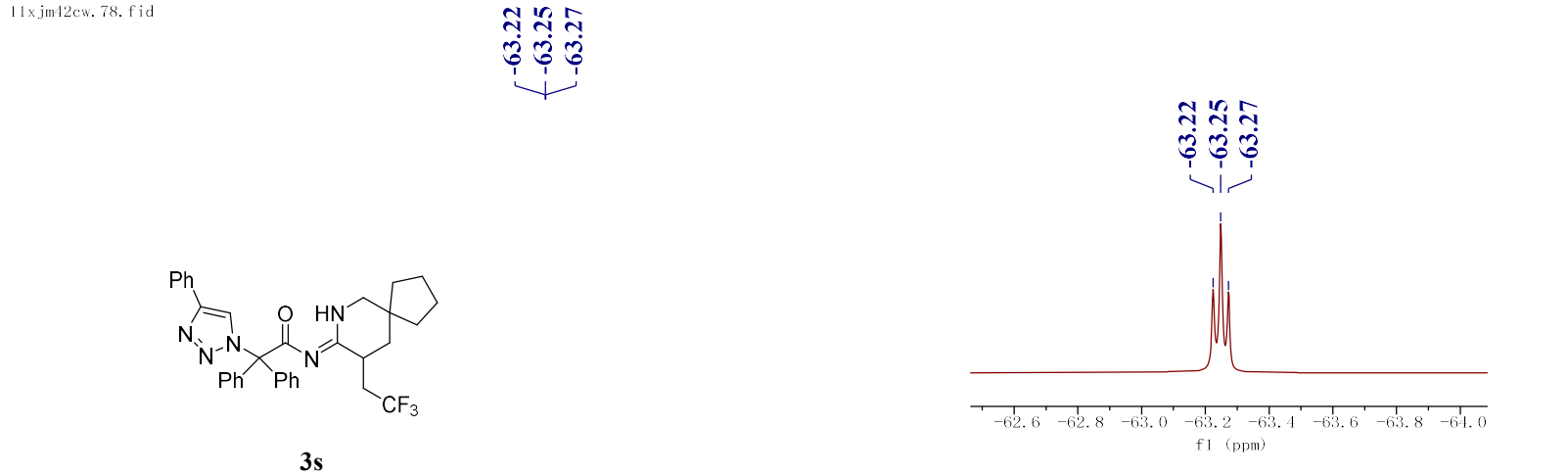
3s

^{1}H NMR (500 MHz, $CDCl_3$)



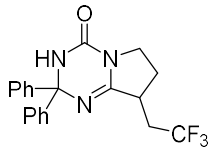
3s

^{13}C NMR (125 MHz, $CDCl_3$)



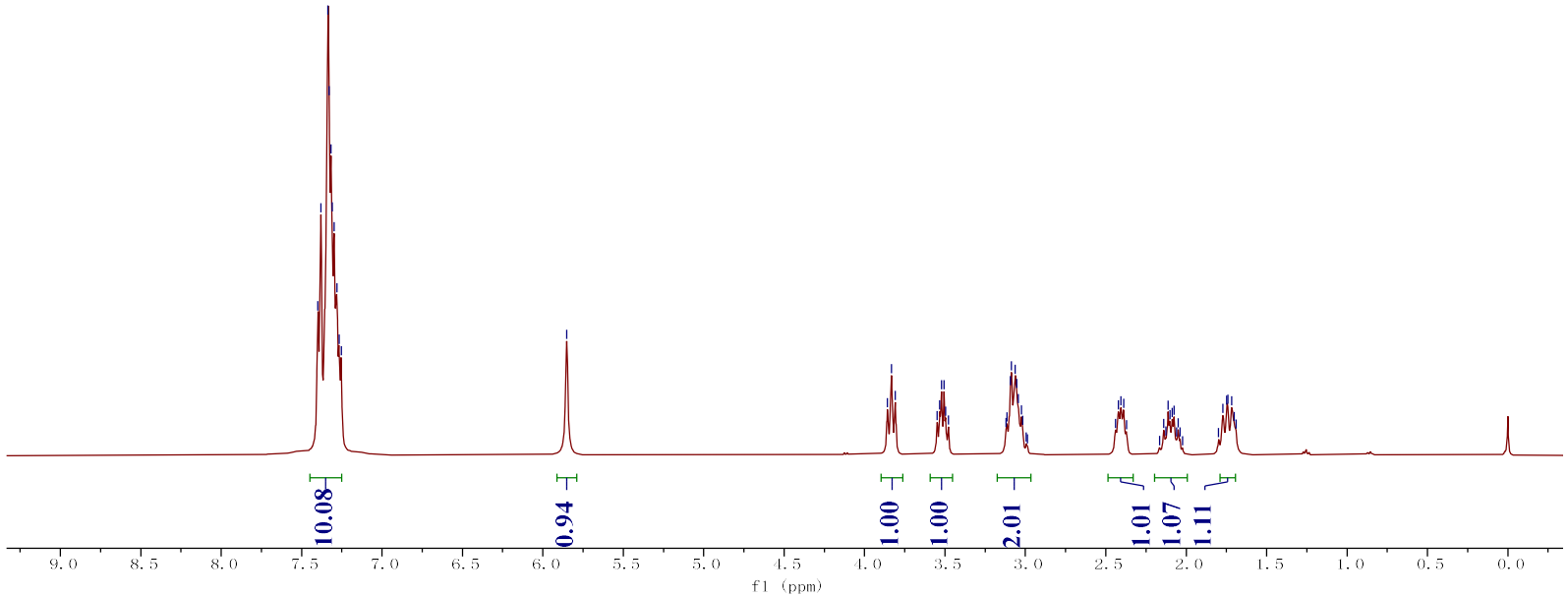
3s

^{19}F NMR (470 MHz, $CDCl_3$)



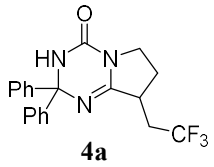
4a

^{1}H NMR (400 MHz, $CDCl_3$)



9XJM-C.12.fid

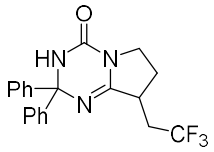
157.41
151.11
145.35
145.25
130.89
128.52
128.51
128.42
128.14
126.44
126.14
125.39
122.64
79.36
43.32
36.82
36.79
36.76
36.73
36.32
36.03
35.74
35.45
27.34



4a

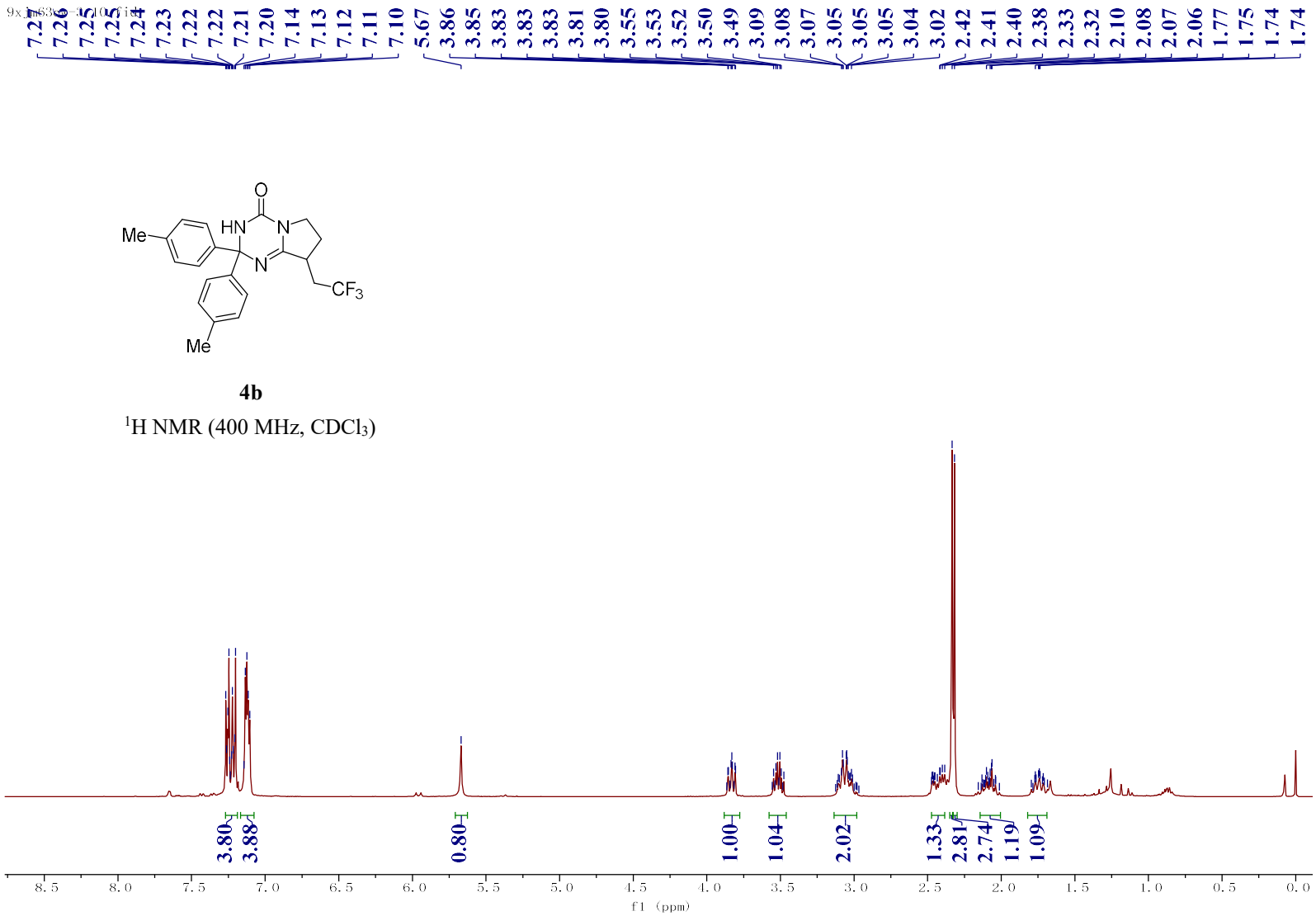
^{13}C NMR (100 MHz, $CDCl_3$)

9xjm.11.fid



4a

^{19}F NMR (376 MHz, $CDCl_3$)

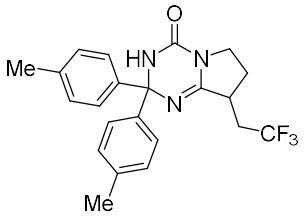


4b

^{1}H NMR (400 MHz, $CDCl_3$)

9xjm63cw-3.12.fid

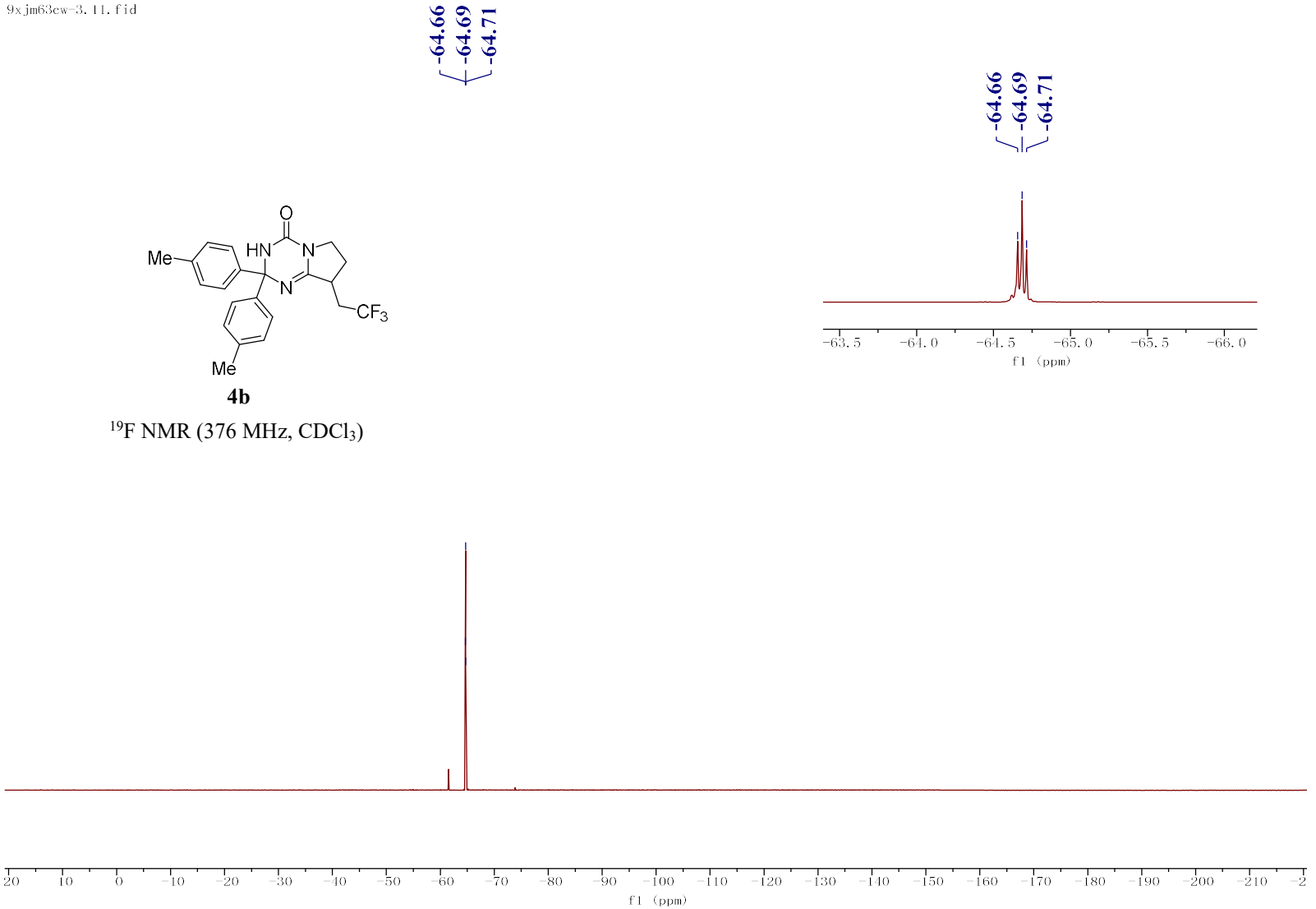
157.14
151.14
142.71
142.52
137.77
137.60
129.16
129.16
129.07
128.17
126.34
126.03
125.42
79.17
43.30
36.78
36.76
36.72
36.70
36.35
36.06
35.77
35.48
27.36
21.19
21.16



4b

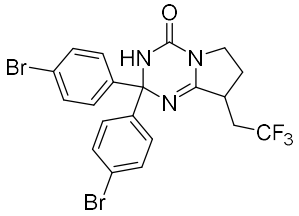
^{13}C NMR (100 MHz, $CDCl_3$)

9xjm63cw-3.11.fid



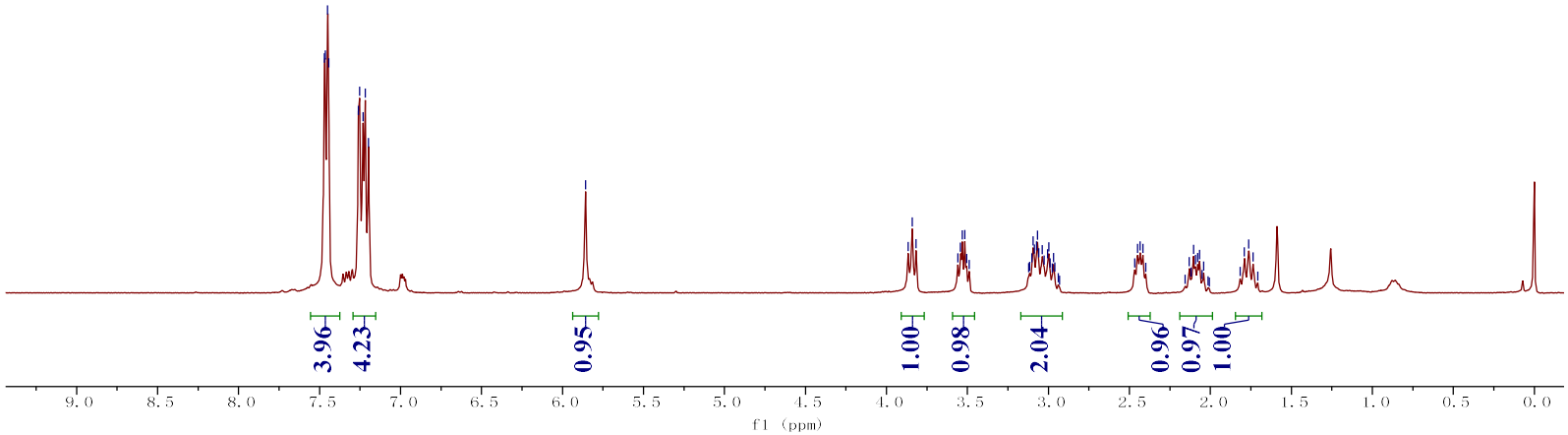
4b

^{19}F NMR (376 MHz, $CDCl_3$)



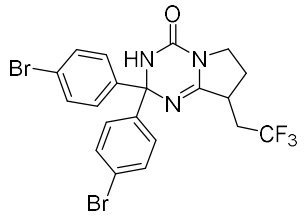
4c

^{1}H NMR (400 MHz, $CDCl_3$)



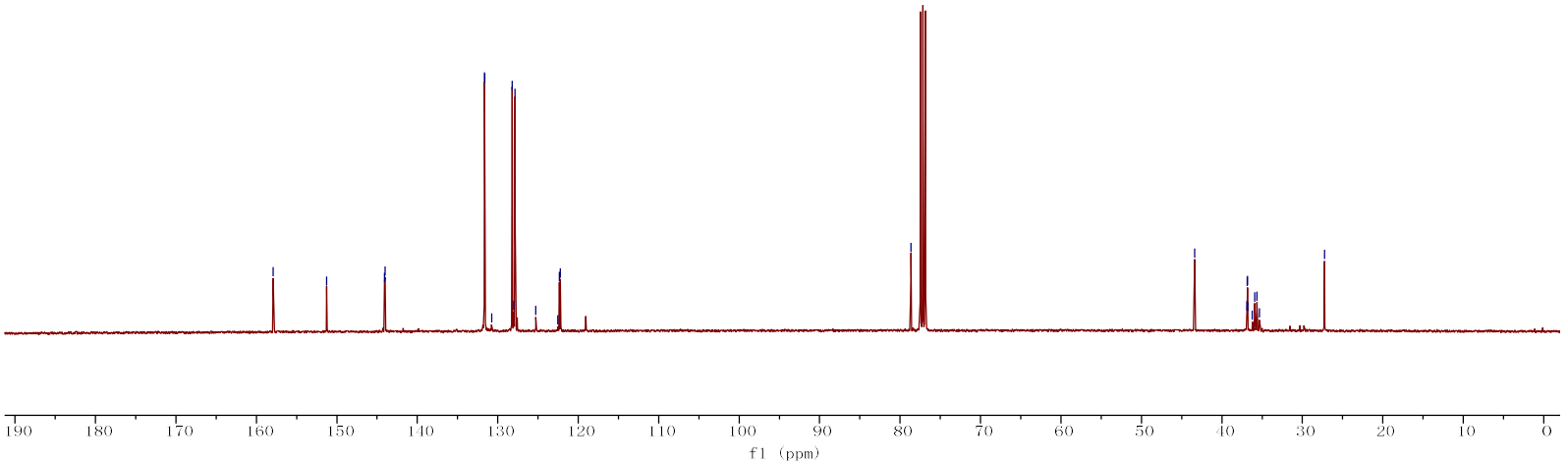
9xjm57bcw-c1024.16.fid

157.91
151.26
144.06
143.98
131.66
131.63
130.77
128.22
128.02
127.86
125.27
122.52
122.36
122.22
78.65
43.40
36.88
36.85
36.82
36.79
36.22
35.93
35.64
35.35
27.26

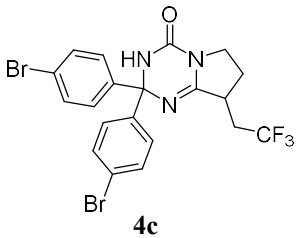


4c

^{13}C NMR (100 MHz, $CDCl_3$)

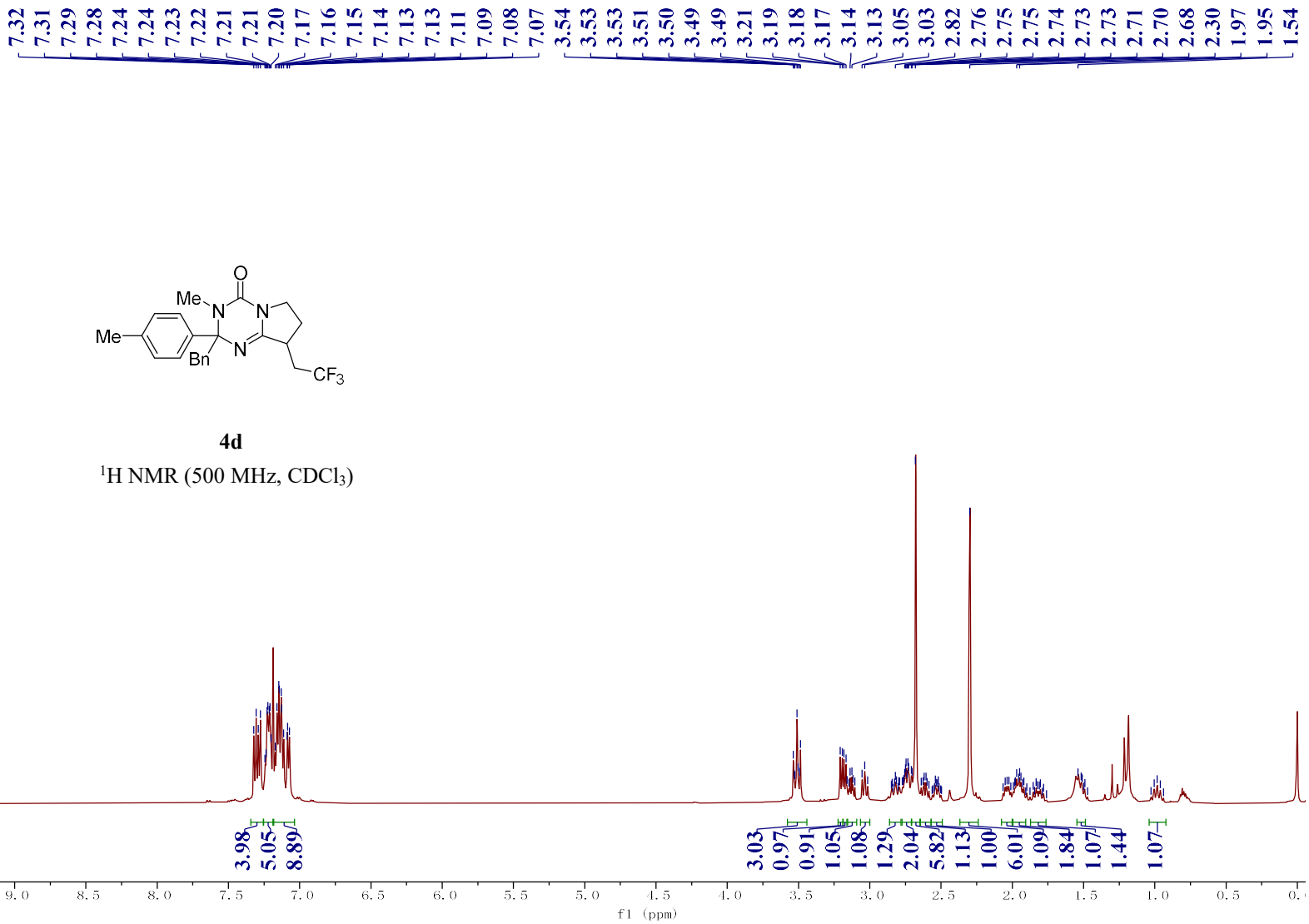


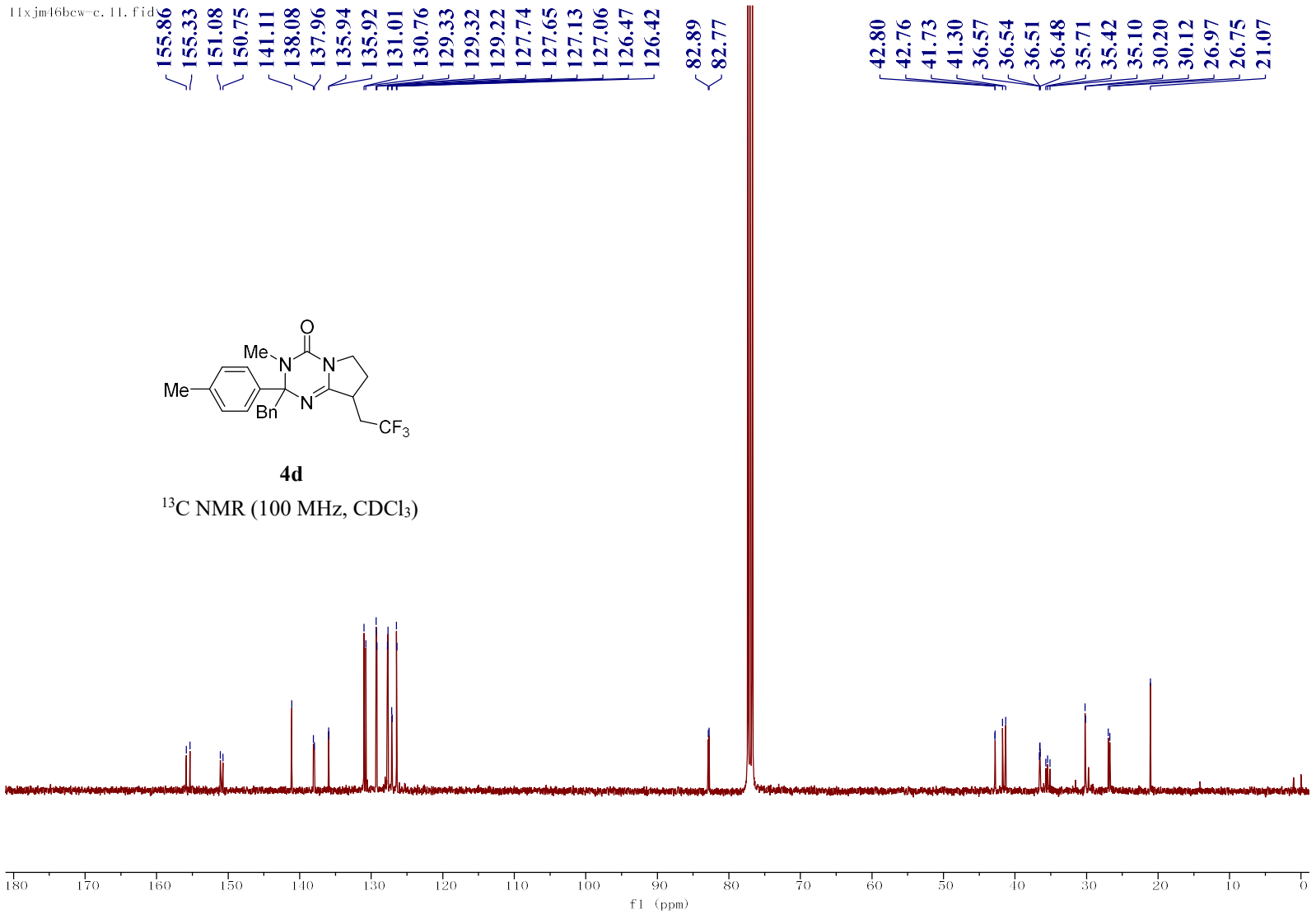
9XJM57CW-3.11.fid



4c

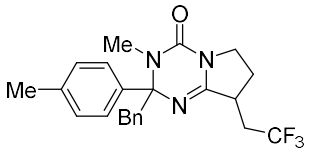
^{19}F NMR (376 MHz, $CDCl_3$)


7.32
7.31
7.29
7.28
7.24
7.24
7.23
7.22
7.21
7.21
7.20
7.17
7.16
7.15
7.14
7.13
7.13
7.11
7.09
7.08
7.07
3.54
3.53
3.53
3.51
3.50
3.49
3.49
3.21
3.19
3.18
3.17
3.14
3.13
3.05
3.03
2.82
2.76
2.75
2.75
2.74
2.73
2.73
2.71
2.70
2.68
2.30
1.97
1.95
1.54
O
Me
N
N
Me
Bn
N
CF3
4d
1H NMR (500 MHz, CDCl3)
3.98
5.05
8.89
3.03
0.97
0.91
1.05
1.08
1.29
2.04
5.82
1.13
1.00
6.01
1.09
1.84
1.07
1.44
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



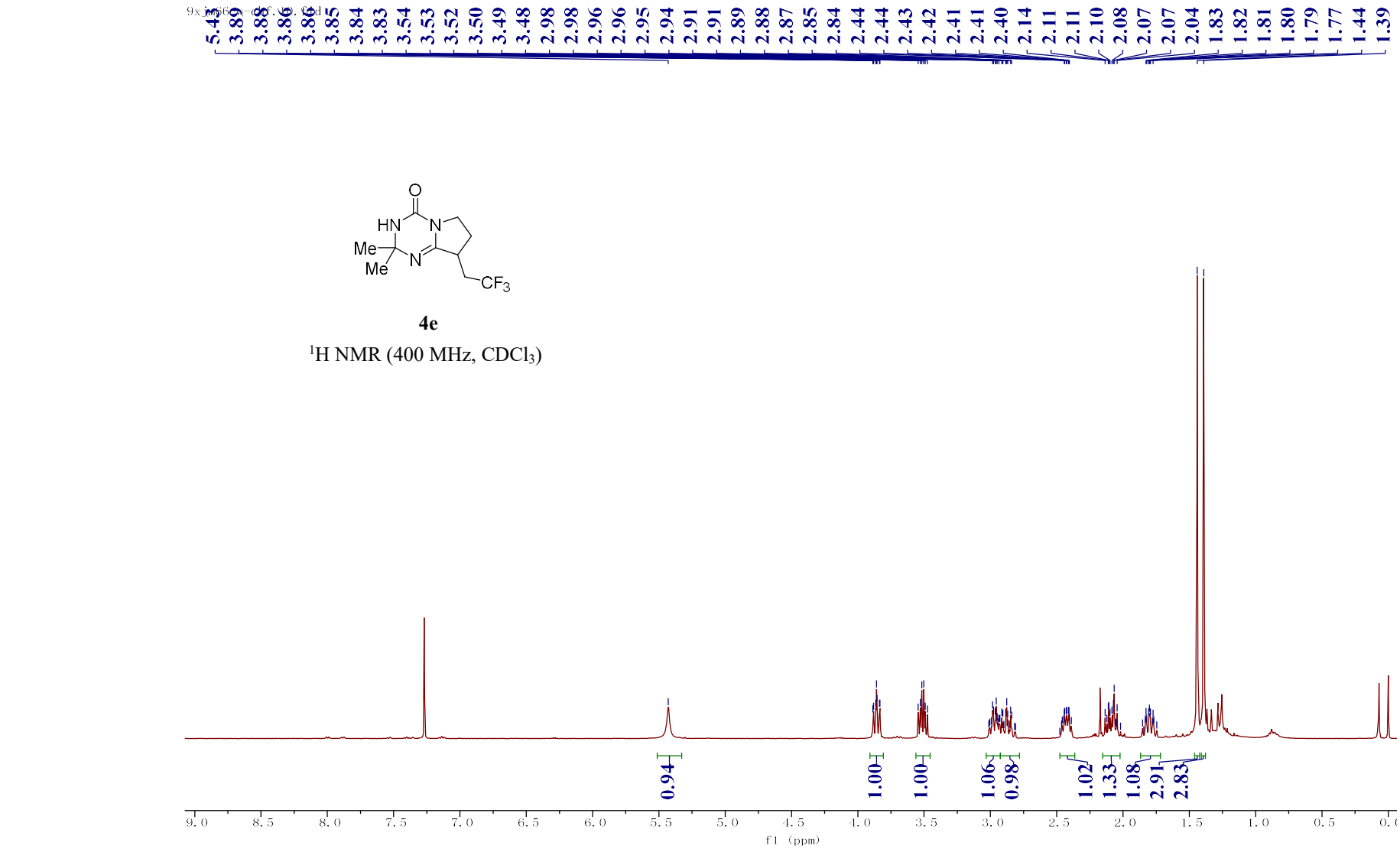
4d

^{13}C NMR (100 MHz, $CDCl_3$)



4d

^{19}F NMR (470 MHz, $CDCl_3$)

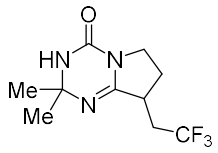


4e

^{1}H NMR (400 MHz, $CDCl_3$)

9xjm66cw-chf.13.fid

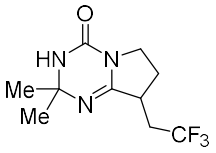
156.50
151.82
130.87
128.12
125.37
122.62
72.39
43.04
36.49
36.47
36.44
36.41
36.36
36.07
35.78
35.49
31.08
30.59
27.40



4e

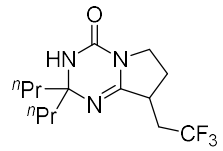
^{13}C NMR (100 MHz, $CDCl_3$)

9xjm66cw-chf.14.fid



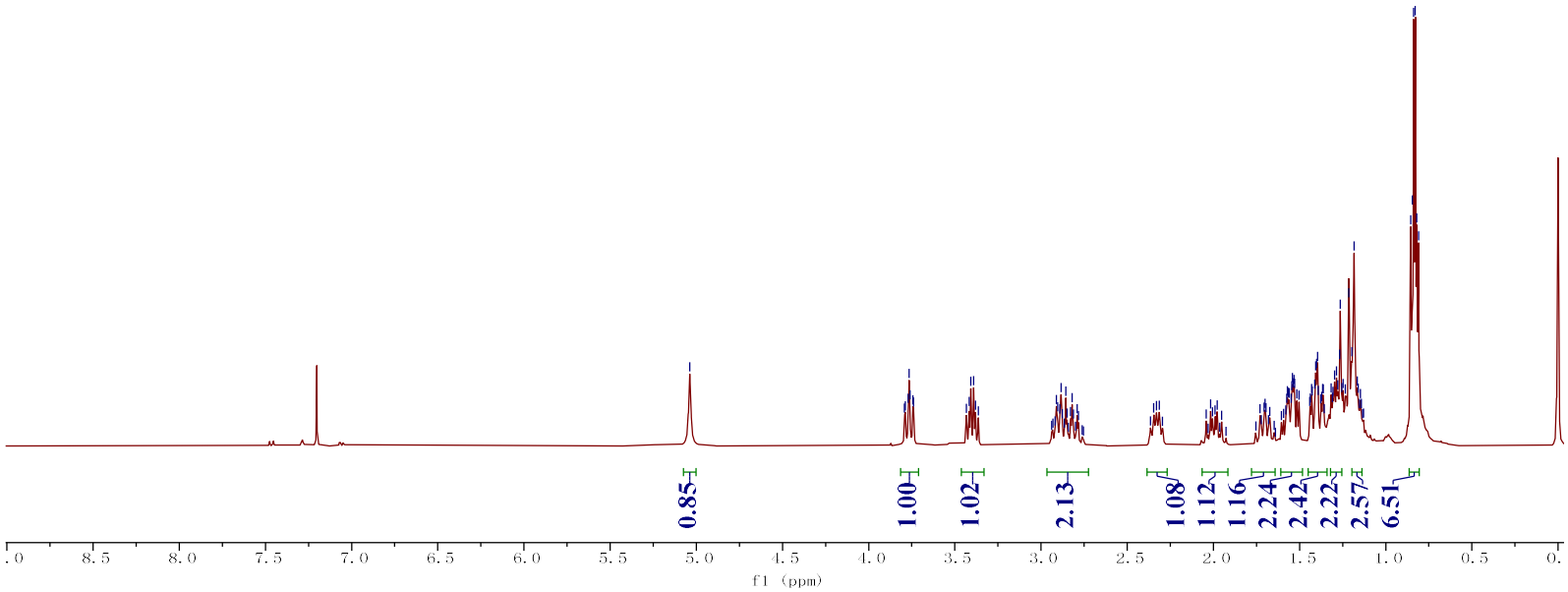
4e

^{19}F NMR (376 MHz, $CDCl_3$)



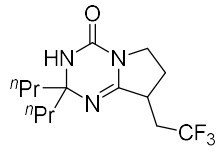
4f

^{1}H NMR (400 MHz, $CDCl_3$)



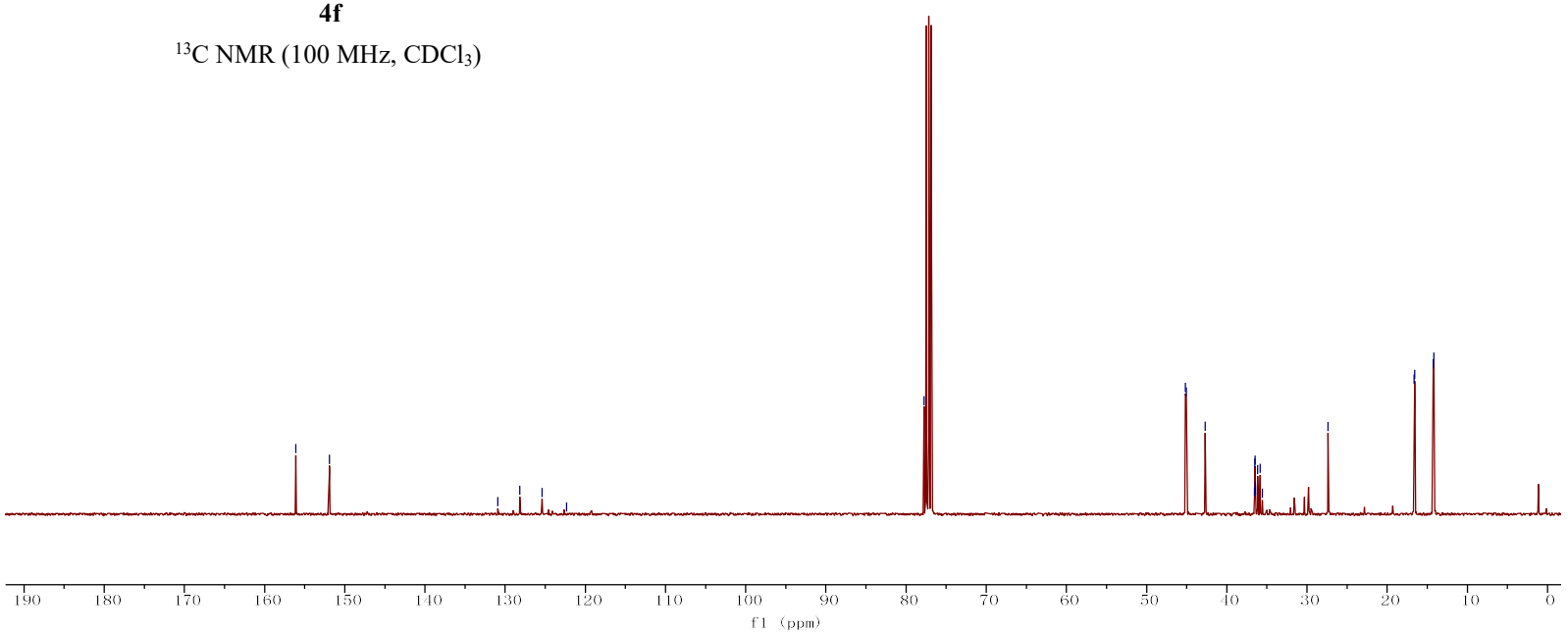
9xjm114cw-2.12.fid

156.12
151.92
130.91
128.16
125.41
122.35
77.77
45.15
45.04
42.71
36.54
36.51
36.48
36.45
36.43
36.15
35.86
35.57
27.37
16.65
16.55
14.26
14.18

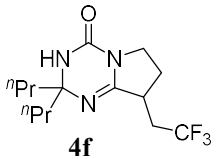


4f

^{13}C NMR (100 MHz, $CDCl_3$)

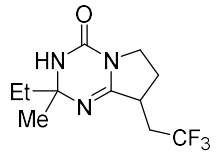


9xjm114cw-2.11.fid



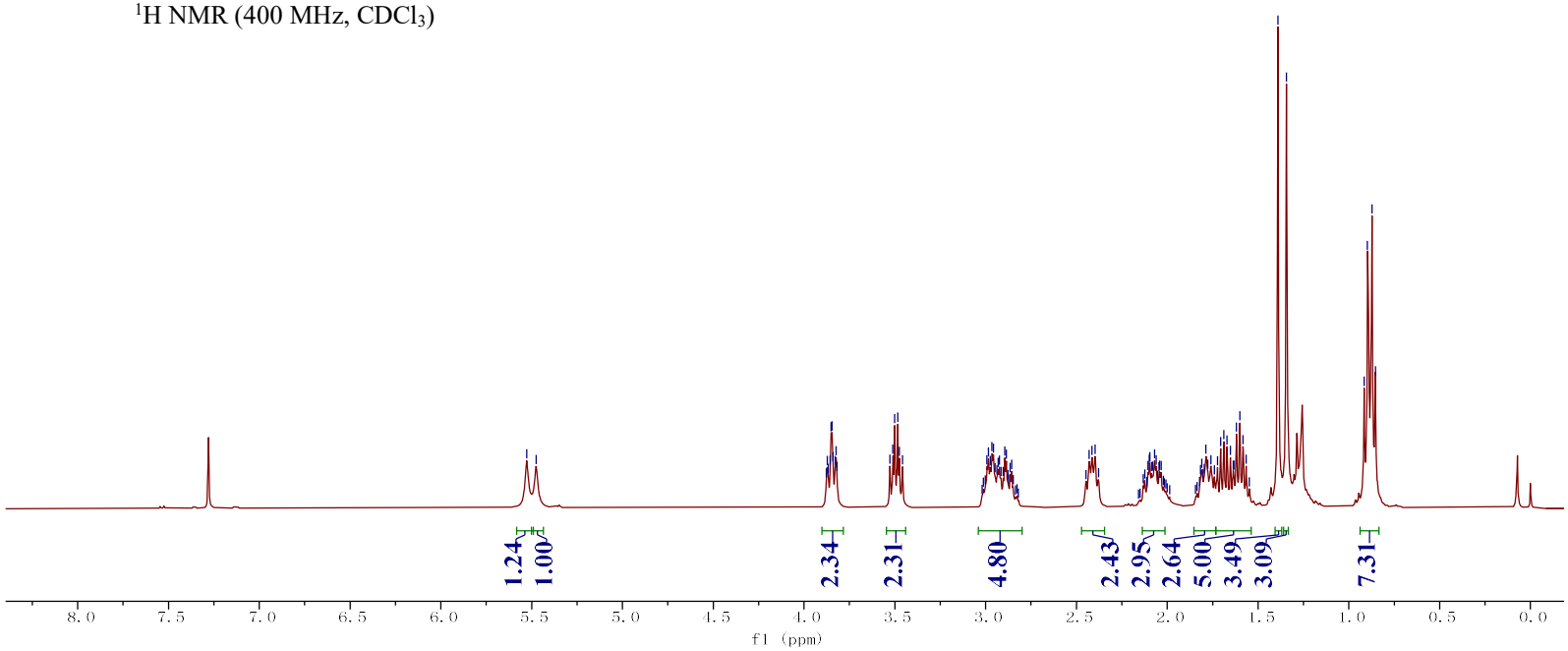
4f

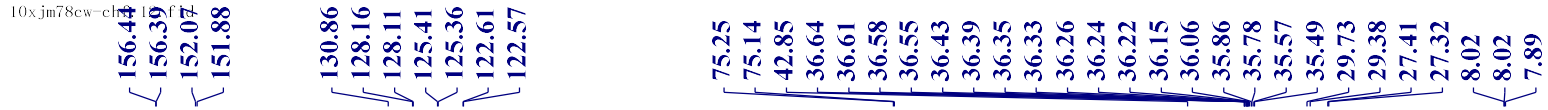
^{19}F NMR (376 MHz, $CDCl_3$)

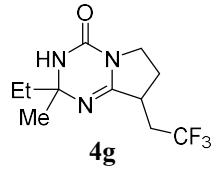


4g

^{1}H NMR (400 MHz, $CDCl_3$)

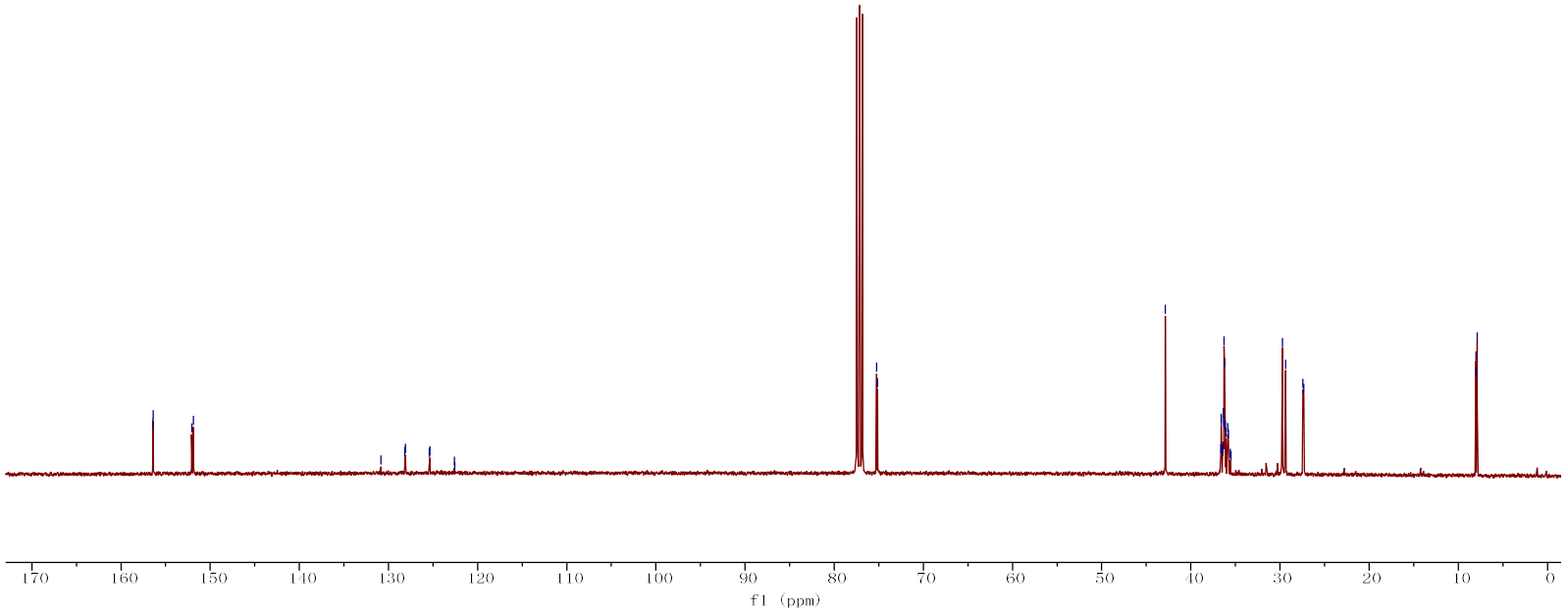




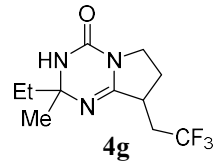


4g

^{13}C NMR (100 MHz, $CDCl_3$)

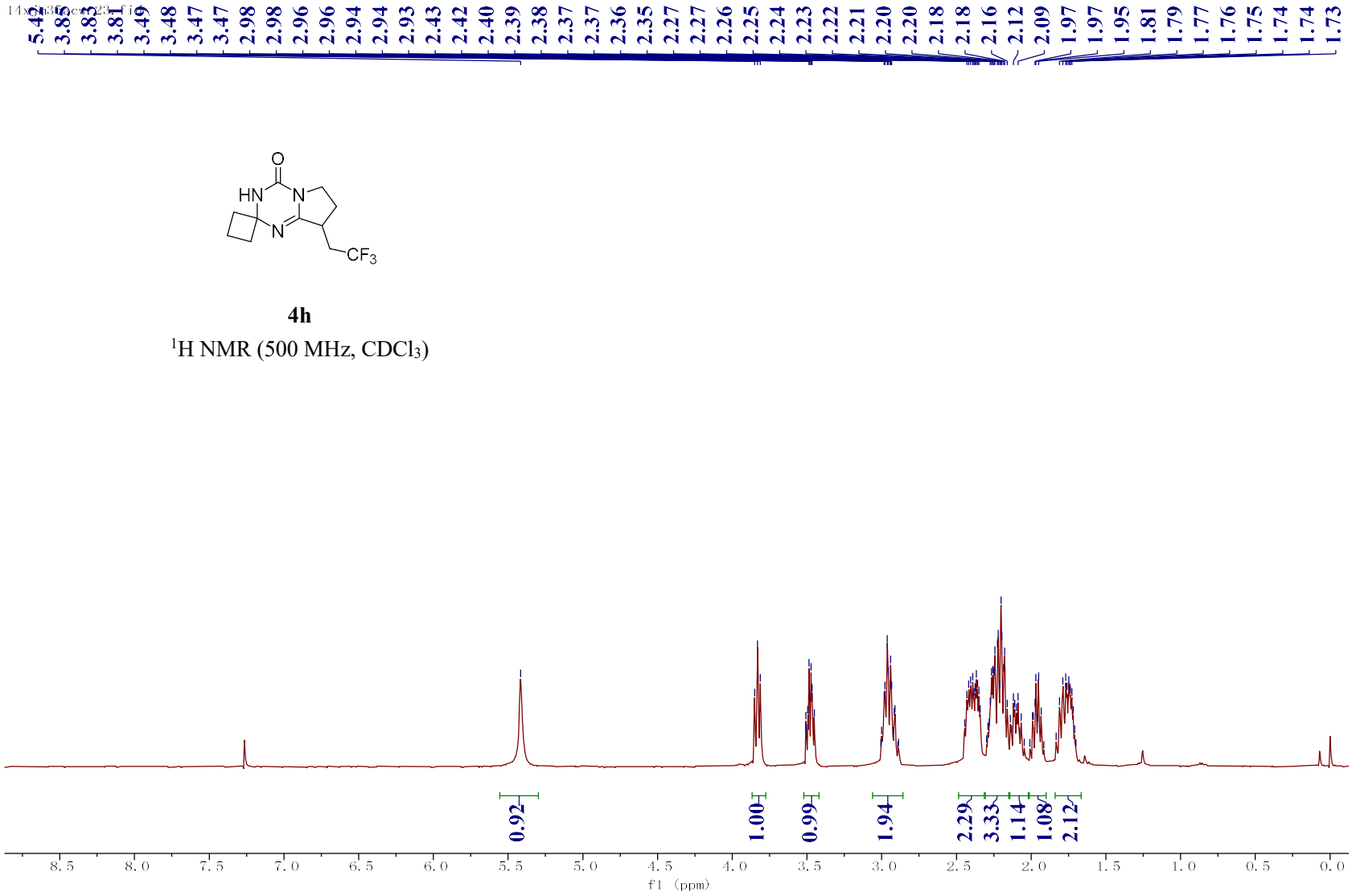


10xjm78cw-chf.11.fid



4g

^{19}F NMR (376 MHz, $CDCl_3$)

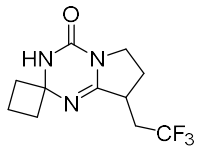


4h

^{1}H NMR (500 MHz, $CDCl_3$)

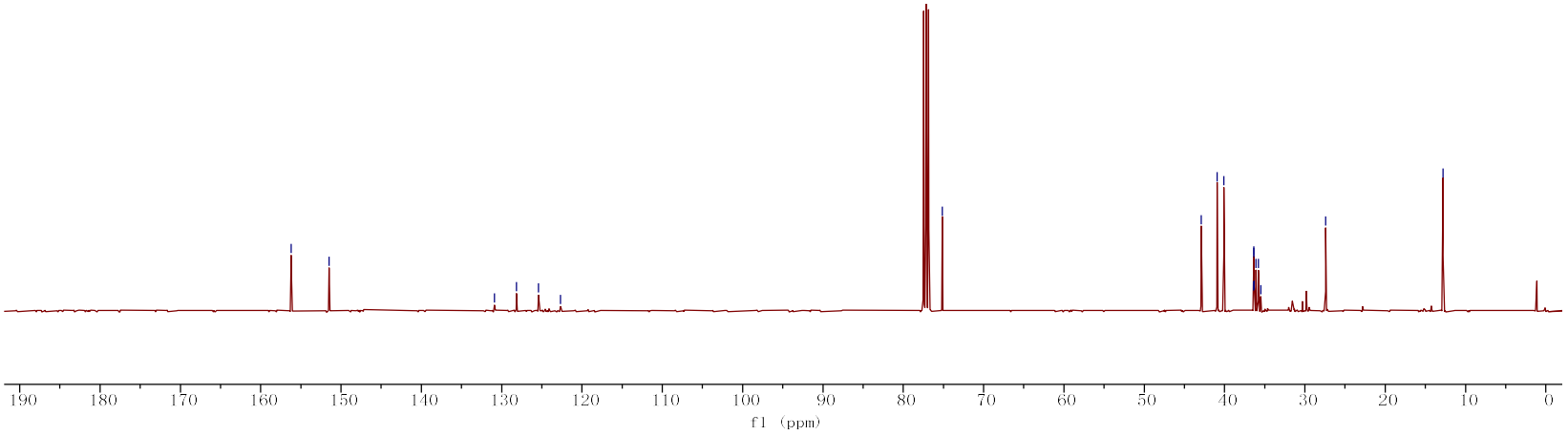
9xjm106cw.12.fid

156.19
151.51
130.91
128.16
125.41
122.66
75.14
42.89
40.93
40.07
36.40
36.37
36.34
36.31
36.07
35.79
35.50
27.40
12.80

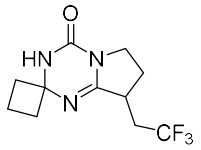


4h

^{13}C NMR (100 MHz, $CDCl_3$)

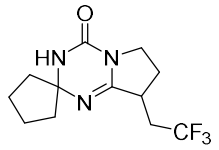


9xjm106cw.11.fid



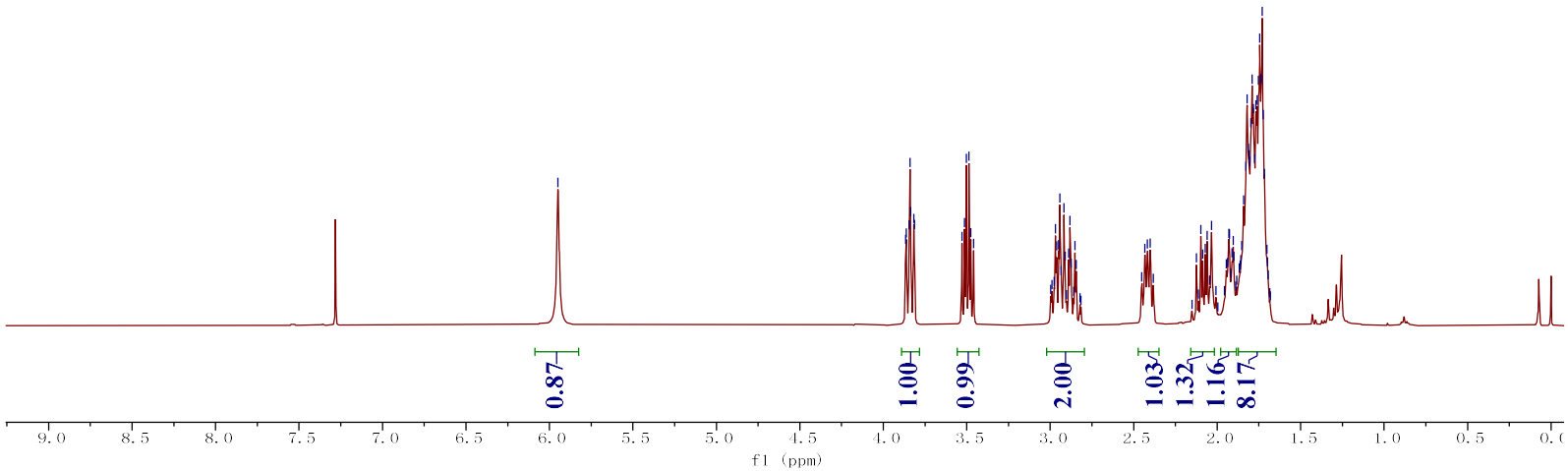
4h

^{19}F NMR (376 MHz, $CDCl_3$)



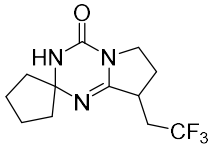
4i

^{1}H NMR (400 MHz, $CDCl_3$)



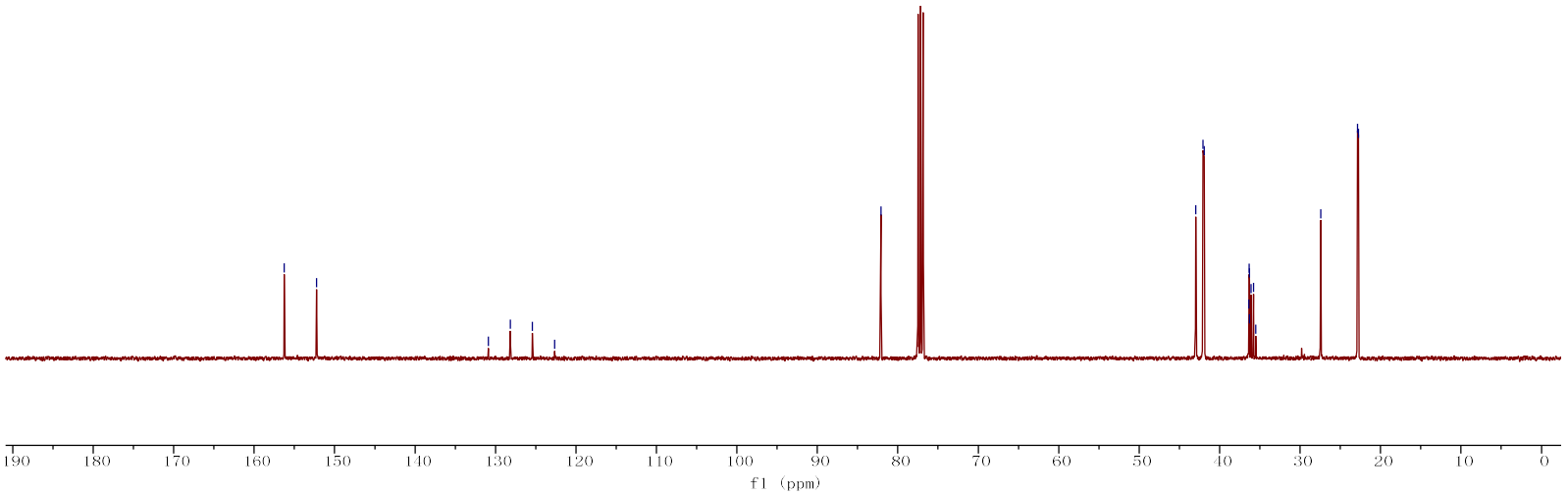
10xjm76cw-chf.12.fid

156.25
152.23
130.91
128.16
125.41
122.66
82.09
42.96
42.06
41.91
36.36
36.33
36.30
36.27
36.08
35.79
35.51
27.43
22.87
22.75

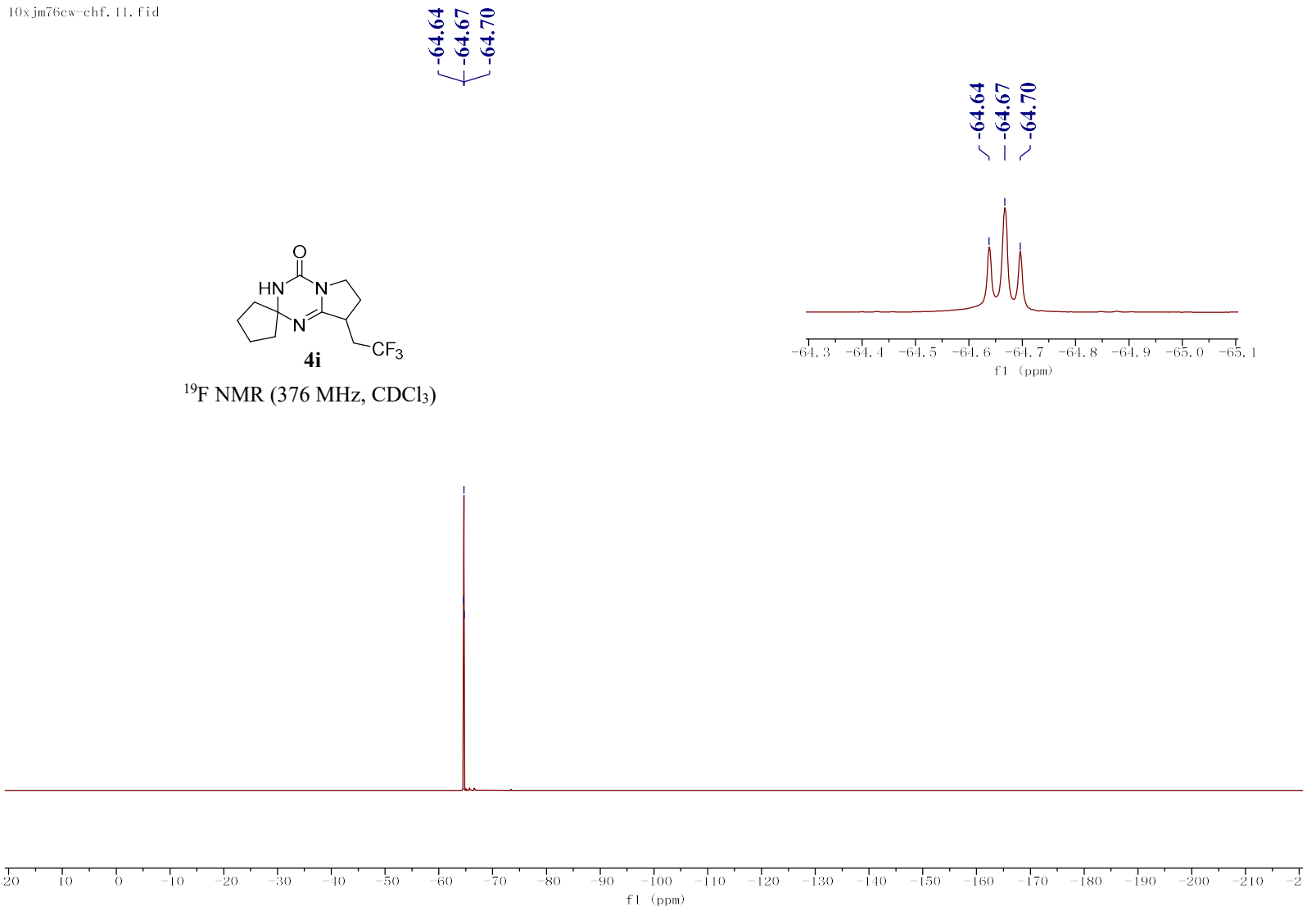


4i

^{13}C NMR (100 MHz, $CDCl_3$)

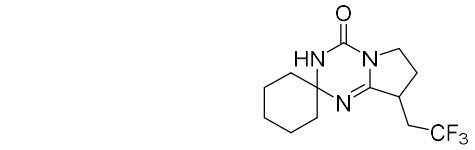


10xjm76cw-chf.11.fid



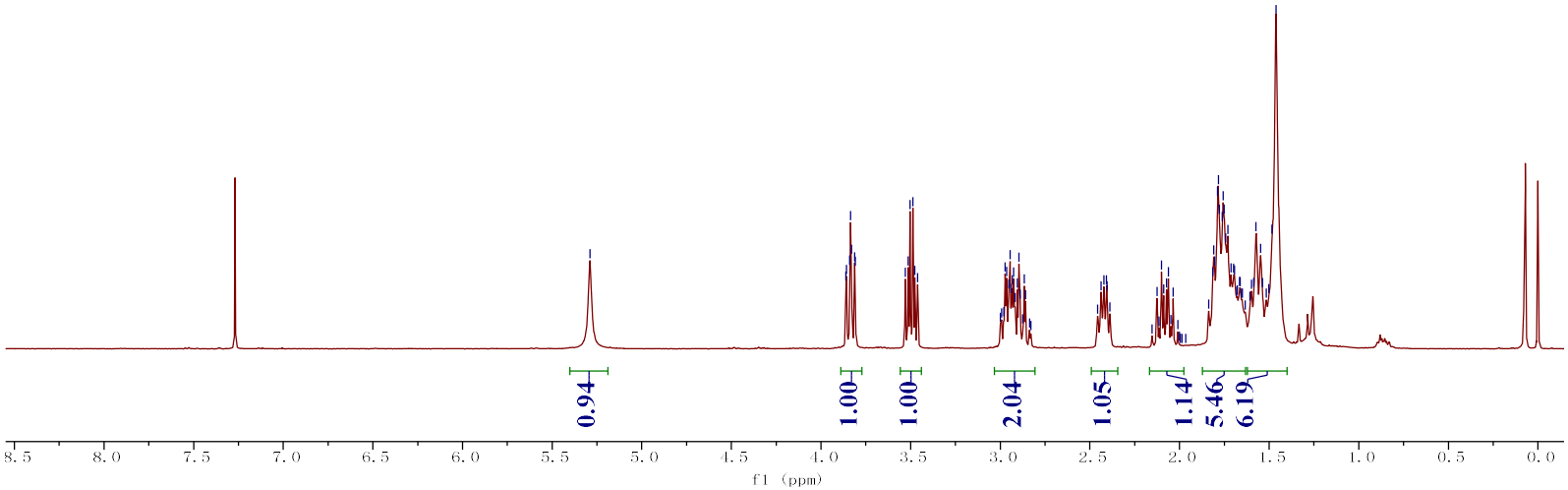
4i

^{19}F NMR (376 MHz, $CDCl_3$)



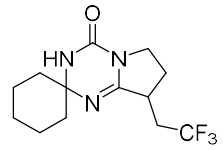
4k

^{1}H NMR (400 MHz, $CDCl_3$)



9xjm78cw-chf.11.fid

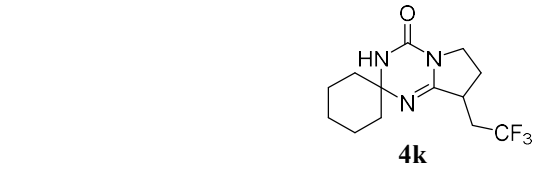
156.12
151.77
130.93
128.18
125.43
122.68
73.62
42.98
39.45
39.12
36.46
36.43
36.40
36.37
36.14
35.86
35.57
27.49
25.15
21.94
21.85



4k

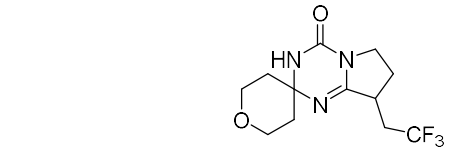
^{13}C NMR (100 MHz, $CDCl_3$)

9xjm78cw-chf.12.fid



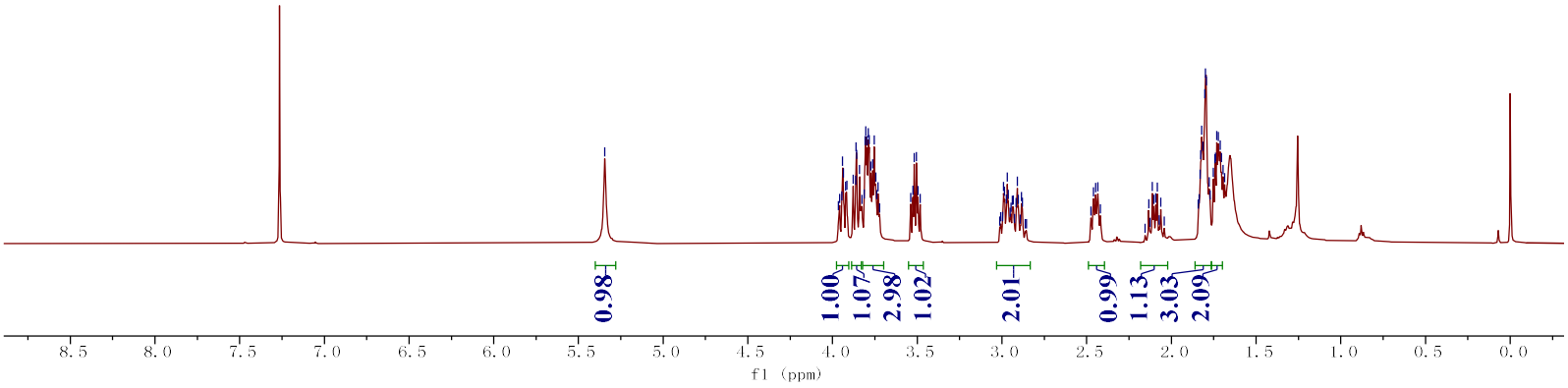
4k

^{19}F NMR (376 MHz, $CDCl_3$)



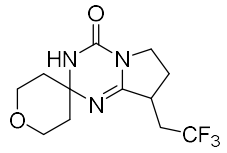
4l

^{1}H NMR (500 MHz, $CDCl_3$)



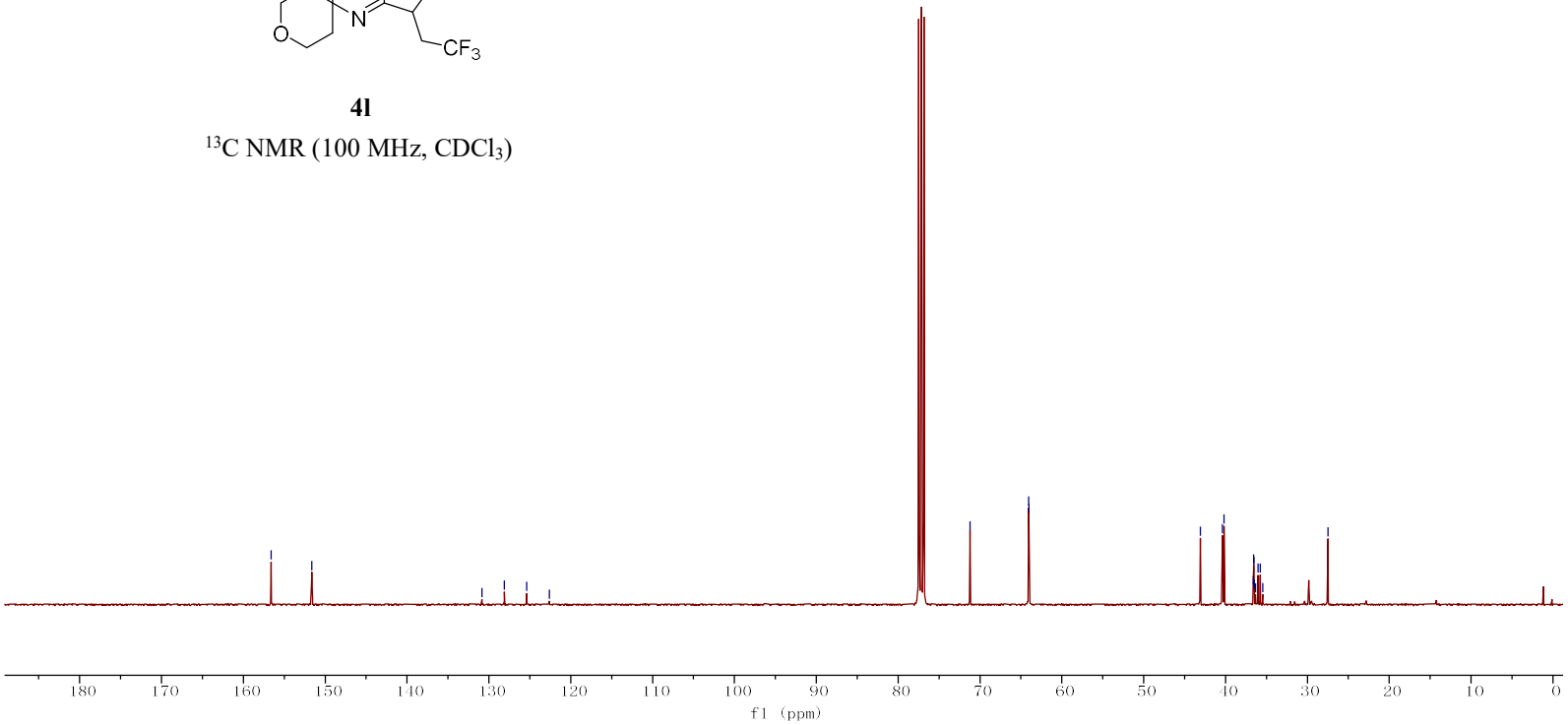
9XJM87CW-3.12.fid

156.59
151.65
130.87
128.12
125.37
122.62
71.23
64.04
64.01
43.08
40.39
40.17
36.59
36.57
36.54
36.51
36.32
36.03
35.74
35.45
27.49



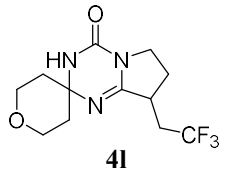
4l

^{13}C NMR (100 MHz, $CDCl_3$)



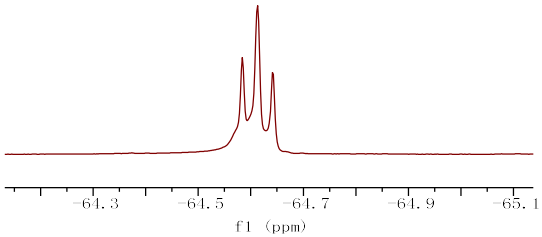
9XJM87CW-3.13.fid

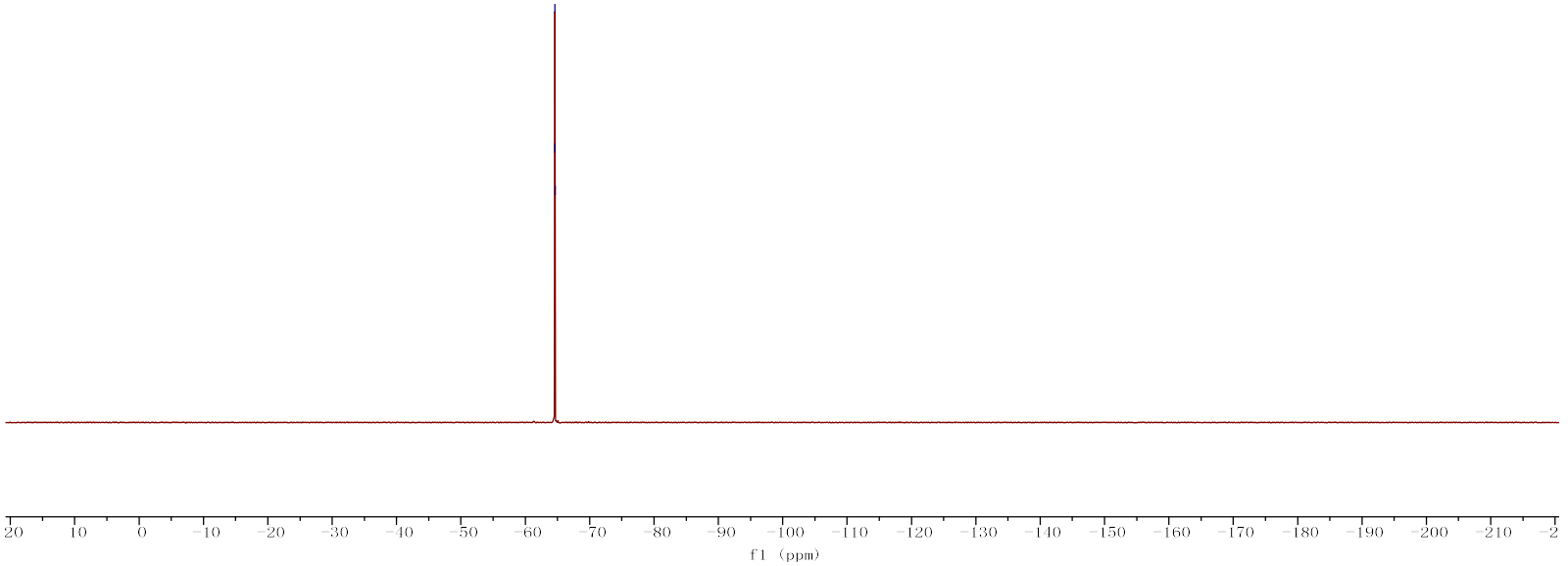
-64.58
-64.61
-64.64

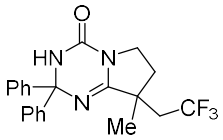


4l

^{19}F NMR (376 MHz, $CDCl_3$)

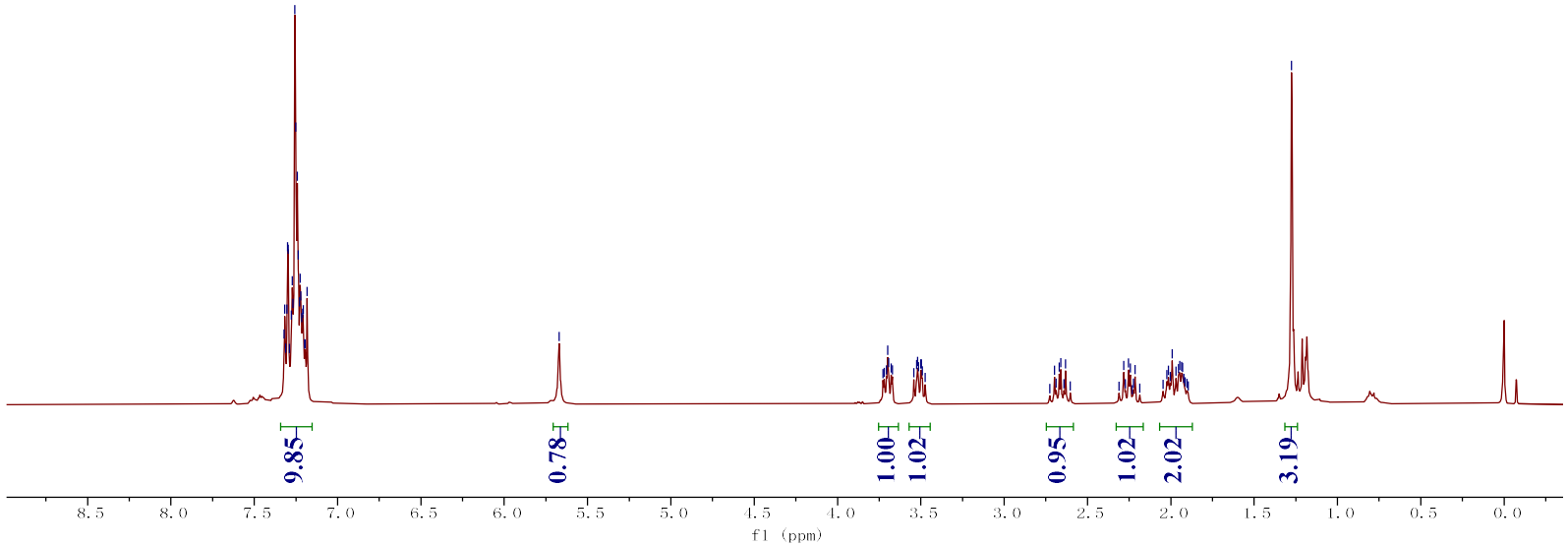






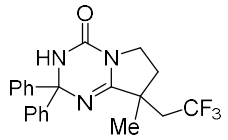
4m

^{1}H NMR (400 MHz, $CDCl_3$)



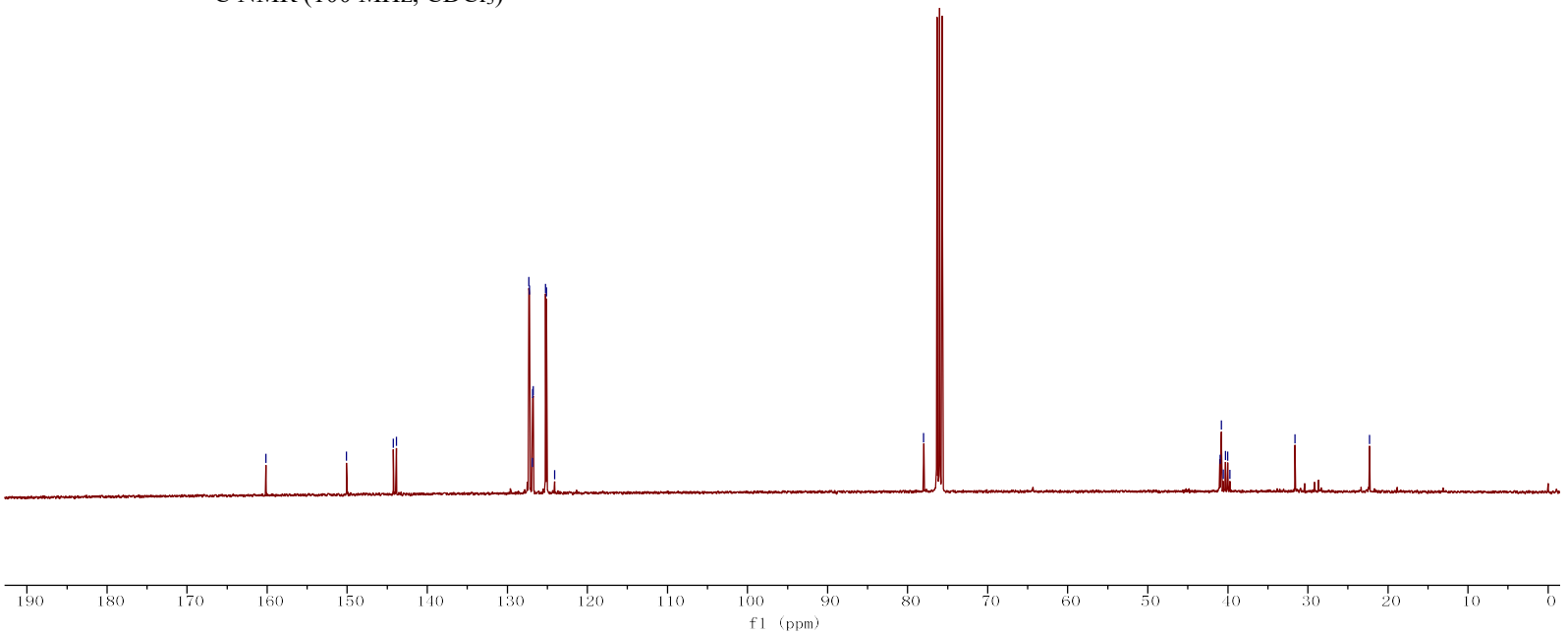
9xjm51cw.12.fid

160.14
150.08
144.24
143.87
127.31
127.24
126.87
126.84
126.78
125.22
125.11
124.11
77.99
40.98
40.81
40.59
40.31
40.04
39.76
31.61
22.29

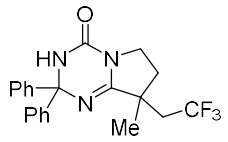


4m

^{13}C NMR (100 MHz, $CDCl_3$)

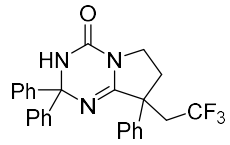


9xjm51cw.11.fid



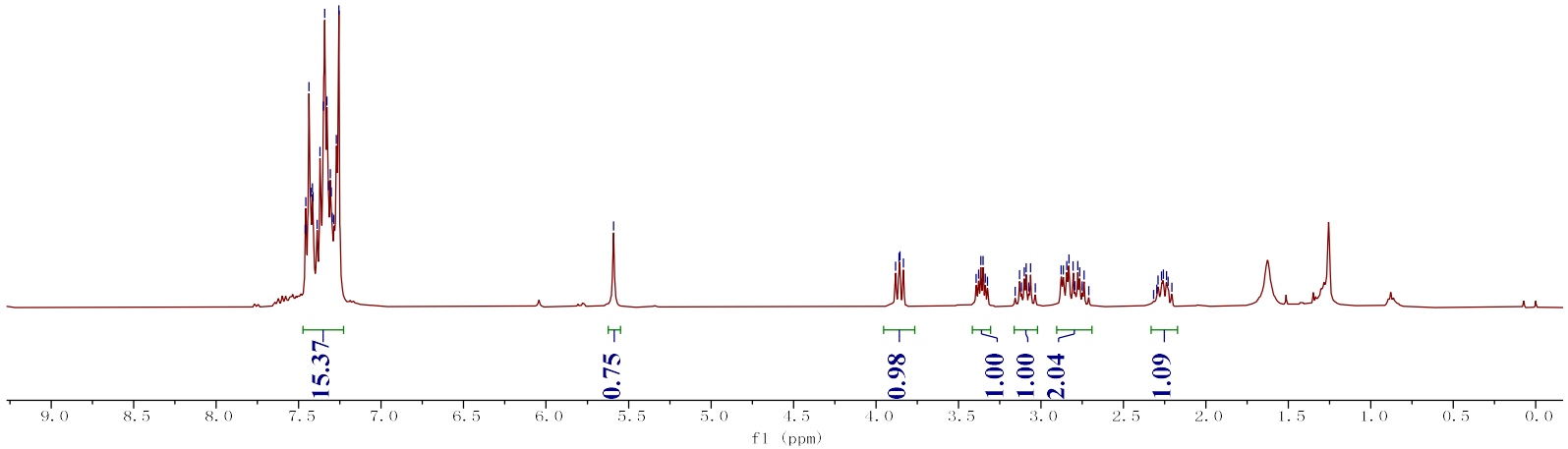
4m

^{19}F NMR (376 MHz, $CDCl_3$)



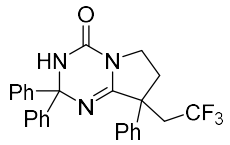
4n

^{1}H NMR (400 MHz, $CDCl_3$)



x-28-2.12.fid

159.27
151.01
145.12
144.86
137.88
129.00
128.90
128.49
128.08
128.06
126.63
126.34
126.23
79.66
49.24
49.22
43.34
43.06
42.79
42.52
41.90
31.32



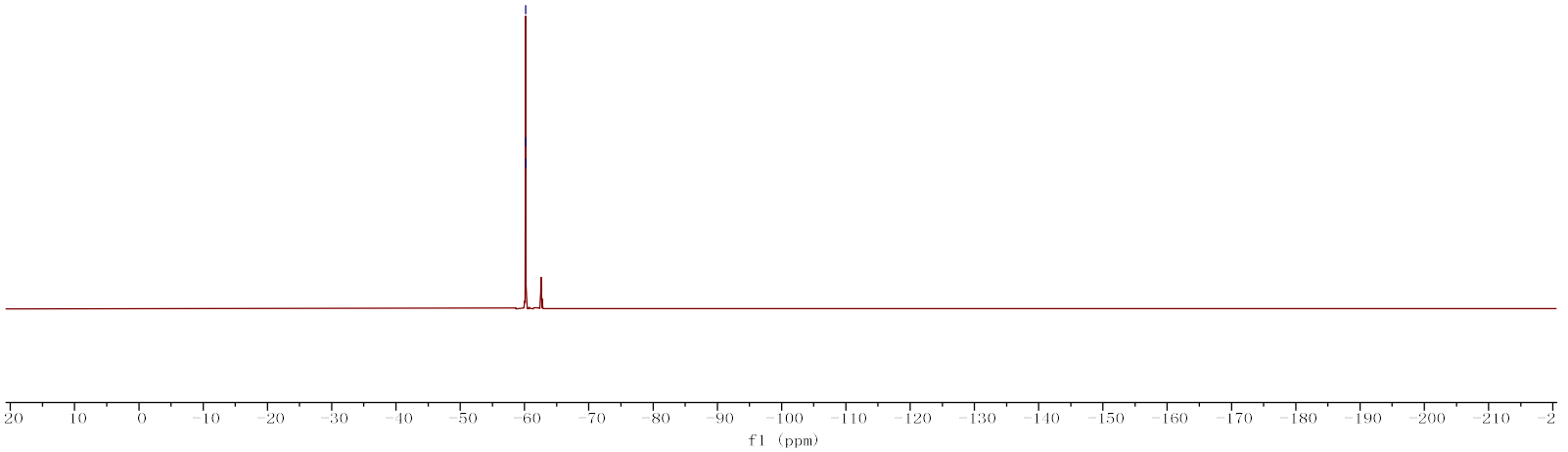
4n

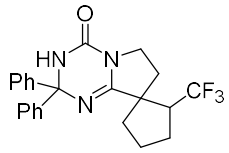
^{13}C NMR (100 MHz, $CDCl_3$)

x-28-2.11.fid

4n

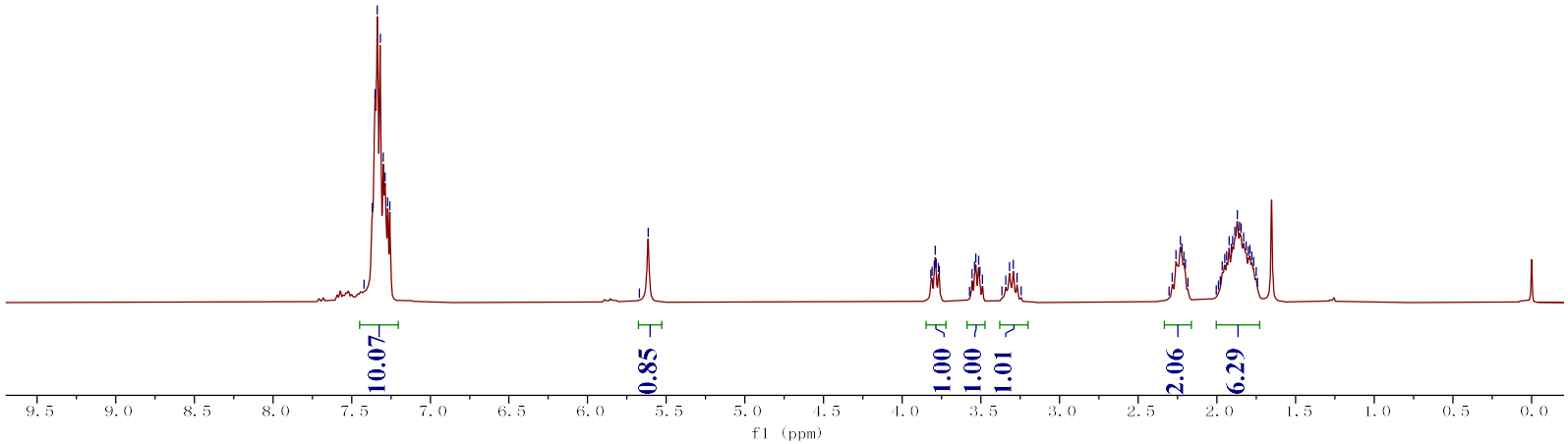
^{19}F NMR (376 MHz, $CDCl_3$)

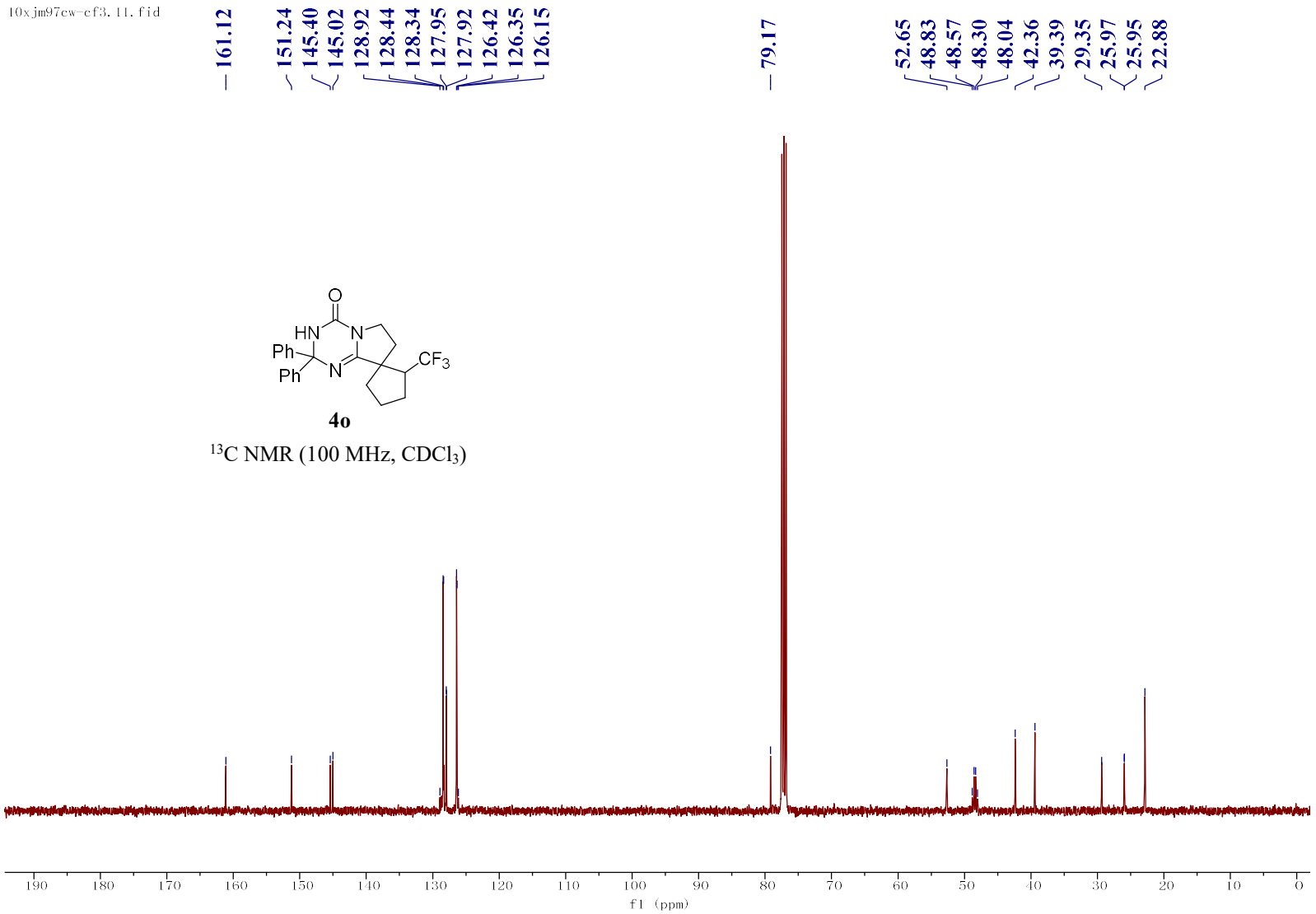




4o

^{1}H NMR (400 MHz, $CDCl_3$)

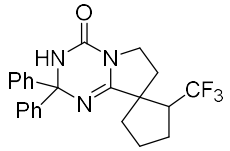




4o

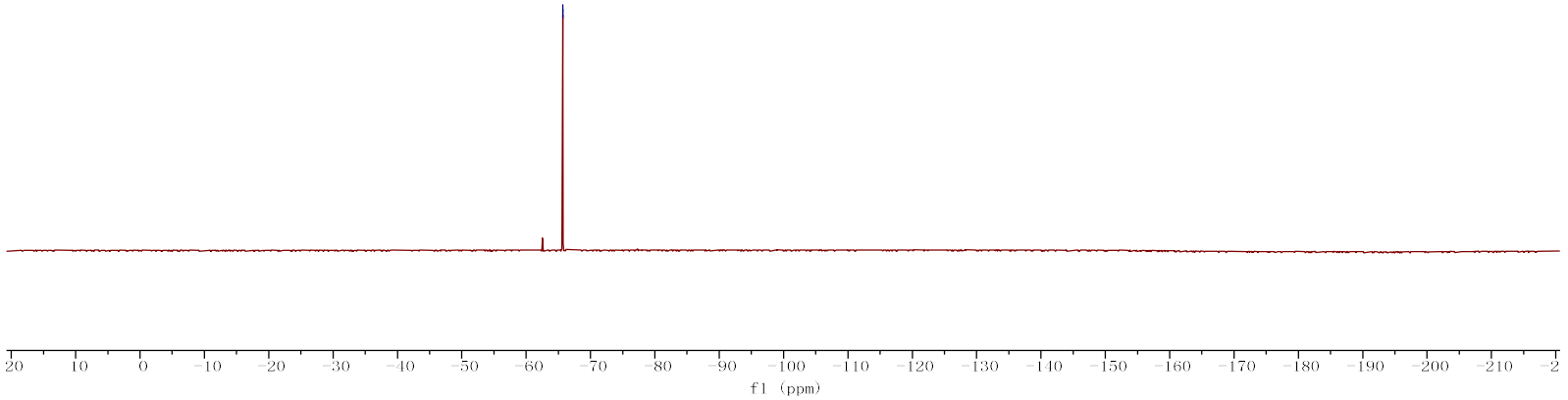
^{13}C NMR (100 MHz, $CDCl_3$)

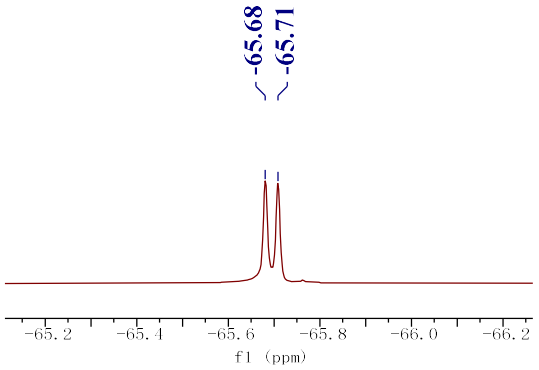
10xjm90-cf3-f-2.11.fid

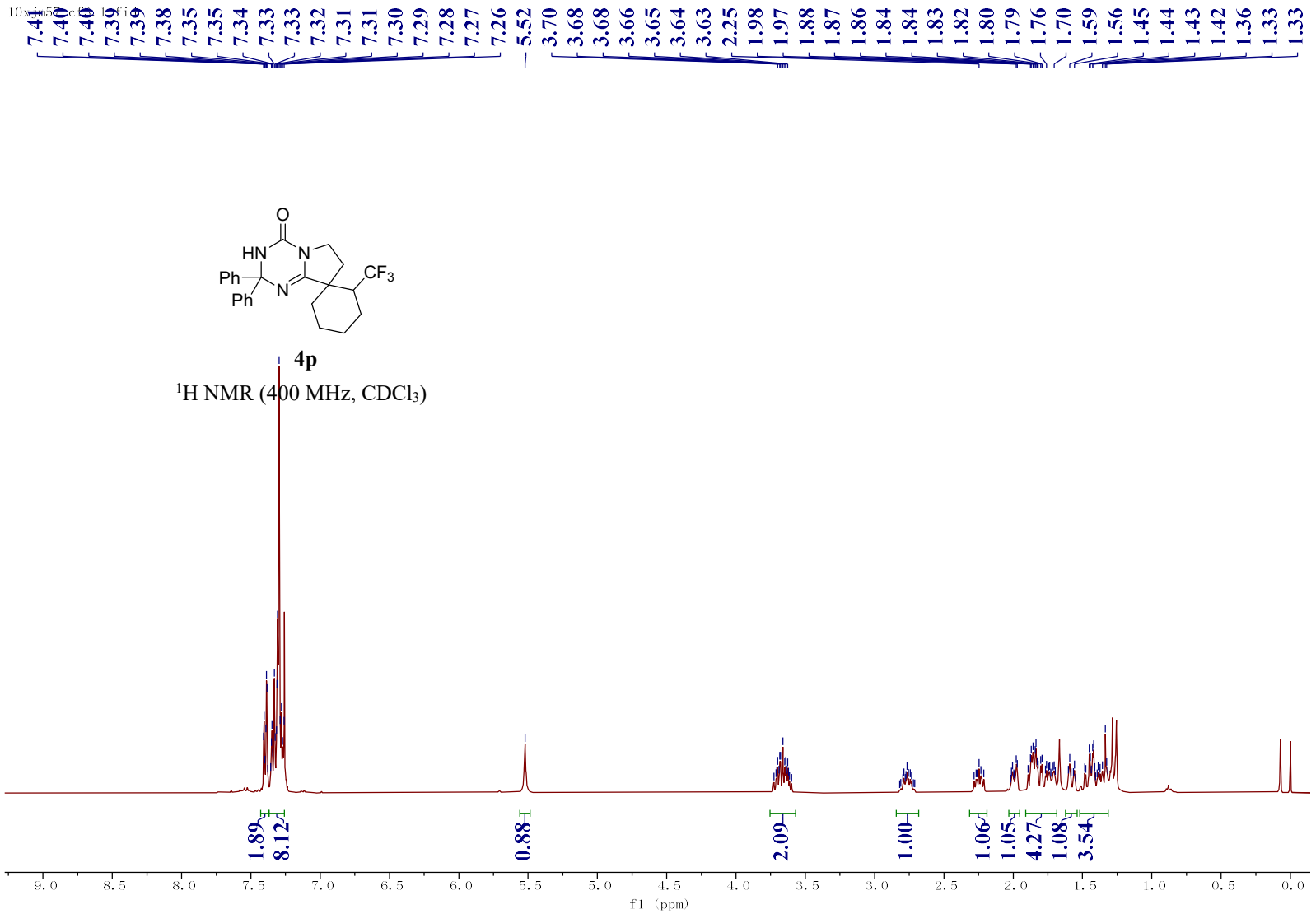


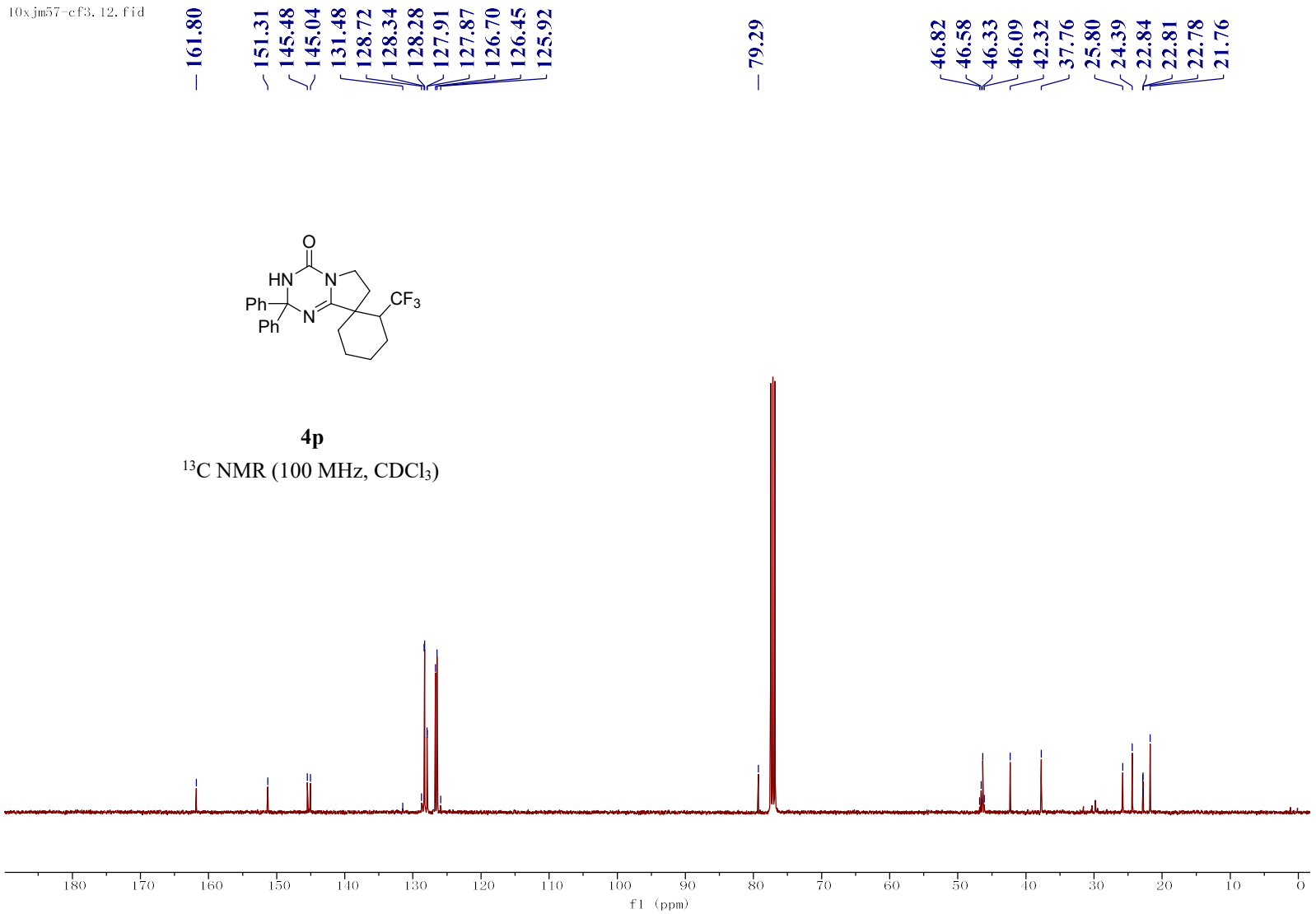
4o

^{19}F NMR (376 MHz, $CDCl_3$)





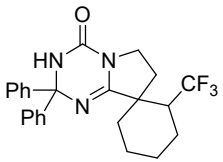

7.41
7.40
7.40
7.39
7.39
7.38
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.26
5.52
3.70
3.68
3.68
3.66
3.65
3.64
3.63
2.25
1.98
1.97
1.88
1.87
1.86
1.84
1.84
1.83
1.82
1.80
1.79
1.76
1.70
1.59
1.56
1.45
1.44
1.43
1.42
1.36
1.33
1.33
O
HN
N
Ph
N
Ph
CF3
4p
1H NMR (400 MHz, CDCl3)
1.89
8.12
0.88
2.09
1.00
1.06
1.05
4.27
1.08
3.54
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



4p

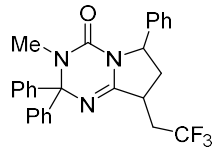
^{13}C NMR (100 MHz, $CDCl_3$)

10XJM57D2-CJJ.11.fid



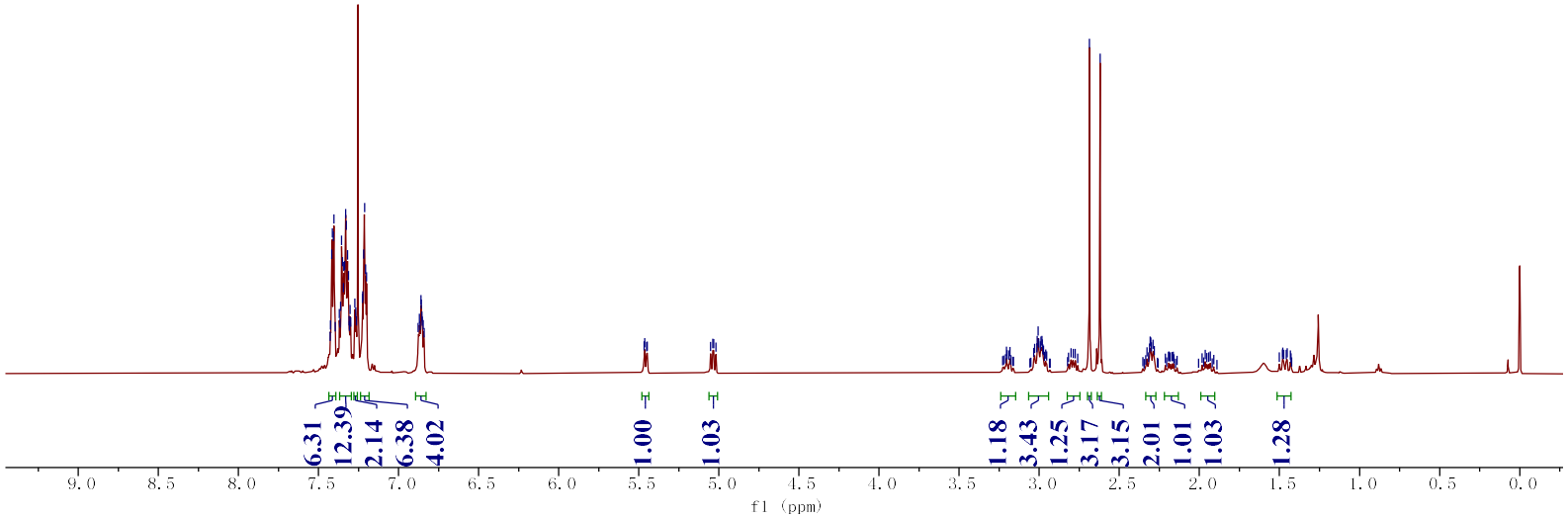
4p

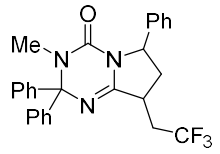
^{19}F NMR (376 MHz, $CDCl_3$)



4q

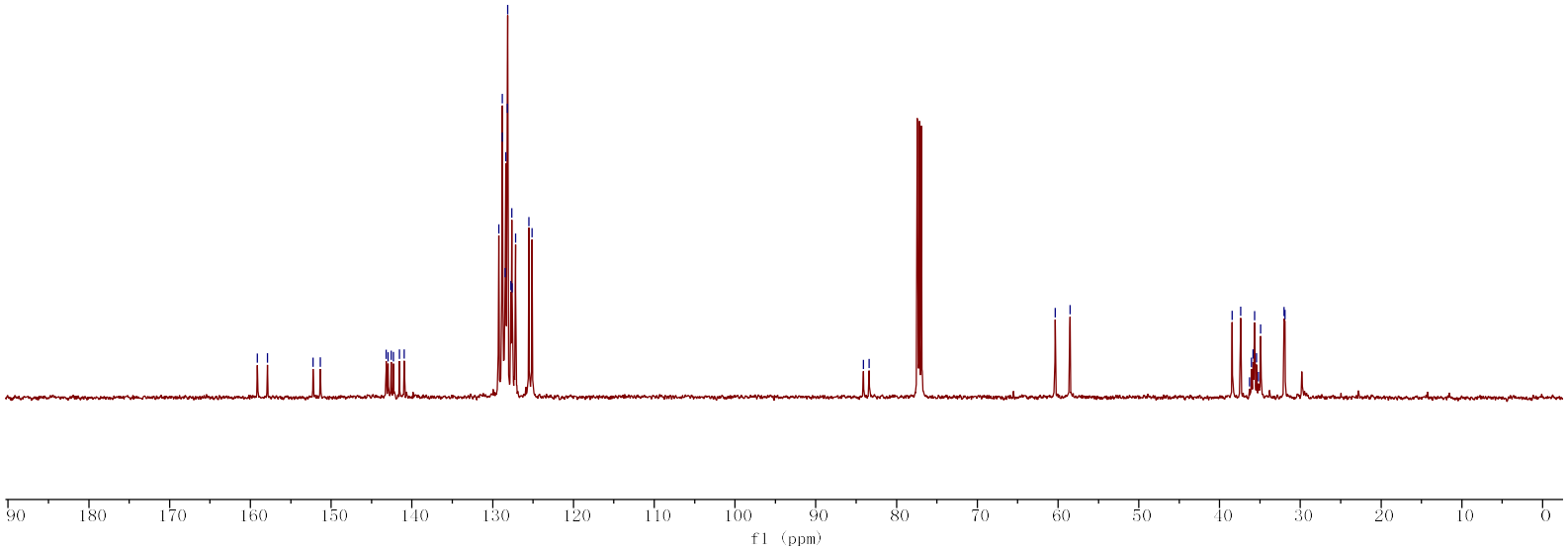
^{1}H NMR (500 MHz, $CDCl_3$)

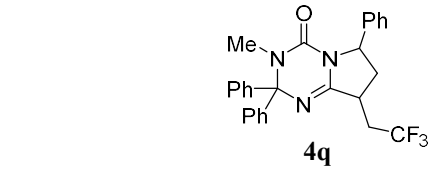




4q

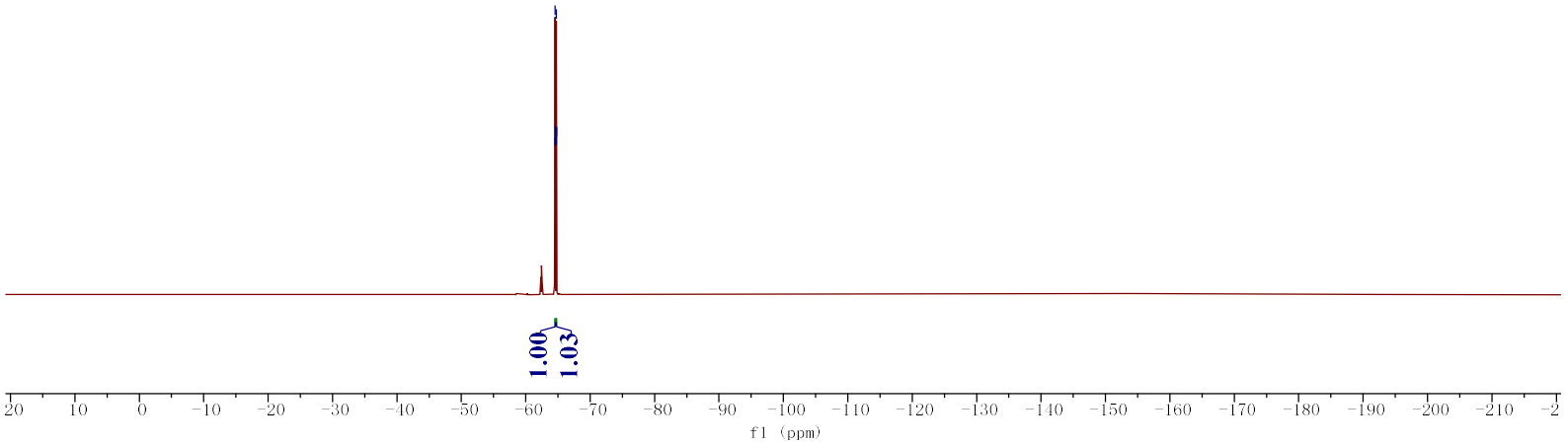
^{13}C NMR (125 MHz, $CDCl_3$)

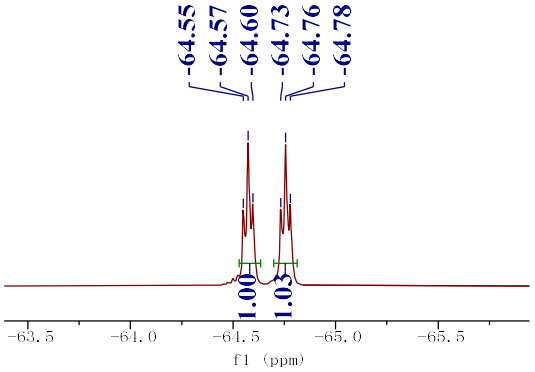


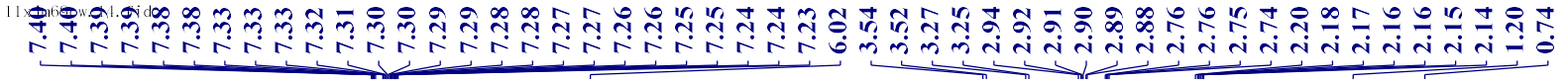


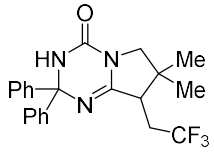
4q

^{19}F NMR (470 MHz, $CDCl_3$)



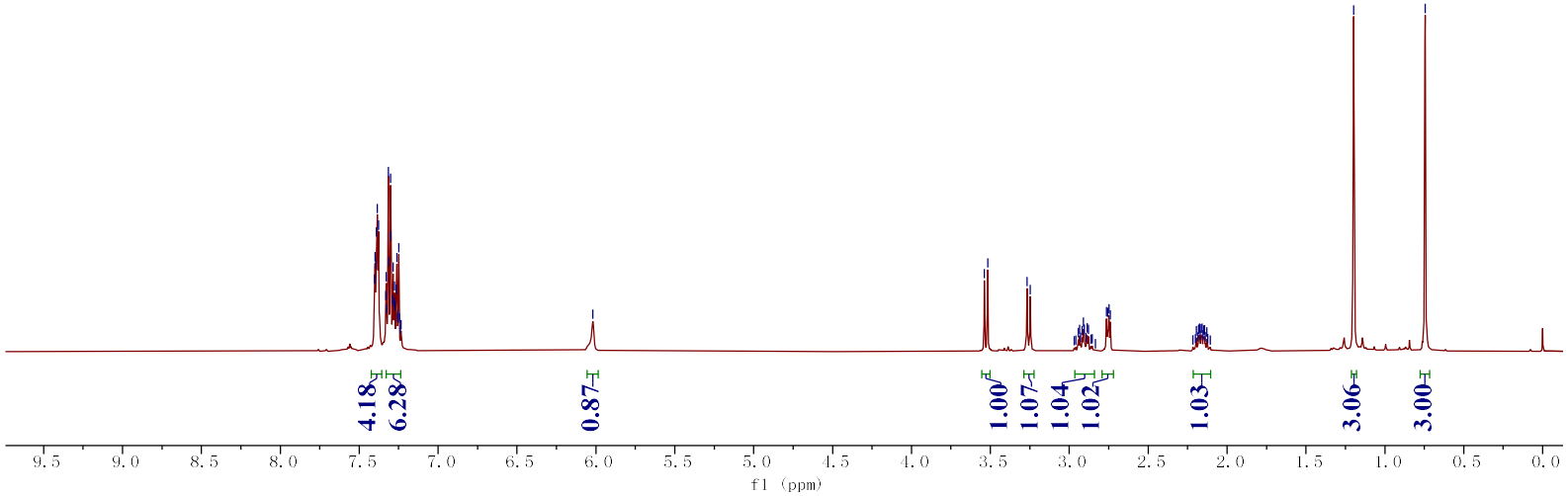






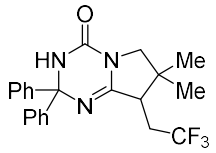
4r

^{1}H NMR (500 MHz, $CDCl_3$)



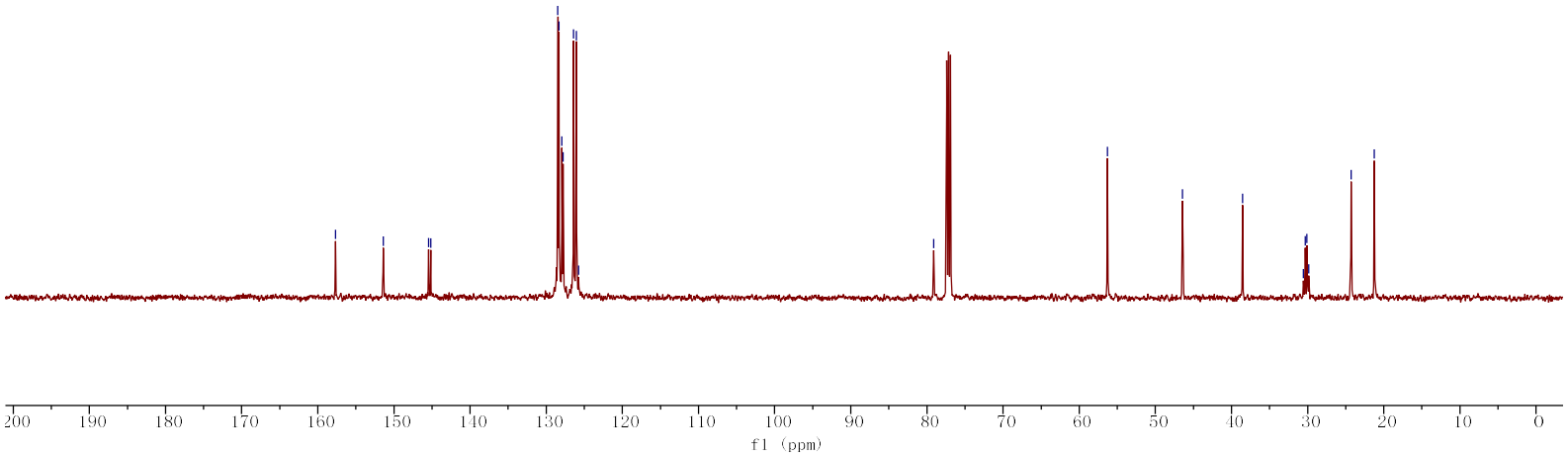
11xjm69cw.16.fid

157.68
151.41
145.45
145.16
128.47
128.32
127.94
127.78
126.41
126.05
125.74
79.09
56.29
46.42
38.56
30.56
30.33
30.09
29.85
24.29
21.24

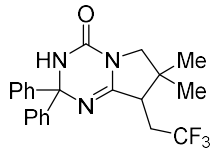


4r

^{13}C NMR (125 MHz, $CDCl_3$)

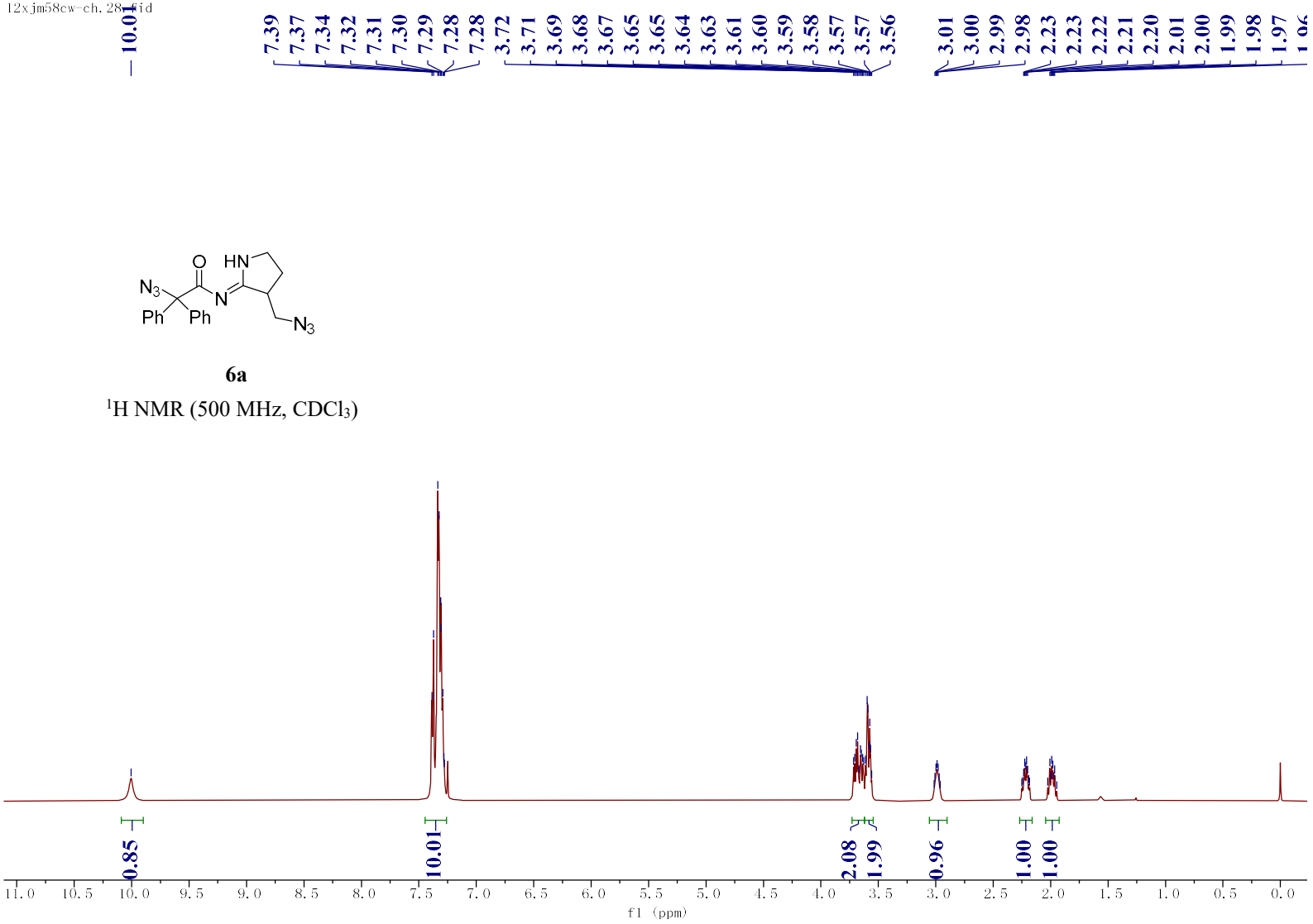


11xjm69cw.15.fid



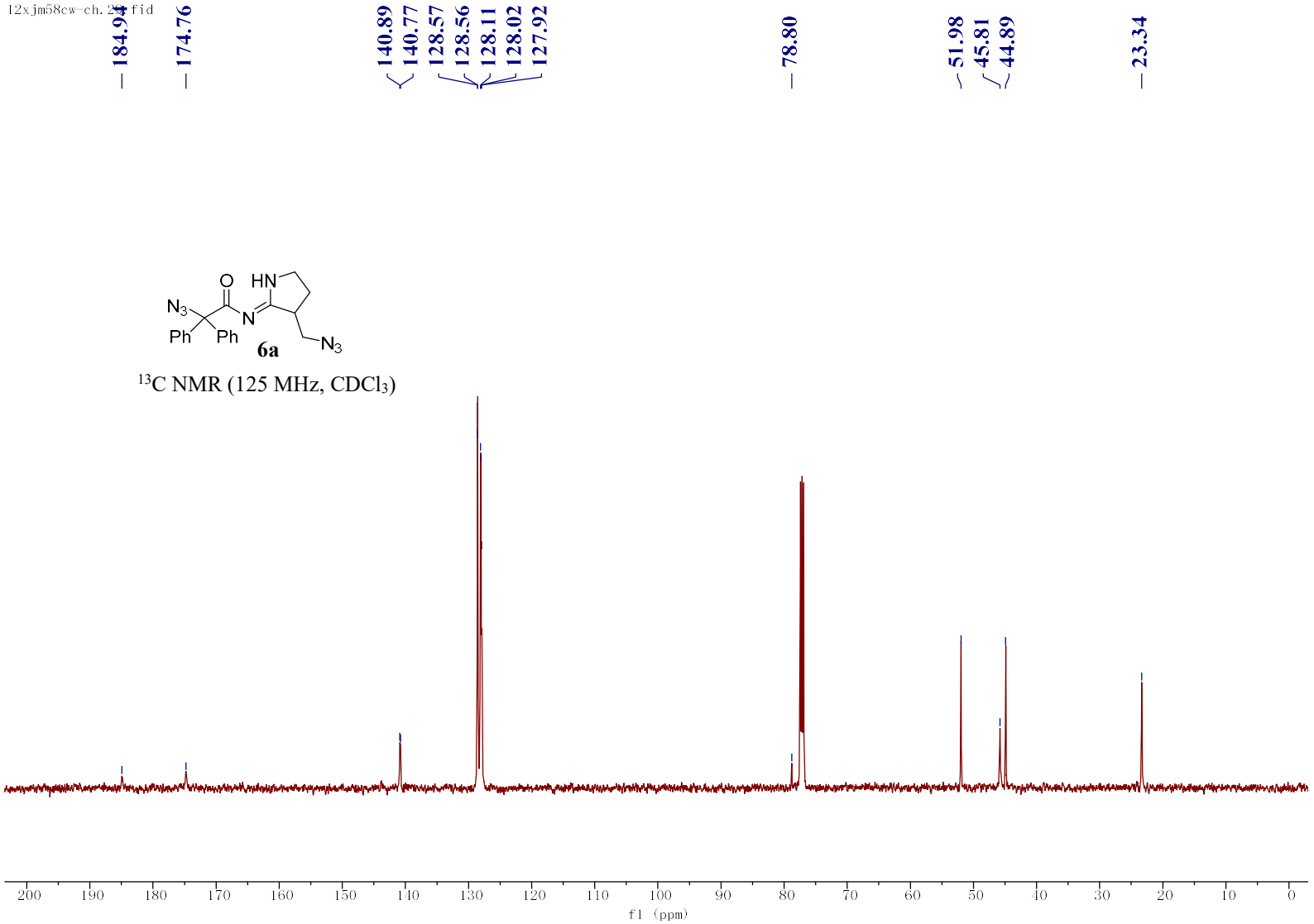
4r

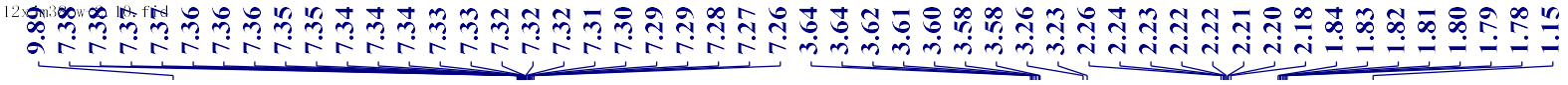
^{19}F NMR (470 MHz, $CDCl_3$)

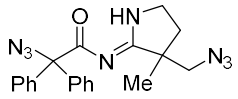


6a

^{1}H NMR (500 MHz, $CDCl_3$)

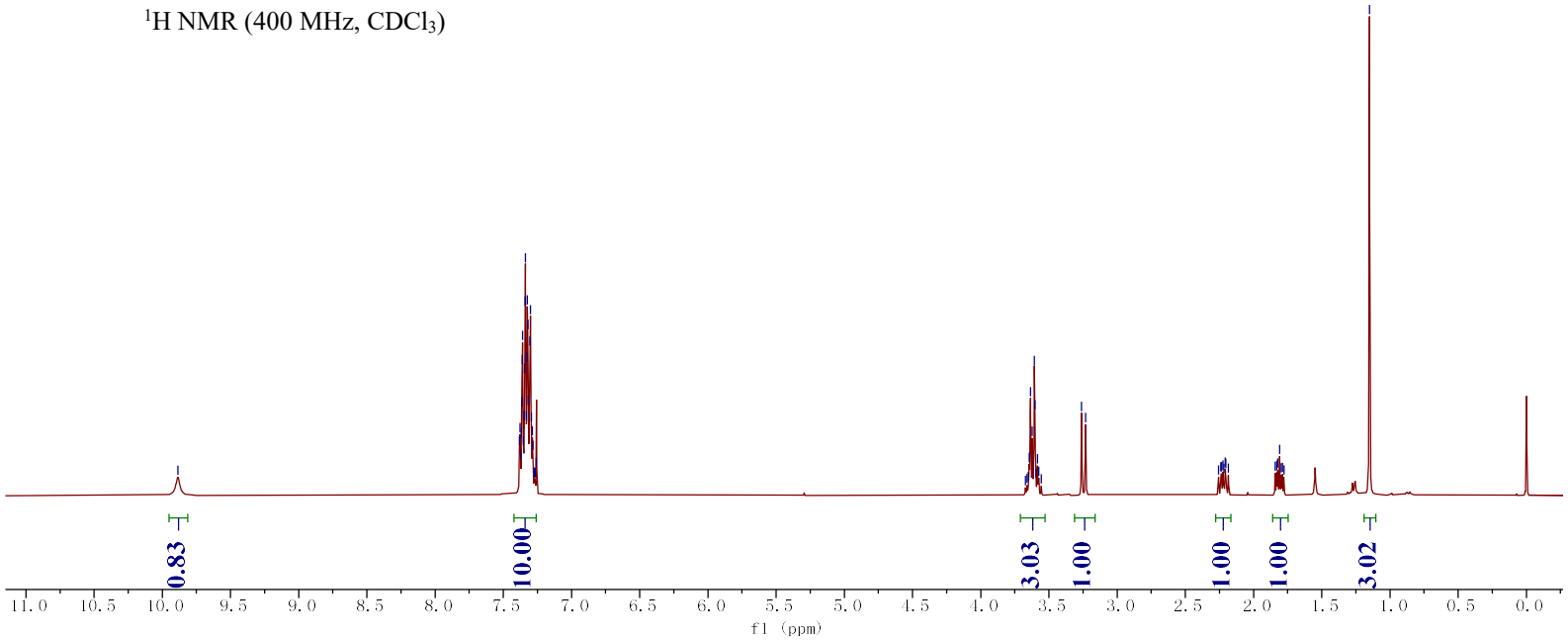

12xjm58cw-ch.2 fid
184.94
174.76
140.89
140.77
128.57
128.56
128.11
128.02
127.92
78.80
51.98
45.81
44.89
23.34
O
HN
N3
N
Ph
Ph
N3
6a
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

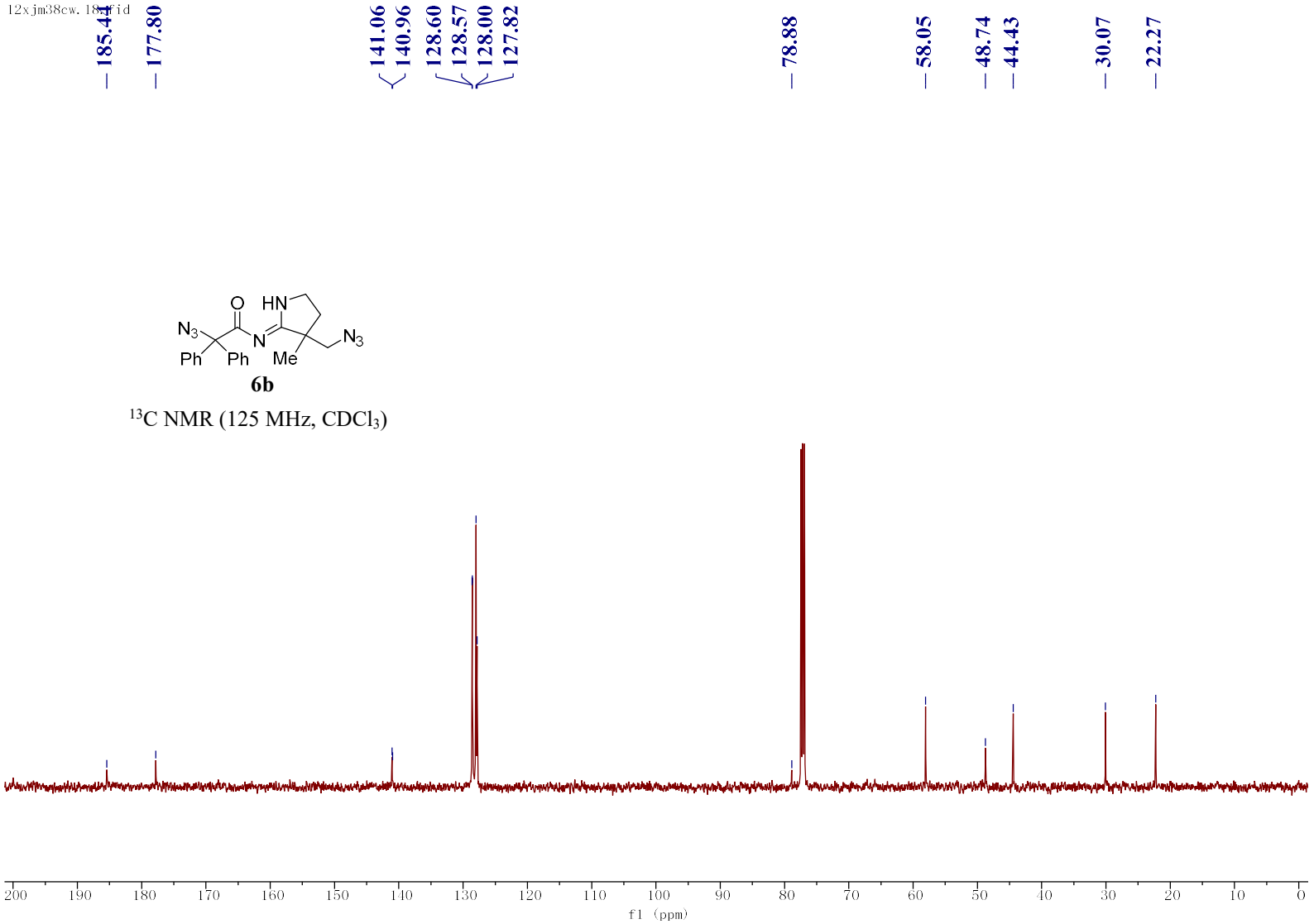




6b

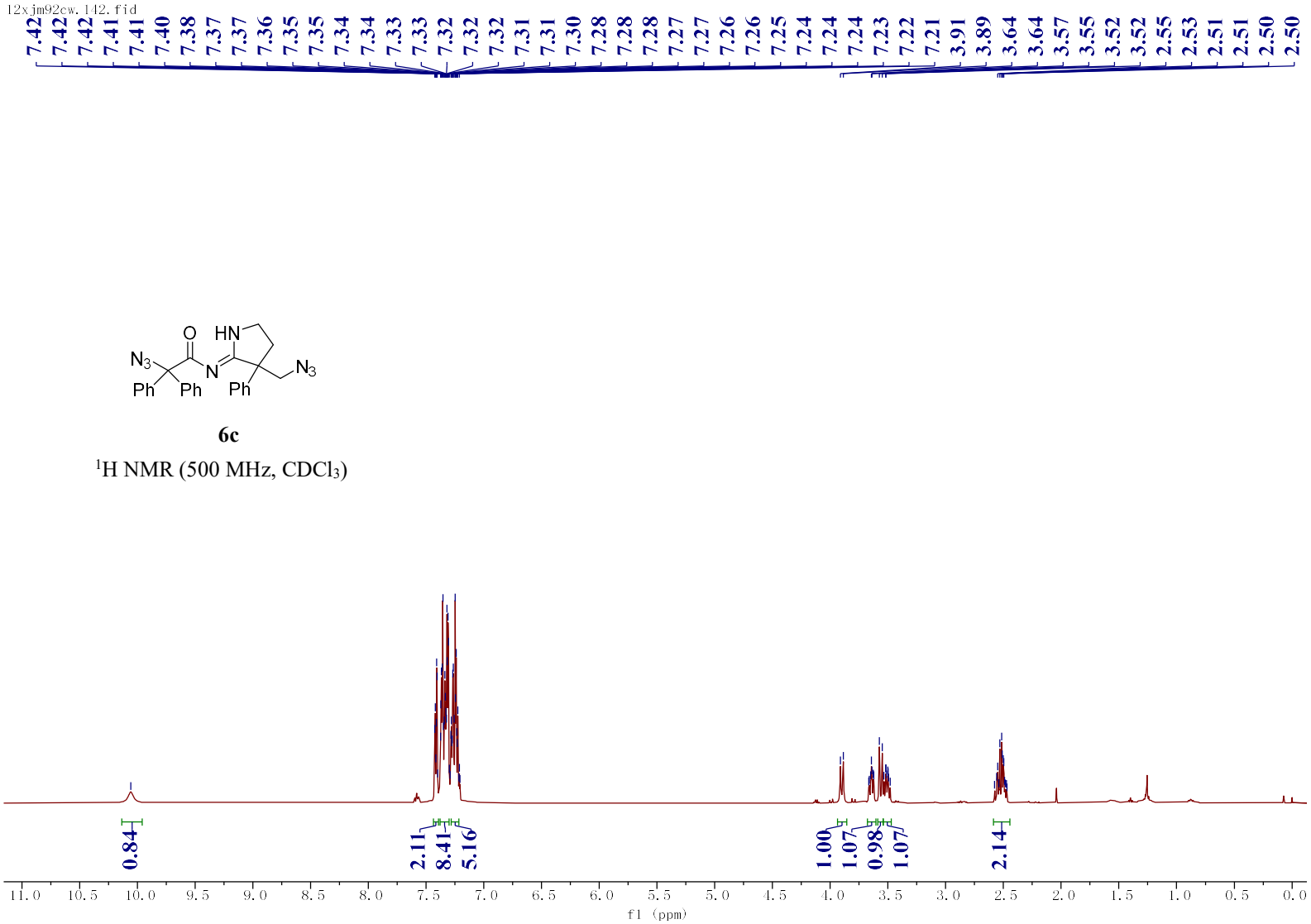
^{1}H NMR (400 MHz, $CDCl_3$)





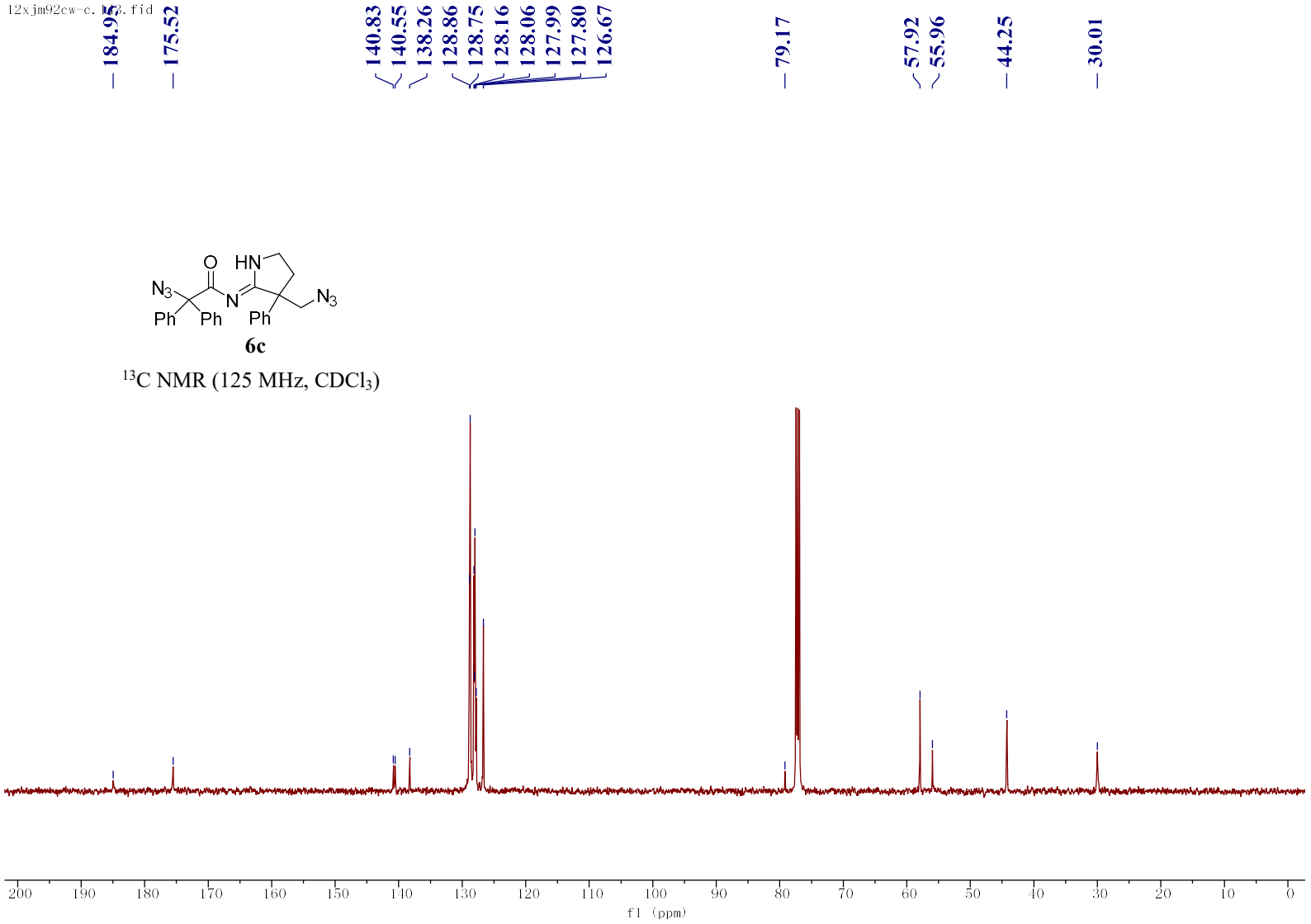
6b

^{13}C NMR (125 MHz, $CDCl_3$)



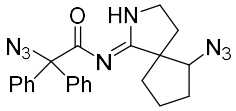
6c

^{1}H NMR (500 MHz, $CDCl_3$)



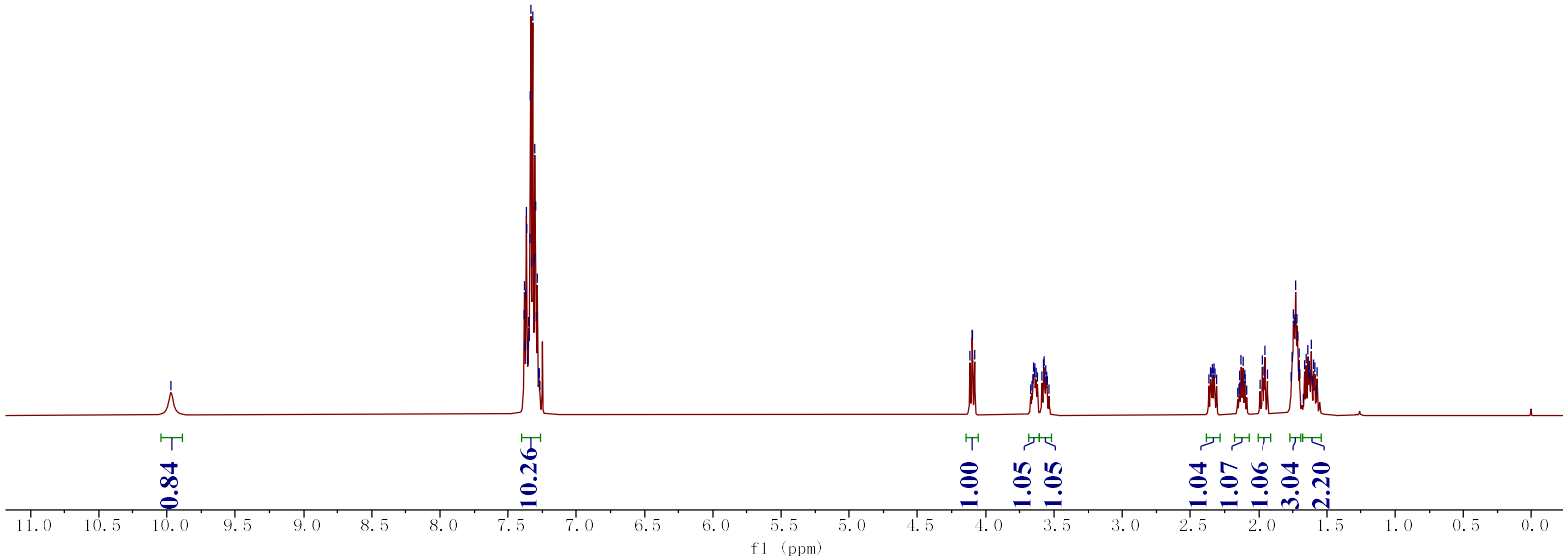
6c

^{13}C NMR (125 MHz, $CDCl_3$)



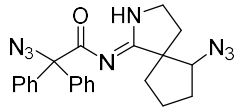
6d

^{1}H NMR (500 MHz, $CDCl_3$)



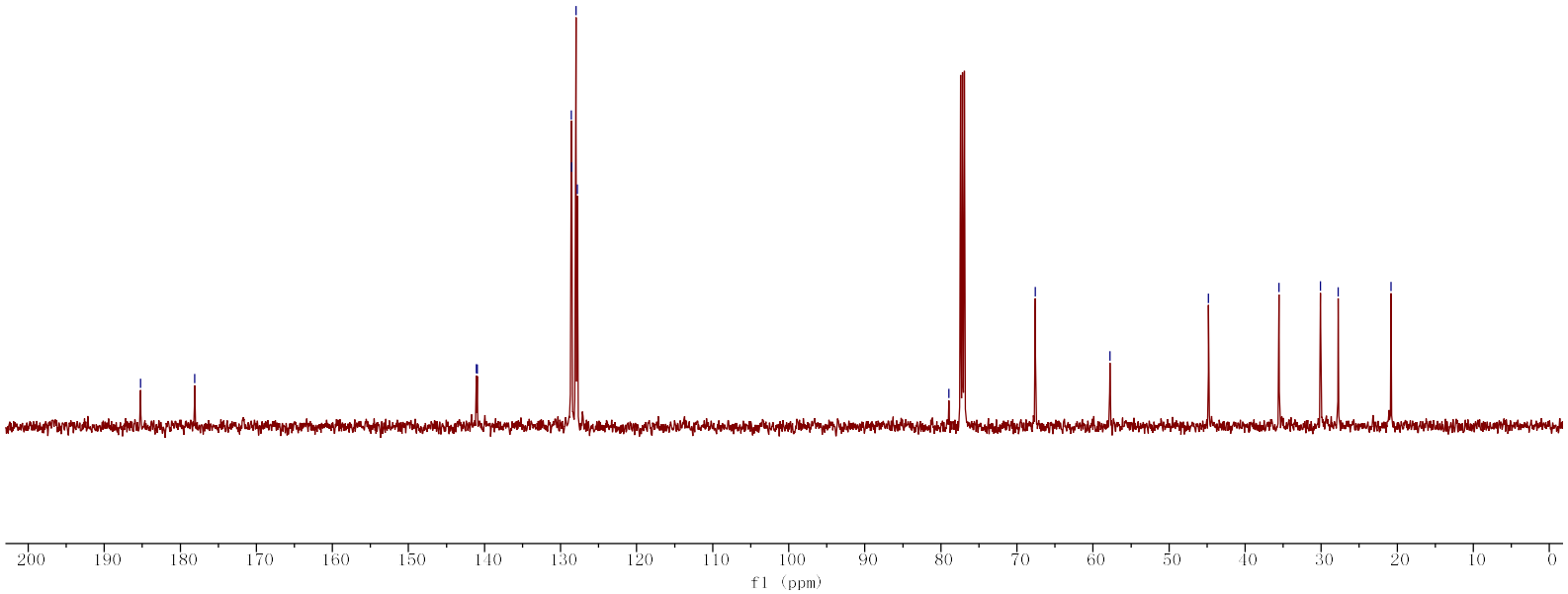
12xjm91cw-c.4.1.1fid

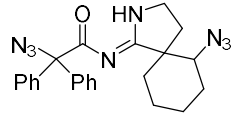
185.22
178.10
141.09
140.95
128.58
128.56
127.98
127.79
78.96
67.60
57.78
44.82
35.54
30.09
27.77
20.83



6d

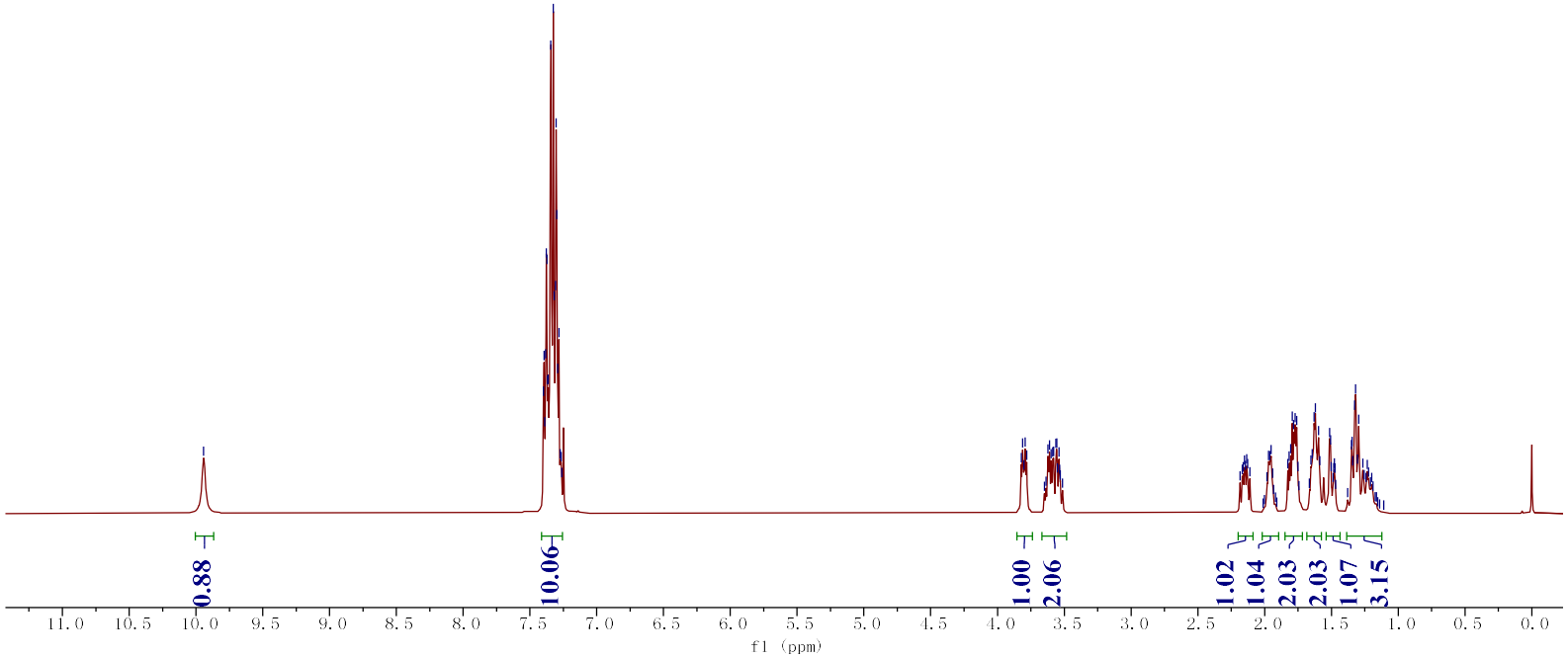
^{13}C NMR (125 MHz, $CDCl_3$)

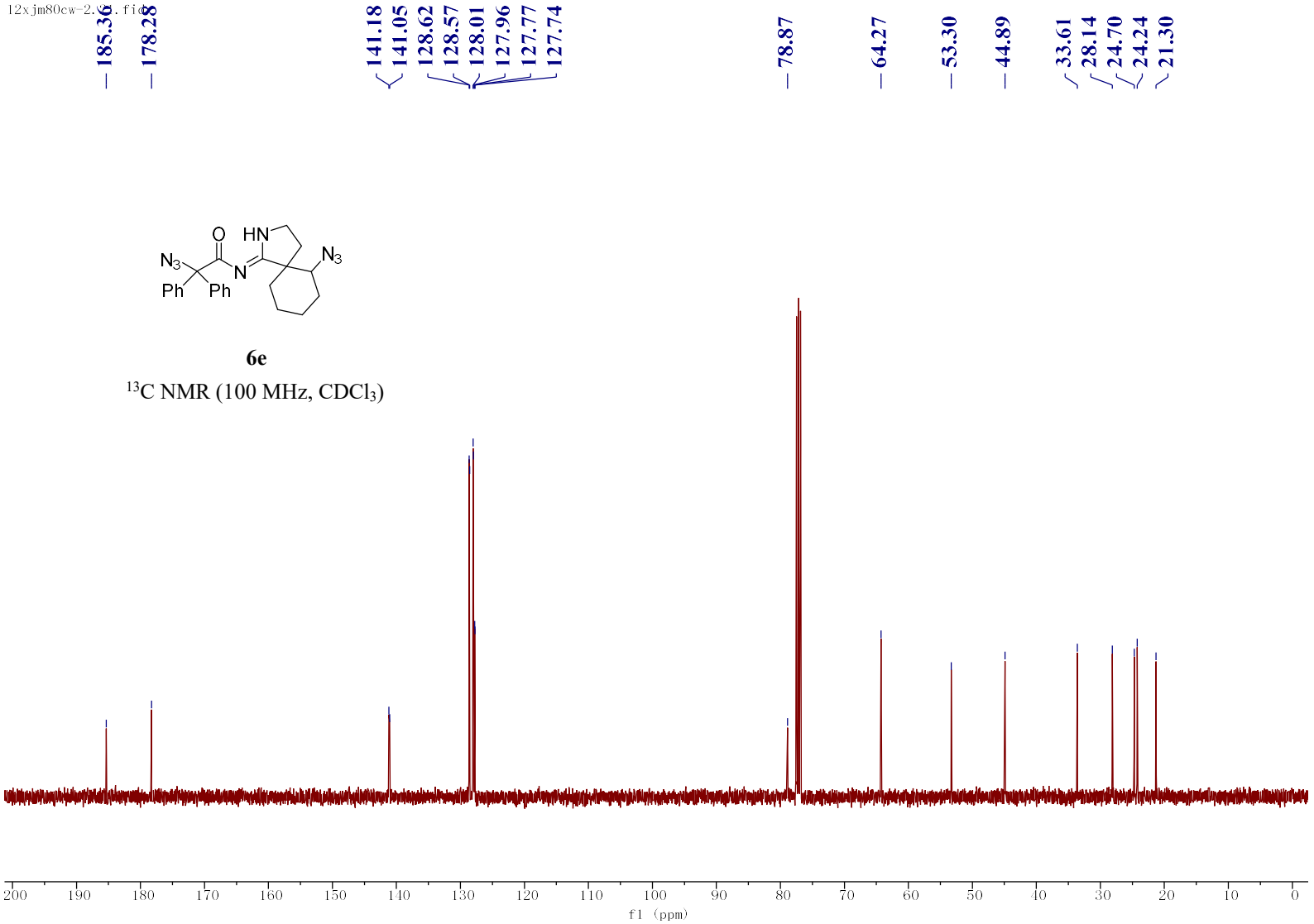




6e

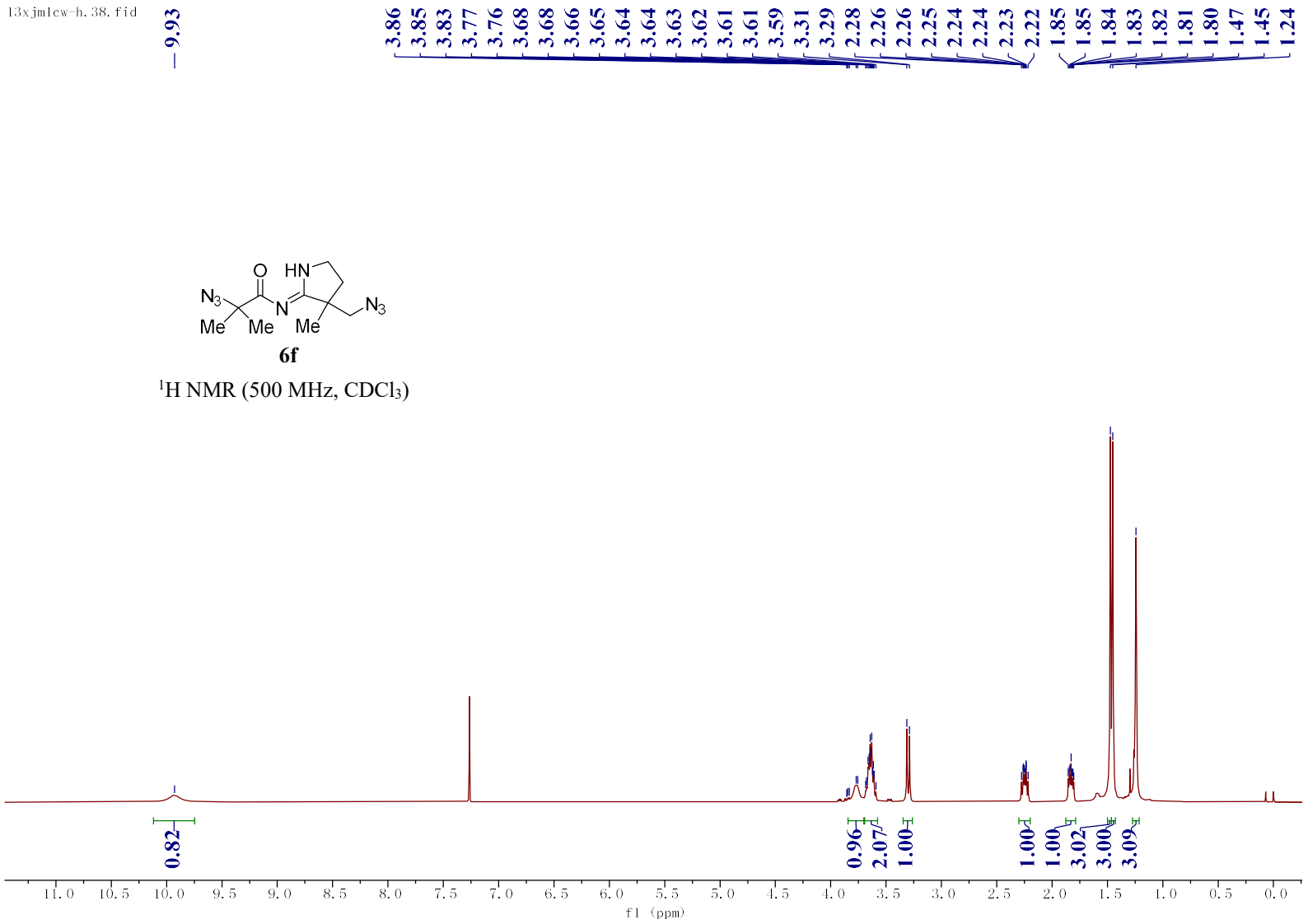
^{1}H NMR (400 MHz, $CDCl_3$)





6e

^{13}C NMR (100 MHz, $CDCl_3$)

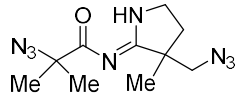


6f

^{1}H NMR (500 MHz, $CDCl_3$)

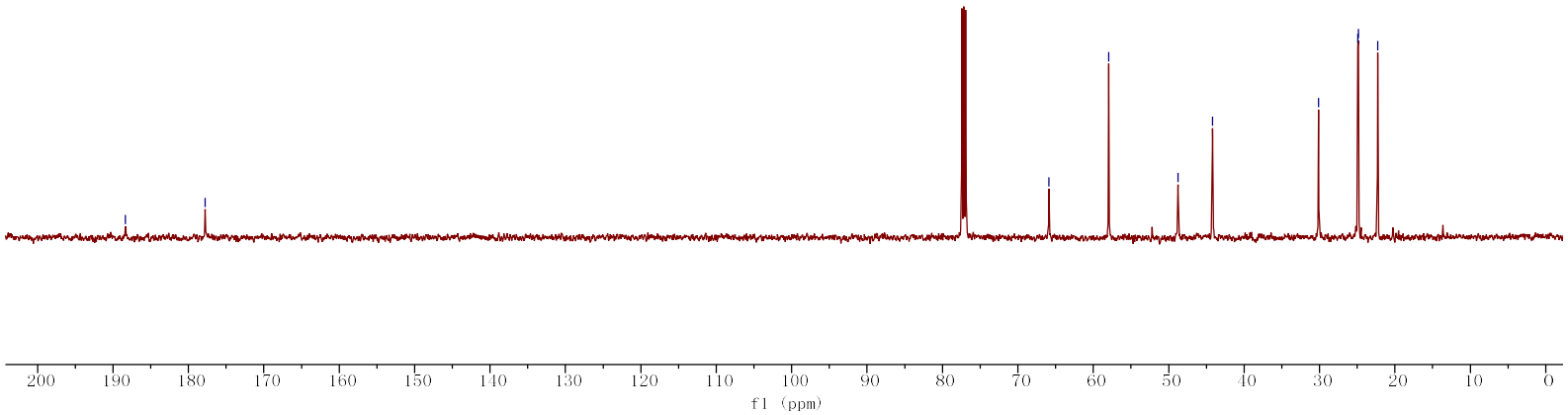
13xjmlcw-c.40.fid

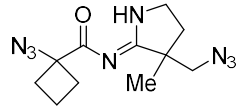
188.35
177.77
65.87
57.94
48.76
44.19
30.12
24.91
24.83
22.29



6f

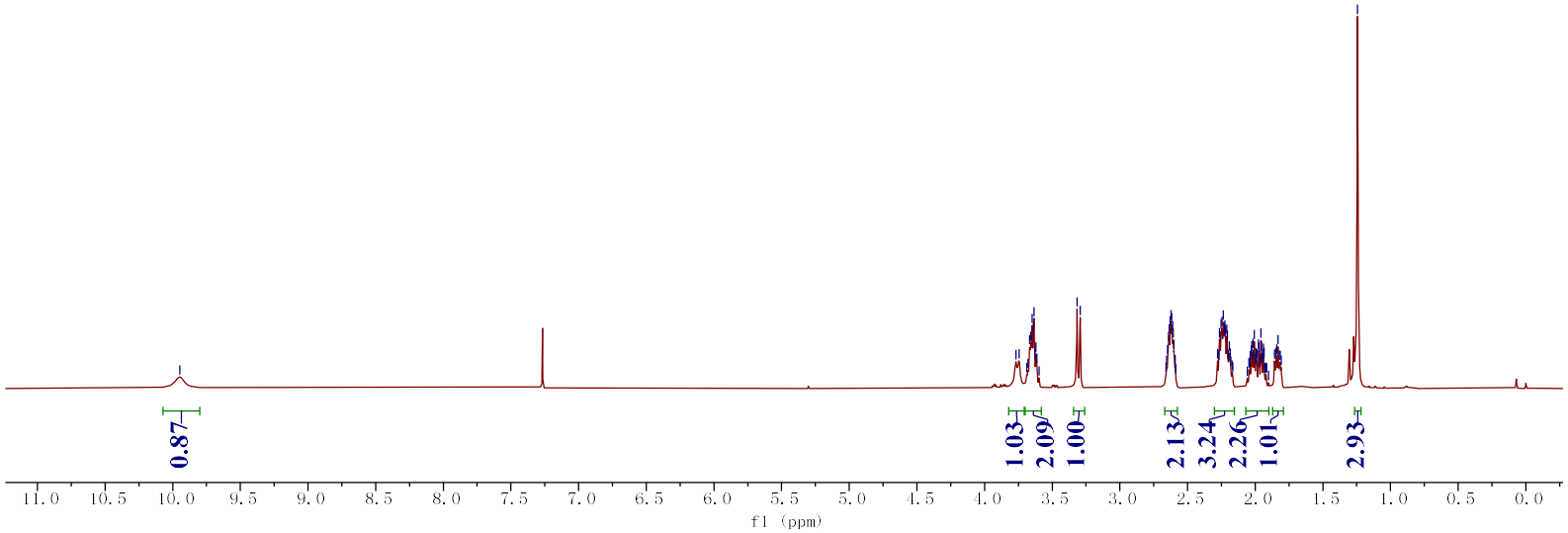
^{13}C NMR (125 MHz, $CDCl_3$)





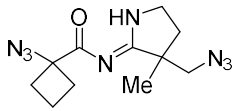
6g

^{1}H NMR (500 MHz, $CDCl_3$)



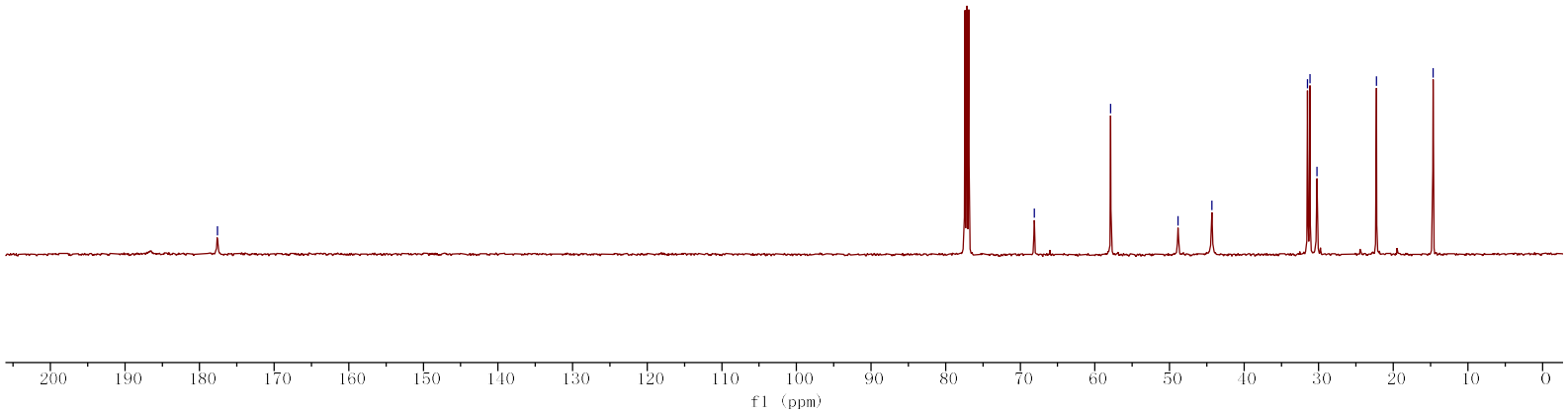
13xjm8cw-3.100071.fid

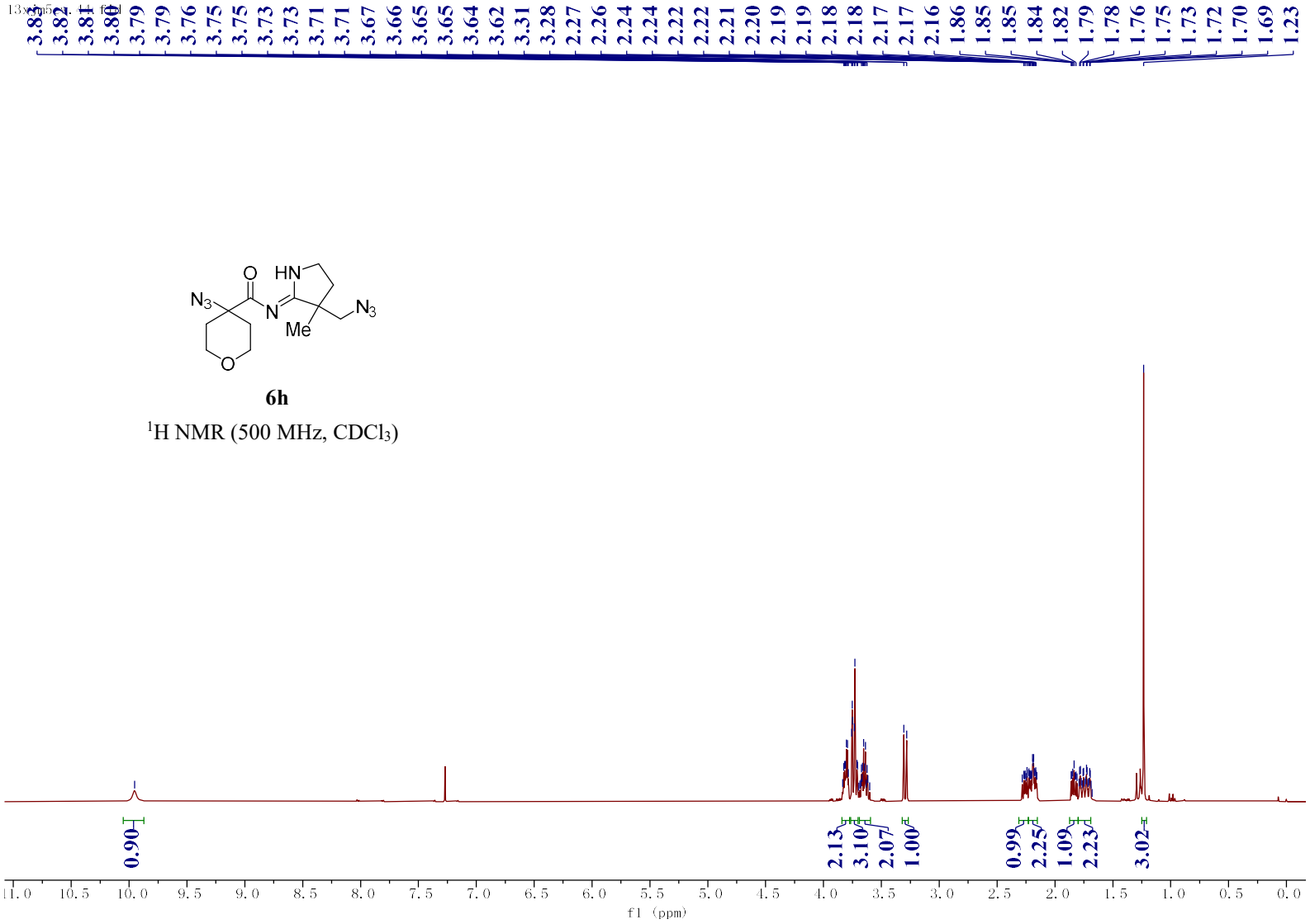
177.62
68.11
57.88
48.85
44.32
31.49
31.17
30.23
22.27
14.68



6g

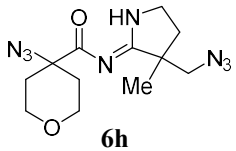
^{13}C NMR (125 MHz, $CDCl_3$)




3.82
3.82
3.81
3.80
3.79
3.79
3.76
3.75
3.75
3.73
3.73
3.71
3.71
3.67
3.66
3.65
3.65
3.64
3.62
3.31
3.28
2.27
2.26
2.24
2.24
2.22
2.22
2.21
2.20
2.19
2.19
2.18
2.18
2.17
2.17
2.16
1.86
1.85
1.85
1.84
1.82
1.79
1.78
1.76
1.75
1.73
1.72
1.70
1.69
1.23
O
HN
N3
N
N3
Me
O
6h
1H NMR (500 MHz, CDCl3)
0.90
2.13
3.10
2.07
1.00
0.99
2.25
1.09
2.23
3.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

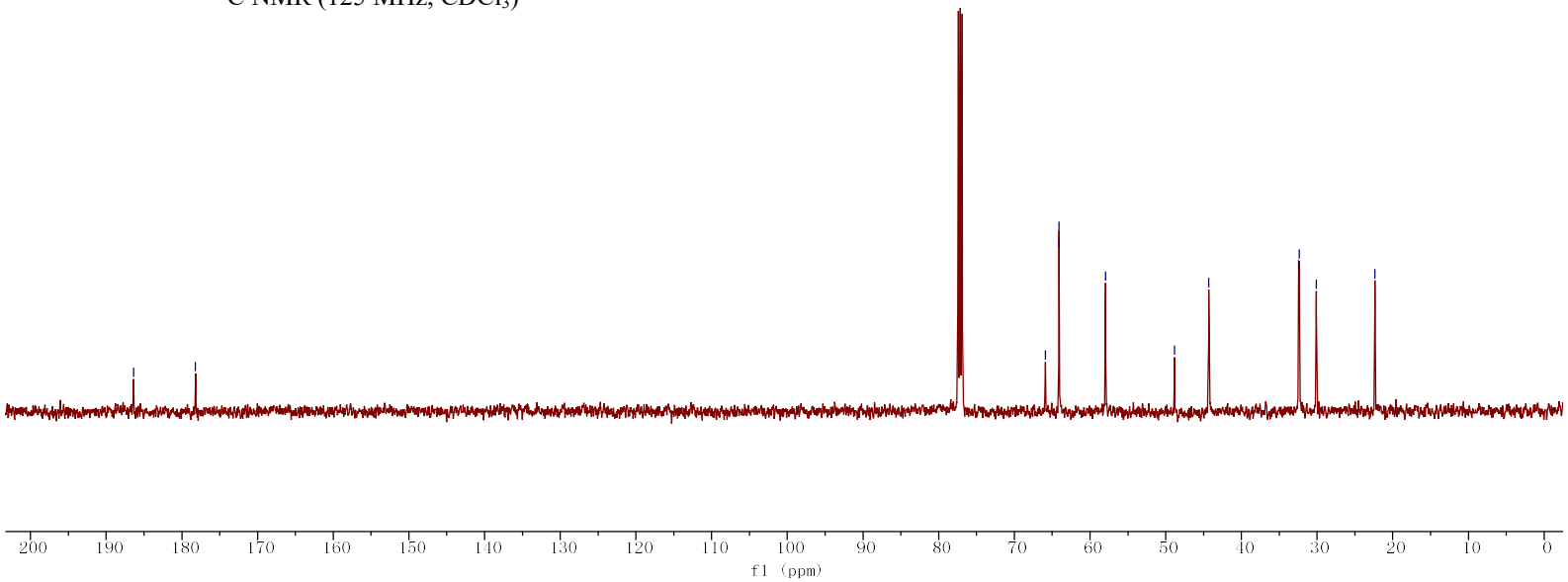
13xjm5cw.43.1r

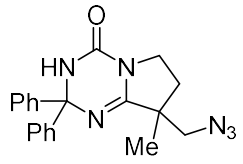
186.39
178.21
65.91
64.11
64.08
57.96
48.84
44.30
32.42
32.33
30.10
22.37



6h

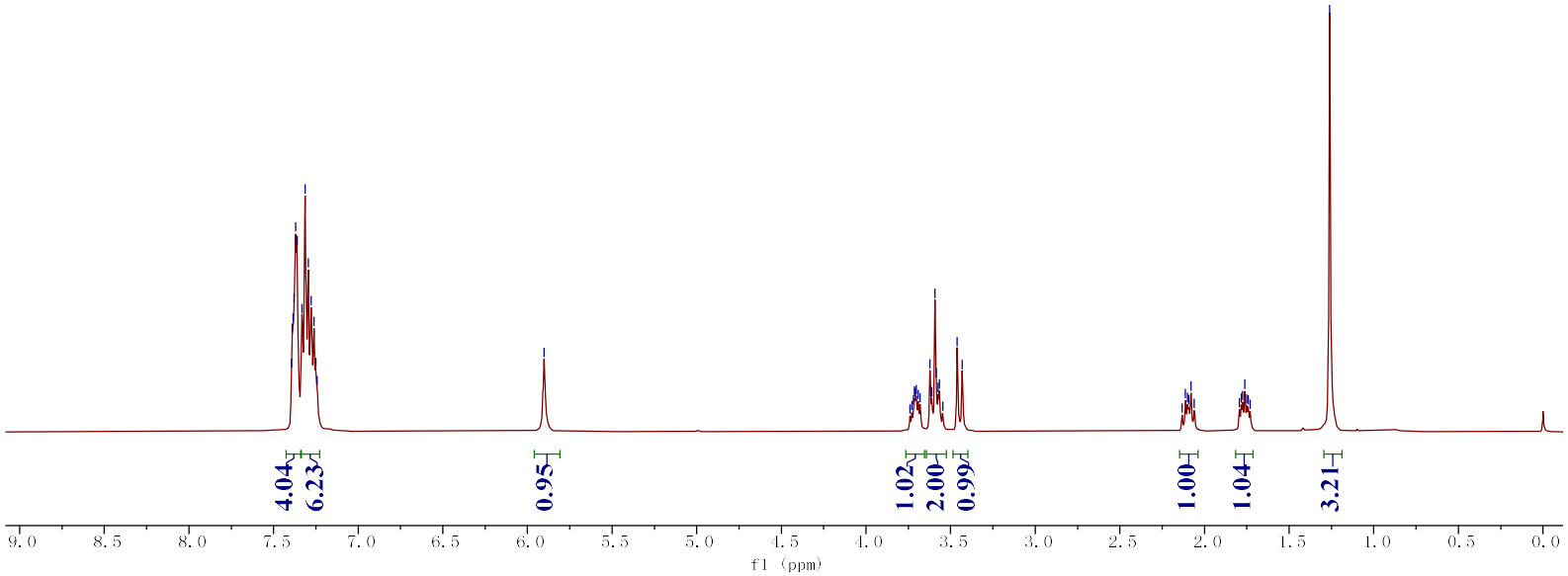
^{13}C NMR (125 MHz, $CDCl_3$)





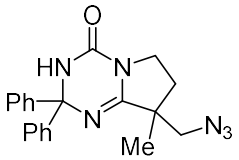
7b

^{1}H NMR (400 MHz, $CDCl_3$)



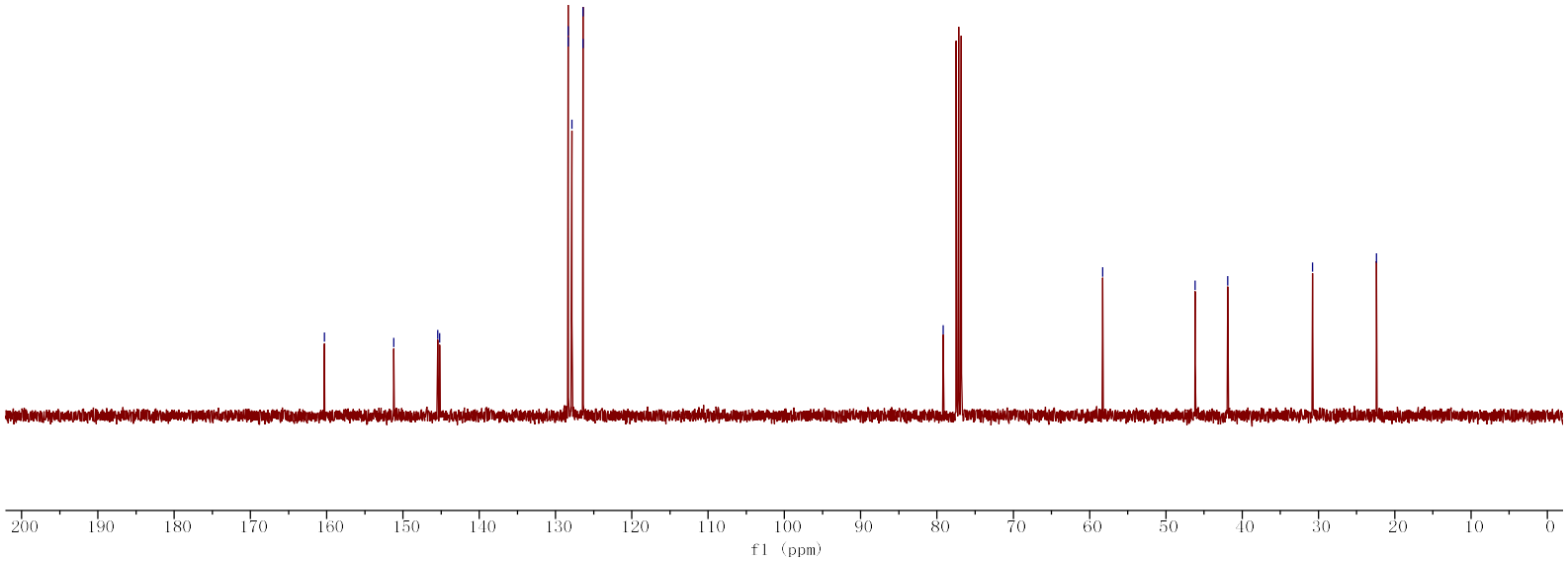
12xjm33cw.21.fid

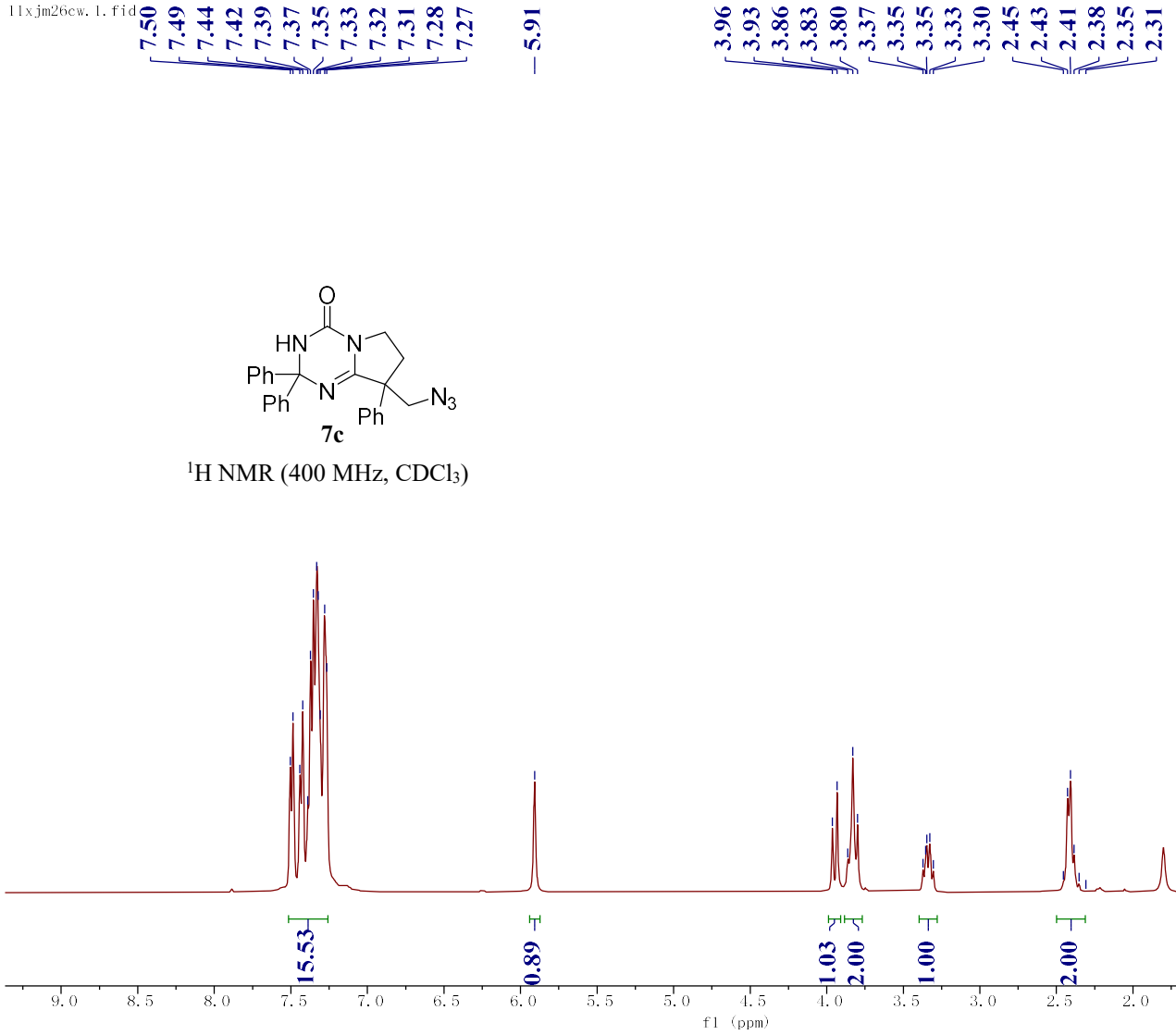
160.32
151.21
145.46
145.22
128.36
128.35
127.87
126.42
126.41
79.20
58.29
46.18
41.90
30.76
22.39



7b

^{13}C NMR (100 MHz, $CDCl_3$)



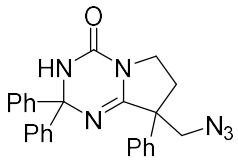


7c

^{1}H NMR (400 MHz, $CDCl_3$)

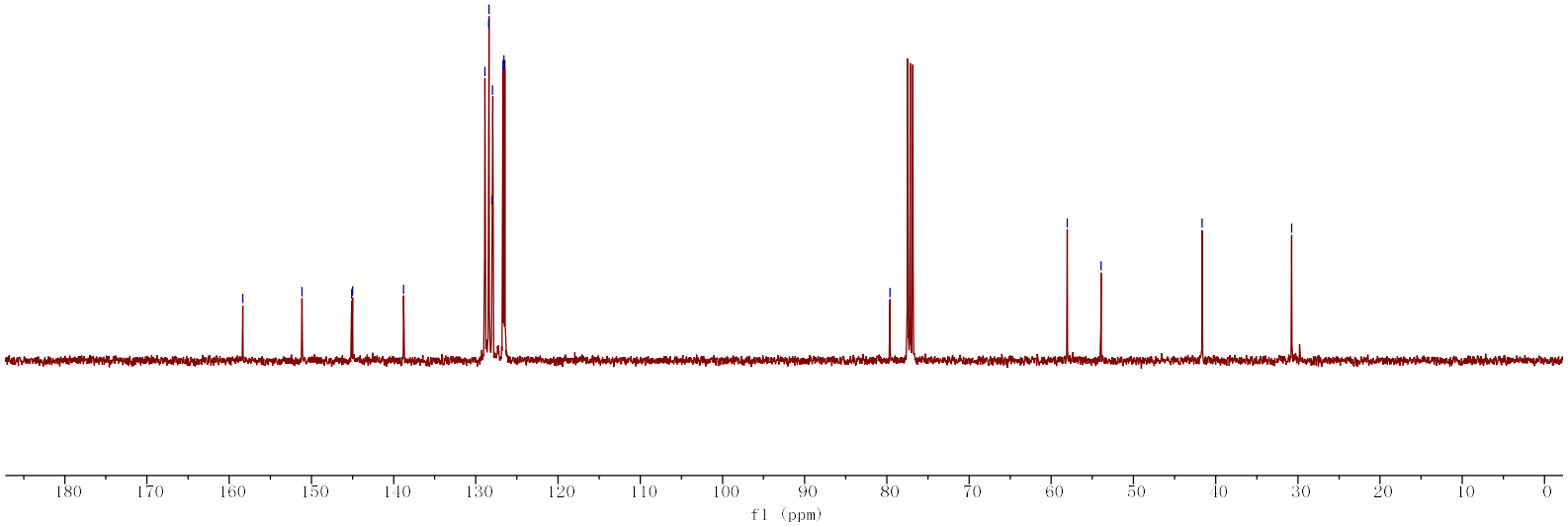
11xjm26cw.2.fid

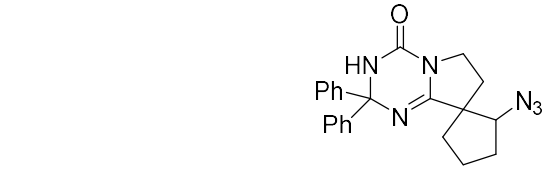
158.37
151.14
145.12
144.99
138.78
128.91
128.44
128.41
128.03
127.95
126.70
126.58
126.46
79.62
58.07
53.95
41.65
30.74



7c

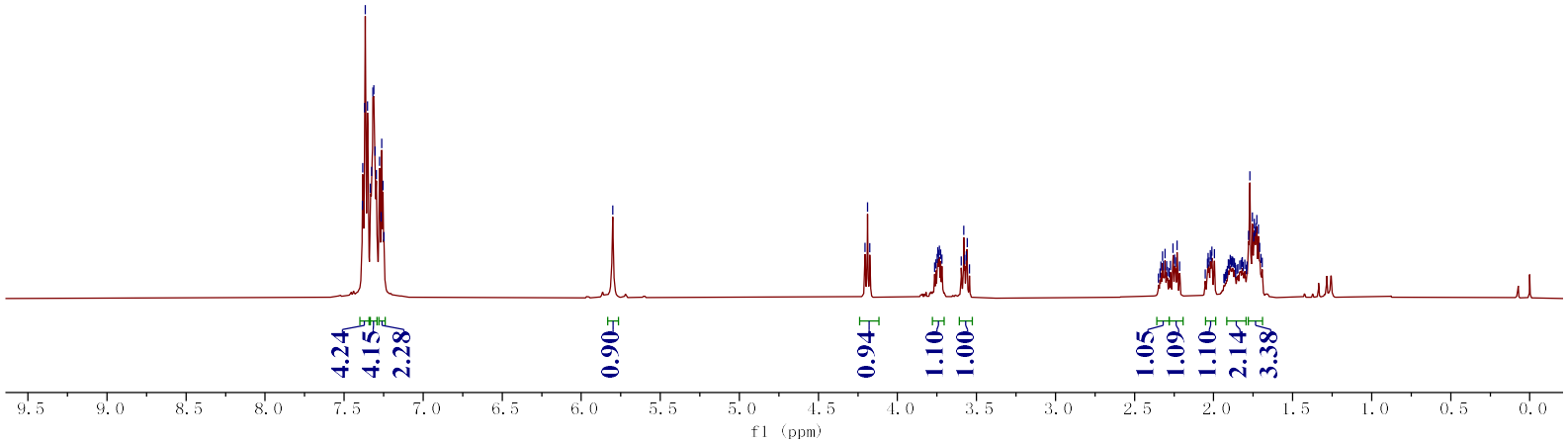
^{13}C NMR (100 MHz, $CDCl_3$)





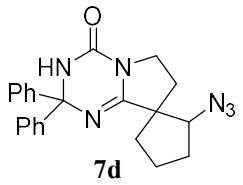
7d

^{1}H NMR (500 MHz, $CDCl_3$)



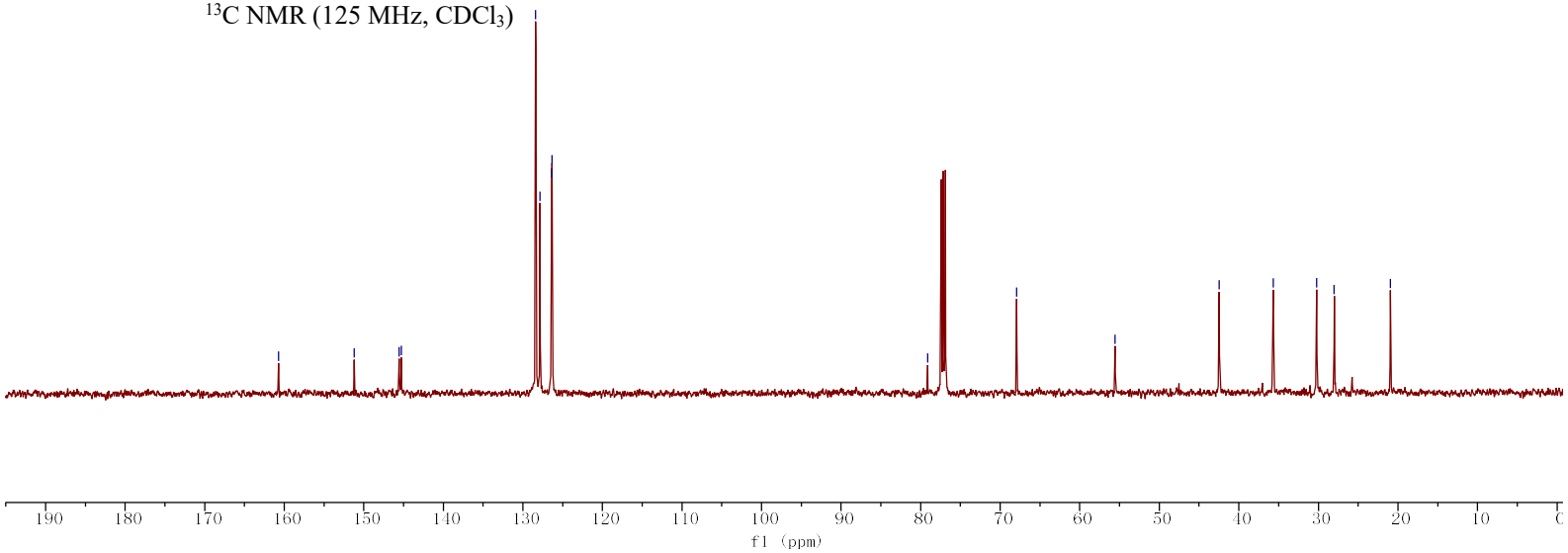
10xjm91cw-2.26.fid

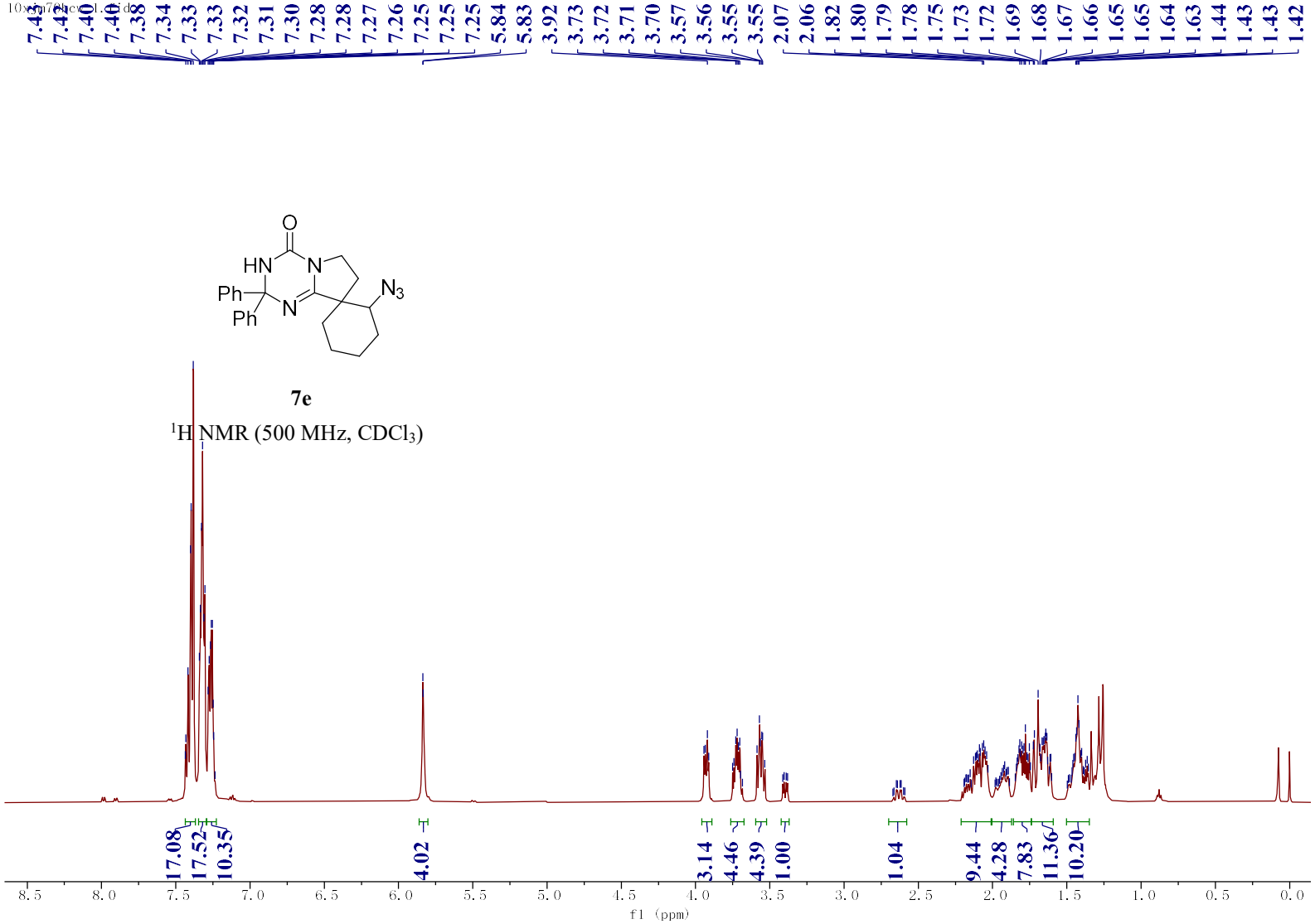
160.71
151.19
145.54
145.28
128.39
127.86
126.38
126.32
79.13
67.94
55.56
42.47
35.67
30.23
28.01
20.94



7d

^{13}C NMR (125 MHz, $CDCl_3$)



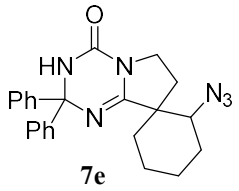


7e

^{1}H NMR (500 MHz, $CDCl_3$)

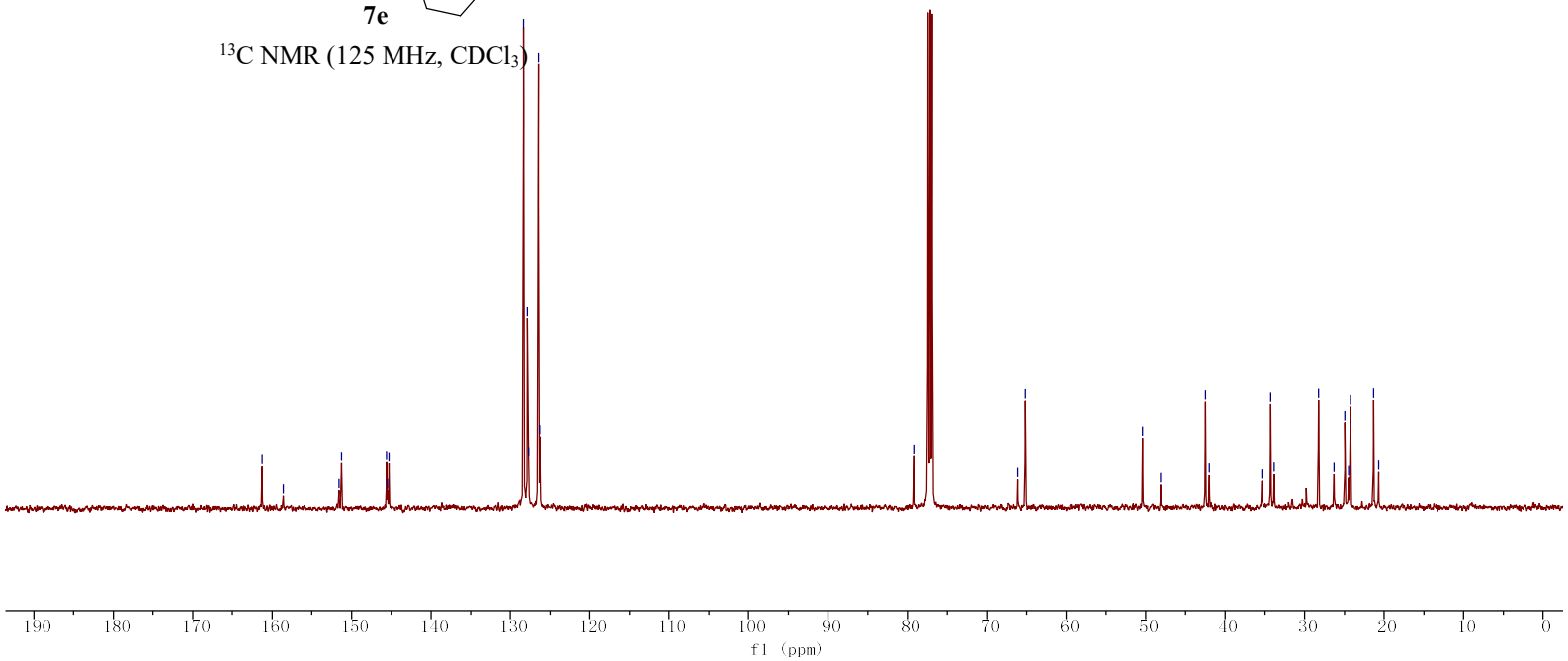
10xjm70bcw-c.1.fid

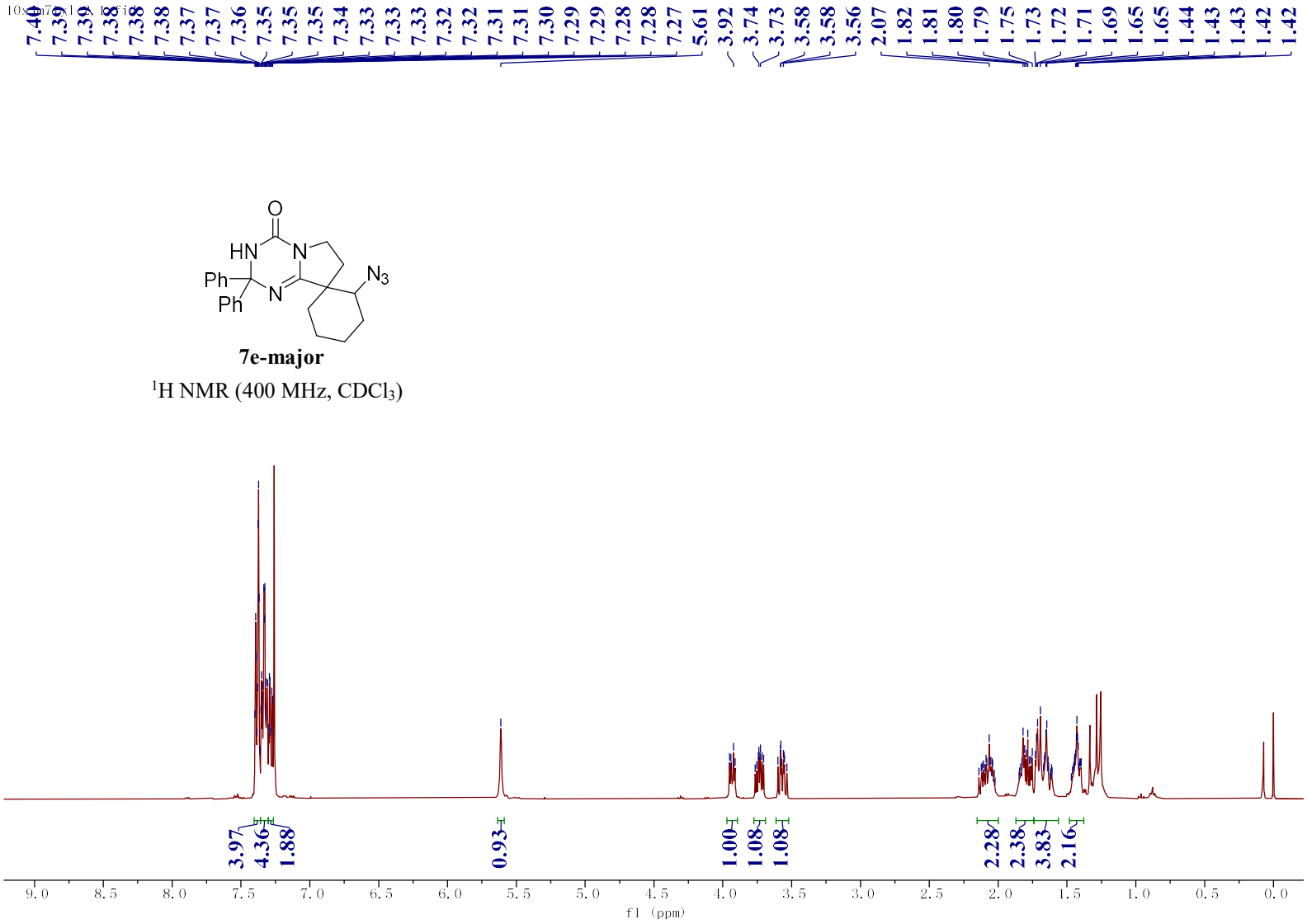
161.28
158.57
151.59
151.27
145.59
145.49
145.29
128.34
127.85
127.71
126.49
126.31
79.23
66.11
65.17
50.41
48.15
42.50
42.02
35.40
34.28
33.82
28.26
26.30
24.94
24.49
24.25
21.33
20.69



7e

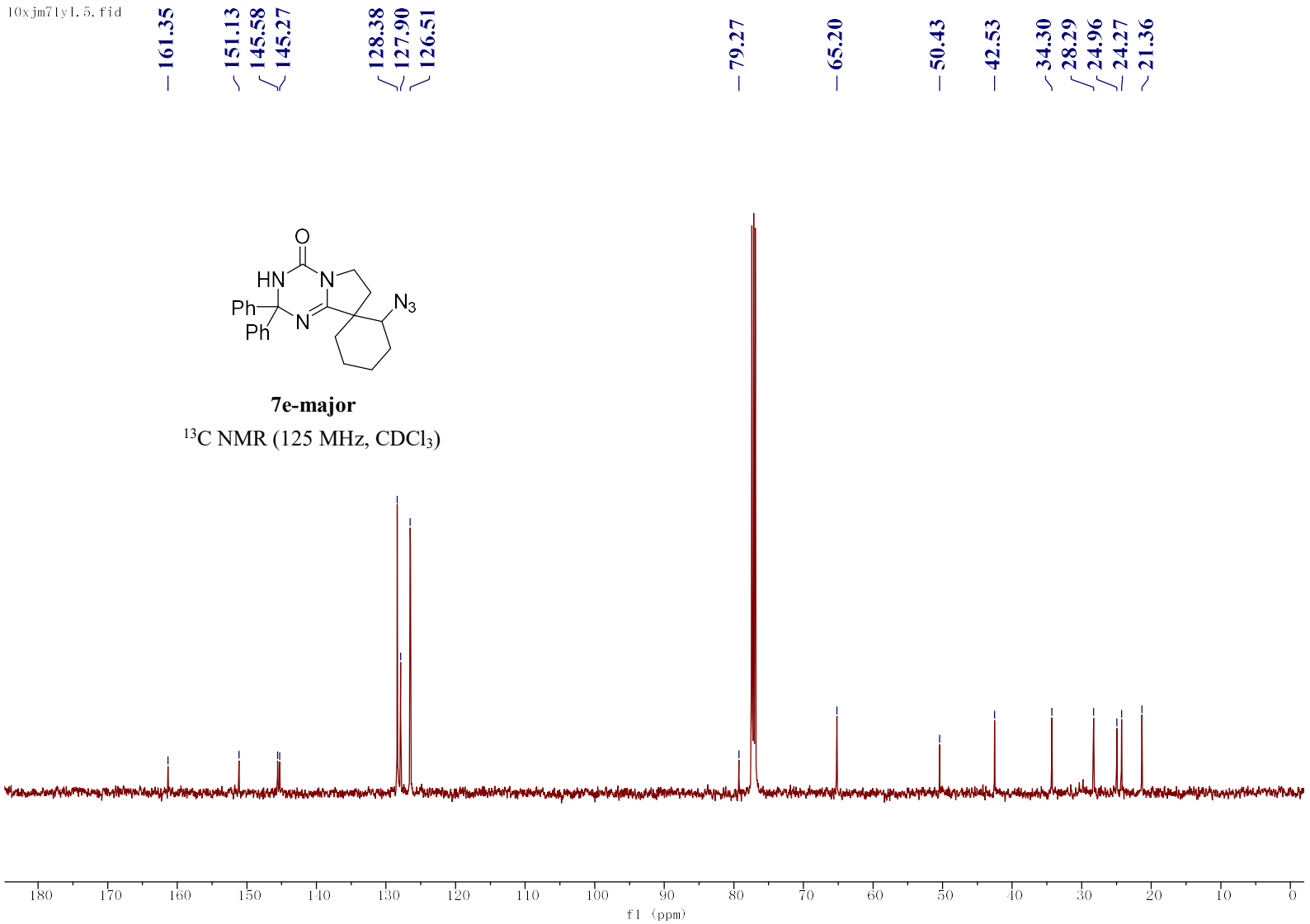
^{13}C NMR (125 MHz, $CDCl_3$)





7e-major

^{1}H NMR (400 MHz, $CDCl_3$)

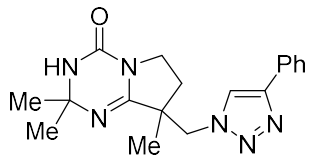


7e-major

^{13}C NMR (125 MHz, $CDCl_3$)

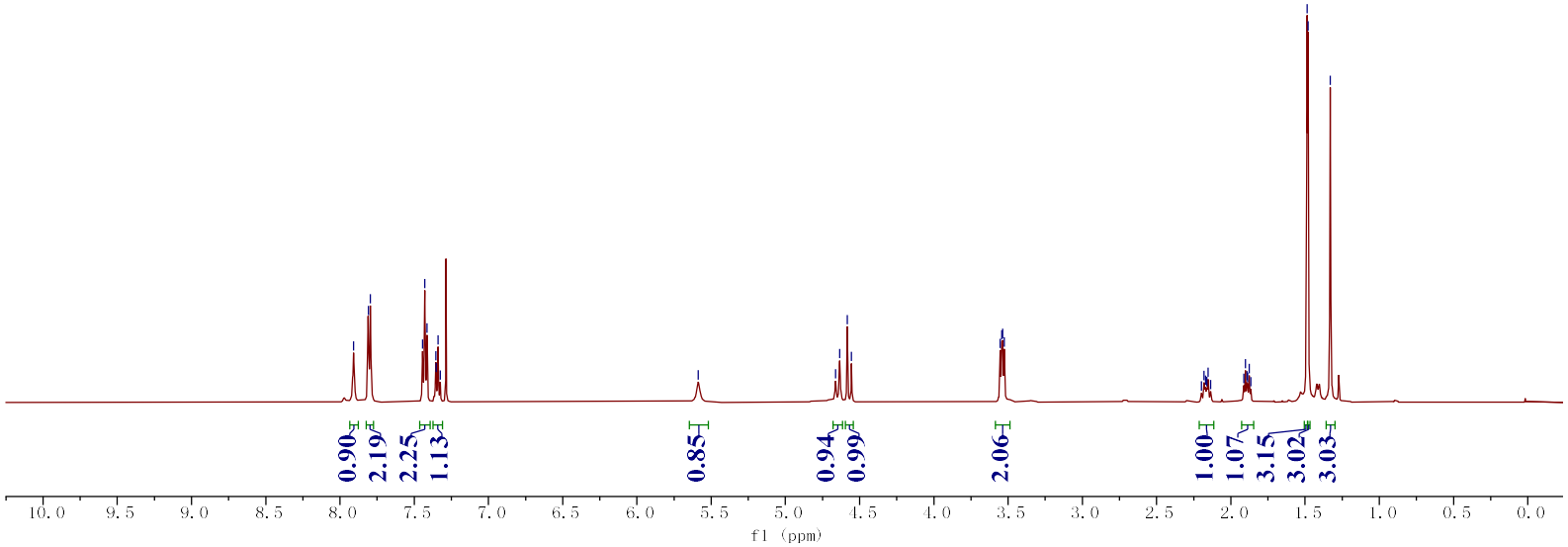
13xjm7bcw-2.100072.fid

7.91 7.81 7.79 7.44 7.43 7.41 7.35 7.35 7.34 7.33 — 5.59 4.66 4.63 4.58 4.55 3.55 3.54 3.54 3.53 2.20 2.18 2.17 2.16 2.15 2.14 1.91 1.90 1.89 1.89 1.88 1.87 1.49 1.48 1.33



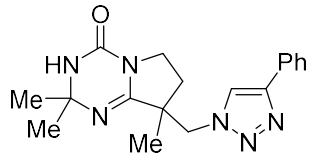
7f

^{1}H NMR (500 MHz, $CDCl_3$)



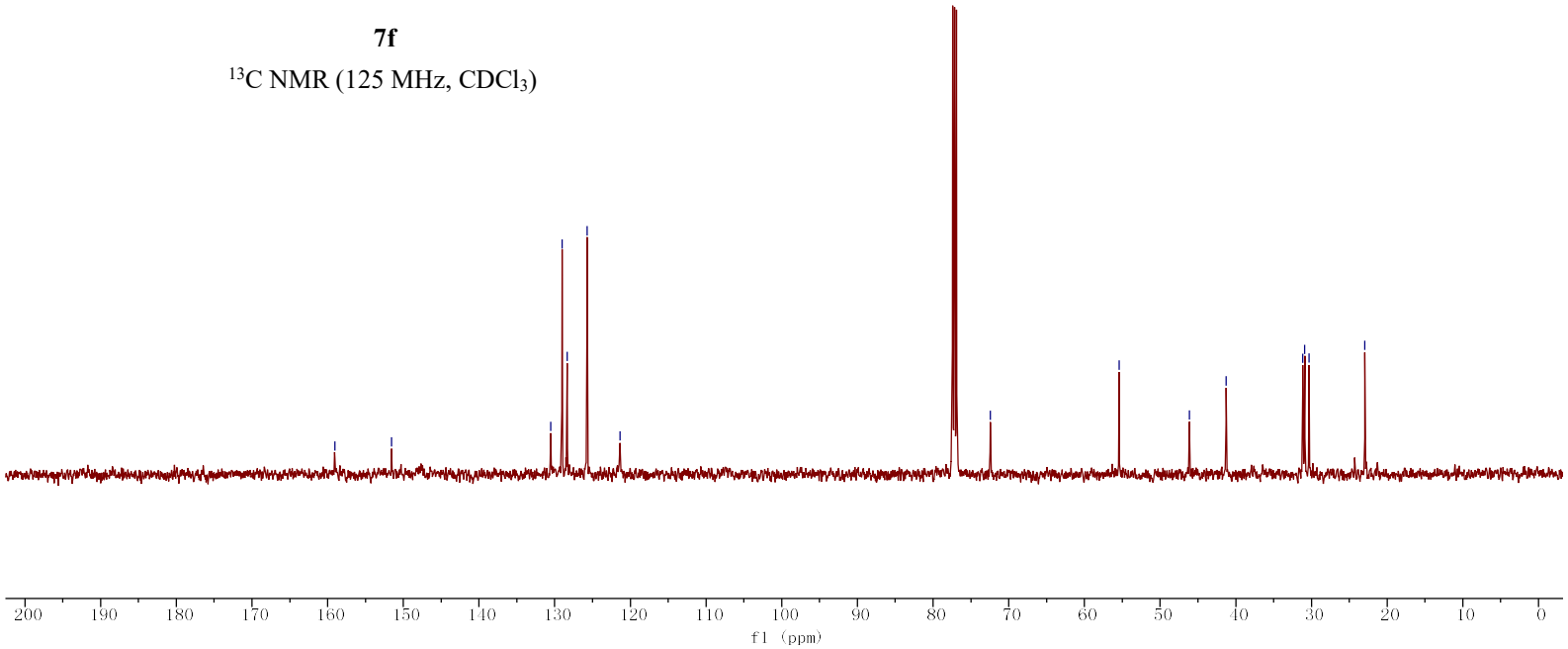
13xjm7bcw-2.100073.fid

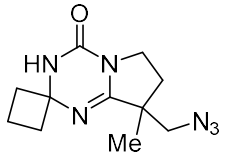
159.06
151.56
130.51
129.02
128.35
125.72
121.37
72.44
55.43
46.14
41.27
31.14
30.88
30.33
22.94



7f

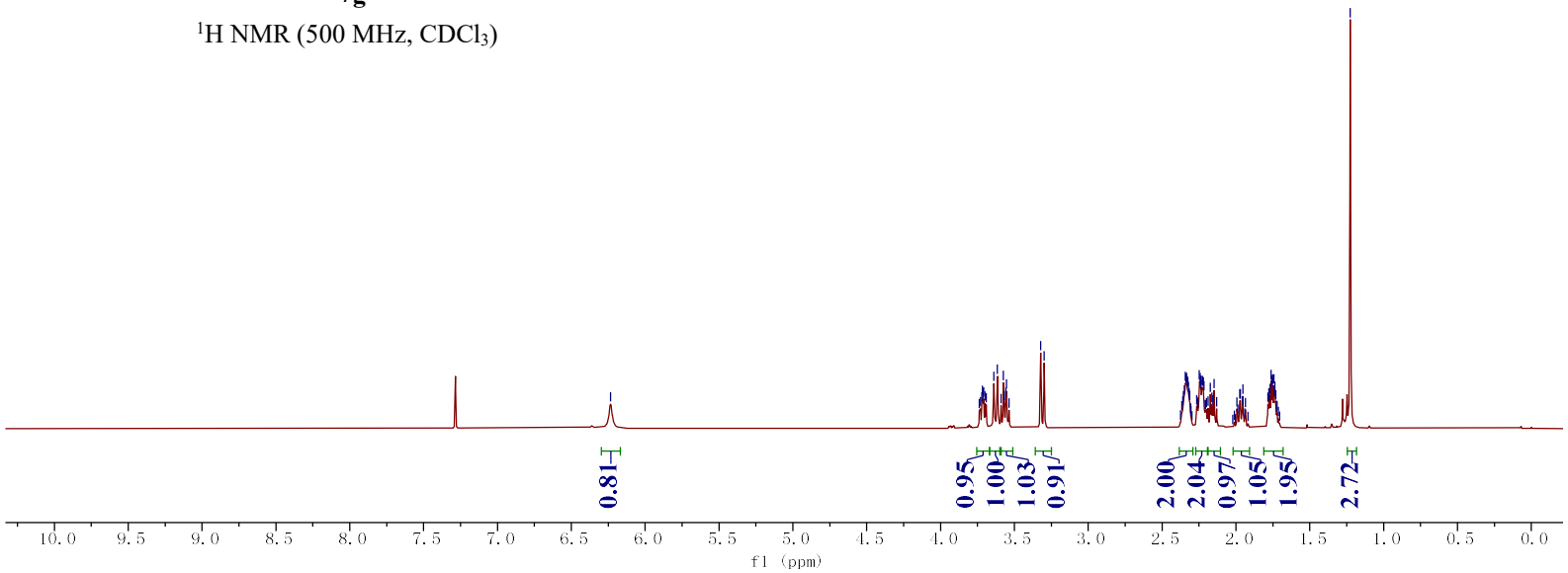
^{13}C NMR (125 MHz, $CDCl_3$)





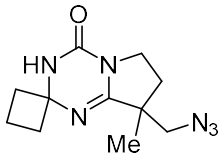
7g

^{1}H NMR (500 MHz, $CDCl_3$)



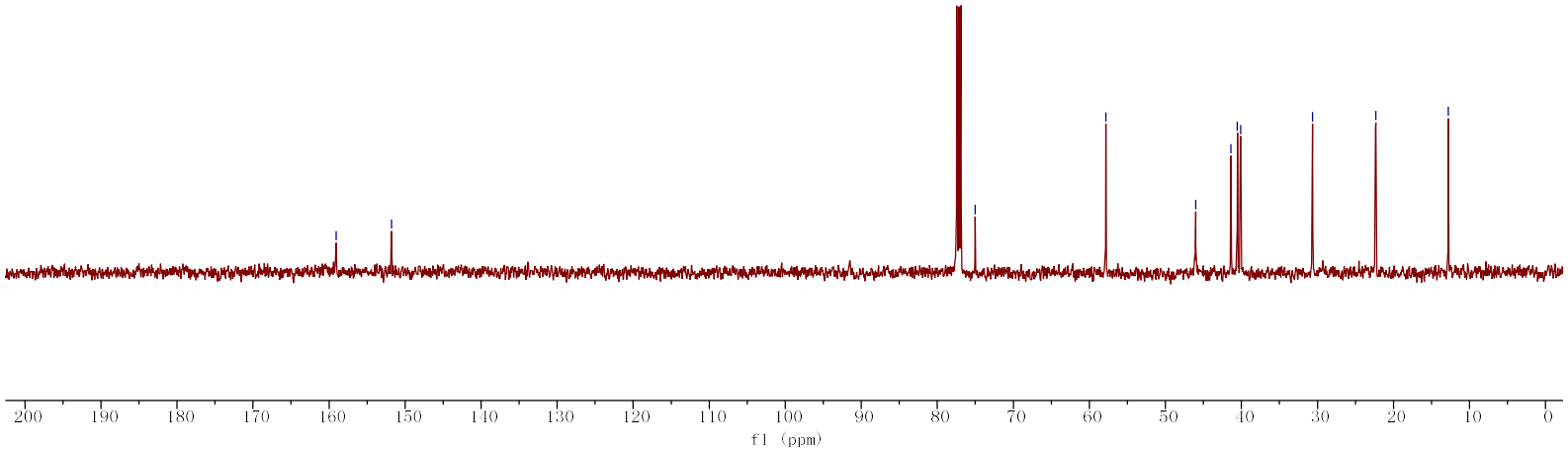
13xjm9cw-c-2.100070.fid

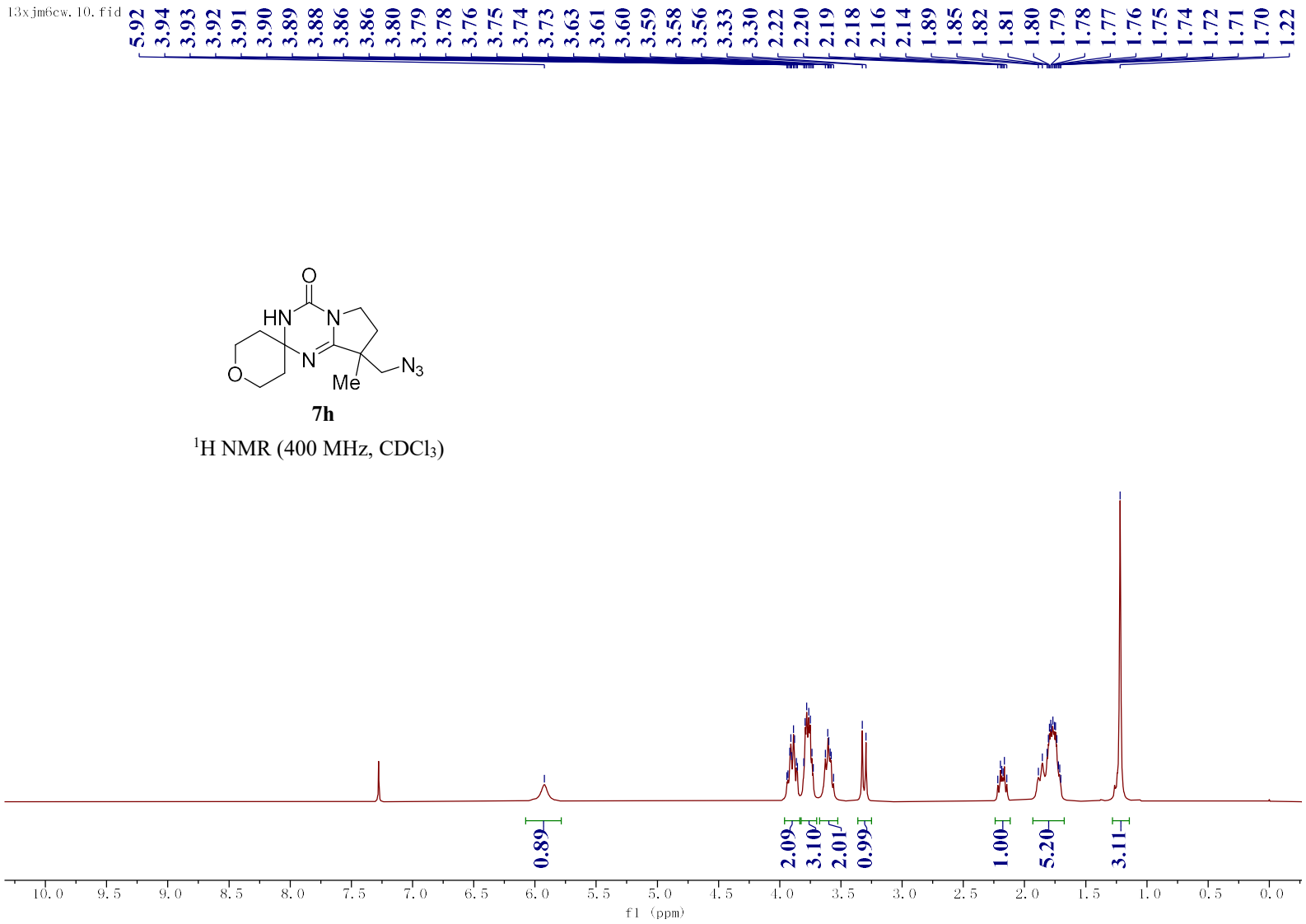
159.06
151.77
75.02
57.83
46.02
41.38
40.53
40.11
30.66
22.34
12.79



7g

^{13}C NMR (125 MHz, $CDCl_3$)



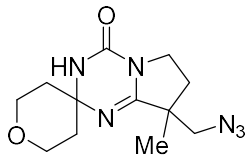


7h

^{1}H NMR (400 MHz, $CDCl_3$)

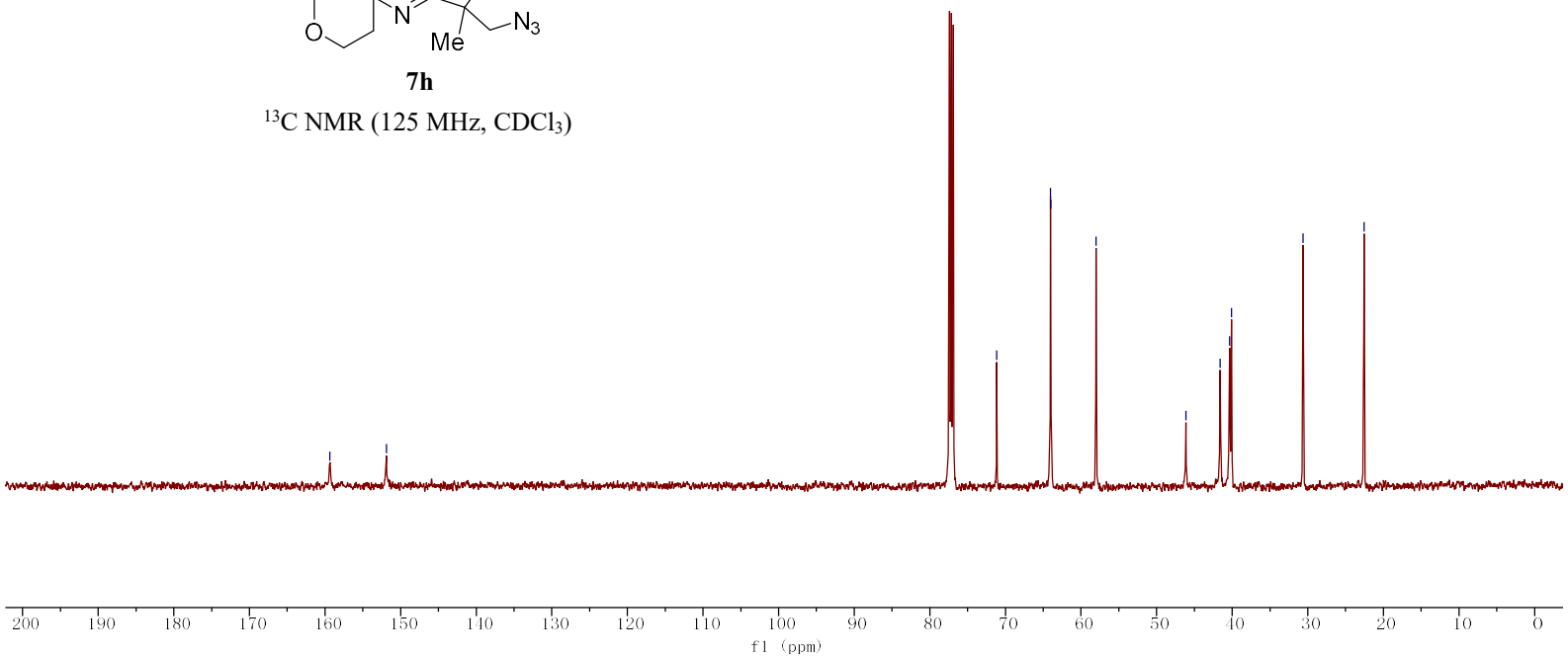
13xjm6cw-c.18.fid

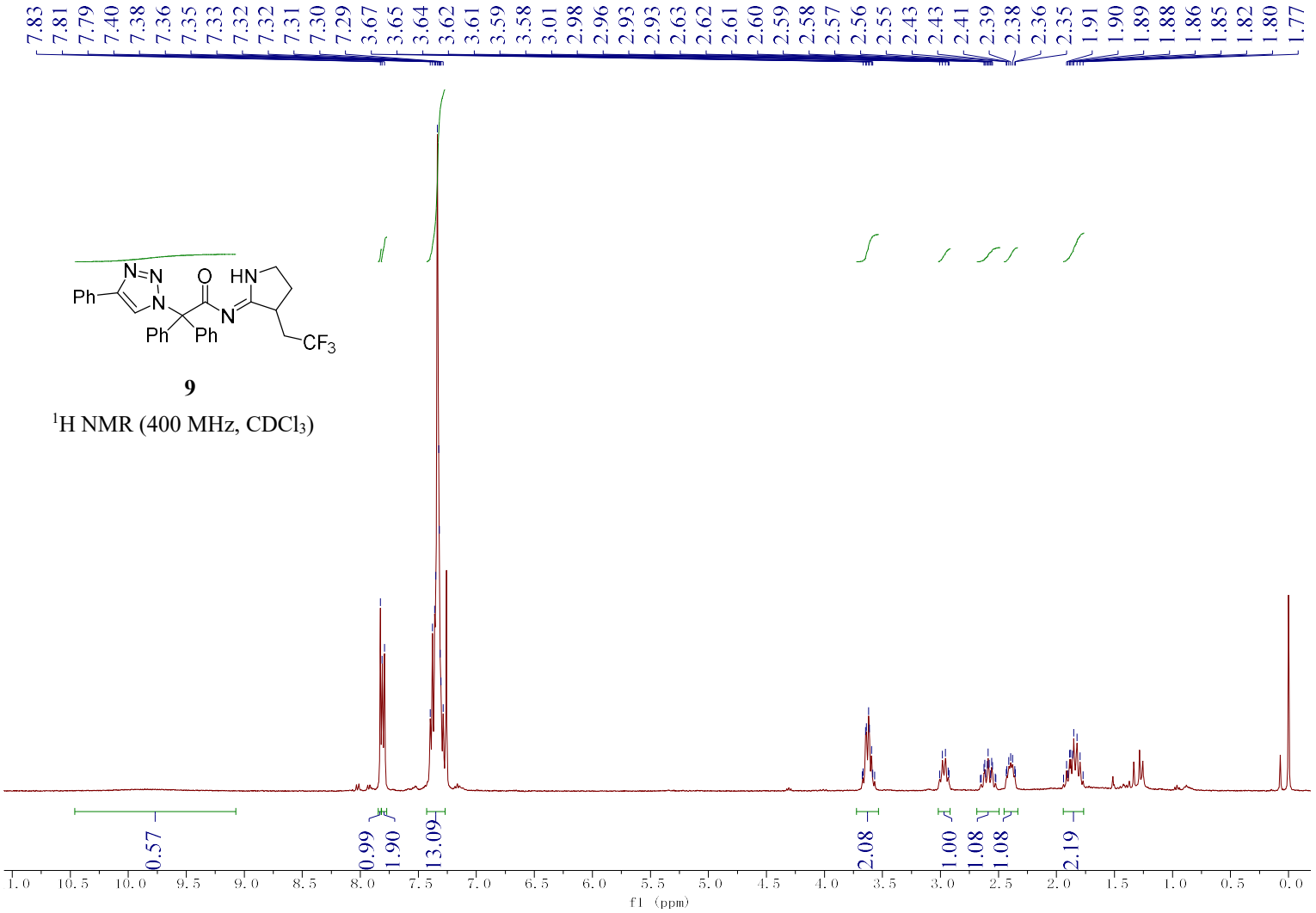
159.35
151.88
71.16
64.03
63.99
58.00
46.12
41.58
40.35
40.10
30.62
22.56



7h

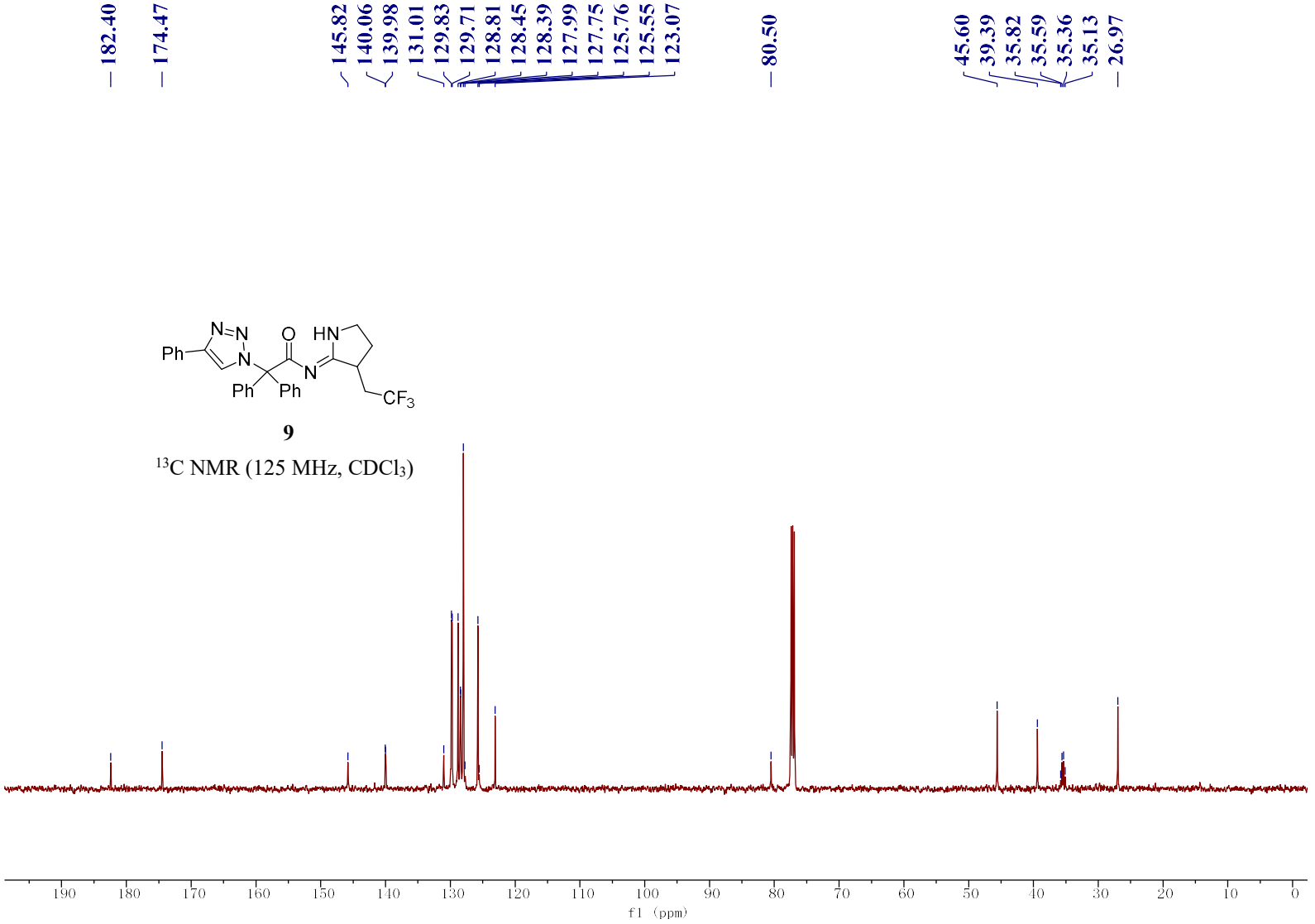
^{13}C NMR (125 MHz, $CDCl_3$)





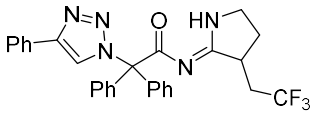
9

^{1}H NMR (400 MHz, $CDCl_3$)



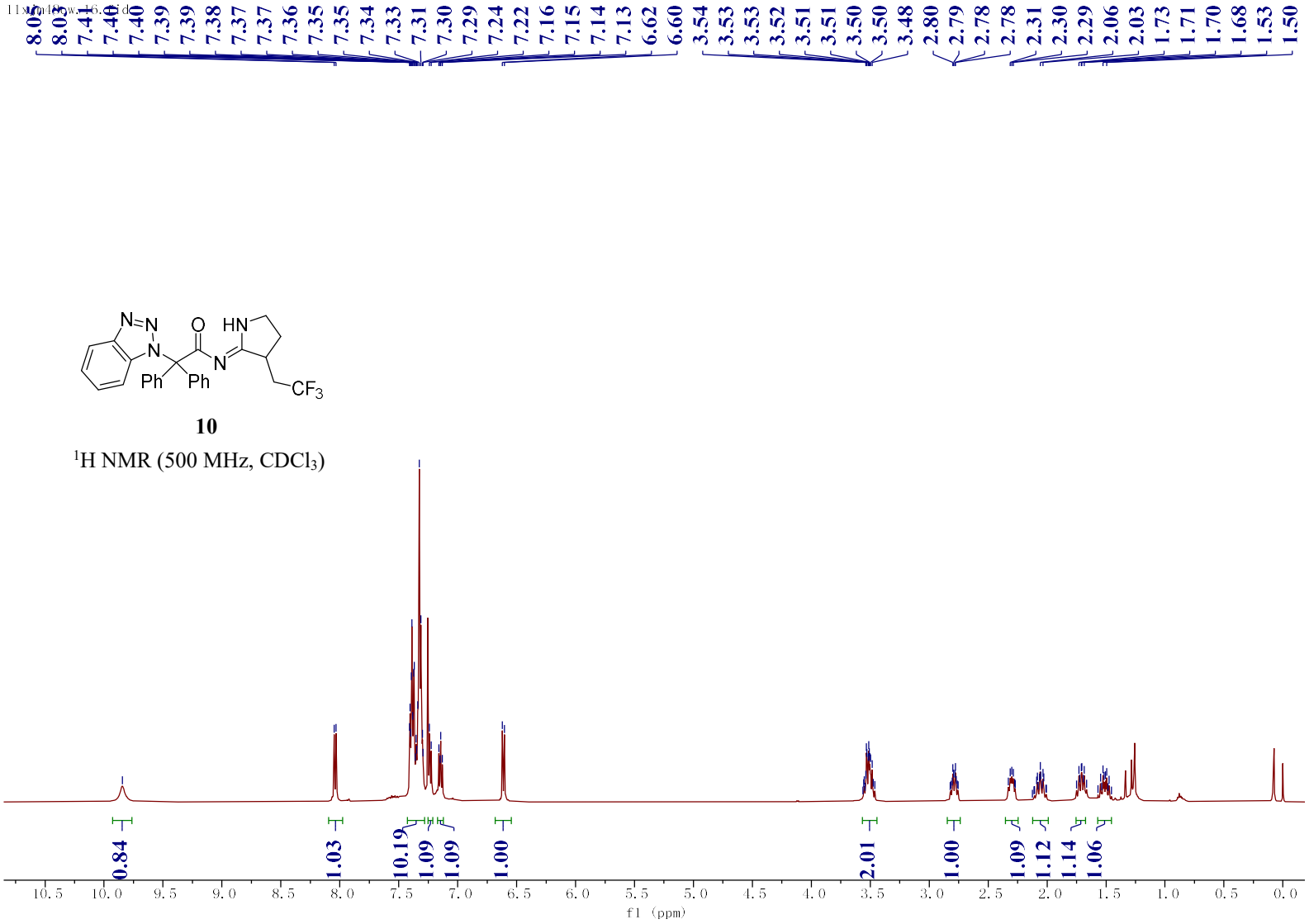
9

^{13}C NMR (125 MHz, $CDCl_3$)



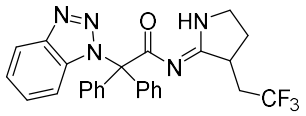
9

^{19}F NMR (470 MHz, $CDCl_3$)



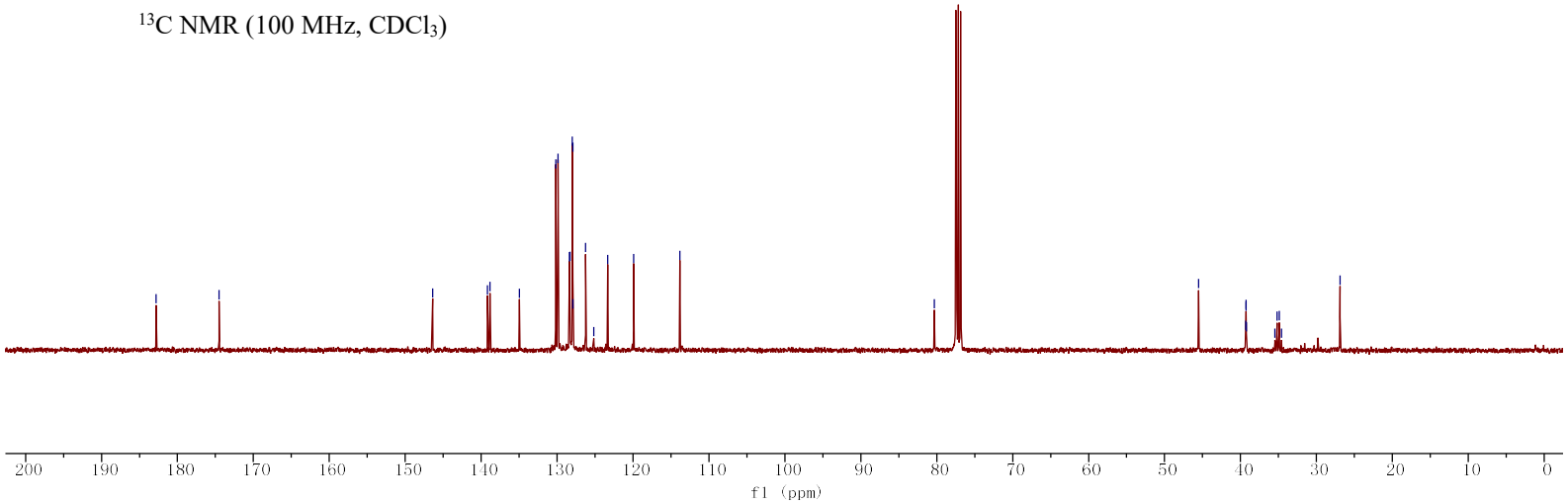
10

^{1}H NMR (500 MHz, $CDCl_3$)

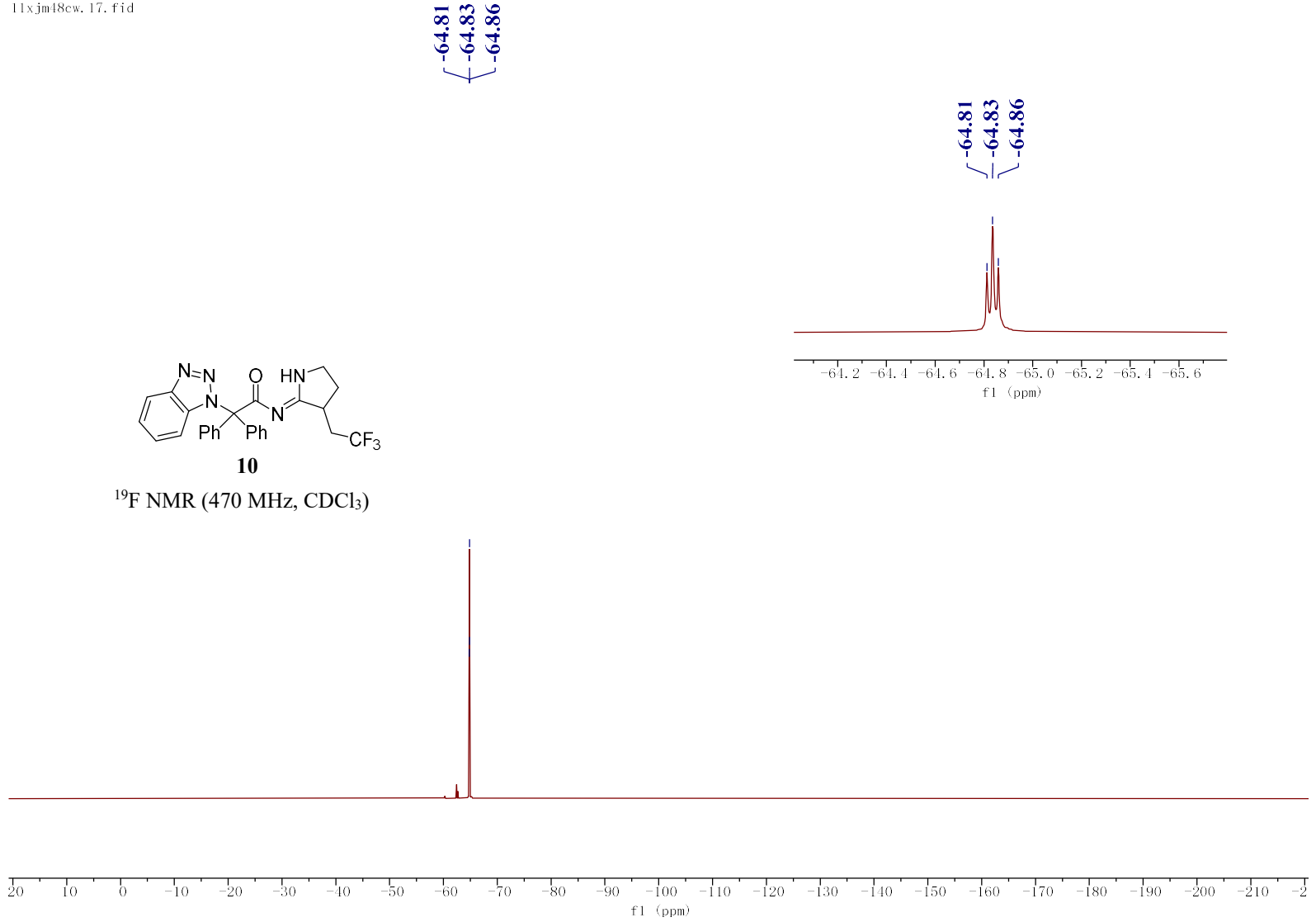


10

^{13}C NMR (100 MHz, $CDCl_3$)

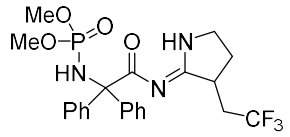


11xjm48cw.17.fid



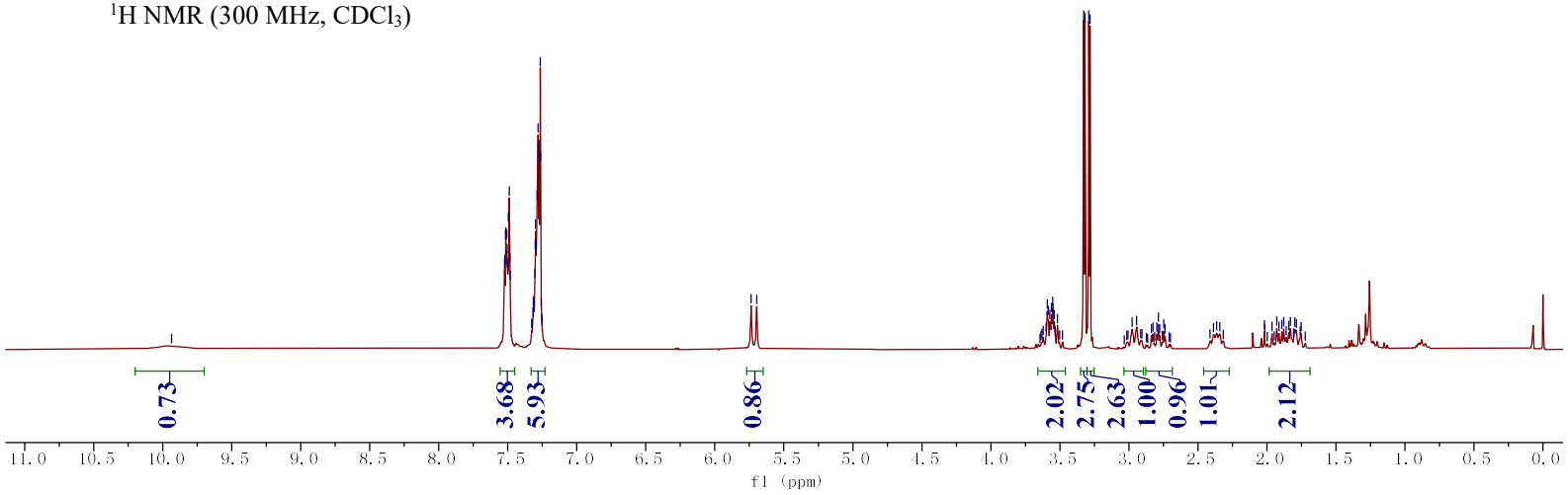
10

^{19}F NMR (470 MHz, $CDCl_3$)



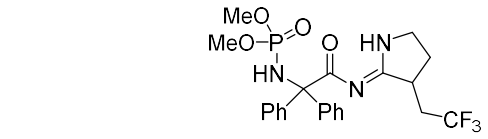
11

^{1}H NMR (300 MHz, $CDCl_3$)



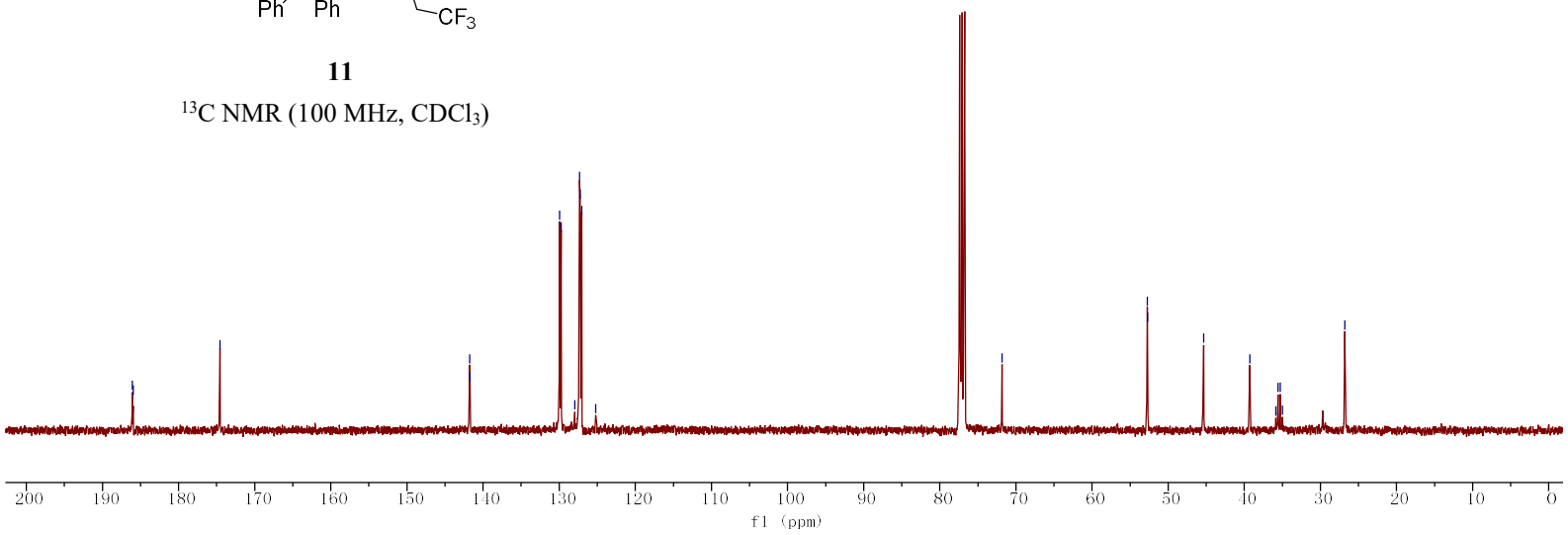
11xjm66cw.10.fid

186.09
185.92
174.57
141.75
141.71
129.93
129.74
127.96
127.33
127.23
127.05
125.20
71.81
52.75
52.69
45.33
39.29
35.86
35.57
35.27
34.99
26.79

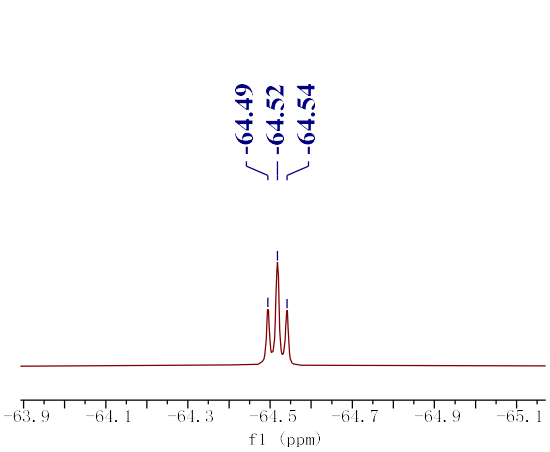


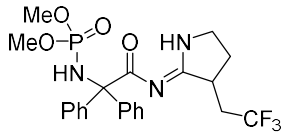
11

^{13}C NMR (100 MHz, $CDCl_3$)



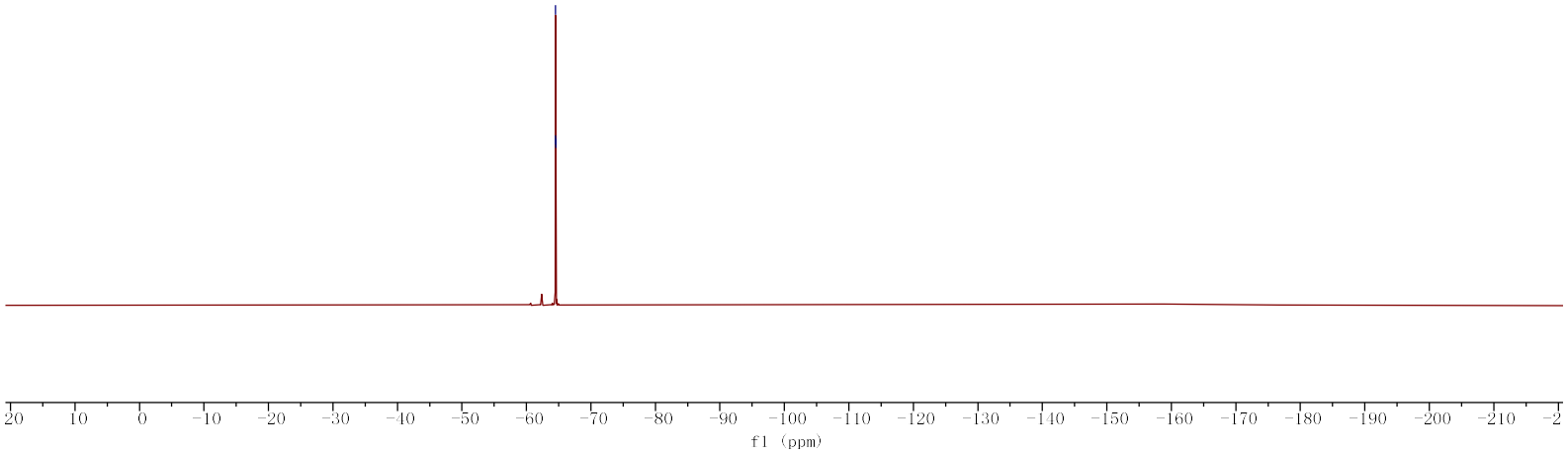
11xjm66cw-2.31.fid





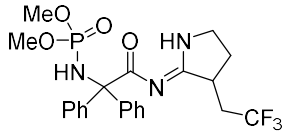
11

^{19}F NMR (470 MHz, $CDCl_3$)



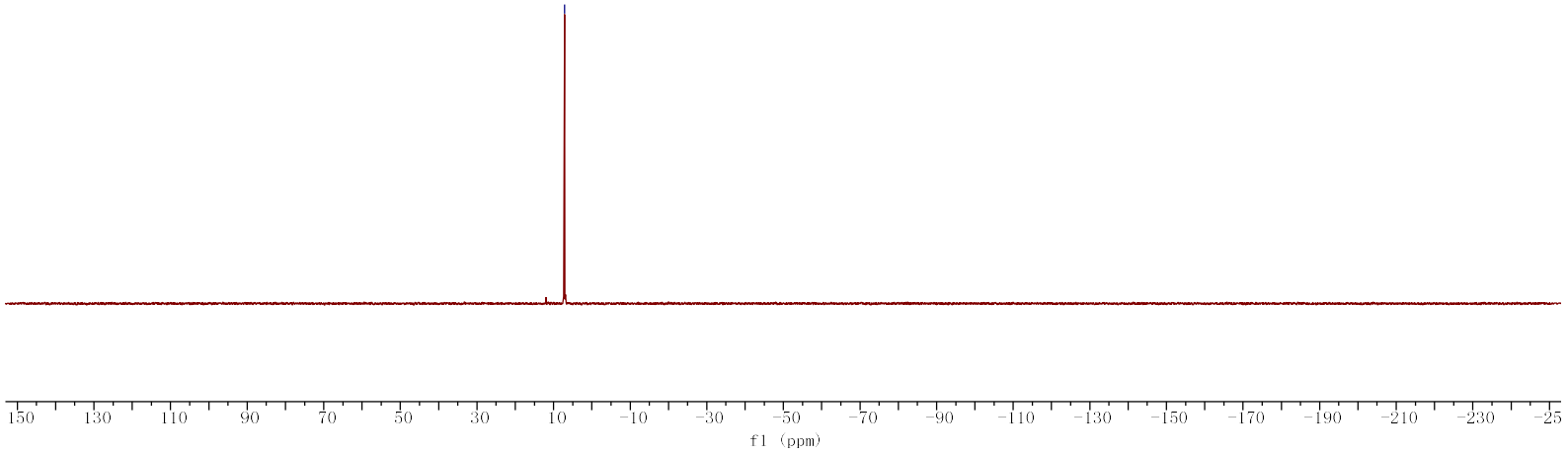
11xjm66cw.13.fid

7.14

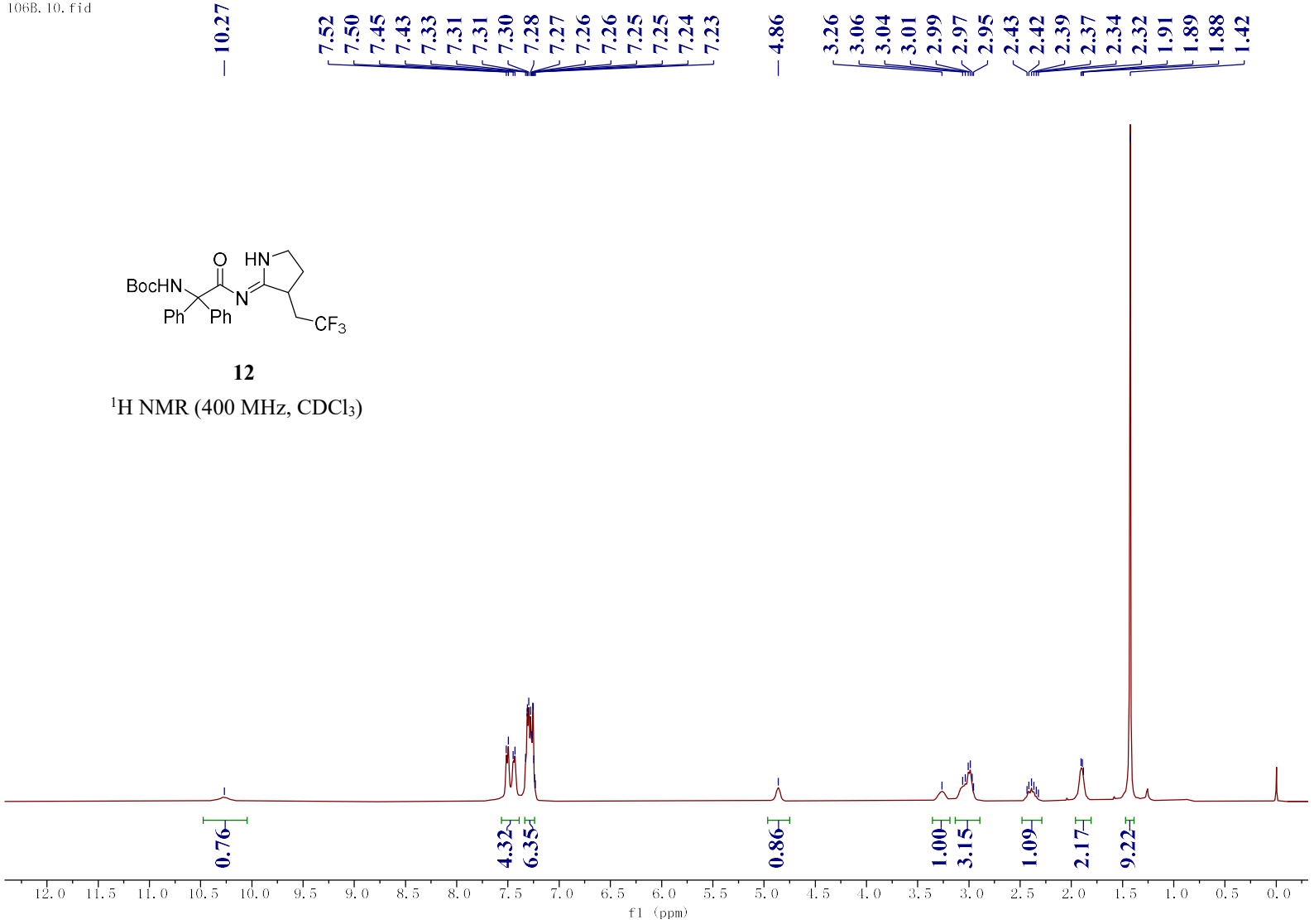


11

^{31}P NMR (162 MHz, $CDCl_3$)

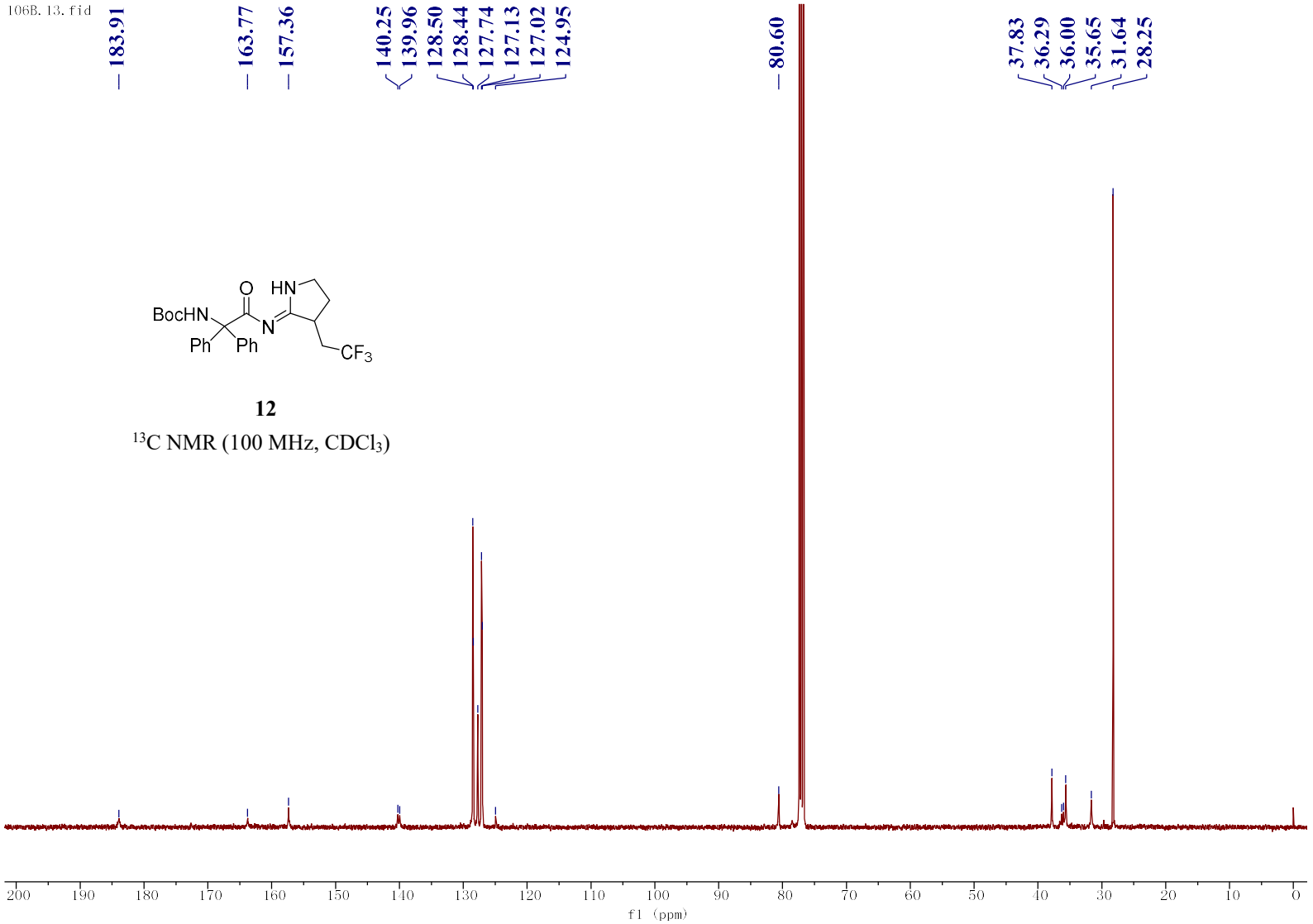


106B.10.fid



12

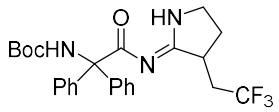
^{1}H NMR (400 MHz, $CDCl_3$)



12

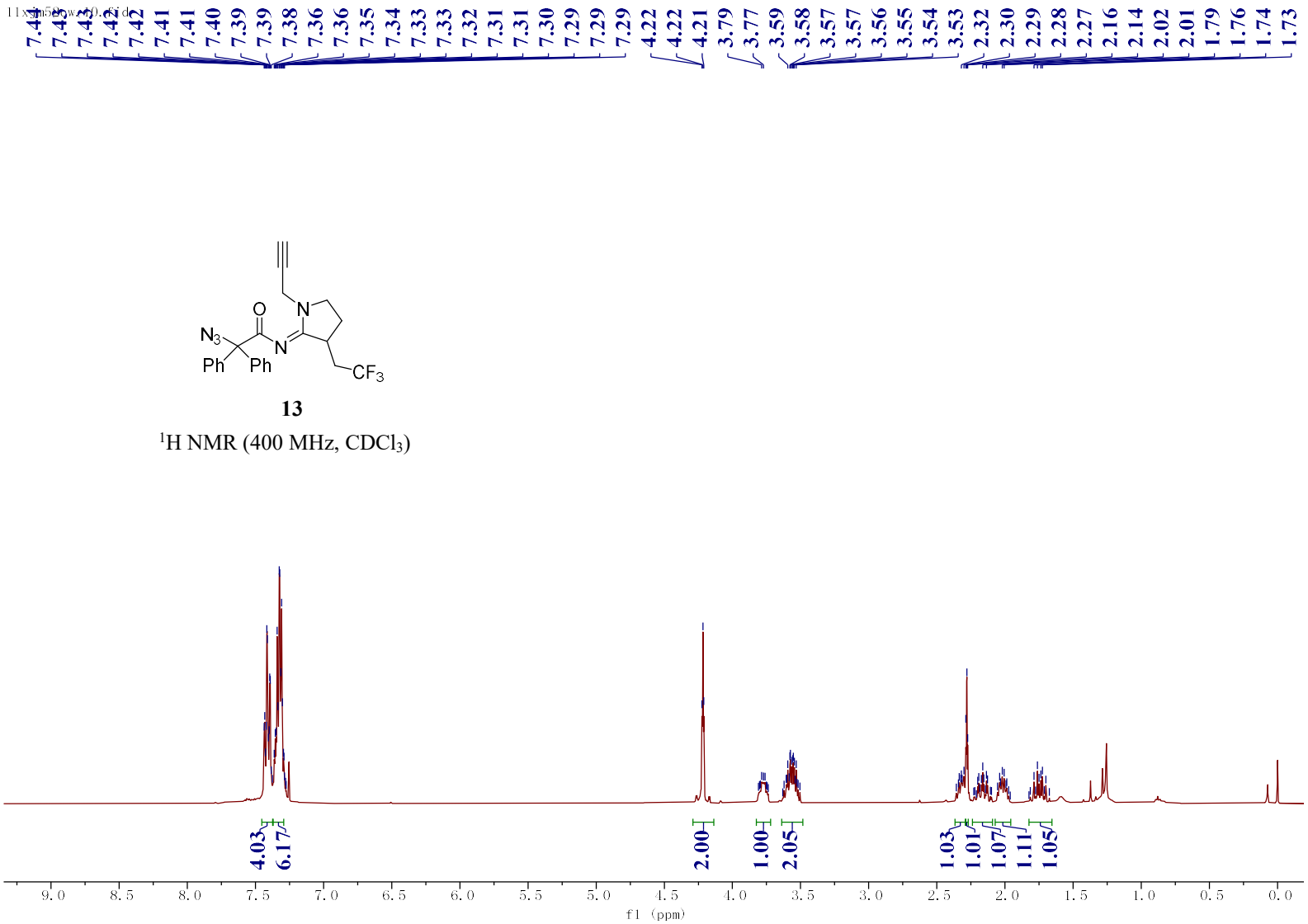
^{13}C NMR (100 MHz, $CDCl_3$)

106B.11.fid



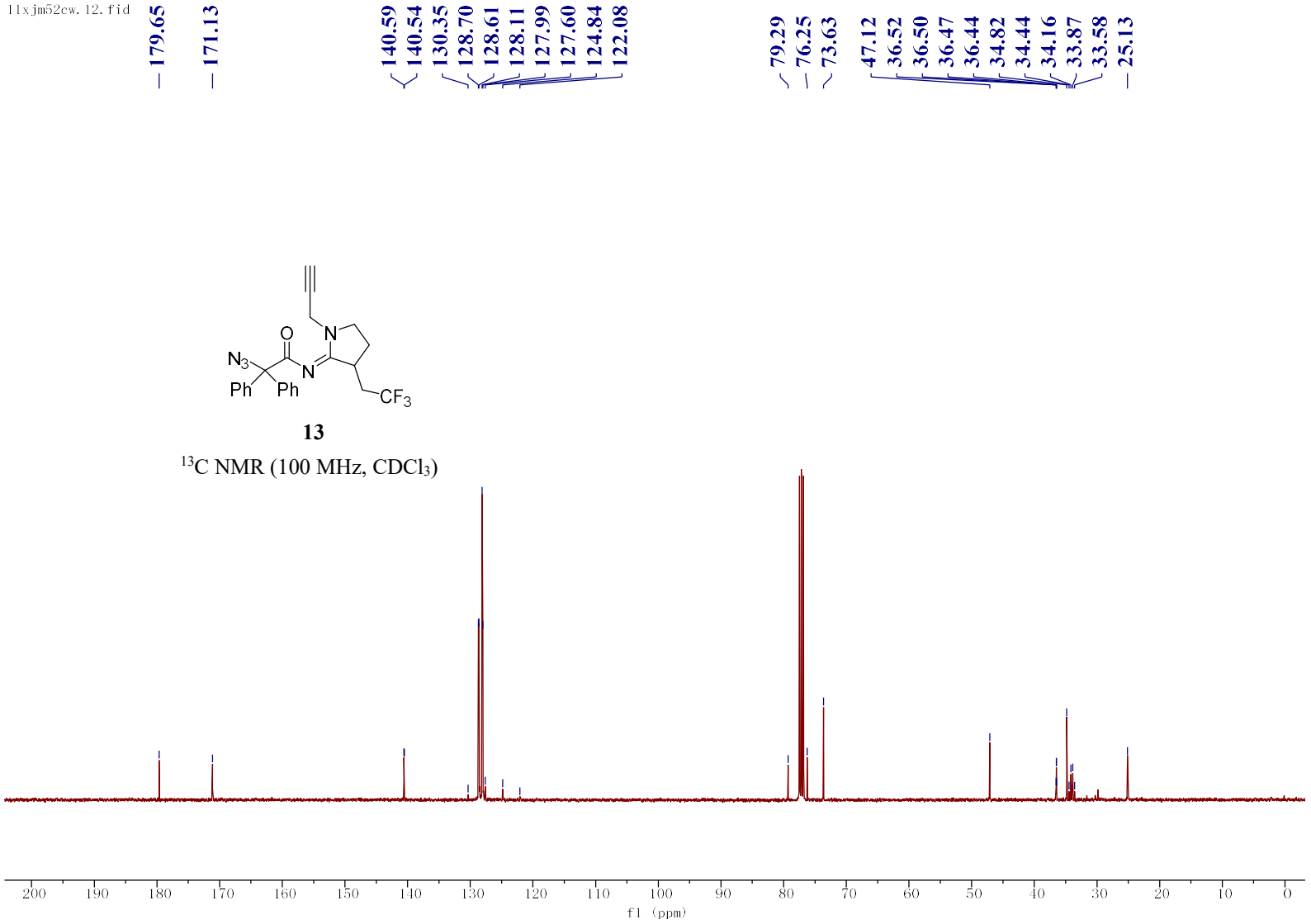
12

^{19}F NMR (376 MHz, $CDCl_3$)



13

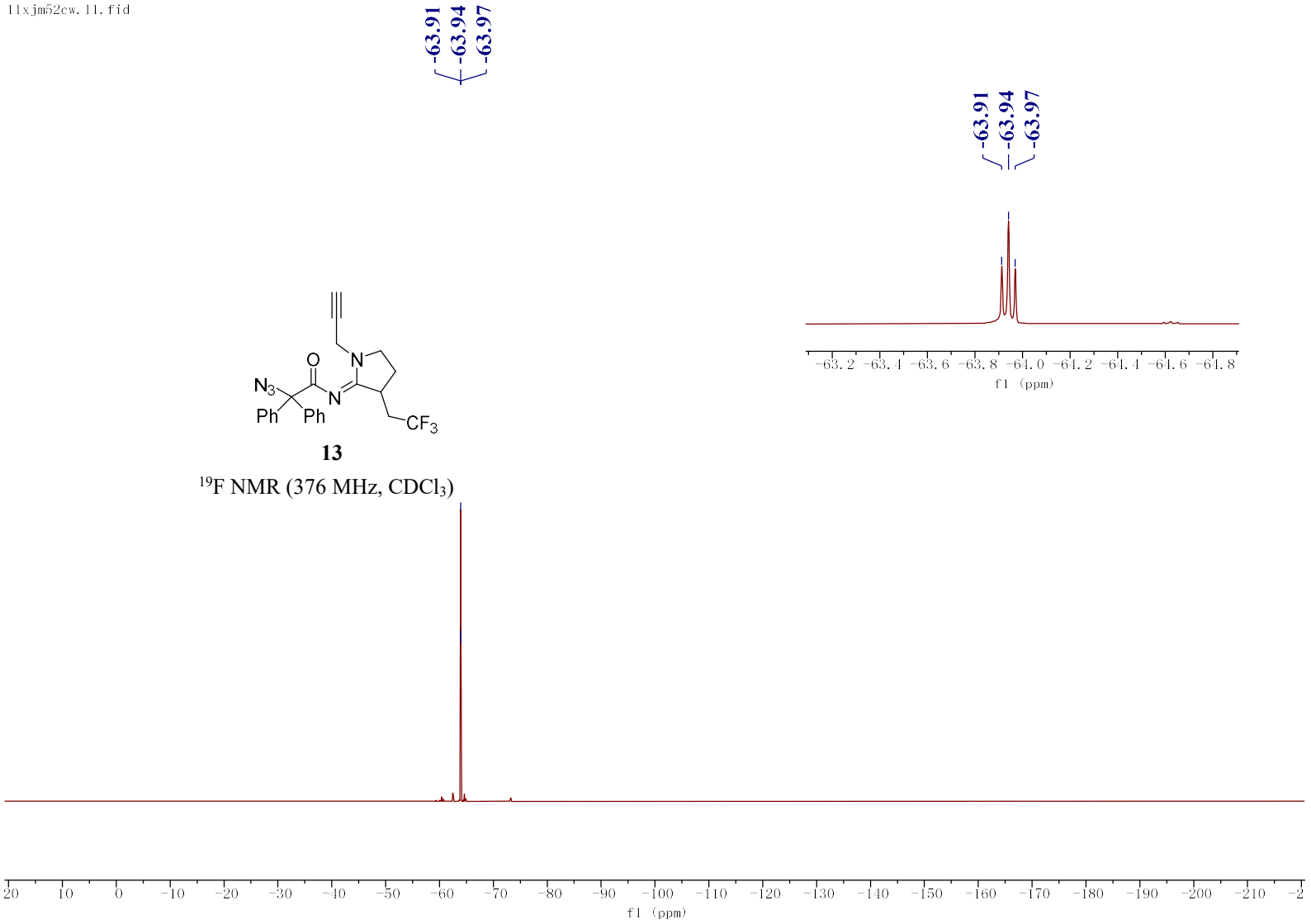
^{1}H NMR (400 MHz, $CDCl_3$)



13

^{13}C NMR (100 MHz, $CDCl_3$)

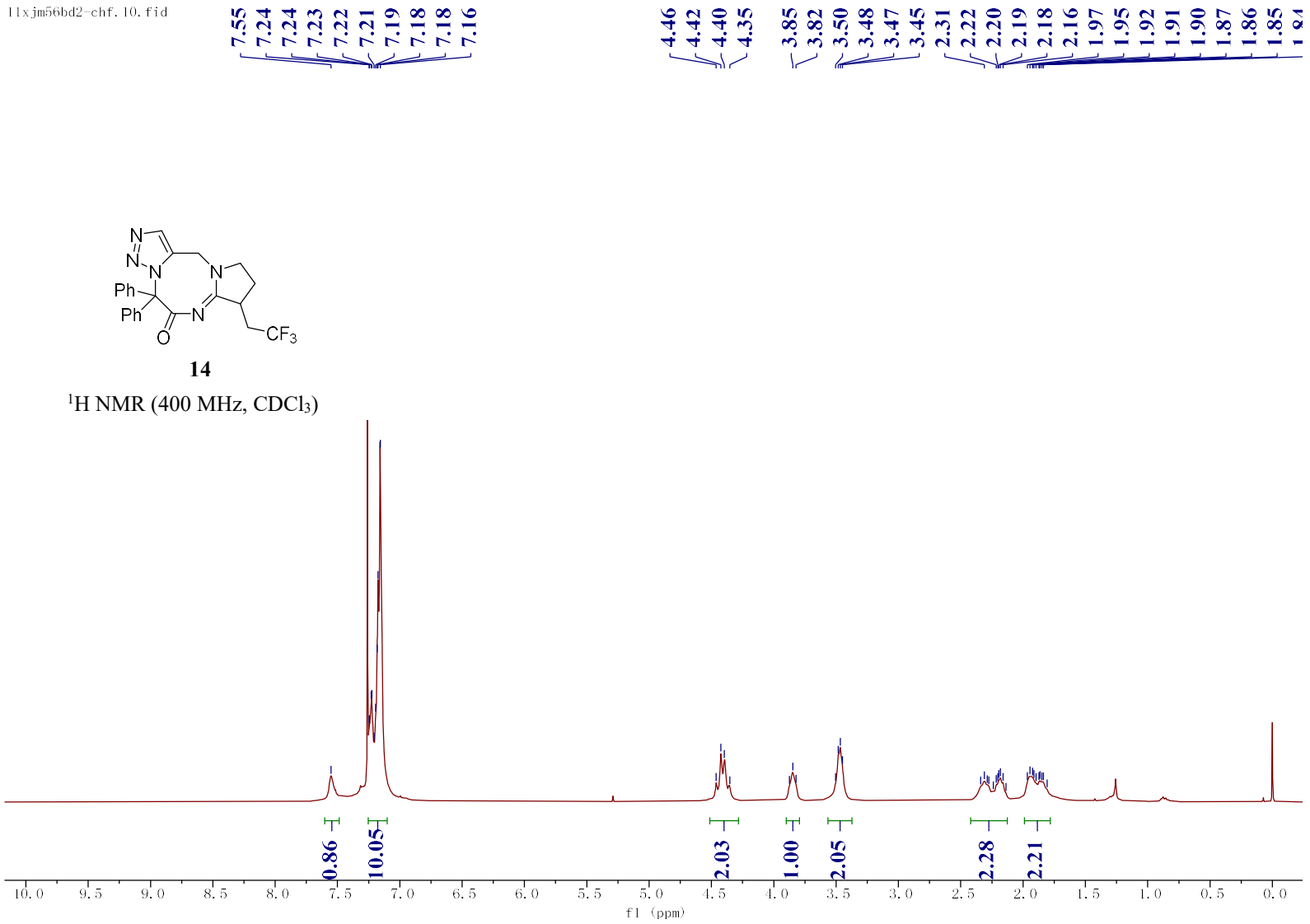
11xjm52cw.11.fid



13

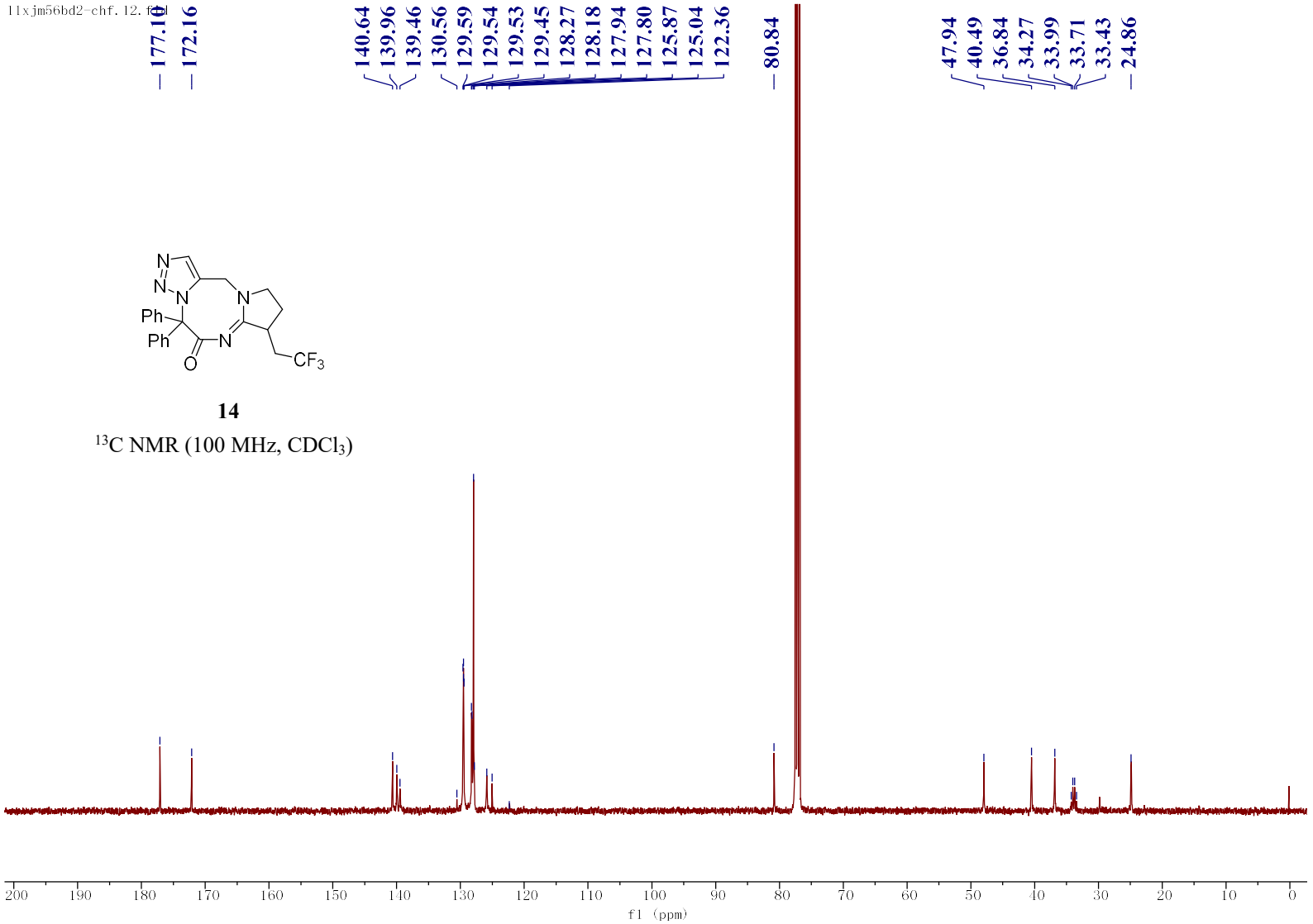
^{19}F NMR (376 MHz, $CDCl_3$)

11xjm56bd2-chf.10.fid



14

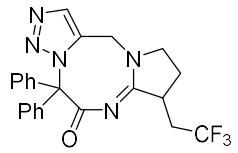
^{1}H NMR (400 MHz, $CDCl_3$)



14

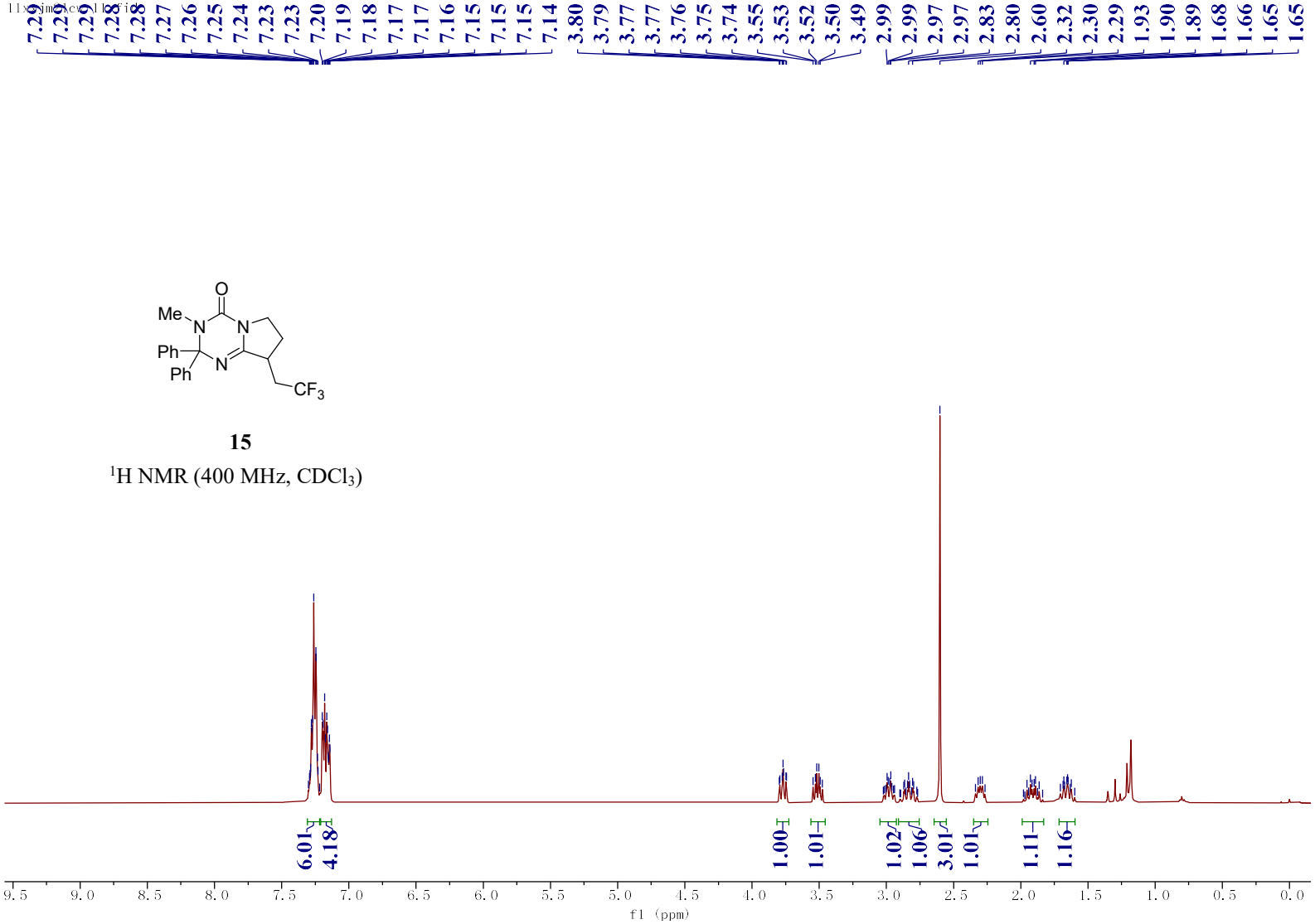
^{13}C NMR (100 MHz, $CDCl_3$)

11xjm56bd2-chf.11.fid



14

^{19}F NMR (376 MHz, $CDCl_3$)

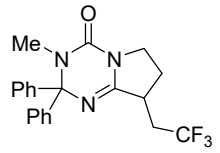


15

^{1}H NMR (400 MHz, $CDCl_3$)

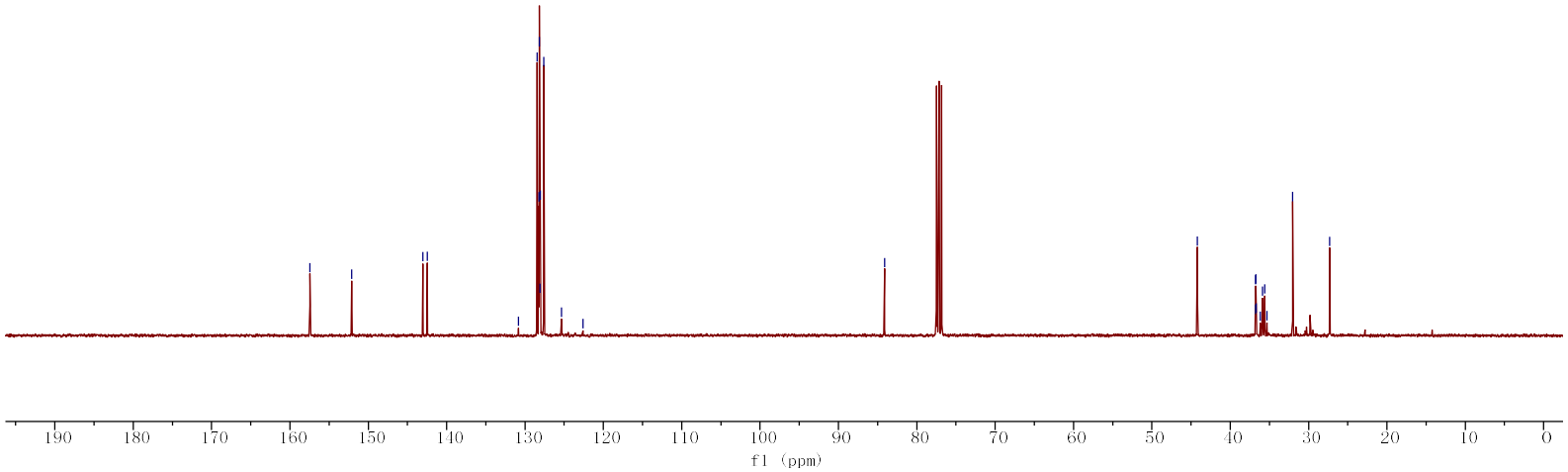
11xxjm21cw.10.fid

157.45
152.13
143.03
142.45
130.85
128.47
128.23
128.16
128.10
128.06
127.62
125.35
122.60
84.12
44.20
36.78
36.75
36.72
36.69
36.16
35.87
35.59
35.30
32.04
27.31

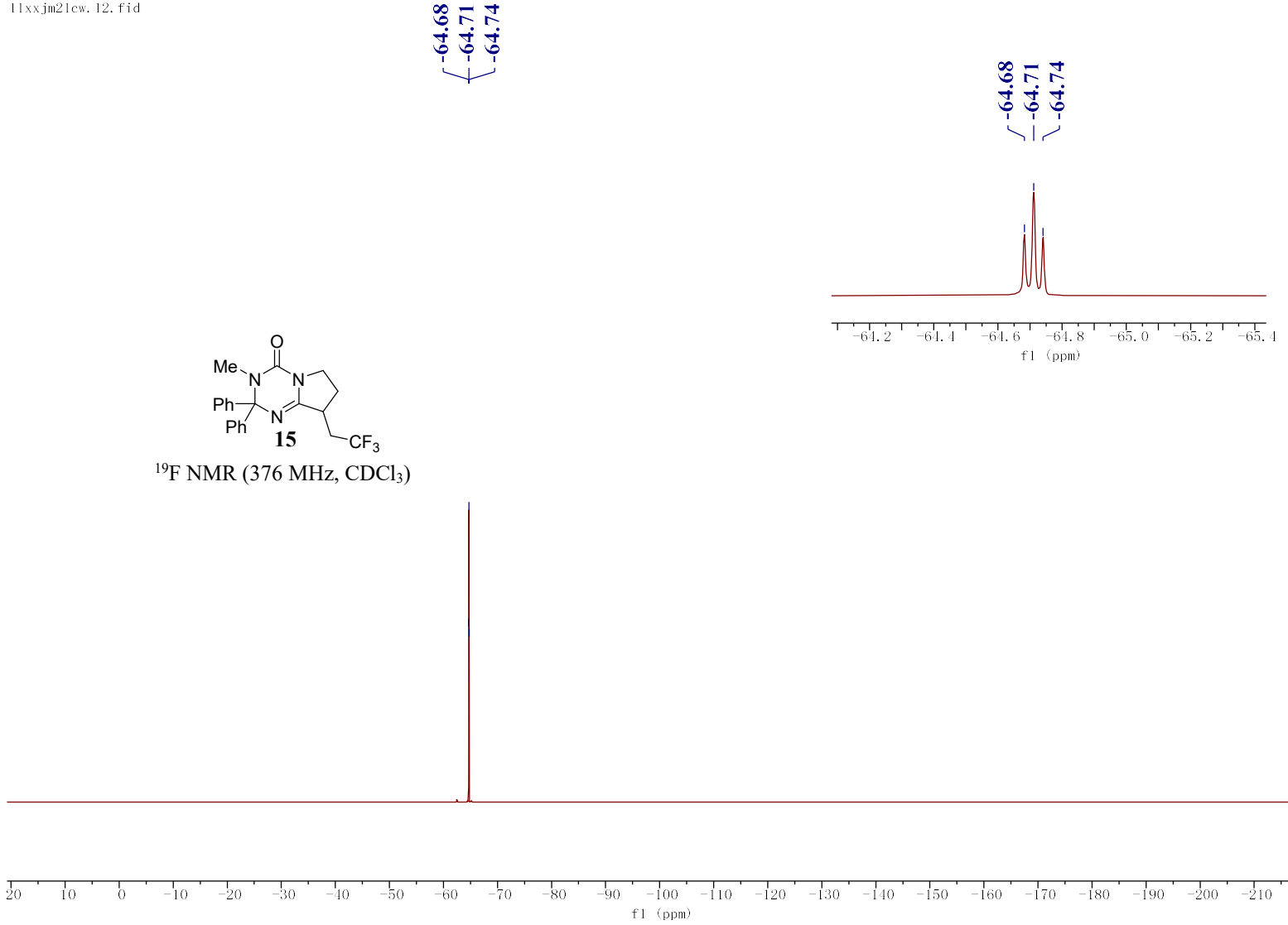


15

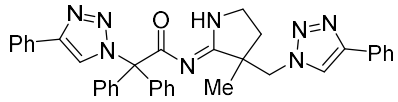
^{13}C NMR (100 MHz, $CDCl_3$)



11xxjm21cw.12.fid

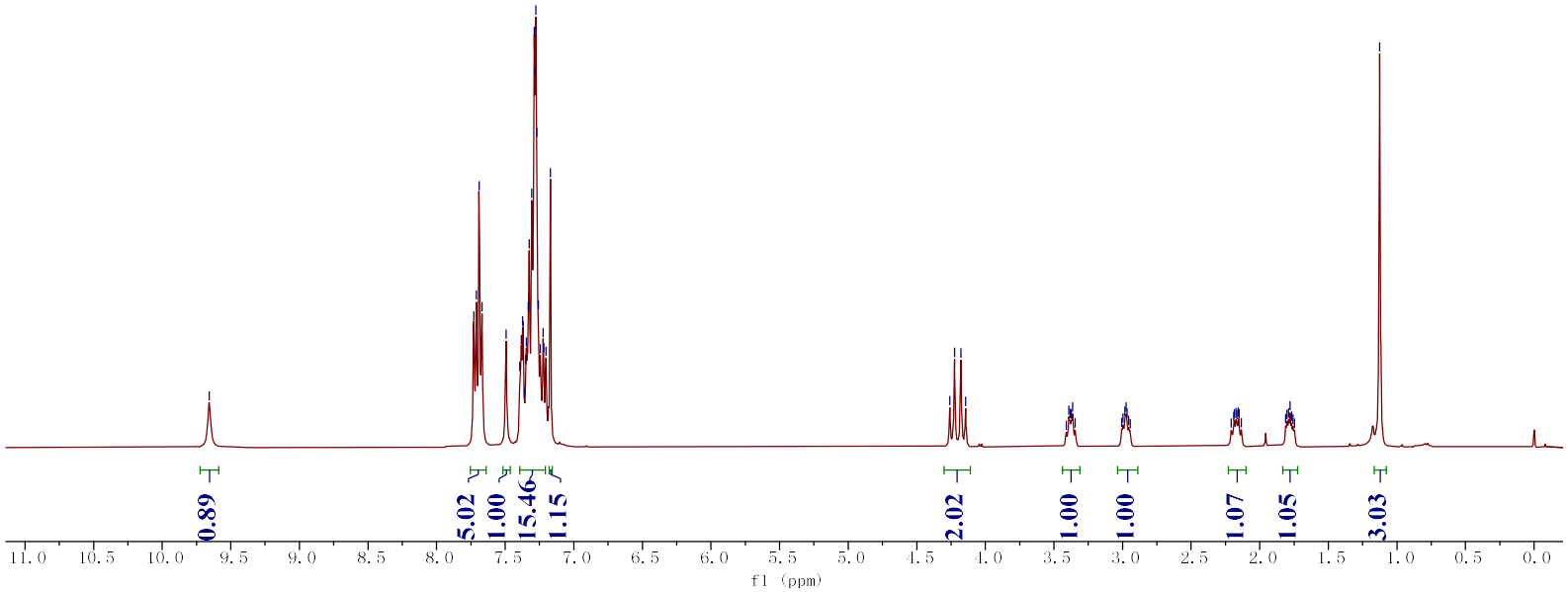


^{19}F NMR (376 MHz, $CDCl_3$)



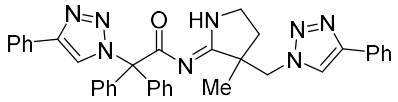
16

^{1}H NMR (400 MHz, $CDCl_3$)



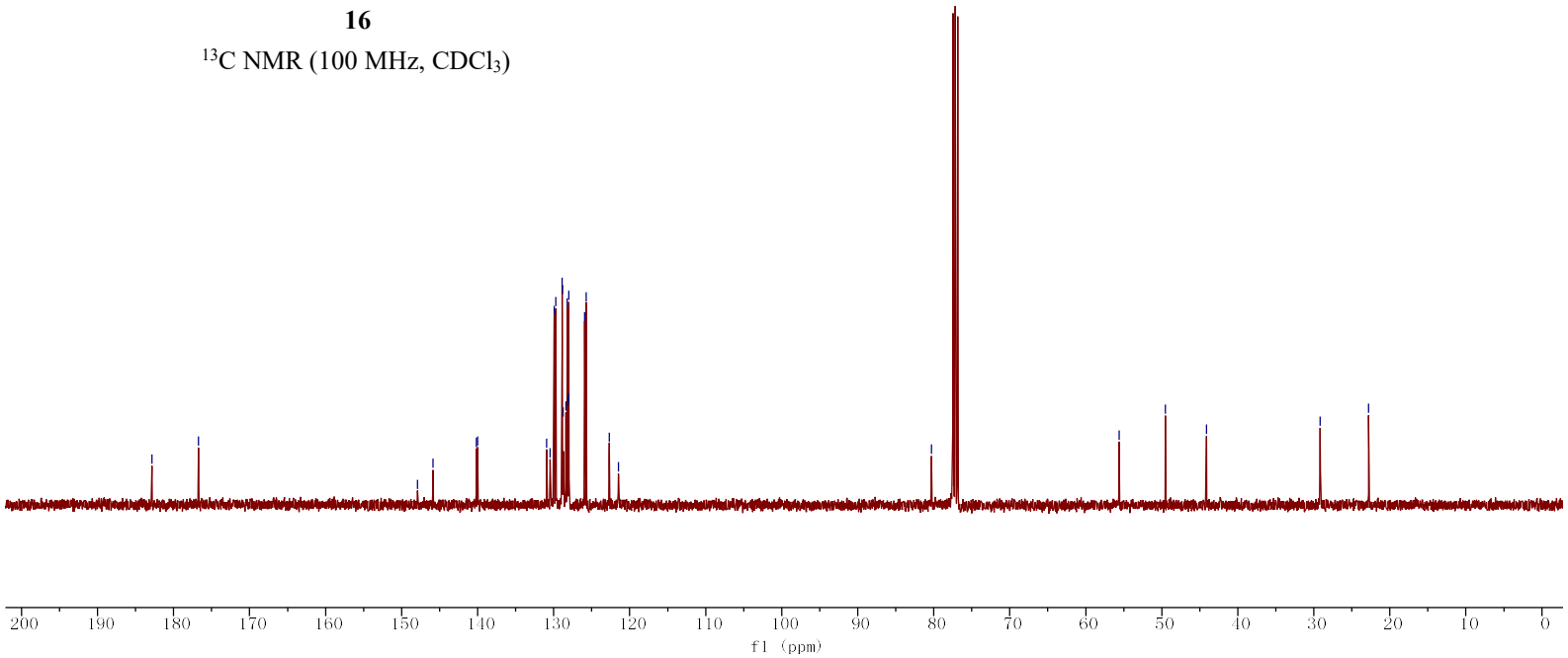
12xjm97cw.11.fid

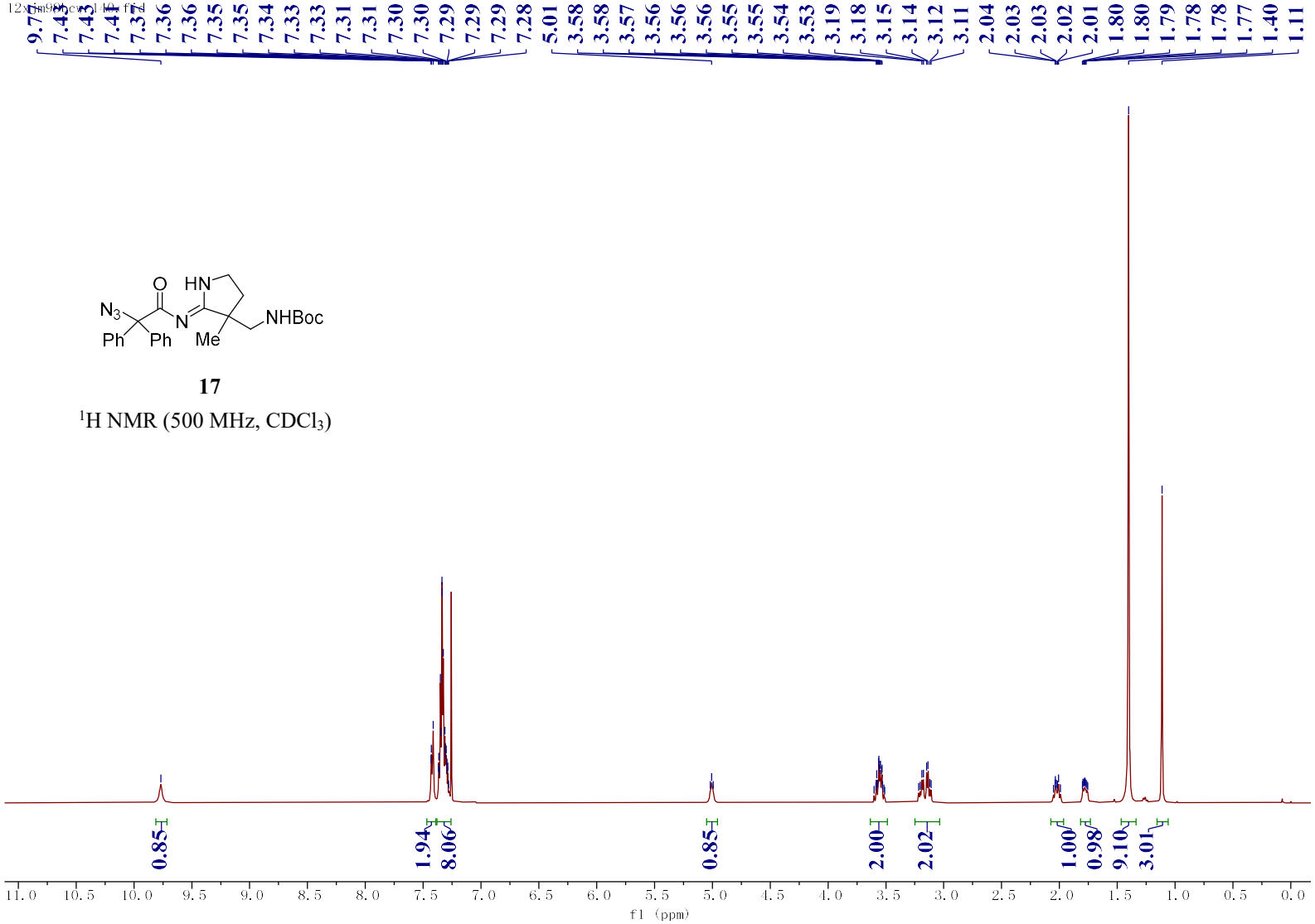
182.86 176.73 147.92 145.89 140.17 139.99 130.91 130.45 129.94 129.71 128.88 128.84 128.74 128.40 128.23 128.15 128.04 128.01 125.92 125.70 122.70 121.47 80.31 55.63 49.52 44.13 29.16 22.79



16

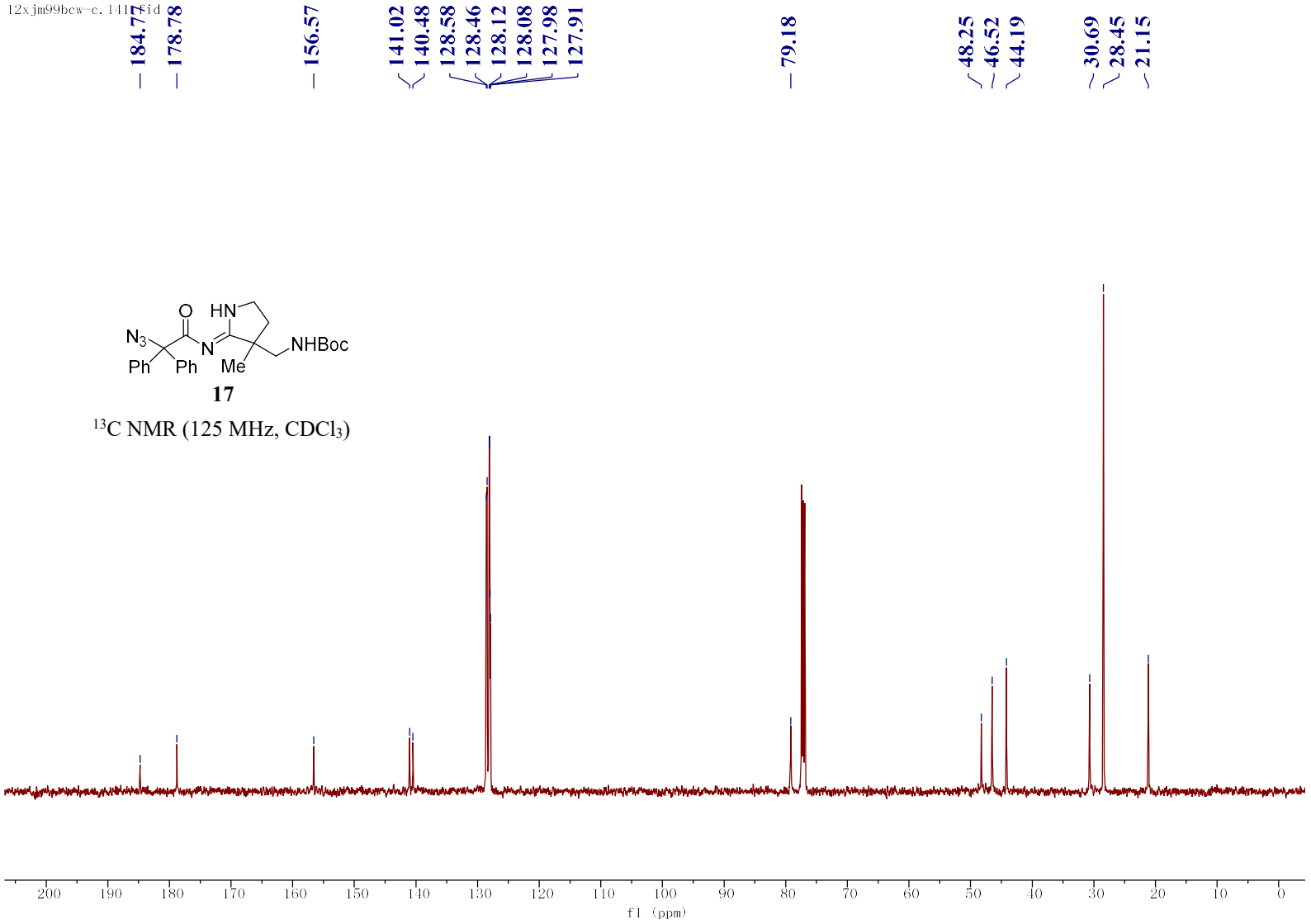
^{13}C NMR (100 MHz, $CDCl_3$)

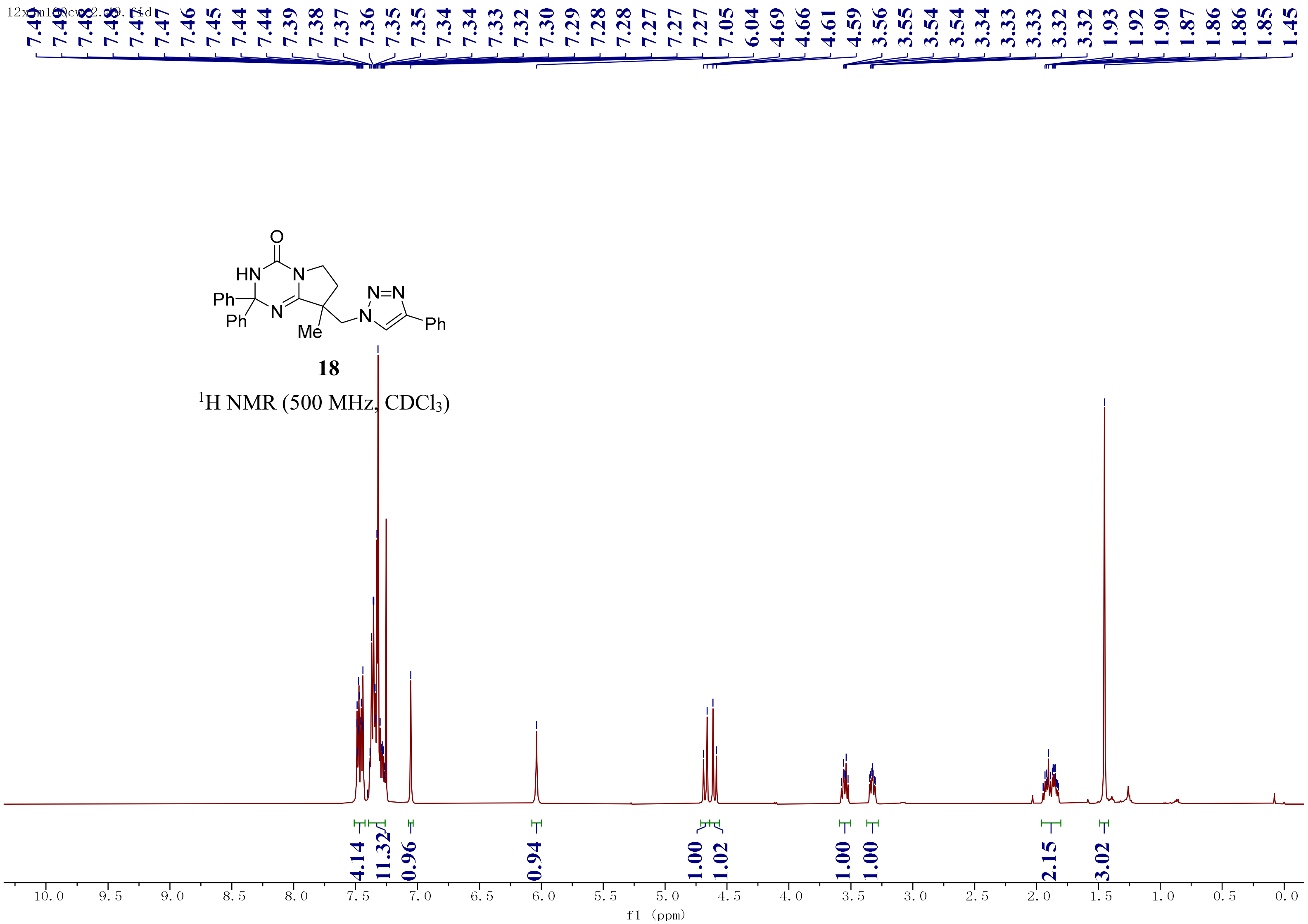




17

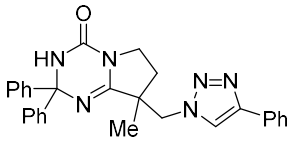
^{1}H NMR (500 MHz, $CDCl_3$)


12xjm99bcw-c.1411.fid
184.77
178.78
156.57
141.02
140.48
128.58
128.46
128.12
128.08
127.98
127.91
79.18
48.25
46.52
44.19
30.69
28.45
21.15
O
HN
N3
N
NHBoc
Ph
Ph
Me
17
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
HN
N
O
N
Me
N
N=N
Ph
18
¹H NMR (500 MHz, CDCl₃)
f1 (ppm)

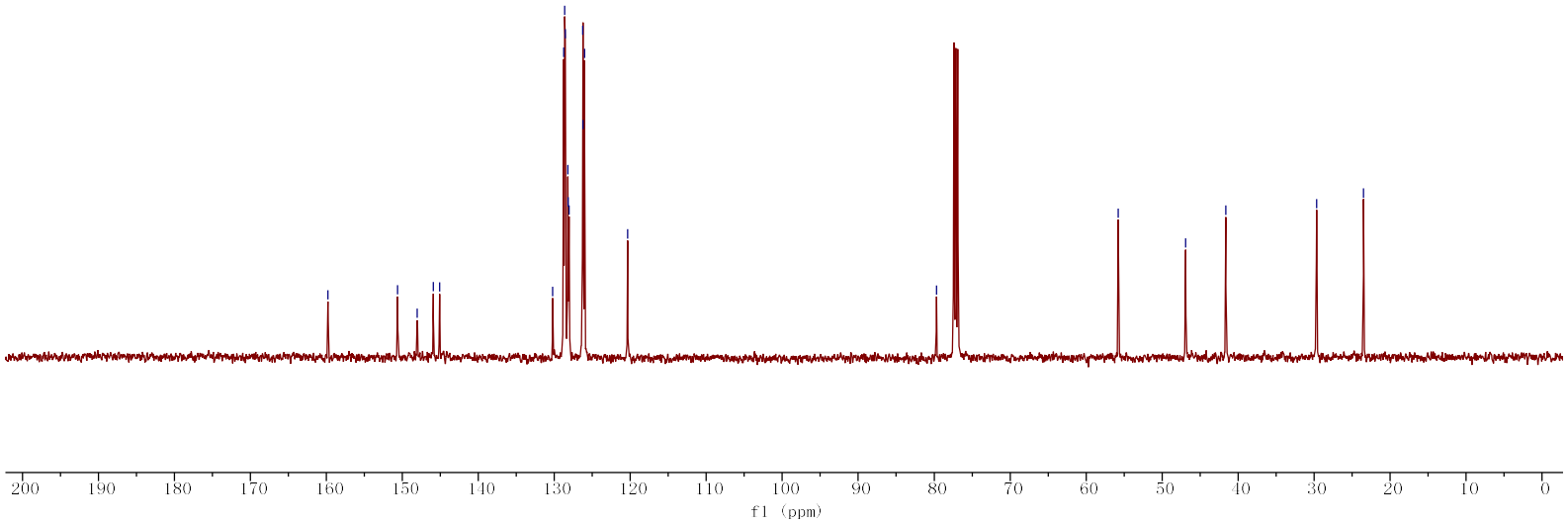
12xjm100cw.24.fid

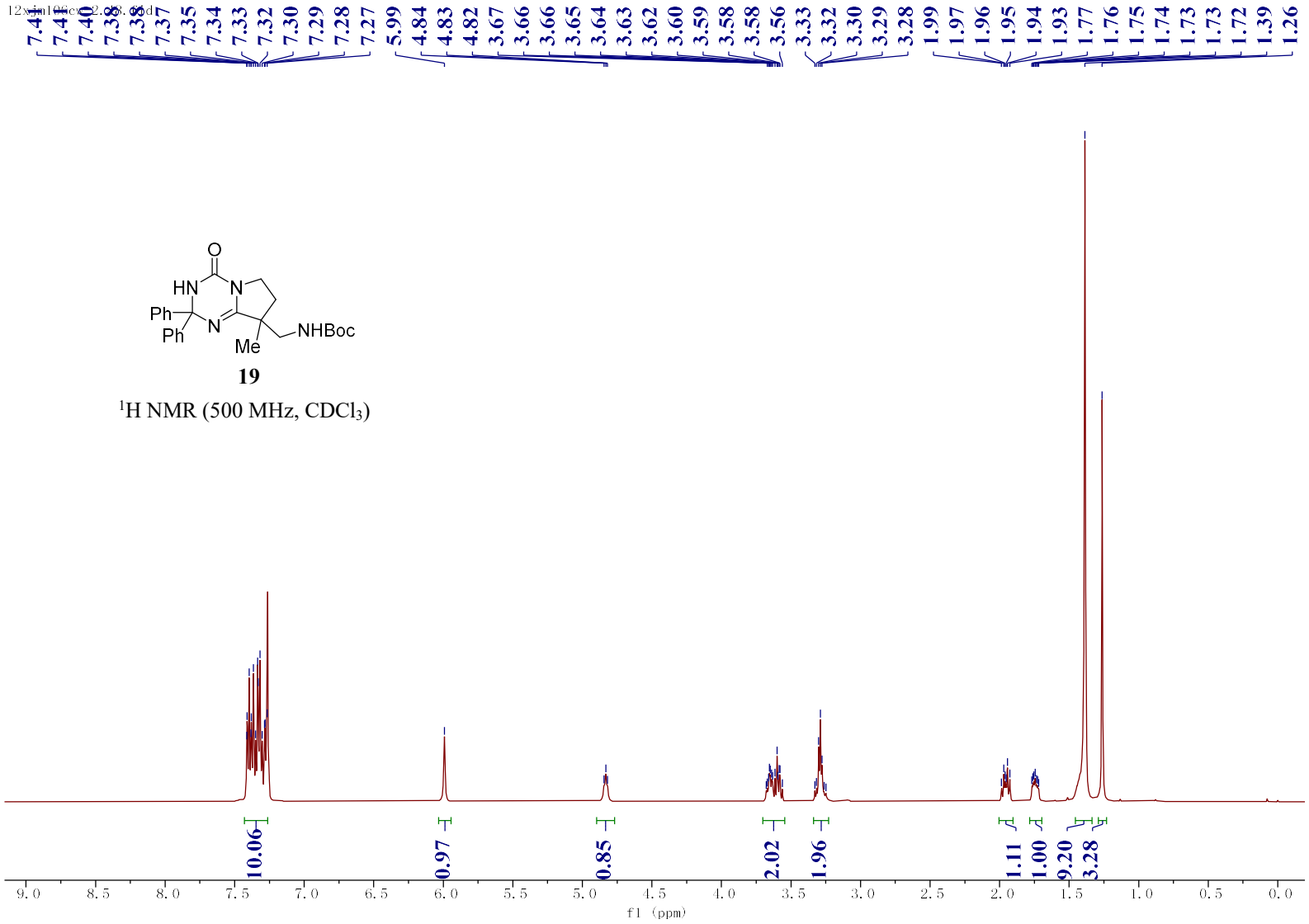
159.79
150.61
148.03
145.93
145.11
130.20
128.77
128.64
128.56
128.23
128.20
128.05
126.27
126.24
126.03
120.35
79.70
55.77
46.90
41.62
29.67
23.48



18

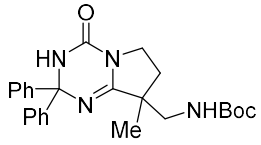
^{13}C NMR (125 MHz, $CDCl_3$)




7.43 7.41 7.40 7.38 7.38 7.37 7.35 7.34 7.33 7.32 7.30 7.29 7.28 7.27
5.99 4.84 4.83 4.82 3.67 3.66 3.66 3.65 3.64 3.63 3.62 3.60 3.59 3.58 3.58 3.56
3.33 3.32 3.30 3.29 3.28
1.99 1.97 1.96 1.95 1.94 1.93 1.77 1.76 1.75 1.74 1.73 1.73 1.72 1.39 1.26
O
HN
N
Ph
Ph
N
Me
NHBoc
19
1H NMR (500 MHz, CDCl3)
10.06
0.97
0.85
2.02
1.96
1.11
1.00
9.20
3.28
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

12xjm106cw-2.47.fid

161.62
156.39
151.25
145.33
128.53
128.41
127.90
127.88
126.45
125.92
79.27
79.03
46.89
45.95
41.93
30.65
28.43
21.87



19

^{13}C NMR (125 MHz, $CDCl_3$)