Supporting Information

Stereoselective synthesis of 2,5-disubstituted pyrrolidines through gold-catalyzed anti-Markovnikov hydroamination-initiated tandem reactions

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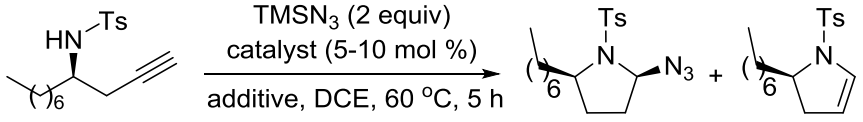
General Information. Ethyl acetate (ACS grade), hexanes (ACS grade) and anhydrous 1,2-dichloroethane (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization.

^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration).

^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

More Reaction Condition, Scope and Mechanism Studies

Table S1 Optimization of reaction conditions of hydroamination/azidation [a]

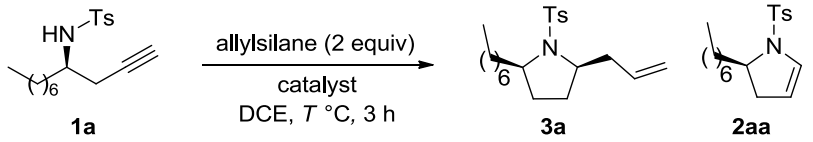


1a **2a** **2aa**

			Yield[b] (%)		
Entry	Catalyst	Additive	**2a**	**2aa**	**1a**
1	$IPrAuNTf_2$ (5 mol %)	-	47	<1	7
2	$IPrAuNTf_2$ (5 mol %)	Et_3N (1 mol %)	69	<1	7
3	$IPrAuNTf_2$ (5 mol %)	Et_3N (1.5 mol %)	52	2	14
4	$IPrAuNTf_2$ (5 mol %)	Et_3N (2 mol %)	36	3	24
5	**$IPrAuNTf_2$ (6 mol %)**	**Et_3N (1 mol %)**	**88**	**<1**	**<1**
6	$Ph_3PAuNTf_2$ (6 mol %)	Et_3N (1 mol %)	70	4	<1
7[c]	CyJohnPhosAuNTf$_2$ (6 mol %)	Et_3N (1 mol %)	49	5	46
8[c]	BrettPhosAuNTf$_2$ (6 mol %)	Et_3N (1 mol %)	25	5	44
9[c,d]	(**Ar**O)$_3$PAuNTf$_2$ (6 mol %)	Et_3N (1 mol %)	12	2	75
10[e]	Au (III) (6 mol %)	Et_3N (1 mol %)	55	<1	14
11[c]	$AgNTf_2$ (10 mol %)	-	44	<5	33

[a] Reaction conditions: **1a** (0.05 mmol), $TMSN_3$ (0.1 mmol), catalyst (5-10 mol %), DCE (0.5 mL), 60 °C, in vials. [b] Measured by ^1H NMR using diethyl phthalate as the internal standard. [c] Reaction time: 24 h. [d] Ar = 2,4-di-*tert*-butylphenyl. [e] Dichloro(2-picolinato)gold(III).

Table S2 Optimization of reaction conditions of hydroamination/allylation[a]

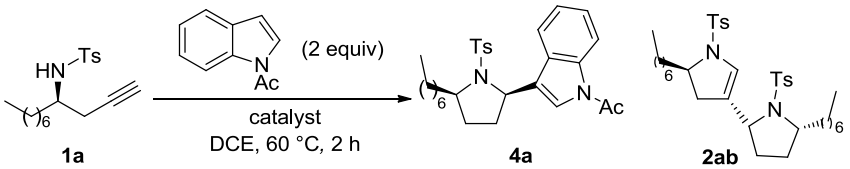


1a **3a** **2aa**

Entry	Catalyst	*T* (°C)	Yield[b] (%) **3a**	**2aa**
1	PPh_3AuNTf_2 (5 mol %)	60	56	<1
2	CyJohnPhosAuNTf$_2$ (5 mol %)	60	24	4
3	XPhosAuNTf$_2$ (5 mol %)	60	43	<1
4	BrettPhosAuNTf$_2$ (5 mol %)	60	43	<1
5	(**Ar**O)$_3$PAuNTf$_2$ (5 mol %)	60	30	<1
6[c]	Au (III) (5 mol %)	60	43	<1
7	**IPrAuNTf$_2$ (5 mol %)**	**60**	**95**	**<1**
8	IPrAuNTf$_2$ (5 mol %)	40	74	7
9	IPrAuNTf$_2$ (5 mol %)	80	60	9
10	AgNTf$_2$ (10 mol %)	60	61	<5
11[d]	CuOTf (10 mol %)	60	<1	<1

[a] Reaction conditions: [**1a**] = 0.1 M, allylsilane (2 equiv), catalyst (5-10 mol %) in DCE at 60 °C, in vials. [b] Measured by ^{1}H NMR using diethyl phthalate as internal standard. [c] Dichloro(2-picolinato)gold(III). [d] Reaction time: 24 h, >95% of **1a** remained unreacted.

Table S3 Optimization of reaction conditions of hydroamination/indolation[a]

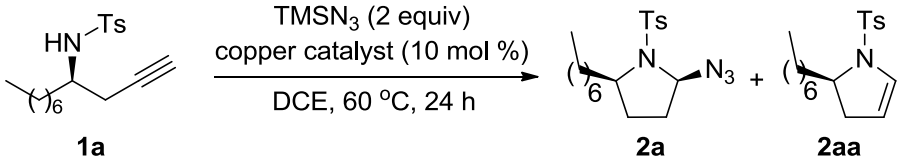


1a **4a** **2ab**

Entry	Catalyst	Yield[b] (%) **4a**	**2ab**
1	IPrAuNTf$_2$ (5 mol %)	17	10
2	BrettPhosAuNTf$_2$ (5 mol %)	<1	<5
3	CyJohnPhosAuNTf$_2$ (5 mol %)	27	6
4	PPh_3AuNTf_2 (5 mol %)	60	10
5	$(ArO)_3PAuNTf_2$ (5 mol %)	49	<1
6[c]	**PPh_3AuNTf_2 (5 mol %)**	**75**	**<1**
7[d]	CuOTf (10 mol %)	16	4

[a] Reaction conditions: [**1a**] = 0.1 M, indole (2 equiv), catalyst (5-10 mol %) in DCE at 60 °C, in vials. [b] Measured by ^{1}H NMR using diethyl phthalate as internal standard. [c] 5 equiv of indole was used. [d] Reaction time: 24 h, 50% of **1a** remained unreacted.

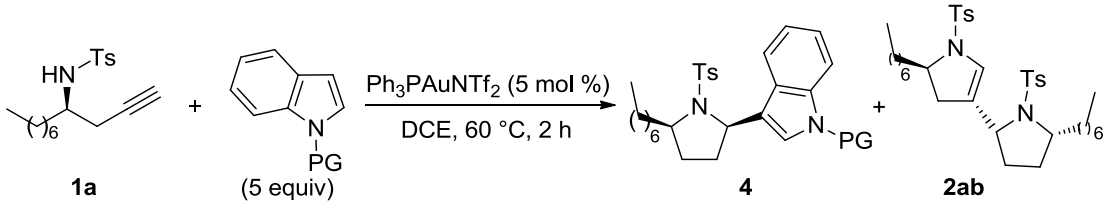
1. The effect of copper catalysts on the reaction of chiral homopropargyl sulfonamide **1a** with $TMSN_3$.



1a **2a** **2aa**

CuOTf: only **1a** (90%) was recovered.
$Cu(CH_3CN)_4PF_6$: only **1a** (>95%) was recovered.

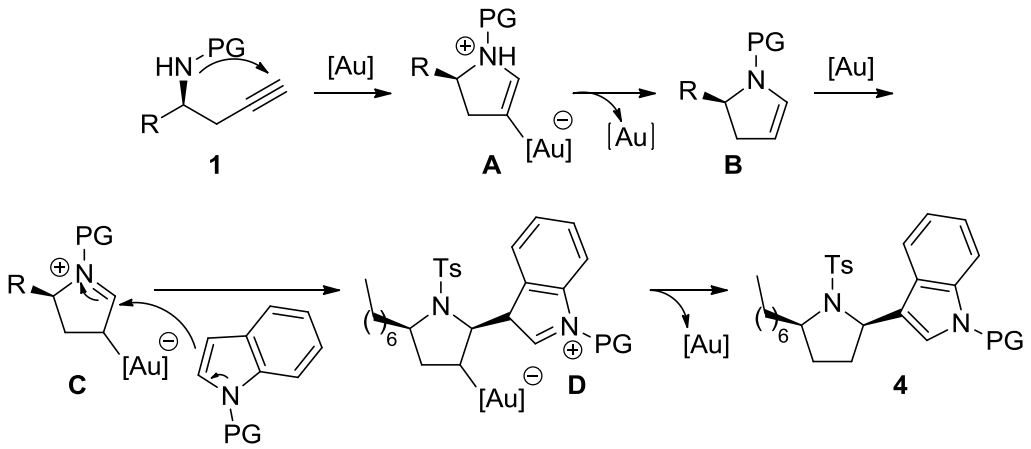
2. The effect of *N*-protecting group of the indole ring.



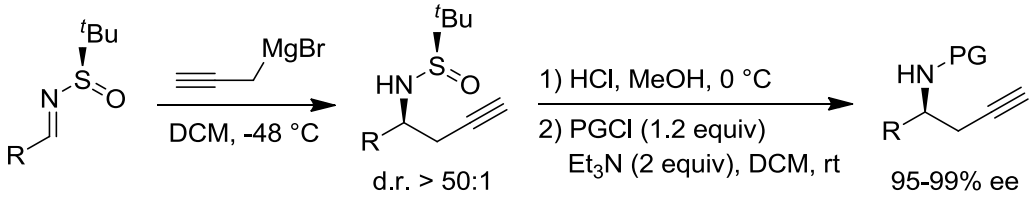
1a (5 equiv) **4** **2ab**

PG = H: **4**, 50%; **2ab**, <1%
PG = Ts: **4**, 7%; **2ab**, 16%
PG = Boc: **4**, 15%; **2ab**, 13%
PG = Bz: **4**, 34%; **2ab**, 12%

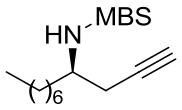
3. Plausible mechanism of hydroamination/indolation.



Compounds **1a-1l** were prepared according to the following known procedures[1] and their data were reported in our previous work.[1]

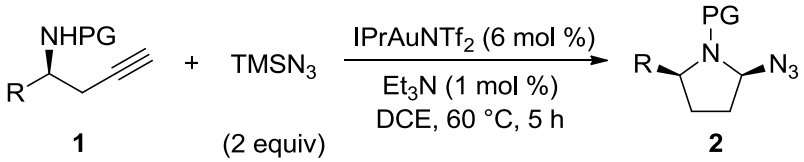


(*R*)-4-methoxy-*N*-(undec-1-yn-4-yl)benzenesulfonamide (1b)



1b

Pale yellow oil. $[\alpha]_D^{20}$ = +33.9 º(c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.88 (d, *J* = 9.2 Hz, 1H), 3.87 (s, 3H), 3.35 – 3.26 (m, 1H), 2.29 (d, *J* = 2.4 Hz, 2H), 1.98 (s, 1H), 1.59 – 1.39 (m, 2H), 1.28 – 1.10 (m, 10H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 132.5, 129.1, 114.1, 79.5, 71.3, 55.5, 51.7, 33.9, 31.6, 29.0, 28.9(8), 25.4, 24.9, 22.5, 14.0; IR (neat): 3281(br), 2928, 2120, 1598, 1428, 1326, 1157, 1081, 913, 814, 668; HRESIMS Calcd for $[C_{18}H_{27}NNaO_3S]^+$ (M + Na^+) 360.1604, found 360.1606.

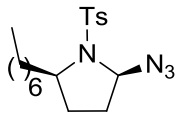


General procedure for the synthesis of azido-substituted pyrrolidines 2:

$TMSN_3$ (53.0 µl, 0.40 mmol), Et_3N (10.0 µl, 0.2 mmol/mL in DCE) and $IPrAuNTf_2$ (10.4 mg, 0.012 mmol) were added in this order to a solution of homopropargyl amide **1** (0.20 mmol) in DCE (2.0 mL) at room temperature (RT). The reaction mixture was then stirred at 60 ^{o}C, and the reaction progress was monitored by TLC. The reaction typically took 5 h. Upon completion, the mixture was concentrated under reduced

pressure and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired product **2**.

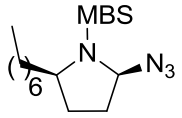
(2*R*,5*R*)-2-azido-5-heptyl-1-tosylpyrrolidine (2a)



2a

Compound **2a** was prepared in 85% yield (62.0 mg) according to the general procedure (Table 2, entry 1). Pale yellow oil. $[\alpha]_D^{20}$ = -20.3 º(c = 1.0, $CHCl_3$). 99% ee (determined by HPLC: Chiralpak ASH Column, 1/99 *i*-PrOH/hexane, 0.6 mL/min, 254 nm; TR = 13.65 min (major), 18.97 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.41 (d, *J* = 6.4 Hz, 1H), 3.57 – 3.49 (m, 1H), 2.43 (s, 3H), 2.07 – 1.93 (m, 1H), 1.90 – 1.82 (m, 1H), 1.76 – 1.65 (m, 2H), 1.59 – 1.46 (m, 1H), 1.45 – 1.37 (m, 1H), 1.36 – 1.25 (m, 10H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 135.4, 129.8, 127.3, 77.3, 61.8, 36.3, 31.7, 29.6, 29.4, 29.1, 25.6, 22.6, 21.5, 14.0; IR (neat): 2923, 2852, 2358, 2110, 1349, 1260, 1160, 1094, 801, 669; HRESIMS Calcd for $[C_{18}H_{28}N_4NaO_2S]^+$ ($M + Na^+$) 387.1825, found 387.1818.

(2*R*,5*R*)-2-azido-5-heptyl-1-((4-methoxyphenyl)sulfonyl)pyrrolidine (2b)

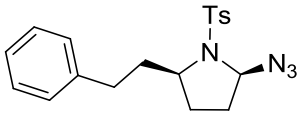


2b

Compound **2b** was prepared in 60% yield (45.6 mg) according to the general procedure (Table 2, entry 2). Pale yellow oil. $[\alpha]_D^{20}$ = -36.5 º(c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 9.2 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.40 (d, *J* = 6.4 Hz, 1H), 3.88 (s, 3H), 3.57 – 3.49 (m, 1H), 2.02 – 1.92 (m, 1H), 1.91 – 1.83 (m, 1H), 1.76 – 1.66 (m, 2H), 1.58 – 1.49 (m, 1H), 1.47 – 1.37 (m, 1H), 1.36 – 1.19 (m, 10H), 0.89 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 130.1, 129.4, 114.4, 77.2, 61.8, 55.6, 36.3, 31.8, 31.7, 29.6, 29.4, 29.2, 25.6, 22.6, 14.0; IR (neat):

2924, 2853, 2359, 2340, 2110, 1596, 1497, 1158, 1094, 803; HRESIMS Calcd for $[C_{18}H_{28}N_4NaO_3S]^+$ (M + Na^+) 403.1774, found 403.1769.

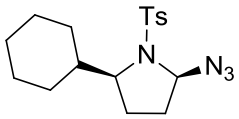
(2*R*,5*R*)-2-azido-5-phenethyl-1-tosylpyrrolidine (2c)



2c

Compound **2c** was prepared in 75% yield (45.6 mg) according to the general procedure (Table 2, entry 3). Pale yellow oil. $[\alpha]_D^{20}$ = -56.4 º(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.25 (m, 4H), 7.23 – 7.19 (m, 3H), 5.41 (d, *J* = 5.2 Hz, 1H), 3.54 – 3.46 (m, 1H), 2.80 – 2.72 (m, 1H), 2.63 – 2.54 (m, 1H), 2.45 – 2.35 (m, 4H), 1.94 – 1.84 (m, 2H), 1.78 – 1.67 (m, 2H), 1.43 – 1.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.1, 135.2, 129.9, 128.4, 127.4, 126.0, 77.4, 61.0, 37.6, 31.9, 31.8, 29.7, 21.5; IR (neat): 2921, 2850, 2358, 2108, 1598, 1455, 1351, 1259, 1161, 814; HRESIMS Calcd for $[C_{19}H_{22}N_4NaO_2S]^+$ (M + Na^+) 393.1356, found 393.1349.

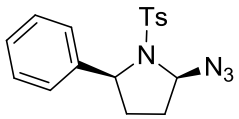
(2*R*,5*S*)-2-azido-5-cyclohexyl-1-tosylpyrrolidine (2d)



2d

Compound **2d** was prepared in 65% yield (45.3 mg) according to the general procedure (Table 2, entry 4). Yellow oil. $[\alpha]_D^{20}$ = -34.2 º(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.44 (d, *J* = 6.0 Hz, 1H), 3.50 – 3.44 (m, 1H), 2.44 (s, 3H), 1.92 – 1.53 (m, 10H), 1.41 – 1.31 (m, 1H), 1.29 – 1.08 (m, 2H), 1.04 – 0.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 135.5, 129.8, 127.5, 77.5, 66.6, 40.8, 31.4, 30.6, 26.5, 26.4, 26.3, 26.0, 25.2, 21.5; IR (neat): 2921, 2850, 2358, 2107, 1453, 1351, 1260, 1160, 1093, 814; HRESIMS Calcd for $[C_{17}H_{24}N_4NaO_2S]^+$ (M + Na^+) 371.1512, found 371.1517.

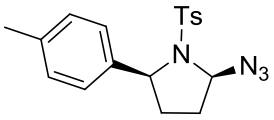
(2*R*,5*S*)-2-azido-5-phenyl-1-tosylpyrrolidine (2e)



2e

Compound **2e** was prepared in 82% yield (56.1 mg) according to the general procedure (Table 2, entry 5). Pale yellow oil. $[\alpha]_D^{20}$ = -118.4 °(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.19 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.76 (d, *J* = 5.6 Hz, 1H), 4.64 – 4.58 (m, 1H), 2.36 (s, 3H), 2.28 – 2.20 (m, 1H), 2.08 – 1.96 (m, 1H), 1.88 – 1.82 (m, 1H), 1.77 – 1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 140.8, 135.6, 129.5, 128.3, 127.5, 127.4, 126.8, 77.6, 65.3, 34.9, 32.2, 21.4; IR (neat): 2918, 2854, 2110, 1606, 1511, 1354, 1260, 1158, 1093, 815, 671; HRESIMS Calcd for $[C_{17}H_{18}N_4NaO_2S]^+$ ($M + Na^+$) 365.1043, found 365.1047.

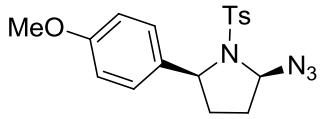
(2*R*,5*S*)-2-azido-5-(*p*-tolyl)-1-tosylpyrrolidine (2f)



2f

Compound **2f** was prepared in 76% yield (54.2 mg) according to the general procedure (Table 2, entry 6). Pale yellow oil. $[\alpha]_D^{20}$ = -157.6 °(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.18 – 7.13 (m, 4H), 7.04 (d, *J* = 7.6 Hz, 2H), 5.75 (d, *J* = 6.0 Hz, 1H), 4.60 – 4.55 (m, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 2.27 – 2.19 (m, 1H), 2.08 – 1.97 (m, 1H), 1.89 – 1.83 (m, 1H), 1.78 – 1.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.8, 137.2, 135.8, 129.4, 129.0, 127.6, 126.8, 77.6, 65.1, 34.9, 32.3, 21.4, 21.0; IR (neat): 2922, 2851, 2109, 1597, 1514, 1354, 1260, 1160, 1093, 813; HRESIMS Calcd for $[C_{18}H_{20}N_4NaO_2S]^+$ ($M + Na^+$) 379.1199, found 379.1192.

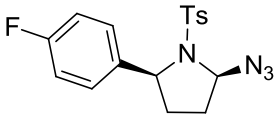
(2*R*,5*S*)-2-azido-5-(4-methoxyphenyl)-1-tosylpyrrolidine (2g)



2g

Compound **2g** was prepared in 84% yield (62.6 mg) according to the general procedure (Table 2, entry 7). Pale yellow oil. $[\alpha]_D^{20}$ = -122.2 °(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.15 (m, 4H), 6.76 (d, *J* = 8.8 Hz, 2H), 5.76 (d, *J* = 5.2 Hz, 1H), 4.62 – 4.56 (m, 1H), 3.77 (s, 3H), 2.37 (s, 3H), 2.27 – 2.18 (m, 1H), 2.08 – 2.04 (m, 1H), 1.98 – 1.86 (m, 1H), 1.85 – 1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 143.6, 136.0, 132.7, 129.4, 128.1, 127.5, 113.8, 77.5, 64.9, 55.2, 34.8, 32.3, 21.4; IR (neat): 2920, 2850, 2359, 2109, 1514, 1353, 1247, 1160, 814, 669; HRESIMS Calcd for $[C_{18}H_{20}N_4NaO_3S]^+$ ($M + Na^+$) 395.1148, found 395.1141.

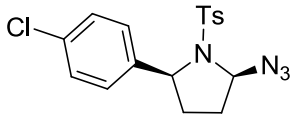
(2*R*,5*S*)-2-azido-5-(4-fluorophenyl)-1-tosylpyrrolidine (2h)



2h

Compound **2h** was prepared in 73% yield (52.6 mg) according to the general procedure (Table 2, entry 8). Pale yellow oil. $[\alpha]_D^{20}$ = -115.9 °(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.17 (m, 4H), 6.93 – 6.88 (m, 2H), 5.77 (d, *J* = 6.0 Hz, 1H), 4.64 – 4.59 (m, 1H), 2.38 (s, 3H), 2.29 – 2.22 (m, 1H), 2.05 – 1.94 (m, 1H), 1.91 – 1.85 (m, 1H), 1.81 – 1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 244.0 Hz), 143.9, 136.6 (d, *J* = 3.0 Hz), 135.7, 129.5, 128.6 (d, *J* = 8.0 Hz), 127.5, 115.2 (d, *J* = 22.0 Hz), 77.6, 64.6, 34.9, 32.3, 21.4; IR (neat): 2918, 2849, 2110, 1511, 1354, 1260, 1160, 1093, 815, 671; HRESIMS Calcd for $[C_{17}H_{17}FN_4NaO_2S]^+$ ($M + Na^+$) 383.0948, found 383.0942.

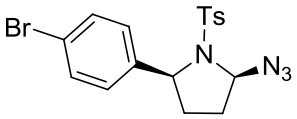
(2*R*,5*S*)-2-azido-5-(4-chlorophenyl)-1-tosylpyrrolidine (2i)



2i

Compound **2i** was prepared in 74% yield (55.8 mg) according to the general procedure (Table 2, entry 9). Pale yellow oil. $[\alpha]_D^{20}$ = -123.9 °(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.13 (m, 6H), 5.78 (d, *J* = 5.2 Hz, 1H), 4.62 – 4.57 (m, 1H), 2.40 (s, 3H), 2.30 – 2.22 (m, 1H), 2.05 – 1.93 (m, 1H), 1.91 – 1.85 (m, 1H), 1.82 – 1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 139.4, 135.6, 133.3, 129.5, 128.5, 128.3, 127.6, 77.6, 64.6, 34.9, 32.3, 21.5; IR (neat): 2920, 2850, 2110, 1597, 1493, 1354, 1259, 1093, 816, 671; HRESIMS Calcd for $[C_{17}H_{17}ClN_4NaO_2]^+$ ($M + Na^+$) 399.0653, found 399.0658.

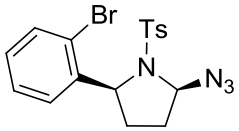
(2*R*,5*S*)-2-azido-5-(4-bromophenyl)-1-tosylpyrrolidine (2j)



2j

Compound **2j** was prepared in 70% yield (59.0 mg) according to the general procedure (Table 2, entry 10). White solid (mp 154-155 °C). $[\alpha]_D^{20}$ = -162.0 °(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.77 (d, *J* = 5.6 Hz, 1H), 4.59 – 4.54 (m, 1H), 2.40 (s, 3H), 2.29 – 2.21 (m, 1H), 2.03 – 1.92 (m, 1H), 1.90 – 1.84 (m, 1H), 1.80 – 1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 139.9, 135.5, 131.4, 129.6, 128.6, 127.5, 121.4, 77.5, 64.6, 34.8, 32.3, 21.5; IR (neat): 2920, 2359, 2341, 2110, 1488, 1455, 1354, 1160, 815, 668; HRESIMS Calcd for $[C_{17}H_{17}BrN_4NaO_2S]^+$ ($M + Na^+$) 443.0148, found 443.0141.

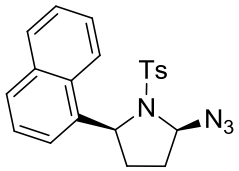
(2*R*,5*S*)-2-azido-5-(2-bromophenyl)-1-tosylpyrrolidine (2k)



2k

Compound **2k** was prepared in 66% yield (55.6 mg) according to the general procedure (Table 2, entry 11). Pale yellow oil. $[\alpha]_D^{20}$ = -66.5 °(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.11 – 7.06 (m, 1H), 5.72 (d, *J* = 5.6 Hz, 1H), 5.04 – 4.99 (m, 1H), 2.41 (s, 3H), 2.39 – 2.32 (m, 1H), 1.88 – 1.77 (m, 2H), 1.68 – 1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 140.5, 134.7, 132.4, 129.8, 128.8, 128.2, 127.9, 127.8, 122.0, 78.0, 64.4, 33.2, 32.0, 21.5; IR (neat): 2359, 2341, 2111, 1356, 1260, 1161, 1093, 814, 669; HRESIMS Calcd for $[C_{17}H_{17}BrN_4NaO_2S]^+$ ($M + Na^+$) 443.0148, found 443.0153.

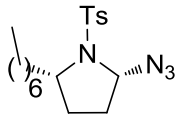
(2*R*,5*S*)-2-azido-5-(naphthalen-1-yl)-1-tosylpyrrolidine (2l)



2l

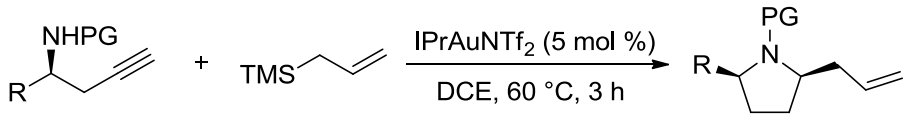
Compound **2l** was prepared in 65% yield (51.0 mg) according to the general procedure (Table 2, entry 12). Pale yellow oil. $[\alpha]_D^{20}$ = -174.0 °(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.89 – 5.86 (m, 1H), 5.52 – 5.47 (m, 1H), 2.45 – 2.36 (m, 1H), 2.34 (s, 3H), 2.10 – 1.99 (m, 1H), 1.96 – 1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.3, 135.3, 133.6, 130.2, 129.4, 128.9, 127.8, 127.6, 126.1, 125.5, 125.4, 124.4, 122.3, 77.9, 62.0, 33.9, 32.1, 21.4; IR (neat): 2919, 2359, 2340, 2110, 1355, 1259, 1160, 1093, 800, 669; HRESIMS Calcd for $[C_{21}H_{20}N_4NaO_2S]^+$ ($M + Na^+$) 415.1199, found 415.1192.

(2*S*,5*S*)-2-azido-5-heptyl-1-tosylpyrrolidine (2a′)



2a′

Compound **2a′** was prepared in 84% yield (61.2 mg) according to the general procedure (Table 2, entry 13). Pale yellow oil. $[\alpha]_D^{20}$ = +23.6 º(c = 1.0, $CHCl_3$).

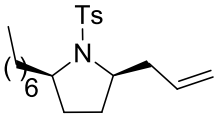


1 (2 equiv) **3**

General procedure for the synthesis of allyl- substituted pyrrolidines 3:

Allylsilane (64.0 µl, 0.40 mmol) and $IPrAuNTf_2$ (9.0 mg, 0.01 mmol) were added in this order to a solution of homopropargyl amide **1** (0.20 mmol) in DCE (2.0 mL) at RT. The reaction mixture was stirred at 60 ^oC, and the reaction progress was monitored by TLC. The reaction typically took 3 h. Upon completion, the mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired product **3**.

(2*R*,5*R*)-2-allyl-5-heptyl-1-tosylpyrrolidine (3a)

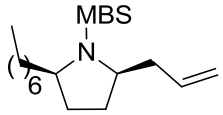


3a

Compound **3a** was prepared in 92% yield (66.9 mg) according to the general procedure (Table 3, entry 1). Pale yellow oil. $[\alpha]_D^{20}$ = -3.1 º(c = 1.0, $CHCl_3$). 99% ee (determined by HPLC: Chiralpak ASH Column, 1/99 *i*-PrOH/hexane, 0.6 mL/min, 254 nm; TR = 13.33 min (minor), 15.03 min (major)). ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.84 – 5.74 (m, 1H), 5.11 – 5.05 (m, 2H), 3.65 – 3.53 (m, 2H), 2.64 – 2.58 (m, 1H), 2.43 (s, 3H), 2.31 – 2.24 (m, 1H), 1.86 – 1.81 (m, 1H), 1.57 – 1.48 (m, 1H), 1.44 – 1.33 (m, 4H), 1.30 – 1.25 (m, 10H), 0.89 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 135.1, 134.8, 129.6, 127.6,

117.4, 61.9, 60.9, 41.4, 36.9, 31.8, 29.5, 29.4, 29.3, 28.9, 26.3, 22.7, 21.5, 14.1; IR (neat): 2921, 2111, 1348, 1260, 1161, 1093, 802, 667, 591, 564; HRESIMS Calcd for $[C_{21}H_{33}NNaO_2S]^+$ (M + Na^+) 386.2124, found 386.2127.

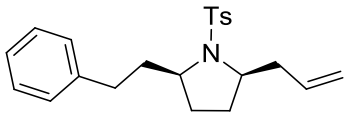
(2*R*,5*R*)-2-allyl-5-heptyl-1-((4-methoxyphenyl)sulfonyl)pyrrolidine (3b)



3b

Compound **3b** was prepared in 80% yield (60.7 mg) according to the general procedure (Table 3, entry 2). Pale yellow oil. $[\alpha]_D^{20}$ = -33.5 º(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 5.84 – 5.74 (m, 1H), 5.10 – 5.05 (m, 2H), 3.87 (s, 3H), 3.64 – 3.52 (m, 2H), 2.63 – 2.57 (m, 1H), 2.31 – 2.26 (m, 1H), 1.82 – 1.80 (m, 1H), 1.62 – 1.51 (m, 1H), 1.48 – 1.37 (m, 4H), 1.34 – 1.28 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 134.8, 130.0, 129.5, 117.4, 114.1, 61.9, 60.9, 55.5, 41.4, 36.9, 31.8, 29.5(1), 29.4(5), 29.3, 28.9, 26.3, 22.7, 14.1; IR (neat): 2924, 2853, 2359, 2340, 2110, 1596, 1497, 1353, 1261, 1158, 1094, 835; HRESIMS Calcd for $[C_{21}H_{33}NNaO_3S]^+$ (M + Na^+) 402.2073, found 402.2078.

(2*R*,5*R*)-2-allyl-5-phenethyl-1-tosylpyrrolidine (3c)

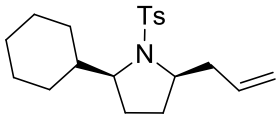


3c

Compound **3c** was prepared in 80% yield (59.1 mg) according to the general procedure (Table 3, entry 3). Pale yellow oil. $[\alpha]_D^{20}$ = -22.6 º(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.25 (m, 4H), 7.23 – 7.18 (m, 3H), 5.85 – 5.76 (m, 1H), 5.15 – 5.06 (m, 2H), 3.72 – 3.54 (m, 2H), 2.76 – 2.69 (m, 2H), 2.67 – 2.60 (m, 1H), 2.41 (s, 3H), 2.35 – 2.31 (m, 1H), 2.29 – 2.22 (m, 1H), 1.79 – 1.71 (m, 1H), 1.65 – 1.44 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 141.6, 134.8, 134.6, 129.6, 128.4(2), 128.3(6), 127.6, 125.8, 117.6, 61.2, 61.1, 41.4, 38.2,

32.5, 29.6, 28.8, 21.5; IR (neat): 3365, 2922, 2852, 2109, 1598, 1494, 1453, 1344, 1260, 802; HRESIMS Calcd for $[C_{22}H_{27}NNaO_2S]^+$ (M + Na^+) 392.1651, found 392.1658.

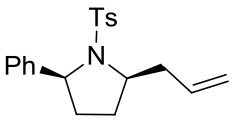
(2*R*,5*S*)-2-allyl-5-cyclohexyl-1-tosylpyrrolidine (3d)



3d

Compound **3d** was prepared in 89% yield (61.9 mg) according to the general procedure (Table 3, entry 4). Pale yellow oil. $[\alpha]_D^{20}$ = -43.7 º(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 5.74 – 5.64 (m, 1H), 5.07 – 5.02 (m, 2H), 3.96 – 3.92 (m, 1H), 3.79 – 3.76 (m, 1H), 2.85 – 2.78 (m, 1H), 2.41 (s, 3H), 2.21 – 2.16 (m, 1H), 2.00 – 1.94 (m, 2H), 1.74 – 1.67 (m, 4H), 1.61 – 1.57 (m, 1H), 1.50 – 1.47 (m, 2H), 1.24 – 1.17 (m, 1H), 1.09 – 0.92 (m, 2H), 0.89 – 0.79 (m, 1H), 0.73 – 0.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 139.7, 135.1, 129.3, 126.8, 117.4, 64.8, 61.1, 40.0, 39.0, 30.6, 28.9, 26.5, 26.4(8), 26.3, 25.8, 24.3, 21.4; IR (neat): 2923, 2851, 2110, 1598, 1446, 1339, 1261, 1157, 1095, 813; HRESIMS Calcd for $[C_{20}H_{29}NNaO_2S]^+$ (M + Na^+) 370.1811, found 370.1816.

(2*R*,5*S*)-2-allyl-5-phenyl-1-tosylpyrrolidine (3e)

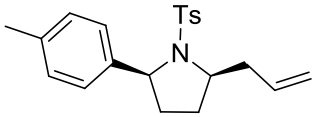


3e

Compound **3e** was prepared in 85% yield (58.0 mg) according to the general procedure (Table 3, entry 5). Pale yellow oil. $[\alpha]_D^{20}$ = -54.2 º(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.08 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.97 (m, 2H), 5.80 – 5.71 (m, 1H), 5.12 – 5.06 (m, 2H), 4.98 (d, *J* = 8.0 Hz, 1H), 4.19 – 4.14 (m, 1H), 2.90 – 2.86 (m, 1H), 2.41 – 2.32 (m, 1H), 2.31 – 2.29 (m, 4H), 2.28 – 2.16 (m, 1H) 1.85 – 1.80 (m, 1H), 1.71 – 1.66 (m, 1H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 142.3, 142.2, 138.6, 134.8, 128.9, 128.0, 126.8, 126.7(5), 126.5, 117.7, 64.0, 60.7, 39.1, 33.0, 27.5, 21.3; IR (neat): 2922, 2851, 1641, 1494, 1453, 1341, 1261, 1156, 1095, 812; HRESIMS Calcd for $[C_{20}H_{23}NNaO_2S]^+$ (M + Na^+) 364.1342, found 364.1347.

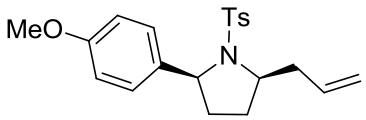
(2*R*,5*S*)-2-allyl-5-(*p*-tolyl)-1-tosylpyrrolidine (3f)



3f

Compound **3f** was prepared in 85% yield (60.4 mg) according to the general procedure (Table 3, entry 6). Pale yellow oil. $[\alpha]_D^{20}$ = -46.6 º(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.92 – 6.87 (m, 4H), 5.80 – 5.70 (m, 1H), 5.11 – 5.06 (m, 2H), 4.93 (d, *J* = 8.5 Hz, 1H), 4.18 – 4.14 (m, 1H), 2.89 – 2.84 (m, 1H), 2.40 – 2.34 (m, 4H), 2.33 – 2.30 (m, 4H), 2.28 – 2.25 (m, 1H), 1.85 – 1.80 (m, 1H), 1.70 – 1.65 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 139.3, 138.8, 136.4, 134.8, 128.8, 128.6, 126.9, 126.5, 117.6, 63.8, 60.7, 39.2, 33.1, 27.6, 21.3, 20.9; IR (neat): 2960, 2922, 2109, 1598, 1529, 1452, 1346, 1181, 1157, 811; HRESIMS Calcd for $[C_{21}H_{25}NNaO_2S]^+$ (M + Na^+) 378.1498, found 378.1494.

(2*R*,5*S*)-2-allyl-5-(4-methoxyphenyl)-1-tosylpyrrolidine (3g)

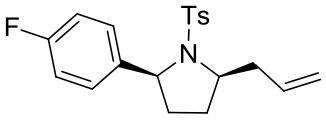


3g

Compound **3g** was prepared in 93% yield (69.1 mg) according to the general procedure (Table 3, entry 7). Pale yellow oil. $[\alpha]_D^{20}$ = +26.9 º(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.25 (m, 4H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.85 – 5.76 (m, 1H), 5.13 – 5.06 (m, 2H), 4.65 – 4.61 (m, 1H), 3.88 – 3.83 (m, 1H), 3.80 (s, 3H), 2.85 – 2.79 (m, 1H), 2.42 (s, 3H), 2.37 – 2.30 (m, 1H), 1.90 – 1.82 (m, 2H), 1.63 – 1.58 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 143.3,

135.1, 134.8, 134.6, 129.5, 127.7, 127.4, 117.6, 113.7, 64.4, 61.5, 55.3, 41.3, 34.2, 29.1, 21.5; IR (neat): 2922, 2852, 1529, 1513, 1453, 1347, 1260, 1159, 1094, 812; HRESIMS Calcd for $[C_{21}H_{25}NNaO_3S]^+$ (M + Na^+) 394.1447, found 394.1442.

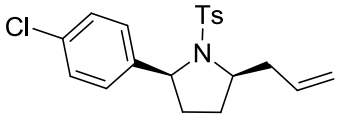
(2*R*,5*S*)-2-allyl-5-(4-fluorophenyl)-1-tosylpyrrolidine (3h)



3h

Compound **3h** was prepared in 82% yield (59.0 mg) according to the general procedure (Table 3, entry 8). Pale yellow oil. $[\alpha]_D^{20}$ = -29.7 º(c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.81 – 6.76 (m, 2H), 5.80 – 5.71 (m, 1H), 5.12 – 5.07 (m, 2H), 4.95 (d, *J* = 8.5 Hz, 1H), 4.20 – 4.16 (m, 1H), 2.95 – 2.86 (m, 1H), 2.45 – 2.26 (m, 5H), 2.17 – 2.11 (m, 1H), 1.87 – 1.82 (m, 1H), 1.69 – 1.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7 (d, *J* = 243.8 Hz), 142.6, 138.7, 138.1 (d, *J* = 3.8 Hz), 134.7, 129.0, 128.1 (d, *J* = 7.5 Hz), 126.8, 117.8, 114.7 (d, *J* = 21.3 Hz), 63.2, 60.9, 39.1, 33.0, 27.5, 21.3; IR (neat): 2920, 2850, 1510, 1454, 1343, 1261, 1156, 846, 1095, 812; HRESIMS Calcd for $[C_{20}H_{22}FNNaO_2S]^+$ (M + Na^+) 382.1247, found 382.1241.

(2*R*,5*S*)-2-allyl-5-(4-chlorophenyl)-1-tosylpyrrolidine (3i)

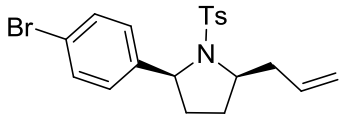


3i

Compound **3i** was prepared in 84% yield (63.2 mg) according to the general procedure (Table 3, entry 9). Yellow oil. $[\alpha]_D^{20}$ = -31.1 º(c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.05 (m, 4H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.79 – 5.69 (m, 1H), 5.12 – 5.07 (m, 2H), 4.92 (d, *J* = 8.5 Hz, 1H), 4.21 – 4.17 (m, 1H), 2.88 – 2.80 (m, 1H), 2.49 – 2.36 (m, 4H), 2.32 – 2.25 (m, 1H), 2.16 – 2.06 (m, 1H), 1.87 – 1.82 (m, 1H), 1.69 – 1.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 140.9, 138.6, 134.6, 132.6, 129.0, 128.1, 127.9, 126.8, 117.8, 63.2, 61.0, 39.1,

33.0, 27.4, 21.4; IR (neat): 2921, 2851, 1529, 1493, 1453, 1344, 1261, 1181, 1156, 1095, 812; HRESIMS Calcd for $[C_{20}H_{22}ClNNaO_2S]^+$ (M + Na^+) 398.0952, found 398.0956.

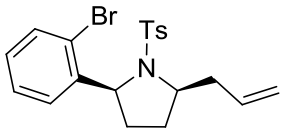
(2*R*,5*S*)-2-allyl-5-(4-bromophenyl)-1-tosylpyrrolidine (3j)



3j

Compound **3j** was prepared in 94% yield (79.0 mg) according to the general procedure (Table 3, entry 10). Pale yellow oil. $[\alpha]_D^{20}$ = -27.8 °(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.78 – 5.69 (m, 1H), 5.12 – 5.07 (m, 2H), 4.90 (d, *J* = 9.0 Hz, 1H), 4.21 – 4.16 (m, 1H), 2.87 – 2.84 (m, 1H), 2.45 – 2.36 (m, 4H), 2.32 – 2.25 (m, 1H), 2.15 – 2.06 (m, 1H), 1.87 – 1.84 (m, 1H), 1.68 – 1.63 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 141.3, 138.6, 134.6, 131.0, 129.0, 128.3, 126.8, 120.7, 117.8, 63.2, 61.0, 39.0, 32.9, 27.4, 21.4; IR (neat): 2922, 2851, 2359, 2341, 1529, 1453, 1345, 1261, 1156, 1095, 812; HRESIMS Calcd for $[C_{20}H_{22}BrNNaO_2S]^+$ (M + Na^+) 442.0447, found 442.0441.

(2*R*,5*S*)-2-allyl-5-(2-bromophenyl)-1-tosylpyrrolidine (3k)

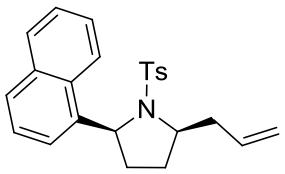


3k

Compound **3k** was prepared in 73% yield (61.4 mg) according to the general procedure (Table 3, entry 11). Pale yellow oil. $[\alpha]_D^{20}$ = -83.2 °(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.11 (m, 2H), 7.06 – 7.02 (m, 1H), 5.69 – 5.59 (m, 1H), 5.31 (d, *J* = 8.5 Hz, 1H), 5.07 – 5.02 (m, 2H), 4.36 – 4.30 (m, 1H), 2.85 – 2.81 (m, 1H), 2.43 – 2.31 (m, 4H), 2.16 – 2.09 (m, 1H), 2.05 – 1.95 (m, 1H), 1.79 – 1.74 (m, 1H),

1.72 – 1.67 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 141.6, 138.6, 134.5, 132.6, 129.4, 128.2, 128.0, 127.1, 126.9, 121.5, 117.9, 63.2, 61.4, 37.9, 31.8, 26.1, 21.4; IR (neat): 2920, 2359, 2341, 1343, 1155, 1095, 1023, 813, 668; HRESIMS Calcd for $[C_{20}H_{22}BrNNaO_2S]^+$ (M + Na^+) 442.0447, found 442.0439.

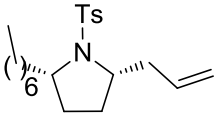
(2*R*,5*S*)-2-allyl-5-(naphthalen-1-yl)-1-tosylpyrrolidine (3l)



3l

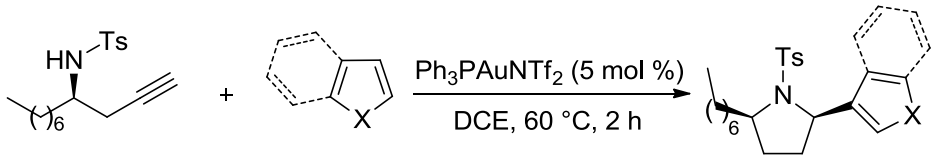
Compound **3l** was prepared in 85% yield (66.6 mg) according to the general procedure (Table 3, entry 12). Yellow oil. $[\alpha]_D^{20}$ = -37.7 º(c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.25 – 7.16 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.82 (d, *J* = 8.0 Hz, 1H), 5.77 – 5.68 (m, 1H), 5.11 – 5.06 (m, 2H), 4.36 – 4.32 (m, 1H), 3.00 – 2.93 (m, 1H), 2.53 – 2.42 (m, 1H), 2.34 (s, 3H), 2.30 – 2.23 (m, 1H), 2.11 – 2.02 (m, 1H), 1.84 – 1.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 138.8, 137.3, 134.8, 133.7, 129.8, 129.1, 128.9, 127.3, 127.1, 126.0, 125.3, 124.8, 124.0, 122.6, 117.8, 61.0, 60.9, 38.4, 32.0, 27.1, 21.4; IR (neat): 2920, 2359, 2341, 1340, 1260, 1154, 1096, 800, 669; HRESIMS Calcd for $[C_{24}H_{25}NNaO_2S]^+$ (M + Na^+) 414.1498, found 414.1496.

(2*S*,5*S*)-2-allyl-5-heptyl-1-tosylpyrrolidine (3a′)



3a′

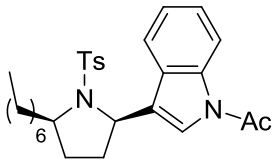
Compound **3a′** was prepared in 90% yield (65.4 mg) according to the general procedure (Table 3, entry 13). Pale yellow oil. $[\alpha]_D^{20}$ = +6.5 º(c = 1.0, $CHCl_3$).



General procedure for the synthesis of heterocycle-substituted pyrrolidines 4:

Heterocycle (1.00 mmol) and $Ph_3PAuNTf_2$ (7.4 mg, 0.01 mmol) were added in this order to a solution of homopropargyl amide **1a** (0.20 mmol) in DCE (2.0 mL) at RT. The reaction mixture was stirred at 60 ^oC, and the reaction progress was monitored by TLC. The reaction typically took 2 h. Upon completion, the mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired product **4**.

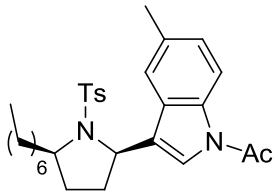
1-(3-((2*R*,5*R*)-5-heptyl-1-tosylpyrrolidin-2-yl)-1*H*-indol-1-yl)ethan-1-one (4a)



4a

Compound **4a** was prepared in 71% yield (68.3 mg) according to the general procedure (Table 4, entry 1). Pale yellow solid (mp 94-95 ^oC). $[\alpha]_D^{20}$ = +55.6 ^{o}(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.41 (s, 1H), 7.35 – 7.28 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 5.01 – 4.97 (m, 1H), 3.76 – 3.73 (m, 1H), 2.61 (s, 3H), 2.42 (s, 3H), 2.17 – 2.09 (m, 1H), 2.02 – 1.95 (m, 1H), 1.93 – 1.85 (m, 1H), 1.76 – 1.68 (m, 1H), 1.60 – 1.52 (m, 2H), 1.43 – 1.25 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 143.5, 136.5, 134.8, 129.6, 128.2, 127.6, 125.2, 124.9, 123.3, 123.0, 118.9, 116.9, 62.1, 58.0, 37.1, 31.7, 31.5, 30.0, 29.5, 29.3, 26.6, 23.9, 22.6, 21.5, 14.0; IR (neat): 2955, 2926, 2855, 2360, 2337, 1707, 1598, 1451, 1383, 1347, 1330, 1220, 1160, 1091, 749, 665, 587, 550; HRESIMS Calcd for $[C_{28}H_{36}N_2NaO_3S]^+$ ($M + Na^+$) 503.2339, found 503.2349.

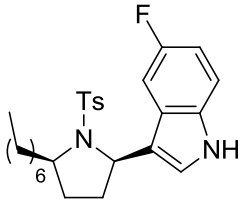
1-(3-((2*R*,5*R*)-5-heptyl-1-tosylpyrrolidin-2-yl)-5-methyl-1*H*-indol-1-yl)ethan-1-one (4b)



4b

Compound **4b** was prepared in 71% yield (70.2 mg) according to the general procedure (Table 4, entry 2). Pale yellow oil. $[\alpha]_D^{20}$ = +59.5 º(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.36 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 (s, 1H), 7.17 – 7.14 (m, 1H), 4.98 – 4.94 (m, 1H), 3.78 – 3.70 (m, 1H), 2.59 (s, 3H), 2.43 (s, 6H), 2.20 – 2.10 (m, 1H), 2.02 – 1.94 (m, 1H), 1.93 – 1.84 (m, 1H), 1.77 – 1.68 (m, 1H) 1.60 – 1.51 (m, 2H), 1.38 – 1.25 (m, 10H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 143.5, 134.9, 134.7, 132.9, 129.6, 128.4, 127.6, 126.5, 124.7, 123.1, 118.8, 116.6, 62.1, 58.1, 37.1, 31.8, 31.5, 30.1, 29.5, 29.3, 26.7, 23.8, 22.6, 21.5, 21.4, 14.0; IR (neat): 2955, 2924, 2855, 1701, 1636, 1598, 1459, 1383, 1346, 1326, 1218, 1158, 1090, 938, 812, 666, 638, 587, 550; HRESIMS Calcd for $[C_{29}H_{38}N_2NaO_3S]^+$ ($M + Na^+$) 517.2495, found 517.2502.

5-fluoro-3-((2*R*,5*R*)-5-heptyl-1-tosylpyrrolidin-2-yl)-1*H*-indole (4c)

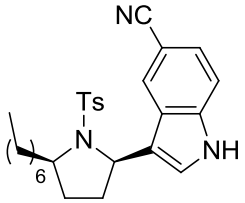


4c

Compound **4c** was prepared in 61% yield (55.7 mg) according to the general procedure (Table 4, entry 3). Pale yellow oil. $[\alpha]_D^{20}$ = +50.4 º(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.15 (m, 3H), 6.89 – 6.84 (m, 1H), 4.99 – 4.96 (m, 1H), 3.76 – 3.69 (m, 1H), 2.42 (s, 3H), 2.16 – 2.12 (m, 1H), 2.02 – 1.96 (m, 1H), 1.75 – 1.60 (m, 2H), 1.58

– 1.53 (m, 2H), 1.38 – 1.25 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4 (d, *J* = 232.5 Hz), 143.3, 135.0, 133.3, 129.5, 127.6, 125.4 (d, *J* = 10.0 Hz), 124.6, 118.1 (d, *J* = 5.0 Hz), 112.1 (d, *J* = 15.0 Hz), 110.2 (d, *J* = 26.3 Hz), 103.9 (d, *J* = 23.8 Hz), 62.1, 58.7, 37.3, 32.0, 31.8, 30.0, 29.5, 29.3, 26.8, 22.6, 21.5, 14.1; IR (neat): 3385, 2955, 2926, 2856, 1627, 1579, 1486, 1457, 1339, 1158, 1091, 1036, 815, 798, 666, 587, 550; HRESIMS Calcd for $[C_{26}H_{33}FN_2NaO_2S]^+$ (M + Na^+) 479.2139, found 479.2134.

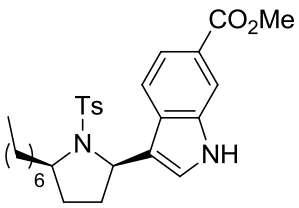
3-((2*R*,5*R*)-5-heptyl-1-tosylpyrrolidin-2-yl)-1*H*-indole-5-carbonitrile (4d)



4d

Compound **4d** was prepared in 68% yield (63.1 mg) according to the general procedure (Table 4, entry 4). Pale yellow oil. $[\alpha]_D^{20}$ = +64.8 °(c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.85 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.27 (m, 3H), 5.02 – 4.98 (m, 1H), 3.75 – 3.69 (m, 1H), 2.45 (s, 3H), 2.19 – 2.13 (m, 1H), 1.99 – 1.92 (m, 1H), 1.89 – 1.81 (m, 1H), 1.74 – 1.67 (m, 1H), 1.62 – 1.55 (m, 2H), 1.41 – 1.24 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 138.4, 134.5, 129.8, 127.6, 124.9, 124.6, 124.3, 120.7, 119.2, 112.3, 103.3, 102.2, 62.2, 58.4, 37.2, 32.4, 31.8, 30.0, 29.5, 29.3, 26.7, 22.6, 21.5, 14.1; IR (neat): 3373, 2953, 2925, 2855, 2219, 1619, 1598, 1470, 1436, 1337, 1157, 1090, 1034, 808, 666, 588, 551; HRESIMS Calcd for $[C_{27}H_{33}N_3NaO_2S]^+$ (M + Na^+) 486.2186, found 486.2182.

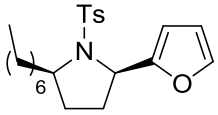
methyl 3-((2*R*,5*R*)-5-heptyl-1-tosylpyrrolidin-2-yl)-1*H*-indole-6-carboxylate (4e)



4e

Compound **4e** was prepared in 60% yield (59.6 mg) according to the general procedure (Table 4, entry 5). Pale yellow oil. $[\alpha]_D^{20}$ = +86.5 º(c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.02 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.72 – 7.69 (m, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.38 (s, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 5.08 – 5.04 (m, 1H), 3.93 (s, 3H), 3.76 – 3.69 (m, 1H), 2.43 (s, 3H), 2.20 – 2.12 (m, 1H), 2.04 – 1.96 (m, 1H), 1.87 – 1.79 (m, 1H), 1.74 – 1.67 (m, 1H), 1.60 – 1.52 (m, 2H), 1.34 – 1.25 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 143.3, 136.1, 134.9, 129.6, 128.6, 127.6, 126.2, 123.3, 120.2, 118.6, 118.2, 113.8, 62.1, 58.6, 51.9, 37.3, 32.3, 31.8, 30.1, 29.5, 29.3, 26.7, 22.6, 21.5, 14.1; IR (neat): 3412, 2950, 2923, 2851, 1708, 1690, 1649, 1624, 1457, 1437, 1317, 1212, 1157, 773, 662, 588, 549; HRESIMS Calcd for $[C_{28}H_{36}N_2NaO_4S]^+$ (M + Na^+) 519.2288, found 519.2293.

(2*R*,5*R*)-2-(furan-2-yl)-5-heptyl-1-tosylpyrrolidine (4f)



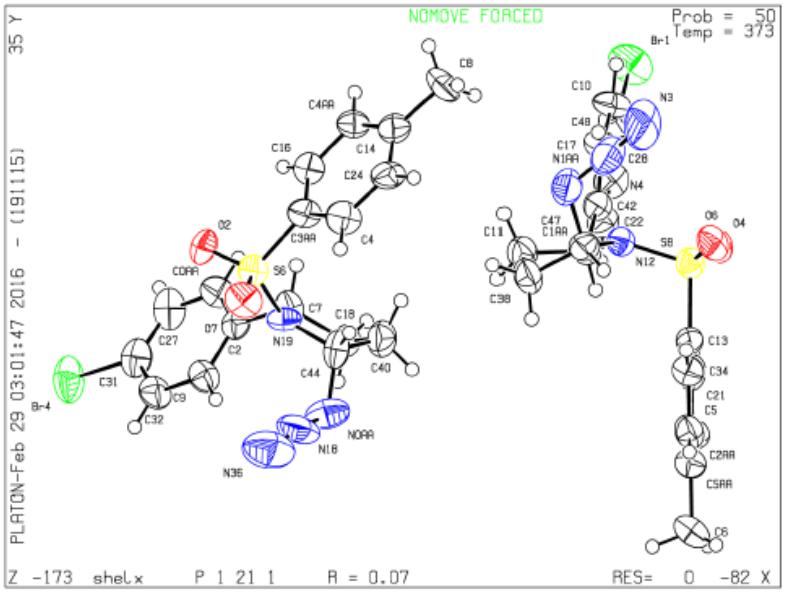
4f

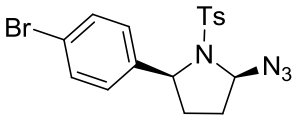
Compound **4f** was prepared in 58% yield (45.2 mg) according to the general procedure (Table 4, entry 6). Yellow oil. $[\alpha]_D^{20}$ = +23.0 º(c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.25 (m, 3H), 6.30 – 6.26 (m, 2H), 4.85 – 4.81 (m, 1H), 3.75 – 3.67 (m, 1H), 2.42 (s, 3H), 2.07 – 1.94 (m, 2H), 1.77 – 1.52 (m, 3H), 1.50 – 1.33 (m, 1H), 1.29 – 1.25 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 143.2, 141.7, 135.7, 129.5, 127.5, 110.2, 107.1, 62.0, 58.1, 36.5, 31.8, 30.4, 30.3, 29.4, 29.2, 26.3, 22.6, 21.5, 14.1; IR (neat): 2955, 2926, 2855, 1636, 1599, 1460, 1350, 1162, 1093, 1006, 815, 730, 665, 588, 550; HRESIMS Calcd for $[C_{22}H_{31}NNaO_3S]^+$ (M + Na^+) 412.1917, found 412.1924.

Reference:

1. a) T.-D. Tan, X.-Q. Zhu, H.-Z. Bu, G.-C. Deng, Y.-B. Chen, R.-S. Liu, L.-W. Ye, *Angew. Chem., Int. Ed.* **2019**, *58*, 9632; b) Y.-F. Yu, C. Shu, T.-D. Tan, L. Li, S. Rafique, L.-W. Ye, *Org. Lett.* **2016**, *18*, 5178; c) C. Shu, L. Li, C.-H. Shen, P.-P. Ruan, C.-Y. Liu, L.-W. Ye, *Chem. Eur. J.* **2016**, *22*, 2282; d) Y.-F. Yu, C. Shu, B. Zhou, J.-Q. Li, J.-M. Zhou, L.-W. Ye, *Chem. Commun.* **2015**, *51*, 2126; e) C. Shu, M.-Q. Liu, Y.-Z. Sun, L.-W. Ye, *Org. Lett.* **2012**, *14*, 4958.

Compound 2j. CCDC Number = 1937618





Bond precision: C-C = 0.0195 A Wavelength=0.71073

Cell: a=12.51500 b=13.74000 c=12.60700
alpha=90 beta=120.1900 gamma=90

Temperature: 373 K

	Calculated	Reported
Volume	1873.809	1874
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C17 H17 Br N4 O2 S	4(C17 H17 Br N4 O2 S)
Sum formula	C17 H17 Br N4 O2 S	C68 H68 Br4 N16 O8 S4
Mr	421.31	1685.26
Dx,g cm-3	1.493	1.493
Z	4	1
Mu (mm-1)	2.323	2.323
F000	856.0	856.0
F000'	855.63	
h,k,lmax	16,17,16	16,17,16
Nref	8560[4462]	8504
Tmin,Tmax	0.665,0.739	0.279,1.000
Tmin'	0.622	

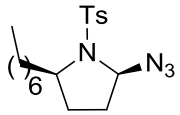
Correction method= # Reported T Limits: Tmin=0.279 Tmax=1.000
AbsCorr = MULTI-SCAN

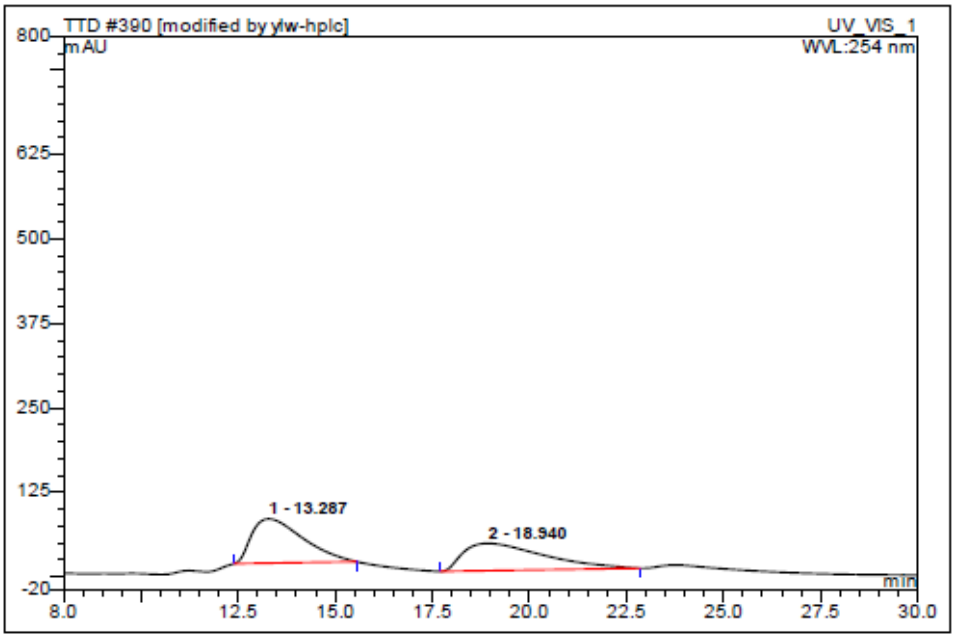
Data completeness= 1.91/0.99 Theta(max)= 27.448

R(reflections)= 0.0729(3855) wR2(reflections)= 0.2339(8504)

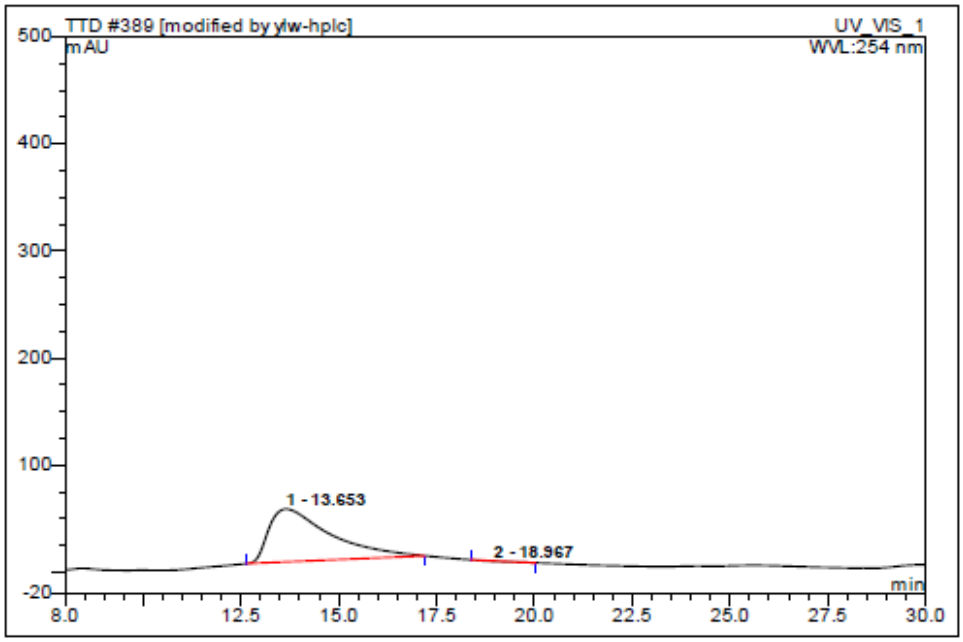
S = 0.971 Npar= 453

Compound **2a**



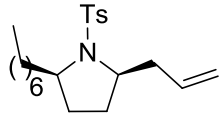


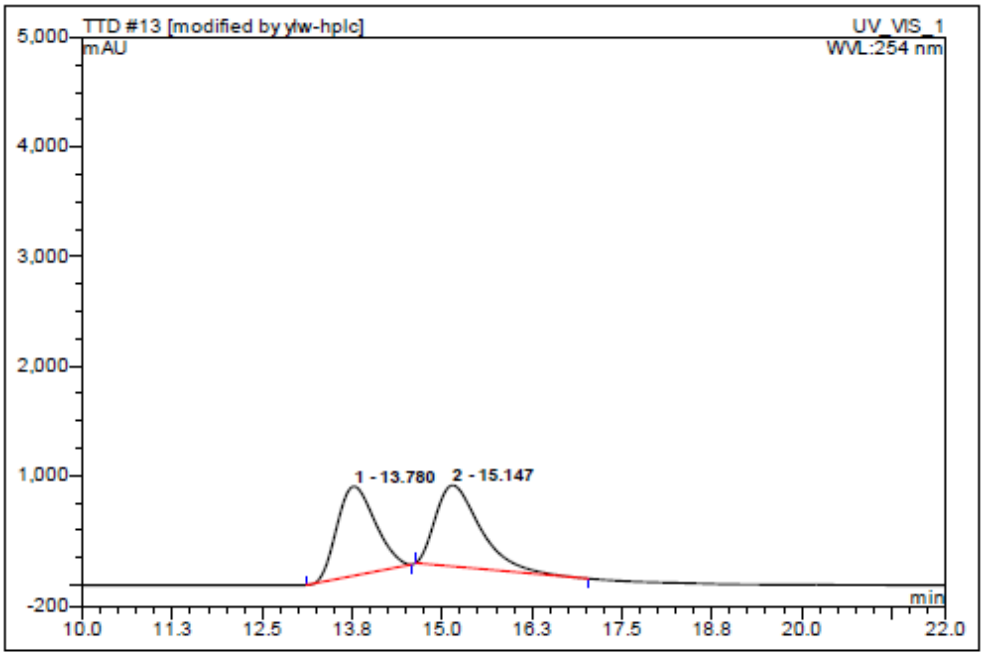
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	13.29	n.a.	65.418	100.404	50.83	n.a.	BMB*
2	18.94	n.a.	40.383	97.129	49.17	n.a.	BMB*
Total:			105.801	197.533	100.00	0.000	



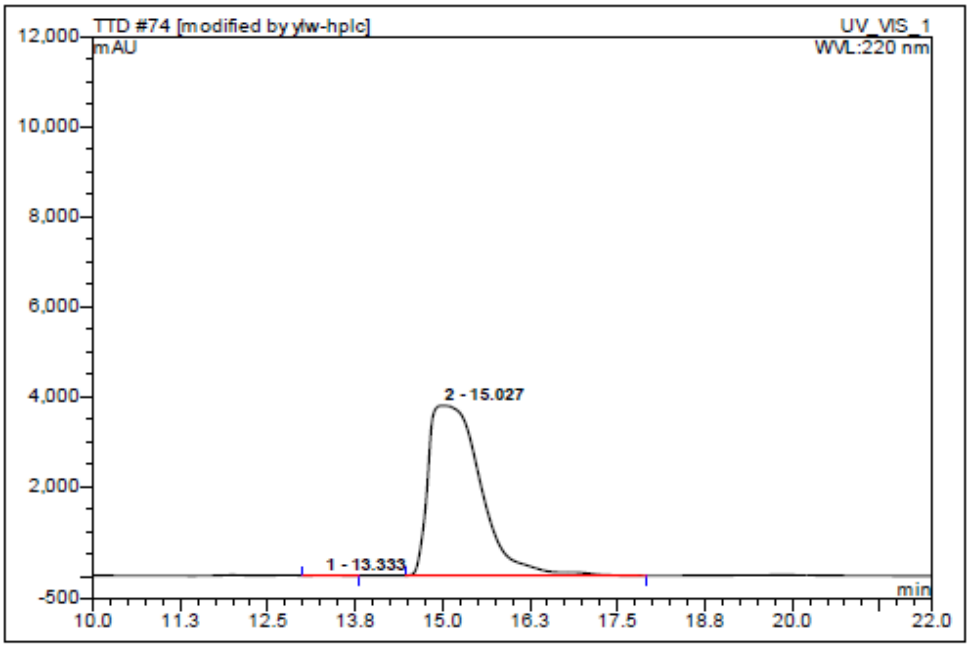
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	13.65	n.a.	49.304	89.578	99.62	n.a.	BMB*
2	18.97	n.a.	0.386	0.345	0.38	n.a.	BMB*
Total:			49.690	89.923	100.00	0.000	

Compound **3a**



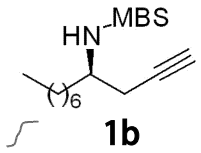


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	13.78	n.a.	814.159	499.572	48.31	n.a.	BMB*
2	15.15	n.a.	739.763	534.607	51.69	n.a.	BMB*
Total:			1553.922	1034.179	100.00	0.000	

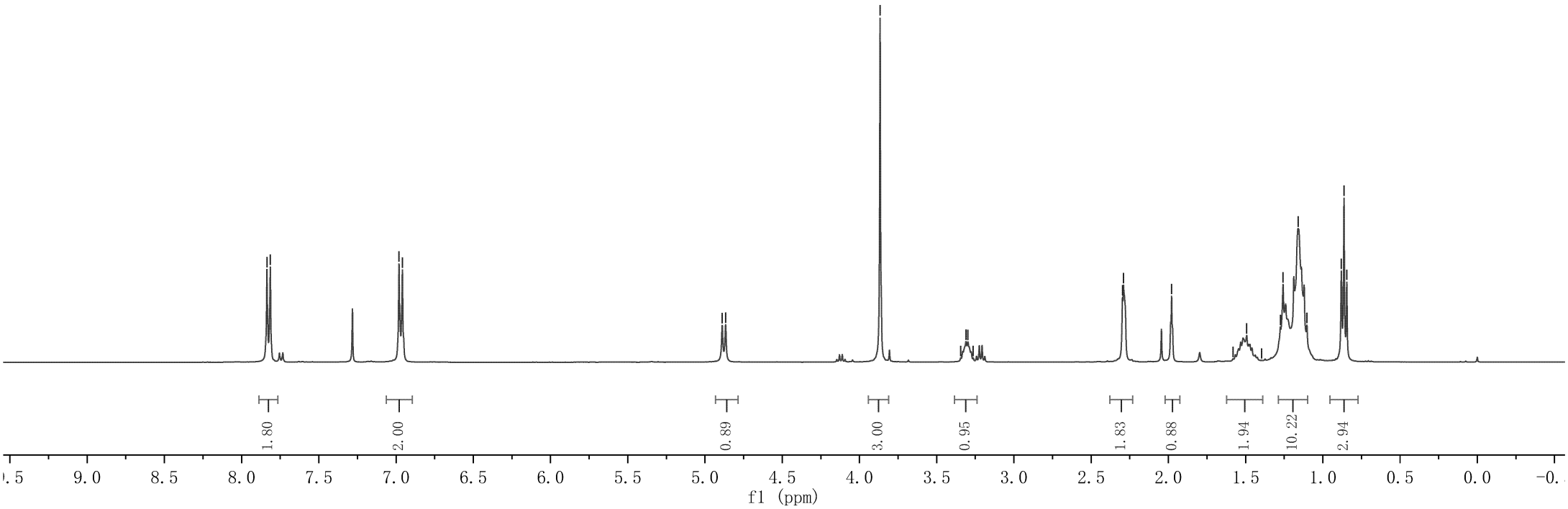


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	13.33	n.a.	2.810	1.176	0.04	n.a.	BMB*
2	15.03	n.a.	3781.454	3282.142	99.96	n.a.	BMB*
Total:			3784.264	3283.318	100.00	0.000	

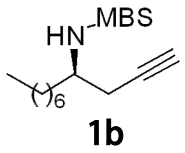
	Parameter	Value
1	Title	ttd-2-117
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	292.7
5	Number of Scans	19
6	Acquisition Time	3.9846
7	Acquisition Date	2016-03-11T14:34:28
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7



1b

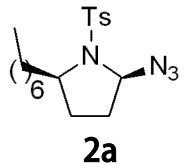


	Parameter	Value
1	Title	ttd-2-117-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	292.9
5	Number of Scans	63
6	Acquisition Time	1.3631
7	Acquisition Date	2016-03-11T14:38:11
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5



1b

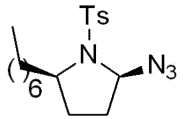
	Parameter	Value
1	Title	ttd-1-91-chun
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	297.0
5	Number of Scans	12
6	Acquisition Time	3.9846
7	Acquisition Date	2015-09-11T11:17:12
8	Spectrometer Frequency	400.03
9	Spectral Width	8223.7



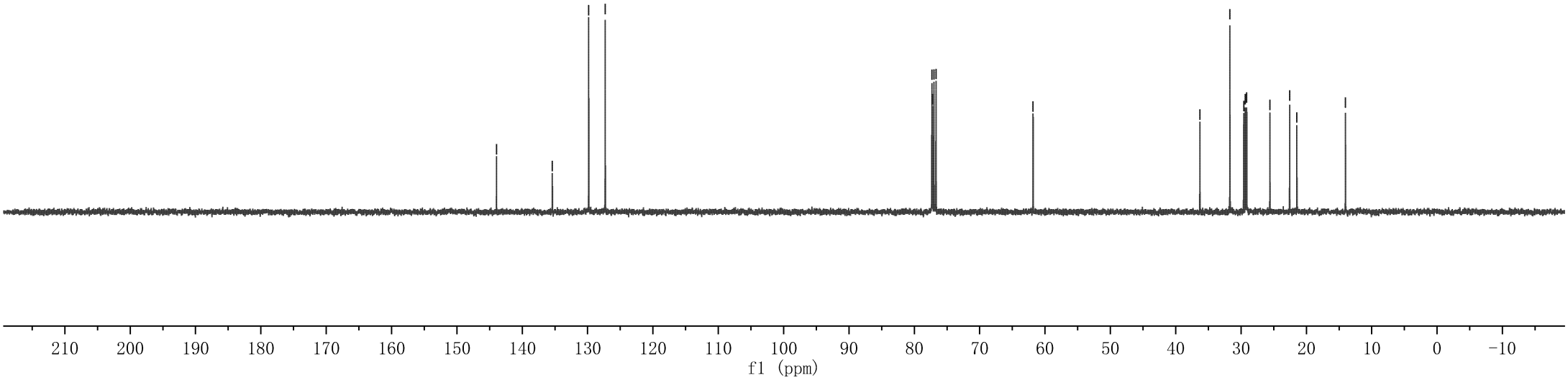
2a

	Parameter	Value
1	Title	ttd-1-91-chun-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	297.3
5	Number of Scans	36
6	Acquisition Time	1.3631
7	Acquisition Date	2015-09-11T11:21:56
8	Spectrometer Frequency	100.59
9	Spectral Width	24038.5

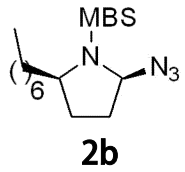
143.93
135.40
129.83
127.30
77.32
77.24
77.00
76.68
61.83
36.30
31.71
29.59
29.35
29.13
25.58
22.56
21.46
14.02



2a

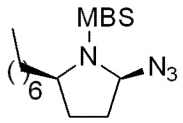


	Parameter	Value
1	Title	ttd-2-121-1
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	293.5
5	Number of Scans	16
6	Acquisition Time	3.9846
7	Acquisition Date	2016-03-14T21:00:34
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7

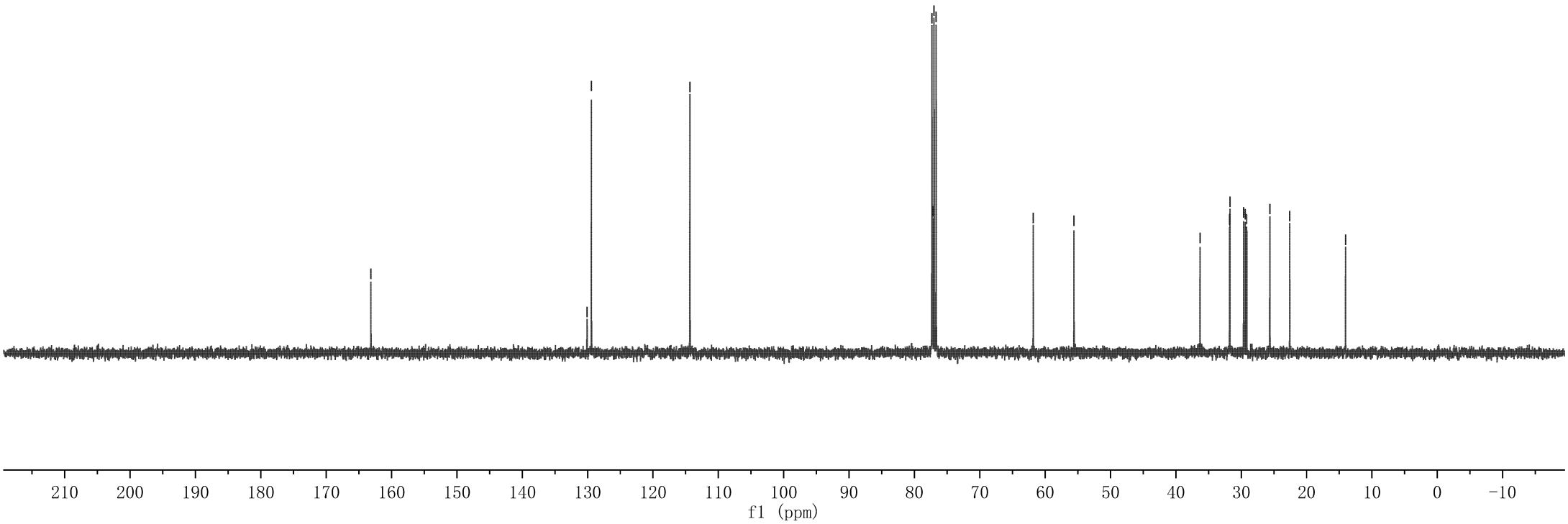


2b

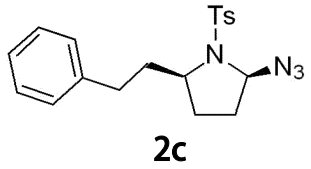
	Parameter	Value
1	Title	ttd-2-121-1-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	293.6
5	Number of Scans	38
6	Acquisition Time	1.3631
7	Acquisition Date	2016-03-14T21:03:40
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5



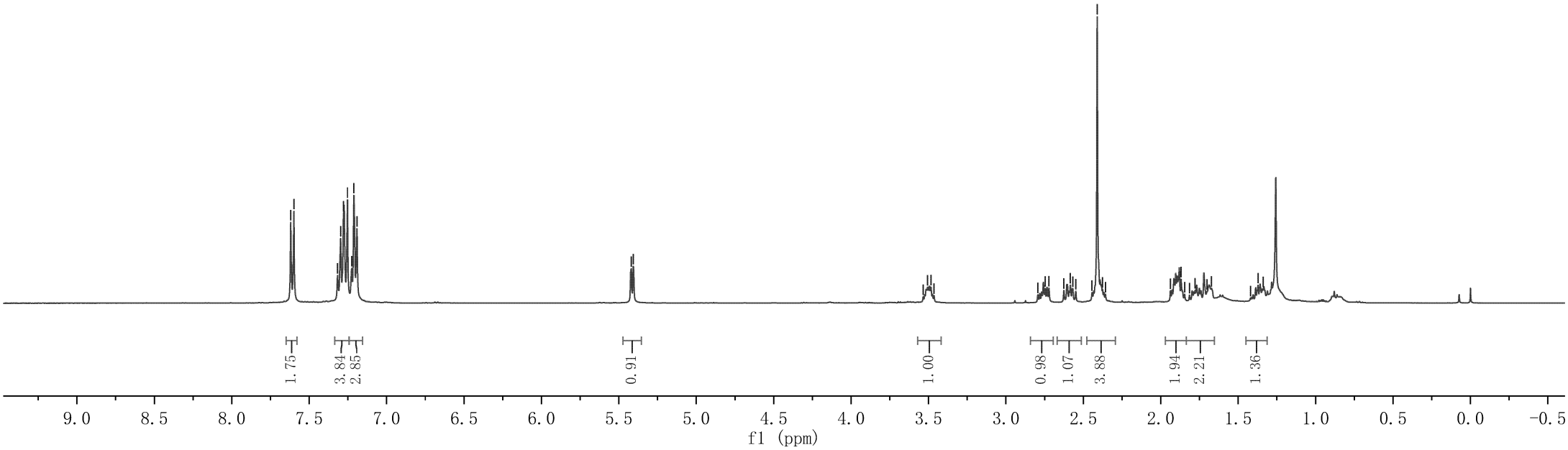
2b



	Parameter	Value
1	Title	ttd-1-117
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	299.9
5	Number of Scans	13
6	Acquisition Time	3.9846
7	Acquisition Date	2015-09-26T08:23:36
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7

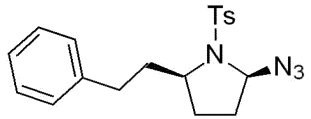


2c

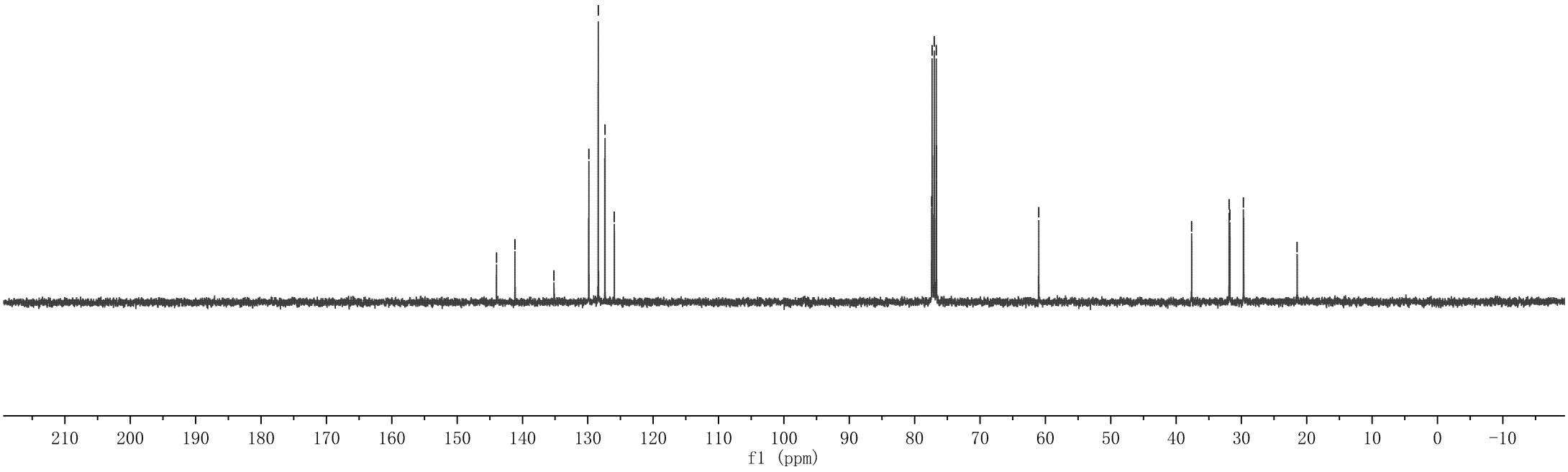


	Parameter	Value
1	Title	ttd-1-117-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	299.8
5	Number of Scans	107
6	Acquisition Time	1.3631
7	Acquisition Date	2015-09-26T08:26:16
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

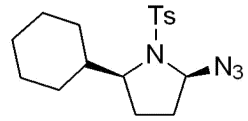
143.97
141.14
135.19
129.85
128.41
127.39
125.95
77.40
77.32
77.00
76.68
61.01
37.61
31.88
31.77
29.69
21.48



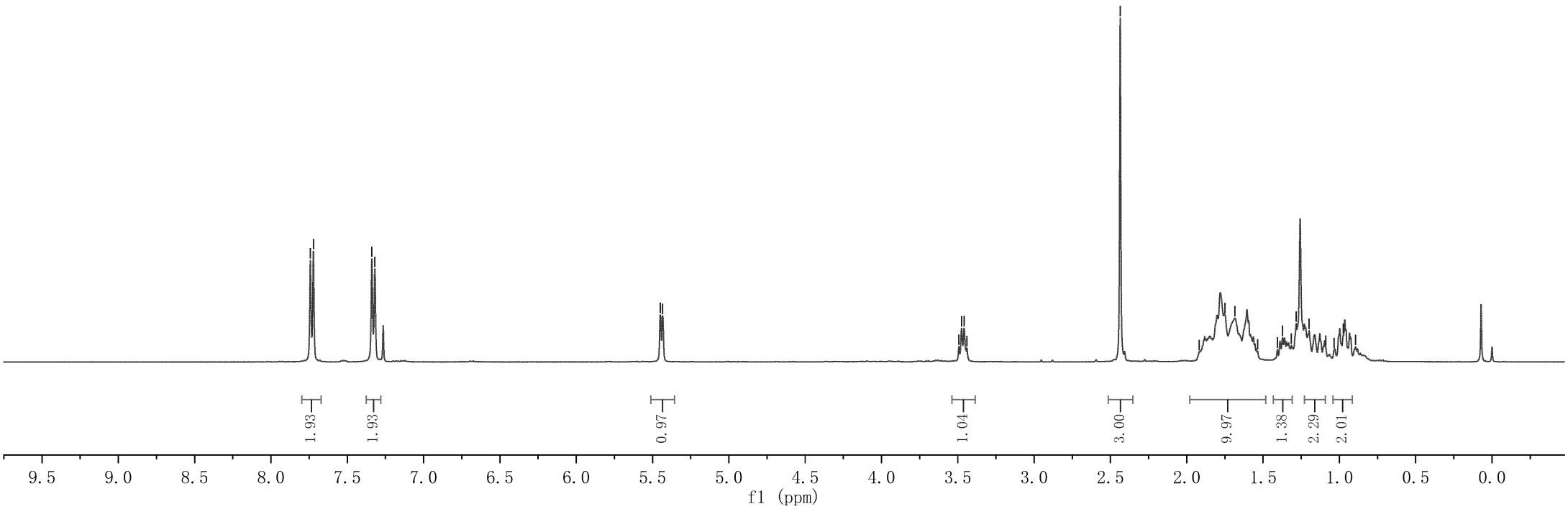
2c



	Parameter	Value
1	Title	ttd-1-130
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	299.2
5	Number of Scans	8
6	Acquisition Time	3.9846
7	Acquisition Date	2015-10-07T10:22:46
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7

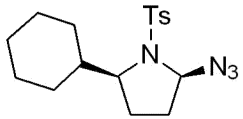


2d

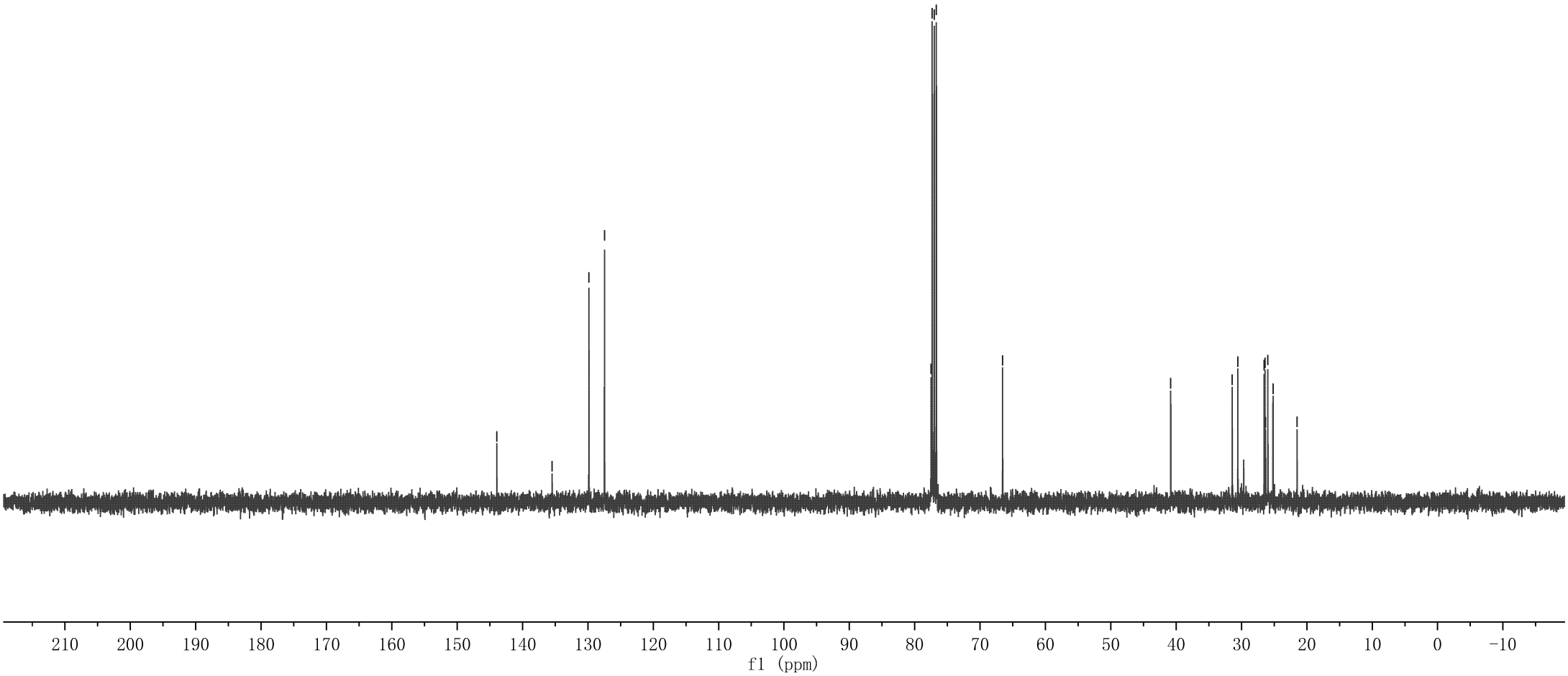


	Parameter	Value
1	Title	ttd-1-130-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	299.3
5	Number of Scans	74
6	Acquisition Time	1.3631
7	Acquisition Date	2015-10-07T10:25:21
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

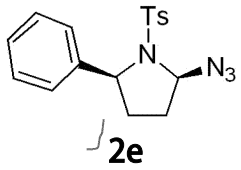
143.94
135.49
129.84
127.46
77.50
77.32
77.00
76.68
66.55
40.83
31.43
30.56
26.53
26.40
26.33
25.97
25.18
21.49



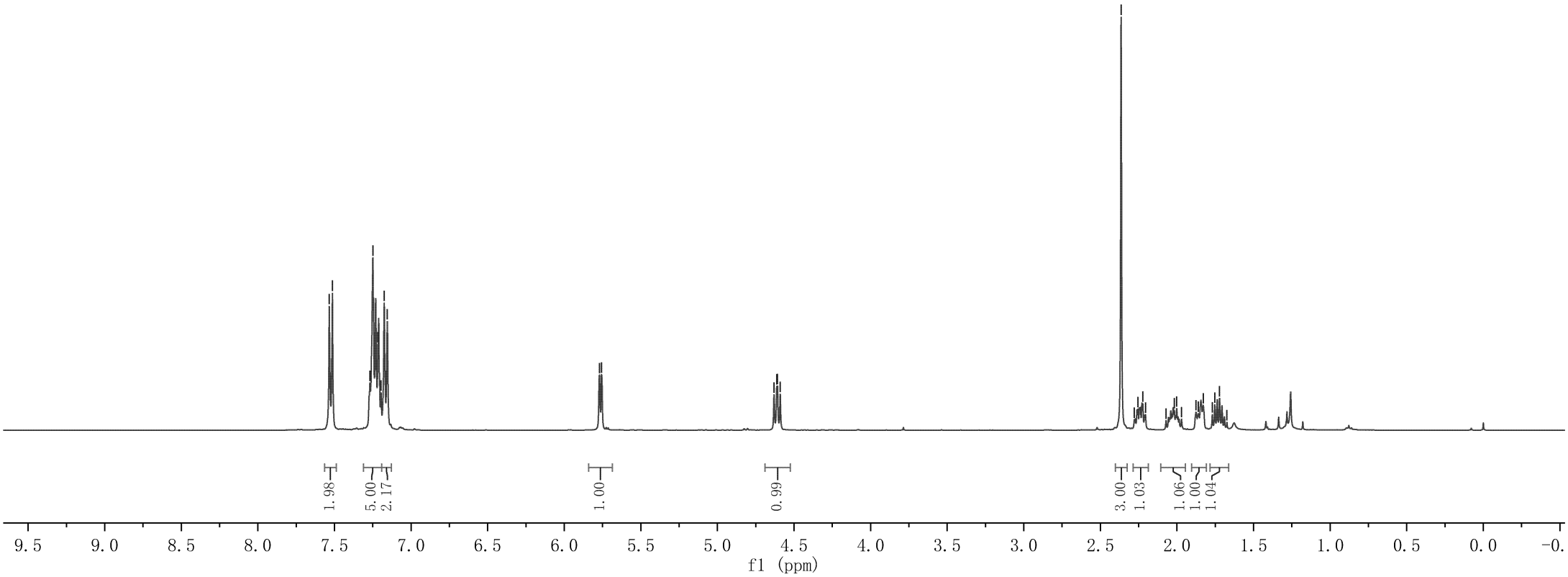
2d



	Parameter	Value
1	Title	ttd-1-100
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	296.1
5	Number of Scans	18
6	Acquisition Time	3.9846
7	Acquisition Date	2015-09-12T09:29:26
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7

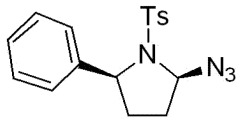


2e

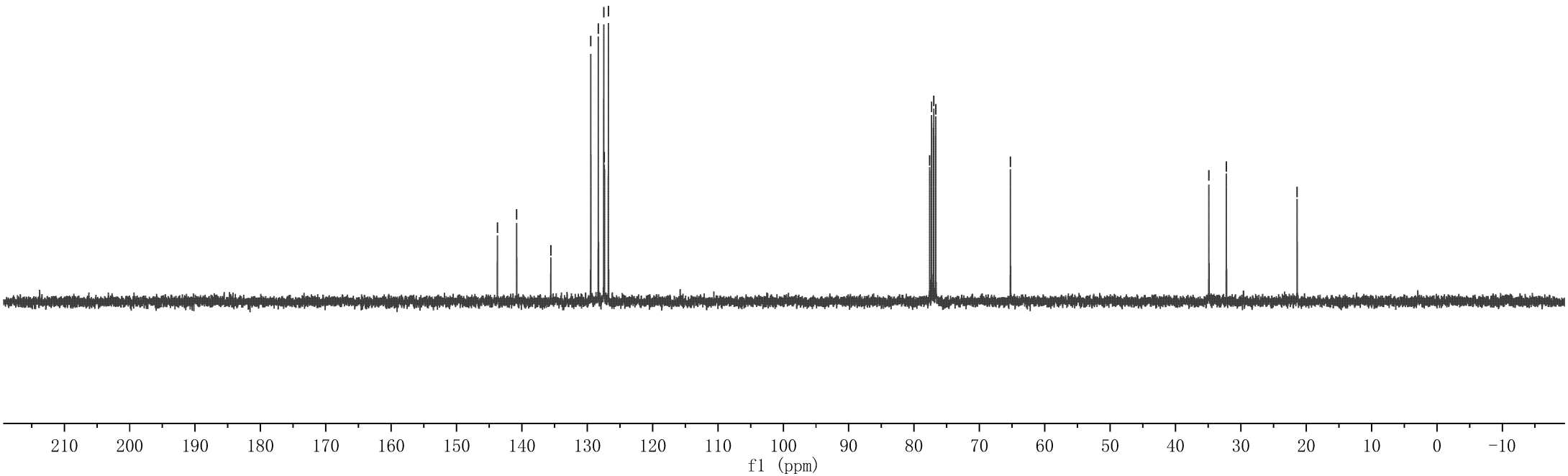


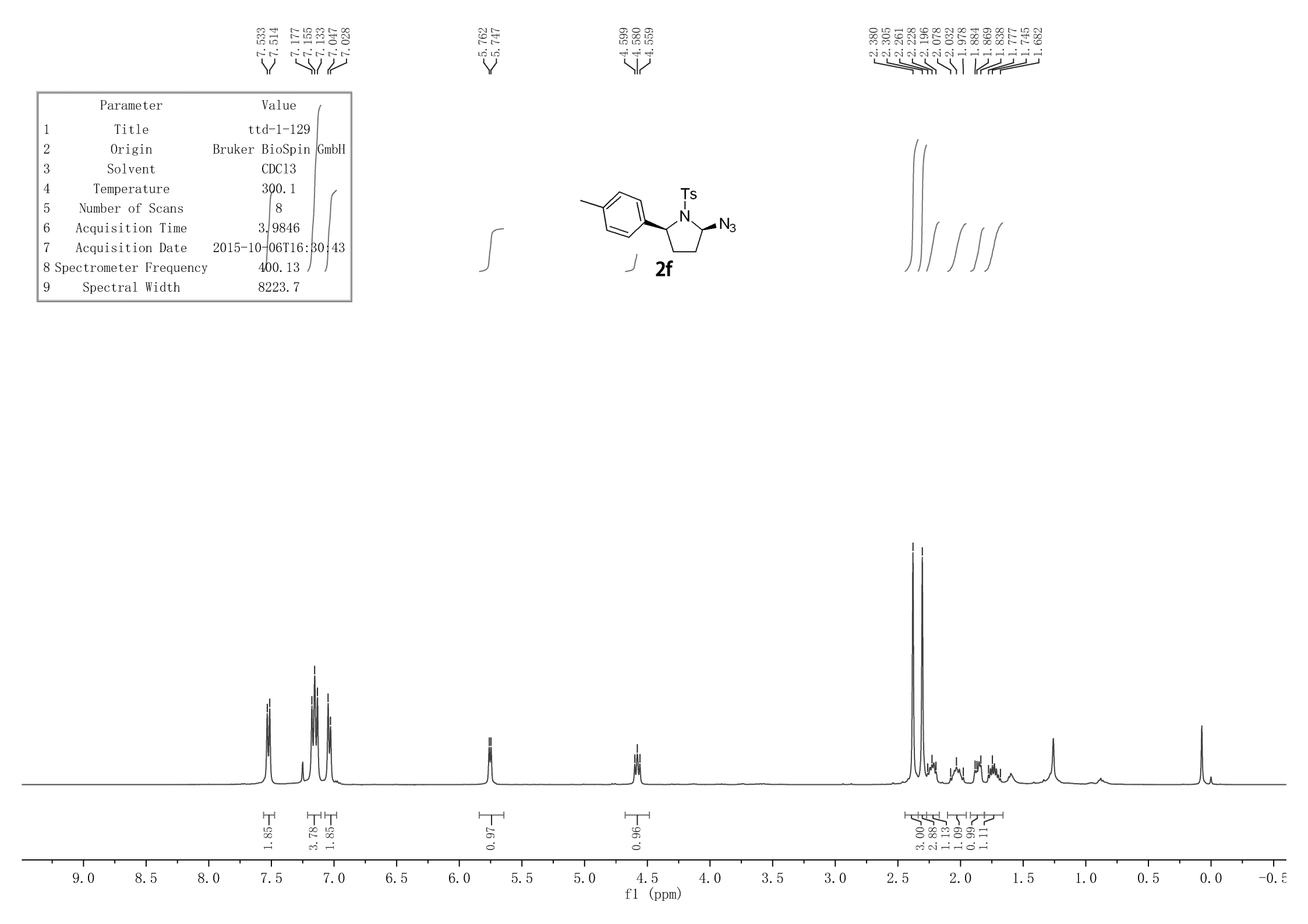
	Parameter	Value
1	Title	ttd-1-100-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	296.0
5	Number of Scans	21
6	Acquisition Time	1.3631
7	Acquisition Date	2015-09-12T09:32:59
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

143.74
140.80
135.57
129.46
128.30
127.47
127.37
126.76
77.60
77.32
77.00
76.68
65.25
34.89
32.21
21.39



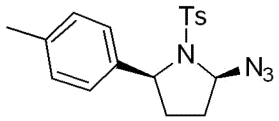
2e



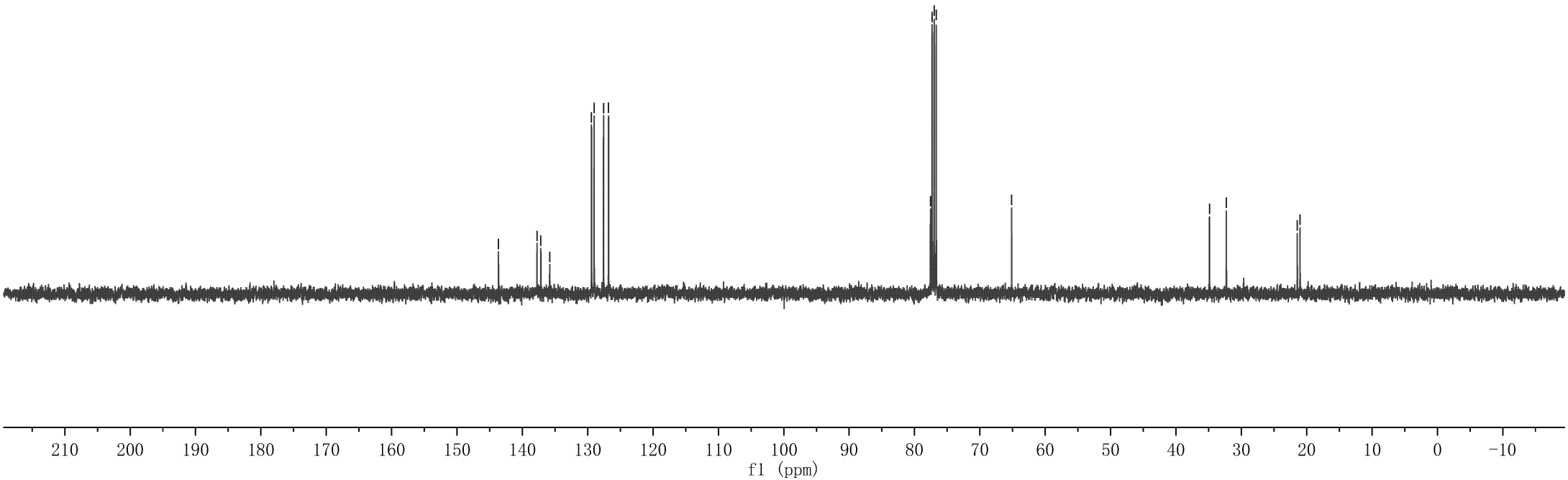

7.533
7.514
7.177
7.155
7.133
7.047
7.028
5.762
5.747
4.599
4.580
4.559
2.380
2.305
2.261
2.228
2.196
2.078
2.032
1.978
1.884
1.869
1.838
1.777
1.745
1.682
Parameter Value
1 Title ttd-1-129
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.1
5 Number of Scans 8
6 Acquisition Time 3.9846
7 Acquisition Date 2015-10-06T16:30:43
8 Spectrometer Frequency 400.13
9 Spectral Width 8223.7
Ts
N
N3
2f
1.85
3.78
1.85
0.97
0.96
3.00
2.88
1.13
1.09
0.99
1.11
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)

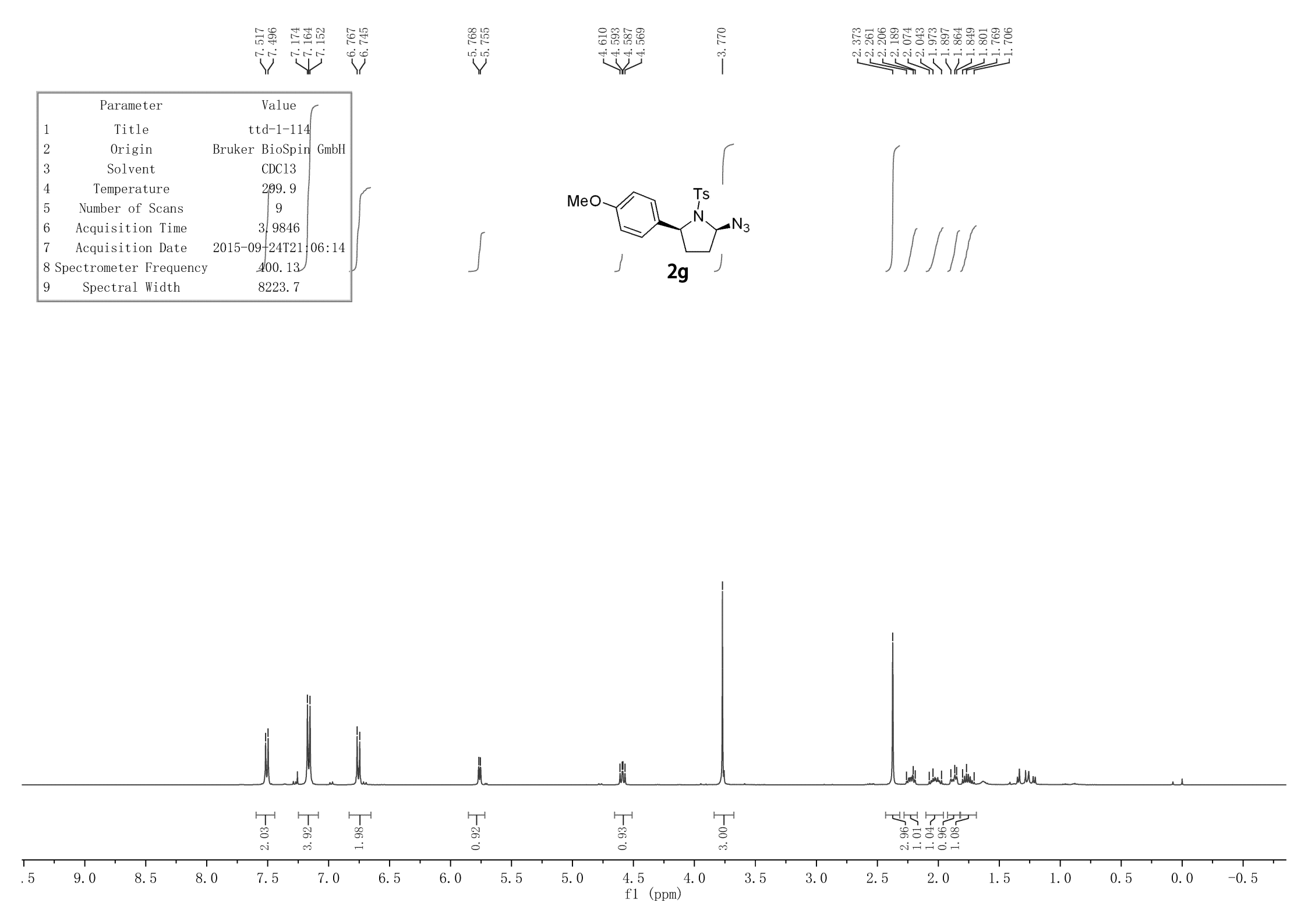
	Parameter	Value
1	Title	ttd-1-129-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.1
5	Number of Scans	28
6	Acquisition Time	1.3631
7	Acquisition Date	2015-10-06T16:33:34
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

143.65
137.76
137.16
135.82
129.41
129.02
127.58
126.81
77.56
77.32
77.00
76.68
65.14
34.87
32.29
21.43
21.01



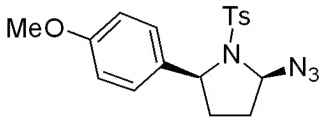
2f



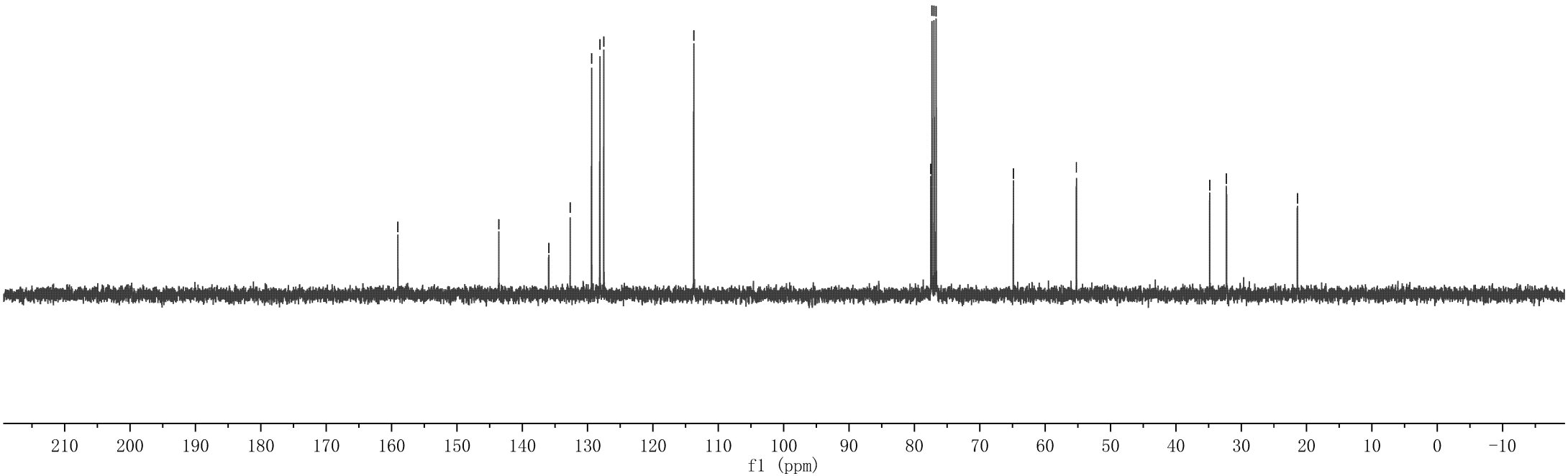

7.517
7.496
7.174
7.164
7.152
6.767
6.745
5.768
5.755
4.610
4.593
4.587
4.569
3.770
2.373
2.261
2.206
2.189
2.074
2.043
1.973
1.897
1.864
1.849
1.801
1.769
1.706
Parameter Value
1 Title ttd-1-114
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 299.9
5 Number of Scans 9
6 Acquisition Time 3.9846
7 Acquisition Date 2015-09-24T21:06:14
8 Spectrometer Frequency 400.13
9 Spectral Width 8223.7
MeO
Ts
N
N3
2g
2.03
3.92
1.98
0.92
0.93
3.00
2.96
1.01
1.04
0.96
1.08
f1 (ppm)

159.03
143.58
135.95
132.66
129.39
128.12
127.53
113.76
77.49
77.32
77.00
76.68
64.87
55.22
34.82
32.26
21.41

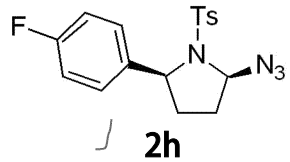
	Parameter	Value
1	Title	ttd-1-114-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.1
5	Number of Scans	21
6	Acquisition Time	1.3631
7	Acquisition Date	2015-09-24T21:09:12
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5



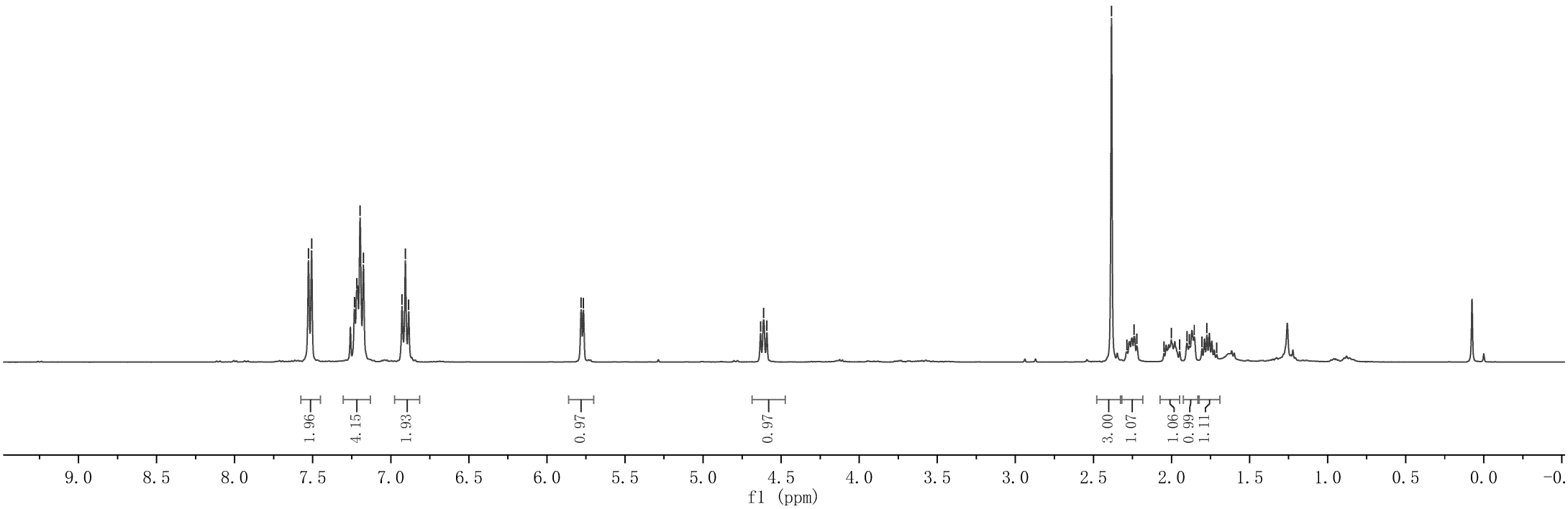
2g

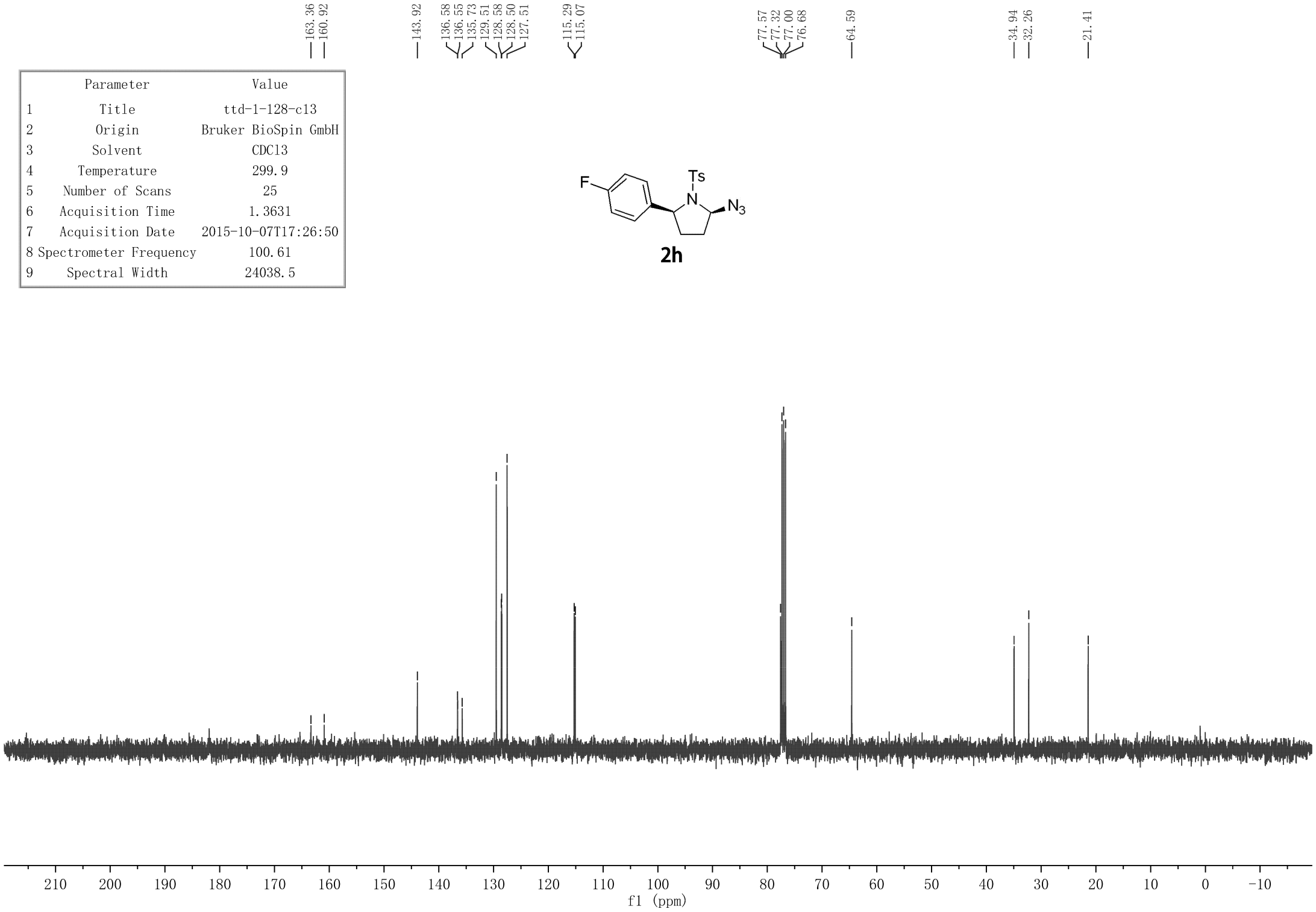


	Parameter	Value
1	Title	ttd-1-128
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Number of Scans	7
6	Acquisition Time	3.9846
7	Acquisition Date	2015-10-07T17:23:01
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7

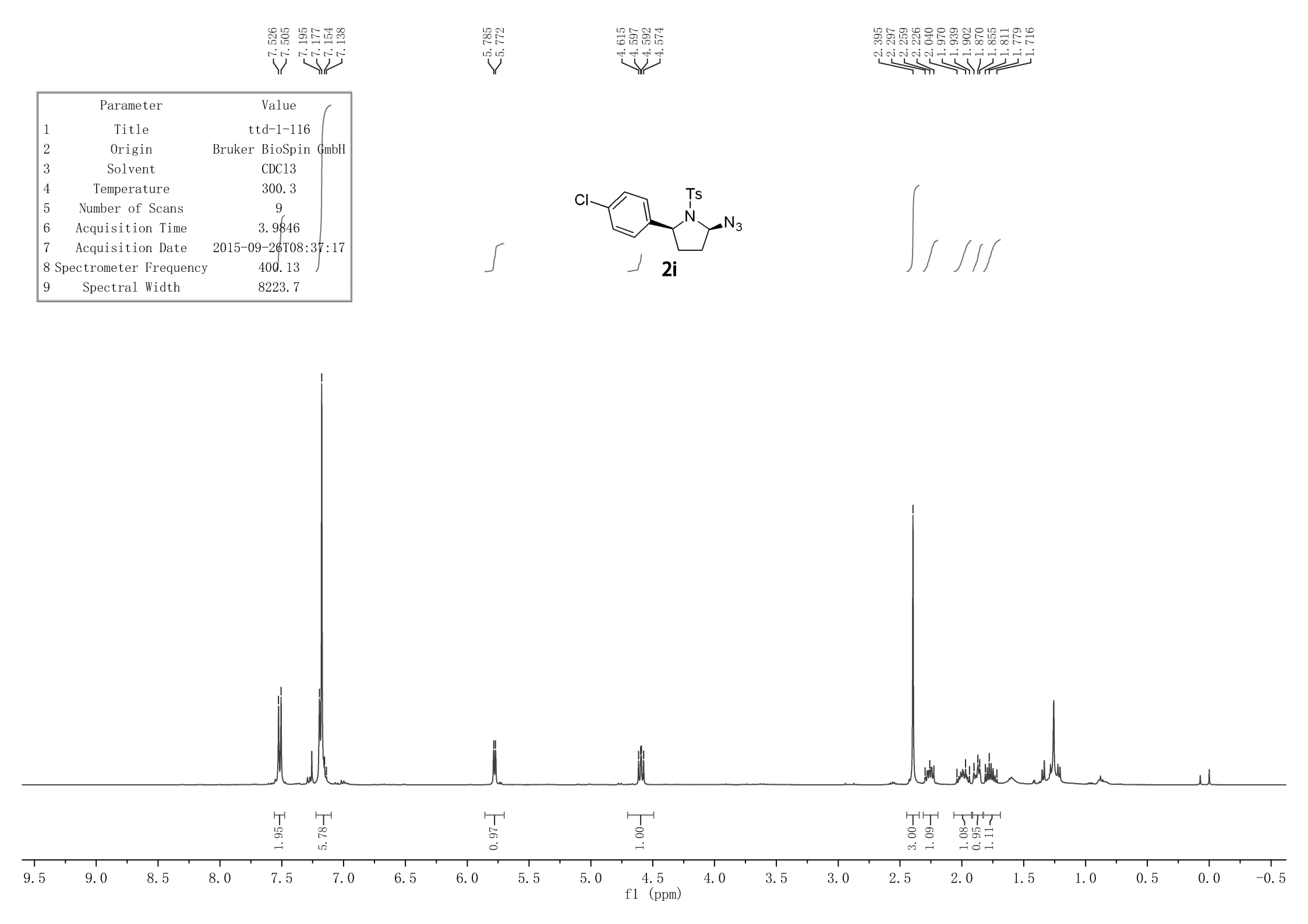


2h



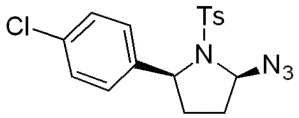


	Parameter	Value
1	Title	ttd-1-128-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	299.9
5	Number of Scans	25
6	Acquisition Time	1.3631
7	Acquisition Date	2015-10-07T17:26:50
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

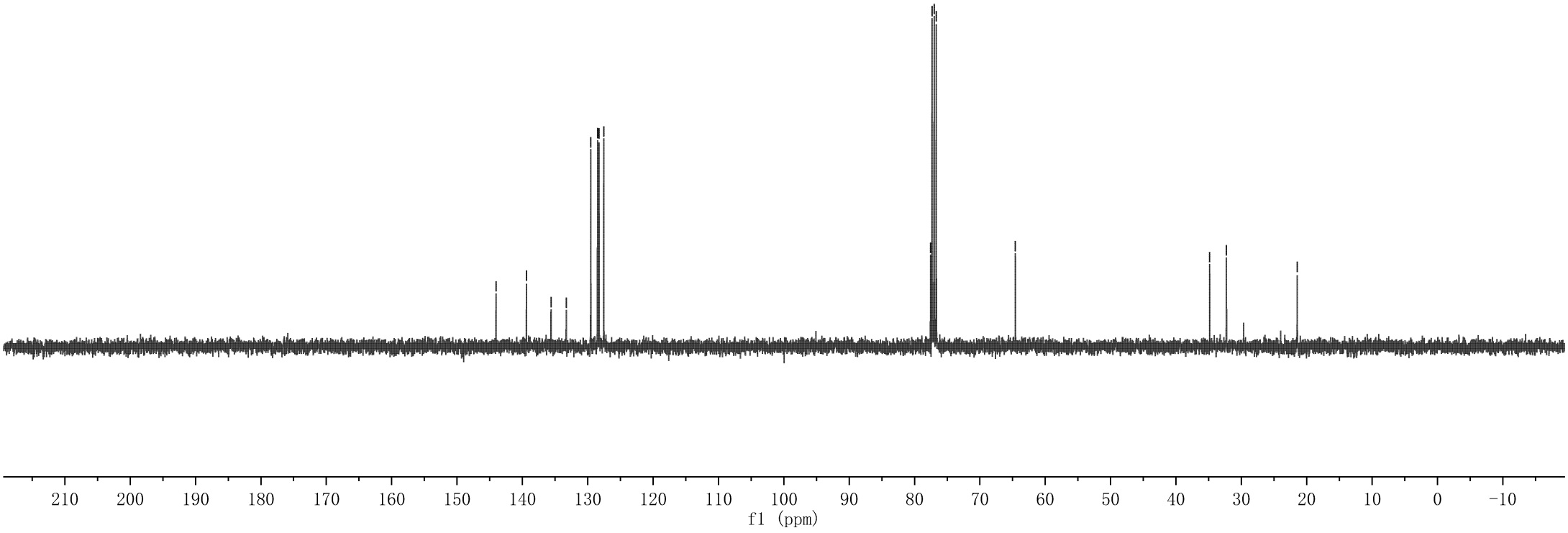

7.526
7.505
7.195
7.177
7.154
7.138
5.785
5.772
4.615
4.597
4.592
4.574
2.395
2.297
2.259
2.226
2.040
1.970
1.939
1.902
1.870
1.855
1.811
1.779
1.716
Parameter Value
1 Title ttd-1-116
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.3
5 Number of Scans 9
6 Acquisition Time 3.9846
7 Acquisition Date 2015-09-26T08:37:17
8 Spectrometer Frequency 400.13
9 Spectral Width 8223.7
Cl
Ts
N
N3
2i
1.95
5.78
0.97
1.00
3.00
1.09
1.08
0.95
1.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

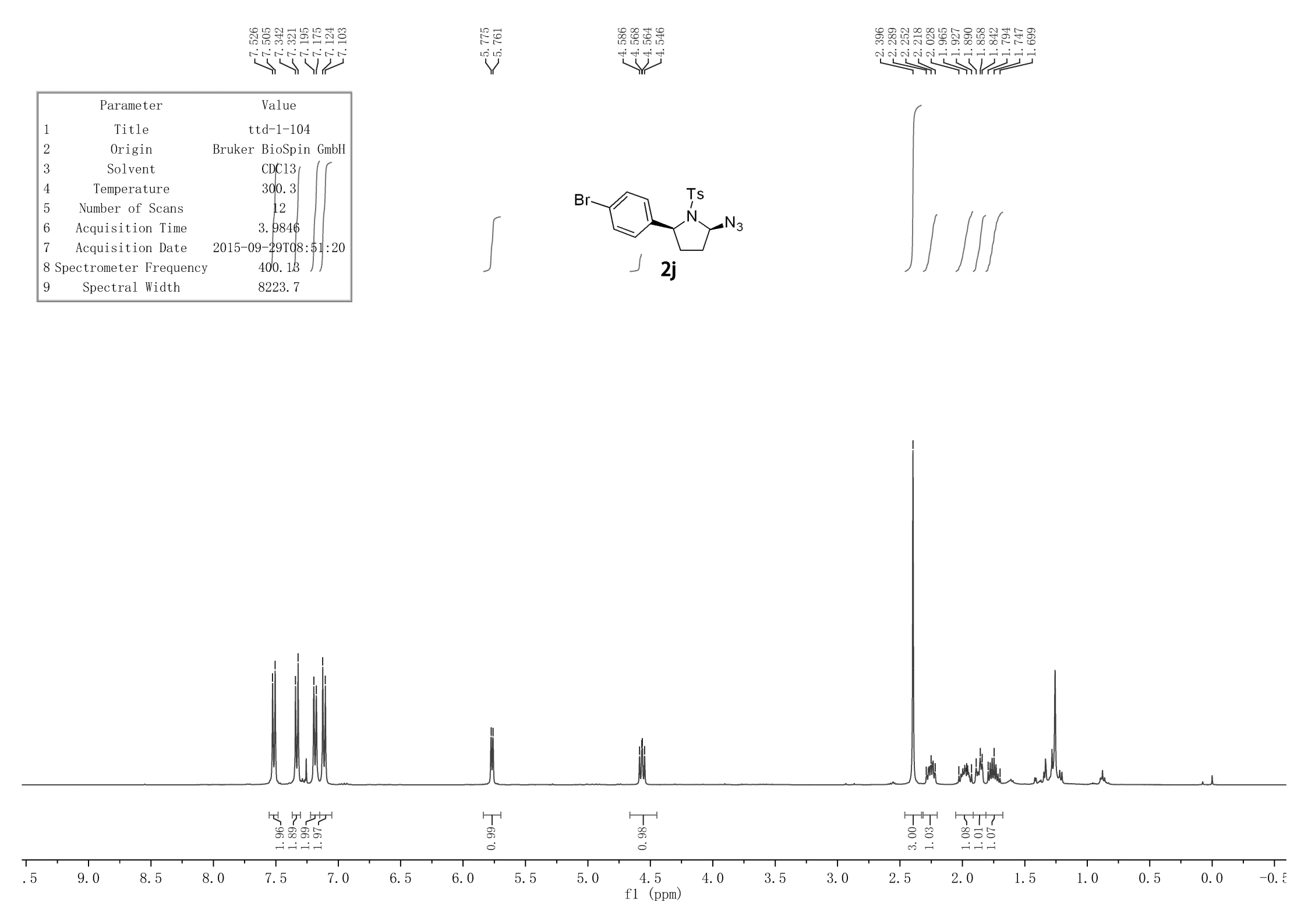
	Parameter	Value
1	Title	ttd-1-116-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Number of Scans	21
6	Acquisition Time	1.3631
7	Acquisition Date	2015-09-24T21:17:29
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

144.03
139.38
135.62
133.29
129.54
128.49
128.26
127.55
77.55
77.32
77.00
76.68
64.58
34.85
32.29
21.45



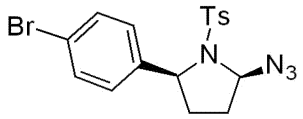
2i



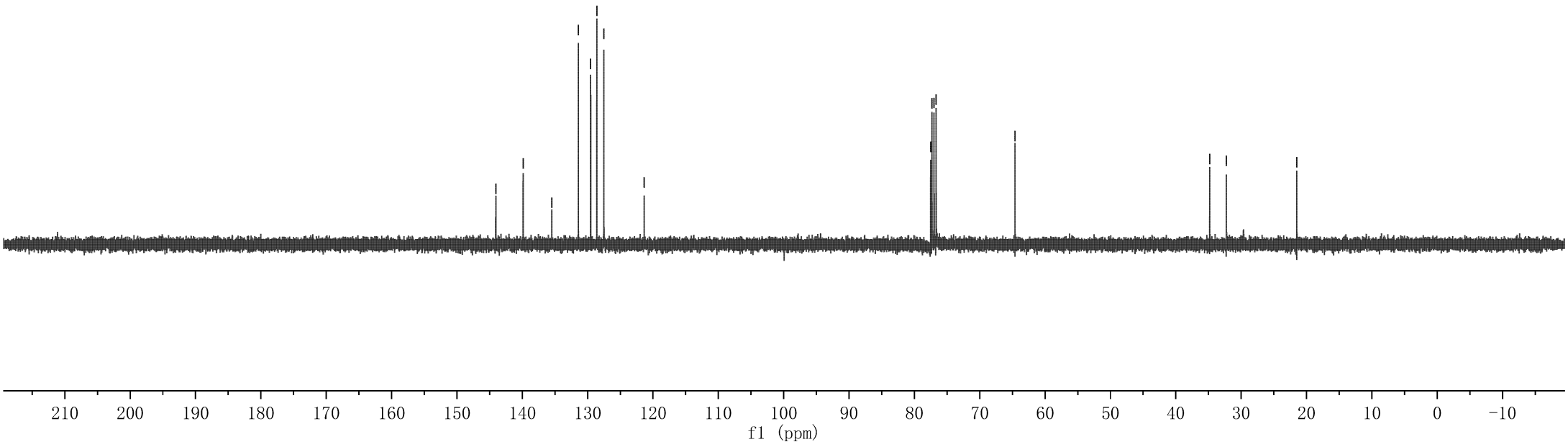

7.526
7.505
7.342
7.321
7.195
7.175
7.124
7.103
5.775
5.761
4.586
4.568
4.564
4.546
2.396
2.289
2.252
2.218
2.028
1.965
1.927
1.890
1.858
1.842
1.794
1.747
1.699
Parameter Value
1 Title ttd-1-104
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.3
5 Number of Scans 12
6 Acquisition Time 3.9846
7 Acquisition Date 2015-09-29T08:51:20
8 Spectrometer Frequency 400.13
9 Spectral Width 8223.7
Br
Ts
N
N3
2j
1.96
1.89
1.99
1.97
0.99
0.98
3.00
1.03
1.08
1.01
1.07
f1 (ppm)

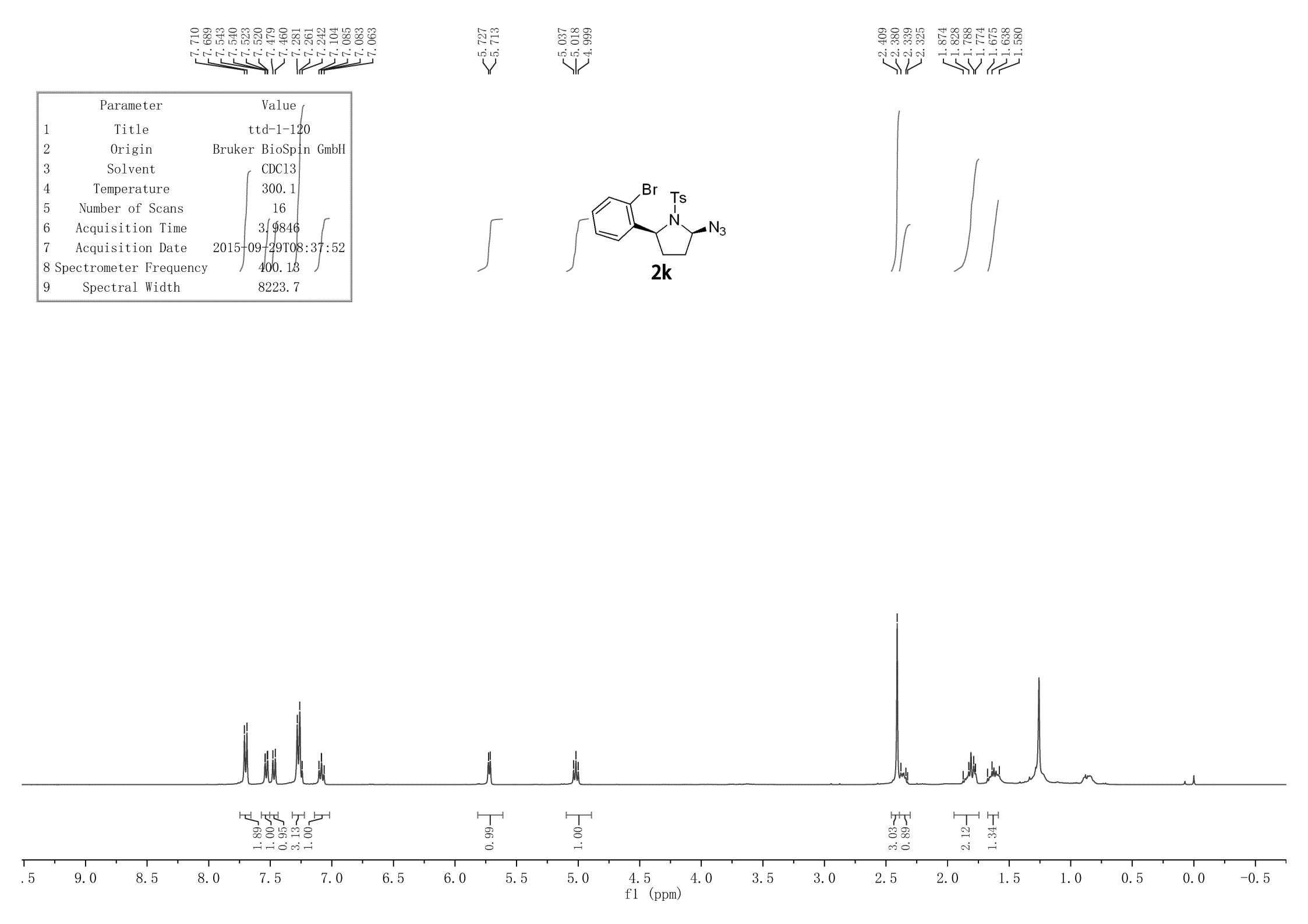
	Parameter	Value
1	Title	ttd-1-104-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	297.4
5	Number of Scans	60
6	Acquisition Time	1.3631
7	Acquisition Date	2015-09-16T17:03:05
8	Spectrometer Frequency	100.60
9	Spectral Width	24038.5

144.05
139.86
135.49
131.43
129.55
128.59
127.51
121.35
77.51
77.32
77.00
76.68
64.60
34.81
32.27
21.48



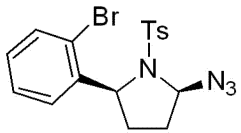
2j



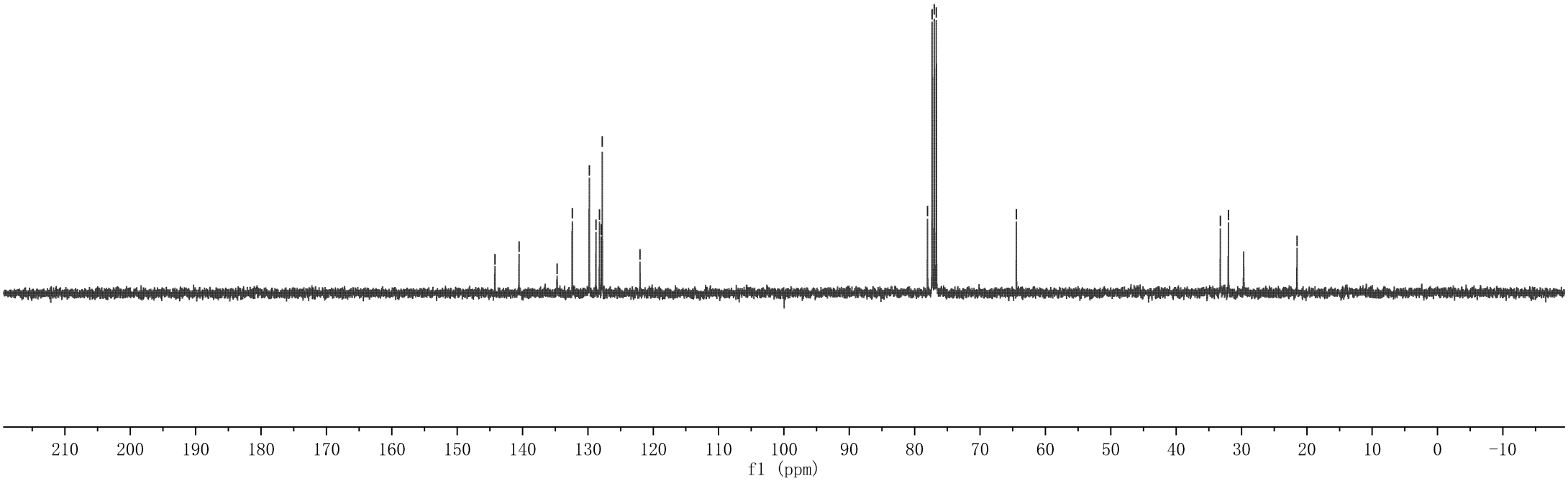

7.710
7.689
7.543
7.540
7.523
7.520
7.479
7.460
7.281
7.261
7.242
7.104
7.085
7.083
7.063
5.727
5.713
5.037
5.018
4.999
2.409
2.380
2.339
2.325
1.874
1.828
1.788
1.774
1.675
1.638
1.580
Parameter Value
1 Title ttd-1-120
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.1
5 Number of Scans 16
6 Acquisition Time 3.9846
7 Acquisition Date 2015-09-29T08:37:52
8 Spectrometer Frequency 400.13
9 Spectral Width 8223.7
Br
Ts
N
N3
2k
1.89
1.00
0.95
3.13
1.00
0.99
1.00
3.03
0.89
2.12
1.34
f1 (ppm)

	Parameter	Value
1	Title	ttd-1-120-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.1
5	Number of Scans	79
6	Acquisition Time	1.3631
7	Acquisition Date	2015-09-29T08:41:02
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

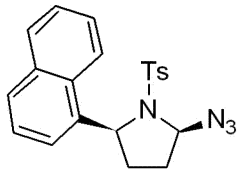
144.23
140.53
134.72
132.40
129.78
128.76
128.23
127.93
127.80
122.02
78.04
77.32
77.00
76.68
64.44
33.23
32.00
21.50



2k



	Parameter	Value
1	Title	ttd-1-138-2
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	296.4
5	Number of Scans	10
6	Acquisition Time	3.9846
7	Acquisition Date	2015-10-13T08:07:05
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7



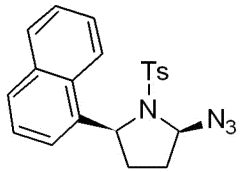
2l

f1 (ppm)

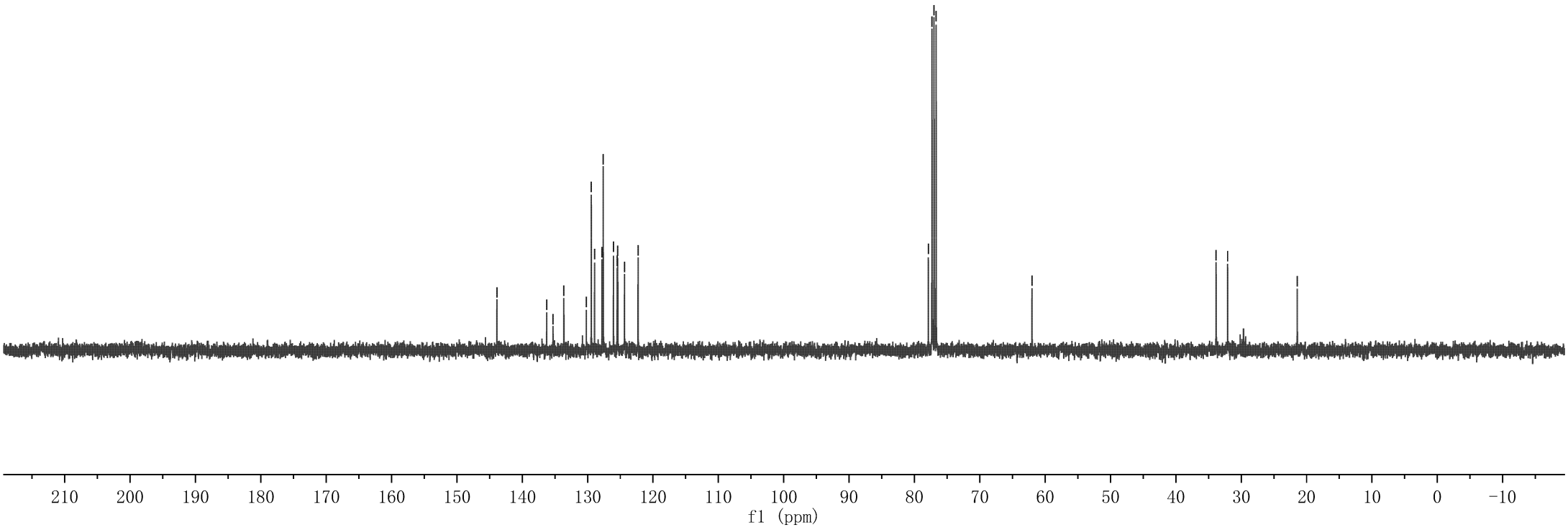
f1 (ppm)

	Parameter	Value
1	Title	ttd-1-138-2-c13
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	296.3
5	Number of Scans	25
6	Acquisition Time	1.3631
7	Acquisition Date	2015-10-13T08:10:11
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

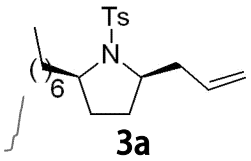
143.88
136.26
135.30
133.63
130.20
129.44
128.94
127.79
127.62
126.05
125.48
125.39
124.36
122.28
77.87
77.32
77.00
76.68
62.02
33.85
32.08
21.42



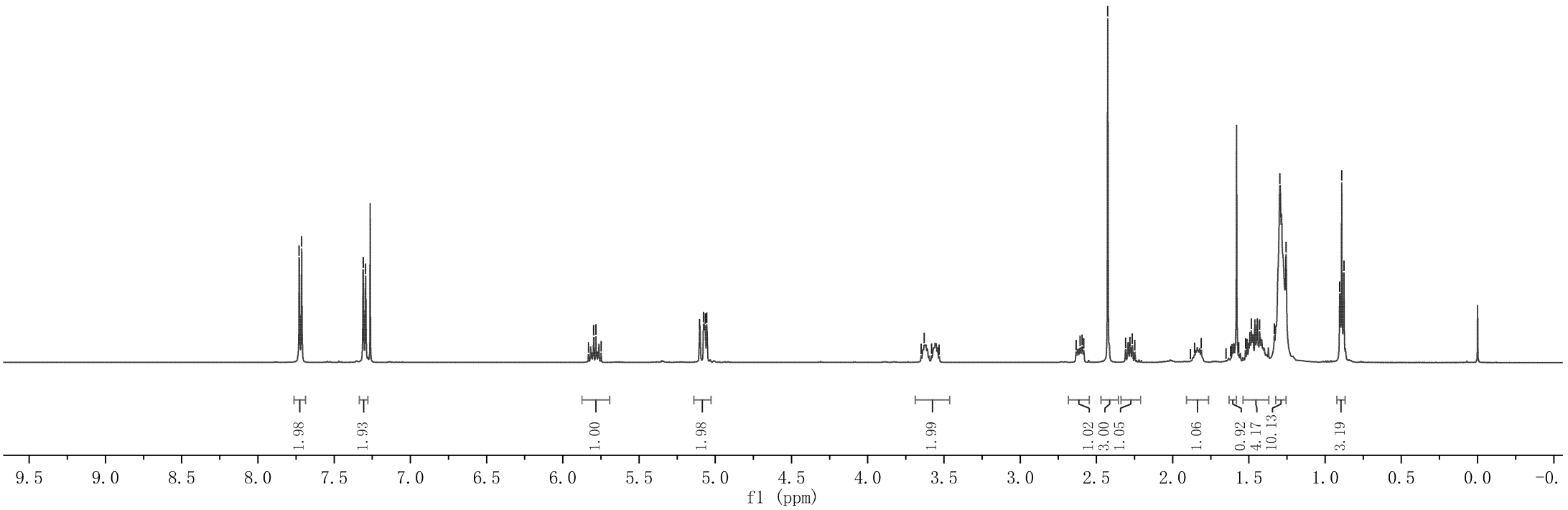
2l



	Parameter	Value
1	Title	ttd-2-81-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-22T16:20:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0

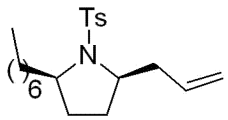


3a

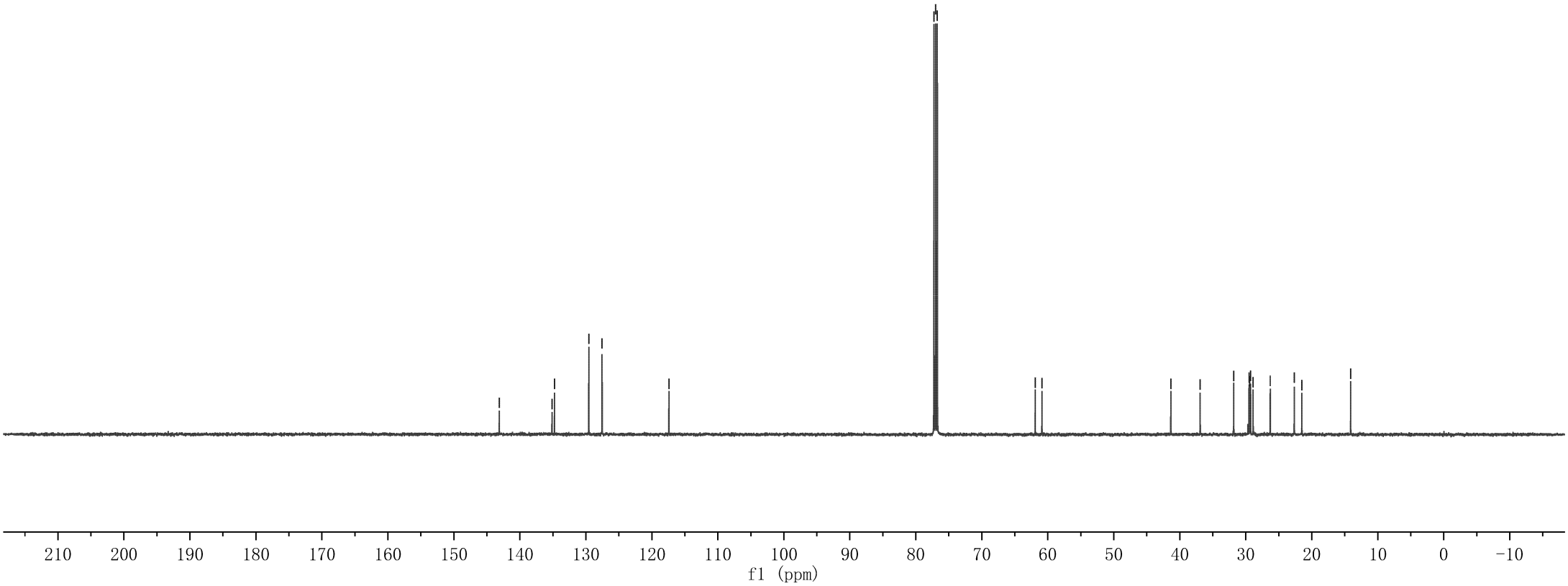


	Parameter	Value
1	Title	ttd-2-81-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-22T16:48:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

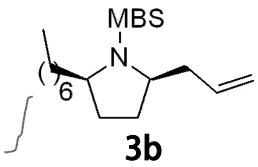
143.13
135.13
134.75
129.56
127.55
117.42
77.25
77.00
76.75
61.91
60.89
41.36
36.92
31.83
29.51
29.42
29.27
28.89
26.30
22.65
21.50
14.11



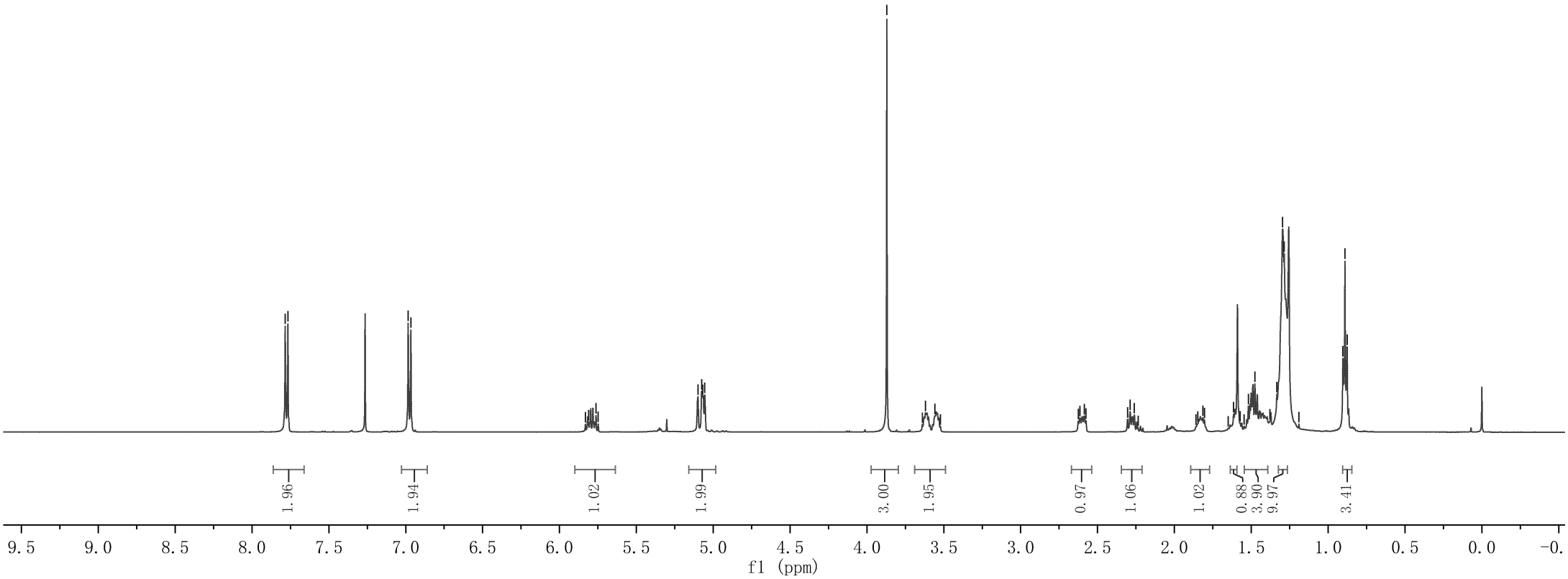
3a

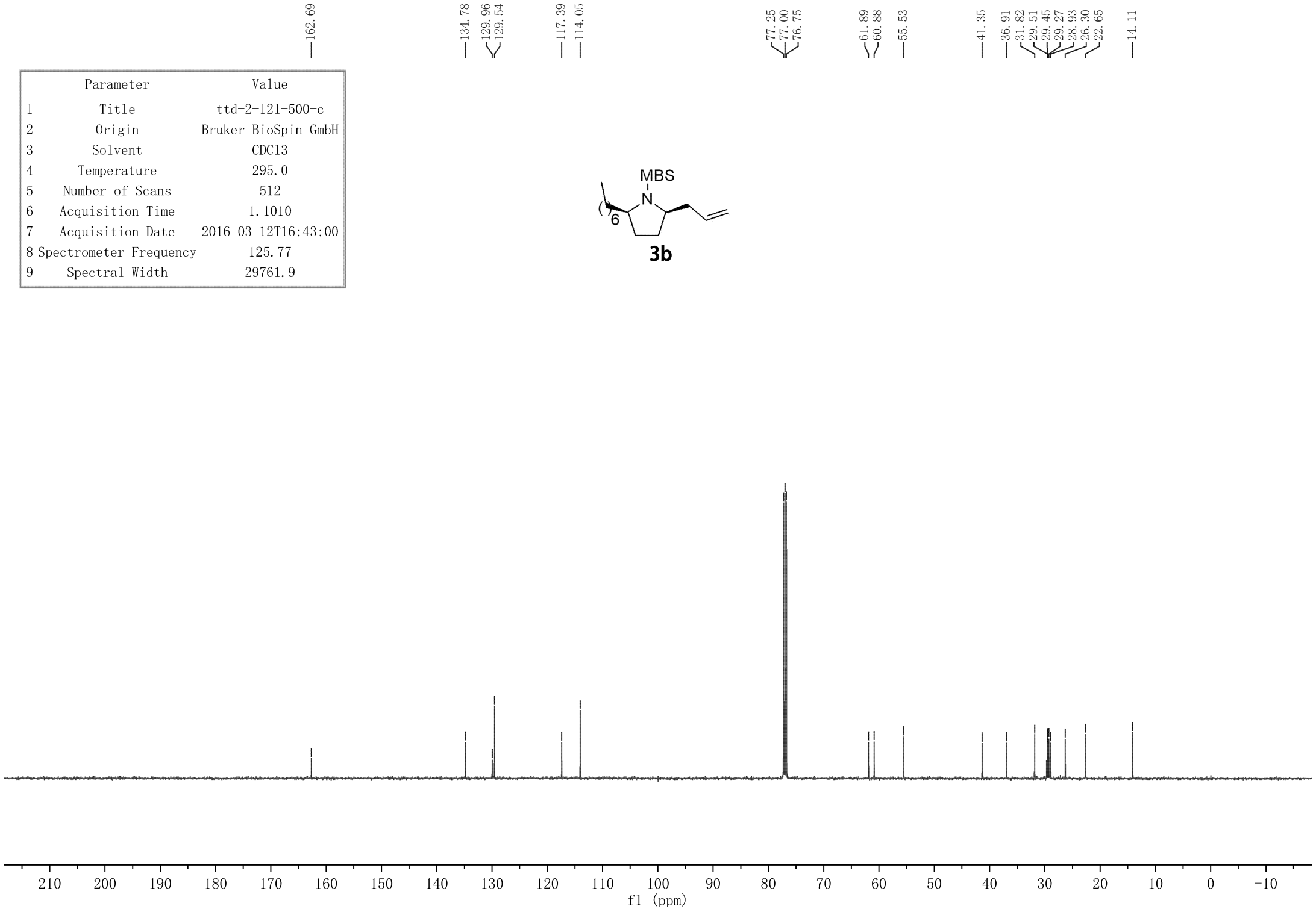


	Parameter	Value
1	Title	ttd-2-121-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-03-12T16:14:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0

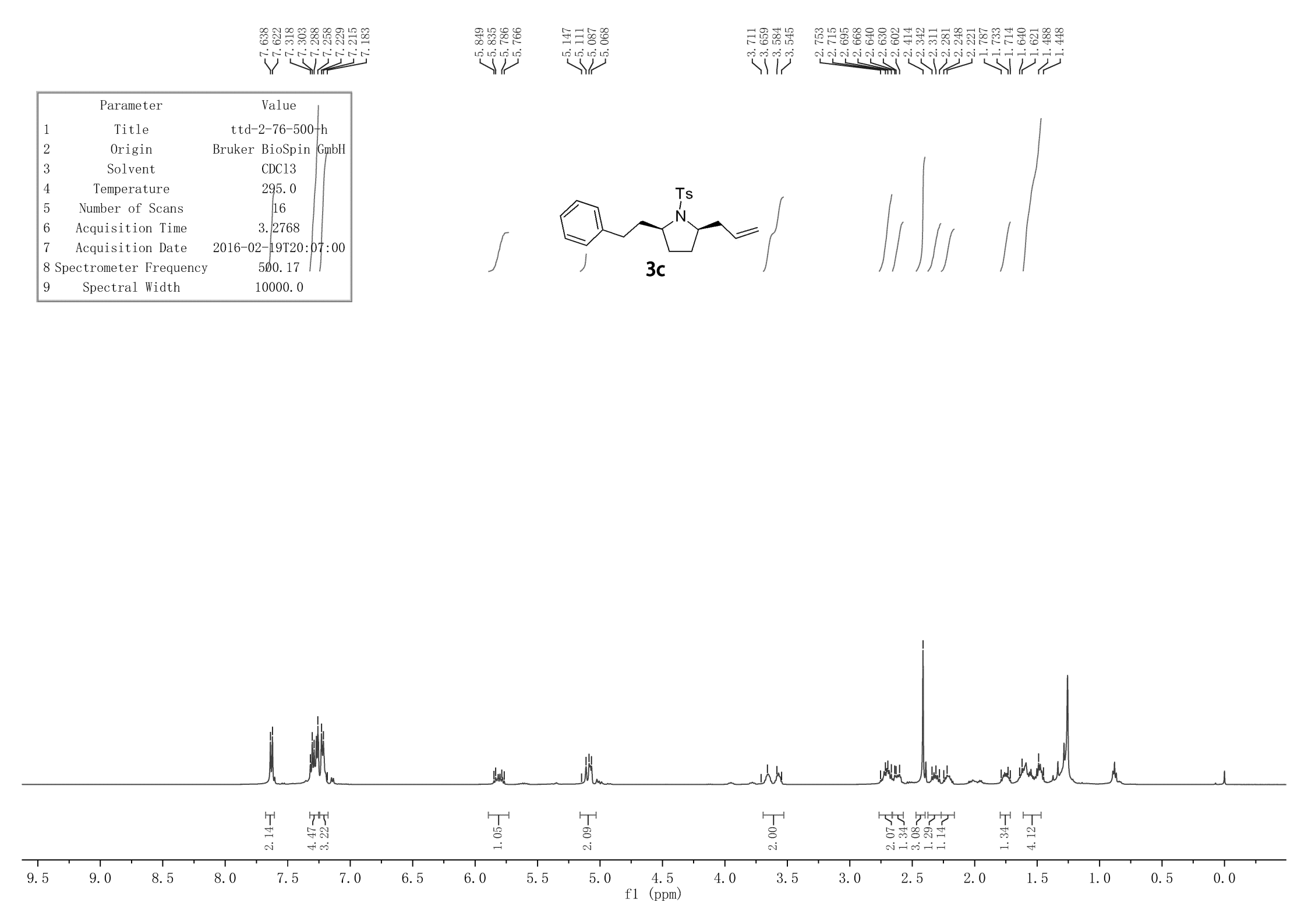


3b



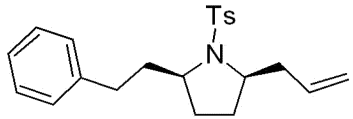


	Parameter	Value
1	Title	ttd-2-121-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-03-12T16:43:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

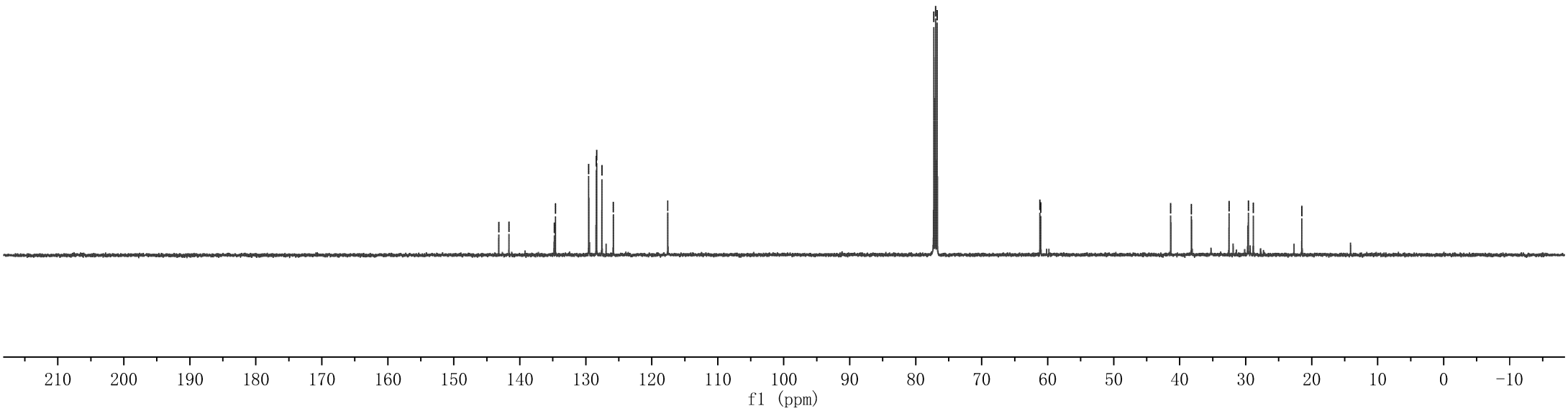

7.638
7.622
7.318
7.303
7.288
7.258
7.229
7.215
7.183
5.849
5.835
5.786
5.766
5.147
5.111
5.087
5.068
3.711
3.659
3.584
3.545
2.753
2.715
2.695
2.668
2.640
2.630
2.602
2.414
2.342
2.311
2.281
2.248
2.221
1.787
1.733
1.714
1.640
1.621
1.488
1.448
Parameter Value
1 Title ttd-2-76-500-h
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.0
5 Number of Scans 16
6 Acquisition Time 3.2768
7 Acquisition Date 2016-02-19T20:07:00
8 Spectrometer Frequency 500.17
9 Spectral Width 10000.0
Ts
N
3c
2.14
4.47
3.22
1.05
2.09
2.00
2.07
1.34
3.08
1.29
1.14
1.34
4.12
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)

	Parameter	Value
1	Title	ttd-2-76-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	256
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-19T20:22:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

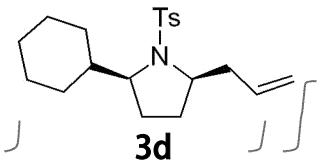
143.19
141.64
134.78
134.61
129.55
128.42
128.36
127.55
125.82
117.58
77.25
77.00
76.75
61.17
61.05
41.36
38.22
32.52
29.59
28.84
21.49



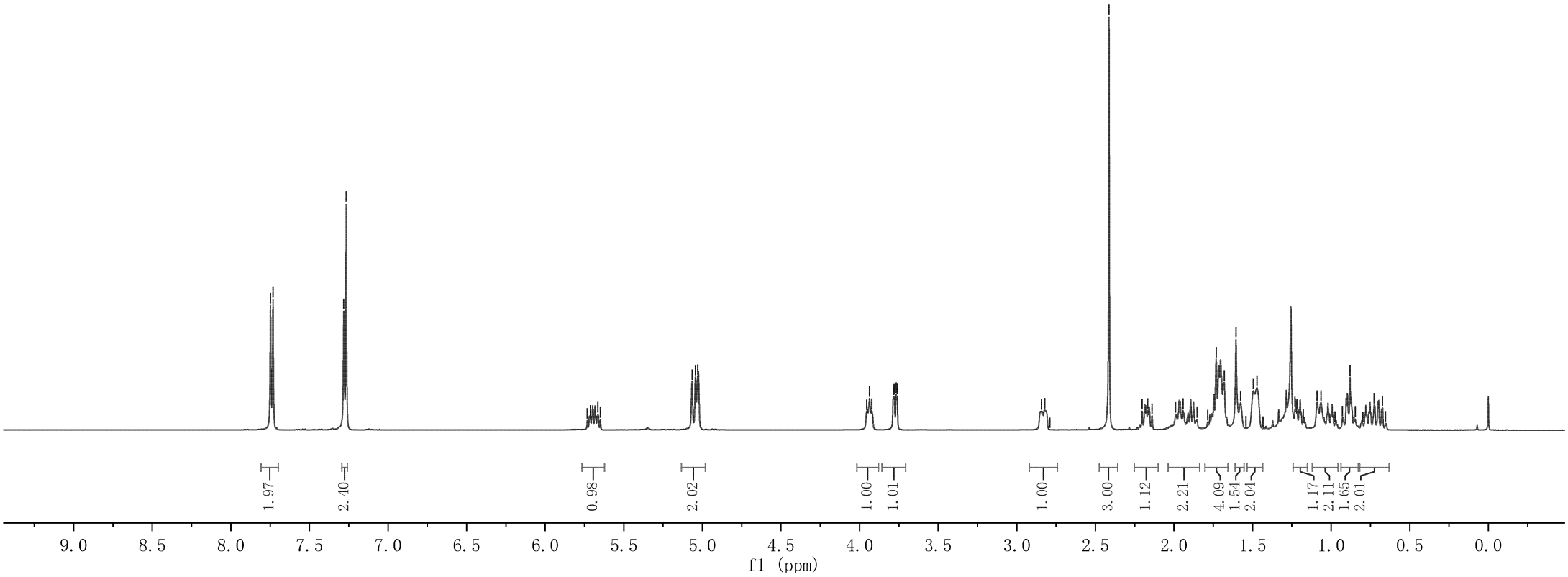
3c



	Parameter	Value
1	Title	ttd-2-79-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.1
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-20T11:18:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0

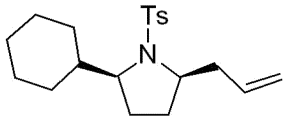


3d

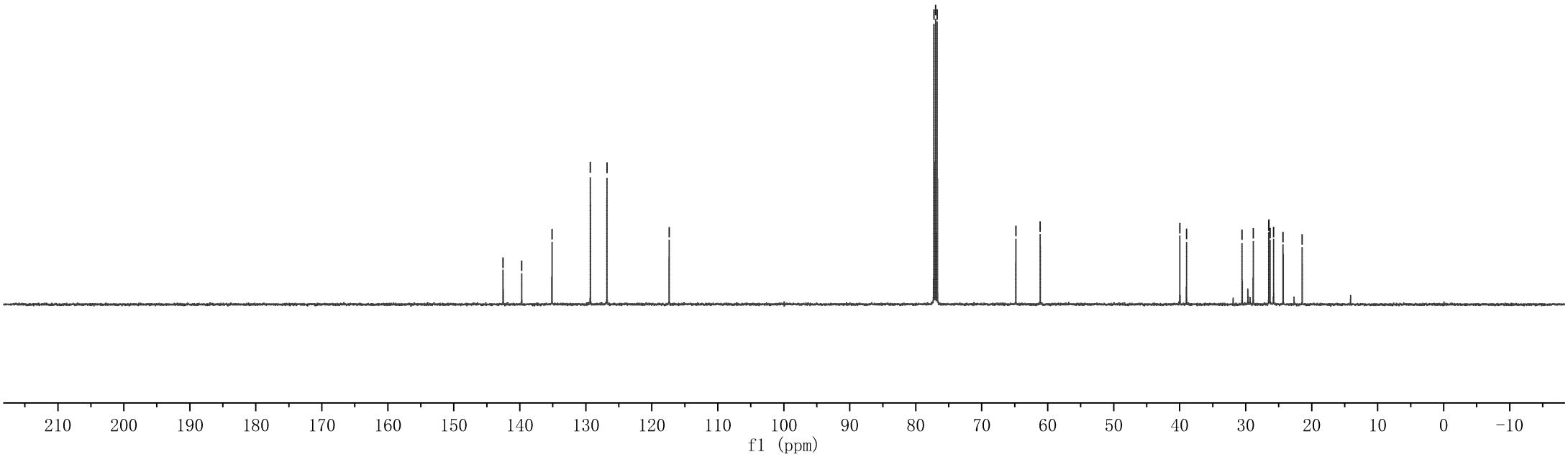


	Parameter	Value
1	Title	ttd-2-79-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-20T11:46:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

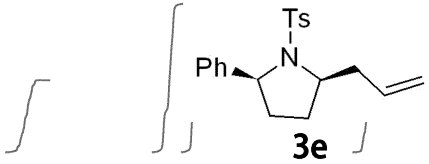
142.54
139.72
135.12
129.31
126.79
117.37
77.25
77.00
76.75
64.83
61.14
39.98
38.97
30.55
28.86
26.50
26.48
26.32
25.78
24.34
21.44



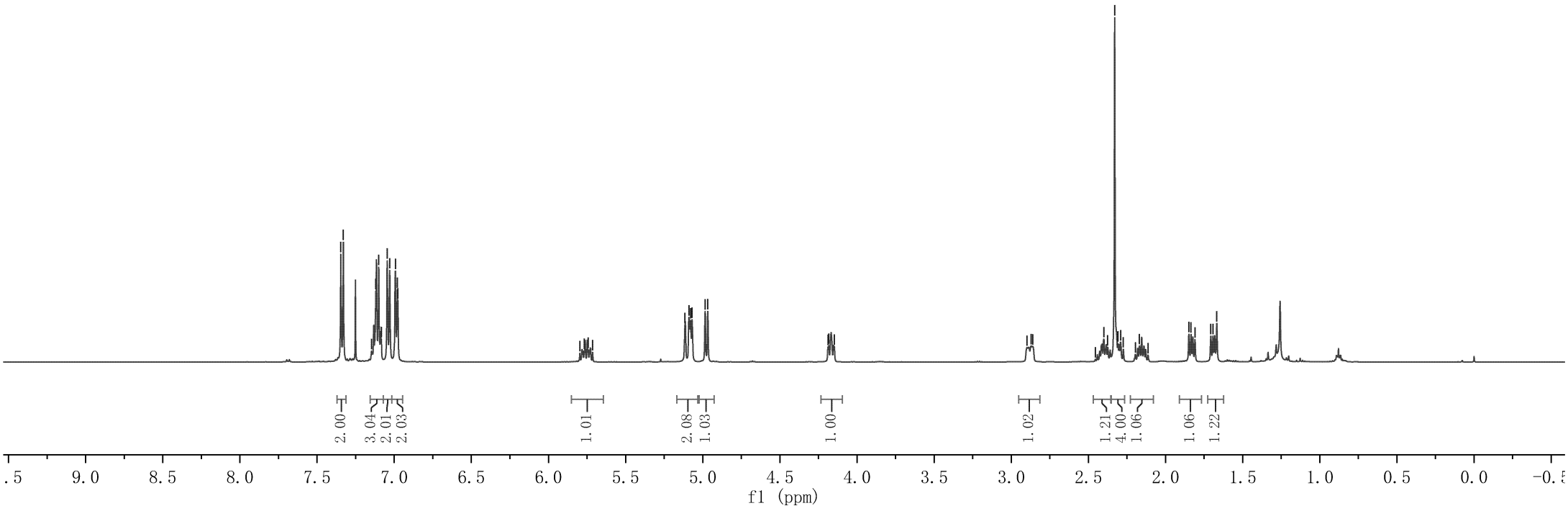
3d



	Parameter	Value
1	Title	ttd-2-82-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-22T20:51:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0

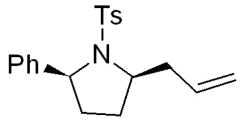


3e



	Parameter	Value
1	Title	ttd-2-82-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-22T21:19:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

142.31
142.23
138.61
134.76
128.90
127.95
126.82
126.75
126.50
117.66
77.25
77.00
76.75
64.04
60.74
39.14
33.00
27.52
21.31



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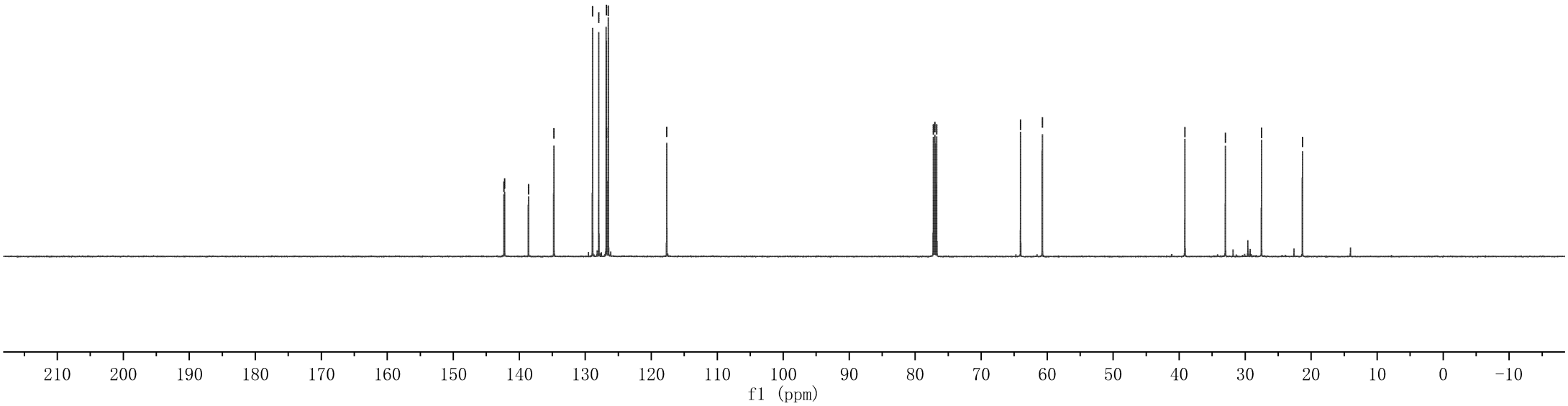
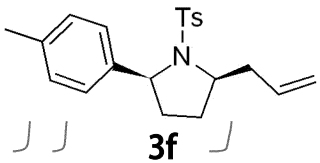


	Parameter	Value
1	Title	ttd-2-73-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-17T22:15:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0



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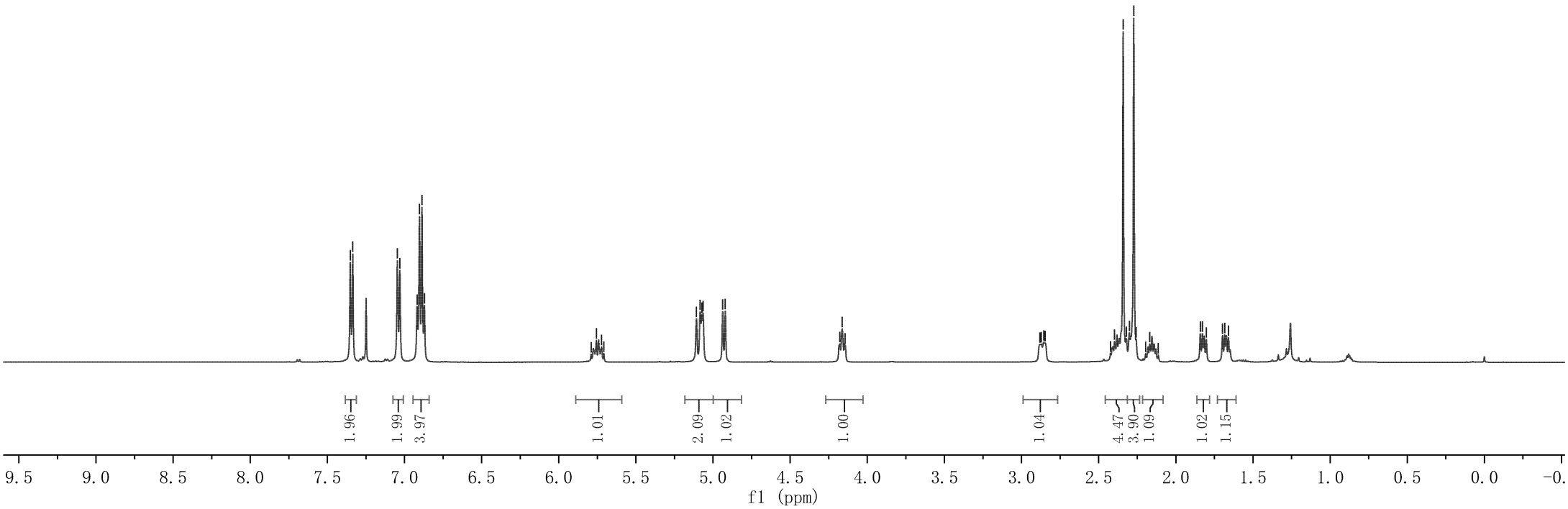
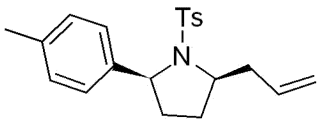


	Parameter	Value
1	Title	ttd-2-73-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-17T22:44:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

142.23
139.34
138.75
136.41
134.82
128.82
128.59
126.86
126.47
117.62
77.25
77.00
76.75
63.79
60.73
39.16
33.08
27.56
21.33
20.93



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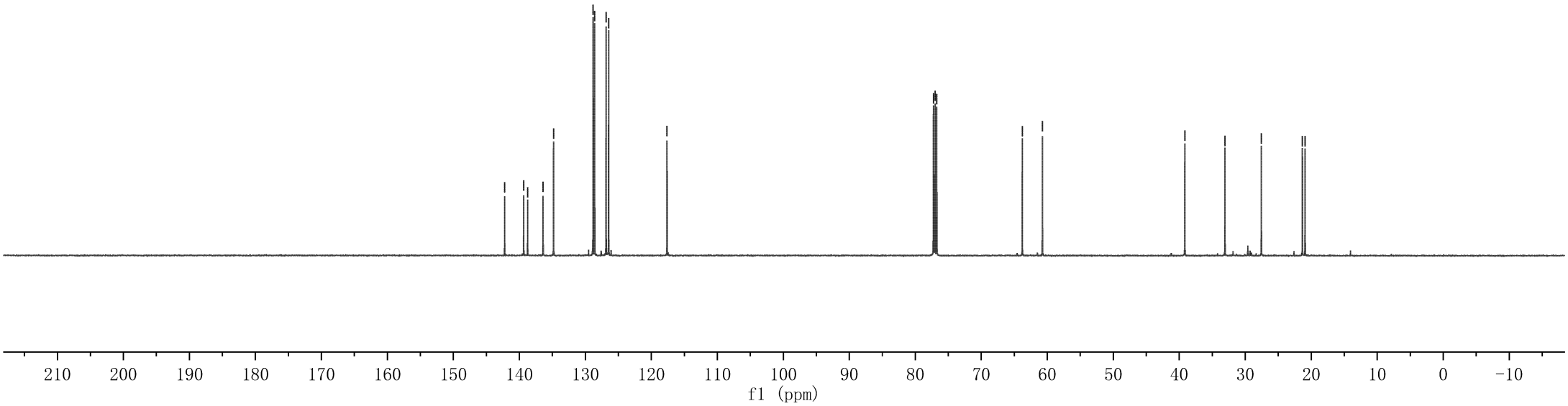
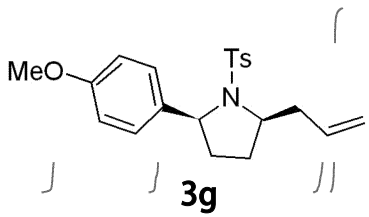
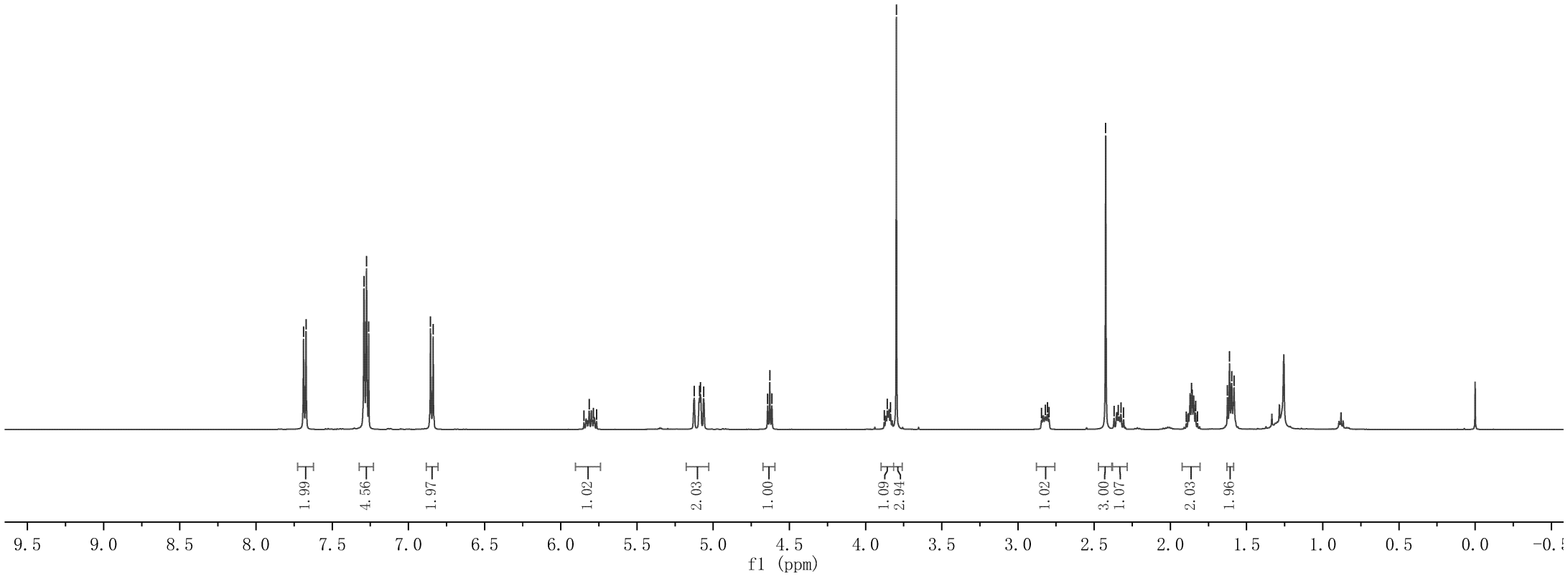


	Parameter	Value
1	Title	ttd-2-84-1-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-23T16:52:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0

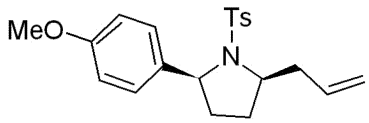


3g

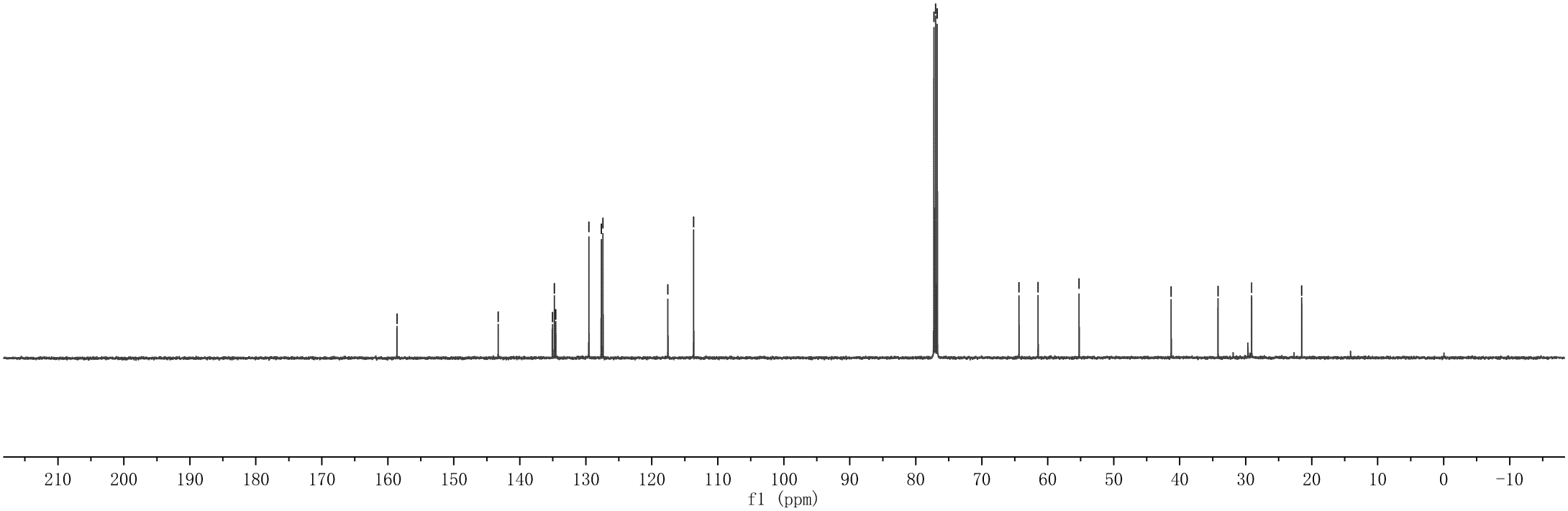


158.61
143.28
135.06
134.77
134.55
129.53
127.66
127.40
117.56
113.66
77.25
77.00
76.75
64.36
61.47
55.25
41.30
34.20
29.11
21.51

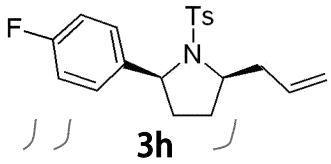
	Parameter	Value
1	Title	ttd-2-84-1-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-23T17:20:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9



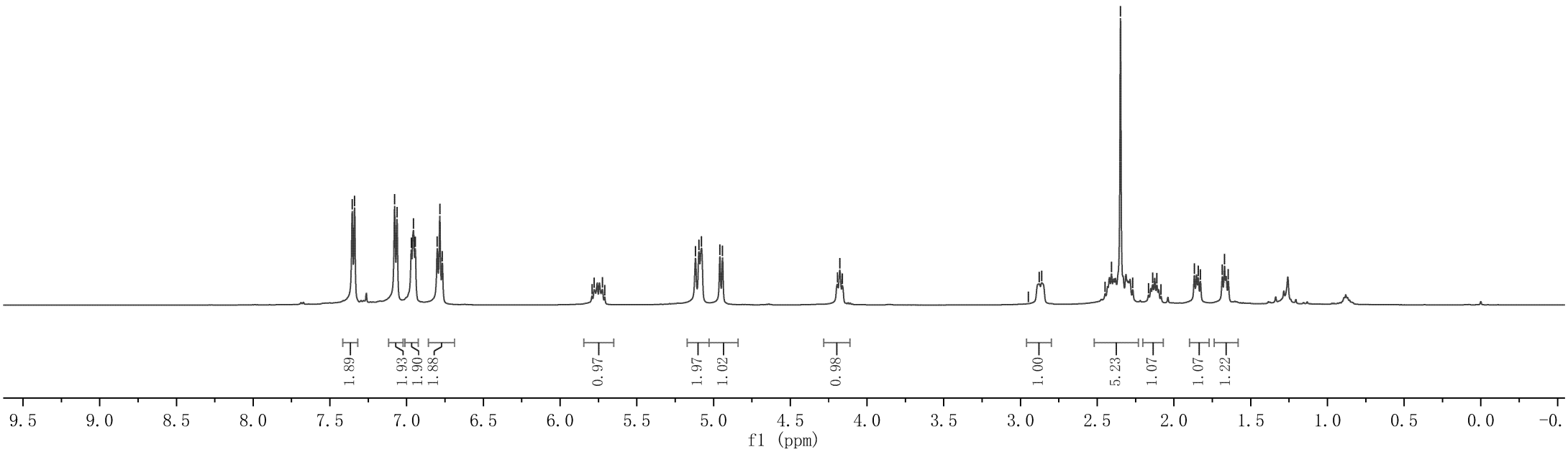
3g

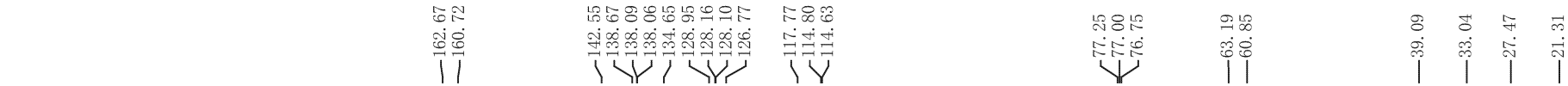


	Parameter	Value
1	Title	ttd-2-71-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-17T15:44:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0

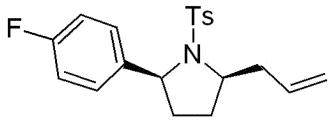


3h

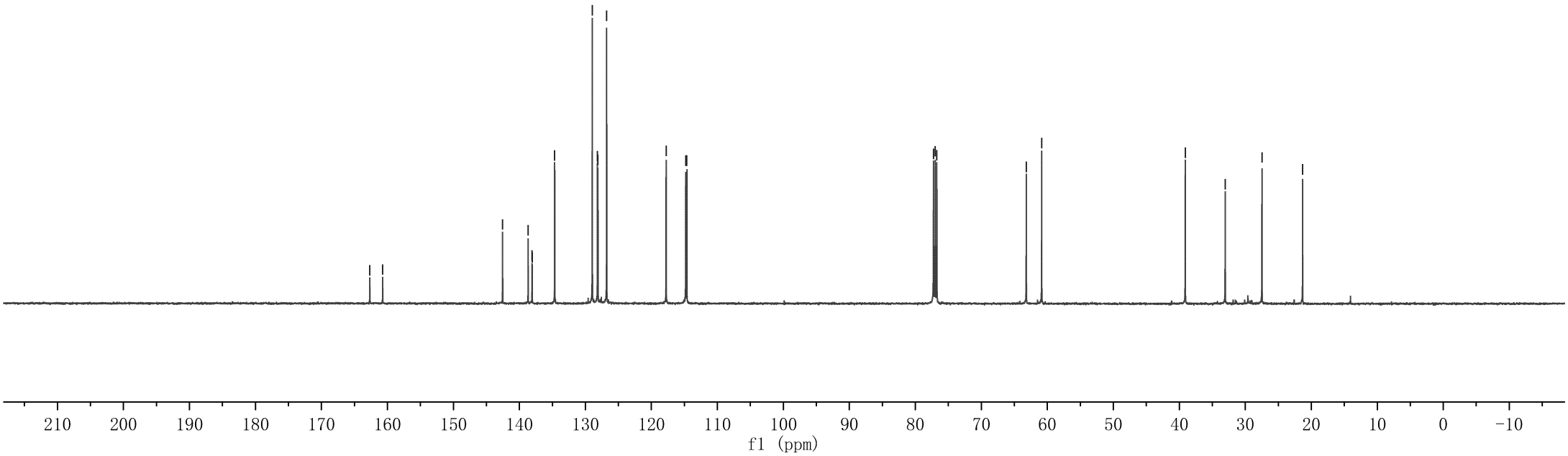




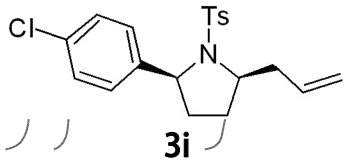
	Parameter	Value
1	Title	ttd-2-71-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	528
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-17T16:13:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9



3h



	Parameter	Value
1	Title	ttd-2-75-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-18T21:17:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0



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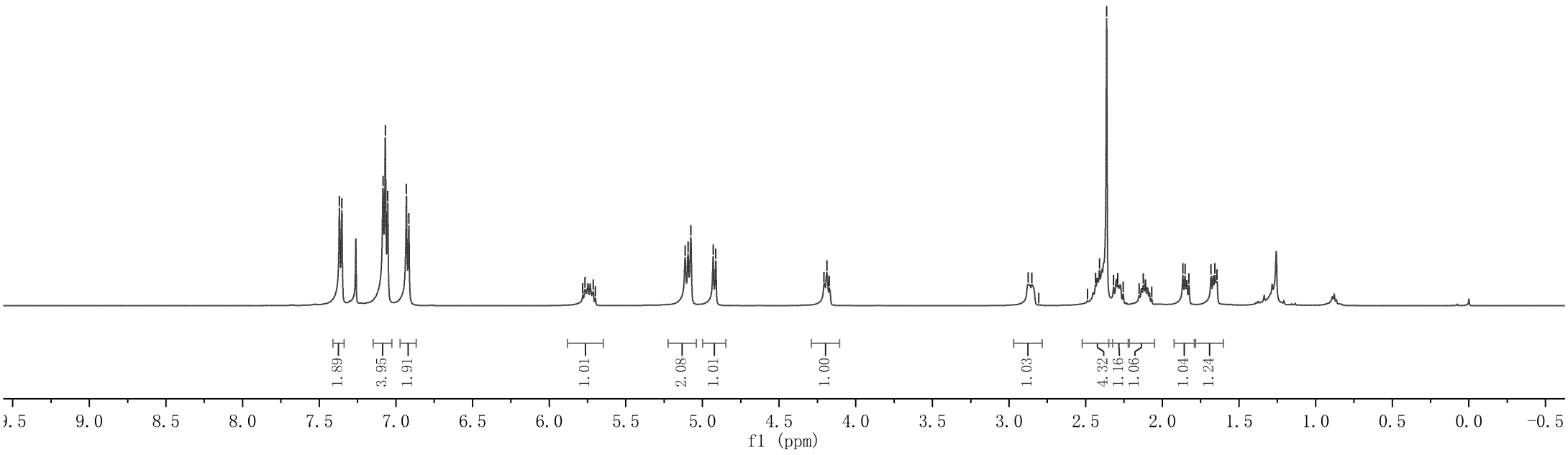

	Parameter	Value
1	Title	ttd-2-75-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-18T21:46:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

142.70
140.87
138.61
134.60
132.60
129.01
128.05
127.91
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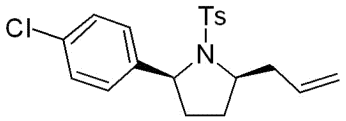
63.19
60.96
39.05
32.99
27.44
21.35



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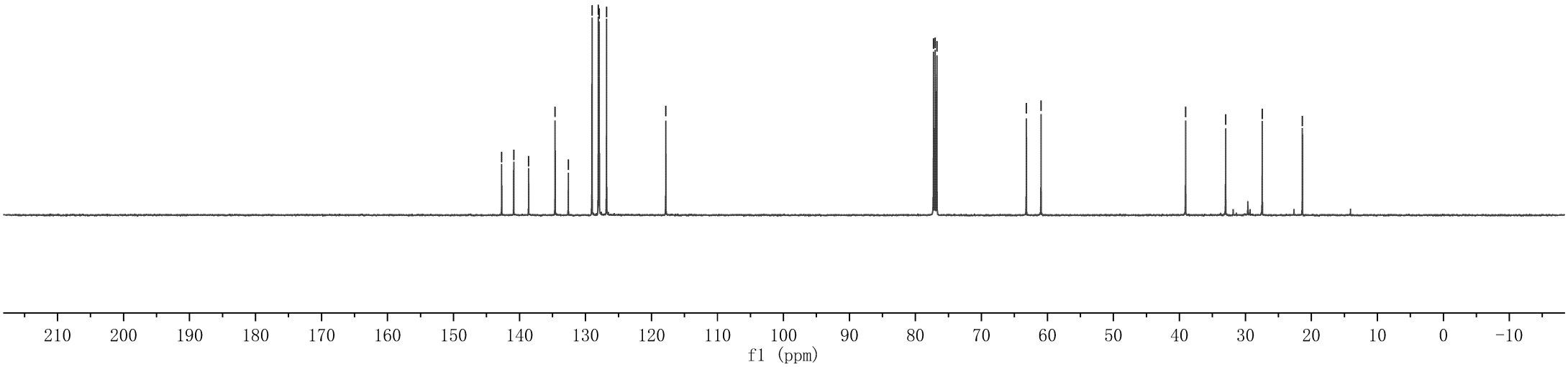
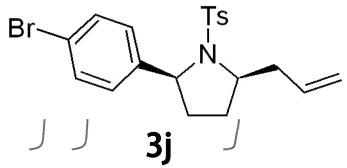


	Parameter	Value
1	Title	ttd-2-80-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-20T16:31:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0



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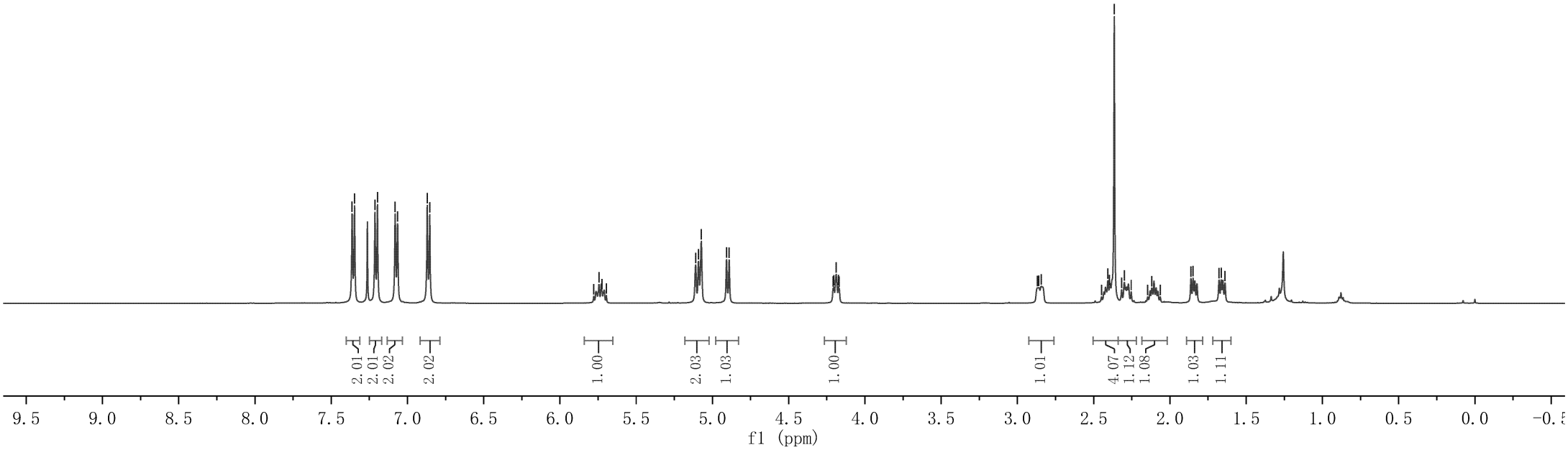

	Parameter	Value
1	Title	ttd-2-80-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-20T16:59:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

142.69
141.33
138.56
134.55
130.96
128.99
128.25
126.75
120.65
117.80
77.25
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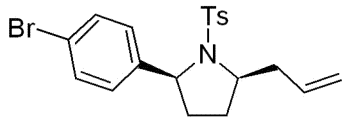
63.17
60.97
39.03
32.90
27.41
21.35



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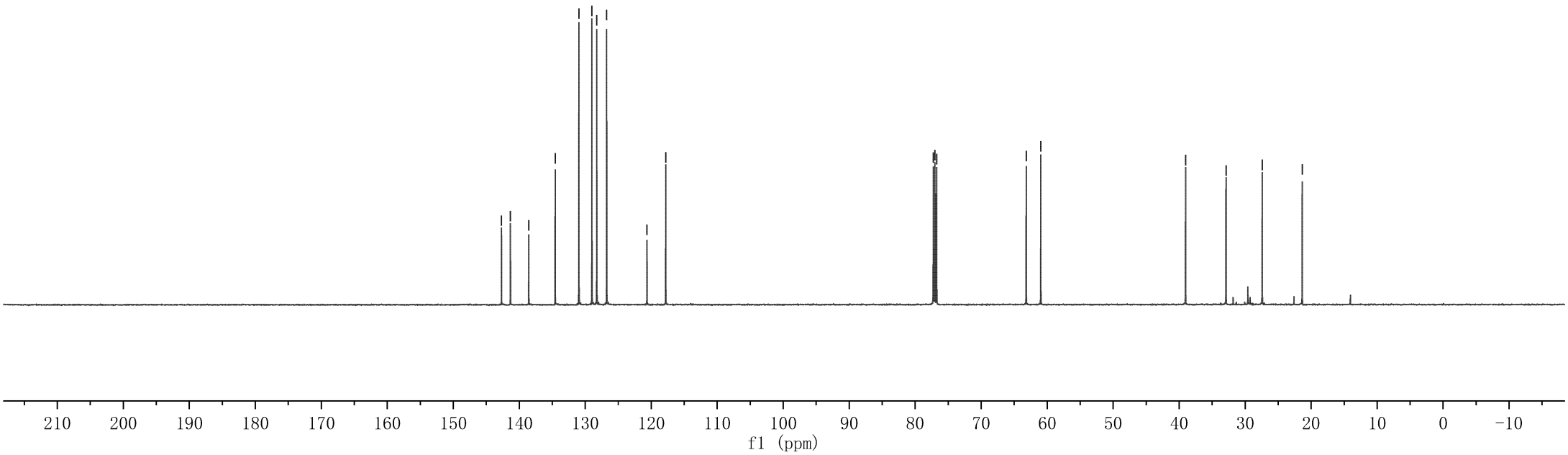
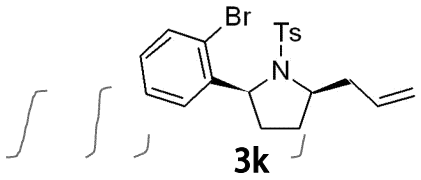
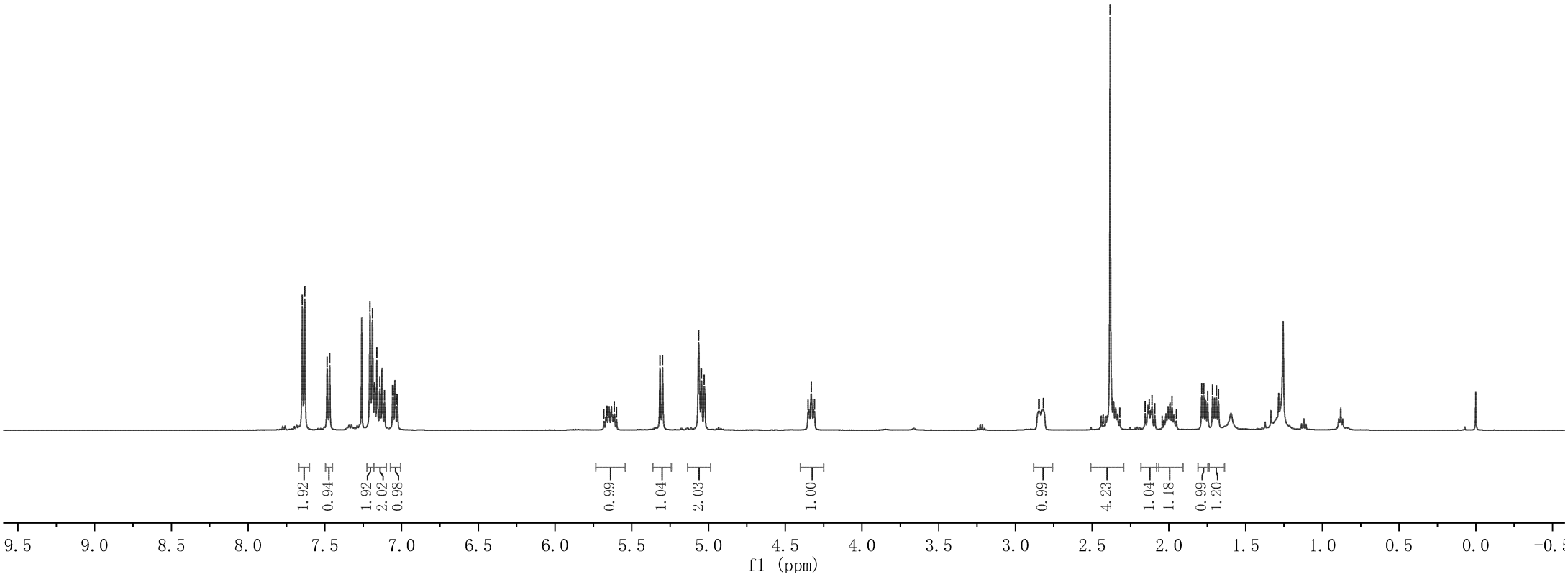


	Parameter	Value
1	Title	ttd-2-95-2328-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-29T17:30:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0

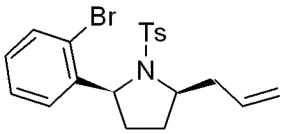


3k

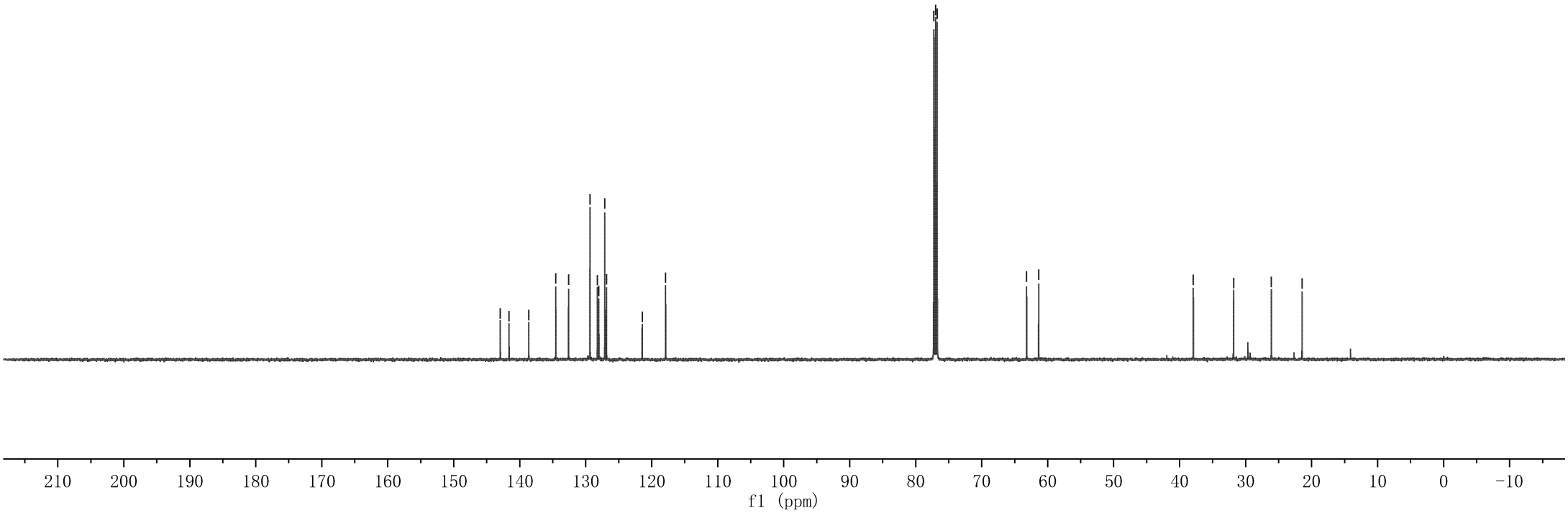


	Parameter	Value
1	Title	ttd-2-95-2328-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	325
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-29T17:48:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

142.95
141.62
138.63
134.53
132.61
129.36
128.23
128.02
127.11
126.85
121.45
117.89
77.25
77.00
76.75
63.19
61.36
37.93
31.82
26.10
21.44



3k



	Parameter	Value
1	Title	ttd-2-74-500-h
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	294.9
5	Number of Scans	16
6	Acquisition Time	3.2768
7	Acquisition Date	2016-02-18T14:07:00
8	Spectrometer Frequency	500.17
9	Spectral Width	10000.0

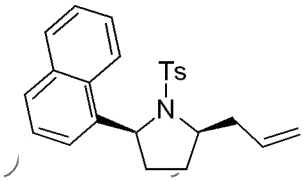
7.982 7.966 7.833 7.817 7.670 7.654 7.541 7.525 7.502 7.459 7.445 7.243 7.220 7.182 7.168 7.095 7.079

5.829 5.813 5.763 5.714 5.695 5.681

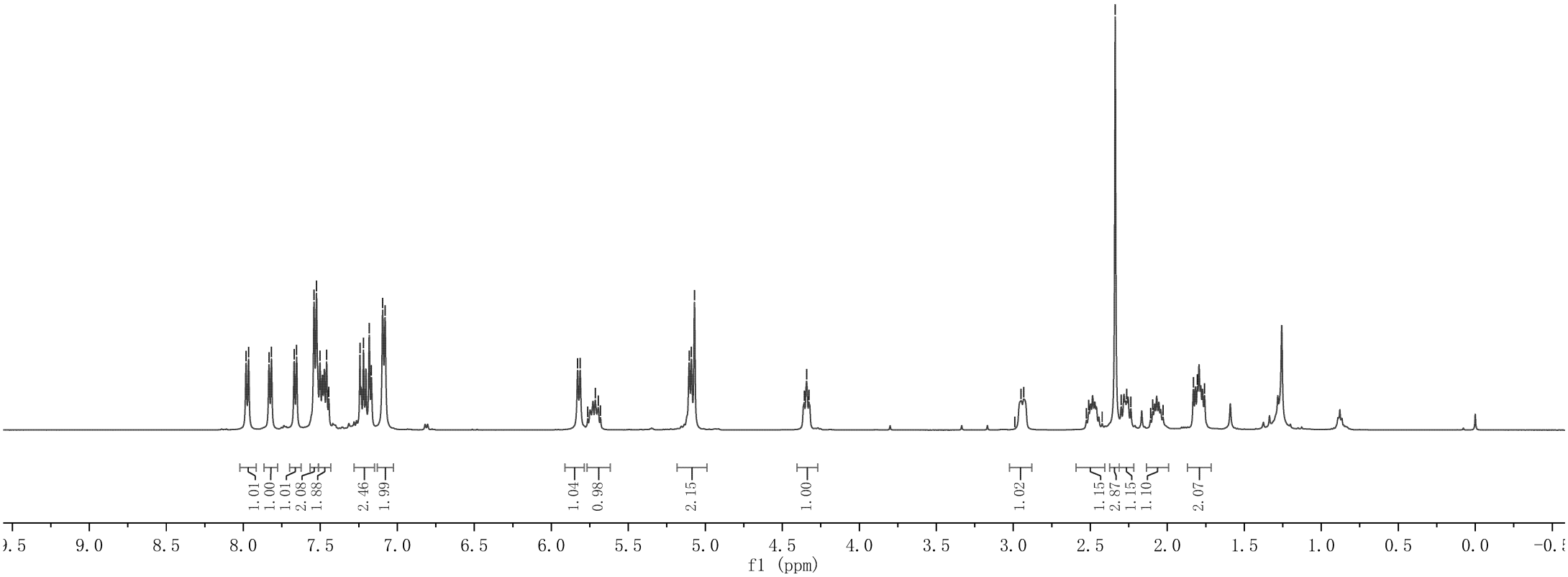
5.104 5.090 5.070

4.357 4.342 4.327

2.990 2.949 2.931 2.525 2.510 2.423 2.338 2.299 2.263 2.237 2.109 2.094 2.028 1.830 1.805 1.758



3l



	Parameter	Value
1	Title	ttd-2-74-500-c
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.0
5	Number of Scans	512
6	Acquisition Time	1.1010
7	Acquisition Date	2016-02-18T14:35:00
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

142.69
138.82
137.30
134.76
133.71
129.84
129.11
128.86
127.30
127.05
125.96
125.30
124.77
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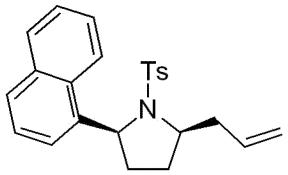
60.95
60.93
38.38
32.01
27.14
21.37



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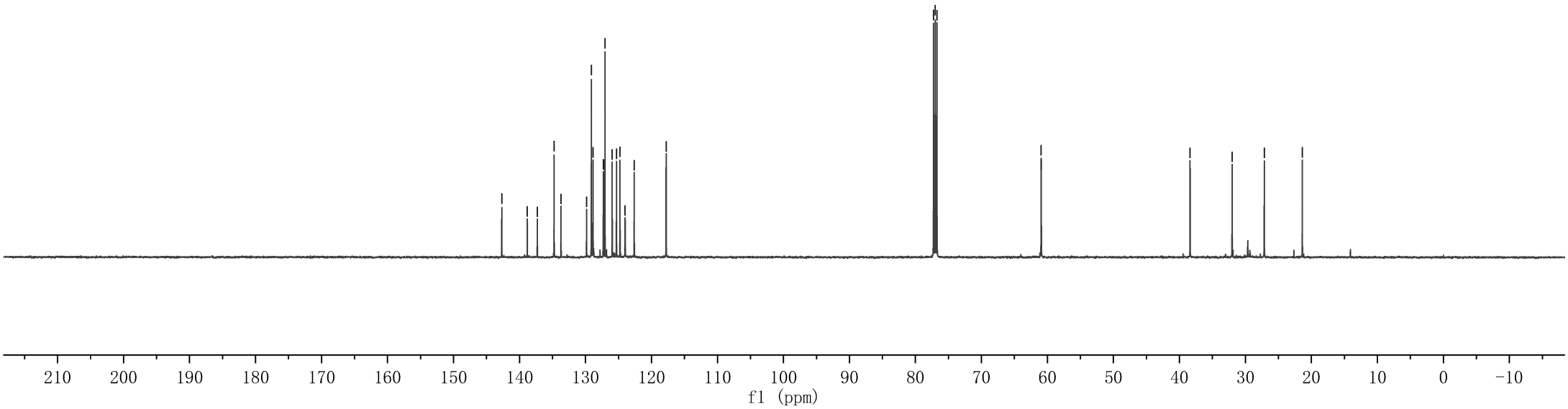
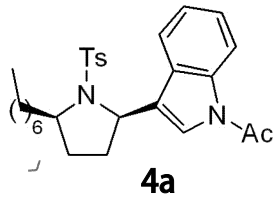
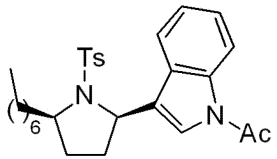


	Parameter	Value
1	Title	LTY-1-38-P1
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	297.6
5	Number of Scans	8
6	Acquisition Time	3.1719
7	Acquisition Date	2019-03-02T04:18:09
8	Spectrometer Frequency	500.17
9	Spectral Width	10330.6



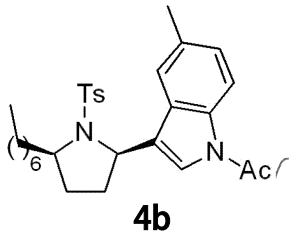
4a

	Parameter	Value
1	Title	LTY-1-38-P1-C
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.2
5	Number of Scans	28
6	Acquisition Time	1.1010
7	Acquisition Date	2019-03-02T04:20:55
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9



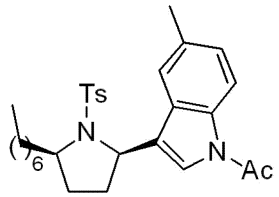
4a

	Parameter	Value
1	Title	LTY-1-65a2
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.4
5	Number of Scans	8
6	Acquisition Time	3.9846
7	Acquisition Date	2019-03-18T13:36:13
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7



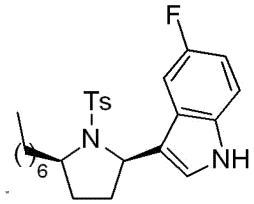
4b

	Parameter	Value
1	Title	LTY-1-65a-C
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Number of Scans	58
6	Acquisition Time	1.1010
7	Acquisition Date	2019-03-17T04:32:11
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9



4b

	Parameter	Value
1	Title	LTY-1-78
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	297.3
5	Number of Scans	7
6	Acquisition Time	3.1719
7	Acquisition Date	2019-03-26T00:43:05
8	Spectrometer Frequency	500.17
9	Spectral Width	10330.6



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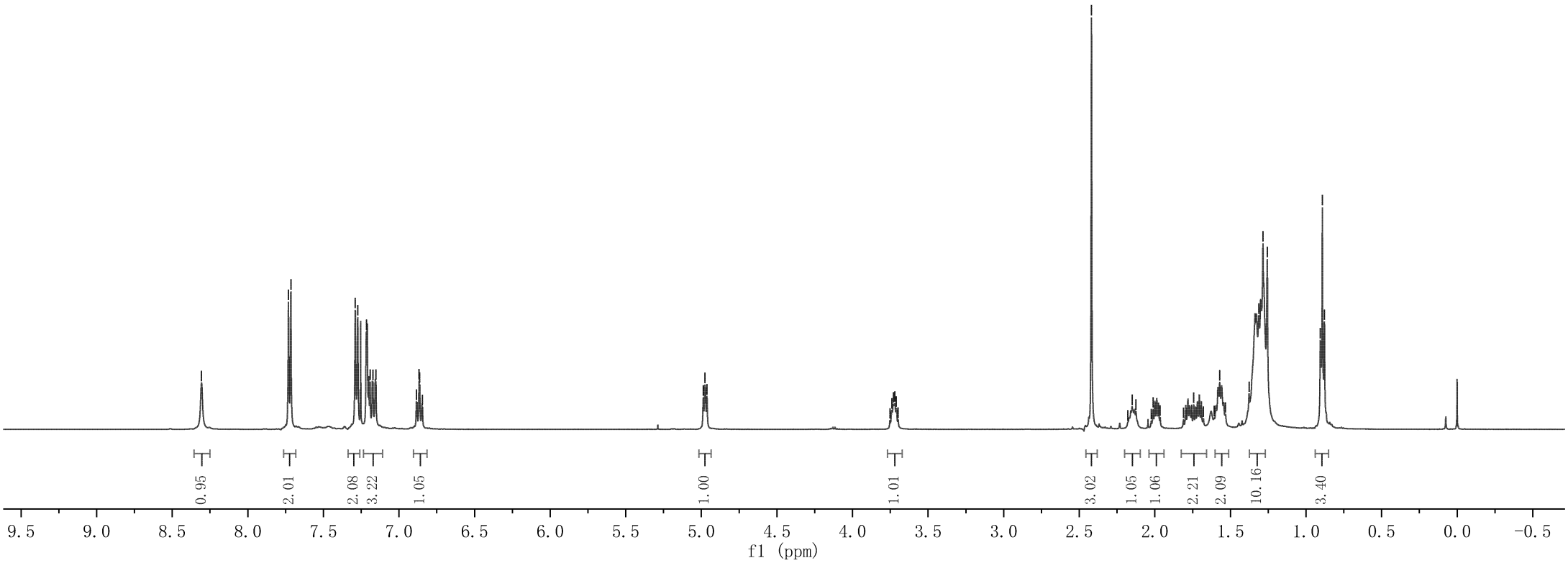
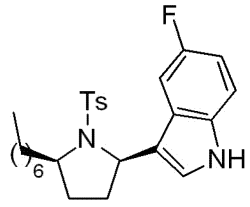


158.38
156.52
143.28
134.99
133.33
129.53
127.59
125.40
125.32
124.56
118.10
118.06
112.06
111.98
110.19
109.98
103.88
103.69
77.25
77.00
76.75
62.08
58.67
37.34
32.00
31.80
30.03
29.49
29.28
26.75
22.62
21.47
14.08

	Parameter	Value
1	Title	LTY-1-78-C
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Number of Scans	77
6	Acquisition Time	1.1010
7	Acquisition Date	2019-03-26T00:45:44
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9



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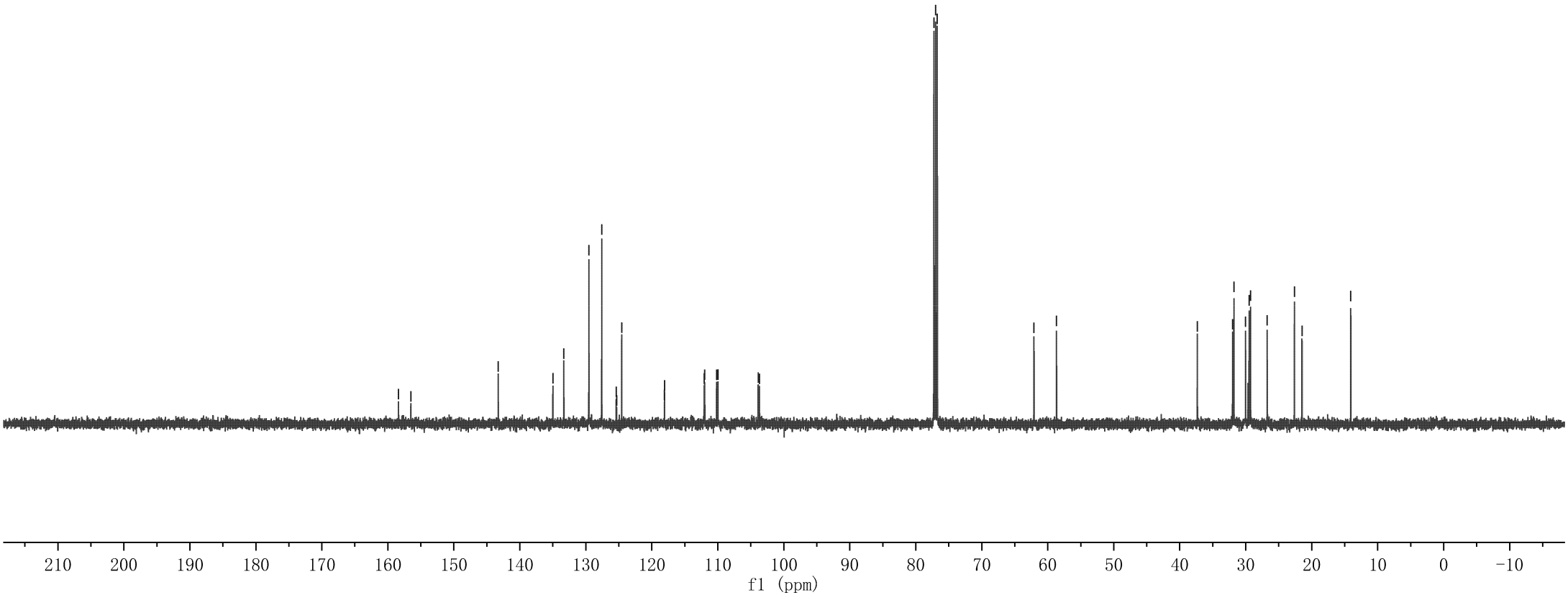
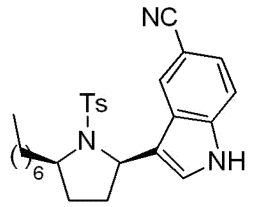


	Parameter	Value
1	Title	LTY-1-74-P1
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.5
5	Number of Scans	12
6	Acquisition Time	3.1719
7	Acquisition Date	2019-03-21T04:31:26
8	Spectrometer Frequency	500.17
9	Spectral Width	10330.6



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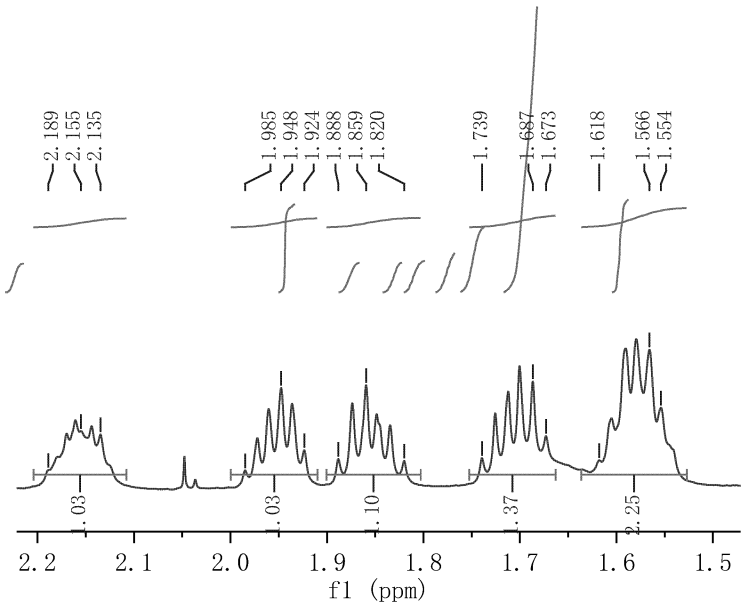

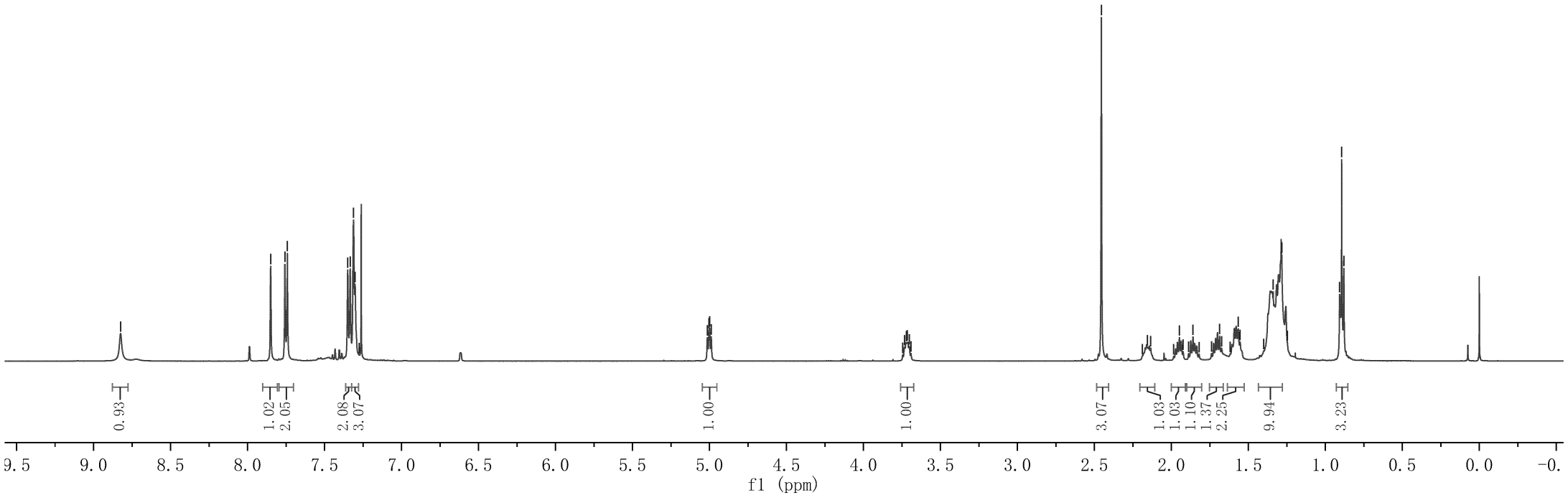

	Parameter	Value
1	Title	LTY-1-74-P1-C
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	299.0
5	Number of Scans	79
6	Acquisition Time	1.1010
7	Acquisition Date	2019-03-21T04:34:24
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9

143.69
138.41
134.52
129.76
127.57
124.89
124.63
124.33
120.74
119.15
112.33
103.34
102.23
77.25
77.00
76.75
62.18
58.38
37.24
32.42
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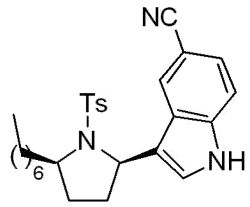
29.46
29.27
26.73
22.62
21.52
14.07



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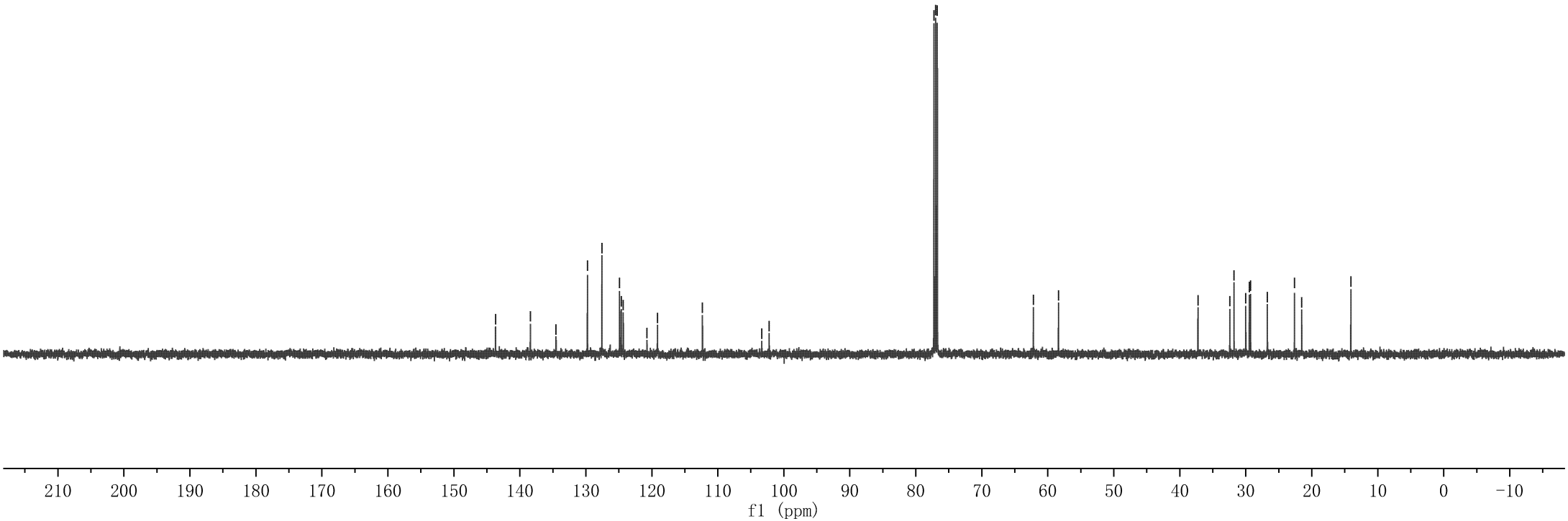
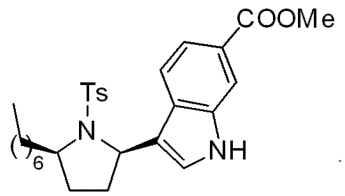
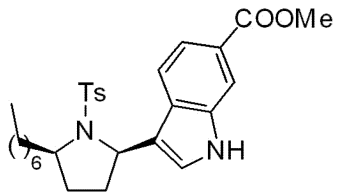


	Parameter	Value
1	Title	LTY-1-79
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Number of Scans	8
6	Acquisition Time	3.1719
7	Acquisition Date	2019-03-23T04:37:49
8	Spectrometer Frequency	500.17
9	Spectral Width	10330.6

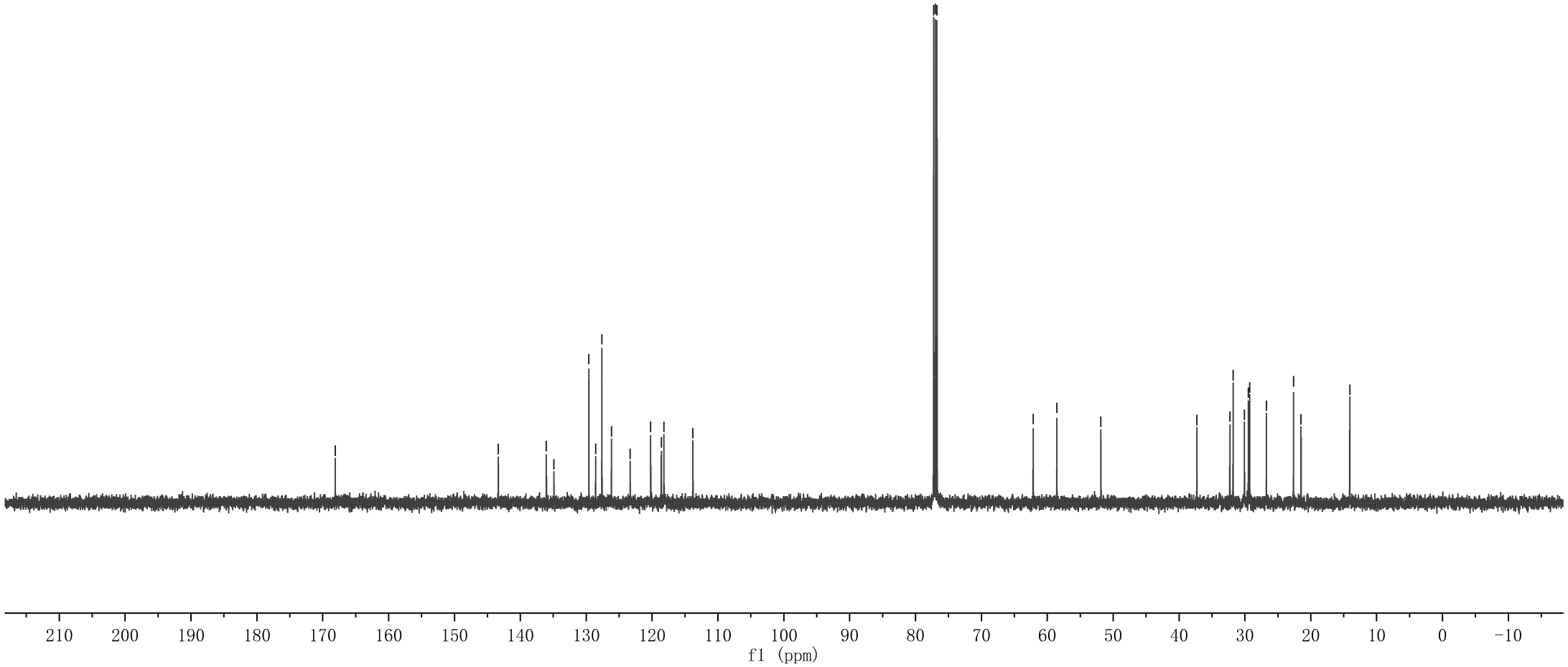


4e

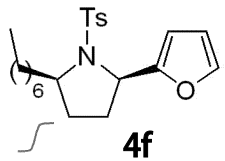
	Parameter	Value
1	Title	LTY-1-79-C
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.7
5	Number of Scans	63
6	Acquisition Time	1.1010
7	Acquisition Date	2019-03-23T04:40:55
8	Spectrometer Frequency	125.77
9	Spectral Width	29761.9



4e



	Parameter	Value
1	Title	LTY-1-66
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.4
5	Number of Scans	10
6	Acquisition Time	3.9846
7	Acquisition Date	2019-03-18T13:39:20
8	Spectrometer Frequency	400.13
9	Spectral Width	8223.7



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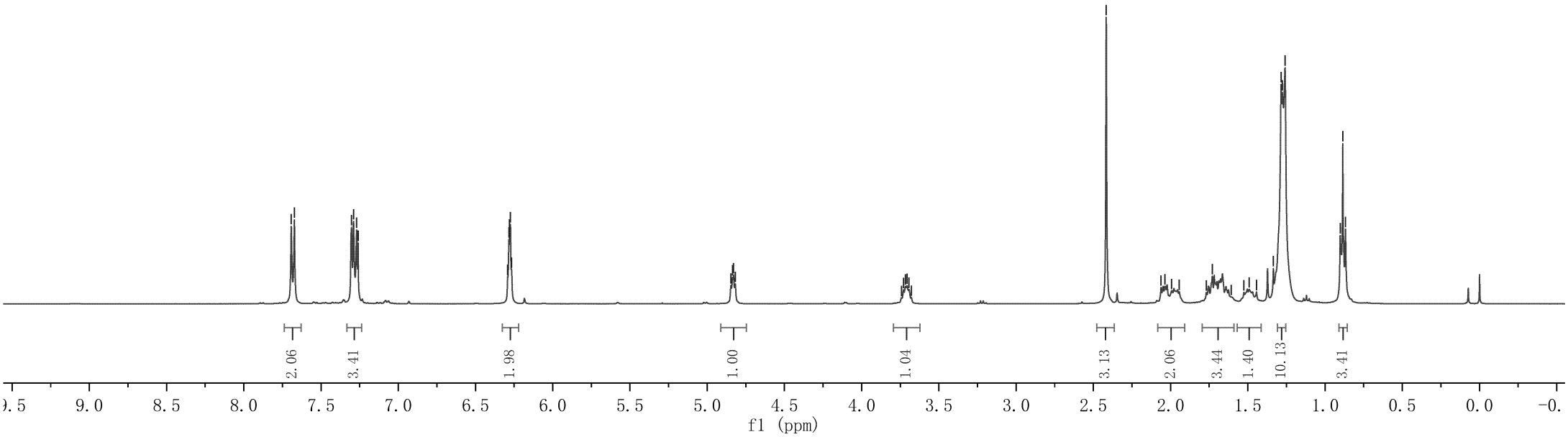
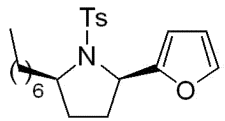


	Parameter	Value
1	Title	LTY-1-66-C
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	295.4
5	Number of Scans	35
6	Acquisition Time	1.3631
7	Acquisition Date	2019-03-18T13:41:37
8	Spectrometer Frequency	100.61
9	Spectral Width	24038.5

154.95
143.19
141.67
135.71
129.53
127.47
110.24
107.09
77.32
77.00
76.68
62.00
58.08
36.52
31.76
30.37
30.29
29.44
29.21
26.26
22.61
21.47
14.06



4f