Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Merging strain-release and copper catalysis: the selective ring-opening cross-coupling of 1,2-oxazetidines with boronic acids

Ji-Hang Xu,[a] Zi-Kui Liu,[a] Yan-Liu Tang,[a] Yang Gao*[b] and Xiao-Qiang Hu*[a] ‡

† Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, School of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, China.

‡ School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, 510006, China.

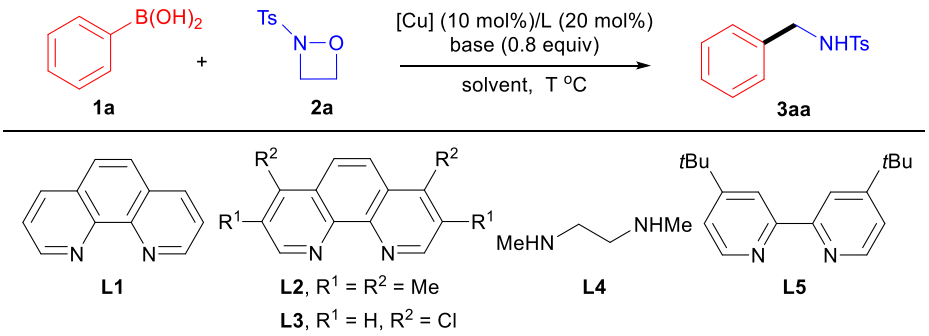
hxq071303127@126.com

Table of Contents

1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers (Alfa, TCI and Sigma-Aldrich etc.), and used without further purification. All the solvents were treated according to general methods. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI. Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

2. Optimization of the reaction conditions

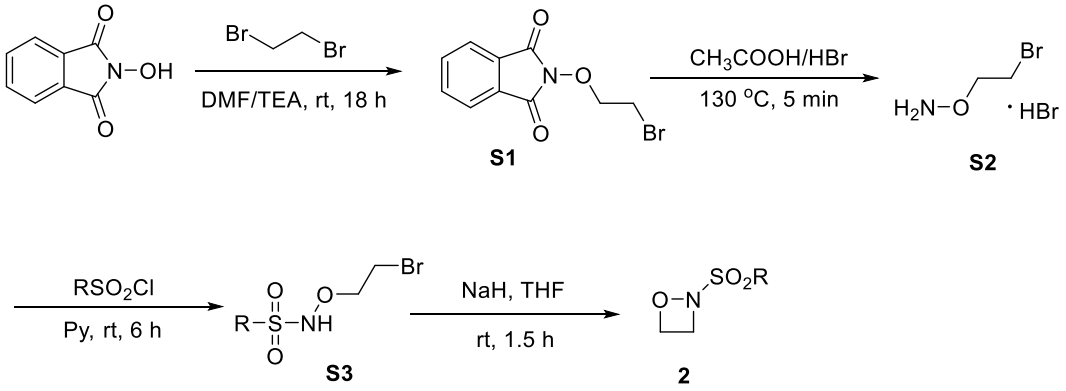


entry	catalyst	base	solvent	yield [b] (%)
1	$Cu(OAc)_2/L_1$	K_2CO_3	DMSO	39
2	$CuBr_2/L_1$	K_2CO_3	DMSO	55
4	$CuCl/L_1$	K_2CO_3	DMSO	62
5	$CuBr/L_1$	K_2CO_3	DMSO	33
6	CuI/L_1	K_2CO_3	DMSO	75
7	CuI/L_1	K_2CO_3	toluene	17
8	CuI/L_1	K_2CO_3	DMF	44
9	CuI/L_1	K_2CO_3	DCE	82
10	CuI/L_1	Cs_2CO_3	DCE	59
11	CuI/L_1	CsF	DCE	69
12	CuI/L_1	K_3PO_4	DCE	84(80)[c]
13[d]	CuI/L_1	K_3PO_4	DCE	81
14[e]	CuI/L_1	K_3PO_4	DCE	33
15	CuI/L_2	K_3PO_4	DCE	82
16	CuI/L_3	K_3PO_4	DCE	76
17	CuI/L_4	K_3PO_4	DCE	trace
18	CuI/L_5	K_3PO_4	DCE	77
19[f]	CuI/L_1	K_3PO_4	DCE	56
20[g]	$--/L_1$	K_3PO_4	DCE	<5
21[h]	CuI/--	K_3PO_4	DCE	18

[a]Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (10 mol%), ligand (20 mol%), base (80 mol%), solvent (2.0 mL), 140 °C for 10 h. [b]GC yield using *n*-tetradecane as the internal standard. [c]Isolated yield. [d]K_3PO_4 (1.0 equiv). [e]K_3PO_4 (0.5 equiv). [f]At 100 °C. [g]Without copper catalyst. [h]Without ligand.

3. Preparation of substrates

3.1 General procedure for preparation of 1,2-oxazetidines



1) To a solution of *N*-hydroxyphthalimide (9.7 g, 60 mmol) in *N*, *N*-dimethyl formamide (80 mL) was added 1, 2-dibromoethane (120 mmol) and triethylamine (120 mmol). The solution was allowed to stand at room temperature with stirring, until the red color of the mixture turned colorless. The precipitate of triethylammonium bromide was filtered at suction. The filtrate was diluted with ice cold water (500 mL) and the solid precipitate was filtered off. The precipitate was recrystallized by ethanol to afford the desired product **S1** (30.4 mmol, 51% yield).

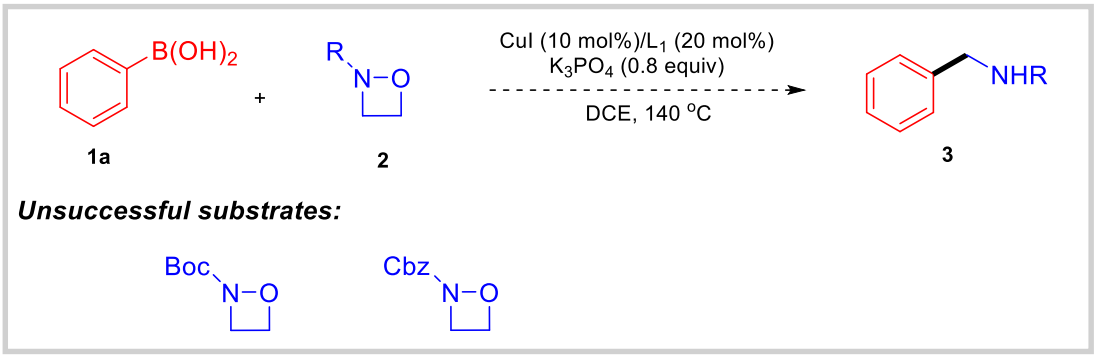
2) A suspension of phthalimidoxyethyl bromide **S1** (3.8 g, 0.012 mol) in glacial acetic acid (10 mL) and 48% hydrobromic acid (15 mL) was stirred at 130 °C for 5 min. After cooling down, 1,2-phthalic acid was filtered off. Removal of the solvent afforded the crude product **S2** as a yellow solid.

A suspension of **S2** (8.70 mmol, 1.0 equiv) in pyridine (15 mL) was stirred for 5 min at room temperature.

3) Then arylsulfonyl chloride (20.87 mmol, 2.4 equiv) was added in portions. The resulting brown suspension was stirred for 5 h. The reaction mixture was poured into 1.0 M HCl solution and extracted with EtOAc. Purification by flash column chromatography (EtOAc/PE 1:3) afforded the product **S3**.

4) To a solution of **S3** (0.166 mmol, 1.0 equiv) in anhydrous THF (4 mL) under argon was added NaH (60% in mineral oil, 0.374 mmol, 2.25 equiv). After stirring for 1.5 h, the reaction mixture was carefully poured into 1.0 M HCl solution and extracted with EtOAc. Purification by flash column chromatography (EtOAc/PE 1:2) afforded the final product **2** as a white solid.

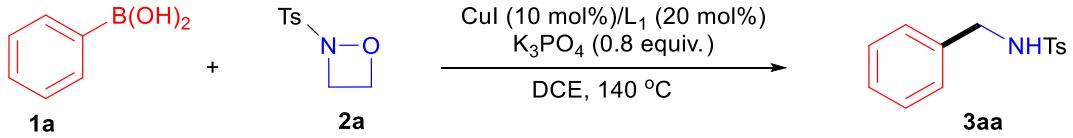
3.2 Unsuccessful Substrates



It should be noted that N-tert-butyloxycarbonyl (Boc) and N-carbobenzyloxy (Cbz) substituted 1,2-oxazetidines were not compatible in current reaction system.

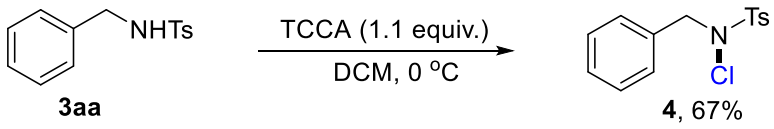
4. General Procedure and Spectral Data of the Products

4.1 General procedure for the synthesis of 3aa-ra, 3ab-3an.



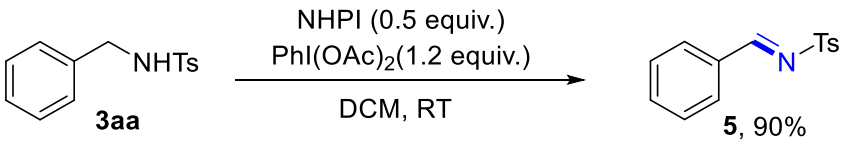
1a (24.2 mg, 0.2 mmol), **2a** (63.9 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), 1, 10-Phenanthroline (7.2 mg, 0.04 mmol) and K_3PO_4 (34.0 mg, 0.16 mmol) were dissolved in dichloroethane (2.0 mL). Then, the mixture was stirred at 140 ℃ for 10 h, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **3aa** in 80 % isolated yield as a white solid. Other products **3ba-ra, 3ab-3an** were prepared according to the above procedure. (Note: a heating module was used as the heating source.)

4.2 General procedure for the synthesis of 4, 5, 6, 7, 8, 9 and 10

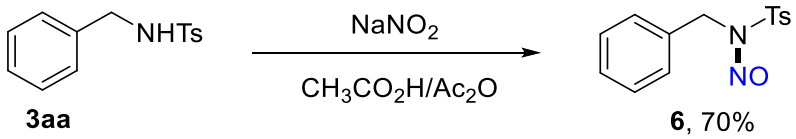


To an ice-cooled solution of **3aa** (109.6 mg, 0.418 mmol) in CH_2Cl_2 (4 mL) is added TCCA (107 mg, 0.460 mmol).Then the mixture is stirred for about 3 h at 0 ℃ before quenched by water (5 mL). The

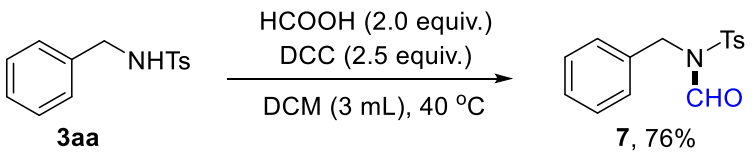
organic layer is separated and the aqueous layer is extracted with CH_2Cl_2.The combined organic phase is washed with brine and then dried over Na_2SO_4.After filtrated, the solvent is concentrated in vacuo. The crude product is purified by flash chromatography afforded the product **4** in 67 % isolated yield as a white solid.



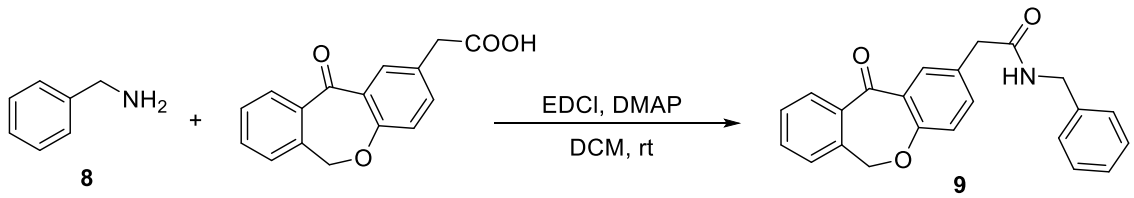
A dried reflux tube equipped with a magenetic stir bar charged with **3aa** (130.5 mg, 0.5 mmol), NHPI (40.8 mg, 0.25 mmol), and DCM (1 mL), then $PhI(OAc)_2$ (193.3 mg, 0.6 mmol) was added in one portion, The mixture was stirred at rt for 0.5 h under air. Then, the mixture was directly purified by flash column chromatography eluting with ethyl acetate and hexane to afford the product **5** in 90% isolated yield as a white solid.



The powered $NaNO_2$ (73.5 mg, 10.6 mmol) was added cautiously in five portions over a period of 6 h to a solution of **3aa** (130.5 mg, 0.5 mmol) in the mixture of AcOH and Ac_2O (1:4, 3.5 mL) at 0 ^oC. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for overnight. The mixture was then quenched with ice water (5 mL) with vigorous stirring and cooled for 1 h. The pale yellow precipitate was filtered and washed several times with water and then recrystallized from ethanol to yield white tiny crystals in 70% isolated yield.



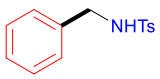
3aa (130.4 mg, 0.50 mmol) was dissolved in dry DCM (3 mL). Then, the reaction mixture was added successively formic acid (46.0 mg, 1 mmol) and DCC (257.5 mg, 1.25 mmol). The reaction was heated to 40 ℃ for 24 h. The product was purified by flash column chromatography (PE/EA=8:2) to afford the product **7** as a white solid in 76% yield.



To a solution of **8** (21.4 mg, 0.2 mmol), Isoxepac (44.8 mg, 0.17 mmol), EDCl (41.4 mg, 0.22 mmol), DMAP (28.6 mg, 0.23 mmol) in CH_2Cl_2 (2 mL).The reaction mixture was stirred at rt for 12 h. The crude product was purified by chromatography to give the product **9** as a white solid in 95% yield. The product **10** was prepared according to the same procedure as a white solid in 96% yield.

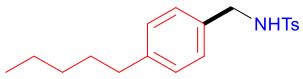
4.3 Spectral data of the products 3aa-ra, 3ab-3an, 5, 6 ,7,9 and 10

Product 3aa (Known compound, CAS: 1576-37-0)



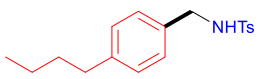
Yield of **3aa**: 44 mg, 80% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.21 – 7.18 (m, 2H), 4.71 (s, 1H), 4.12 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.6, 136.8, 136.2, 129.8, 128.7, 127.9, 127.9, 127.2, 47.3, 21.6.

Product 3ba



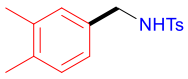
Yield of **3ba**: 48 mg, 70% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 4H), 4.66 (s, 1H), 4.08 (d, *J* = 6.1 Hz, 2H), 2.58 – 2.52 (m, 2H), 2.44 (s, 3H), 1.60 – 1.52 (m, 2H), 1.35 – 1.24 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.4, 142.8, 136.9, 133.4, 129.7, 128.7, 127.9, 127.2, 47.1, 35.5, 31.4, 31.1, 22.5, 21.5, 14.0. M.P.: 58.0 – 58.5 °C. HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{19}H_{25}NO_2SNa$: 354.1498; found: 354.1495.

Product 3ca



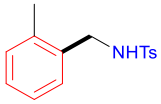
Yield of **3ca**: 38 mg, 61% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 4H), 4.78 (s, 1H), 4.07 (d, *J* = 6.1 Hz, 2H), 2.55 (s, 2H), 2.43 (s, 3H), 1.58 – 1.51 (m, 2H), 1.37 – 1.29 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5, 142.8, 136.9, 133.4, 129.7, 128.7, 127.9, 127.2, 47.1, 35.3, 33.6, 22.3, 21.6, 14.0. M.P.: 64.0 – 64.5 °C HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{18}H_{23}NO_2SNa$: 340.1342; found: 340.1340.

Product 3da (Known compound, CAS: 1392847-62-9)



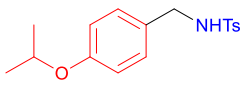
Yield of **3da**: 40 mg, 69% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.74 (s, 1H), 4.03 (d, *J* = 5.8 Hz, 2H), 2.43 (s, 3H), 2.20 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5, 137.0, 136.9, 136.3, 133.6, 129.9, 129.7, 129.2, 127.2, 125.3, 47.1, 21.6, 19.7, 19.4.

Product 3ea (Known compound, CAS: 191085-60-6)



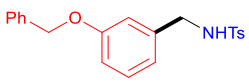
Yield of **3ea**: 32 mg, 59% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.14 – 7.07 (m, 3H), 4.54 (s, 1H), 4.08 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.6, 136.8, 136.6, 133.9, 130.6, 129.8, 128.9, 128.3, 127.2, 126.2, 45.4, 21.6, 18.8.

Product 3fa (Known compound, CAS: 1310996-52-1)



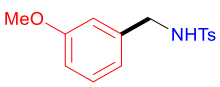
Yield of **3fa**: 26 mg, 40% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* =f 8.6 Hz, 2H), 4.65 (s, 1H), 4.53 – 4.47 (m, 1H), 4.04 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.6, 143.5, 136.9, 129.7, 129.3, 128.0, 127.2, 116.0, 69.9, 46.8, 22.0, 21.6.

Product 3ga



Yield of **3ga**: 48 mg, 66% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.35 – 7.26 (m, 3H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.87 – 6.75 (m, 3H), 4.96 (s, 2H), 4.89 (s, 1H), 4.08 (d, *J* = 6.2 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0, 143.6, 137.9, 136.9, 136.8, 129.8, 128.6, 128.0, 127.5, 127.2, 120.3, 114.5, 114.1, 69.9, 47.2, 21.6. M.P.: 98.0 – 98.5 ^{o}C HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{21}H_{21}NO_3SNa$: 390.1134; found: .390.1128.

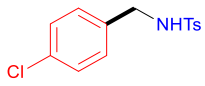
Product 3ha (Known compound, CAS: 191085-63-9)



Yield of **3ha**: 38 mg, 65% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 – 7.73 (m, 2H), 7.32 – 7.26 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 6.83 – 6.68 (m, 3H),

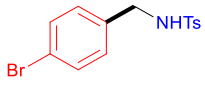
4.85 (s, 1H), 4.09 (d, *J* = 6.2 Hz, 2H), 3.74 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.8, 143.5, 137.9, 136.8, 129.7, 129.7, 127.2, 120.0, 113.6, 113.1, 55.2, 47.2, 21.6.

Product 3ia (Known compound, CAS: 10504-98-0)



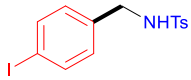
Yield of **3ia**: 47 mg, 80% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 4.97 (s, 1H), 4.08 (d, *J* = 6.3 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.7, 136.7, 134.9, 133.7, 129.8, 129.2, 128.8, 127.1, 46.6, 21.6.

Product 3ja (Known compound, CAS: 10504-96-8)



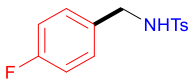
Yield of **3ja**: 46 mg, 68% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 4.98 (s, 1H), 4.06 (d, *J* = 6.3 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.7, 136.7, 135.4, 131.8, 129.8, 129.5, 127.1, 121.8, 46.6, 21.6.

Product 3ka (Known compound, CAS: 1377577-60-0)



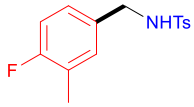
Yield of **3ka**: 48 mg, 62% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 1H), 4.05 (d, *J* = 6.3 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.7, 137.7, 136.7, 136.1, 129.8, 127.1, 93.4, 46.7, 21.6.

Product 3la (Known compound, CAS: 570417-42-4)



Yield of **3la**: 33 mg, 59% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.17 (s, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 4.82 (s, 1H), 4.09 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.3 (d, *J* = 245.0 Hz), 143.7, 136.8, 132.1 (d, *J* = 3.2 Hz), 129.8, 129.7 (d, *J* = 8.1 Hz), 127.2, 115.6 (d, *J* = 21.5 Hz), 46.6, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.25 (s, 1F).

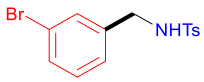
Product 3ma



Yield of **3ma**: 28 mg, 48% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.99 – 6.95 (m, 2H), 6.99 – 6.95 (t, *J* = 9.0 Hz, 1H), 4.77 (s, 1H), 4.05 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

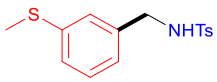
= 160.9 (d, *J* = 243.8 Hz), 143.6, 136.9, 131.7 (d, *J* = 3.6 Hz), 131.1 (d, *J* = 5.4 Hz), 129.7, 127.2, 126.9 (d, *J* = 8.2 Hz), 125.2 (d, *J* = 5.4 Hz), 115.1 (d, *J* = 17.5 Hz), 77.4, 77.2, 77.0, 76.7, 46.6, 21.6, 14.4. M.P.: 96.0 – 96.5 ºC HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{15}H_{16}FNO_2SNa$: 316.0078; found:316.0794. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -118.72 (s, 1F).

Product 3na (Known compound, CAS: 894156-93-5)



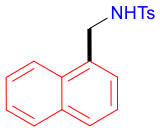
Yield of **3na**: 28 mg, 42% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 7.9 Hz, 2H), 7.36 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 1H), 7.14 (d, *J* = 4.7 Hz, 2H), 4.93 (s, 1H), 4.10 (d, *J* = 6.3 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.8, 138.6, 136.7, 130.9, 130.8, 130.2, 129.8, 127.1, 126.4, 122.6, 46.6, 21.6.

Product 3oa



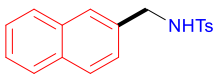
Yield of **3oa**: 18 mg, 30% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.01 (s, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 4.85 (s, 1H), 4.08 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.7, 139.2, 137.0, 136.7, 129.8, 129.1, 127.2, 125.8, 125.5, 124.4, 47.1, 21.6, 15.5. M.P.: 69.0 – 69.5 ºC HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{15}H_{17}NO_2S_2Na$: 330.0593; found: 330.0595.

Product 3pa (Known compound, CAS: 86328-84-9)



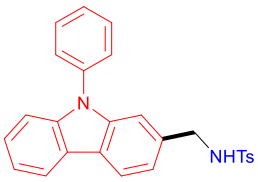
Yield of **3pa**: 28 mg, 45% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.92 – 7.86 (m, 1H), 7.86 – 7.81 (m, 1H), 7.77 (d, *J* = 8.3 Hz, 3H), 7.51 – 7.46 (m, 2H), 7.36 – 7.27 (m, 4H), 4.73 (s, 1H), 4.53 (d, *J* = 5.9 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.6, 136.5, 133.8, 131.3, 131.2, 129.7, 129.1, 128.7, 127.3, 127.0, 126.7, 126.1, 125.2, 123.3, 45.5, 21.6.

Product 3qa (Known compound, CAS: 125640-81-5)



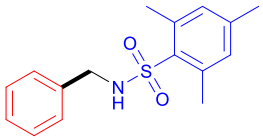
Yield of **3qa**: 30 mg, 49% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 – 7.76 (m, 2H), 7.75 – 7.70 (m, 3H), 7.59 (s, 1H), 7.48 – 7.44 (m, 2H), 7.34 – 7.31 – 7.25 (m, 3H), 4.88 (s, 1H), 4.27 (d, *J* = 6.2 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.6, 136.9, 133.6, 129.7, 128.6, 127.8, 127.7, 127.2, 126.7, 126.4, 126.2, 125.7, 47.5, 21.5.

Product 3ra



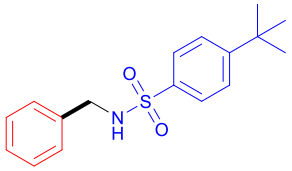
Yield of **3ra**: 44 mg, 51% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.50 – 7.47 (mf, 3H), 7.43 – 7.34 (m, 2H), 7.30 – 7.26 (m, 1H), 7.26 – 7.19 (m, 3H), 7.09 (dd, *J* = 8.0, 1.4 Hz, 1H), 4.72 (s, 1H), 4.24 (d, *J* = 6.1 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5, 141.3, 141.0, 137.3, 136.8, 134.1, 130.0, 129.7, 127.7, 127.2, 127.1, 126.1, 123.1, 122.9, 120.6, 120.3, 120.1, 119.8, 109.9, 109.1, 48.0, 21.5. M.P.: 168.0 – 168.5 ºC HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{26}H_{22}N_2O_2SNa$:449.1294; found: 449.1289.

Product 3ab (Known compound, CAS: 85045-43-8)



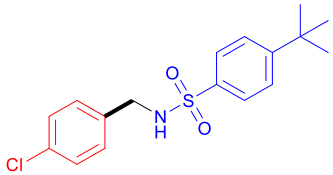
Yield of **3ab**: 43 mg, 74% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 7.25 (m, 2H), 7.18 – 7.16 (m, 2H), 6.96 (s, 2H), 4.75 (s, 1H), 4.07 (d, *J* = 6.2 Hz, 2H), 2.64 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.3, 139.2, 136.4, 133.5, 132.0, 128.7, 127.9, 127.9, 46.8, 23.0, 21.0.

Product 3ac (Known compound, CAS: 321704-15-8)



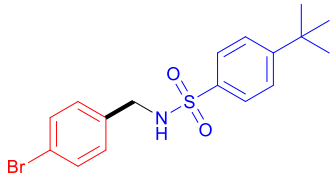
Yield of **3ac**: 37 mg, 61% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 6.7 Hz, 3H), 7.19 (d, *J* = 7.6 Hz, 2H), 4.88 (s, 1H), 4.14 (d, *J* = 6.0 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.5, 136.8, 136.3, 128.7, 127.9, 127.0, 126.1, 47.3, 35.2, 31.1.

Product 3ad



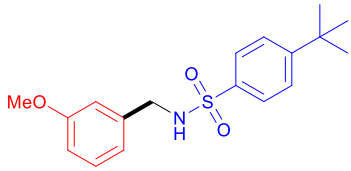
Yield of **3ad**: 57 mg, 84% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.28 (s, 1H), 4.11 (d, *J* = 6.3 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.6, 136.7, 134.9, 133.5, 129.3, 128.7, 126.9, 126.1, 46.5, 35.2, 31.1. M.P.: 163.0 – 163.5 ºC HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{17}H_{20}ClNO_2SNa$:360.0795; found: 360.0787.

Product 3ae



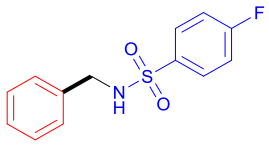
Yield of **3ae**: 57 mg, 75% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 5.02 (s, 1H), 4.10 (d, *J* = 6.4 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.7, 136.7, 135.4, 131.7, 129.6, 126.9, 126.1, 121.7, 46.6, 35.2, 31.1. M.P.: 173.0 – 173.5 ºC HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{17}H_{20}BrNO_2SNa$:404.0290; found: 404.0297.

Product 3af



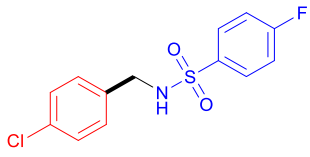
Yield of **3af**: 59 mg, 88% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.78 – 6.68 (m, 3H), 5.08 (s, 1H), 4.12 (d, *J* = 6.3 Hz, 2H), 3.71 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.7, 156.4, 137.9, 136.8, 129.6, 127.0, 126.1, 120.0, 113.6, 113.0, 55.2, 47.2, 35.2, 31.1. M.P.: 88.0 – 88.5 ºC HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{18}H_{23}NO_3SNa$:356.1291; found: 356.1285.

Product 3ag (Known compound, CAS: 727-36-6)



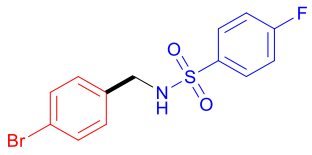
Yield of **3ag**: 38 mg, 72% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.72 (m, 2H), 7.43 – 7.03 (m, 7H), 5.08 (s, 1H), 4.14 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.0 (d, *J* = 243.8 Hz), 136.1 (d, *J* = 3.2 Hz), 136.0, 129.9 (d, *J* = 9.2 Hz), 128.7, 128.0, 127.9, 116.4 (d, *J* = 22.5 Hz), 47.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.32 (s, 1F).

Product 3ah



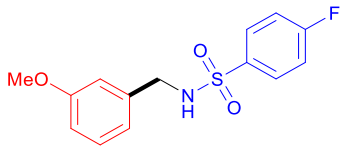
Yield of **3ah**: 40 mg, 66% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.80 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.24 (s, 1H), 4.09 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.1 (d, *J* = 253.6 Hz), 135.9 (d, *J* = 3.3 Hz), 134.6, 133.8, 129.9 (d, *J* = 9.3 Hz), 129.2, 128.8, 116.4 (d, *J* = 22.5 Hz), 46.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.84 (s, 1F). M.P.: 96.0 – 96.5 ºC HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{11}ClFNO_2SNa$:322.0075; found: 322.0076.

Product 3ai



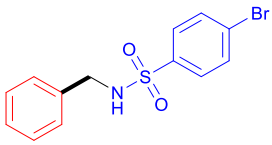
Yield of **3ai**: 32 mg, 46% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.38 (s, 1H), 4.06 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.1 (d, *J* = 253.4 Hz), 135.8 (d, *J* = 3.3 Hz), 135.2, 131.8, 129.8 (d, *J* = 9.2 Hz), 129.6, 121.9, 116.4 (d, *J* = 22.5 Hz), 46.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.81 (s, 1F). M.P.: 87.0 – 87.5 °C HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{11}BrFNO_2SNa$:365.9570; found: 365.9565.

Product 3aj



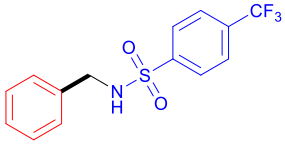
Yield of **3aj**: 36 mg, 61% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.82 (m, 2H), 7.15 (q, *J* = 8.3 Hz, 3H), 6.77 – 6.70 (m, 3H), 5.15 (s, 1H), 4.10 (d, *J* = 6.2 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.0 (d, *J* = 253.1 Hz), 159.8, 137.6, 136.0 (d, *J* = 3.2 Hz), 129.9, 129.80, 129.75, 120.0, 116.4 (d, *J* = 22.5 Hz), 113.4 (d, *J* = 25.8 Hz), 55.2, 47.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.29 (s, 1F). M.P.: 62.0 – 62.5 °C HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}FNO_3SNa$:318.0571; found: 318.0571.

Product 3ak (Known compound, CAS: 3609-87-8)



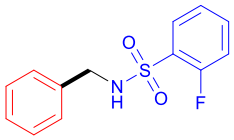
Yield of **3ak**: 37 mg, 57% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 – 7.69 (m, 2H), 7.65 – 7.46 (m, 2H), 7.29 – 7.26 (m, 3H), 7.20 – 7.17 (m, 2H), 4.80 (s, 1H), 4.16 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.9, 132.4, 129.4, 128.8, 128.7, 128.6, 128.1, 127.9, 47.3.

Product 3al (Known compound, CAS: 321704-24-9)



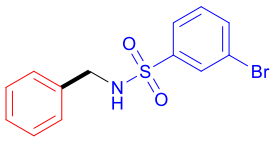
Yield of **3al**: 42 mg, 67% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.33 (m, 5H), 4.34 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 135.7, 134.3 (q, *J* = 32.7 Hz), 134.2, 128.8, 128.1, 127.9, 127.6, 126.3 (q, *J* = 271.1 Hz), 124.6, 121.9, 47.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.14 (s, 3F).

Product 3am (Known compound, CAS: 568566-59-6)



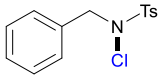
Yield of **3am**: 32 mg, 60% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (t, *J* = 7.6 Hz, 1H), 7.54 (q, *J* = 7.3, 6.6 Hz, 1H), 7.23 (t, *J* = 3.9 Hz, 4H), 7.21 – 7.10 (m, 3H), 5.20 (s, 1H), 4.18 (d, *J* = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.0 (d, *J* = 252.3 Hz), 135.9, 135.1 (d, *J* = 8.5 Hz), 130.3, 128.7, 128.1, 128.0, 127.9, 124.5 (d, *J* = 3.7 Hz), 116.8 (d, *J* = 21.1 Hz), 47.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -110.56 (s, 1F).

Product 3an (Known compound, CAS: 625470-36-2)



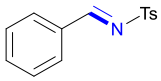
Yield of **3an**: 23 mg, 35% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.79 – 7.76 (m, 2H), 7.38 (s, 1H), 7.28 (s, 2H), 7.19 (d, *J* = 5.9 Hz, 2H), 4.83 (s, 1H), 4.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.9, 135.8, 135.7, 130.6, 130.1, 128.8, 128.2, 127.9, 125.6, 123.1, 47.4.

Product 4 (Known compound, CAS: 14070-53-2)



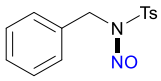
Yield of **4**: 83 mg, 67% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.31 (m, 5H), 4.34 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.7, 133.7, 129.9, 129.7, 129.1, 128.7, 128.6, 60.6, 21.8.

Product 5 (Known compound, CAS: 13707-41-0)



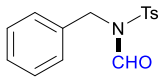
Yield of **5**: 117 mg, 90% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.03 (s, 1H), 7.92 (d, *J* = 7.4 Hz, 2H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 144.7, 135.1, 135.0, 132.3, 131.3, 129.8, 129.2, 128.1, 21.7.

Product 6 (Known compound, CAS: 33528-13-1)



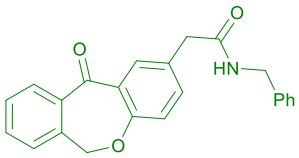
Yield of **6**: 102 mg, 70% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.18 (m, 5H), 7.14 – 7.08 (m, 2H), 4.91 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.0, 134.9, 133.5, 130.1, 129.8, 128.6, 128.4, 128.1, 46.0, 21.7.

Product 7 (Known compound, CAS: 312329-77-4)



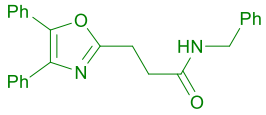
Yield of **7**: 110 mg, 76% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.19 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.19 (m, 7H), 4.72 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.5, 145.3, 135.4, 134.6, 130.0, 128.4, 128.4, 127.8, 127.3, 45.7, 21.6.

Product 9



Yield of **9**: 71 mg, 95% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 2.4 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.29 – 7.16 (m, 5H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.15 (s, 1H), 5.14 (s, 2H), 4.39 (d, *J* = 5.8 Hz, 2H), 3.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.9, 170.7, 160.6, 140.4, 138.1, 136.5, 135.5, 132.9, 132.4, 129.4, 129.3, 128.7, 128.7, 127.9, 127.6, 127.5, 125.2, 121.5, 73.6, 43.7, 42.6. M.P.: 136.0 –136.5 ºC HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{23}H_{19}NO_3Na$: 380.1257; found: 380.1253.

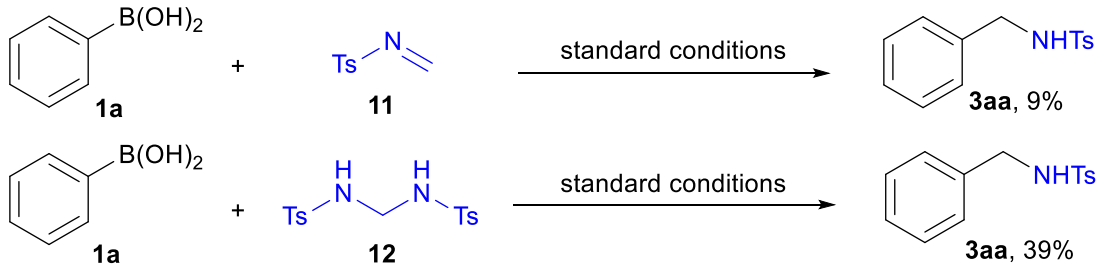
Product 10



Yield of **10**: 73 mg, 96% yield as a white solid. ^{11}H NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.49 (m, 4H), 7.35 – 7.33 (m, 6H), 7.25 – 7.24 (m, 5H), 6.48 (s, 1H), 4.47 (d, *J* = 5.6 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.82 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 164.2, 145.5, 138.1, 135.0, 132.4, 128.9, 128.67. 128.66, 128.56, 128.51, 128.07, 127.8, 127.7, 127.4, 126.5, 43.8, 33.0, 24.1. M.P.: 118.0 – 118.5 ºC HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $C_{25}H_{22}N_2O_2$: 383.1754; found: 383.1752.

5. Mechanistic studies

a) Control experiments: *Examining the involvement of formaldimine intermediate*

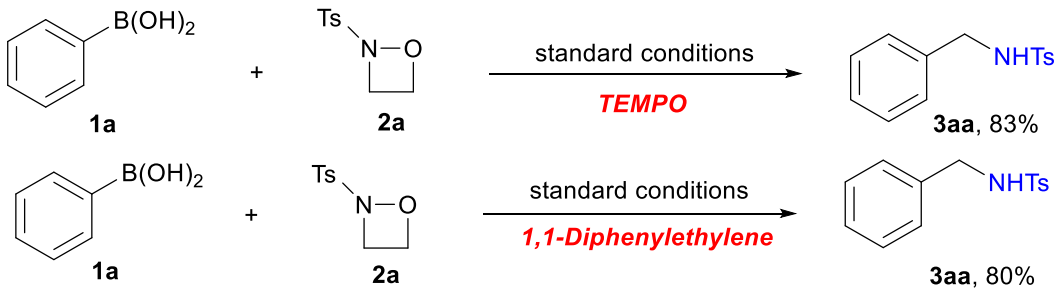


1a (24.2 mg, 0.2 mmol), **11** (55.0 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), 1,10-phenanthroline (7.2 mg, 0.04 mmol) and K_3PO_4 (34.0 mg, 0.16 mmol) were dissolved in dichloroethane (2.0 mL). Then, the mixture was stirred at 140 °C for 10 h. Product **3aa** can be obtained in 9% yield (GC).

1a (24.2 mg, 0.2 mmol), **12** (106.3 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), 1,10-phenanthroline (7.2 mg, 0.04 mmol) and K_3PO_4 (34.0 mg, 0.16 mmol) were dissolved in dichloroethane (2.0 mL). Then, the mixture was stirred at 140 °C for 10 h. Product **3aa** can be obtained in 39% yield (GC).

These two experiments indicated the intermediacy of a formaldimine species in this reaction, which should be generated in a slow fashion due to its inherent instability in the reaction system.

b) Radical trapping experiments:



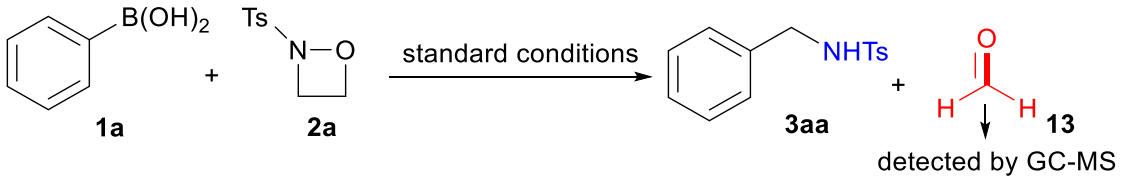
1a (24.2 mg, 0.2 mmol), **2a** (63.9 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), 1,10-phenanthroline (7.2 mg, 0.04 mmol), K_3PO_4 (34.0 mg, 0.16 mmol) and TEMPO (62.5 mg, 0.04 mmol) were dissolved in dichloroethane (2.0 mL). Then, the mixture was stirred at 140 °C for 10 h. Product **3aa** can be obtained in 83% yield (GC).

1a (24.2 mg, 0.2 mmol), **2a** (63.9 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), 1,10-phenanthroline (7.2 mg, 0.04 mmol), K_3PO_4 (34.0 mg, 0.16 mmol) and 1,1-diphenylenthylene (62.5 mg, 0.04 mmol) were

dissolved in dichloroethane (2.0 mL). Then, the mixture was stirred at 140 °C for 10 h. Product **3aa** can be obtained in 80% yield (GC).

These two experiments suggest that radical mechanism might not be involved in this transformation.

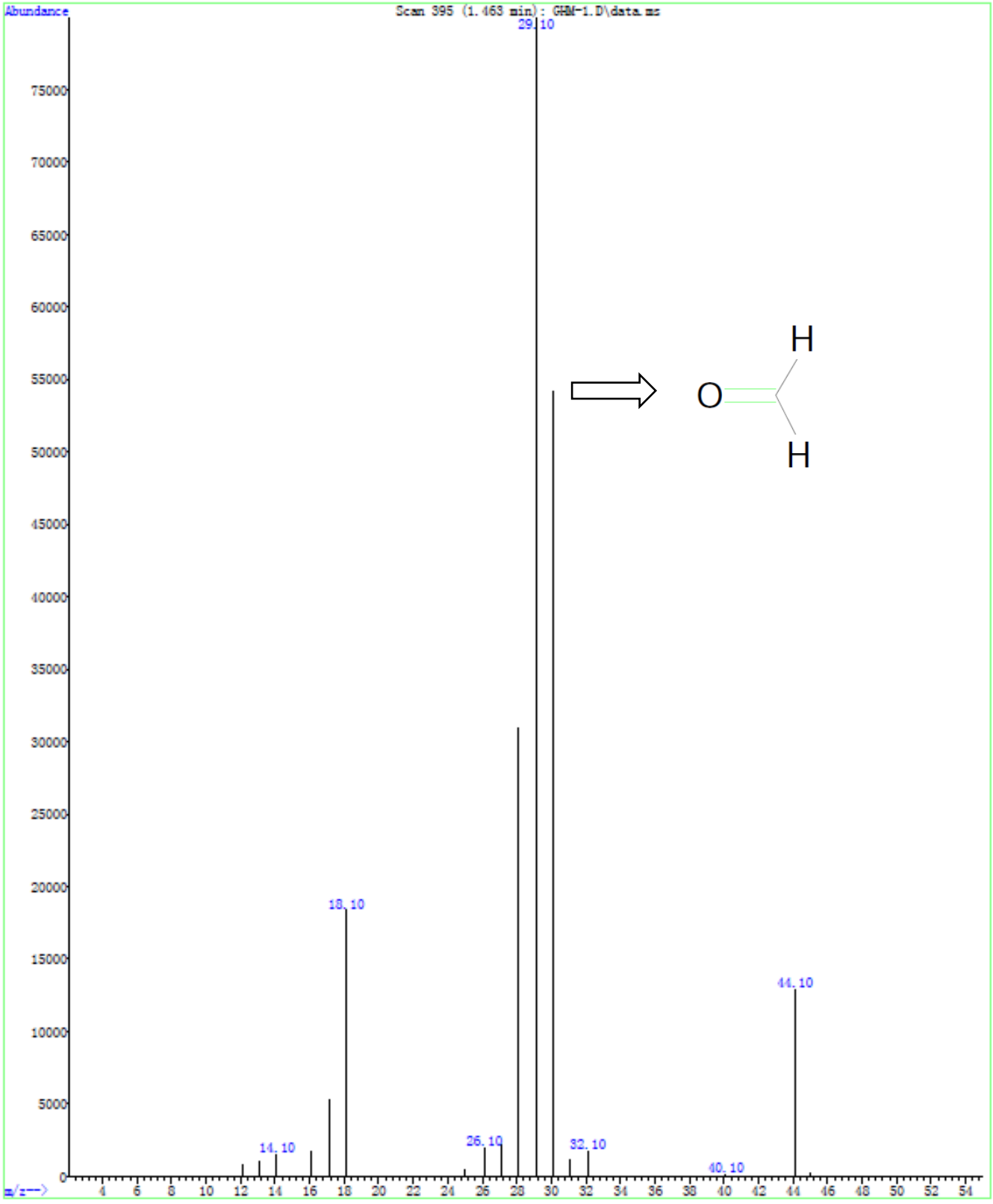
c) Investigation of crude reaction mixture : *Detection of formaldehyde by-product*



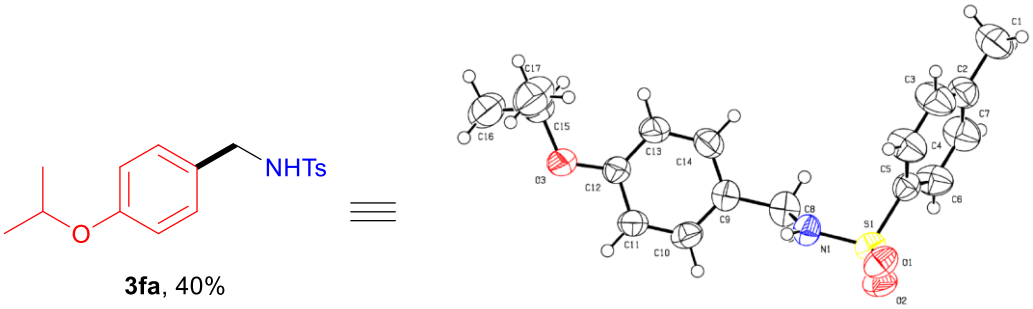
1a (24.2 mg, 0.2 mmol), **2a** (63.9 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), 1,10-phenanthroline (7.2 mg, 0.04 mmol) and K_3PO_4 (34.0 mg, 0.16 mmol) were dissolved in dichloroethane (2.0 mL). Then, the mixture was stirred at 140 °C for 10 h.

The by-product formaldehyde 13 can be detected by GC-MS analysis of the crude reaction mixture

File :D:\2021DATA\20211227\GHM-1.D
Operator :
Acquired : 28 Dec 2021 8:24 using AcqMethod 20210716.M
Instrument : GCMSD
Sample Name:
Misc Info :
Vial Number: 8



6. X-Ray structure of 3fa

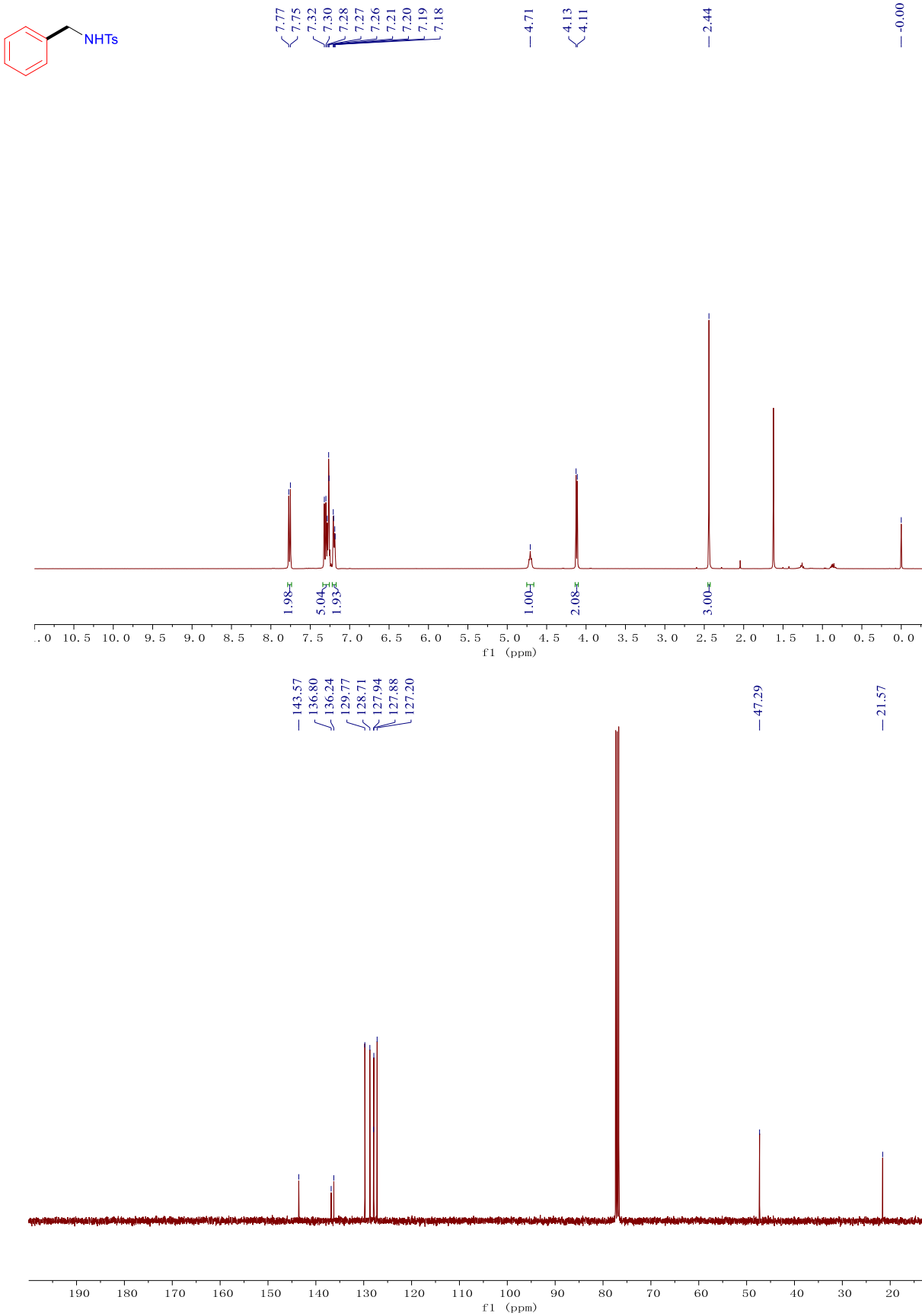


3fa, 40%

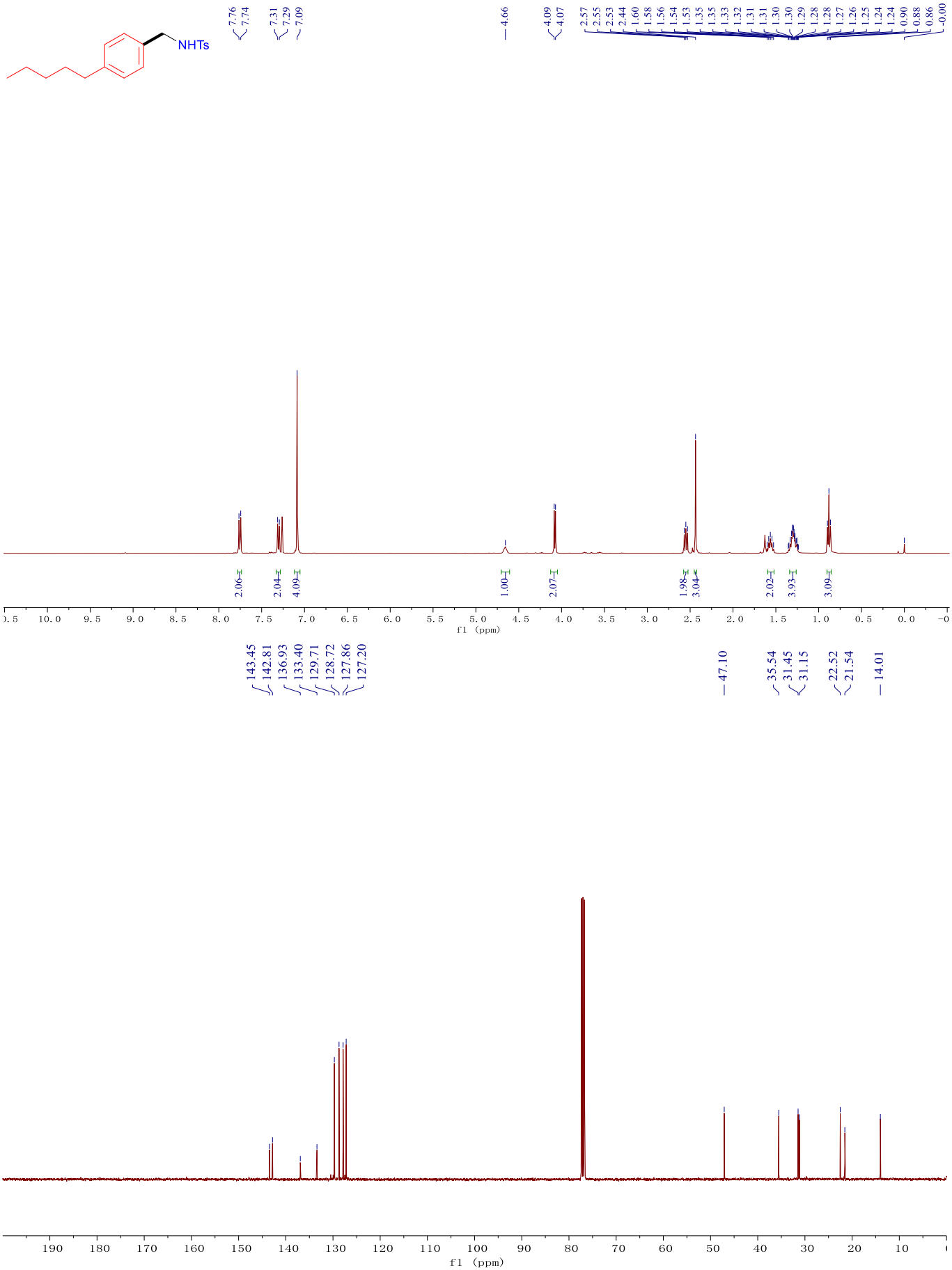
CCDC number: 2131523

7. NMR Spectra of products 3aa-3ra, 3ab-3an, 5, 6, 7, 9 and 10

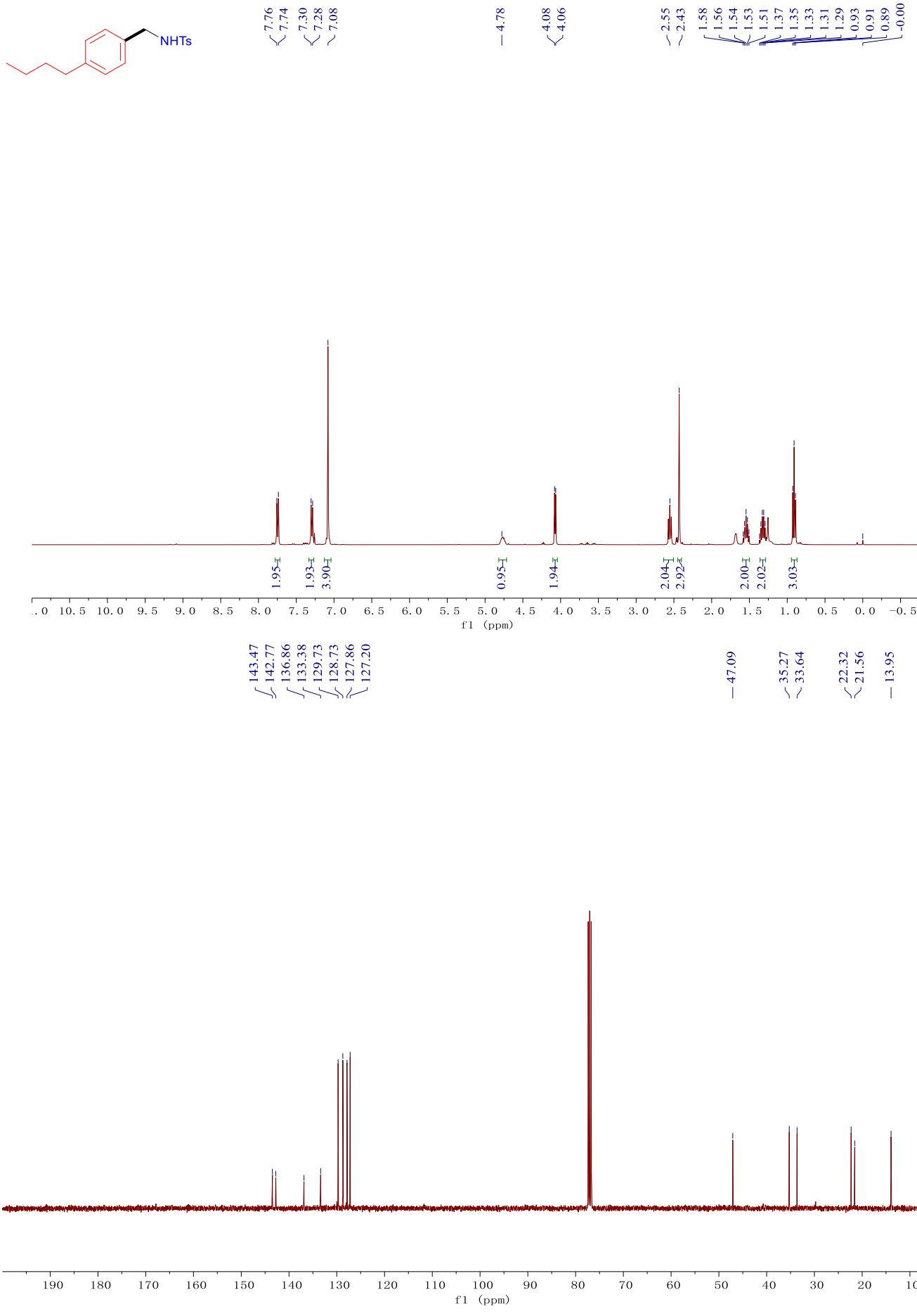
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3aa



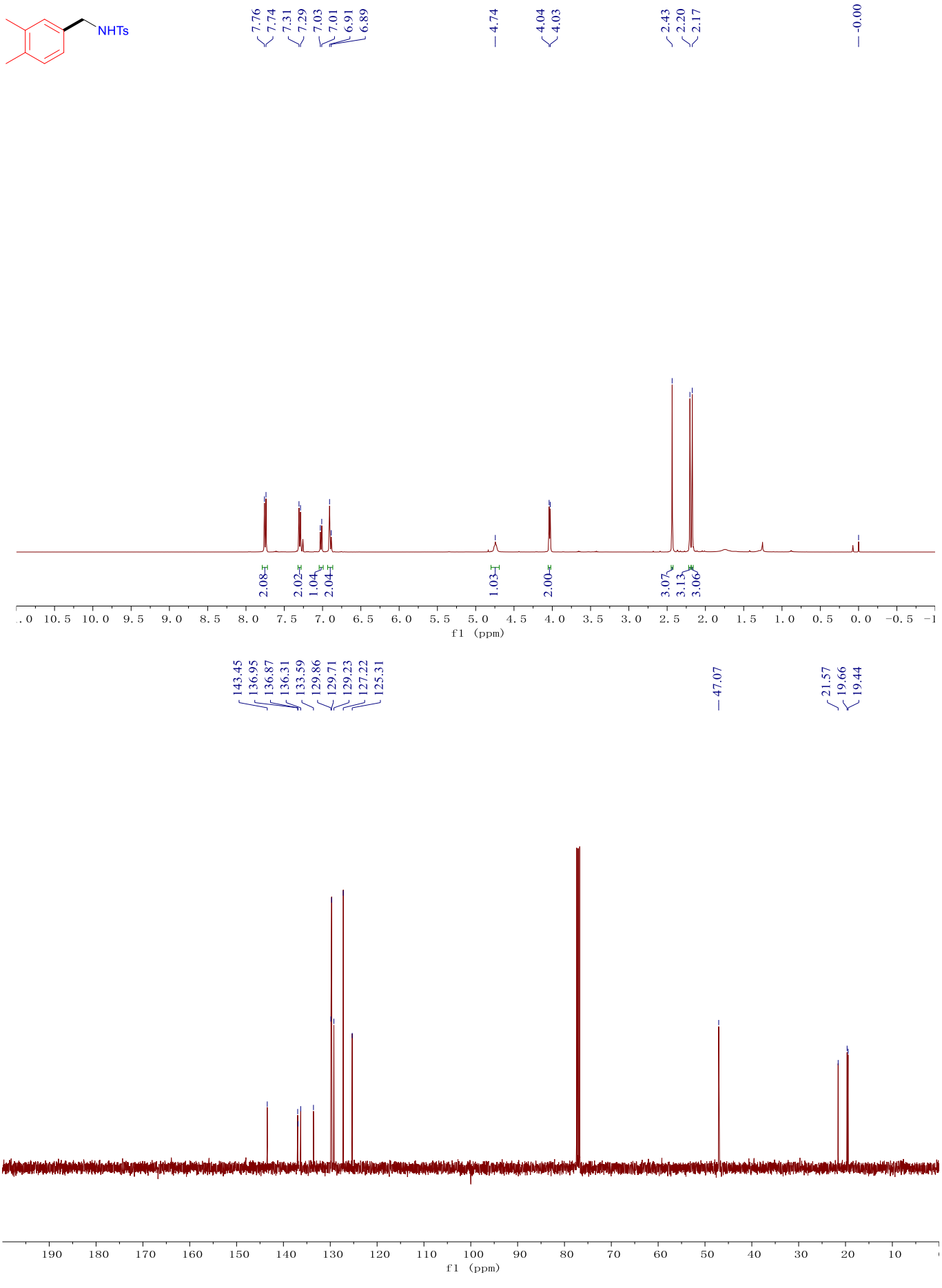
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ba



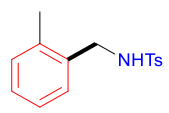
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3ca

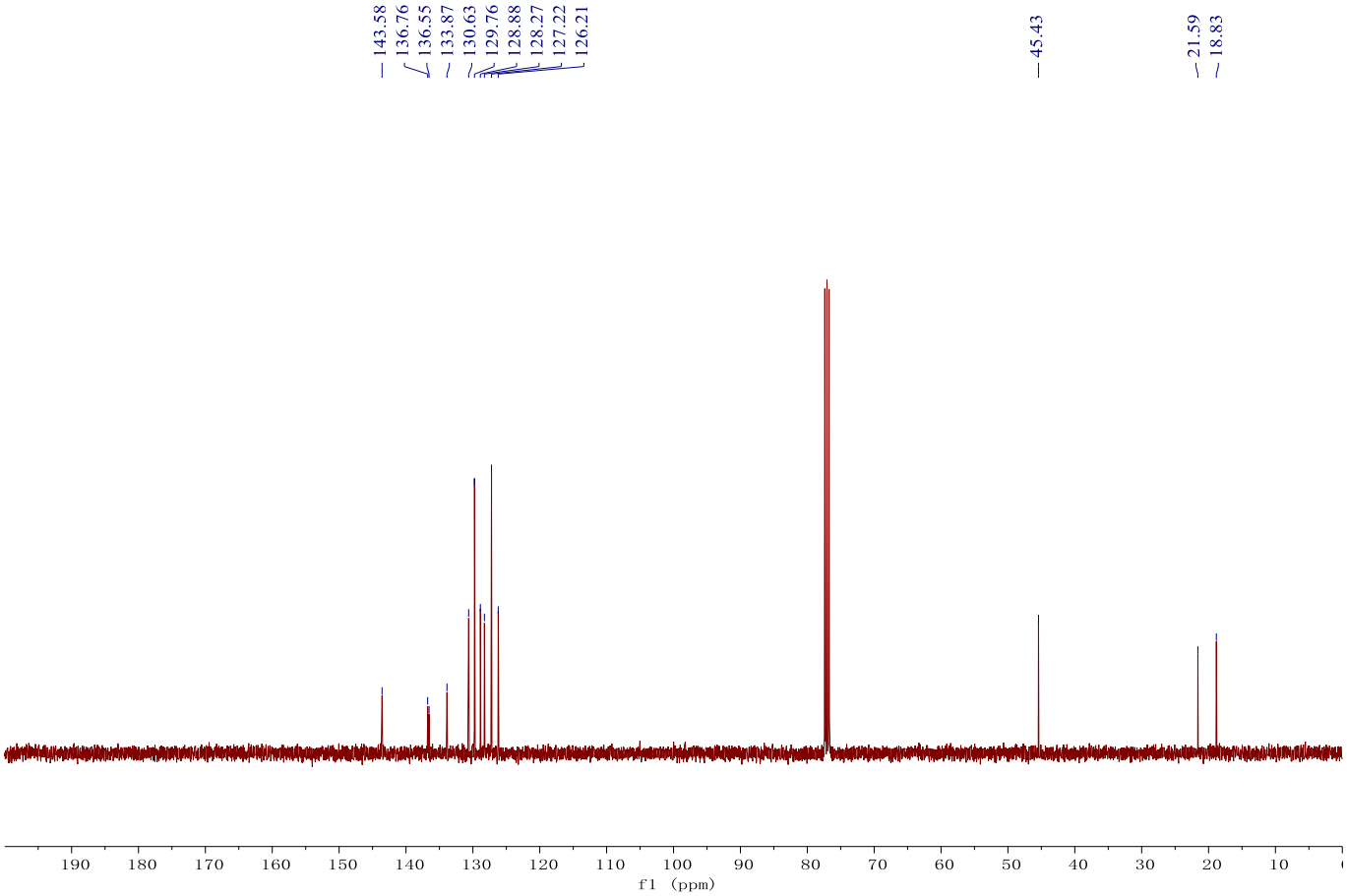


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3da

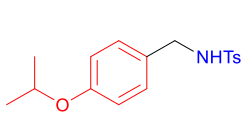


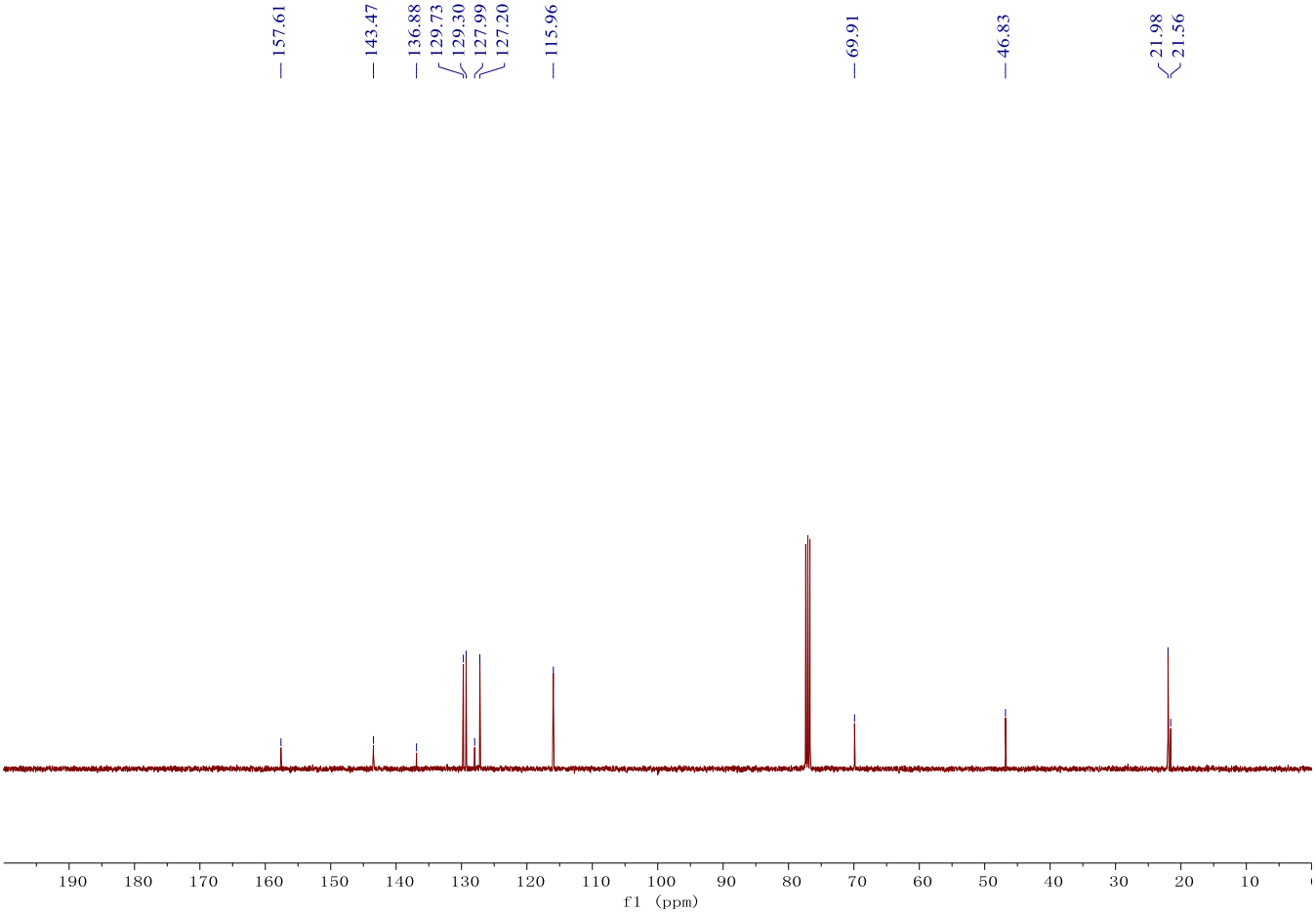
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ea



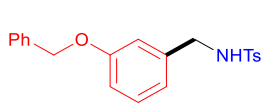


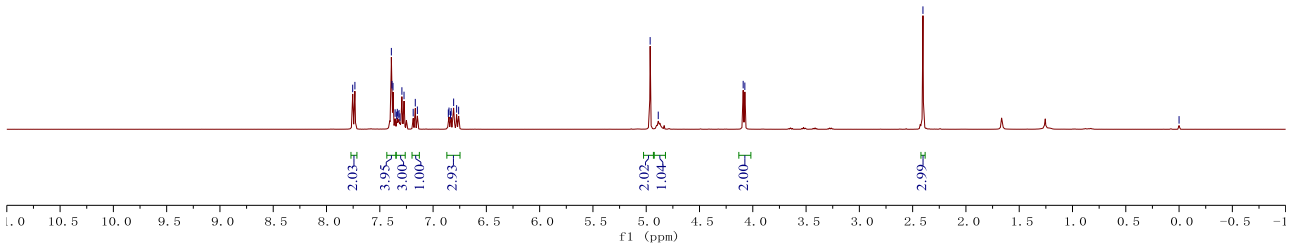
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3fa

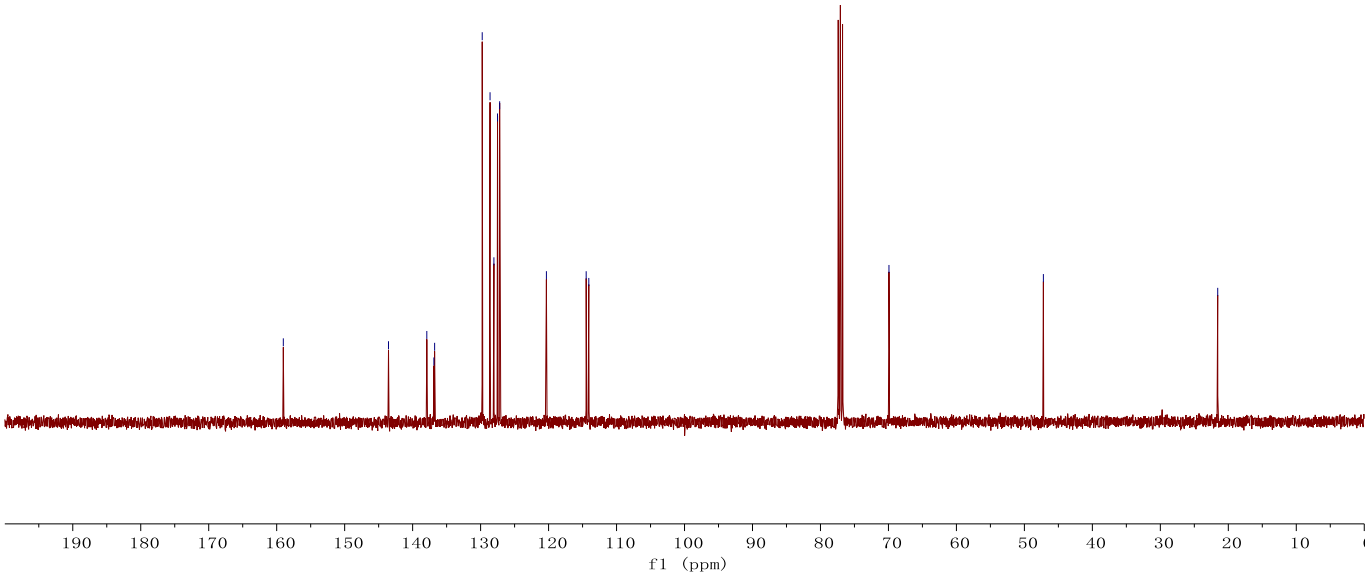




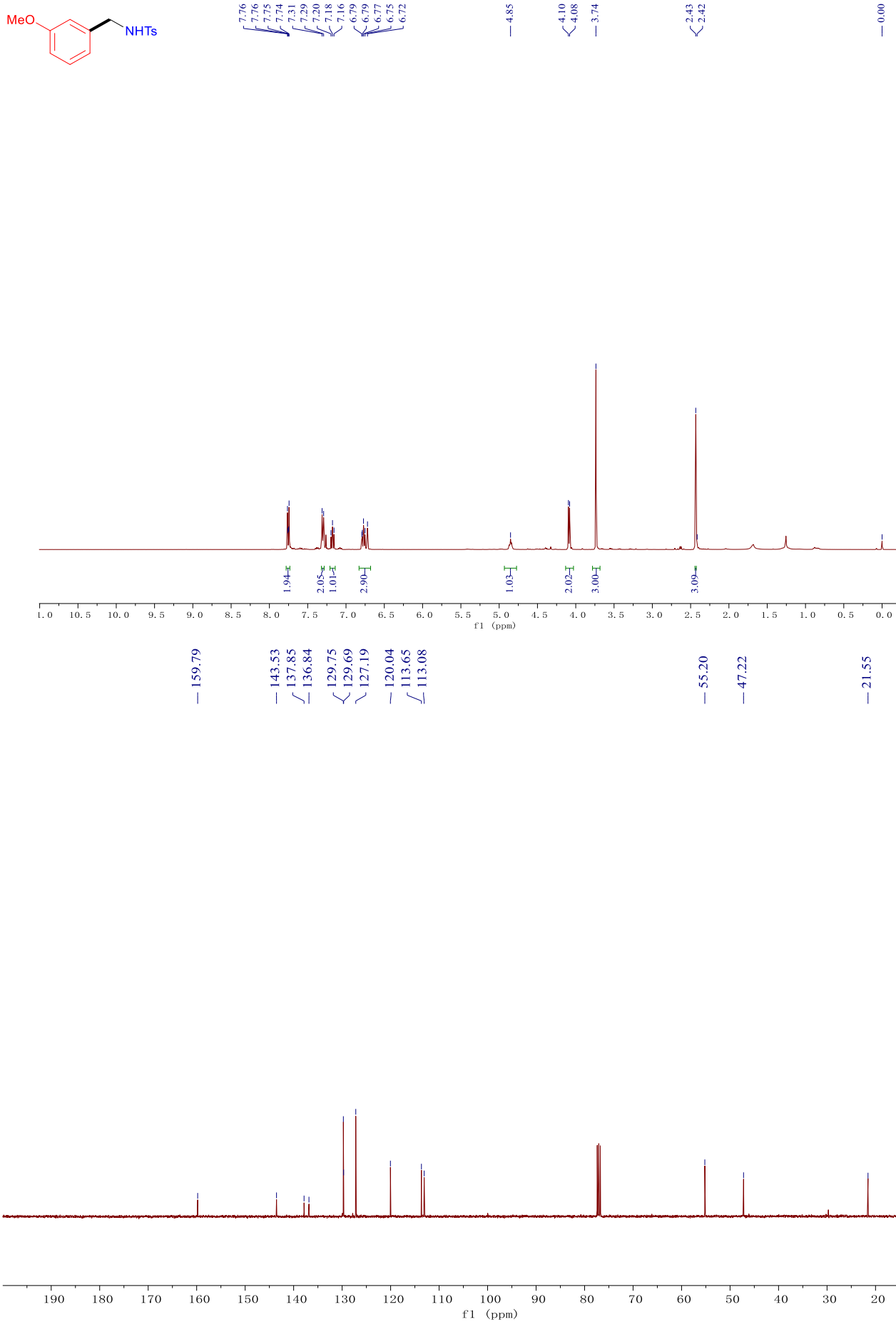
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ga



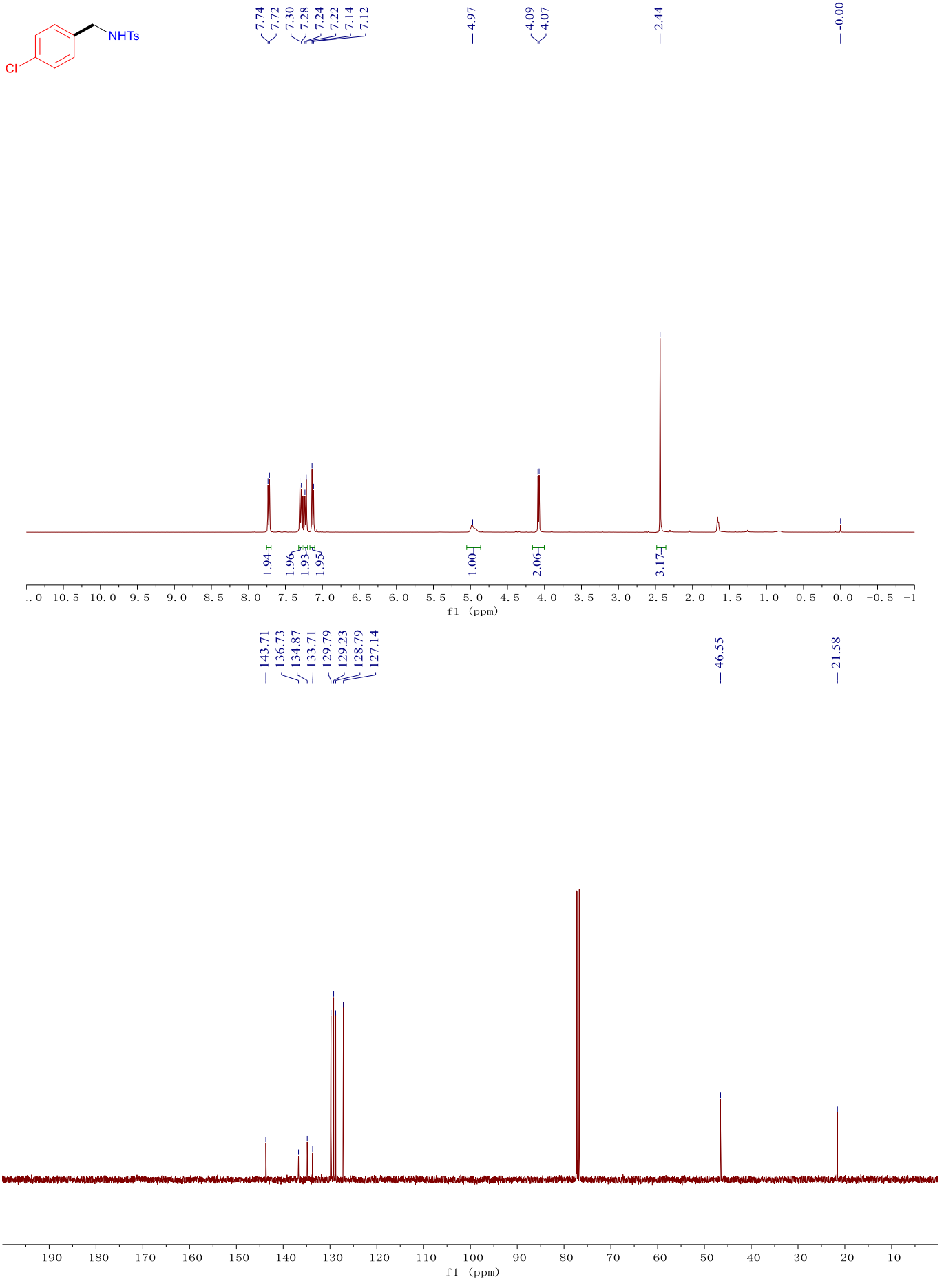




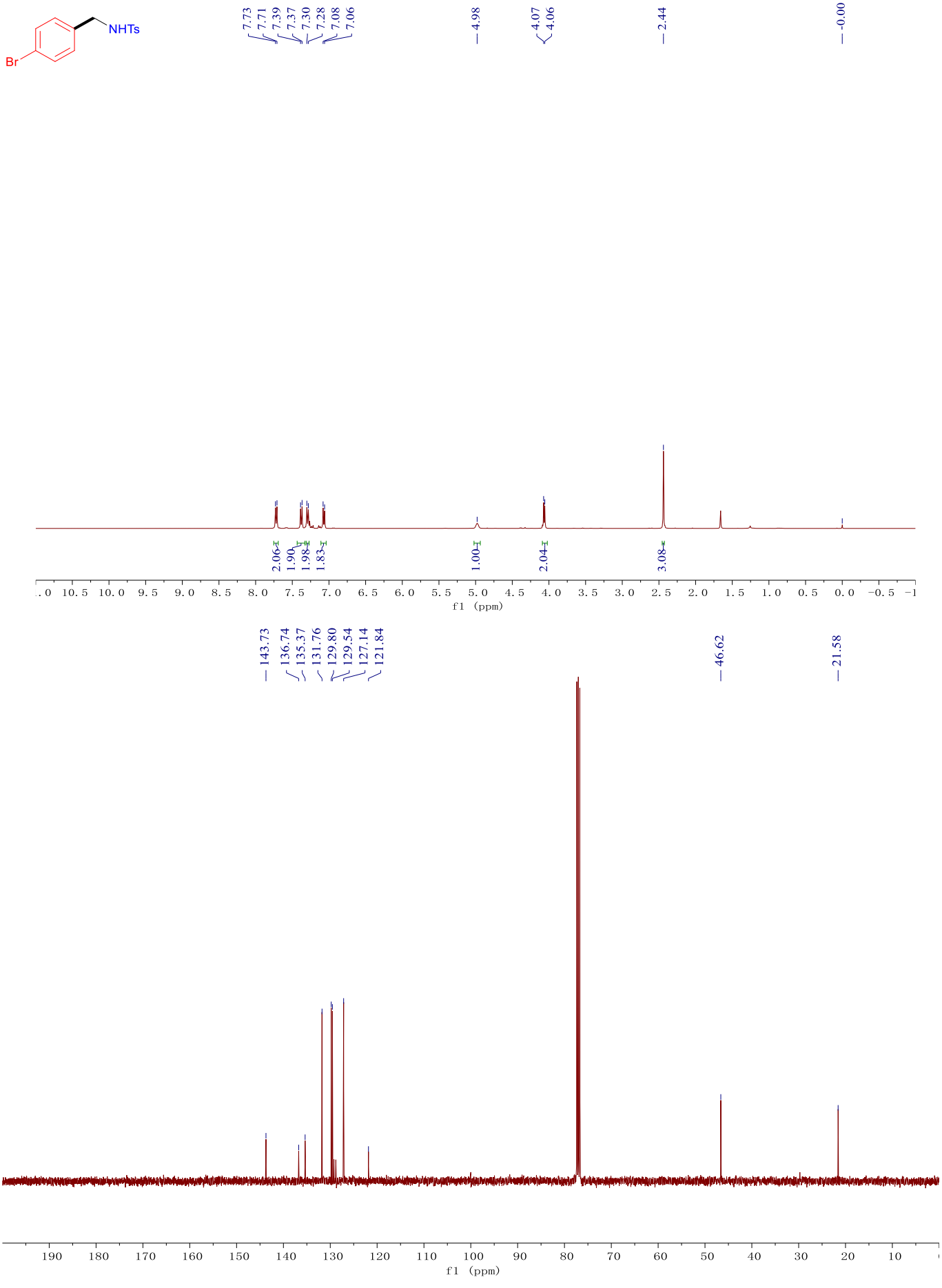
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3ha



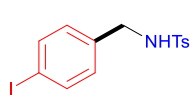
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ia

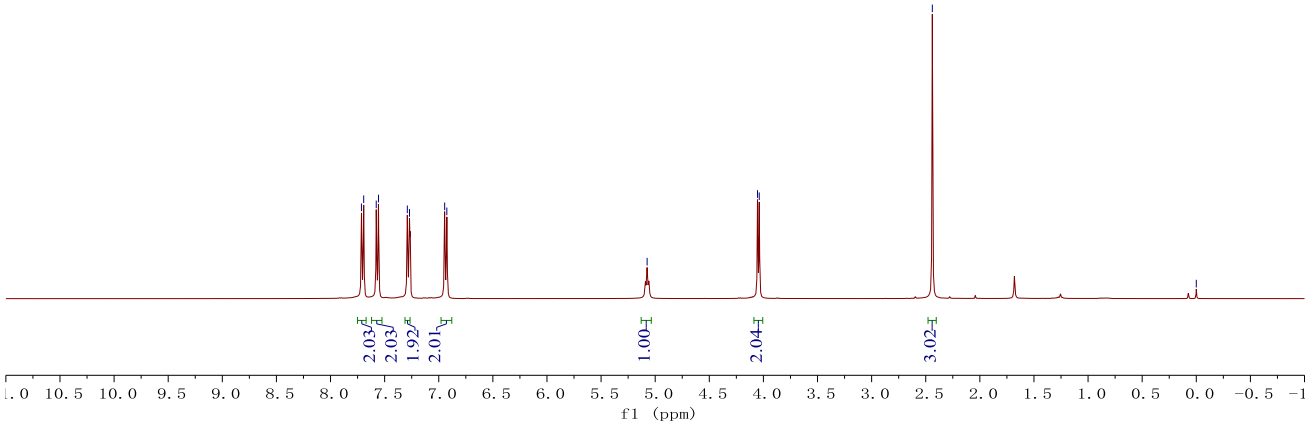


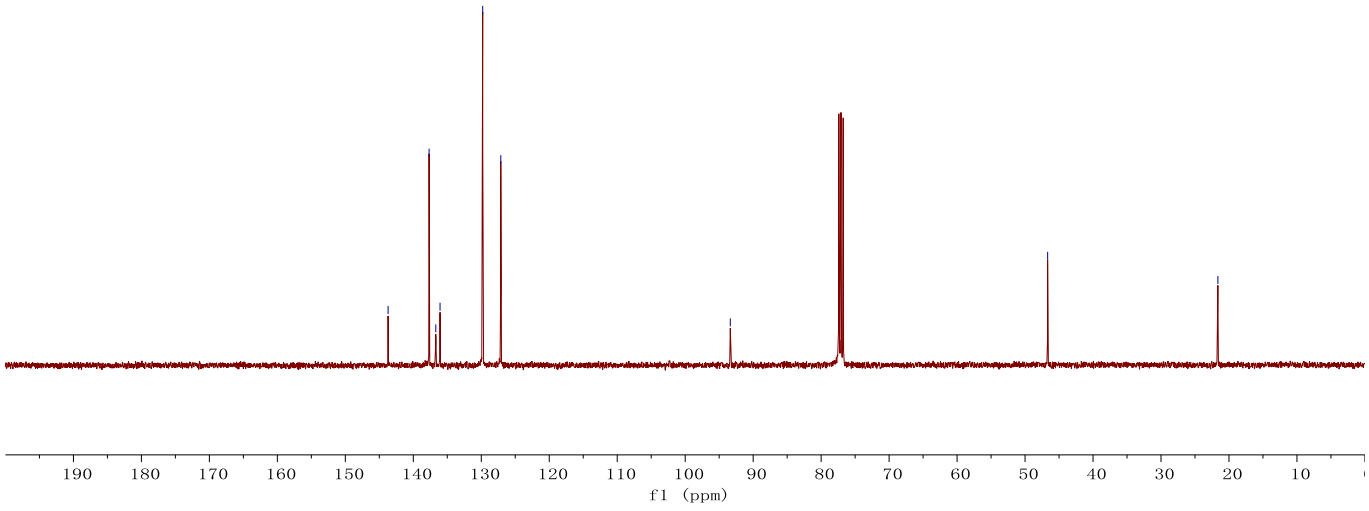
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ja



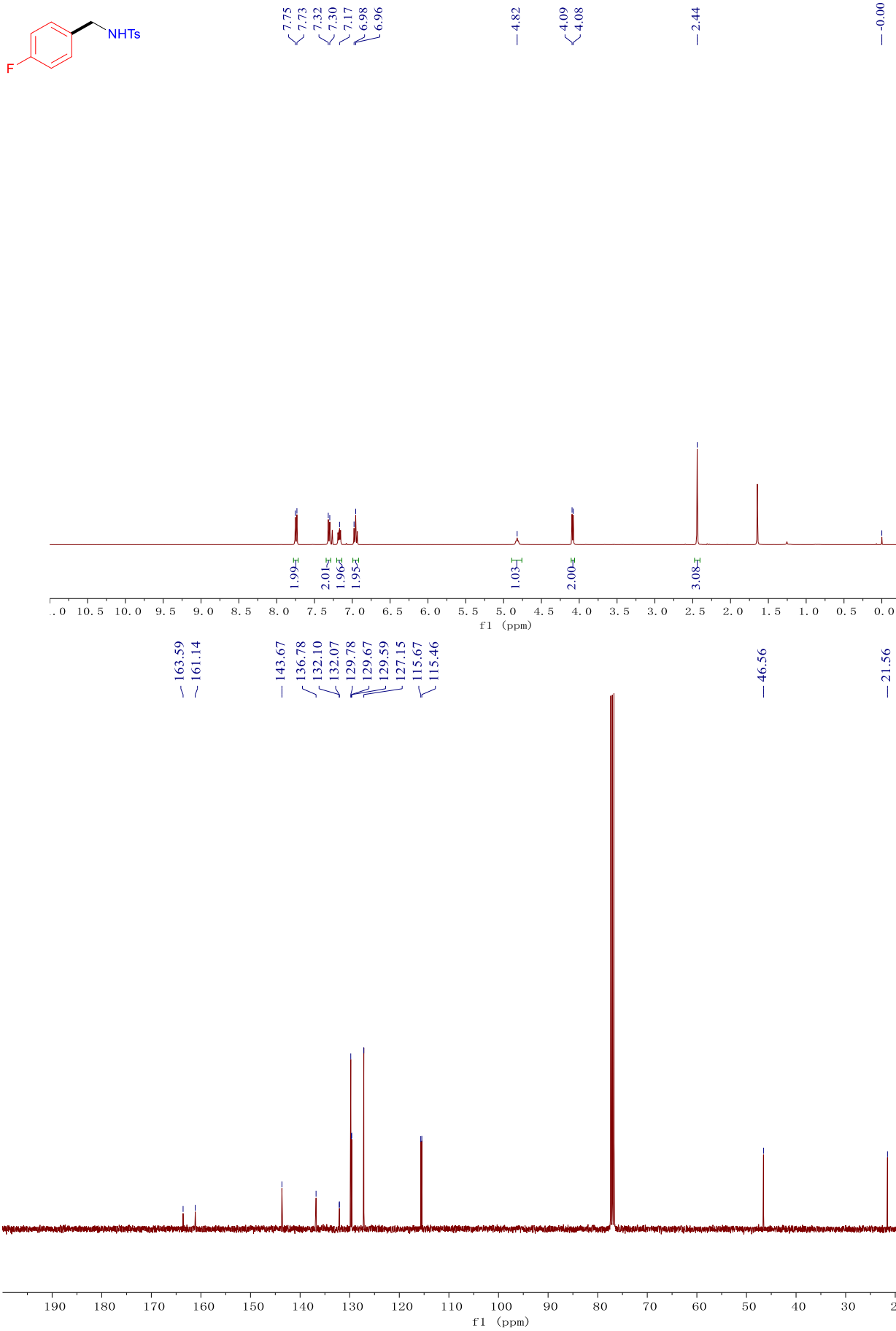
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3ka

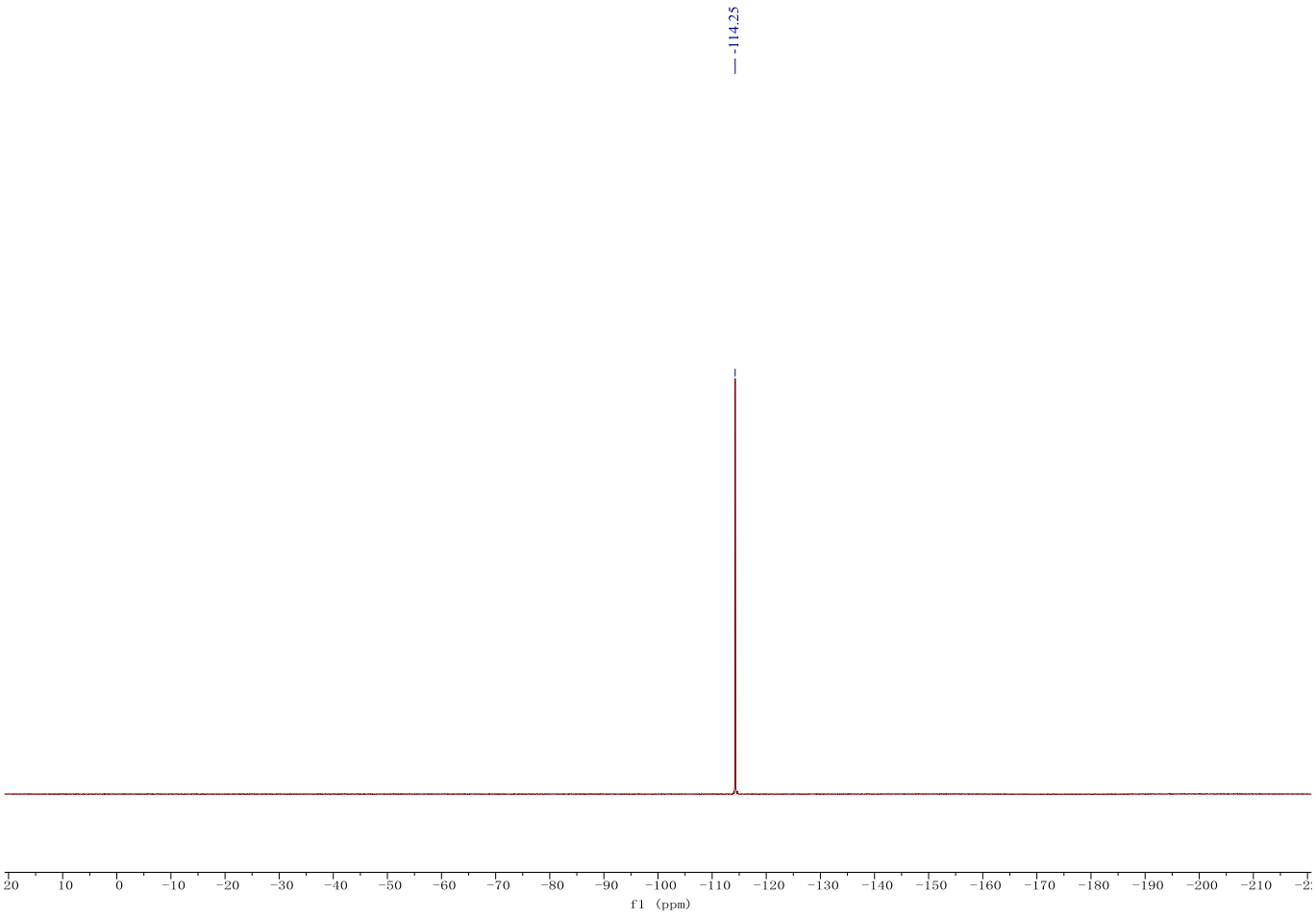




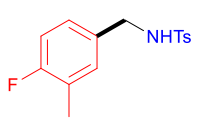


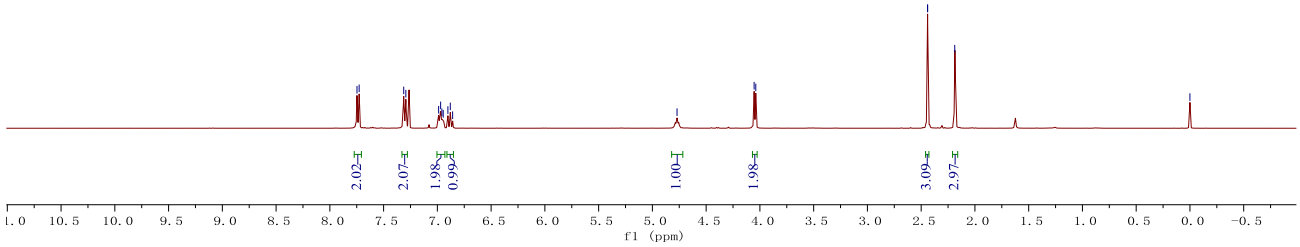
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3la

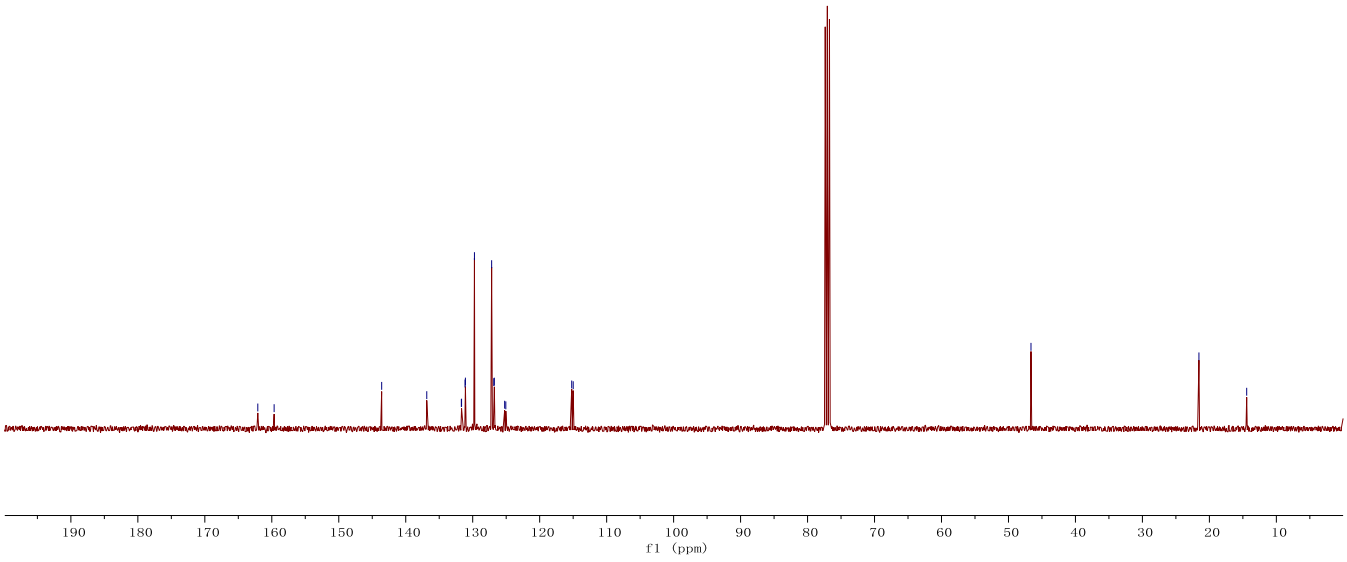


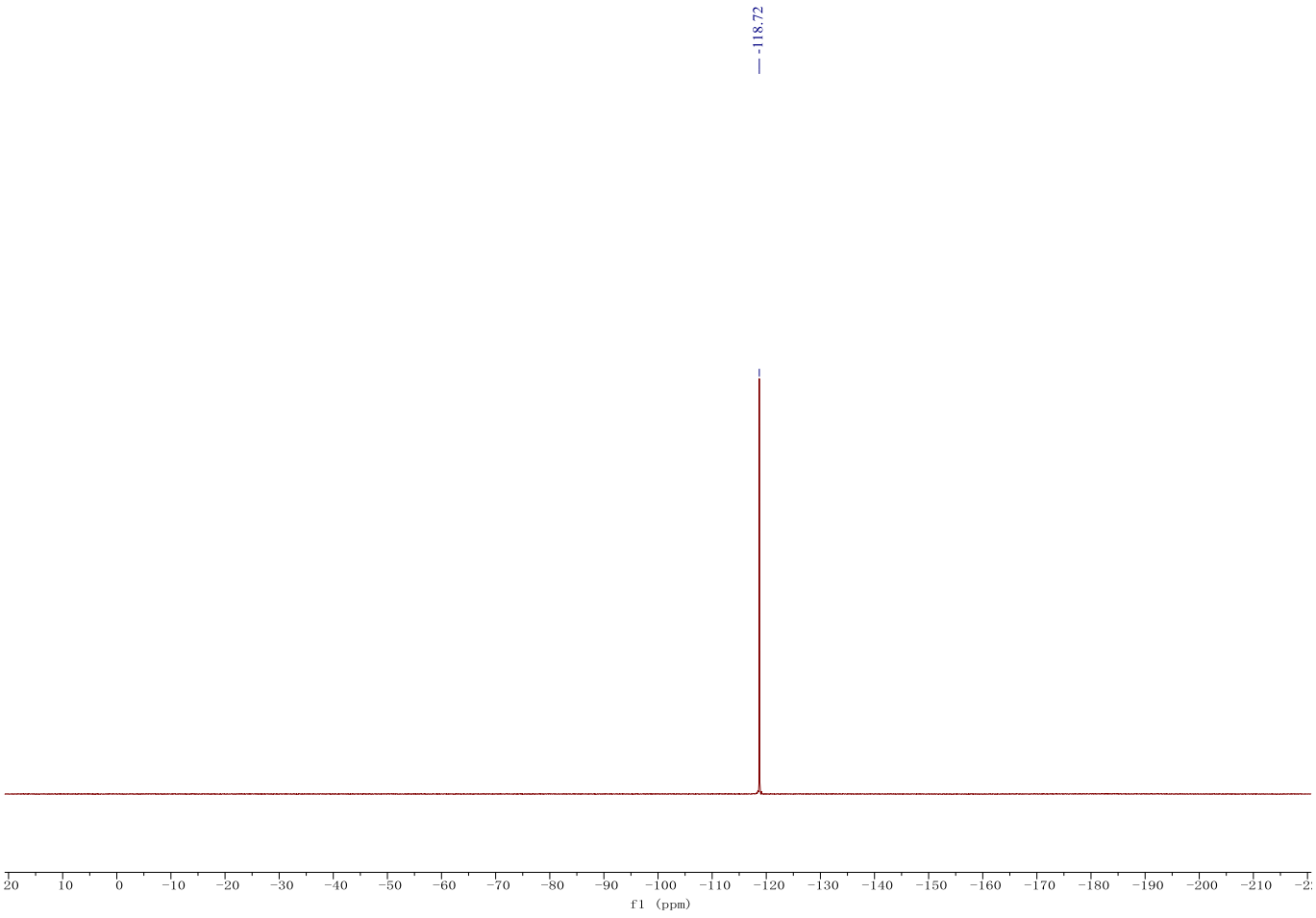

-114.25
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ma

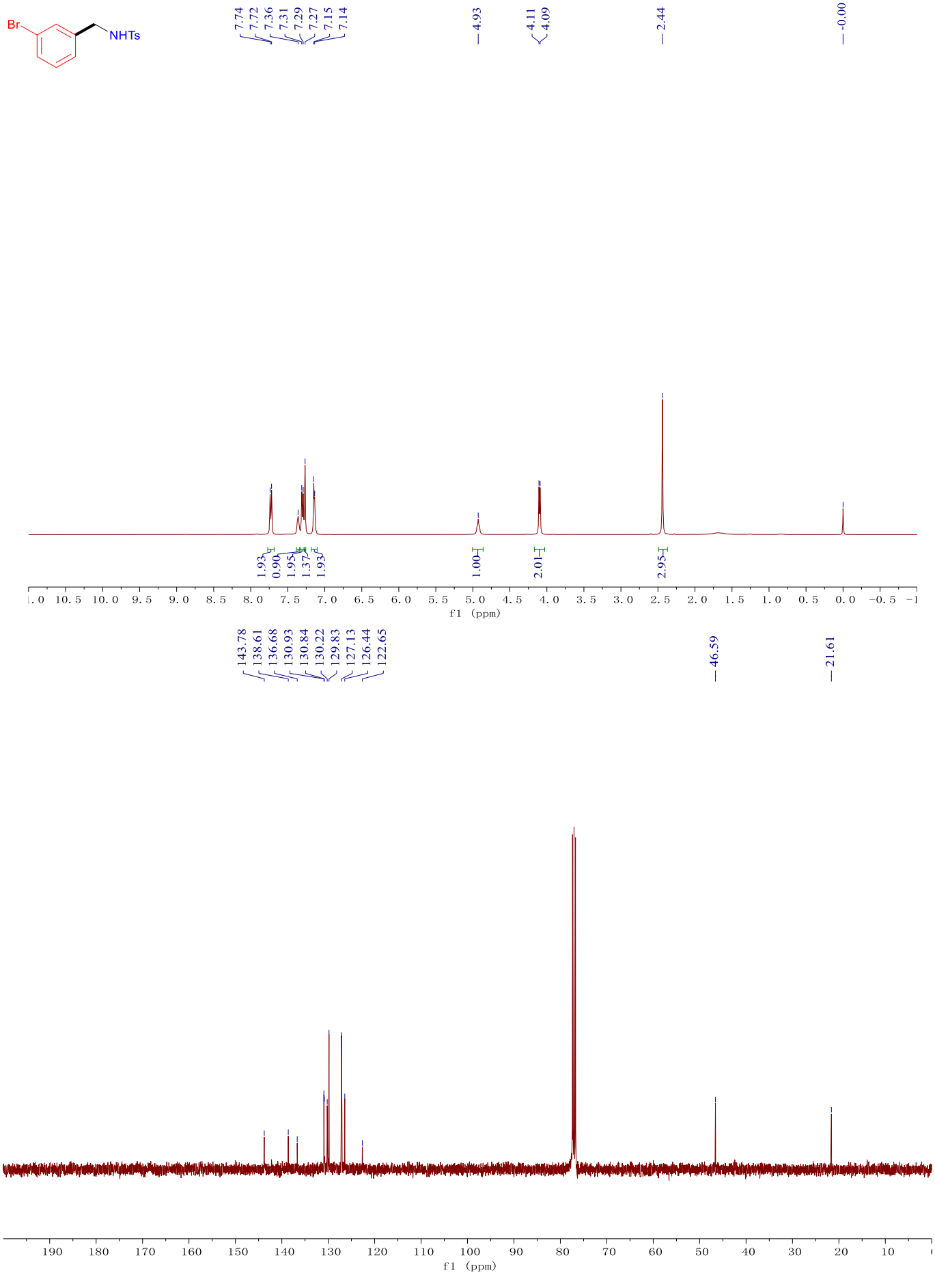




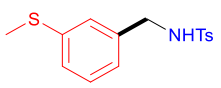


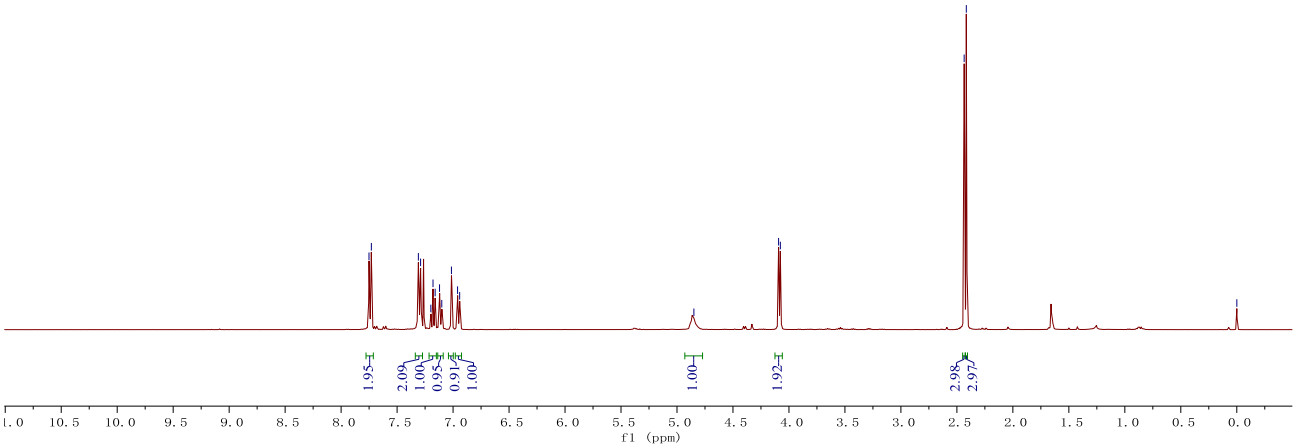

-118.72
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

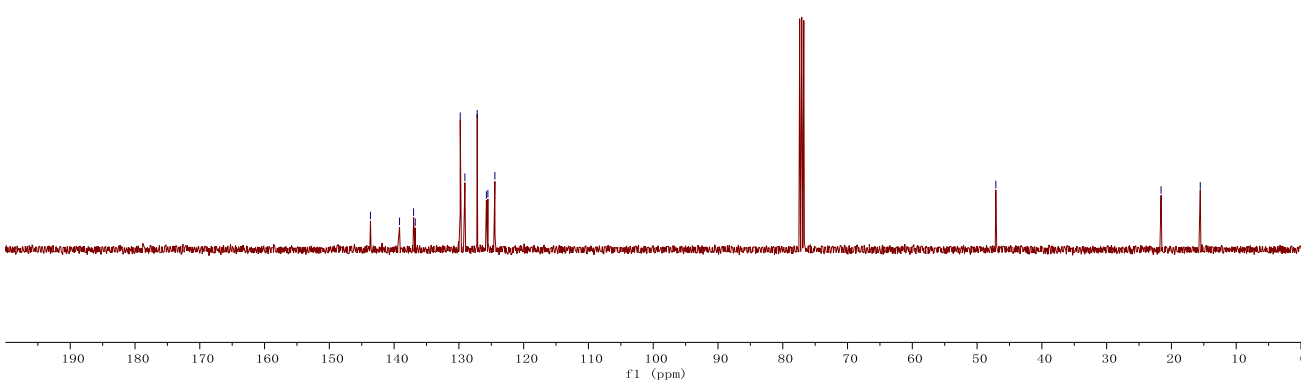
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3na



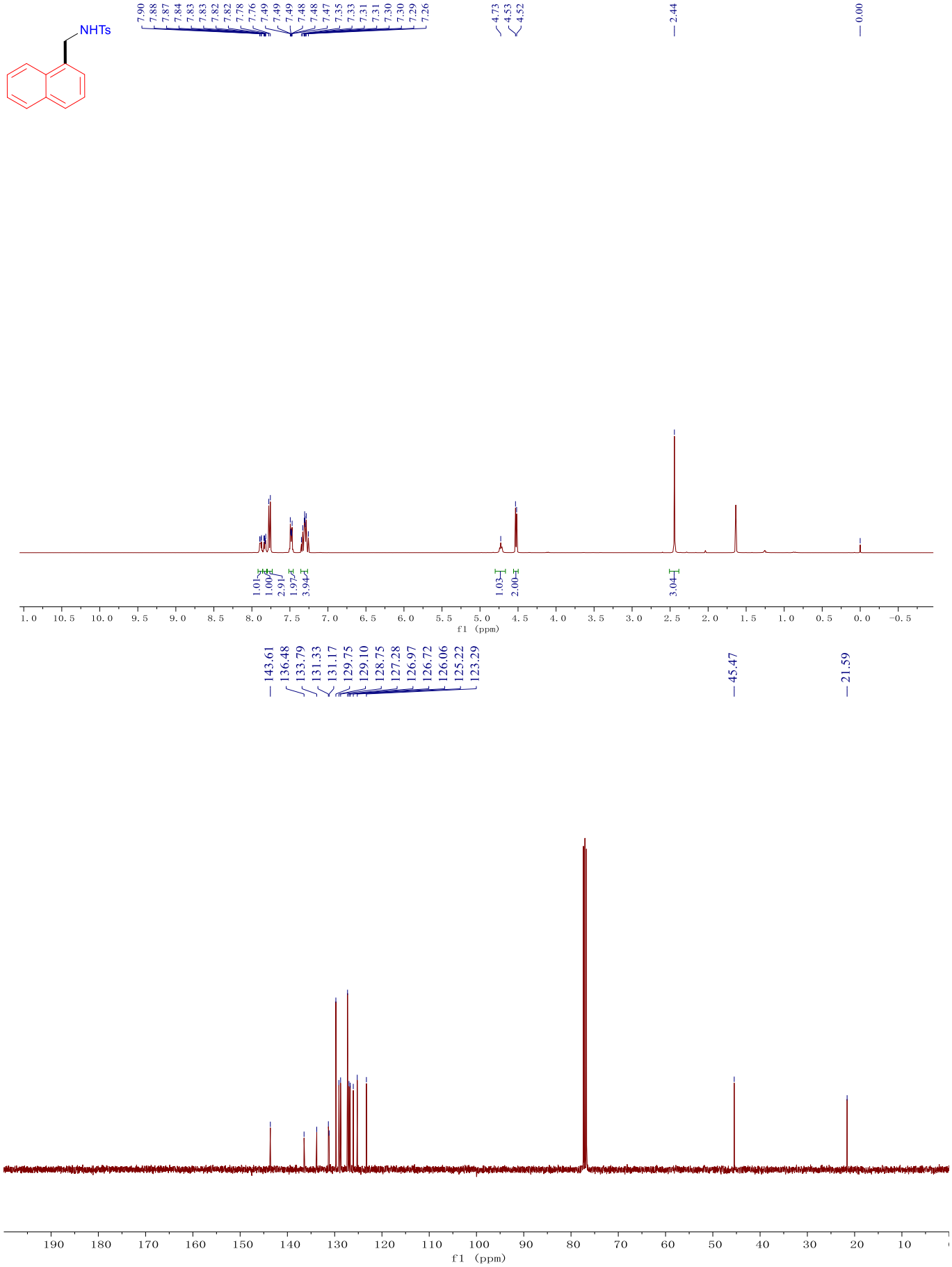
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3oa



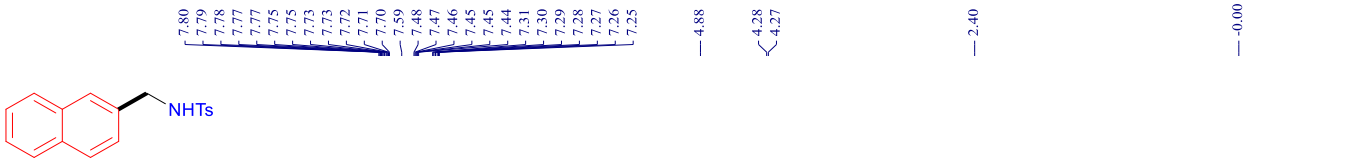


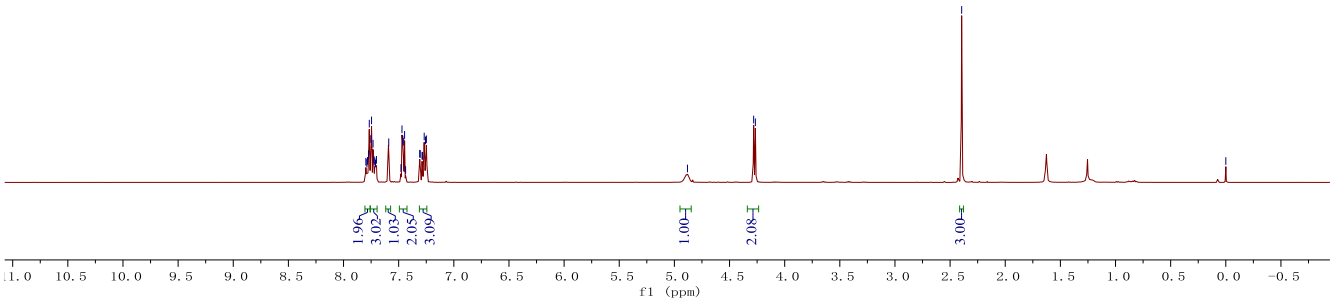


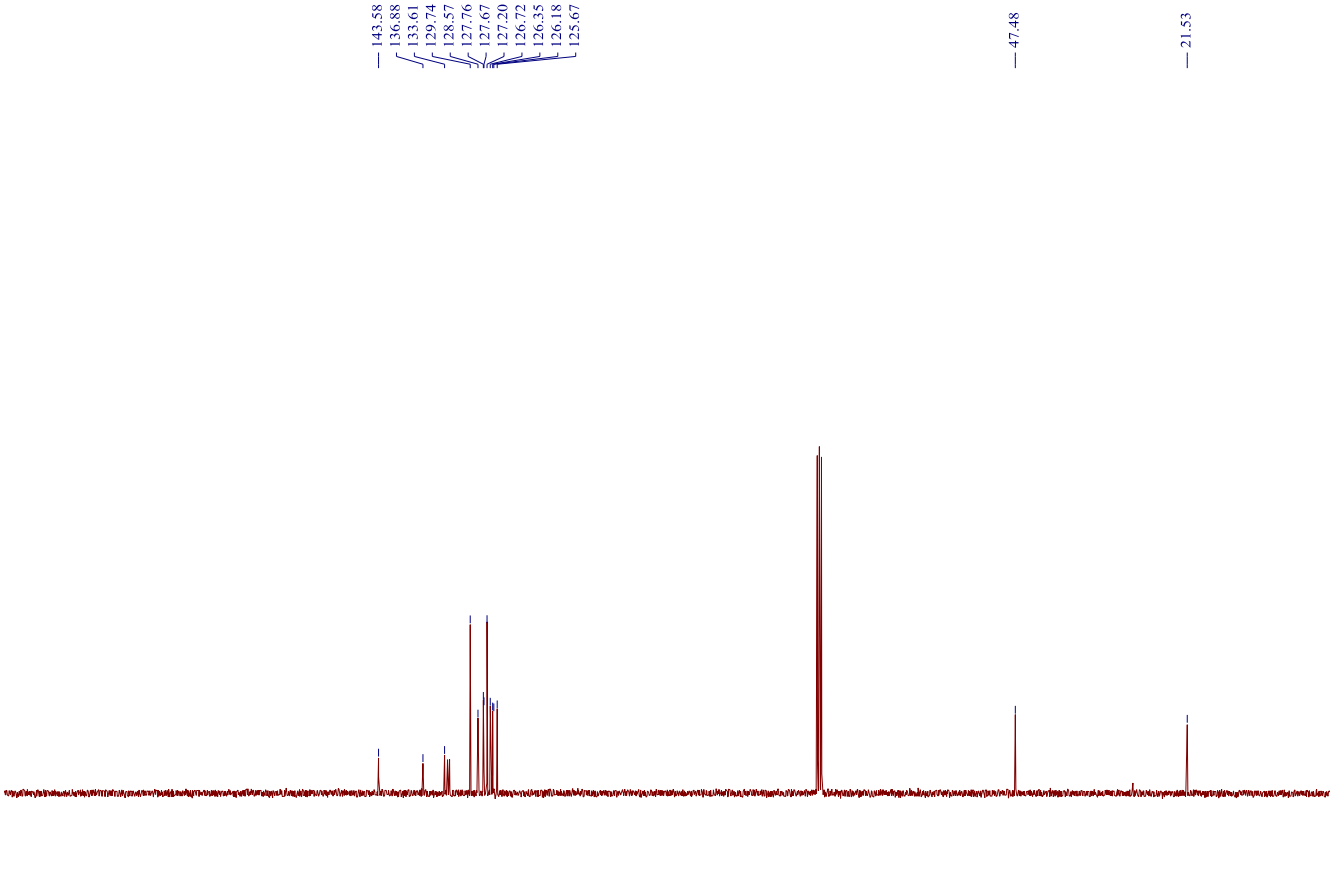
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3pa



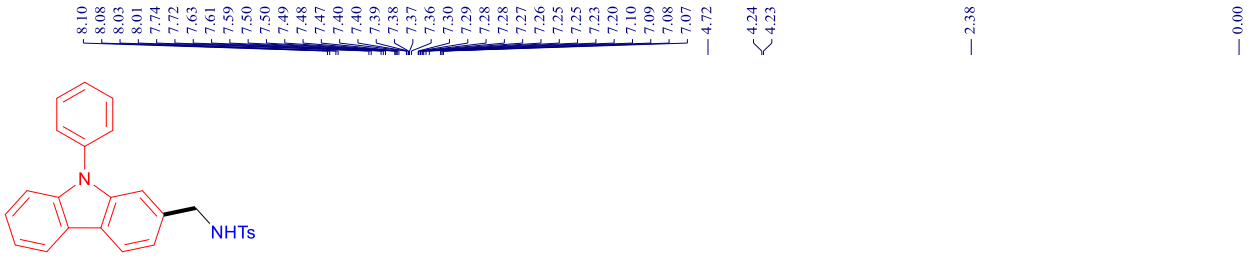
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3qa

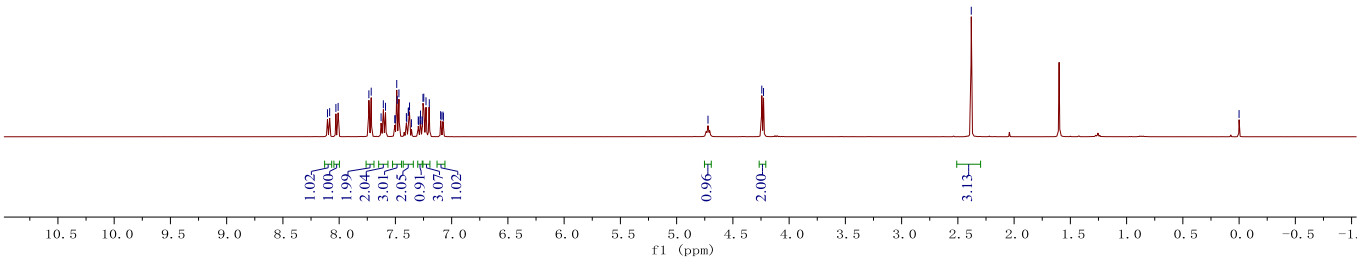


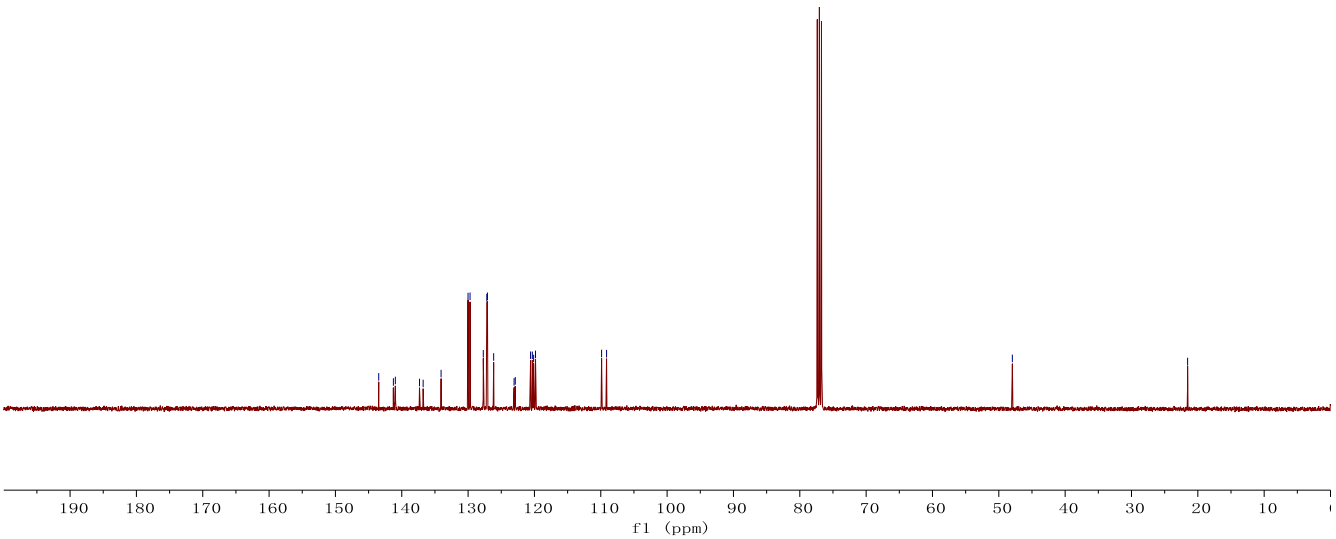




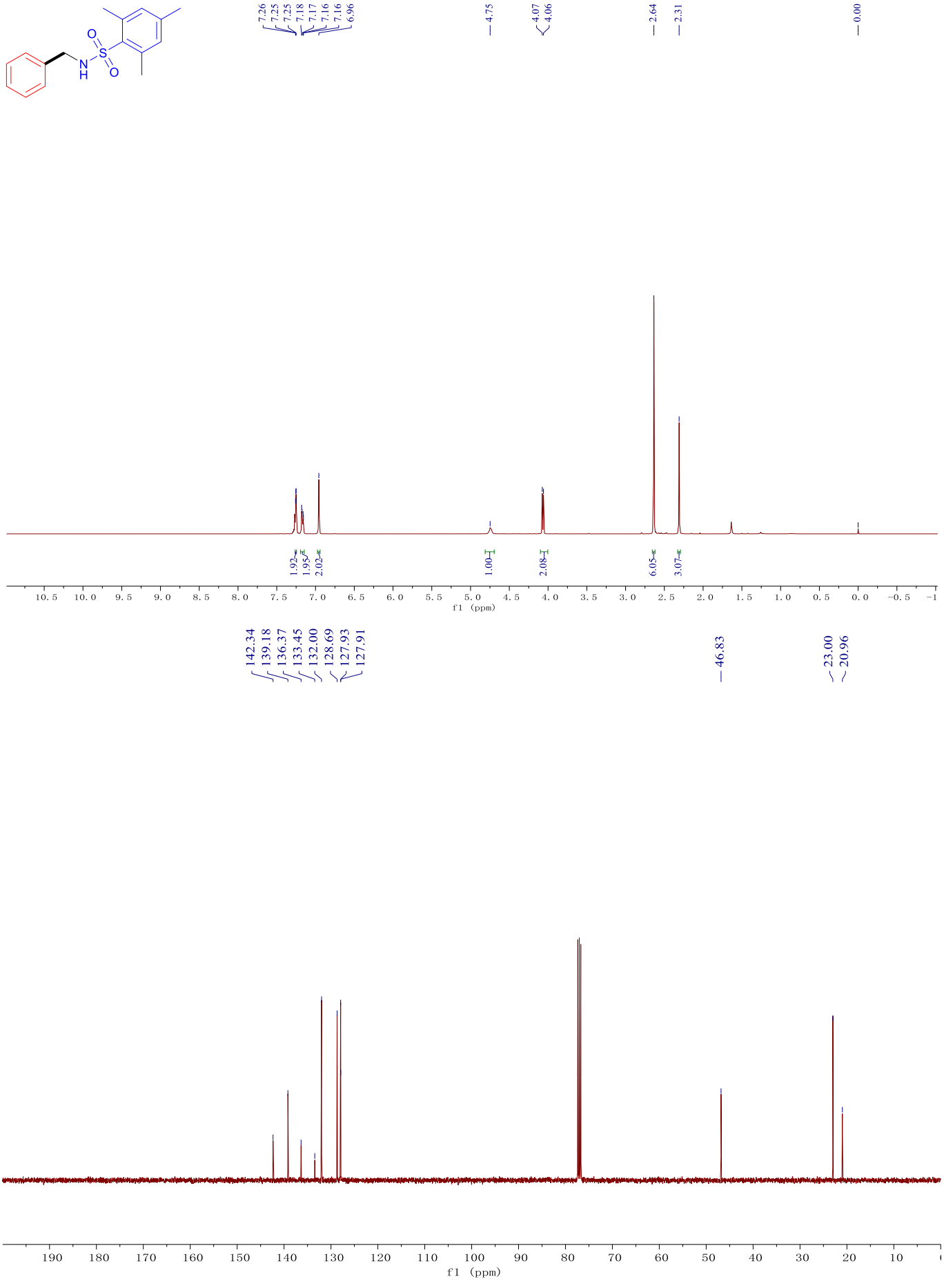
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ra



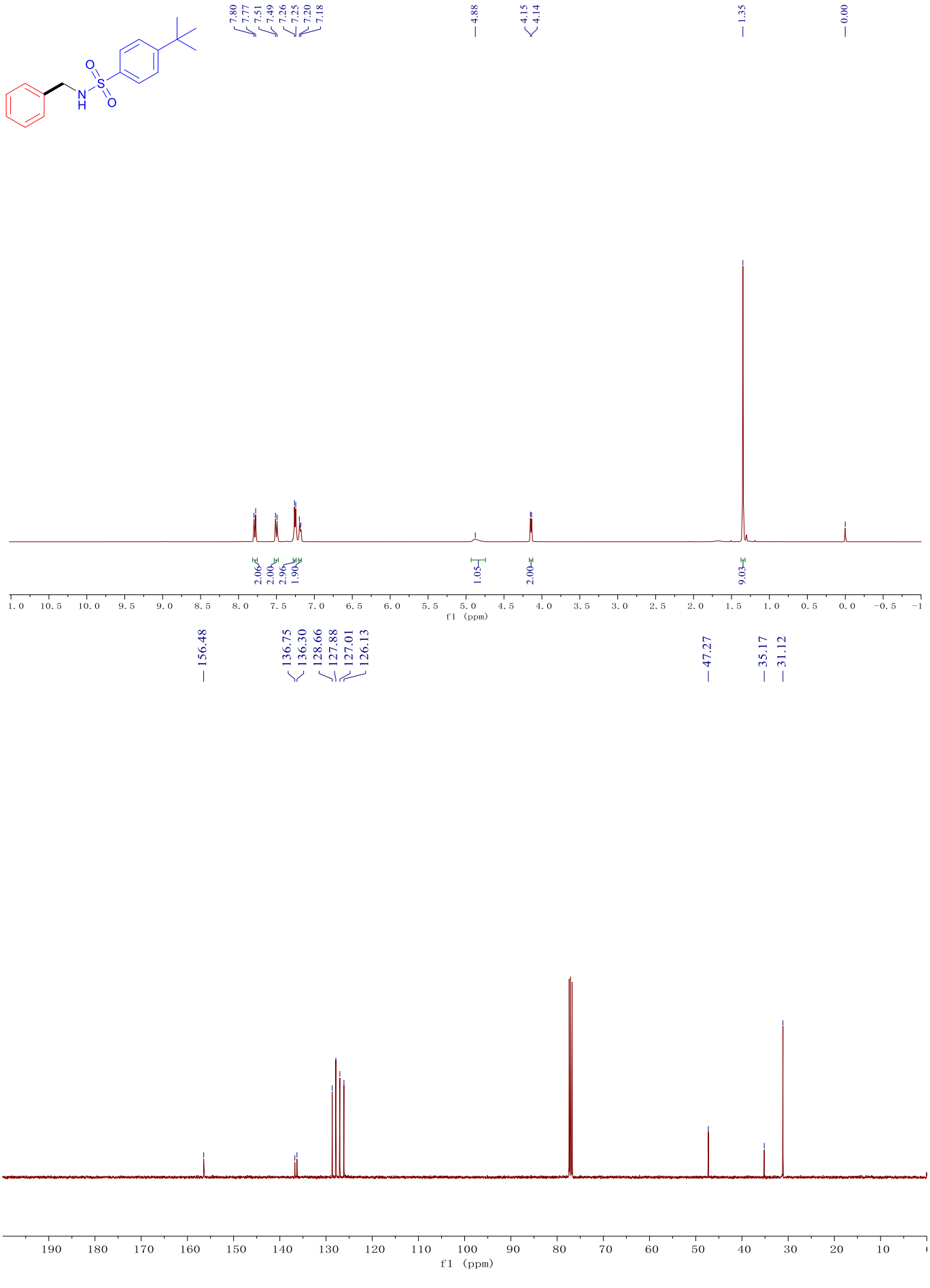




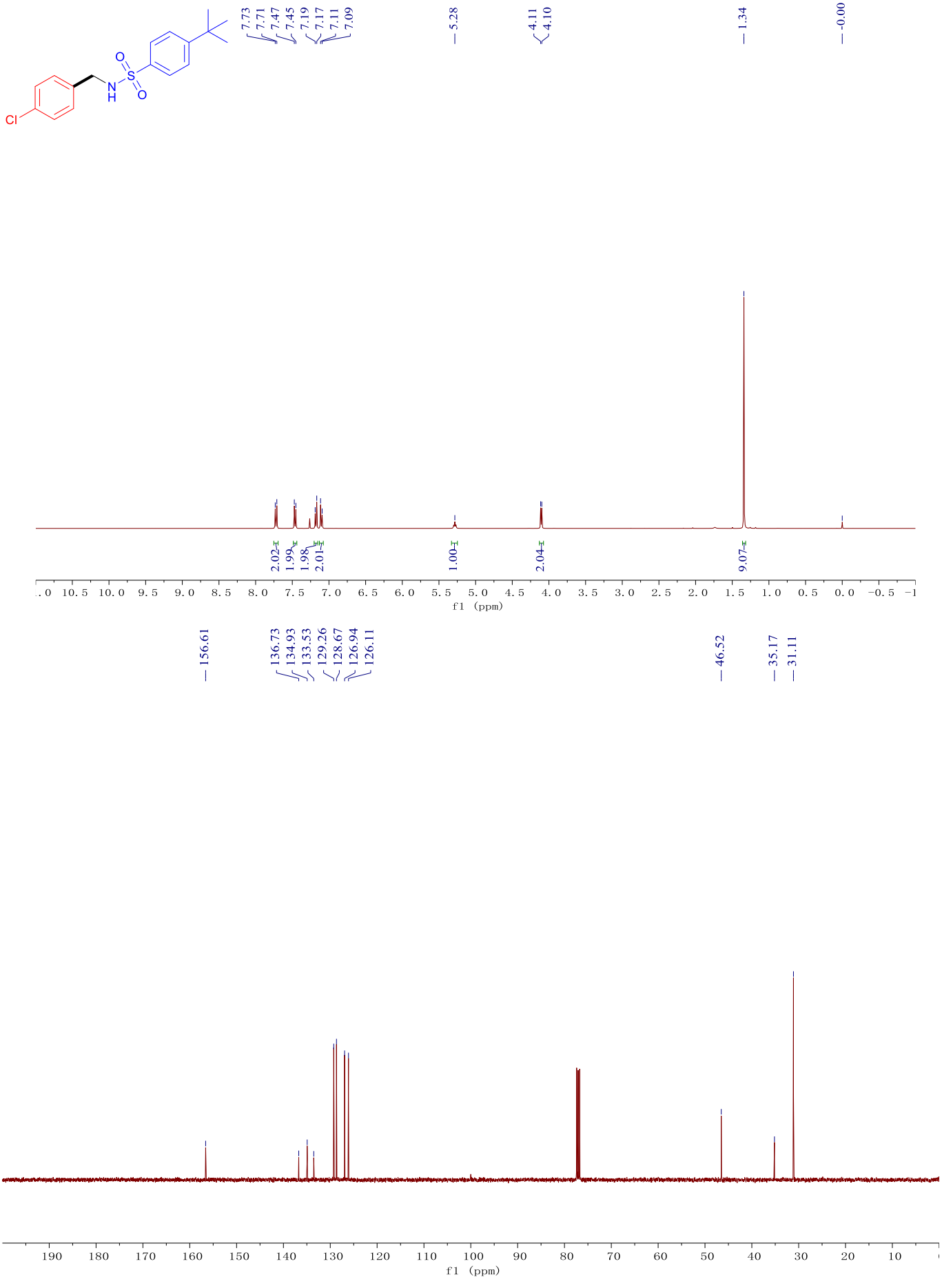
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ab



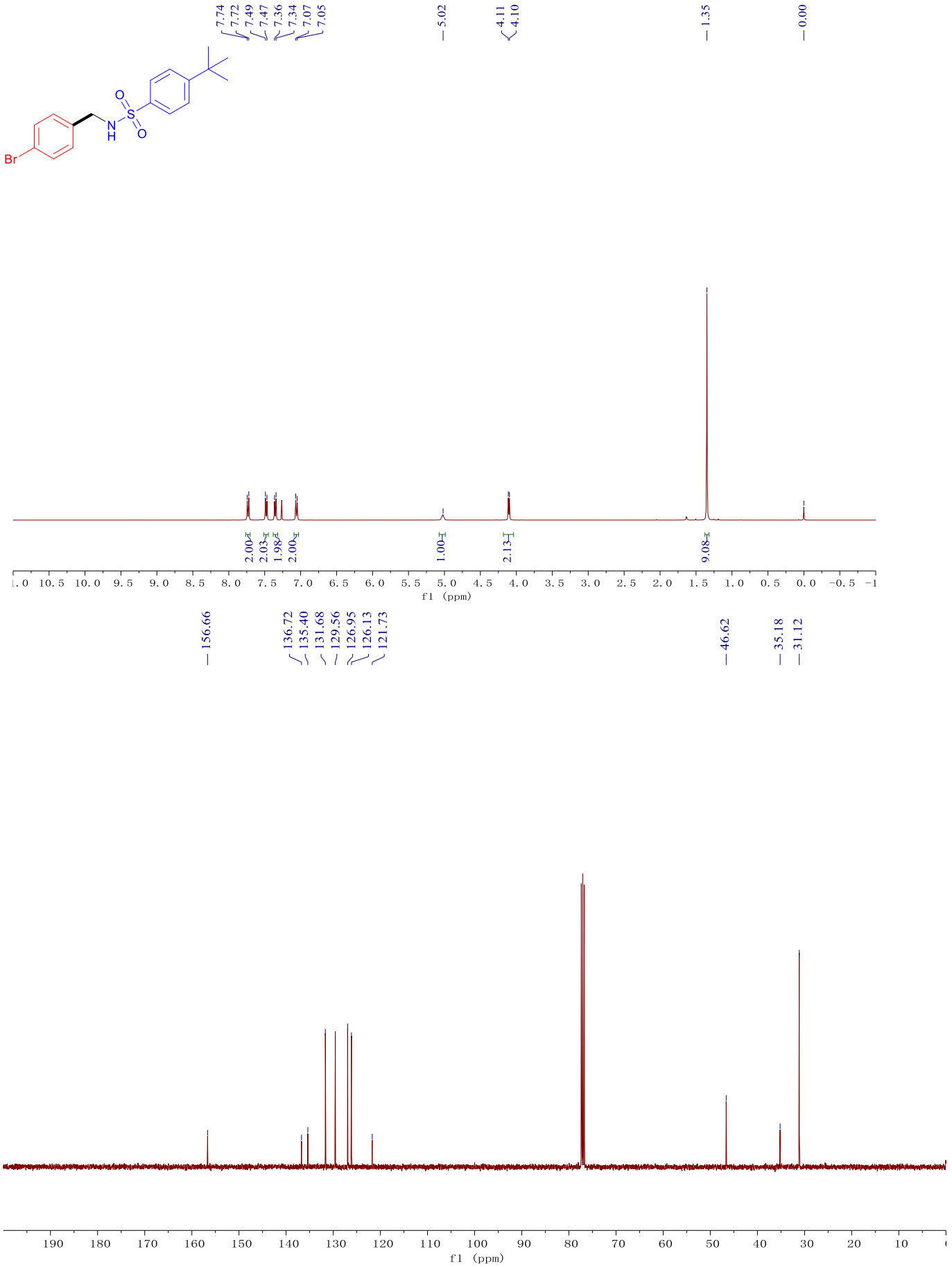
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3ac



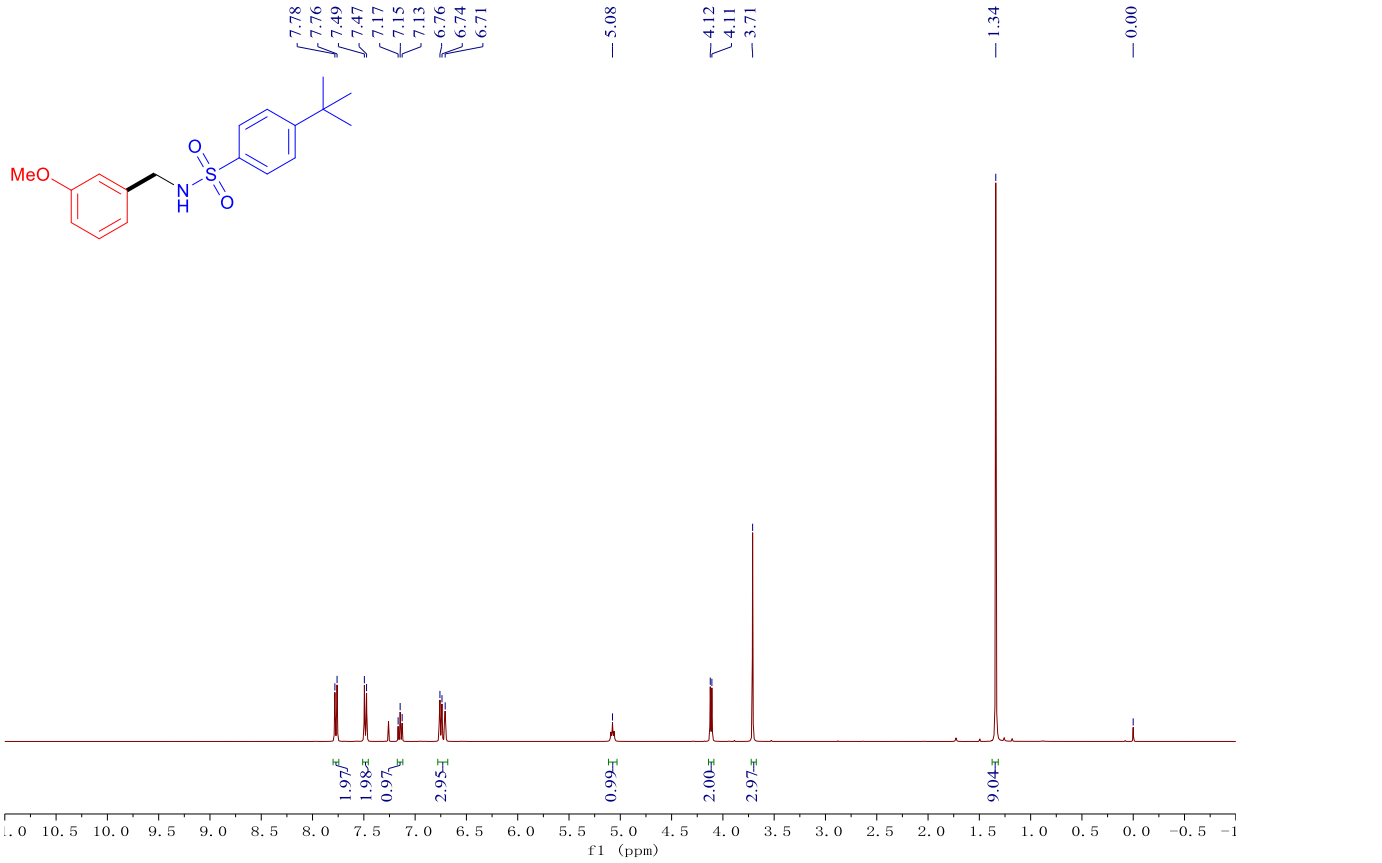
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3ad

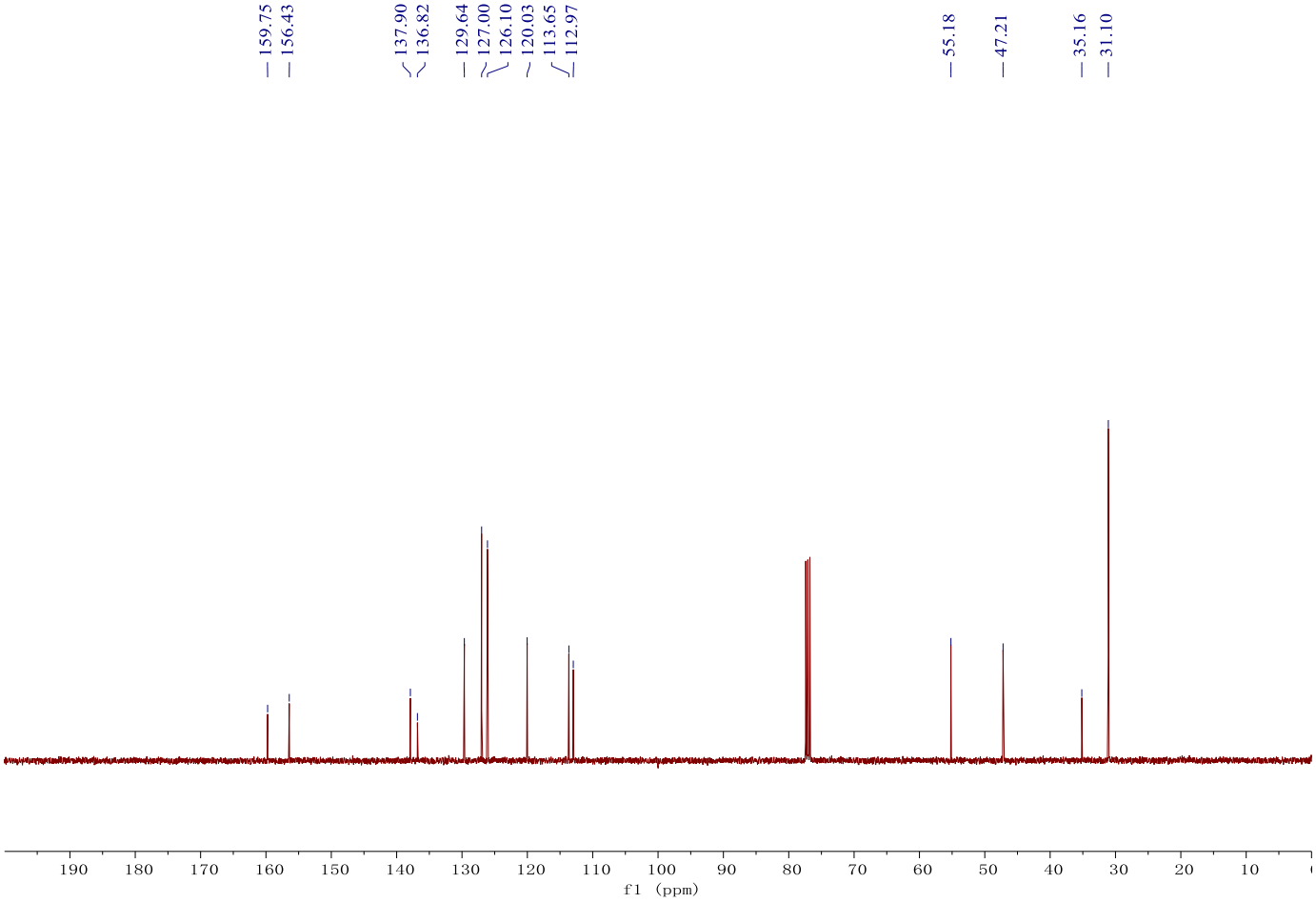


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3ae

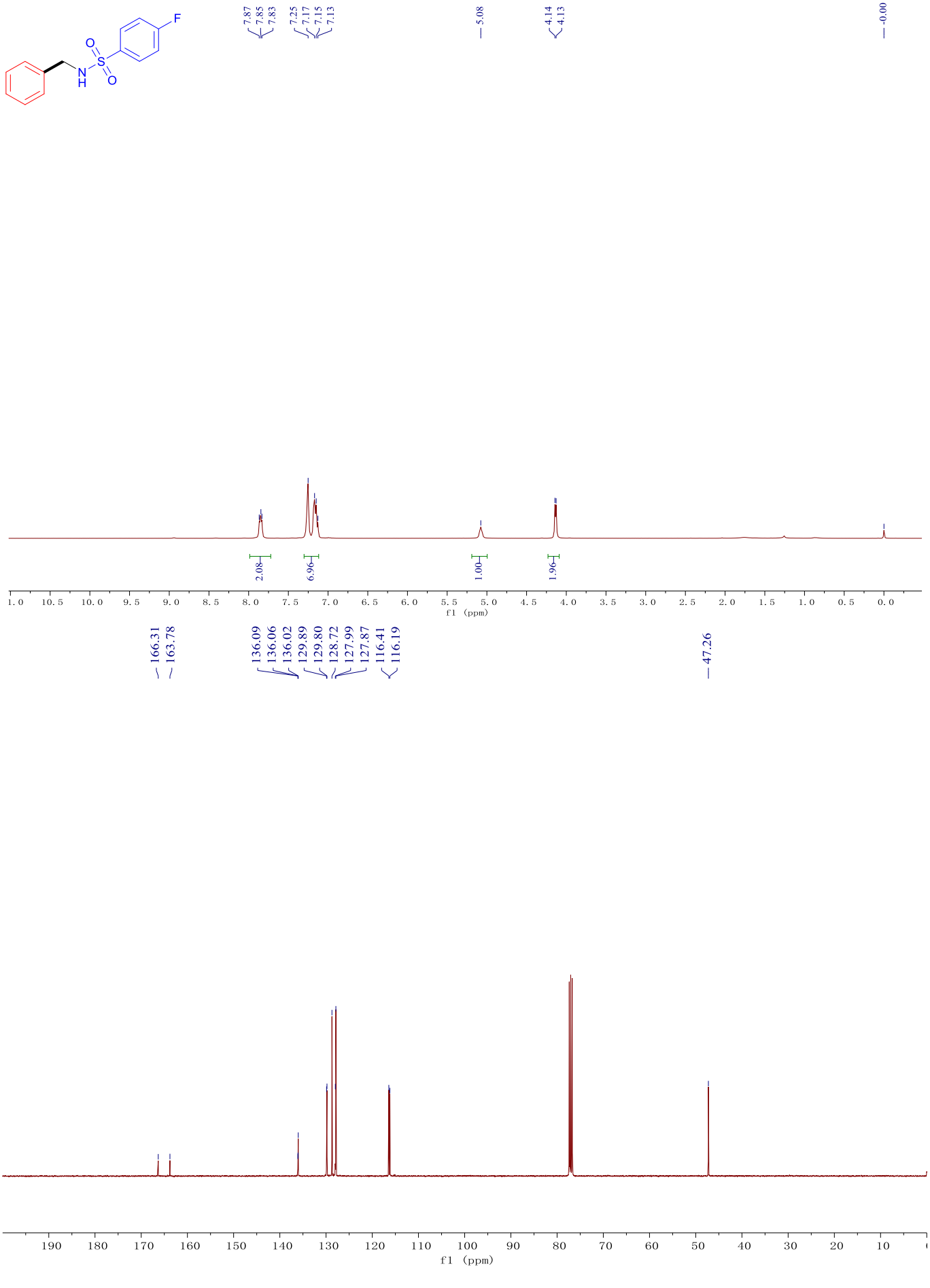


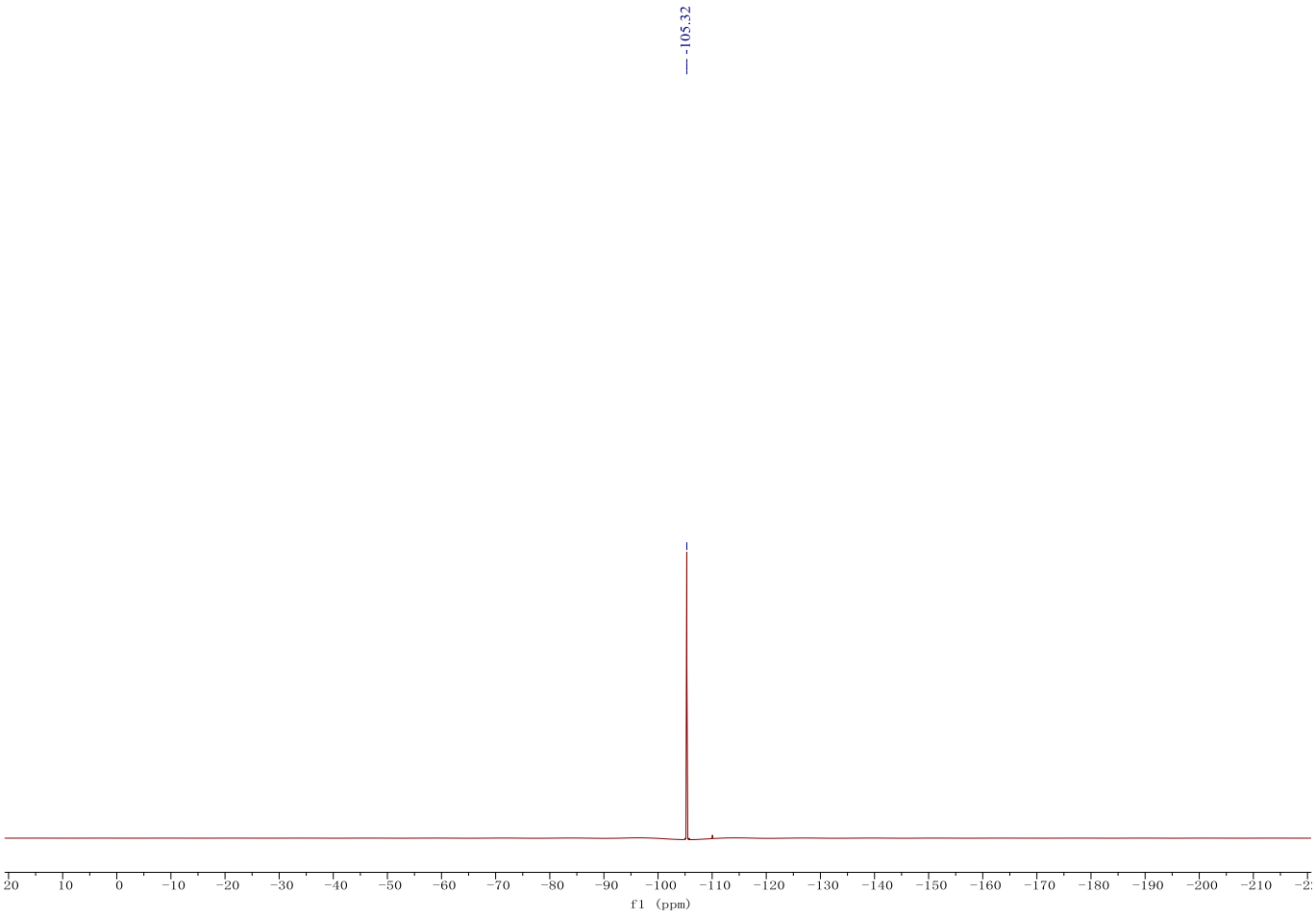
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3af



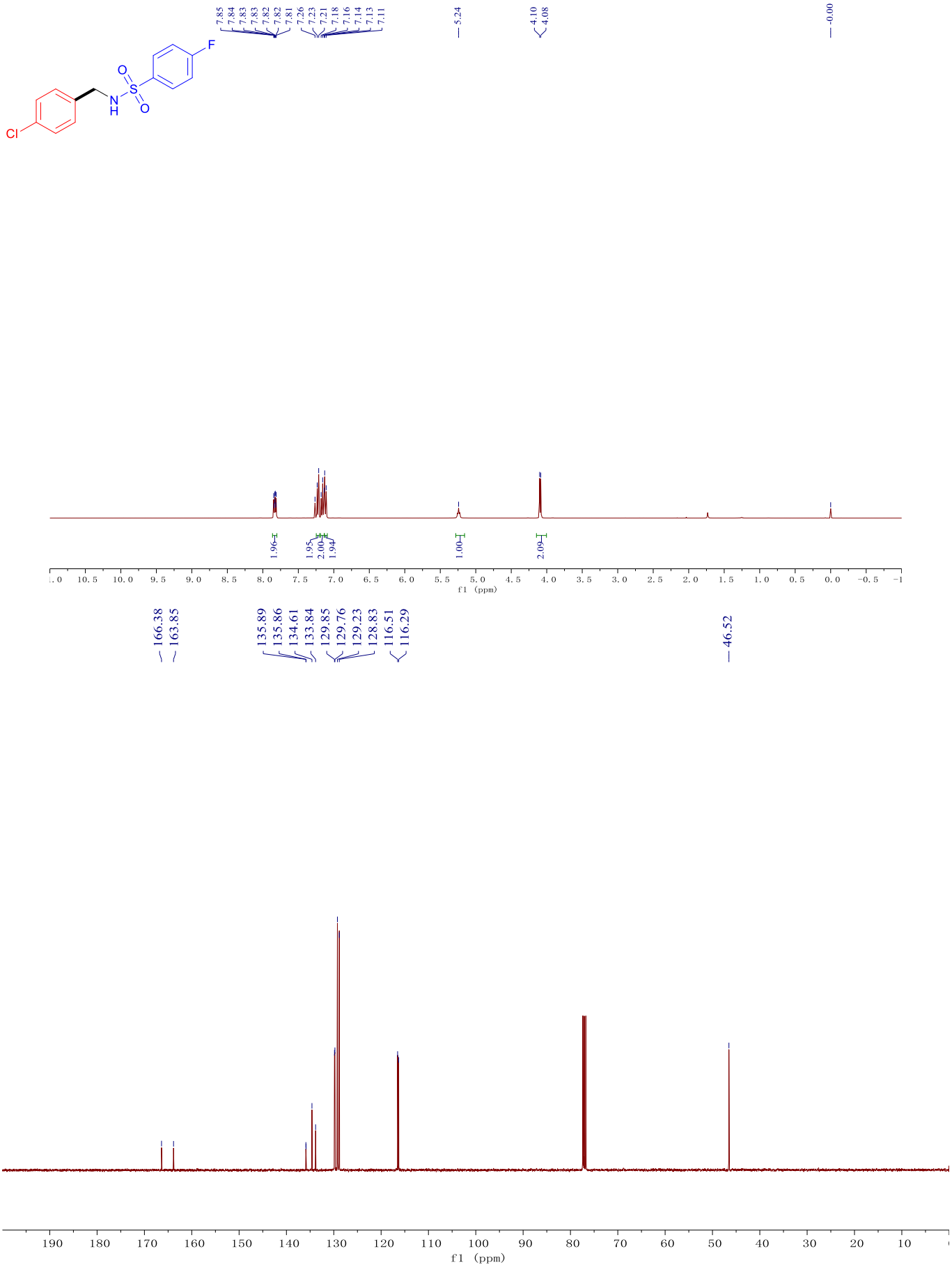


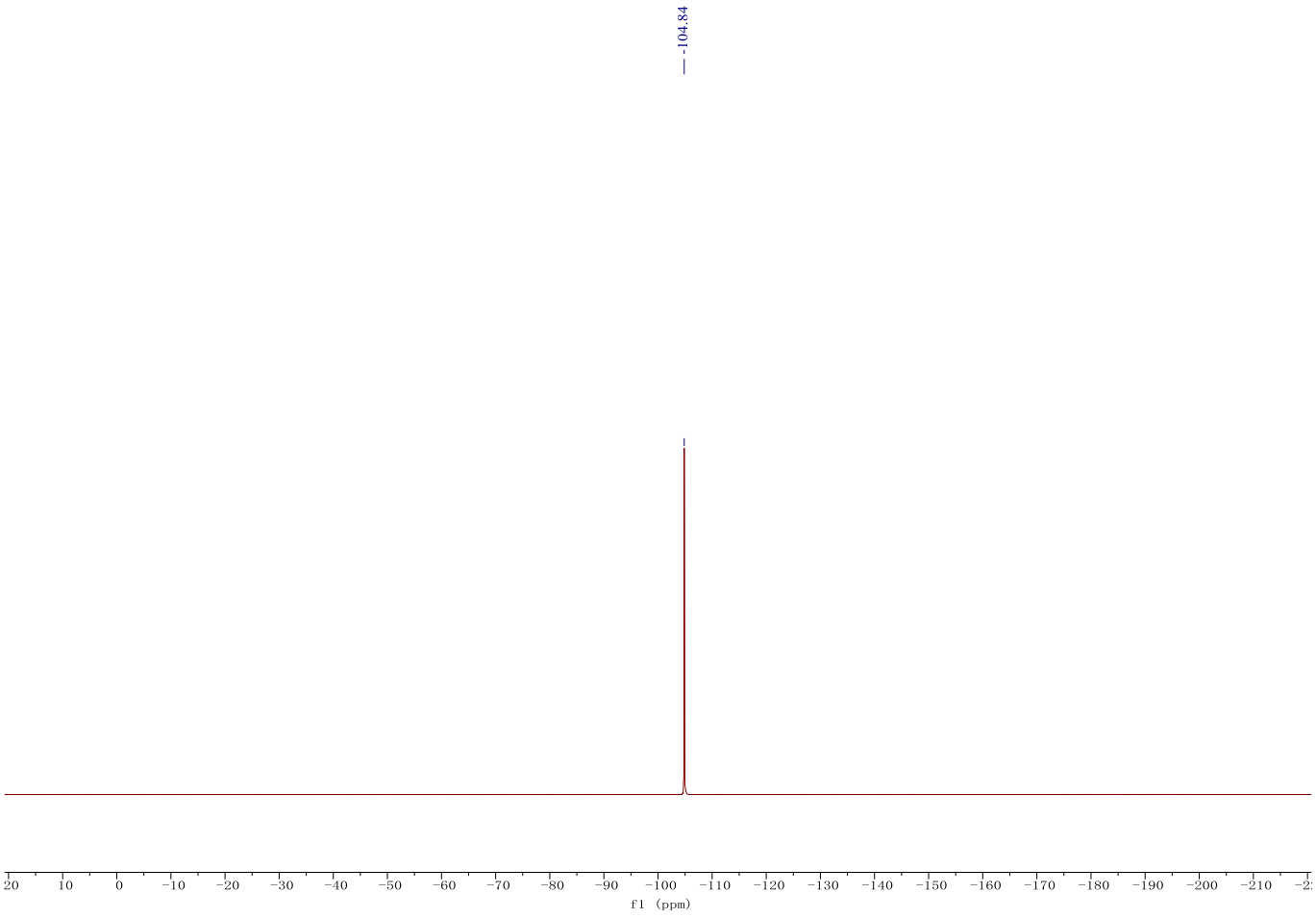
^{1}H NMR (400 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ag



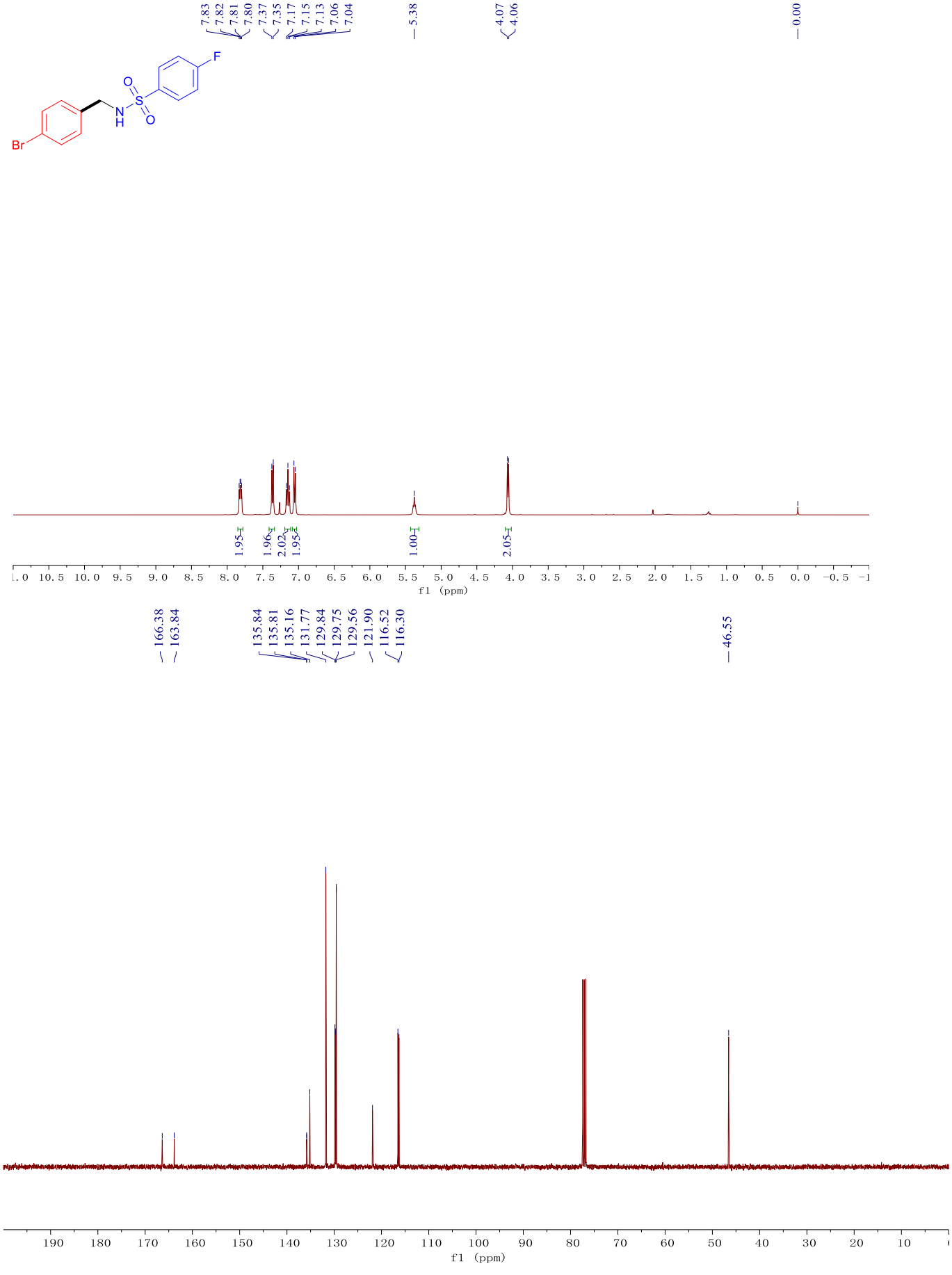

-105.32
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

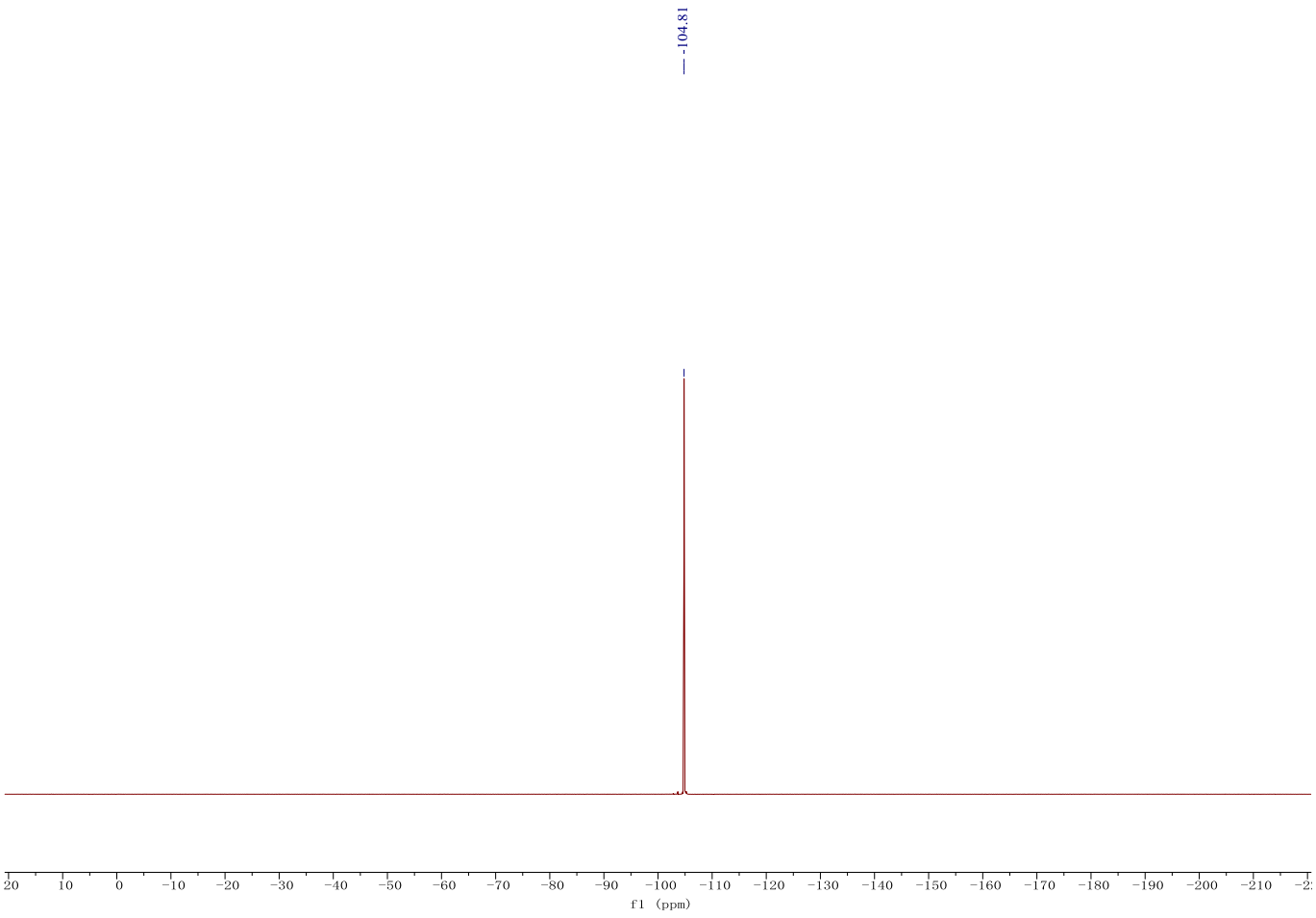
^{1}H NMR (400 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 3ah



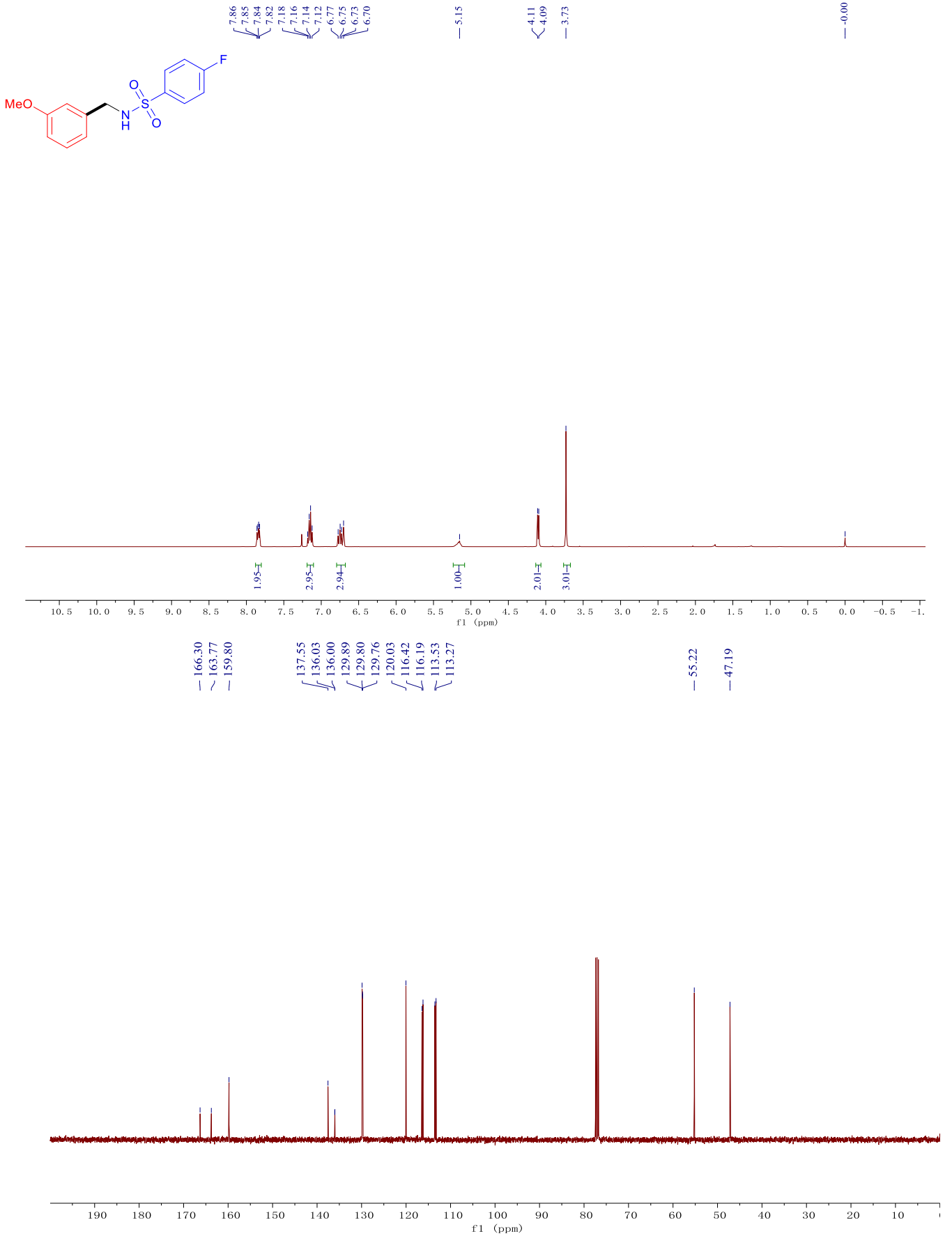

-104.84
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

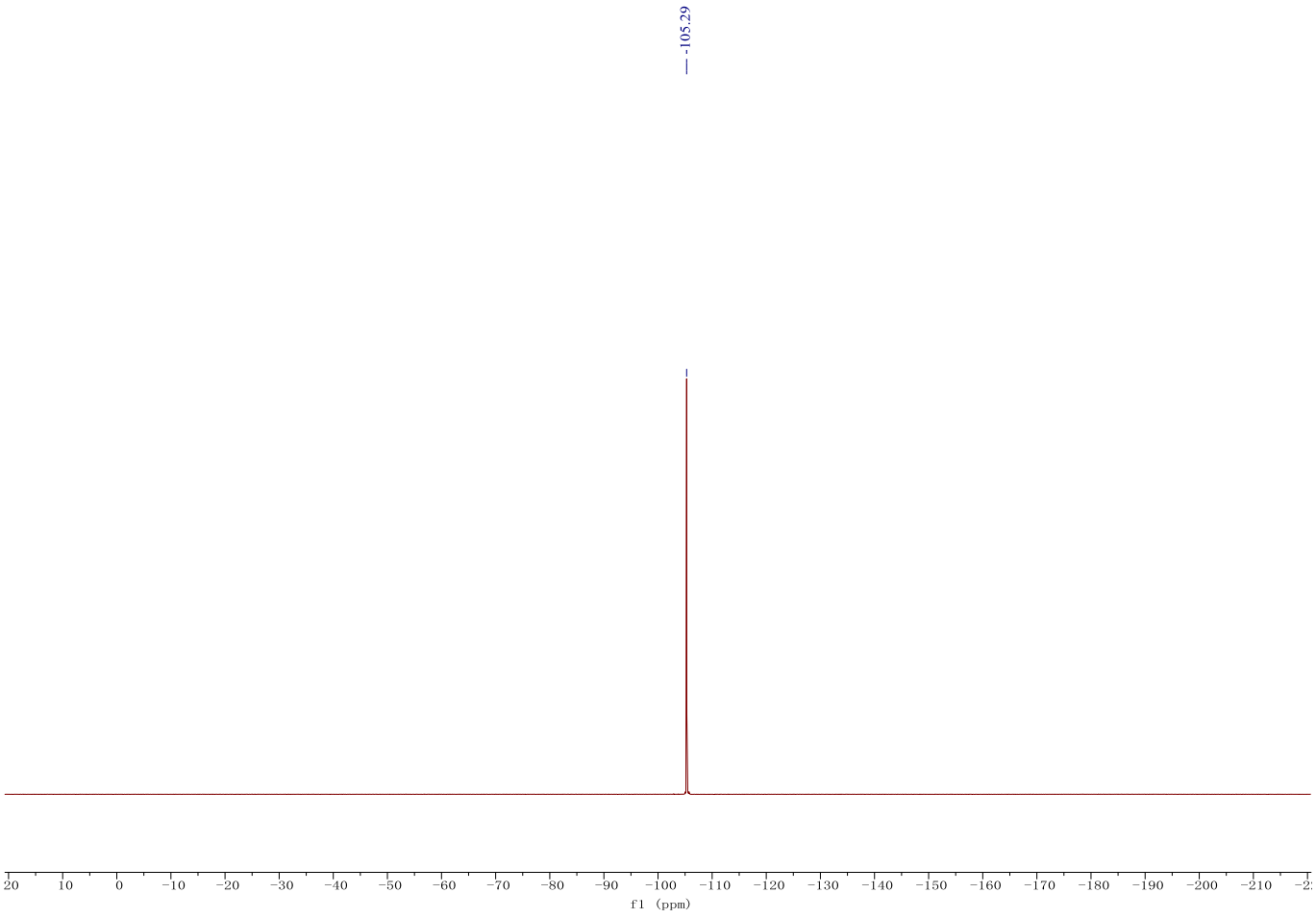
^{1}H NMR (400 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 3ai



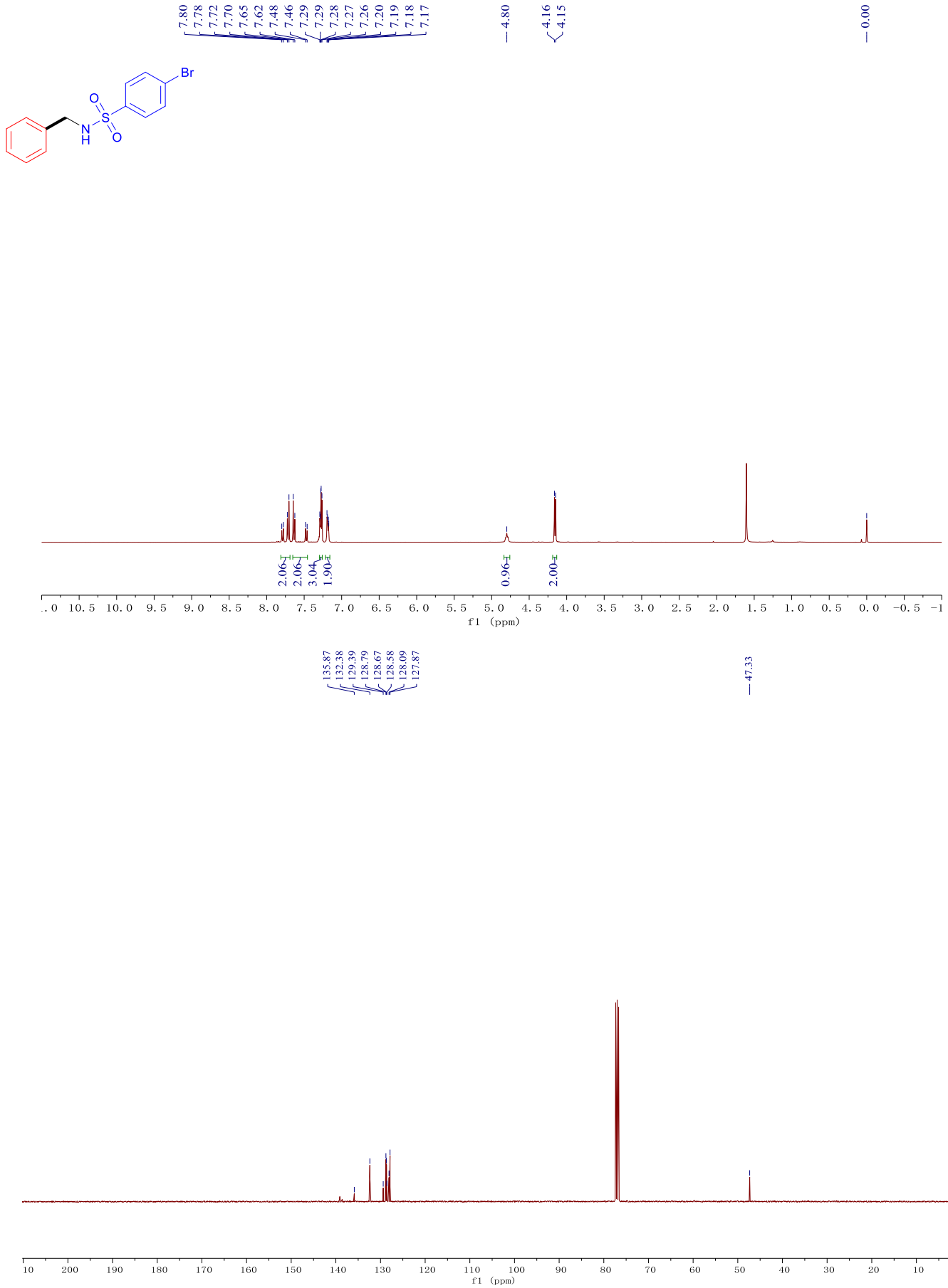

-104.81
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 3aj

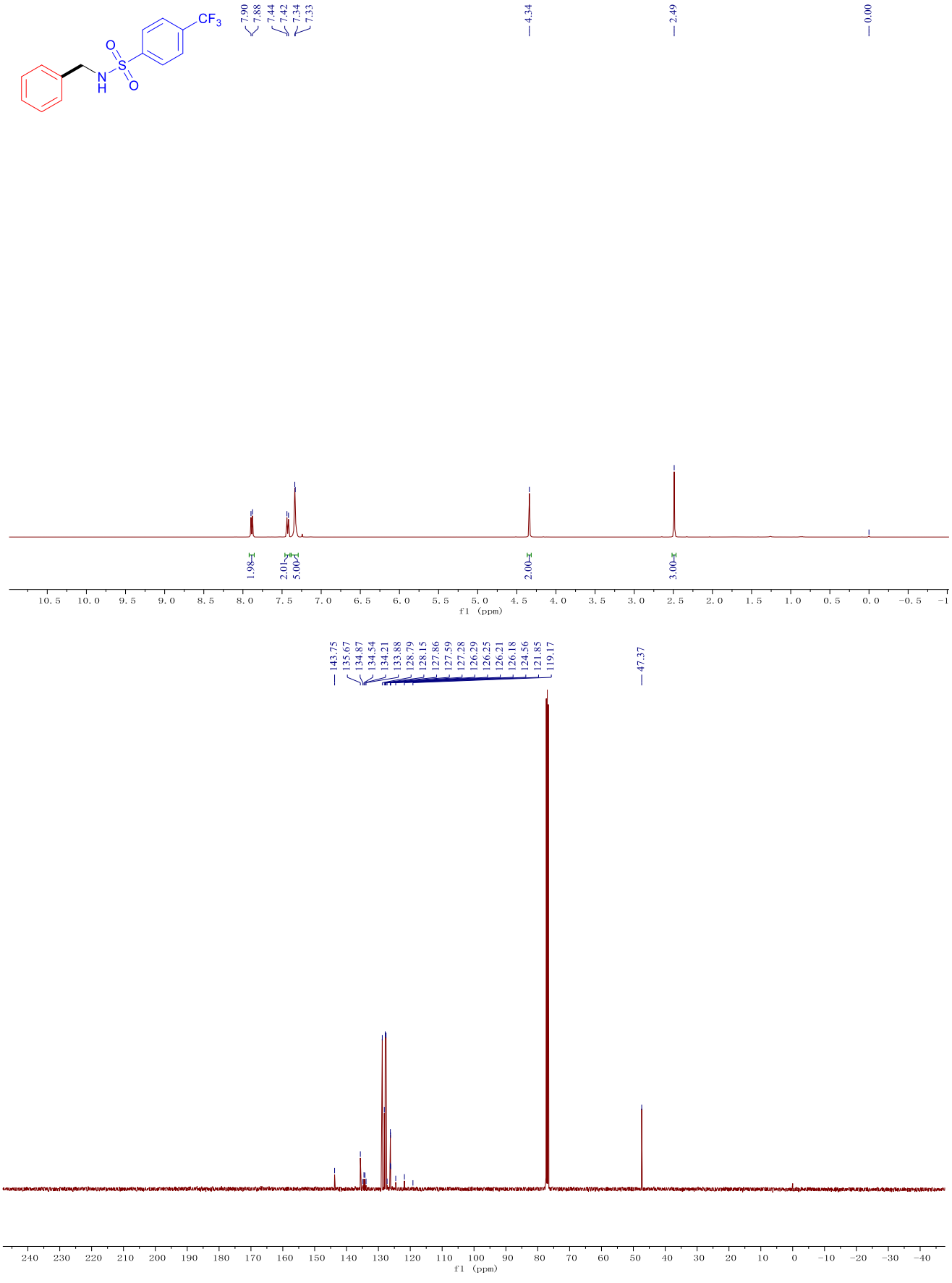


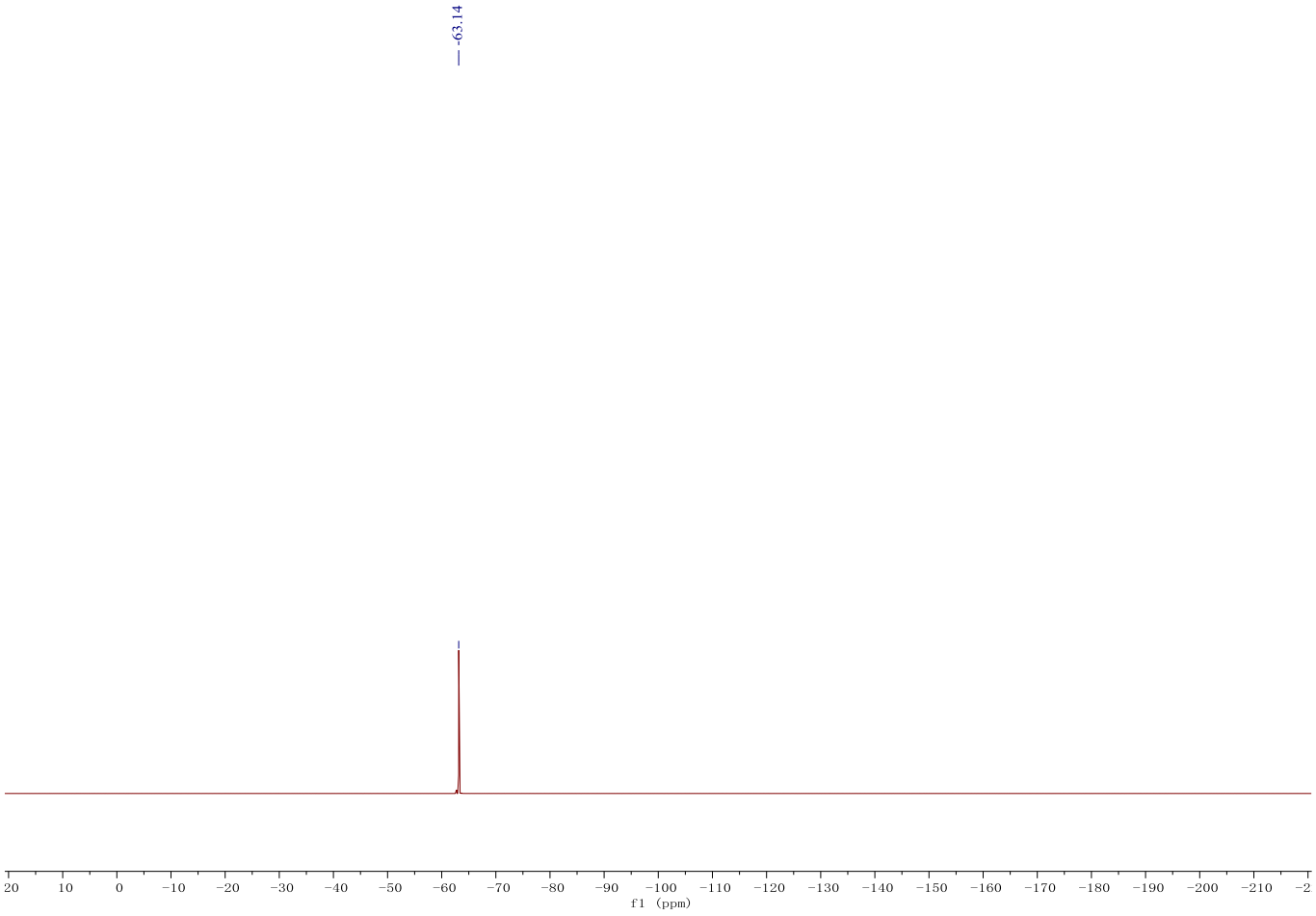

-105.29
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ak

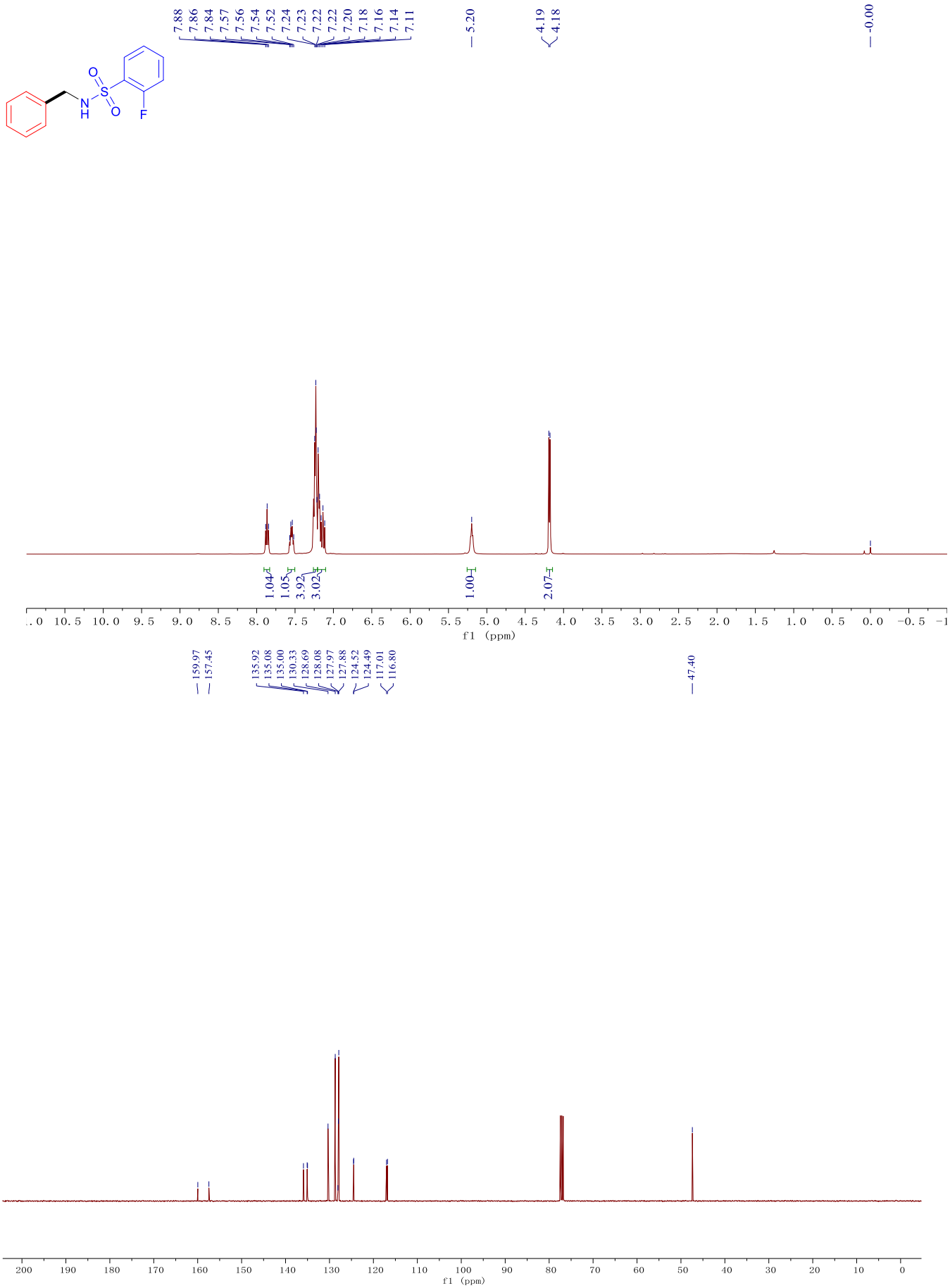


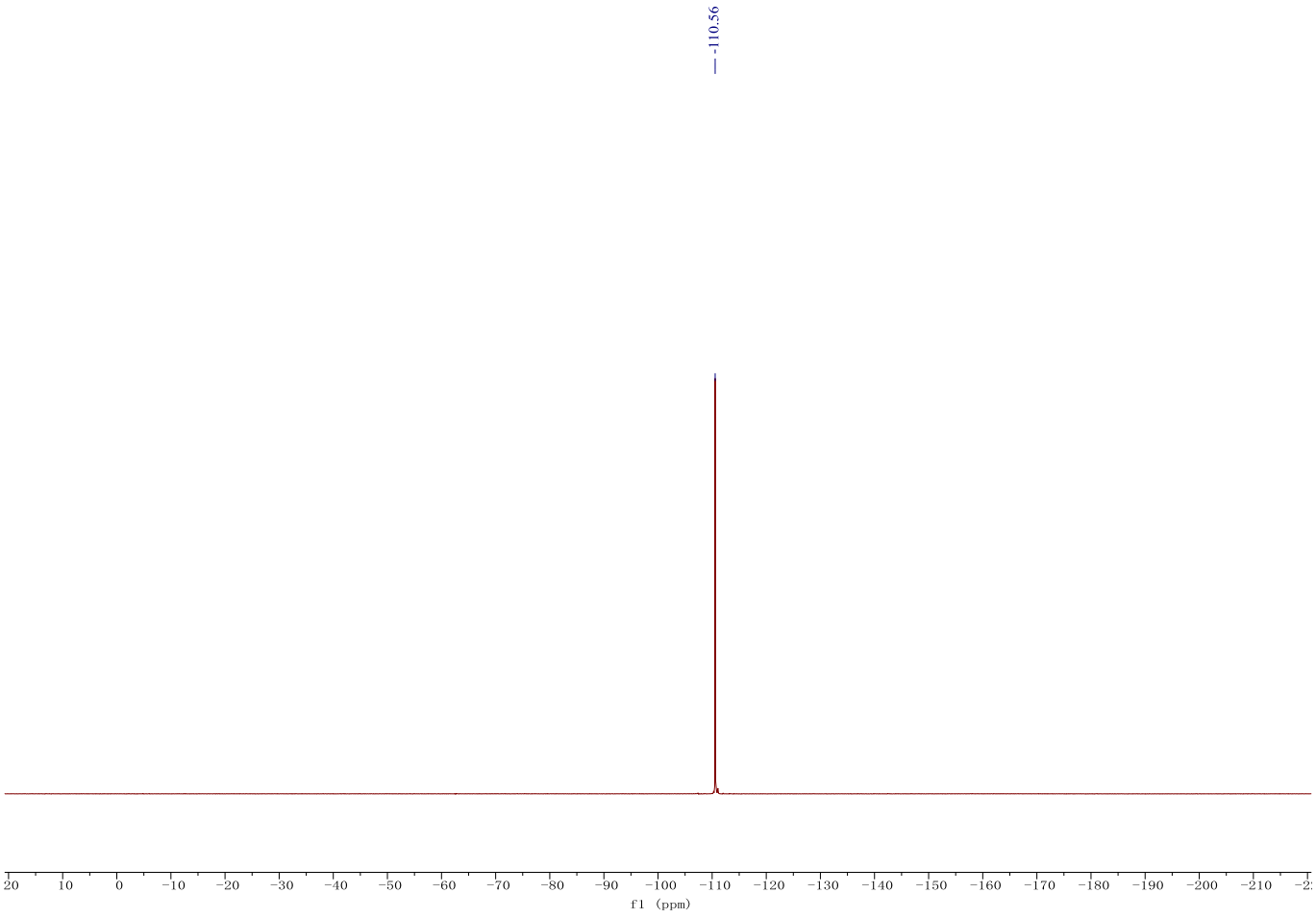
^{1}H NMR (400 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3al



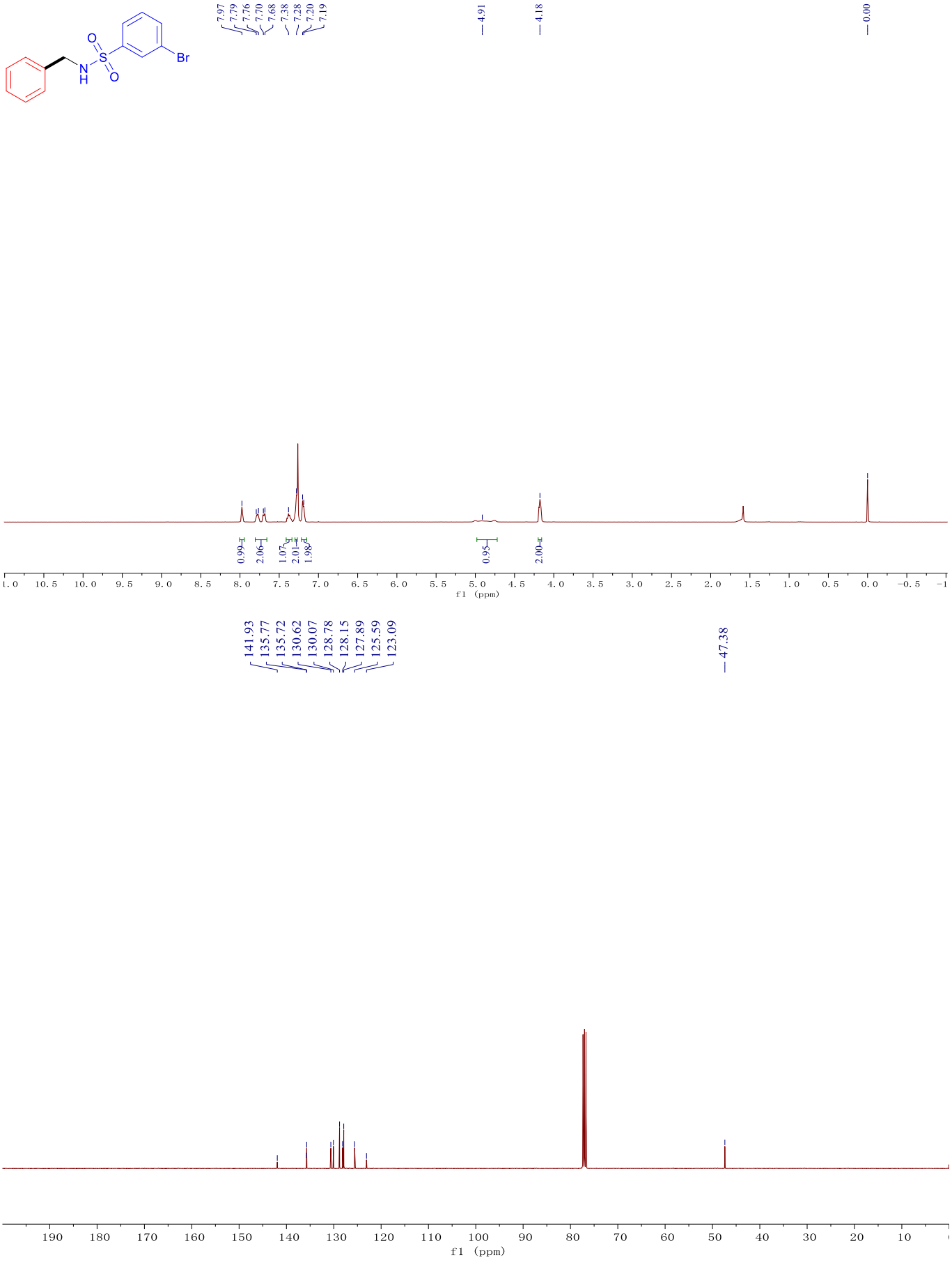

-63.14
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 3am

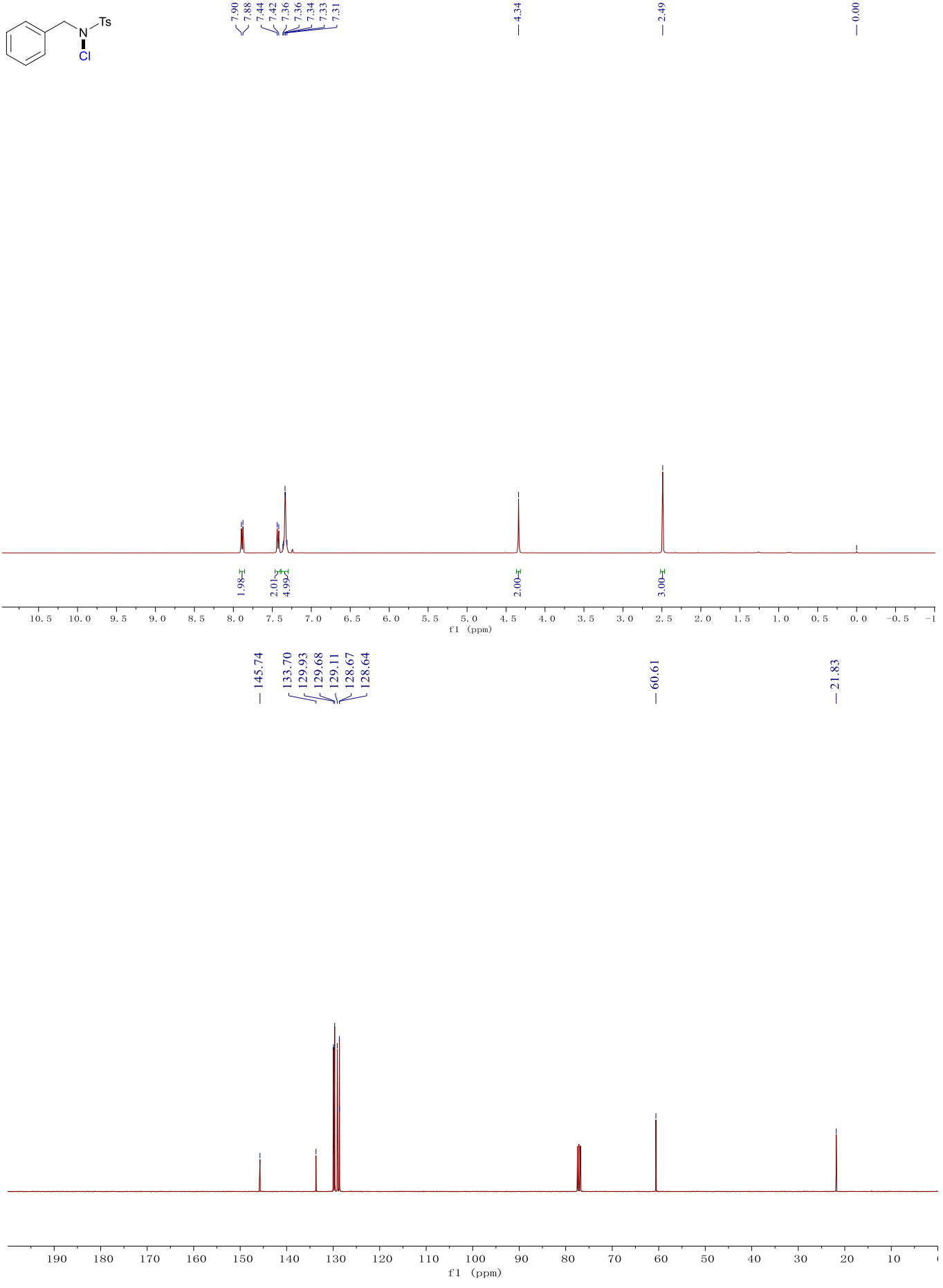



-110.56
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

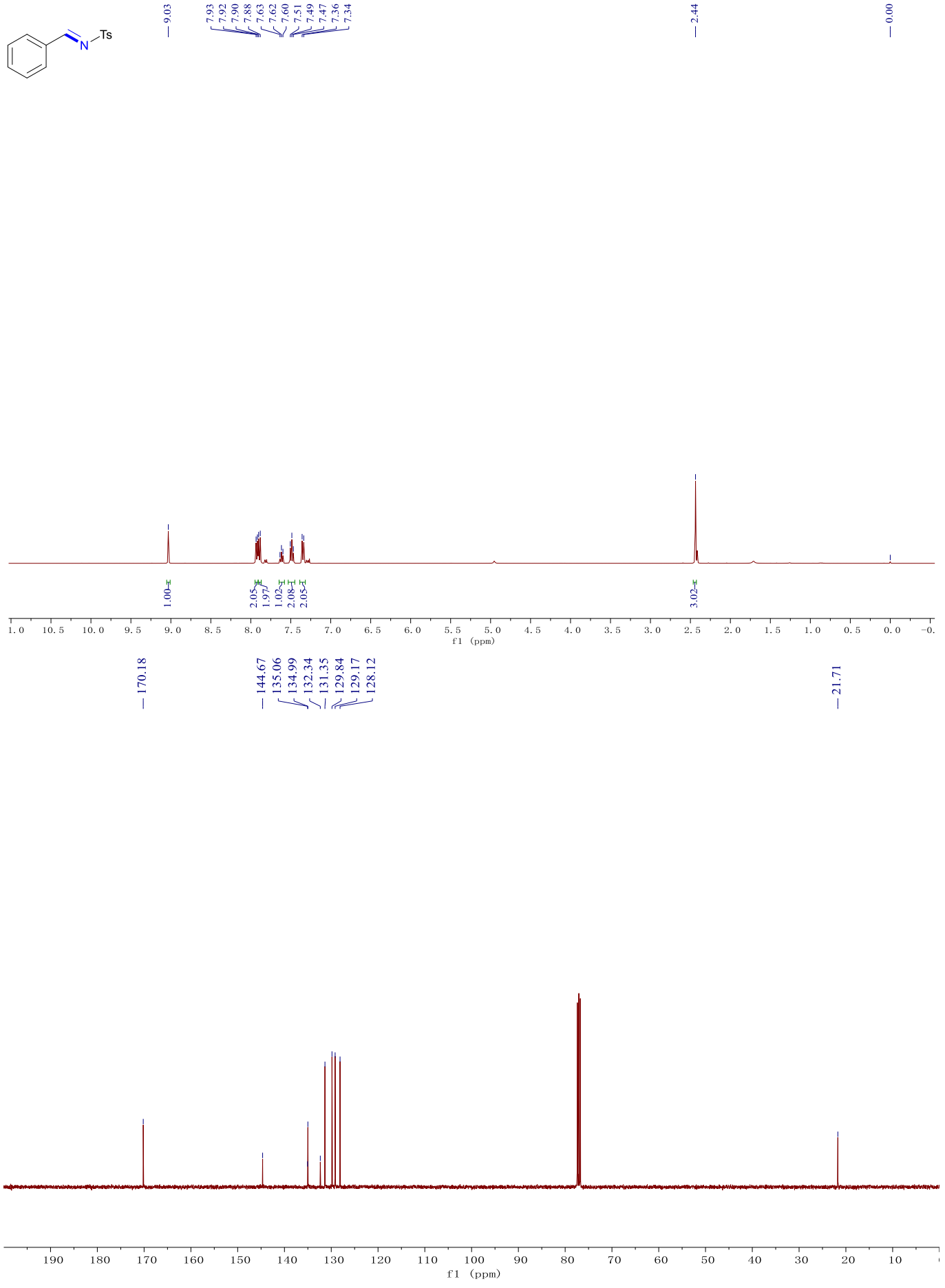
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3an



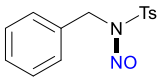
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4

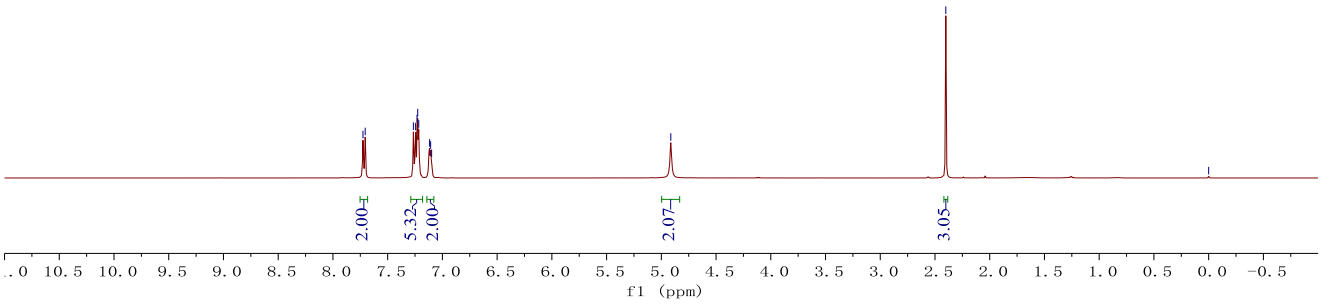


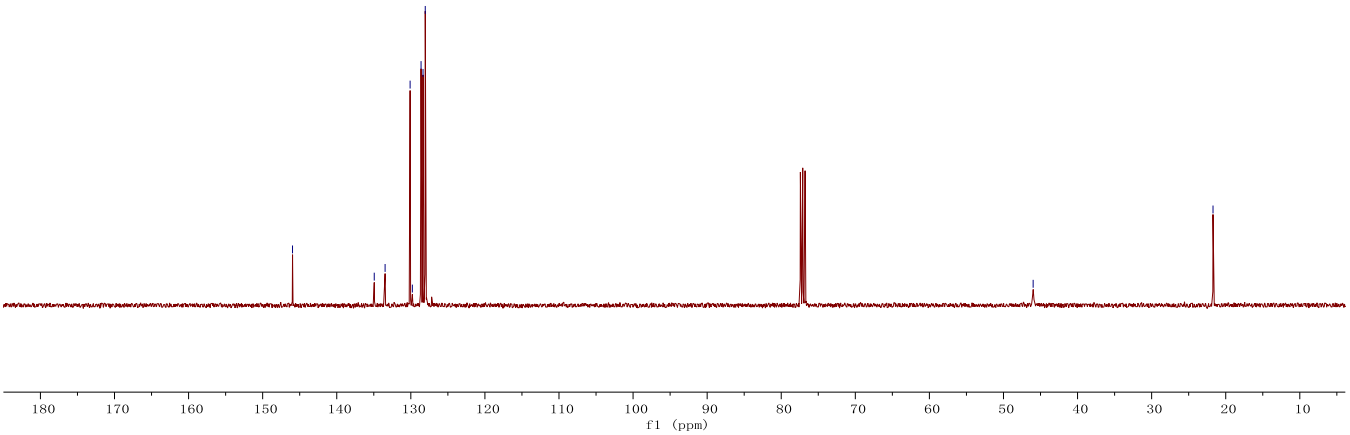
H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 5



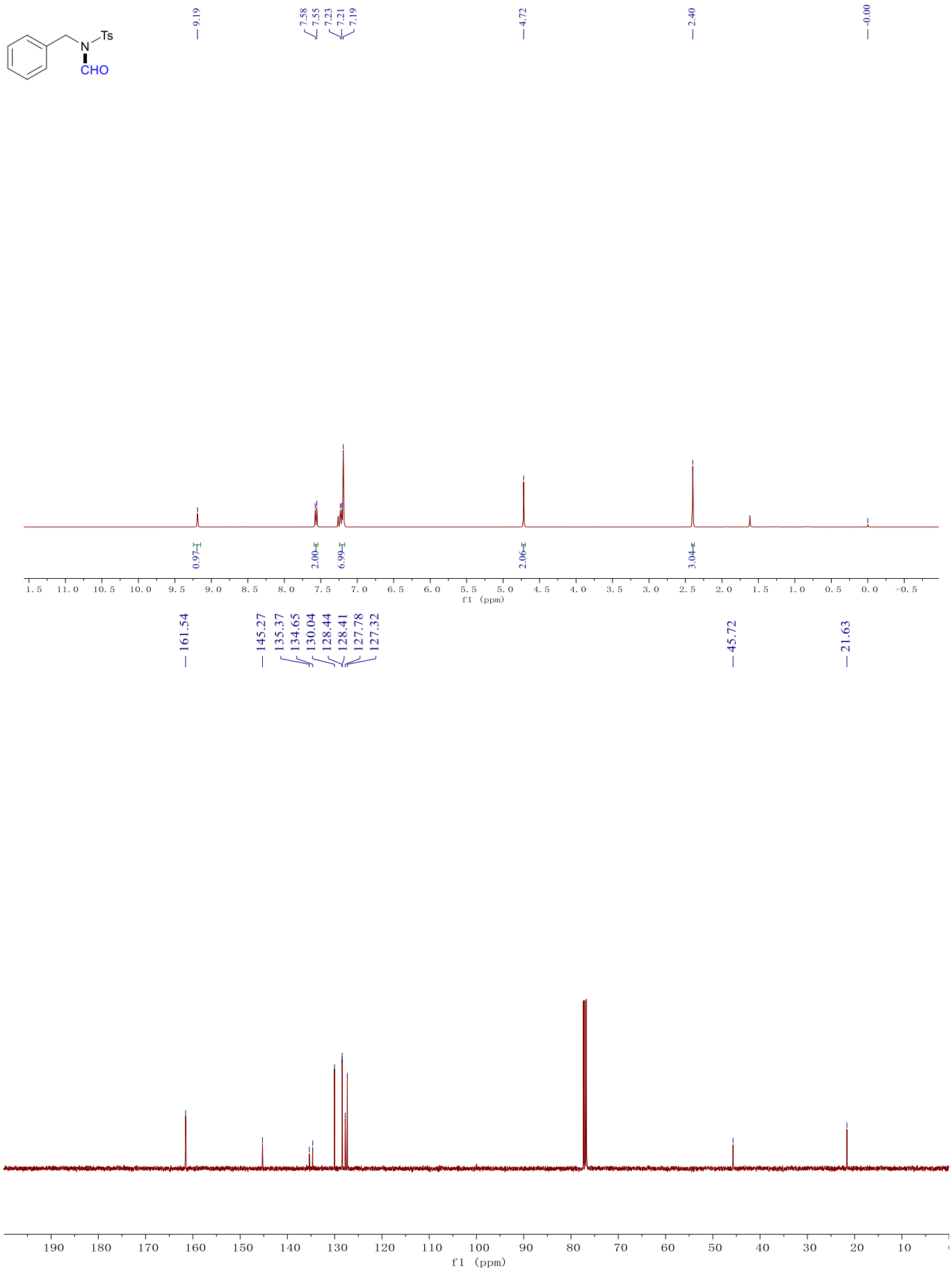
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 6



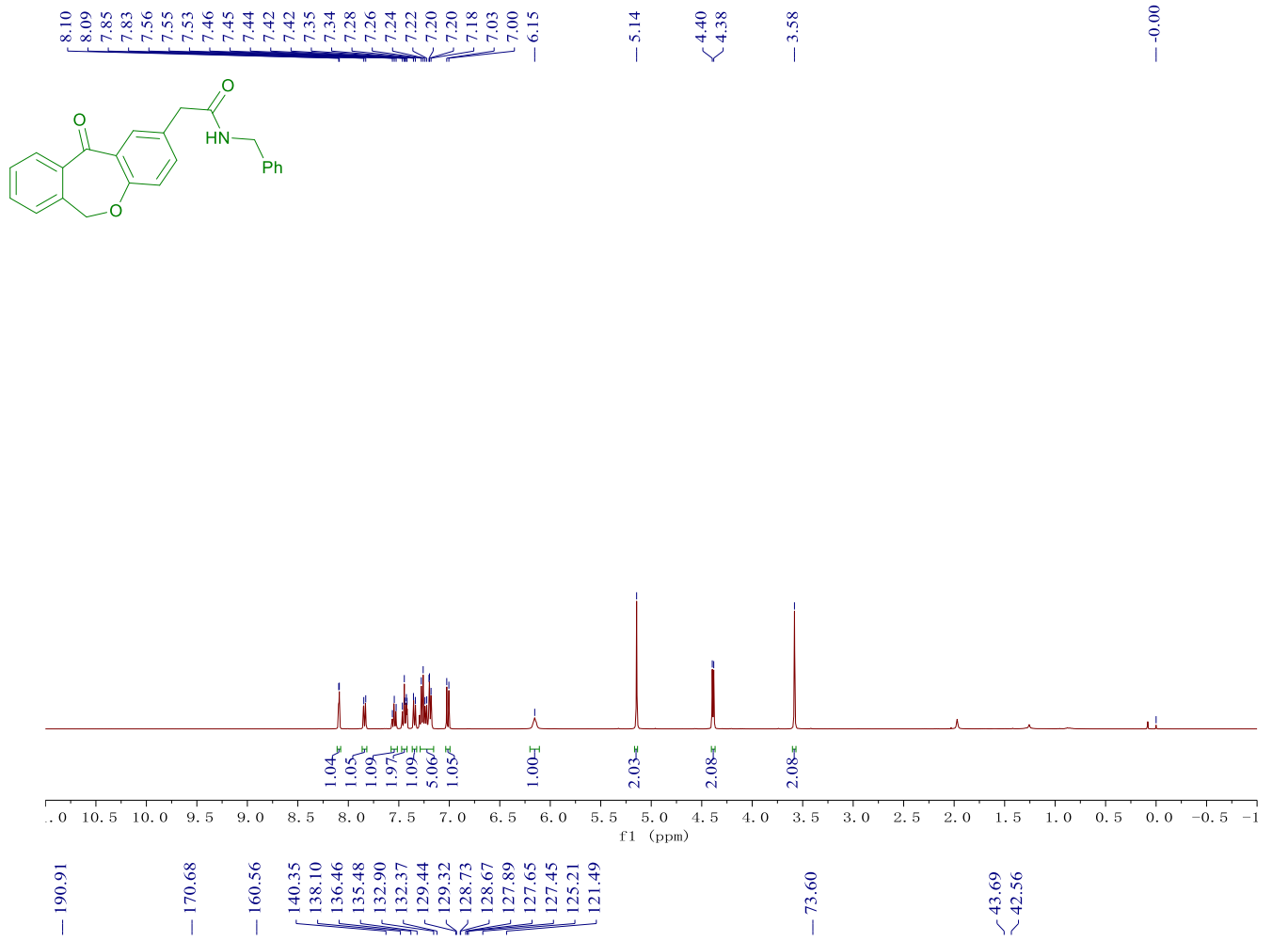




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 7



H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 9



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 10