Visible-Light-Driven Nickel-Catalyzed Reductive Cross-Electrophile Coupling of Benzyltrimethylammonium Triflates with Aryl Bromides

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Supporting Information

Table of Contents

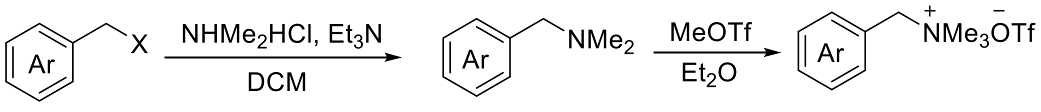
General Information

The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz, 101 MHz respectively) or on a Bruker AC-500 FT spectrometer (500 MHz, 126 MHz, respectively). The chemical shifts of ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced internally with tetramethylsilane (δ H 0.00, δ C 0.00), or residual protio solvent signals ($CDCl_3$ (δ C 77.16). Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). ESI-mass data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. Melting points are uncorrected.

Chemicals were purchased from the Accela, Adamas, Alfa Aesar, Bidepharm, Energy Chemical, Macklin and TCI, and used as received.

Abbreviations: acac = acetylacetonate, Ar = aryl, TEMPO = 2,2,6,6-tetramethyl-1-piperinedinyloxy, DABCO = 1,4-diaza[2.2.2]bicyclooctane , DCM = dichloromethane.

General Procedure for the Preparation of Quaternary Ammonium Triflates[1]



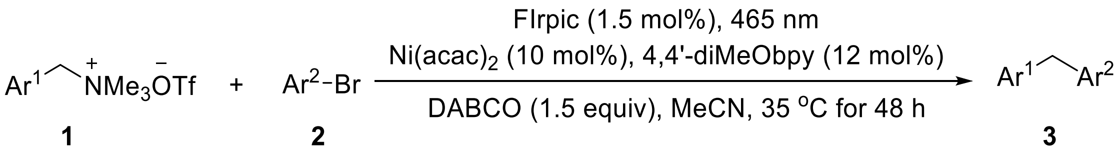
S1
(X = Cl, Br, I)

S2

To a stirred solution of benzyl halides **S1** (10.0 mmol) in DCM (50 mL) at room temperature were added Et_3N (1.67 mL, 1.21 g, 12 mmol), $NHMe_2HCl$ (0.978 g, 12.0 mmol). The mixture was stirred at room temperature for 6 hours and 30 mL brine was added in, followed by extractions with DCM (3x30 mL). The organic layer was combined, washed with brine (2 × 30 mL), dried with anhydrous sodium sulfate, filtered and concentrated in vacuo to give crude tertiary amines **S2**.

To a solution of crude amine **S2** in diethyl ether (20 mL) at 0 °C was added dropwise MeOTf (1.36 mL, 1.97 g, 12 mmol). The mixture was stirred at room temperature for 4 h. The precipitate was isolated by filtration and washed with diethyl ether (3 × 20 mL). The resulting solid was dried under vacuum to give benzyltrimethylammonium triflates **1**. If no precipitate was generated, the ammonium triflates was separated by column chromatography (DCM/MeOH = 20/1).

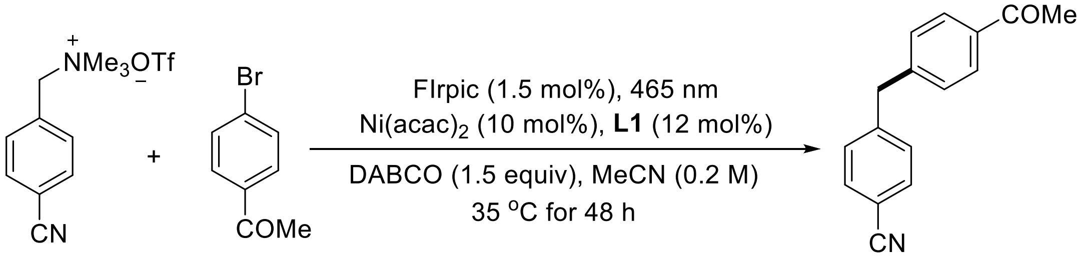
General Procedure for the Visible-Light-Driven Nickel-Catalyzed Reductive Cross-Electrophile Coupling of Benzyltrimethylammonium Triflates with Aryl Bromides



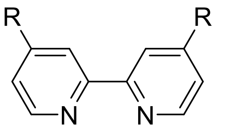
1 **2** **3**

To a flame-dried Schlenk tube equipped with a stir bar were added benzyltrimethylammonium triflates **1** (0.20 mmol), aryl bromides **2** (0.5 mmol), FIrpic (2.1 mg, 0.003 mmol), $Ni(acac)_2$ (5.1 mg, 0.02 mmol), 4,4'-dimethoxy-2,2'-bipyridine (5.2 mg, 0.024 mmol) and DABCO (33.7 mg, 0.30 mmol). The tube was evacuated and refilled nitrogen three times and added MeCN (1.0 mL) via syringe. The mixture was stirred under blue light (465 nm, 10 W) irradiation for 48 h at 35 °C. The reaction mixture was then filtered and concentrated under reduced pressure. The crude residue was finally purified by silica gel chromatography, using a mixture of ethyl acetate and petroleum ether (1:10 to 1:4) as the eluent, to give products **1**.

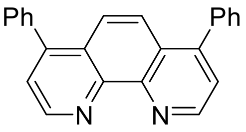
Table S1 : Optimization of the Reaction Conditions[a]



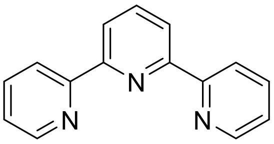
1a **2a** **3a**



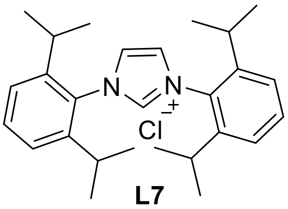
L1, R = OMe
L2, R = COOMe
L3, R = ^{t}Bu
L4, R = H



L5



L6



L7

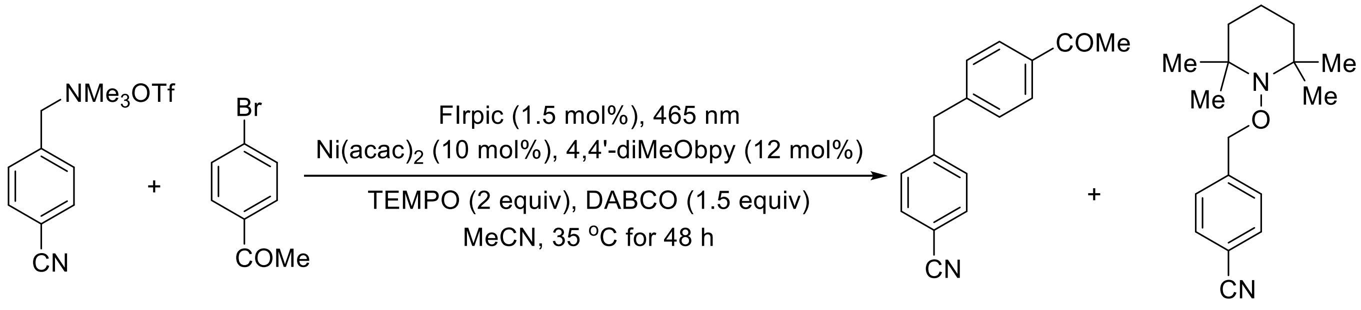
Entry	variation of standard conditions	Yield (%)[b]
1	none	71
2	I instead of Br	41
3	Cl instead of Br	trace
4	$[Ir(dtbbpy)(ppy)_2]PF_6$ instead of FIrpic	38
5	$Ir(ppy)_3$ instead of FIrpic	46
6	$Ru(bpy)_3Cl_2.6H_2O$ instead of FIrpic	trace
7	without FIrpic	0
8	NiI_2 instead of $Ni(acac)_2$	43
9	$NiBr_2$ instead of $Ni(acac)_2$	38
10	$Ni(OTf)_2$ instead of $Ni(acac)_2$	25
11	without $Ni(acac)_2$	0
12	**L2** instead of **L1**	trace
13	**L3** instead of **L1**	52
14	**L4** instead of **L1**	25
15	**L5** instead of **L1**	36
16	**L6** instead of **L1**	0

17	**L7** instead of **L1**	0
18	without Ligand	11
19	Et_3N instead of DABCO	25
20	without DABCO	0
21	DMF instead of MeCN	40
22	THF instead of MeCN	trace
23	PhMe	0
24	12 h instead of 48 h	48
25	24 h instead of 48 h	65
26	dark for 48 h	0

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.50 mmol), FIrpic (1.5 mol%), $Ni(acac)_2$ (10 mol%), **L1** (12 mol%), DABCO (0.30 mmol), MeCN (1.0 mL), 465 nm blue light (35 °C), 48 h. [b]Isolated yield.

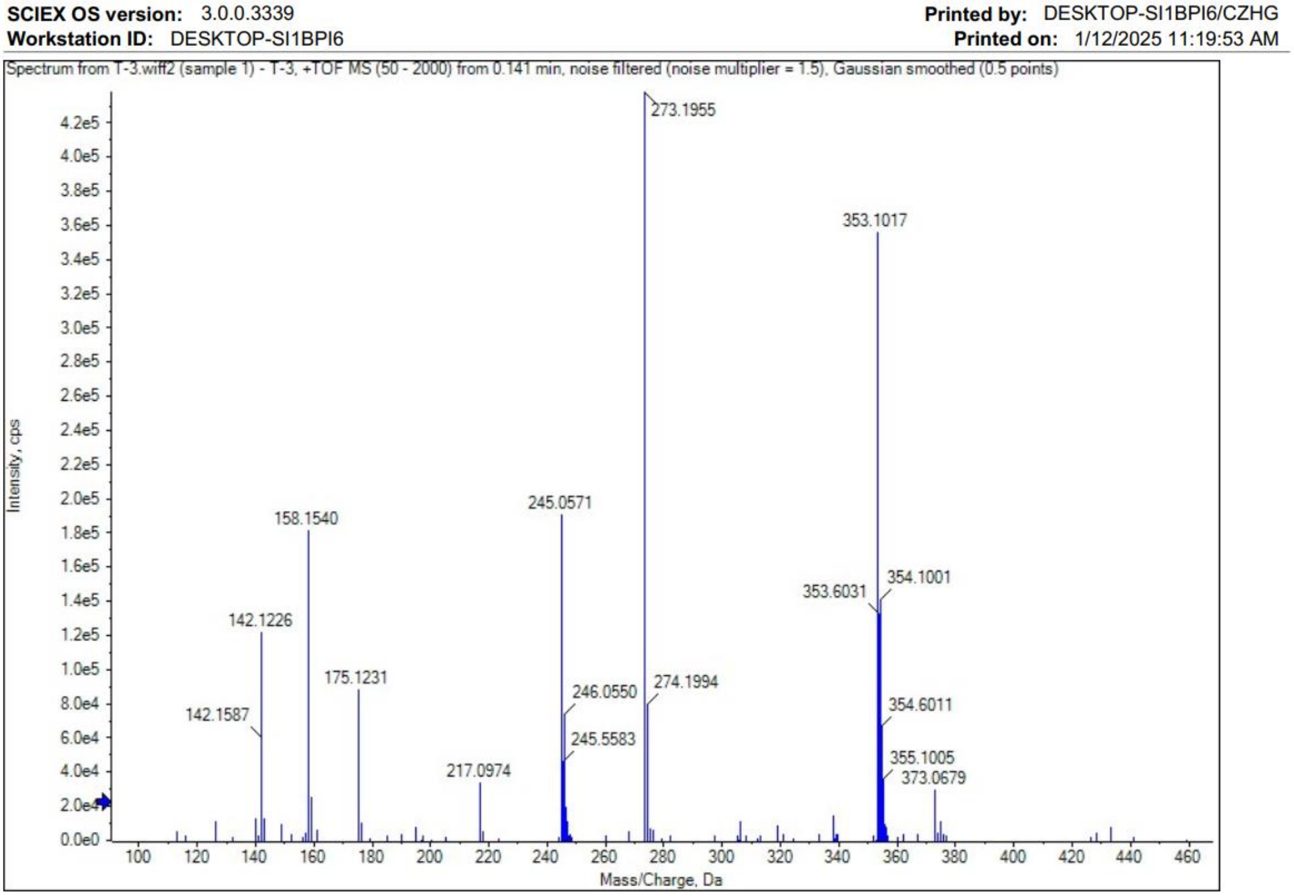
Mechanistic Studies :

(a)



1a **2a** **3a**, trace **4** Detected by ESI-MS

To a flame-dried Schlenk tube equipped with a stir bar were added benzyltrimethylammonium triflates **1a** (64.8 mg, 0.20 mmol), **2a** (99.5 mg, 0.5 mmol), FIrpic (2.1 mg, 0.003 mmol), $Ni(acac)_2$ (5.1 mg, 0.02 mmol), 4,4'-dimethoxy-2,2'-bipyridine (5.2 mg, 0.024 mmol), DABCO (33.7 mg, 0.30 mmol) and TEMPO (62.5 mg, 0.40 mmol). The tube was evacuated and refilled nitrogen three times and added MeCN (1.0 mL) via syringe. The mixture was stirred under blue light (465 nm, 10 W) irradiation for 48 h at 35 °C and subjected to ESI-MS analysis. Copied below is the spectrum we obtained. TEMPO-adduct **4**: HRMS (ESI) calcd for $C_{17}H_{25}N_2O^+$ $(M + H)^+$ 273.1962, found 273.1955.



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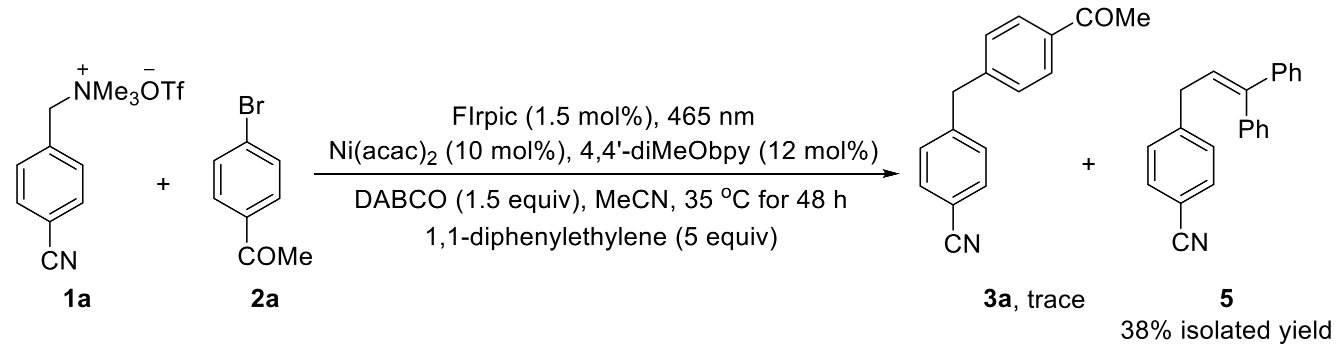
Workstation ID: DESKTOP-SI1BPI6 **Printed on:** 1/12/2025 11:19:53 AM

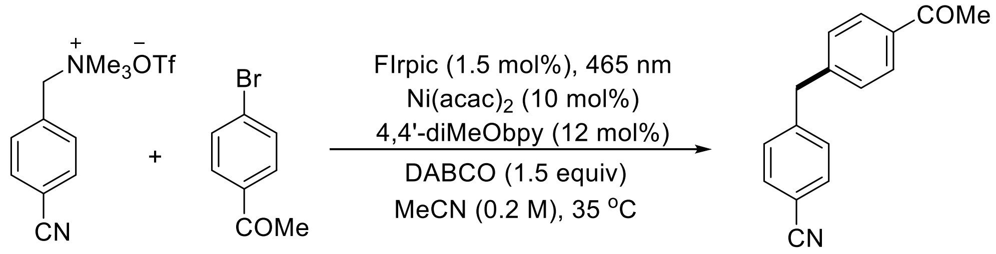
Spectrum from T-3.wiff2 (sample 1) - T-3, +TOF MS (50 - 2000) from 0.141 min, noise filtered (noise multiplier = 1.5), Gaussian smoothed (0.5 points)

(b)



To a flame-dried Schlenk tube equipped with a stir bar were added benzyltrimethylammonium triflate **1a** (64.8 mg, 0.20 mmol), **2a** (99.5 mg, 0.5 mmol), FIrpic (2.1 mg, 0.003 mmol), Ni(acac)$_2$ (5.1 mg, 0.02 mmol), 4,4'-dimethoxy-2,2'-bipyridine (5.2 mg, 0.024 mmol) and DABCO (33.7 mg, 0.30 mmol). The tube was evacuated and refilled nitrogen three times and added 1,1-diphenylethylene (176 μL, 180 mg, 1.0 mmol) and MeCN (1.0 mL) via syringe. The mixture was stirred under blue light (465 nm, 10 W) irradiation for 48 h at 35 ℃. The reaction mixture was then filtered and concentrated under reduced pressure. The crude residue was finally purified by silica gel chromatography, using a mixture of ethyl acetate and petroleum ether (1:9 to 1:5) as the eluent, to give product **5** (22.4 mg, 38% yield).

The on/off-light Experiment :



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

To a flame-dried Schlenk tube equipped with a stir bar were added benzyltrimethylammonium triflate **1a** (64.8 mg, 0.20 mmol), **2a** (99.5 mg, 0.5 mmol), FIrpic (2.1 mg, 0.003 mmol), $Ni(acac)_2$ (5.1 mg, 0.02 mmol), 4,4'-dimethoxy-2,2'-bipyridine (5.2 mg, 0.024 mmol) and DABCO (33.7 mg, 0.30 mmol). The tube was evacuated and refilled nitrogen three times and added MeCN (1.0 mL) via syringe. The tube was then sealed and the mixture was stirred for 18 h at 35 °C was conducted for light-dark experiment.

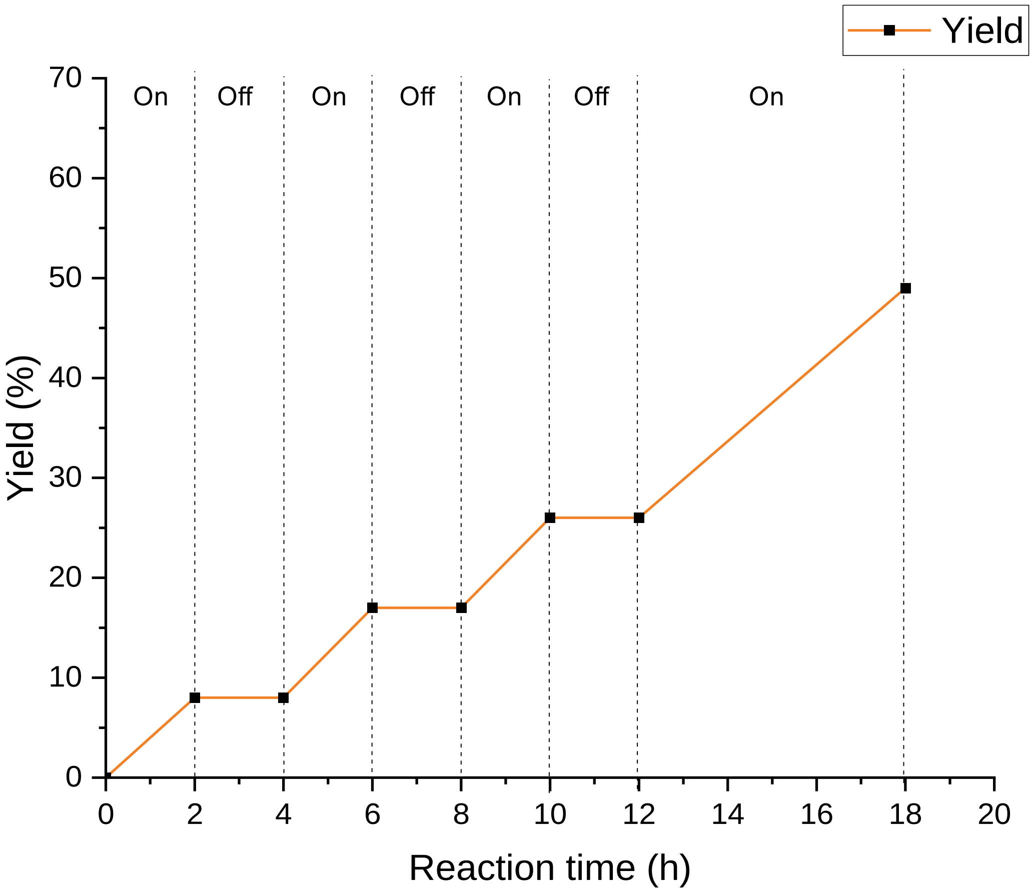
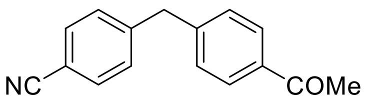


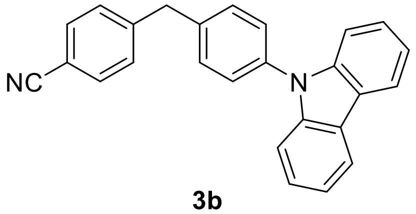
Figure S1. The on/off-light experiment.

Analytical Data for the Products (Scheme 2-3)



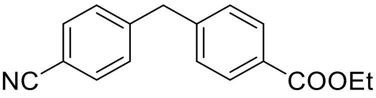
3a

4-(4-Acetylbenzyl)benzonitrile (**3a**) was obtained (33.4 mg, 71% yield) as a white solid.[2] m. p. 102-103 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.09 (s, 2H), 2.58 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 197.7, 145.7, 144.9, 135.9, 132.6, 129.8, 129.3, 129.0, 118.9, 110.6, 41.9, 26.7.



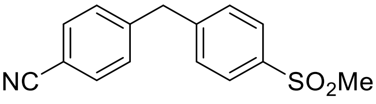
3b

4-(4-(9*H*-Carbazol-9-yl)benzyl)benzonitrile (**3b**) was obtained (30.8 mg, 43% yield) as a white solid.[2] m. p. 178-179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.42-7.38 (m, 8H), 7.31-7.28 (m, 2H), 4.16 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.3, 140.9, 138.8, 136.4, 132.6, 130.4, 129.9, 127.5, 126.0, 123.5, 120.5, 120.1, 119.1, 110.5, 109.8, 41.8.



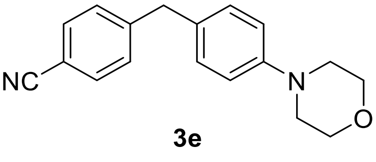
3c

Ethyl 4-(4-cyanobenzyl)benzoate (**3c**) was obtained (37.1 mg, 70% yield) as a colorless oil.[3] m. p. 79-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 4.07 (s, 2H), 1.37 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.4, 145.8, 144.5, 132.5, 130.1, 129.7, 129.1, 129.0, 118.9, 110.4, 61.1, 41.9, 14.4.



3d

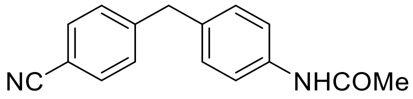
4-(4-(Methylsulfonyl)benzyl)benzonitrile (**3d**) was obtained (42.8 mg, 79% yield) as a white solid. m. p. 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 4.12 (s, 2H), 3.04 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.9, 145.0, 139.1, 132.7, 130.0, 129.8, 128.0, 118.8, 110.8, 44.6, 41.8. HRMS (ESI) calcd for $C_{15}H_{14}NO_2S^+$ $(M + H)^+$ 272.0740, found 272.0744.



3e

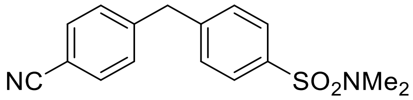
4-(4-Morpholinobenzyl)benzonitrile (**3e**) was obtained (22.8 mg, 41% yield) as a white solid.[4] m.

p. 105-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.90-6.89 (m, 2H), 3.96 (s, 2H), 3.87 (m, 4H), 3.16-3.13 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.4, 132.3, 129.8, 129.4, 119.1, 116.1, 110.0, 67.0, 49.5, 41.2.



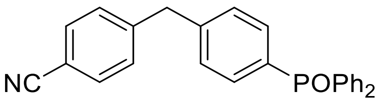
3f

N-(4-(4-Cyanobenzyl)phenyl)acetamide (**3f**) was obtained (25.0 mg, 50% yield) as a white solid.[5] m. p. 138-139 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.31 (br, 1H), 7.26 (d, J = 8.2 Hz,, 2H), 7.10 (d, J = 8.2 Hz, 2H), 3.98 (s, 2H), 2.16 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.5, 146.9, 136.6, 135.4, 132.4, 129.7, 129.6, 120.4, 119.1, 110.1, 41.5, 24.7.



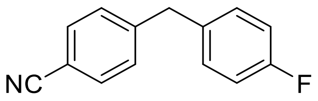
3g

4-(4-Cyanobenzyl)-*N*,*N*-dimethylbenzenesulfonamide (**3g**) was obtained (39.0 mg, 65% yield) as a white solid. m. p. 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 4.10 (s, 2H), 2.69 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.2, 144.7, 134.0, 132.6, 129.8, 129.6, 128.3, 118.8, 110.7, 41.7, 38.0. HRMS (ESI) calcd for $C_{16}H_{17}N_2O_2S^+$ $(M + H)^+$ 301.1005, found 301.1010.



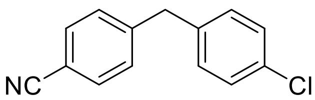
3h

4-(4-(Diphenylphosphoryl)benzyl)benzonitrile (**3h**) was obtained (39.3 mg, 52% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.53 (m, 10H), 7.47-7.44 (m, 4H), 7.28-7.24 (m, 4H), 4.07 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.5, 143.6, 132.9, 132.7, 132.6, 132.5, 132.1, 132.1, 132.05, 132.01, 131.9, 131.4, 130.4, 129.8, 129.2, 129.1, 128.6, 128.5, 118.9, 110.4, 41.9. HRMS (ESI) calcd for $C_{26}H_{19}NOP^-$ $(M - H)^-$ 392.1210, found 392.1201.



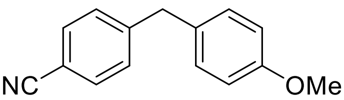
3i

4-(4-Fluorobenzyl)benzonitrile (**3i**) was obtained (19.0 mg, 45% yield) as a white solid.[2] m. p. 49-50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.12 (dd, J = 8.4, 5.5 Hz, 2H), 7.03-6.97 (m, 2H), 4.01 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J_{C-F} = 245.1 Hz), 146.6, 135.1 (d, J_{C-F} = 3.3 Hz), 132.5, 130.5 (d, J_{C-F} = 8.0 Hz), 129.6, 119.0, 115.7 (d, J_{C-F} = 21.3 Hz), 110.3, 41.2.



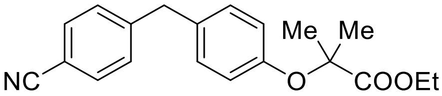
3j

4-(4-Chlorobenzyl)benzonitrile (**3j**) was obtained (23.6 mg, 52% yield) as a white solid.[2] m. p. 75-76 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, J = 8.2 Hz, 2H), 7.29-7.25 (m, 4H), 7.09 (d, J = 8.3 Hz, 2H), 4.00 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 146.2, 137.9, 132.7, 132.5, 130.4, 129.7, 129.0, 119.0, 110.4, 41.4.



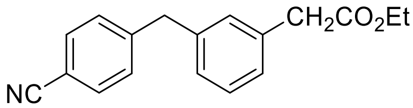
3k

4-(4-Methoxybenzyl)benzonitrile (**3k**) was obtained (21.9 mg, 48% yield) as a white solid.[2] m. p. 36-37 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.97 (s, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 158.5, 147.4, 132.4, 131.5, 130.1, 129.6, 119.2, 114.3, 110.0, 55.4, 41.2.



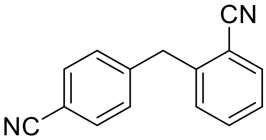
3l

Ethyl 2-(4-(4-cyanobenzyl)phenoxy)-2-methylpropanoate (**3l**) was obtained (26.5 mg, 41% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.86 (s, 2H), 1.48 (s, 6H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 174.3, 154.2, 147.0, 133.0, 132.3, 129.7, 129.6, 119.5, 119.1, 110.0, 79.2, 61.5, 41.2, 25.4, 14.1. HRMS (ESI) calcd for $C_{20}H_{22}NO_3^+$ $(M + H)^+$ 324.1594, found 324.1588.



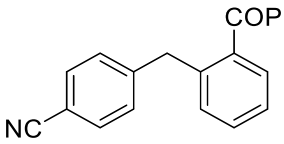
3m

Ethyl 2-(3-(4-cyanobenzyl)phenyl)acetate (**3m**) was obtained (26.8 mg, 48% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, J = 8.4 Hz, 2H), 7.29-7.25 (m, 3H), 7.16 (d, J = 7.7 Hz, 1H), 7.09-7.05 (m, 2H), 4.14 (q, J = 7.1 Hz, 2H), 4.02 (s, 2H), 3.58 (s, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 171.6, 146.7, 139.7, 134.8, 132.4, 130.0, 129.8, 129.1, 127.8, 127.7, 119.1, 110.2, 61.0, 42.0, 41.4, 14.3. HRMS (ESI) calcd for $C_{18}H_{18}NO_2^+$ $(M + H)^+$ 280.1332, found 280.1331.



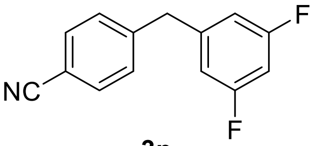
3n

2-(4-Cyanobenzyl)benzonitrile (**3n**) was obtained (27.0 mg, 62% yield) as a white solid. m. p. 70-71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.55 (t, J = 7.7 Hz, 1H), 7.38-7.33 (m, 3H), 7.29 (d, J = 7.7 Hz, 1H), 4.26 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.3, 143.1, 133.33, 133.31, 132.6, 130.2, 129.8, 127.6, 118.8, 118.0, 112.8, 110.8, 40.3. HRMS (ESI) calcd for $C_{15}H_9N_2^-$ (M - H)$^-$ 271.0771, found 271.0768.



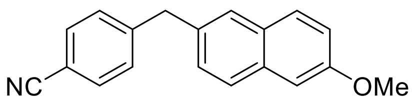
3o

4-(2-Benzoylbenzyl)benzonitrile (**3o**) was obtained (30.3 mg, 51% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.58-7.55 (m, 1H), 7.47-7.39 (m, 5H), 7.33-7.28 (m, 3H), 7.20 (d, J = 8.3 Hz, 2H), 4.14 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.3, 146.3, 138.73, 138.68, 137.5, 133.5, 132.2, 131.2, 130.8, 130.2, 130.0, 129.4, 128.5, 126.3, 119.1, 110.0, 39.2. HRMS (ESI) calcd for $C_{21}H_{16}NO^+$ (M + H)$^+$ 298.1227, found 298.1219.



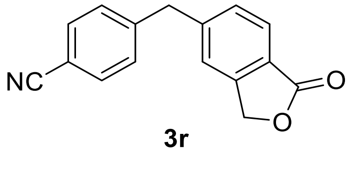
3p

4-(3,5-Difluorobenzyl)benzonitrile (**3p**) was obtained (27.9 mg, 61% yield) as a white solid. m. p. 54-55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 6.56 (d, J = 7.2 Hz, 3H), 3.89 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.42 (d, $J_{C\text{-}F}$ = 12.8 Hz), 161.95 (d, $J_{C\text{-}F}$ = 12.9 Hz), 145.0, 143.20 (t, $J_{C\text{-}F}$ = 9.0 Hz), 132.6, 129.7, 118.8, 111.9 (dd, $J_{C\text{-}F\,=}$ 18.5 Hz, 6.8 Hz), 110.7, 102.27 (t, $J_{C\text{-}F}$ = 25.3 Hz), 41.5. HRMS (ESI) calcd for $C_{14}H_8F_2N^-$ (M - H)$^-$ 228.0630, found 228.0630.



3q

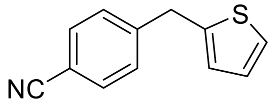
4-((6-Methoxynaphthalen-2-yl)methyl)benzonitrile (**3q**) was obtained (21.3 mg, 39% yield) as a white solid.[6] m. p. 95-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.0, 5.3 Hz, 2H), 7.58-7.54 (m, 3H), 7.32 (d, J = 7.5 Hz, 2H), 7.22 (dd, J = 8.4, 1.5 Hz, 1H), 7.16-7.14 (m, 1H), 7.12-7.11 (m, 1H), 4.15 (s, 2H), 3.92 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.7, 147.0, 134.5, 133.4, 132.4, 129.8, 129.13, 129.09, 127.9, 127.45, 127.35, 119.21, 119.15, 110.1, 105.7, 55.4, 42.0.



3r

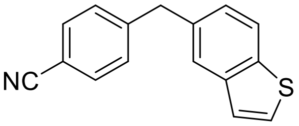
4-((1-Oxo-1,3-dihydroisobenzofuran-5-yl)methyl)benzonitrile (**3r**) was obtained (24.4 mg, 49% yield) as a white solid. m. p. 188-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 7.9 Hz, 1H), 7.30-7.26 (m, 3H), 5.28 (s, 2H), 4.17 (s, 2H). $^{13}C\{^1H\}$

NMR (126 MHz, $CDCl_3$) δ 170.8, 147.5, 146.5, 145.1, 132.7, 130.2, 129.9, 126.3, 124.5, 122.5, 118.8, 110.9, 69.6, 42.2. HRMS (ESI) calcd for $C_{16}H_{10}NO_2^-$ $(M - H)^-$ 248.0717, found 248.0713.



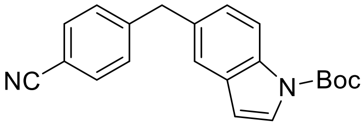
3s

4-(Thiophen-2-ylmethyl)benzonitrile (**3s**) was obtained (17.1 mg, 43% yield) as a colorless oil.[5] ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.19 (dd, J = 5.1, 1.0 Hz, 1H), 6.95 (dd, J = 5.1, 3.5 Hz, 1H), 6.82 (d, J = 3.4 Hz, 1H), 4.21 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.0, 141.8, 132.5, 129.4, 127.2, 126.0, 124.8, 119.0, 110.6, 36.1.



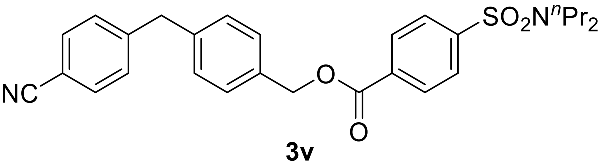
3t

4-(Benzo[*b*]thiophen-5-ylmethyl)benzonitrile (**3t**) was obtained (29.9 mg, 60% yield) as a white solid.[7] m. p. 98-99 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.62-7.56 (m, 3H), 7.44 (d, J = 8.4 Hz, 1H), 7.38 (s, 1H), 7.29 (d, J = 7.7 Hz, 2H), 7.08 (d, J = 8.3 Hz, 1H), 6.72 (s, 1H), 4.11 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.0, 147.4, 145.6, 134.0, 132.4, 129.7, 128.0, 125.4, 121.4, 119.2, 111.7, 110.1, 106.5, 42.0.



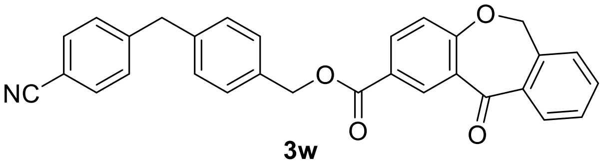
3u

Tert-butyl 5-(4-cyanobenzyl)-1*H*-indole-1-carboxylate (**3u**) was obtained (43.2 mg, 65% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.9 Hz, 1H), 7.59 (d, J = 3.5 Hz, 1H), 7.55 (d, J = 8.2 Hz, 2H), 7.33 (s, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.11 (dd, J = 8.5, 1.6 Hz, 1H), 6.51 (d, J = 3.7 Hz, 1H), 4.11 (s, 2H), 1.67 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.8, 147.5, 134.1, 133.8, 132.3, 131.1, 129.7, 126.5, 125.4, 121.2, 119.2, 115.5, 109.9, 107.1, 83.9, 41.9, 28.3. HRMS (ESI) calcd for $C_{21}H_{21}N_2O_2^+$ $(M + H)^+$ 333.1598, found 333.1599.



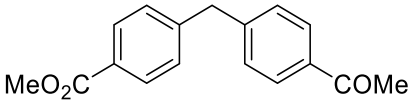
3v

4-(4-Cyanobenzyl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**3v**) was obtained (58.8 mg, 60% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 5.35 (s, 2H), 4.03 (s, 2H), 3.10-3.06 (m, 4H), 1.57-1.48 (m, 4H), 0.85 (t, J = 7.4 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.1, 146.4, 144.3, 139.8, 133.9, 133.4, 132.4, 130.3, 129.7, 129.3, 128.9, 127.0, 119.0, 110.1, 67.0, 49.9, 41.7, 21.9, 11.2. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_4S^+$ $(M + H)^+$ 491.1999, found 491.1990.



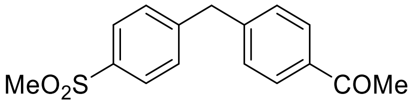
3w

4-(4-Cyanobenzyl)benzyl 11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepine-2-carboxylate (**3w**) was obtained (44.1 mg, 48% yield) as a yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 8.12 (d, *J* = 2.3 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.57-7.55 (m, 3H), 7.48-7.45 (m, 1H), 7.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.37-7.36 (m, 1H), 7.29-7.26 (m, 4H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 2H), 5.12 (s, 2H), 4.02 (s, 2H), 3.68 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) *δ* 190.8, 171.3, 160.6, 146.5, 140.5, 139.6, 136.4, 135.6, 134.3, 132.9, 132.6, 132.4, 129.7, 129.5, 129.3, 129.2, 128.8, 127.9, 127.7, 125.2, 121.1, 119.0, 110.2, 73.7, 66.5, 41.7, 40.3. HRMS (ESI) calcd for $C_{31}H_{24}NO_4^+$ $(M + H)^+$ 474.1700, found 474.1695.



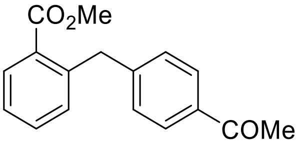
3x

Methyl 4-(4-acetylbenzyl)benzoate (**3x**) was obtained (38.1 mg, 71% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.96 (d, *J* = 8.3 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.27-7.23 (m, 4H), 4.07 (s, 2H), 3.89 (s, 3H), 2.57 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) *δ* 197.9, 167.0, 145.8, 145.5, 135.5, 130.1, 129.2, 129.1, 128.8, 128.5, 52.2, 41.9, 26.7. HRMS (ESI) calcd for $C_{17}H_{17}O_3^+$ $(M + H)^+$ 269.1172, found 269.1168.



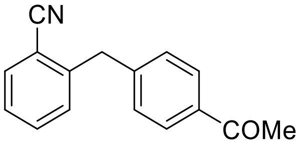
3y

1-(4-(4-(Methylsulfonyl)benzyl)phenyl)ethan-1-one (**3y**) was obtained (28.8 mg, 50% yield) as a white solid. m. p. 103-104 °C. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.91 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 4.12 (s, 2H), 3.04 (s, 3H), 2.58 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) *δ* 197.7, 146.7, 145.0, 138.9, 135.8, 129.9, 129.3, 129.0, 127.9, 44.7, 41.8, 26.7. HRMS (ESI) calcd for $C_{16}H_{17}O_3S^+$ $(M + H)^+$ 289.0893, found 289.0892.



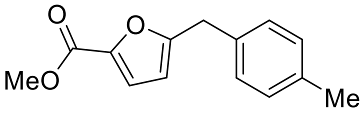
3z

Methyl 2-(4-acetylbenzyl)benzoate (**3z**) was obtained (31.1 mg, 58% yield) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.94 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (td, *J* = 7.8, 1.5 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 3H), 4.44 (s, 2H), 3.81 (s, 3H), 2.56 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.0, 167.9, 146.9, 141.3, 135.2, 132.4, 131.9, 131.1, 129.9, 129.0, 128.6, 126.8, 52.1, 39.9, 26.7. HRMS (ESI) calcd for $C_{17}H_{17}O_3^+$ $(M + H)^+$ 269.1172, found 269.1169.



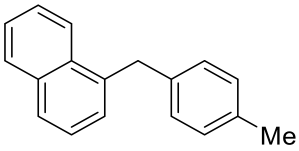
3aa

2-(4-Acetylbenzyl)benzonitrile (**3aa**) was obtained (25.9 mg, 55% yield) as a white solid. m. p. 66-67 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.65 (dd, J = 7.7, 1.2 Hz, 1H), 7.52 (td, J = 7.7, 1.4 Hz, 1H), 7.36-7.26 (m, 4H), 4.25 (s, 2H), 2.57 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.8, 144.3, 143.9, 135.8, 133.2, 130.2, 129.3, 128.9, 127.3, 118.1, 112.8, 40.2, 26.7. HRMS (ESI) calcd for $C_{16}H_{14}NO^+$ $(M + H)^+$ 236.1070, found 236.1069.



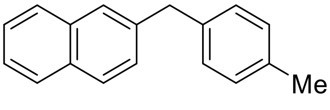
3ab

Methyl 5-(4-methylbenzyl)furan-2-carboxylate (**3ab**) was obtained (20.7 mg, 45% yield) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.15-7.11 (m, 4H), 7.09 (d, J = 3.4 Hz, 1H), 6.05 (d, J = 3.4 Hz, 1H), 4.00 (s, 2H), 3.87 (s, 3H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 160.1, 159.3, 143.4, 136.6, 133.7, 129.5, 128.8, 119.4, 108.8, 51.9, 34.5, 21.1. HRMS (ESI) calcd for $C_{14}H_{15}O_3^+$ $(M + H)^+$ 231.1016, found 231.1012.



3ac

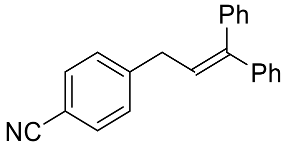
1-(4-Methylbenzyl)naphthalene (**3ac**) was obtained (25.5 mg, 55% yield) as a colorless oil.[8] ^1H NMR (500 MHz, $CDCl_3$) δ 8.03-8.01 (m, 1H), 7.88-7.86 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.48-7.41 (m, 3H), 7.30 (d, J = 7.0 Hz, 1H), 7.12-7.08 (m, 4H), 4.43 (s, 2H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.7, 137.0, 135.6, 134.0, 132.3, 129.3, 128.8, 128.7, 127.4, 127.2, 126.1, 125.68, 125.65, 124.4, 38.8, 21.2.



3ad

2-(4-Methylbenzyl)naphthalene (**3ad**) was obtained (18.6 mg, 40% yield) as a colorless oil.[9] ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 3H), 7.65 (s, 1H), 7.49-7.42 (m, 2H), 7.33 (dd, J = 8.4, 1.8

Hz, 1H), 7.16-7.11 (m, 4H), 4.12 (s, 2H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.0, 138.1, 135.8, 133.7, 132.2, 129.3, 129.0, 128.2, 127.8, 127.74, 127.67, 127.1, 126.1, 125.4, 41.8, 21.2.



5

4-(3,3-Diphenylallyl)benzonitrile (**5**) was obtained (22.4 mg, 38% yield) as a colorless oil.[10] ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.34-7.31 (m, 1H), 7.26 -7.19 (m, 9H), 6.19 (t, *J* = 7.6 Hz, 1H), 3.50 (d, *J* = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) 146.6, 144.0, 141.9, 139.4, 132.3, 129.7, 129.2, 128.5, 128.2, 127.5, 127.5, 127.3, 125.5, 119.0, 109.9, 77.4, 77.2, 76.9, 36.0.

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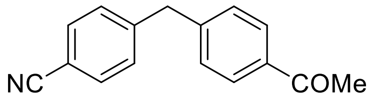
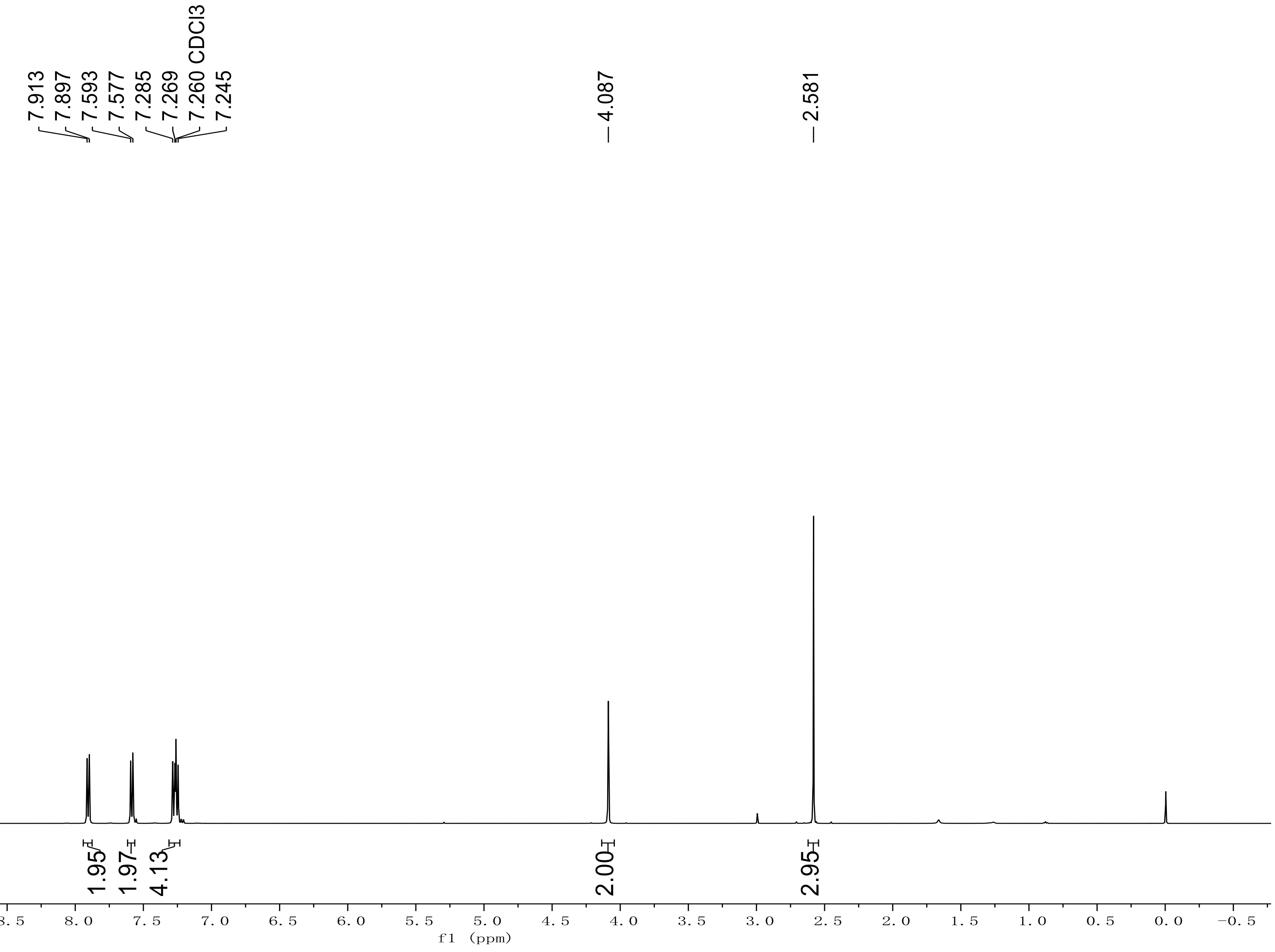
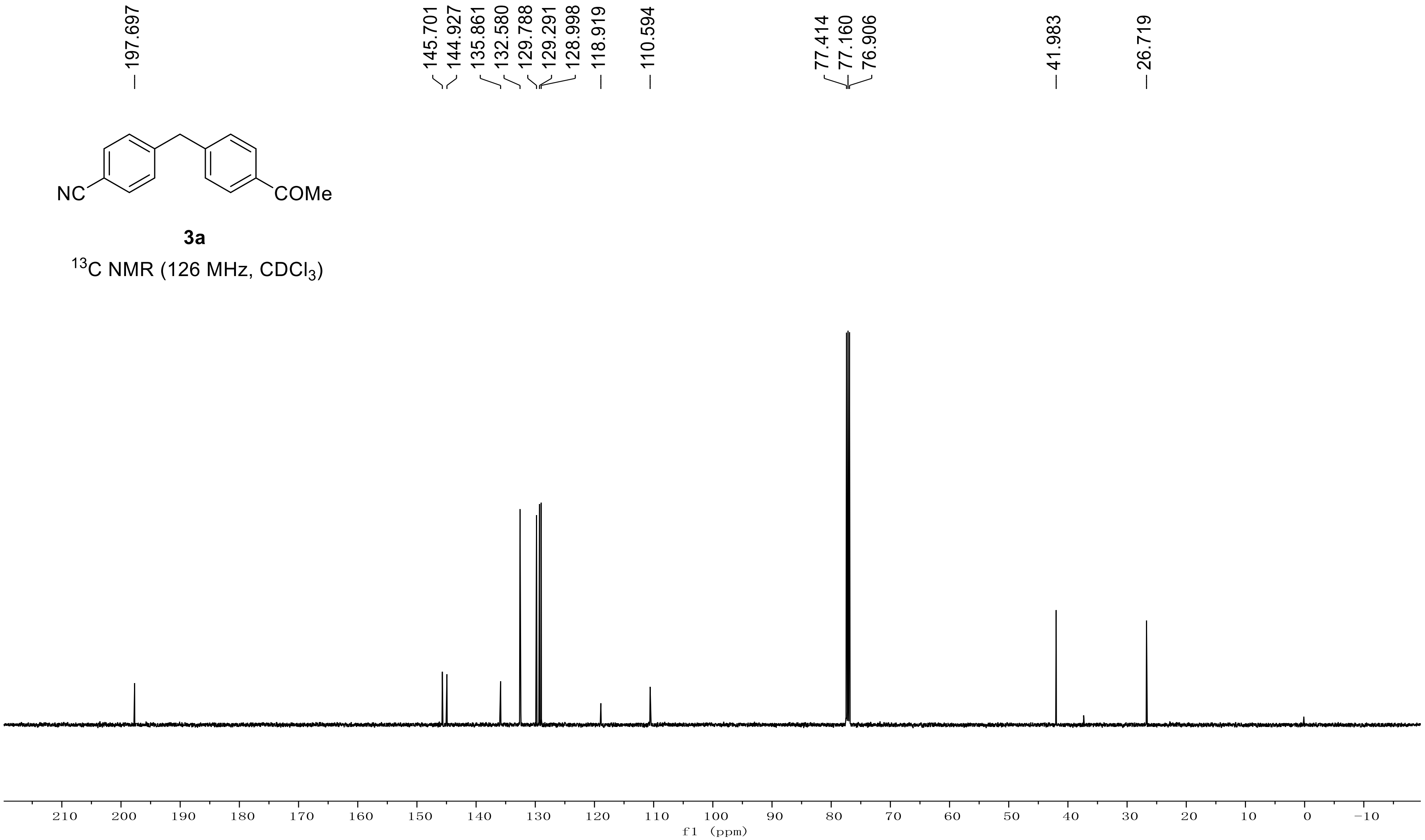
Copies of NMR Spectra



3a

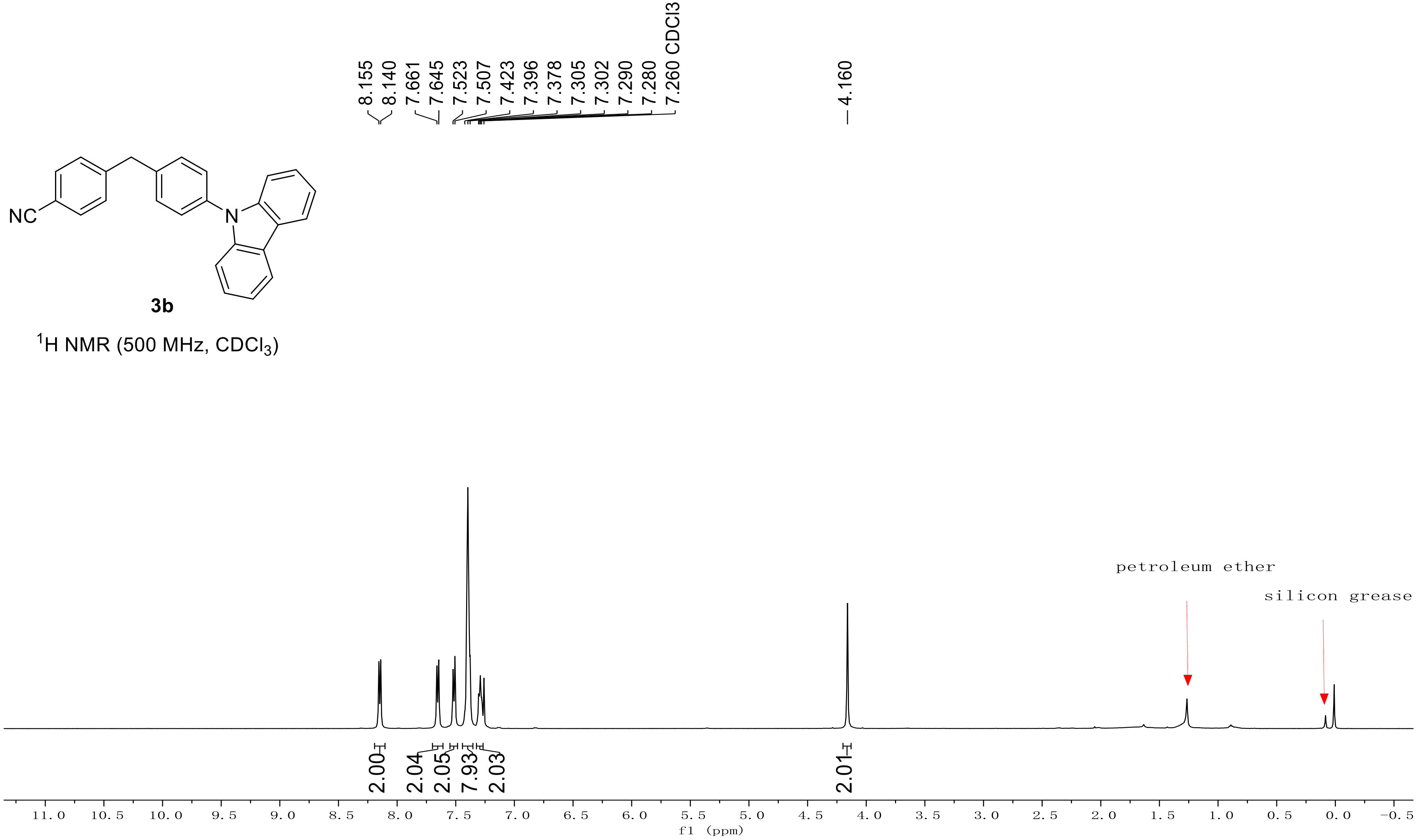
^{1}H NMR (500 MHz, $CDCl_3$)





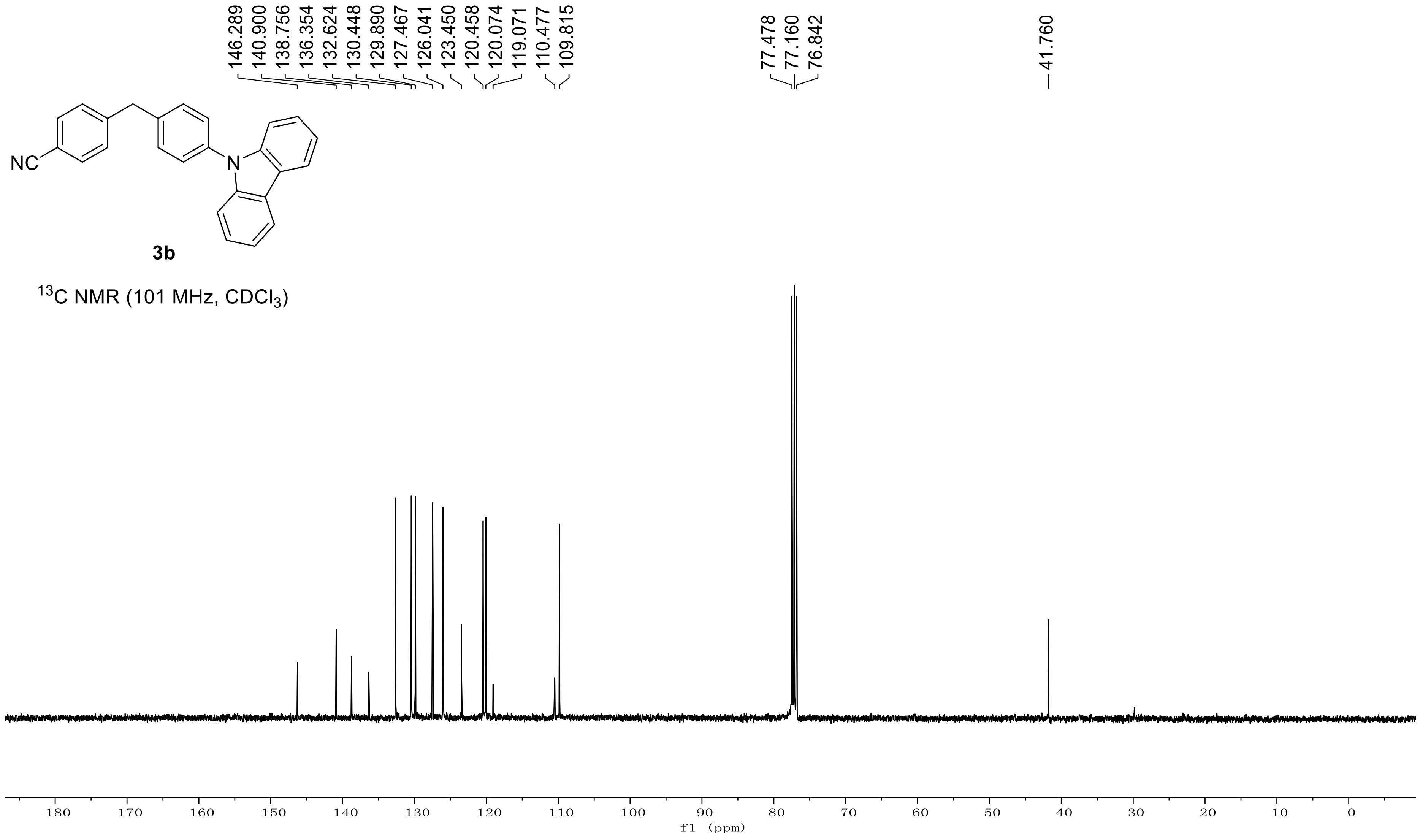
3a

^{13}C NMR (126 MHz, CDCl$_3$)



3b

^{1}H NMR (500 MHz, $CDCl_3$)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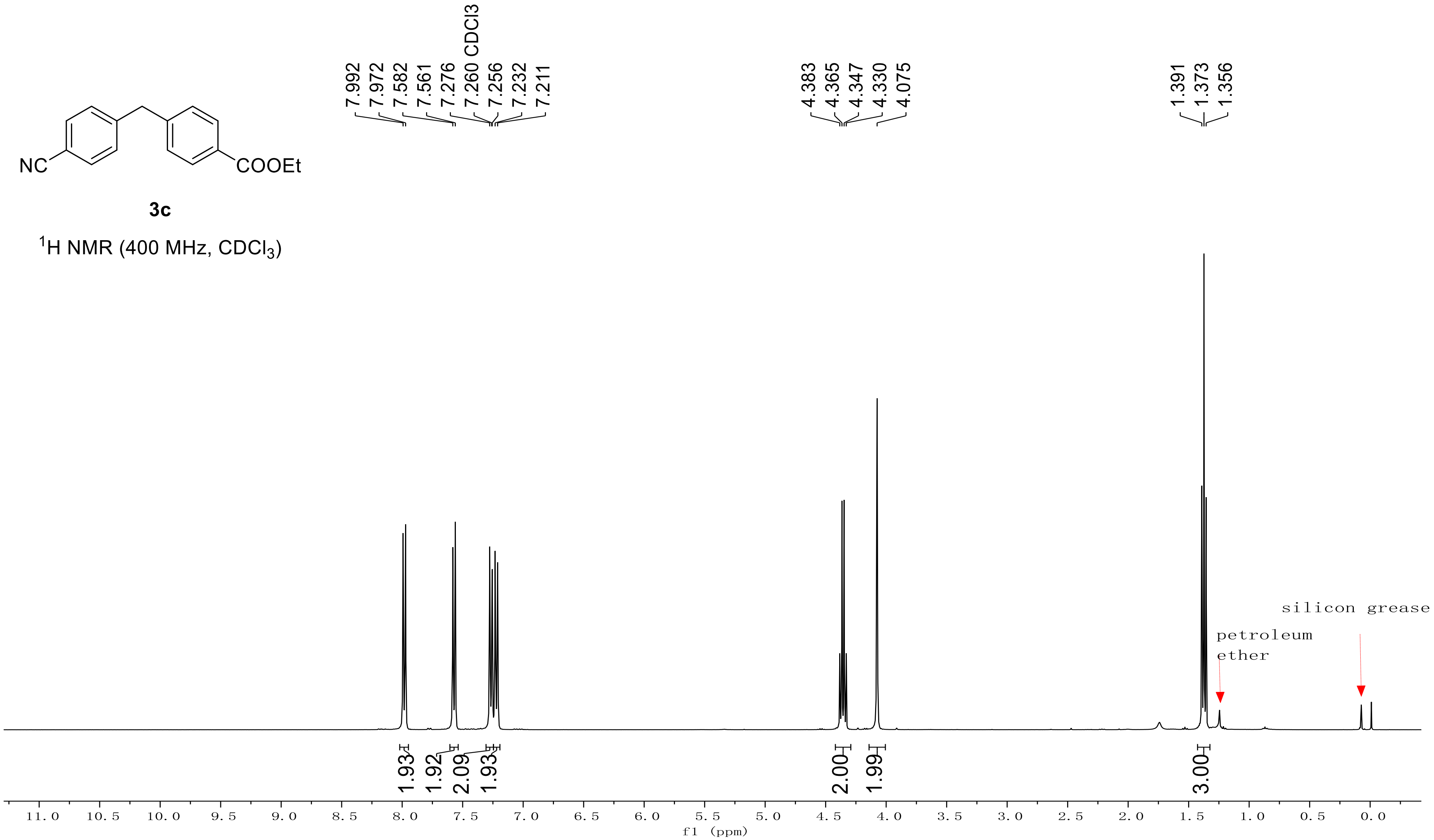
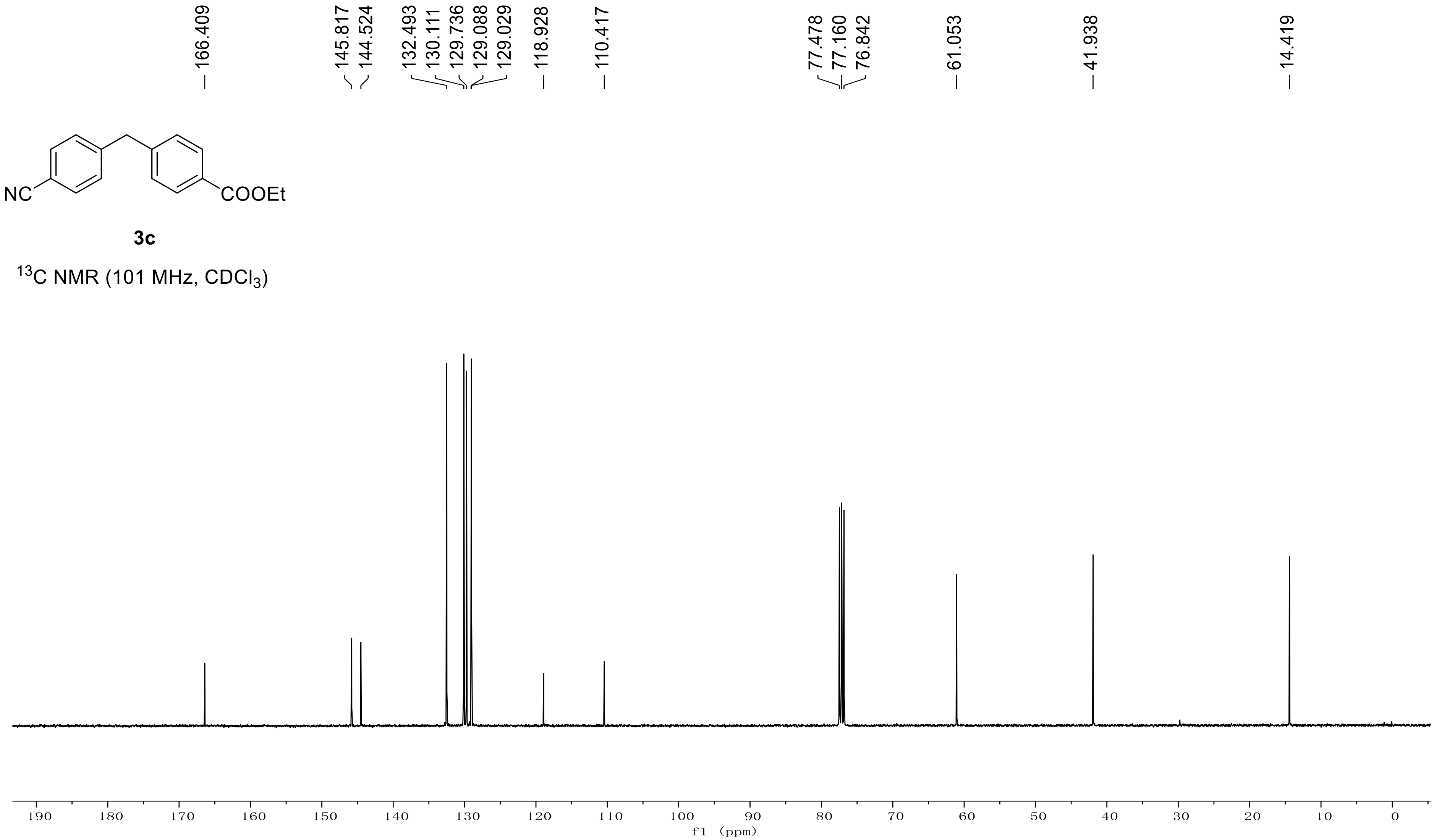
140.900
138.756
136.354
132.624
130.448
129.890
127.467
126.041
123.450
120.458
120.074
119.071
110.477
109.815
77.478
77.160
76.842
41.760
NC
N
3b
^{13}C NMR (101 MHz, CDCl$_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



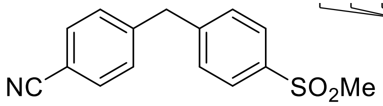
3c

^{1}H NMR (400 MHz, CDCl$_3$)



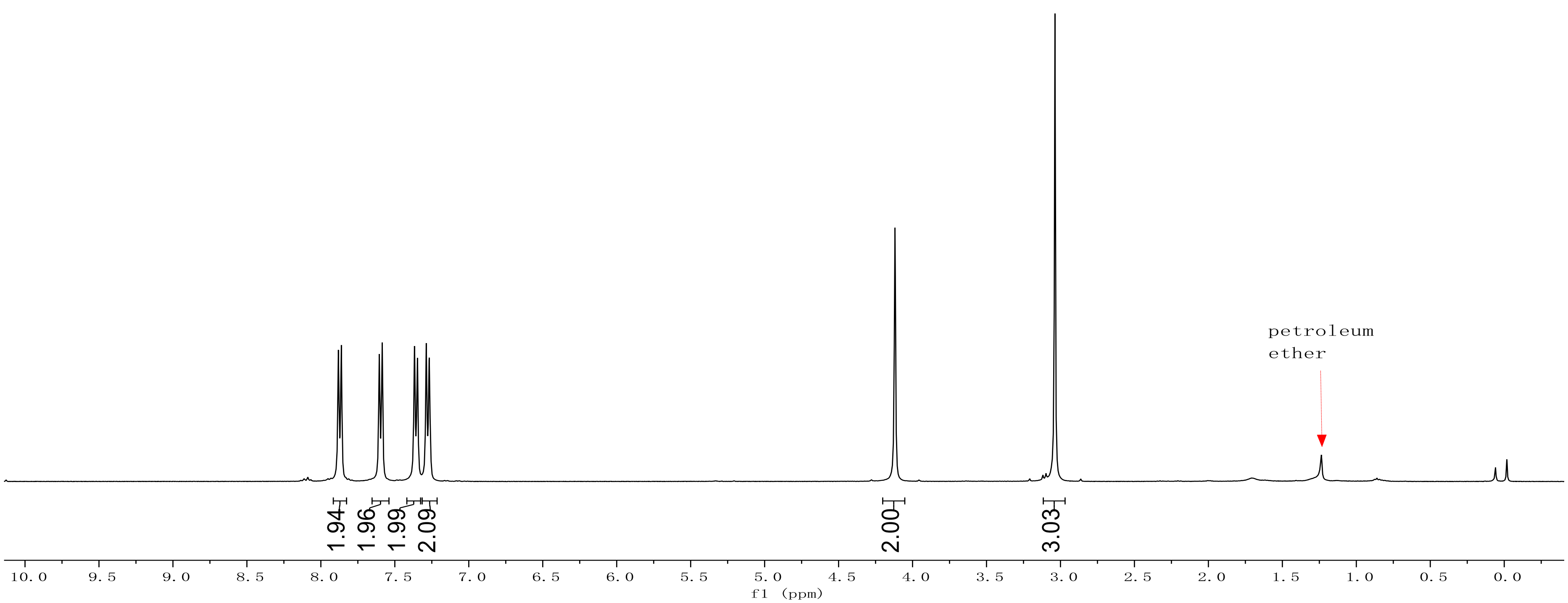
3c

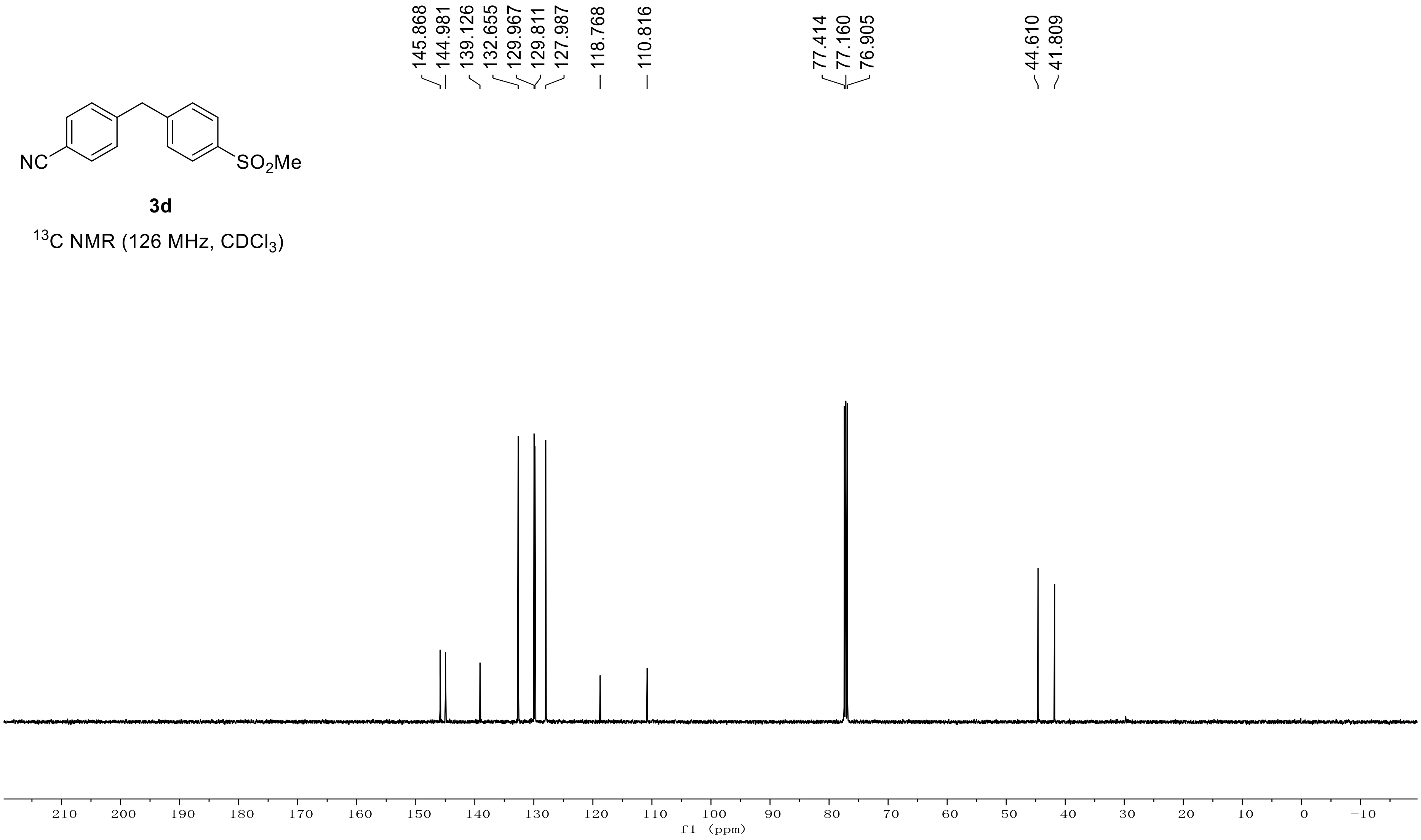
^{13}C NMR (101 MHz, CDCl$_3$)



3d

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



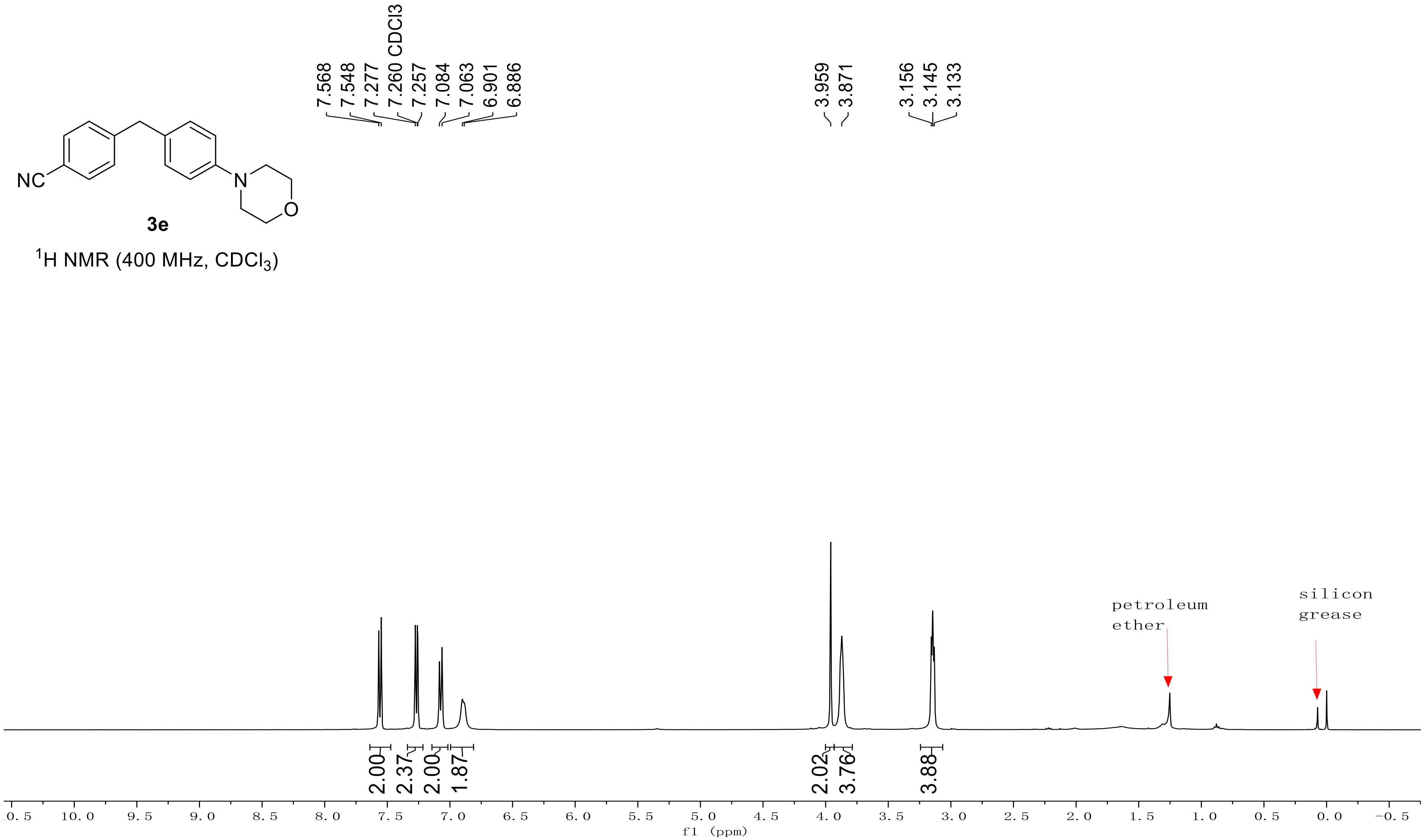


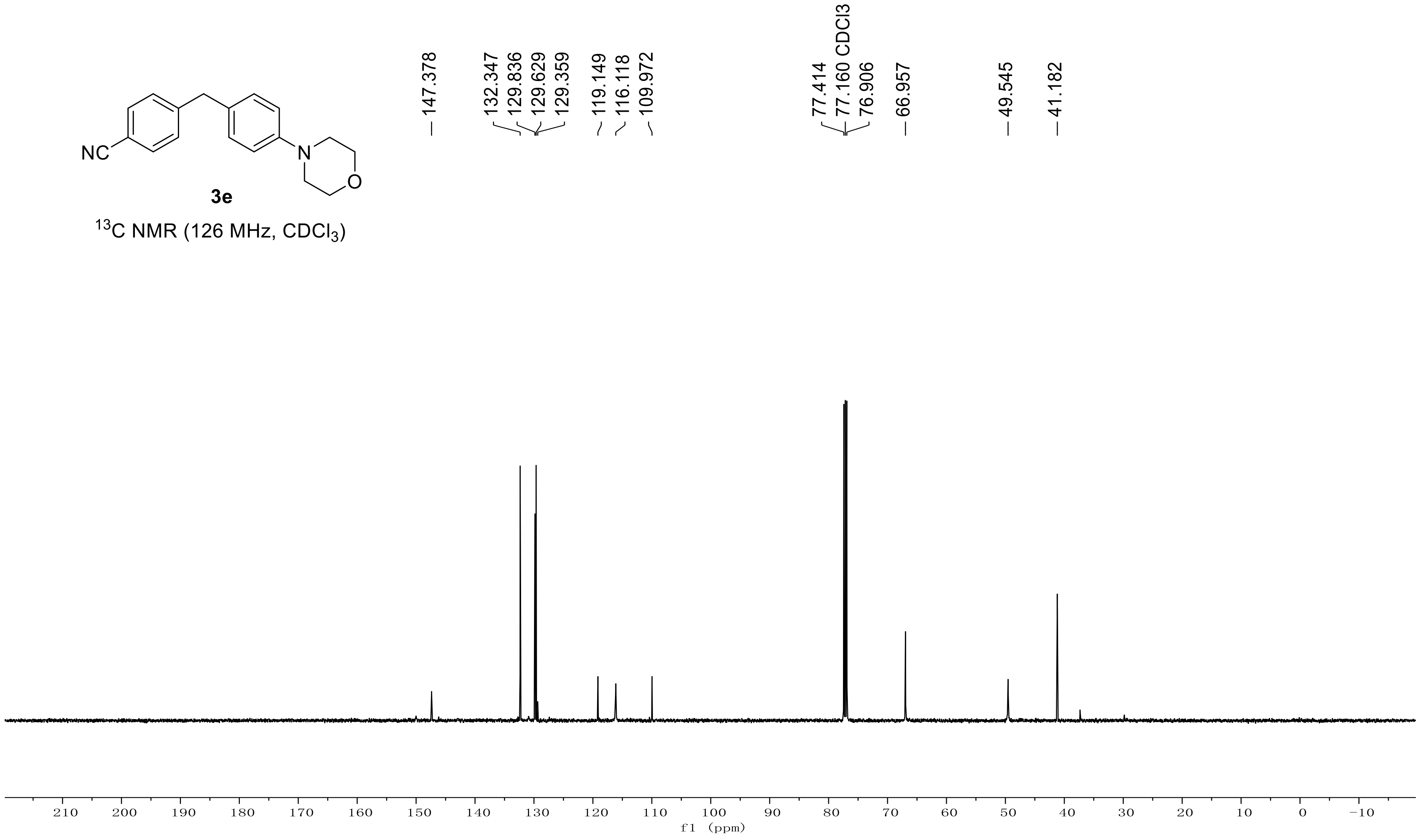
3d

^{13}C NMR (126 MHz, $CDCl_3$)

3e

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



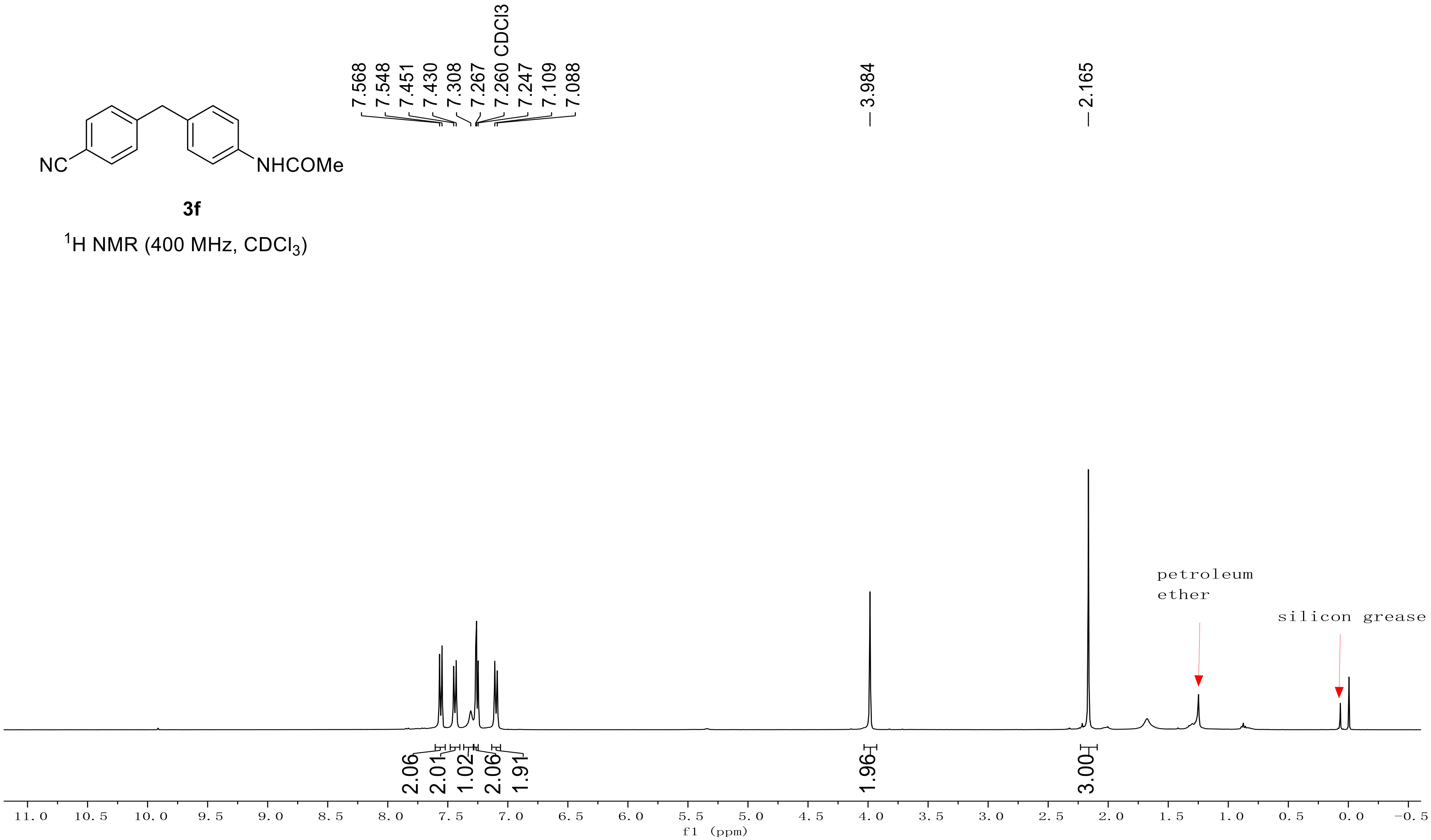


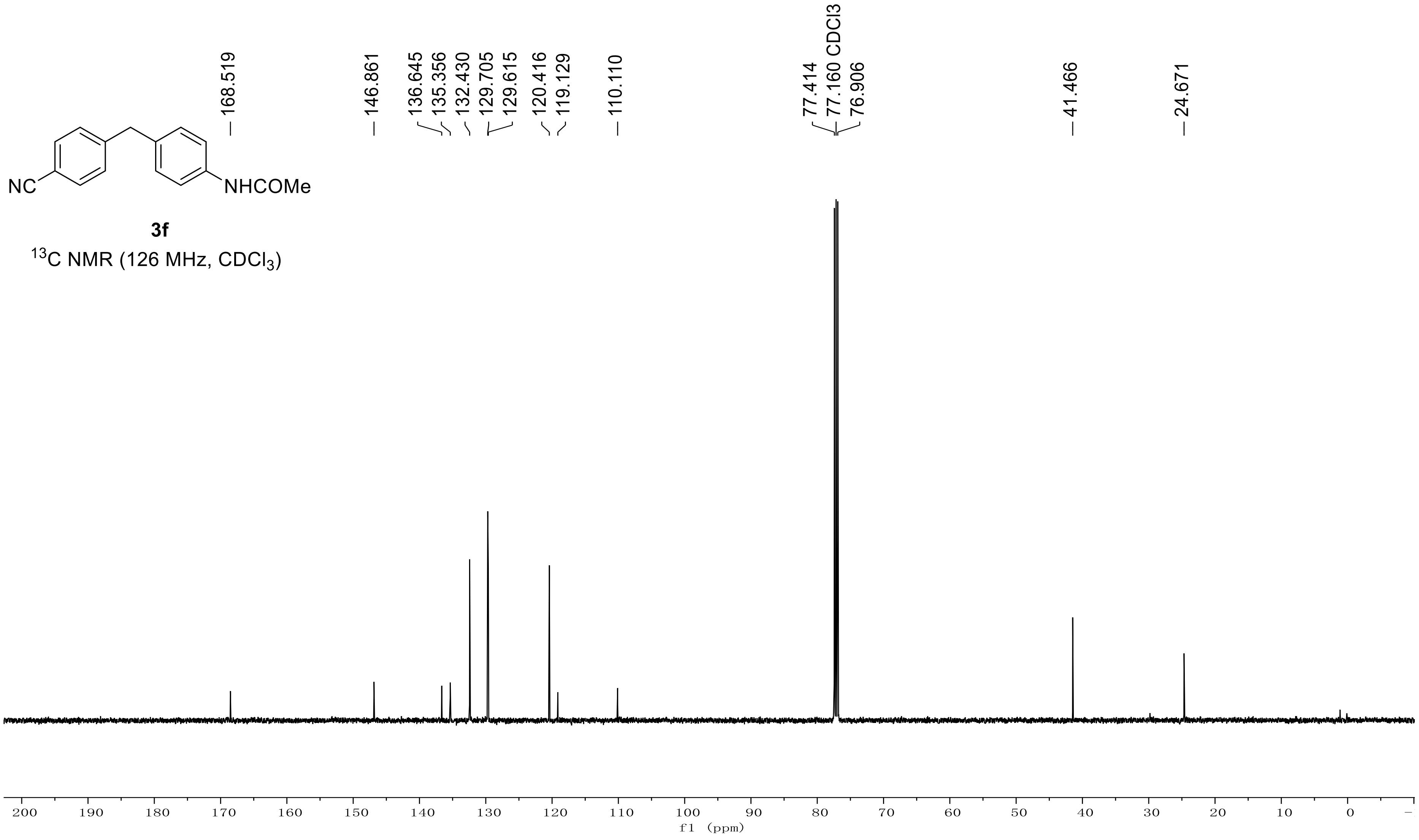
3e

^{13}C NMR (126 MHz, CDCl$_3$)

3f

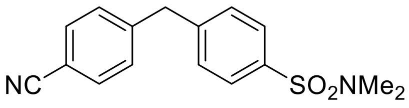
^{1}H NMR (400 MHz, $CDCl_3$)





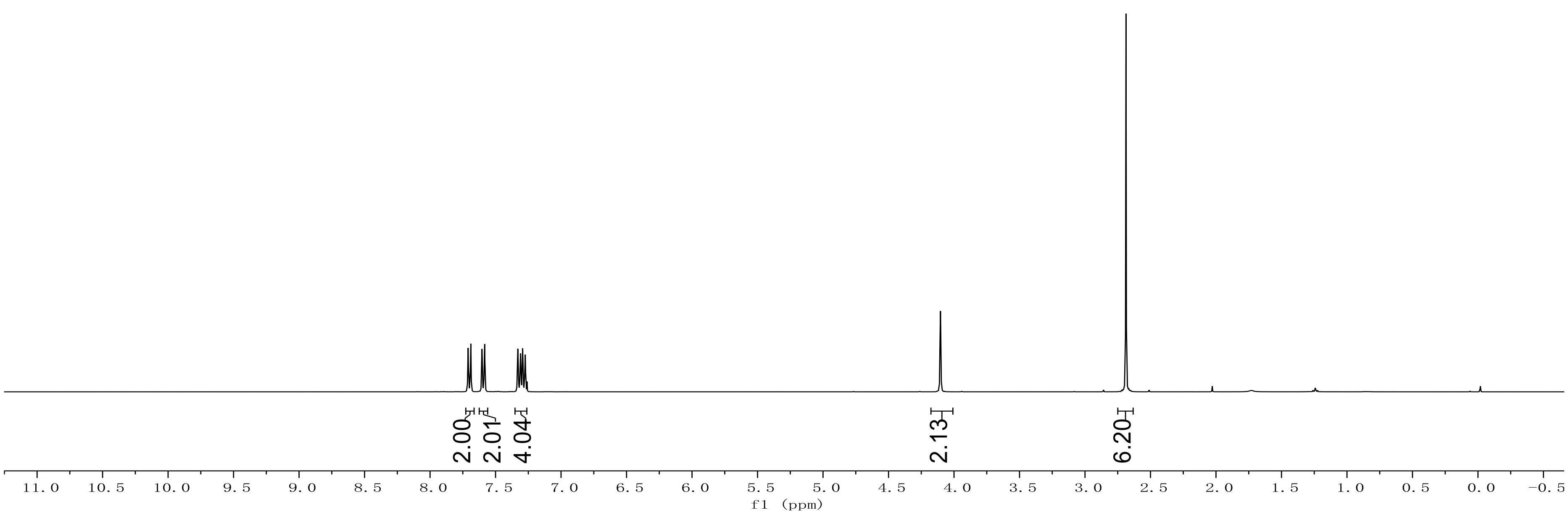
3f

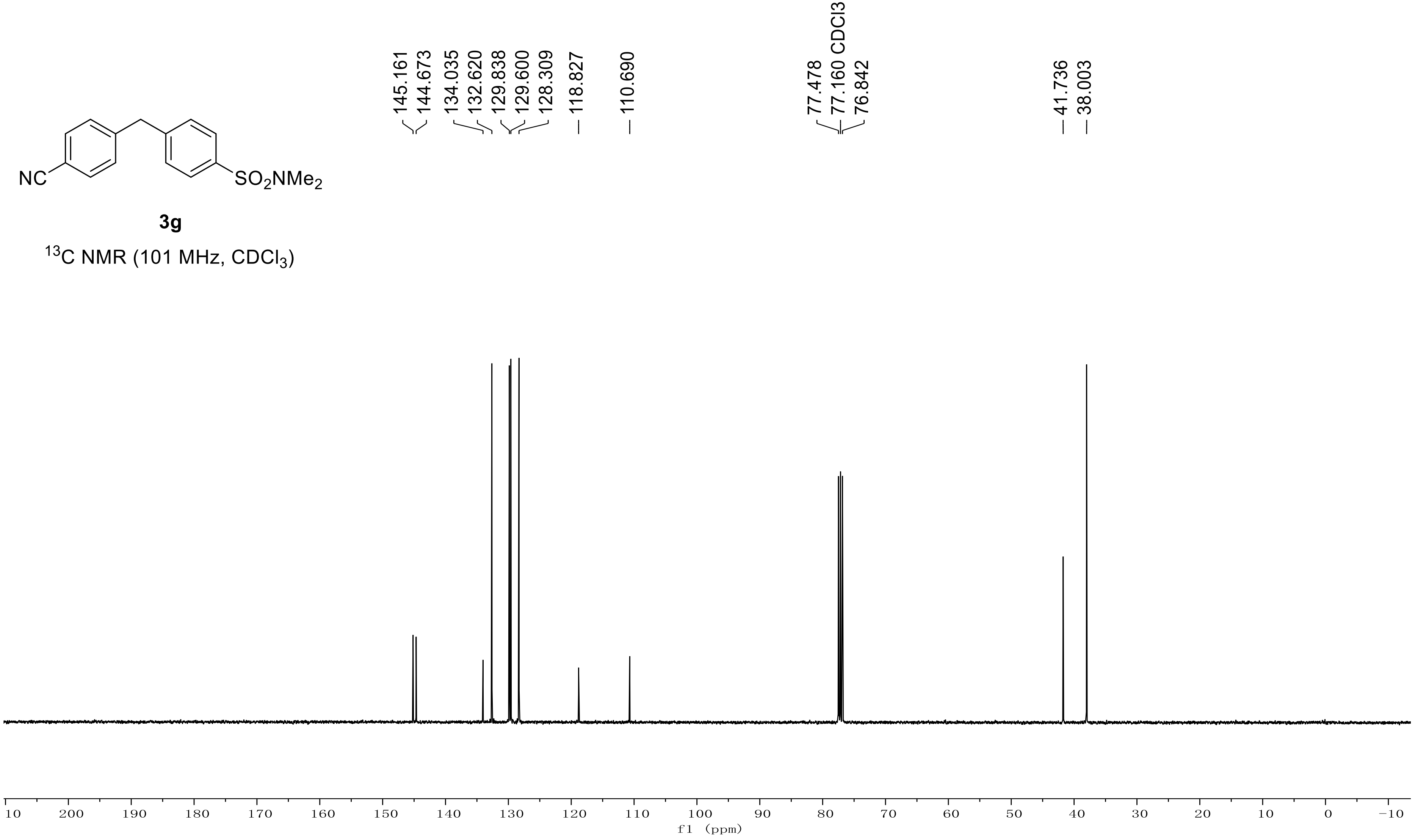
^{13}C NMR (126 MHz, $CDCl_3$)



3g

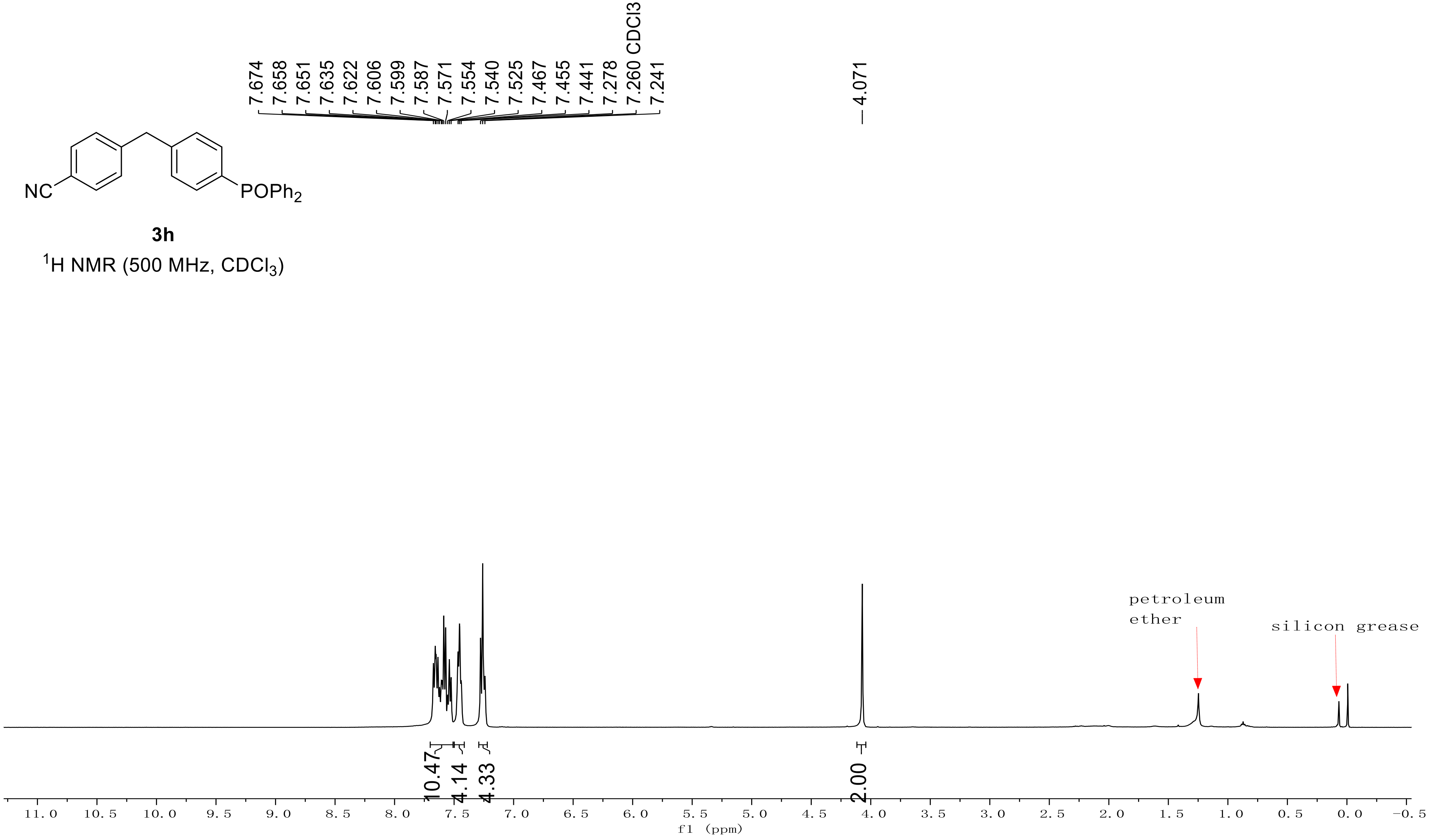
^{1}H NMR (400 MHz, $CDCl_3$)





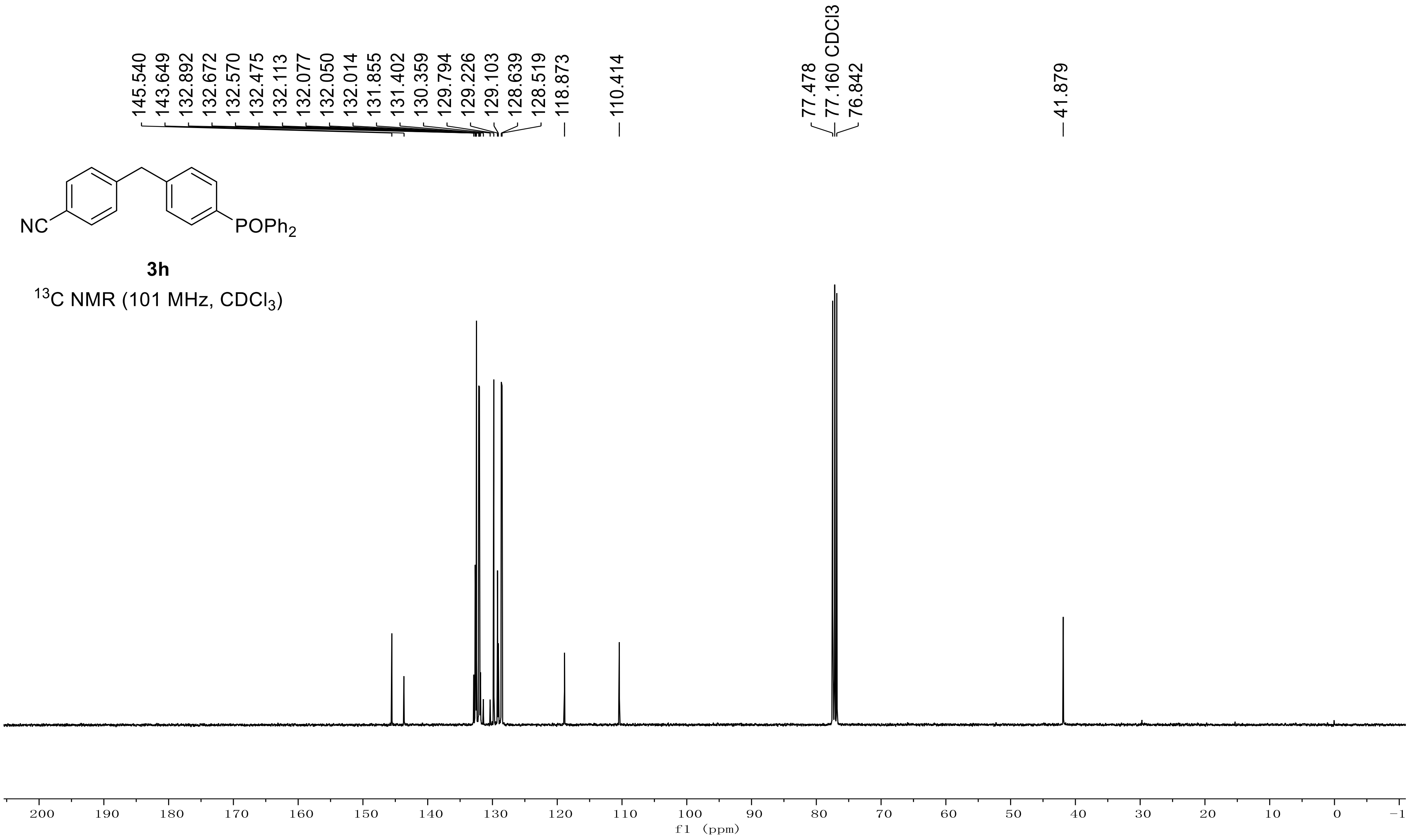
3g

^{13}C NMR (101 MHz, CDCl$_3$)



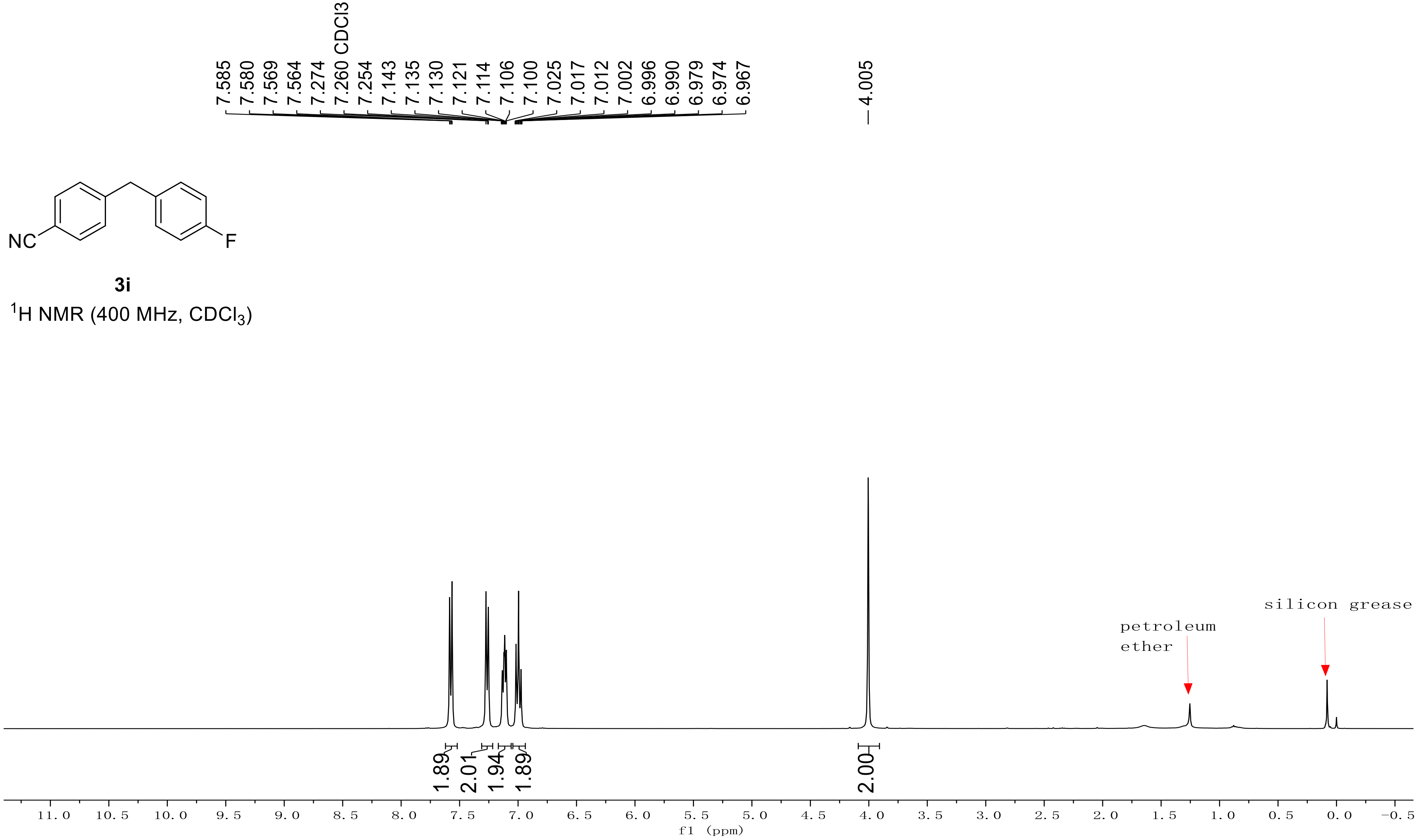
3h

^{1}H NMR (500 MHz, CDCl$_3$)



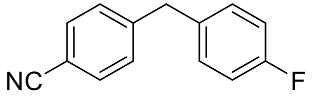
3h

^{13}C NMR (101 MHz, $CDCl_3$)



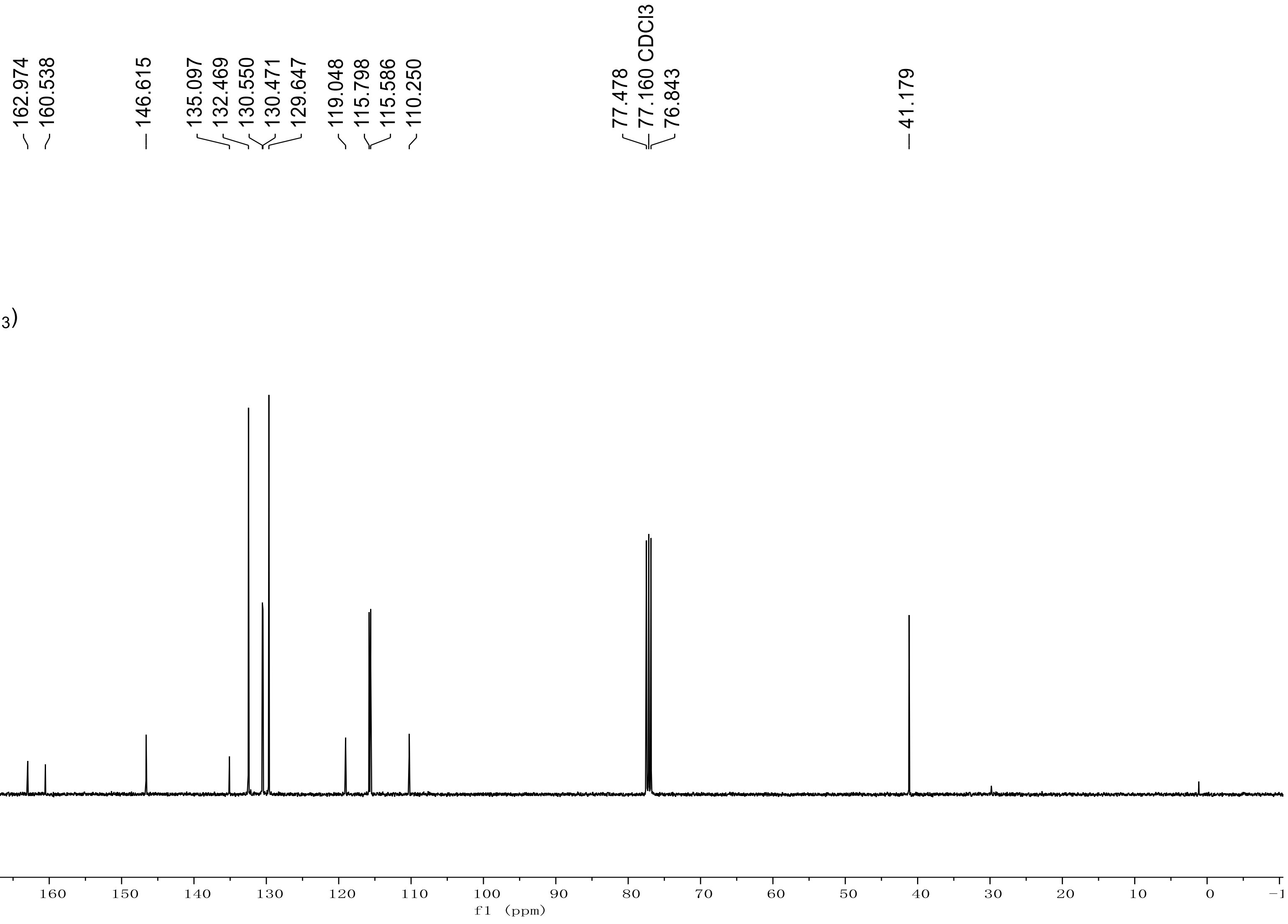
3i

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



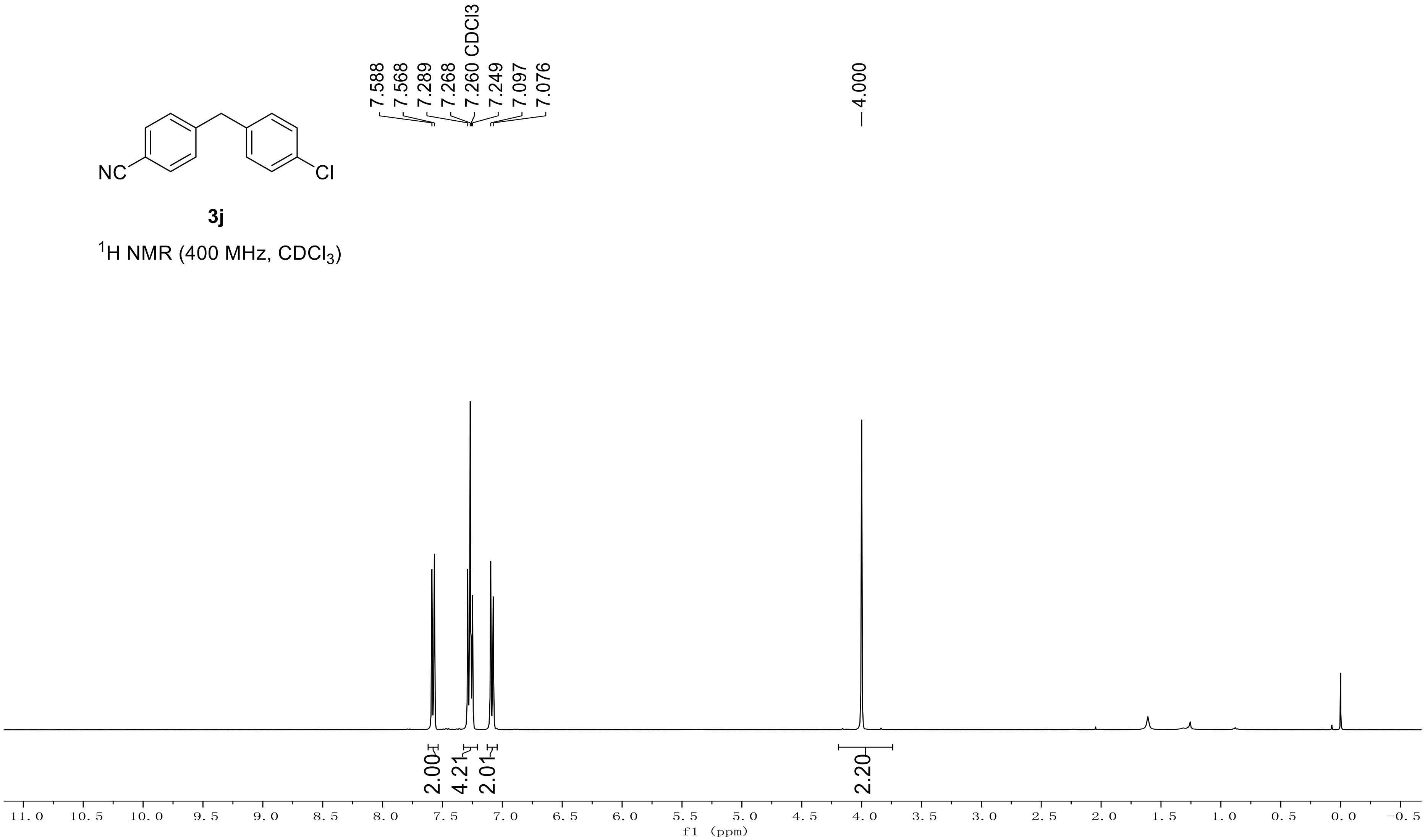
3i

^{13}C NMR (101 MHz, $CDCl_3$)



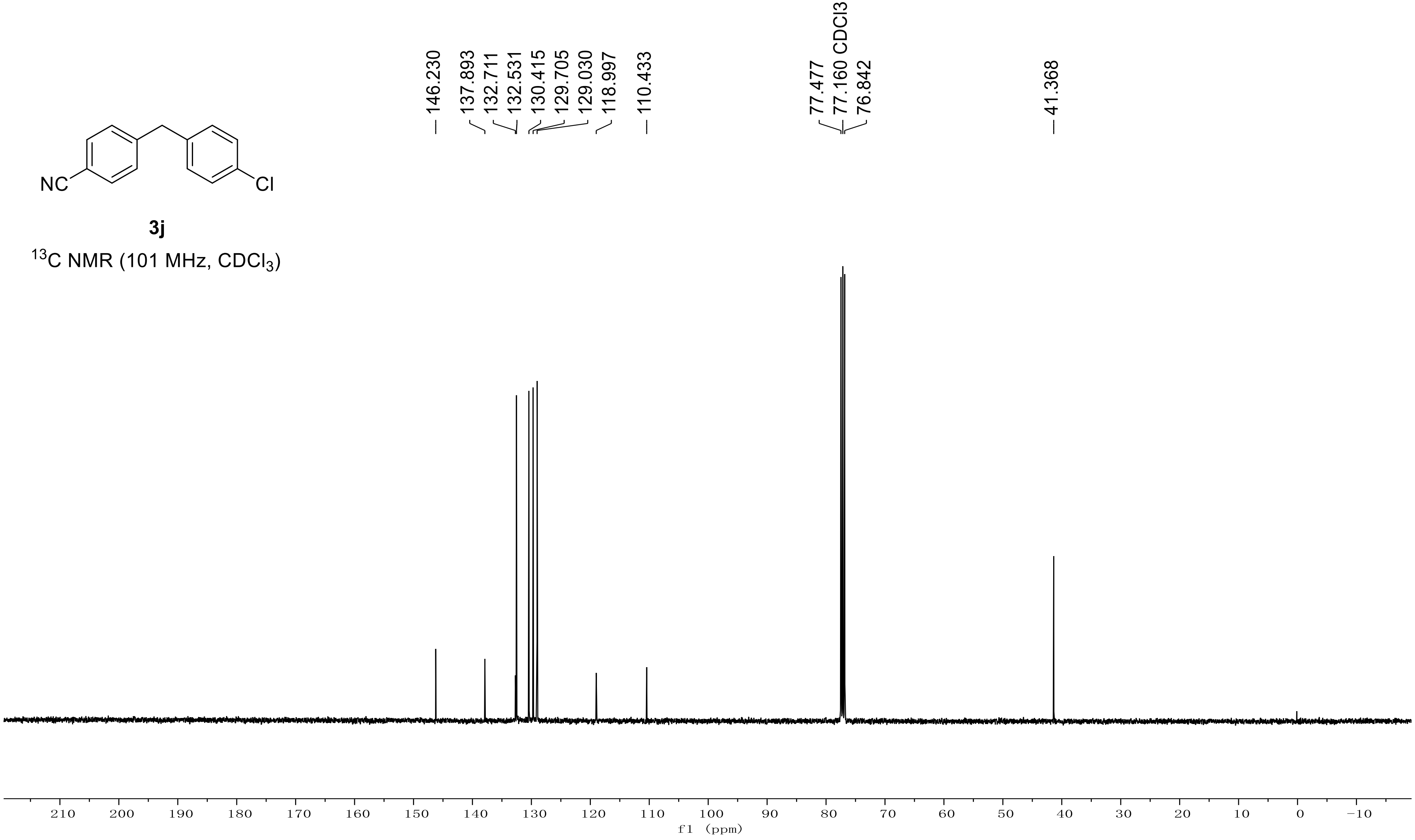
3j

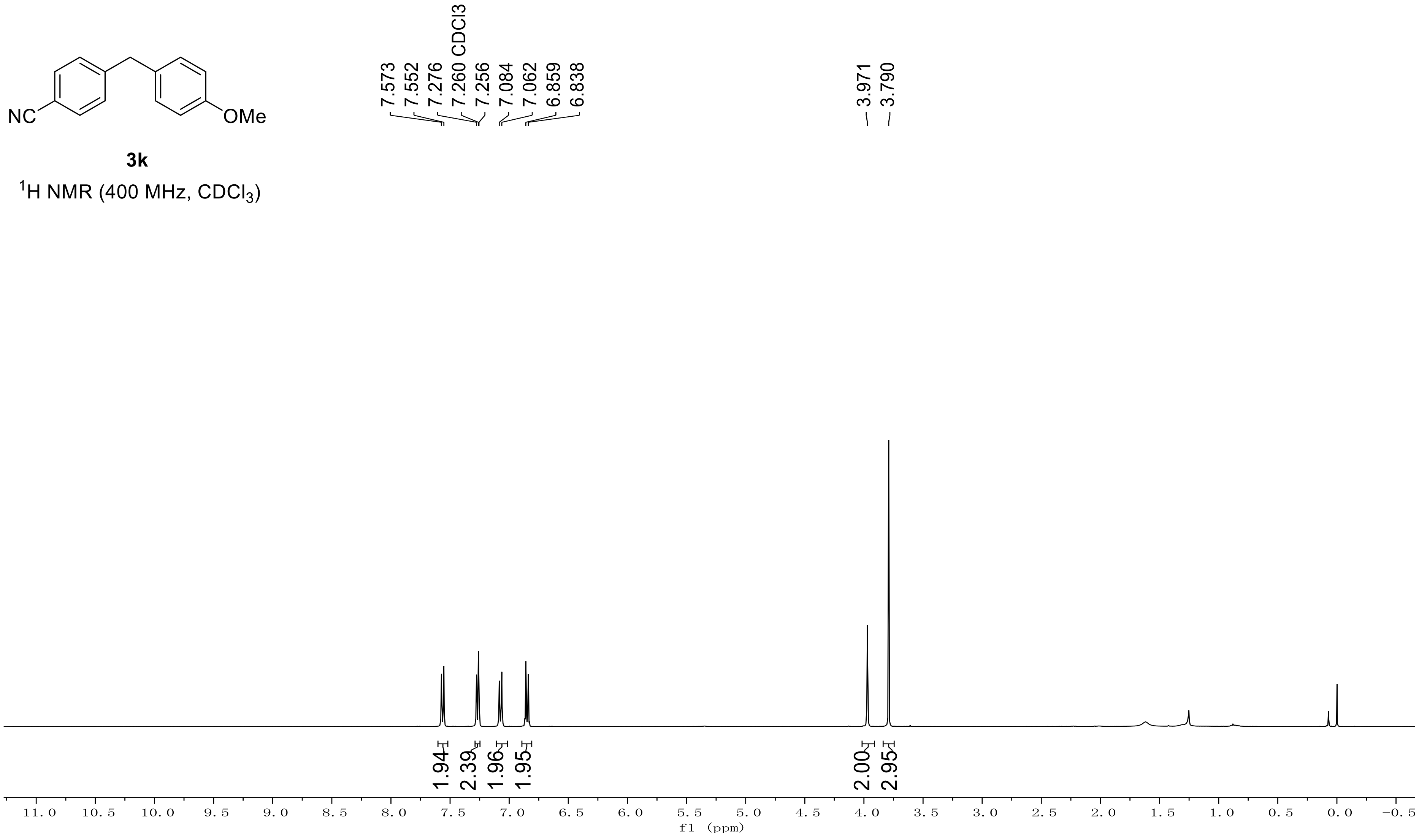
^{1}H NMR (400 MHz, CDCl$_3$)



3j

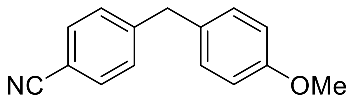
^{13}C NMR (101 MHz, CDCl$_3$)





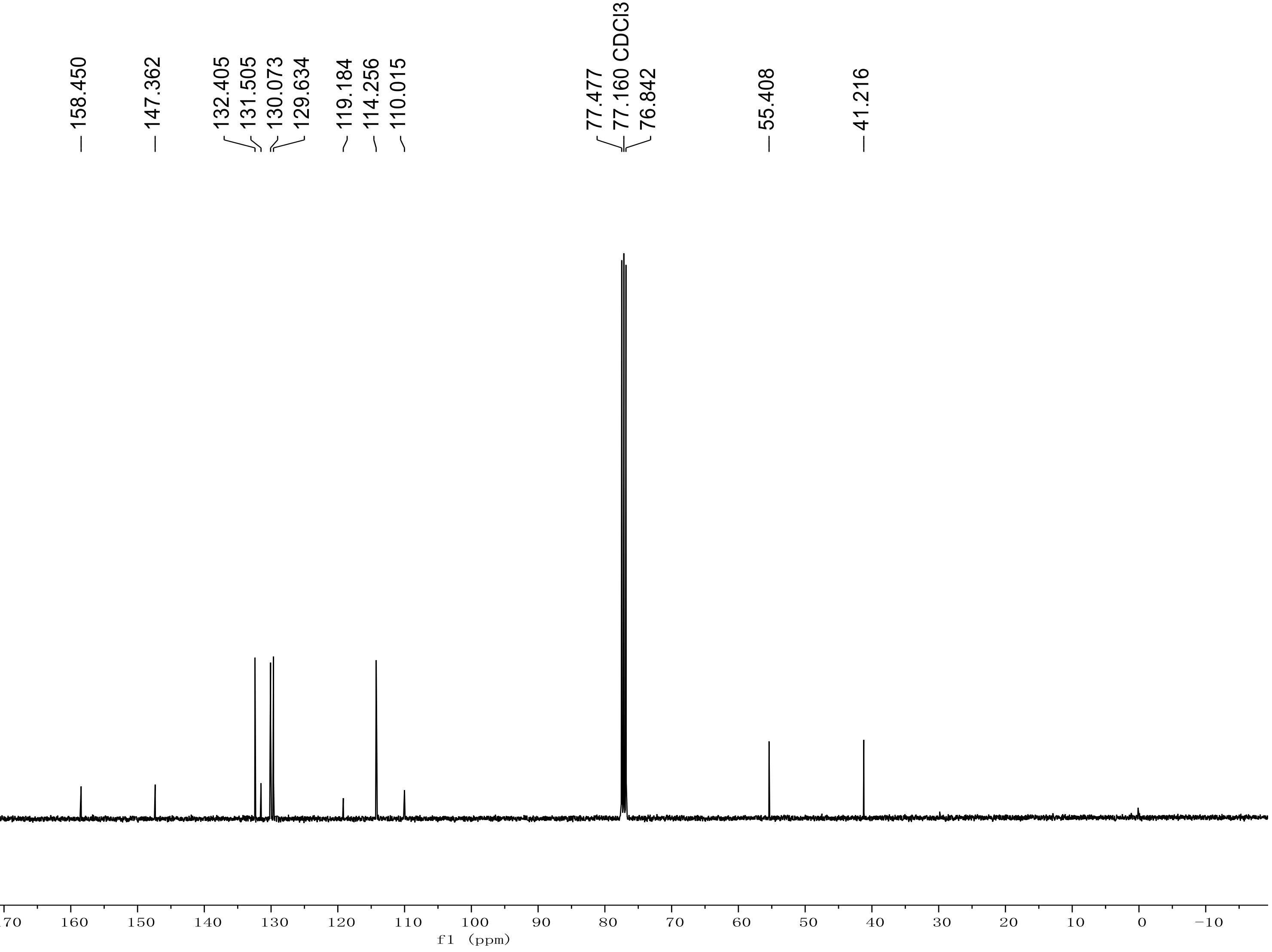
3k

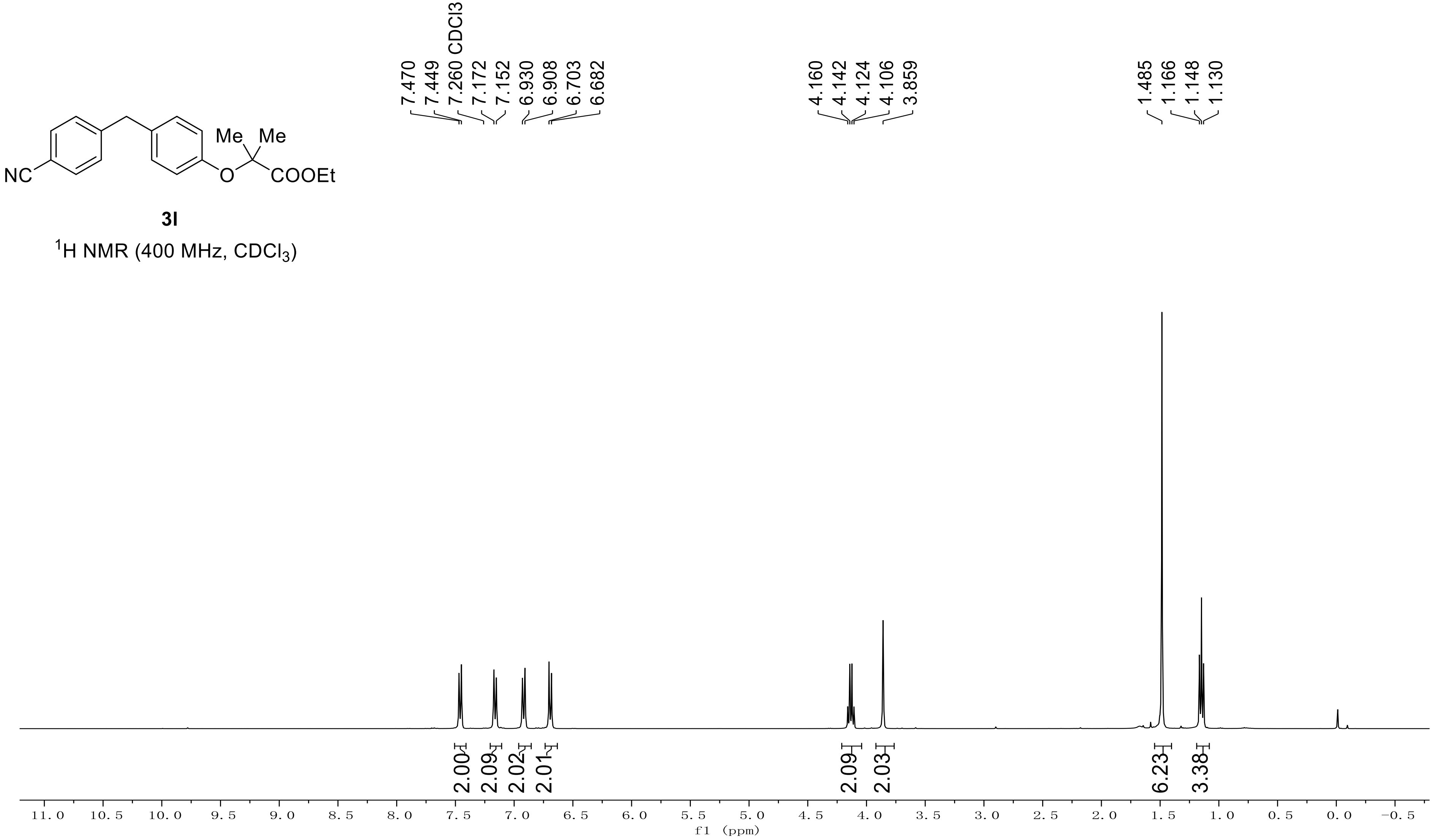
^{1}H NMR (400 MHz, CDCl$_3$)



3k

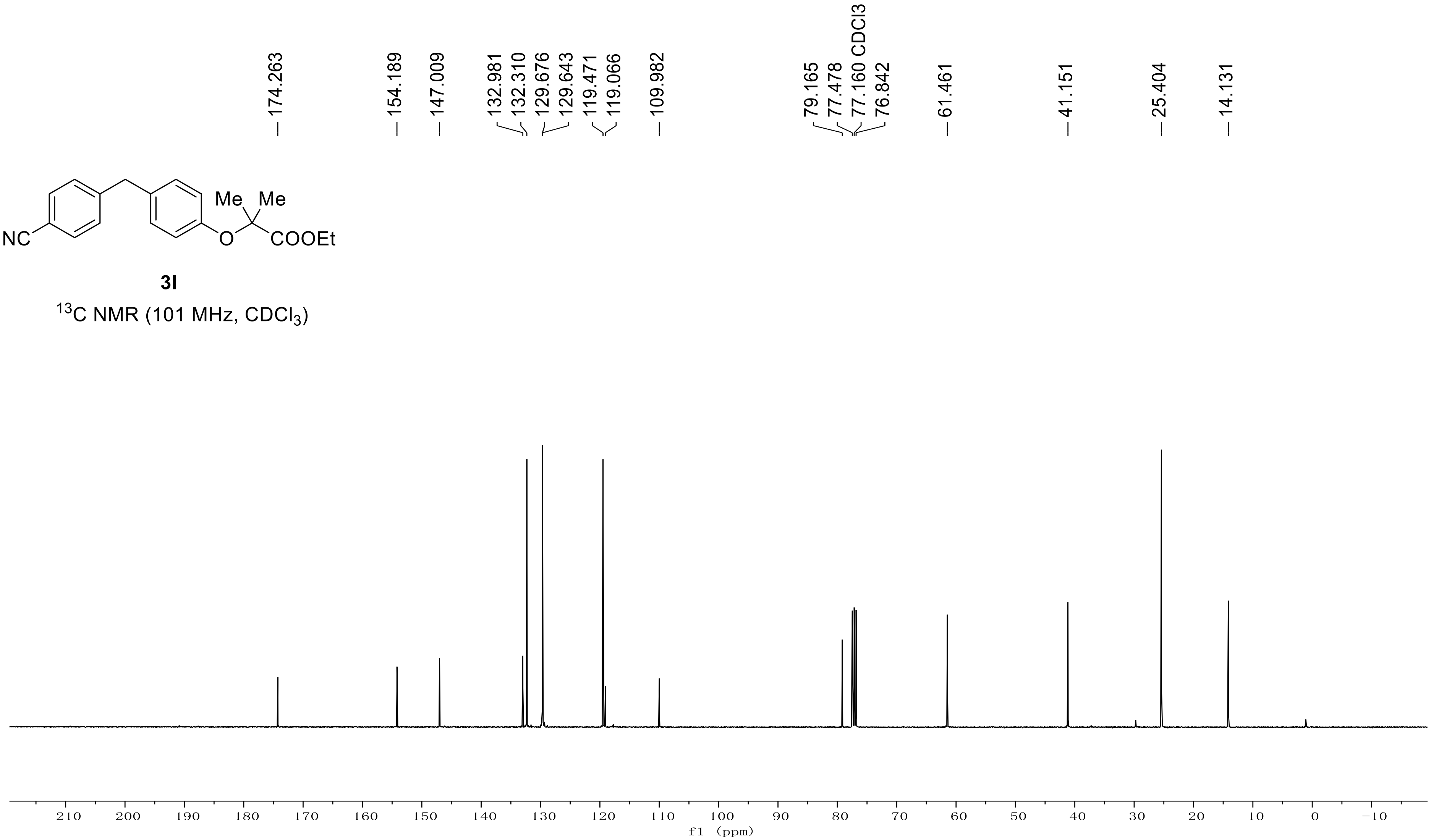
^{13}C NMR (101 MHz, CDCl$_3$)





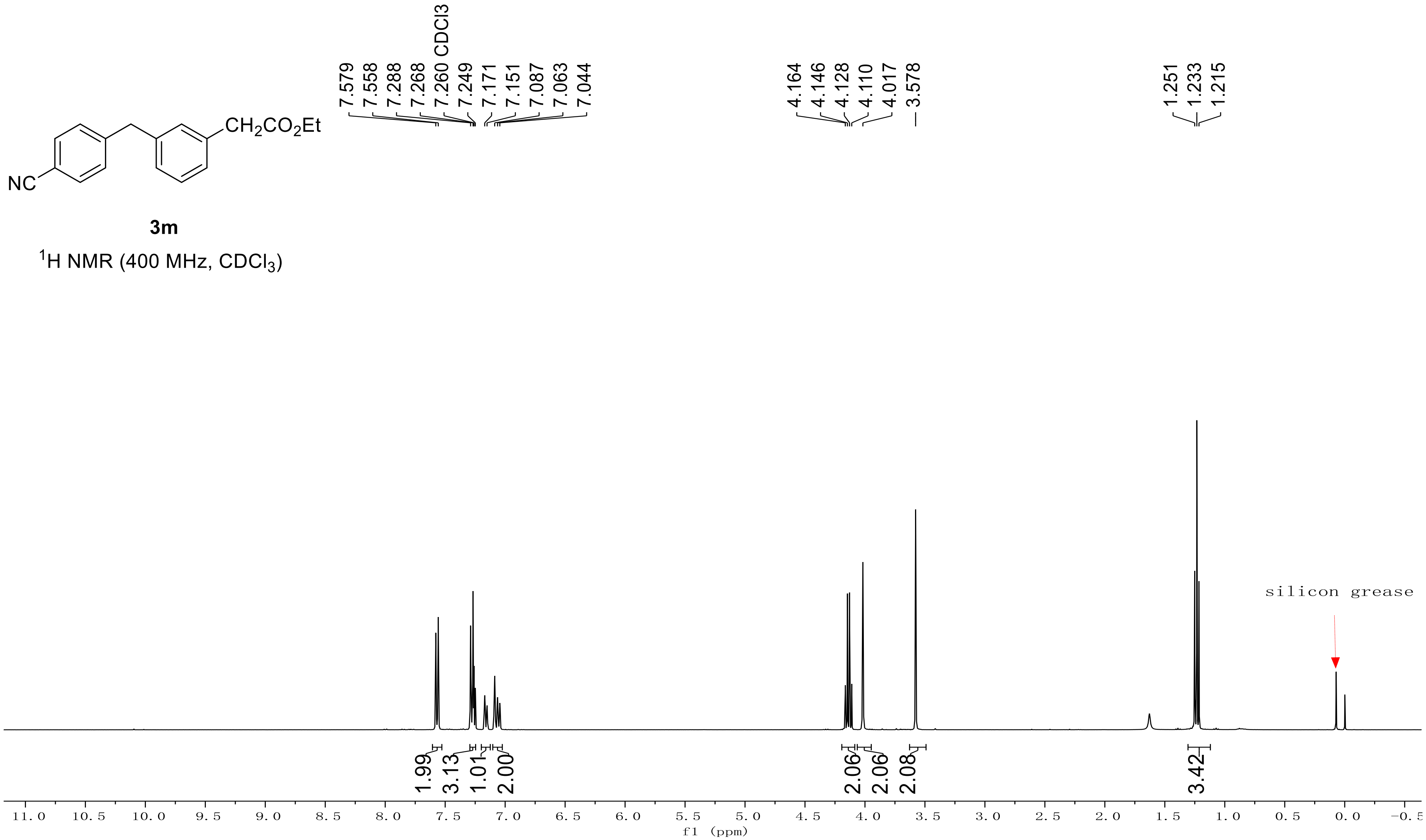
3l

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



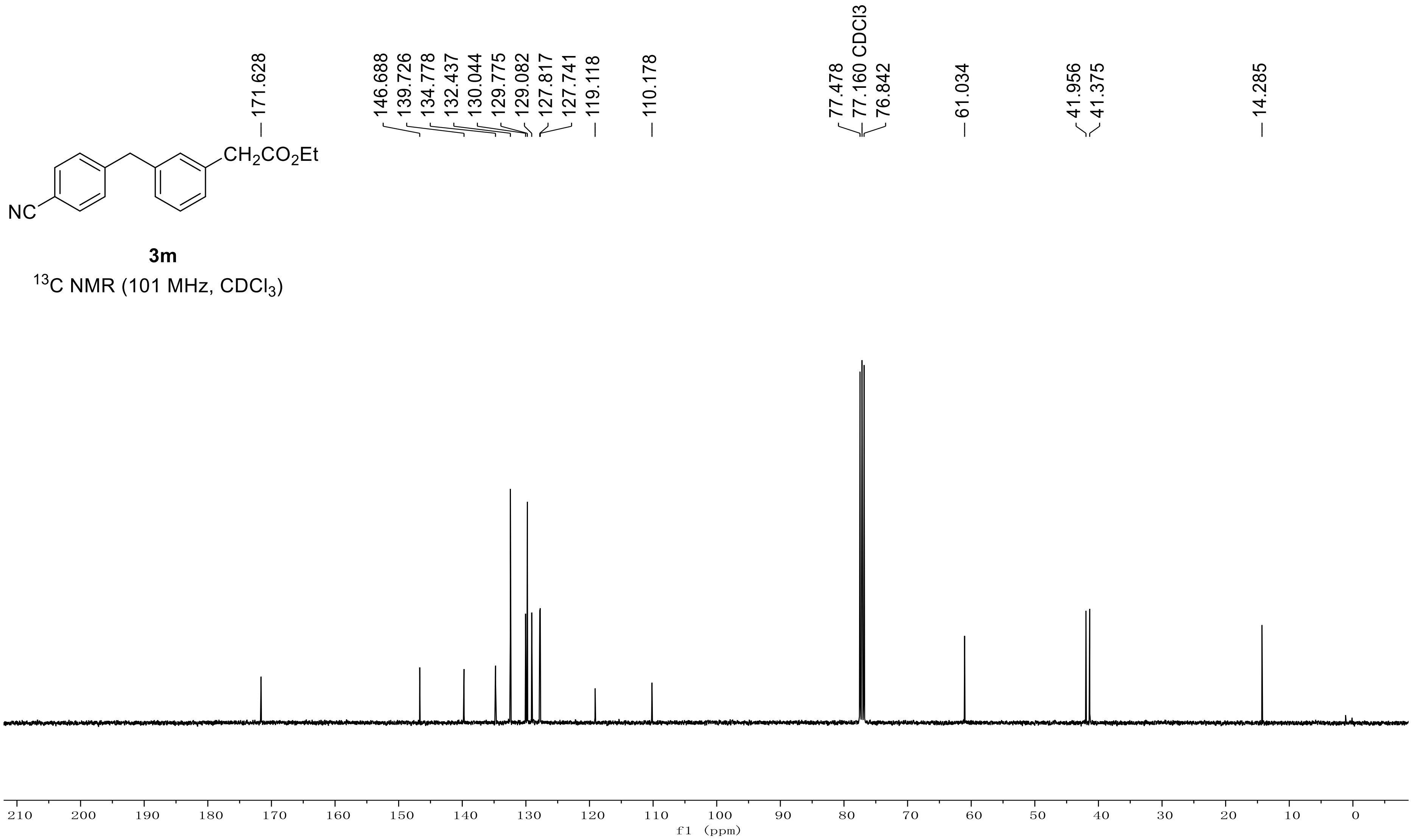
3l

^{13}C NMR (101 MHz, $CDCl_3$)



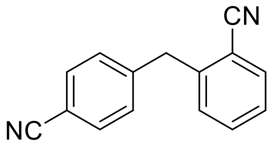
3m

^{1}H NMR (400 MHz, CDCl$_3$)



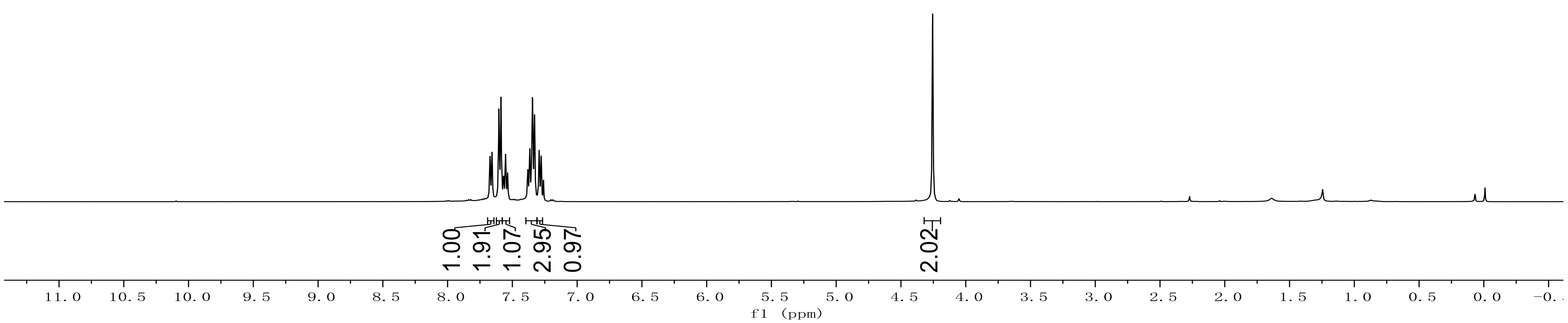
3m

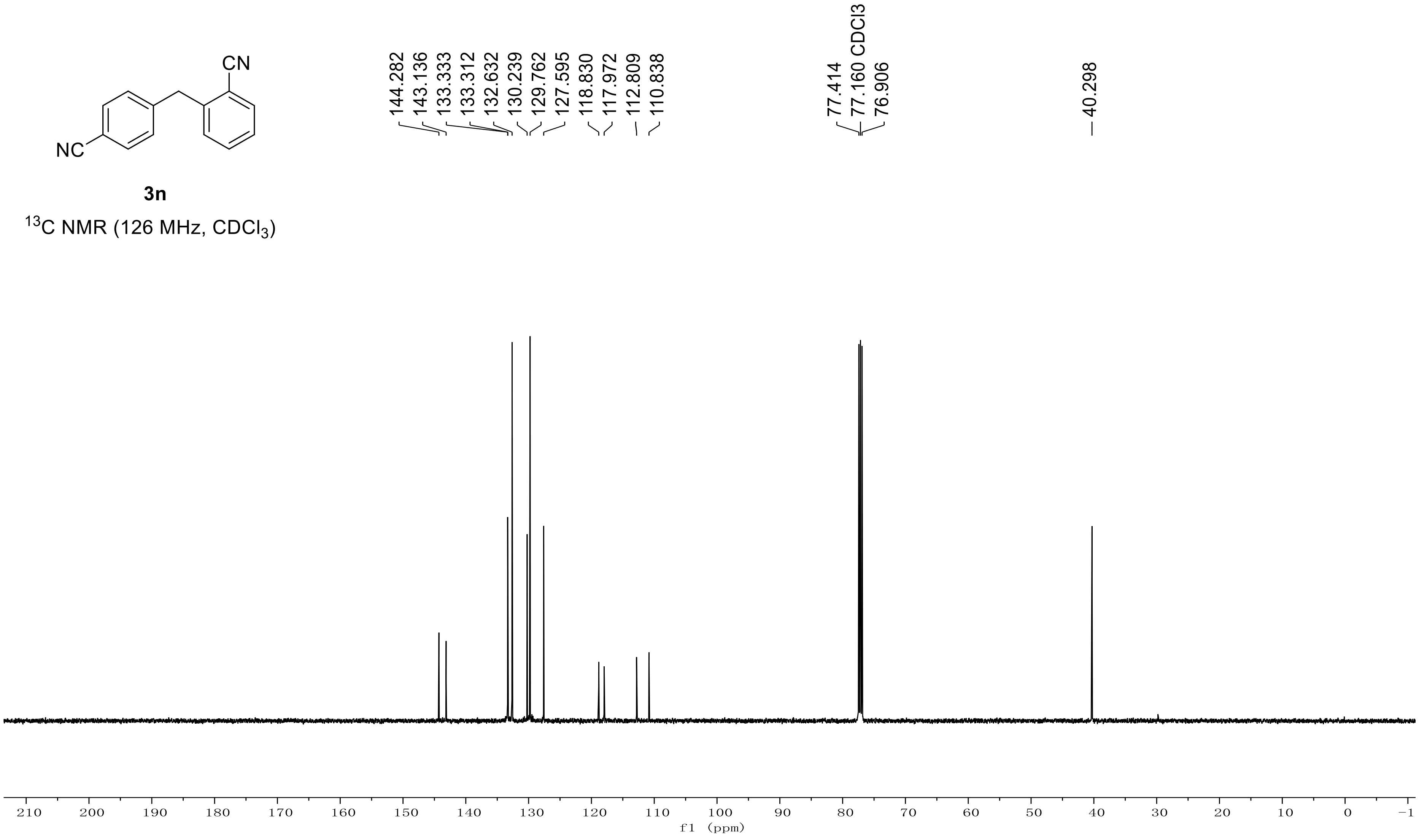
^{13}C NMR (101 MHz, CDCl$_3$)



3n

^{1}H NMR (500 MHz, CDCl$_3$)



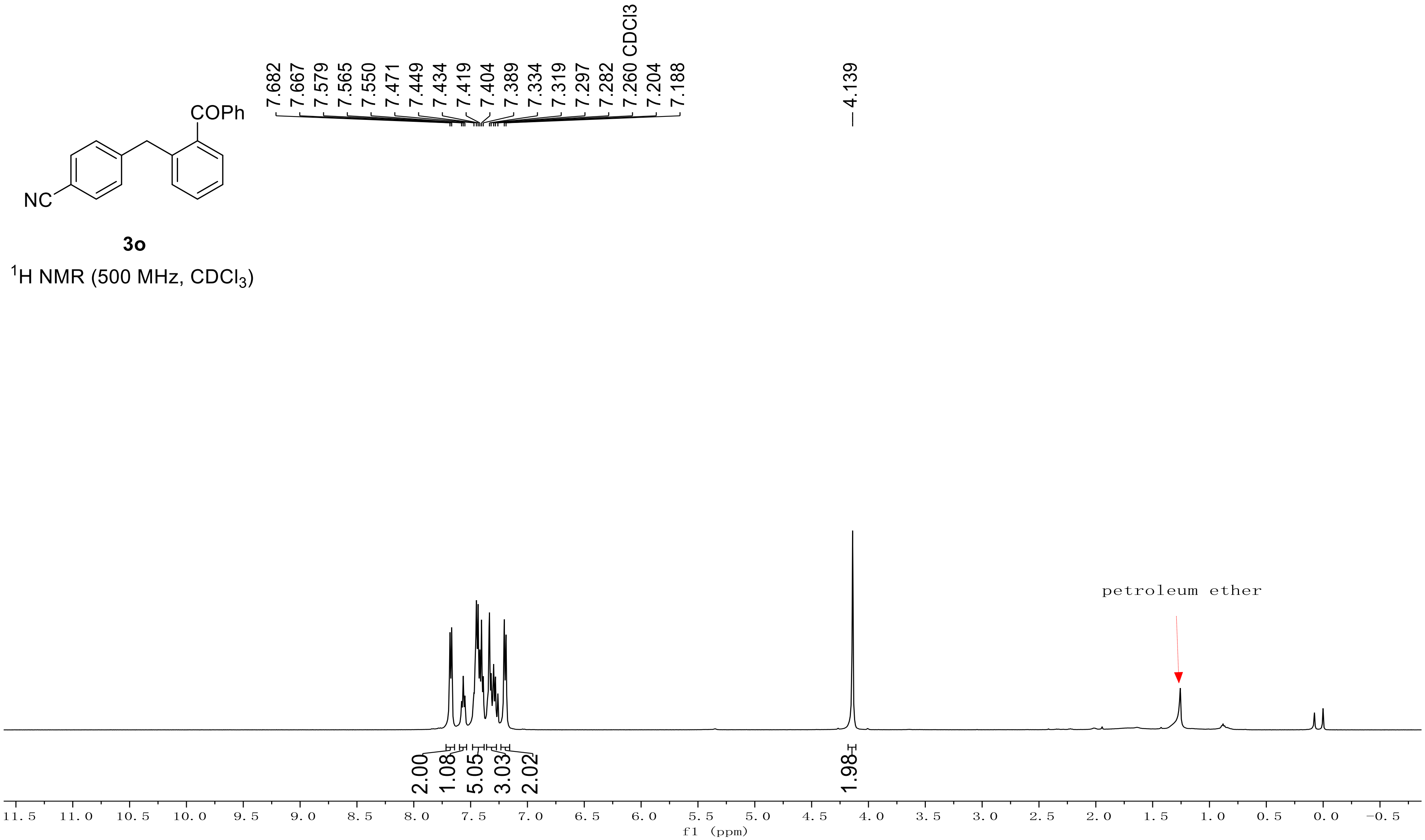


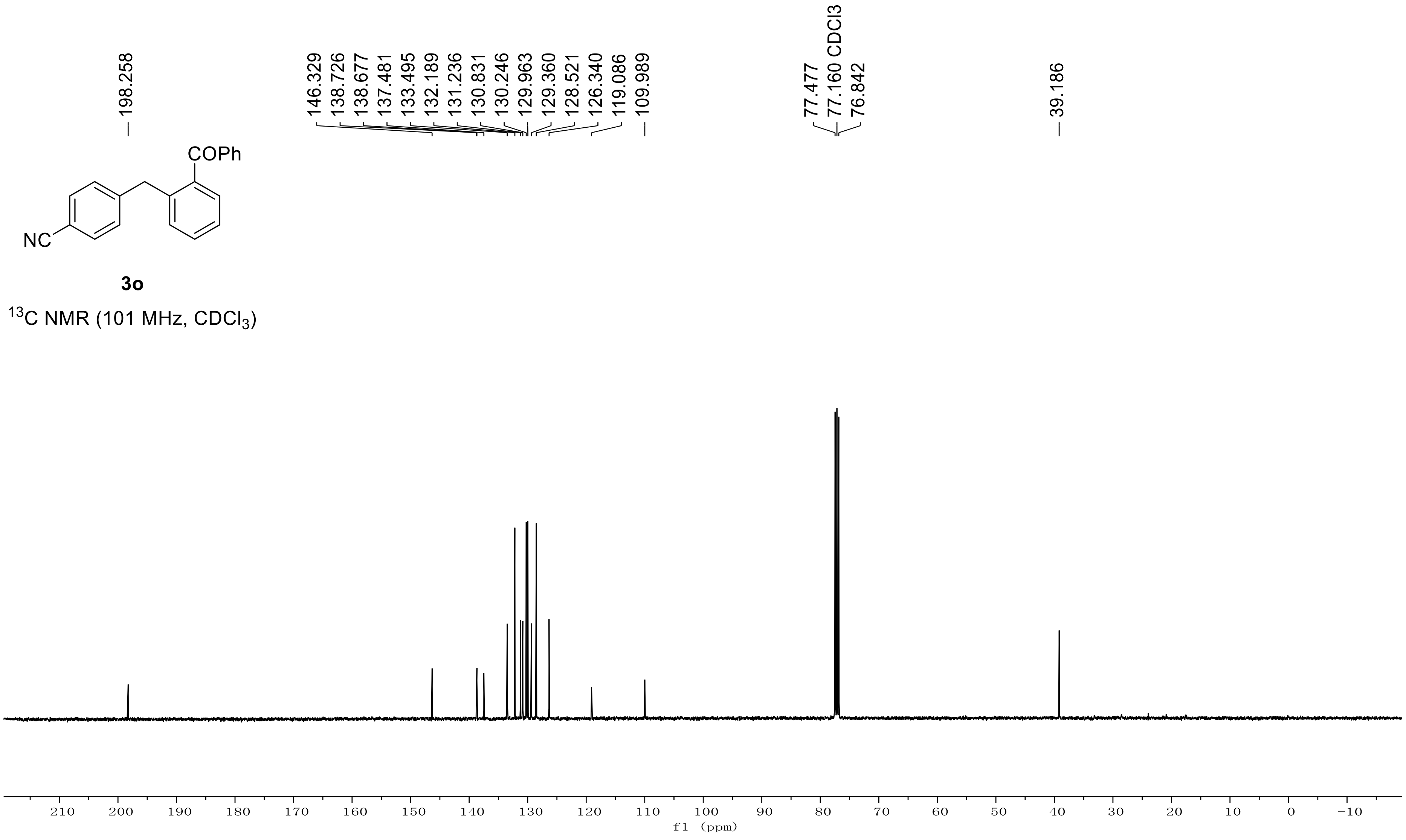
3n

^{13}C NMR (126 MHz, CDCl$_3$)

3o

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



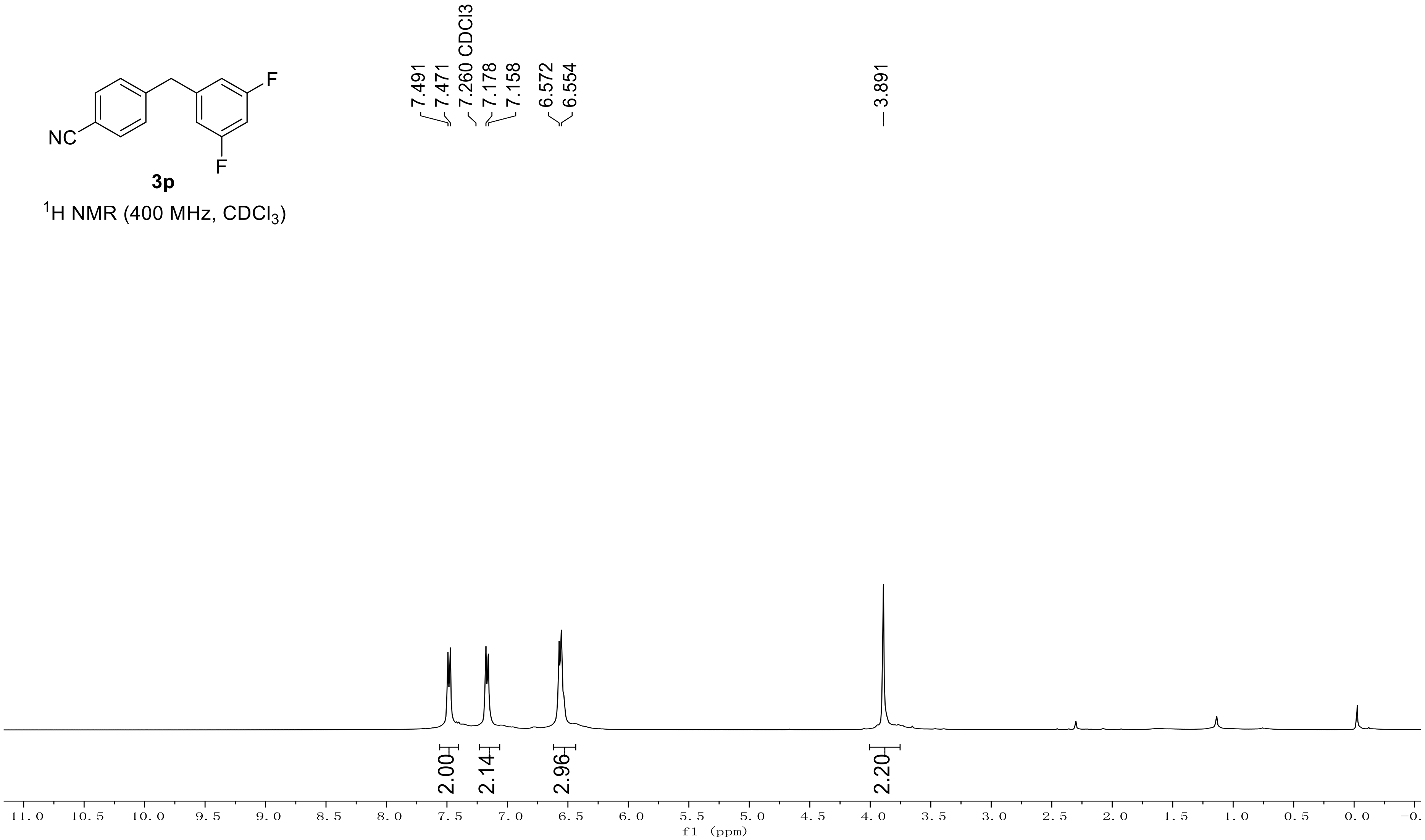


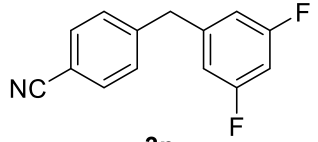
3o

^{13}C NMR (101 MHz, CDCl$_3$)

3p

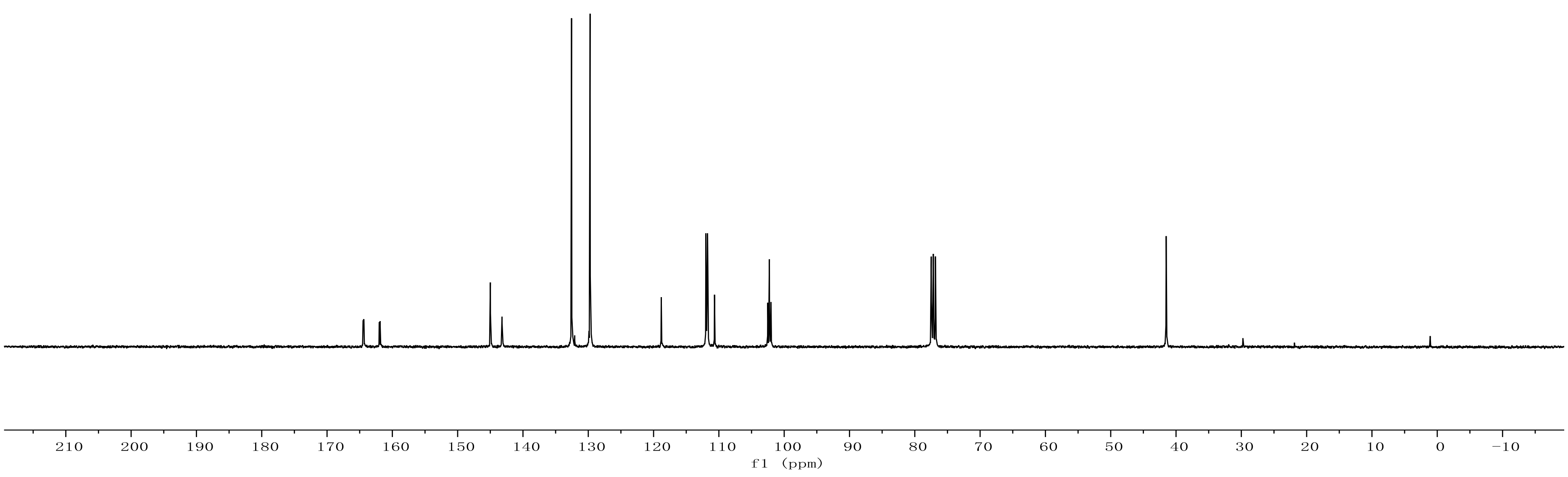
^{1}H NMR (400 MHz, $CDCl_3$)

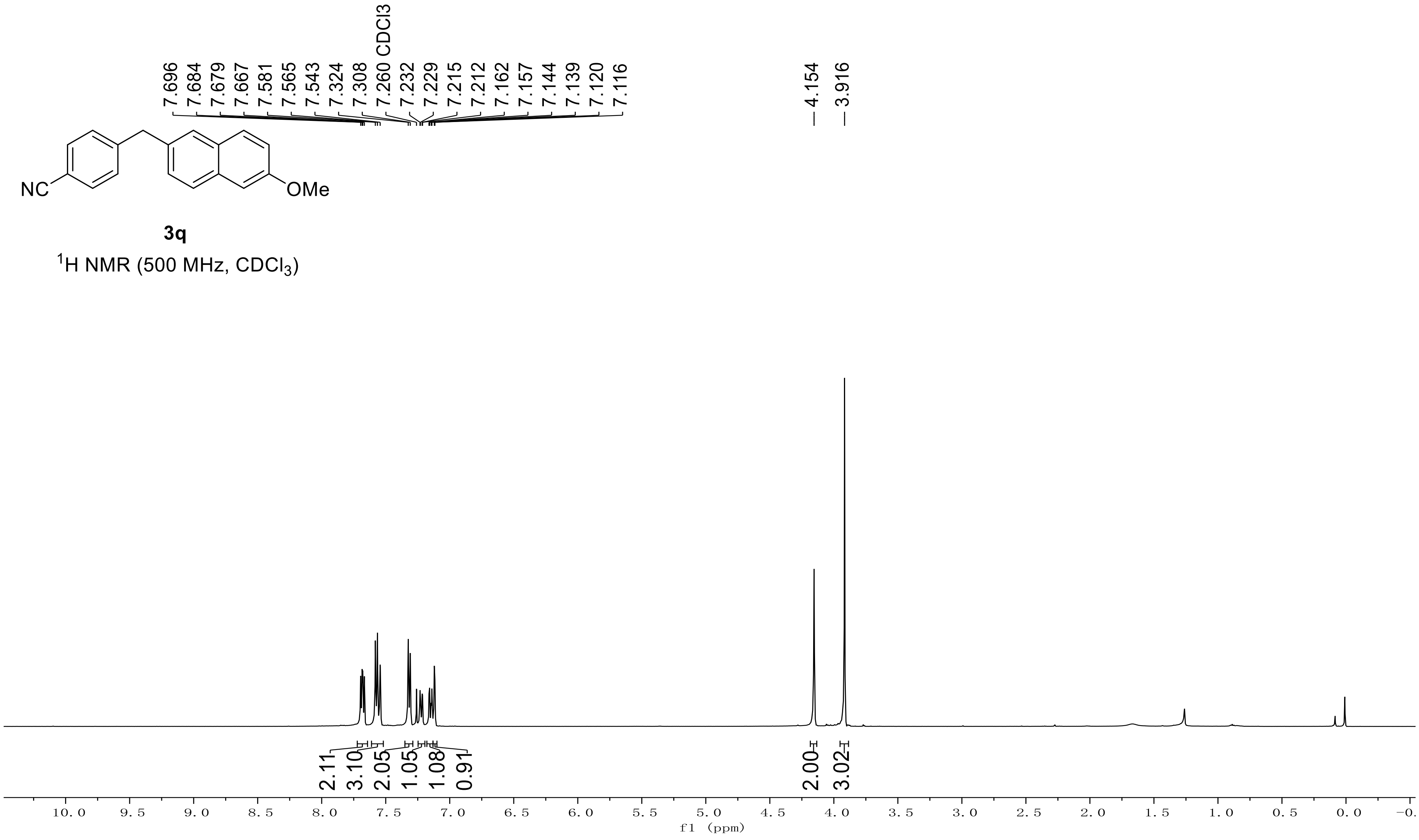




3p

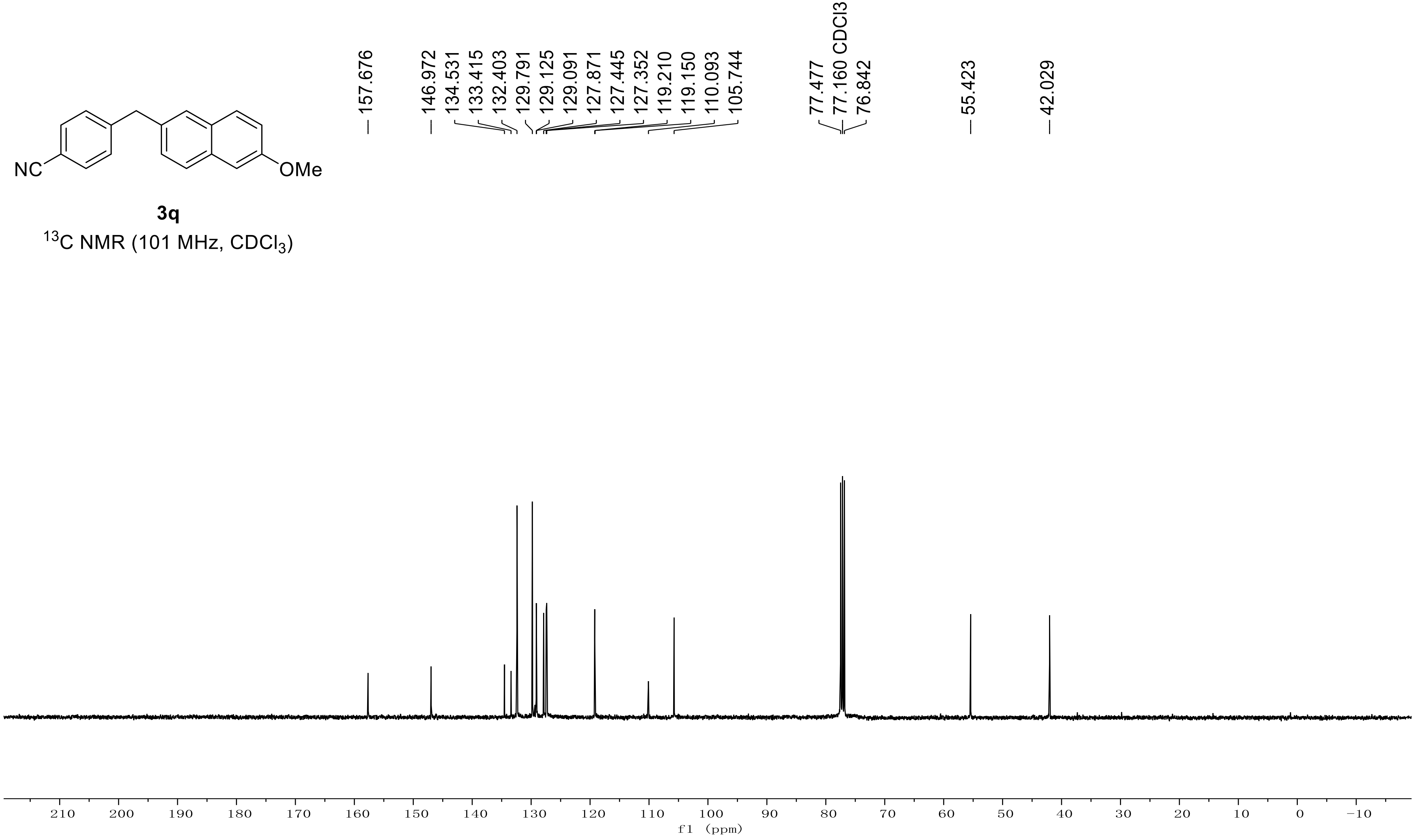
^{13}C NMR (101 MHz, CDCl$_3$)





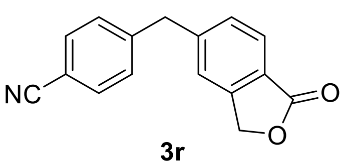
3q

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



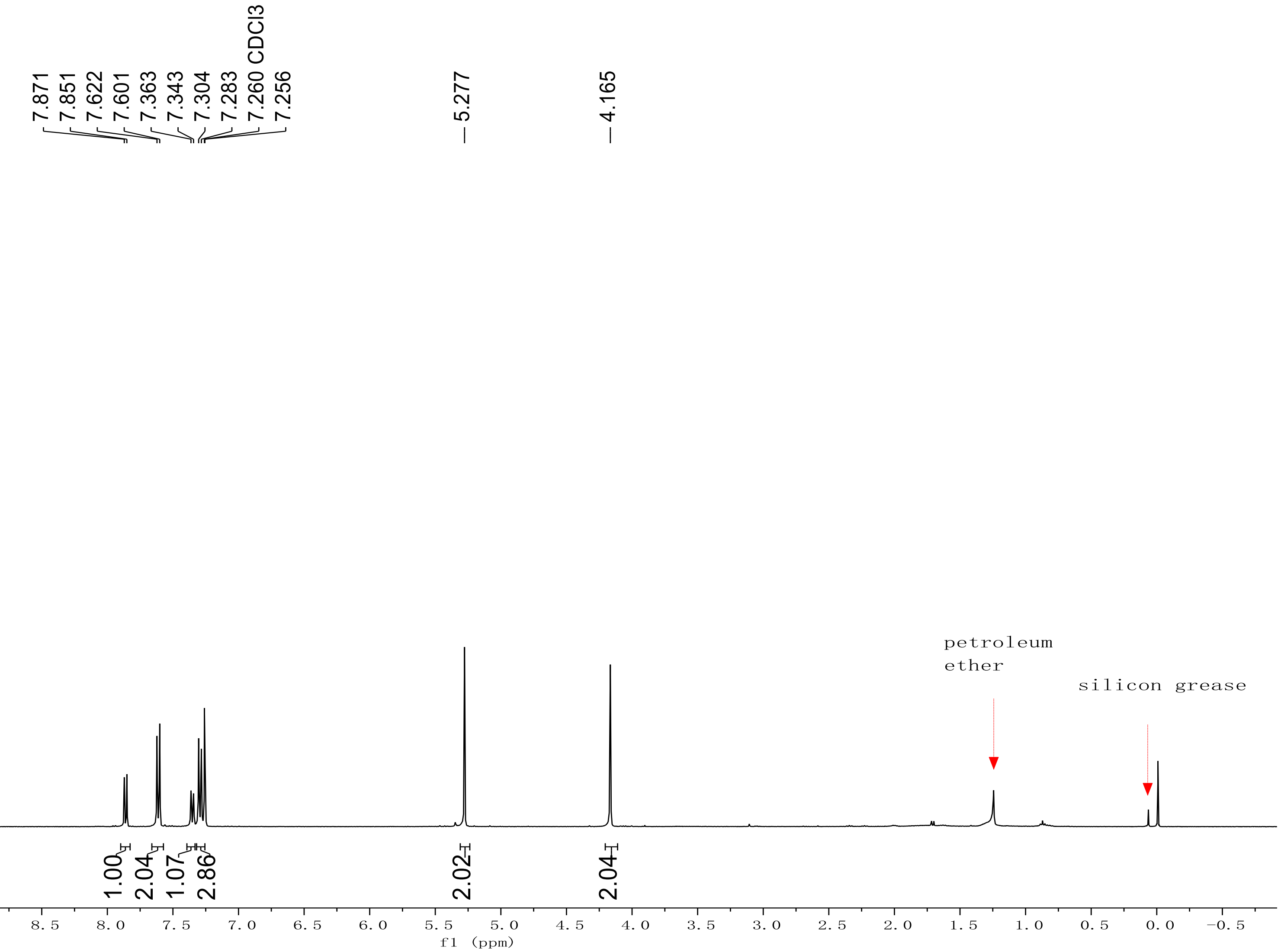
3q

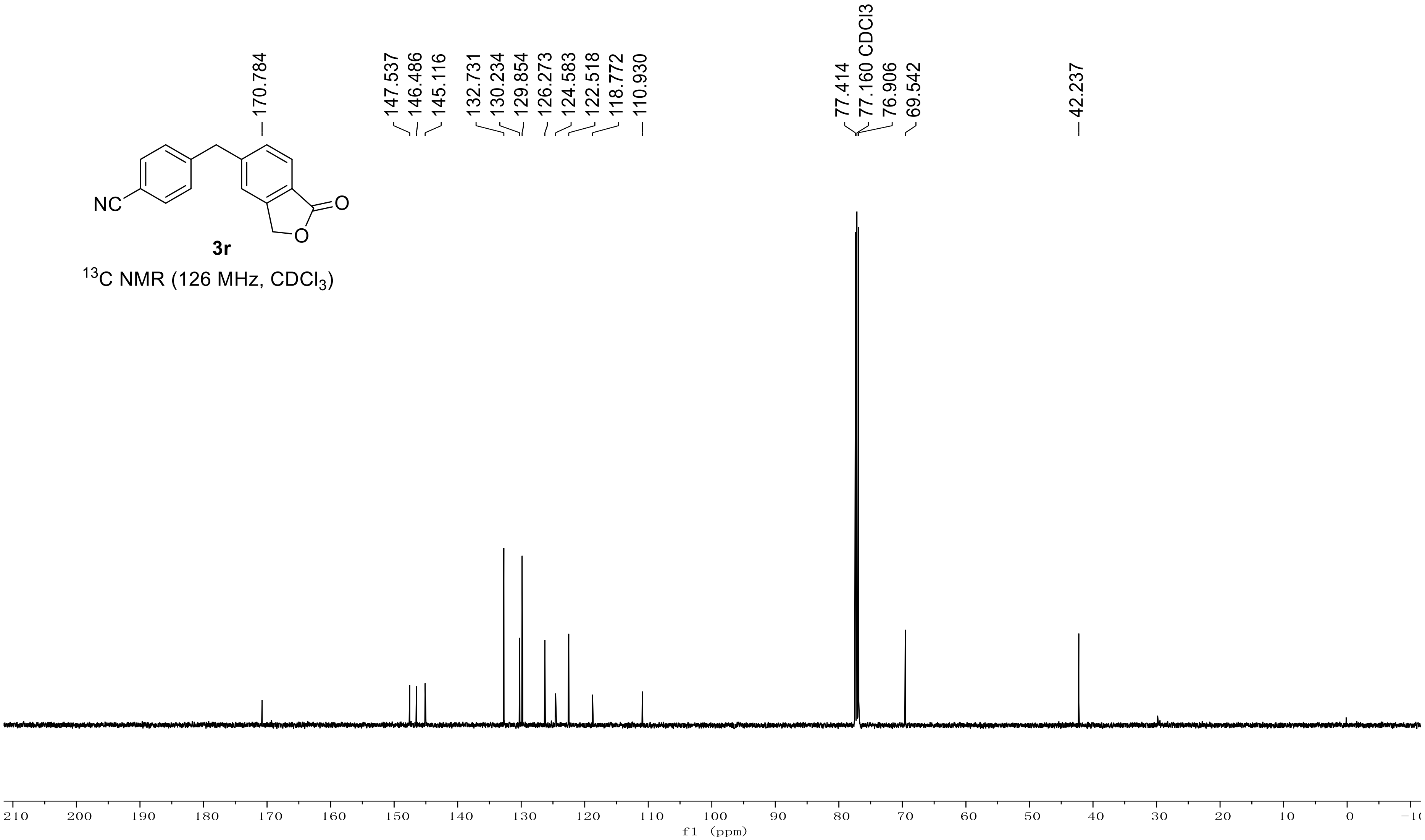
^{13}C NMR (101 MHz, CDCl$_3$)



3r

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



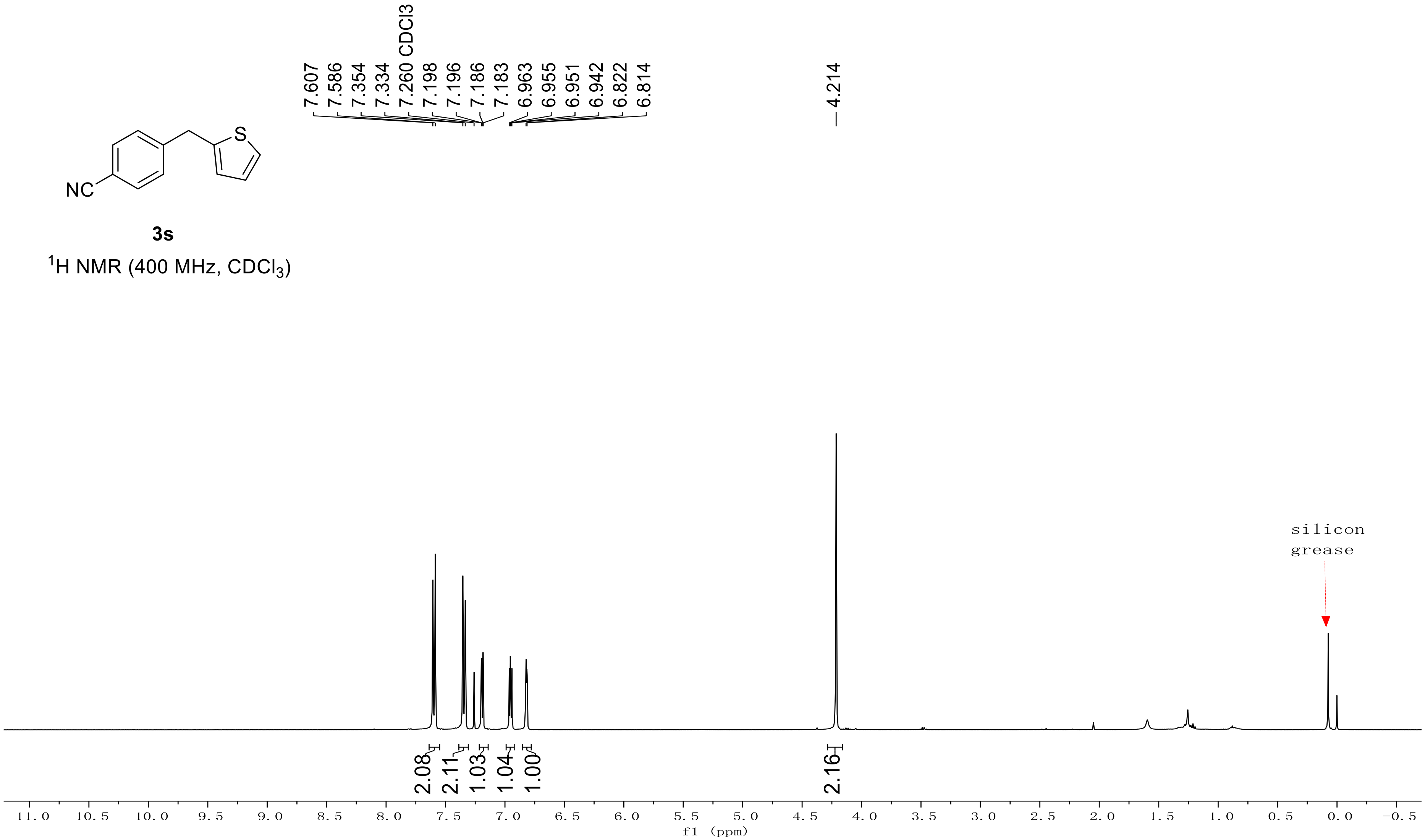


3r

^{13}C NMR (126 MHz, CDCl$_3$)

3s

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



3s

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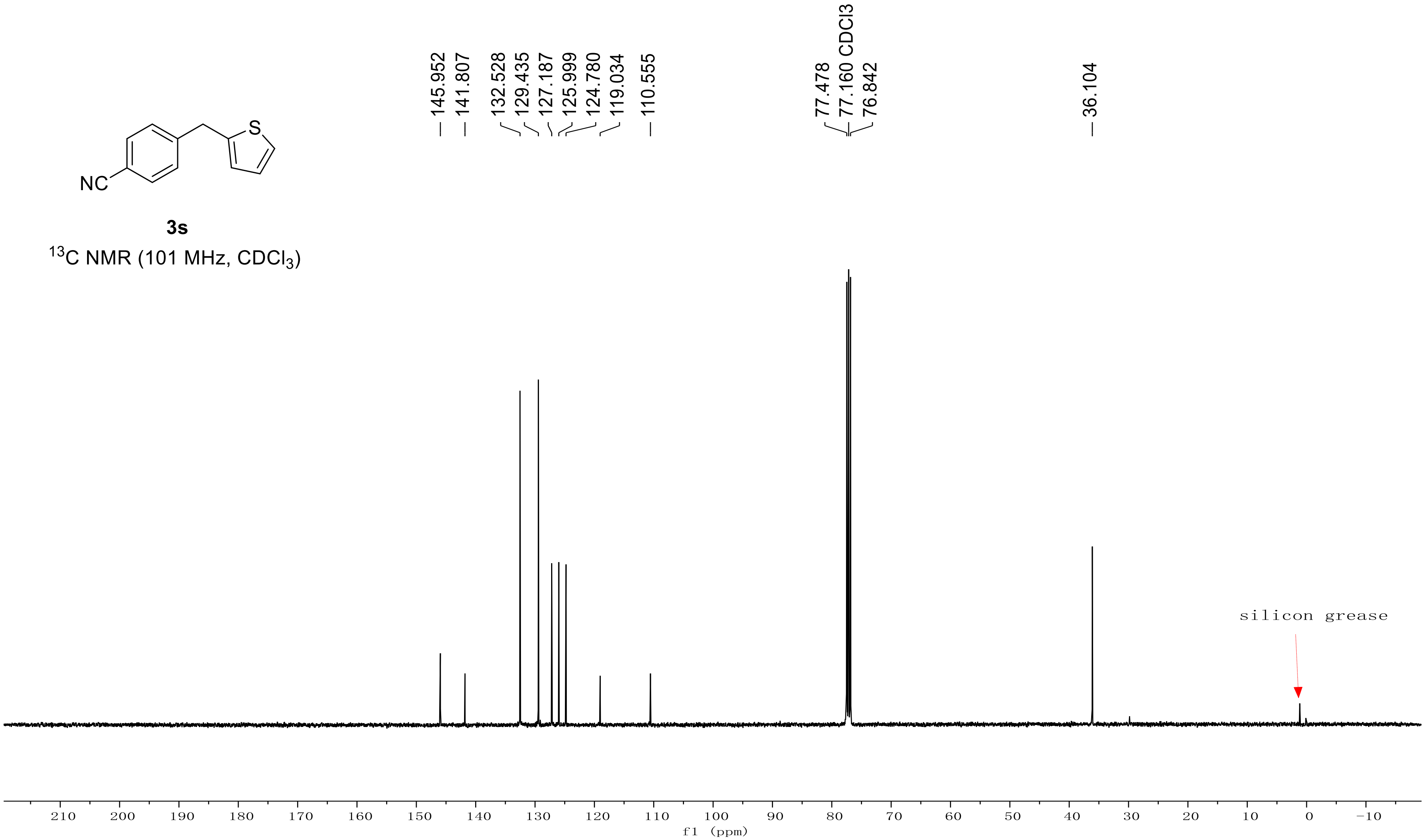
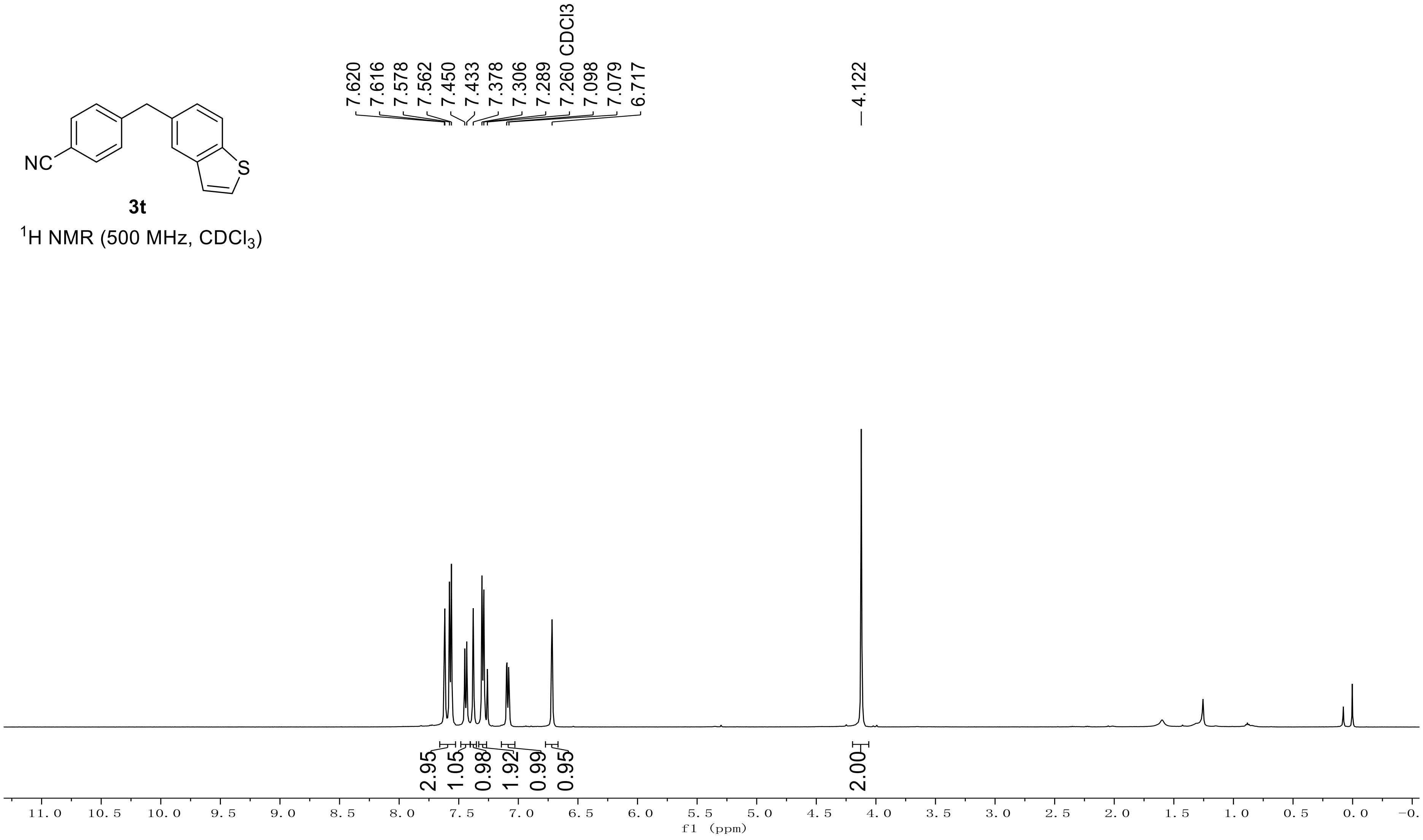
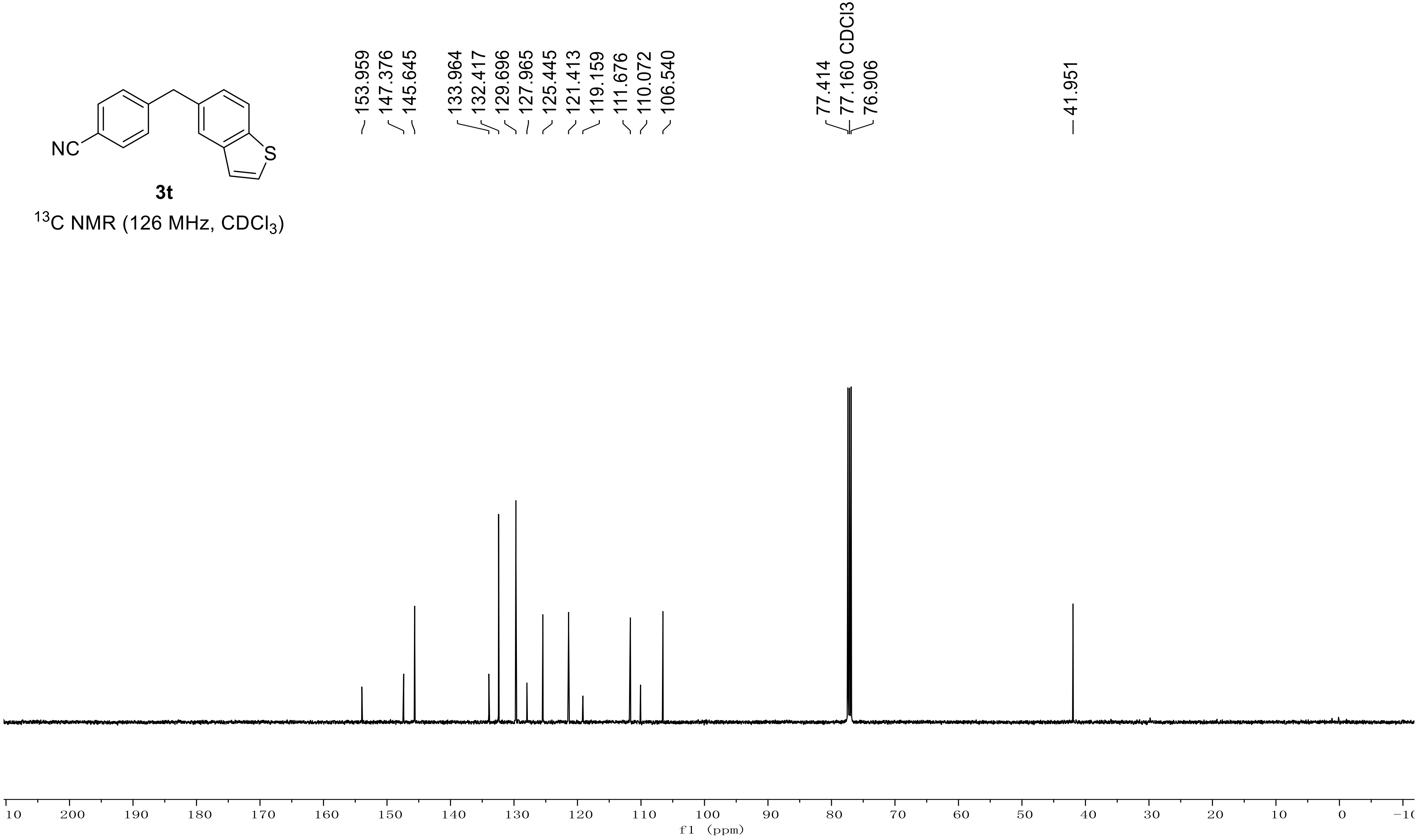




3t

^{1}H NMR (500 MHz, CDCl$_3$)



3t

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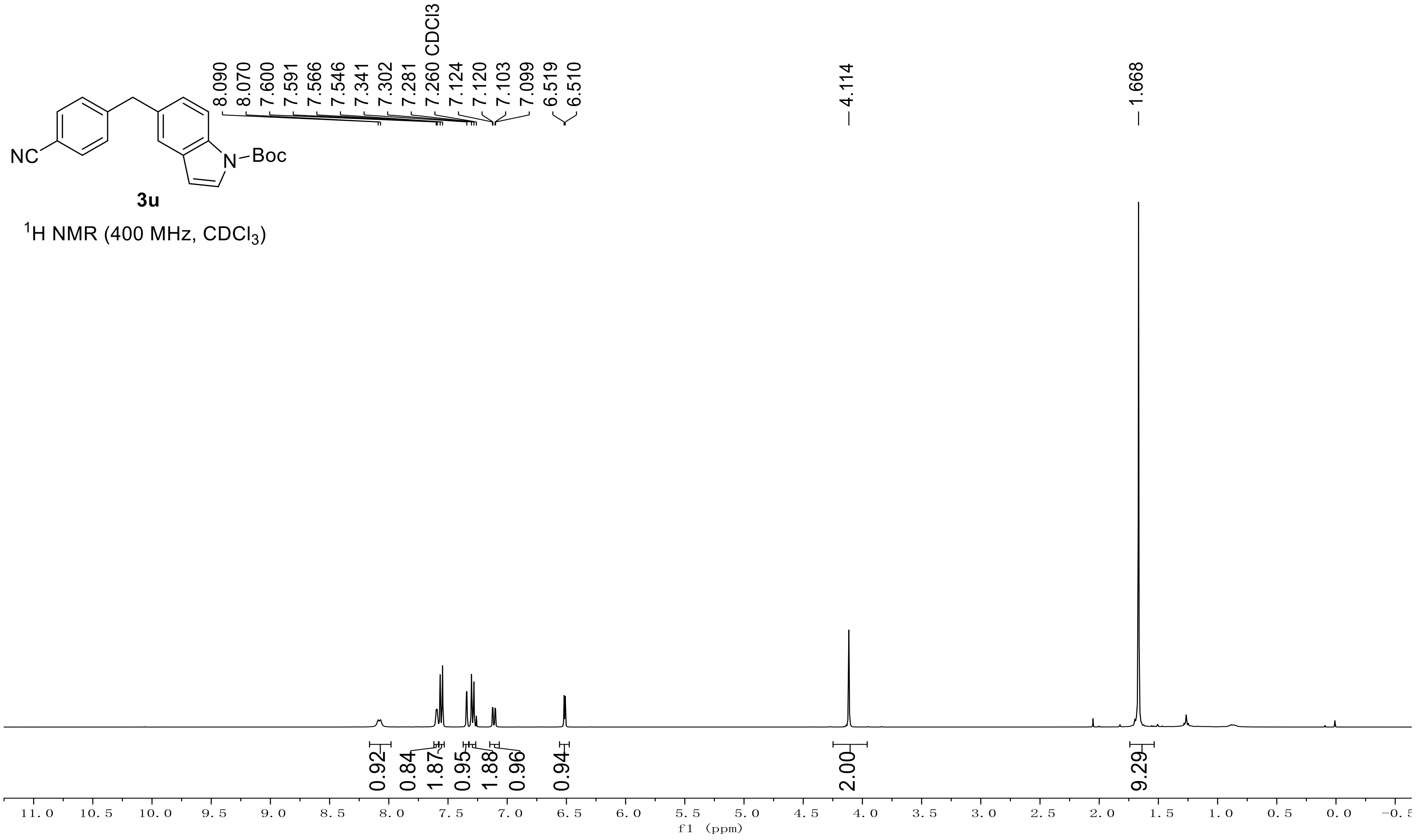
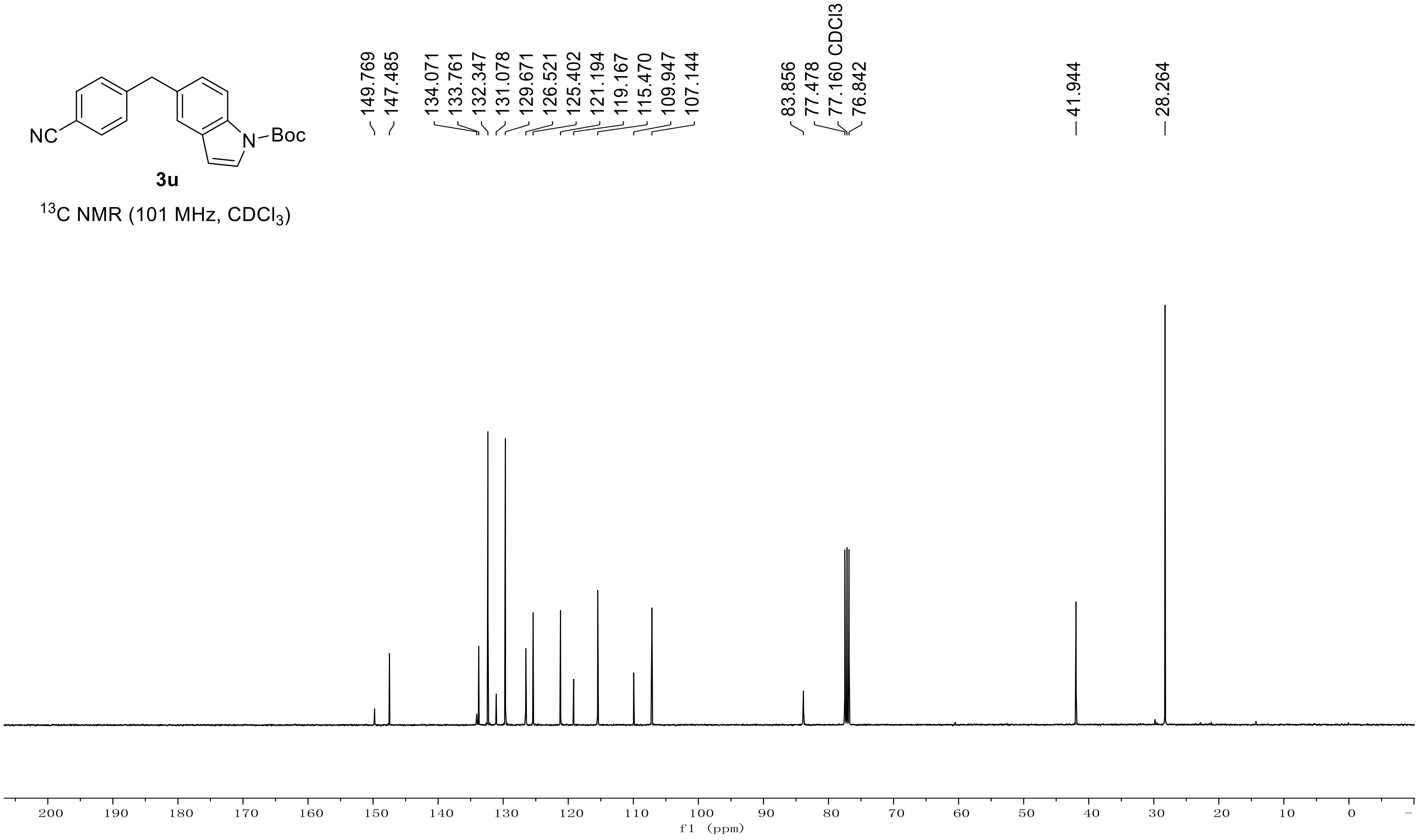


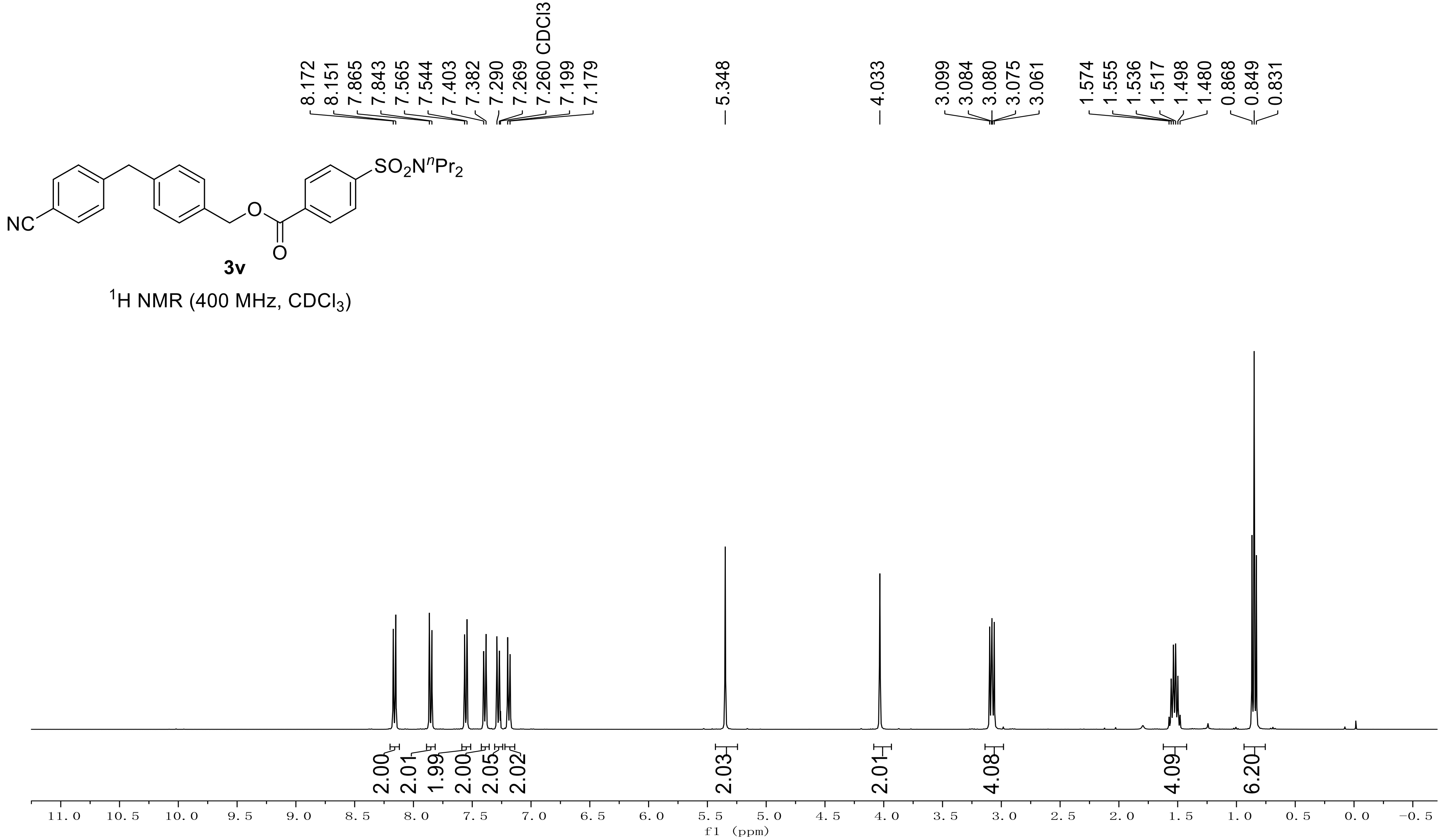
3u

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



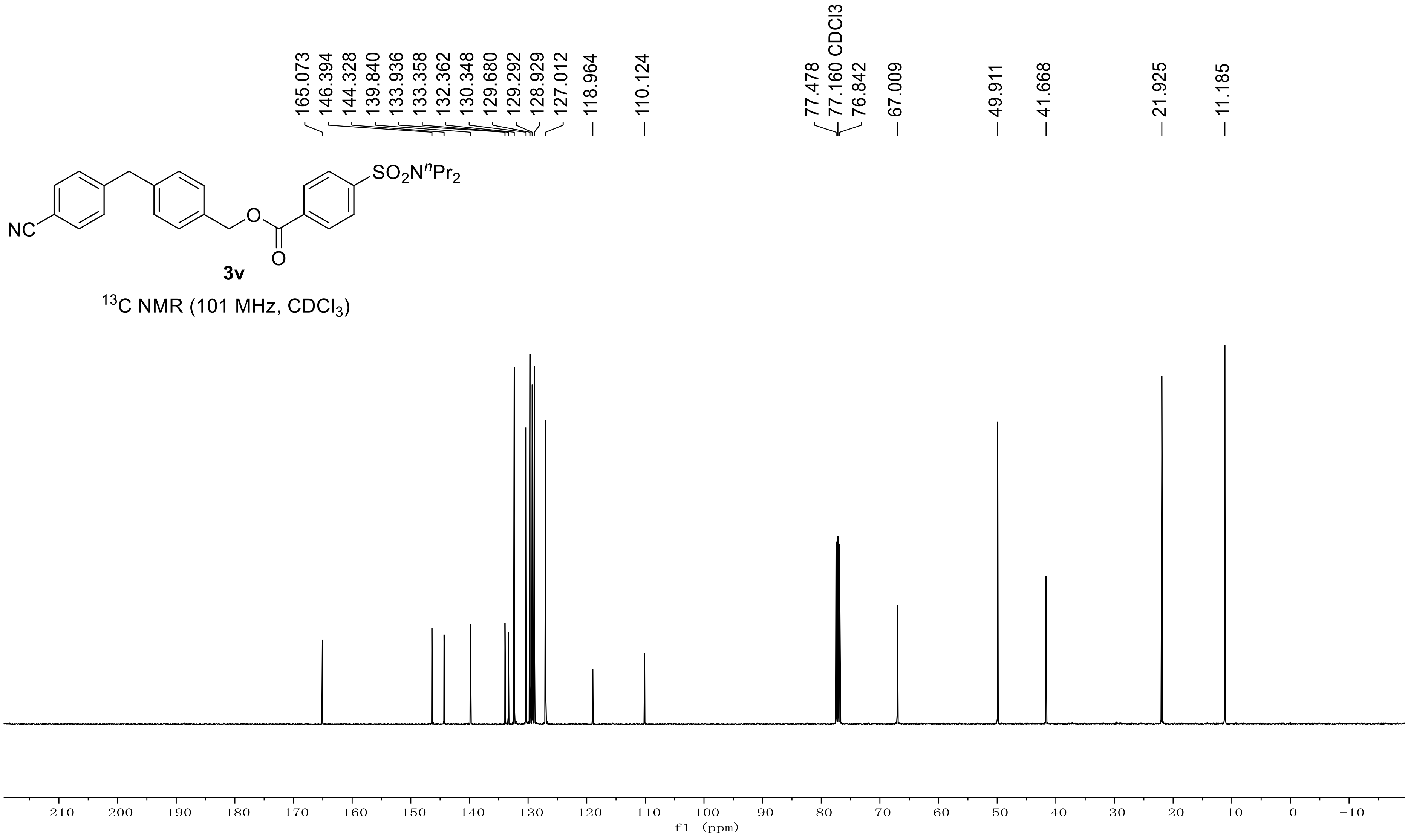
3u

^{13}C NMR (101 MHz, CDCl$_3$)



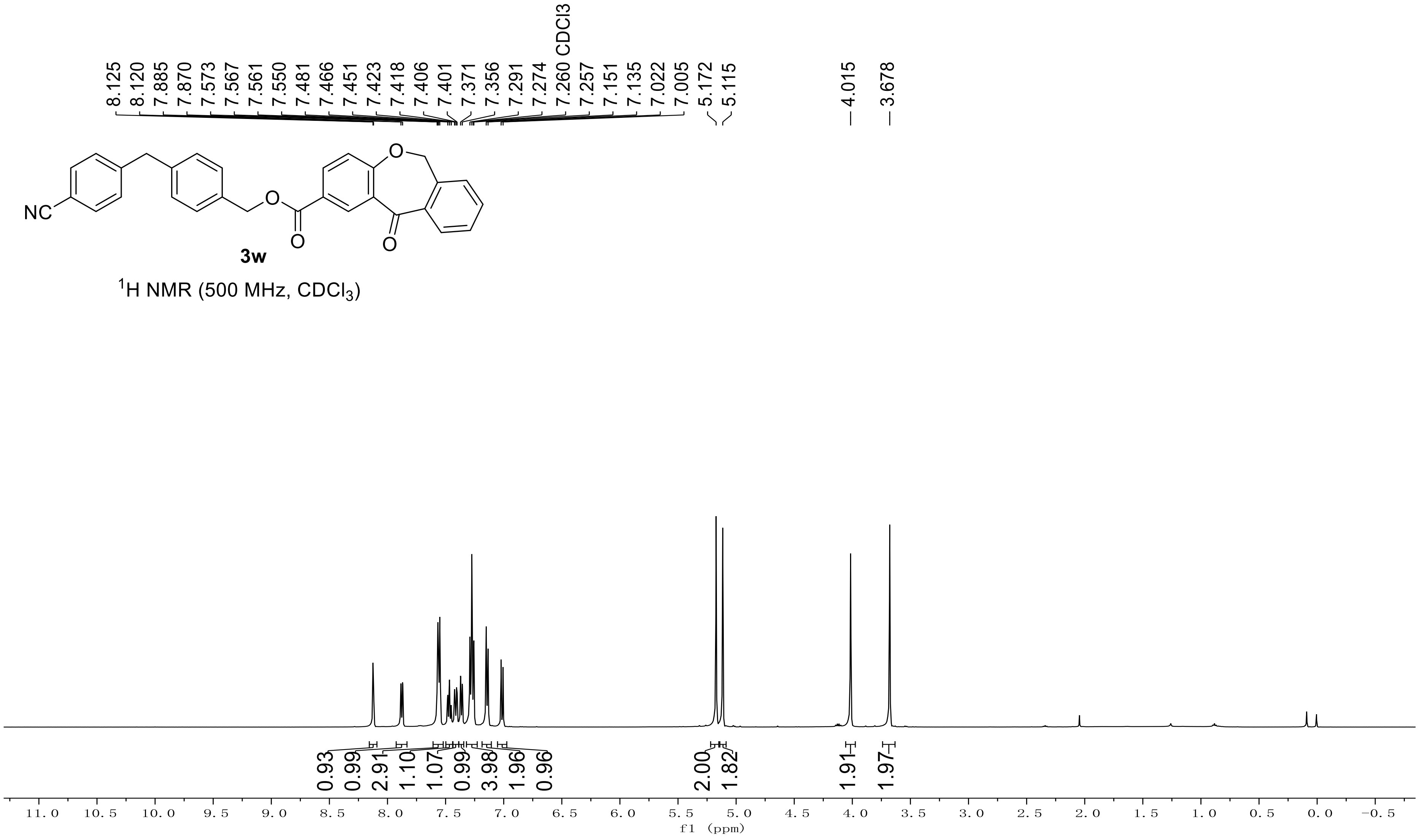
3v

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



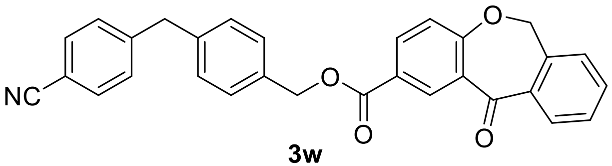
3v

^{13}C NMR (101 MHz, CDCl$_3$)



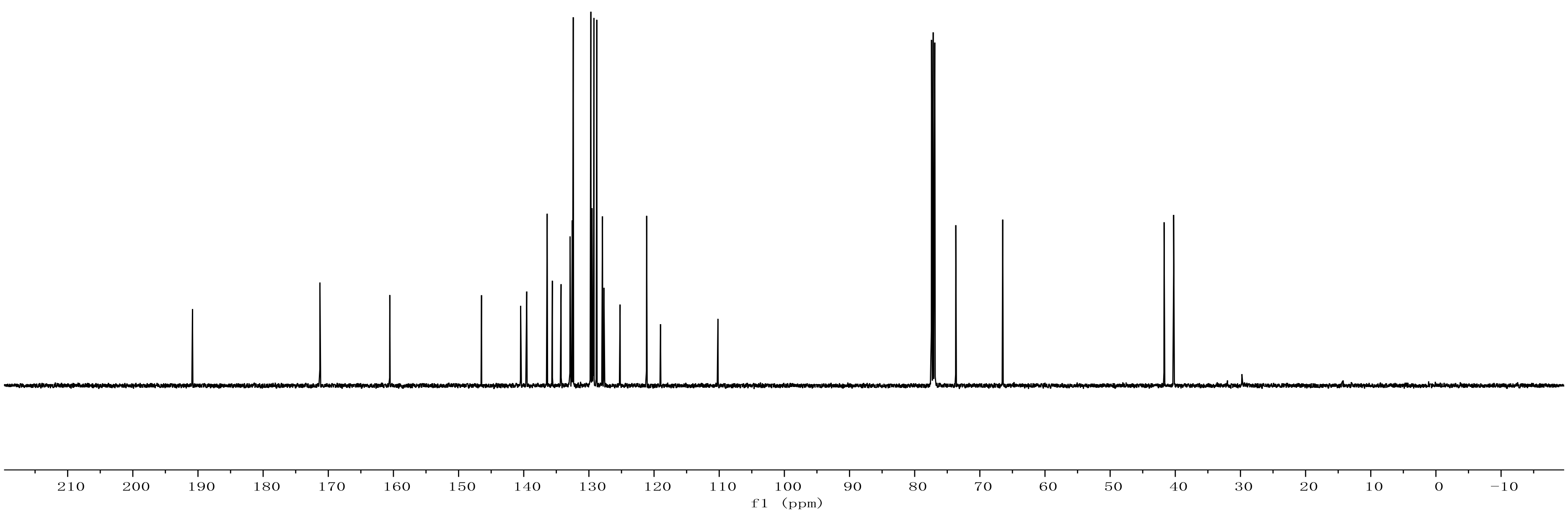
3w

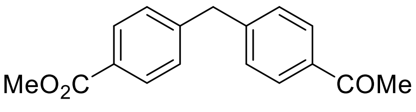
^{1}H NMR (500 MHz, CDCl$_3$)



3w

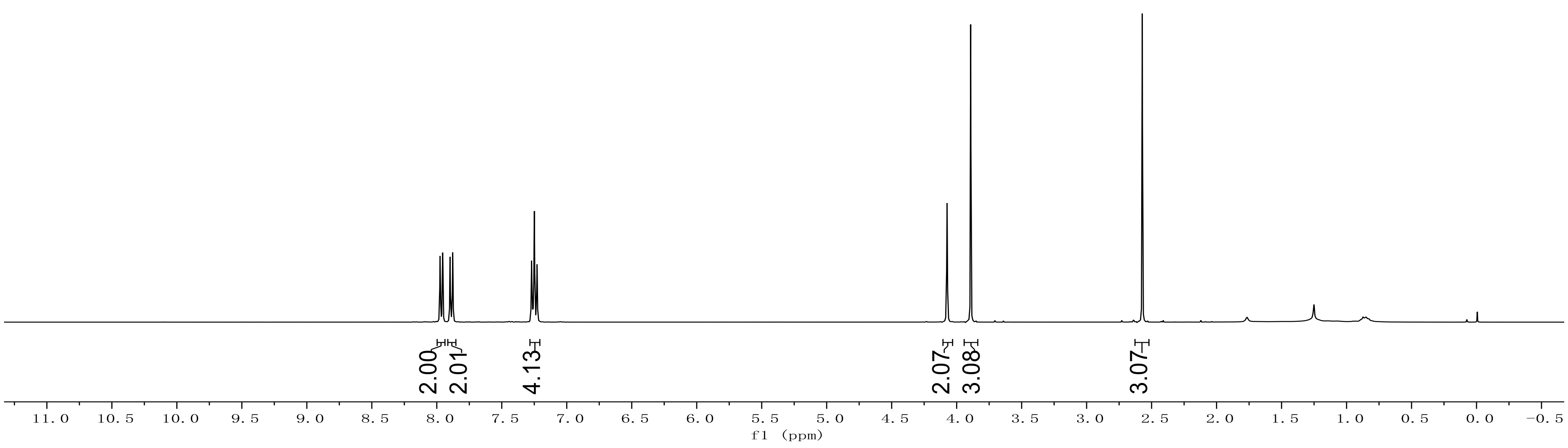
^{13}C NMR (126 MHz, $CDCl_3$)

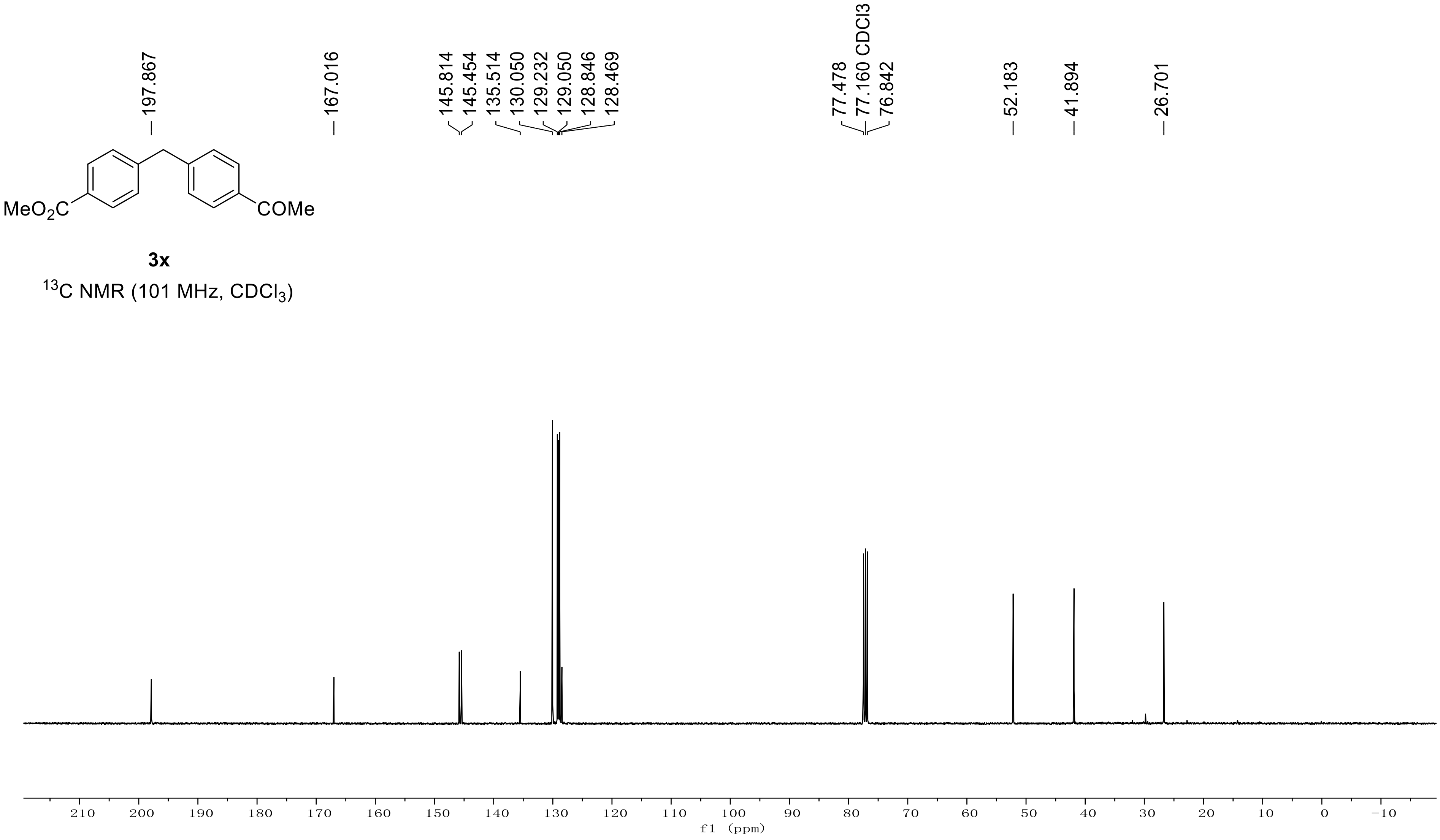




3x

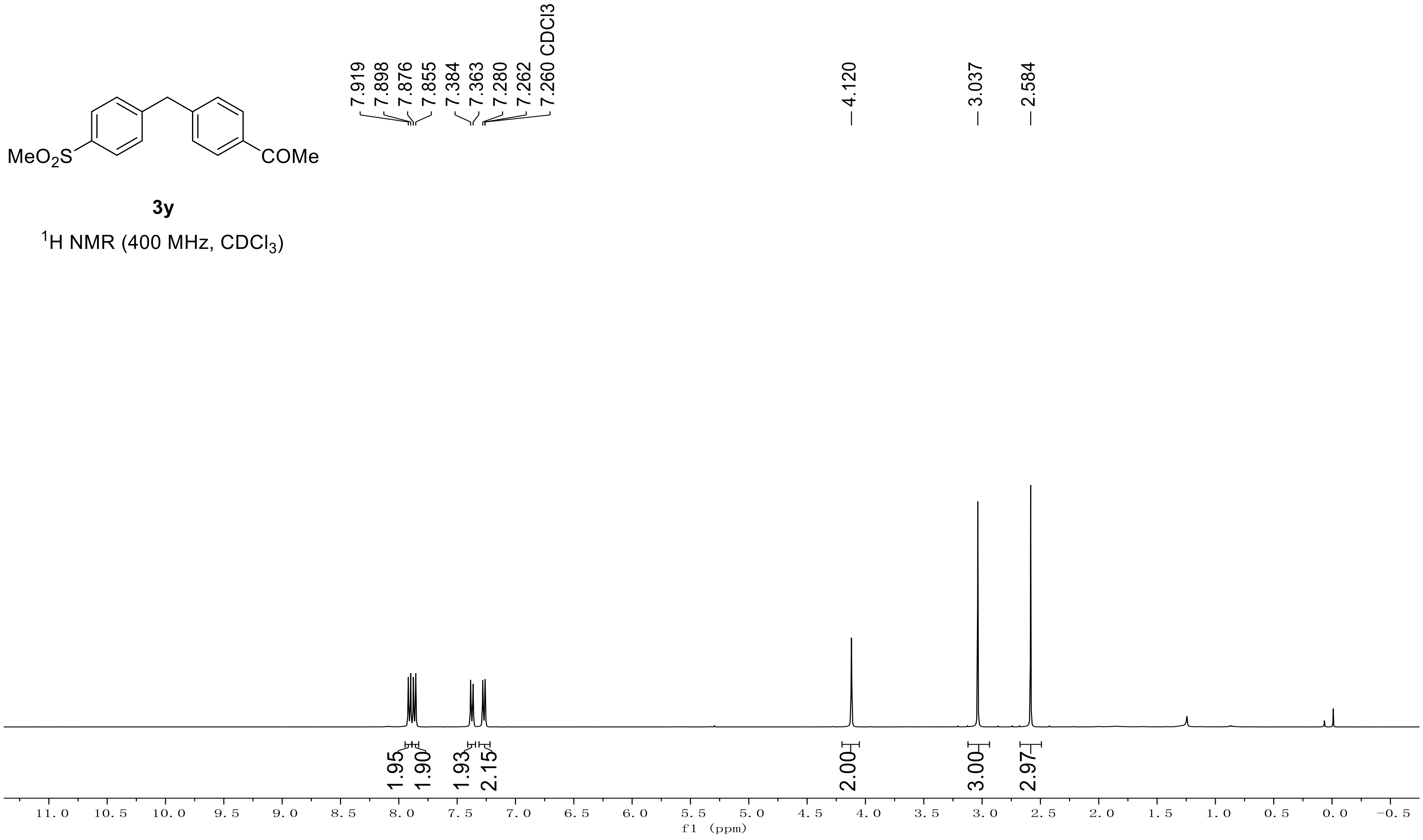
^{1}H NMR (400 MHz, CDCl$_3$)





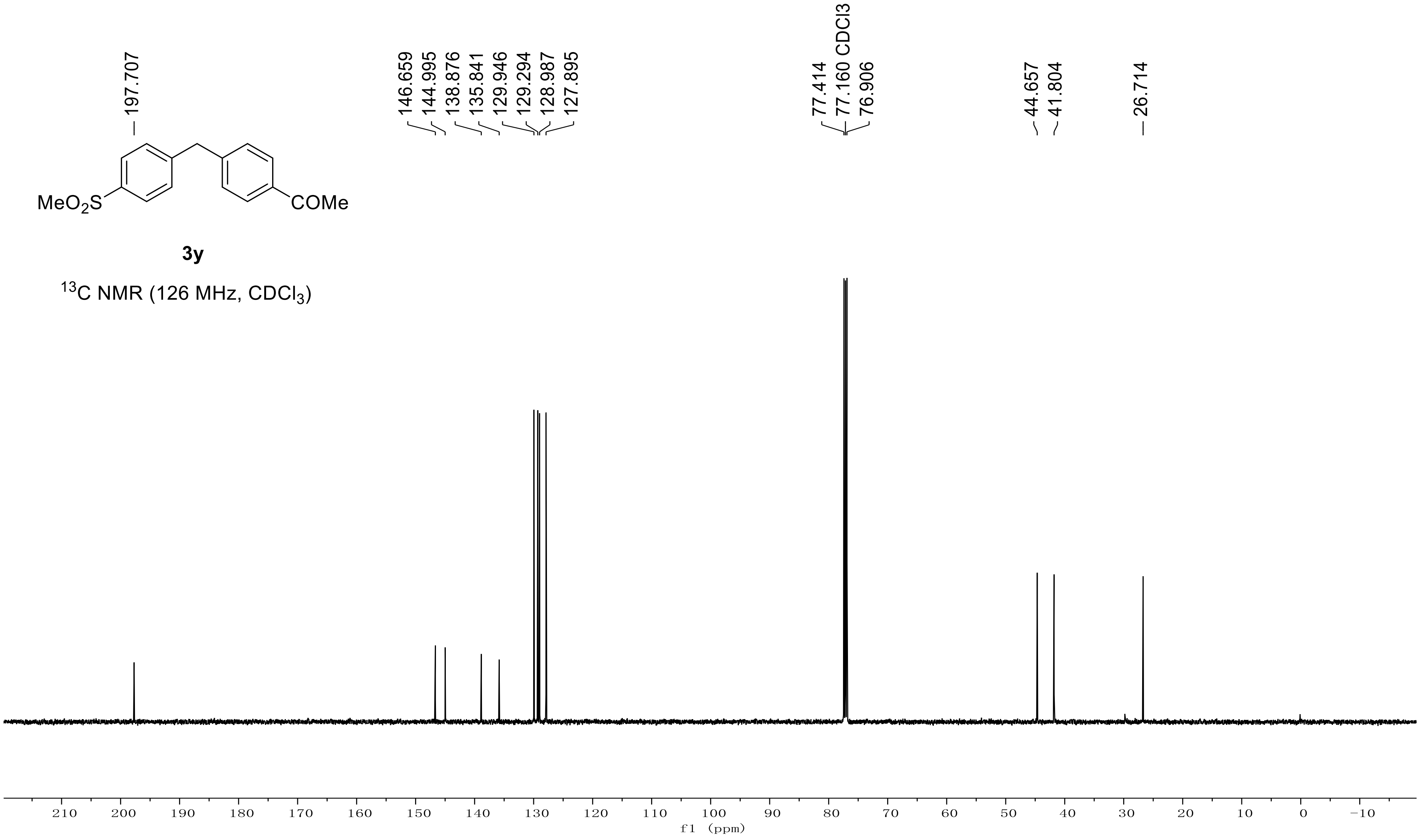
3x

^{13}C NMR (101 MHz, CDCl$_3$)



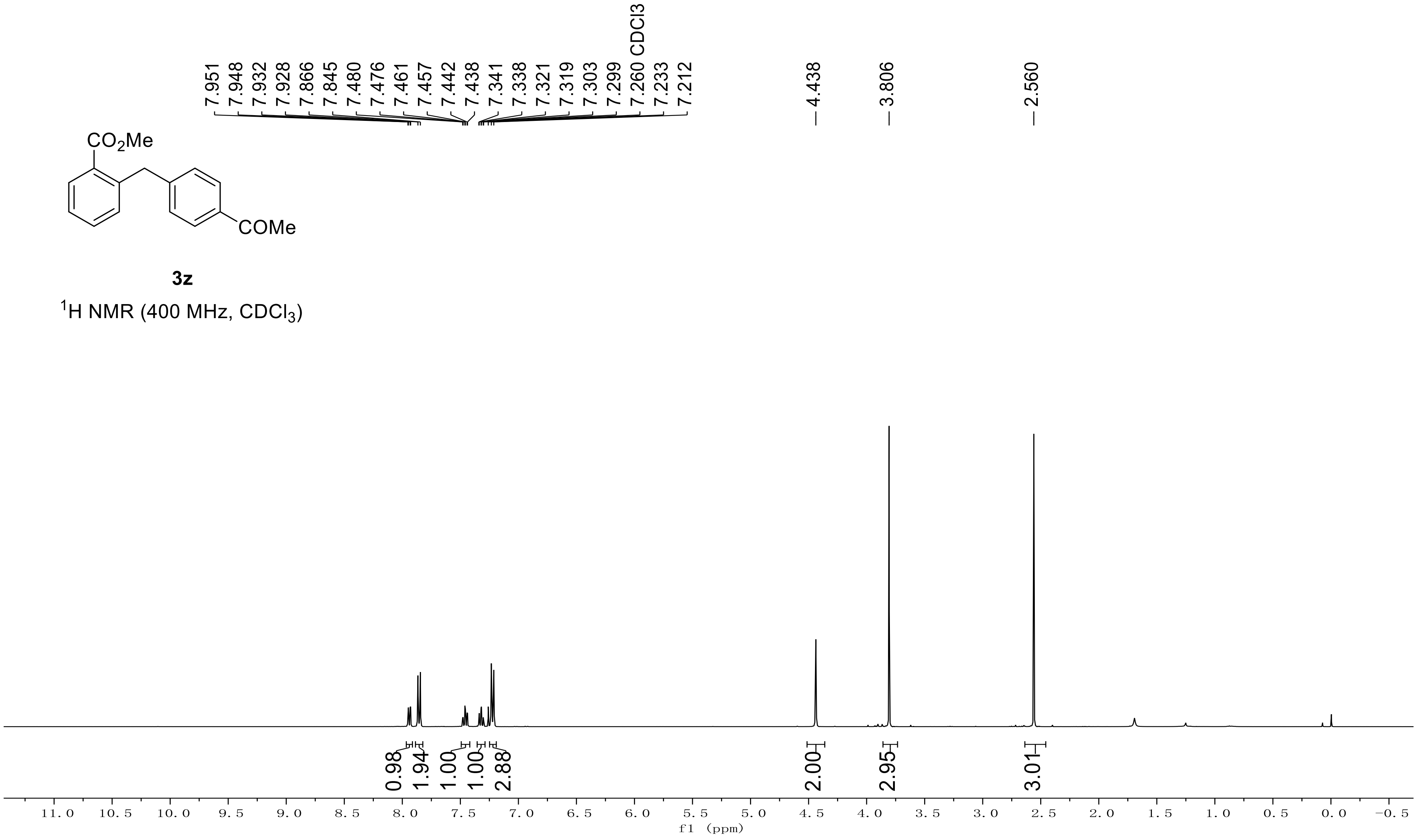
3y

^{1}H NMR (400 MHz, CDCl$_3$)



3y

^{13}C NMR (126 MHz, CDCl$_3$)



3z

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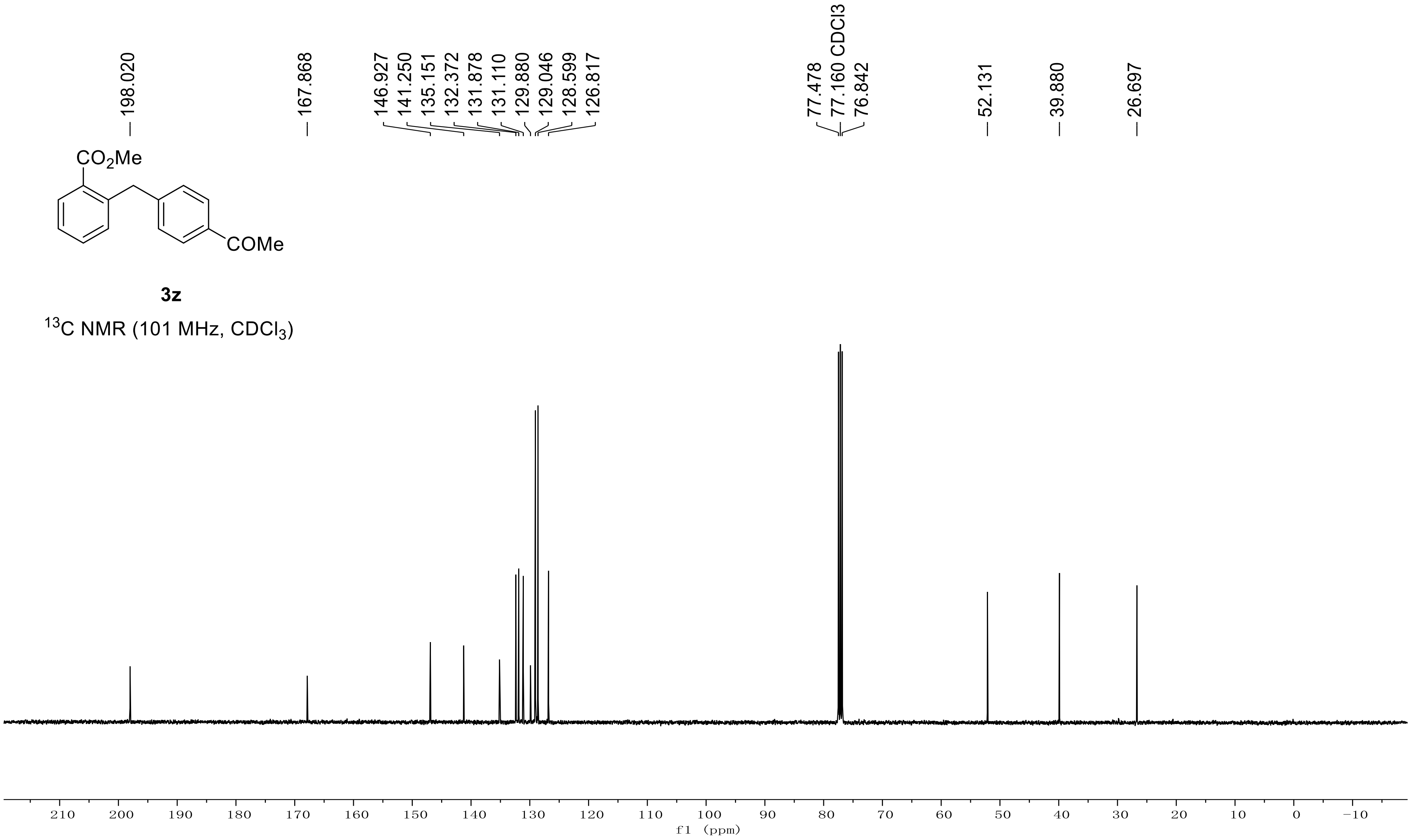

3z

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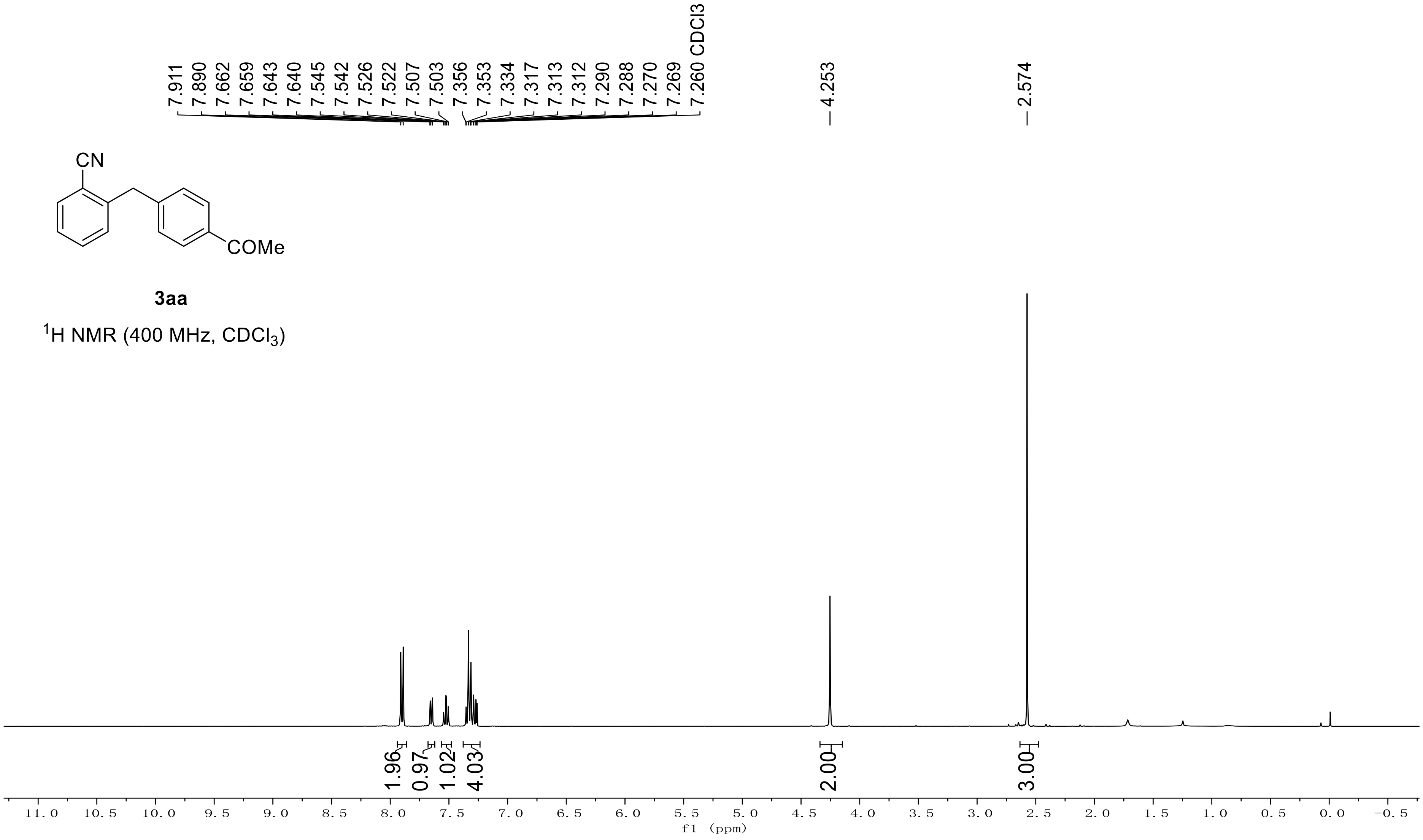
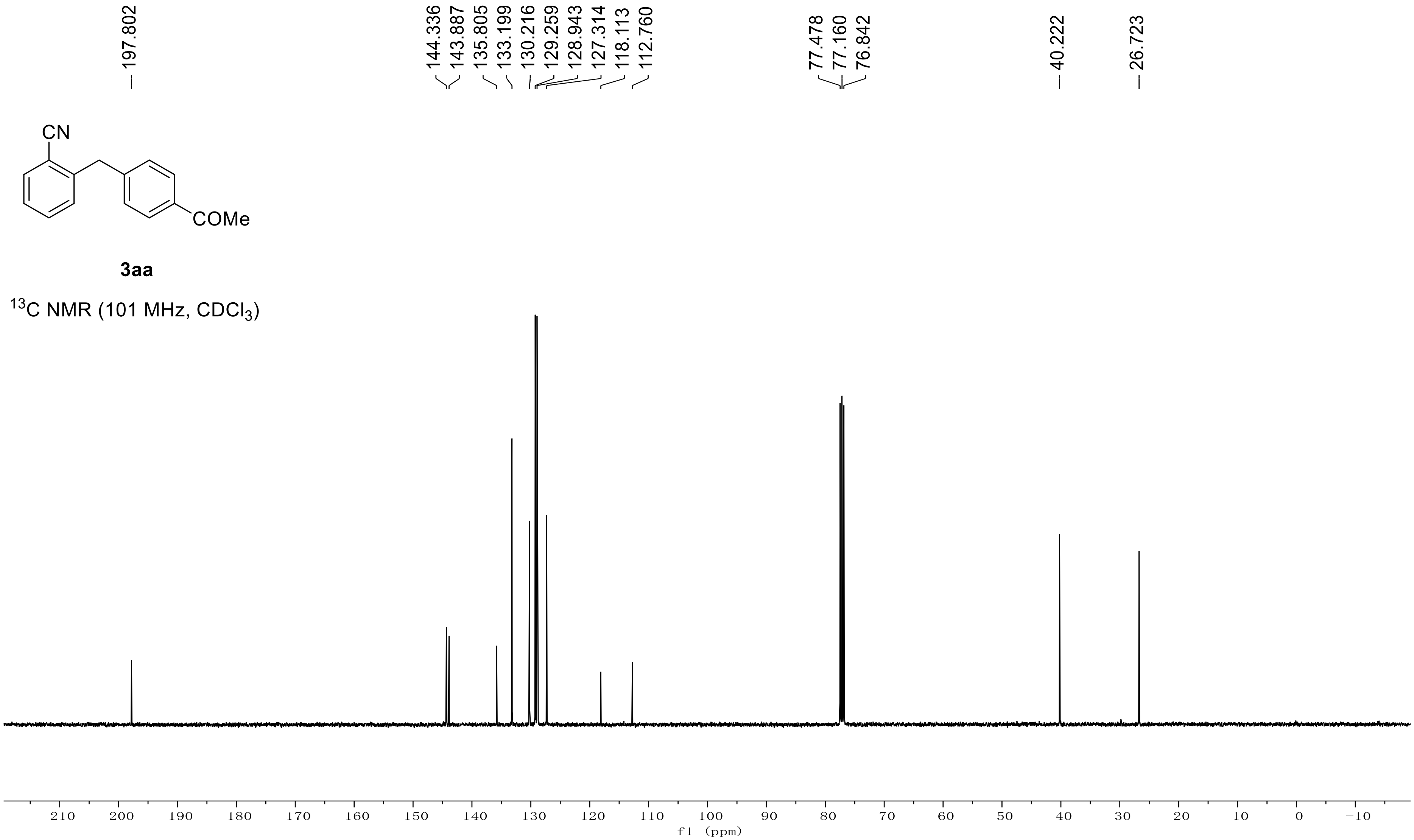


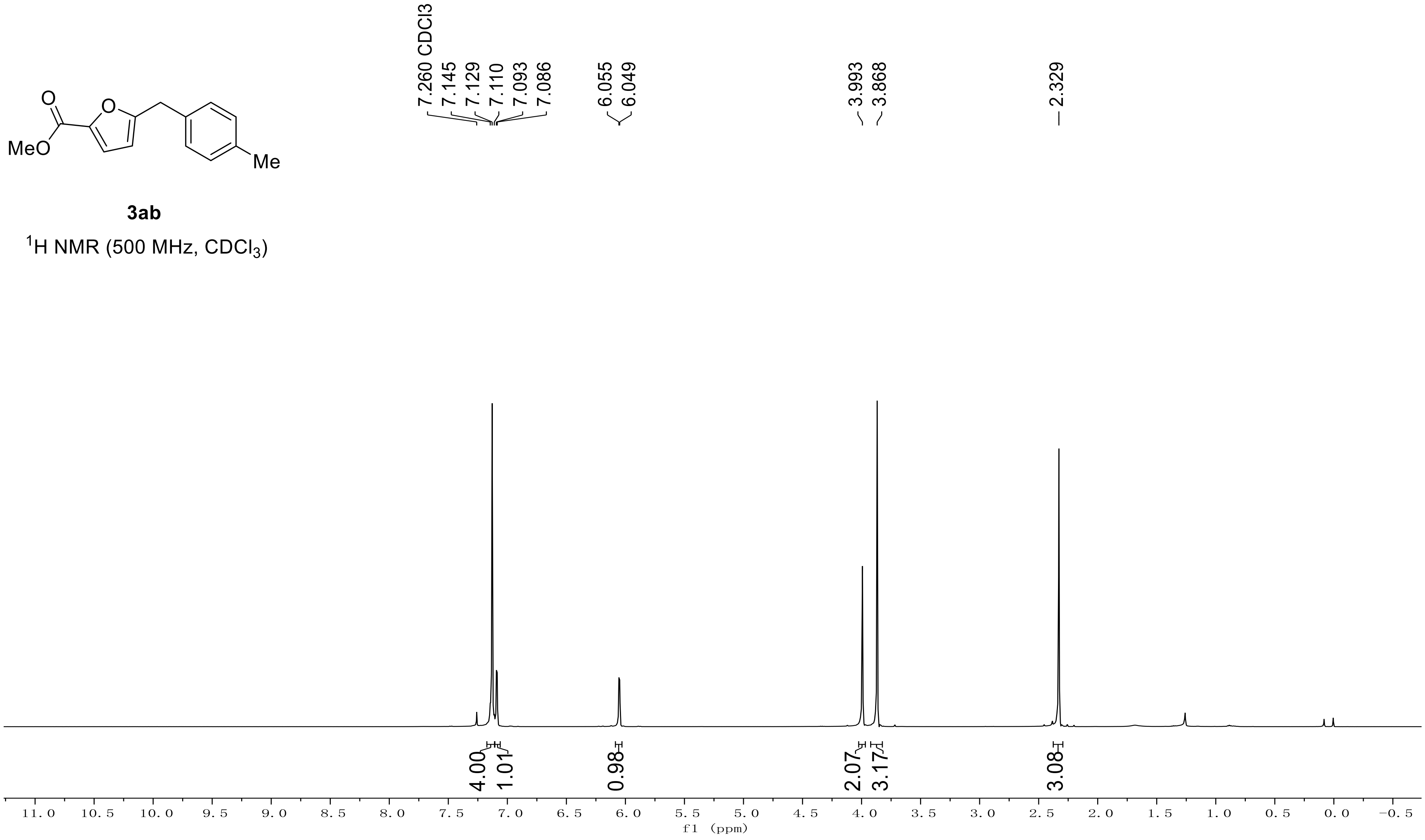
3aa

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



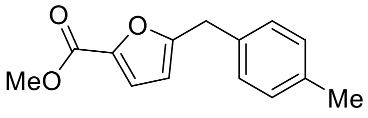
3aa

^{13}C NMR (101 MHz, CDCl$_3$)



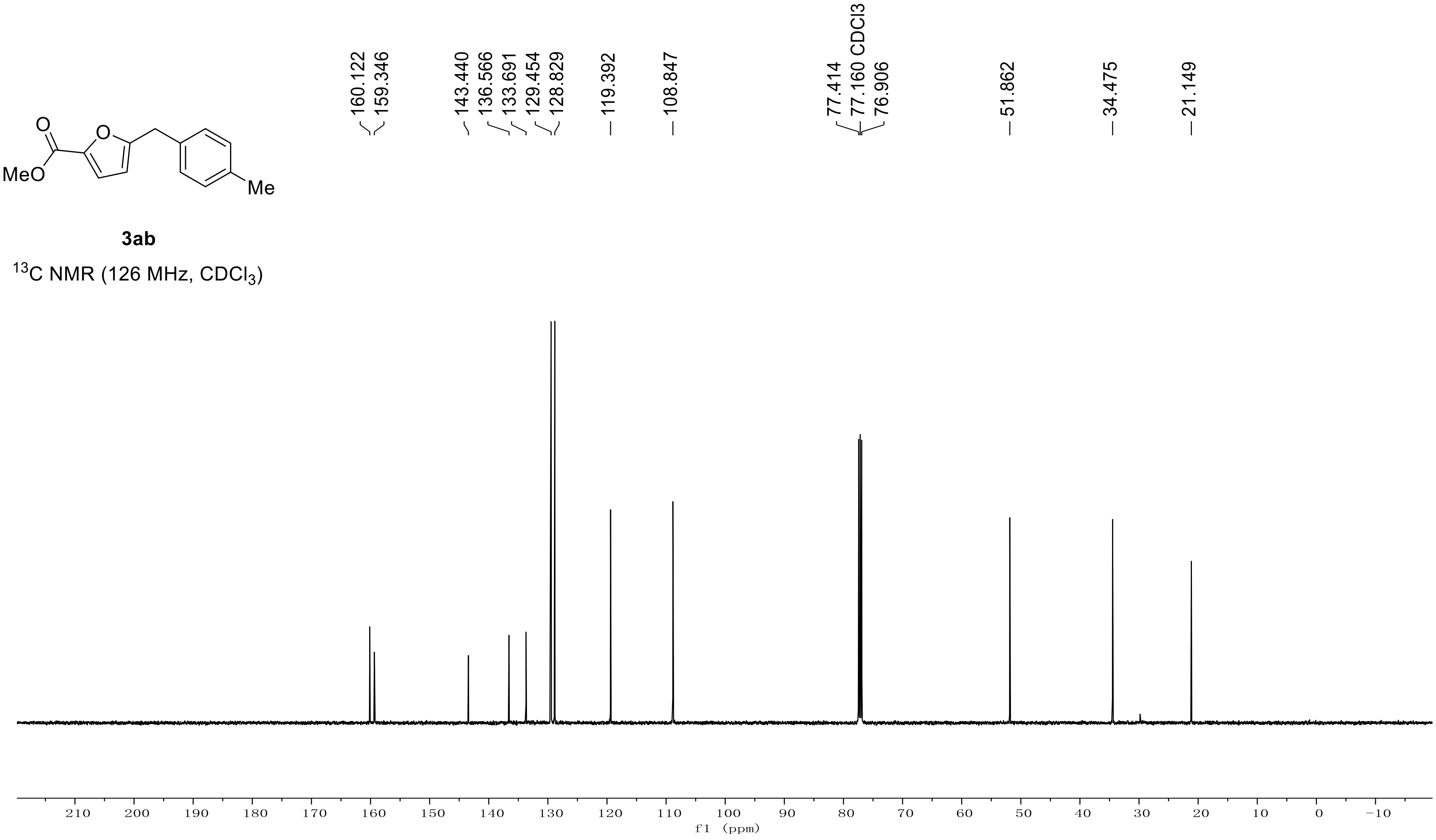
3ab

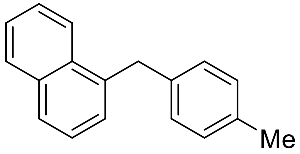
^{1}H NMR (500 MHz, CDCl$_3$)



3ab

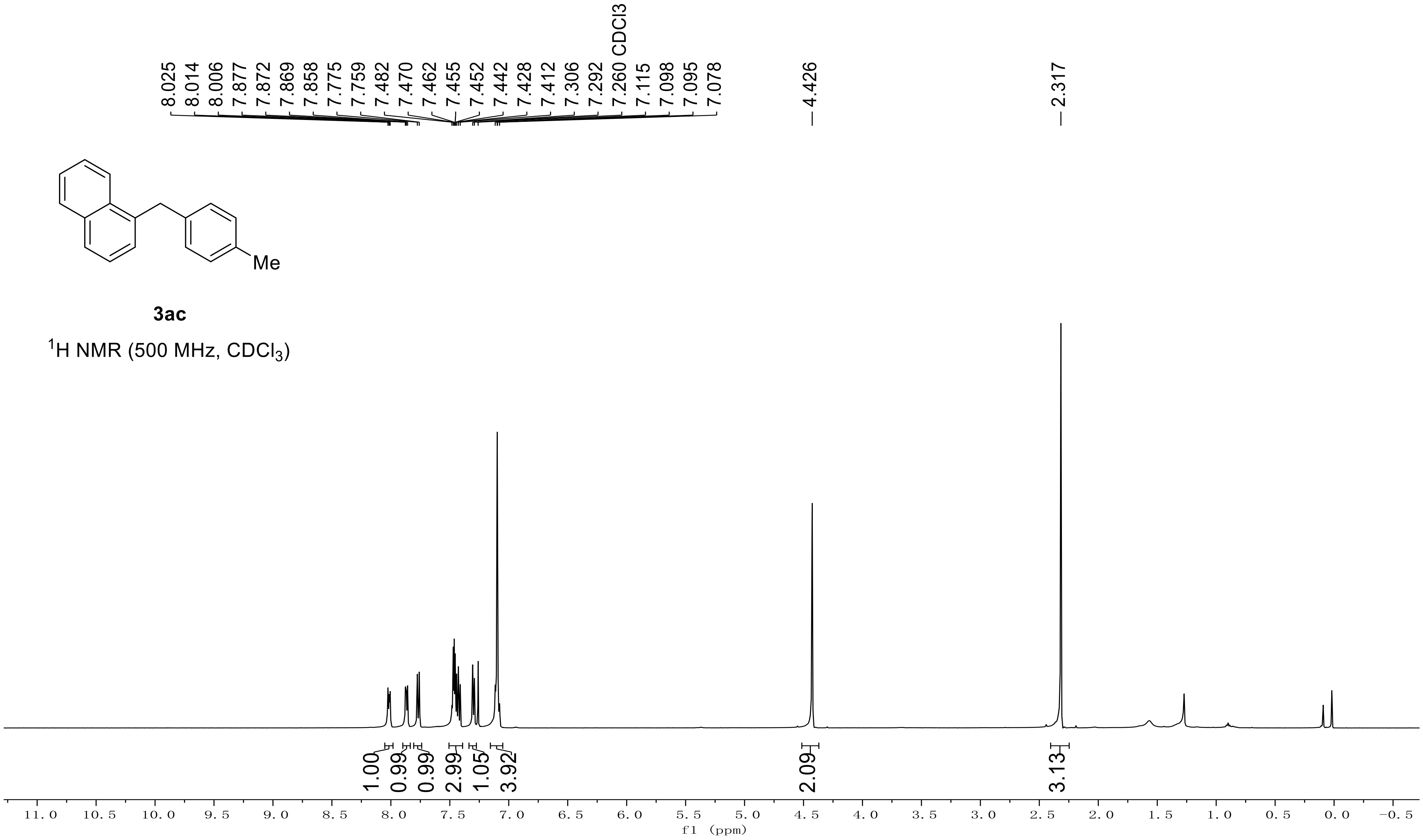
^{13}C NMR (126 MHz, $CDCl_3$)

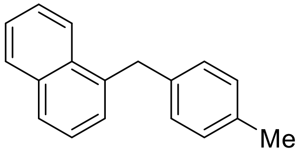




3ac

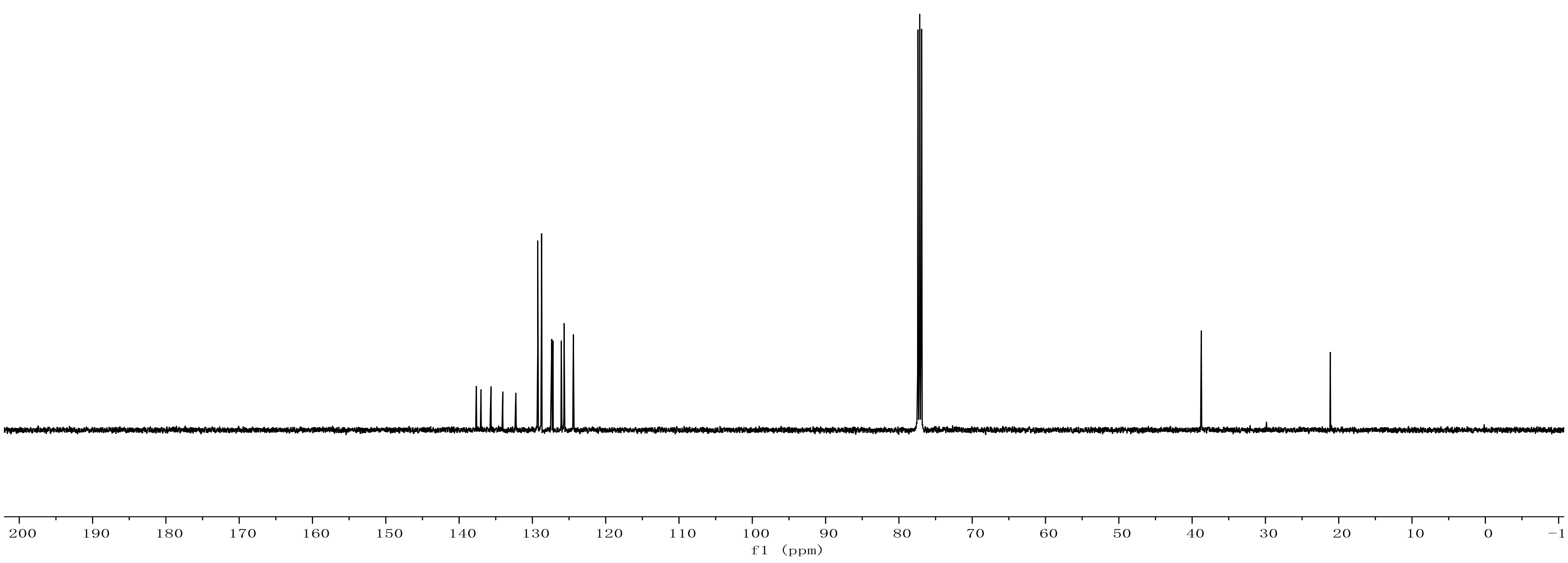
^{1}H NMR (500 MHz, $CDCl_3$)

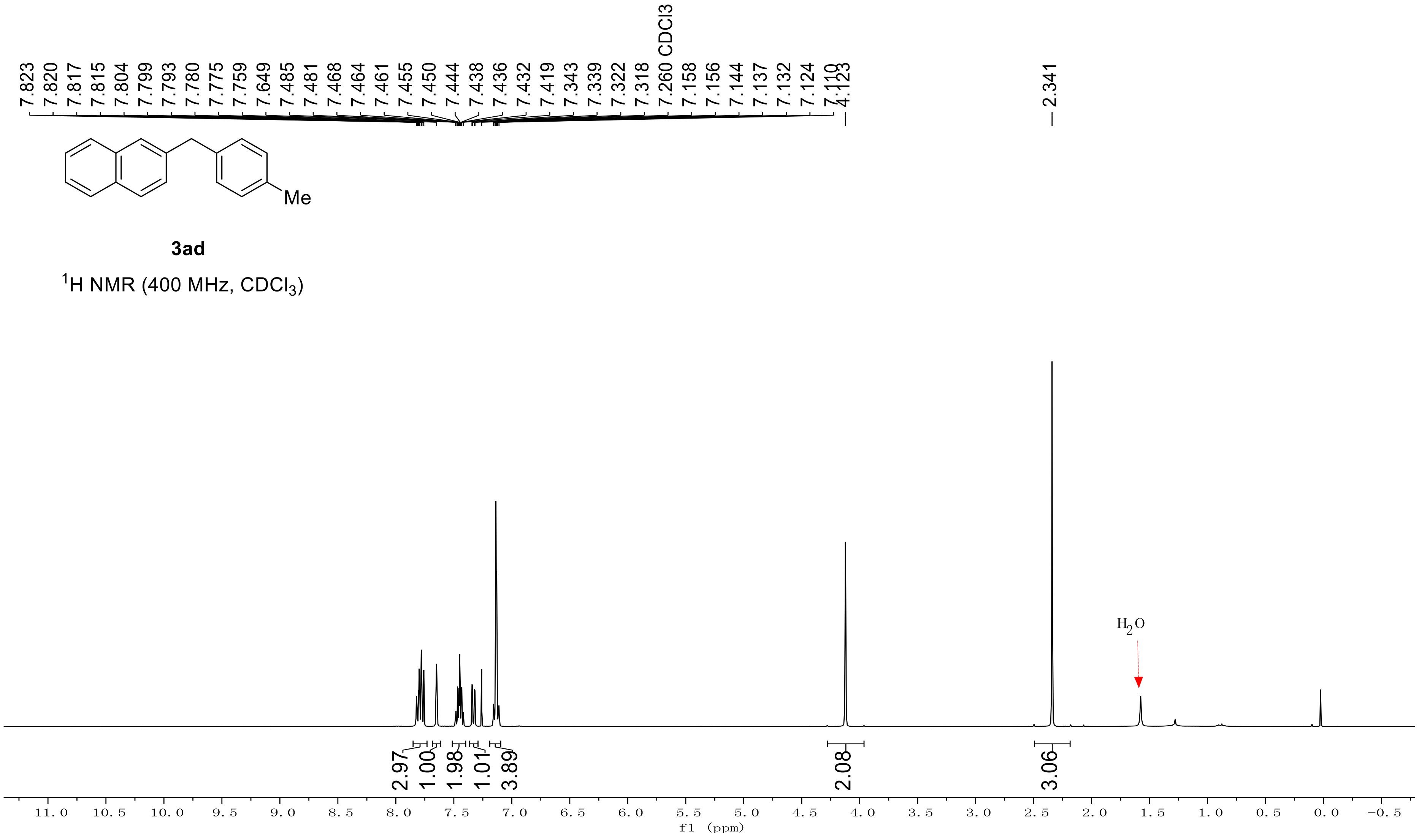




3ac

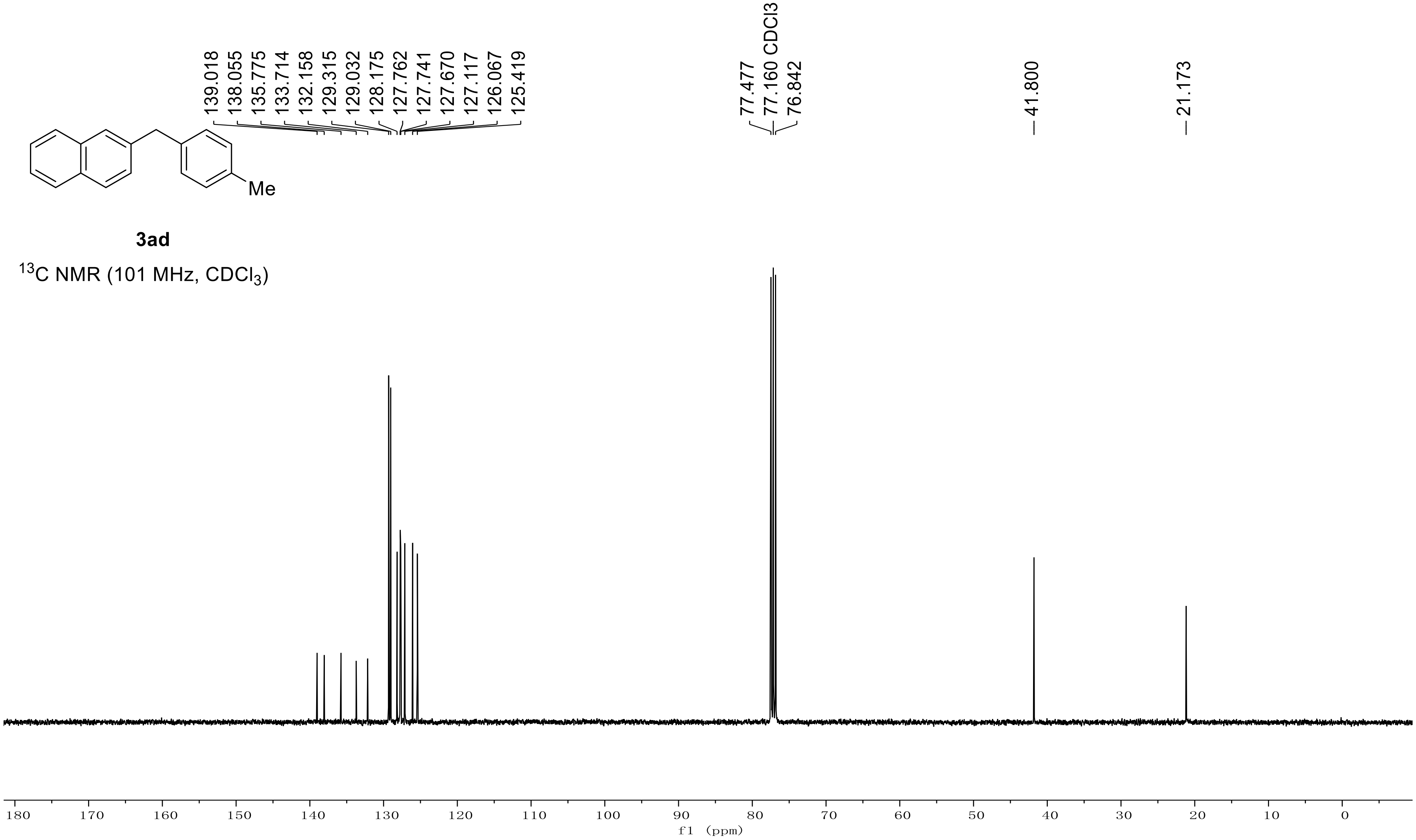
^{13}C NMR (126 MHz, CDCl$_3$)





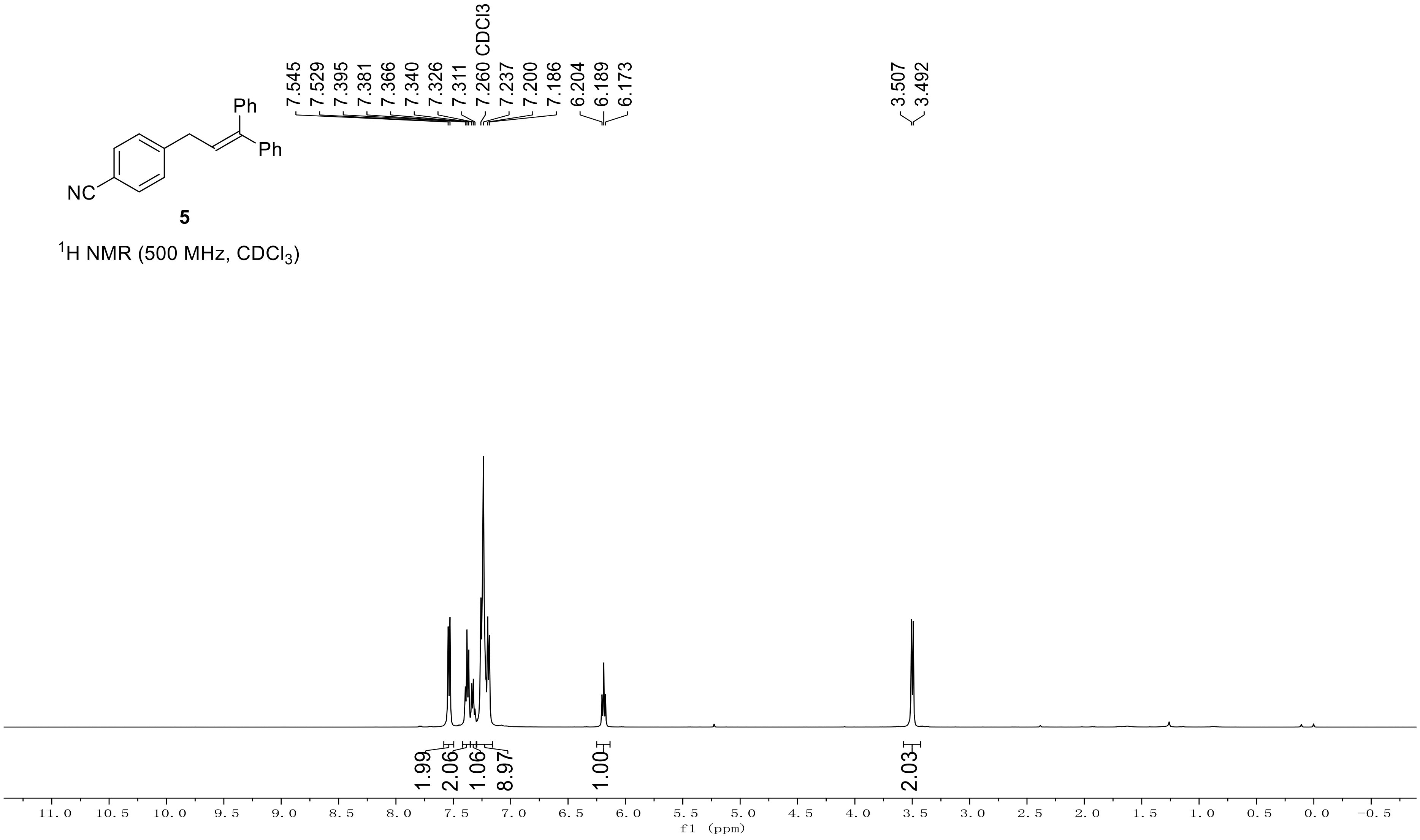
3ad

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



3ad

^{13}C NMR (101 MHz, CDCl$_3$)



5

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

5

^{13}C NMR (126 MHz, $CDCl_3$)