Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Reductive Cross-Coupling to Access C-N Bond from Aryl Halides and Diazoesters under Dual Nickel/Photoredox-Catalyzed Conditions

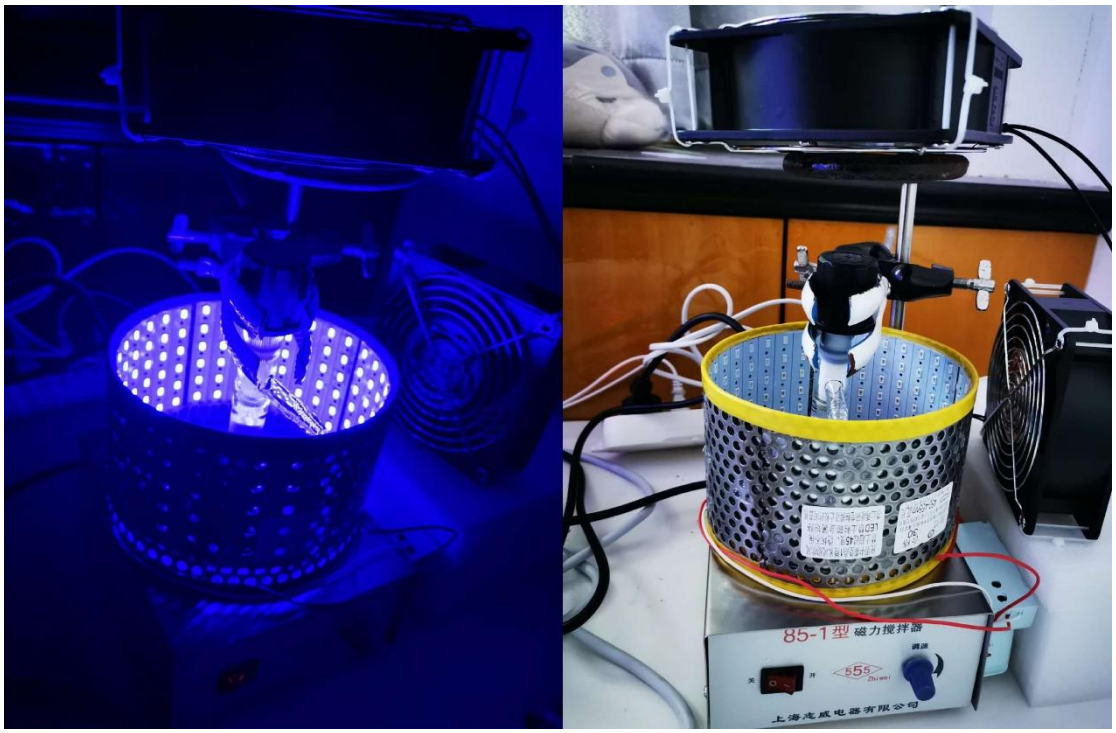
1. General Information

All commercially available compounds were used as received. ^{1}H and ^{13}C spectra were recorded on a Bruker Avance 400, 600 spectrometers, and $CDCl_3$ was purchased from J&K. Chemical shifts (δ) are given in ppm with the internal standards as TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Solvents were dried and purified according to the procedure from 'Purification of Laboratory Chemicals book'. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

2. Light Sources

Reactions were optimized with 30 W blue LED lamps (450-455 nm) purchased from www.taobao.com.
https://item.taobao.com/item.htm?spm=a1z10.3-c.w4002-15754154531.36.2e3cdeabd55EgT&id=603545564757

The Schlenk tube was kept 1-2 cm away from the lights, with cooling fan to keep the reaction temperature at 20-30 °C. A fan was placed 6 cm above the LED lamps for cooling and a second fan was placed in front (**Supplementary Figure S1**).



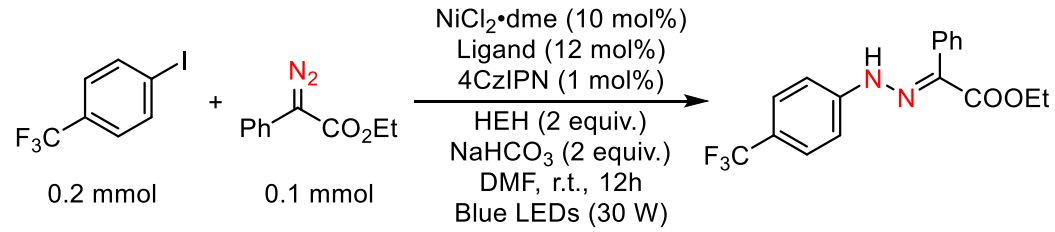
Supplementary Figure S1. Photochemical Setup

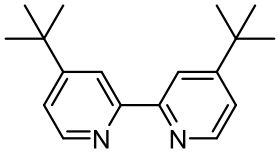
3. Screening Results

The standard condition was listed below and the screening experiments were tested by changing the relevant parameters based on this procedure:

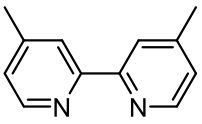
In the nitrogen filled glovebox, a 25 mL oven-dried Schlenk tube with a magnetic bar were charged with nickel catalyst (10 mol%), ligand (12 mol%), base (2.0 equiv.), reductant (2.0 equiv.) and the photocatalyst (0.001 mmol, 1 mol%). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, solvent (2 mL), aryl halide (0.2 mmol) and aryl diazoacetate (0.1 mmol) were added to the reaction vial, then it was immediately set to stir at 800 rpm and irradiated by 30 W blue LEDs for 12 h. The reaction mixture was quenched by saturated NaCl aqueous solution before the internal standard (dodecane) was added to the reaction vial, and extracted with ethyl acetate (2 mL ×2). The crude product was submitted to GC for analysis.

Table S1 screening results on the ligand.

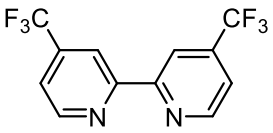




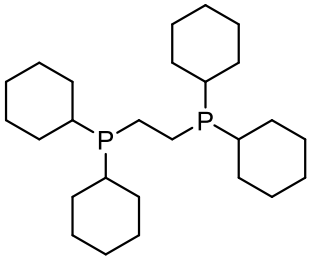
L1 dtbpy
23%



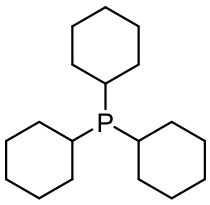
L2
16%



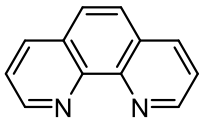
L3
0%



L4
0%

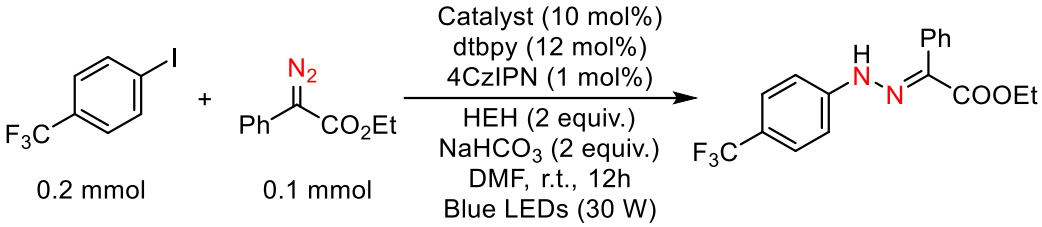


L5
13%



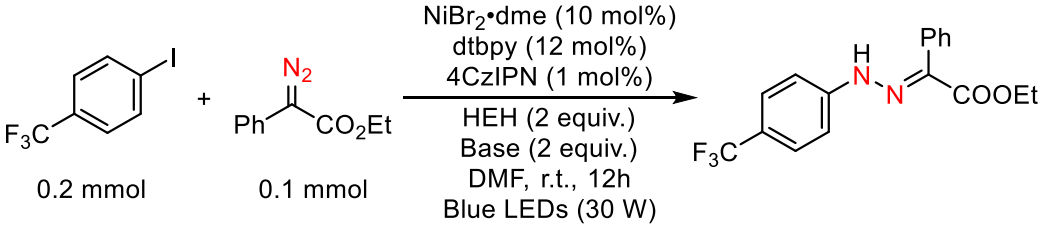
L6 phen
14%

Table S2 screening results on the catalyst.



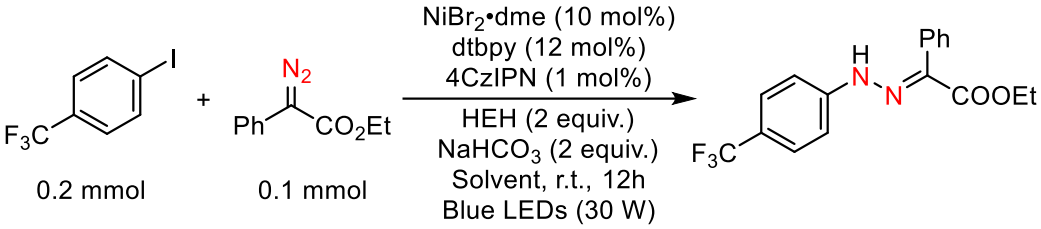
Entry	Catalyst	Yield (%)
1	$Ni(acac)_2$	n.d.
2	NiI_2	n.d.
3	$NiBr_2$·dme	40%
4	$NiCl_2$·dme	23%
5	$Ni(cod)_2$	trace
6	$Ni(OTf)_2$	n.d.

Table S3 screening results on the base.



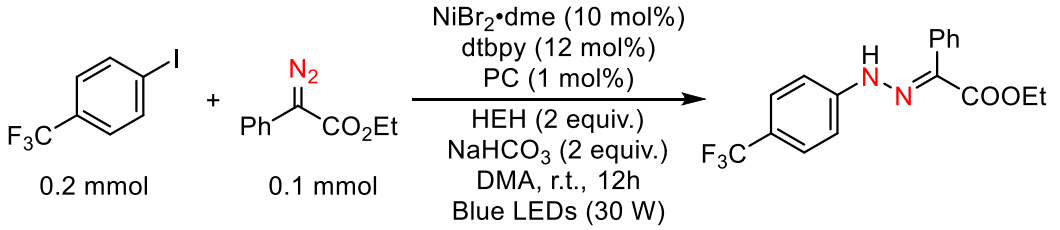
Entry	Base	Yield (%)
1	K_2CO_3	12%
2	K_3PO_4	trace
3	K_2HPO_4	8%
4	Na_2CO_3	20%
5	DIPEA	trace
6	DIPA	trace
7	TMEDA	n.d.
8	Et_3N	n.d.
9	$NaHCO_3$	40%
10	$KHCO_3$	24%
11	Li_2CO_3	10%
12	DABCO	24%
13	KF	trace
14	NaOAc	trace
15	LiOH	12%

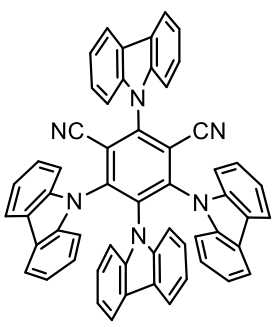
Table S4 screening results on the solvent.



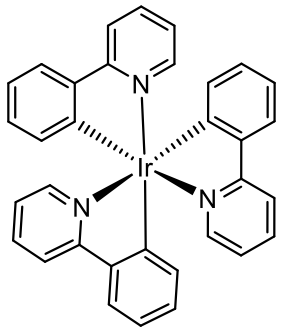
Entry	Solvent	Yield (%)
1	DMF	40%
2	DMA	66%
3	MeCN	trace
4	DMSO	10%
5	DCE	trace
6	DCM	trace
7	1,4-dioxane	trace
8	THF	trace

Table S5 screening results on the photocatalyst.

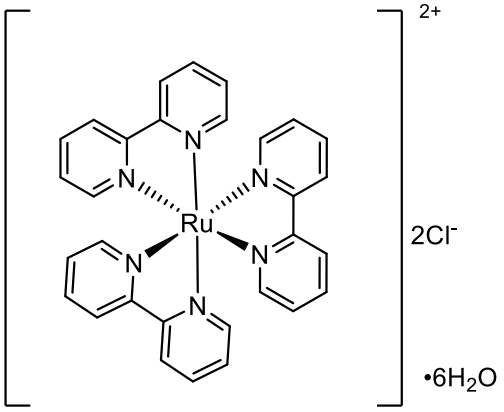




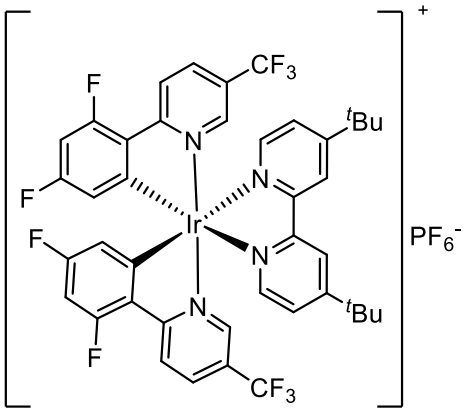
66%



0%

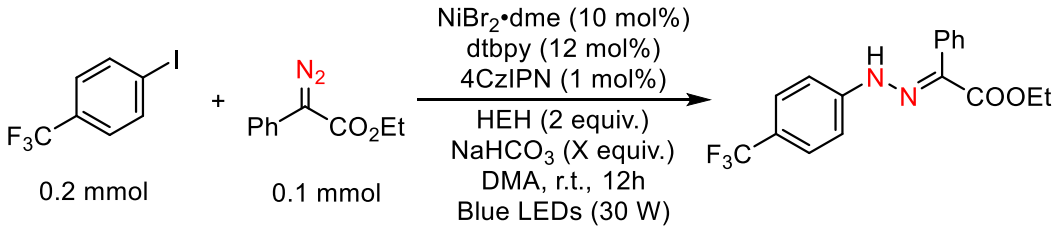


10%



26%

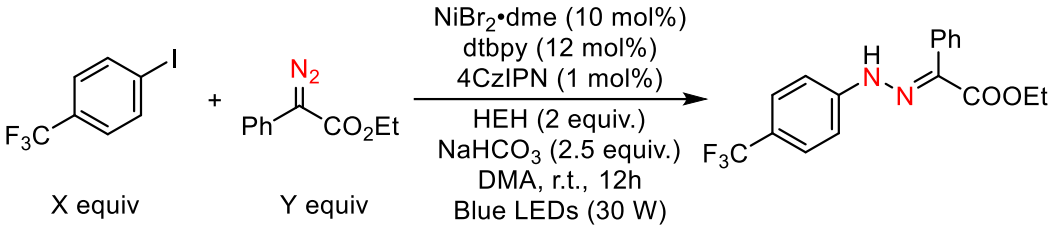
Table S6 screening results on the equivalent of the base.



Entry	X equiv	Yield (%)
1	1.0	9%
2	2.0	66%

3	2.5	69%
4	3.0	65%
5	3.5	60%

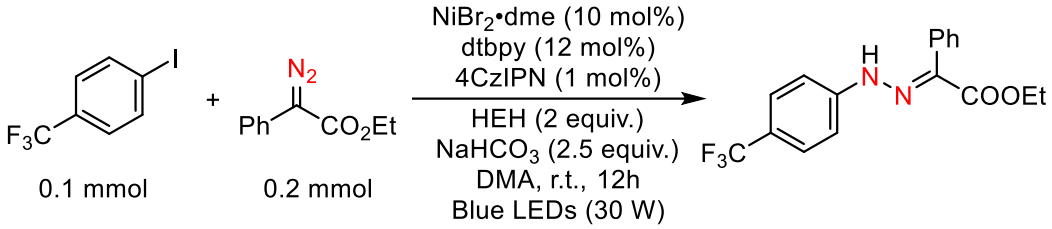
Table S7 screening results on the ratio of the substrate.



X equiv Y equiv

Entry	X:Y	Yield(%)
1	1.0:1.0	16%
2	1.5:1.0	33%
3	2.0:1.0	69%
4	2.5:1.0	69%
5	3.0:1.0	71%
6	4.0:1.0	71%
7	1.0:1.5	23%
8	1.0:2.0	73%
9	1.0:3.0	55%

Table S8 control experiments



0.1 mmol 0.2 mmol

Entry	Change from standard conditionds	Yield (%)
1	None	73%
2	Without Ni	n.d.
3	Without Ligand	10%
4	Without PC	n.d.
5	Without $NaHCO_3$	n.d.
6	Without HEH	n.d.

4. General Procedures

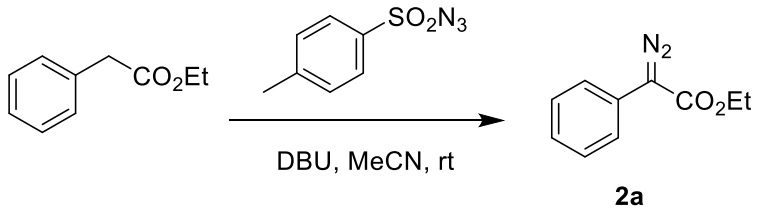
4.1. General procedure for synthesis of hydrazones

In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with $NiBr_2$•DME (0.02 mmol, 10 mol%), dtbpy (0.024 mmol, 12

mol%), $NaHCO_3$ (0.5 mmol, 42.0 mg, 2.5 equiv.),HEH (0.4 mmol, 101.2 mg, 2 equiv.) and 4CzIPN (0.002 mmol, 1 mol%). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, anhydrous DMA (4 mL), aryl halide (0.2 mmol) and aryl diazoacetate (0.4 mmol, 2 equiv.) were added to the reaction vial, then it was immediately set to stir at 800 rpm and irradiated by 30 W blue LEDs for 12 h. The reaction mixture was quenched by saturated NaCl aqueous solution (2 mL) and the aqueous layer was extracted with ethyl acetate (2 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified carefully by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate affording the product.

On 1 mmol scale: In the nitrogen filled glovebox, a 50 mL oven-dried Schlenk tube with a magnetic bar was charged with $NiBr_2$•DME (0.1 mmol, 10 mol%), dtbpy (0.12 mmol, 12 mol%), $NaHCO_3$ (2.5 mmol, 210.0 mg, 2.5 equiv.), HEH (2 mmol, 506.0 mg, 2 equiv.) and the 4CzIPN (0.01 mmol, 1 mol%). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, anhydrous DMA (20 mL), aryl halide (1.0 mmol) and aryl diazoacetate (2.0 mmol, 2 equiv.) were added to the reaction vial, then it was immediately set to stir at 800 rpm and irradiated by 30 W blue LEDs for 30 h. The reaction mixture was quenched by saturated NaCl aqueous solution (10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified carefully by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate affording the product **3a** (40% isolated yield, 134.8 mg).

4.2. Preparation of diazoacetates[1]

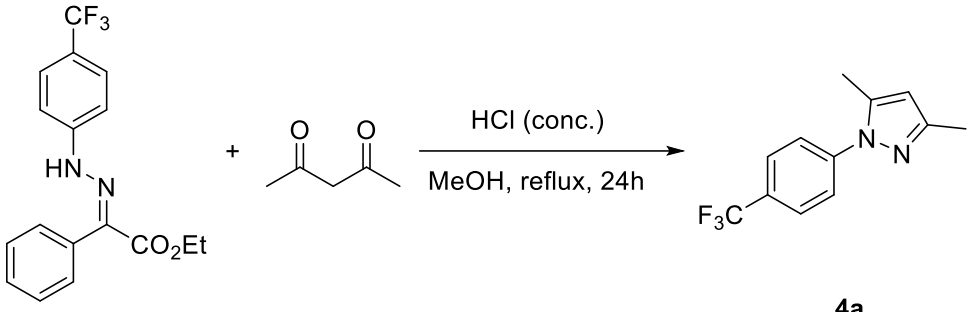


2a

To a solution of ethyl phenylacetate (1.64 g, 10 mmol) and tosyl azide (2.37 g, 12 mmol) in dry CH_3CN (20 mL) was added 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.79 mL, 13 mmol) dropwise at 0 °C. Then the mixture was stirred overnight at room temperature. The reaction was then quenched with saturated NH_4Cl aqueous solution, followed by extraction with ethyl acetate (2×20 mL). The combined organic extracts

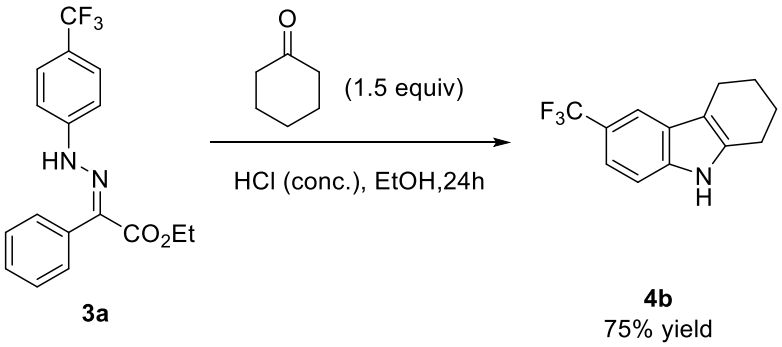
were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether:ethyl aceate = 30:1) to give the product **2a** as a yellow oil (1.76 g, 93% yield). The other *α*-aryl *α*-diazoesters were prepared by the similar procedure.

4.3. Procedure for synthesis of compound 4a



To a 25 mL round bottomed flask equipped with a condenser and a magnetic stirrer was added **3a** (0.1 mmol, 33.6 mg), 2.0 mL methanol (0.10 M), acetylacetone (51 μL, 0.975 g/mL, 0.5 mmol), and 120 μL conc. HCl. The reaction mixture was warmed up to 70 °C, and stirred for 24 h. After cooling to room temperature, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate to afford the desired product **4a** (20.3 mg, 85% yield). ^{1}H NMR was in agreement with the literature[2].

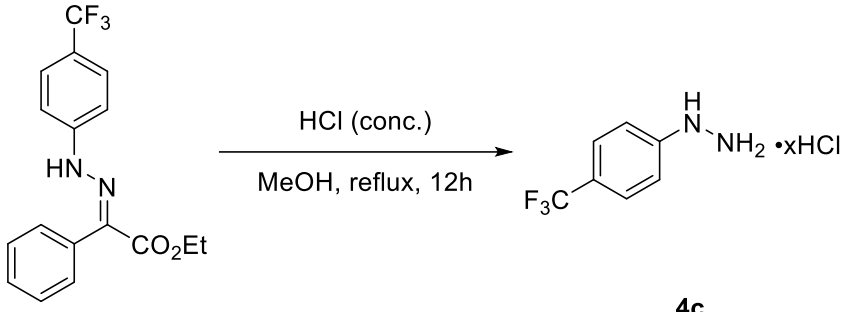
4.4. Procedure for synthesis of compound 4b



To a 25 mL round bottomed flask equipped with a condenser and a magnetic stirrer was added **3a** (0.1 mmol, 33.6mg), 16 μL (0.947 g/mL, 0.15 mmol) of cyclohexanone, 100 μL of conc. HCl, and 3 mL of anhydrous ethanol. The reaction mixture was warmed up to 85 °C, and stirred for 24 h until complete conversion (monitored by TLC). After cooling to room temperature, the reaction mixture was quenched with water (10 mL)

and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate to afford the desired product **4b** (18.0 mg, 75% yield). ^{1}H NMR was in agreement with the literature[3].

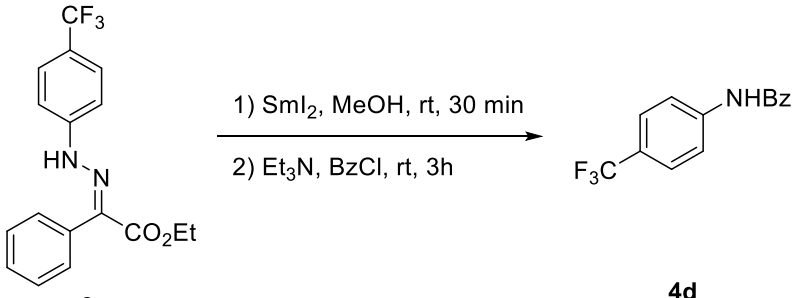
4.5. Procedure for synthesis of compound 4c



3a **4c**
62% yield

To a 25 mL round-bottom flask equipped with a condenser and a magnetic stirrer were added **3a** (0.1mmol, 33.6mg) and 3 mL of MeOH. Then 100 μL of conc. HCl was added slowly. The reaction mixture was warmed up to 80 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was quenched with water (5 mL). And ethyl acetate (10 mL × 3) was added, the solvent was removed under reduced pressure. After H_2O was removed, the colorless solid precipitated out of the solvent. The solid residues were washed three times with Et_2O (10 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate to afford the desired product **4c** (13.1 mg, 62% yield, beige solid). ^{1}H NMR was in agreement with the literature[4].

4.6. Procedure for synthesis of compound 4d

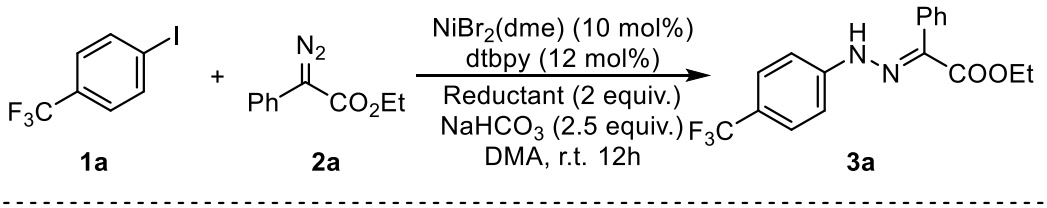


3a **4d**
65% yield

Step A : To a 25 mL round bottomed flask equipped with a magnetic stirrer, it was vacuumed and flushed with N_2 and repeated for three times. To the flask, 33.6mg (0.1

mmol) of **3a**, 3 mL of anhydrous MeOH was added. Then, a solution of samarium(II) iodide (5 mL of a 0.1 M solution in THF) was added rapidly dropwise. The solution maintained blue for a few minutes. After complete addition, the reaction was allowed to stir for 30 min. The solution was concentrated to afford a yellow oil which was used for the next step without further purification. **Step B :** To the above oil, 3 mL (0.1 M) of THF, 35 μL (1.211 g/mL, 0.3 mmol) of BzCl, and 54 μL (0.728 g/mL, 0.4 mmol) of Et_3N were added, followed by 3 h stirring. The mixture was quenched with water (10 mL) and then extracted with EtOAc (10 mL × 4). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate to afford the desired product **4d** (17.2 mg, 65% yield). ^{1}H NMR was in agreement with the literature[5].

4.7. Comparison reactions



'Standard condition'	Zn	Mn	B_2Pin_2 LiOMe	Me_2N NMe_2 Me_2N NMe_2
65% (*E*/*Z*>20:1)	0	0	0	0

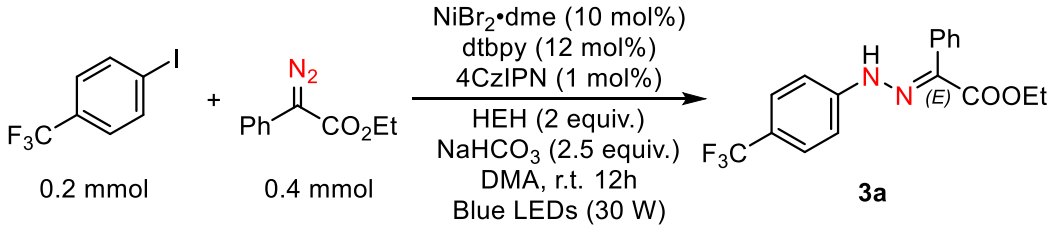
In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with $NiBr_2$•DME (0.02 mmol, 10 mol%), dtbpy (0.024 mmol, 12 mol%), $NaHCO_3$ (0.5 mmol, 42.0 mg, 2.5 equiv.), HEH (0.4 mmol, 101.2 mg, 2 equiv.) and 4CzIPN (0.002 mmol, 1 mol%). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, anhydrous DMA (4 mL), aryl halide (0.2 mmol) and aryl diazoacetate (0.4 mmol, 2 equiv.) were added to the reaction vial, then it was immediately set to stir at 800 rpm and irradiated by 30 W blue LEDs for 12 h. Upon completed, the mixture was diluted with EtOAc and n-Dodecane as a GC internal standard was added. The yield was determined by GC analysis.

4.8. Origin of Z/E-selectivity: time study

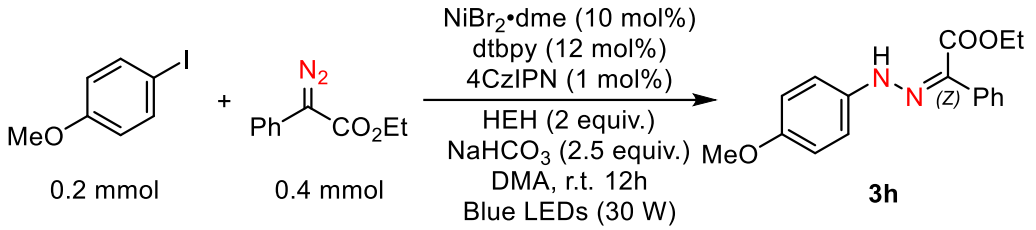
According to General Procedure (**SI 4.1**), the reaction was stopped at different time points. The yield was determined by ^{1}H NMR with use CH_2Br_2 as an internal

standard. Z:E ratios were determined using crude products via ^{1}H NMR.

Table S9 time study

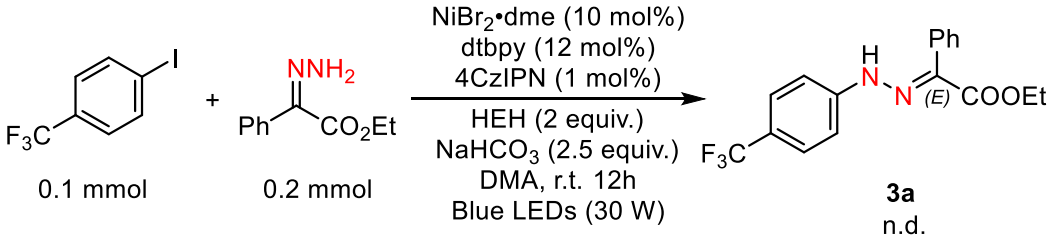


Entry	Time	Yield (%)	E:Z(**3a**)
1	4 hour	28	1:2
2	8 hour	45	3:1
3	12 hour	70	>20:1



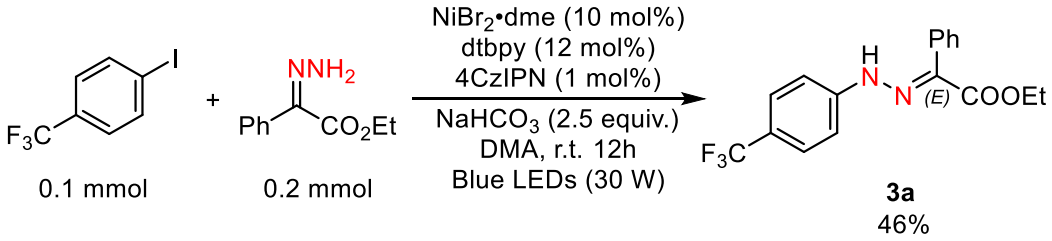
Entry	Time	Yield (%)	Z:E(**3h**)
1	4 hour	18	2:1
2	8 hour	33	16:1
3	12 hour	54	>20:1

5. Mechanism Studies.

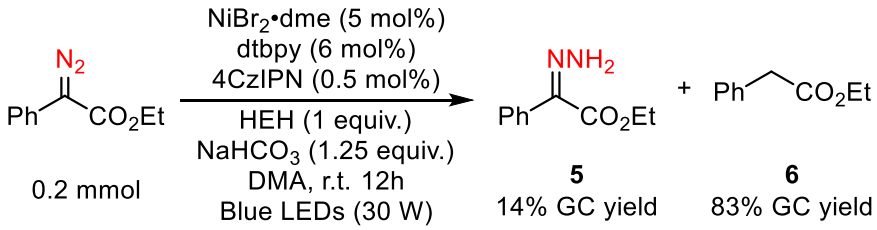


In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with $NiBr_2$•DME (0.01 mmol, 10 mol%), dtbpy (0.012 mmol, 12 mol%), $NaHCO_3$ (0.25 mmol, 21.0 mg, 2.5 equiv.),HEH (0.2 mmol, 50.6 mg, 2 equiv.) and 4CzIPN (0.001 mmol, 1 mol%). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, anhydrous DMA (2 mL), aryl halide (0.1 mmol) and *E*-hydrazine (0.2 mmol, 2 equiv.) were added to the reaction vial, then it was immediately set to stir at 800 rpm and irradiated by 30 W blue LEDs for 12 h. The reaction mixture was quenched by saturated NaCl aqueous solution before the internal

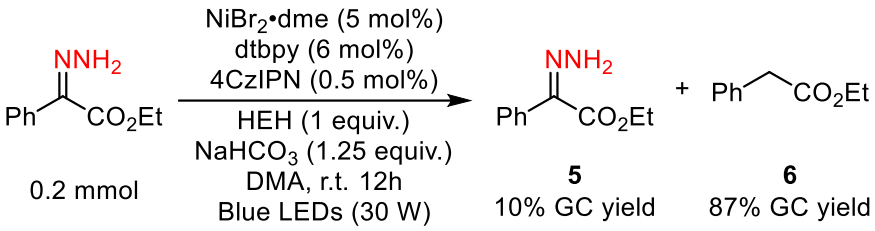
standard (dodecane) was added to the reaction vial, and extracted with ethyl acetate (2 mL ×2). The crude product was submitted to GC for analysis.



In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with $NiBr_2$•DME (0.01 mmol, 10 mol%), dtbpy (0.012 mmol, 12 mol%), $NaHCO_3$ (0.25 mmol, 21.0 mg, 2.5 equiv.) and 4CzIPN (0.001 mmol, 1 mol%). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, anhydrous DMA (2 mL), aryl halide (0.1 mmol) and *E*-hydrazine (0.2 mmol, 2 equiv.) were added to the reaction vial, then it was immediately set to stir at 800 rpm and irradiated by 30 W blue LEDs for 12 h. The reaction mixture was quenched by saturated NaCl aqueous solution (2 mL) and the aqueous layer was extracted with ethyl acetate (2 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified carefully by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate affording the product **3a** (30.9 mg, 46% yield, white solid).

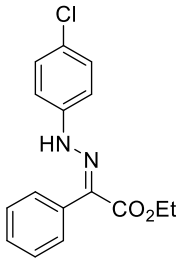


In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with $NiBr_2$•DME (0.01 mmol, 5 mol%), dtbpy (0.012 mmol, 6 mol%), $NaHCO_3$ (0.25 mmol, 21.0 mg, 1.25 equiv.),HEH (0.2 mmol, 50.6 mg, 1 equiv.) and 4CzIPN (0.001 mmol, 0.5 mol%). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, anhydrous DMA (2 mL), aryl diazoacetate (0.2 mmol) were added to the reaction vial, then it was immediately set to stir at 800 rpm and irradiated by 30 W blue LEDs for 12 h. The reaction mixture was quenched by saturated NaCl aqueous solution before the internal standard (dodecane) was added to the reaction vial, and extracted with ethyl acetate (2 mL ×2). The crude product was submitted to GC for analysis.

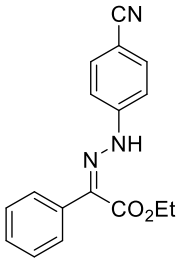


In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with $NiBr_2$•DME (0.01 mmol, 5 mol%), dtbpy (0.012 mmol, 12 mol%), $NaHCO_3$ (0.25 mmol, 21.0 mg, 1.25 equiv.),HEH (0.2 mmol, 50.6 mg, 1 equiv.) and 4CzIPN (0.001 mmol, 0.5 mol%). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, anhydrous DMA (2 mL), *E*-hydrazine (0.2 mmol) were added to the reaction vial, then it was immediately set to stir at 800 rpm and irradiated by 30 W blue LEDs for 12 h. The reaction mixture was quenched by saturated NaCl aqueous solution before the internal standard (dodecane) was added to the reaction vial, and extracted with ethyl acetate (2 mL ×2). The crude product was submitted to GC for analysis.

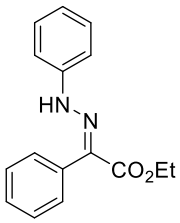
6. The Characterization of the New Products



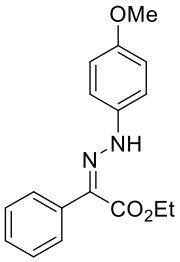
3c



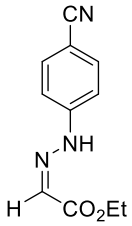
3d



3g

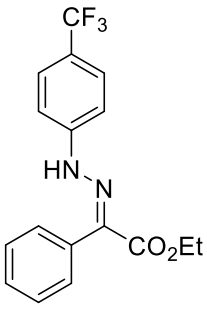


3h



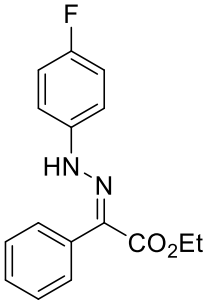
3y

Compounds **3c**[6], **3d**[7], **3g**[8], **3h**[7], **3y**[9] were synthesized according to General Procedure (**SI 4.1**), and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate. The spectral data match those previously reported.



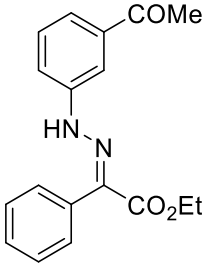
3a

The title compound **3a** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (43.6 mg, 65% yield, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.55 (m, 5H), 7.40 – 7.30 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.14, 145.35, 136.64, 129.90, 129.56, 129.44, 128.84, 126.62 (q, *J* = 3.8 Hz), 123.86 (q, *J* = 32.7 Hz), 121.65 (q, *J* = 273.2 Hz), 113.73, 61.53, 14.27. HRMS: m/z (ESI) calculated $[M+Na]^+$:359.0983, found: 359.0980.



3b

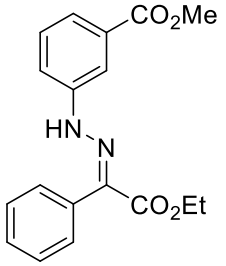
The title compound **3b** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (34.8 mg, 61% yield, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.61 – 7.45 (m, 3H), 7.39 – 7.30 (m, 2H), 7.13 – 7.04 (m, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.41, 158.44 (d, *J* = 239.9 Hz), 139.01, 134.57, 129.82, 129.63, 129.49, 128.99, 115.92 (d, *J* = 22.8 Hz), 115.17 (d, *J* = 7.9 Hz), 61.30, 14.32. HRMS: m/z (ESI) calculated $[M+Na]^+$:309.1015, found: 309.1010.



3e

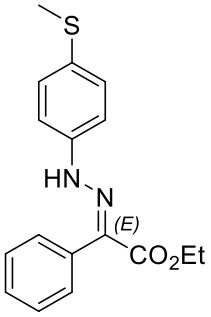
The title compound **3e** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (43.1 mg, 66% yield, yellow solid). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.59 – 7.49 (m, 6H), 7.42 – 7.38 (m, 1H), 7.36 – 7.33 (m, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

197.9, 164.3, 143.1, 138.0, 135.7, 129.8, 129.7, 129.6, 129.6, 128.9, 122.2, 118.5, 113.3, 61.4, 26.7, 14.3. HRMS: m/z (ESI) calculated $[M+Na]^+$:333.1215, found: 333.1197.

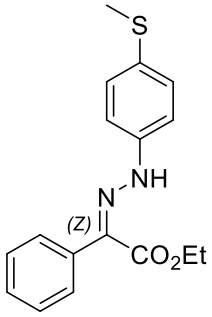


3f

The title compound **3f** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (43.9 mg, 67% yield, yellow solid). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.40 – 7.32 (m, 3H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 164.3, 142.9, 135.6, 131.1, 129.7, 129.6, 129.5, 129.5, 128.9, 123.1, 118.3, 114.9, 61.4, 52.1, 14.3. HRMS: m/z (ESI) calculated $[M+Na]^+$:349.1164, found: 349.1151.



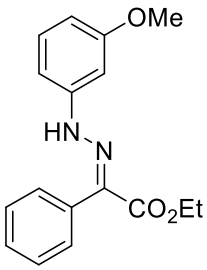
E**-3i**



Z**-3i**

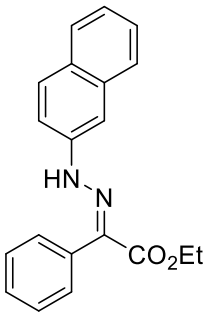
The title compound **3i** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (33.3 mg, 53% yield, E/Z= 3:1, yellow solid). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.44 (s, 0.24H), 8.08 (s, 0.76H), 7.67 – 7.63 (m, 0.50H), 7.54 (t, *J* = 7.5 Hz, 1.55H), 7.51 – 7.46 (m, 0.77H), 7.38 (t, *J* = 7.6 Hz, 0.57H), 7.35 – 7.31 (m, 1.81H), 7.27 (dd, *J* = 7.3, 5.2 Hz, 0.65H), 7.24 – 7.20 (m, 2.09H), 7.11 – 7.05 (m, 1.60H), 4.34 (m, 2.12H), 2.46 (s, 0.78H), 2.44 (s, 2.26H), 1.36 (m, 3.18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.37, 163.72, 141.40, 140.86, 136.40, 134.55, 130.96, 130.68, 129.78, 129.57, 129.44, 129.30, 129.27, 128.97, 128.56, 128.00, 127.82, 127.53,

114.80, 114.64, 61.25, 61.03, 29.65, 17.43, 14.29, 14.13. HRMS: m/z (ESI) calculated $[M+Na]^+$:337.0987, found:337.0974.



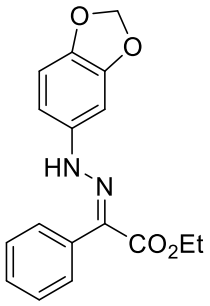
3j

The title compound **3j** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (17.8 mg, 30% yield, white solid).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.61 – 7.44 (m, 3H), 7.38 – 7.30 (m, 2H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.79 (t, *J* = 2.3 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.51 (dd, *J* = 8.1, 2.5 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 160.8, 144.0, 134.6, 130.1, 129.9, 129.6, 129.5, 129.0, 108.1, 106.6, 99.8, 61.3, 55.3, 14.3. HRMS: m/z (ESI) calculated $[M+Na]^+$:321.1215, found: 321.1210.



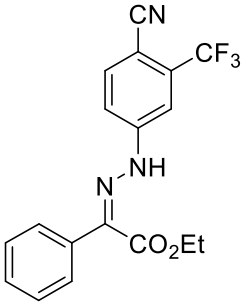
3k

The title compound **3k** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (30.5 mg, 48% yield, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.82 – 7.67 (m, 3H), 7.62 – 7.48 (m, 3H), 7.48 – 7.35 (m, 5H), 7.32 (t, *J* = 7.5 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 140.3, 134.9, 134.2, 129.9, 129.9, 129.7, 129.5, 129.4, 129.1, 127.8, 126.9, 126.7, 123.9, 115.5, 109.2, 61.4, 14.4. HRMS: m/z (ESI) calculated $[M+Na]^+$:341.1266, found: 341.1260.



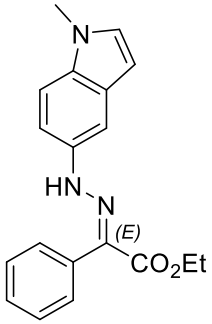
3l

The title compound **3l** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (25.3 mg, 40% yield, yellow solid). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.54 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.35 – 7.30 (m, 2H), 6.89 (d, *J* = 2.2 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.40 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.93 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 148.6, 142.9, 138.1, 133.6, 129.9, 129.5, 129.5, 129.0, 108.3, 106.3, 101.1, 96.7, 61.2, 14.3. HRMS: m/z (ESI) calculated $[M+Na]^+$:335.1008, found: 335.1002.

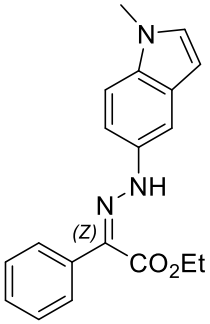


3m

The title compound **3m** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (41.4 mg, 57% yield, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.57 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.68 – 7.55 (m, 3H), 7.43 (m, 4H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.42, 146.70, 136.18, 135.10, 134.51 (q, *J* = 33.0 Hz), 133.34, 128.77, 128.74, 128.11, 122.28 (q, *J* = 273.8 Hz), 116.22, 116.16, 111.98 (q, *J* = 5.4 Hz), 101.39, 62.03, 14.04. HRMS: m/z (ESI) calculated $[M+Na]^+$:384.0936, found: 384.0930.

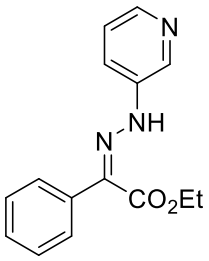


E-**3n**



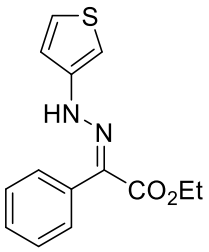
Z-**3n**

The title compound **3n** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (30.8 mg, 48% yield, E/Z = 10:1, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.63 (s, 0.09H), 8.20 (s, 0.91H), 7.70 (d, *J* = 7.6 Hz, 0.20H), 7.60 – 7.43 (m, 2.99H), 7.42 – 7.31 (m, 3.14H), 7.22 (d, *J* = 8.8 Hz, 1.04H), 7.09 (dd, *J* = 8.8, 2.2 Hz, 0.98H), 7.01 (d, *J* = 3.0 Hz, 1.08H), 6.49-6.34 (m, 0.98H), 4.34 (m, 2.19H), 3.75 (d, 3.20H), 1.37 (m, *J* = 7.1 Hz, 3.58H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.79, 163.98, 137.09, 136.17, 133.62, 132.44, 130.36, 129.72, 129.39, 129.27, 128.90, 128.58, 127.96, 127.77, 127.08, 127.00, 110.48, 110.23, 109.82, 109.78, 105.46, 105.22, 100.75, 100.57, 61.03, 60.68, 32.94, 31.91, 31.61, 29.68, 29.34, 22.68, 14.40, 14.10. HRMS: m/z (ESI) calculated $[M+Na]^+$:344.1375, found:344.1380.



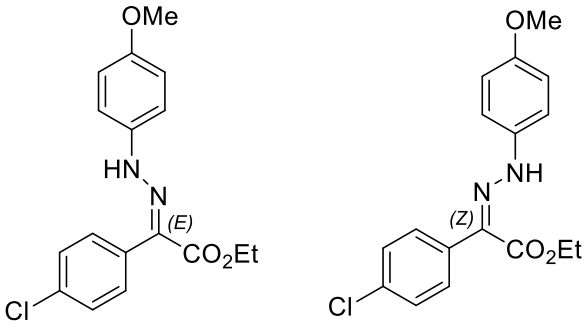
3o

The title compound **3o** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (16.7 mg, 31% yield, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.39 (s, 1H), 8.53 (d, *J* = 2.6 Hz, 1H), 8.25 (d, *J* = 4.7 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 3H), 7.39 (m, 3H), 7.24 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 143.6, 139.6, 136.9, 136.0, 128.6, 128.0, 127.9, 123.9, 120.8, 93.9, 61.4, 14.1. HRMS: m/z (ESI) calculated $[M+Na]^+$:292.1062, found: 292.1065.



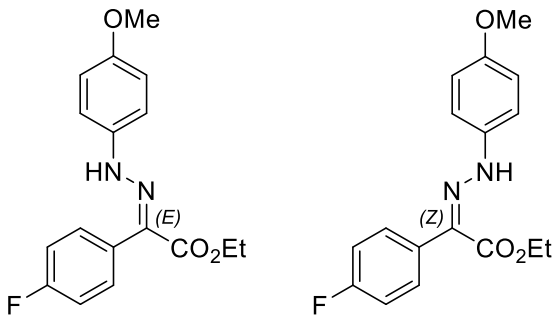
3p

The title compound **3p** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (20.2 mg, 37% yield, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.59 – 7.43 (m, 3H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.22 (dd, *J* = 5.2, 3.2 Hz, 1H), 6.95 (d, *J* = 5.2 Hz, 1H), 6.69 (d, *J* = 3.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 142.8, 134.3, 129.8, 129.5, 129.4, 129.0, 125.8, 118.3, 102.3, 61.2, 14.3. HRMS: m/z (ESI) calculated $[M+Na]^+$:297.0674, found: 297.0660.



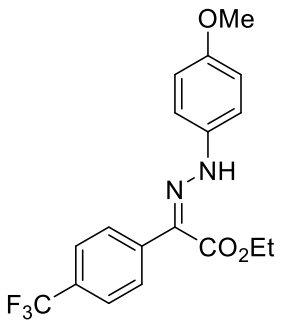
E-**3q** Z-**3q**

The title compound **3q** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (35.8 mg, 54% yield, E/Z = 5:1, yellow oil). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.50 (s, 0.16H), 7.99 (s, 0.84H), 7.59 (d, *J* = 8.6 Hz, 0.33H), 7.53 – 7.48 (m, 1.59H), 7.35 – 7.31 (m, 0.43H), 7.31 – 7.27 (m, 1.60H), 7.23 – 7.20 (m, 0.40H), 7.10 – 7.06 (m, 1.65H), 6.91 – 6.87 (m, 0.34H), 6.86 – 6.81 (m, 1.64H), 4.33 (m, 2.04H), 3.80 (s, 0.56H), 3.77 (s, 2.42H), 1.35 (m, 3.05H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.31, 163.62, 155.68, 155.40, 136.86, 136.35, 135.49, 135.19, 131.98, 130.64, 129.77, 129.74, 128.69, 128.36, 127.95, 127.85, 115.45, 115.31, 114.72, 114.63, 61.24, 60.95, 55.58, 55.55, 14.32, 14.17. HRMS: m/z (ESI) calculated $[M+Na]^+$:355.0825, found: 355.0820.



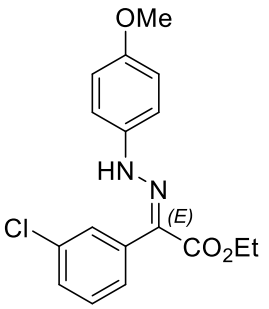
E-**3r** Z-**3r**

The title compound **3r** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (35.4 mg, 56% yield, E/Z = 9:1, yellow solid). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.47 (s, 0.1H), 7.97 (s, 0.89H), 7.62 (m, 0.25H), 7.33 (ddd, *J* = 8.8, 5.3, 1.8 Hz, 1.87H), 7.23 (m, 2.30H), 7.12 – 7.01 (m, 2.26H), 6.92 – 6.79 (m, 2.17H), 4.32 (m, 2.12H), 3.80 (d, *J* = 1.6 Hz, 0.35H), 3.78 (d, *J* = 1.6 Hz, 2.51H), 1.36 (m,, 3.36H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.50, 155.35, 136.41, 132.28, 131.26 (d, *J* = 8.8 Hz), 130.22 (d, *J* = 8.7 Hz), 125.59, 116.68 (d, *J* = 21.9 Hz), 115.28, 114.64, 61.23, 55.57, 14.34. HRMS: m/z (ESI) calculated $[M+Na]^+$:339.1121, found:339.1129.

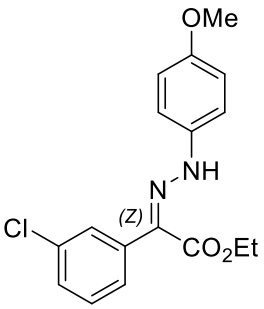


3s

The title compound **3s** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (43.9 mg, 60% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.62 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 5.6 Hz, 2H), 6.95 – 6.86 (m, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.59, 155.96, 140.21, 136.68, 128.90 (q, *J* = 32.6 Hz), 128.57, 125.08, 124.72 (q, *J* = 3.8 Hz), 121.62 (q, *J* = 271.7 Hz), 115.67, 114.78, 61.06, 55.60, 14.19. HRMS: m/z (ESI) calculated $[M+Na]^+$:389.1089, found:389.1092.

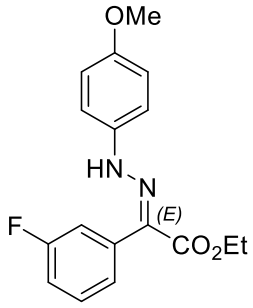


E-**3t**

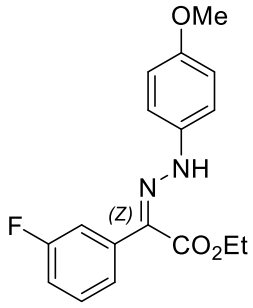


Z-**3t**

The title compound **3t** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (37.2 mg, 56% yield, E/Z = 13:1, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.55 (s, 0.07H), 7.99 (s, 0.93H), 7.47 (d, *J* = 7.2 Hz, 1.90H), 7.33 (d, *J* = 2.0 Hz, 1.11H), 7.22 (m, 1.03H), 7.13 – 7.03 (m, 1.89H), 6.85 (d, *J* = 8.9 Hz, 1.79H), 4.32 (m, 2.11H), 3.78 (s, 0.31H), 3.8 (s, 2.65H), 1.35 (m, 2.90H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 163.6, 155.8, 155.5, 138.5, 136.8, 136.3, 135.5, 133.7, 131.8, 131.6, 130.7, 129.7, 129.3, 128.9, 128.5, 127.3, 127.1, 126.6, 125.1, 115.6, 115.4, 114.7, 114.6, 61.3, 61.0, 55.6, 29.7, 14.3, 14.2. HRMS: m/z (ESI) calculated $[M+Na]^+$:355.0825, found:355.0832.



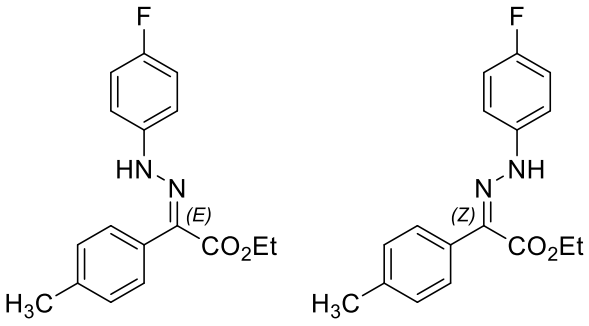
E-**3u**



Z-**3u**

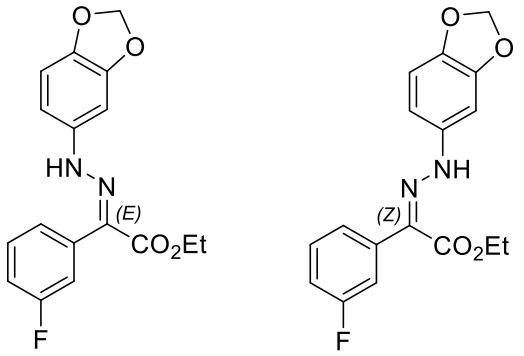
The title compound **3t** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (35.4 mg, 56% yield, E/Z = 3:1 yellow solid). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.54 (s, 0.27H), 8.02 (s, 0.73H), 7.55 – 7.45 (m, 1.08H), 7.42 – 7.28 (m, 0.75H), 7.25 – 7.15 (m, 1.38H), 7.14 – 7.04 (m, 2.99H), 6.99 (m, 0.39H), 6.93 – 6.82 (m, 2.07H), 4.34 (m, 2.07H), 3.79 (d, *J* = 15.2 Hz, 3.03H), 1.37 (m, 3.15H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.21, 164.09, 163.61, 162.44, 155.77, 155.44, 136.81, 136.32, 132.05 (d, *J* = 7.7 Hz), 131.71, 131.14 (d, *J* = 8.0 Hz), 129.10 (d, *J* = 8.6 Hz), 125.21 (d, *J* = 3.3 Hz), 124.79 (d, *J* = 3.3 Hz), 124.02 (d, *J* = 2.2 Hz), 116.64, 116.50,

116.35, 115.56, 115.37, 115.20, 114.74, 114.64, 113.93 (d, *J* = 21.8 Hz), 61.25, 61.00, 55.59, 55.56, 14.32, 14.18. HRMS: m/z (ESI) calculated $[M+Na]^+$:339.1121, found:339.1129.



E-**3v** Z-**3v**

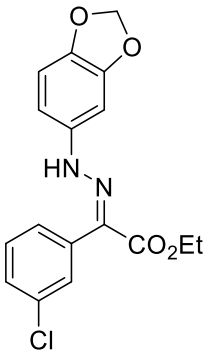
The title compound **3v** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (33.6 mg, 56% yield, Z/E = 16:1, yellow oil). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.38 (s, 0.94H), 8.07 (s, 0.06H), 7.58 – 7.50 (m, 1.79H), 7.34 (s, 0.16H), 7.24 – 7.14 (m, 3.84H), 7.11 – 7.05 (m, 0.18H), 7.04 – 6.93 (m, 1.98H), 4.35 (m, 2.08H), 2.43 (s, 0.22H), 2.38 (s, 2.81H), 1.36 (m, 3.17H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.88, 158.58 (d, *J* = 240.5 Hz), 139.66 (d, *J* = 2.4 Hz), 137.50, 133.64, 128.65, 128.52, 128.04, 115.99 (d, *J* = 23.1 Hz), 115.18 (d, *J* = 7.8 Hz), 61.06, 21.24, 14.21.HRMS: m/z (ESI) calculated $[M+Na]^+$:323.1172, found:323.1177.



E-**3w** Z-**3w**

The title compound **3w** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (38.9 mg, 59% yield, yellow solid, E/Z = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.51 (s, 0.40H), 8.01 (s, 0.59H), 7.55 – 7.27 (m, 2.30H), 7.09 (m, 3.18H), 6.90 (m, 0.66H), 6.76 (d, *J* = 8.3 Hz, 0.40H), 6.69 (d, *J* = 8.3 Hz, 0.65H), 6.62 (dd, *J* = 8.3, 2.2 Hz, 0.45H), 6.42 (dd, *J* = 8.3, 2.2 Hz, 0.65H), 5.94 (d, *J* = 7.2 Hz,

2.13H), 4.44 – 4.24 (m, 2.36H), 1.37 (m, 3.62H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.50, 164.12, 163.57, 162.02, 148.71, 148.61, 143.49, 143.19, 138.67 (d, *J* = 8.5 Hz), 138.38, 137.88, 131.92 (d, *J* = 7.7 Hz), 131.16 (d, *J* = 8.4 Hz), 129.13 (d, *J* = 8.4 Hz), 124.72 (d, *J* = 3.2 Hz), 124.03 (d, *J* = 2.5 Hz), 116.76, 116.52 (d, *J* = 5.9 Hz), 116.27, 115.31 (d, *J* = 23.2 Hz), 114.06 (d, *J* = 21.6 Hz), 108.45, 108.31, 107.07, 106.47, 101.20 (d, *J* = 1.6 Hz), 96.78, 96.51, 61.31, 61.09, 29.68, 29.64, 14.31, 14.16. HRMS: m/z (ESI) calculated $[M+Na]^+$:353.0914, found:353.0917.



3x

The title compound **3x** was synthesized according to General Procedure **(SI 4.1)**, and purified by column chromatography on silica gel with a gradient eluent of petroleum/ethyl acetate (38.0 mg, 55% yield, yellow solid). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.51 – 7.43 (m, 2H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.21 (d, *J* = 6.7 Hz, 1H), 6.90 (d, *J* = 2.3 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.43 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.93 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 148.6, 143.2, 137.8, 135.5, 131.9, 131.7, 130.7, 129.8, 129.3, 127.2, 108.3, 106.5, 101.2, 96.8, 61.3, 14.3. HRMS: m/z (ESI) calculated $[M+Na]^+$:369.0618, found:369.0614.

7. References

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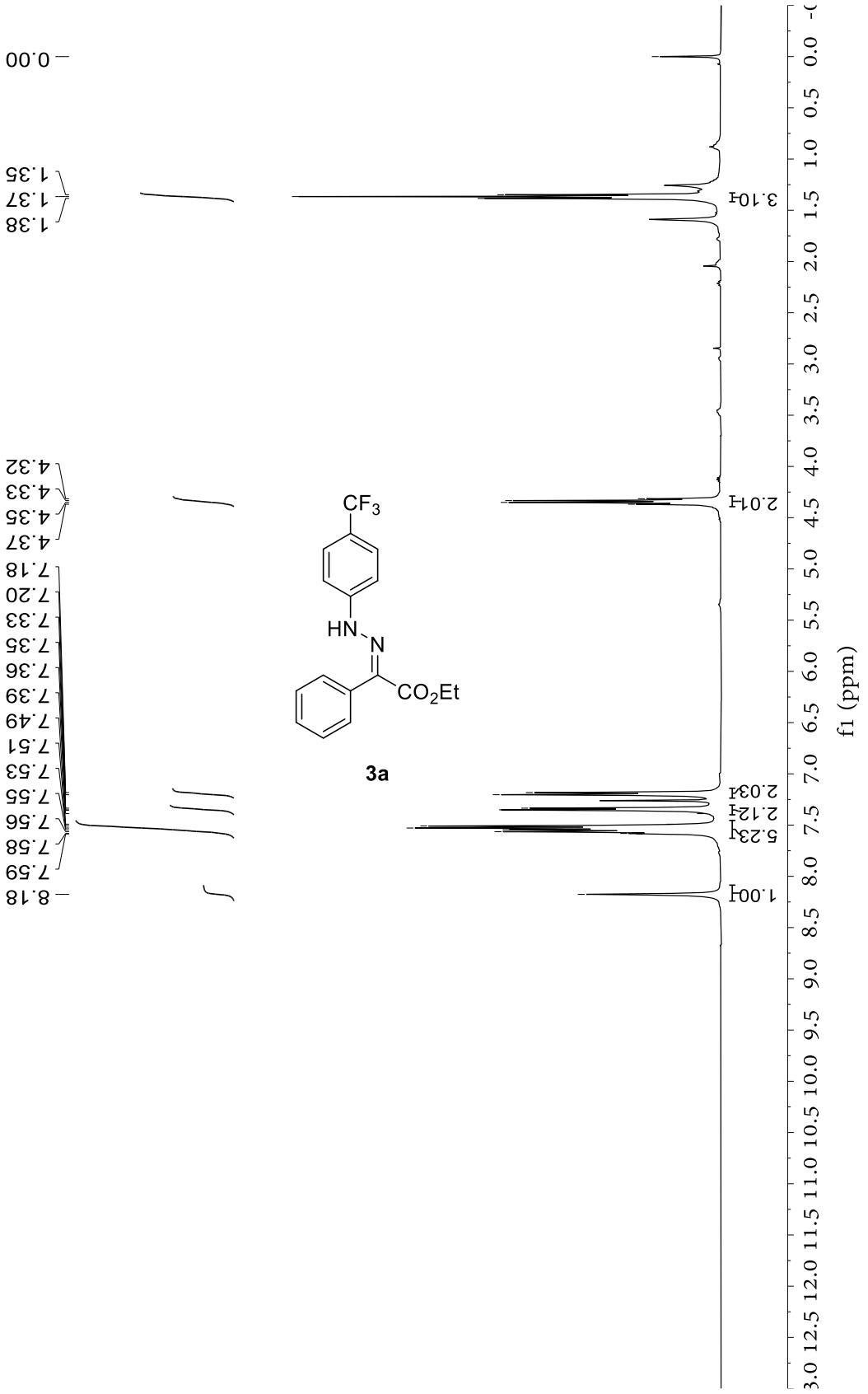
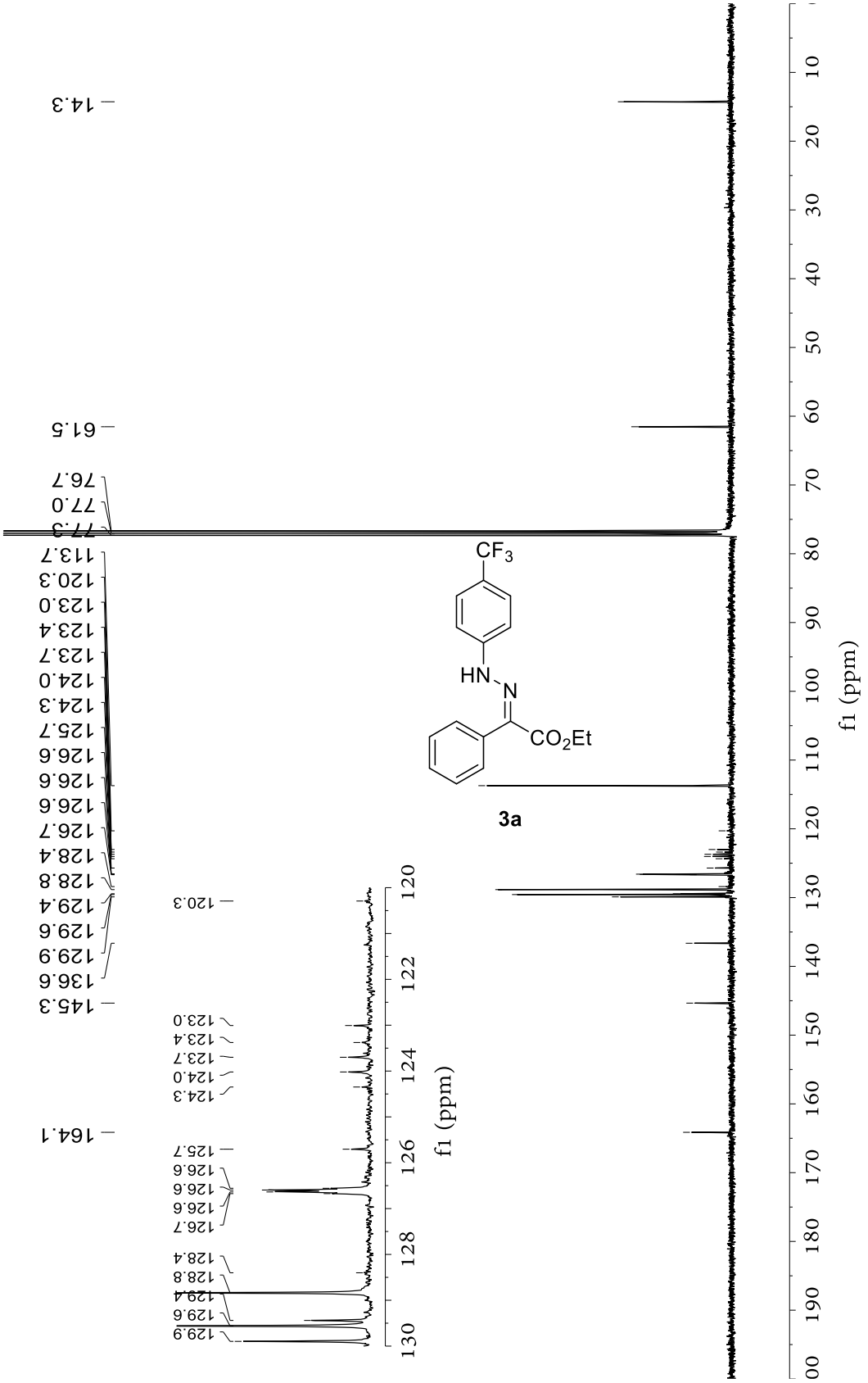
8. The Spectra of the New Products

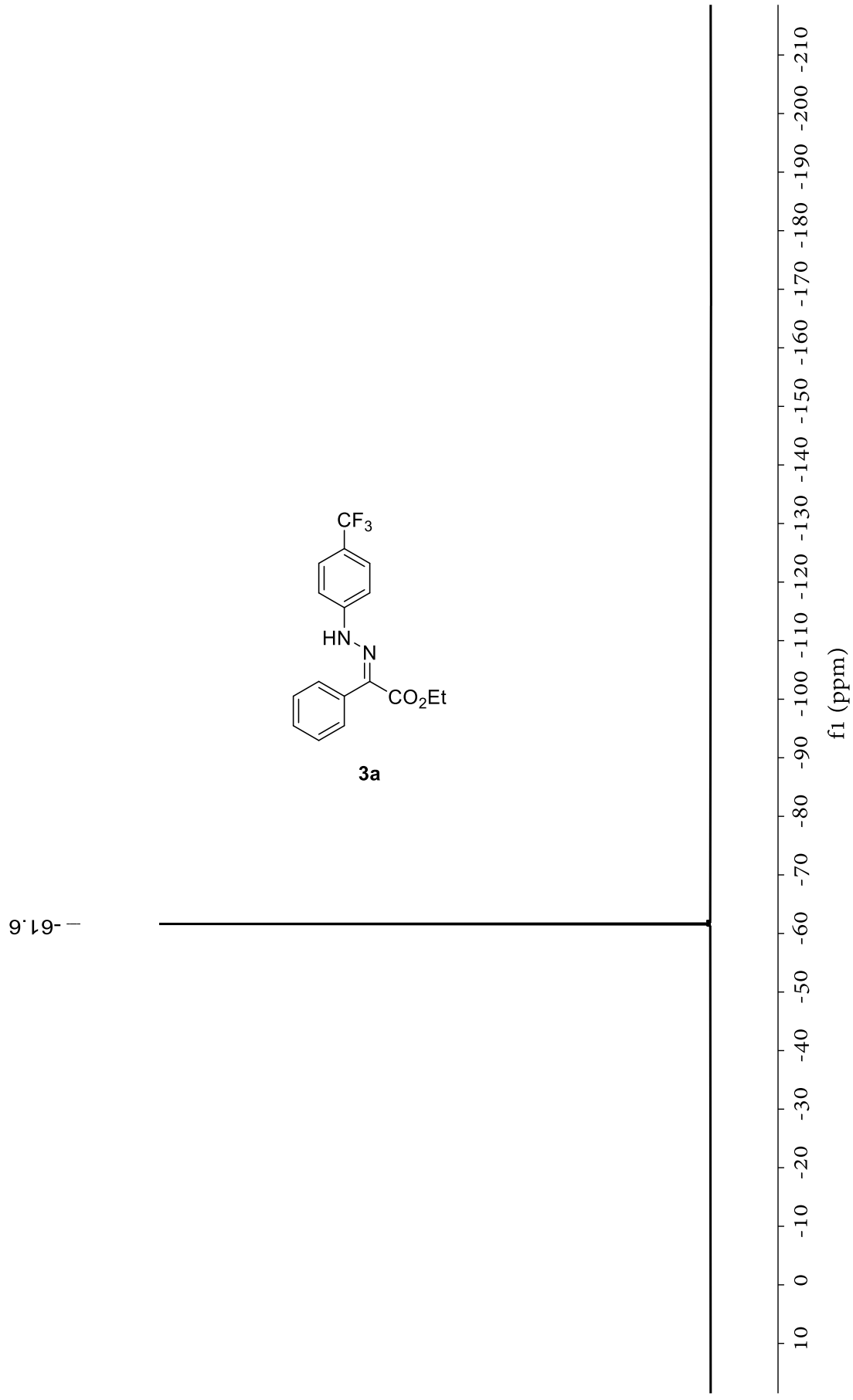
Compound **3a** ^{1}H NMR (400 MHz, $CDCl_3$)



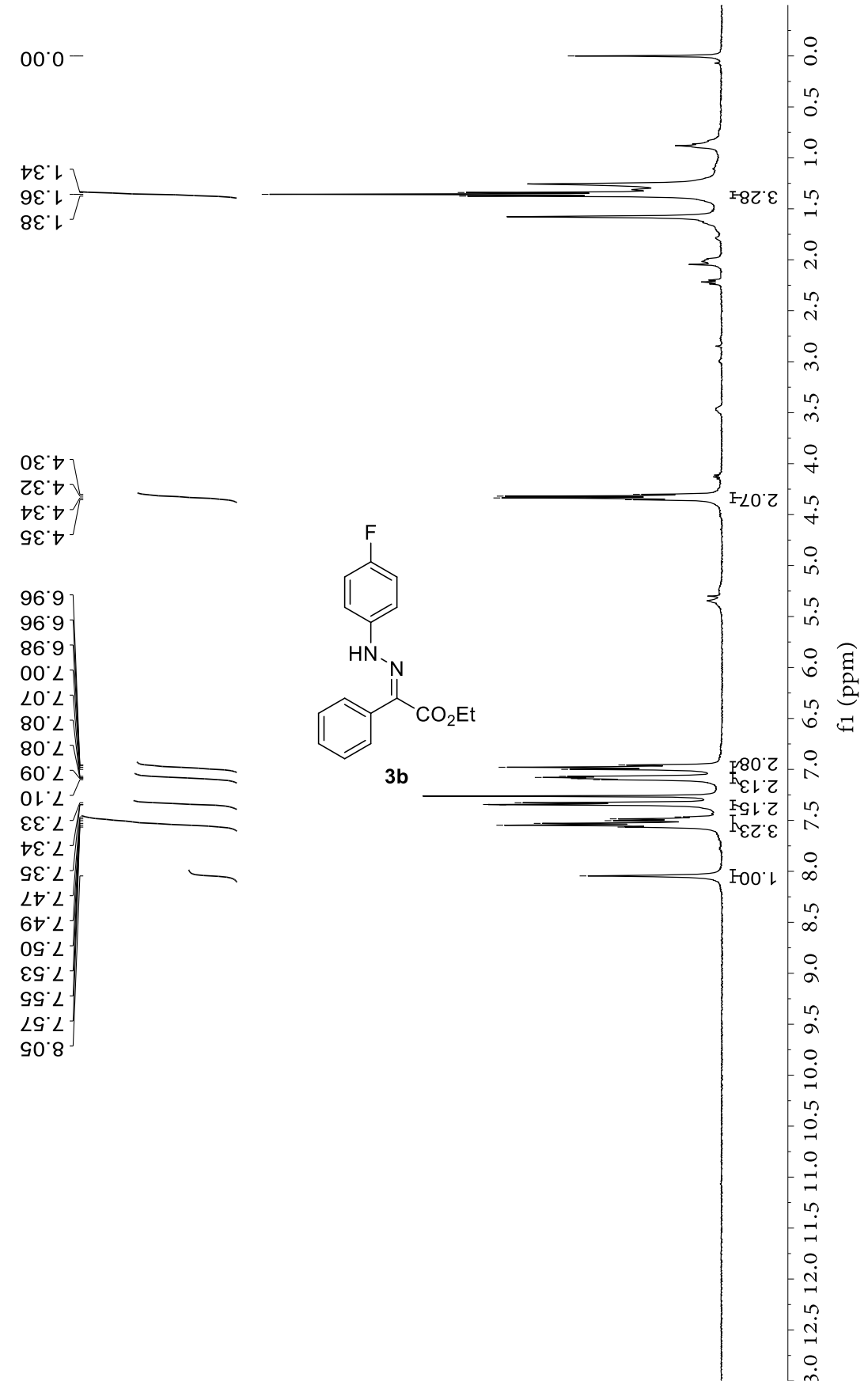
Compound **3a** ^{13}C NMR (101 MHz, $CDCl_3$)



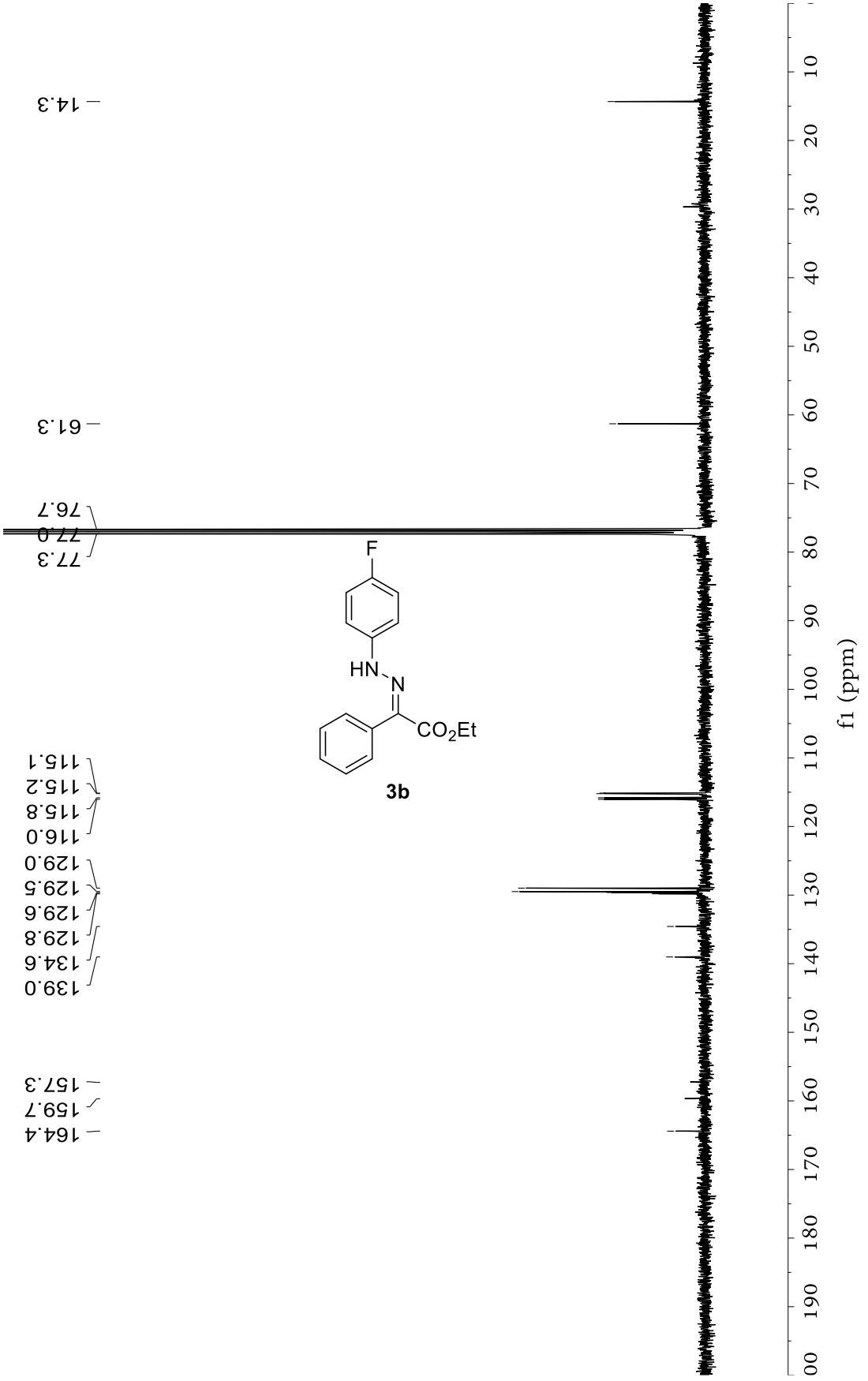
Compound **3a** ^{19}F NMR (376 MHz, $CDCl_3$)



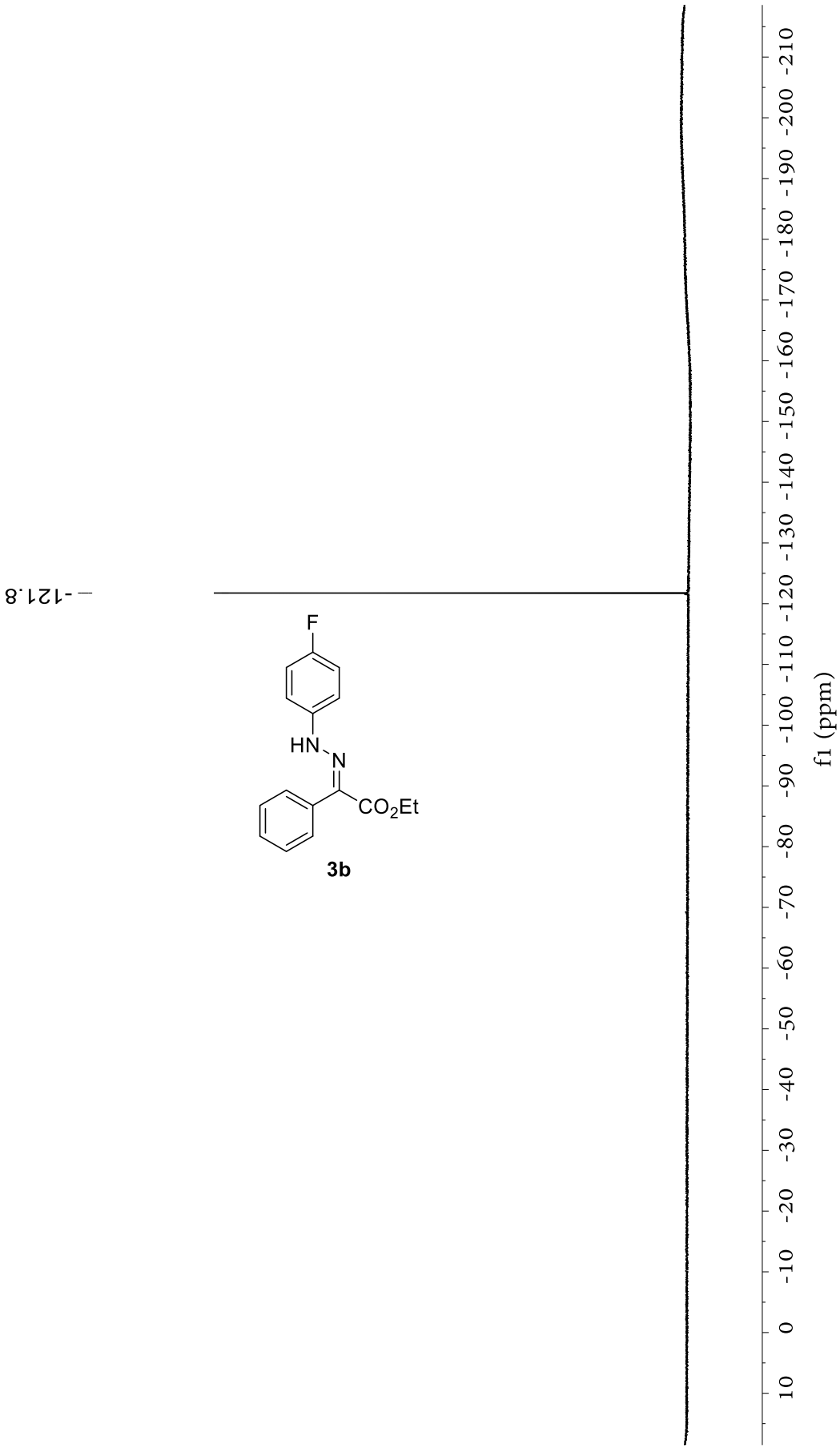
Compound **3b** ^{1}H NMR (400 MHz, $CDCl_3$)



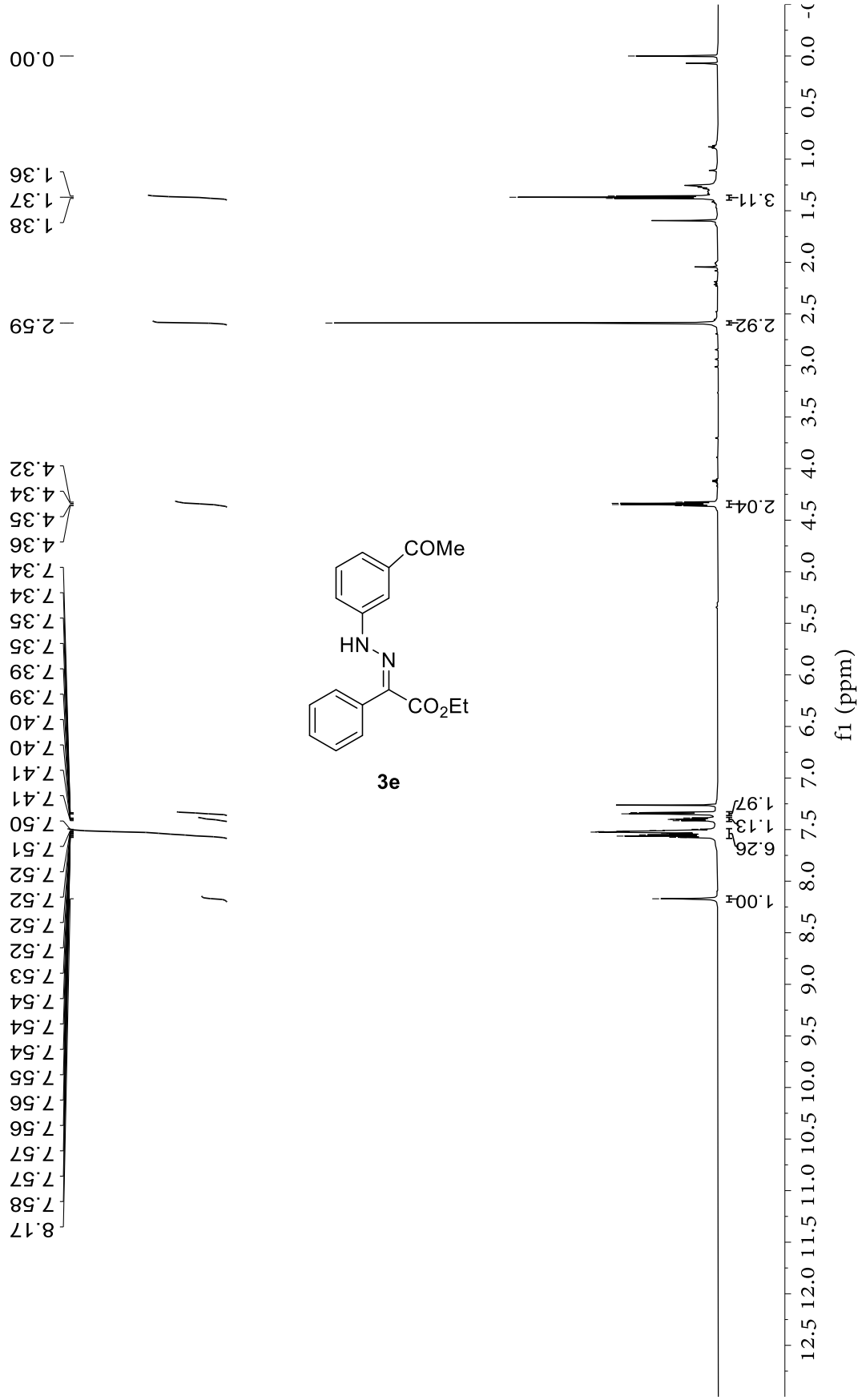
Compound **3b** ^{13}C NMR (101 MHz, $CDCl_3$)



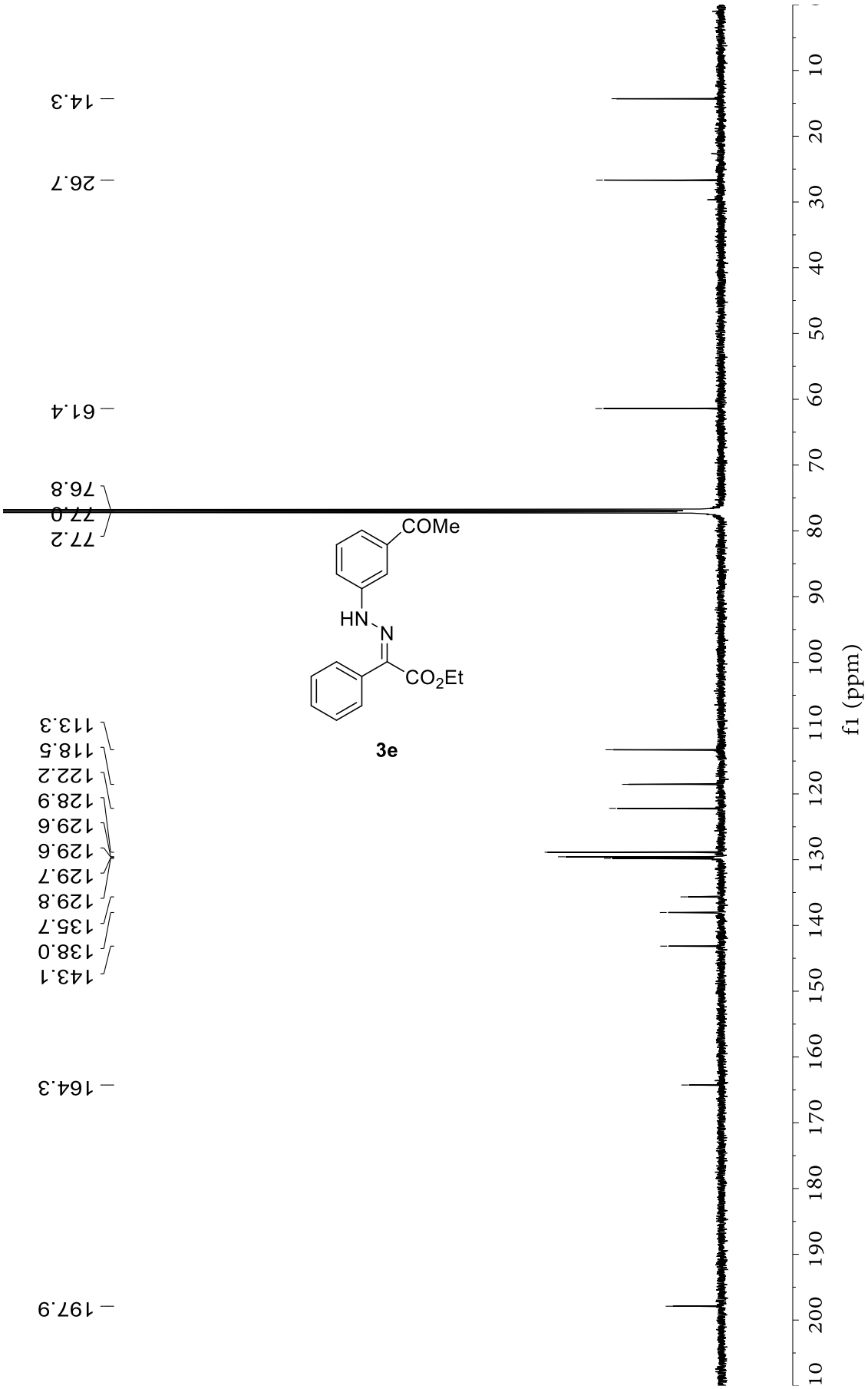
Compound **3b** ^{19}F NMR (376 MHz, $CDCl_3$)



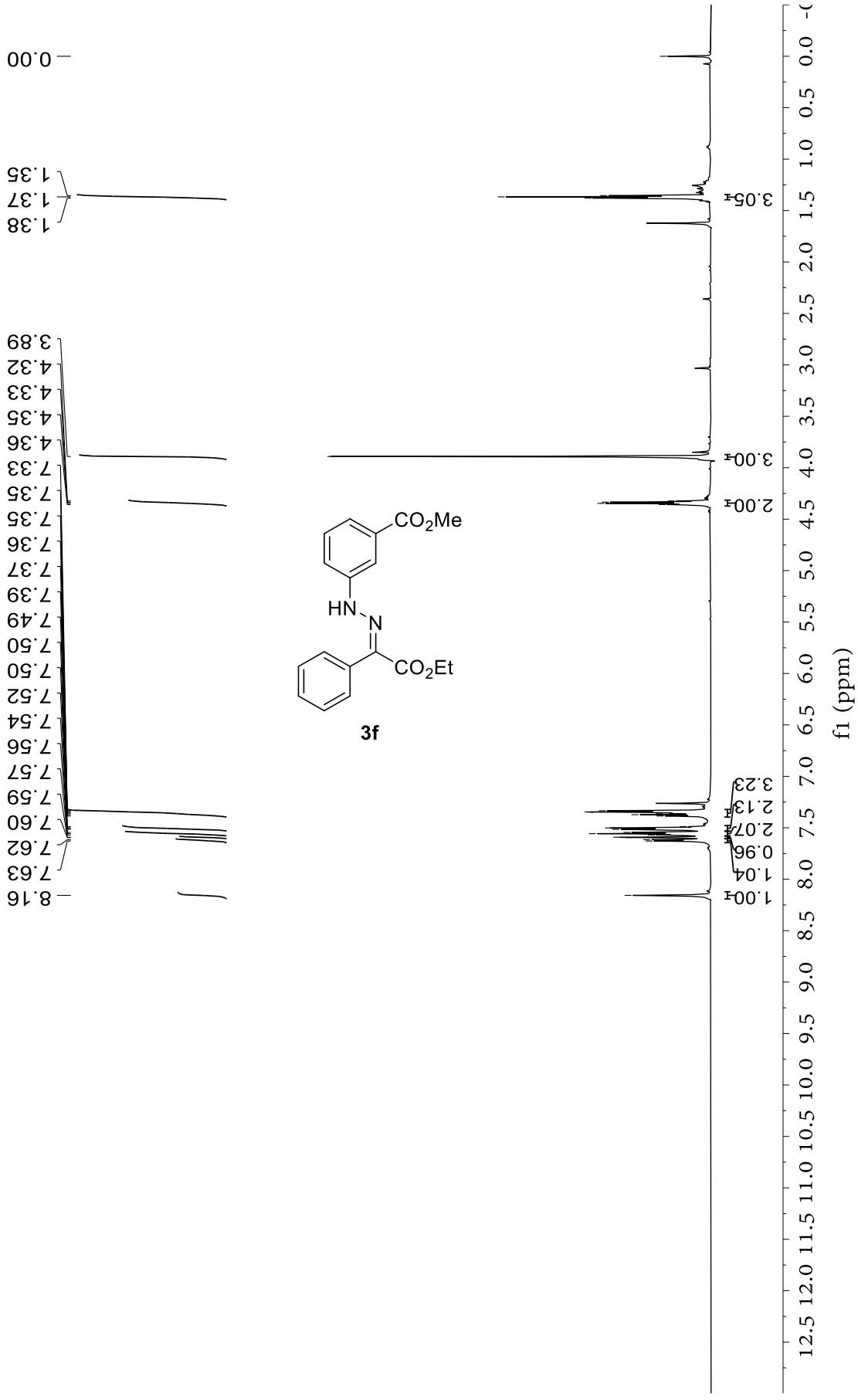
Compound **3e** ^{1}H NMR (600 MHz, $CDCl_3$)



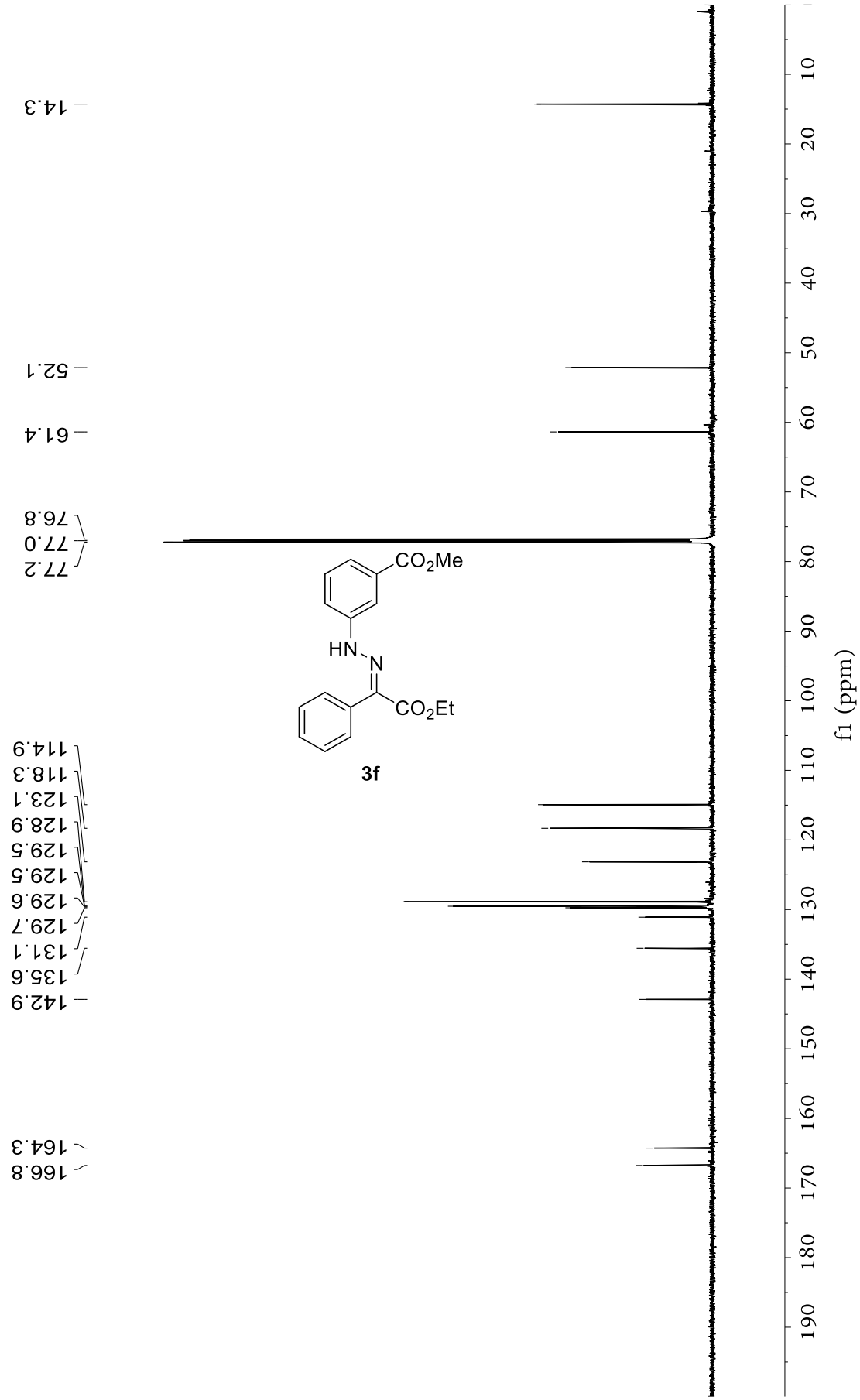
Compound **3e** ^{13}C NMR (151 MHz, $CDCl_3$)



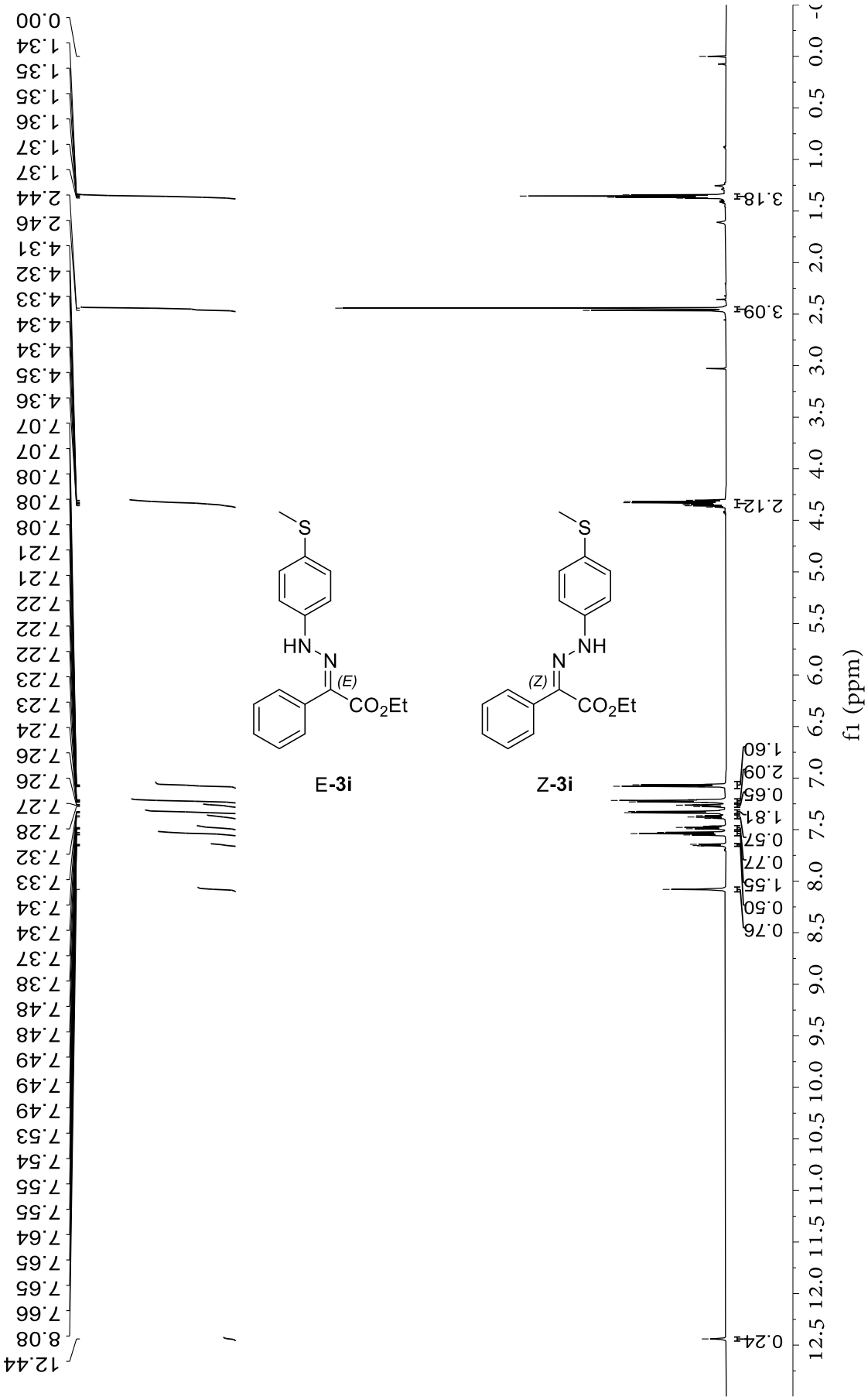
Compound **3f** ^{1}H NMR (600 MHz, $CDCl_3$)



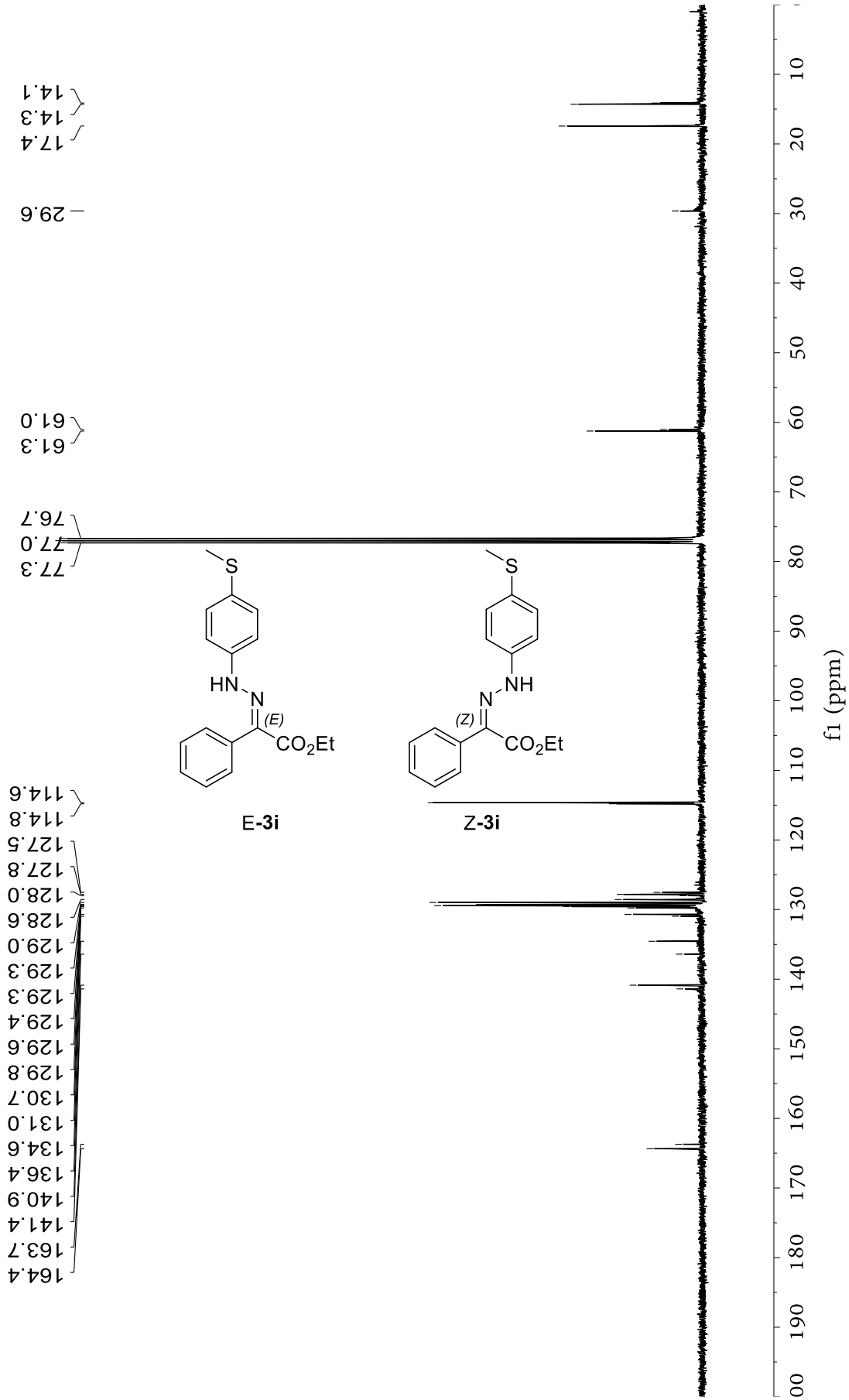
Compound **3f** ^{13}C NMR (151 MHz, $CDCl_3$)



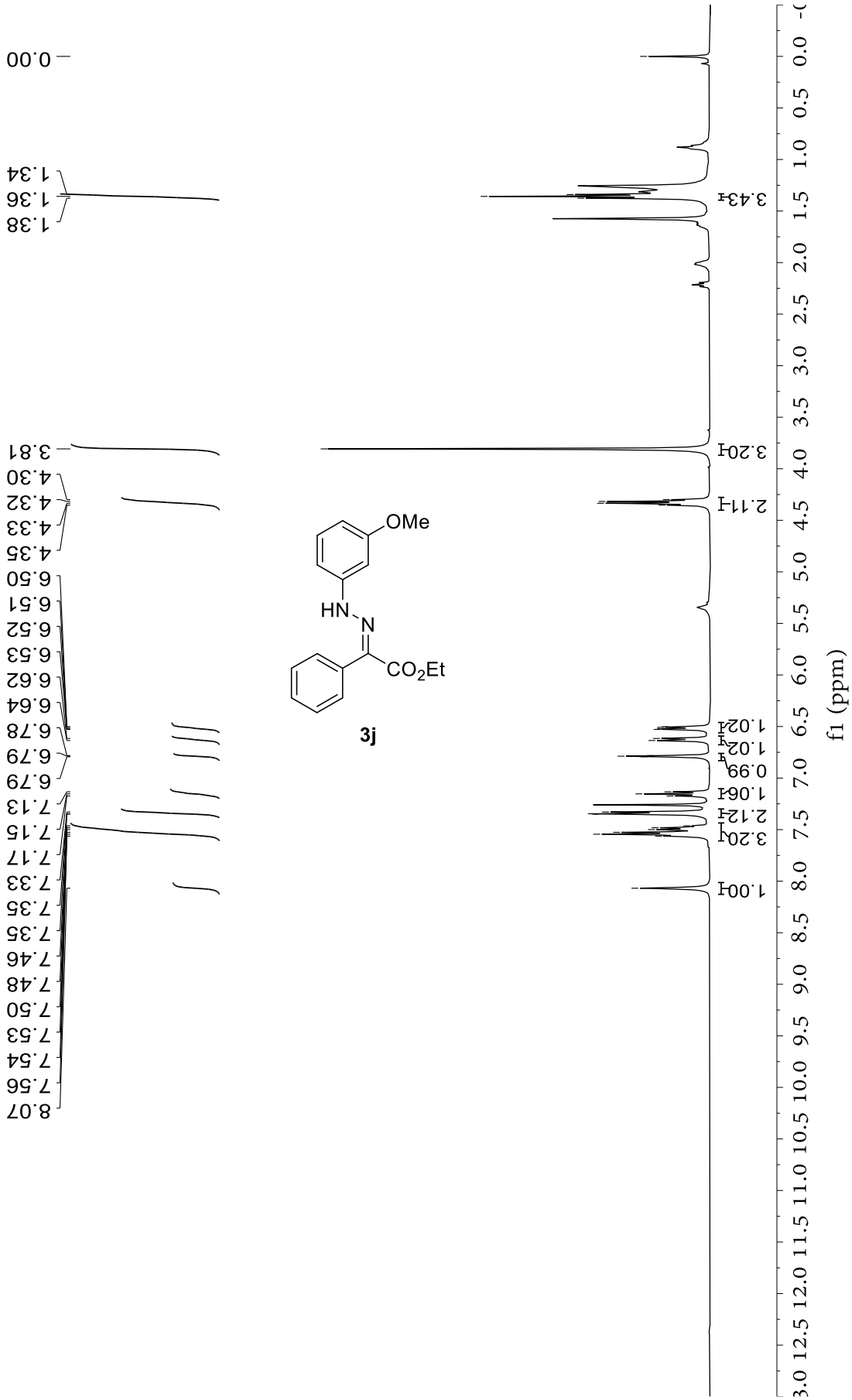
Compound **3i** ^{1}H NMR (600 MHz, $CDCl_3$)



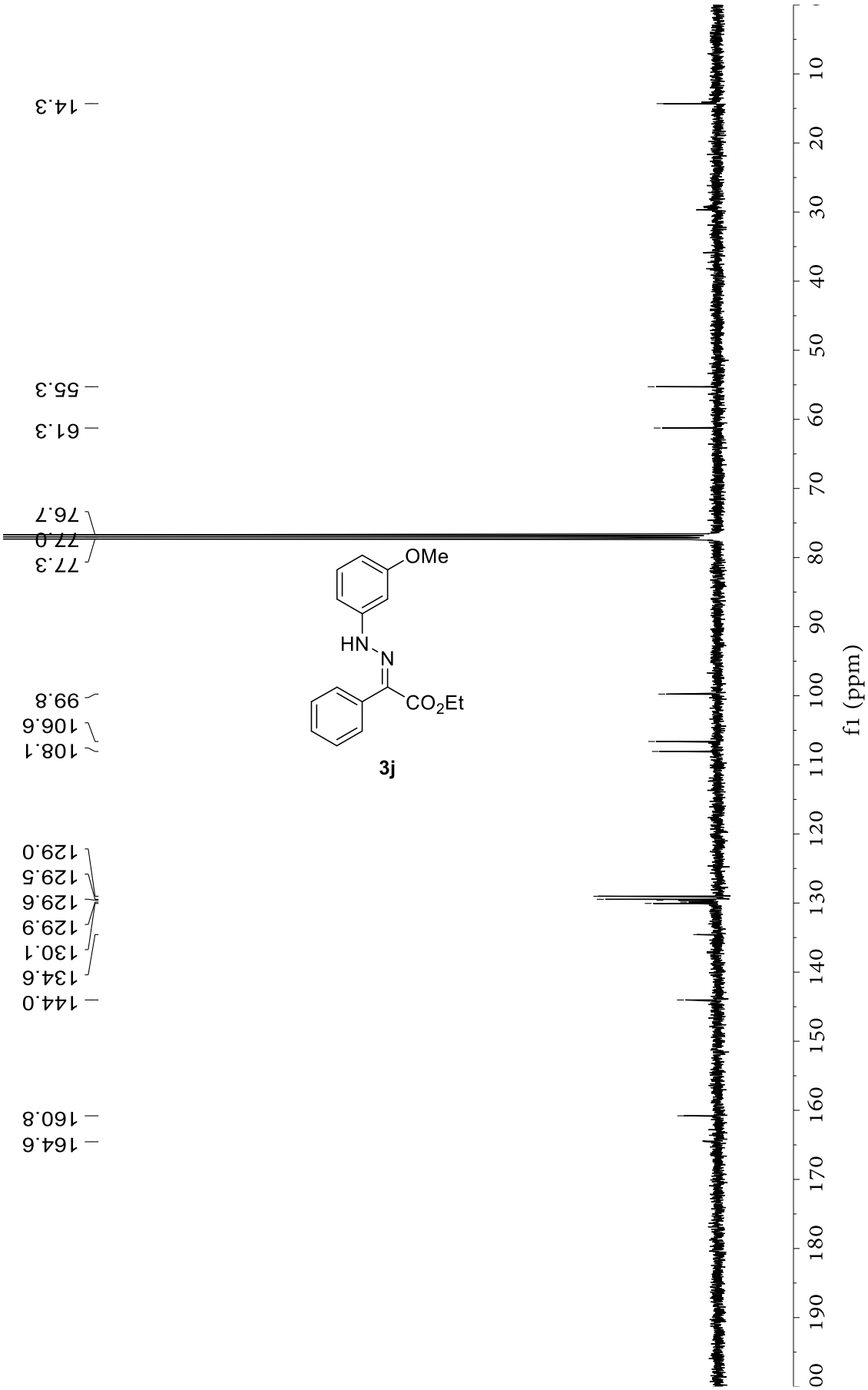
Compound **3i** ^{13}C NMR (151 MHz, $CDCl_3$)



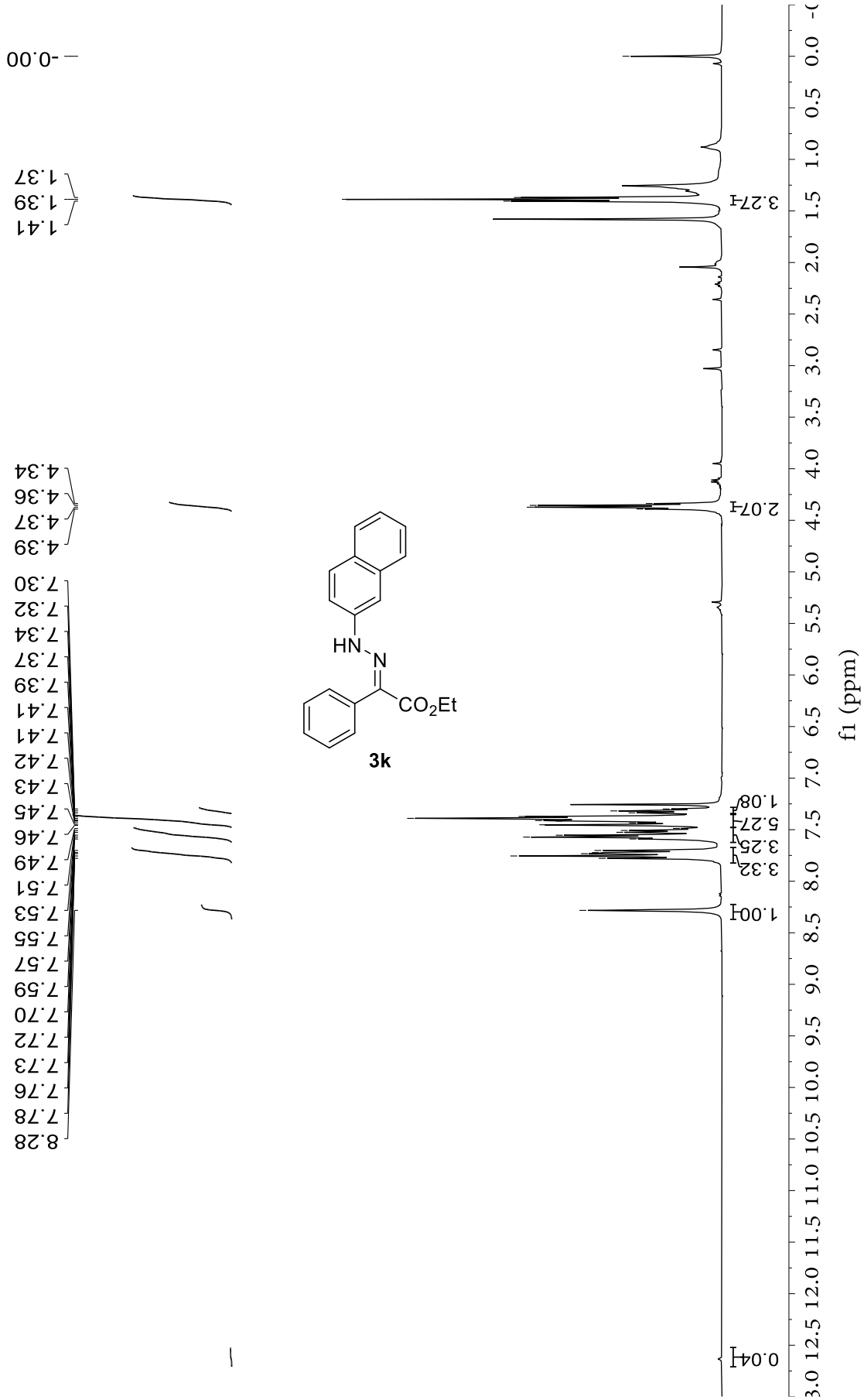
Compound **3j** ^{1}H NMR (400 MHz, $CDCl_3$)



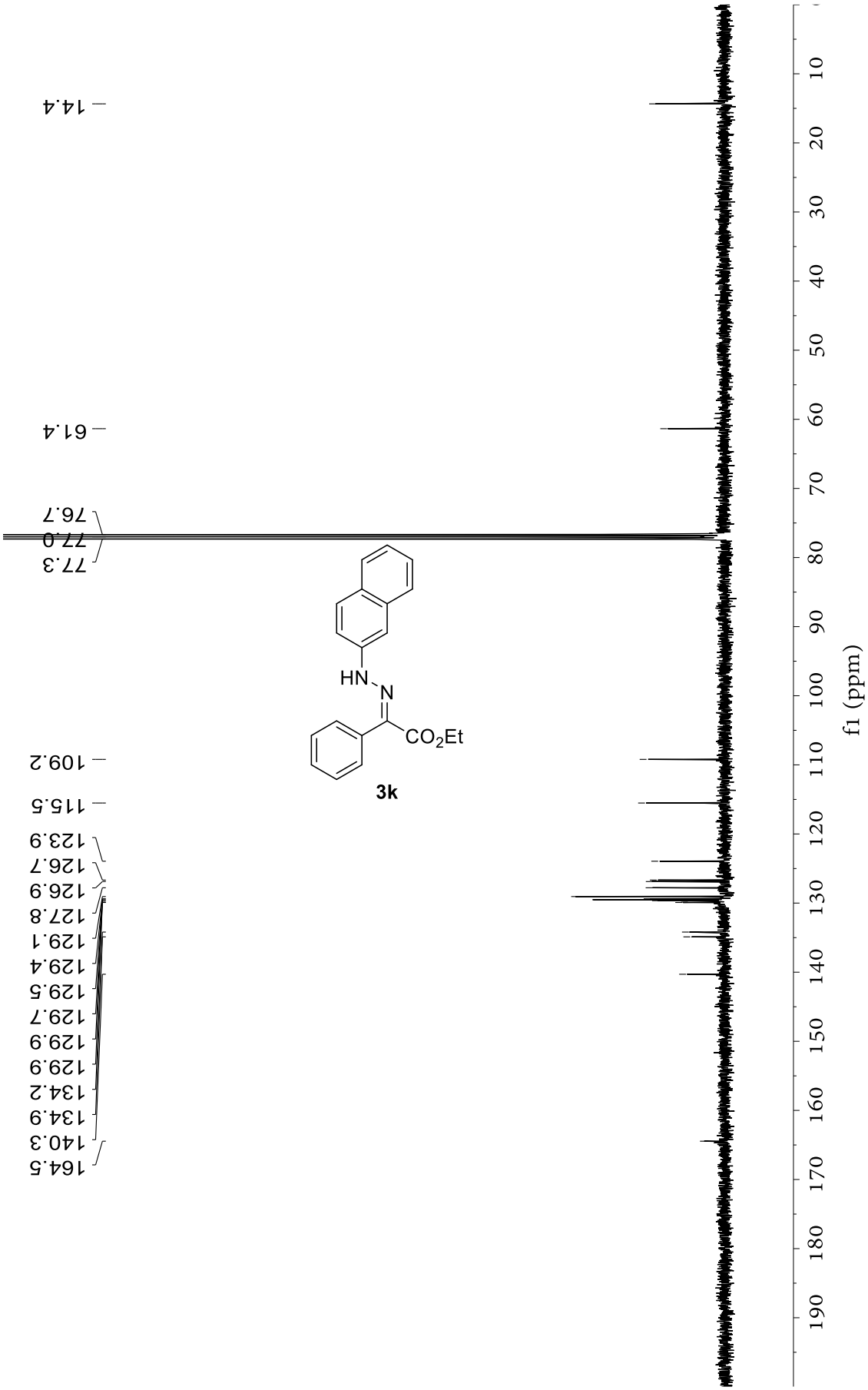
Compound **3j** ^{13}C NMR (101 MHz, $CDCl_3$)



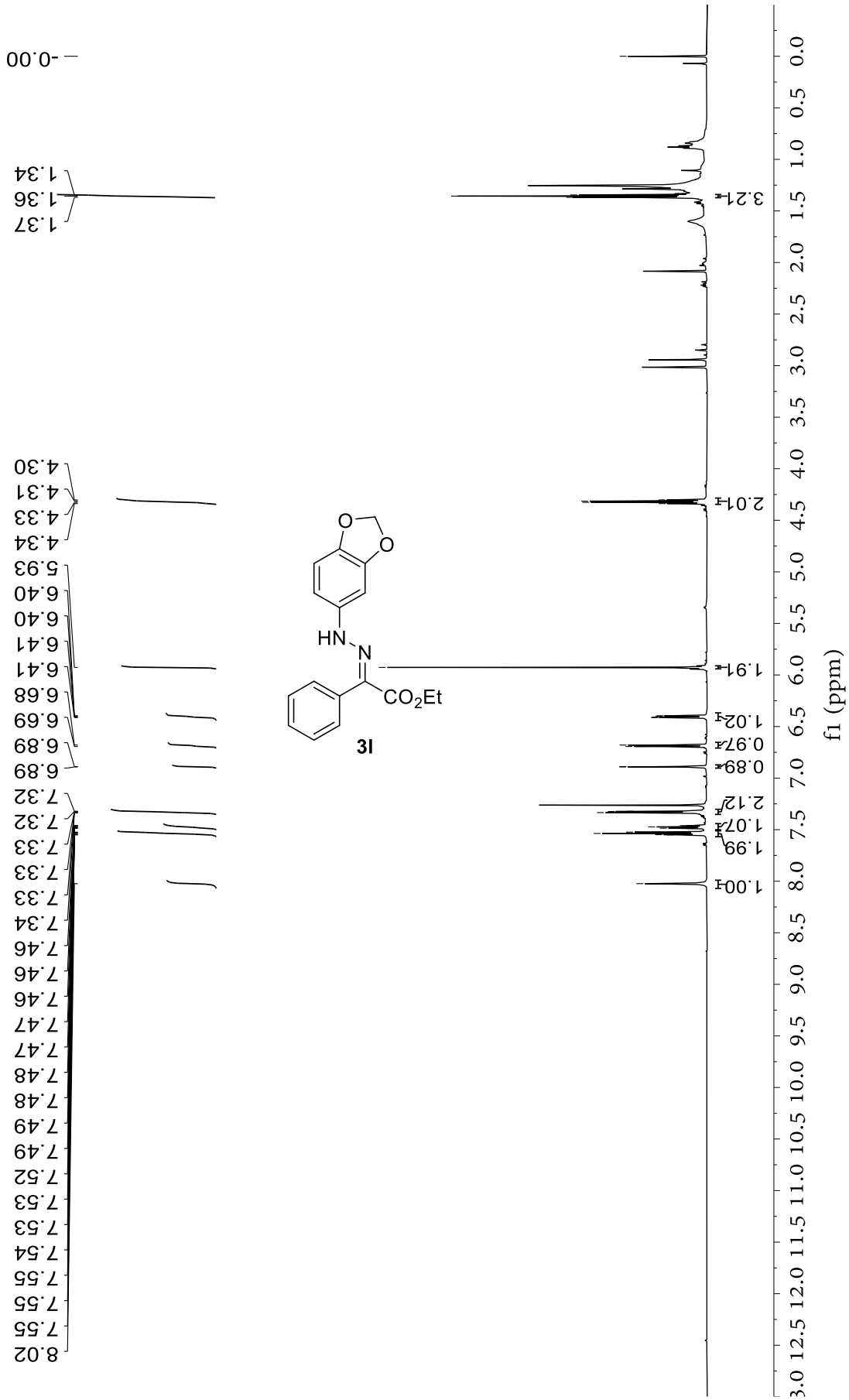
Compound **3k** ^{1}H NMR (400 MHz, $CDCl_3$)



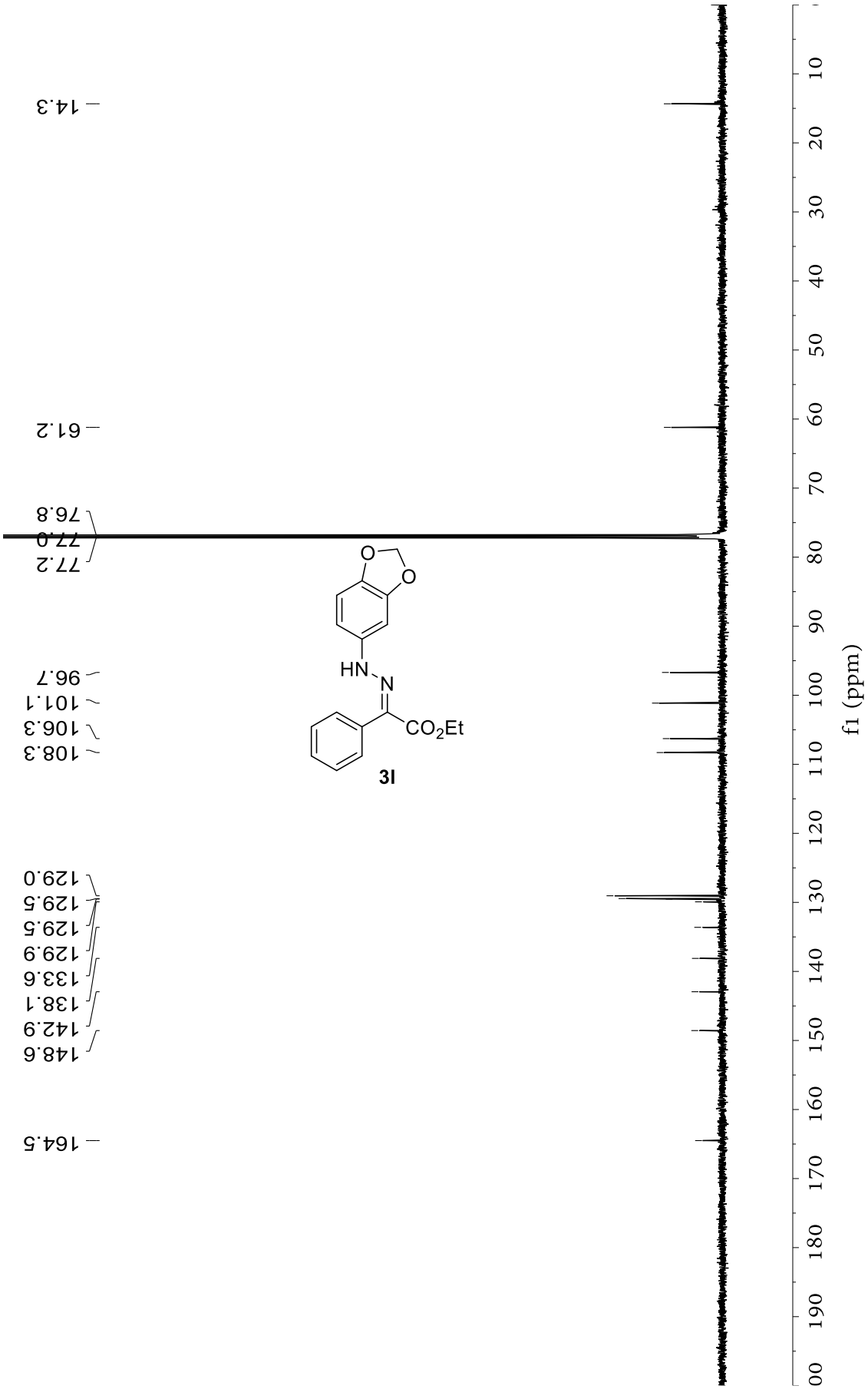
Compound **3k** ^{13}C NMR (101 MHz, $CDCl_3$)



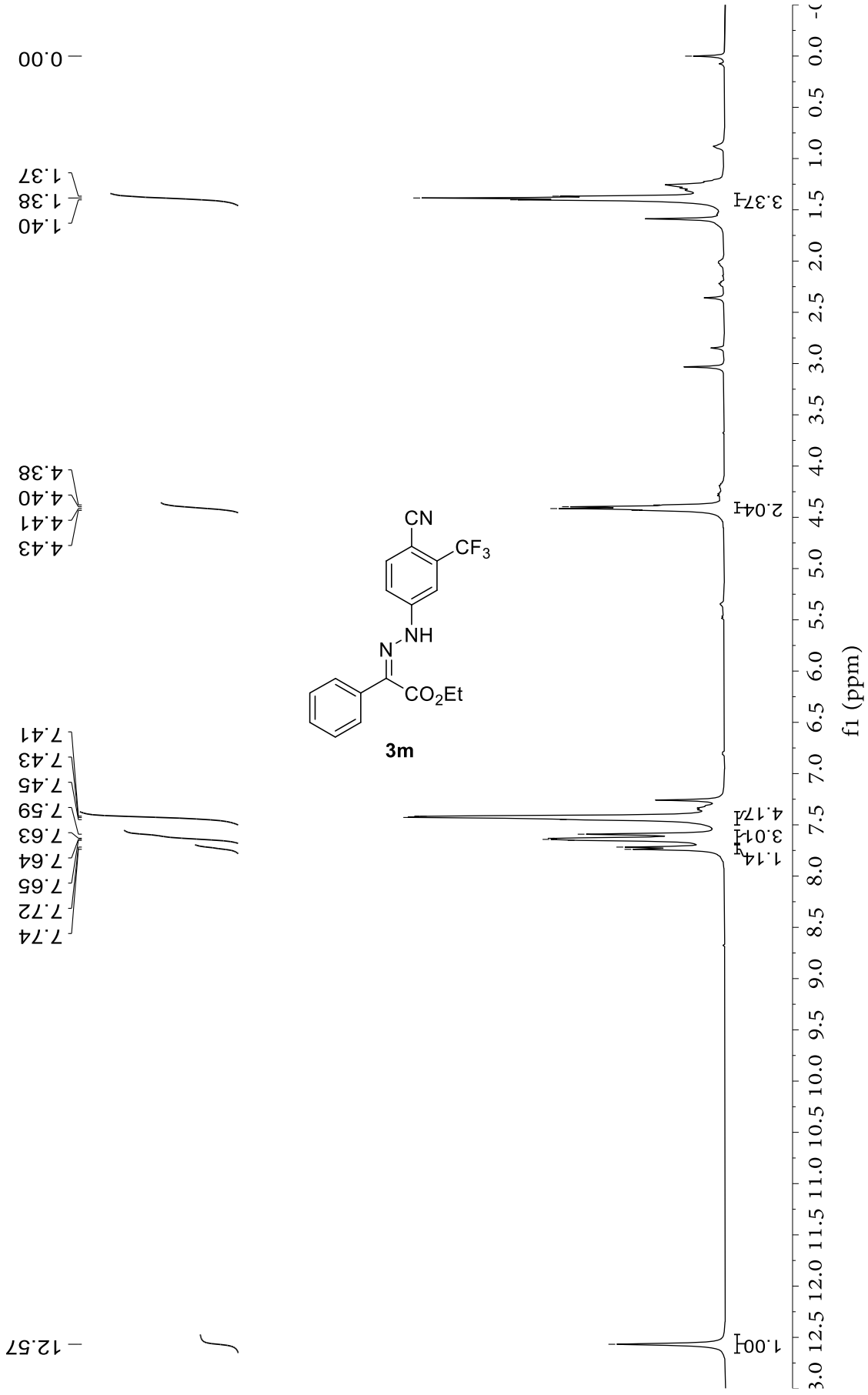
Compound **3l** ^{1}H NMR (600 MHz, $CDCl_3$)



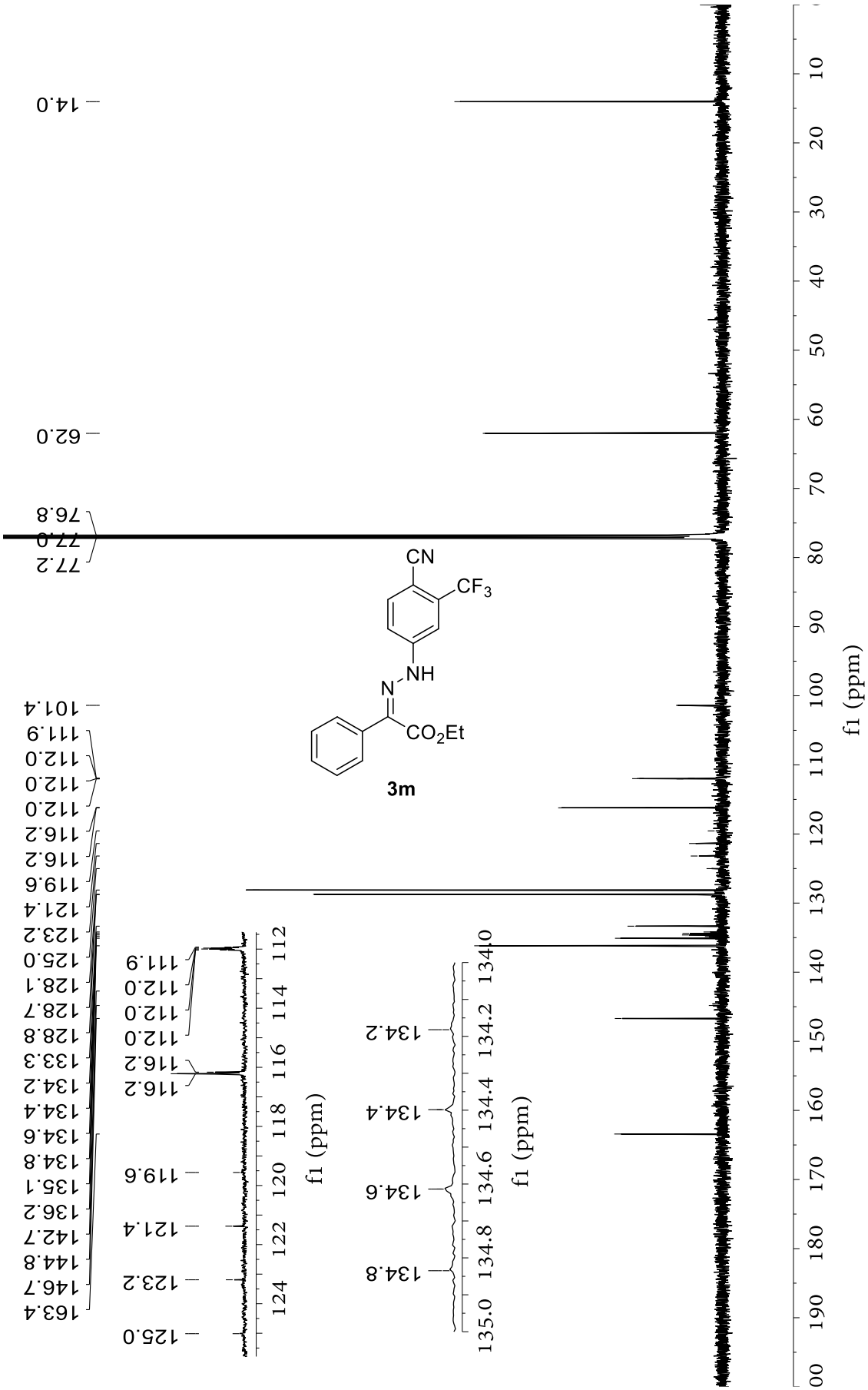
Compound **3l** ^{13}C NMR (151 MHz, $CDCl_3$)



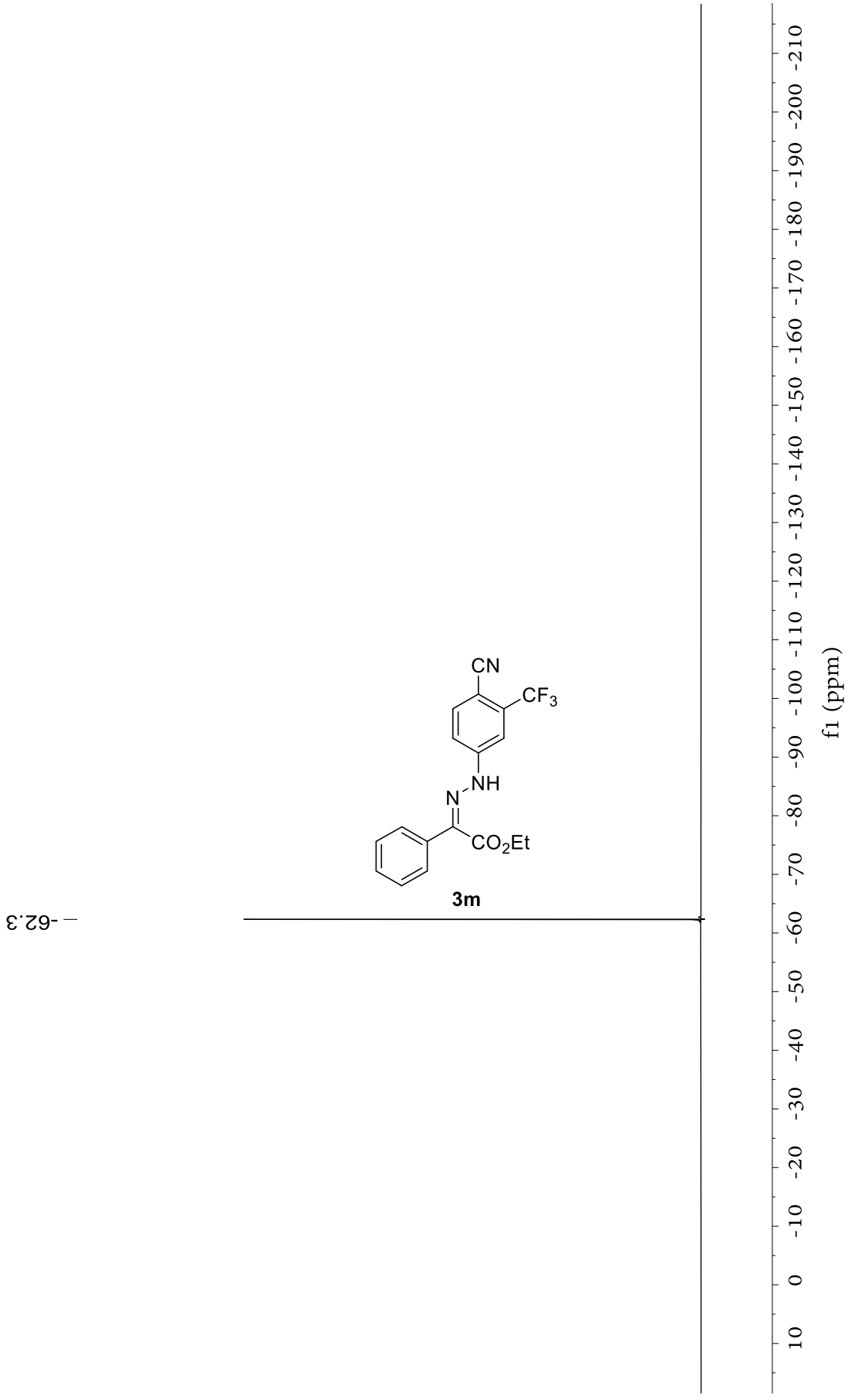
Compound **3m** ^{1}H NMR (400 MHz, $CDCl_3$)



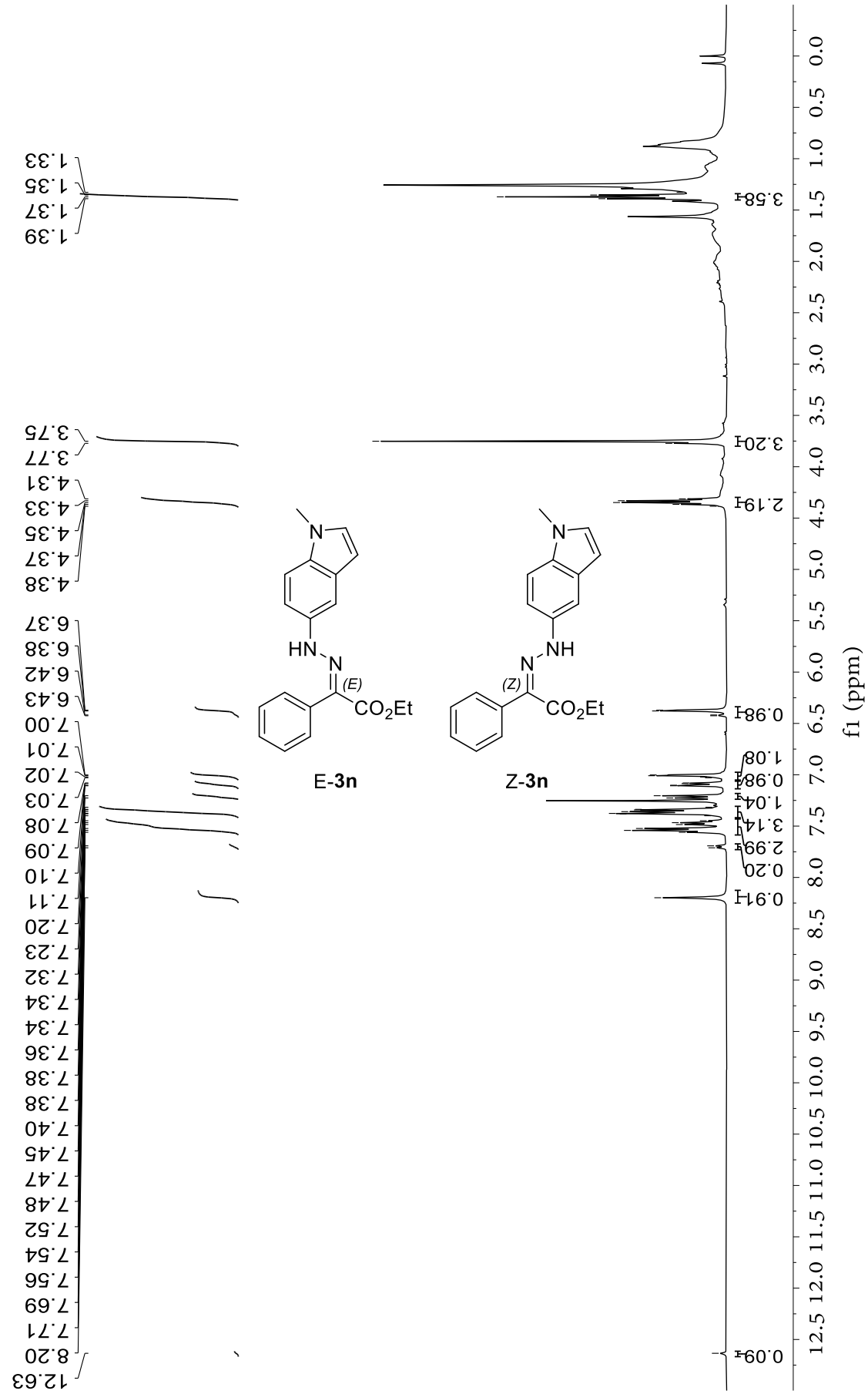
Compound **3m** ^{13}C NMR (101 MHz, $CDCl_3$)



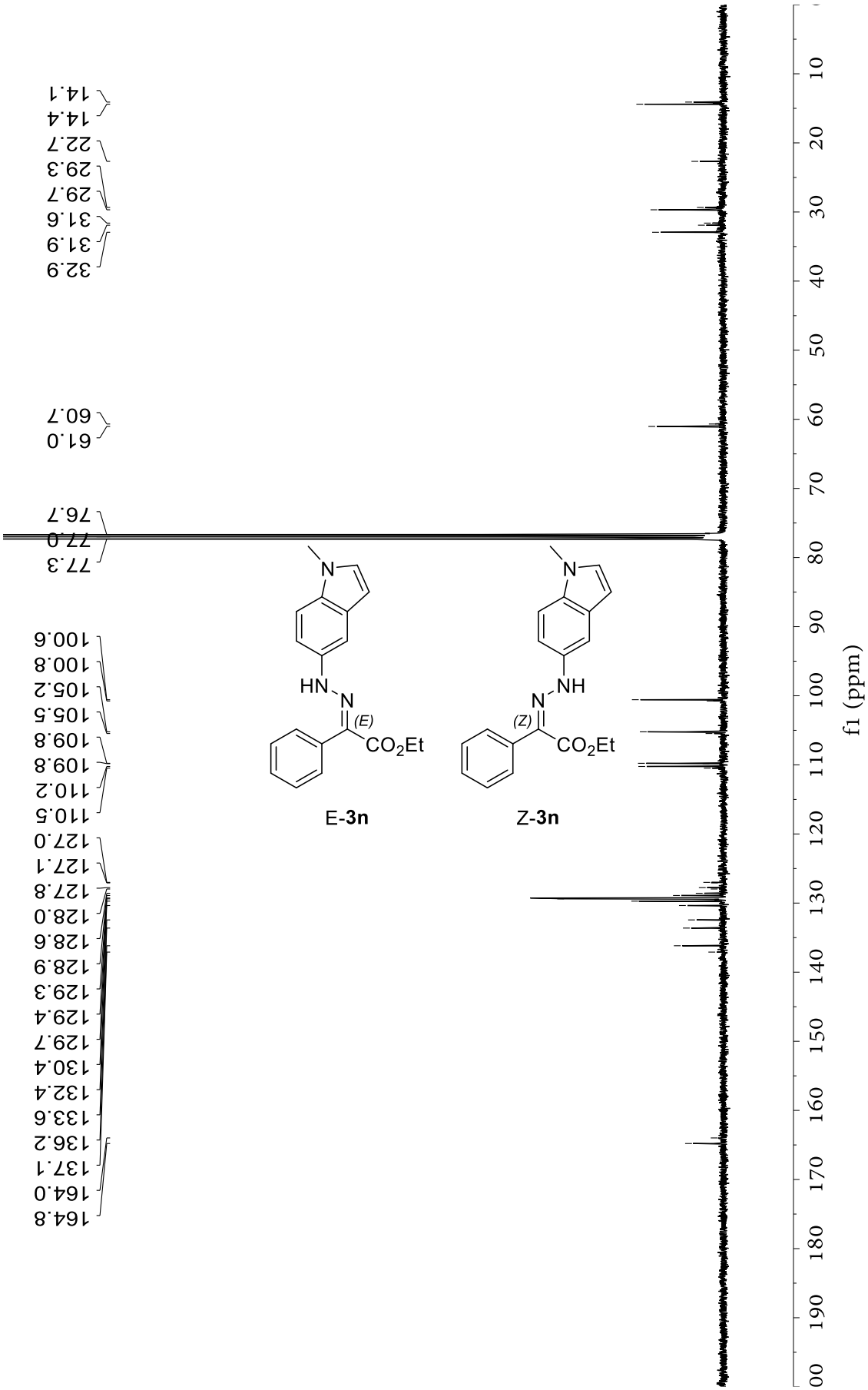
Compound **3m** ^{19}F NMR (565 MHz, $CDCl_3$)



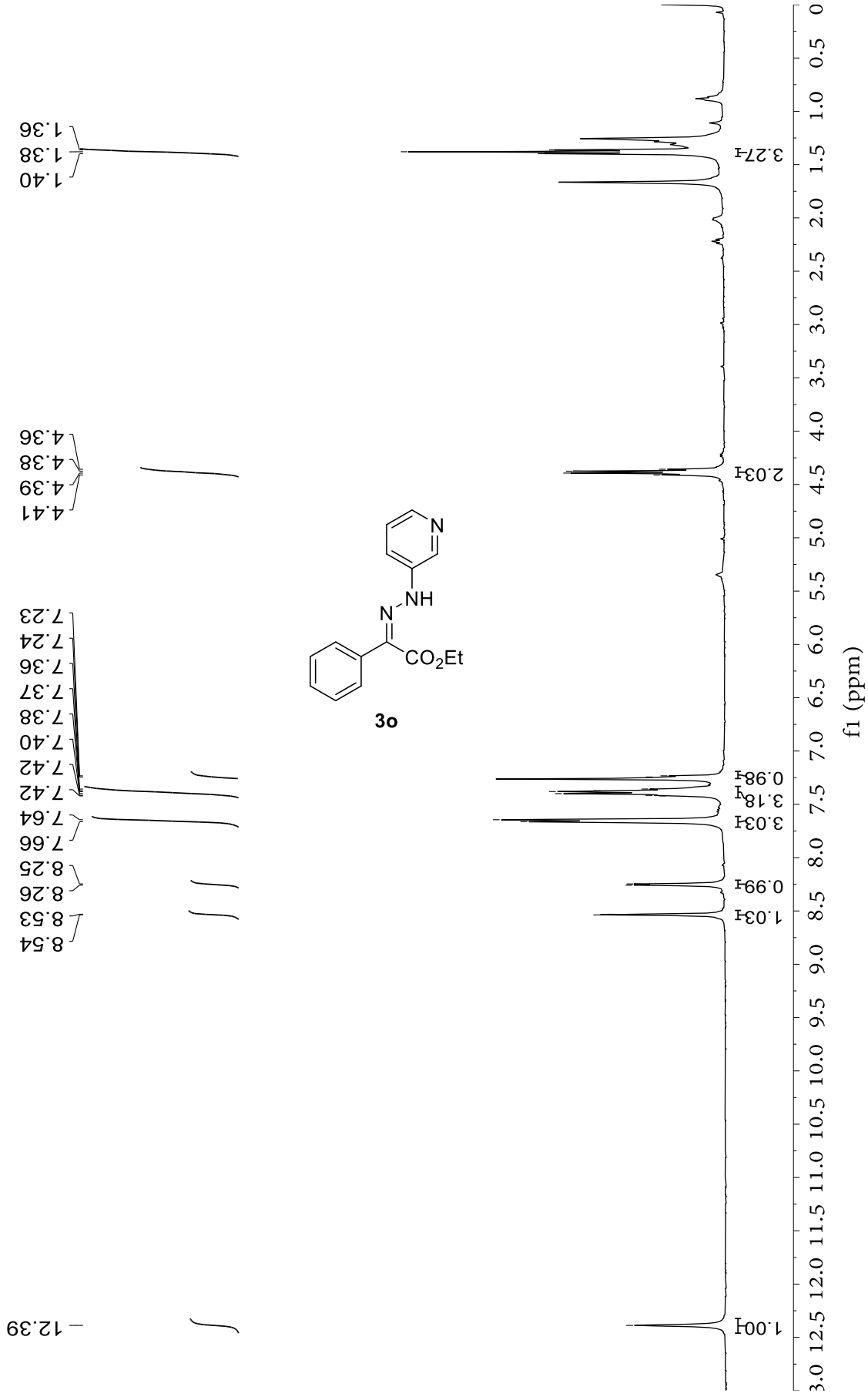
Compound **3n** ^{1}H NMR (400 MHz, $CDCl_3$)



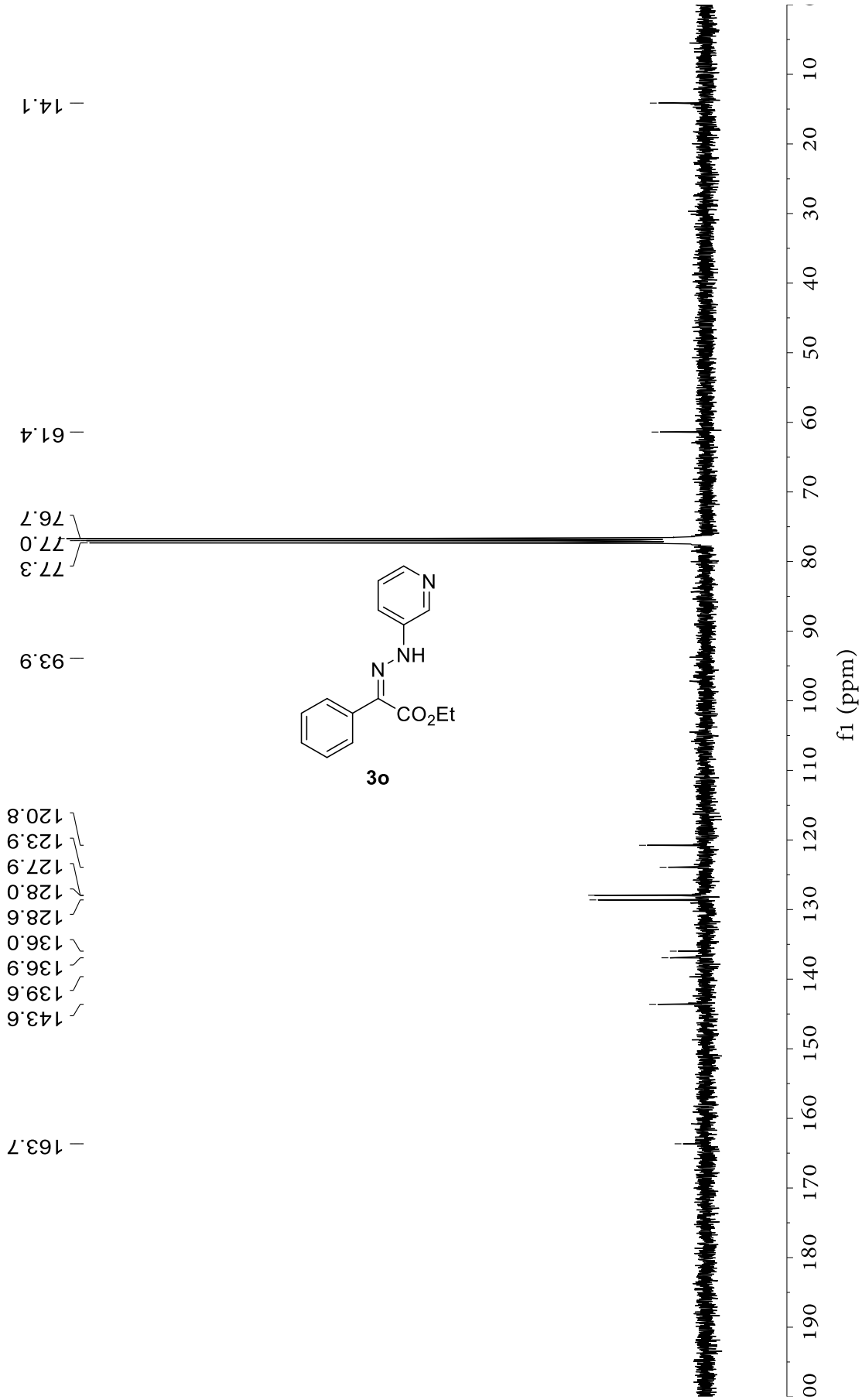
Compound **3n** ^{13}C NMR (101 MHz, $CDCl_3$)



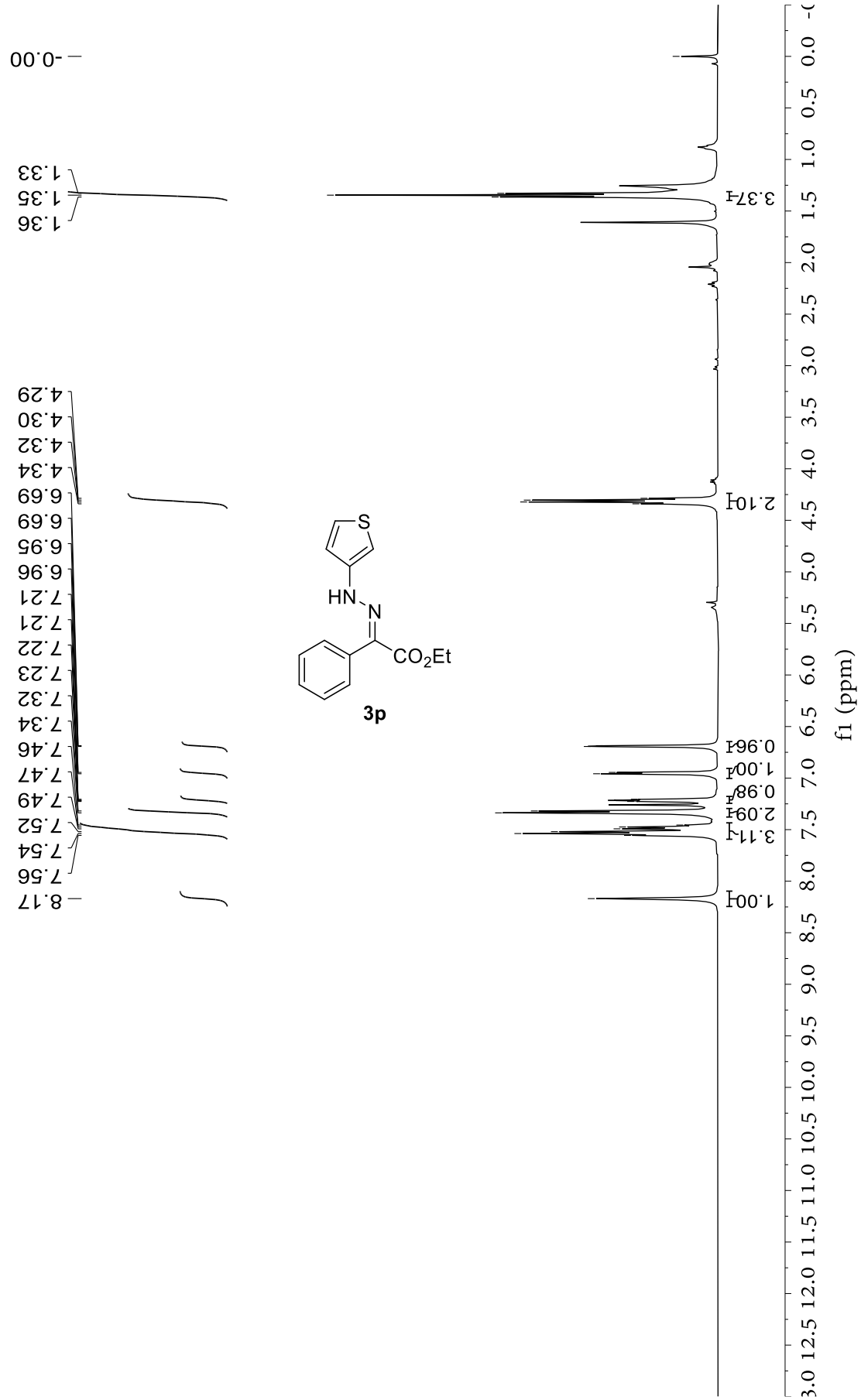
Compound **3o** ^{1}H NMR (400 MHz, $CDCl_3$)



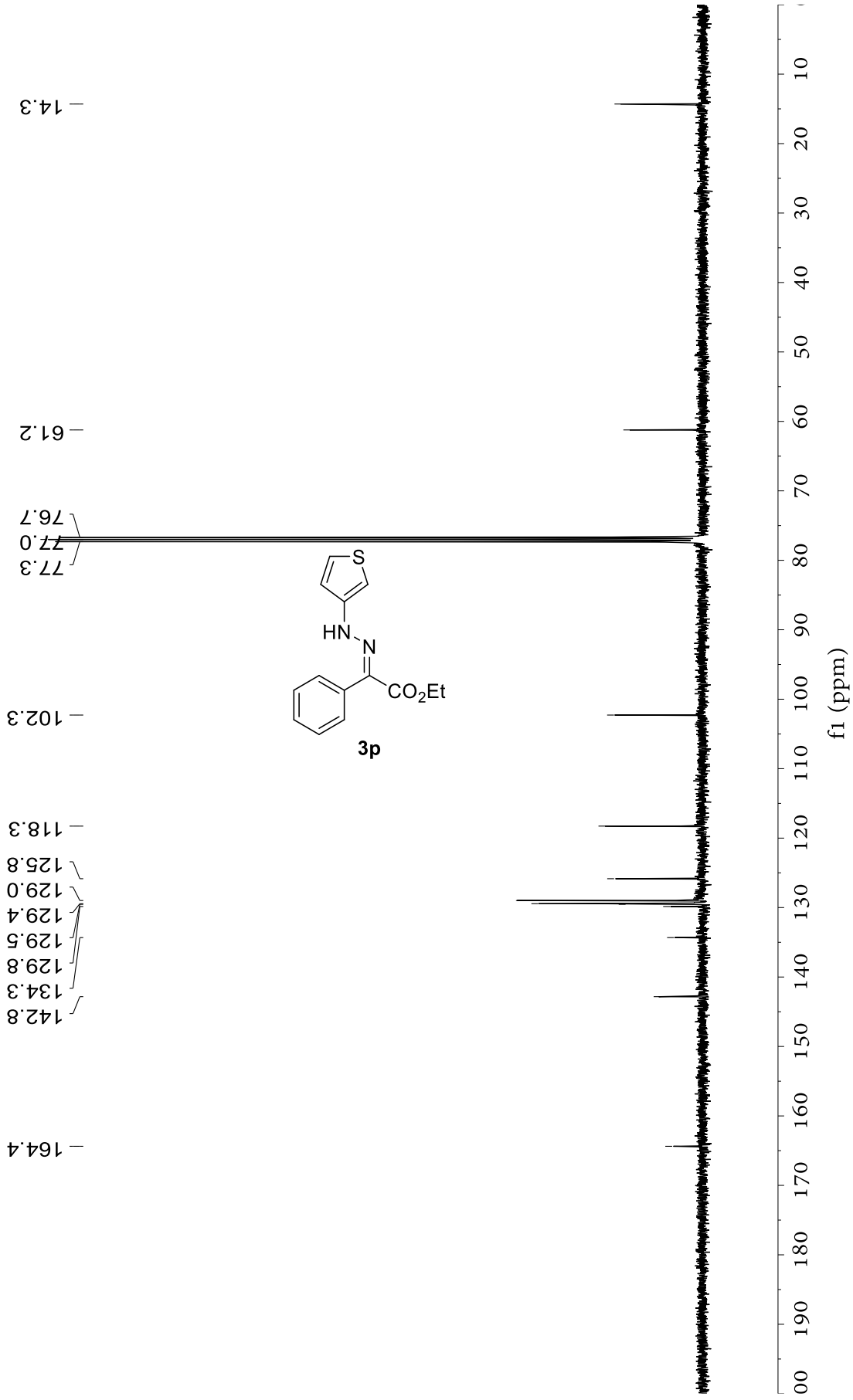
Compound **3o** ^{13}C NMR (101 MHz, $CDCl_3$)



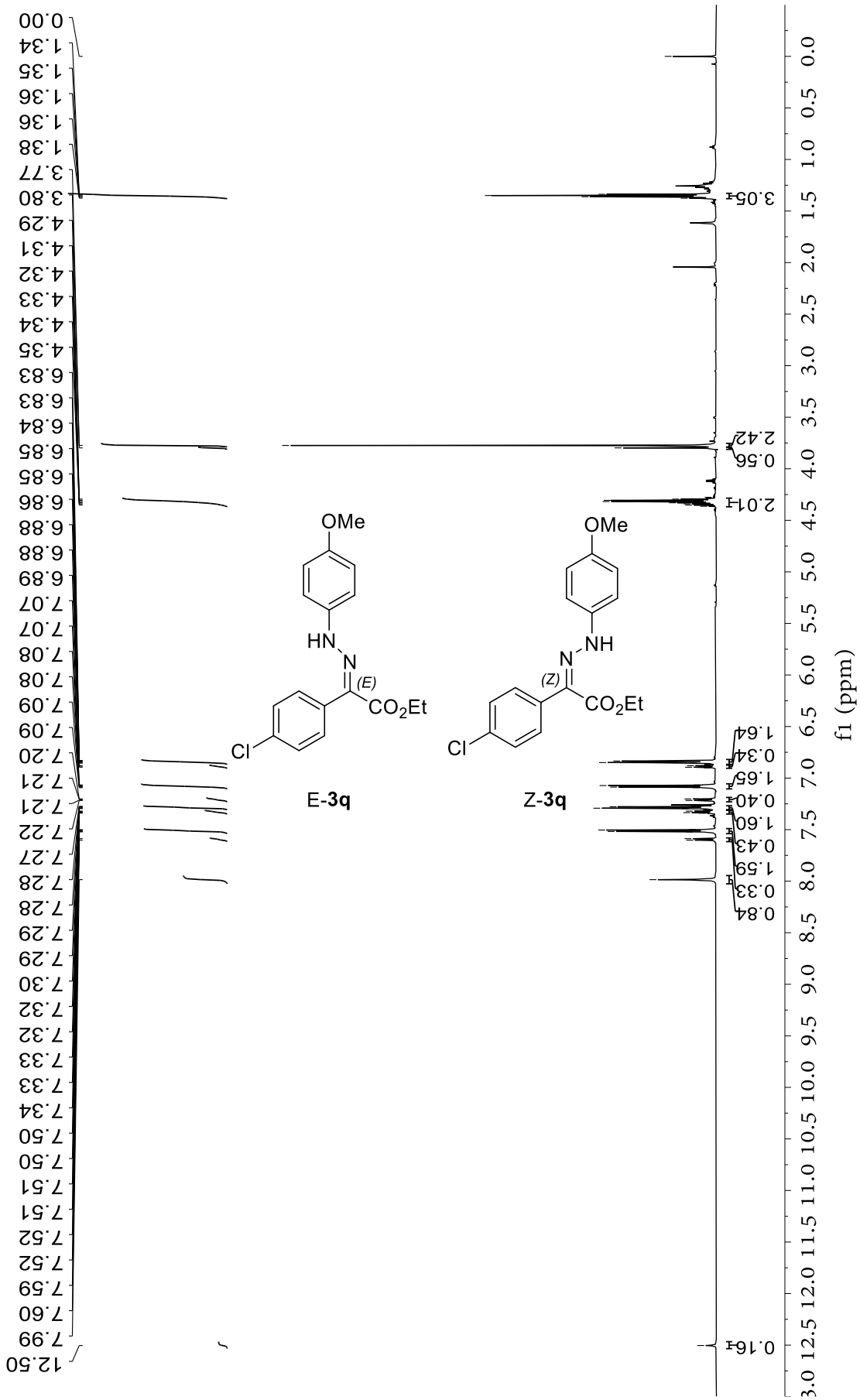
Compound **3p** ^{1}H NMR (400 MHz, $CDCl_3$)



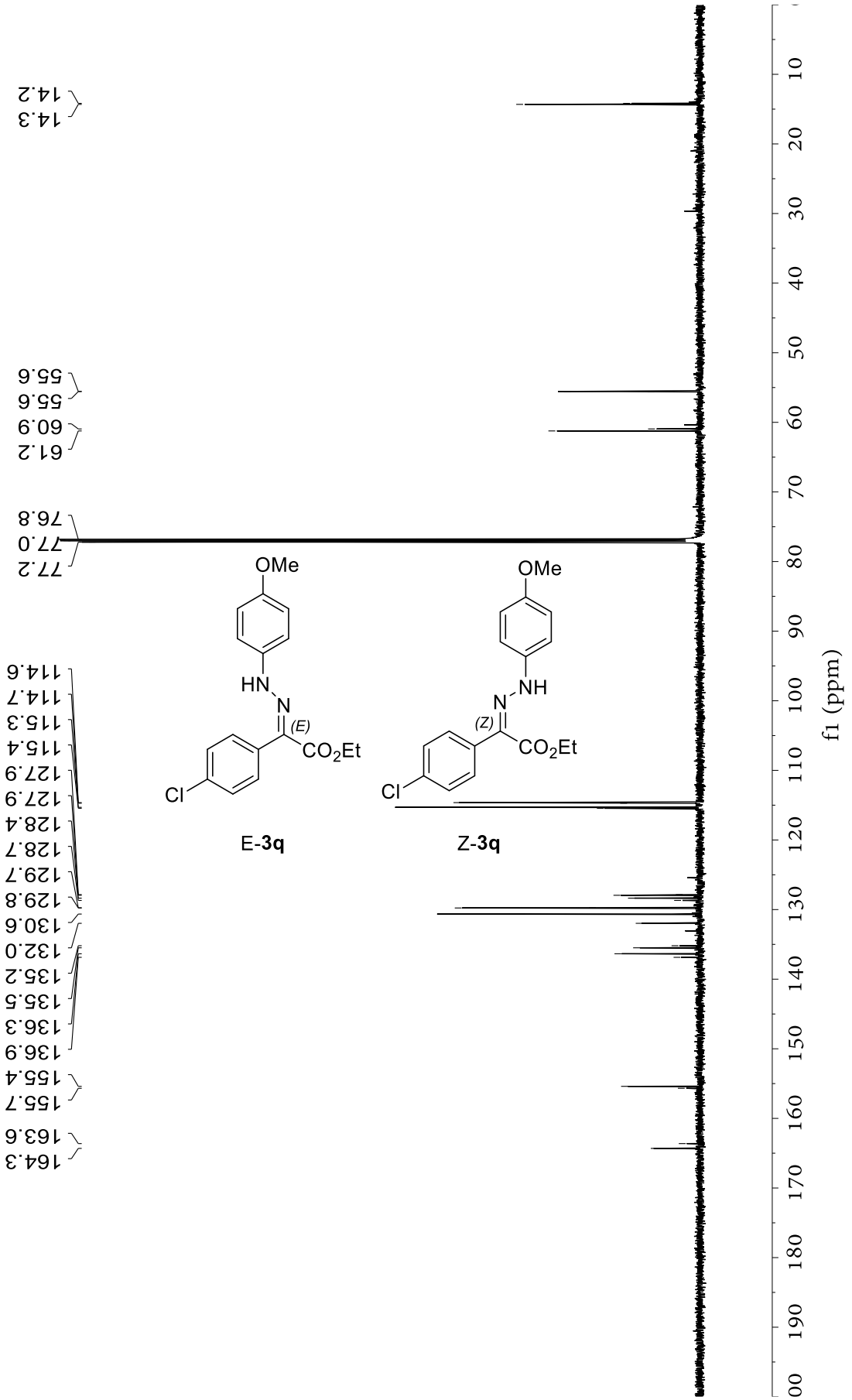
Compound **3p** ^{13}C NMR (101 MHz, $CDCl_3$)



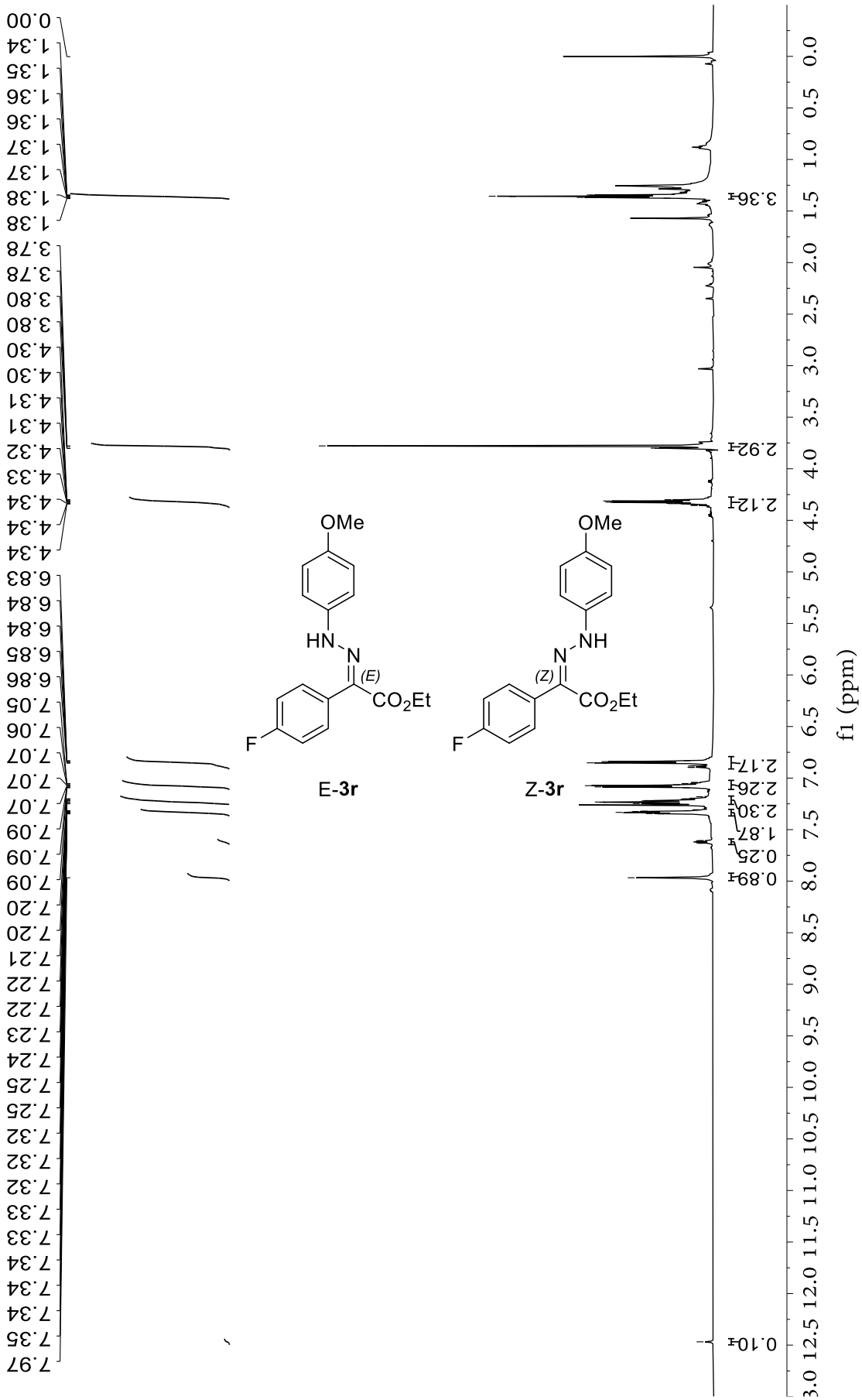
Compound **3q** ^{1}H NMR (600 MHz, $CDCl_3$)



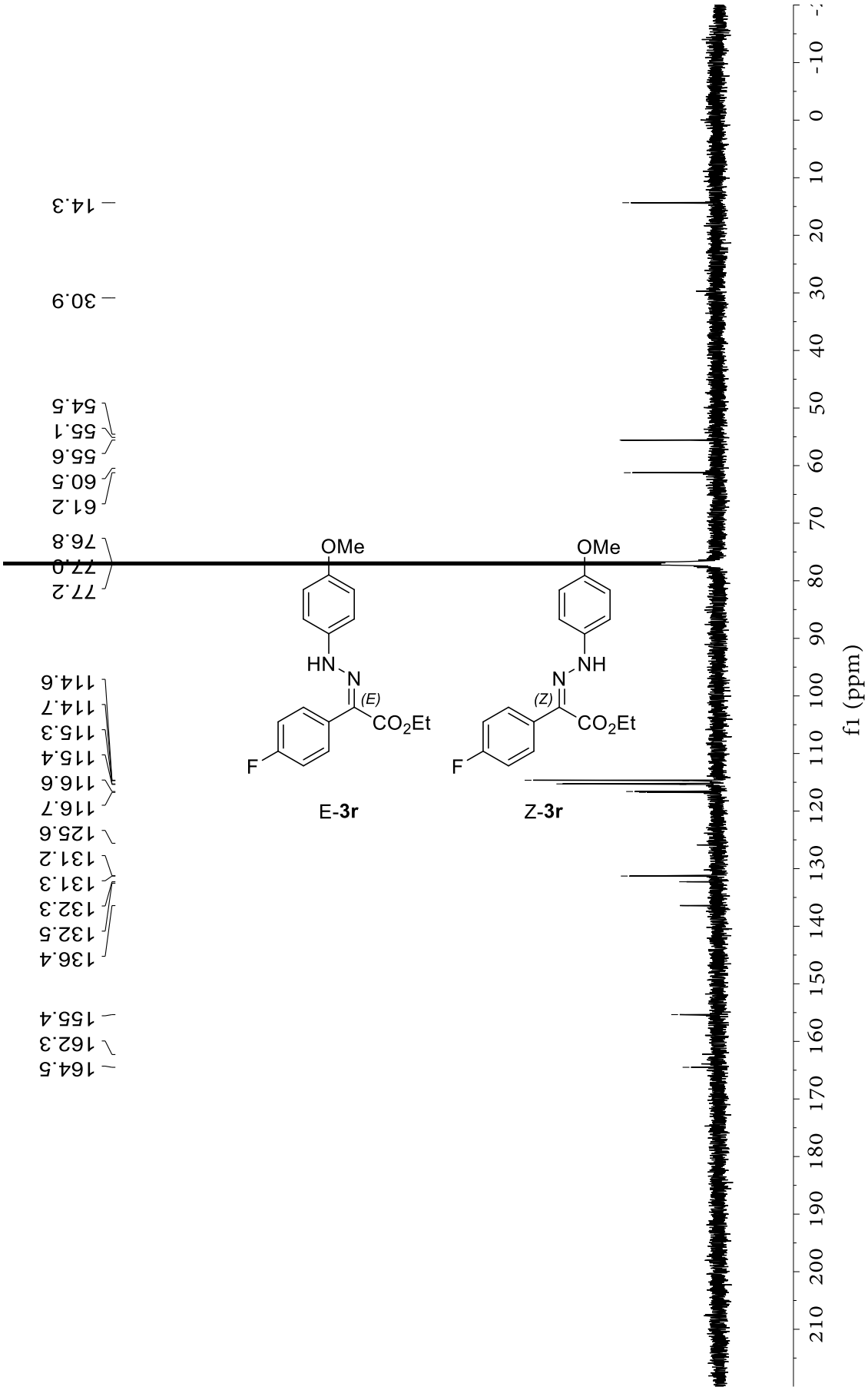
Compound **3q** ^{13}C NMR (151 MHz, $CDCl_3$)



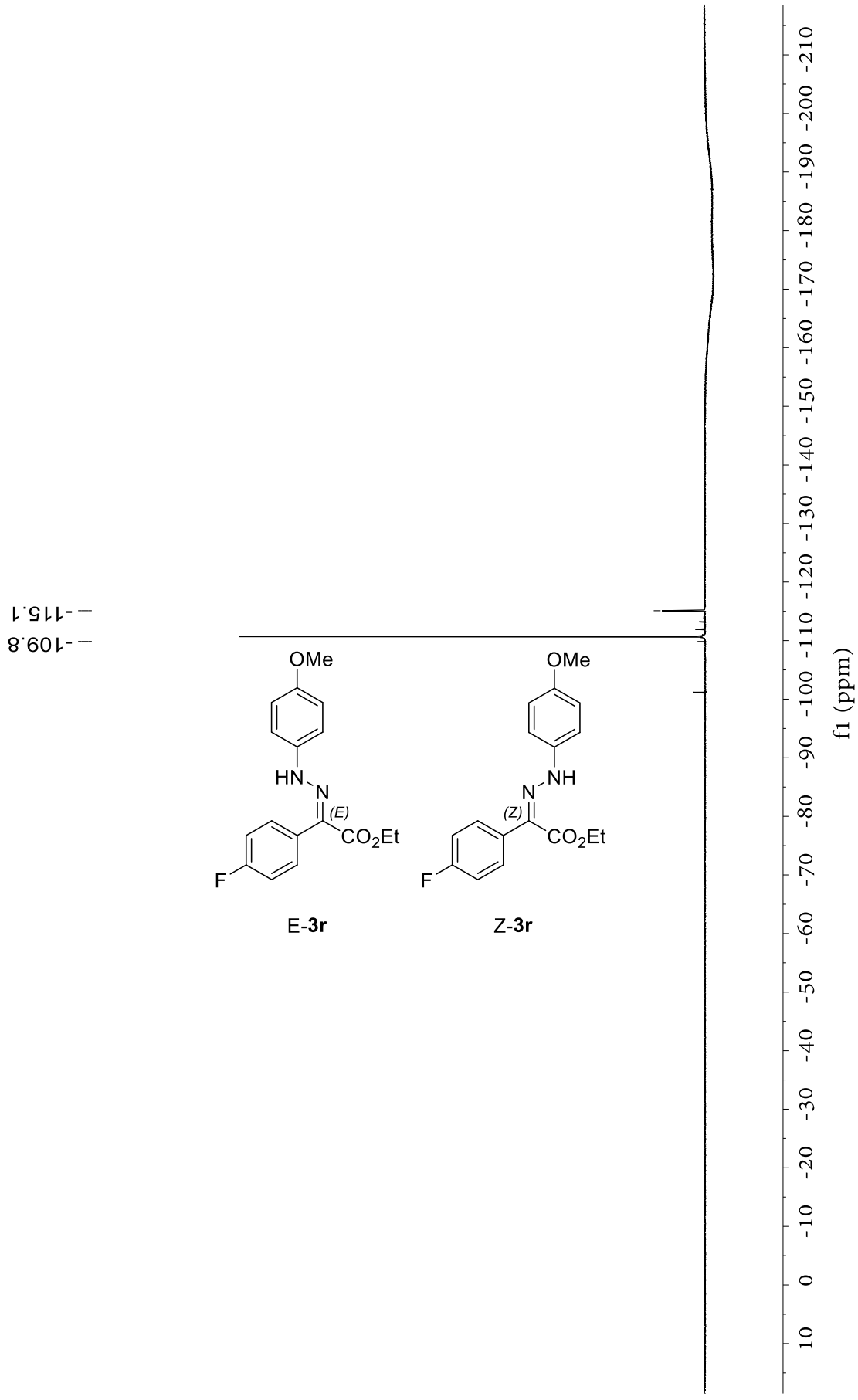
Compound **3r** ^{1}H NMR (600 MHz, $CDCl_3$)



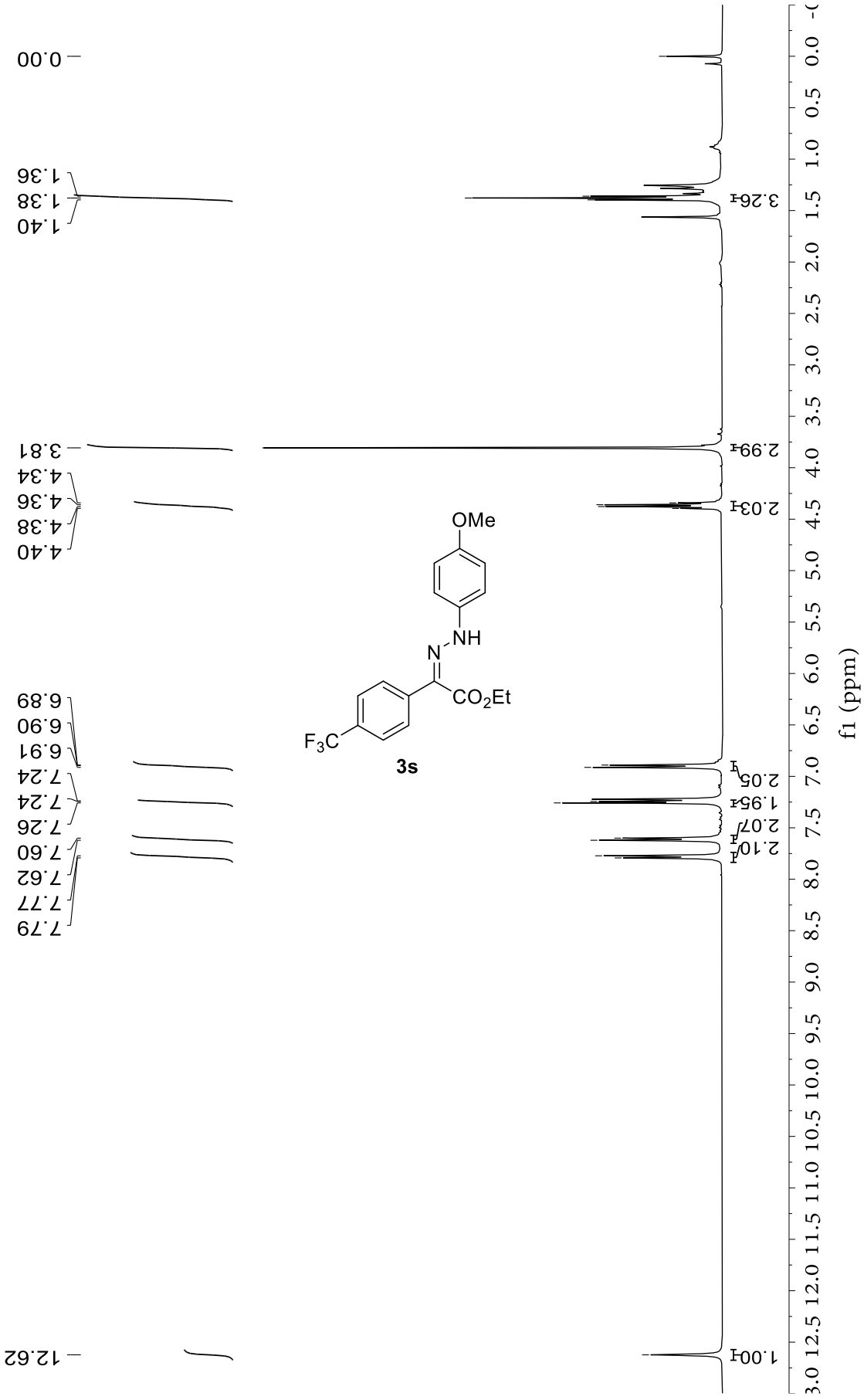
Compound **3r** ^{13}C NMR (151 MHz, $CDCl_3$)



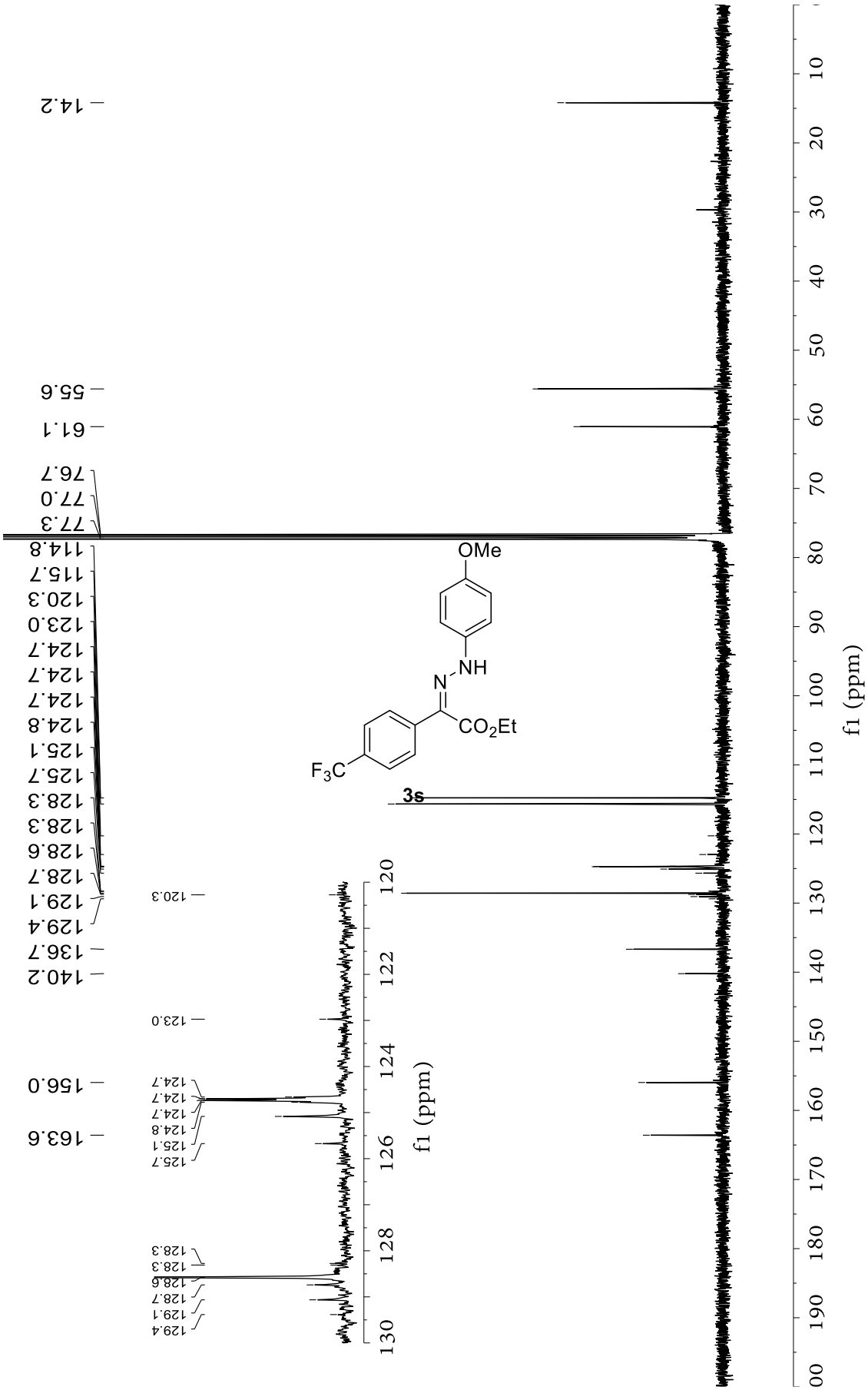
Compound **3r** ^{19}F NMR (565 MHz, $CDCl_3$)



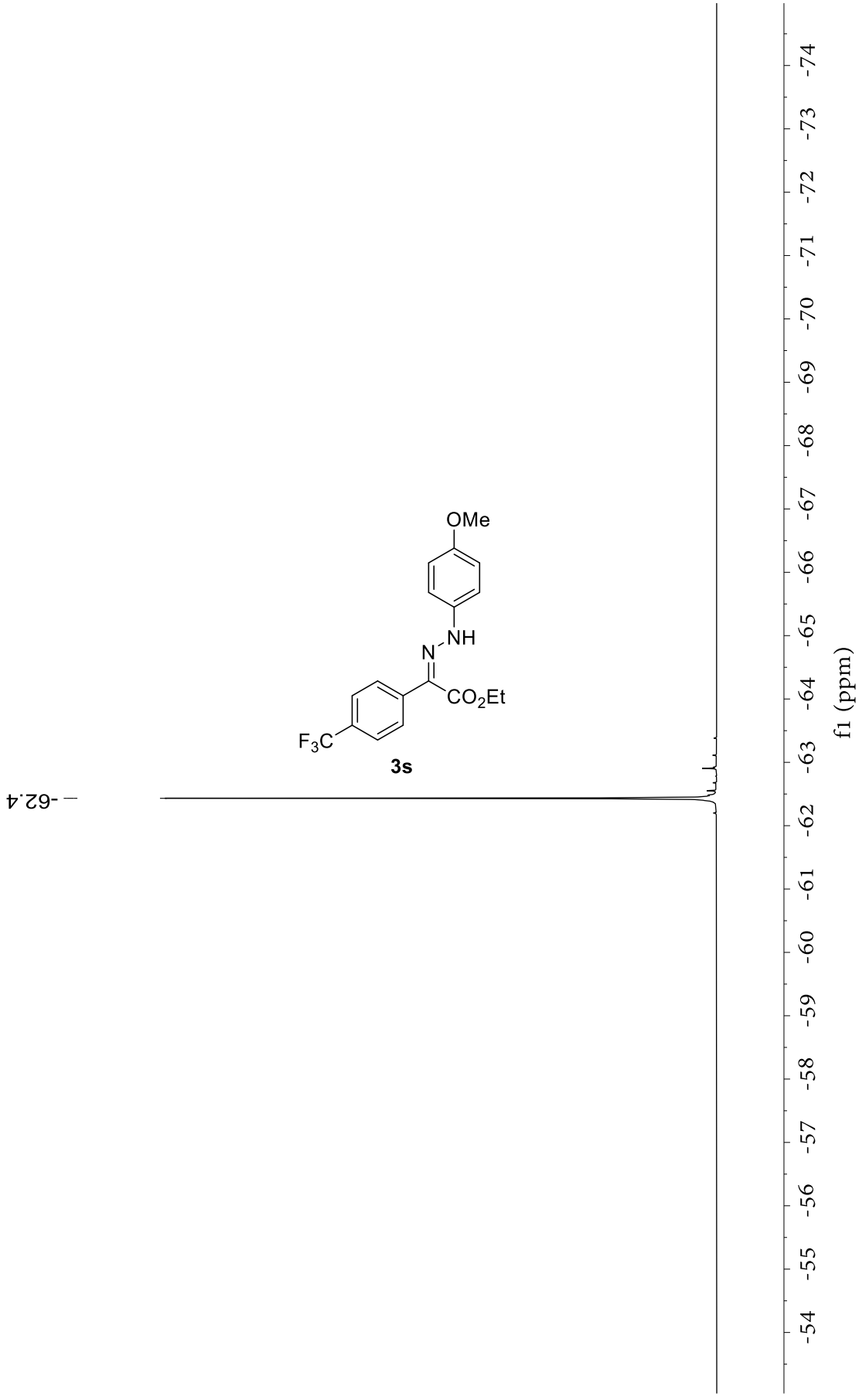
Compound **3s** ^{1}H NMR (400 MHz, $CDCl_3$)



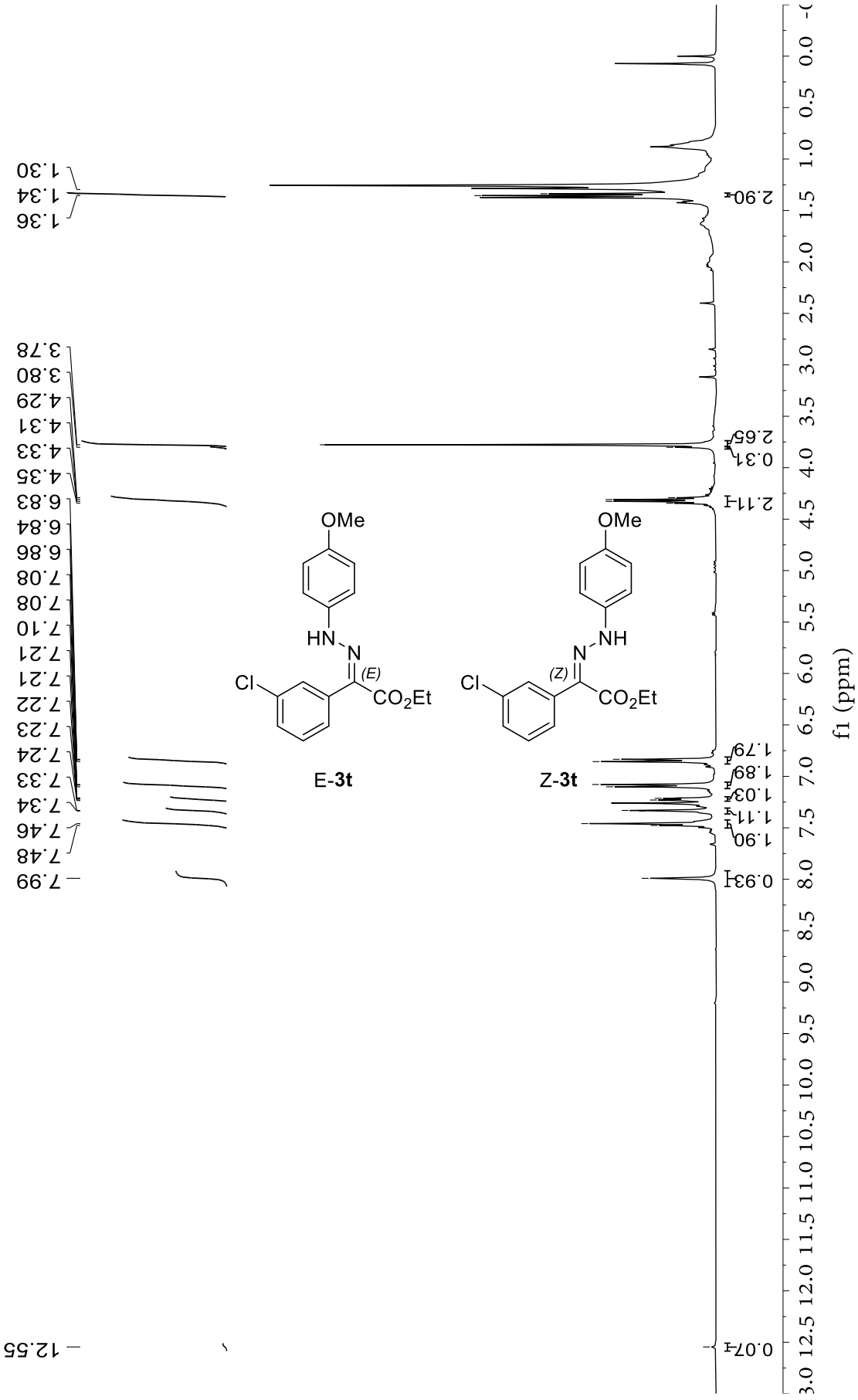
Compound **3s** ^{13}C NMR (101 MHz, $CDCl_3$)



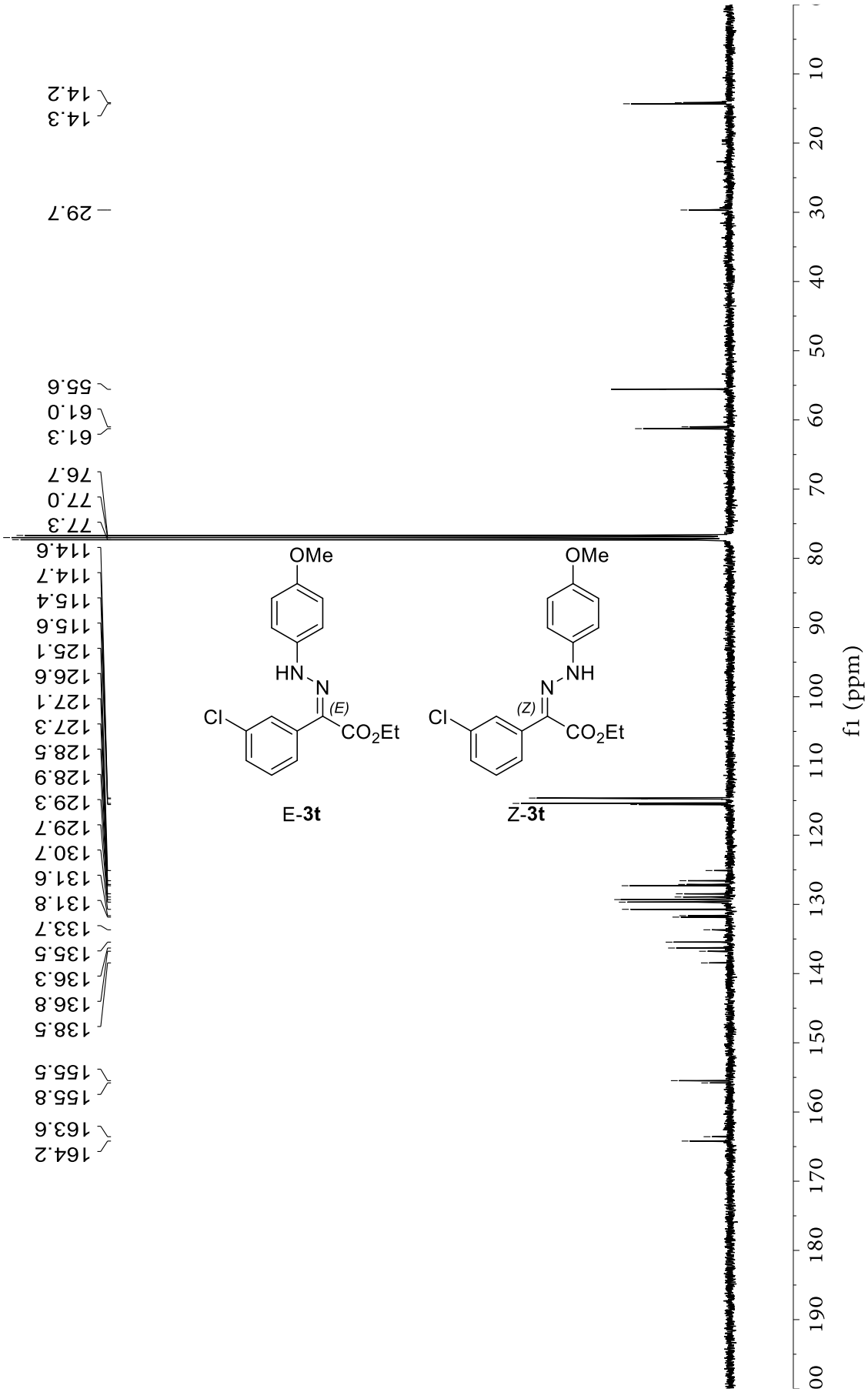
Compound **3s** ^{19}F NMR (376 MHz, $CDCl_3$)



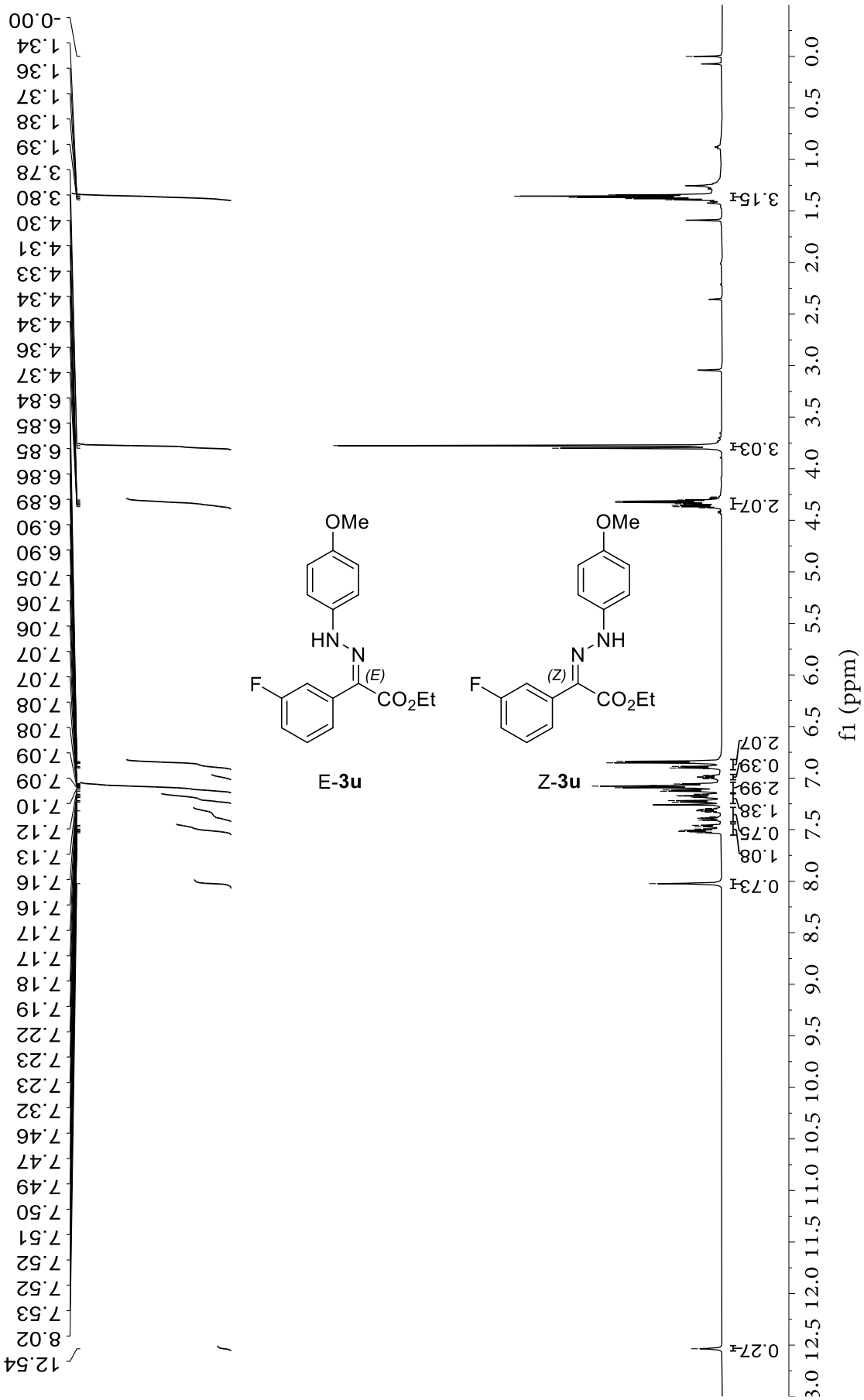
Compound **3t** ^{1}H NMR (400 MHz, $CDCl_3$)



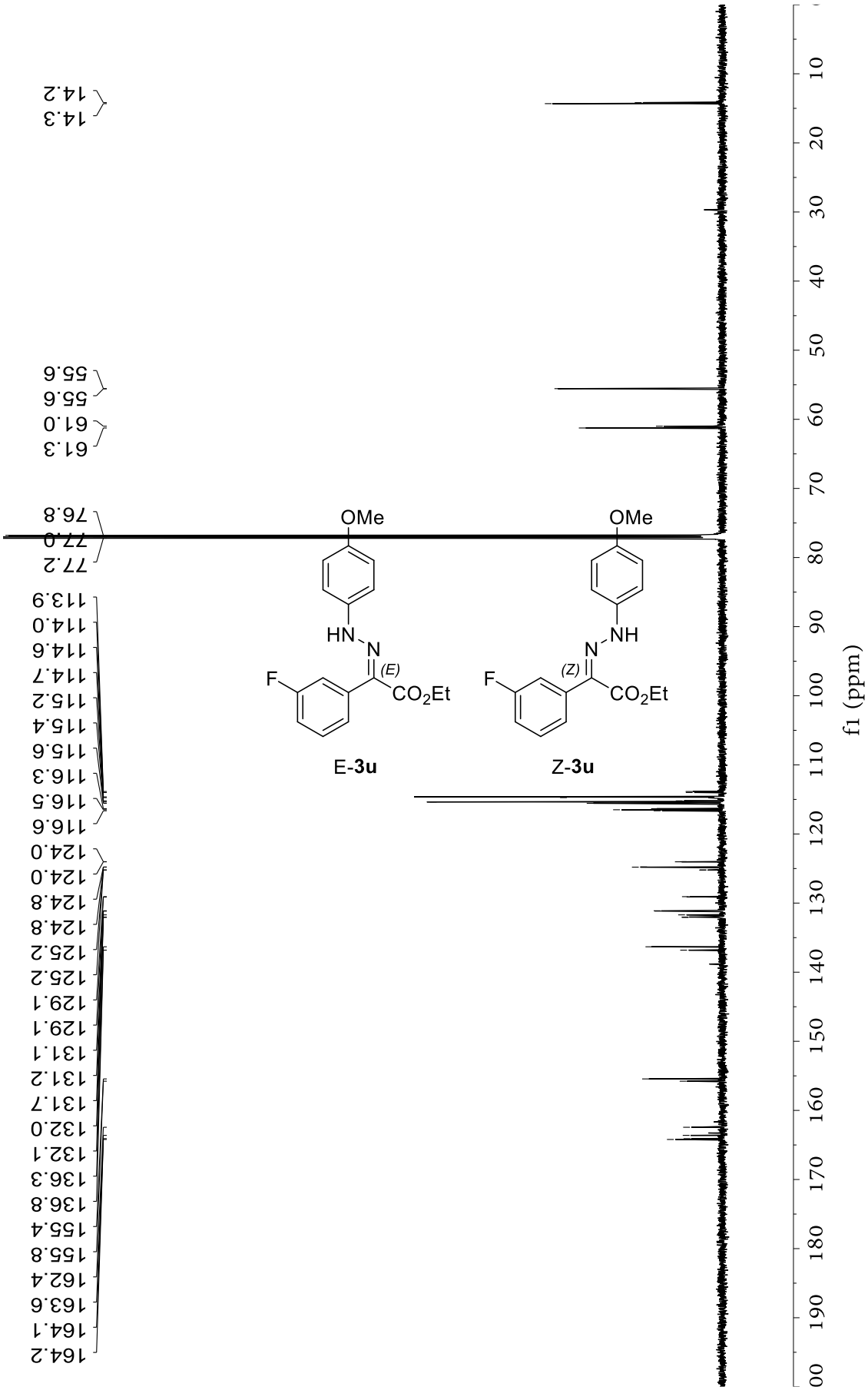
Compound **3t** ^{13}C NMR (101 MHz, $CDCl_3$)



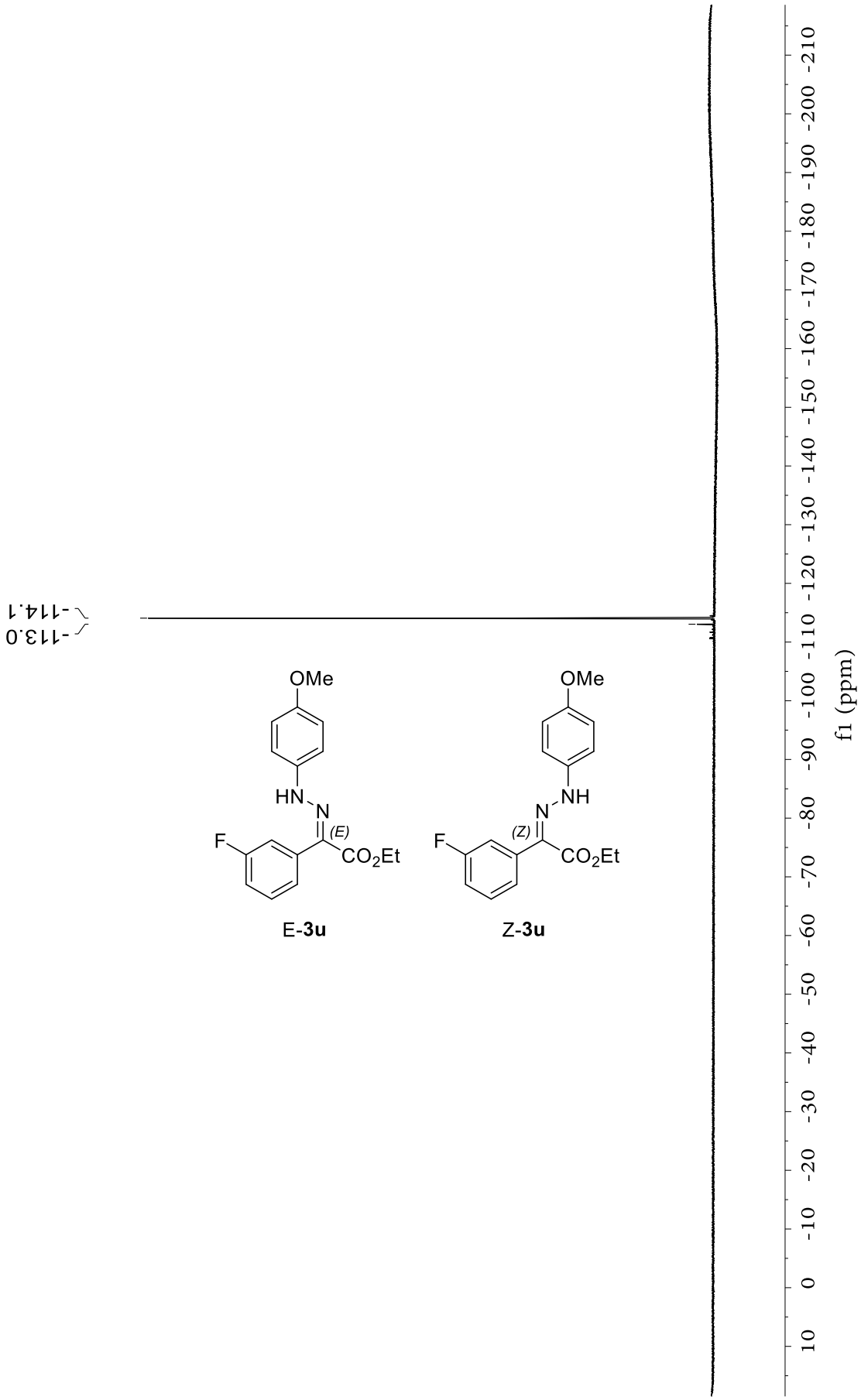
Compound **3u** ^{1}H NMR (600 MHz, $CDCl_3$)



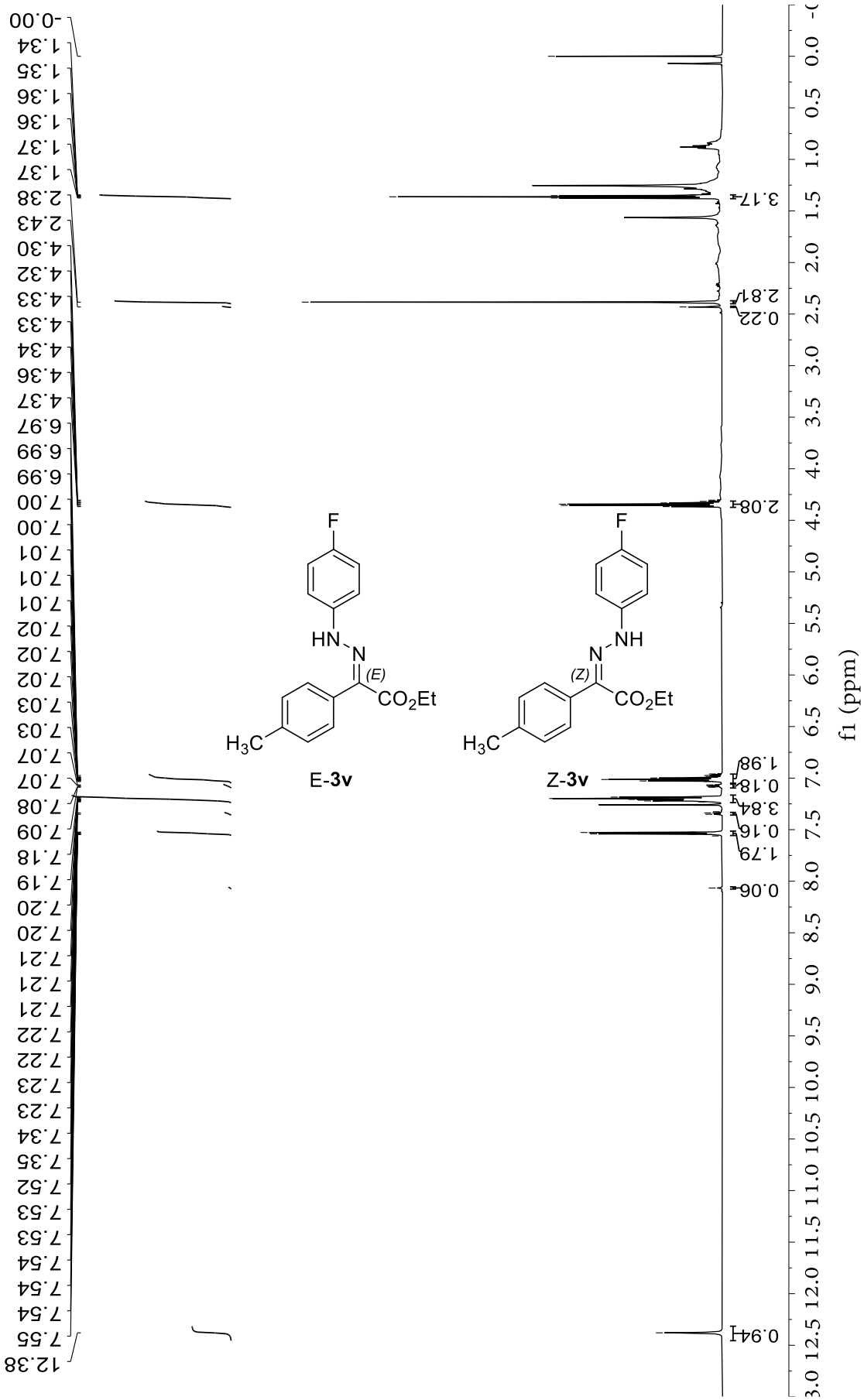
Compound **3u** ^{13}C NMR (151 MHz, $CDCl_3$)



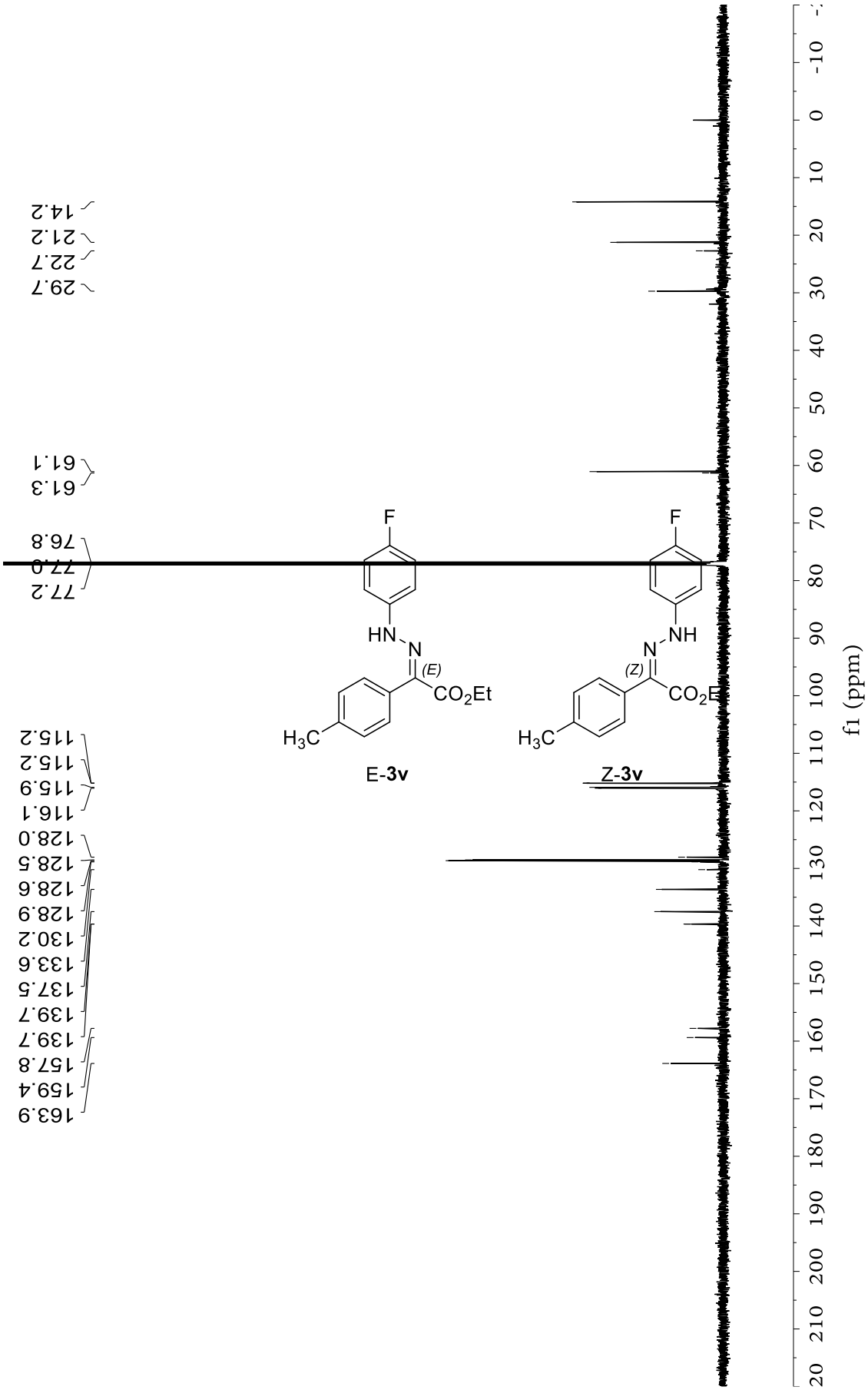
Compound **3u** ^{19}F NMR (565 MHz, $CDCl_3$)



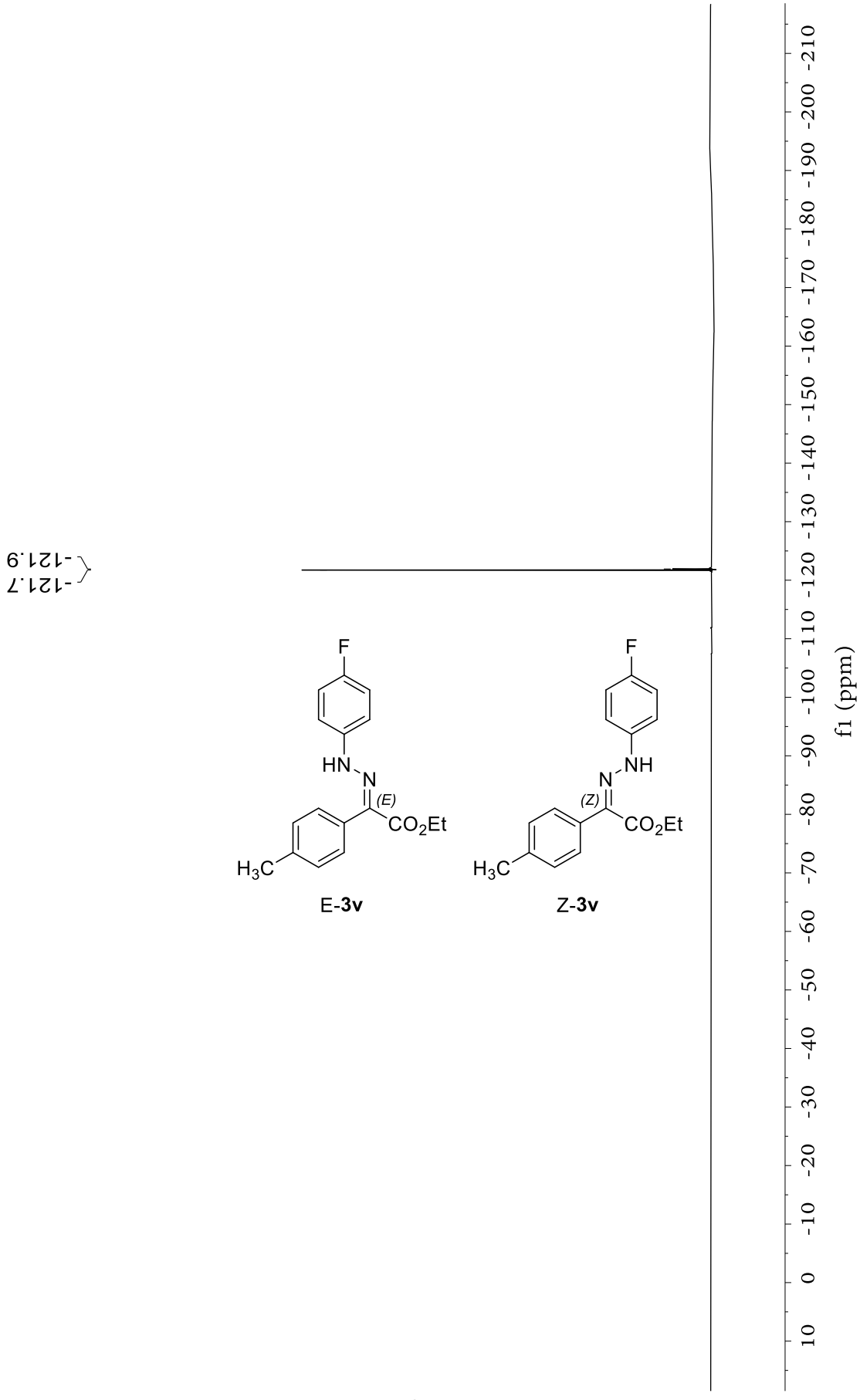
Compound **3v** ^{1}H NMR (600 MHz, $CDCl_3$)



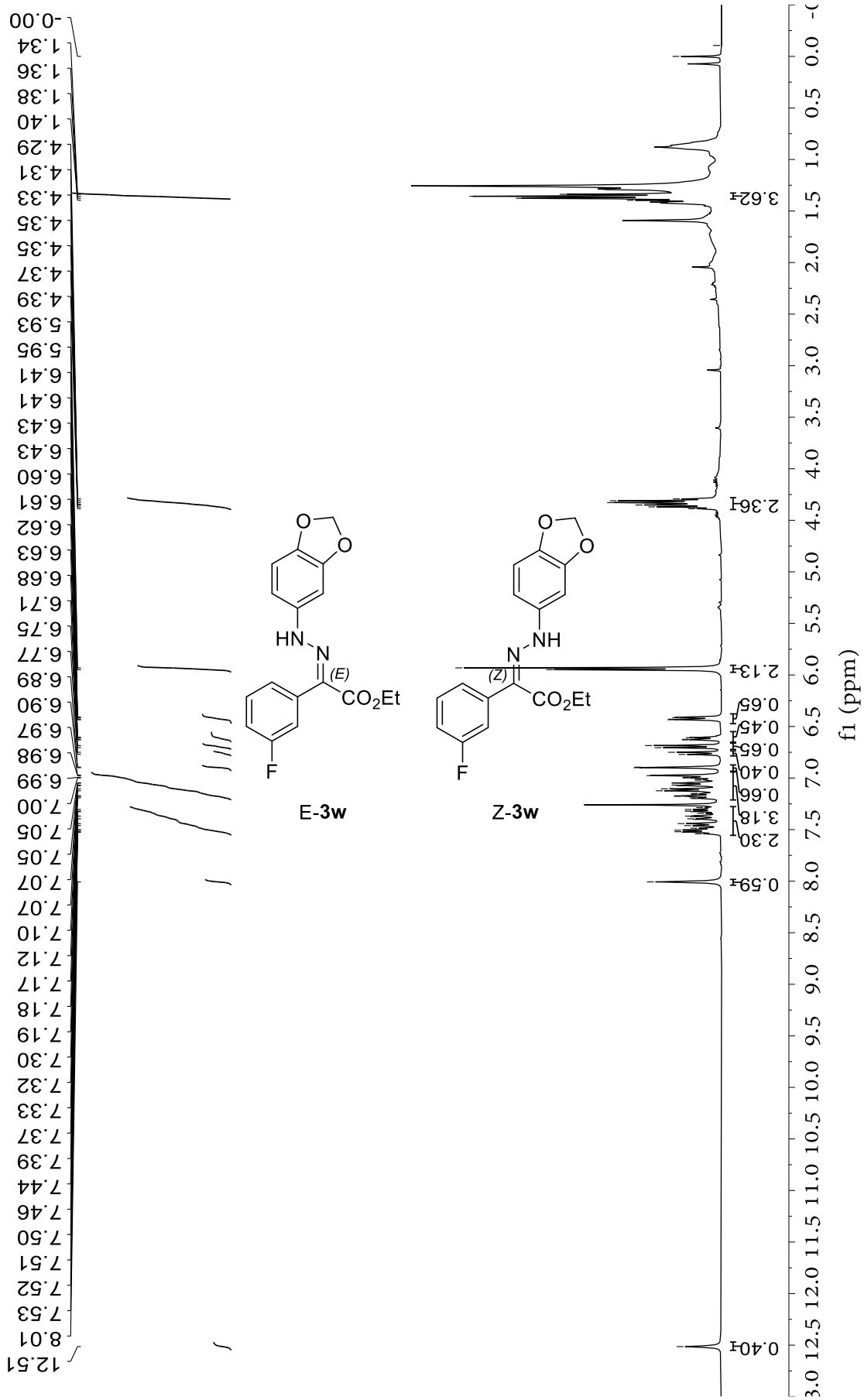
Compound **3v** ^{13}C NMR (151 MHz, $CDCl_3$)



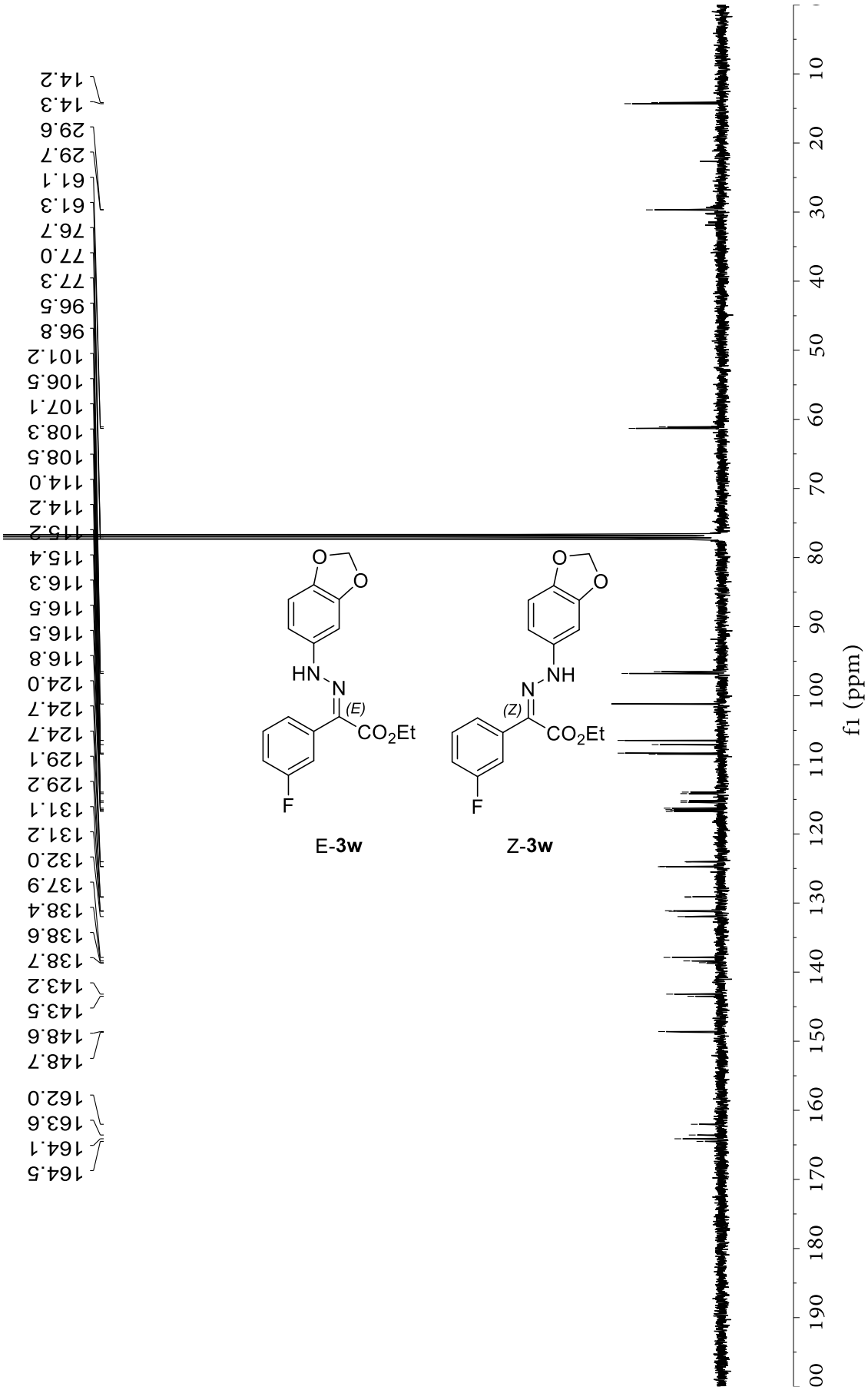
Compound **3v** ^{19}F NMR (565 MHz, $CDCl_3$)



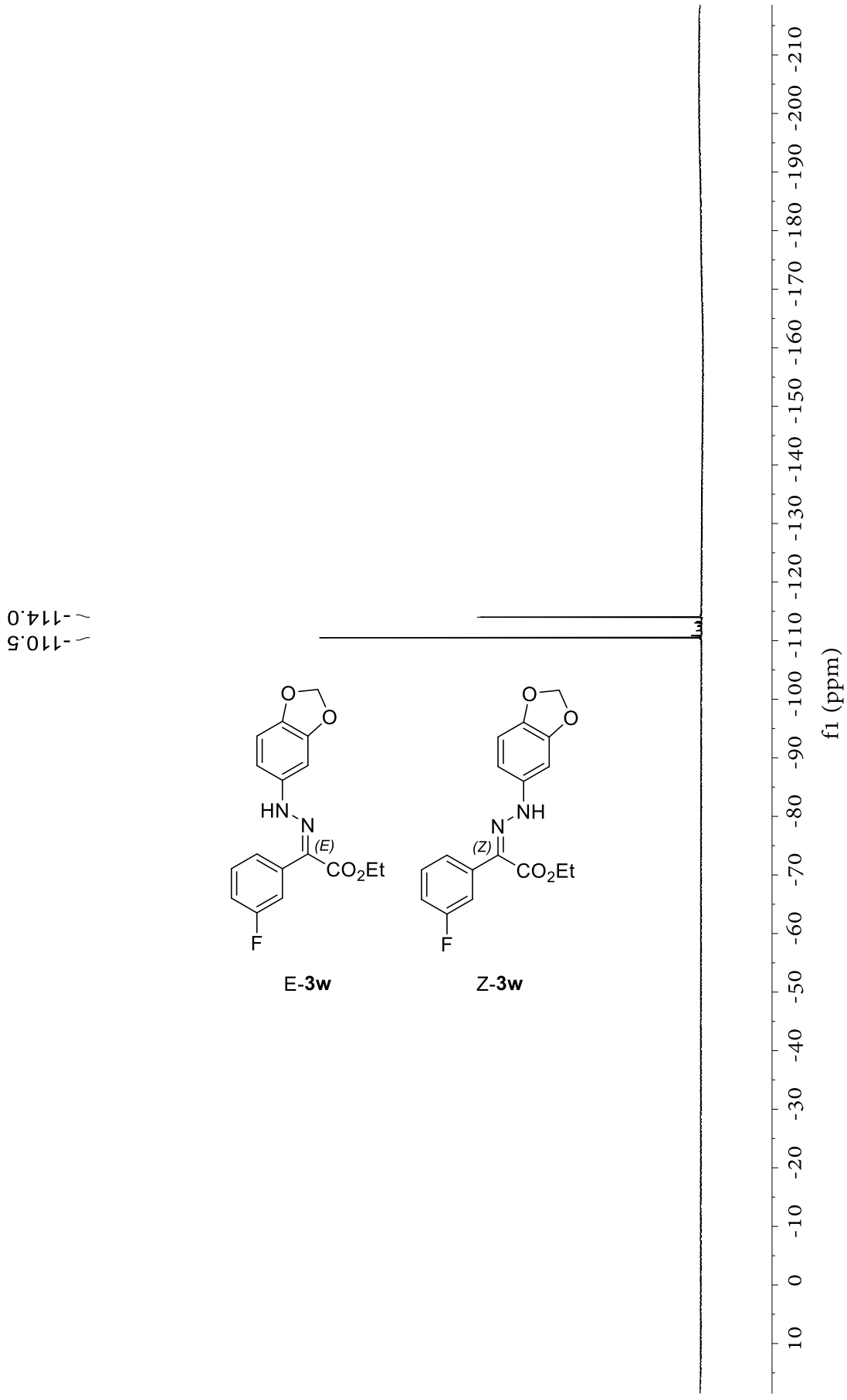
Compound **3v** ^{1}H NMR (600 MHz, $CDCl_3$)



Compound **3w** ^{13}C NMR (151 MHz, $CDCl_3$)

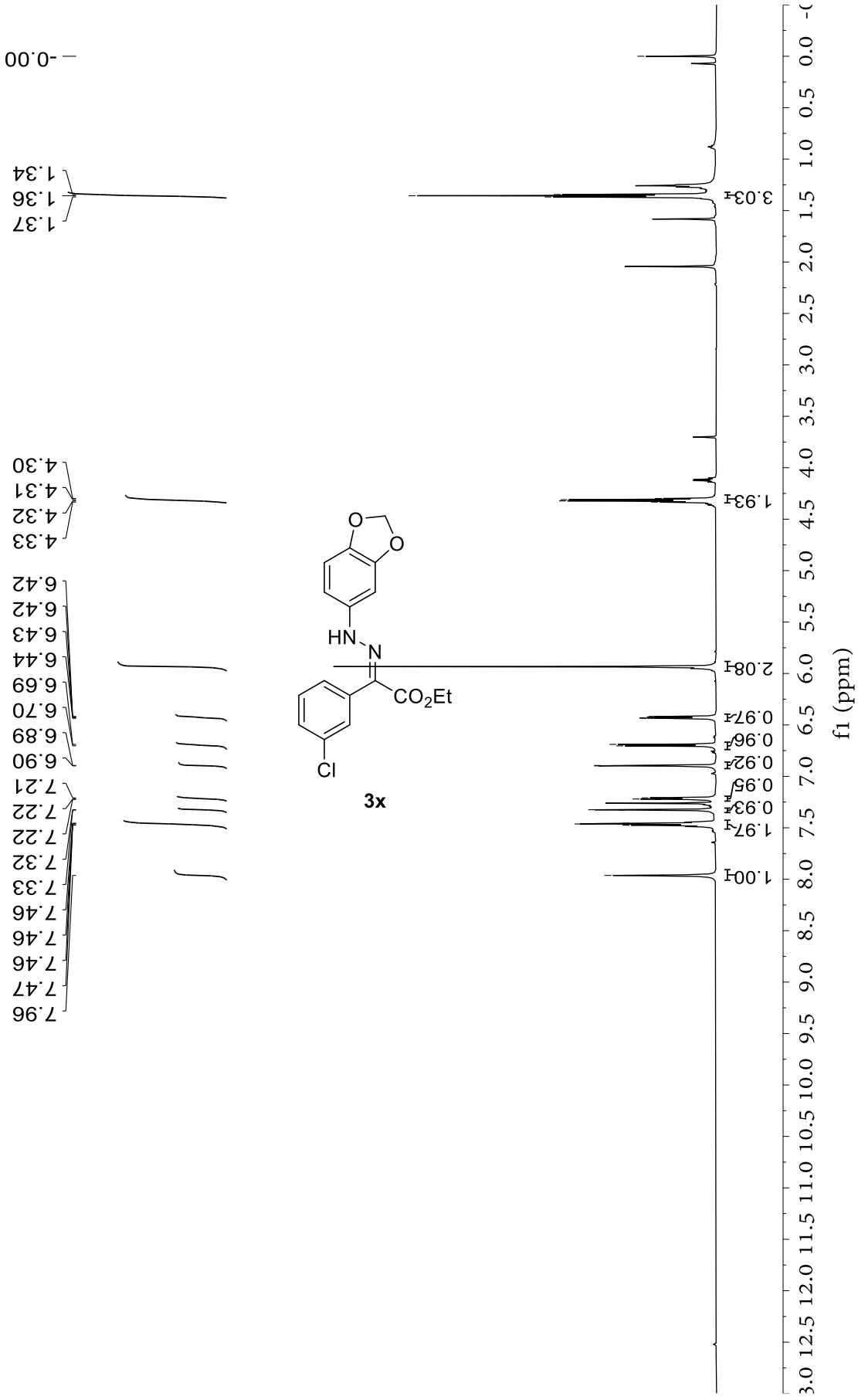


Compound **3w** ^{19}F NMR (565 MHz, $CDCl_3$)



E-**3w** Z-**3w**

Compound **3x** ^{1}H NMR (600 MHz, $CDCl_3$)



Compound **3w** ^{13}C NMR (151 MHz, $CDCl_3$)