Electronic Supplementary Information

Visible Light-Mediated-*ipso*-Annulation of Activated Alkynes: Access to 3-Alkylated Spiro[4,5]-trienones, Thiaspiro[4,5]-trienones and Azaspiro[4,5]-trienones

Sabyasachi Manna, Puneeth Kumar Someswara Ashwathappa and Kandikere Ramaiah Prabhu*

Department of Organic Chemistry,

Indian Institute of Science,

Bangalore 560 012,

Karnataka, India

*To whom correspondence should be addressed. E-mail: prabhu@iisc.ac.in

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1. General experimental

All reactions were carried out using distilled solvents. Reactions were monitored by using precoated silica TLC plates. Mass spectra were recorded on EI, and ESI (TOF) modes. NMR spectra were recorded in at 400 MHz spectrometers in $CDCl_3$, DMSO-d_6, and tetramethylsilane (TMS; δ = 0.00 ppm) served as an internal standard for ^1H NMR. The corresponding residual non-deuterated solvent signal ($CDCl_3$; δ = 77.00 ppm and DMSO-d_6; δ = 39.52 ppm) was used as internal standard for ^{13}C NMR. Column chromatography was carried out on silica gel 230-400 mesh or 100-200 mesh (Merck), and thin-layer chromatography was carried out using SILICA GEL GF-254. Chemicals obtained from commercial suppliers were used without further purification. The pK_a of **2a** was measured with an eutech pH meter (model no. - pH 700) and found to be 10.1 in water and 10.7 in $CH_3CN:H_2O$ (1:1). $(Ir[df(CF_3)ppy]_2(dtbpy))PF_6$ was prepared according to the literature report.[1]

Emission Spectra of Blue LED Strip:

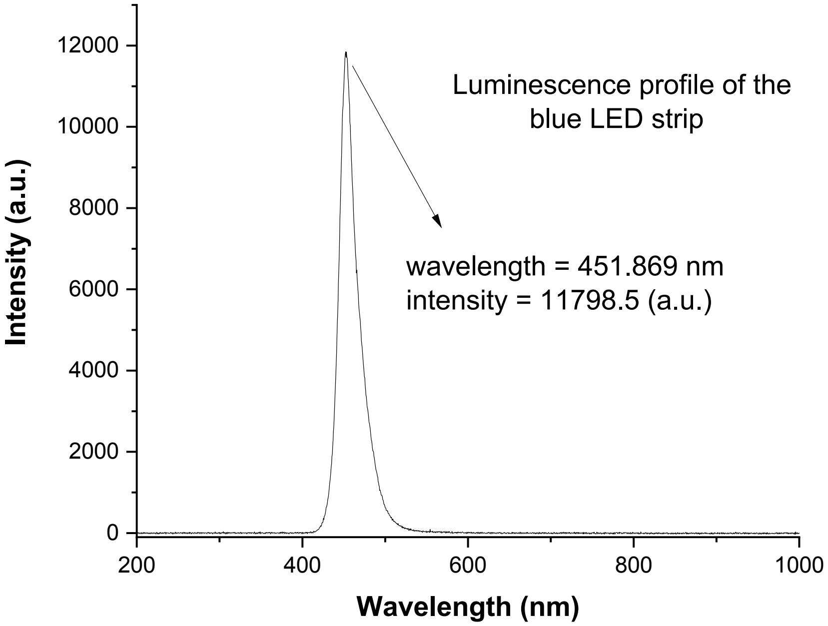


Fig 1: Plot of Intensity versus wavelength for the emission from the blue LED strip

An Ocean Optics spectrometer was used to record the emission spectrum of the blue LED strip, which was oriented toward the aperture of the spectrometer unit at a distance of approximately 8 cm.

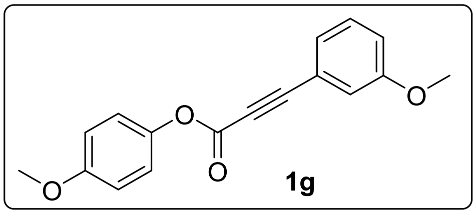
2. Preparation for aryl-alkynoates, N-arylpropiolamide and S-aryl prop-2-ynethioates:

Aryl alkynoates, *N*-arylpropiolamides, and S-aryl prop-2-ynethioates were prepared according to the literature procedure.[2, 3] The data for the known arylalkynoates, N-arylpropiolamides, and S-aryl prop-2-ynethioates matched with the reported data.[2, 3]

General procedure for the synthesis of aryl-alkynoate and *N*-arylpropiolamides: EDC.HCl (1.5 equiv) was added to a well-stirred solution of phenol or aniline (1.2 mmol for phenols or 3 mmol for anilines, 1 equiv), propiolic acid derivative (1.1 equiv) and DMAP (0.30 equiv) in CH_2Cl_2 (5 mL). The clear reaction mixture was stirred at 0 °C for 1 h, followed by 2-5 h at room temperature (monitored by TLC). After completion of the reaction, the solvent was evaporated under reduced pressure, and the crude reaction mixture was purified on a silica gel column (100-200 mesh) using EtOAc/petroleum ether as eluent.
General procedure for the synthesis of *N*-alkyl-*N*,arylpropiolamides: To a solution of appropriate *N*-arylpropiolamides (1.2 mmol) in THF (8 mL) was added NaH (60% in oil, 3.0 mmol) and appropriate alkyl iodide or alkylbromide (3.0 mmol). The mixture was stirred for 30 min then poured into ice water (20 mL), extracted with CH_2Cl_2 (3 x 20 mL), washed (brine), dried (Na_2SO_4) and evaporated the solvent. The crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to afford corresponding *N*-arylpropiolamides.

Characterization data for unknown aryl alkynoates and N-alkyl-N,arylpropiolamides:

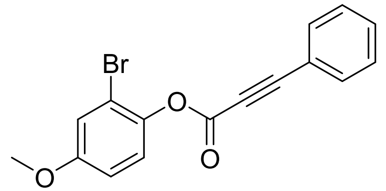
4-Methoxyphenyl 3-(3-methoxyphenyl)propiolate (1g):



1g

Yellowish Solid; Yield – (183 mg, 54%); ***mp***: 55-57 °C R_f (5% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 2940, 2837, 2218, 1713, 1603; **^{1}H NMR δ ($CDCl_3$, 400 MHz):** 7.31-7.27 (t, *J* = 8Hz, 1H), 7.22-7.20 (d, *J* = 7.6Hz, 1H), 7.11-7.09 (d, *J* = 9.2Hz, 3H), 7.03-7.01 (d, *J* = 8.4Hz, 1H), 6.92-6.90 (d, *J* = 9.2Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H); **^{13}C NMR δ ($CDCl_3$, 100 MHz):**159.54, 157.8, 152.9, 143.7, 129.9, 125.8, 122.4, 120.3, 118.0, 117.7, 114.7, 88.7, 80.1, 55.7, 55.5; **HRESI-MS** *(m/z)***:** Calculated for $C_{17}H_{14}O_4$ $[M+H]^+$: 283.0970, found $[M+H]^+$: 283.0971.

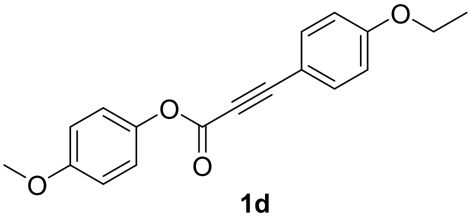
2-Bromo-4-methoxyphenyl 3-phenylpropiolate (1l)



1l

White solid; Yield – (151 mg, 38%); ***mp***: 65-67 °C; R_f (5% EtOAc/petroleum ether) 0.7; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 2231, 1730, 1487, 1141; **^{1}H NMR δ ($CDCl_3$, 400 MHz):** 7.65-7.63 (d, *J* = 7.2Hz, 2H), 7.51-7.47 (t, *J* = 7.2Hz, 1H), 7.42-7.39 (t, *J* = 7.6Hz, 2H), 7.169 (s, 1H), 7.13-7.11 (d, *J* = 8.8Hz, 1H), 6.90-6.87 (dd, *J* = 8.8Hz, 1), 3.80 (s, 3H); **^{13}C NMR δ ($CDCl_3$, 100 MHz):**158.4, 152.0, 141.2, 133.5, 131.3, 128.8, 123.9, 119.3, 118.4, 116.4, 114.4, 89.4, 80.0, 56.0; **HRESI-MS** ***(m/z)*:** Calculated for C16H11O3Br $[M+H]^+$: 330.9970, found $[M+H]^+$: 330.9971.

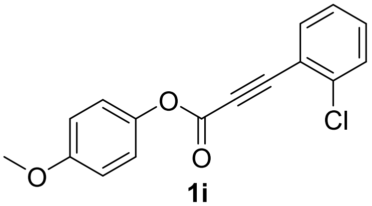
4-Methoxyphenyl 3-(4-ethoxyphenyl)propiolate (1d)



1d

White solid; Yield – (151 mg, 38%); ***mp***: 91-93 °C; R_f (5% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (a). **IR** (Neat, cm^{-1}): 2197, 1718, 1599, 1504; **^{1}H NMR δ ($CDCl_3$, 400 MHz):** 7.57-7.54 (d, *J* = 8.4Hz, 2H), 7.114-7.092 (d, *J* = 8.8Hz, 2H), 6.92-6.87 (m, 4H), 4.09-4.04 (q, *J* = 6.8Hz, 2H), 1.45-1.41 (t, *J* = 6.8Hz, 3H), 3.80 (s, 3H); **^{13}C NMR δ ($CDCl_3$, 100 MHz):**161.4, 157.7, 153.3, 143.8, 135.3, 122.5, 114.9, 114.7, 110.9, 89.9, 79.9, 63.9, 55.7, 14.8; **HRESI-MS** ***(m/z)*:** Calculated for $C_{18}H_{16}O_4$ $[M+H]^+$: 297.1127, found $[M+Na]^+$: 297.1130.

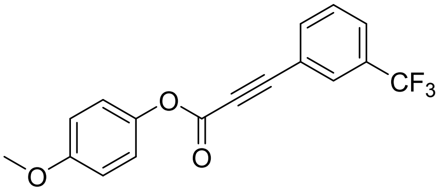
4-Methoxyphenyl 3-(2-chlorophenyl)propiolate (1i)



1i

Yellowish liquid; Yield – (155 mg, 45%); R_f (5% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 2216, 1725, 1502, 1192; **^{1}H NMR δ ($CDCl_3$, 400 MHz):** 7.65-7.63(d, *J* = 7.6Hz, 1H), 7.476-7.457(d, *J* = 7.6Hz, 1H), 7.429-7.390(t, *J* = 7.6Hz, 1H), 7.31-7.25(m, 1H), 7.13-7.11(d, *J* = 8.8Hz, 2H), 6.93-6.90(d, *J* = 8.8Hz, 2H),3.81(s, 3H; **^{13}C NMR δ ($CDCl_3$, 100 MHz):**157.68, 152.6, 143.8, 135.1, 132.1, 129.8, 126.9, 122.4, 114.8, 84.9, 84.6, 55.8, 29.9; **HRESI-MS** ***(m/z)*:** Calculated for $[M+H]^+$: 287.0475, found $[M+H]^+$: 287.0474.

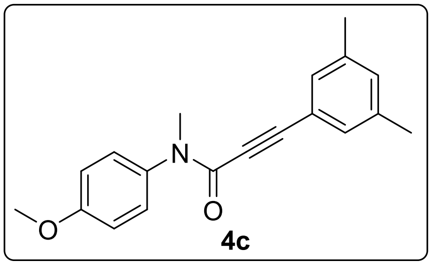
4-Methoxyphenyl 3-(3-(trifluoromethyl)phenyl)propiolate (1h)



1h

Yellowish liquid; Yield – (196 mg, 51%); R_f (5% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 2235, 1727, 1502, 1333; **^{1}H NMR δ (CDCl$_3$, 400 MHz):** 7.79-7.77(d, *J* = 7.6Hz, 1H), 7.73-7.71(d, *J* = 8Hz, 1H), 7.56-7.52(t, *J* = 7.6Hz, 1H), 7.12-7.10(d, *J* = 9.2Hz, 2H), 6.93-6.90(d, *J* = 9.2Hz, 2H), 3.80(s, 3H); **^{13}C NMR δ (CDCl$_3$, 100 MHz):** 157.9, 152.4, 143.7, 136.2, 131.6 (q, *J* = 34Hz), 130.0 (q, *J* = 5Hz), 129.9, 127.6 (q, *J* = 5Hz), 122.1 (q, *J* = 272Hz), 122.28, 120.5, 114.7, 86.3, 81.4, 55.7; **HRESI-MS** *(m/z)***:** Calculated for $C_{17}H_{11}F_3O_3$ [M+H]$^+$: 321.0739, found [M+H]$^+$: 321.0738.

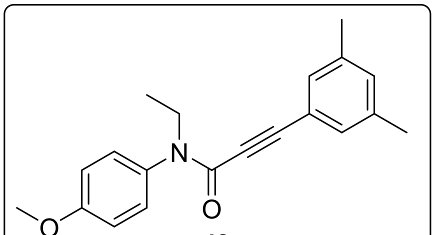
3-(3,5-Dimethylphenyl)-N-(4-methoxyphenyl)-N-methylpropiolamide (4c)



4c

Yellowish liquid; Yield – (288 mg, 82%) R$_f$ (30% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 2918, 2212, 1637, 1511; **^{1}H NMR δ (CDCl$_3$, 400 MHz):** 7.26-7.24(t, *J* = 8.8Hz, 2H), 6.95-6.93(d, *J* = 6.4Hz, 3H), 6.77(s, 2H), 3.84(s, 3H), 3.33(s, 3H), 2.2(s, 6H); **^{13}C NMR δ (CDCl$_3$, 100 MHz):**159.1, 154.8, 137.9, 136.3, 131.9, 130.1, 128.7, 120.2, 114.3, 91.7, 82.2, 55.6, 36.6, 21.1; **HRESI-MS** *(m/z)***:** Calculated for $C_{19}H_{19}NO_2$ [M+H]$^+$: 294.1498, found [M+H]$^+$: 294.1494.

3-(3,5-Dimethylphenyl)-N-(4-methoxyphenyl)-N-ethylpropiolamide (4f)



4f

Yellowish liquid; Yield – (284 mg, 77%) R$_f$ (30% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 2928, 2213, 1633, 1510; **^{1}H NMR δ (CDCl$_3$, 400 MHz):** 7.22-7.20(d, *J* = 6.8Hz, 2H), 6.95-6.93(m, 3H), 6.73(s, 2H), 3.84(s, 3H), 3.82-3.80(m, 2H), 2.19(s, 6H), 1.17-1.13(t, *J* = 7.2Hz, 3H); **^{13}C NMR δ (CDCl$_3$, 100 MHz):** 159.3, 154.5, 137.9, 134.6, 131.80, 130.2, 129.9, 128.4, 120.3, 114.4, 91.5, 82.5, 68.0, 55.6, 43.5, 25.7, 21.1, 13.0; **HRESI-MS** *(m/z)***:** Calculated for $C_{20}H_{21}NO_2$ [M+H]$^+$: 308.1651, found [M+H]$^+$: 308.1652.

3. Optimization and Control Studies

In an 8 mL screw cap reaction vial equipped with a magnetic stirrer bar was added 4-methoxyphenyl 3-phenylpropiolate (0.2 mmol, 1 equiv.), triethyl methanetricarboxylate, appropriate oxidant, appropriate photocatalyst. The appropriate solvent was added to the vial and it was purged three times with argon and was sealed with a cap containing TFE-lined silicone septa. The reaction vial was then degassed with argon for 15 min via an inlet needle. After this the cap was changed with a solid-top cap under argon flow and the vial was irradiated with 2 × 27 W CFL for 6-24 h. The temperature of the reaction was maintained at approximately 25 °C *via* a fan. After the reaction was stopped, the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (10 mL) and water (10 mL). The residue was extracted with EtOAc (10 mL x 3) and washed with brine (saturated aq NaCl, 10 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed in rotatory evaporator followed by *in vacuo*. The reaction mixture was analyzed by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

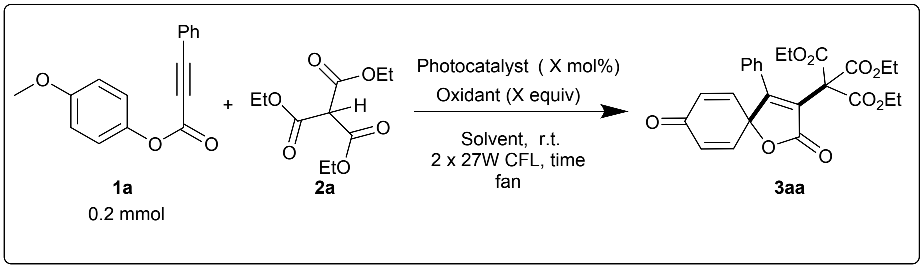


Table 1 Optimization studies [a]

Entry	2a (equiv)	Oxidant (equiv)	Atmosphere	Time (h)	Photocatalyst (mol%)	Solvent	NMR Yield of 3aa (%)[b]
1	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	$CH_3CN:H_2O$ (1:1) 2 mL	68
2	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN	n.d.
3	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	$CH_3CN:H_2O$ (1:1) 2 mL	6
4	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	$C_3H_7CN:H_2O$ (1:1) 2 mL	n.d.

5	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	DCM:H_2O (1:1) 2 mL	trace
6	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	DMSO:H_2O (1:1) 2 mL	31
7	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	DMF:H_2O (1:1) 2 mL	n.d.
8	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	TFE:H_2O (1:1) 2 mL	n.d.
9	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	HFIP:H_2O (1:1) 2 mL	n.d.
10	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3(PF_6)_2$ (2)	CH_3CN:H_2O (1:1) 2 mL	71
11	2	$K_2S_2O_8$ (2)	air	12	Eosin Y (5)	CH_3CN:H_2O (1:1) 2 mL	n.d.
12	2	$K_2S_2O_8$ (2)	air	12	$Ir[\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (2)	CH_3CN:H_2O (1:1) 2 mL	n.d.
13	2	$K_2S_2O_8$ (2)	air	12	Mes-Acr-$PhBF_4$ (5)	CH_3CN:H_2O (1:1) 2 mL	n.d.
14	2	$Na_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:1) 2 mL	45
15	2	$(NH_4)_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:1) 2 mL	61
16	2	70% aq. TBHP(2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:1) 2 mL	n.d.
17	2	O_2	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:1) 2 mL	n.d.
18	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:1) 1 mL	37

19	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:1) 4 mL	26
20	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (3:1) 2 mL	55
21	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:3) 2 mL	48
22	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (1)	CH_3CN:H_2O (1:1) 2 mL	47
23	2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (3)	CH_3CN:H_2O (1:1) 2 mL	67
24	2	$K_2S_2O_8$ (2)	air	24	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:1) 2 mL	66
25	2	$K_2S_2O_8$ (2)	air	6	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	CH_3CN:H_2O (1:1) 2 mL	61
26 [d]	2	$K_2S_2O_8$ (2)	purged and degassed with Ar	12	$Ru(bpy)_3(PF_6)_2$ (2)	CH_3CN:H_2O (1:1) 2 mL	79
27 [c, d]	2	$K_2S_2O_8$ (2)	purged and degassed with Ar	12	$Ru(bpy)_3(PF_6)_2$ (2)	CH_3CN:H_2O (1:1) 2 mL	85
28 [c, d]	1.5	$K_2S_2O_8$ (2)	purged and degassed with Ar	12	$Ru(bpy)_3(PF_6)_2$ (2)	CH_3CN:H_2O (1:1) 2 mL	84
29 [c, d]	1.2	$K_2S_2O_8$ (2)	purged and degassed with Ar	12	$Ru(bpy)_3(PF_6)_2$ (2)	CH_3CN:H_2O (1:1) 2 mL	84
30 [c, d]	1.1	$K_2S_2O_8$ (2)	purged and degassed with Ar	12	$Ru(bpy)_3(PF_6)_2$ (2)	CH_3CN:H_2O (1:1) 2 mL	80

31 [c, d]	1.2	$K_2S_2O_8$ (2.5)	purged and degassed with Ar	12	$Ru(bpy)_3(PF_6)_2$ (2)	$CH_3CN:H_2O$ (1:1) 2 mL	84
32 [c, d]	1.2	$K_2S_2O_8$ (1.5)	purged and degassed with Ar	12	$Ru(bpy)_3(PF_6)_2$ (2)	$CH_3CN:H_2O$ (1:1) 2 mL	79
33	1.2	$K_2S_2O_8$ (2)	air	12	none	$CH_3CN:H_2O$ (1:1) 2 mL	n.d.
34	1.2	none	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	$CH_3CN:H_2O$ (1:1) 2 mL	n.d.
35 [e]	1.2	$K_2S_2O_8$ (2)	air	12	$Ru(bpy)_3Cl_2$. 6 H_2O (2)	$CH_3CN:H_2O$ (1:1) 2 mL	n.d.

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (X mmol), oxidant (X mmol), Photocatalyst (x mol%), Solvent (x mL) under 2 × 27W CFL for 6-12 h. [b] NMR yield (using 1,3,5-trimethoxybenzene as an internal standard).[c] Reaction mixture was degassed with Ar for 15 min. [d] Reaction was performed under blue LED strip (452 nm, 1.5 mW/cm^2). [e] Reaction was performed in the dark.

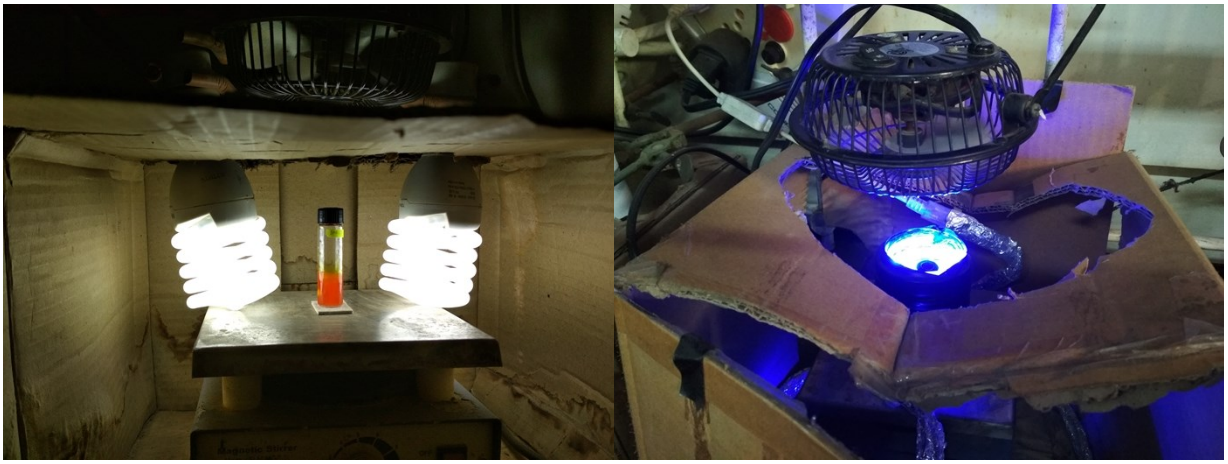


Fig 2: Reaction set-up under CFL (left) and Blue LED strips (right)

4. General Experimental Procedure

(a) General experimental procedure for spirocyclization of alkynoate with tricarbonyls:

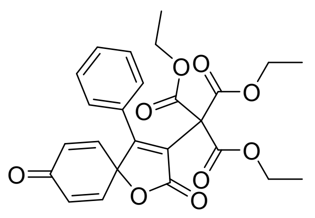
In a 8 mL screw cap reaction vial equipped with a magnetic stirrer bar was added alkynoate (0.2 mmol, 1 equiv.), tricarbonyl (0.24 mmol, 1.2 equiv.), $K_2S_2O_8$ (0.4 mmol, 2 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.004 mmol, 2 mol%). 2 mL of $CH_3CN:H_2O$ (1:1) was added to the vial and it was purged three times with argon and was sealed with a cap containing TFE-lined silicone septa. The reaction vial was then degassed with argon for 15 min via an inlet needle. After this, the cap was changed with a solid-top cap under argon flow and the vial was irradiated with a blue LED strip (0.11 W/cm^2, measured through a Newport optical power meter 1916-R at a distance of 2 cm) for 6-24 h. The temperature of the reaction vial was maintained at approximately 25 °C *via* a fan. After the reaction was stopped, the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (10 mL) and water (10 mL). The residue was extracted with EtOAc (10 mL x 3) and washed with brine (saturated aq NaCl, 10 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed in rotatory evaporator followed by *in vacuo*. The crude products were then purified on a silica gel column (230-400 mesh) using EtOAc/petroleum ether mixture to get the pure product.

(b) Experimental Procedure for the scale-up reaction for spirocyclization of acrylamide with triethylmethane tricarboxylate:

In a 50 mL screw cap reaction vial equipped with a magnetic stirrer bar was added the N-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide (2 mmol, 1 equiv.), tricarbonyl (2.4 mmol, 1.2 equiv.), $K_2S_2O_8$ (4 mmol, 2 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.04 mmol, 2 mol%). 20 mL of $CH_3CN:H_2O$ (1:1) was added to the reaction vial then and it was purged three times with argon and was sealed with a cap containing TFE-lined silicone septa. The reaction vial was then degassed with argon for 15 min via an inlet needle. After this, the cap was changed with a solid-top cap under argon flow and the vial was irradiated with a blue LED strip (0.11 W/cm^2, measured through a optical power meter 1916-R at a distance of 2 cm) for 12 h. The temperature of the reaction vial was maintained at approximately 25 °C *via* a fan. After the reaction was stopped, the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (20 mL) and water (20 mL). The residue was extracted with EtOAc (20 mL x 3) and washed with brine (saturated aq NaCl, 20 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed in rotatory evaporator followed by *in vacuo*. The crude products were then purified on a silica gel column (230-400 mesh) using EtOAc/petroleum ether mixture to get the pure product **4aa** in 69% yield (664 mg).

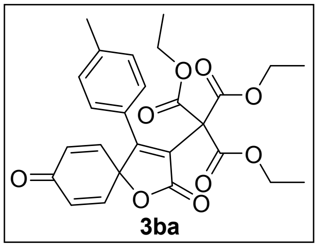
5. Characterization data for the products:

1. **Triethyl (2,8-dioxo-4-phenyl-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3aa).** White solid; Yield – (74 mg, 79%); ***mp***: 112-114 °C; R_f (30% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1778, 1740, 1672, 1631, 1211, 1058; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 3 H), 7.08 (d. *J* = 6.5 Hz, 2 H), 6.68 (d, *J* = 10 Hz, 2 H), 6.30 (d, *J* = 10 Hz, 2 H), 3.95 (q, *J* = 7.16 Hz, 6 H) ,1.19 (t, *J* = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.5, 169.9, 163.1, 159.7, 141.9, 132.1, 130.0, 128.3, 128.1, 127.7, 126.2, 83.1, 65.3, 63.0, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{24}O_9Na$ (M + Na): 491.1318, found (M + Na): 491.1319.



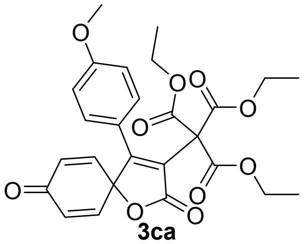
3aa

2. **Triethyl (2,8-dioxo-4-(p-tolyl)-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3ba).** Pale Yellow liquid; Yield – (80.1 mg, 83%); R_f (30% EtOAc/ petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (KBr, cm^{-1}): 1781, 1737, 1676, 1638, 1289, 1215, 1069; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8 Hz, 2 H), 6.95 (d, *J* = 8 Hz, 2 H), 6.66 (d,.*J* = 10 Hz, 2 H), 6.30 (d, *J* = 10 Hz, 2 H), 3.96 (q, *J* = 7.2 Hz, 6 H), 2.31 (s, 3 H), 1.19 (t, *J* = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.7, 170.0, 163.1, 160.0, 142.1, 140.2, 132.0, 128.8, 127.5, 126.0, 125.4, 83.1, 65.3, 62.9, 21.2, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{26}O_9$ (M + Na): 505.1475, found (M + Na): 505.1476.



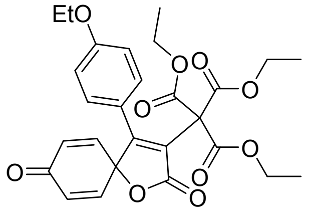
3ba

3. **Triethyl (4-(4-methoxyphenyl)-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3ca).** Yellowish liquid; Yield – (76.7 mg, 77%); R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1785, 1734, 1673, 1635, 1605, 1511, 1296, 1211, 1065; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.04 (d, *J* = 7.6 Hz, 2 H), 6.84 (d, *J* = 7.2 Hz, 2 H), 6.68 (d. *J* = 9.2 Hz., 2 H), 6.33 (d, *J* = 9.2 Hz, 2 H), 4.01 (q, *J* = 7.2 Hz, 6 H), 3.80 (s, 3 H), 1.22 (t, *J* = 6.8 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 183.6, , 170.2, 163.2, 160.8, 159.8, 142.2, 131.9, 129.1, 126.0, 120.5, 113.6, 83.0, 65.4, 62.9, 55.2, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{26}O_{10}Na$ (M + Na): 521.1424, found (M + Na): 521.1420.



3ca

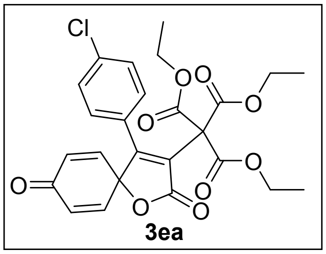
4. **Triethyl (4-(4-ethoxyphenyl)-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3da).** Yellowish liquid; Yield – (74.8 mg, 73%); R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1784, 1674, 1637, 1211, 1064; **^{1}H NMR**



3da

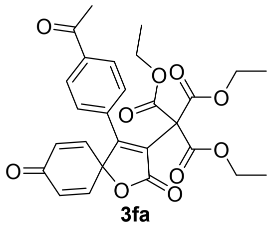
(400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.4 Hz, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 10 Hz, 2 H), 6.31 (d, *J* =10 Hz, 2 H), 4.02 – 3.96 (m, 8 H), 1.39 (t, *J* =6.8 Hz, 3 H), 1.21 (t, *J* = 6.8 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.6, 170.0, 163.2, 160.1, 159.9, 142.3, 132.0, 129.1, 125.9, 120.3, 114.1, 83.1, 65.4, 63.6, 63.0, 14.6, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{27}H_{28}O_{10}Na$ (M + Na): 535.1580, found (M + Na): 535.1583.

5. **Triethyl (4-(4-chlorophenyl)-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3ea).** Yellowish liquid; Yield – (71.4 mg, 71%); R_f (30% EtOAc/petroleum ether) 0.5; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1785, 1738, 1674, 1213; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.66 (d, *J* = 10 Hz, 2 H), 6.33 (d, *J* = 10 Hz, 2 H), 3.99 (q, *J* = 7.2 Hz, 6 H), 1.21 (t, *J* = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.3, 169.5, 163.1, 158.5, 141.7, 136.4, 132.3, 129.1, 128.5, 127.0, 126.7, 82.9, 65.3, 63.1, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{23}O_9ClH$ (M + H): 503.1109, found (M + H): 503.1110.



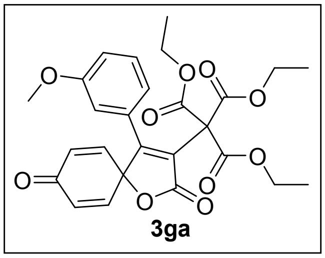
3ea

6. **Triethyl (4-(4-acetylphenyl)-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3fa).** Yellowish liquid; Yield – (87.8 mg, 86%); R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1784, 1738, 1687, 1635, 1212; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 6.69 (d, *J* = 10 Hz, 2 H), 6.32 (d, *J* = 9.6 Hz, 2 H), 3.96 (q, *J* = 7.2 Hz, 6 H), 2.59 (s, 3 H), 1.2 (t, *J* = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 183.2, 169.4, 163.0, 158.6, 141.6, 137.9, 133.0, 132.3, 128.2, 127.8, 127.1, 82.9, 65.3. 63.1, 26.6, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{27}H_{26}O_{10}H$ (M + H): 511.1604, found (M + H): 511.1604.



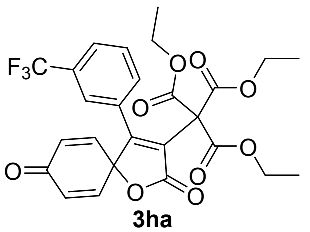
3fa

7. **Triethyl (4-(3-methoxyphenyl)-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3ga).** Yellowish liquid; Yield – (75.7 mg, 76%); R_f (30% EtOAc/ petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1784, 1737, 1674, 1208, 1060; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.0 Hz, 1 H), 6.88 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.69-6.62 (m, 4 H), 6.32 (d, *J* = 10 Hz, 2 H), 3.98 (q, *J* = 7.2 Hz, 6 H), 3.76 (s, 3 H), 1.20 (t, *J* = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.6, 169.9, 163.2, 159.6, 159.0, 142.0, 132.0, 129.7, 129.4, 126.2, 119.7, 115.6, 113.4, 82.9, 65.4, 63.0, 55.2, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{26}O_{10}Na$ (M + Na): 521.1424, found (M + Na): 521.1422.



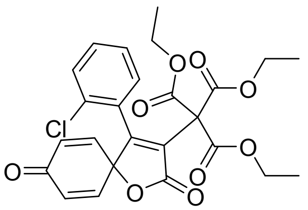
3ga

8. **Triethyl (2,8-dioxo-4-(3-(trifluoromethyl)phenyl)-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3ha).** White solid; Yield – (68.6 mg, 64%); ***mp***: 159-161 °C; R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1787, 1739, 1676, 1636, 1214, 1067; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.35-7.29 (m, 2 H), 6.70 (d, *J*=10 Hz, 2 H), 6.33 (d, *J*=10.4 Hz, 2 H), 3.98 (q, *J* = 6.8 Hz, 6 H), 1.21 (t, J = 6.8 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.1, 169.3, 162.9, 157.9, 141.4, 132.4, 131.3, 130.7 (q, $J_{C\text{-}F}$ = 33.0 Hz), 129.2, 128.9, 127.5, 126.8 (q, $J_{C\text{-}F}$ = 4.0 Hz), 124.5 (q, $J_{C\text{-}F}$ = 4.0 Hz), 123.2 (q, $J_{C\text{-}F}$ = 271.0 Hz), 83.0, 65.3, 63.2, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{23}F_3O_9H$ (M + H): 537.1372, found (M + H): 537.1375.



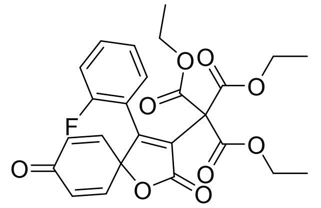
3ha

9. **Triethyl (4-(2-chlorophenyl)-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3ia).** White solid; Yield – (51.3 mg, 51%); ***mp***: 120-122 °C; R_f (30% EtOAc/petroleum ether) 0.5; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1785, 1738, 1675, 1209; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 1 H), 7.33-7.29 (m, 1 H), 7.25-7.21 (m, 1 H), 6.98-6.95 (m, 2 H), 6.63 (dd, *J* = 10.0, 3.1 Hz, 1 H), 6.31 (dd, *J* = 10.2, 1.4 Hz, 1 H), 6.23 (dd, *J* = 10.2, 1.4 Hz, 1 H), 4.03-3.92 (m, 6 H), 1.22 (t, *J* = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.5, 169.7, 162.8, 156.64, 142.1, 141.8, 133.2, 132.1, 131.2, 131.1, 130.7, 129.8, 128.4, 126.6, 125.9, 84.1, 65.2, 63.0, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{23}ClO_9H$ (M + H): 503.1109, found (M + H): 503.1111.



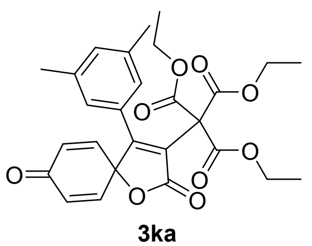
3ia

10. **Triethyl (4-(2-fluorophenyl)-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3ja).** Yellowish liquid; Yield – (34.9 mg, 36%); R_f (30% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (KBr, cm^{-1}): 1783, 1741, 1679, 1212; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 1 H), 7.14-7.04 (m, 2 H), 6.98-6.94 (m, 1 H), 6.71-6.68 (m, 2 H), 6.28 (d, *J* = 10.0 Hz, 2 H) 3.98 (q, *J* = 10.0 Hz, 6 H), 1.22 (t, *J* = 7.0 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.5, 169.6, 162.9, 158.8 (d, $J_{C\text{-}F}$ = 249.0 Hz), 154.6, 141.9, 132.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 131.9, 130.6 (d, $J_{C\text{-}F}$ = 1.7 Hz), 129.1, 123.7 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 115.7 (d, $J_{C\text{-}F}$ = 16.0 Hz), 83.6, 65.4, 63.2, 13.7. **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{23}FO_9$ (M + Na): 509.1224, found (M + Na): 509.1222.



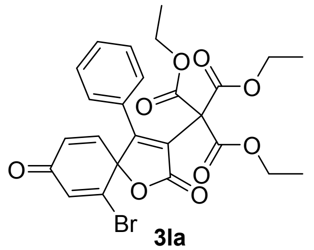
3ja

11. **Triethyl (4-(3,5-dimethylphenyl)-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3ka).**Yellowish liquid; Yield – (54.6 mg, 55%); R$_f$ (30% EtOAc/petroleum ether) 0.5; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1785, 1738, 1674, 1220, 1064; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.97 (s, 1 H), 6.68-6.65 (m, 4 H), 3.95 (q. *J* = 6.8 Hz, 6 H), 2.25 (s, 6 H), 1.19 (t, *J* = 7.2 Hz , 9 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 183.7, 170.1, 163.2, 160.1, 142.1, 137.8, 131.9, 131.5, 128.3, 125.9, 125.2, 83.0, 65.3, 62.8, 21.1, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{27}H_{28}O_9H$ (M + H): 497.1812, found (M + H): 497.1814.



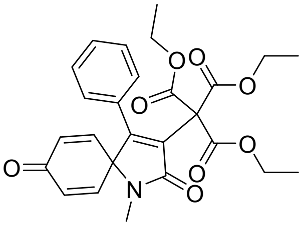
3ka

12. **Triethyl (6-bromo-2,8-dioxo-4-phenyl-1-oxaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (3la).** White semi solid; Yield – (94.1 mg, 86%); R$_f$ (30% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1791, 1738, 1676, 1639, 1601, 1212, 1059; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.41-7.32 (m, 3 H) 7.15 (d, *J* = 7.2 Hz, 2 H) ,6.85 (d. *J* = 10.0 Hz, 1 H), 6.71 (d, *J* = 1.2 Hz, 1 H), 6.41 (dd, *J* = 9.8, 1.6 Hz, 1 H) ,4.03-3.88 (m, 6 H), 1.20 (t, *J* = 6.8 Hz, 9 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 181.7, 169.5, 163.0, 158.2, 141.8, 141.3, 135.7, 131.2, 130.3, 128.3, 127.9, 127.7, 127.6, 84.6, 65.3, 63.0, 13.7; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{23}BrO_9H$ (M + H): 547.0604, found (M + H): 547.0603.

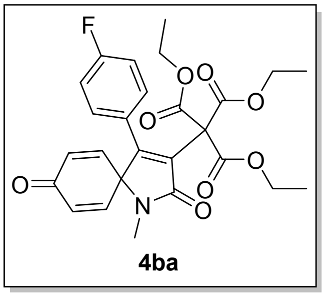


3la

13. **Triethyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4aa).** White solid; Yield – (78 mg, 81%); ***mp***: 154-156 °C; R$_f$ (50% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1741, 1704, 1670, 1630, 1229, 1065; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.31-7.26 (m, 3 H), 7.07 (dd, *J* = 7.6, 1.6 Hz, 2 H), 6.55 (d, *J* = 10.0 Hz, 2 H), 6.38 (d, *J* = 10.4 Hz, 2 H), 3.93 (q, *J* = 6.8 Hz, 6 H), 2.9 (s, 3 H), 1.18 (t, *J* = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 183.8, 168.8, 163.9, 150.7, 144.6, 133.4, 132.0, 129.8, 129.2, 128.4, 127.8, 68.6, 65.7, 62.5, 26.3, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{27}NO_8H$ (M + H): 482.1815, found (M + H): 482.1812.

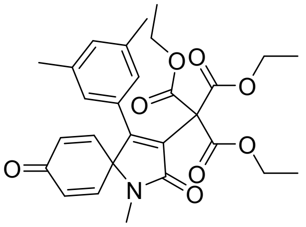


4aa



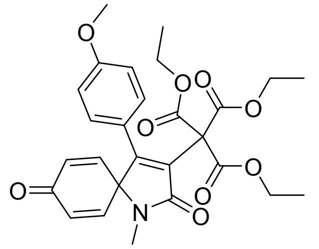
4ba

14. **Triethyl (4-(4-fluorophenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4ba).** Pale yellow solid; Yield – (78.9 mg, 79%); ***mp***: 135-137 °C; R_f (50% EtOAc/ petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1742, 1706, 1669, 1226, 1063; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09-7.06 (m, 2 H), 6.99 (t, J = 8.4 Hz, 2 H), 6.53 (d, J = 10.0 Hz, 2 H), 6.40 (d, J = 10.0 Hz, 2 H), 3.97 (q, J = 6.8 Hz, 6 H), 2.91 (s, 3 H), 1.20 (t, J = 6.8 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.6, 168.6, 163.8, 163.0 (d, $J_{C\text{-}F}$ = 249.0 Hz), 149.7, 144.5, 133.5, 132.7, 130.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 125.7 (d, $J_{C\text{-}F}$= 4.0 Hz), 115.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 68.6, 65.7, 62.7, 26.3, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{26}FNO_8H$ (M + H): 500.1721, found (M + H): 500.1722.



4ca

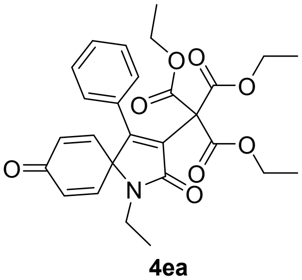
15. **Triethyl (4-(3,5-dimethylphenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4ca).** White solid; Yield – (74.4 mg, 73%); ***mp***: 139-141 °C; R_f (50% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1741, 1706, 1669, 1211, 1064; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91 (s, 1 H), 6.65 (s, 2 H), 6.53 (d, J = 10.0 Hz, 2 H), 6.38 (d, J = 10.0 Hz, 2 H), 3.93 (d, J = 7.2 Hz, 6 H), 2.90 (s, 3 H), 2.24 (s, 6 H), 1.18 (t, J = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.1, 169.1, 164.0, 151.2, 144.9, 137.4, 133.2, 131.6, 130.8, 129.7, 126.0, 68.6, 65.7, 62.5, 26.2, 21.1, 13.7; **HRESI-MS** *(m/z)*: Calculated for $C_{28}H_{31}NO_8H$ (M + H): 510.2128, found (M + H): 510.2125.



4da

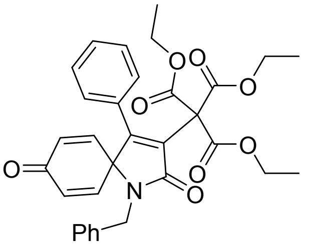
16. **Triethyl (4-(4-methoxyphenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4da).** White semi solid; Yield – (84.9 mg, 83%); R_f (50% EtOAc/petroleum ether) 0.2; Prepared as shown in the general experimental procedure (a). **IR** (KBr, cm^{-1}): 1739, 1705, 1669; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, J = 8.8 Hz, 2 H), 6.79 (d, J = 8.4 Hz, 2 H), 6.54 (d, J = 10.0 Hz, 2 H) 6.39 (d, J = 10.0 Hz, 2 H), 3.96 (q, J = 6.8 Hz, 6 H), 3.77 (s, 3 H), 2.90 (s, 3 H), 1.19 (t, J = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.0, 169.1, 164.1, 160.3, 150.9, 145.0, 133.4, 132.0, 129.8, 122.0, 113.4, 68.8, 65.8, 62.7, 55.3, 26.4, 13.7; **HRESI-MS** *(m/z)*: Calculated for $C_{27}H_{29}NO_9Na$ (M + Na): 534.1740, found (M + Na): 534.1740.

17. **Triethyl (1-ethyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4ea).** White semi solid; Yield – (31.7 mg, 32%); R_f (50% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1740, 1703, 1669, 1630, 1226, 1064; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.32-7.25 (m, 3 H), 7.06-7.04 (m, 2 H), 6.60 (d. J = 10.0 Hz, 2 H), 6.34 (d, J = 10.0 Hz, 2 H), 3.92 (q, J = 7.2 Hz, 6 H), 3.38 (q, J = 7.2 Hz, 2 H), 1.23-1.16 (m, 12 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 184.0, 168.7, 163.9, 150.5, 145.1, 132.8, 132.3, 129.8, 129.2, 128.5, 127.8, 69.0, 65.7, 62.5, 29.6, 15.1, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{27}H_{29}NO_8H$ (M + H): 496.1971, found (M + H): 496.1971.



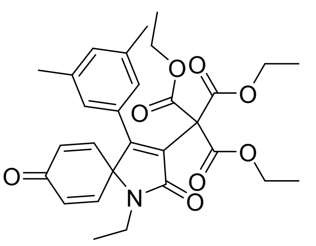
4ea

18. **Triethyl (1-benzyl-4-(3,5-dimethylphenyl)-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4fa).** White solid; Yield – (70.3 mg, 63%); ***mp***: 108-110 °C; R_f (50% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1766, 1740, 1669, 1228, 1064; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.25-7.24 (m, 8 H) , 7.02-7.00 (m, 2 H), 6.36 (d, J = 10.0 Hz, 2 H), 6.14 (d, J = 10.0 Hz, 2 H), 4.56 (s, 2 H), 3.94 (q, J = 7.2 Hz, 6 H), 1.19 (t, J = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 184.0, 169.0, 163.8, 150.9, 144.8, 137.4, 132.4, 131.8, 129.5, 129.2, 128.5, 128.45, 128.43, 127.7, 68.9, 65.7, 62.6, 44.7, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{32}H_{31}NO_8H$ (M + H): 558.2128, found (M + H): 558.2131.



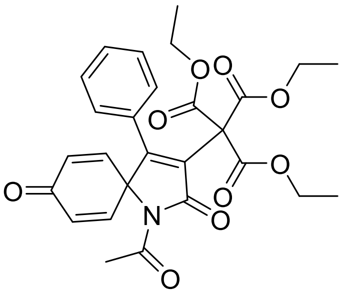
4fa

19. **Triethyl (4-(3,5-dimethylphenyl)-1-ethyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4ga).** White solid; Yield – (52.4 mg, 50%); ***mp***: 98-100 °C; R_f (50% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1740, 1703, 1668, 1209, 1063; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.91 (s, 1 H) , 6.64 (s, 2 H), 6.58 (d, J = 10.0 Hz, 2 H), 6.35 (d, J = 10.4 Hz, 2 H), 3.93 (q, J = 7.2 Hz, 6 H), 3.36 (q, J = 7.2 Hz, 2 H), 2.23 (s, 6 H), 1.22-1.16 (m, 12 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 184.3, 168.9, 163.9, 150.9, 145.4, 137.4, 132.6, 131.9, 130.7, 129.7, 126.1, 68.9, 65.7, 62.5, 36.1, 21.1, 15.1, 13.7; **HRESI-MS** *(m/z)*: Calculated for $C_{29}H_{33}NO_8H$ (M + H): 524.2284, found (M + H): 524.2286.

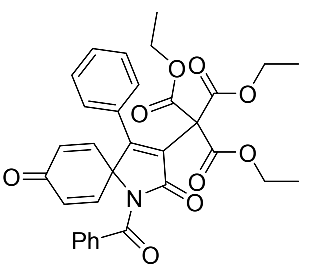


4ga

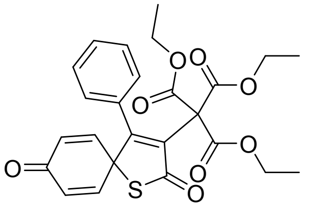
20. **Triethyl (1-acetyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4ha).** White solid; Yield – (80.5 mg, 79%); ***mp***: 153-155 °C; R$_f$ (50% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1767, 1738, 1708, 1669, 1277, 1227, 1064; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.35-7.26 (m, 3 H), 7.05-7.03 (m, 2 H), 6.58 (d, *J* = 10.0 Hz, 2 H), 6.31 (d, *J* = 10.1 Hz, 2 H), 3.94 (q, *J* = 7.1 Hz, 6 H), 2.61 (s, 3 H), 2.23 (s, *J* = 10.1 Hz, 9 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 183.8, 168.8, 167.7, 163.5, 154.5, 143.6, 132.3, 131.4, 129.7, 128.8, 127.9, 127.5, 68.3, 65.8, 62.8, 25.5, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{27}H_{27}NO_9H$ (M + H): 510.1764, found (M + H): 510.1754.


4ha

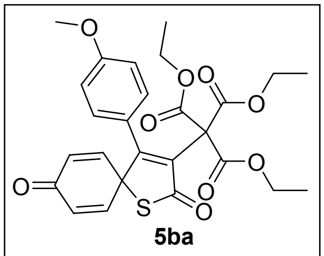
21. **triethyl (1-benzoyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (4ia).** White solid; Yield – (58.3 mg, 51%); ***mp***: 60-62 °C; R$_f$ (50% EtOAc/petroleum ether) 0.5; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1767, 1739, 1693, 1669, 1297, 1217, 1063; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.73-7.71 (m, 2 H) , 7.57-7.54 (m, 1 H), 7.46-7.42 (m, 2 H), 7.37-7.32 (m, 3 H), 7.11-7.09 (m, 2 H), 6.77-6.75 (m, 2 H), 6.36-6.34 (m, 2 H), 3.91 (q, *J* = 7.1 Hz, 6 H), 1.18 (t, *J* = 7.1 Hz, 9 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 183.8, 168.1, 167.3, 163.5, 154.2, 143.9, 133.3, 132.8, 132.4, 131.5, 129.8, 129.2, 129.1, 128.1, 127.6, 68.8, 65.8, 62.9, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{32}H_{29}NO_9H$ (M + H): 572.1921, found (M + H): 572.1910.


4ia

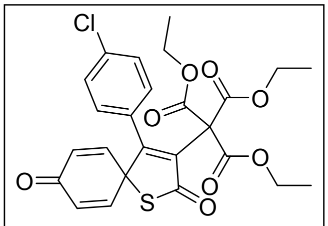
22. **Triethyl (2,8-dioxo-4-phenyl-1-thiaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (5aa).** White semi solid; Yield – (53.3 mg, 55%); R$_f$ (30% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1765, 1738, 1664, 1223, 1063; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.36-7.27 (m, 3 H), 7.12 (dd, J = 8.2, 1.2 Hz, 2 H), 6.88 (d, J = 10.0 Hz, 2 H), 6.26 (d, J = 10.0 Hz, 2 H), 3.92 (q, j = 7.2 Hz, 6 H), 1.20 (t, J = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 194.3, 183.6, 163.5, 160.8, 145.0, 136.6, 130.7, 129.9, 127.9, 127.8, 66.9, 62.9, 60.9, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{24}O_8SNa$ (M + Na): 507.1090, found (M + Na): 507.1094.


5aa

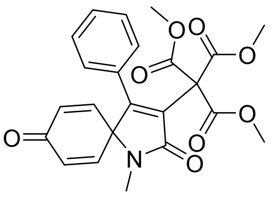
23. **Triethyl (4-(4-methoxyphenyl)-2,8-dioxo-1-thiaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (5ba). Pale** White semi solid; Yield – (54.5 mg, 53%); R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in the general experimental procedure (a). **IR** (KBr, cm^{-1}):1738, 1695, 1664; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.8 Hz, 2 H), 6.86 (d, J = 10.0 Hz, 2 H), 6.79 (d, J = 8.8 Hz, 2 H), 6.28 (d, J = 10.0 Hz, 2 H), 3.96 (q, J = 6.8 Hz, 6 H), 3.78 (s, 3 H), 1.21 (t, J = 6.8 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.3, 183.7, 163.6, 161.0, 160.7, 145.3, 136.4, 130.6, 129.4, 123.0, 113.3, 67.0, 62.9, 60.9, 55.3, 13.7; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{26}O_9SNa$ (M + Na): 537.1195, found (M + Na): 537.1196.


5ba

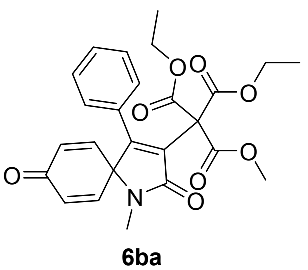
24. **Triethyl (4-(4-chlorophenyl)-2,8-dioxo-1-thiaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (5ca).** Pale white solid; Yield – (52.9 mg, 51%); ***mp***: 88-90 °C; R_f (30% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1765, 1738, 1698; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2 H), 7.08 (d, J = 8.4 Hz, 2 H), 6.85 (d, 10.0 Hz, 2 H), 6.29 (d, J = 10.0 Hz, 2 H), 3.96 (q, J = 7.2 Hz, 6 H), 1.21 (t, J = 7.2 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 183.4, 163.4, 159.5, 144.7, 137.2, 136.2, 130.9, 129.4, 129.0, 128.2, 66.9, 63.0, 60.7, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{23}ClO_8SH$ (M + H): 519.0880, found (M + H): 519.0880.


5ca

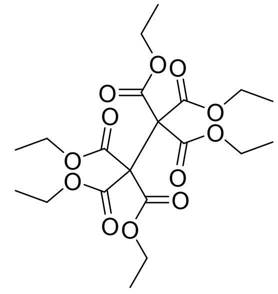
25. **Trimethyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (6aa).** White solid; Yield – (82.6 mg, 94%); ***mp***: 220-222 °C; R_f (50% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1744, 1704, 1629; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 3 H), 7.07-7.05 (m, 2 H), 6.57 (d, J = 10.0 Hz, 2 H), 6.39 (d, J = 10.0 Hz, 2 H), 3.52 (s, 9 H), 2.92 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.7, 168.7, 164.3, 151.2, 144.4, 133.4, 131.6, 129.5, 129.2, 128.3, 127.9, 68.7, 65.3, 53.4, 26.3; **HRESI-MS** *(m/z)*: Calculated for $C_{23}H_{21}NO_8H$ (M + H): 440.1345, found (M + H): 440.1346.


6aa

26. **1,1-diethyl 1-methyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (6ba).** White solid; Yield – (71 mg, 76%); ***mp***: 146-148 °C; R_f (50% EtOAc/petroleum ether) 0.4; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1740, 1705, 1669, 1629; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.29 (m, 3 H), 7.07-7.06 (m, 2 H), 3.95 (q, J = 7 Hz, 4 H), 3.48 (s, 3 H), 2.91 (s, 3 H), 1.86 (t, J = 7.1 Hz, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.7, 168.8, 164.5, 163.8, 150.9, 144.5, 133.4, 131.8, 129.7, 129.2, 128.3, 127.8, 68.6, 65.6, 62.6, 53.2, 26.3, 13.6; **HRESI-MS** *(m/z)*: Calculated for $C_{23}H_{21}NO_8H$ (M + Na): 490.1478, found (M + Na): 490.1478.

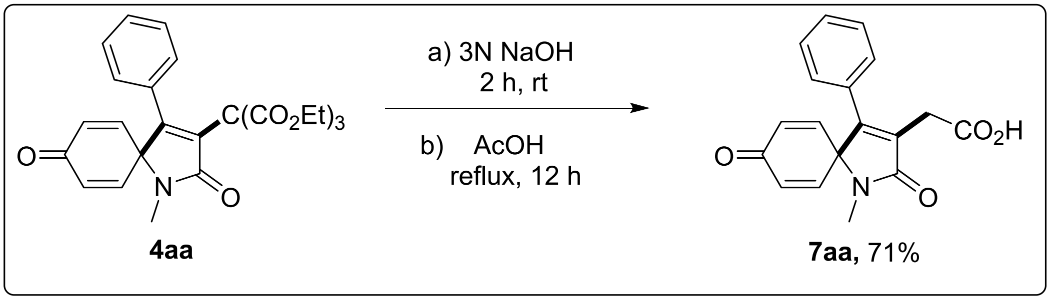

6ba

27. **Hexaethyl ethane-1,1,1,2,2,2-hexacarboxylate.** White solid; ***mp***: 88-90 °C; R_f (30% EtOAc/petroleum ether) 0.45; Prepared as shown in the general experimental procedure (a). **IR** (Neat, cm^{-1}): 1740; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.30 (q, J = 7.2 Hz, 12 H), 1.29 (t, J = 7.2 Hz, 18 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 69.1, 62.7, 13.7; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{30}O_{12}H$ (M + H): 463.1816, found (M + H): 463.1818.



6. Product modification

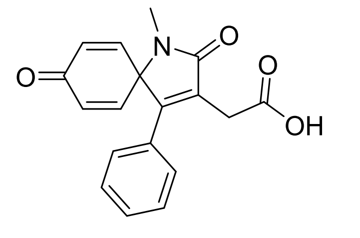
(i) Synthesis of alkenyl acetic acid (7aa):



A solution of the **4aa** (0.2 mmol) in MeOH (2 mL) was treated with a solution 3N NaOH (0.6 mL, 0.4 mmol) in water, and the resulting mixture was stirred at room temperature and monitored by TLC. When no starting material remained, volatiles were removed in vacuo, and the crude tris-acid was taken up in AcOH (2 mL) and heated to reflux. The reaction was monitored by TLC analysis, and when no starting material remained (12 h), the solvent was concentrated in vacuo. The resultant crude acid was dissolved in water (3 mL), extracted with EtOAc (5 mL × 3), and the combined extracts were dried (Na_2SO_4) and concentrated in vacuo to give the acid product (44 mg) in a yield of 71%.

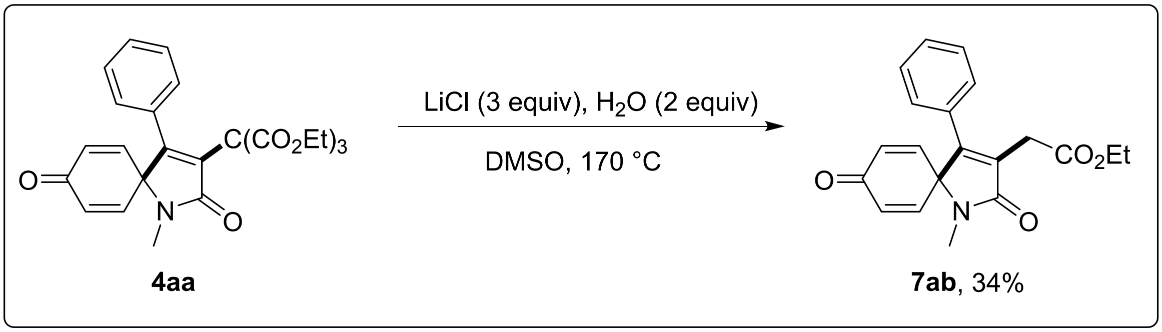
2-(1-Methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)acetic acid (7aa).

White Semi solid; Yield – (44 mg, 71%); **^{1}H NMR δ ($CDCl_3$, 400 MHz):** 7.30-7.27 (m, 3H), 7.14-7.12 (m, 2H), 6.48-6.38 (m, 4H), 3.3 (s, 2H), 2.8 (s, 3H); **^{13}C NMR δ ($CDCl_3$, 100 MHz):** 184.06, 172.58, 171.03, 153.30, 153.30, 145.29, 144.76, 133.54, 133.36, 130.97, 130.39, 130.01, 129.79, 128.96, 128.83, 128.10, 68.27, 31.33, 30.59, 26.29; **IR (Neat, cm^{-1}):** 3809, 3779, 3755, 3626, 3583, 3432, 32723080, 2866, 2697, 2550; **HRMS (ESI) (*m/z*):** Calculated for $C_{18}H_{15}NO_4$ [M+H]$^+$: 310.1079, found [M+H]$^+$: 310.1080.



7aa

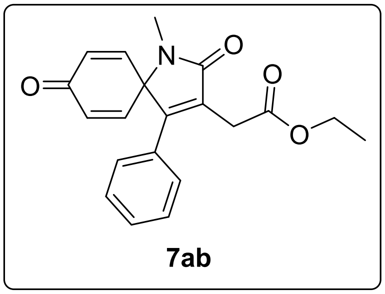
(ii) Synthesis of monoesterified product (7ab):



DMSO (3 mL) solution of triethyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)methanetricarboxylate (97 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.44 mg, 0.6 mmol, 3.0

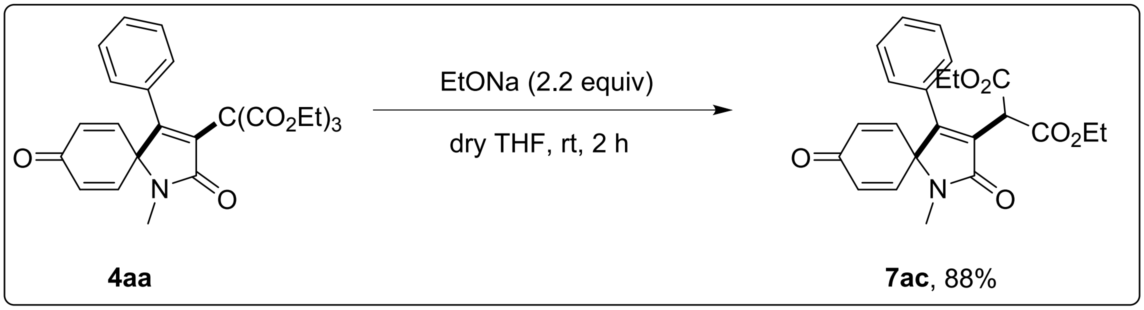
equiv.), and water (7 mg, 0.4 mmol, 2.0 equiv.) was heated at 170°C for 2 h. After cooling down to room temperature, the reaction mixture was washed with water (10 mL), and the aqueous layer was extracted with ether (5x5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure to give a crude product. The product was purified by vacuum distillation, or by flash chromatography on silica gel using EtOAc/n-hexane as the eluant in 34% (23 mg) yield.

Ethyl 2-(1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)acetate (7ab).


7ab

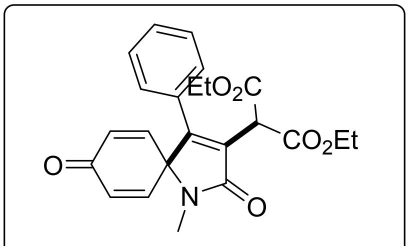
White Semi solid; **IR (Neat, cm^{-1}):** 2235, 1727, 1502, 1333; **^{1}H NMR δ ($CDCl_3$, 400 MHz):** 9.31-7.22 (m, 3H), 7.12-7.10 (m, 2H), 6.49-6.46 (d, *J* = 8.4Hz, 2H), 6.39-6.36(d, *J* = 8.4Hz, 2H), 4.09-4.03 (q, 2H), 3.30 (s, 2H), 2.83 (s, 3H), 1.18-1.17 (t, *J* = 1.6Hz 3H); **^{13}C NMR δ ($CDCl_3$, 100 MHz):** 184.21, 170.11, 169.82, 152.48, 145.4, 144.26, 133.32, 131.73, 130.81, 129.74, 128.81, 128.06, 67.89, 63.03, 61.42, 32.04, 30.8, 29.81, 29.48, 26.15, 22.81, 14.25, 14.2; **HRMS (ESI) (*m/z*):** Calculated for $C_{20}H_{19}NO_4$ $[M+H]^+$: 338.1392, found $[M+H]^+$: 338.1394.

(iii) **Synthesis of diester 7ac:**



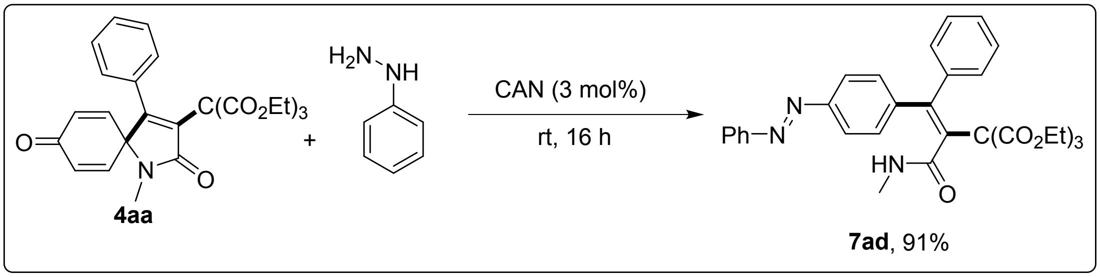
The compound **4aa** (0.1 mmol, 1 equiv) in dry THF (1 mL) was added dropwise to a well stirred solution of sodium ethoxide (0.22 mmol, 2.2 equiv) in THF (1 mL) under argon at rt. After stirring at rt for 2 h the solution was acidified with 1N HCl and diluted with ethyl acetate (5 mL), followed by washing with water, sat. $NaHCO_3$ solution, brine, dried (MgSO4). The organic layer collected was concentrated and purified by silica gel column chromatography (60% EtOAc:petroleum ether) to provide diester **7ac** (36 mg, 88% yield)

Diethyl 2-(1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)malonate (7ac)

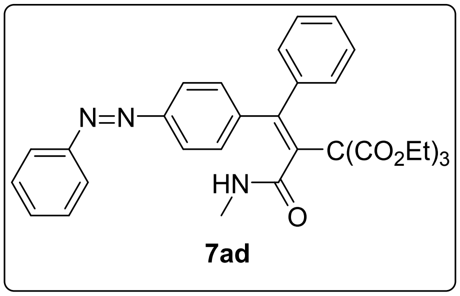

7ac

White sticky liquid; R_f (50% EtOAc/petroleum ether) 0.4; **^{1}H NMR δ ($CDCl_3$, 400 MHz):** 7.36-7.28(m, 3 H), 7.19-7.17(m, 2 H), 6.56 (d, *J* = 10Hz, 2 H), 6.43 (d, *J* = 10Hz, 2 H), 4.60 (s, 1 H), 4.05-3.92 (m, 4 H), 2.91 (s, 3 H), 1.82 (t, *J* = 7.1 Hz, 6 H); **^{13}C NMR δ ($CDCl_3$, 100 MHz):** 183.9, 169.0, 166.4, 153.2, 144.7, 133.4, 131.0, 129.9, 129.6, 128.3, 128.2, 68.2, 61.9, 49.4, 26.2, 13.8; **IR ν_{max} (Neat, cm^{-1}):** 2926, 1738, 1707, 1669; **HRMS (ESI) (*m/z*):** Calculated for $C_{23}H_{23}NO_6$ [M+Na]: 432.1423, found [M+Na]: 432.1422.

(iv) Aromatization of 4aa via spirolactam ring opening:

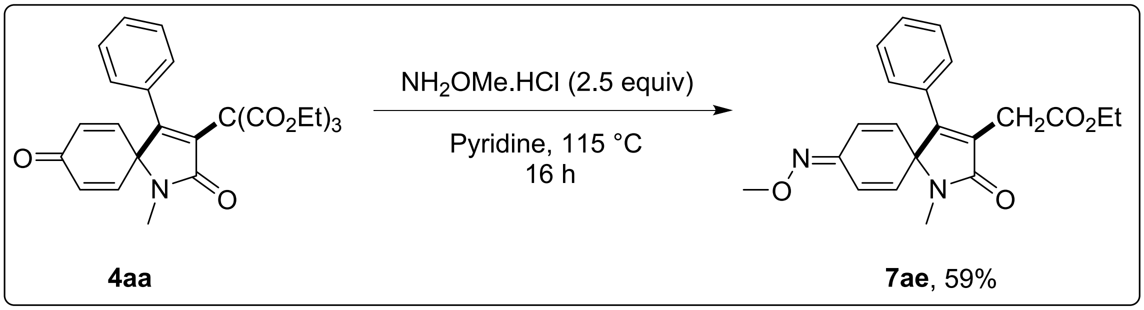


The azobenzene **7ad** was synthesized by incubating **4aa** (0.2 mmol) with phenylhydrazine (100 mM) in 2 mL acetonitrile in the presence of 3 mol% of cerium (IV) ammonium nitrate (CAN) at room temperature for 16 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to yield the desired product (104 mg, 91% yield).



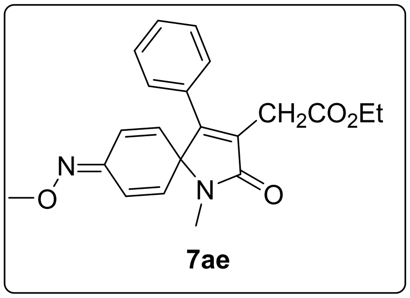
Triethyl (2Z)-2-(methylcarbamoyl)-3-phenyl-3-(4-(phenyldiazenyl)phenyl)prop-2-ene-1,1,1-tricarboxylate (7ad). White Semi solid; Yield – (104 mg, 91%); **IR (Neat, cm^{-1}):** 3288, 1738, 1680, 1601, 1550; **^{1}H NMR δ (CDCl$_3$, 400 MHz):** 7.26-7.25 (m, 5H), 7.14-7.13 (t, *J* = 3.2Hz, 2H), 7.07-7.05 (d, *J* = 8Hz, 2H), 6.89-6.85 (t, *J* = 15.2Hz, 2H), 6.64-6.61 (d, *J* = 10Hz, 1H), 5.81-5.78 (d, *J* = 10.4Hz, 1H), 5.56-5.54 (d, *J* = 10Hz, 1H), 3.92-3.88 (m, 6H), 2.81 (s, 3H), 1.17-1.14 (t, *J* = 6.8Hz, 9H); **^{13}C NMR δ (CDCl$_3$, 100 MHz):** 168.71, 164.43, 154.20, 144.83, 149.83, 134.48, 133.56, 132.71, 132.29, 131.59, 129.81 129.37, 128.84, 128.60, 128.51, 127.85, 124.98, 121.19, 118.78, 113.31, 69.97, 65.73, 62.79, 62.62, 29.79, 25.99, 13.81]=[-p: **HRMS (ESI) (*m/z*):** Calculated for $C_{32}H_{33}N_3O_7$ [M+H]$^+$: 572.2397, found [M+H]$^+$: 572.2396.

(v) Synthesis of ketoxime 7ae:



The compound **4aa** (0.2 mmol, 1 equiv) and methoxyamine hydrochloride (0.5 mmol, 2.5 equiv) were taken in an oven dried screw cap reaction vial with a magnetic stir bar. Then, dry pyridine (2 mL) was added, and the mixture was allowed to stir at 115 °C for 15 h. After completion of the reaction (monitored by TLC), volatiles were removed under reduced pressure and the crude reaction mixture was directly purified by silica gel column chromatography (20% EtOAc:petroleum ether) to provide ketoxime **7ae** (43 mg, 59% yield) as yellow sticky liquid.

Ethyl 2-(8-(methoxyimino)-1-methyl-2-oxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)acetate (7ae)

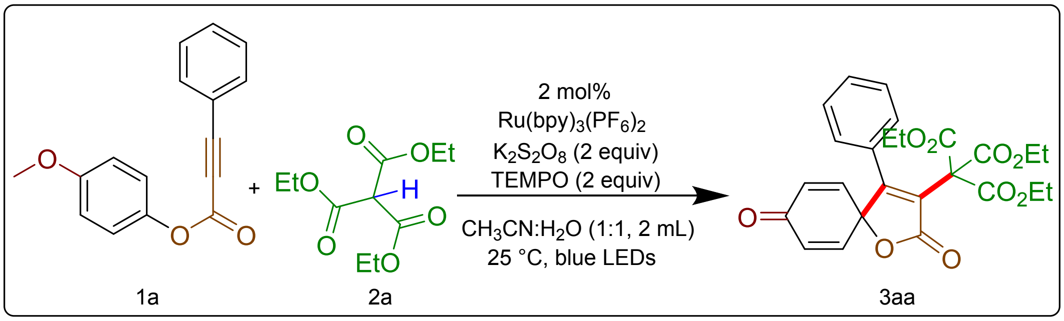


7ae

^{1}H NMR δ (CDCl$_3$, 400 MHz): 7.33-7.31(m, 3H), 7.30-7.22(m, 2H), 7.12-7.10(d, *J* = 10Hz, 1H), 6.54-6.51(d, *J* = 10Hz, 1H), 5.85-5.82(d, *J* = 10Hz, 1H), 5.74-5.72(d, *J* = 10Hz, 1H), 4.15+4.09(q, 2H), 3.93(s, 3H), 3.36(s, 2H), 2.80(s, 3H), 1.24-1.21(t, *J* = 7.6Hz, 9H); **^{13}C NMR δ (CDCl$_3$, 100 MHz):** 170.16, 169.88, 154.84, 146.28, 134.98, 131.96, 130.74, 129.75, 129.75, 129.28, 128.65, 128.54, 128.19, 120.36, 68.54, 62.59, 61.29, 32.03,6, 30.71, 29.83, 29.49, 25..65, 22.83, 14.23; **IR ν_{max} (Neat, cm^{-1}):** 2928, 1737, 1695; **HRMS (ESI) (*m/z*):** Calculated for $C_{21}H_{22}N_2O_4$ [M+H]$^+$: 367.1658, found [M+H]$^+$: 367.1659.

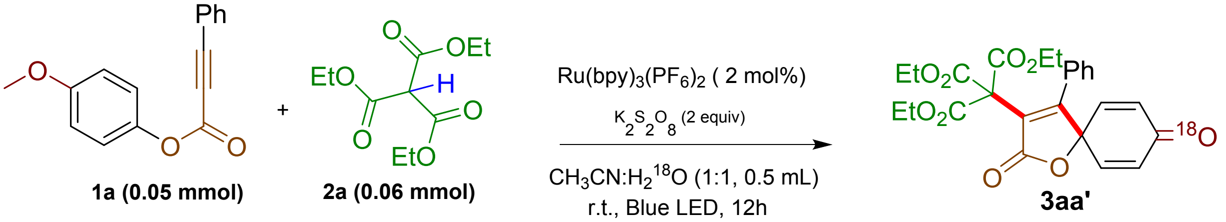
7. Mechanistic Studies

(i) Tempo Quenching Studies



In a 8 mL screw cap reaction vial equipped with a magnetic stirrer bar was added alkynoate (0.2 mmol, 1 equiv.), tricarbonyl (0.24 mmol, 1.2 equiv.), $K_2S_2O_8$ (0.4 mmol, 2 equiv.), 2,2,6,6-tetramethyl-1-piperidinyloxy (0.4 mmol, 2 equiv.), Ru(bpy)$_3$(PF$_6$)$_2$ (0.004 mmol, 2 mol%). 2 mL of CH_3CN:H_2O (1:1) was added to the vial then and it was purged three times with argon and was sealed with a cap containing PTFE-lined silicone septa. The reaction vial was then degassed with argon for 15 min via an inlet needle. After this, the cap was changed with a PTFE-lined solid-top cap under argon flow and the vial was irradiated with a blue LED strip (1.5 mW/cm^2, at a distance of 2 cm) for 12 h. The temperature of the reaction vial was maintained at approximately 25 °C *via* a fan. After the reaction was stopped, the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (10 mL) and water (10 mL). The residue was extracted with EtOAc (10 mL x 3) and washed with brine (saturated aq NaCl, 10 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed in rotatory evaporator followed by *in vacuo*. The crude product was then purified by column chromatography on silica gel (230-400 mesh) using EtOAc/petroleum ether mixture to get the pure product.

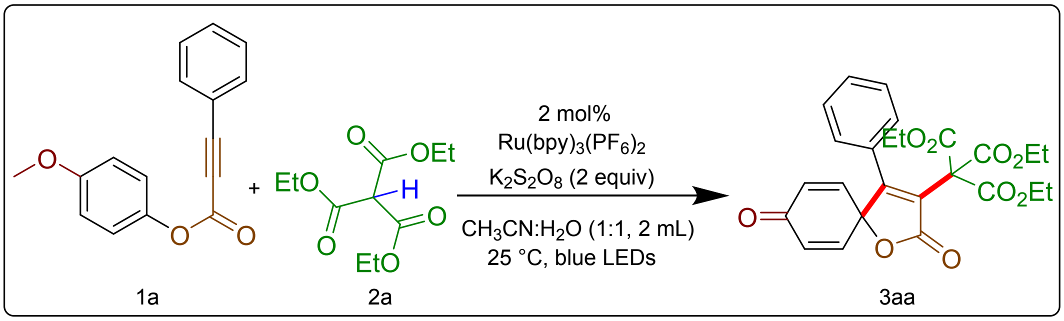
(ii) Reaction using $H_2{}^{18}O$:



In a 8 mL screw cap reaction vial equipped with a magnetic stirrer bar was added alkynoate (0.05 mmol, 1 equiv.), tricarbonyl (0.06 mmol, 1.2 equiv.), $K_2S_2O_8$ (0.1 mmol, 2 equiv.), Ru(bpy)$_3$(PF$_6$)$_2$ (0.001 mmol, 2 mol%). 0.5 mL of CH_3CN:$H_2{}^{18}O$ (1:1) was added to the vial and it was purged three times with argon and was sealed with a cap containing PTFE-lined silicone septa. The reaction vial was then degassed with argon for 15 min via an inlet needle. After this, the cap was changed with a PTFE-lined solid-top cap under argon flow and the vial was irradiated with a blue LED strip (1.5 mW/cm^2, at a distance of 2 cm) for 12 h. The temperature of the reaction vial was maintained at approximately 25 °C *via* a fan. After the reaction was stopped, the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (5 mL) and water (5 mL). The residue was extracted with EtOAc (5 mL x 3) and washed with brine (saturated aq NaCl, 5 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed in rotatory evaporator followed by *in vacuo* to obtain **3aa’** as the only product. The crude **3aa’** was subjected to mass spectroscopic analysis which has shown the formation of **3aa’** as the product. The crude product was then purified on a silica gel (230-400 mesh) using EtOAc/petroleum ether which has shown a mixture of **3aa** and **3aa’** (51%).

(iii) Light/dark study:

To rule out the involvement of a radical-chain-reaction pathway, through SET between persulfate anion and the intermediate **C**, a light on-off study was performed. In this experiment, the progress of the reaction was monitored by alternating periods of light-irradiation and darkness, which ascertains the non-progression of the reaction in the absence of light, and the absence of a self-sustaining radical chain mechanism.



In a 8 mL screw cap reaction vial equipped with a magnetic stirrer bar was added alkynoate (0.2 mmol, 1 equiv.), tricarbonyl (0.24 mmol, 1.2 equiv.), $K_2S_2O_8$ (0.4 mmol, 2 equiv $Ru(bpy)_3(PF_6)_2$ (0.004 mmol, 2 mol%). 2 mL of $CH_3CN:H_2O$ (1:1) was added to the vial then and it was purged three times with argon and was sealed with a cap containing PTFE-lined silicone septa. The reaction vial was then degassed with argon for 15 min via an inlet needle. After this, the cap was changed with a PTFE-lined solid-top cap under argon flow and the vial was irradiated with a blue LED strip (1.5 mW/cm^2, at a distance of 2 cm) for 12 h. The temperature of the reaction vial was maintained at approximately 25 °C *via* a fan. After completion of the reaction, the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (10 mL) and water (10 mL). The residue was extracted with EtOAc (10 mL x 3) and washed with brine (saturated aq NaCl, 10 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed in rotatory evaporator followed by *in vacuo*. The reaction was analyzed by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Entry	**Light on-off conditions**	**NMR yield (%)** ^{a}
1	Light off for 30 min	0
2	Light off for 30 min, on for 30 min	28
3	Light off for 30 min, on for 30 min, off for 30 min	29
4	Light off for 30 min, on for 30 min, off for 30 min, on for 30 min	46
5	Light off for 30 min, on for 30 min, off for 30 min, on for 30 min, off for 30 min	45

6	Light off for 30 min, on for 30 min, off for 30 min, on for 30 min, off for 30 min, on for 30 min	63
7	Light off for 30 min, on for 30 min, off for 30 min, on for 30 min, off for 30 min, on for 30 min, off for 30 min	63
8	Light off for 30 min, on for 30 min, off for 30 min, on for 30 min, off for 30 min, on for 30 min, off for 30 min, on for 30 min	72

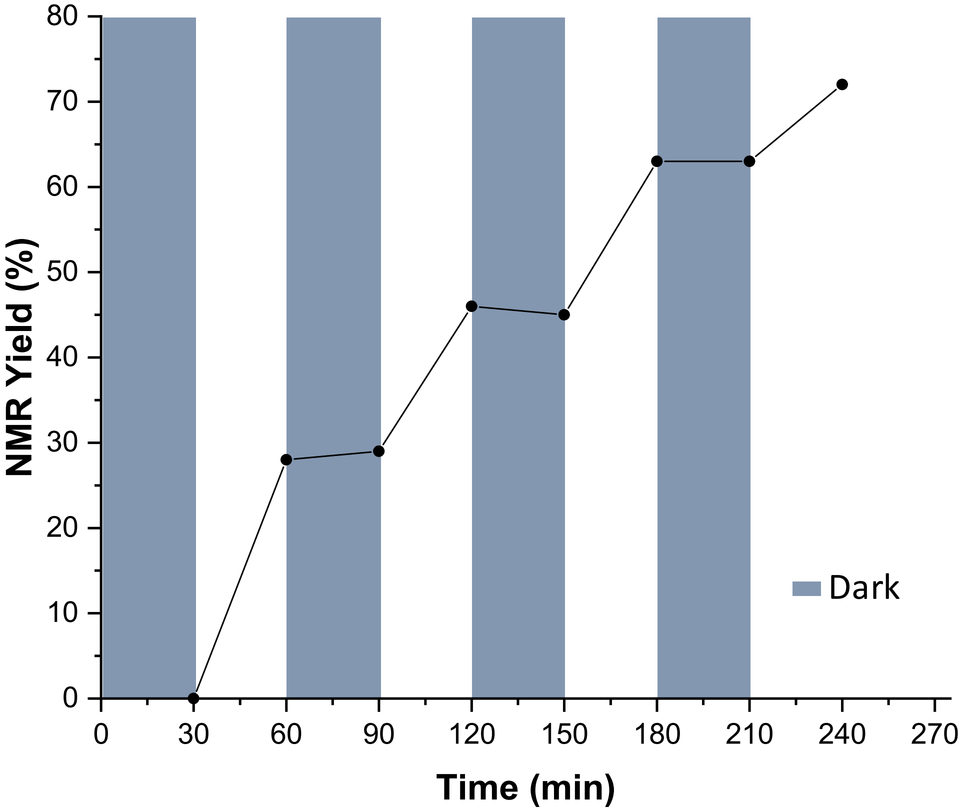


Fig 3: Plot of effect of light source on the reaction over time

(iv) Stern-Volmer Emission Quenching Studies

General: Absorption peak (452 nm) for Ru(bpy)$_3$(PF$_6$)$_2$ was found out using UV-Vis spectroscopy (Shimadzu 3600 spectrophotometer). Then, the Stern-Volmer fluorescence quenching experiment was performed using a Cary Fluorescence Spectrophotometer with an excitation wavelength of 452 nm and emission at 608 nm was recorded.

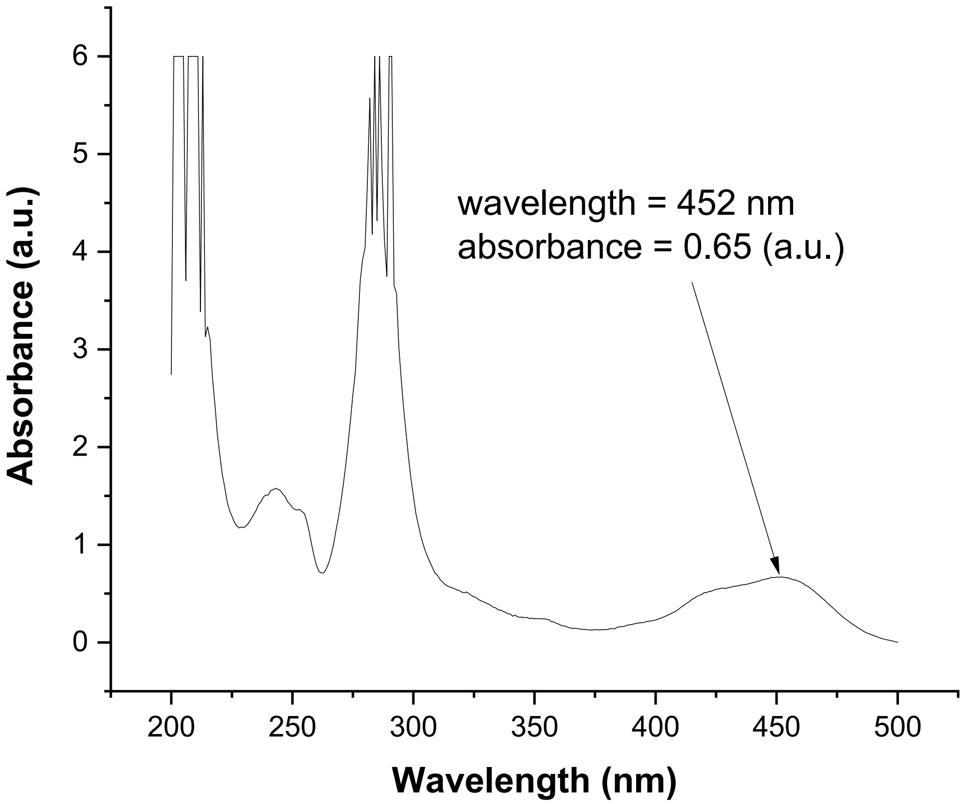


Fig 4: Plot of absorbance of $Ru(bpy)_3(PF_6)_2$ in 1:1 degassed $CH_3CN:H_2O$

Fluorescence emission of photocatalyst $Ru(bpy)_3(PF_6)$: To a quartz cuvette with a PTFE lined silicone septa was added 1 mL of 2×10^{-4} M solution of $Ru(bpy)_3(PF_6)_2$ in $CH_3CN:H_2O$. To the solution was added 1 mL of $CH_3CN:H_2O$ (1:1) to achieve a final concentration of 1×10^{-4} M of $Ru(bpy)_3(PF_6)_2$ in $CH_3CN:H_2O$ (1:1). The solution was degassed with argon for 15 min, and the PTFE lined silicone septa was changed to a solid-top cap under the argon flow. Then the emission of the sample without quencher was measured. The intensity was plotted against wavelength.

Fluorescence quenching ability of the alkynoate (1a): To a quartz cuvette with a PTFE lined silicone septa was added 1 mL of 2×10^{-4} M solution of $Ru(bpy)_3(PF_6)_2$ in anhydrous $CH_3CN:H_2O$ (1:1). To the solution was added 1 mL alkynoate (**1a**) in an appropriate concentration in $CH_3CN:H_2O$ (1:1) ($[Ru(bpy)_3(PF_6)_2]$ =1 x 10-4 M, [quencher] = 0.001 M, 0.002 M, 0.004 M, 0.008 M, 0.016 M, 0.032 M). The solution was degassed with argon for 15 min, and the PTFE lined silicone septa was changed to a solid-top cap under the argon flow. Then the emission of the sample was measured without changing the settings of the previous measurements. The intensity was plotted against wavelength at each different concentration of the quencher.

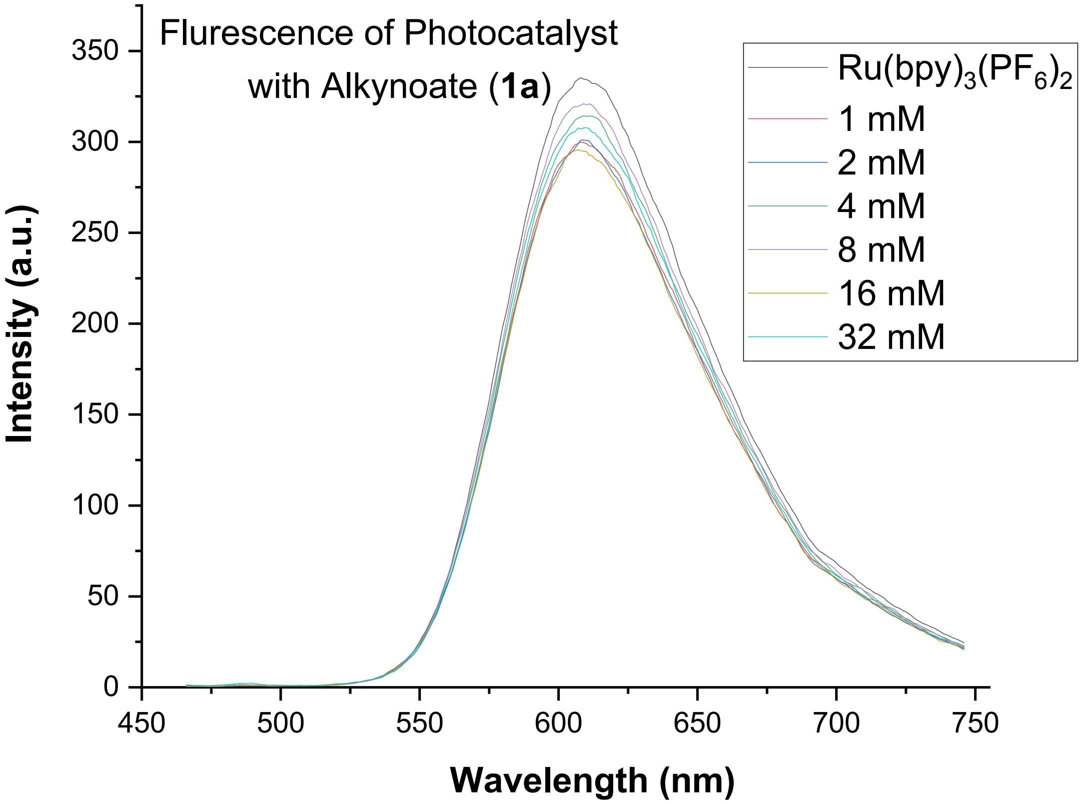


Fig 5: Plot of Fluorescence Quenching Ability of 1a Versus Wavelength

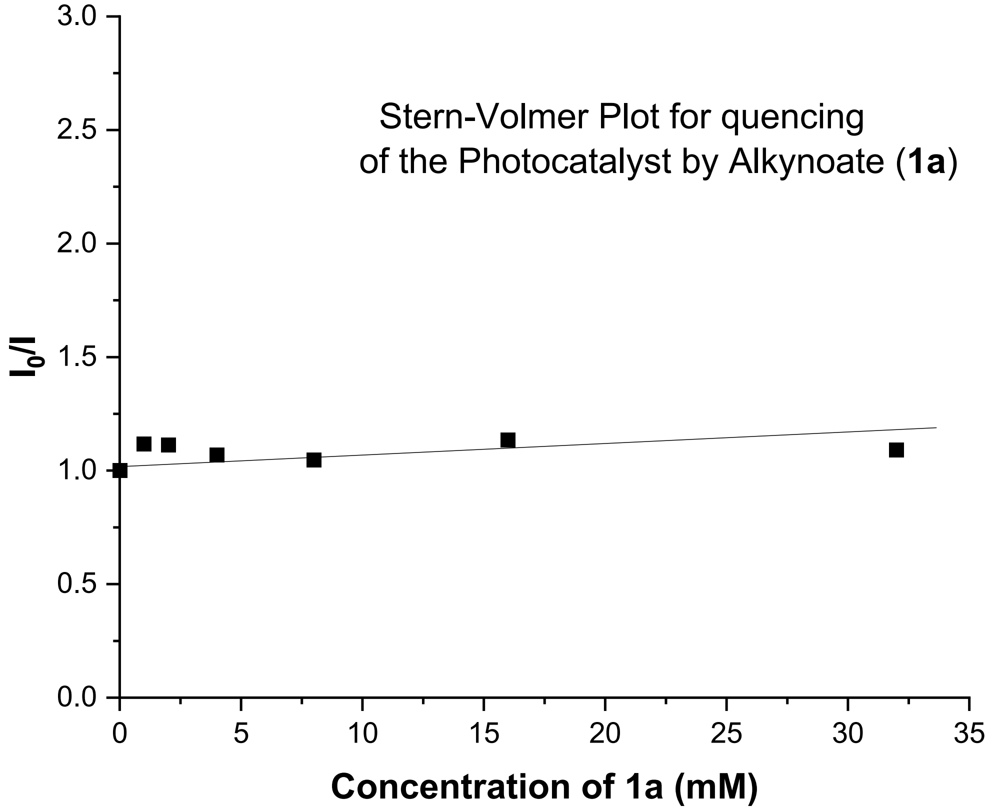


Fig 6: Stern-Volmer relationship for Alkynoate (1a)

Fluoroscence quenching ability of the tricarbonyl (2a): To a quartz cuvette with a PTFE lined silicone septa was added 1 mL of 2×10^{-4} M solution of $Ru(bpy)_3(PF_6)_2$ in anhydrous $CH_3CN:H_2O$ (1:1). To the solution was added 1 mL $HC(CO_2Et)_3$ (**2a)** in an appropriate concentration in $CH_3CN:H_2O$ (1:1) ($[Ru(bpy)_3(PF_6)_2]$ =1 x 10-4 M, [quencher] = 0.001 M, 0.002 M, 0.004 M, 0.008 M, 0.016 M, 0.032 M). The solution was degassed with argon for 15 min, and the PTFE lined silicone septa was changed to a solid-top cap under the argon flow. Then the emission of the sample was measured without changing the settings of the previous measurements. The intensity was plotted against wavelength at each different concentration of the quencher.

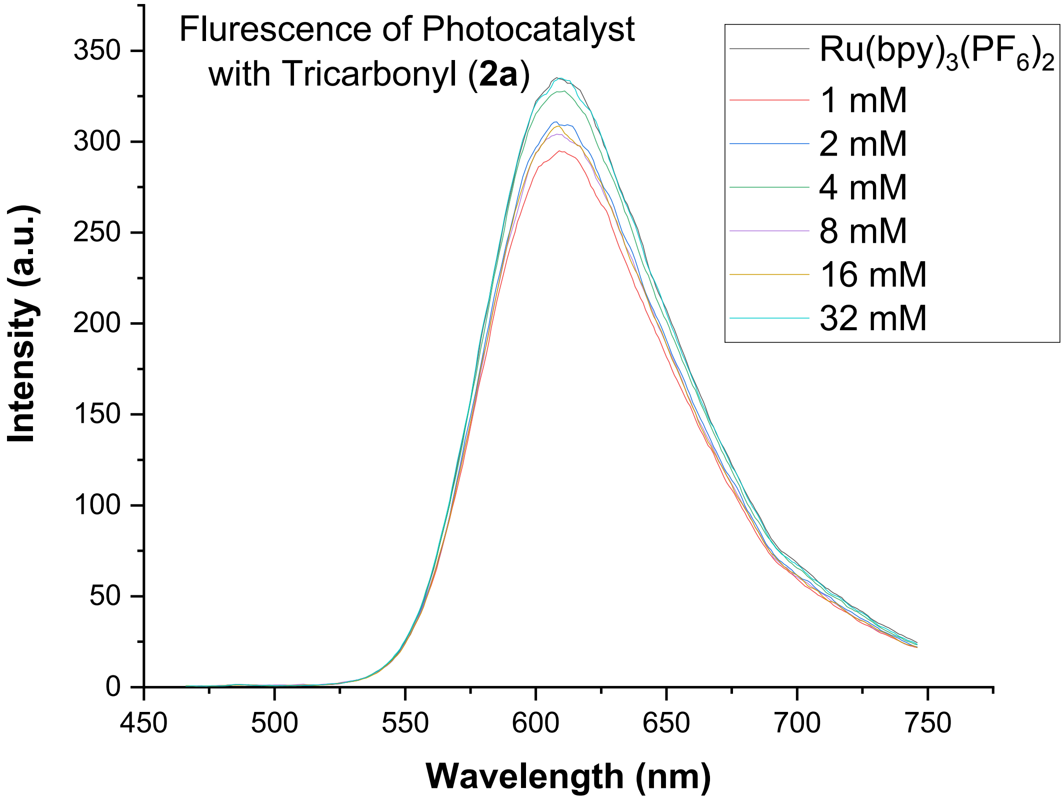


Fig 7: Plot of Fluorescence Quenching Ability of 1a Versus Wavelength

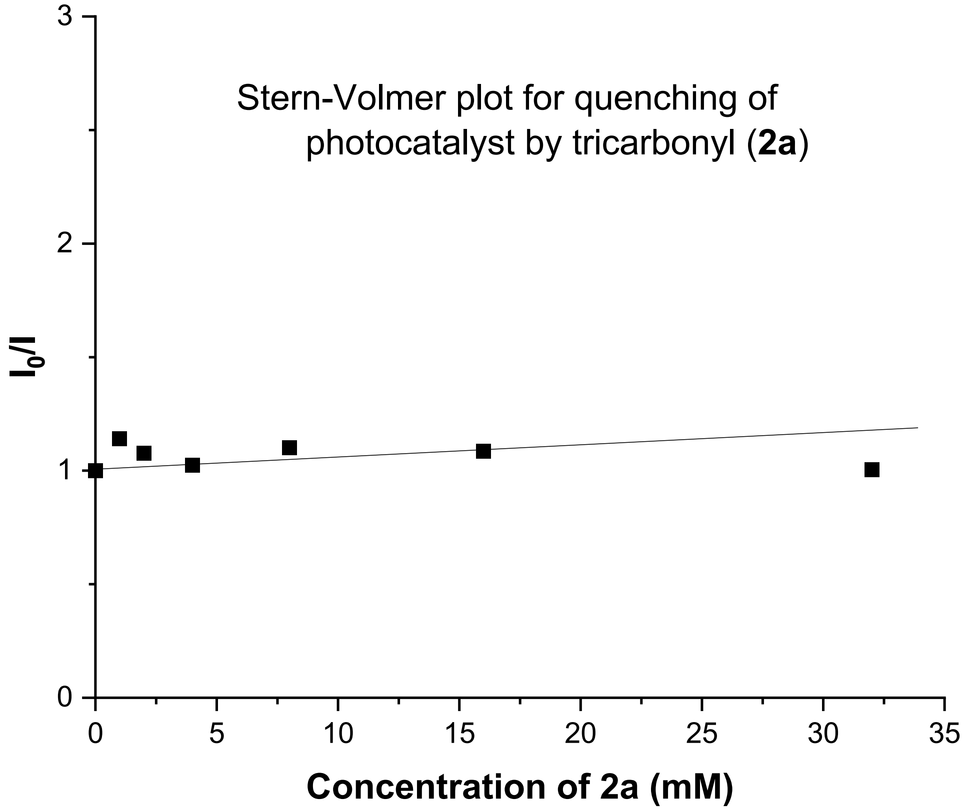


Fig 8: Stern-Volmer relationship for tricarbonyl (2a)

Fluorescence quenching ability of the oxidant ($K_2S_2O_8$): To a quartz cuvette with a PTFE lined silicone septa was added 1 mL of 2×10^{-4} M solution of $Ru(bpy)_3(PF_6)_2$ in anhydrous $CH_3CN:H_2O$ (1:1). To the solution was added 1 mL of $K_2S_2O_8$ in an appropriate concentration in $CH_3CN:H_2O$ (1:1) ($[Ru(bpy)_3(PF_6)_2]$ =1 x 10-4 M, [quencher] = 0.001 M, 0.002 M, 0.004 M, 0.008 M, 0.016 M, 0.032 M). The solution was degassed with argon for 15 min, and the PTFE lined silicone septa was changed to a solid-top cap under the argon flow. Then the emission of the sample was measured without changing the settings of the previous measurements. Intensity was plotted against wavelength at each different concentration of the quencher.

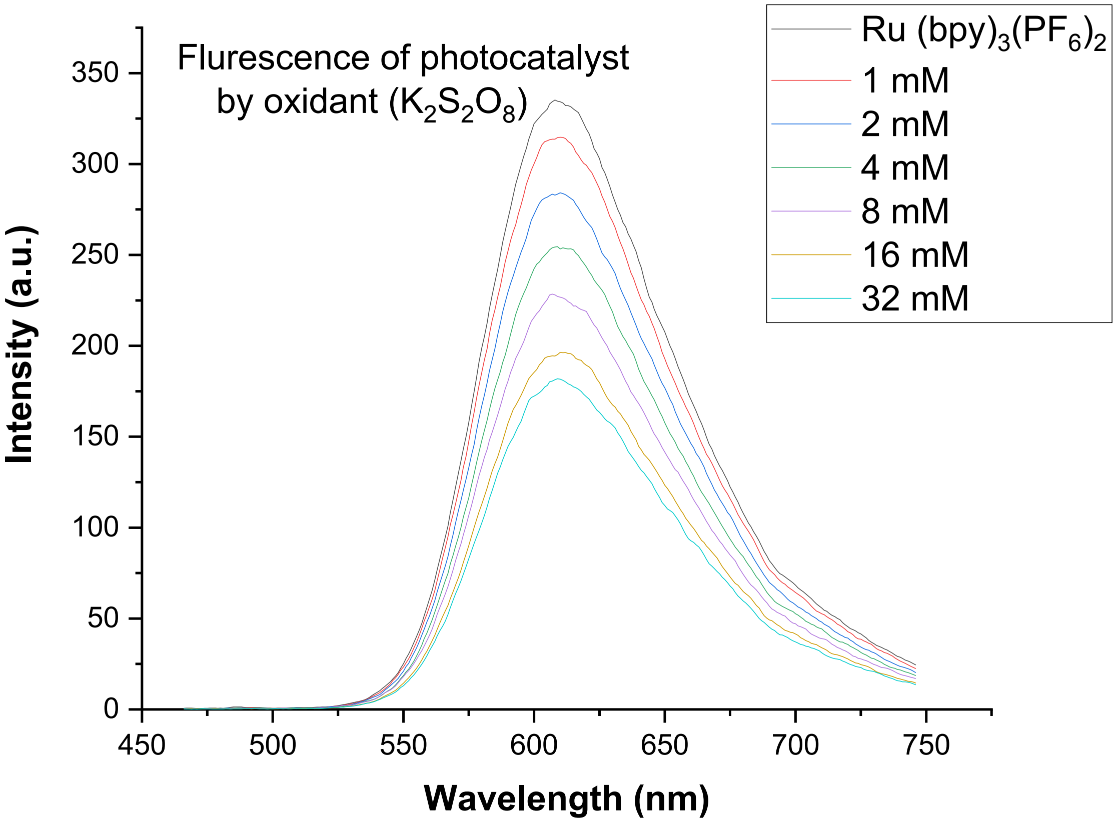


Fig 9: Plot of Fluorescence Quenching Ability of $K_2S_2O_8$ Versus Wavelength

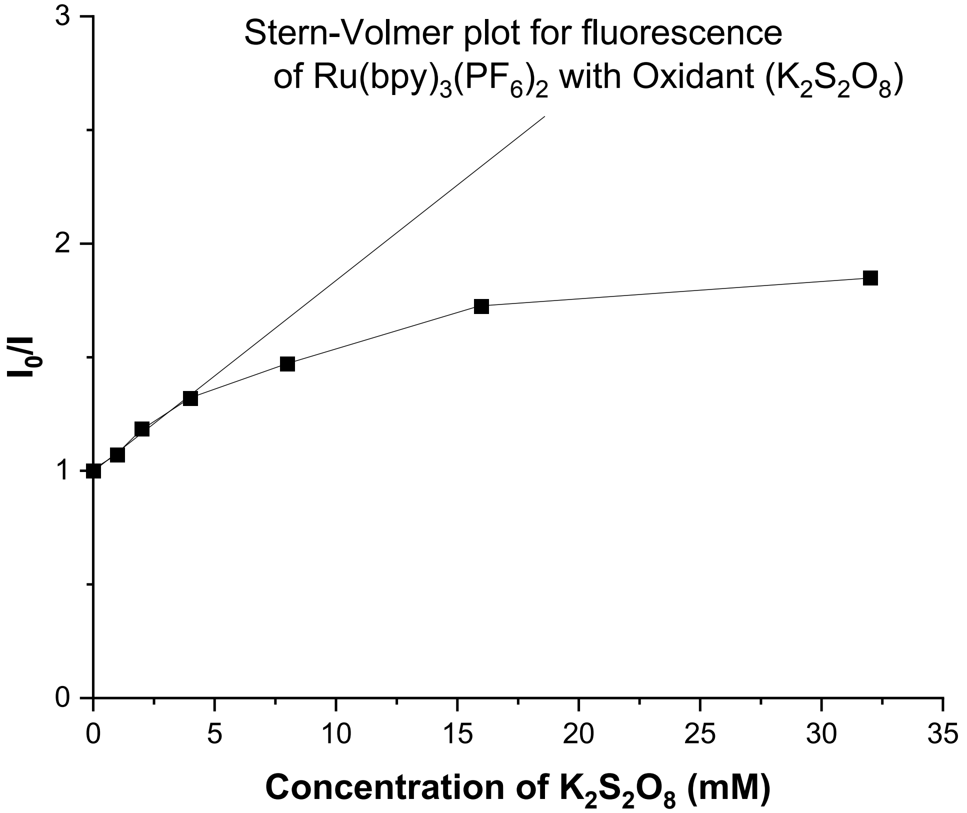


Fig 10: Stern-Volmer relationship for oxidant ($K_2S_2O_8$)

Consolidated plots of Stern-Volmer quenching study:

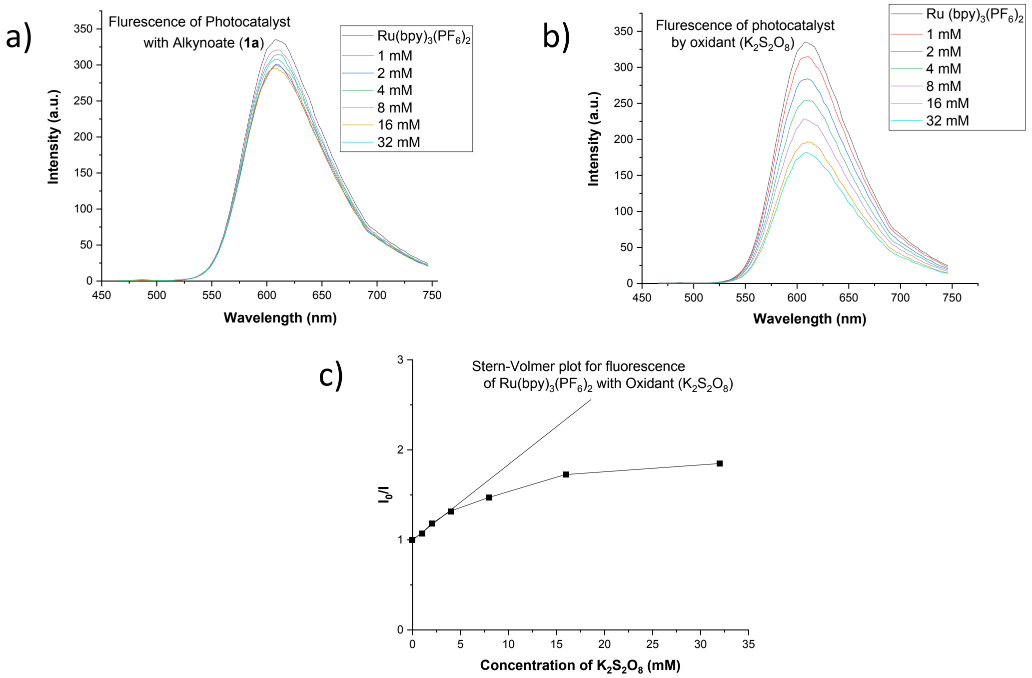


Fig 11 : a) Plot of fluorescence quenching ability of $HC(CO_2Et)_3$ versus wavelength b) Plot of fluorescence quenching ability of $K_2S_2O_8$ versus wavelength c) Stern-Volmer relationship for $K_2S_2O_8$.

Conclusion of Stern-Volmer quenching study:

This study suggested that there was no luminescence quenching by tricarbonyl or alkynoate, rather it was persulfate that was quenching the catalyst from its photo-excited state.

(v) Cyclic Voltammetry data

Cyclic Voltammetry was performed on a CH Instruments electrochemical analyzer (CHI 645D). A 0.005 M MeCN/H_2O (v/v 1:1) solution of $Ru(bpy)_3(PF_6)_2$ or $HC(CO_2Et)_3$ was prepared with 0.1 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) as supporting electrolyte, using a glassy carbon working electrode, a Pt counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Scan rate = 0.05 V/s.

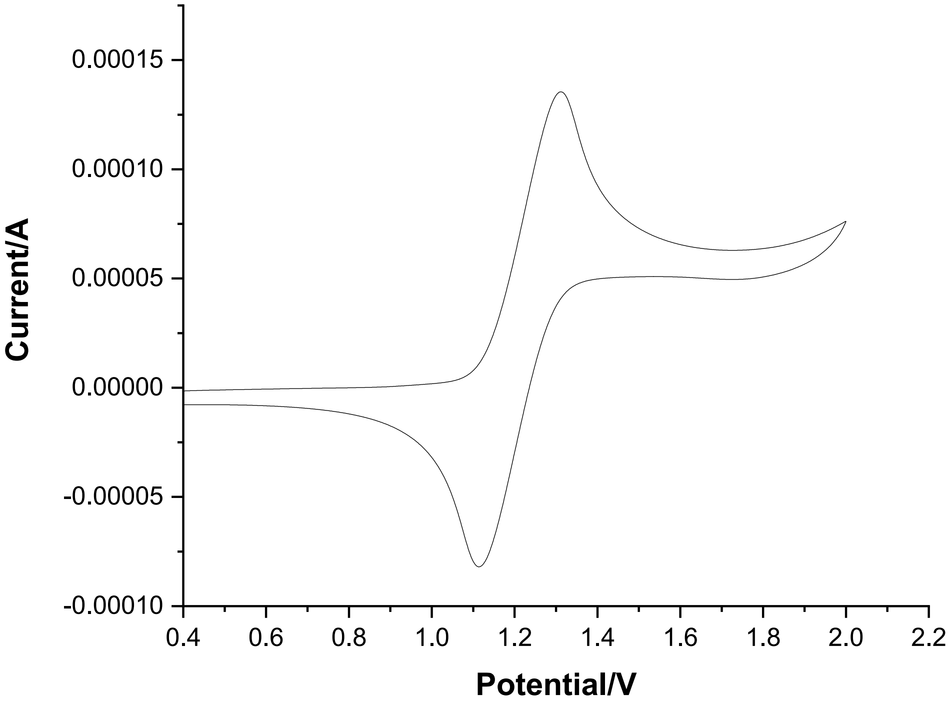


Fig 12: Cyclic Voltammogram for $Ru(bpy)_3(PF_6)_2$ in 1:1 CH_3CN:H_2O

Ground state redox potential obtained:

$E_{1/2}^{IV/III}$ = [(1.31+1.11)/2] V = 1.21 V vs SCE

Excited state redox potential calculated from ground-state potential and λ_{max}(emission) = 608 nm:

$E_{0,0}$ = 2.04 eV

$E_{1/2}^{*IV/III}$ = -0.83 V vs. SCE

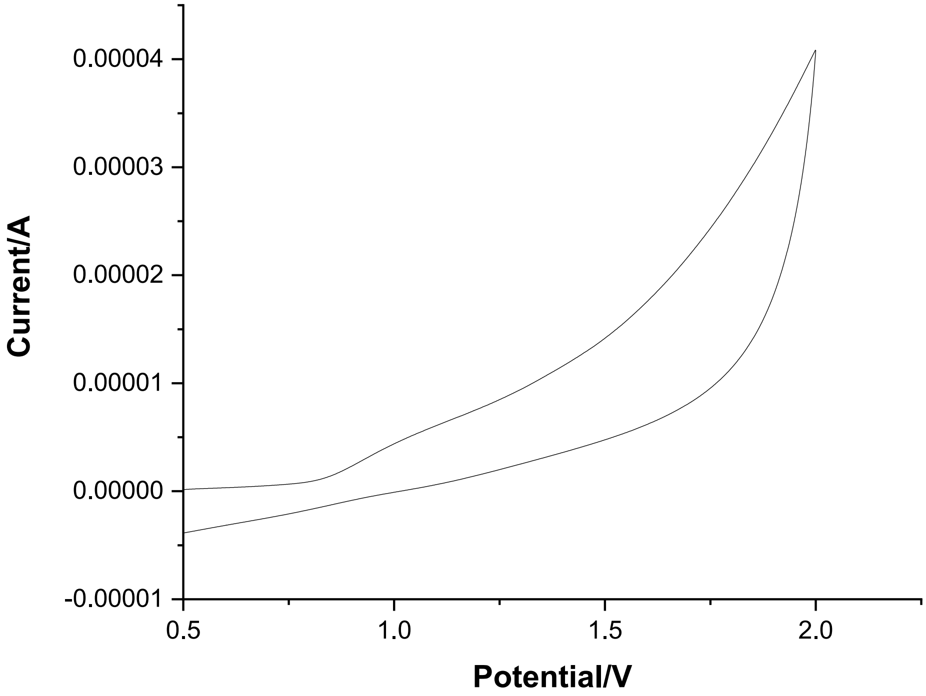
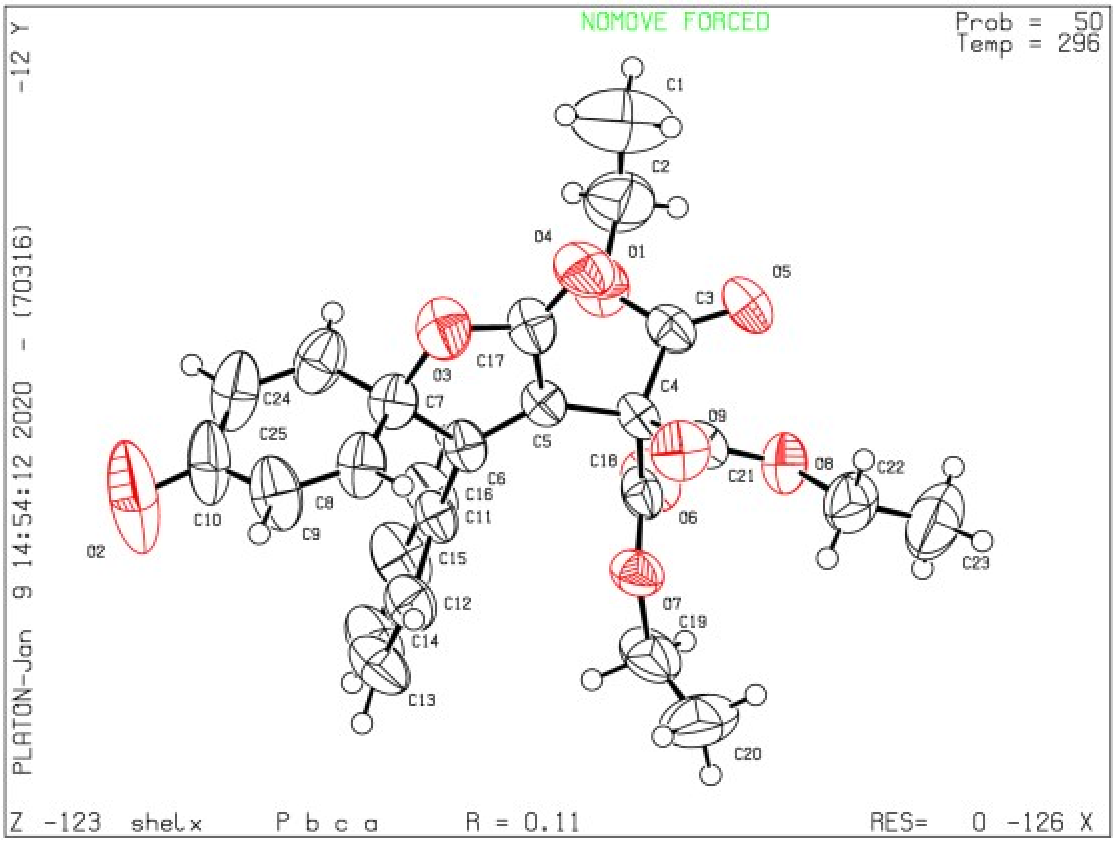


Fig 12: Cyclic Voltammogram for tricarbonyl $HC(CO_2Et)_3$ in 1:1 $CH_3CN:H_2O$

The cyclic voltammetry of the tricarbonyl $HC(CO_2Et)_3$ shows an irreversible oxidation at around +0.9 V. This suggests that a direct single electron oxidation of the tricarbonyl by persulfate radical anion (non-HAT pathway) is not completely ruled out.

8. Crystal Data for 3aa:

The ORTEP diagram and Crystal Parameters of **3aa** in thermal ellipsoids are drawn at 50% probability level. The crystal of suitable quality was obtained from slow evaporation of the solution of pure isolated **3aa** in DCM/Petroleum ether and was analyzed by single-crystal diffractometer. Atomic coordinates, bond lengths, bond angles, and thermal parameters for this compound have been deposited at the Cambridge Crystallographic Data Centre. CCDC 1976359 contains supplementary crystallographic data.



Bond precision: C-C = 0.0054 A Wavelength = 0.71073

Cell: a=22.085 (7) b=9.856 c=22.387 (7)

alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	4873 (3)	4873 (3)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	$C_{25}H_{24}O_9$	$C_{25}H_{24}O_9$
Sum formula	$C_{25}H_{24}O_9$	$C_{25}H_{24}O_9$
Mr	468.44	468.44
Dx, g cm-3	1.277	1.277
Z	8	8
Mu (mm-1)	0.098	0.098
F000	1968.0	1968.0
F000’	1969.21	
h, k, lmax	28, 12, 29	28, 12, 29
Nref	5671	5649
Tmin, Tmax	0.983, 0.988	0.982, 0.987

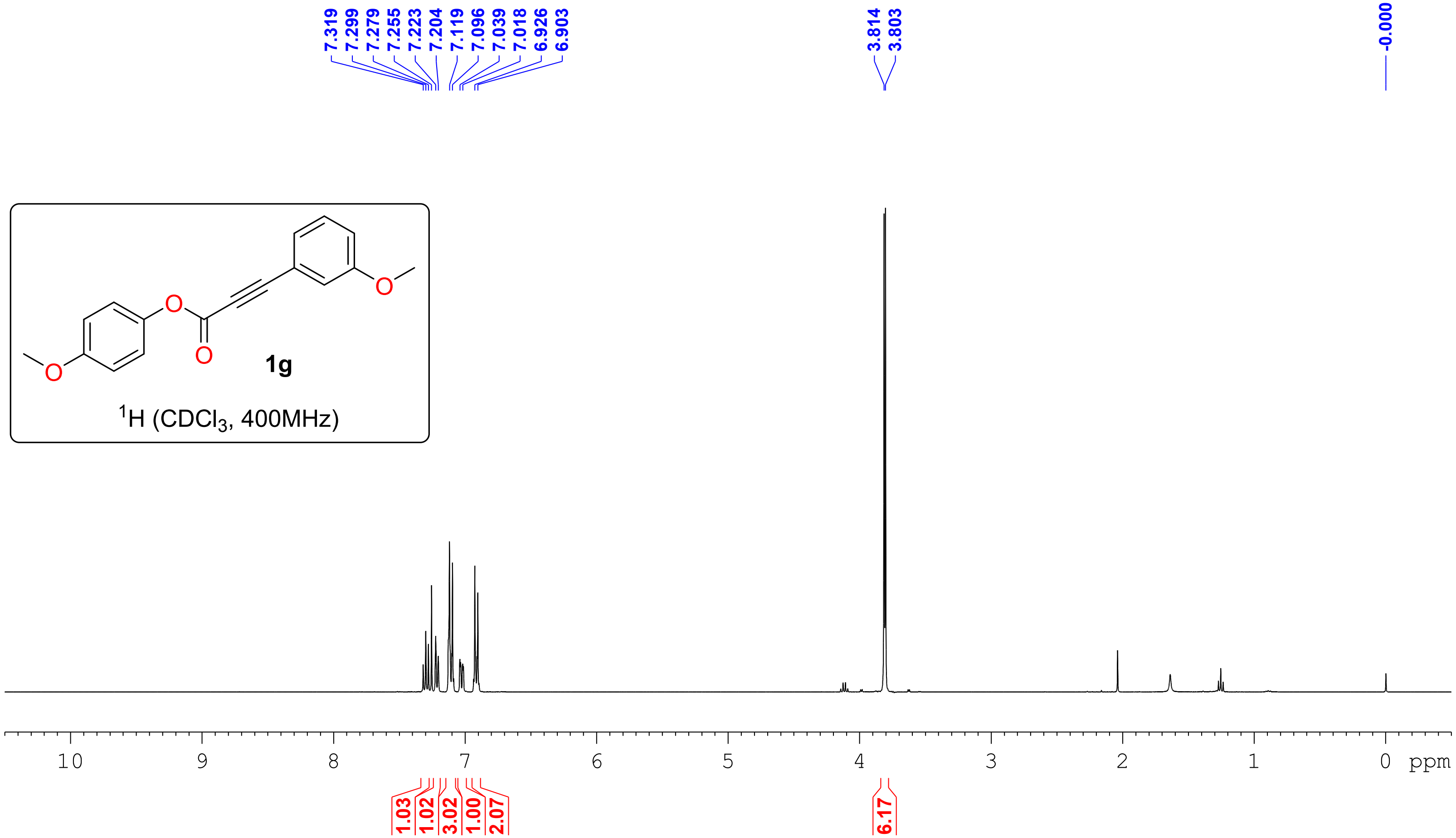
Tmin′	0.976	

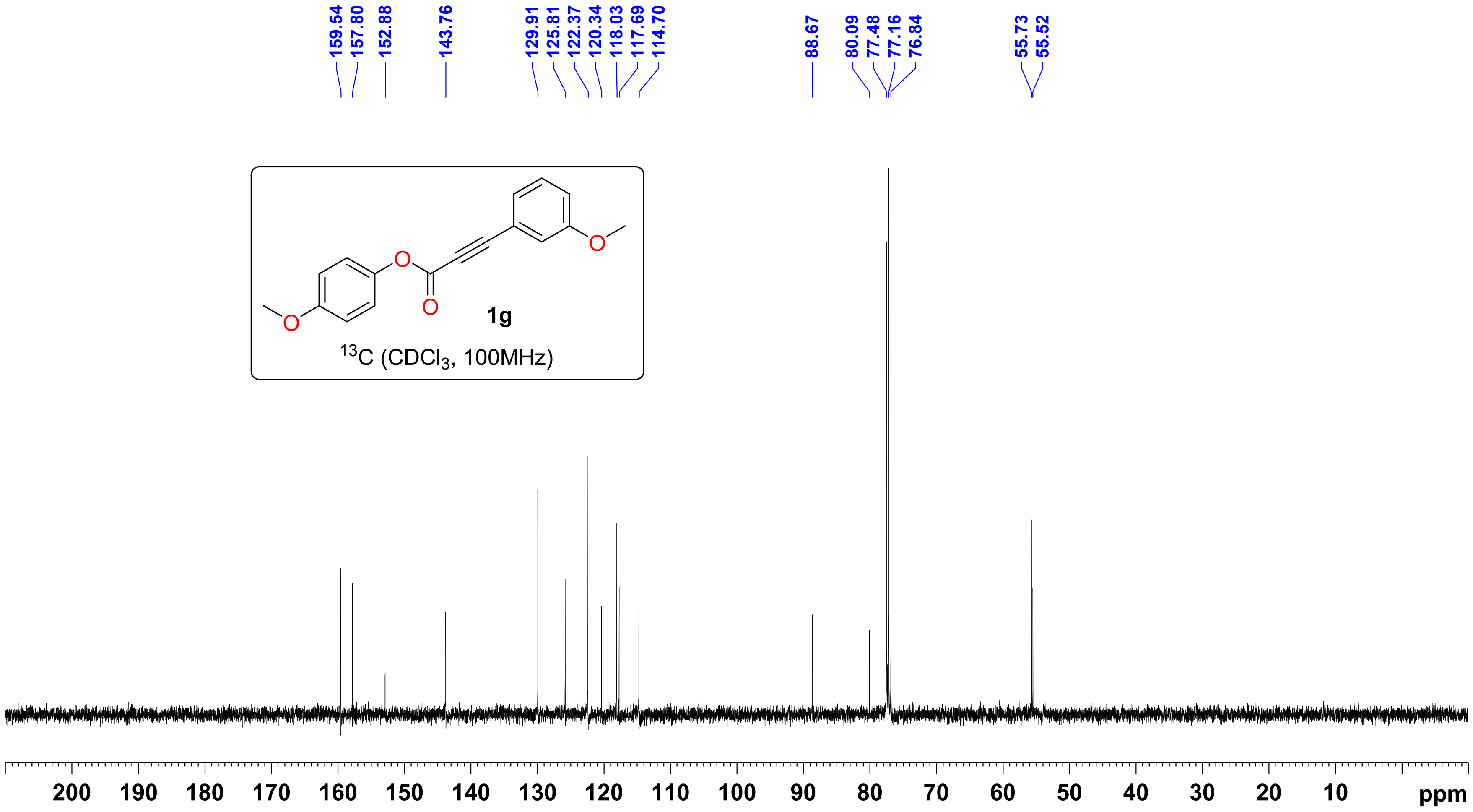
Correction method= # Reported T Limits: Tmin=0.982 Tmax=0.987
AbsCorr = EMPIRICAL
Data completeness= 0.996 Theta (max)= 27.632
R (reflections) = 0.1068 (3302) wR2 (reflections) = 0.2903 (5649)
S = 1.739 Npar= 310

9. References:

1. C. B. Kelly, N. R. Patel, D. N. Primer, M. Jouffroy, J. C. Tellis, G. A. Molander, *Nat. Protoc.,* 2017, **12**, 472.
2. A. H. Bansode, S. R. Shaikh, R. G. Gonnade and N. T. Patil, *Chem. Commun.*, 2017, **53**, 9081.
3. D. Qian, J. Zhang, *Chem. Commun.*, 2012, **48**, 7082.

10. ^{1}H and ^{13}C spectra

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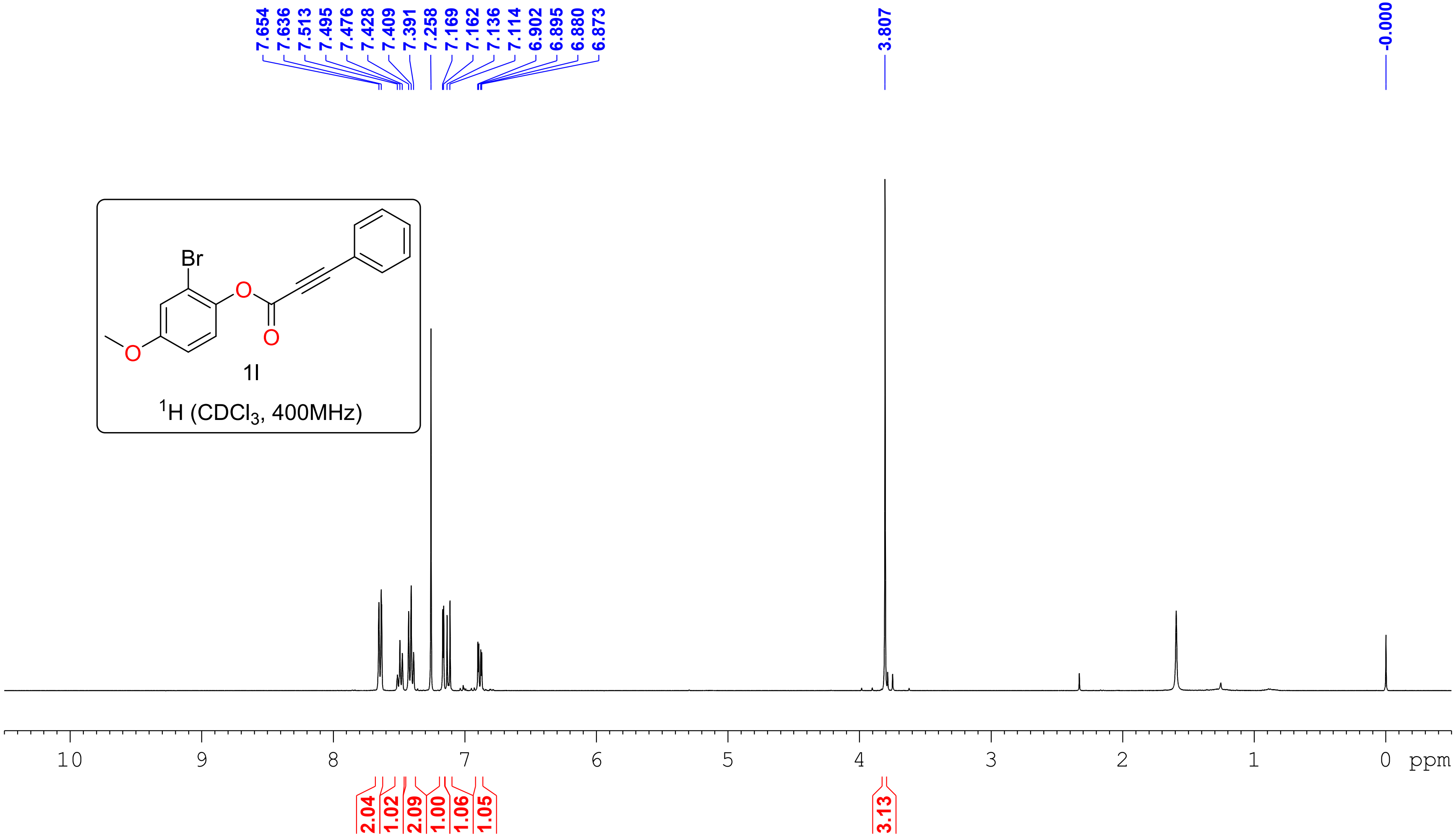
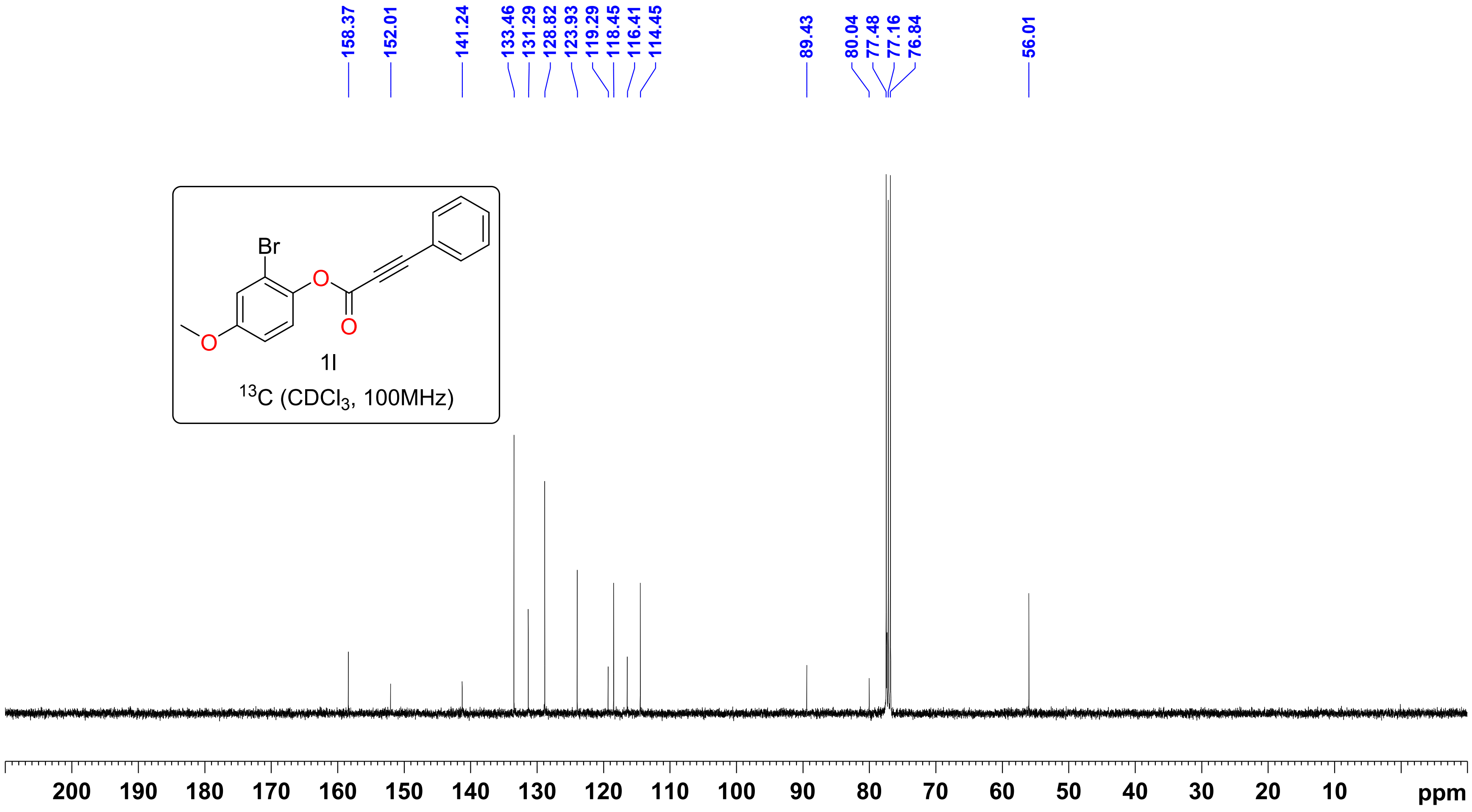
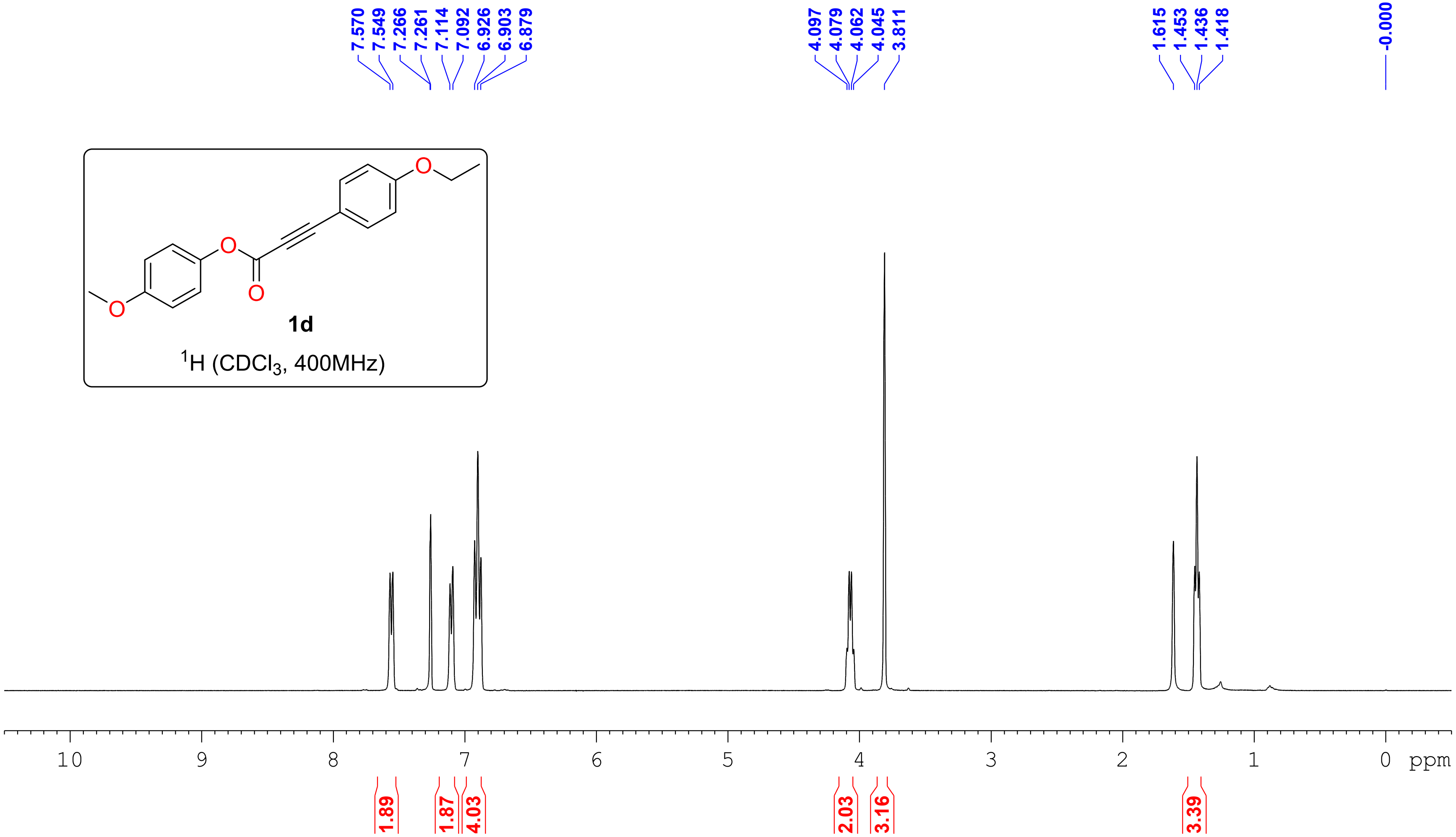
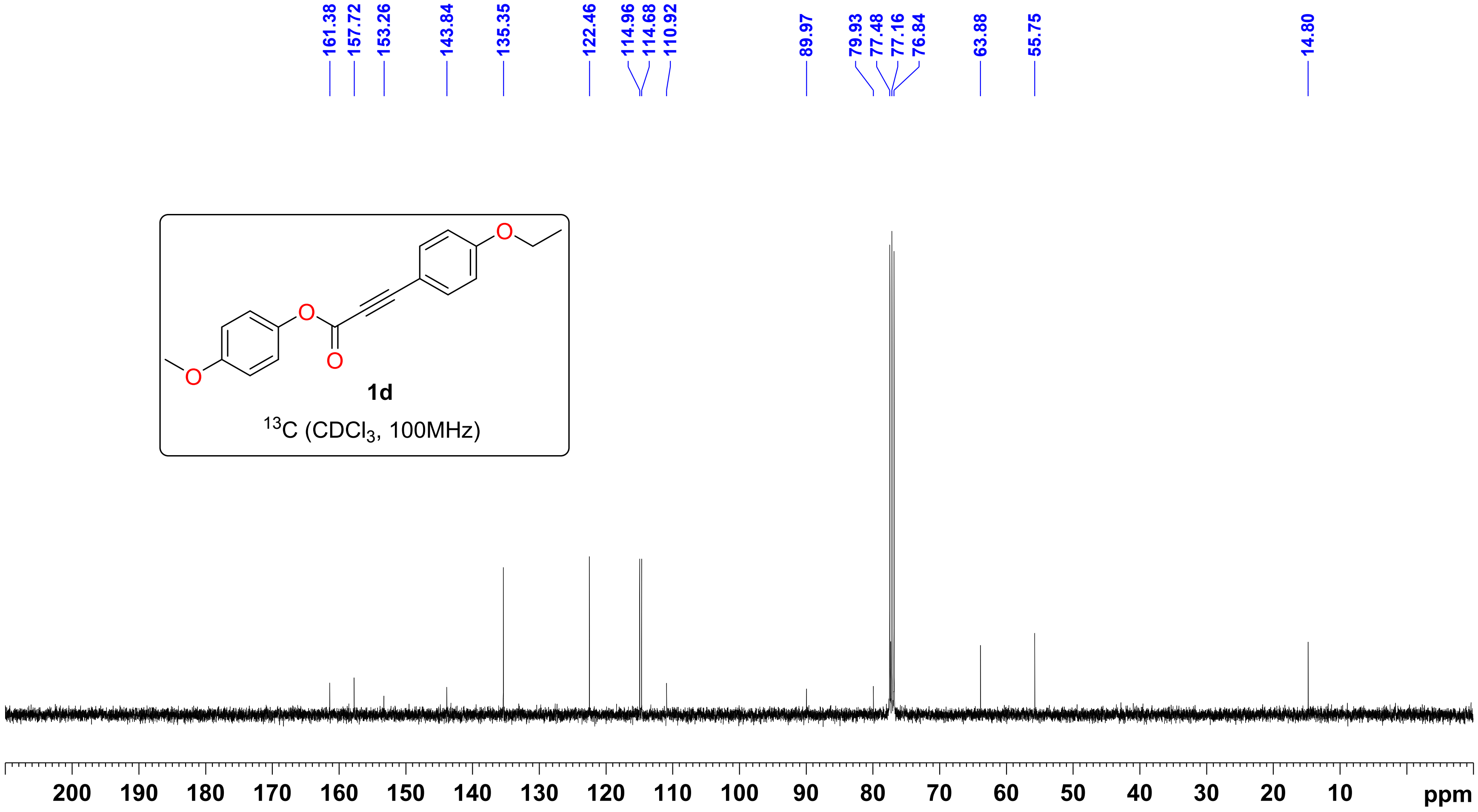
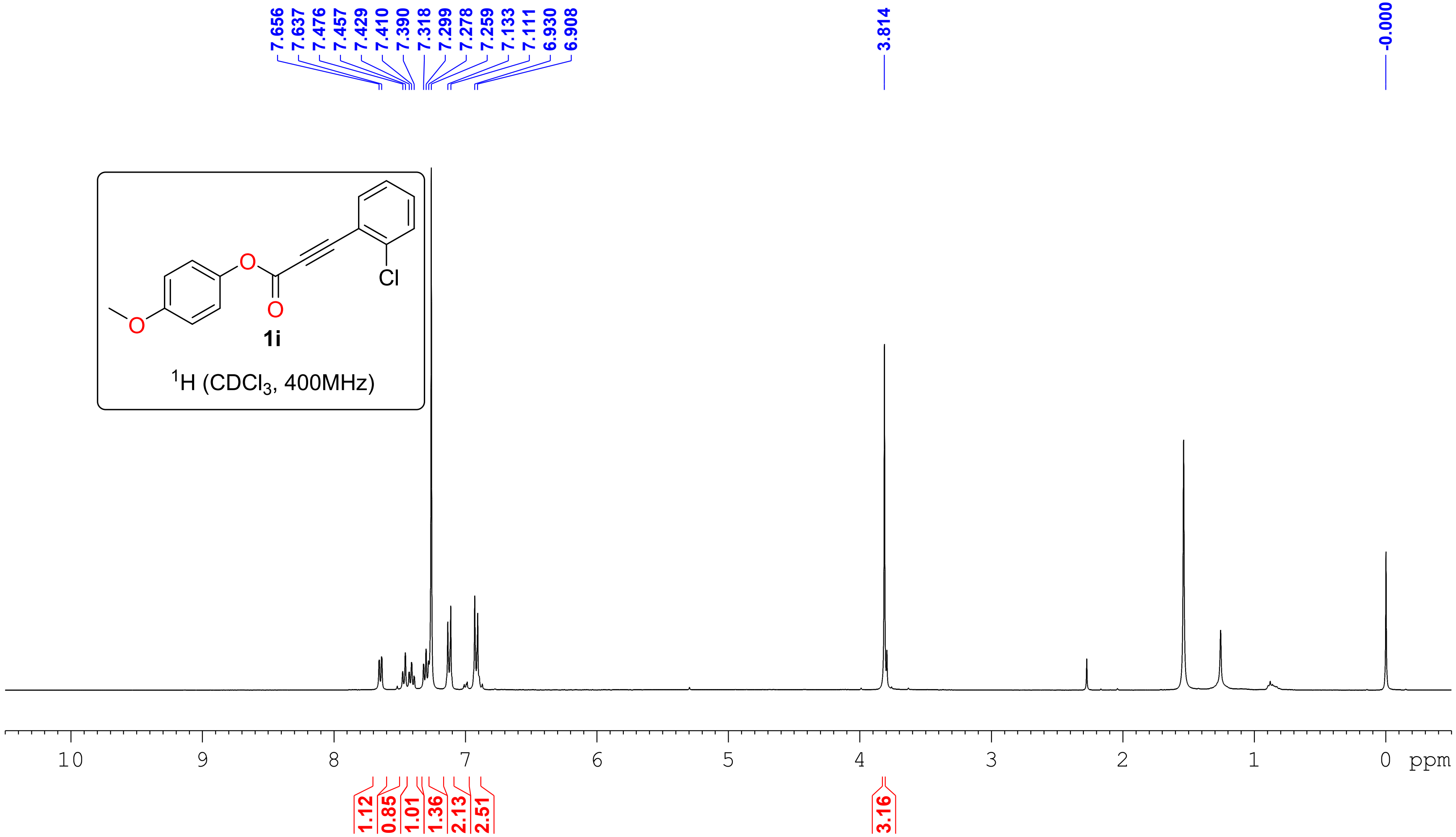
157.80
152.88
143.76
129.91
125.81
122.37
120.34
118.03
117.69
114.70
88.67
80.09
77.48
77.16
76.84
55.73
55.52
O
O
O
O
1g
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

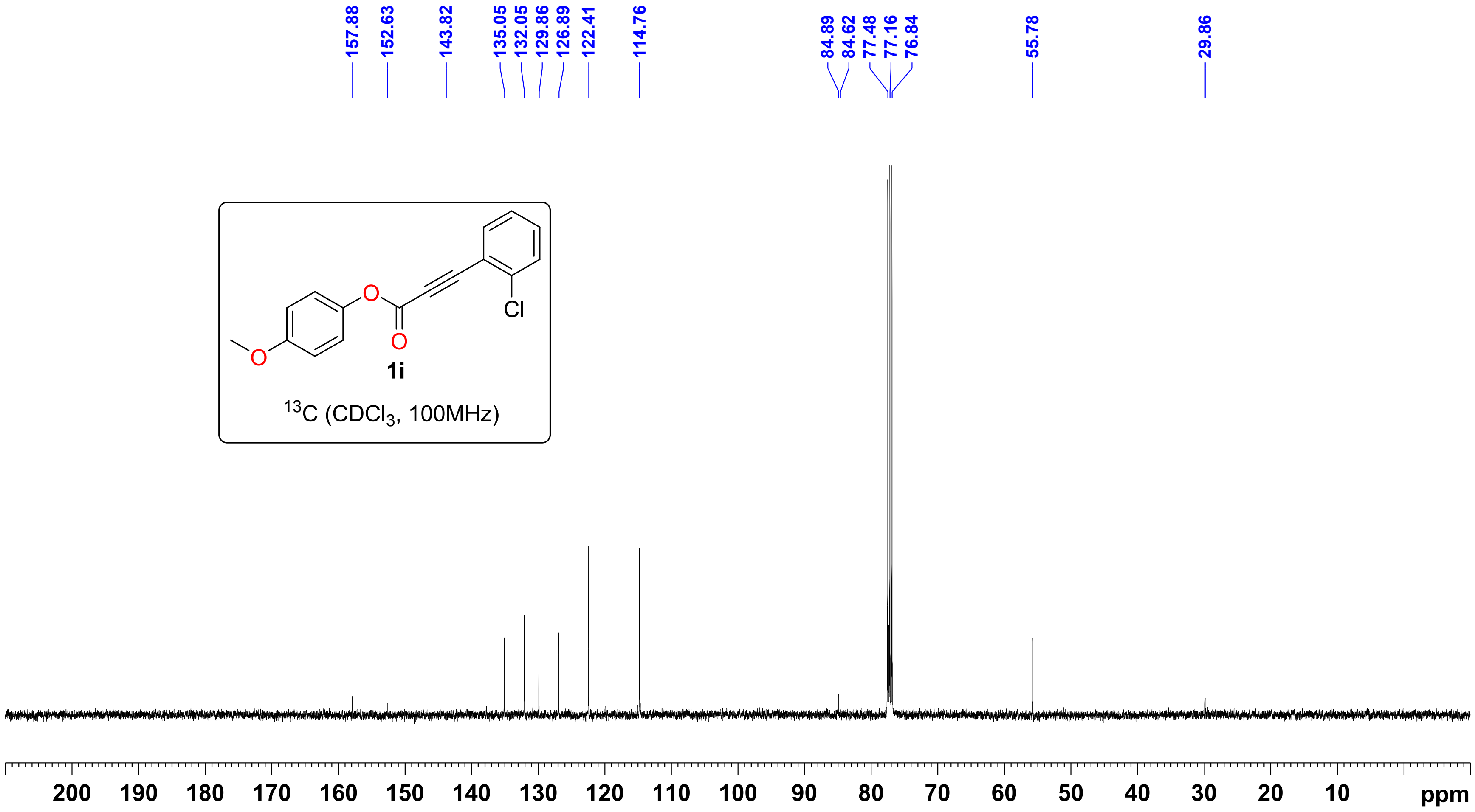

7.654
7.636
7.513
7.495
7.476
7.428
7.409
7.391
7.258
7.169
7.162
7.136
7.114
6.902
6.895
6.880
6.873
3.807
-0.000
Br
O
O
O
1l
¹H (CDCl₃, 400MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.04
1.02
2.09
1.00
1.06
1.05
3.13

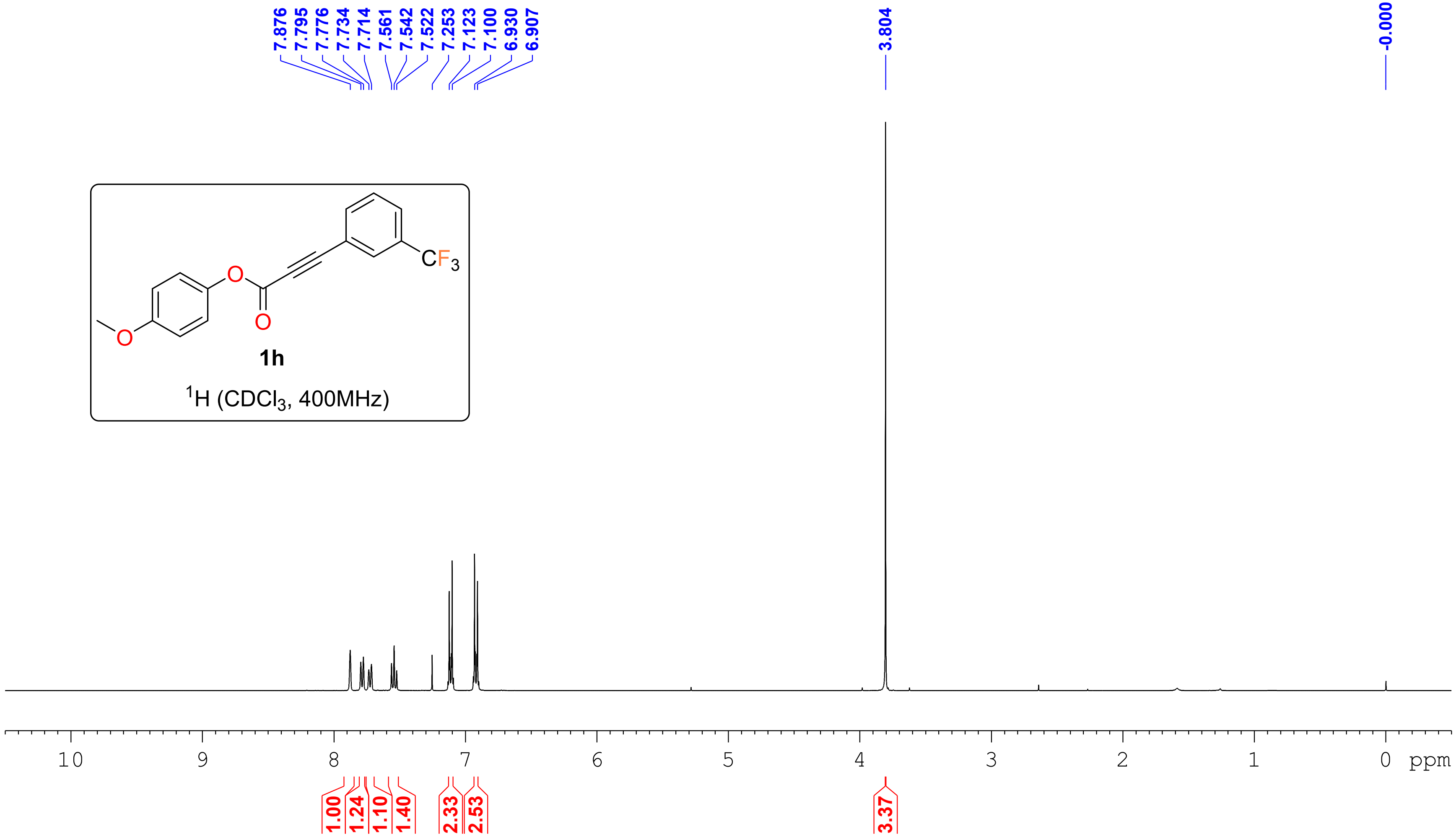

158.37
152.01
141.24
133.46
131.29
128.82
123.93
119.29
118.45
116.41
114.45
89.43
80.04
77.48
77.16
76.84
56.01
Br
O
O
O
1l
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

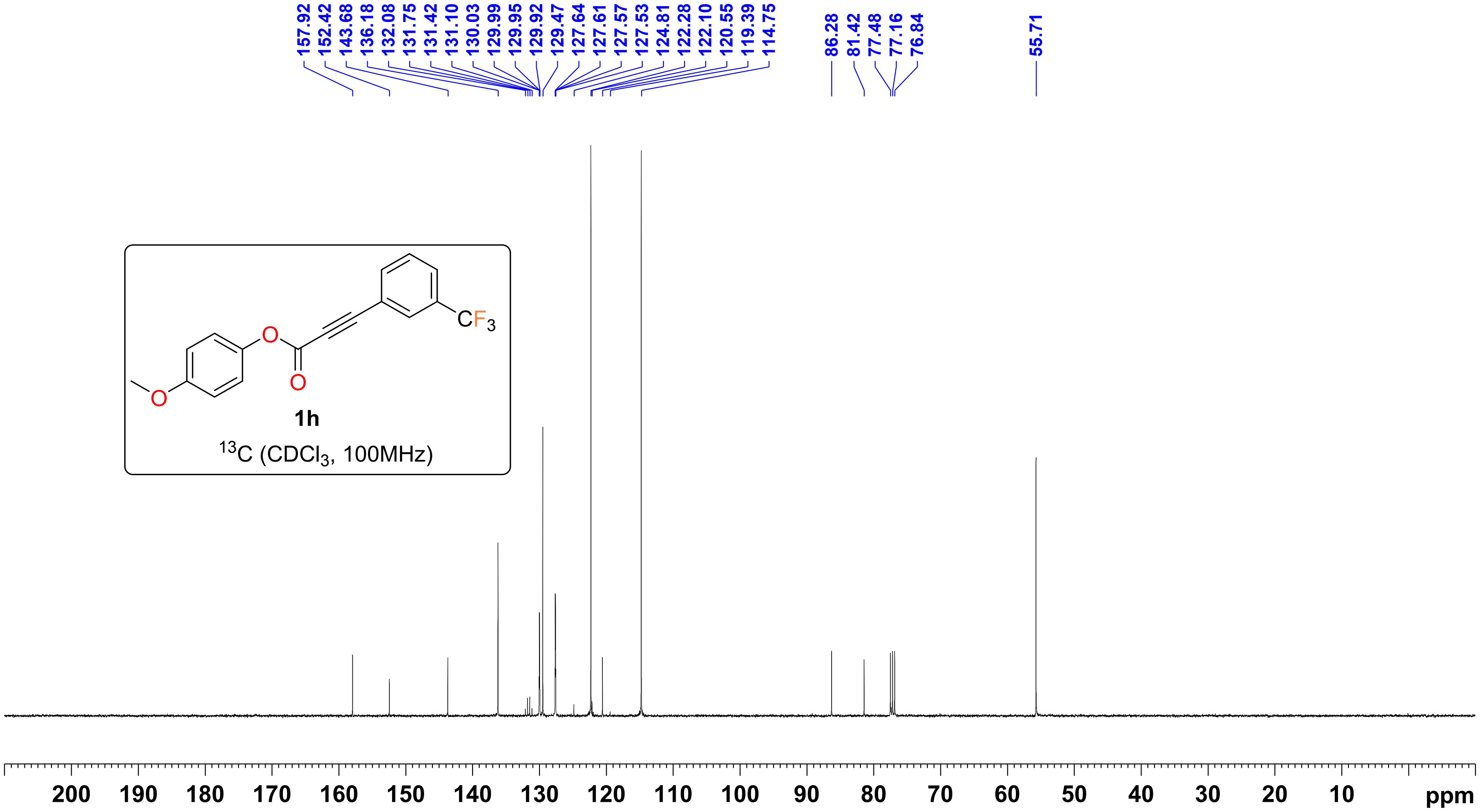

7.570
7.549
7.266
7.261
7.114
7.092
6.926
6.903
6.879
4.097
4.079
4.062
4.045
3.811
1.615
1.453
1.436
1.418
-0.000
1d
^{1}H (CDCl$_3$, 400MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.89
1.87
4.03
2.03
3.16
3.39


161.38
157.72
153.26
143.84
135.35
122.46
114.96
114.68
110.92
89.97
79.93
77.48
77.16
76.84
63.88
55.75
14.80
1d
^{13}C ($CDCl_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.656
7.637
7.476
7.457
7.429
7.410
7.390
7.318
7.299
7.278
7.259
7.133
7.111
6.930
6.908
3.814
-0.000
O
O
O
Cl
1i
¹H (CDCl₃, 400MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.12
0.85
1.01
1.36
2.13
2.51
3.16

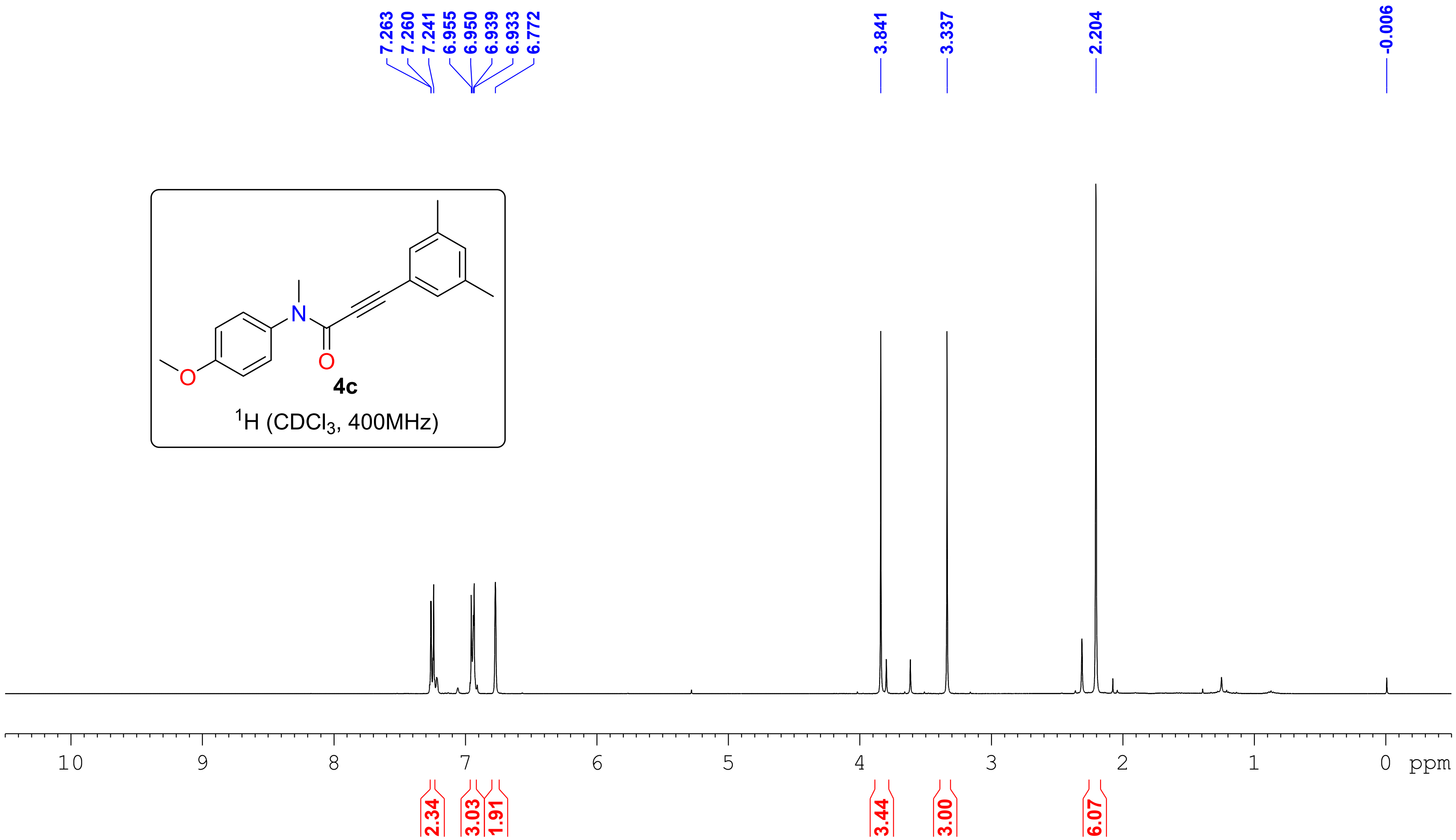

157.88
152.63
143.82
135.05
132.05
129.86
126.89
122.41
114.76
84.89
84.62
77.48
77.16
76.84
55.78
29.86
O
O
O
Cl
1i
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

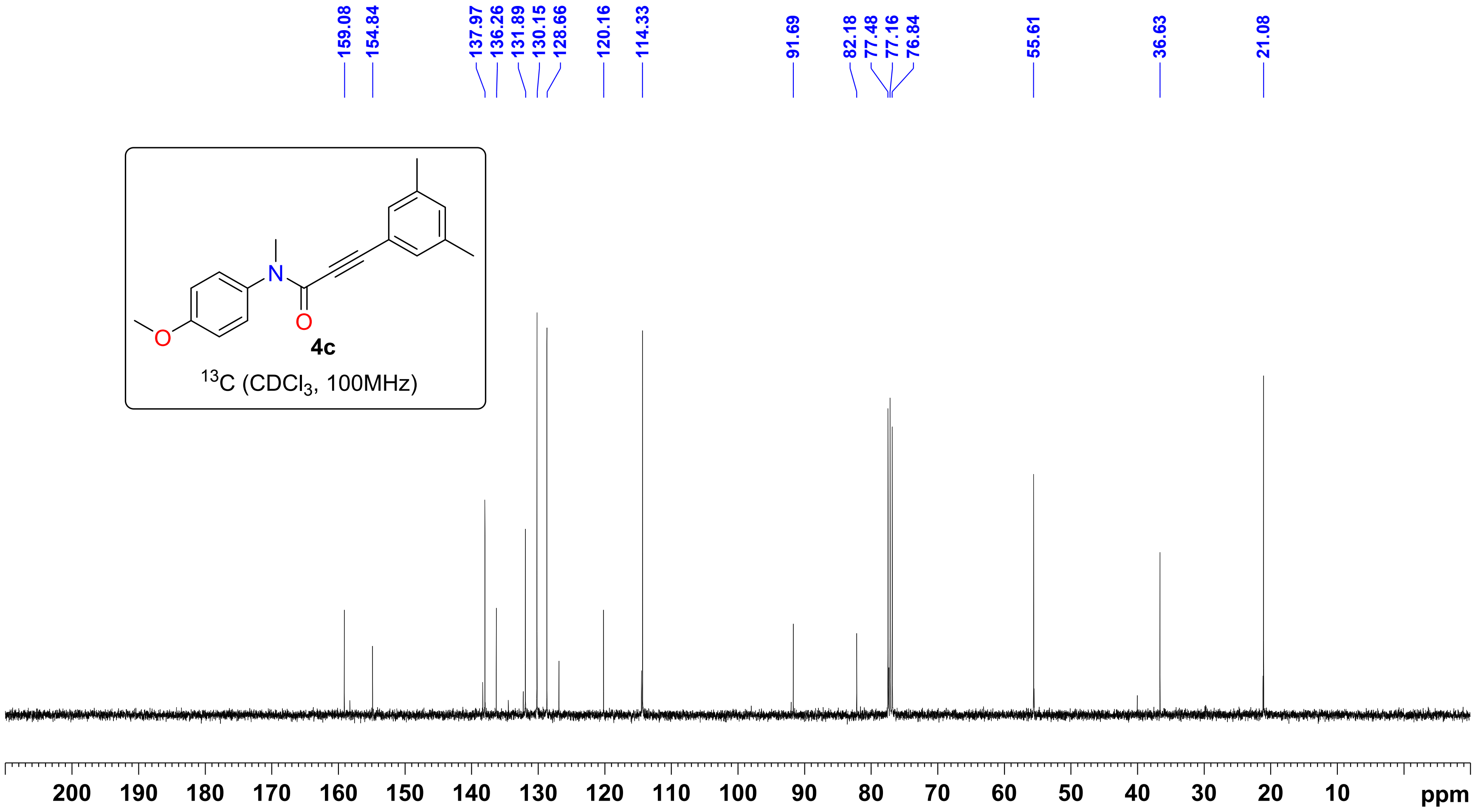

7.876
7.795
7.776
7.734
7.714
7.561
7.542
7.522
7.253
7.123
7.100
6.930
6.907
3.804
-0.000
CF3
O
O
O
1h
1H (CDCl3, 400MHz)
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.24
1.10
1.40
2.33
2.53
3.37

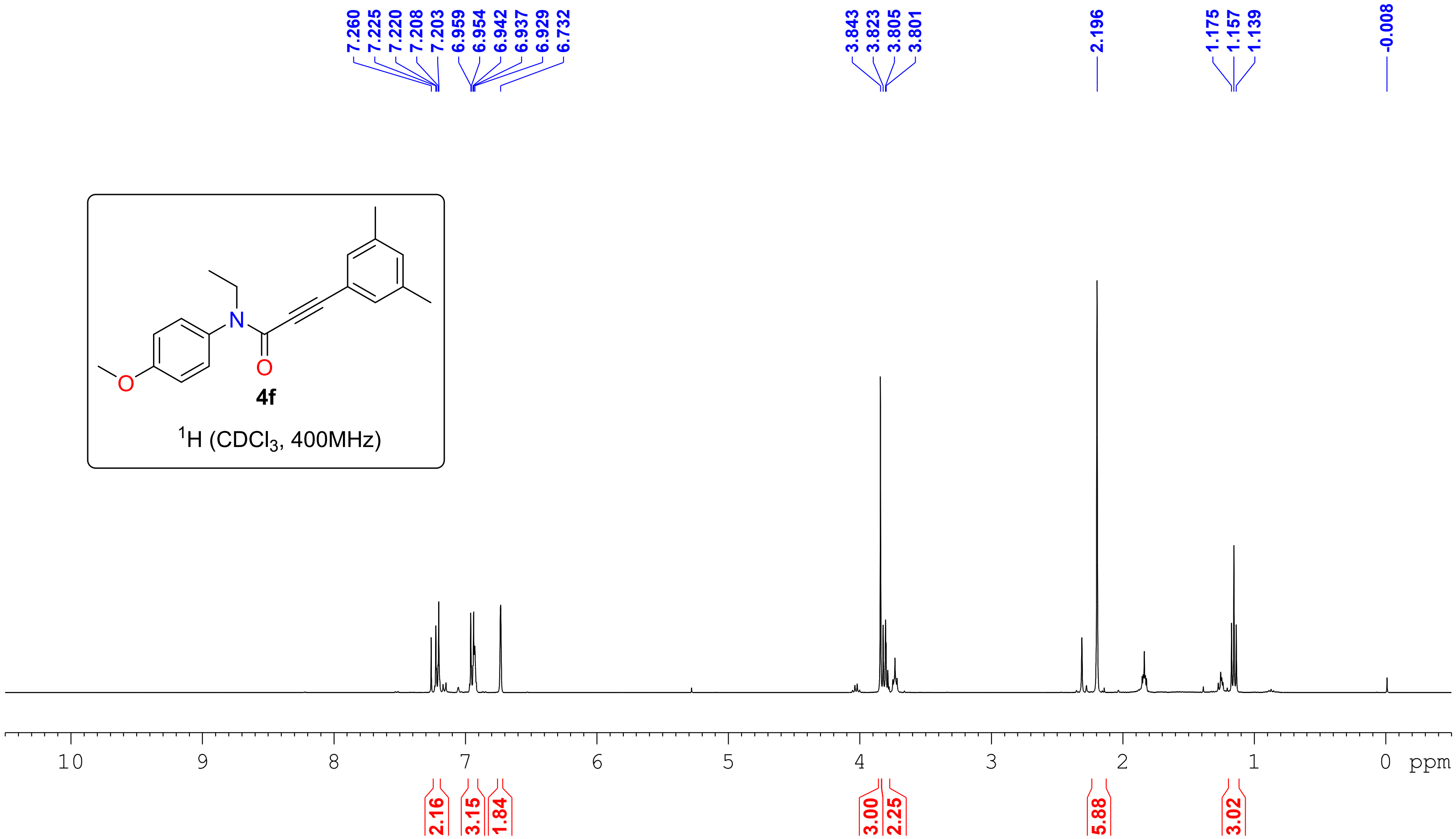


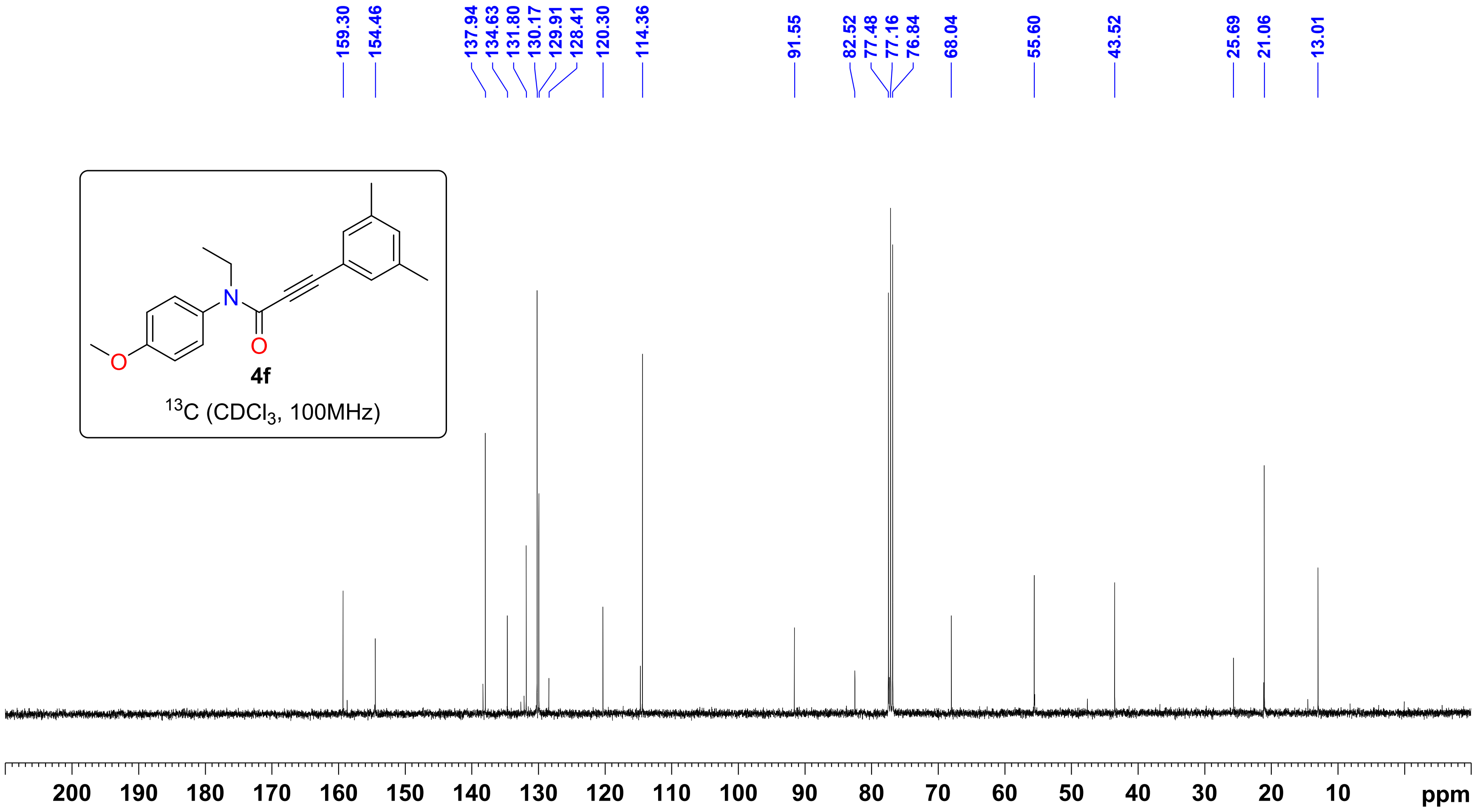
1h

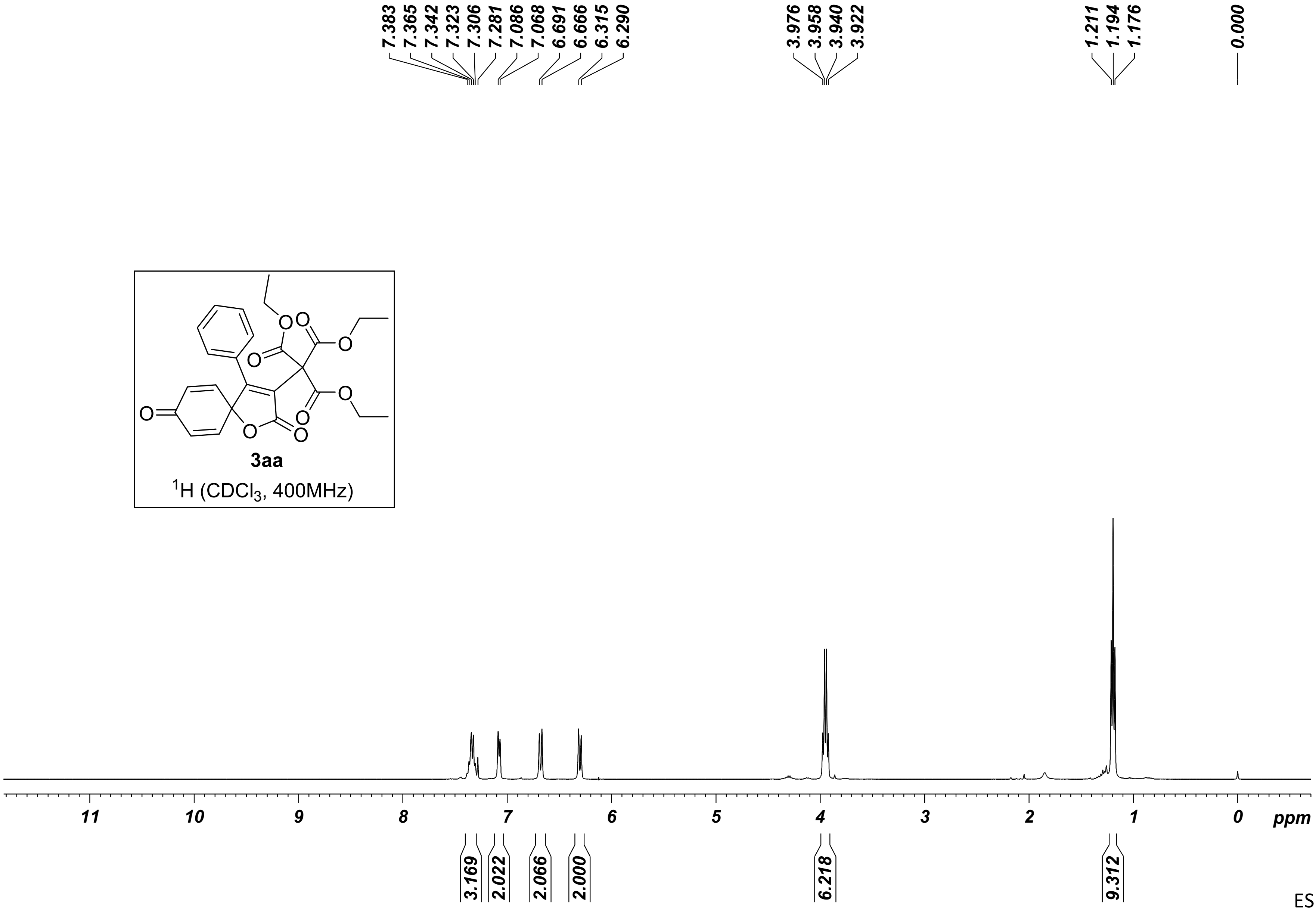
^{13}C (CDCl$_3$, 100MHz)

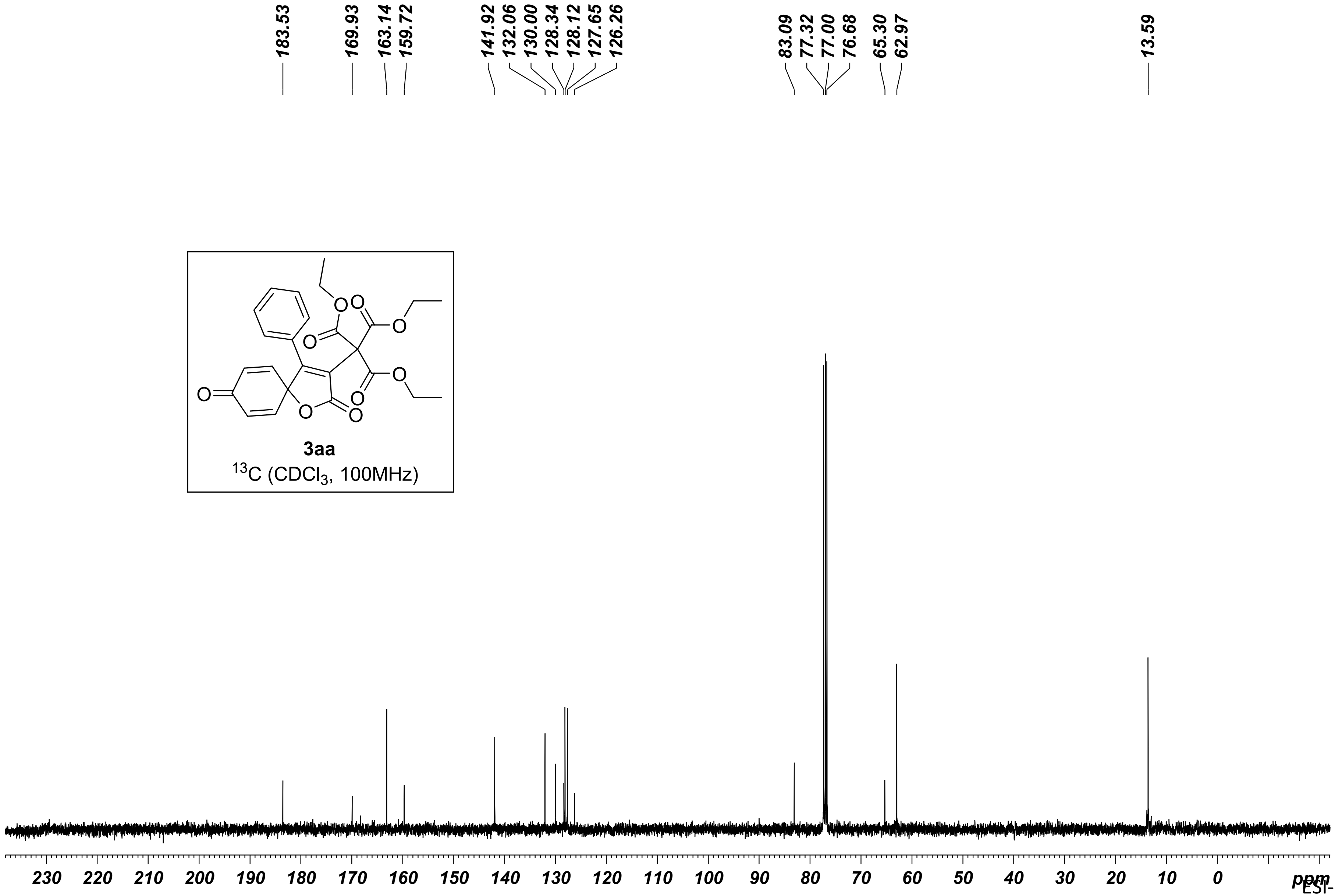

7.263
7.260
7.241
6.955
6.950
6.939
6.933
6.772
3.841
3.337
2.204
-0.006
N
O
O
4c
^{1}H (CDCl$_3$, 400MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.34
3.03
1.91
3.44
3.00
6.07


159.08
154.84
137.97
136.26
131.89
130.15
128.66
120.16
114.33
91.69
82.18
77.48
77.16
76.84
55.61
36.63
21.08
N
O
O
4c
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.260
7.225
7.220
7.208
7.203
6.959
6.954
6.942
6.937
6.929
6.732
3.843
3.823
3.805
3.801
2.196
1.175
1.157
1.139
-0.008
O
N
O
4f
¹H (CDCl₃, 400MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.16
3.15
1.84
3.00
2.25
5.88
3.02


159.30
154.46
137.94
134.63
131.80
130.17
129.91
128.41
120.30
114.36
91.55
82.52
77.48
77.16
76.84
68.04
55.60
43.52
25.69
21.06
13.01
O
N
O
4f
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.383
7.365
7.342
7.323
7.306
7.281
7.086
7.068
6.691
6.666
6.315
6.290
3.976
3.958
3.940
3.922
1.211
1.194
1.176
0.000
3aa
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.169
2.022
2.066
2.000
6.218
9.312

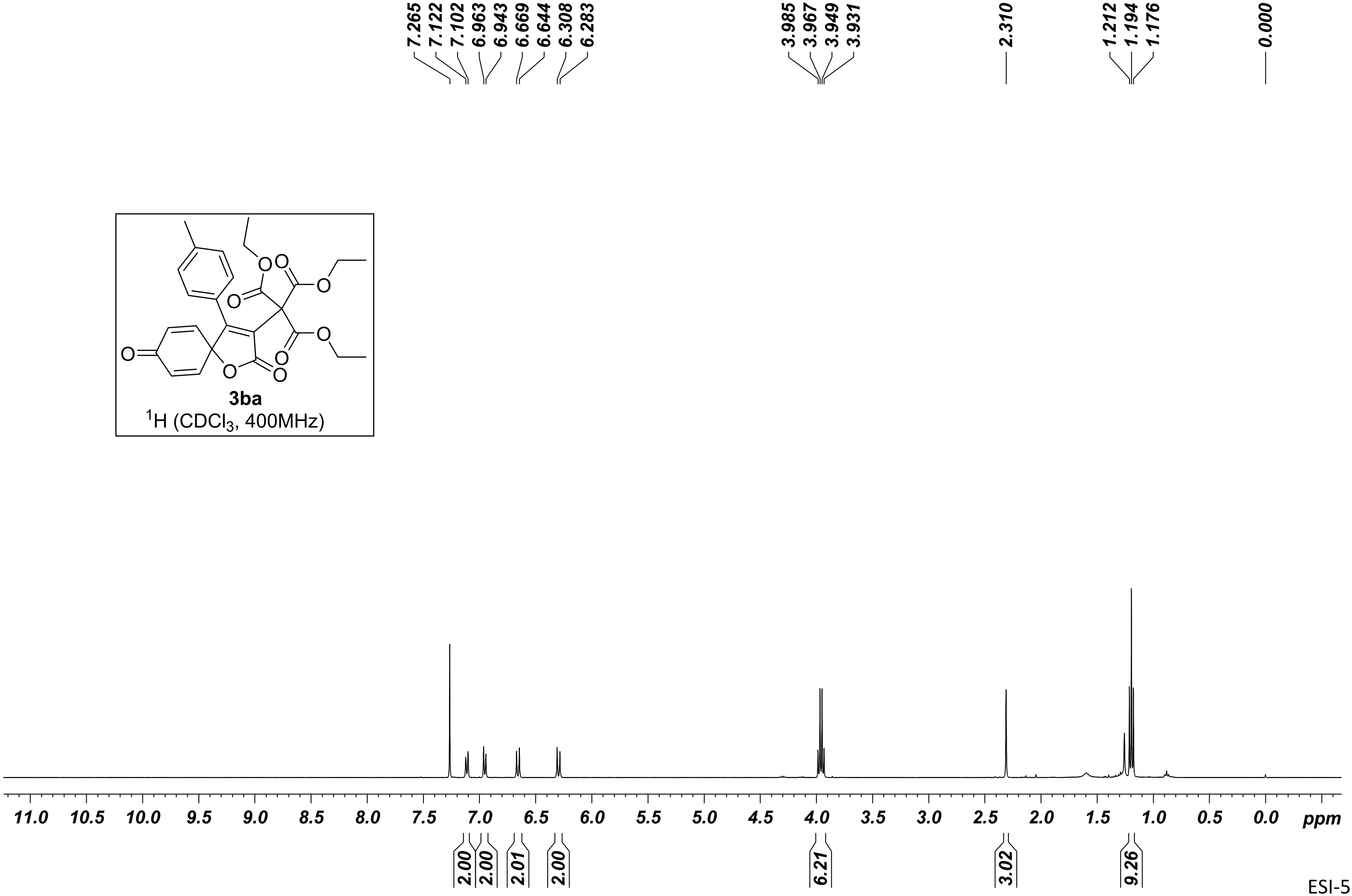


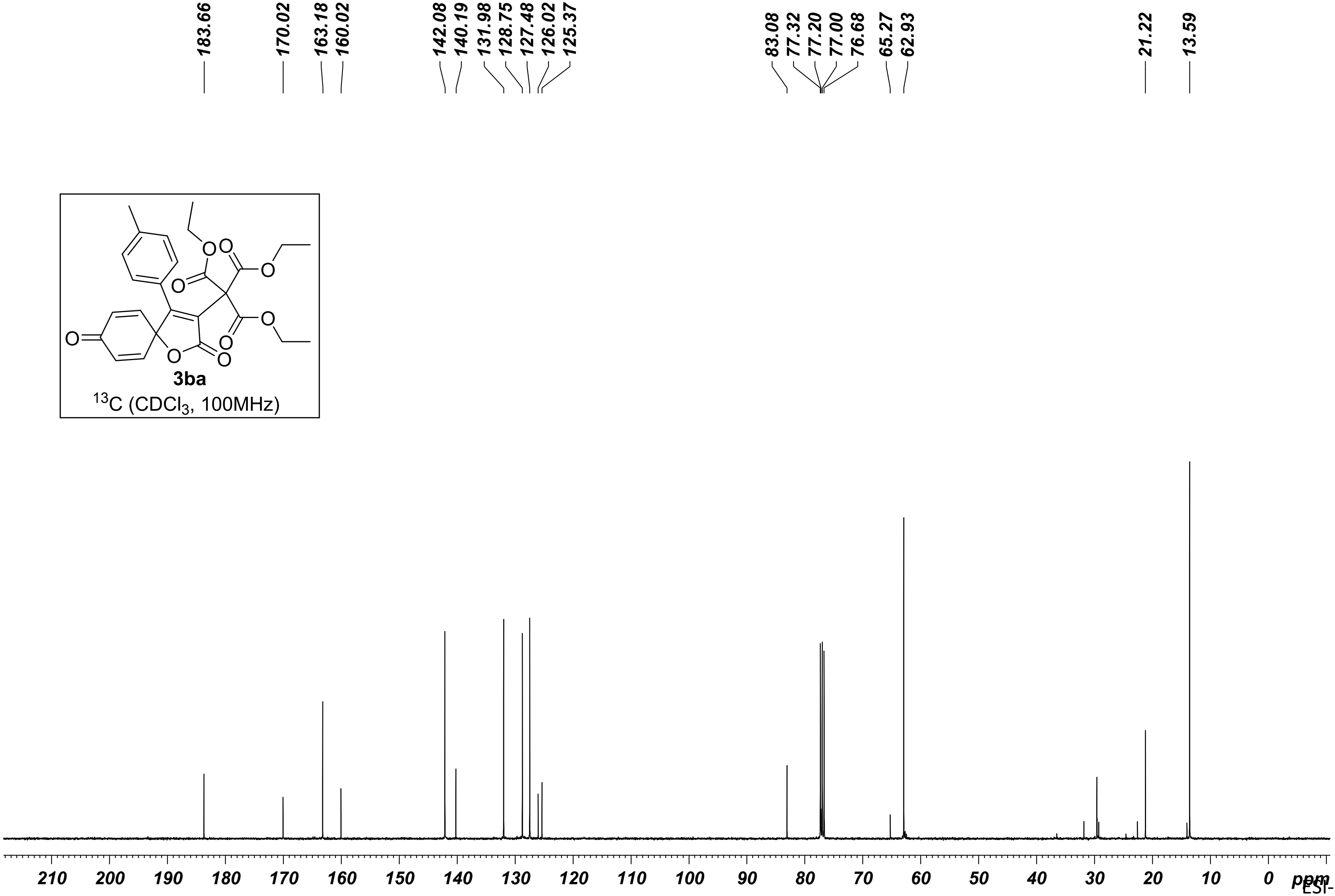
3aa

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

3ba

^1H (CDCl$_3$, 400MHz)



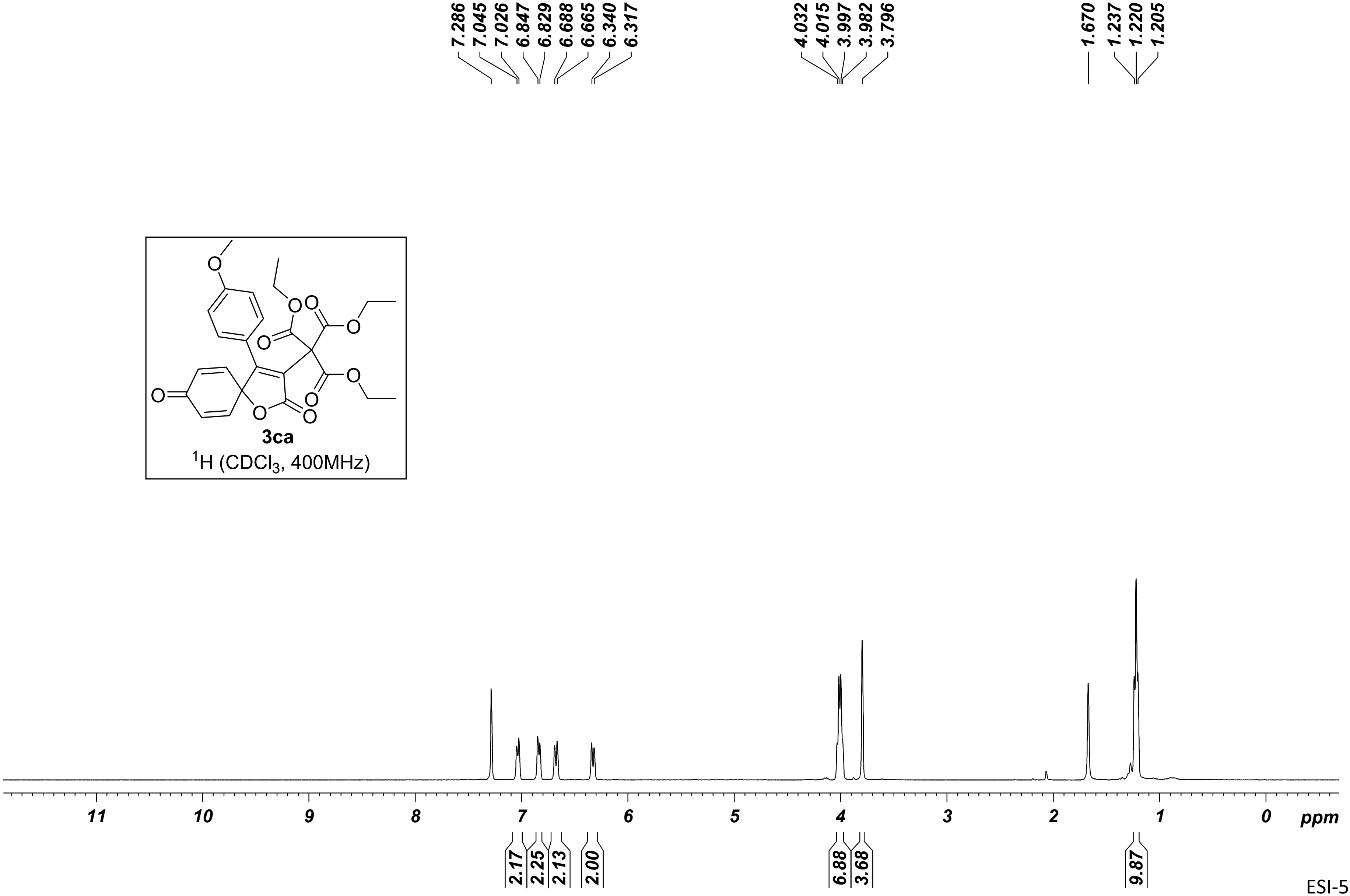


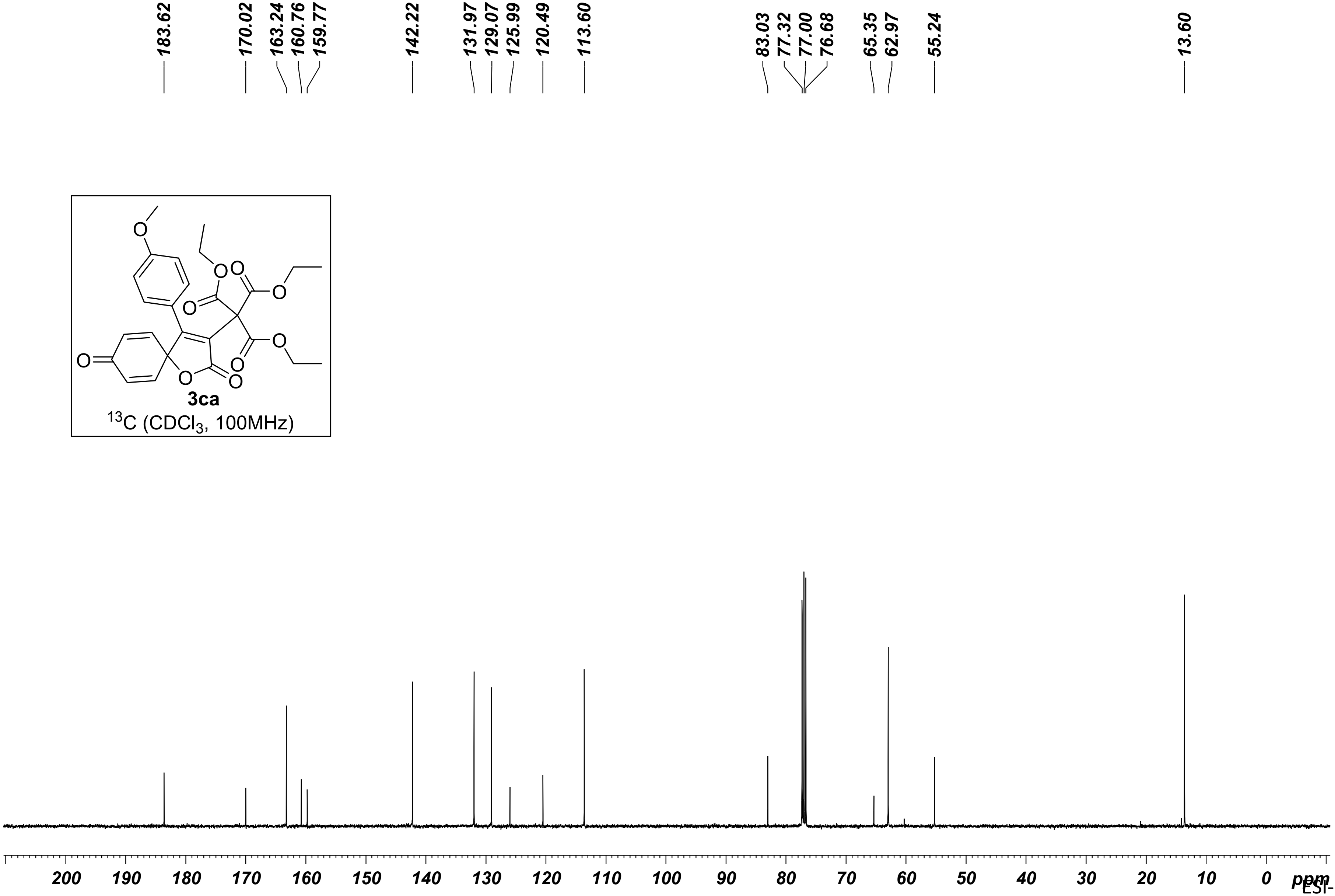
3ba

^{13}C (CDCl$_3$, 100MHz)

3ca

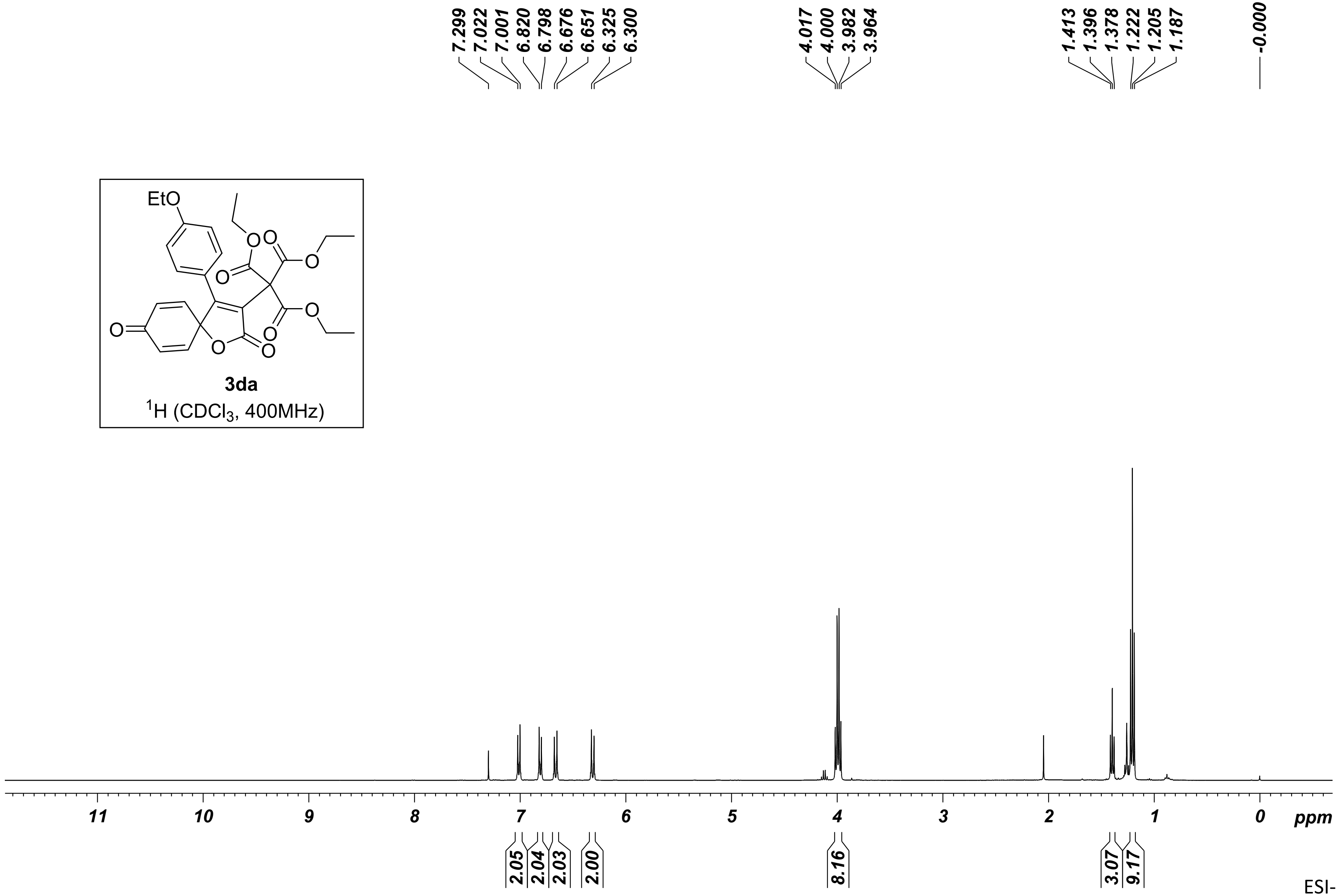
^{1}H (CDCl$_3$, 400MHz)





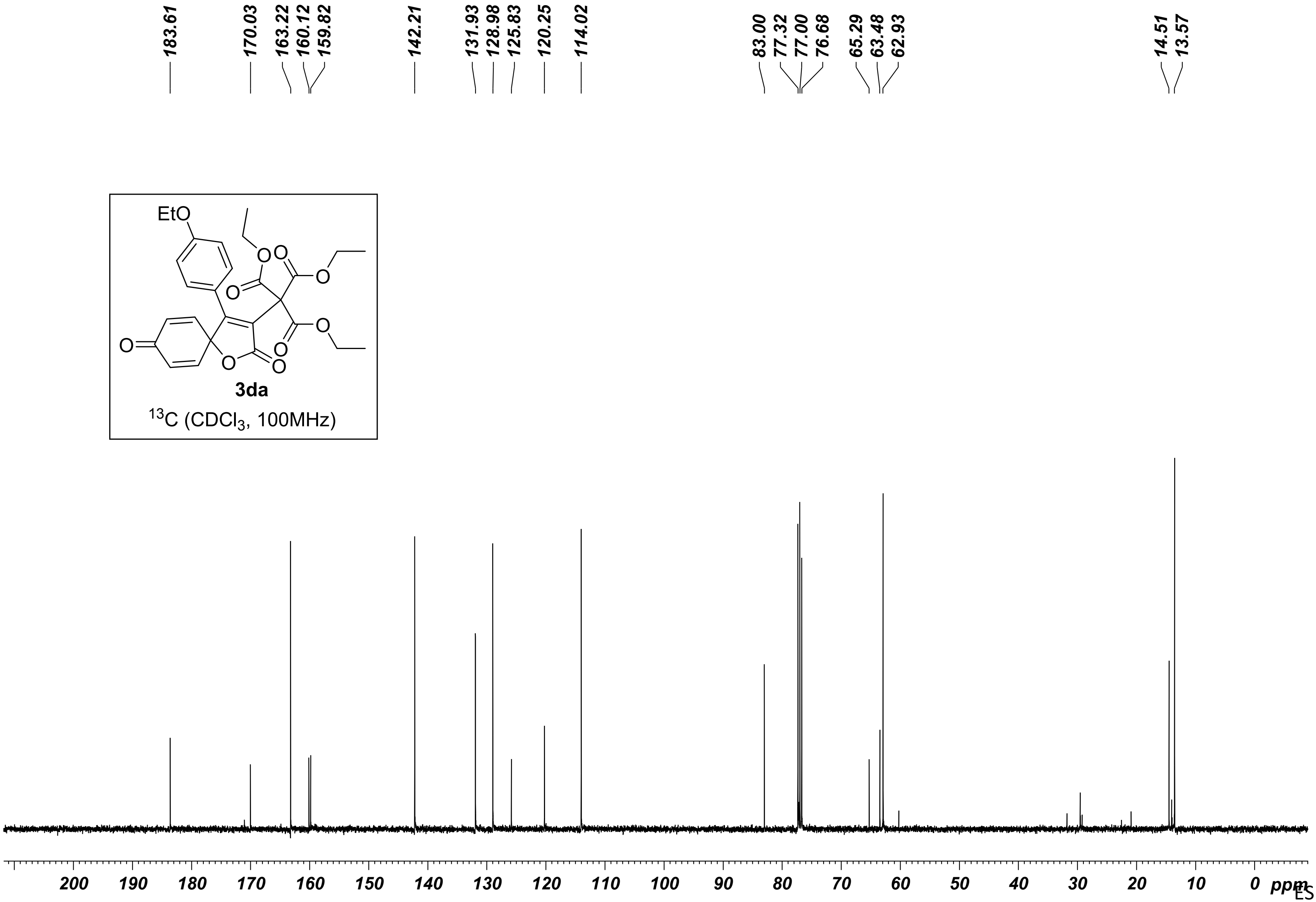
3ca

^{13}C (CDCl$_3$, 100MHz)



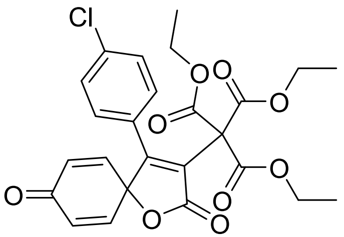
3da

^1H (CDCl$_3$, 400MHz)



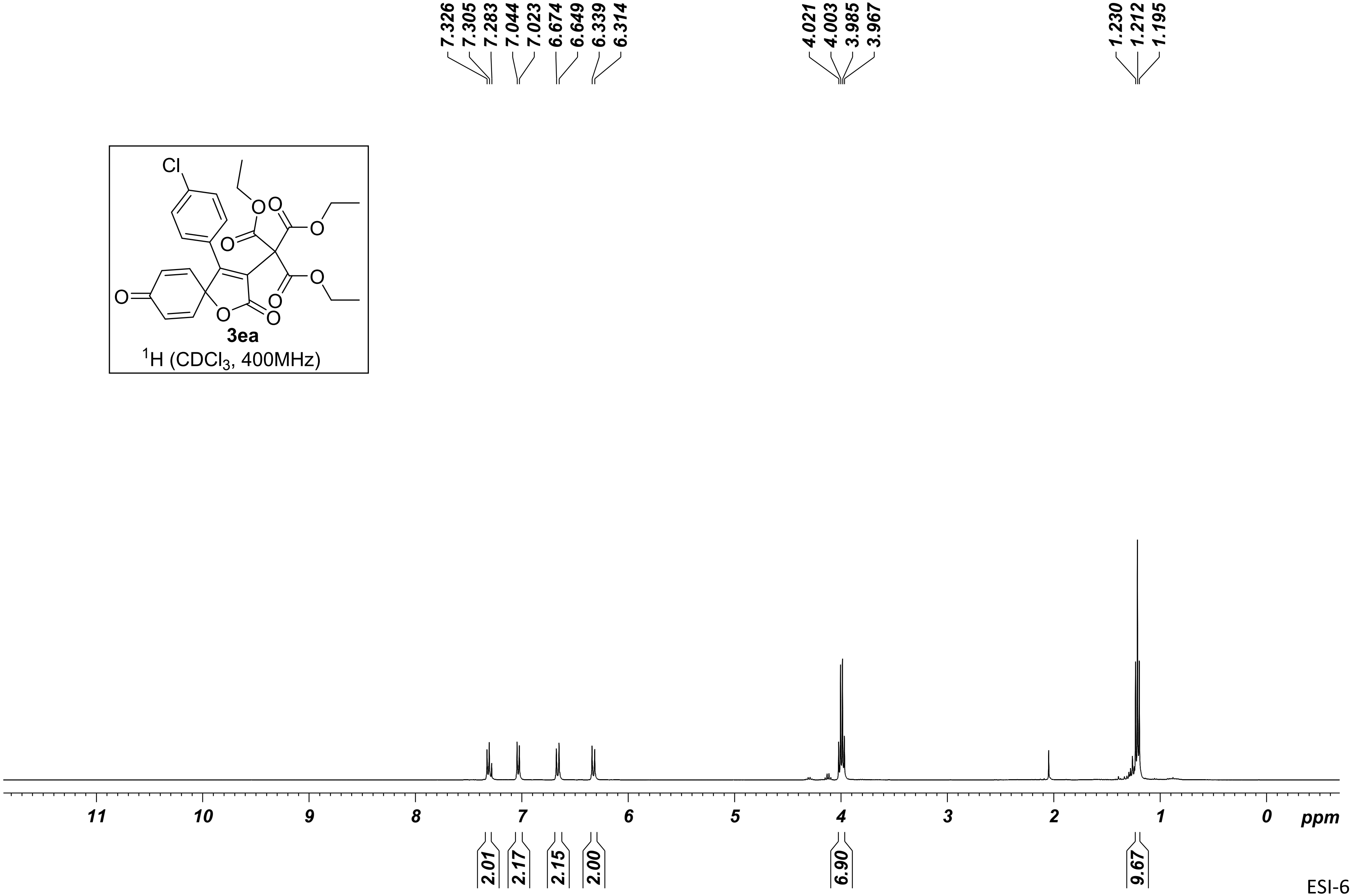
3da

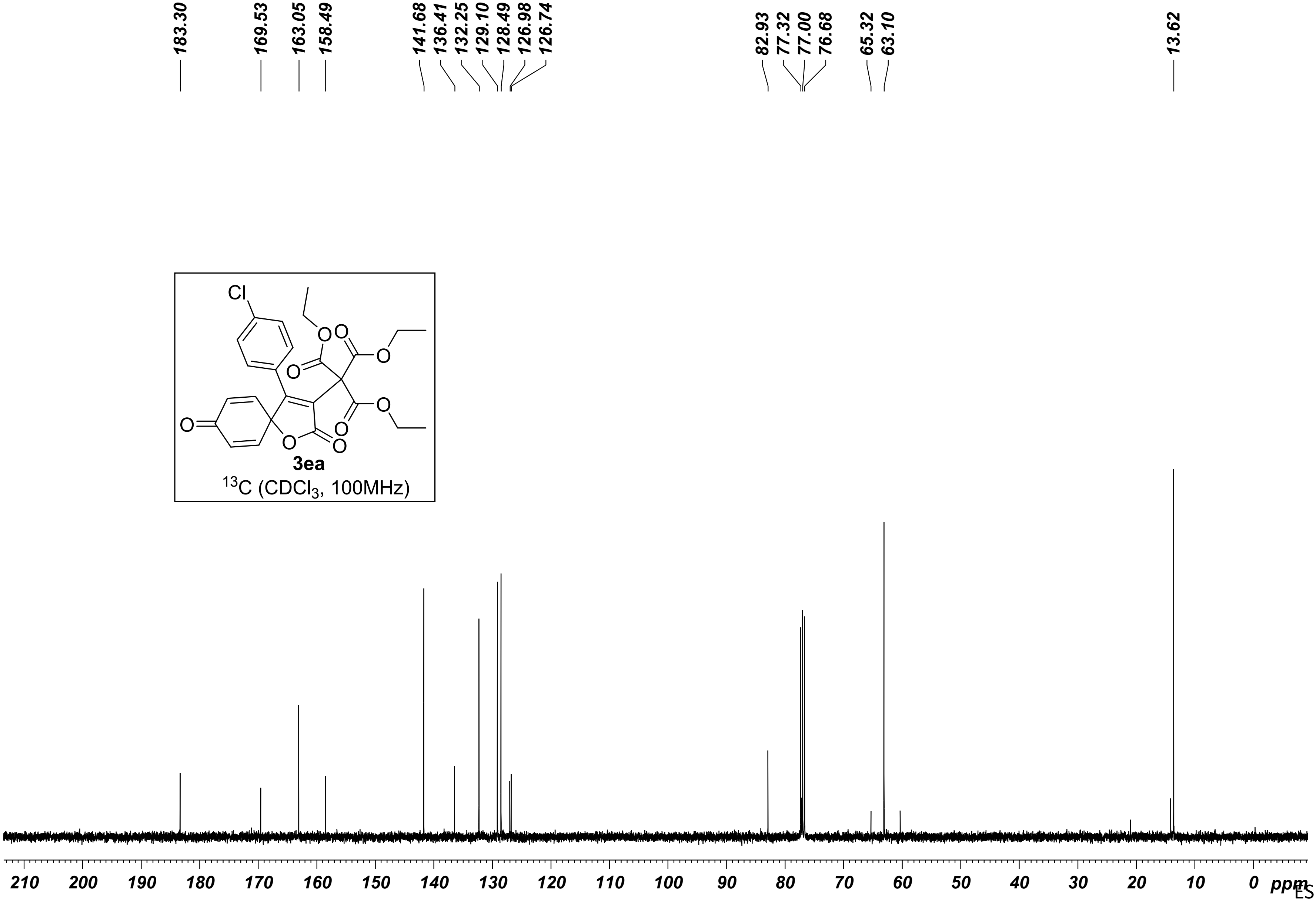
^{13}C (CDCl$_3$, 100MHz)



3ea

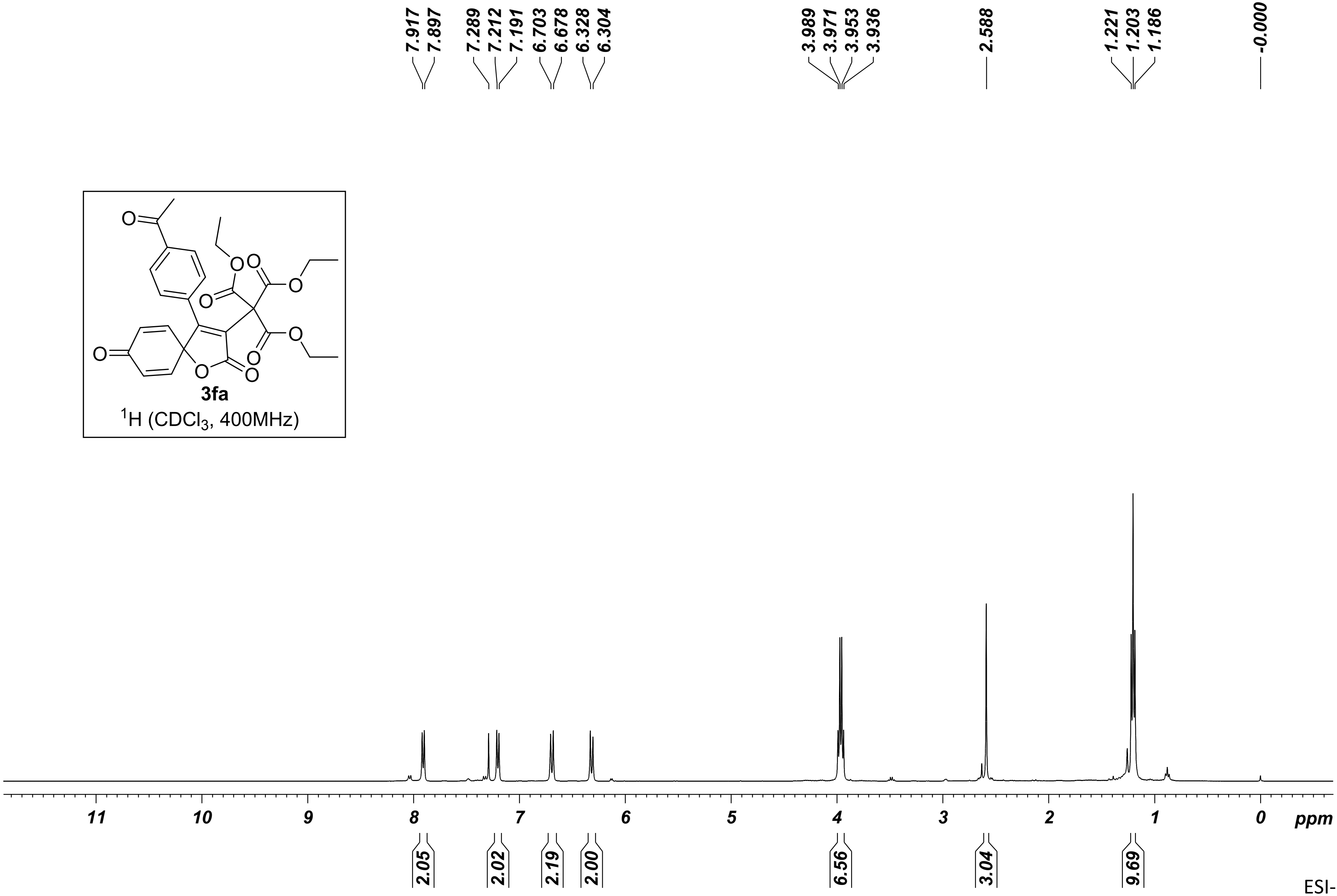
^{1}H (CDCl$_3$, 400MHz)





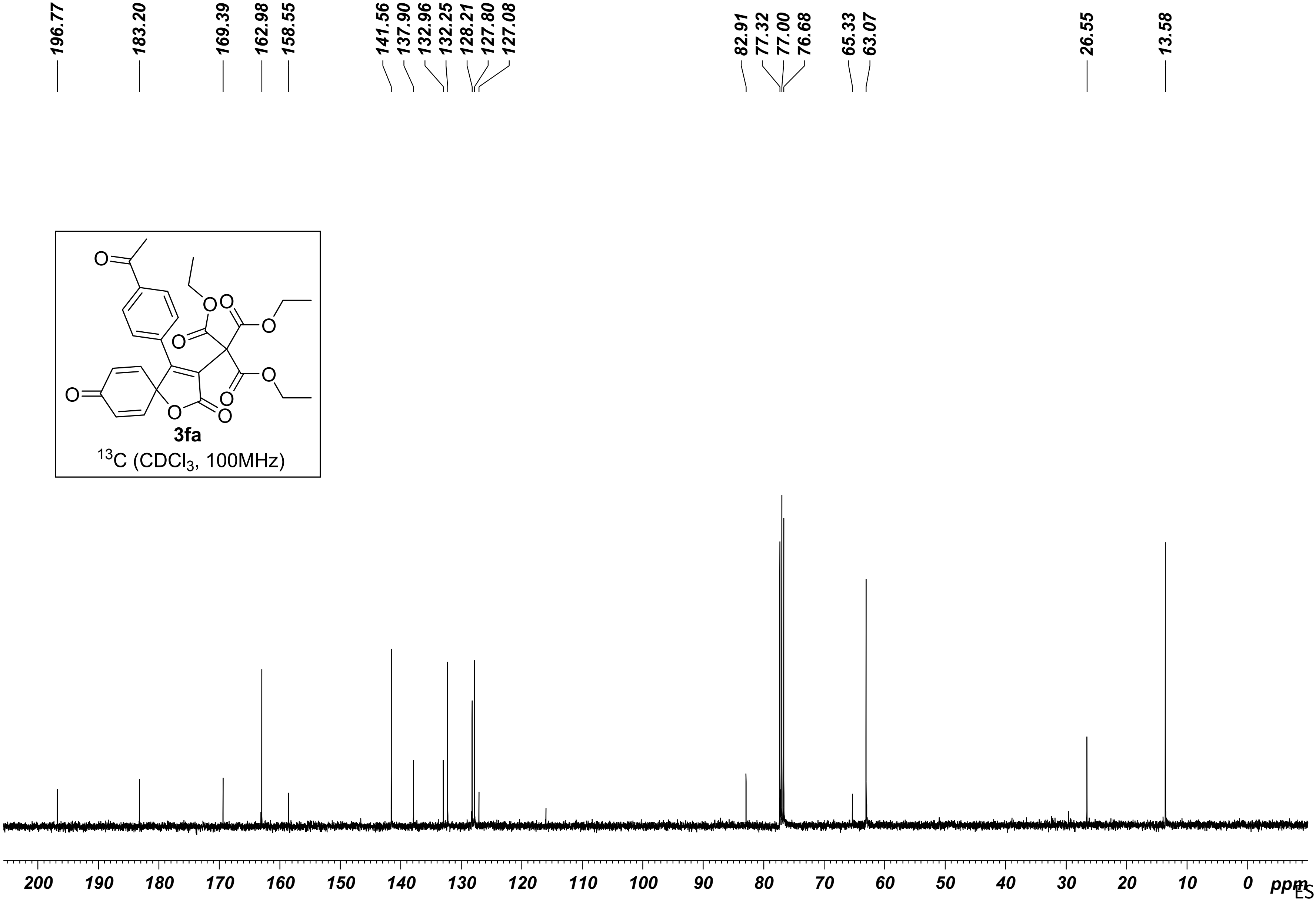
3ea

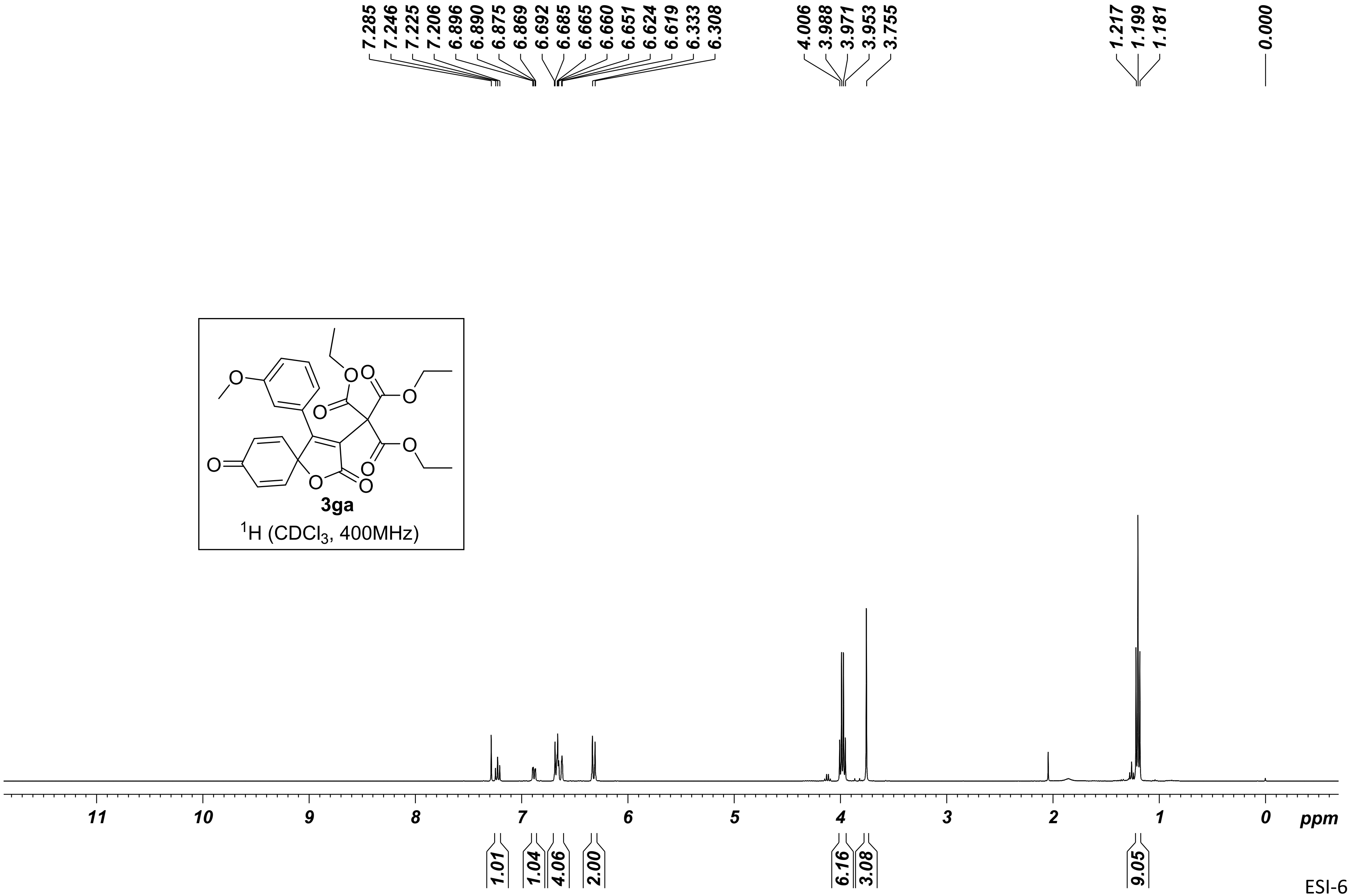
^{13}C (CDCl$_3$, 100MHz)

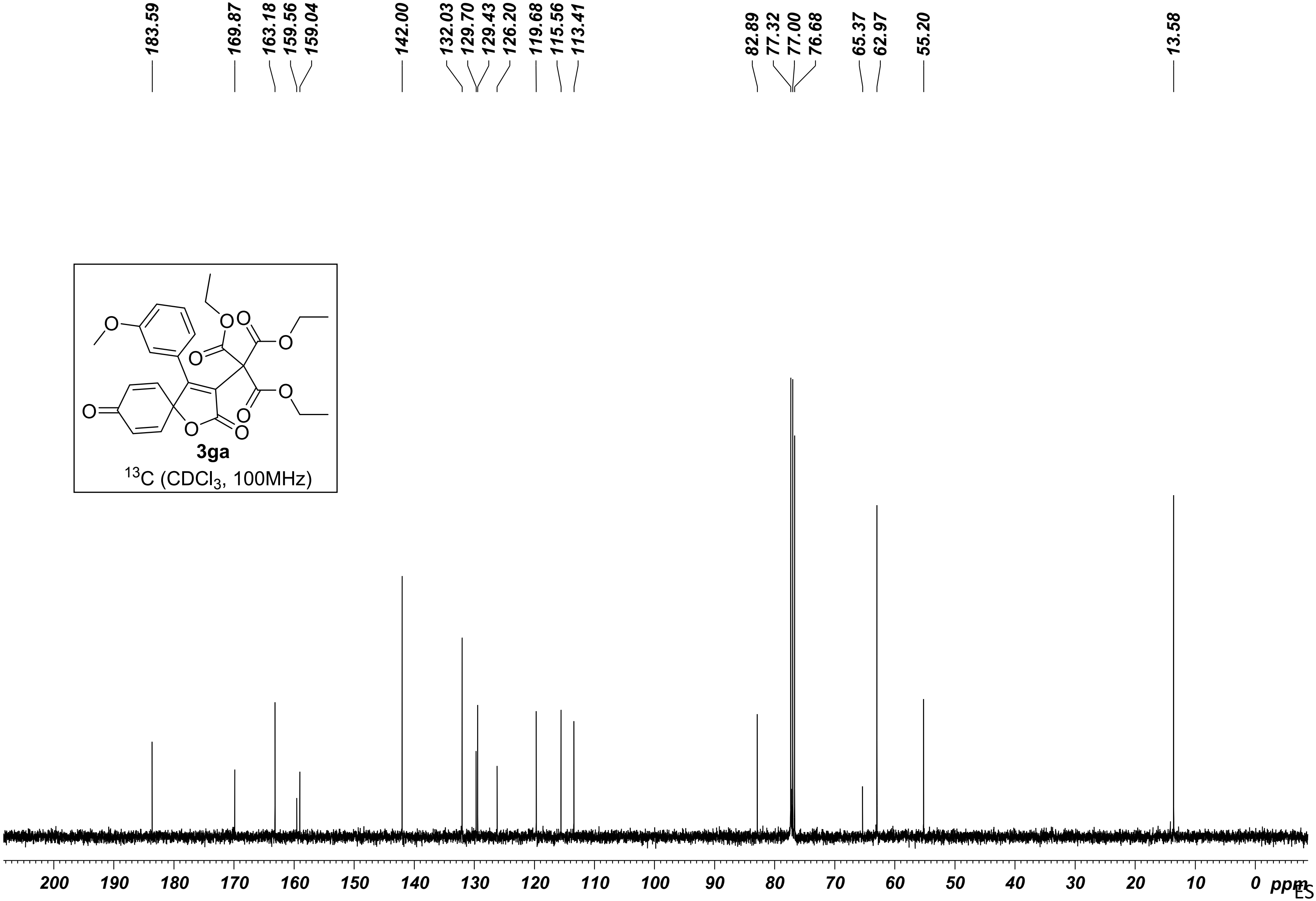


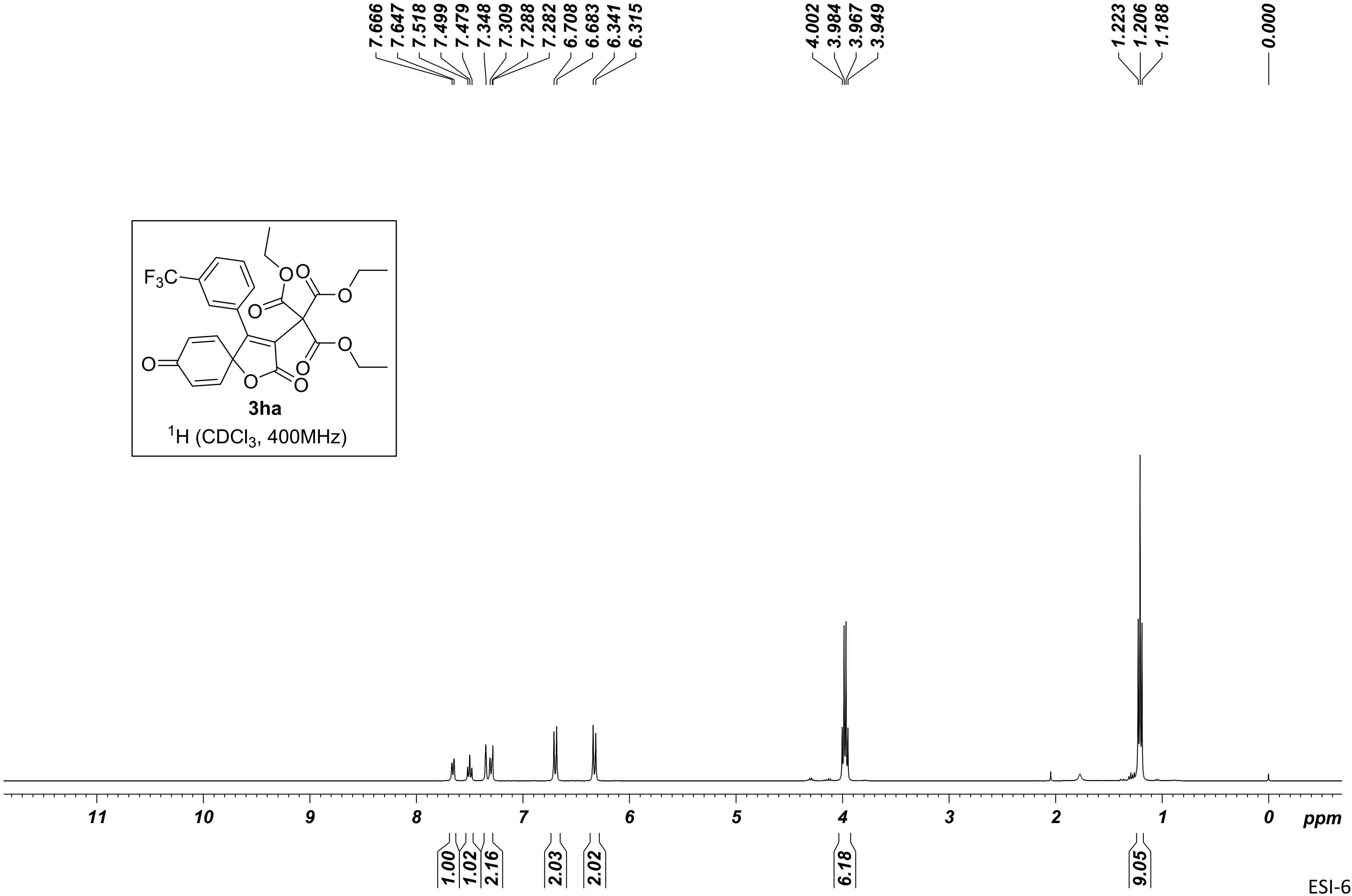
3fa

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


196.77
183.20
169.39
162.98
158.55
141.56
137.90
132.96
132.25
128.21
127.80
127.08
82.91
77.32
77.00
76.68
65.33
63.07
26.55
13.58
O
O
O
O
O
O
O
O
O
O
3fa
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.285
7.246
7.225
7.206
6.896
6.890
6.875
6.869
6.692
6.685
6.665
6.660
6.651
6.624
6.619
6.333
6.308
4.006
3.988
3.971
3.953
3.755
1.217
1.199
1.181
0.000
O
O
O
O
O
O
O
O
O
3ga
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.04
4.06
2.00
6.16
3.08
9.05


183.59
169.87
163.18
159.56
159.04
142.00
132.03
129.70
129.43
126.20
119.68
115.56
113.41
82.89
77.32
77.00
76.68
65.37
62.97
55.20
13.58
O
O
O
O
O
O
O
O
O
O
3ga
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

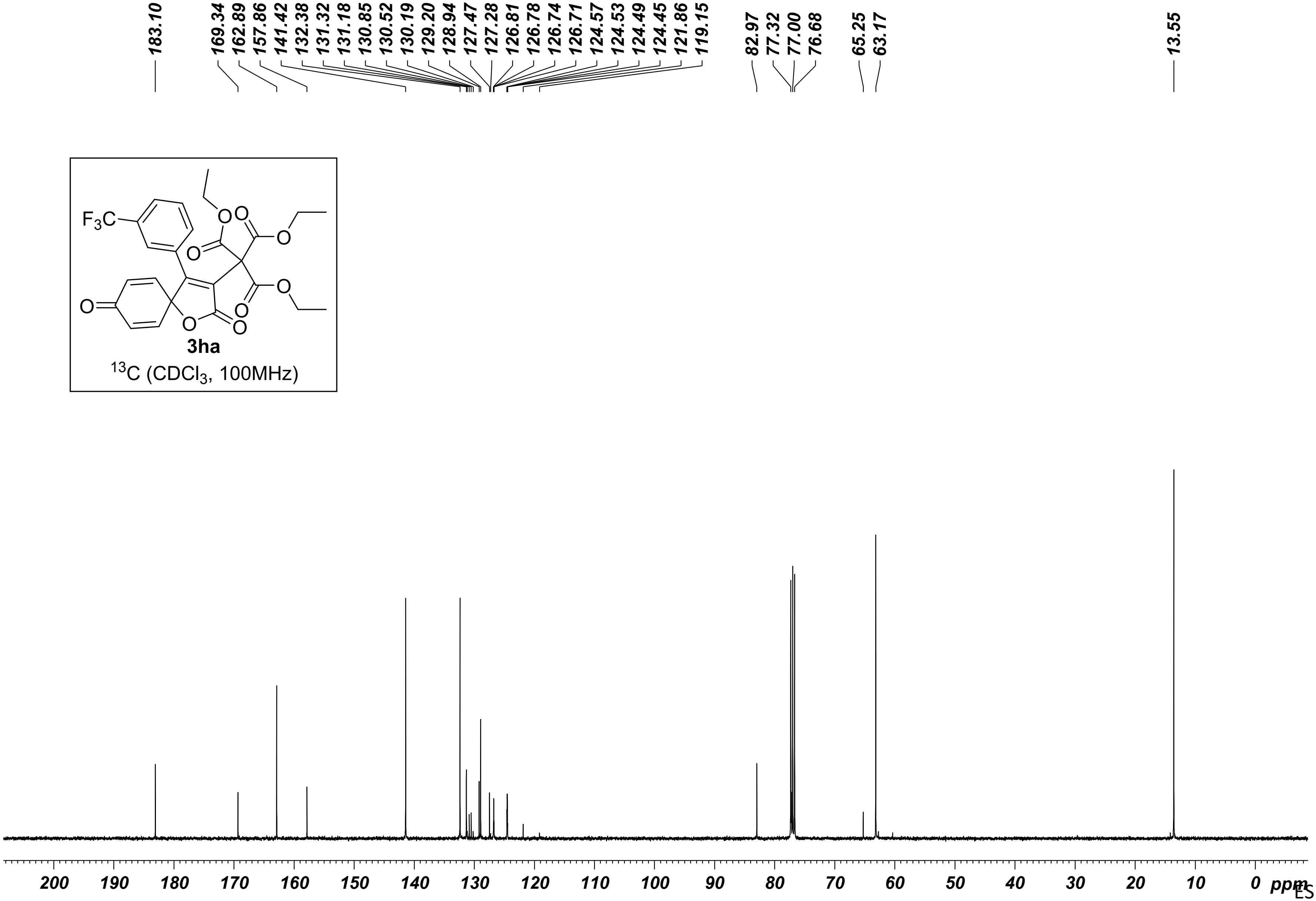


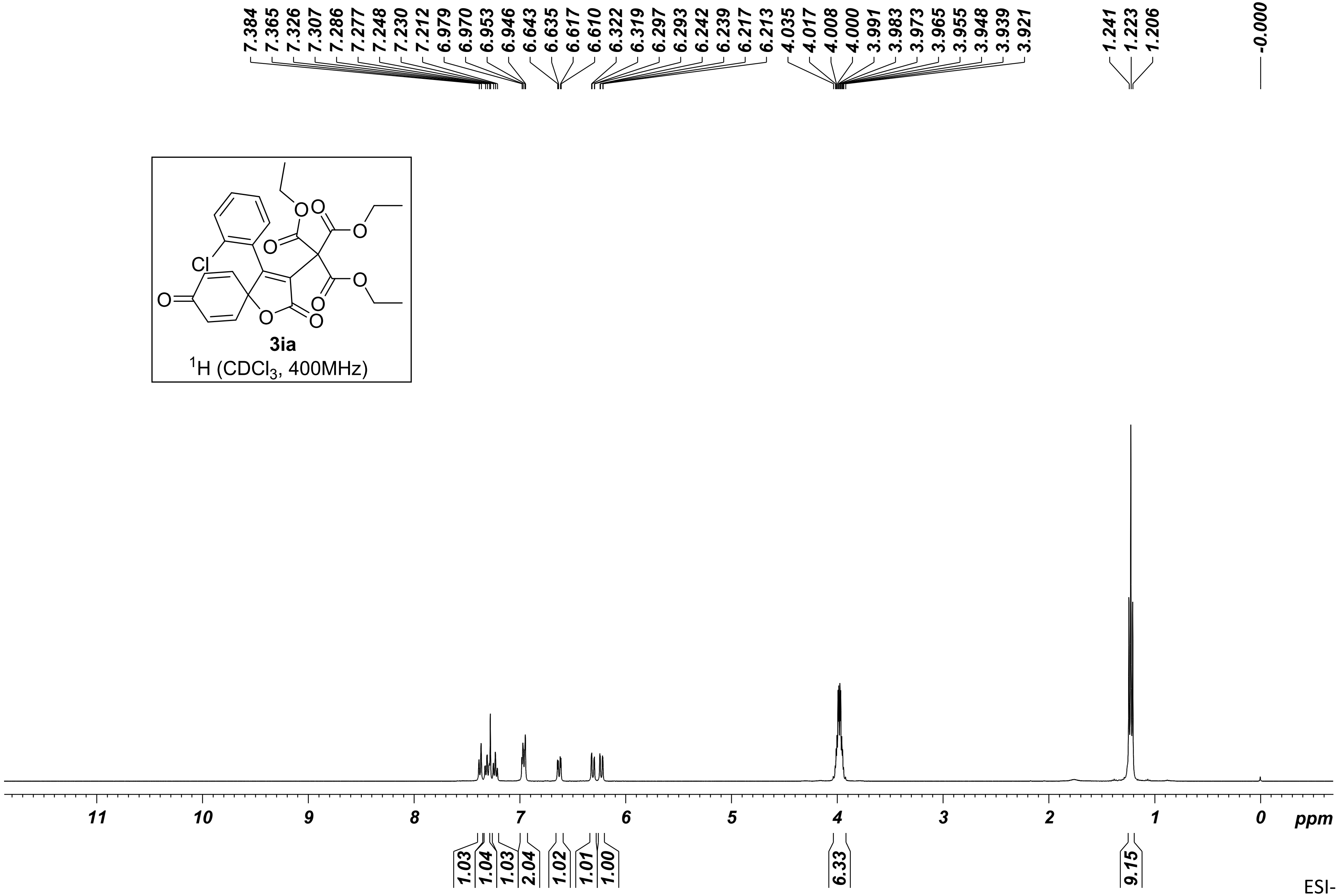
3ha

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

3ha

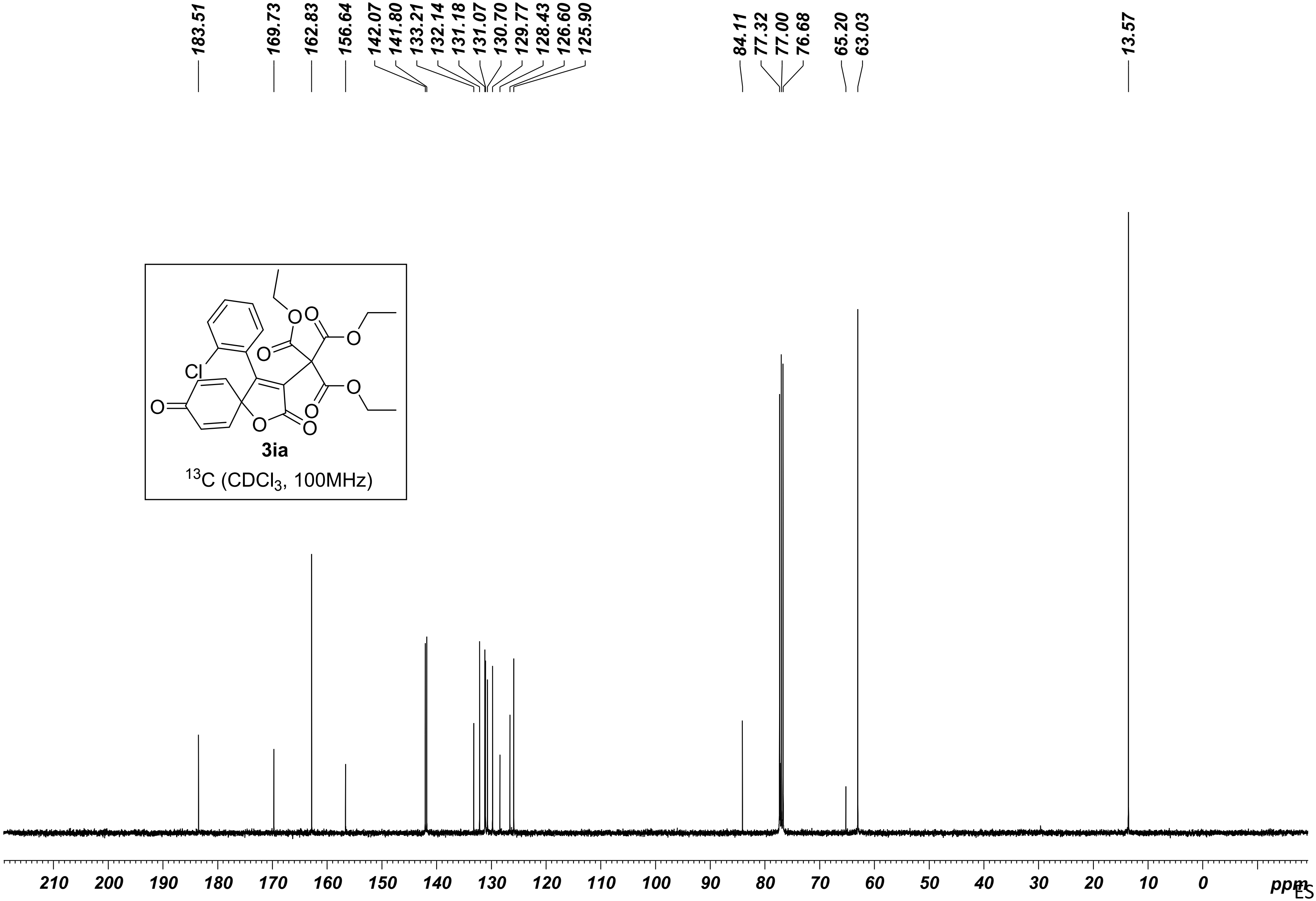
^{13}C (CDCl$_3$, 100MHz)

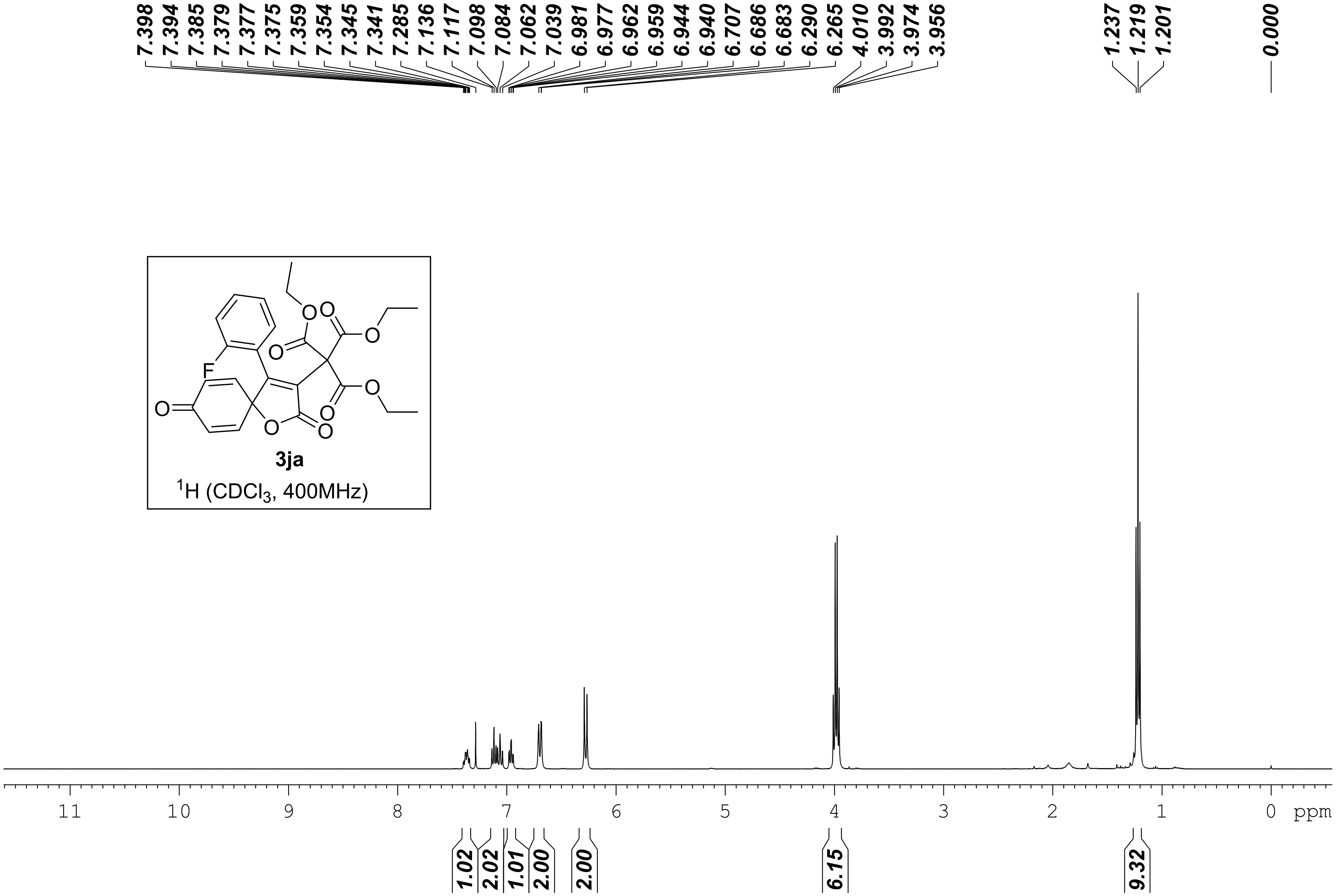




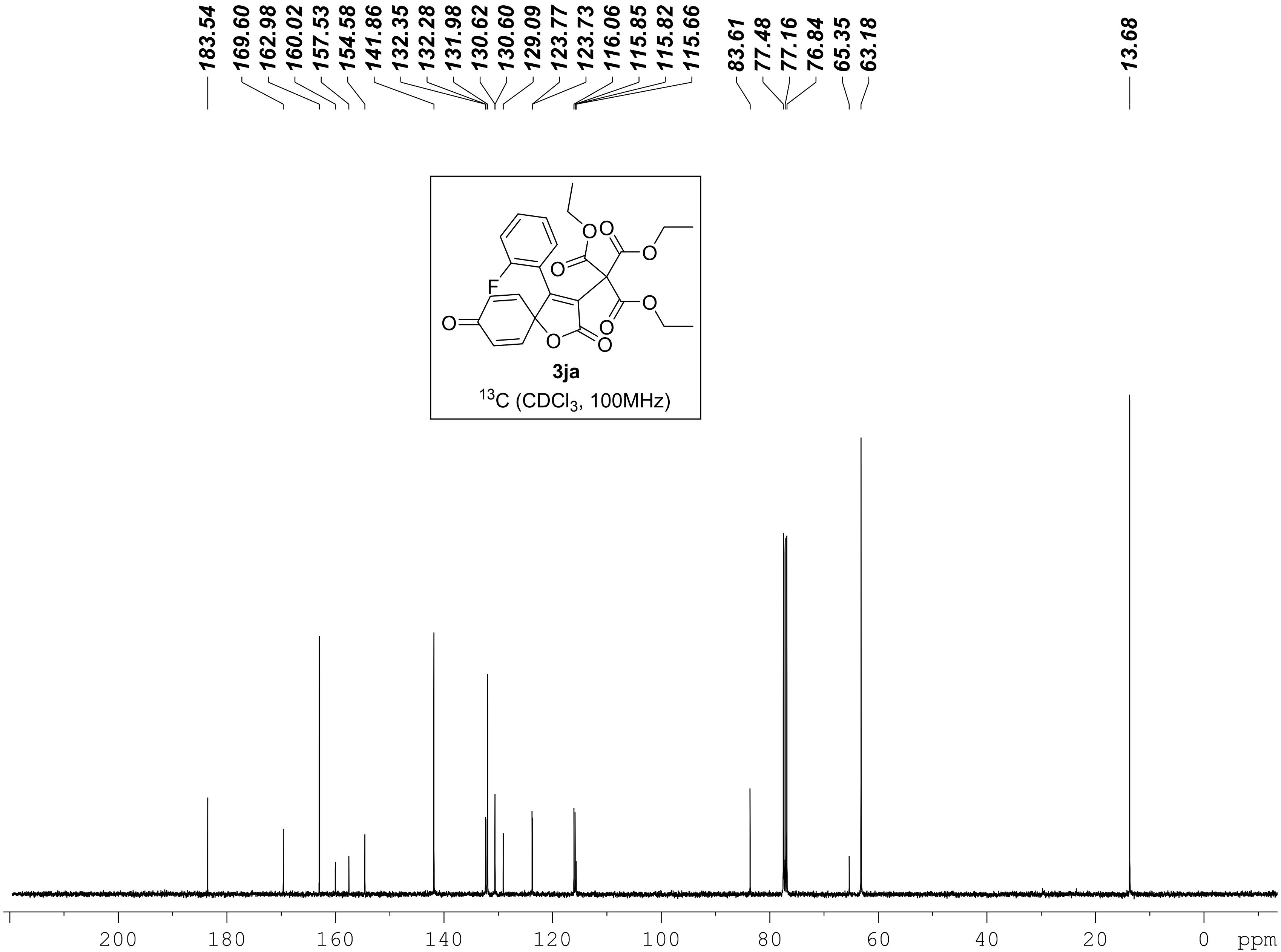
3ia

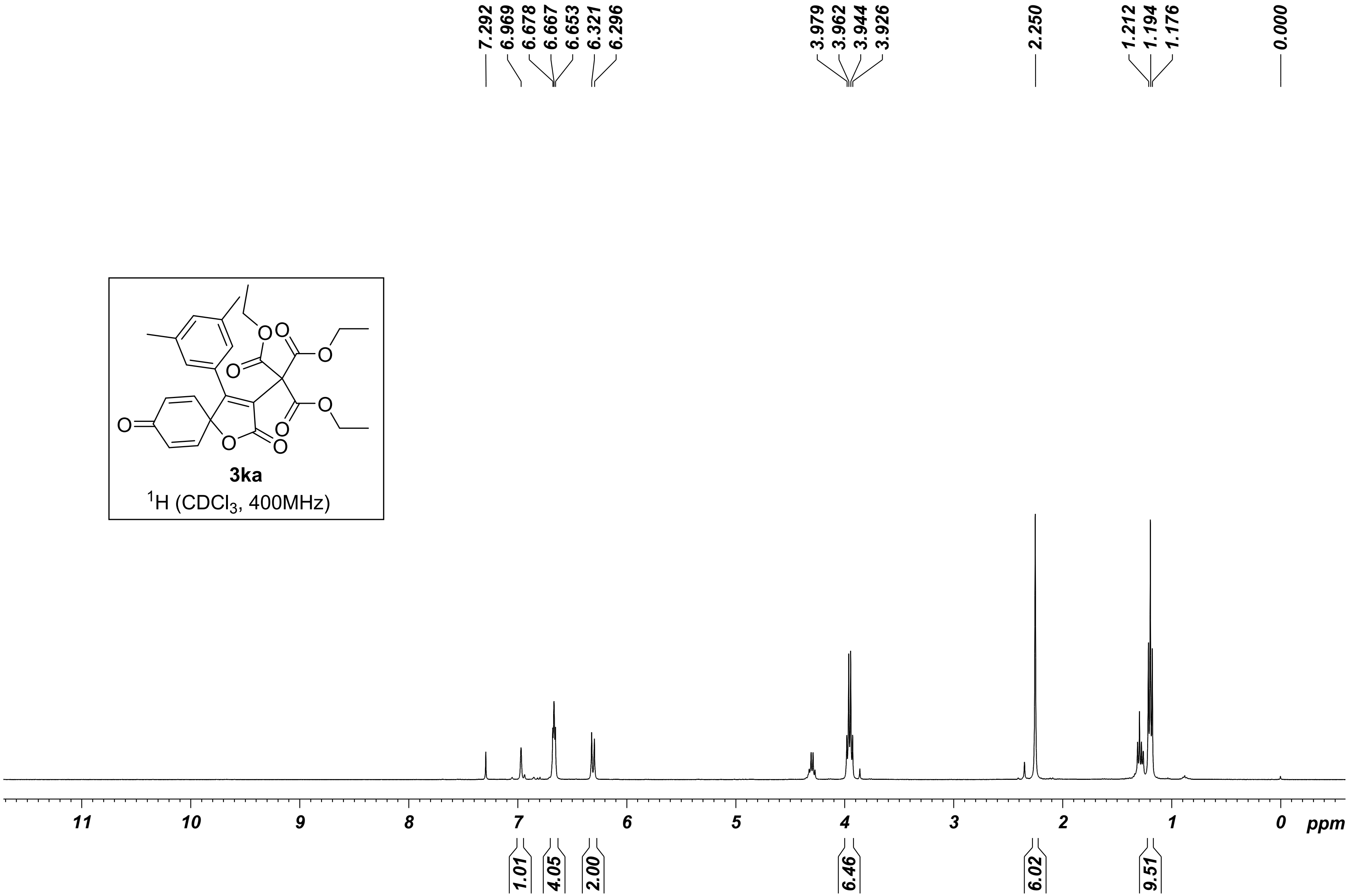
^{1}H (CDCl$_3$, 400MHz)

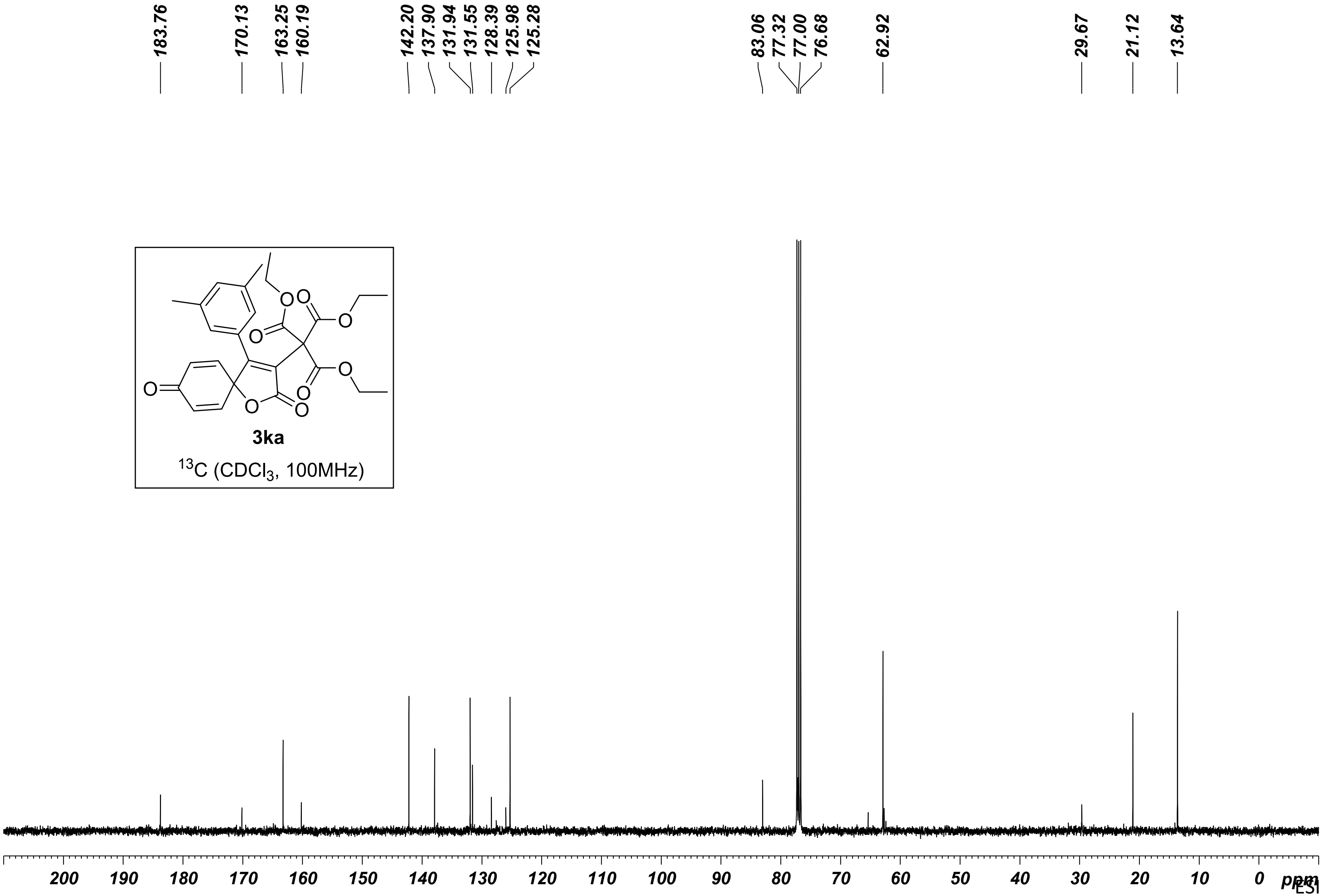

183.51
169.73
162.83
156.64
142.07
141.80
133.21
132.14
131.18
131.07
130.70
129.77
128.43
126.60
125.90
84.11
77.32
77.00
76.68
65.20
63.03
13.57
Cl
O
3ia
^{13}C (CDCl$_3$, 100MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

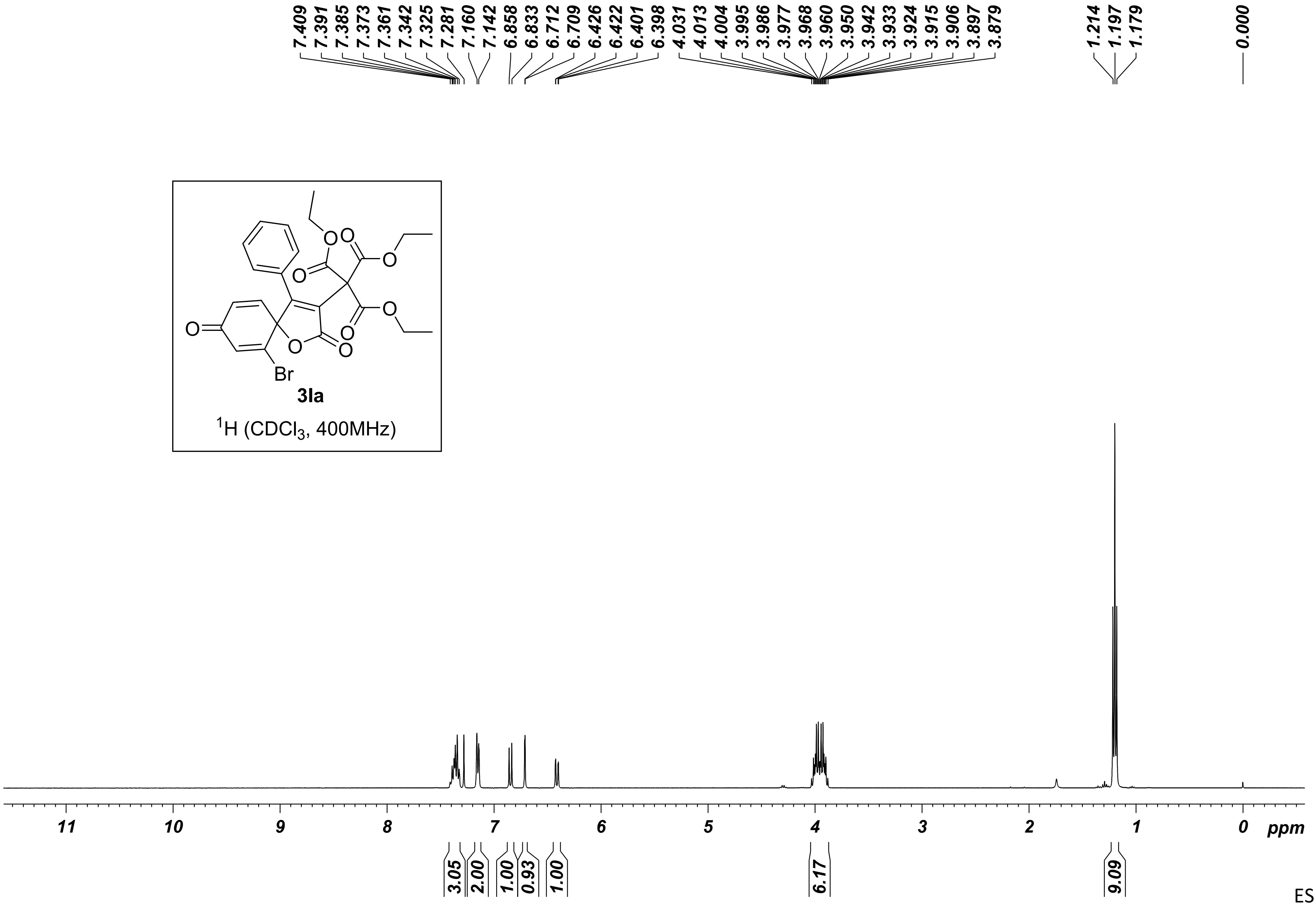

3ja

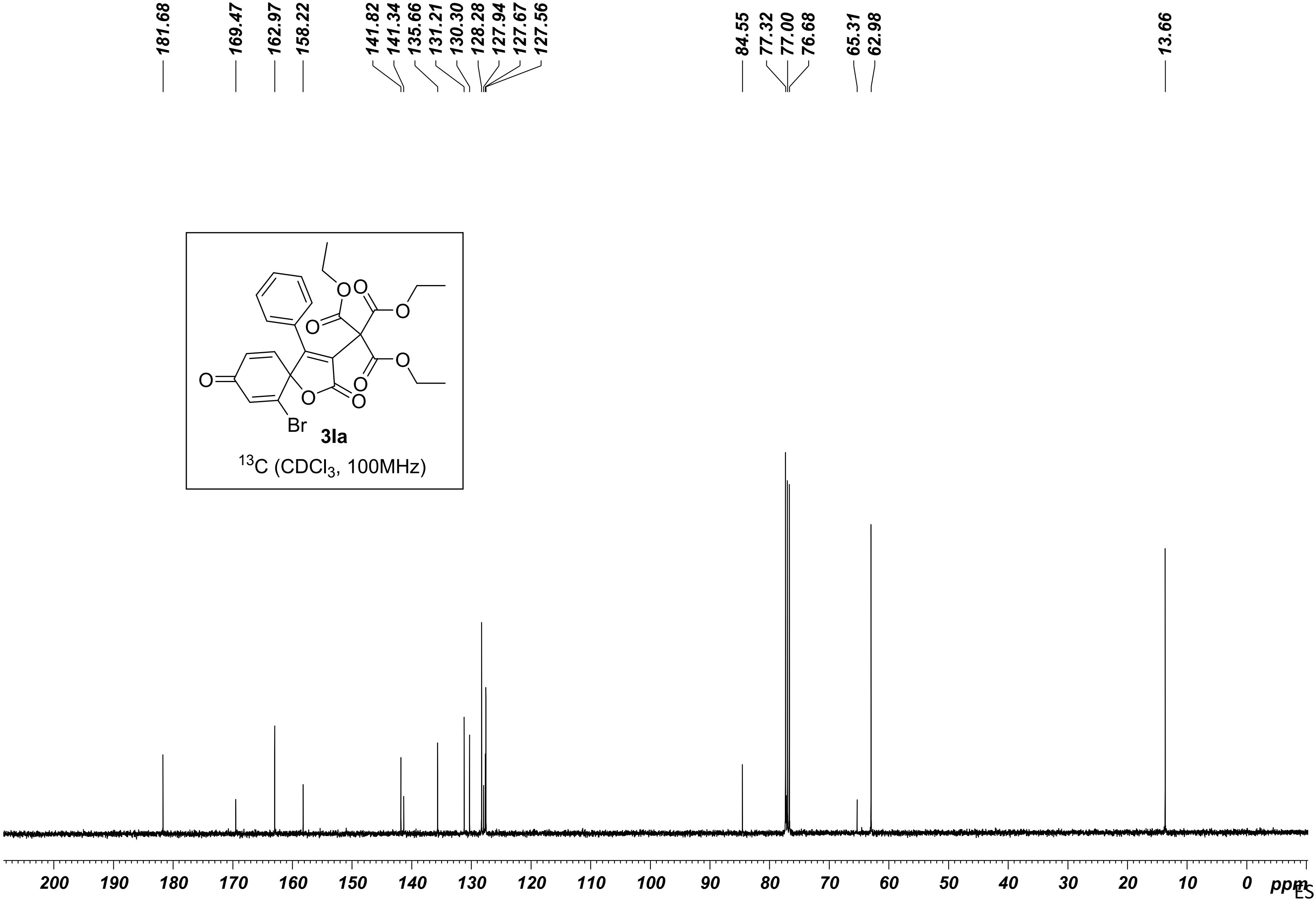
^{1}H (CDCl$_3$, 400MHz)


183.54
169.60
162.98
160.02
157.53
154.58
141.86
132.35
132.28
131.98
130.62
130.60
129.09
123.77
123.73
116.06
115.85
115.82
115.66
83.61
77.48
77.16
76.84
65.35
63.18
13.68
F
O
3ja
13C (CDCl3, 100MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm


7.292
6.969
6.678
6.667
6.653
6.321
6.296
3.979
3.962
3.944
3.926
2.250
1.212
1.194
1.176
0.000
3ka
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
4.05
2.00
6.46
6.02
9.51

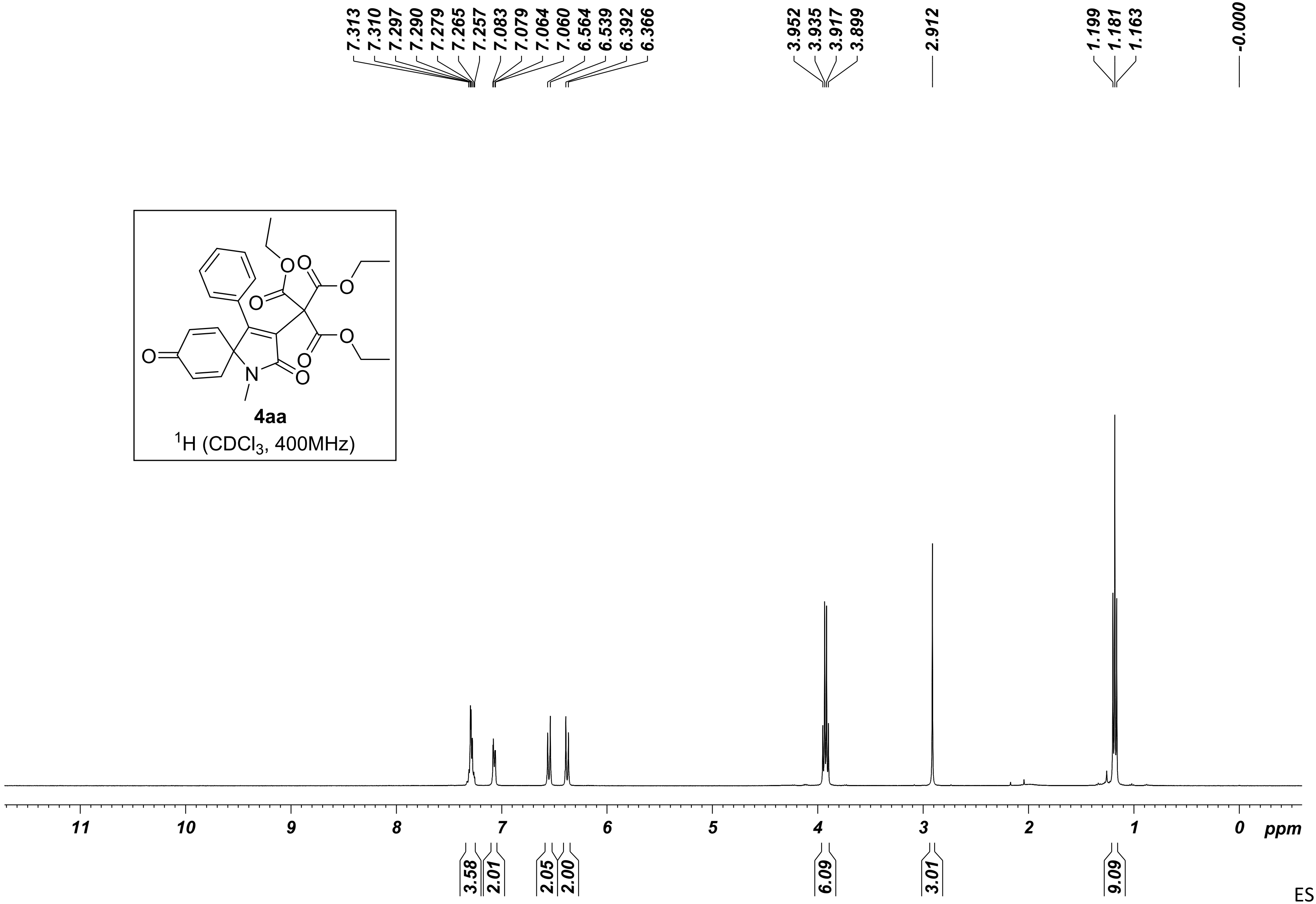

183.76
170.13
163.25
160.19
142.20
137.90
131.94
131.55
128.39
125.98
125.28
83.06
77.32
77.00
76.68
62.92
29.67
21.12
13.64
3ka
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

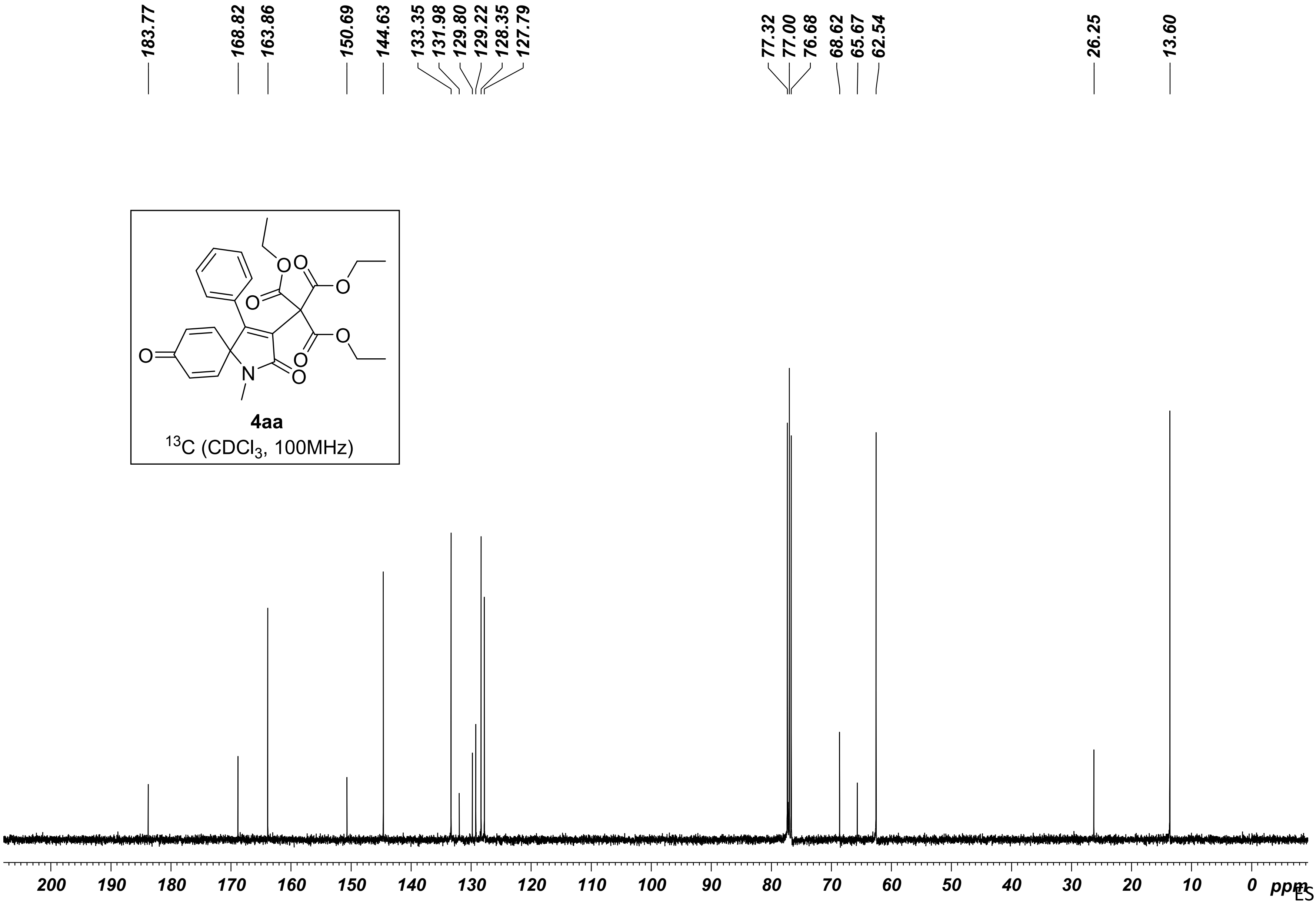

7.409
7.391
7.385
7.373
7.361
7.342
7.325
7.281
7.160
7.142
6.858
6.833
6.712
6.709
6.426
6.422
6.401
6.398
4.031
4.013
4.004
3.995
3.986
3.977
3.968
3.960
3.950
3.942
3.933
3.924
3.915
3.906
3.897
3.879
1.214
1.197
1.179
0.000
O
O
O
O
O
O
O
O
Br
3la
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.05
2.00
1.00
0.93
1.00
6.17
9.09

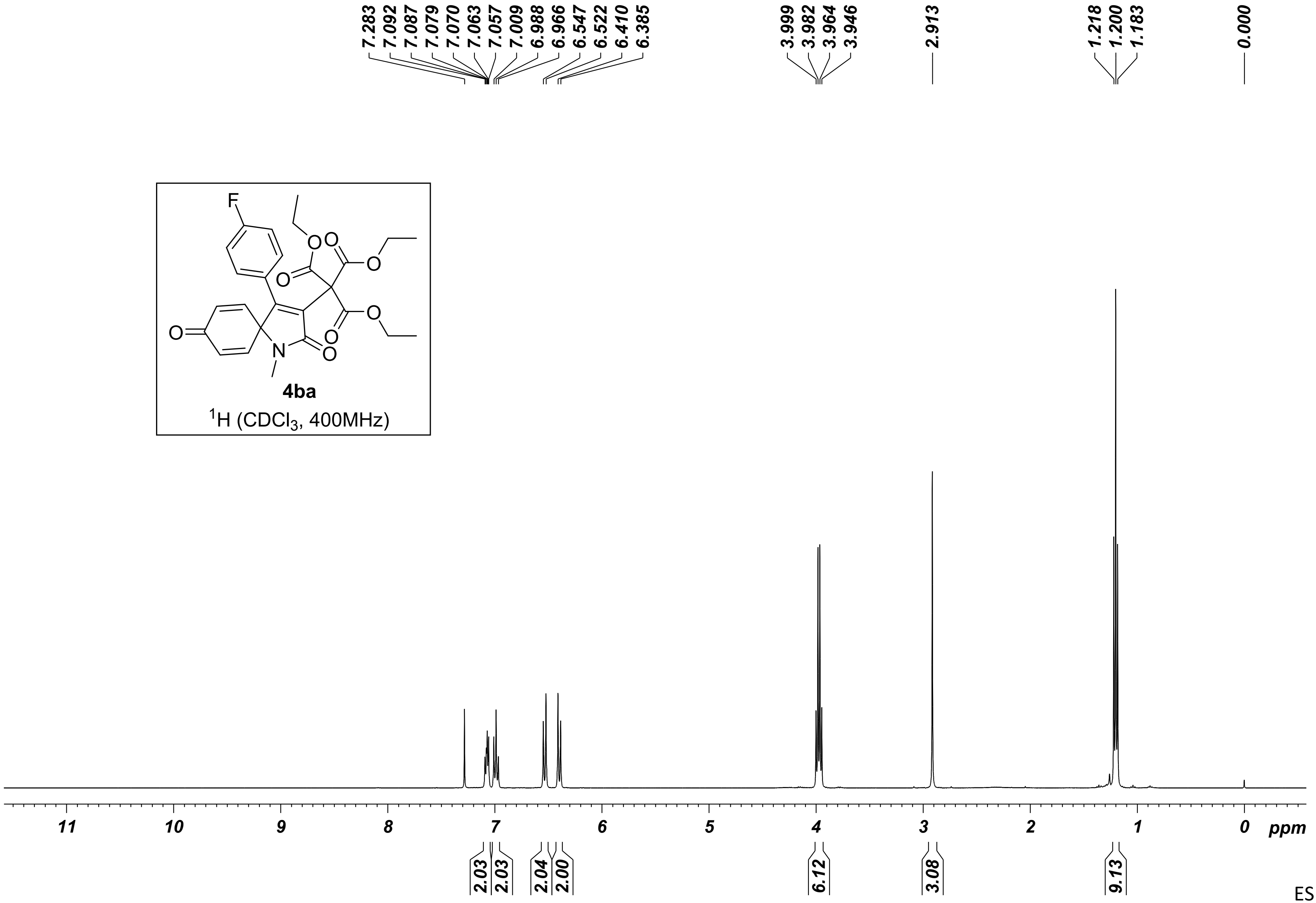


3la

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

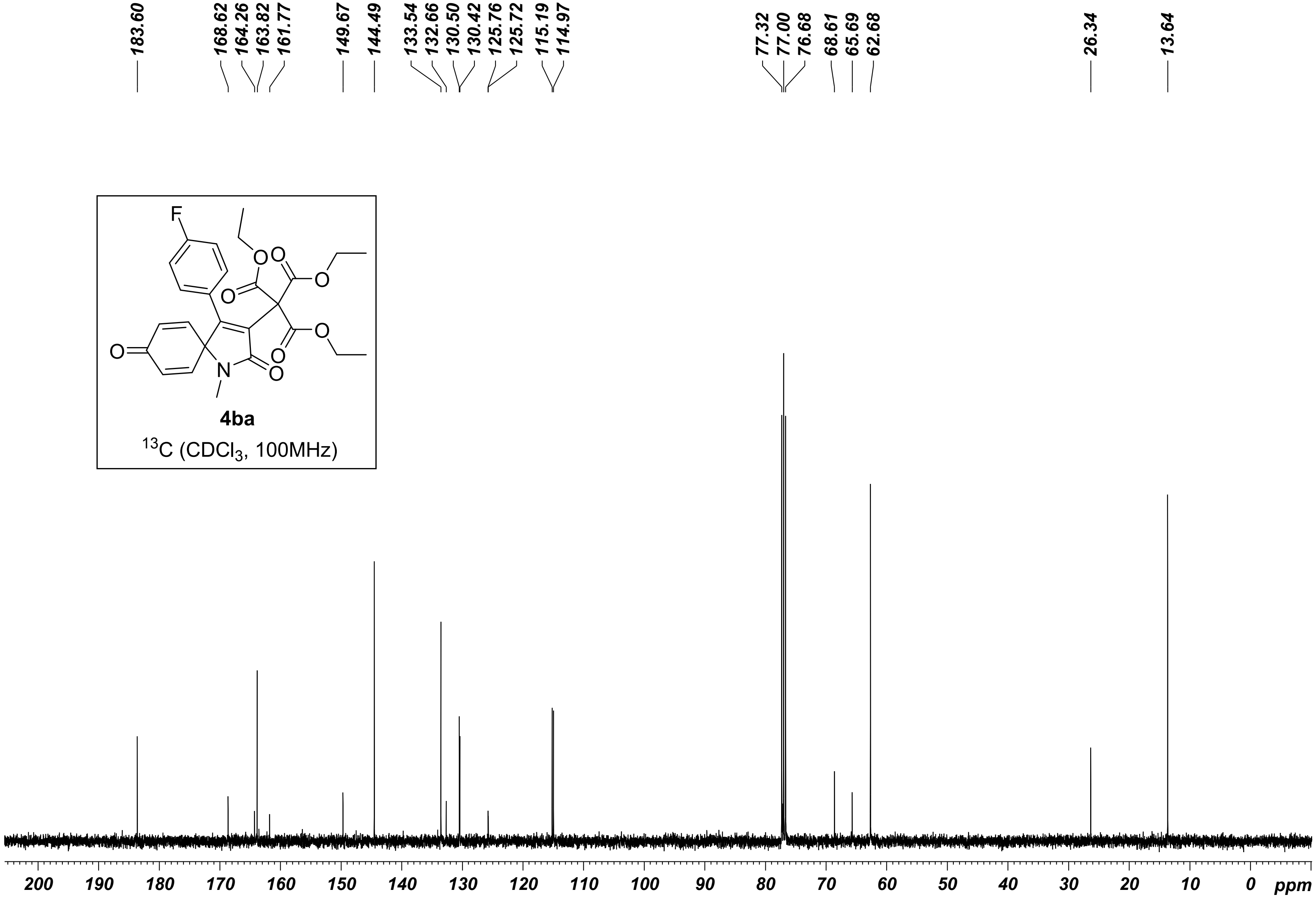

7.313
7.310
7.297
7.290
7.279
7.265
7.257
7.083
7.079
7.064
7.060
6.564
6.539
6.392
6.366
3.952
3.935
3.917
3.899
2.912
1.199
1.181
1.163
-0.000
O
O
O
O
O
O
N
O
4aa
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.58
2.01
2.05
2.00
6.09
3.01
9.09

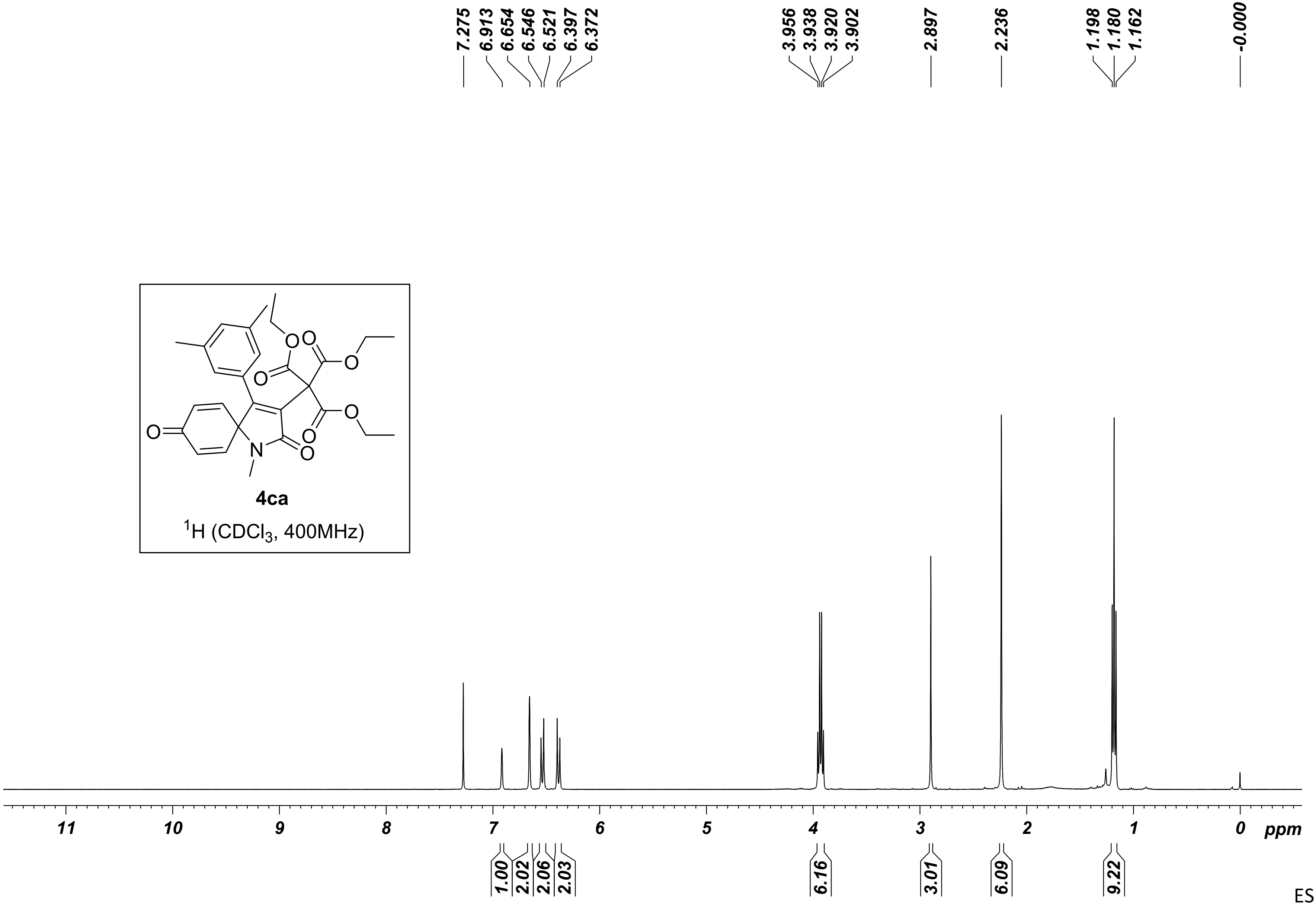

183.77
168.82
163.86
150.69
144.63
133.35
131.98
129.80
129.22
128.35
127.79
77.32
77.00
76.68
68.62
65.67
62.54
26.25
13.60
4aa
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



4ba

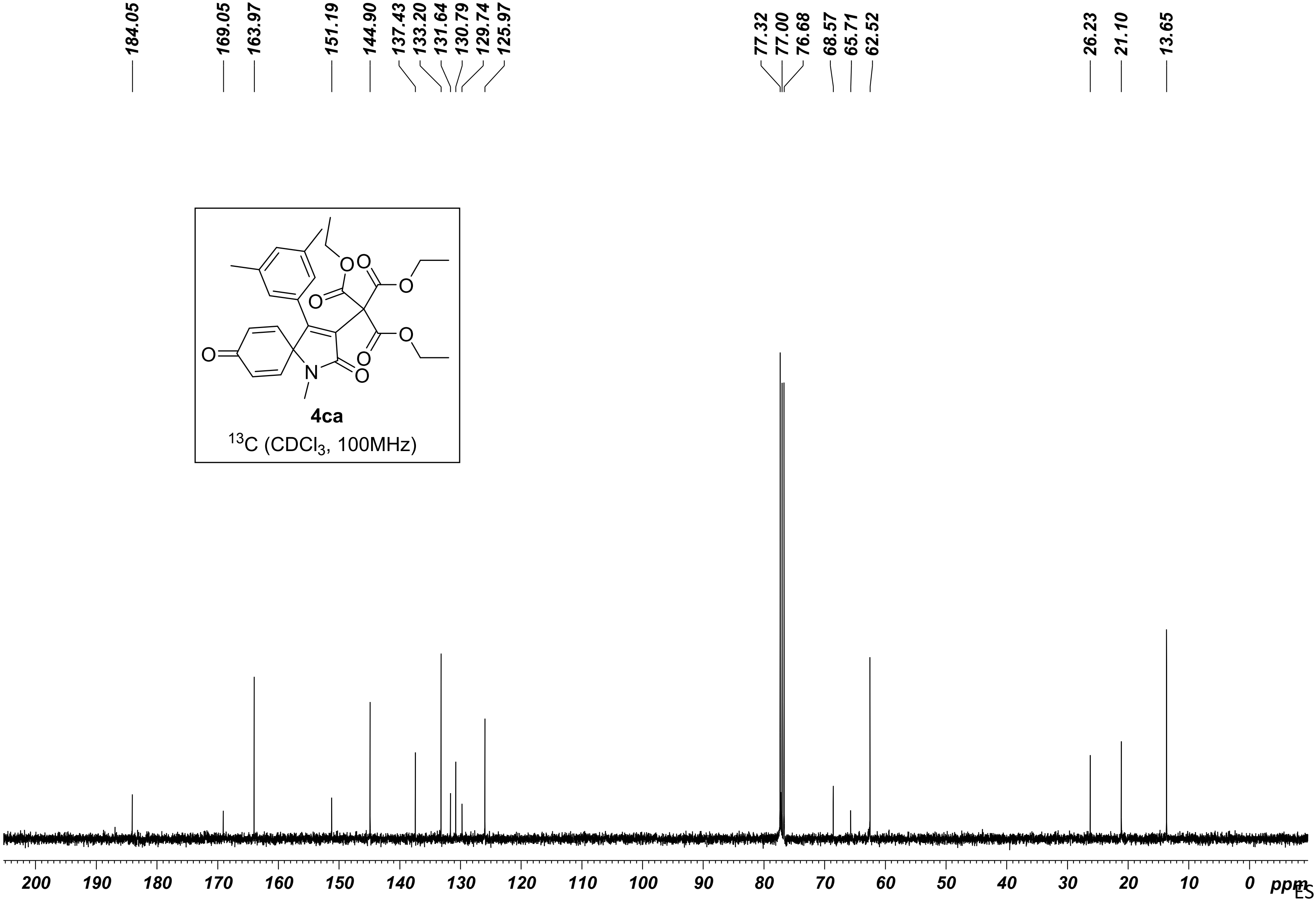
^1H ($CDCl_3$, 400MHz)

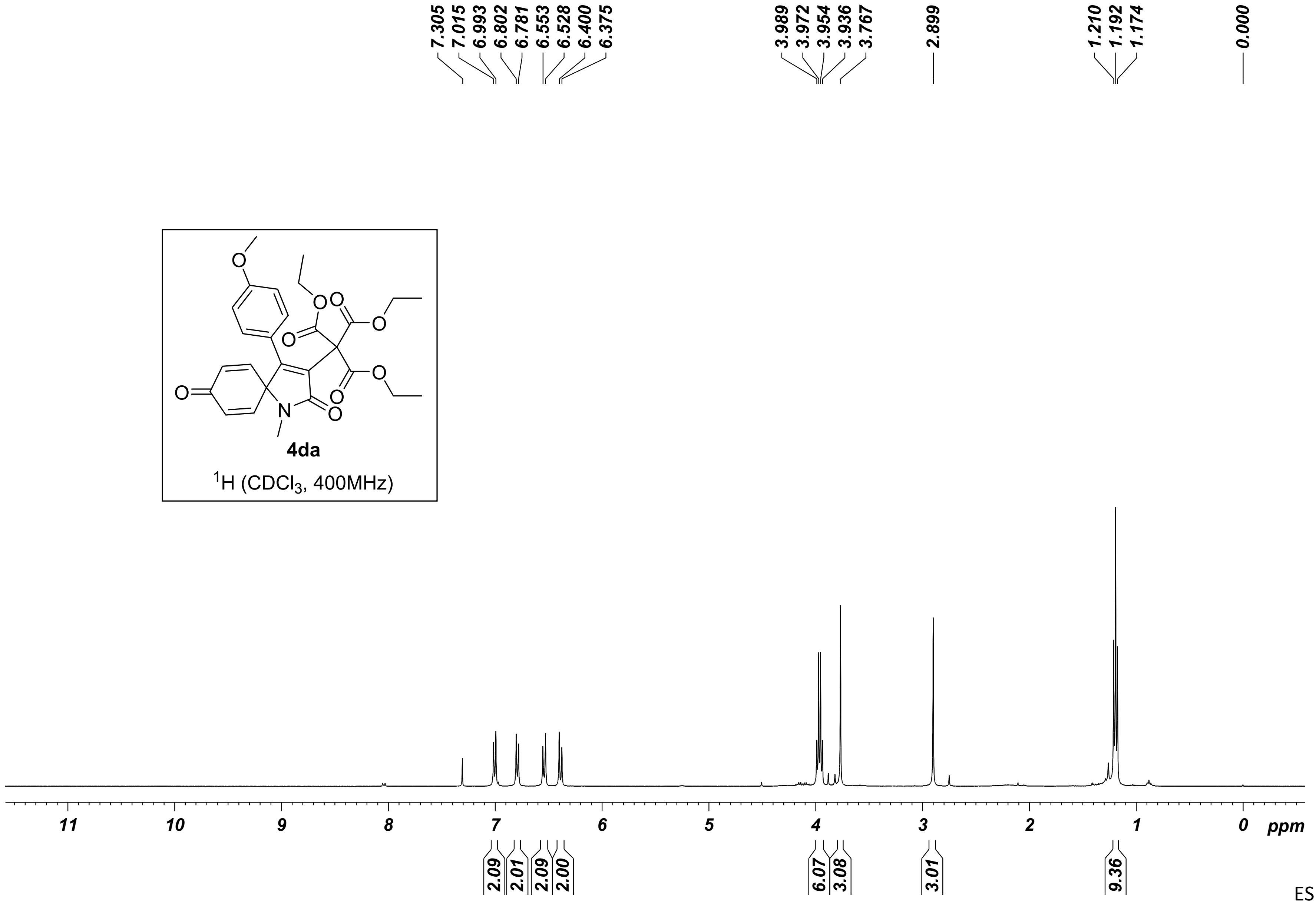

183.60
168.62
164.26
163.82
161.77
149.67
144.49
133.54
132.66
130.50
130.42
125.76
125.72
115.19
114.97
77.32
77.00
76.68
68.61
65.69
62.68
26.34
13.64
F
O
N
4ba
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

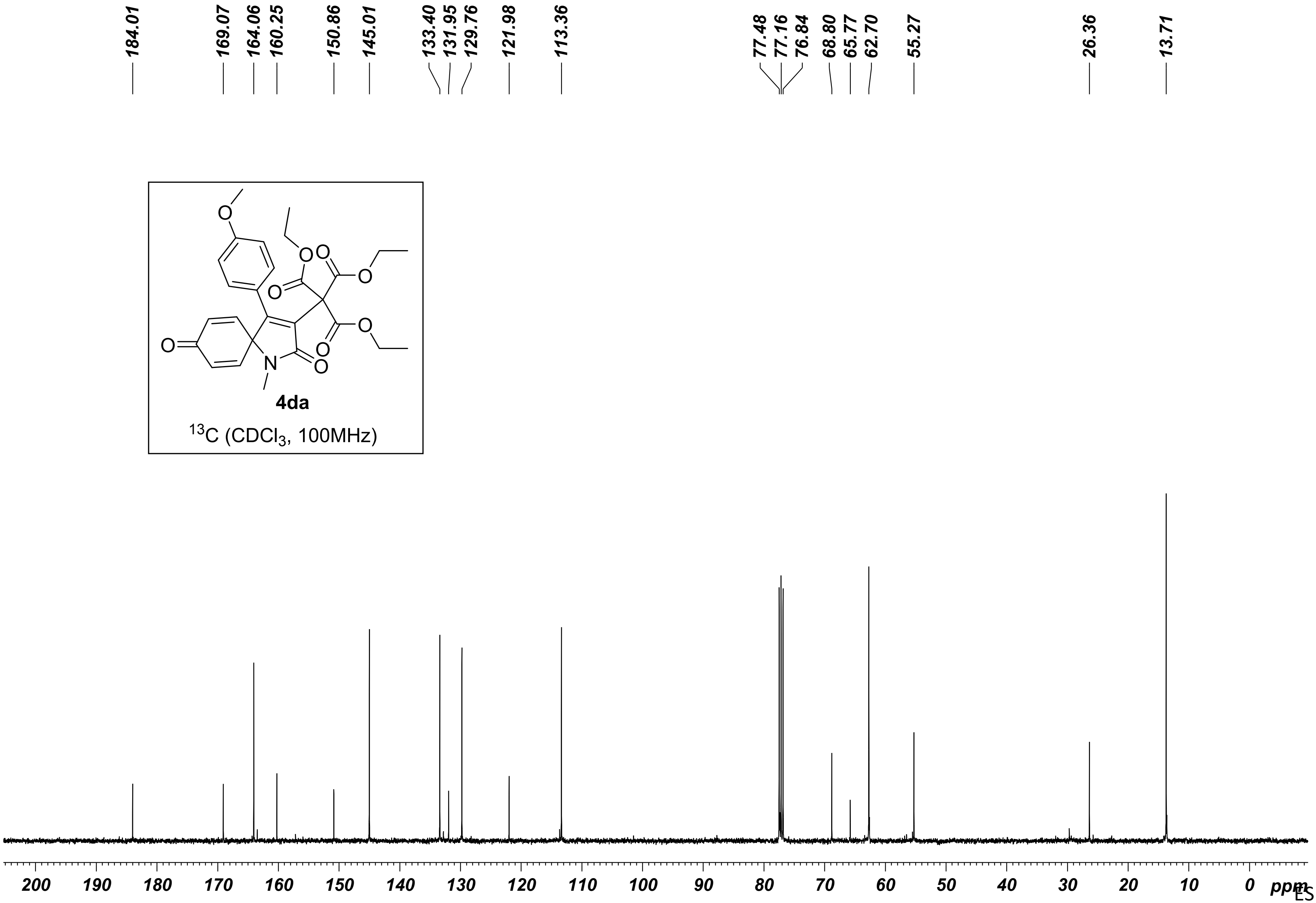


4ca

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

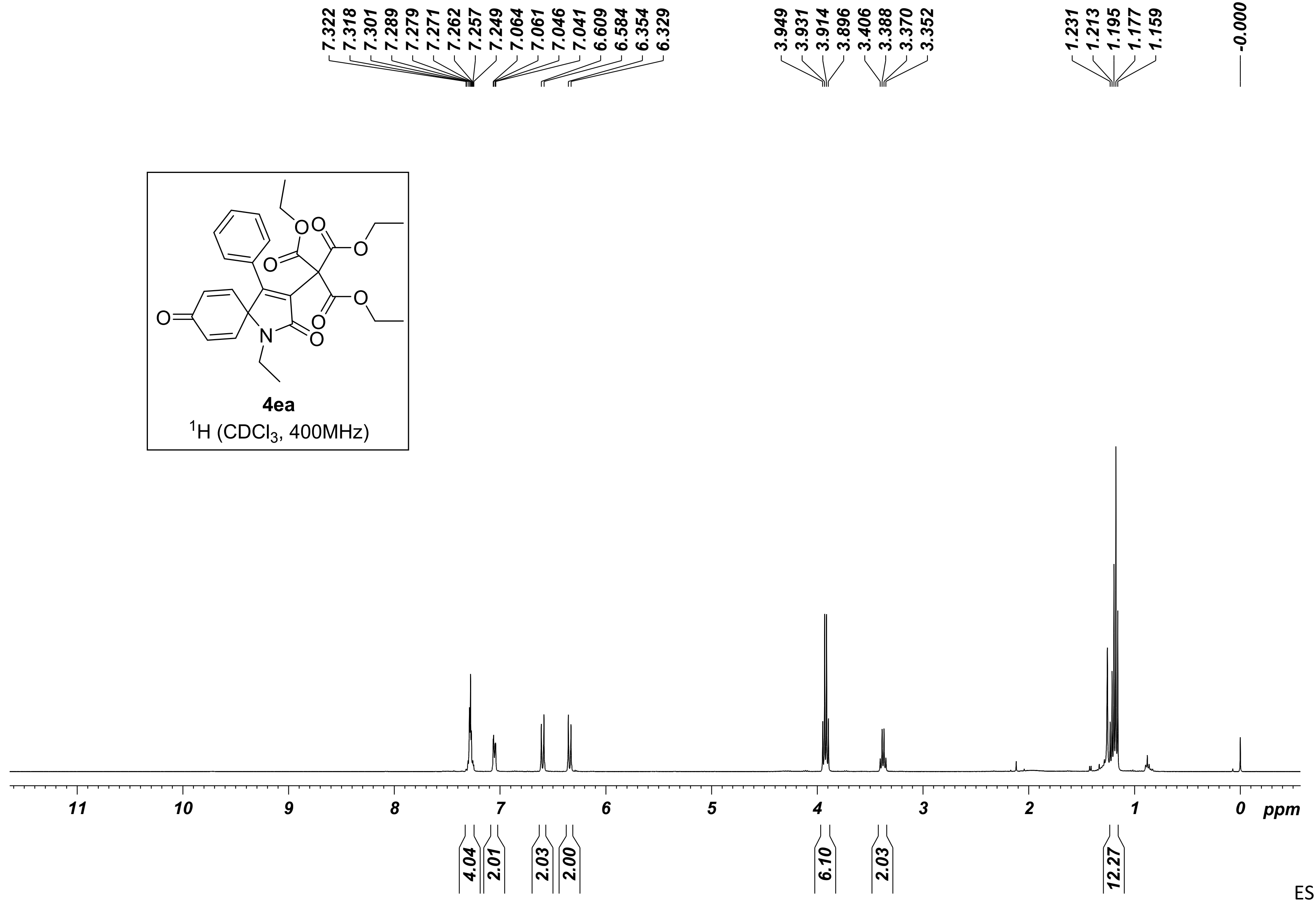

184.05
169.05
163.97
151.19
144.90
137.43
133.20
131.64
130.79
129.74
125.97
77.32
77.00
76.68
68.57
65.71
62.52
26.23
21.10
13.65
O
O
O
O
O
O
O
N
O
4ca
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

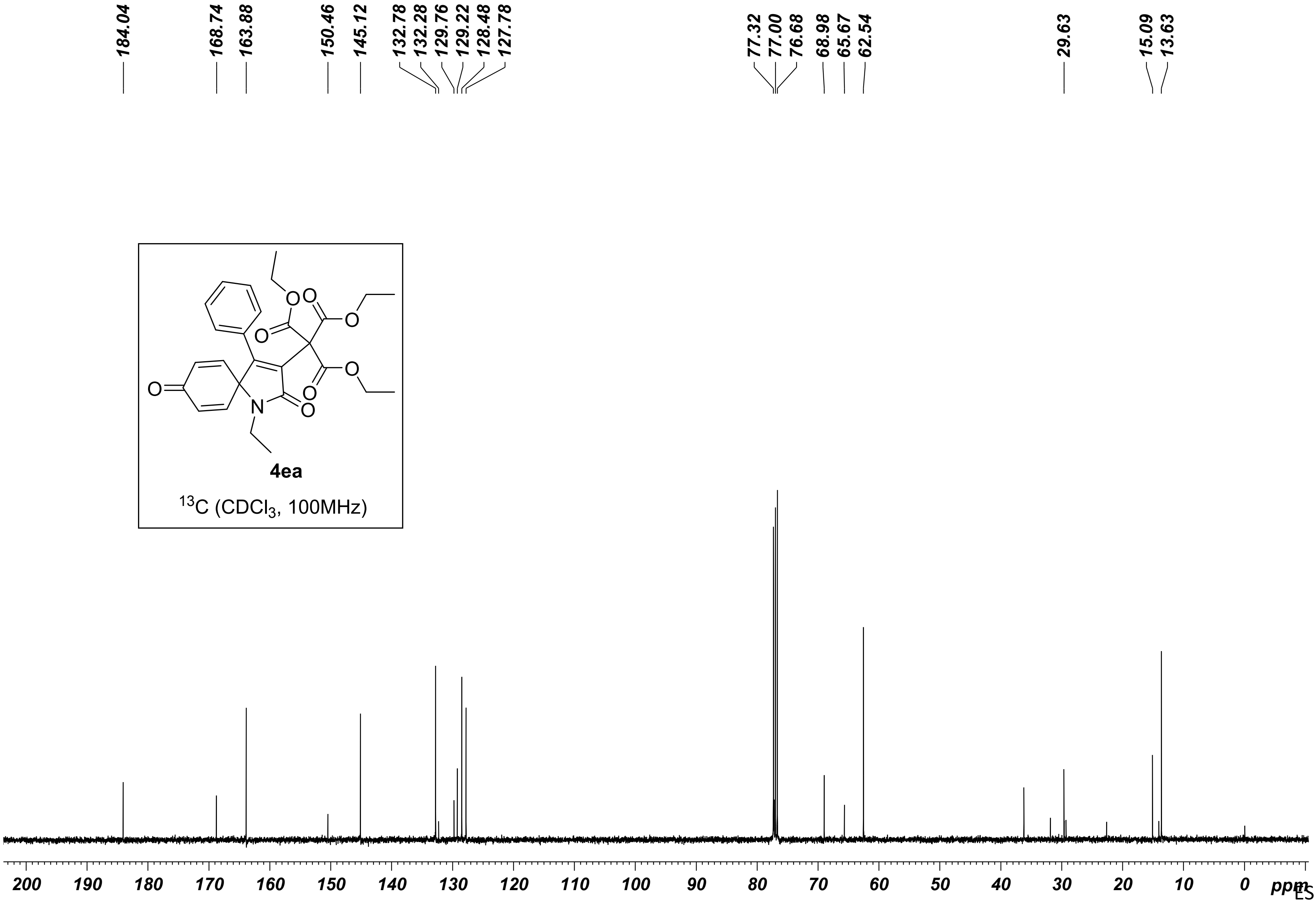

7.305
7.015
6.993
6.802
6.781
6.553
6.528
6.400
6.375
3.989
3.972
3.954
3.936
3.767
2.899
1.210
1.192
1.174
0.000
O
O
O
O
O
O
O
O
N
4da
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.09
2.01
2.09
2.00
6.07
3.08
3.01
9.36

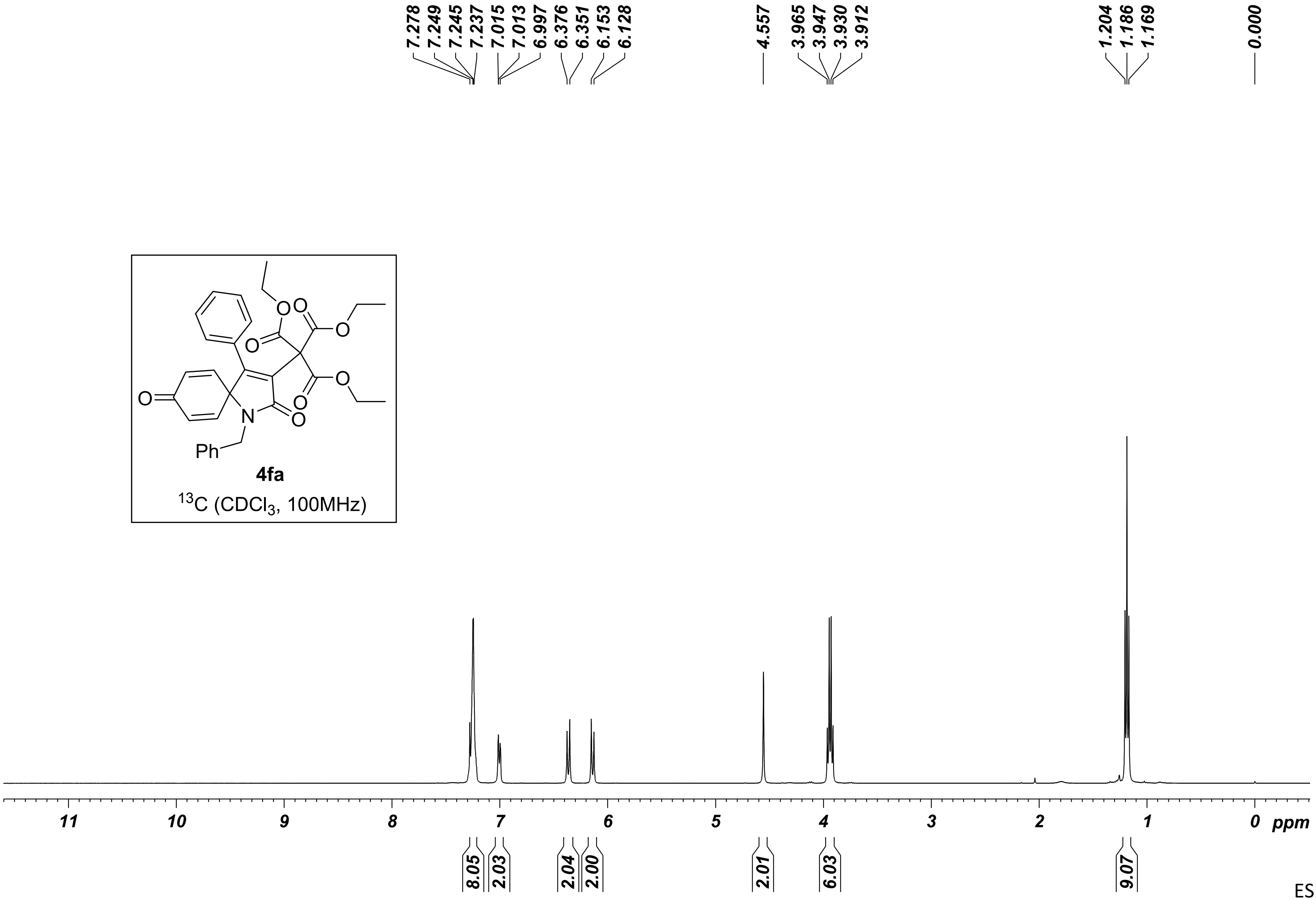


4da

^{13}C (CDCl$_3$, 100MHz)

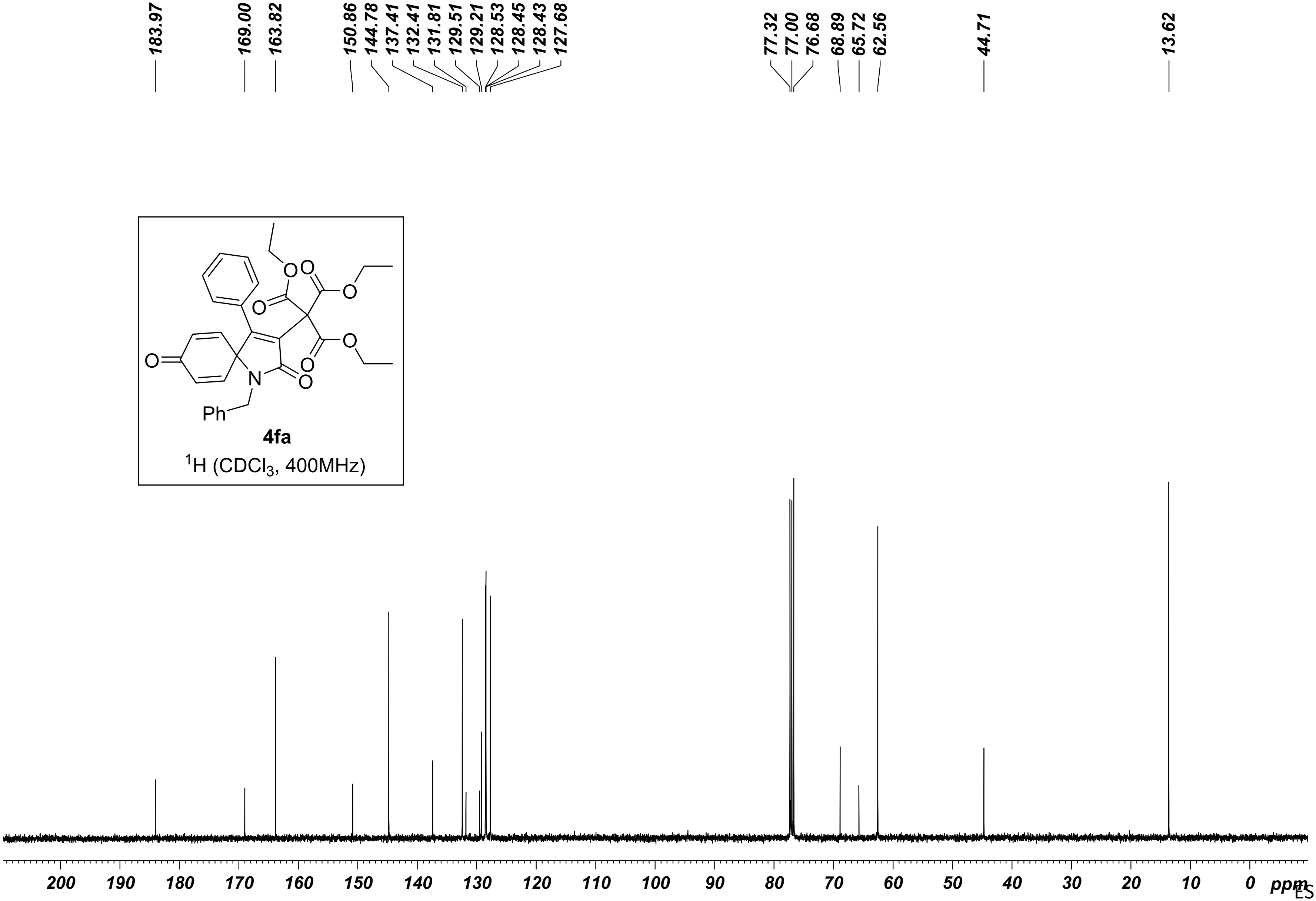

7.322
7.318
7.301
7.289
7.279
7.271
7.262
7.257
7.249
7.064
7.061
7.046
7.041
6.609
6.584
6.354
6.329
3.949
3.931
3.914
3.896
3.406
3.388
3.370
3.352
1.231
1.213
1.195
1.177
1.159
-0.000
4ea
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.04
2.01
2.03
2.00
6.10
2.03
12.27


184.04
168.74
163.88
150.46
145.12
132.78
132.28
129.76
129.22
128.48
127.78
77.32
77.00
76.68
68.98
65.67
62.54
29.63
15.09
13.63
4ea
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



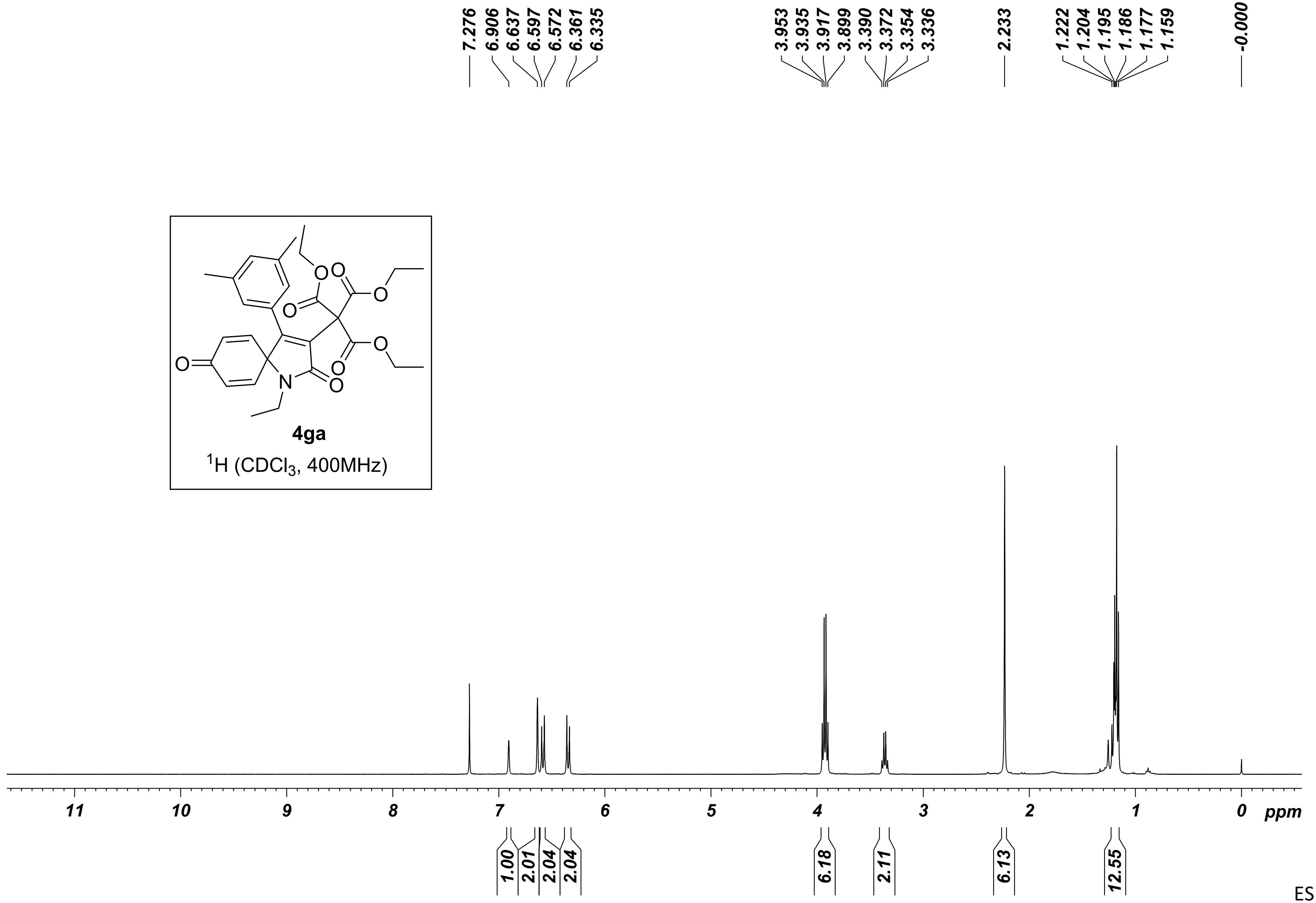
4fa

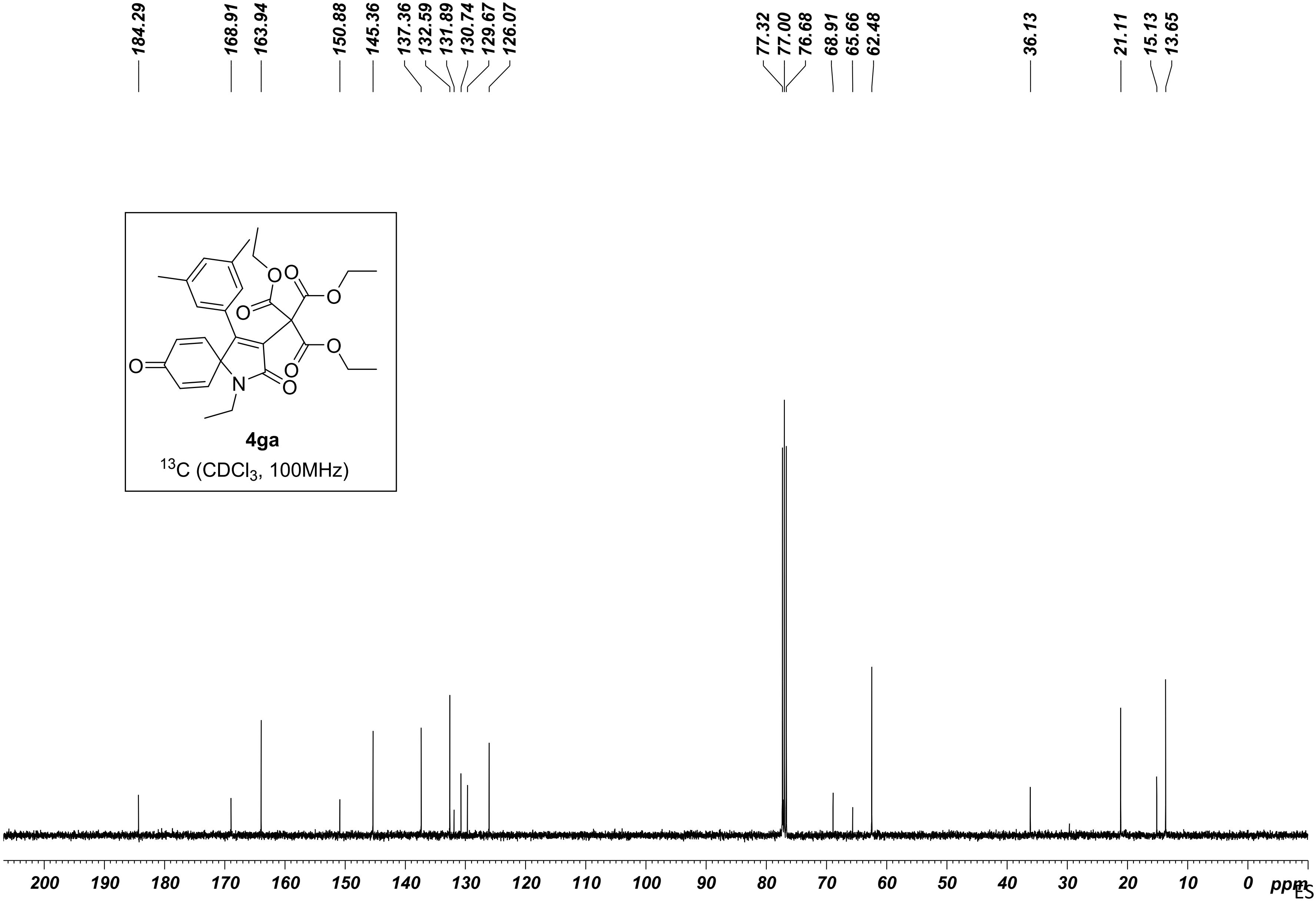
^{13}C (CDCl$_3$, 100MHz)



4fa

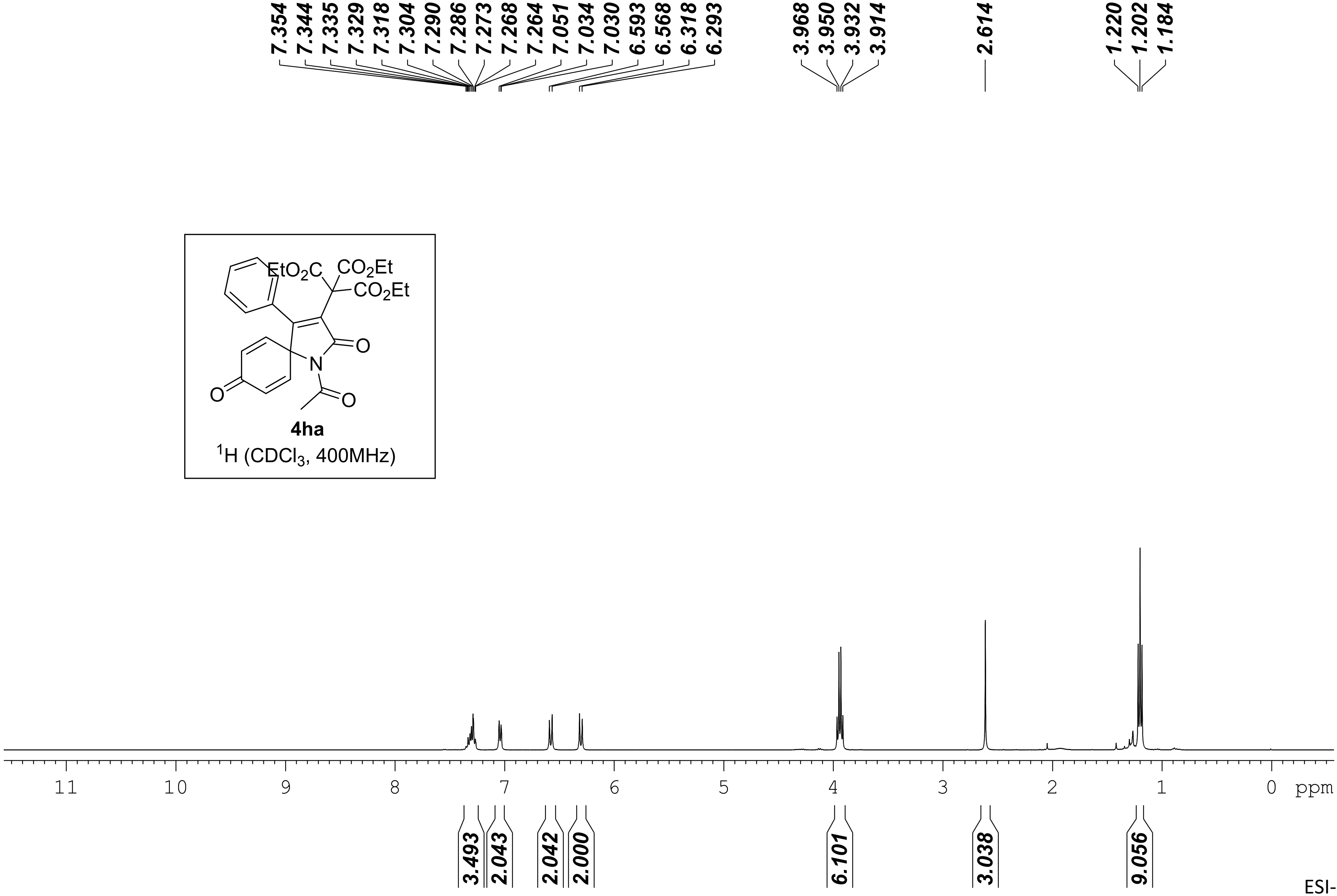
^{1}H (CDCl$_3$, 400MHz)

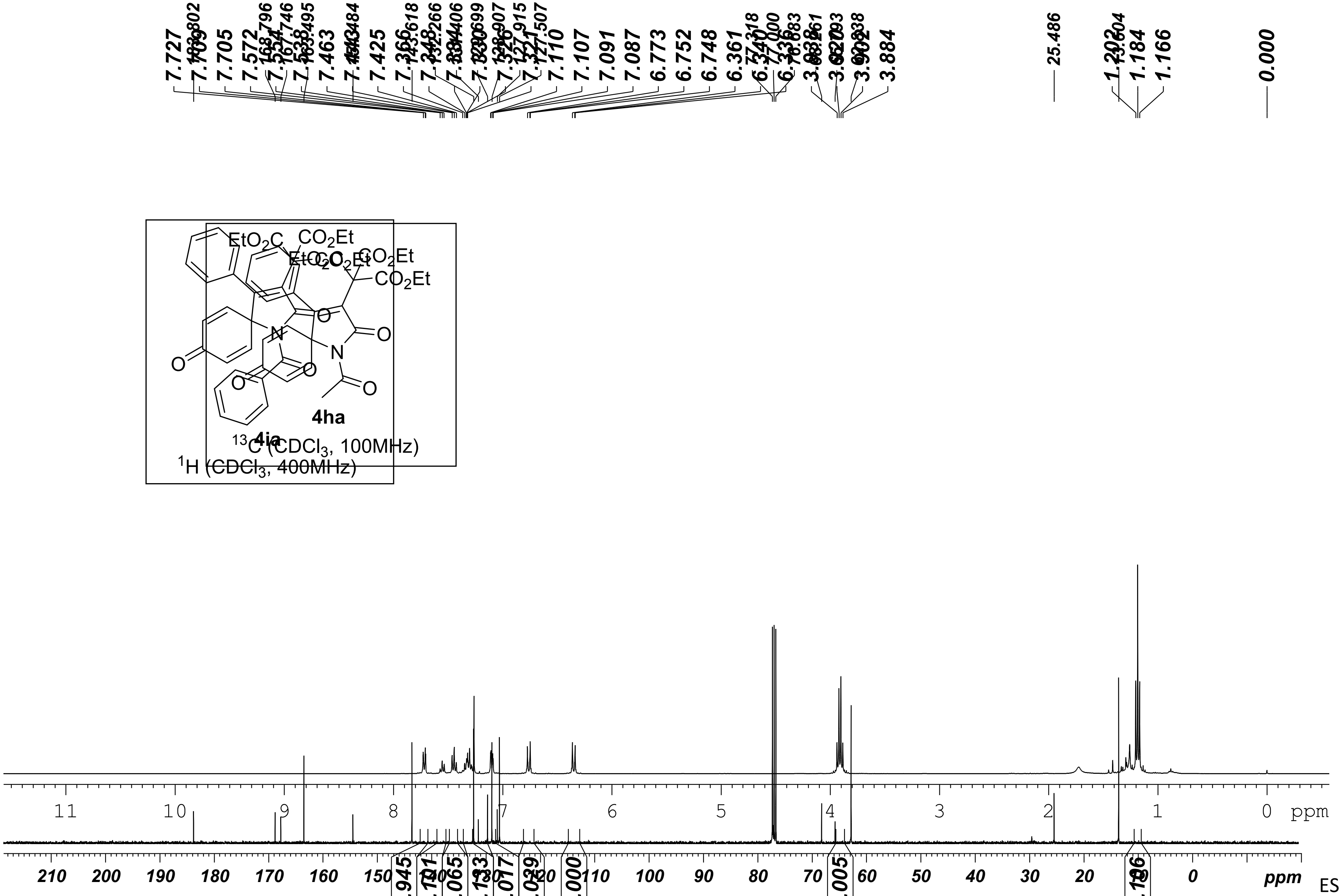

7.276
6.906
6.637
6.597
6.572
6.361
6.335
3.953
3.935
3.917
3.899
3.390
3.372
3.354
3.336
2.233
1.222
1.204
1.195
1.186
1.177
1.159
-0.000
4ga
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.01
2.04
2.04
6.18
2.11
6.13
12.55

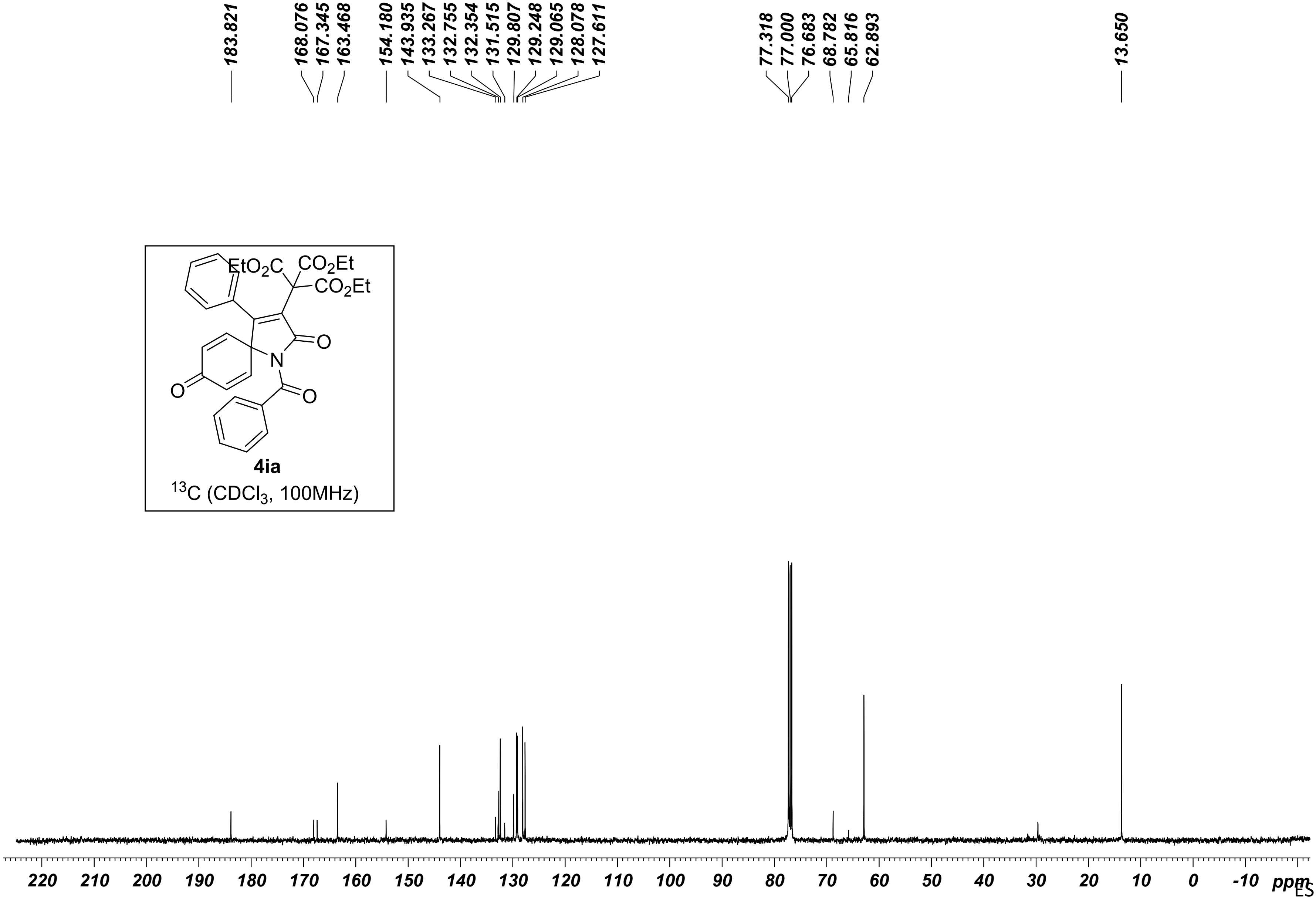


4ga

^{13}C (CDCl$_3$, 100MHz)

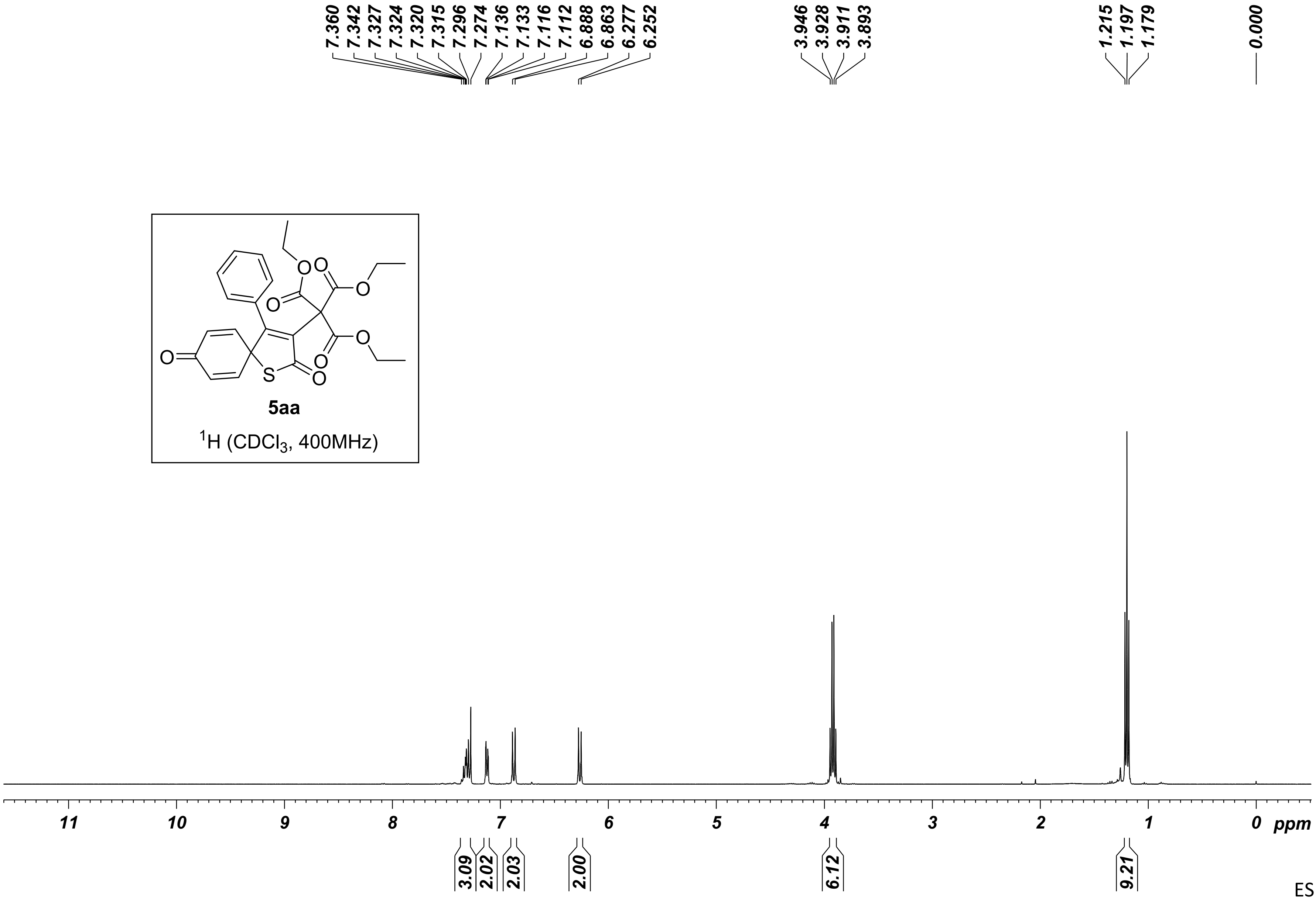

7.354
7.344
7.335
7.329
7.318
7.304
7.290
7.286
7.273
7.268
7.264
7.051
7.034
7.030
6.593
6.568
6.318
6.293
3.968
3.950
3.932
3.914
2.614
1.220
1.202
1.184
EtO2C
CO2Et
CO2Et
O
N
O
O
4ha
1H (CDCl3, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.493
2.043
2.042
2.000
6.101
3.038
9.056

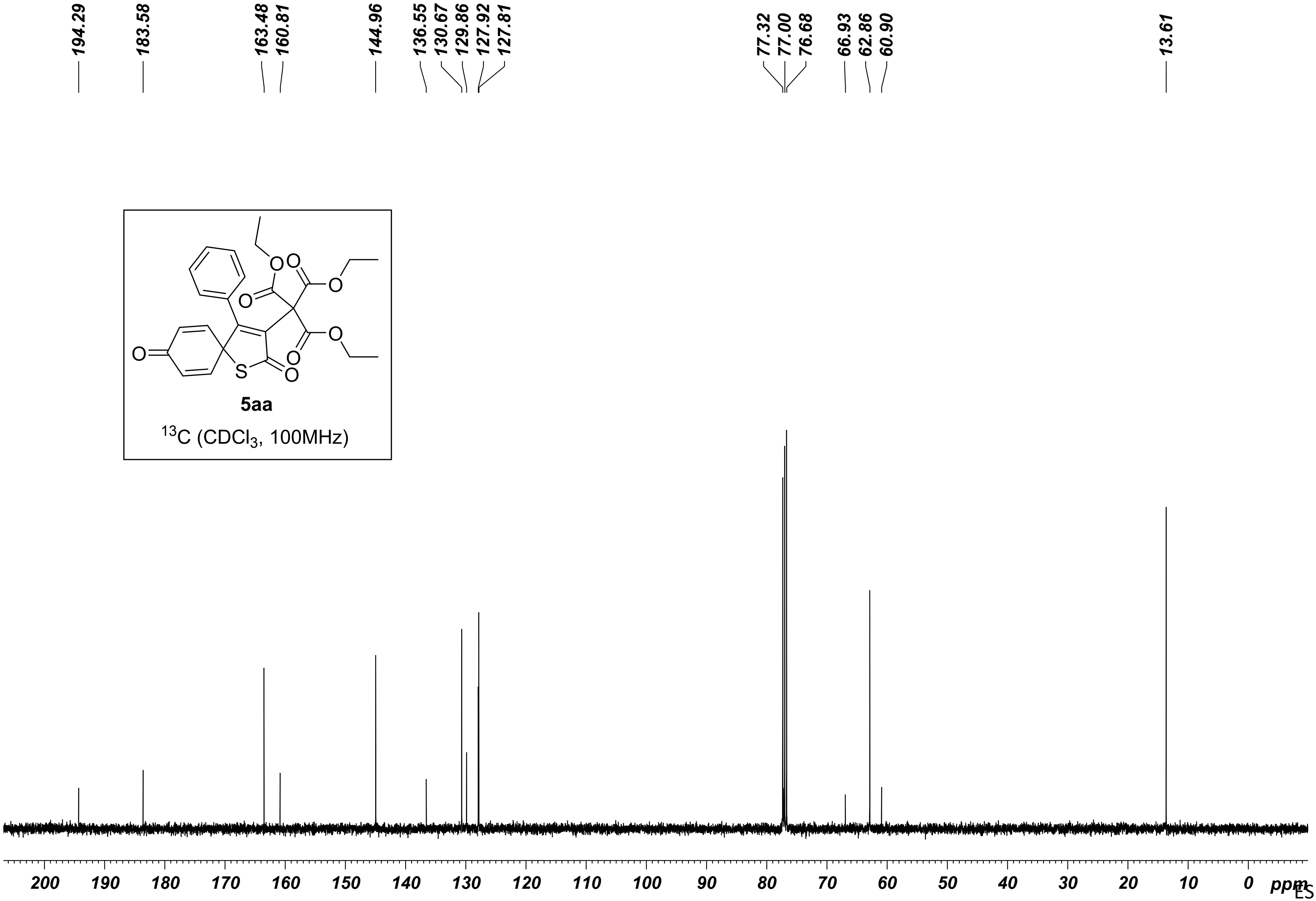

7.727
7.709
7.705
7.572
7.554
7.538
7.463
7.443
7.425
7.366
7.348
7.344
7.330
7.326
7.321
7.110
7.107
7.091
7.087
6.773
6.752
6.748
6.361
6.340
6.336
3.938
3.920
3.902
3.884
1.202
1.184
1.166
0.000
183.802
168.796
167.746
163.495
154.484
143.618
132.266
130.406
130.099
128.907
127.915
127.507
77.318
77.000
76.683
63.261
62.093
62.038
25.486
13.604
EtO2C
CO2Et
EtO2C
CO2Et
CO2Et
O
N
O
N
O
O
O
O
4ha
4ia
13C (CDCl3, 100MHz)
1H (CDCl3, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
1.945
1.101
2.065
3.133
2.077
2.029
2.000
6.005
9.106

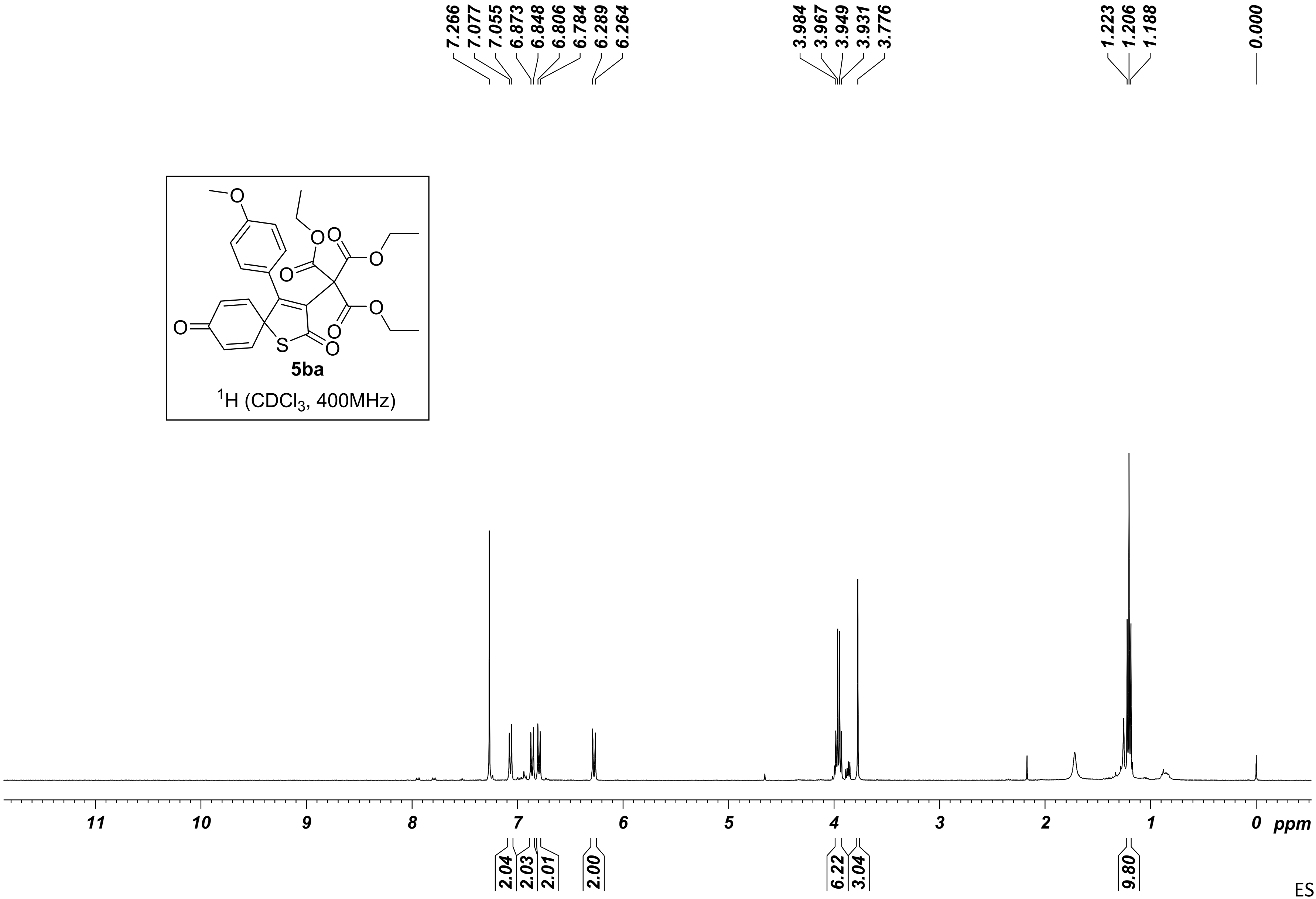


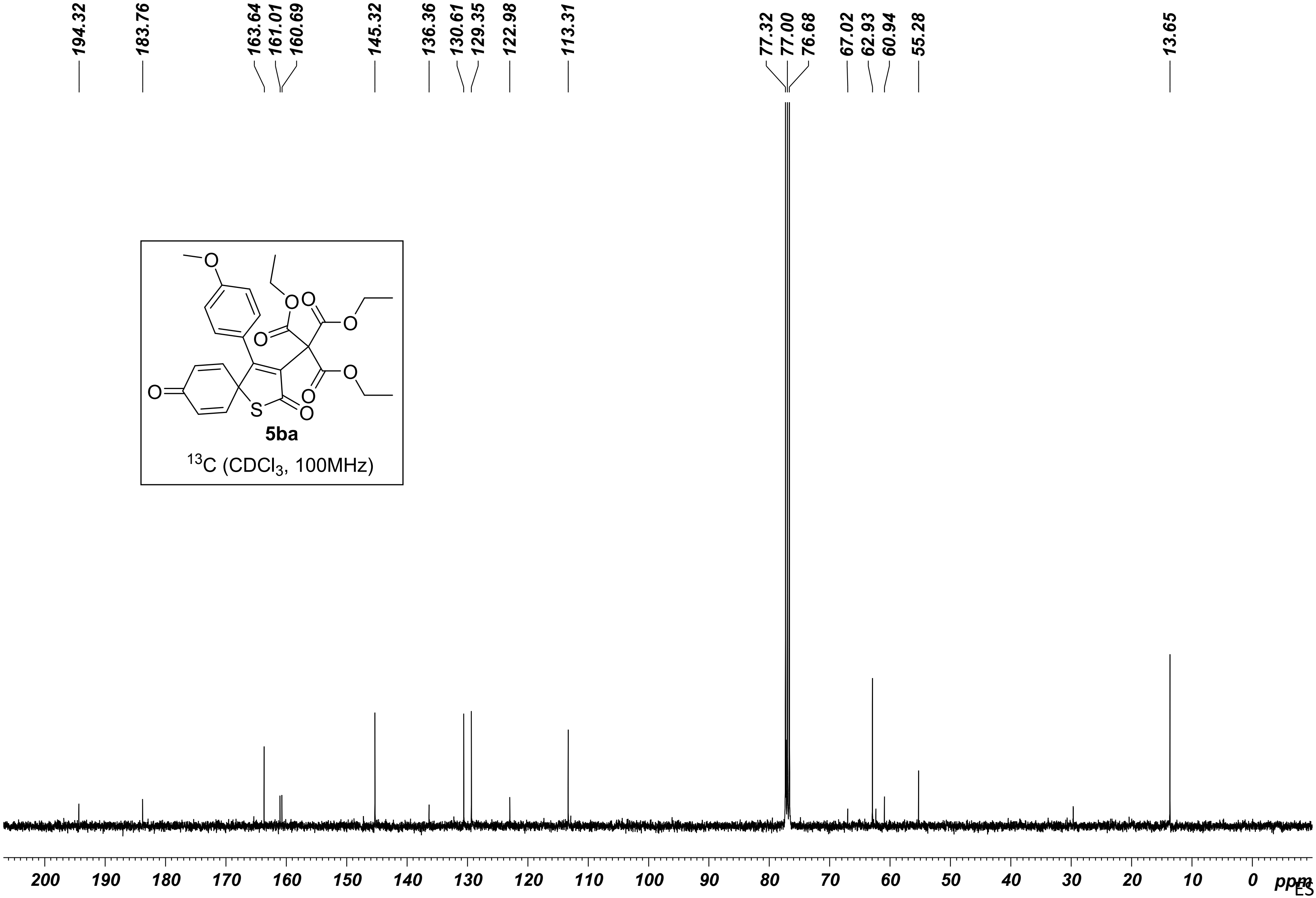
4ia

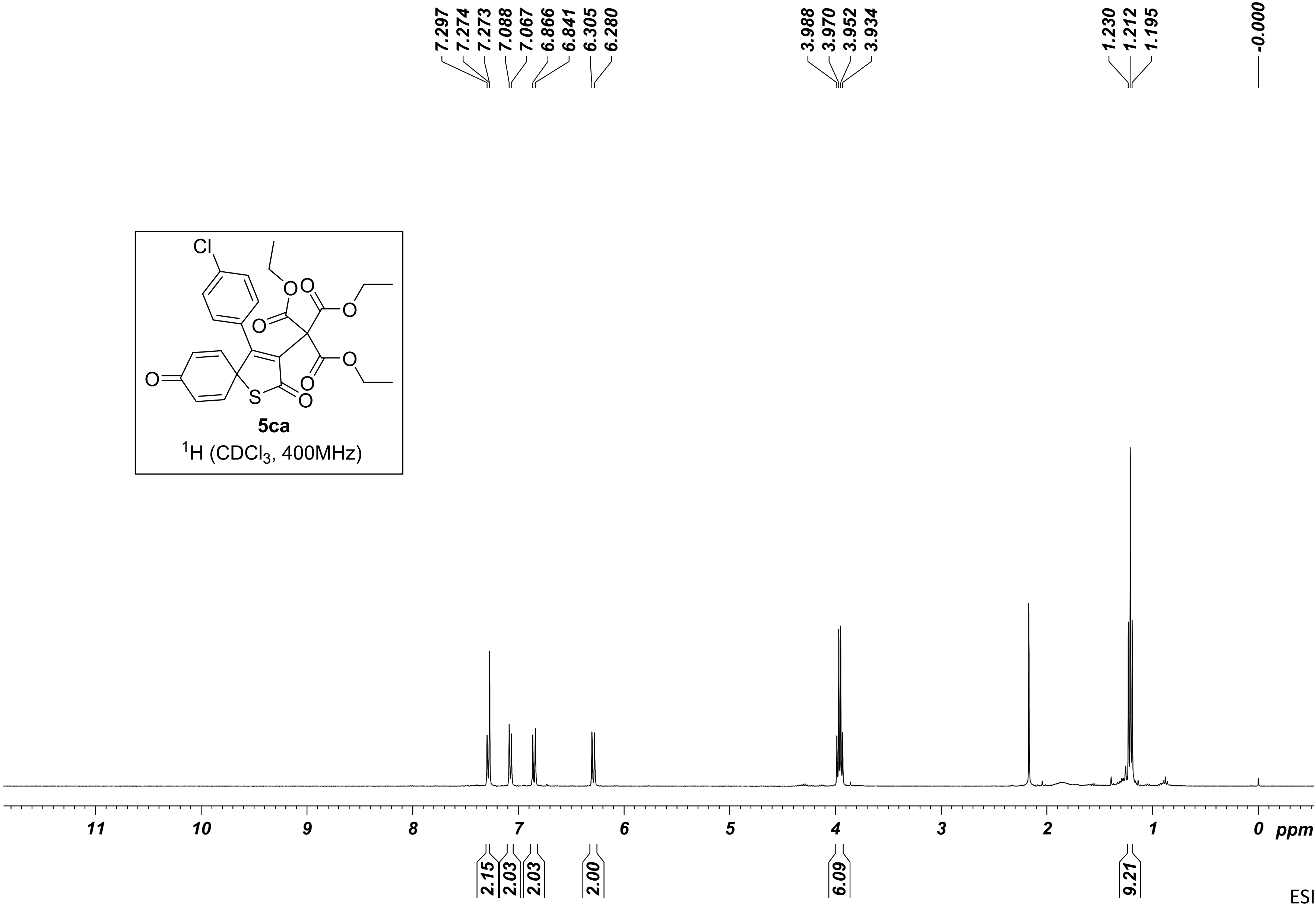
^{13}C (CDCl$_3$, 100MHz)


7.360
7.342
7.327
7.324
7.320
7.315
7.296
7.274
7.136
7.133
7.116
7.112
6.888
6.863
6.277
6.252
3.946
3.928
3.911
3.893
1.215
1.197
1.179
0.000
O
S
5aa
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.09
2.02
2.03
2.00
6.12
9.21


194.29
183.58
163.48
160.81
144.96
136.55
130.67
129.86
127.92
127.81
77.32
77.00
76.68
66.93
62.86
60.90
13.61
O
O
O
O
O
O
S
O
5aa
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

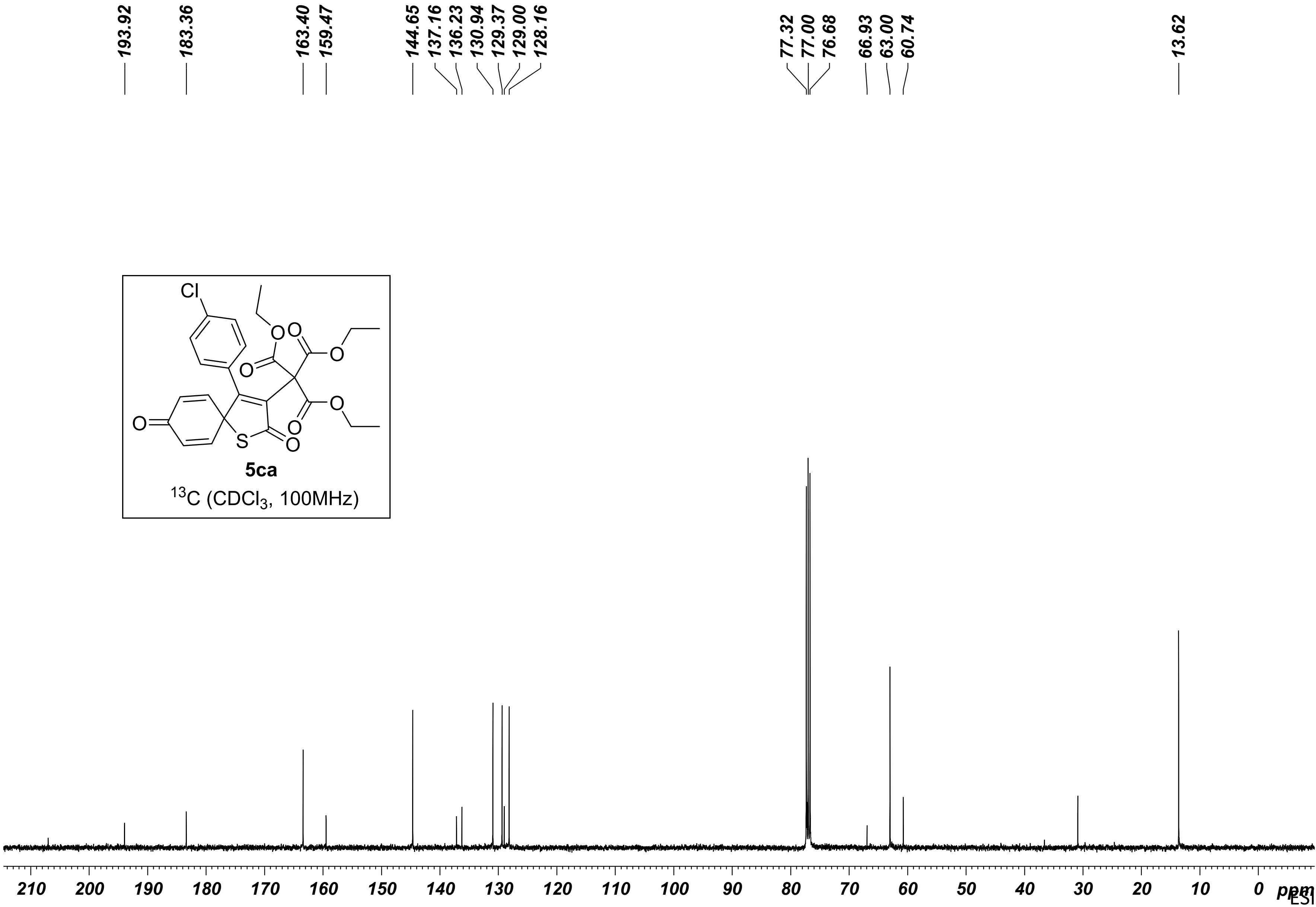

7.266
7.077
7.055
6.873
6.848
6.806
6.784
6.289
6.264
3.984
3.967
3.949
3.931
3.776
1.223
1.206
1.188
0.000
O
O
O
O
O
O
O
O
S
O
5ba
^{1}H (CDCl$_3$, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.04
2.03
2.01
2.00
6.22
3.04
9.80


194.32
183.76
163.64
161.01
160.69
145.32
136.36
130.61
129.35
122.98
113.31
77.32
77.00
76.68
67.02
62.93
60.94
55.28
13.65
5ba
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



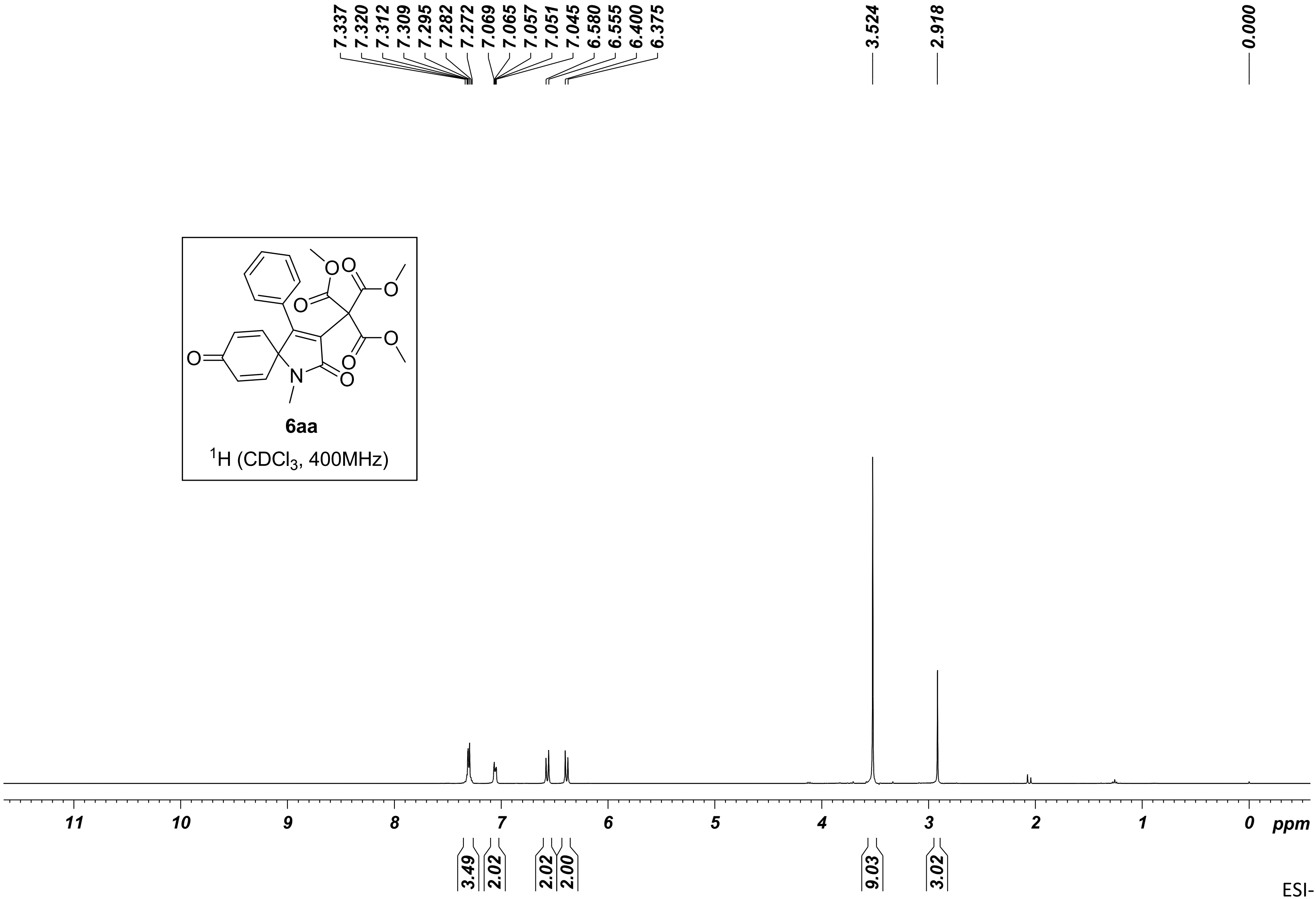
5ca

^1H ($CDCl_3$, 400MHz)



5ca

^{13}C (CDCl$_3$, 100MHz)

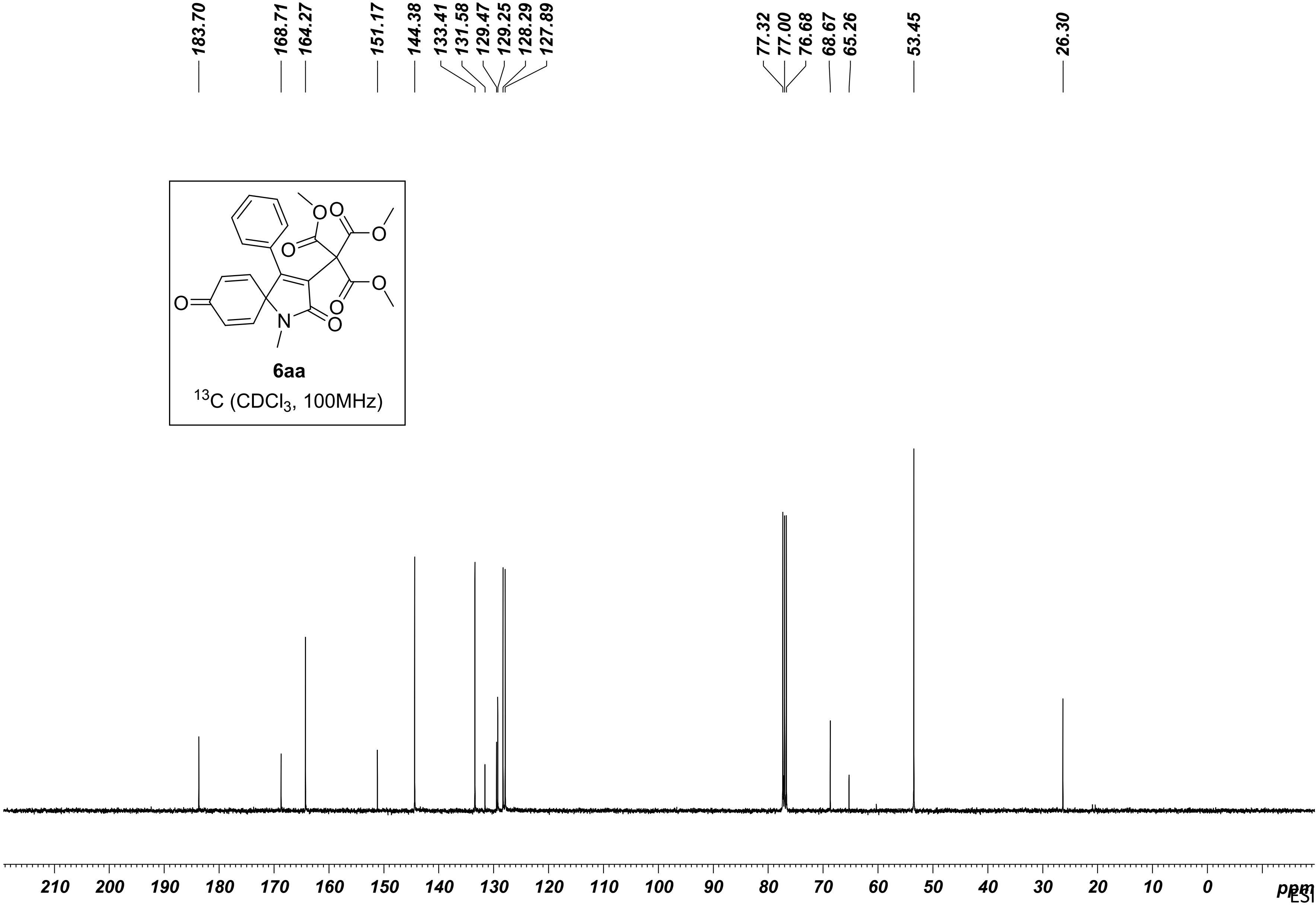


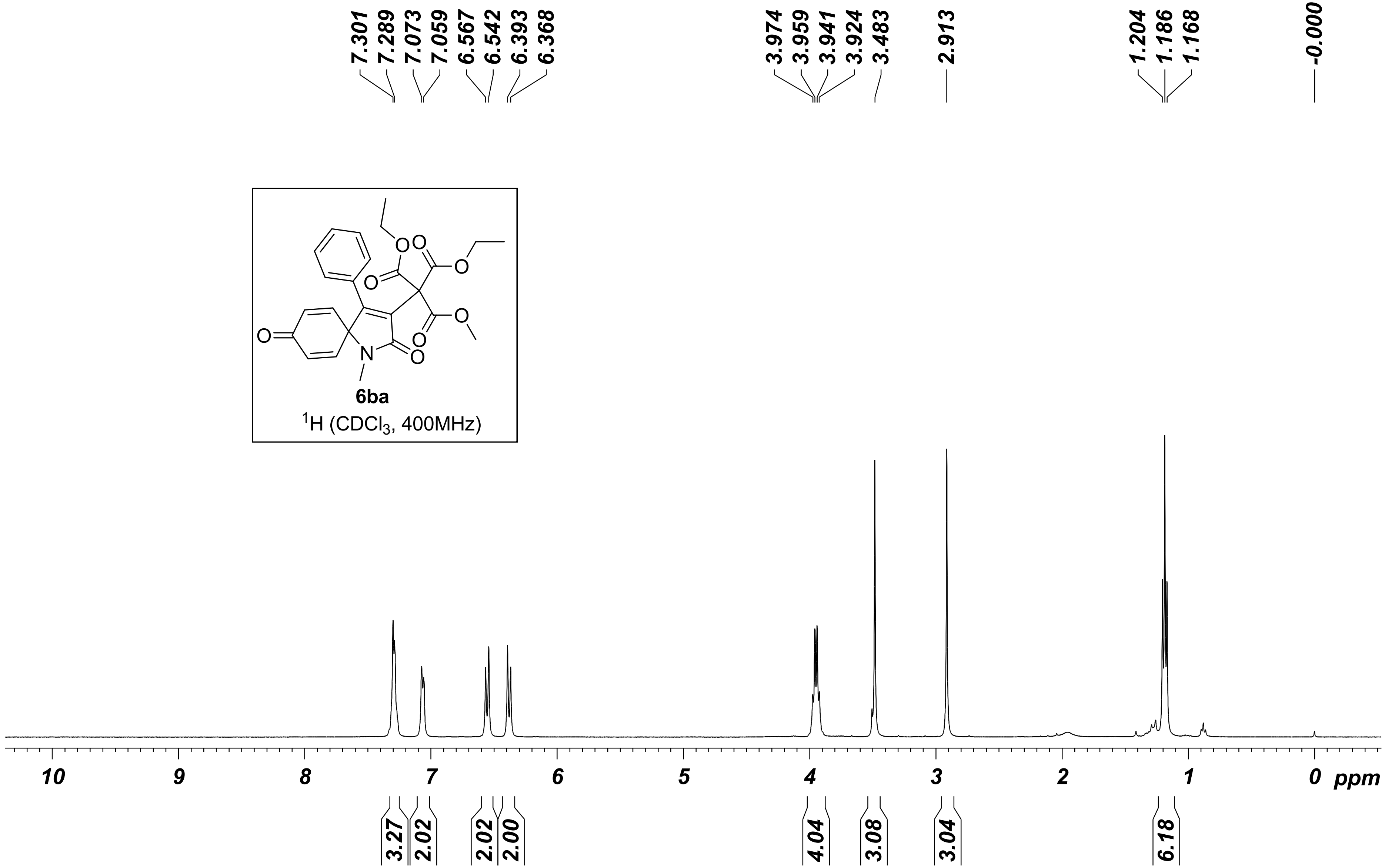
6aa

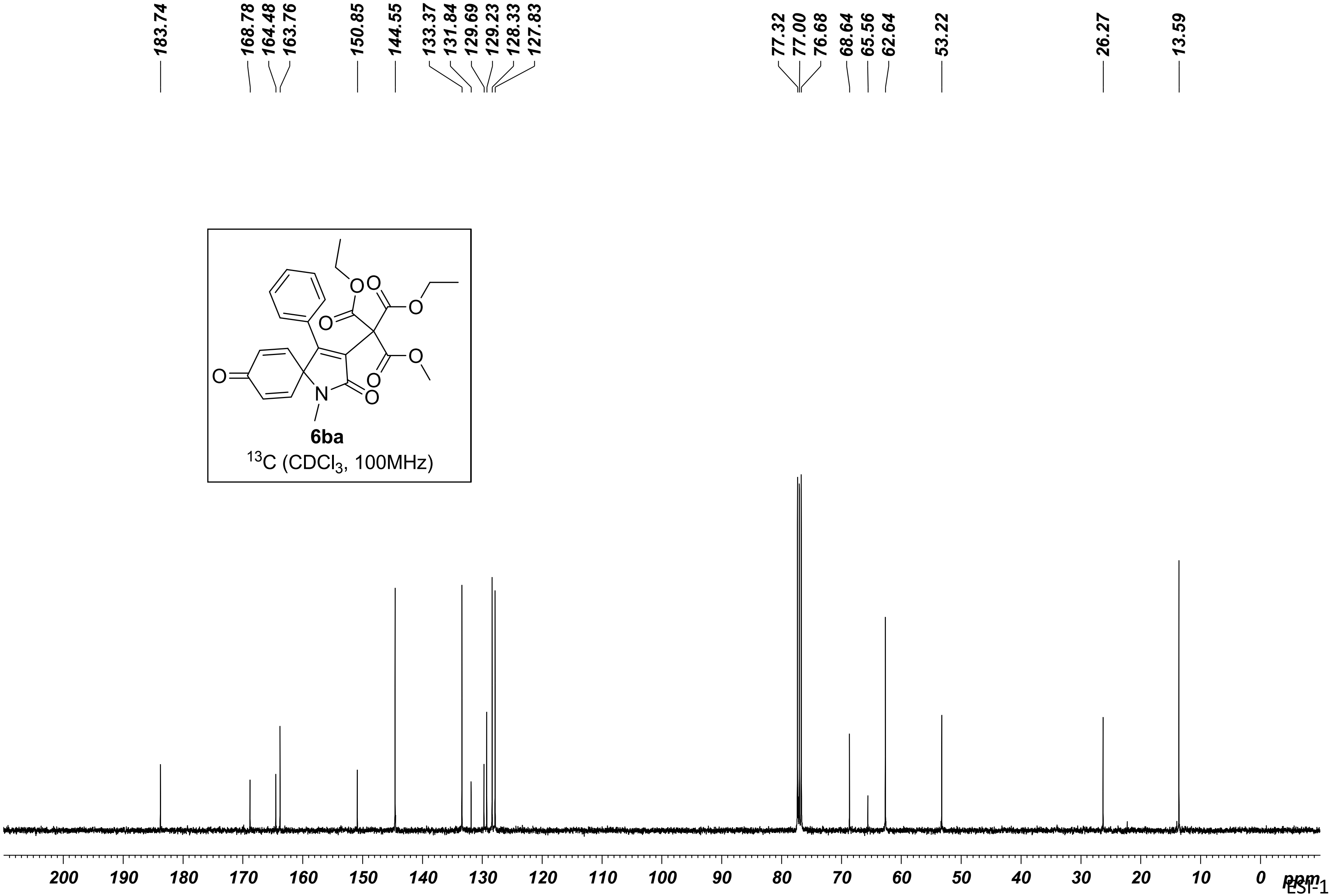
^1H ($CDCl_3$, 400MHz)

6aa

^{13}C (CDCl$_3$, 100MHz)

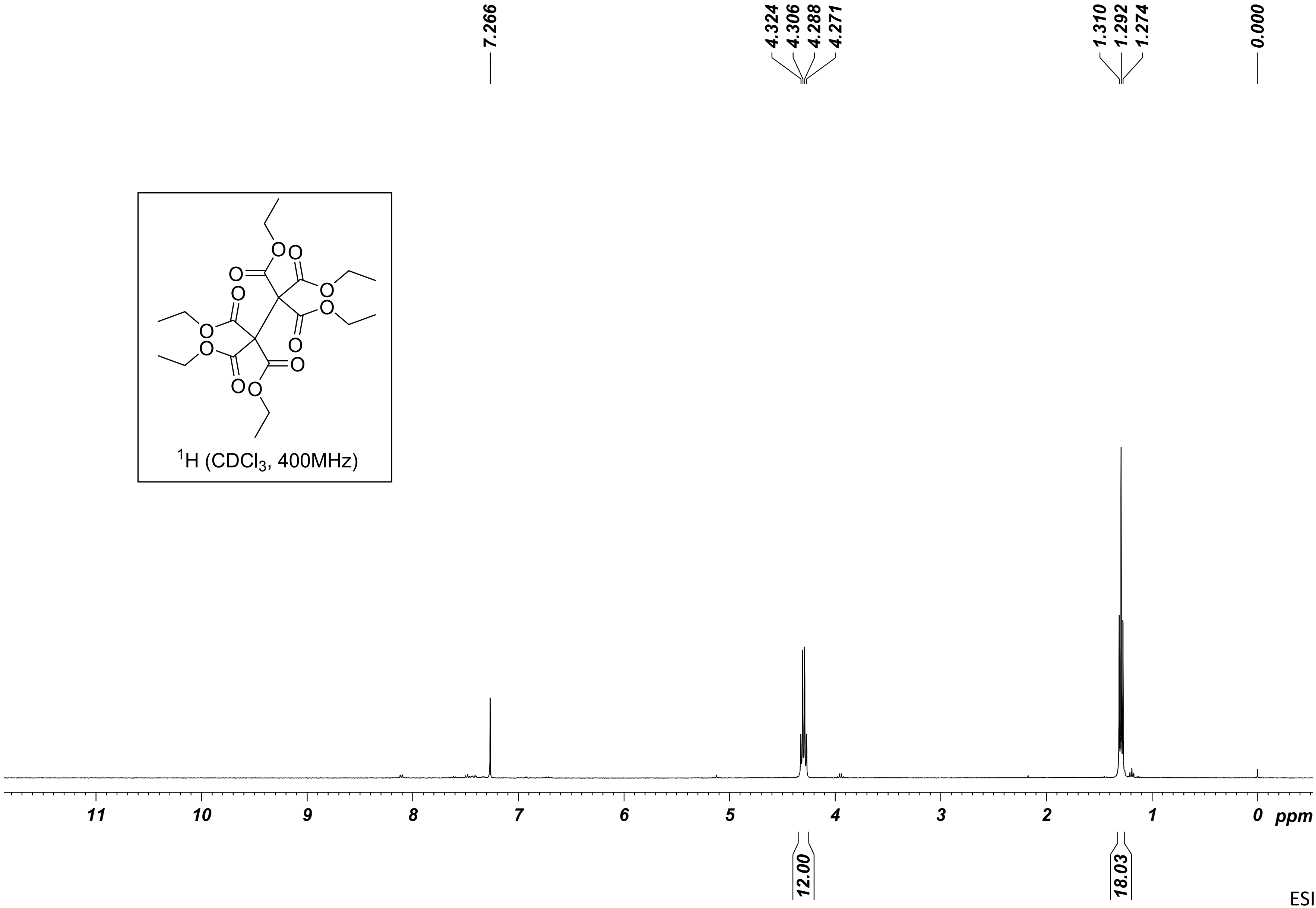


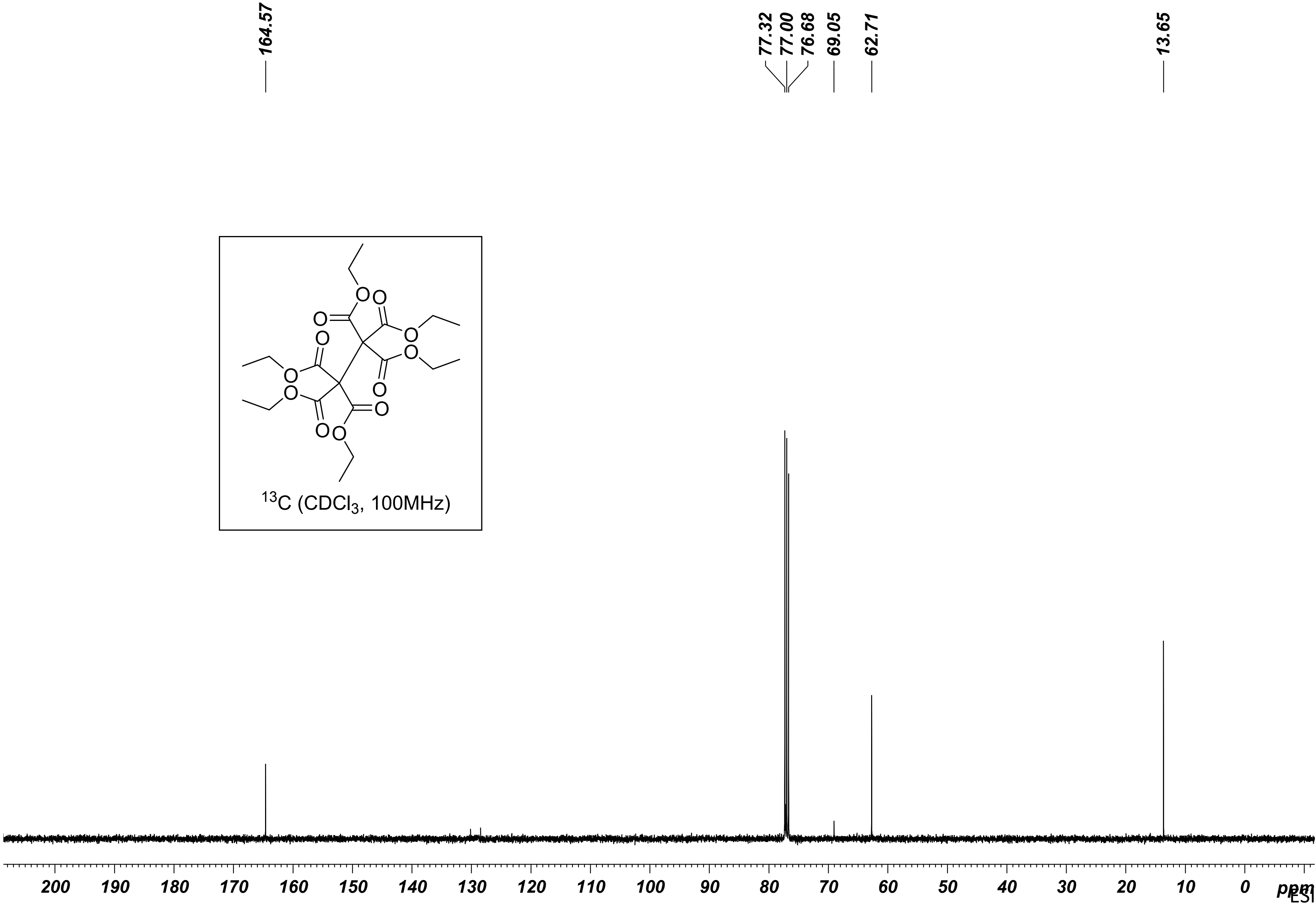

7.301
7.289
7.073
7.059
6.567
6.542
6.393
6.368
3.974
3.959
3.941
3.924
3.483
2.913
1.204
1.186
1.168
-0.000
O
O
O
O
O
O
O
N
O
6ba
^{1}H (CDCl$_3$, 400MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
3.27
2.02
2.02
2.00
4.04
3.08
3.04
6.18

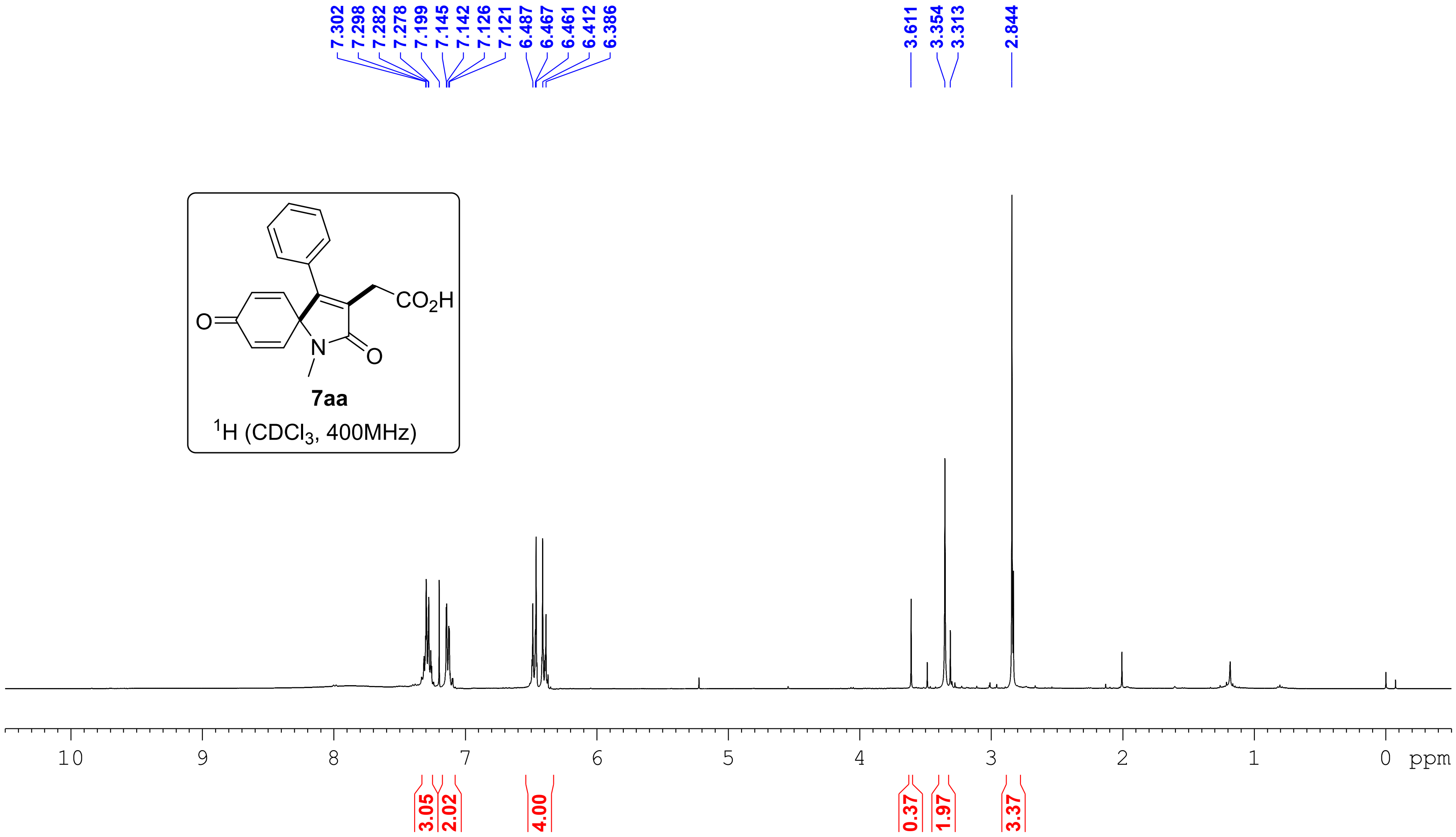


6ba

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

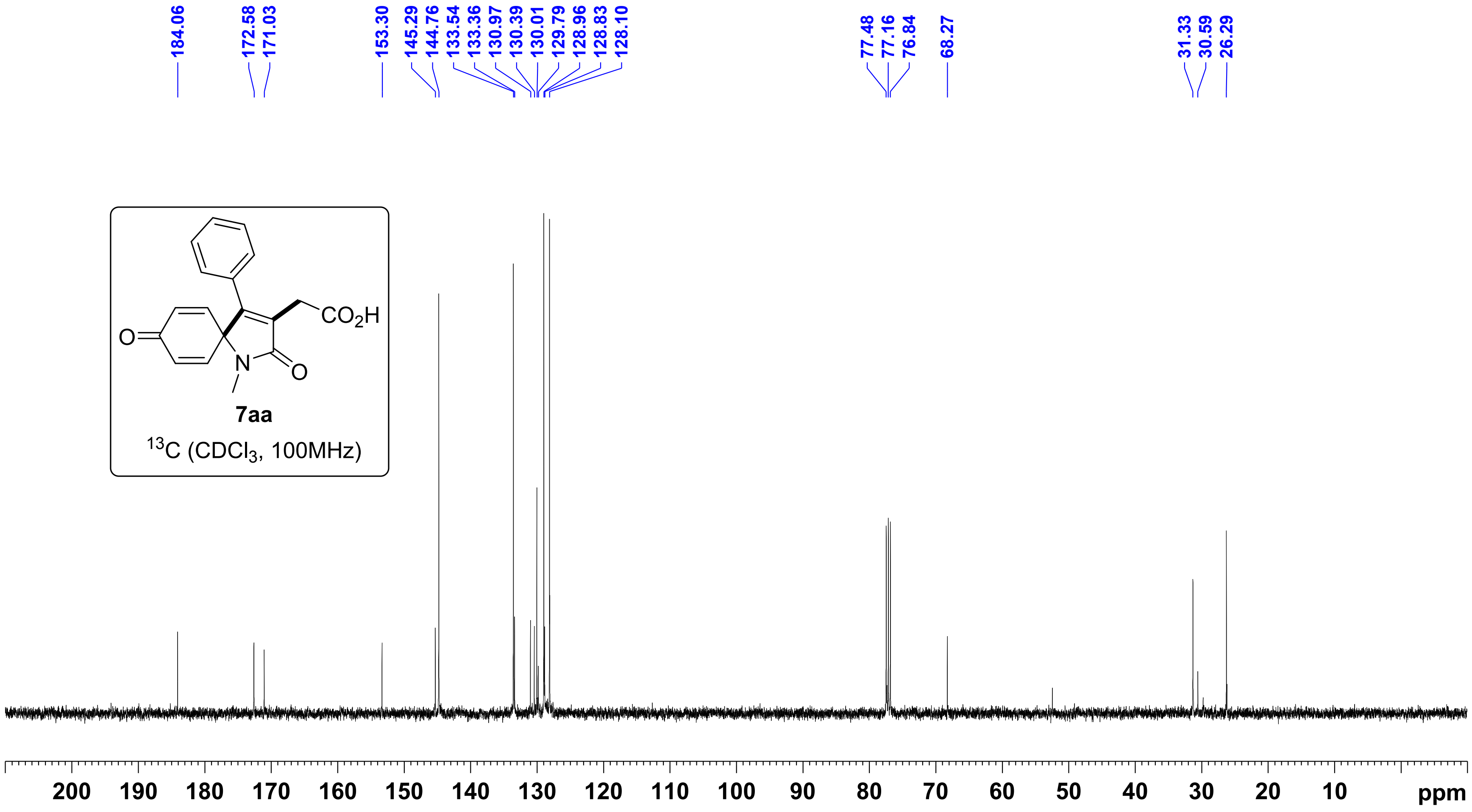

7.266
4.324
4.306
4.288
4.271
1.310
1.292
1.274
0.000
¹H (CDCl₃, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
12.00
18.03


164.57
77.32
77.00
76.68
69.05
62.71
13.65
^{13}C (CDCl$_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



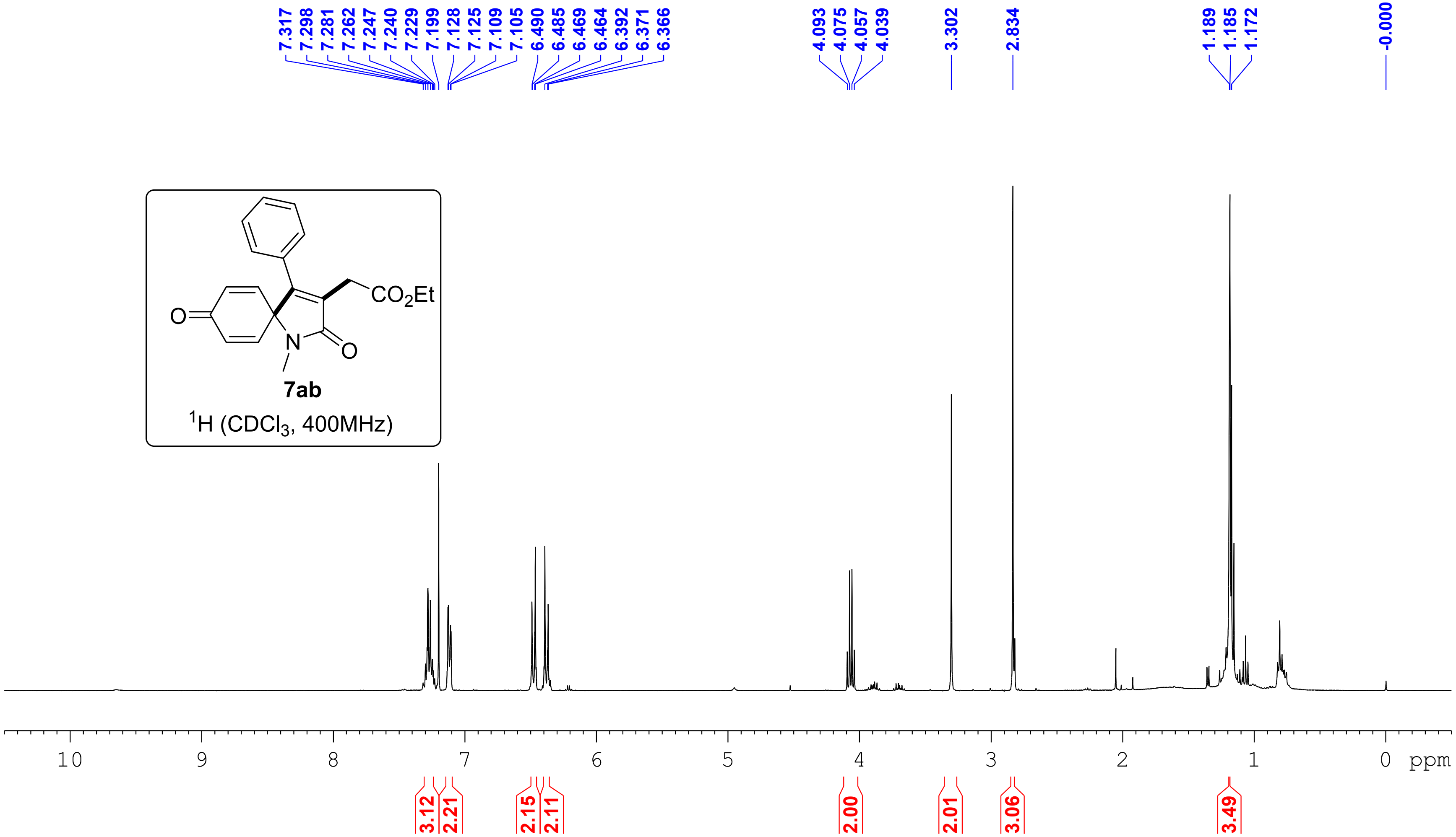
7aa

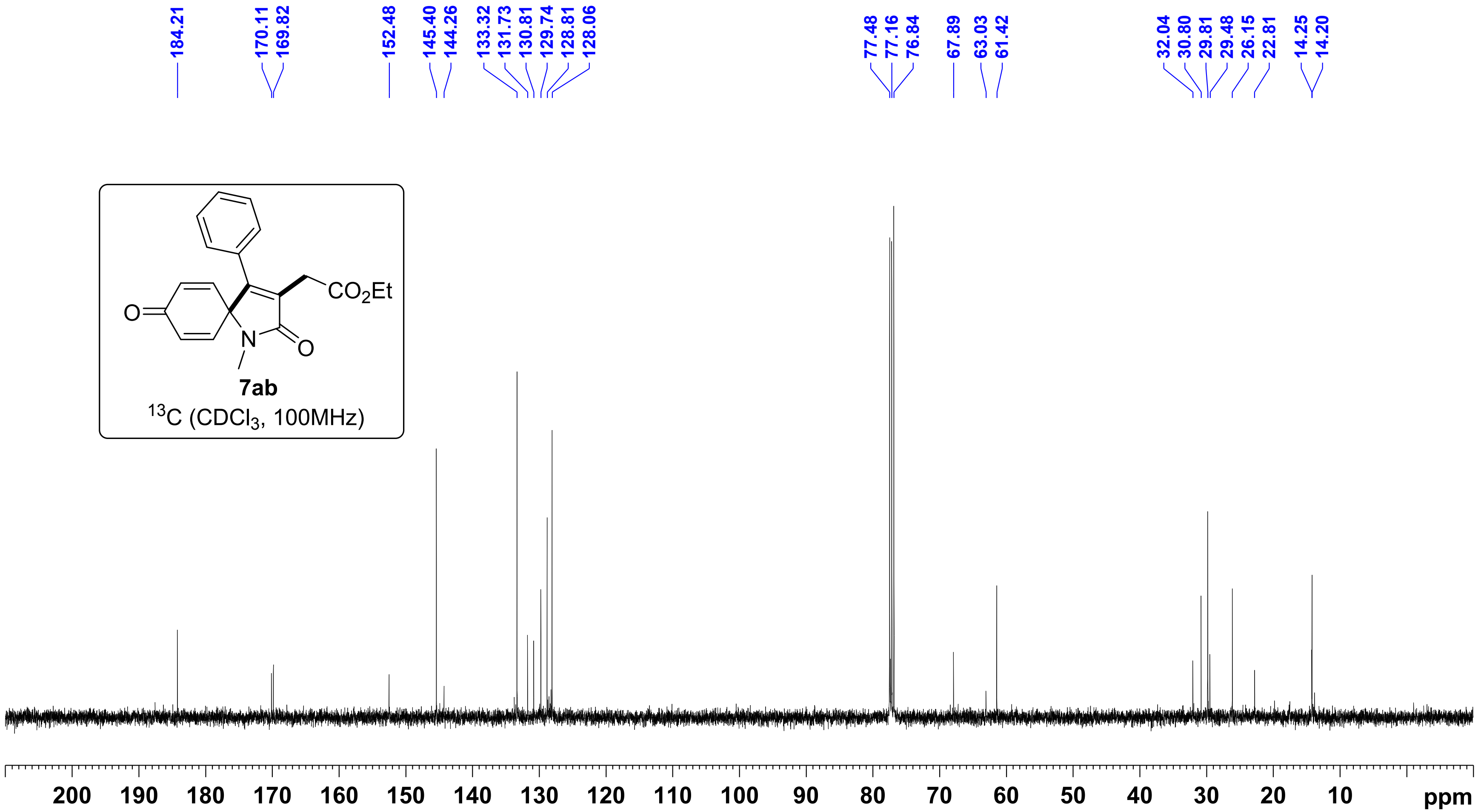
^1H ($CDCl_3$, 400MHz)

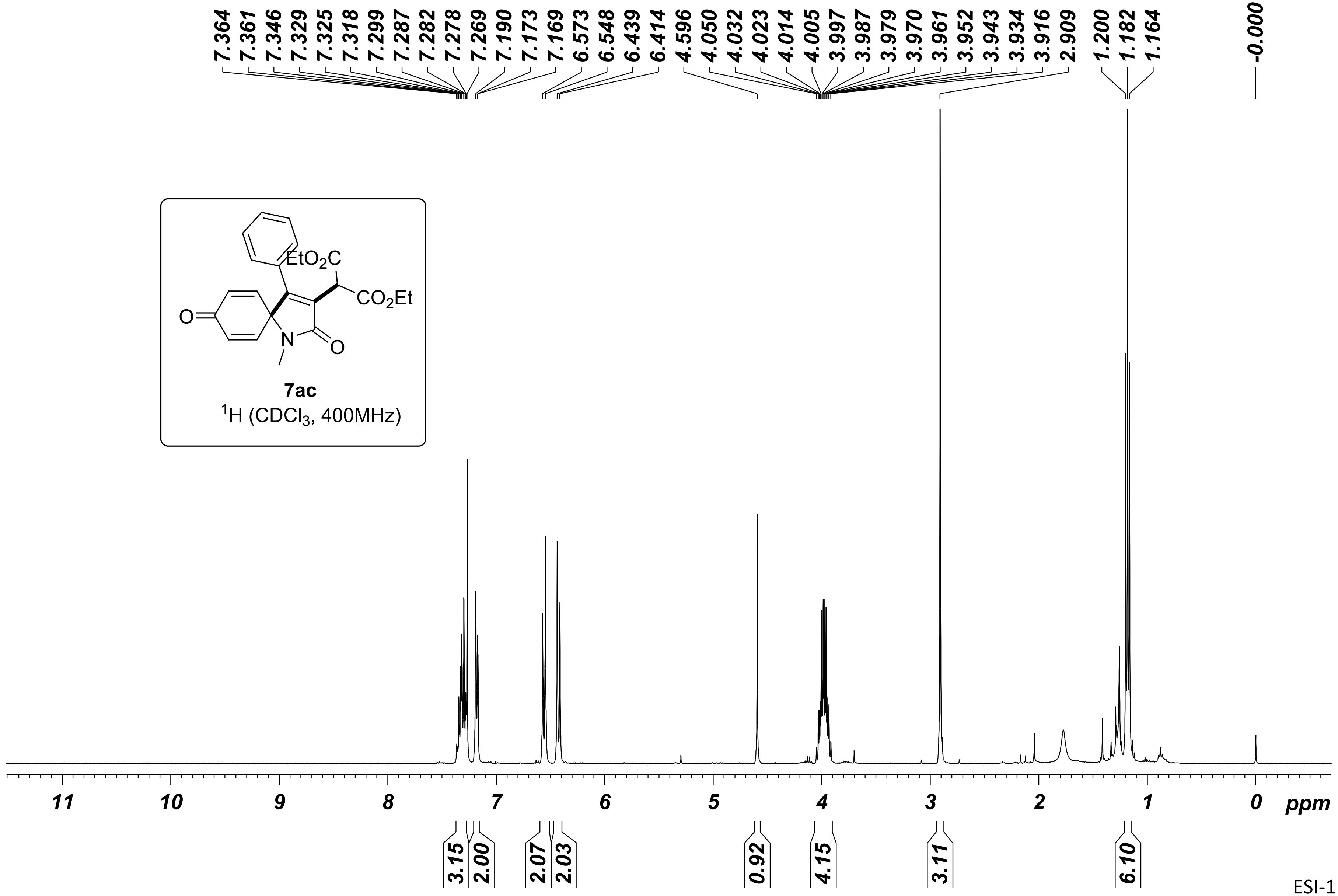


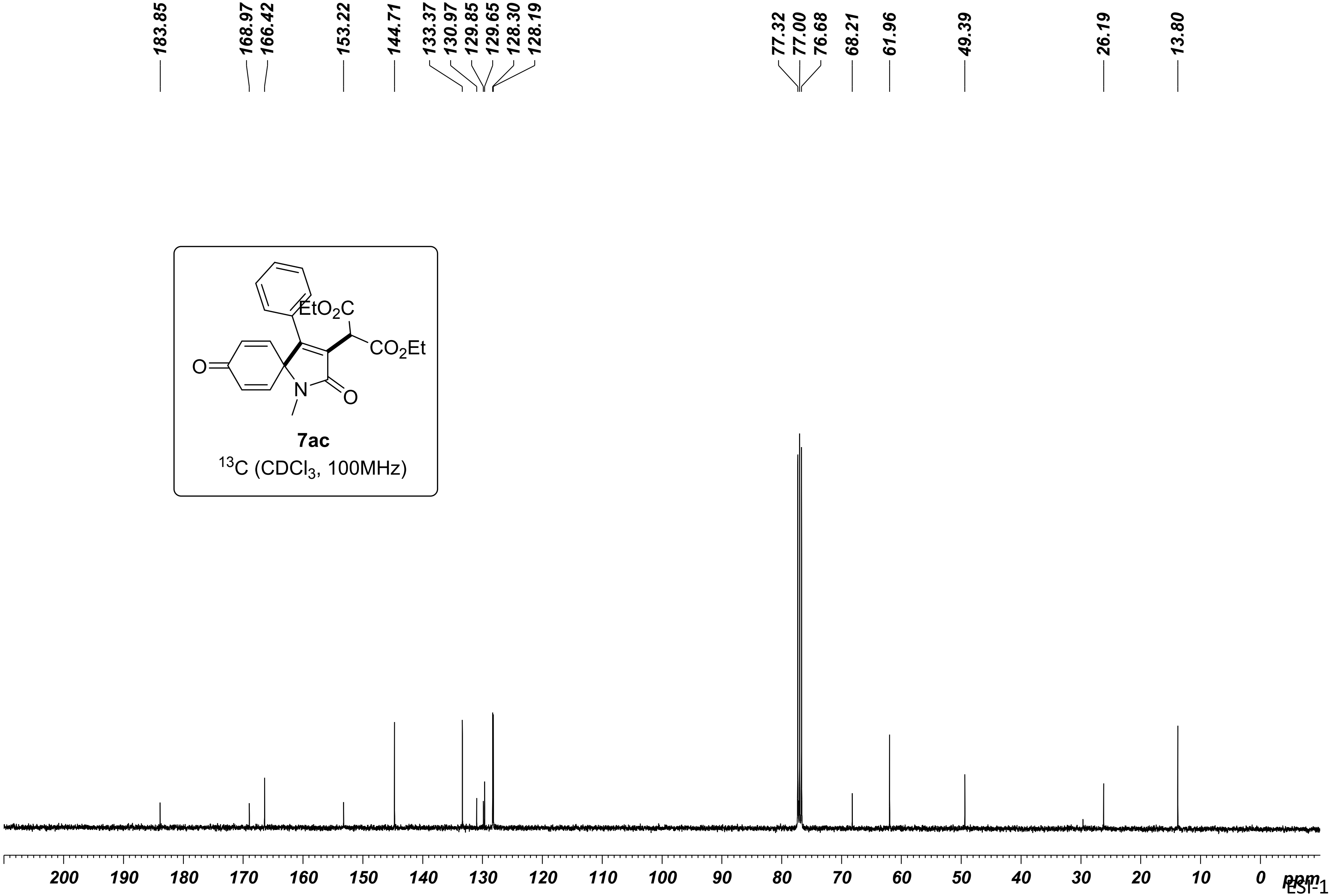
7aa

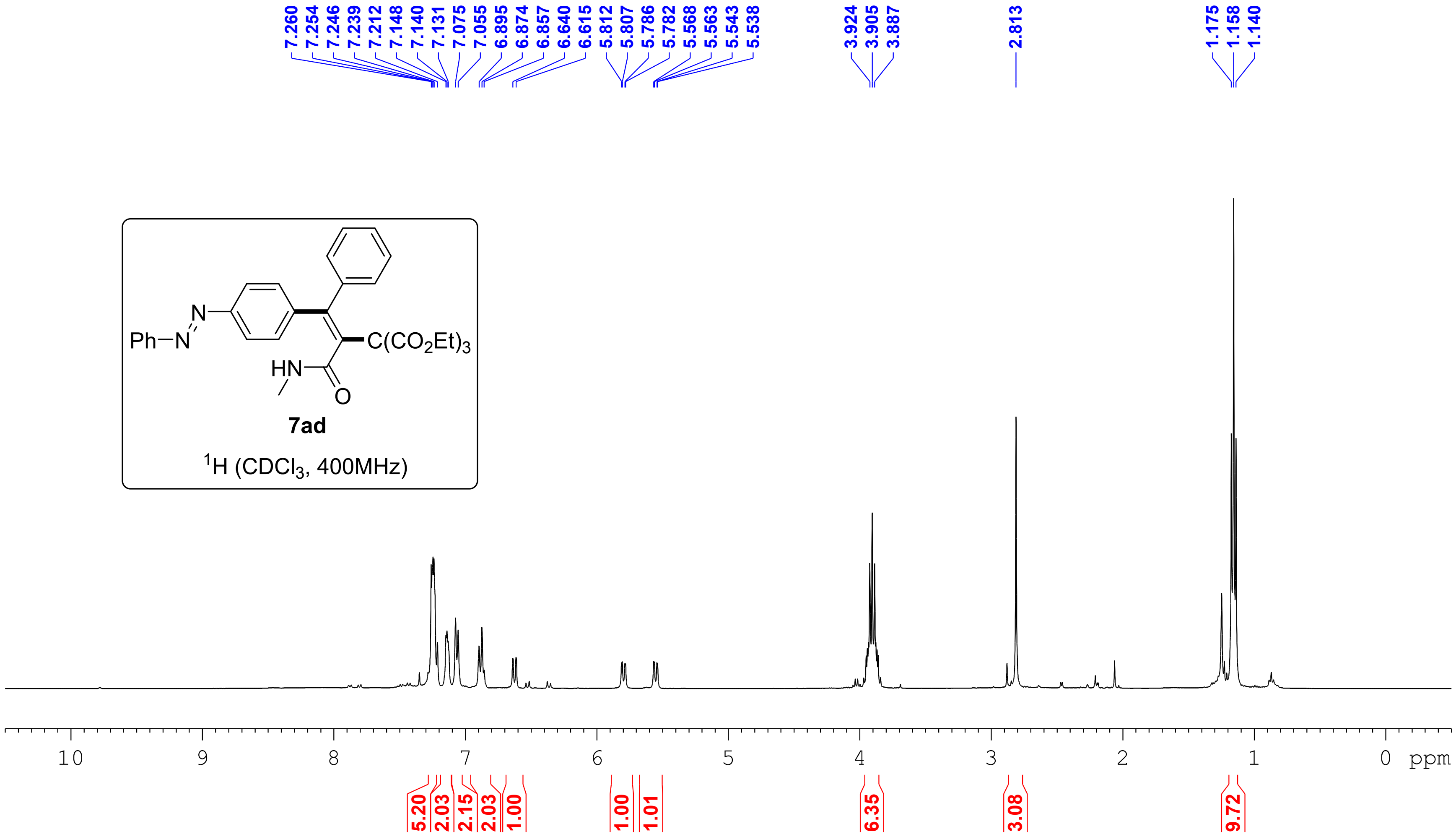
^{13}C ($CDCl_3$, 100MHz)

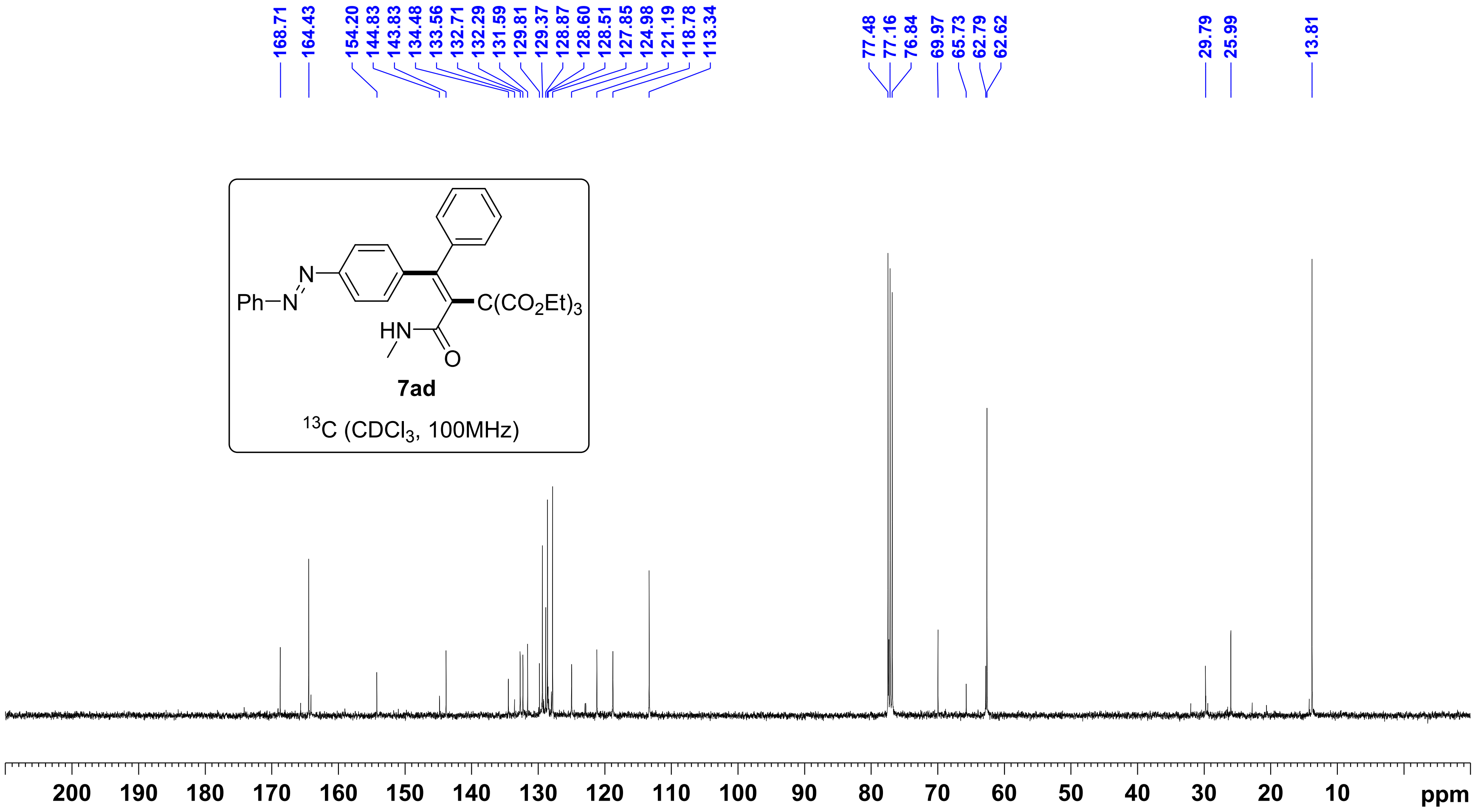

7.317
7.298
7.281
7.262
7.247
7.240
7.229
7.199
7.128
7.125
7.109
7.105
6.490
6.485
6.469
6.464
6.392
6.371
6.366
4.093
4.075
4.057
4.039
3.302
2.834
1.189
1.185
1.172
-0.000
O
N
O
CO$_2$Et
7ab
^{1}H (CDCl$_3$, 400MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
3.12
2.21
2.15
2.11
2.00
2.01
3.06
3.49


184.21
170.11
169.82
152.48
145.40
144.26
133.32
131.73
130.81
129.74
128.81
128.06
77.48
77.16
76.84
67.89
63.03
61.42
32.04
30.80
29.81
29.48
26.15
22.81
14.25
14.20
O
N
O
CO_2Et
7ab
^{13}C ($CDCl_3$, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.364
7.361
7.346
7.329
7.325
7.318
7.299
7.287
7.282
7.278
7.269
7.190
7.173
7.169
6.573
6.548
6.439
6.414
4.596
4.050
4.032
4.023
4.014
4.005
3.997
3.987
3.979
3.970
3.961
3.952
3.943
3.934
3.916
2.909
1.200
1.182
1.164
-0.000
EtO2C
CO2Et
O
N
O
7ac
1H (CDCl3, 400MHz)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.15
2.00
2.07
2.03
0.92
4.15
3.11
6.10

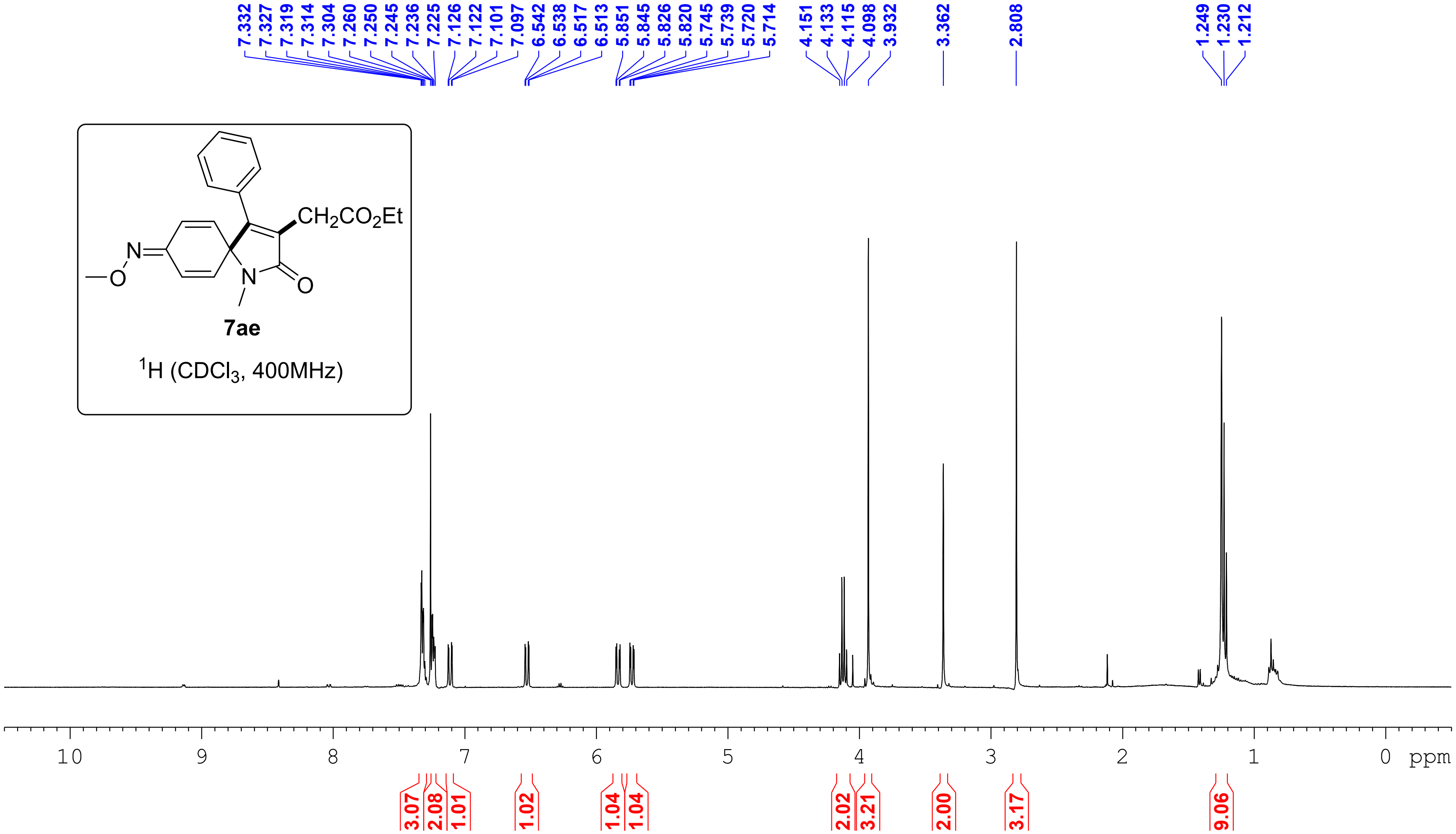

183.85
168.97
166.42
153.22
144.71
133.37
130.97
129.85
129.65
128.30
128.19
77.32
77.00
76.68
68.21
61.96
49.39
26.19
13.80
EtO₂C
CO₂Et
O
N
O
7ac
¹³C (CDCl₃, 100MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.260
7.254
7.246
7.239
7.212
7.148
7.140
7.131
7.075
7.055
6.895
6.874
6.857
6.640
6.615
5.812
5.807
5.786
5.782
5.568
5.563
5.543
5.538
3.924
3.905
3.887
2.813
1.175
1.158
1.140
Ph–N=N
HN
O
C(CO2Et)3
7ad
1H (CDCl3, 400MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
5.20
2.03
2.15
2.03
1.00
1.00
1.01
6.35
3.08
9.72



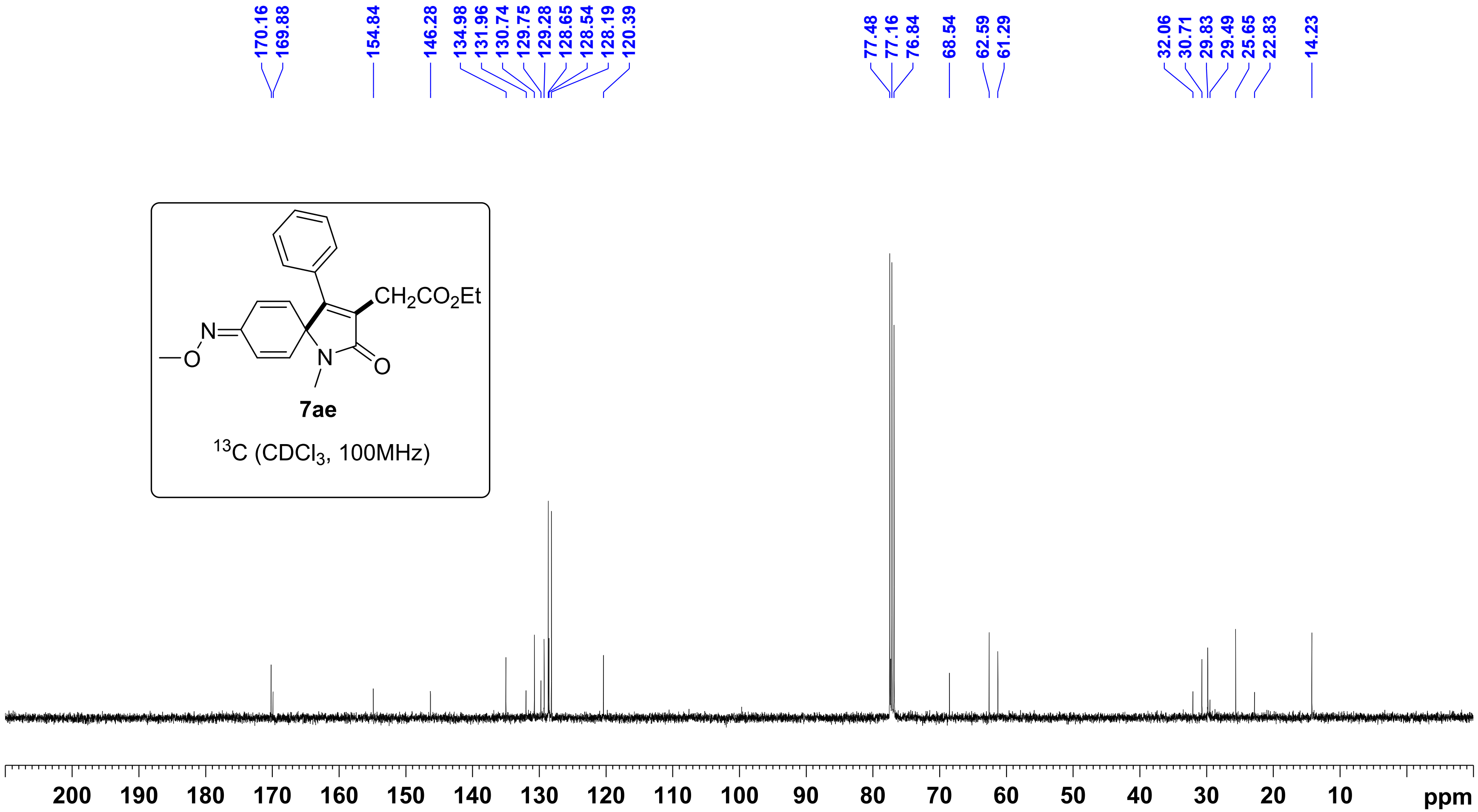
7ad

^{13}C (CDCl$_3$, 100MHz)



7ae

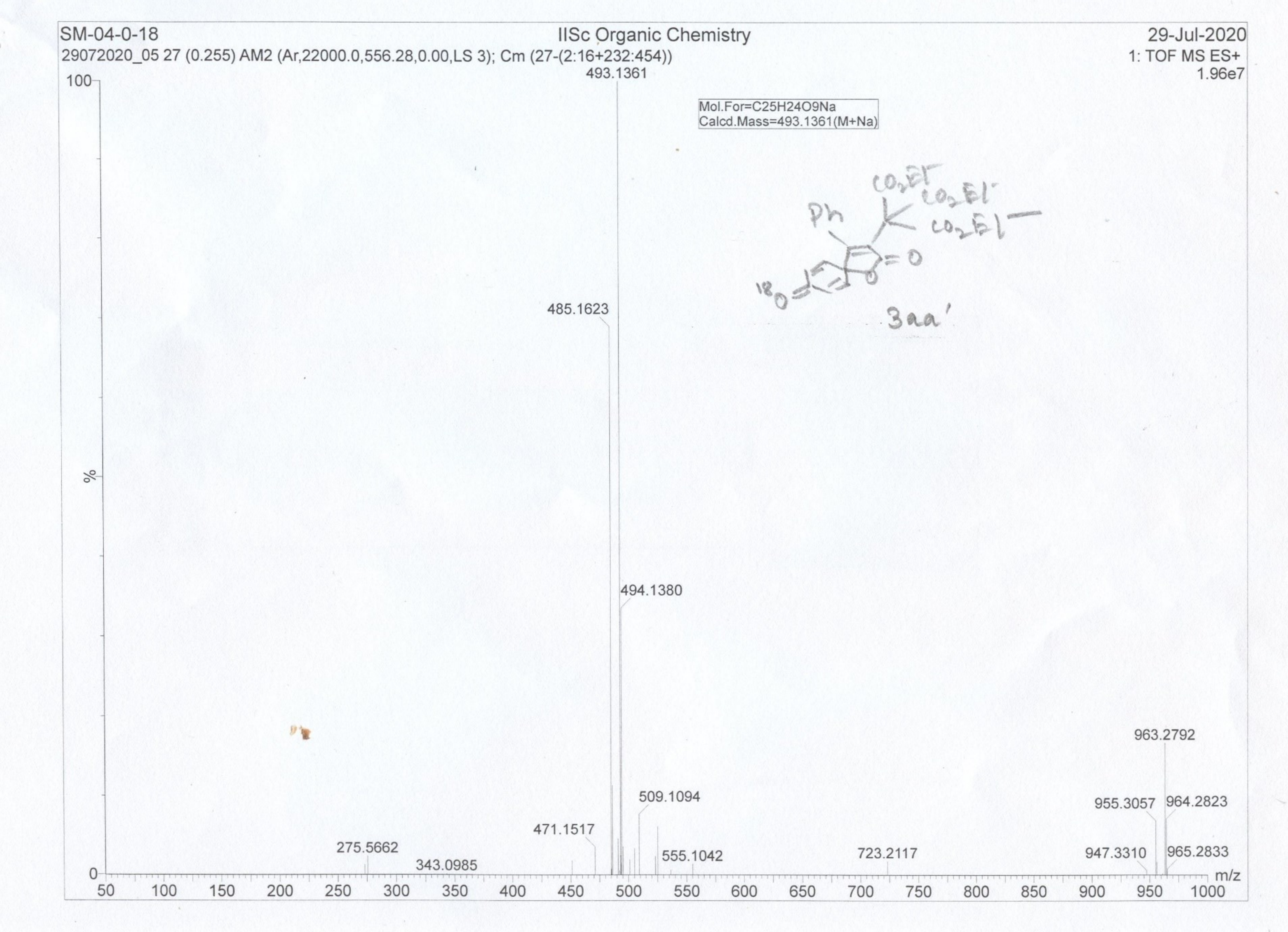
^{1}H (CDCl$_3$, 400MHz)

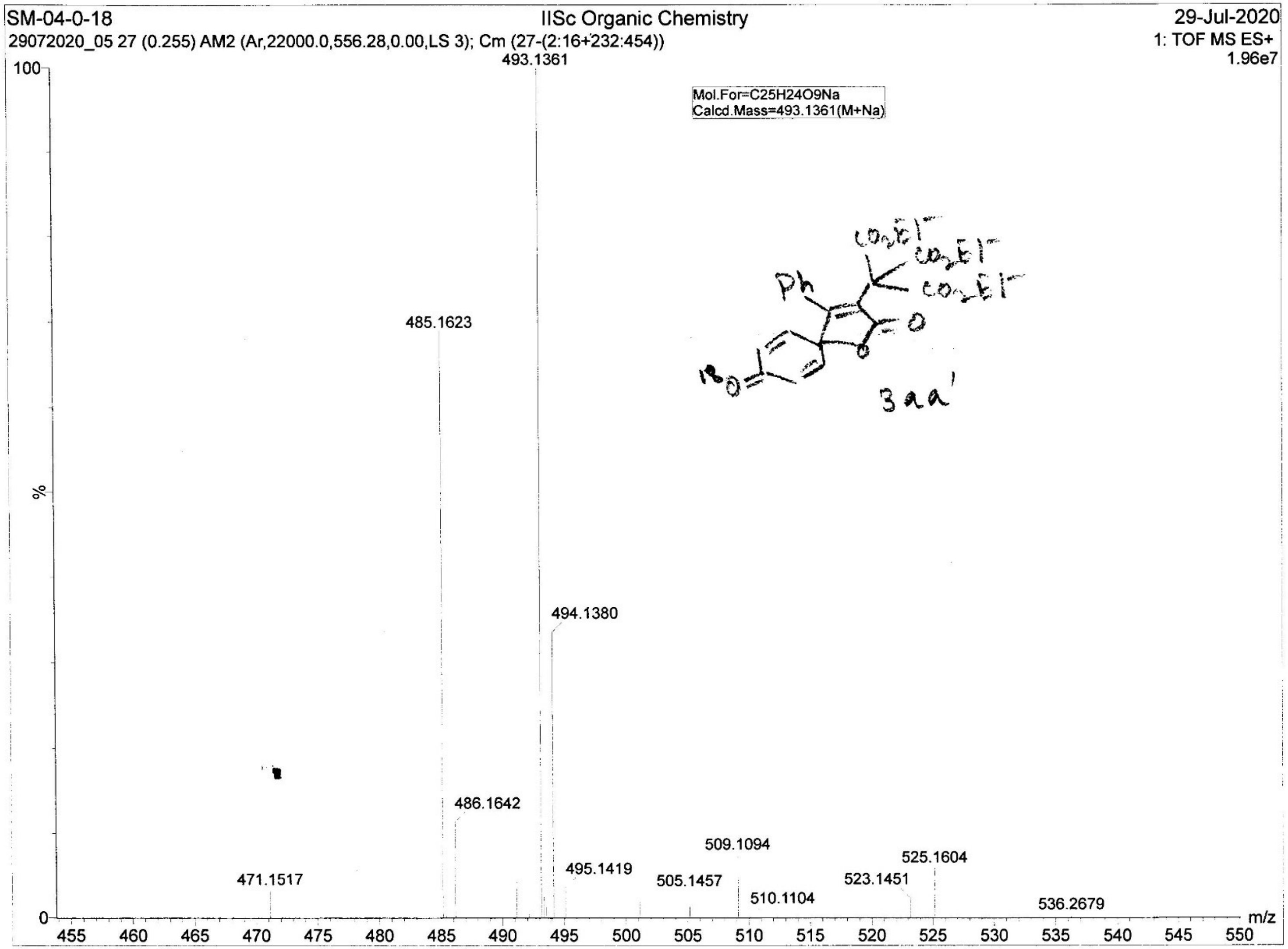


7ae

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

11. Mass spectrum of ^{18}O labelled compound **3aa’**




SM-04-0-18
IISc Organic Chemistry
29-Jul-2020
29072020_05 27 (0.255) AM2 (Ar,22000.0,556.28,0.00,LS 3); Cm (27-(2:16+232:454))
1: TOF MS ES+
1.96e7
Mol.For=C25H24O9Na
Calcd.Mass=493.1361(M+Na)
Ph
CO2Et
CO2Et
CO2Et
O
18O
3aa'
100
%
0
493.1361
485.1623
494.1380
486.1642
471.1517
495.1419
505.1457
509.1094
510.1104
523.1451
525.1604
536.2679
455
460
465
470
475
480
485
490
495
500
505
510
515
520
525
530
535
540
545
550
m/z