Supplementary Information

Proline-catalyzed synthesis of α-substituted (*E*)-α,β-unsaturated aldehydes from epoxides

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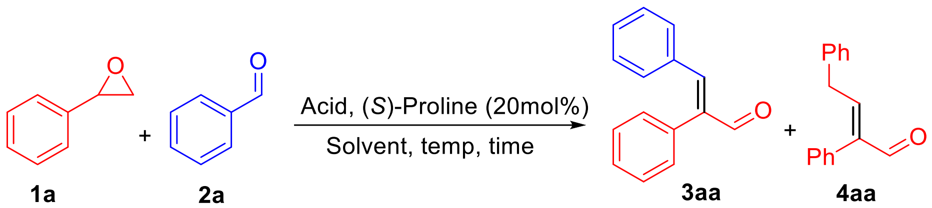
1. General information: All the chemicals and solvents were used as received without further purification from Merck, Spectrochem and TCI. Organic extracts were dried over anhydrous sodium sulfate. Progress of the reactions was monitored by TLC using precoated aluminum plates of Merck Kieselgel 60 F254. An oil bath was used for heating. Organic extracts were dried over anhydrous sodium sulfate. Column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate/n-hexane. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in $CDCl_3$ (unless otherwise mentioned) on JEOL ECS and Brucker operating at 500/126 MHz and 600/151 MHz, respectively. Chemical shifts are reported in δ (ppm), referenced to TMS and were reported as s (singlet), d (doublet), t (triplet), q (quadruple), dd (doublet of doublet), m (multiplet) etc. The coupling constants *J*, are reported in Hertz (Hz). Mass spectra were recorded on SCIEX X500R QTOF (TOF-MS).

2. Optimization: Table S1: Screening of acid catalysis and solvent in the presence of (*S*)-proline**.**

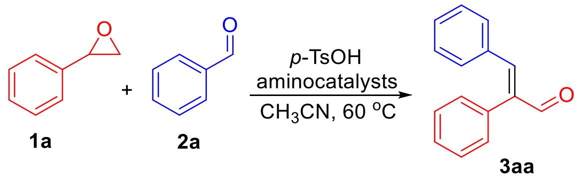


Sr. No.	Acid (1.0 equiv)	Solvent	benzaldehyde 2a (*x* equiv)	temp. (ºC)	time (h)	yield[b] of 3aa (%)	yield[b] of 4aa (%)
1.	TfOH	HFIP	1	rt	12	0	0
2.	TfOH	HFIP	1	45	12	0	0
3.	TfOH	toluene	1	rt	12	0	0
4.	TfOH	toluene	1	45	5	30	15
5.	TfOH	toluene	1	60	5	37	20
6.	TfOH	THF	1	60	5	40	17
7.	TfOH	1,4-dioxane	1	60	5	30	trace
8.	TfOH	DCM	1	60	5	0	0
9.	TfOH	MeOH	1	60	5	0	0
10.	TfOH	$CHCl_3$	1	60	5	0	0
11.	TfOH	DMSO	1	60	5	0	0
12.	TfOH	DMF	1	60	5	0	0
13.	TfOH	CH_3CN	1	60	5	47	22
14.	TfOH	CH_3CN	1	90	5	25	---
15.	TfOH	CH_3CN	1	rt	12	trace	0
16.	TfOH	CH_3CN	1.5	60	5	58	0
17.	TfOH	CH_3CN	1.2	60	3	60	0
18.	TfOH	CH_3CN	0.8	60	5	30	41
19.	TFA	CH_3CN	1.2	60	3	59	0
20.	MsOH	CH_3CN	1.2	60	3	34	0
21.	***p*-TsOH**	**CH_3CN**	**1.2**	**60**	**3**	**78**	**0**
22.	*p*-TsOH	THF	1.2	60	3	71	0
23.	*p*-TsOH	DCM	1.2	60	3	46	0
24.	*p*-TsOH	Toluene	1.2	60	3	70	0

General conditions: Epoxide **1a** (1.0 mmol), benzaldehyde **2a** (*x* mmol), (*S*)-proline (20 mol%) and acid (1.0 mmol) in solvent (10 mL) at a specified temp for a specified time, except otherwise noted. Isolated yields

Our investigation commenced by employing styrene oxide **1a** and benzaldehyde **2a** as the model substrates, in the presence of TfOH and (*S*)-proline as an organocatalyst (Table S1). We were delighted to achieve the expected product **3aa** with a 30% yield at 45°C in a span of 5 hours using toluene as the solvent (entry 4). Nonetheless, the aldol self-condensation product **4aa** from styrene oxide **1a** was also obtained with a 15% yield (entry 4). This encouraging result prompted us to conduct a detailed study of the reaction in order to establish the optimal reaction conditions for the synthesis of acrylaldehydes **3aa.** Evaluation of various aprotic and protic solvents at different temperatures revealed that the reaction demonstrated better yields in acetonitrile at 60 ºC (Table S1, entry 13). In order to enhance the yield of **3aa** while minimizing the formation of **4aa**, we optimized the quantity of benzaldehyde **2a**. It was ascertained that the addition of 1.2 equivalents of benzaldehyde was optimal in preventing the formation of **4aa** and the desired product **3aa** was obtained in 60% yield (Table S1, entry 17). Then, when we tested some other acids such as TFA, MsOH, and *p*-TsOH, we noticed an exciting rise in yield and the combination of *p*-TsOH in CH_3CN furnished the desired acrylaldehydes **3aa** in 78% yield at 60 ºC within 3h (Table S1, entry 21). Furthermore, we also examined the effects of different aminocatalysts, however, it was observed that apart from proline, the other tested aminocatalysts did not exhibit catalytic activity in the reactions (Table S2). Motivated by these findings, the impact of *p*-TsOH proportion and temperature was reevaluated at this stage (Table S3) and found that 0.8 eq. of *p*-TsOH at 60 °C was optimal to get the maximum yield of **3aa** in 81% yield. Therefore, 0.8 equiv of *p*-TsOH in CH_3CN at 60 °C for 3 h in the presence of 20 mol% (*S*)-proline were found to be the optimal conditions for the synthesis of acrylaldehydes **3aa** (Table S3, entry 6).

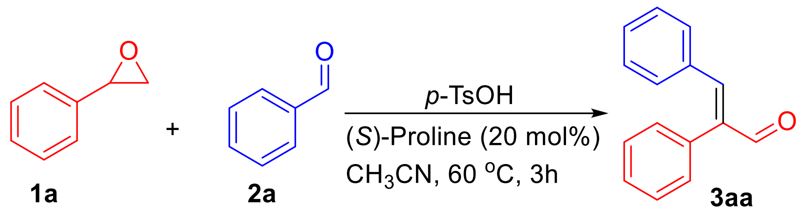
Table S2: Screening of aminocatalysts.



entry	aminocatalysts (*x* mole%)	time (h)	yield[b] of **3aa** (%)
1	Pyrrolidine (20 mol%)	3	0
2	Piperidine (20 mol%)	3	0
3	Morpholine (20 mol%)	3	0
4	Triethylamine (20 mol%)	3	0
5	Triethylamine (50 mol%)	3	0
6	Triethylamine (100 mol%)	3	0
7	Alanine (20 mol%)	3	0
8	(*S*)-proline (20 mol%)	3	78
9	(*R, S*)-proline (20 mol%)	3	76
10	(*S*)-proline (30 mol%)	3	76
11	(*S*)-proline (10 mol%)	3	64

General conditions: Epoxide **1a** (1.0 mmol), benzaldehyde **2a** (1.20 mmol), aminocatalyst (*x* mol%) and *p*-TsOH (1.0 mmol) in CH_3CN (10 mL) at 60 ºC for a specified time, except otherwise noted. Isolated yields

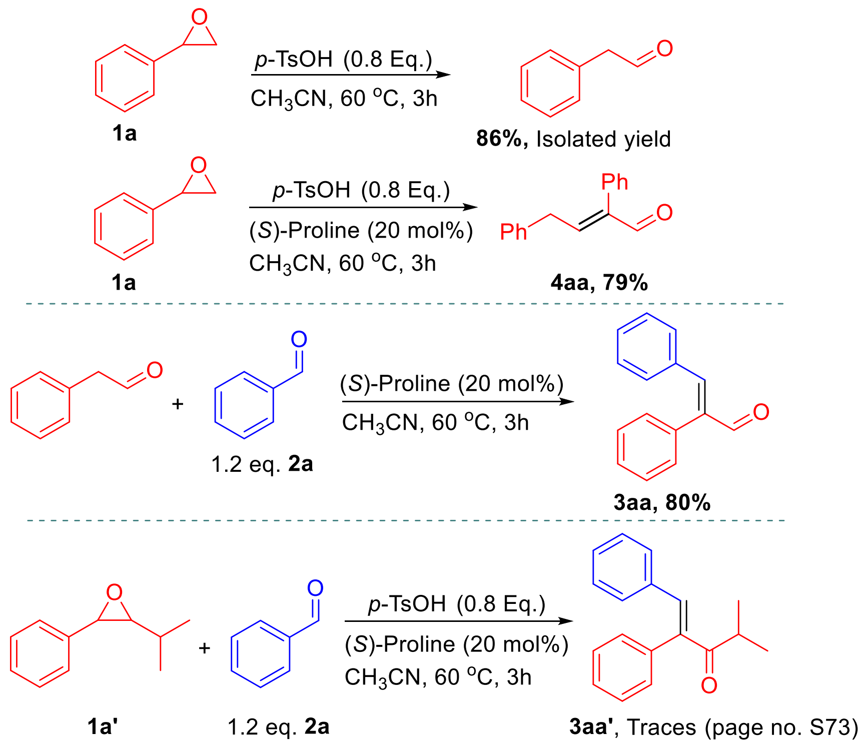
Table S3: Acid catalyst loading and temperature variations.



entry	*p*-TsOH (*x* equiv)	temp. (°C)	time (h)	yield[b] of **3aa** (%)
1	1.0	rt	12	30
2	1.0	60	3	78
3	1.0	90	3	56
4	1.0	45	3	71
5	1.5	60	3	68
6	0.8	60	3	81
7	0.5	60	3	61

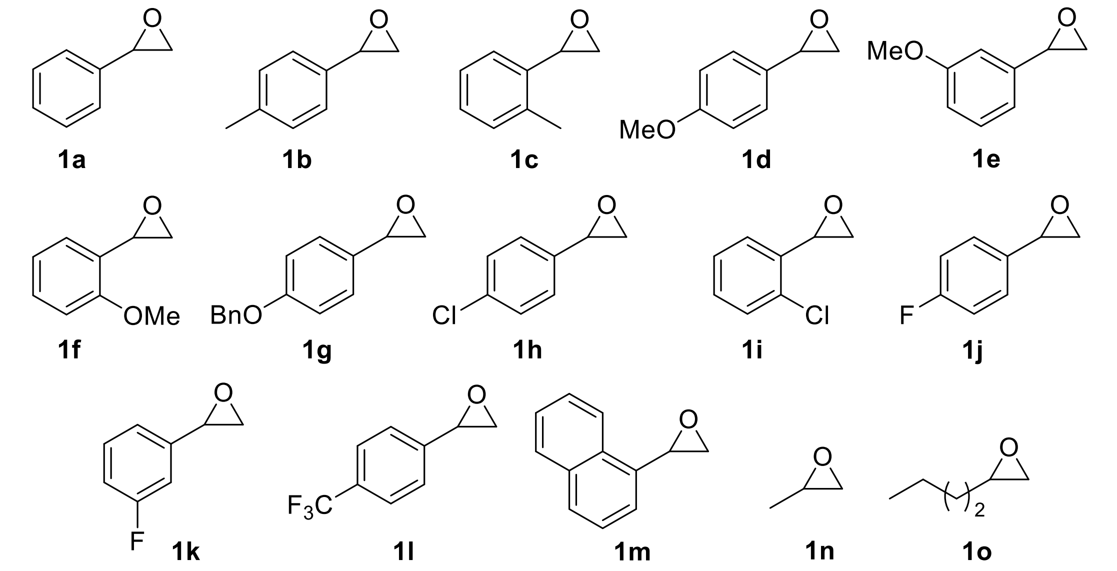
General conditions: Epoxide **1a** (1.0 mmol), benzaldehyde **2a** (1.20 mmol), (*S*)-proline (20 mol%) and *p*-TsOH (*x* mmol) in CH_3CN (10 mL) at a specified temp, for a specified time, except otherwise noted. Isolated yields

3. Control experiments:



HRMS (ESI-TOF) m/z: $[M + H]^+$
Calcd. 251.1430
Found 251.1437

4. Structures of epoxides 1 used in the study:

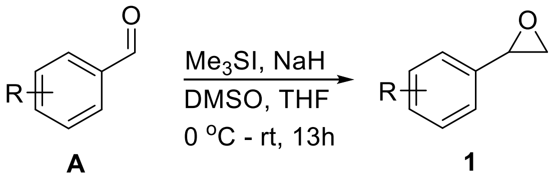


5. Experimental Section:

5.1 Synthesis of substrate epoxides, 1

1a, 1b, 1h, 1j, 1n and **1o** were purchased and used without further purification. Other epoxides were synthesized according to known literature.[1]

General procedure for the synthesis of epoxides, 1



A solution of NaH (8.80 mmol, 2.2 equiv.) and Me_3SI (8.80 mmol, 2.2 equiv.) in DMSO (7 mL) and THF (5 mL) stirred for 30 min at room temperature under N_2 atmosphere. Then a solution of aldehyde **A** (4.0 mmol, 1.0 equiv.) in THF was added dropwise at 0 ˚C. After complete addition, the mixture was warmed to room temperature and allowed to stir for 12 hours. After completion of the reaction as monitored by TLC, the reaction mixture was quenched with sat. NH_4Cl and then extracted with Et_2O (3 x 10 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 concentrated in *vacuo* and the crude products were purified by column chromatography with Et_3N to afforded the desired epoxides **1** in stated yields.

5.2 General procedure for the synthesis of compound, 3

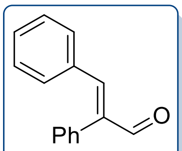
To a stirred solution of epoxide **1** (0.50 mmol, 1.0 equiv.) in CH_3CN (5 mL) were added aldehydes **2** (0.60 mmol, 1.20 equiv.), *p*-TsOH (0.40 mmol, 0.80 equiv.) and (*S*)-proline (20 mol%).

The resulting mixture was stirred at 60 °C for 3 h. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature, quenched with saturated aqueous $NaHCO_3$ and then extracted with DCM (3 x 10 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 concentrated in *vacuo* and the crude products were purified by column chromatography (silica gel, 100-200 mesh) which afforded the desired acrylaldehydes **3** in moderate to good yields.

Note: Reaction performed in a sealed tube with 1.0 mmol of acetaldehyde for the synthesis of **3at** derivative. Acrylaldehydes **3as**, **3at** and **3au** were not stable. These acrylaldehydes were converted into corresponding alcohol for analysis (After removing solvent, the reaction mixture was treated with $NaBH_4$ in MeOH at 0 ^oC).

5.3 Characterization of Compounds, 3

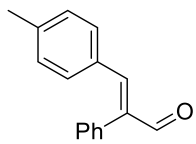
(*E*)-2,3-Diphenylacrylaldehyde, 3aa[2b]



3aa

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); White solid (84 mg, 81%); mp: 90–92 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.77 (s, 1H), 7.43–7.36 (m, 4H), 7.30–7.26 (m, 1H), 7.24–7.18 (m, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 194.0, 150.2, 141.9, 134.2, 133.5, 130.9, 130.4, 129.5, 129.0, 128.6, 128.5.

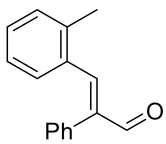
(*E*)-2-Phenyl-3-(p-tolyl)acrylaldehyde, 3ab[2e]



3ab

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); White solid (85 mg, 77%); mp: 98–100 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.74 (s, 1H), 7.42–7.35 (m, 4H), 7.19 (d, J = 6.8 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 2.30 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 194.1, 150.5, 141.2, 141.0, 133.8, 131.4, 130.9, 129.5, 129.4, 129.0, 128.4, 21.6.

(*E*)-2-Phenyl-3-(o-tolyl)acrylaldehyde, 3ac[2e]

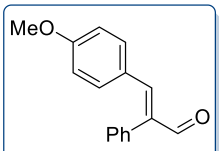


3ac

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); White solid (84 mg, 76%); mp: 97–99 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.82 (s, 1H), 7.60 (s, 1H), 7.32–7.30 (m, 3H), 7.21–7.17 (m, 4H), 6.92–6.87 (m, 2H), 2.43 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 193.9, 148.8, 142.3, 137.9, 133.4, 132.9, 130.6, 129.8, 129.74, 129.70, 128.6, 128.2, 125.7, 20.2.

(*E*)-3-(4-Methoxyphenyl)-2-phenylacrylaldehyde, 3ad[2e]

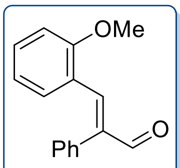
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (84 mg, 71%); mp: 140–142 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.72 (s, 1H), 7.44–7.37 (m, 3H), 7.33 (s, 1H), 7.21 (d, J = 7.4 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 194.0, 161.4, 150.3, 139.9, 133.9, 132.9, 129.5, 129.1, 128.3, 126.8, 114.2, 55.4.



3ad

(*E*)-3-(2-Methoxyphenyl)-2-phenylacrylaldehyde, 3ae

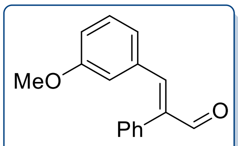
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (86 mg, 73%); mp: 142–144 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.80 (s, 1H), 7.82 (s, 1H), 7.39–7.33 (m, 3H), 7.26 (d, J = 7.2 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H), 6.89 (t, J = 9.2 Hz, 2H), 6.64 (t, J = 7.5 Hz, 1H), 3.90 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 194.3, 158.3, 145.3, 141.5, 133.6, 131.8, 130.7, 129.6, 128.8, 128.2, 123.2, 120.2, 110.9, 55.7. **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ calcd. for $C_{16}H_{14}NaO_2$ 261.0886; Found 261.0881; **IR** (KBr, cm^{-1}): 3004, 2837, 1682, 1619, 1467, 778.



3ae

(*E*)-3-(3-Methoxyphenyl)-2-phenylacrylaldehyde, 3af

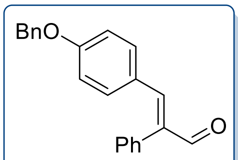
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (95 mg, 80%); mp: 145–147 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.45–7.36 (m, 4H), 7.21–7.15 (m, 3H), 6.87–6.83 (m, 2H), 6.66 (s, 1H), 3.50 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 193.7, 159.6, 149.6, 142.3, 135.5, 133.9, 129.6, 128.9, 128.4, 123.9, 117.3, 114.9, 55.0. **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ calcd. for $C_{16}H_{14}NaO_2$ 261.0886; Found 261.0880; **IR** (KBr, cm^{-1}): 3014, 2952, 2850, 1662, 1598, 1442, 789.



3af

(*E*)-3-(4-(Benzyloxy)phenyl)-2-phenylacrylaldehyde, 3ag

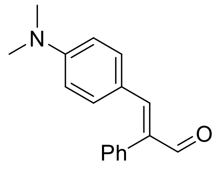
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Yellow solid (116 mg, 74%); mp: 150–152 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.72 (s, 1H), 7.44–7.32 (m, 9H), 7.20 (d, J = 7.4 Hz, 2H), 7.16 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 5.04 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 193.9, 160.6, 150.1, 140.1, 136.5, 133.9, 132.9, 129.5, 129.1, 128.8, 128.3, 127.5, 127.1, 115.0, 70.2. **HRMS** (ESI-TOF) m/z: [M + H]$^+$ calcd. for $C_{22}H_{19}O_2$ 315.1380; Found 315.1370; **IR** (KBr, cm^{-1}): 3353, 3032, 2854, 1683, 1605, 1510, 835.



3ag

(*E*)-3-(4-(Dimethylamino)phenyl)-2-phenylacrylaldehyde, 3ah

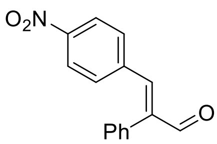
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.8/9.2); Yellow solid (92 mg, 74%); mp: 153–155 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 9.66 (s, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.37 (d, J = 7.1 Hz, 1H), 7.28 (s, 1H), 7.23 (d, J = 7.5 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.50 (d, J = 8.4 Hz, 2H), 2.98 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 193.9, 151.6, 151.5, 137.6, 134.9, 133.1, 129.7, 129.0, 127.9, 121.9, 111.5, 40.1. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{17}H_{17}NNaO$ 274.1202; Found 274.1195; **IR** (KBr, cm^{-1}): 3008, 2835, 1685, 1235, 790.



3ah

(*E*)-3-(4-Nitrophenyl)-2-phenylacrylaldehyde, 3ai[2f]

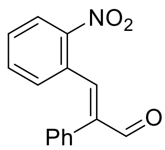
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Brown solid (107 mg, 85%); mp: 140–142 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.77 (s, 1H), 8.01 (d, J = 8.2 Hz, 2H), 7.38–7.35 (m, 4H), 7.28 (d, J = 8.4 Hz, 2H), 7.10 (dd, J = 6.0, 2.6 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 193.2, 148.1, 145.9, 144.6, 140.5, 132.3, 131.2, 129.3, 129.2, 129.1, 123.7.



3ai

(*E*)-3-(2-Nitrophenyl)-2-phenylacrylaldehyde, 3aj

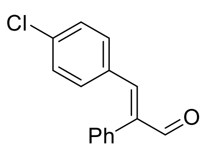
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Brown solid (106 mg, 84%); mp: 145–147 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.89 (s, 1H), 8.14 (d, J = 8.3 Hz, 1H), 7.80 (s, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.28–7.26 (m, 3H), 7.12–7.10 (m, 2H), 7.01 (d, J = 7.7 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 193.0, 148.1, 146.1, 143.2, 133.4, 131.8, 131.9, 131.1, 130.0, 129.8, 128.6, 128.5, 124.9. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{15}H_{12}NO_3$ 254.0812; Found 254.0812; **IR** (KBr, cm^{-1}): 3037, 2844, 1683, 1606, 1570, 1367, 792.



3aj

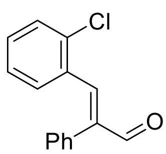
(*E*)-3-(4-Chlorophenyl)-2-phenylacrylaldehyde, 3ak[2e]

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (100 mg, 83%); mp: 152–154 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.45–7.37 (m, 3H), 7.34 (s, 1H), 7.21–7.16 (m, 4H), 7.13 (d, J = 9.0 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 193.7, 148.4, 142.3, 136.3, 133.1, 132.6, 131.9, 129.4, 129.1, 128.9, 128.7.



3ak

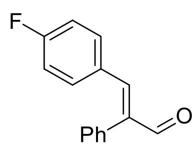
(*E*)-3-(2-Chlorophenyl)-2-phenylacrylaldehyde, 3al[2b]



3al

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (101 mg, 84%); mp: 151–153 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.72 (s, 1H), 7.43 (dd, J = 8.1, 1.0 Hz, 1H), 7.35–7.33 (m, 3H), 7.22–7.19 (m, 1H), 7.17–7.15 (m, 2H), 6.95–6.90 (m, 2H); **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$) δ: 193.7, 146.1, 143.2, 135.3, 132.8, 132.4, 131.2, 130.8, 129.9, 129.7, 128.9, 128.6, 126.5.

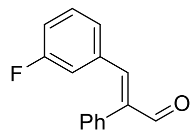
(*E*)-3-(4-Fluorophenyl)-2-phenylacrylaldehyde, 3am[2e]



3am

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); White solid (96 mg, 85%); mp: 135–137 °C; **^{1}H NMR** (600 MHz, CDCl$_3$) δ: 9.75 (s, 1H), 7.43–7.38 (m, 3H), 7.35 (s, 1H), 7.20–7.17 (m, 4H), 6.92 (t, *J* = 8.6 Hz, 2H); **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$) δ: 193.8 (s), 163.7 (d, *J* = 252.7 Hz), 148.8, 141.6, 133.3, 132.9 (d, *J* = 8.4 Hz), 130.4 (d, *J* = 2.8 Hz), 129.4, 129.1, 128.6, 115.9 (d, *J* = 22.0 Hz). **^{19}F{^{1}H} NMR** (471 MHz, CDCl$_3$) δ: –111.15.

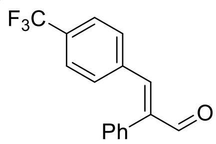
(*E*)-3-(3-Fluorophenyl)-2-phenylacrylaldehyde, 3an[2b]



3an

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); White solid (94 mg, 84%); mp: 132–134 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ: 9.78 (s, 1H), 7.44–7.38 (m, 3H), 7.35 (s, 1H), 7.24–7.16 (m, 3H), 7.02–6.97 (m, 2H), 6.85 (d, *J* = 9.5 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, CDCl$_3$) δ: 193.7, 162.5 (d, *J* = 246.4 Hz), 148.2, 142.9, 136.2 (d, *J* = 8.1 Hz), 132.9, 130.1 (d, *J* = 8.3 Hz), 129.3, 129.1, 128.9, 126.7 (d, *J* = 2.4 Hz), 117.3, 117.1 (d, *J* = 2.8 Hz), 116.9; **^{19}F{^{1}H} NMR** (471 MHz, CDCl$_3$) δ: –112.13.

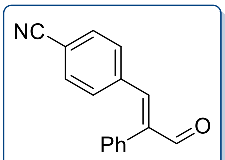
(*E*)-2-Phenyl-3-(4-(trifluoromethyl)phenyl)acrylaldehyde, 3ao[2e]



3ao

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (118 mg, 86%); mp: 122–124 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ: 9.80 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.40 (s, 4H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 6.4 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, CDCl$_3$) δ: 193.6, 147.6, 143.6, 137.6, 132.7, 131.5 (q, *J* = 32.9 Hz), 130.8, 129.3, 129.1, 128.8, 125.5 (d, *J* = 3.4 Hz), 124.9 (q, *J* = 272.4 Hz); **^{19}F{^{1}H} NMR** (471 MHz, CDCl$_3$) δ: –62.87.

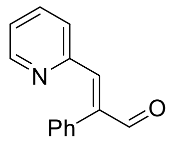
(*E*)-4-(3-Oxo-2-phenylprop-1-en-1-yl)benzonitrile, 3ap



3ap

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (94 mg, 81%); mp: 124–126 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ: 9.75 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.35–7.34 (m, 3H), 7.31 (s, 1H), 7.23–7.19 (m, 2H), 7.09 (dd, *J* = 6.4, 2.4 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, CDCl$_3$) δ: 193.3, 146.6, 144.2, 138.6, 132.4, 132.3, 130.9, 129.3, 129.2, 129.0, 118.4, 113.2. **HRMS** (ESI-TOF) m/z: [M + H]$^+$ calcd. for $C_{16}H_{12}NO$ 234.0913; Found 234.0909; **IR** (KBr, cm^{-1}): 3051, 2842, 2228, 1667, 1626, 836.

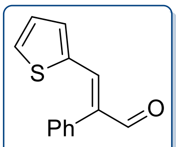
(*E*)-2-Phenyl-3-(pyridin-2-yl)acrylaldehyde, 3aq



3aq

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); White solid (84 mg, 81%); mp: 160–162 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*: 9.86 (s, 1H), 8.67 (s, 1H), 7.55 (s, 1H), 7.43–7.41 (m, 4H), 7.20–7.17 (m, 3H), 6.95 (d, *J* = 7.9 Hz, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) *δ*: 194.1, 153.6, 150.2, 149.9, 144.1, 136.0, 132.7, 129.4, 129.0, 128.9, 125.4, 123.8. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{14}H_{11}NNaO$ 232.0733; Found 232.0731; **IR** (KBr, cm^{-1}): 3058, 2926, 1778, 1688, 749.

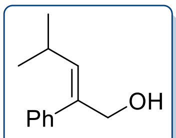
(*E*)-2-Phenyl-3-(thiophen-2-yl)acrylaldehyde, 3ar



3ar

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); Brown solid (82 mg, 77%); mp: 135–137 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 9.72 (s, 1H), 7.61 (s, 1H), 7.49–7.44 (m, 3H), 7.35 (d, *J* = 4.9 Hz, 1H), 7.25 (dd, *J* = 26.9, 5.2 Hz, 3H), 7.00 (t, *J* = 4.2 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) *δ*: 192.9, 142.3, 139.6, 138.2, 134.4, 133.1, 132.3, 129.7, 129.3, 128.9, 127.3. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{13}H_{10}NaOS$ 237.0345; Found 237.0343; **IR** (KBr, cm^{-1}): 3049, 2824, 1668, 1596, 840.

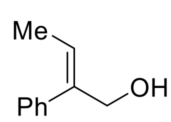
(*E*)-4-Methyl-2-phenylpent-2-en-1-ol, 3as[2d]



3as

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Colorless liquid (63 mg, 72%); **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*: 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 5.70 (d, *J* = 9.6 Hz, 0.04H, *Z*-isomer, minor), 5.51 (d, *J* = 10.1 Hz, 1H), 4.58 (s, 0.08H, *Z*-isomer, minor), 4.27 (s, 2H), 2.42–2.32 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) *δ*: 138.9, 138.0, 136.3, 128.7, 128.4, 127.2, 68.3, 27.7, 23.3. (*E/Z* isomers are inseparable through column chromatography)

(*E*)-2-Phenylbut-2-en-1-ol, 3at[2a]

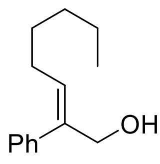


3at

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Colorless liquid (54 mg, 73%); **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*: 7.36 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.1 Hz, 2H), 5.96 (q, *J* = 6.4 Hz, 0.03H, *Z*-isomer, minor), 5.82 (q, *J* = 6.9 Hz, 1H), 4.58 (s, 0.05H, *Z*-isomer, minor), 4 .30 (s, 2H), 1.64 (t, *J* = 10.5 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) *δ*: 141.1, 138.4, 128.8, 128.4, 127.2, 123.5, 68.2, 14.5. (*E/Z* isomers are inseparable through column chromatography)

(*E*)-2-Phenyloct-2-en-1-ol, 3au[2a]

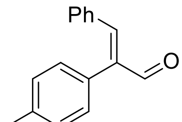
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Colorless liquid (66 mg, 65%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.35–7.32 (m, 2H), 7.28–7.24 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 5.89 (t, J = 7.5 Hz, 0.03 H, Z-isomer, minor), 5.72 (t, *J* = 7.4 Hz, 1H), 4.57 (d, J = 4.4 Hz, 0.06 H, Z-isomer, minor), 4.30 (d, *J* = 5.9 Hz, 2H), 1.99 (q, *J* = 7.4 Hz, 2H), 1.65 (t, *J* = 6.1 Hz, 1H), 1.39–1.32 (m, 2H), 1.27–1.17 (m, 4H), 0.84 (t, *J* = 6.8 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 140.2, 138.7, 129.4, 128.8, 128.4, 127.1, 68.2, 31.5, 29.6, 28.6, 22.6, 14.1. (*E/Z* isomers are inseparable through column chromatography)



3au

(*E*)-3-Phenyl-2-(p-tolyl)acrylaldehyde, 3ba[2b]

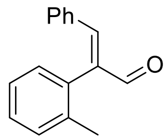
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); White solid (93 mg, 84%); mp: 100–102 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.36 (s, 1H), 7.29 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.26–7.20 (m, 6H), 7.08 (d, *J* = 7.7 Hz, 2H), 2.39 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 194.3, 150.0, 141.9, 138.3, 134.3, 130.8, 130.3, 130.2, 129.7, 129.3, 128.6, 21.5.



3ba

(*E*)-3-Phenyl-2-(o-tolyl)acrylaldehyde, 3ca[2b]

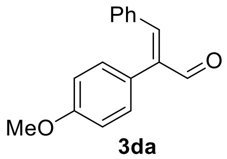
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); White solid (91 mg, 82%); mp: 99–101 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 7.46 (s, 1H), 7.35–7.27 (m, 3H), 7.26–7.20 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 1H), 2.07 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 194.0, 150.4, 141.9, 136.3, 134.3, 133.5, 130.7, 130.6, 129.2, 128.8, 128.7, 126.6, 19.6.



3ca

(*E*)-2-(4-Methoxyphenyl)-3-phenylacrylaldehyde, 3da[2g]

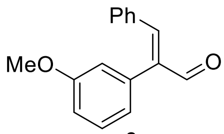
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (101 mg, 85%); mp: 138–140 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.35 (s, 1H), 7.30–7.25 (m, 5H), 7.13 (d, *J* = 7.3 Hz, 2H), 6.94 (d, *J* = 7.3 Hz, 2H), 3.84 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 194.5, 159.7, 150.1, 141.5, 134.4, 130.8, 130.2, 128.6, 125.4, 114.5, 55.4.



3da

(*E*)-2-(3-Methoxyphenyl)-3-phenylacrylaldehyde, 3ea[2b]

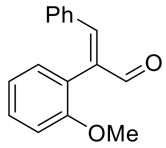
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (94 mg, 79%); mp: 145–147 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.38 (s, 1H), 7.32 (dd, *J* = 15.6, 7.6 Hz, 2H), 7.25–7.22 (m, 4H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H),



3ea

6.73 (s, 1H), 3.76 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) *δ*: 193.9, 160.1, 150.2, 141.8, 134.8, 134.0, 130.9, 130.4, 130.1, 128.6, 121.7, 114.7, 114.2, 55.3.

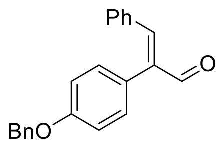
(*E*)-2-(2-Methoxyphenyl)-3-phenylacrylaldehyde, 3fa



3fa

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (98 mg, 83%); mp: 146–148 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 9.74 (s, 1H), 7.46 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.31–7.20 (m, 5H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 2H), 3.68 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) *δ*: 193.9, 157.2, 149.8, 139.0, 134.6, 130.7, 130.5, 130.2, 130.1, 128.6, 122.9, 121.3, 111.6, 55.7. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{16}H_{15}O_2$ 239.1067; Found 239.1063; **IR** (KBr, cm^{-1}): 3003, 2835, 1685, 1597, 1493, 787.

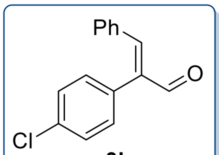
(*E*)-2-(4-(Benzyloxy)phenyl)-3-phenylacrylaldehyde, 3ga



3ga

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Yellow solid (131 mg, 84%); mp: 155–157 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 9.75 (s, 1H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (s, 2H), 7.31–7.21 (m, 5H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 5.09 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) *δ*: 194.4, 158.9, 150.1, 141.4, 136.9, 134.3, 130.8, 130.7, 130.2, 128.7, 128.6, 128.1, 127.7, 125.6, 115.4, 70.1. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{22}H_{19}O_2$ 315.1380; Found 315.1377; **IR** (KBr, cm^{-1}): 3034, 2864, 1685, 1602, 1509, 851.

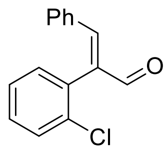
(*E*)-2-(4-Chlorophenyl)-3-phenylacrylaldehyde, 3ha[2b]



3ha

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (98 mg, 81%); mp: 146–148 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 9.75 (s, 1H), 7.44–7.36 (m, 3H), 7.33 (t, *J* = 7.1 Hz, 1H), 7.30–7.19 (m, 4H), 7.15 (d, *J* = 7.8 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) *δ*: 193.6, 150.9, 140.7, 134.5, 133.8, 131.7, 131.0, 130.8, 130.6, 129.3, 128.8.

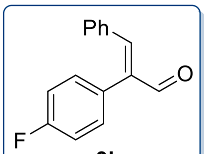
(*E*)-2-(2-Chlorophenyl)-3-phenylacrylaldehyde, 3ia[2b]



3ia

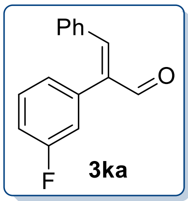
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (94 mg, 78%); mp: 140–142 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*: 9.76 (s, 1H), 7.53 (s, 1H), 7.51 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.37 (td, *J* = 7.7, 1.7 Hz, 1H), 7.32 (q, *J* = 6.7 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.12 (dd, *J* = 7.5, 1.6 Hz, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) *δ*: 192.9, 150.8, 139.7, 133.9, 133.7, 133.3, 131.1, 130.8, 130.6, 130.1, 130.0, 128.8, 127.5.

(*E*)-2-(4-Fluorophenyl)-3-phenylacrylaldehyde, 3ja[2c]


3ja

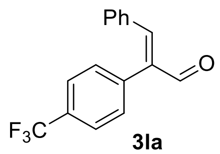
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (84 mg, 75%); mp: 128–130 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 9.76 (s, 1H), 7.40 (s, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.23–7.14 (m, 4H), 7.10 (t, *J* = 8.5 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) *δ*: 193.8, 163.8, 161.8, 150.8, 140.9, 133.9, 131.4 (d, *J* = 8.2 Hz), 130.8, 130.5, 129.1 (d, *J* = 2.7 Hz), 128.7, 116.1 (d, *J* = 21.2 Hz); **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) *δ*: –113.07.

(*E*)-2-(3-Fluorophenyl)-3-phenylacrylaldehyde, 3ka[2b]


3ka

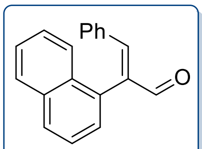
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (89 mg, 79%); mp: 131–133 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 9.75 (s, 1H), 7.42 (s, 1H), 7.38 (dd, *J* = 14.4, 7.4 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.29–7.18 (m, 4H), 7.08 (t, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 9.4 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) *δ*: 193.4, 163.1 (d, *J* = 247.0 Hz), 150.9, 140.6, 135.6 (d, *J* = 8.2 Hz), 133.7, 130.9, 130.6 (d, *J* = 11.7 Hz), 128.8, 125.3 (d, *J* = 2.5 Hz), 116.6 (d, *J* = 21.8 Hz), 115.5 (d, *J* = 21.2 Hz); **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) *δ*: –112.16.

(*E*)-3-Phenyl-2-(4-(trifluoromethyl)phenyl)acrylaldehyde, 3la[2b]


3la

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (110 mg, 80%); mp: 125–127 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 9.78 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.47 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 3H), 7.30–7.23 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) *δ*: 193.3, 151.3, 140.6, 137.3, 133.6, 130.8, 130.1, 128.9, 125.9 (d, *J* = 2.7 Hz); **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) *δ*: –62.53.

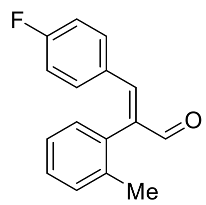
(*E*)-2-(Naphthalen-1-yl)-3-phenylacrylaldehyde, 3ma[2b]


3ma

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (98 mg, 76%); mp: 150–152 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*: 9.86 (s, 1H), 7.84 (t, *J* = 8.5 Hz, 2H), 7.64 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.48–7.44 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) *δ*: 194.1, 151.3, 140.6, 133.9, 131.9, 131.3, 131.0, 130.6, 129.0, 128.8, 128.7, 127.2, 126.7, 126.3, 125.9, 125.0.

(*E*)-3-(4-Fluorophenyl)-2-(o-tolyl)acrylaldehyde, 3cm

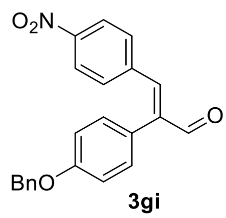
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); White solid (100 mg, 84%); mp: 153–155 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.77 (s, 1H), 7.43 (s, 1H), 7.36–7.23 (m, 3H), 7.16–7.10 (m, 2H), 7.01 (d, J = 7.5 Hz, 1H), 6.92 (t, J = 8.3 Hz, 2H), 2.07 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 193.9, 163.8 (d, J = 253.6 Hz), 148.9, 141.5, 136.3, 133.2, 132.7 (d, J = 8.4 Hz), 130.8, 130.6 (d, J = 3.2 Hz), 129.2, 128.8, 126.8, 116.0 (d, J = 21.5 Hz), 19.6.; **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ: –108.25. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{16}H_{14}FO$ 241.1023; Found 241.1021; **IR** (KBr, cm^{-1}): 3068, 2928, 1685, 1600, 1235, 835.



3cm

(*E*)-2-(4-(Benzyloxy)phenyl)-3-(4-nitrophenyl)acrylaldehyde, 3gi

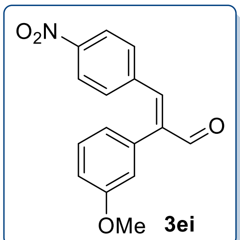
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Orange solid (161 mg, 90%); mp: 161–163 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 9.81 (s, 1H), 8.08 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.42–7.33 (m, 6H), 7.10 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 5.09 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 193.6, 159.4, 147.9, 145.7, 144.1, 140.8, 136.7, 131.1, 130.8, 128.7, 128.2, 127.7, 124.3, 123.7, 115.6, 70.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{22}H_{18}NO_4$ 360.1230; Found 360.1240; **IR** (KBr, cm^{-1}): 3037, 2858, 1676, 1593, 1341, 829.



3gi

(*E*)-2-(3-Methoxyphenyl)-3-(4-nitrophenyl)acrylaldehyde, 3ei

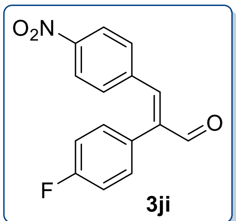
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Orange solid (120 mg, 85%); mp: 165–167 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 9.82 (s, 1H), 8.09 (d, J = 8.8 Hz, 2H), 7.43 (s, 1H), 7.41–7.31 (m, 3H), 6.96 (dd, J = 8.3, 2.2 Hz, 1H), 6.72 (dd, J = 12.8, 4.7 Hz, 2H), 3.78 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 193.1, 160.2, 148.1, 145.9, 144.5, 140.4, 133.7, 131.3, 130.5, 123.7, 121.4, 114.9, 114.5, 55.4. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{16}H_{14}NO_4$ 284.0917; Found 284.0923; **IR** (KBr, cm^{-1}): 3042, 2843, 1682, 1596, 1577, 1437, 1343, 847.



3ei

(*E*)-2-(4-Fluorophenyl)-3-(4-nitrophenyl)acrylaldehyde, 3ji

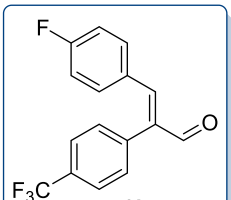
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Yellow solid (116 mg, 86%); mp: 140–142 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.83 (s, 1H), 8.11 (d, J = 7.8 Hz, 2H), 7.45 (s, 1H), 7.36 (d, J = 7.8 Hz, 2H), 7.19–7.09 (m, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 193.1, 163.2 (d, J = 249.8 Hz), 148.1, 146.6, 143.6, 140.2, 131.4 (d, J



3ji

= 8.2 Hz), 131.1, 127.9 (d, *J* = 3.2 Hz), 123.9, 116.4 (d, *J* = 21.7 Hz); **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) *δ*: –111.51. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{15}H_{11}FNO_3$ 272.0717; Found 272.0722; **IR** (KBr, cm^{-1}): 3063, 2850, 1668, 1594, 1343, 830.

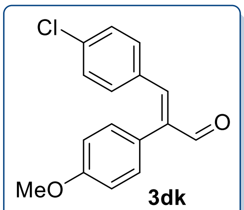
(*E*)-3-(4-Fluorophenyl)-2-(4-(trifluoromethyl)phenyl)acrylaldehyde, 3lm



3lm

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Yellow solid (104 mg, 71%); mp: 158–160 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 9.78 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.43 (s, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.24 (s, 1H), 7.04 (t, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 9.9 Hz, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) *δ*: 193.0, 162.6 (d, *J* = 247.8 Hz), 149.4, 141.5, 136.7, 135.6 (d, *J* = 8.1 Hz), 130.5 (d, *J* = 8.3 Hz), 130.0, 126.6 (d, *J* = 2.6 Hz), 126.0 (q, *J* = 7.0, Hz), 117.7 (d, *J* = 20.9 Hz), 117.1 (d, *J* = 22.3 Hz); **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) *δ*: –62.59, –111.58. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{16}H_{11}F_4O$ 295.0741; Found 295.0748; **IR** (KBr, cm^{-1}): 2957, 2850, 1682, 1323, 1129, 798.

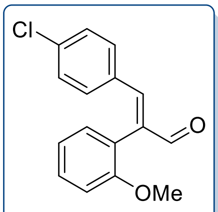
(*E*)-3-(4-Chlorophenyl)-2-(4-methoxyphenyl)acrylaldehyde, 3dk



3dk

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Yellow solid (121 mg, 89%); mp: 167–169 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*: 9.75 (s, 1H), 7.29 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.94 (d, *J* = 7.3 Hz, 2H), 3.84 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) *δ*: 194.0, 159.8, 148.1, 141.7, 136.0, 132.7, 131.8, 130.6, 128.8, 124.8, 114.5, 55.3. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{16}H_{14}ClO_2$ 273.0677; Found 273.0671; **IR** (KBr, cm^{-1}): 3003, 2836, 1685, 1596, 1460, 825, 755.

(*E*)-3-(4-Chlorophenyl)-2-(2-methoxyphenyl)acrylaldehyde, 3fk

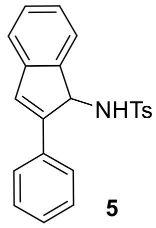


3fk

Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Yellow solid (119 mg, 88%); mp: 165–167 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*: 9.73 (s, 1H), 7.41 (s, 1H), 7.40–7.37 (m, 1H), 7.22–7.18 (m, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.04–6.97 (m, 3H), 3.69 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) *δ*: 193.6, 157.1, 147.9, 139.4, 136.2, 133.2, 131.6, 130.7, 130.4, 128.9, 122.6, 121.4, 111.6, 55.7. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{16}H_{14}ClO_2$ 273.0677; Found 273.0675; **IR** (KBr, cm^{-1}): 3024, 2834, 1671, 1605, 805, 768.

5.4 Synthesis of 4-methyl-*N*-(2-phenyl-1*H*-inden-1-yl)benzenesulfonamide, 5[3]

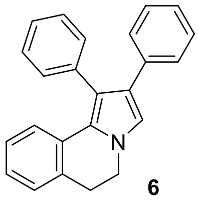
To a stirred solution of acrylaldehyde **3aa** (104 mg, 0.50 mmol, 0.50 equiv.) in toluene (3 mL) were added *p*-toluenesulfonamide (102 mg, 0.60 mmol, 1.20 equiv.) and $FeCl_3$ (33 mg, 20 mol %). The resulting mixture was stirred at 60 °C for 8 h. After completion of the reaction as monitored by TLC, the reaction mixture was quenched with H_2O and then extracted with EtOAc (3 x 10 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 concentrated in *vacuo* and then purified by column chromatography over silica gel (EtOAc:hexane, 1.5:8.5) to afford the indenamine derivative **5** (153 mg, 85%) as a white solid. mp: 144–147 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.2 Hz, 2H), 7.30 (dd, *J* = 15.4, 7.5 Hz, 4H), 7.24–7.16 (m, 6H), 7.09–7.06 (m, 1H), 6.97 (s, 1H), 5.42 (d, *J* = 9.1 Hz, 1H), 4.51 (d, *J* = 9.2 Hz, 1H), 2.49 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 146.4, 144.3, 143.8, 142.3, 138.6, 133.4, 129.9, 128.8, 128.7, 128.6, 127.9, 127.6, 127.0, 126.4, 124.8, 121.5, 59.7, 21.7.



5

5.5 Synthesis of 1,2-diphenyl-5,6-dihydropyrrolo[2,1-a]isoquinoline, 6[4]

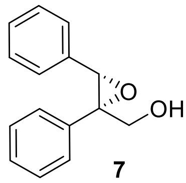
To a stirred solution of acrylaldehyde **3aa** (104 mg, 0.50 mmol, 0.50 equiv.) in toluene (3 mL) were added 1,2,3,4-tetrahydroisoquinoline (133 mg, 1.0 mmol, 2.0 equiv.) and TfOH (75 mg, 0.50 mmol, 1.0 equiv.). The resulting mixture was stirred at 130 °C for 5 h. After completion of the reaction as monitored by TLC, the reaction mixture was concentrated in *vacuo* and then purified by column chromatography over silica gel (EtOAc:hexane, 0.2:9.8) to afford the isoquinolines: derivative **6** (138 mg, 86%) as a white solid. mp: 50–52 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.32–7.26 (m, 5H), 7.15 (t, *J* = 6.8 Hz, 3H), 7.11–7.14 (m, 3H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.86 (s, 1H), 4.09 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 6.5 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 136.7, 135.7, 131.9, 131.1, 129.7, 128.7, 128.2, 128.1, 128.0, 126.8, 126.3, 125.6, 125.5, 124.8, 124.2, 120.5, 119.1, 44.7, 30.2.



6

5.6 Synthesis of ((2*S*,3*S*)-2,3-diphenyloxiran-2-yl)methanol, 7[5]

To a stirred solution of acrylaldehyde **3aa** (208 mg, 1.0 mmol, 1.0 equiv.) in $CHCl_3$ (10 mL) at 4 °C was added (*R*)-*α,α*-diphenylprolinol trimethylsilyl ether (65 mg, 0.20 mmol, 20 mol%), followed by 35% aq. H_2O_2 (0.15 mL, 1.50 mmol, 1.50 equiv.) addition and the reaction mixture was stirred for 16 h. After completion of the reaction as monitored by TLC, the reaction mixture was quenched with water and then extracted with DCM (3 x 10 mL). The organic layer was washed with brine, dried over Na_2SO_4 (anhyd.), concentrated in *vacuo* for the next step without further purification.

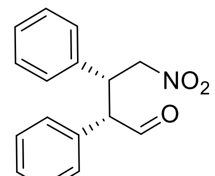


7

To a stirred solution of above synthesized crude product in MeOH at 0 °C was added $NaBH_4$ (19.0 mg, 0.50 mmol, 0.5 equiv.) and the reaction mixture was stirred for 0.5 h. After completion of the

reaction as monitored by TLC, the reaction mixture was quenched with aq. saturated NH_4Cl and then extracted with DCM (3 x 10 mL). The organic layer was washed with brine, dried over over anhydrous Na_2SO_4, concentrated in *vacuo* and then purified by column chromatography over silica gel (EtOAc:hexane, 1.0:9.0) to afford the epoxy alcohol **7** (189 mg, 84%) with ≥97% ee as a colourless oil. $[\alpha]_D^{25}$ −49.4 (*c* 2.4, $CHCl_3$); [lit.[6] $[\alpha]_D^{25}$ −49.6 (*c* 2.4, $CHCl_3$]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.20 (s, 5H), 7.13–7.09 (m, 3H), 7.04–7.02 (m, 3H), 4.51 (s, 1H), 4.04 (s, 2H), 2.02 (s, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 134.9, 134.5, 128.2, 128.02, 127.9, 127.8, 127.7, 126.7, 69.2, 65.1, 60.9.
The enantiomeric purity was determined by HPLC analysis (chiral column-Chiralcel AD-H, 4.6 x 250 mm; 25 °C; mobile phase hexane/EtOH, 8.5:1.5; flow rate 1 mL/min; PDA detection at 225 nm): minor (2*R*, 3*R*) enantiomer: *t*R = 10.24 min, major (2*S*, 3*S*) enantiomer: *t*R = 11.52 min.

5.7 Synthesis of 4-nitro-2,3-diphenylbutanal, 8[7]



8

To a stirred solution of acrylaldehyde **3aa** (208 mg, 1.0 mmol, 1.0 equiv.) in MeOH (5 mL) was added (*R*)-diphenylprolinol silyl ether (65 mg, 0.20 mmol, 20 mol%), PhCOOH (12.2 mg, 0.10 mmol, 10 mol%) and nitromethane (0.16 mL, 3.0 mmol, 3.0 equiv.) at the room temperature, and the reaction mixture was stirred for 24 h. After completion of the reaction as monitored by TLC, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and then extracted with EtOAc (3 x 10 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. ^{1}H NMR of the crude mixture showed a dr (*anti:syn*) = 87:13 and the chiral HPLC showed er (*anti*) = 86:14. After column chromatography (EtOAc:hexane, 0.5:9.5), the major (*anti:* determined by comparison with known literature data[7]) isomer of Michael product **8** was isolated as a white solid (71%, 190 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 9.55 (s, 1H), 7.44 (t, *J* = 7.0 Hz, 2H), 7.41–7.38 (m, 1H), 7.34 (t, *J* = 6.9 Hz, 2H), 7.31–7.25 (m, 5H), 4.49 (t, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 14.5 Hz, 1H), 4.31 (t, *J* = 10.3 Hz, 1H), 4.07 (d, *J* = 10.5 Hz, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 196.9, 137.2, 132.5, 129.9, 129.5, 129.2, 129.1, 128.3, 128.2, 78.5, 61.8, 44.5.
The enantiomeric purity was determined by HPLC analysis of the corresponding alcohol (chiral column-Chiralcel AD-H, 4.6 x 250 mm; 25 °C; mobile phase hexane/EtOH, 9.0:1.0; flow rate 1 mL/min; PDA detection at 220 nm): minor enantiomer: *t*R = 12.58 min, major enantiomer: *t*R = 27.59 min.

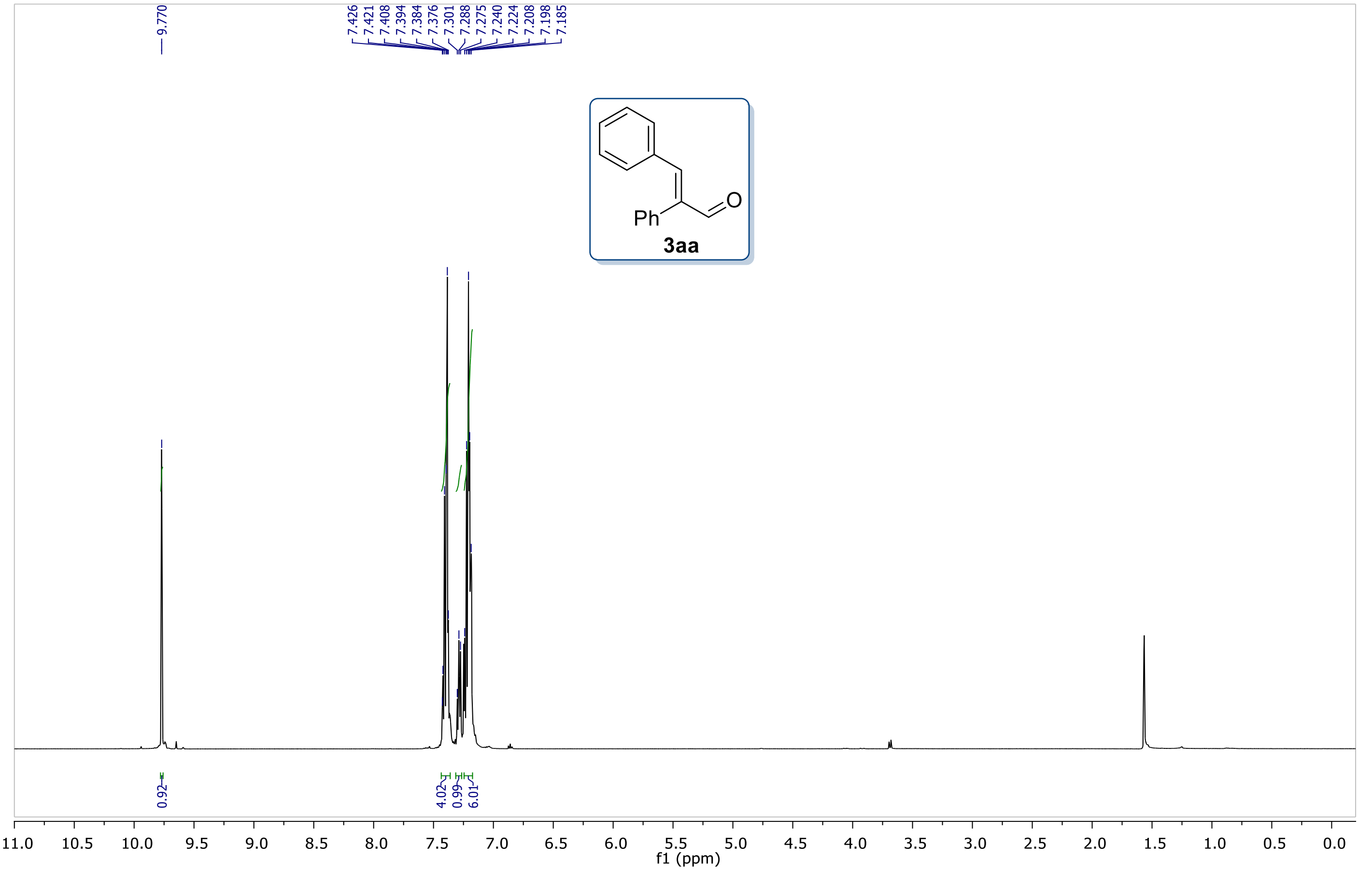
6. References:

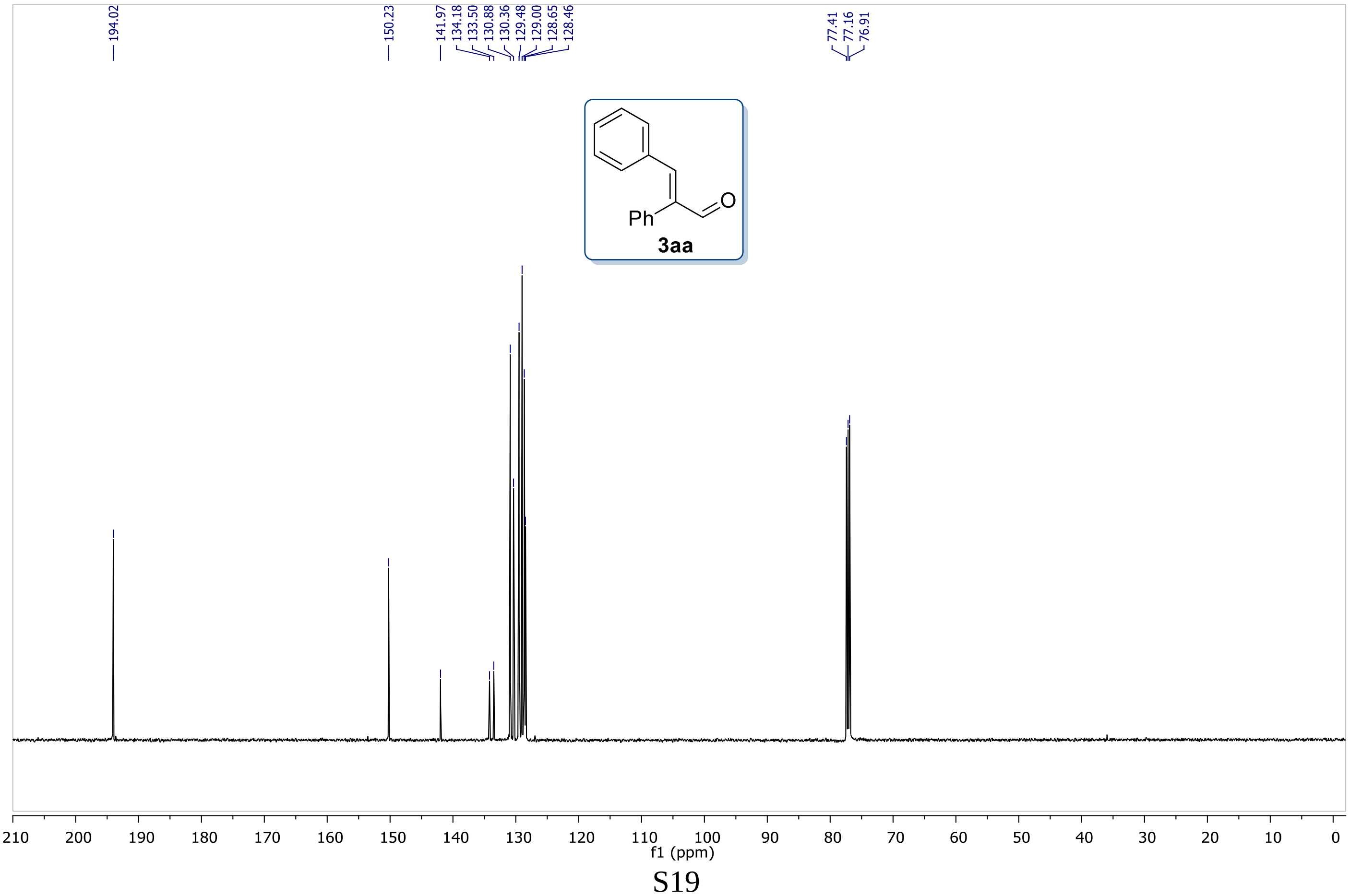
1. J. Qu, Z. Yan, X. Wang, J. Deng, F. Liu and Z. -Q. Rong, *Chem. Commun.*, 2022, **58**, 9214.
2. (a) Q. Zeng, F. Gao, J. Benet-Buchholz and A. W. Kleij, *ACS Catal.*, 2023, **13**, 7514; (b) S. Yuan, G. Gao, L. Wang, C. Liu, L. Wan, H. Huang, H. Geng and M. Chang, *Nat. Commun.*, 2020, **11**, 621; (c) X. -L. Zhang, G. -F. Pan, X. -Q. Zhu, Y. -R. Y. -R. Guo, Gao and Y. -Q. Wang, *Org.*

Lett., 2019, **21**, 2731; (d) Y. Wang, Z. Shao, K. Zhang and Q. Liu, *Angew. Chem. Int. Ed.*, 2018, **57**, 15143; (e) P. Gandeepan, P. Rajamalli and C. -H. Cheng, *ACS Catal.*, 2014, **4**, 4485; (f) W. Zhang, F. Ning, L. Varadi, D. E. Hibbs, J. A. Platts, M. Nyerges, R. J. Anderson and P. W. Groundwater, *Tetrahedron.*, 2014, **70**, 3621; (g) P. Wang, H. Rao, F. Zhou, R. Hua, C. -J. Li, *J. Am. Chem. Soc.*, 2012, **134**, 16468.

3. X. Fan, H. Lv, Y. -G. Guan, X. -M. Cui and K. Guo, *Chem. Commun.*, 2014, **50**, 4119.
4. G. -Q. Hou, W. Zhao, C. Deng, C. Dong, C. W. L. Liu and J. Li, *ACS Omega*, 2022, **7**, 37050.
5. W. Zhang, A. Basak, Y. Kosugi, Y. Hoshino and H. Yamamoto, *Angew. Chem. Int. Ed.*, 2005, **44**, 4389.
6. Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765.
7. N. Mase, K. Watanabe, H. Yoda, K. Takabe, F. Tanaka and C. F. Barbas, *J. Am. Chem. Soc.*, 2006, **128**, 4966.

^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3aa**





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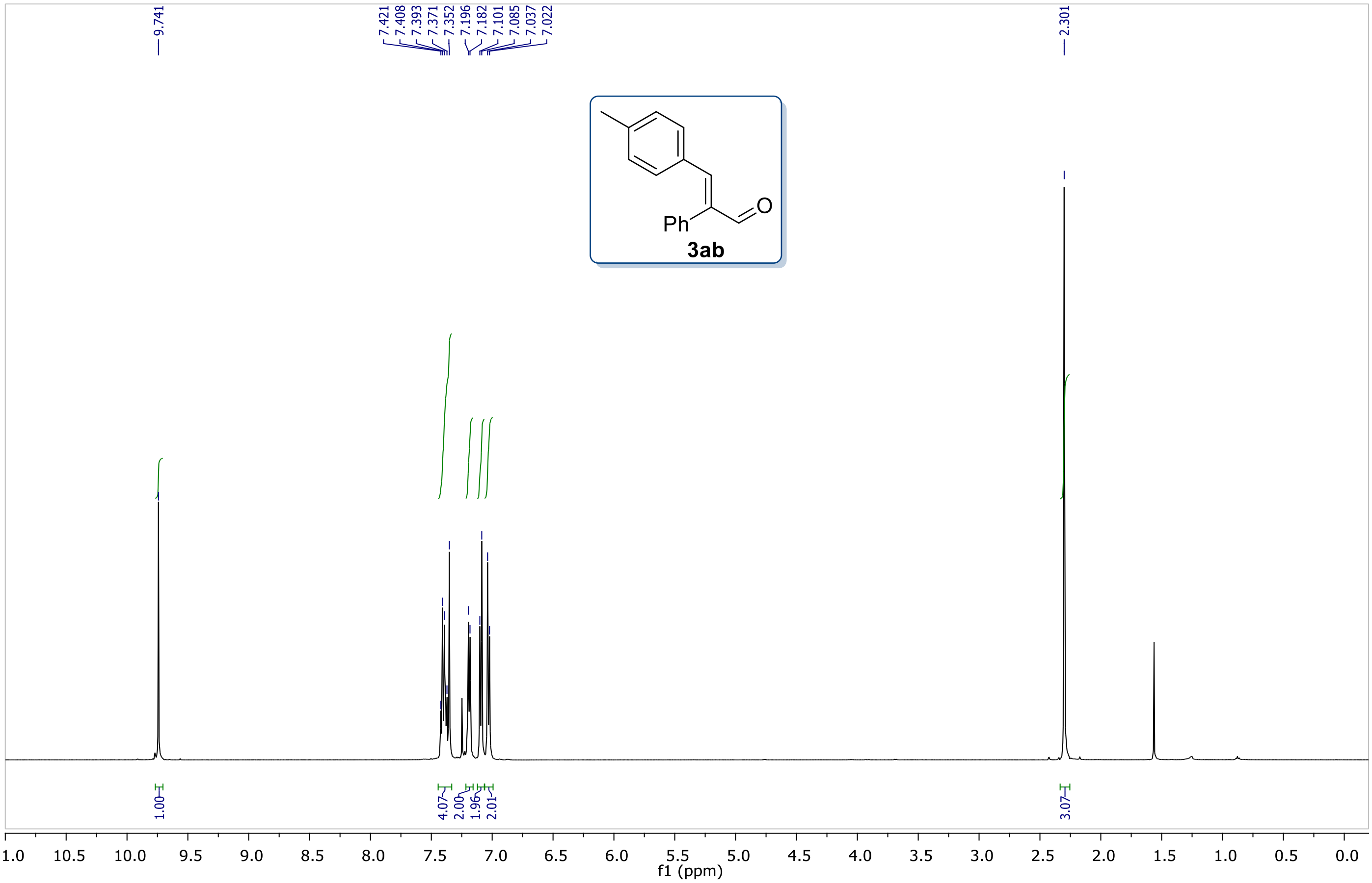

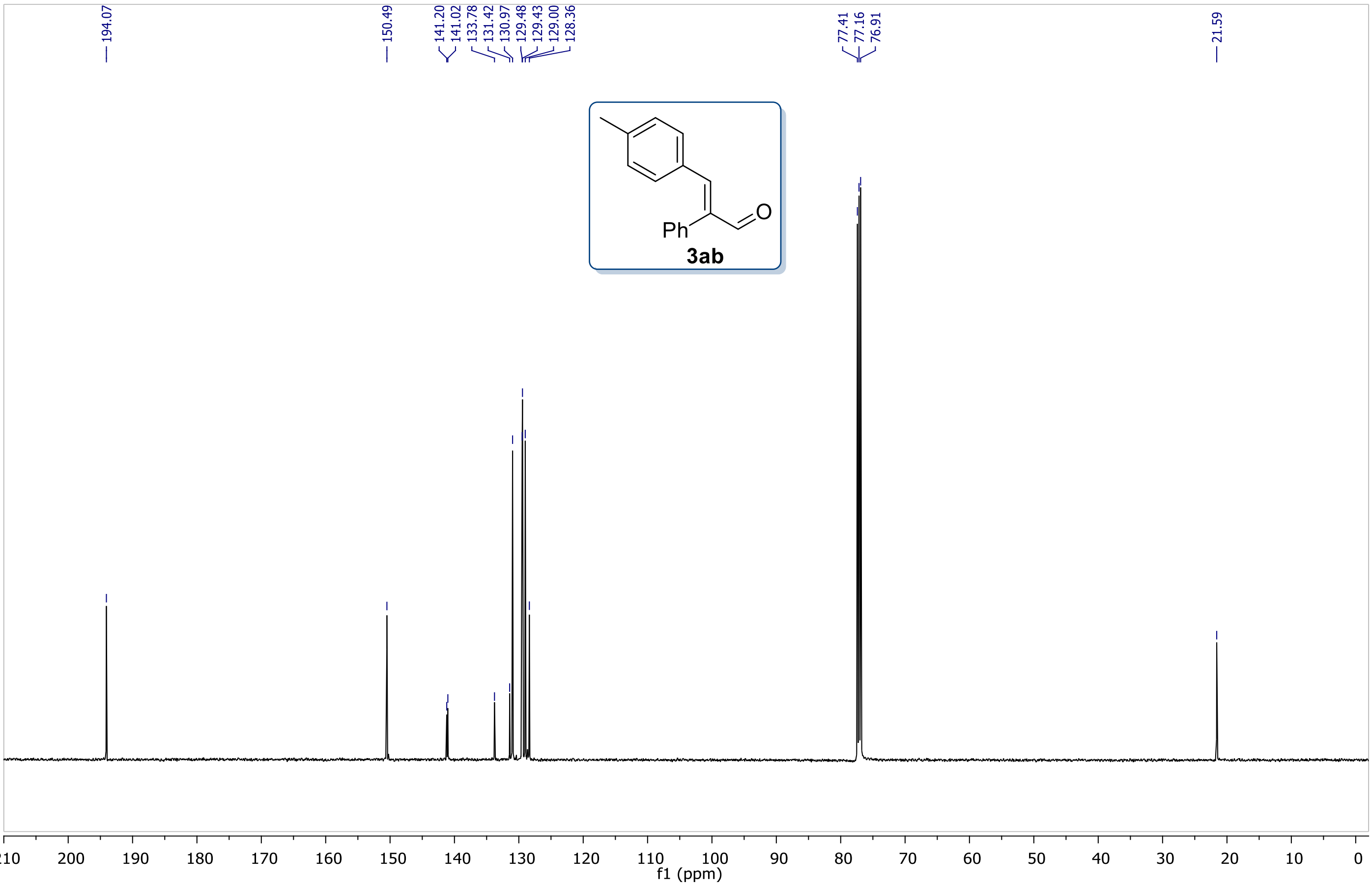

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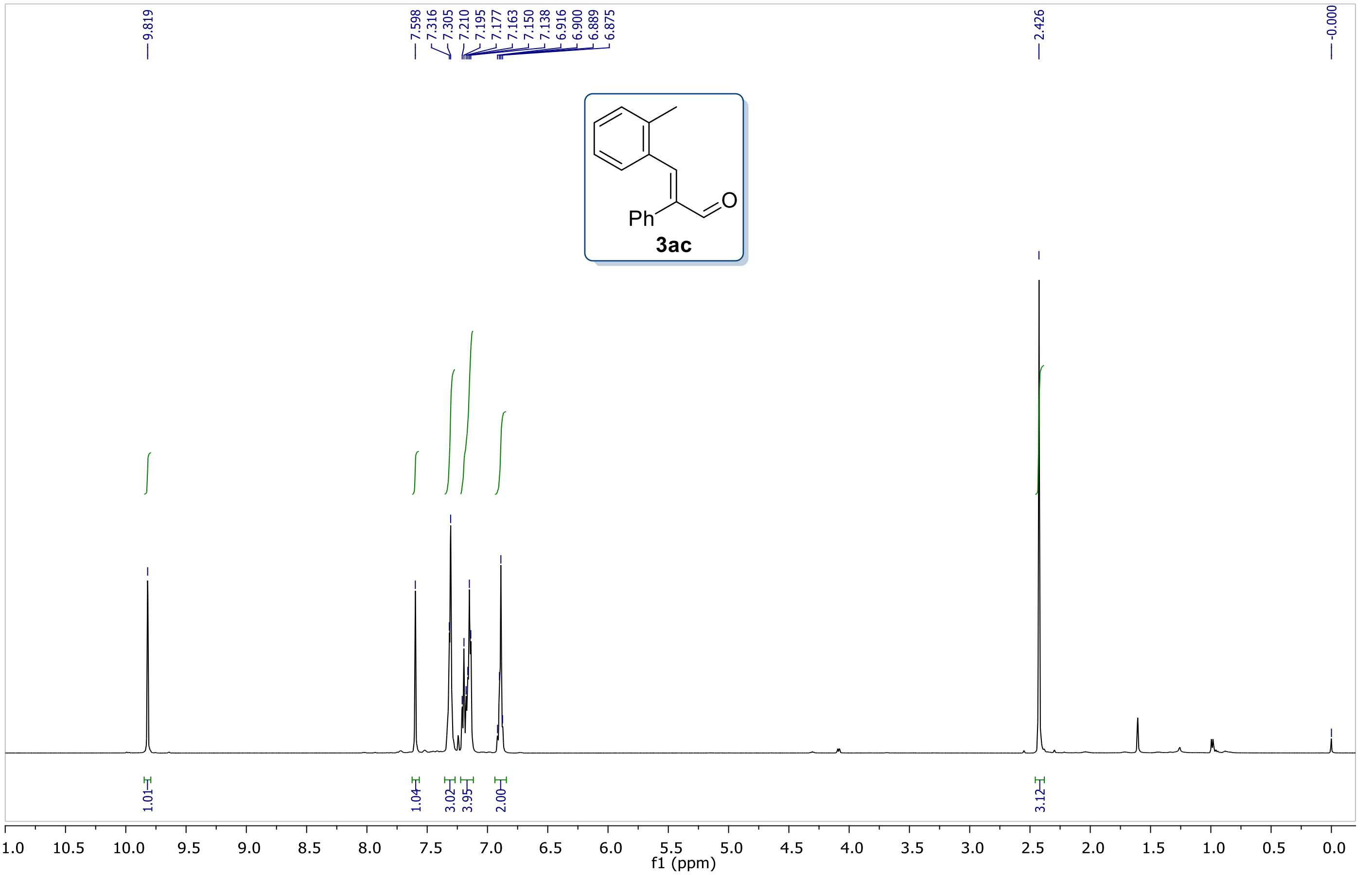

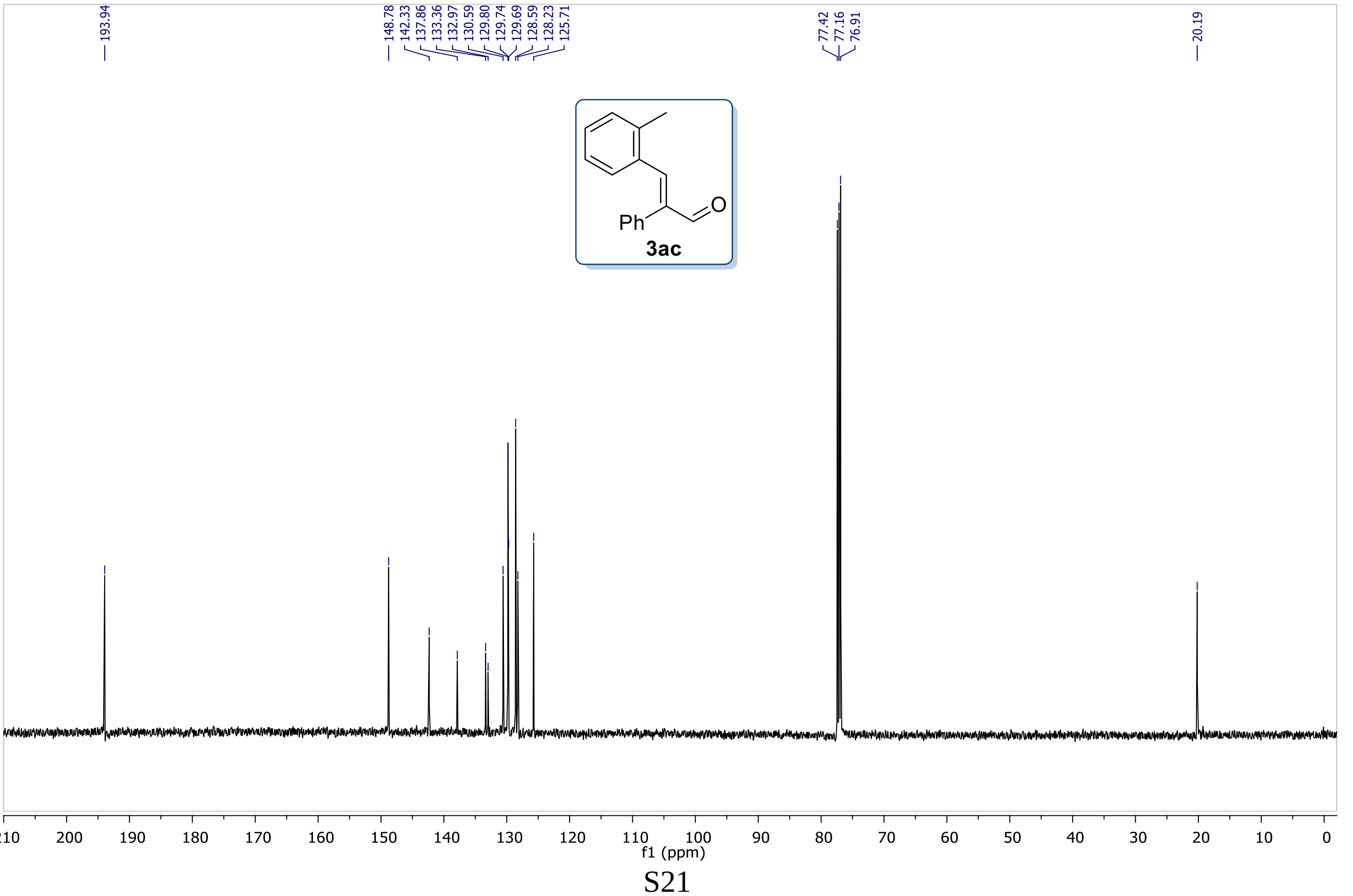

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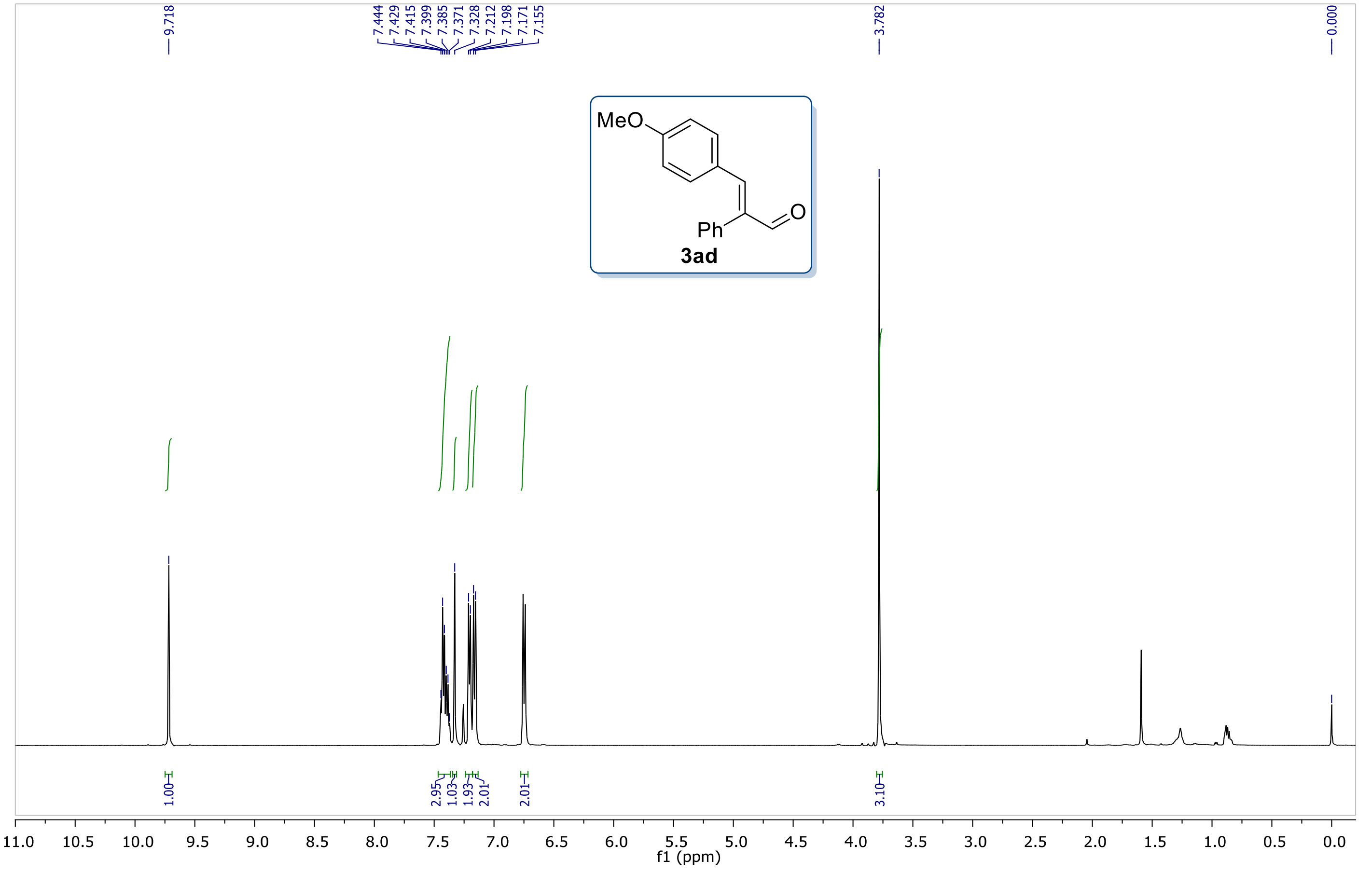

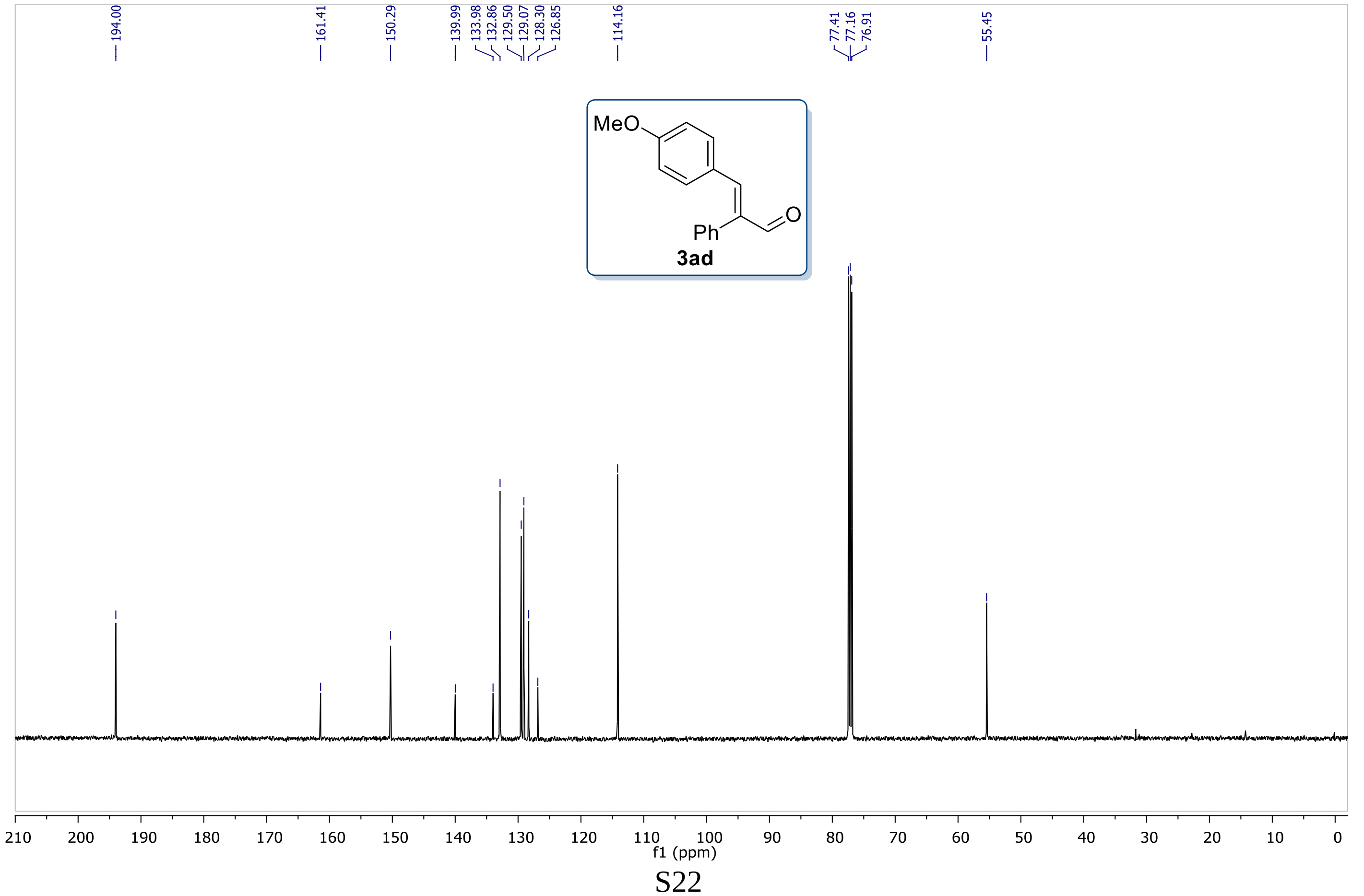

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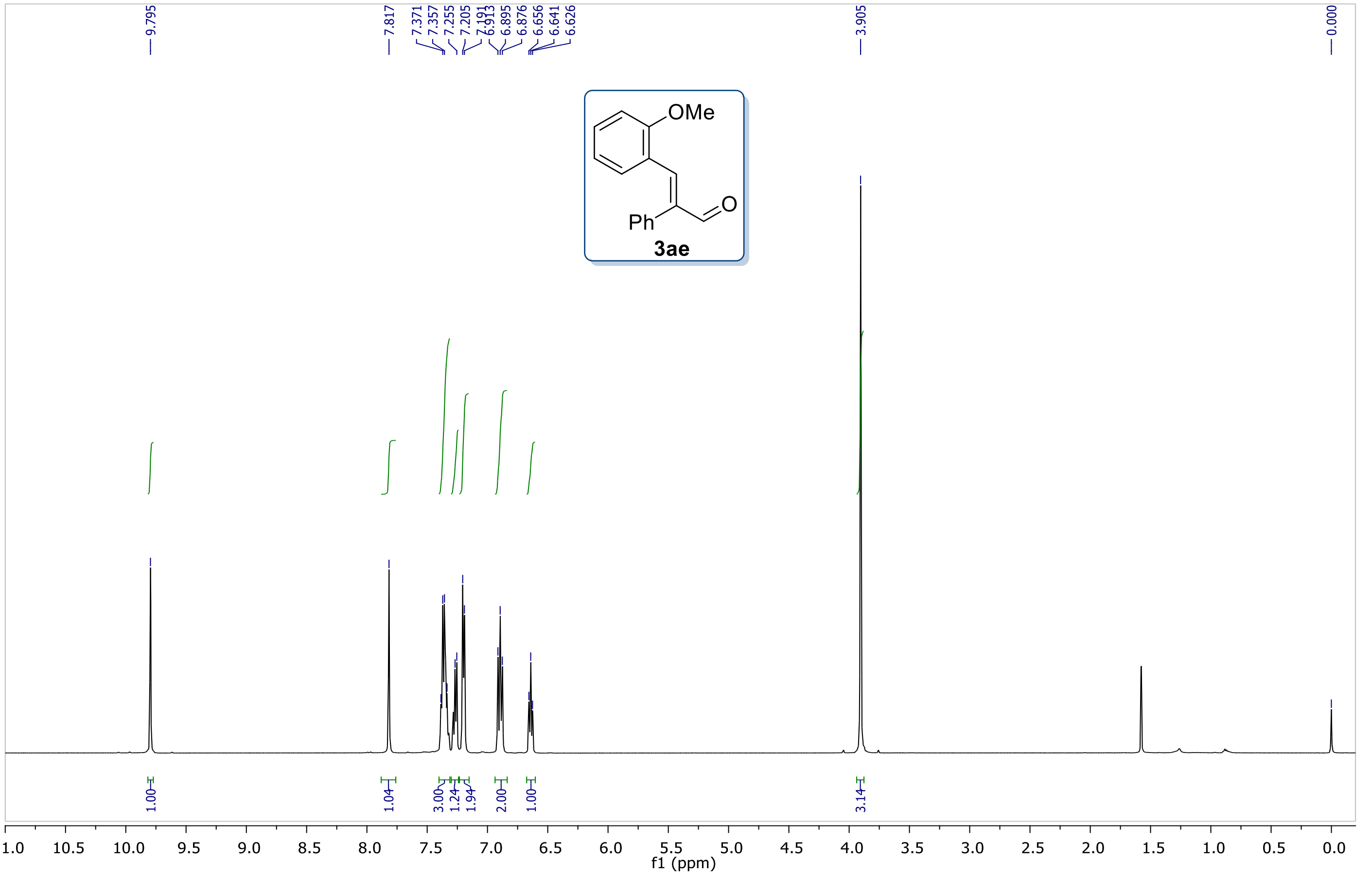
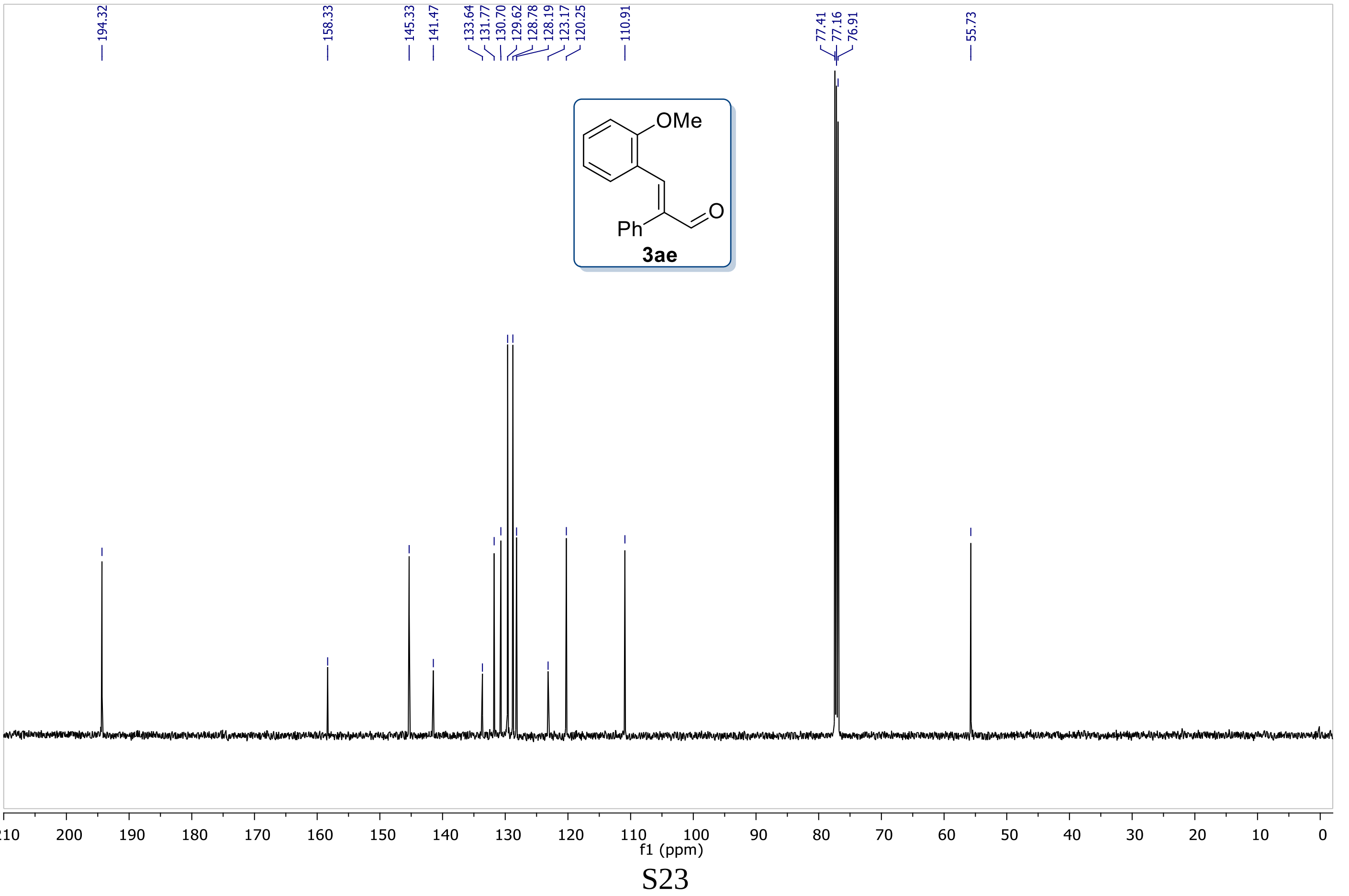
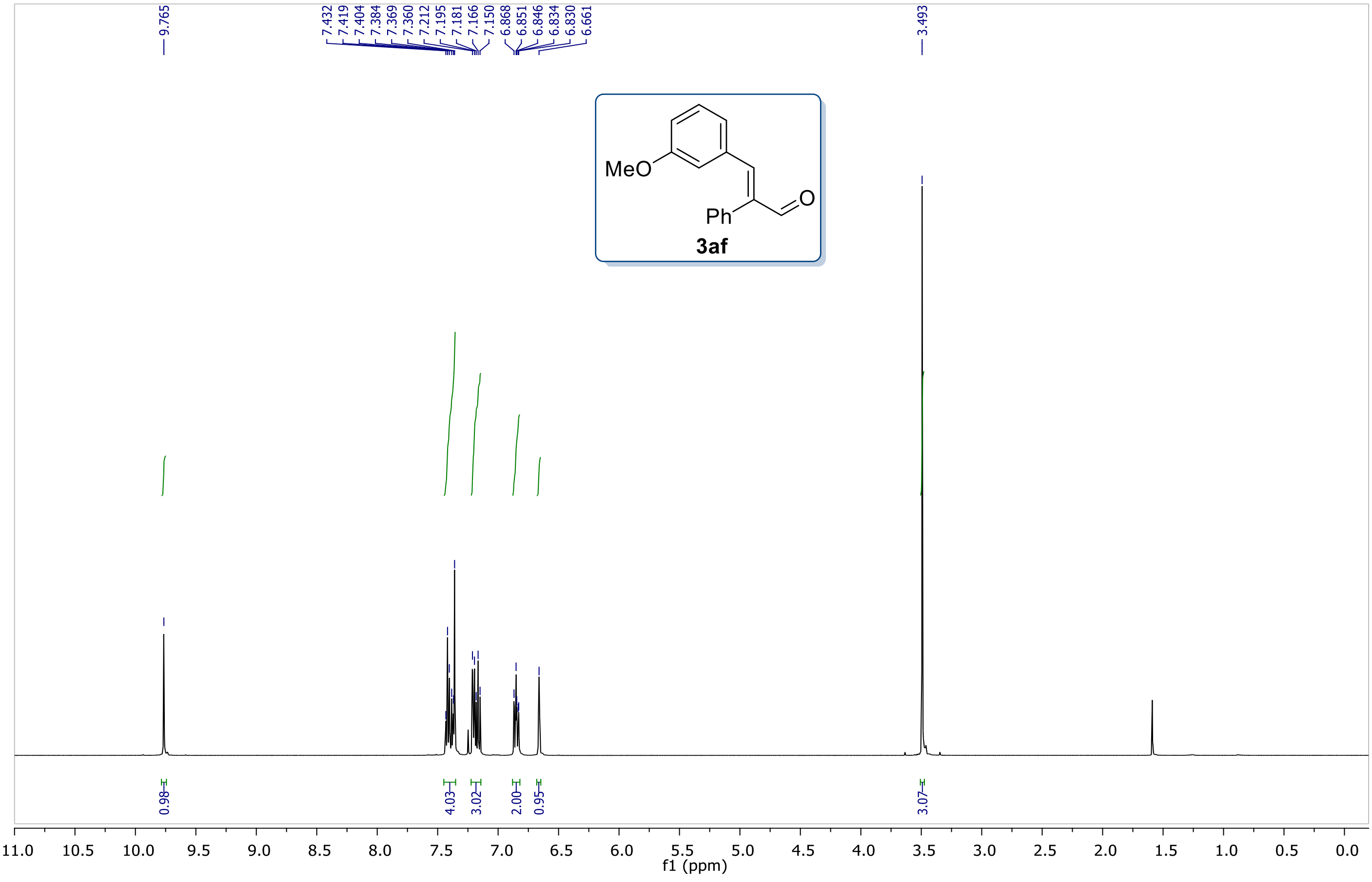
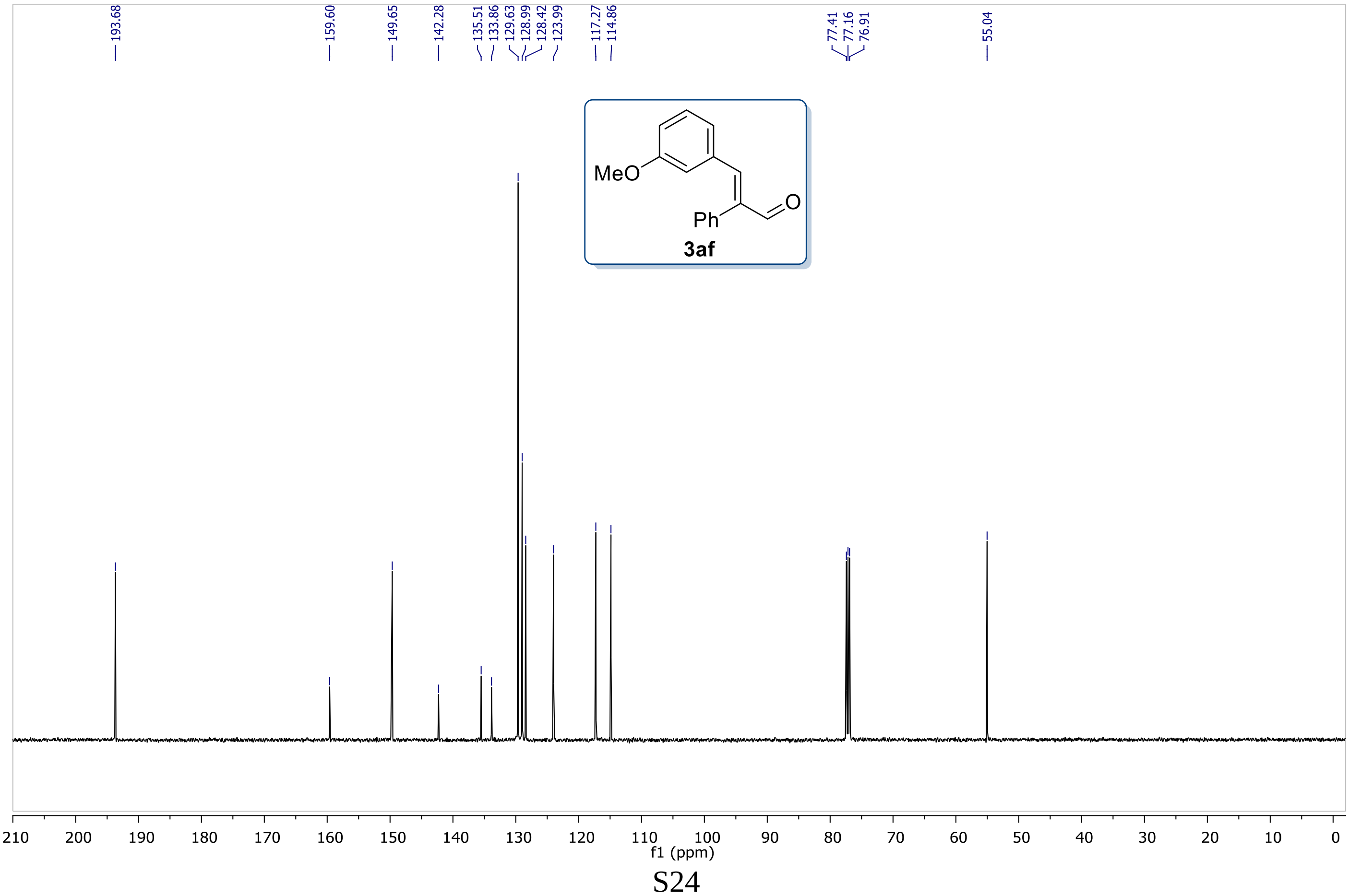


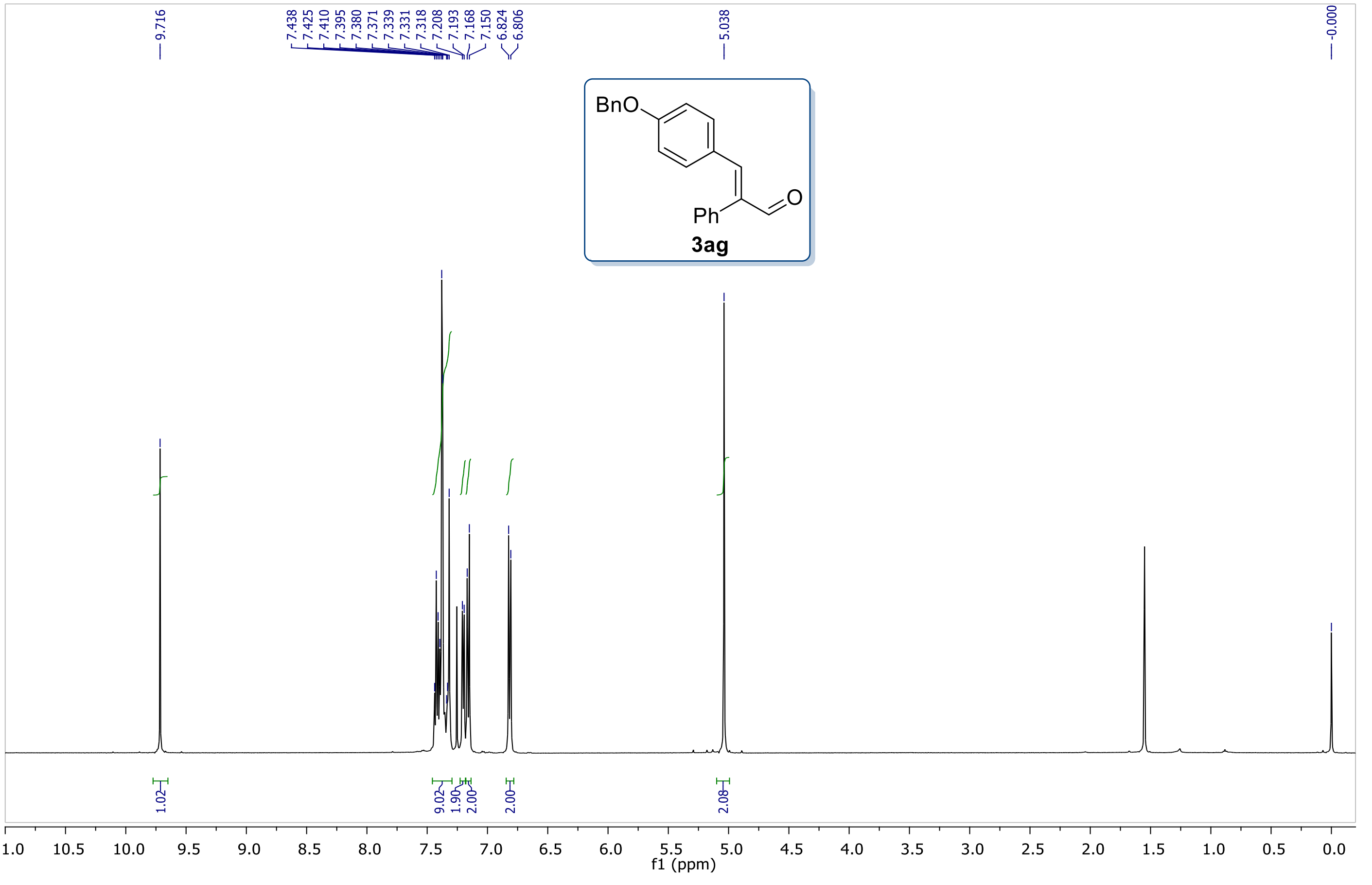


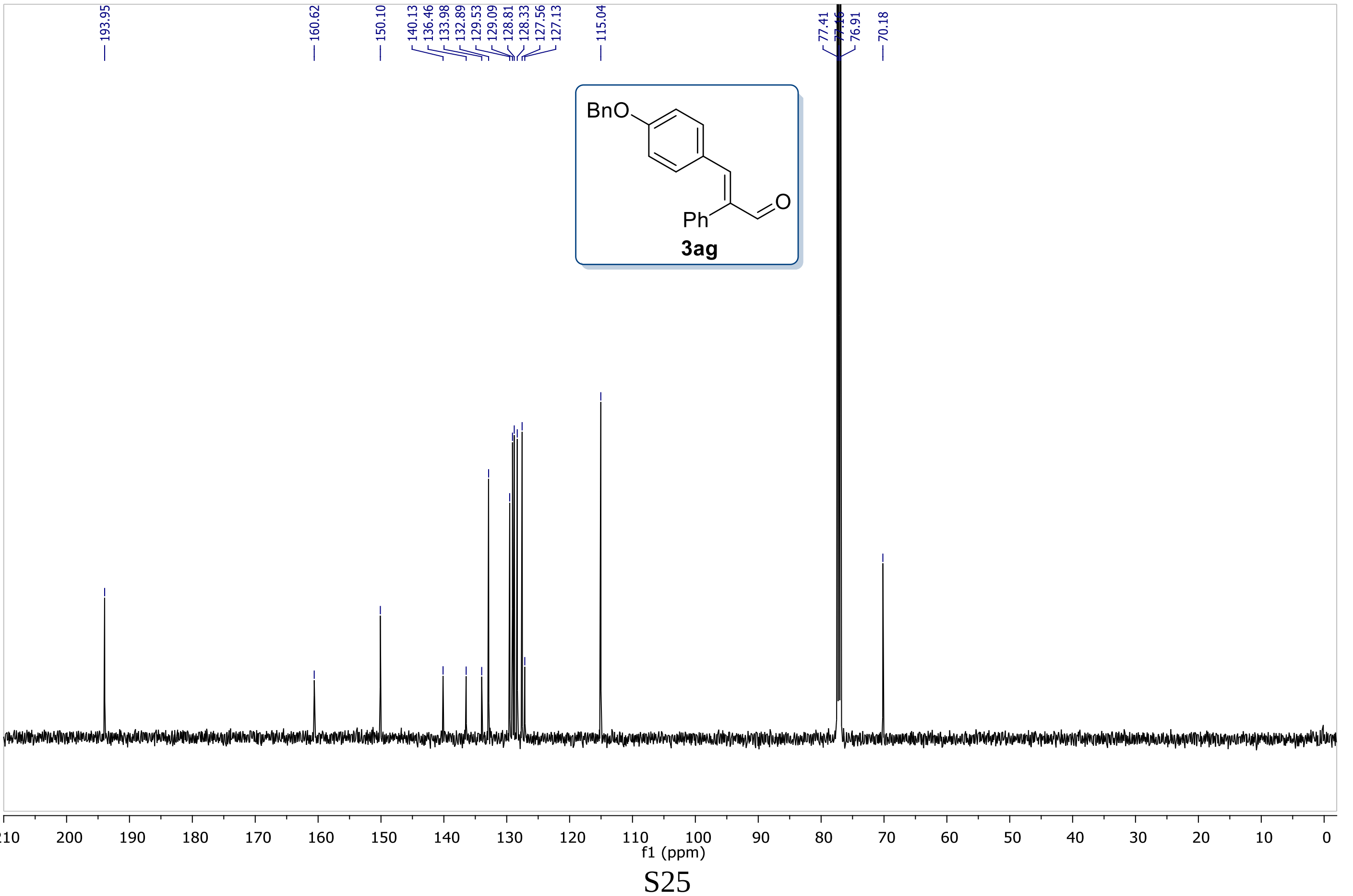
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3af**



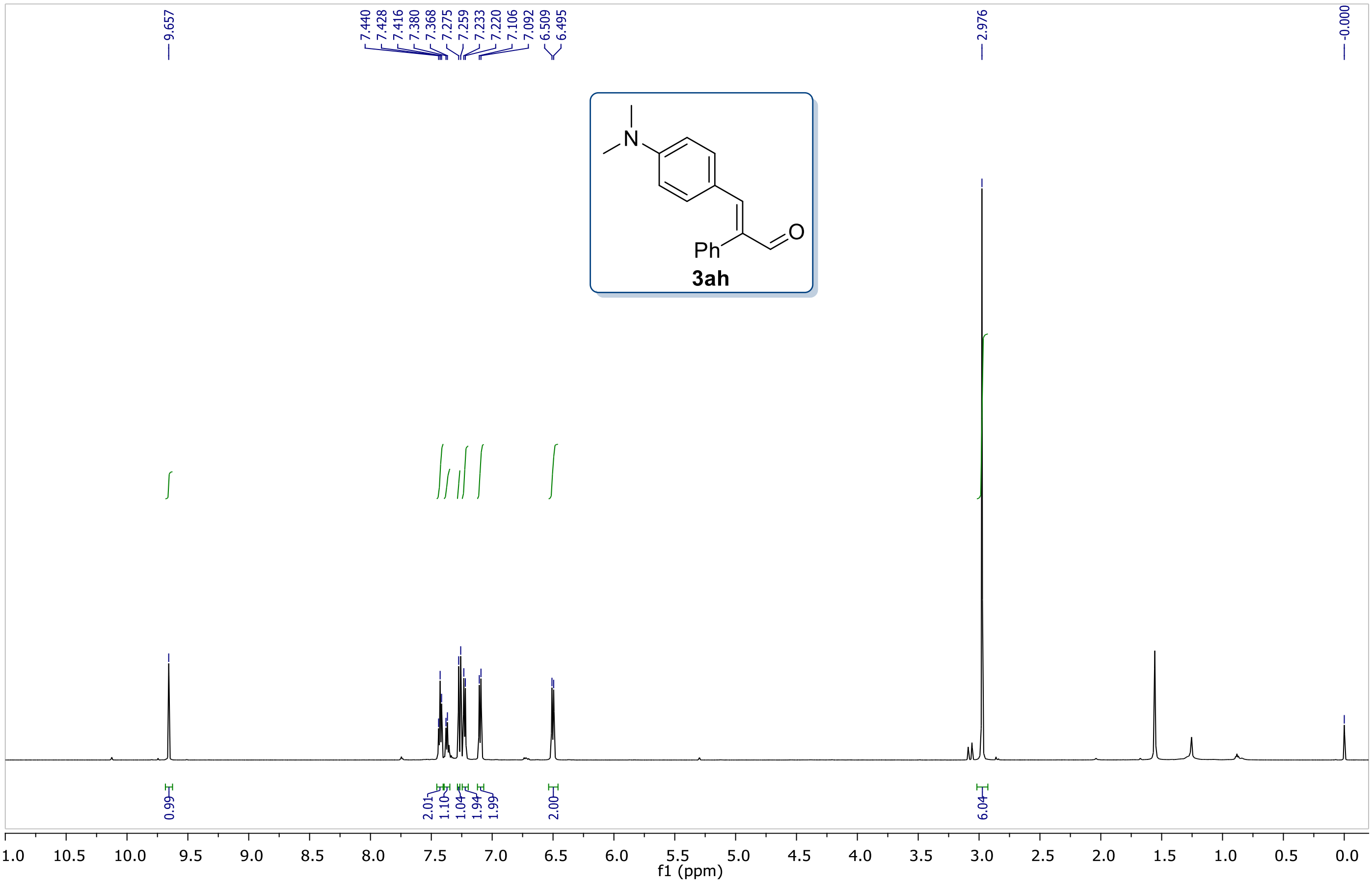


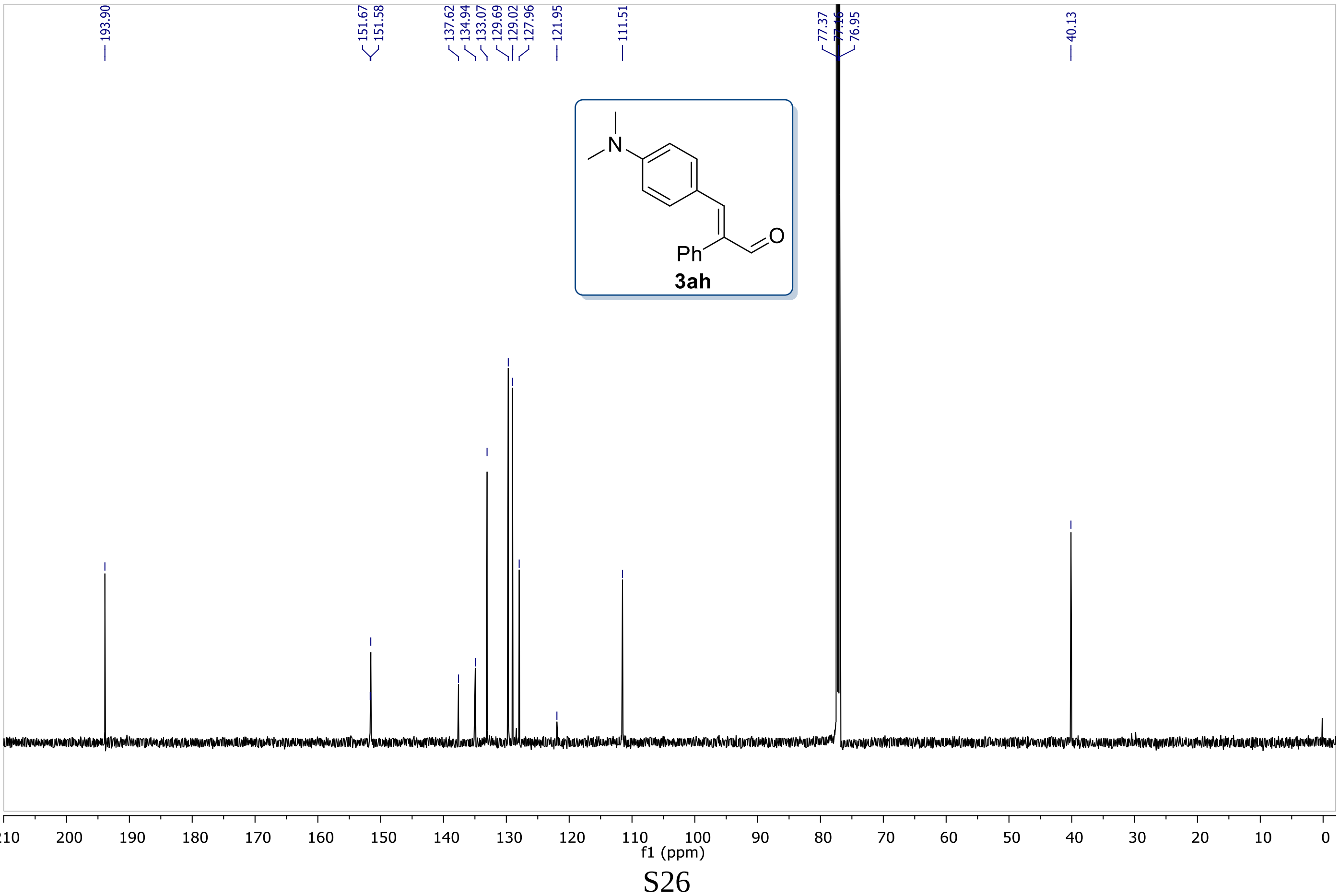
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3ag**





^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$), **3ah**





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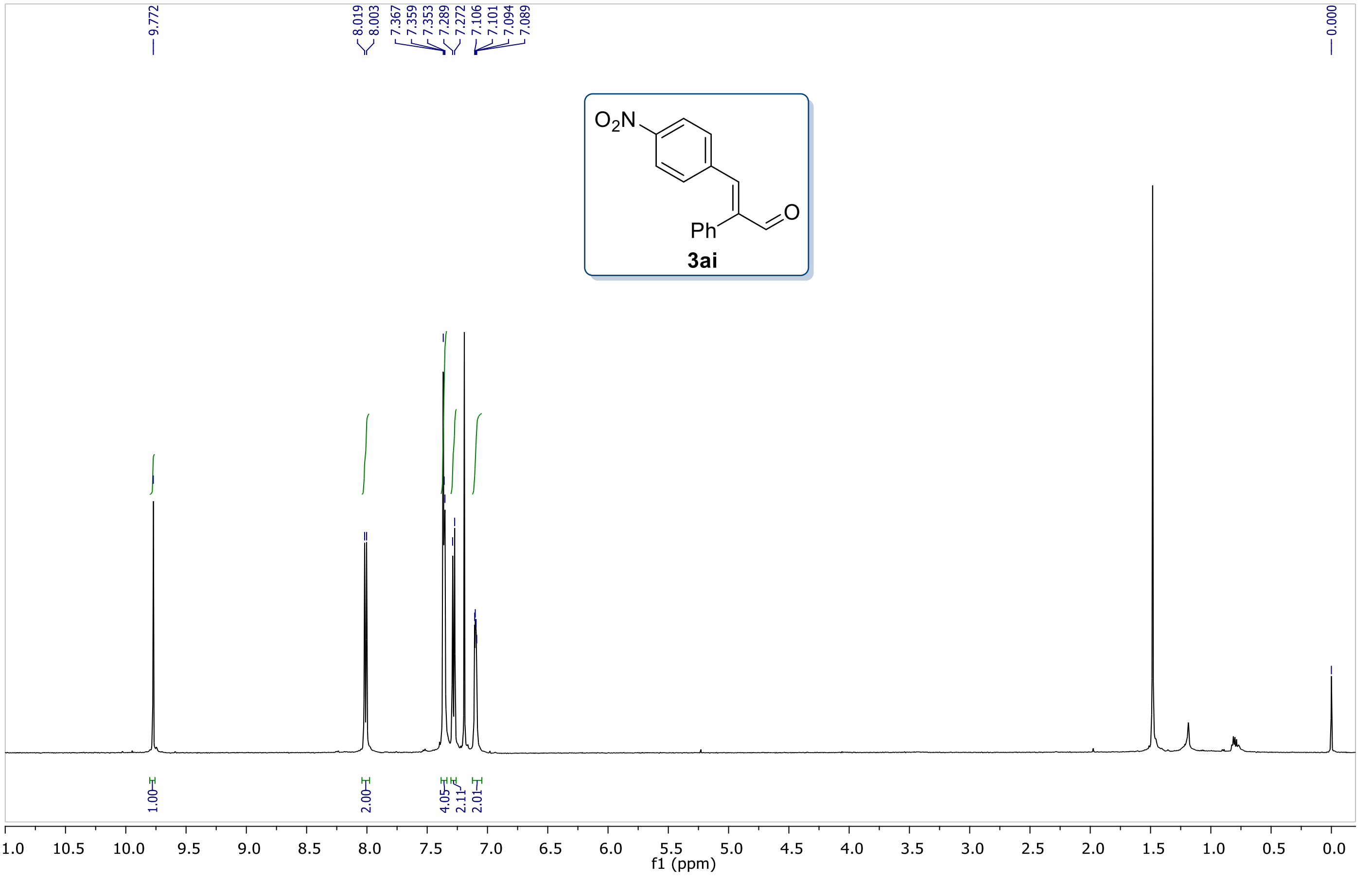
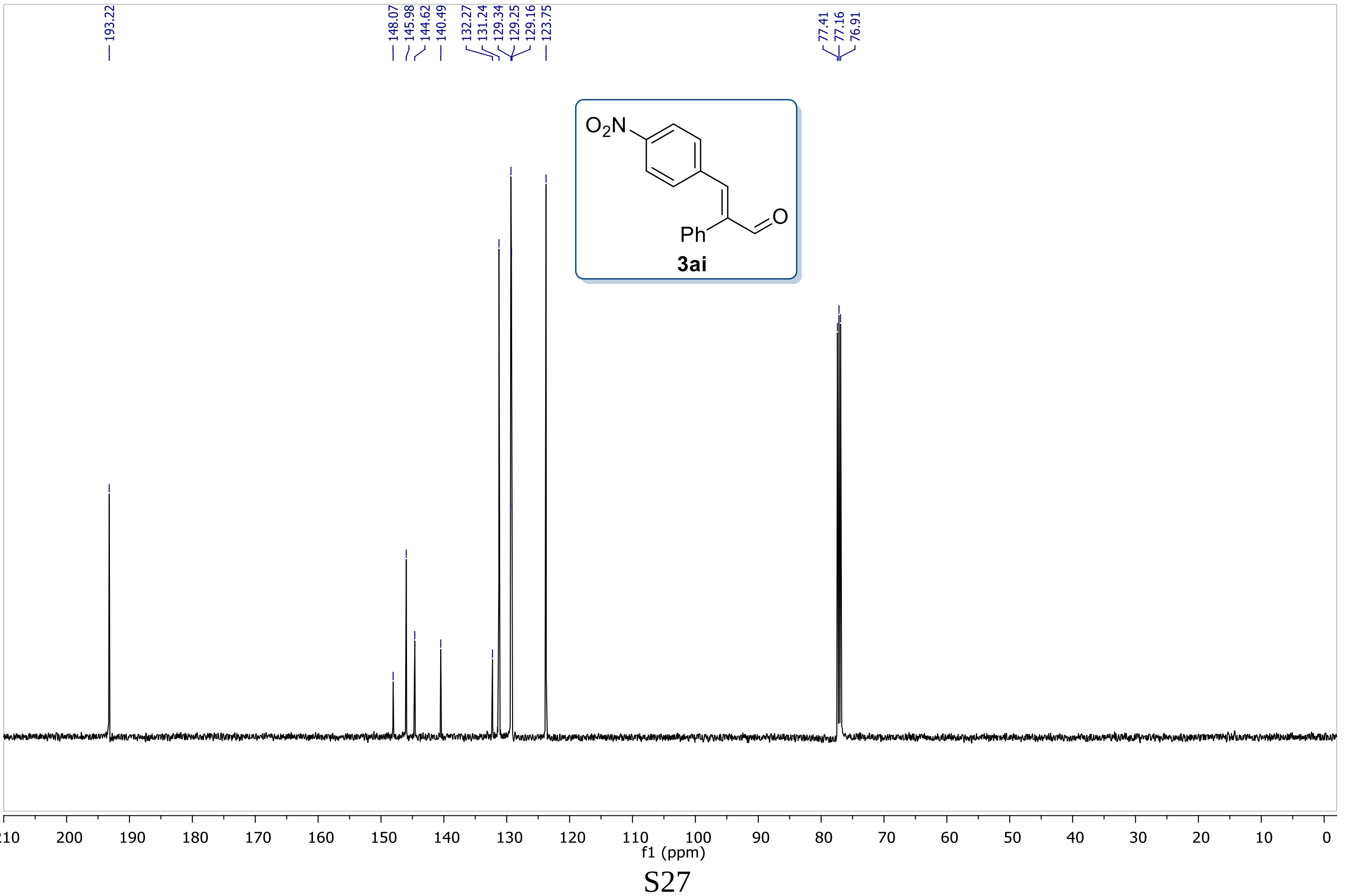
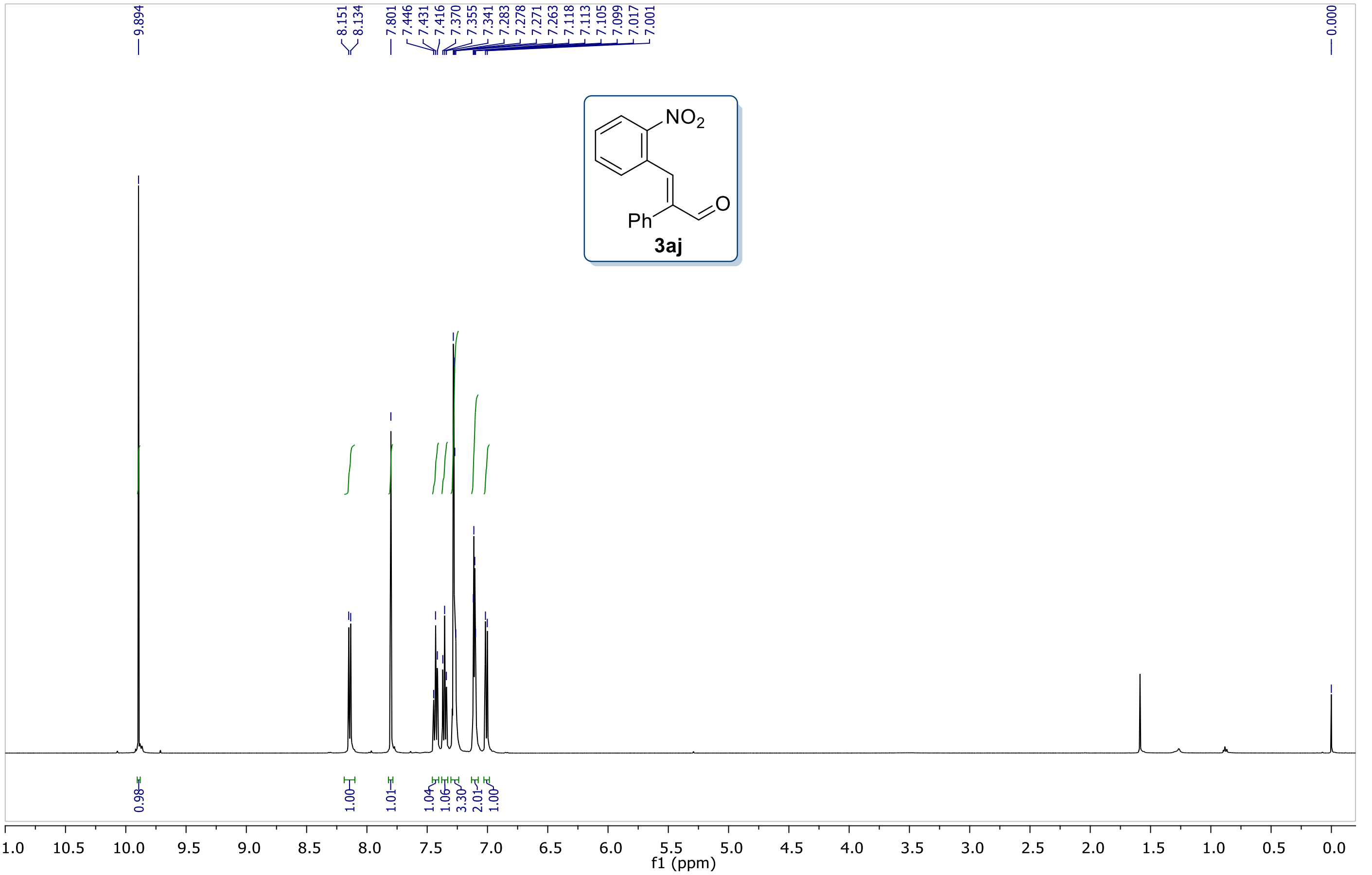
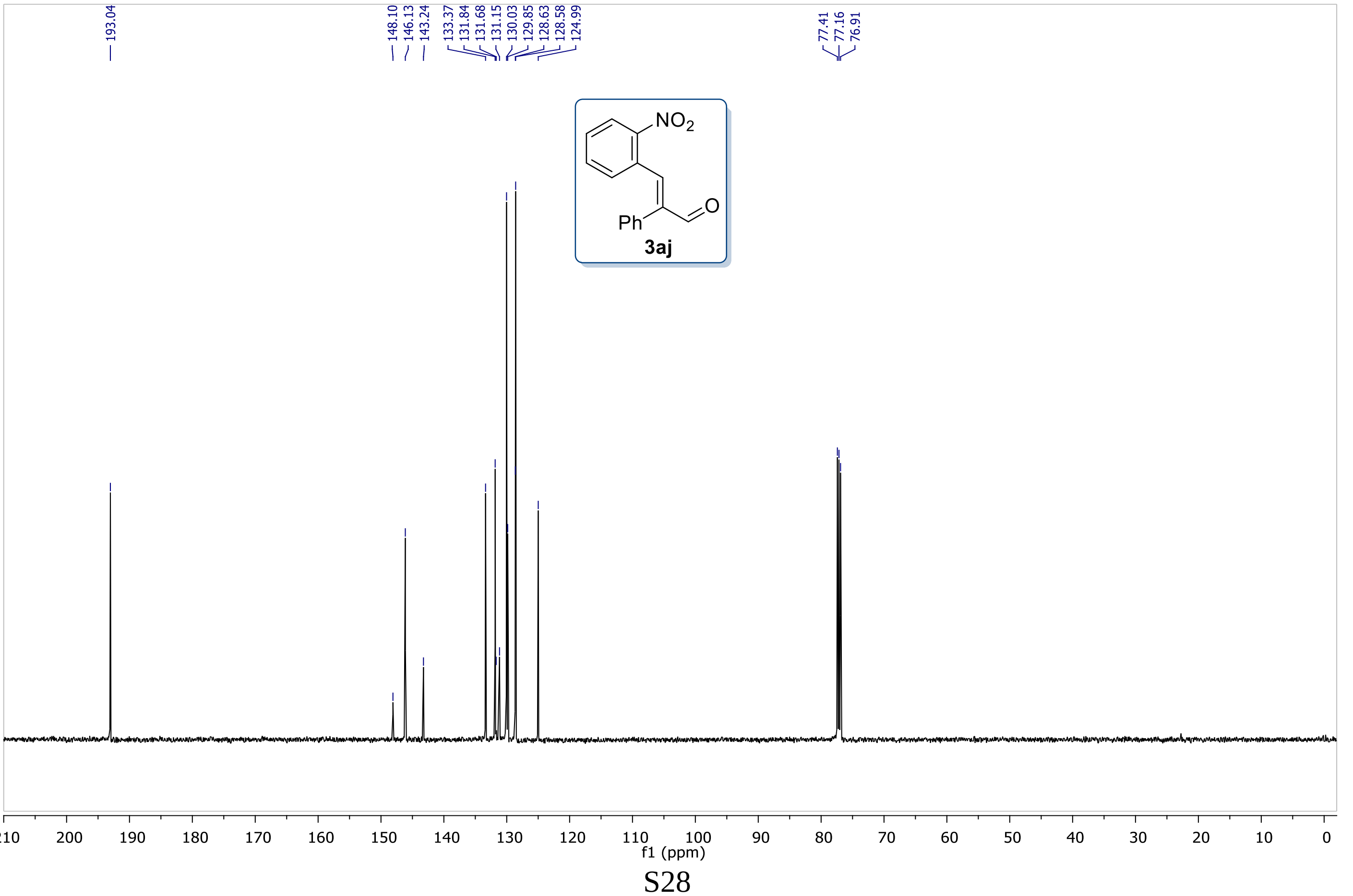


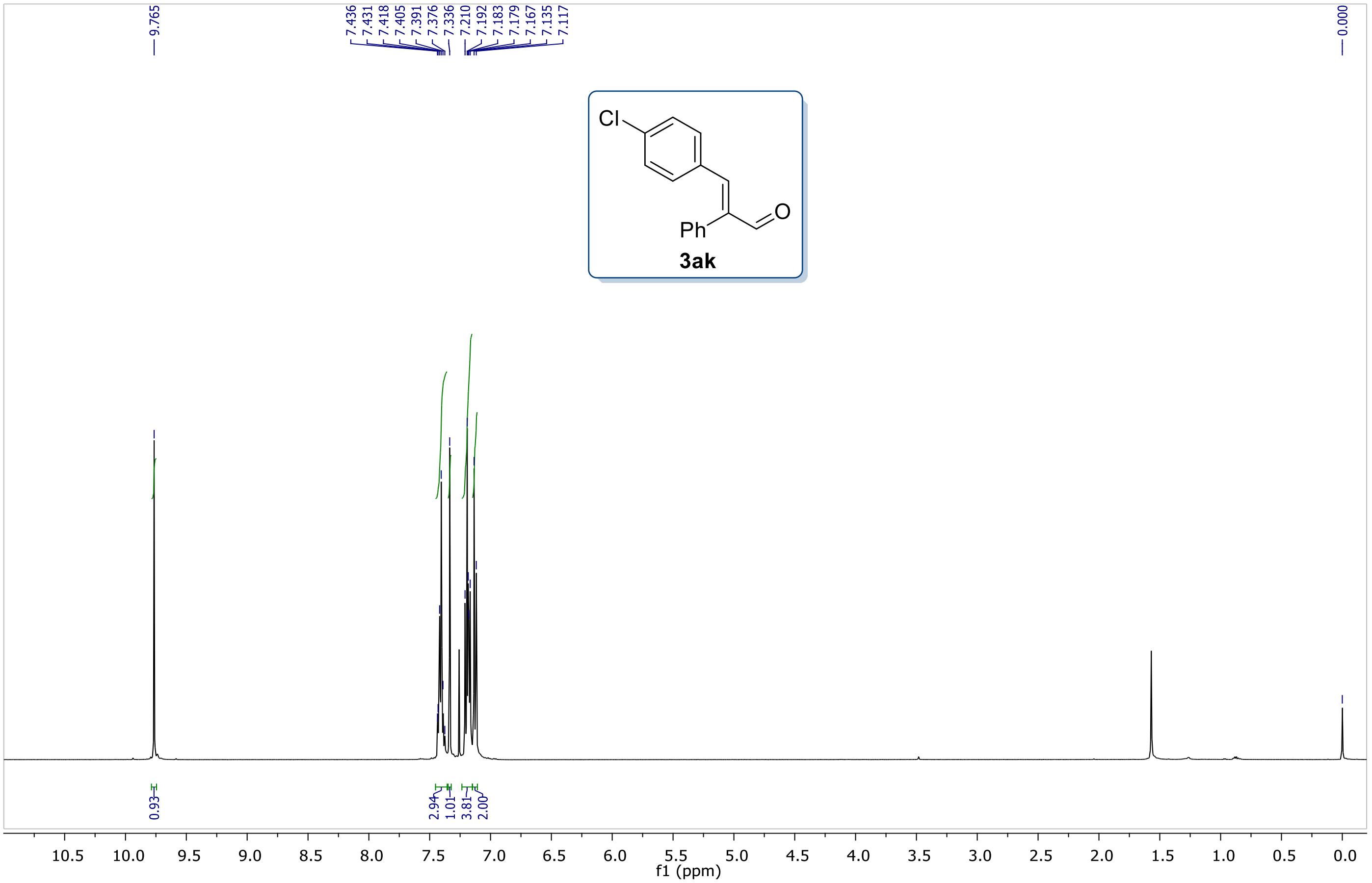


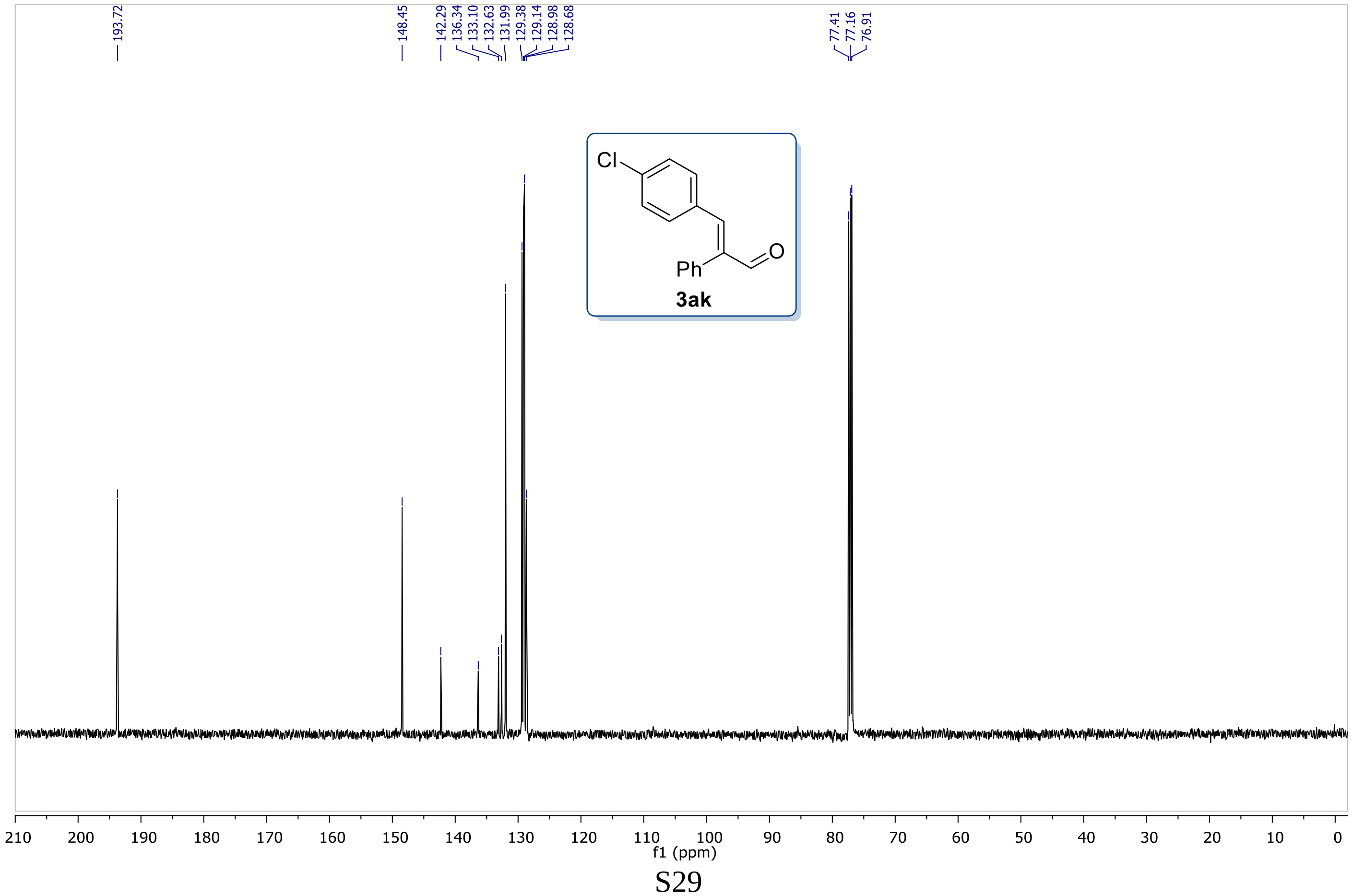
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3aj**



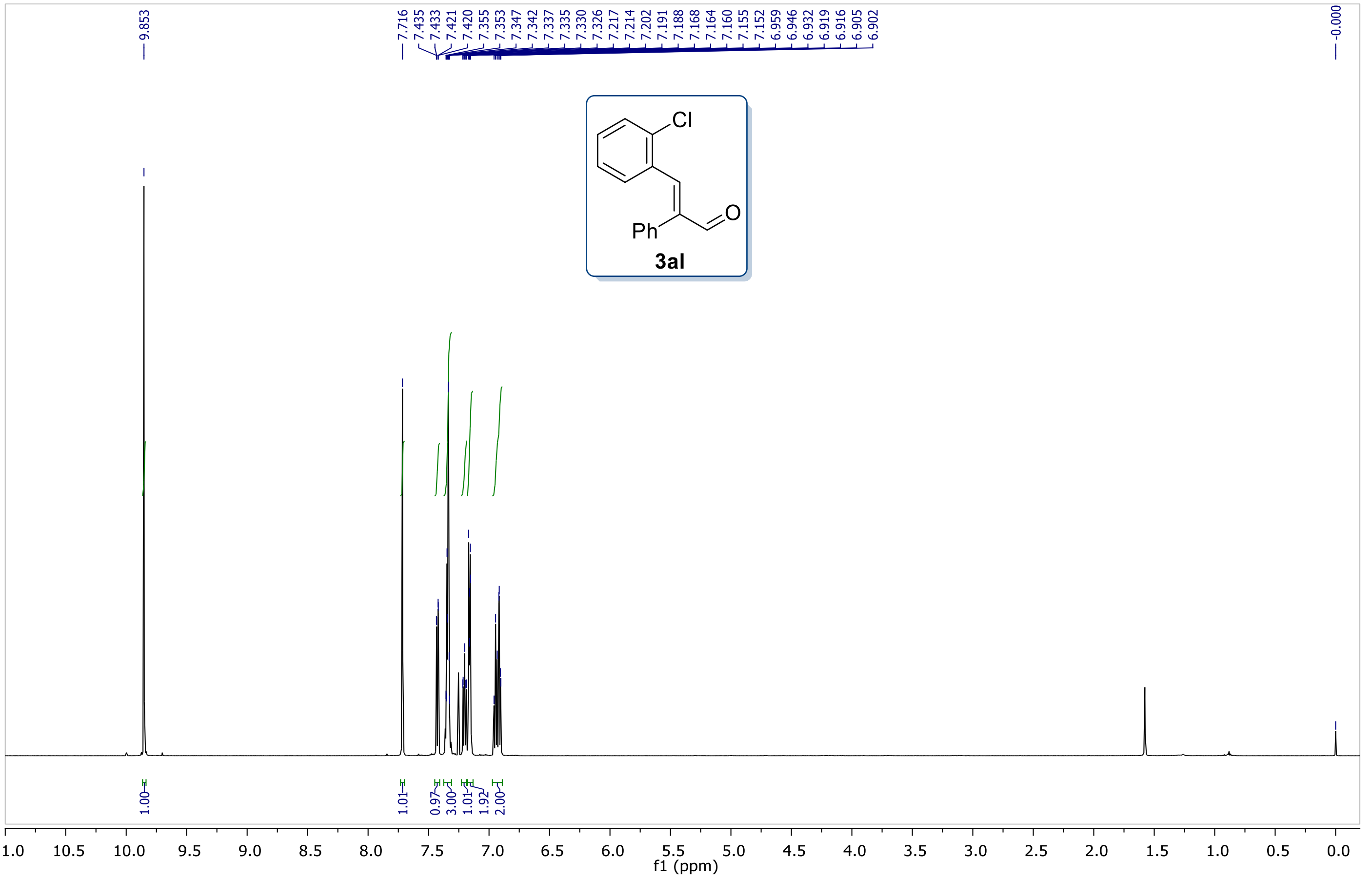


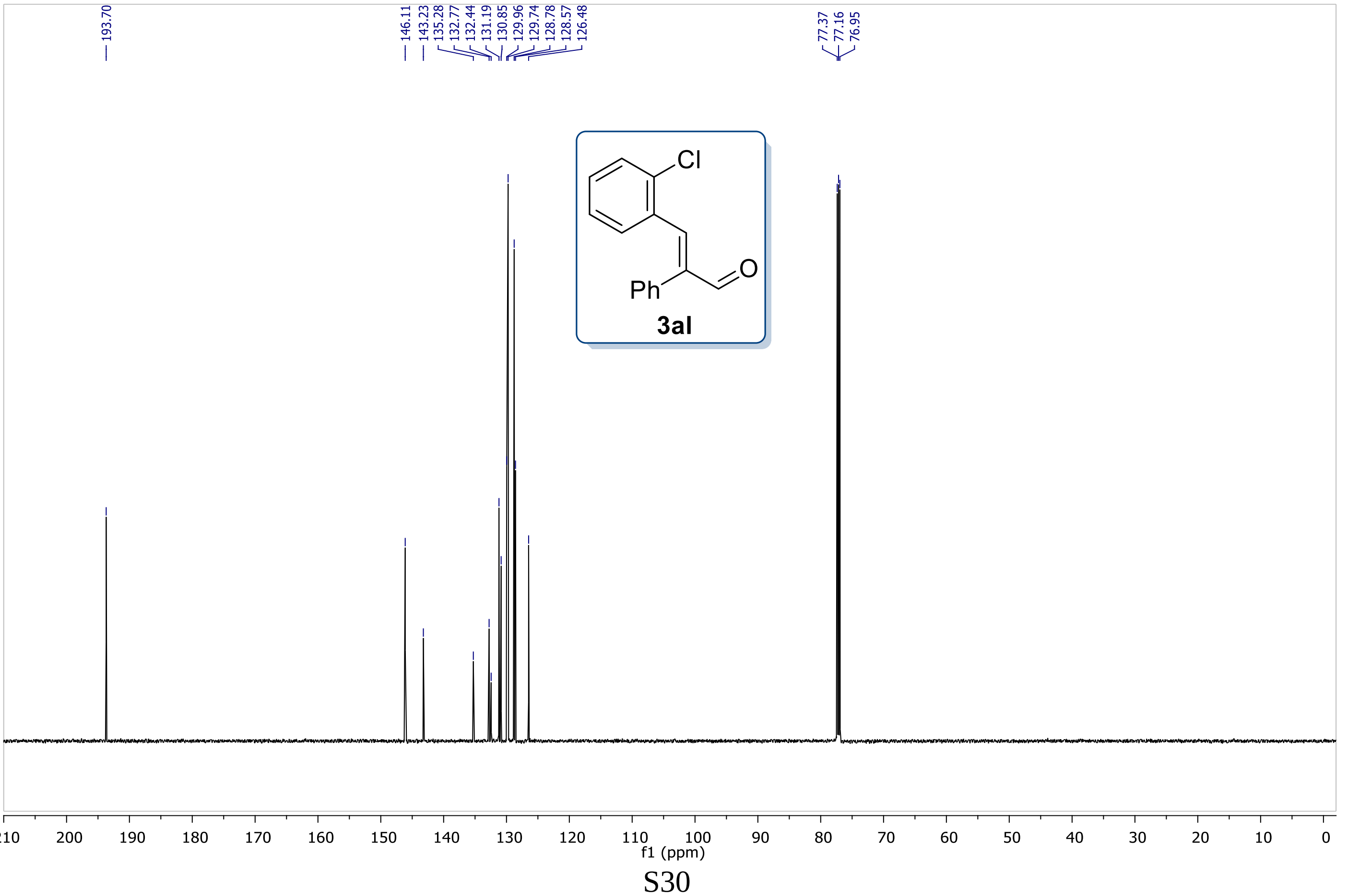
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3ak**



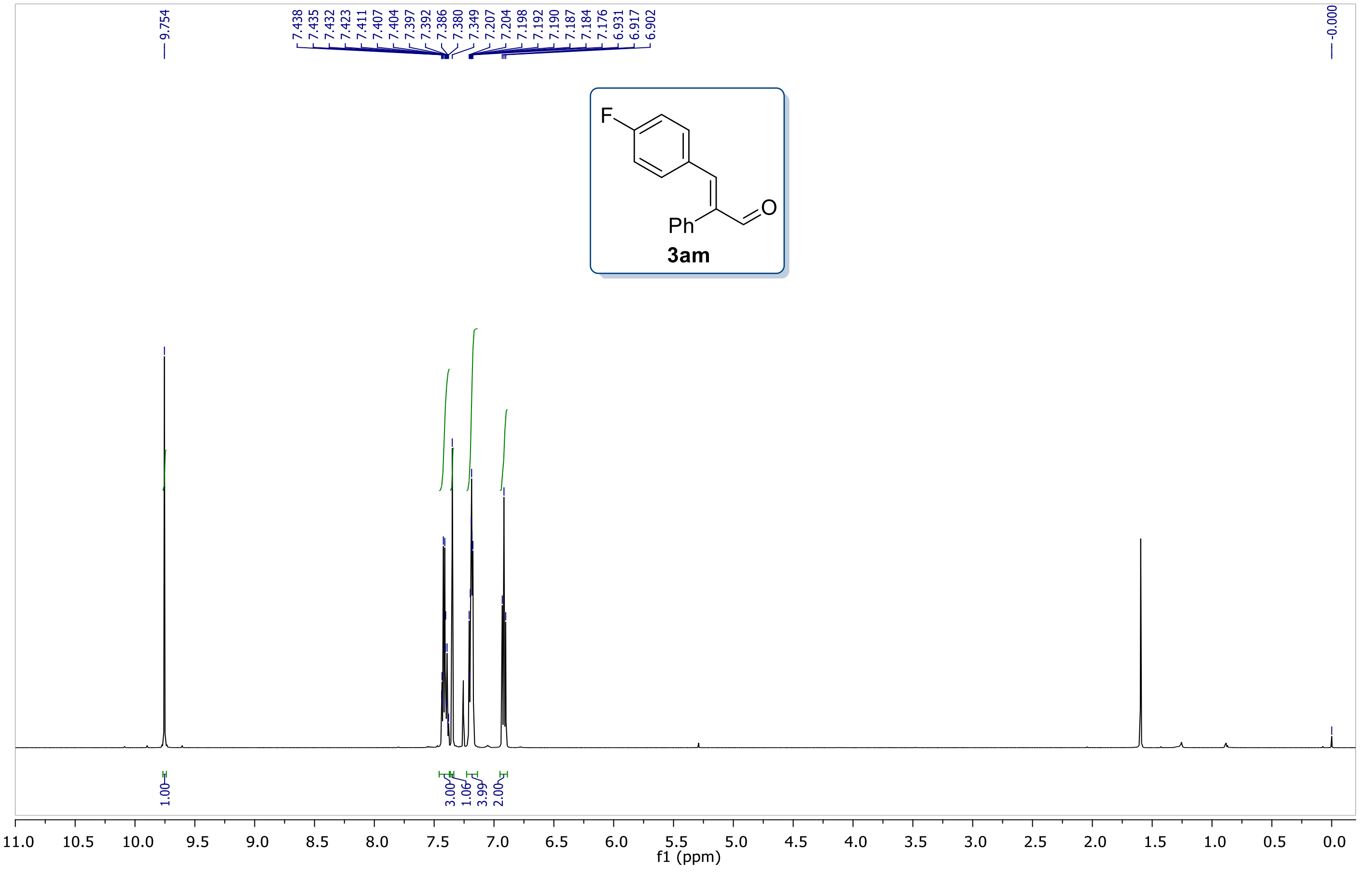


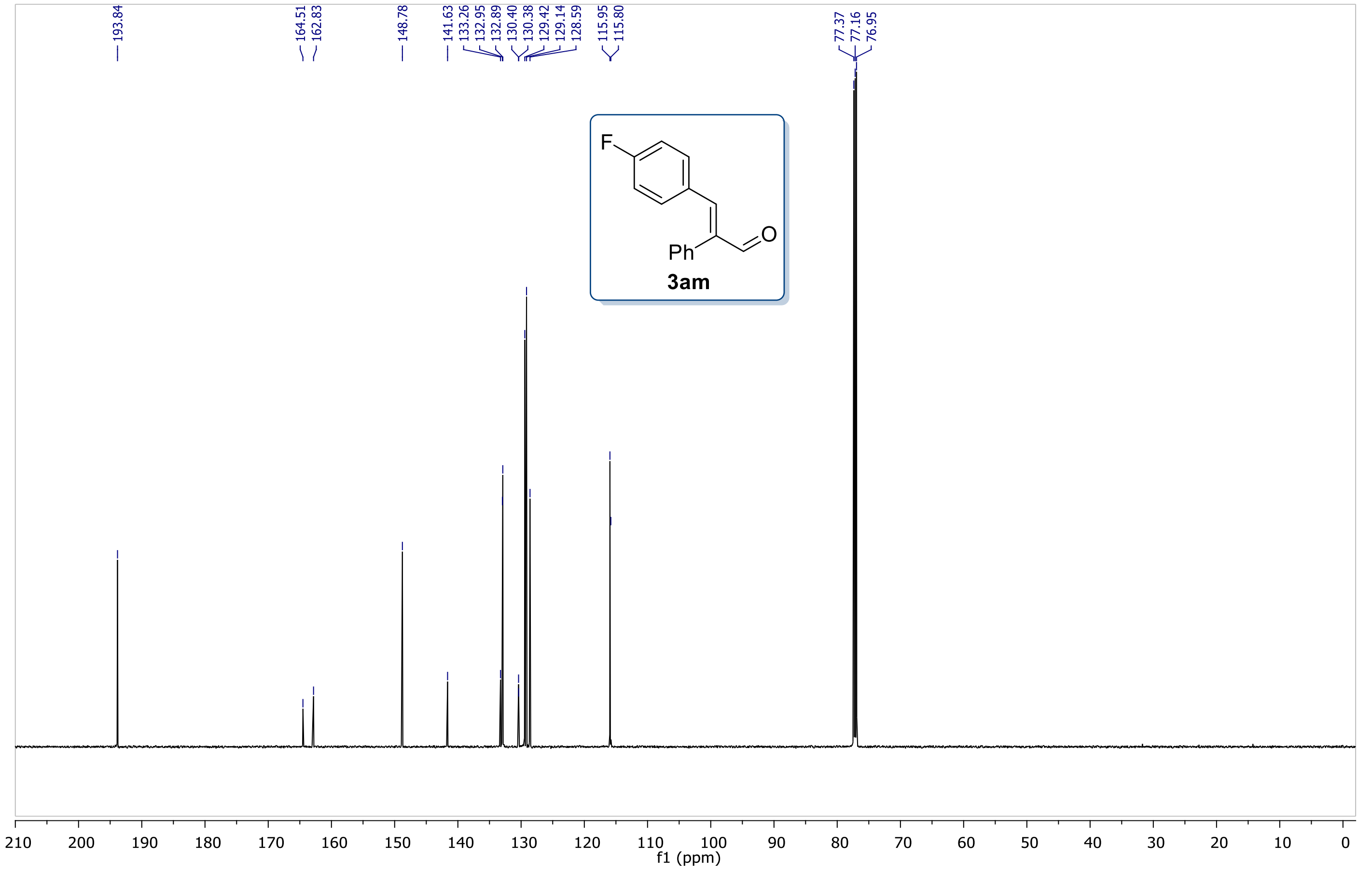
[1]H NMR (600 MHz, $CDCl_3$) and [13]C{[1]H} NMR (151 MHz, $CDCl_3$), **3al**



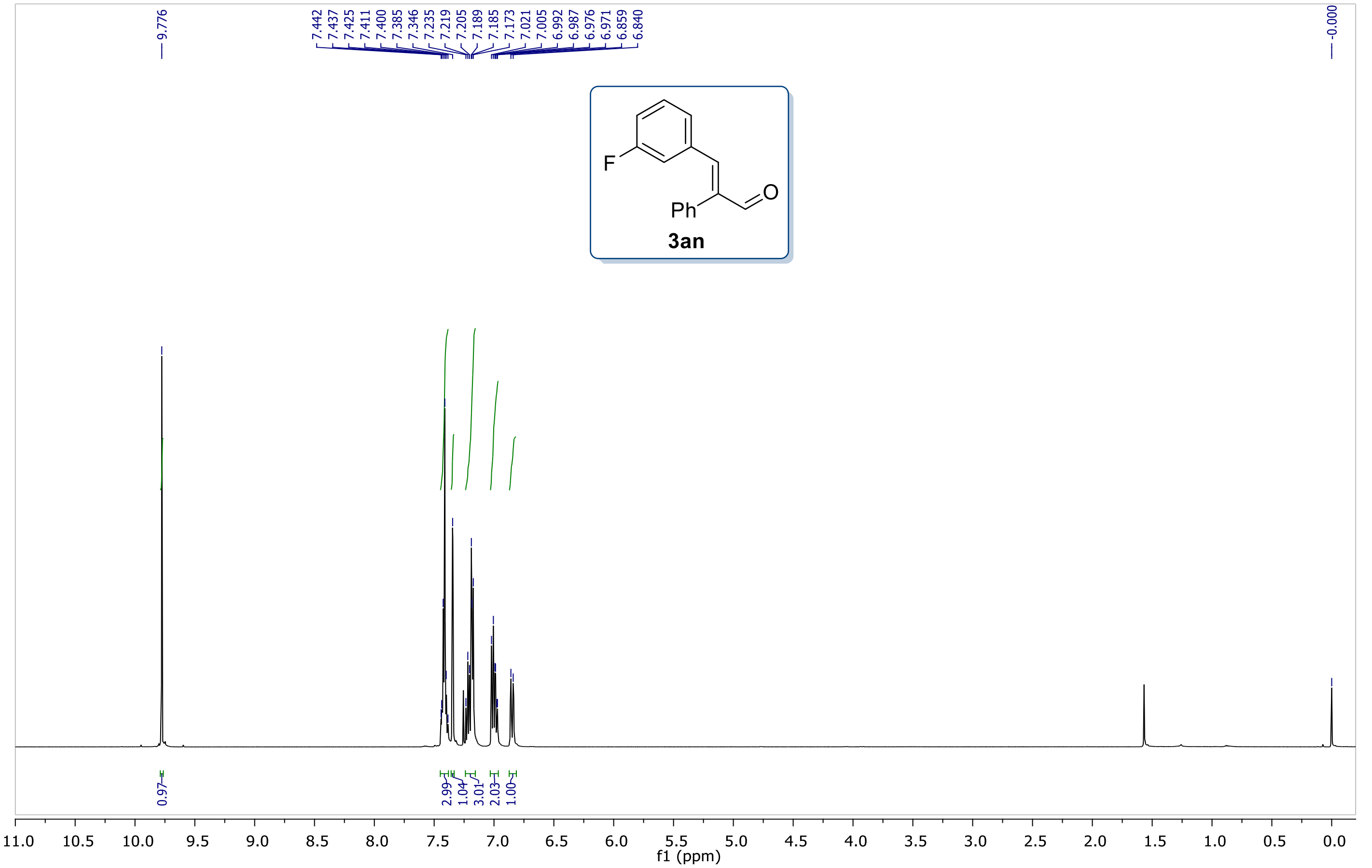


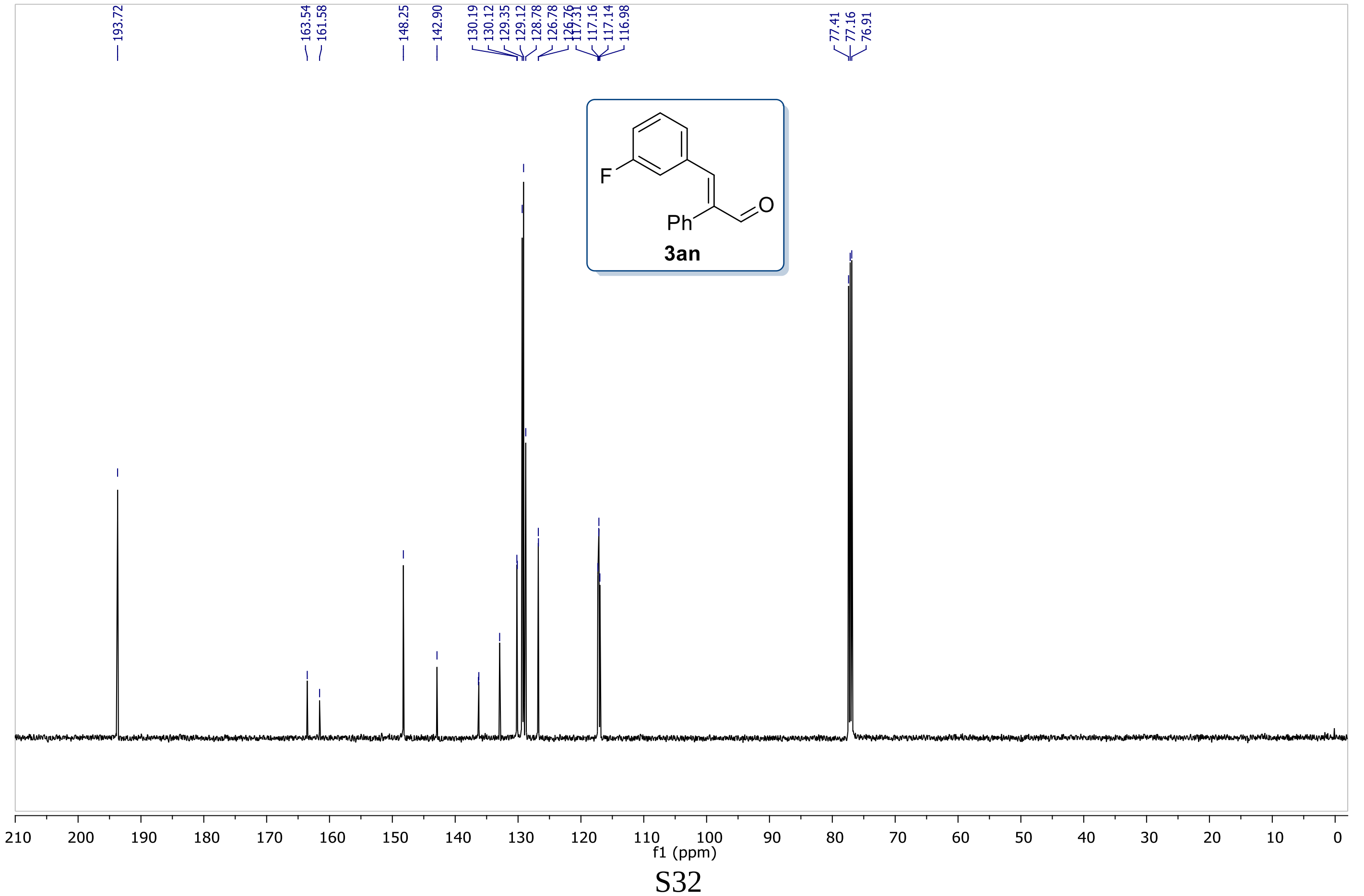
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$), **3am**



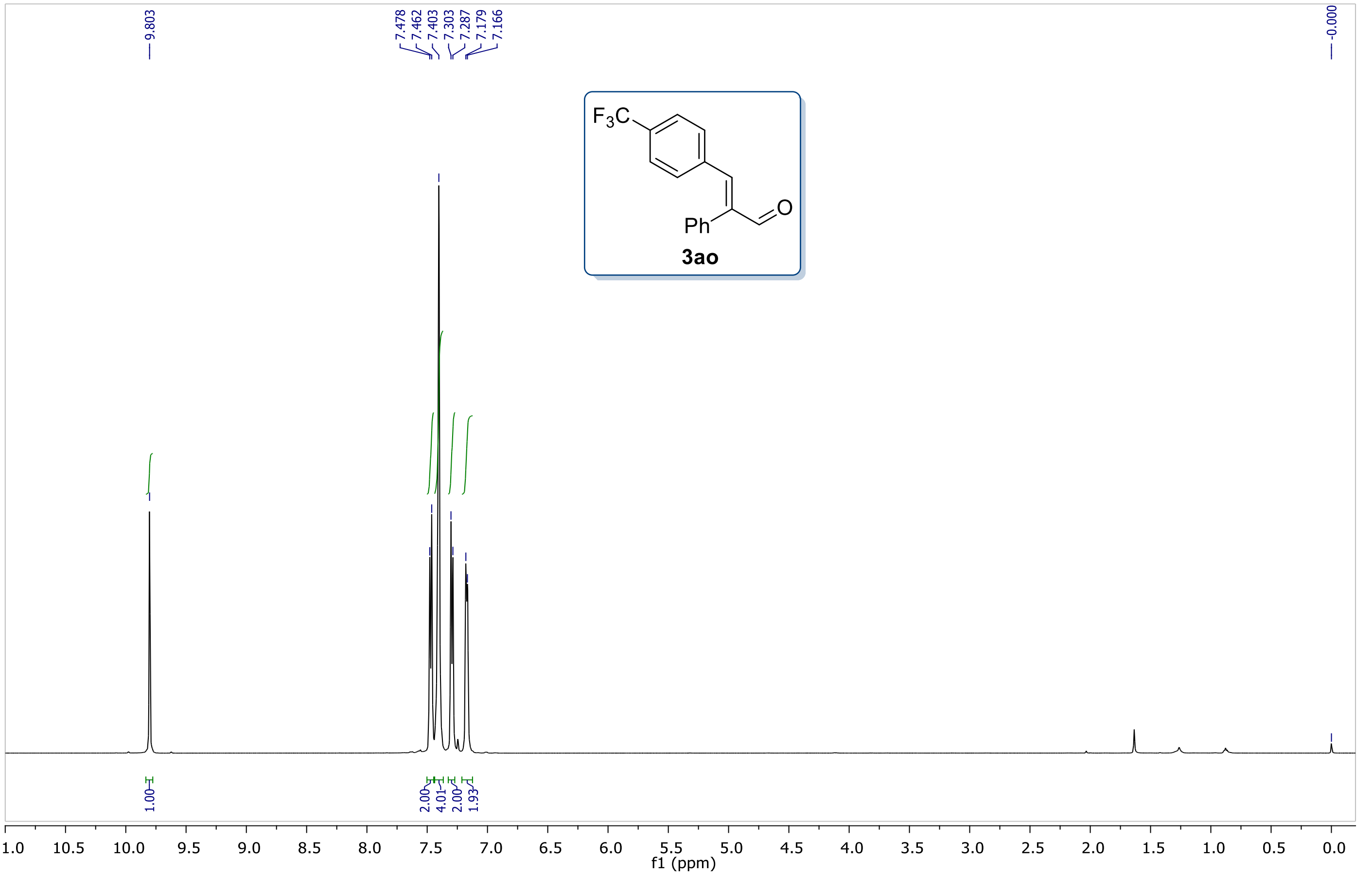


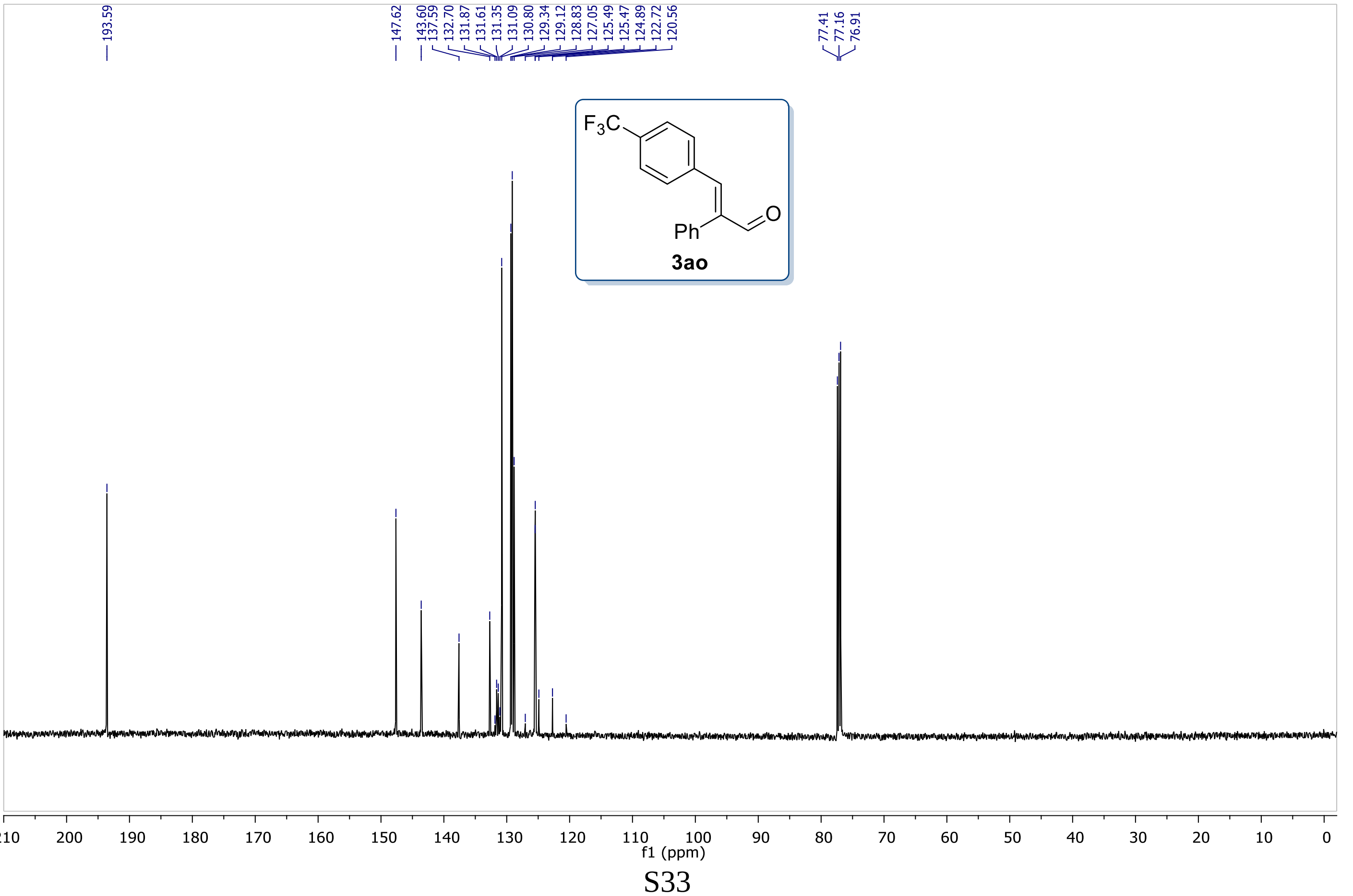
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3an**



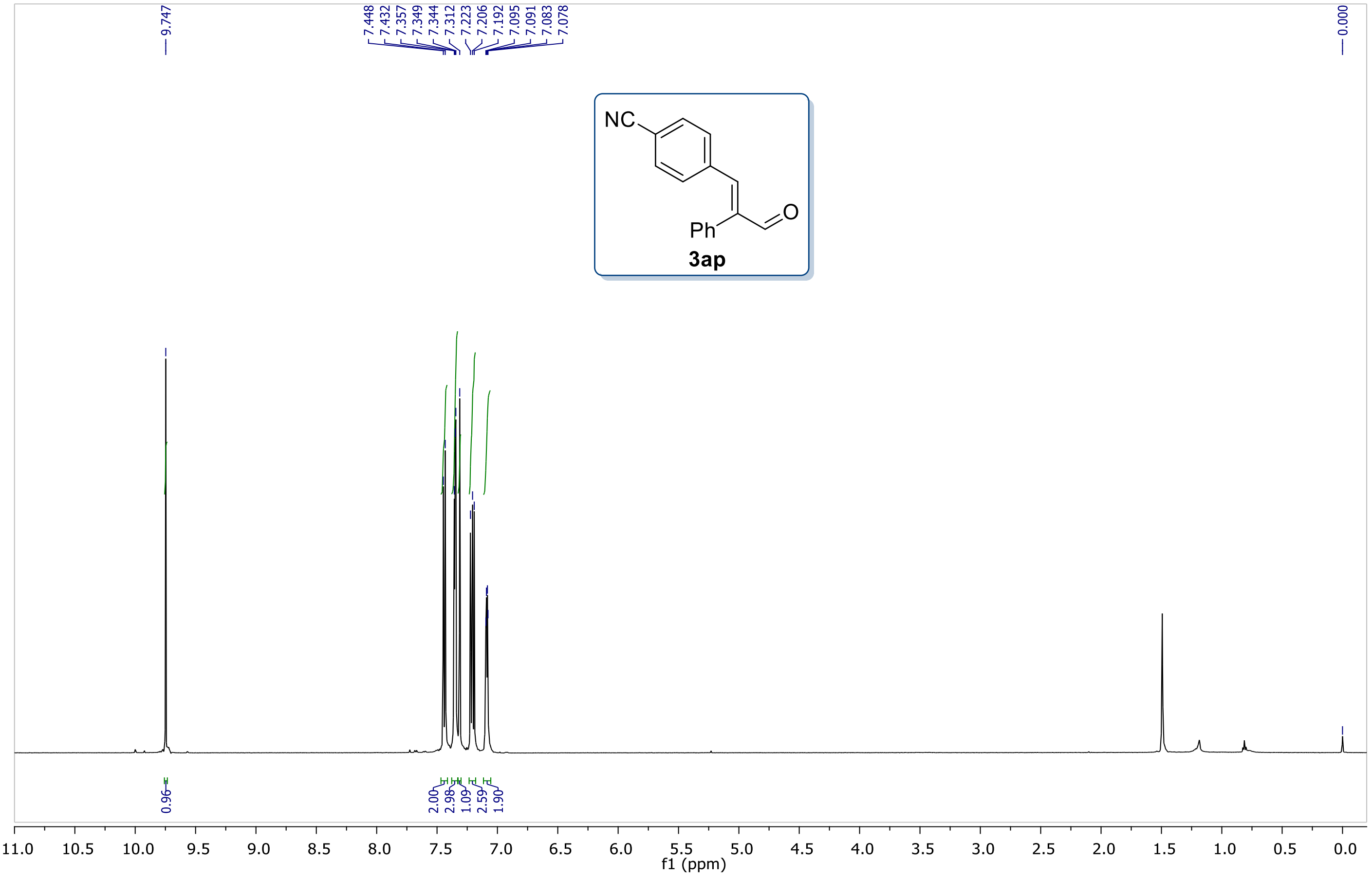


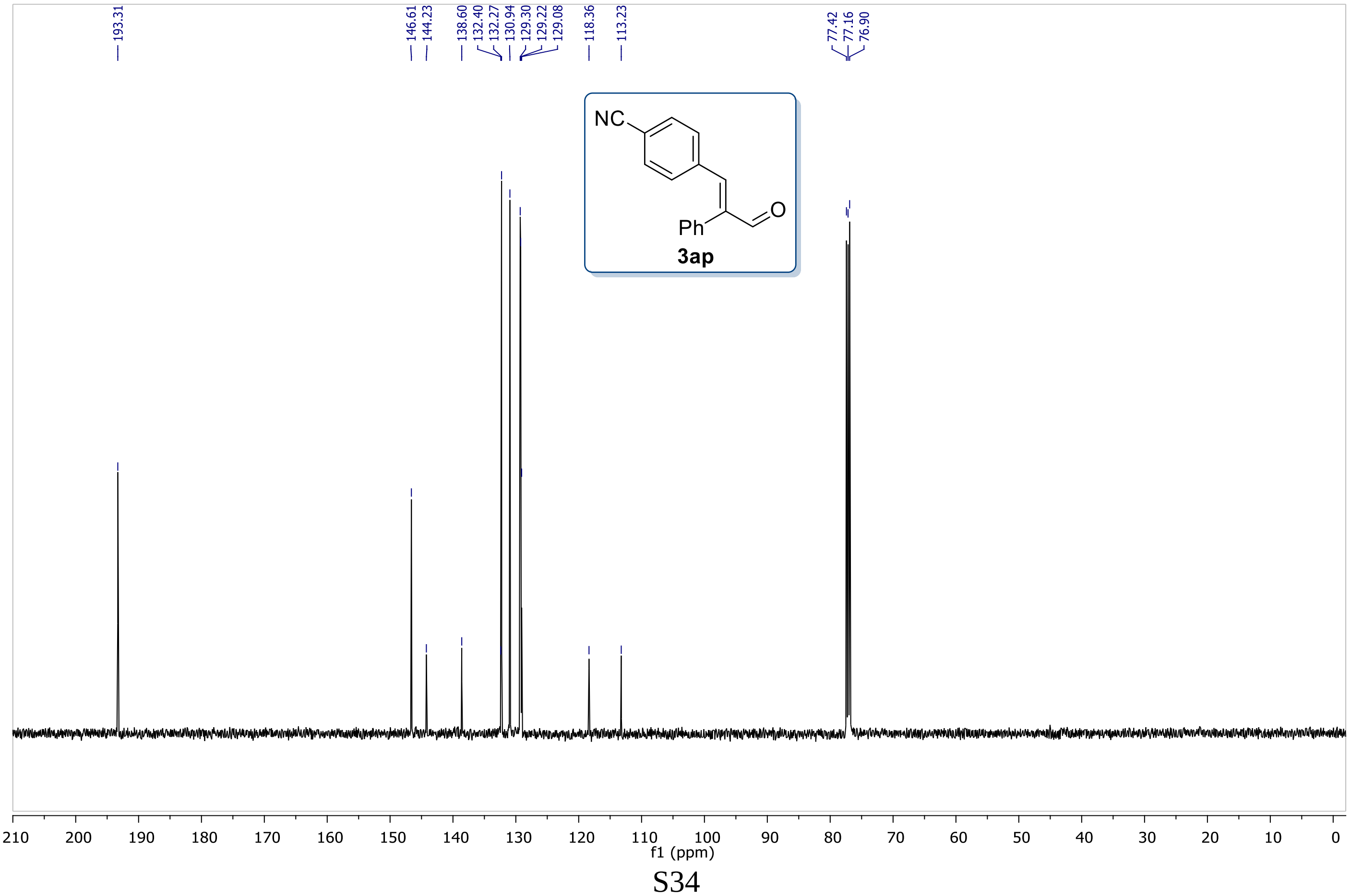
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3ao**



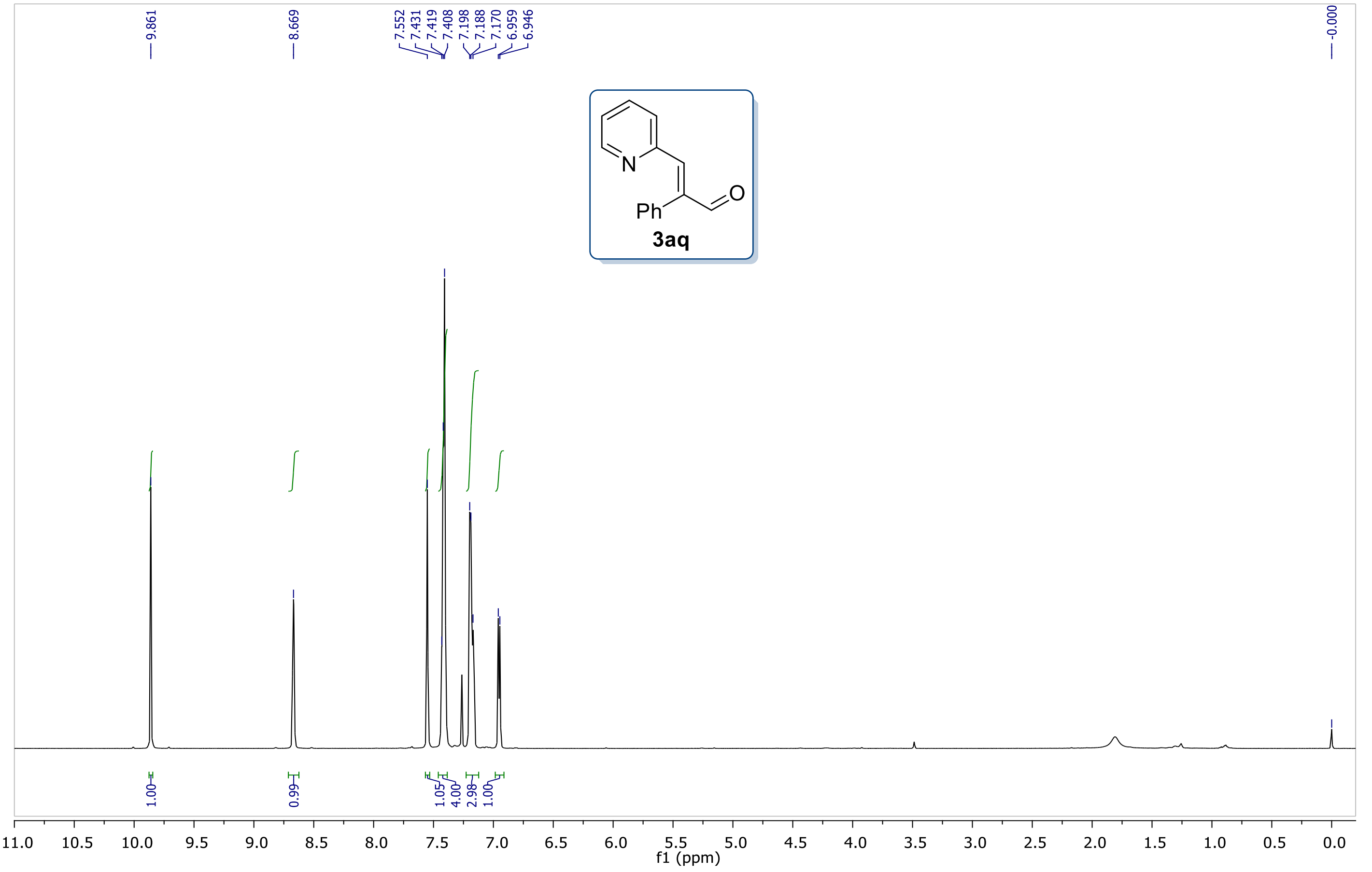


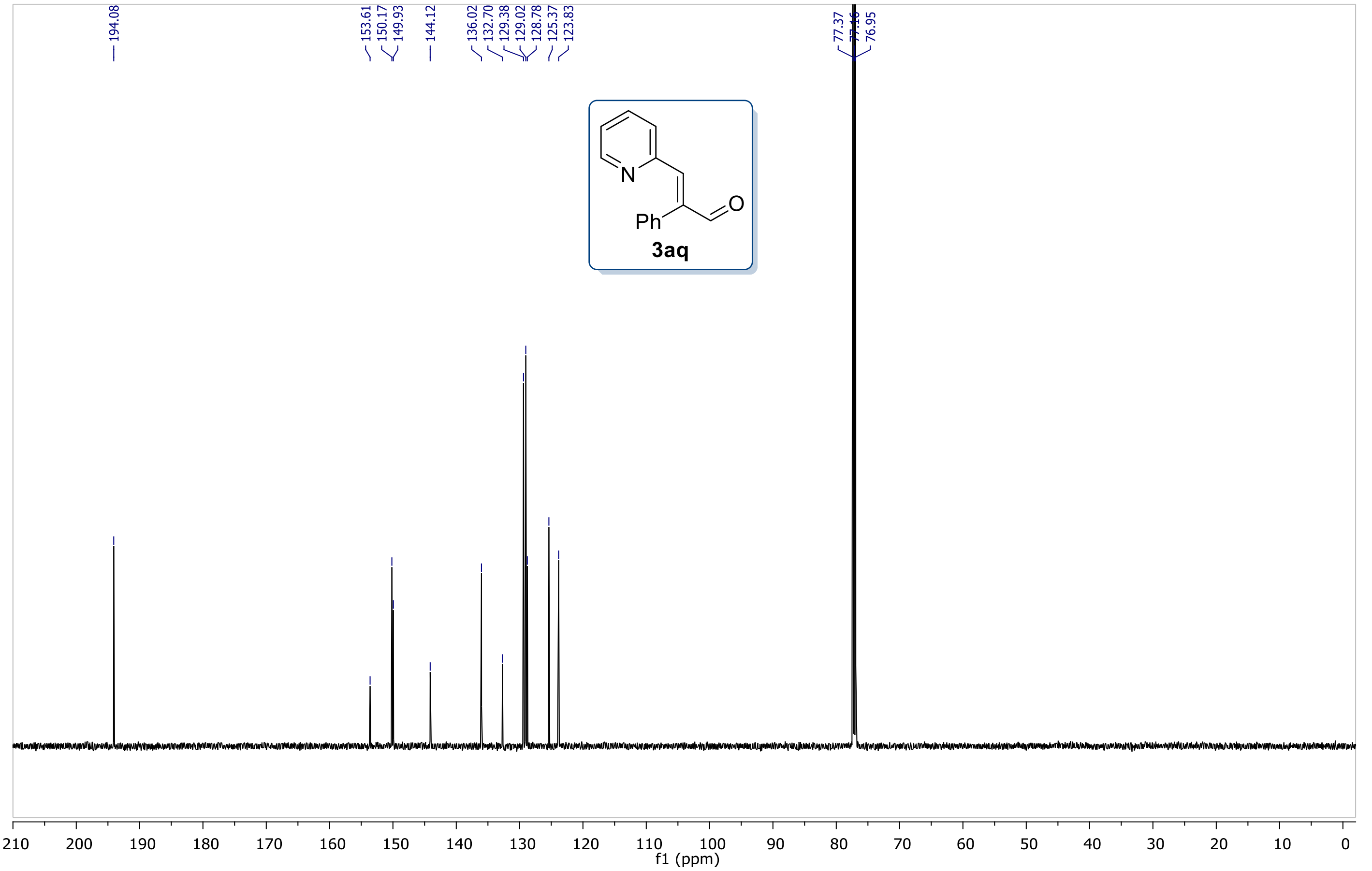
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **3ap**



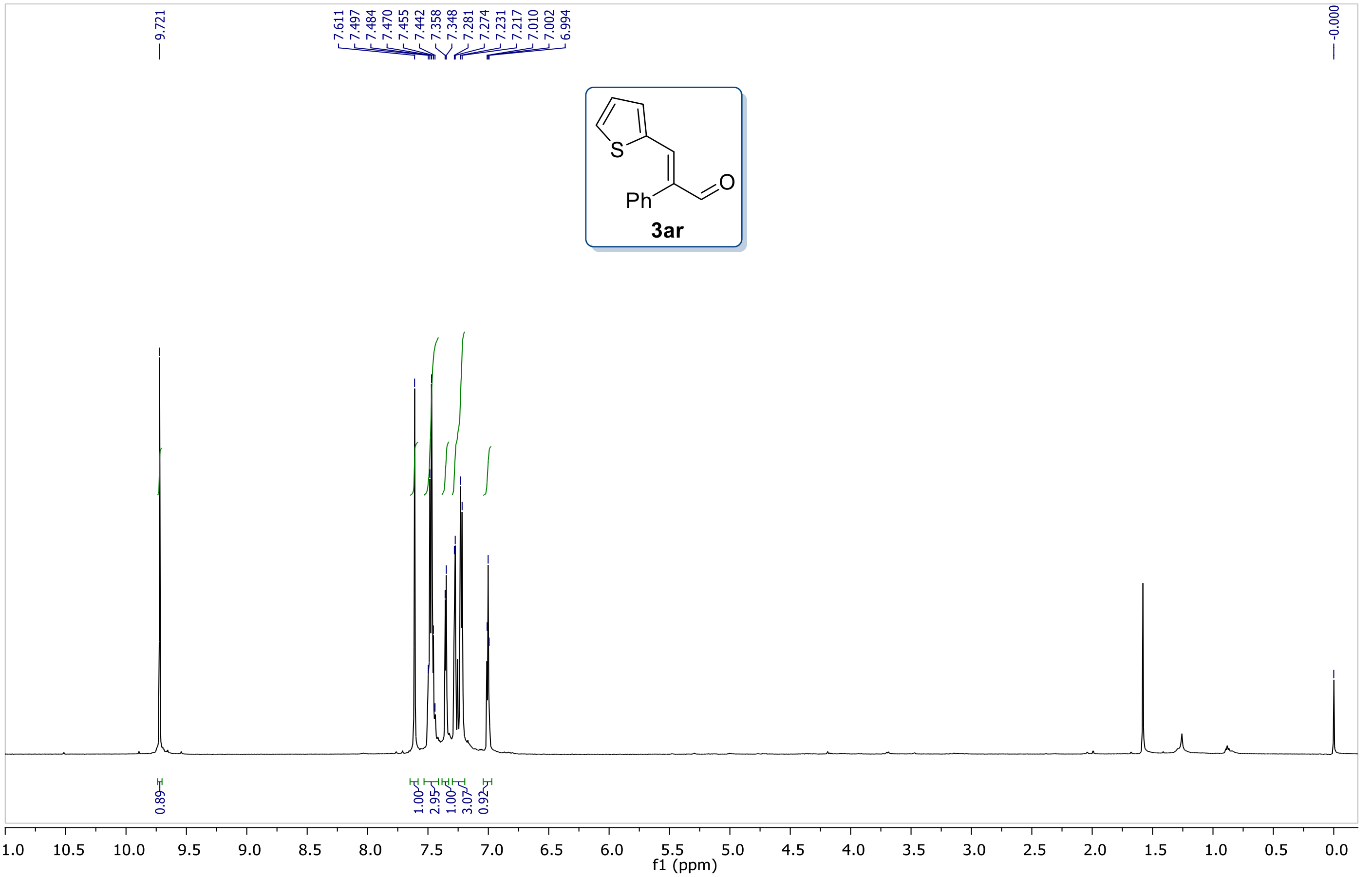


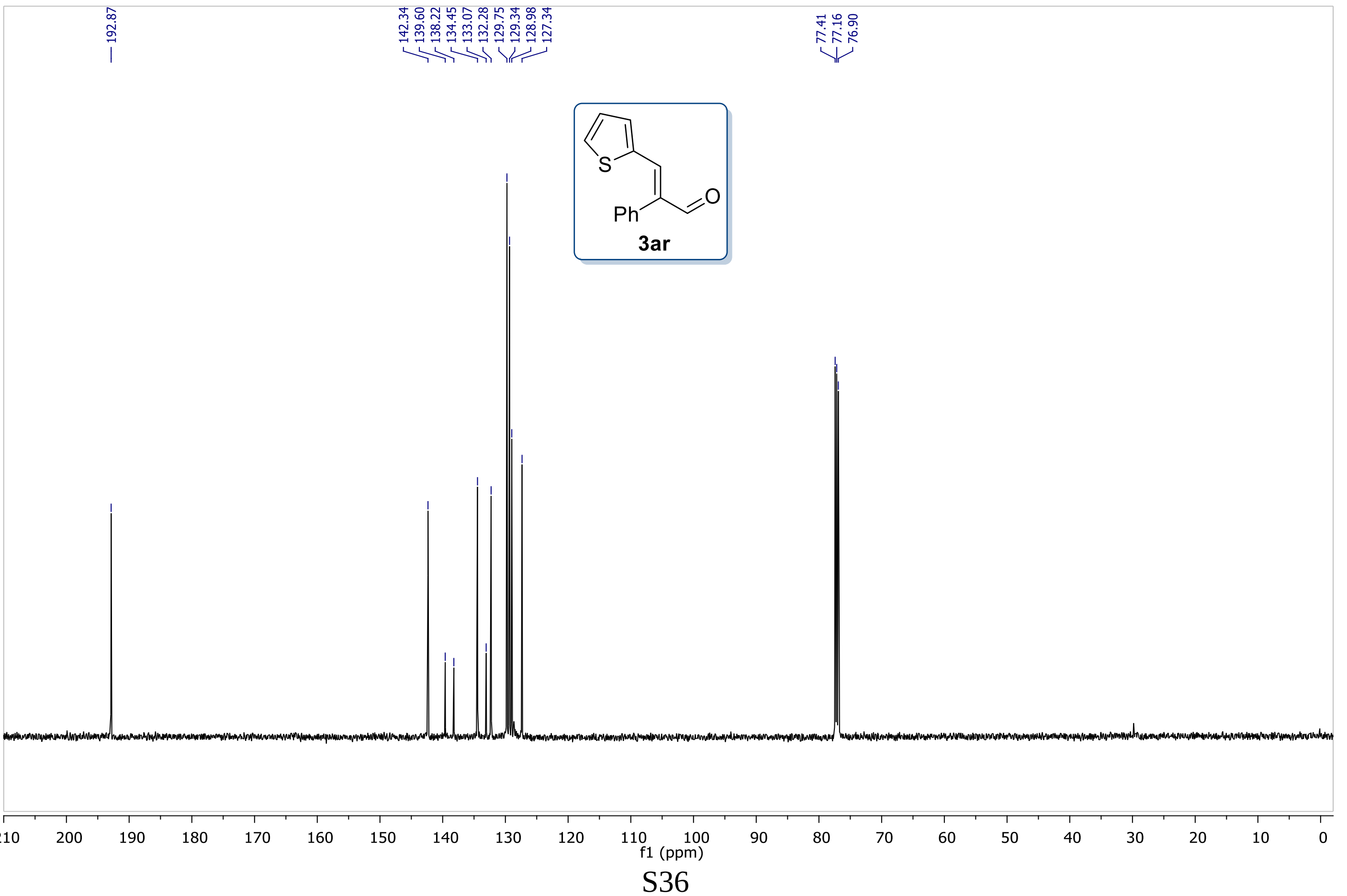
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3aq**



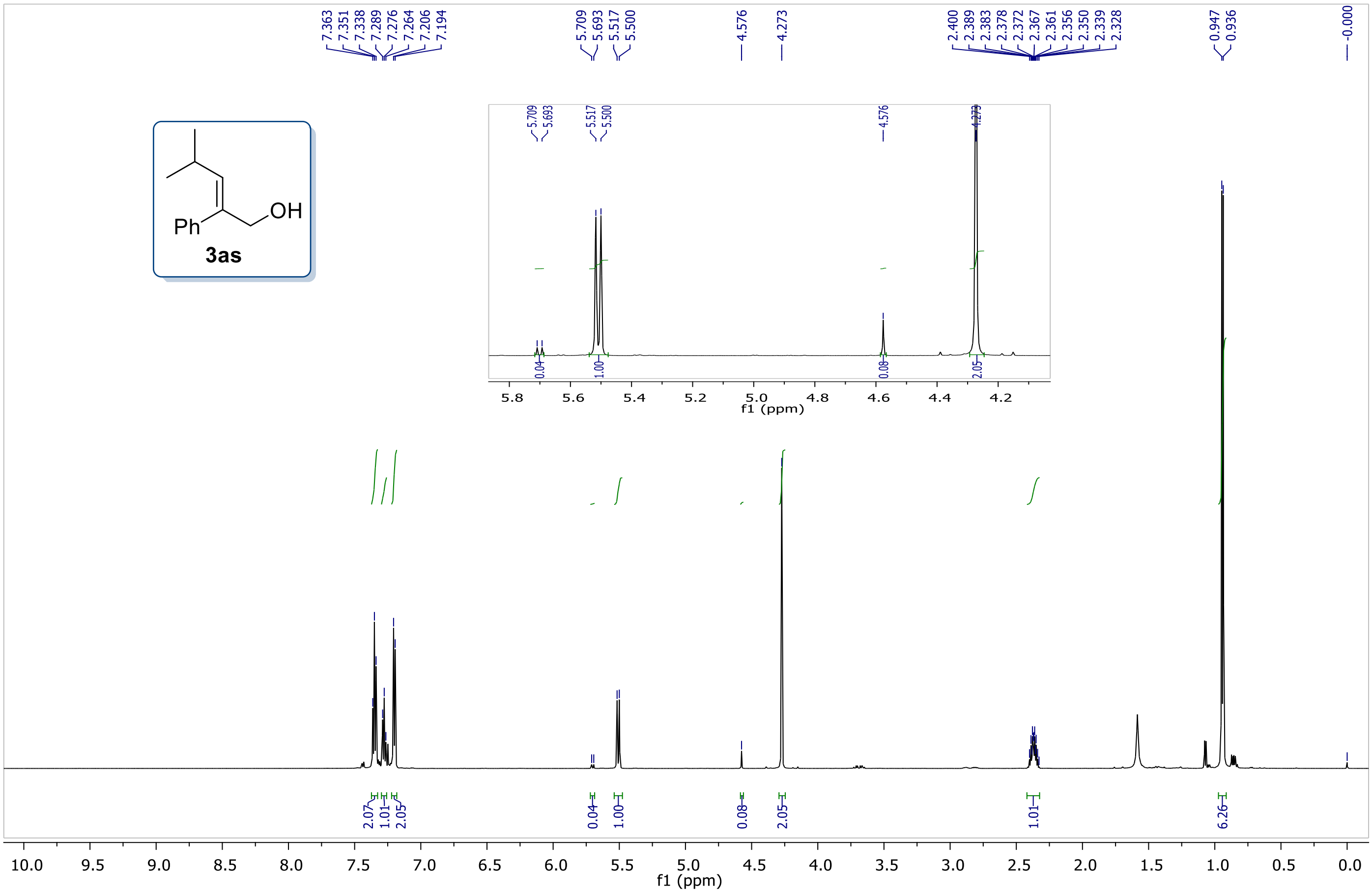


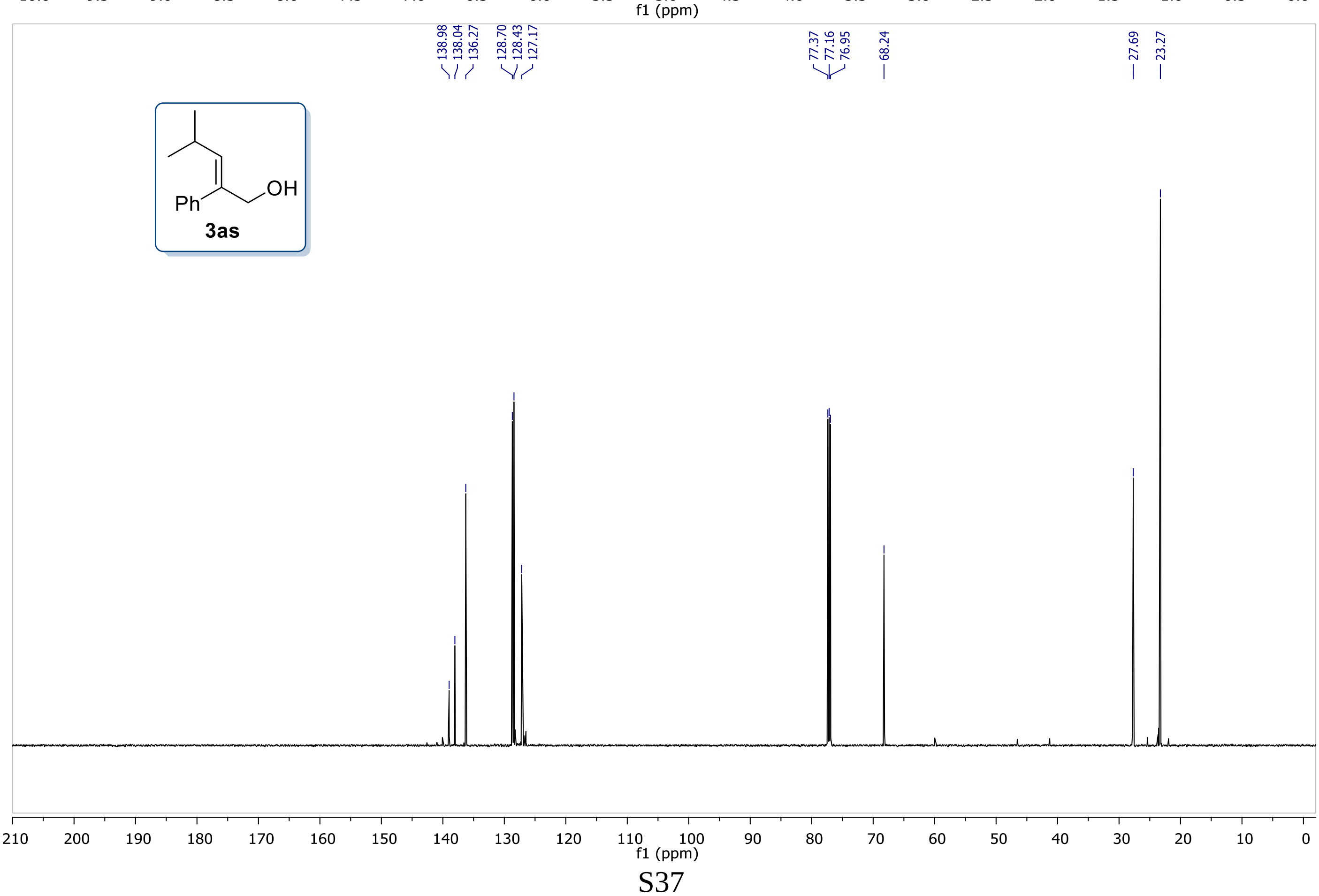
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3ar**



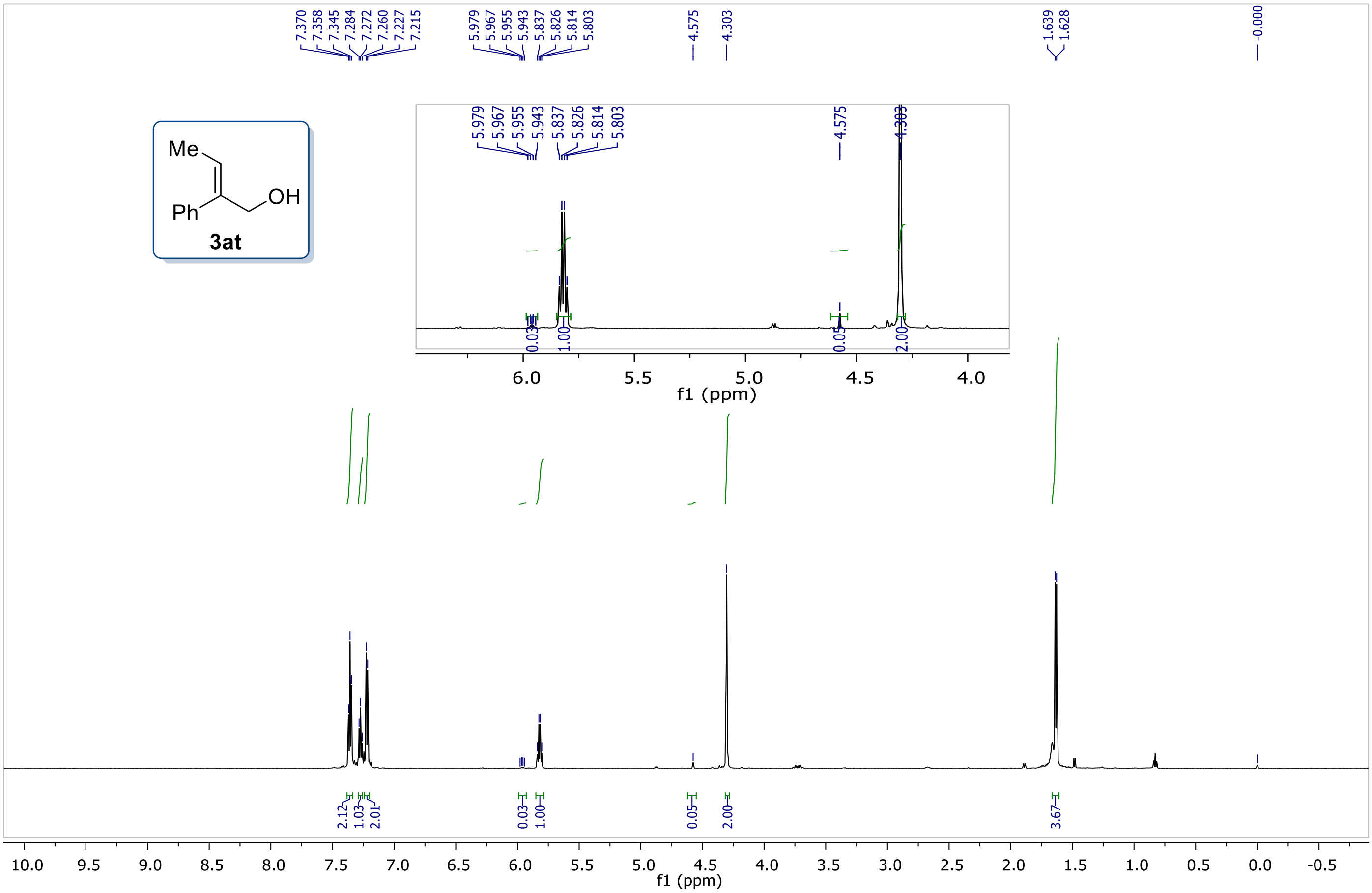


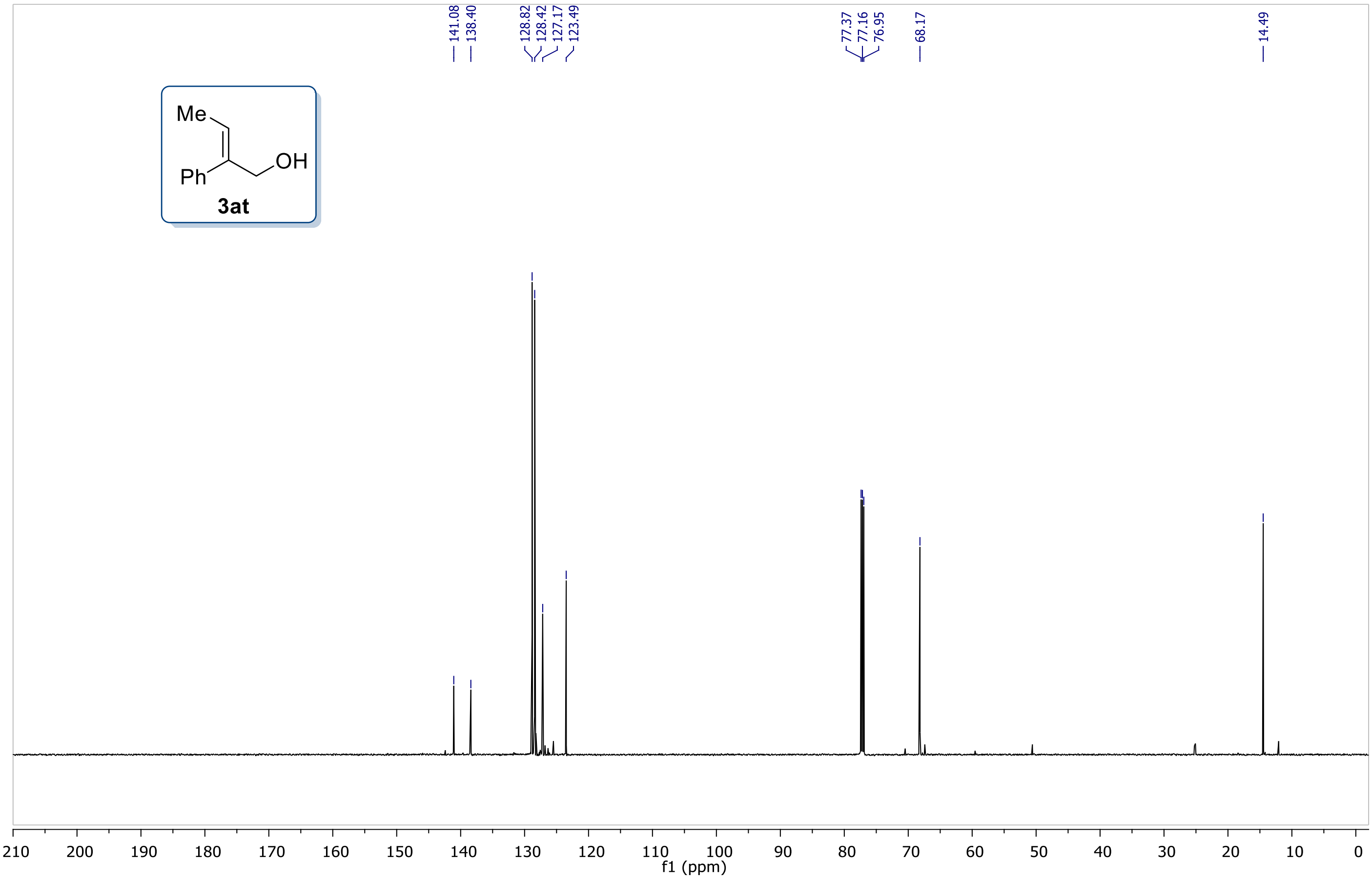
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), **3as**



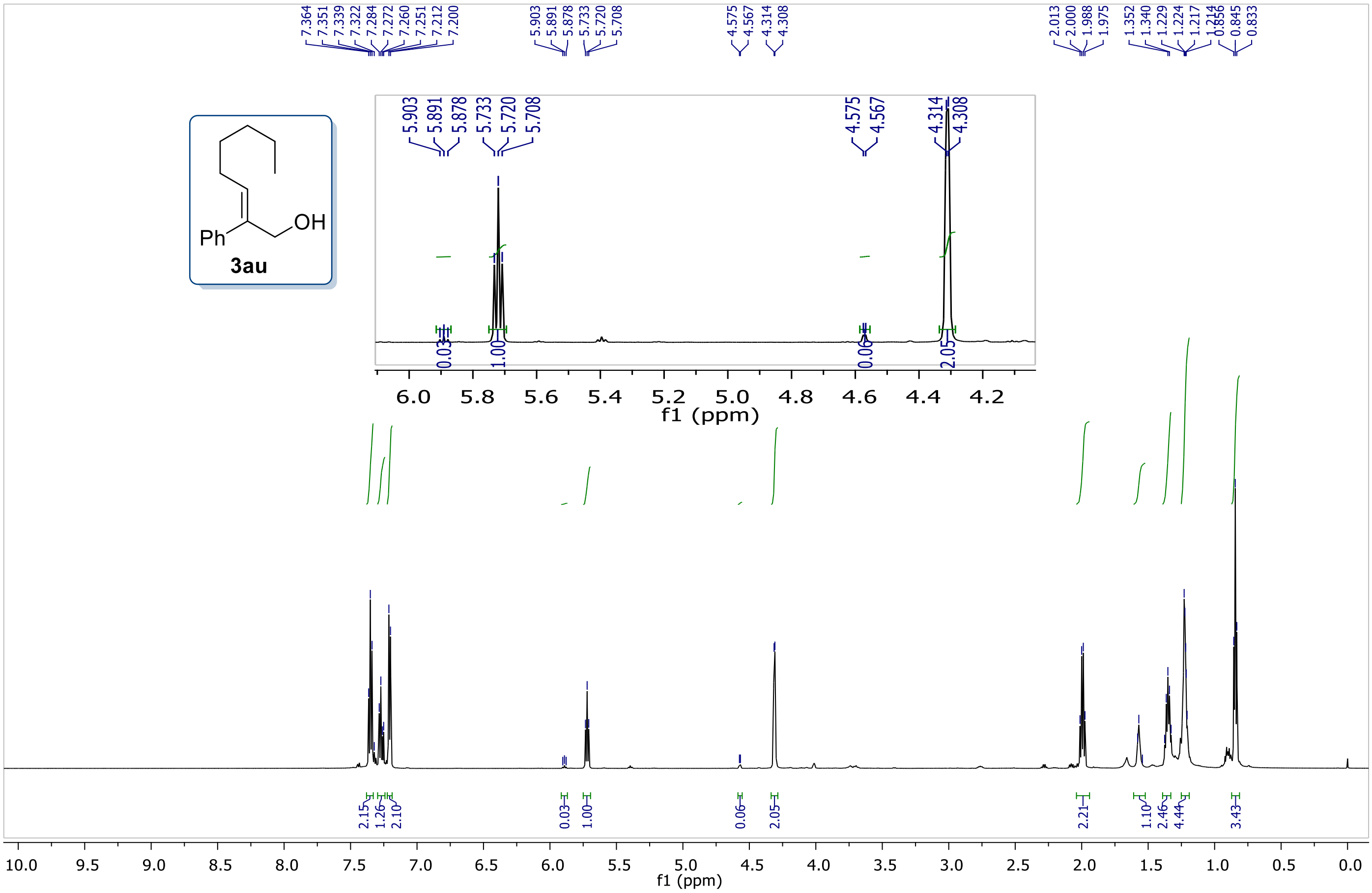


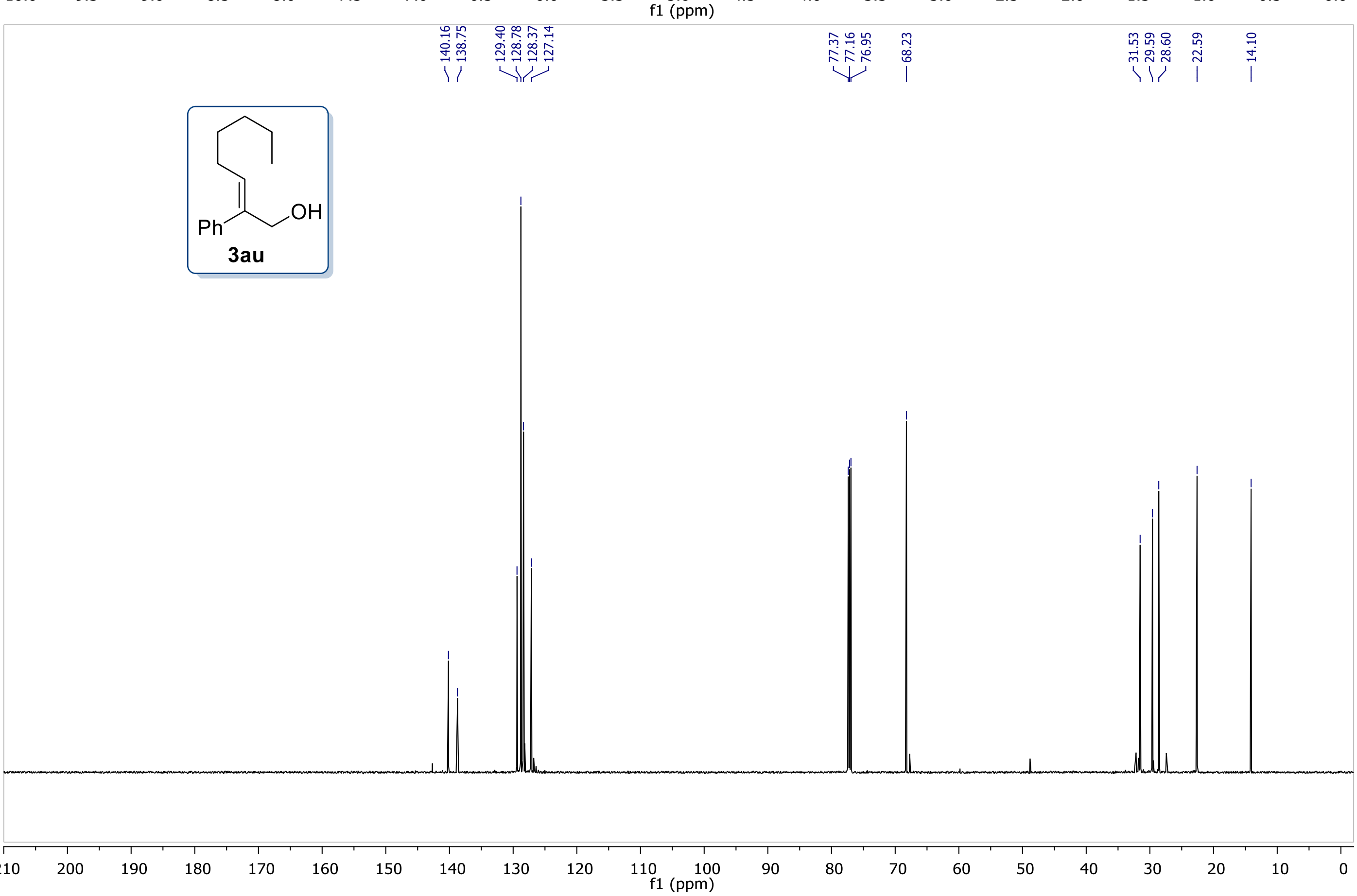
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3at**



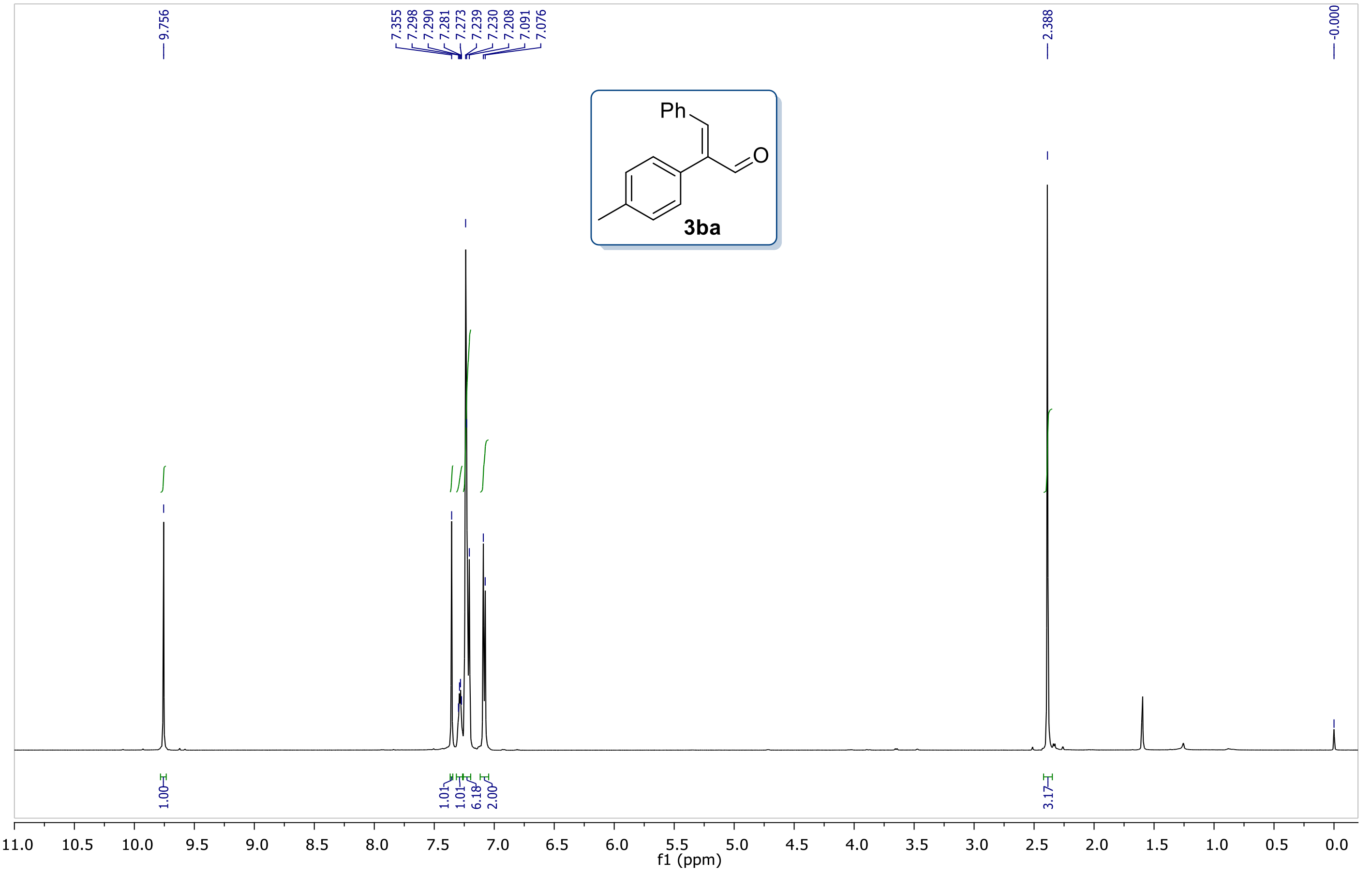


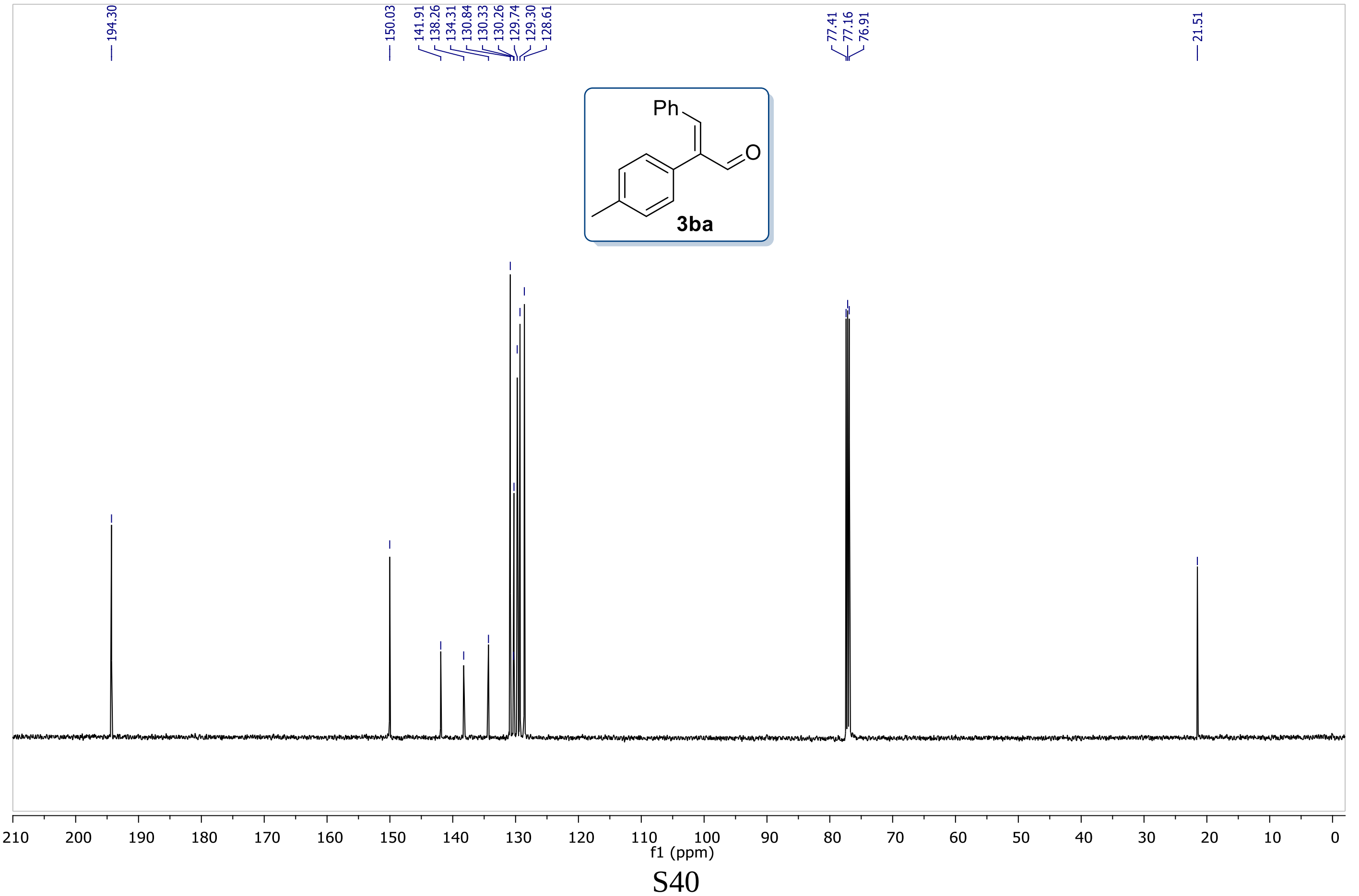
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3au**





[1]H NMR (500 MHz, $CDCl_3$) and [13]C{[1]H} NMR (126 MHz, $CDCl_3$), **3ba**





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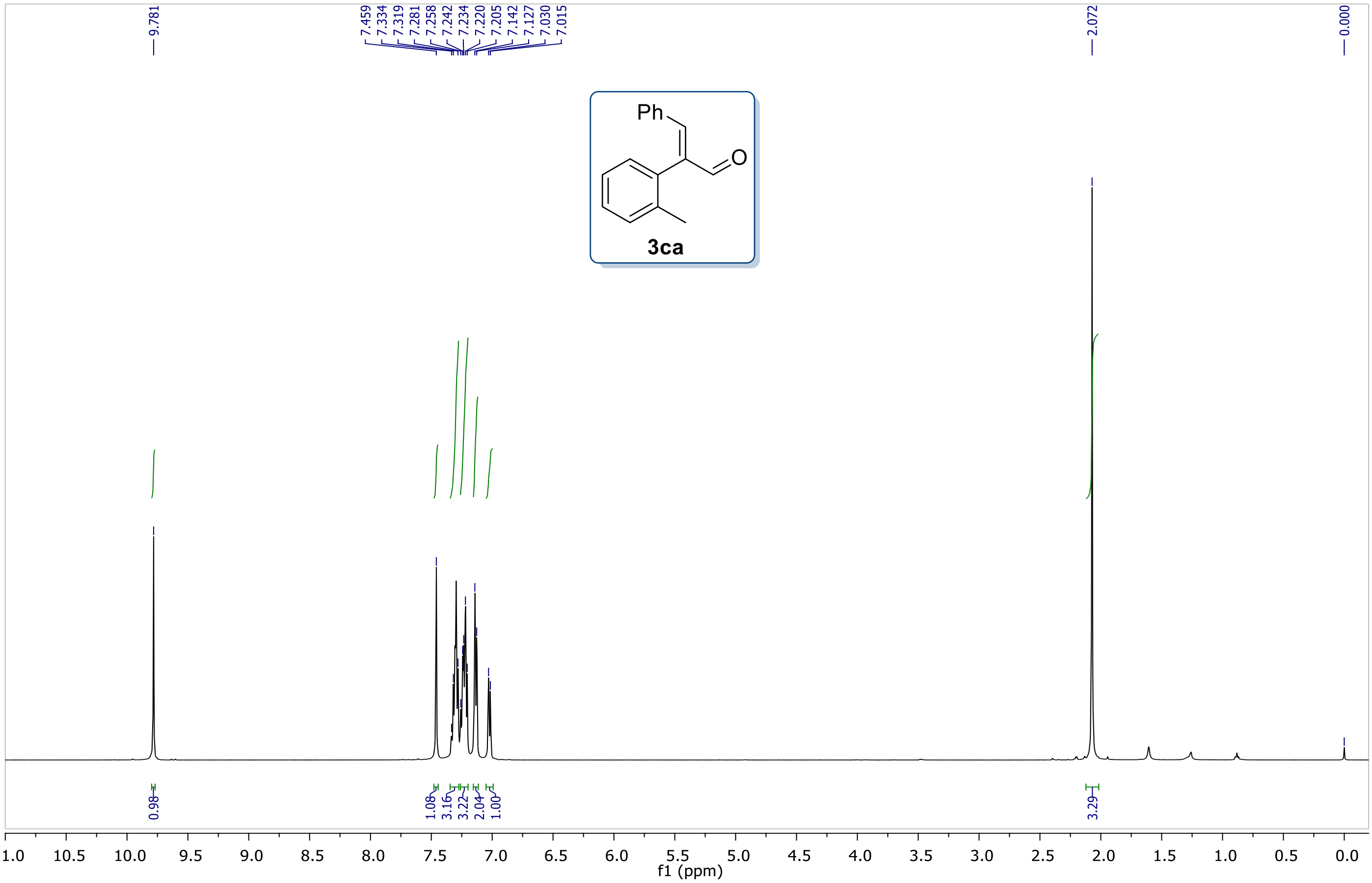
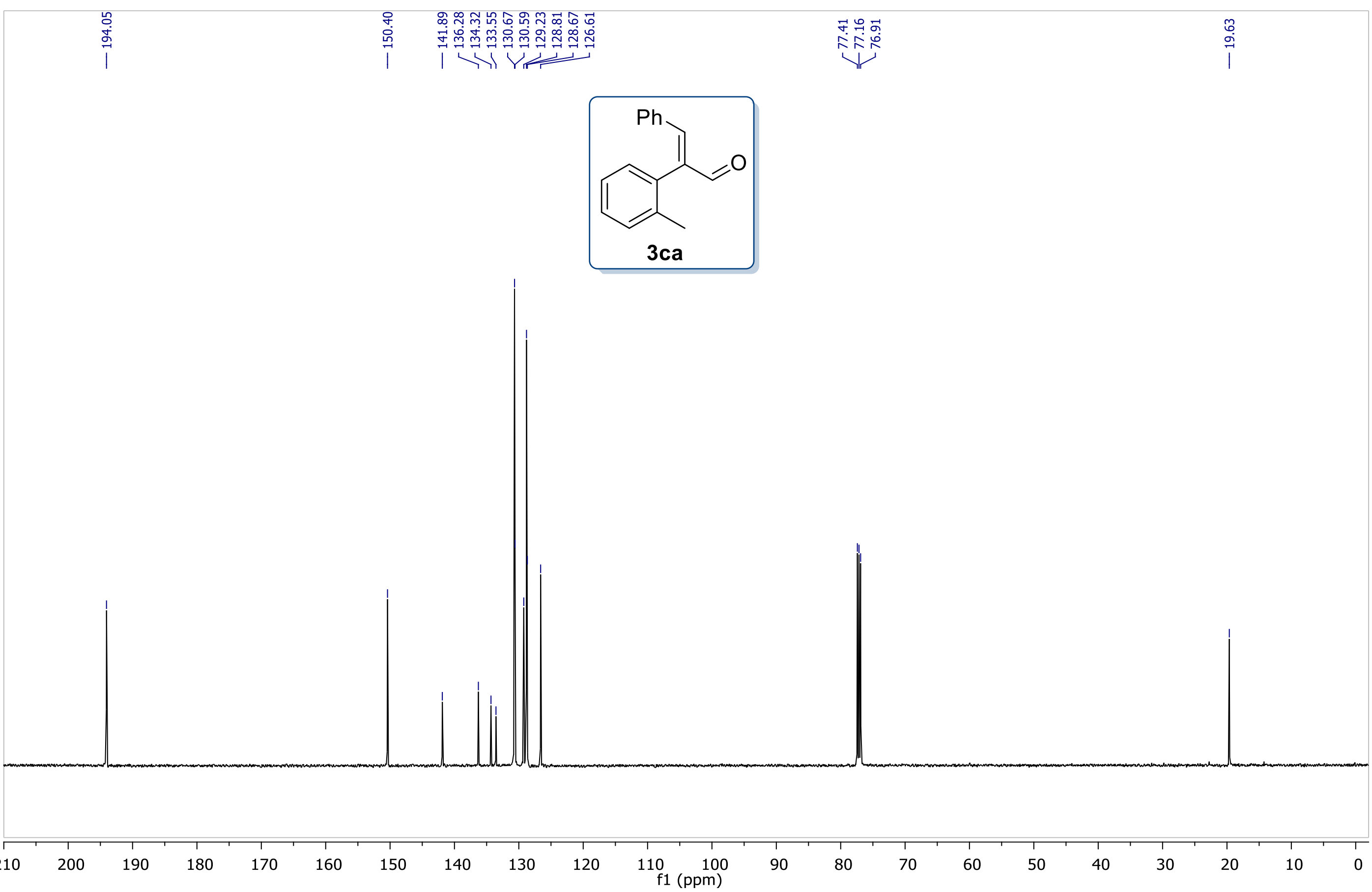
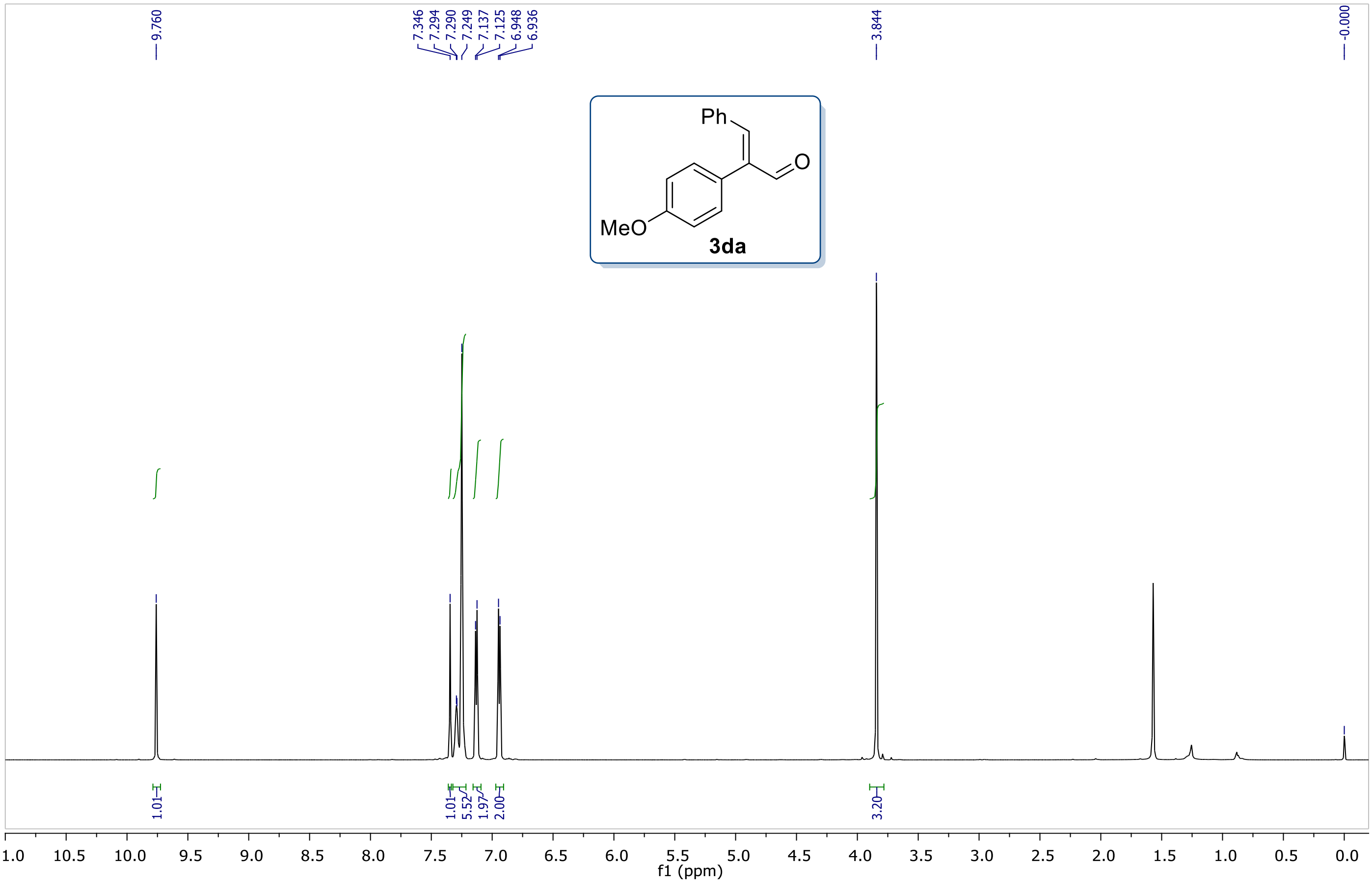
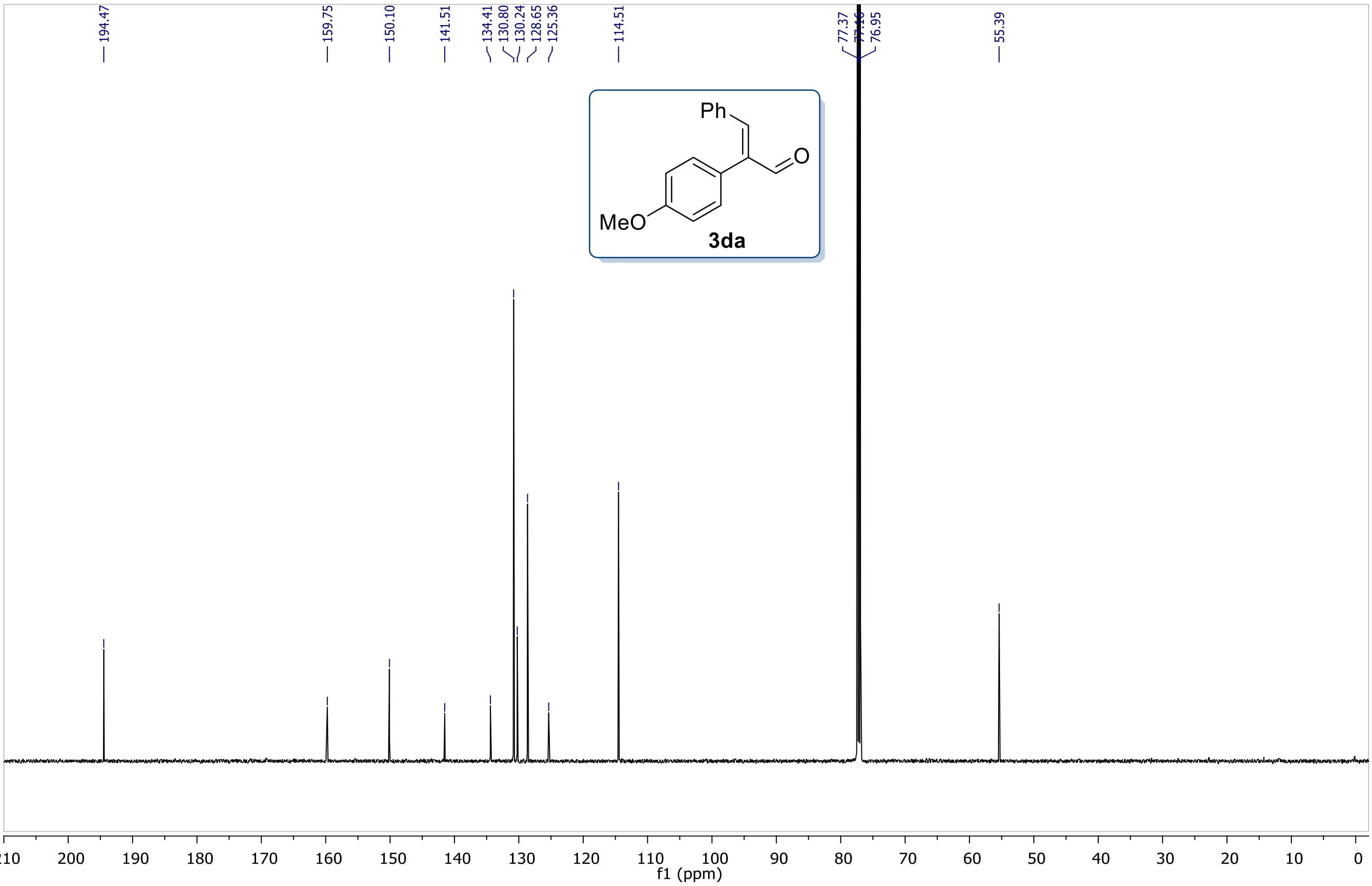




^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$), **3da**





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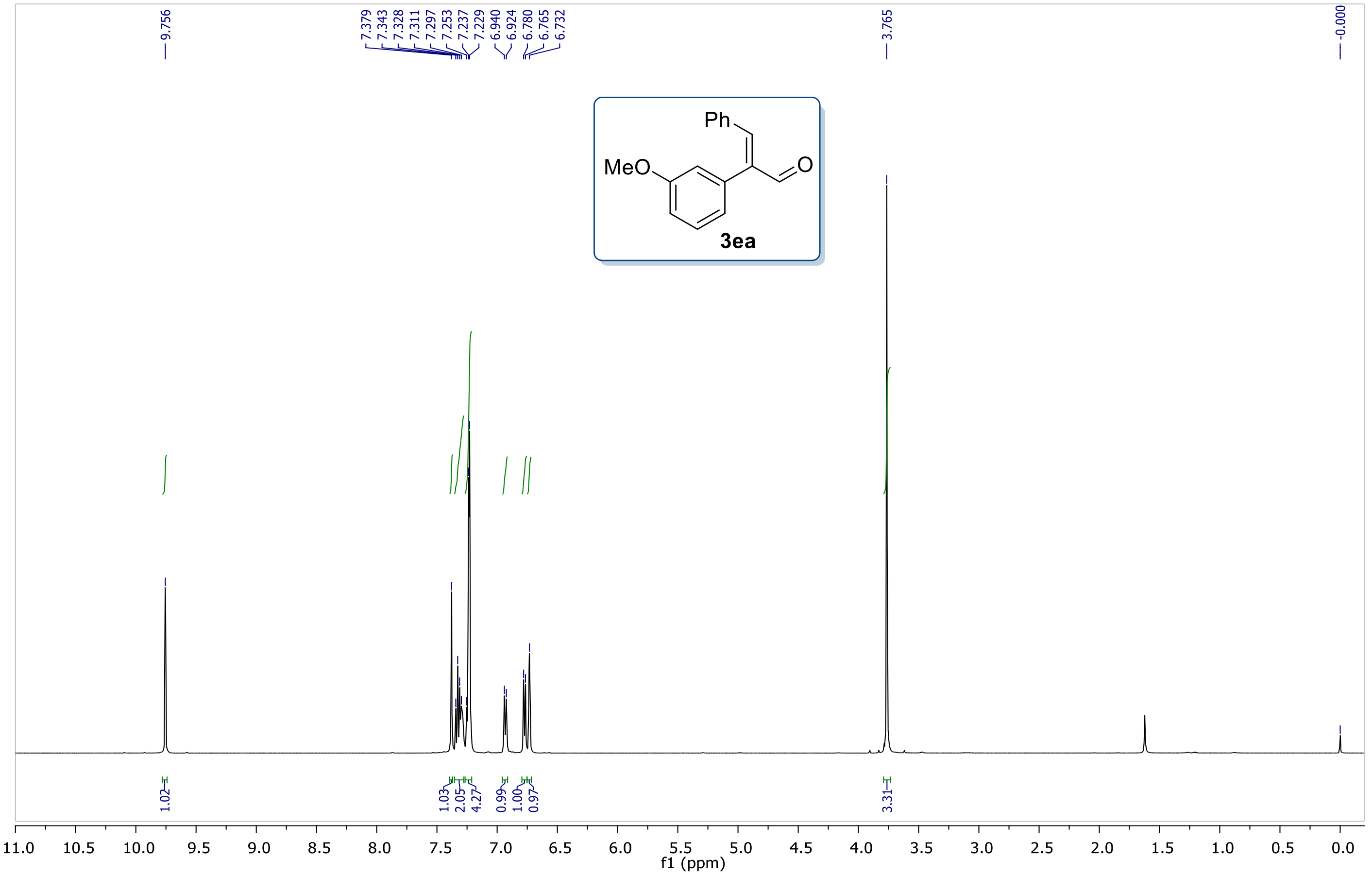
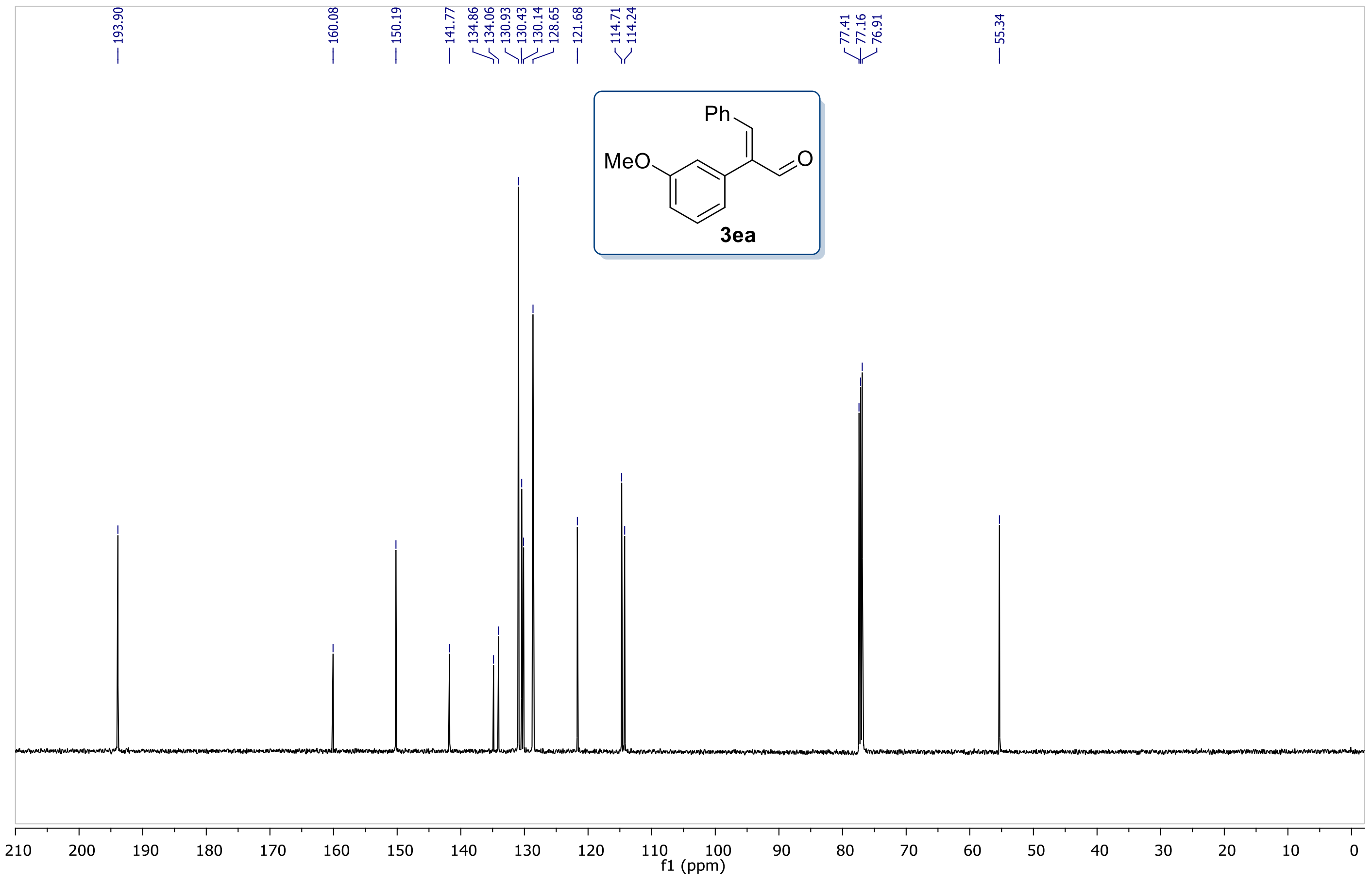
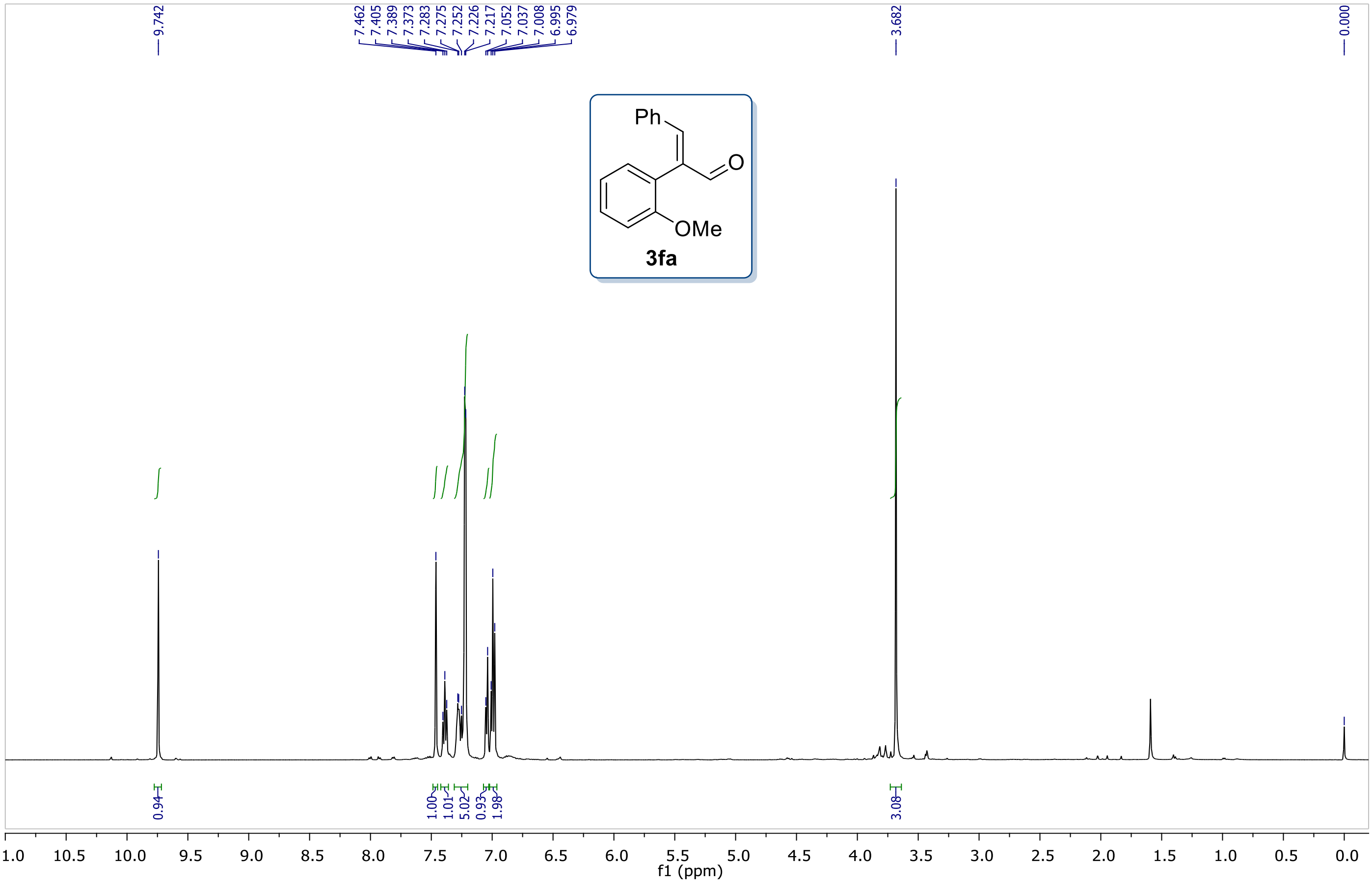
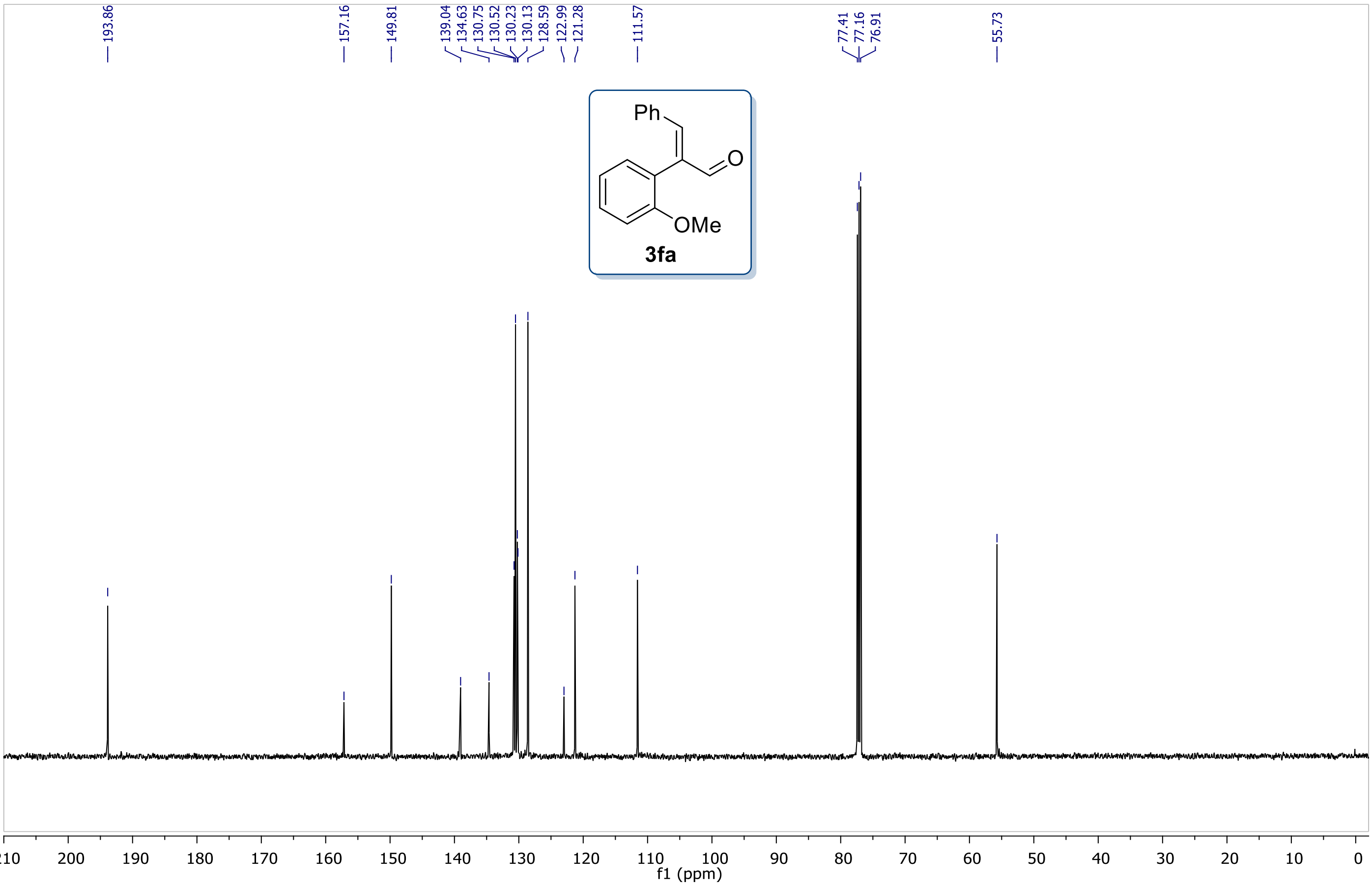




^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3fa**





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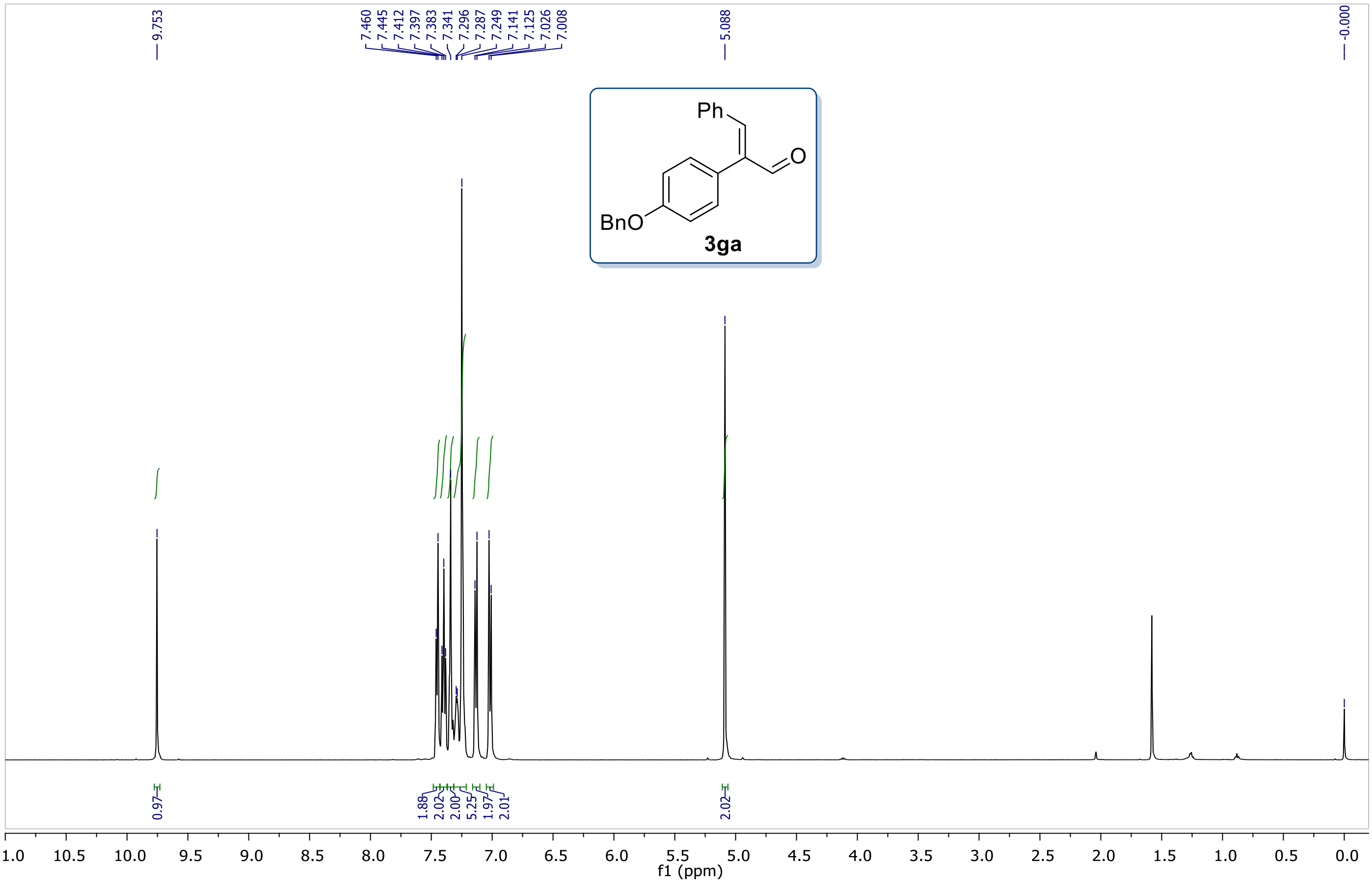

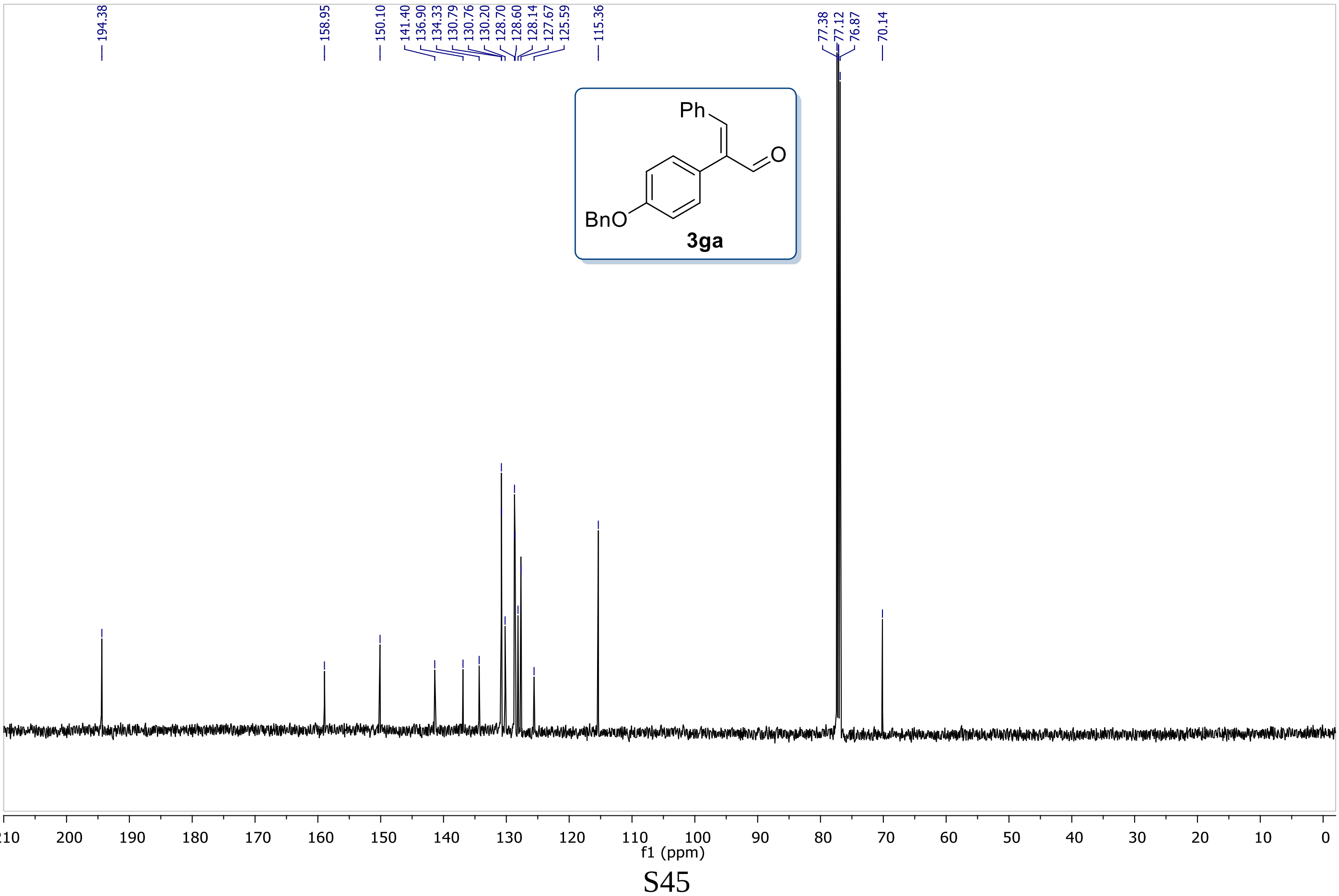

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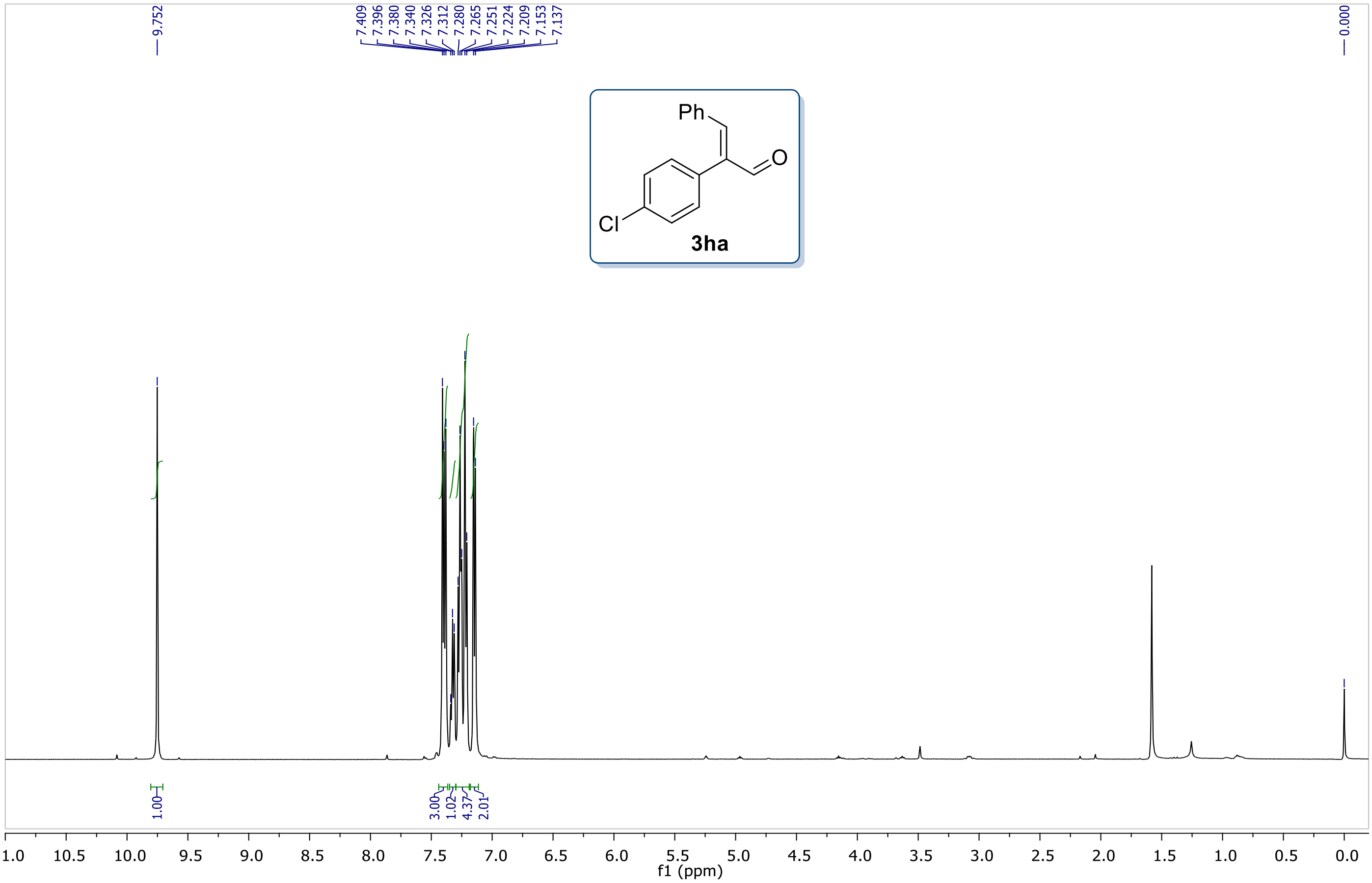
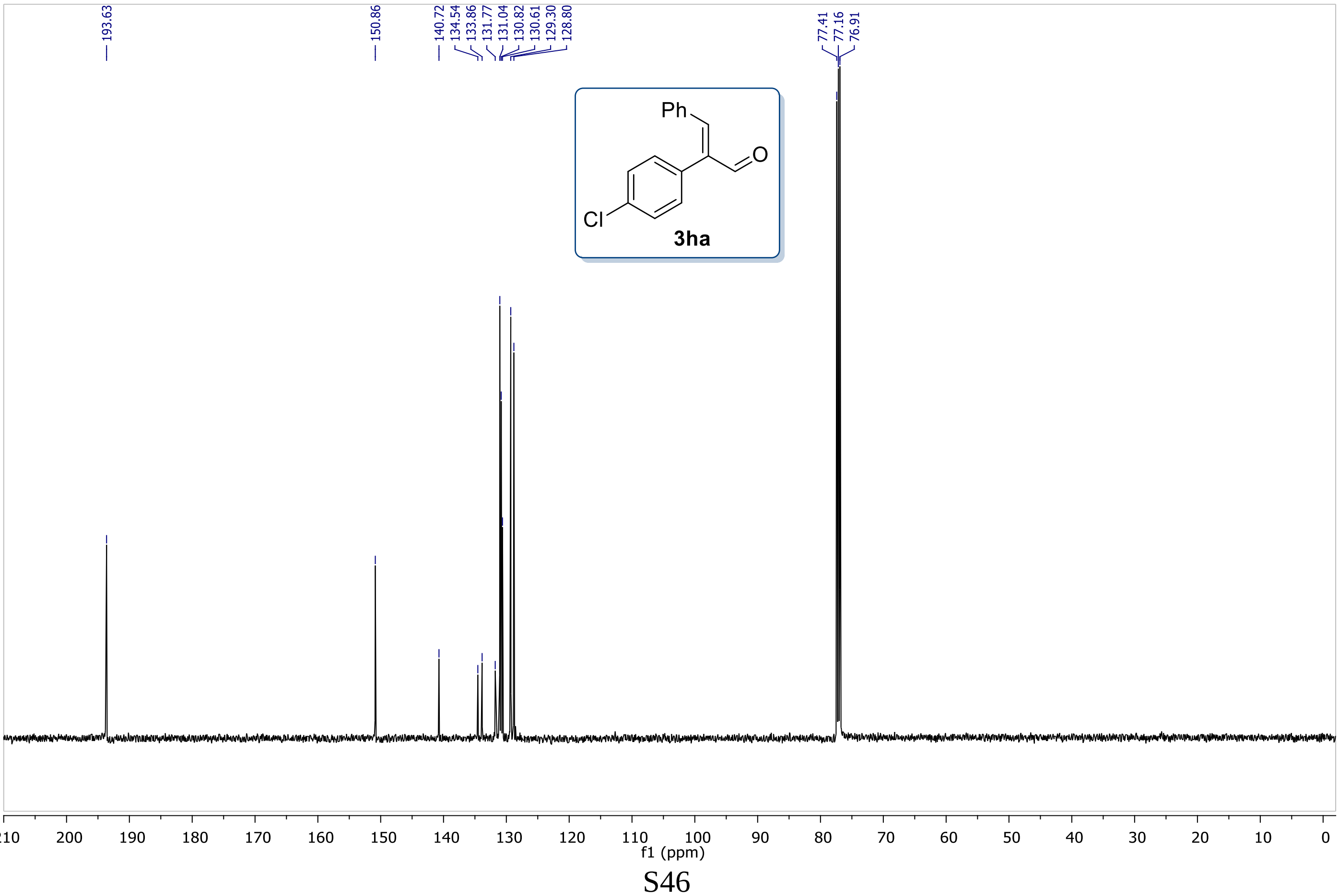
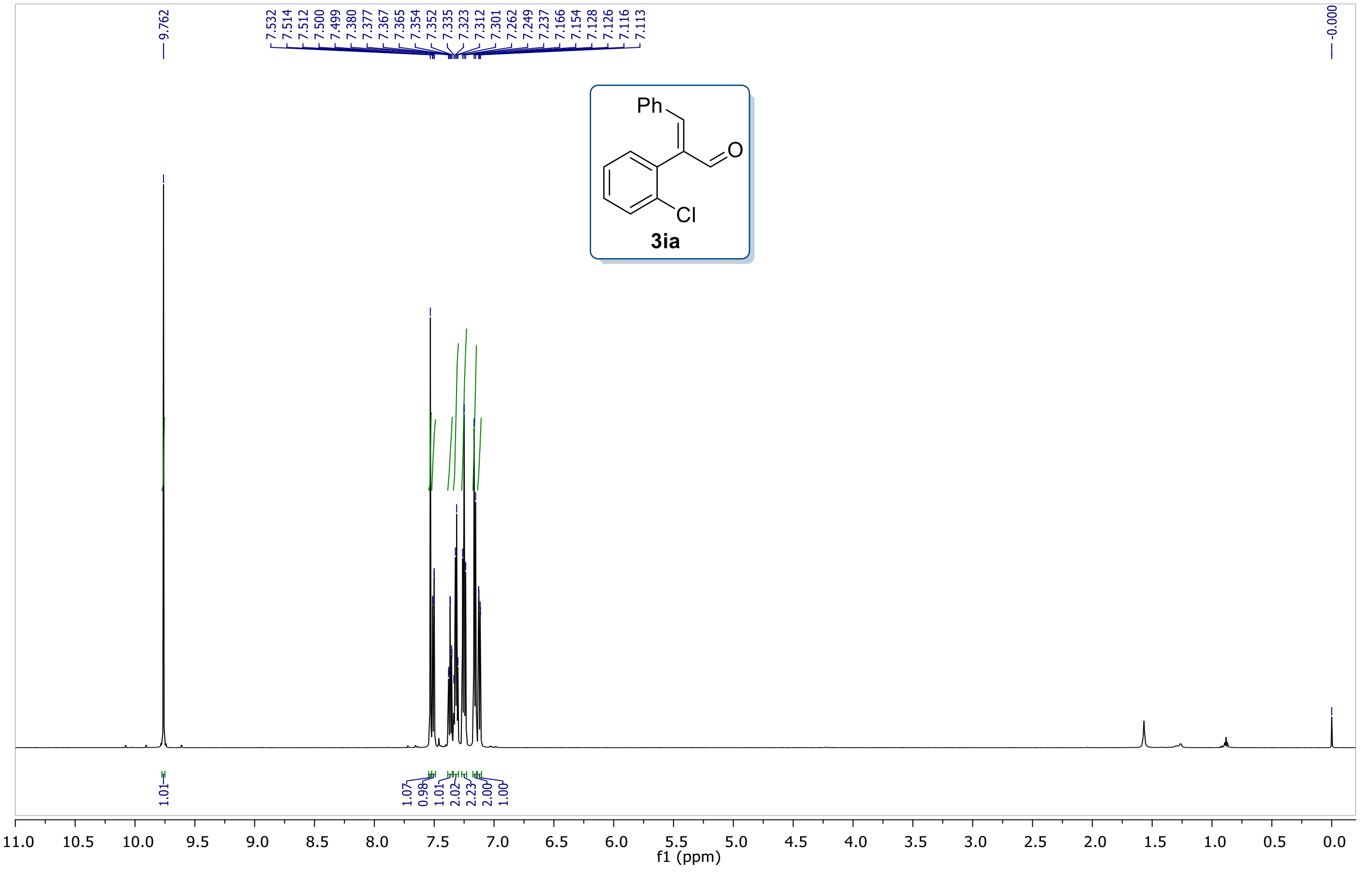
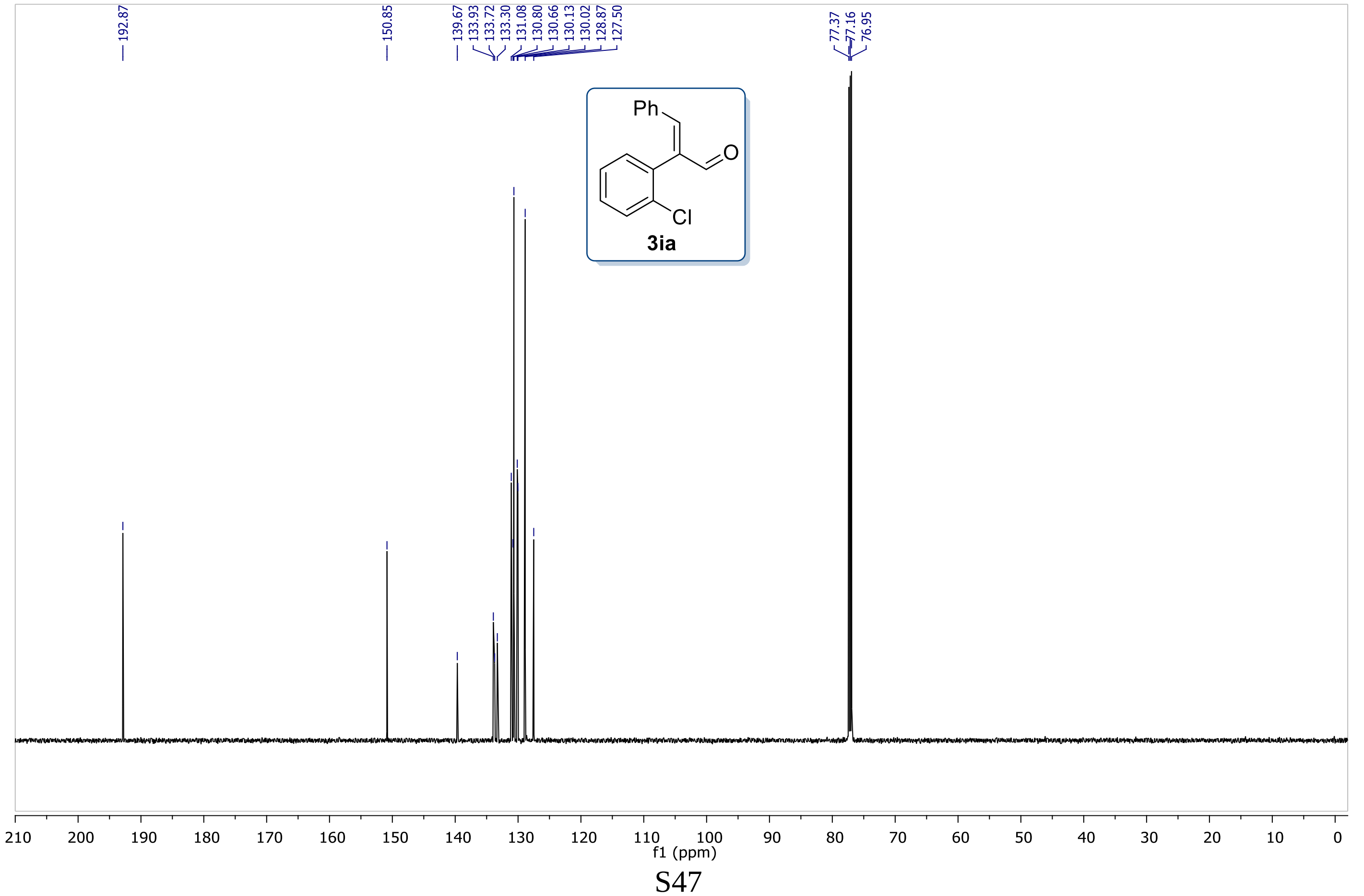


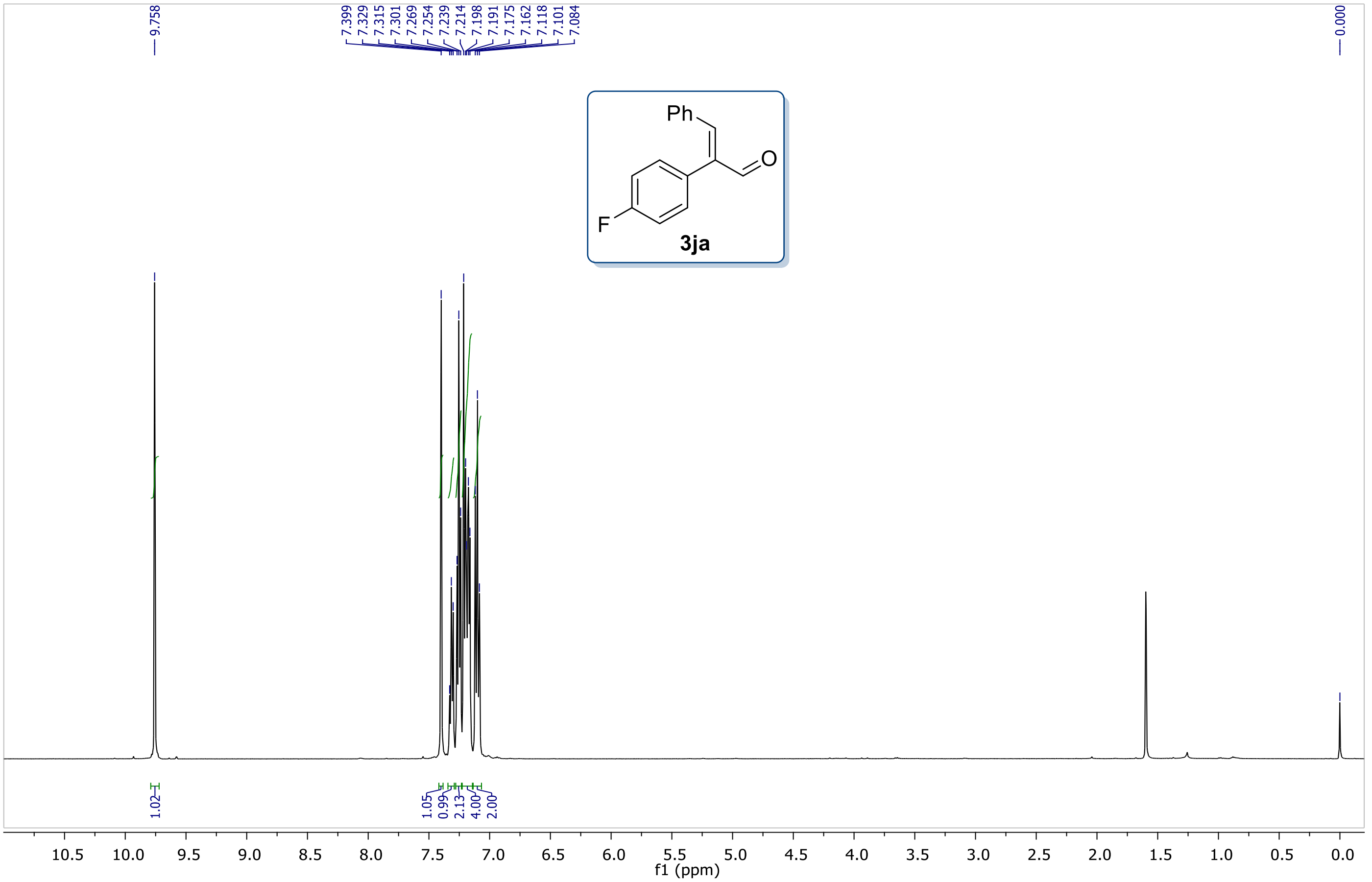


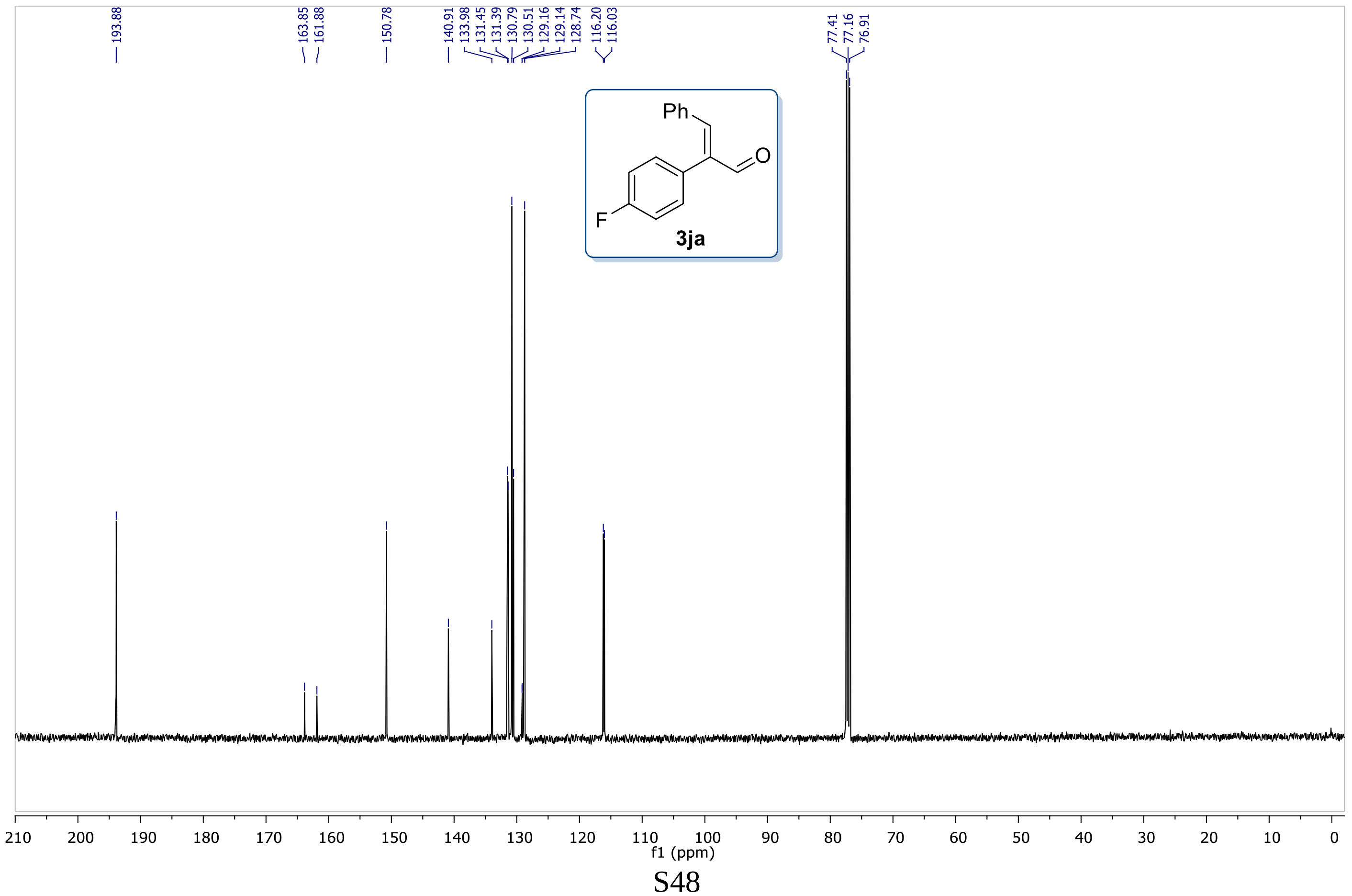
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3ia**



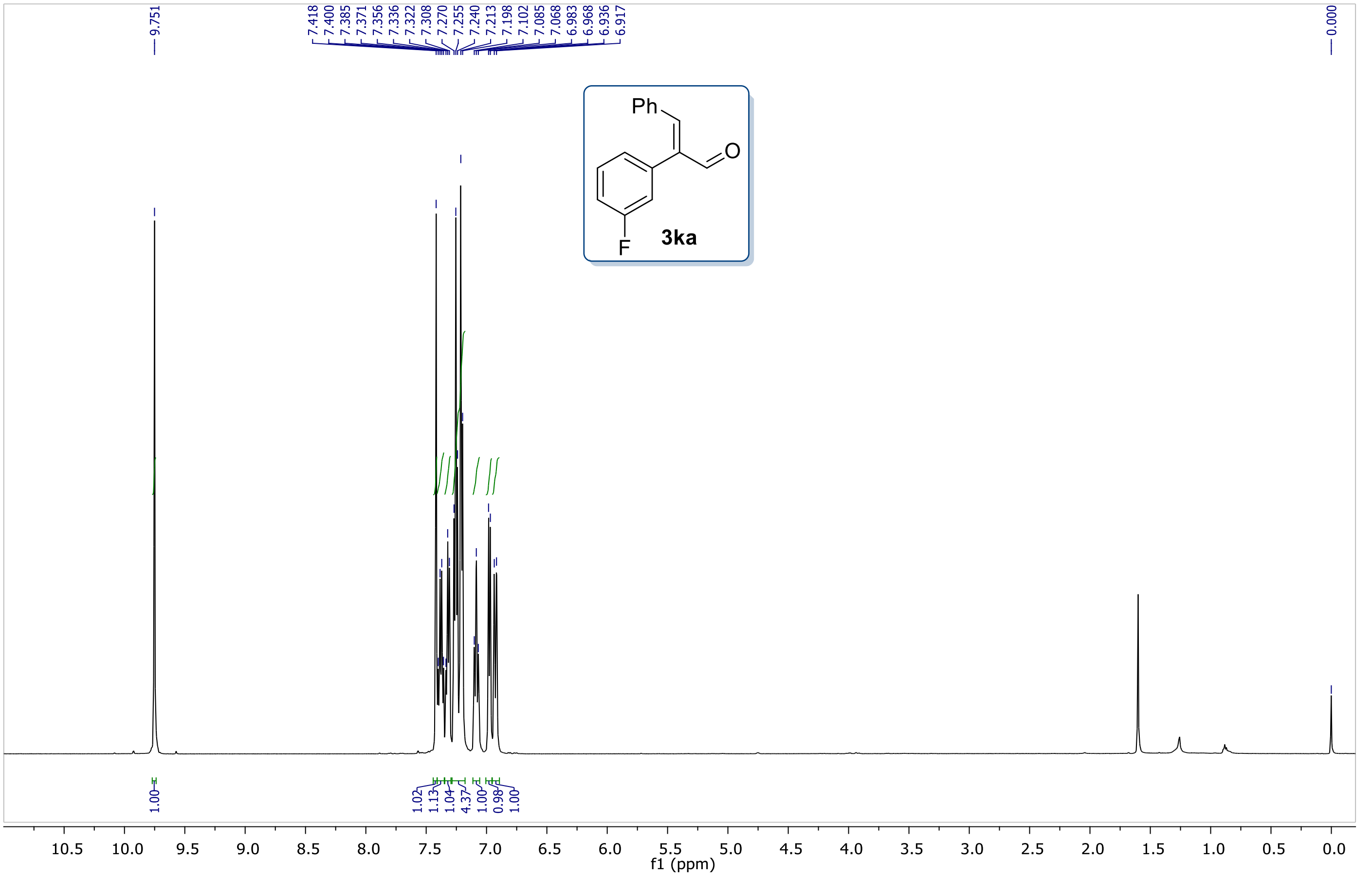


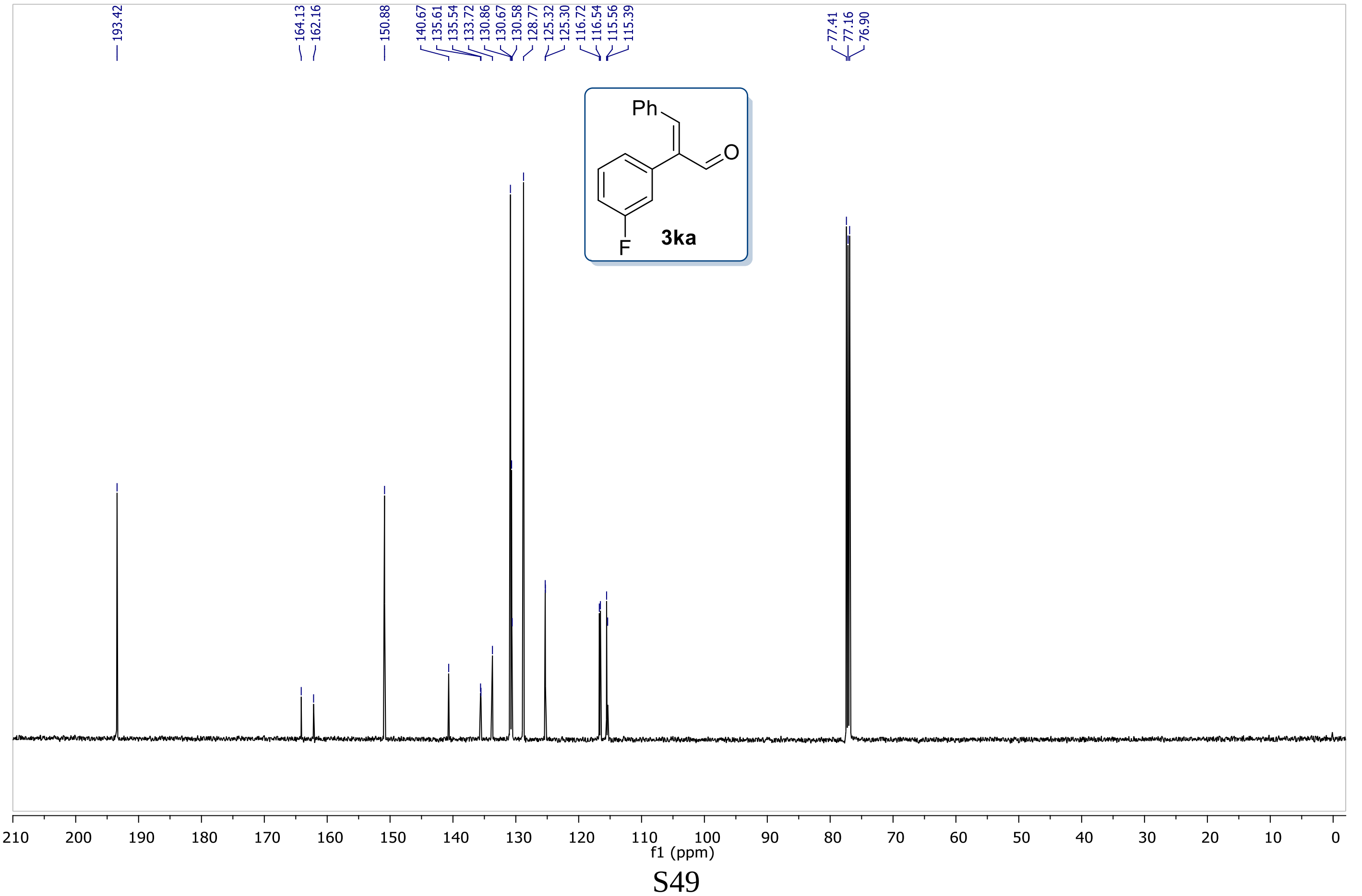
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3ja**



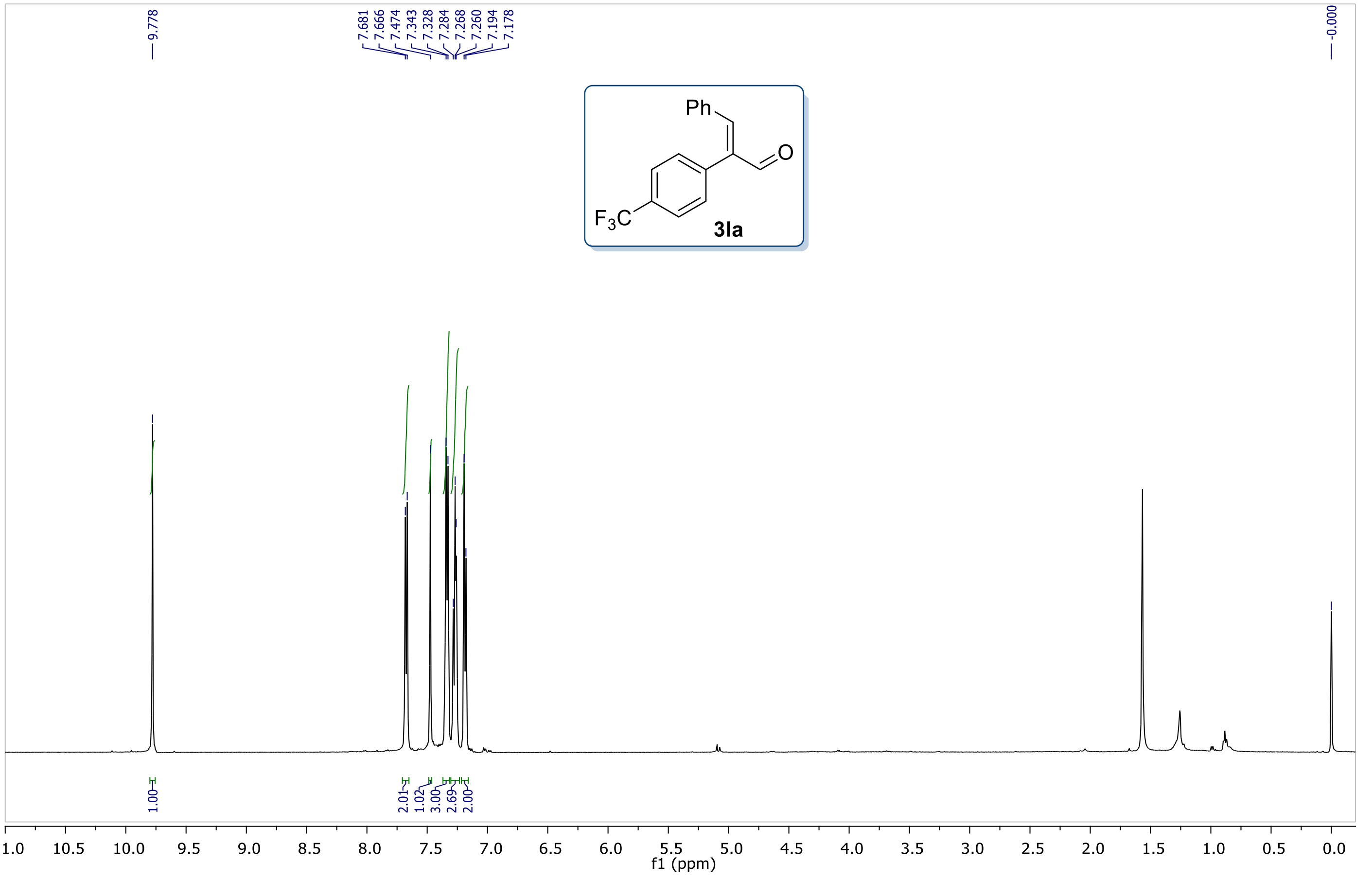


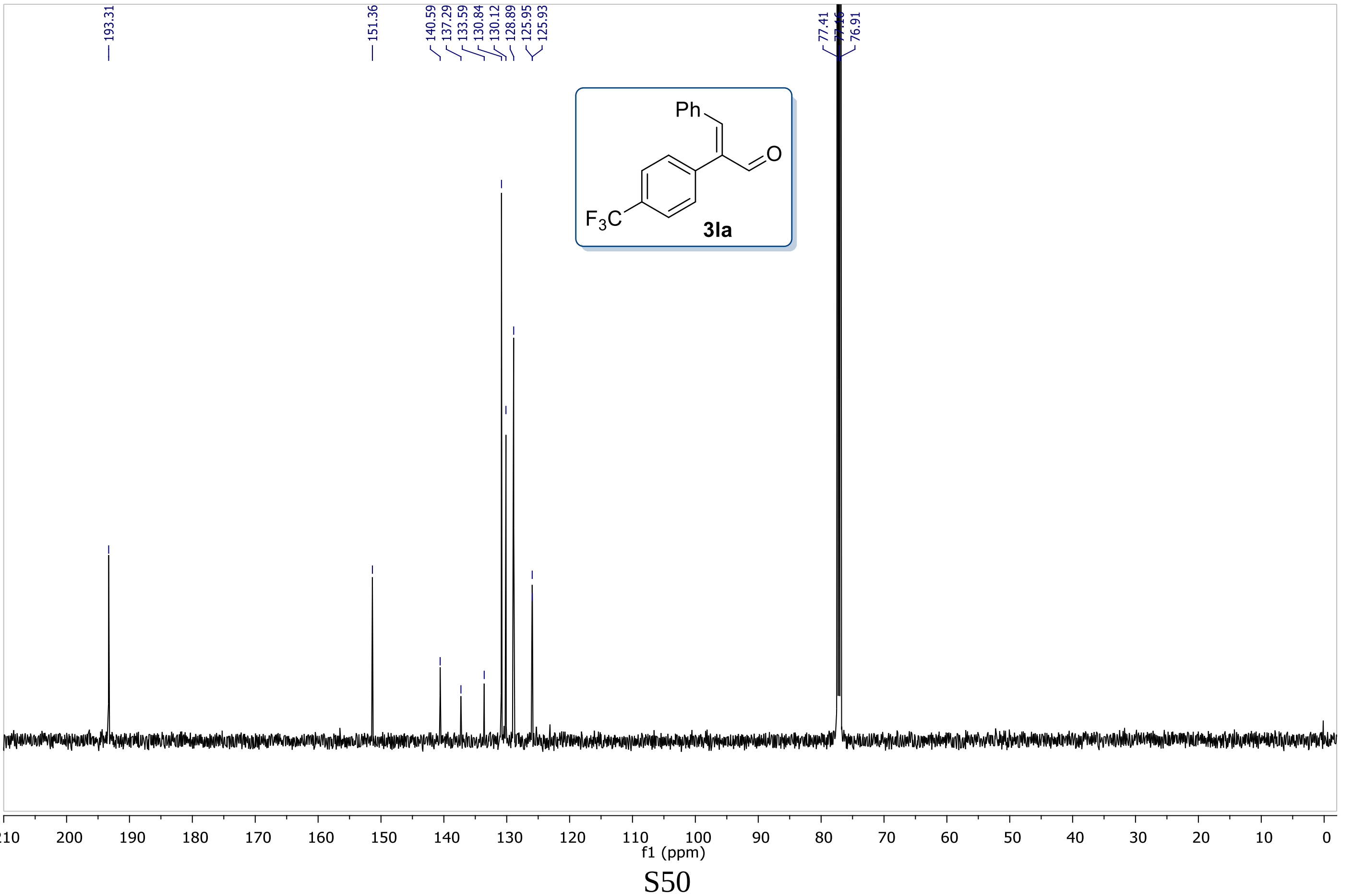
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3ka**



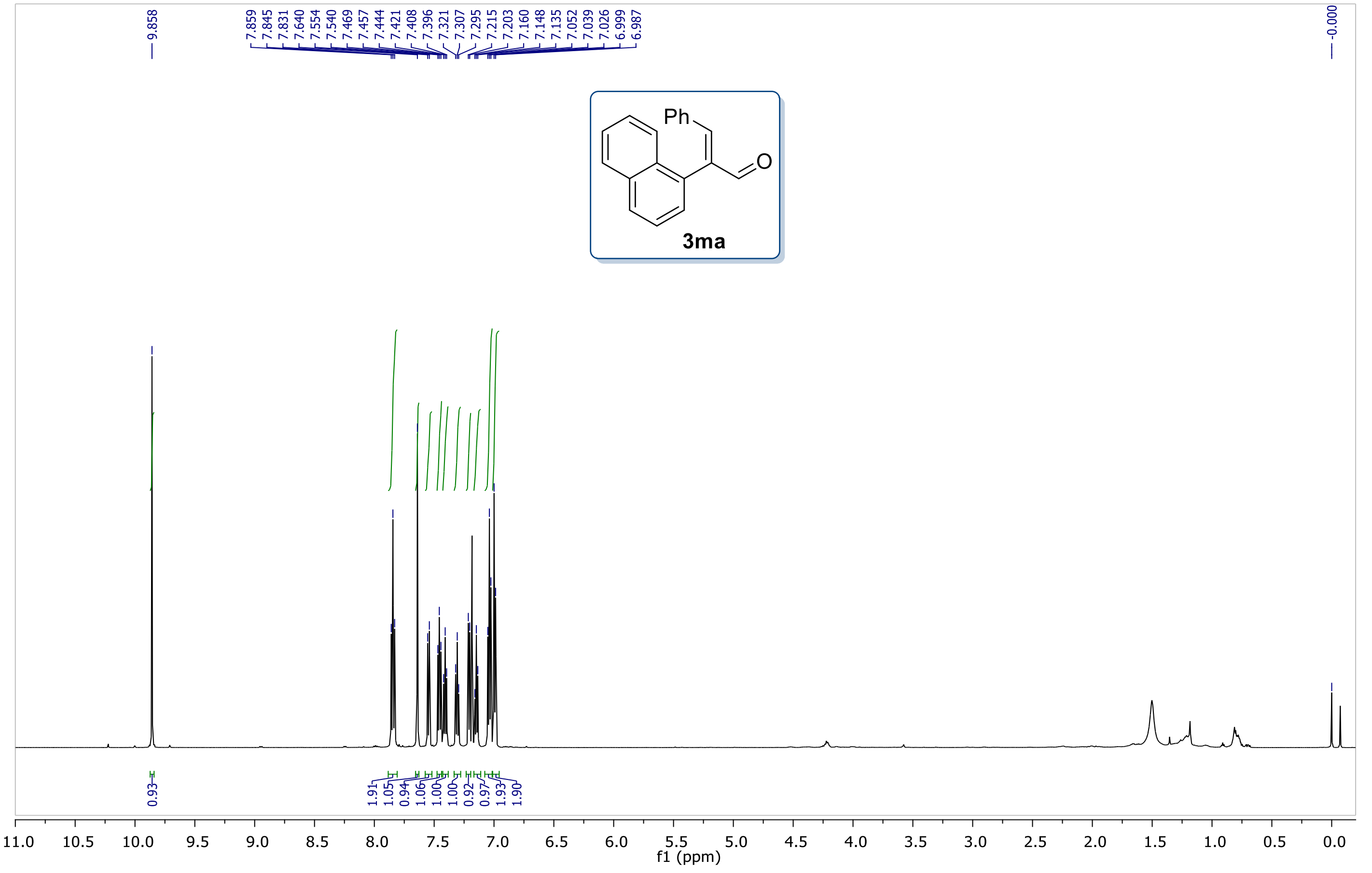


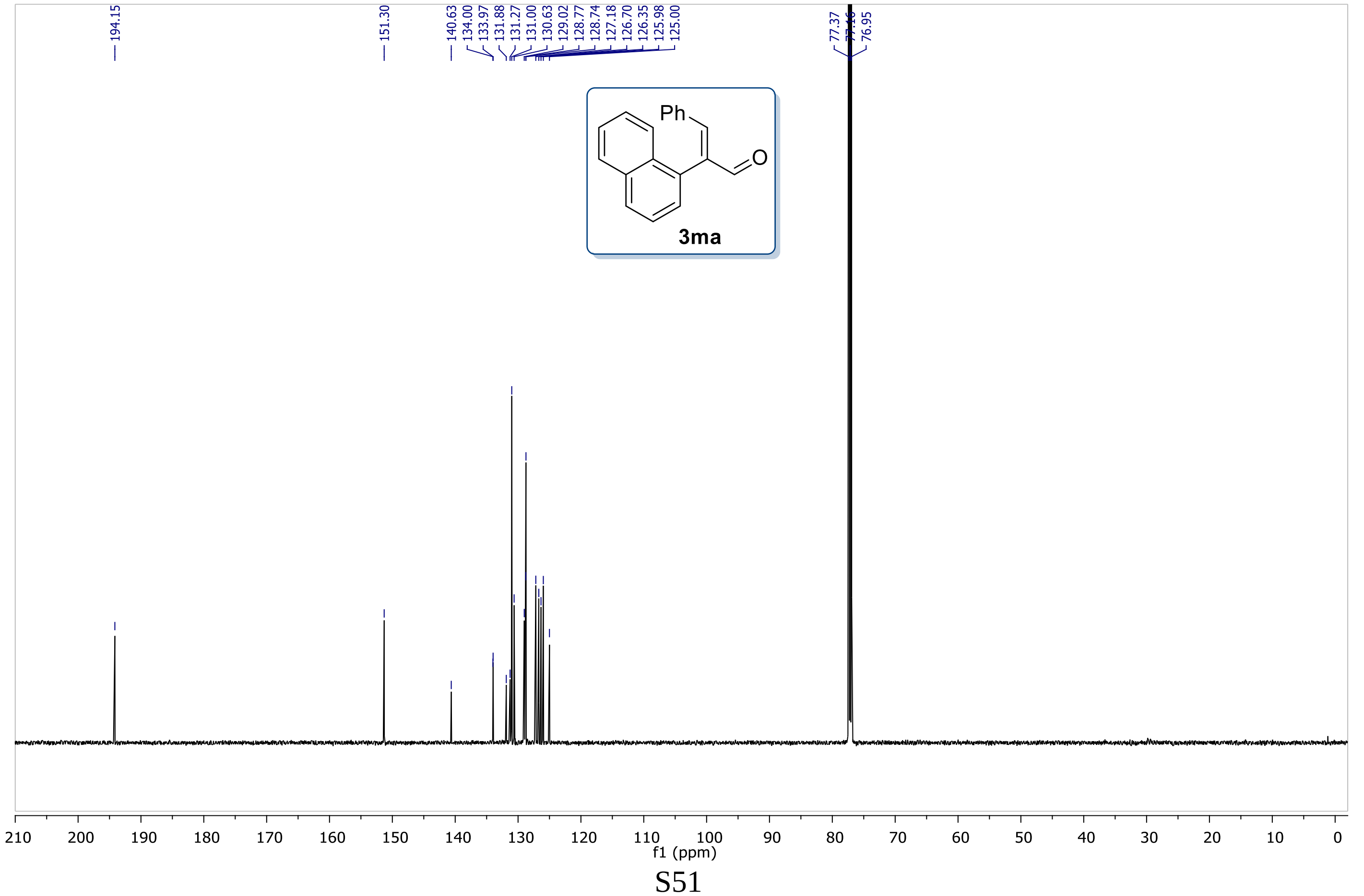
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3la**





^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3ma**





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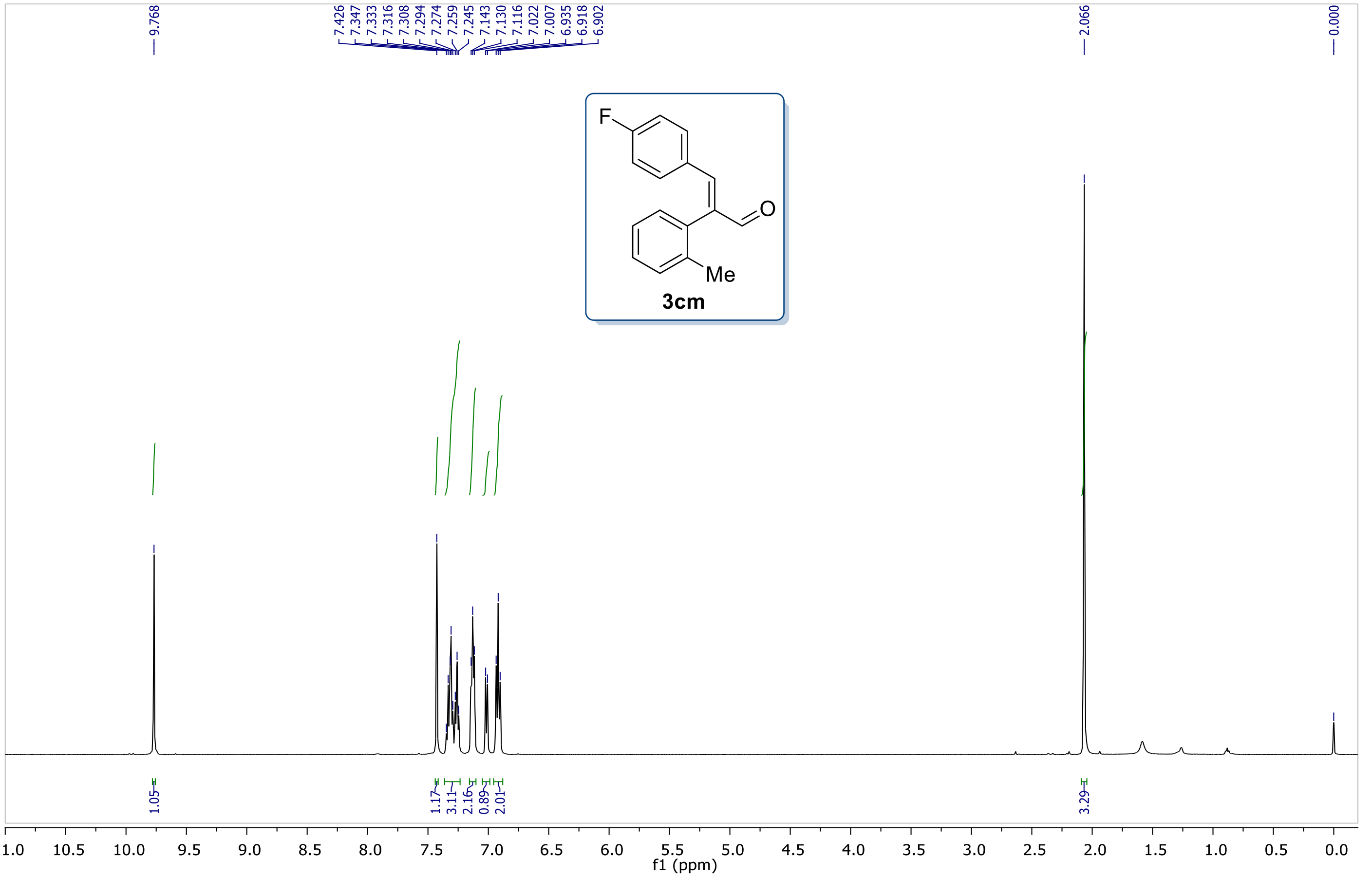
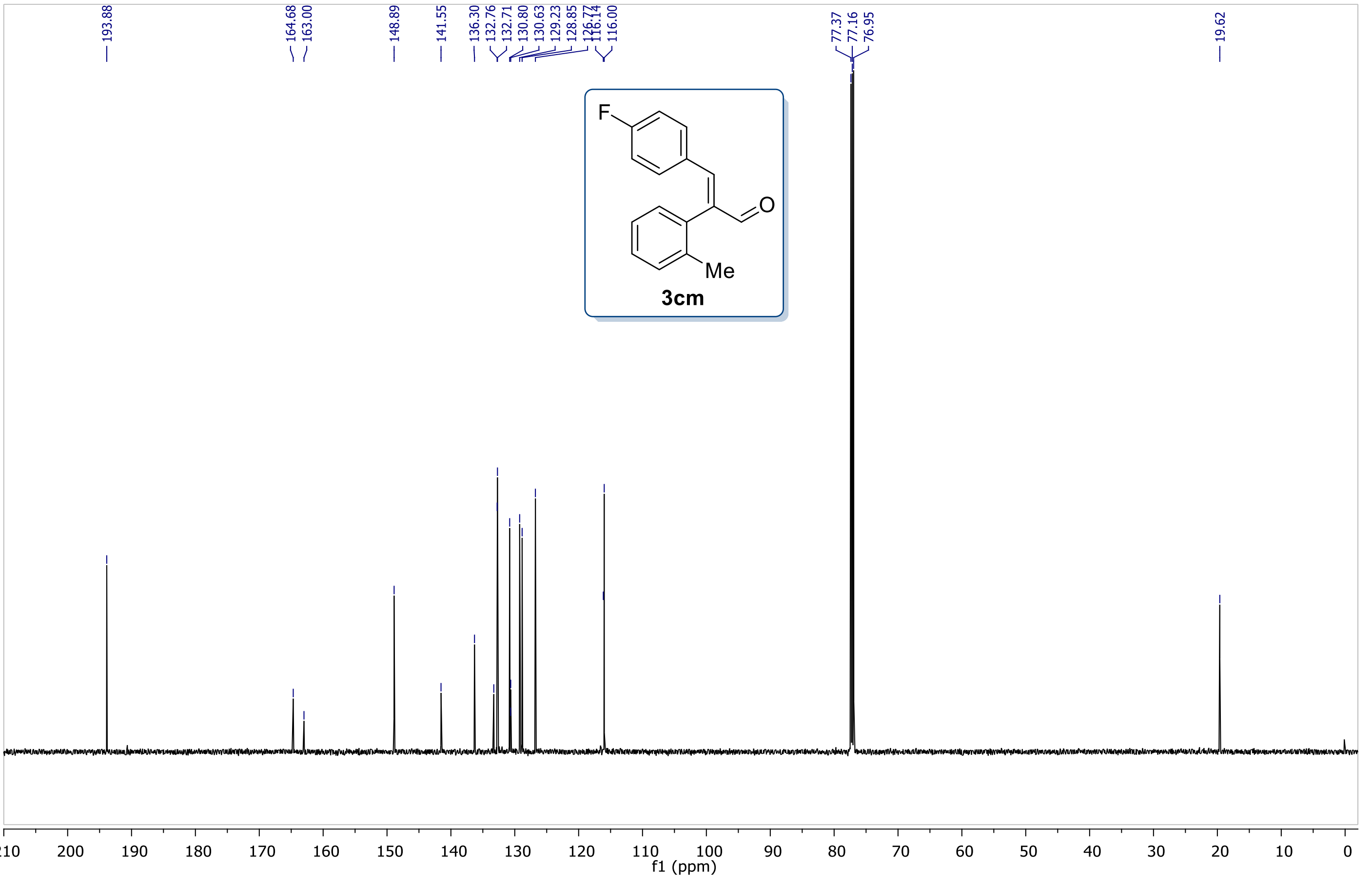
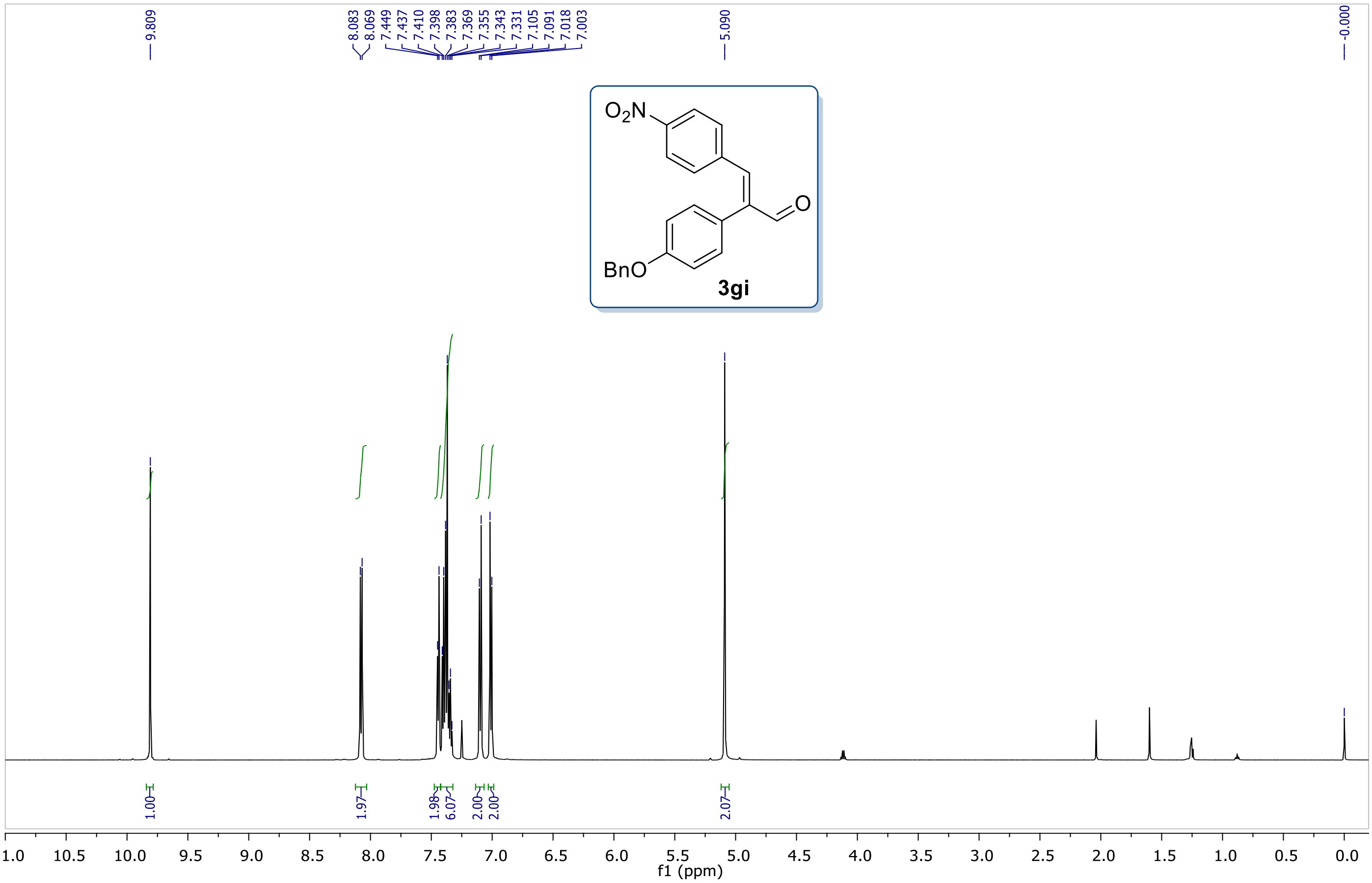
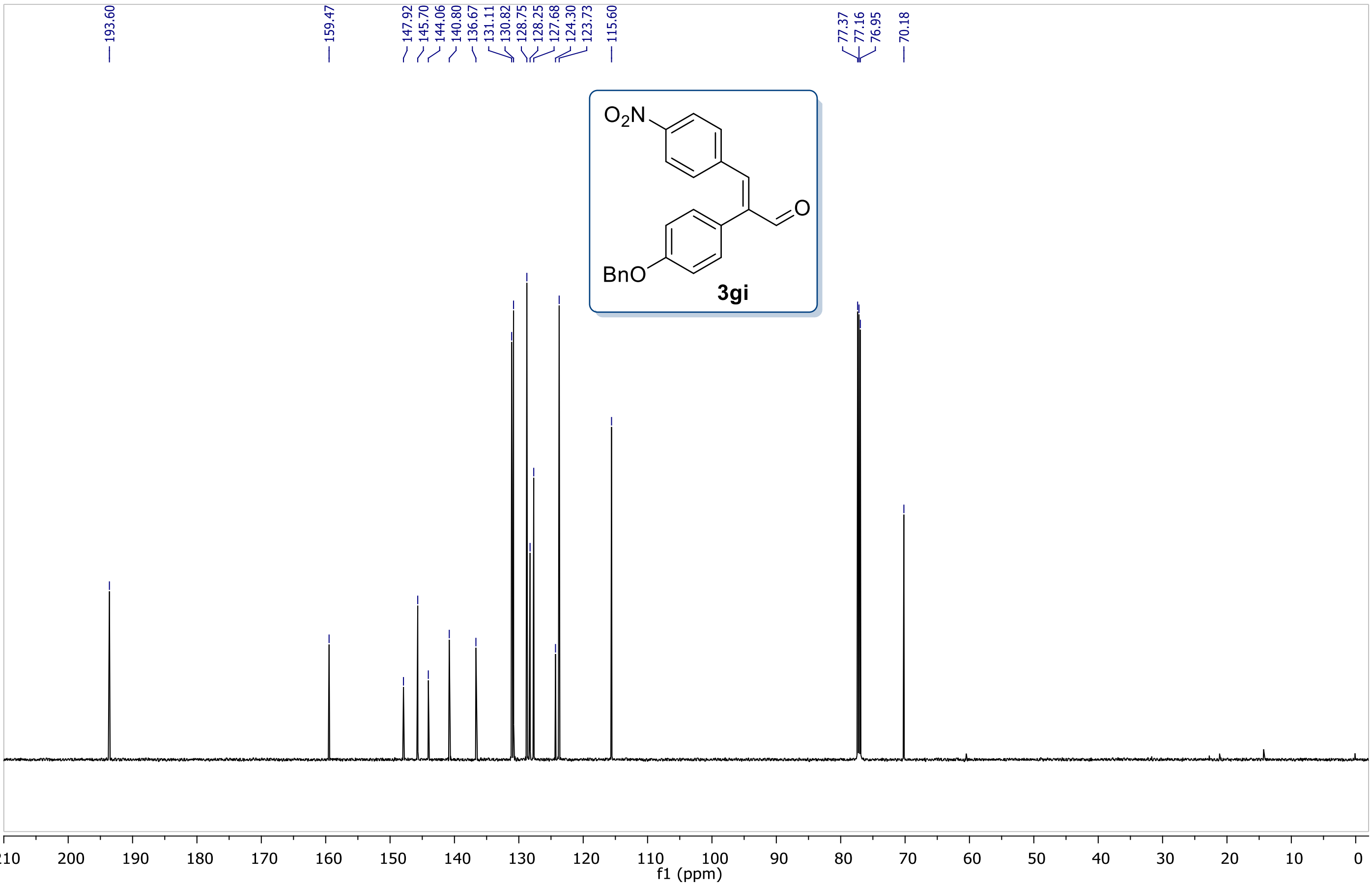


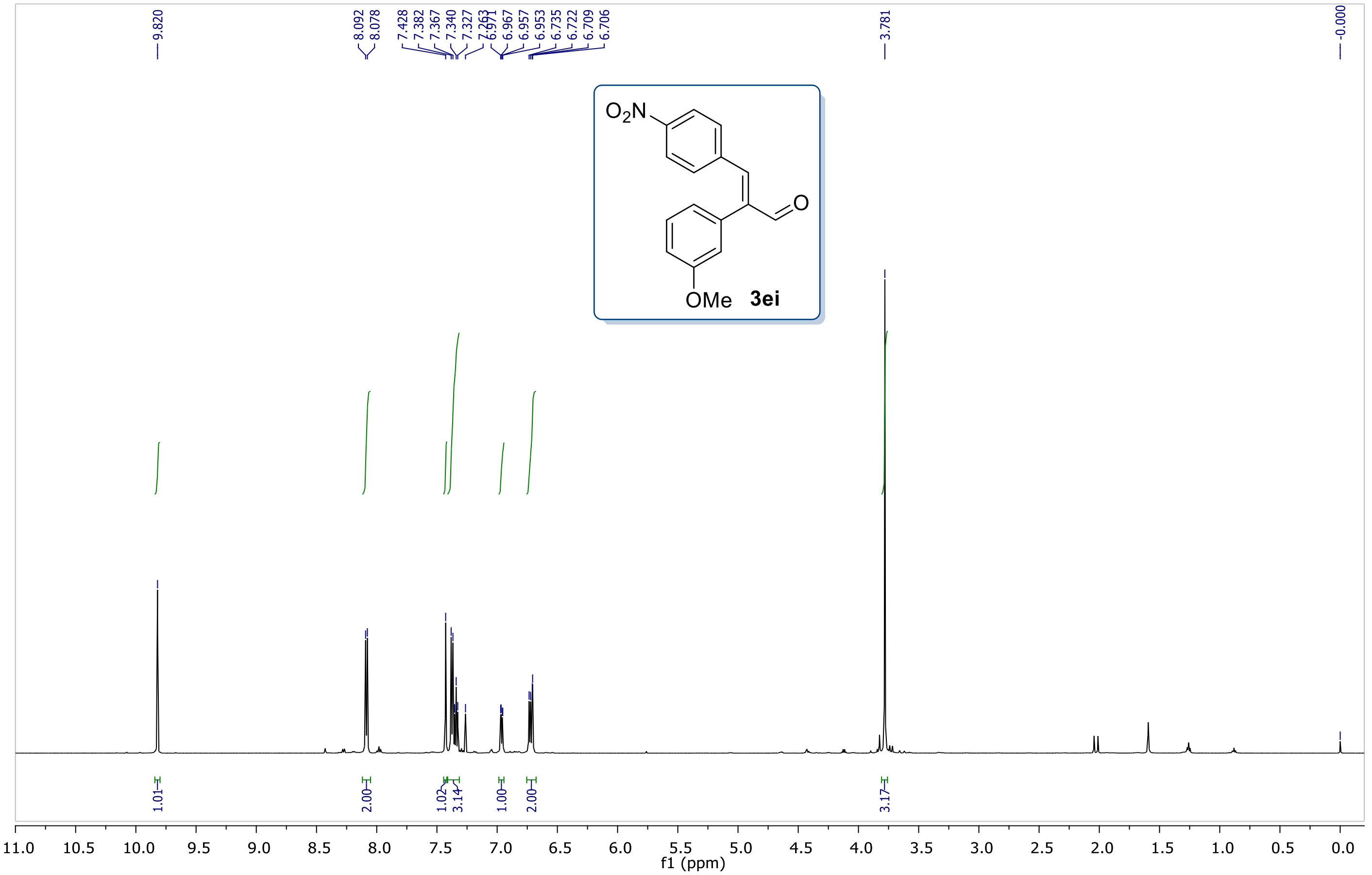


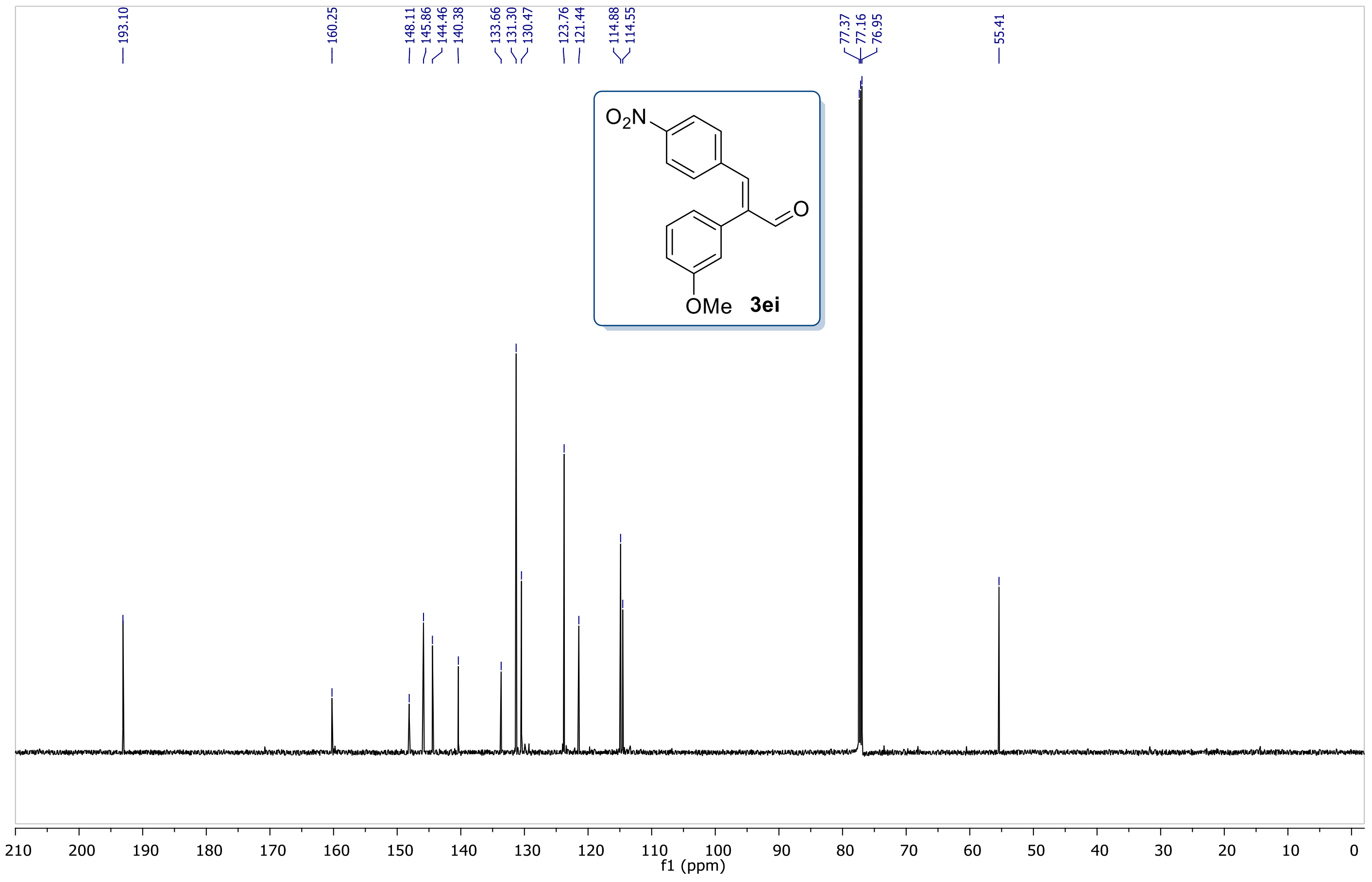
^1H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$), **3gi**



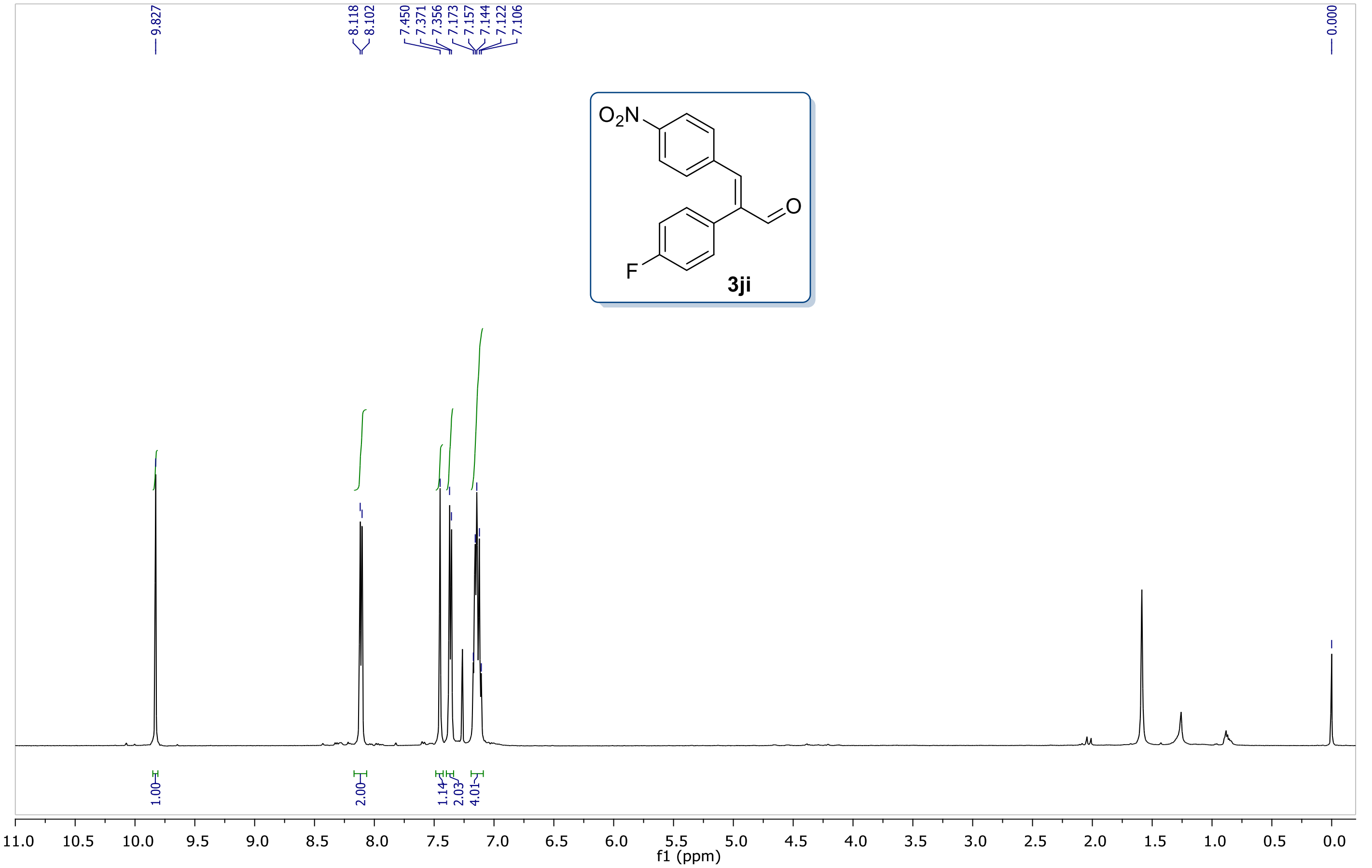


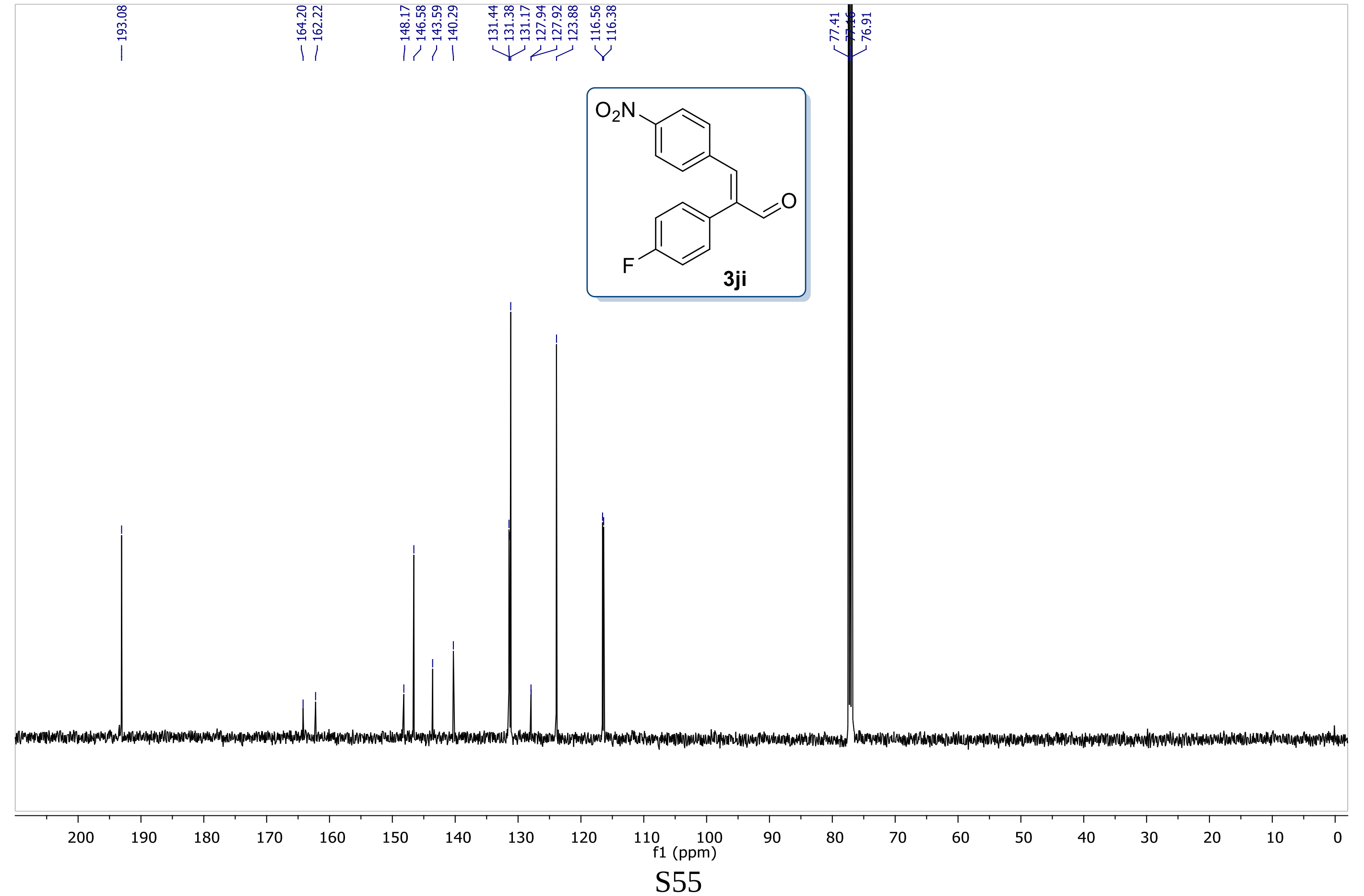
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3ei**



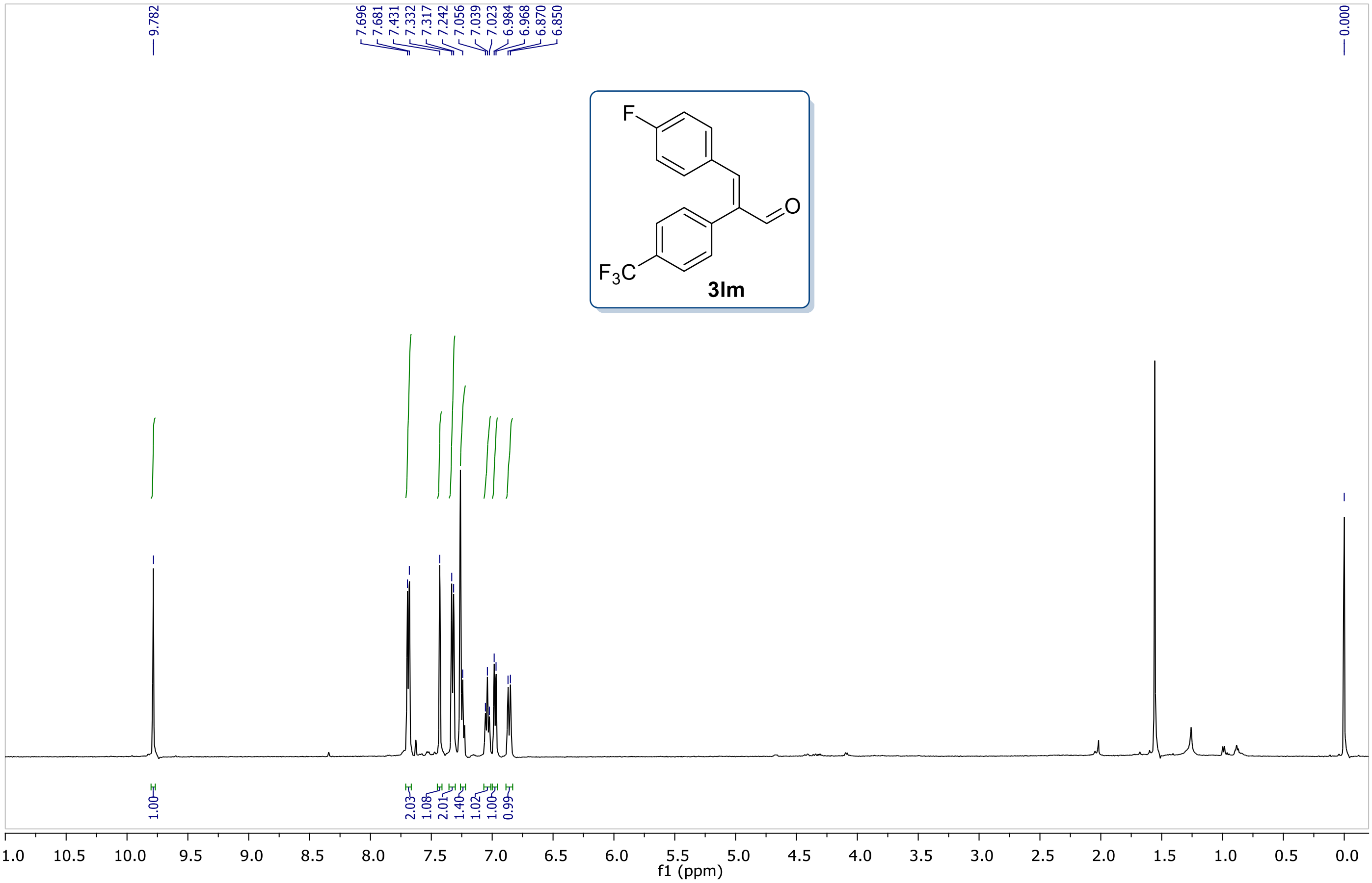


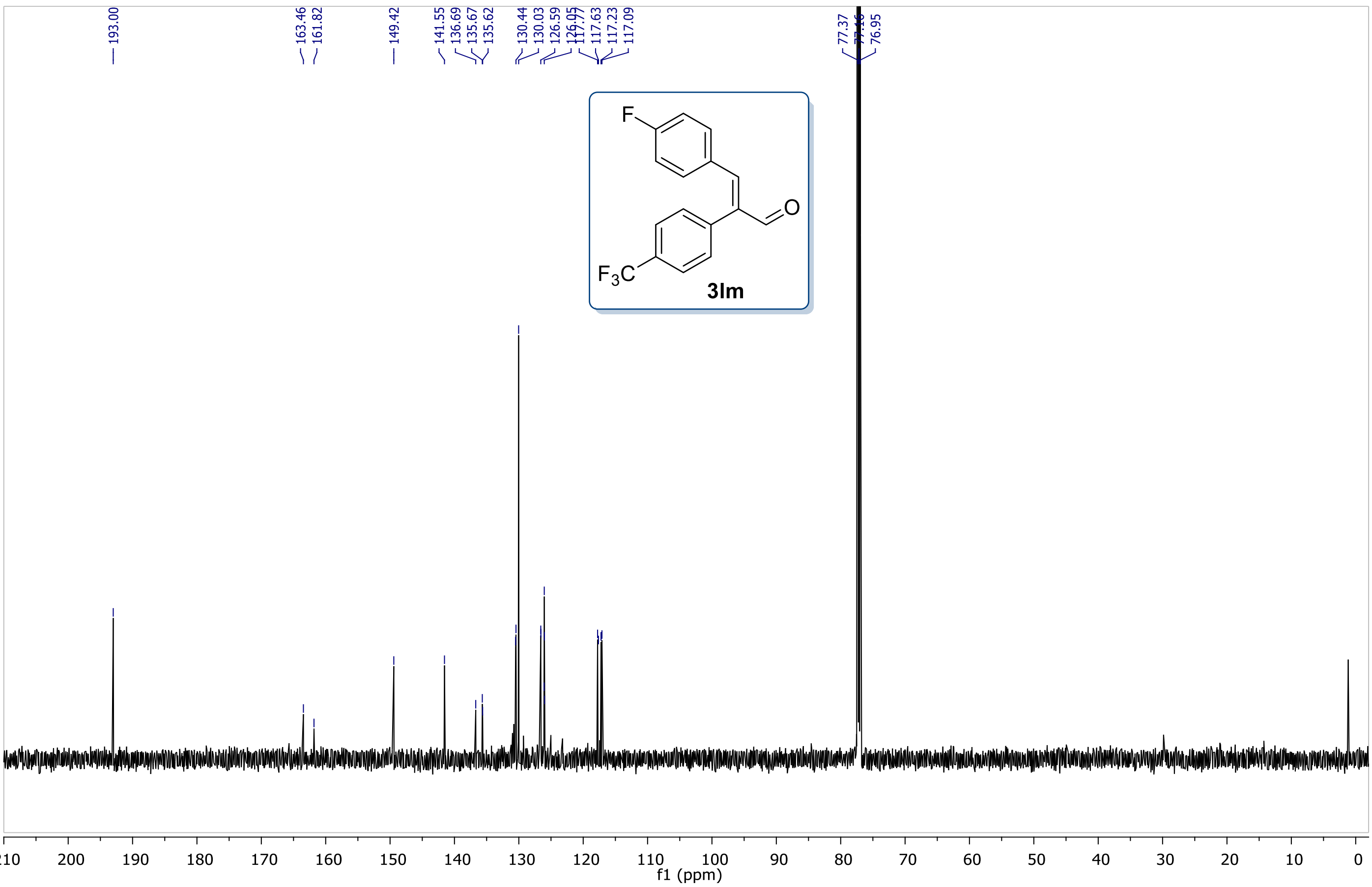
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3ji**



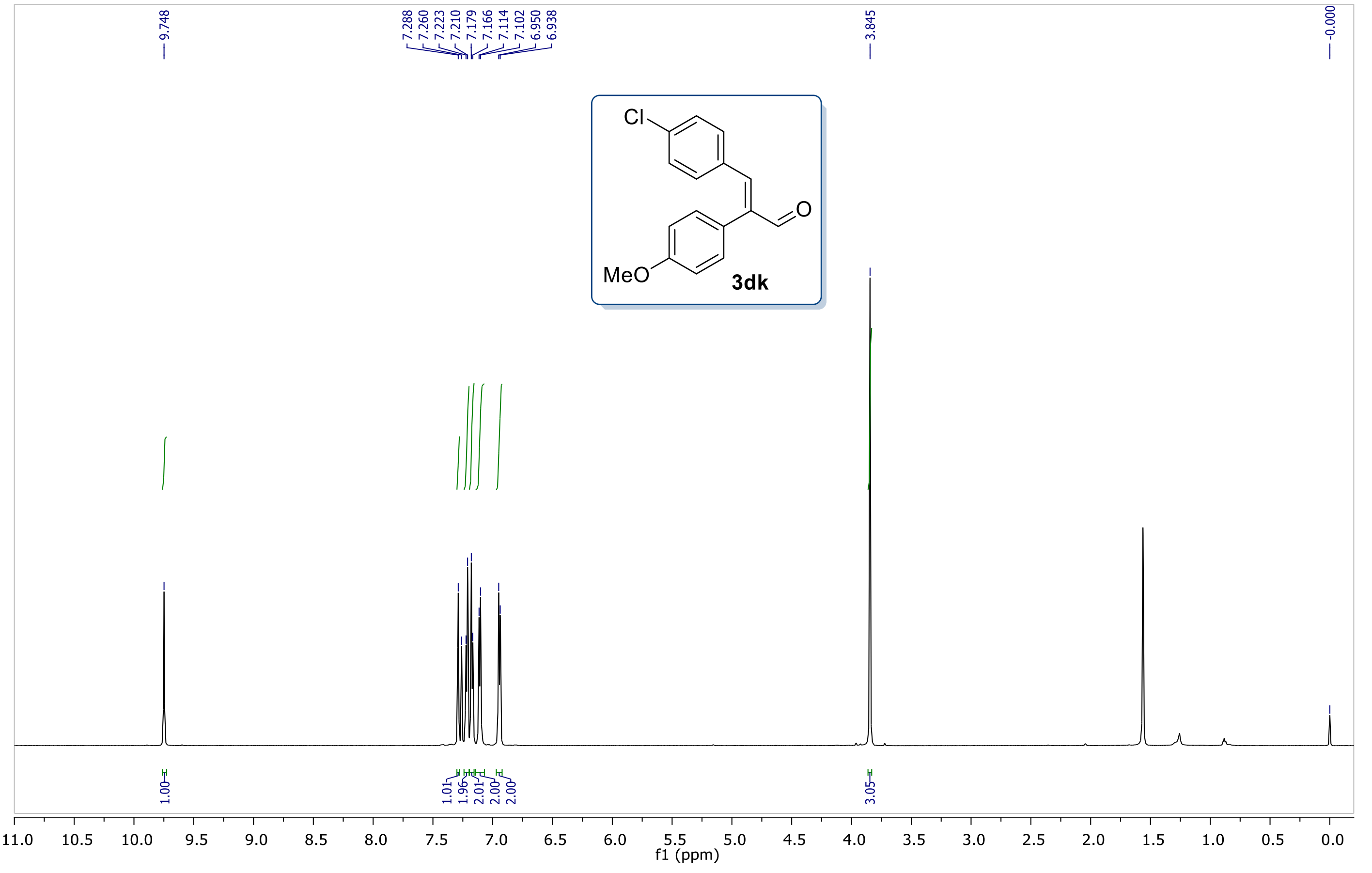


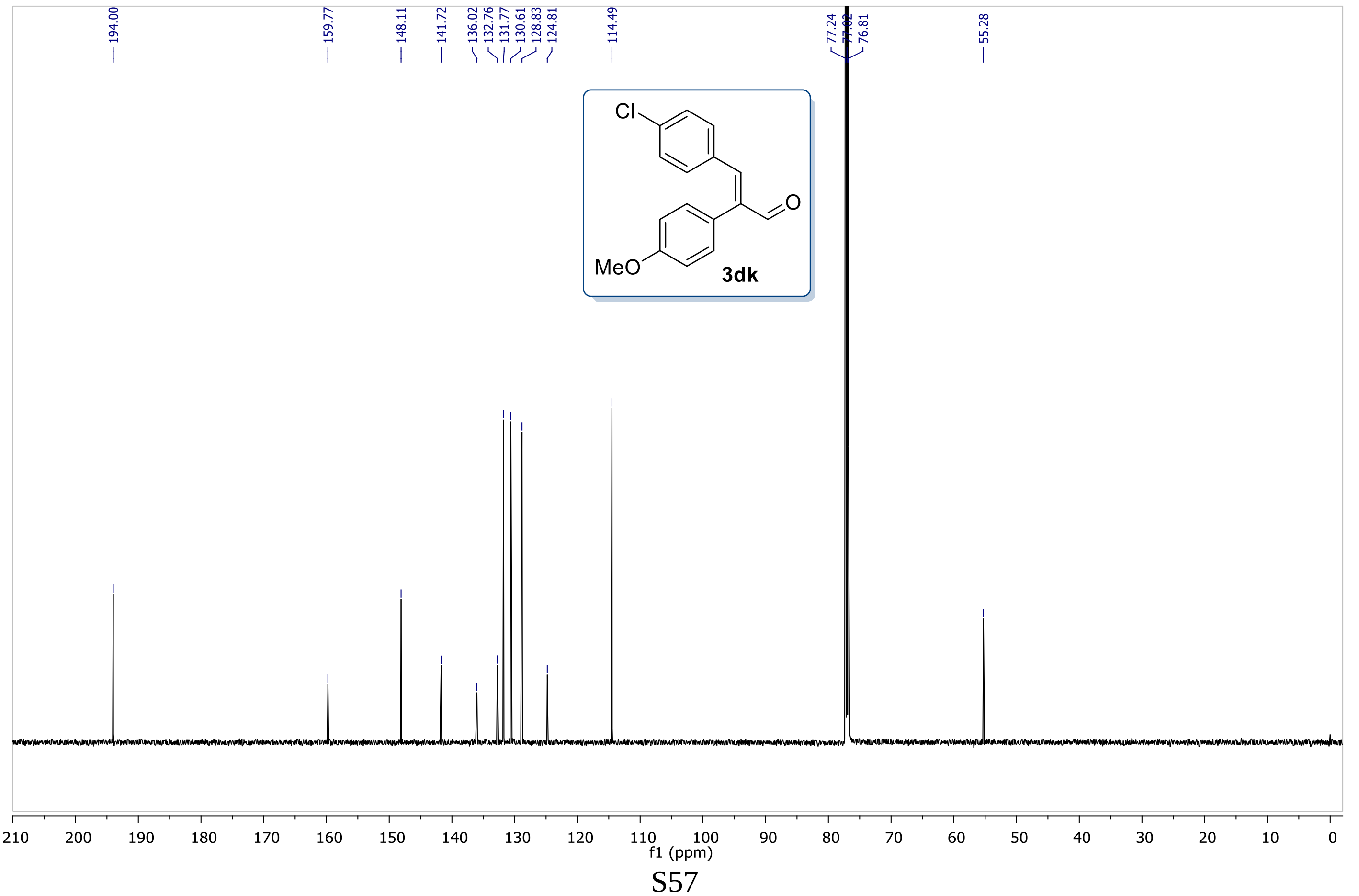
^1H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$), **3lm**



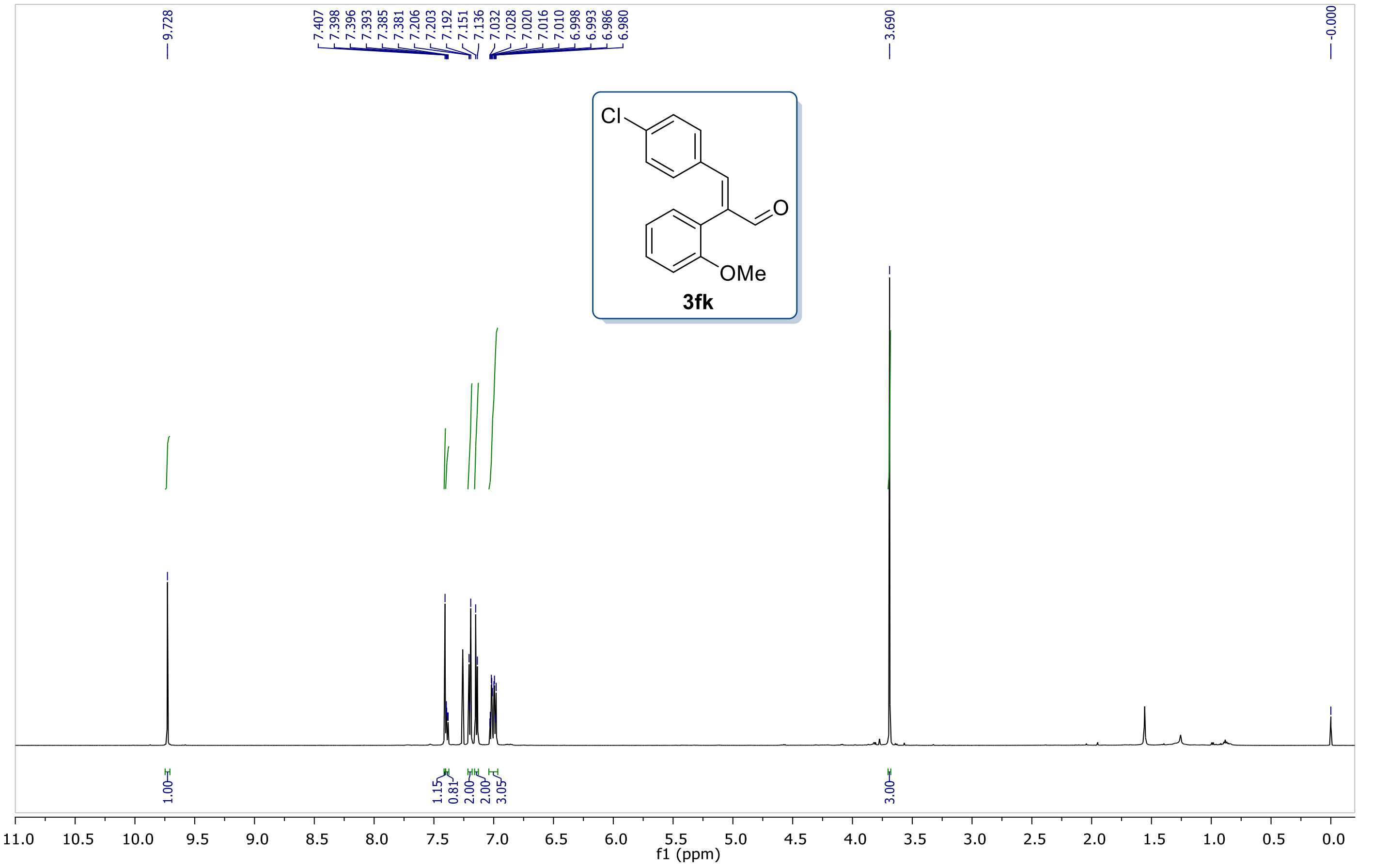


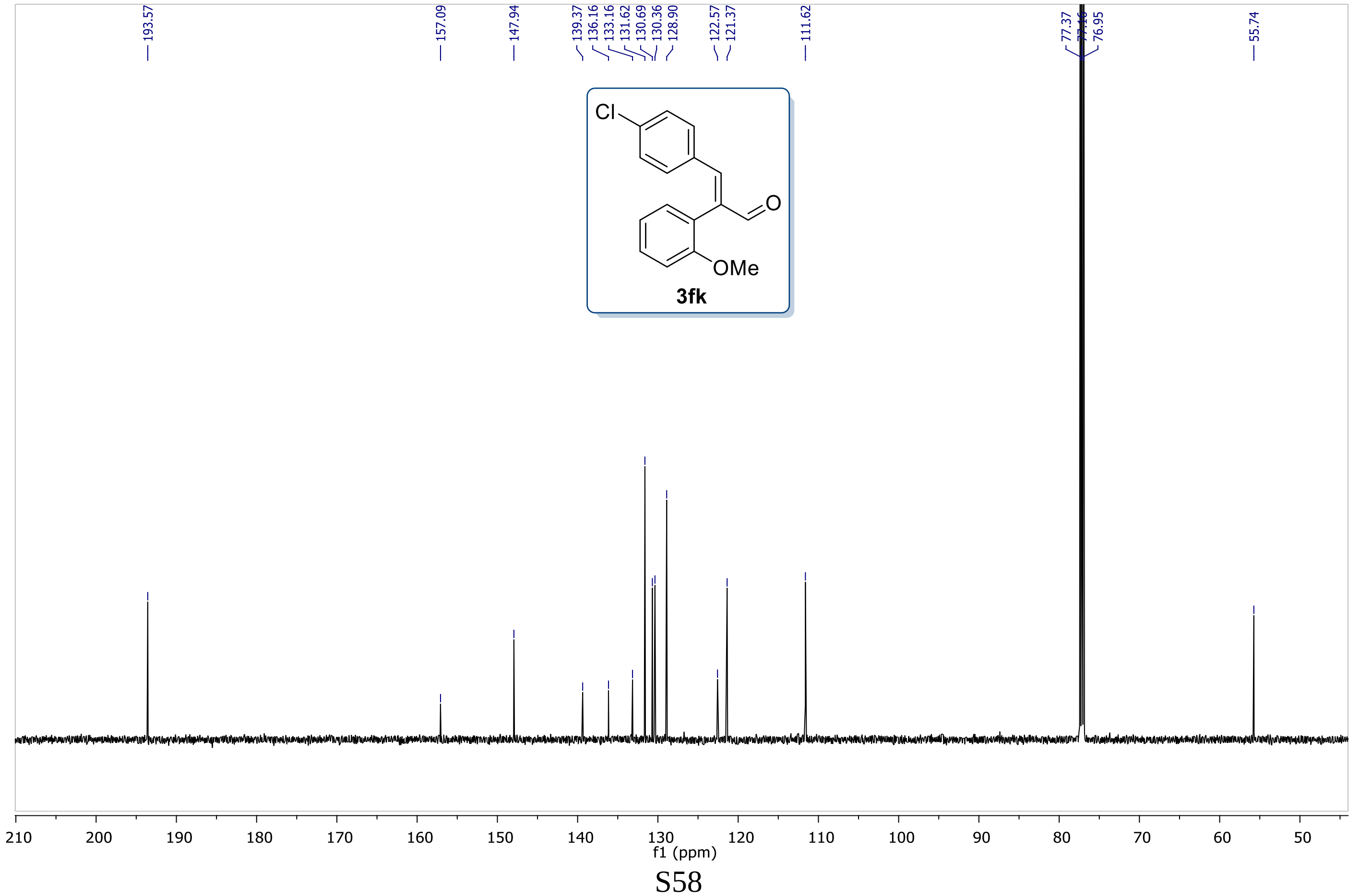
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3dk**



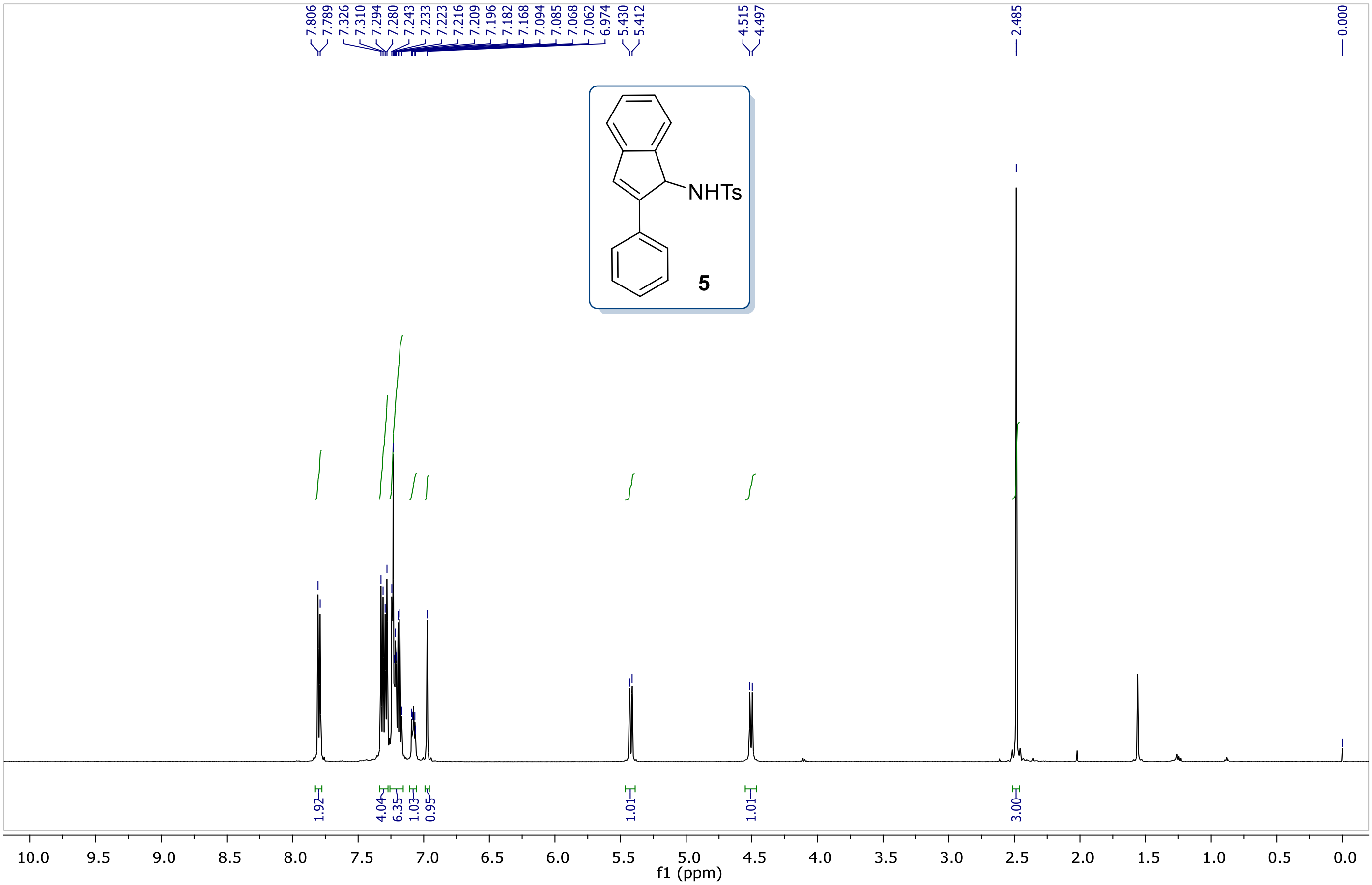


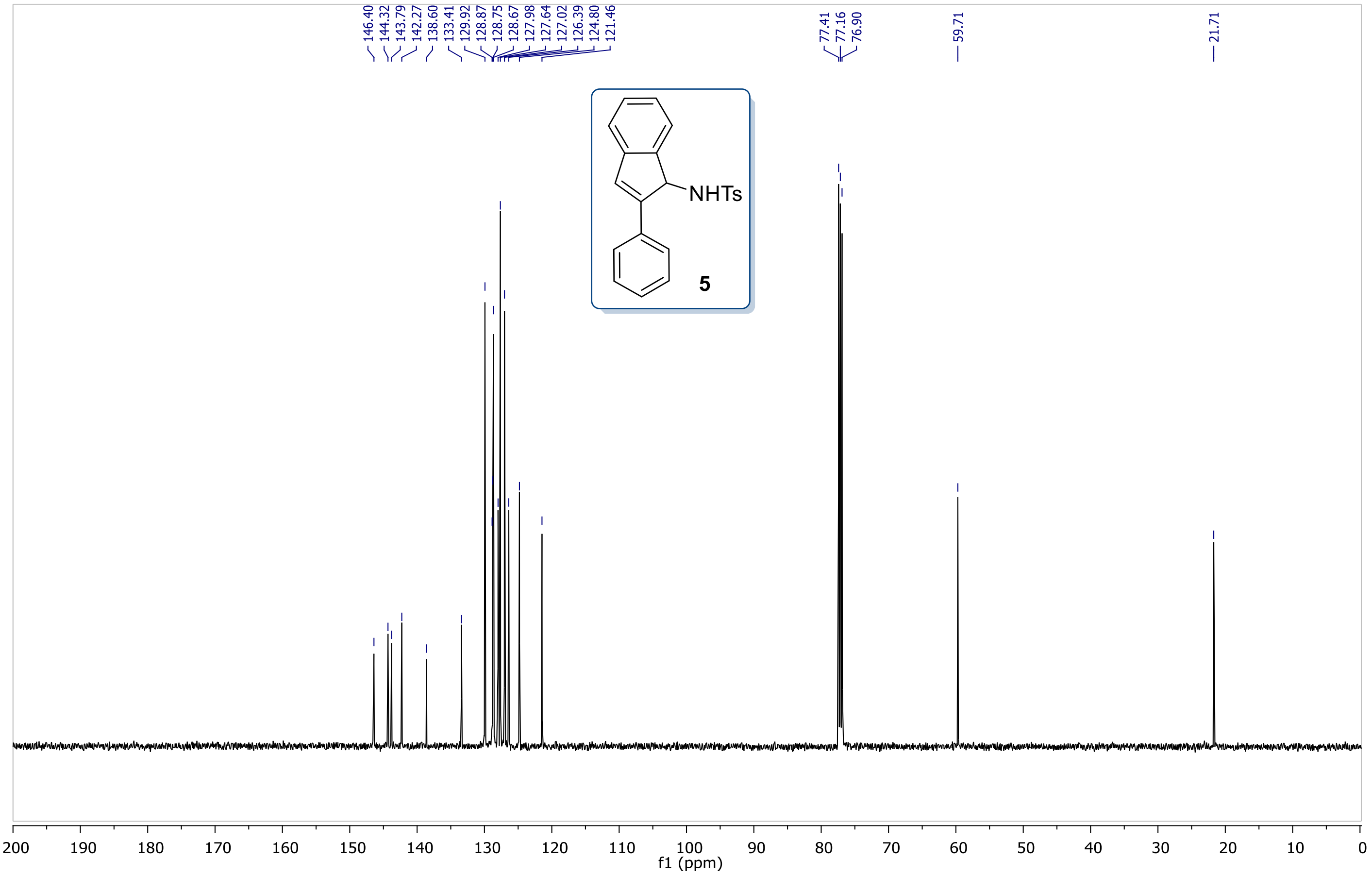
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3fk**



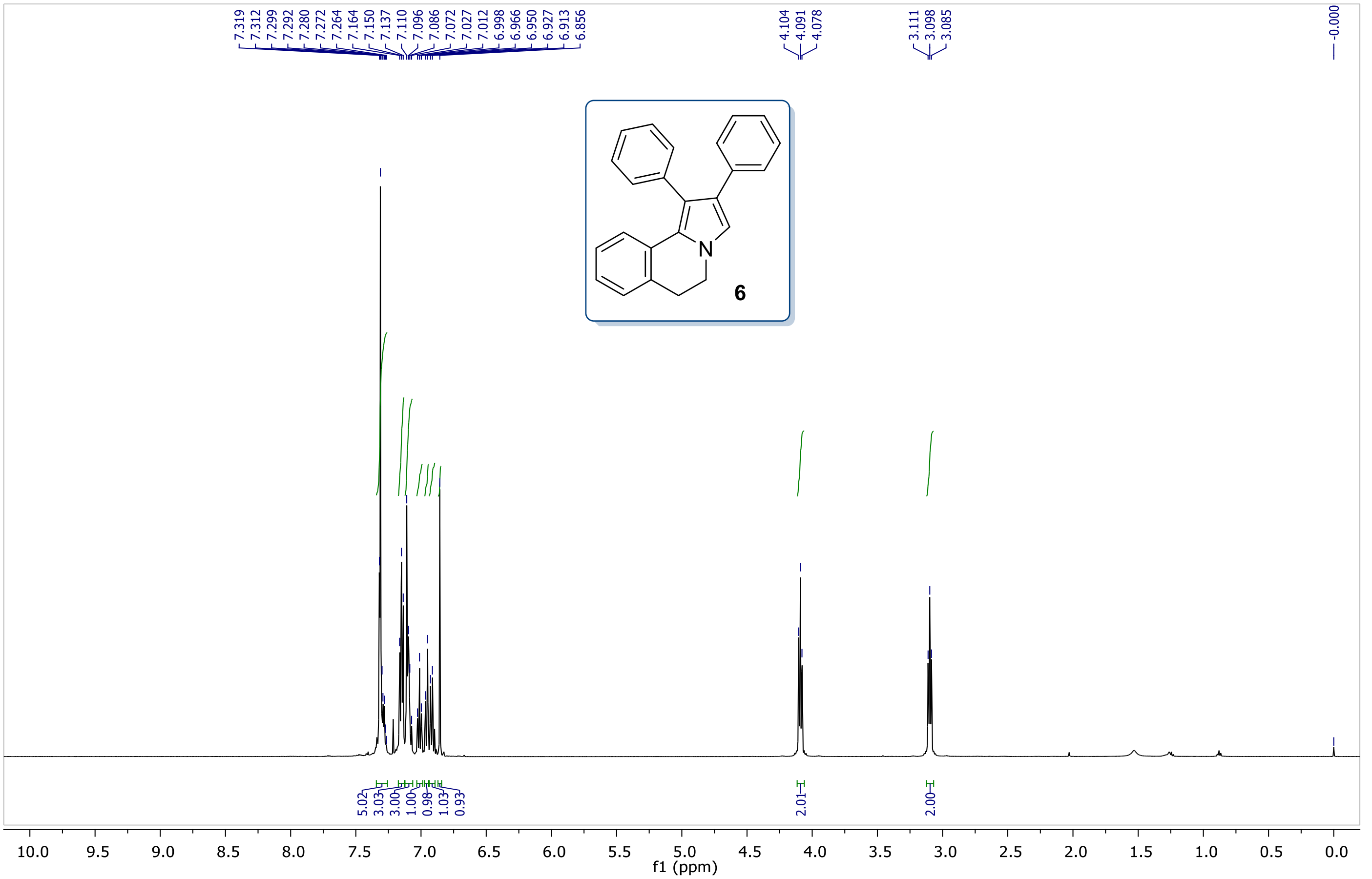


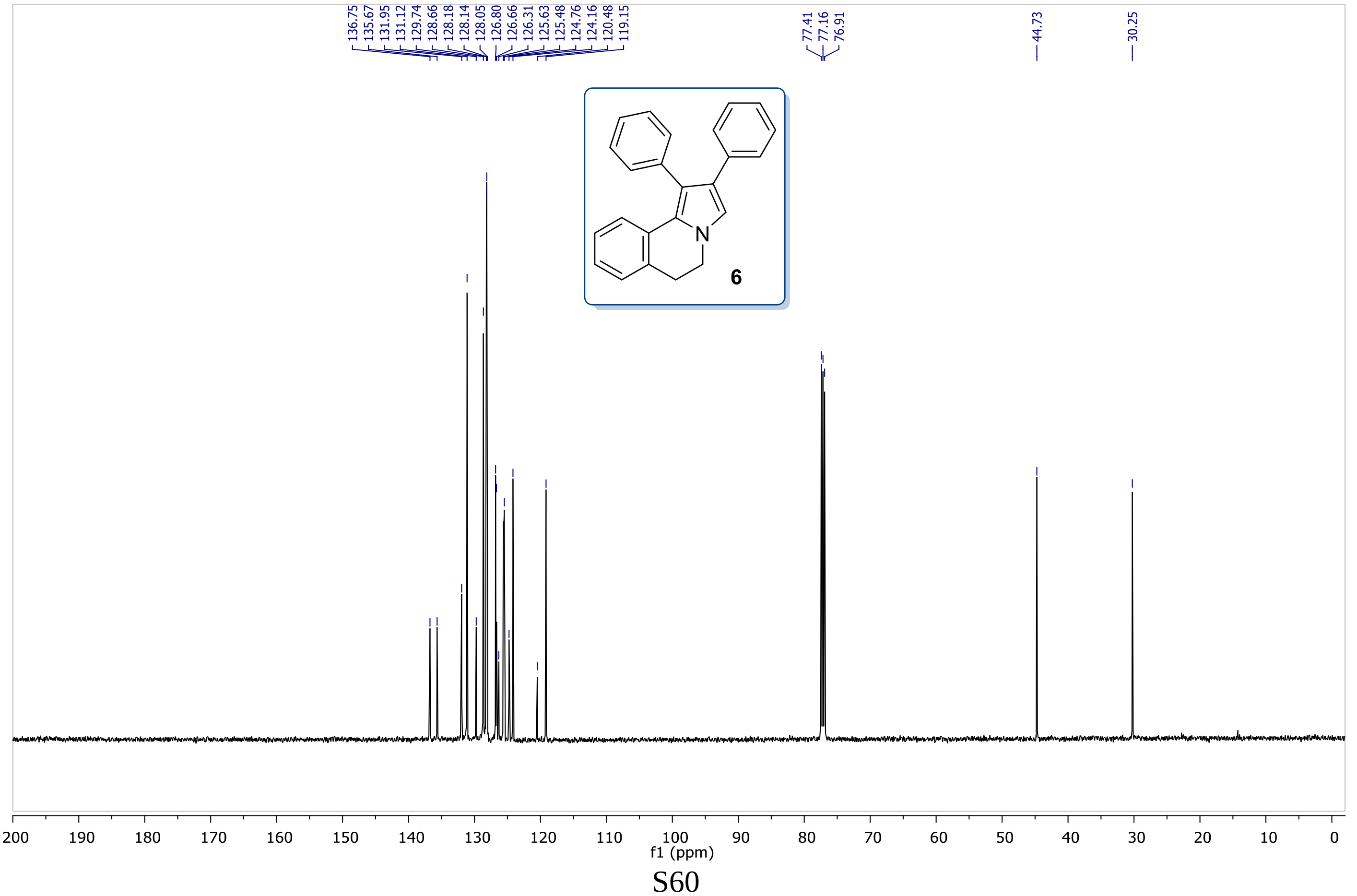
^1H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), **5**



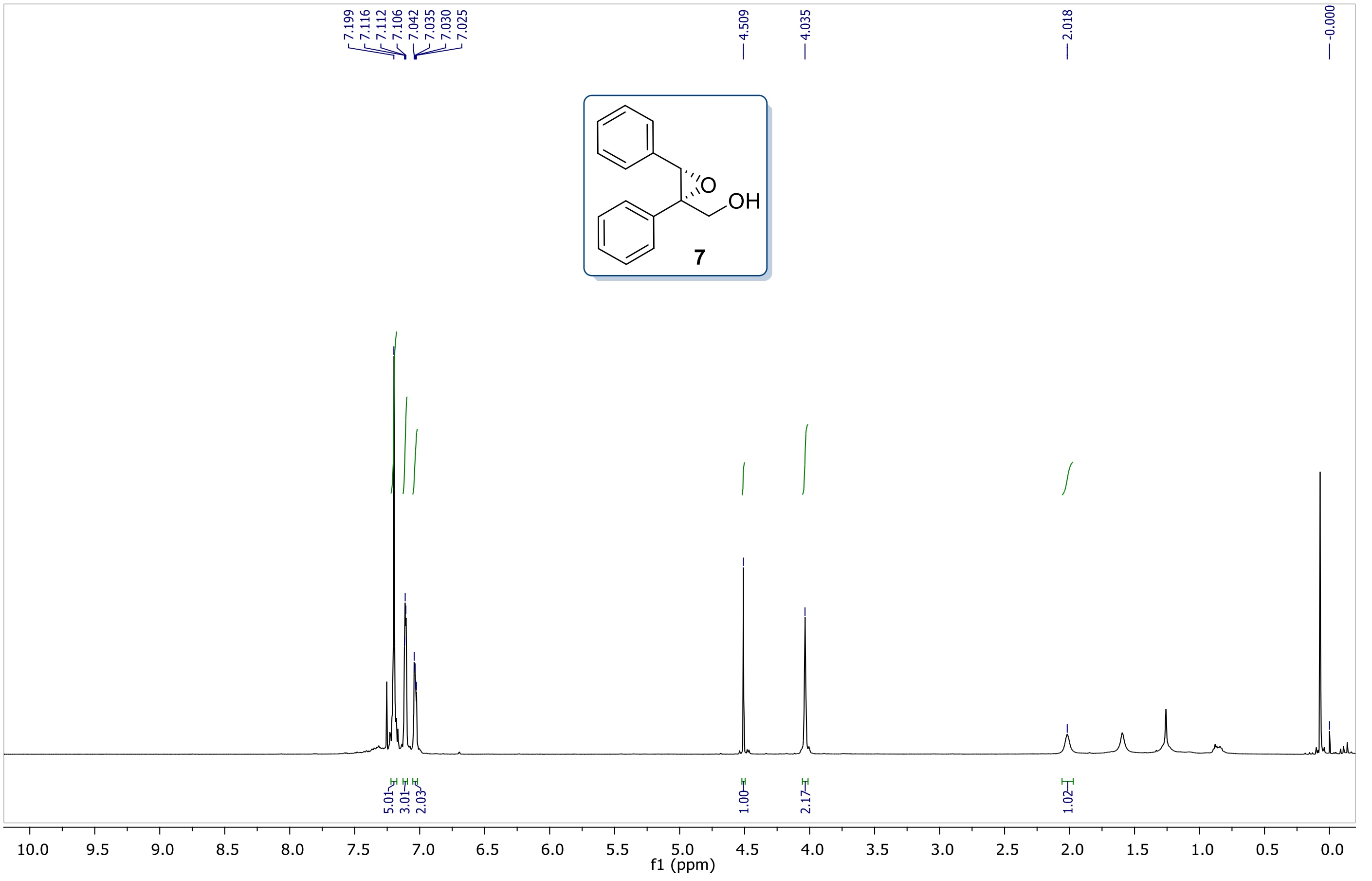


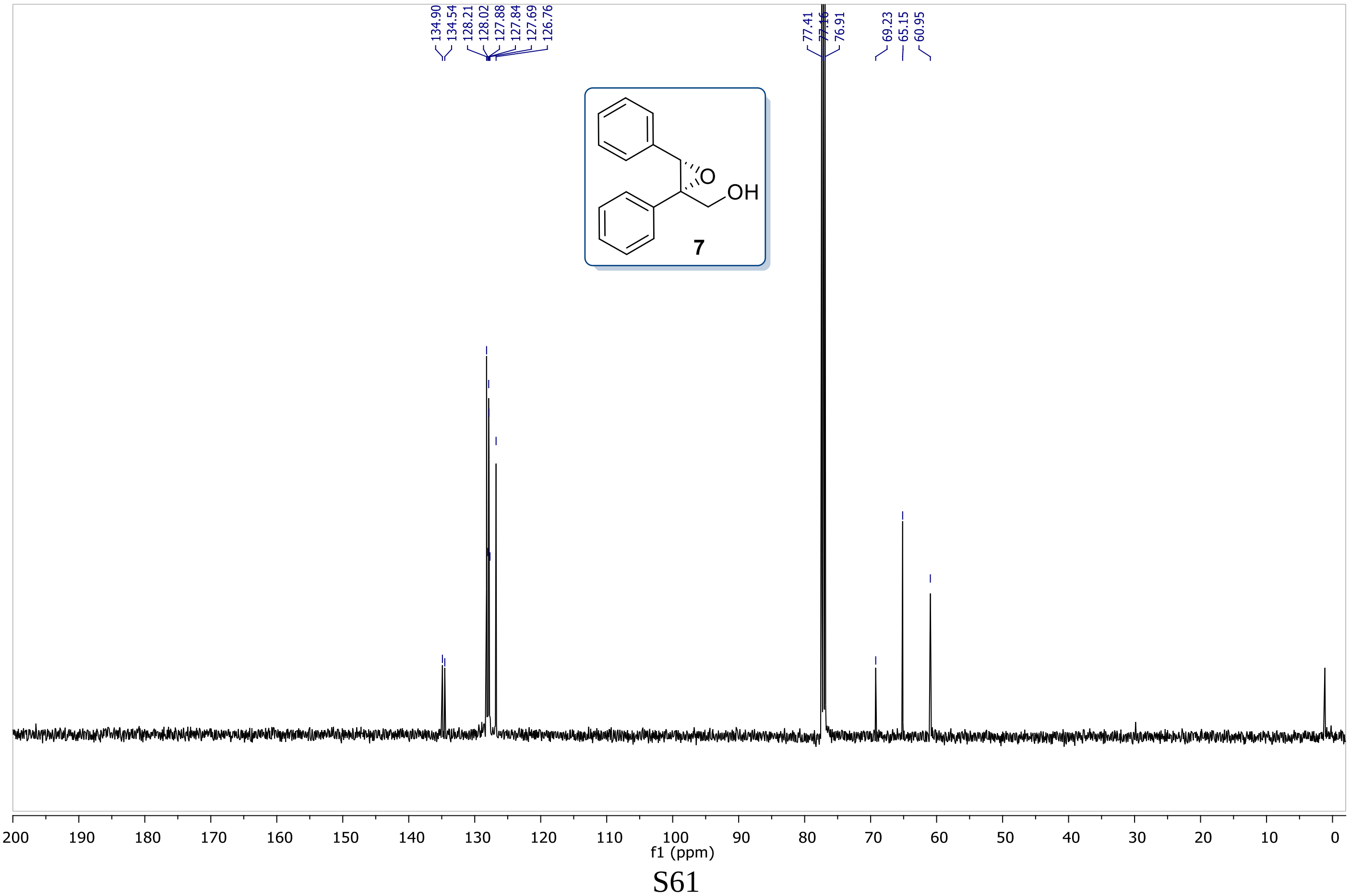
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), **6**



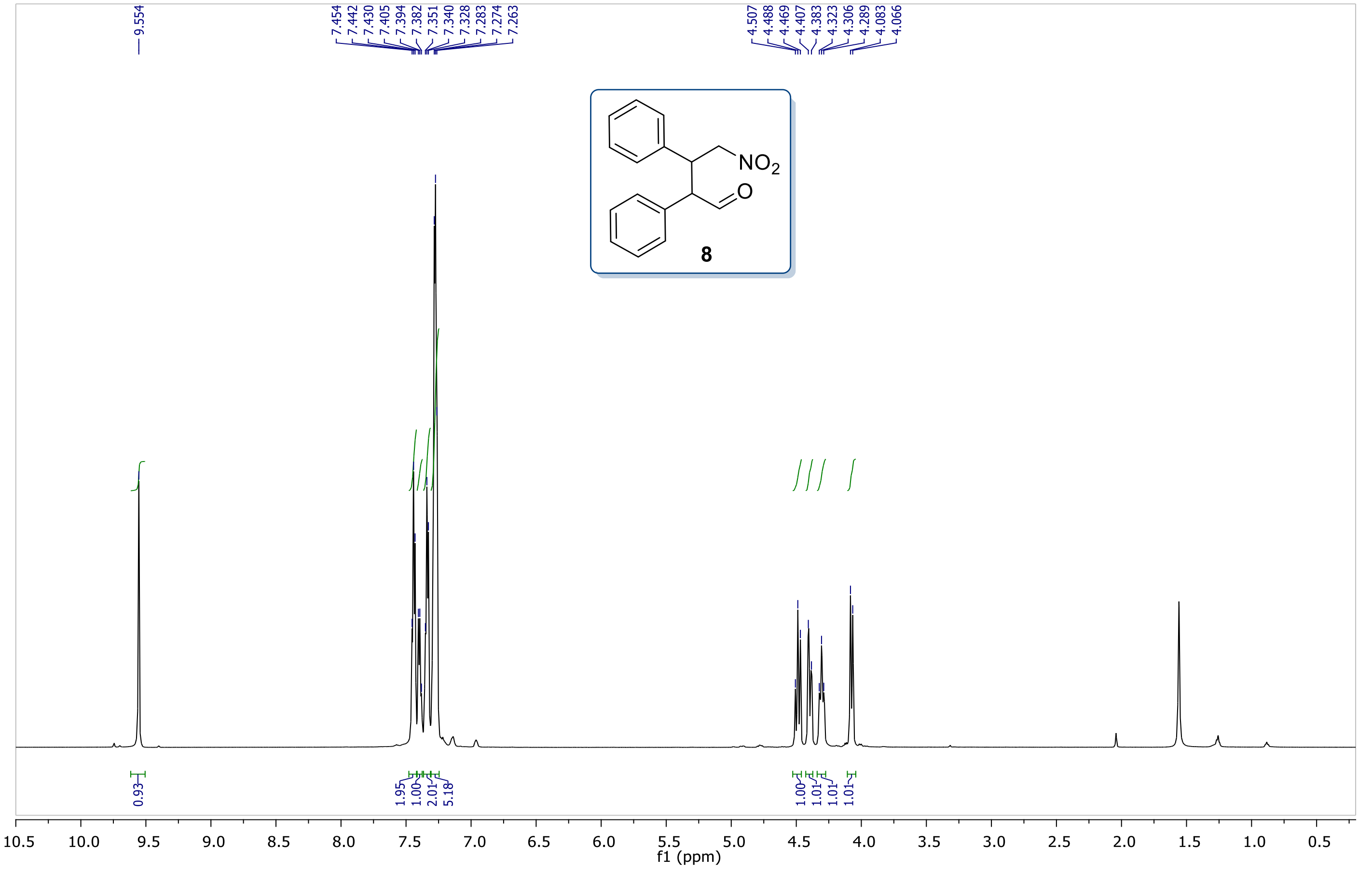


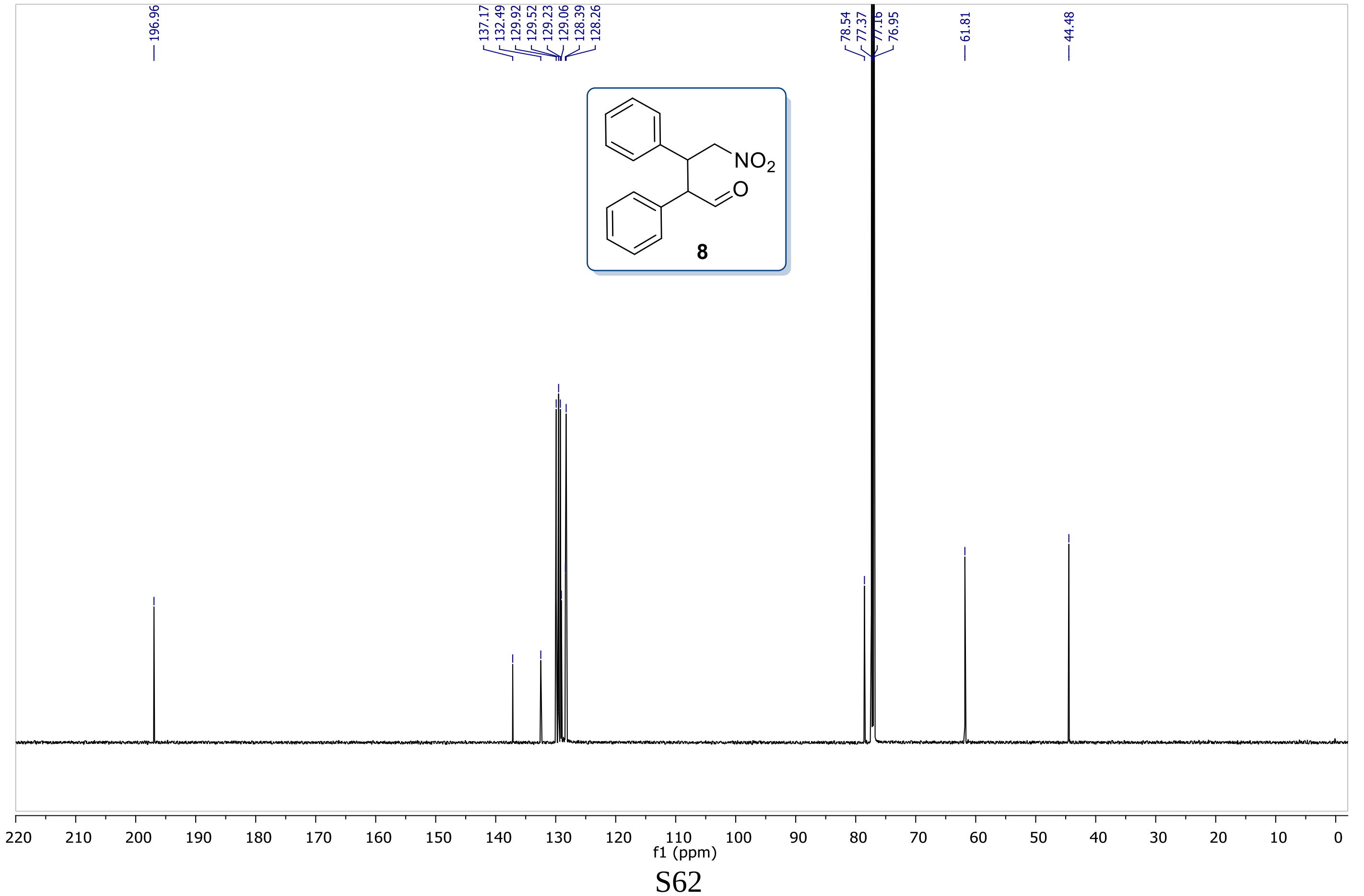
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **7**



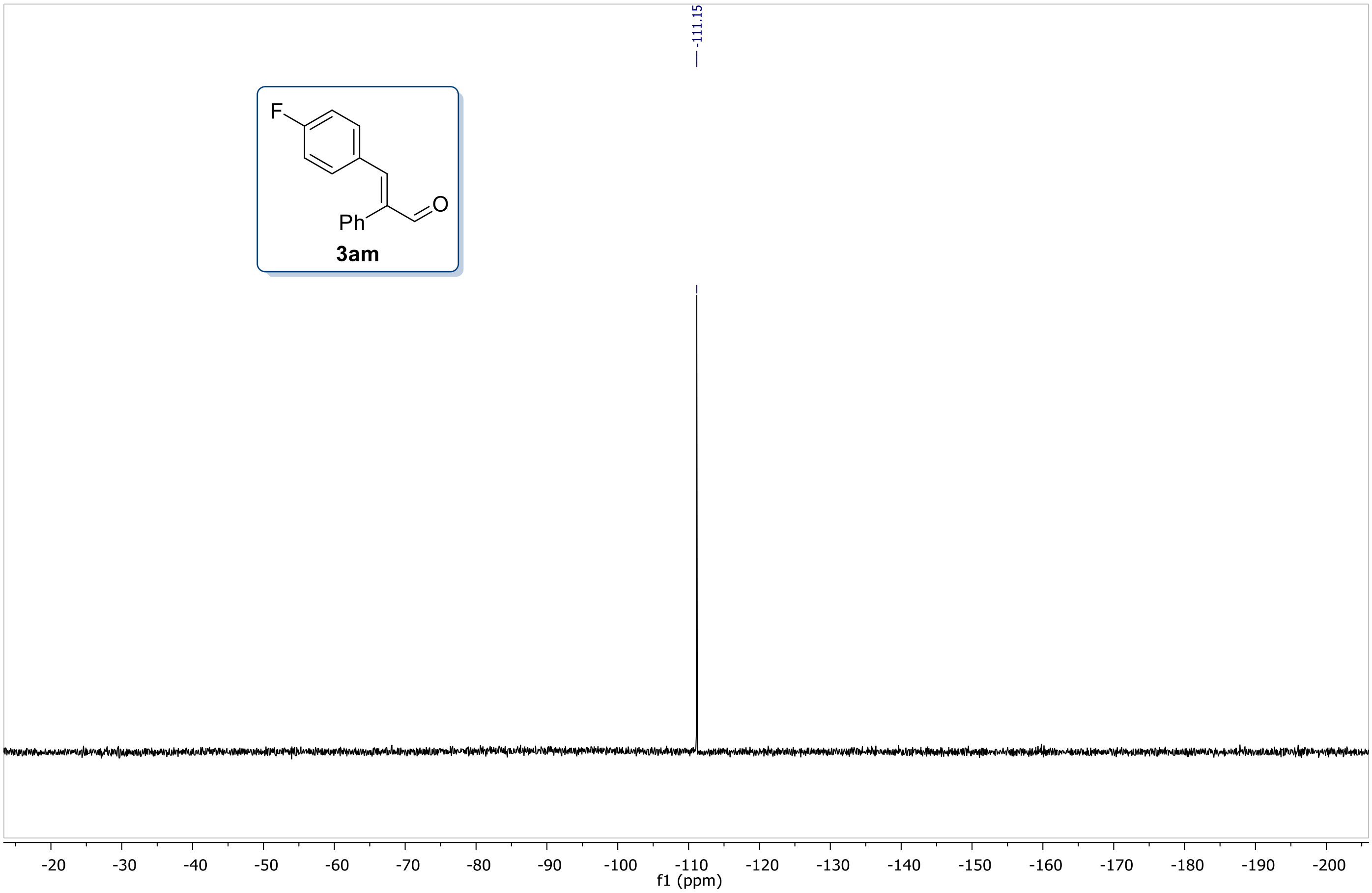


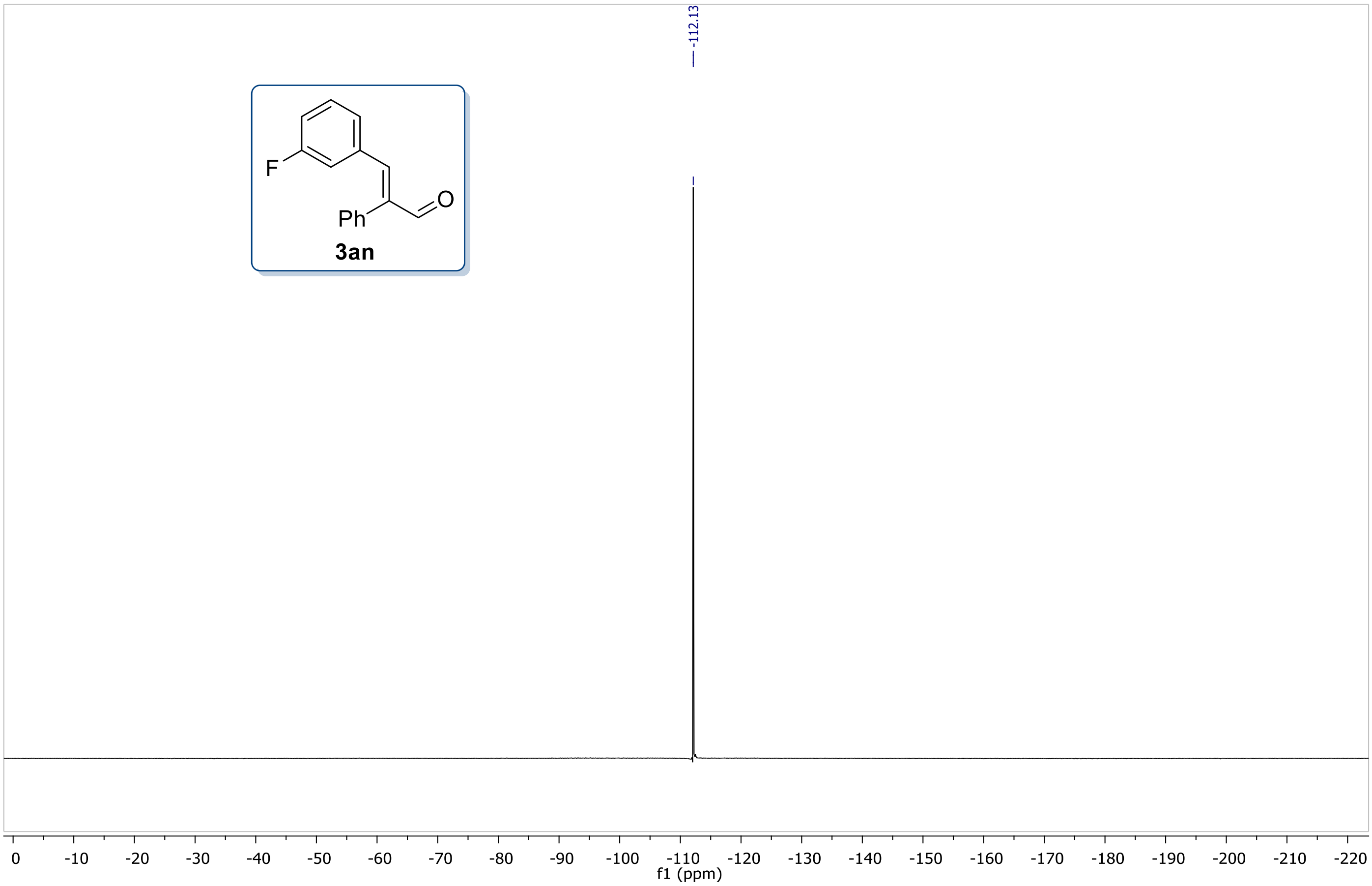
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), 8



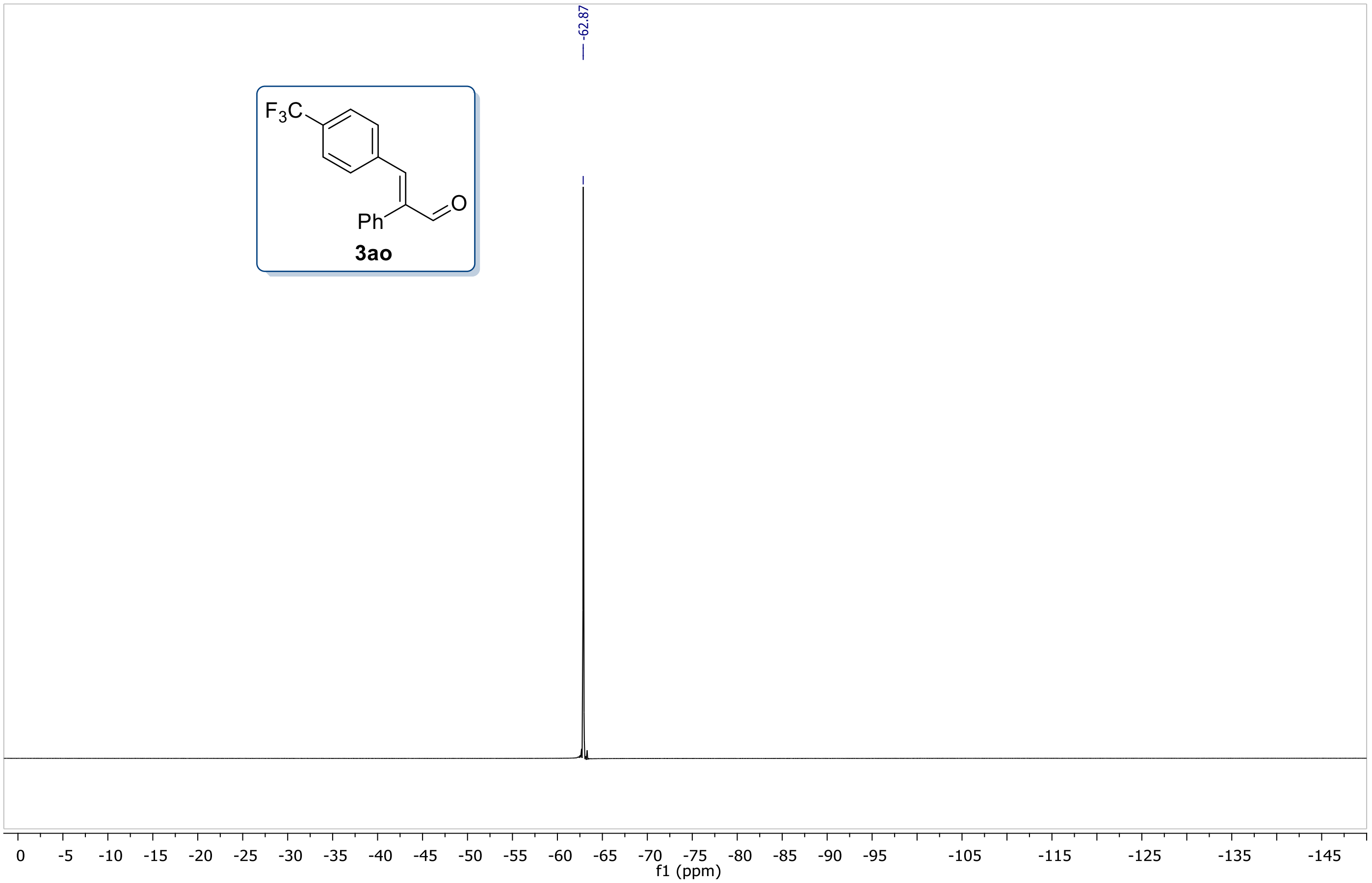


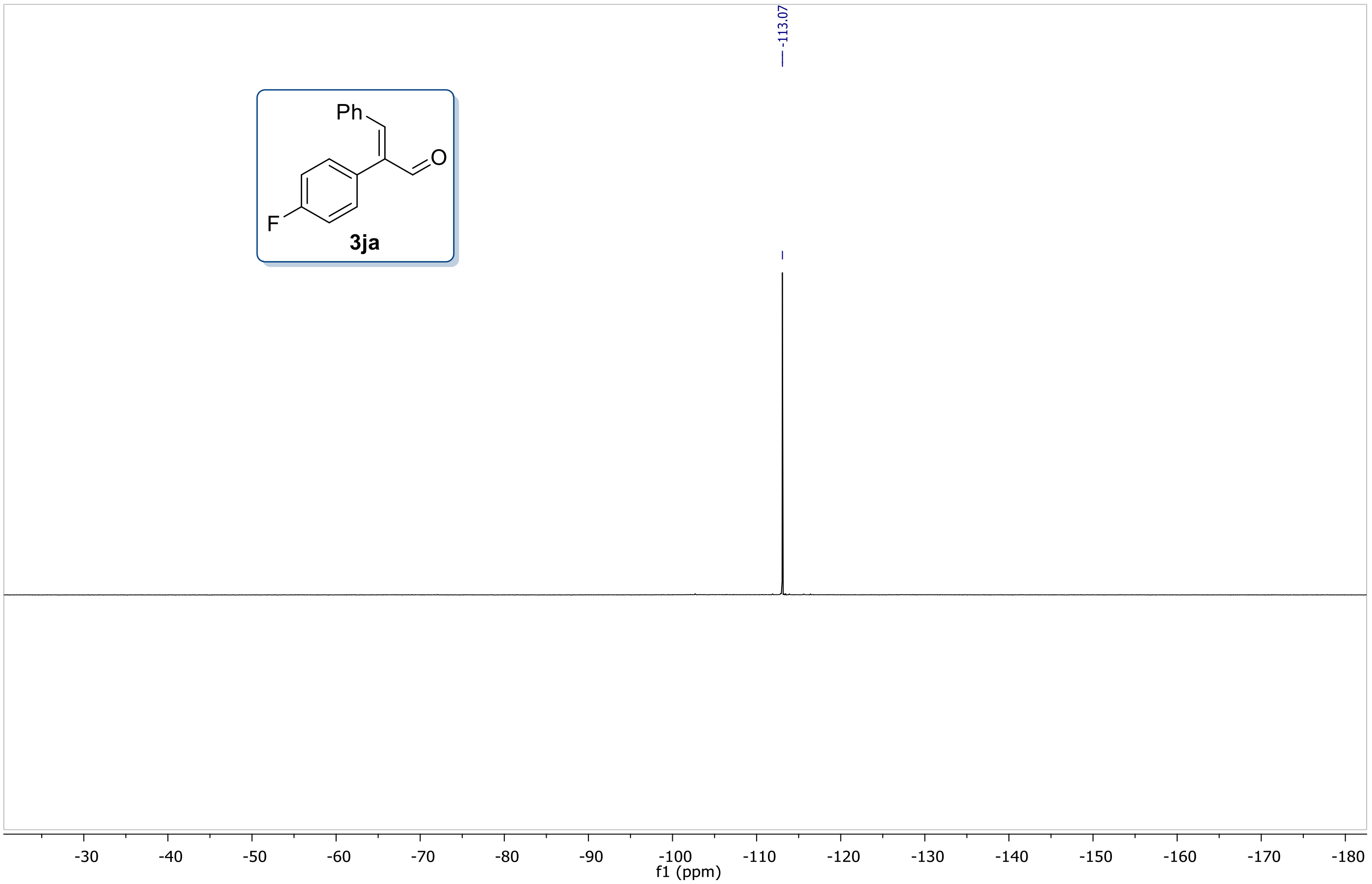
$^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$), **3am** and **3an**



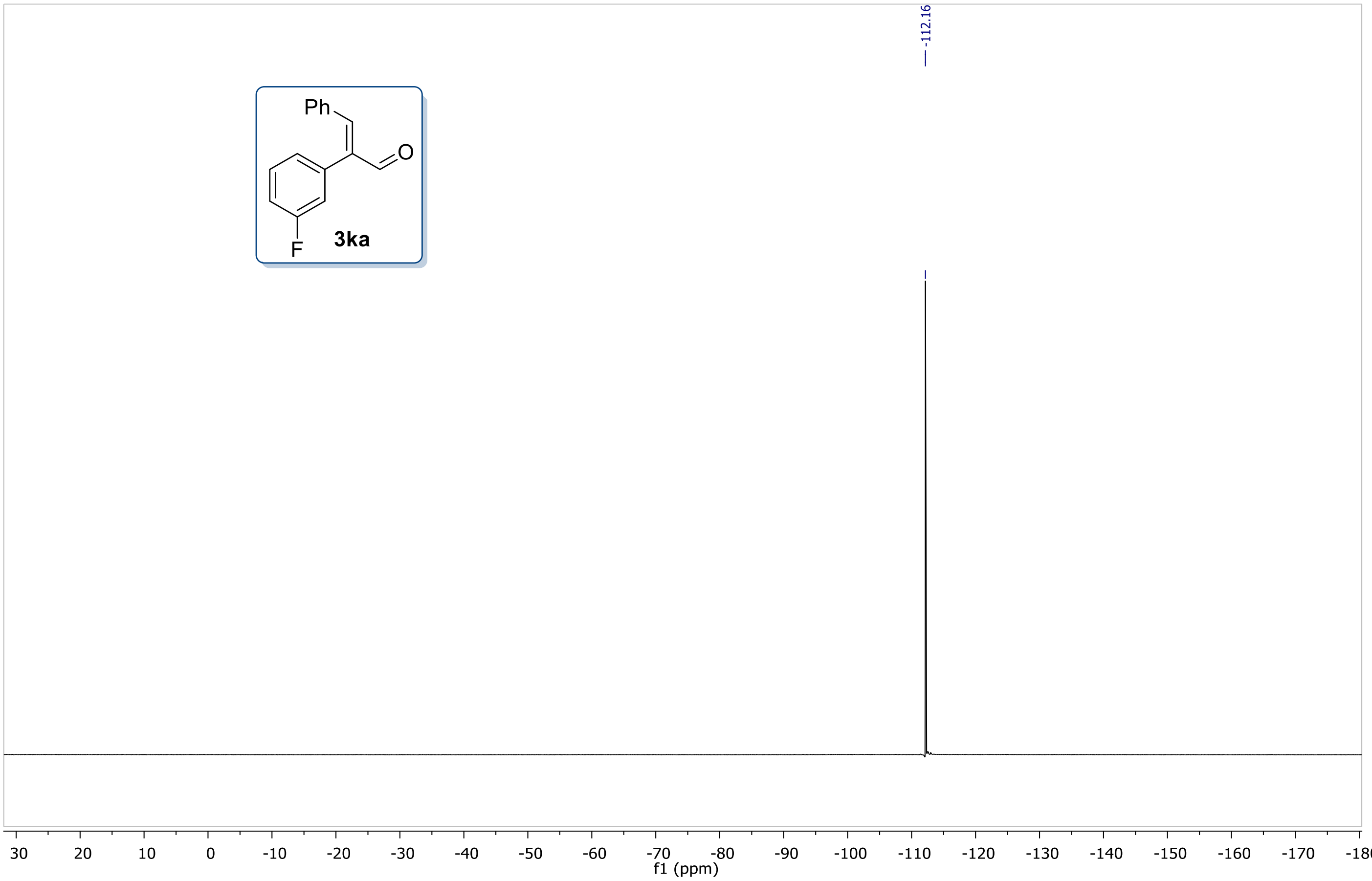


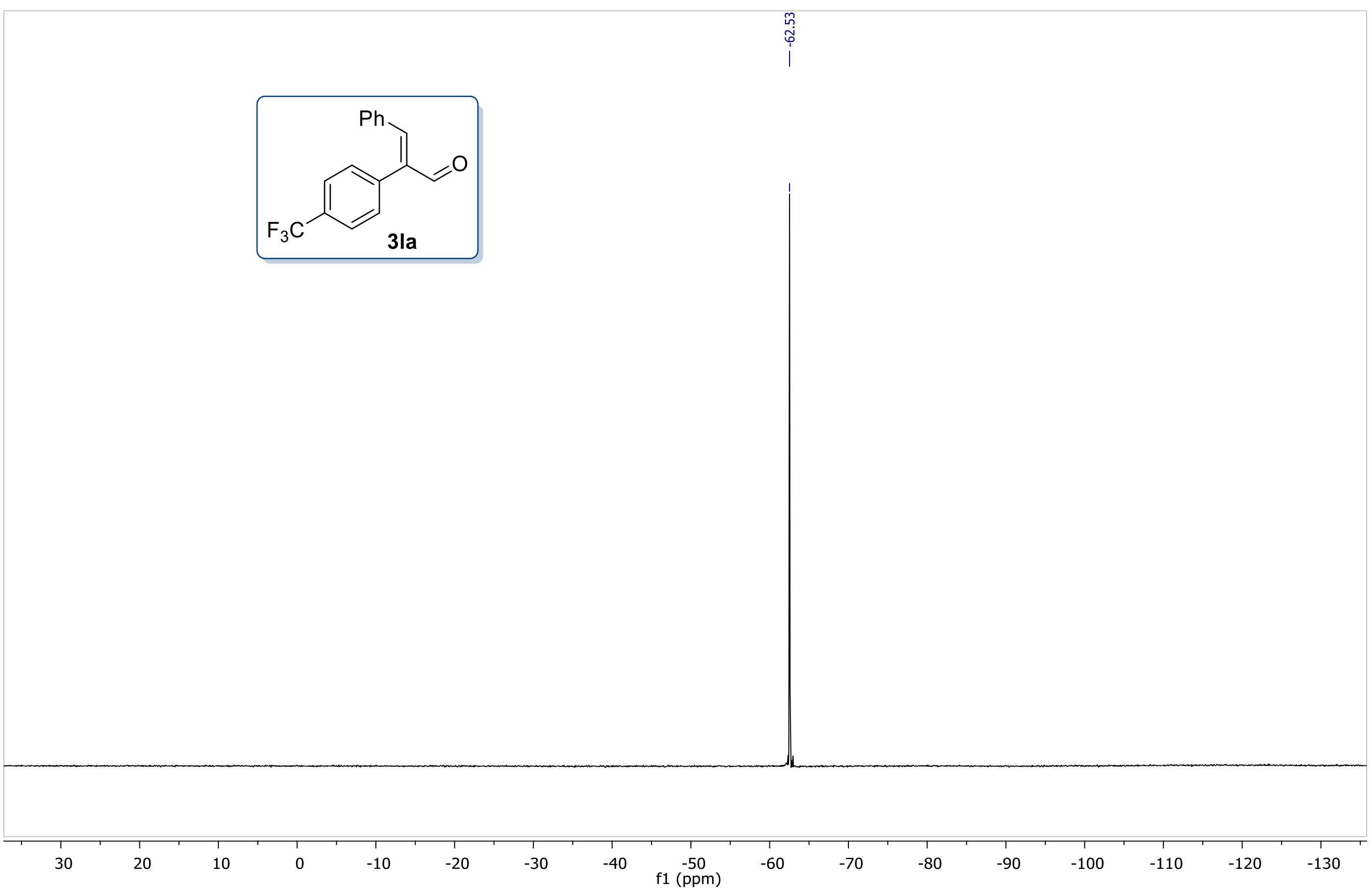
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$), **3ao** and **3ja**



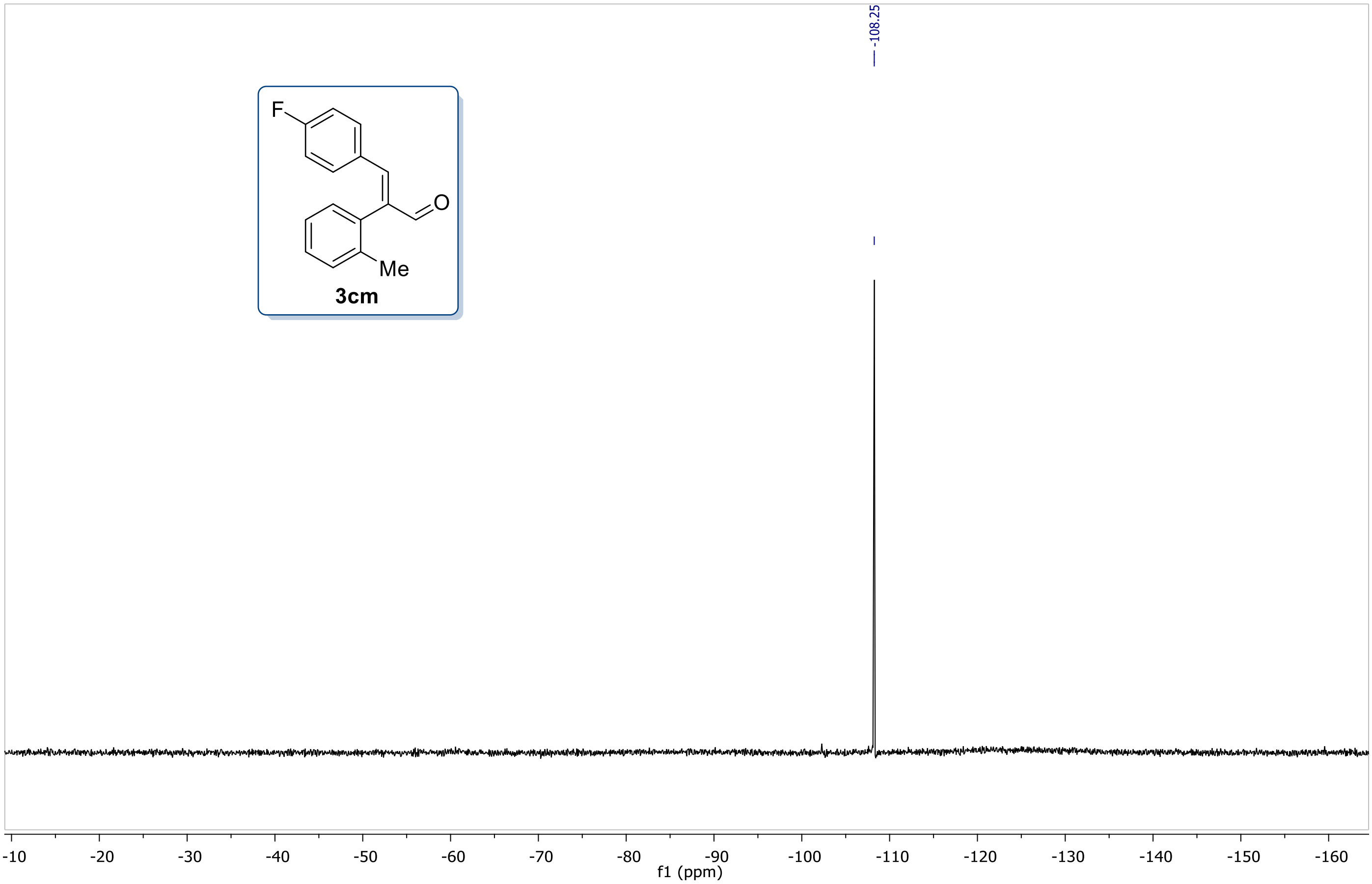


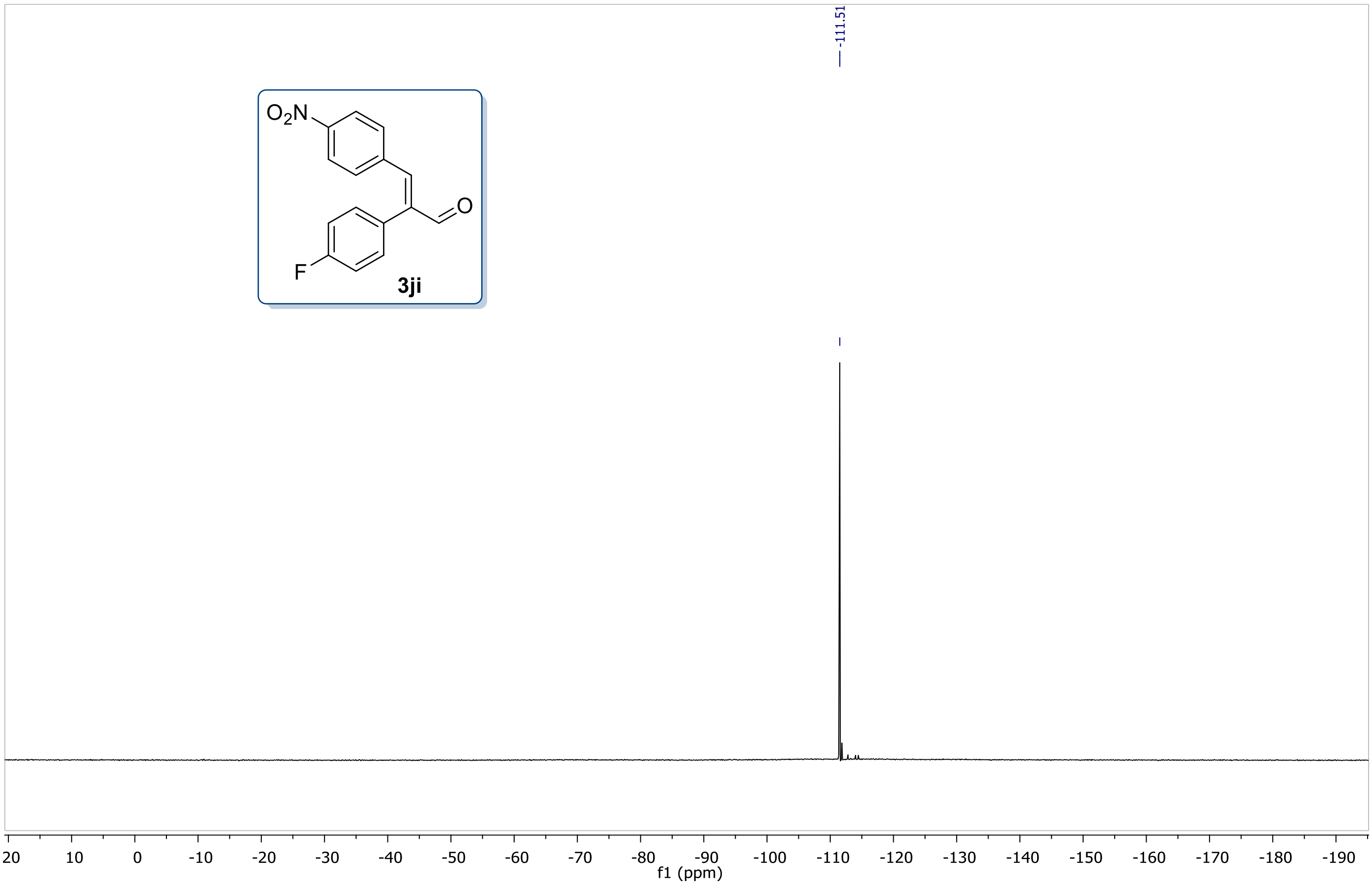
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$), **3ka** and **3la**



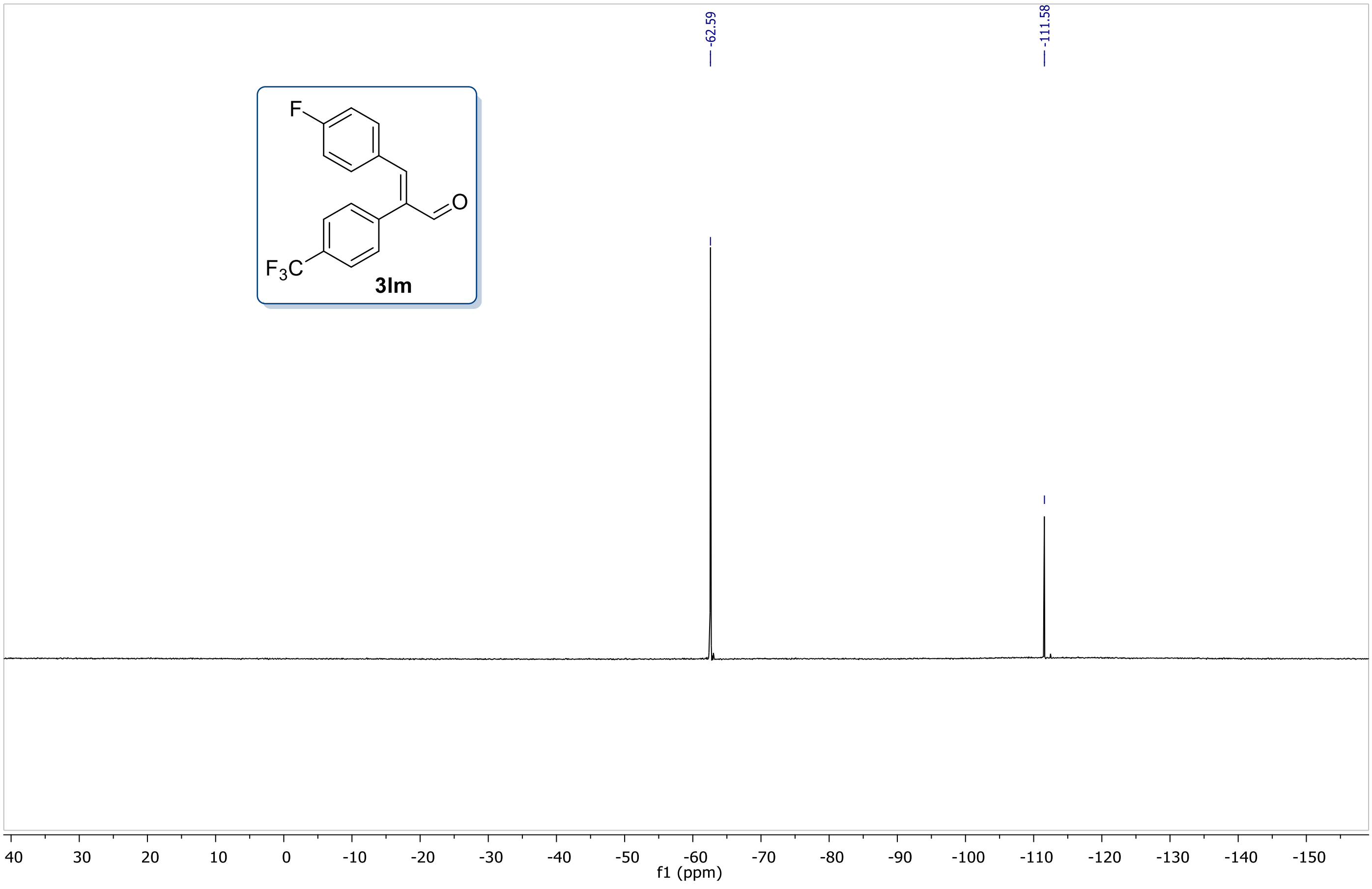


$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$), **3cm** and **3ji**

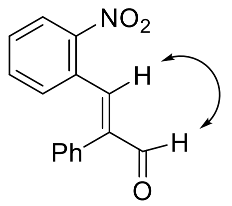




$^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$), **3lm**



NOESY spectrum ($CDCl_3$) , **3aj**



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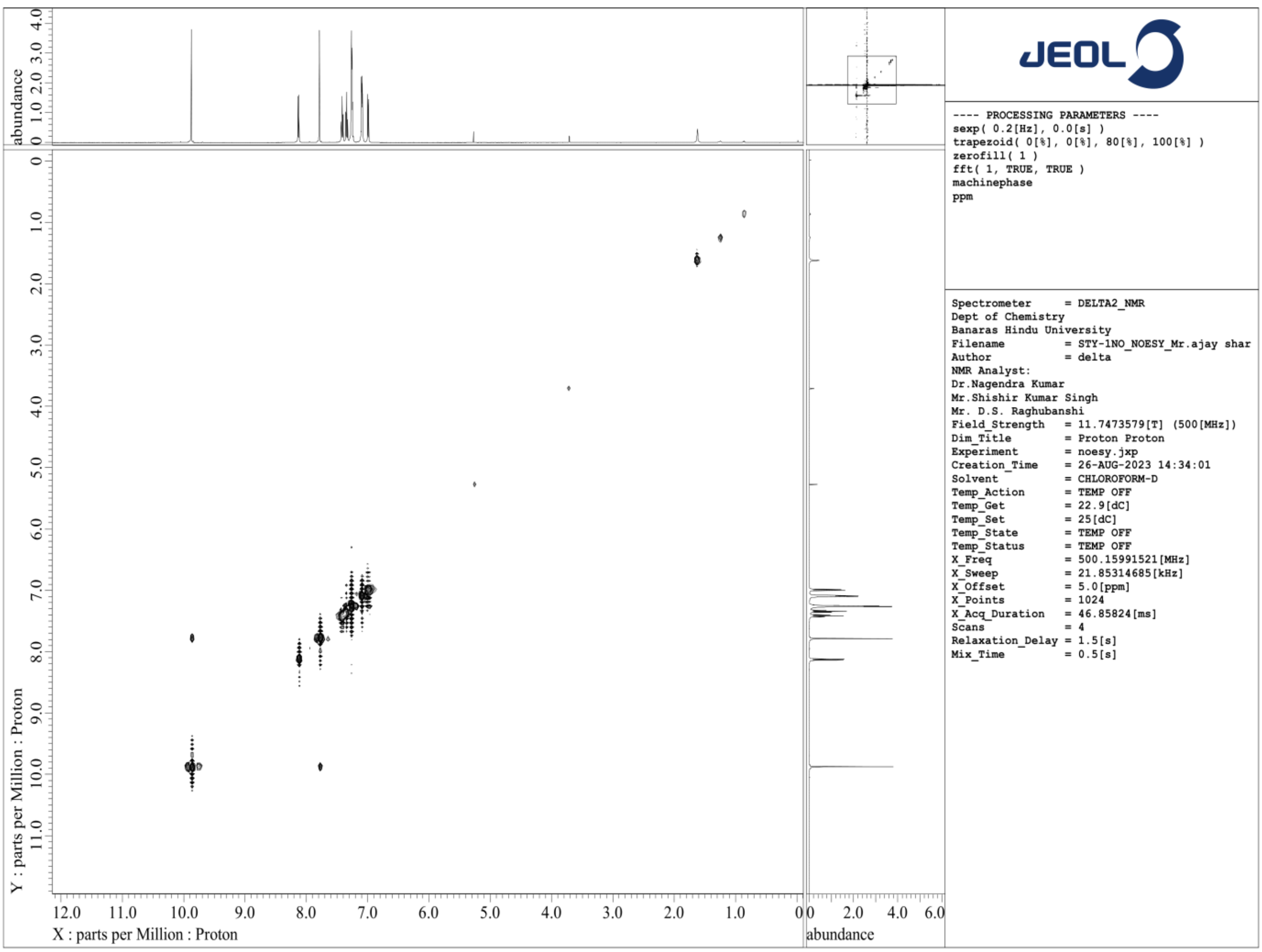

Racemic, **7**

Empower™ 3 SOFTWARE

Default Individual Report

SAMPLE INFORMATION

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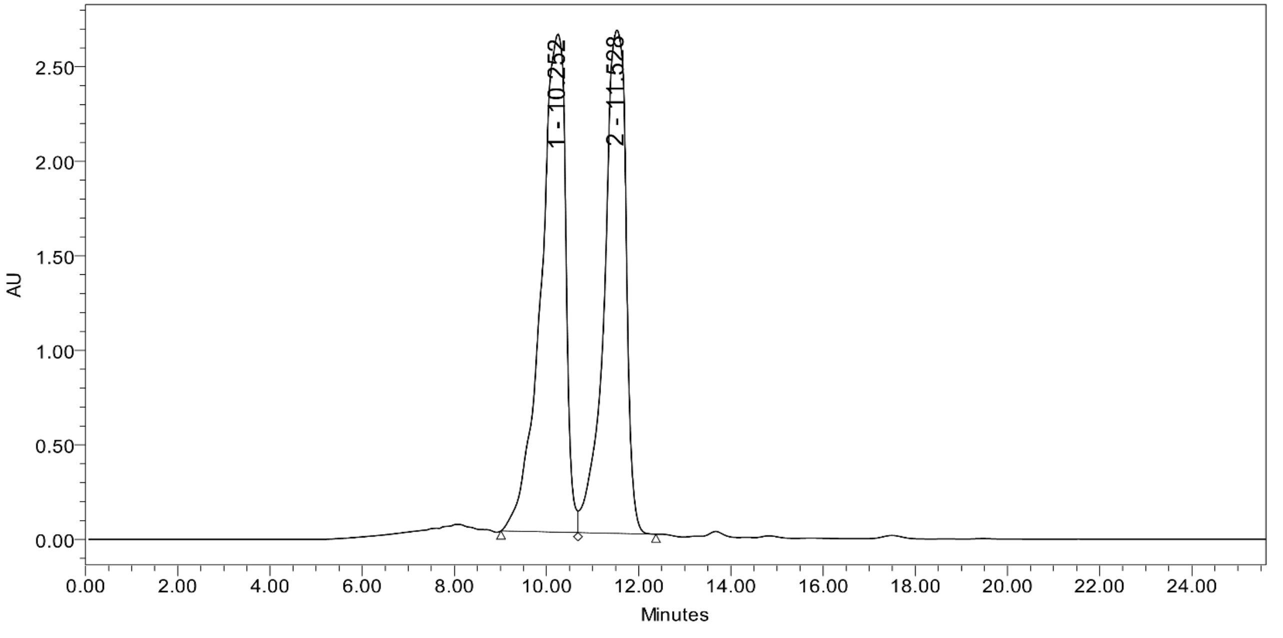
Vial:	1	Acq. Method Set:	35% 25 254
Injection #:	1	Processing Method:	Sty Epo
Injection Volume:	10.00 ul	Channel Name:	225.0nm
Run Time:	100.0 Minutes	Proc. Chnl. Descr.:	2998 PDA 225.0 nm (2998
Date Acquired:	09-06-2023 14:04:16 IST		
Date Processed:	09-09-2023 12:32:36 IST		



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2	2	11.528	87969043	47.22	2661199

Reported by User: System
Report Method: Default Individual Report
Report Method ID: 1009
Page: 1 of 1

Project Name: DEMO
Date Printed:
09-09-2023
12:51:54 Asia/Calcutta

Chiral, **7**

Default Individual Report

SAMPLE INFORMATION

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Vial:	1	Acq. Method Set:	35% 25 254
Injection #:	1	Processing Method:	ch
Injection Volume:	10.00 ul	Channel Name:	225.0nm@2
Run Time:	100.0 Minutes	Proc. Chnl. Descr.:	2998 PDA 225.0 nm (2998
Date Acquired:	09-06-2023 13:10:51 IST		
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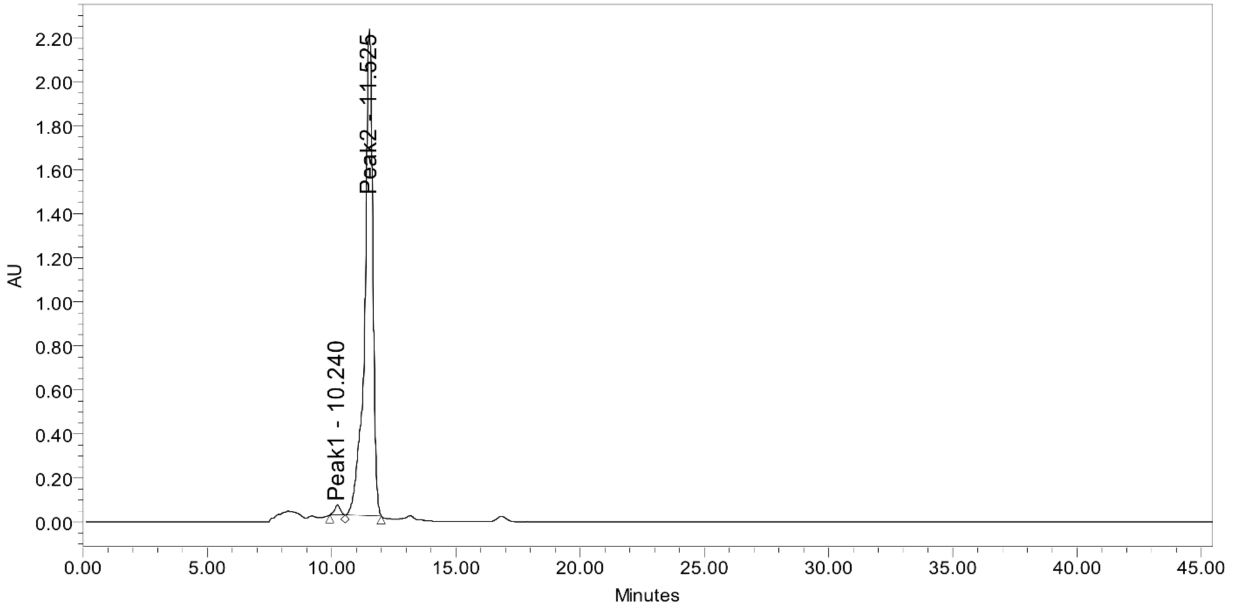

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Report Method ID: 1009
Page: 1 of 1

Project Name: DEMO
Date Printed:
09-09-2023
12:59:32 Asia/Calcutta

Racemic, **8**

Empower™ 3 SOFTWARE

Default Individual Report

SAMPLE INFORMATION

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Sample Type:	Standard	Sample Set Name:	
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Injection Volume:	20.00 ul	Channel Name:	220.0nm
Run Time:	184.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm (200-400)nm
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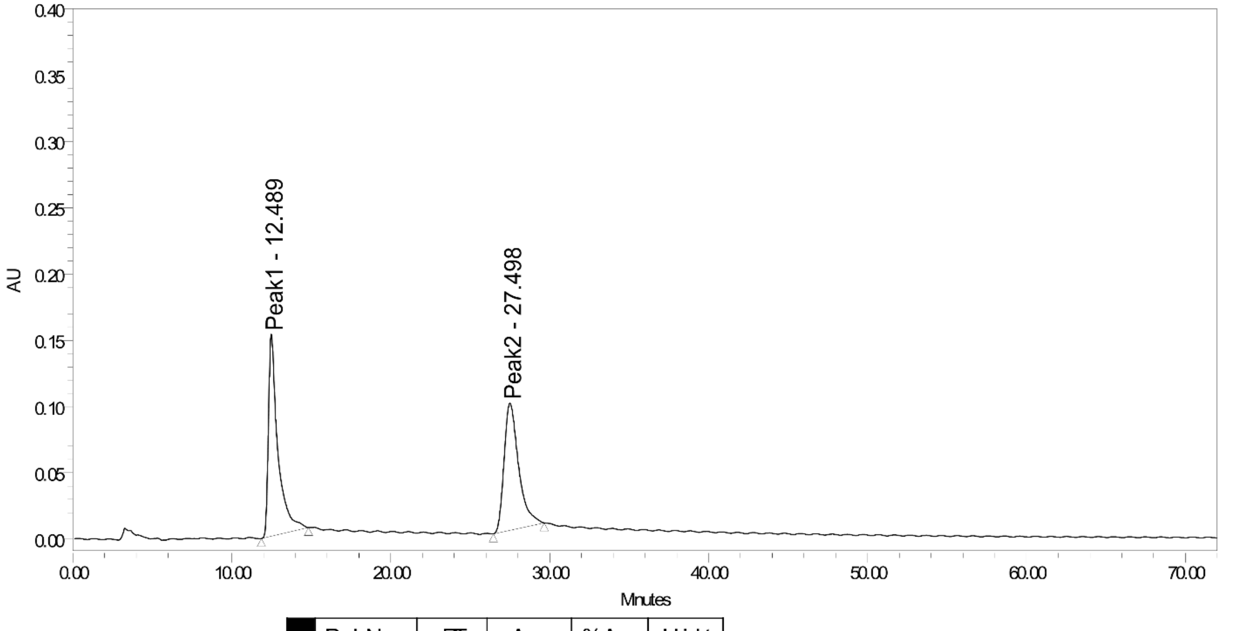

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Empower™ 3 SOFTWARE

Default Individual Report

SAMPLE INFORMATION

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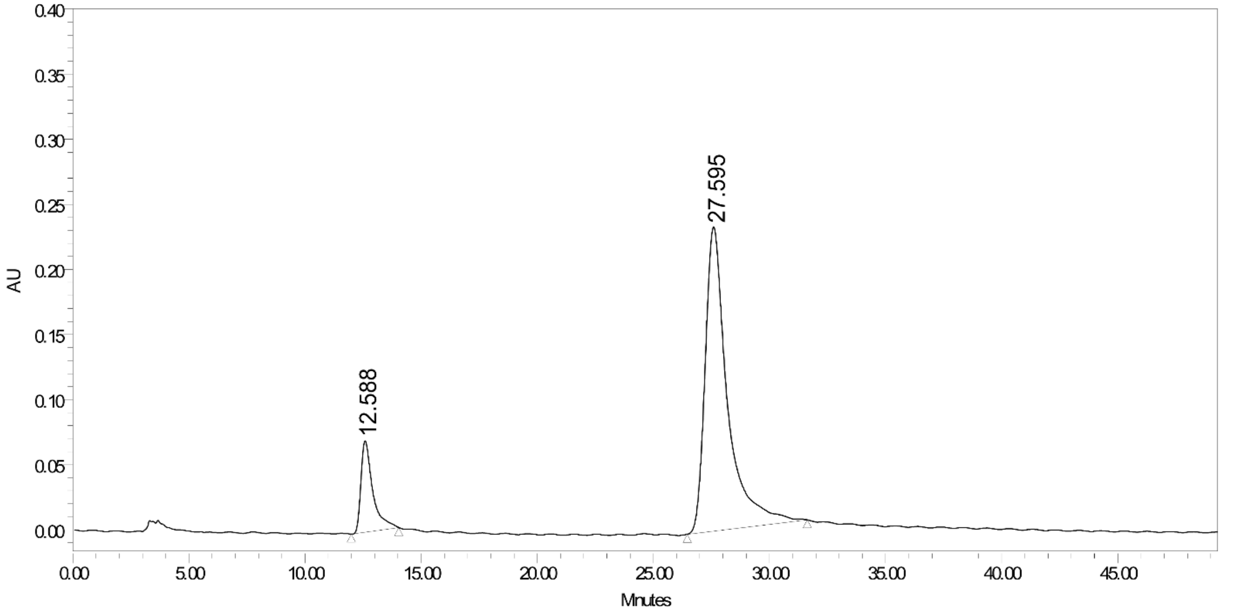

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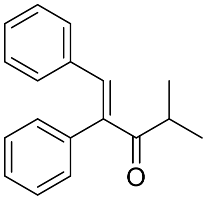
HRMS spectra, **3aa’**



3aa'