Electronic Supplementary Information

Value-added chemicals from biomass-derived furans: radical functionalizations of 5-chloromethylfurfural (CMF) by metal-free ATRA reactions

Rajesh Dasi,[a] Daniel Schmidhuber,[b] Lisa Marie Gronbach,[a]
Julia Rehbein*[b] and Malte Brasholz*[a]

a) Institute of Chemistry – Organic Chemistry, University of Rostock, Albert-Einstein-Str. 3A, 18059 Rostock, Germany

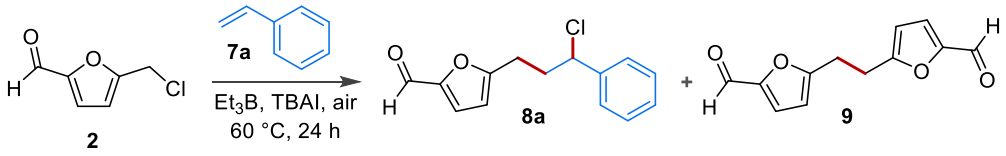
e-mail: malte.brasholz@uni-rostock.de

b) Institute of Organic Chemistry, University of Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany

e-mail: julia.rehbein@chemie.uni-regensburg.de

1. Reaction optimization

Table ESI-1. Reaction optimization.



#	Et_3B (eq.)	TBAI (eq.)	**7a** (eq.)	solvent	conv. **2** [%][a]	yield **8a** [%][a]	yield **9** [%][a]
1	2.0	0	15	MeCN	29	0	0
2	2.0	1	15	MeCN	87	23	10
3[b]	2.0	1	15	MeCN	0	0	0
4	2.0	0.5	8	MeCN	100	16	2
5	2.0	1	8	MeCN	100	30	2
6	2.0	2	8	MeCN	100	31	3
7	2.0	4	8	MeCN	100	40	3
8	2.0	6	8	MeCN	100	38	4
9	2.0	4	4	MeCN	95	30	2
10	2.0	4	10	MeCN	100	42	3
11	2.0	4	15	MeCN	82	42	6
12	2.0	4	20	MeCN	100	30	2
13	4.0	4	10	MeCN	100	33	5
14	1.0	4	10	MeCN	98	51	5
15	**0.5**	**4**	**10**	**MeCN**	**96**	**74**	**3**
16	0.25	4	10	MeCN	91	38	3
17	**0.5**	**4**	**10**	**acetone**	**97**	**75 (78)[c]**	**3**
18	0.5	4	10	THF	74	50	2
19	0.5	4	10	DMF	63	28	2
20	0.5	4	10	DMSO	77	35	1

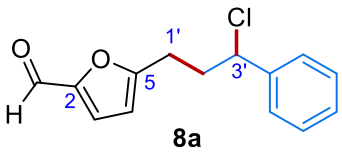
Reactions were performed on 0.30 mmol scale of **1**. [a] Determined by ^{1}H NMR spectros-copy against CH_2Br_2 as internal standard. [b] Reaction in the absence of O_2. [c] Yield of isolated product after chromatography.

2. Synthetic experiments

General Experimental Procedure:

5-Chloromethylfurfural **2** (0.30 mmol, 1.0 equiv.) and tetrabutylammonium iodide (TBAI, 1.20 mmol, 4.0 equiv.) were combined in a 10 mL crimp cap vial and the vial was sealed. Dry acetone (2.00 mL) and styrene derivative **7** (or **10** or **12**, respectively; 3.00 mmol, 10 equiv., freshly distilled) were added and the mixture was heated to 60 °C. After 30 min, triethylborane (Et_3B, 1.0 M solution in hexanes, 0.15 mmol, 0.5 equiv.) was added. Then, the septum was pierced with a cannula to allow the capture of oxygen from the ambient air (the cannula remained in the septum membrane throughout the reaction). After 24 h of reaction time, the solvent was evaporated. The crude mixture was diluted with DCM and washed with water and brine (3 × 20 mL). The organic layer was collected and dried over anhydrous $MgSO_4$ and filtered, followed by concentration under reduced pressure. The crude mixture was subjected to column chromatography (silica gel, 230 – 400 mesh) to afford the desired compounds **8** (or **11** or **13**, respectively).

5-(3-Chloro-3-phenylpropyl)furan-2-carbaldehyde (8a)



8a

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), styrene **7a** (345 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8a** (58 mg, 78%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, $\mathbf{R_f}$ = 0.39 (EtOAc /heptane 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.37–2.57 (m, 2 H, CH_2, C-1'), 2.79–3.00 (m, 2 H, CH_2, C-2'), 4.86 (dd, *J* = 6.1, 8.3 Hz, 1 H, C-3'), 6.27 (d, *J* = 3.6 Hz, 1 H, 4-H), 7.16 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.27–7.40 (m, 5 H, Ar-H), 9.52 (s, 1 H, CHO).

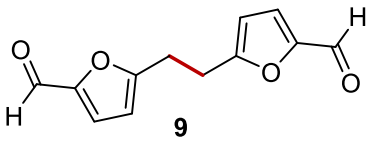
^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.2 (t, C-1'), 37.7 (t, C-2'), 62.5 (d, C-3'), 109.5 (d, C-4), 123.3 (d, C-3), 127.0 (d, Ar), 128.7 (d, Ar), 128.9 (d, Ar), 140.9 (s, Ar), 152.2 (s, C-2), 161.7 (s, C-5), 177.1 (d, CHO).

IR: ṽ = 3030, 2920, 2815 (C-H), 1670 (CO), 1515, 1395, 1195 (C-Cl), 1020, 955, 800, 695 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{14}H_{13}ClO_2^+$ $[M]^+$: 248.0599, found: 248.0596.

From the reaction optimization experiments, a sample of furan dimer **9** could be obtained, in ~90% purity after chromatography.

5,5'-(ethane-1,2-diyl)bis(furan-2-carbaldehyde) (9)



9

Orange solid, **m.p.** 113 °C – 116 °C.

R_f = 0.20 (EtOAc /heptane 1:2)

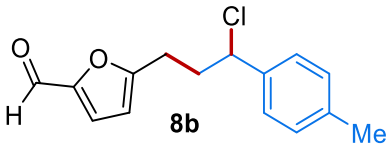
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.14 (s, 4 H, 2 × CH_2, C-1'), 6.24 (d, *J* = 3.5 Hz, 2 H, 4-H), 7.14 (d, *J* = 3.5 Hz, 2 H, 3-H), 9.52 (s, 2 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 26.6 (t, C-1'), 109.6 (d, C-4), 123.3 (d, C-3), 152.2 (s, C-2), 160.9 (s, C-5), 177.1 (d, CHO).

IR: ṽ = 1676, 1521, 1222, 1024, 786, 775, 762, 757, 730, 667 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{12}H_{11}O_4$ $[M+H]^+$: 219.0657, found: 219.0658.

5-(3-Chloro-3-(p-tolyl)propyl)furan-2-carbaldehyde



8b

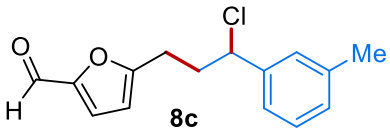
According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-methylstyrene **7b** (400 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8b** (52.7 mg, 67%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, **R_f** = 0.39 (EtOAc /heptane 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.35 (s, 3 H, Ar-CH_3), 2.38–2.56 (m, 2 H, CH_2, C-1'), 2.79–2.99 (m, 2 H, CH_2, C-2'), 4.83 (dd, *J* = 6.1, 8.4 Hz, 1 H, CH, C-3'), 6.27 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.14–7.16 (m, 1 H, 3-H), 7.18 (dt, *J* = 1.8 Hz, 0.6, 2 H, Ar-H), 7.24–7.29 (m, 2 H, Ar-H), 9.53 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 21.3 (q, Ar-CH_3), 26.3 (t, C-1'), 37.7 (t, C-2'), 62.6 (d, C-3'), 109.5 (d, C-4), 126.3 (d, C-3), 126.9 (d, Ar), 129.6 (d, Ar), 138.0 (s, Ar), 138.6 (s, Ar), 152.3 (s, C-2), 161.9 (s, C-5), 177.1 (d, CHO).
IR: ṽ = 3025, 2955, 2920 (C-H), 1715, 1675 (CO), 1515, 1395, 1205 (C-Cl), 1020, 955, 800, 755 cm^{-1}.
HRMS (ESI+): *m/z* calc.: $C_{15}H_{15}ClO_2^+$ $[M]^+$: 262.0755, found: 262.0762.

5-(3-Chloro-3-(m-tolyl)propyl)furan-2-carbaldehyde (8c)

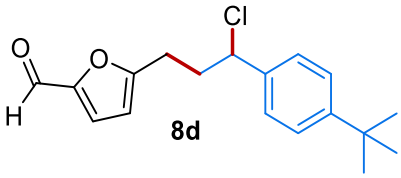


8c

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 3-methylstyrene **7c** (400 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8c** (66 mg, 84%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, $\mathbf{R_f}$ = 0.39 (EtOAc /heptane 1:3)
^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.36 (s, 3 H, Ar-CH_3), 2.39–2.53 (m, 2 H, C-1'), 2.82–2.97 (m, 2 H, C-2'), 4.82 (dd, *J* = 5.8, 8.6 Hz, 1 H, CH, C-3'), 6.28 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.13 (d, *J* = 7.5 Hz, 1 H, Ar-H), 7.16–7.21 (m, 3 H, 3-H, Ar-H), 7.22–7.29 (m, 1 H, Ar-H), 9.53 (s, 1 H, CHO).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 21.5(q, Ar-CH_3), 26.2 (t, C-1'), 37.7 (t, C-2'), 62.7 (d, C-3'), 109.5 (d, C-4), 123.4 (d, C-3), 124.1 (d, Ar), 127.7 (d, Ar), 128.8 (d, Ar), 129.5 (d, Ar), 138.7 (s, Ar), 140.9 (s, Ar), 152.2 (s, C-2), 161.8 (s, C-5), 177.1 (d, CHO).
IR: ṽ = 3115, 2930, 2830 (C-H), 1670 (CO), 1515, 1260, 1150 (C-Cl), 1020, 750, 690 cm^{-1}.
HRMS (ESI+): *m/z* calc.: $C_{15}H_{15}ClO_2^+$ $[M]^+$: 262.0755, found: 262.0762.

5-(3-(4-(Tert-butyl)phenyl)-3-chloropropyl)furan-2-carbaldehyde (8d)



8d

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-tert-butyl styrene **7d** (550 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8d** (63 mg, 69%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, $\mathbf{R_f}$ = 0.42 (EtOAc /heptane 1:3)

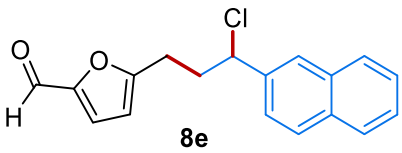
^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.31 (s, 9 H, CH_3), 2.37–2.57 (m, 2 H, CH_2, C-1'), 2.79–3.03 (m, 2 H, CH_2, C-2'), 4.86 (dd, *J* = 6.1, 8.3 Hz, 1 H, CH, C-3'), 6.27 (d, *J* = 3.4 Hz, 1 H, 4-H), 7.16 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.28-7.40 (m, 4 H, Ar-H), 9.53 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.2 (t, C-1'), 31.4 (q, 3 × CH_3), 34.7 (s, *t*-Bu), 37.6 (t, C-2'), 62.5 (d, C-3'), 109.4 (d, C-4), 123.4 (d, C-3), 125.8 (d, Ar), 126.7 (d, Ar), 137.9 (s, Ar), 151.8 (s, Ar), 152.2 (s, C-2), 161.9 (s, C-5), 177.1 (d, CHO).

IR: ṽ = 2960, 2860, 2810 (C-H), 1675 (CO), 1510, 1395, 1365, 1200 (C-Cl), 1020, 950, 800, 750 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{18}H_{21}ClO_2^+$ $[M]^+$: 304. 1225, found: 304. 1225.

5-(3-Chloro-3-(naphthalen-2-yl)propyl)furan-2-carbaldehyde (8e)



8e

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 2-Vinylnaphthalene **7e** (463 mg, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8e** (33.8 mg, 40%) after chromatography (silica, EtOAc/heptane 1:6).

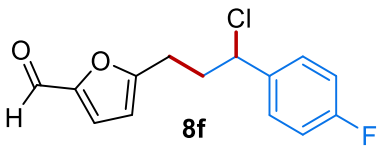
Pale yellow oil, $\mathbf{R_f}$ = 0.37 (EtOAc /heptane 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.47–2.67 (m, 2 H, CH_2, C-1'), 2.83–3.03 (m, 2 H, CH_2, C-2'), 5.04 (dd, *J* = 6.2, 8.3 Hz, 1 H, CH, C-3'), 6.27 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.16 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.48–7.56 (m, 3 H, Ar-H), 7.78–7.90 (m, 4 H, Ar-H), 9.53 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.3 (t, C-1'), 37.6 (t, C-2'), 62.8 (d, C-3'), 109.5 (d, C-4), 123.3 (d, C-3), 124.5 (d, Ar), 126.2 (d, Ar), 126.7 (d, Ar), 127.8 (d, Ar), 128.2 (d, Ar), 129.0 (d, Ar), 133.1 (s, Ar), 133.4 (s, Ar), 138.1 (s, Ar), 152.3 (s, C-2), 161.7 (s, C-5), 177.1 (d, CHO).

IR: ṽ = 3115, 3055, 2920, 2820 (C-H), 1670 (CO), 1510, 1400, 1240 (C-Cl), 1020, 955, 750, 480 cm^{-1}.

5-(3-Chloro-3-(4-fluorophenyl)propyl)furan-2-carbaldehyde (8f)



8f

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-fluorostyrene **7f** (330 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8f** (44 mg, 55%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, $\mathbf{R_f}$ = 0.36 (EtOAc /heptane 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.35–2.54 (m, 2 H, CH_2, C-1'), 2.80–2.99 (m, 2 H, CH_2, C-2'), 4.84 (dd, *J* = 6.0, 8.4 Hz, 1 H, CH, C-3'), 6.28 (d, *J* = 3.5 Hz, 1 H, 4-H), 6.99–7.08 (m, 2 H, Ar-H), 7.17 (d, *J* = 3.6, 1 H, 3-H), 7.30–7.40 (m, 2 H, Ar-H), 9.53 (s, 1 H, CHO).

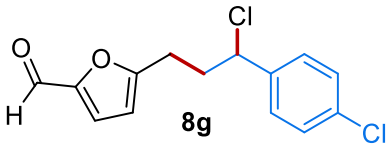
^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.2 (t, C-1'), 37.8 (t, C-2'), 61.7 (d, C-3'), 109.5 (d, C-4), 115.7 (d, Ar), 115.9 (d, $J_{C,F}$ = 22.5 Hz, Ar), 123.4 (d, C-3), 128.9 (d, $J_{C,F}$ = 7.5 Hz, Ar), 136.9 (s, Ar), 152.3 (s, C-2), 161.5 (s, C-5), 162.4 (d, $J_{C,F}$ = 285.0 Hz, Ar), 177.1 (d, CHO).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -112.99 (s, 1 F, Ar-F).

IR: ṽ = 3115, 2915, 2820 (C-H), 1670 (CO), 1600, 1395, 1220 (C-Cl), 1160, 1020, 950, 760, 525 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{14}H_{12}ClFO_2^+$ $[M]^+$: 266.0504, found: 266.0503.

5-(3-Chloro-3-(4-chlorophenyl)propyl)furan-2-carbaldehyde (8g)



8g

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-chlorostyrene **7g** (360 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8g** (55 mg, 65%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, $\mathbf{R_f}$ = 0.36 (EtOAc /heptane 1:3)

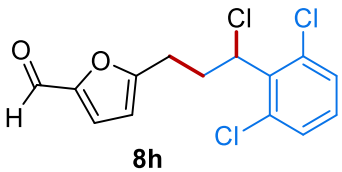
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.34–2.53 (m, 2, CH_2, C-1'), 2.79 – 3.01 (m, 2 H, CH_2, C-2'), 4.82 (dd, *J* = 6.1, 8.4 Hz, 1 H, CH, C-3'), 6.28 (d, *J* = 3.6 Hz, 1 H, 4-H), 7.17 (d, *J* = 3.6 Hz, 1 H, 3-H), 7.28–7.37 (m, 4 H, Ar-H), 9.53 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.1 (t, C-1'), 37.7 (t, C-2'), 61.6 (d, C-3'), 109.6 (d, C-4), 123.4 (d, C-3), 128.4 (d, Ar), 129.1 (d, Ar), 134.5 (s, Ar), 139.5 (s, Ar), 152.3 (s, C-2), 161.4 (s, C-5), 177.1 (d, CHO).

IR: ṽ = 3115, 2960, 2820 (C-H), 1670 (CO), 1515, 1395, 1190 (C-Cl), 1090, 1010, 950, 800, 620 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{14}H_{12}Cl_2O_2^+$ $[M]^+$: 282.0209, found: 282.0207.

5-(3-Chloro-3-(2,6-dichlorophenyl)propyl)furan-2-carbaldehyde (8h)



8h

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 2,6-dichlorostyrene **7h** (410 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8h** (33.2 mg, 35%) after chromatography (silica, EtOAc/heptane 1:4).

Pale yellow oil, $\mathbf{R_f}$ = 0.38 (EtOAc /heptane 1:3)

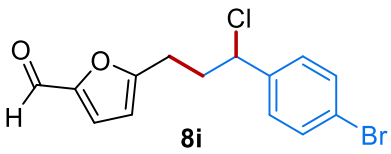
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.58–3.06 (m, 4 H, CH_2, C-1', C-2'), 5.71–5.80 (m, 1 H, CH, C-3'), 6.30 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.12–7.21 (m, 2 H, 3-H, Ar-H), 7.25 – 7.36 (m, 2 H, Ar-H), 9.52 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.3 (t, C-1'), 33.2 (t, C-2'), 56.7 (d, C-3'), 109.6 (d, C-4), 123.2 (d, C-3), 128.7 (d, Ar), 130.0 (d, Ar), 131.0 (d, Ar), 134.6 (s, Ar), 135.0 (s, Ar), 136.0 (s, Ar), 152.3 (s, C-2), 161.3 (s, C-5), 177.2 (d, CHO).

IR: ṽ = 3115, 2925, 2815 (C-H), 1670 (CO), 1510, 1435, 1185 (C-Cl), 1020, 950, 760, 710 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{14}H_{11}Cl_3O_2^+$ $[M]^+$: 315.9819, found: 315.9815.

5-(3-(4-Bromophenyl)-3-chloropropyl)furan-2-carbaldehyde (8i)



8i

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-bromostyrene **7i** (392 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8i** (69.4 mg, 71%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow colour oil, $\mathbf{R_f}$ = 0.35 (EtOAc /heptane 1:3)

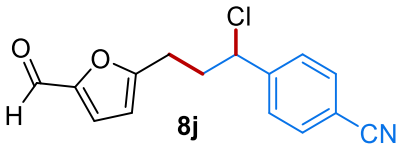
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.33–2.54 (m, 2 H, CH_2, C-1'), 2.81–3.00 (m, 2 H, CH_2, C-2'), 4.82 (dd, *J* = 6.1, 8.3 Hz, 1 H, CH, C-3'), 6.29 (d, *J* = 3.6 Hz, 1 H, 4-H), 7.18 (d, *J* = 3.6 Hz, 1 H, 3-H), 7.23–7.31 (m, 2 H, Ar-H), 7.47–7.54 (m, 2 H, Ar-H), 9.55 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.1 (t, C-1'), 37.7 (t, C-2'), 61.6 (d, C-3'), 109.6 (d, C-4), 122.6 (s, Ar), 123.4 (d, C-3), 128.7 (d, Ar), 132.1 (d, Ar), 140.0 (s, Ar), 152.3 (s, C-2), 161.4 (s, C-5), 177.1 (d, CHO).

IR: ṽ = 3120, 2925, 2815 (C-H), 1670 (CO), 1510, 1490, 1200 (C-Cl), 1070, 1010, 750, 620 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{14}H_{12}BrClO_2^+$ $[M]^+$: 325.9704, found: 325.9701.

4-(1-Chloro-3-(5-formylfuran-2-yl)propyl)benzonitrile (8j)



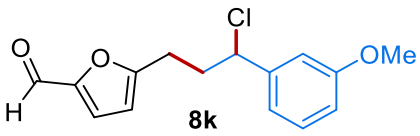
8j

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-cyanostyrene **7j** (360 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8j** (48.3 mg, 59%) after chromatography (silica, EtOAc/heptane 1:4).

Pale yellow oil, $\mathbf{R_f}$ = 0.30 (EtOAc /heptane 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.37–2.48 (m, 2 H, CH_2, C-1'), 2.84–2.98 (m, 2 H, CH_2, C-2'), 4.86 (dd, *J* = 5.9, 8.4 Hz, 1 H, CH, C-3'), 6.28 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.16 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.47–7.53 (m, 2 H, Ar-H), 7.62–7.68 (m, 2 H, Ar-H), 9.51 (s, 1 H, CHO).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 25.9 (t, C-1'), 37.5 (t, C-2'), 61.1 (d, C-3'), 109.7 (d- C-4), 112.5 (s, Ar), 118.4 (s, CN), 123.5 (d, C-3), 127.8 (d, Ar), 132.7 (d, Ar), 146.0 (s, Ar), 152.3 (s, C-2), 161.0 (s, C-5), 177.0 (d, CHO).
IR: ṽ = 3115, 2930, 2820 (C-H), 2230 (CN), 1670 (CO), 1515, 1190 (C-Cl), 1020, 950, 750, 560 cm^{-1}.
HRMS (ESI+): *m/z* calc.: $C_{15}H_{12}ClNaNO_2^+$ $[M+Na]^+$: 296.0449, found: 296.0449.

5-(3-Chloro-3-(3-methoxyphenyl)propyl)furan-2-carbaldehyde (8k)

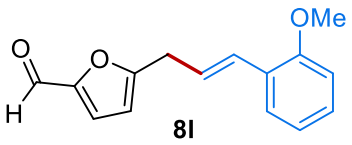


8k

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 3-methoxystyrene **7k** (416 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8k** (60.8 mg, 73%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, $\mathbf{R_f}$ = 0.35 (EtOAc /heptane 1:3)
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.35–2.55 (m, 2 H, CH_2, C-1'), 2.78–2.99 (m, 2 H, CH_2, C-2'), 3.81 (s, 3 H, CH_3, OMe), 4.82 (dd, *J* = 6.2, 8.2 Hz, 1 H, CH, C-3'), 6.27 (d, *J* = 3.6 Hz, 1 H, 4-H), 6.82–6.87 (m, 1 H, Ar-H), 6.90–6.97 (m, 2 H, Ar-H), 7.16 (d, *J* =3.5 Hz, 1 H, 3-H), 7.22–7.31 (m, 1 H, Ar-H), 9.52 (s, 1 H, CHO).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.2 (t, C-1'), 37.7 (t, C-2'), 55.4 (q, OMe), 62.4 (d, C-3'), 109.5 (d, C-4), 112.7 (d, Ar), 114.1 (d, Ar), 119.2 (d, Ar), 123.3 (d, C-3), 129.9 (d, Ar), 142.4 (s, Ar), 152.2 (s, C-2), 159.9 (s, C-5), 161.7 (s, Ar), 177.1 (d, CHO).
IR: ṽ = 3115, 2940, 2835 (C-H), 1670 (CO), 1515, 1260, 1150 (C-Cl), 1020, 750, 690 cm^{-1}.
HRMS (ESI+): *m/z* calc.: $C_{15}H_{15}ClO_3^+$ $[M]^+$: 278.0704, found: 278.0703.

(*E*)-5-(3-(2-Methoxyphenyl)allyl)furan-2-carbaldehyde (8l)

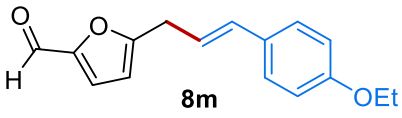


8l

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 2-methoxystyrene **7l** (416 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **8l** (30 mg, 41%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, $\mathbf{R_f}$ = 0.36 (EtOAc /heptane 1:3)
^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.67 (d, *J* = 7.1 Hz, 2 H, CH_2, C-1'), 3.85 (s, 3 H, CH_3, OMe), 6.31 (td, *J* = 7.1, 15.9 Hz, 1 H, 2'-H), 6.32 (d, *J* = 3.5 Hz, 1 H, 4-H), 6.84–6.96 (m, 3 H, Ar-H, 3'-H), 7.17–7.24 (m, 2 H, 3-H, Ar-H), 7.42 (dd, *J* = 1.7, 7.6 Hz, 1 H, Ar-H), 9.55 (s, 1 H, CHO).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 32.7 (t- C-1'), 55.6 (q, CH_3, OCH_3), 109.4 (d, C-4), 111.0 (d, Ar), 120.8 (d, Ar), 123.4 (d, C-3), 123.9 (d, C-2'), 125.9 (s, Ar), 127.0 (d, Ar), 128.6 (d, C-3'), 128.9 (d, Ar), 152.2 (s, C-2), 156.7 (s, C-5), 162.0 (s, Ar), 177.3 (d, CHO).
IR: ṽ = 2935, 2835 (C-H), 1670 (CO), 1510, 1490, 1395, 1240 (C-Cl), 965, 750 cm^{-1}.
HRMS (ESI+): *m/z* calc.: $C_{15}H_{14}NaO_3^+$ $[M+Na]^+$: 265.0835, found: 265.0839.

(*E*)-5-(3-(4-ethoxyphenyl)allyl)furan-2-carbaldehyde (8m)



8m

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-ethoxystyrene **7m** (450 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in Acetone (2.0 mL) gave, after 24 h reaction time, compound **8l** (23 mg, 30%) after chromatography (silica, EtOAc/heptane 1:6).

Pale yellow oil, $\mathbf{R_f}$ = 0.36 (EtOAc /heptane 1:3).
^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.41 (t, *J* = 7.0 Hz, 3 H, CH_3), 3.62 (d, *J* = 6.9 Hz, 2 H, C-1'), 4.03 (q, *J* = 7.0 Hz, 2 H, OCH_2), 6.14 (td, *J* = 6.9, 15.7 Hz, 1 H, C-2'), 6.30 (d, *J* = 3.6 Hz, 1 H,

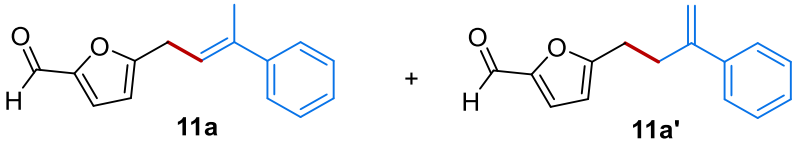
4-H), 6.49 (d, *J* = 15.7 Hz, 1 H, C-3'), 6.81–6.88 (m, 2 H, Ar-H), 7.19 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.25–7.32 (m, 2 H, Ar-H), 9.55 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.9 (q, CH_3), 32.2 (t- C-1'), 63.6 (t- CH_2), 109.3 (d- C-4), 114.7 (d, Ar), 120.9 (d, C-2'), 123.4 (d, C-3), 127.6 (s, Ar), 129.5 (d, Ar), 133.1 (d, C-3'), 152.3 (s, C-2), 158.8 (s, C-5), 161.9 (s, Ar), 177.3 (d, CHO).

IR: ṽ = 3110, 2980, 2830 (C-H), 1670 (CO), 1510, 1390, 1230 (C-Cl), 1175, 975, 755 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{16}H_{16}NaO_3^+$ $[M+Na]^+$: 279.0992, found: 279.0994.

(*E*)-5-(3-Phenylbut-2-en-1-yl)furan-2-carbaldehyde (11a) and 5-(3-Phenylbut-3-en-1-yl)furan-2-carbaldehyde (11a')



According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), α-methylstyrene **10a** (400 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compounds **11a, 11a'** (16 mg, 25%, inseparable mixture, ratio 1:1) after chromatography (silica, EtOAc/heptane 1:7).

Brown oil, $\mathbf{R_f}$ = 0.40 (EtOAc /heptane 1:3)

11a:

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.12 (m_c, 3 H, CH_3, 4'-H), 3.67 (d, *J* = 7.4 Hz, 2 H, CH_2, 1'-H), 5.92 (qt, *J* = 1.5, 7.3 Hz, 1 H, 2'-H), 6.29 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.18 (d, *J* = 3.6 Hz, 1 H, 3-H), 7.27–7.44 (m, 5 H, Ar-H), 9.55 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 16.1 (q, CH_3, C-4'), 28.1 (t, C-1'), 108.9 (d, C-4), 119.8 (d, C-2'), 123.4 (d, C-3), 126.0, (d, Ar), 129.2 (d, Ar), 137.5 (s, C-3'), 138.4 (s, Ar), 152.1 (s, C-2), 163.0 (s, C-5), 177.0 (d, CHO).

11a':

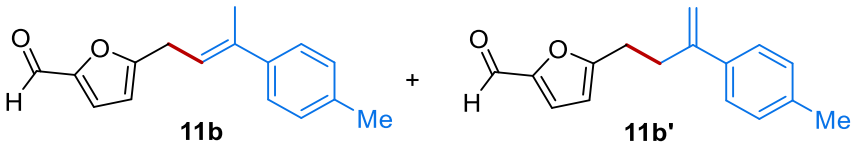
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.91 (dt, *J* = 2.3, 4.5 Hz, 4 H, CH_2, 1'-H, 2'-H), 5.08 (d, *J* = 1.2 Hz, 1 H, 4'-H^a), 5.30 (d, *J* = 1.2 Hz, 1 H, 4'-H^b), 6.21 (d, *J* = 3.5 Hz,1 H, 4-H), 7.15 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.27–7.44 (m, 5 H, Ar-H), 9.52 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 27.5 (t, C-1'), 33.3 (t, C-2'), 109.1 (d, C-4), 112.7 (t, C-4'), 123.4 (d, C-3), 125.7 (d, Ar), 129.0 (d, Ar), 140.1 (s, Ar), 146.5 (s, C-3'), 151.9 (s, C-2), 162.1 (s, C-5), 177.0 (d, CHO).

IR: ṽ = 3055, 2920, 2815 (C-H), 1670 (CO), 1510, 1395, 1190 (C-Cl), 1120, 965, 750, 695 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{15}H_{14}NaO_2^+$ $[M+Na]^+$: 249.0886, found: 249.0888.

(*E*)-5-(3-(p-tolyl)but-2-en-1-yl)furan-2-carbaldehyde (11b) and 5-(3-(p-tolyl)but-3-en-1-yl)furan-2-carbaldehyde (11b')



According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4,α-dimethylstyrene **10b** (440 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compounds **11b, 11b'** (20.2 mg, 28%, inseparable mixture, ratio 40:60) after chromatography (silica, EtOAc/heptane 1:7).

Brown oil, $\mathbf{R_f}$ = 0.42 (EtOAc /heptane 1:3)

11b:

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.09 (dt, *J* = 0.9, 1.5 Hz, 3 H, CH_3, 4'-H), 2.35 (s, 3 H, Ar-CH_3), 3.65 (d, *J* = 7.4, 2 H, CH_2, 1'-H), 5.89 (tt, *J* = 1.4, 7.3 Hz, 1 H, 2'-H), 6.28 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.12–7.17 (m, 2 H, Ar-H), 7.18 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.27–7.32 (m, 2 H, Ar-H), 9.54 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 16.3 (q, CH_3, C-4'), 21.2 (q, Ar-CH_3), 28.3 (t, C-1'), 109.0 (d, C-4), 119.9 (d, C-2'), 123.5 (d, C-3), 125.8 (d, Ar), 129.1 (d, Ar), 137.2 (s, C-3'), 137.6 (s, Ar), 138.5 (s, Ar), 152.0 (s, C-2), 163.1 (s, C-5), 177.2 (d, CHO).

11b':

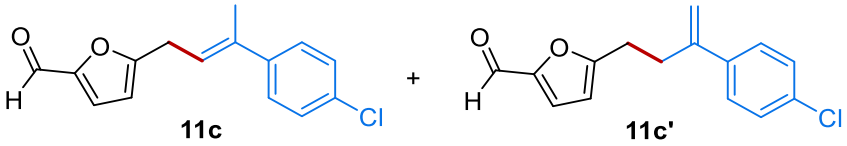
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.35 (s, 3 H, Ar-CH_3), 2.89 (d, *J* = 0.7 Hz, 4 H, CH_2, 1'-H, 2'-H), 5.03 (d, *J* = 1.2 Hz, 1 H, 4'-H^a), 5.28 (d, *J* = 1.2 Hz, 1 H, 4'-H^b), 6.21 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.12–7.17 (m, 3 H, 3-H, Ar-H), 7.27–7.32 (m, 2 H, Ar-H), 9.52 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.2 (q, CH_3, Ar-CH_3), 27.6 (t, C-1'), 33.4 (t, C-2'), 109.2 (d, C-4), 112.8 (t, C-4'), 123.5 (d, C-3), 126.1 (d, Ar), 129.3 (d, Ar), 137.6 (s, Ar), 146.6 (s, C-3'), 152.0 (s, C-2), 163.1 (s, C-5), 177.1 (d, CHO).

IR: ṽ = 3020, 2915, 2815 (C-H), 1670 (CO), 1510, 1400, 1280, 1190 (C-Cl), 1015, 965, 795, 755 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{16}H_{16}O_2^+$ $[M]^+$: 240.1145, found: 240.1144.

(*E*)-5-(3-(4-Chlorophenyl)but-2-en-1-yl)furan-2-carbaldehyde (11c) and 5-(3-(4-Chlorophenyl)but-3-en-1-yl)furan-2-carbaldehyde (11c')



According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-chloro-α-methylstyrene **10c** (430 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compounds **11c, 11c'** (25.7 mg, 33%, inseparable mixture, ratio 60:40) after chromatography (silica, EtOAc/heptane 1:7).

Brown oil, $\mathbf{R_f}$ = 0.40 (EtOAc /heptane 1:3)

11c:

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.09 (s, 3 H, CH_3, 4'-H), 3.65 (d, *J* = 7.3 Hz, 2 H, CH_2, 1'-H), 5.91 (t, *J* = 7.3 Hz, 1 H, =CH, 2'-H), 6.28 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.18 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.27–7.36 (m, 4 H, Ar-H) 9.55 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 16.2 (q, CH_3, C-4'), 28.3 (t- C-1'), 109.1 (d, C-4), 121.4 (d, C-2'), 123.5 (d, C-3), 127.2 (d, Ar), 128.6 (d, Ar), 133.2 (s, Ar), 137.6 (s, Ar), 141.5 (s, C-3'), 152.3 (s, C-2), 161.7 (s, C-5), 177.2 (d, CHO).

11c':

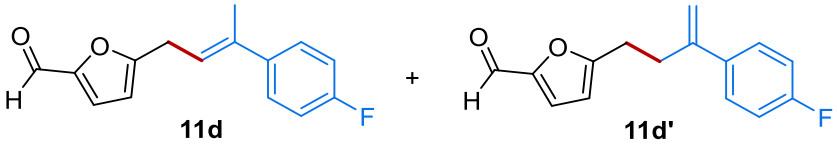
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.88 (s, 4 H, CH_2, 1'-H, 2'-H), 5.10 (d, *J* = 1.0 Hz, 1 H, 4'-H^a), 5.29 (d, *J* = 1.0 Hz, 1 H, 4'-H^b), 6.20 (d, *J* = 3.6 Hz, 1 H, 4-H), 7.14 (d, *J* = 3.5 Hz, 1 H, 3-H), 7.27–7.36 (m, 4 H Ar-H), 9.52 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 27.5 (t- C-1'), 33.3 (t- C-2'), 109.3 (d, C-4), 114.2 (t, C-4'), 123.5 (d, C-3), 127.6 (d, Ar), 128.8 (d, Ar), 133.7(s, Ar), 139.0 (s, Ar), 145.8 (s, C-3'), 152.1 (s, C-2), 162.6 (s, C-5), 177.1 (d, C-6).

IR: ṽ = 3015, 2920, 2820 (C-H), 1670 (CO), 1510, 1400, 1190 (C-Cl), 1090, 1010, 795, 755, 545 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{15}H_{13}ClO_2^+$ $[M]^+$: 260.0599, found: 260.0602.

(*E*)-5-(3-(4-fluorophenyl)but-2-en-1-yl)furan-2-carbaldehyde (11d) and 5-(3-(4-fluorophenyl)but-3-en-1-yl)furan-2-carbaldehyde (11d')



According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 4-fluoro-α-methylstyrene **10d** (400 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compounds **11d, 11d'** (21.2 mg, 29%, inseparable mixture, ratio 54:46) after chromatography (silica, EtOAc/heptane 1:7).

Brown colour oil, $\mathbf{R_f}$ = 0.40 (EtOAc /heptane 1:3)

11d:

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.09 (s, 3 H, CH_3, 4'-H), 3.65 (d, *J* = 7.3 Hz, 2 H, CH_2, 1'-H), 5.86 (qt, *J* = 1.4, 7.3 Hz, 1 H, 2'-H), 6.28 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.01 (tdd, *J* = 2.1, 3.7, 8.7 Hz, 2 H, Ar-H), 7.18 (dd, *J* = 3.7 Hz, 1 H, 3-H), 7.32–7.40 (m, 2 H, Ar-H), 9.54 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 16.4 (q, CH_3, C-4'), 28.2 (t, C-1'), 109.3 (d, C-4), 115.1 (d, Ar), 115.3 (d, Ar), 120.8 (d, C-2'), 123.5 (d, C-3), 127.4 (d, Ar), 127.9 (d, Ar), 137.7 (s, C-3'), 139.2 (s, Ar), 152.3 (s, C-2), 162.7 (s, C-5), 164.2 (s, Ar), 177.1 (d, CHO).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -115.53, (s, 1 F, Ar-F)

11d':

^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.88 (s, 4 H, CH_2, 1'-H, 2'-H), 5.07 (d, *J* = 1.0 Hz, 1 H, 4'-H^a), 5.25 (d, *J* = 1.0 Hz, 1 H, 4'-H^b), 6.20 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.01 (tdd, *J* = 2.2, 3.8, 8.7 Hz, 2 H, Ar-H), 7.14 (d, *J* = 3.5 Hz, 1 H, 3-H) , 7.32–7.39 (m, 2 H, Ar-H), 9.52 (s, 1 H, CHO).

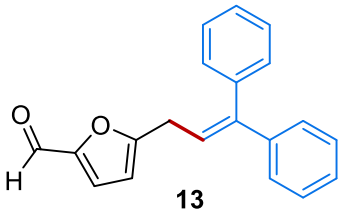
^{13}C NMR (75 MHz, $CDCl_3$) δ = 27.5 (t, C-1'), 33.5 (t, C-2'), 109.1 (d, C-4), 113.6 (t, C-4'), 115.3 (d, Ar), 115.6 (d, Ar), 123.5 (d, C-3), 127.5 (d, Ar), 127.8 (d, Ar), 139.1 (s, Ar), 145.8 (s, C-3'), 152.1 (s, C-2), 161.9 (s, C-5), 163.9 (s, Ar), 177.2 (d, CHO).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.77, (s, 1 F, Ar-F)

IR: ṽ = 3020, 2925, 2815 (C-H), 1670 (CO), 1505, 1395, 1220 (C-Cl), 1160, 1015, 800, 760, 550 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{15}H_{13}FO_2^+$ $[M]^+$: 244.0894, found: 244.0892.

5-(3,3-Diphenylallyl)furan-2-carbaldehyde (13)



13

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), 1,1-diphenylethylene **12** (529 µL, 3.00 mmol, 10 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, compound **13** (25 mg, 29%) after chromatography (silica, EtOAc/heptane 1:7).

Pale yellow oil, R_f = 0.49 (EtOAc /heptane 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.56 (d, *J* = 7.5 Hz, 2 H, CH_2, C-1'), 6.24 (t, *J* = 7.6 Hz, 1 H, =CH, C-2'), 6.29 (d, *J* = 3.6 Hz, 1 H 4-H), 7.16–7.23 (m, 3 H, Ph-H), 7.23–7.31 (m, 5 H, Ph-H), 7.32–7.42 (m, 3 H, 3-H, Ph-H), 9.54 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 29.5 (t- C-1'), 109.1 (d, C-4), 121.7 (d, C-2'), 123.4 (d, C-3), 127.5 (d, Ph), 127.7 (d, Ph), 128.4 (d, Ph), 128.6 (d, Ph), 129.8 (d, Ph), 139.2 (s, Ph), 141.9 (s, Ph), 145.2 (d, C-3'), 152.3 (s, C-2), 162.0 (s, C-5), 177.2 (d, CHO).

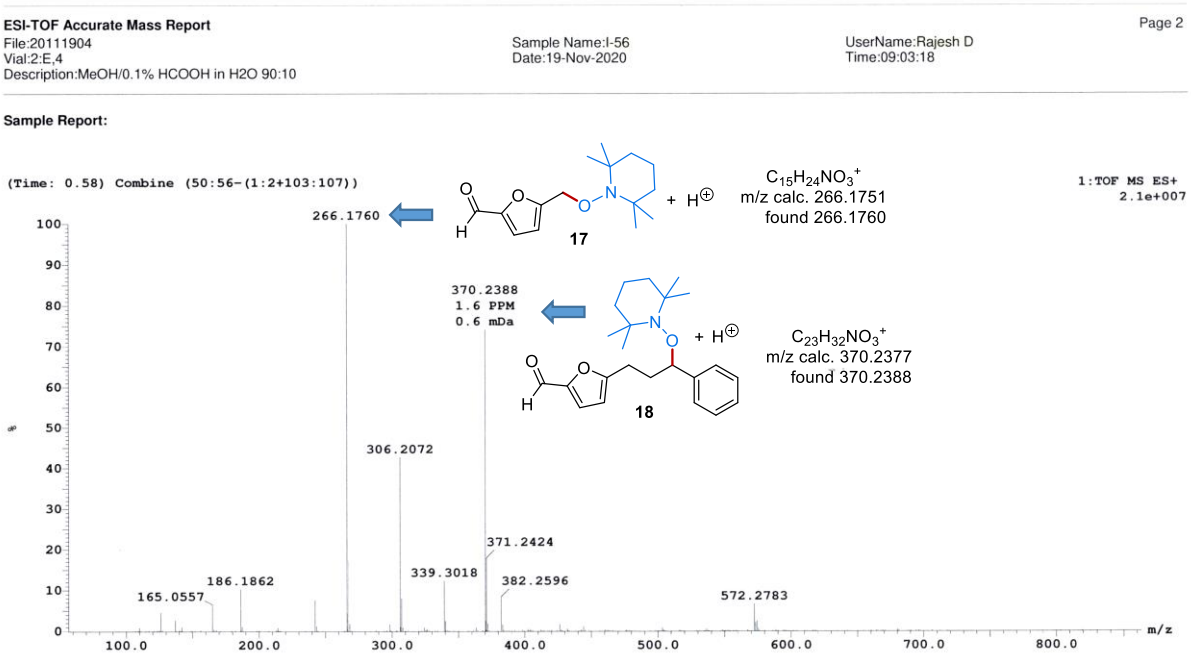
IR: ṽ = 3050, 3020, 2815 (C-H), 1670 (CO), 1515, 1440, 1395, 1190 (C-Cl), 1020, 755, 695 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{20}H_{16}O_2$ $[M]^+$: 288.1145, found: 288.1144.

3. TEMPO trapping experiments

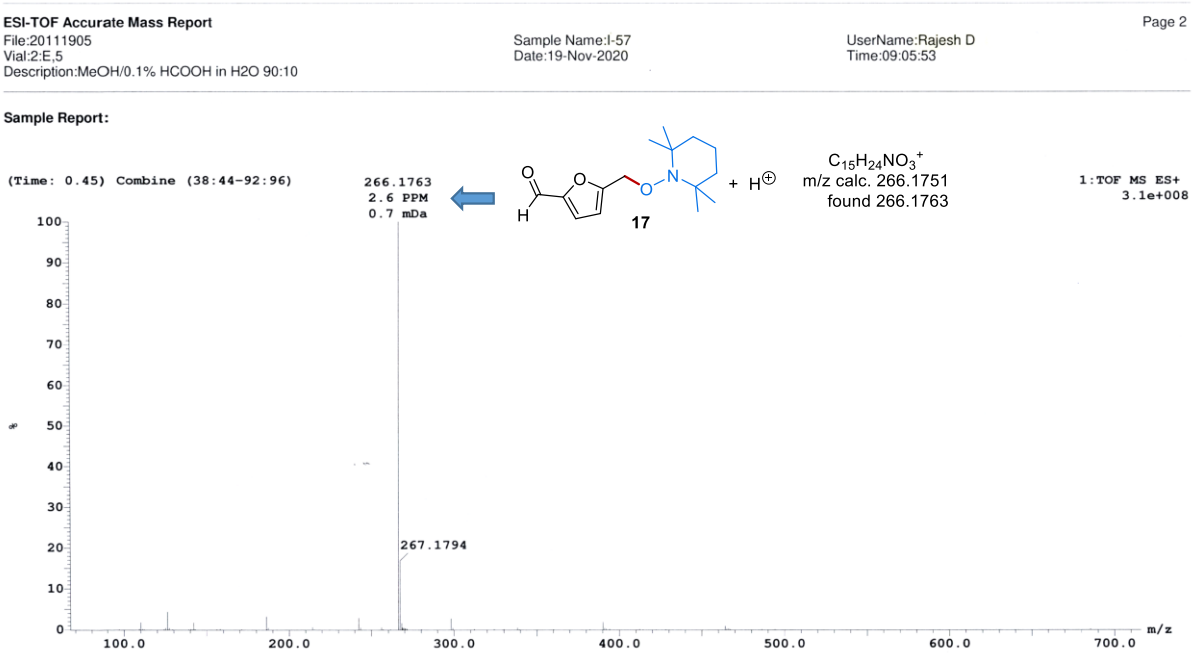
a) Trapping experiment with TEMPO in the presence of styrene:

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), styrene **7a** (345 µL, 3.00 mmol, 10 equiv), TEMPO (46.9 mg, 0.30 mmol, 1 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, a crude product that was analyzed by ESI-TOF mass spectrometry. TEMPO adducts **17** and **18** were unambigiously confirmed.

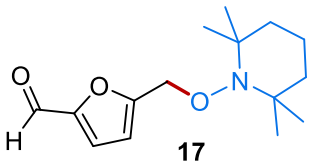


b) Trapping experiment with TEMPO in the absence of styrene:

According to the General Procedure, **2** (43.4 mg, 0.30 mmol, 1.0 equiv), TBAI (443 mg, 1.20 mmol, 4.0 equiv), TEMPO (46.9 mg, 0.30 mmol, 1 equiv), Et_3B (1.0 M solution in hexanes, 150 µL, 0.15 mmol, 0.5 equiv) in acetone (2.00 mL) gave, after 24 h reaction time, a crude product that was analyzed by ESI-TOF mass spectrometry. TEMPO adduct **17** was the only species present. Chromatography of the crude product (silica, EtOAc/heptane 1:6) gave pure compound **17** (35 mg, 44%).



5-{[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]methyl}furan-2-carbaldehyde (17)



Colorless oil, R_f = 0.42 (EtOAc /heptane 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.11 (s, 6 H, CH_3), 1.22 (s, 6 H, CH_3), 1.29 – 1.70 (m, 6 H, 3 × CH_2), 4.84 (s, 2 H, CH_2, C-1'), 6.51 (d, *J* = 3.5 Hz, 1 H, 4-H), 7.21 (d, *J* = 3.5 Hz, 1 H, 3-H), 9.61 (s, 1 H, CHO).

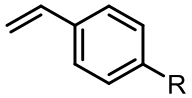
^{13}C NMR (126 MHz, $CDCl_3$) δ = 17.1 (t, CH_2), 20.2 (q, CH_3), 33.0 (q, CH_3), 39.8 (t, CH_2), 60.2 (s, $C(CH_3)_2$), 71.7 (t, C-1'), 110.9 (d, C-4), 122.2 (d, C-3), 152.4 (s, C-2), 158.5 (s, C-5), 177.8 (d, CHO).

HRMS (ESI+): *m/z* calc.: $C_{15}H_{24}NO_3^+$ $[M+H]^+$: 266.1751, found: 266.1763.

4. Computational studies

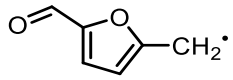
All calculations were performed with the Gaussian09 Revision E.01[1] suite of programs. The calculations were carried out either on a uMP2/6-311+G**[2]–[17] level of theory or a uM06-2X/6-311+G**[2]–[12],[18] level of theory. Stationary points were confirmed as ground or transition states with the computation of the harmonic vibrational frequencies and evaluating the number of imaginary frequencies (0 for ground state, 1 for transition state). Further confirmation of the TS being associated to the reaction coordinate of interest was obtained by visualization of the imaginary frequency. Reported energies are unscaled Gibbs free energies that include a zero-point energy correction and are based on the frequency calculations within the harmonic oscillator approximation. To obtain information about spin densities and FMO energies population analyses were performed with the NBO6[19] software.

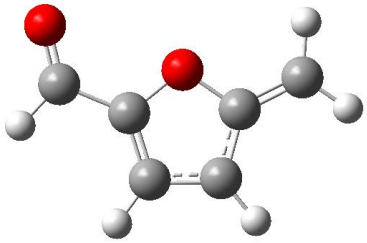
Table ESI-2. SOMO energies of radicals **3**-**6**, LUMO energies of 4-substituted styrenes **7** and energy gaps ΔE (in eV) calculated using NBOs at the uMP2/6-311+G** level of theory.

radicals	SOMO (eV)	**3** -8.828	**4** -8.167	**5** -9.168	**6** -8.771
 **7**	LUMO (eV)	Δε (eV)	Δε (eV)	Δε (eV)	Δε (eV)
R = H	1,762	-10,590	-9,929	-10,930	-10,533
R = Me	1,773	-10,601	-9,940	-10,941	-10,544
R = OMe	1,710	-10,538	-9,877	-10,878	-10,481
R = F	1,701	-10,529	-9,868	-10,869	-10,472
R = CN	1,192	-10,020	-9,359	-10,360	-9,963

Ground state optimizations

3



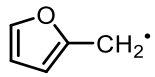
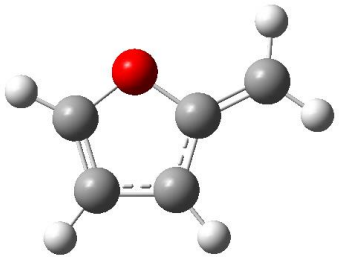


Level of theory: uMP2/6-311+G**

C	1.43203	-0.23181	-0.00036
C	1.38765	1.16412	-0.00044
C	0.02790	1.51339	0.00001
C	-0.66792	0.34829	0.00089
O	0.15794	-0.71657	0.00053
C	-2.13816	0.11712	0.00021
H	-2.69552	1.08331	0.00084
O	-2.67588	-0.93693	-0.00079
C	2.48883	-1.11985	0.00007
H	2.24724	1.81779	-0.00113
H	-0.40165	2.50568	0.00006
H	2.31083	-2.18626	0.00065
H	3.50070	-0.74011	-0.00065

Zero-point correction= 0.095818 (Hartree/Particle)
Thermal correction to Energy= 0.102759
Thermal correction to Enthalpy= 0.103703
Thermal correction to Gibbs Free Energy= 0.063899
Sum of electronic and zero-point Energies= -380.950128
Sum of electronic and thermal Energies= -380.943187
Sum of electronic and thermal Enthalpies= -380.942243
Sum of electronic and thermal Free Energies= -380.982047

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	64.482	25.538	83.775

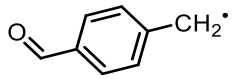
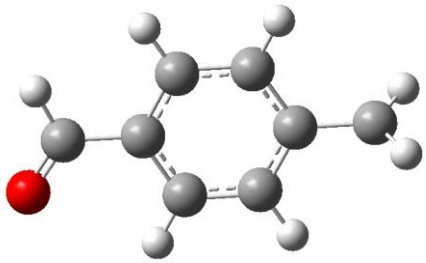
4	
	

Level of theory: uMP2/6-311+G**

C	-1.46886	0.62471	0.00003
C	-1.32349	-0.71427	0.00002
O	-0.02473	-1.07518	0.00001
C	0.71710	0.08155	-0.00009
C	-0.15314	1.16180	-0.00007
C	2.09816	-0.01220	-0.00004
H	-2.40467	1.16326	0.00030
H	-2.03336	-1.52727	0.00006
H	0.14075	2.20074	-0.00028
H	2.69019	0.89180	0.00088
H	2.58631	-0.97663	-0.00008

Zero-point correction= 0.085339 (Hartree/Particle)
Thermal correction to Energy= 0.090250
Thermal correction to Enthalpy= 0.091194
Thermal correction to Gibbs Free Energy= 0.056819
Sum of electronic and zero-point Energies= -267.887282
Sum of electronic and thermal Energies= -267.882371
Sum of electronic and thermal Enthalpies= -267.881427
Sum of electronic and thermal Free Energies= -267.915802

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	56.633	18.815	72.349

5	
	

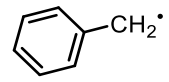
Level of theory: uMP2/6-311+G**

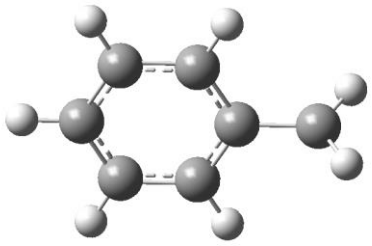
C	0.16485	1.34407	-0.01171
C	0.99118	0.20820	0.01554
C	0.41611	-1.07536	0.00901
C	-0.97498	-1.21155	0.01648
C	-1.81705	-0.07907	-0.00715
C	-1.22810	1.20016	-0.00627
C	2.46368	0.37960	-0.00500
O	3.26558	-0.53898	-0.00235
C	-3.29018	-0.23345	-0.00383
H	0.61216	2.33655	-0.01490
H	1.06710	-1.94539	0.02195
H	-1.42205	-2.20269	0.02288
H	-1.86648	2.07992	-0.02644
H	2.80913	1.43475	-0.02366
H	-3.81101	-0.57900	-0.88835
H	-3.86663	-0.00790	0.88491

Zero-point correction= 0.121599 (Hartree/Particle)
Thermal correction to Energy= 0.130172
Thermal correction to Enthalpy= 0.131116
Thermal correction to Gibbs Free Energy= 0.088028
Sum of electronic and zero-point Energies= -383.075480
Sum of electronic and thermal Energies= -383.066906
Sum of electronic and thermal Enthalpies= -383.065962
Sum of electronic and thermal Free Energies= -383.109051

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	81.684	32.168	90.687

6





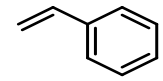
Level of theory: uMP2/6-311+G**

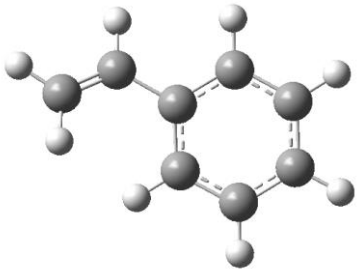
C	0.25383	-1.21103	-0.00868
C	-1.14890	-1.21201	-0.00911
C	-1.85399	-0.00000	-0.00002
C	-1.14891	1.21201	0.00914
C	0.25383	1.21103	0.00865
C	0.97311	-0.00000	0.00001
C	2.45496	0.00001	0.00000
H	0.79768	-2.15252	-0.01938
H	-1.68734	-2.15615	-0.01634
H	-2.94064	-0.00000	0.00000
H	-1.68734	2.15615	0.01633
H	0.79768	2.15252	0.01939
H	3.00817	0.22846	-0.90277
H	3.00819	-0.22848	0.90275

Zero-point correction= 0.111844 (Hartree/Particle)
Thermal correction to Energy= 0.118610
Thermal correction to Enthalpy= 0.119554
Thermal correction to Gibbs Free Energy= 0.081236
Sum of electronic and zero-point Energies= -270.003007
Sum of electronic and thermal Energies= -269.996241
Sum of electronic and thermal Enthalpies= -269.995297
Sum of electronic and thermal Free Energies= -270.033615

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	74.429	25.786	80.648

7a





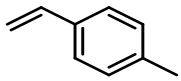
Level of theory: uMP2/6-311+G**

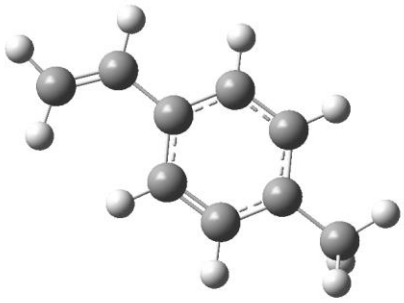
C	0.51829	-0.22196	-0.10104
C	-0.39180	-1.29025	-0.00008
C	-1.76581	-1.05422	0.10872
C	-2.25612	0.25685	0.08022
C	-1.36118	1.32806	-0.03871
C	0.01131	1.08991	-0.15430
C	1.96348	-0.50063	-0.18541
C	2.93281	0.32808	0.24558
H	-0.01276	-2.31005	0.02330
H	-2.45330	-1.89172	0.19417
H	-3.32377	0.44301	0.15961
H	-1.73696	2.34711	-0.08238
H	0.69574	1.92457	-0.28416
H	2.24346	-1.46951	-0.59925
H	3.97943	0.05716	0.15237
H	2.70232	1.28442	0.70644

Zero-point correction= 0.132065 (Hartree/Particle)
Thermal correction to Energy= 0.139130
Thermal correction to Enthalpy= 0.140074
Thermal correction to Gibbs Free Energy= 0.100880
Sum of electronic and zero-point Energies= -308.630904
Sum of electronic and thermal Energies= -308.623839
Sum of electronic and thermal Enthalpies= -308.622895
Sum of electronic and thermal Free Energies= -308.662089

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	87.305	27.384	82.491

7b





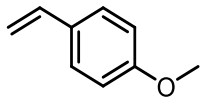
Level of theory: uMP2/6-311+G**

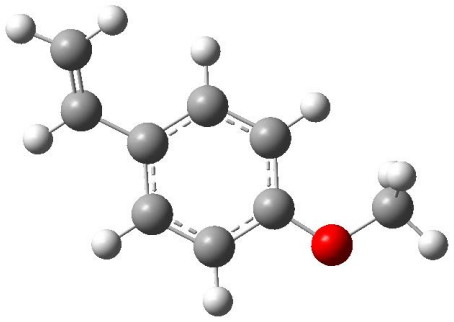
C	1.03651	0.22751	-0.09632
C	0.19002	1.34769	-0.01307
C	-1.19783	1.19640	0.05706
C	-1.79027	-0.07501	0.00676
C	-0.94460	-1.19164	-0.09944
C	0.44270	-1.04572	-0.17530
C	2.49700	0.41448	-0.14871
C	3.40537	-0.48474	0.27464
C	-3.28616	-0.24146	0.11204
H	0.62748	2.34366	0.02472
H	-1.83077	2.07915	0.12749
H	-1.38176	-2.18640	-0.16633
H	1.06995	-1.92553	-0.29760
H	2.84530	1.37404	-0.53146
H	4.46826	-0.27763	0.20463
H	3.10807	-1.43690	0.70483
H	-3.80753	0.63298	-0.28793
H	-3.62253	-1.12325	-0.44106
H	-3.59295	-0.36519	1.15676

Zero-point correction= 0.159808 (Hartree/Particle)
Thermal correction to Energy= 0.168714
Thermal correction to Enthalpy= 0.169658
Thermal correction to Gibbs Free Energy= 0.125921
Sum of electronic and zero-point Energies= -347.803462
Sum of electronic and thermal Energies= -347.794556
Sum of electronic and thermal Enthalpies= -347.793611
Sum of electronic and thermal Free Energies= -347.837349

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	105.870	33.415	92.053

7n





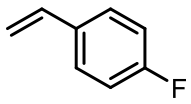
Level of theory: uMP2/6-311+G**

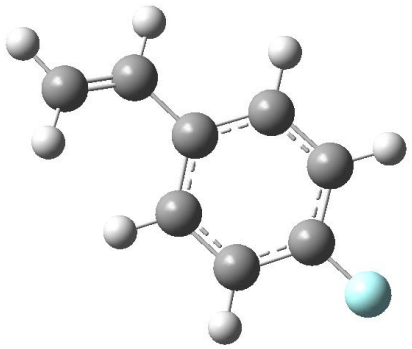
C	-1.47152	0.20927	0.10068
C	-0.77294	1.42985	0.00449
C	0.61667	1.46307	-0.07053
C	1.35495	0.26980	-0.01365
C	0.68039	-0.95522	0.10123
C	-0.71787	-0.97153	0.18306
C	-2.94320	0.20548	0.15141
C	-3.72833	-0.80200	-0.27518
O	2.71098	0.40807	-0.08432
C	3.47489	-0.78804	-0.03979
H	-1.33206	2.36229	-0.04158
H	1.15590	2.40251	-0.15351
H	1.22262	-1.89138	0.17378
H	-1.22479	-1.92508	0.31024
H	-3.41298	1.10955	0.53966
H	-4.80886	-0.73572	-0.20082
H	-3.31056	-1.70452	-0.71235
H	4.51591	-0.47659	-0.11909
H	3.32331	-1.32098	0.90568
H	3.22543	-1.44871	-0.87778

Zero-point correction= 0.165092 (Hartree/Particle)
Thermal correction to Energy= 0.174794
Thermal correction to Enthalpy= 0.175738
Thermal correction to Gibbs Free Energy= 0.129979
Sum of electronic and zero-point Energies= -422.856986
Sum of electronic and thermal Energies= -422.847284
Sum of electronic and thermal Enthalpies= -422.846340
Sum of electronic and thermal Free Energies= -422.892099

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	109.685	36.542	96.307

7f



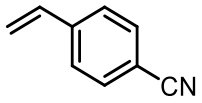
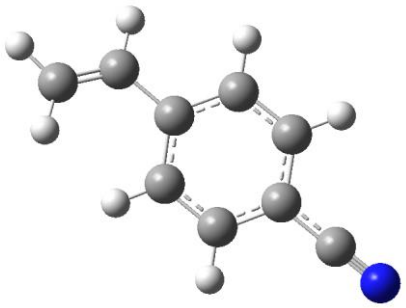


Level of theory: uMP2/6-311+G**

C	-0.98112	0.22912	-0.10640
C	-0.12969	1.34518	-0.01040
C	1.25759	1.19499	0.07235
C	1.78830	-0.09059	0.02938
C	0.98334	-1.22082	-0.08588
C	-0.40074	-1.05140	-0.17386
C	-2.44067	0.42593	-0.16562
C	-3.35402	-0.45930	0.27466
F	3.12829	-0.24791	0.09994
H	-0.56072	2.34322	0.02493
H	1.92171	2.04958	0.15522
H	1.44227	-2.20317	-0.13954
H	-1.03582	-1.92425	-0.29963
H	-2.78169	1.37872	-0.57045
H	-4.41557	-0.24862	0.19738
H	-3.06263	-1.40289	0.72727

Zero-point correction= 0.124005 (Hartree/Particle)
Thermal correction to Energy= 0.131864
Thermal correction to Enthalpy= 0.132808
Thermal correction to Gibbs Free Energy= 0.091513
Sum of electronic and zero-point Energies= -407.716615
Sum of electronic and thermal Energies= -407.708756
Sum of electronic and thermal Enthalpies= -407.707812
Sum of electronic and thermal Free Energies= -407.749107

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	82.746	30.249	86.911

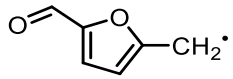
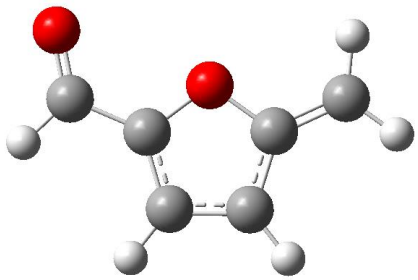
7j	
	

Level of theory: uMP2/6-311+G**

C	-1.31675	0.22203	-0.10033
C	-0.49775	1.36354	-0.01451
C	0.89148	1.25414	0.05200
C	1.48947	-0.01668	-0.01048
C	0.68782	-1.16802	-0.11383
C	-0.69899	-1.04040	-0.18546
C	-2.78131	0.37558	-0.14248
C	-3.66041	-0.54399	0.29790
C	2.91767	-0.14200	0.05954
N	4.08983	-0.24452	0.11708
H	-0.95972	2.34726	0.03265
H	1.51502	2.14021	0.12981
H	1.15749	-2.14552	-0.17786
H	-1.31038	-1.93108	-0.30395
H	-3.15521	1.32402	-0.52739
H	-4.72880	-0.36401	0.24000
H	-3.33455	-1.48451	0.73308

Zero-point correction= 0.130013 (Hartree/Particle)
Thermal correction to Energy= 0.138982
Thermal correction to Enthalpy= 0.139926
Thermal correction to Gibbs Free Energy= 0.095906
Sum of electronic and zero-point Energies= -400.671735
Sum of electronic and thermal Energies= -400.662766
Sum of electronic and thermal Enthalpies= -400.661822
Sum of electronic and thermal Free Energies= -400.705842

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	87.212	33.634	92.648

3	
	

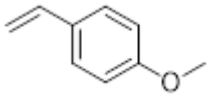
Level of theory: uM06-2X/6-311+G**

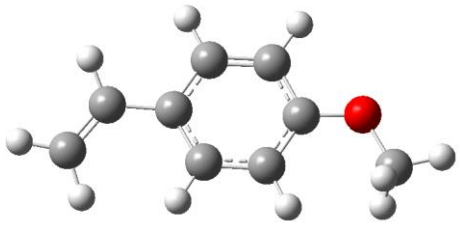
C	1.43187	-0.24576	-0.00021
C	1.38425	1.17083	0.00014
C	0.04194	1.52564	-0.00023
C	-0.68469	0.34186	0.00009
O	0.14619	-0.71967	0.00010
C	-2.12135	0.13617	0.00014
H	-2.69944	1.07897	0.00022
O	-2.66260	-0.94431	-0.00010
C	2.47752	-1.12315	-0.00002
H	2.24628	1.81823	0.00046
H	-0.38272	2.51771	-0.00026
H	2.30006	-2.18861	0.00007
H	3.48990	-0.74803	0.00009

Zero-point correction= 0.094526 (Hartree/Particle)
Thermal correction to Energy= 0.101284
Thermal correction to Enthalpy= 0.102228
Thermal correction to Gibbs Free Energy= 0.062869
Sum of electronic and zero-point Energies= -381.876224
Sum of electronic and thermal Energies= -381.869466
Sum of electronic and thermal Enthalpies= -381.868522
Sum of electronic and thermal Free Energies= -381.907881

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	63.557	25.198	82.838

7n





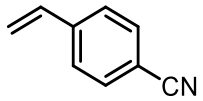
Level of theory: uM06-2X/6-311+G**

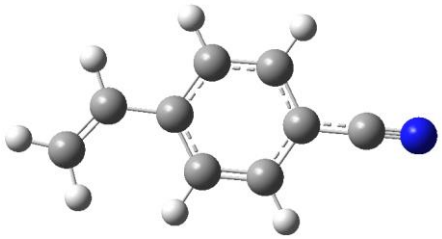
C	-1.46177	0.20941	0.05720
C	-0.76122	1.42205	0.00146
C	0.62051	1.45857	-0.03569
C	1.35007	0.26851	-0.00873
C	0.67558	-0.95133	0.06227
C	-0.71471	-0.96742	0.09762
C	-2.93410	0.22447	0.07432
C	-3.74290	-0.81129	-0.14470
O	2.70092	0.39683	-0.04686
C	3.47547	-0.78342	-0.02469
H	-1.31756	2.35332	-0.02017
H	1.16210	2.39511	-0.08390
H	1.21619	-1.88730	0.10090
H	-1.21971	-1.92344	0.17322
H	-3.37967	1.19614	0.27452
H	-4.81834	-0.69349	-0.10564
H	-3.36732	-1.80119	-0.37853
H	4.51379	-0.46352	-0.07161
H	3.31016	-1.34789	0.89829
H	3.25128	-1.41962	-0.88657

Zero-point correction= 0.167054 (Hartree/Particle)
Thermal correction to Energy= 0.176315
Thermal correction to Enthalpy= 0.177259
Thermal correction to Gibbs Free Energy= 0.132197
Sum of electronic and zero-point Energies= -423.927653
Sum of electronic and thermal Energies= -423.918392
Sum of electronic and thermal Enthalpies= -423.917448
Sum of electronic and thermal Free Energies= -423.962510

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	110.639	34.997	94.840

7j





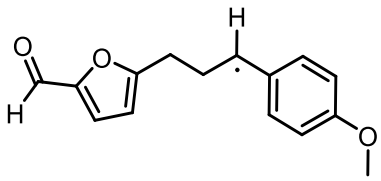
Level of theory: uM06-2X/6-311+G**

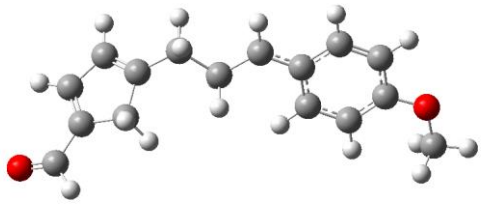
C	-1.30211	0.22364	0.00001
C	-0.48232	1.35702	0.00000
C	0.89985	1.24627	-0.00000
C	1.48782	-0.01868	-0.00001
C	0.68374	-1.16368	-0.00001
C	-0.69364	-1.03848	0.00000
C	-2.76431	0.40551	0.00001
C	-3.68376	-0.55762	0.00002
C	2.91816	-0.14673	-0.00001
N	4.06397	-0.25050	-0.00002
H	-0.93858	2.34060	0.00001
H	1.52605	2.12954	-0.00001
H	1.14835	-2.14176	-0.00001
H	-1.30103	-1.93482	0.00000
H	-3.09546	1.44055	0.00002
H	-4.73832	-0.31311	0.00002
H	-3.42943	-1.61111	0.00002

Zero-point correction= 0.132796 (Hartree/Particle)
Thermal correction to Energy= 0.140470
Thermal correction to Enthalpy= 0.141414
Thermal correction to Gibbs Free Energy= 0.100256
Sum of electronic and zero-point Energies= -401.688524
Sum of electronic and thermal Energies= -401.680851
Sum of electronic and thermal Enthalpies= -401.679906
Sum of electronic and thermal Free Energies= -401.721064

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	88.146	29.944	86.623

14n





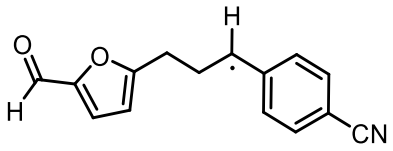
Level of theory: uM06-2X/6-311+G**

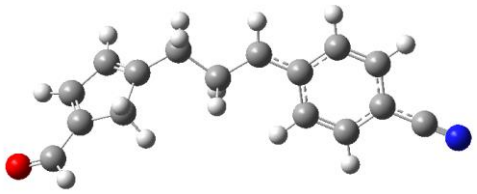
C	-4.76161	0.56479	-0.11771
C	-4.99689	-0.28257	0.90906
C	-3.88448	-1.21404	1.03244
C	-2.96061	-0.94483	0.08440
C	-3.43460	0.22413	-0.73591
C	-5.63956	1.65018	-0.55957
O	-6.70526	1.91716	-0.05661
C	-1.66866	-1.65604	-0.15871
C	-0.44398	-0.73836	-0.03977
C	0.83807	-1.47814	-0.24079
C	2.11510	-0.87781	-0.15531
C	3.29319	-1.64660	-0.36202
C	4.54356	-1.08495	-0.28415
C	4.68965	0.28167	0.00578
C	3.55485	1.06697	0.21460
C	2.29284	0.49345	0.13444
O	5.96472	0.73994	0.06084
C	6.16125	2.10780	0.35191
H	-5.87954	-0.25987	1.53521
H	-3.81523	-2.00340	1.76986
H	-3.52092	-0.04256	-1.79679
H	-2.73263	1.06573	-0.67957
H	-5.26440	2.24383	-1.41781
H	-1.57330	-2.48114	0.55259
H	-1.67603	-2.09813	-1.16242
H	-0.52568	0.07597	-0.77363
H	-0.45703	-0.25252	0.94598
H	0.78712	-2.53797	-0.46980
H	3.19367	-2.70327	-0.58622
H	5.43944	-1.67300	-0.44171
H	3.64148	2.12145	0.43995
H	1.42575	1.12181	0.30135
H	7.23719	2.26531	0.34946
H	5.69806	2.74355	-0.40899
H	5.75763	2.36340	1.33651

Zero-point correction= 0.289066 (Hartree/Particle)
Thermal correction to Energy= 0.306414
Thermal correction to Enthalpy= 0.307358
Thermal correction to Gibbs Free Energy= 0.240443
Sum of electronic and zero-point Energies= -769.878718
Sum of electronic and thermal Energies= -769.861371
Sum of electronic and thermal Enthalpies= -769.860426
Sum of electronic and thermal Free Energies= -769.927341

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	192.278	64.950	140.835

14j





Level of theory: uM06-2X/6-311+G**

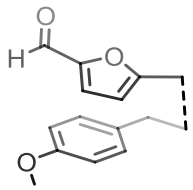
C	4.63929	0.50723	0.11109
C	4.83057	-0.35444	-0.91216
C	3.68274	-1.24577	-1.01410
C	2.78232	-0.93572	-0.05698
C	3.30967	0.21941	0.75040
C	5.56363	1.56324	0.53410
O	6.63023	1.78459	0.01300
C	1.46819	-1.59874	0.20555
C	0.27522	-0.64553	0.04820
C	-1.03180	-1.32999	0.27659
C	-2.28914	-0.70089	0.15570
C	-3.48201	-1.43305	0.39504
C	-4.71958	-0.84129	0.28411
C	-4.81840	0.51346	-0.07220
C	-3.65599	1.25971	-0.31421
C	-2.41640	0.66657	-0.20301
C	-6.10408	1.13257	-0.18819
N	-7.13805	1.63079	-0.28127
H	5.70515	-0.36881	-1.54960
H	3.57607	-2.03816	-1.74388
H	3.40429	-0.04649	1.81085
H	2.64079	1.08809	0.70249
H	5.22379	2.17655	1.39294
H	1.34882	-2.44333	-0.47866
H	1.45787	-2.00648	1.22346
H	0.37965	0.19424	0.74891
H	0.30086	-0.20067	-0.95566
H	-1.01665	-2.37858	0.55797
H	-3.40764	-2.47912	0.67010
H	-5.62232	-1.41005	0.46892
H	-3.74346	2.30367	-0.58878
H	-1.52812	1.25633	-0.39378

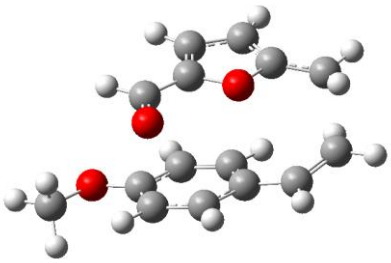
Zero-point correction= 0.254890 (Hartree/Particle)
Thermal correction to Energy= 0.271485
Thermal correction to Enthalpy= 0.272429
Thermal correction to Gibbs Free Energy= 0.206957
Sum of electronic and zero-point Energies= -747.640552
Sum of electronic and thermal Energies= -747.623957
Sum of electronic and thermal Enthalpies= -747.623013
Sum of electronic and thermal Free Energies= -747.688485

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	170.359	61.812	137.797

Transition state optimizations

TS 3 – 7n





Level of theory: uM06-2X/6-311+G**

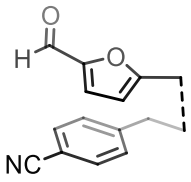
C	-0.57331	1.75790	0.22973
C	-0.66656	1.55678	1.58771
C	-1.87545	0.87522	1.81073
C	-2.46224	0.69876	0.56137
O	-1.66572	1.24691	-0.39105
C	0.48244	2.37189	-0.54860
O	0.49401	2.49028	-1.75241
C	-3.59489	-0.01486	0.12602
C	-2.78206	-1.99944	-0.44785
C	-1.65836	-1.75367	-1.18920
C	-0.33423	-1.49915	-0.65221
C	0.02103	-1.77144	0.68408
C	1.26831	-1.44673	1.17353
C	2.21448	-0.83261	0.34346
C	1.89689	-0.57096	-0.98928
C	0.63639	-0.90565	-1.46789
H	1.32083	2.73395	0.07827
H	0.06920	1.85951	2.31683
H	-2.28699	0.54044	2.74925
H	-4.29810	-0.34969	0.87747
H	-3.98582	0.20953	-0.85667
H	-2.70714	-2.28459	0.59500
H	-3.69810	-2.28842	-0.94881
H	-1.76968	-1.60612	-2.25958
H	0.38487	-0.65890	-2.49364
H	-0.69245	-2.24519	1.34787
H	1.54299	-1.65191	2.20109
H	2.60003	-0.08646	-1.65296
O	3.40254	-0.52751	0.92241
C	4.38306	0.09684	0.11792
H	4.66938	-0.54308	-0.72204
H	4.02719	1.05919	-0.26320
H	5.24422	0.25692	0.76238

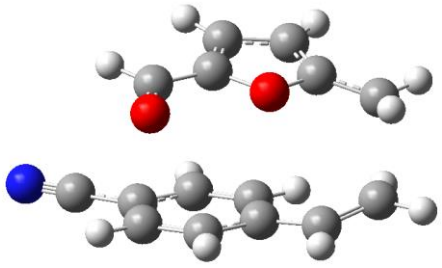
υ_{imag} = -545.37 cm^{-1}

Zero-point correction= 0.263768 (Hartree/Particle)
Thermal correction to Energy= 0.280102
Thermal correction to Enthalpy= 0.281046
Thermal correction to Gibbs Free Energy= 0.218548
Sum of electronic and zero-point Energies= -805.800117
Sum of electronic and thermal Energies= -805.783784
Sum of electronic and thermal Enthalpies= -805.782839
Sum of electronic and thermal Free Energies= -805.845337

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	175.766	62.792	131.538

TS 3 – 7j





Level of theory: uM06-2X/6-311+G**

C	0.47722	1.76205	-0.22764
C	0.43007	1.55939	-1.58678
C	1.58523	0.82839	-1.92217
C	2.28256	0.63114	-0.73528
O	1.60077	1.20677	0.28735
C	-0.46724	2.41750	0.66160
O	-0.33625	2.50984	1.85913
C	3.43341	-0.10967	-0.40501
C	2.63506	-2.05582	0.33131
C	1.58942	-1.74673	1.15618
C	0.23252	-1.47497	0.71544
C	-0.22109	-1.78091	-0.58072
C	-1.49602	-1.43758	-0.98865
C	-2.35751	-0.77668	-0.10544
C	-1.93375	-0.48245	1.19471
C	-0.65720	-0.83315	1.59445
C	-3.66750	-0.38840	-0.54232
H	-1.35006	2.82885	0.13724
H	-0.35681	1.89680	-2.24381
H	1.89306	0.48214	-2.89573
H	4.04158	-0.48665	-1.21694
H	3.93143	0.12051	0.52656
H	2.46598	-2.38096	-0.68814
H	3.58769	-2.33907	0.76213
H	1.79343	-1.55829	2.20569
H	-0.31865	-0.56638	2.58911
H	0.43094	-2.29185	-1.27803
H	-1.83556	-1.67113	-1.99027
H	-2.59788	0.03827	1.87354
N	-4.71320	-0.06825	-0.90161

υ_{imag} = -557.87 cm^{-1}

Zero-point correction= 0.229289 (Hartree/Particle)
Thermal correction to Energy= 0.244965
Thermal correction to Enthalpy= 0.245909
Thermal correction to Gibbs Free Energy= 0.184573
Sum of electronic and zero-point Energies= -783.561043
Sum of electronic and thermal Energies= -783.545368
Sum of electronic and thermal Enthalpies= -783.544423
Sum of electronic and thermal Free Energies= -783.605760

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	153.718	59.880	129.094

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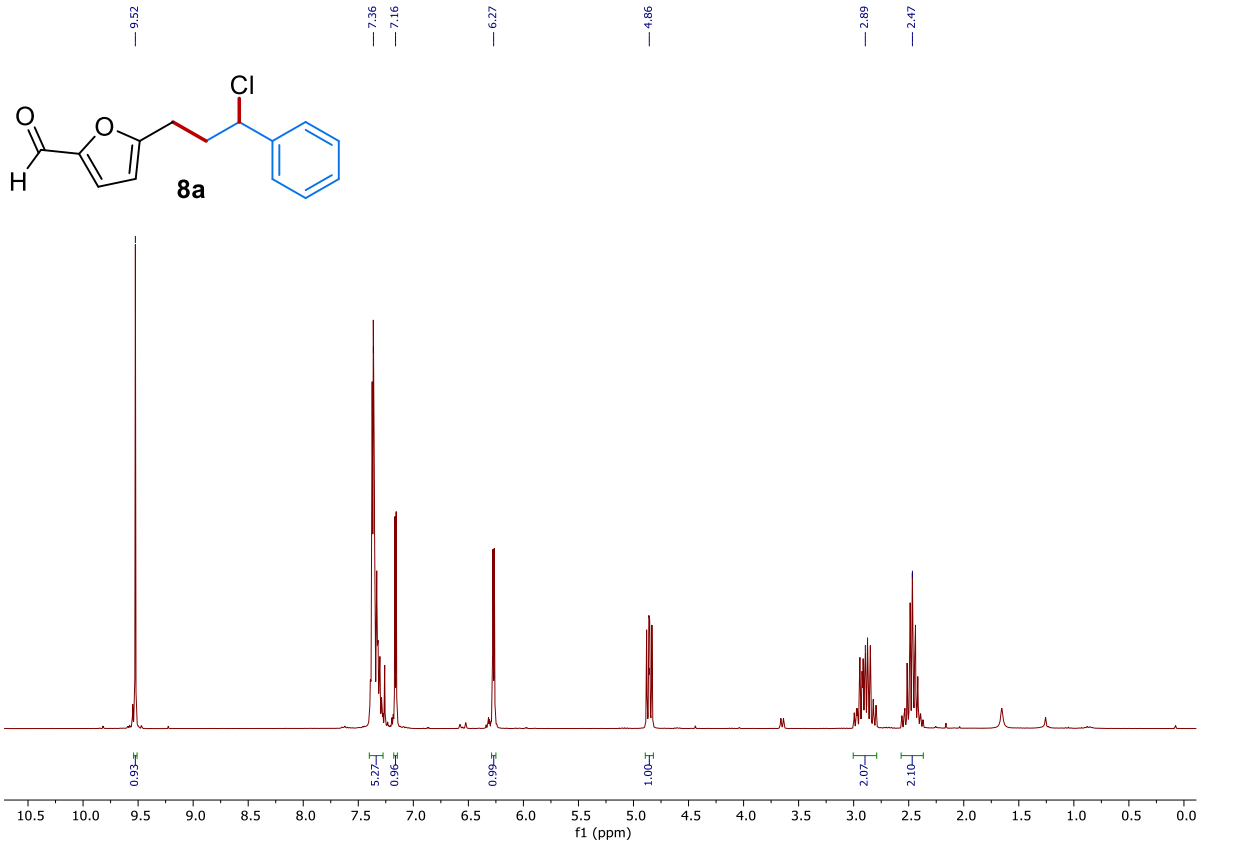
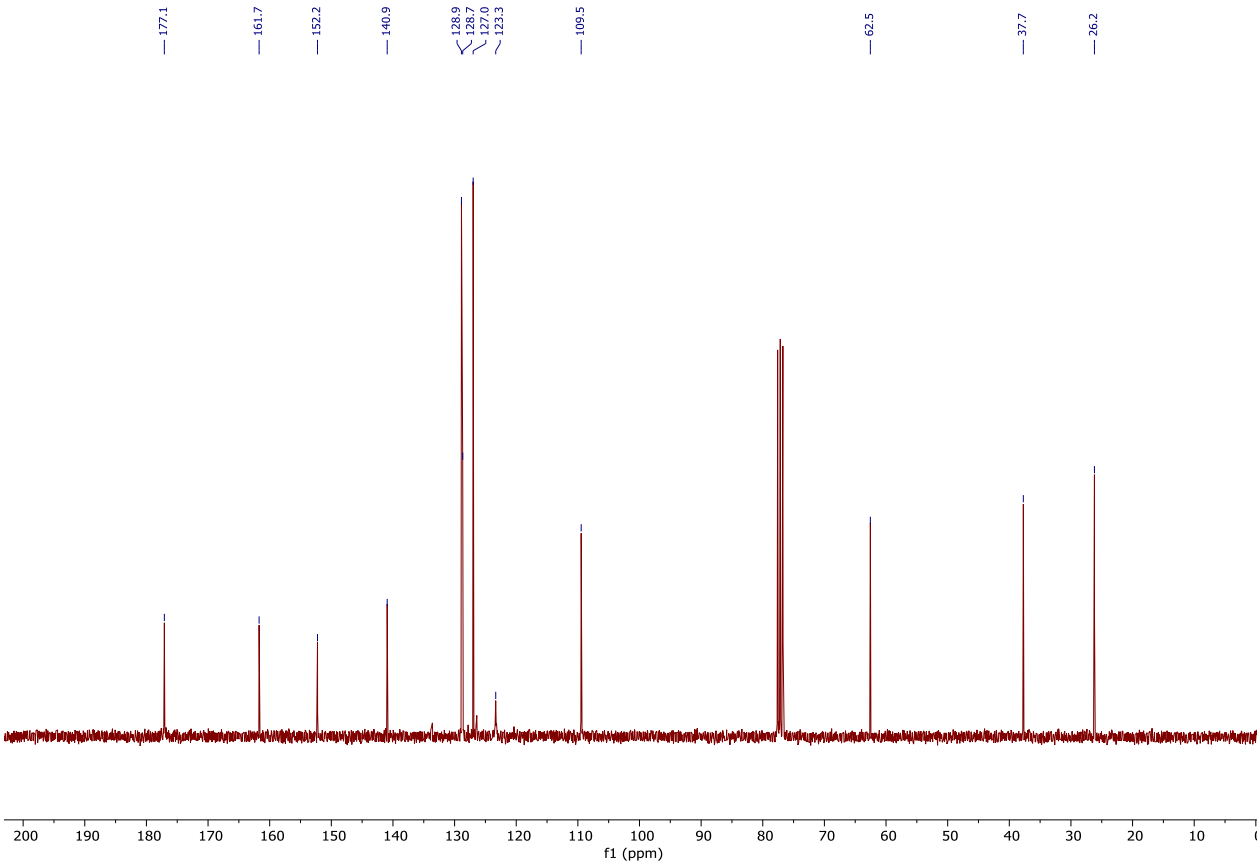
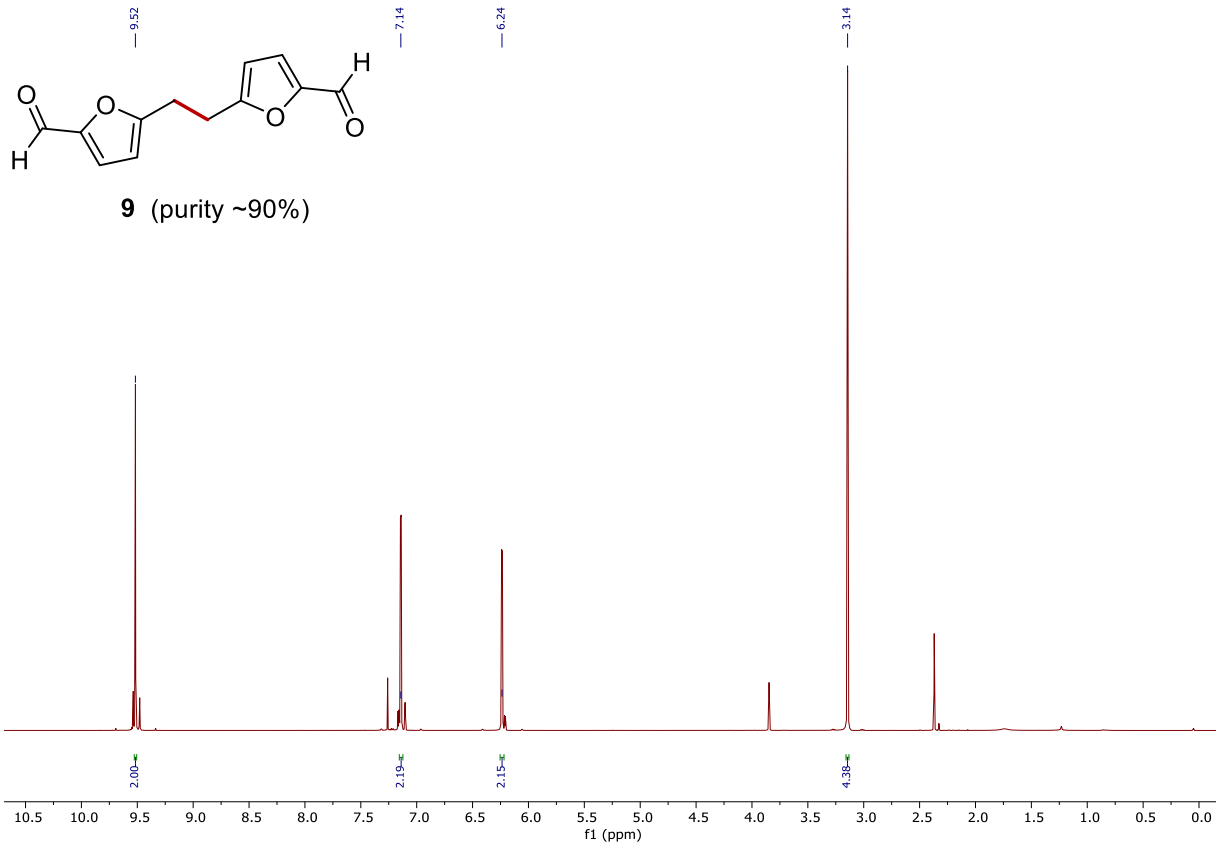
5. NMR spectra



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7.14
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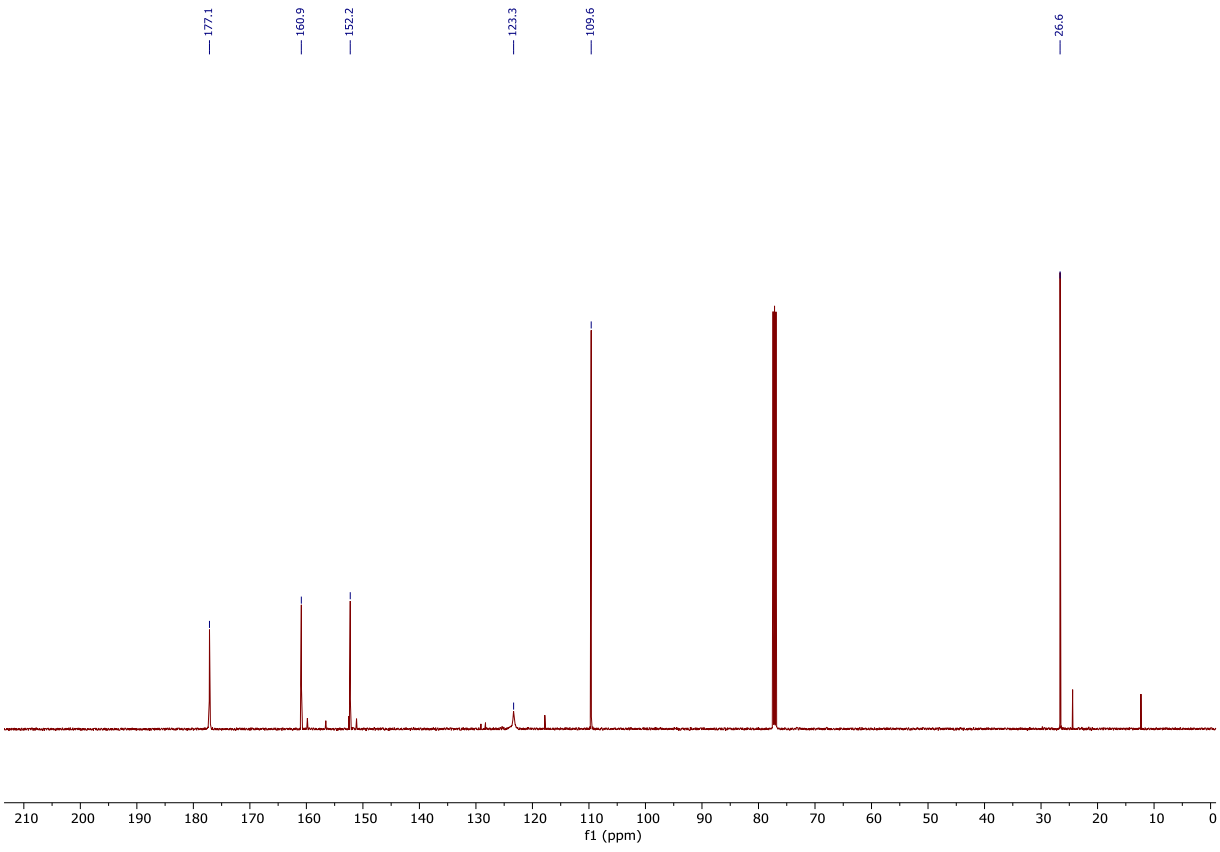
3.14
2.00
2.19
2.15
4.38
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

9 (purity ~90%)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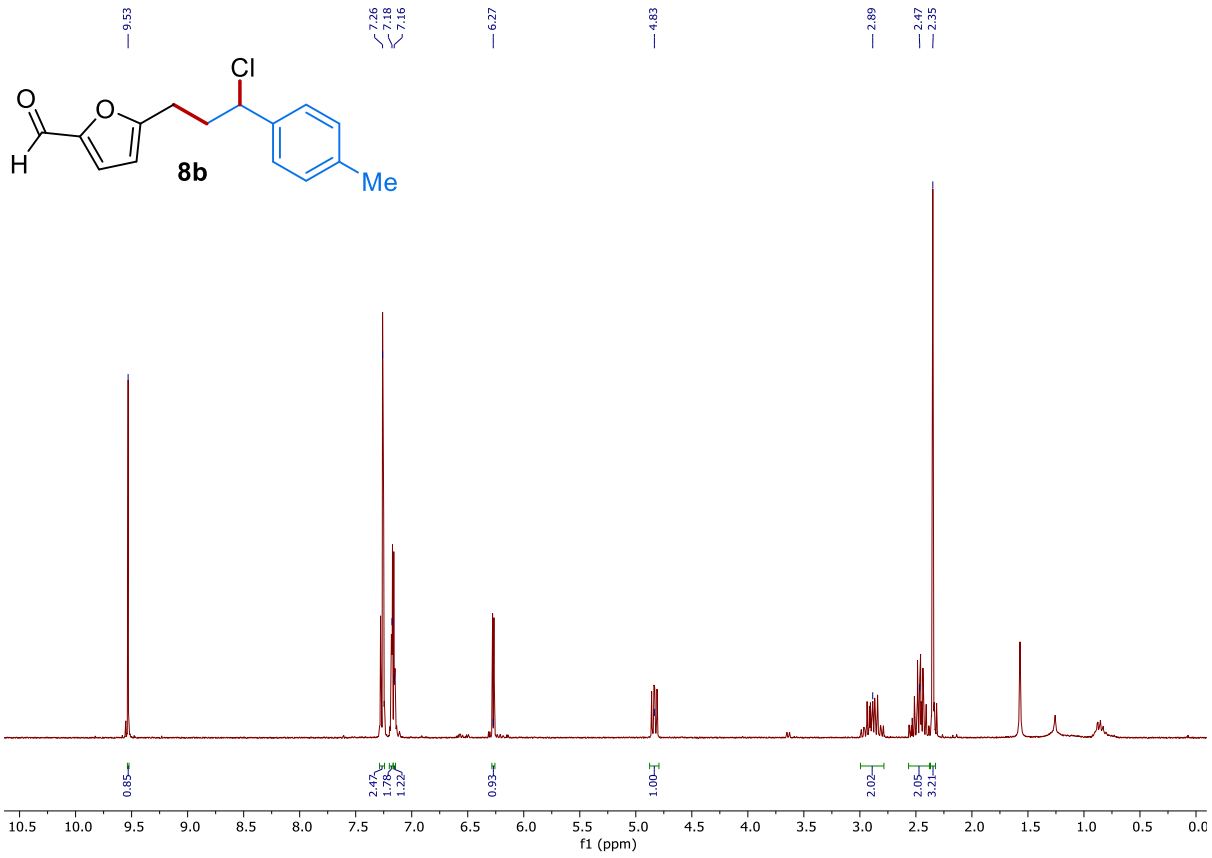
152.2
123.3
109.6
26.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.26
7.18
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6.27
4.83
2.89
2.47
2.35
Cl
O
O
H
8b
Me
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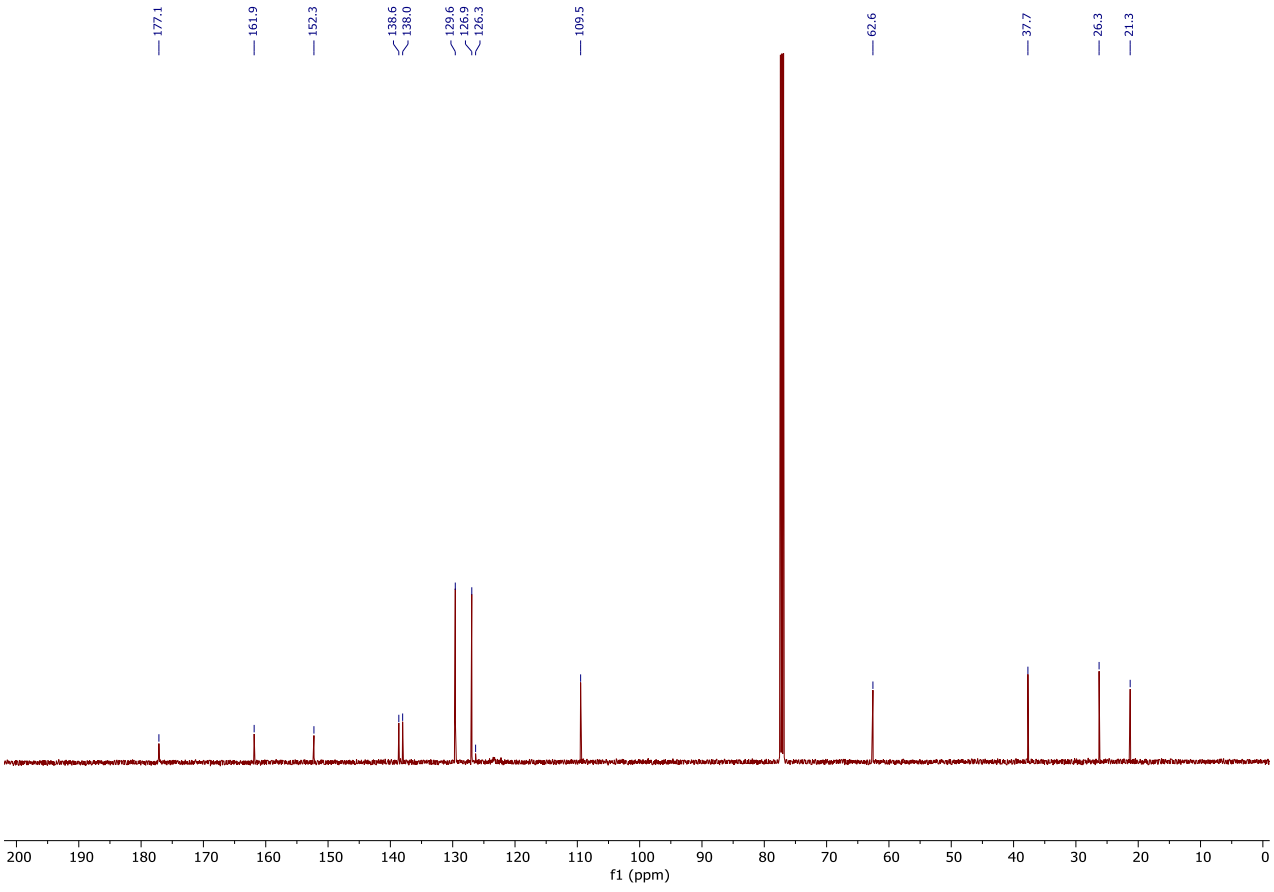
2.47
1.78
1.22
0.93
1.00
2.02
2.05
3.21
f1 (ppm)


177.1
161.9
152.3
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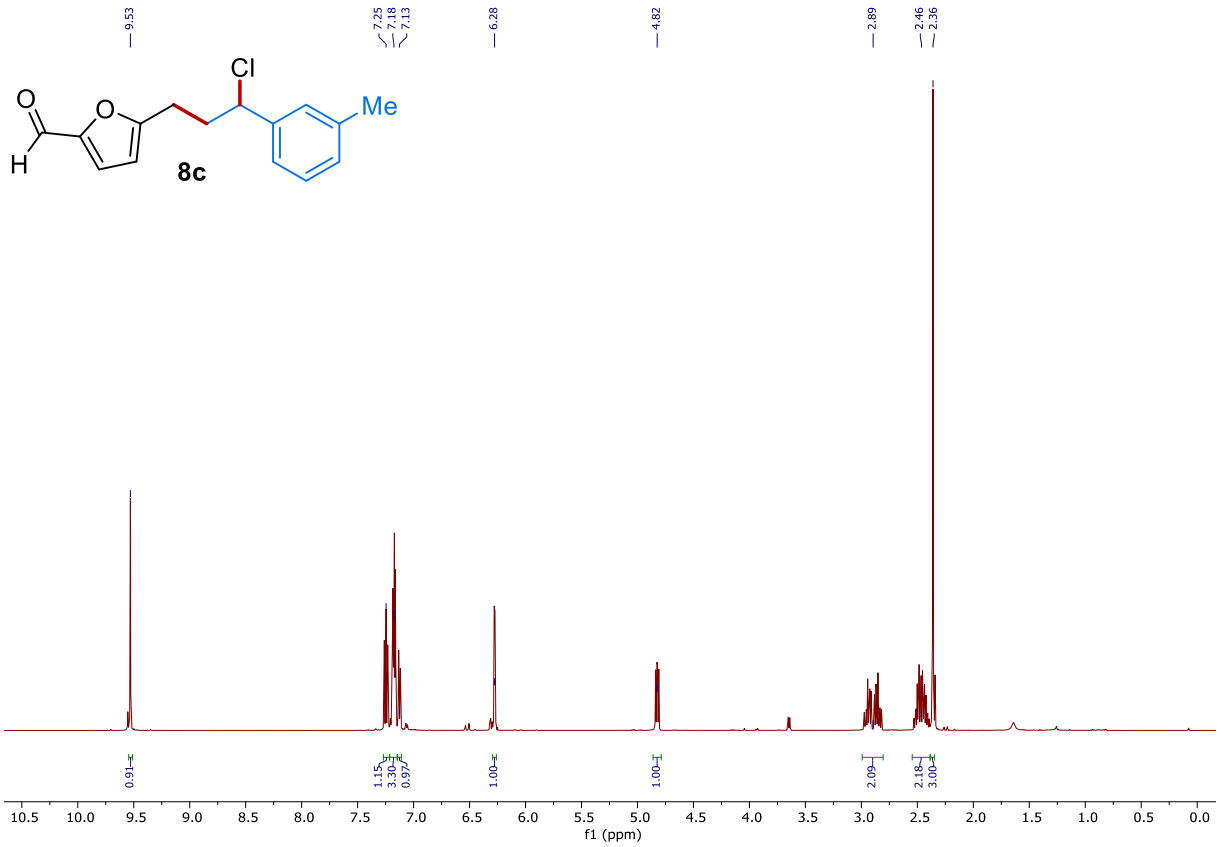
138.0
129.6
126.9
126.3
109.5
62.6
37.7
26.3
21.3
f1 (ppm)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6.28
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Cl
O
O
H
Me
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0.97
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1.00
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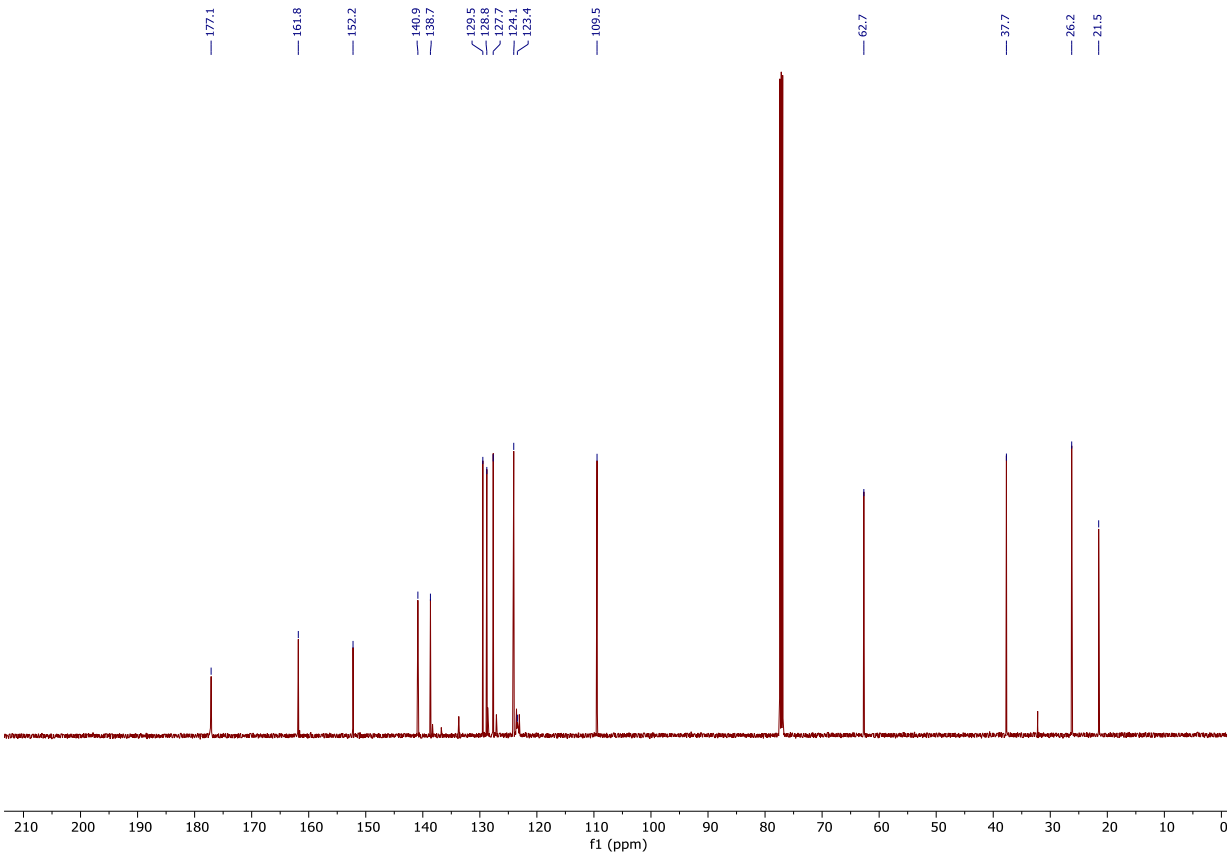
3.00
f1 (ppm)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127.7
124.1
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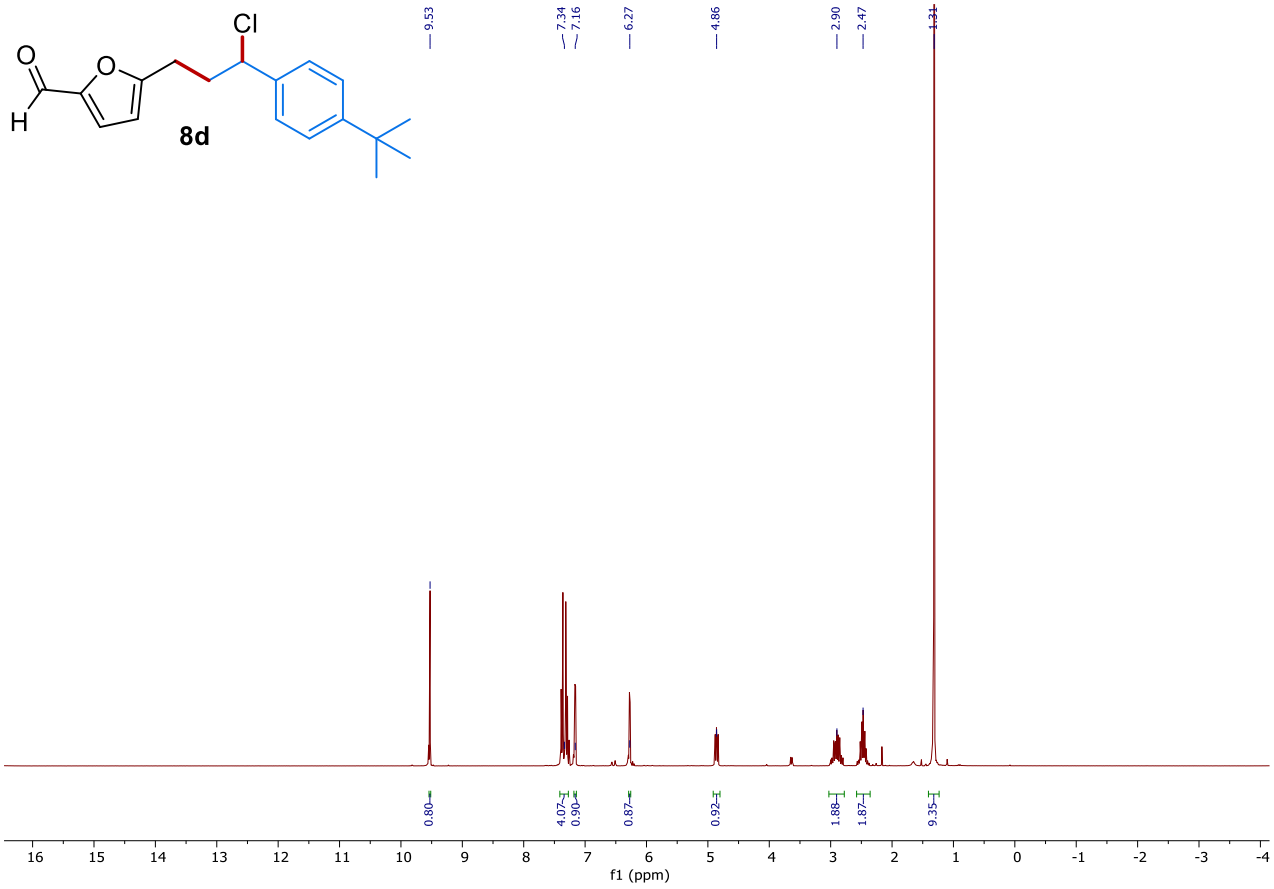
109.5
62.7
37.7
26.2
21.5
f1 (ppm)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O
O
H
8d
9.53
7.34
7.16
6.27
4.86
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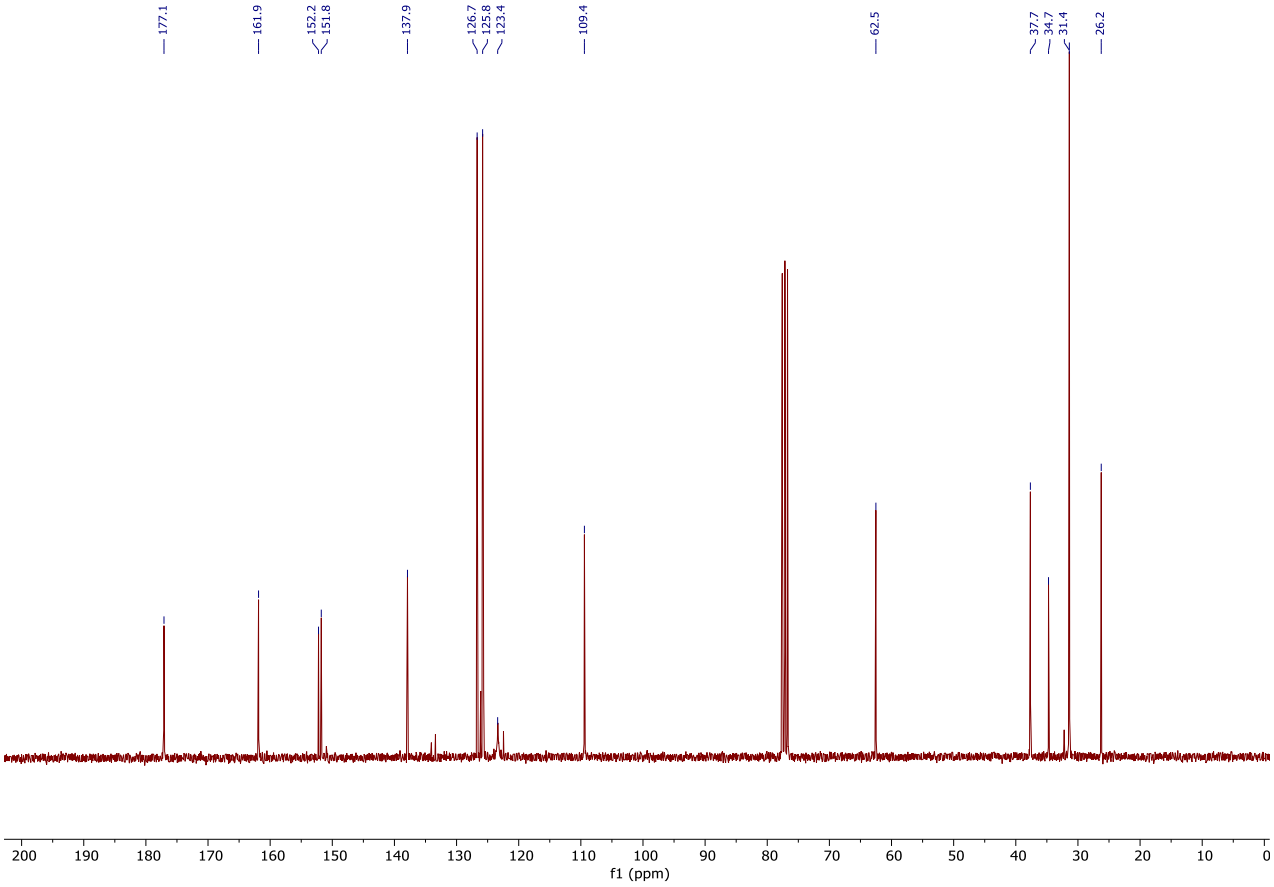
4.07
0.90
0.87
0.92
1.88
1.87
9.35
f1 (ppm)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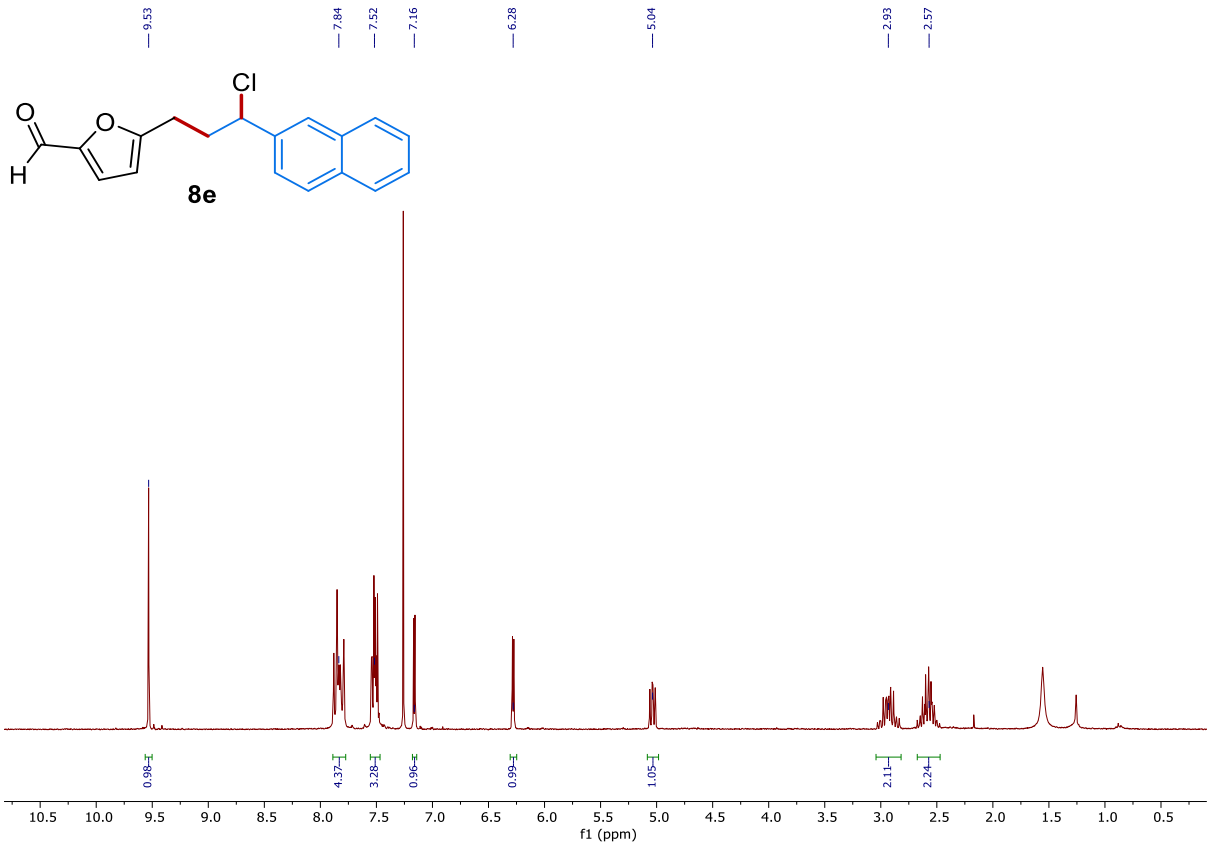
123.4
109.4
62.5
37.7
34.7
31.4
26.2
f1 (ppm)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5.04
2.93
2.57
Cl
O
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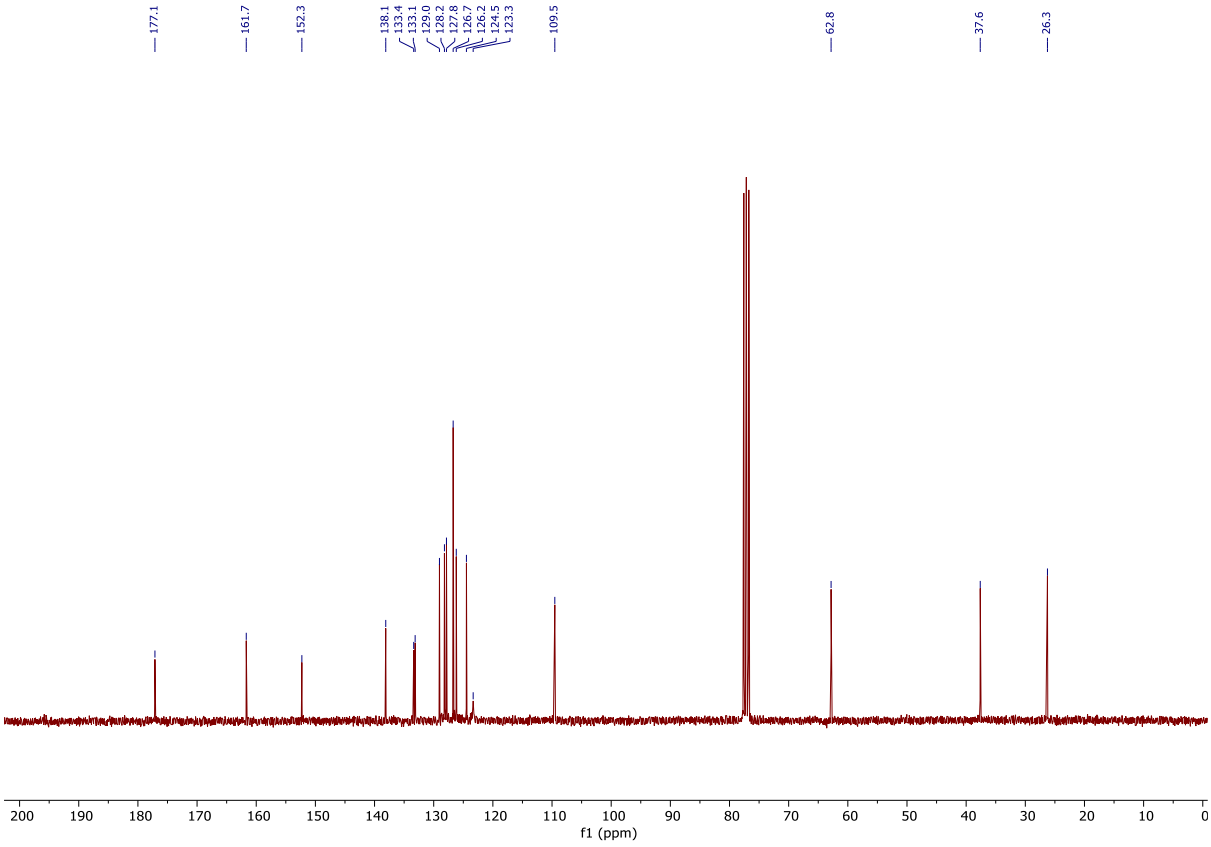
4.37
3.28
0.96
0.99
1.05
2.11
2.24
f1 (ppm)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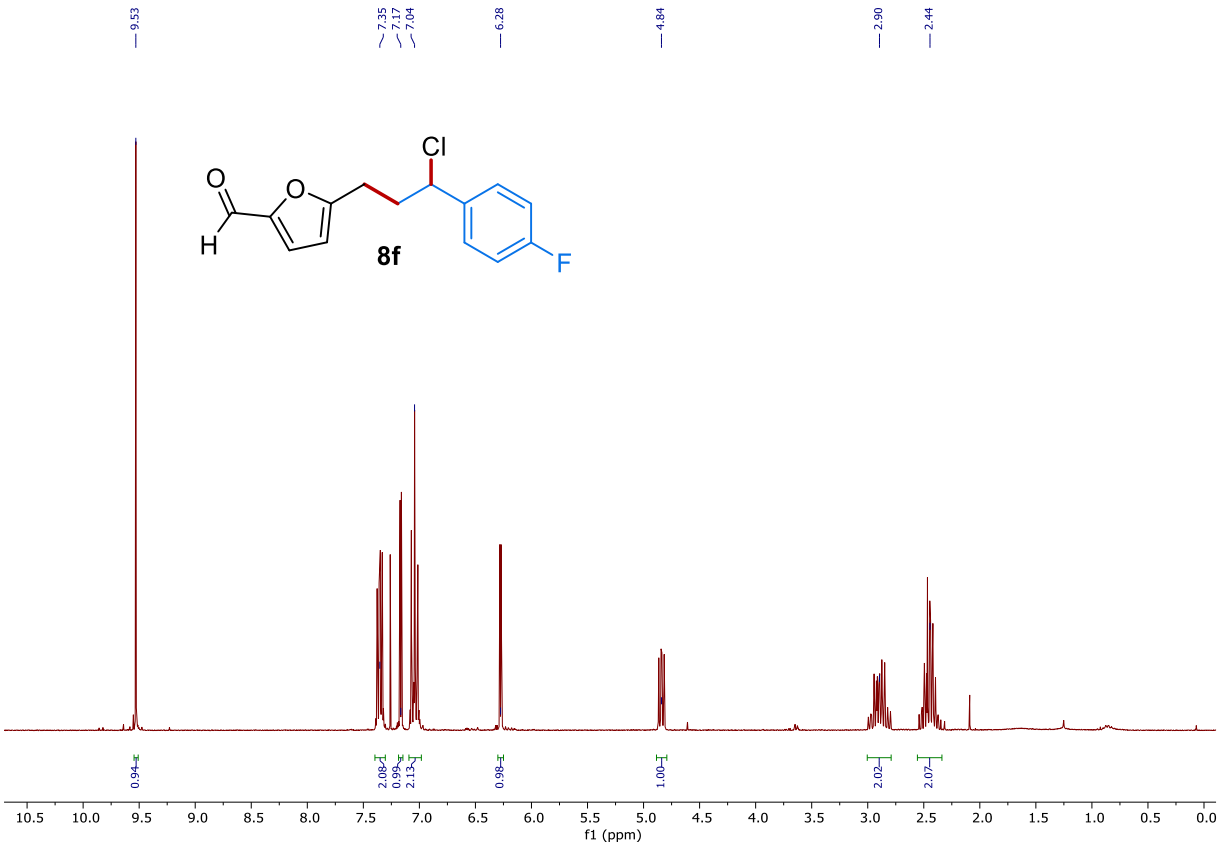
109.5
62.8
37.6
26.3
f1 (ppm)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O
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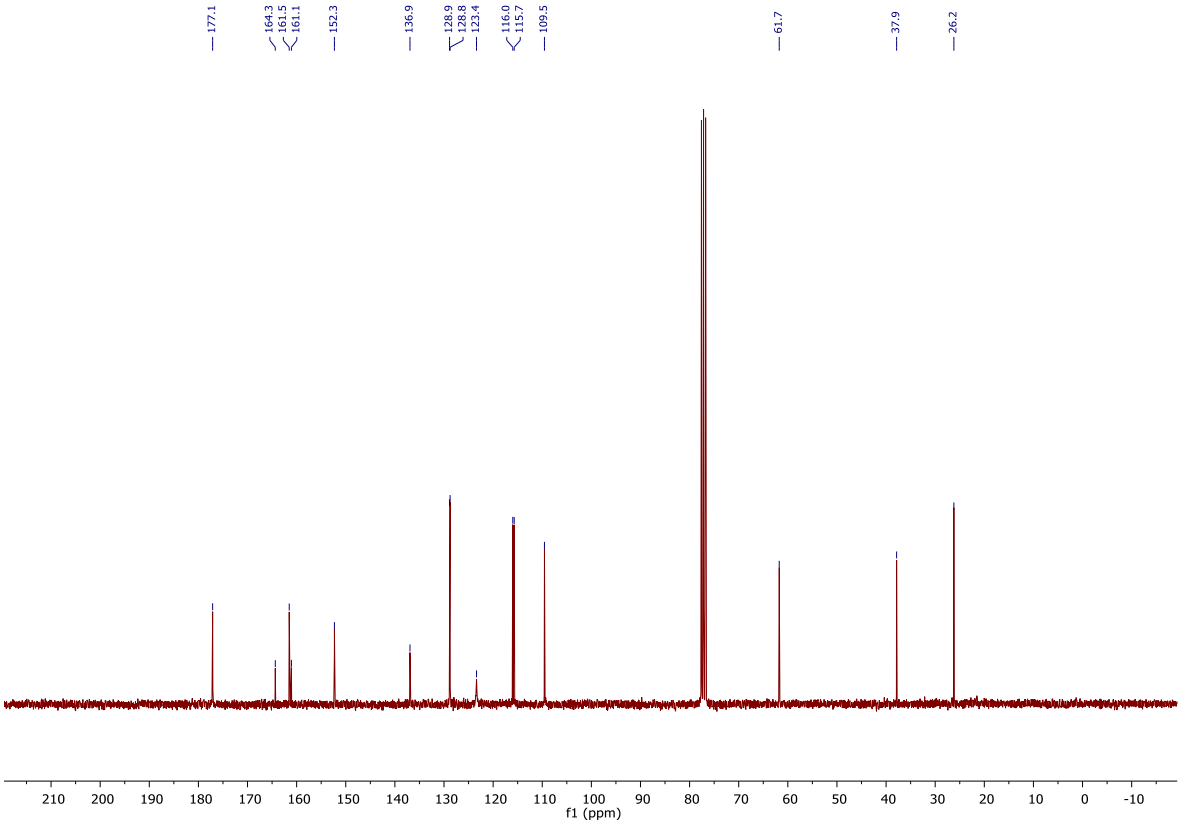
H
F
8f
0.94
2.08
0.99
2.13
0.98
1.00
2.02
2.07
f1 (ppm)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161.5
161.1
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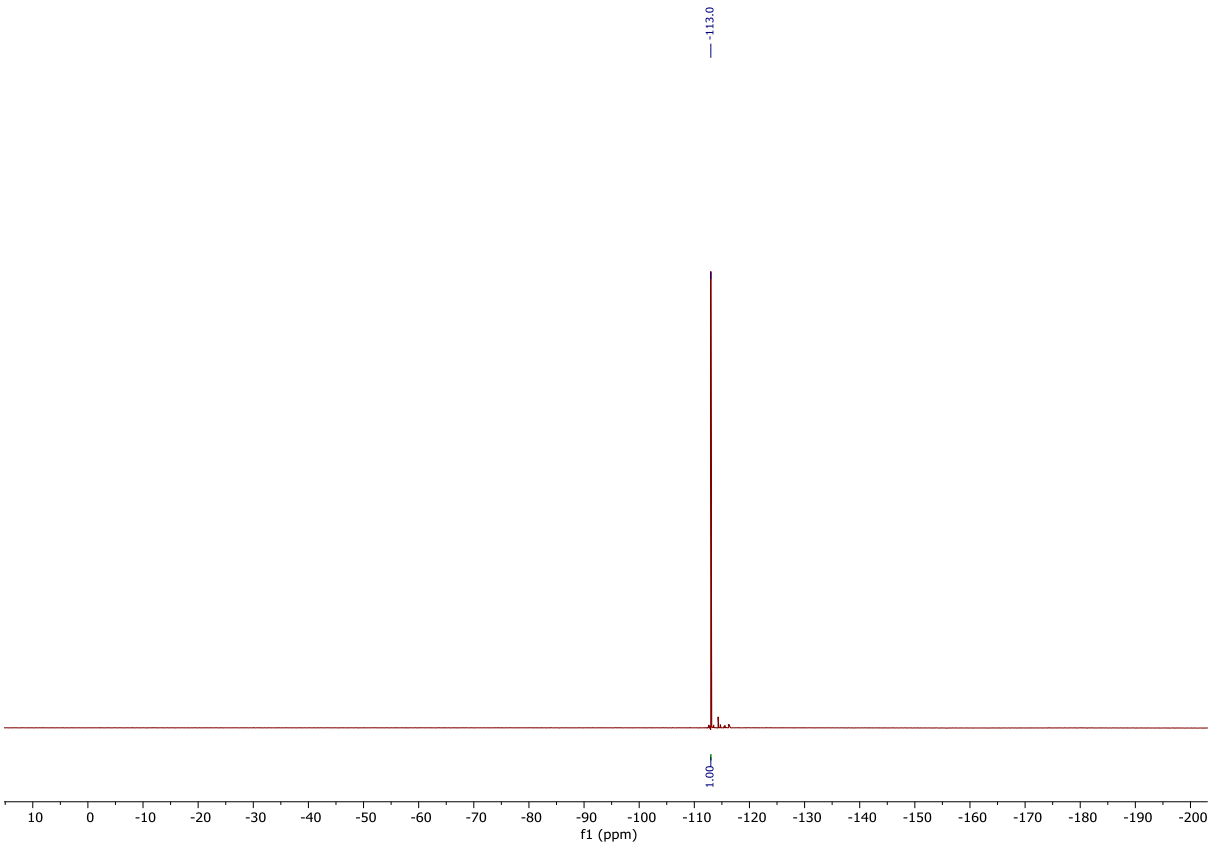
128.8
123.4
116.0
115.7
109.5
61.7
37.9
26.2
f1 (ppm)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1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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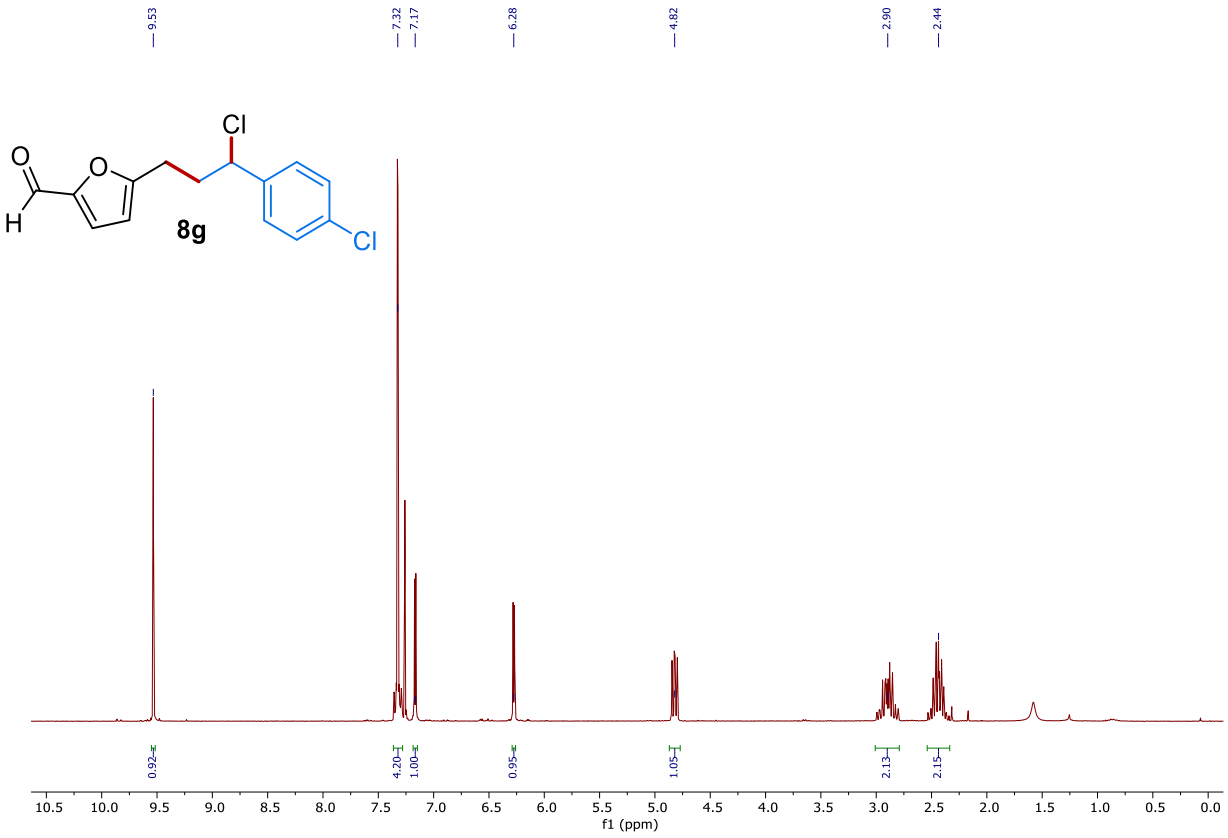
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)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7.17
6.28
4.82
2.90
2.44
O
O
H
Cl
Cl
8g
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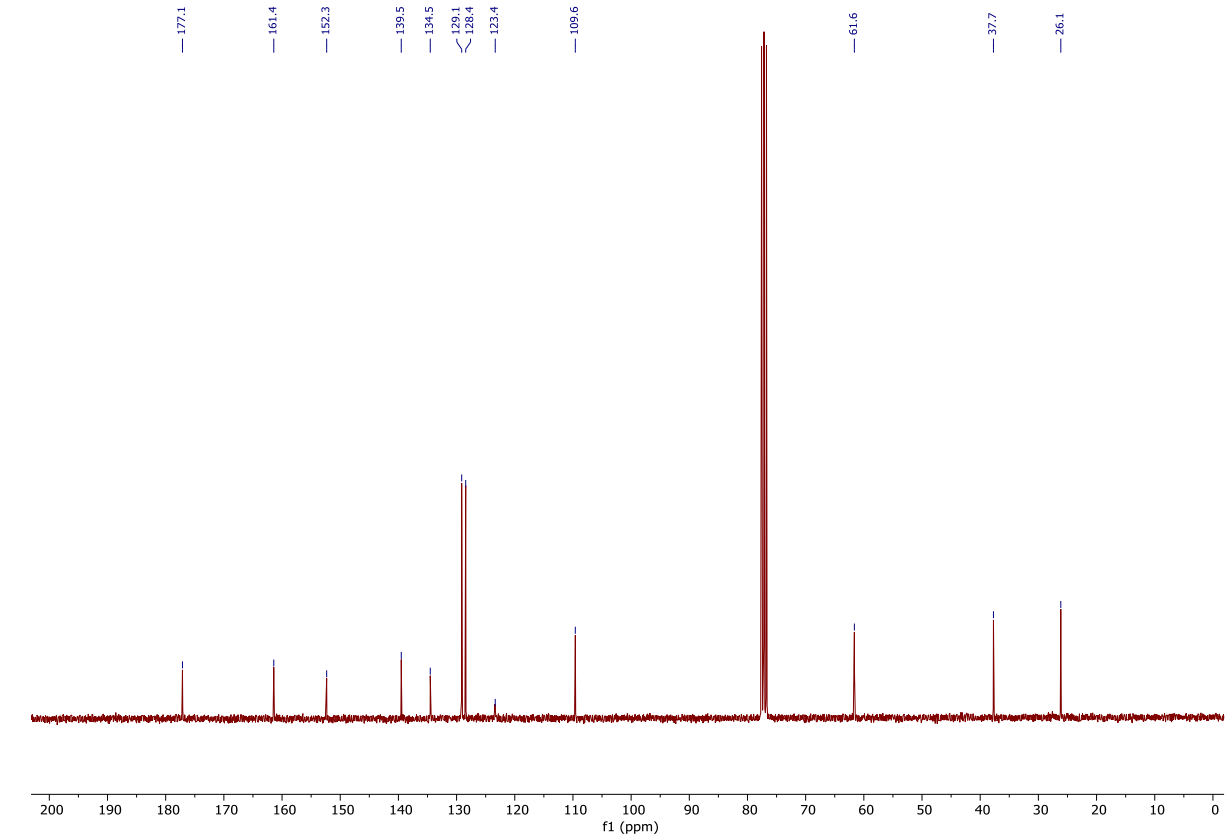
4.20
1.00
0.95
1.05
2.13
2.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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152.3
139.5
134.5
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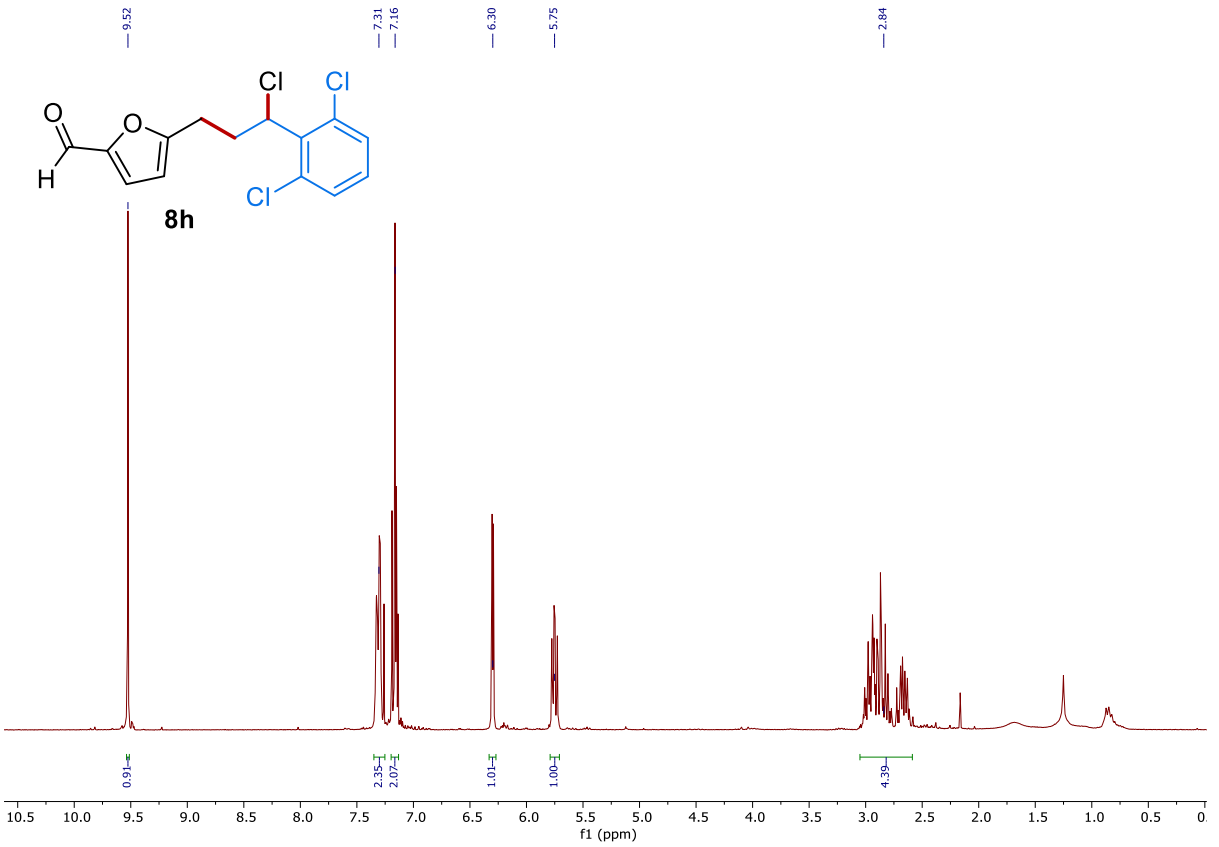
123.4
109.6
61.6
37.7
26.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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Cl
Cl
Cl
O
O
H
8h
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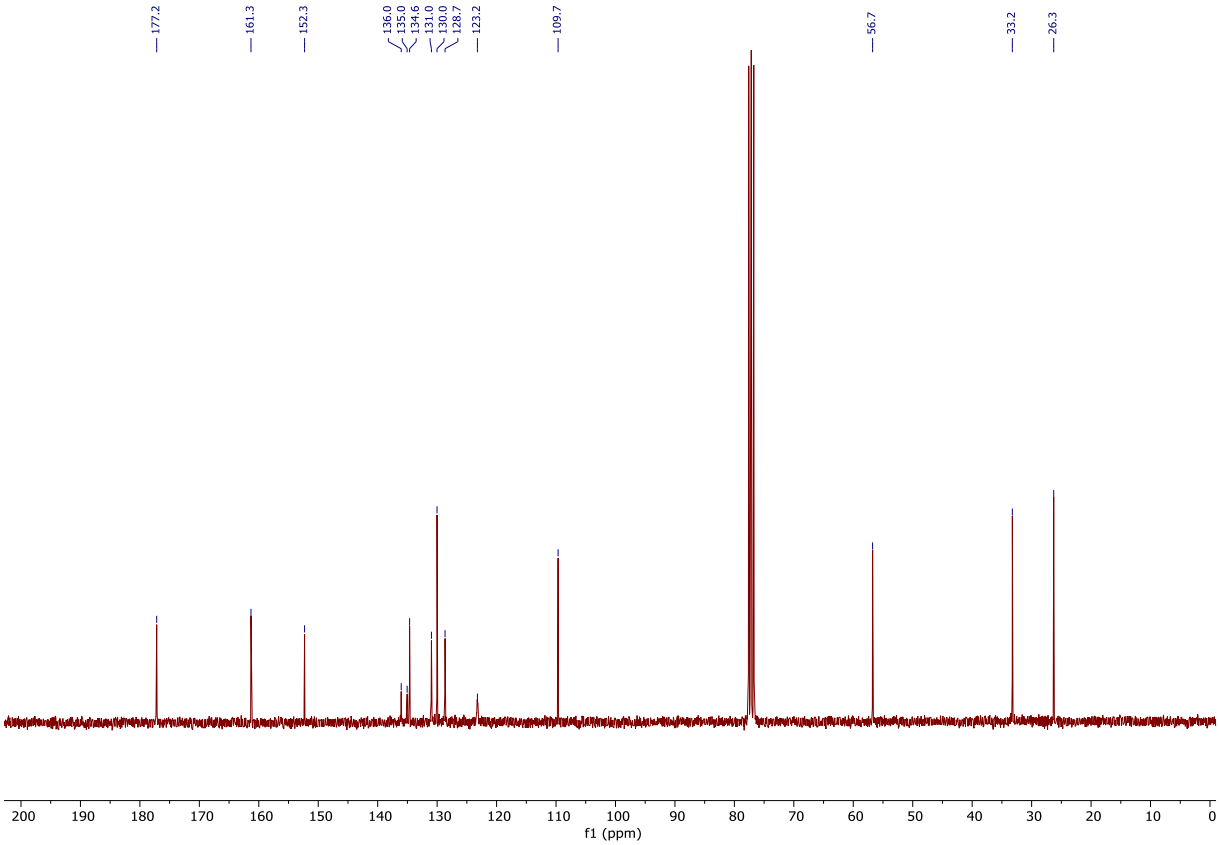
2.07
1.01
1.00
4.39
f1 (ppm)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128.7
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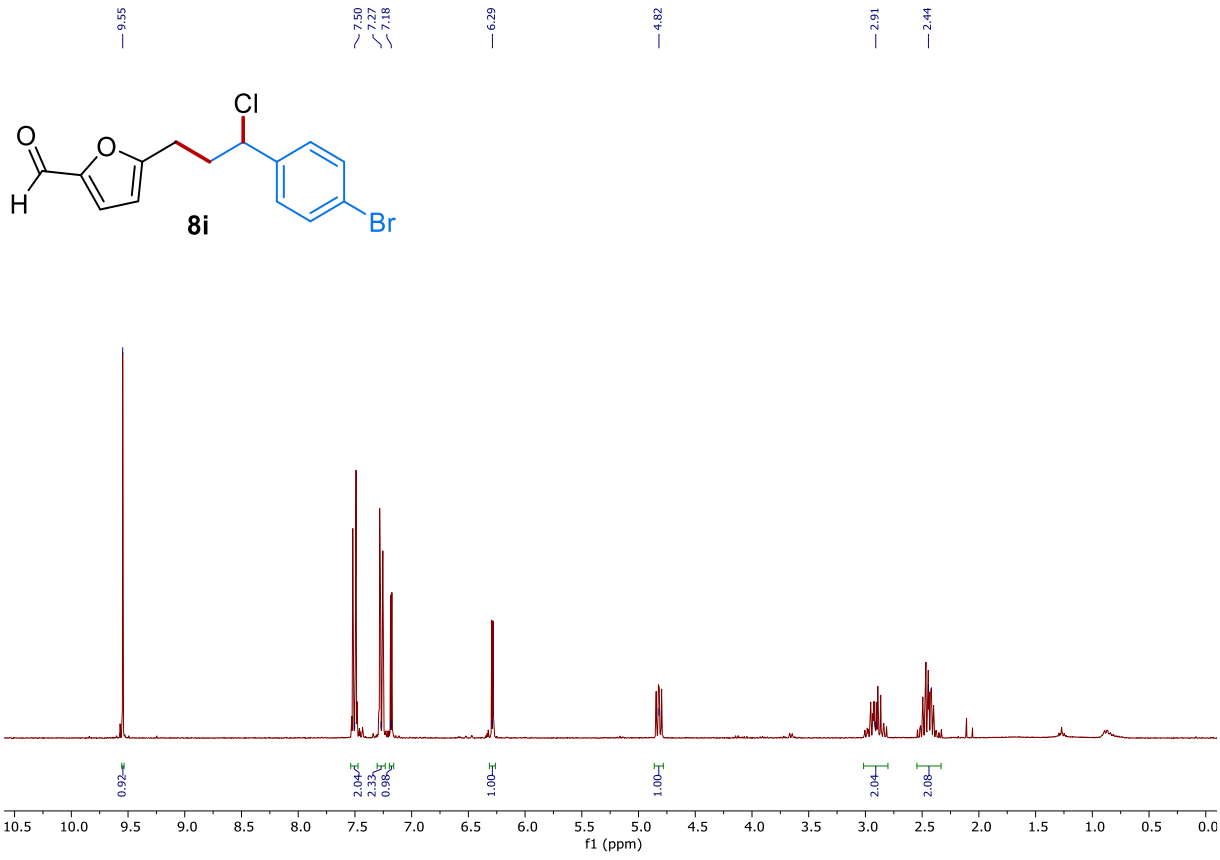
33.2
26.3
f1 (ppm)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Cl
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O
H
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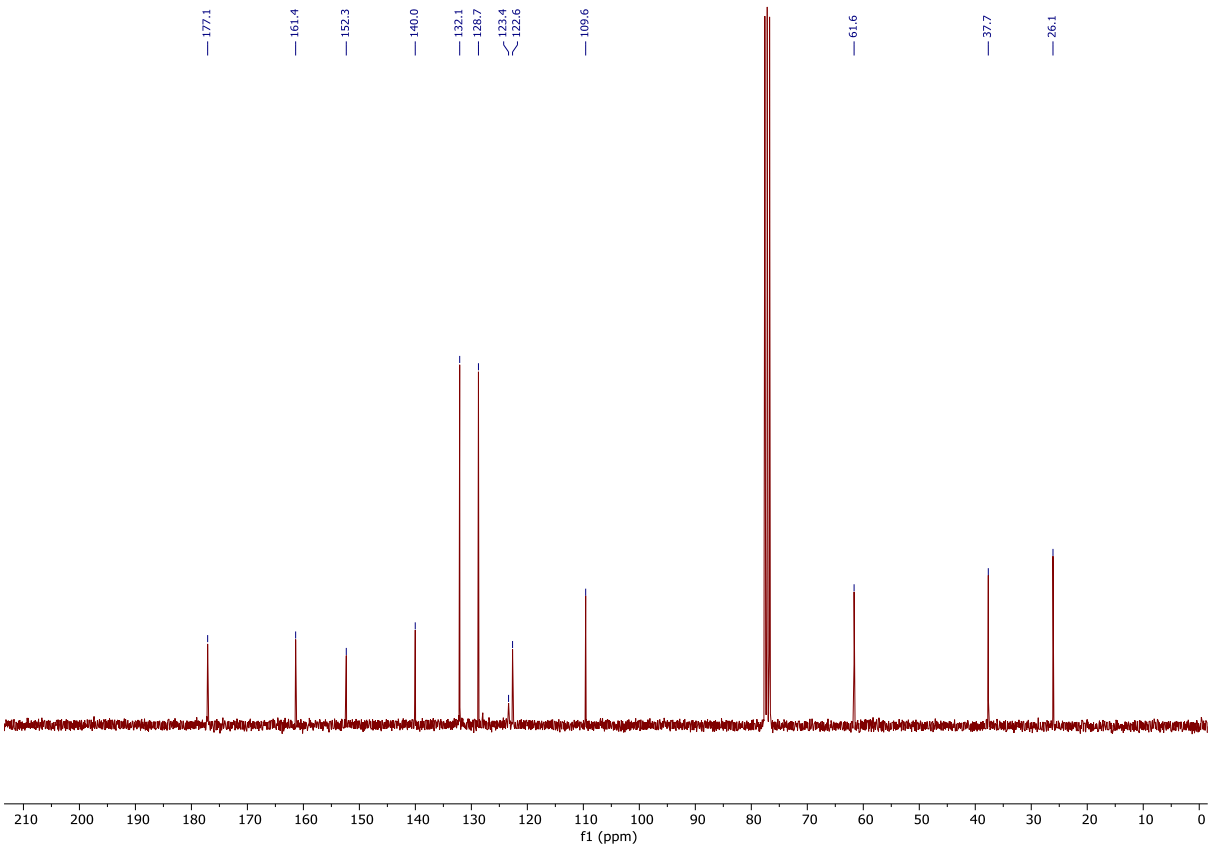
1.00
2.04
2.08
f1 (ppm)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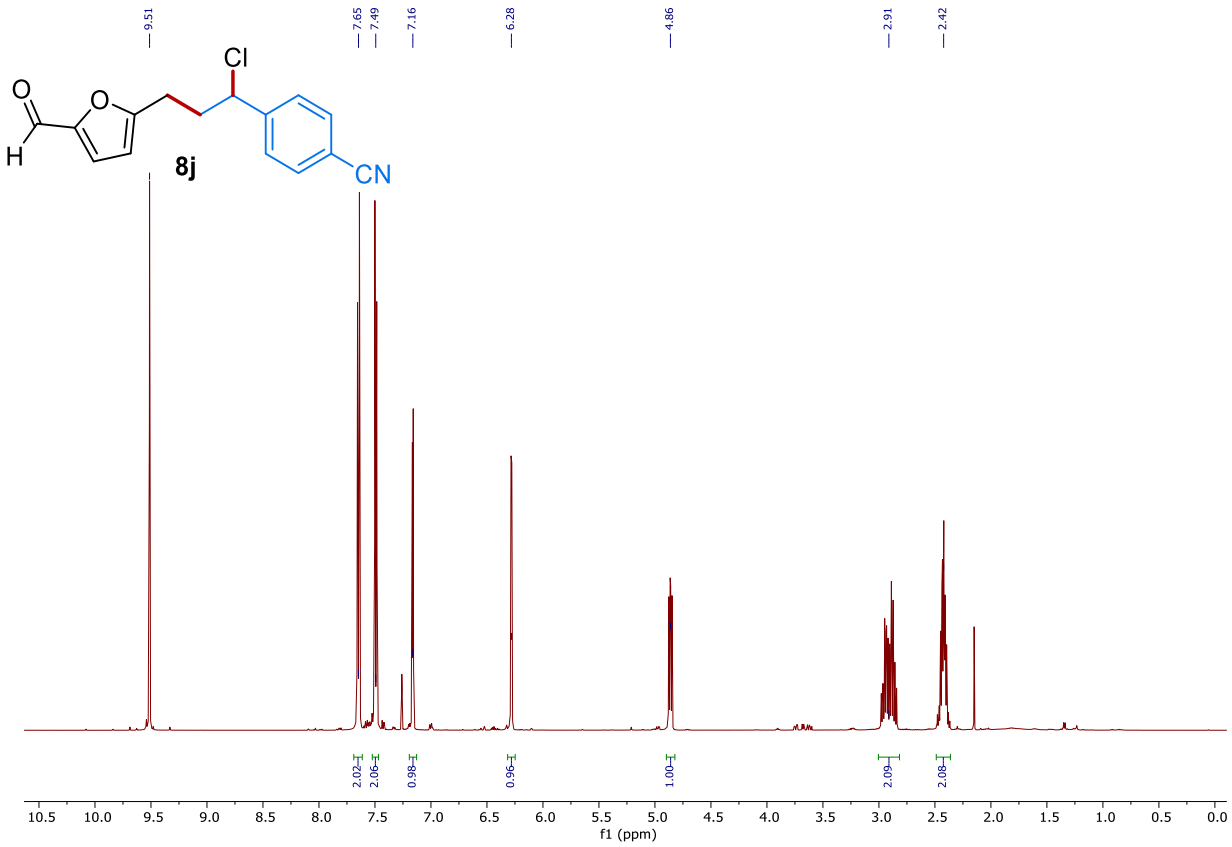
132.1
128.7
123.4
122.6
109.6
61.6
37.7
26.1
f1 (ppm)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6.28
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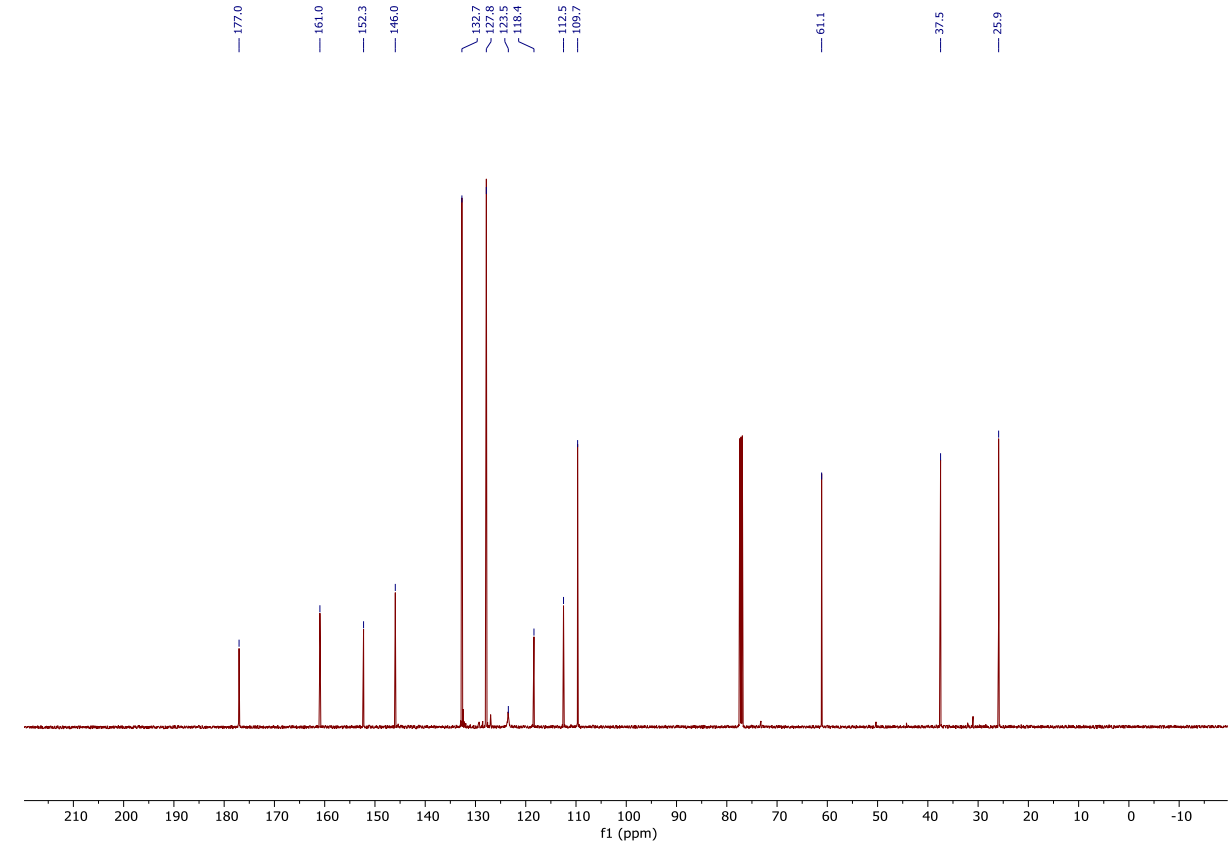
2.42
Cl
O
O
H
CN
8j
2.02
2.06
0.98
0.96
1.00
2.09
2.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.7
127.8
123.5
118.4
112.5
109.7
61.1
37.5
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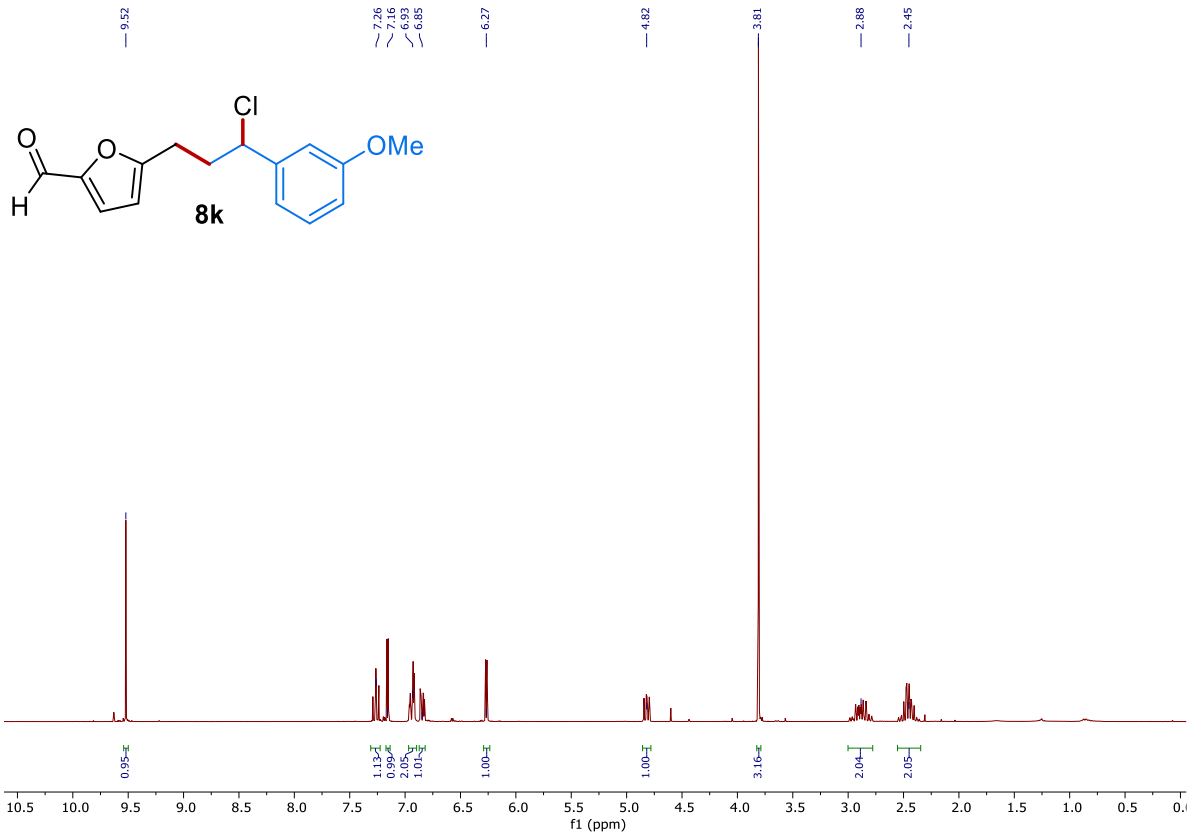
f1 (ppm)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2.45
Cl
O
O
H
OMe
8k
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0.99
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1.00
3.16
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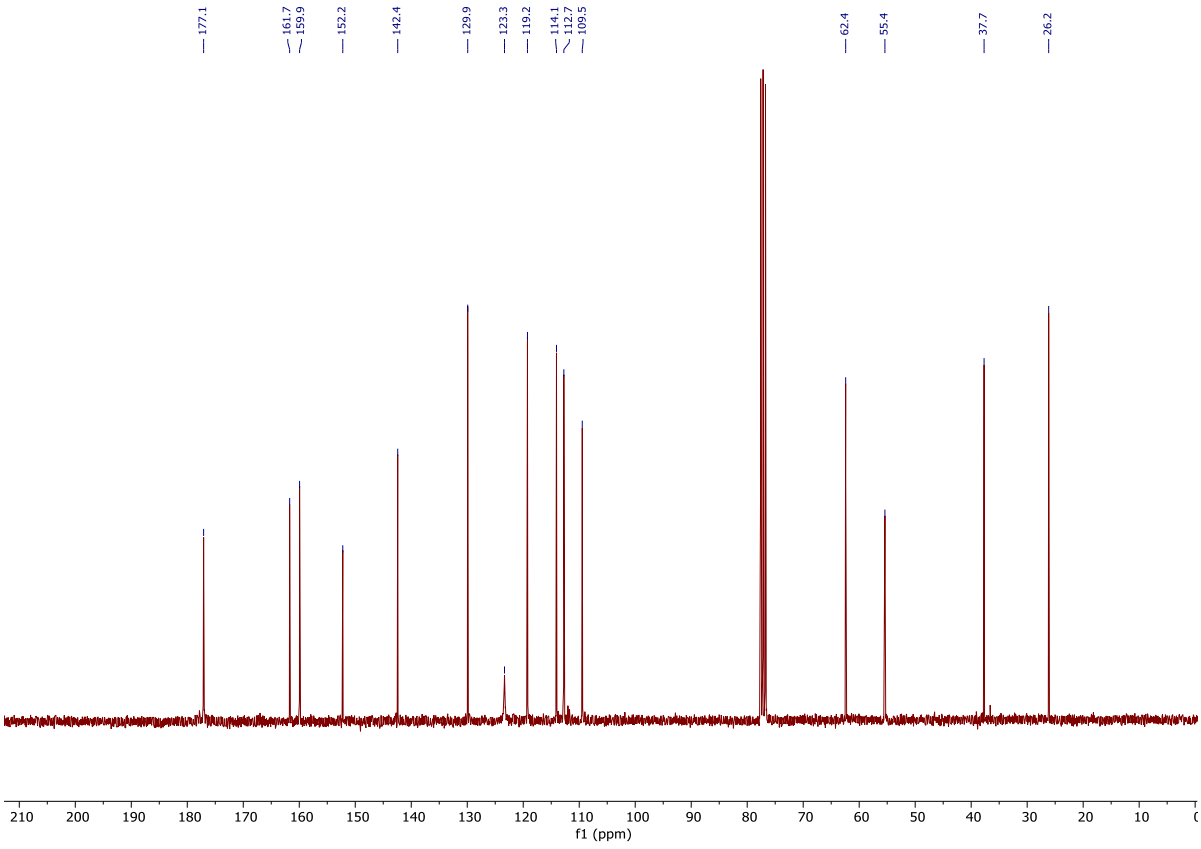
2.05
f1 (ppm)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152.2
142.4
129.9
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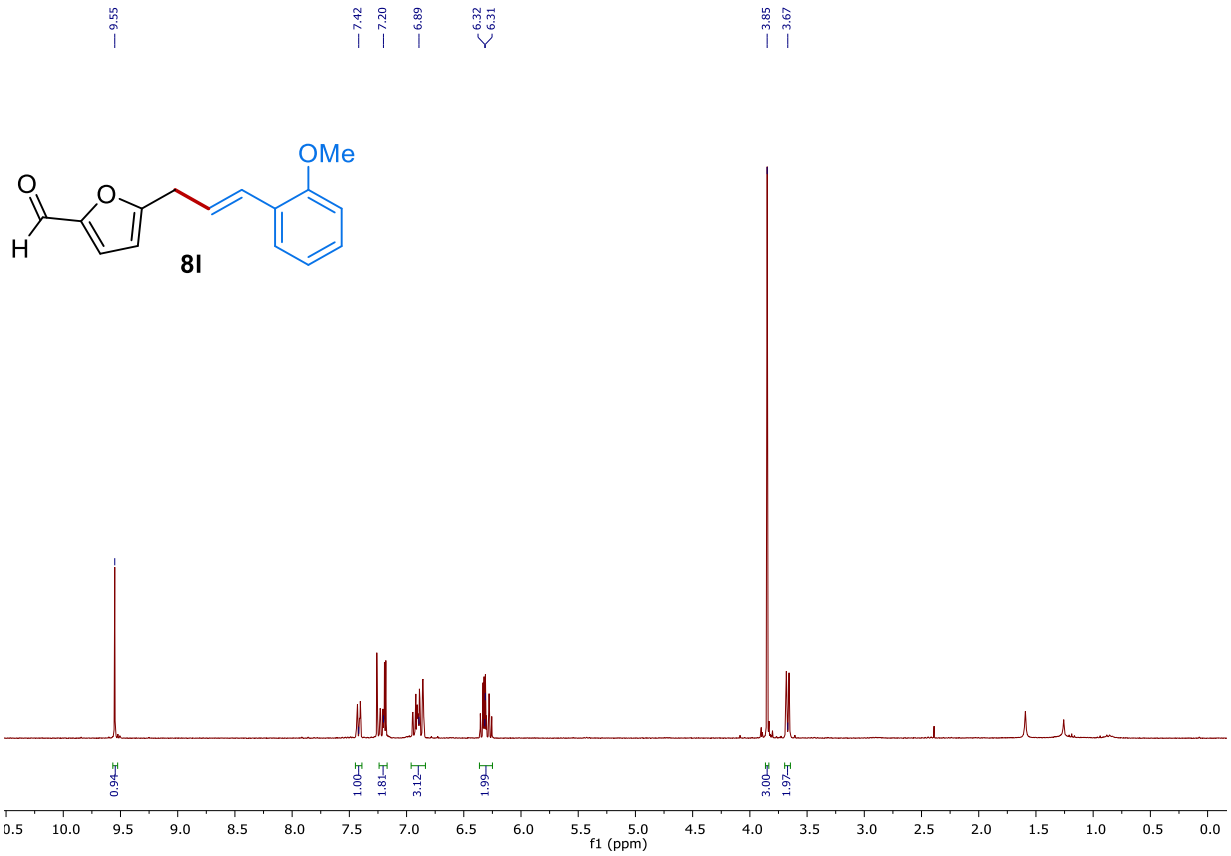
114.1
112.7
109.5
62.4
55.4
37.7
26.2
f1 (ppm)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6.32
6.31
3.85
3.67
OMe
O
O
H
8l
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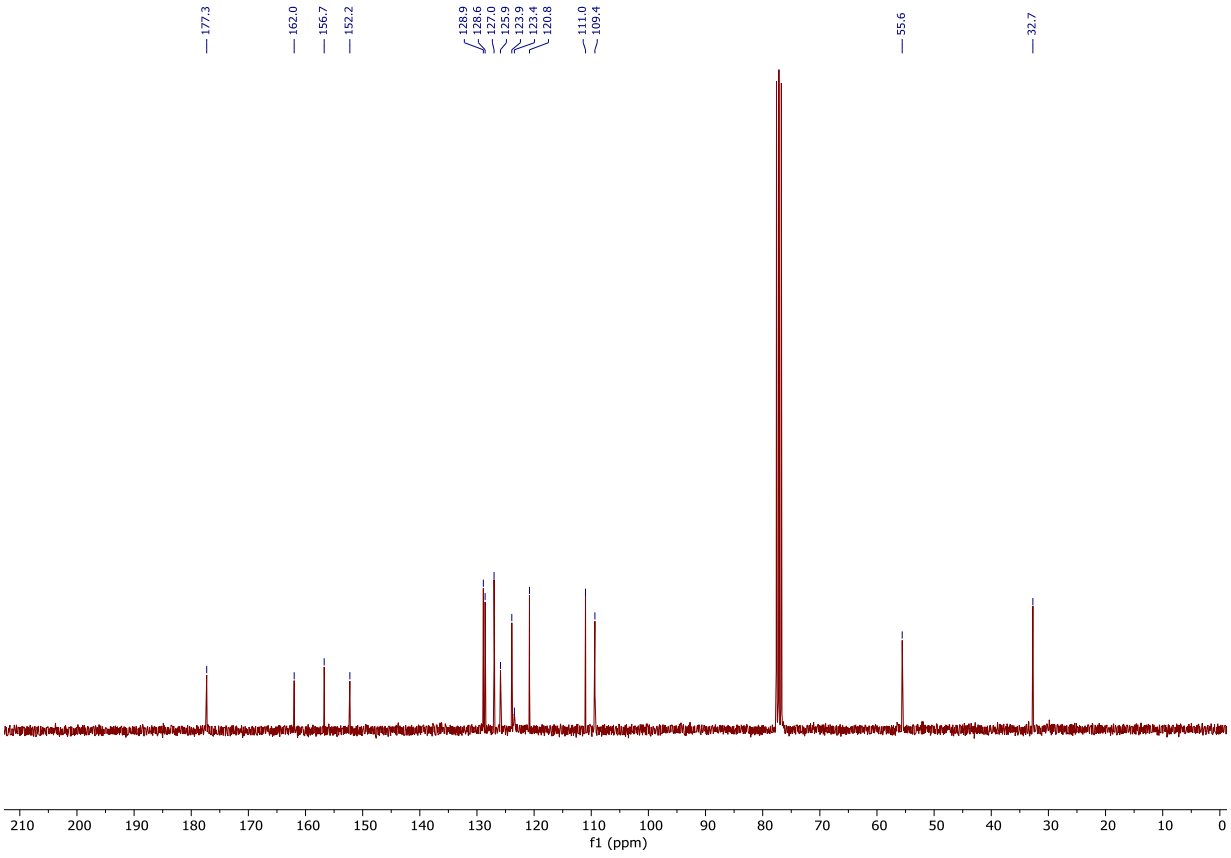
1.00
1.81
3.12
1.99
3.00
1.97
f1 (ppm)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152.2
128.9
128.6
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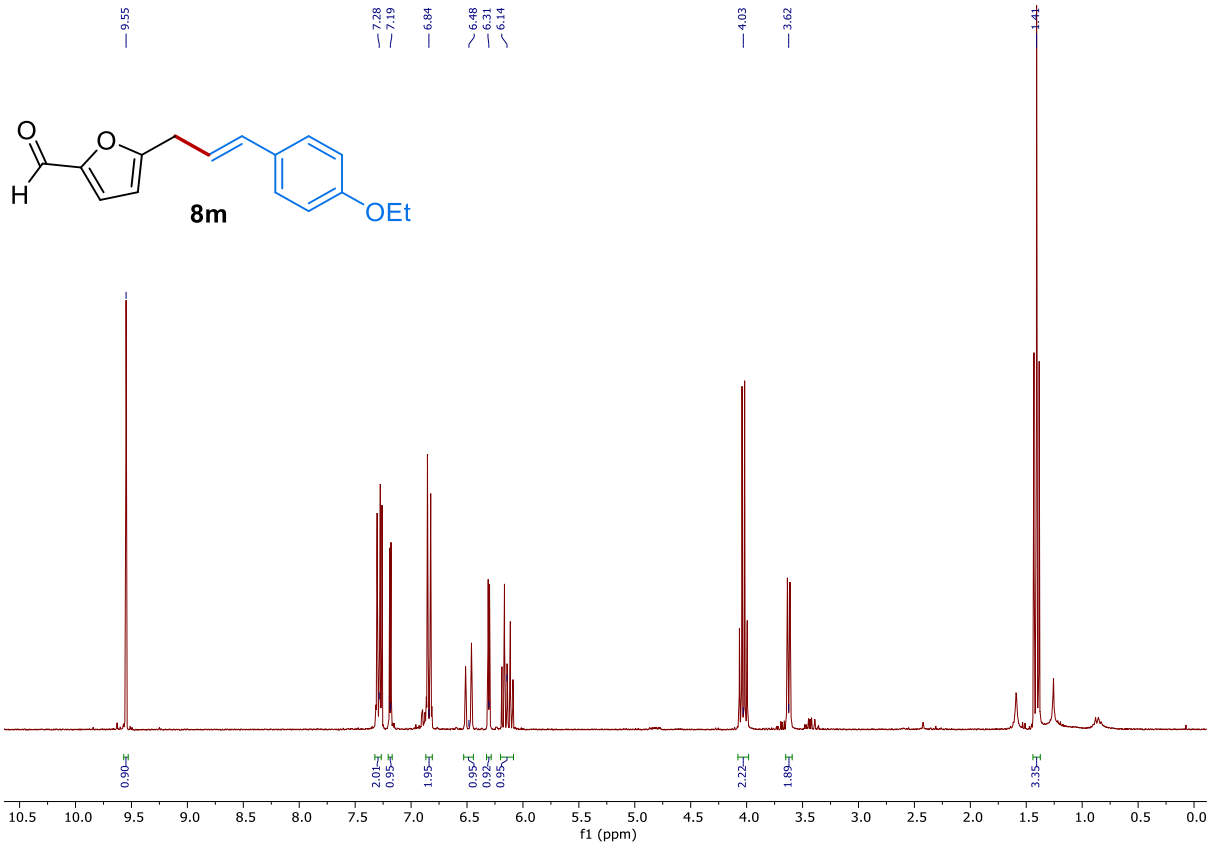
125.9
123.9
123.4
120.8
111.0
109.4
55.6
32.7
f1 (ppm)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6.84
6.48
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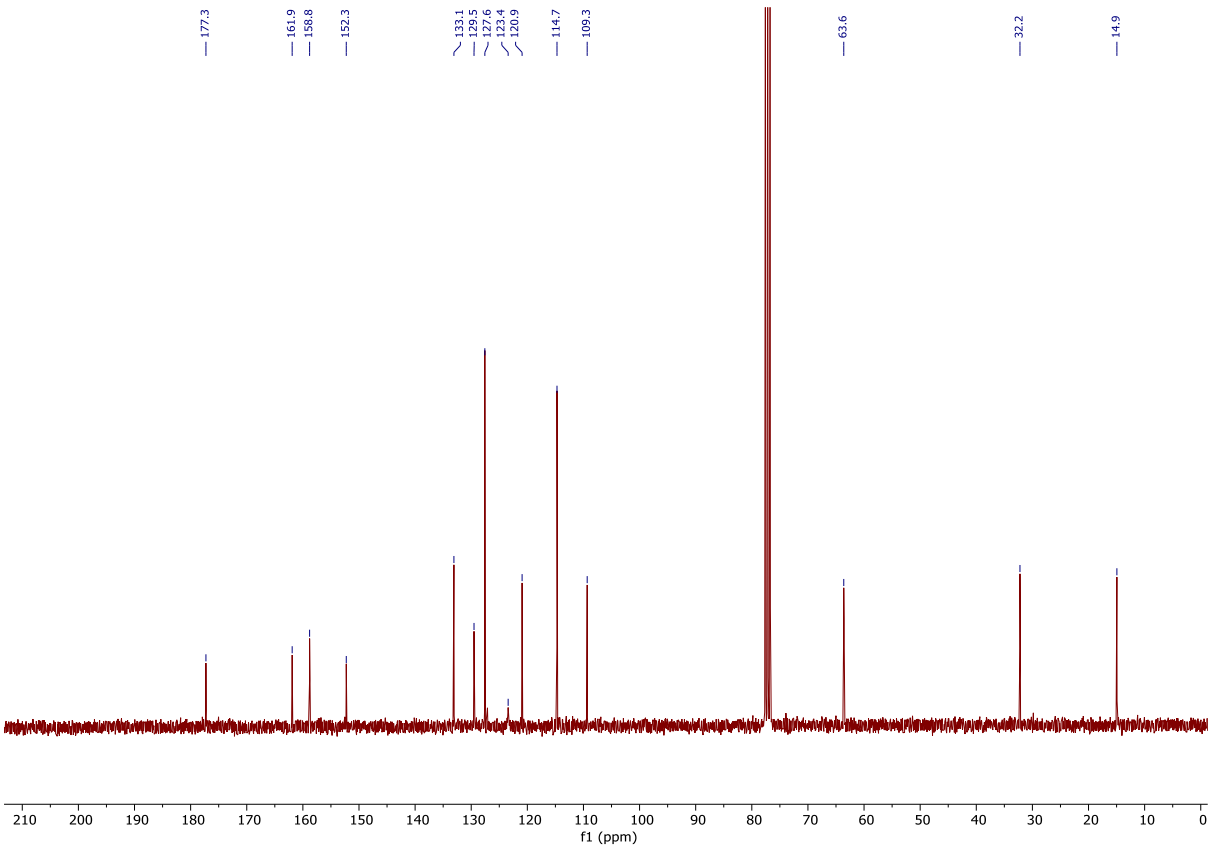
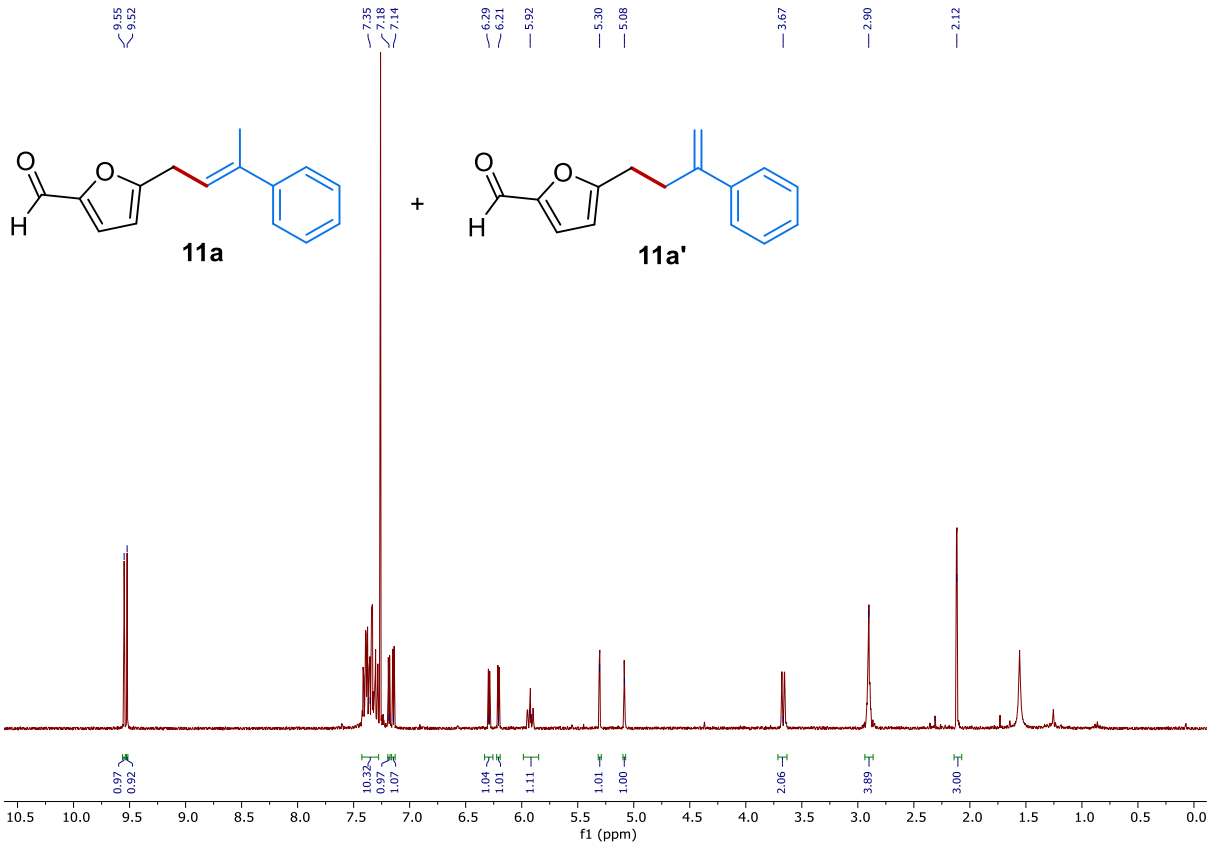
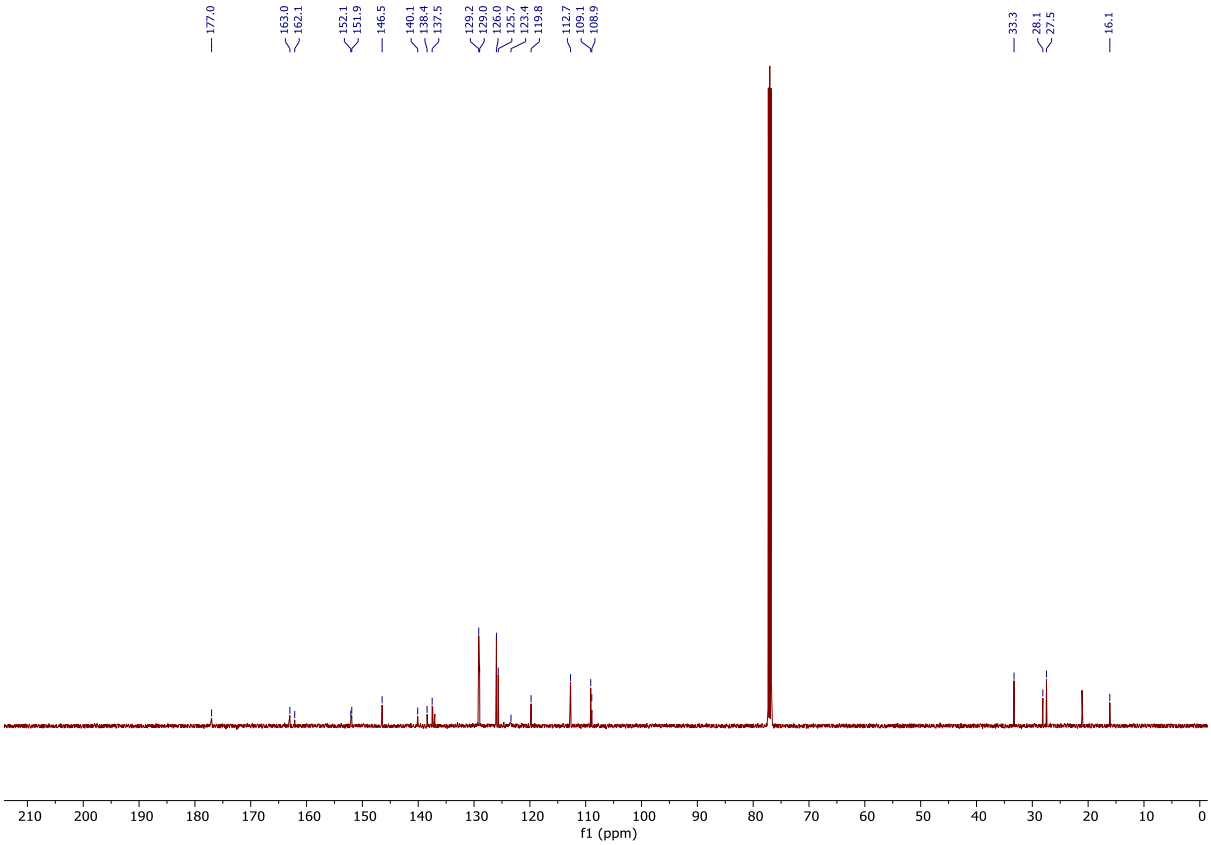
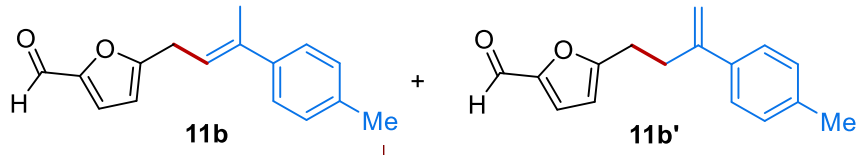
6.14
4.03
3.62
1.41
O
O
H
8m
OEt
0.90
2.01
0.95
1.95
0.95
0.92
0.95
2.22
1.89
3.35
f1 (ppm)

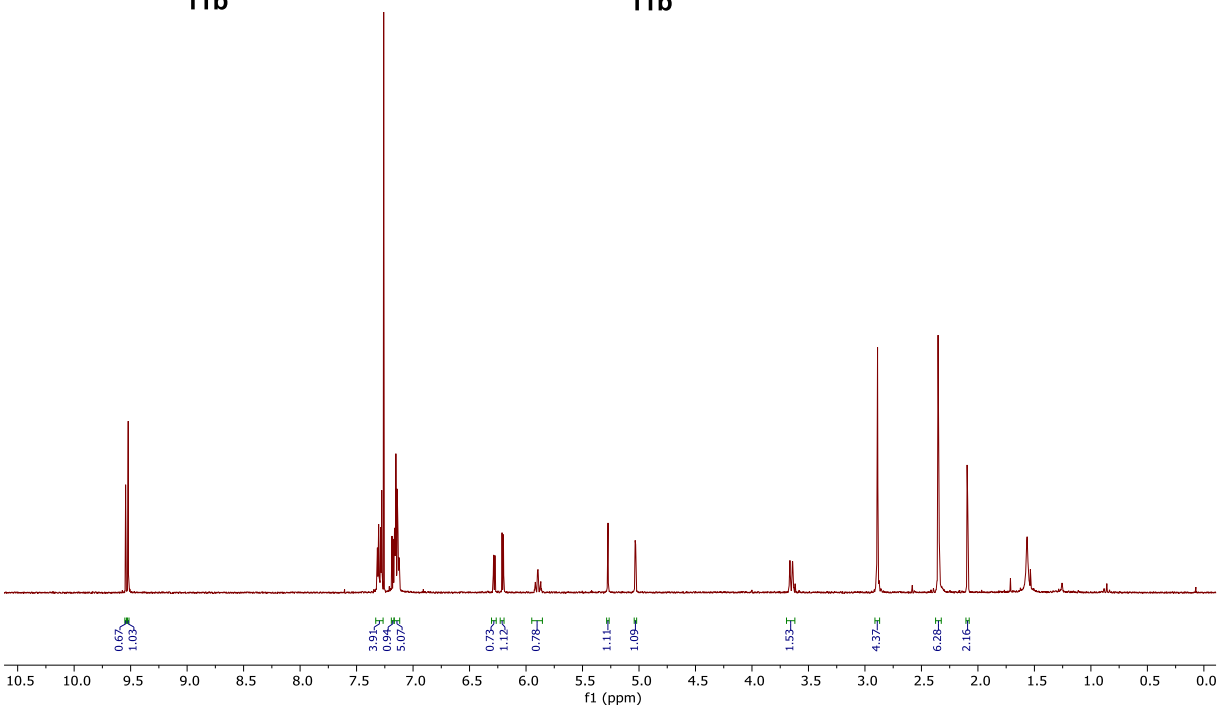

177.3
161.9
158.8
152.3
133.1
129.5
127.6
122.4
120.9
114.7
109.3
63.6
32.2
14.9
f1 (ppm)

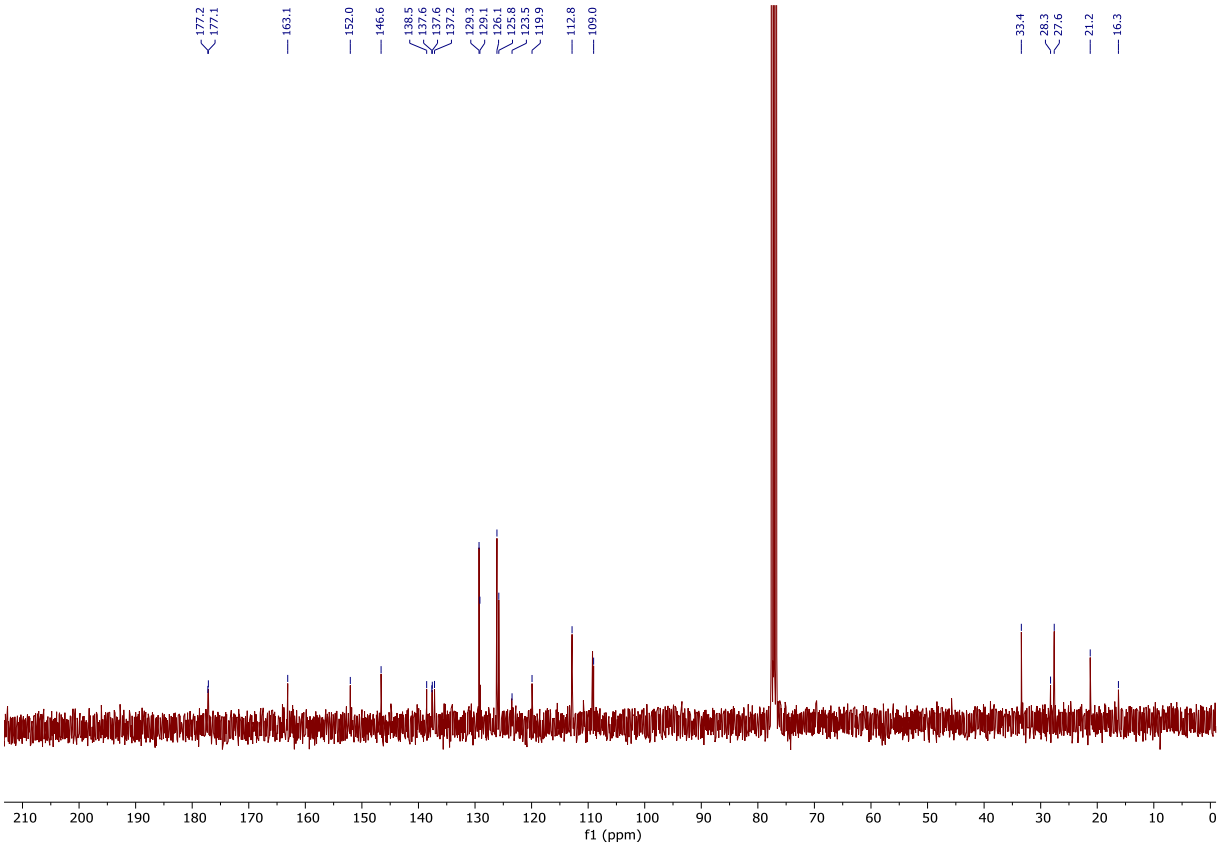

9.55
9.52
7.35
7.18
7.14
6.29
6.21
5.92
5.30
5.08
3.67
2.90
2.12
O
O
H
11a
+
O
O
H
11a'
0.97
0.92
10.32
0.97
1.07
1.04
1.01
1.11
1.01
1.00
2.06
3.89
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

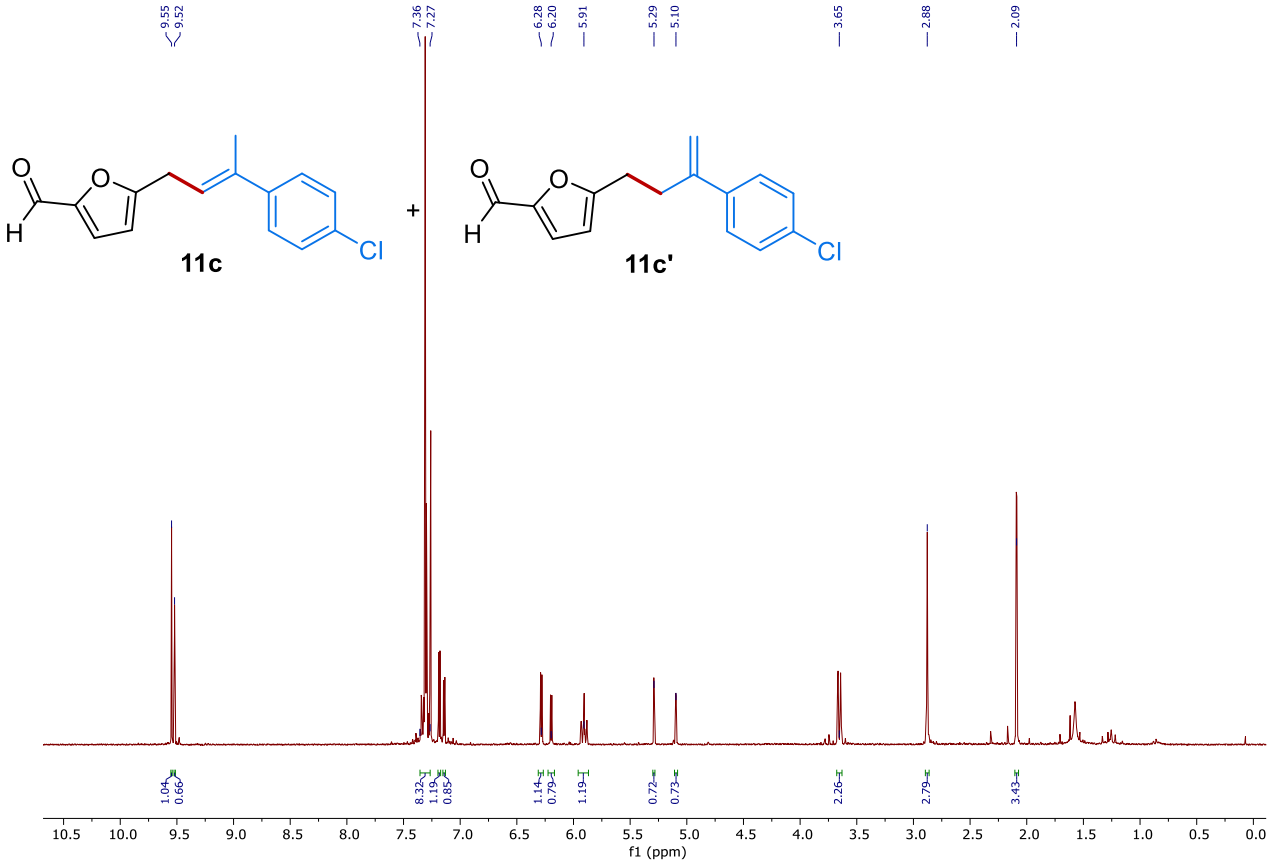

177.0
163.0
162.1
152.1
151.9
146.5
140.1
138.4
137.5
129.2
129.0
126.0
125.7
123.4
119.8
112.7
109.1
108.9
33.3
28.1
27.5
16.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

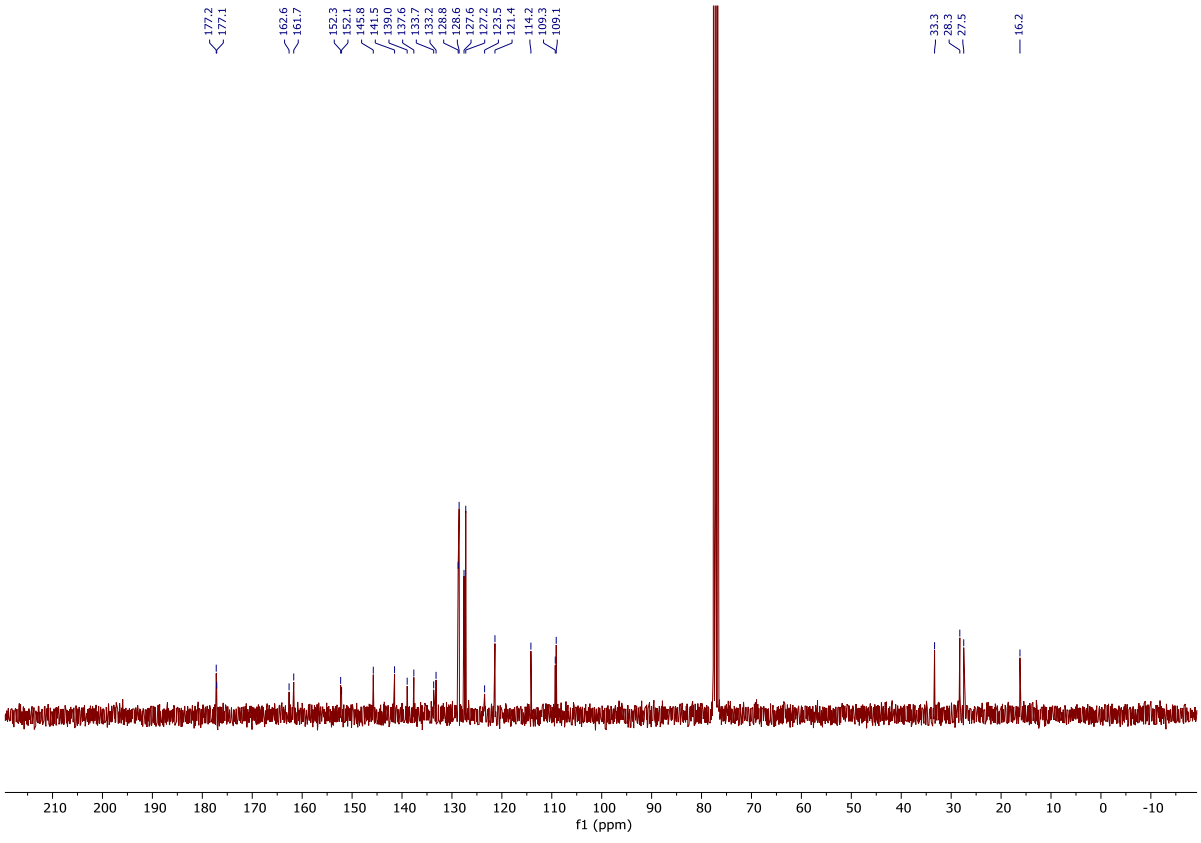

O
O
H
Me
+
O
O
H
Me

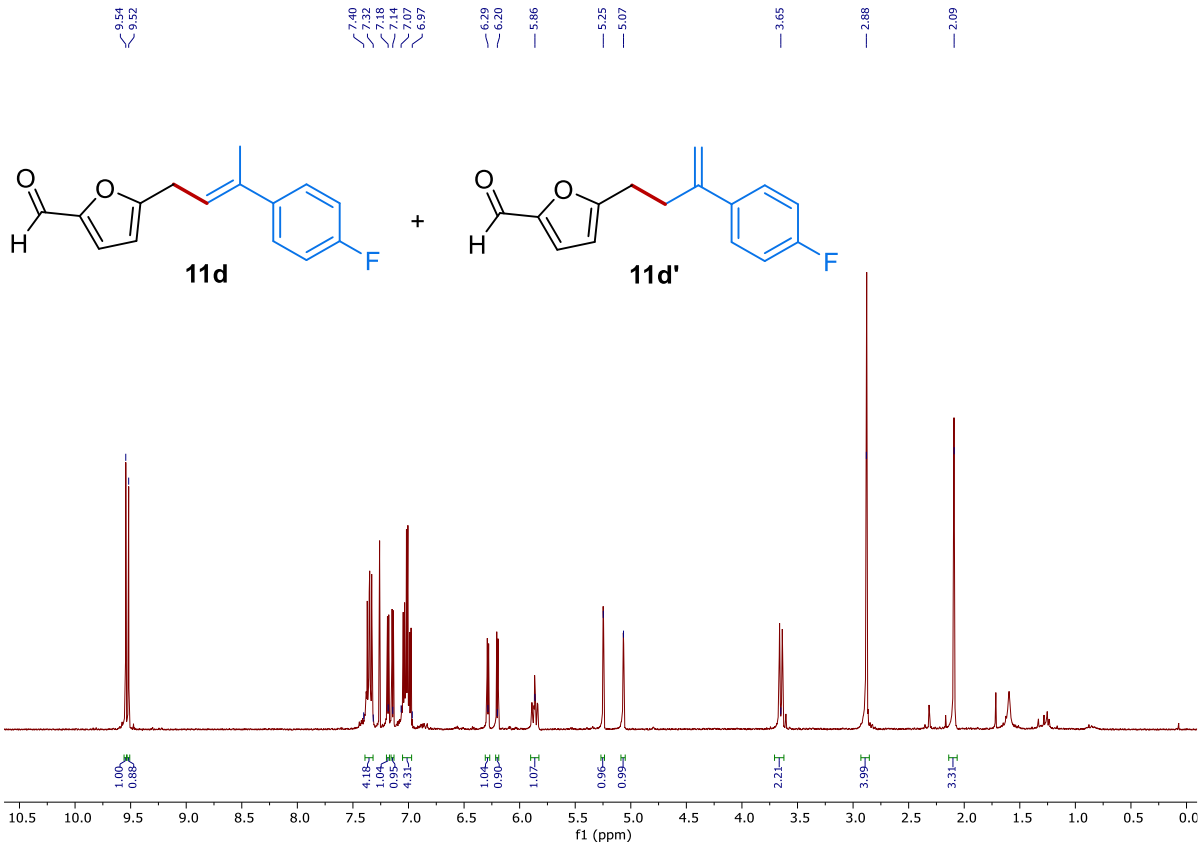
11b **11b'**

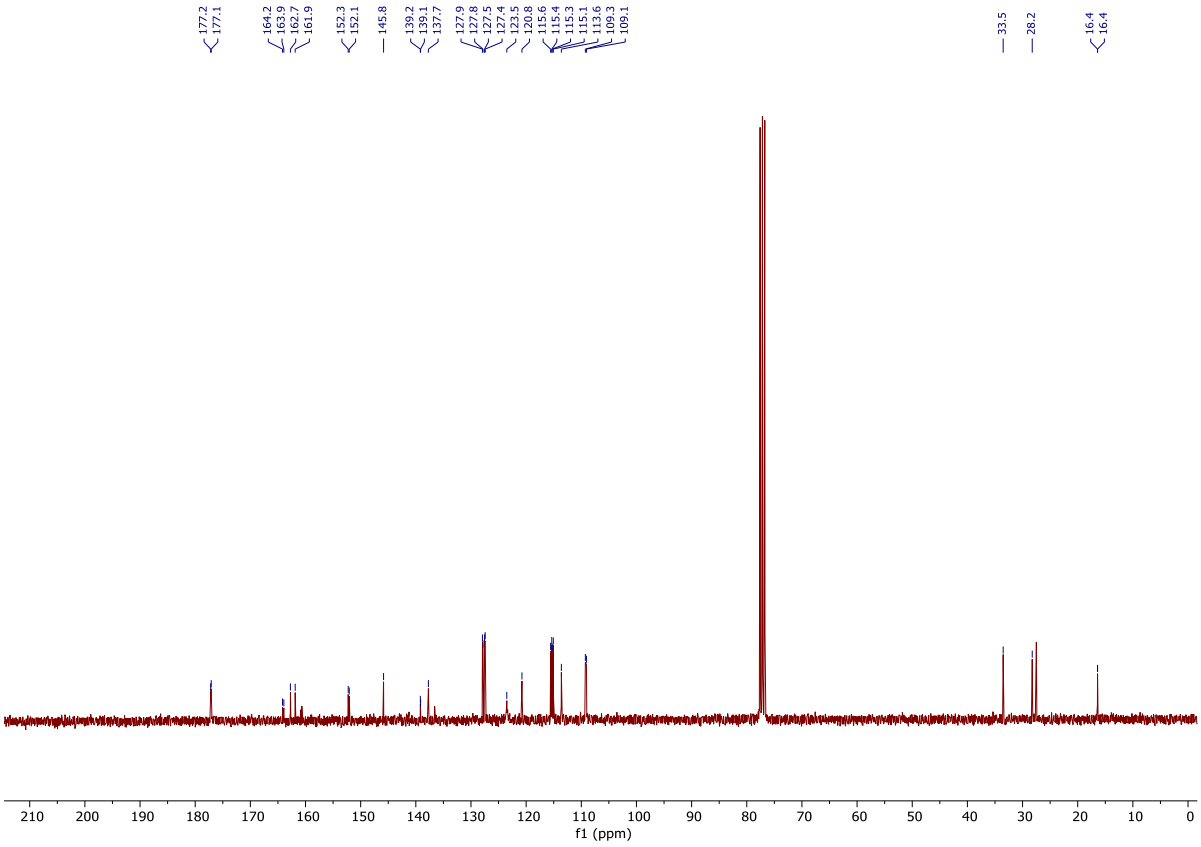

0.67
1.03
3.91
0.94
5.07
0.73
1.12
0.78
1.11
1.09
1.53
4.37
6.28
2.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

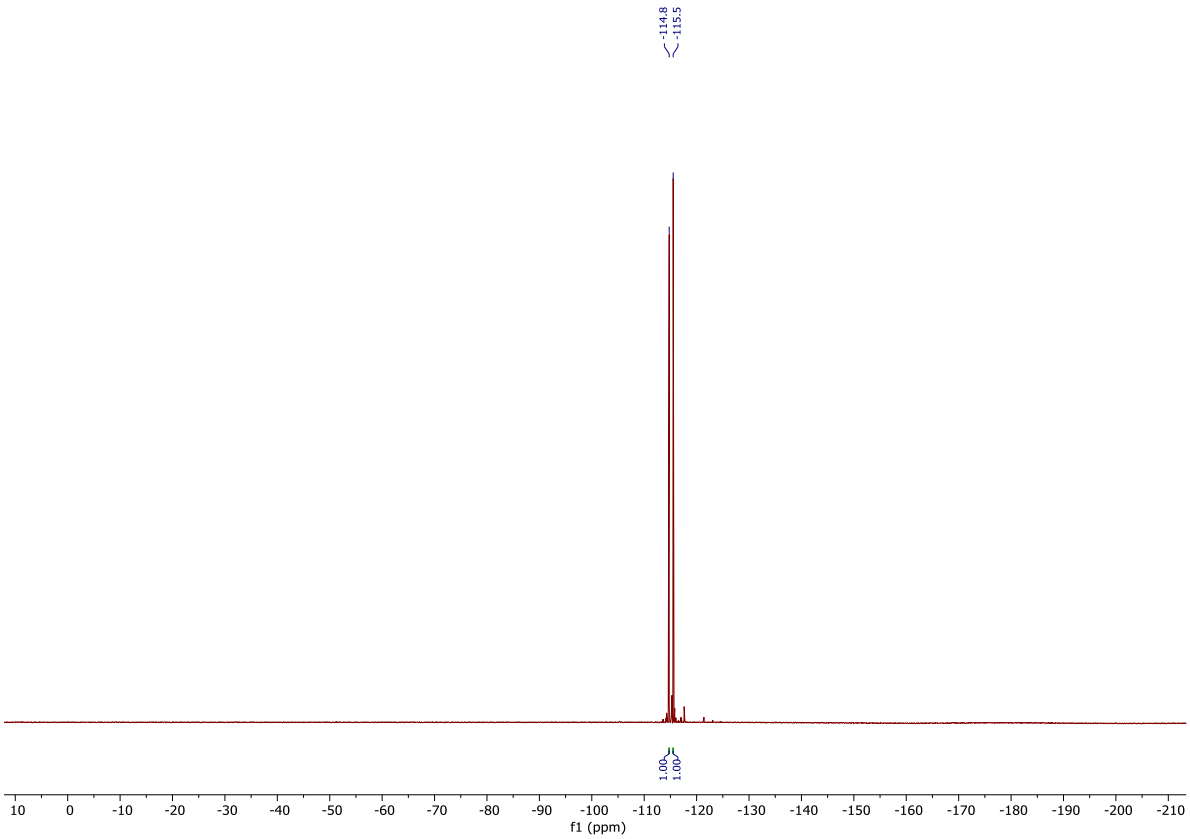

177.2
177.1
163.1
152.0
146.6
138.5
137.6
137.6
137.2
129.3
129.1
126.1
125.8
123.5
119.9
112.8
109.0
33.4
28.3
27.6
21.2
16.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

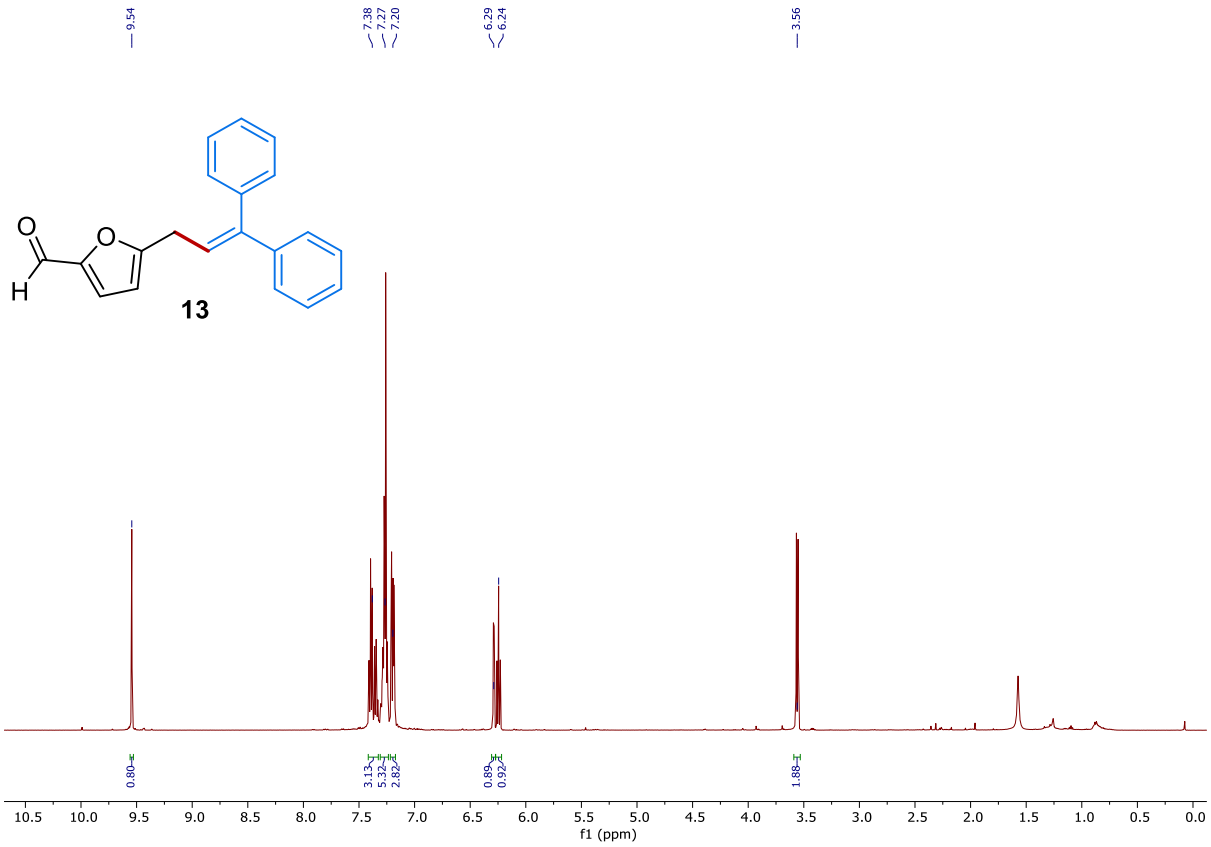

9.55
9.52
7.36
7.27
6.28
6.20
5.91
5.29
5.10
3.65
2.88
2.09
O
O
H
Cl
11c
+
O
O
H
Cl
11c'
1.04
0.66
8.32
1.19
0.85
1.14
0.79
1.19
0.72
0.73
2.26
2.79
3.43
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

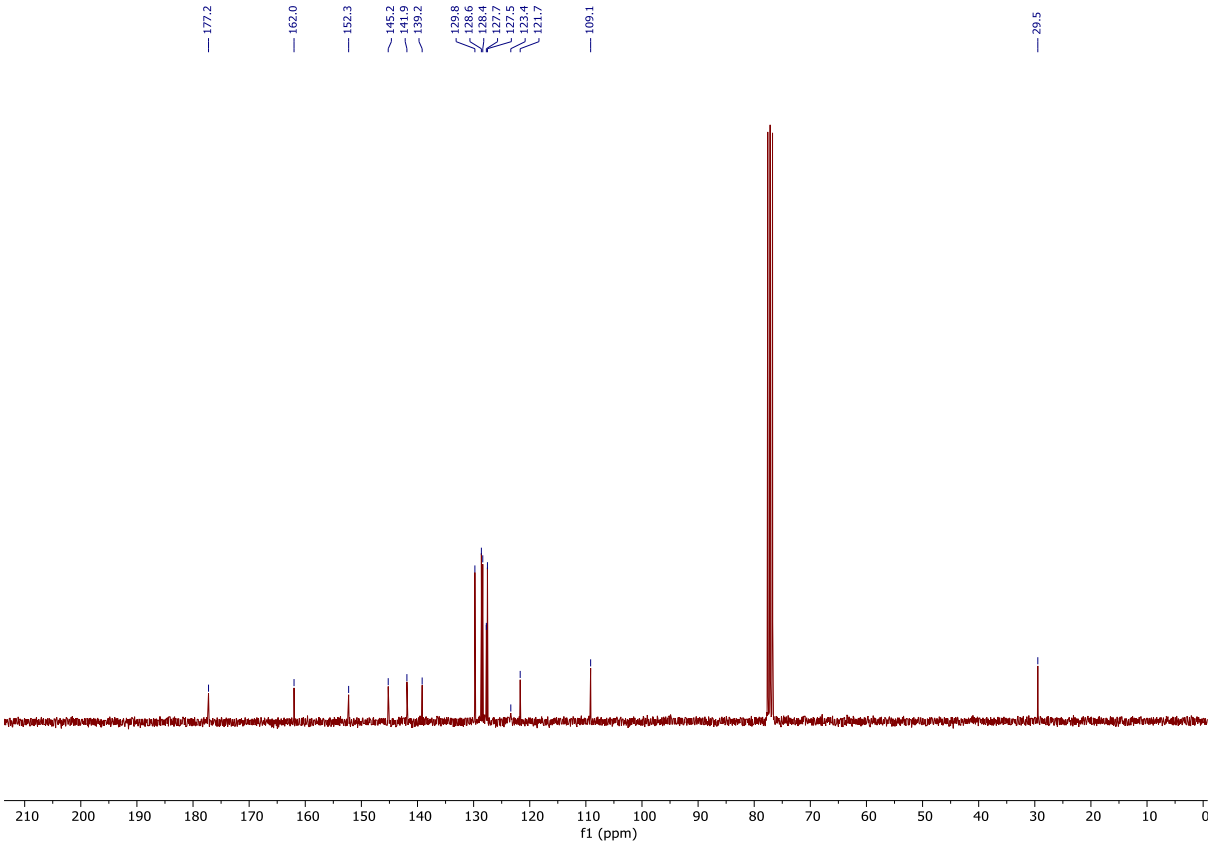

177.2
177.1
162.6
161.7
152.3
152.1
145.8
141.5
139.0
137.6
133.7
133.2
128.8
128.6
127.6
127.2
123.5
121.4
114.2
109.3
109.1
33.3
28.3
27.5
16.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

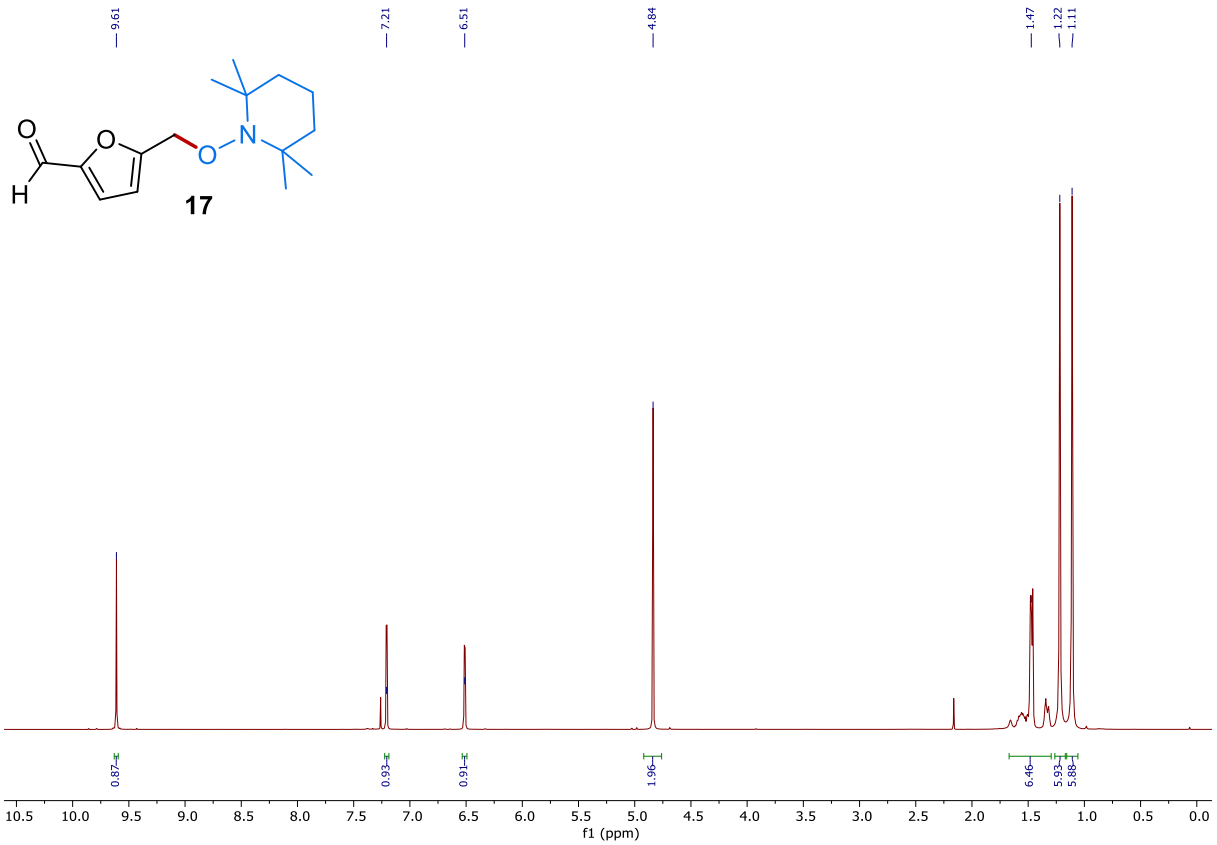

9.54
9.52
7.40
7.32
7.18
7.14
7.07
6.97
6.29
6.20
5.86
5.25
5.07
3.65
2.88
2.09
11d
+
11d'
F
1.00
0.88
4.18
1.04
0.95
4.31
1.04
0.90
1.07
0.96
0.99
2.21
3.99
3.31
f1 (ppm)

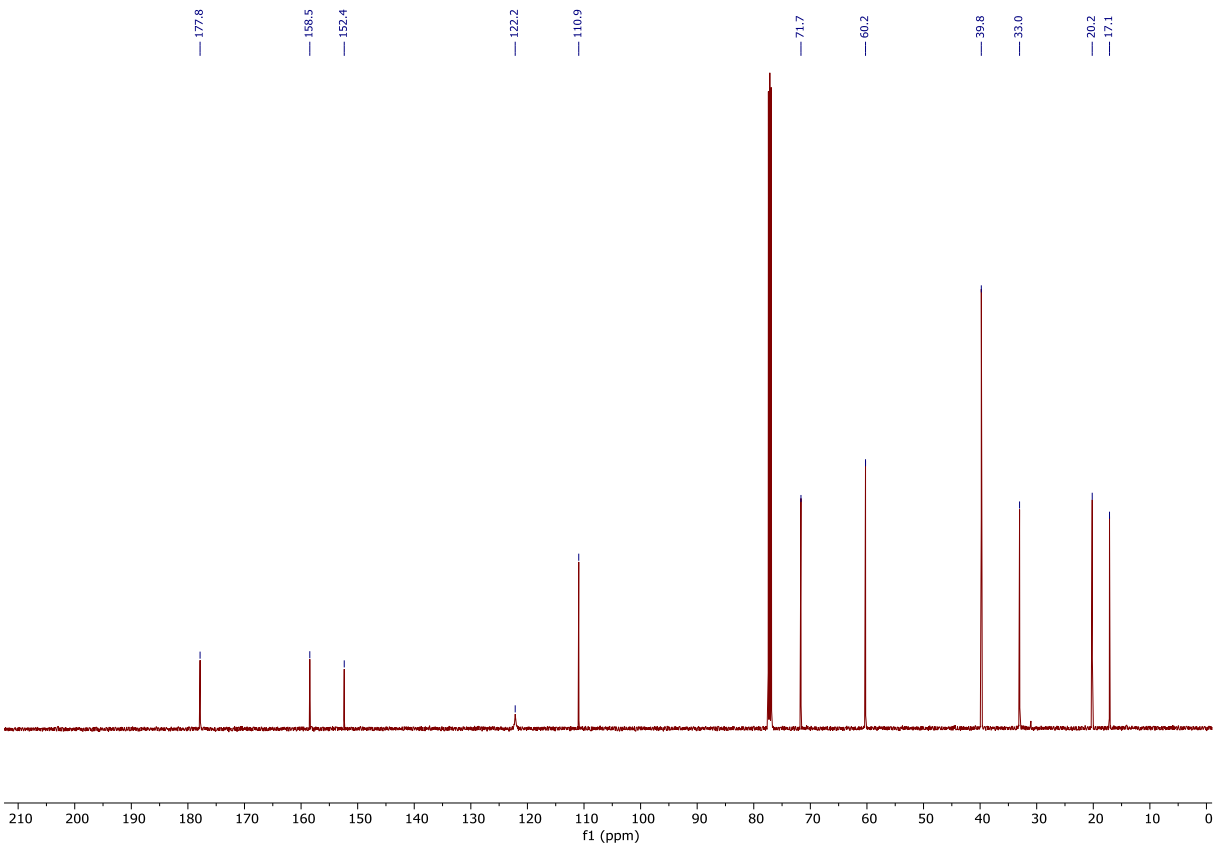

177.2
177.1
164.2
163.9
162.7
161.9
152.3
152.1
145.8
139.2
139.1
137.7
127.9
127.8
127.5
127.4
123.5
120.8
115.6
115.4
115.3
115.1
113.6
109.3
109.1
33.5
28.2
16.4
16.4
f1 (ppm)


-114.8
-115.5
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


9.54
7.38
7.27
7.20
6.29
6.24
3.56
O
O
H
13
0.80
3.13
5.32
2.82
0.89
0.92
1.88
f1 (ppm)


177.2
162.0
152.3
145.2
141.9
139.2
129.8
128.6
128.4
127.7
127.5
123.4
121.7
109.1
29.5
f1 (ppm)


9.61
7.21
6.51
4.84
1.47
1.22
1.11
O
O
N
O
H
17
0.87
0.93
0.91
1.96
6.46
5.93
5.88
f1 (ppm)


177.8
158.5
152.4
122.2
110.9
71.7
60.2
39.8
33.0
20.2
17.1
f1 (ppm)