Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Manganese-catalyzed Selective C-H Activation and Deuteration by means of a Catalytic Transient Directing Group Strategy

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1 General comments

All reactions were carried out in 25 mL Schlenk pressure tubes (FengTecEx) under an atmosphere of argon using standard Schlenk techniques. DCE was purchased from AlfaAesar. D_2O (99.90%) was purchased from Deutero. Aldehydes were purchased from Sigma-Aldrich, Fluorochem, AlfaAesar, and TCI and stored under argon. Anhydrous sodium acetate was purchased from Fisher. Manganese carbonyl complexes were purchased from Sigma-Aldrich and stored under argon at 4 °C. All solvents and reagents were used as received. NMR spectra were recorded on Bruker Avance 300 (300 MHz) or 400 (400 MHz) NMR spectrometers. Chemical shifts δ (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C), for CD_3OD 3.31 ppm (^{1}H) and 49.00 ppm (^{13}C). Multiplets of NMR were assigned as s (singlet), br s (broad singlet) d (doublet), t (triplet), dd (doublet of doublet), dq (doublet of quartet), ddd (doublet of doublet of doublet), and m (multiplet). All measurements were carried out at room temperature. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). The data is given as mass units per charge (m/z).

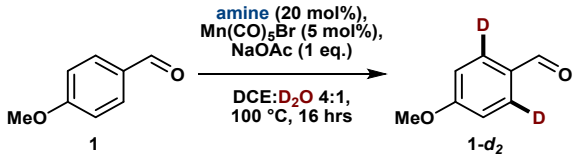
2 General procedure for the deuteration of aromatic aldehydes

A. The aldehyde (0.5 mmol), sodium acetate (41 mg, 0.5 mmol, 1.0 eq.) and manganese pentacarbonyl bromide (6.9 mg, 25 µmol, 5 mol%) were weighed into a 25 mL pressure-resistent Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was evacuated and backfilled with argon three times before DCE (400 µL), D_2O (100 µL) and *n*-butylamine (7.3 mg, 0.1 mmol, 20 mol%) were added. Liquid aldehydes were also added at this stage. The reaction mixture was subsequently heated to 100 °C and stirred at this temperature for the indicated reaction time. The resulting suspension was diluted with DCM, washed with distilled water (20 mL), and extracted with DCM (2x 20 mL). The combined organic layers were dried over sodium sulfate and concentrated. The deuterated products were then purified by silica gel column chromatography.

B. The aldehyde (0.5 mmol), 4-chlorobenzoic acid (39 mg, 0.25 mmol, 0.5 eq.) and manganese pentacarbonyl bromide (6.9 mg, 25 µmol, 5 mol%) were weighed into a 25 mL pressure-resistent Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was evacuated and backfilled with argon three times before DCE (400 µL), D_2O (100 µL) and benzylamine (11 µL, 0.1 mmol, 20 mol%) were added. Liquid aldehydes were also added at this stage. The reaction mixture was subsequently heated to 100 °C and stirred at this temperature for the indicated reaction time. The resulting suspension was diluted with DCM, washed with an aqueous saturated solution of sodium bicarbonate (20 mL), and extracted with DCM (2x 20 mL). The combined organic layers were washed with water (20 mL), dried over sodium sulfate and concentrated. The deuterated products were then purified by silica gel column chromatography.

3 Optimization details

Table 1 The effect of different catalytic amines.

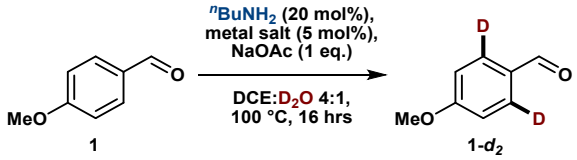


Entry	Catalytic amine [20 mol%]	Deuterium incorporation [%]
1	-	0
2	2-aminobenzotrifluoride	0
3	benzylamine	66
4	2-methylbenzylamine	65
5	2,6-dimethylbenzylamine	69

6	3-methoxybenzylamine	57
7	4-methoxybenzylamine	67
8	2-(trifluoromethyl)benzylamine	67
9	3-(trifluoromethyl)benzylamine	56
10	4-(trifluoromethyl)benzylamine	54
11	3,4-difluorobenzylamine	52
12	1-phenylethylamine	32
13	**n-butylamine**	**73**
14	n-octylamine	72
15	cyclopentylamine	48
16	4-phenylbutylamine	72
17	glycine	0

Scale: 0.5 mmol **1**. Deuterium incorporation was determined by ^{1}H NMR through the decrease of the doublet at 7.81 ppm while referencing on the protons in *meta* position.

Table 2 The effect of different catalyst precursors.

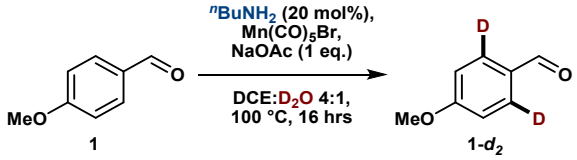


Entry	Catalyst precursor [5 mol%]	Deuterium incorporation [%]
1	-	0
2	$Mn(CO)_5Br$	73
3	$Mn_2(CO)_{10}$	85
4	$MnCl_2$	0
5	$Mn(OAc)_2$	0

Scale: 0.5 mmol **1**. Deuterium incorporation was determined by ^{1}H NMR through the decrease of the doublet at 7.81 ppm while referencing on the protons in *meta* position.

Since dimanganese decacarbonyl was completely ineffective for the deuteration of 2-nitrobenzaldehyde, the model substrate for acidic deuteration conditions, while manganese pentacarbonyl bromide was an efficient catalyst under these conditions, the latter was used as a catalyst for further experiments to allow for a broader scope of the reaction.

Table 3 The effect of catalyst loading.

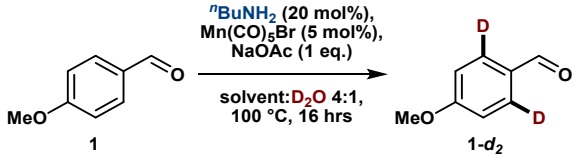


Entry	Catalyst loading [mol%]	Deuterium incorporation [%]
1	0	0
2	2.5	62
3	5	73
4	10	81
5	20	94

Scale: 0.5 mmol **1**. Deuterium incorporation was determined by ^{1}H NMR through the decrease of the doublet at 7.81 ppm while referencing on the protons in *meta* position.

Aiming for a cost-efficient procedure, a catalyst loading of 5 mol% was used for the evaluation of the substrate scope. Indeed, most substrates were sufficiently reactive with this lower catalyst loading.

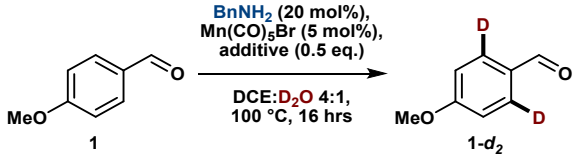
Table 4 Effect of solvents.



Entry	Co-solvent	Deuterium incorporation [%]
1	DCE	73
2	DME	80
3	PhCl	54
4	Toluene	55
5	D_2O	88
6	DMF	23
7	1,4-Dioxane	62

Scale: 0.5 mmol **1**. Deuterium incorporation was determined by ^{1}H NMR through the decrease of the doublet at 7.81 ppm while referencing on the protons in *meta* position.

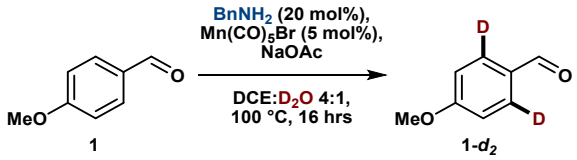
Table 5 Effect of base and acid additives.



Entry	Additive (0.5 eq.)	Deuterium incorporation [%]
1	**NaOAc**	**60**
2	K_2CO_3	0
3	Cy_2NH	9
4	AcOH	50
5	TFA	0
6	PivOH	21
7	$AdCO_2H$	22
8	$PhCO_2H$	21
9	4-Cl-$PhCO_2H$	21
10	4-OMe-$PhCO_2H$	29
11	4-CF_3-$PhCO_2H$	10

Scale: 0.5 mmol **1**. Deuterium incorporation was determined by ^{1}H NMR through the decrease of the doublet at 7.81 ppm while referencing on the protons in *meta* position. $AdCO_2H$ = adamantane carboxylic acid.

Table 6 Effect of base loading.



Entry	NaOAc loading [eq.]	Deuterium incorporation [%]
1	0.25	51
2	0.5	60
3	**1**	**66**
4	2	59

4 Characterization data for deuterated compounds

***p*-Anisaldehyde-2,6-d_2 (1-d_2)**. Procedure A, 16 hrs. Purification with pentane:ethyl acetate 9:1. 73% Deuterium incorporation on average in positions 2 and 6, 80% isolated yield (average of two runs). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.86 (s, 1H), 7.81 (d, J = 9.1 Hz, 28% ^{1}H, 2H), 6.99–6.97 (m, 2H), 3.86 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.8, 164.7, 131.7 (t, J = 24.7 Hz), 129.9 (t, J = 5.5 Hz), 114.3, 55.6. **HRMS** (EI): *m/z*: calcd. for [M]: 138.0644, found 138.0640. **MS** (EI, 70 eV): *m/z* (%): 138 (49.2) M-d_2, 137 (100.0) M-d_2-H, 136 (55.9) M-*d*-H, 109 (8.0), 94 (10.6), 79 (16.3).

***p*-Fluorobenzaldehyde-2,6-d_2 (2-d_2)**. Procedure A, 16 hrs. Purification with pentane:ethyl acetate 20:1 → 10:1. 93% Deuterium incorporation on average in positions 2 and 6, 89% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.98 (s, 1H), 7.91 (dd, J = 9.1, 5.3 Hz, 7% ^{1}H, 2H), 7.22 (d, J = 8.4 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.6, 166.6 (d, J = 255.7 Hz), 133.0 (m), 132.4–131.6 (m), 116.4 (d, J = 22.3 Hz). **MS** (EI, 70 eV): *m/z* (%): 126 (79.9) M-d_2, 125 (100.0) M-d_2-H, 124 (16.6) M-*d*-H, 97 (70.7).

***p*-Chlorobenzaldehyde-2,6-d_2 (3-d_2)**. Procedure A, 16 hrs. Purification with pentane:ethyl acetate 10:1. 91% Deuterium incorporation on average in positions 2 and 6, 48% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.98 (s, 1H), 7.84–7.81 (d, J = 8.8 Hz, 19% ^{1}H, 2H), 7.53–7.51 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.0, 141.1, 134.7, 130.7 (t, J = 24.5 Hz), 129.5. **HRMS** (EI): *m/z*: calcd. for [M-H]: 141.0071, found 141.0074. **MS** (EI, 70 eV): *m/z* (%): 144 (21.1) M(^{37}Cl)-d_2, 143 (36.9) M(^{37}Cl)-d_2-H, 142 (69.1) M(^{35}Cl)-d_2, 141 (100.0) M(^{35}Cl)-d_2-H, 140 (17.9) M(^{35}Cl)-*d*-H, 115 (14.9), 113 (45.2).

***o*-Chlorobenzaldehyde-6-*d* (4-*d*)**. Procedure B, 2.5 mol% $Mn(CO)_5Br$, 19 hrs. Purification with pentane:ethyl acetate 10:1. 88 % Deuterium incorporation in position 6, 32 % isolated yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 7.92 (ddd, J = 7.7, 1.8, 0.4 Hz, 12% ^{1}H, 1H), 7.53 (dd, J = 8.0, 7.1 Hz, 1H), 7.45 (d, J = 8.1, 1.4 Hz, 1H), 7.42–7.35 (m, 1H). **HRMS** (EI): *m/z*: calcd. For [M-H]: 140.0008, found 140.0005. **MS** (EI, 70 eV): *m/z* (%): 142 (38.6) [M-H](^{37}Cl)-*d*, 141 (72.9) [M-H](^{37}Cl), 140 (100.0) [M-H](^{35}Cl)-*d*, 139 (14.5) [M-H](^{35}Cl), 112 (36.9).

***m*-Bromobenzaldehyde-2,6-d_2 (5-d_2)**. Procedure A, 72 hrs. Purification with pentane:ethyl acetate 20:1. 70% Deuterium incorporation in positions 2 and 6, 79% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.95 (m, 1H), 8.00–7.99 (m, 30% ^{1}H, 1H), 7.82–7.78 (m, 30% ^{1}H, 1H), 7.76–7.72 (m, 1H), 7.44–7.39 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.9, 138.1, 137.4, 132.5, 130.7, 128.5, 123.4. **HRMS** (EI): *m/z*: calcd. for [M-H]: 186.9545, found 186.9545. **MS** (EI, 70 eV): *m/z* (%): 187 (96.5) M(^{81}Br)-d_2, 186 (99.9) M(^{81}Br)-*d*, 185 (100.0) M(^{79}Br)-d_2, 184 (53.9) M(^{79}Br)-*d*, 159 (27.1), 158 (26.6), 157 (29.3), 156 (23.9), 78 (30.0), 77 (23.8), 51 (23.2).

4-Bromo-2-fluorobenzaldehyde-6-*d* (6-*d*). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 20:1. 96% Deuterium incorporation in position 6, 78% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.30 (d, J = 0.6 Hz, 1H), 7.76–7.71 (m, 4% ^{1}H, 1H), 7.42–7.42 (m, 1H), 7.38 (dd, J = 9.7, 1.7 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 186.2 (d, J = 6.3 Hz), 164.2 (d, J = 263.1 Hz), 130.3 (d, J = 10.0 Hz), 129.8–129.1 (m), 128.4 (d, J = 3.7 Hz), 123.2 (d, J = 8.3 Hz), 120.4 (d, J = 23.6 Hz). **HRMS** (EI): *m/z*: calcd. for [M-H]: 201.9409, found 201.9411. **MS** (EI, 70 eV): *m/z* (%): 205 (57.6) M(^{81}Br)-*d*, 204 (100.0) M(^{81}Br)-*d*-H, 203 (62.0) M(^{79}Br)-*d*, 202 (97.9) M(^{79}Br)-*d*-H, 176 (19.9), 174 (20.6), 95 (29.7).

5-Chloro-2-fluorobenzaldehyde-6-*d* (7-*d*). Procedure A, 16 hrs. 90% Deuterium incorporation in position 6. Purification on silica gel was unsuccessful. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.29 (s, 1H), 7.81 (dd, *J* = 5.9, 2.8 Hz, 10% ^{1}H, 1H), 7.54 (dd, *J* = 8.8, 4.5 Hz, 1H), 7.14 (dd, *J* = 9.2 Hz, 1H). **HRMS** (EI): *m/z*: calcd. for [M-H] (^{37}Cl): 159.9884, found 159.9888. **MS** (EI, 70 eV): *m/z* (%): 161 (20.5) [M](^{37}Cl)-*d*, 160 (36.5) [M-H](^{37}Cl)-*d*, 159 (69.3) [M](^{35}Cl)-*d*, 158 (100.0) [M-H](^{35}Cl)-*d*, 157 (22.4) [M-H](^{35}Cl), 130 (36.8), 110 (8.4), 95 (29.2), 75 (31.0).

***p*-(Trifluoromethyl)benzaldehyde-2,6-d_2 (8-d_2)**. Procedure A, 16 hrs. Purification with pentane:ethyl acetate 10:1. 76% Deuterium incorporation on average in positions 2 and 6, 30% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.10 (s, 1H), 8.00 (dq, *J* = 8.5, 0.7 Hz, 34% ^{1}H, 2H), 7.82–7.79 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.2, 138.8, 136.1, 130.0, 126.2, 121.8. **HRMS** (EI): *m/z*: calcd. For [M-H]: 175.0334, found 175.0335. **MS** (EI, 70 eV): *m/z* (%): 176 (56.2) M-d_2, 175 (100.0) M-H-d_2/M-*d*, 174 (44.4) M-H-*d*, 147 (73.2), 146 (44.1).

1-Naphthaldehyde-2-*d* (9-*d*). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 10:1. 81% Deuterium incorporation in position 2, 85% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.41 (s, 1H), 9.28–9.24 (m, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.99 (dd, *J* = 7.1, 1.3 Hz, 19% ^{1}H, 1H), 7.94–7.91 (m, 1H), 7.70 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.66–7.57 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 193.6, 136.4 (t, *J* = 24.4 Hz), 135.4, 133.8, 131.5, 130.6, 129.2, 128.6, 127.1, 125.0. **HRMS** (EI): *m/z*: calcd. For [M]: 157.0632, found 157.0630.

Benzaldehyde-2,6-d_2 (10-d_2). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 9:1. 50% Deuterium incorporation on average in positions 2 and 6, 79% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.02 (s, 1H), 7.90–7.86 (m, 50% ^{1}H, 2H), 7.66–7.60 (m, 1H), 7.56–7.50 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 192.5, 136.5, 134.6, 129.9, 129.0.

***o*-Tolualdehyde-6-*d* (11-*d*)**. Procedure A, 72 hrs. Purification with pentane:ethyl acetate 20:1. 61% Deuterium incorporation in position 6, 61% isolated yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.28 (s, 1H), 7.80 (dd, *J* = 7.6, 1.5 Hz, 5% ^{1}H, 1H), 7.51–7.46 (m, 1H), 7.39–7.35 (m, 1H), 7.28–7.25 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 193.0, 140.8, 134.3, 133.8, 132.2, 131.9, 126.4, 19.7. **HRMS** (EI): *m/z*: calcd. for [M-H]: 120.0554, found 120.0553. **MS** (EI, 70 eV): *m/z* (%): 121 (71.7) M-*d*, 120 (100.0) M-H-*d*, 119 (35.0) M-H, 92 (79.8), 65 (15.6), 51 (7.2), 39 (9.2).

Biphenyl-4-carboxaldehyde-3,5-d_2 (12-d_2). Procedure A, 72 hrs. Purification with pentane:ethyl acetate 10:1. 44% Deuterium incorporation on average in positions 3 and 5, 83% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.06 (s, 1H), 7.97–7.93 (m, 57% ^{1}H, 2H), 7.77–7.73 (m, 2H), 7.66–7.62 (m, 2H), 7.52–7.39 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.9, 147.2, 139.8, 130.3, 129.1, 128.6, 127.7, 127.6, 127.4. **HRMS** (EI): *m/z*: calcd. for [M-H]: 183.0774, found 183.0780. **MS** (EI, 70 eV): *m/z* (%): 184 (22.7) M-d_2, 183 (76.7) M-d_2-H, 182 (100.0) M-*d*-H, 181 (44.9) M-H, 154 (34.3), 153 (54.8), 152 (42.5).

***p-tert*-Butylbenzaldehyde-2,6-d_2 (13-d_2)**. Procedure A, 72 hrs. Purification with pentane:ethyl acetate 20:1. 18% Deuterium incorporation on average in positions 2 and 6, 77% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.98 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 83% ^{1}H, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 1.35 (s, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 192.1, 158.6, 134.2, 129.8, 126.1, 35.5, 31.2. **HRMS** (EI): *m/z*: calcd. for [M-H] (monodeuterated compound): 162.1024, found 162.1029. **MS** (EI, 70 eV): *m/z* (%): 163 (14.2) M-*d*, 162 (23.8) M-*d*-H, 148 (58.7), 147 (100.0), 120 (12.6), 119 (24.2), 92 (19.4), 91 (42.7).

3,4-Dimethoxybenzaldehyde-2,6-d_2 (14-d_2). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 4:1 → 2:1. 79% Deuterium incorporation in position 2, 62% deuterium incorporation in position 6, 77% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.81 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 38% ^{1}H, 1H), 7.36 (br s, 21% ^{1}H, 1H), 6.95–6.92 (m, 1H), 3.92 (s, 3H), 3.89 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.9, 154.5, 149.6, 130.0, 126.8, 110.3, 108.9, 56.2, 56.0. **MS** (EI, 70 eV): *m/z* (%): 168 (62.8) M-d_2, 167 (100.0) M-*d*, 166 (55.9) M-*d*-H, 165 (10.1) M-H), 96 (17.6).

***p*-Dimethylaminobenzaldehyde-2,6-d_2 (15-d_2)**. Procedure A, 72 hrs. Purification with pentane:ethyl acetate 4:1. 51% Deuterium incorporation on average in positions 2 and 6, 100% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.29 (br s, 1H), 8.28 (d, *J* = 9.2 Hz, 49% ^{1}H, 2H), 7.27–7.23 (m, 2H), 3.63 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.3, 154.4, 132.0, 125.1, 111.0, 40.1. **HRMS** (EI): *m/z*: calcd. For [M]: 151.0961, found 151.0959. **MS** (EI, 70 eV): *m/z* (%): 151 (33.1) M-d_2, 150 (94.3) M-*d*, 149 (100.0) M, 148 (32.8).

Piperonal-2,6-d_2 (16-d_2). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 4:1. 95% Deuterium incorporation in position 2, 39% deuterium incorporation in position 6, 78% isolated yield. **^{1}H NMR (300 MHz,**

$CDCl_3$) δ 9.78 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 61% ^{1}H, 1H), 7.30 (m, 5% ^{1}H, 1H), 6.92–6.89 (m, 1H), 6.05 (s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.3, 153.2, 148.7, 131.9, 128.7, 108.4, 106.7 (t, *J* = 26.3 Hz), 102.2. **HRMS** (EI): *m/z*: calcd. for [M]: 152.0437, found 152.0434. **MS** (EI, 70 eV): *m/z* (%): 152 (38.2) M-d_2, 151 (100.0) M-*d*, 150 (74.3) M, 123 (12.0), 122 (19.0).

6-Bromopiperonal-*d* (17-*d*). Procedure B, 2.5 mol% $Mn(CO)_5Br$, 17 hrs. Purification with pentane:ethyl acetate 9:1. 77% Deuterium incorporation, 85% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.15 (s, 1H), 7.34 (s, 5% ^{1}H, 1H), 7.03 (s, 1H), 6.07 (s, 2H).). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.4, 160.6, 153.5, 148.2, 128.1, 121.7, 113.4, 102.9. **HRMS** (EI): *m/z*: calcd. For [M]: 228.9479, found 228.9484. **MS** (EI, 70 eV): *m/z* (%): 231 (82.5) M(^{81}Br)-*d*, 230 (100.0) M(^{81}Br)-H-*d*, 229 (88.1) M(^{79}Br)-*d*, 228 (95.7) M(^{79}Br)-H-*d*, 202 (19.7), 200 (22.8), 144 (10.4), 121 (9.5), 91 (6.1), 64 (23.2), 63 (28.8).

***p*-Formylacetanilide-3,5-d_2 (18-d_2)**. Procedure A, 72 hrs. Purification with pentane:ethyl acetate 1:1. 75% Deuterium incorporation on average in positions 3 and 5, 96% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.92 (br s), 7.85 (d, *J* = 9.0 Hz, 25% ^{1}H, 2H), 7.71–7.69 (m, 3H), 2.23 (s, 3H).). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.3, 168.9, 143.7, 132.2, 131.3, 119.3, 24.9. **HRMS** (EI): *m/z*: calcd. for [M]: 165.0753, found 165.0756. **MS** (EI, 70 eV): *m/z* (%): 165 (27.0) M-d_2, 164 (20.4) M-*d*, 123 (43.2), 122 (100.0), 121 (62.3), 94 (10.7), 66 (10.6), 43 (26.6).

***p*-Cyanobenzaldehyde-2,6-d_2 (19-d_2)**. Procedure B, 16 hrs. Purification with pentane:ethyl acetate 10:1 → 9:1. 88% Deuterium incorporation on average in positions 2 and 6, 100% isolated yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.09 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 12% ^{1}H, 2H), 7.85–7.83 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.7, 138.7, 132.9, 129.7 (t, *J* = 25.3 Hz), 117.8, 117.7. **HRMS** (EI): *m/z*: calcd. For [M-H]: 132.0413, found 131.0412. **MS** (EI, 70 eV): *m/z* (%): 133 (59.5) M-d_2, 132 (100.0) M-H-d_2, 131 (22.5) M-H-*d*, 104 (47.4), 77 (16.9), 51 (9.4).

***m*-Cyanobenzaldehyde-2,6-d_2 (20-d_2)**. Procedure B, 2.5 mol% $Mn(CO)_5Br$, 8 hrs. Purification with pentane:ethyl acetate 9:1. 89% Deuterium incorporation in position 2, 78% deuterium incorporation in position 6, 90 % isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.05 (s, 1H), 8.17–8.10 (m, 35% ^{1}H, 2H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.72–7.67 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.0, 137.3, 136.8, 133.4, 133.2, 130.1, 117.6, 113.7. **HRMS** (EI): *m/z*: calcd. for [M-H]: 132.0413, found 132.0413. **MS** (EI, 70 eV): *m/z* (%): 133 (55.8) M-d_2,132 (100.0) M-H-d_2, 131 (36.1) M-H-*d*, 104 (41.9), 77 (17.6), 51 (9.8).

***p*-Nitrobenzaldehyde-2,6-d_2 (21-d_2)**. Procedure B, 16 hrs. Purification with pentane:ethyl acetate 9:1. 91% Deuterium incorporation on average in positions 2 and 6, 81% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.16 (s, 1H), 8.42–8.38 (m, 2H), 8.08 (d, *J* = 9.0 Hz, 9% ^{1}H, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.4, 151.2, 140.0, 130.3 (t, *J* = 25.5 Hz), 124.3. **HRMS** (EI): *m/z*: calcd. For [M]: 153.0390, found 131.0387. **MS** (EI, 70 eV): *m/z* (%): 153 (88.9) M-d_2, 152 (100.0) M-H-d_2, 151 (21.8) M-H-*d*, 137 (2.7), 122 (4.4), 107 (18.0), 106 (18.6), 94 (9.3), 79 (49.7), 67 (7.8), 52 (28.7).

***m*-Nitrobenzaldehyde-2,6-d_2 (22-d_2)**. Procedure B, 2.5 mol% $Mn(CO)_5Br$, 19 hrs. Purification with pentane:ethyl acetate 10:1 → 9:1. 50% Deuterium incorporation in position 2, 90% deuterium incorporation in position 6, 100 % isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.11 (s, 1H), 8.69 (dd, *J* = 2.3, 0.4 Hz, 50% ^{1}H, 1H), 8.49–8.46 (m, 1H), 8.26–8.21 (m, 10% ^{1}H, 1H), 7.79–7.74 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 189.8, 148.9, 137.3, 134.5 (t, *J* = 25.4 Hz), 130.4, 128.7, 124.5. **HRMS** (EI): *m/z*: calcd. For [M-H]: 152.0327, found 152.0324. **MS** (EI, 70 eV): *m/z* (%): 153 (45.7) M-d_2, 152 (100.0) M-H-d_2, 151 (59.1) M-H-*d*, 106 (29.7), 78 (47.1), 52 (27.4).

***o*-Nitrobenzaldehyde-6-*d* (23-*d*)**. Procedure B, 2.5 mol% $Mn(CO)_5Br$, 8 hrs. Purification with pentane:ethyl acetate 9:1. 95 % Deuterium incorporation in position 6, 77 % isolated yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.41 (d, *J* = 0.7 Hz, 1H), 8.11 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.96–7.93 (m, 5% ^{1}H, 1H), 7.81–7.74 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 188.3, 149.7, 134.1, 133.8, 131.4, 129.8, 129.5 (t, *J* = 20.6 Hz), 124.6.

Indole-3-carboxaldehyde-2-*d* (24-*d*). Procedure B, 16 hrs. Purification with DCM:acetone 20:1. 84% Deuterium incorporation in position 2, 82% isolated yield. **^{1}H NMR (300 MHz, CD_3OD)** δ 9.88 (s, 1H), 8.17–8.14 (m, 1H), 8.09 (s, 16% ^{1}H, 1H), 7.49–7.46 (m, 1H), 7.30–7.21 (m, 2H). **^{13}C NMR (75 MHz, CD_3OD)** δ 187.4, 139.3 (t, *J* = 28.9 Hz), 138.9, 125.7, 125.0, 123.6, 122.4, 120.0, 133.1. **HRMS** (ESI-TOF): *m/z*: calcd. For $[M+H]^+$: 147.0668, found 147.0673.

Indole-6-carboxaldehyde-3,7-d_2 (25-d_2). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 2:1. 91% Deuterium incorporation in position 3, 10% deuterium incorporation in position 5, 92% deuterium incorporation in position 7, 89% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.45 (br s, 5% ^{1}H, 1H), 9.87 (s, 1H), 7.85 (s, 8% ^{1}H, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 90% ^{1}H, 1H), 7.37 (s, 1H), 6.49 (d, *J* = 2.9 Hz, 9% ^{1}H, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 193.6, 135.4, 133.3, 130.2, 129.5, 120.7, 120.3, 114.8, 102.5. **HRMS** (EI): *m/z*: calcd. for [M]: 147.0648, found 147.0646. **MS** (EI, 70 eV): *m/z* (%): 148 (37.6) M-d_3, 147 (100.0) M-d_2, 146 (77.3) M-*d*, 145 (13.4) M, 119 (26.8), 118 (53.5), 91 (23.4).

Thiophene-3-carboxaldehyde-d_2 (26-d_2). Procedure B, 2.5 mol% $Mn(CO)_5Br$, 17 hrs. Purification with pentane:ethyl acetate 20:1 → 10:1. 94% Deuterium incorporation in position 2, 39% deuterium incorporation in position 4, 66% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.92 (s, 1H), 9.12 (dd, *J* = 2.9, 1.1 Hz, 6% ^{1}H, 1H), 7.53 (d, *J* = 5.1 Hz, 61% ^{1}H, 1H), 7.37–7.35 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 185.0, 143.0, 136.6 (t, *J* = 28.0 Hz), 127.3, 125.5.

Benzothiophene-3-carboxaldehyde-2-*d* (27-*d*). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 10:1. 96% Deuterium incorporation in position 2, 100% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.13 (s, 1H), 8.68 (ddd, *J* = 8.0, 1.6, 0.7 Hz, 1H), 8.29 (s, 4% ^{1}H, 1H), 7.87 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.54–7.42 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 185.5, 143.1 (t, *J* = 27.9 Hz), 140.5, 136.4, 135.2, 126.2, 126.2, 124.9, 122.5. **HRMS** (EI): *m/z*: calcd. for [M]: 163.0181, found 163.0186. **MS** (EI, 70 eV): *m/z* (%): 163 (89.4) M-*d*, 162 (100.0) M, 134 (23.3), 90 (31.3).

3-Formyl-6-methyl-chromone-d_2 (28-d_2). Procedure A, 10 mol% $Mn(CO)_5Br$, 16 hrs. Purification with pentane:ethyl acetate 4:1. 72% Deuterium incorporation in position 2, 68% formyl D, 48% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.38 (s, 32% ^{1}H, 1H), 8.52 (m, 28% ^{1}H, 1H), 8.07 (m, 1H), 7.57–7.53 (m, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 188.9, 176.2, 160.7, 154.6, 137.1, 136.1, 125.7, 125.1, 120.2, 118.5, 21.1. **HRMS** (EI): *m/z*: calcd. For $[M]^-$: 189.0531, found 189.0531.

Cinnamaldehyde-2-*d* (29-*d*). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 20:1 → 10:1. 60% Deuterium incorporation in position 2, 100% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.72–9.70 (m, 1H), 7.59–7.54 (m, 2H), 7.51–7.41 (m, 4H), 6.72 (dd, *J* = 16.0, 7.7 Hz, 40% ^{1}H, 1H). **HRMS** (EI): *m/z*: calcd. For $[M]^-$: 133.0632, found 133.0634. **MS** (EI, 70 eV): *m/z* (%): 133 (46.6) M-*d*, 132 (100.0) M, 131 (48.5), 105 (20.0), 104 (45.1), 103 (30.9), 78 (40.1), 77 (28.8), 51 (20.1).

Acetocinnamone-3-*d* (30-*d*). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 9:1. 64% Deuterium incorporation in the olefinic α position, 90% deuterium incorporation in the α-carbonyl position, 84% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.55–7.47 (m, 3H), 7.40–7.36 (m, 3H), 6.70 (d, *J* = 16.3 Hz, 36% ^{1}H, 1H), 2.36–2.32 (m, 10% ^{1}H, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 198.6, 143.5, 134.5, 130.6, 129.0, 128.3, 127.3. **HRMS** (EI): *m/z*: calcd. For [M+H]: 148.0867, found 148.0866. **MS** (EI, 70 eV): *m/z* (%): 150 (53.9) M-d_3, 149 (94.1) M-d_2, 148 (48.6) M-*d*, 132 (100.0), 131 (50.6), 104 (90.1), 103 (56.0), 78 (26.1), 77 (40.2), 51 (23.1).

Citral-3,4,6-d_6 (31-*d*). Procedure A, 16 hrs. Purification with pentane:ethyl acetate 20:1. 89% Deuterium incorporation in the olefinic α position, 97% deuterium incorporation in the allylic methyl group, 65% deuterium incorporation in the allylic methylene group, 41% isolated yield. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.99–9.87 (m, 1H), 5.88–5.85 (m, 11% ^{1}H, 1H), 5.12–5.02 (m, 1H), 2.60–2.51 (m, 3% ^{1}H, 3H), 2.22–2.16 (35% ^{1}H, 6H), 1.67 (m, 3H), 1.60–1.58 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.5, 190.9, 163.8, 133.8, 133.0, 127.7, 122.7, 122.4, 41.7, 32.1, 27.0, 25.8, 25.7, 17.8. The ratio of *E*/*Z* isomers was conserved during the reaction. **HRMS** (EI): *m/z*: calcd. For [M-H]: 157.1494, found 157.1477.

5 Unsuccessful substrates

Free hydroxy groups in the benzaldehyde moiety, terminal alkynes, heterocycles with the aldehyde moiety α to the heteroatom and pyridine were not tolerated and either led to recovery of undeuterated starting material (***Figure 1***) or, in some cases, to decomposition (***Figure 2***). Further, the methodology could not be extended to ketones (***Figure 1***).

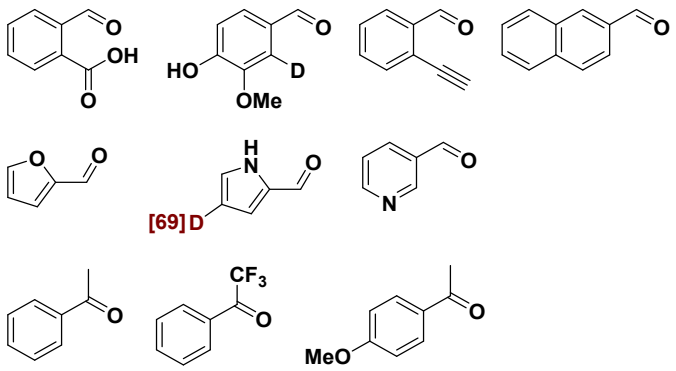


Figure 1 List of substrates that were not deuterated under the reaction conditions.

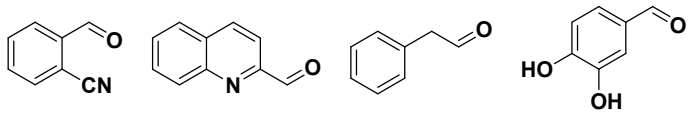


Figure 2 List of substrates that decomposed under the reaction conditions.

Some other substrates only afforded low deuteration levels and are listed in ***Figure 3***.

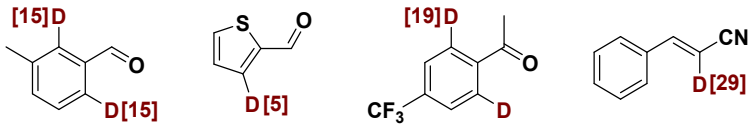
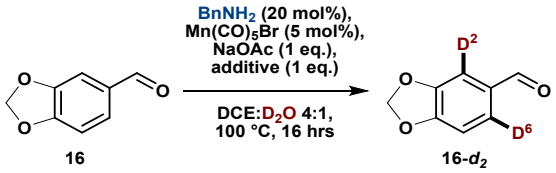


Figure 3 List of poorly reactive substrates.

6 Functional group tolerance

The functional group tolerance of the reaction was evaluated using General Procedure A with piperonal as the substrate and equimolar additives (***Table 7***).

Table 7 Test of functional group tolerance.

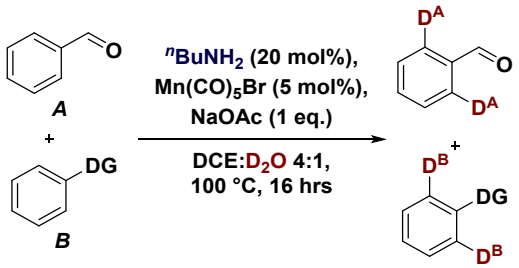


Entry	additive	D^2 [%]	D^6 [%]
1	none	95	39
2	4-(trifluoromethyl)styrene	90	40
3	acetophenone	93	26
4	phenylboronic acid	91	68
5	phenol	93	43
6	phenylsulfonamide	91	7
7	*N*-methylbenzamide	94	35
8	propyl benzoate	93	35
9	phenyl acetate	59	6
10	pyridine	26	0
11	1-ethynyl-4-(trifluoromethyl)benzene	9	0

7 Competition experiments with other directing groups

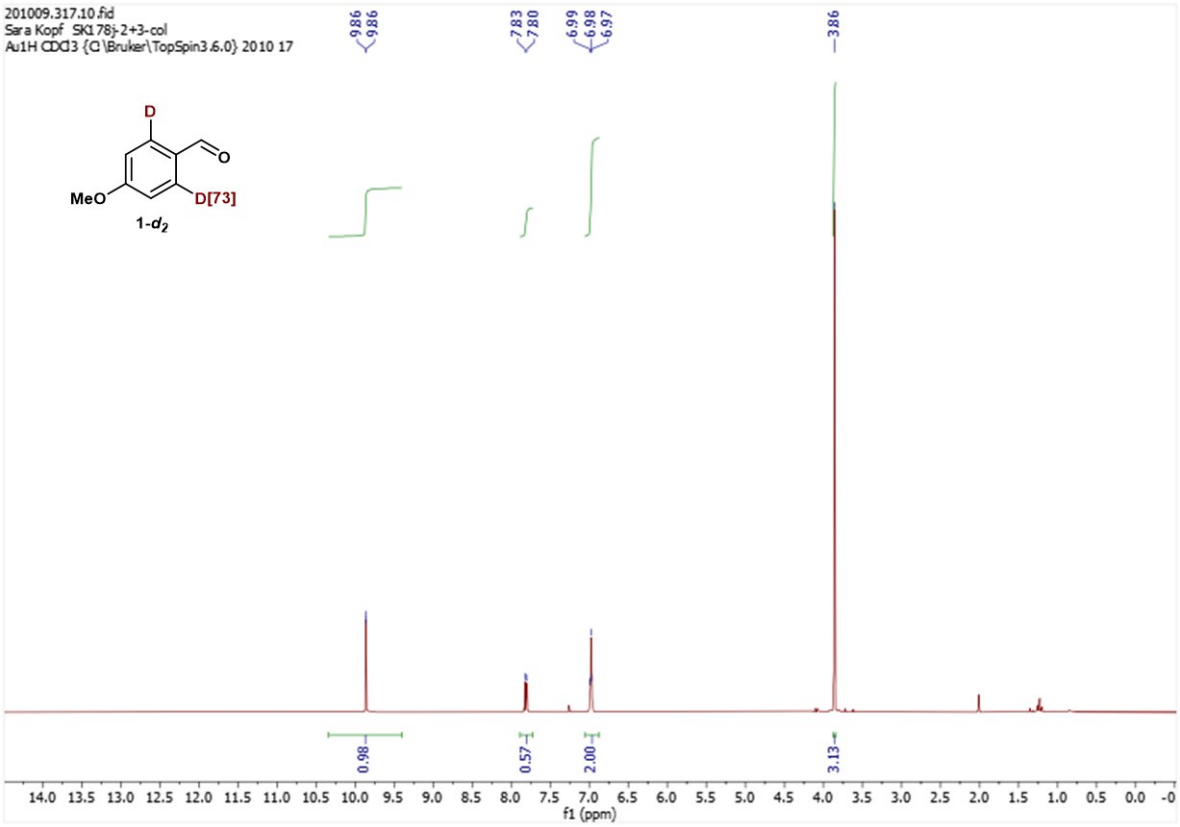
Following General Procedure A and using benzaldehyde as the substrate, equimolar amounts of substrates containing other potential directing groups were added to the reaction mixture in order to compare them in intermolecular competition experiments (***Table 8***).

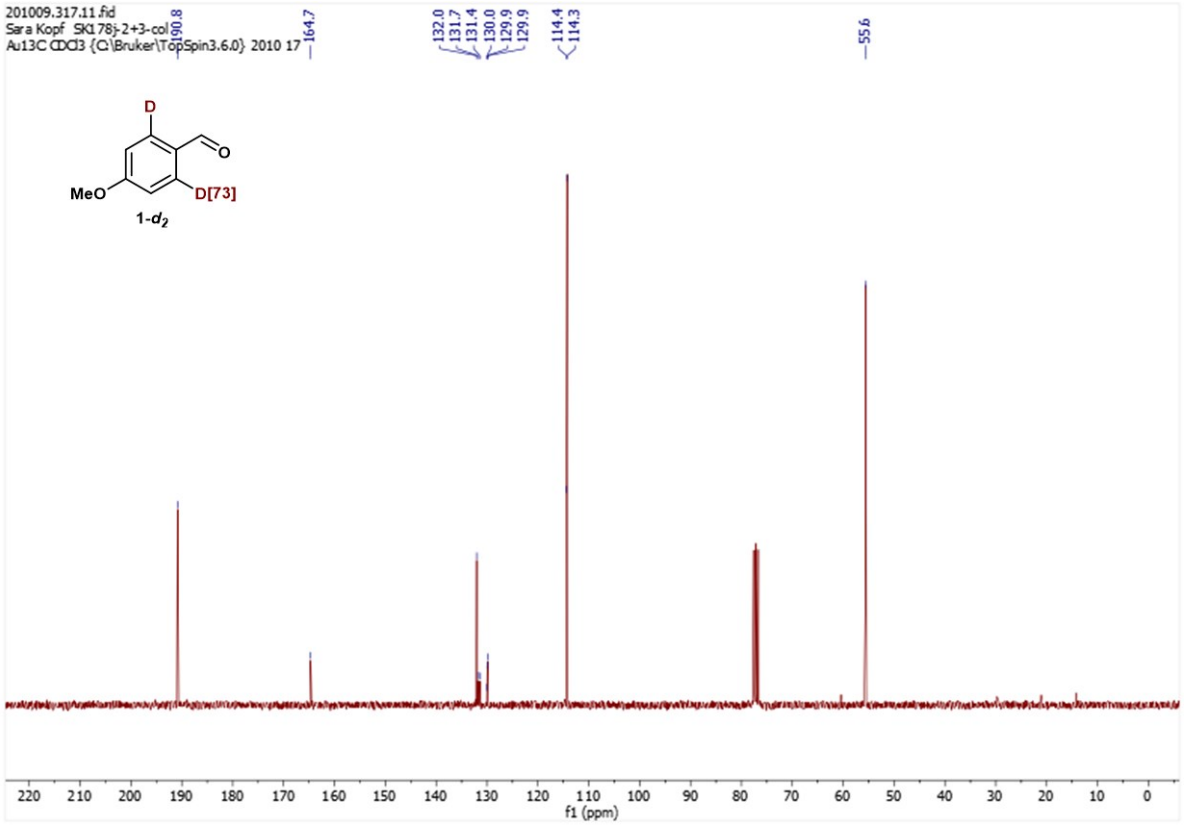
Table 8 Intermolecular competition experiments with other directing groups.



Entry	DG	D^A [%]	D^B [%]
1	none	50	-
2	2-pyridine	45	91
3	1-pyrazole	35	39
4	2-imidazole	27	55
5	*N*-methylamide	46	0
6	propyl ester	46	0
7	acetate	14	0

8 NMR spectra

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132.0
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130.0
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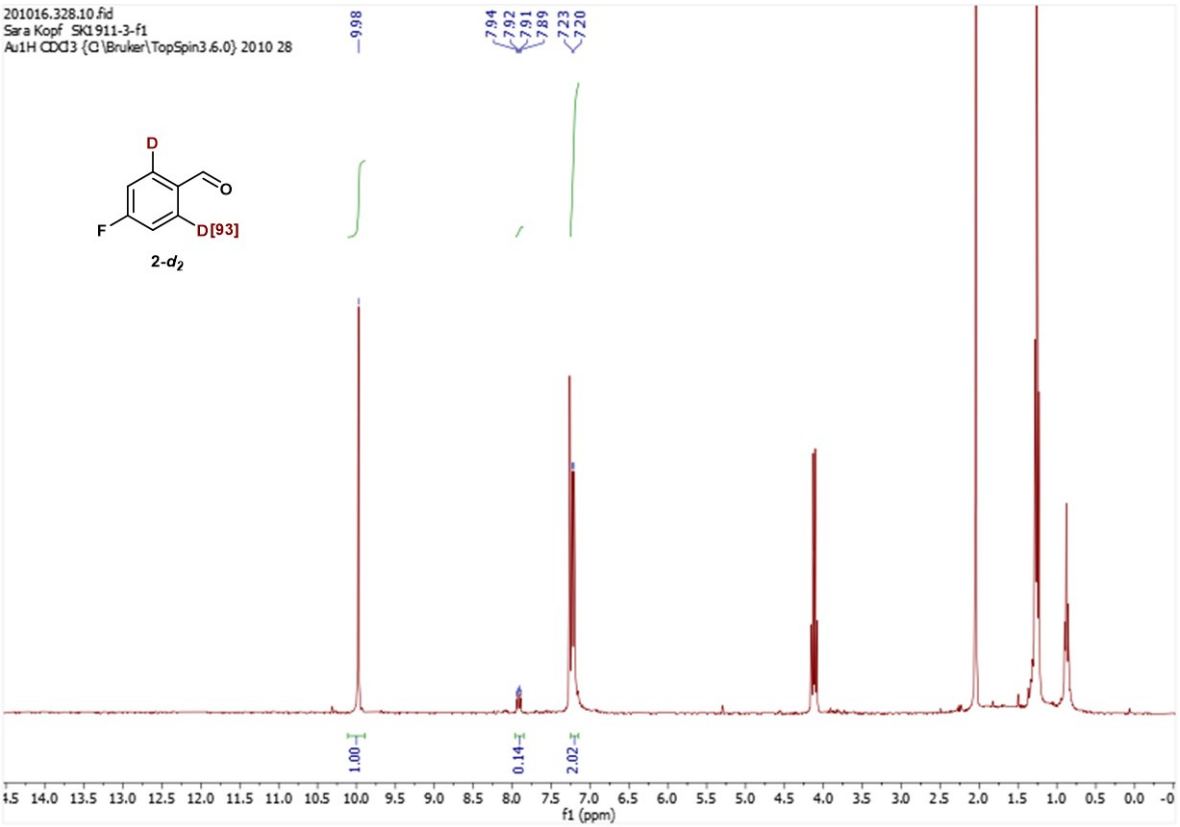
114.3
55.6
D
O
MeO
D[73]
1-d_2
f1 (ppm)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D
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F
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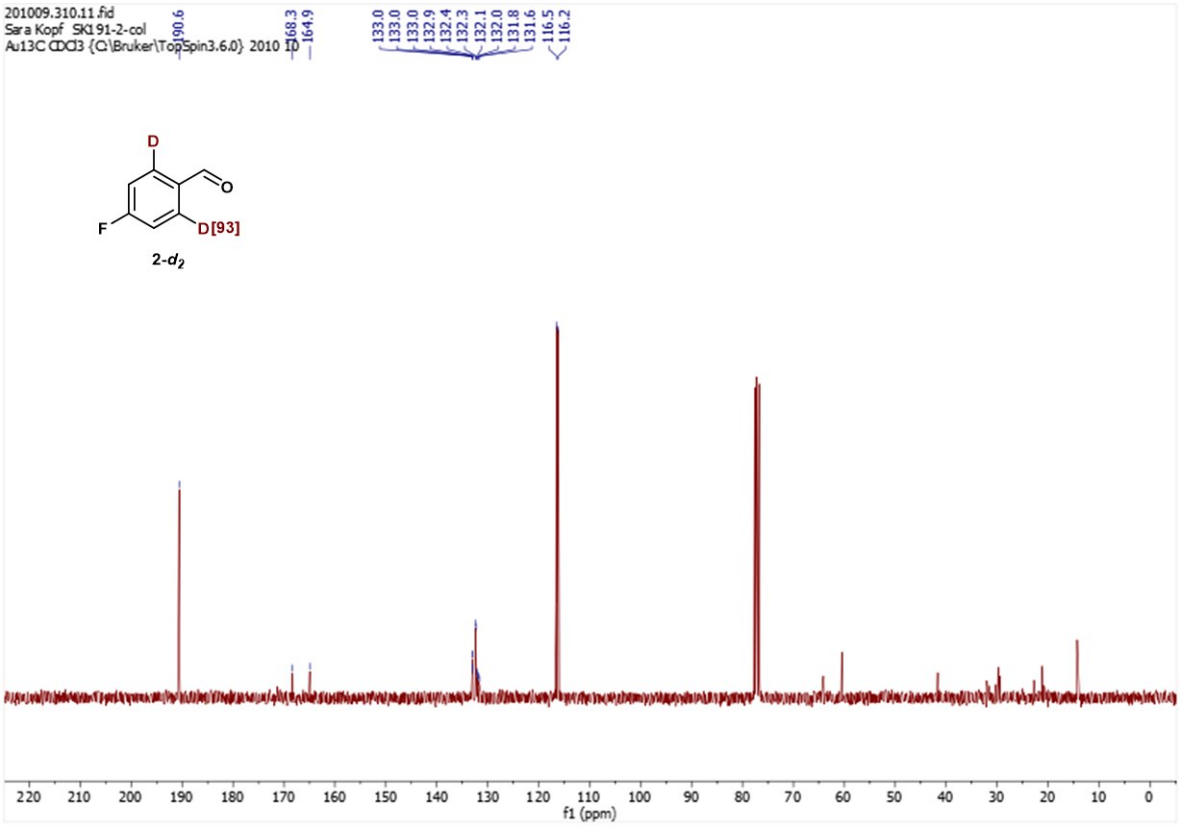
f1 (ppm)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O
F
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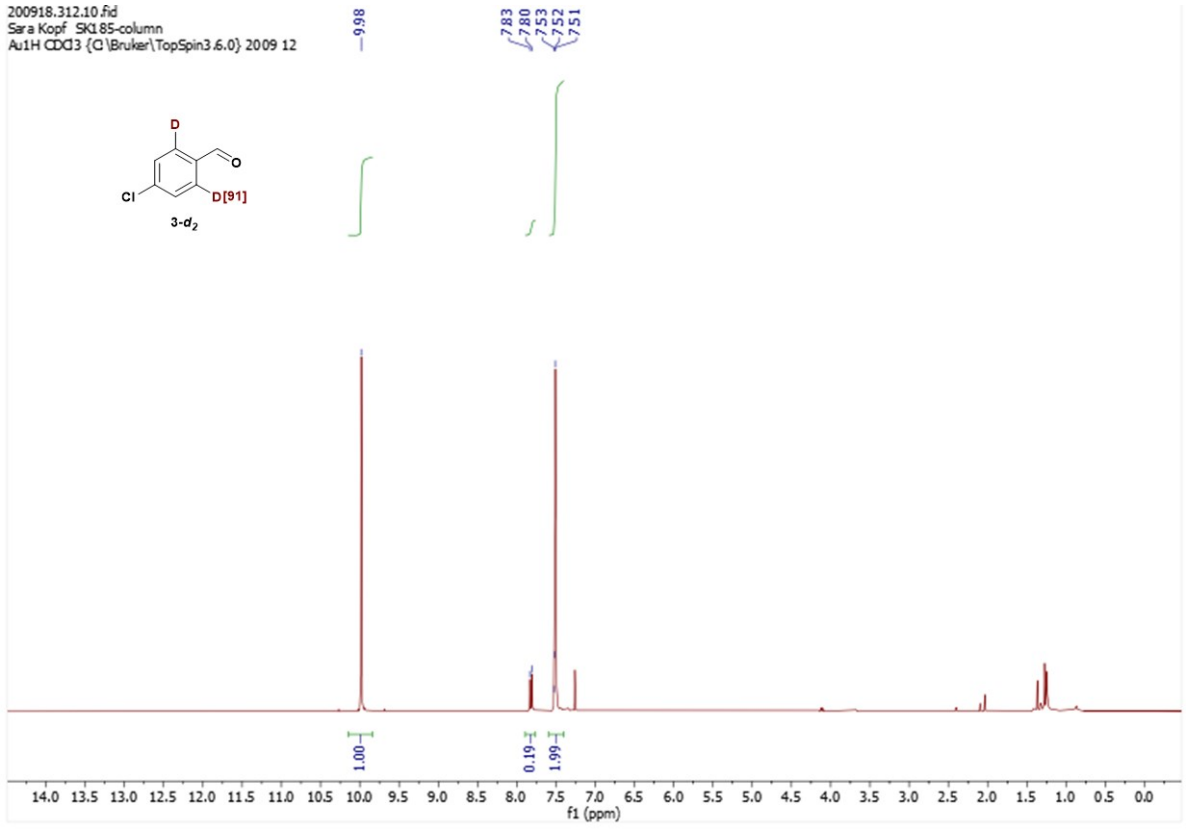
2-d_2
f1 (ppm)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7.52
7.51
D
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Cl
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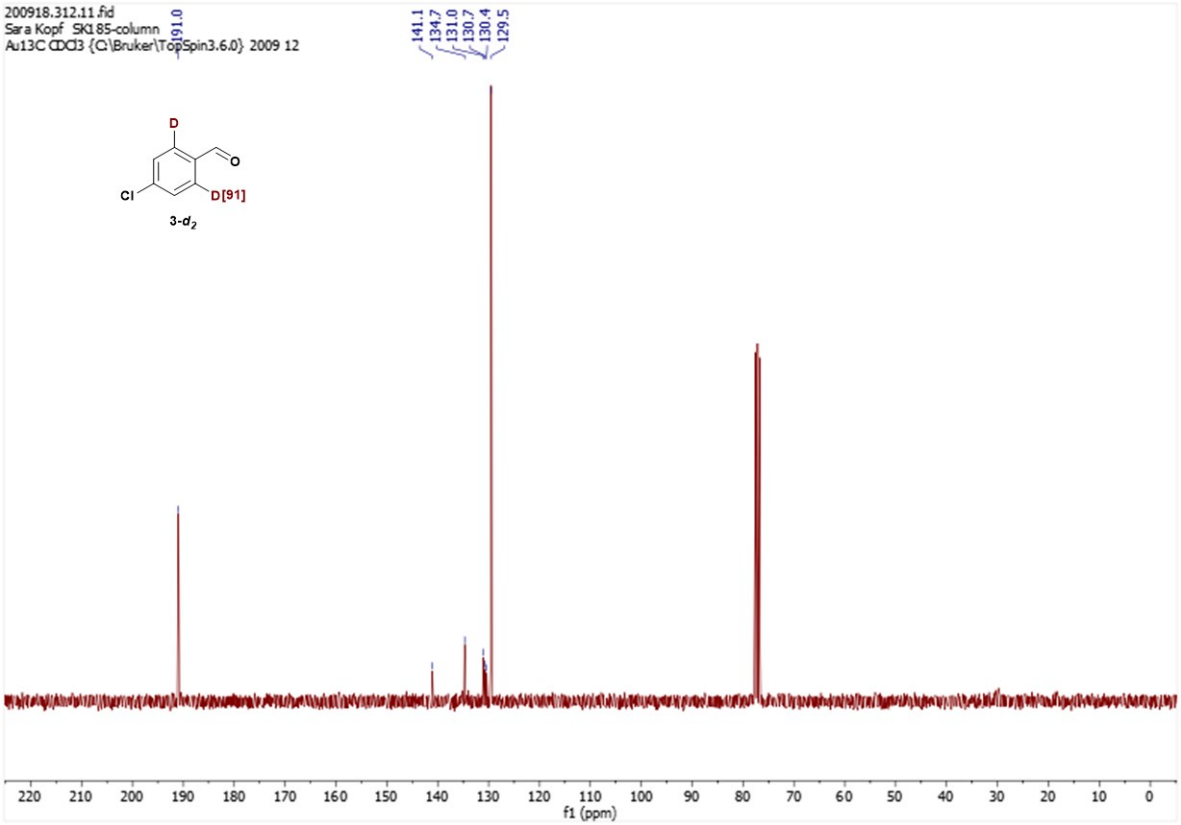
1.99
f1 (ppm)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Cl
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3-d_2
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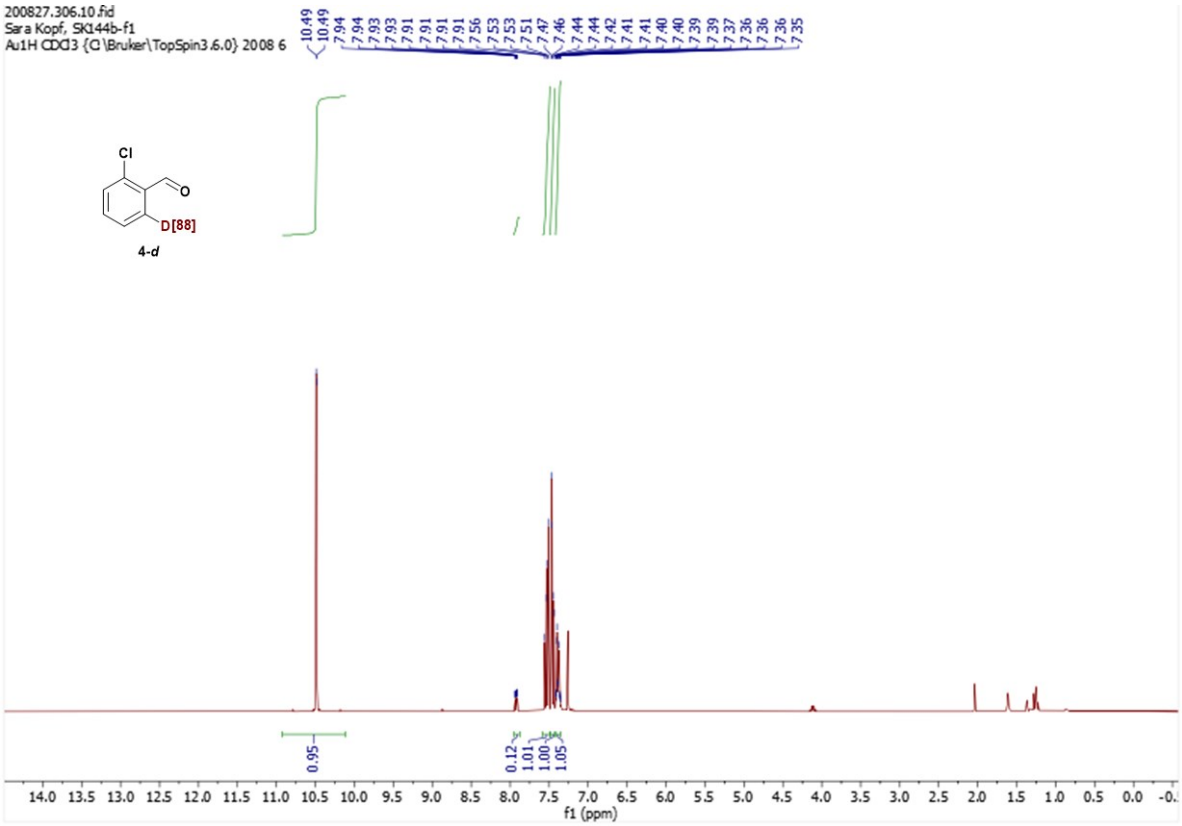
f1 (ppm)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7.35
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O
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1.01
1.00
1.05
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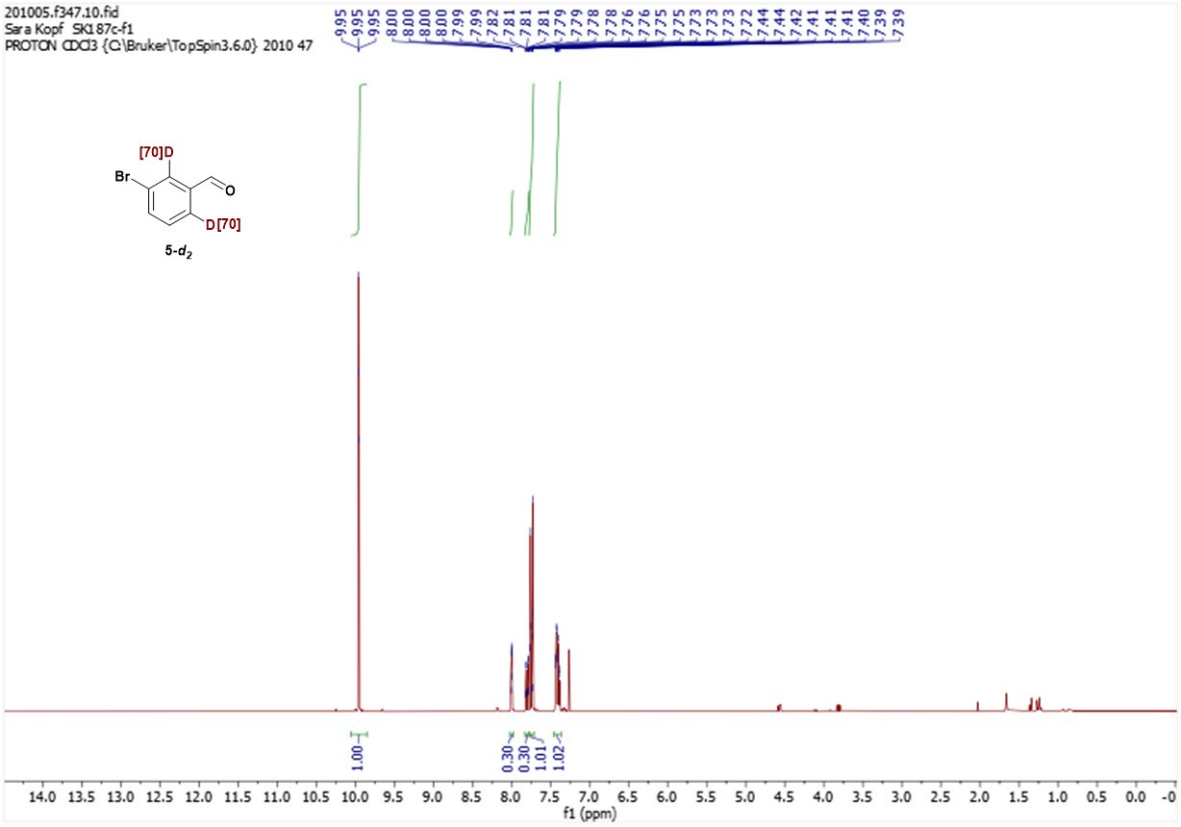
f1 (ppm)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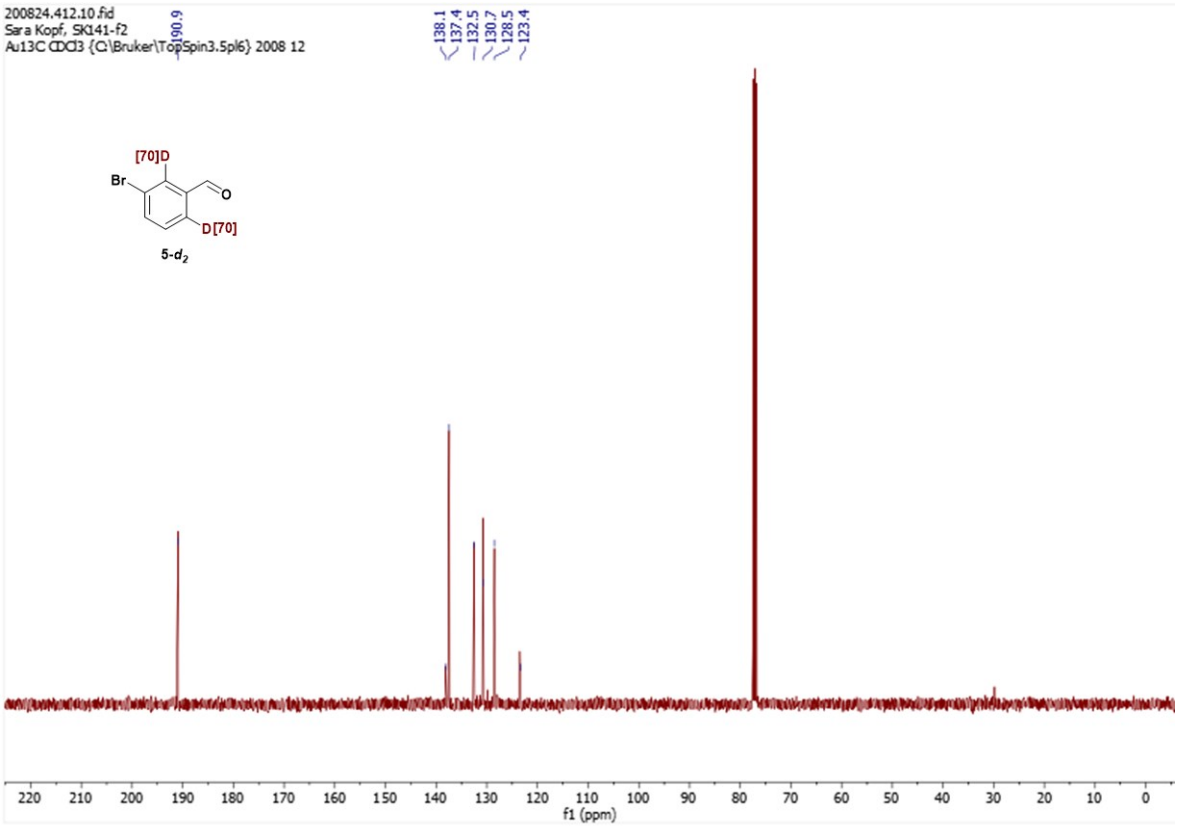
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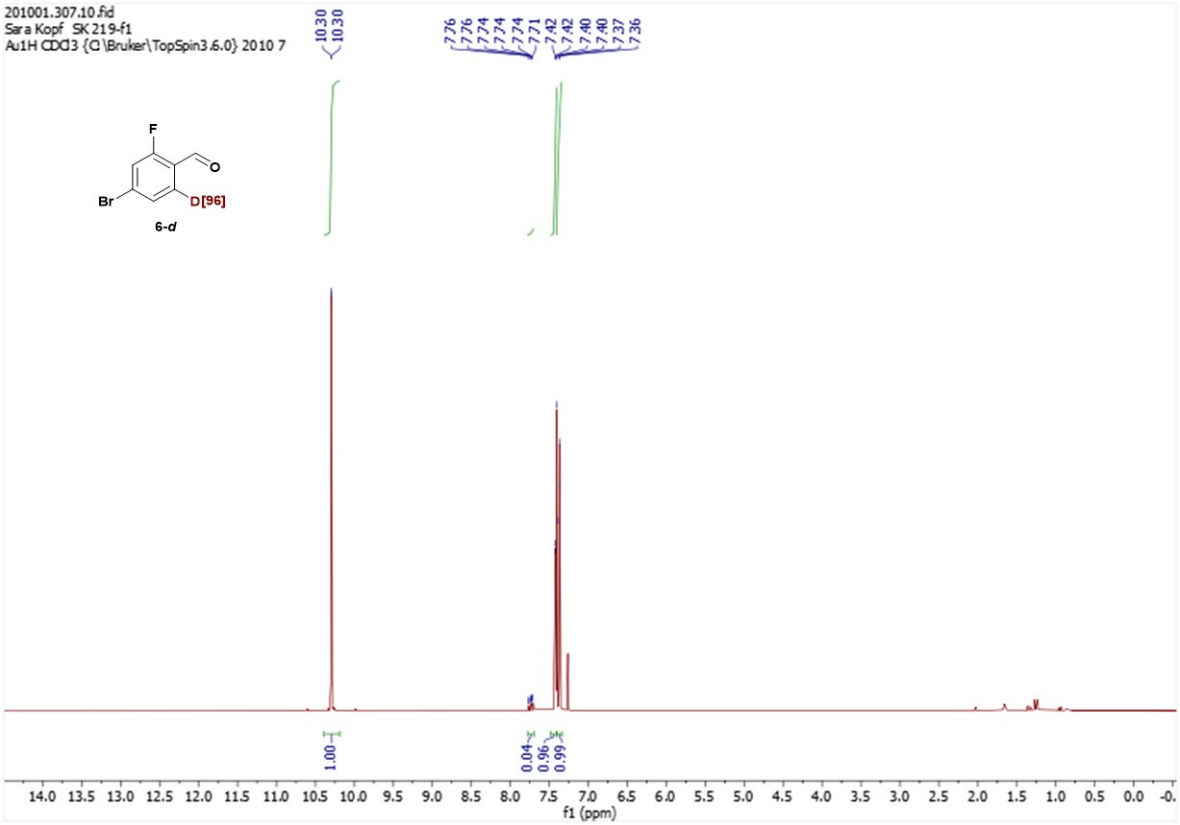
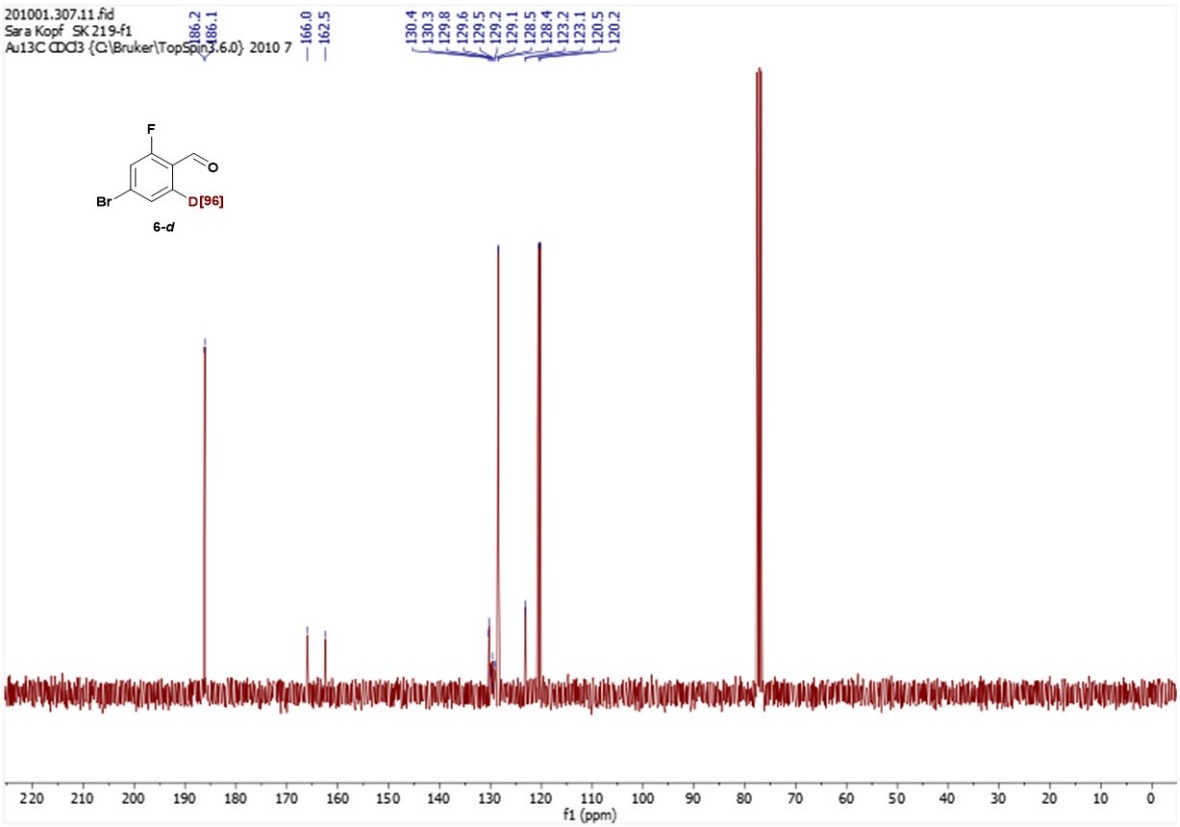
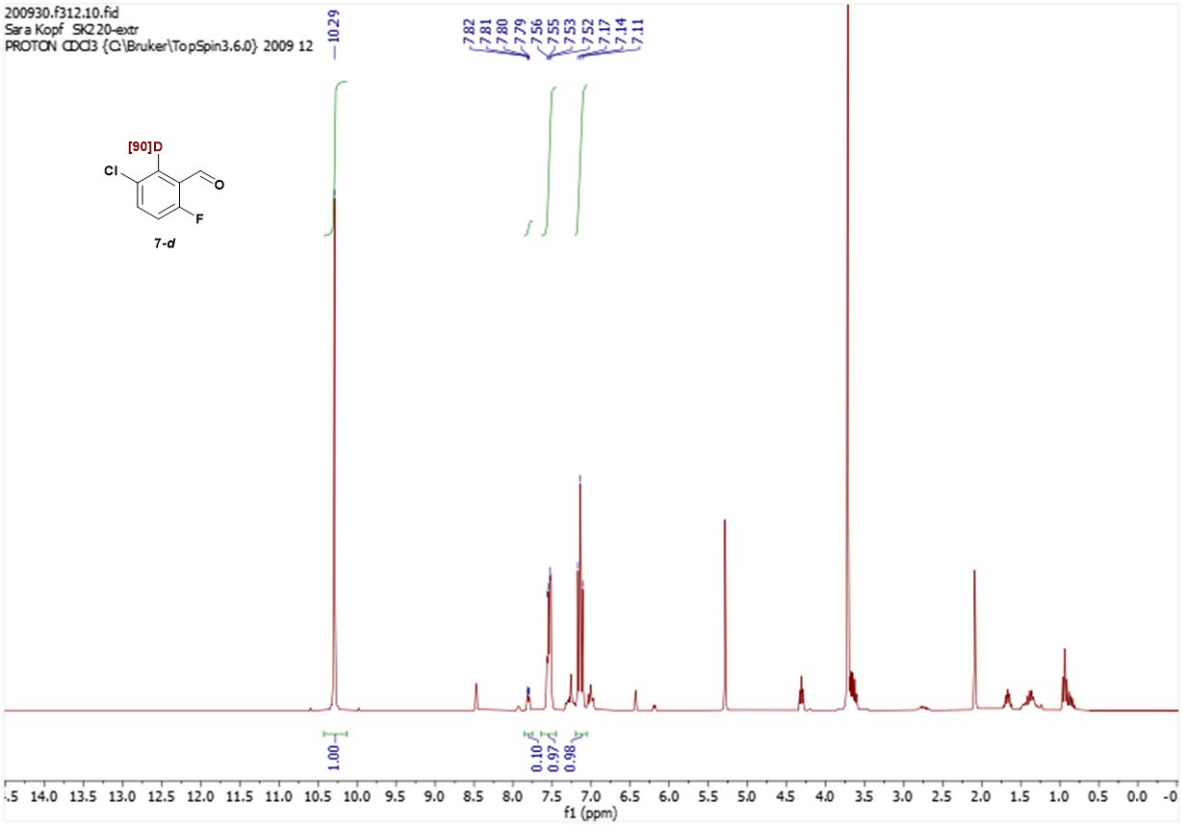
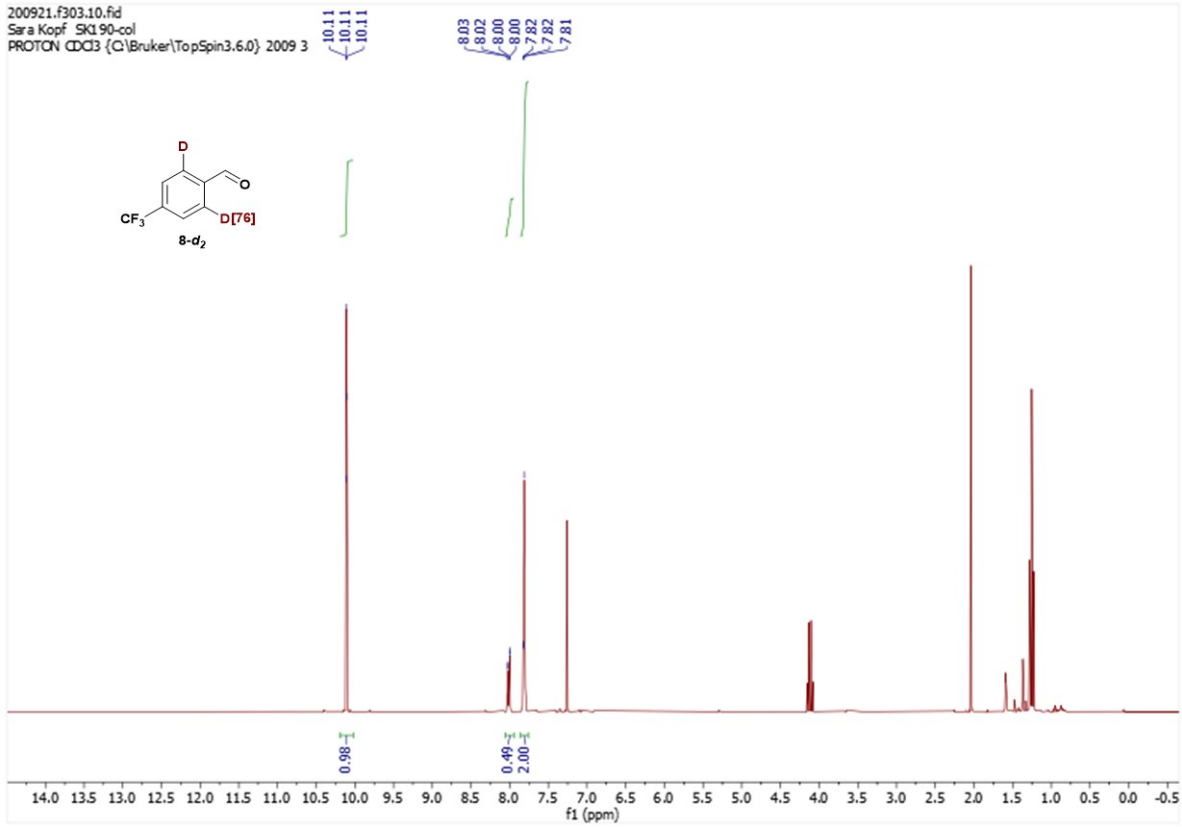
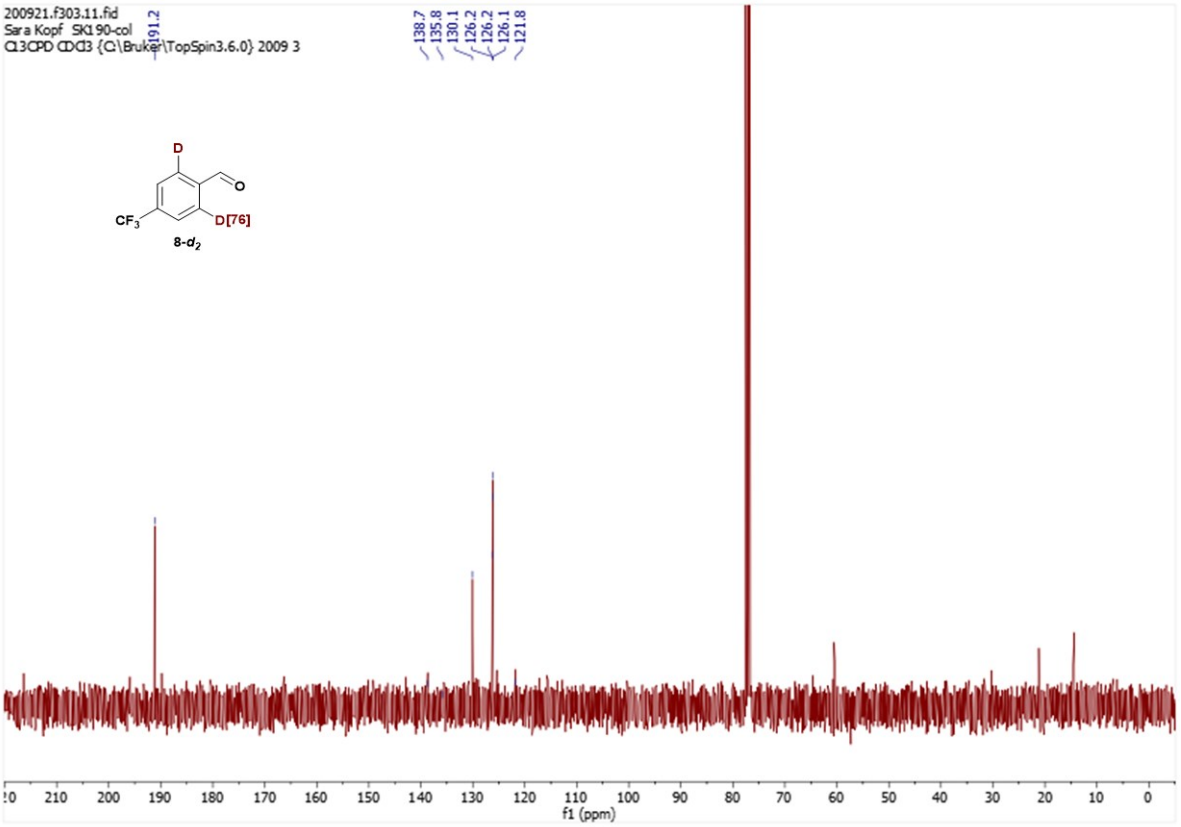
5-d_2
f1 (ppm)

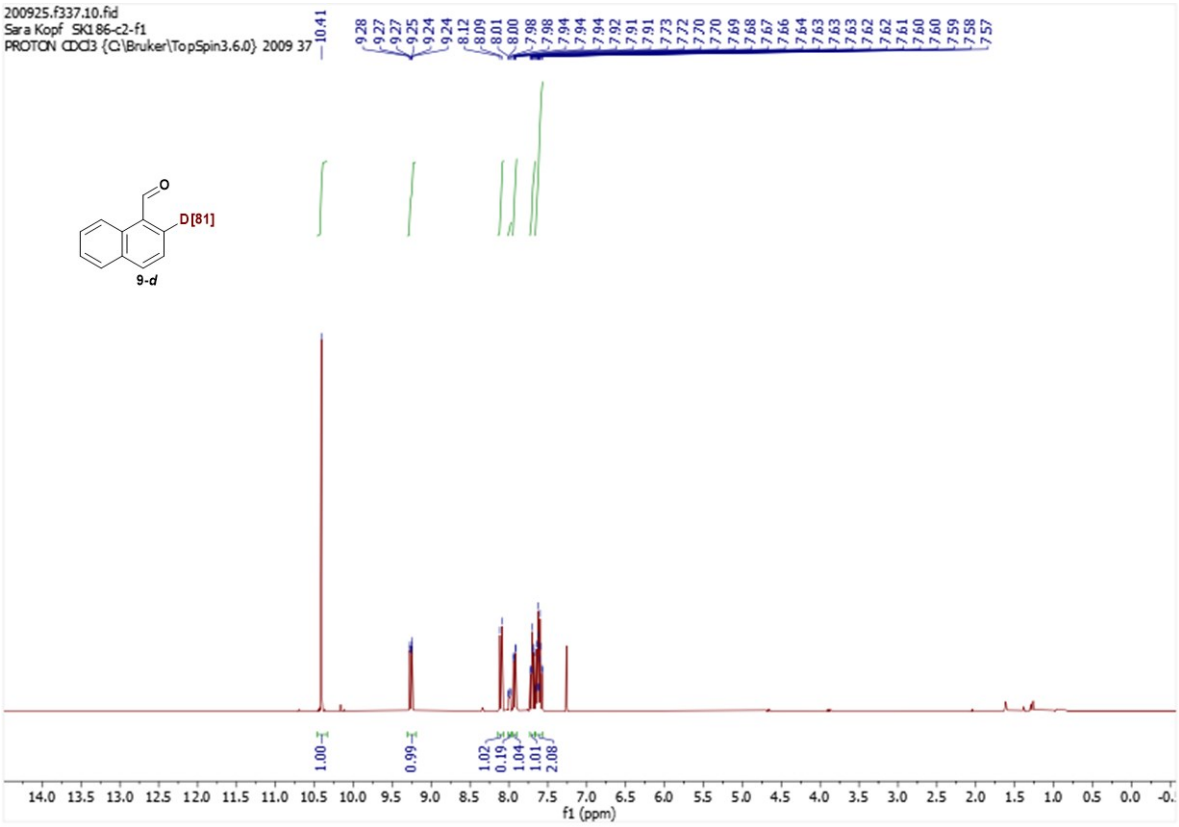

201001.307.10.fid
Sara Kopf SK 219-f1
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 7
10.30
10.30
7.76
7.76
7.74
7.74
7.74
7.71
7.42
7.42
7.40
7.40
7.37
7.36
F
O
Br
D[96]
6-d
1.00
0.04
0.96
0.99
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

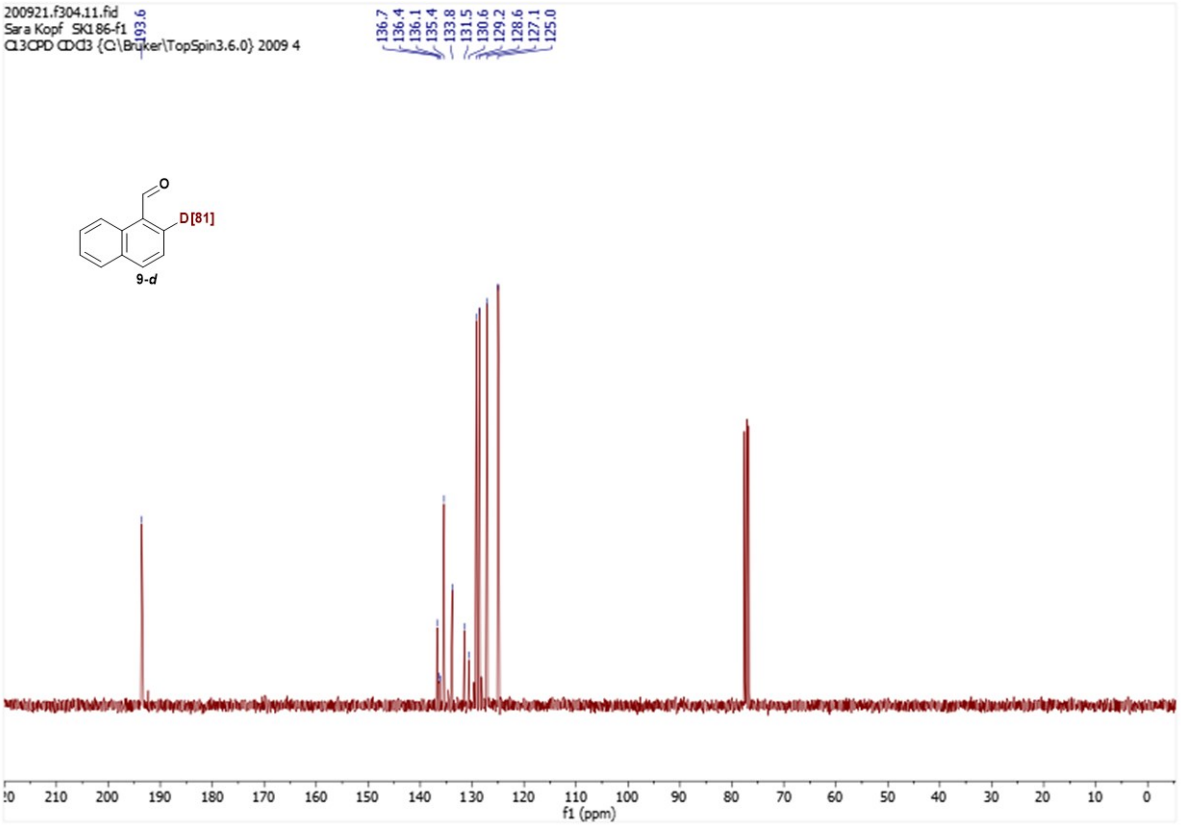

201001.307.11.fid
Sara Kopf SK 219-f1
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 7
186.2
186.1
166.0
162.5
130.4
130.3
129.8
129.6
129.5
129.2
129.1
128.5
128.4
123.2
123.1
120.5
120.2
F
O
Br
D[96]
6-d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

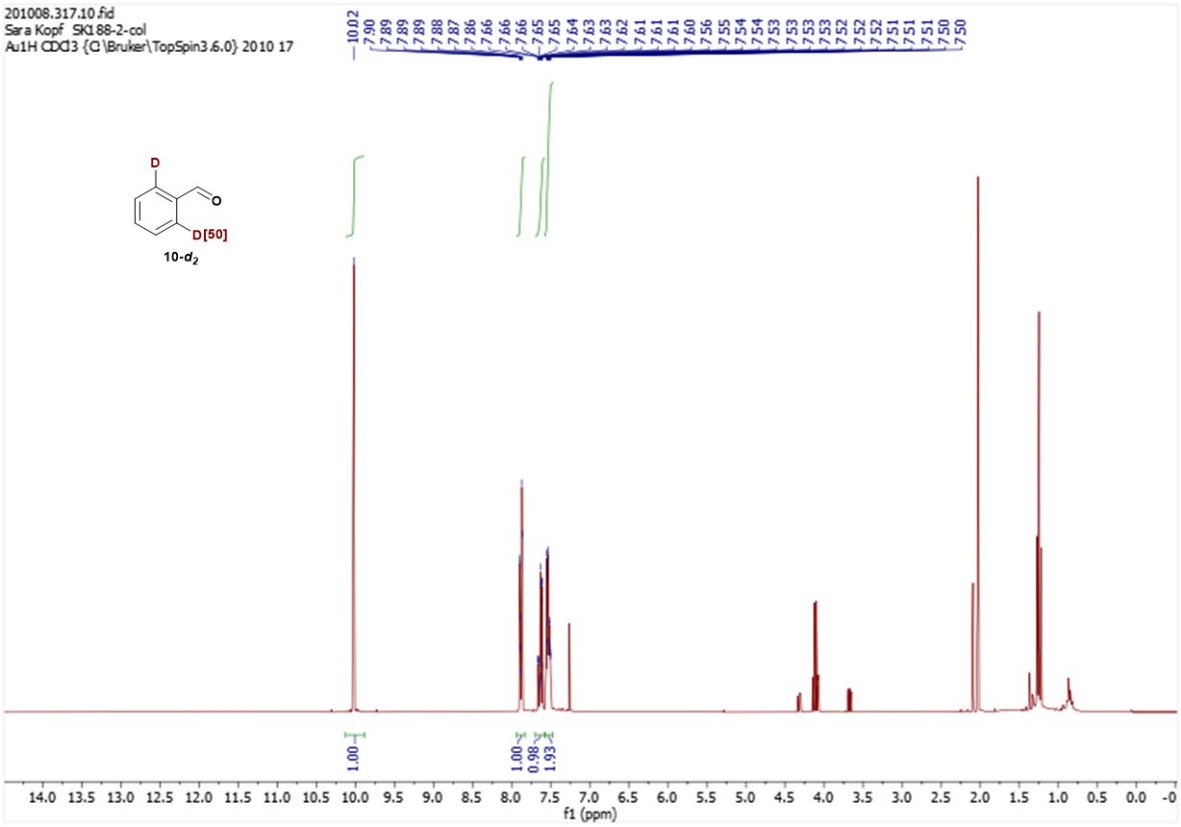

200930.f312.10.fid
Sara Kopf SK220-extr
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 12
10.29
7.82
7.81
7.80
7.79
7.56
7.55
7.53
7.52
7.17
7.14
7.11
[90]D
Cl
O
F
7-d
1.00
0.10
0.97
0.98
f1 (ppm)

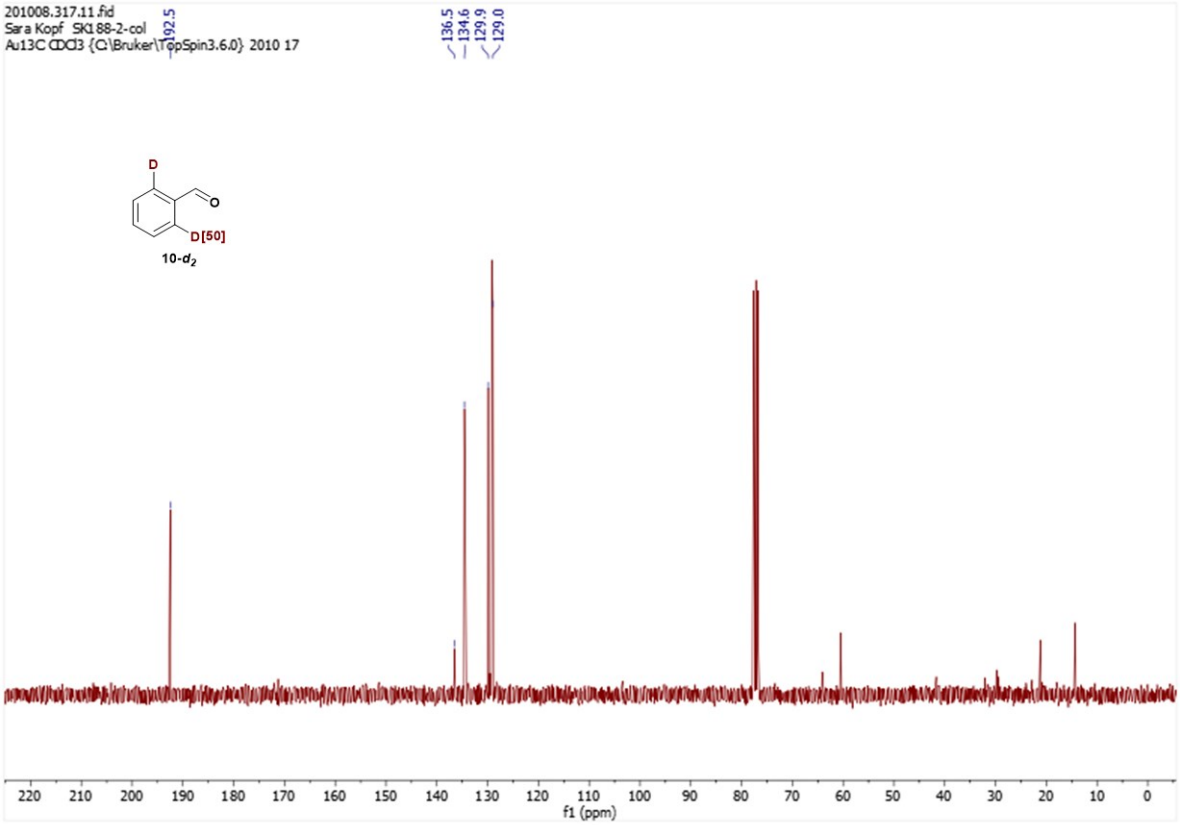

200921.f303.10.fid
Sara Kopf SK190-col
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 3
10.11
10.11
10.11
8.03
8.02
8.00
8.00
7.82
7.82
7.81
D
O
CF3
D[76]
8-d2
0.98
0.49
2.00
f1 (ppm)

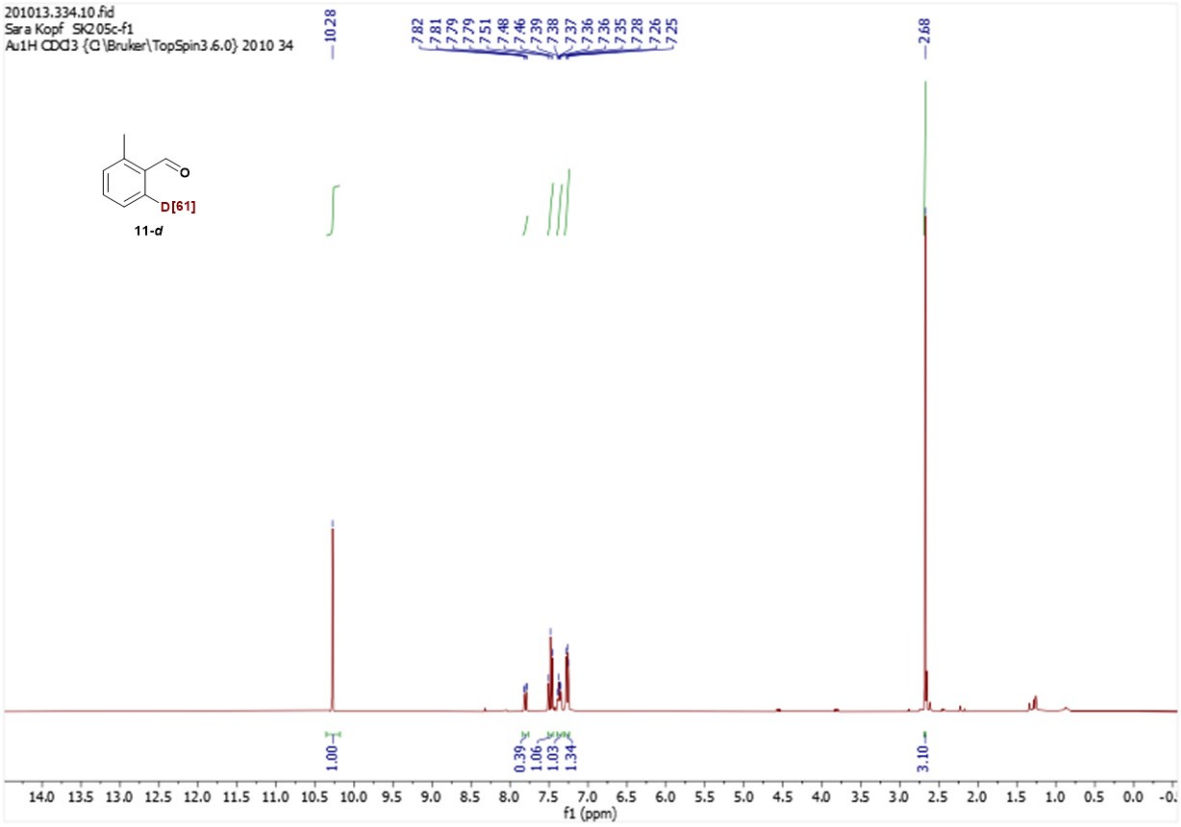

200921.f303.11.fid
Sara Kopf SK190-col
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 3
191.2
138.7
135.8
130.1
126.2
126.2
126.1
121.8
D
O
CF3
D[76]
8-d2
f1 (ppm)

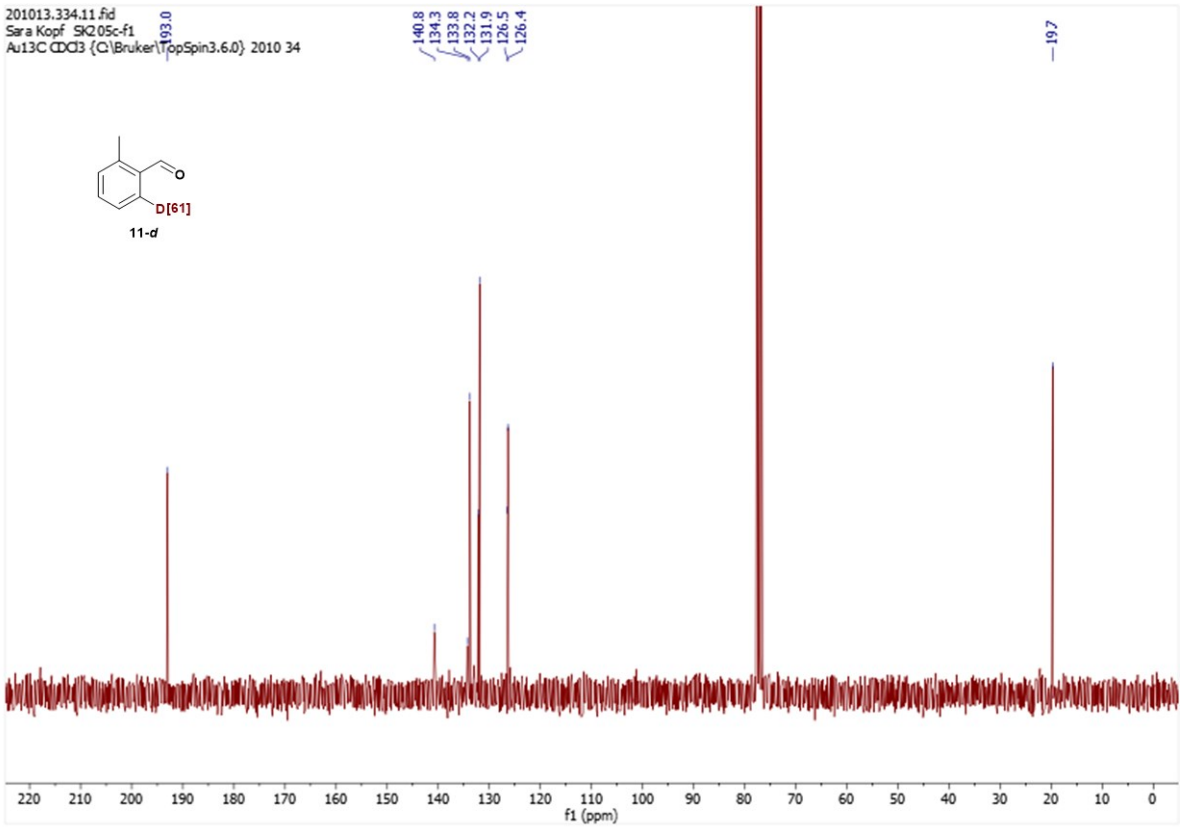

200925.f337.10.fid
Sara Kopf SK186-c2-f1
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 37
10.41
9.28
9.27
9.27
9.25
9.24
9.24
8.12
8.09
8.01
8.00
7.98
7.98
7.94
7.94
7.94
7.92
7.91
7.91
7.73
7.72
7.70
7.70
7.69
7.68
7.67
7.66
7.64
7.63
7.63
7.62
7.62
7.61
7.60
7.60
7.59
7.58
7.57
O
D[81]
9-d
1.00
0.99
1.02
0.19
1.04
1.01
2.08
f1 (ppm)

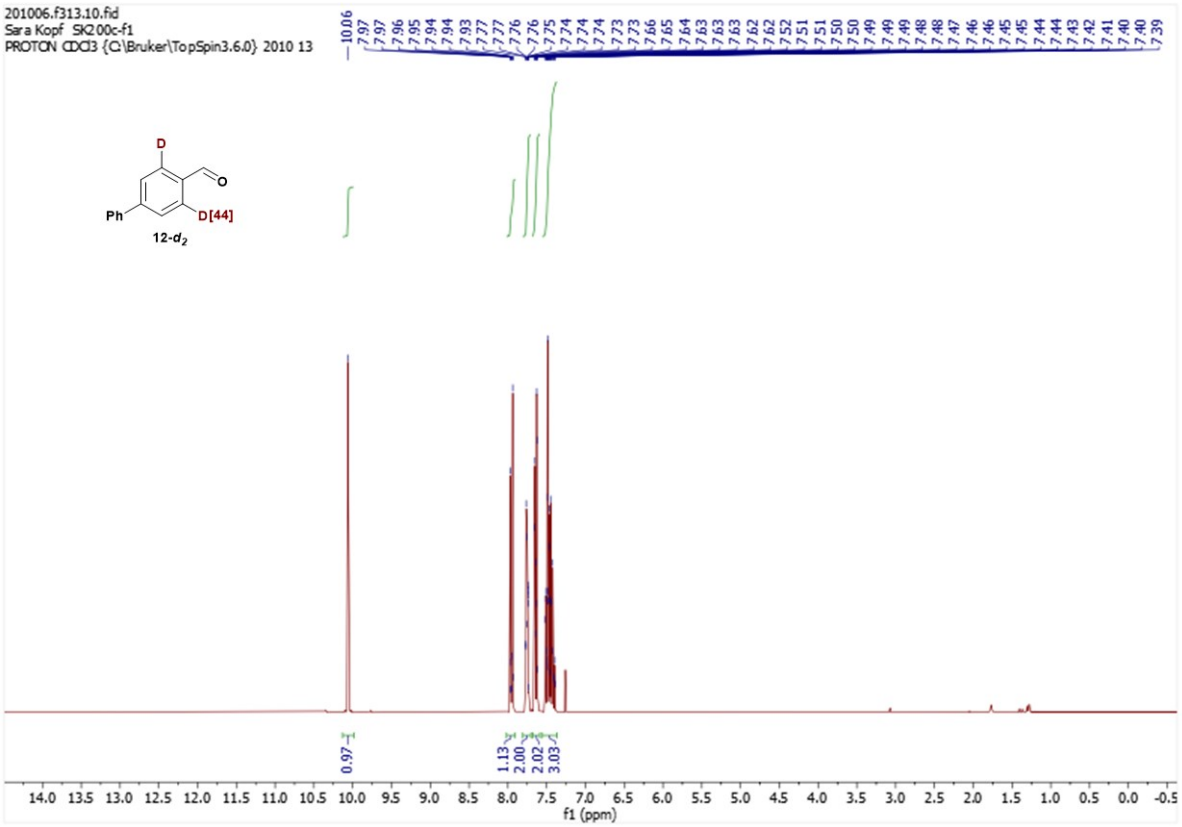

200921.f304.11.fid
Sara Kopf SK186-f1
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 4
193.6
136.7
136.4
136.1
135.4
133.8
131.5
130.6
129.2
128.6
127.1
125.0
O
D[81]
9-d
f1 (ppm)

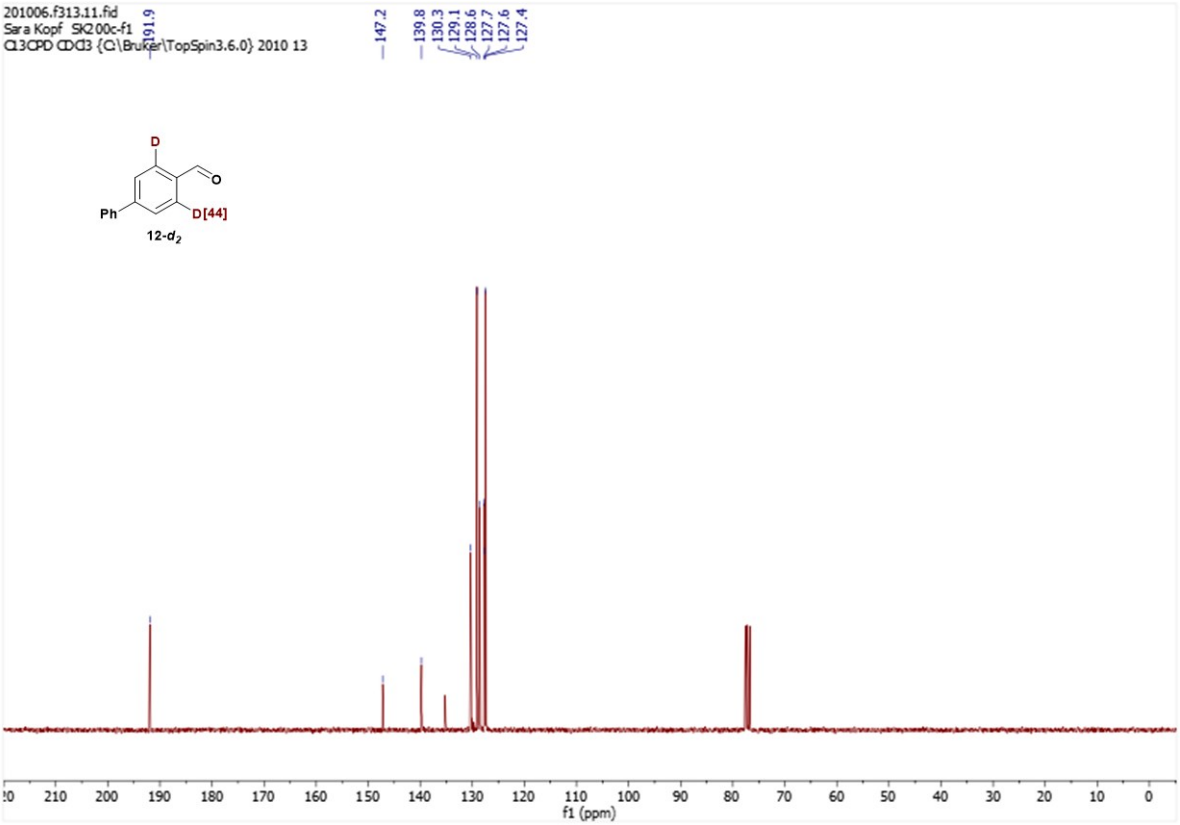

201008.317.10.fid
Sara Kopf SK188-2-col
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 17
10.02
7.90
7.89
7.89
7.89
7.88
7.87
7.86
7.66
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.61
7.60
7.56
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.51
7.50
7.50
D
O
D[50]
10-d2
1.00
1.00
0.98
1.93
f1 (ppm)

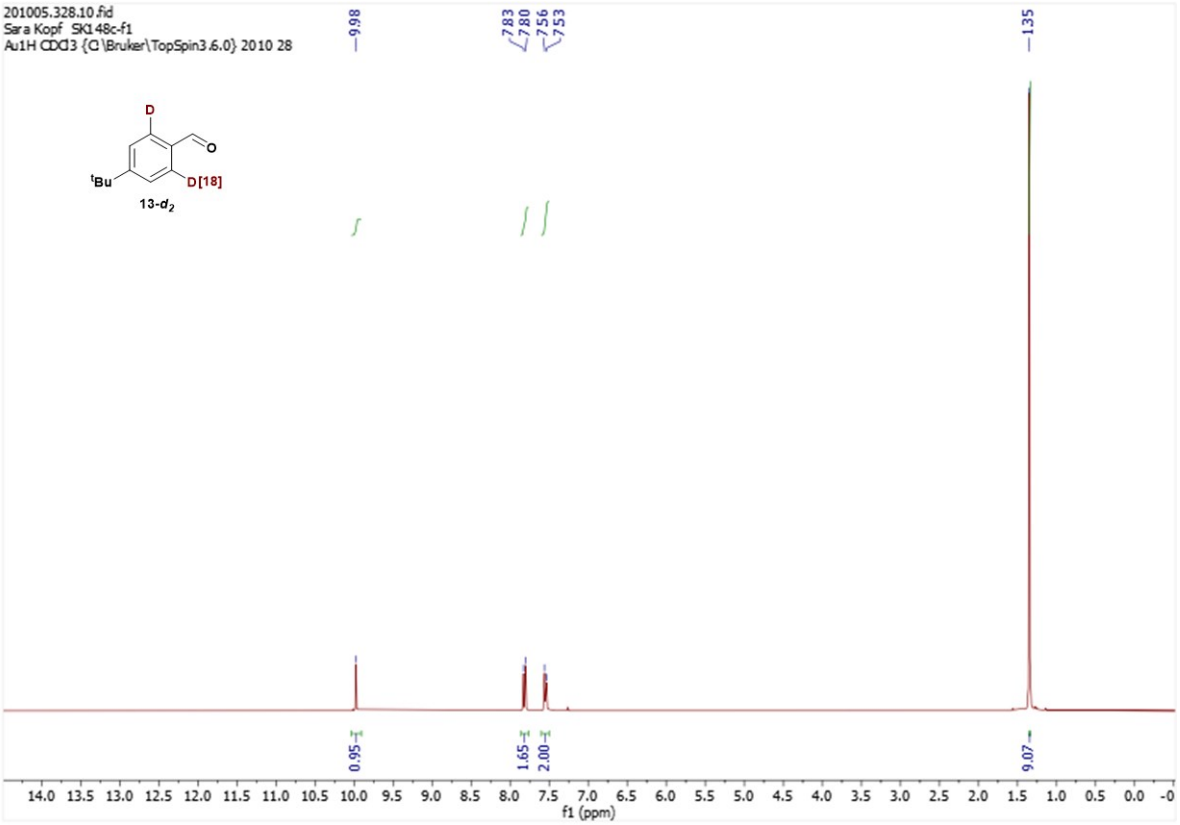

201008.317.11.fid
Sara Kopf SK188-2-col
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 17
192.5
136.5
134.6
129.9
129.0
D
O
D[50]
10-d_2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

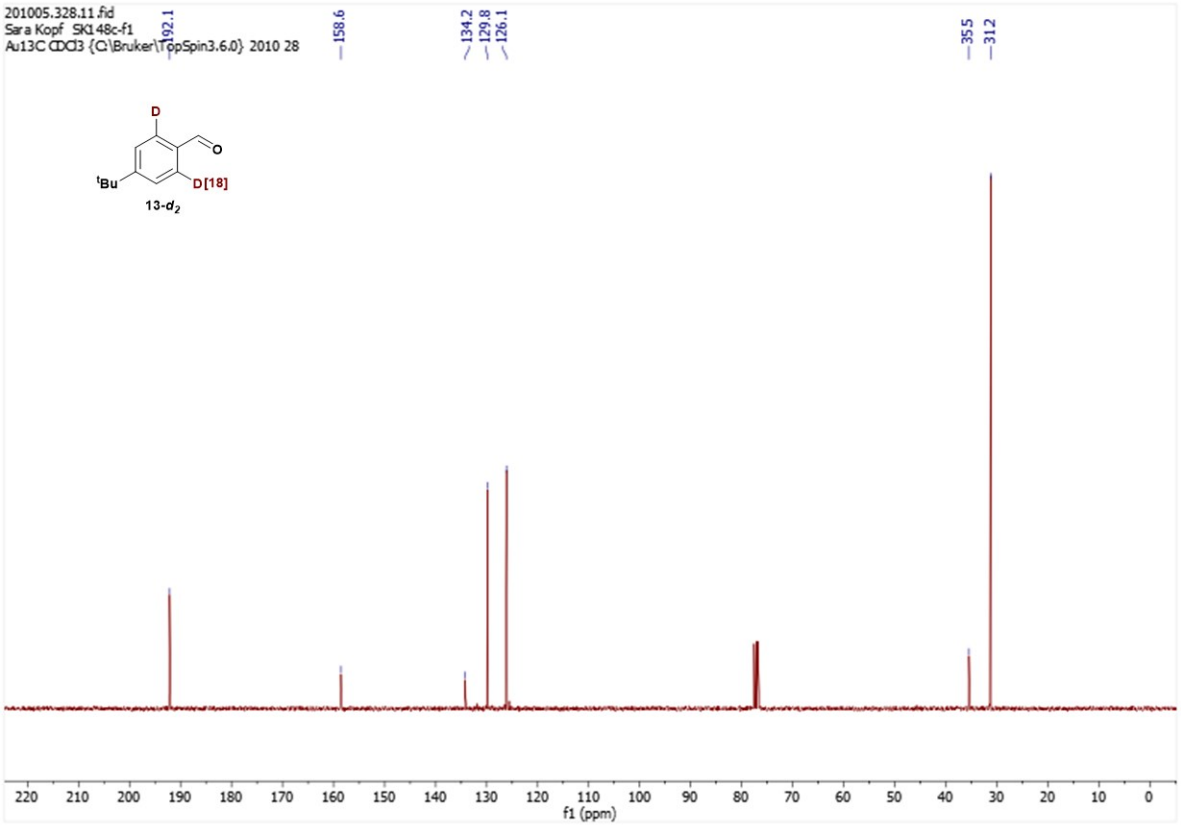

201013.334.10.fid
Sara Kopf SK205c-f1
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 34
10.28
7.82
7.81
7.79
7.79
7.51
7.48
7.46
7.39
7.38
7.37
7.36
7.36
7.35
7.28
7.26
7.25
2.68
O
D[61]
11-d
1.00
0.39
1.06
1.03
1.34
3.10
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

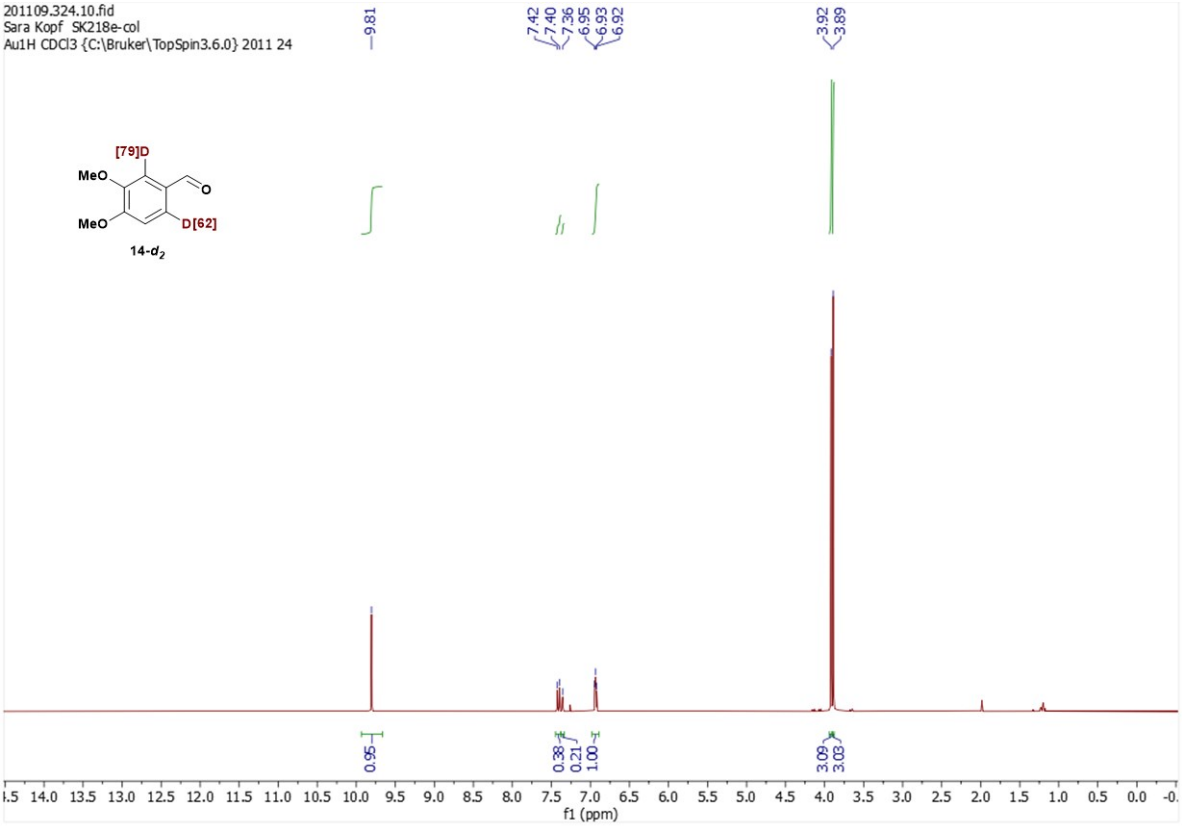

201013.334.11.fid
Sara Kopf SK205c-f1
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 34
193.0
140.8
134.3
133.8
132.2
131.9
126.5
126.4
19.7
D[61]
11-d
f1 (ppm)

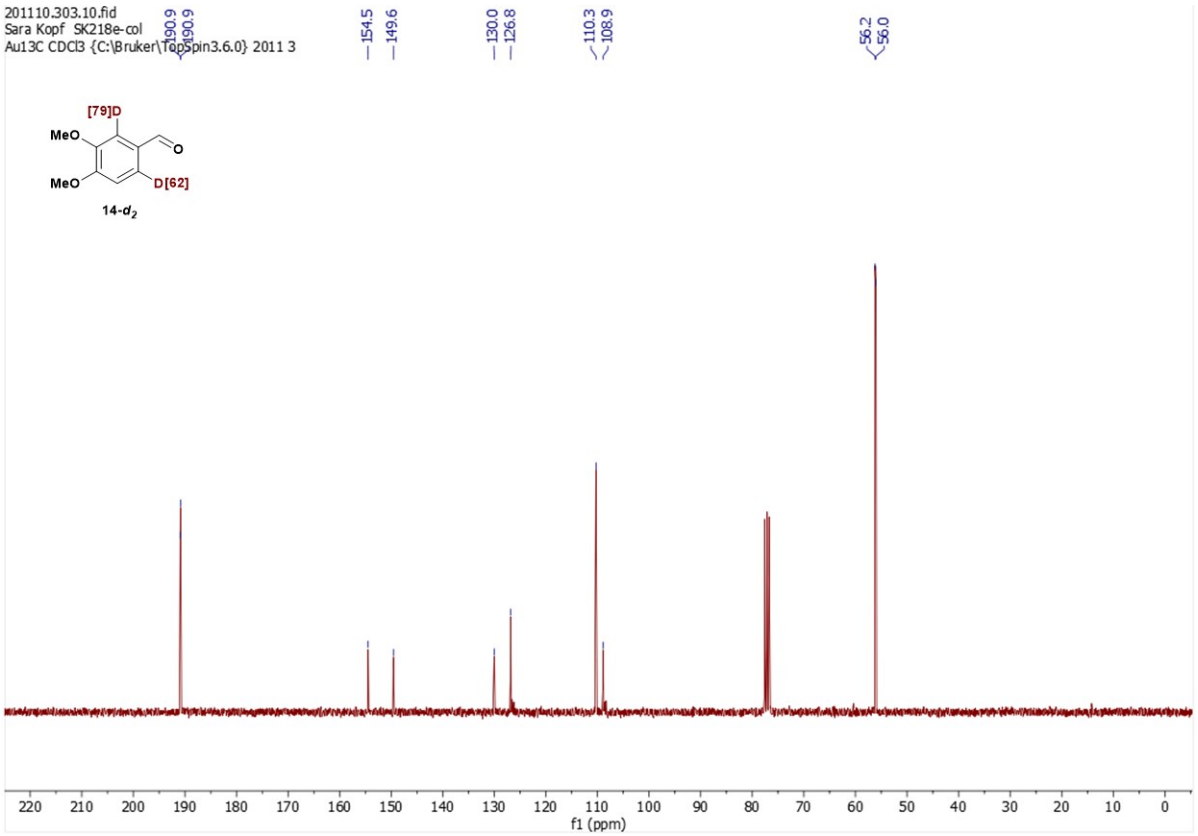

201006.f313.10.fid
Sara Kopf SK200c-f1
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 13
10.06
D
Ph
D[44]
12-d2
0.97
1.13
2.00
2.02
3.03
f1 (ppm)

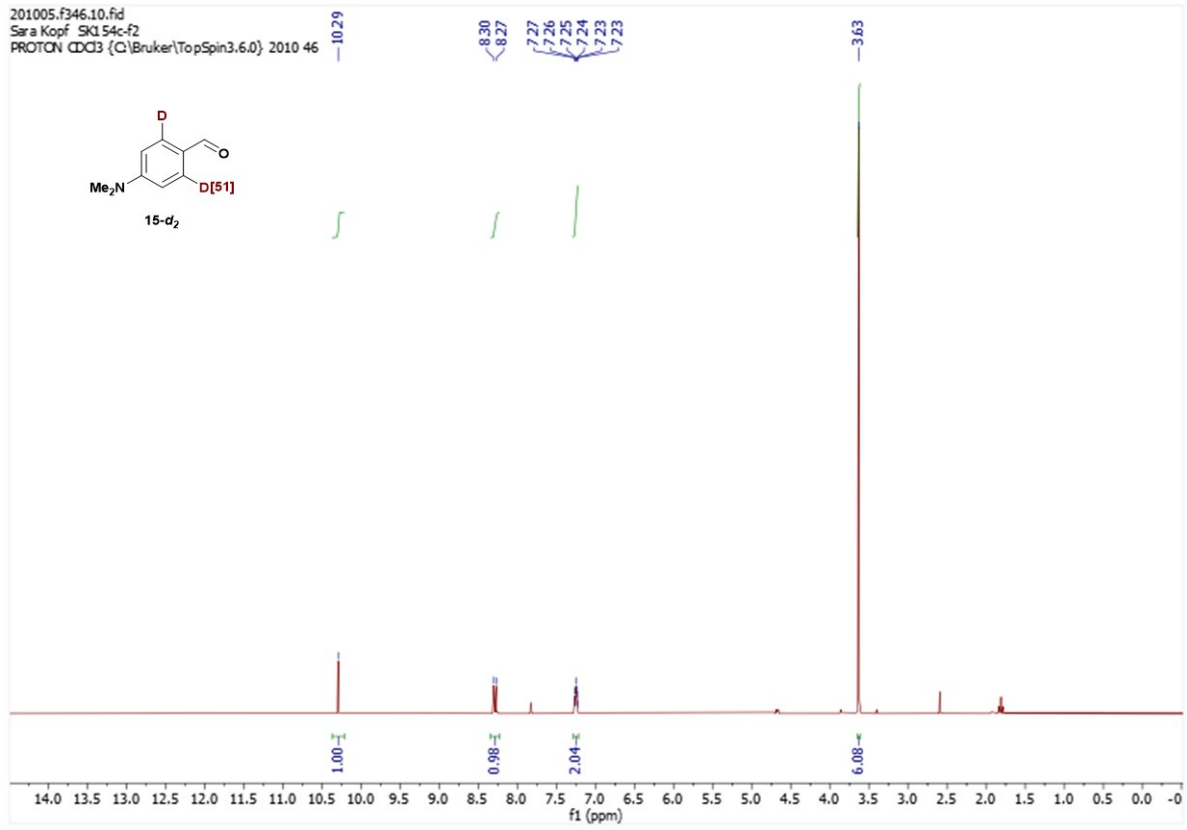

201006.f313.11.fid
Sara Kopf SK200c-f1
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 13
191.9
147.2
139.8
130.3
129.1
128.6
127.7
127.6
127.4
D
O
Ph
D[44]
12-d_2
f1 (ppm)

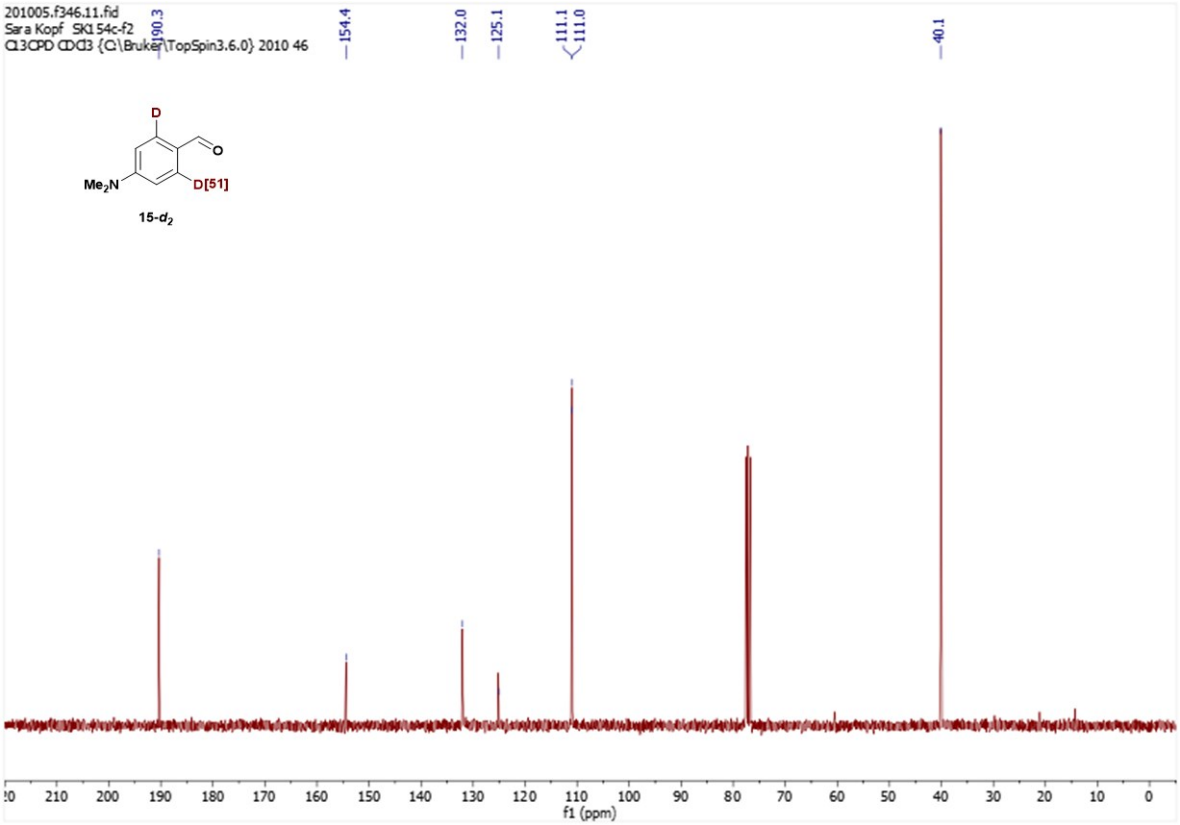

201005.328.10.fid
Sara Kopf SK148c-f1
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 28
9.98
7.83
7.80
7.56
7.53
1.35
D
O
tBu
D[18]
13-d_2
0.95
1.65
2.00
9.07
f1 (ppm)

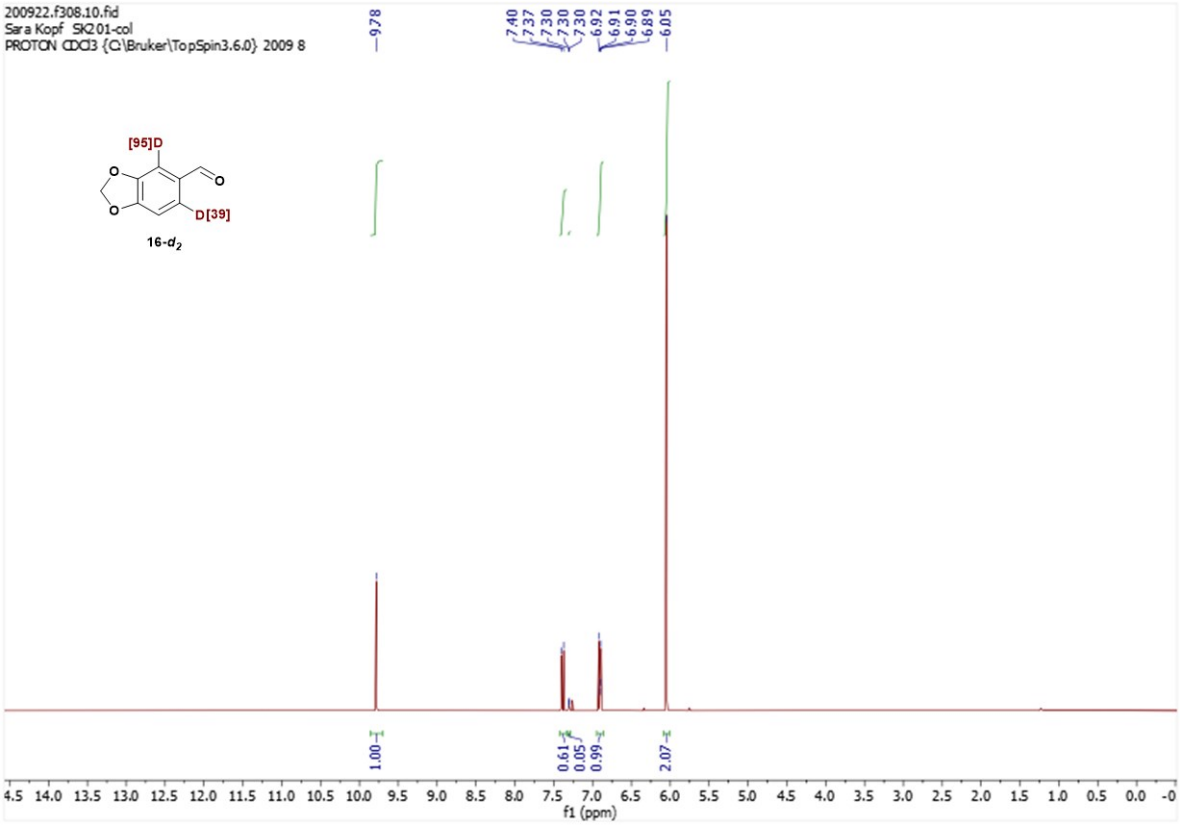

201005.328.11.fid
Sara Kopf SK148c-f1
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 28
192.1
158.6
134.2
129.8
126.1
35.5
31.2
D
O
tBu
D[18]
13-d2
f1 (ppm)

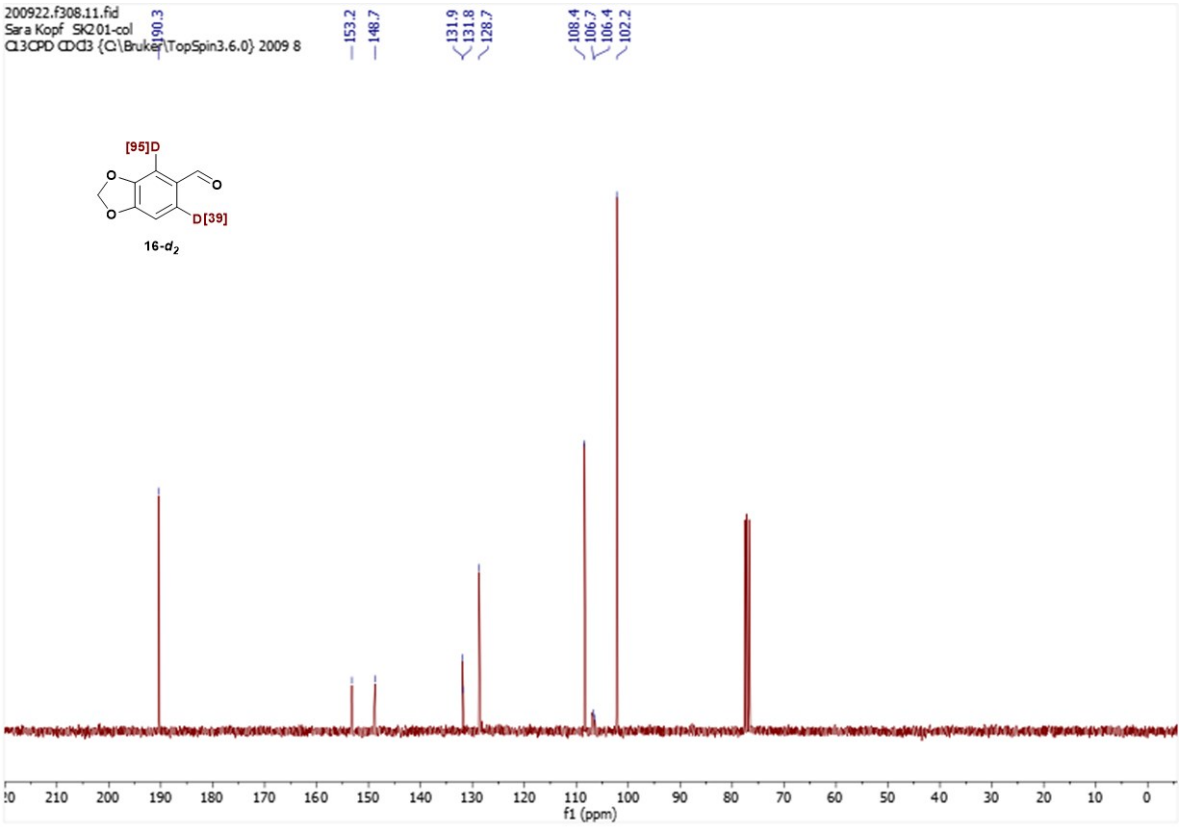

201109.324.10.fid
Sara Kopf SK218e-col
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 24
9.81
7.42
7.40
7.36
6.95
6.93
6.92
3.92
3.89
[79]D
MeO
MeO
O
D[62]
14-d2
0.95
0.38
0.21
1.00
3.09
3.03
f1 (ppm)

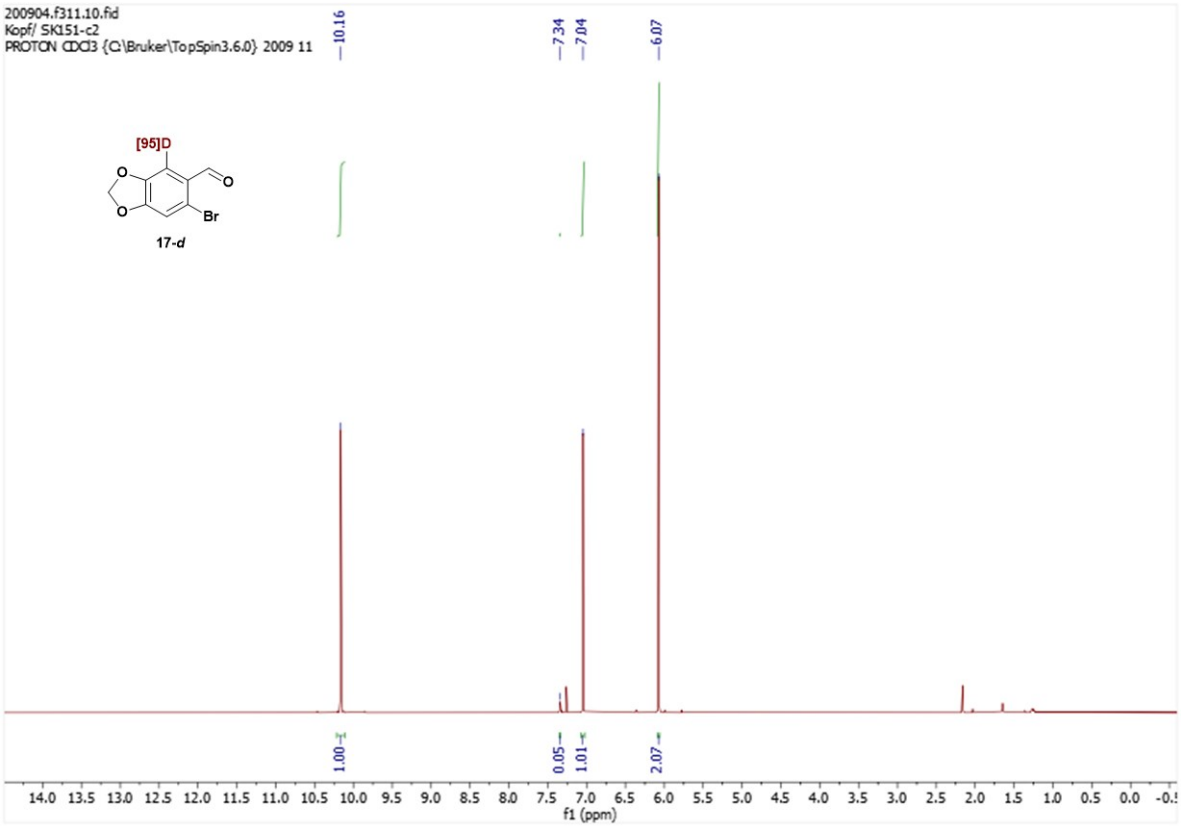

201110.303.10.fid
Sara Kopf SK218e-col
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 3
190.9
190.9
154.5
149.6
130.0
126.8
110.3
108.9
56.2
56.0
[79]D
MeO
MeO
O
D[62]
14-d_2
f1 (ppm)

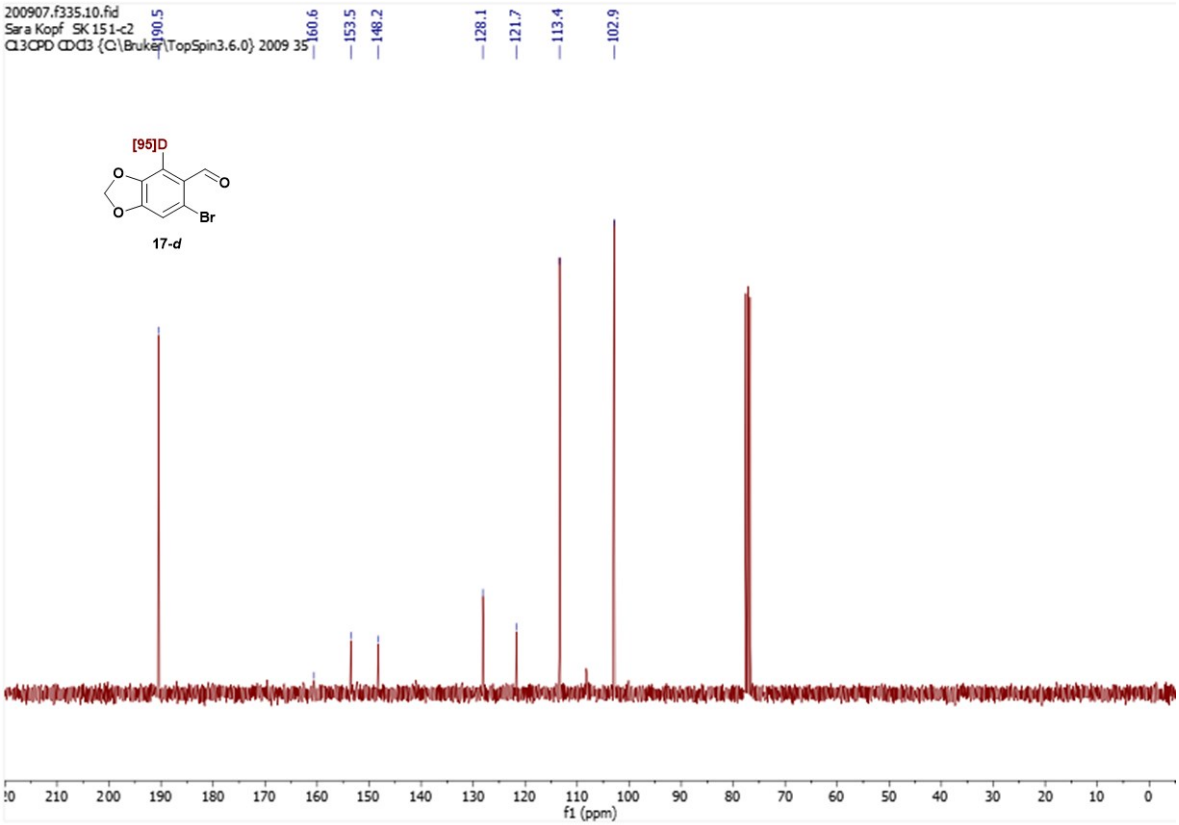

201005.f346.10.fid
Sara Kopf SK154c-f2
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 46
10.29
8.30
8.27
7.27
7.26
7.25
7.24
7.23
7.23
3.63
D
O
Me_2N
D[51]
15-d_2
1.00
0.98
2.04
6.08
f1 (ppm)

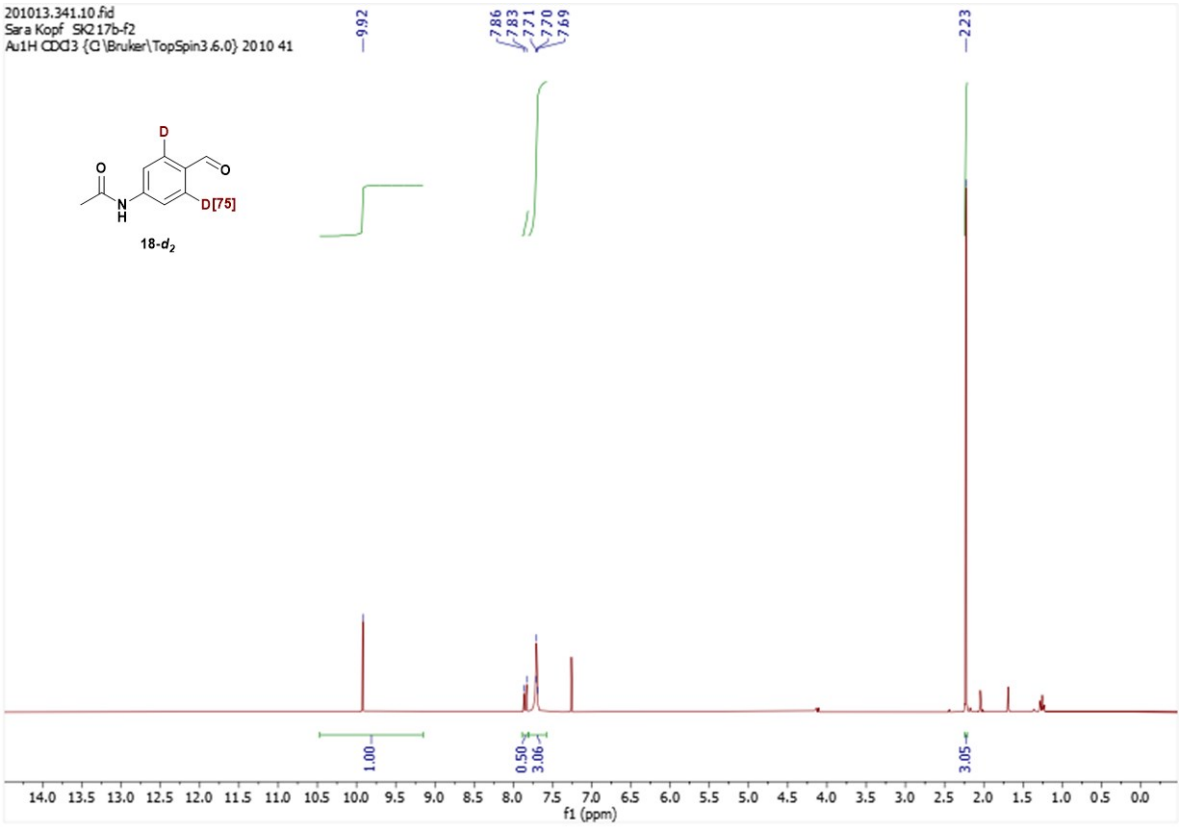

201005.f346.11.fid
Sara Kopf SK154c-f2
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 46
190.3
154.4
132.0
125.1
111.1
111.0
40.1
D
O
Me2N
D[51]
15-d2
f1 (ppm)

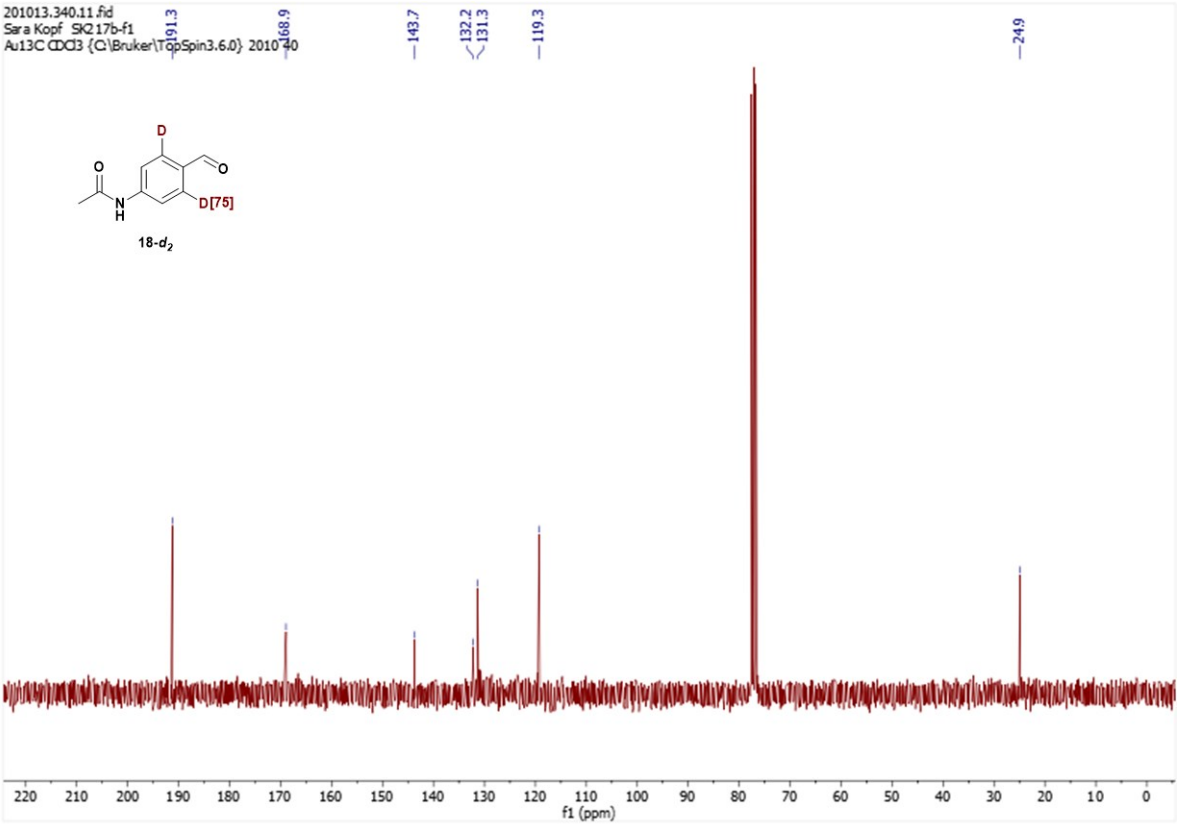

200922.f308.10.fid
Sara Kopf SK201-col
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 8
9.78
7.40
7.37
7.30
7.30
7.30
6.92
6.91
6.90
6.89
6.05
[95]D
O
O
O
D[39]
16-d2
1.00
0.61
0.05
0.99
2.07
f1 (ppm)

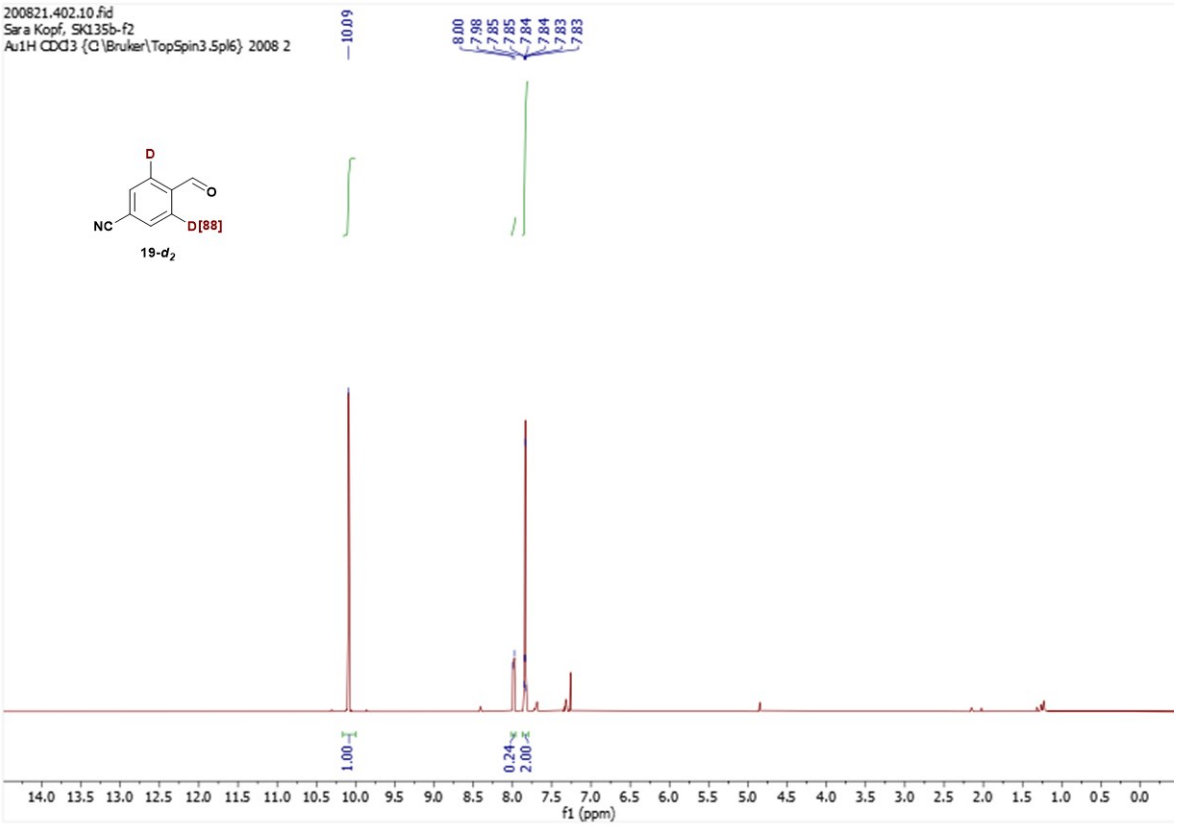

200922.f308.11.fid
Sara Kopf SK201-col
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 8
190.3
153.2
148.7
131.9
131.8
128.7
108.4
106.7
106.4
102.2
[95]D
D[39]
16-d_2
f1 (ppm)

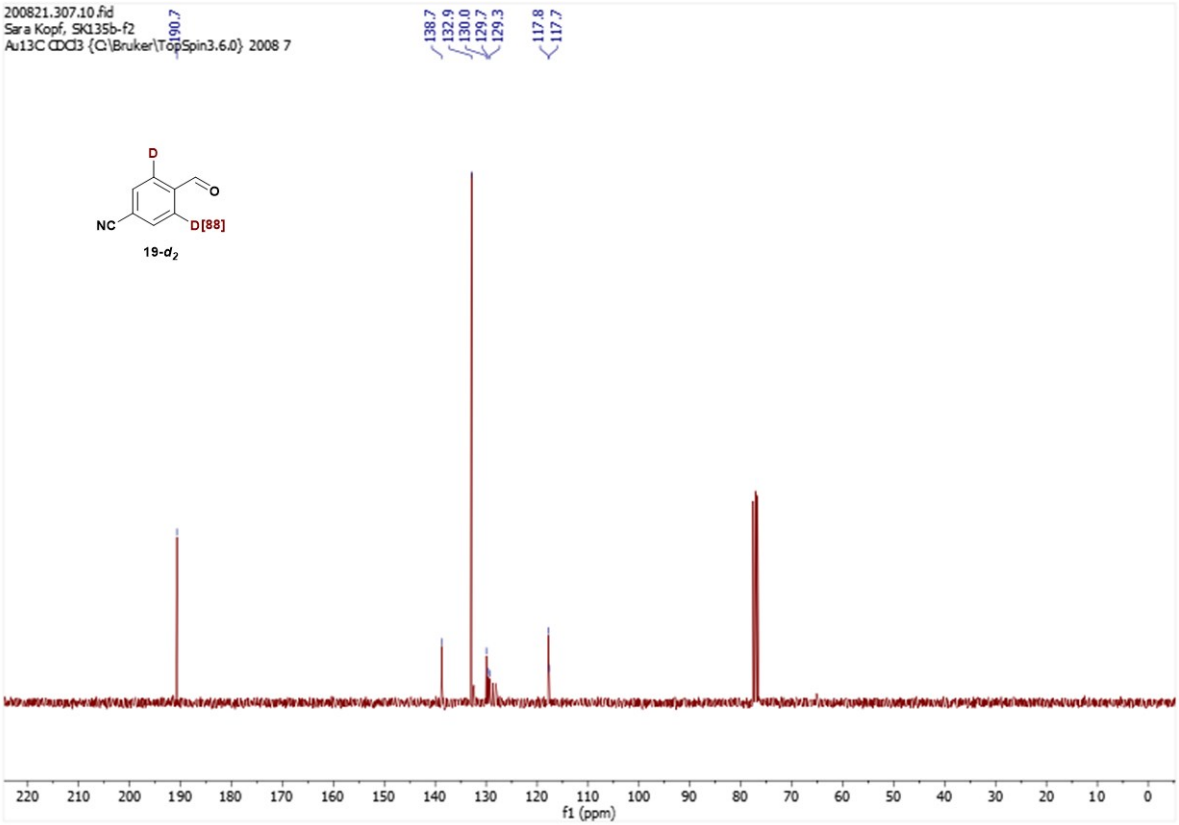

200904.f311.10.fid
Kopf/ SK151-c2
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 11
10.16
7.34
7.04
6.07
[95]D
Br
17-d
1.00
0.05
1.01
2.07
f1 (ppm)

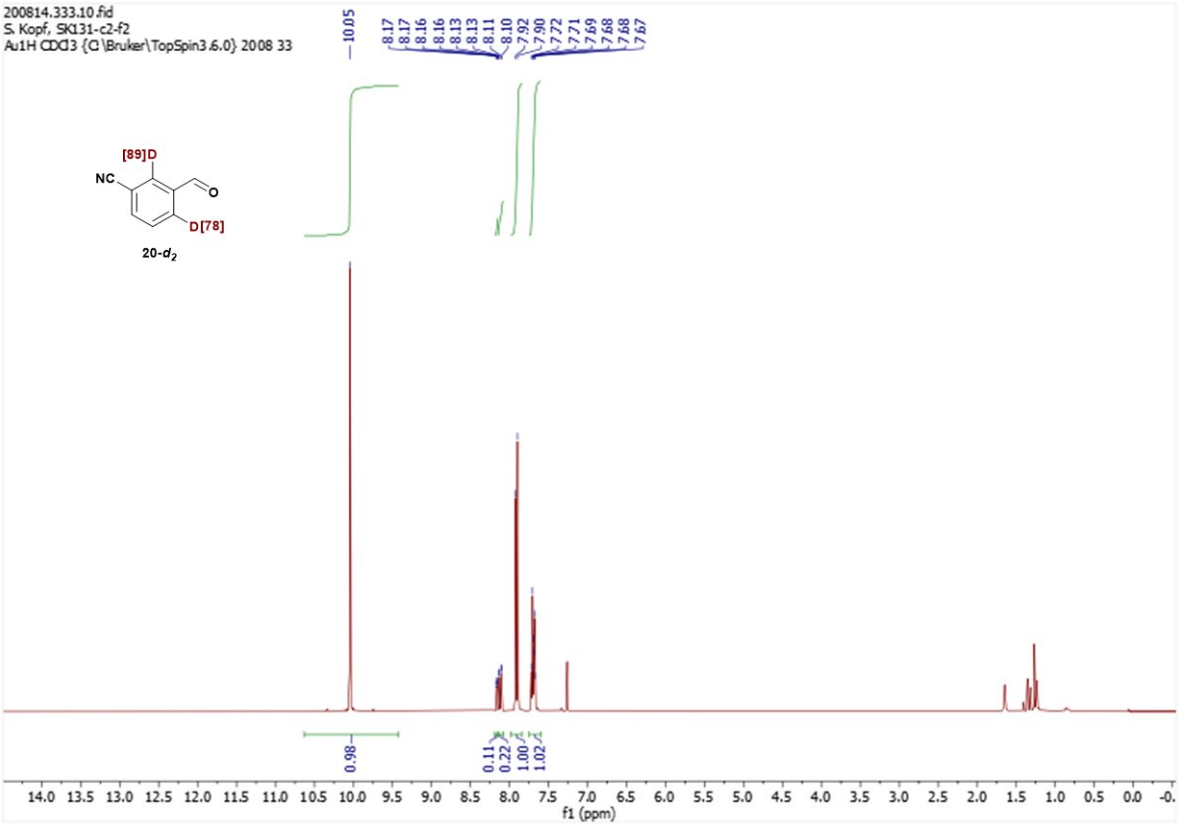

200907.f335.10.fid
Sara Kopf SK 151-c2
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 35
190.5
160.6
153.5
148.2
128.1
121.7
113.4
102.9
[95]D
O
O
O
Br
17-d
f1 (ppm)

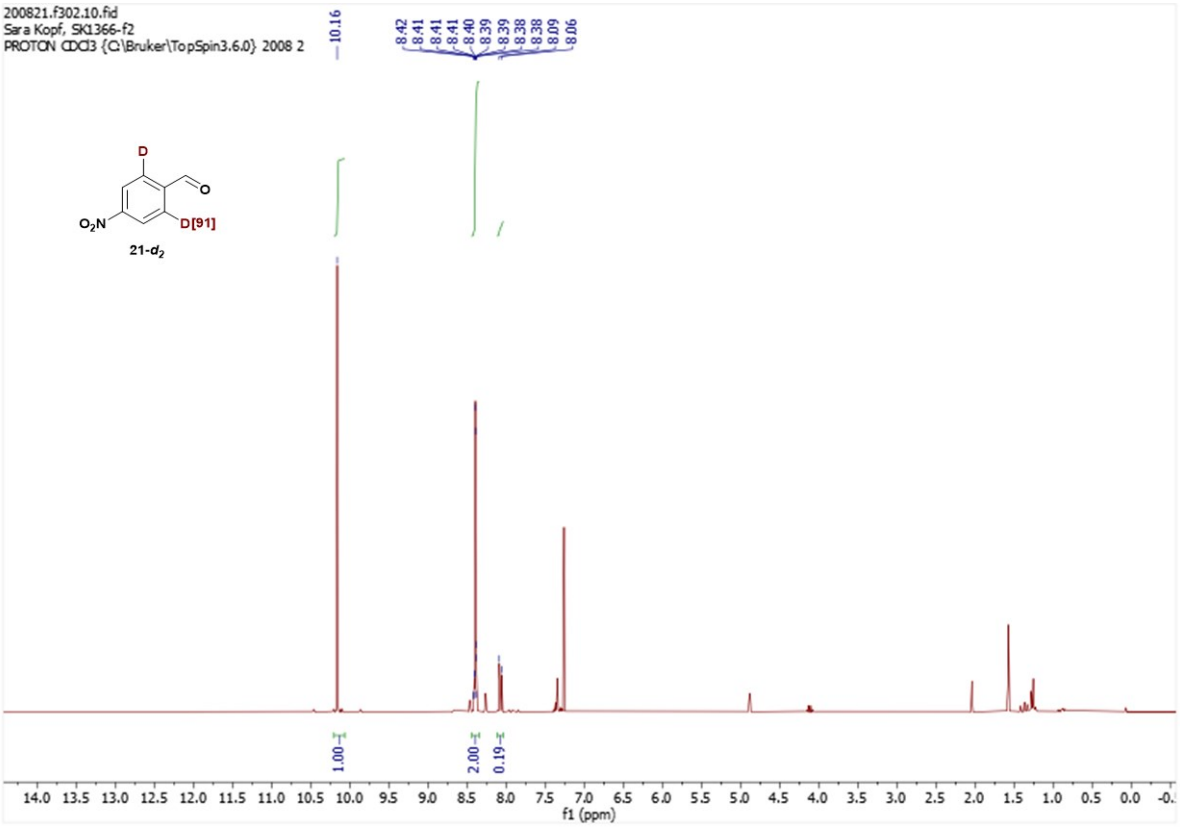

201013.341.10.fid
Sara Kopf SK217b-f2
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 41
9.92
7.86
7.83
7.71
7.70
7.69
2.23
D
O
O
N
H
D[75]
18-d2
1.00
0.50
3.06
3.05
f1 (ppm)

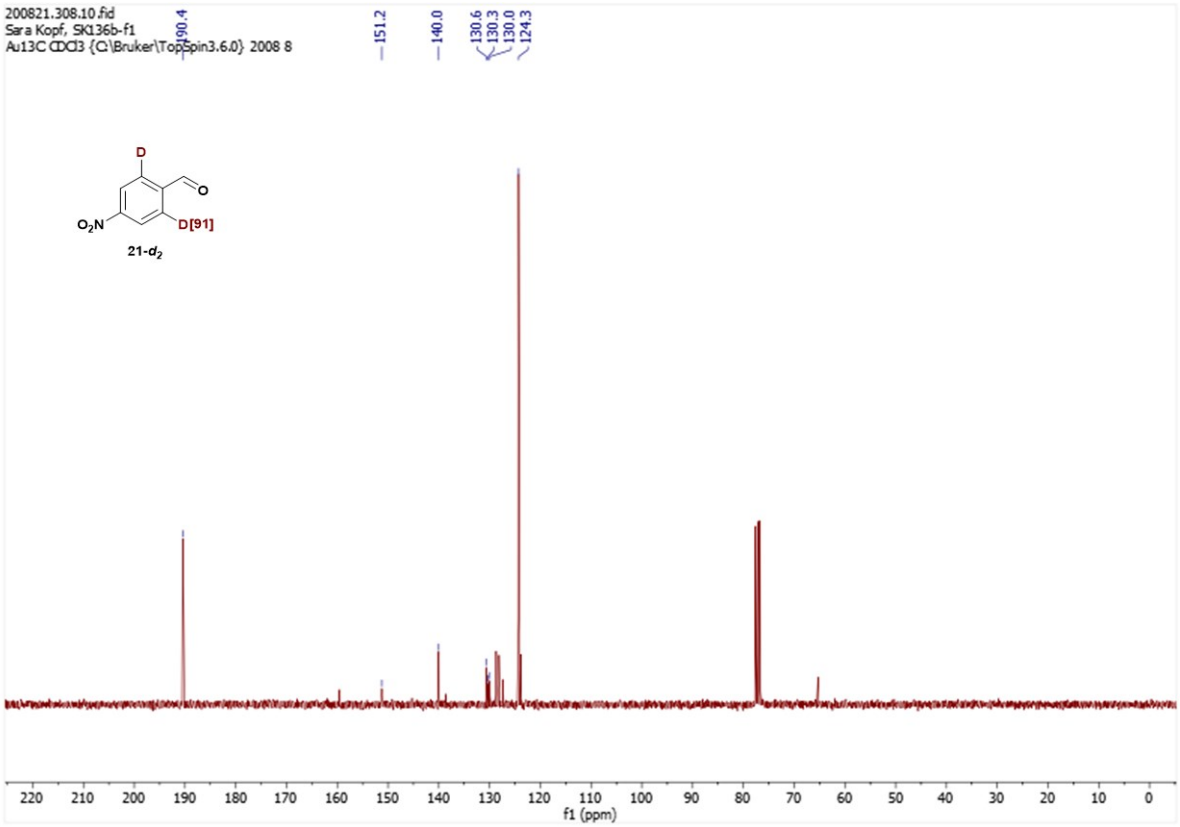

201013.340.11.fid
Sara Kopf SK217b-f1
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 40
191.3
168.9
143.7
132.2
131.3
119.3
24.9
D
O
O
N
H
D[75]
18-d_2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

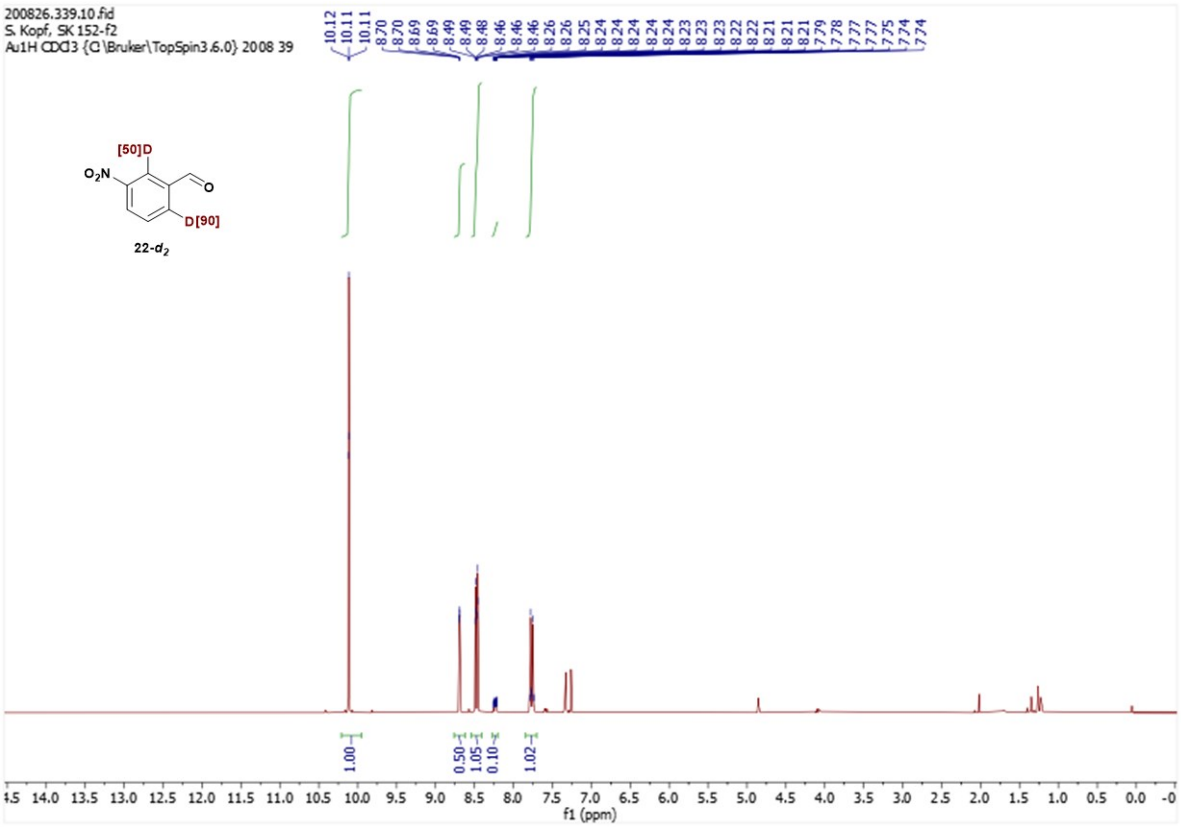

200821.402.10.fid
Sara Kopf, SK135b-f2
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 2008 2
10.09
8.00
7.98
7.85
7.85
7.84
7.84
7.83
7.83
D
O
NC
D[88]
19-d_2
1.00
0.24
2.00
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

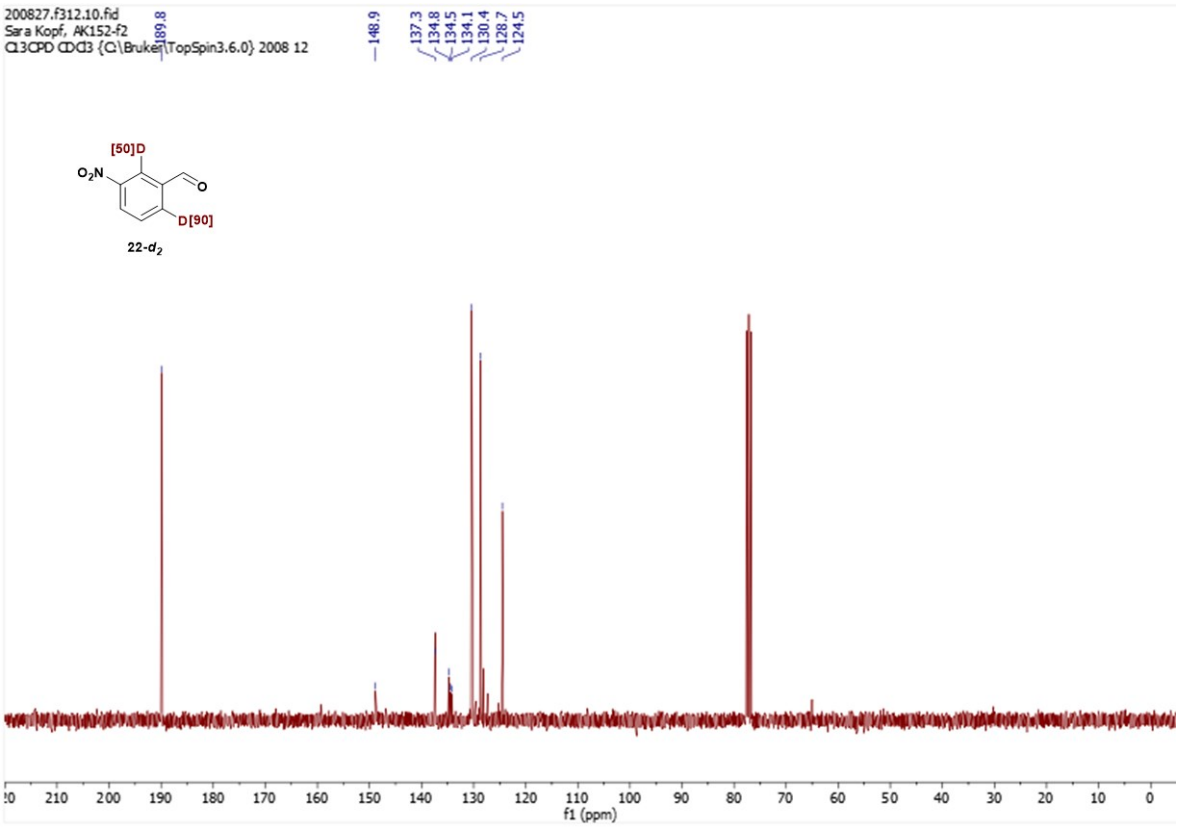

200821.307.10.fid
Sara Kopf, SK135b-f2
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 7
190.7
138.7
132.9
130.0
129.7
129.3
117.8
117.7
D
O
NC
D[88]
19-d_2
f1 (ppm)

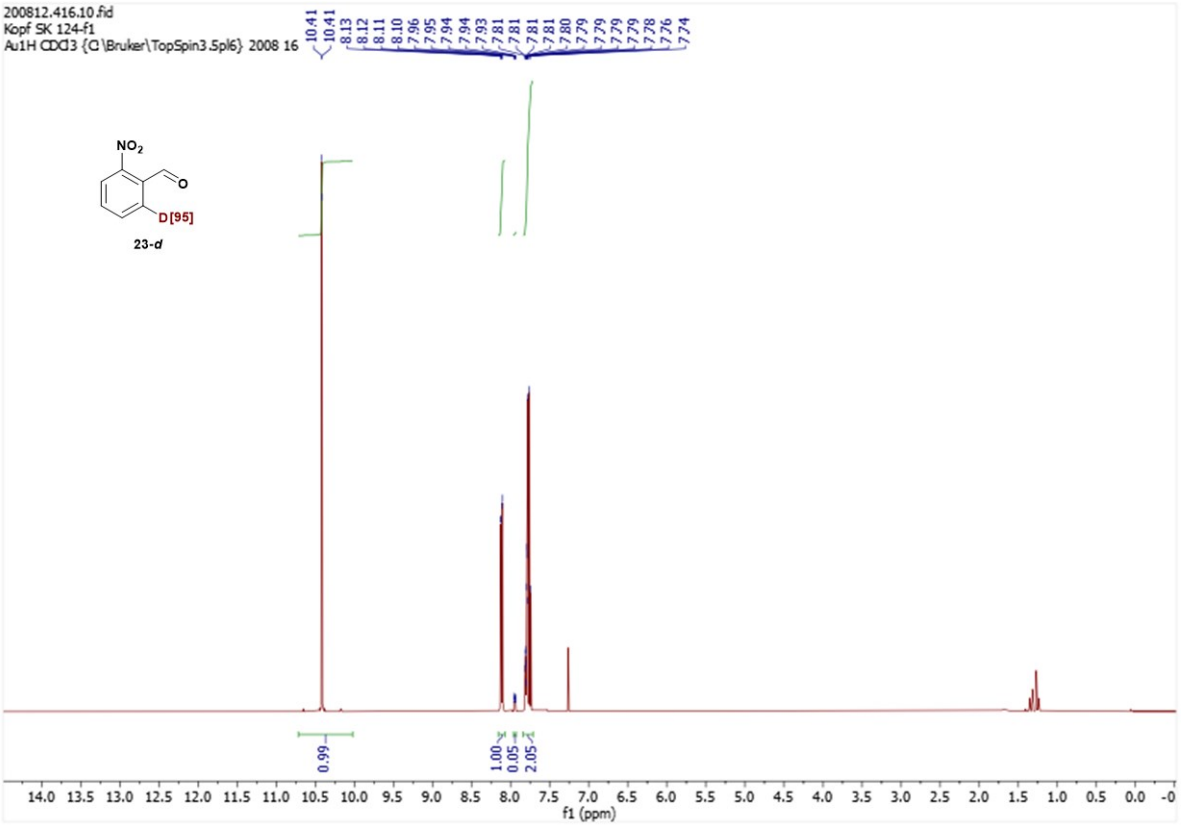

200814.333.10.fid
S. Kopf, SK131-c2-f2
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 33
10.05
8.17
8.17
8.16
8.16
8.13
8.13
8.11
8.10
7.92
7.90
7.72
7.71
7.69
7.68
7.68
7.67
[89]D
NC
O
D[78]
20-d_2
0.98
0.11
0.22
1.00
1.02
f1 (ppm)

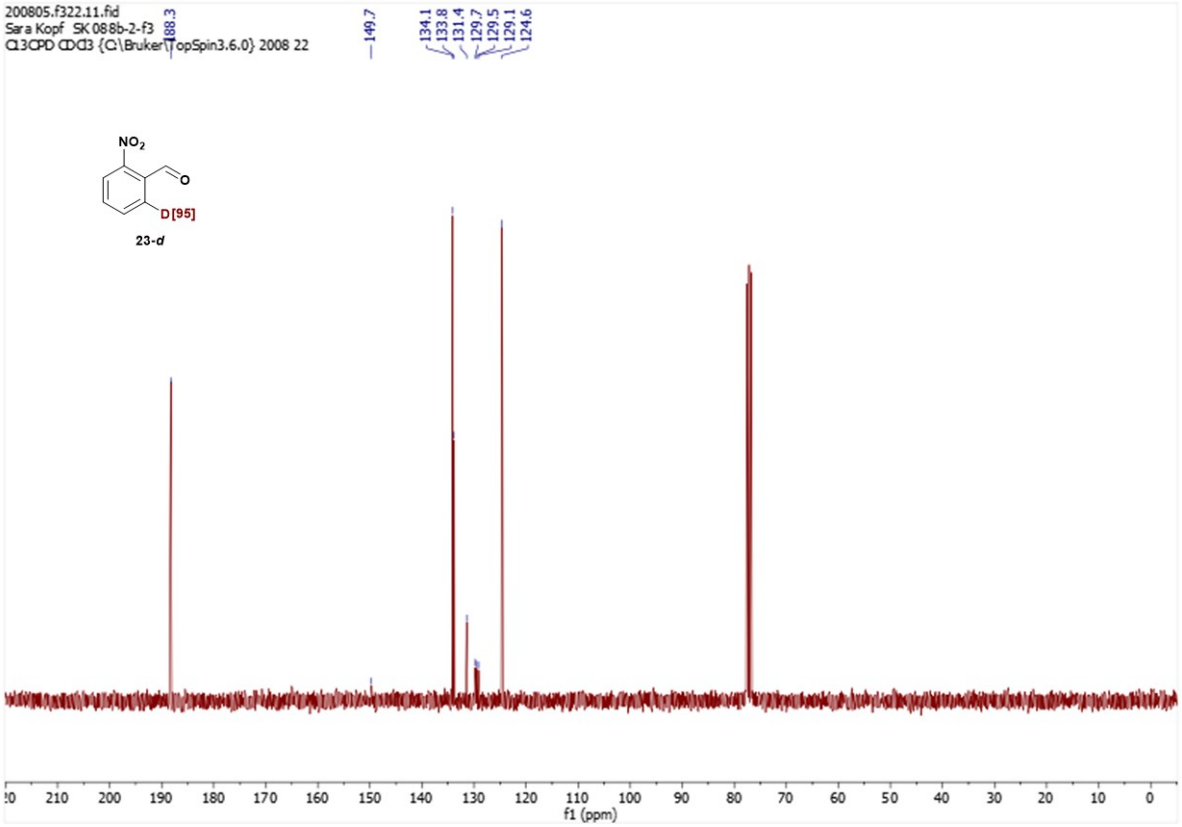

200821.f302.10.fid
Sara Kopf, SK1366-f2
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 2
10.16
8.42
8.41
8.41
8.41
8.40
8.39
8.39
8.38
8.38
8.09
8.06
D
O
O2N
D[91]
21-d2
1.00
2.00
0.19
f1 (ppm)

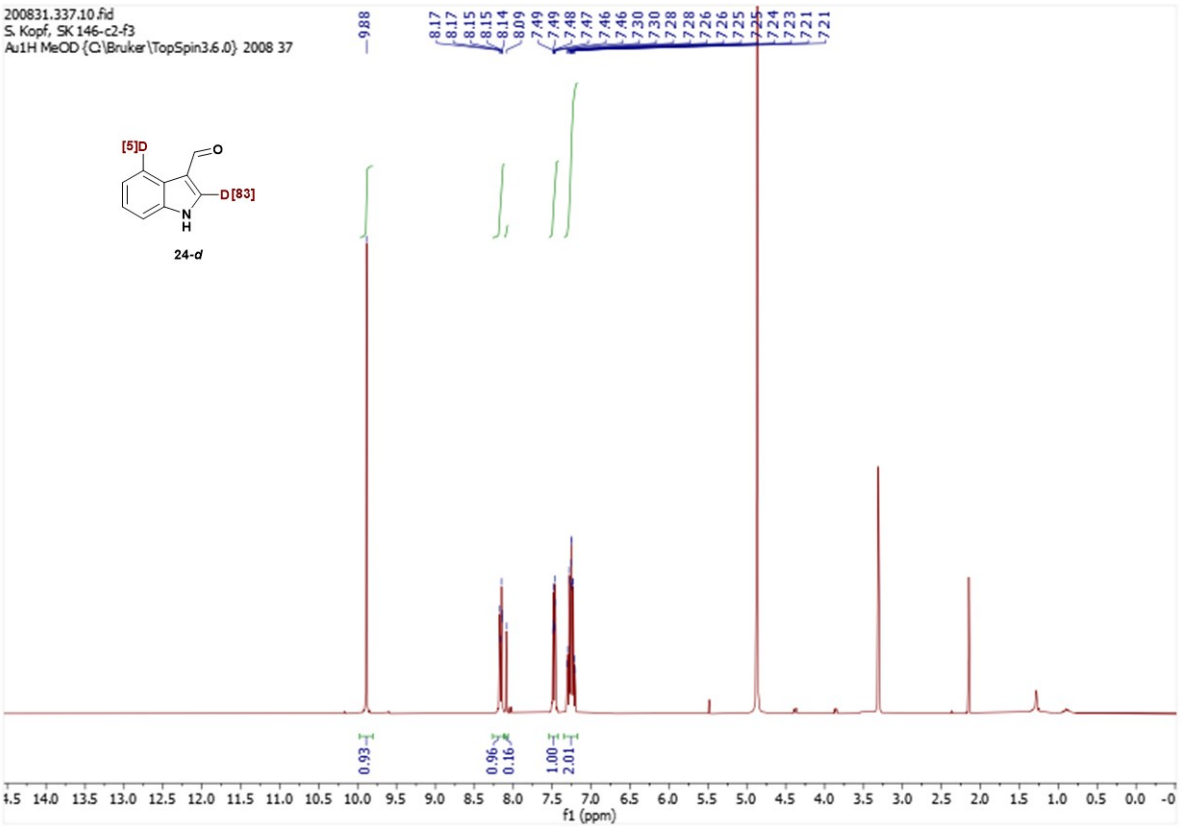

200821.308.10.fid
Sara Kopf, SK136b-f1
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 8
190.4
151.2
140.0
130.6
130.3
130.0
124.3
D
O
O2N
D[91]
21-d2
f1 (ppm)

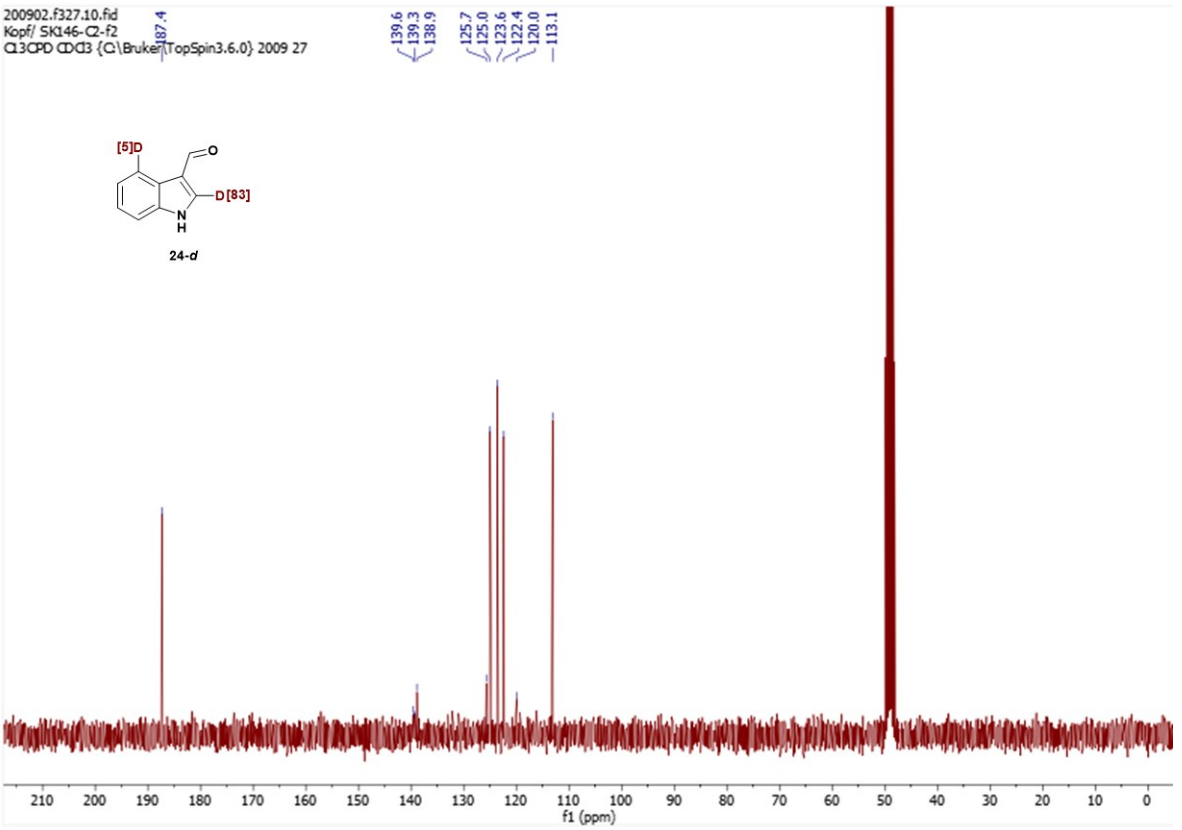

200826.339.10.fid
S. Kopf, SK 152-f2
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 39
[50]D
O2N
O
D[90]
22-d2
f1 (ppm)

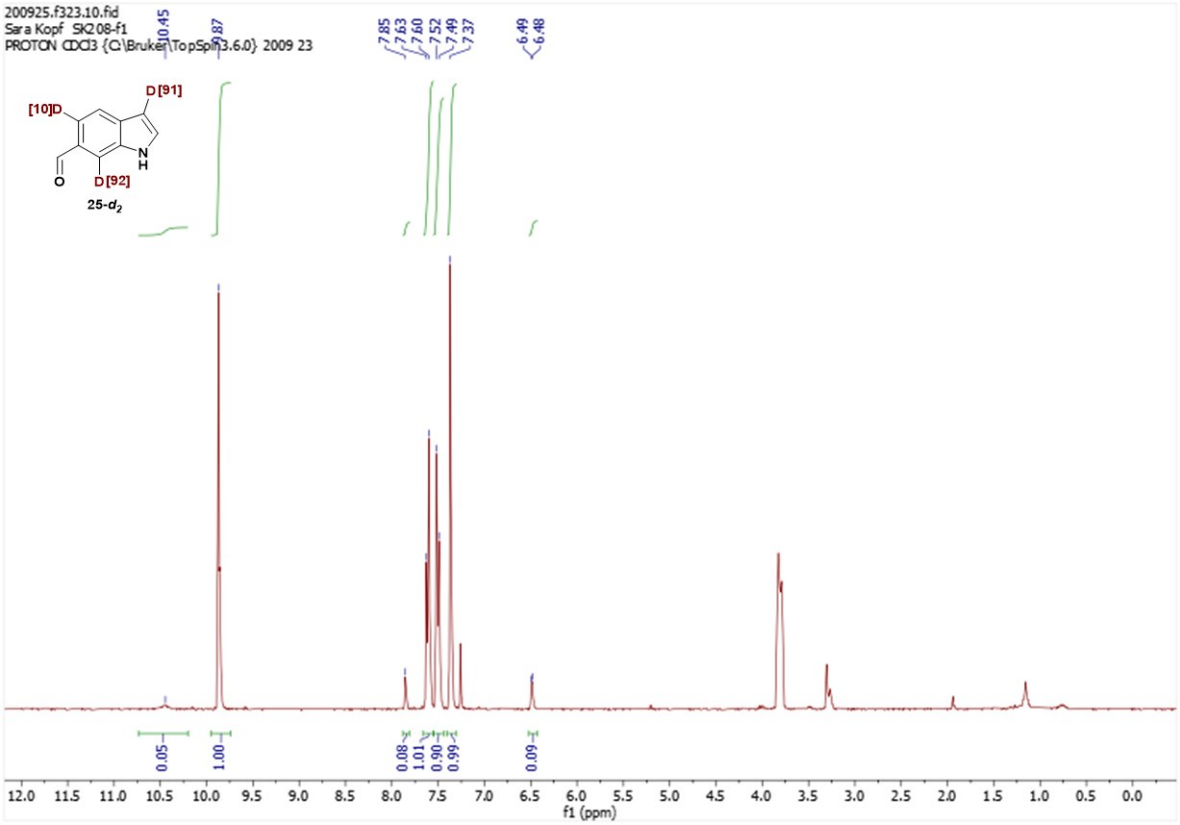

200827.f312.10.fid
Sara Kopf, AK152-f2
CL3CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 12
[50]D
O2N
O
D[90]
22-d2
f1 (ppm)

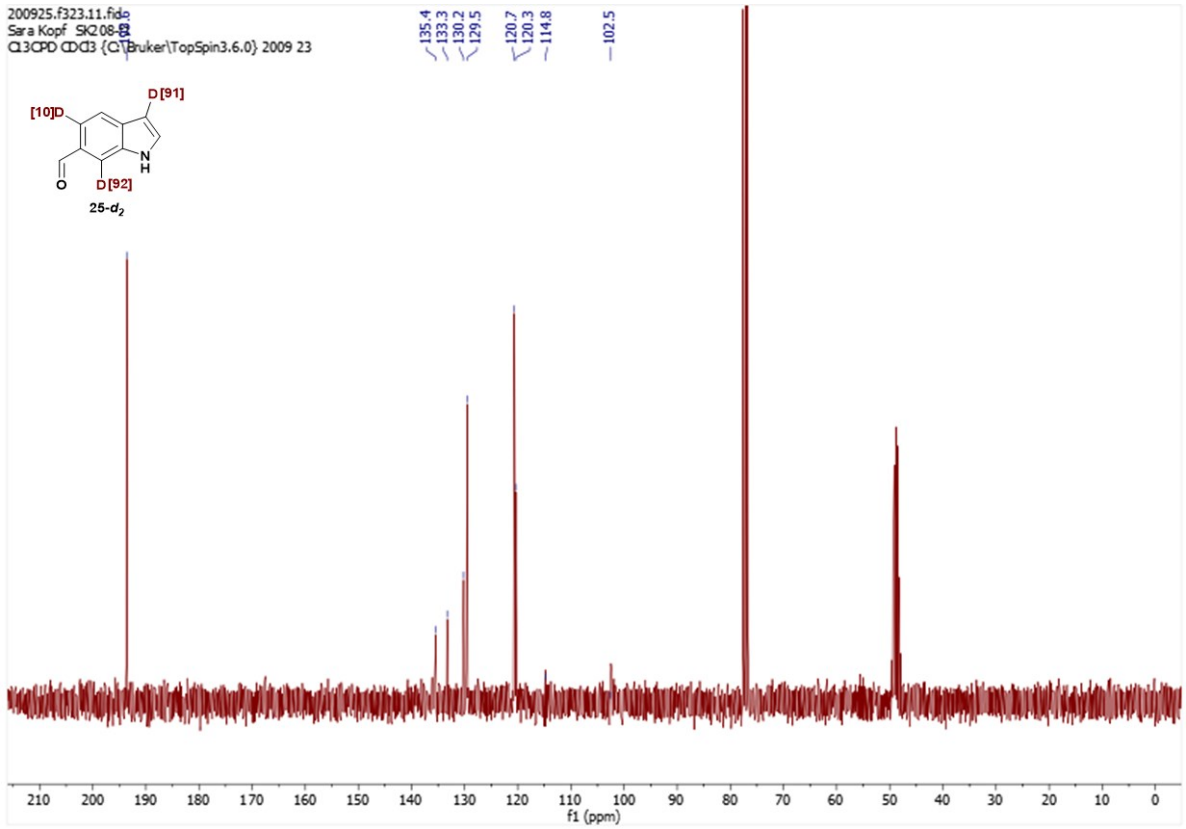

200812.416.10.fid
Kopf SK 124-f1
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 2008 16
10.41
10.41
8.13
8.12
8.11
8.10
7.96
7.95
7.94
7.94
7.93
7.81
7.81
7.81
7.81
7.80
7.79
7.79
7.79
7.79
7.78
7.76
7.74
NO2
O
D[95]
23-d
0.99
1.00
0.05
2.05
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 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 -0
f1 (ppm)

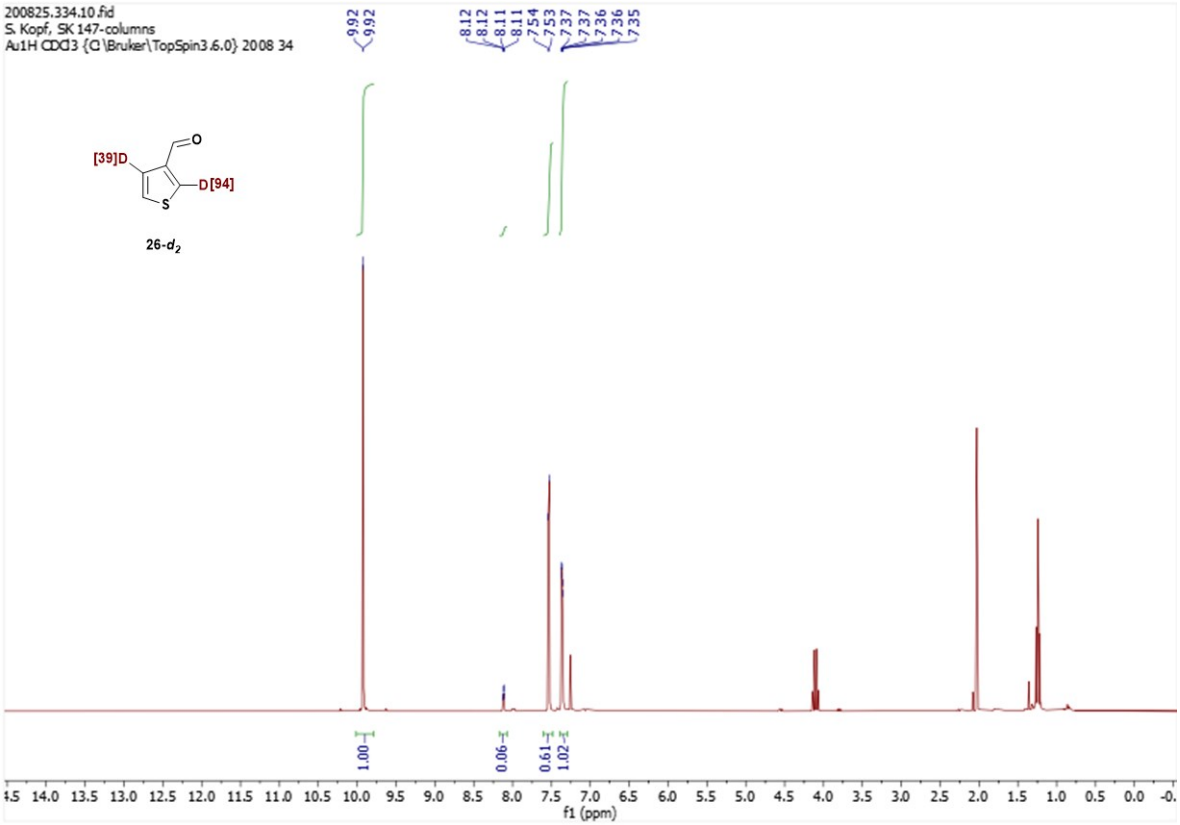

200805.f322.11.fid
Sara Kopf SK 088b-2-f3
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 22
188.3
149.7
134.1
133.8
131.4
129.7
129.5
129.1
124.6
NO2
O
D[95]
23-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

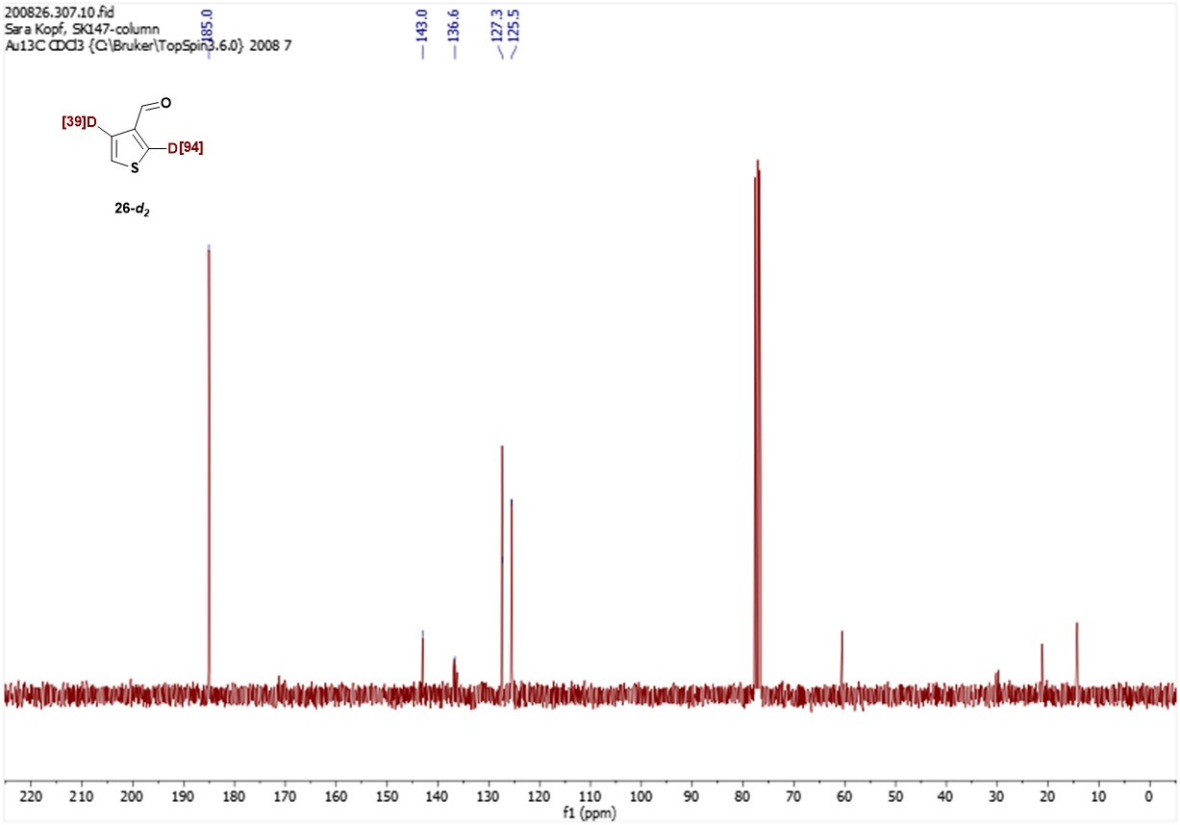

200831.337.10.fid
S. Kopf, SK 146-c2-f3
Au1H MeOD {C:\Bruker\TopSpin3.6.0} 2008 37
[5]D
D [83]
N
H
24-d
f1 (ppm)

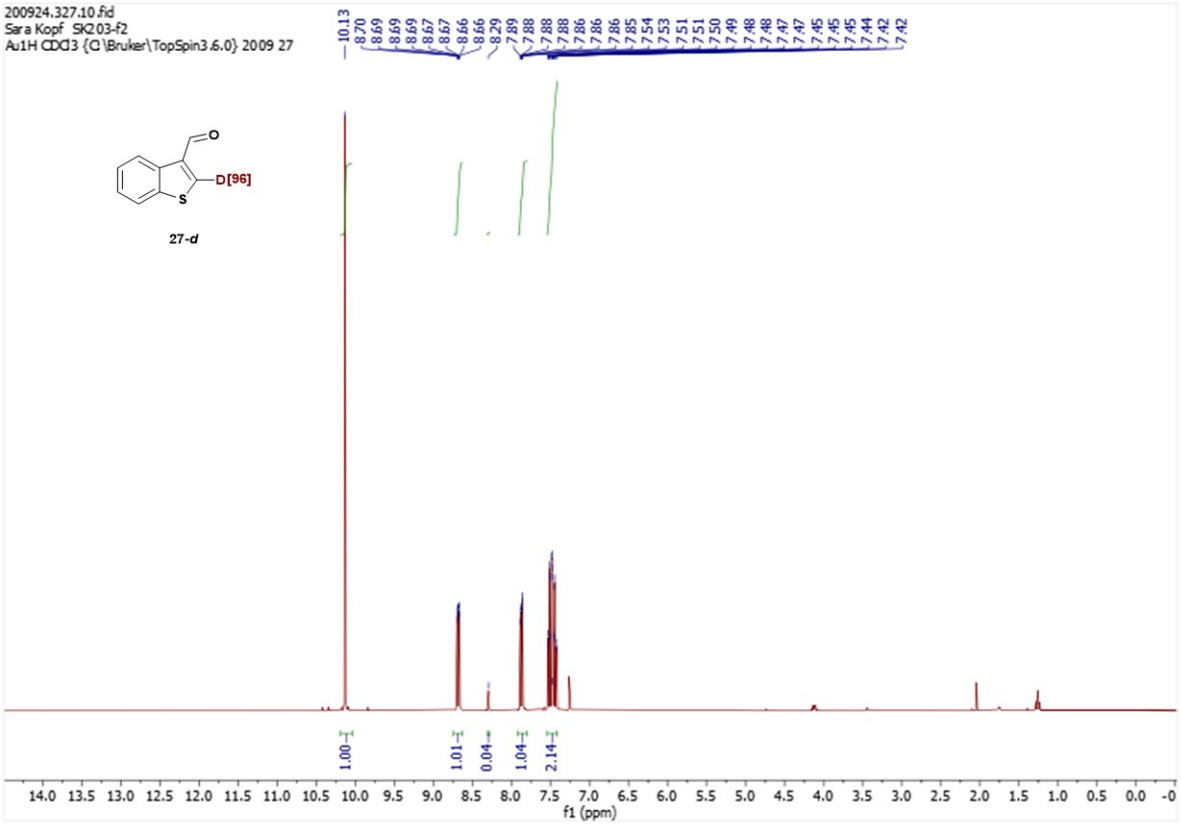

200902.f327.10.fid
Kopf/ SK146-C2-f2
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 27
[5]D
D [83]
N
H
24-d
f1 (ppm)

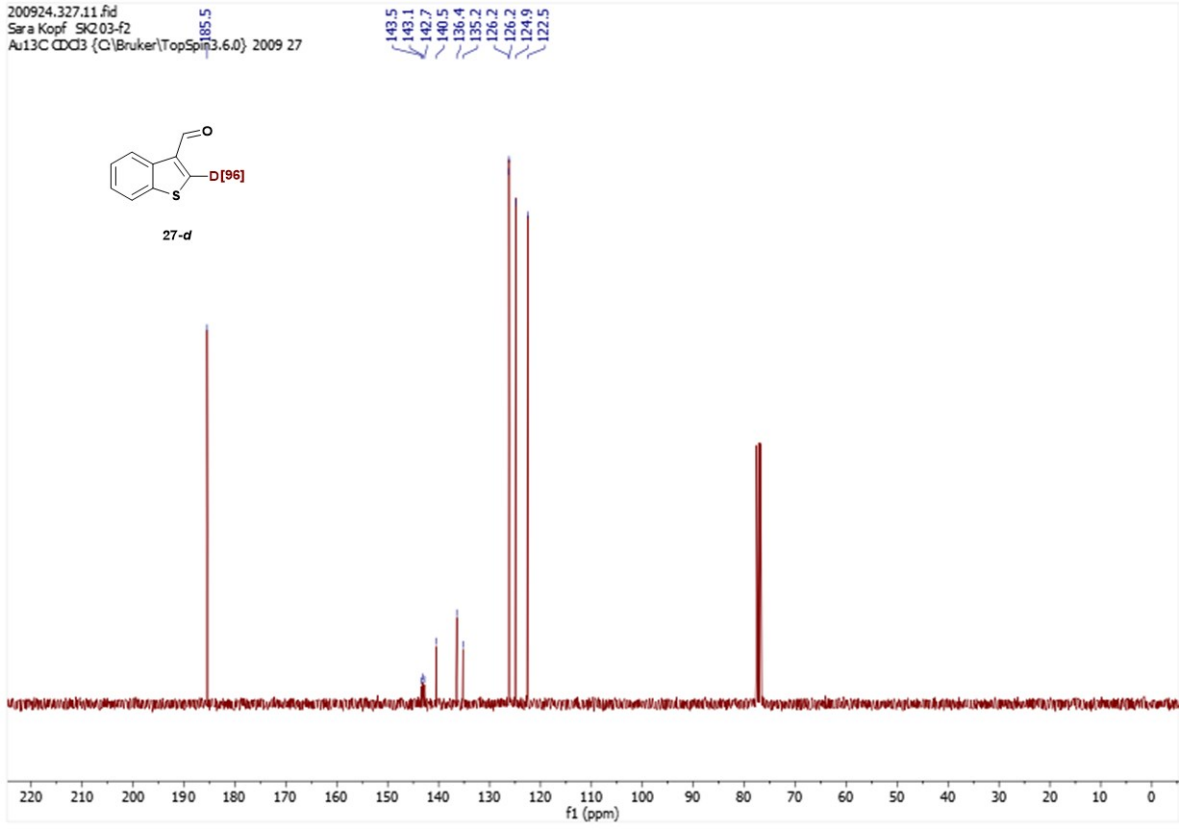

200925.f323.10.fid
Sara Kopf SK208-f1
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 23
10.45
9.87
7.85
7.63
7.60
7.52
7.49
7.37
6.49
6.48
D [91]
[10]D
N
H
O
D [92]
25-d_2
0.05
1.00
0.08
1.01
0.90
0.99
0.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

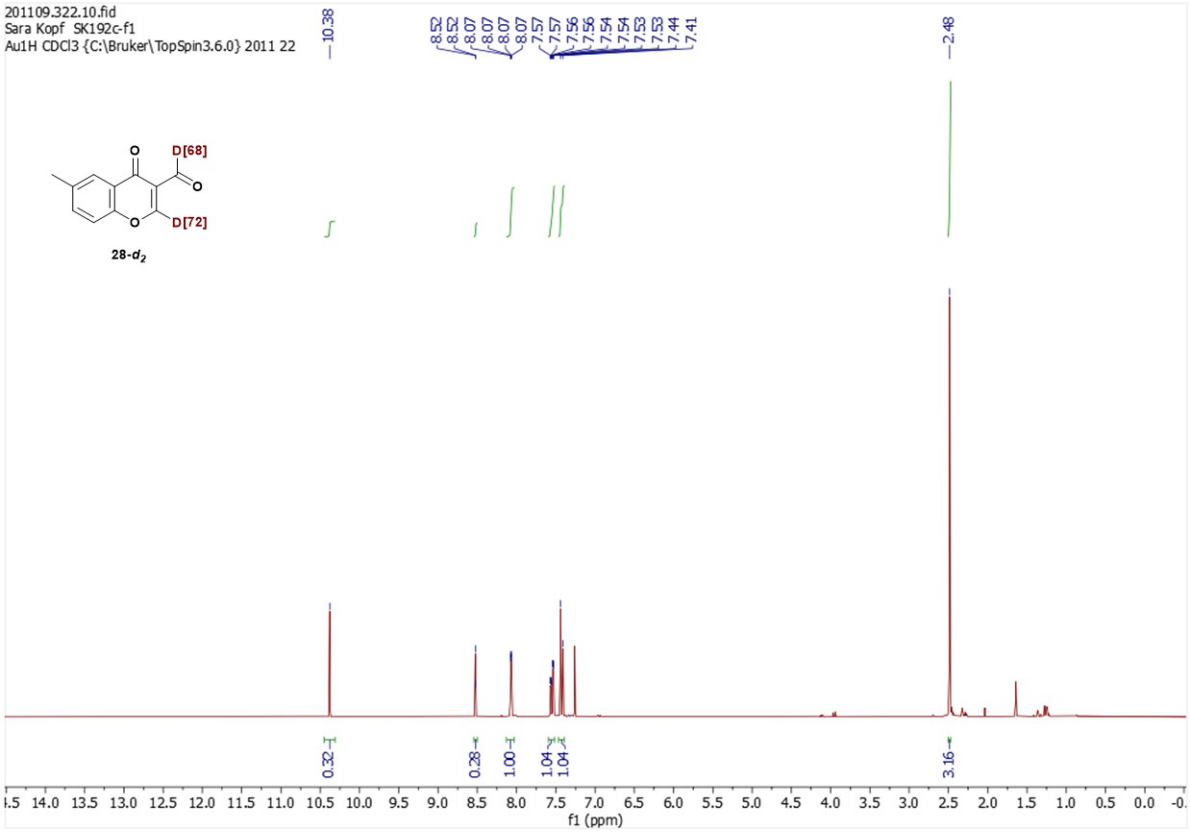

200925.f323.11.fid
Sara Kopf SK208-f3
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 23
135.4
133.3
130.2
129.5
120.7
120.3
114.8
102.5
D [91]
[10]D
N
H
O
D [92]
25-d_2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

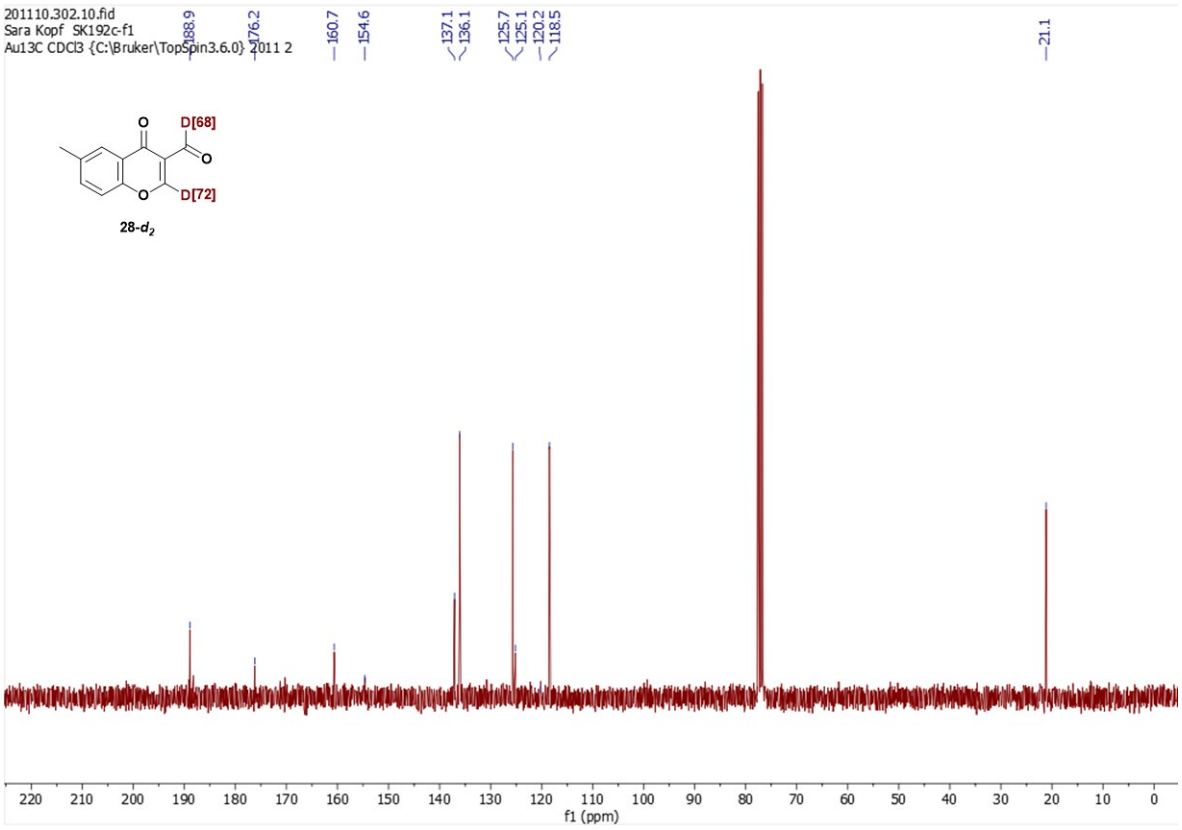

200825.334.10.fid
S. Kopf, SK 147-columns
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 34
9.92
9.92
8.12
8.12
8.11
8.11
7.54
7.53
7.37
7.37
7.36
7.36
7.35
[39]D
D[94]
O
S
26-d_2
1.00
0.06
0.61
1.02
f1 (ppm)

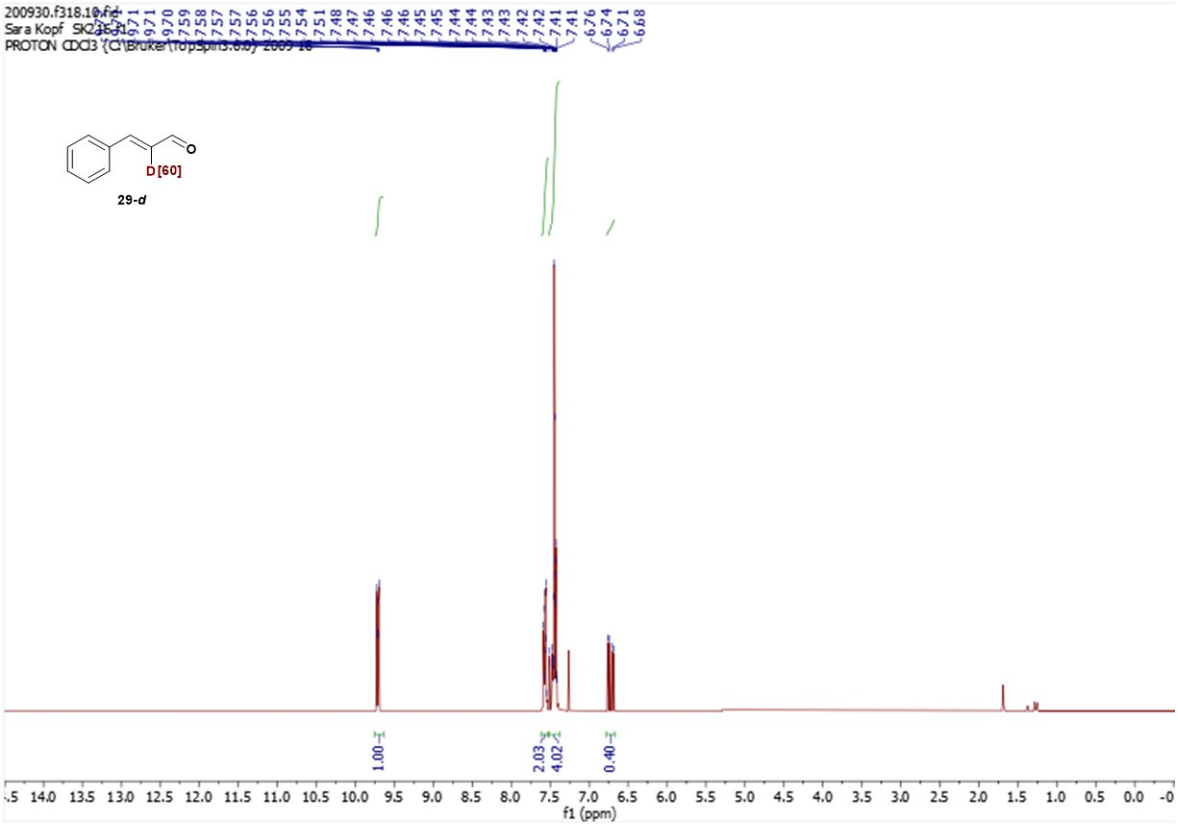

200826.307.10.fid
Sara Kopf, SK147-column
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 7
185.0
143.0
136.6
127.3
125.5
[39]D
D[94]
O
S
26-d_2
f1 (ppm)

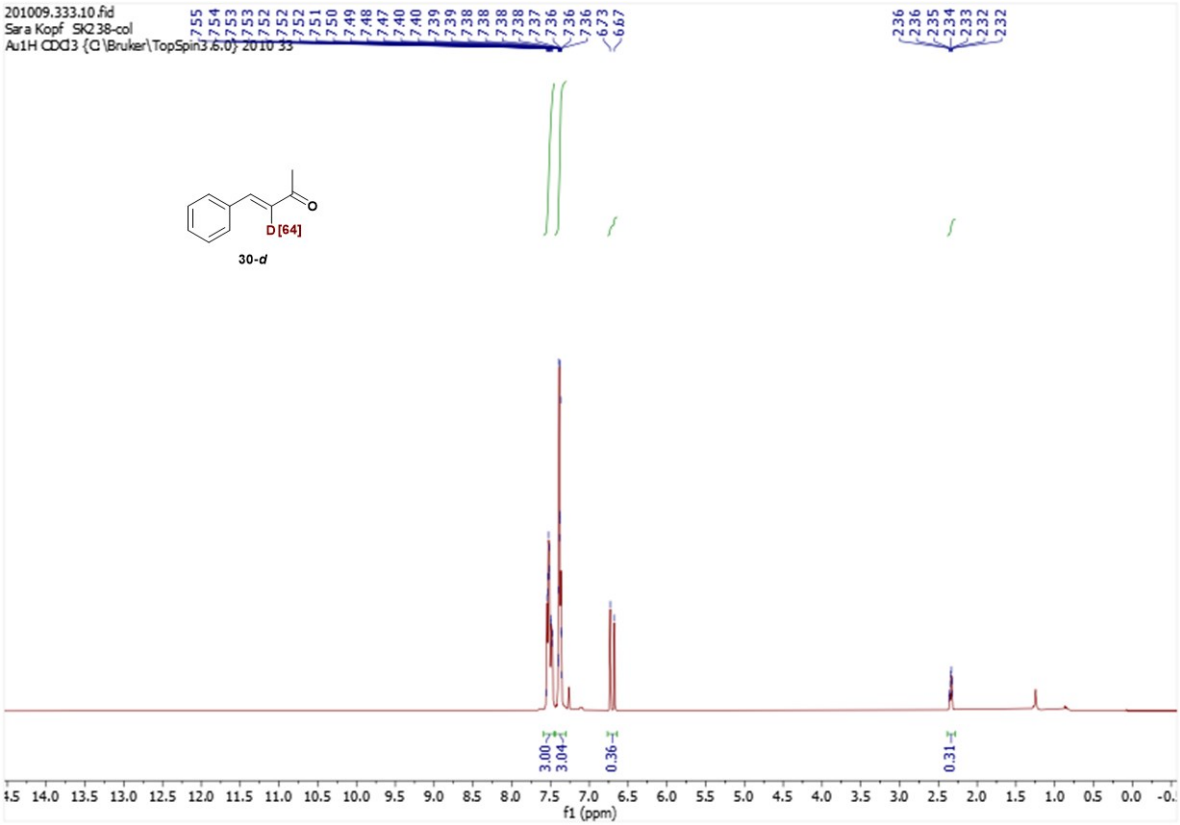

200924.327.10.fid
Sara Kopf SK203-f2
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 27
D[96]
27-d
f1 (ppm)

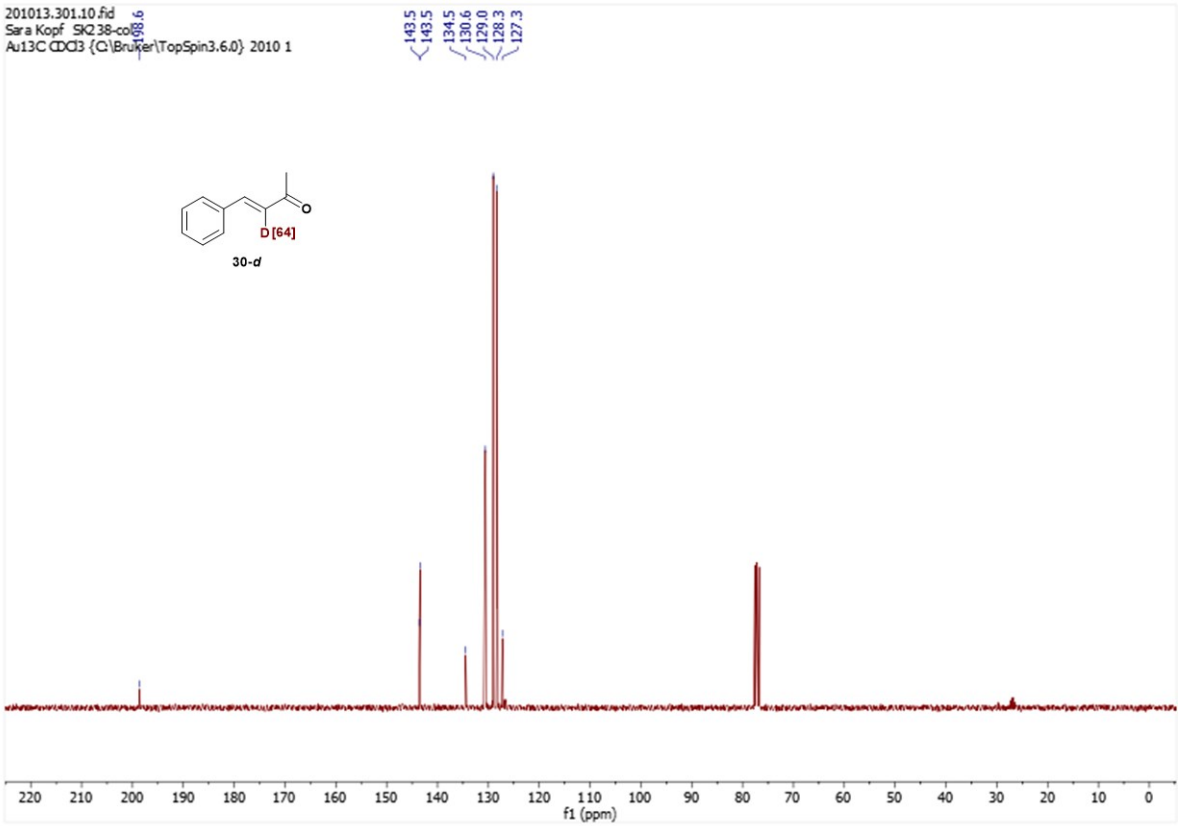

200924.327.11.fid
Sara Kopf SK203-f2
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 27
D[96]
27-d
f1 (ppm)

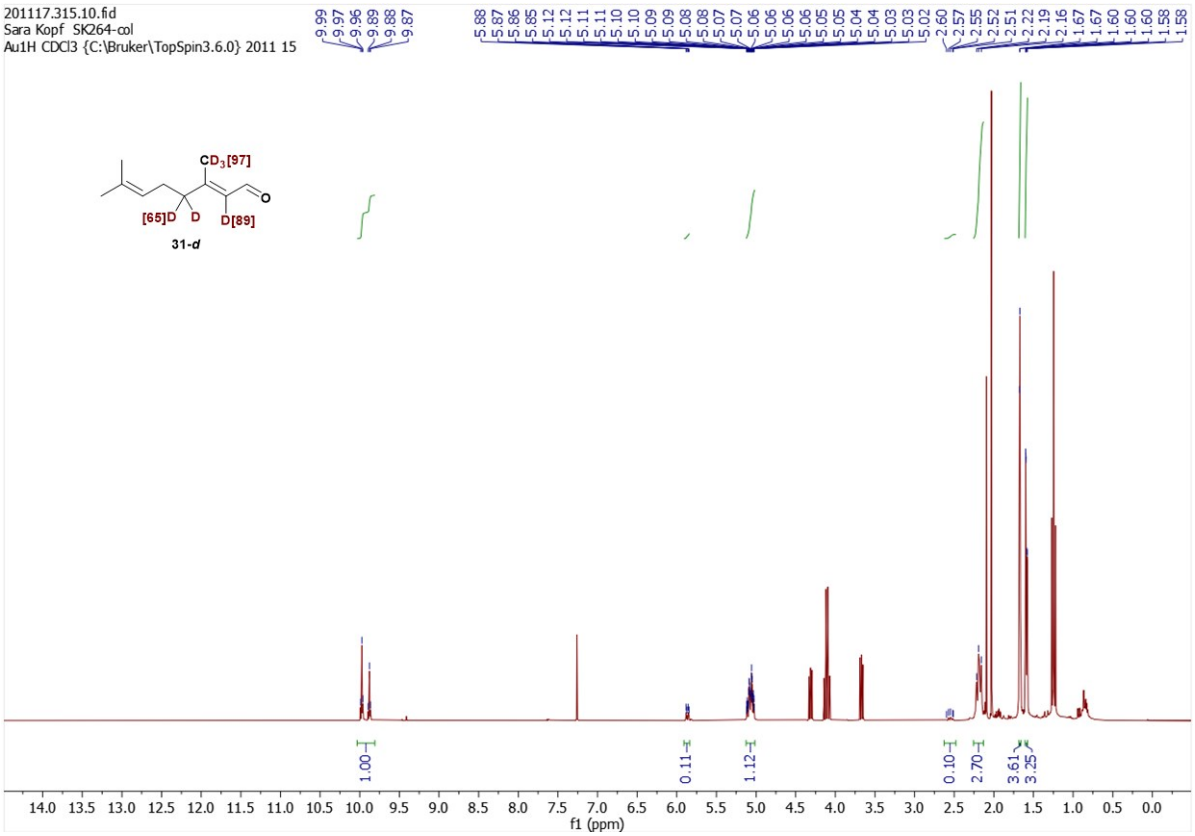

201109.322.10.fid
Sara Kopf SK192c-f1
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 22
10.38
8.52
8.52
8.07
8.07
8.07
8.07
7.57
7.57
7.56
7.56
7.54
7.54
7.53
7.53
7.44
7.41
2.48
D[68]
D[72]
28-d_2
0.32
0.28
1.00
1.04
1.04
3.16
f1 (ppm)

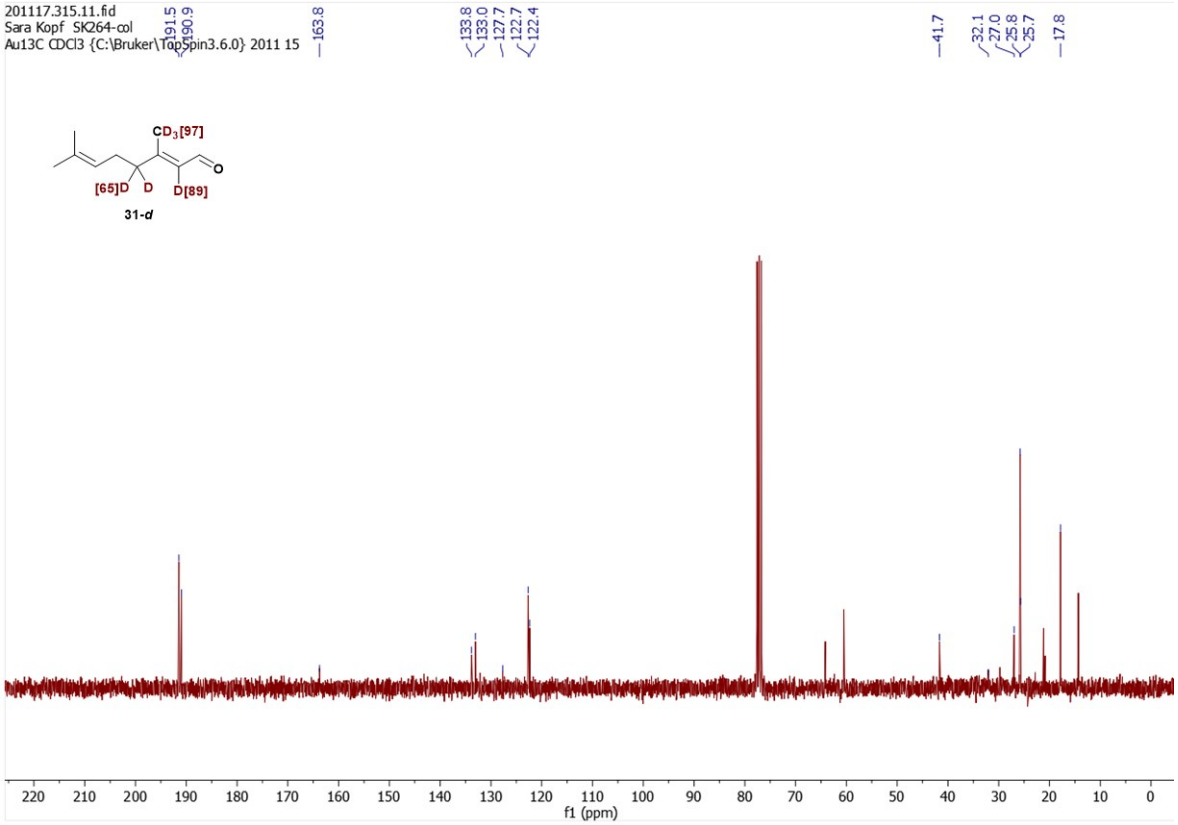

201110.302.10.fid
Sara Kopf SK192c-f1
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 2
188.9
176.2
160.7
154.6
137.1
136.1
125.7
125.1
120.2
118.5
21.1
D[68]
D[72]
28-d_2
f1 (ppm)


200930.f318.10.fid
Sara Kopf SK238-H
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 18
D [60]
29-d
1.00
2.03
4.02
0.40
f1 (ppm)

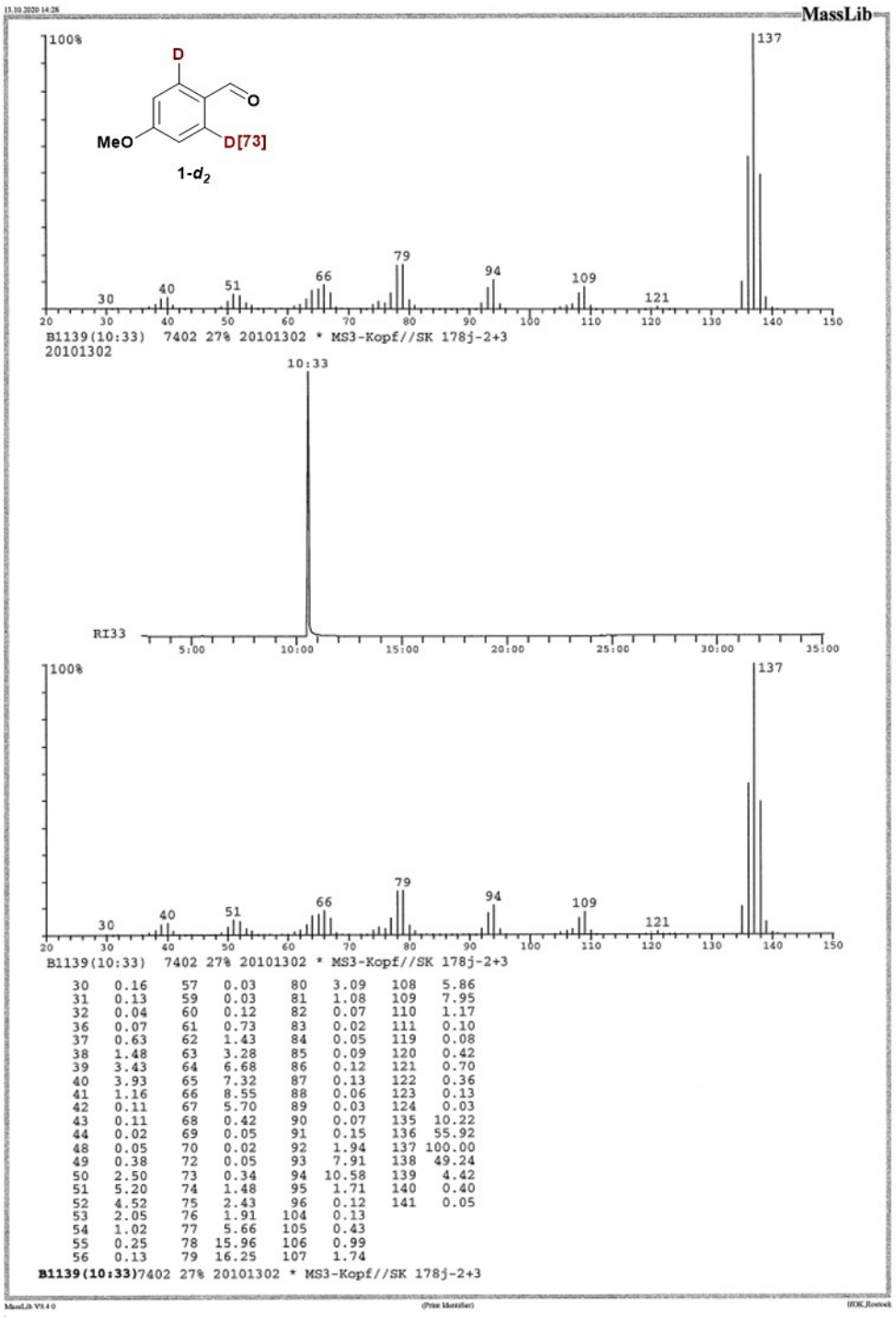

201009.333.10.fid
Sara Kopf SK238-col
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 33
D [64]
30-d
3.00
3.04
0.36
0.31
f1 (ppm)


201013.301.10.fid
Sara Kopf SK238-col
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 1
143.5
143.5
134.5
130.6
129.0
128.3
127.3
D [64]
30-d
f1 (ppm)


201117.315.10.fid
Sara Kopf SK264-col
Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 15
CD3 [97]
[65]D
D
D [89]
31-d
1.00
0.11
1.12
0.10
2.70
3.61
3.25
f1 (ppm)

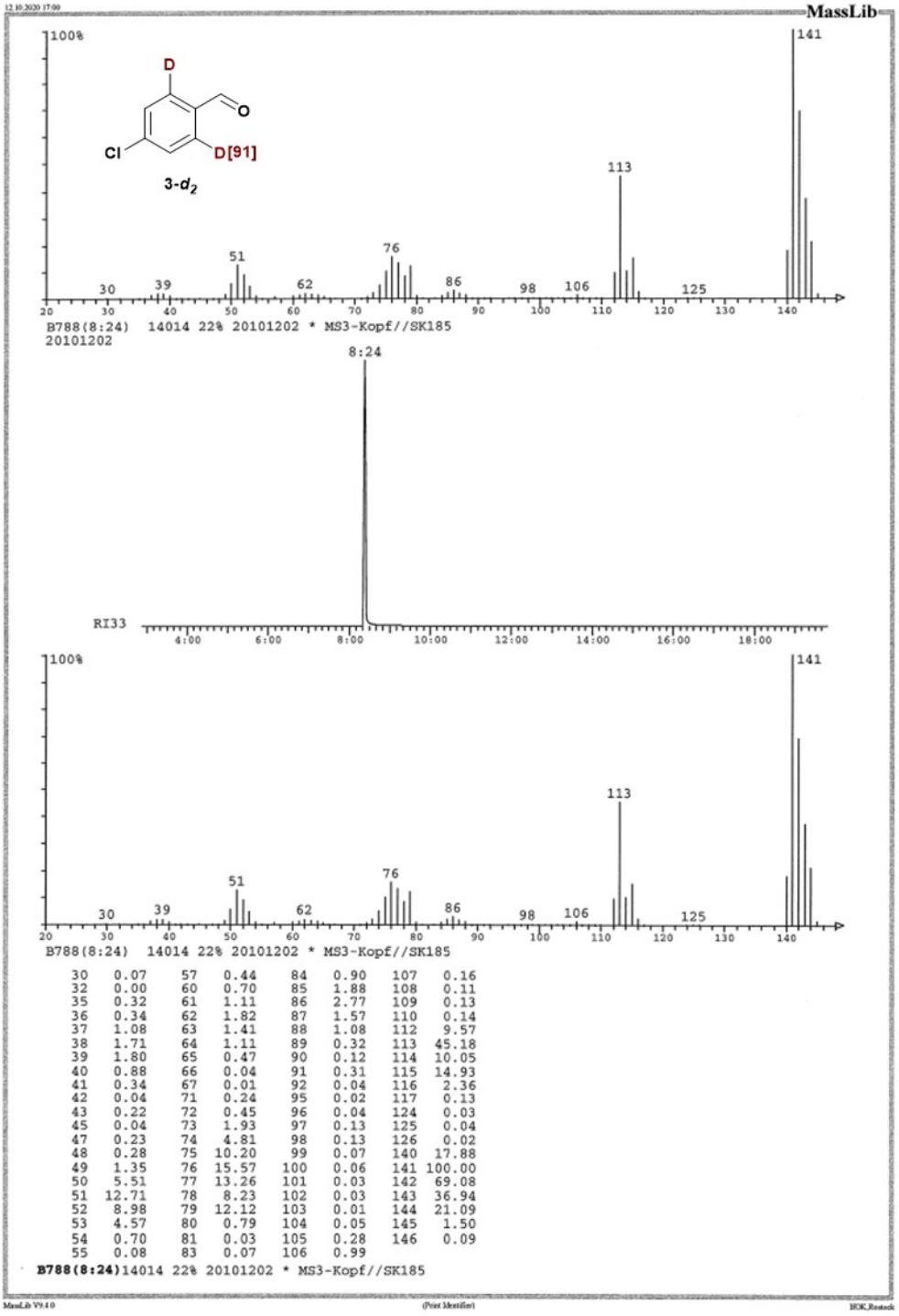

201117.315.11.fid
Sara Kopf SK264-col
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 15
191.5
190.9
163.8
133.8
133.0
127.7
122.7
122.4
41.7
32.1
27.0
25.8
25.7
17.8
CD3[97]
O
[65]D
D
D[89]
31-d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

9 Mass spectra



30	0.16	57	0.03	80	3.09	108	5.86
31	0.13	59	0.03	81	1.08	109	7.95
32	0.04	60	0.12	82	0.07	110	1.17
36	0.07	61	0.73	83	0.02	111	0.10
37	0.63	62	1.43	84	0.05	119	0.08
38	1.48	63	3.28	85	0.09	120	0.42
39	3.43	64	6.68	86	0.12	121	0.70
40	3.93	65	7.32	87	0.13	122	0.36
41	1.16	66	8.55	88	0.06	123	0.13
42	0.11	67	5.70	89	0.03	124	0.03
43	0.11	68	0.42	90	0.07	135	10.22
44	0.02	69	0.05	91	0.15	136	55.92
48	0.05	70	0.02	92	1.94	137	100.00
49	0.38	72	0.05	93	7.91	138	49.24
50	2.50	73	0.34	94	10.58	139	4.42
51	5.20	74	1.48	95	1.71	140	0.40
52	4.52	75	2.43	96	0.12	141	0.05
53	2.05	76	1.91	104	0.13		
54	1.02	77	5.66	105	0.43		
55	0.25	78	15.96	106	0.99		
56	0.13	79	16.25	107	1.74		

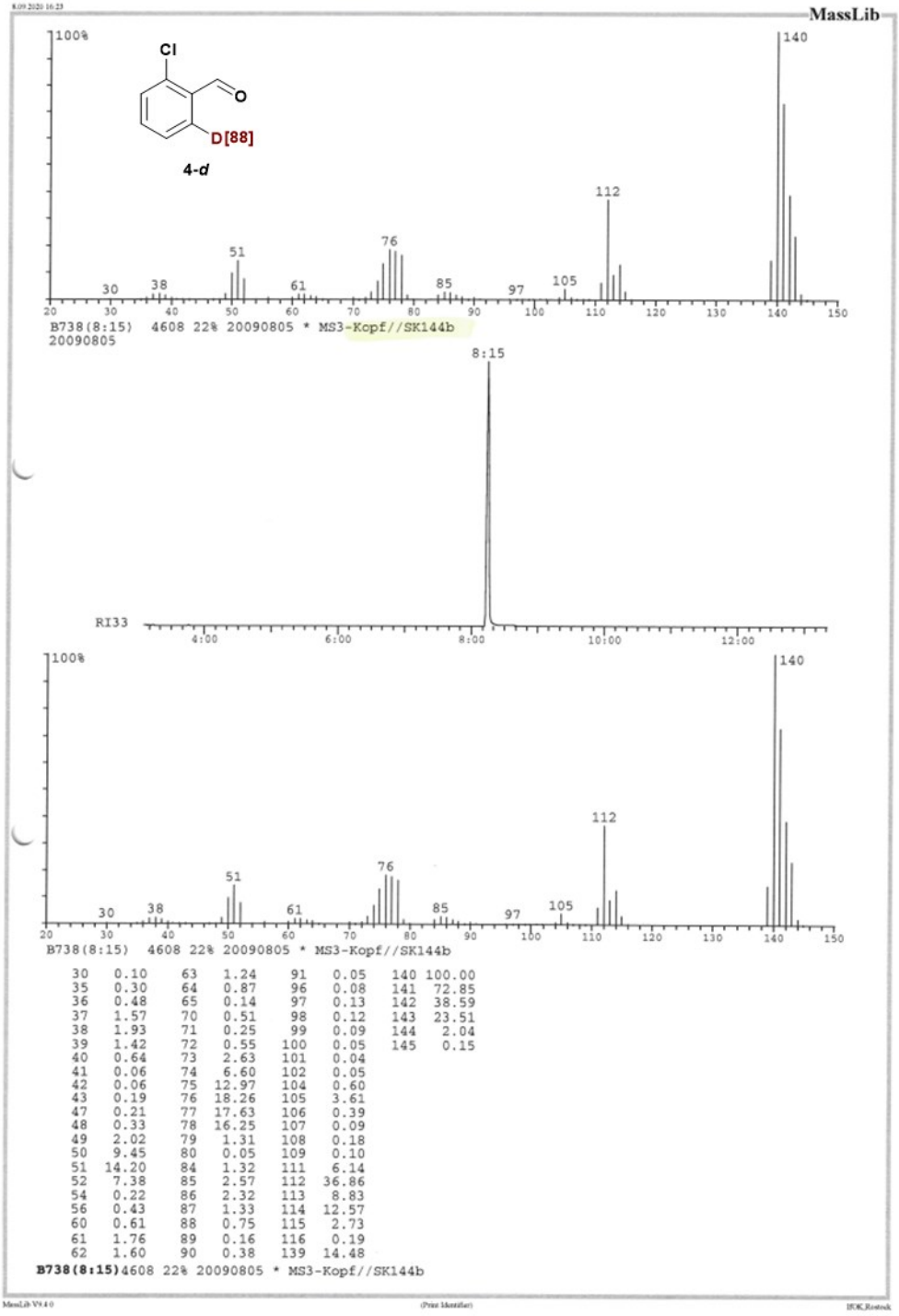
B1139(10:33)7402 27% 20101302 * MS3-Kopf//SK 178j-2+3



B788(8:24) 14014 22% 20101202 * MS3-Kopf//SK185

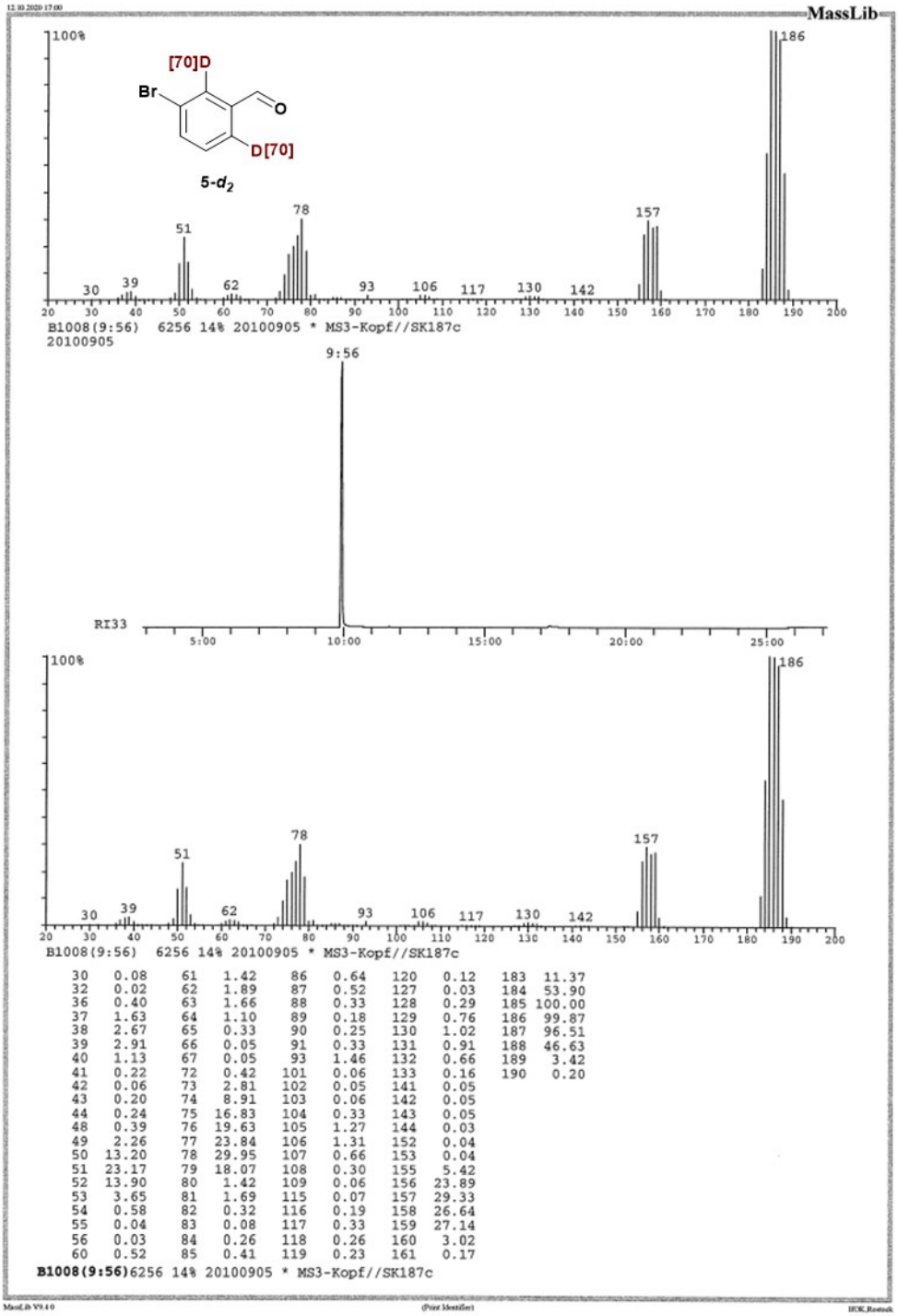
30	0.07	57	0.44	84	0.90	107	0.16
32	0.00	60	0.70	85	1.88	108	0.11
35	0.32	61	1.11	86	2.77	109	0.13
36	0.34	62	1.82	87	1.57	110	0.14
37	1.08	63	1.41	88	1.08	112	9.57
38	1.71	64	1.11	89	0.32	113	45.18
39	1.80	65	0.47	90	0.12	114	10.05
40	0.88	66	0.04	91	0.31	115	14.93
41	0.34	67	0.01	92	0.04	116	2.36
42	0.04	71	0.24	95	0.02	117	0.13
43	0.22	72	0.45	96	0.04	124	0.03
45	0.04	73	1.93	97	0.13	125	0.04
47	0.23	74	4.81	98	0.13	126	0.02
48	0.28	75	10.20	99	0.07	140	17.88
49	1.35	76	15.57	100	0.06	141	100.00
50	5.51	77	13.26	101	0.03	142	69.08
51	12.71	78	8.23	102	0.03	143	36.94
52	8.98	79	12.12	103	0.01	144	21.09
53	4.57	80	0.79	104	0.05	145	1.50
54	0.70	81	0.03	105	0.28	146	0.09
55	0.08	83	0.07	106	0.99		

B788(8:24)14014 22% 20101202 * MS3-Kopf//SK185



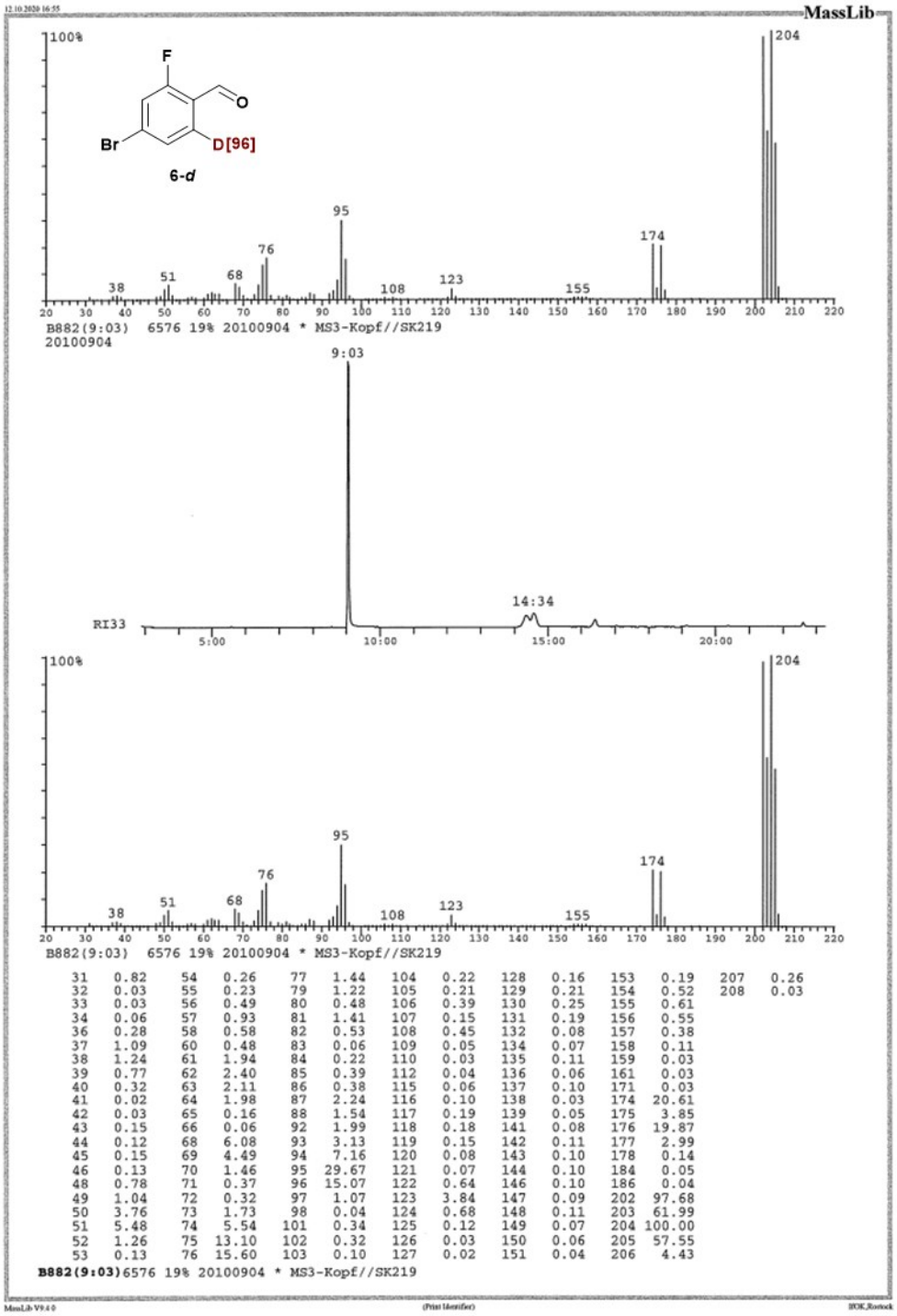
30	0.10	63	1.24	91	0.05	140	100.00
35	0.30	64	0.87	96	0.08	141	72.85
36	0.48	65	0.14	97	0.13	142	38.59
37	1.57	70	0.51	98	0.12	143	23.51
38	1.93	71	0.25	99	0.09	144	2.04
39	1.42	72	0.55	100	0.05	145	0.15
40	0.64	73	2.63	101	0.04		
41	0.06	74	6.60	102	0.05		
42	0.06	75	12.97	104	0.60		
43	0.19	76	18.26	105	3.61		
47	0.21	77	17.63	106	0.39		
48	0.33	78	16.25	107	0.09		
49	2.02	79	1.31	108	0.18		
50	9.45	80	0.05	109	0.10		
51	14.20	84	1.32	111	6.14		
52	7.38	85	2.57	112	36.86		
54	0.22	86	2.32	113	8.83		
56	0.43	87	1.33	114	12.57		
60	0.61	88	0.75	115	2.73		
61	1.76	89	0.16	116	0.19		
62	1.60	90	0.38	139	14.48		

B738(8:15)4608 22% 20090805 * MS3-Kopf//SK144b

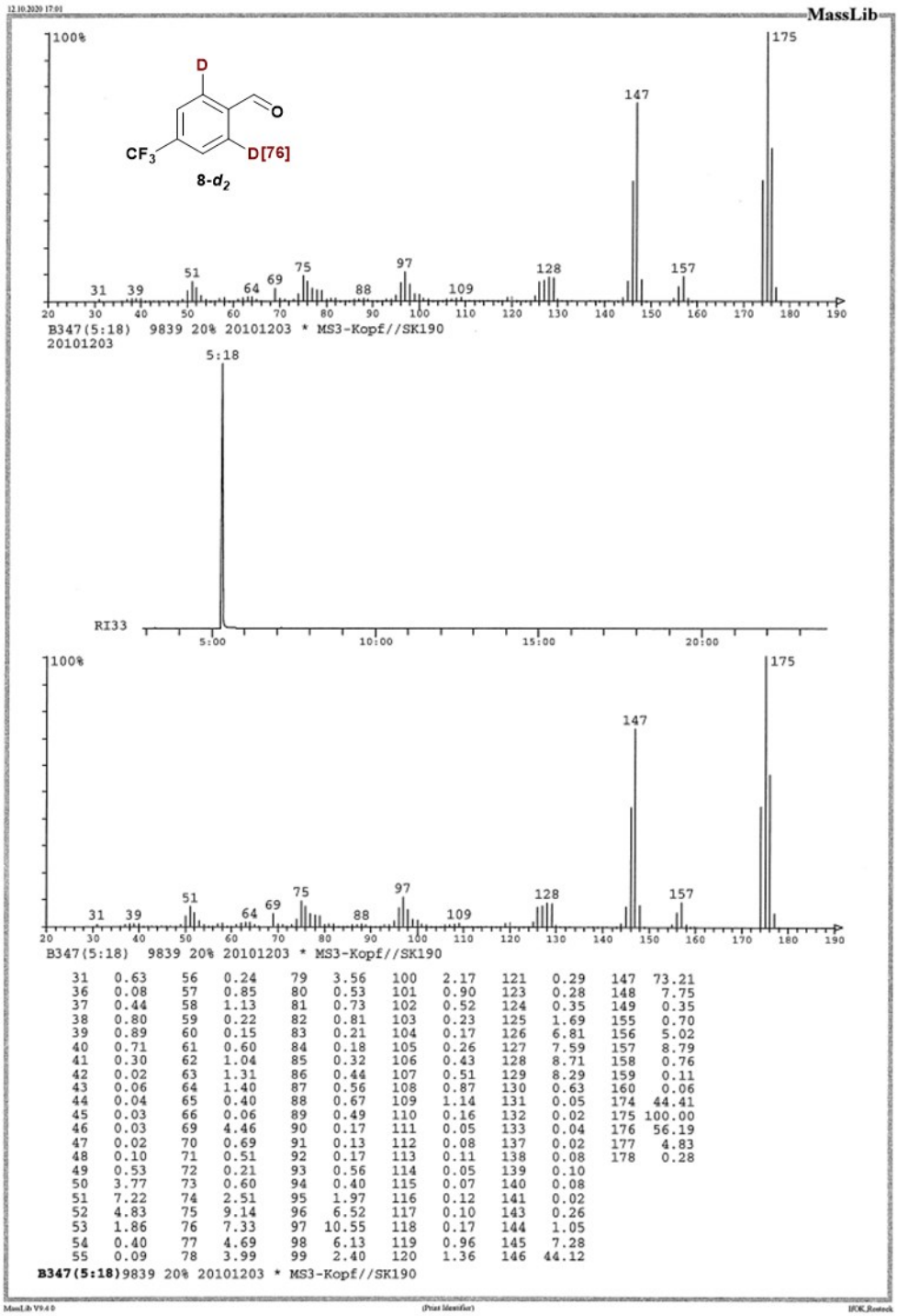


30	0.08	61	1.42	86	0.64	120	0.12	183	11.37
32	0.02	62	1.89	87	0.52	127	0.03	184	53.90
36	0.40	63	1.66	88	0.33	128	0.29	185	100.00
37	1.63	64	1.10	89	0.18	129	0.76	186	99.87
38	2.67	65	0.33	90	0.25	130	1.02	187	96.51
39	2.91	66	0.05	91	0.33	131	0.91	188	46.63
40	1.13	67	0.05	93	1.46	132	0.66	189	3.42
41	0.22	72	0.42	101	0.06	133	0.16	190	0.20
42	0.06	73	2.81	102	0.05	141	0.05		
43	0.20	74	8.91	103	0.06	142	0.05		
44	0.24	75	16.83	104	0.33	143	0.05		
48	0.39	76	19.63	105	1.27	144	0.03		
49	2.26	77	23.84	106	1.31	152	0.04		
50	13.20	78	29.95	107	0.66	153	0.04		
51	23.17	79	18.07	108	0.30	155	5.42		
52	13.90	80	1.42	109	0.06	156	23.89		
53	3.65	81	1.69	115	0.07	157	29.33		
54	0.58	82	0.32	116	0.19	158	26.64		
55	0.04	83	0.08	117	0.33	159	27.14		
56	0.03	84	0.26	118	0.26	160	3.02		
60	0.52	85	0.41	119	0.23	161	0.17		

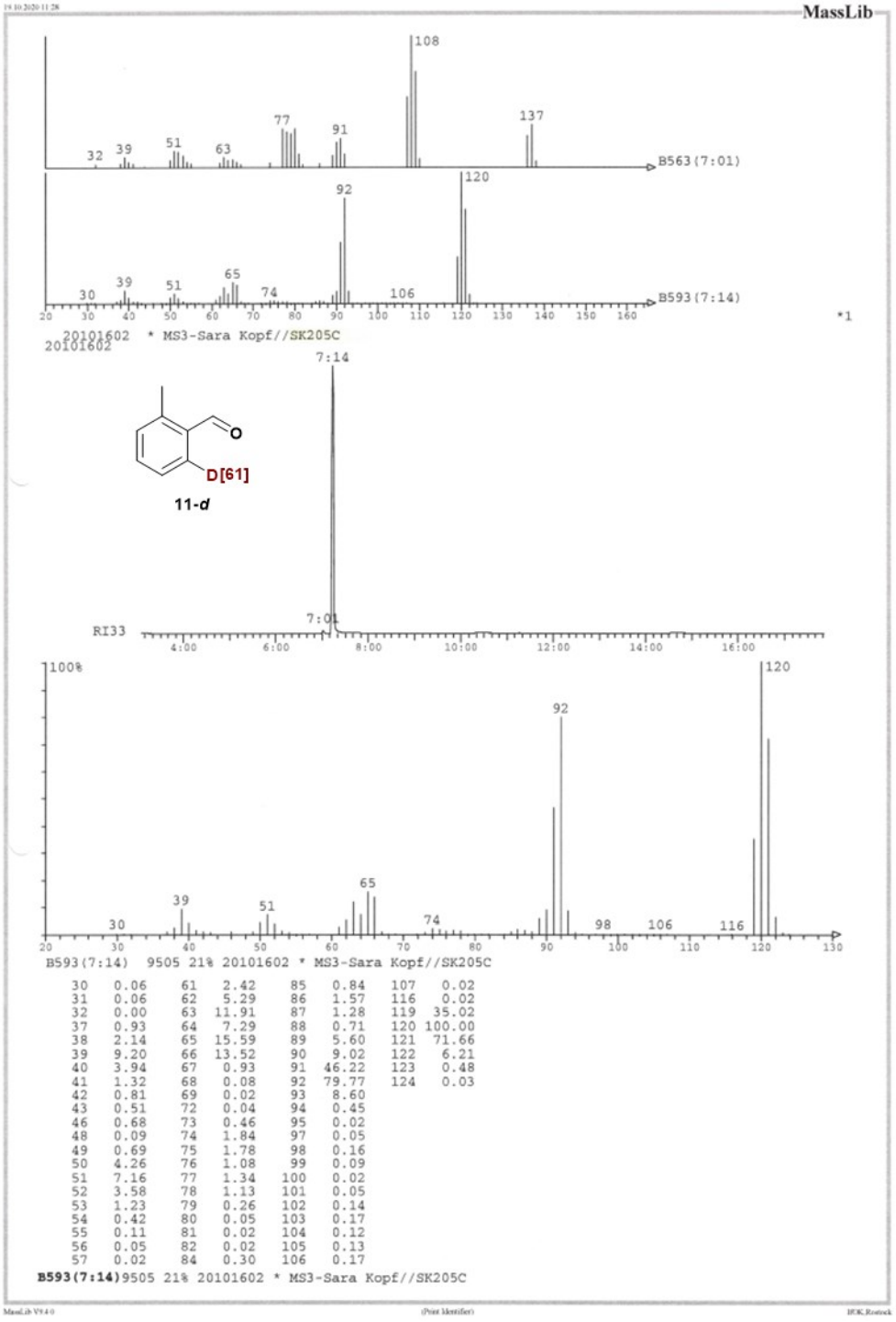
B1008(9:56) 6256 14% 20100905 * MS3-Kopf//SK187c



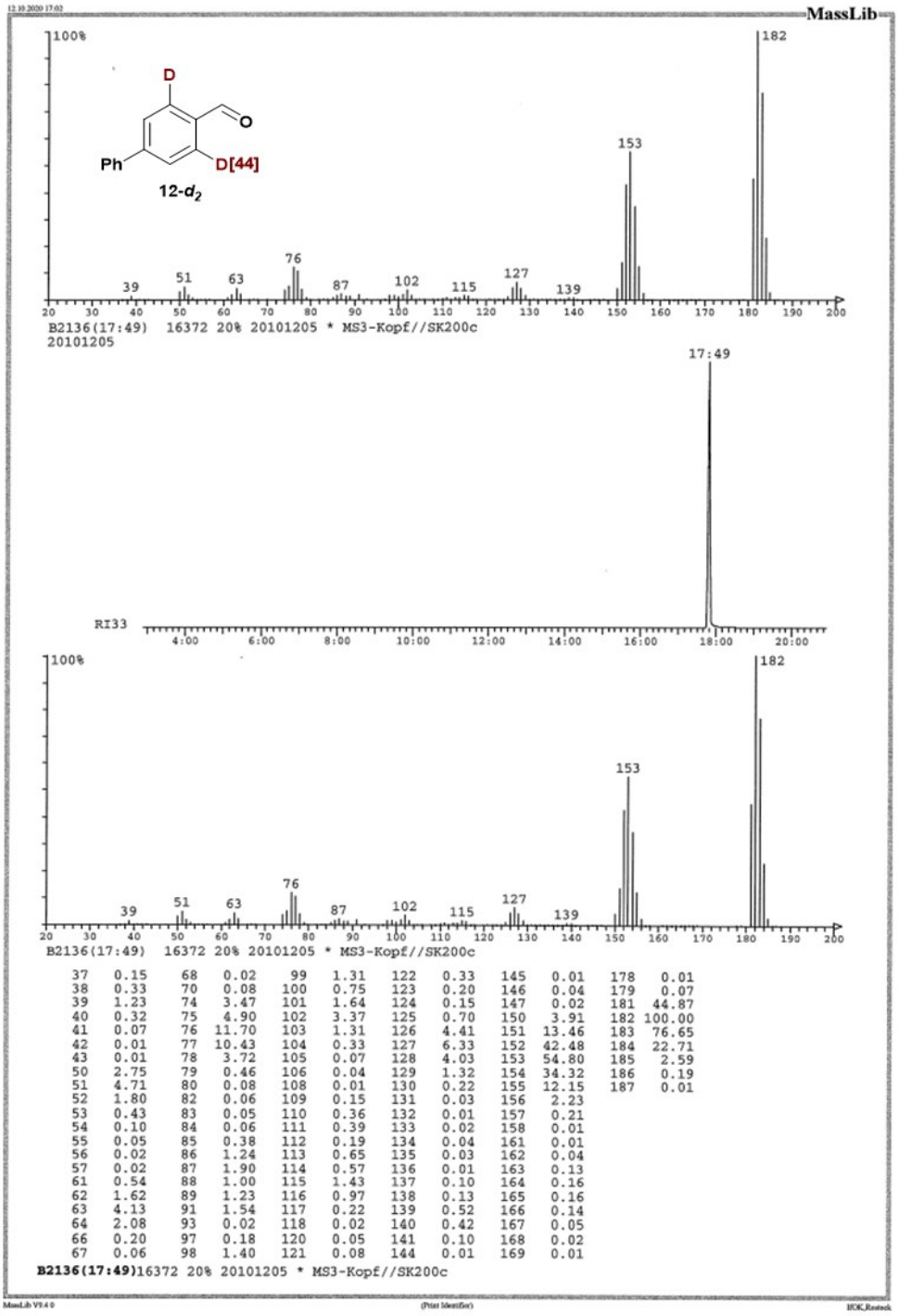
31	0.82	54	0.26	77	1.44	104	0.22	128	0.16	153	0.19	207	0.26
32	0.03	55	0.23	79	1.22	105	0.21	129	0.21	154	0.52	208	0.03
33	0.03	56	0.49	80	0.48	106	0.39	130	0.25	155	0.61		
34	0.06	57	0.93	81	1.41	107	0.15	131	0.19	156	0.55		
36	0.28	58	0.58	82	0.53	108	0.45	132	0.08	157	0.38		
37	1.09	60	0.48	83	0.06	109	0.05	134	0.07	158	0.11		
38	1.24	61	1.94	84	0.22	110	0.03	135	0.11	159	0.03		
39	0.77	62	2.40	85	0.39	112	0.04	136	0.06	161	0.03		
40	0.32	63	2.11	86	0.38	115	0.06	137	0.10	171	0.03		
41	0.02	64	1.98	87	2.24	116	0.10	138	0.03	174	20.61		
42	0.03	65	0.16	88	1.54	117	0.19	139	0.05	175	3.85		
43	0.15	66	0.06	92	1.99	118	0.18	141	0.08	176	19.87		
44	0.12	68	6.08	93	3.13	119	0.15	142	0.11	177	2.99		
45	0.15	69	4.49	94	7.16	120	0.08	143	0.10	178	0.14		
46	0.13	70	1.46	95	29.67	121	0.07	144	0.10	184	0.05		
48	0.78	71	0.37	96	15.07	122	0.64	146	0.10	186	0.04		
49	1.04	72	0.32	97	1.07	123	3.84	147	0.09	202	97.68		
50	3.76	73	1.73	98	0.04	124	0.68	148	0.11	203	61.99		
51	5.48	74	5.54	101	0.34	125	0.12	149	0.07	204	100.00		
52	1.26	75	13.10	102	0.32	126	0.03	150	0.06	205	57.55		
53	0.13	76	15.60	103	0.10	127	0.02	151	0.04	206	4.43		



31	0.63	56	0.24	79	3.56	100	2.17	121	0.29	147	73.21
36	0.08	57	0.85	80	0.53	101	0.90	123	0.28	148	7.75
37	0.44	58	1.13	81	0.73	102	0.52	124	0.35	149	0.35
38	0.80	59	0.22	82	0.81	103	0.23	125	1.69	155	0.70
39	0.89	60	0.15	83	0.21	104	0.17	126	6.81	156	5.02
40	0.71	61	0.60	84	0.18	105	0.26	127	7.59	157	8.79
41	0.30	62	1.04	85	0.32	106	0.43	128	8.71	158	0.76
42	0.02	63	1.31	86	0.44	107	0.51	129	8.29	159	0.11
43	0.06	64	1.40	87	0.56	108	0.87	130	0.63	160	0.06
44	0.04	65	0.40	88	0.67	109	1.14	131	0.05	174	44.41
45	0.03	66	0.06	89	0.49	110	0.16	132	0.02	175	100.00
46	0.03	69	4.46	90	0.17	111	0.05	133	0.04	176	56.19
47	0.02	70	0.69	91	0.13	112	0.08	137	0.02	177	4.83
48	0.10	71	0.51	92	0.17	113	0.11	138	0.08	178	0.28
49	0.53	72	0.21	93	0.56	114	0.05	139	0.10		
50	3.77	73	0.60	94	0.40	115	0.07	140	0.08		
51	7.22	74	2.51	95	1.97	116	0.12	141	0.02		
52	4.83	75	9.14	96	6.52	117	0.10	143	0.26		
53	1.86	76	7.33	97	10.55	118	0.17	144	1.05		
54	0.40	77	4.69	98	6.13	119	0.96	145	7.28		
55	0.09	78	3.99	99	2.40	120	1.36	146	44.12		

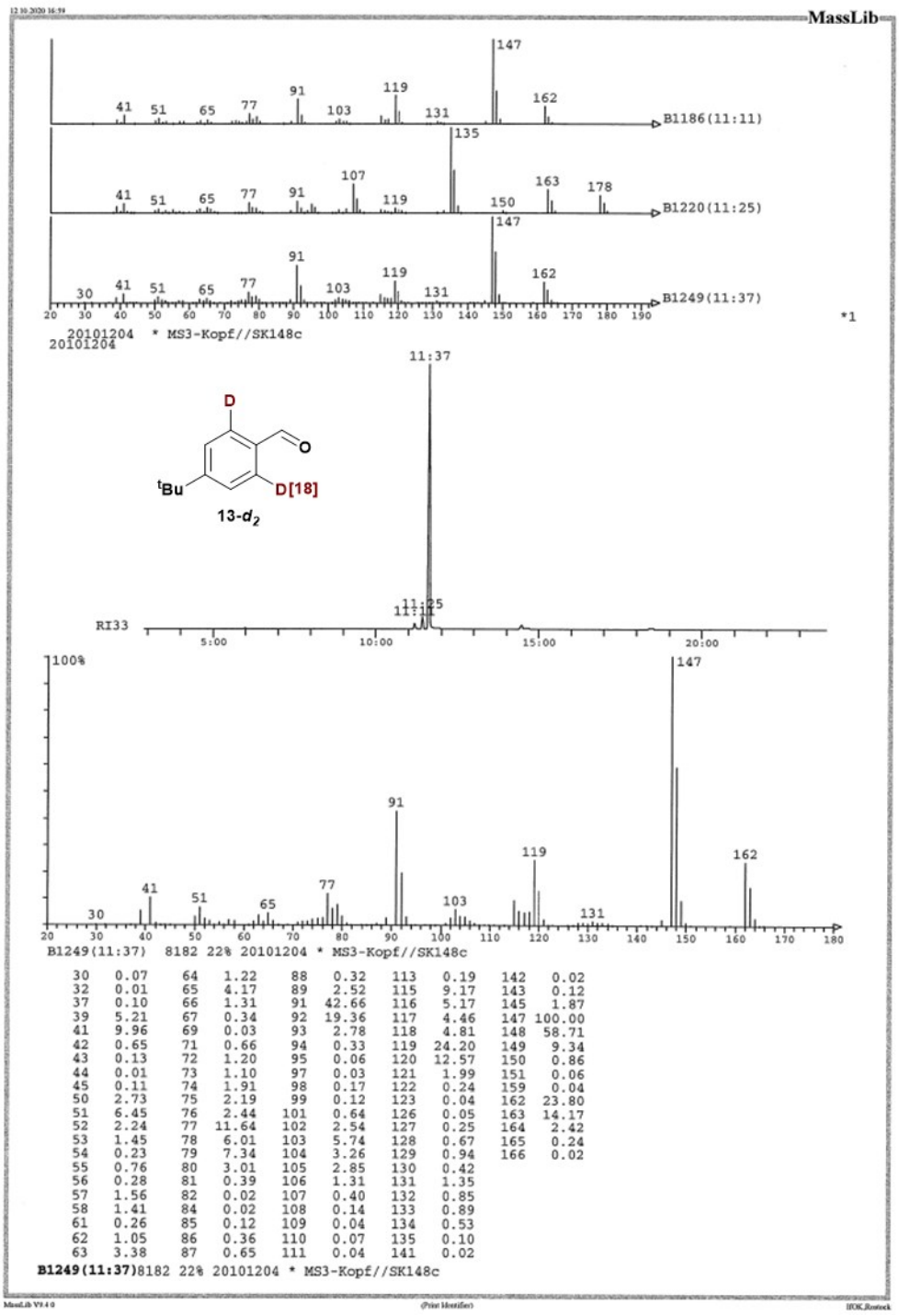


30	0.06	61	2.42	85	0.84	107	0.02
31	0.06	62	5.29	86	1.57	116	0.02
32	0.00	63	11.91	87	1.28	119	35.02
37	0.93	64	7.29	88	0.71	120	100.00
38	2.14	65	15.59	89	5.60	121	71.66
39	9.20	66	13.52	90	9.02	122	6.21
40	3.94	67	0.93	91	46.22	123	0.48
41	1.32	68	0.08	92	79.77	124	0.03
42	0.81	69	0.02	93	8.60		
43	0.51	72	0.04	94	0.45		
46	0.68	73	0.46	95	0.02		
48	0.09	74	1.84	97	0.05		
49	0.69	75	1.78	98	0.16		
50	4.26	76	1.08	99	0.09		
51	7.16	77	1.34	100	0.02		
52	3.58	78	1.13	101	0.05		
53	1.23	79	0.26	102	0.14		
54	0.42	80	0.05	103	0.17		
55	0.11	81	0.02	104	0.12		
56	0.05	82	0.02	105	0.13		
57	0.02	84	0.30	106	0.17		



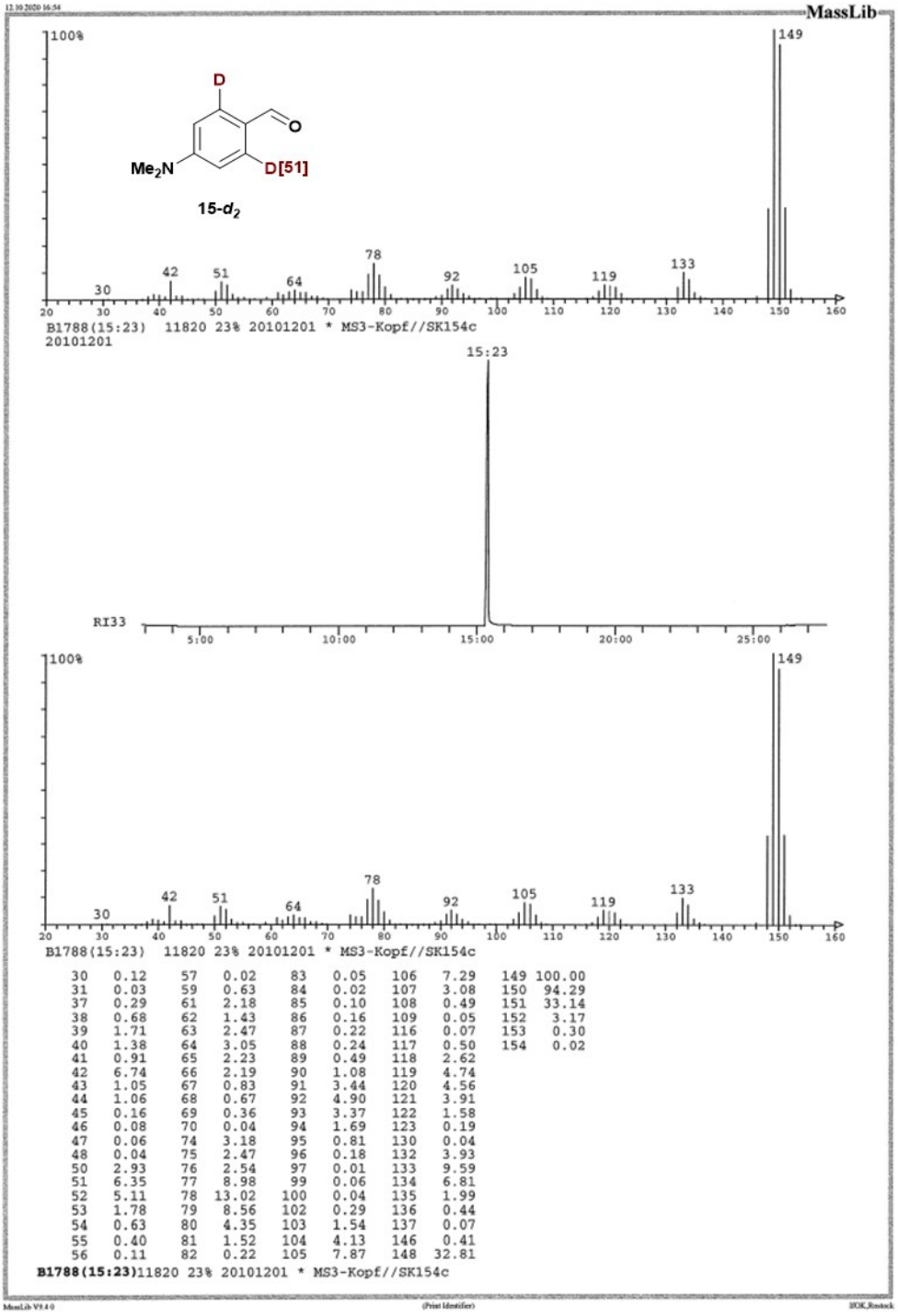
37	0.15	68	0.02	99	1.31	122	0.33	145	0.01	178	0.01
38	0.33	70	0.08	100	0.75	123	0.20	146	0.04	179	0.07
39	1.23	74	3.47	101	1.64	124	0.15	147	0.02	181	44.87
40	0.32	75	4.90	102	3.37	125	0.70	150	3.91	182	100.00
41	0.07	76	11.70	103	1.31	126	4.41	151	13.46	183	76.65
42	0.01	77	10.43	104	0.33	127	6.33	152	42.48	184	22.71
43	0.01	78	3.72	105	0.07	128	4.03	153	54.80	185	2.59
50	2.75	79	0.46	106	0.04	129	1.32	154	34.32	186	0.19
51	4.71	80	0.08	108	0.01	130	0.22	155	12.15	187	0.01
52	1.80	82	0.06	109	0.15	131	0.03	156	2.23		
53	0.43	83	0.05	110	0.36	132	0.01	157	0.21		
54	0.10	84	0.06	111	0.39	133	0.02	158	0.01		
55	0.05	85	0.38	112	0.19	134	0.04	161	0.01		
56	0.02	86	1.24	113	0.65	135	0.03	162	0.04		
57	0.02	87	1.90	114	0.57	136	0.01	163	0.13		
61	0.54	88	1.00	115	1.43	137	0.10	164	0.16		
62	1.62	89	1.23	116	0.97	138	0.13	165	0.16		
63	4.13	91	1.54	117	0.22	139	0.52	166	0.14		
64	2.08	93	0.02	118	0.02	140	0.42	167	0.05		
66	0.20	97	0.18	120	0.05	141	0.10	168	0.02		
67	0.06	98	1.40	121	0.08	144	0.01	169	0.01		

B2136(17:49)16372 20% 20101205 * MS3-Kopf//SK200c



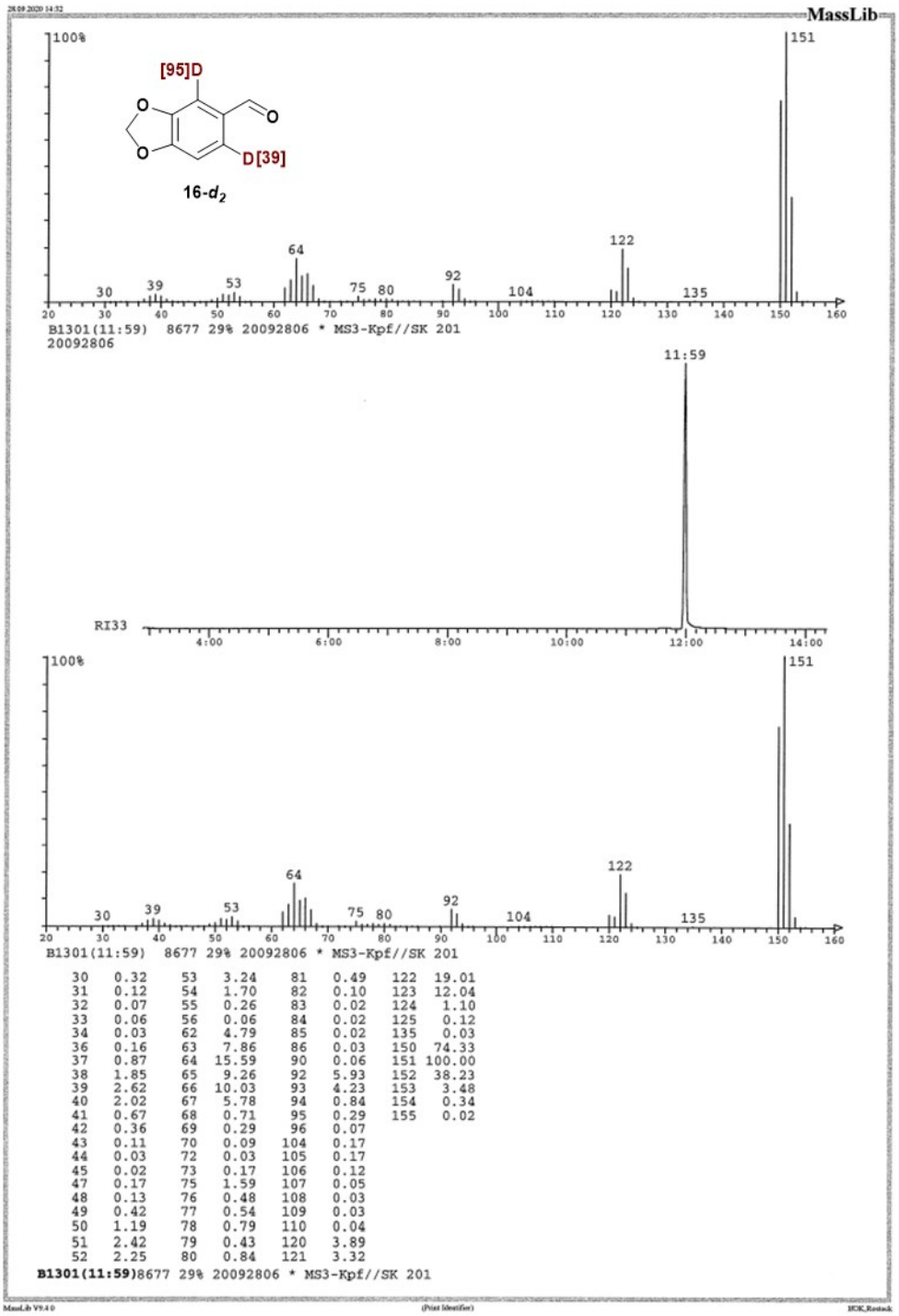
30	0.07	64	1.22	88	0.32	113	0.19	142	0.02
32	0.01	65	4.17	89	2.52	115	9.17	143	0.12
37	0.10	66	1.31	91	42.66	116	5.17	145	1.87
39	5.21	67	0.34	92	19.36	117	4.46	147	100.00
41	9.96	69	0.03	93	2.78	118	4.81	148	58.71
42	0.65	71	0.66	94	0.33	119	24.20	149	9.34
43	0.13	72	1.20	95	0.06	120	12.57	150	0.86
44	0.01	73	1.10	97	0.03	121	1.99	151	0.06
45	0.11	74	1.91	98	0.17	122	0.24	159	0.04
50	2.73	75	2.19	99	0.12	123	0.04	162	23.80
51	6.45	76	2.44	101	0.64	126	0.05	163	14.17
52	2.24	77	11.64	102	2.54	127	0.25	164	2.42
53	1.45	78	6.01	103	5.74	128	0.67	165	0.24
54	0.23	79	7.34	104	3.26	129	0.94	166	0.02
55	0.76	80	3.01	105	2.85	130	0.42		
56	0.28	81	0.39	106	1.31	131	1.35		
57	1.56	82	0.02	107	0.40	132	0.85		
58	1.41	84	0.02	108	0.14	133	0.89		
61	0.26	85	0.12	109	0.04	134	0.53		
62	1.05	86	0.36	110	0.07	135	0.10		
63	3.38	87	0.65	111	0.04	141	0.02		

B1249(11:37)8182 22% 20101204 * MS3-Kopf//SK148c



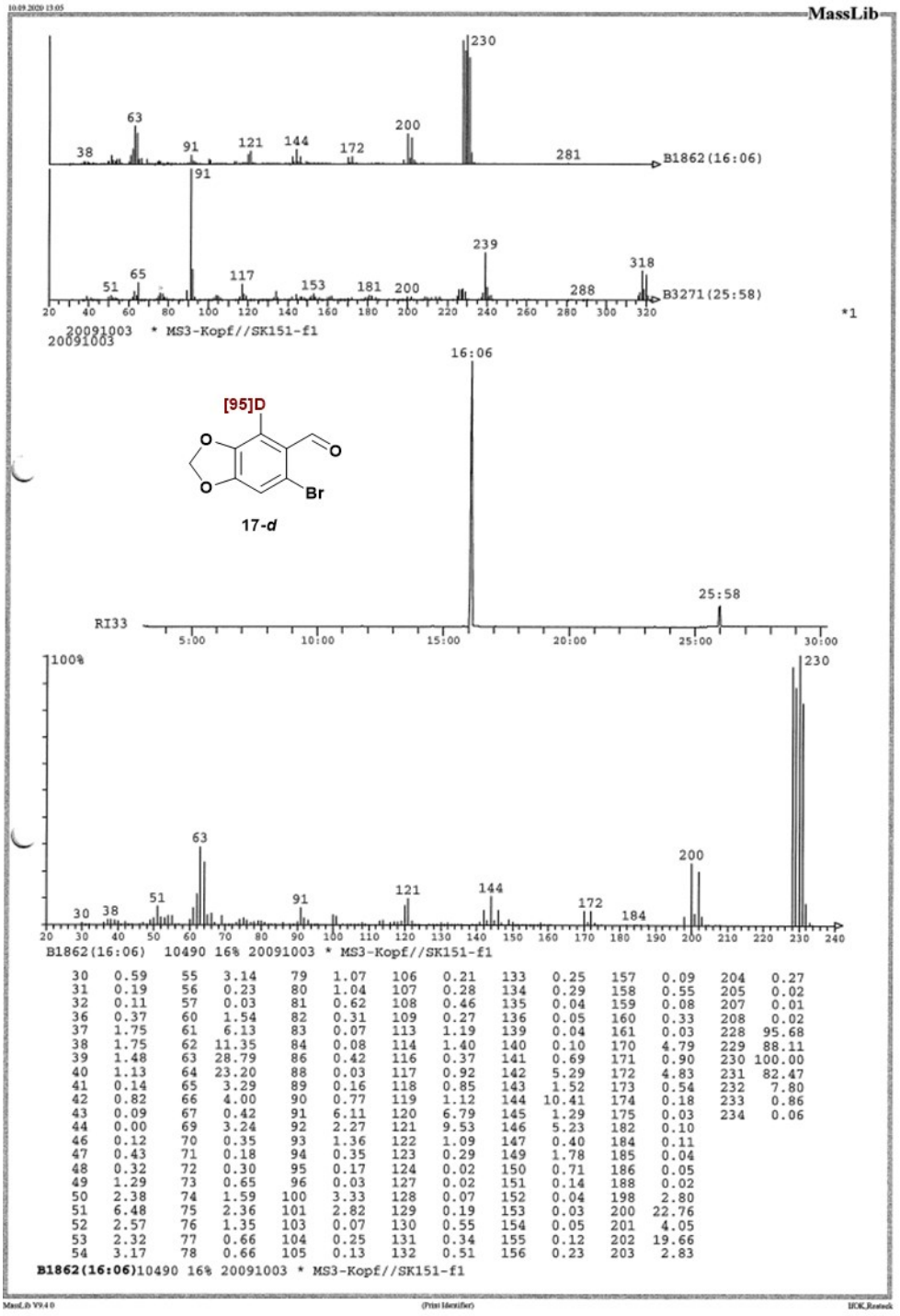
30	0.12	57	0.02	83	0.05	106	7.29	149	100.00
31	0.03	59	0.63	84	0.02	107	3.08	150	94.29
37	0.29	61	2.18	85	0.10	108	0.49	151	33.14
38	0.68	62	1.43	86	0.16	109	0.05	152	3.17
39	1.71	63	2.47	87	0.22	116	0.07	153	0.30
40	1.38	64	3.05	88	0.24	117	0.50	154	0.02
41	0.91	65	2.23	89	0.49	118	2.62		
42	6.74	66	2.19	90	1.08	119	4.74		
43	1.05	67	0.83	91	3.44	120	4.56		
44	1.06	68	0.67	92	4.90	121	3.91		
45	0.16	69	0.36	93	3.37	122	1.58		
46	0.08	70	0.04	94	1.69	123	0.19		
47	0.06	74	3.18	95	0.81	130	0.04		
48	0.04	75	2.47	96	0.18	132	3.93		
50	2.93	76	2.54	97	0.01	133	9.59		
51	6.35	77	8.98	99	0.06	134	6.81		
52	5.11	78	13.02	100	0.04	135	1.99		
53	1.78	79	8.56	102	0.29	136	0.44		
54	0.63	80	4.35	103	1.54	137	0.07		
55	0.40	81	1.52	104	4.13	146	0.41		
56	0.11	82	0.22	105	7.87	148	32.81		

B1788(15:23)11820 23% 20101201 * MS3-Kopf//SK154c



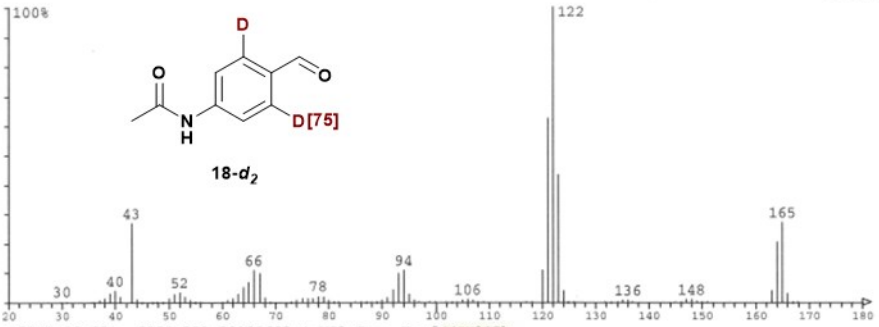
30	0.32	53	3.24	81	0.49	122	19.01
31	0.12	54	1.70	82	0.10	123	12.04
32	0.07	55	0.26	83	0.02	124	1.10
33	0.06	56	0.06	84	0.02	125	0.12
34	0.03	62	4.79	85	0.02	135	0.03
36	0.16	63	7.86	86	0.03	150	74.33
37	0.87	64	15.59	90	0.06	151	100.00
38	1.85	65	9.26	92	5.93	152	38.23
39	2.62	66	10.03	93	4.23	153	3.48
40	2.02	67	5.78	94	0.84	154	0.34
41	0.67	68	0.71	95	0.29	155	0.02
42	0.36	69	0.29	96	0.07		
43	0.11	70	0.09	104	0.17		
44	0.03	72	0.03	105	0.17		
45	0.02	73	0.17	106	0.12		
47	0.17	75	1.59	107	0.05		
48	0.13	76	0.48	108	0.03		
49	0.42	77	0.54	109	0.03		
50	1.19	78	0.79	110	0.04		
51	2.42	79	0.43	120	3.89		
52	2.25	80	0.84	121	3.32		

B1301(11:59)8677 29% 20092806 * MS3-Kpf//SK 201

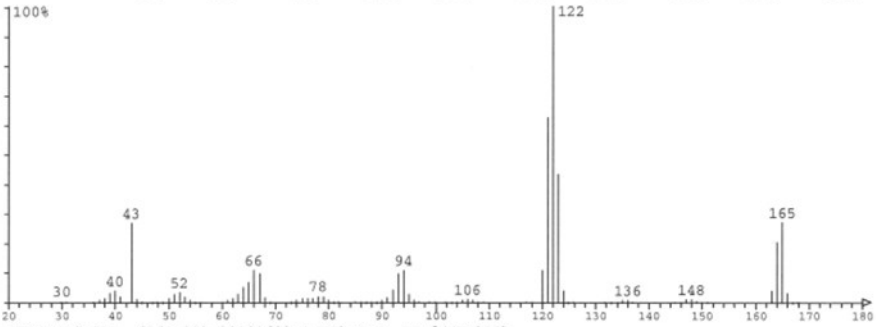


30	0.59	55	3.14	79	1.07	106	0.21	133	0.25	157	0.09	204	0.27
31	0.19	56	0.23	80	1.04	107	0.28	134	0.29	158	0.55	205	0.02
32	0.11	57	0.03	81	0.62	108	0.46	135	0.04	159	0.08	207	0.01
36	0.37	60	1.54	82	0.31	109	0.27	136	0.05	160	0.33	208	0.02
37	1.75	61	6.13	83	0.07	113	1.19	139	0.04	161	0.03	228	95.68
38	1.75	62	11.35	84	0.08	114	1.40	140	0.10	170	4.79	229	88.11
39	1.48	63	28.79	86	0.42	116	0.37	141	0.69	171	0.90	230	100.00
40	1.13	64	23.20	88	0.03	117	0.92	142	5.29	172	4.83	231	82.47
41	0.14	65	3.29	89	0.16	118	0.85	143	1.52	173	0.54	232	7.80
42	0.82	66	4.00	90	0.77	119	1.12	144	10.41	174	0.18	233	0.86
43	0.09	67	0.42	91	6.11	120	6.79	145	1.29	175	0.03	234	0.06
44	0.00	69	3.24	92	2.27	121	9.53	146	5.23	182	0.10		
46	0.12	70	0.35	93	1.36	122	1.09	147	0.40	184	0.11		
47	0.43	71	0.18	94	0.35	123	0.29	149	1.78	185	0.04		
48	0.32	72	0.30	95	0.17	124	0.02	150	0.71	186	0.05		
49	1.29	73	0.65	96	0.03	127	0.02	151	0.14	188	0.02		
50	2.38	74	1.59	100	3.33	128	0.07	152	0.04	198	2.80		
51	6.48	75	2.36	101	2.82	129	0.19	153	0.03	200	22.76		
52	2.57	76	1.35	103	0.07	130	0.55	154	0.05	201	4.05		
53	2.32	77	0.66	104	0.25	131	0.34	155	0.12	202	19.66		
54	3.17	78	0.66	105	0.13	132	0.51	156	0.23	203	2.83		

B1862(16:06)10490 16% 20091003 * MS3-Kopf//SK151-f1



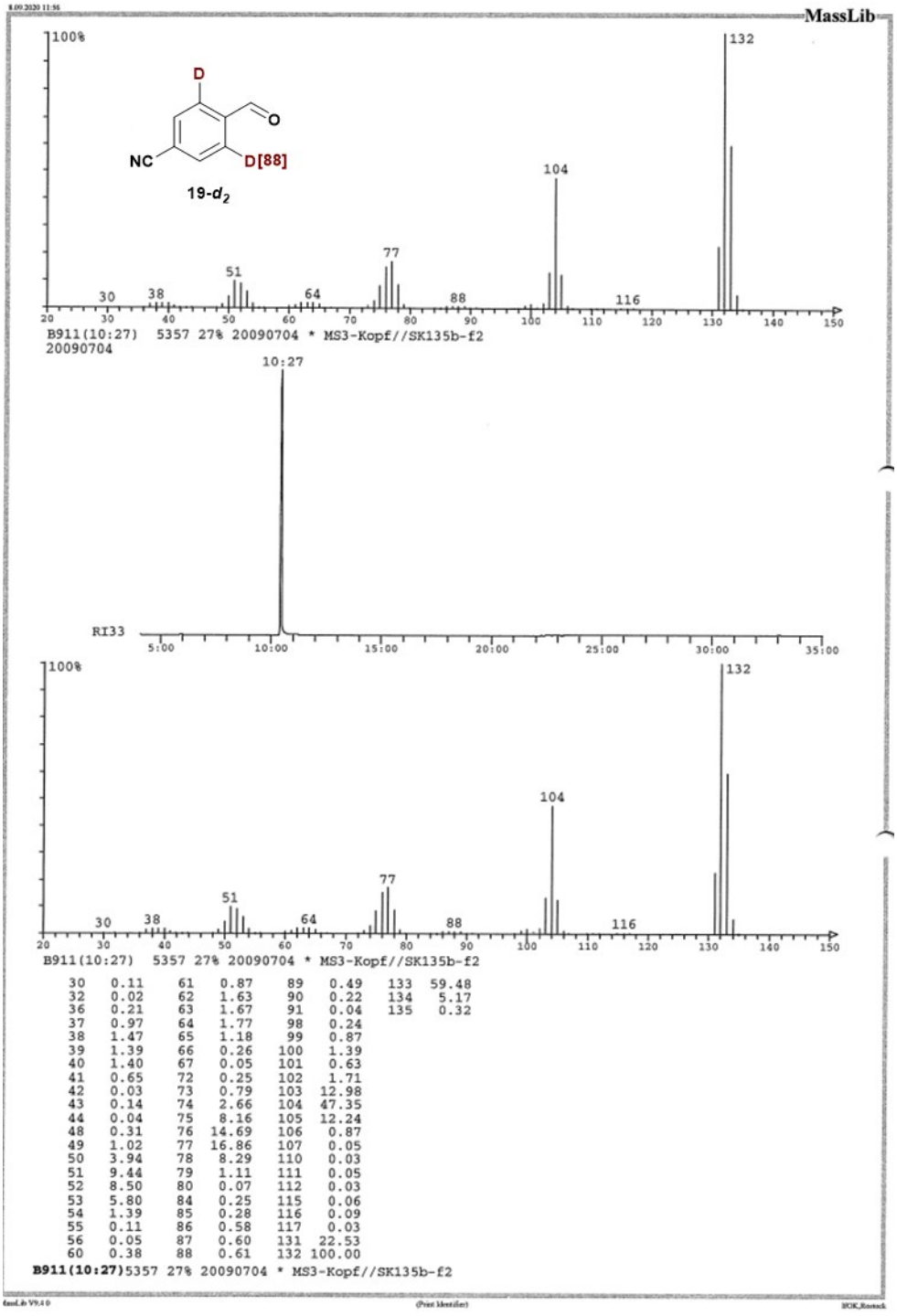
B2141(18:03) 6864 25% 20101603 * MS3-Sara Kopf//SK217b
20101603



B2141(18:03) 6864 25% 20101603 * MS3-Sara Kopf//SK217b

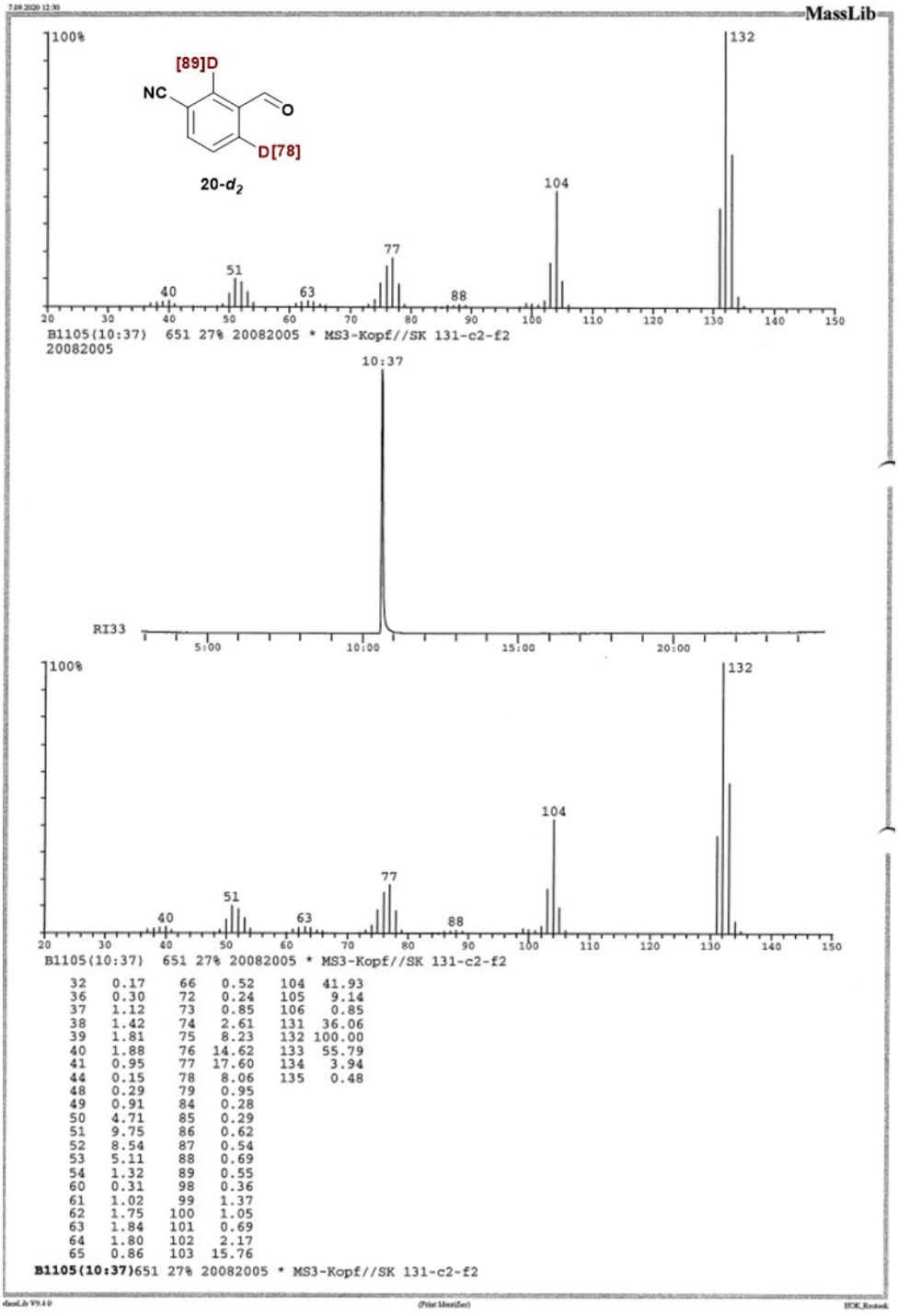
30	0.07	60	0.11	86	0.08	109	0.04	150	0.33
31	0.03	61	0.45	87	0.16	117	0.04	151	0.03
36	0.03	62	1.05	88	0.19	118	0.11	163	3.64
37	0.45	63	2.56	89	0.21	120	10.78	164	20.38
38	1.06	64	4.87	90	0.43	121	62.33	165	27.03
39	2.83	65	6.60	91	1.32	122	100.00	166	2.93
40	3.81	66	10.62	92	4.08	123	43.24	167	0.31
41	1.67	67	9.49	93	9.61	124	3.70	168	0.03
43	26.61	68	1.52	94	10.68	125	0.26		
44	0.85	69	0.14	95	2.65	126	0.02		
45	0.11	73	0.17	96	0.45	132	0.03		
47	0.12	74	0.65	97	0.03	133	0.10		
48	0.03	75	1.11	99	0.02	134	0.20		
49	0.16	76	0.97	100	0.03	135	0.40		
50	1.09	77	1.12	102	0.03	136	0.47		
51	2.42	78	1.81	103	0.09	137	0.08		
52	3.15	79	1.77	104	0.19	145	0.05		
53	1.69	80	0.44	105	0.39	146	0.16		
54	0.55	81	0.21	106	0.69	147	0.70		
55	0.28	82	0.04	107	0.52	148	0.78		
56	0.08	85	0.03	108	0.20	149	0.36		

B2141(18:03)6864 25% 20101603 * MS3-Sara Kopf//SK217b



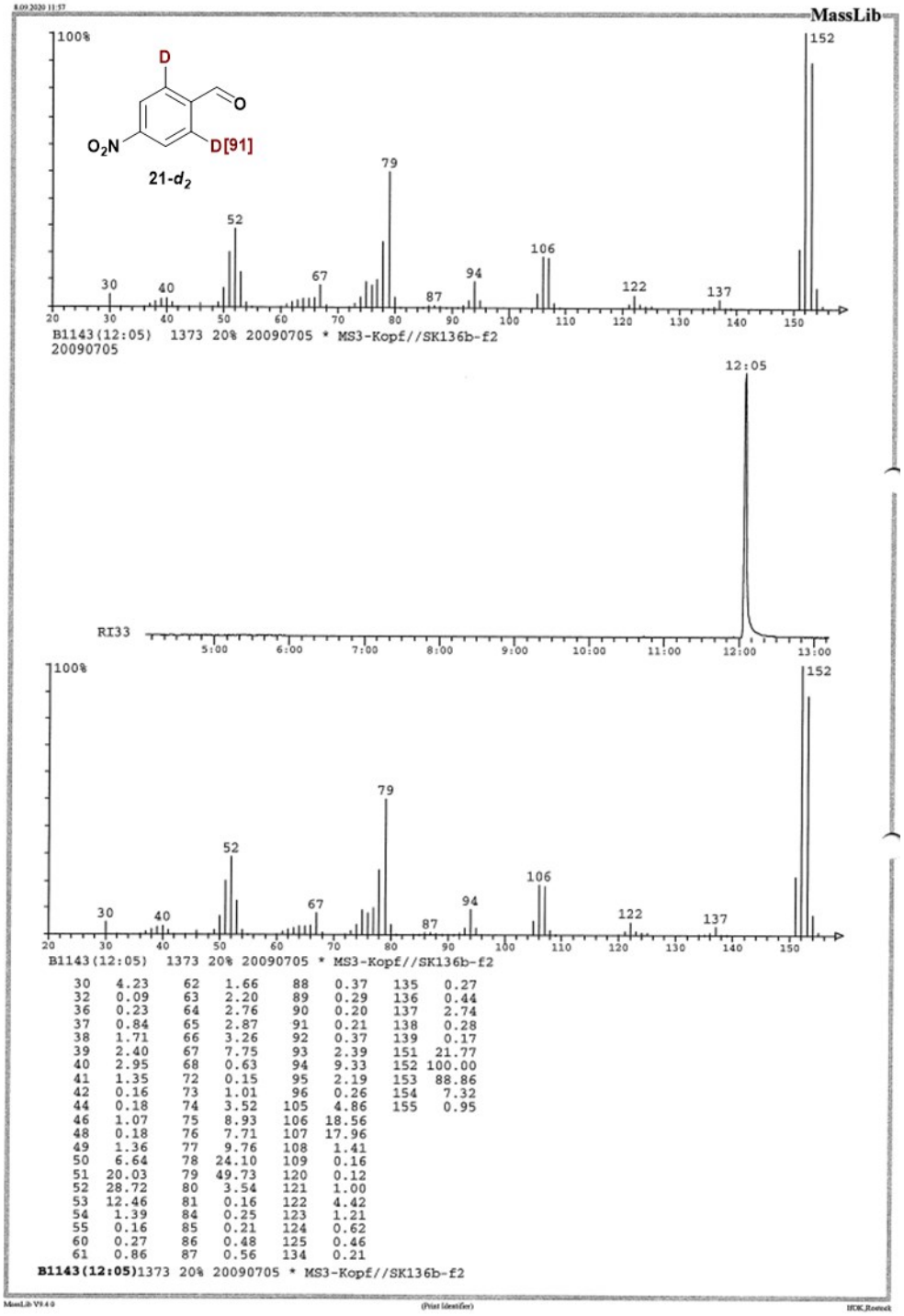
30	0.11	61	0.87	89	0.49	133	59.48
32	0.02	62	1.63	90	0.22	134	5.17
36	0.21	63	1.67	91	0.04	135	0.32
37	0.97	64	1.77	98	0.24		
38	1.47	65	1.18	99	0.87		
39	1.39	66	0.26	100	1.39		
40	1.40	67	0.05	101	0.63		
41	0.65	72	0.25	102	1.71		
42	0.03	73	0.79	103	12.98		
43	0.14	74	2.66	104	47.35		
44	0.04	75	8.16	105	12.24		
48	0.31	76	14.69	106	0.87		
49	1.02	77	16.86	107	0.05		
50	3.94	78	8.29	110	0.03		
51	9.44	79	1.11	111	0.05		
52	8.50	80	0.07	112	0.03		
53	5.80	84	0.25	115	0.06		
54	1.39	85	0.28	116	0.09		
55	0.11	86	0.58	117	0.03		
56	0.05	87	0.60	131	22.53		
60	0.38	88	0.61	132	100.00		

B911(10:27)5357 27% 20090704 * MS3-Kopf//SK135b-f2



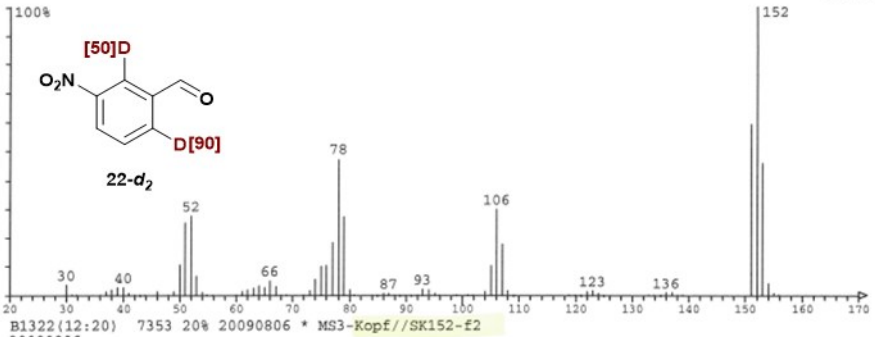
32	0.17	66	0.52	104	41.93
36	0.30	72	0.24	105	9.14
37	1.12	73	0.85	106	0.85
38	1.42	74	2.61	131	36.06
39	1.81	75	8.23	132	100.00
40	1.88	76	14.62	133	55.79
41	0.95	77	17.60	134	3.94
44	0.15	78	8.06	135	0.48
48	0.29	79	0.95		
49	0.91	84	0.28		
50	4.71	85	0.29		
51	9.75	86	0.62		
52	8.54	87	0.54		
53	5.11	88	0.69		
54	1.32	89	0.55		
60	0.31	98	0.36		
61	1.02	99	1.37		
62	1.75	100	1.05		
63	1.84	101	0.69		
64	1.80	102	2.17		
65	0.86	103	15.76		

B1105(10:37)651 27% 20082005 * MS3-Kopf//SK 131-c2-f2

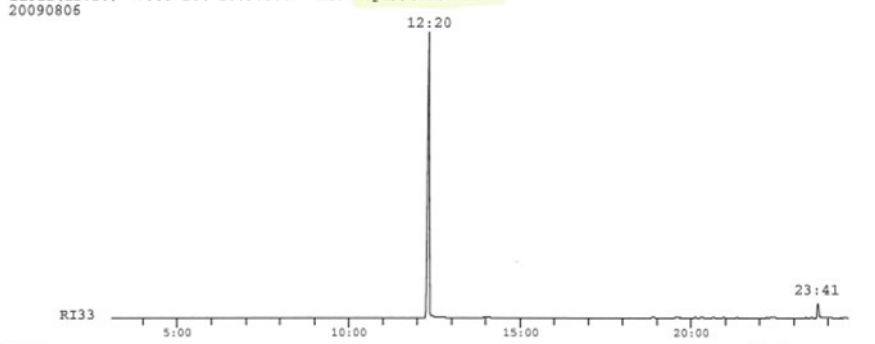


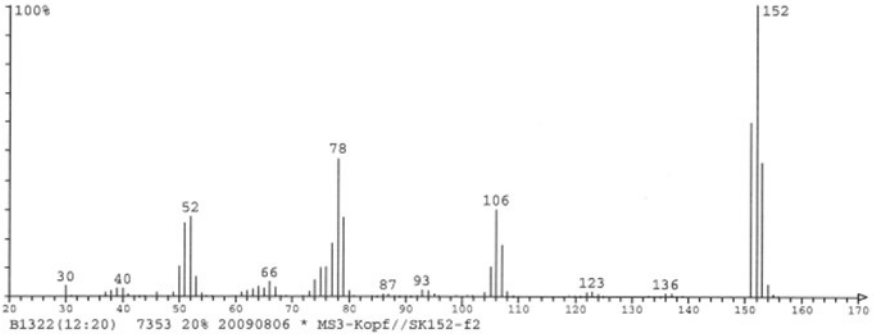
30	4.23	62	1.66	88	0.37	135	0.27
32	0.09	63	2.20	89	0.29	136	0.44
36	0.23	64	2.76	90	0.20	137	2.74
37	0.84	65	2.87	91	0.21	138	0.28
38	1.71	66	3.26	92	0.37	139	0.17
39	2.40	67	7.75	93	2.39	151	21.77
40	2.95	68	0.63	94	9.33	152	100.00
41	1.35	72	0.15	95	2.19	153	88.86
42	0.16	73	1.01	96	0.26	154	7.32
44	0.18	74	3.52	105	4.86	155	0.95
46	1.07	75	8.93	106	18.56		
48	0.18	76	7.71	107	17.96		
49	1.36	77	9.76	108	1.41		
50	6.64	78	24.10	109	0.16		
51	20.03	79	49.73	120	0.12		
52	28.72	80	3.54	121	1.00		
53	12.46	81	0.16	122	4.42		
54	1.39	84	0.25	123	1.21		
55	0.16	85	0.21	124	0.62		
60	0.27	86	0.48	125	0.46		
61	0.86	87	0.56	134	0.21		

B1143(12:05)1373 20% 20090705 * MS3-Kopf//SK136b-f2



B1322(12:20) 7353 20% 20090806 * MS3-Kopf//SK152-f2
20090806

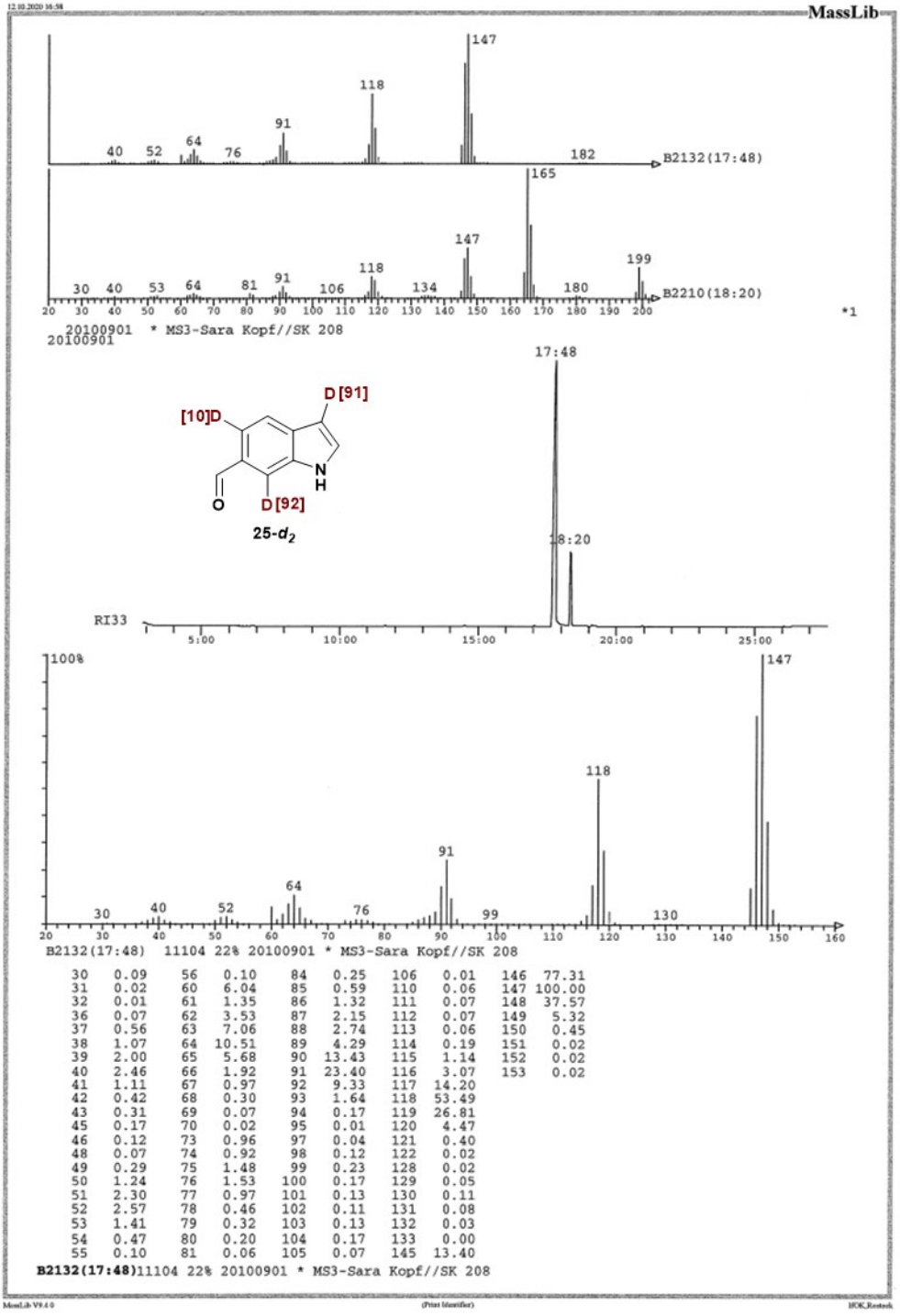




B1322(12:20) 7353 20% 20090806 * MS3-Kopf//SK152-f2

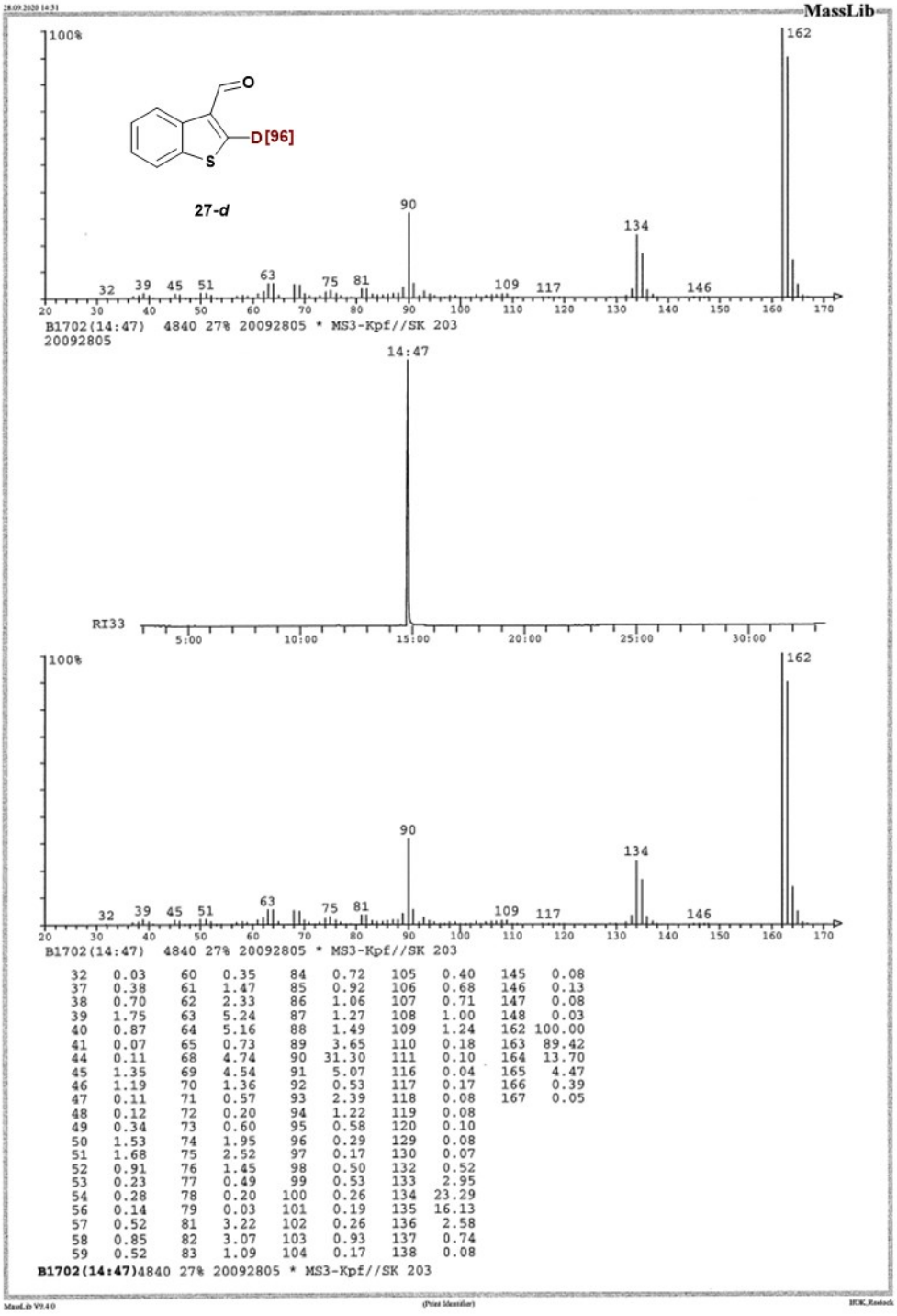
30	3.30	56	0.05	84	0.11	109	0.09
31	0.05	60	0.29	85	0.29	119	0.02
32	0.03	61	1.17	86	0.47	120	0.07
36	0.18	62	1.81	87	0.48	121	0.23
37	1.08	63	2.35	88	0.32	122	1.12
38	1.77	64	3.06	89	0.25	123	1.32
39	2.41	65	2.43	90	0.14	124	0.53
40	2.53	66	4.86	91	0.14	125	0.11
41	0.59	67	2.97	92	0.36	133	0.03
42	0.09	68	0.23	93	1.84	134	0.05
43	0.08	69	0.03	94	1.64	135	0.12
44	0.04	72	0.16	95	0.38	136	0.85
46	1.08	73	1.32	96	0.04	137	0.70
48	0.16	74	5.34	99	0.02	138	0.08
49	1.19	75	9.78	101	0.04	139	0.03
50	10.30	76	10.22	102	0.03	151	59.13
51	25.22	77	18.09	104	1.19	152	100.00
52	27.41	78	47.08	105	10.18	153	45.71
53	6.57	79	27.22	106	29.74	154	3.99
54	0.80	80	1.75	107	17.49	155	0.39
55	0.07	81	0.07	108	1.36	156	0.03

B1322(12:20)7353 20% 20090806 * MS3-Kopf//SK152-f2



30	0.09	56	0.10	84	0.25	106	0.01	146	77.31
31	0.02	60	6.04	85	0.59	110	0.06	147	100.00
32	0.01	61	1.35	86	1.32	111	0.07	148	37.57
36	0.07	62	3.53	87	2.15	112	0.07	149	5.32
37	0.56	63	7.06	88	2.74	113	0.06	150	0.45
38	1.07	64	10.51	89	4.29	114	0.19	151	0.02
39	2.00	65	5.68	90	13.43	115	1.14	152	0.02
40	2.46	66	1.92	91	23.40	116	3.07	153	0.02
41	1.11	67	0.97	92	9.33	117	14.20		
42	0.42	68	0.30	93	1.64	118	53.49		
43	0.31	69	0.07	94	0.17	119	26.81		
45	0.17	70	0.02	95	0.01	120	4.47		
46	0.12	73	0.96	97	0.04	121	0.40		
48	0.07	74	0.92	98	0.12	122	0.02		
49	0.29	75	1.48	99	0.23	128	0.02		
50	1.24	76	1.53	100	0.17	129	0.05		
51	2.30	77	0.97	101	0.13	130	0.11		
52	2.57	78	0.46	102	0.11	131	0.08		
53	1.41	79	0.32	103	0.13	132	0.03		
54	0.47	80	0.20	104	0.17	133	0.00		
55	0.10	81	0.06	105	0.07	145	13.40		

B2132(17:48)11104 22% 20100901 * MS3-Sara Kopf//SK 208



32	0.03	60	0.35	84	0.72	105	0.40	145	0.08
37	0.38	61	1.47	85	0.92	106	0.68	146	0.13
38	0.70	62	2.33	86	1.06	107	0.71	147	0.08
39	1.75	63	5.24	87	1.27	108	1.00	148	0.03
40	0.87	64	5.16	88	1.49	109	1.24	162	100.00
41	0.07	65	0.73	89	3.65	110	0.18	163	89.42
44	0.11	68	4.74	90	31.30	111	0.10	164	13.70
45	1.35	69	4.54	91	5.07	116	0.04	165	4.47
46	1.19	70	1.36	92	0.53	117	0.17	166	0.39
47	0.11	71	0.57	93	2.39	118	0.08	167	0.05
48	0.12	72	0.20	94	1.22	119	0.08		
49	0.34	73	0.60	95	0.58	120	0.10		
50	1.53	74	1.95	96	0.29	129	0.08		
51	1.68	75	2.52	97	0.17	130	0.07		
52	0.91	76	1.45	98	0.50	132	0.52		
53	0.23	77	0.49	99	0.53	133	2.95		
54	0.28	78	0.20	100	0.26	134	23.29		
56	0.14	79	0.03	101	0.19	135	16.13		
57	0.52	81	3.22	102	0.26	136	2.58		
58	0.85	82	3.07	103	0.93	137	0.74		
59	0.52	83	1.09	104	0.17	138	0.08		

B1702(14:47)4840 27% 20092805 * MS3-Kpf//SK 203