Supporting Information

Ir(III)-Catalyzed *ortho* C-H Alkylations of (Hetero)aromatic Aldehydes Using Alkyl Boron Reagents

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General Information

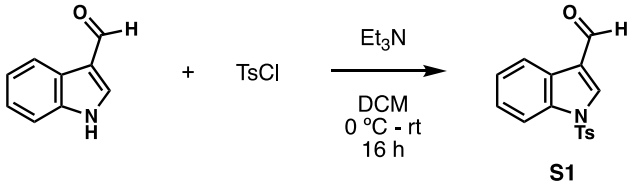
All commercially available reagents were purchased from Alfa Aesar, Ark Pharm Inc., Combi-Blocks, Enamine Building Blocks, Fisher Scientific, Frontier Scientific, Oakwood Chemicals, Sigma Aldrich, and TCI America, and were used directly without further purifications. $[Cp^*IrCl_2]_2$ was synthesized from $IrCl_3$ and Cp* according to a known procedure.[1] Dichloroethane and acetic acid were freeze-pump-thawed three times before use. Other reaction solvents were purified according to the method of Grubbs.[2] Reactions were monitored by thin layer chromatography (TLC) carried out on 250 μm Merck silica gel plates (60 F254) containing a fluorescent indicator (254 nm). Visualization of the developed TLC plate was performed by irradiation with UV light. Organic solvents were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath (25 °C). Filtration was performed using Celite®. Preparative thin layer chromatography was undertaken using Analtech Uniplate silica gel chromatography plates containing a fluorescent indicator (254 nm) (20x20 cm, 250, 500 or 1000 micron). Flash column chromatography was performed using Silicycle SiliaFlash P60 silica gel (60 Å pore size, 40 – 63 μm particle size, 230 – 400 mesh).

^{1}H NMR spectra were recorded on a Bruker 500 (500 MHz) and are referenced relative to residual $CHCl_3$ (in $CDCl_3$) proton signals at δ 7.26 ppm. Data for ^{1}H spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, ap = apparent), integration, coupling constant (Hz) and assignment. ^{13}C NMR spectra were recorded on a Bruker 500 (126 MHz) and are referenced relative to residual $CHCl_3$ (in $CDCl_3$) at δ 77.16 ppm. Data for ^{13}C NMR spectra are reported in terms of chemical shift and multiplicity where appropriate. ^{19}F NMR spectra were recorded on a Bruker 300 (282 MHz). Data for ^{19}F NMR spectra are reported in terms of chemical shift and multiplicity where appropriate. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a 30000-200 cm^{-1} diamond and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained from Princeton University Mass Spectrometry Facility using an Agilent 6210 TOF LC/MS (Electrospray Ionization). X-ray crystallographic analyses were performed using Bruker SMART APEX DUO diffractometer equipped with a copper or molybdenum X-ray tube on a Bruker Kappa APEX-II CCD diffractometer.

Experimental Procedures and Characterization Data

Syntheses of Substrates

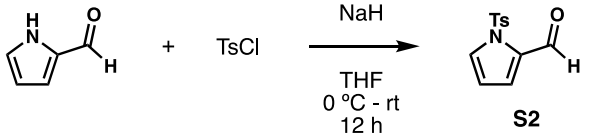
Synthesis of 1-tosyl-1*H*-indole-3-carbaldehyde (**S1**)



S1

Following a previously reported procedure,[3] a 25 mL oven-dried round bottom flask equipped with a magnetic stir bar was charged with 1*H*-indole-3-carbaldehyde (0.29 g, 2.0 mmol). The flask was capped with a rubber septum before being evacuated and filled with argon three times. Anhydrous DCM (5 mL) was added, and the reaction flask was cooled to 0 ºC, followed by the addition of Et_3N (0.56 mL, 4.0 mmol). The resulting mixture was stirred at 0 ºC for 10 min before TsCl (0.42 g, 2.2 mmol) was added. The solution was allowed to warm to r.t. and stirred for 16 h. After this time, the reaction was quenched with water (10 mL) and saturated aqueous $NaHCO_3$ (10 mL), and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and the solvent removed *in vacuo*. Purification was undertaken by flash silica gel column chromatography using hexane/EtOAc (4:1) as the eluting solvent to give the product as a white solid (0.53 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.25 (dt, *J* = 7.7, 1.0 Hz, 1H), 8.23 (s, 1H), 7.95 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.43 – 7.34 (m, 2H), 7.31 – 7.28 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.49, 146.31, 136.36, 135.35, 134.47, 130.47, 127.38, 126.45, 126.42, 125.20, 122.75, 122.50, 113.38, 21.82. MS-ESI m/z 300.0678 ([M + H]$^+$, $C_{16}H_{14}NO_3S$, calc. 300.0689). IR (neat): 2961, 2933, 2873, 1739, 1668, 1539, 1434, 1377.

Synthesis of 1-tosyl-1*H*-pyrrole-2-carbaldehyde (**S2**)

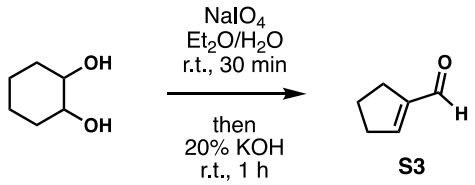


S2

Following a previously reported procedure,[4] a 25 mL oven-dried round bottom flask equipped with a magnetic stir bar was charged with 1*H*-pyrazole-2-carbaldehyde (0.19 g, 2.0 mmol). The flask was capped with a rubber septum before being evacuated and filled with argon three times. Anhydrous THF (5 mL) was added, and the reaction flask was cooled to 0 ºC, followed by the addition of NaH (60% in mineral oil, 0.12 g, 3.0 mmol). The resulting mixture was stirred at 0 ºC for 10 min before TsCl (0.57 g, 3.0 mmol) was added. The solution was allowed to warm to r.t. and stirred for 12 h. After this time, the reaction was quenched with water (10 mL) and saturated aqueous NH_4Cl (10 mL), and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and the solvent removed *in vacuo*. Purification was undertaken

by flash silica gel column chromatography using hexane/EtOAc/DCM (5:1:1) as the eluting solvent to give the product as a light orange solid (0.46 g, 93%).[1]H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.85 – 7.75 (m, 2H), 7.62 (dd, J = 3.1, 1.8 Hz, 1H), 7.32 (dt, J = 7.2, 0.9 Hz, 2H), 7.16 (dd, J = 3.8, 1.7 Hz, 1H), 6.40 (t, J = 3.4 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.12, 146.10, 135.33, 133.63, 130.29, 129.58, 127.63, 124.63, 112.54, 21.85. MS-ESI m/z 250.0536 ($[M + H]^+$, $C_{12}H_{12}NO_3S$, calc. 250.0532). IR (neat): 3137, 3124, 1732, 1689, 1666, 1593, 1538, 1422, 1363, 1250.

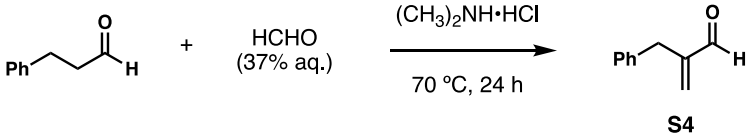
Synthesis of 1-cyclopentene-1-carboxaldehyde (**S3**)



S3

Following a previously reported procedure,[5] to a solution of sodium periodate (28.3 g, 0.132 mol) in water (250 mL) was added an Et_2O solution (150 mL) of 1,2-cyclohexanediol (12.0 g, 0.103 mol). The solution was stirred for 30 min at r.t., followed by the addition of 20% aqueous KOH (40 mL). The reaction mixture was stirred for 1 h. The layers were separated, and the organic layer was washed with water, brine, dried over Na_2SO_4 and the solvent removed *in vacuo*. Kugelrohr distillation (50 ºC, 1 mmHg) gave the desired product as a colorless oil (4.5 g, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 6.87 (ddd, *J* = 4.4, 2.8, 1.8 Hz, 1H), 2.60 (ddt, *J* = 7.7, 5.0, 2.5 Hz, 2H), 2.52 (tt, *J* = 6.6, 2.1 Hz, 2H), 1.99 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.04, 153.30, 148.05, 33.81, 28.44, 23.05.

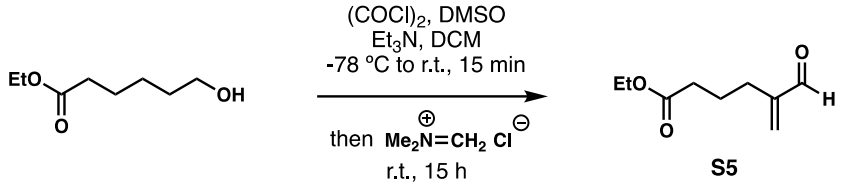
Synthesis of 2-benzylacrylaldehyde (**S4**)



S4

Following a previously reported procedure,[6] hydrocinnamaldehyde (2.6 mL, 20 mmol), formaldehyde (37% aqueous solution, 1.8 mL, 24 mmol) and dimethylamine hydrochloride (1.96 g, 24 mmol) were placed in a round bottom flask and stirred at 70 ºC for 24 h. After cooling to r.t., the reaction was diluted with H_2O (20 mL) and extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and the solvent removed *in vacuo*. Purification was undertaken by flash silica gel column chromatography using hexane/Et_2O (25:1) as the eluting solvent to give the product as a colorless oil (1.39 g, 47%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.31 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.21 – 7.18 (m, 2H), 6.11 (d, *J* = 1.6 Hz, 1H), 6.07 (d, *J* = 0.9 Hz, 1H), 3.58 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.09, 149.80, 138.21, 135.34, 129.23, 128.63, 126.53, 34.22. MS-ESI m/z 147.0807 ($[M + H]^+$, $C_{10}H_{11}O$, calc. 147.0804). IR (neat): 3029, 2928, 2824, 1690, 1496, 1454.

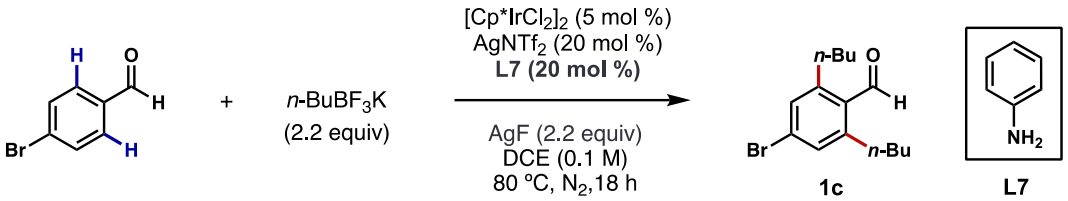
Synthesis of ethyl 5-formylhex-5-enoate (**S5**)



Following a previously reported procedure,[7] to a solution of oxalyl chloride (1.7 mL, 20 mmol) in DCM (15 mL) was added DMSO (4.3 mL, 60 mmol) dropwise at -78 ºC. The solution was stirred for 15 min before ethyl 6-hydroxyhexanoate (1.6 mL, 10 mmol) and Et_3N (15.6 mL, 0.112 mol) were added at the same temperature. The solution was allowed to warm to r.t. followed by the addition of methylene-*N*,*N*-dimethylammonium chloride (1.9 g, 20 mmol). After 15 h of stirring at r.t., the mixture was diluted with DCM (30 mL), washed with saturated aqueous $NaHCO_3$, brine, dried over Na_2SO_4, and the solvent removed *in vacuo*. Purification was undertaken by flash silica gel column chromatography using hexane/EtOAc (8:1) as the eluting solvent to give the product as a light-yellow oil (1.5 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (d, *J* = 1.7 Hz, 1H), 6.28 (d, *J* = 1.6 Hz, 1H), 6.03 (s, 1H), 4.15 – 4.08 (m, 2H), 2.33 – 2.26 (m, 4H), 1.84 – 1.75 (m, 2H), 1.24 (td, *J* = 7.1, 1.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.60, 173.35, 149.43, 134.65, 60.48, 33.79, 27.27, 23.06, 14.36. MS-ESI m/z 193.0825 ($[M + Na]^+$, $C_9H_{14}NaO_3$, calc. 193.0835). IR (neat): 3029, 2938, 2825, 1734, 1694, 1454, 1374, 1245.

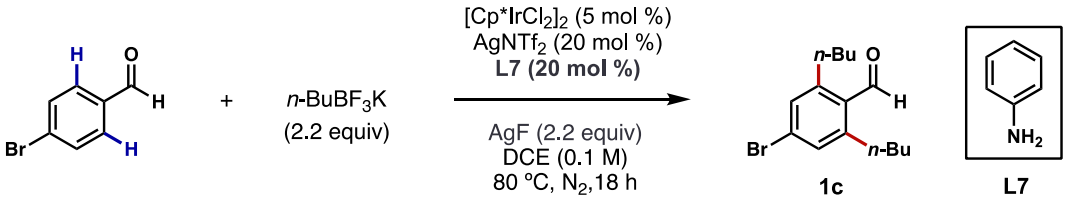
Optimization Experiments

Table S1. Evaluation of Catalysts



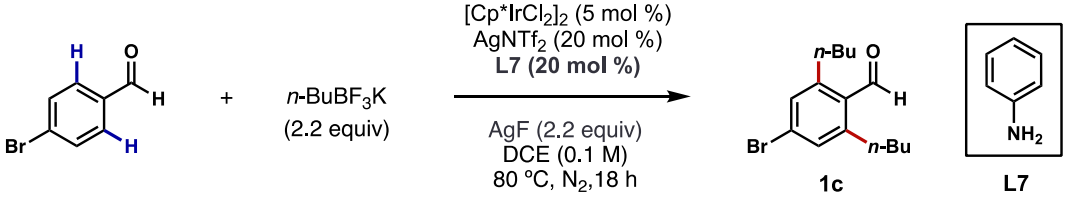
entry	variation from the standard condition	yield of **1c** (%)
1	none	**58**
2	no $[Cp^*IrCl_2]_2$	0
3	$[Cp^*RhCl_2]_2$ instead of $[Cp^*IrCl_2]_2$	26 (mono:di 1:1.6)
4	$[Ru(p\text{-cymene})Cl_2]_2$ instead of $[Cp^*IrCl_2]_2$	4 (mono)

Table S2. Evaluation of Additives



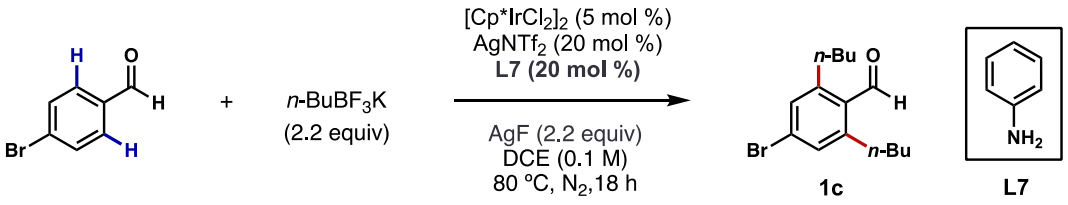
entry	variation from the standard condition	yield of **1c** (%)
1	none	**58**
2	$AgSbF_6$ instead of $AgNTf_2$	44
3	$AgPF_6$ instead of $AgNTf_2$	50
4	$AgBF_4$ instead of $AgNTf_2$	32

Table S3. Evaluation of Oxidants



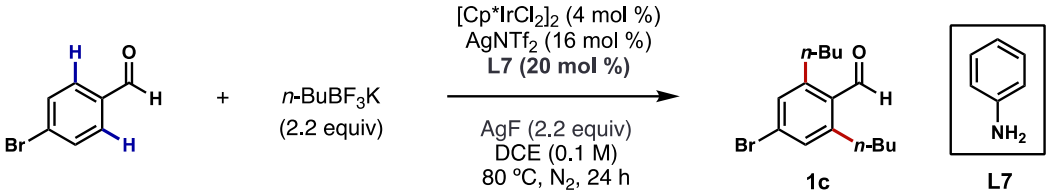
entry	variation from the standard condition	yield of **1c** (%)
1	none	**58**
2	AgOAc instead of AgF	0
3	AgTFA instead of AgF	0
4	AgOTs instead of AgF	36 (mono:di 1:5)
5	AgOTf instead of AgF	10
6	Ag_2CO_3 instead of AgF	0
7	Ag_3PO_4 instead of AgF	18
8	$PhI(OAc)_2$ instead of AgF	0
9	benzoquinone instead of AgF	0
10	$K_2S_2O_8$ instead of AgF	10
11	Oxone® instead of AgF	0
12	2,4,6-trimethyl-F-pyridinium OTf instead of AgF	46
13	2,4,6-trimethyl-F-pyridinium BF_4 instead of AgF	8
14	NFSI instead of AgF	40
15	Selectfluor® instead of AgF	30
16	$Ce(SO_4)_2$ instead of AgF	6
17	$Cu(OAc)_2$ instead of AgF	6

Table S4. Evaluation of Catalyst/Additive Loadings and Reaction Time



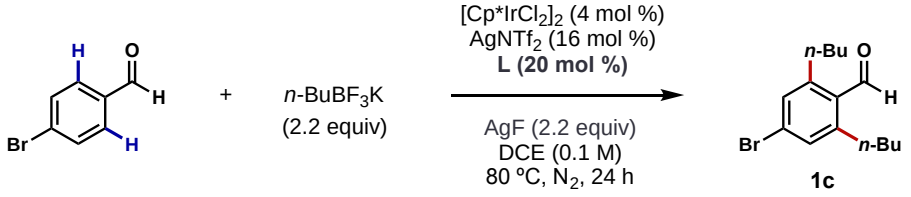
entry	variation from the standard condition	yield of **1c** (%)
1	none	58
2	$[Cp^*IrCl_2]_2$ (4 mol%), $AgNTf_2$ (16 mol %), 24 h	**68**

Table S5. Evaluation of Solvents



entry	variation from the standard condition	yield of **1c** (%)
1	none	**68**
2	DCE/HFIP (9:1) instead of DCE	10
3	with 5 equiv of TFA	12 (mono:di 2:1)
4	HFIP instead of DCE	0
5	PhCl instead of DCE	52
6	$PhCF_3$ instead of DCE	50
7	toluene instead of DCE	30
8	DCM instead of DCE	36
9	chloroform instead of DCE	40
10	MeCN instead of DCE	0
11	THF instead of DCE	58
12	1,4-dioxane instead of DCE	42
13	DMF instead of DCE	0
14	MeOH instead of DCE	0
15	AcOH instead of DCE	**72 (mono:di 1:17)**

Table S6. Evaluation of Catalytic Ligands



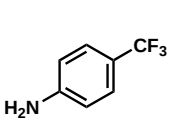
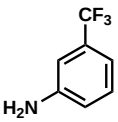
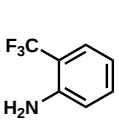
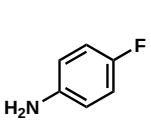
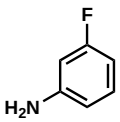
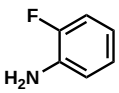
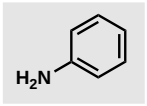
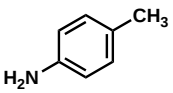
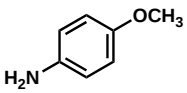
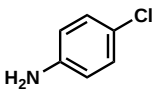
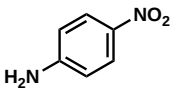
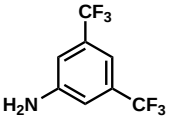
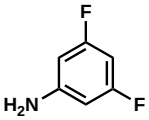
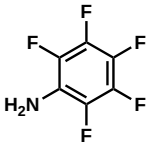
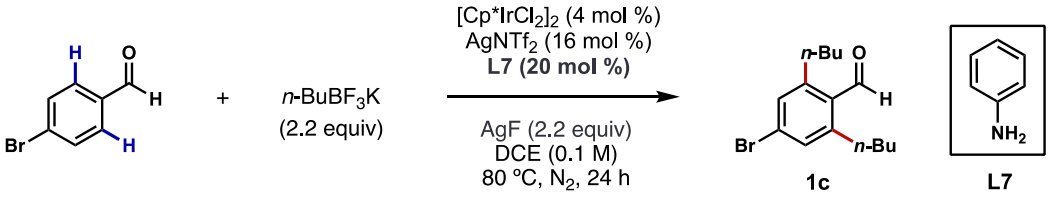
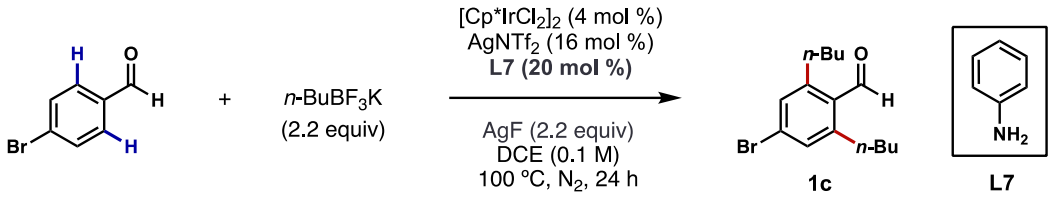
 **L1** (62%)	 **L2** (60%)	 **L3** (22%)	 **L4** (50%)	 **L5** (56%)
 **L6** (50%)	 **L7** (68%)	 **L8** (16%)	 **L9** (12%)	 **L10** (38%)
 **L11** (32%)	 **L12** (30%)	 **L13** (30%)	 **L14** (6%)	**No TDG** (0%)

Table S7. Evaluation of the Reaction Concentration and Temperature



entry	variation from the standard condition	yield of **1c** (%)
1	none	68
2	0.15 M instead of 0.1 M	62
3	0.2 M instead of 0.1 M	50
4	0.067 M instead of 0.1 M	68
5	60 ºC instead of 80 ºC	40
6	100 ºC instead of 80 ºC	**72**

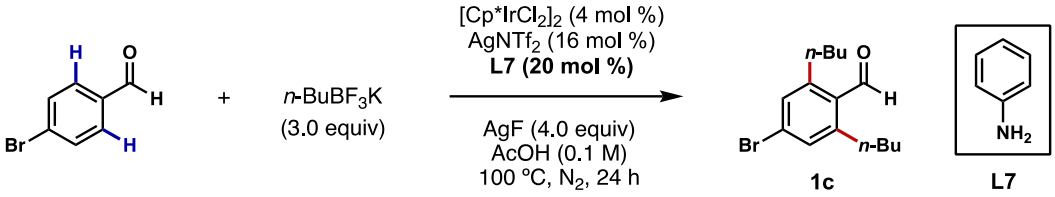
Table S8. Evaluation of the Amounts of AgF and *n*-$BuBF_3K$



entry	variation from the standard condition	yield of **1c** (%)
1	none	72
2	AgF (4 equiv), *n*-$BuBF_3K$ (3 equiv)	**78 (94)**[a]

[a] AcOH (0.1 M) was used as the reaction solvent

Table S9. Evaluation of Scale-up Reactions



entry	variation from the standard condition	yield of **1c** (%)
1	None (0.1 mmol scale)	94
2	0.3 mmol scale	88
3	0.3 mmol scale (20 mL scintillation vial with a cross-shaped stir-bar)	**94**

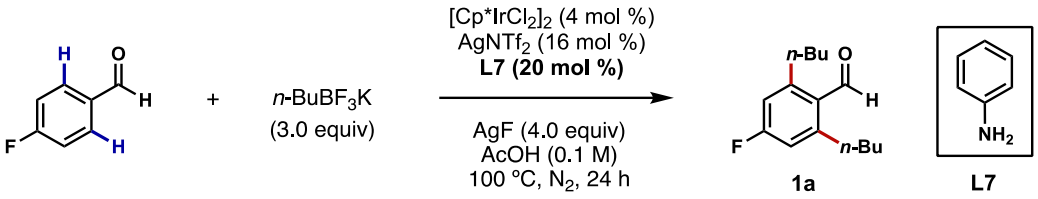
Standard Procedures

General Procedure for the Optimization Experiments (using **Table S8, entry 2** as an example)

A 10-mL oven-dried microwave-vial equipped with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.2 mg, 0.004 mmol), 4-bromobenzaldehyde (18.5 mg, 0.10 mmol), AgF (50.8 mg, 0.40 mmol) and *n*-$BuBF_3K$ (49.2 mg, 0.30 mmol). The vial was transferred to a glovebox filled with N_2, wherein $AgNTf_2$ (6.2 mg, 0.016 mmol) and aniline (1.8 µL, 0.020 mmol) were added. The vial was sealed with a PTFE-lined aluminum cap and taken out of the glovebox. Degassed DCE or AcOH (1 mL) was added through a syringe, and the vial was heated in a pie-block at 100 ºC under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (10 mL). The filtrate was then concentrated *in vacuo* before CH_2Br_2 (6.95 µL, 0.1 mmol) was added. The yield of the desired product was determined by crude ^1H NMR using CH_2Br_2 as the internal standard.

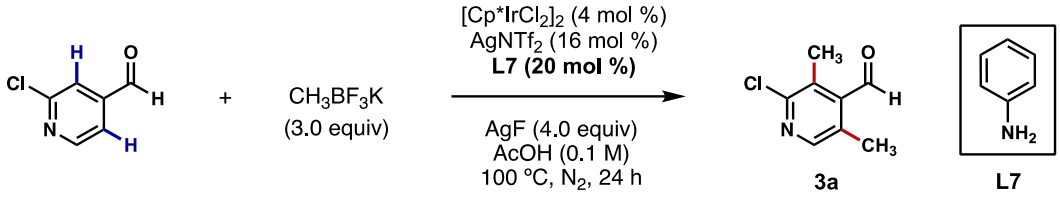
Note: All control experiments were conducted on a 0.1 mmol scale unless otherwise noted, and changes were made based on the "standard condition" described above.

General Procedure **A** for the (Hetero)aromatic Aldehyde Substrate Scope Experiments (using **1a** as an example)



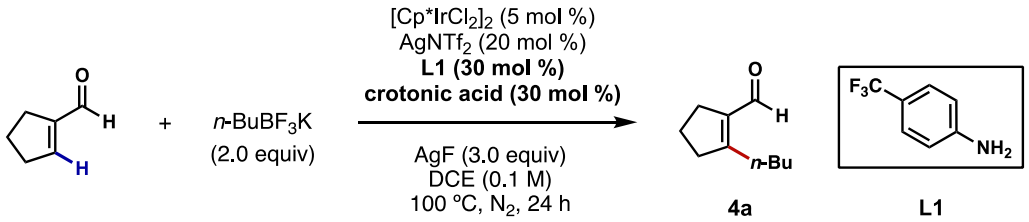
A 20-mL oven-dried scintillation vial equipped with a cross-shaped stir bar was charged with $[Cp^*IrCl_2]_2$ (9.6 mg, 0.012 mmol), AgF (0.152 g, 1.20 mmol) and *n*-$BuBF_3K$ (0.147 g, 0.90 mmol). The vial was transferred to a glovebox filled with N_2, wherein $AgNTf_2$ (18.6 mg, 0.048 mmol), 4-fluorobenzaldehyde (32.2 µL, 0.30 mmol) and aniline (5.6 µL, 0.060 mmol) were added. The vial was capped tightly with a PTFE-lined green cap and taken out of the glovebox. Degassed AcOH (3 mL) was added through a syringe, and the vial was heated in a pie-block at 100 ºC under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (15 mL). The filtrate was then concentrated *in vacuo* and the resulting residue was purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent.

General Procedure **B** for the Potassium Alkyl Trifluoroborate Scope Experiments (using **3a** as an example)



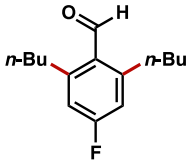
A 20-mL oven-dried scintillation vial equipped with a cross-shaped stir bar was charged with $[Cp^*IrCl_2]_2$ (9.6 mg, 0.012 mmol), 2-chloroisonicotinaldehyde (42.5 mg, 0.30 mmol), AgF (0.152 g, 1.20 mmol) and *n*-$BuBF_3K$ (0.147 g, 0.90 mmol). The vial was transferred to a glovebox filled with N_2, wherein $AgNTf_2$ (18.6 mg, 0.048 mmol) and aniline (5.6 µL, 0.060 mmol) were added. The vial was capped tightly with a PTFE-lined green cap and taken out of the glovebox. Degassed AcOH (3 mL) was added through a syringe, and the vial was heated in a pie-block at 100 °C under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (15 mL). The filtrate was then concentrated *in vacuo* and the resulting residue was purified by flash silica gel column chromatography using hexane/Et_2O (10:1) as the eluting solvent.

General Procedure **C** for the α,β-Unsaturated Aldehyde Scope Experiments (using **4a** as an example)



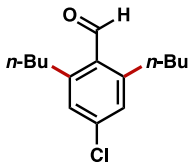
A 20-mL oven-dried scintillation vial equipped with a cross-shaped stir bar was charged with $[Cp^*IrCl_2]_2$ (12.0 mg, 0.015 mmol), AgF (0.114 g, 0.90 mmol), crotonic acid (7.7 mg, 0.09 mmol) and *n*-$BuBF_3K$ (98.4 mg, 0.60 mmol). The vial was transferred to a glovebox filled with N_2, wherein $AgNTf_2$ (23.3 mg, 0.060 mmol), 1-cyclopentene-1-carboxaldehyde (29.5 µL) and 4-(trifluoromethyl)aniline (11.3 µL, 0.090 mmol) were added. The vial was capped tightly with a PTFE-lined green cap and taken out of the glovebox. Degassed DCE (3 mL) was added through a syringe, and the vial was heated in a pie-block at 100 °C under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (15 mL). The filtrate was then concentrated *in vacuo* and the resulting residue was purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the eluting solvent.

Substrate Scope Experiments



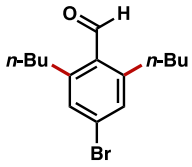
1a

This compound was synthesized from 4-fluorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a yellow oil (60.3 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 6.79 (d, *J* = 9.4 Hz, 2H), 3.06 – 2.73 (m, 4H), 1.67 – 1.49 (m, 4H), 1.40 (q, *J* = 7.4 Hz, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.98, 164.82 (d, *J* = 254.8 Hz), 150.13 (d, *J* = 8.8 Hz), 128.41 (d, *J* = 2.7 Hz), 115.66 (d, *J* = 20.8 Hz), 34.36, 33.58 (d, *J* = 1.4 Hz), 22.79, 14.04. ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.91 (t, *J* = 9.5 Hz). MS-ESI m/z 237.1645 ($[M + H]^+$, $C_{15}H_{22}FO$, calc. 237.1649). IR (neat): 2960, 2933, 2874, 1694, 1596, 1459, 1282.



1b

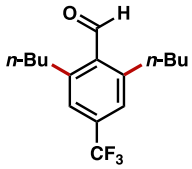
This compound was synthesized from 4-chlorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a light-yellow oil (65.9 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.08 (s, 2H), 2.96 – 2.76 (m, 4H), 1.55 (ddt, *J* = 10.1, 7.9, 3.5 Hz, 4H), 1.46 – 1.35 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.45, 148.17, 138.66, 130.33, 128.87, 34.45, 33.29, 22.79, 14.01. MS-ESI m/z 253.1342 ($[M + H]^+$, $C_{15}H_{22}ClO$, calc. 253.1354). IR (neat): 2959, 2932, 2873, 1695, 1579, 1465, 1403.



1c

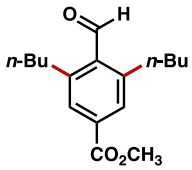
This compound was synthesized from 4-bromobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a light-yellow solid (83.5 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.26 (s, 2H), 2.96 – 2.80 (m, 4H), 1.66 – 1.48 (m, 4H), 1.39 (q, *J* = 7.4 Hz, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.75, 148.15, 131.87, 130.79, 127.65, 34.52, 33.24, 22.82, 14.03. MS-ESI m/z 297.0839 ($[M + H]^+$, $C_{15}H_{22}BrO$, calc. 297.0849). IR (neat): 2959, 2931, 2872,

1692, 1574, 1465, 1401.



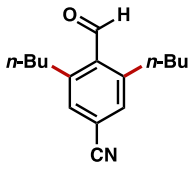
1d

This compound was synthesized from 4-(trifluoromethyl)benzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a light-yellow solid (76.6 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.34 (s, 2H), 2.98 – 2.88 (m, 4H), 1.58 (td, *J* = 7.5, 6.9, 3.9 Hz, 4H), 1.46 – 1.36 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.27, 146.46, 135.09 (q, *J* = 1.2 Hz), 133.70 (q, *J* = 32.2 Hz), 125.45 (q, *J* = 3.7 Hz), 123.71 (q, *J* = 272.9 Hz), 34.55, 33.33, 22.82, 13.97. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.36. MS-ESI m/z 287.1609 ($[M + H]^+$, $C_{16}H_{22}F_3O$, calc. 287.1617). IR (neat): 2959, 2935, 2874, 2862, 1697, 1578, 1466, 1411, 1350, 1323.



1e

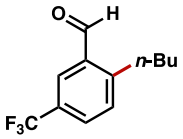
This compound was synthesized from methyl-4-formylbenzoate following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a white solid (82.5 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.74 (s, 2H), 3.93 (s, 3H), 3.02 – 2.82 (m, 4H), 1.62 – 1.53 (m, 4H), 1.40 (h, *J* = 7.4 Hz, 4H), 0.93 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.80, 166.60, 145.83, 135.78, 133.06, 129.76, 52.53, 34.62, 33.28, 22.83, 14.04. MS-ESI m/z 277.1793 ($[M + H]^+$, $C_{17}H_{25}O_3$, calc. 277.1798). IR (neat): 2958, 2932, 2873, 1727, 1697, 1570, 1458, 1436, 1297.



1f

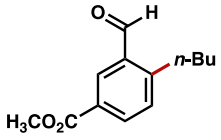
This compound was synthesized from 4-formylbenzonitrile following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a yellow oil (25.3 mg, 35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.38 (s, 2H), 2.96 – 2.83 (m, 4H), 1.56 (tt, *J* = 7.9, 6.5 Hz, 4H), 1.39 (dq, *J* = 14.6, 7.4 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.05, 146.30, 135.90, 132.04, 118.28, 115.70, 34.30, 32.93, 22.71, 13.97. MS-ESI m/z 244.1692 ($[M + H]^+$, $C_{16}H_{22}NO$, calc. 244.1696). IR (neat): 2959,

2932, 2873, 2231, 1700, 1601, 1561, 1465.



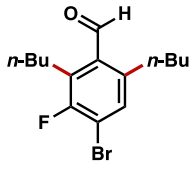
1g

This compound was synthesized from 3-(trifluoromethyl)benzaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by flash silica gel column chromatography using hexane/Et$_2$O (33:1) as the eluting solvent to give the product as a light-yellow oil (58.8 mg, 85%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.32 (s, 1H), 8.09 (d, *J* = 2.1 Hz, 1H), 7.72 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 3.13 – 3.03 (m, 2H), 1.67 – 1.56 (m, 2H), 1.48 – 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 190.80, 149.65 (d, *J* = 1.2 Hz), 133.93, 131.81, 130.04 (q, *J* = 3.5 Hz), 129.24 (q, *J* = 33.3 Hz), 127.94 (q, *J* = 3.8 Hz), 123.81 (q, *J* = 272.1 Hz), 34.45, 32.20, 22.67, 13.95. ^{19}F NMR (282 MHz, CDCl$_3$) δ -62.80. MS-ESI m/z 231.0993 ([M + H]$^+$, $C_{12}H_{14}F_3O$, calc. 231.0991). IR (neat): 2962, 2935, 2875, 1710, 1618, 1577, 1467, 1333, 1270.



1h

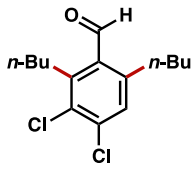
This compound was synthesized from methyl-3-formylbenzoate following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by flash silica gel column chromatography using hexane/Et$_2$O (20:1) as the eluting solvent to give the product as a light-yellow oil (59.9 mg, 91%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.27 (s, 1H), 8.45 (d, *J* = 2.0 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 3.08 – 3.03 (m, 2H), 1.62 – 1.53 (m, 2H), 1.39 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 191.65, 166.18, 150.71, 134.27, 133.74, 133.27, 131.41, 128.70, 52.39, 34.13, 32.55, 22.69, 13.96. MS-ESI m/z 221.1166 ([M + H]$^+$, $C_{13}H_{17}O_3$, calc. 221.1172). IR (neat): 2958, 2933, 2873, 1727, 1705, 1609, 1437, 1293, 1262.



1i

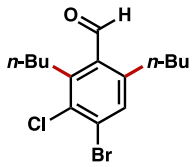
This compound was synthesized from 4-bromo-3-fluorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et$_2$O (50:1) as the eluting solvent to give the product as a light-yellow oil (82.3 mg, 87%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.44

(s, 1H), 7.31 (d, J = 6.6 Hz, 1H), 2.98 – 2.91 (m, 2H), 2.87 – 2.81 (m, 2H), 1.58 – 1.50 (m, 4H), 1.40 (dh, J = 14.6, 7.3 Hz, 4H), 0.93 (td, J = 7.3, 3.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.18 (d, J = 2.7 Hz), 155.98 (d, J = 243.9 Hz), 142.59 (d, J = 4.3 Hz), 133.81 (d, J = 17.0 Hz), 133.02, 132.43 (d, J = 2.7 Hz), 114.46 (d, J = 22.9 Hz), 34.61 (d, J = 1.2 Hz), 33.40, 32.62, 25.11 (d, J = 4.1 Hz), 22.87, 22.73, 14.00, 13.95. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.04 (d, J = 6.3 Hz). MS-ESI m/z 315.0746 ($[M + H]^+$, $C_{15}H_{21}BrFO$, calc. 315.0754). IR (neat): 2958, 2930, 2872, 1696, 1581, 1456, 1404, 1379, 1260.



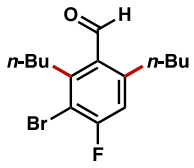
1j

This compound was synthesized from 3,4-dichlorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a white solid (77.7 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.24 (s, 1H), 3.10 – 3.03 (m, 2H), 2.85 – 2.79 (m, 2H), 1.54 (qt, J = 7.5, 3.2 Hz, 4H), 1.46 (q, J = 7.3 Hz, 2H), 1.39 (dt, J = 14.9, 7.3 Hz, 2H), 0.94 (dt, J = 15.1, 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.68, 145.03, 144.76, 137.49, 132.42, 131.46, 130.32, 34.26, 32.87, 32.51, 30.36, 23.03, 22.75, 13.99, 13.93. MS-ESI m/z 287.0960 ($[M + H]^+$, $C_{15}H_{21}Cl_2O$, calc. 287.0964). IR (neat): 2953, 2927, 2871, 2856, 1693, 1566, 1454, 1378.



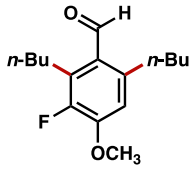
1k

This compound was synthesized from 4-bromo-3-chlorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a light-yellow solid (86.4 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.42 (s, 1H), 3.16 – 3.01 (m, 2H), 2.88 – 2.73 (m, 2H), 1.58 – 1.50 (m, 4H), 1.49 – 1.41 (m, 2H), 1.37 (dt, J = 14.6, 7.4 Hz, 2H), 0.94 (dt, J = 14.8, 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.89, 144.75, 144.74, 133.68, 133.29, 133.09, 128.42, 34.31, 32.79, 32.51, 30.78, 23.03, 22.76, 14.00, 13.94. MS-ESI m/z 331.0453 ($[M + H]^+$, $C_{15}H_{21}BrClO$, calc. 331.0459). IR (neat): 2956, 2928, 2871, 1693, 1562, 1464, 1375.



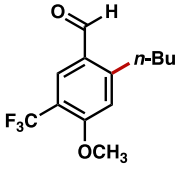
1l

This compound was synthesized from 3-bromo-4-fluorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a light-yellow oil (82.8 mg, 88%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 6.90 (d, *J* = 9.1 Hz, 1H), 3.16 – 3.06 (m, 2H), 2.93 – 2.83 (m, 2H), 1.55 (dddd, *J* = 16.0, 9.0, 7.9, 3.4 Hz, 4H), 1.51 – 1.44 (m, 2H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.95 (dt, *J* = 18.8, 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.09, 161.11 (d, *J* = 253.8 Hz), 147.92 (d, *J* = 1.1 Hz), 147.80 (d, *J* = 8.7 Hz), 130.16 (d, *J* = 3.0 Hz), 116.31 (d, *J* = 22.9 Hz), 111.01 (d, *J* = 19.6 Hz), 34.12, 33.23 (d, *J* = 1.4 Hz), 32.70, 32.08 (d, *J* = 2.4 Hz), 23.02, 22.73, 14.01, 13.95. ^{19}F NMR (282 MHz, $CDCl_3$) δ -95.11 (d, *J* = 9.1 Hz). MS-ESI m/z 315.0748 ($[M + H]^+$, $C_{15}H_{21}BrFO$, calc. 315.0754). IR (neat): 2958, 2930, 2872, 1697, 1571, 1456, 1379, 1297.



1m

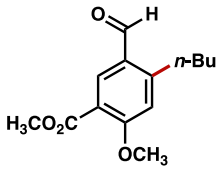
This compound was synthesized from 3-fluoro-4-methoxybenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a light-yellow solid (71.3 mg, 89%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.37 (d, *J* = 0.9 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H), 2.99 (td, *J* = 7.9, 2.7 Hz, 2H), 2.93 – 2.89 (m, 2H), 1.55 (dqd, *J* = 10.6, 7.6, 5.6 Hz, 4H), 1.41 (hd, *J* = 7.3, 3.5 Hz, 4H), 0.94 (td, *J* = 7.3, 4.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.34 (d, *J* = 2.8 Hz), 151.08 (d, *J* = 12.3 Hz), 148.81 (d, *J* = 241.9 Hz), 144.40 (d, *J* = 3.9 Hz), 134.09 (d, *J* = 13.0 Hz), 124.77 (d, *J* = 2.4 Hz), 112.43 (d, *J* = 1.9 Hz), 56.16, 34.95 (d, *J* = 1.1 Hz), 33.69, 33.41, 24.52 (d, *J* = 5.4 Hz), 22.88, 14.07, 14.02. ^{19}F NMR (282 MHz, $CDCl_3$) δ -141.13 – -145.92 (m). MS-ESI m/z 267.1744 ($[M + H]^+$, $C_{16}H_{24}FO_2$, calc. 267.1755). IR (neat): 2957, 2928, 2871, 1688, 1602, 1564, 1492, 1463, 1300.



1n

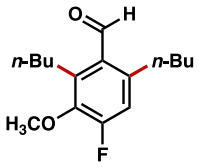
This compound was synthesized from 4-methoxy-3-(trifluoromethyl)benzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O

(20:1) as the eluting solvent to give the product as a yellow oil (77.4 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.04 (s, 1H), 6.83 (s, 1H), 3.97 (s, 3H), 3.08 – 3.02 (m, 2H), 1.60 (tt, *J* = 7.9, 5.7 Hz, 2H), 1.42 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.67, 161.12 (q, *J* = 1.5 Hz), 152.71 (d, *J* = 1.0 Hz), 131.26 (q, *J* = 5.1 Hz), 126.36, 123.22 (q, *J* = 272.2 Hz), 117.29 (q, *J* = 31.9 Hz), 113.81, 56.33, 34.30, 32.75, 22.76, 13.94. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.65. MS-ESI m/z 261.1088 ($[M + H]^+$, $C_{13}H_{16}F_3O_2$, calc. 261.1097). IR (neat): 2960, 2934, 2874, 1700, 1619, 1568, 1505, 1467, 1427, 1396, 1335, 1306, 1257.



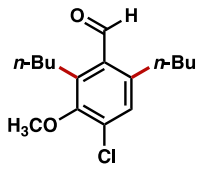
1o

This compound was synthesized from methyl 5-formyl-2-methoxybenzoate following general procedure A and purified by flash silica gel column chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a yellow oil (74.0 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.28 (s, 1H), 6.79 (s, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.05 – 2.97 (m, 2H), 1.62 – 1.52 (m, 2H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.31, 165.45, 162.85, 152.61, 137.14, 126.54, 117.98, 113.90, 56.36, 52.19, 33.98, 32.99, 22.72, 13.93. MS-ESI m/z 251.1263 ($[M + H]^+$, $C_{14}H_{19}O_4$, calc. 251.1278). IR (neat): 2957, 2872, 1733, 1696, 1607, 1558, 1499, 1465, 1436, 1384, 1328, 1262.



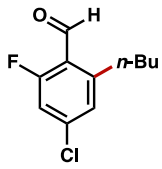
1p

This compound was synthesized from 4-fluoro-3-methoxybenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a light-yellow oil (41.0 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.42 (s, 1H), 6.83 (d, *J* = 12.1 Hz, 1H), 3.90 (d, *J* = 1.5 Hz, 3H), 2.98 – 2.93 (m, 2H), 2.87 – 2.83 (m, 2H), 1.58 – 1.46 (m, 4H), 1.46 – 1.34 (m, 4H), 0.97 – 0.90 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.44, 158.02 (d, *J* = 255.6 Hz), 144.10 (d, *J* = 10.3 Hz), 143.23 (d, *J* = 8.2 Hz), 141.94 (d, *J* = 3.5 Hz), 128.88 (d, *J* = 2.9 Hz), 116.72 (d, *J* = 19.2 Hz), 61.68 (d, *J* = 5.7 Hz), 34.35, 34.25, 33.11 (d, *J* = 1.2 Hz), 25.59 (d, *J* = 2.4 Hz), 23.14, 22.77, 14.06, 14.03. ^{19}F NMR (282 MHz, $CDCl_3$) δ -121.66 (d, *J* = 12.1 Hz). MS-ESI m/z 267.1741 ($[M + H]^+$, $C_{16}H_{24}FO_2$, calc. 267.1755). IR (neat): 2959, 2933, 2873, 1695, 1579, 1480, 1310.



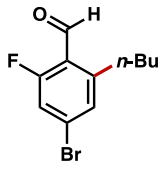
1q

This compound was synthesized from 4-chloro-3-methoxybenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a light-yellow oil (35.3 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.13 (s, 1H), 3.84 (s, 3H), 2.98 – 2.92 (m, 2H), 2.86 – 2.81 (m, 2H), 1.58 – 1.47 (m, 4H), 1.47 – 1.34 (m, 4H), 0.94 (td, *J* = 7.3, 6.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.88, 152.79, 142.62, 141.23, 132.80, 131.88, 130.34, 61.32, 34.52, 34.44, 32.92, 26.10, 23.21, 22.80, 14.05, 13.99. MS-ESI m/z 283.1448 ($[M + H]^+$, $C_{16}H_{24}ClO_2$, calc. 283.1459). IR (neat): 2959, 2932, 2872, 1695, 1576, 1556, 1464, 1394, 1263.



1r

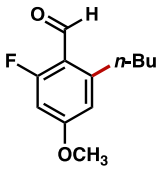
This compound was synthesized from 4-chloro-2-fluorobenzaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by preparative thin layer chromatography using hexane/EtOAc (20:1) as the eluting solvent to give the product as a light-yellow oil (41.3 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.11 – 7.00 (m, 2H), 3.01 – 2.91 (m, 2H), 1.57 – 1.50 (m, 2H), 1.45 – 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.02 (d, *J* = 10.5 Hz), 166.19 (d, *J* = 261.0 Hz), 149.02, 140.48 (d, *J* = 12.6 Hz), 127.24 (d, *J* = 3.4 Hz), 120.80 (d, *J* = 5.2 Hz), 114.72 (d, *J* = 25.4 Hz), 33.34, 33.33, 22.80, 14.02. ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.55 – -120.63 (m). MS-ESI m/z 215.0625 ($[M + H]^+$, $C_{11}H_{13}ClFO$, calc. 215.0633). IR (neat): 2959, 2930, 2873, 1700, 1601, 1564, 1465, 1408, 1263.



1s

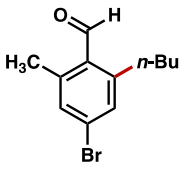
This compound was synthesized from 4-bromo-2-fluorobenzaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by preparative thin layer chromatography using hexane/EtOAc (20:1) as the eluting solvent to give the product as a light-yellow oil (74.2 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.24 – 7.19 (m, 2H), 2.99 – 2.94 (m, 2H), 1.57 – 1.49 (m, 2H), 1.44 – 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 188.18 (d, *J* = 10.6 Hz), 165.86 (d, *J* = 262.0 Hz), 149.02, 130.20 (d, *J* = 3.5 Hz), 128.74 (d, *J* = 11.7 Hz), 121.14 (d, *J* = 5.2 Hz), 117.64 (d, *J* = 25.0 Hz), 33.38, 33.23 (d, *J* = 2.1 Hz), 22.80, 14.01. ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.90 – -120.27 (m). MS-ESI m/z 259.0102 ([M + H]$^+$, $C_{11}H_{13}BrFO$, calc. 259.0128). IR (neat): 2959, 2931, 2873, 1699, 1596, 1552, 1465, 1405, 1249.



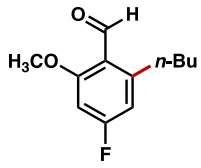
1t

This compound was synthesized from 2-fluoro-4-methoxybenzaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by preparative thin layer chromatography using hexane/EtOAc (15:1) as the eluting solvent to give the product as a light-yellow oil (47.2 mg, 75%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.34 (d, *J* = 1.6 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 6.48 (dt, *J* = 12.9, 2.1 Hz, 1H), 3.84 (d, *J* = 1.7 Hz, 3H), 3.02 – 2.92 (m, 2H), 1.56 – 1.47 (m, 2H), 1.39 (h, *J* = 7.0 Hz, 2H), 0.92 (td, *J* = 7.3, 1.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.50 (d, *J* = 10.6 Hz), 168.29 (d, *J* = 257.7 Hz), 164.73 (d, *J* = 13.5 Hz), 149.42 (d, *J* = 1.7 Hz), 115.83 (d, *J* = 4.9 Hz), 112.95 (d, *J* = 2.6 Hz), 99.13 (d, *J* = 25.7 Hz), 55.85, 33.88 (d, *J* = 2.3 Hz), 33.32, 22.80, 14.04. ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.68 (d, *J* = 13.0 Hz). MS-ESI m/z 211.1121 ([M + H]$^+$, $C_{12}H_{16}FO_2$, calc. 211.1129). IR (neat): 2958, 2932, 2873, 1688, 1618, 1570, 1464, 1435, 1419, 1338, 1283.



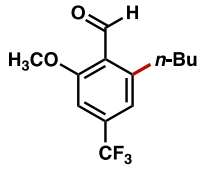
1u

This compound was synthesized from 4-bromo-2-methylbenzaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by preparative thin layer chromatography using hexane/EtOAc (20:1) as the eluting solvent to give the product as a yellow oil (17.8 mg, 23%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.26 (s, 2H), 2.94 – 2.86 (m, 2H), 2.56 (s, 3H), 1.62 – 1.52 (m, 2H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.67, 148.36, 143.05, 132.75, 131.88, 131.02, 127.75, 34.72, 32.92, 22.77, 20.91, 14.00. MS-ESI m/z 255.0383 ([M + H]$^+$, $C_{12}H_{16}BrO$, calc. 255.0379). IR (neat): 2958, 2930, 2872, 1693, 1574, 1464, 1380, 1241.



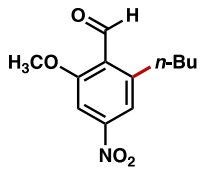
1v

This compound was synthesized from 4-fluoro-2-methoxybenzaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF3K*, and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a light-yellow oil (52.6 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (s, 1H), 6.53 (s, 1H), 6.51 (s, 1H), 3.87 (s, 3H), 2.96 – 2.91 (m, 2H), 1.51 (p, *J* = 8.1, 7.6 Hz, 2H), 1.38 (h, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.62, 166.27 (d, *J* = 254.7 Hz), 165.29 (d, *J* = 11.4 Hz), 150.32 (d, *J* = 10.4 Hz), 119.67 (d, *J* = 2.8 Hz), 110.05 (d, *J* = 21.1 Hz), 97.26 (d, *J* = 25.5 Hz), 56.17, 33.94 (d, *J* = 1.7 Hz), 33.27, 22.83, 14.05. ^{19}F NMR (282 MHz, $CDCl_3$) δ -101.47 (t, *J* = 10.1 Hz). MS-ESI m/z 211.1137 ($[M + H]^+$, $C_{12}H_{16}FO_2$, calc. 211.1129). IR (neat): 2959, 2934, 2873, 1687, 1593, 1458, 1429, 1409, 1311.



1w

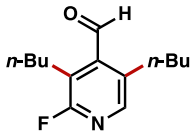
This compound was synthesized from 2-methoxy-4-(trifluoromethyl)benzaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF3K*, and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a yellow oil (67.9 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.08 (s, 1H), 7.03 (d, *J* = 1.6 Hz, 1H), 3.94 (s, 3H), 2.98 – 2.89 (m, 2H), 1.58 – 1.48 (m, 2H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.73, 162.97, 147.86, 135.26 (q, *J* = 32.4 Hz), 125.56 (d, *J* = 1.3 Hz), 123.51 (q, *J* = 273.1 Hz), 119.94 (q, *J* = 3.8 Hz), 105.91 (q, *J* = 3.8 Hz), 56.20, 33.63, 22.89, 14.01. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.57. MS-ESI m/z 261.1091 ($[M + H]^+$, $C_{13}H_{16}F_3O_2$, calc. 261.1097). IR (neat): 2960, 2935, 2874, 1696, 1582, 1477, 1459, 1427, 1409, 1347, 1327, 1304.



1x

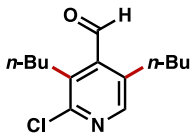
This compound was synthesized from 2-methoxy-4-nitrobenzaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF3K*, and purified by flash silica

gel column chromatography using hexane/Et_2O (25:1) as the eluting solvent to give the product as a yellow solid (66.5 mg, 93%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 4.00 (s, 3H), 3.03 – 2.87 (m, 2H), 1.58 – 1.50 (m, 2H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.34, 163.06, 150.63, 148.36, 127.53, 117.82, 104.04, 56.57, 33.56, 33.42, 22.77, 13.96. MS-ESI m/z 238.1073 ($[M + H]^+$, $C_{12}H_{16}NO_4$, calc. 238.1074). IR (neat): 3101, 2963, 2944, 2896, 2875, 2855, 1684, 1590, 1530, 1474, 1456, 1429, 1401, 1349, 1331, 1299, 1277.



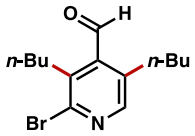
2a

This compound was synthesized from 2-fluoroisonicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (20:1) as the eluting solvent to give the product as a light-yellow oil (17.7 mg, 25%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.98 (s, 1H), 2.95 – 2.69 (m, 4H), 1.59 – 1.50 (m, 4H), 1.40 (ddt, *J* = 14.8, 11.5, 7.3 Hz, 4H), 0.93 (td, *J* = 7.3, 3.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.47 (d, *J* = 4.1 Hz), 161.64 (d, *J* = 237.7 Hz), 146.75 (d, *J* = 14.2 Hz), 142.68 (d, *J* = 4.4 Hz), 135.57 (d, *J* = 5.2 Hz), 124.71 (d, *J* = 31.5 Hz), 34.44 (d, *J* = 1.2 Hz), 33.06, 29.53, 24.71, 22.81, 22.63, 13.93, 13.91. ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.11. MS-ESI m/z 238.1600 ($[M + H]^+$, $C_{14}H_{21}FNO$, calc. 238.1602). IR (neat): 2961, 2933, 2874, 1708, 1592, 1560, 1457, 1397, 1282.



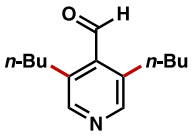
2b

This compound was synthesized from 2-chloroisonicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a yellow oil (64.3 mg, 84%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.16 (s, 1H), 2.95 – 2.89 (m, 2H), 2.80 – 2.74 (m, 2H), 1.59 – 1.48 (m, 4H), 1.43 (dt, *J* = 14.7, 7.3 Hz, 2H), 1.35 (dt, *J* = 14.6, 7.4 Hz, 2H), 0.92 (dt, *J* = 15.7, 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.92, 151.08, 149.32, 141.58, 136.51, 135.98, 34.16, 32.33, 29.57, 28.96, 22.95, 22.62, 13.87, 13.84. MS-ESI m/z 254.1296 ($[M + H]^+$, $C_{14}H_{21}ClNO$, calc. 254.1306). IR (neat): 2960, 2932, 2873, 1709, 1545, 1466, 1371.



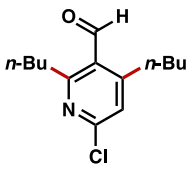
2c

This compound was synthesized from 2-bromoisonicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a yellow oil (67.0 mg, 75%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.46 (s, 1H), 8.14 (s, 1H), 2.94 – 2.87 (m, 2H), 2.77 – 2.71 (m, 2H), 1.53 (ddtd, *J* = 15.4, 9.9, 7.5, 5.5 Hz, 4H), 1.47 – 1.39 (m, 2H), 1.36 (h, *J* = 7.3 Hz, 2H), 0.92 (dt, *J* = 19.9, 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.93, 149.84, 144.28, 141.36, 138.08, 136.76, 34.07, 32.44, 31.21, 29.52, 22.96, 22.61, 13.86, 13.83. MS-ESI m/z 298.0814 ($[M + H]^+$, $C_{14}H_{21}BrNO$, calc. 298.0801). IR (neat): 2959, 2931, 2873, 1708, 1542, 1465, 1430, 1367.



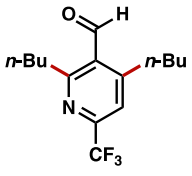
2d

This compound was synthesized from isonicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a light-yellow oil (65.3 mg, 99%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.39 (s, 2H), 2.90 – 2.78 (m, 4H), 1.57 – 1.50 (m, 4H), 1.36 (h, *J* = 7.4 Hz, 4H), 0.90 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.26, 150.19, 137.99, 137.58, 34.43, 29.98, 22.67, 13.88. MS-ESI m/z 220.1686 ($[M + H]^+$, $C_{14}H_{22}NO$, calc. 220.1696). IR (neat): 2959, 2931, 2873, 1706, 1465, 1414.



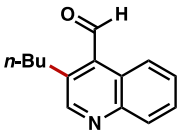
2e

This compound was synthesized from 6-chloronicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a light-yellow oil (10.6 mg, 14%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.09 (s, 1H), 3.09 – 3.03 (m, 2H), 2.93 – 2.87 (m, 2H), 1.72 – 1.63 (m, 2H), 1.61 – 1.52 (m, 2H), 1.47 – 1.36 (m, 4H), 0.94 (td, *J* = 7.3, 2.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.51, 166.59, 157.58, 154.05, 126.72, 123.85, 35.65, 33.15, 33.04, 32.89, 22.90, 22.80, 14.02, 13.96. MS-ESI m/z 254.1296 ($[M + H]^+$, $C_{14}H_{21}ClNO$, calc. 254.1306). IR (neat): 2963, 2935, 2874, 1700, 1596, 1566, 1546, 1466, 1379.



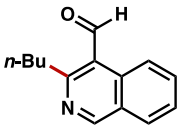
2f

This compound was synthesized from 6-(trifluoromethyl)nicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a yellow oil (62.8 mg, 73%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.41 (s, 1H), 3.15 – 3.08 (m, 2H), 2.99 – 2.92 (m, 2H), 1.73 – 1.64 (m, 2H), 1.59 (tt, *J* = 7.9, 6.5 Hz, 2H), 1.42 (hd, *J* = 7.4, 2.4 Hz, 4H), 0.94 (td, *J* = 7.4, 5.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.05, 165.33, 156.21, 149.67 (q, *J* = 34.3 Hz), 130.19 (d, *J* = 1.1 Hz), 121.20 (q, *J* = 274.8 Hz), 120.24 (q, *J* = 2.9 Hz), 35.71, 33.41, 33.04, 32.76, 22.82, 13.97, 13.91. ^{19}F NMR (282 MHz, $CDCl_3$) δ -68.62. MS-ESI m/z 288.1580 ($[M + H]^+$, $C_{15}H_{21}F_3NO$, calc. 288.1570). IR (neat): 2961, 2934, 2875, 1704, 1593, 1563, 1458, 1390, 1360.



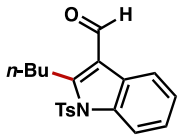
2g

This compound was synthesized from 4-quinolinecarboxaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF₃K*, and purified by flash silica gel column chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a yellow oil (53.6 mg, 84%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.89 (s, 1H), 8.86 (s, 1H), 8.69 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.11 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.70 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.62 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 3.13 – 3.02 (m, 2H), 1.74 – 1.61 (m, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.28, 153.93, 147.77, 137.88, 134.00, 129.98, 129.19, 128.99, 124.31, 124.03, 35.20, 29.85, 22.66, 13.91. MS-ESI m/z 214.1225 ($[M + H]^+$, $C_{14}H_{16}NO$, calc. 214.1226). IR (neat): 2959, 2931, 2872, 1696, 1502, 1461.



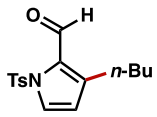
2h

This compound was synthesized from 4-isoquinolinecarboxaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF₃K*, and purified by flash silica gel column chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a yellow oil (52.3 mg, 82%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.82 (s, 1H), 9.29 (d, *J* = 0.8 Hz, 1H), 9.00 (dq, *J* = 8.7, 0.9 Hz, 1H), 7.94 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.78 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.59 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 3.34 – 3.20 (m, 2H), 1.85 – 1.71 (m, 2H), 1.44 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.98, 162.45, 157.17, 133.54, 133.30, 128.35, 127.45, 127.39, 124.44, 121.85, 34.82, 33.97, 22.80, 13.98. MS-ESI m/z 214.1226 ($[M + H]^+$, $C_{14}H_{16}NO$, calc. 214.1226). IR (neat): 2959, 2930, 2872, 1685, 1619, 1573, 1494, 1428, 1376.



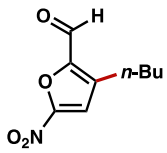
2i

This compound was synthesized from **S1** following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by flash silica gel column chromatography using hexane/EtOAc (10:1) as the eluting solvent to give the product as a yellow oil (28.8 mg, 27%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.29 – 8.23 (m, 1H), 8.21 – 8.15 (m, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.28 – 7.21 (m, 2H), 3.41 – 3.36 (m, 2H), 2.36 (s, 3H), 1.79 (tt, *J* = 8.4, 6.2 Hz, 2H), 1.48 (h, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.83, 153.11, 145.88, 136.11, 135.80, 130.30, 126.63, 126.39, 125.63, 125.22, 121.49, 119.17, 114.63, 34.42, 26.01, 22.87, 21.78, 13.84. MS-ESI m/z 356.1308 ([M + H]$^+$, $C_{20}H_{22}NO_3S$, calc. 356.1315). IR (neat): 2959, 2931, 2872, 1739, 1707, 1667, 1597, 1454, 1376, 1245.



2j

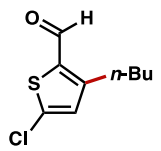
This compound was synthesized from **S2** following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by flash silica gel column chromatography using hexane/EtOAc (30:1) as the eluting solvent to give the product as a yellow solid (78.6 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 3.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 6.28 (d, *J* = 3.1 Hz, 1H), 2.85 – 2.68 (m, 2H), 2.41 (s, 3H), 1.56 – 1.46 (m, 2H), 1.31 (h, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.11, 145.79, 143.50, 135.63, 130.24, 128.87, 128.59, 127.39, 114.08, 31.95, 26.89, 22.57, 21.83, 14.00. MS-ESI m/z 306.1168 ([M + H]$^+$, $C_{16}H_{20}NO_3S$, calc. 306.1158). IR (neat): 2961, 2933, 2873, 1696, 1669, 1596, 1548, 1437, 1399, 1375.



2k

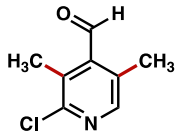
This compound was synthesized from 5-nitro-2-furaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by flash silica gel column chromatography using hexane/EtOAc (25:1) as the eluting solvent to give the product as a yellow oil (40.4 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (d, *J* = 0.6 Hz, 1H), 7.27 (s, 1H), 2.90 – 2.82 (m, 2H), 1.67 – 1.58 (m, 2H), 1.39 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.56, 152.22, 146.88, 137.82, 113.08, 31.55, 24.62, 22.30, 13.80. MS-ESI m/z 198.0750 ([M + H]$^+$, $C_9H_{12}NO_4$, calc. 198.0761). IR (neat): 3132, 2962, 2932, 2874, 1741, 1694, 1588, 1540,

1503, 1467, 1432, 1363.



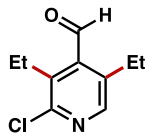
2l

This compound was synthesized from 5-chloro-2-thiophenecarboxaldehyde following general procedure A *with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K*, and purified by flash silica gel column chromatography using hexane/EtOAc (50:1) as the eluting solvent to give the product as a yellow oil (47.8 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 6.85 (s, 1H), 2.91 – 2.87 (m, 2H), 1.67 – 1.59 (m, 2H), 1.38 (h, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.14, 152.94, 141.07, 136.78, 130.14, 33.41, 28.37, 22.43, 13.92. MS-ESI m/z 203.0287 ($[M + H]^+$, $C_9H_{12}ClOS$, calc. 203.0292). IR (neat): 2961, 2933, 2873, 1741, 1662, 1431, 1377.



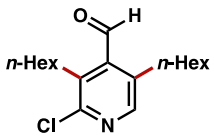
3a

This compound was synthesized using potassium methyltrifluoroborate as the alkylating reagent following general procedure B and purified by preparative thin layer chromatography using hexane/EtOAc (2:1) as the eluting solvent to give the product as a light yellow solid (9.2 mg, 18%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.56 (s, 1H), 8.20 (s, 1H), 2.59 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.84, 151.73, 149.60, 141.36, 131.72, 16.44, 15.57. MS-ESI m/z 170.0373 ($[M + H]^+$, C_8H_9ClNO, calc. 170.0367). IR (neat): 2962, 2934, 2874, 1700, 1596, 1459, 1363, 1279.



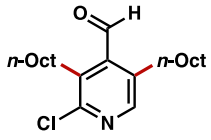
3b

This compound was synthesized using potassium ethyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et_2O (20:1) as the eluting solvent to give the product as a yellow oil (52.0 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.20 (s, 1H), 2.96 (q, J = 7.5 Hz, 2H), 2.82 (q, J = 7.6 Hz, 2H), 1.22 (td, J = 7.5, 2.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.85, 150.97, 148.92, 141.35, 137.80, 137.02, 23.20, 22.73, 16.22, 14.35. MS-ESI m/z 198.0692 ($[M + H]^+$, $C_{10}H_{13}ClNO$, calc. 198.0680). IR (neat): 2969, 2936, 2875, 1709, 1596, 1463, 1378, 1365.



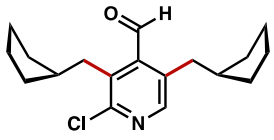
3c

This compound was synthesized using potassium *n*-hexyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as an orange oil (78.2 mg, 84%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.16 (s, 1H), 2.94 – 2.88 (m, 2H), 2.79 – 2.74 (m, 2H), 1.59 – 1.49 (m, 4H), 1.40 (ddt, *J* = 14.5, 10.7, 5.7 Hz, 2H), 1.29 (dqd, *J* = 14.5, 7.8, 7.2, 3.0 Hz, 10H), 0.90 – 0.83 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.90, 151.07, 149.31, 141.55, 136.53, 136.02, 32.05, 31.57, 31.49, 30.21, 29.85, 29.50, 29.24, 29.18, 22.64, 22.62, 14.13, 14.12. MS-ESI m/z 310.1920 ($[M + H]^+$, $C_{18}H_{29}ClNO$, calc. 310.1932). IR (neat): 2961, 2932, 2873, 2860, 1709, 1596, 1466, 1370.



3d

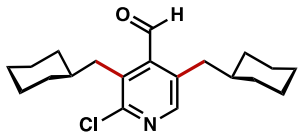
This compound was synthesized using potassium *n*-octyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a white solid (88.8 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.16 (s, 1H), 2.94 – 2.88 (m, 2H), 2.80 – 2.73 (m, 2H), 1.54 (tdd, *J* = 15.0, 9.8, 6.5 Hz, 4H), 1.43 – 1.36 (m, 2H), 1.36 – 1.20 (m, 18H), 0.86 (td, *J* = 6.9, 3.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.90, 151.08, 149.32, 141.55, 136.54, 136.03, 32.09, 31.93, 31.90, 30.26, 29.86, 29.85, 29.53, 29.37, 29.29, 29.28, 29.27, 29.25, 22.75, 22.73, 14.20, 14.18. MS-ESI m/z 366.2544 ($[M + H]^+$, $C_{22}H_{37}ClNO$, calc. 366.2558). IR (neat): 2958, 2929, 2856, 1716, 1578, 1467, 1374, 1283.



3e

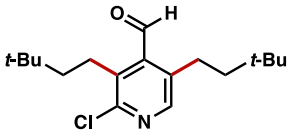
This compound was synthesized using potassium (cyclopentylmethyl)trifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a yellow oil (23.3 mg, 25%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.18 (s, 1H), 3.04 (d, *J* = 7.4 Hz, 2H), 2.80 (d, *J* = 7.4 Hz, 2H), 2.06 (tt, *J* = 9.3, 7.1 Hz, 1H), 1.96 (dtd, *J* = 14.3, 7.1, 1.6 Hz, 1H), 1.69 – 1.62 (m, 8H), 1.56 – 1.46 (m, 4H), 1.25 (tdd, *J* = 11.4, 8.1, 4.8 Hz, 2H), 1.17 (dddd, *J* = 16.4, 12.0, 9.1, 4.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.56, 151.25, 149.58, 142.35, 135.67, 135.43,

42.23, 41.90, 35.35, 33.46, 32.50, 32.37, 24.86, 24.74. MS-ESI m/z 306.1606 ([M + H]$^+$, $C_{18}H_{25}ClNO$, calc. 306.1619). IR (neat): 2961, 2872, 1709, 1595, 1457, 1369.



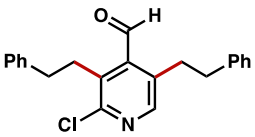
3f

This compound was synthesized using potassium (cyclohexylmethyl)trifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et_2O (33:1) as the eluting solvent to give the product as a yellow oil (64.0 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.12 (s, 1H), 2.89 (d, *J* = 7.0 Hz, 2H), 2.66 (d, *J* = 7.1 Hz, 2H), 1.71 – 1.65 (m, 4H), 1.64 – 1.60 (m, 6H), 1.59 (d, *J* = 3.2 Hz, 1H), 1.39 (dtq, *J* = 14.3, 7.0, 3.5 Hz, 1H), 1.18 – 1.10 (m, 6H), 1.06 (td, *J* = 11.9, 11.5, 2.9 Hz, 2H), 0.95 (qd, *J* = 11.7, 3.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.52, 151.57, 150.04, 142.84, 134.57, 134.56, 40.10, 39.54, 37.20, 35.72, 33.13, 33.11, 26.39, 26.35, 26.20. MS-ESI m/z 334.1928 ([M + H]$^+$, $C_{20}H_{29}ClNO$, calc. 334.1932). IR (neat): 2961, 2930, 2854, 1709, 1596, 1449, 1369.



3g

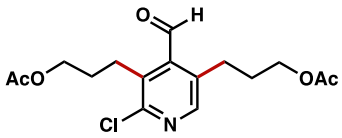
This compound was synthesized using potassium (3,3-dimethylbutyl)trifluoroborate as the alkylating reagent following general procedure B *with the exception of using DCE as the solvent and a lower reaction temperature (80 ºC)*, and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the eluting solvent to give the product as a yellow solid (4.7 mg, 5%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.17 (s, 1H), 2.99 – 2.86 (m, 2H), 2.83 – 2.70 (m, 2H), 1.51 – 1.34 (m, 4H), 1.00 (s, 9H), 0.97 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.68, 151.01, 149.37, 141.39, 137.41, 136.56, 46.87, 44.03, 31.07, 31.02, 29.25, 29.15, 25.40, 24.92. MS-ESI m/z 310.1923 ([M + H]$^+$, $C_{18}H_{29}ClNO$, calc. 310.1932). IR (neat): 2960, 2934, 2873, 1697, 1595, 1459, 1364.



3h

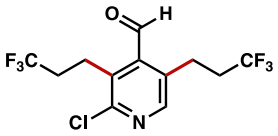
This compound was synthesized using potassium phenethyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et_2O (10:1) as the eluting solvent to give the product as a yellow solid (85.3 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.16 (s, 1H), 7.34 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H),

7.21 – 7.17 (m, 2H), 7.14 – 7.10 (m, 2H), 3.28 – 3.22 (m, 2H), 3.07 (dd, *J* = 8.9, 6.7 Hz, 2H), 2.94 – 2.89 (m, 2H), 2.85 (dd, *J* = 8.9, 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.16, 151.38, 149.82, 142.33, 140.29, 140.01, 134.98, 134.35, 128.76, 128.67, 126.62, 126.61, 37.96, 35.65, 31.78, 31.31. MS-ESI m/z 350.1317 ([M + H]$^+$, $C_{22}H_{21}ClNO$, calc. 350.1306). IR (neat): 3026, 2962, 2935, 2874, 1706, 1601, 1496, 1455, 1371.



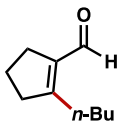
3i

This compound was synthesized using potassium 3-acetoxypropyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/EtOAc (2:1) as the eluting solvent to give the product as a yellow oil (86.9 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.19 (s, 1H), 4.10 (t, *J* = 6.2 Hz, 2H), 4.05 (t, *J* = 6.2 Hz, 2H), 3.04 – 2.96 (m, 2H), 2.89 – 2.81 (m, 2H), 2.02 (s, 3H), 2.01 (s, 3H), 1.89 (dddd, *J* = 15.9, 12.3, 8.0, 6.1 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.29, 170.99, 170.95, 151.54, 149.70, 141.55, 135.22, 134.86, 63.54, 63.25, 30.50, 28.72, 26.32, 25.83, 20.92, 20.91. MS-ESI m/z 342.1106 ([M + H]$^+$, $C_{16}H_{21}ClNO_5$, calc. 342.1103). IR (neat): 2962, 2935, 2874, 1739, 1708, 1595, 1456, 1367, 1246.



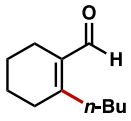
3j

This compound was synthesized using potassium 3,3,3-trifluoropropane-1-trifluoroborate as the alkylating reagent following general procedure B *with the exception of using DCE as the solvent and a lower reaction temperature (80 ºC),* and purified by preparative thin layer chromatography using hexane/acetone (2:1) as the eluting solvent to give the product as a yellow oil (9.8 mg, 10%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.34 (s, 1H), 3.36 – 3.19 (m, 2H), 3.19 – 3.01 (m, 2H), 2.57 – 2.35 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.48, 152.53, 150.74, 141.80, 133.08, 132.78, 126.27 (q, *J* = 277.0 Hz), 126.24 (q, *J* = 277.0 Hz), 35.43 (q, *J* = 29.0 Hz), 33.34 (q, *J* = 29.3 Hz), 22.97 (q, *J* = 3.4 Hz), 22.22 (q, *J* = 3.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.31 (t, *J* = 10.4 Hz), -66.66 (t, *J* = 10.4 Hz). MS-ESI m/z 334.0416 ([M + H]$^+$, $C_{12}H_{11}ClF_6NO$, calc. 334.0428). IR (neat): 2962, 2934, 2874, 1698, 1595, 1459, 1307.



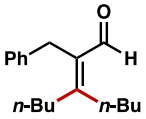
4a

This compound was synthesized from **S3** following general procedure C and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a yellow oil (8.0 mg, 18%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 2.62 – 2.53 (m, 6H), 1.85 (p, *J* = 7.8 Hz, 2H), 1.54 – 1.46 (m, 2H), 1.35 (p, *J* = 7.6 Hz, 2H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.32, 167.28, 138.52, 38.52, 30.63, 30.35, 28.33, 22.69, 21.51, 13.99. MS-ESI m/z 153.1273 ($[M + H]^+$, $C_{10}H_{17}O$, calc. 153.1274).



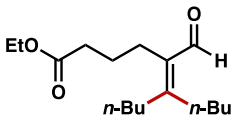
4b

This compound was synthesized from 1-cyclohexene-1-carboxaldehyde following general procedure C *without the addition of crotonic acid*, and purified by preparative thin layer chromatography using hexane/EtOAc (5:1), then hexane/DCM (1:1) as the eluting solvent to give the product as a yellow oil (6.0 mg, 12%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 2.55 – 2.49 (m, 2H), 2.25 (td, *J* = 6.2, 2.2 Hz, 2H), 2.22 – 2.16 (m, 2H), 1.64 – 1.58 (m, 4H), 1.50 (ddd, *J* = 12.9, 5.9, 3.6 Hz, 2H), 1.36 (p, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.16, 161.03, 133.72, 32.43, 32.32, 32.08, 22.88, 22.32, 22.31, 21.86, 14.04. MS-ESI m/z 167.1433 ($[M + H]^+$, $C_{11}H_{19}O$, calc. 167.1430).



4c

This compound was synthesized from **S4** following general procedure C and purified by preparative thin layer chromatography using hexane/EtOAc (5:1), then hexane/DCM (1:1) as the eluting solvent to give the product as a yellow oil (9.1 mg, 12%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.12 (m, 1H), 7.11 – 7.08 (m, 2H), 3.64 (s, 2H), 2.64 – 2.56 (m, 2H), 2.27 (dd, *J* = 9.6, 6.6 Hz, 2H), 1.53 (ddd, *J* = 12.6, 5.9, 3.5 Hz, 2H), 1.40 (p, *J* = 7.5 Hz, 2H), 1.33 (td, *J* = 7.8, 6.3, 3.6 Hz, 4H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.91 – 0.84 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.43, 165.81, 140.55, 135.38, 128.42, 128.13, 125.87, 35.31, 33.35, 30.80, 30.63, 30.30, 23.29, 23.06, 14.04, 14.02. MS-ESI m/z 259.2038 ($[M + H]^+$, $C_{18}H_{27}O$, calc. 259.2056).

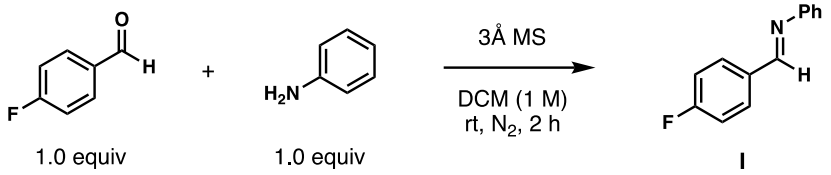


4d

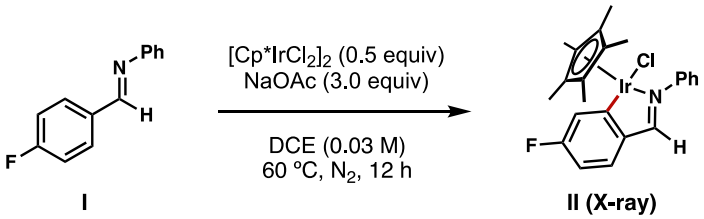
This compound was synthesized from **S5** following general procedure C and purified by preparative thin layer chromatography using hexane/EtOAc (5:1), then DCM as the eluting solvent to give the product as a yellow oil (6.3 mg, 7%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 4.12 (q, *J* = 7.1

Hz, 2H), 2.61 – 2.43 (m, 2H), 2.37 – 2.20 (m, 6H), 1.66 – 1.58 (m, 2H), 1.51 – 1.32 (m, 8H), 1.27 – 1.23 (m, 3H), 0.93 (dt, *J* = 8.4, 7.2 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 191.56, 173.71, 164.59, 136.02, 60.40, 34.67, 34.33, 33.33, 30.80, 30.57, 24.78, 24.75, 23.30, 22.99, 14.40, 14.10, 14.02. MS-ESI m/z 305.2075 ($[M + H]^+$, $C_{17}H_{30}NaO_3$, calc. 305.2087).

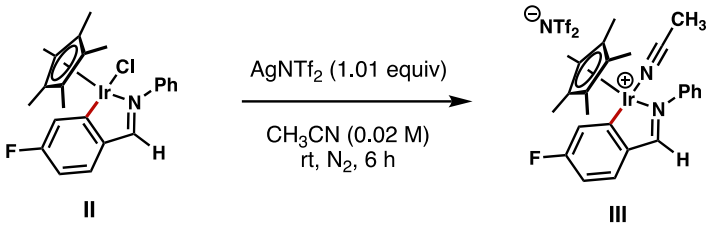
Mechanistic Studies



Following a previously reported procedure,[8] 4-fluorobenzaldehyde (1.07 mL, 10.0 mmol) was dissolved in anhydrous DCM (10 mL) along with 3Å molecular sieves in a 50-mL oven-dried round bottom flask equipped with a magnetic stir bar under an argon atmosphere. To this solution was added aniline (0.91 mL, 10.0 mmol). The reaction was stirred at r.t. for 2 h, at which point Na_2SO_4 was added with subsequent filtration. The solvent was removed *in vacuo* to give the product as a white solid (1.83 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.94 – 7.88 (m, 2H), 7.42 – 7.37 (m, 2H), 7.27 – 7.13 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.84 (d, *J* = 252.1 Hz), 158.99, 151.98, 132.70 (d, *J* = 3.0 Hz), 130.92 (d, *J* = 8.8 Hz), 129.33, 126.16, 120.97, 116.09 (d, *J* = 21.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -108.12 (tt, *J* = 8.5, 5.5 Hz). MS-ESI m/z 200.0870 ($[M + H]^+$, $C_{13}H_{11}FN$, calc. 200.0870). IR (neat): 3066, 2878, 1625. 1586. 1505, 1483, 1235, 1218.

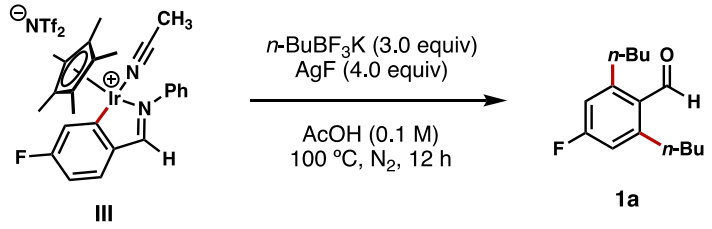


Following a previously reported procedure with slight modifications,[9] NaOAc (73.8 mg, 0.90 mmol) and $[Cp^*IrCl_2]_2$ (119.5 mg, 0.15 mmol) were added to a solution of imine I (59.8 mg, 0.30 mmol) in anhydrous DCE (10 mL) in a 25-mL oven-dried round bottom flask equipped with a magnetic stir bar under an argon atmosphere. The mixture was stirred at 60 ºC for 8 h, then filtered through a pad of Celite®. The filtrate was evaporated *in vacuo* and purified by preparative thin layer chromatography using DCM/EtOAc (100:1) as the eluting solvent to yield the iridacycle as a red solid (109.1 mg, 63%). Single crystal was obtained by slow diffusion of pentane to a solution of iridacycle II in DCM at -20 ºC.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.61 (dd, *J* = 8.3, 5.7 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.49 (dd, *J* = 9.5, 2.4 Hz, 1H), 7.39 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.31 – 7.27 (m, 1H), 6.72 (td, *J* = 8.7, 2.5 Hz, 1H), 1.46 (s, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.96, 173.62 (d, *J* = 6.3 Hz), 165.00 (d, *J* = 257.2 Hz), 151.63, 143.43 (d, *J* = 1.4 Hz), 131.47 (d, *J* = 9.6 Hz), 129.08, 127.39, 122.51, 121.16 (d, *J* = 17.7 Hz), 109.62 (d, *J* = 23.7 Hz), 89.41, 8.76. ^{19}F NMR (282 MHz, $CDCl_3$) δ -106.35 (td, *J* = 9.2, 5.6 Hz). MS-ESI m/z 526.1532 ($[M]^+$, $C_{23}H_{24}FIrN$, calc. 526.1517). IR (neat): 2914, 1599, 1585, 1539, 1484, 1447, 1380, 1343, 1242, 1230.



II III

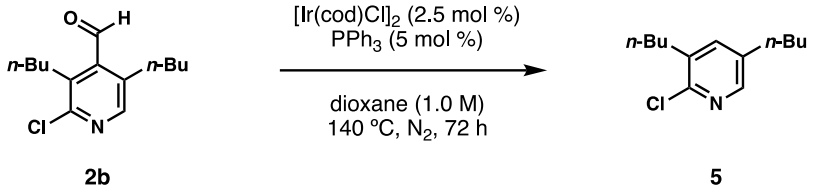
Following a previously reported procedure with slight modifications,[10] iridacycle II (56.1 mg, 0.10 mmol) was added to a 25-mL oven-dried round bottom flask equipped with a magnetic stir bar under air. The flask was then transferred to a glovebox filled with N_2, wherein $AgNTf_2$ (39.2 mg, 0.101 mmol) was added. The flask was sealed with a rubber septum and taken out of the glovebox. Anhydrous acetonitrile (5 mL) was added, and the reaction mixture was stirred at r.t. for 6 h, and then filtered through a pad of Celite®. The filtrate was evaporated *in vacuo* to give iridacycle III as a light orange solid (84.7 mg, quantitative). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.77 (dd, *J* = 8.4, 5.5 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.43 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.31 (m, 2H), 6.89 (td, *J* = 8.6, 2.4 Hz, 1H), 2.51 (s, 3H), 1.50 (s, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.85, 166.67 (d, *J* = 6.5 Hz), 165.44 (d, *J* = 260.5 Hz), 149.62, 143.87 (d, *J* = 1.8 Hz), 132.95 (d, *J* = 9.7 Hz), 130.07, 128.74, 122.19, 121.44 (d, *J* = 18.9 Hz), 120.13, 119.99 (q, *J* = 321.6 Hz), 111.67 (d, *J* = 23.4 Hz), 92.08, 8.65, 4.04. ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.67, -103.40 (dd, *J* = 8.9, 5.6 Hz). MS-ESI m/z 567.1770 ($[M]^+$, $C_{25}H_{27}FIrN_2$, calc. 567.1782). IR (neat): 2947, 2837, 1604, 1589, 1546, 1488, 1452, 1350, 1227.



III 1a

A 10-mL oven-dried microwave-vial equipped with a magnetic stir bar was charged with iridacycle III (84.7 mg, 0.10 mmol), AgF (50.8 mg, 0.40 mmol) and *n*-$BuBF_3K$ (49.2 mg, 0.30 mmol). The vial was sealed with a PTFE-lined aluminum cap, evacuated and filled with argon three times. Degassed AcOH (1 mL) was added through a syringe, and the vial was heated in a pie-block at 100 °C under vigorous stirring for 12 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (10 mL). The filtrate was then concentrated *in vacuo* and the resulting residue was purified by flash silica gel column chromatography using hexane/Et_2O (50:1) as the eluting solvent to give the product as a yellow oil (6.1 mg, 26%).

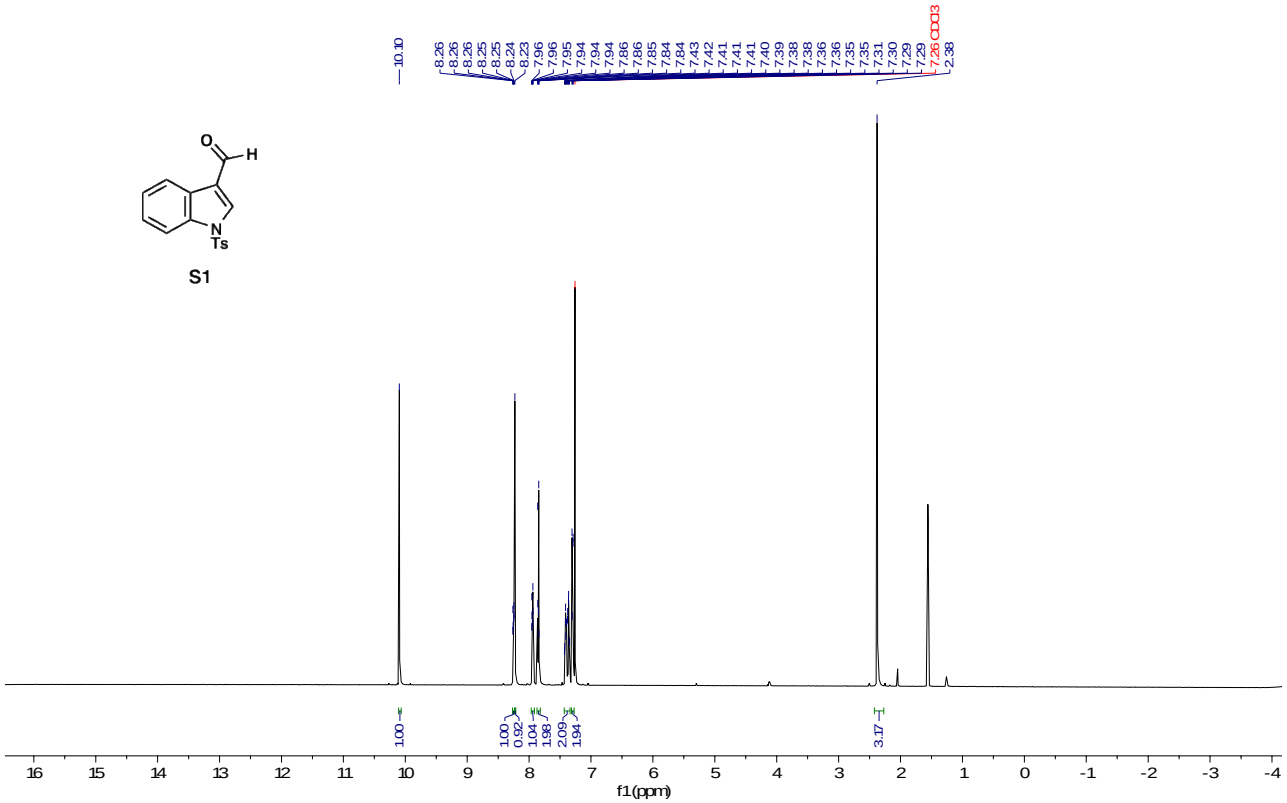
Decarbonylation

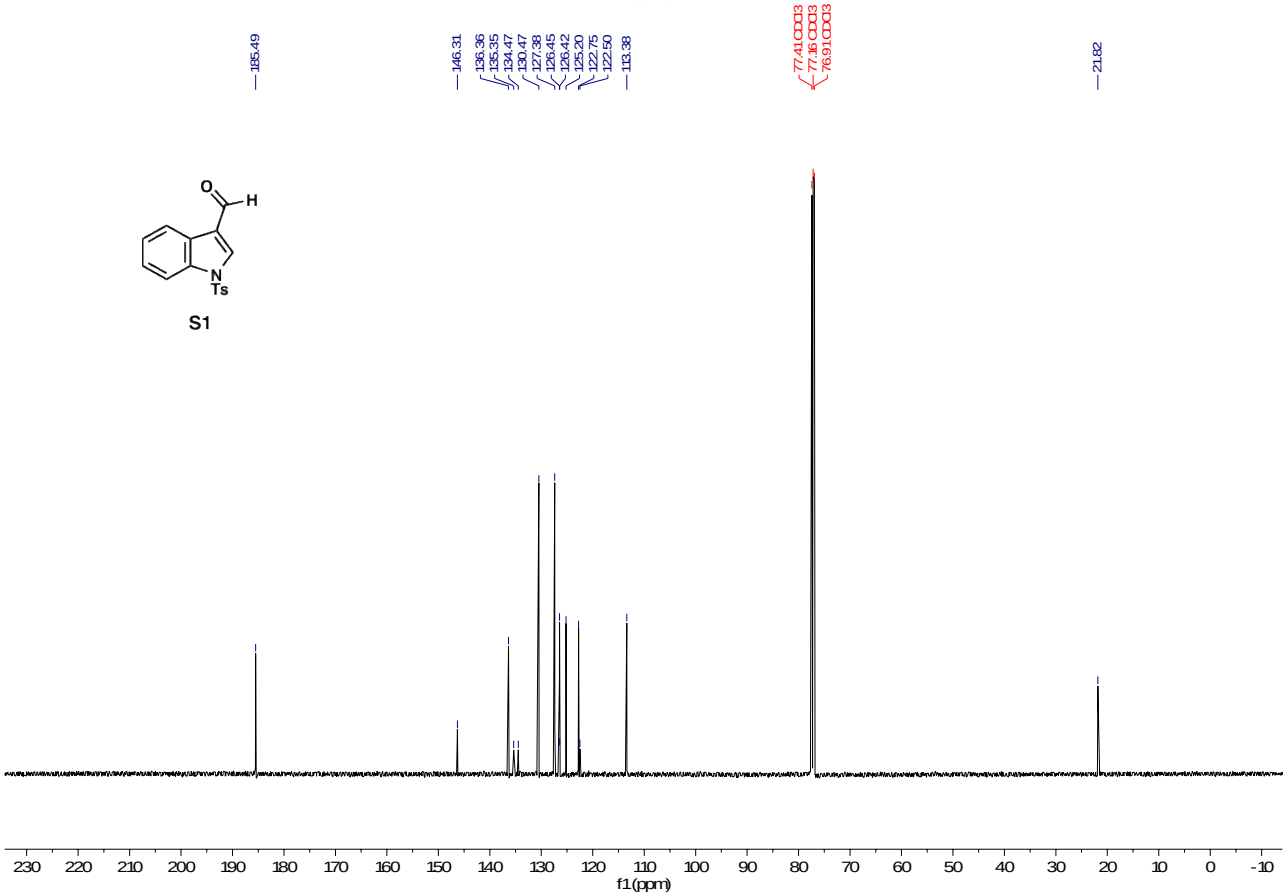


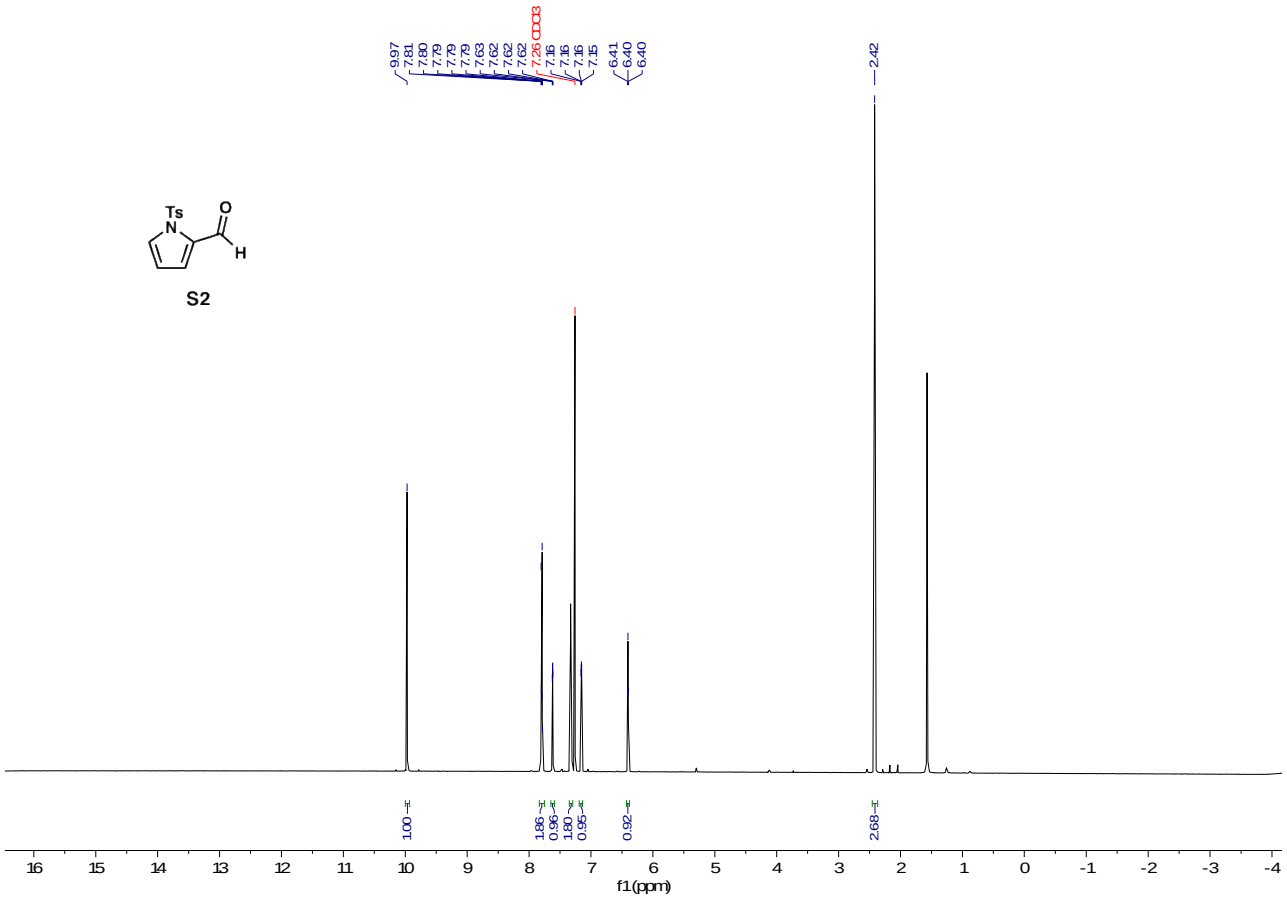
2b **5**

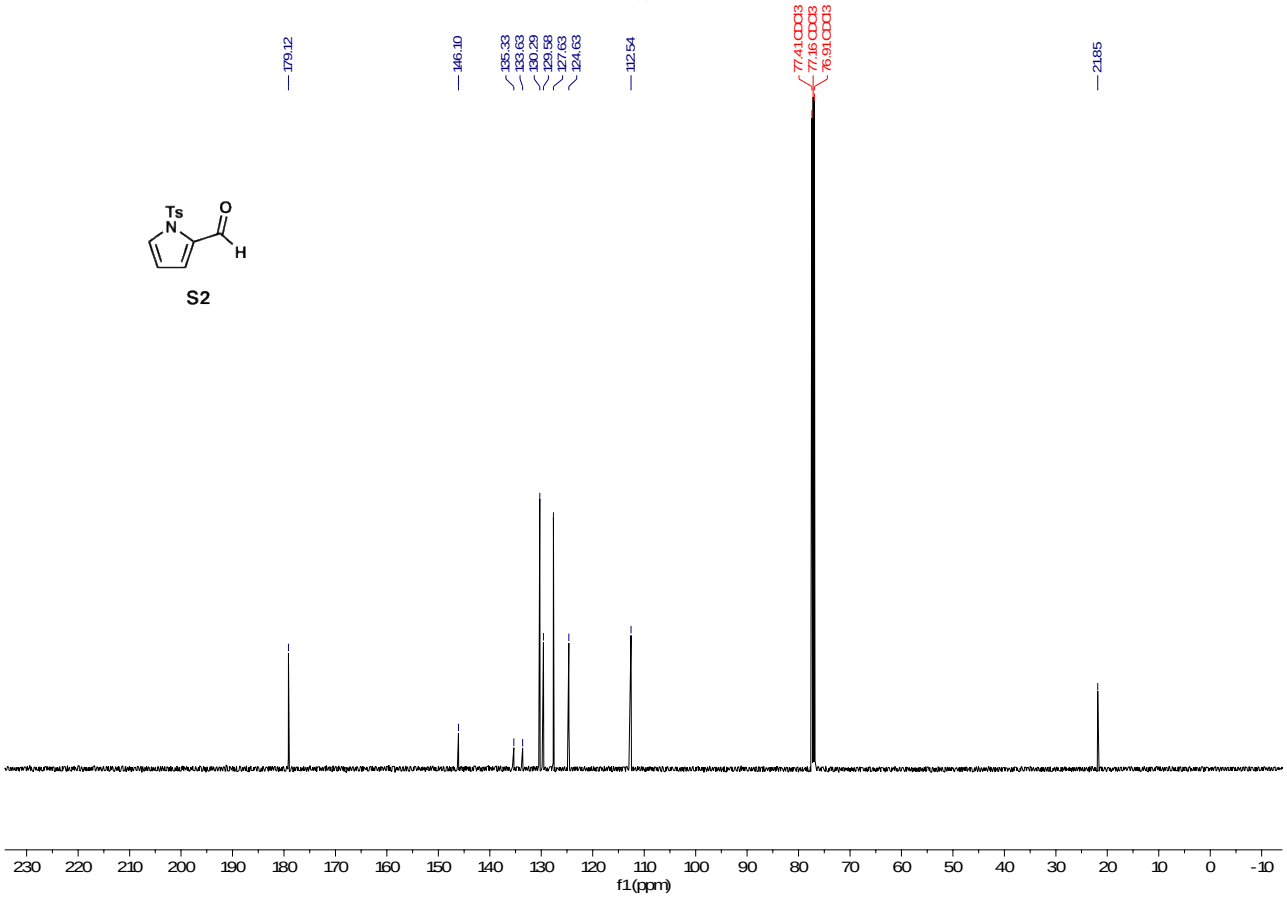
Following a previously reported procedure,11 a 10-mL oven-dried microwave vial equipped with a magnetic stir bar was charged with PPh3 (6.6 mg, 0.025 mmol). The vial was transferred to a glovebox filled with N2, wherein [Ir(cod)Cl]2 (8.4 mg, 0.0125 mmol) was added. The vial was sealed with a PTFE-lined aluminum cap and taken out of the glovebox. A solution of the di-alkylation product 2b (0.5 mmol) in 1,4-dioxane (0.5 mL) was added to the vial via a syringe. The resulting mixture was degassed by the freeze–pump-thaw method for three times and kept under nitrogen atmosphere. The reaction mixture was then heated to 140 °C and stirred for 72 h. The crude product was purified by flash silica gel column chromatography using hexane/EtOAc (50:1) as the eluting solvent to give the product as a colorless oil (97.4 mg, 86%).1H NMR (500 MHz, CDCl3) δ 8.01 (d, J = 2.4 Hz, 1H), 7.31 (d, J = 2.5 Hz, 1H), 2.67 – 2.61 (m, 2H), 2.56 – 2.49 (m, 2H), 1.61 – 1.51 (m, 4H), 1.34 (dh, J = 22.1, 7.4 Hz, 4H), 0.91 (dt, J = 12.9, 7.4 Hz, 6H). 13C NMR (126 MHz, CDCl3) δ 148.57, 146.88, 138.84, 137.17, 136.04, 33.28, 32.84, 31.91, 31.44, 22.50, 22.25, 13.92, 13.88. MS-ESI m/z 226.1357 ([M]+, C13H21ClN, calc. 226.1357). IR (neat): 2957, 2930, 2860, 1561, 1465, 1427, 1405, 1379.

^{1}H, ^{13}C and ^{19}F NMR Spectra of New Compounds






9.97
7.81
7.80
7.79
7.79
7.79
7.63
7.62
7.62
7.62
7.62
7.26 CDCl3
7.16
7.16
7.16
7.15
6.41
6.40
6.40
2.42
Ts
N
O
H
S2
1.00
1.96
0.96
1.80
0.95
0.92
2.68
f1 (ppm)


179.12
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133.63
130.29
129.58
127.63
124.63
112.54
77.41 CDCl3
77.16 CDCl3
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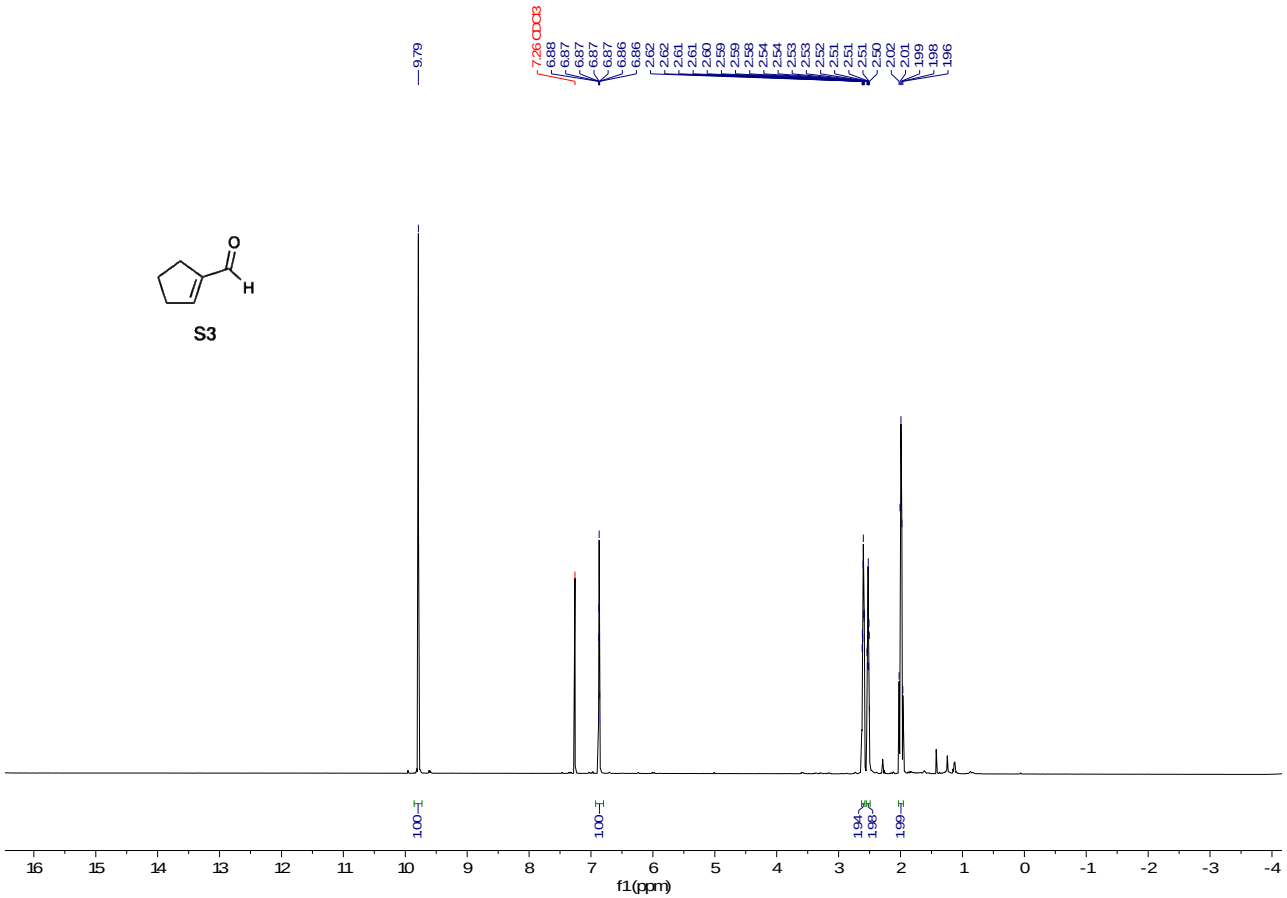
21.85
Ts
N
O
H
S2
f1 (ppm)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7.26 CDCl3
6.88
6.87
6.87
6.87
6.87
6.86
6.86
2.62
2.62
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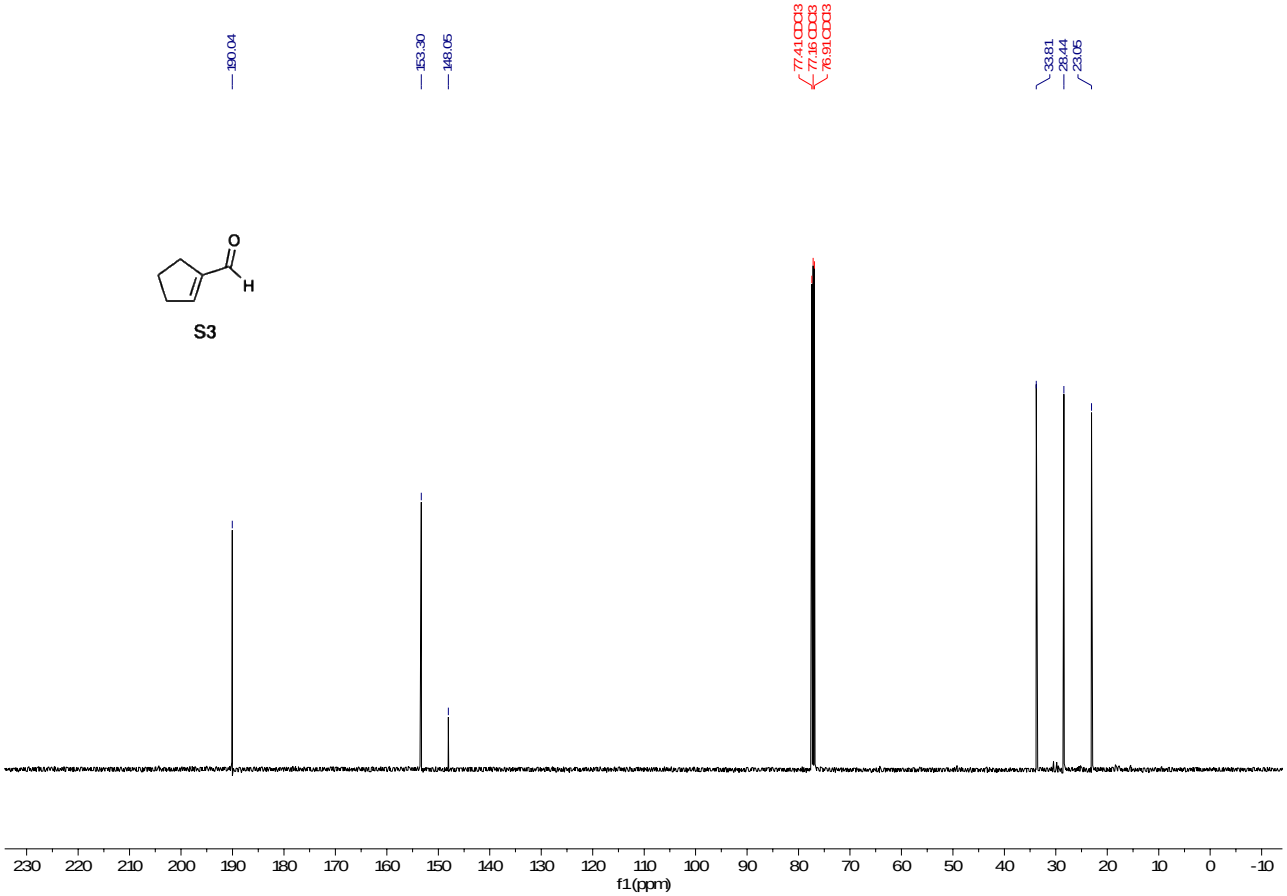
f1 (ppm)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148.05
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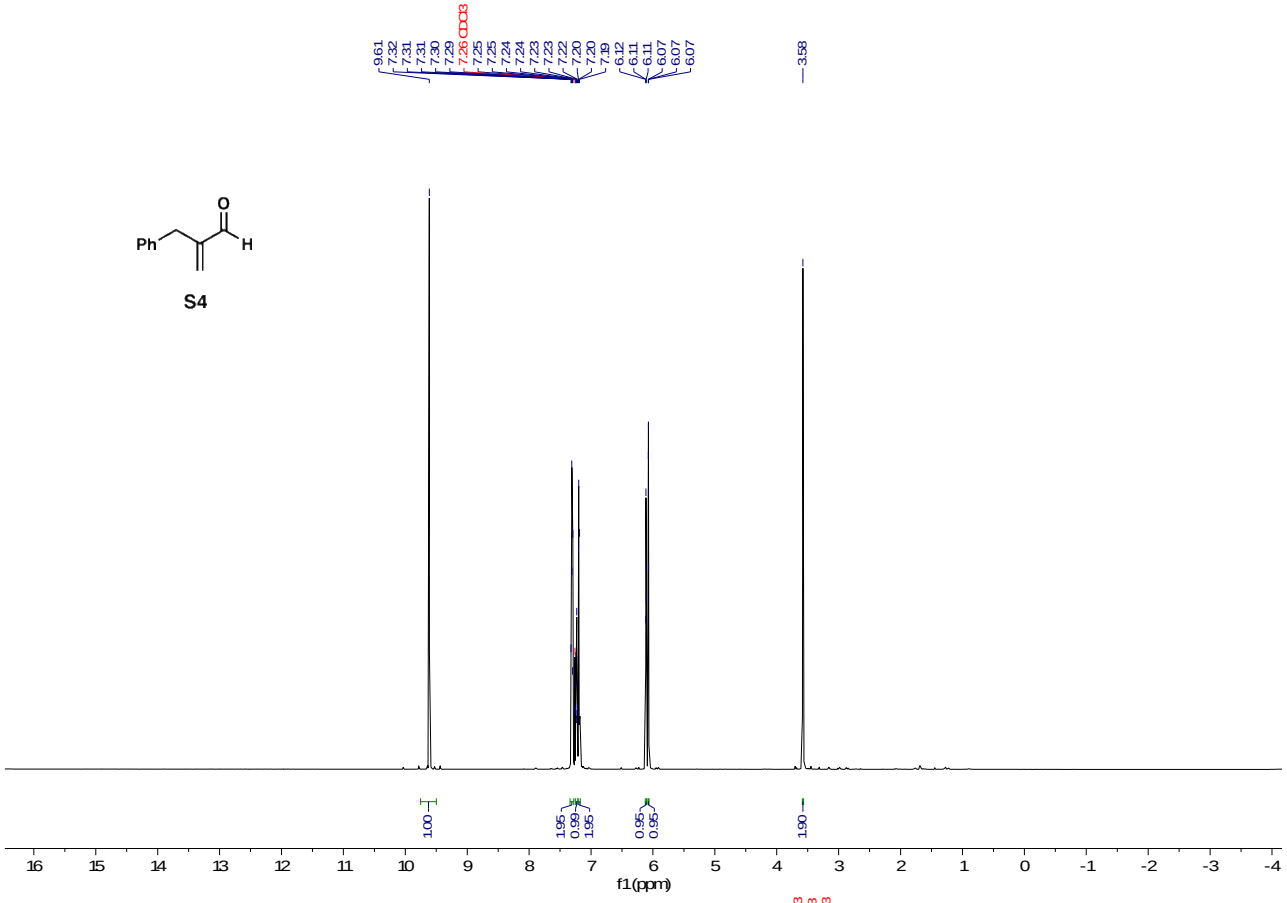
77.16 CDCl3
76.91 CDCl3
33.81
28.44
23.06
O
H
S3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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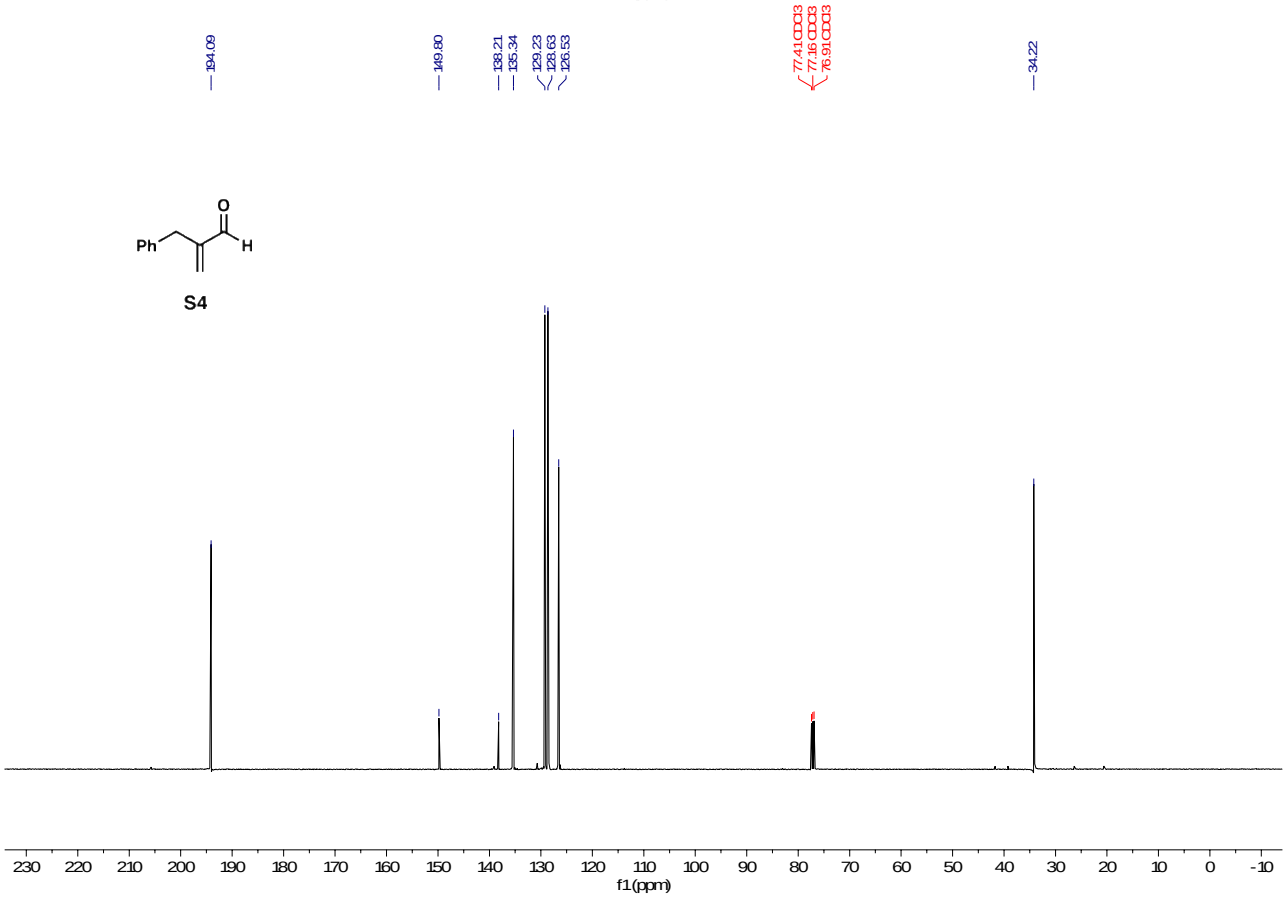
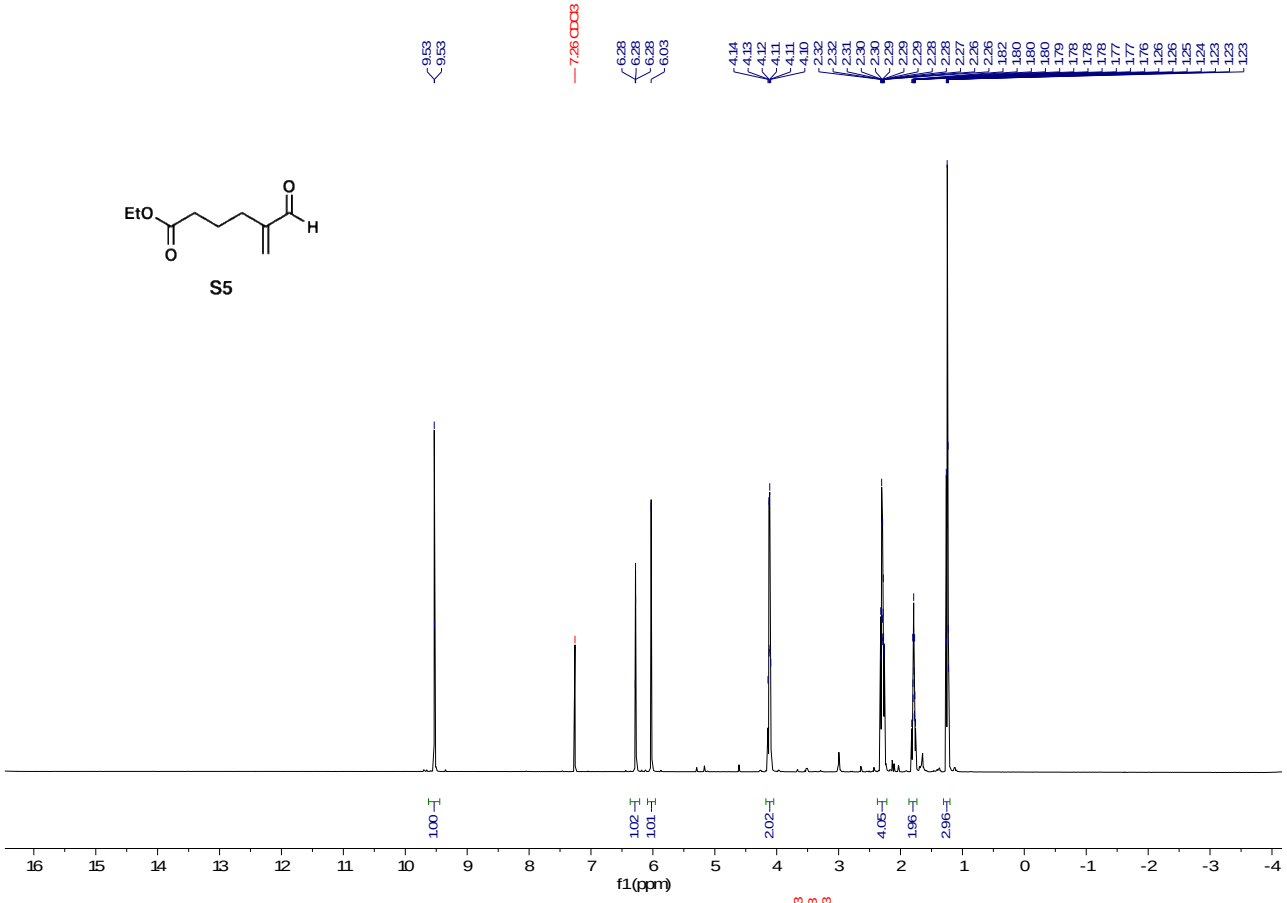
7.32
7.31
7.31
7.30
7.29
7.26 CDCl3
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.20
7.20
7.19
6.12
6.11
6.11
6.07
6.07
6.07
3.58
O
Ph
H
S4
1.00
1.95
0.99
1.95
0.95
0.95
1.90
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


194.09
149.80
138.21
135.34
129.23
128.63
126.53
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.22
O
Ph
H
S4
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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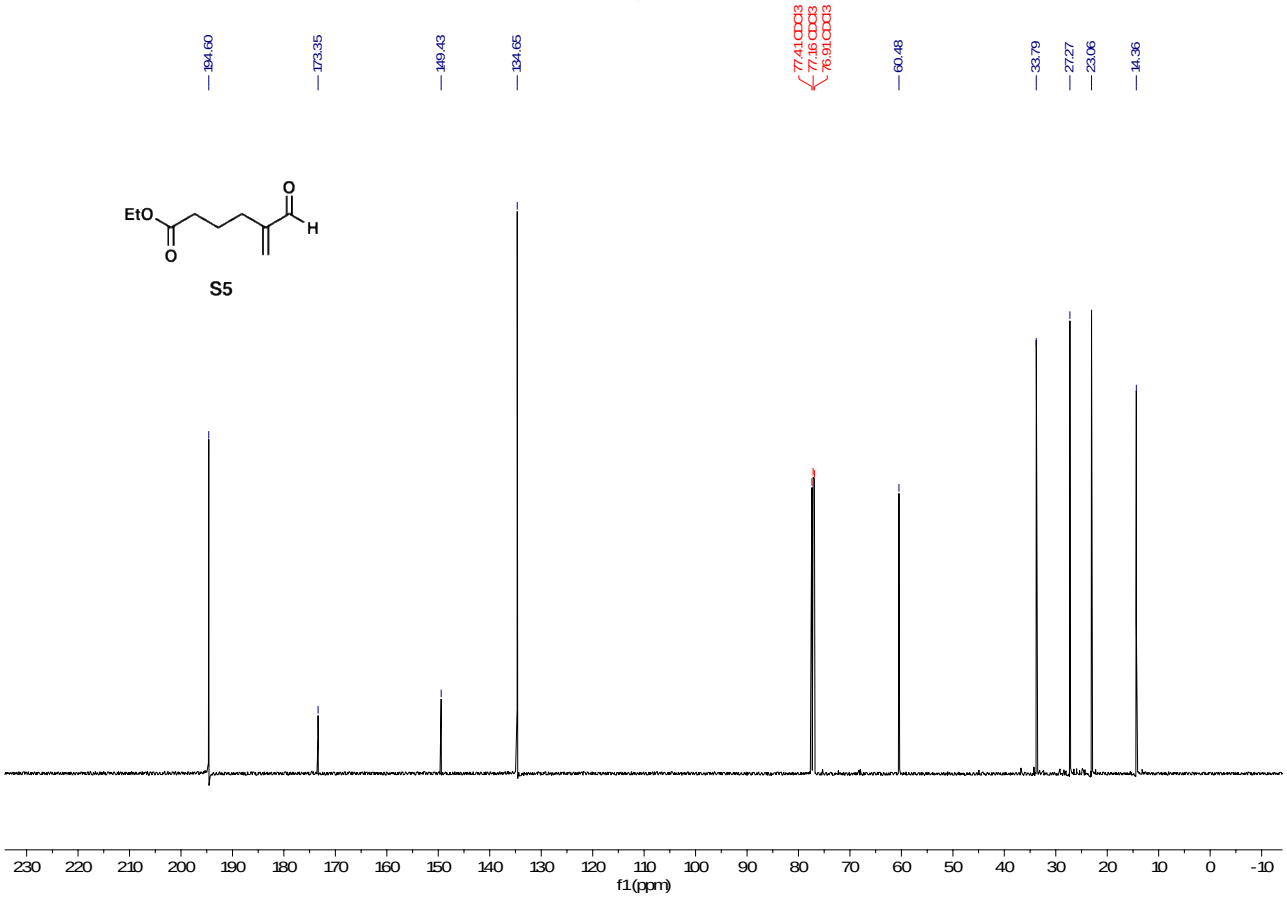
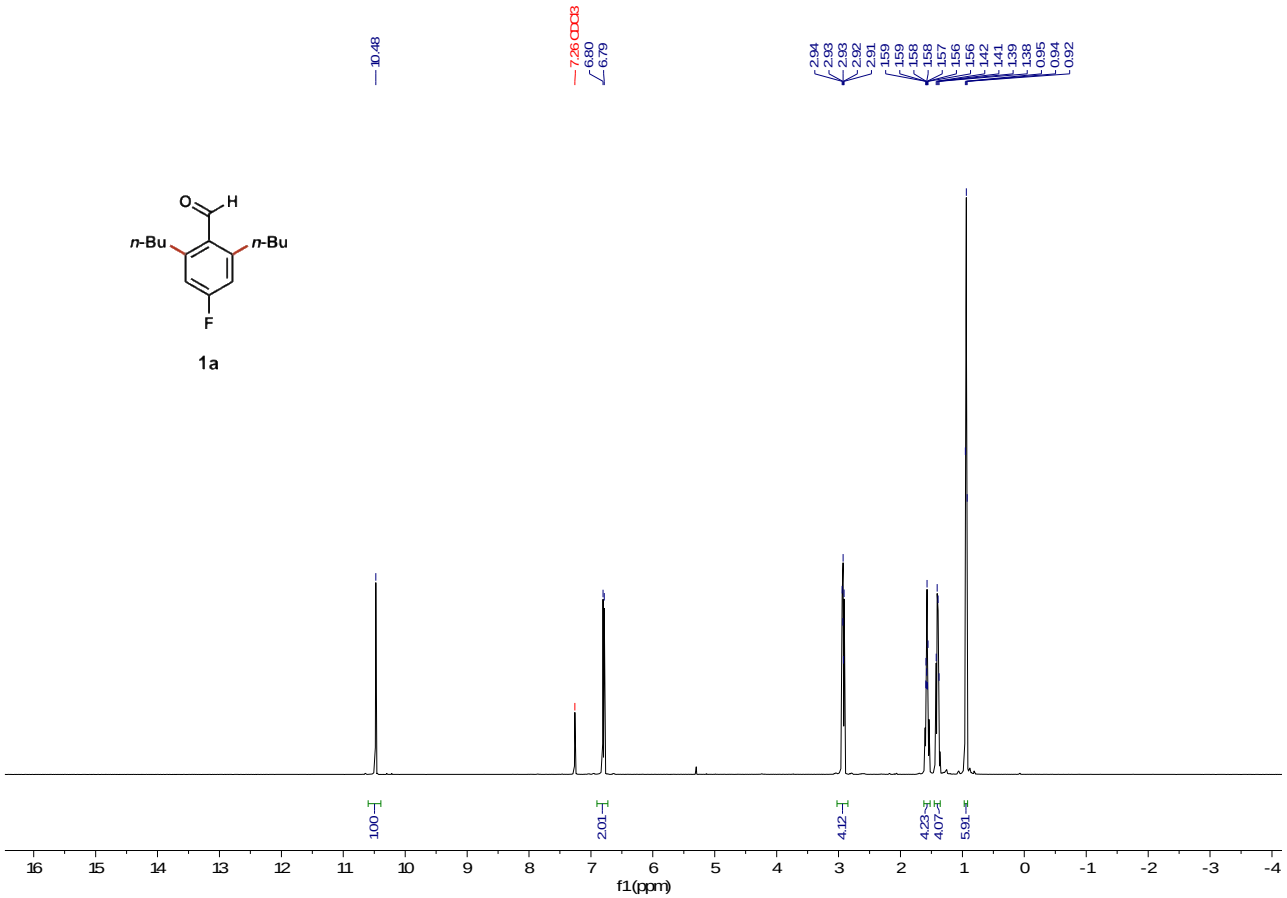
9.53
7.26 CDCl3
6.28
6.28
6.28
6.03
4.14
4.13
4.12
4.11
4.11
4.10
2.32
2.32
2.31
2.30
2.30
2.29
2.29
2.29
2.28
2.28
2.27
2.26
2.25
1.82
1.80
1.80
1.80
1.79
1.78
1.78
1.78
1.77
1.77
1.76
1.26
1.26
1.25
1.24
1.23
1.23
1.23
EtO
O
O
O
H
S5
1.00
1.02
1.01
2.02
4.05
1.96
2.96
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


194.60
173.35
149.43
134.65
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
60.48
33.79
27.27
23.06
14.36
EtO
O
O
O
H
S5
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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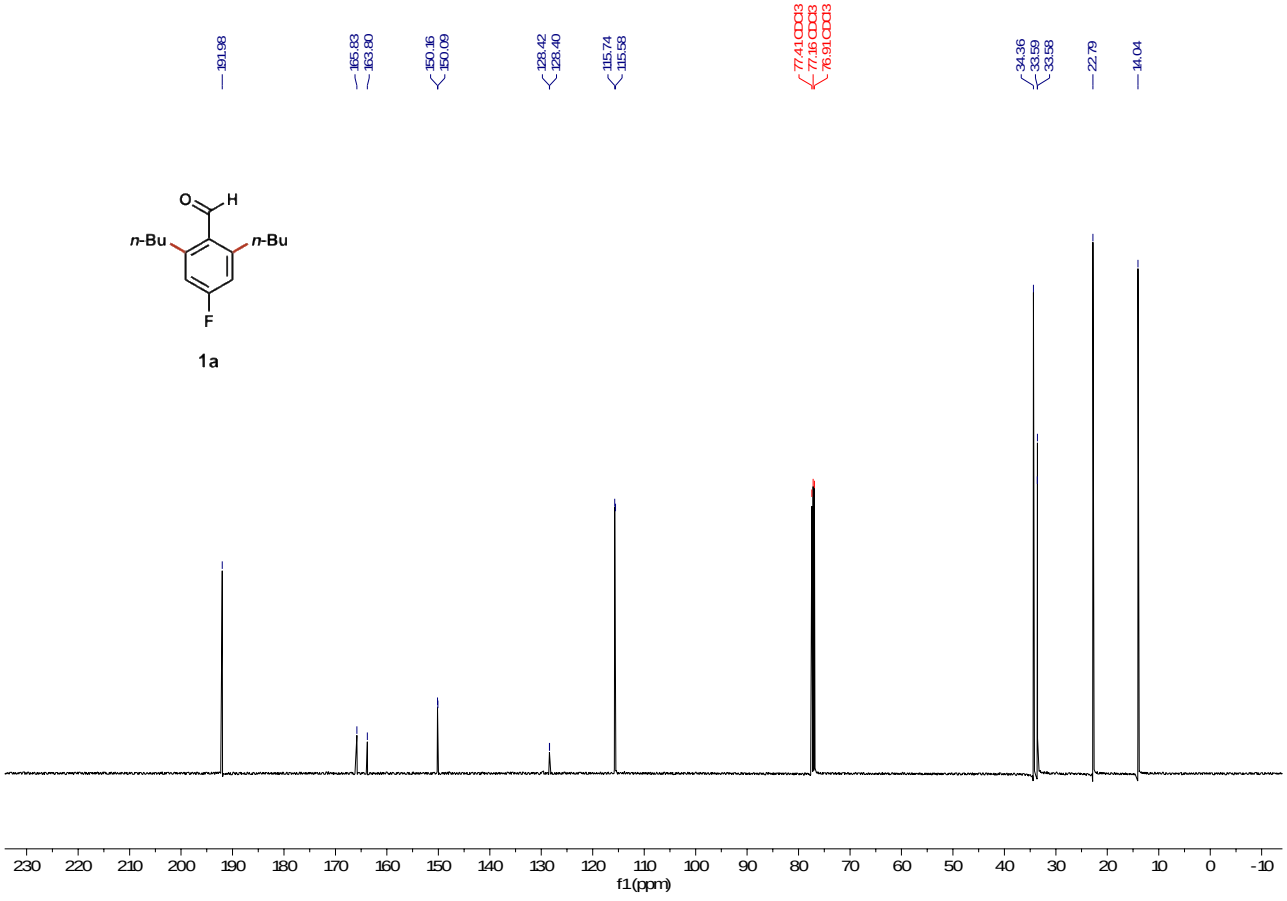
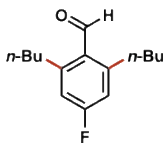
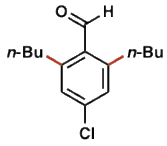
7.26 CDCl3
6.80
6.79
2.94
2.93
2.93
2.92
2.91
1.59
1.59
1.58
1.58
1.57
1.56
1.56
1.42
1.41
1.39
1.38
0.95
0.94
0.92
O
H
n-Bu
n-Bu
F
1a
1.00
2.01
4.12
4.23
4.07
5.91
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


191.98
165.83
163.80
150.16
150.09
128.42
128.40
115.74
115.58
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.36
33.59
33.58
22.79
14.04
O
H
n-Bu
n-Bu
F
1a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
H
n-Bu
n-Bu
F

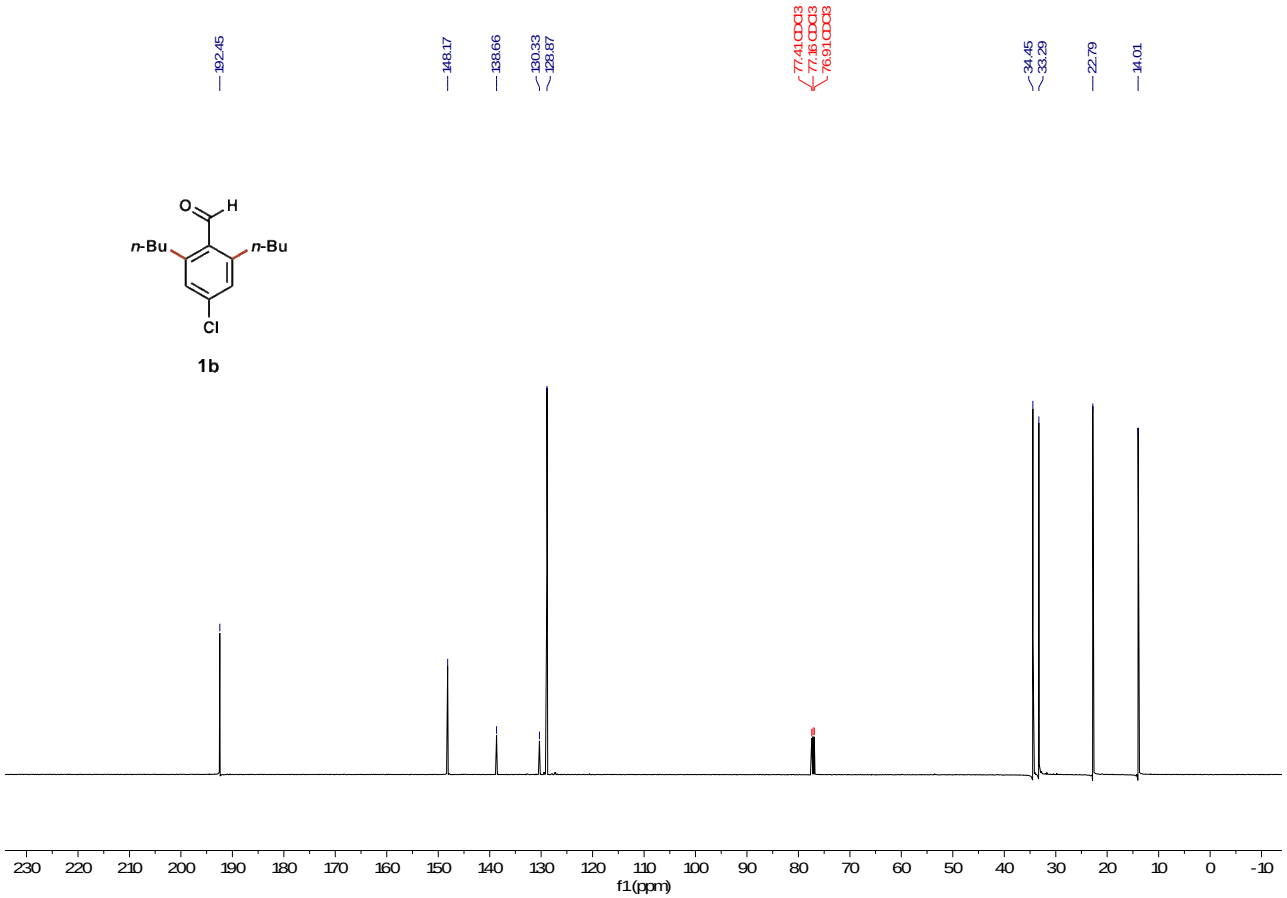
1a

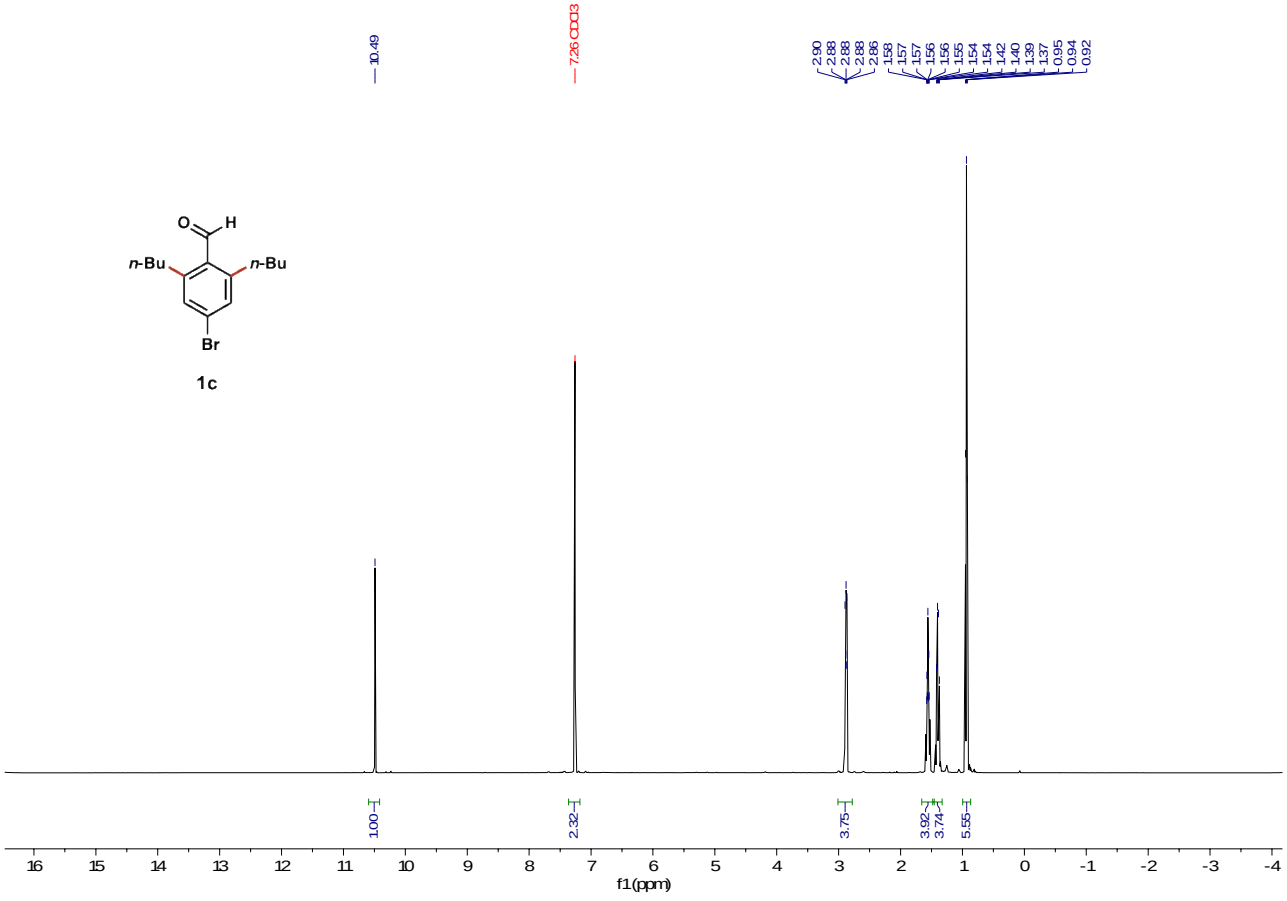
-105.89
-105.91
-105.93
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

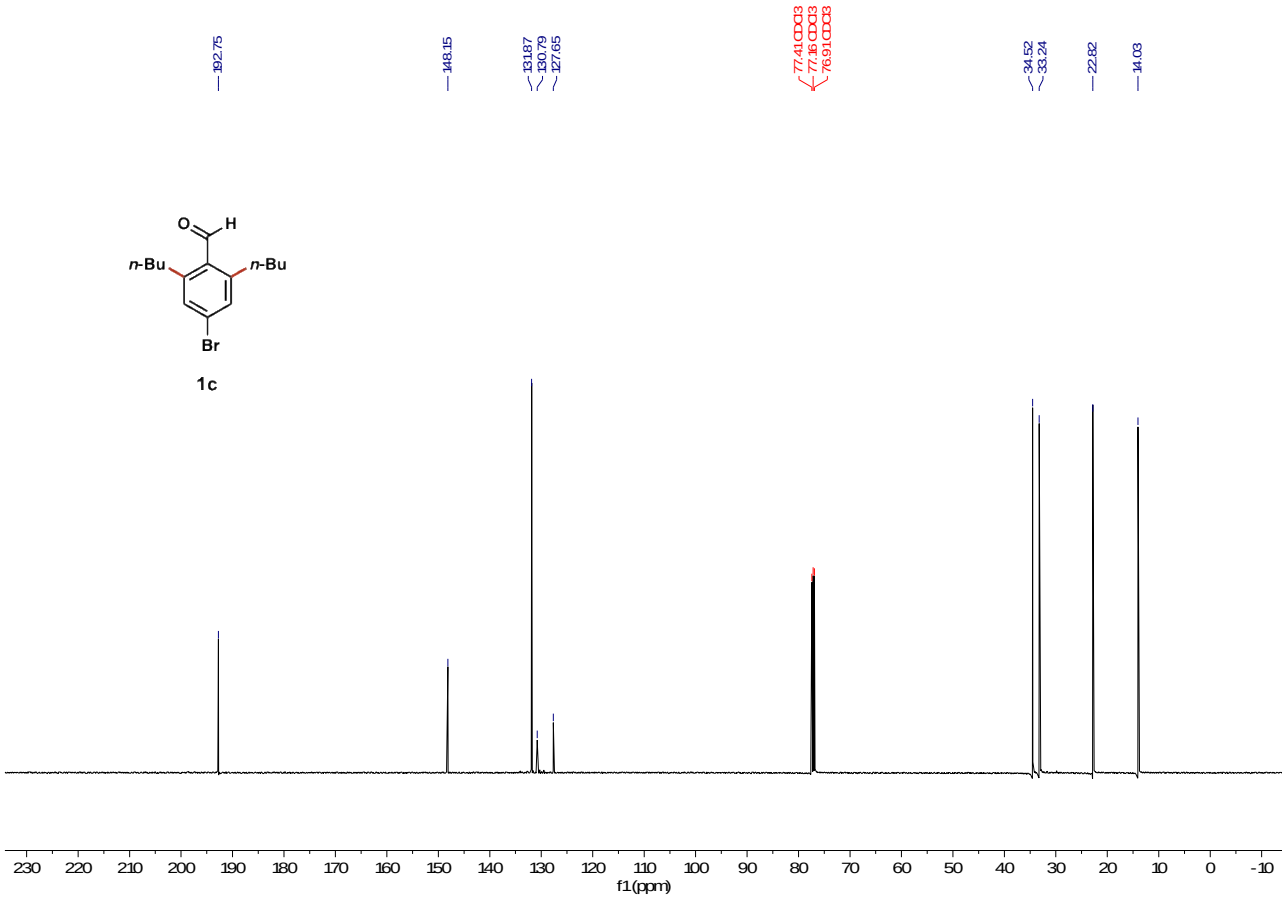

O
H
n-Bu
n-Bu
Cl

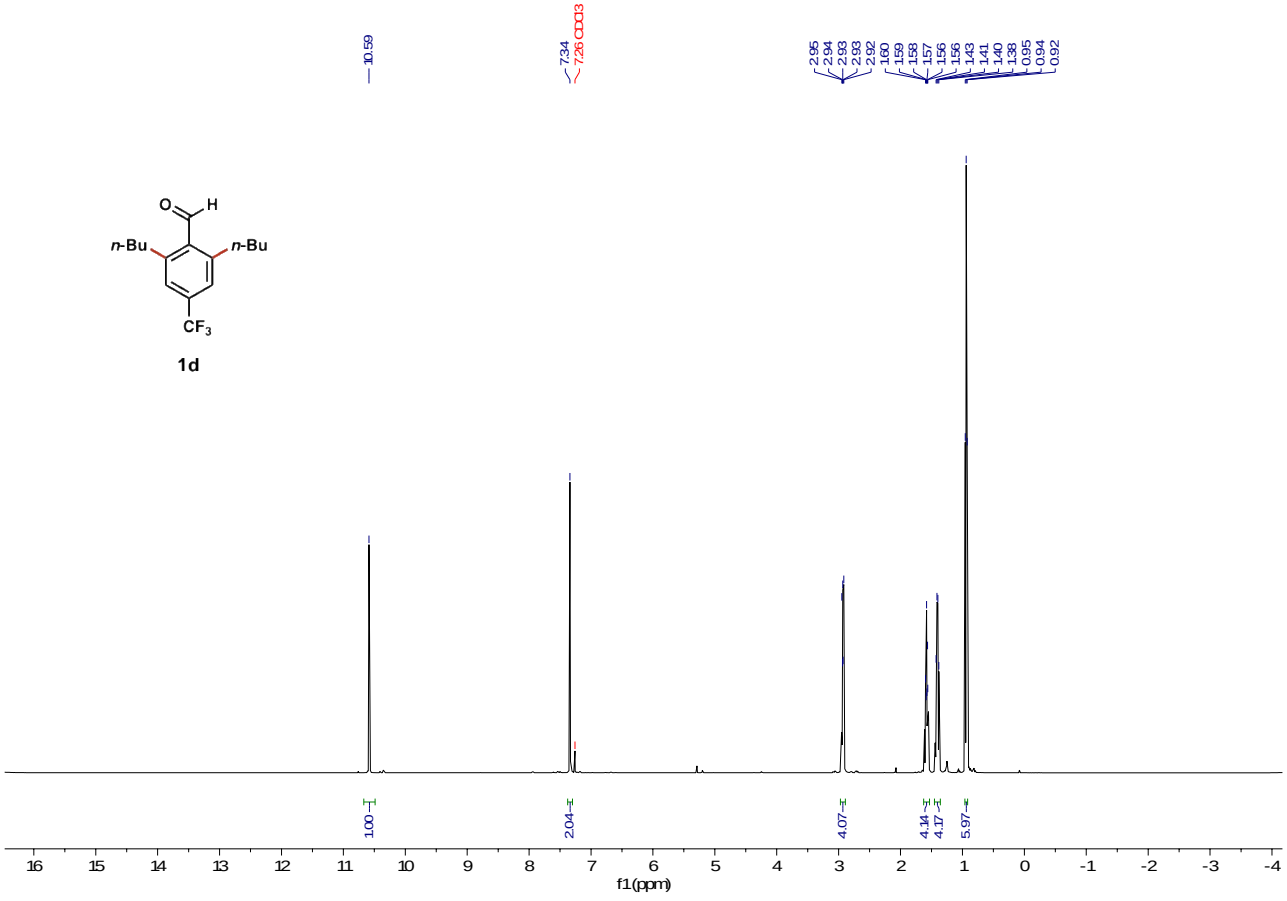
1b

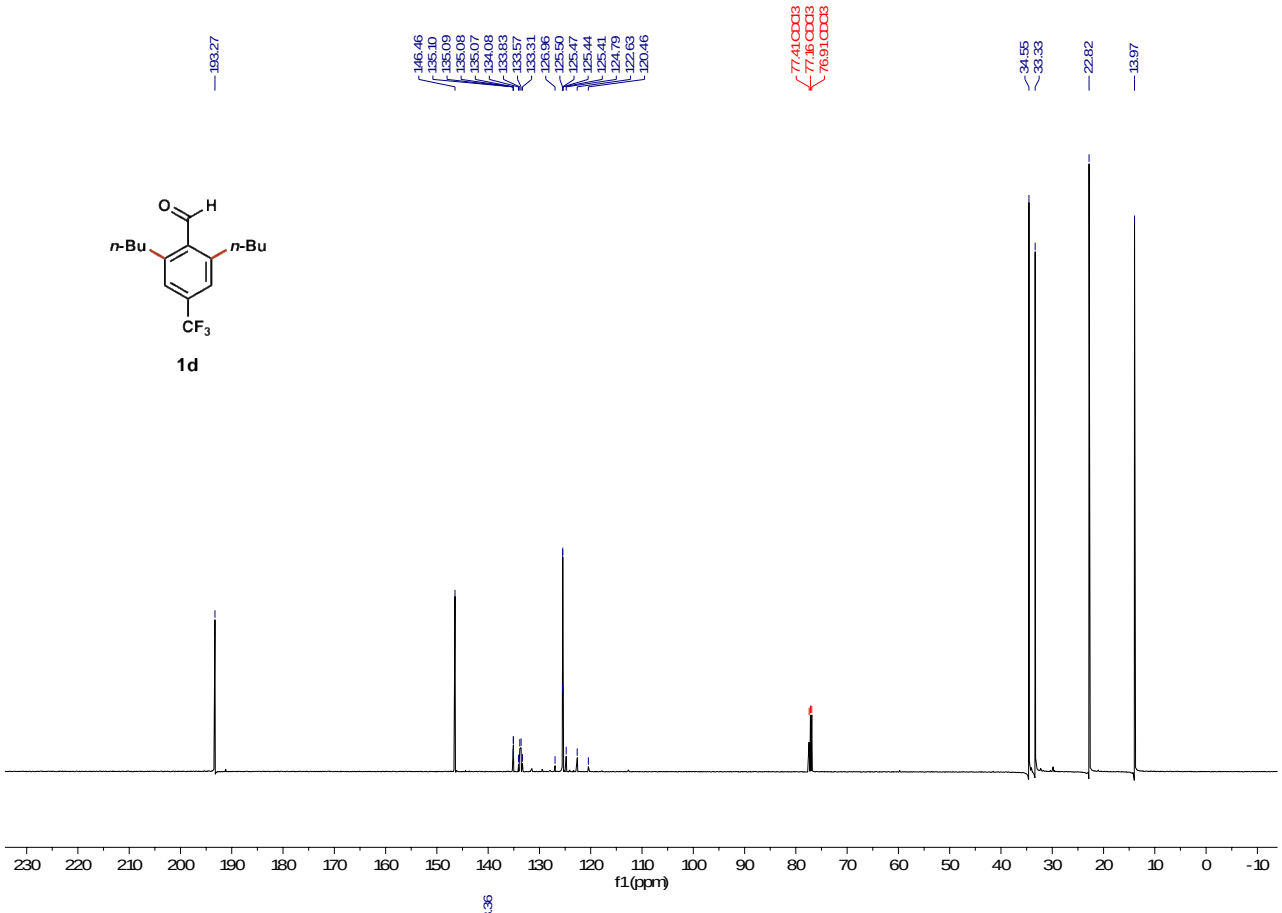
10.48
7.26 CDCl3
7.08
2.90
2.89
2.88
2.88
2.87
1.57
1.57
1.56
1.55
1.55
1.54
1.54
1.53
1.52
1.41
1.40
1.38
1.37
0.94
0.93
0.91
1.00
2.04
4.13
4.13
4.15
6.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


192.45
148.17
138.66
130.33
128.87
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.45
33.29
22.79
14.01
O
H
n-Bu
n-Bu
Cl
1b
f1 (ppm)


10.49
7.26 CDCl3
2.90
2.88
2.88
2.88
2.86
1.58
1.57
1.57
1.56
1.56
1.55
1.54
1.54
1.42
1.40
1.39
1.37
0.95
0.94
0.92
O
H
n-Bu
n-Bu
Br
1c
1.00
2.32
3.75
3.92
3.74
5.55
f1 (ppm)


192.75
148.15
131.87
130.79
127.65
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.52
33.24
22.82
14.03
O
H
n-Bu
n-Bu
Br
1c
f1 (ppm)


10.59
7.34
7.26 CDCl3
2.95
2.94
2.93
2.93
2.92
1.60
1.59
1.58
1.57
1.56
1.56
1.43
1.41
1.40
1.38
0.95
0.94
0.92
O
H
n-Bu
n-Bu
CF3
1d
1.00
2.04
4.07
4.14
4.17
5.97
f1 (ppm)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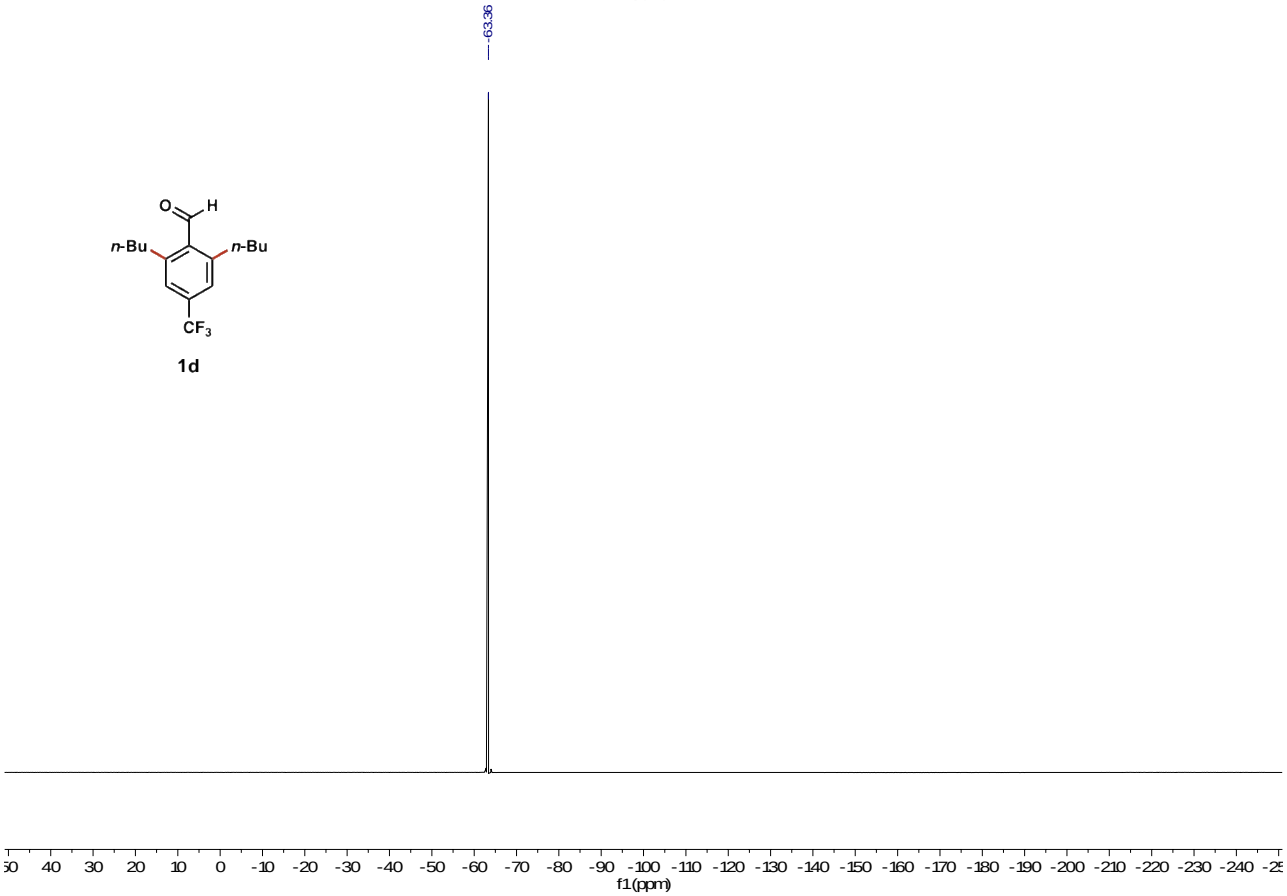
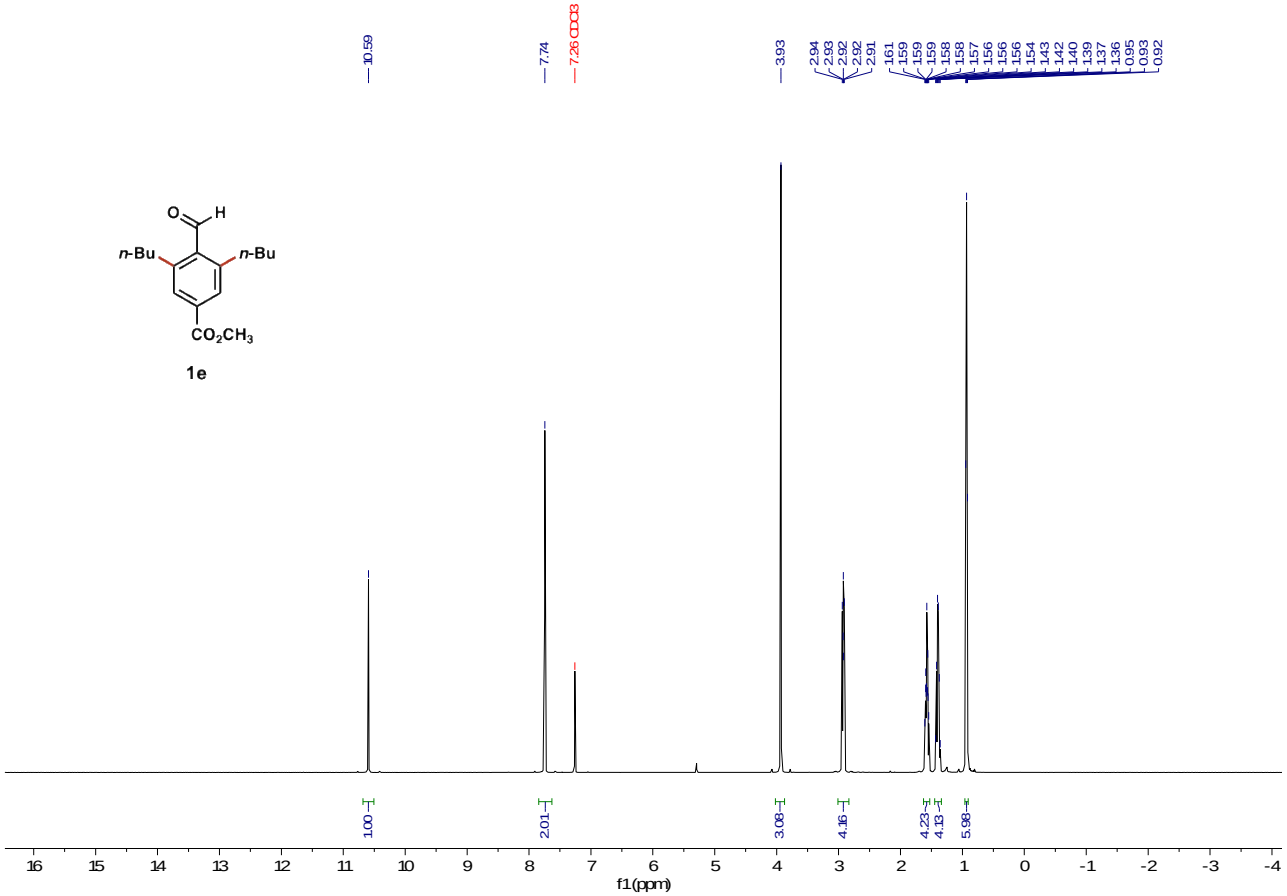
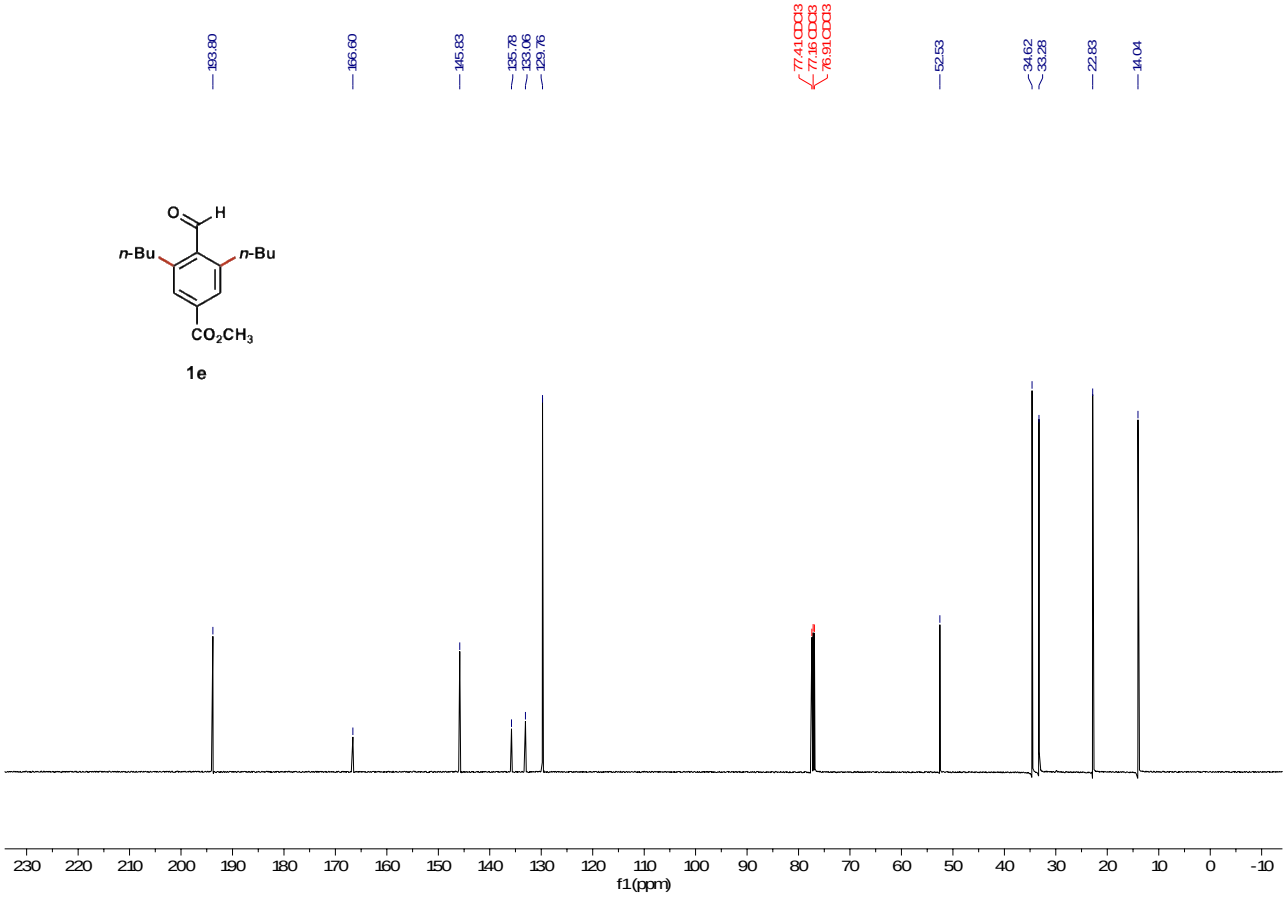
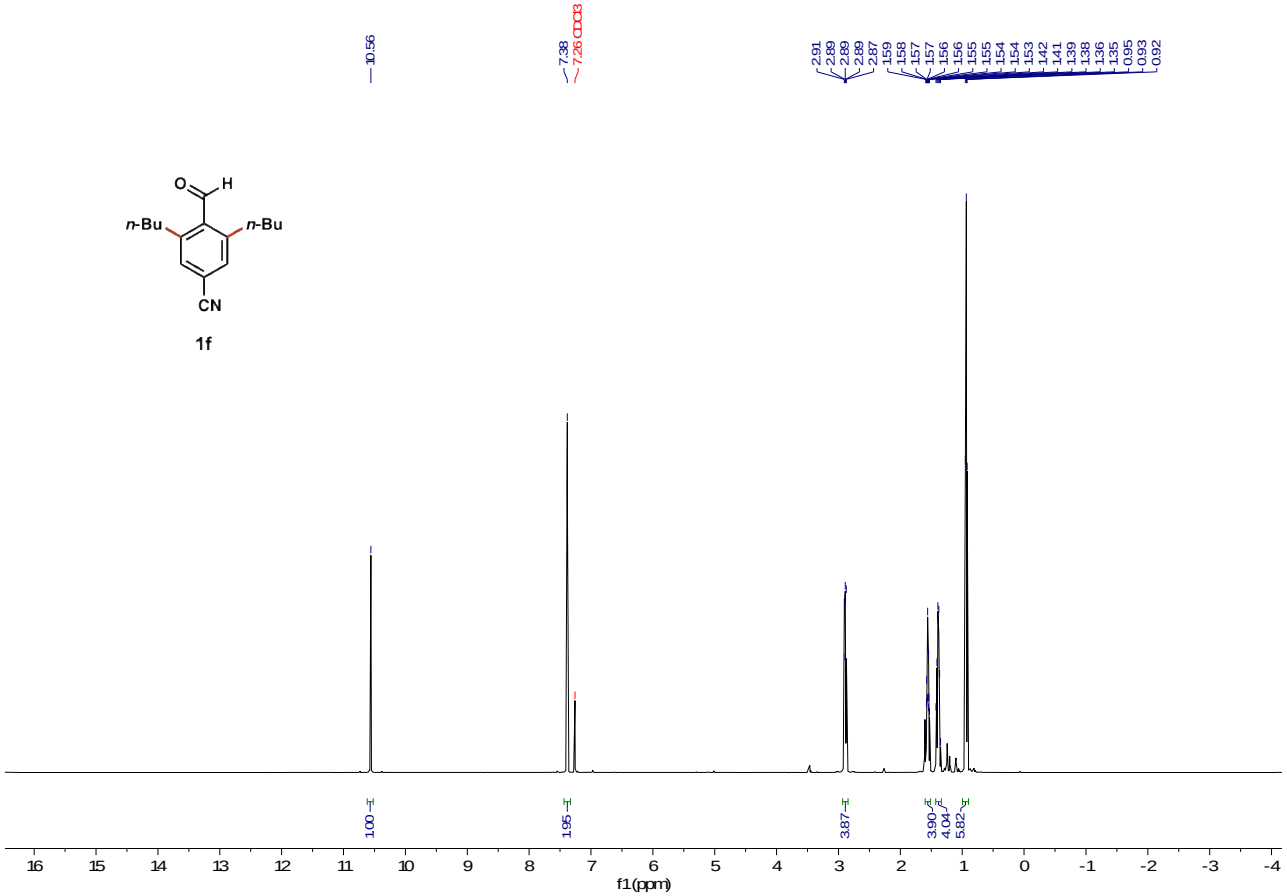
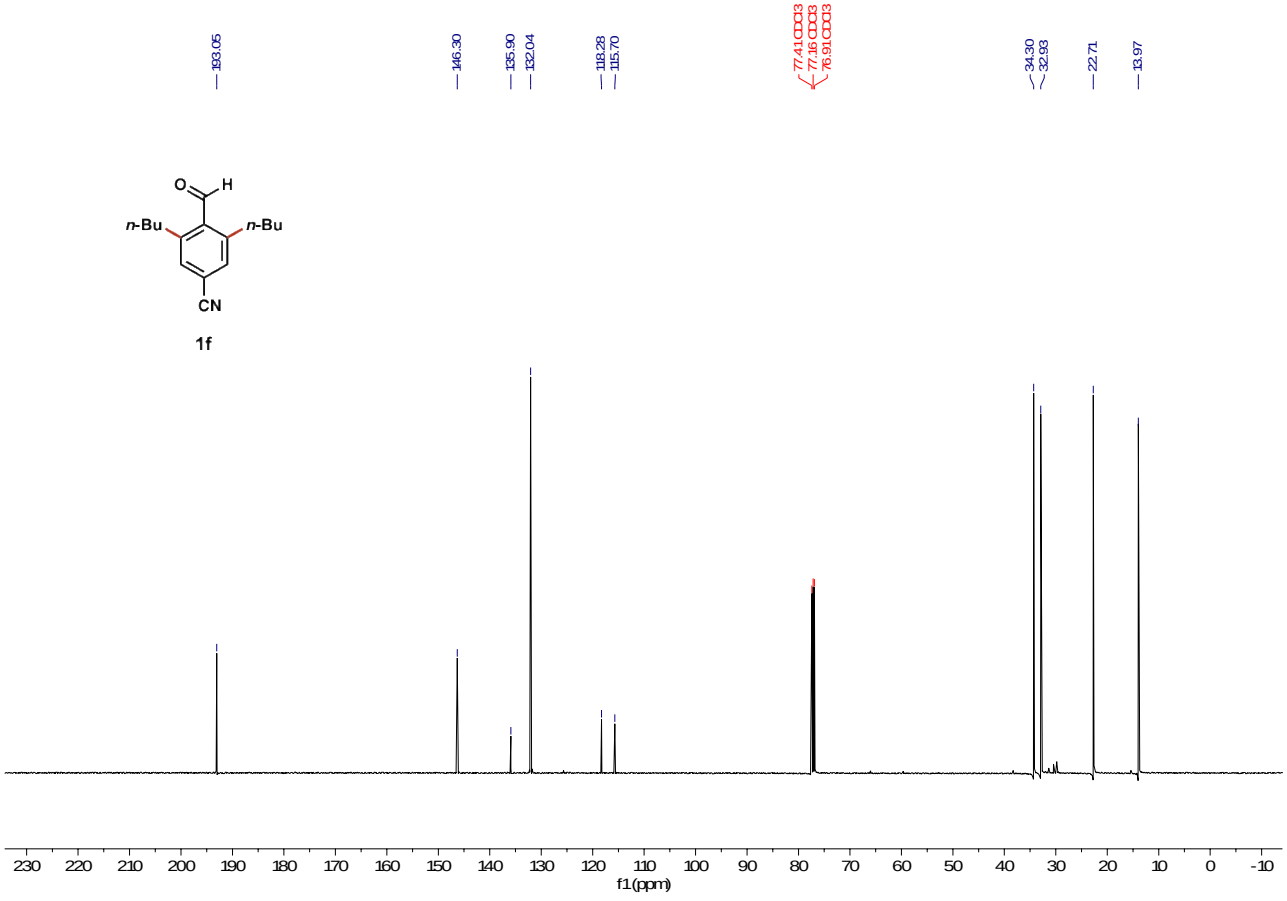
146.46
135.10
135.09
135.08
135.07
134.08
133.83
133.57
133.31
126.96
125.50
125.47
125.44
125.41
124.79
122.63
120.46
77.41
77.16
76.91
34.55
33.33
22.82
13.97
O
H
n-Bu
n-Bu
CF3
1d
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-63.36
O
H
n-Bu
n-Bu
CF3
1d
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25
f1 (ppm)


10.59
7.74
7.26 CDCl3
3.93
2.94
2.93
2.92
2.92
2.91
161
159
159
159
158
158
157
156
156
156
154
143
142
140
139
137
136
0.95
0.93
0.92
O
H
n-Bu
n-Bu
CO2CH3
1e
1.00
2.01
3.08
4.16
4.23
4.13
5.98
f1 (ppm)


193.80
166.60
145.83
135.78
133.06
129.76
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
52.53
34.62
33.28
22.83
14.04
O
H
n-Bu
n-Bu
CO2CH3
1e
f1 (ppm)


10.56
7.38
7.26 CDCl3
2.91
2.89
2.89
2.89
2.87
1.59
1.58
1.57
1.57
1.56
1.56
1.55
1.55
1.54
1.54
1.53
1.42
1.41
1.39
1.38
1.36
1.35
0.95
0.93
0.92
O
H
n-Bu
n-Bu
CN
1f
1.00
1.95
3.87
3.90
4.04
5.82
f1 (ppm)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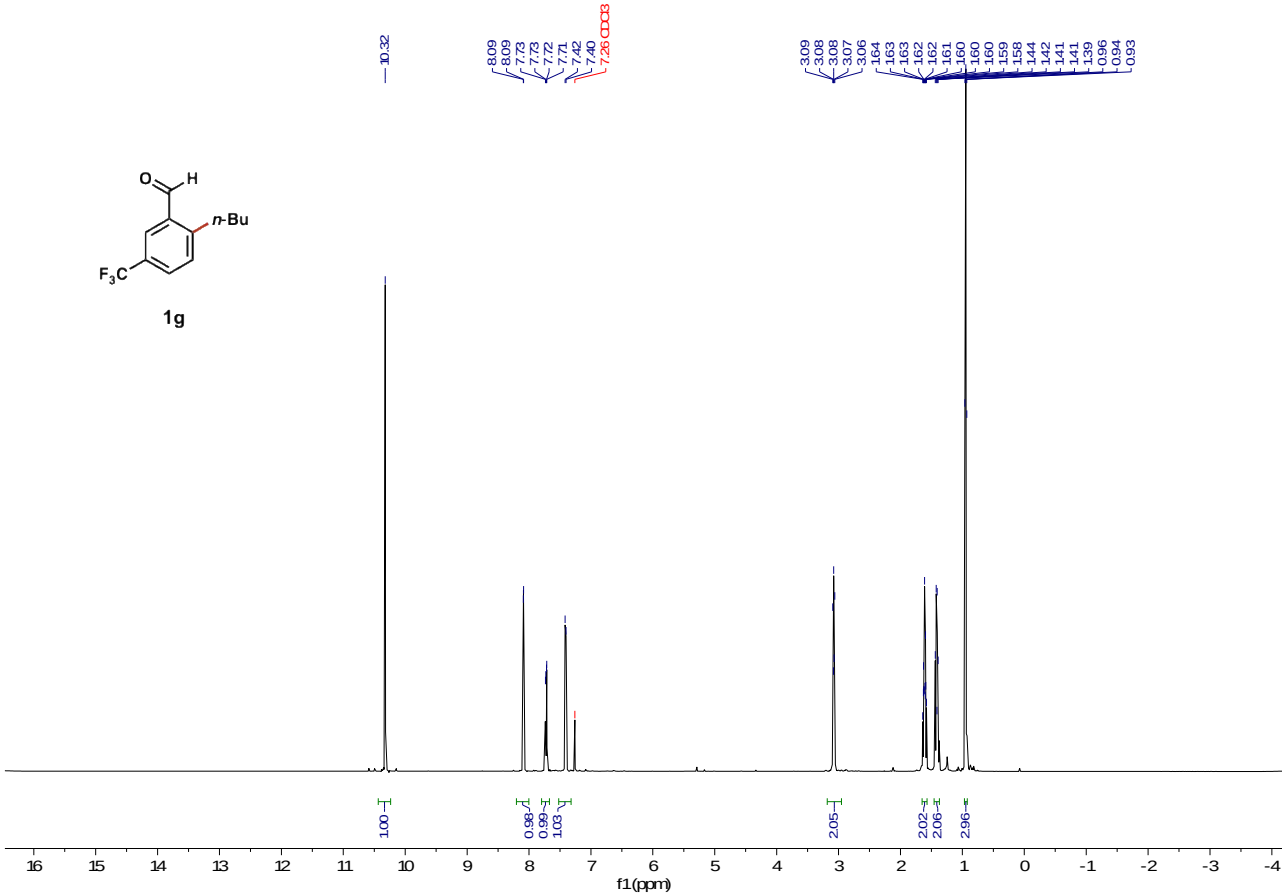
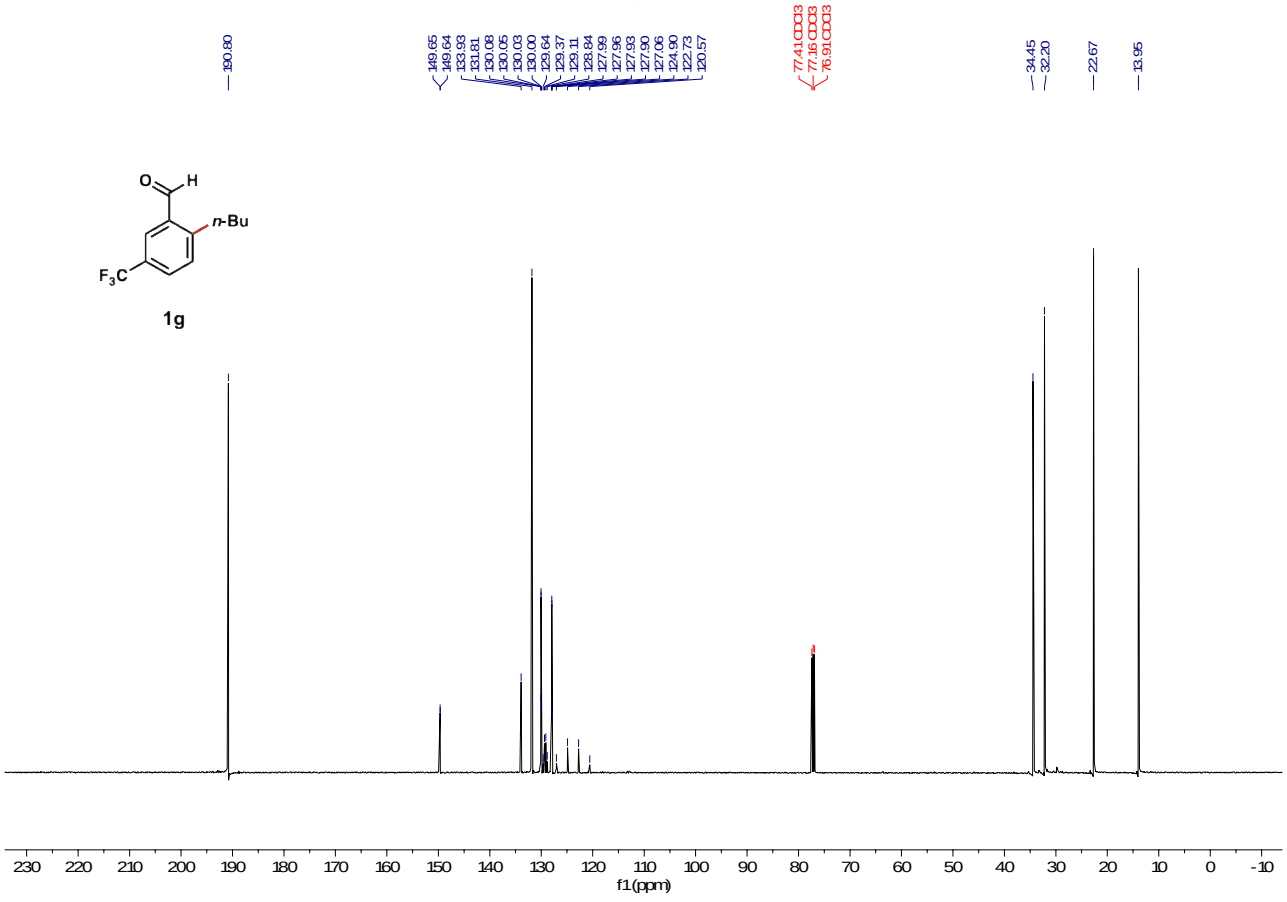
146.30
135.90
132.04
118.28
115.70
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.30
32.93
22.71
13.97
O
H
n-Bu
n-Bu
CN
1f
f1 (ppm)


10.32
8.09
8.09
7.73
7.73
7.72
7.71
7.42
7.40
7.26 CDCl3
3.09
3.08
3.08
3.07
3.06
1.64
1.63
1.63
1.62
1.62
1.61
1.60
1.60
1.60
1.59
1.58
1.44
1.42
1.41
1.41
1.39
0.96
0.94
0.93
O
H
n-Bu
F3C
1g
1.00
0.98
0.99
1.03
2.05
2.02
2.06
2.96
f1 (ppm)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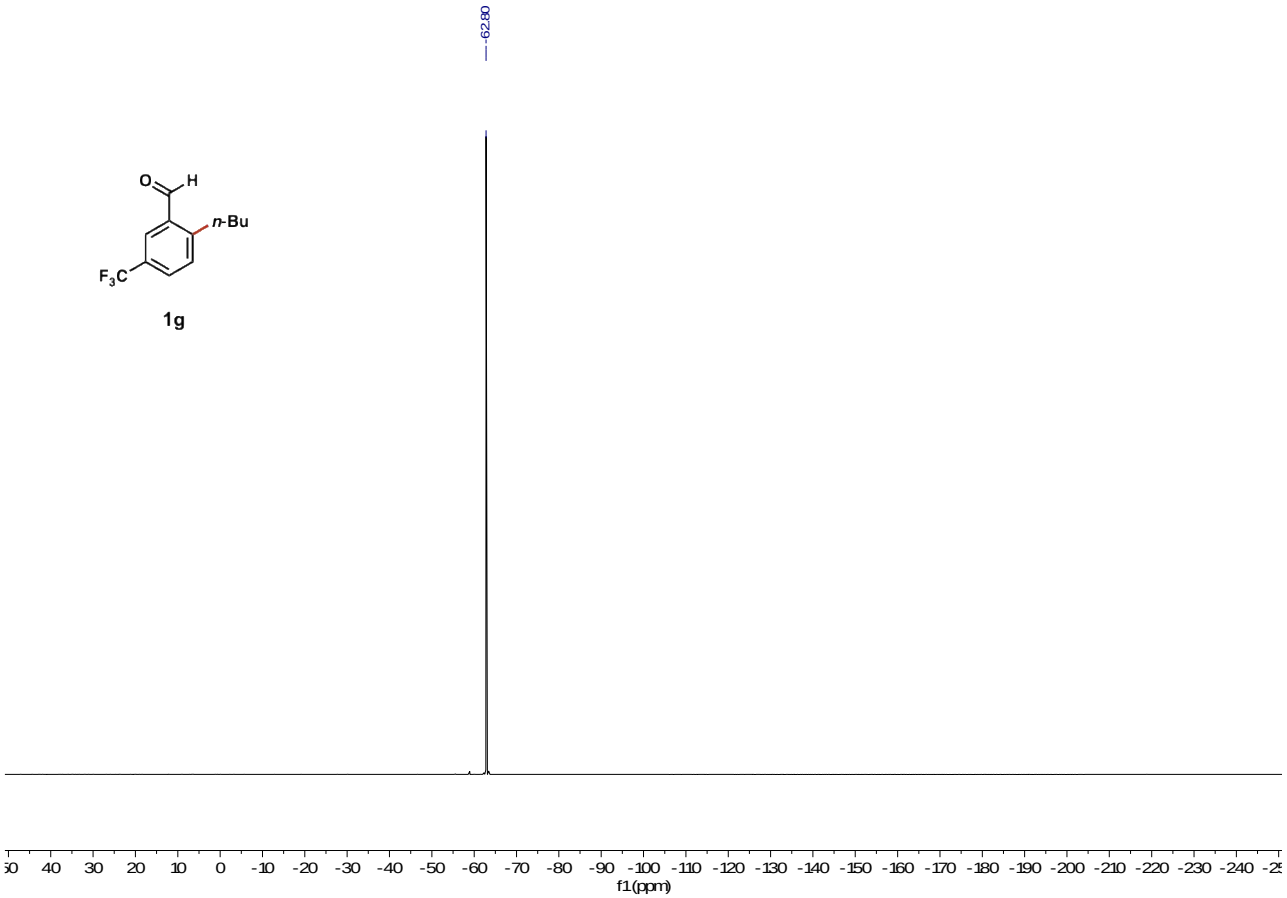
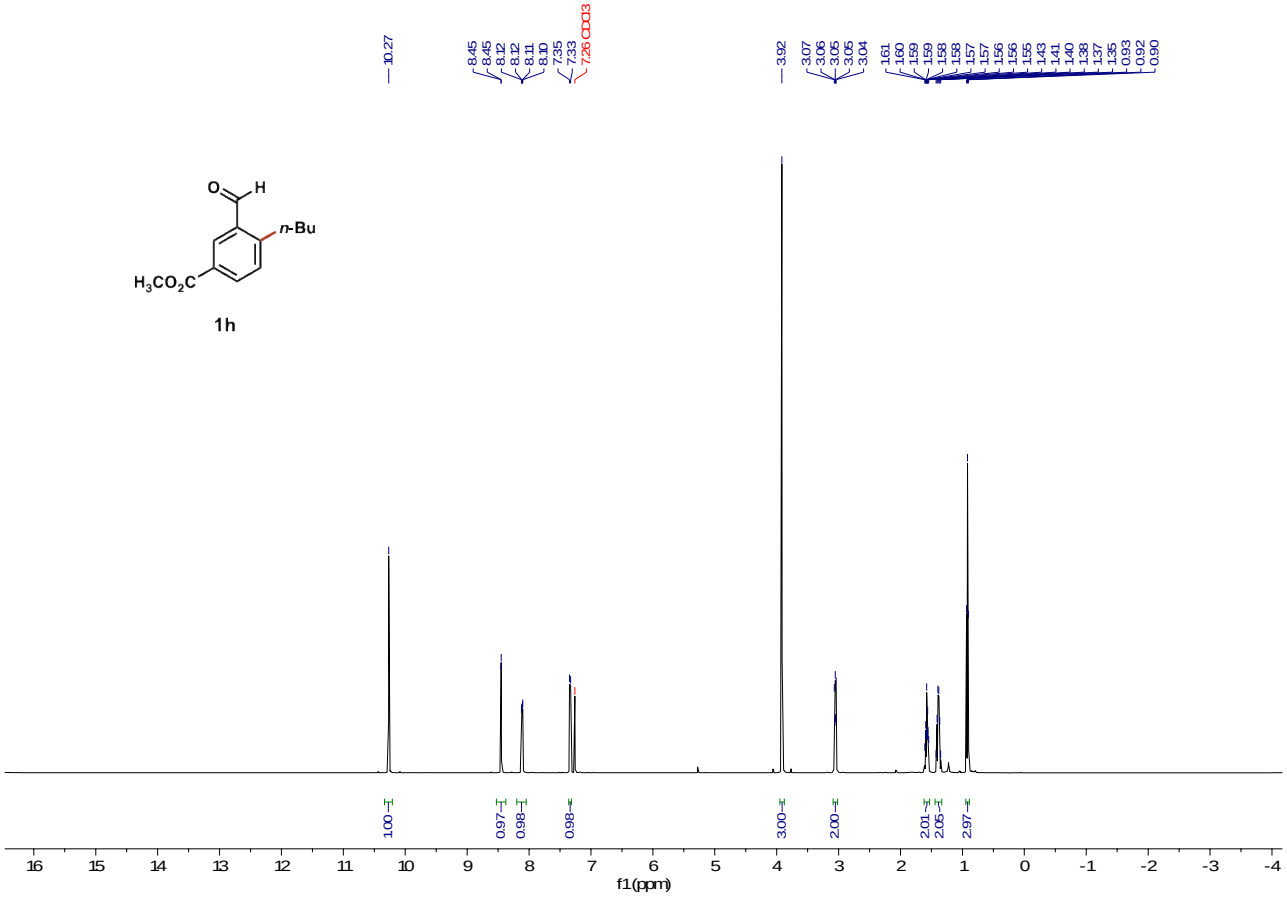
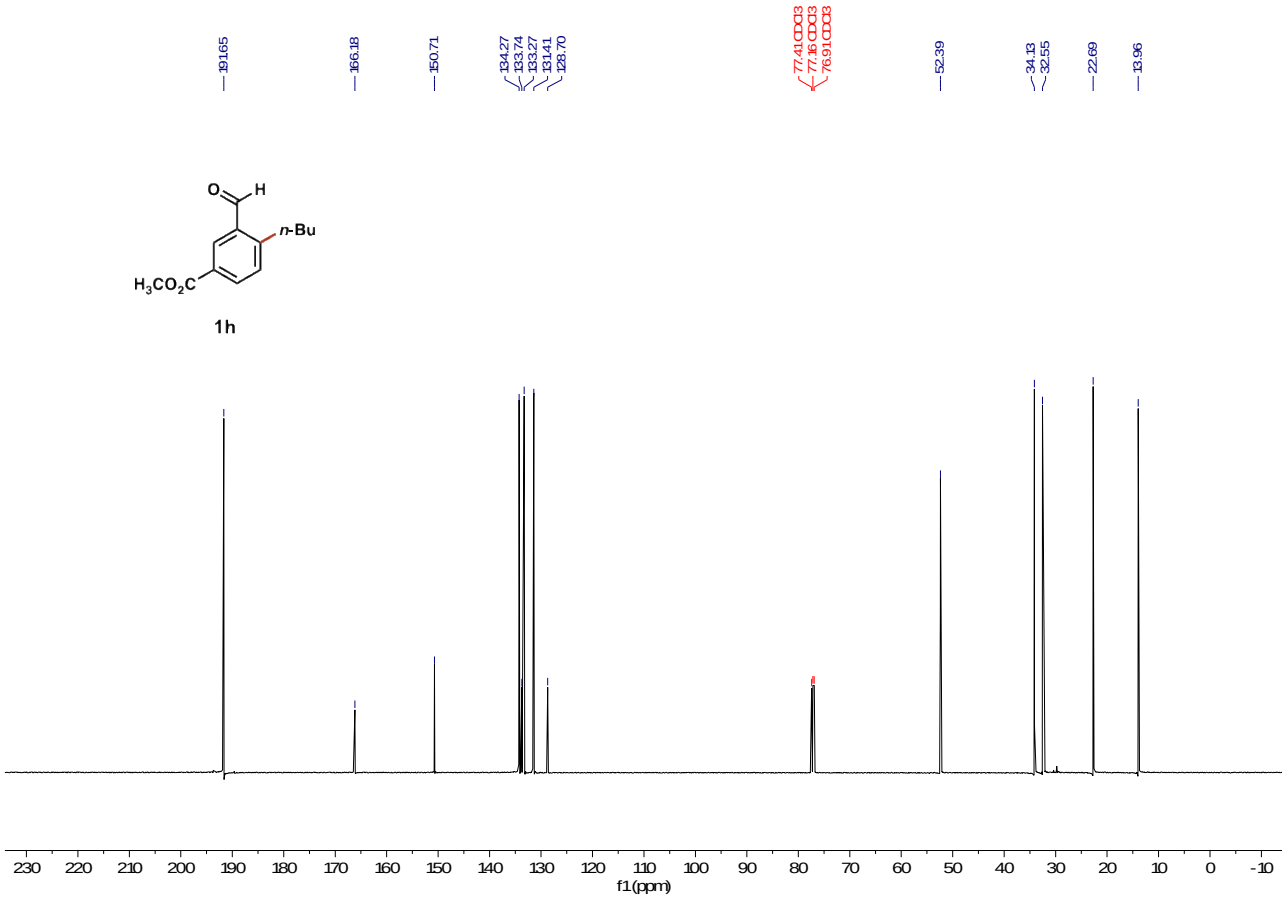
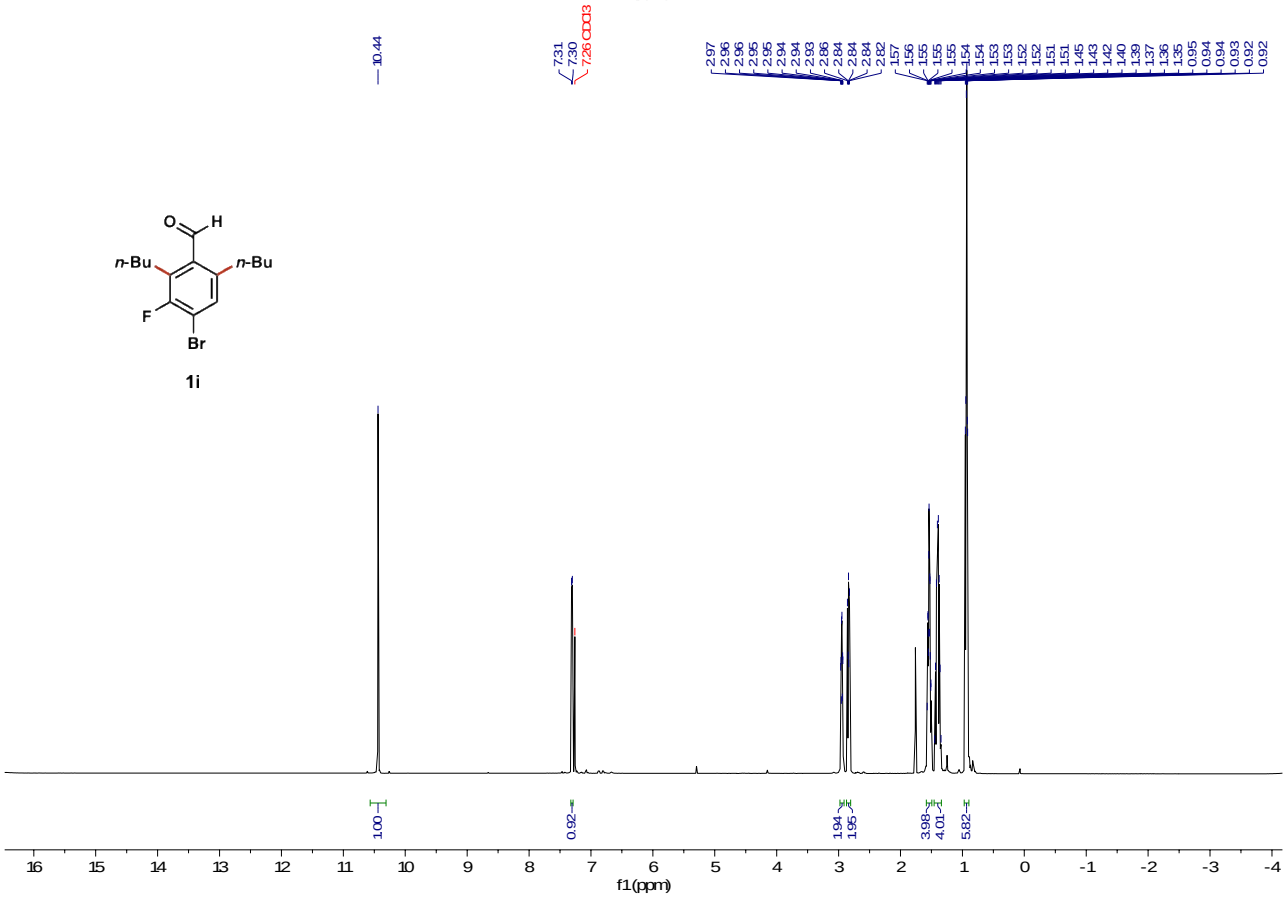
131.81
130.08
130.05
130.03
130.00
129.64
129.37
129.11
128.84
127.99
127.96
127.93
127.90
127.06
124.90
122.73
120.57
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.45
32.20
22.67
13.95
O
H
n-Bu
F3C
1g
f1 (ppm)


-62.80
O
H
n-Bu
F3C
1g
f1 (ppm)


10.27
8.45
8.45
8.12
8.12
8.11
8.10
7.35
7.33
7.26 CDCl3
3.92
3.07
3.06
3.05
3.05
3.04
1.61
1.60
1.59
1.59
1.58
1.58
1.57
1.57
1.56
1.56
1.55
1.43
1.41
1.40
1.38
1.37
1.35
0.93
0.92
0.90
O
H
n-Bu
H3CO2C
1h
1.00
0.97
0.98
0.98
3.00
2.00
2.01
2.05
2.97
f1 (ppm)


191.65
166.18
150.71
134.27
133.74
133.27
131.41
128.70
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
52.39
34.13
32.55
22.69
13.96
O
H
n-Bu
H3CO2C
1h
f1 (ppm)


10.44
7.31
7.30
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2.97
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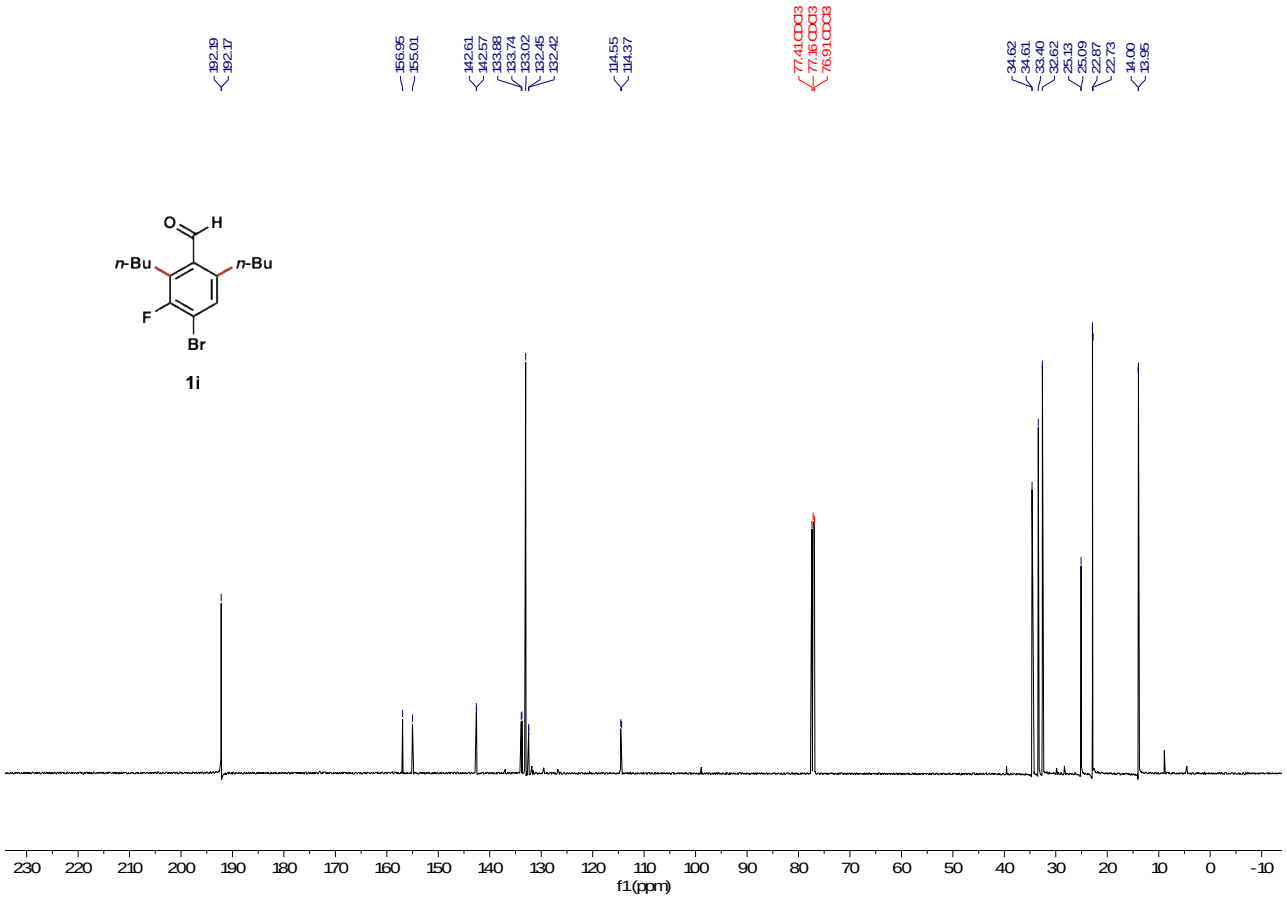
2.96
2.96
2.95
2.95
2.94
2.94
2.93
2.86
2.84
2.84
2.84
2.82
1.57
1.56
1.55
1.55
1.55
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.45
1.43
1.42
1.40
1.39
1.37
1.36
1.35
0.95
0.94
0.94
0.93
0.92
0.92
O
H
n-Bu
n-Bu
F
Br
1i
1.00
0.92
1.94
1.95
3.98
4.01
5.82
f1 (ppm)


192.19
192.17
156.95
155.01
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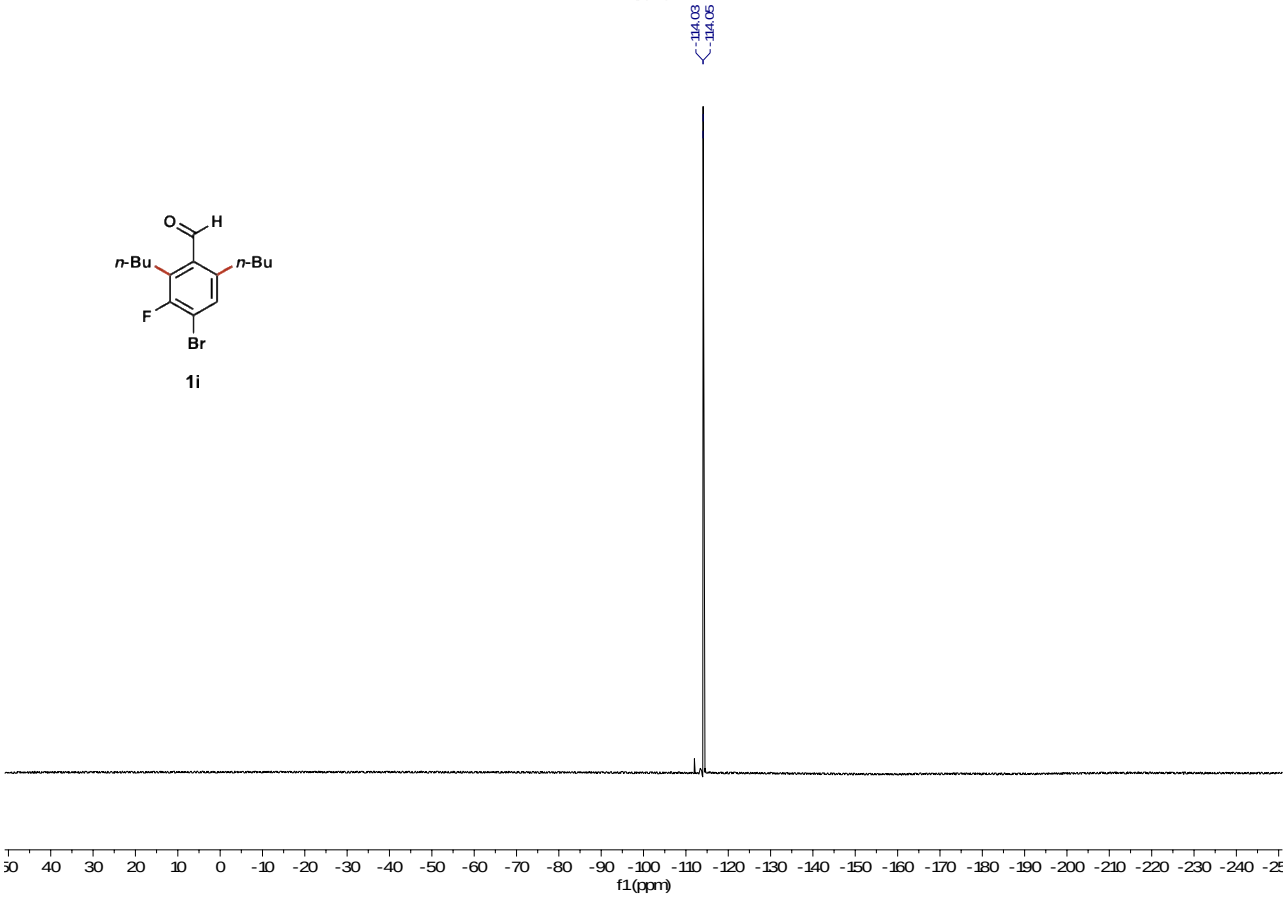
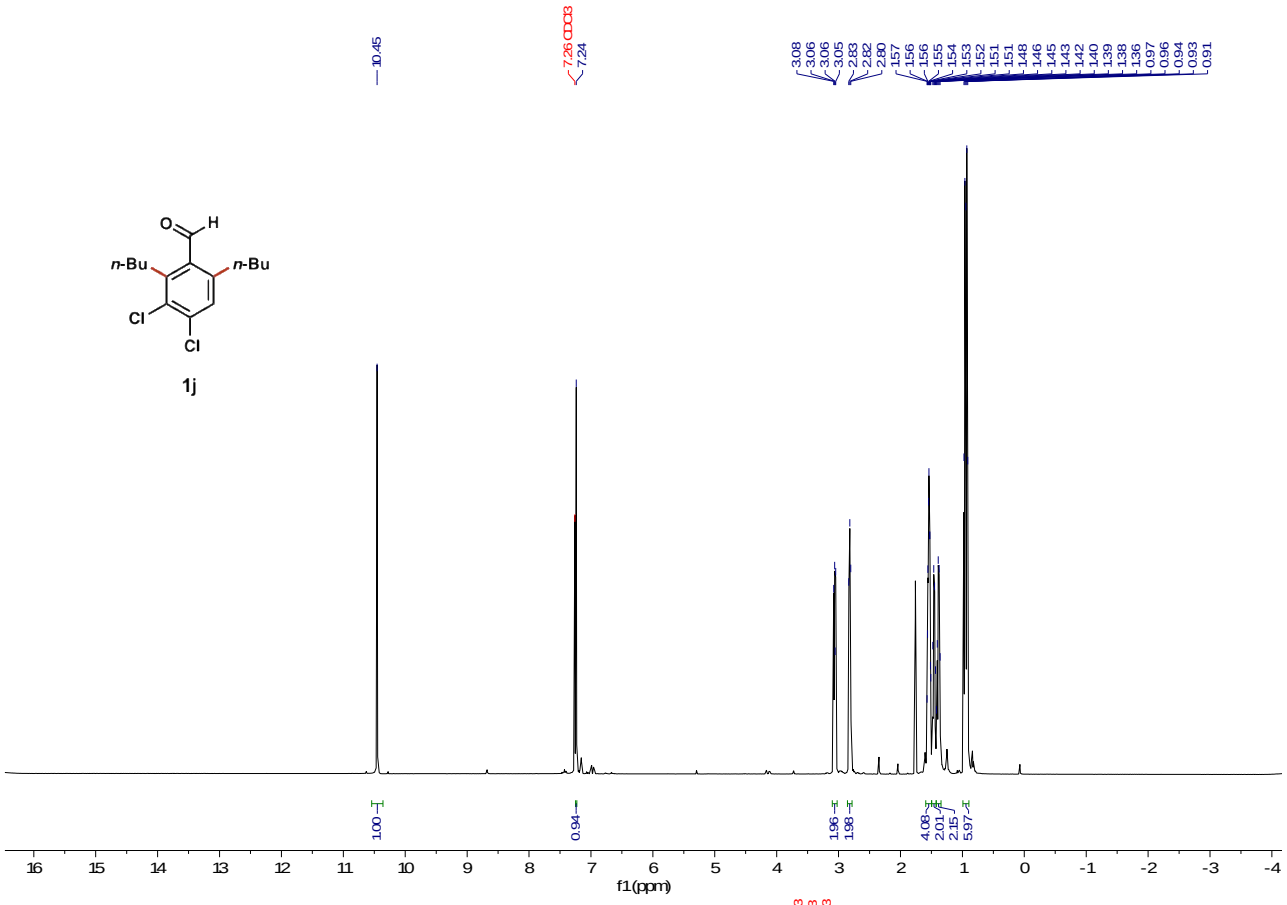
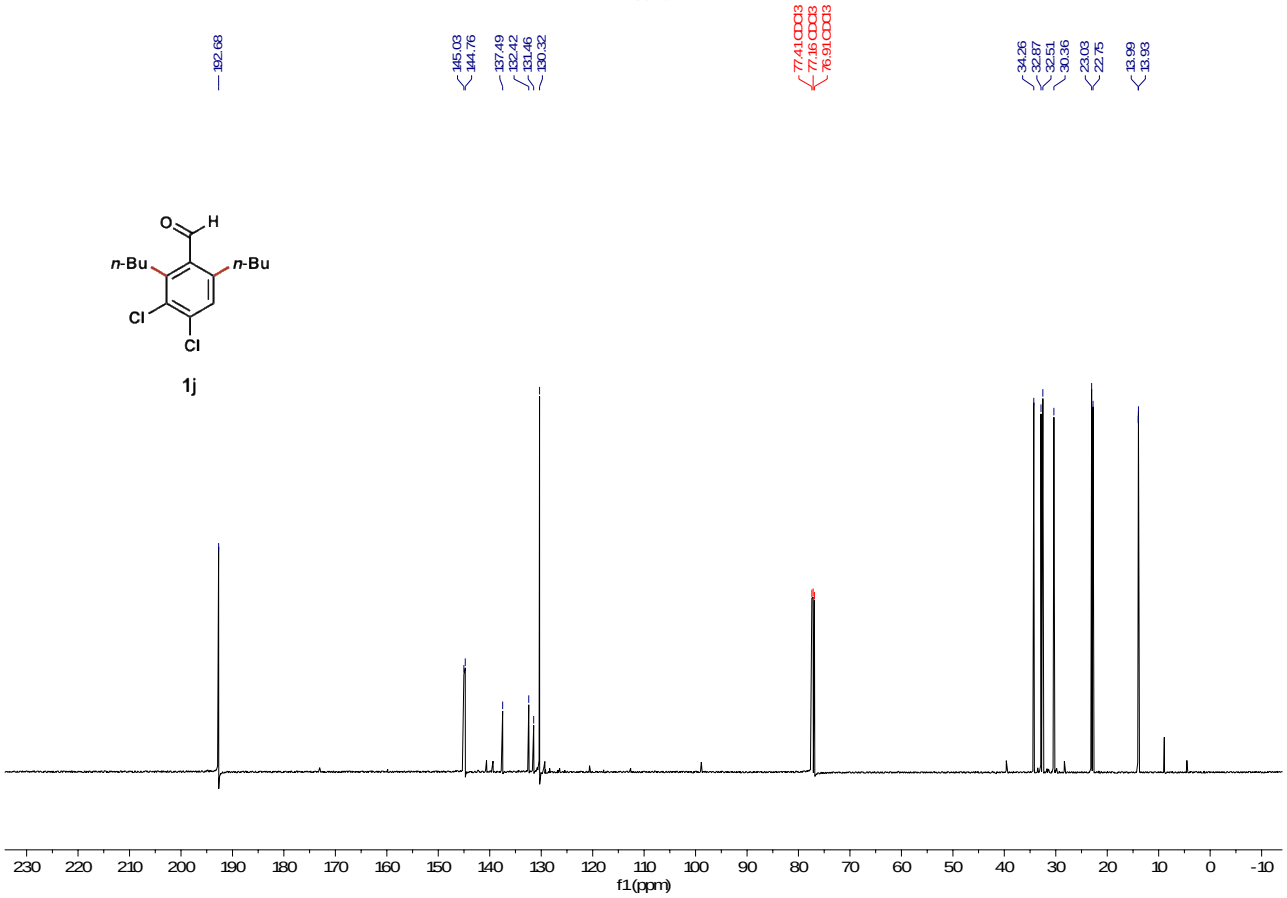
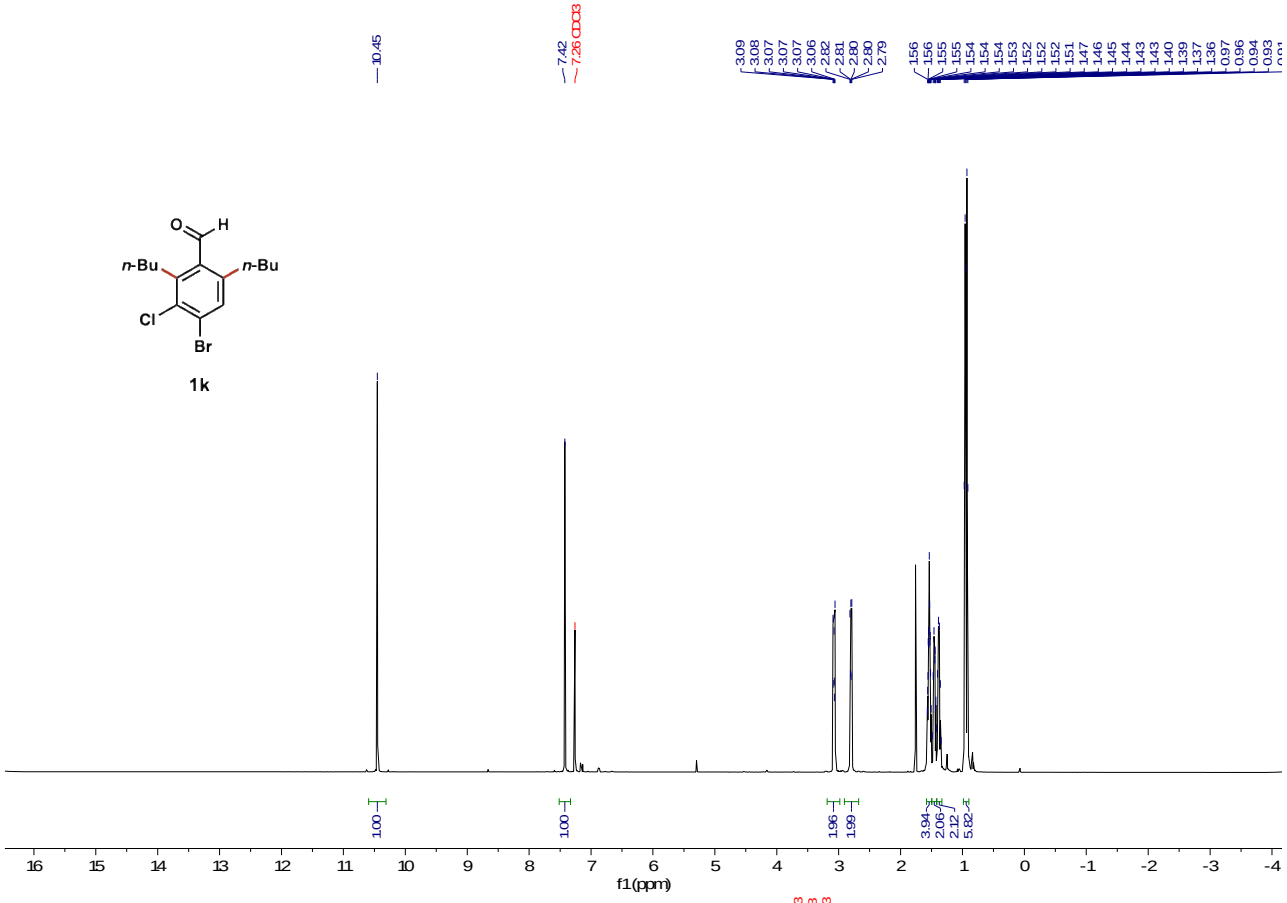
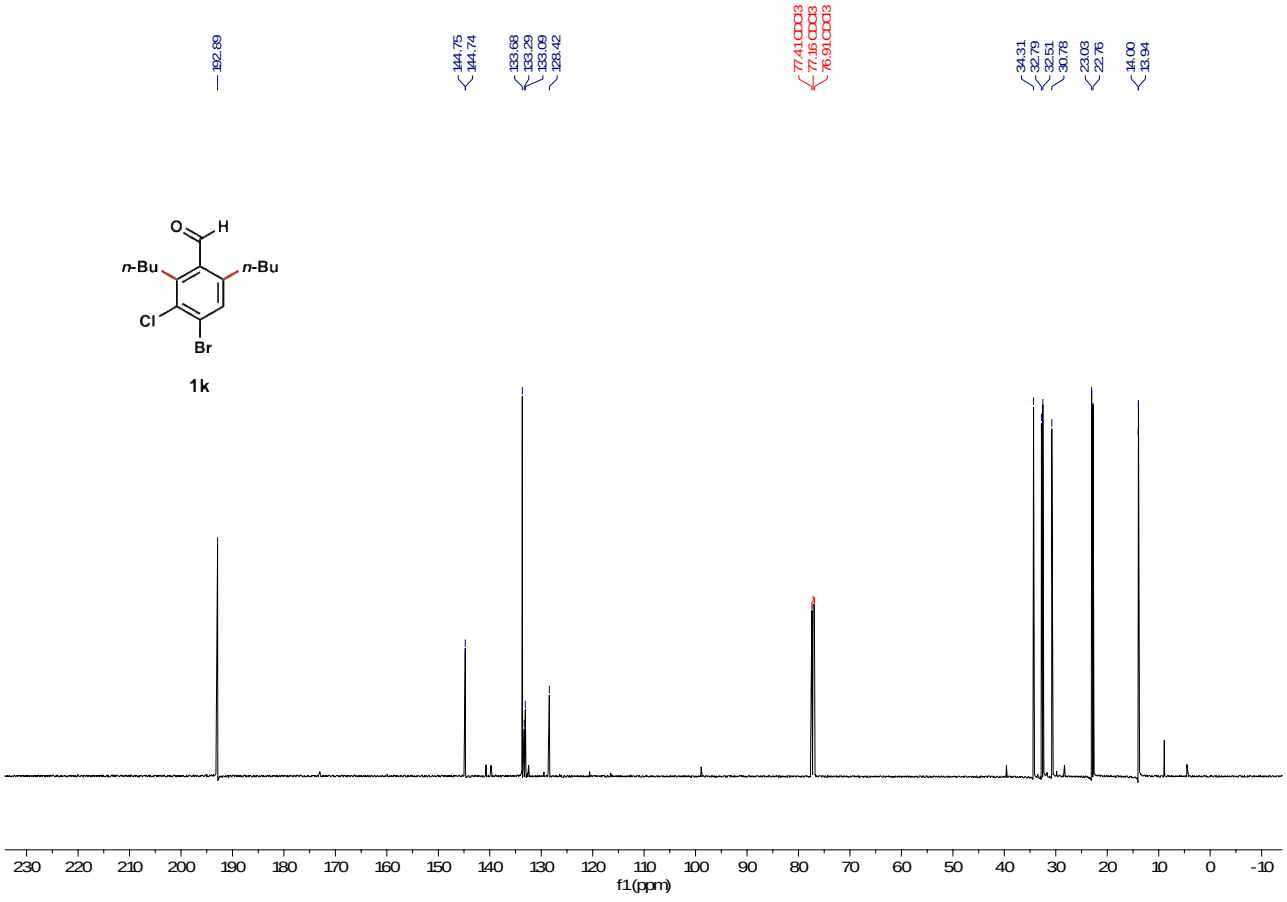
142.57
133.88
133.74
133.02
132.45
132.42
114.55
114.37
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.62
34.61
33.40
32.62
25.13
25.09
22.87
22.73
14.00
13.95
O
H
n-Bu
n-Bu
F
Br
1i
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

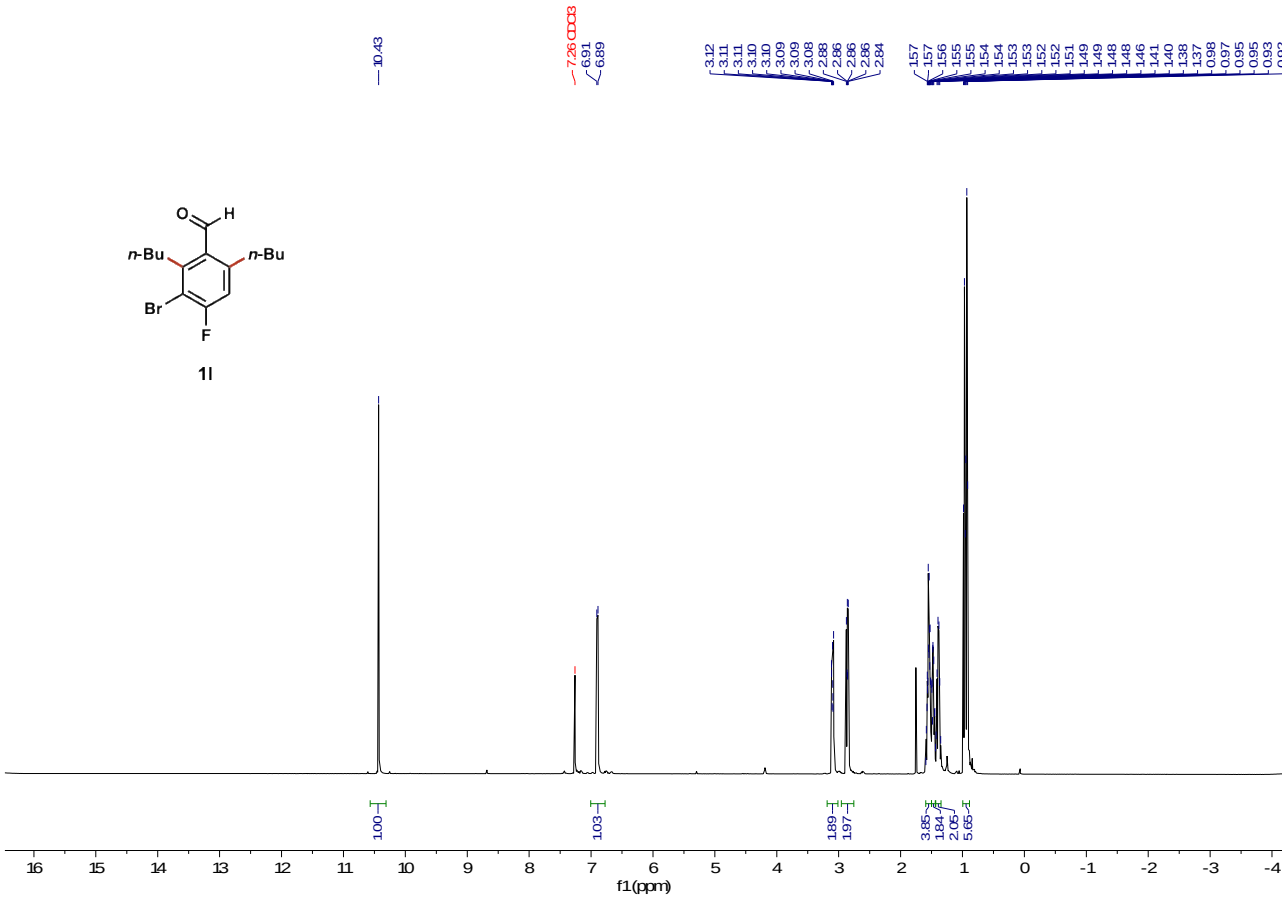

-114.03
-114.05
O
H
n-Bu
n-Bu
F
Br
1i
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25
f1 (ppm)

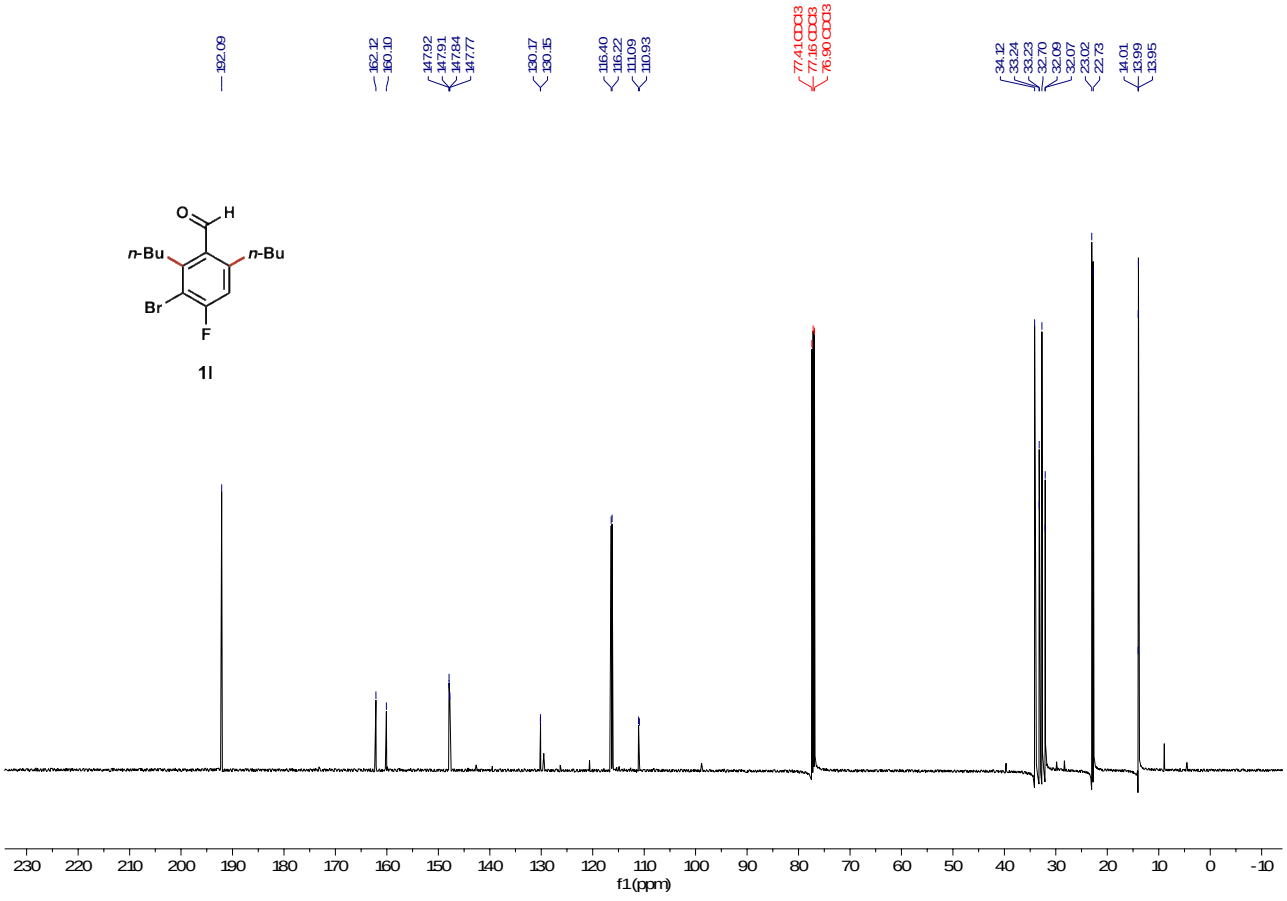

10.45
7.26 CDCl3
7.24
3.08
3.06
3.06
3.05
2.83
2.82
2.80
1.57
1.56
1.56
1.55
1.54
1.53
1.52
1.51
1.51
1.48
1.46
1.45
1.43
1.42
1.40
1.39
1.38
1.36
0.97
0.96
0.94
0.93
0.91
O
H
n-Bu
n-Bu
Cl
Cl
1j
1.00
0.94
1.96
1.98
4.08
2.01
2.15
5.97
f1(ppm)

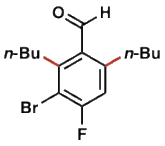

192.68
145.03
144.76
137.49
132.42
131.46
130.32
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.26
32.87
32.51
30.36
23.03
22.75
13.99
13.93
O
H
n-Bu
n-Bu
Cl
Cl
1j
f1(ppm)


10.45
7.42
7.26 CDCl3
3.09
3.08
3.07
3.07
3.07
3.06
2.82
2.81
2.80
2.80
2.79
156
156
155
155
154
154
154
153
152
152
152
151
147
146
145
144
143
140
139
137
136
0.97
0.96
0.94
0.93
O
H
n-Bu
n-Bu
Cl
Br
1k
1.00
1.00
1.96
1.99
3.94
2.06
2.12
5.82
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


192.89
144.75
144.74
133.68
133.29
133.09
128.42
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.31
32.79
32.51
30.78
23.03
22.76
14.00
13.94
O
H
n-Bu
n-Bu
Cl
Br
1k
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

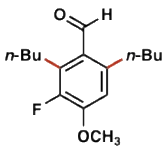

10.43
7.26 CDCl3
6.91
6.89
3.12
3.11
3.11
3.10
3.10
3.09
3.09
3.08
2.88
2.86
2.86
2.86
2.84
157
157
156
155
155
154
154
153
153
152
152
151
149
149
148
148
146
141
140
138
137
98
97
95
95
93
O
H
n-Bu
n-Bu
Br
F
1l
1.00
1.03
1.89
1.97
3.85
1.84
2.05
5.65
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


192.09
162.12
160.10
147.92
147.91
147.84
147.77
130.17
130.15
116.40
116.22
111.09
110.93
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
34.12
33.24
33.23
32.70
32.09
32.07
23.02
22.73
14.01
13.99
13.95
O
H
n-Bu
n-Bu
Br
F
1l
230
220
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)


O
H
n-Bu
n-Bu
Br
F

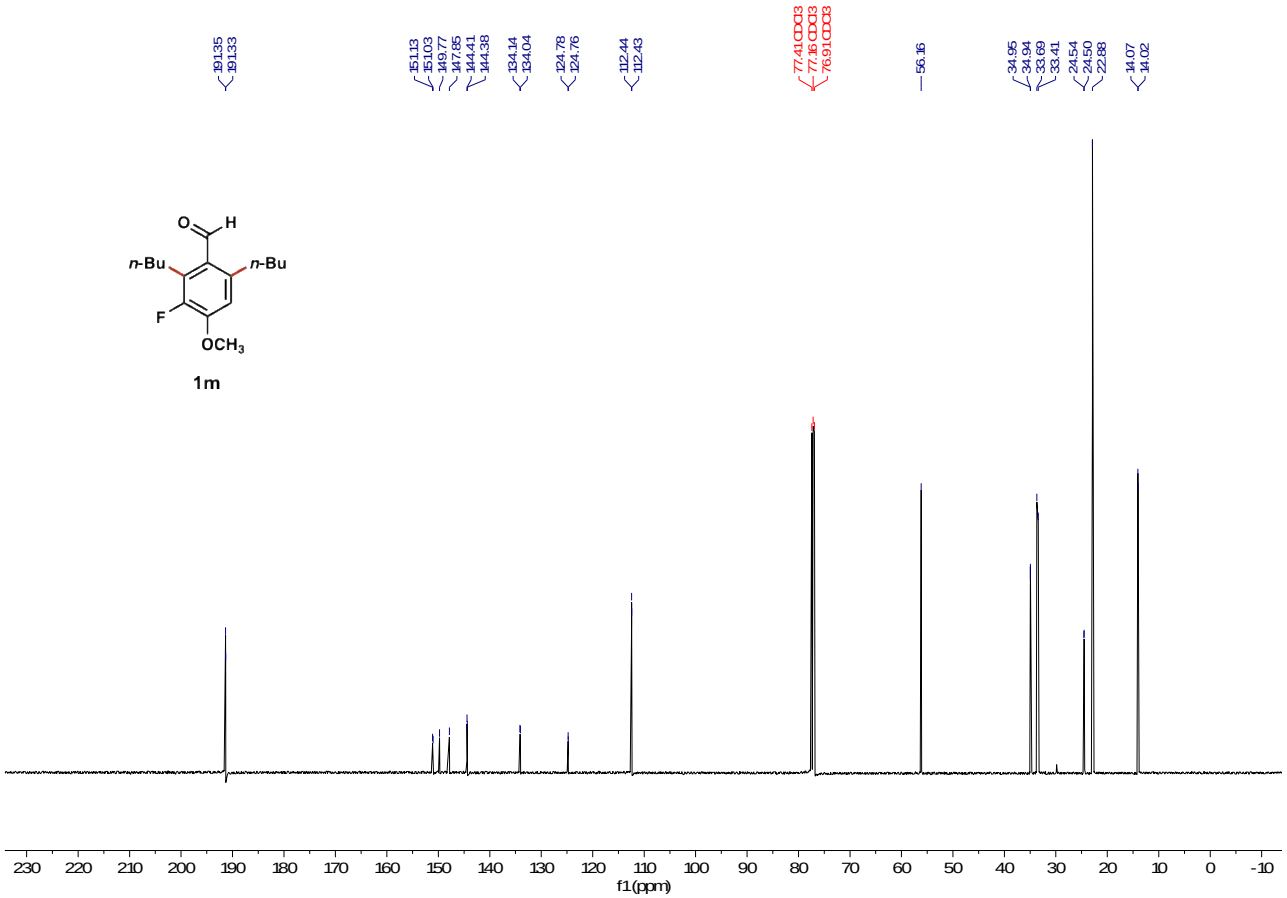
1l

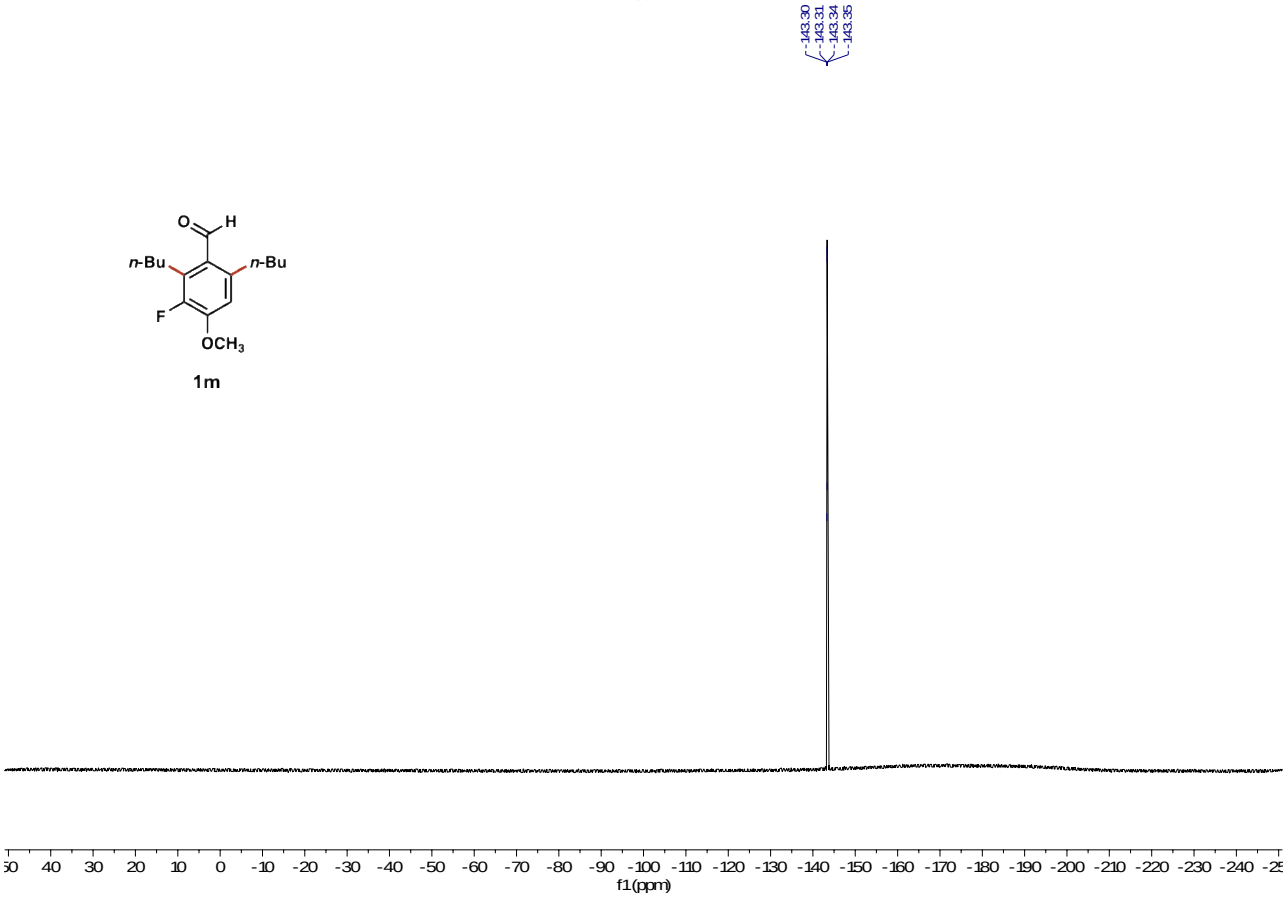
-95.09
-95.12
f1(ppm)

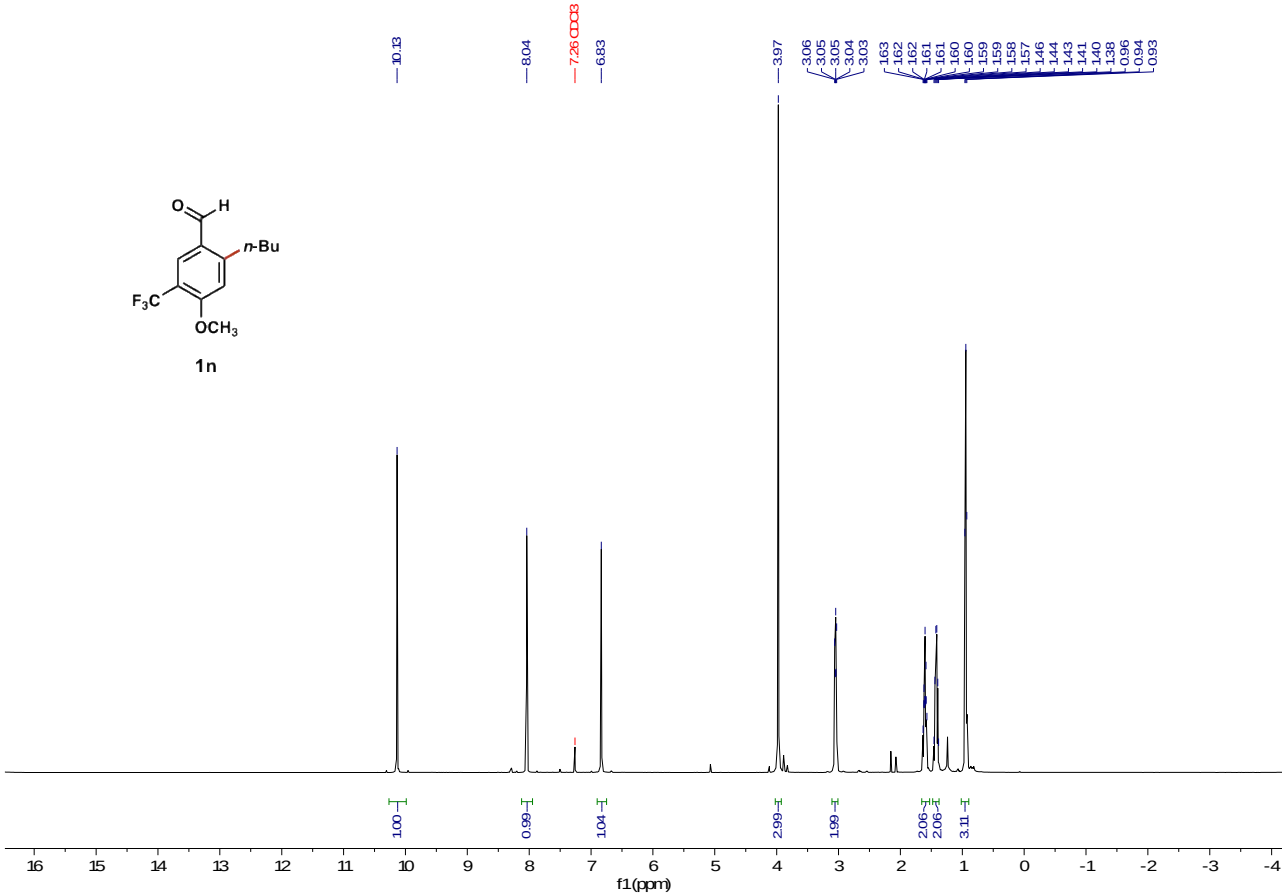

O
H
n-Bu
n-Bu
F
OCH3

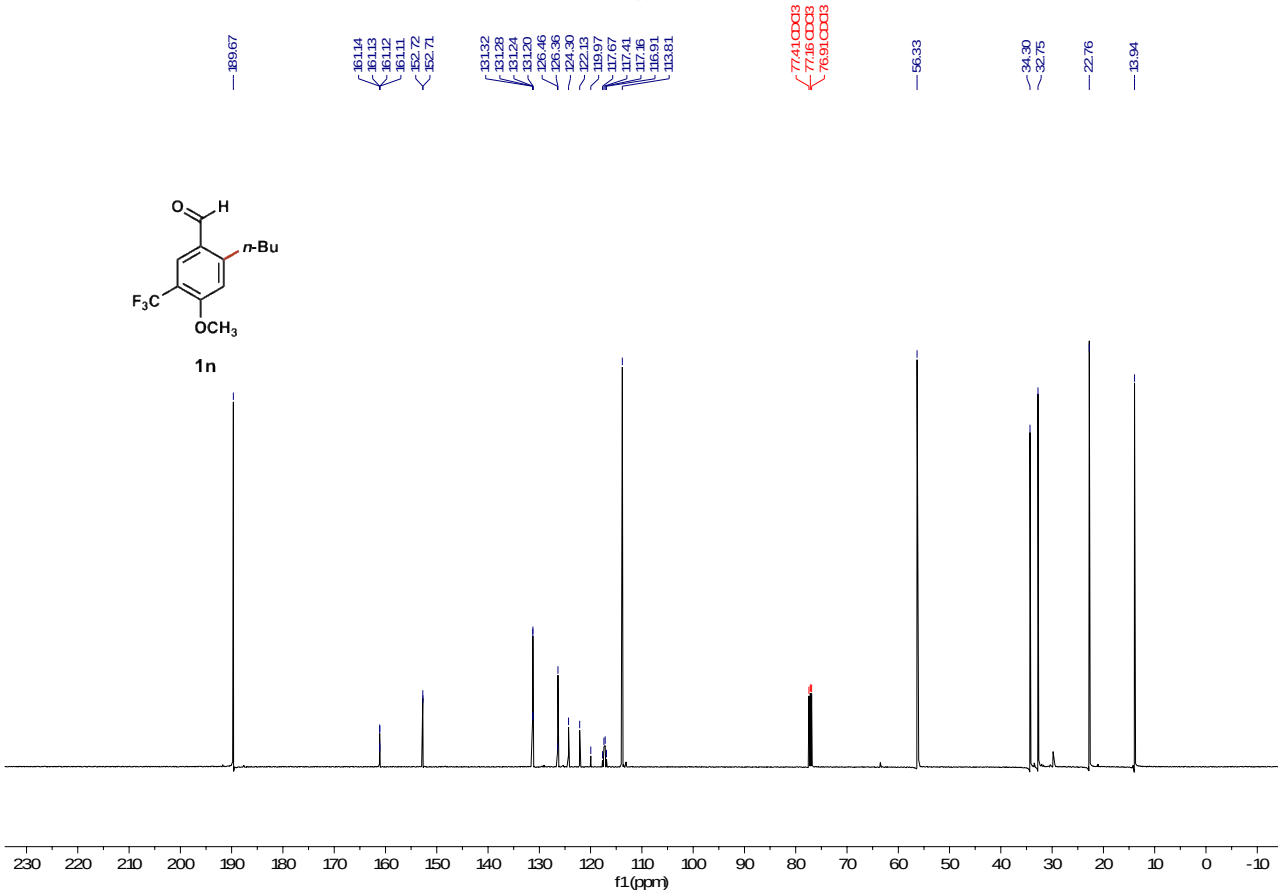
1m

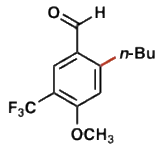
10.37
10.37
7.26 CDCl3
6.65
6.63
3.93
3.01
3.00
2.99
2.99
2.98
2.98
2.97
2.97
2.93
2.92
2.91
2.91
2.90
1.58
1.57
1.56
1.55
1.55
1.55
1.54
1.53
1.53
1.52
1.43
1.43
1.42
1.41
1.40
1.40
1.39
1.38
0.95
0.95
0.94
0.93
0.92
1.00
1.06
3.01
2.01
2.04
4.19
4.16
6.09
f1(ppm)


191.35
191.33
151.13
151.03
149.77
147.85
144.41
144.38
134.14
134.04
124.78
124.76
112.44
112.43
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.16
34.95
34.94
33.69
33.41
24.54
24.50
22.88
14.07
14.02
O
H
n-Bu
n-Bu
F
OCH3
1m
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-143.30
-143.31
-143.34
-143.35
O
H
n-Bu
n-Bu
F
OCH3
1m
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25
f1 (ppm)

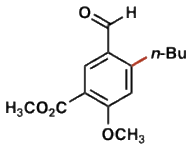

10.13
8.04
7.26
6.83
3.97
1.00
0.99
1.04
2.99
1.99
2.06
2.06
3.11
f1(ppm)
O
H
n-Bu
F3C
OCH3
1n


189.67
161.14
161.13
161.12
161.11
152.72
152.71
131.32
131.28
131.24
131.20
126.46
126.36
124.30
122.13
119.97
117.67
117.41
117.16
116.91
113.81
77.41
77.16
76.91
56.33
34.30
32.75
22.76
13.94
f1(ppm)
O
H
n-Bu
F3C
OCH3
1n


O
H
n-Bu
F3C
OCH3

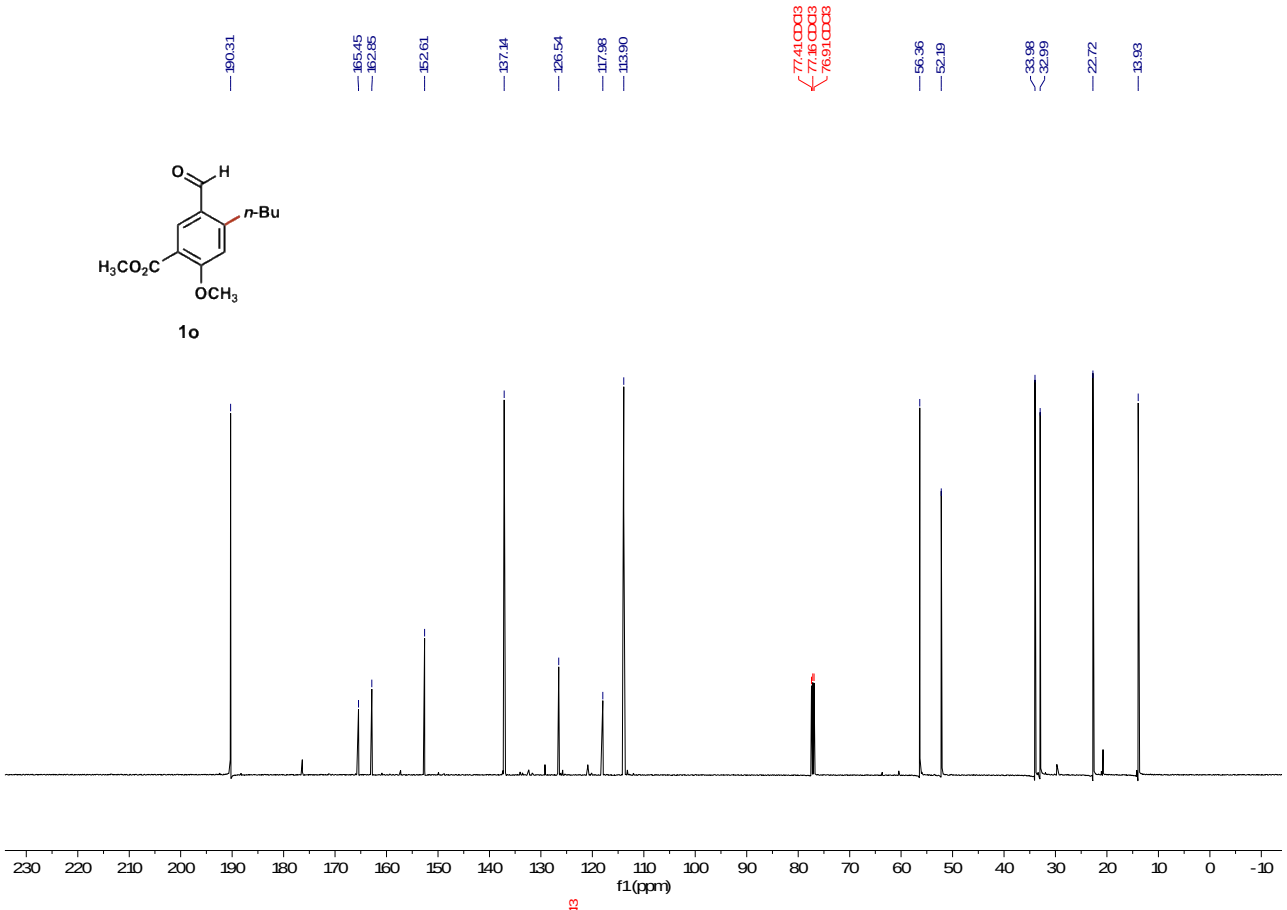
1n

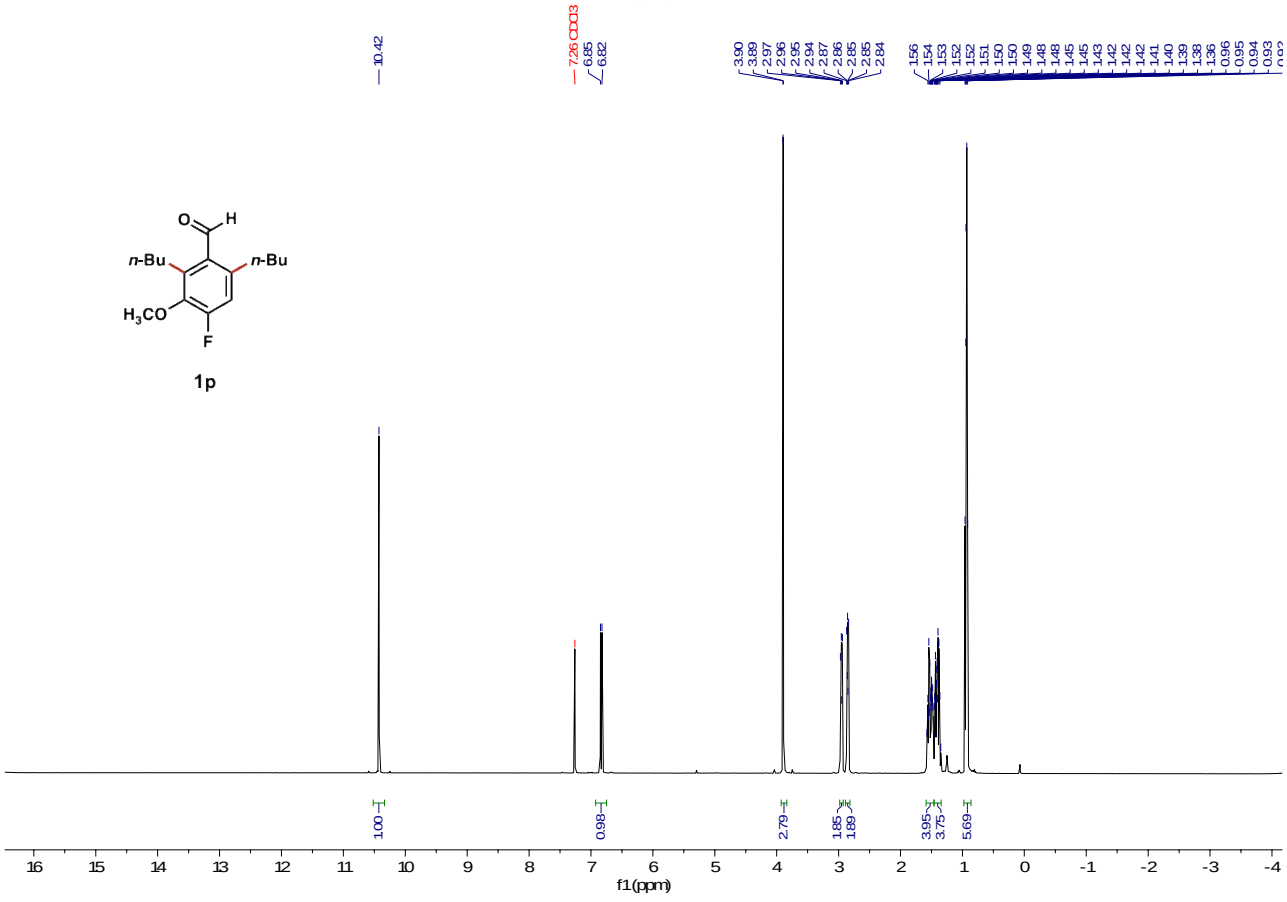
-62.65
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

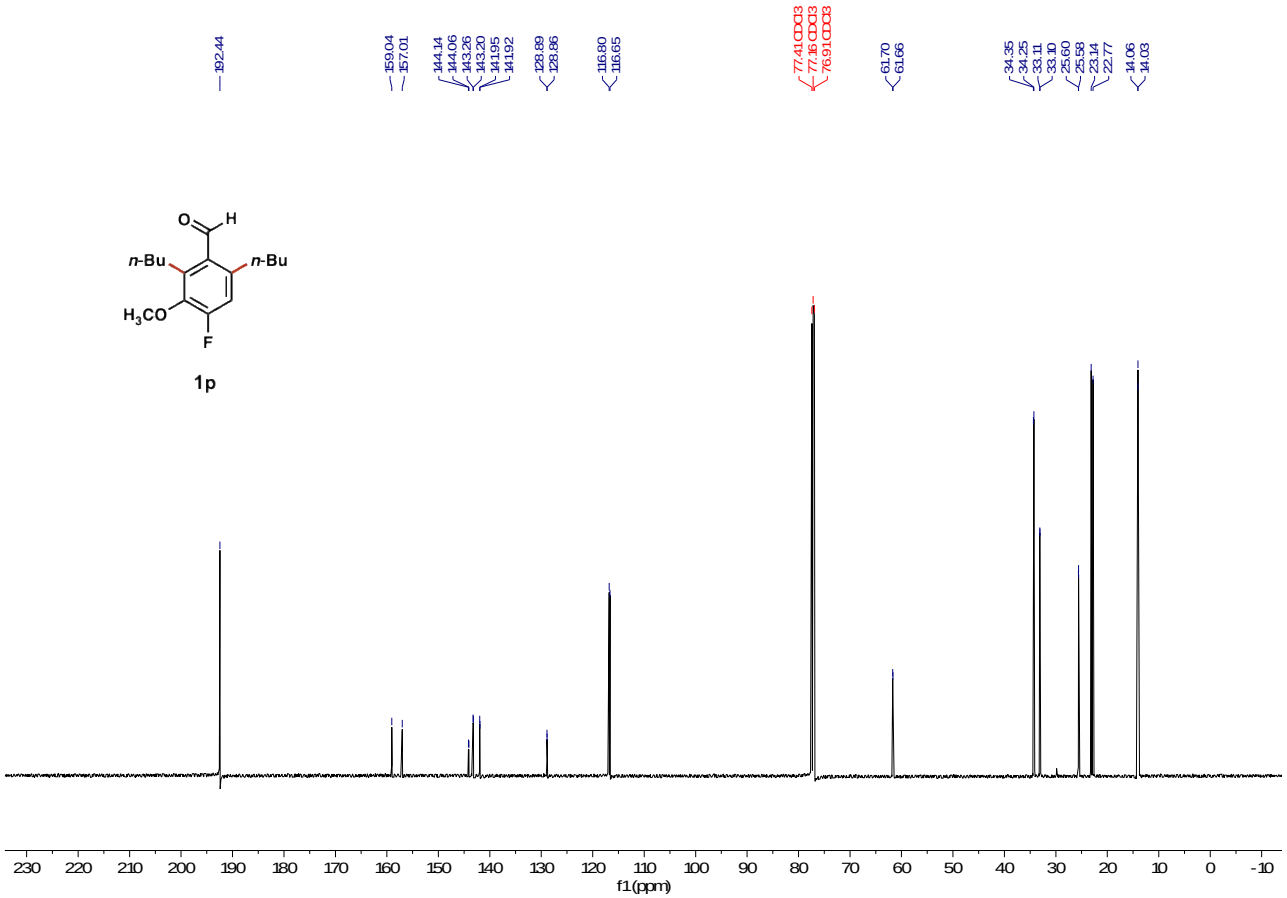

O
H
n-Bu
H3CO2C
OCH3

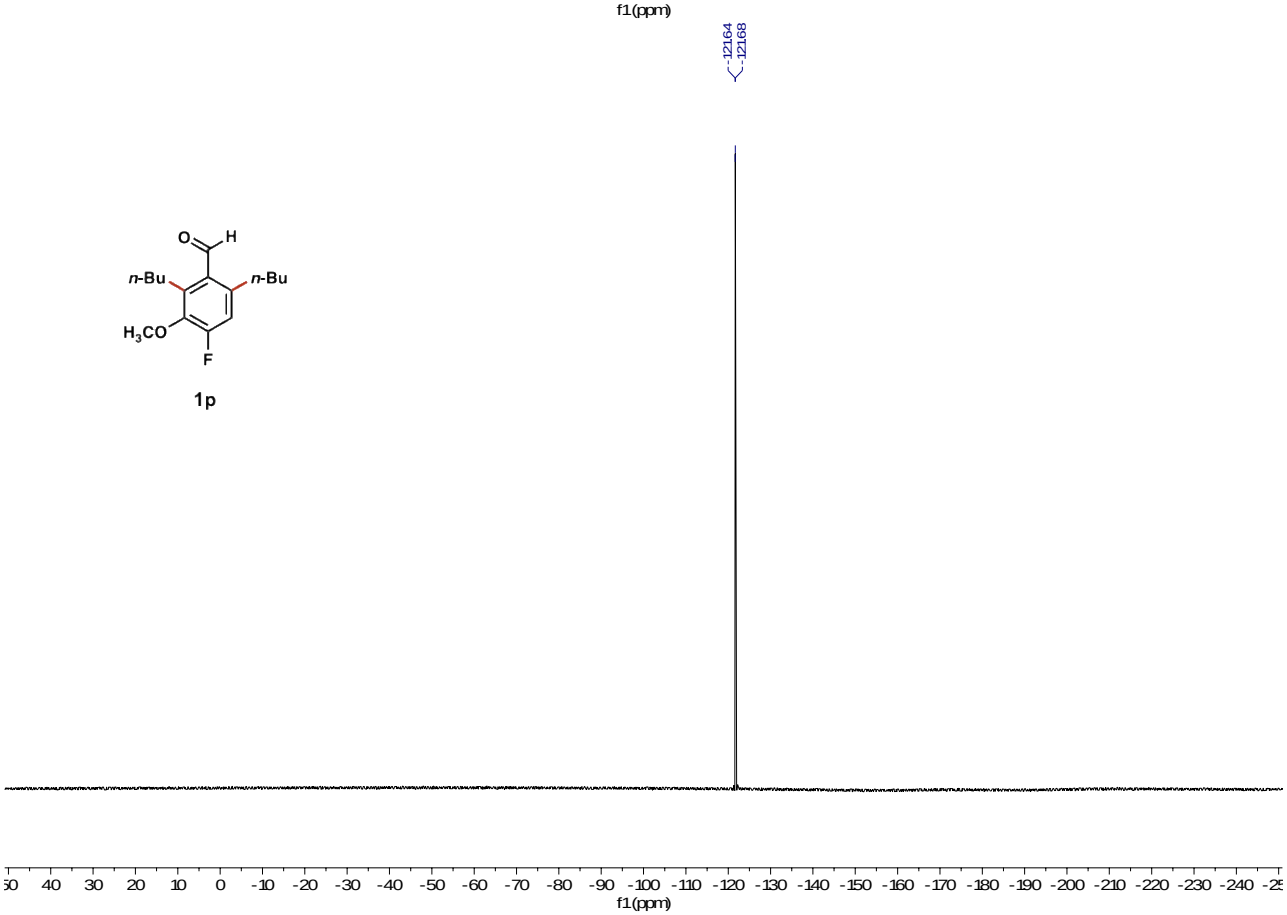
1o

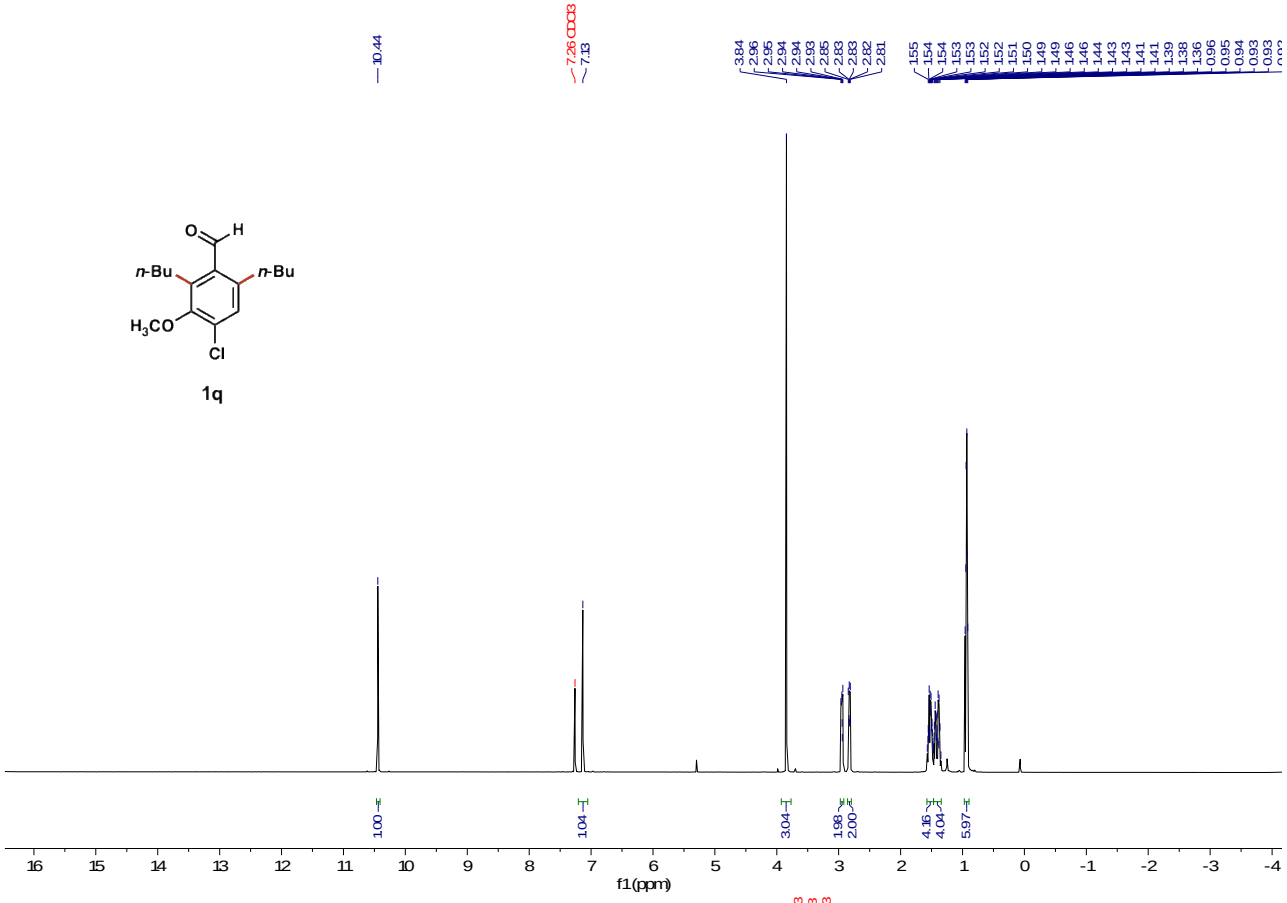
10.07
8.28
7.26 CDCl3
6.79
3.96
3.86
3.03
3.02
3.02
3.01
3.00
1.60
1.58
1.58
1.58
1.57
1.57
1.56
1.55
1.55
1.55
1.53
1.42
1.41
1.39
1.38
1.36
1.35
0.93
0.91
0.90
1.00
0.96
1.01
2.82
2.91
1.95
2.02
2.02
2.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

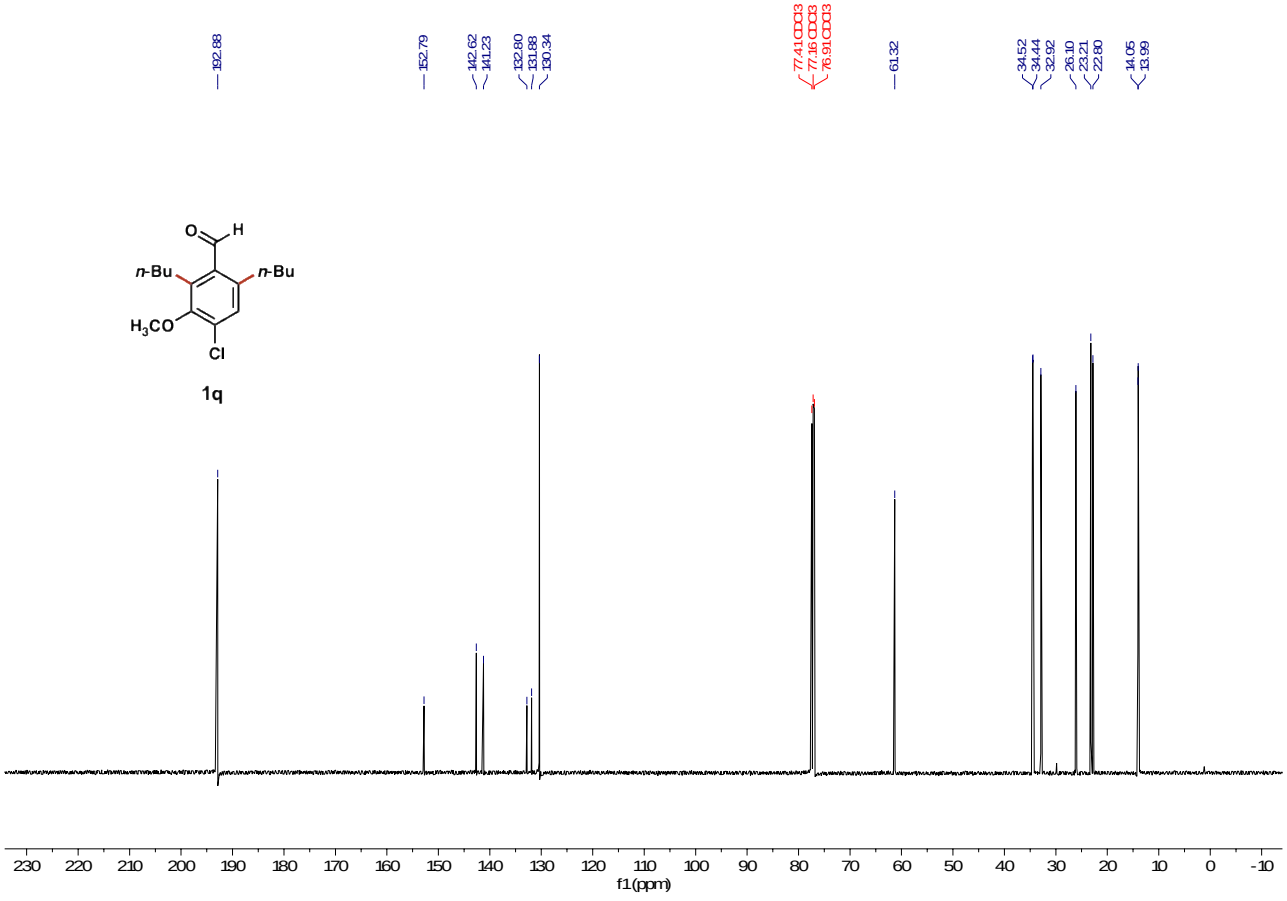

190.31
165.45
162.85
152.61
137.14
126.54
117.98
113.90
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.36
52.19
33.98
32.99
22.72
13.93
O
H
n-Bu
H3CO2C
OCH3
1o
f1 (ppm)

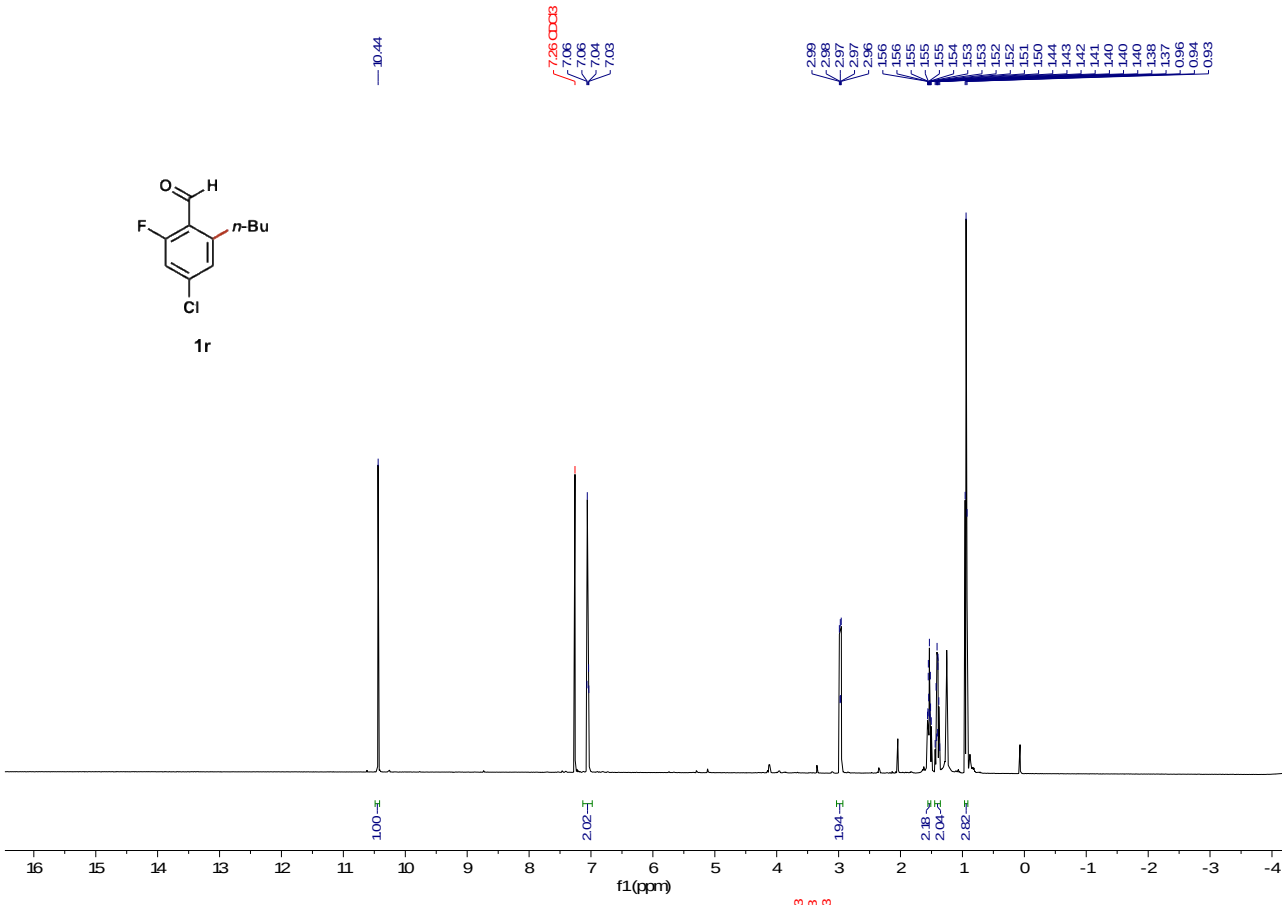

10.42
7.26 CDCl3
6.85
6.82
3.90
3.89
2.97
2.96
2.95
2.94
2.87
2.86
2.85
2.85
2.84
1.56
1.54
1.53
1.52
1.52
1.52
1.51
1.50
1.50
1.49
1.48
1.48
1.48
1.45
1.45
1.43
1.42
1.42
1.42
1.41
1.40
1.39
1.38
1.36
0.96
0.95
0.94
0.93
O
H
n-Bu
n-Bu
H3CO
F
1p
1.00
0.98
2.79
1.85
1.89
3.95
3.75
5.69
f1 (ppm)

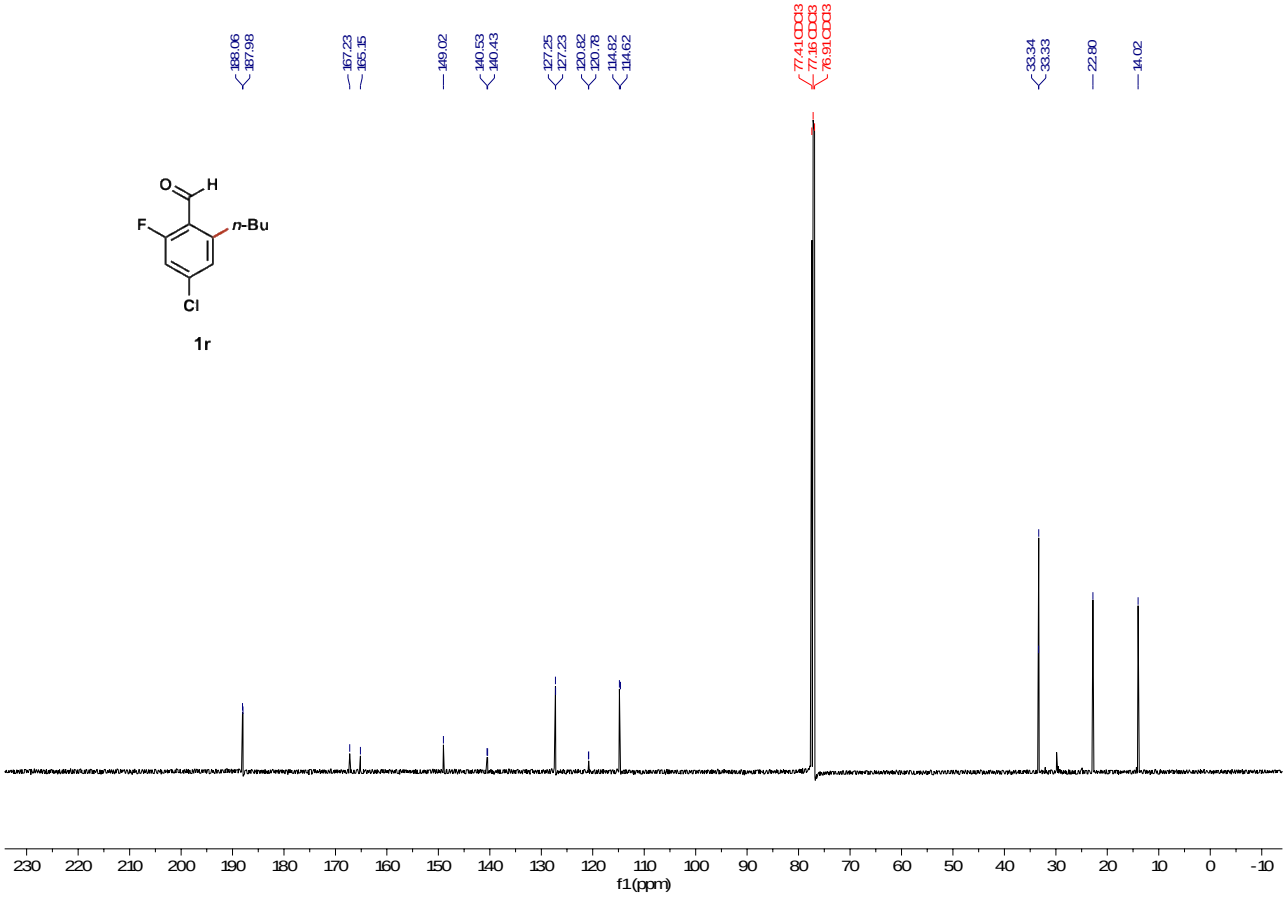

192.44
159.04
157.01
144.14
144.06
143.26
143.20
141.95
141.92
128.89
128.86
116.80
116.65
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
61.70
61.66
34.35
34.25
33.11
33.10
25.60
25.58
23.14
22.77
14.06
14.03
O
H
n-Bu
n-Bu
H3CO
F
1p
f1 (ppm)

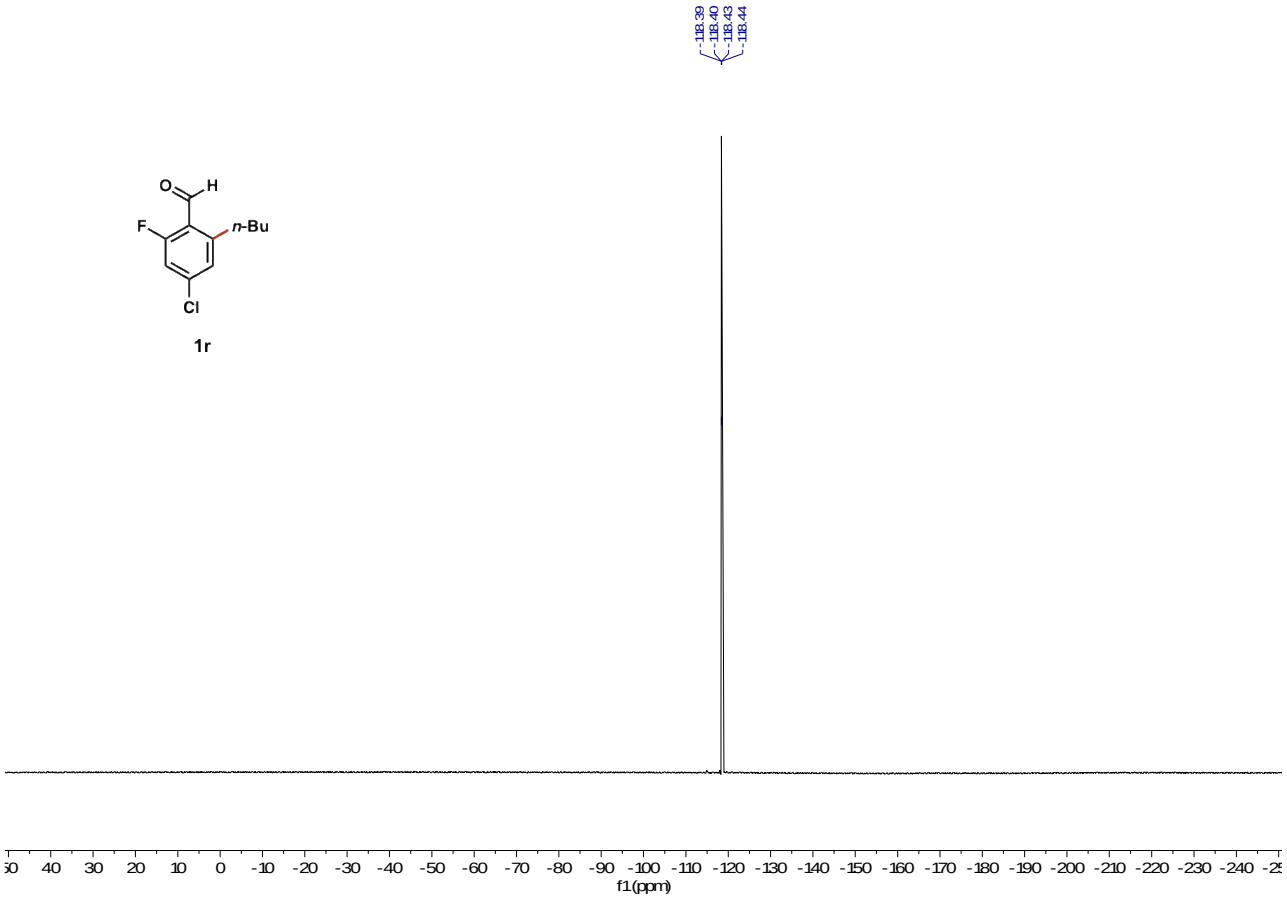

-121.64
-121.68
O
H
n-Bu
n-Bu
H3CO
F
1p
f1 (ppm)


10.44
7.26 CDCl3
7.13
3.84
2.96
2.95
2.94
2.94
2.93
2.85
2.83
2.83
2.82
2.81
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.50
1.49
1.49
1.49
1.46
1.46
1.44
1.44
1.43
1.43
1.41
1.41
1.39
1.38
1.36
0.96
0.95
0.94
0.93
0.93
O
H
n-Bu
n-Bu
H3CO
Cl
1q
1.00
1.04
3.04
1.98
2.00
4.16
4.04
5.97
f1 (ppm)


192.88
152.79
142.62
141.23
132.80
131.88
130.34
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
61.32
34.52
34.44
32.92
26.10
23.21
22.80
14.05
13.99
O
H
n-Bu
n-Bu
H3CO
Cl
1q
f1 (ppm)


10.44
7.26 CDCl3
7.06
7.06
7.04
7.03
2.99
2.98
2.97
2.97
2.96
156
156
155
155
155
154
153
153
152
152
151
150
144
143
142
141
140
140
140
138
137
0.96
0.94
0.93
O
H
F
n-Bu
Cl
1r
1.00
2.02
1.94
2.18
2.04
2.82
f1(ppm)


188.06
187.98
167.23
166.15
149.02
140.53
140.43
127.25
127.23
120.82
120.78
114.82
114.62
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
33.34
33.33
22.80
14.02
O
H
F
n-Bu
Cl
1r
f1(ppm)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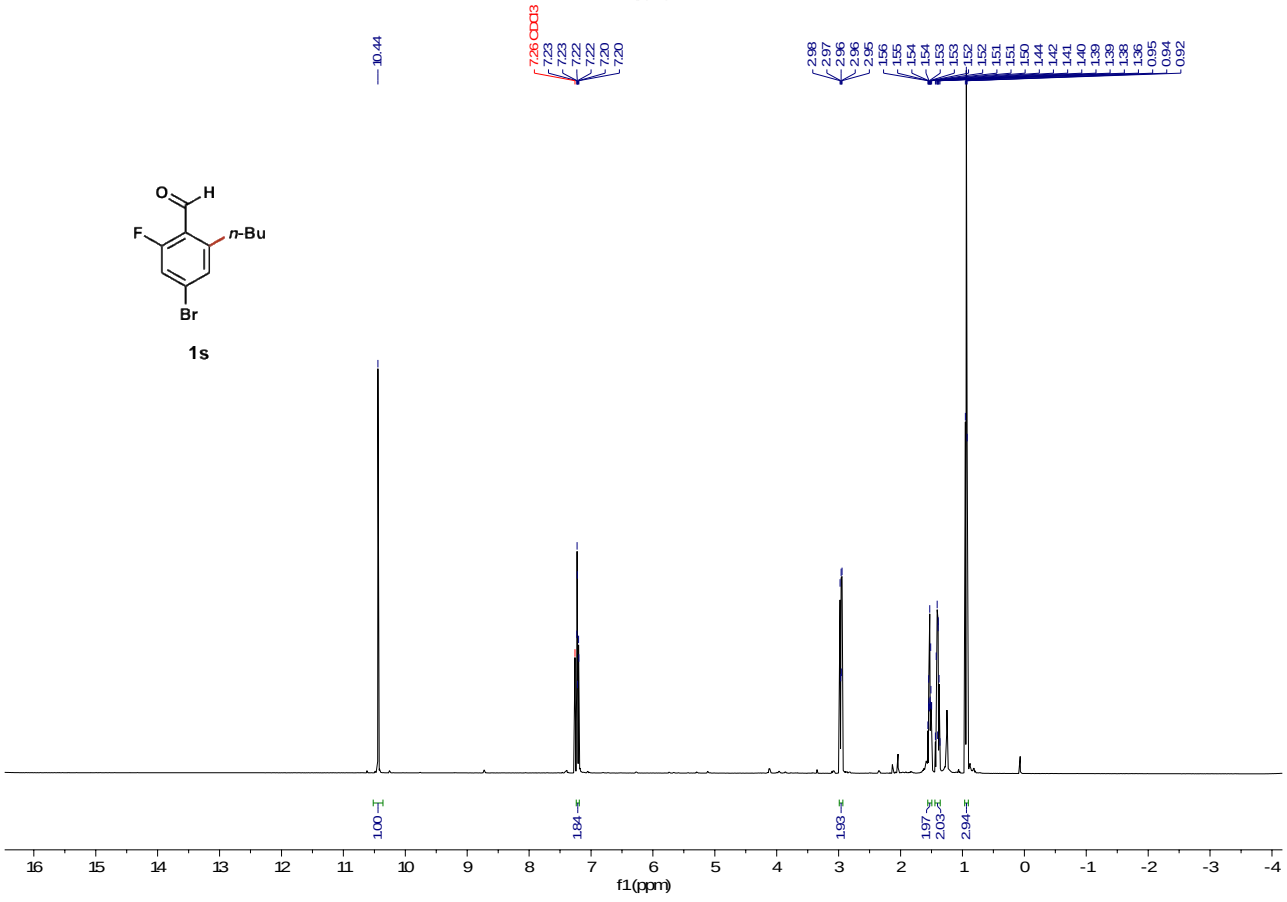
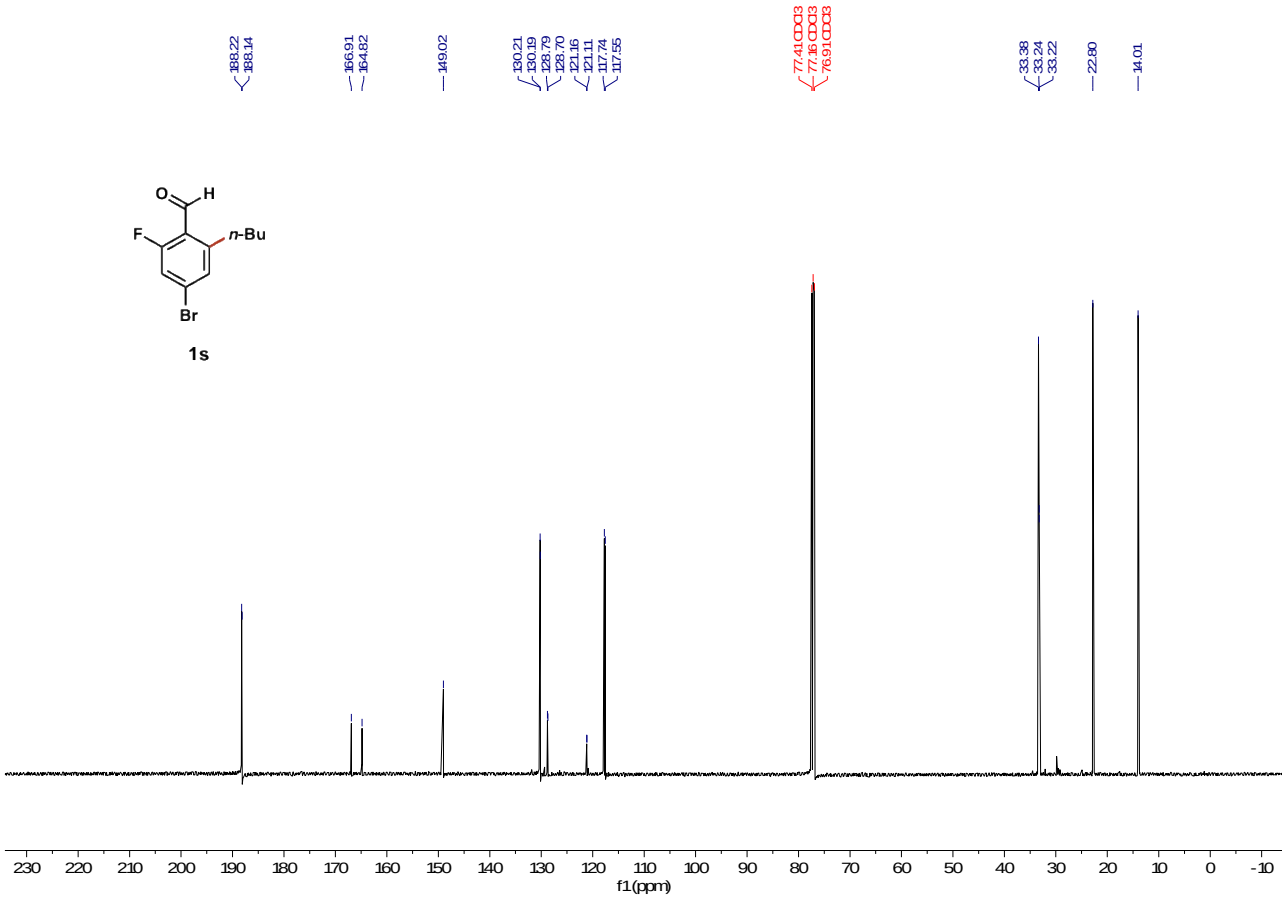
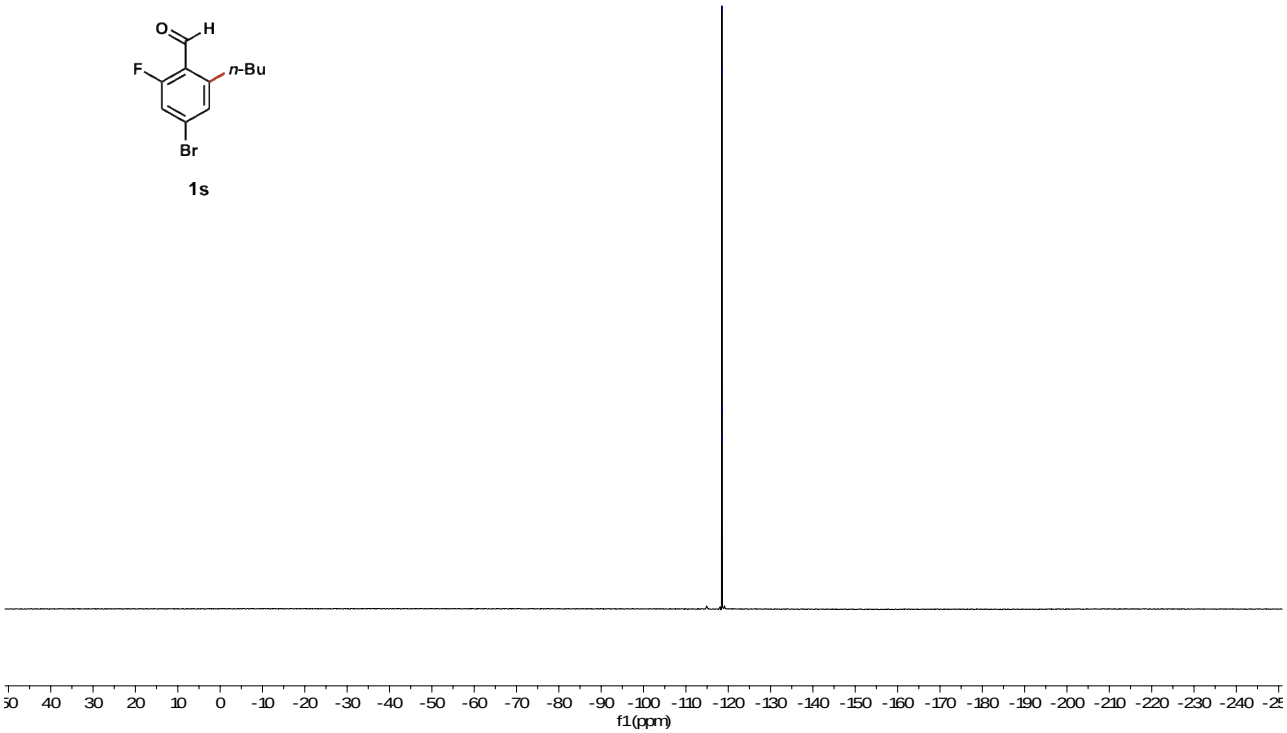
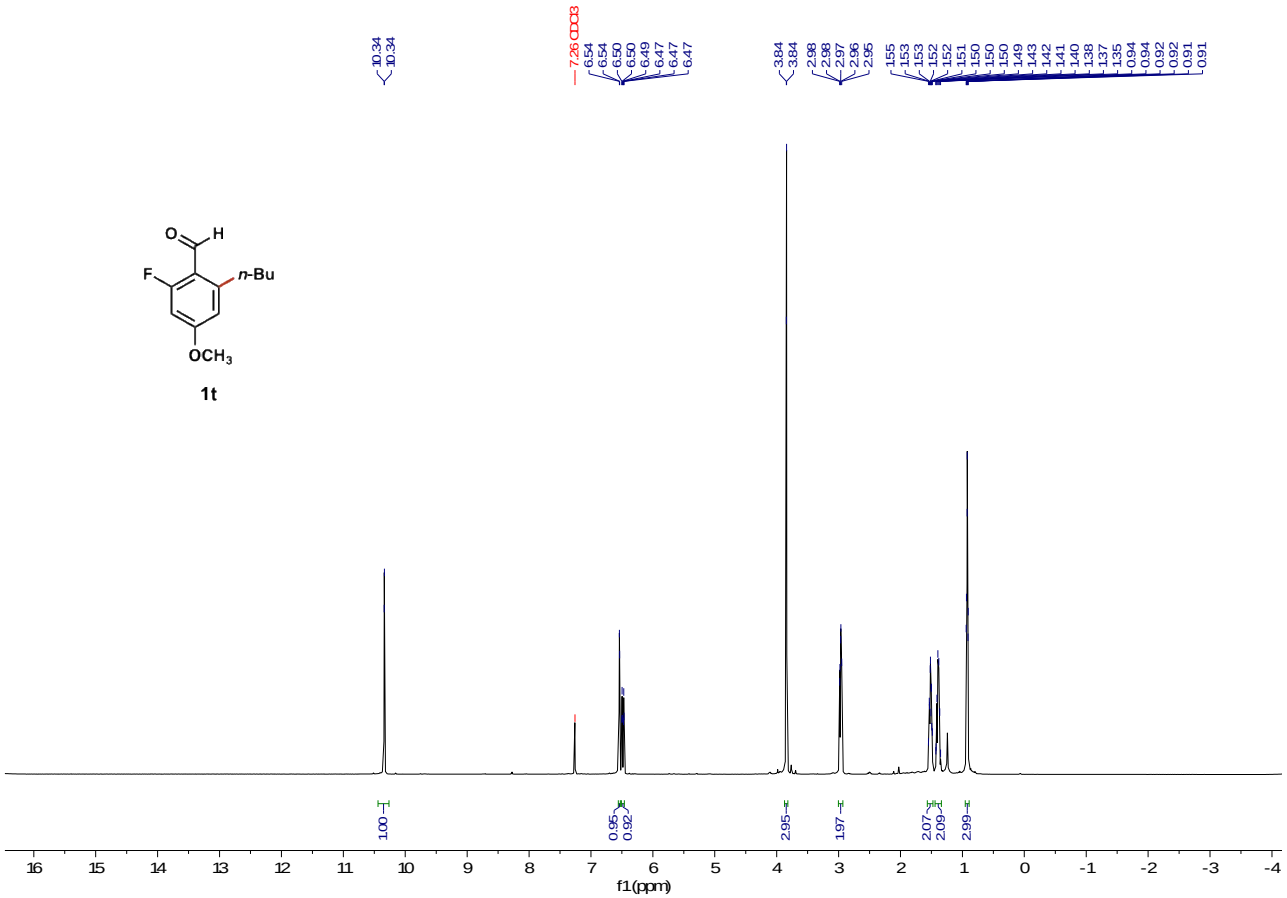
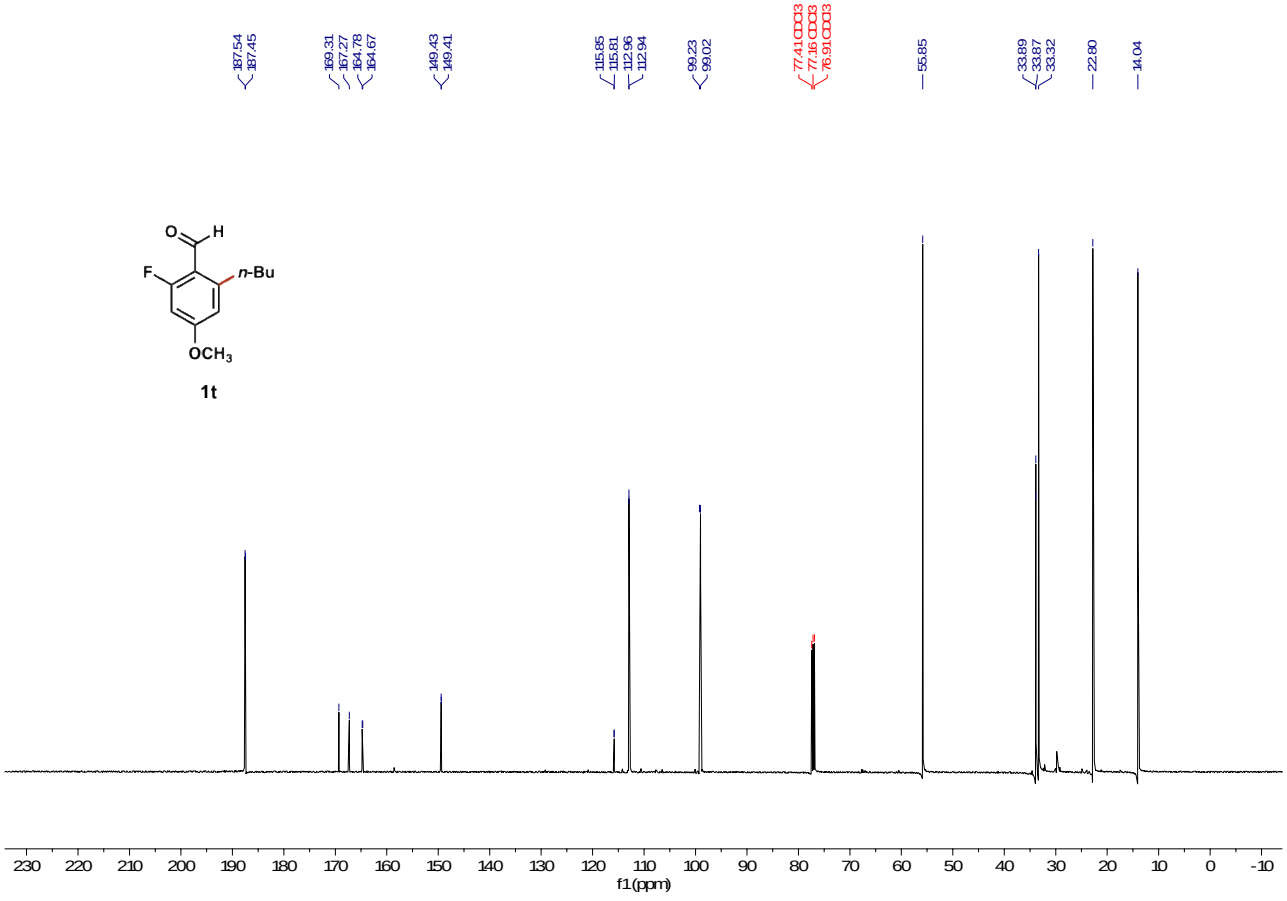
-118.40
-118.43
-118.44
O
H
F
n-Bu
Cl
1r
f1 (ppm)


10.44
7.26 CDCl3
7.23
7.23
7.22
7.22
7.20
7.20
2.98
2.97
2.96
2.96
2.95
1.56
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.50
1.44
1.42
1.41
1.40
1.39
1.39
1.38
1.36
0.95
0.94
0.92
O
H
F
n-Bu
Br
1s
1.00
1.84
1.93
1.97
2.03
2.94
f1 (ppm)


188.22
188.14
166.91
164.82
149.02
130.21
130.19
128.79
128.70
121.16
121.11
117.74
117.55
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
33.38
33.24
33.22
22.80
14.01
O
H
F
n-Bu
Br
1s
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


118.49
118.50
118.53
118.54
O
H
F
n-Bu
Br
1s
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25
f1 (ppm)


10.34
10.34
7.26 CDCl3
6.54
6.54
6.50
6.50
6.49
6.47
6.47
6.47
3.84
3.84
2.98
2.98
2.97
2.96
2.95
1.55
1.53
1.53
1.52
1.52
1.51
1.50
1.50
1.50
1.49
1.43
1.42
1.41
1.40
1.38
1.37
1.35
0.94
0.94
0.92
0.92
0.91
0.91
O
H
F
n-Bu
OCH3
1t
1.00
0.95
0.92
2.95
1.97
2.07
2.09
2.99
f1 (ppm)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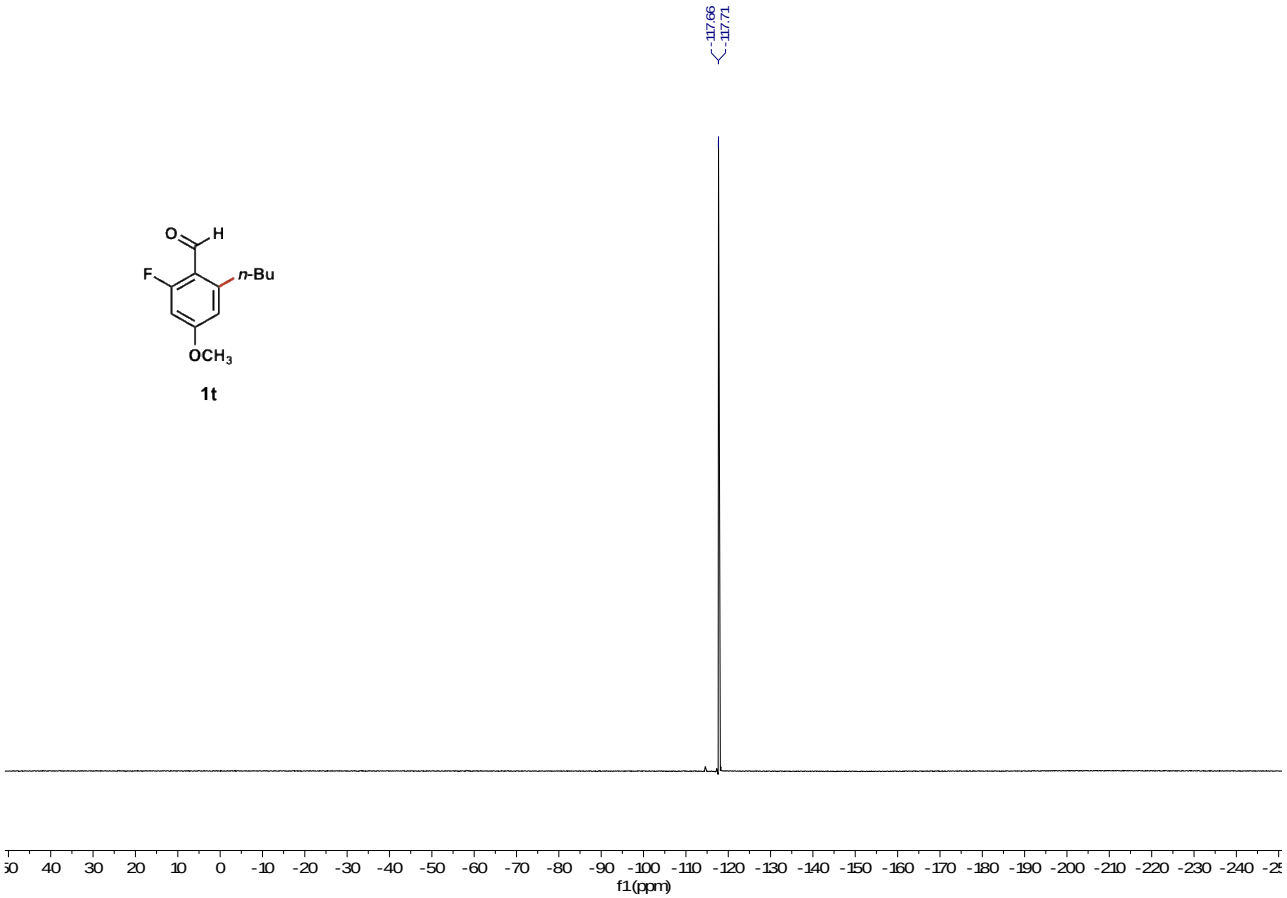
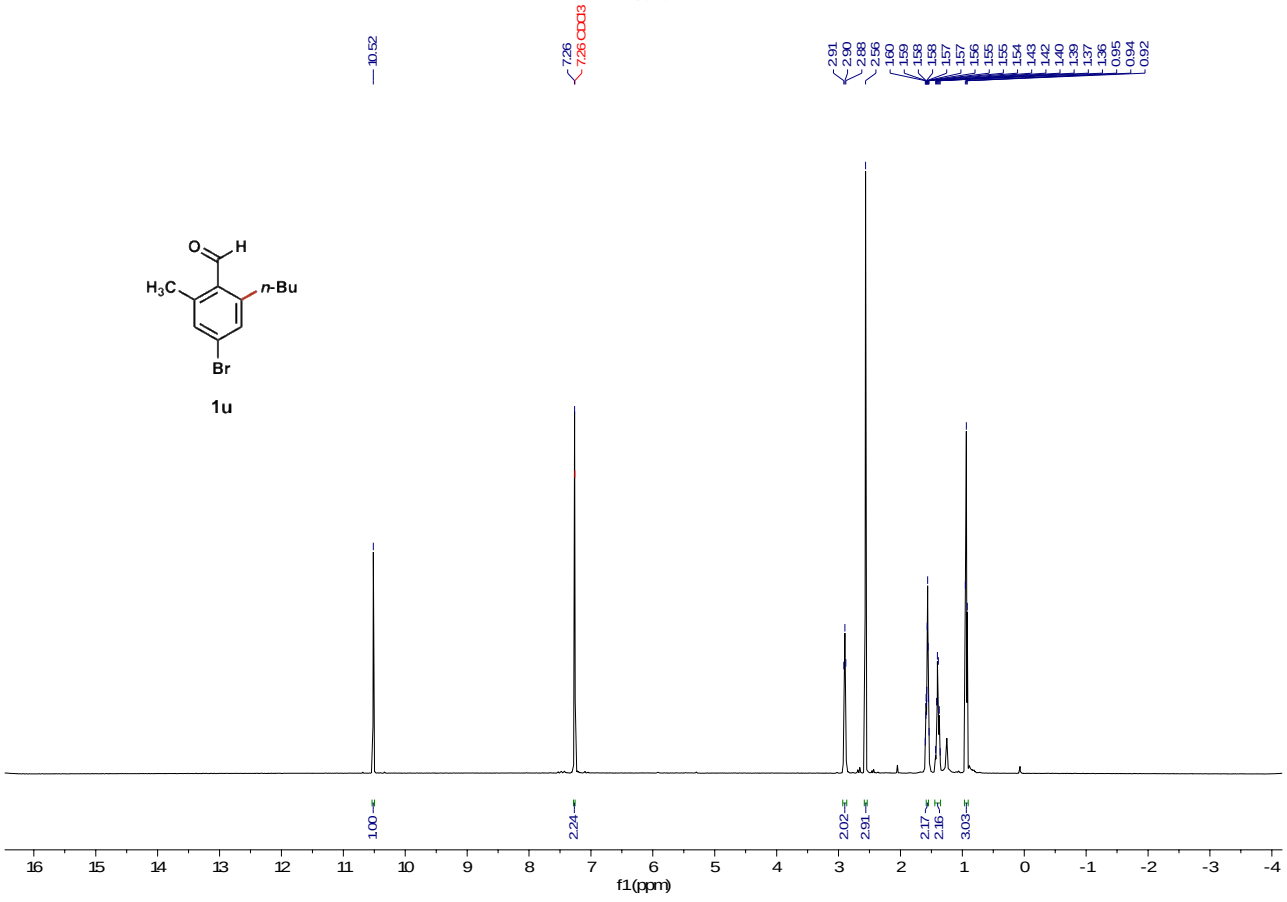
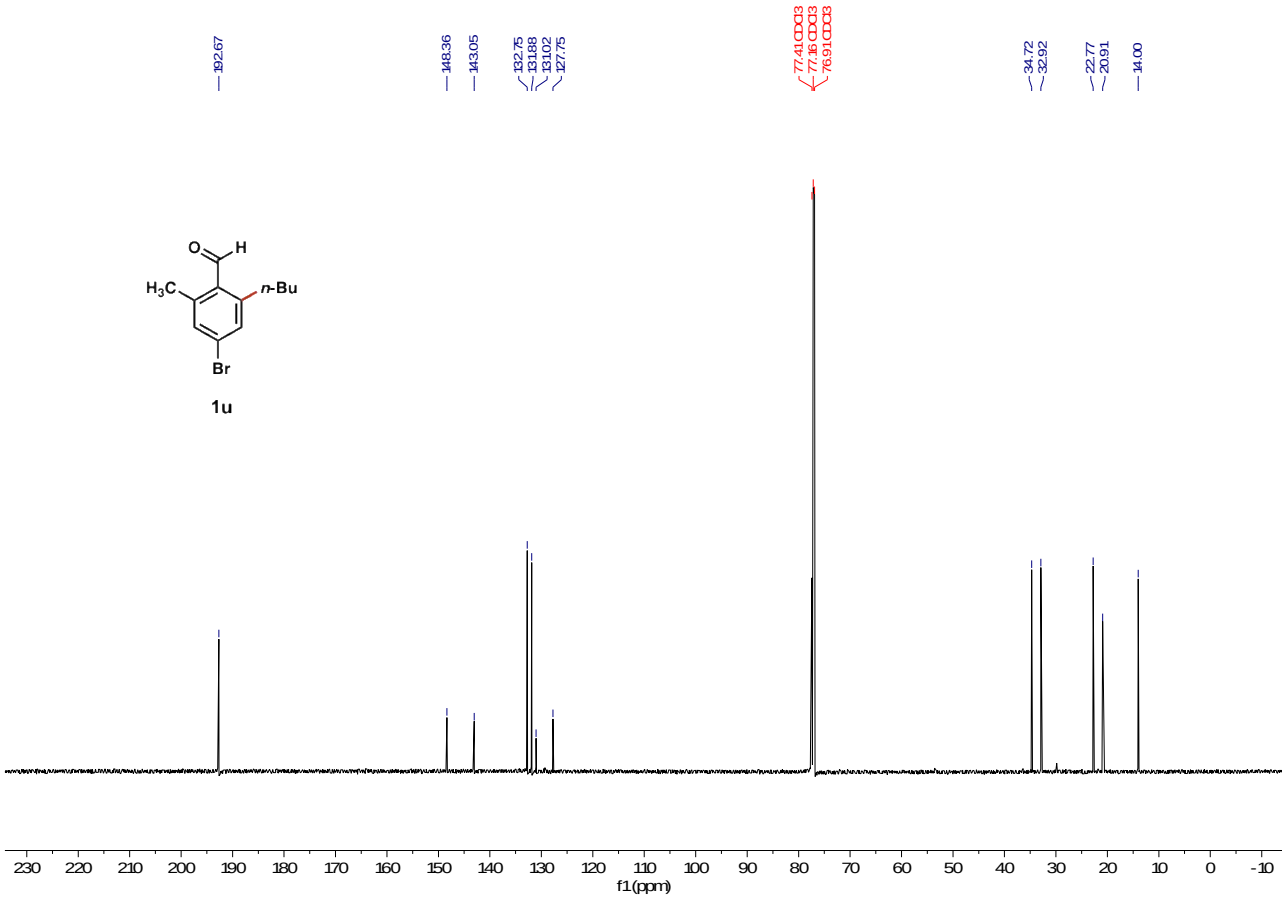
187.45
169.31
167.27
164.78
164.67
149.43
149.41
115.85
115.81
112.96
112.94
99.23
99.02
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
55.85
33.89
33.87
33.32
22.80
14.04
O
H
F
n-Bu
OCH3
1t
f1 (ppm)


-117.66
-117.71
O
H
F
n-Bu
OCH3
1t
f1 (ppm)


10.52
7.26
7.26 CDCl3
2.91
2.90
2.88
2.66
1.60
1.59
1.58
1.58
1.57
1.57
1.56
1.55
1.55
1.54
1.43
1.42
1.40
1.39
1.37
1.36
0.95
0.94
0.92
O
H
H3C
n-Bu
Br
1u
1.00
2.24
2.02
2.91
2.17
2.16
3.03
f1 (ppm)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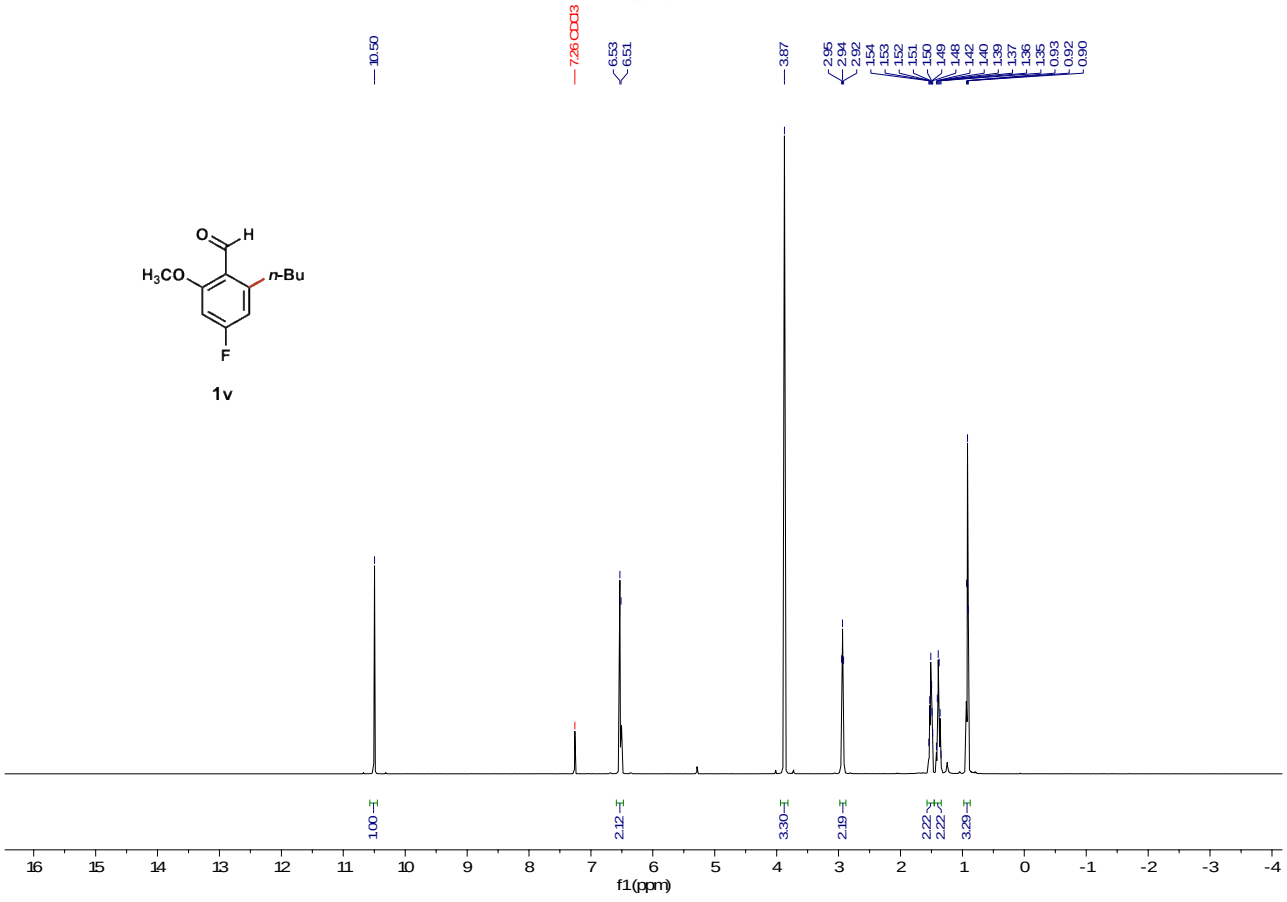
148.36
143.05
132.75
131.88
131.02
127.75
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.72
32.92
22.77
20.91
14.00
O
H
H3C
n-Bu
Br
1u
f1 (ppm)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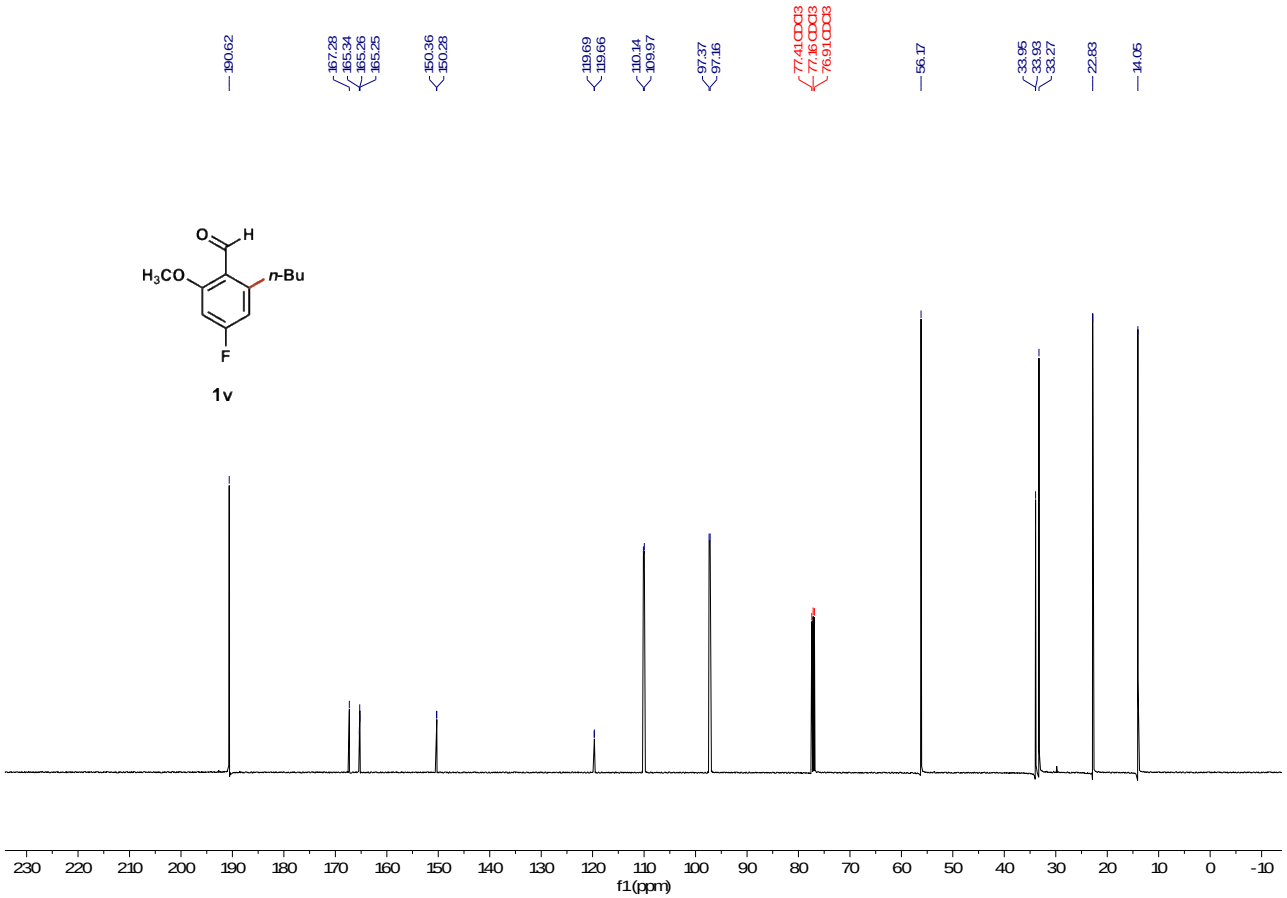
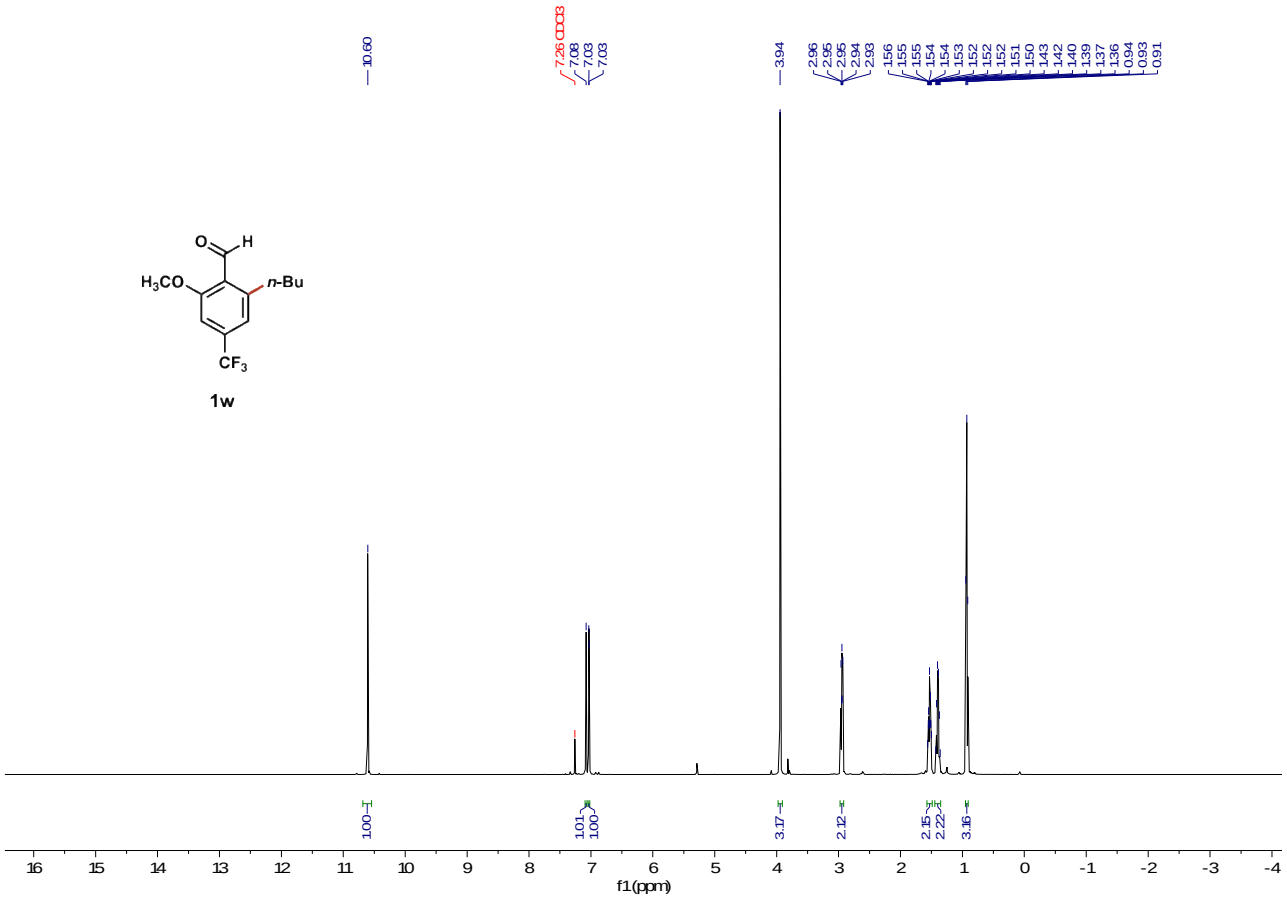
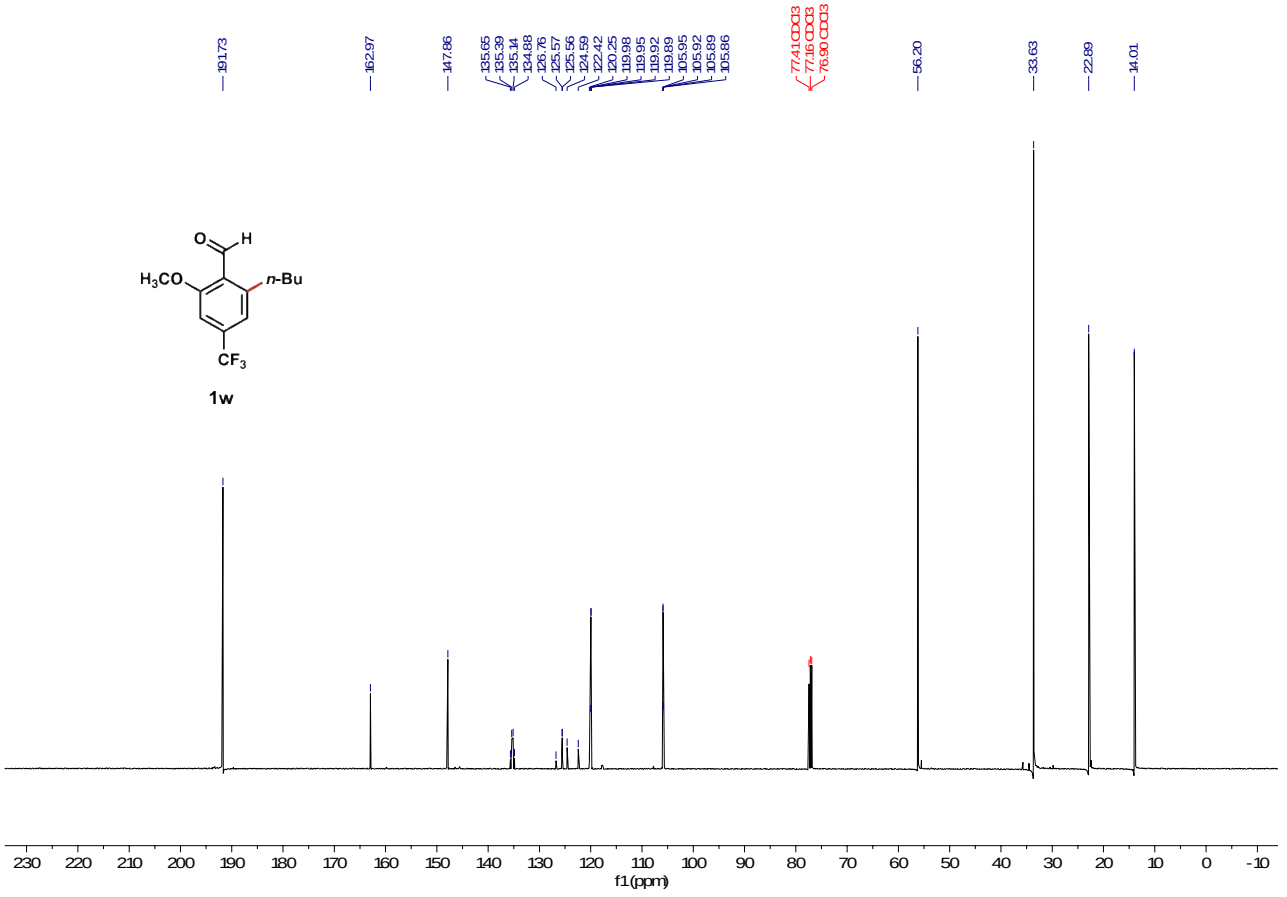
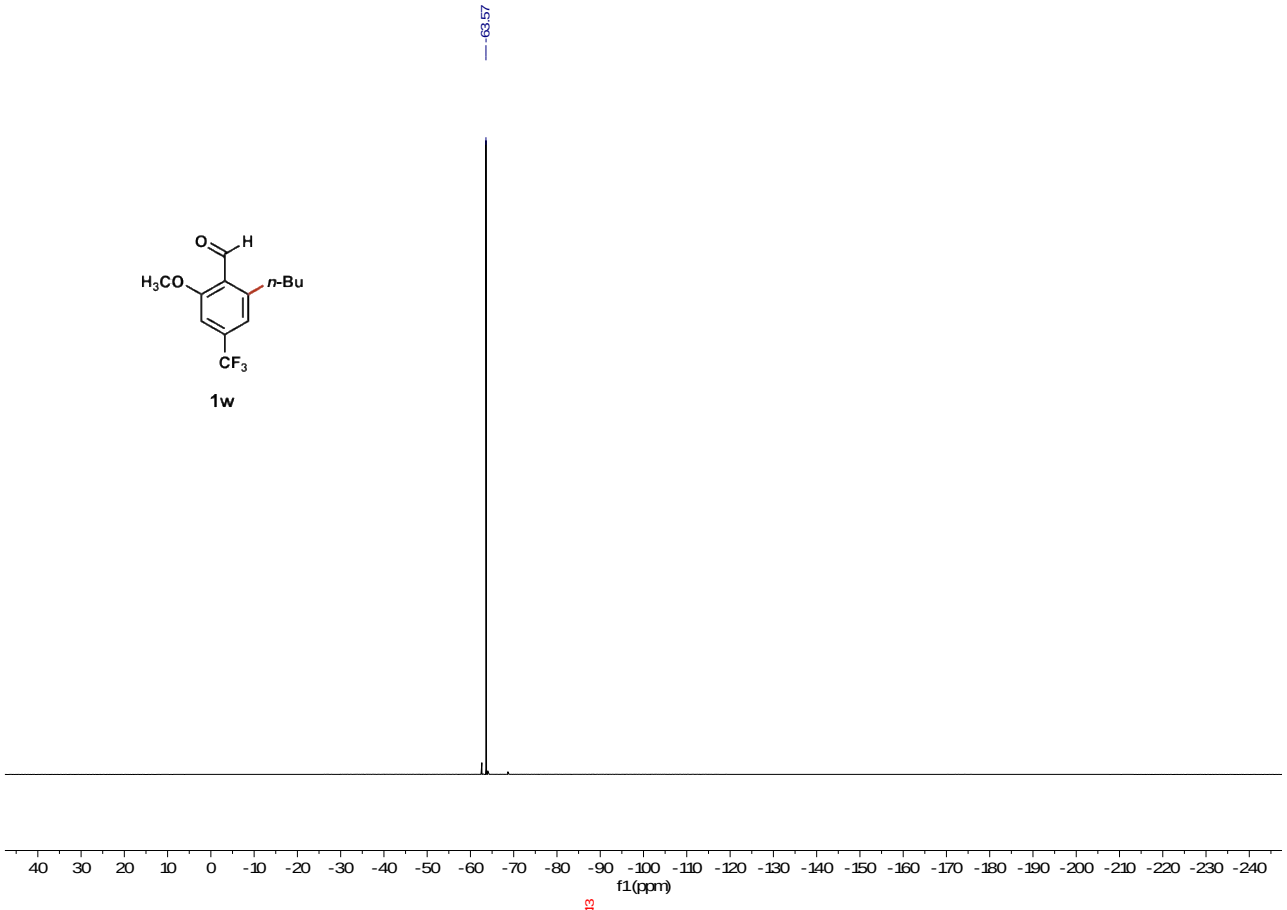
7.26 CDCl3
6.53
6.51
3.87
2.95
2.94
2.92
1.54
1.53
1.52
1.51
1.50
1.49
1.48
1.42
1.40
1.39
1.37
1.36
1.35
0.93
0.92
0.90
O
H
H3CO
n-Bu
F
1v
1.00
2.12
3.30
2.19
2.22
2.22
3.29
f1 (ppm)

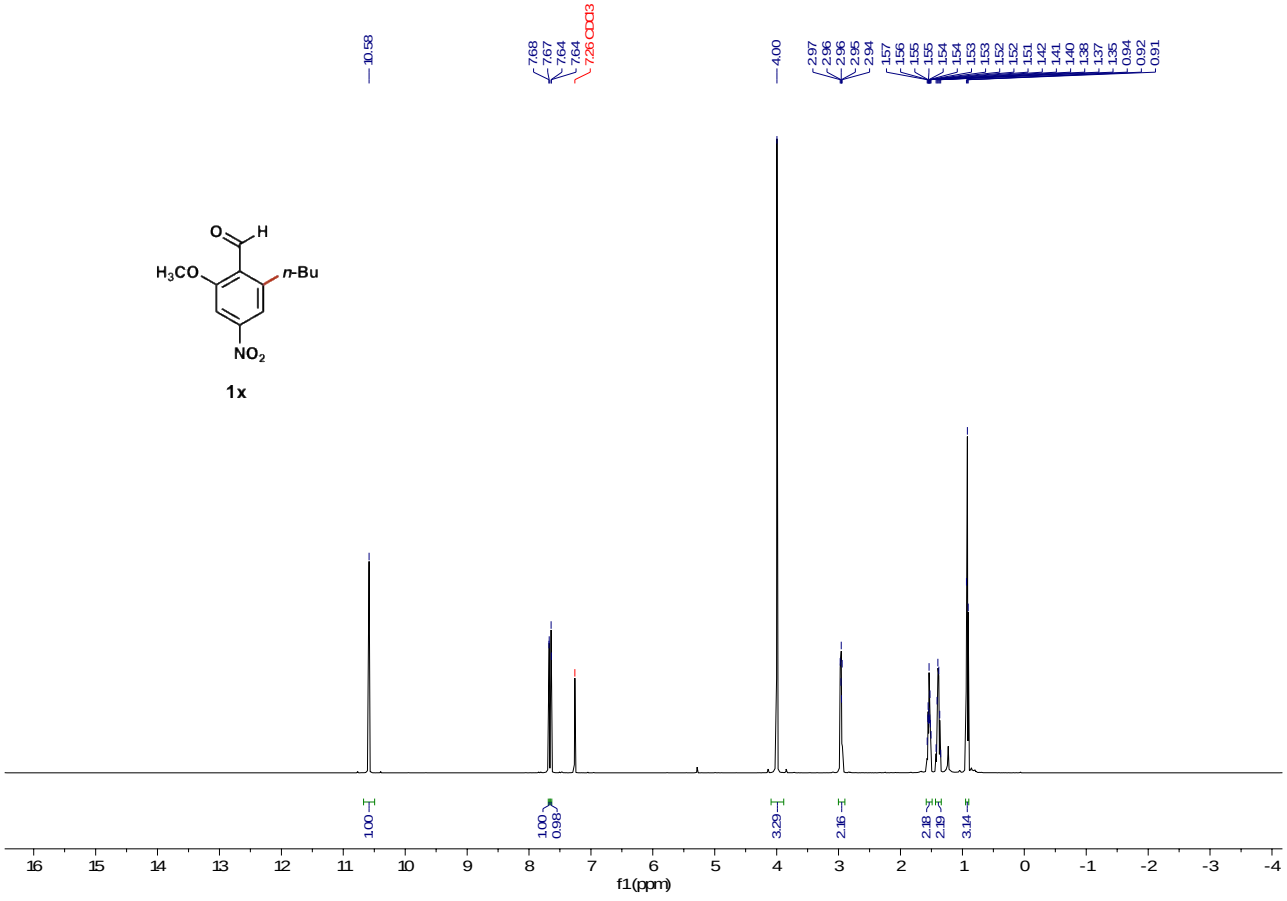

190.62
167.28
165.34
165.26
165.25
150.36
150.28
119.69
119.66
110.14
109.97
97.37
97.16
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.17
33.95
33.93
33.27
22.83
14.05
O
H
H3CO
n-Bu
F
1v
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

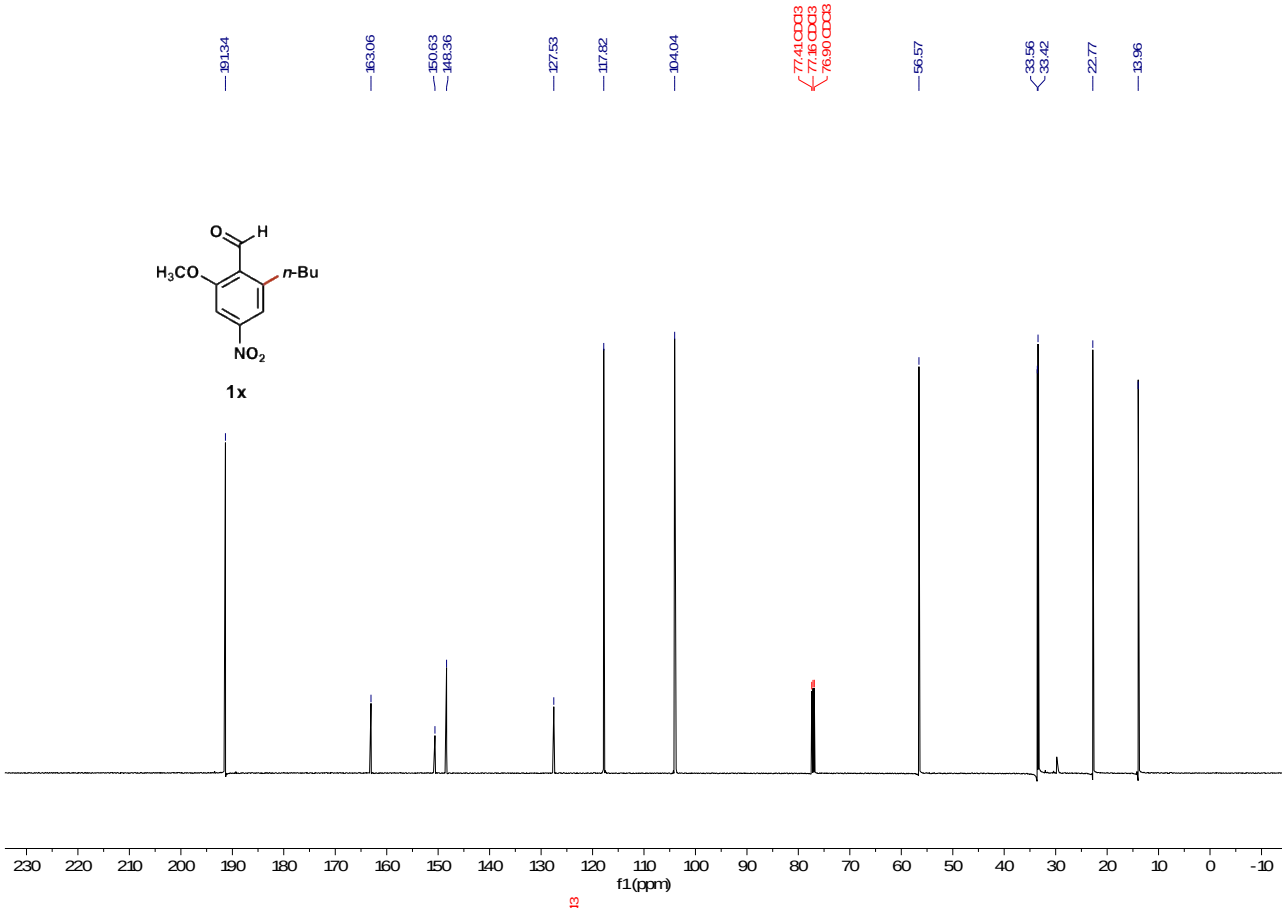

-101.45
-101.47
-101.49
O
H
H3CO
n-Bu
F
1v
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

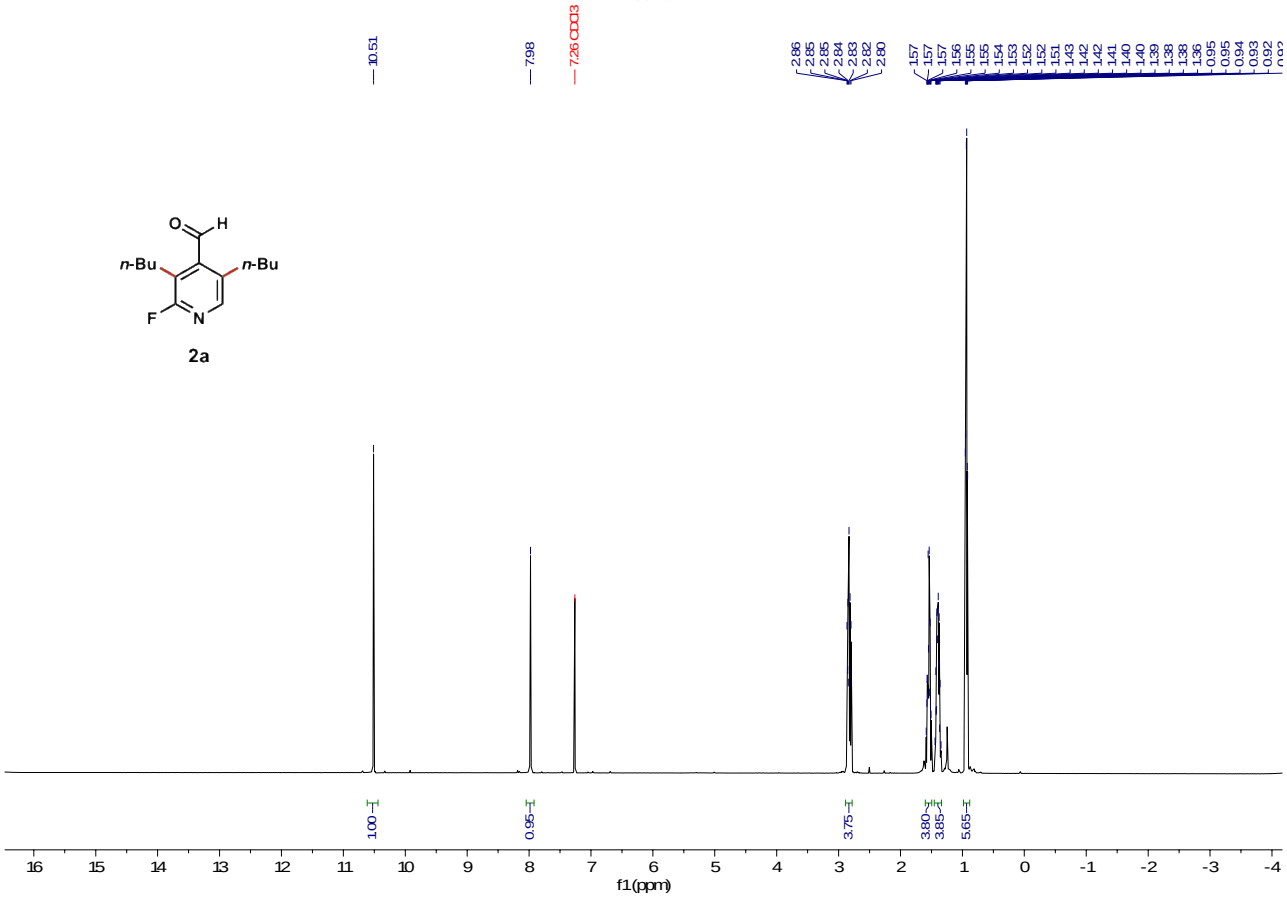

10.60
7.26 CDCl3
7.08
7.03
7.03
3.94
2.96
2.95
2.95
2.94
2.93
156
155
155
155
154
154
153
152
152
152
151
151
150
143
142
140
139
137
136
0.94
0.93
0.91
O
H
H3CO
n-Bu
CF3
1w
1.00
1.01
1.00
3.17
2.12
2.15
2.22
3.16
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1(ppm)

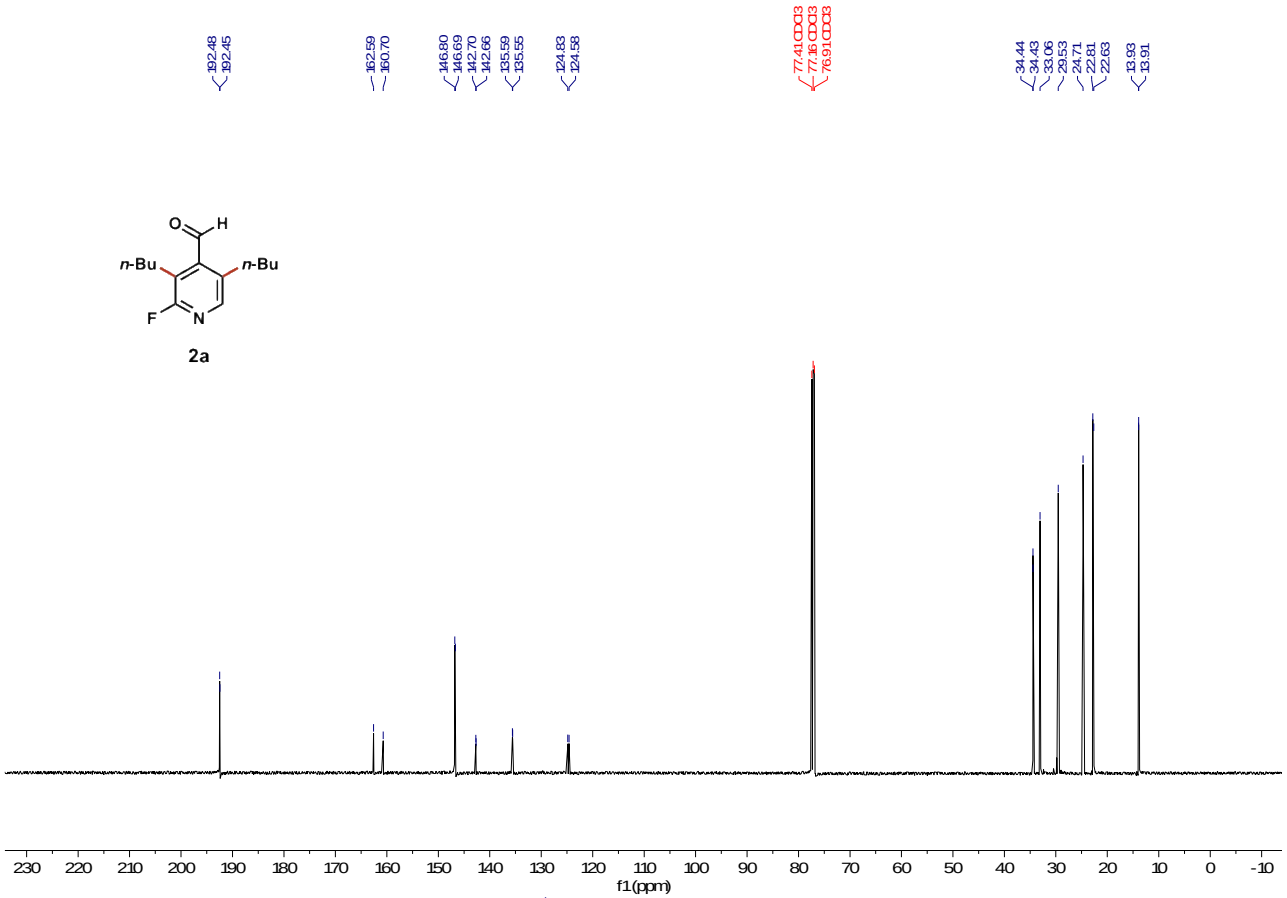

191.73
162.97
147.86
135.65
135.39
135.14
134.88
126.76
125.57
125.56
124.59
122.42
120.25
119.98
119.95
119.92
119.89
105.95
105.92
105.89
105.86
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
56.20
33.63
22.89
14.01
O
H
H3CO
n-Bu
CF3
1w
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1(ppm)


-63.57
O
H
H3CO
n-Bu
CF3
1w
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


10.58
7.68
7.67
7.64
7.64
7.26 CDCl3
4.00
2.97
2.96
2.96
2.95
2.94
1.57
1.56
1.55
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.42
1.41
1.40
1.38
1.37
1.35
0.94
0.92
0.91
O
H
H3CO
n-Bu
NO2
1x
1.00
1.00
0.98
3.29
2.16
2.18
2.29
3.14
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


191.34
163.06
150.63
148.36
127.53
117.82
104.04
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
56.57
33.56
33.42
22.77
13.96
O
H
H3CO
n-Bu
NO2
1x
f1 (ppm)


10.51
7.98
7.26 CDCl3
2.86
2.85
2.85
2.84
2.83
2.82
2.80
1.57
1.57
1.57
1.56
1.55
1.55
1.54
1.53
1.52
1.52
1.51
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.38
1.36
0.95
0.95
0.94
0.93
0.92
O
H
n-Bu
n-Bu
F
N
2a
1.00
0.95
3.75
3.80
3.85
5.65
f1 (ppm)


192.48
192.45
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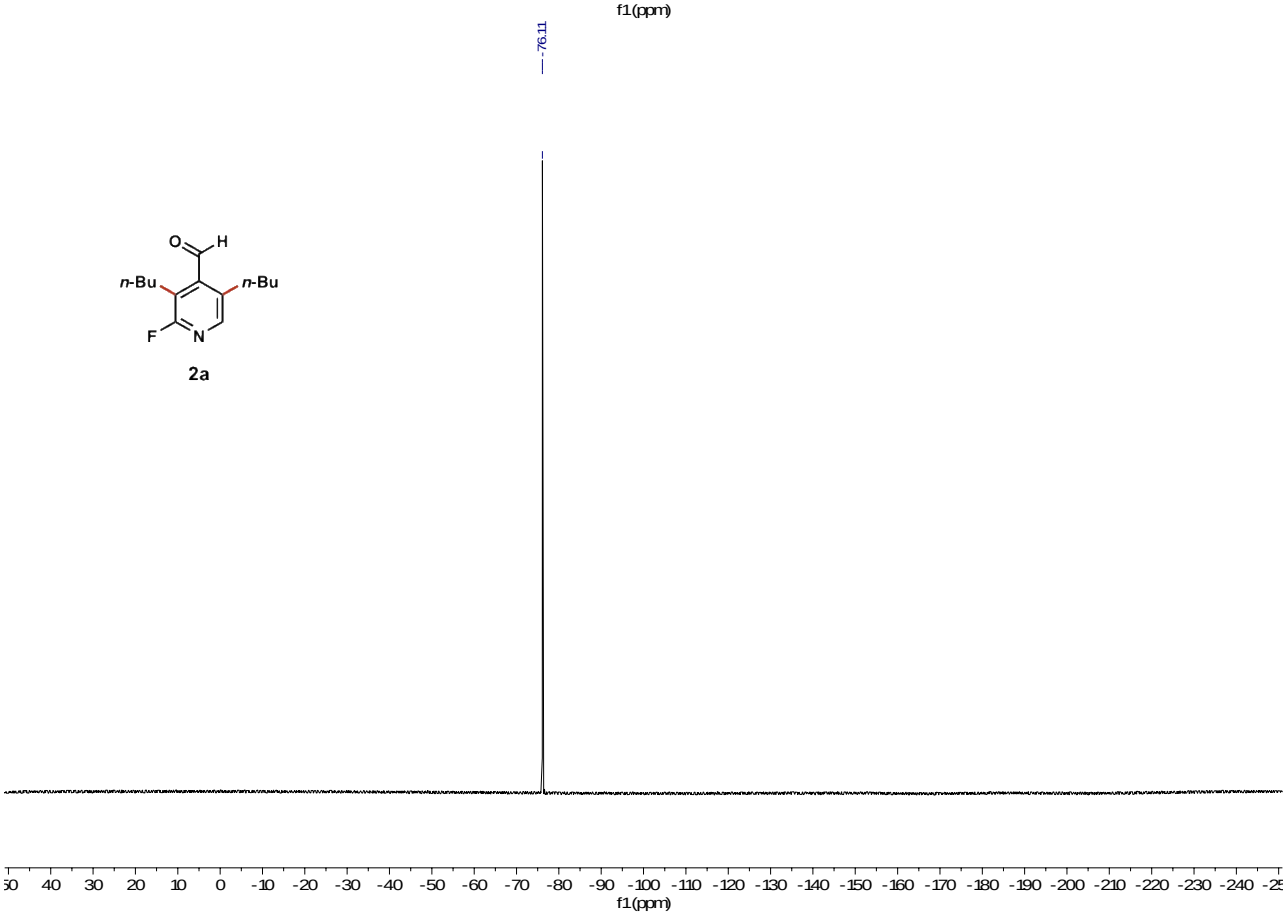
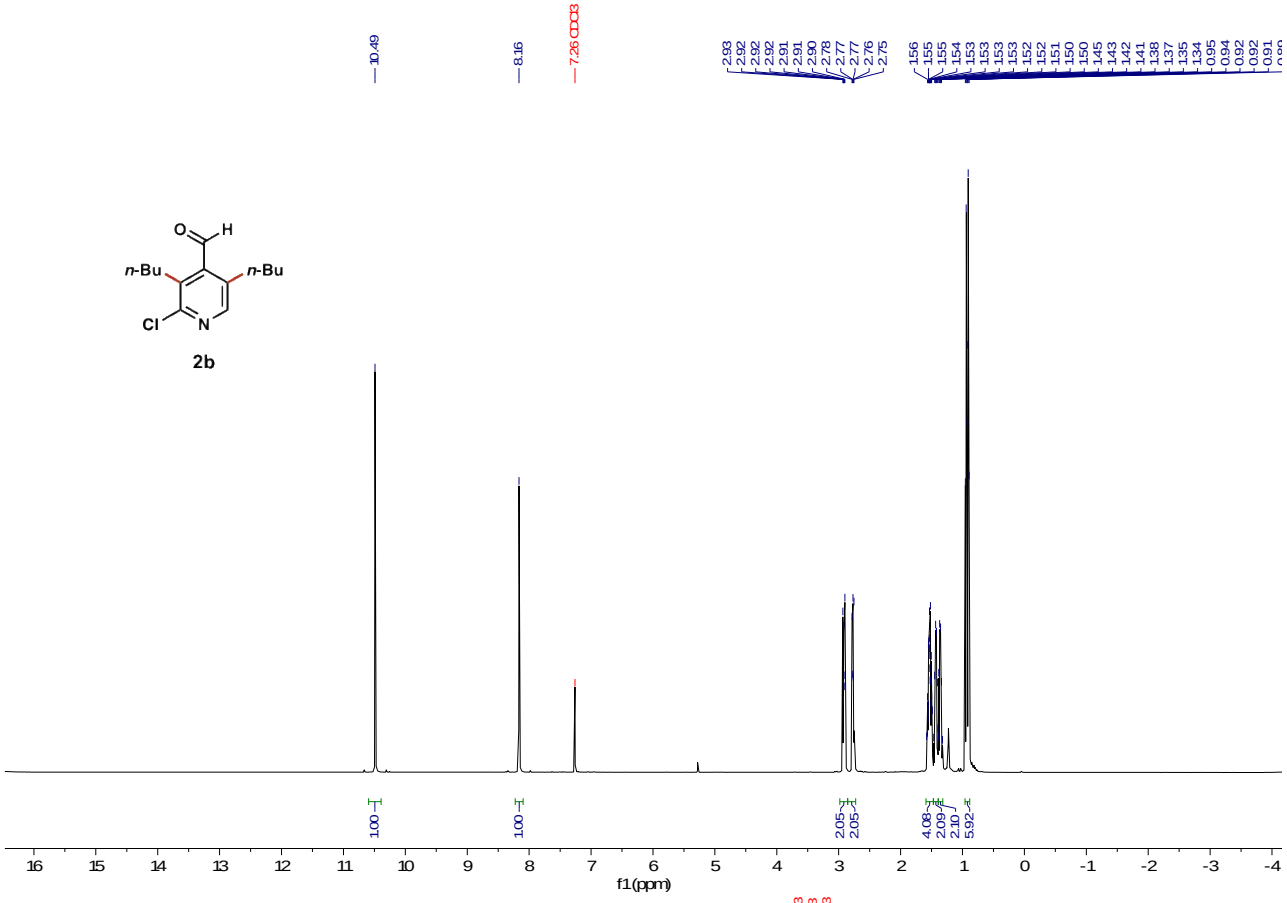
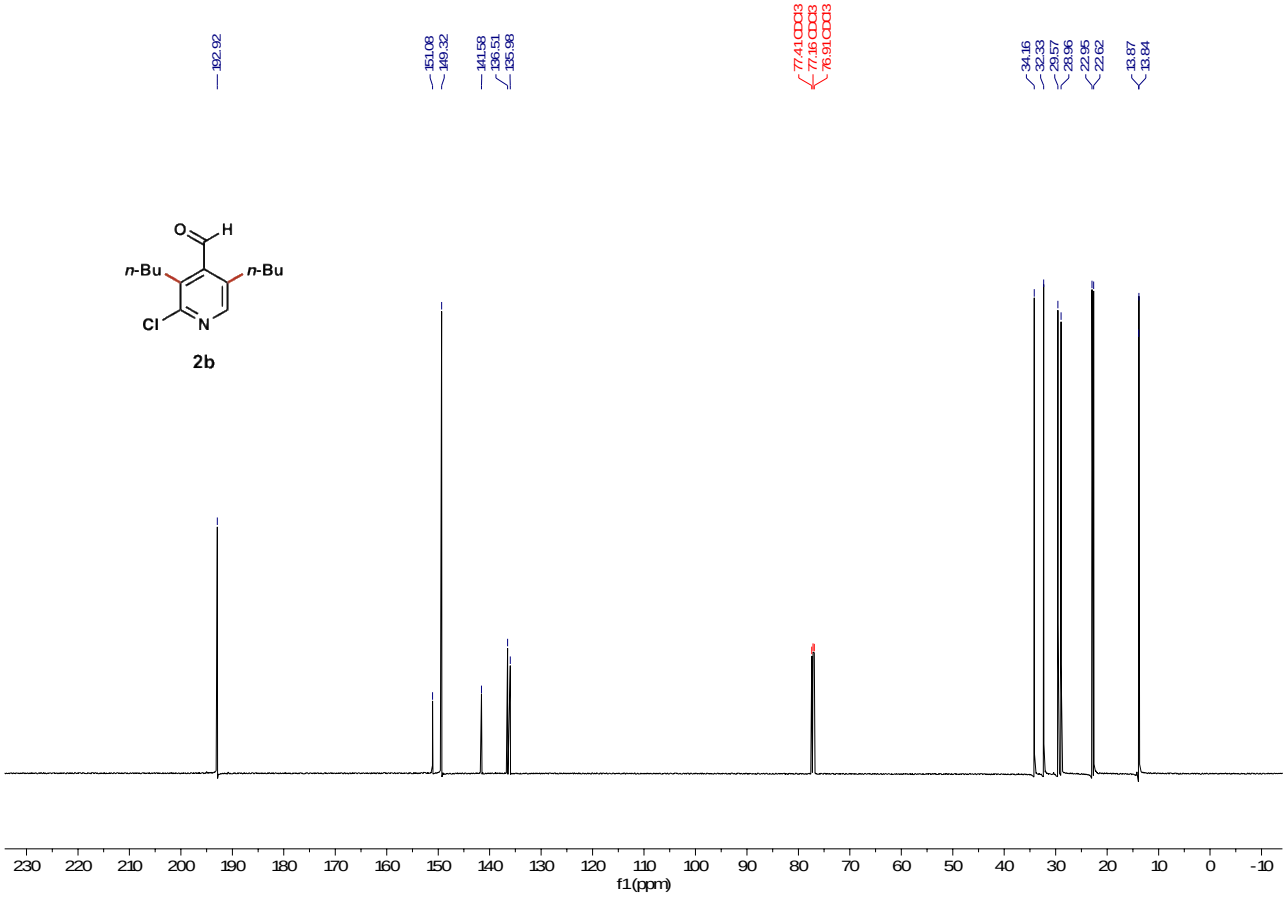
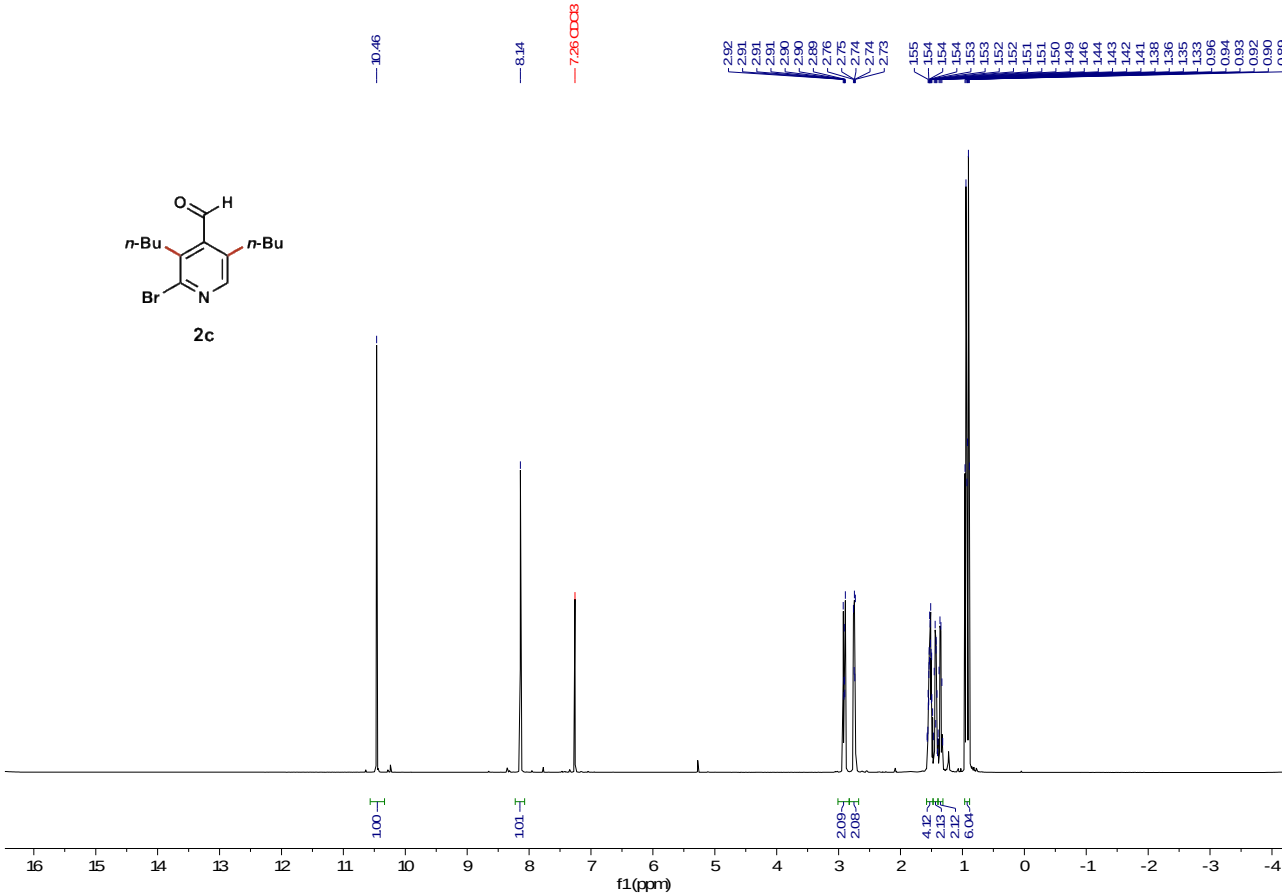
146.80
146.69
142.70
142.66
135.59
135.55
124.83
124.58
77.41
77.16
76.91
34.44
34.43
33.06
29.53
24.71
22.81
22.63
13.93
13.91
O
H
n-Bu
n-Bu
F
N
2a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-76.11
O
H
n-Bu
n-Bu
F
N
2a
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25
f1 (ppm)


10.49
8.16
7.26 CDCl3
1.00
1.00
2.05
2.05
4.08
2.09
2.10
5.92
f1 (ppm)
n-Bu
n-Bu
Cl
N
O
H
2b


192.92
151.08
149.32
141.58
136.51
135.98
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.16
32.33
29.57
28.96
22.95
22.62
13.87
13.84
f1 (ppm)
n-Bu
n-Bu
Cl
N
O
H
2b


10.46
8.14
7.26 CDCl3
n-Bu
n-Bu
Br
N
O
H
2c
1.00
1.01
2.09
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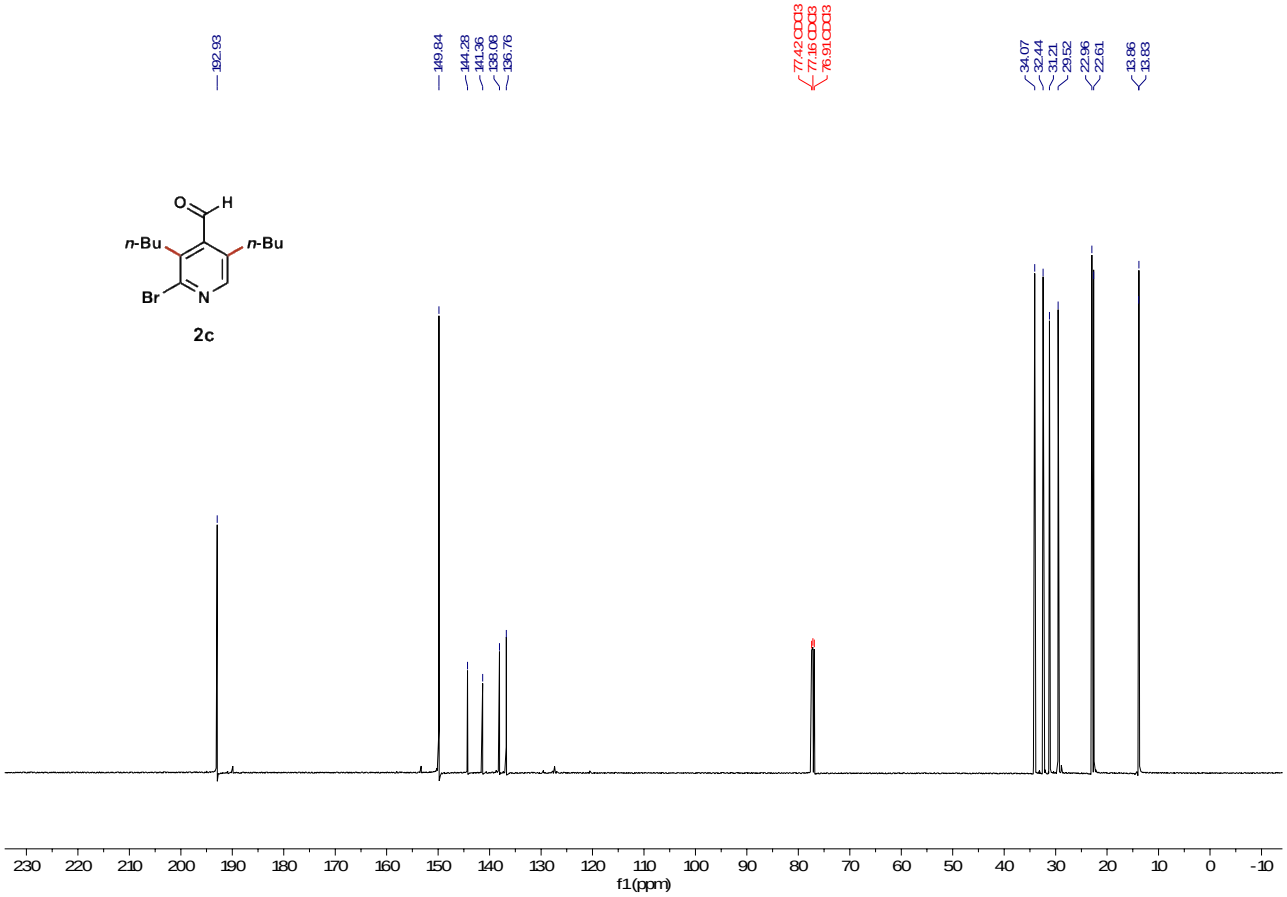
4.12
2.13
2.12
6.04
f1 (ppm)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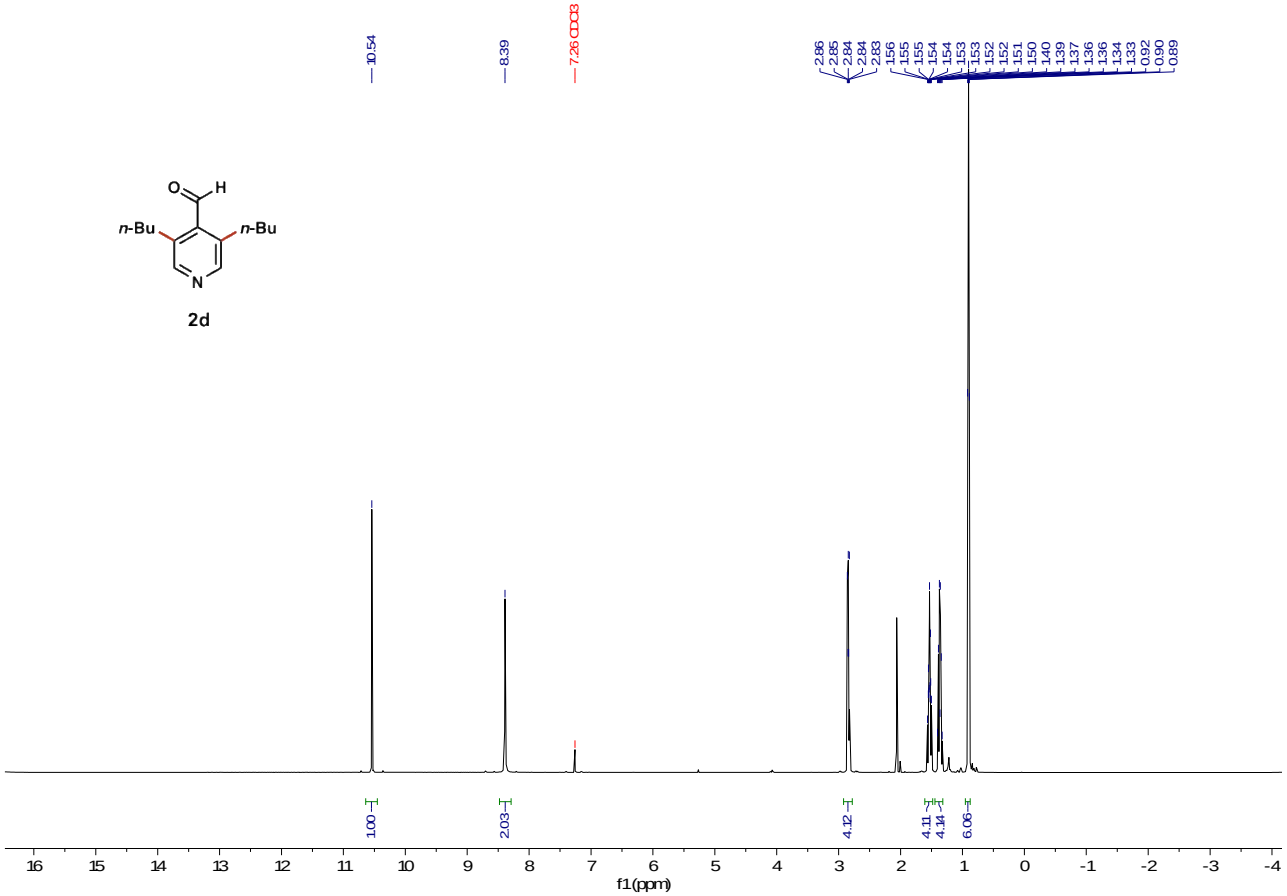
149.84
144.28
141.36
138.08
136.76
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
34.07
32.44
31.21
29.52
22.96
22.61
13.86
13.83
n-Bu
n-Bu
Br
N
O
H
2c
f1 (ppm)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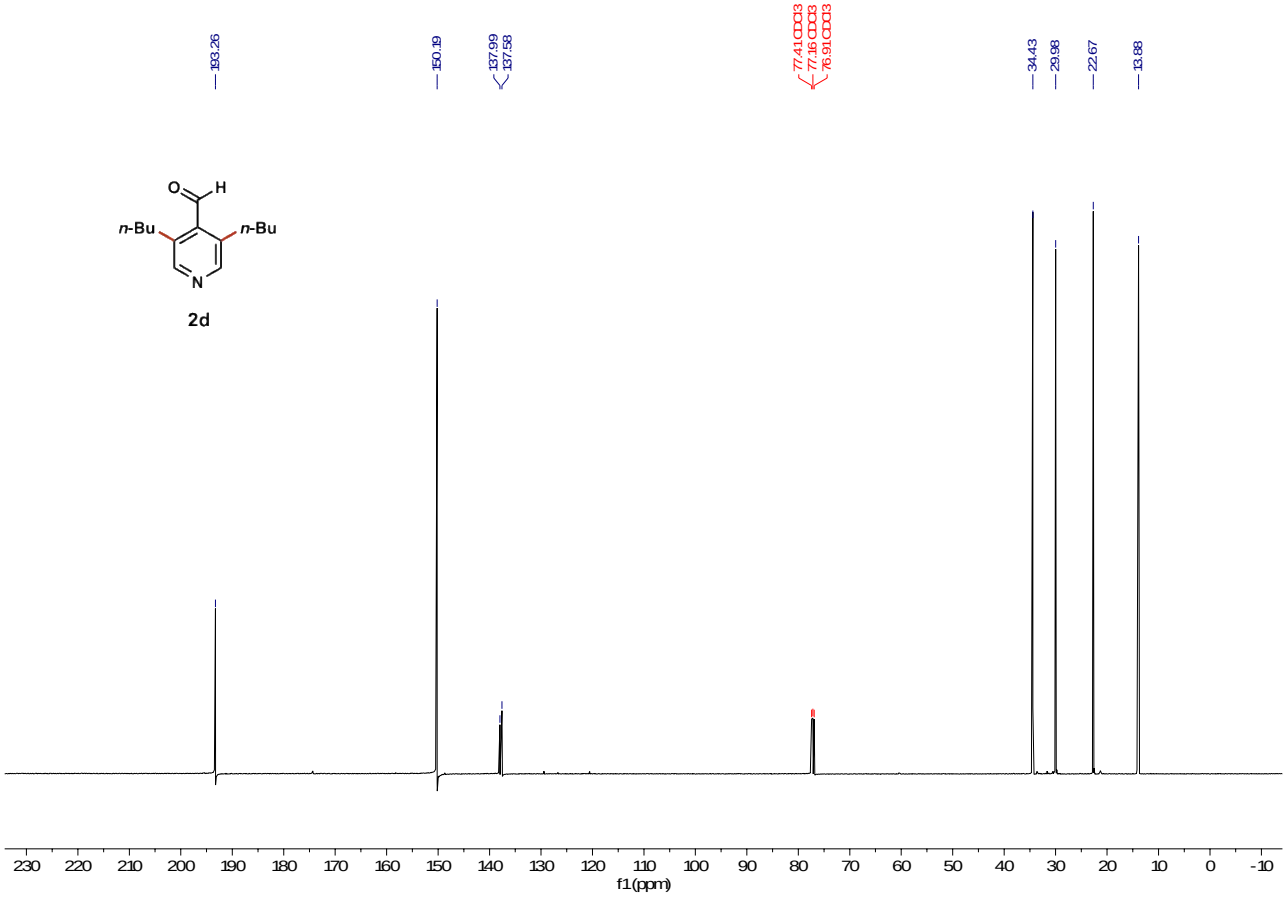
8.39
7.26 CDCl3
2.86
2.85
2.84
2.84
2.83
1.56
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.50
1.40
1.39
1.37
1.36
1.36
1.34
1.33
0.92
0.90
0.89
O
H
n-Bu
n-Bu
N
2d
1.00
2.03
4.12
4.11
4.14
6.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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150.19
137.99
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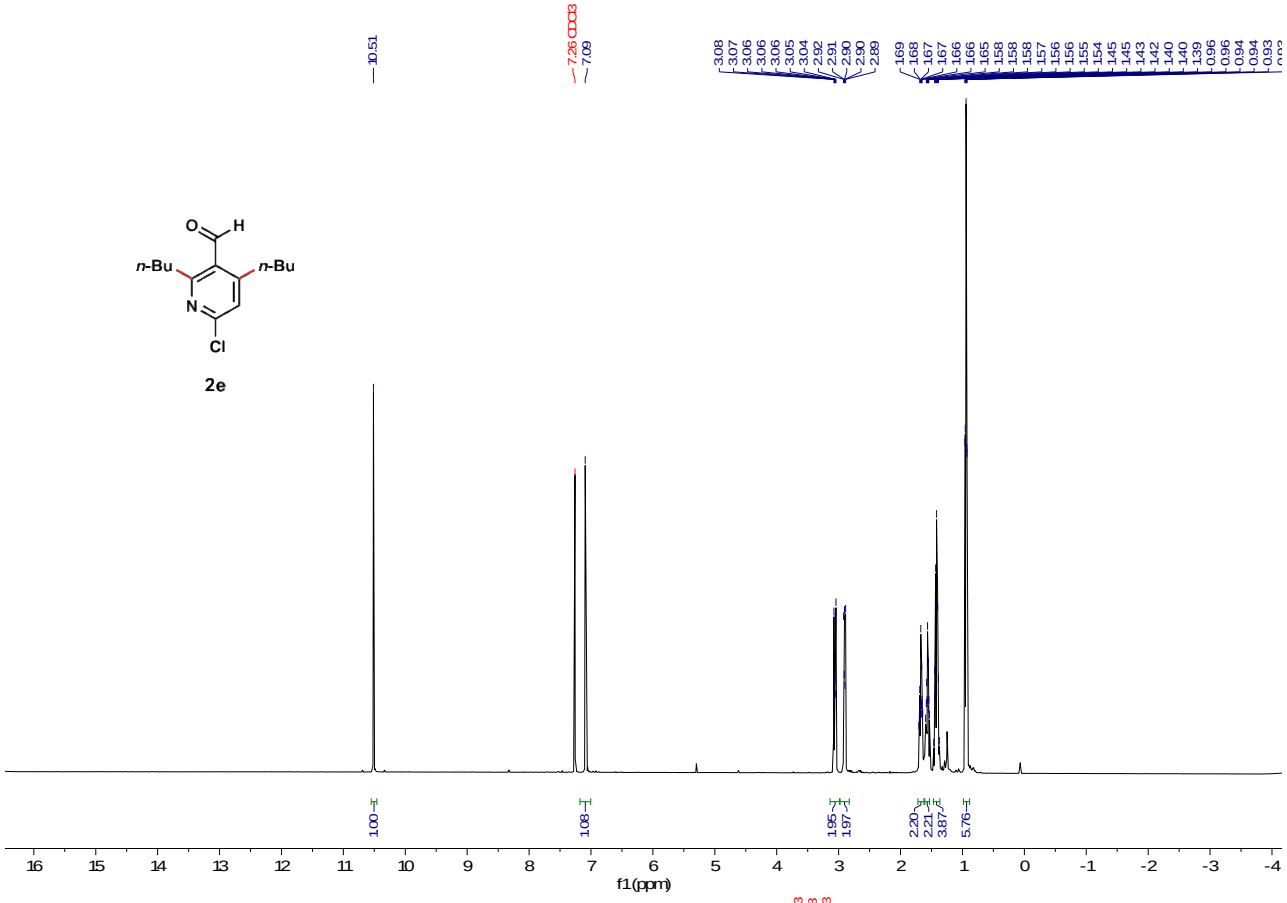
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.43
29.98
22.67
13.88
O
H
n-Bu
n-Bu
N
2d
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.26 CDCl3
7.09
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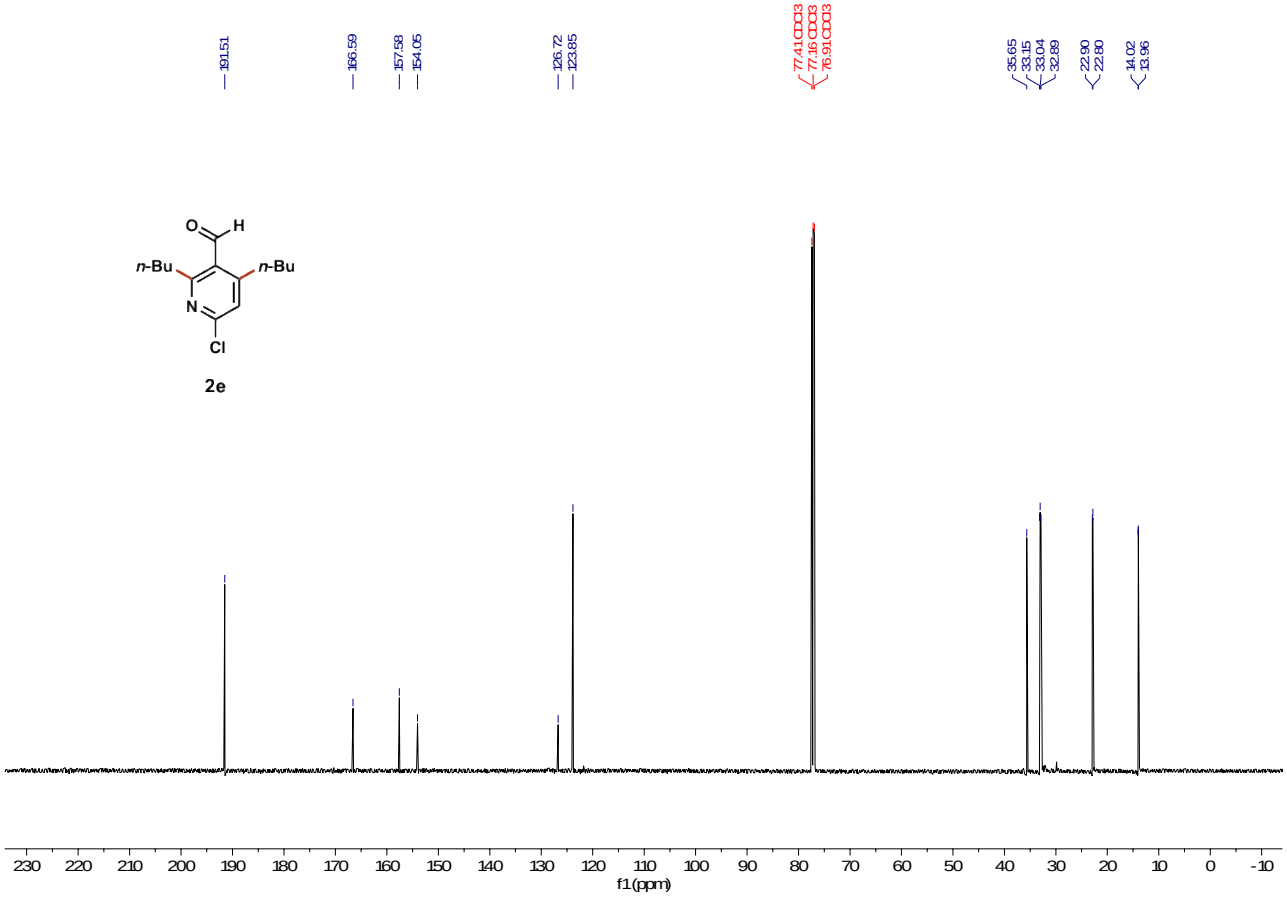
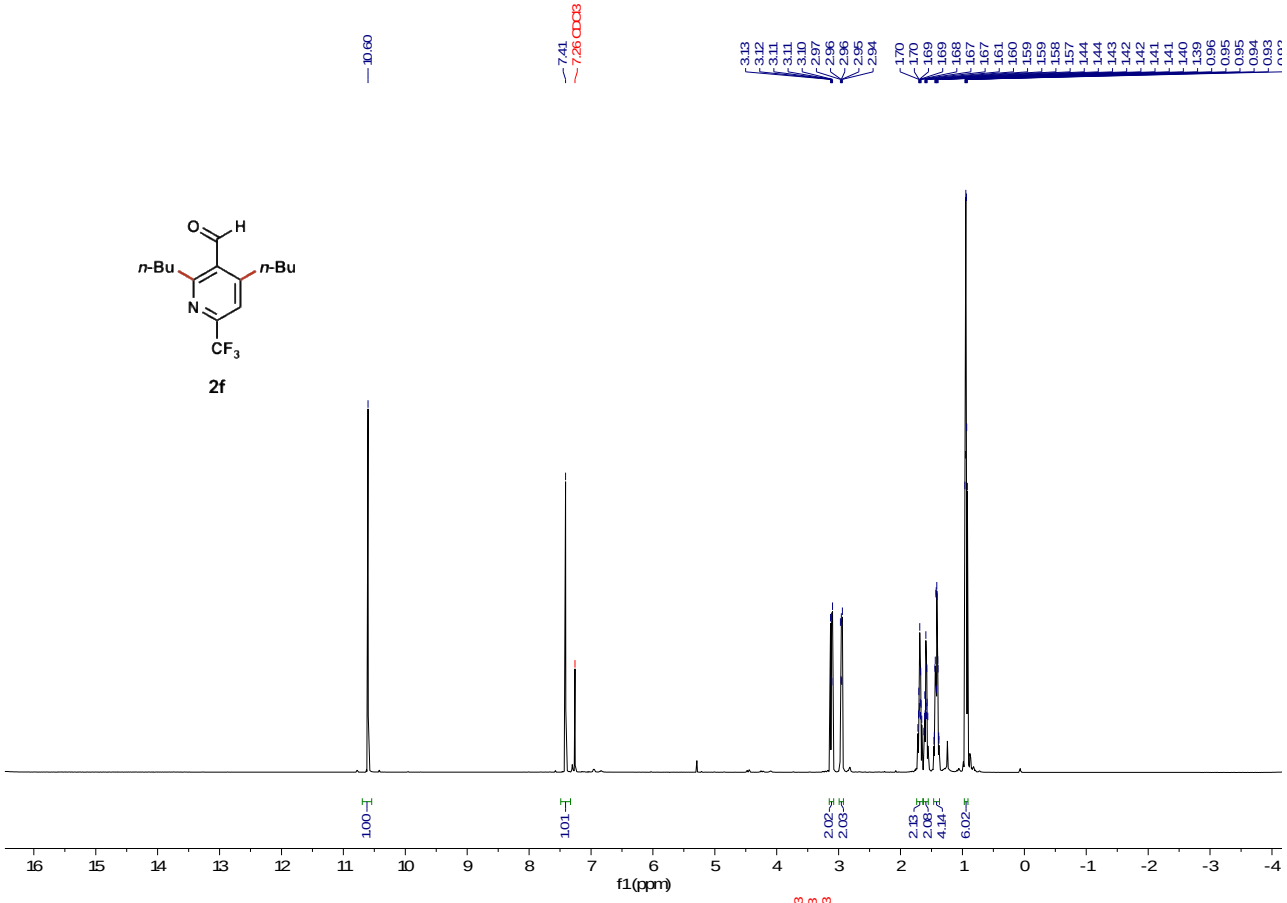
3.07
3.06
3.06
3.06
3.05
3.04
2.92
2.91
2.90
2.90
2.89
1.69
1.68
1.67
1.67
1.66
1.66
1.65
1.58
1.58
1.58
1.57
1.56
1.56
1.55
1.54
1.45
1.45
1.43
1.42
1.40
1.40
1.39
0.96
0.96
0.94
0.94
0.93
O
H
n-Bu
n-Bu
N
Cl
2e
1.00
1.08
1.95
1.97
2.20
2.21
3.87
5.76
f1 (ppm)


191.51
166.59
157.58
154.05
126.72
123.85
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
35.65
33.15
33.04
32.89
22.90
22.80
14.02
13.96
O
H
n-Bu
n-Bu
N
Cl
2e
f1 (ppm)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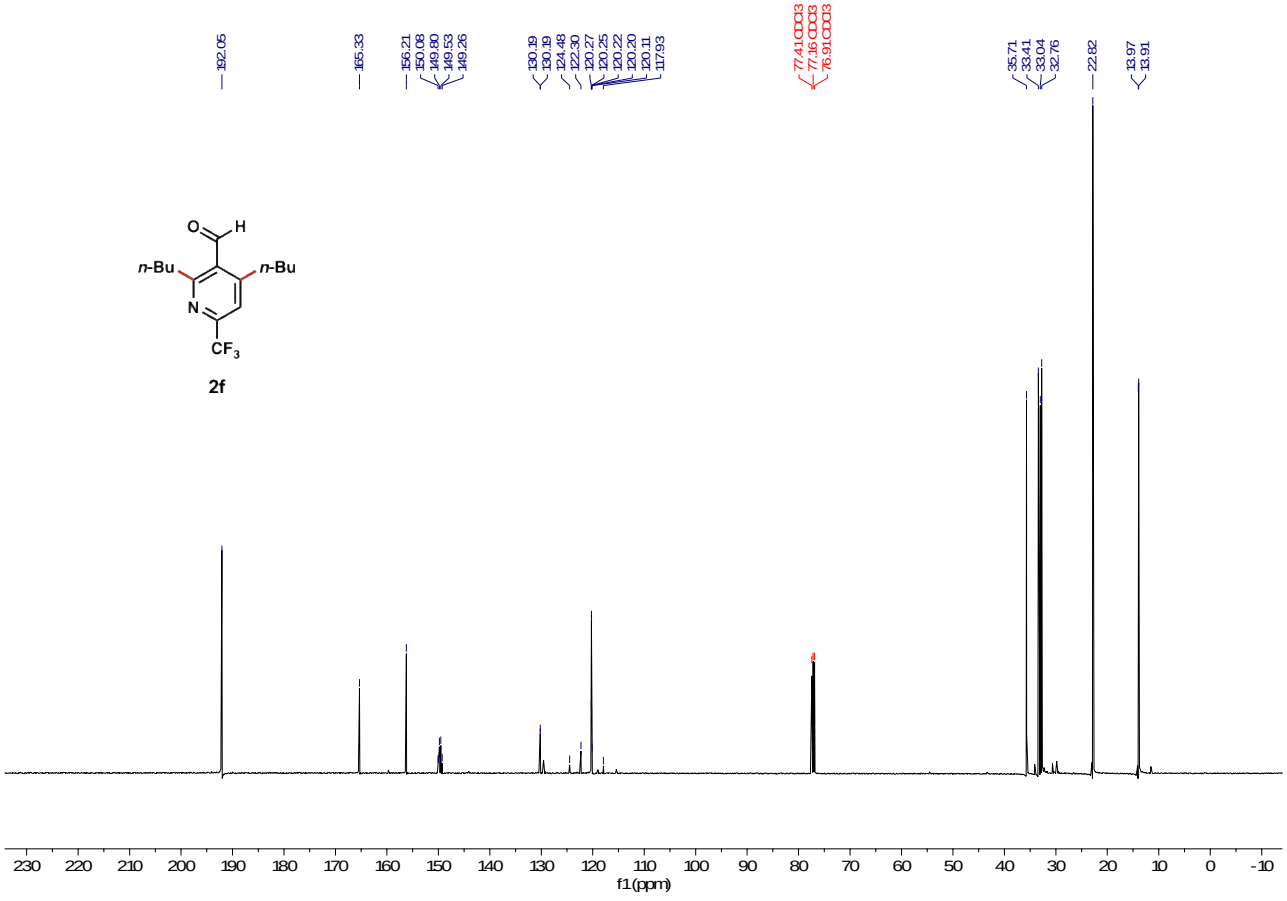
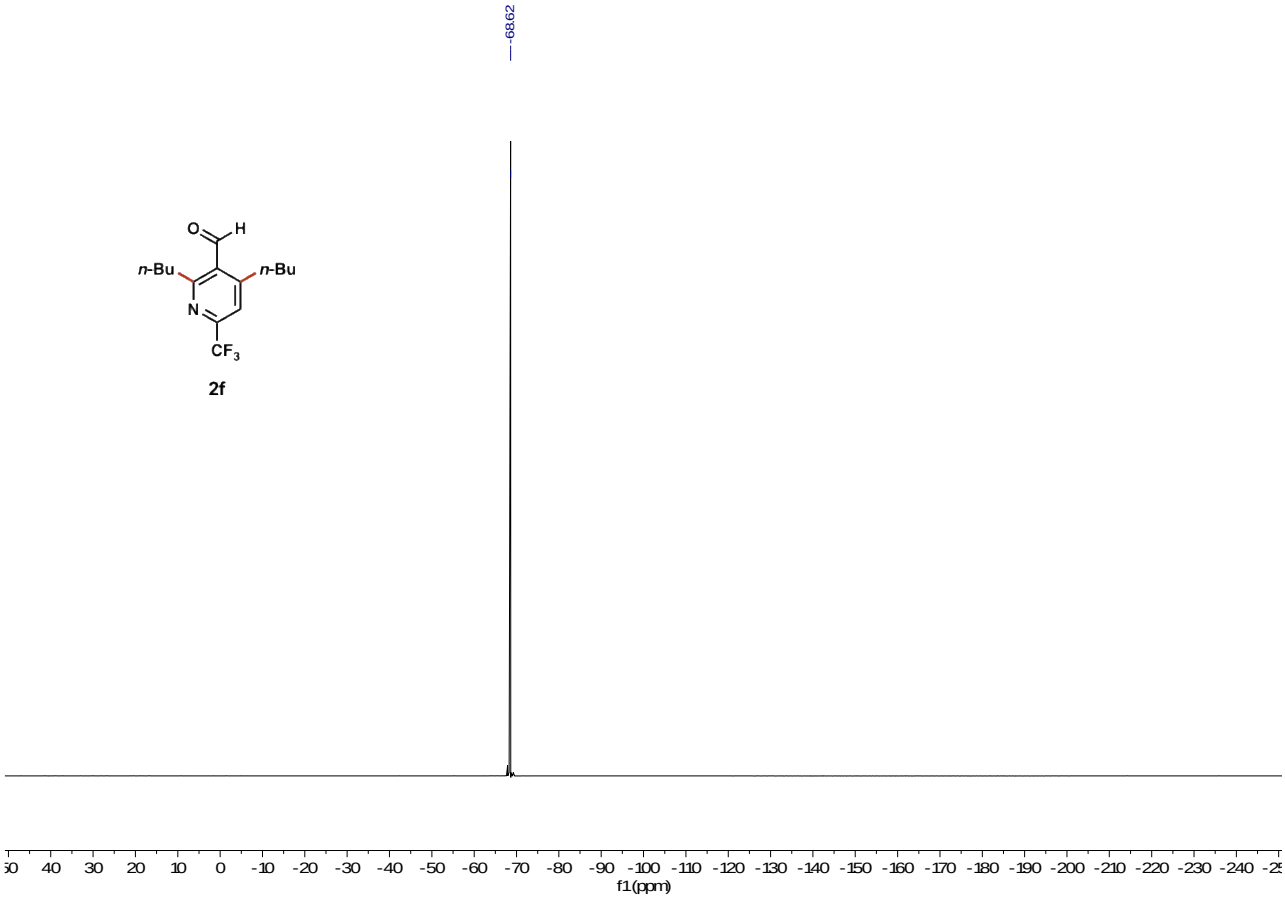
7.41
7.26 CDCl3
3.13
3.12
3.11
3.11
3.10
2.97
2.96
2.96
2.95
2.94
1.70
1.70
1.69
1.69
1.68
1.67
1.67
1.61
1.60
1.59
1.59
1.58
1.57
1.44
1.44
1.43
1.42
1.42
1.41
1.41
1.40
1.39
0.96
0.95
0.95
0.94
0.93
O
H
n-Bu
n-Bu
N
CF3
2f
1.00
1.01
2.02
2.03
2.13
2.08
4.14
6.02
f1 (ppm)


192.05
165.33
156.21
150.08
149.80
149.53
149.26
130.19
130.19
124.48
122.30
120.27
120.25
120.22
120.20
120.11
117.93
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
35.71
33.41
33.04
32.76
22.82
13.97
13.91
O
H
n-Bu
n-Bu
N
CF3
2f
f1 (ppm)


-68.62
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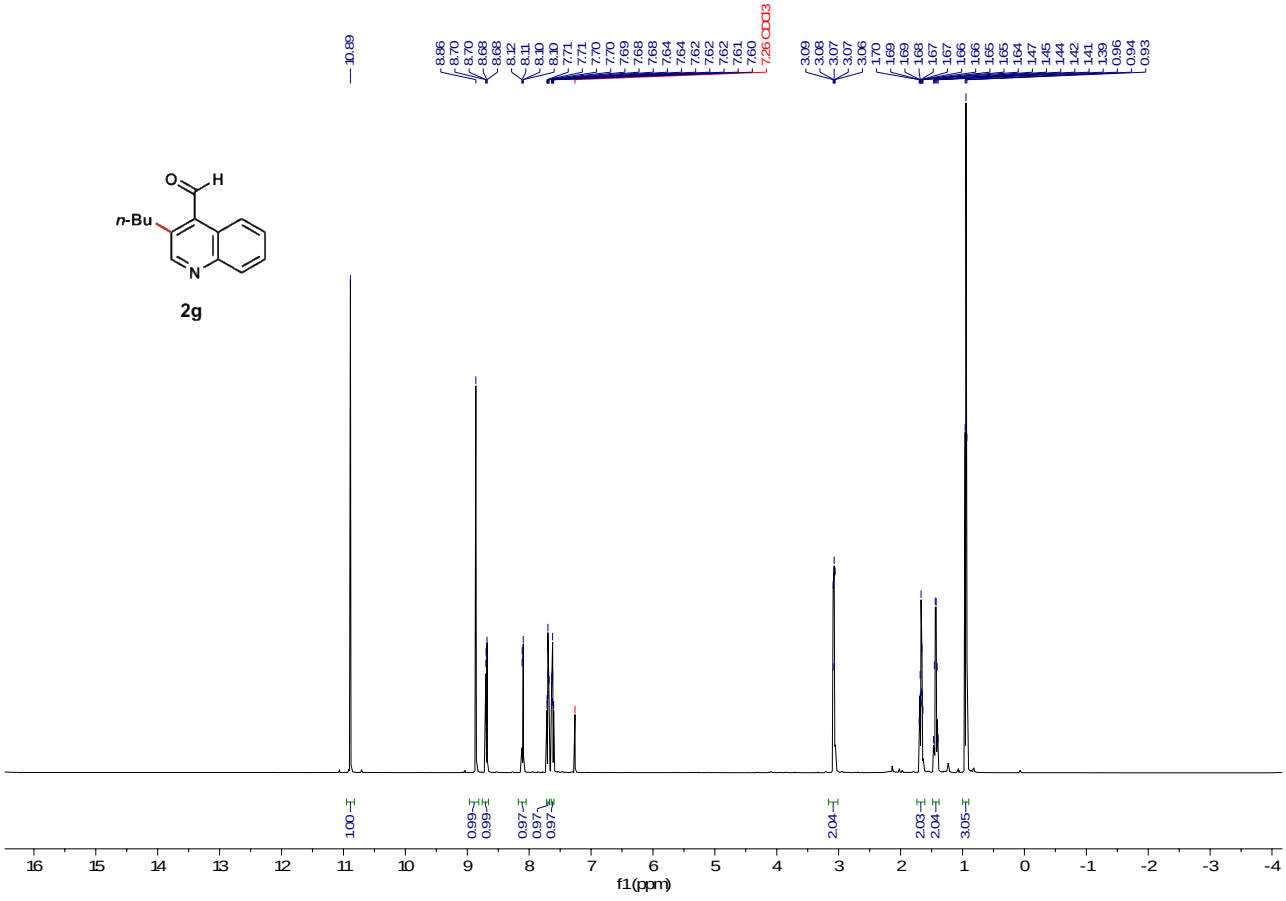
2f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8.68
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7.69
7.69
7.68
7.68
7.64
7.64
7.62
7.62
7.62
7.61
7.60
7.26 CDCl3
3.09
3.08
3.07
3.07
3.07
3.06
1.70
1.69
1.69
1.68
1.67
1.67
1.66
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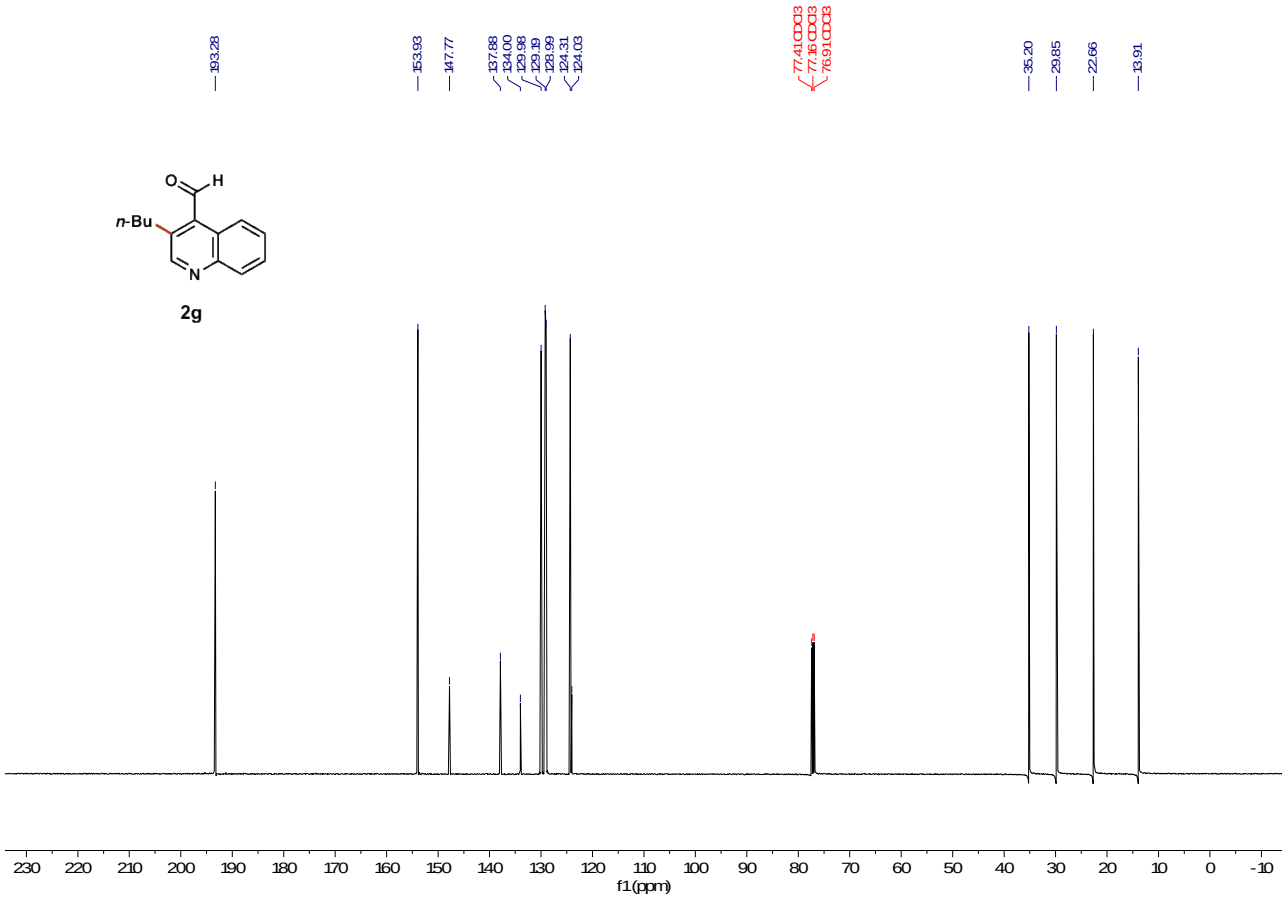
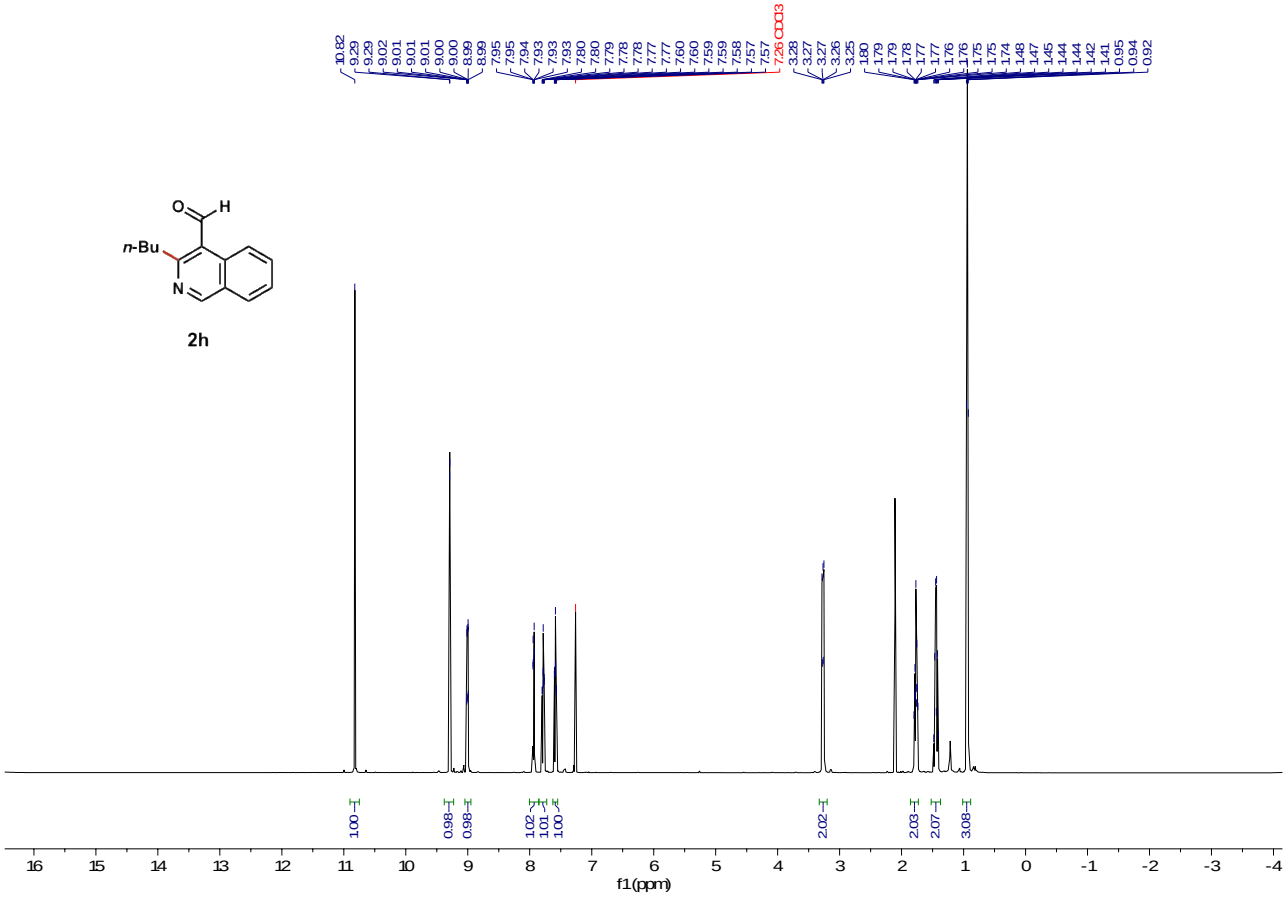
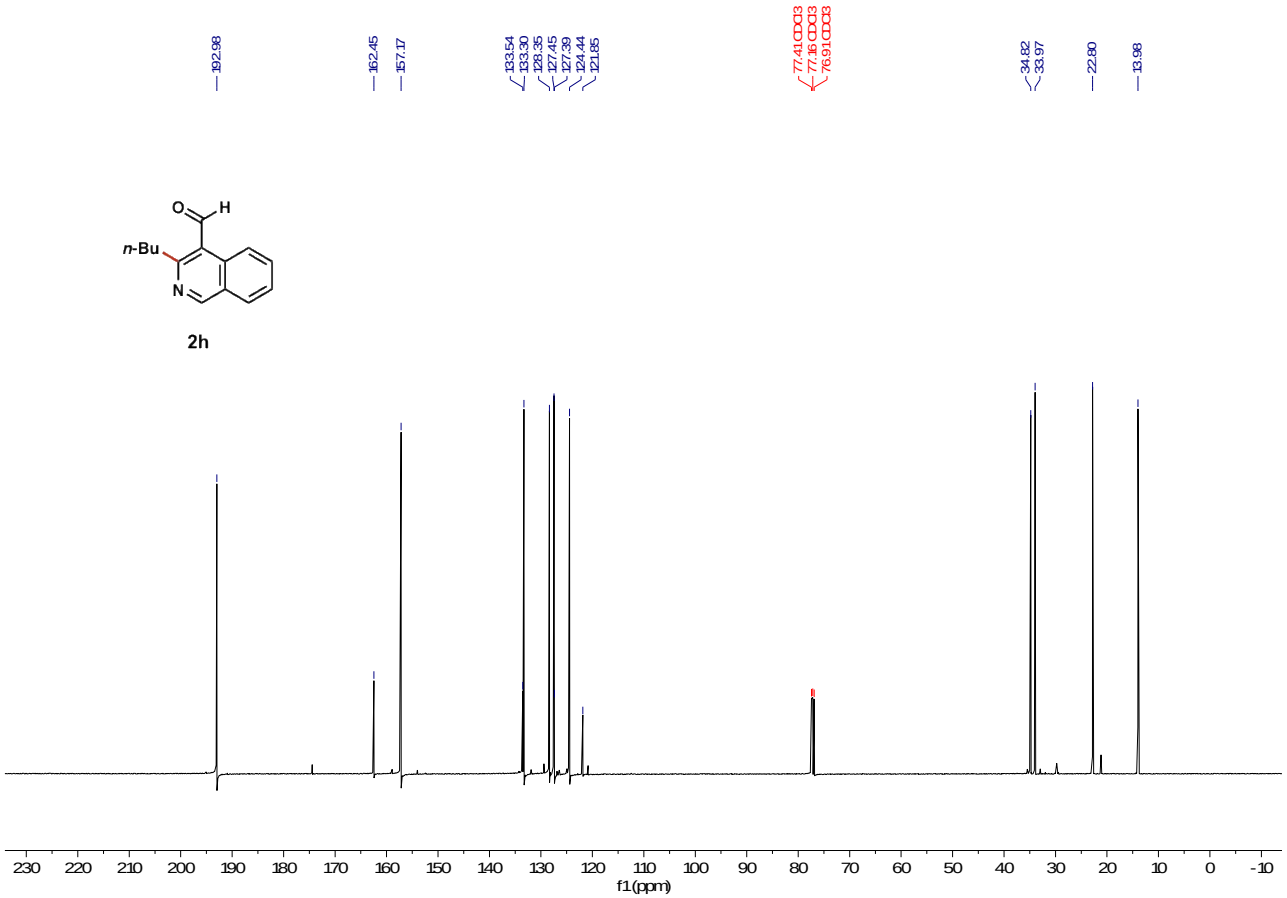
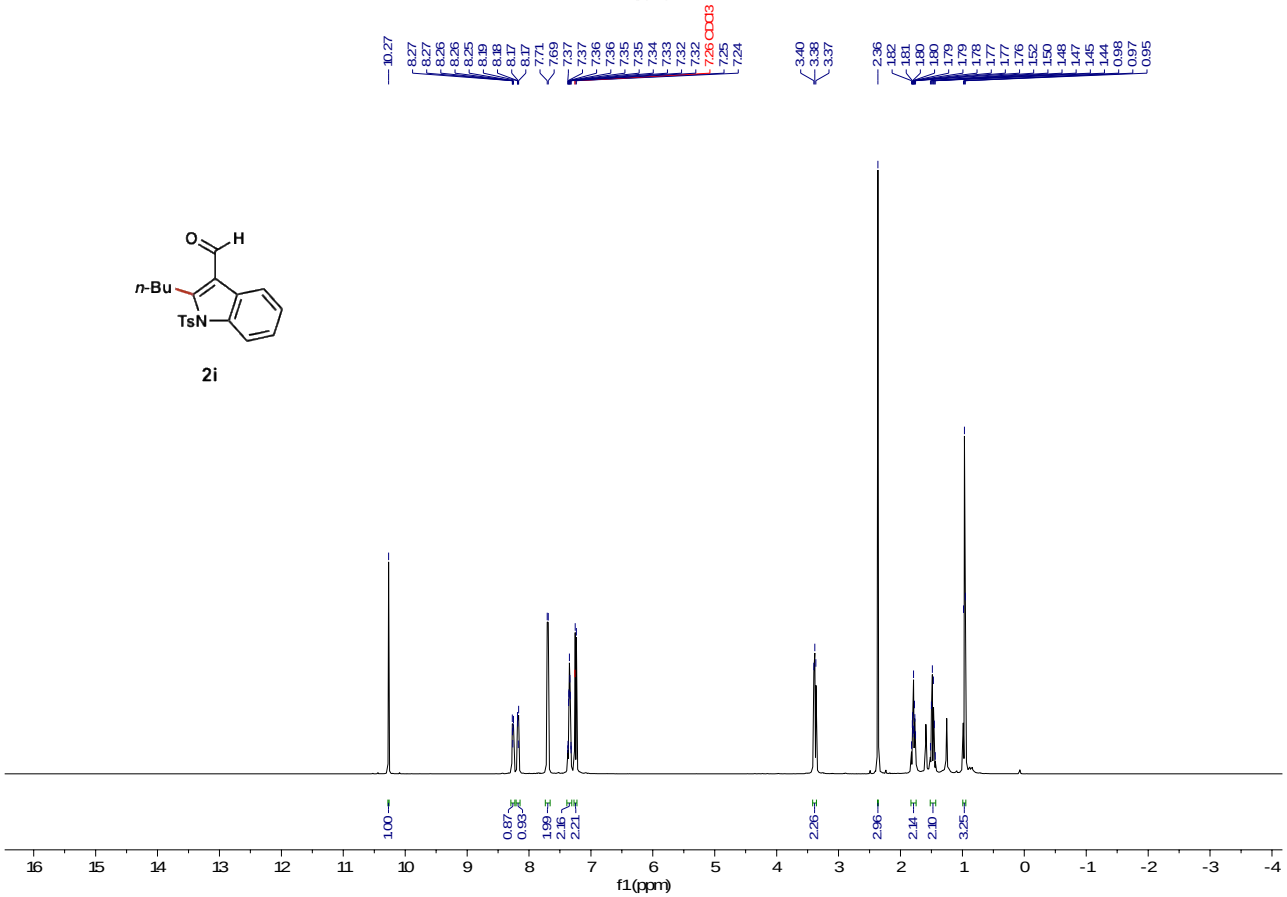
1.65
1.64
1.47
1.45
1.44
1.42
1.41
1.39
0.96
0.94
0.93
1.00
0.99
0.99
0.97
0.97
0.97
2.04
2.03
2.04
3.05
f1 (ppm)

2g


193.28
153.93
147.77
137.88
134.00
129.98
129.49
128.99
124.31
124.03
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
35.20
29.85
22.66
13.91
O
H
n-Bu
N
2g
f1 (ppm)


10.82
9.29
9.29
9.02
9.01
9.01
9.01
9.00
9.00
8.99
8.99
7.95
7.95
7.94
7.93
7.93
7.93
7.80
7.80
7.79
7.78
7.78
7.77
7.77
7.77
7.60
7.60
7.59
7.59
7.58
7.57
7.57
7.26 CDCl3
3.28
3.27
3.27
3.26
3.25
1.80
1.79
1.79
1.78
1.77
1.77
1.77
1.76
1.76
1.76
1.75
1.75
1.74
1.48
1.47
1.45
1.44
1.44
1.42
1.41
0.95
0.94
0.92
O
H
n-Bu
N
2h
1.00
0.98
0.98
1.02
1.01
1.00
2.02
2.03
2.07
3.08
f1 (ppm)


192.98
162.45
157.17
133.54
133.30
128.35
127.45
127.39
124.44
121.85
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.82
33.97
22.80
13.98
O
H
n-Bu
N
2h
f1 (ppm)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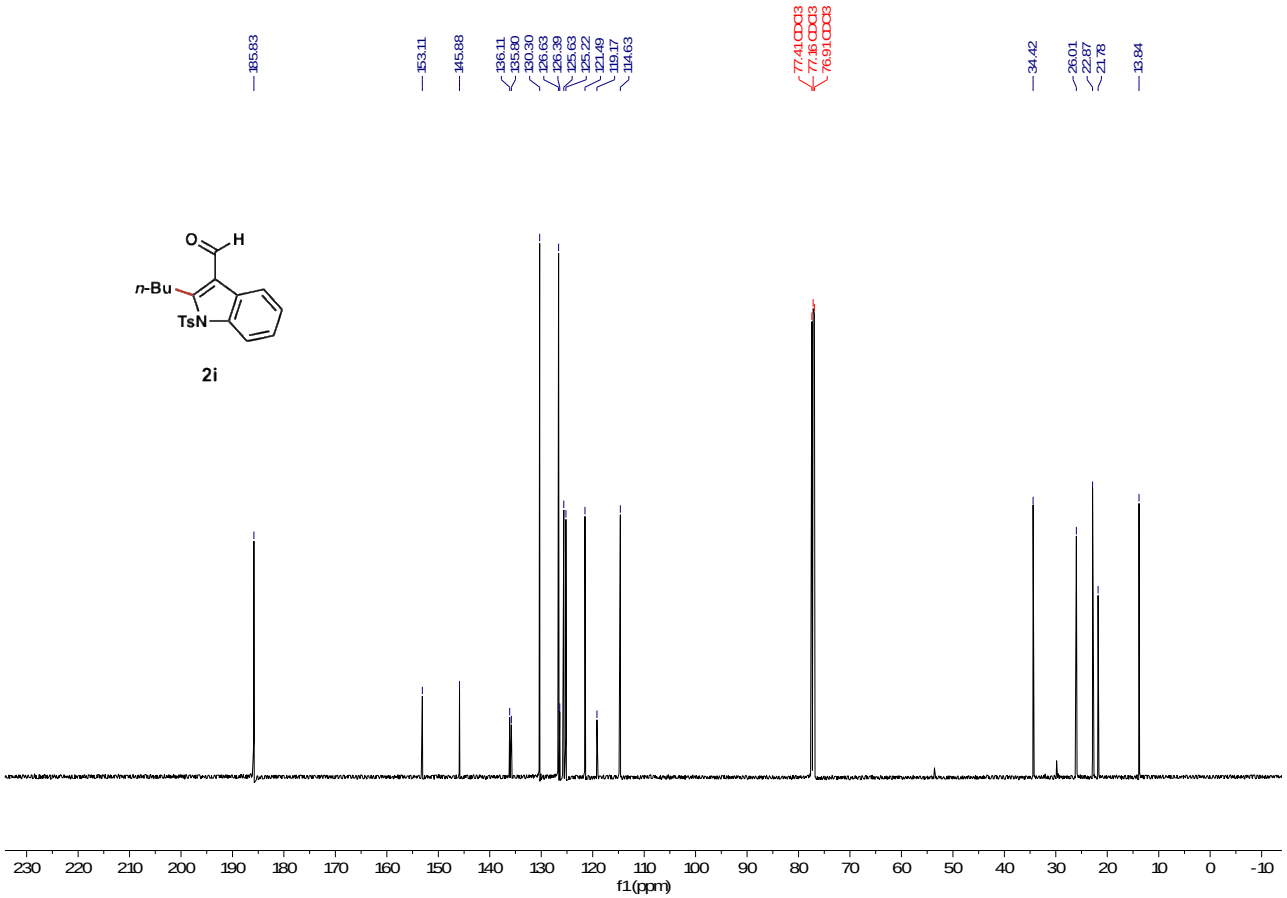
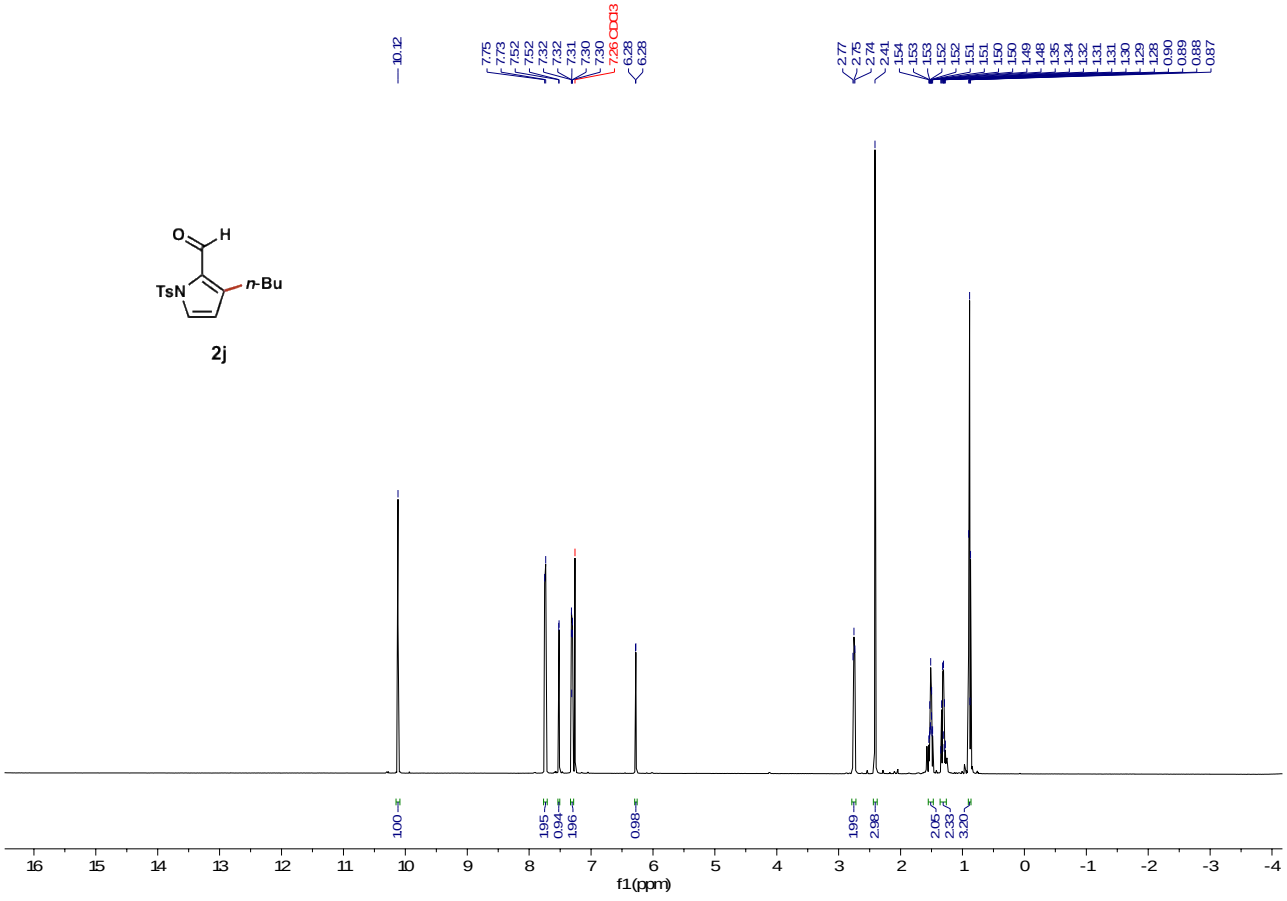
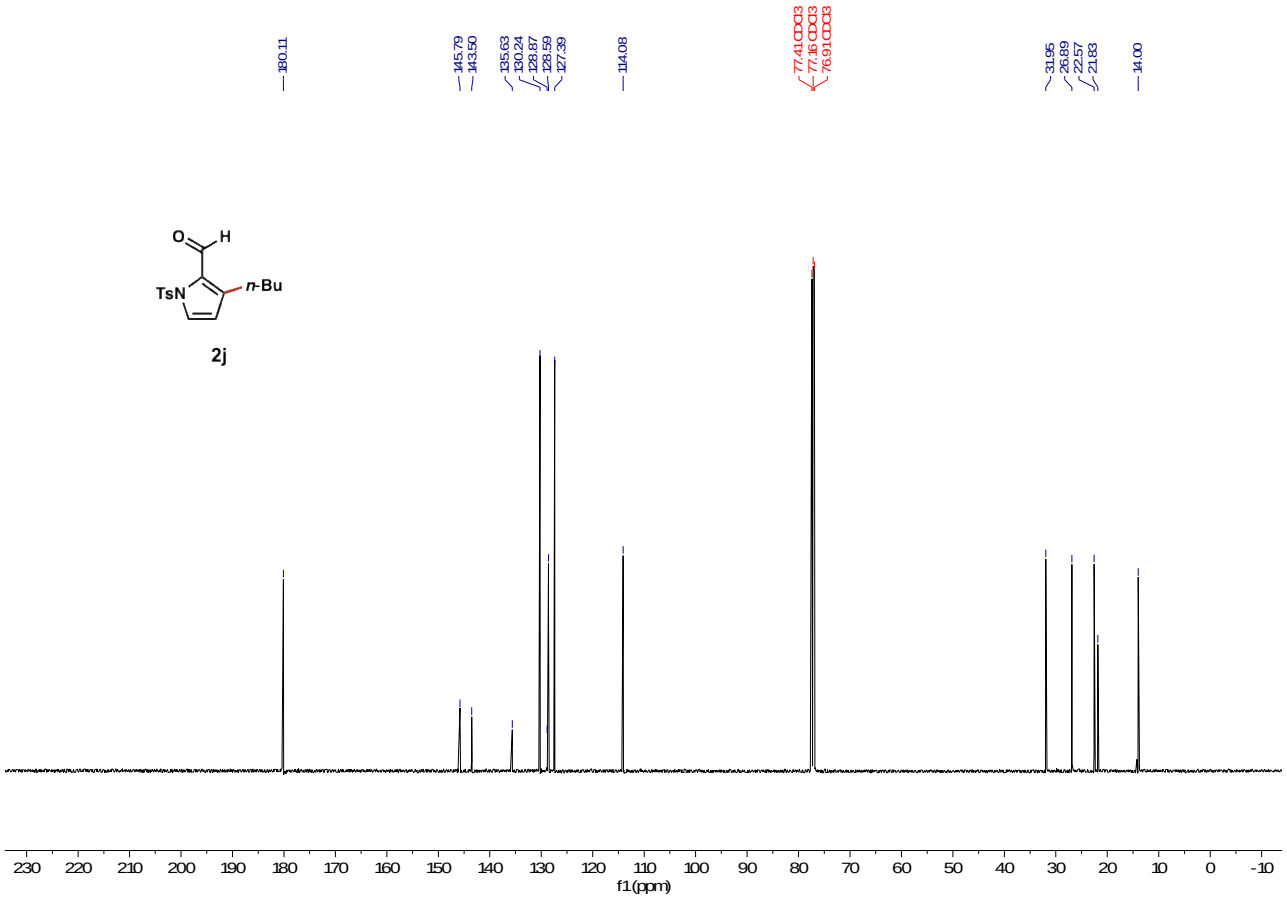
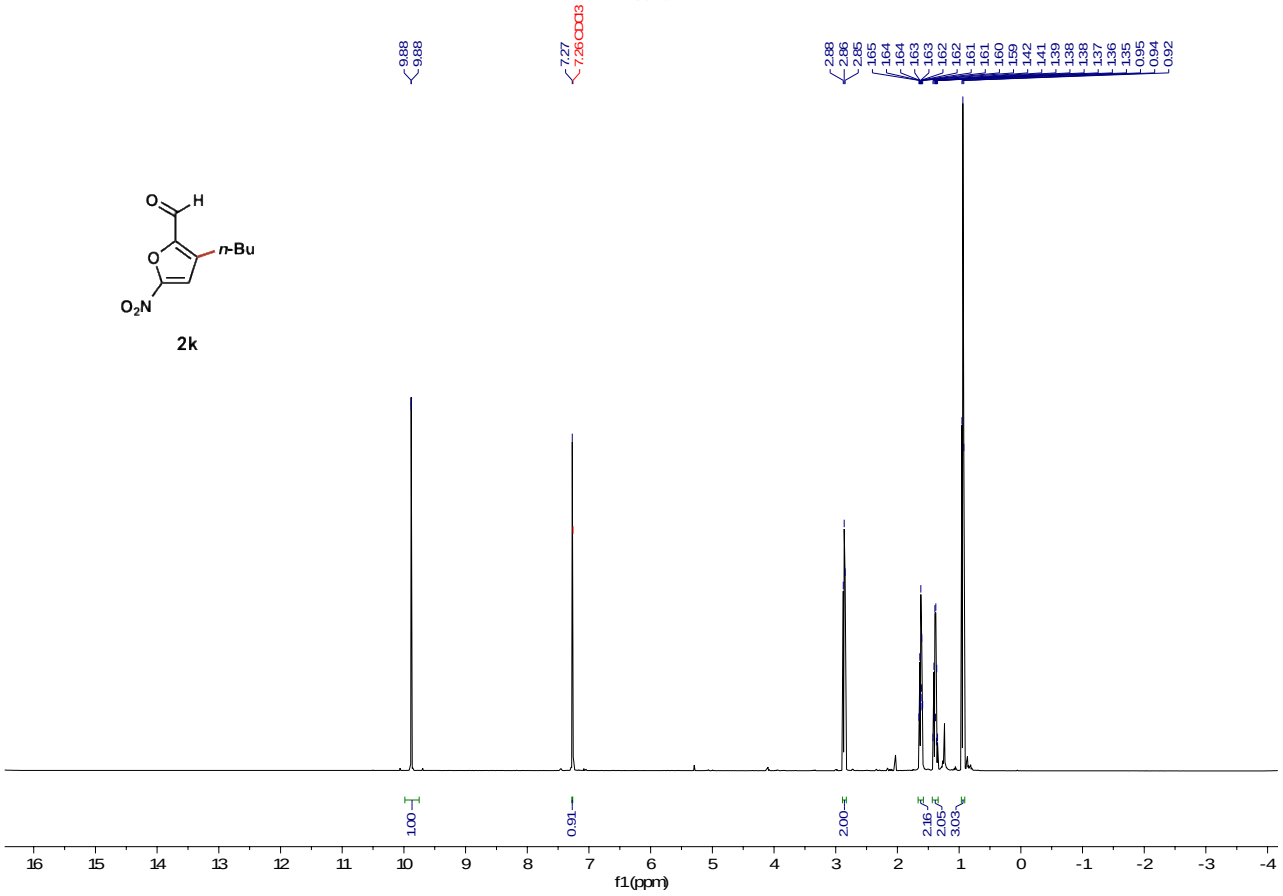
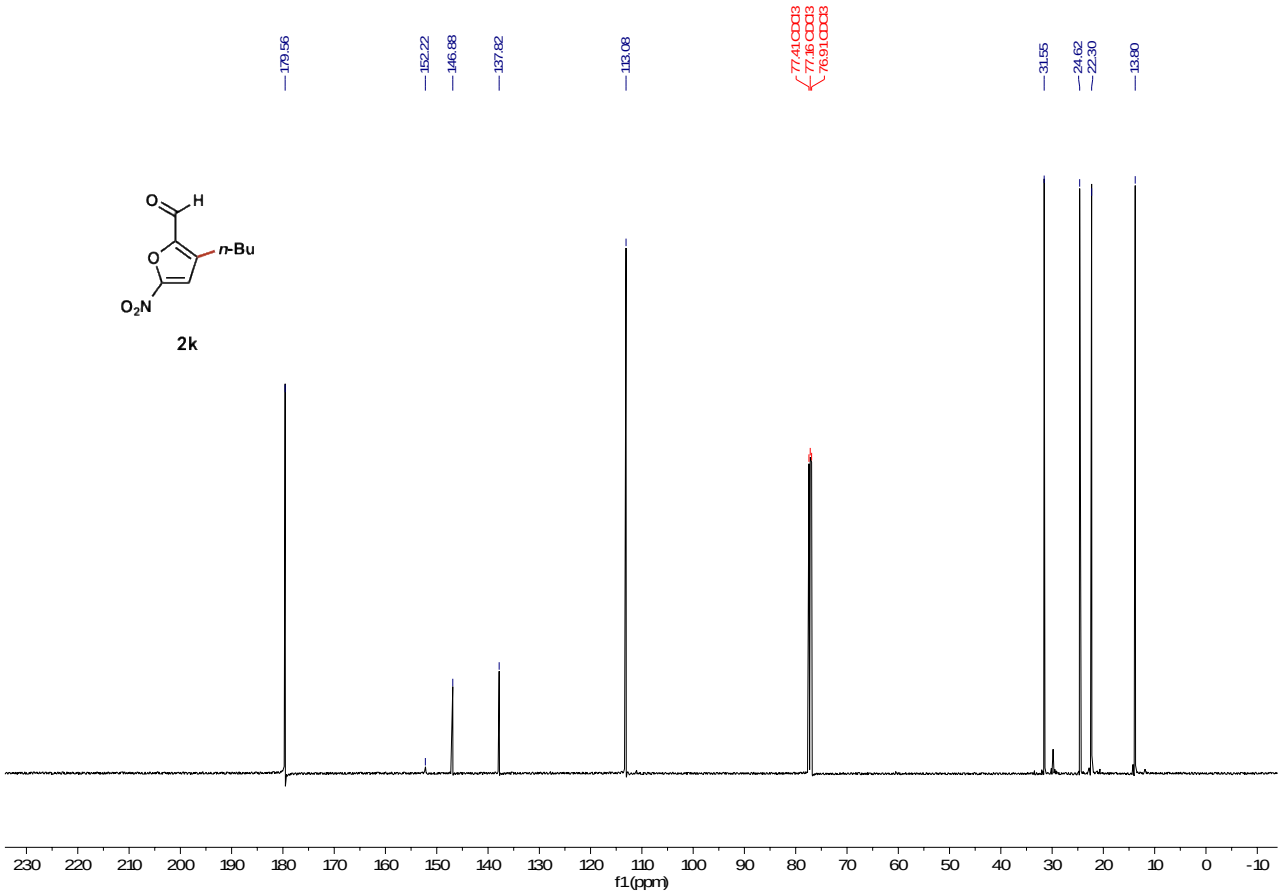
8.27
8.26
8.26
8.25
8.19
8.18
8.17
8.17
7.71
7.69
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.26 CDCl3
7.25
7.24
3.40
3.38
3.37
2.36
1.82
1.81
1.80
1.80
1.79
1.79
1.78
1.77
1.77
1.77
1.76
1.52
1.50
1.48
1.47
1.45
1.44
0.98
0.97
0.95
O
H
n-Bu
TsN
2i
1.00
0.87
0.93
1.99
2.16
2.21
2.26
2.96
2.14
2.10
3.25
f1 (ppm)

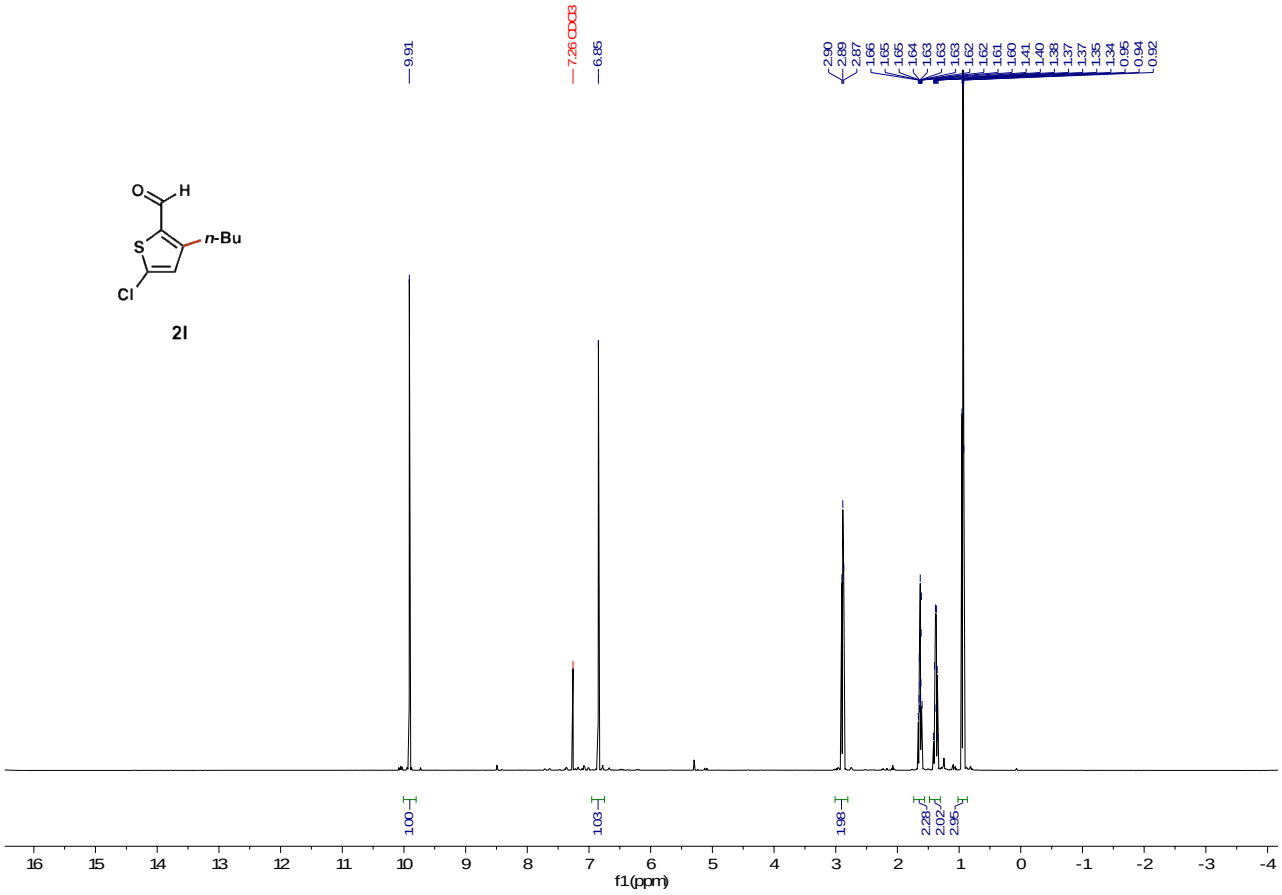

185.83
153.11
145.88
136.11
135.80
130.30
126.63
126.39
125.63
125.22
121.49
119.17
114.63
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
34.42
26.01
22.87
21.78
13.84
O
H
n-Bu
TsN
2i
f1 (ppm)

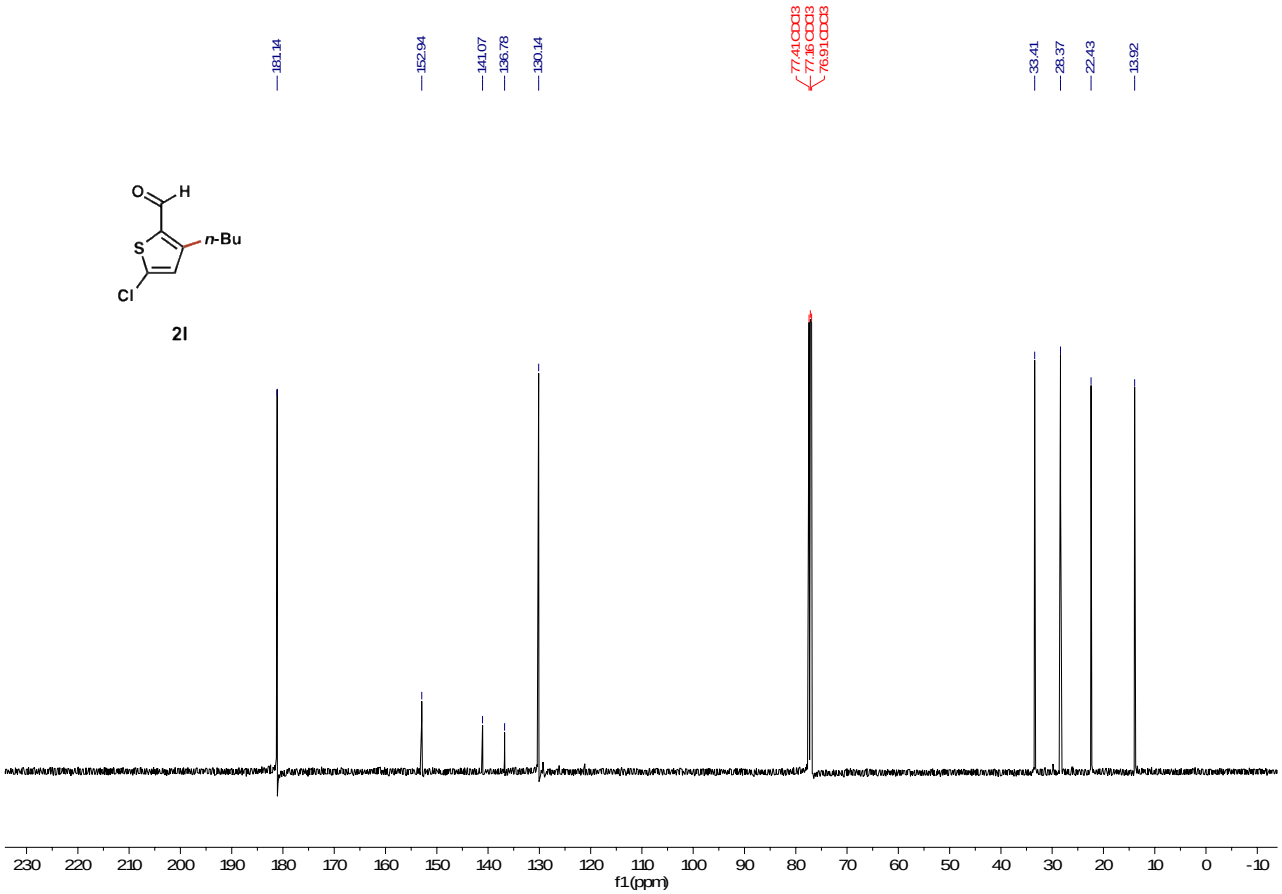

10.12
7.75
7.73
7.52
7.52
7.32
7.32
7.31
7.30
7.30
7.26 CDCl3
6.28
6.28
2.77
2.75
2.74
2.41
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.50
1.50
1.49
1.48
1.35
1.34
1.32
1.31
1.31
1.30
1.29
1.28
0.90
0.89
0.88
0.87
1.00
1.95
0.94
1.96
0.98
1.99
2.98
2.05
2.33
3.20
O
H
TsN
n-Bu
2j
f1 (ppm)

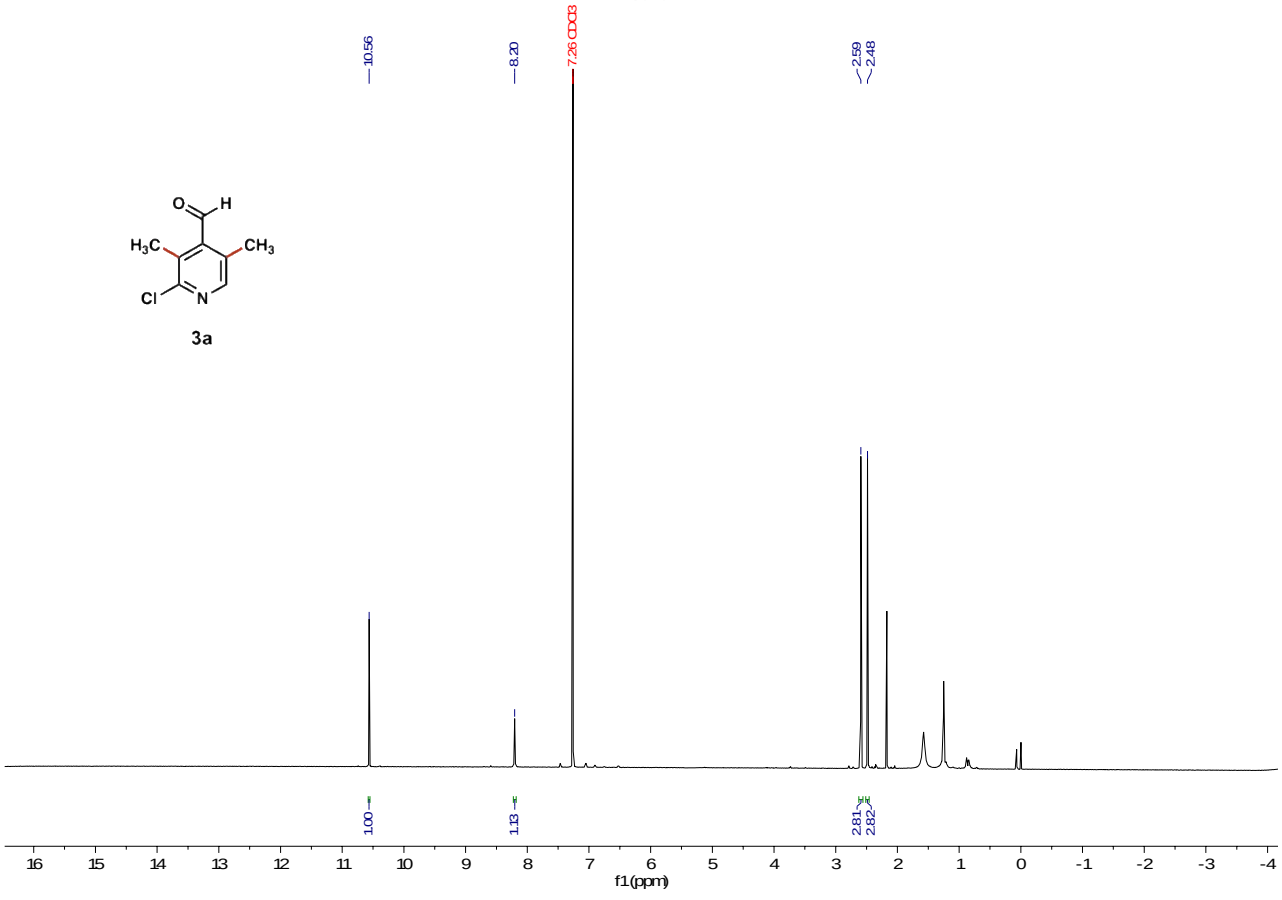

180.11
145.79
143.50
135.63
130.24
128.87
128.59
127.39
114.08
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
31.95
26.89
22.57
21.83
14.00
O
H
TsN
n-Bu
2j
f1 (ppm)

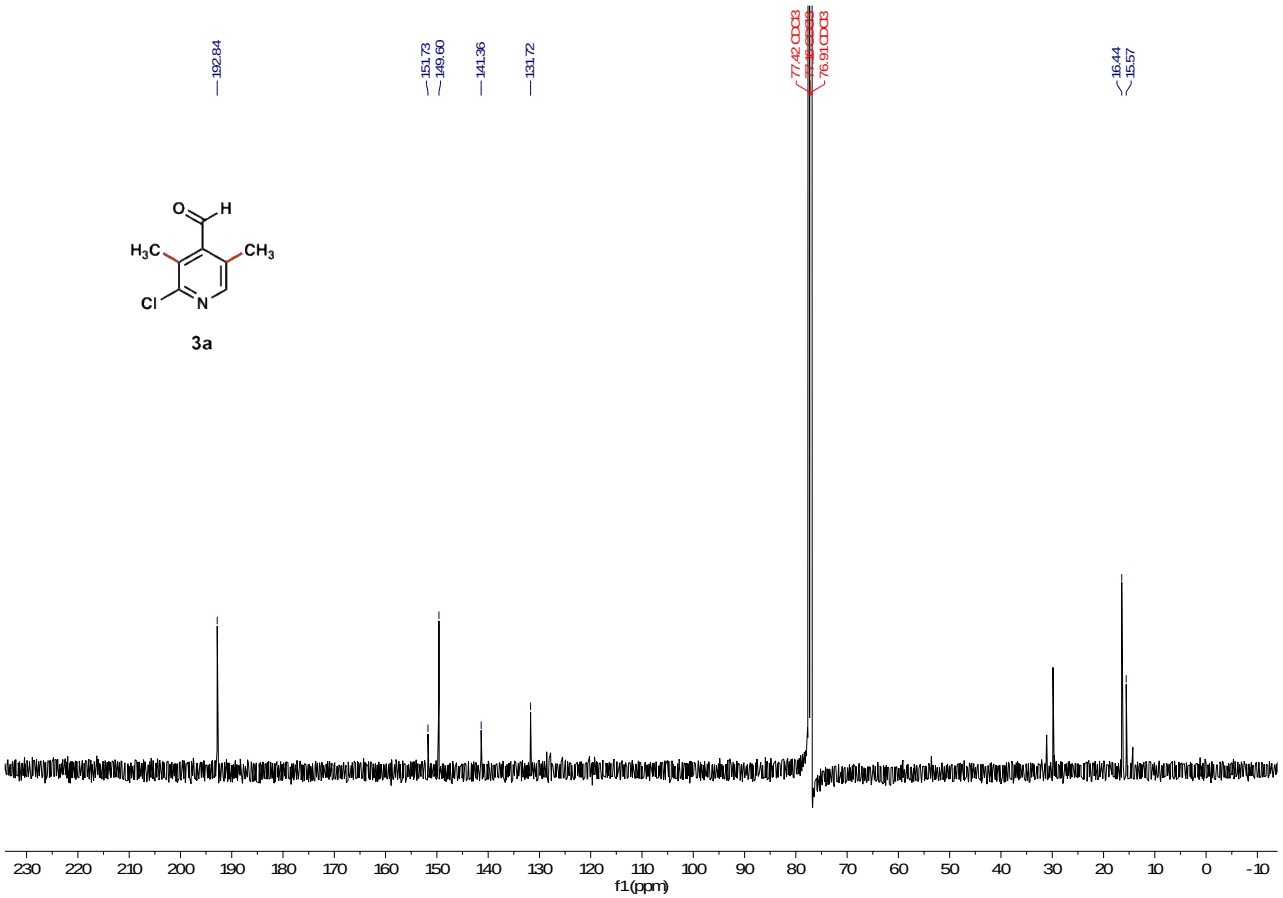

9.88
9.88
7.27
7.26 CDCl3
2.88
2.86
2.85
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.61
1.61
1.60
1.59
1.42
1.41
1.39
1.38
1.38
1.37
1.36
1.35
0.95
0.94
0.92
O
H
O
n-Bu
O2N
2k
1.00
0.91
2.00
2.16
2.05
3.03
f1 (ppm)

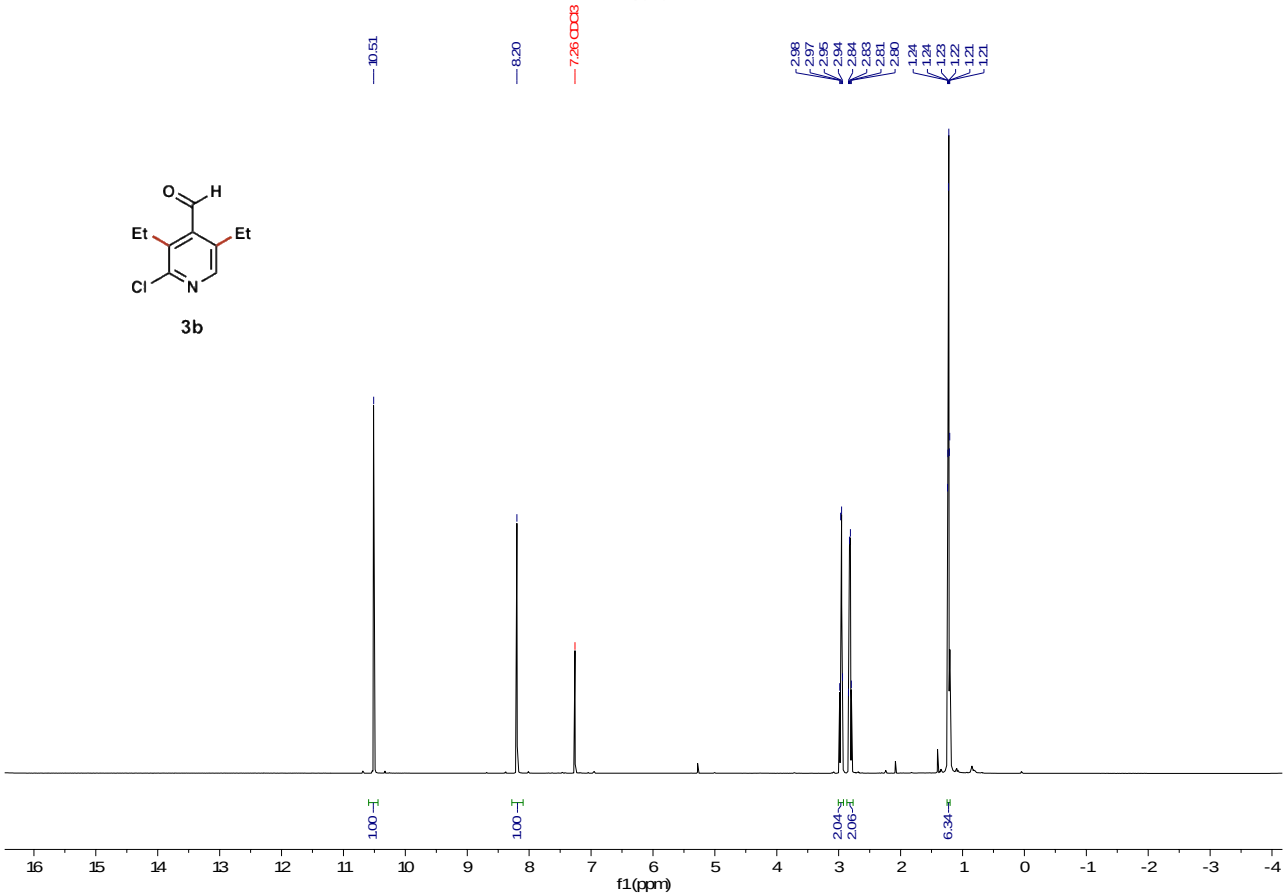

179.56
152.22
146.88
137.82
113.08
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
31.55
24.62
22.30
13.90
O
H
O
n-Bu
O2N
2k
f1 (ppm)

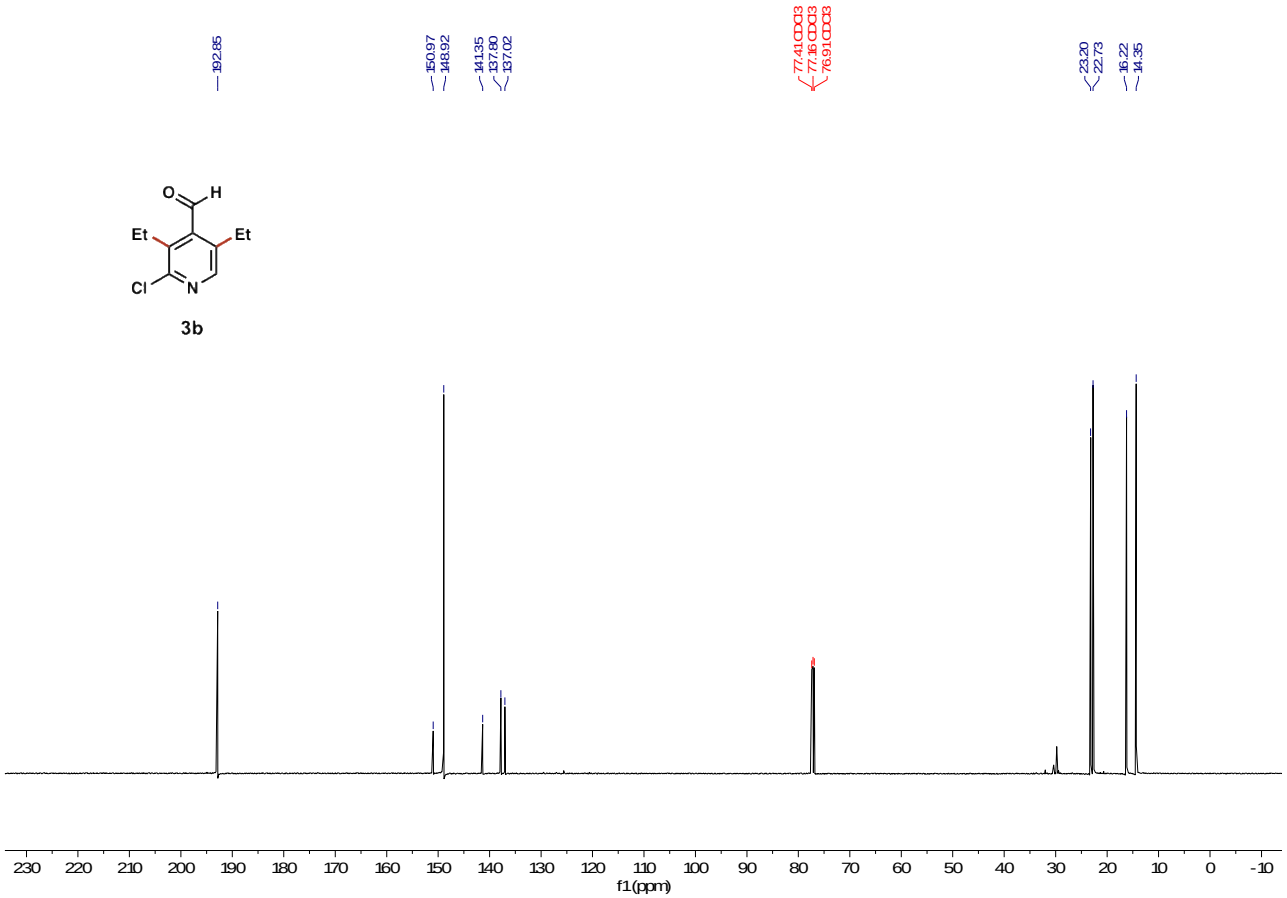

9.91
7.26 CDCl3
6.85
2.90
2.89
2.87
1.66
1.65
1.65
1.64
1.63
1.63
1.63
1.62
1.62
1.61
1.60
1.41
1.40
1.38
1.37
1.37
1.35
1.34
0.95
0.94
0.92
O
H
S
n-Bu
Cl
2l
1.00
1.03
1.98
2.28
2.02
2.95
f1 (ppm)

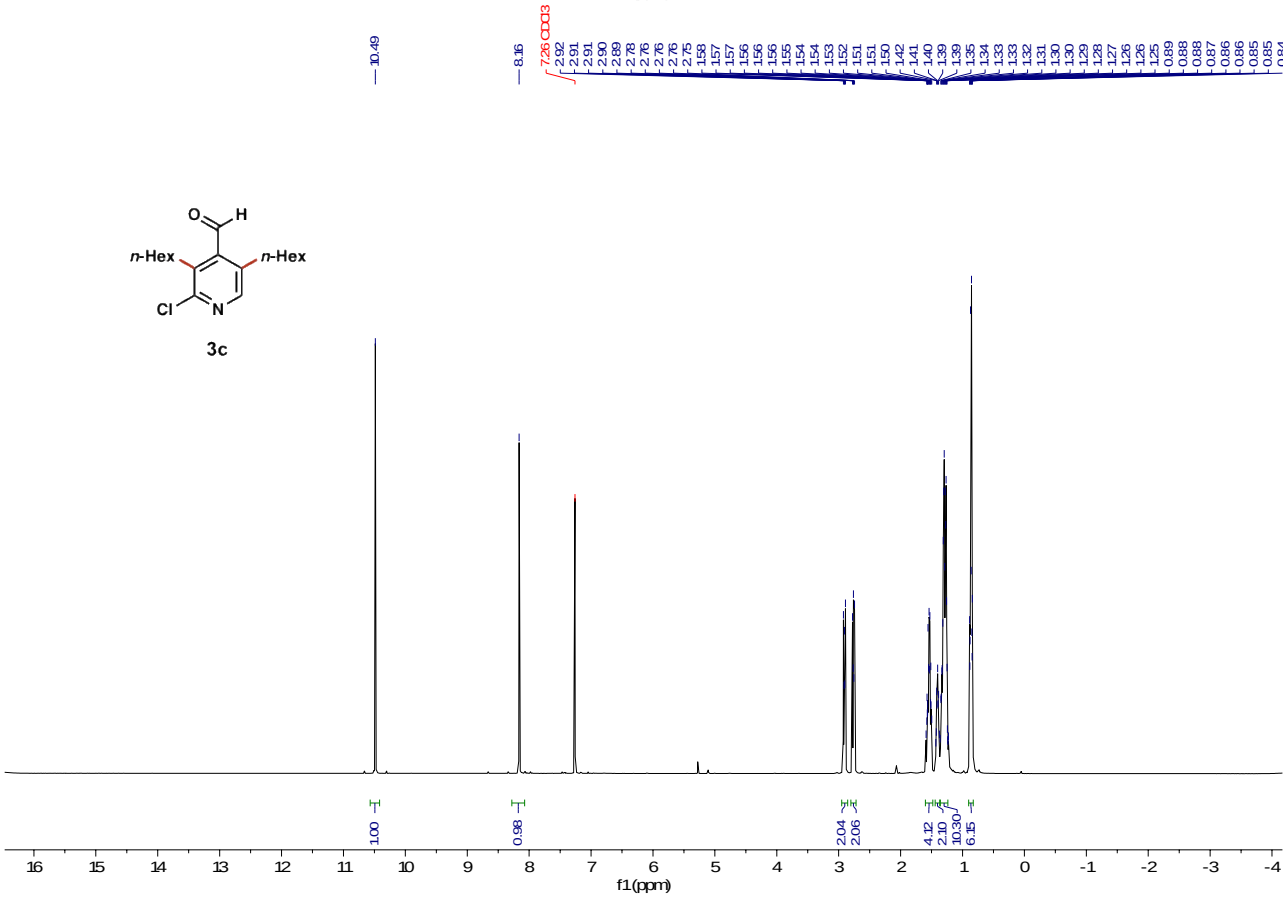

181.14
152.94
141.07
136.78
130.14
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
33.41
28.37
22.43
13.92
O
H
S
n-Bu
Cl
2l
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

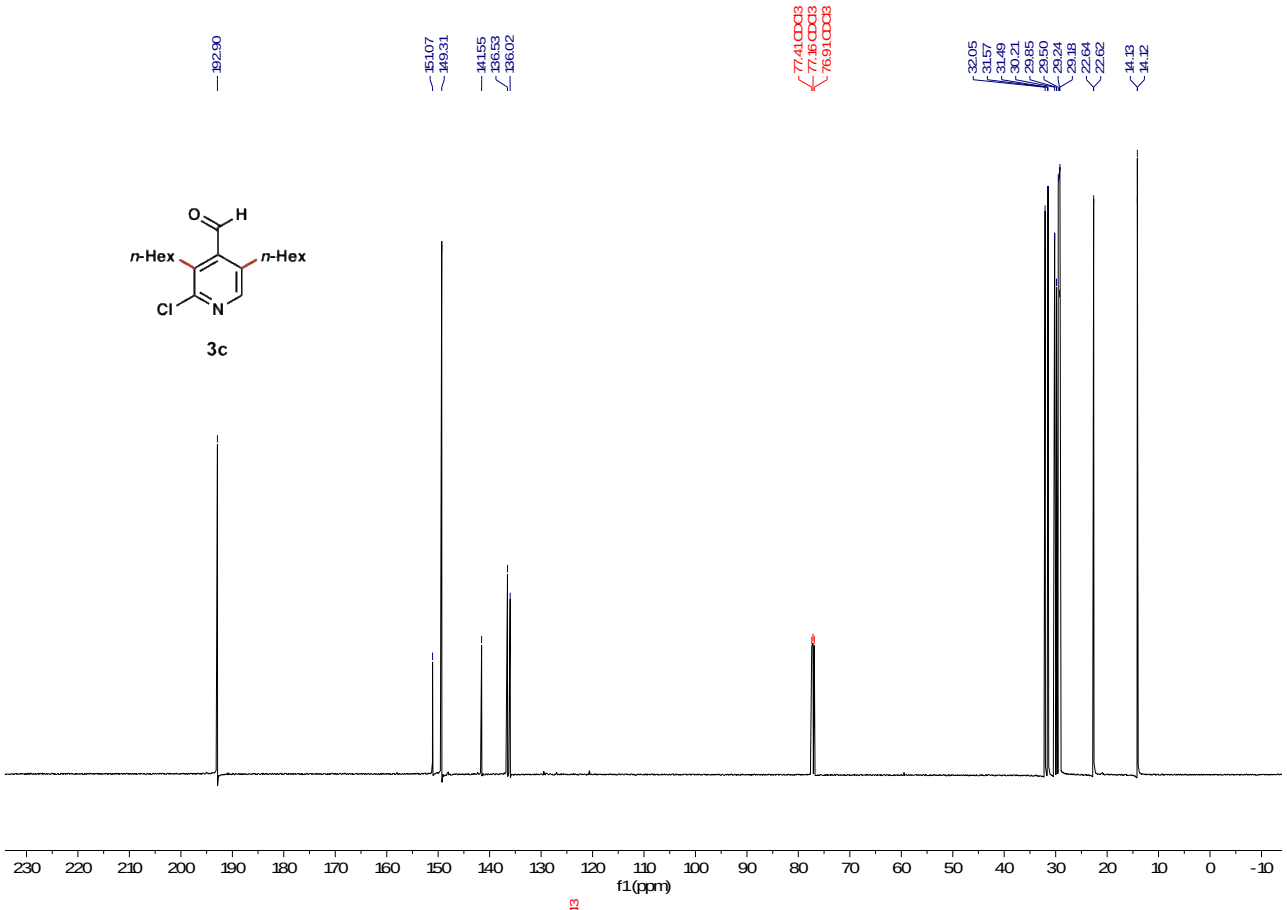

10.56
8.20
7.26 CDCl3
2.59
2.48
O
H
H3C
CH3
Cl
N
3a
1.00
1.13
2.81
2.82
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

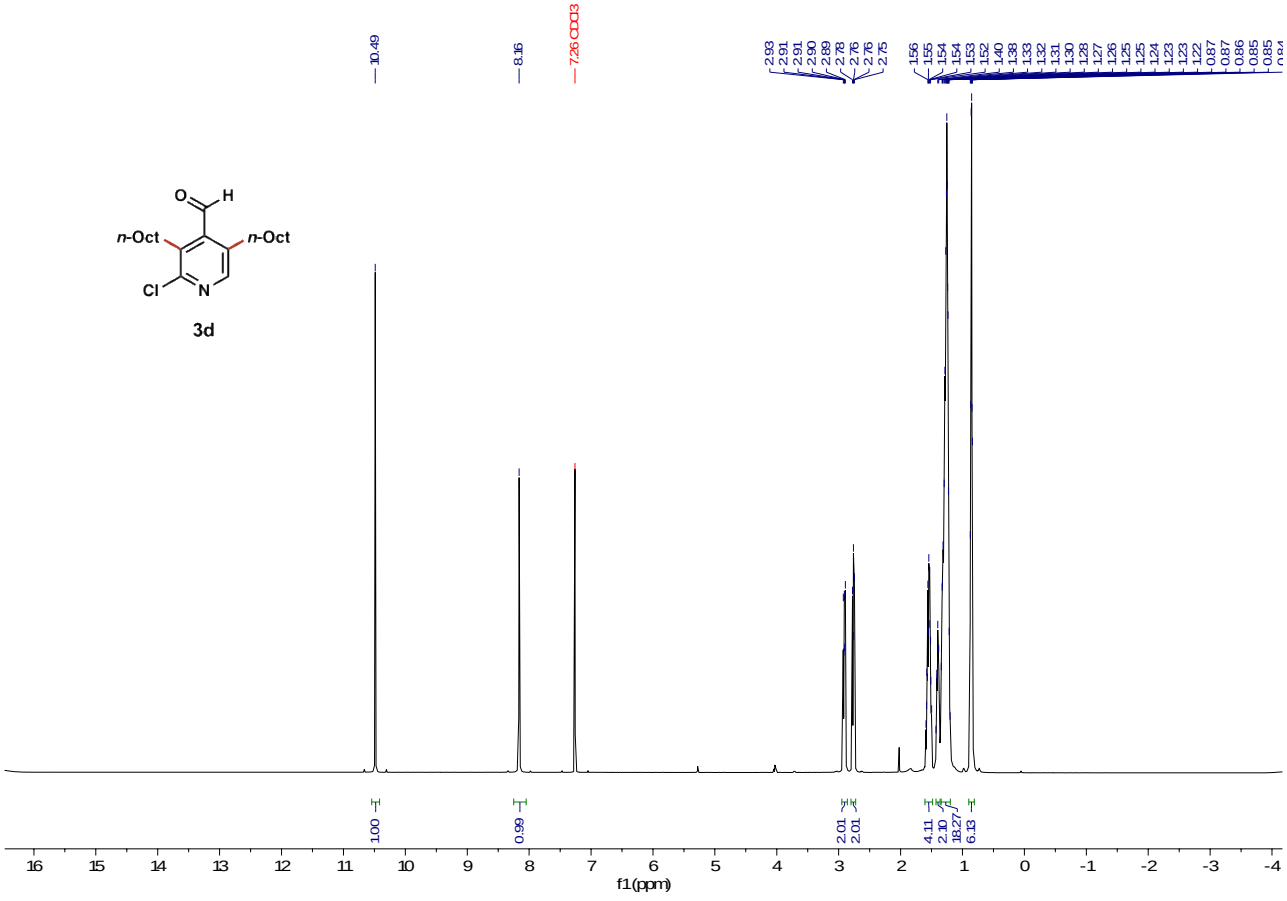

192.84
151.73
149.60
141.36
131.72
77.42 CDCl3
76.91 CDCl3
16.44
15.57
O
H
H3C
CH3
Cl
N
3a
f1 (ppm)

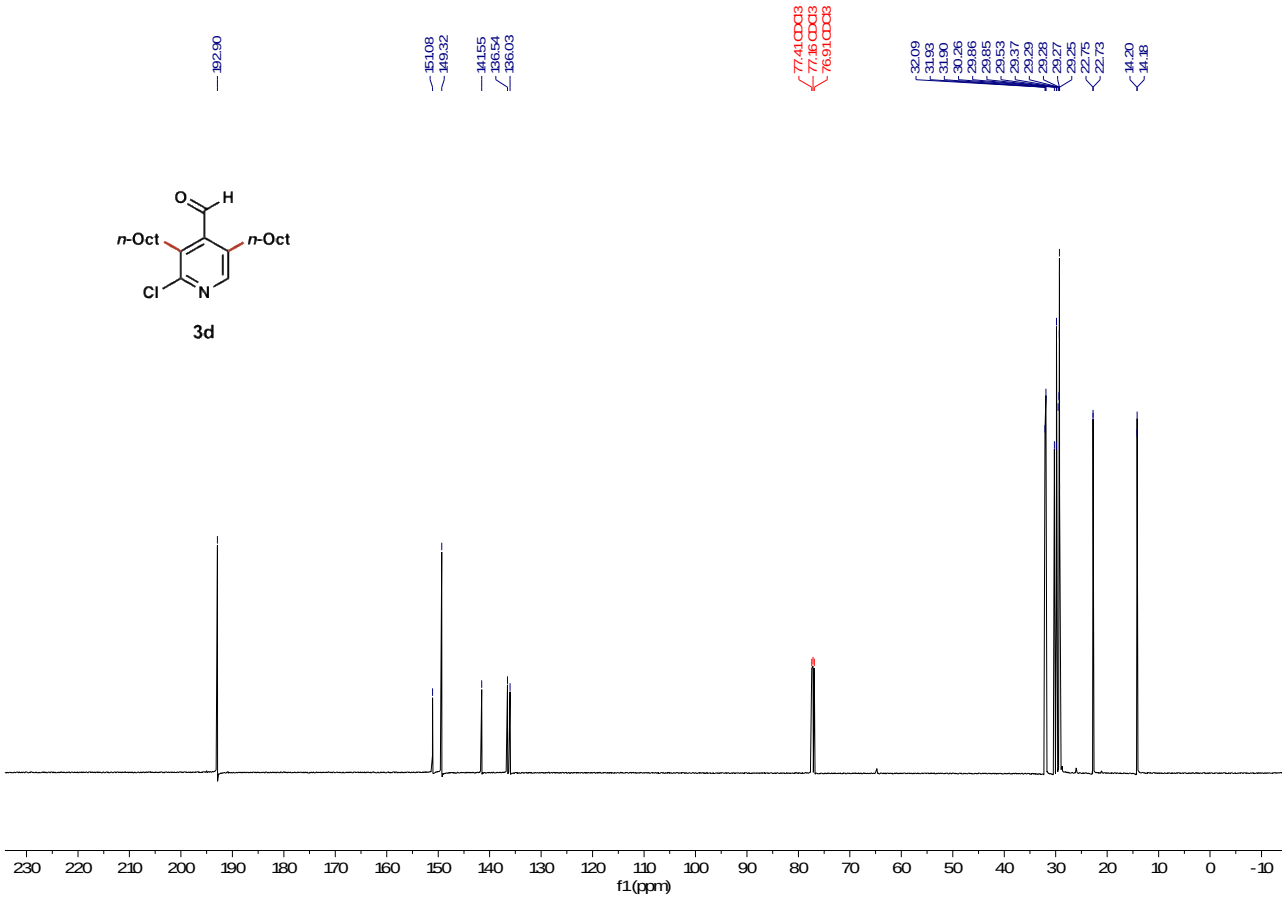

10.51
8.20
7.26 CDCl3
2.98
2.97
2.96
2.94
2.84
2.83
2.81
2.80
1.24
1.24
1.23
1.22
1.21
1.21
O
H
Et
Et
Cl
N
3b
1.00
1.00
2.04
2.06
6.34
f1 (ppm)


192.85
150.97
148.92
141.35
137.80
137.02
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
23.20
22.73
16.22
14.35
O
H
Et
Et
Cl
N
3b
f1 (ppm)


10.49
8.16
7.26 CDCl3
O
H
n-Hex
n-Hex
Cl
N
3c
1.00
0.98
2.04
2.06
4.12
2.10
10.30
6.15
f1 (ppm)


192.90
151.07
149.31
141.55
136.53
136.02
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
32.05
31.57
31.49
30.21
29.65
29.50
29.24
29.18
22.64
22.62
14.13
14.12
O
H
n-Hex
n-Hex
Cl
N
3c
f1 (ppm)


10.49
8.16
7.26 CDCl3
2.93
2.91
2.91
2.90
2.89
2.78
2.76
2.76
2.75
1.56
1.55
1.54
1.54
1.53
1.52
1.40
1.38
1.33
1.32
1.31
1.30
1.28
1.27
1.26
1.25
1.25
1.24
1.23
1.23
1.22
0.87
0.86
0.85
0.85
1.00
0.99
2.01
2.01
4.11
2.10
18.27
6.13
O
H
n-Oct
n-Oct
Cl
N
3d
f1 (ppm)


192.90
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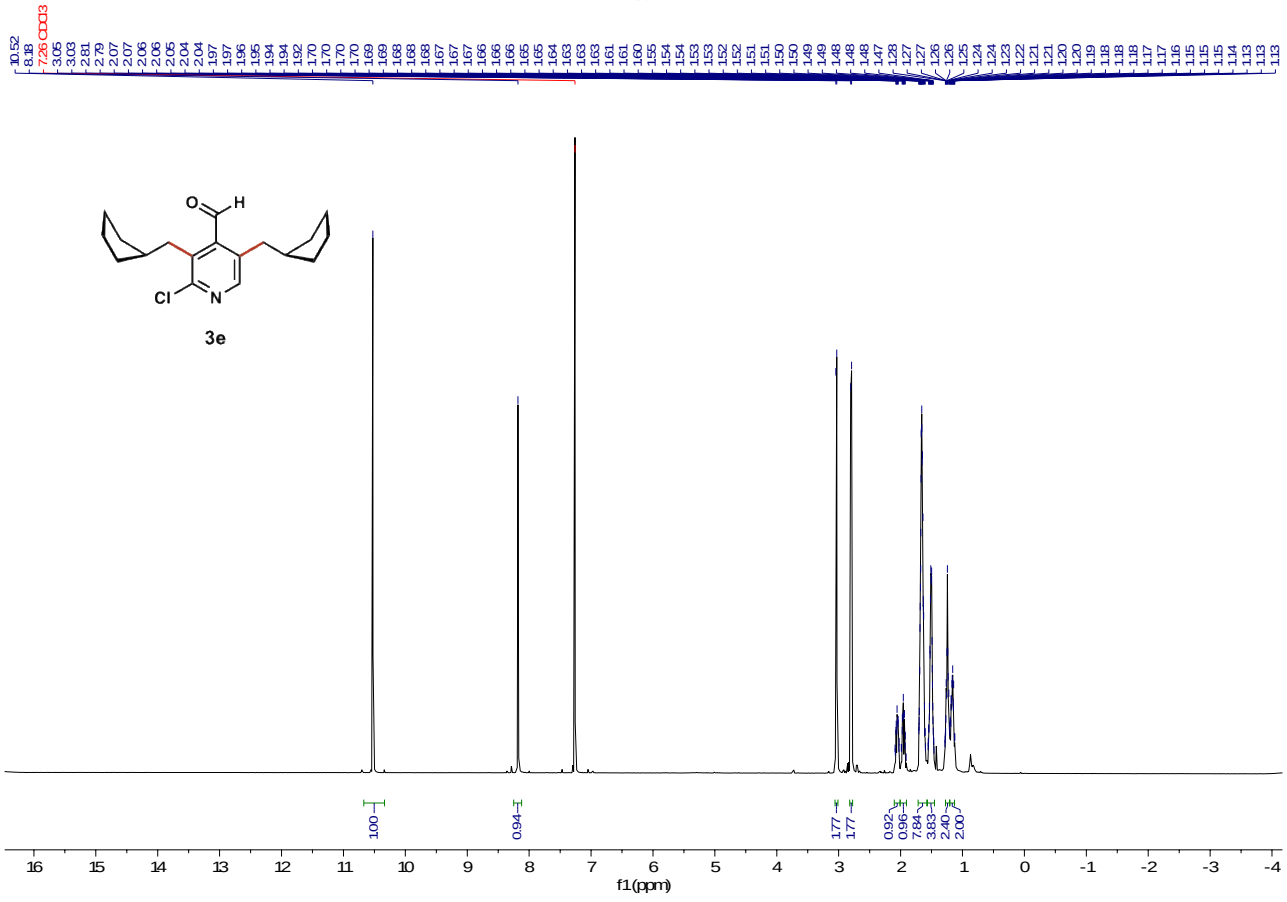
136.54
136.03
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
32.09
31.93
31.90
30.26
29.86
29.85
29.53
29.37
29.29
29.28
29.27
29.25
22.75
22.73
14.20
14.18
O
H
n-Oct
n-Oct
Cl
N
3d
f1 (ppm)


10.52
8.18
7.26 CDCl3
3.05
3.03
2.81
2.79
2.07
2.07
2.06
2.06
2.06
2.05
2.04
2.04
1.97
1.97
1.96
1.95
1.94
1.94
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1.27
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1.25
1.24
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1.22
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1.18
1.18
1.18
1.17
1.17
1.16
1.15
1.15
1.15
1.14
1.13
1.13
1.13
O
H
Cl
N
3e
1.00
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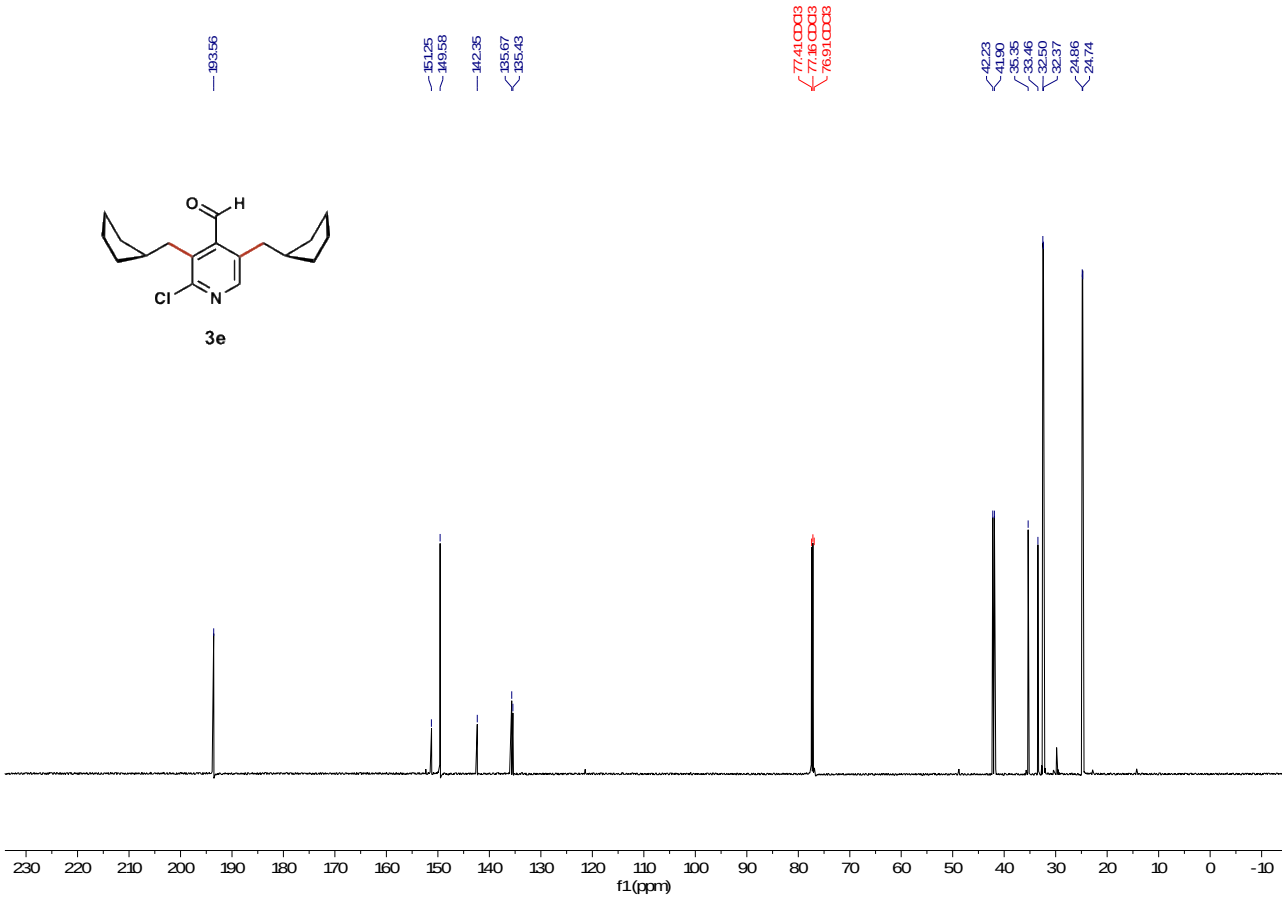
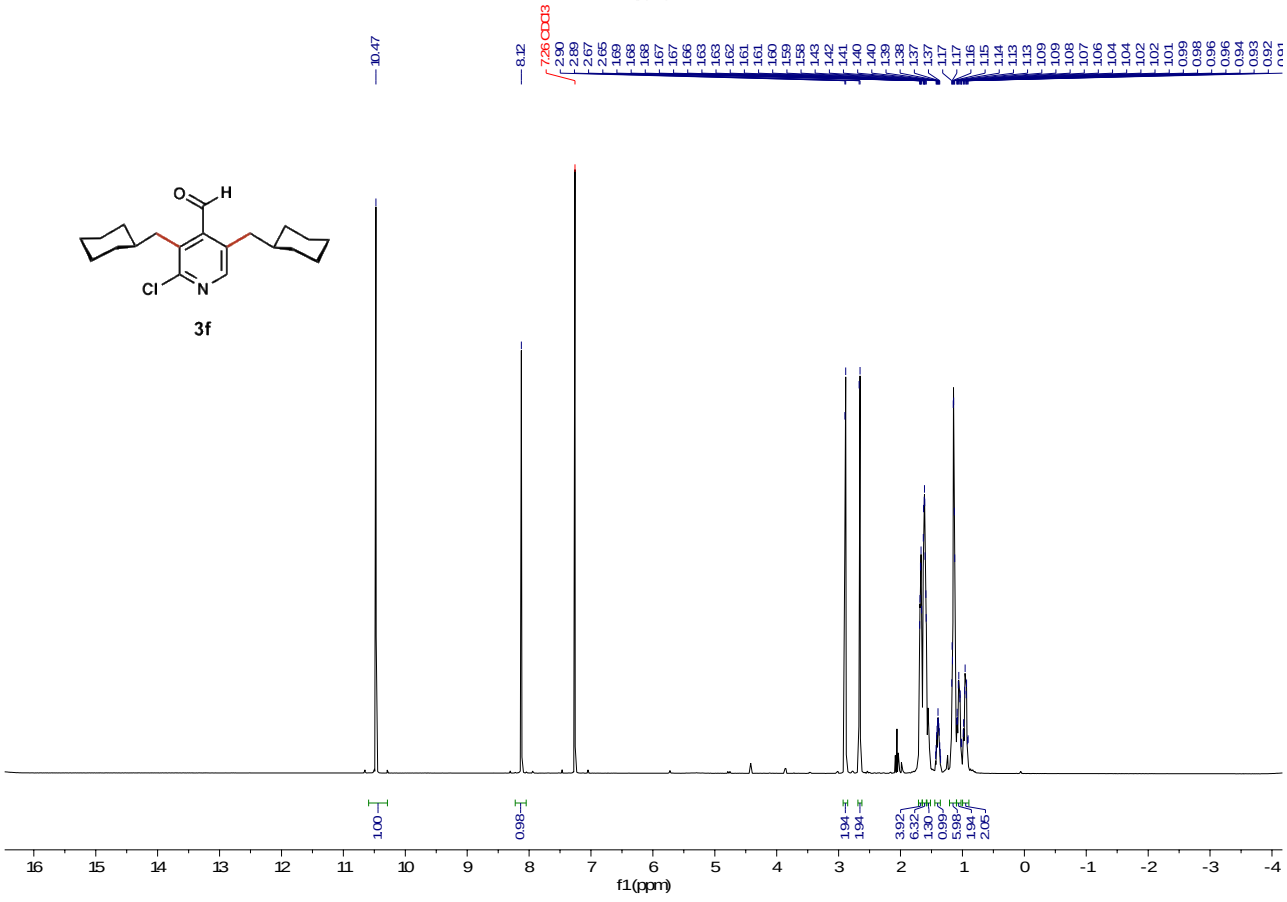
1.77
1.77
0.92
0.96
7.84
3.83
2.40
2.00
f1 (ppm)


193.56
151.25
149.58
142.35
135.67
135.43
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
42.23
41.90
35.35
33.46
32.50
32.37
24.86
24.74
O
H
Cl
N
3e
f1 (ppm)


10.47
8.12
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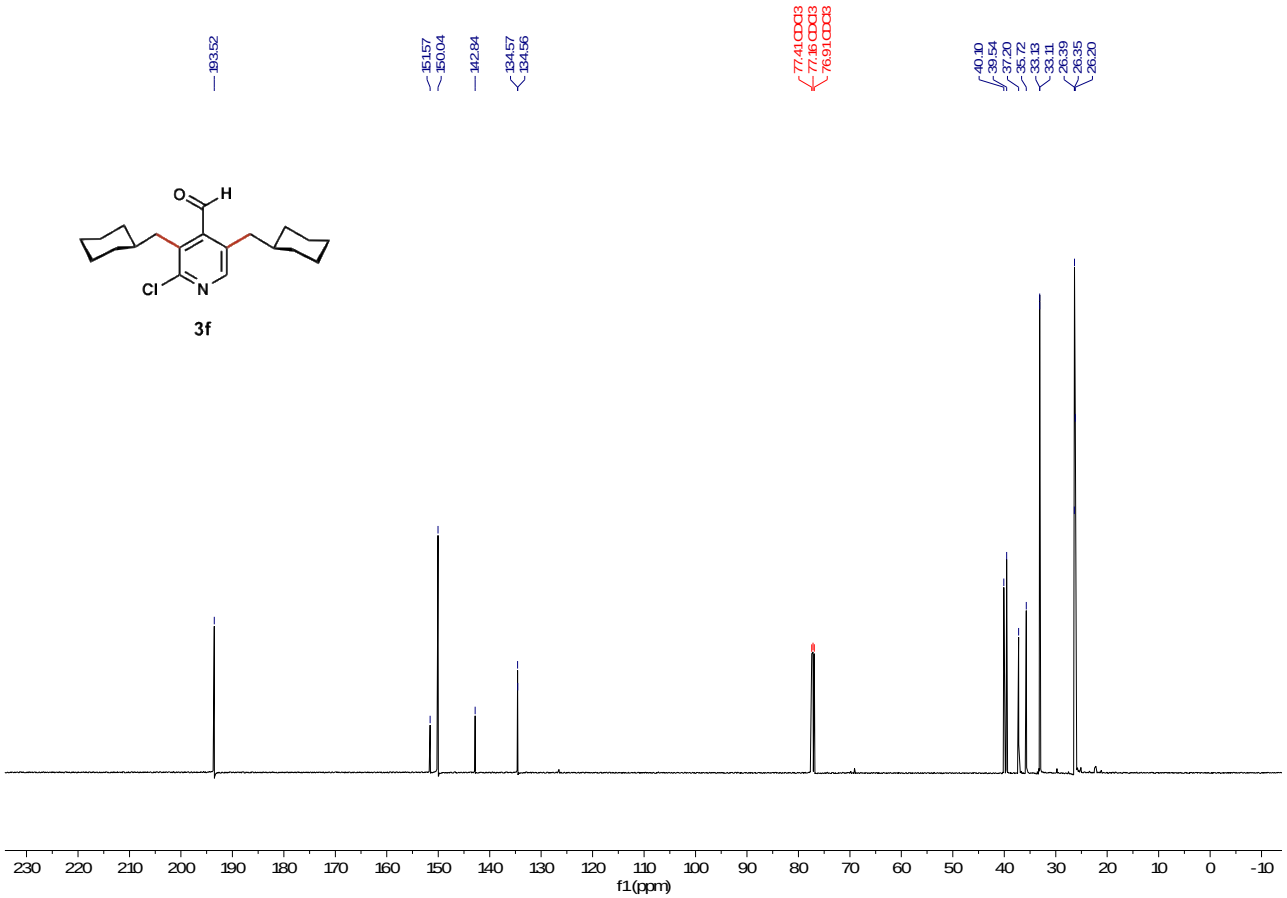
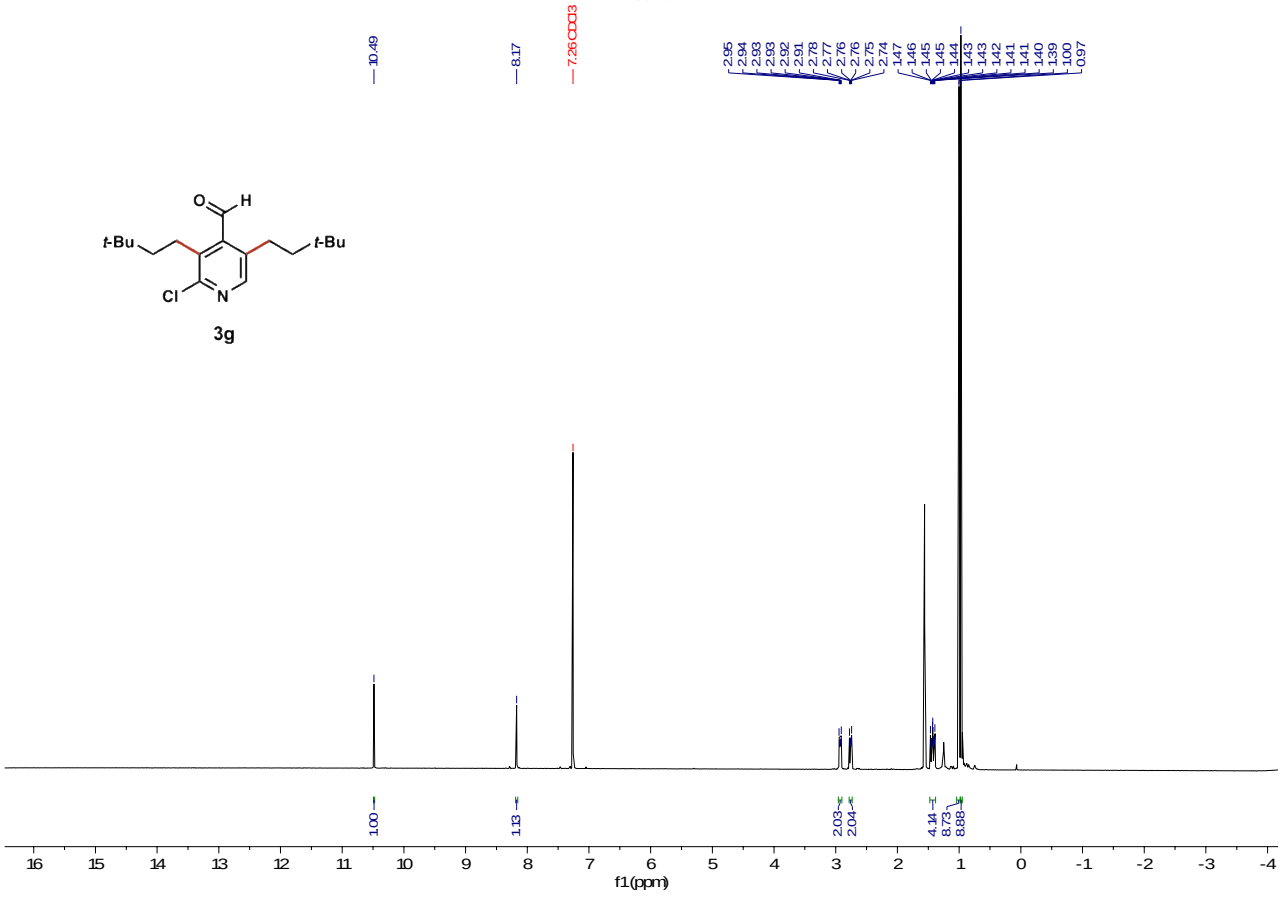
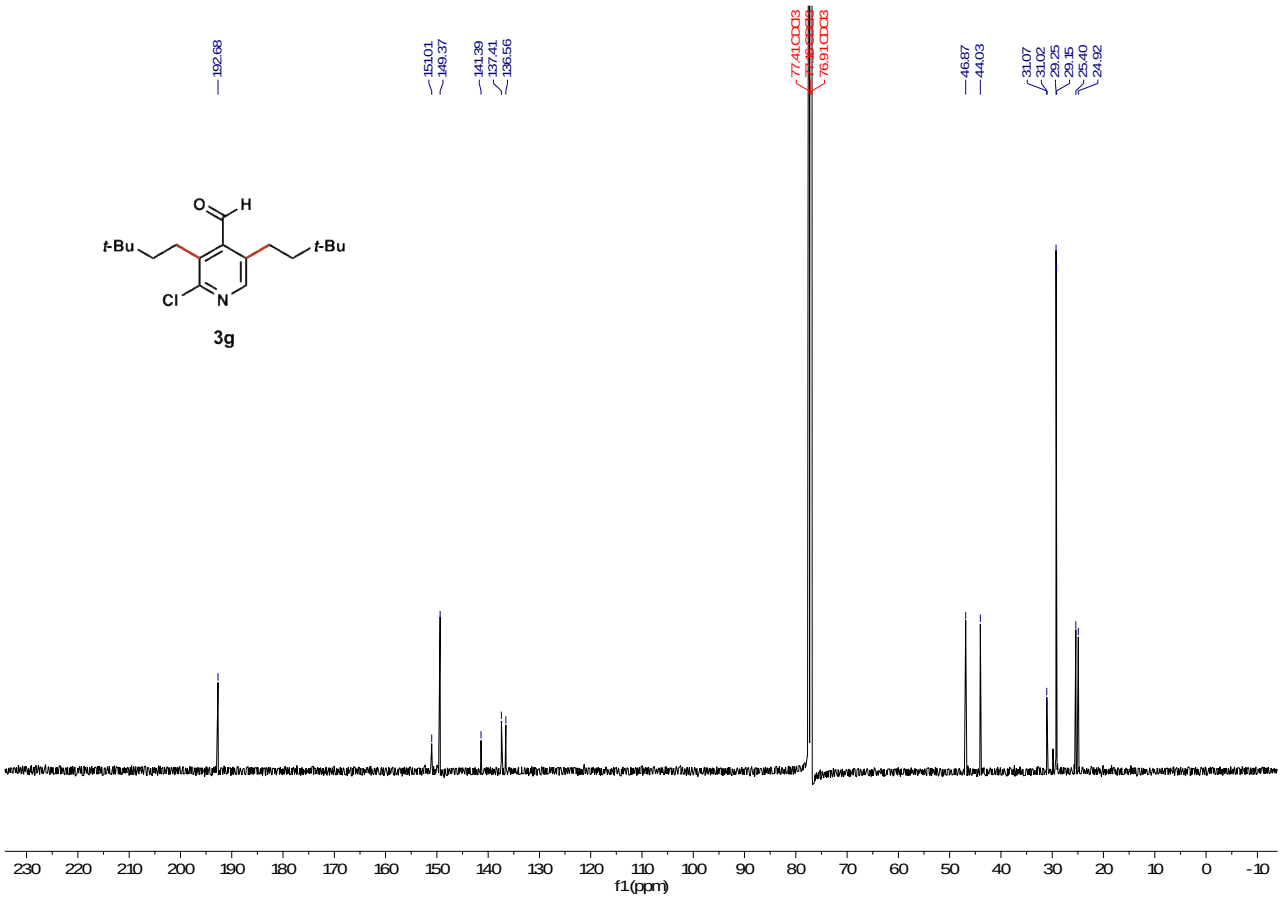
O
H
Cl
N
3f
1.00
0.98
1.94
1.94
3.92
6.32
1.30
0.99
5.98
1.94
2.05
f1 (ppm)


193.52
151.57
150.04
142.84
134.57
134.56
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
40.10
39.54
37.20
35.72
33.13
33.11
26.39
26.35
26.20
O
H
Cl
N
3f
f1 (ppm)


10.49
8.17
7.26 CDCl3
2.95
2.94
2.93
2.93
2.92
2.91
2.78
2.77
2.76
2.76
2.75
2.74
1.47
1.46
1.45
1.45
1.44
1.43
1.43
1.42
1.41
1.41
1.40
1.39
1.00
0.97
O
H
t-Bu
t-Bu
Cl
N
3g
1.00
1.13
2.03
2.04
4.14
8.73
8.88
f1 (ppm)


192.68
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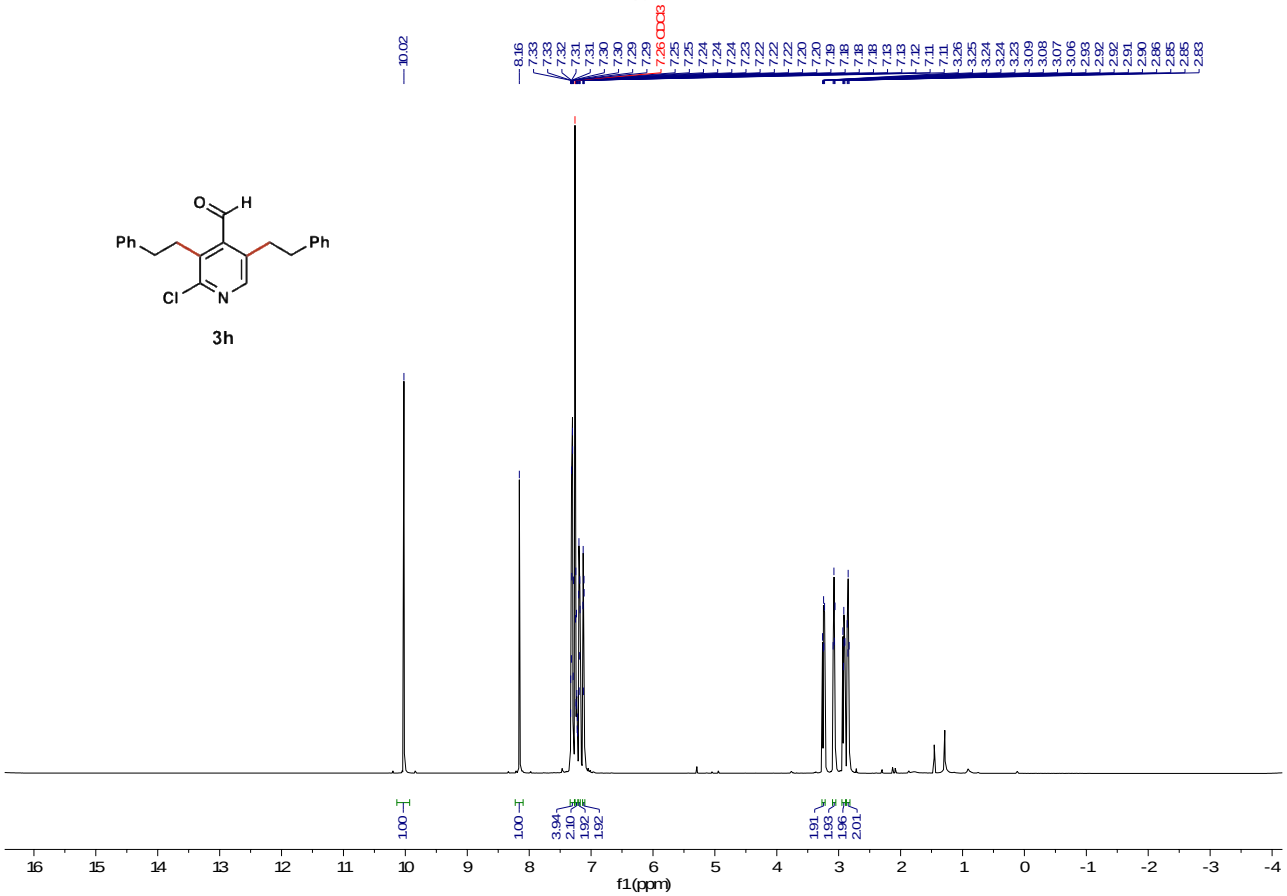
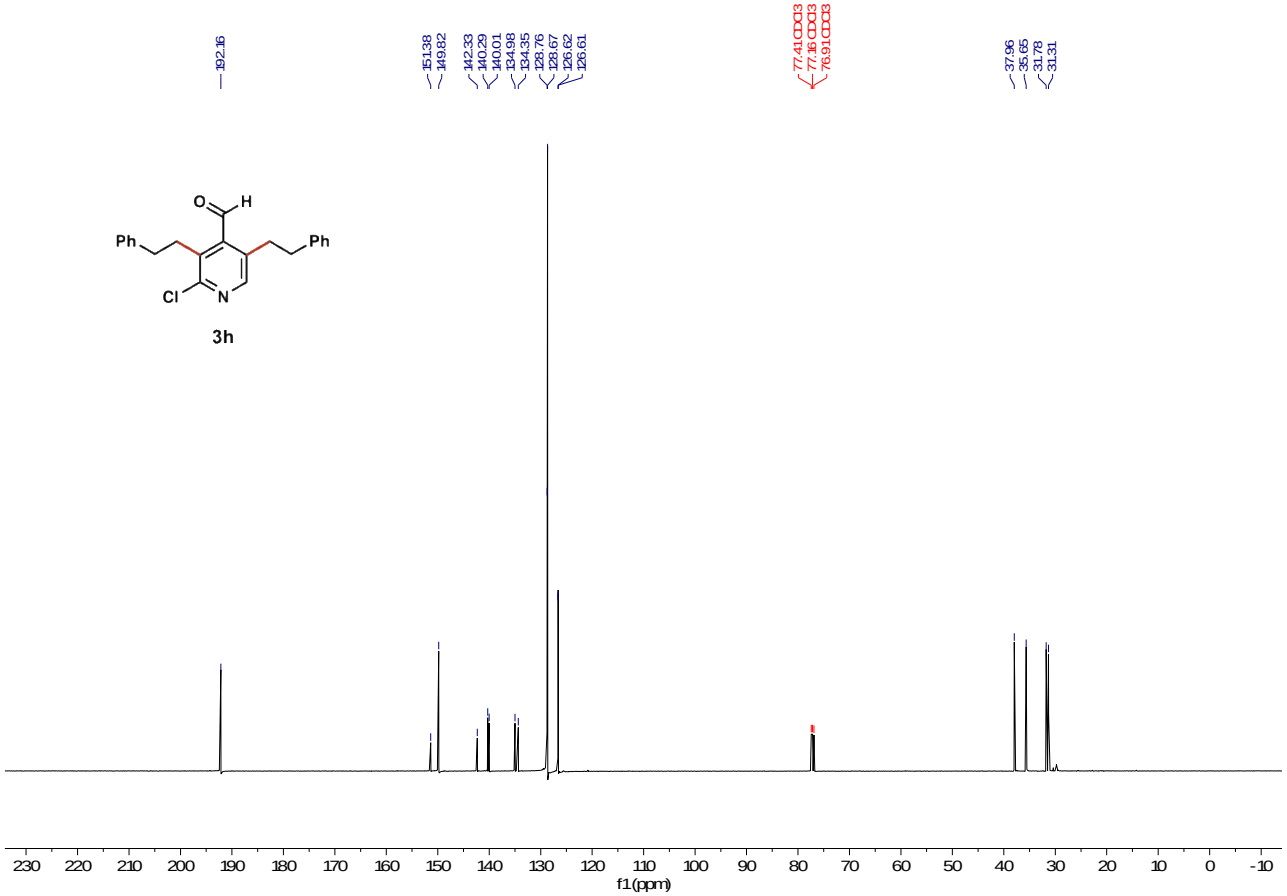
149.37
141.39
137.41
136.56
77.41 CDCl3
76.91 CDCl3
46.87
44.03
31.07
31.02
29.25
29.15
25.40
24.92
O
H
t-Bu
t-Bu
Cl
N
3g
f1 (ppm)


10.02
8.16
7.33
7.32
7.31
7.30
7.29
7.26 CDCl3
7.25
7.24
7.23
7.22
7.20
7.19
7.18
7.13
7.12
7.11
3.26
3.25
3.24
3.23
3.09
3.08
3.07
3.06
2.93
2.92
2.91
2.90
2.86
2.85
2.83
O
H
Ph
Ph
Cl
N
3h
1.00
1.00
3.94
2.10
1.92
1.92
1.91
1.93
1.96
2.01
f1 (ppm)


192.16
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142.33
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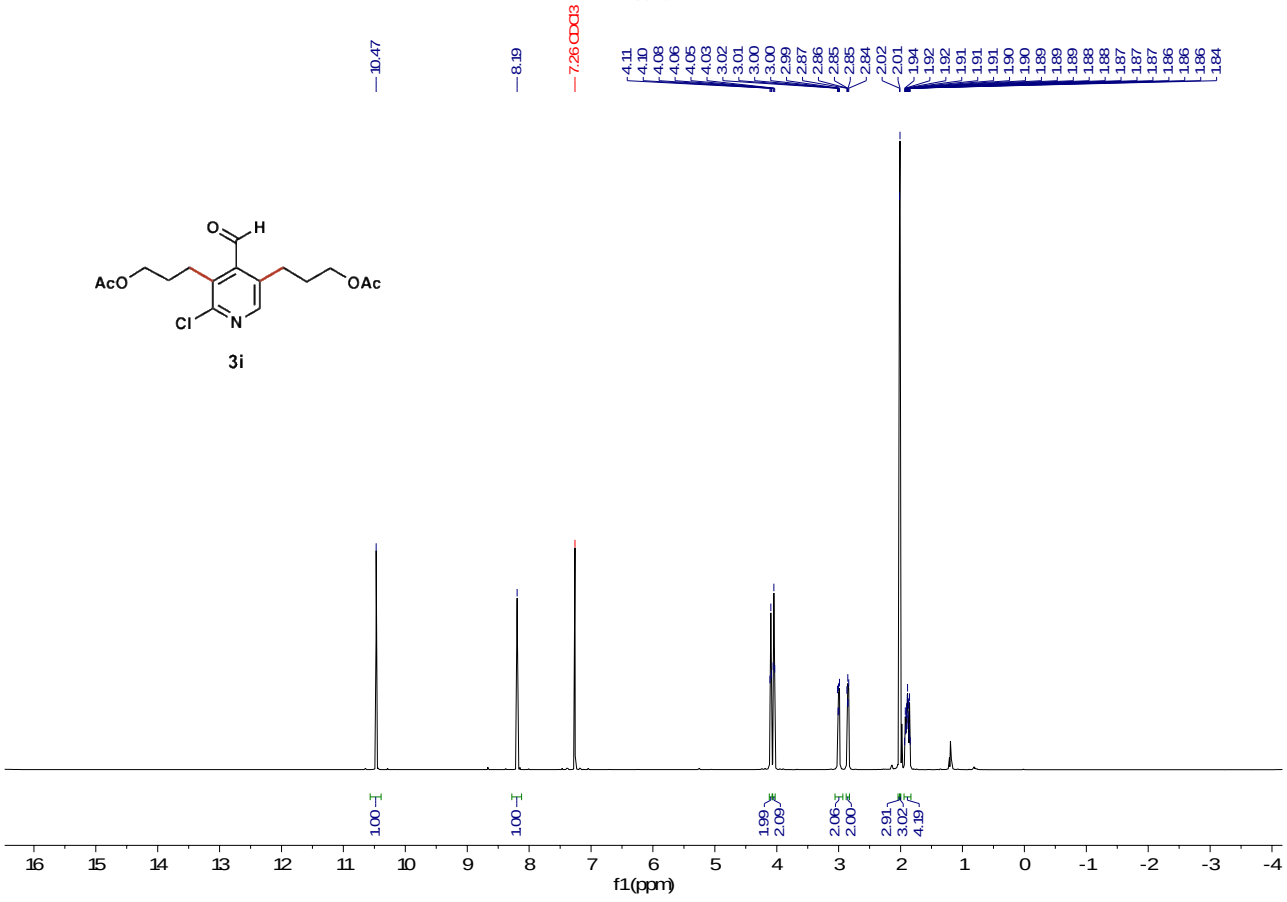
140.01
134.98
134.35
128.76
128.67
126.62
126.61
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
37.96
35.65
31.78
31.31
O
H
Ph
Ph
Cl
N
3h
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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4.03
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3.00
2.99
2.87
2.86
2.85
2.85
2.84
2.02
2.01
1.94
1.92
1.92
1.91
1.91
1.91
1.90
1.90
1.89
1.89
1.89
1.88
1.88
1.87
1.87
1.87
1.86
1.86
1.84
O
H
AcO
OAc
Cl
N
3i
1.00
1.00
1.99
2.09
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3.02
4.19
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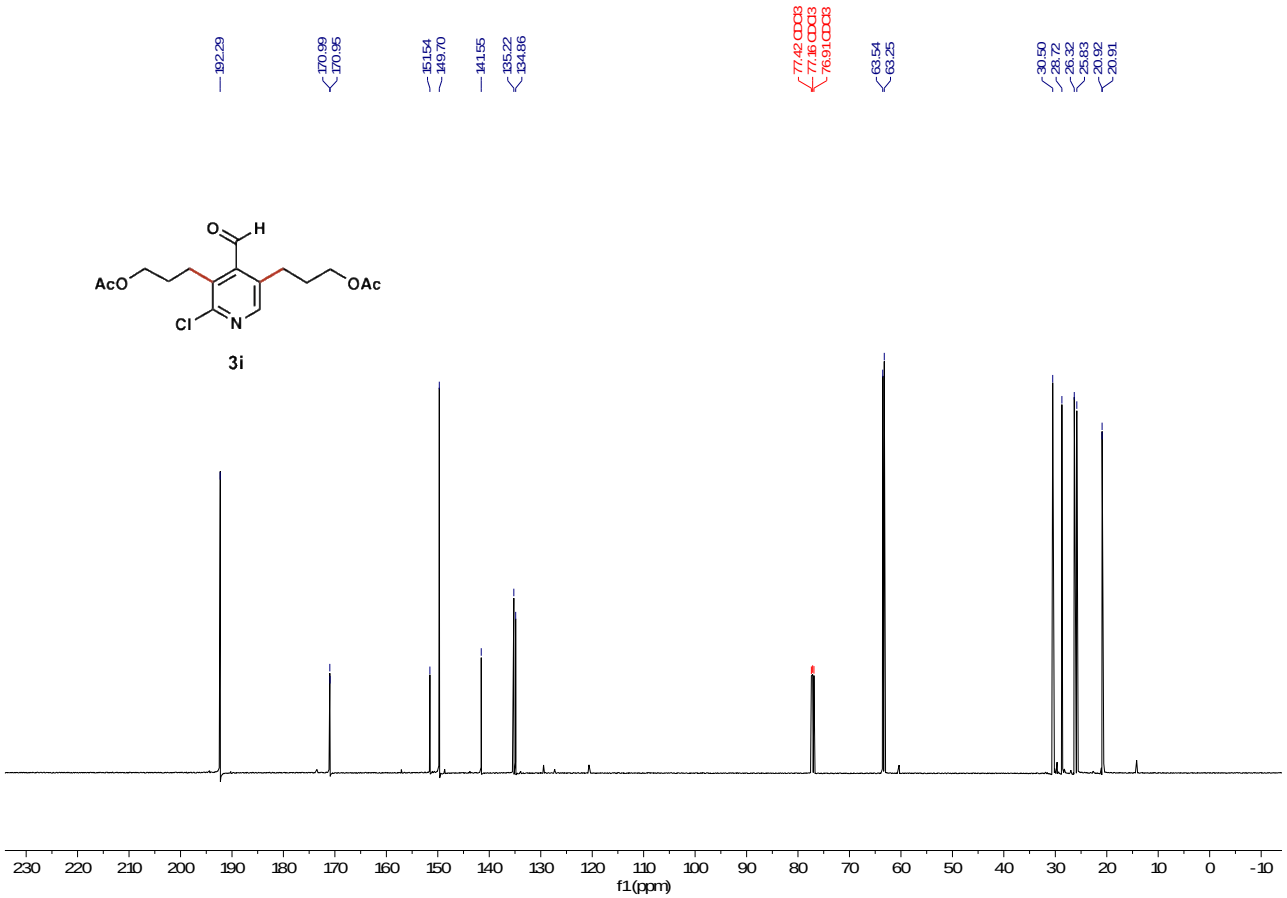
f1 (ppm)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76.91 CDCl3
63.54
63.25
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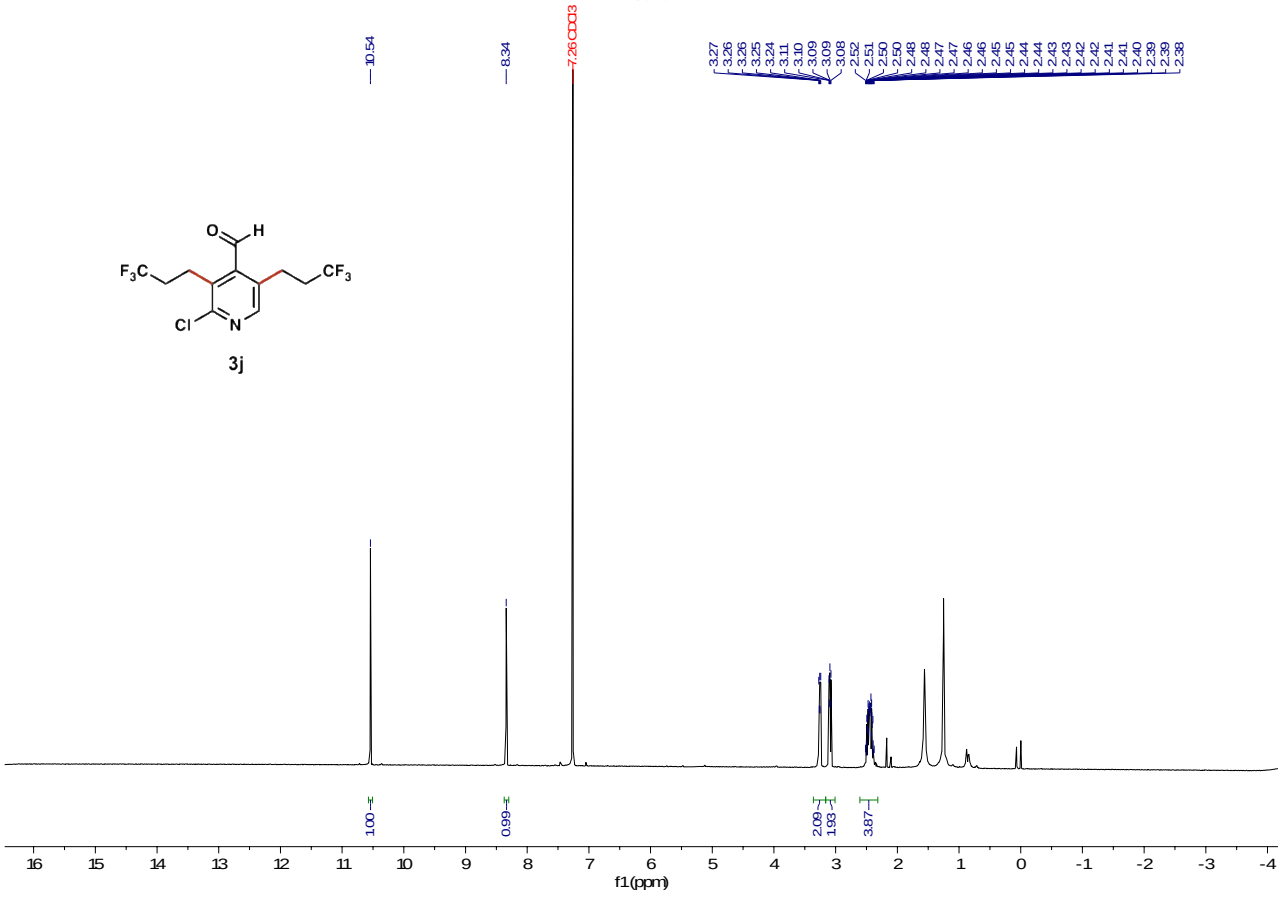
20.92
20.91
O
H
AcO
OAc
Cl
N
3i
f1 (ppm)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2.41
2.41
2.40
2.39
2.39
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CF3
Cl
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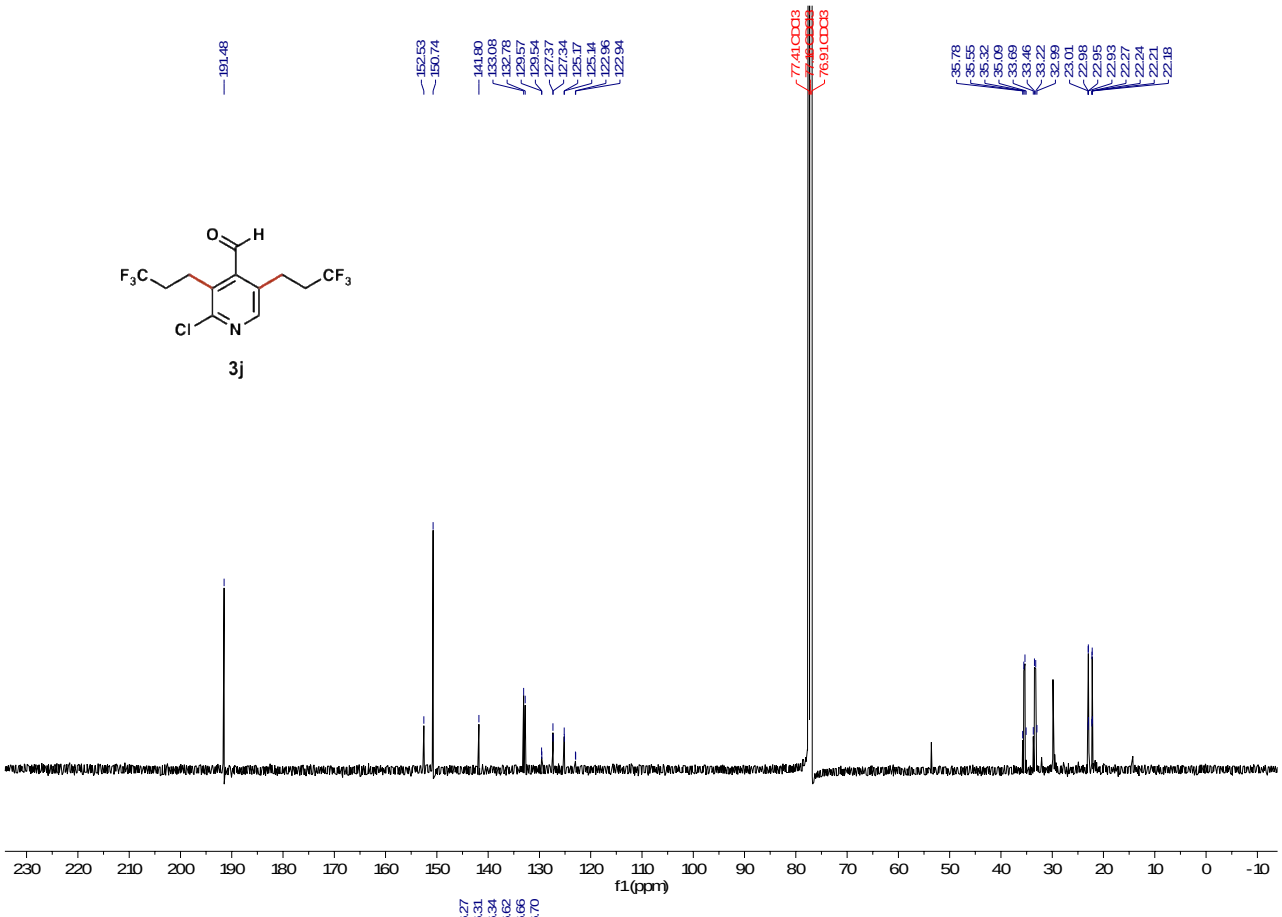
f1 (ppm)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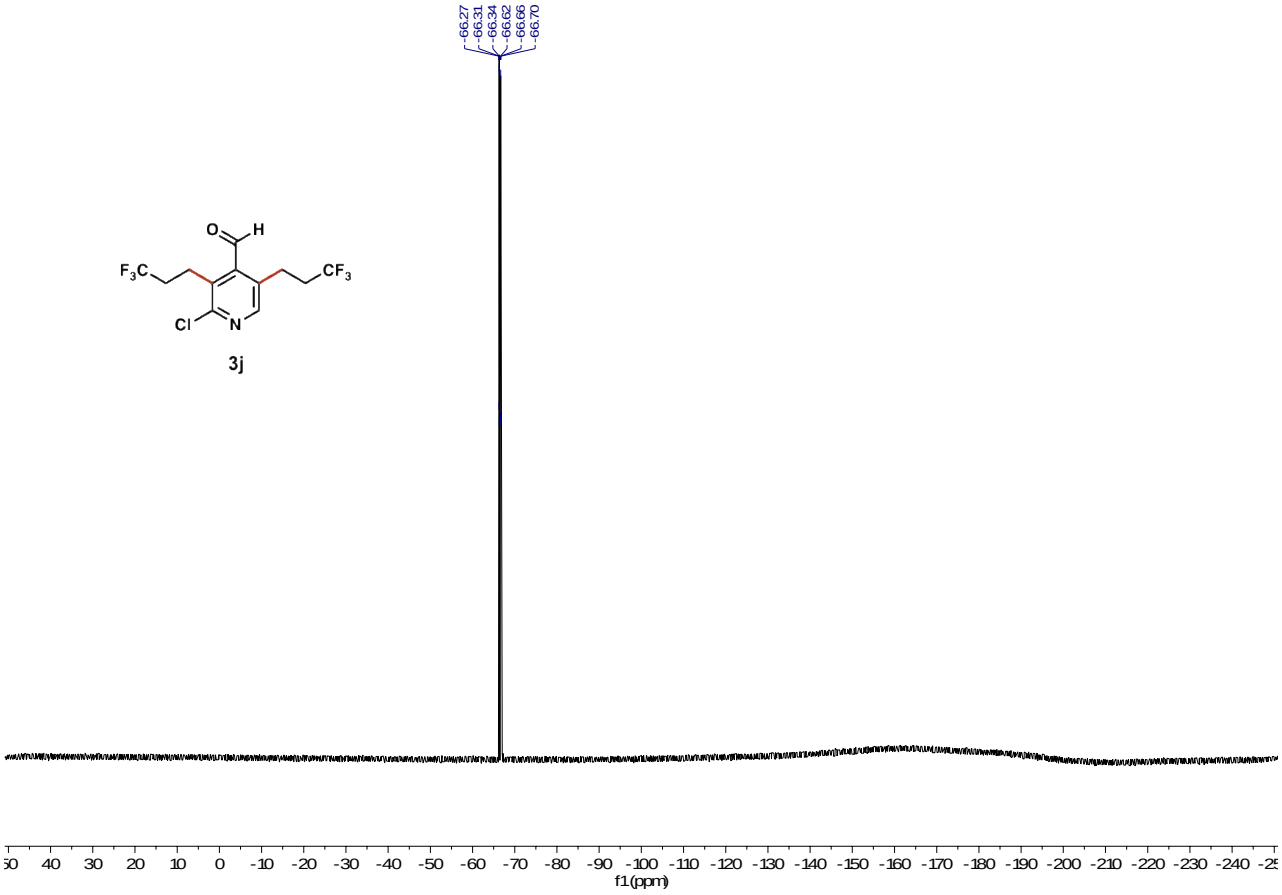
F3C
CF3
Cl
N
3j
f1(ppm)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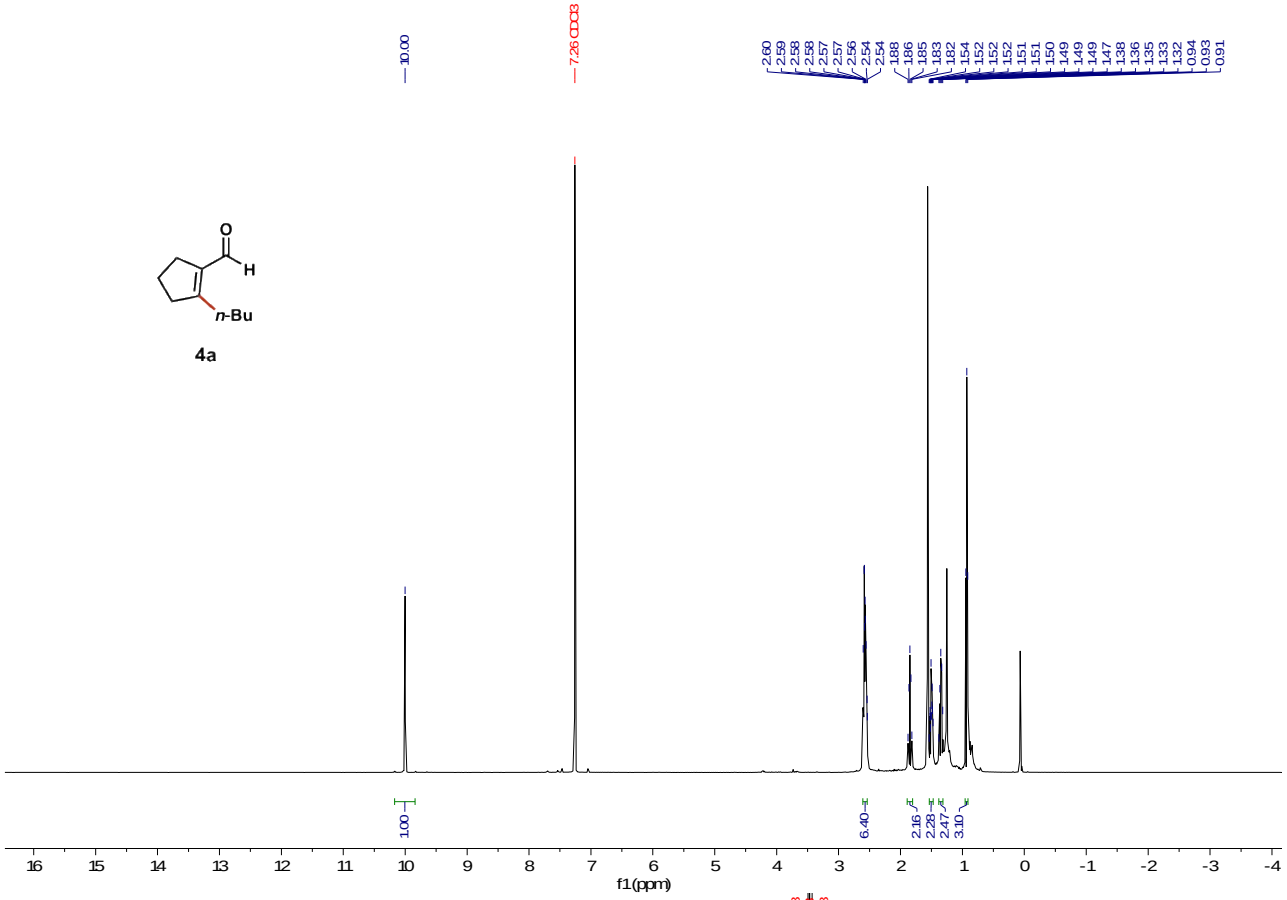
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1.49
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1.47
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1.36
1.35
1.33
1.32
0.94
0.93
0.91
O
H
n-Bu
4a
1.00
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2.47
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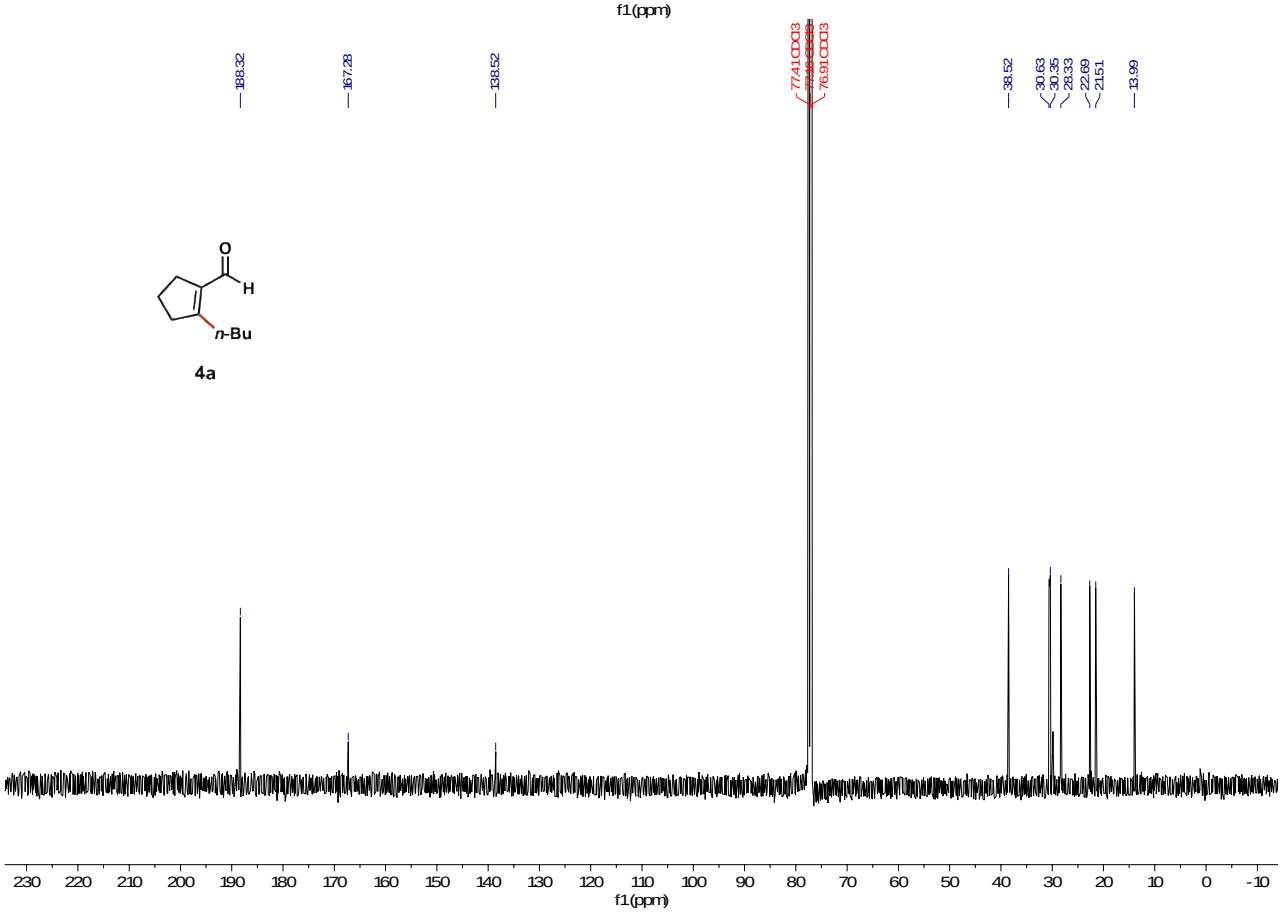
f1(ppm)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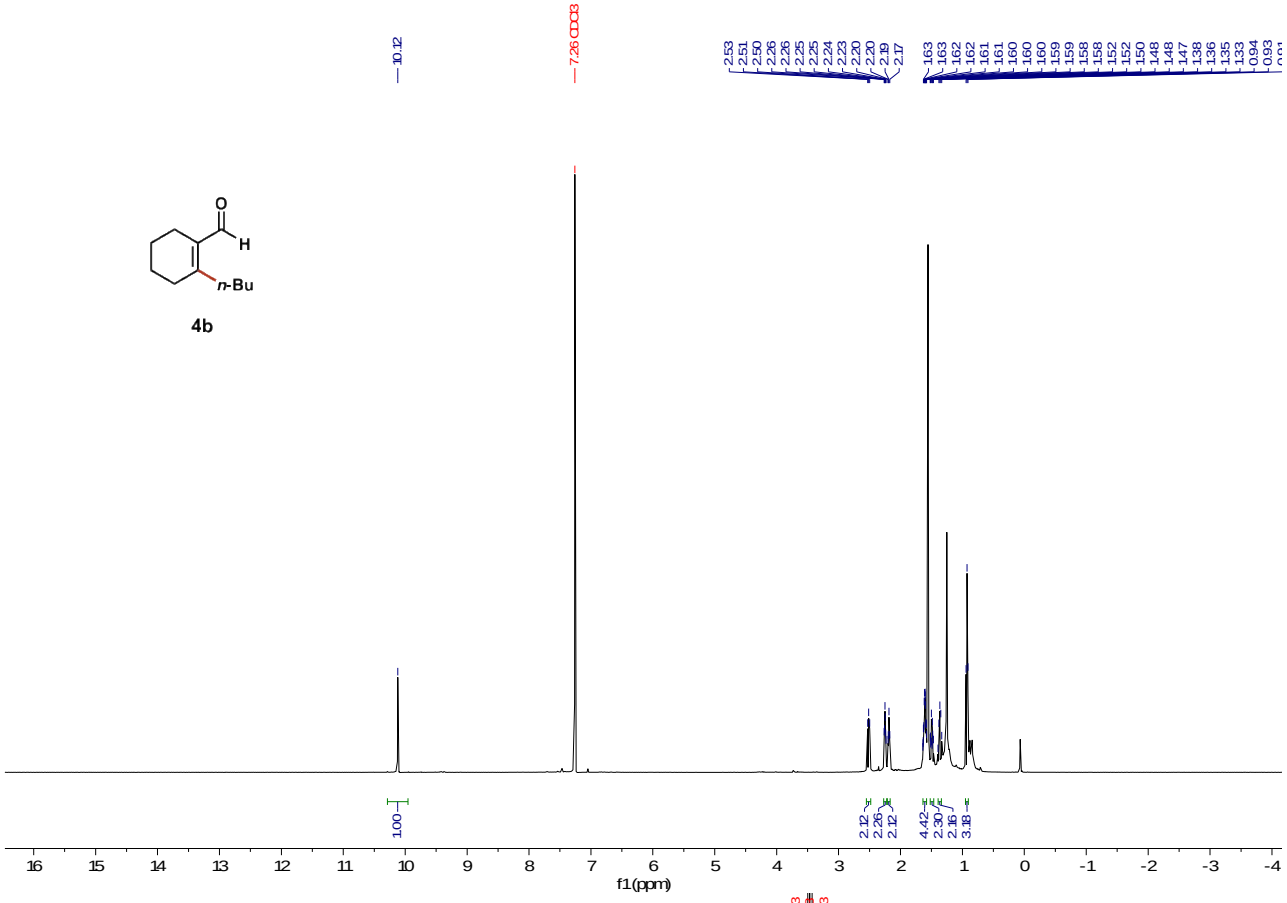
76.91
38.52
30.63
30.35
28.33
22.69
21.51
13.99
O
H
n-Bu
4a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1(ppm)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2.26
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2.24
2.23
2.20
2.19
2.17
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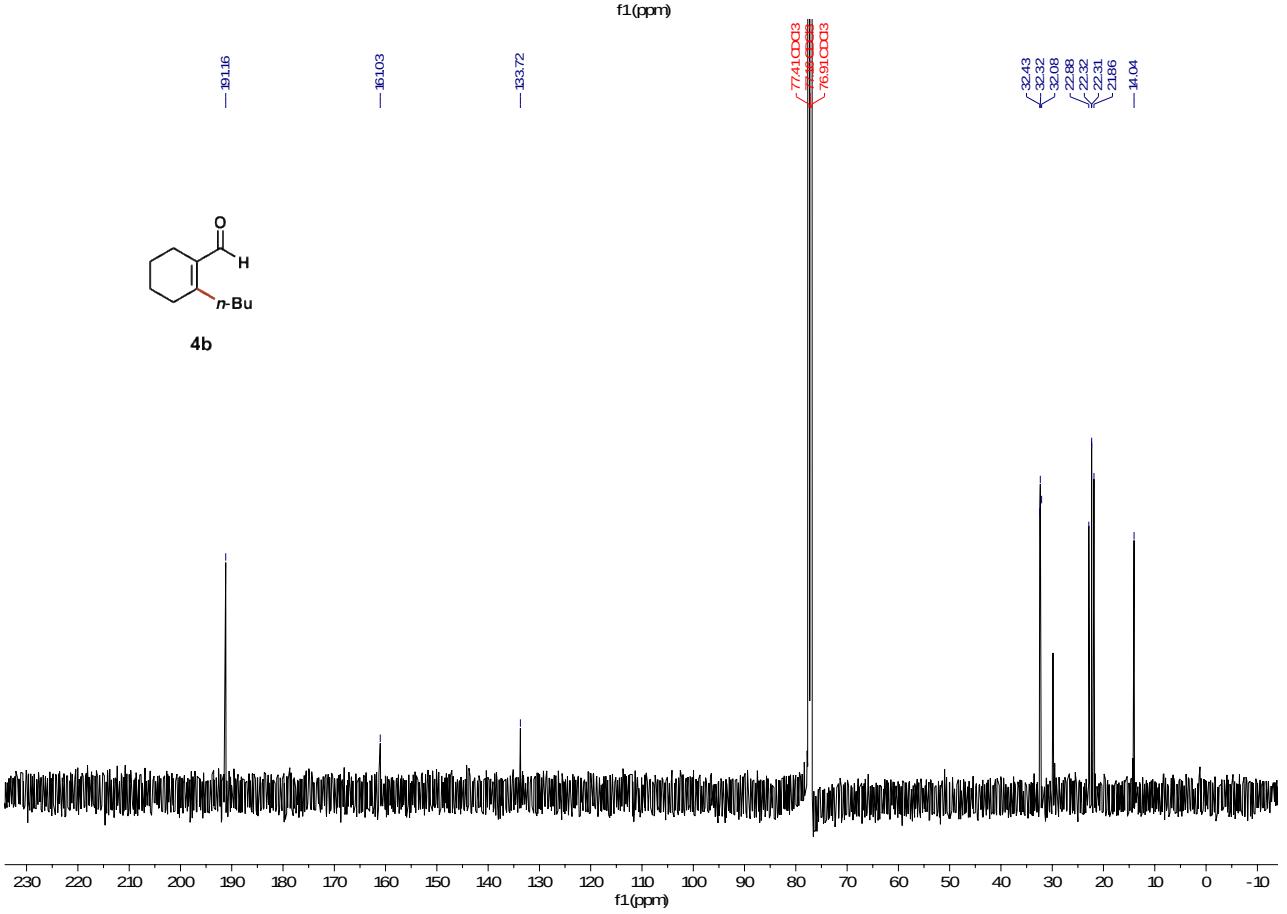
1.62
1.61
1.60
1.59
1.58
1.52
1.50
1.48
1.47
1.38
1.36
1.35
1.33
0.94
0.93
O
H
n-Bu
4b
1.00
2.12
2.26
2.12
4.42
2.30
2.16
3.18
f1(ppm)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22.31
21.86
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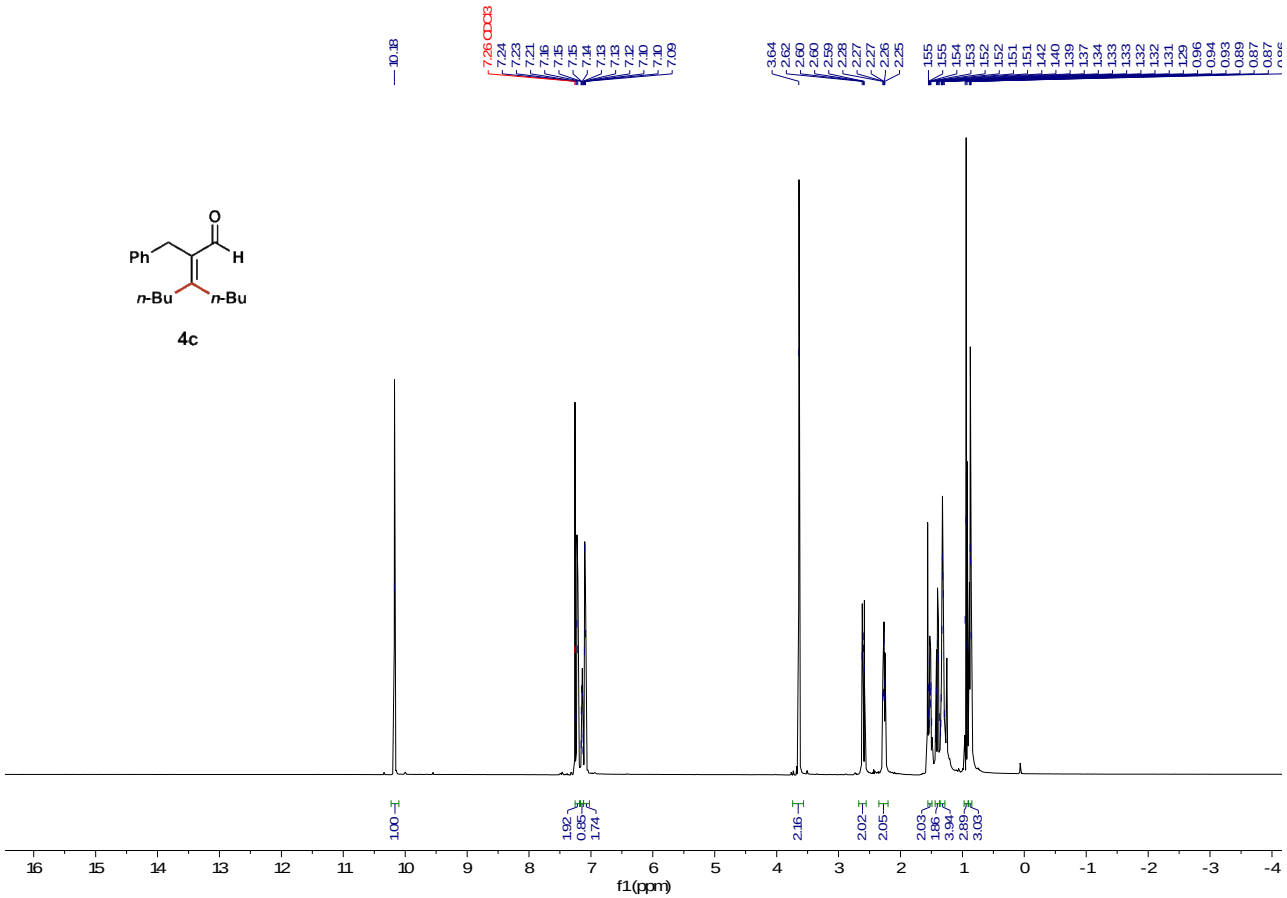
O
H
n-Bu
4b
f1(ppm)


Ph
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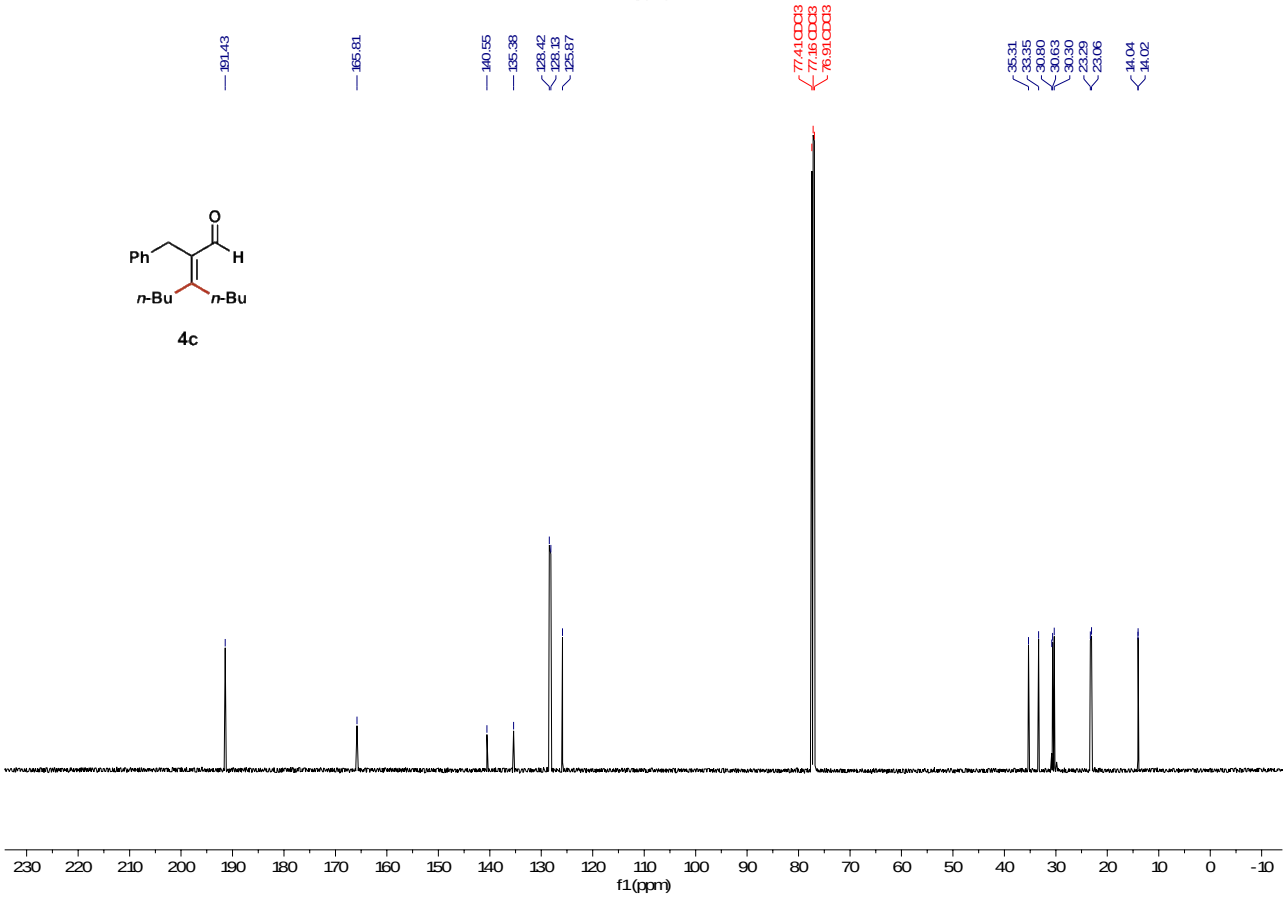
H
n-Bu
n-Bu
4c
f1 (ppm)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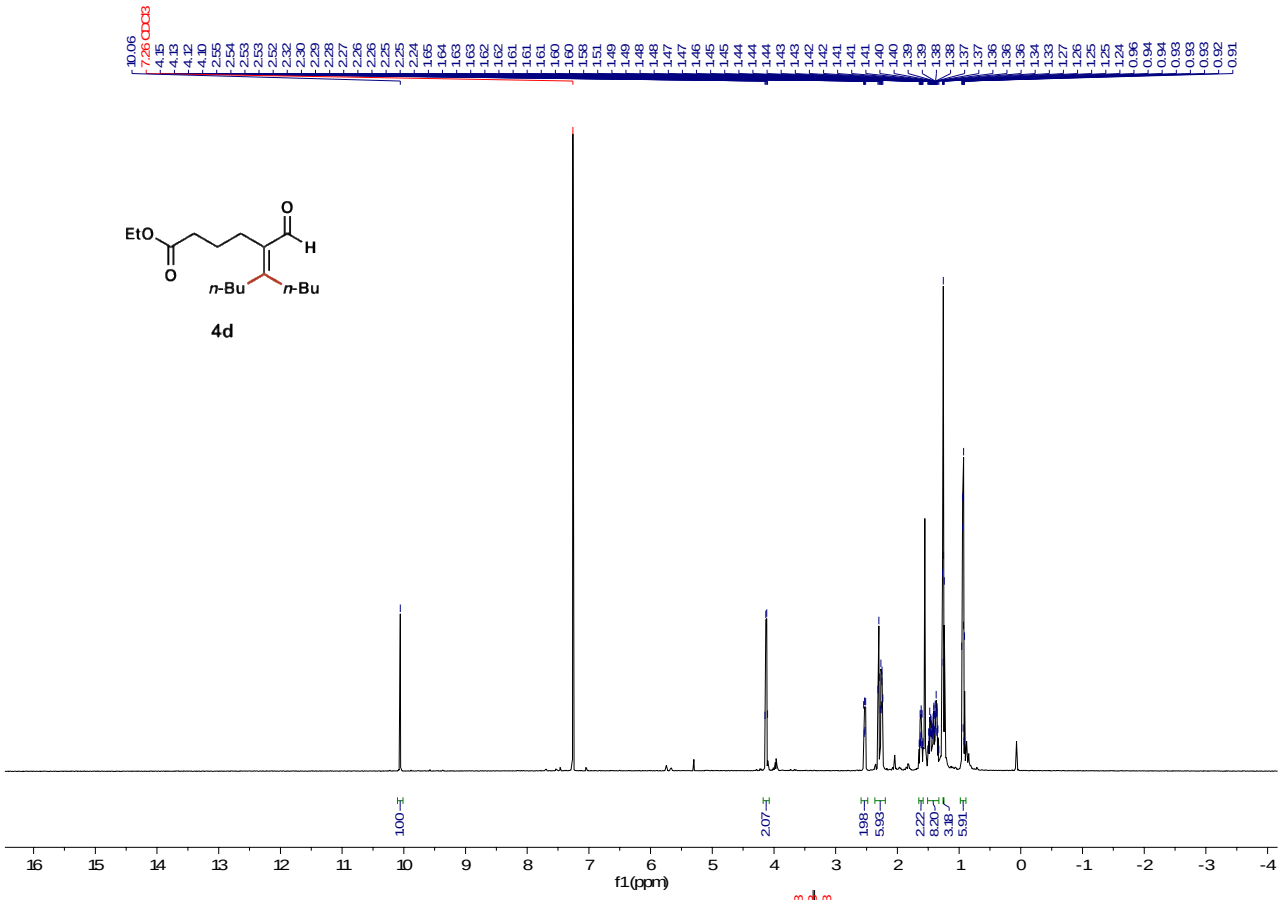
H
n-Bu
n-Bu
4c
f1 (ppm)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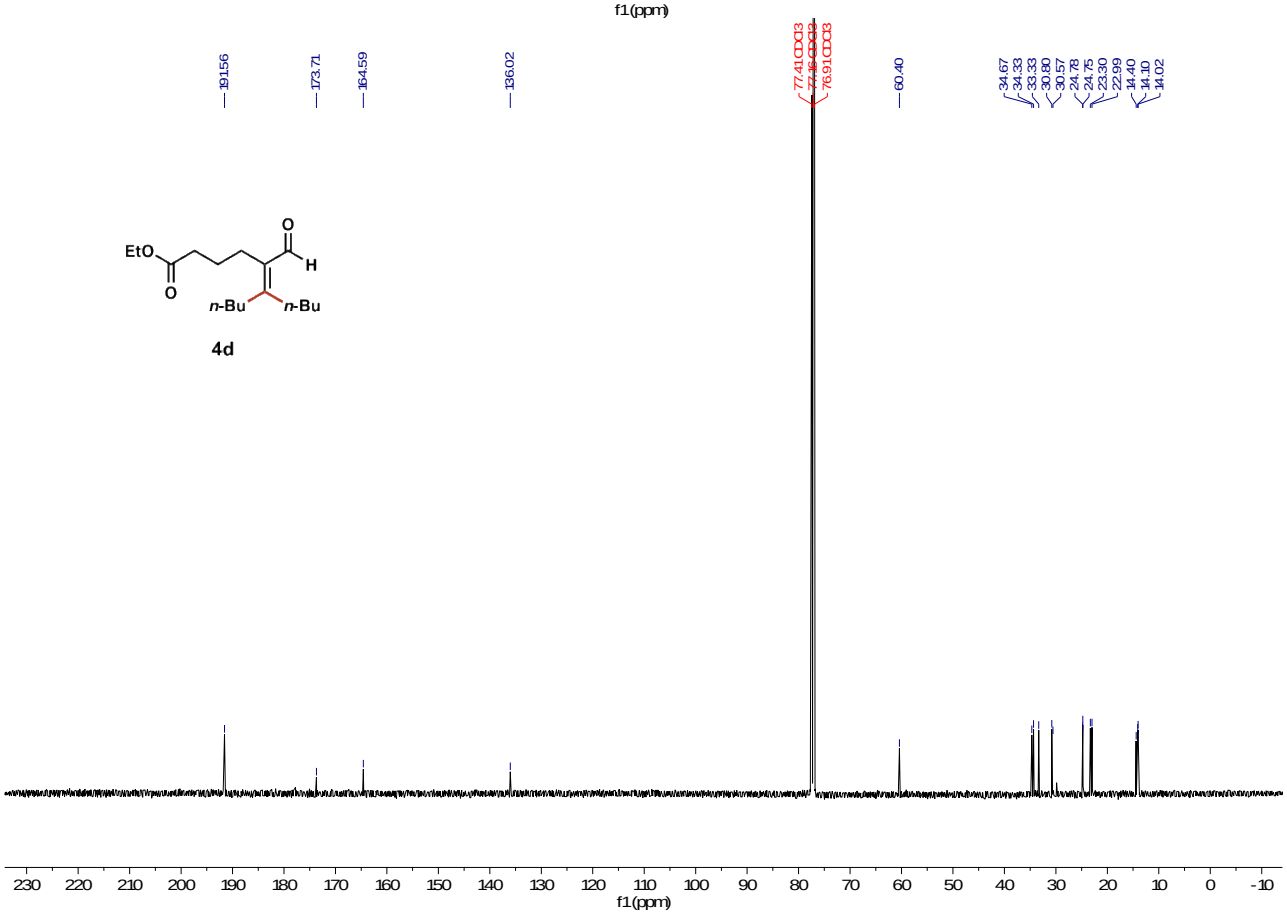
O
O
H
n-Bu
n-Bu
4d
f1 (ppm)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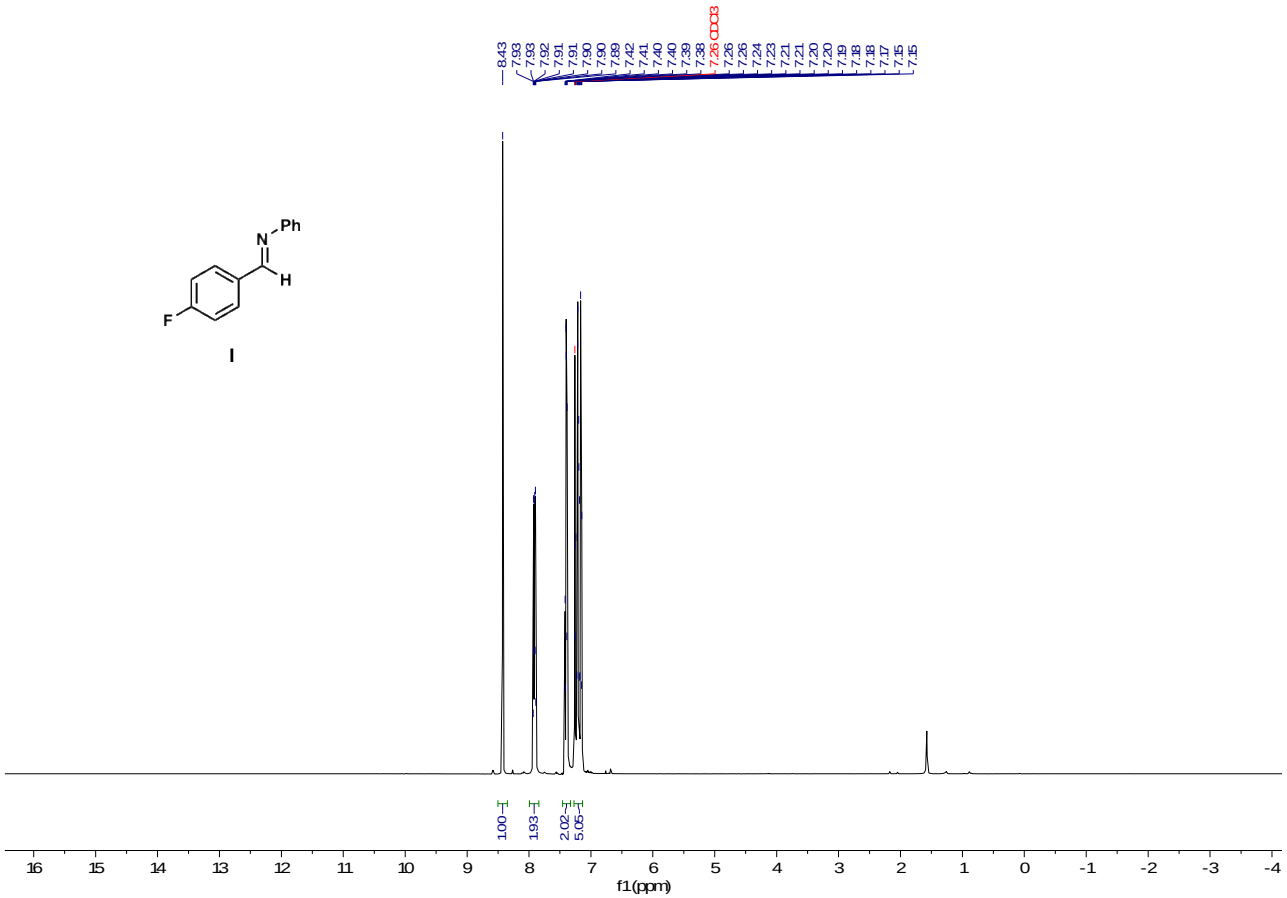
O
O
H
n-Bu
n-Bu
4d
f1 (ppm)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7.90
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7.40
7.40
7.39
7.38
7.26 CDCl3
7.26
7.26
7.24
7.23
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.15
7.15
Ph
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H
F
I
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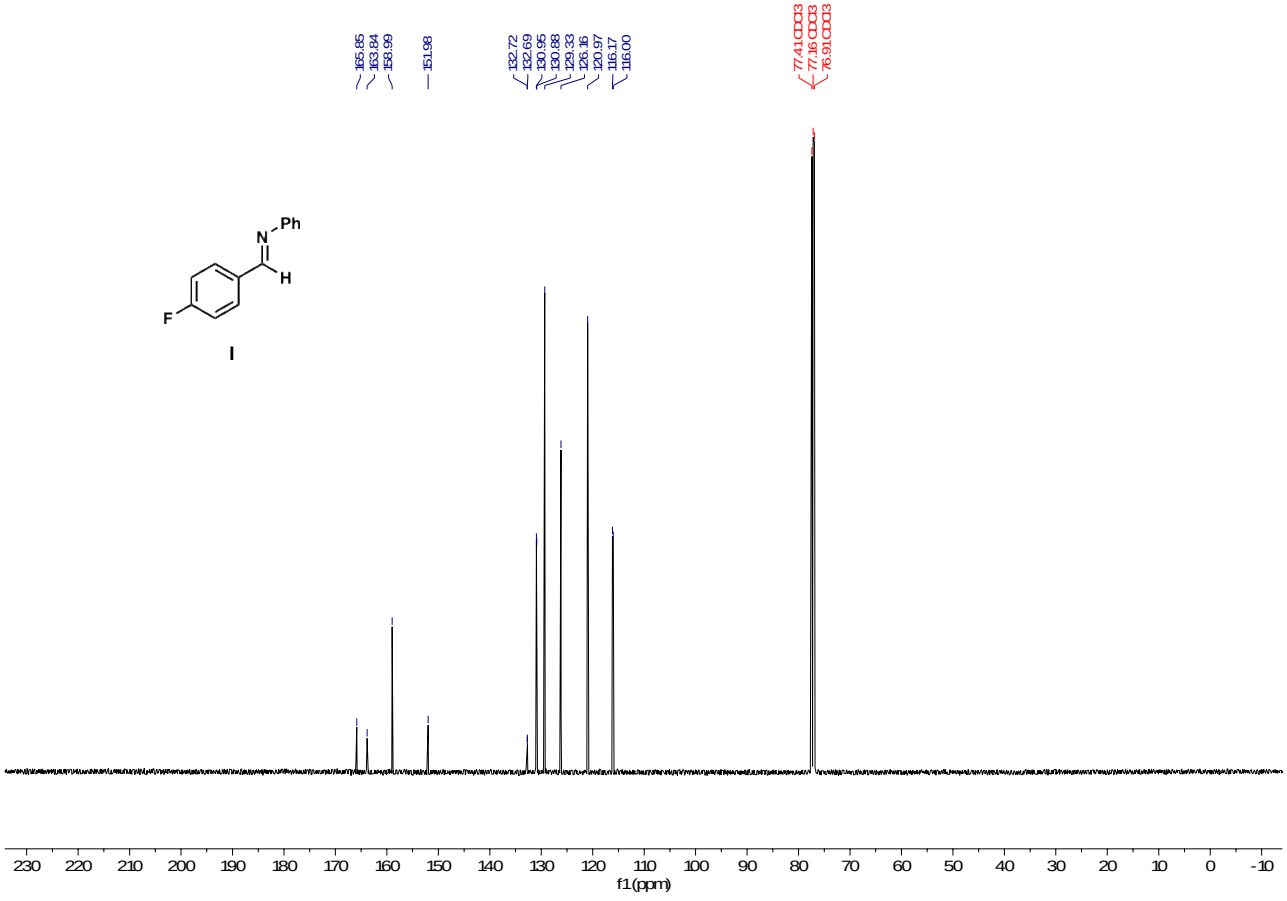
5.05
f1 (ppm)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130.88
129.33
126.16
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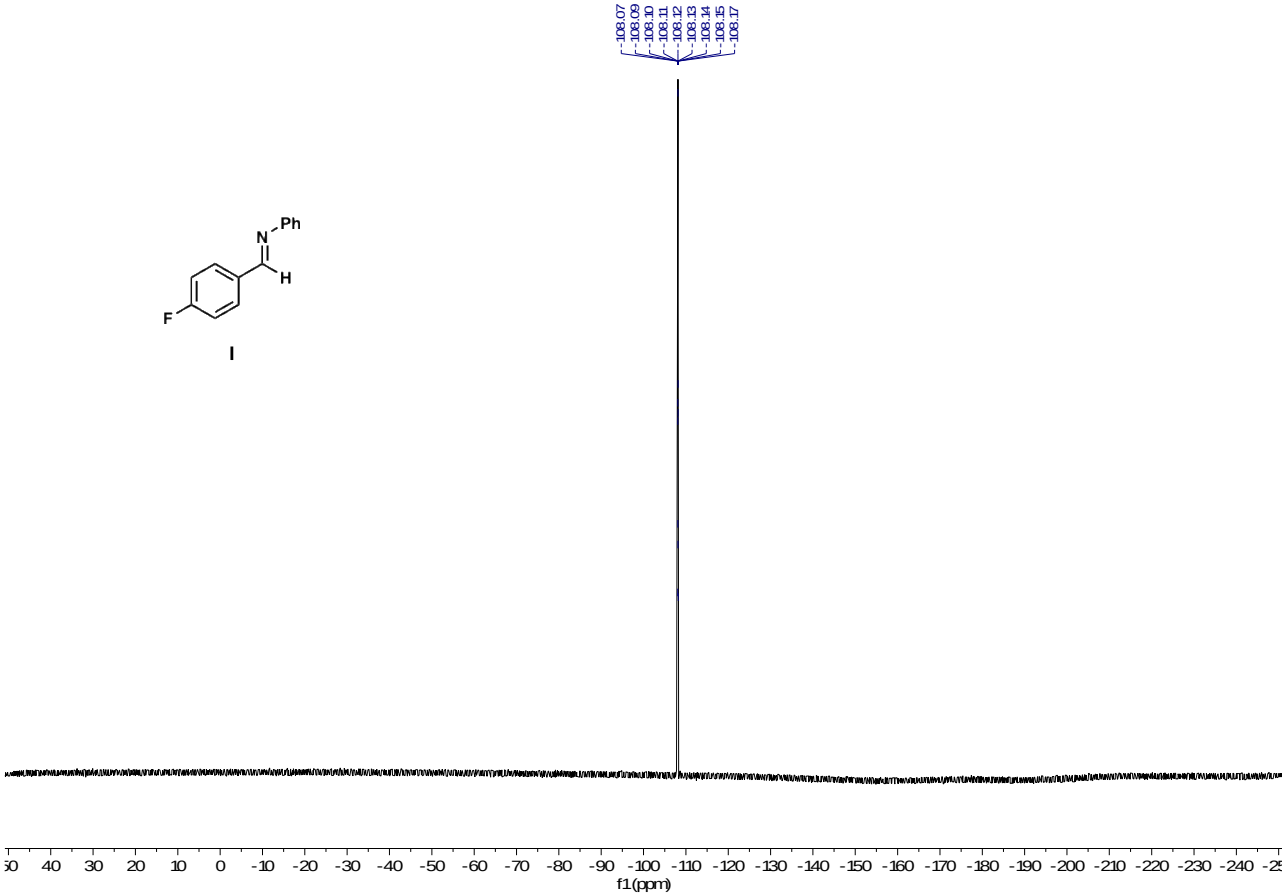
116.00
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
Ph
N
H
F
I
f1 (ppm)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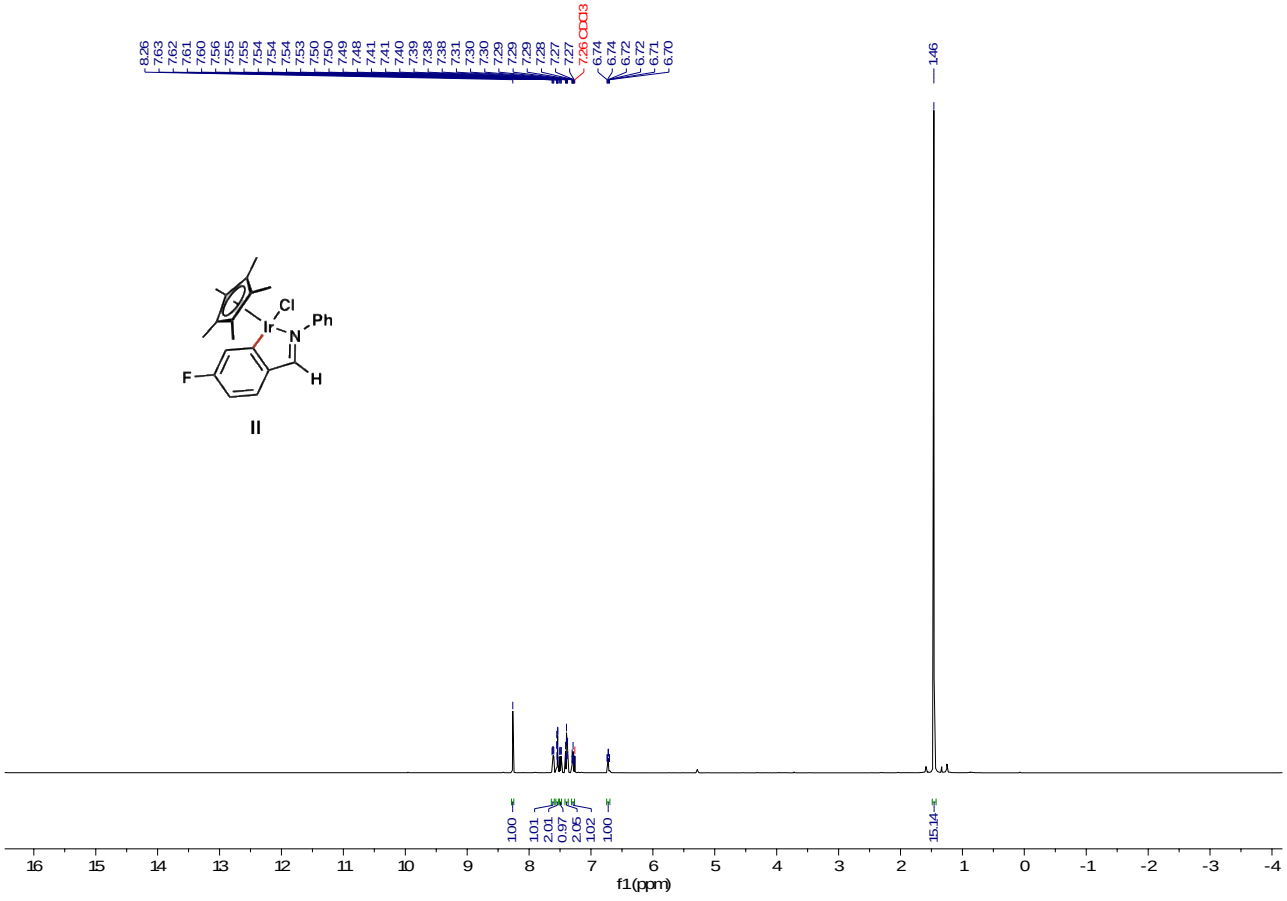
N
Ph
H
F
I
f1 (ppm)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6.72
6.72
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6.70
1.46
Cl
Ir
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Ph
F
H
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1.02
1.00
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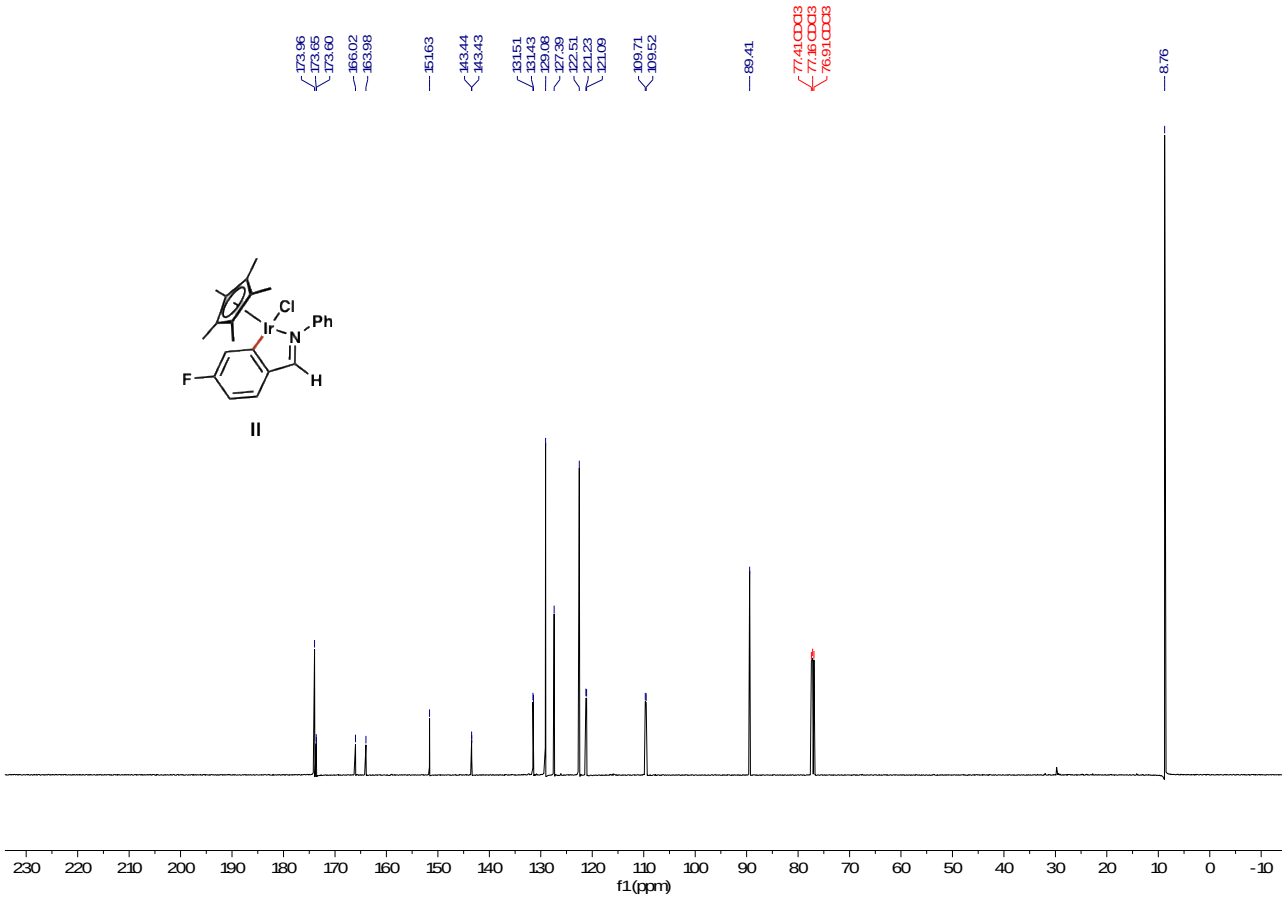
f1 (ppm)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127.39
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121.23
121.09
109.71
109.52
89.41
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
8.76
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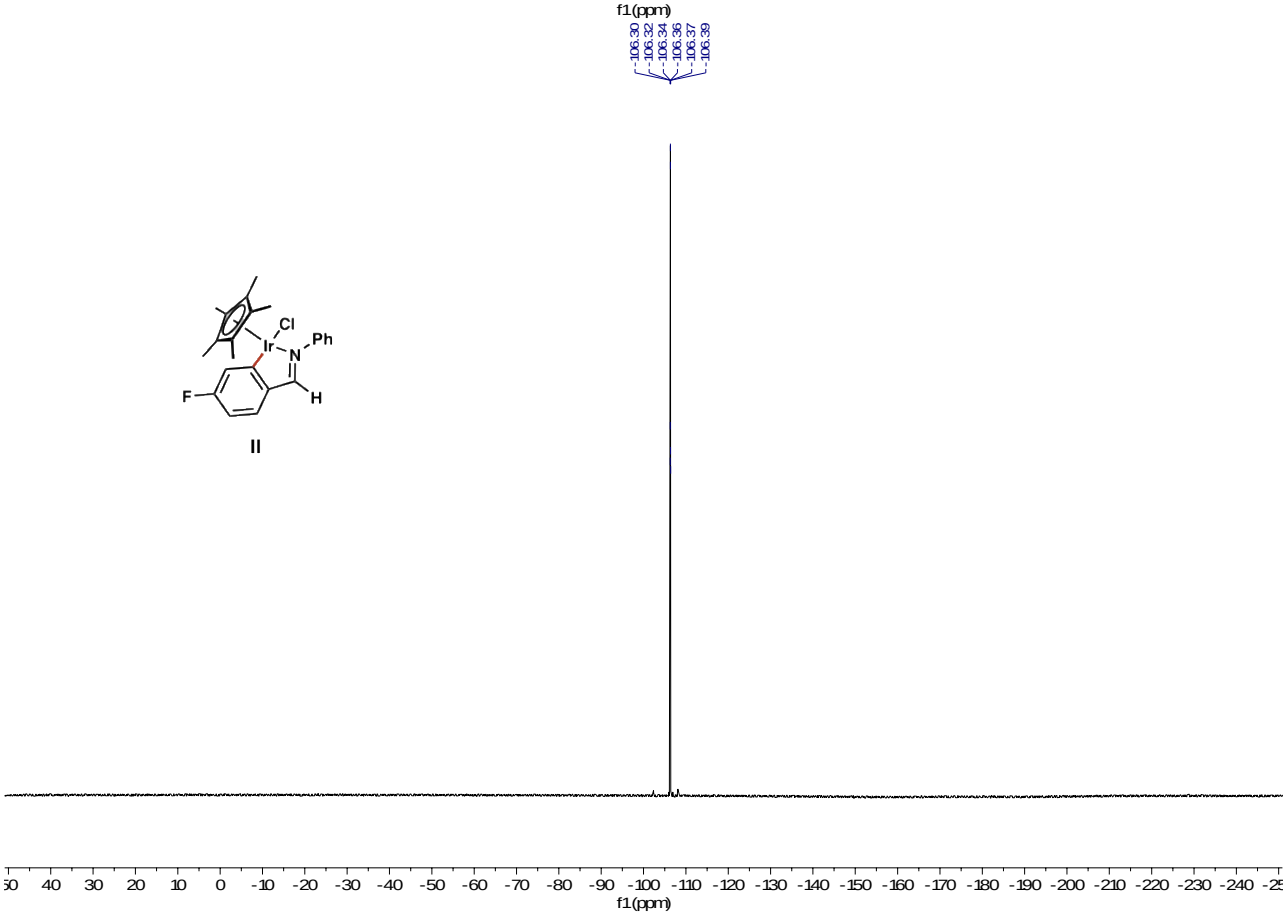
Ir
N
Ph
F
H
II
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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Ir
N
Ph
F
H
II
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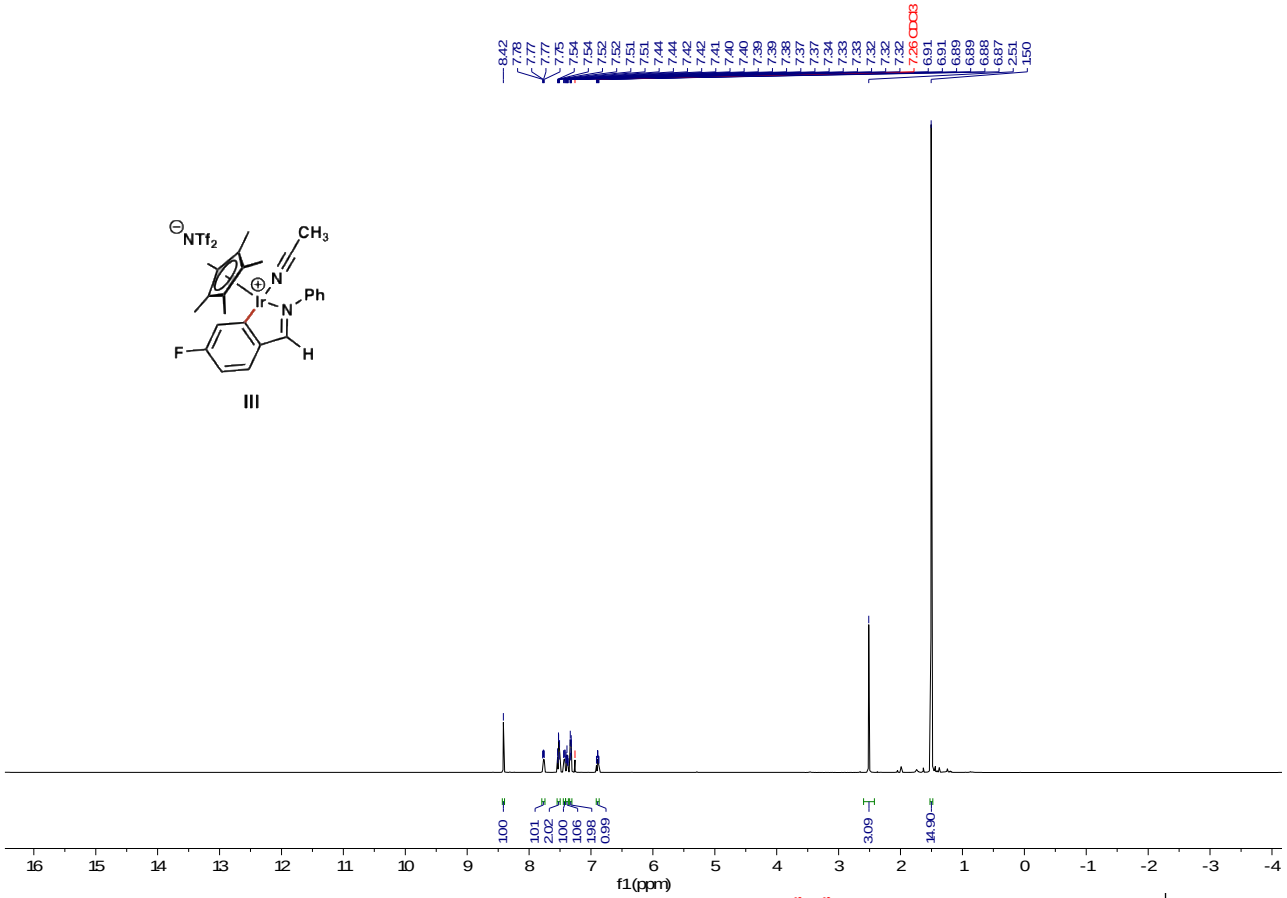
f1 (ppm)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7.37
7.34
7.33
7.33
7.32
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7.32
7.26 CDCl3
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CH3
N
Ir
N
Ph
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1.00
1.06
1.98
0.99
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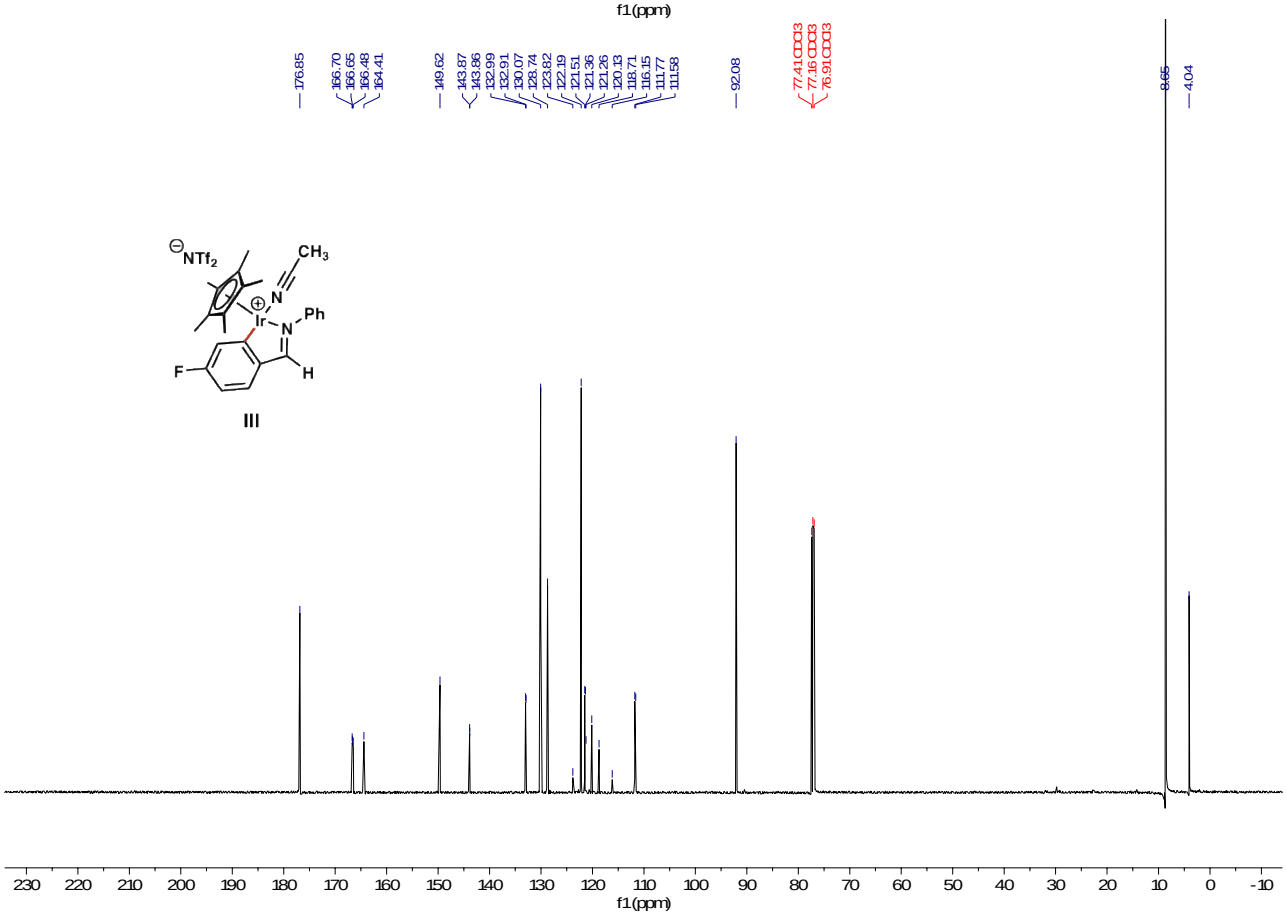
f1 (ppm)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132.99
132.91
130.07
128.74
123.82
122.19
121.51
121.36
121.26
120.13
118.71
116.15
111.77
111.58
92.08
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
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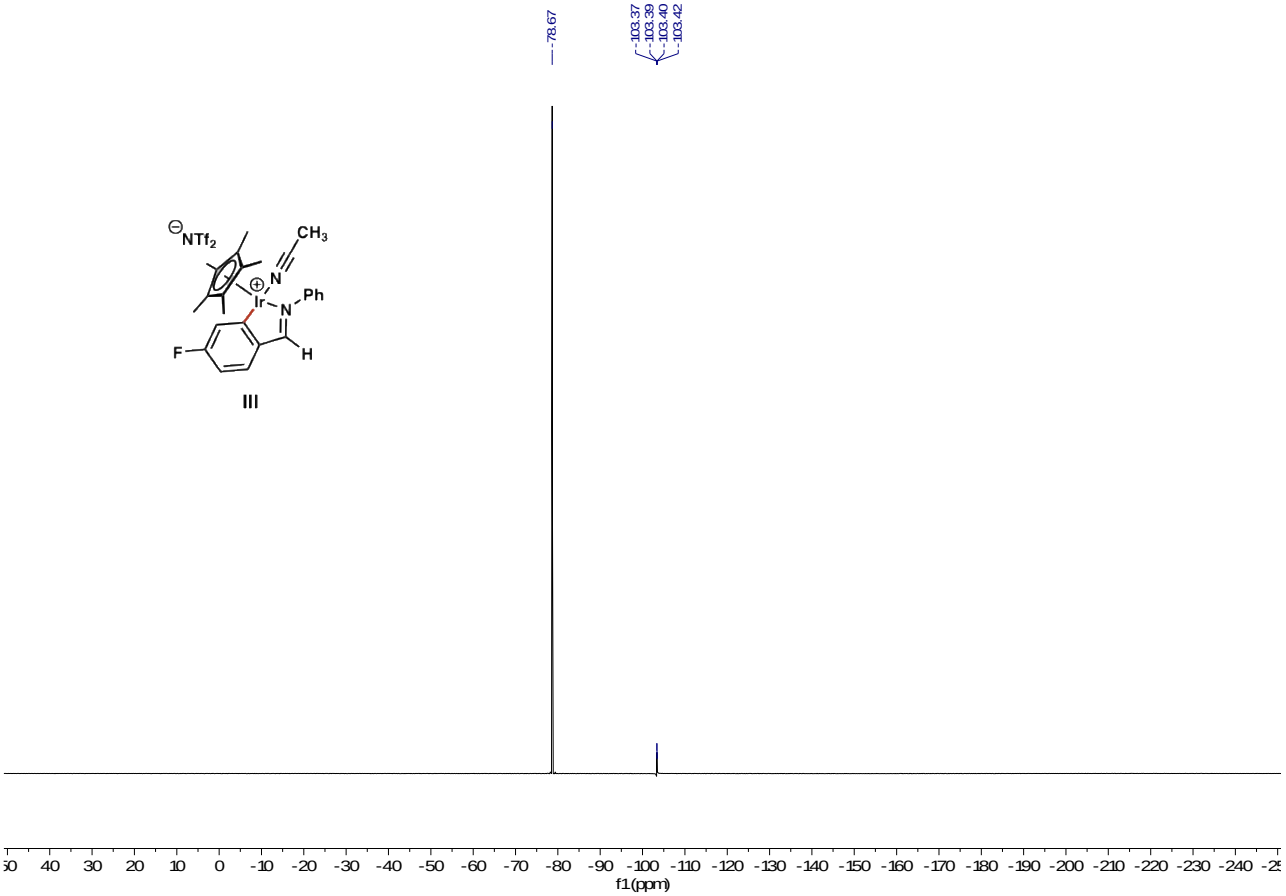
N
Ir
N
Ph
F
H
III
f1 (ppm)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-103.39
-103.40
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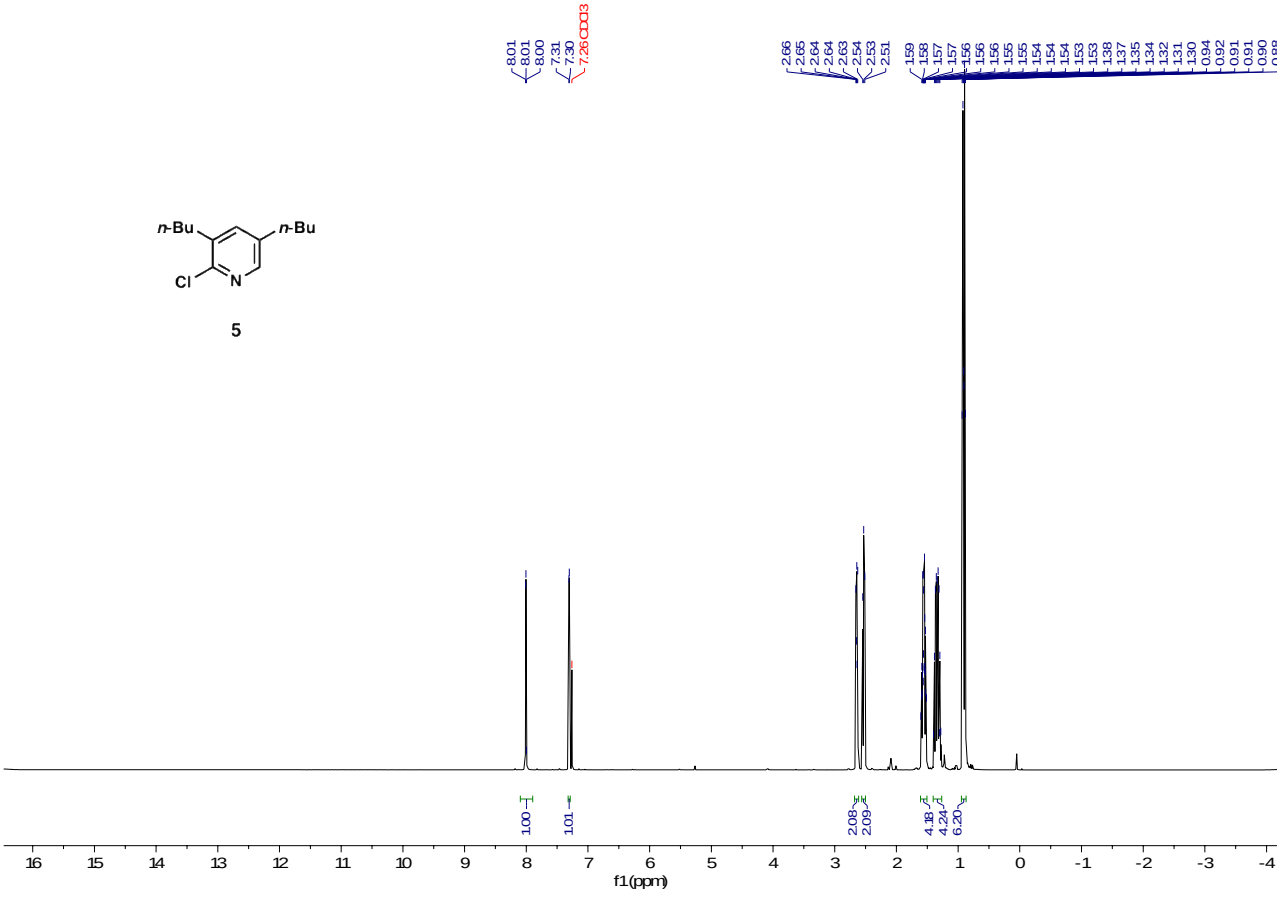
CH3
N
Ir
N
Ph
F
H
III
f1(ppm)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7.26 CDCl3
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1.38
1.37
1.35
1.34
1.32
1.31
1.30
0.94
0.92
0.91
0.91
0.90
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n-Bu
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2.08
2.09
4.18
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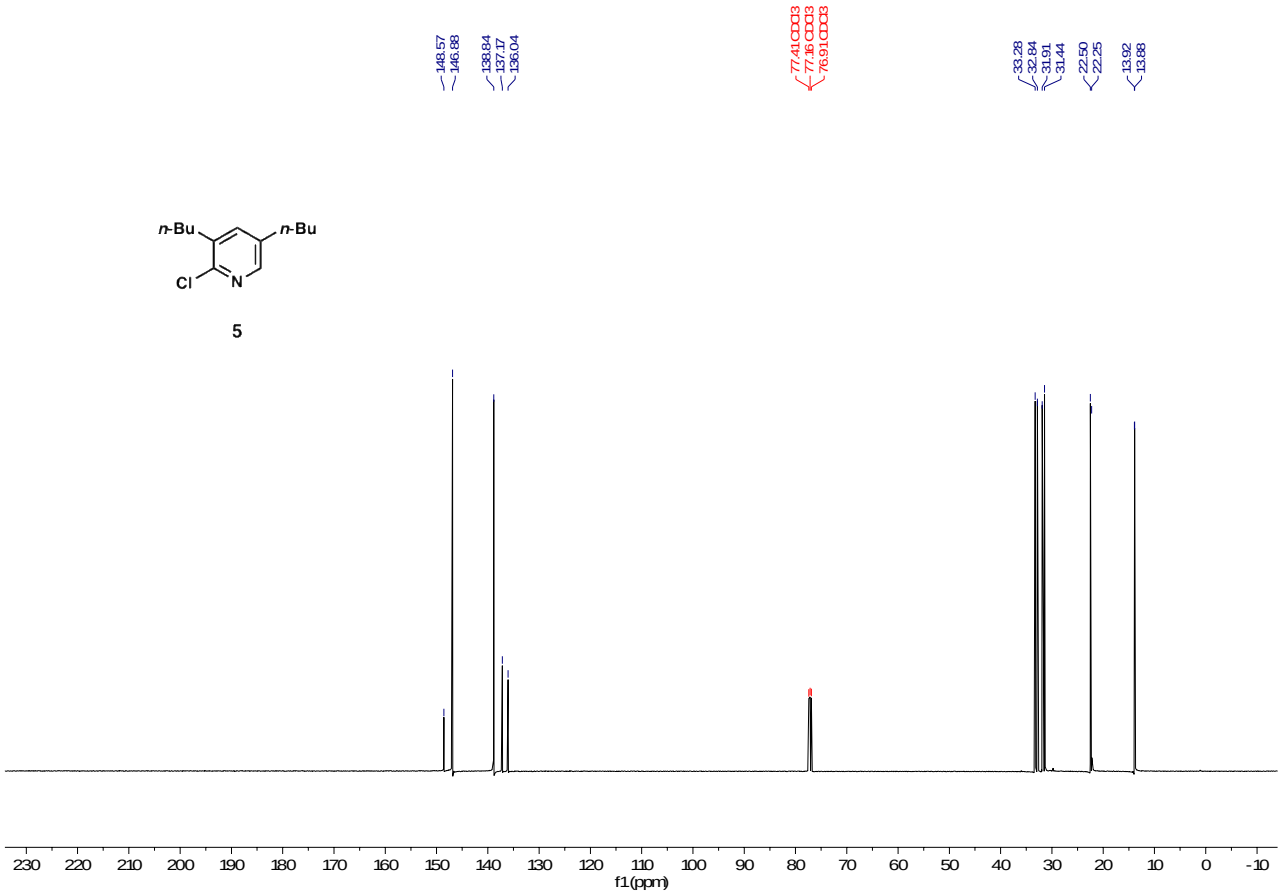
6.20
f1(ppm)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22.50
22.25
13.92
13.88
n-Bu
n-Bu
Cl
N
5
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

X-ray Crystallographic Data

A translucent intense orange prism-like specimen of $C_{23}H_{24}ClFIrN$, approximate dimensions 0.113 mm x 0.166 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table 1: Data collection details for PDJXC7a.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	33.991	35.93	-130.07	0.00	54.74	0.50	303	1.50	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	102.00	54.74	0.50	303	1.50	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	-54.00	54.74	0.50	303	1.50	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	51.00	54.74	0.50	303	1.50	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	153.00	54.74	0.50	303	1.00	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	-105.00	54.74	0.50	303	1.00	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	-156.00	54.74	0.50	303	1.00	0.71073	50	1.0	n/a
Omega	33.991	20.93	-145.07	0.00	54.74	0.50	303	1.00	0.71073	50	1.0	n/a
Omega	33.991	20.93	-145.07	180.00	54.74	0.50	303	1.00	0.71073	50	1.0	n/a
Omega	33.991	20.93	-145.07	270.00	54.74	0.50	303	1.00	0.71073	50	1.0	n/a
Omega	33.991	20.93	-145.07	90.00	54.74	0.50	303	1.00	0.71073	50	1.0	n/a
Phi	33.991	35.93	-130.26	0.00	54.74	0.50	720	1.00	0.71073	50	1.0	n/a

A total of 4053 frames were collected. The total exposure time was 1.29 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 61710 reflections to a maximum θ angle of 33.14° (0.65 Å resolution), of which 7679 were independent (average redundancy 8.036, completeness = 99.8%, R_{int} = 5.68%, R_{sig} = 2.95%) and 7162 (93.27%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 9.2681(5) Å, $\underline{b}$ = 10.4733(5) Å, $\underline{c}$ = 10.8722(5) Å, α = 82.9875(15)°, β = 85.2833(17)°, γ = 74.7986(16)°, volume = 1009.40(9) $Å^3$, are based upon the refinement of the XYZ-centroids of 9791 reflections above 20 σ(I) with 5.245° < 2θ < 72.76°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.728. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2540 and 0.5170.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{23}H_{24}ClFIrN$. The final anisotropic full-matrix least-squares refinement on F^2 with 249 variables converged at R1 = 2.17%, for the observed data and wR2 = 4.83% for all data. The goodness-of-fit was 1.089. The largest peak in the final difference electron density synthesis was 2.289 $e^-/Å^3$ and the largest hole was -0.813 $e^-/Å^3$ with an RMS deviation of 0.145 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.846 g/cm^3 and F(000), 544 e^-.

Table 2. Sample and crystal data for PDJXC7a.

Identification code	PDJXC7a	
Chemical formula	$C_{23}H_{24}ClFIrN$	
Formula weight	561.08 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.113 x 0.166 x 0.280 mm	
Crystal habit	translucent intense orange prism	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.2681(5) Å	α = 82.9875(15)°
	b = 10.4733(5) Å	β = 85.2833(17)°
	c = 10.8722(5) Å	γ = 74.7986(16)°
Volume	1009.40(9) $Å^3$	
Z	2	
Density (calculated)	1.846 g/cm^3	
Absorption coefficient	6.733 mm^{-1}	
F(000)	544	

Table 3. Data collection and structure refinement for PDJXC7a.

Theta range for data collection	2.03 to 33.14°
Index ranges	-14<=h<=14, -16<=k<=16, -16<=l<=16
Reflections collected	61710
Independent reflections	7679 [R(int) = 0.0568]
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.5170 and 0.2540
Structure solution technique	direct methods
Structure solution program	SHELXT (Sheldrick, 2016)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7679 / 0 / 249
Goodness-of-fit on F^2	1.089

Δ/σ_{max}	0.003	
Final R indices	7162 data; I>2σ(I)	R1 = 0.0217, wR2 = 0.0474
	all data	R1 = 0.0251, wR2 = 0.0483
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0197P)^2+0.7300P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.289 and -0.813 eÅ^{-3}	
R.M.S. deviation from mean	0.145 eÅ^{-3}	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for PDJXC7a.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Ir1	0.55443(2)	0.72803(2)	0.24316(2)	0.00981(2)
Cl1	0.63266(6)	0.92600(5)	0.16797(5)	0.01514(9)
F1	0.00695(17)	0.64414(16)	0.55593(15)	0.0248(3)
N1	0.3843(2)	0.84803(17)	0.34651(16)	0.0112(3)
C1	0.6572(2)	0.73178(19)	0.40039(18)	0.0115(3)
C2	0.8082(3)	0.6775(2)	0.4245(2)	0.0145(4)
C3	0.8588(3)	0.6973(2)	0.5352(2)	0.0158(4)
C4	0.7708(3)	0.7677(2)	0.6255(2)	0.0159(4)
C7	0.4159(2)	0.8663(2)	0.45616(18)	0.0122(3)
C6	0.5659(2)	0.8050(2)	0.49199(18)	0.0115(3)
C5	0.6211(3)	0.8225(2)	0.60365(19)	0.0142(4)
C8	0.2401(2)	0.9115(2)	0.3000(2)	0.0135(4)
C9	0.1103(3)	0.9019(2)	0.3707(2)	0.0179(4)
C10	0.9719(3)	0.9621(3)	0.3216(3)	0.0241(5)
C11	0.9629(3)	0.0320(3)	0.2049(3)	0.0243(5)
C12	0.0933(3)	0.0412(2)	0.1348(2)	0.0209(4)
C13	0.2318(3)	0.9798(2)	0.1815(2)	0.0158(4)
C14	0.4418(3)	0.5780(2)	0.2141(2)	0.0146(4)
C15	0.4455(3)	0.6566(2)	0.0952(2)	0.0196(4)
C16	0.5974(3)	0.6487(2)	0.0589(2)	0.0210(5)
C17	0.6922(3)	0.5633(2)	0.1510(2)	0.0167(4)
C18	0.5942(2)	0.5160(2)	0.24591(19)	0.0126(4)
C19	0.3032(3)	0.5574(2)	0.2853(3)	0.0228(5)
C20	0.3147(4)	0.7255(3)	0.0192(3)	0.0358(8)
C21	0.6519(5)	0.7184(3)	0.9426(2)	0.0382(8)
C22	0.8596(3)	0.5167(3)	0.1397(3)	0.0274(6)
C23	0.6444(3)	0.4134(2)	0.3528(2)	0.0191(4)

Table 5. Bond lengths (Å) for PDJXC7a.

Ir1-C1	2.033(2)	Ir1-N1	2.0842(18)
Ir1-C18	2.150(2)	Ir1-C17	2.160(2)
Ir1-C14	2.167(2)	Ir1-C16	2.228(2)
Ir1-C15	2.264(2)	Ir1-Cl1	2.4021(5)
F1-C3	1.365(3)	N1-C7	1.299(3)
N1-C8	1.430(3)	C1-C2	1.399(3)
C1-C6	1.415(3)	C2-C3	1.385(3)
C2-H2	0.95	C3-C4	1.379(3)
C4-C5	1.384(3)	C4-H4	0.95
C7-C6	1.434(3)	C7-H7	0.95
C6-C5	1.405(3)	C5-H5	0.95
C8-C13	1.393(3)	C8-C9	1.393(3)
C9-C10	1.391(3)	C9-H9	0.95
C10-C11	1.383(4)	C10-H10	0.95
C11-C12	1.393(4)	C11-H11	0.95
C12-C13	1.384(3)	C12-H12	0.95
C13-H13	0.95	C14-C18	1.442(3)
C14-C15	1.448(3)	C14-C19	1.495(3)
C15-C16	1.415(4)	C15-C20	1.495(4)
C16-C17	1.445(4)	C16-C21	1.500(3)
C17-C18	1.446(3)	C17-C22	1.499(4)
C18-C23	1.498(3)	C19-H19A	0.98
C19-H19B	0.98	C19-H19C	0.98
C20-H20A	0.98	C20-H20B	0.98
C20-H20C	0.98	C21-H21A	0.98
C21-H21B	0.98	C21-H21C	0.98
C22-H22A	0.98	C22-H22B	0.98
C22-H22C	0.98	C23-H23A	0.98
C23-H23B	0.98	C23-H23C	0.98

Table 6. Bond angles (°) for PDJXC7a.

C1-Ir1-N1	77.75(8)	C1-Ir1-C18	98.49(8)
N1-Ir1-C18	124.96(7)	C1-Ir1-C17	106.48(9)
N1-Ir1-C17	163.46(8)	C18-Ir1-C17	39.21(8)
C1-Ir1-C14	124.57(8)	N1-Ir1-C14	98.87(8)
C18-Ir1-C14	39.03(8)	C17-Ir1-C14	65.35(9)
C1-Ir1-C16	141.89(10)	N1-Ir1-C16	140.32(9)
C18-Ir1-C16	64.01(8)	C17-Ir1-C16	38.41(9)

C14-Ir1-C16	63.38(9)	C1-Ir1-C15	161.69(8)
N1-Ir1-C15	107.42(9)	C18-Ir1-C15	63.93(8)
C17-Ir1-C15	63.74(9)	C14-Ir1-C15	38.08(8)
C16-Ir1-C15	36.72(10)	C1-Ir1-Cl1	85.69(6)
N1-Ir1-Cl1	87.05(5)	C18-Ir1-Cl1	147.93(6)
C17-Ir1-Cl1	109.04(6)	C14-Ir1-Cl1	149.74(6)
C16-Ir1-Cl1	93.30(6)	C15-Ir1-Cl1	111.82(6)
C7-N1-C8	120.48(18)	C7-N1-Ir1	116.69(15)
C8-N1-Ir1	122.81(13)	C2-C1-C6	117.03(19)
C2-C1-Ir1	127.47(15)	C6-C1-Ir1	115.38(15)
C3-C2-C1	118.8(2)	C3-C2-H2	120.6
C1-C2-H2	120.6	F1-C3-C4	117.7(2)
F1-C3-C2	117.6(2)	C4-C3-C2	124.7(2)
C3-C4-C5	117.6(2)	C3-C4-H4	121.2
C5-C4-H4	121.2	N1-C7-C6	116.52(18)
N1-C7-H7	121.7	C6-C7-H7	121.7
C5-C6-C1	122.7(2)	C5-C6-C7	123.60(19)
C1-C6-C7	113.62(18)	C4-C5-C6	119.3(2)
C4-C5-H5	120.4	C6-C5-H5	120.4
C13-C8-C9	120.6(2)	C13-C8-N1	118.8(2)
C9-C8-N1	120.50(19)	C10-C9-C8	119.0(2)
C10-C9-H9	120.5	C8-C9-H9	120.5
C11-C10-C9	120.6(2)	C11-C10-H10	119.7
C9-C10-H10	119.7	C10-C11-C12	120.0(2)
C10-C11-H11	120.0	C12-C11-H11	120.0
C13-C12-C11	120.1(2)	C13-C12-H12	119.9
C11-C12-H12	119.9	C12-C13-C8	119.6(2)
C12-C13-H13	120.2	C8-C13-H13	120.2
C18-C14-C15	108.0(2)	C18-C14-C19	126.6(2)
C15-C14-C19	125.3(2)	C18-C14-Ir1	69.85(12)
C15-C14-Ir1	74.58(12)	C19-C14-Ir1	124.84(15)
C16-C15-C14	107.5(2)	C16-C15-C20	125.6(2)
C14-C15-C20	126.8(3)	C16-C15-Ir1	70.26(13)
C14-C15-Ir1	67.34(12)	C20-C15-Ir1	131.06(17)
C15-C16-C17	109.62(19)	C15-C16-C21	125.2(3)
C17-C16-C21	125.2(3)	C15-C16-Ir1	73.02(13)
C17-C16-Ir1	68.26(12)	C21-C16-Ir1	125.07(17)
C16-C17-C18	106.8(2)	C16-C17-C22	126.0(2)
C18-C17-C22	126.6(2)	C16-C17-Ir1	73.33(13)
C18-C17-Ir1	70.01(11)	C22-C17-Ir1	128.72(17)

C14-C18-C17	107.95(19)	C14-C18-C23	126.6(2)
C17-C18-C23	125.3(2)	C14-C18-Ir1	71.12(11)
C17-C18-Ir1	70.77(12)	C23-C18-Ir1	126.93(15)
C14-C19-H19A	109.5	C14-C19-H19B	109.5
H19A-C19-H19B	109.5	C14-C19-H19C	109.5
H19A-C19-H19C	109.5	H19B-C19-H19C	109.5
C15-C20-H20A	109.5	C15-C20-H20B	109.5
H20A-C20-H20B	109.5	C15-C20-H20C	109.5
H20A-C20-H20C	109.5	H20B-C20-H20C	109.5
C16-C21-H21A	109.5	C16-C21-H21B	109.5
H21A-C21-H21B	109.5	C16-C21-H21C	109.5
H21A-C21-H21C	109.5	H21B-C21-H21C	109.5
C17-C22-H22A	109.5	C17-C22-H22B	109.5
H22A-C22-H22B	109.5	C17-C22-H22C	109.5
H22A-C22-H22C	109.5	H22B-C22-H22C	109.5
C18-C23-H23A	109.5	C18-C23-H23B	109.5
H23A-C23-H23B	109.5	C18-C23-H23C	109.5
H23A-C23-H23C	109.5	H23B-C23-H23C	109.5

Table 7. Torsion angles (°) for PDJXC7a.

C6-C1-C2-C3	0.5(3)	Ir1-C1-C2-C3	176.28(16)
C1-C2-C3-F1	-179.49(19)	C1-C2-C3-C4	-0.1(3)
F1-C3-C4-C5	179.41(19)	C2-C3-C4-C5	0.1(3)
C8-N1-C7-C6	-176.44(18)	Ir1-N1-C7-C6	1.9(2)
C2-C1-C6-C5	-0.8(3)	Ir1-C1-C6-C5	-177.12(16)
C2-C1-C6-C7	175.23(18)	Ir1-C1-C6-C7	-1.1(2)
N1-C7-C6-C5	175.48(19)	N1-C7-C6-C1	-0.5(3)
C3-C4-C5-C6	-0.4(3)	C1-C6-C5-C4	0.8(3)
C7-C6-C5-C4	-174.9(2)	C7-N1-C8-C13	130.8(2)
Ir1-N1-C8-C13	-47.4(2)	C7-N1-C8-C9	-51.0(3)
Ir1-N1-C8-C9	130.82(18)	C13-C8-C9-C10	-0.3(3)
N1-C8-C9-C10	-178.5(2)	C8-C9-C10-C11	-0.8(4)
C9-C10-C11-C12	0.8(4)	C10-C11-C12-C13	0.4(4)
C11-C12-C13-C8	-1.6(3)	C9-C8-C13-C12	1.5(3)
N1-C8-C13-C12	179.7(2)	C18-C14-C15-C16	-3.3(2)
C19-C14-C15-C16	-179.0(2)	Ir1-C14-C15-C16	58.97(15)
C18-C14-C15-C20	172.5(2)	C19-C14-C15-C20	-3.2(4)
Ir1-C14-C15-C20	-125.2(2)	C18-C14-C15-Ir1	-62.26(14)
C19-C14-C15-Ir1	122.1(2)	C14-C15-C16-C17	1.5(2)
C20-C15-C16-C17	-174.4(2)	Ir1-C15-C16-C17	58.67(15)

C14-C15-C16-C21	-178.5(2)	C20-C15-C16-C21	5.6(4)
Ir1-C15-C16-C21	-121.3(2)	C14-C15-C16-Ir1	-57.15(14)
C20-C15-C16-Ir1	127.0(2)	C15-C16-C17-C18	0.8(2)
C21-C16-C17-C18	-179.2(2)	Ir1-C16-C17-C18	62.41(14)
C15-C16-C17-C22	172.3(2)	C21-C16-C17-C22	-7.7(4)
Ir1-C16-C17-C22	-126.1(2)	C15-C16-C17-Ir1	-61.58(16)
C21-C16-C17-Ir1	118.4(2)	C15-C14-C18-C17	3.8(2)
C19-C14-C18-C17	179.4(2)	Ir1-C14-C18-C17	-61.54(14)
C15-C14-C18-C23	-172.2(2)	C19-C14-C18-C23	3.4(3)
Ir1-C14-C18-C23	122.5(2)	C15-C14-C18-Ir1	65.35(14)
C19-C14-C18-Ir1	-119.0(2)	C16-C17-C18-C14	-2.9(2)
C22-C17-C18-C14	-174.3(2)	Ir1-C17-C18-C14	61.76(14)
C16-C17-C18-C23	173.2(2)	C22-C17-C18-C23	1.8(4)
Ir1-C17-C18-C23	-122.2(2)	C16-C17-C18-Ir1	-64.62(14)
C22-C17-C18-Ir1	124.0(2)		

Table 8. Anisotropic atomic displacement parameters (Å^2) for PDJXC7a.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	0.01495(4)	0.00801(3)	0.00732(3)	-0.00095(2)	0.00039(2)	-0.00464(2)
Cl1	0.0194(2)	0.0132(2)	0.0147(2)	0.00080(16)	0.00042(17)	-0.00897(18)
F1	0.0197(7)	0.0266(8)	0.0270(8)	-0.0008(6)	-0.0102(6)	-0.0019(6)
N1	0.0144(8)	0.0088(7)	0.0109(7)	0.0006(6)	-0.0006(6)	-0.0049(6)
C1	0.0160(9)	0.0081(8)	0.0108(8)	0.0003(6)	0.0004(7)	-0.0048(7)
C2	0.0165(10)	0.0120(9)	0.0148(9)	-0.0011(7)	-0.0021(7)	-0.0028(7)
C3	0.0172(10)	0.0115(9)	0.0176(9)	0.0022(7)	-0.0054(8)	-0.0021(7)
C4	0.0259(11)	0.0116(9)	0.0113(8)	0.0021(7)	-0.0042(8)	-0.0074(8)
C7	0.0158(9)	0.0106(8)	0.0101(8)	-0.0023(6)	0.0030(7)	-0.0038(7)
C6	0.0168(9)	0.0089(8)	0.0089(8)	-0.0003(6)	0.0004(7)	-0.0040(7)
C5	0.0229(11)	0.0101(8)	0.0100(8)	-0.0004(7)	-0.0020(7)	-0.0048(7)
C8	0.0148(9)	0.0105(8)	0.0162(9)	-0.0022(7)	-0.0016(7)	-0.0044(7)
C9	0.0164(10)	0.0172(10)	0.0200(10)	-0.0022(8)	0.0013(8)	-0.0047(8)
C10	0.0140(10)	0.0256(12)	0.0333(13)	-0.0041(10)	0.0003(9)	-0.0060(9)
C11	0.0166(11)	0.0244(12)	0.0323(13)	-0.0023(10)	-0.0081(9)	-0.0043(9)
C12	0.0218(11)	0.0190(10)	0.0232(11)	-0.0006(9)	-0.0094(9)	-0.0058(9)
C13	0.0174(10)	0.0151(9)	0.0165(9)	-0.0011(7)	-0.0031(8)	-0.0068(8)
C14	0.0203(10)	0.0092(8)	0.0169(9)	-0.0034(7)	-0.0023(8)	-0.0069(7)
C15	0.0346(13)	0.0121(9)	0.0151(9)	-0.0033(7)	-0.0099(9)	-0.0079(9)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	0.0440(15)	0.0144(9)	0.0076(8)	-0.0052(7)	0.0044(9)	-0.0126(10)
C17	0.0241(11)	0.0136(9)	0.0139(9)	-0.0067(7)	0.0085(8)	-0.0081(8)
C18	0.0170(9)	0.0092(8)	0.0118(8)	-0.0017(6)	0.0016(7)	-0.0041(7)
C19	0.0158(10)	0.0186(10)	0.0365(13)	-0.0081(10)	0.0026(9)	-0.0077(8)
C20	0.056(2)	0.0194(12)	0.0350(15)	-0.0065(11)	-0.0318(14)	-0.0044(12)
C21	0.082(3)	0.0254(13)	0.0116(10)	-0.0030(9)	0.0111(13)	-0.0254(15)
C22	0.0246(12)	0.0274(13)	0.0339(14)	-0.0176(11)	0.0161(11)	-0.0120(10)
C23	0.0247(12)	0.0121(9)	0.0195(10)	0.0021(8)	-0.0011(8)	-0.0044(8)

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for PDJXC7a.

	x/a	y/b	z/c	U(eq)
H2	0.8747	0.6281	0.3659	0.017
H4	0.8115	0.7783	0.6999	0.019
H7	0.3435	0.9175	0.5098	0.015
H5	0.5563	0.8714	0.6635	0.017
H9	0.1162	0.8548	0.4514	0.021
H10	-0.1172	0.9551	0.3686	0.029
H11	-0.1321	1.0738	0.1725	0.029
H12	0.0870	1.0898	0.0548	0.025
H13	0.3208	0.9841	0.1330	0.019
H19A	0.3273	0.5199	0.3704	0.034
H19B	0.2633	0.4958	0.2453	0.034
H19C	0.2282	0.6428	0.2867	0.034
H20A	0.3326	0.8074	-0.0257	0.054
H20B	0.2241	0.7475	0.0738	0.054
H20C	0.3016	0.6669	-0.0404	0.054
H21A	0.7534	0.7259	-0.0475	0.057
H21B	0.5850	0.8075	-0.0734	0.057
H21C	0.6529	0.6673	-0.1274	0.057
H22A	0.8974	0.4743	0.2202	0.041
H22B	0.9017	0.5930	0.1134	0.041
H22C	0.8893	0.4525	0.0780	0.041
H23A	0.5640	0.4207	0.4180	0.029
H23B	0.7334	0.4280	0.3857	0.029
H23C	0.6685	0.3245	0.3246	0.029

References

1. M. Jakoobi, N. Halcovitch, G. F. S. Whitehead and A. G. Sergeev, *Angew. Chem. Int. Ed.*, 2017, **56**, 3266-3269.
2. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.
3. A. P. Dieskau, M. S. Holzwarth and B. Plietker, *J. Am. Chem. Soc.*, 2012, **134**, 5048-5051.
4. C. Bosset, P. Angibaud, I. Stanfield, L. Meerpoel, D. Berthelot, A. Guérinot and J. Cossy, *J. Org. Chem.*, 2015, **80**, 12509-12525.
5. M. J. Meyers, G. B. Arhancet, S. L. Hockerman, X. Chen, S. A. Long, M. W. Mahoney, J. R. Rico, D. J. Garland, J. R. Blinn, J. T. Collins, S. Yang, H.-C. Huang, K. F. McGee, J. M. Wendling, J. D. Dietz, M. A. Payne, B. L. Homer, M. I. Heron, D. B. Reitz and X. Hu, *J. Med. Chem.*, 2010, **53**, 5979-6002.
6. M. van Gemmeren, M. Börjesson, A. Tortajada, S.-Z. Sun, K. Okura and R. Martin, *Angew. Chem. Int. Ed.*, 2017, **56**, 6558-6562.
7. S. Takano, K. Inomata, K. Samizu, S. i. Tomita, M. Yanase, M. Suzuki, Y. Iwabuchi, T. Sugihara and K. Ogasawara, *Chem. Lett.*, 1989, **18**, 1283-1284.
8. C. Wang, K. Huang, J. Wang, H. Wang, L. Liu, W. Chang and J. Li, *Adv. Synth. Catal.*, 2015, **357**, 2795-2802.
9. L. Li, W. W. Brennessel and W. D. Jones, *J. Am. Chem. Soc.*, 2008, **130**, 12414-12419.
10. Y.-K. Sau, X.-Y. Yi, K.-W. Chan, C.-S. Lai, I. D. Williams and W.-H. Leung, *J. Organomet. Chem.*, 2010, **695**, 1399-1404.
11. P.-S. Lee and N. Yoshikai, *Angew. Chem. Int. Ed.*, 2013, **52**, 1240-1244.