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Supplementary Information

Light-switchable divergent C–H activation and cross-coupling of cyclic ethers with aromatic aldehydes

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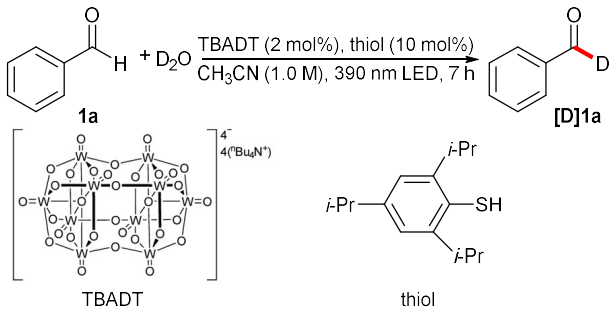
I、 General Methods

All reactions were conducted under argon atmosphere in glass vessels with magnetic stirring. Petroleum ether, ethyl acetate, and other solvents were dried and purified following the procedures described in 'Purification of Laboratory Chemicals'.[1] The Reactions were monitored by thin-layer chromatography (TLC) on silica gel GF 254 plates. Column chromatography was performed through silica gel (200−300 mesh). The specifications for preparative thin-layer chromatography (PTLC) were as follows: plate dimensions (20 × 20 cm), silica gel type (GF254), layer thickness (1.0 mm), with visualization under ultraviolet light (254/365 nm). ^{1}H, ^{19}F and ^{13}C NMR spectra were collected on a Bruker AVANCE III HD 400 (^{1}H 400 MHz, ^{13}C 101 MHz, ^{19}F 376 MHz), spectrometers at room temperature. Chemical shift values (δ) are given in ppm and coupling constants (J) in Hertz (Hz). Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference ($CDCl_3$: δ H 7.26, δ C 77.0 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), hept (heptet), dd (doublet of doublets), td (triplet of doublets), dt (doublet of triplets) and m (multiplet). HRMS was performed on Bruker Apex II FT-ICR mass instrument using ESI (Electrospray Ionization) at the Analytical Testing Center of Lanzhou University.

The light-reaction setup consisted of the following equipment: 365 nm insect-attracting UV blacklight tube (T8-15 W × 2, total 30 W, Haining Haihong Optoelectronics Technology Co., Ltd); 254 nm UV tube (T5-8 W × 4, total 32 W, Royal Philips, Netherlands); a multi-channel photoreactor with 10 W purple LED (390 nm, composed of 2 LED units in series, manufacturer: Shanghai Yukang Science and Education Instrument and Equipment company); cooling fan (30 W, 50Hz, specification 160 mm, Model number YZS-180, Taizhou Jiaojiang Liyu Plastic Electrical Appliance Factory).

II、 Preparation of Substrates

Procedure for Preparation of Deuterated Benzaldehyde



Deuterated benzaldehyde was prepared according to the literature procedure.[2] A mixture of aldehyde substrate **1a** (0.2 mmol), TBADT (13.2 mg, 2 mol%), thiol (5 μL, 10 mol%), D_2O (180

μL, 50 equiv.) and CH_3CN (200 μL, 1.0 M) was added to a 10 mL quartz tube equipped with a stir bar. The mixture was operated by freeze-pump-thaw procedures three times before charging the tube with argon. The reactor was then sealed and irradiated with a 390 nm LED light (10 W) while stirring for 7 h. Then, the crude reaction mixture was extracted with diethyl ether (3 × 2 mL). The combined organic layer was concentrated and purified by flash column chromatography over silica gel to afford the deuterated product **[D]1a** as pale-yellow oil (94% yield).

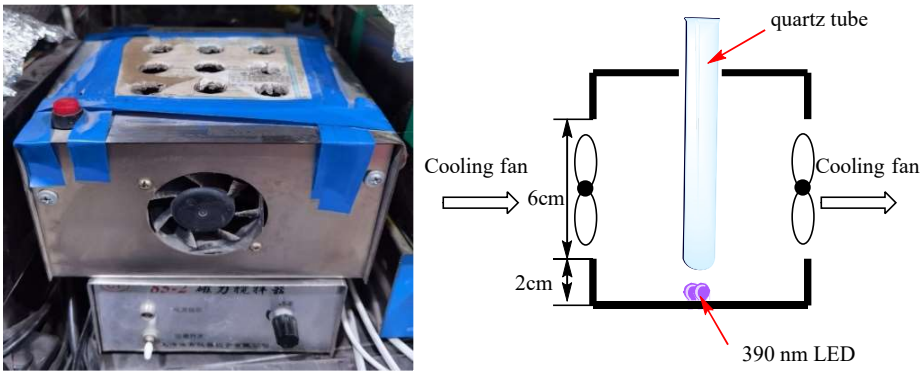
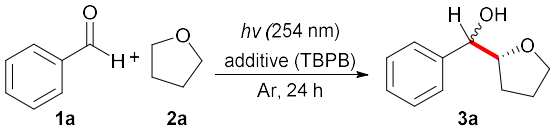


Figure S1. Photochemical Reaction Setup under 390 nm Illumination: Physical object picture of the 390 nm LED (Left), Schematic diagram of the 390 nm LED internal structure (Right).

III、Optimization of the Reaction Conditions of α-hydroxyarylation

Table S1-1 Exploring temperature effects on α-hydroxyarylation reaction[a]

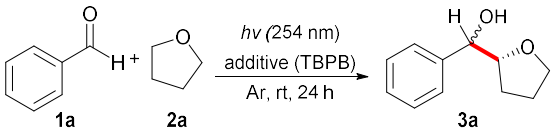


Entry	reaction temperature/°C	Yield (%) [b]	Threo/erythro
1	-7	55	1.04
2	4	60	1.07
3	8	62	1.00
4	room temperature	64	1.03
5	80	8	0.6
6	100	5	0

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), and solvent (3.0 mL THF) was irradiated with four 254 nm UV tubes (8 W each, total 32 W) for 24 h under an argon atmosphere

at different temperatures. [b] Isolated yields.

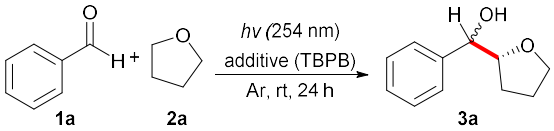
Table S1-2 Exploring the amount of TBPB[a]



Entry	TBPB (equiv.)	Yield (%) [b]	Threo/erythro
1	0.2	46	0.95
2	0.5	49	1.13
3	0.8	49	1.13
4	1	52	1.08
5	1.5	55	1.04

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (different molar equivalents), and solvent (3.0 mL THF) was irradiated with four 254 nm UV tubes (8 W each, total 32 W) for 24 h under an argon atmosphere at room temperature. [b] Isolated yields.

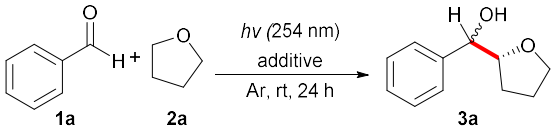
Table S1-3 Exploring the amount of solvent[a]



Entry	solvent (mL)	Yield (%) [b]	Threo/erythro
1	0.5	39	1.17
2	1	54	1.08
3	2	53	1.04

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), and solvent (THF) was irradiated with four 254 nm UV tubes (8 W each, total 32 W) for 24 h under an argon atmosphere at room temperature. [b] Isolated yields.

Table S1-4 Exploring the different additives[a]

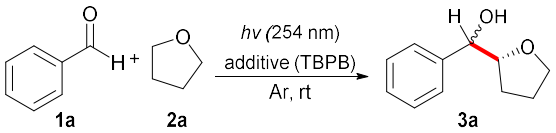


Entry	Additices	Yield (%) [b]	Threo/erythro
1	*tert*-Butyl hydroperoxide	26	1.00

2	Di-*tert*-butyl peroxide	36	1.00
3	2-Me-TBPB	30	1.14
4	4-*t*-Bu-TBPB	44	1.00
5	2-MeO-TBPB	12	0
6	4-MeO-TBPB	56	1.07
7	Pyridine	41	0.95
8	Triethylenediamine	47	1.04
9	N, N-diisopropylethylamine	50	1.08
10	Quinuclidine	49	1.04
11	Pachycarpine	29	0.93
12	3-Chloroperoxybenzoic acid	26	1.17
13	0.1 eq CuOTf	23	1.00
14	0.1 eq $FeCl_2$	16	0.78
15	0.1 eq $Cu(OTf)_2$	trace	-
16	0.2 eq NHPI + 2 eq TBPB	63	0.97
17	0.2 eq NBS + 2 eq TBPB	12	1.00
18	0.2 eq NCS + 2 eq TBPB	42	0.88

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), additive (0.4 mmol or the labeled molar equivalents), and solvent (3.0 mL THF) was irradiated with four 254 nm UV tubes (8 W each, total 32 W) for 24 h under an argon atmosphere at room temperature. [b] Isolated yields.

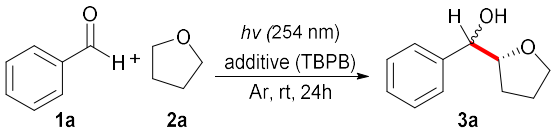
Table S1-5 Exploring the reaction time[a]



Entry	reaction time (h)	Yield (%) [b]	Threo/erythro
1	36	58	1.07
2	48	60	1.00

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), and solvent (3.0 mL THF) was irradiated with four 254 nm UV tubes (8 W each, total 32 W) for different reaction times under an argon atmosphere at room temperature. [b] Isolated yields.

Table S1-6 Exploring for mixed solvents[a]

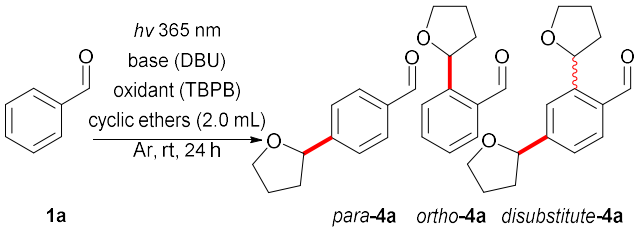


Entry	Solvents	Yield (%) [b]	Threo/erythro
1	THF/EA	55	1.20
2	THF/DMF	53	1.15
3	THF/DMSO	39	1.05
4	THF/DMAc	48	1.00
5	THF/Toluene	53	1.12
6	THF/ Trifluorotoluene	45	1.14
7	THF/MeCN	52	1.08
8	THF/MeOH	56	1.07
9	THF/EtOH	50	1.08
10	THF/*i*-Pr-OH	50	1.17
11	THF/DCE	30	1.50
12	THF/DCM	32	1.46
13	1.0 equiv. THF	trace	-
14	2.0 equiv. THF	7%	0.50

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), and solvent (THF/others = 5:1 v/v, total 3.0 mL) was irradiated with four 254 nm UV tubes (8 W each, total 32 W) for 24 h under an argon atmosphere at room temperature. [b] Isolated yields.

IV、 Optimization Of the Reaction Conditions of Dehydrogenative Coupling

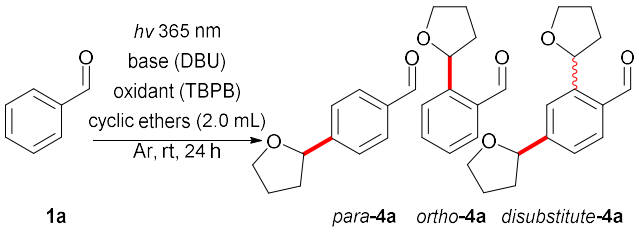
Table S2-1 Exploring the amount of TBPB[a]



Entry	TBPB (equiv.)	Yield (All, %) [b]
1	0	11
2	1.0	29
3	1.5	47
4	3.0	50
5	4.0	45

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (different molar equivalents), DBU (0.4 mmol), and THF (2.0 mL) was irradiated with two 365 nm UV tubes (15 W each, total 30 W) for 24 h under an argon atmosphere at room temperature; [b] isolated yields were given.

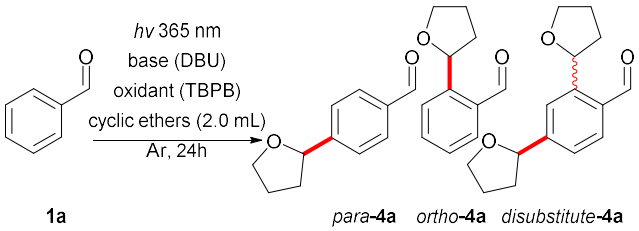
Table S2-2 Exploring the amount of DBU[a]



Entry	DBU (equiv.)	Yield (All, %) [b]
1	0	6
2	1.0	29
3	1.5	47
4	3.0	50

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), DBU (different molar equivalents), and THF (2.0 mL) was irradiated with two 365 nm UV tubes (15 W each, total 30 W) for 24 h under an argon atmosphere at room temperature; [b] isolated yields were given.

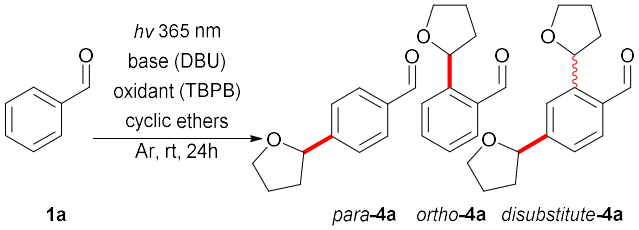
Table S2-3 Exploring of reaction temperature[a]



Entry	Temperature (°C)	Yield (All, %) [b]
1	50	53
2	80	45
3	100	43

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), DBU (0.4 mmol), and THF (2.0 mL) was irradiated with two 365 nm UV tubes (15 W each, total 30 W) for 24 h under an argon atmosphere at different reaction temperatures; [b] isolated yields were given.

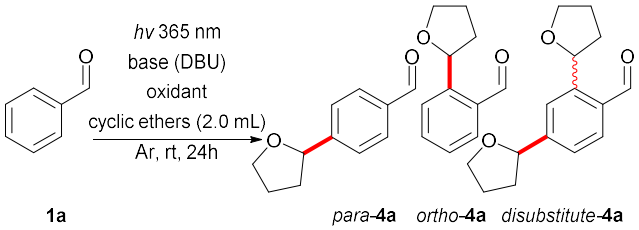
Table S2-4 Exploring for mixed solvents[a]



Entry	Solvents	Yield (All, %) [b]
1	THF/MeCN	46
2	THF/Acetone	48
3	THF/DCM	48
4	THF/*o*-Xylene	44
5	THF/EA	47
6	THF/Trifluorotoluene	44

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), DBU (0.4 mmol), and solvent (THF/others = 1:1 v/v, total 2.0 mL) was irradiated with two 365 nm UV tubes (15 W each, total 30 W) for 24 h under an argon atmosphere at room temperature; [b] isolated yields were given.

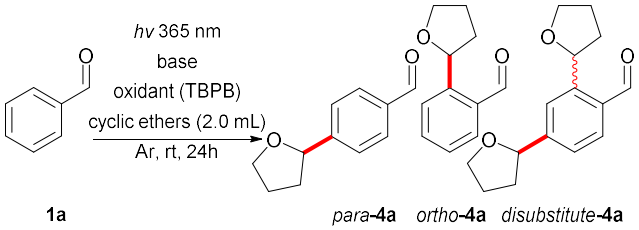
Table S2-5 Exploring for different oxidants[a]



Entry	Oxidants	Yield (All, %) [b]
1	*tert*-Butyl hydroperoxide	19
2	(Diacetoxyiodo)benzene	16
3	Dibenzoyl peroxide	Trace
4	Dimethanesulfonyl peroroxyde	N.D.
5	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone	N.D.

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), oxidant (0.4 mmol), DBU (0.4 mmol), and THF (2.0 mL) was irradiated with two 365 nm UV tubes (15 W each, total 30 W) for 24 h under an argon atmosphere at room temperature; [b] isolated yields were given.

Table S2-6 Exploring for different bases[a]

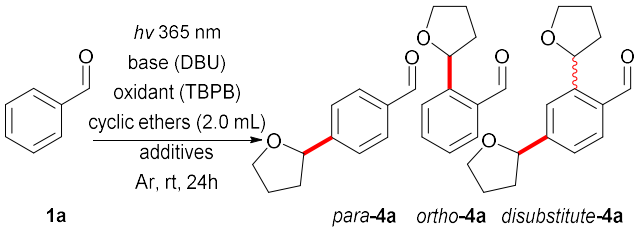


Entry	Bases	Yield (All, %) [b]
1	Morpholine	24
2	N, N-Diisopropylethylamine	7
3	Quinuclidine	21
4	Triethylenediamine	47
5	1,5-Diazabicyclo[4.3.0]non-5-ene	50
6	Tetramethylguanidine	42
7	1,5,7-Triazabicyclo[4.4.0]dec-5-ene	37
8	1,3,4,6,7,8-hexahydro-1-methyl-2h-pyrimidol[1,2-a]pyrimidine	31
9	4-Dimethylaminopyridine	25

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), base (0.4 mmol), and THF (2.0 mL) was irradiated with two 365 nm UV tubes (15 W each, total 30 W) for 24 h under an argon

atmosphere at room temperature; [b] isolated yields were given.

Table S2-7 Exploring for different additives[a]

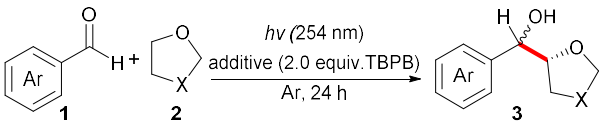


Entry	Additives	Yield (All, %) [b]
1	Sc $(OTf)_3$	49
2	LiCl	46
3	LiBr	49
4	N-Chlorosuccinimide	49
5	$AlCl_3$	48
6	$ZnCl_2$	50
7	NHPI	51
8	NH_4I	48
9	Tetrabutyl ammonium chloride	50
10	CsF	51

[a] Reaction conditions: A mixture of **1a** (0.2 mmol), TBPB (0.4 mmol), DBU (0.4 mmol), additives (0.04 mmol), and THF (2.0 mL) was irradiated with two 365 nm UV tubes (15 W each, total 30 W) for 24 h under an argon atmosphere at room temperature; [b] isolated yields were given.

V、 General Procedures

1. General procedures for the *α*- Hydroxyarylation

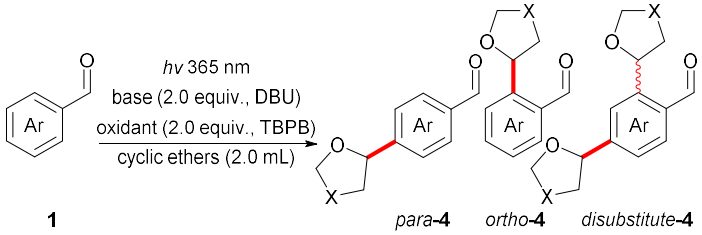


In an argon-filled glovebox, a 10 mL quartz tube equipped with a stir bar was charged with cyclic ether (3.0 mL), additive (0.4 mmol, 2.0 equiv.). Substrate **1** (0.2 mmol) was then added to the glass tube, which was subsequently sealed and removed from the glovebox. The mixture was stirred under irradiation from four 254 nm UV tubes (254 nm, 8 W each, total 32 W) at room temperature for the indicated time, with a cooling fan providing thermal regulation of the lamp assembly. Experimental results confirmed that the cooling fan effectively dissipated heat generated by the lamps. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated

under reduced pressure and purified by flash column chromatography on silica gel (petroleum ether/EA, v/v = 5/1) to afford the desired product. The isomeric mixtures can be isolated using preparative thin-layer chromatography (PTLC). This was accomplished through multiple developments (typically 5-10 runs) utilizing the compounds' intrinsic weak fluorescence for band visualization. Target bands were scraped off and extracted with ethyl acetate (EA), followed by three washes with saturated $NaHCO_3$(aq) to remove acidic impurities. The EA phase was then dried over Na_2SO_4, concentrated in vacuo to yield the pure product.

Figure S2. Photochemical reaction setup under 254 nm conditions. Physical object picture of the 254 nm setup with cooling fan (Left) and lamps (right).

2. General Procedures for Dehydrogenative Coupling Reactions



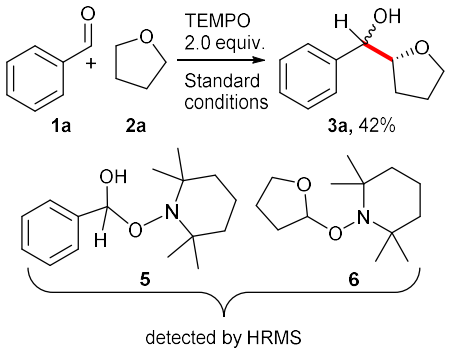
In an argon-filled glovebox, a 10 mL quartz tube equipped with a stir bar was charged with cyclic ether (2.0 mL), oxidant (0.4 mmol, 2.0 equiv.), and base (0.4 mmol, 2.0 equiv.). Substrate **1** (0.2 mmol) was then added to the glass tube, which was subsequently sealed and removed from the glovebox. The mixture was stirred under irradiation from two 365 nm UV tubes (365 nm insect-attracting blacklight tube, 15 W each, total 30 W) irradiation at room temperature for the indicated time, with a cooling fan providing thermal regulation of the lamp assembly. Experimental results confirmed that the cooling fan effectively dissipated heat generated by the lamps. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (petroleum ether/EtOAc, v/v = 5/1) to afford the desired product. For mixtures that were challenging to separate by column chromatography (e.g., SR/RR diastereomers), purification was primarily achieved using preparative thin-layer

chromatography (PTLC) with a PE/DCM gradient (v/v = 5:1 → 0:1). Critical to the separation was the addition of a small amount of acid (formic, acetic, or trifluoroacetic acid; 40 drops or 1 wt% per 120 mL eluent). The crude mixture-coated silica plate was developed multiple times until complete separation. Target bands were scraped off and extracted with ethyl acetate (EA), followed by three washes with saturated $NaHCO_3$(aq) to remove acidic impurities. The EA phase was then dried over Na_2SO_4, concentrated in vacuo to yield the pure product.

Figure S3. Photochemical reaction setup under 365 nm conditions. Physical object picture of the 365 nm setup with cooling fan (Left) and lamps (right).

VI、 Control experiments

1. Radical Trapping Experiments of *α*- Hydroxyarylation



In an argon-filled glovebox, a 10 mL quartz tube equipped with a stir bar was charged with cyclic ether THF (3.0 mL), additive TBPB (0.4 mmol, 2.0 equiv.). Substrate **1a** (0.2 mmol) and TEMPO (0.4 mmol, 2.0 equiv.) were then added to the tube, which was subsequently sealed and removed from the glovebox. The mixture was stirred under irradiation from four 254-nm UV tubes (8 W each, total 32 W) at room temperature for 24 h, with a cooling fan directed at the light source. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (petroleum ether/EtOAc, v/v =

5/1) to afford the desired product.

TEMPO did not completely suppress the formation of product **3a** (42% yield), suggesting that the reaction proceeds through an ionic rather than radical-based mechanism. HRMS analysis (ESI) detected compound **5** (calcd for $C_{16}H_{25}NO_2$ $[M + K]^+$ 302.1517, found 302.1519), potentially indicating the presence of a ketyl radical intermediate (Figure S4). Similarly, TEMPO-trapped THF radicals were identified as compound **6** (calcd for $C_{13}H_{25}NO_2$ $[M + H]^+$ 228.1958, found 228.1953) by HRMS (Figure S5). Despite the abundant THF radicals, the reaction appears to follow an ionic pathway. Consequently, the coupling between ketyl radicals and THF radicals must occur via an ionic mechanism.

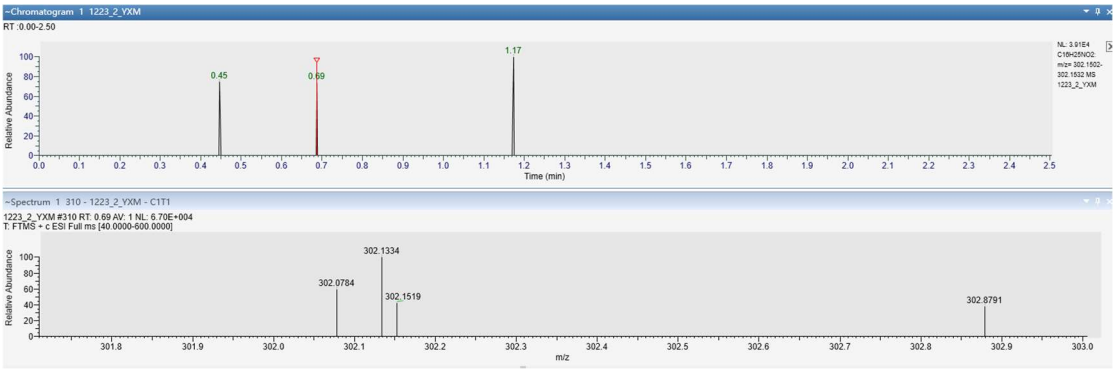


Figure S4. HRMS of reaction intermediate **5** captured by TEMPO

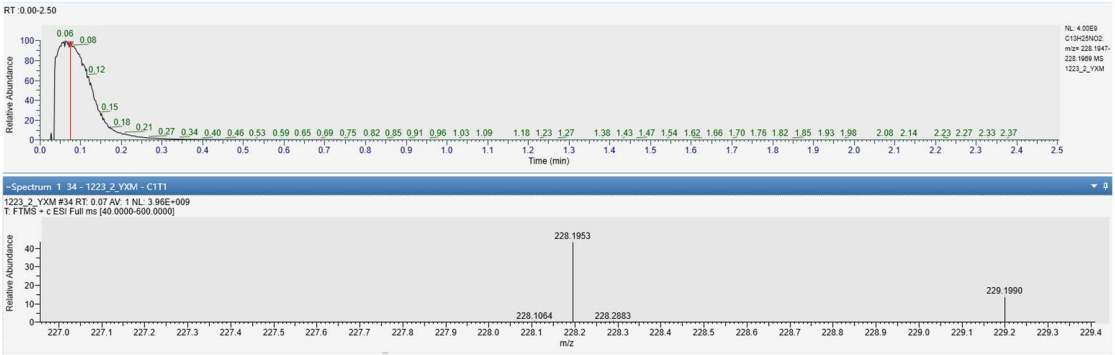
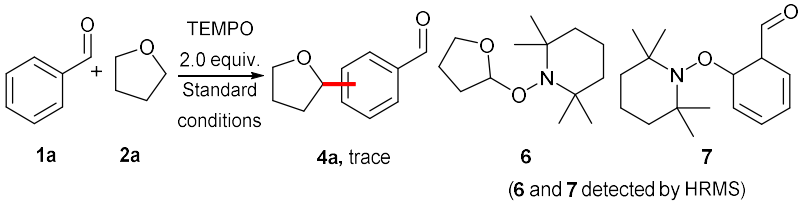


Figure S5. HRMS of reaction intermediate **6** captured by TEMPO

2. Radical Trapping Experiments of Dehydrogenative coupling



In an argon-filled glovebox, a 10 mL quartz tube equipped with a stir bar was charged with cyclic ether (2.0 mL), oxidant (0.4 mmol, 2.0 equiv.), and base (0.4 mmol, 2.0 equiv.). Substrate **1a** (0.2 mmol) and TEMPO (0.4 mmol, 2.0 equiv.) were then added to the tube, which was subsequently

sealed and removed from the glovebox. The reaction mixture was stirred under 365 nm UV irradiation (insect-attracting blacklight, 15 W each, total 30 W) at room temperature for 24 h, with a cooling fan directed at the light source. Reaction progress was monitored by TLC.

The formation of **4a** (trace yield) was fully suppressed by TEMPO, suggesting the reaction proceeds through a radical-involved pathway. HRMS analysis (ESI) detected compound **6** (calcd for $C_{13}H_{25}NO_2$ $[M + H]^+$ 228.1958, found 228.1955; Figure S6) and compound **7** (calcd for $C_{16}H_{25}NO_2$ $[M + H]^+$ 302.1517, found 302.1528; Figure S7), providing evidence for the generation of corresponding radical intermediates.

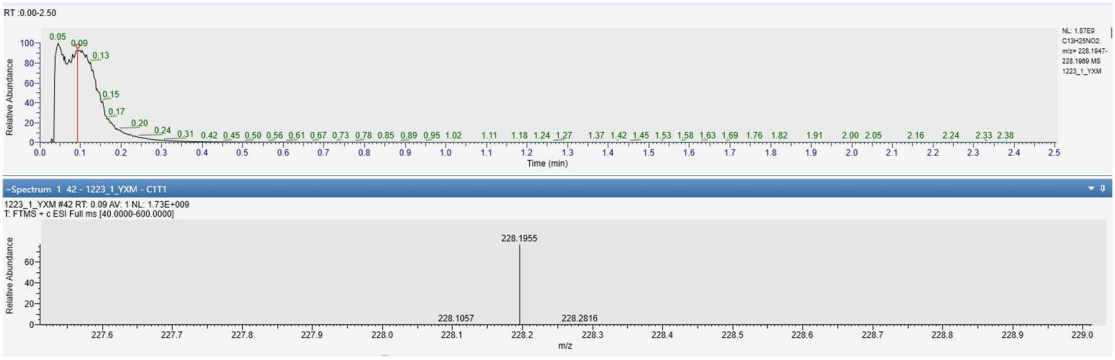


Figure S6. HRMS of reaction intermediate **6** captured by TEMPO

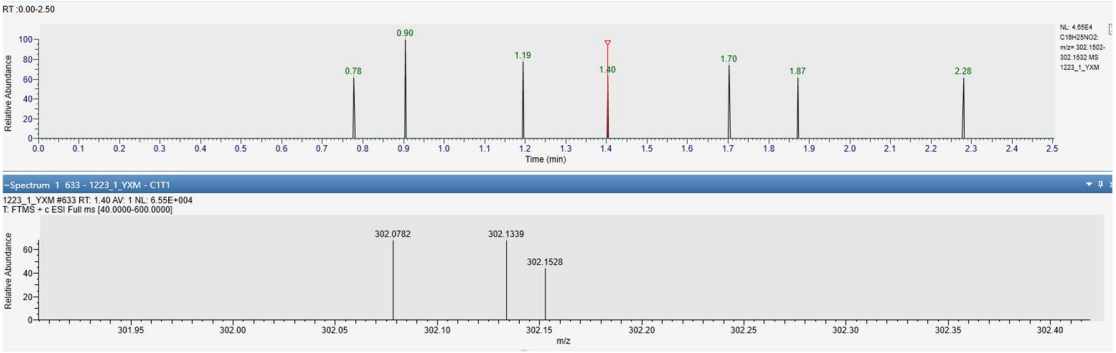
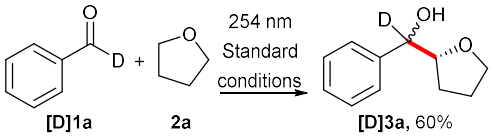


Figure S7. HRMS of reaction intermediate **7** captured by TEMPO

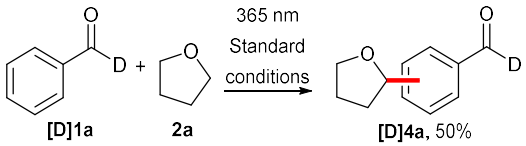
3. Deuterium Labelling Experiments of *α*- Hydroxyarylation



In an argon-filled glovebox, a 10 mL quartz tube equipped with a stir bar was charged with cyclic ether THF (3.0 mL) and additive TBPB (0.4 mmol, 2.0 equiv.). Deuterated benzaldehyde **[D]1a** (0.2 mmol) was then added to the tube, which was subsequently sealed and removed from

the glovebox. The reaction mixture was stirred under 254 nm UV irradiation (8 W each, total 32 W) at room temperature for 24 h, with a cooling fan directed at the light source. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (petroleum ether/EtOAc, v/v = 5/1) to afford the desired product. For difficult-to-separate products, separation methods can be found in Part V: General Procedures.

4. Deuterium Labelling Experiments of Dehydrogenative coupling



In an argon-filled glovebox, a 10 mL quartz tube equipped with a stir bar was charged with cyclic ether THF (2.0 mL), oxidant TBPB (0.4 mmol, 2.0 equiv.), and base (0.4 mmol, 2.0 equiv.). Deuterated benzaldehyde **[D]1a** (0.2 mmol) was then added to the tube, which was subsequently sealed and removed from the glovebox. The reaction mixture was stirred under 365 nm UV irradiation (insect-attracting blacklight, 15 W each, total 30 W) at room temperature for 24 h, with a cooling fan directed at the light source. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (petroleum ether/EtOAc, v/v = 5/1) to afford the desired product. For difficult-to-separate products, separation methods can be found in Part V: General Procedures.

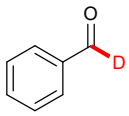
VII、 References

1. Yokoyama A.; Maruyama T.; Tagami K.; Masu H.; Katagiri K.; Azumaya I.; Yokozawa T. *Org. Lett.*, 2008, **10**, 3207−3210.
2. Y. Kuang, H. Cao, H. Tang, J. Chew, W. Chen, X. Shi and J. Wu, *Chem. Sci.*, 2020, **11**, 8912−8918.

VIII、Characterization Data of Products

1. Characterization Data of the Partial Substrate

Deuterated benzaldehyde ([D]**1a**)

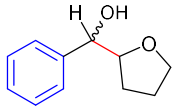


^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 0.06H), 7.91 - 7.88 (m, 2H), 7.66 – 7.62 (m, 1H),

7.56 – 7.53 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.46 (CHO), 192.15 (t, J = 26.26 Hz, COD), 136.32, 134.51, 129.77, 129.03

2. Characterization Data of the α- Hydroxyarylation Products

phenyl(tetrahydrofuran-2-yl)methanol (3a)

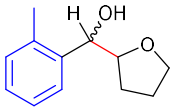


Threo-**3a** and *erythro*-**3a** were synthesized via **General Procedure V-1**, affording colorless oils (23 mg, 64%, threo/erythro = 1.03).

Threo-**3a**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 5H), 4.44 (d, *J* = 7.5 Hz, 1H), 4.03 – 3.98(m, 1H), 3.94 – 3.82 (m, 2H), 3.11 (s, 1H), 1.97 – 1.81 (m, 2H), 1.75 – 1.60 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.72, 128.41, 127.97, 127.02, 83.49, 68.45, 27.93, 26.08.

Erythro-**3a**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.23 (m, 5H), 4.93 (d, *J* = 3.8 Hz, 1H), 4.16 – 4.01 (m, 1H), 3.97 – 3.76 (m, 2H), 2.68 (s, 1H), 1.97 – 1.74 (m, 3H), 1.70 – 1.51 (m, 1H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.58, 128.28, 127.44, 126.05, 83.17, 74.03, 69.07, 26.05, 24.78.

(tetrahydrofuran-2-yl)(o-tolyl)methanol (3b)

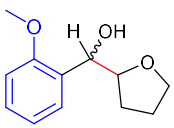


Threo-**3b** and *erythro*-**3b** were synthesized via **General Procedure V-1**, affording colorless oils (21 mg, 41%, threo/erythro = 1.16).

Threo-**3b**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.26 – 7.09 (m, 3H), 4.76 (d, *J* = 7.2 Hz, 1H), 4.19 – 4.09 (m, 1H), 4.01 – 3.83 (m, 2H), 2.40 (s, 3H), 2.02 – 1.72 (m, 3H), 1.67 – 1.53 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.84, 135.64, 130.54, 127.66, 126.97, 126.21, 83.02, 72.65, 68.47, 27.89, 26.11, 19.64.

Erythro-**3b**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.27 – 7.07 (m, 3H), 5.19 (d, *J* = 3.6 Hz, 1H), 4.12 – 4.02 (m, 1H), 4.01 – 3.91 (m, 1H), 3.88 – 3.76 (m, 1H), 2.34 (s, 3H), 2.07 – 1.77 (m, 3H), 1.64 – 1.49 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.59, 134.62, 130.14, 127.26, 126.11, 125.70, 81.30, 70.64, 69.00, 26.18, 24.70, 19.19.

(2-methoxyphenyl)(tetrahydrofuran-2-yl)methanol (3c)

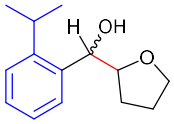


Threo-**3c** and *erythro*-**3c** were synthesized via **General Procedure V-1**, affording colorless oils (20 mg, 40%, threo/erythro = 1.11).

Threo-**3c**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.02 – 6.94 (m, 1H), 6.88 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.90 (d, *J* = 7.0 Hz, 1H), 4.14 – 4.05 (m, 1H), 4.00 – 3.90 (m, 1H), 3.84 (s, 4H), 2.03 – 1.79 (m, 2H), 1.78 – 1.70 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.64, 129.30, 128.67, 127.80, 120.84, 110.49, 82.99, 70.81, 68.46, 55.38, 27.72, 26.07.

Erythro-**3c**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 1H), 7.25 (td, *J* = 7.8, 1.7 Hz, 1H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.85 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.17 (d, *J* = 4.1 Hz, 1H), 4.28 – 4.19 (m, 1H), 3.98 – 3.84 (m, 1H), 3.83 (s, 3H), 3.83 – 3.75 (m, 2H), 2.71 (s, 1H), 1.98 – 1.77 (m, 4H), 1.66 – 1.52 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.19, 128.76, 128.29, 127.10, 120.67, 110.08, 80.82, 70.10, 68.95, 55.24, 26.14, 25.11.

(2-isopropylphenyl)(tetrahydrofuran-2-yl)methanol (3d)

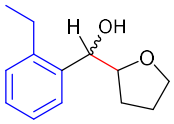


Threo-**3d** and *erythro*-**3d** were synthesized via **General Procedure V-1**, affording colorless oils (24 mg, 51%, threo/erythro = 1.04).

Threo-**3d**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.20 (td, *J* = 7.3, 1.8 Hz, 1H), 4.86 (d, *J* = 7.2 Hz, 1H), 4.21 – 4.09 (m, 1H), 4.01 – 3.76 (m, 5H), 3.34 (hept, *J* = 6.8 Hz, 1H), 1.97 – 1.74 (m, 2H), 1.63 – 1.54 (m, 2H), 1.31 – 1.21 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.71, 137.25, 128.06, 127.17, 125.93, 125.48, 83.22, 72.22, 68.50, 28.43, 28.10, 26.13, 24.89, 23.58.

Erythro-**3d**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 1H), 7.30 – 7.18 (m, 3H), 5.30 (d, *J* = 3.6 Hz, 1H), 4.09 – 4.02 (m, 1H), 4.00 – 3.91 (m, 1H), 3.87 – 3.78 (m, 1H), 3.16 (hept, *J* = 6.8 Hz, 1H), 2.42 (s, 1H), 2.04 – 1.79 (m, 3H), 1.61 – 1.50 (m, 1H), 1.29 – 1.19 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.59, 136.72, 127.64, 125.88, 125.71, 125.13, 82.29, 70.04, 69.01, 28.16, 26.20, 24.76, 24.63, 23.65.

(2-ethylphenyl)(tetrahydrofuran-2-yl)methanol (3e)

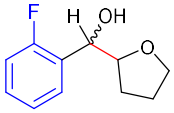


Threo-**3e** and *erythro*-**3e** were synthesized via **General Procedure V-1**, affording colorless oils (20 mg, 42%, threo/erythro = 1.15).

Threo-**3e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 – 7.39 (m, 1H), 7.26 – 7.16 (m, 3H), 4.78 (d, *J* = 7.3 Hz, 1H), 4.25 – 4.11 (m, 1H), 4.02 – 3.82 (m, 2H), 2.85 – 2.62 (m, 2H), 2.02 – 1.82 (m, 2H), 1.86 – 1.70 (m, 1H), 1.64 – 1.51 (m, 1H), 1.25 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-

d) δ 141.99, 138.09, 128.81, 127.93, 127.13, 126.20, 83.17, 72.20, 68.49, 28.02, 26.12, 25.65, 15.93. *Erythro*-**3e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 5.6, 3.7 Hz, 1H), 7.28 – 7.13 (m, 3H), 5.21 (d, *J* = 3.7 Hz, 1H), 4.11 – 4.02 (m, 1H), 4.00 – 3.89 (m, 1H), 3.87 – 3.76 (m, 1H), 2.81 – 2.68 (m, 1H), 2.68 – 2.54 (m, 1H), 2.06 – 1.77 (m, 3H), 1.65 – 1.54 (m, 1H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.87, 137.80, 128.32, 127.55, 126.06, 125.88, 82.05, 70.25, 68.95, 26.17, 25.06, 24.85, 15.57.

(2-fluorophenyl)(tetrahydrofuran-2-yl)methanol (3f)

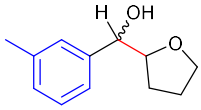


Threo-**3f** and *erythro*-**3f** were synthesized via **General Procedure V-1**, affording colorless oils (21 mg, 47%, threo/erythro = 1.14).

Threo-**3f**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (td, *J* = 7.4, 1.9 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 7.05 – 7.00 (m, 1H), 4.86 (d, *J* = 7.2 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.99 – 3.89 (m, 1H), 3.86 (td, *J* = 7.8, 5.9 Hz, 1H), 2.08 – 1.82 (m, 2H), 1.84 – 1.65 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.05 (d, *J* = 245.7 Hz), 129.23 (d, *J* = 8.4 Hz), 128.34 (d, *J* = 4.3 Hz), 128.04 (d, *J* = 13.2 Hz), 124.37 (d, *J* = 3.5 Hz), 115.24 (d, *J* = 22.3 Hz), 83.11 (d, *J* = 1.7 Hz), 69.70 (d, *J* = 1.9 Hz), 68.54, 27.52 (d, *J* = 1.6 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -118.52.

Erythro-**3f**: **^{1}H NMR** (400 MHz, Chloroform-*d*)δ 7.56 (td, *J* = 7.5, 1.9 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.09 – 6.94 (m, 1H), 5.24 (d, *J* = 3.8 Hz, 1H), 4.22 – 4.17 (m, 1H), 3.96 – 3.86 (m, 1H), 3.86 – 3.76 (m, 1H), 1.89 – 1.78 (m, 3H), 1.67 – 1.53 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.66 (d, *J* = 245.3 Hz), 128.83 (d, *J* = 8.1 Hz), 127.66 (d, *J* = 13.4 Hz), 127.63 (d, *J* = 4.6 Hz), 124.19 (d, *J* = 3.4 Hz), 114.94 (d, *J* = 21.7 Hz), 81.27 (d, *J* = 1.6 Hz), 69.09, 68.28 (d, *J* = 0.77 Hz), 26.06, 24.95. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -118.80.

(tetrahydrofuran-2-yl)(m-tolyl)methanol (3g)



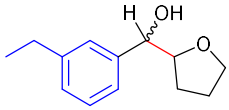
Threo-**3g** and *erythro*-**3g** were synthesized via **General Procedure V-1**, affording colorless oils (20 mg, 51%, threo/erythro = 1.04).

Threo-**3g**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.18 (m, 2H), 7.18 – 7.12 (m, 1H), 7.17 – 7.07 (m, 1H), 4.41 (d, *J* = 7.5 Hz, 1H), 4.06 – 3.97 (m, 1H), 3.97 – 3.77 (m, 2H), 2.35 (s, 3H), 2.01 – 1.82 (m, 2H), 1.79 – 1.55 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.59, 138.07, 128.75, 128.28, 127.61, 124.13, 83.44, 68.43, 27.94, 26.08, 21.47.

Erythro-**3g**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.16 (m, 2H), 7.19 – 7.11 (m, 1H), 7.08

(dd, *J* = 7.3, 1.9 Hz, 1H), 4.90 (d, *J* = 3.9 Hz, 1H), 4.15 – 4.03 (m, 1H), 3.98 – 3.87 (m, 1H), 3.87 – 3.75 (m, 1H), 2.35 (s, 3H), 1.97 – 1.75 (m, 3H), 1.69 – 1.53 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.45, 137.92, 128.21, 128.19, 126.66, 123.09, 83.12, 74.09, 69.06, 26.07, 24.82, 21.51.

(3-ethylphenyl)(tetrahydrofuran-2-yl)methanol (3h)

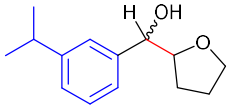


Threo-**3h** and *erythro*-**3h** were synthesized via **General Procedure V-1**, affording colorless oils (23 mg, 53%, threo/erythro = 1.04).

Threo-**3h**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.10 (m, 4H), 4.42 (d, *J* = 7.5 Hz, 1H), 4.06 – 3.97 (m, 1H), 3.97 – 3.81 (m, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.99 – 1.81 (m, 2H), 1.79 – 1.56 (m, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.42, 140.61, 128.35, 127.53, 126.49, 124.34, 83.44, 77.11, 68.43, 28.86, 27.95, 26.09, 15.57.

Erythro-**3h**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.14 (m, 3H), 7.11 (d, *J* = 7.3 Hz, 1H), 4.93 (d, *J* = 3.8 Hz, 1H), 4.14 – 4.05 (m, 1H), 3.98 – 3.75 (m, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.98 – 1.77 (m, 3H), 1.65 – 1.53 (m, 1H), 1.24 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.29, 140.50, 128.23, 127.00, 125.52, 123.38, 83.15, 74.17, 69.05, 28.91, 26.07, 24.80, 15.61.

(3-isopropylphenyl)(tetrahydrofuran-2-yl)methanol (3i)

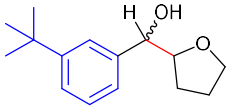


Threo-**3i** and *erythro*-**3i** were synthesized via **General Procedure V-1**, affording colorless oils (28 mg, 61%, threo/erythro = 1.07).

Threo-**3i**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.21 (m, 3H), 7.20 – 7.15 (m, 2H), 4.43 (d, *J* = 7.6 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 1H), 3.96 – 3.82 (m, 2H), 2.91 (hept, *J* = 6.9 Hz, 1H), 1.97 – 1.86 (m, 2H), 1.80 – 1.56 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.04, 140.55, 128.34, 126.05, 125.18, 124.44, 83.44, 77.19, 68.43, 34.13, 27.95, 26.09, 24.05, 23.99.

Erythro-**3i**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 2H), 7.18 – 7.15 (m, 2H), 4.93 (d, *J* = 3.7 Hz, 1H), 4.14 – 4.05 (m, 1H), 3.98 – 3.88 (m, 1H), 3.84 – 3.74 (m, 1H), 2.91 (hept, *J* = 7.0 Hz, 1H), 1.96 – 1.79 (m, 3H), 1.65 – 1.55 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.95, 140.39, 128.21, 125.53, 124.15, 123.56, 83.16, 81.52, 74.24, 69.07, 34.16, 26.07, 24.73, 24.11, 23.97.

(3-(tert-butyl)phenyl)(tetrahydrofuran-2-yl)methanol (3j)

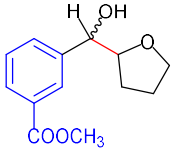


Threo-**3j** and *erythro*-**3j** were synthesized via **General Procedure V-1**, affording colorless oils (30 mg, 59%, threo/erythro = 1.03).

Threo-**3j**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 – 7.24 (m, 3H), 7.23 – 7.16 (m, 1H), 4.44 (d, *J* = 7.6 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 1H), 3.97 – 3.82 (m, 2H), 2.01 – 1.80 (m, 2H), 1.79 – 1.55 (m, 2H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.24, 140.21, 128.08, 124.98, 124.07, 124.02, 83.48, 77.37, 68.42, 34.70, 31.38, 27.95, 26.09.

Erythro-**3j**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.34 – 7.23 (m, 2H), 7.17 (dt, *J* = 6.9, 1.8 Hz, 1H), 4.94 (d, *J* = 3.7 Hz, 1H), 4.14 – 4.05 (m, 1H), 4.00 – 3.75 (m, 2H), 1.97 – 1.76 (m, 3H), 1.64 – 1.56 (m, 1H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.16, 140.06, 127.92, 124.43, 123.26, 123.02, 83.21, 74.40, 69.04, 34.71, 31.39, 26.06, 24.71.

methyl 3-(hydroxy(tetrahydrofuran-2-yl)methyl)benzoate (3k)

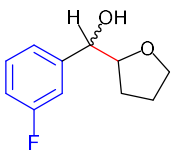


Threo-**3k** and *erythro*-**3k** were synthesized via **General Procedure V-1**, affording colorless oils (18 mg, 34%, threo/erythro = 0.89).

Threo-**3k**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 4.99 (d, *J* = 3.8 Hz, 1H), 4.15 – 4.06 (m, 1H), 3.92 (s, 4H), 3.86 – 3.77 (m, 1H), 2.65 (s, 1H), 1.92 – 1.76 (m, 3H), 1.63 – 1.51 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.06, 140.98, 130.61, 130.18, 128.70, 128.41, 127.19, 82.87, 73.61, 69.13, 52.14, 26.00, 24.79.

Erythro-**3k**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 8.01 – 7.94 (m, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 4.52 (d, *J* = 7.2 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.96 – 3.82 (m, 5H), 3.06 (s, 1H), 2.00 – 1.82 (m, 2H), 1.80 – 1.61 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.98, 141.23, 131.49, 130.28, 129.19, 128.57, 128.17, 83.25, 76.50, 68.54, 52.15, 27.86, 26.08.

(3-fluorophenyl)(tetrahydrofuran-2-yl)methanol (3l)



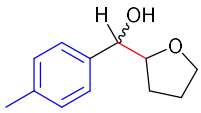
Threo-**3l** and *erythro*-**3l** were synthesized via **General Procedure V-1**, affording colorless oils (17 mg, 38%, threo/erythro = 1.00).

Threo-**3l**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 1H), 7.13 (t, *J* = 9.8 Hz, 2H), 6.98

(td, *J* = 8.5, 1.9 Hz, 1H), 4.45 (d, *J* = 7.2 Hz, 1H), 4.02 – 3.80 (m, 3H), 3.11 (s, 1H), 2.01 – 1.81 (m, 2H), 1.81 – 1.60 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.88 (d, *J* = 245.8 Hz), 143.42 (d, *J* = 7.0 Hz), 129.88 (d, *J* = 8.2 Hz), 122.57 (d, *J* = 2.9 Hz), 114.80 (d, *J* = 21.1 Hz), 113.88 (d, *J* = 21.9 Hz), 83.23, 76.30 (d, *J* = 1.7 Hz), 68.52, 27.90, 26.06. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.04.

Erythro-**3l**: **^{1}H NMR** (400 MHz, Chloroform-*d*)δ 7.35 – 7.24 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.00 – 6.91 (m, 1H), 4.94 (d, *J* = 3.7 Hz, 1H), 4.11 – 4.02 (m, 1H), 3.98 – 3.88 (m, 1H), 3.87 – 3.75 (m, 1H), 2.71 (s, 1H), 1.94 – 1.75 (m, 5H), 1.63 – 1.51 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.93 (d, *J* = 245.5 Hz), 143.20 (d, *J* = 7.1 Hz), 129.74 (d, *J* = 8.2 Hz), 121.57, 114.25 (d, *J* = 21.2 Hz), 113.02 (d, *J* = 22.3 Hz), 82.91, 73.34 (d, *J* = 1.7 Hz), 69.14, 26.01, 24.69. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.11.

(tetrahydrofuran-2-yl)(p-tolyl)methanol (3m)

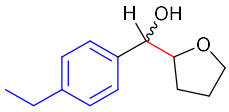


Threo-**3m** and *erythro*-**3m** were synthesized via **General Procedure V-1**, affording colorless oils (25 mg, 61%, threo/erythro = 1.10).

Threo-**3m**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.41 (d, *J* = 7.6 Hz, 1H), 4.05 – 3.95 (m, 1H), 3.97 – 3.80 (m, 2H), 2.34 (s, 3H), 2.00 – 1.81 (m, 2H), 1.78 – 1.55 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.67, 129.11, 126.92, 83.48, 76.86, 68.43, 27.91, 26.08, 21.19.

Erythro-**3m**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.90 (d, *J* = 3.9 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.97 – 3.84 (m, 1H), 3.84 – 3.75 (m, 1H), 2.34 (s, 3H), 1.97 – 1.74 (m, 3H), 1.67 – 1.54 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.53, 137.10, 128.99, 125.96, 83.16, 74.02, 69.04, 26.05, 24.87, 21.16.

(4-ethylphenyl)(tetrahydrofuran-2-yl)methanol (3n)



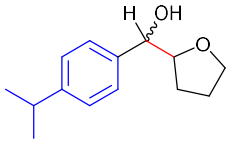
Threo-**3n** and *erythro*-**3n** were synthesized via **General Procedure V-1**, affording colorless oils (26 mg, 61%, threo/erythro = 1.03).

Threo-**3n**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.42 (d, *J* = 7.6 Hz, 1H), 4.06 – 3.97 (m, 1H), 3.97 – 3.81 (m, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.99 – 1.82 (m, 2H), 1.79 – 1.56 (m, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.03, 137.91, 127.92, 126.97, 83.45, 76.85, 68.43, 28.58, 27.95, 26.09, 15.57.

Erythro-**3n**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H),

4.90 (d, *J* = 3.9 Hz, 1H), 4.14 – 4.03 (m, 1H), 3.98 – 3.87 (m, 1H), 3.85 – 3.75 (m, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.98 – 1.77 (m, 3H), 1.66 – 1.58 (m, 1H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.48, 137.80, 127.80, 126.04, 83.15, 74.09, 69.04, 28.55, 26.06, 24.93, 15.58.

(4-isopropylphenyl)(tetrahydrofuran-2-yl)methanol (3o)

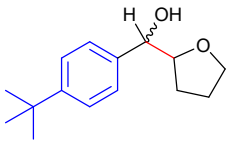


Threo-**3o** and *erythro*-**3o** were synthesized via **General Procedure V-1**, affording colorless oils (27 mg, 66%, threo/erythro = 1.03).

Threo-**3o**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 2H), 7.25 – 7.17 (m, 2H), 4.42 (d, *J* = 7.5 Hz, 1H), 4.08 – 3.97 (m, 1H), 3.97 – 3.79 (m, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 1.99 – 1.80 (m, 2H), 1.81 – 1.57 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.63, 138.05, 126.94, 126.48, 83.40, 76.81, 68.44, 33.85, 27.98, 26.08, 23.99, 23.98.

Erythro-**3o**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.17 (m, 2H), 4.88 (d, *J* = 4.0 Hz, 1H), 4.17 – 4.01 (m, 1H), 3.95 – 3.75 (m, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 1.96 – 1.76 (m, 3H), 1.68 – 1.60 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.11, 137.96, 126.36, 126.04, 83.12, 74.15, 69.02, 33.81, 26.06, 25.00, 24.01, 24.00.

(4-(tert-butyl)phenyl)(tetrahydrofuran-2-yl)methanol (3p)

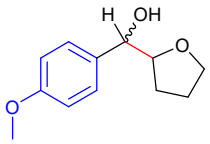


Threo-**3p** and *erythro*-**3p** were synthesized via **General Procedure V-1**, affording colorless oils (30 mg, 59%, threo/erythro = 1.11).

Threo-**3p**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 2H), 7.34 – 7.26 (m, 2H), 4.42 (d, *J* = 7.4 Hz, 1H), 4.13 – 3.98 (m, 1H), 3.98 – 3.78 (m, 2H), 1.99 – 1.80 (m, 2H), 1.81 – 1.60 (m, 2H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.85, 137.68, 126.65, 125.33, 83.35, 68.45, 34.54, 31.35, 28.01, 26.09.

Erythro-**3p**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.89 (d, *J* = 4.0 Hz, 1H), 3.97 – 3.76 (m, 2H), 1.99 – 1.75 (m, 3H), 1.69 – 1.61 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.36, 137.58, 125.78, 125.23, 83.09, 74.11, 69.03, 34.51, 31.37, 26.07, 25.04.

(4-methoxyphenyl)(tetrahydrofuran-2-yl)methanol (3q)

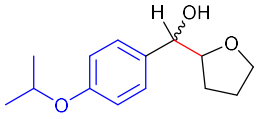


Threo-**3q** and *erythro*-**3q** were synthesized via **General Procedure V-1**, affording colorless oils (25 mg, 55%, threo/erythro = 1.11).

Threo-**3q**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 2H), 6.92 – 6.84 (m, 2H), 4.39 (d, *J* = 7.7 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.97 – 3.81 (m, 2H), 3.80 (s, 3H), 1.98 – 1.82 (m, 2H), 1.76 – 1.67 (m, 1H), 1.66 – 1.53 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.36, 132.78, 128.20, 113.81, 83.51, 76.65, 68.43, 55.28, 27.91, 26.09.

Erythro-**3q**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 6.92 – 6.84 (m, 2H), 4.86 (d, *J* = 4.0 Hz, 1H), 4.10 – 4.01 (m, 1H), 3.97 – 3.87 (m, 1H), 3.85 – 3.75 (m, 1H), 3.80 (s, 3H), 1.93 – 1.77 (m, 2H), 1.71 – 1.58 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.98, 132.71, 127.25, 113.71, 83.14, 73.87, 69.01, 55.26, 26.02, 25.02.

(4-isopropoxyphenyl)(tetrahydrofuran-2-yl)methanol (3r)

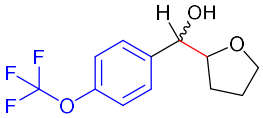


Threo-**3r** and *erythro*-**3r** were synthesized via **General Procedure V-1**, affording colorless oils (23 mg, 50%, threo/erythro = 1.00).

Threo-**3r**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 2H), 6.90 – 6.82 (m, 2H), 4.54 (hept, *J* = 6.0 Hz, 1H), 4.38 (d, *J* = 7.8 Hz, 1H), 4.03 – 3.81 (m, 3H), 2.00 – 1.80 (m, 2H), 1.78 – 1.51 (m, 2H), 1.33 (dd, *J* = 6.0, 1.3 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.67, 132.52, 128.23, 115.73, 83.49, 76.68, 69.84, 68.43, 27.94, 26.09, 22.07, 22.04.

Erythro-**3r**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.1 Hz, 2H), 6.90 – 6.82 (m, 2H), 4.86 (d, *J* = 4.0 Hz, 1H), 4.54 (hept, *J* = 6.1 Hz, 1H), 4.10 – 4.01 (m, 1H), 3.97 – 3.87 (m, 1H), 3.85 – 3.75 (m, 1H), 1.94 – 1.78 (m, 3H), 1.69 – 1.62 (m, 1H), 1.33 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.29, 132.47, 127.27, 115.64, 83.14, 73.90, 69.84, 69.02, 26.05, 25.01, 22.09, 22.07.

(tetrahydrofuran-2-yl)(4-(trifluoromethoxy)phenyl)methanol (3s)



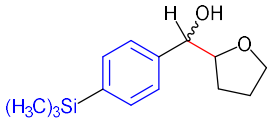
Threo-**3s** and *erythro*-**3s** were synthesized via **General Procedure V-1**, affording colorless oils (24 mg, 44%, threo/erythro = 1.00).

Threo-**3s**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 2H), 7.23 – 7.17 (m, 2H), 4.47 (d,

J = 7.3 Hz, 1H), 4.02 – 3.81 (m, 3H), 2.01 – 1.83 (m, 2H), 1.81 – 1.72 (m, 1H), 1.69 – 1.60 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.84, 139.47, 128.37, 120.90, 120.46 (q, *J* = 257.0 Hz), 83.25, 76.17, 68.54, 27.90, 26.06. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.87.

Erythro-**3s**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.95 (d, *J* = 3.9 Hz, 1H), 4.11 – 4.02 (m, 1H), 3.97 – 3.78 (m, 2H), 1.94 – 1.77 (m, 3H), 1.63 – 1.55 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.47, 139.22, 127.43, 120.79, 120.48 (q, *J* = 256.8 Hz), 82.90, 73.38, 69.11, 25.98, 24.82. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.88, -57.93.

(tetrahydrofuran-2-yl)(4-(trimethylsilyl)phenyl)methanol (t)

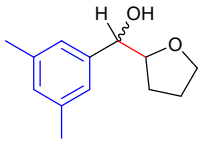


Threo-**3t** and *erythro*-**3t** were synthesized via **General Procedure V-1**, affording colorless oils (23 mg, 43%, threo/erythro = 1.09).

Threo-**3t**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 4.44 (d, *J* = 7.4 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.98 – 3.80 (m, 2H), 2.99 (s, 1H), 2.01 – 1.81 (m, 2H), 1.80 – 1.57 (m, 2H), 0.25 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.37, 141.24, 134.55, 127.41, 84.46, 77.99, 69.58, 29.09, 27.19, -0.00.

Erythro-**3t**: **^{1}H NMR** (400 MHz, Chloroform-*d*)δ 7.52 – 7.46 (m, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 4.91 (d, *J* = 3.9 Hz, 1H), 4.13 – 4.04 (m, 1H), 3.99 – 3.89 (m, 1H), 3.84 – 3.76 (m, 1H), 2.48 (s, 1H), 1.94 – 1.78 (m, 4H), 1.67 – 1.57 (m, 1H), 0.25 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.24, 140.61, 134.42, 126.52, 84.17, 75.28, 70.15, 27.16, 26.04, -0.00.

(3,5-dimethylphenyl)(tetrahydrofuran-2-yl)methanol (3u)

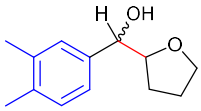


Threo-**3u** and *erythro*-**3u** were synthesized via **General Procedure V-1**, affording colorless oils (24 mg, 51%, threo/erythro = 0.96).

Threo-**3u**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.98 (s, 2H), 6.93 (s, 1H), 4.36 (d, *J* = 7.6 Hz, 1H), 4.06 – 3.96 (m, 1H), 3.97 – 3.79 (m, 2H), 2.31 (s, 6H), 1.99 – 1.81 (m, 2H), 1.78 – 1.59 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.52, 137.93, 129.66, 124.79, 83.42, 68.42, 27.97, 26.09, 21.36.

Erythro-**3u**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.98 (s, 2H), 6.90 (s, 1H), 4.86 (d, *J* = 3.9 Hz, 1H), 4.12 – 4.03 (m, 1H), 3.97 – 3.75 (m, 2H), 2.31 (s, 6H), 1.96 – 1.75 (m, 3H), 1.70 – 1.55 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.46, 137.82, 129.13, 123.78, 83.13, 74.14, 69.06, 26.10, 24.90, 21.40.

(3,4-dimethylphenyl)(tetrahydrofuran-2-yl)methanol (3v)

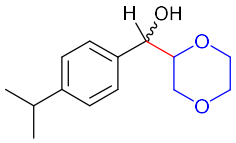


Threo-**3v** and *erythro*-**3v** were synthesized via **General Procedure V-1**, affording colorless oils (26 mg, 58%, threo/erythro = 1.07).

Threo-**3v**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 (s, 1H), 7.12 – 7.07 (m, 2H), 4.38 (d, *J* = 7.6 Hz, 1H), 4.06 – 3.96 (m, 1H), 3.97 – 3.79 (m, 2H), 1.98 – 1.82 (m, 2H), 1.77 – 1.58 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.10, 136.63, 136.31, 129.62, 128.16, 124.47, 83.46, 76.86, 68.40, 27.96, 26.08, 19.86, 19.52.

Erythro-**3v**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.14 (s, 1H), 7.12 – 7.08 (m, 2H), 4.85 (d, *J* = 4.0 Hz, 1H), 4.11 – 4.02 (m, 1H), 3.97 – 3.89 (m, 1H), 3.82 – 3.77 (m, 1H), 2.25 (d, *J* = 7.2 Hz, 6H), 1.95 – 1.79 (m, 3H), 1.69 – 1.55 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.04, 136.47, 135.75, 129.55, 127.28, 123.47, 83.15, 74.12, 69.02, 26.07, 25.01, 19.89, 19.49.

(1,4-dioxan-2-yl)(4-isopropylphenyl)methanol (3w)

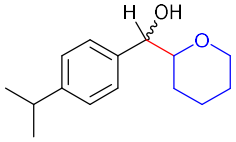


Threo-**3w** and *erythro*-**3w** were synthesized via **General Procedure V-1**, affording colorless oils (25 mg, 53%, threo/erythro = 1.04).

Threo-**3w**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 6.3 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.48 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.82 – 3.53 (m, 4H), 3.46 – 3.30 (m, 2H), 2.91 – 2.82 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.17, 136.54, 126.86, 126.68, 78.99, 74.01, 67.92, 66.64, 66.26, 33.88, 23.98.

Erythro-**3w**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.77 (d, *J* = 4.9 Hz, 1H), 3.86 – 3.70 (m, 3H), 3.72 – 3.61 (m, 2H), 3.65 – 3.51 (m, 2H), 2.90 (hept, *J* = 7.0 Hz, 1H), 1.24 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.59, 136.91, 126.54, 126.19, 78.24, 73.97, 67.12, 66.86, 66.35, 33.83, 24.01, 23.99.

(4-isopropylphenyl)(tetrahydro-2H-pyran-2-yl)methanol (3x)



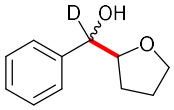
Threo-**3x** and *erythro*-**3x** were synthesized via **General Procedure V-1**, affording colorless oils (23 mg, 47%, threo/erythro = 1.14).

Threo-**3x**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 4.41

(d, *J* = 8.0 Hz, 1H), 4.11 – 4.06 (m, 1H), 3.54 – 3.43 (m, 1H), 3.37 – 3.27 (m, 1H), 2.89 (hept, *J* = 6.9 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.69 – 1.46 (m, 3H), 1.45 – 1.25 (m, 2H), 1.24 (d, *J* = 7.0 Hz, 6H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.65, 137.42, 127.27, 126.37, 81.96, 77.69, 68.53, 33.86, 27.50, 25.89, 24.04, 24.00, 22.91.

Erythro-**3x**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.79 (d, *J* = 3.8 Hz, 1H), 4.06 – 4.02 (m, 1H), 3.53 – 3.44 (m, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.63 – 1.28 (m, 5H), 1.24 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.96, 137.67, 126.40, 126.20, 81.12, 75.74, 68.92, 33.81, 26.04, 24.19, 24.03, 23.00.

phenyl((S)-tetrahydrofuran-2-yl)methan-d-ol ([D]-3a)



[D]*threo*-**3a** and [D]*erythro*-**3a** were synthesized via **General Procedure V-1**, affording colorless oils (23 mg, 60%, threo/erythro = 1.14).

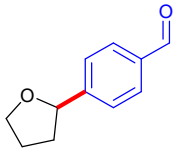
[D]*threo*-**3a**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 5H), 4.45 (d, *J* = 7.5 Hz, 0.08H), 4.03 – 3.75 (m, 3H), 2.97 (s, 1H), 2.02 – 1.81 (m, 2H), 1.78 – 1.54 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.63, 128.41, 127.98, 126.99, 83.38, 76.55, 68.45, 27.91, 26.07.

[D]*erythro*-**3a**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 4H), 7.29 – 7.24 (m, 1H), 4.94 (d, *J* = 3.8 Hz, 1H), 4.11 – 4.05 (m, 1H), 3.96 – 3.89 (m, 1H), 3.84 – 3.77 (m, 1H), 1.92 – 1.77 (m, 3H), 1.63 – 1.55 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.46, 128.28, 127.46, 126.03, 83.06, 69.07, 26.04, 24.76.

3. Characterization Data of the Dehydrogenative Coupling Reaction Products

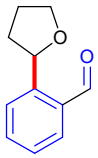
4a: *para*-**4a**, *ortho*-**4a** and *2,4-disubstituted*-**4a** were synthesized via **General Procedure V-2**, affording colorless oils (21 mg, 52%, *para*-**4a**/*ortho*-**4a**/*2,4-disubstituted*-**4a** = 0.42/0.35/0.23).

4-(tetrahydrofuran-2-yl)benzaldehyde (*para*-4a)



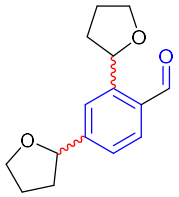
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.89 – 7.82 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 4.98 (t, *J* = 7.2 Hz, 1H), 4.13 (dt, *J* = 8.4, 6.8 Hz, 1H), 3.98 (dt, *J* = 8.3, 6.9 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.09 – 1.96 (m, 2H), 1.86 – 1.72 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.94, 146.47, 134.04, 133.79, 132.49, 127.20, 125.77, 77.54, 69.09, 34.54, 25.92.

2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-4a)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 7.82 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.60 (td, *J* = 7.6, 1.5 Hz, 1H), 7.45 (td, *J* = 7.5, 1.3 Hz, 1H), 5.69 (t, *J* = 7.0 Hz, 1H), 4.17 (dt, *J* = 7.8, 5.6 Hz, 1H), 3.98 (dt, *J* = 8.3, 7.1 Hz, 1H), 2.63 – 2.55 (m, 1H), 2.10 – 1.89 (m, 2H), 1.67 – 1.59 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.94, 146.47, 134.04, 133.79, 132.49, 130.15, 127.20, 125.77, 77.54, 69.09, 34.54, 25.92.

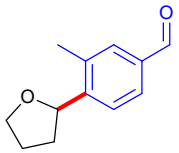
2,4-bis(tetrahydrofuran-2-yl)benzaldehyde (*2,4-disubstituted*-4a)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.14 (s, 1H), 7.78 (dd, *J* = 7.8, 6.2 Hz, 1H), 7.65 (dd, *J* = 22.1, 1.6 Hz, 1H), 7.51 – 7.39 (m, 1H), 5.67 (t, *J* = 7.1 Hz, 1H), 4.96 (td, *J* = 7.2, 2.3 Hz, 1H), 4.20 – 4.09 (m, 2H), 4.00 – 3.94 (m, 2H), 2.62 – 2.54 (m, 1H), 2.43 – 2.34 (m, 1H), 2.07 – 1.88 (m, 4H), 1.83 – 1.74 (m, 1H), 1.66 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.47, 192.45, 150.39, 150.29, 146.53, 146.42, 134.29, 134.14, 131.54, 131.52, 124.16, 123.89, 123.15, 122.57, 81.52, 80.38, 80.30, 77.65, 77.62, 69.00, 68.97, 68.41, 34.79, 34.68, 34.48, 34.45, 28.19, 26.11, 26.00, 25.93, 25.92.

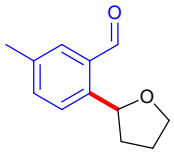
4b: *para*-**4b,** *ortho*-**4b** and *2,4-disubstituted*-**4b** were synthesized via **General Procedure V-2**, affording colorless oils (18 mg, 45%, *para*-4**b**/*ortho*-4**b**/*2,4-disubstituted*-**4b** = 0.65/0.27/0.08)

3-methyl-4-(tetrahydrofuran-2-yl)benzaldehyde (*para*-4b)



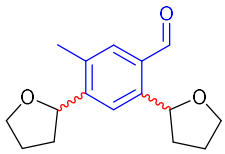
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 7.71 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 5.10 (t, *J* = 7.2 Hz, 1H), 4.18 (dt, *J* = 8.4, 6.6 Hz, 1H), 3.97 (dt, *J* = 8.4, 7.0 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.37 (s, 3H), 2.10 – 1.96 (m, 2H), 1.69 – 1.60 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.39, 149.44, 135.08, 134.99, 131.08, 128.11, 125.14, 77.78, 68.96, 33.15, 26.05, 19.22.

5-methyl-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-4b)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 7.62 (d, *J* = 2.6 Hz, 1H), 7.59 (s, 1H), 7.40 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.64 (t, *J* = 7.0 Hz, 1H), 4.21 – 4.11 (m, 1H), 4.06 – 3.91 (m, 1H), 2.58 – 2.51 (m, 1H), 2.42 (s, 3H), 2.09 – 1.87 (m, 2H), 1.66 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 193.04, 143.48, 136.97, 134.76, 134.10, 132.45, 125.86, 77.48, 68.99, 34.61, 25.91, 20.80.

5-methyl-2,4-bis(tetrahydrofuran-2-yl)benzaldehyde (*2,4-disubstituted*-**4b**)

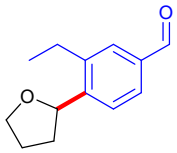


(2-S-4-R) *2,4-disubstituted*-**4b**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.13 (s, 1H), 7.79 (s, 1H), 7.55 (s, 1H), 5.64 (t, *J* = 7.1 Hz, 1H), 5.07 (t, *J* = 7.3 Hz, 1H), 4.25 – 4.13 (m, 2H), 4.01 – 3.92 (m, 2H), 2.58 – 2.48 (m, 1H), 2.45 – 2.38 (m, 1H), 2.35 (s, 3H), 2.07 – 1.92 (m, 4H), 1.70 – 1.57 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.52, 148.61, 144.08, 135.28, 133.04, 131.18, 122.00, 77.52, 68.95, 68.93, 34.51, 33.10, 26.06, 25.93, 18.66.

(2-R-4-R) *2,4-disubstituted*-**4b**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 7.73 (s, 1H), 7.58 (s, 1H), 5.57 (t, *J* = 7.1 Hz, 1H), 5.07 (t, *J* = 7.3 Hz, 1H), 4.24 – 4.10 (m, 2H), 4.01 – 3.89 (m, 2H), 2.61 – 2.46 (m, 1H), 2.47 – 2.36 (m, 1H), 2.35 (s, 3H), 2.07 – 1.90 (m, 4H), 1.71 – 1.60 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.55, 148.37, 143.82, 134.87, 133.32, 131.42, 122.64, 78.13, 78.02, 68.84, 34.71, 33.09, 26.06, 25.91, 18.74.

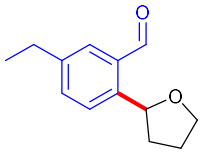
4c: *para*-**4c**, *ortho*-**4c** and *2,4-disubstituted*-**4c** were synthesized via **General Procedure V-2**, affording colorless oils (19 mg, 40%, *para*-**4c**/*ortho*-**4c**/*2,4-disubstituted*-**4c** = 0.48/0.35/0.18)

3-ethyl-4-(tetrahydrofuran-2-yl)benzaldehyde (*para*-*4*c)



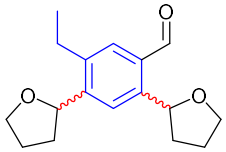
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.68 – 7.59 (m, 1H), 5.14 (t, *J* = 7.3 Hz, 1H), 4.19 (dt, *J* = 8.4, 6.6 Hz, 1H), 3.97 (dt, *J* = 8.3, 7.0 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.48 – 2.35 (m, 1H), 2.11 – 1.98 (m, 2H), 1.74 – 1.63 (m, 1H), 1.29 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.46, 148.71, 141.11, 135.34, 129.19, 128.00, 125.54, 77.28, 68.98, 34.22, 26.21, 25.05, 14.90.

5-ethyl-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-4c)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 7.66 – 7.63 (m, 1H), 7.61 (s, 1H), 7.42 (dd, *J* = 7.9, 2.0 Hz, 1H), 5.64 (t, *J* = 7.0 Hz, 1H), 4.21 – 4.11 (m, 1H), 4.02 – 3.91 (m, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.59 – 2.51 (m, 1H), 2.09 – 1.87 (m, 2H), 1.69 – 1.56 (m, 1H), 1.27 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 193.07, 143.70, 143.28, 133.64, 132.89, 132.55, 125.93, 77.49, 69.00, 34.57, 28.19, 25.93, 15.41.

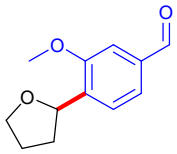
5-ethyl-2,4-bis(tetrahydrofuran-2-yl)benzaldehyde (*2,4-disubstituted***-4c)**



(2-S-4-R) *2,4-disubstituted*-**4c**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 7.80 (s, 1H), 7.61 (s, 1H), 5.64 (t, *J* = 7.1 Hz, 1H), 5.12 (t, *J* = 7.4 Hz, 1H), 4.26 – 4.13 (m, 2H), 4.01 – 3.93 (m, 2H), 2.77 – 2.62 (m, 2H), 2.57 – 2.49 (m, 1H), 2.43 – 2.35 (m, 1H), 2.12 – 1.92 (m, 4H), 1.75 – 1.58 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.65, 147.89, 143.92, 139.22, 133.53, 131.46, 122.34, 77.55, 77.39, 77.24, 68.97, 34.44, 34.17, 26.24, 25.94, 24.67, 15.01. (2-R-4-R) *2,4-disubstituted*-**4c**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.21 (s, 1H), 7.73 (s, 1H), 7.63 (s, 1H), 5.57 (t, *J* = 7.1 Hz, 1H), 5.12 (t, *J* = 7.3 Hz, 1H), 4.22 – 4.11 (m, 2H), 3.96 (dt, *J* = 8.3, 7.1 Hz, 2H), 2.76 – 2.62 (m, 2H), 2.57 – 2.49 (m, 1H), 2.44 – 2.35 (m, 1H), 2.10 – 1.91 (m, 4H), 1.74 – 1.61 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.63, 147.70, 143.64, 139.47, 132.99, 131.75, 122.95, 78.07, 77.55, 68.87, 68.83, 34.68, 34.16, 26.20, 25.91, 24.70, 15.01.

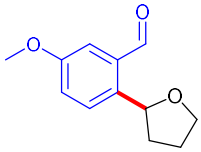
4d: *para*-**4d**, *ortho*-**4d** were synthesized via **General Procedure V-2**, affording colorless oils (19 mg, 43%, *para*-**4d**/*ortho*-**4d**/*2,4-disubstituted*-**4d** = 0.74/0.26/0.00)

3-methoxy-4-(tetrahydrofuran-2-yl)benzaldehyde (*para-4***d)**



^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 7.67 – 7.58 (m, 1H), 7.45 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (d, *J* = 1.5 Hz, 1H), 5.18 (t, *J* = 7.1 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.95 (dt, *J* = 8.2, 6.9 Hz, 1H), 3.89 (s, 3H), 2.49 – 2.41 (m, 1H), 2.06 – 1.87 (m, 2H), 1.70 – 1.61 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.09, 156.56, 140.18, 136.37, 125.80, 124.81, 108.00, 75.88, 68.75, 55.50, 33.06, 25.86.

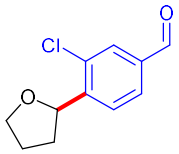
5-methoxy-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-4d)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.63 (s, 1H), 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.46 (dd, *J* = 9.5, 6.7 Hz, 1H), 4.11 (dt, *J* = 8.6, 6.8 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.86 (s, 3H), 2.49 – 2.40 (m, 1H), 2.26 – 1.99 (m, 2H), 1.88 – 1.79 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 193.71, 156.90, 136.87, 132.24, 128.24, 120.33, 114.69, 75.73, 68.03, 55.96, 34.01, 26.47.

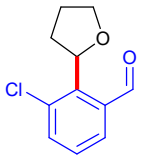
4e: *para*-**4e,** *ortho*-**4e**, 3-Cl-*2,4-disubstituted*-**4e** and 5-Cl-*2,4-disubstituted*-**4e** were synthesized via **General Procedure V-2**, affording colorless oils and white solids (25 mg, 49%, *para*-**4e**/*ortho*-**4e**/*2,4-disubstituted*-**4e** = 0.34/0.14/0.52).

3-chloro-4-(tetrahydrofuran-2-yl)benzaldehyde (*para*-4e)



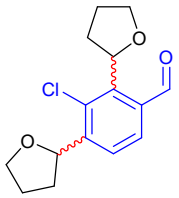
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 7.84 (t, *J* = 1.2 Hz, 1H), 7.77 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 5.23 (t, *J* = 7.1 Hz, 1H), 4.23 – 4.13 (m, 1H), 4.05 – 3.94 (m, 1H), 2.63 – 2.54 (m, 1H), 2.11 – 1.91 (m, 2H), 1.73 – 1.65 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.75, 148.67, 136.33, 132.47, 130.08, 128.33, 126.98, 77.79, 69.26, 33.13, 25.87.

3-chloro-2-(tetrahydrofuran-2-yl)benzaldehyde(*ortho*-4e)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.58 (s, 1H), 7.64 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 5.43 (dd, *J* = 9.5, 6.7 Hz, 1H), 4.14 (dt, *J* = 8.7, 7.0 Hz, 1H), 3.91 (dt, *J* = 8.6, 7.1 Hz, 1H), 2.65 – 2.52 (m, 1H), 2.20 – 2.07 (m, 2H), 1.91 – 1.81 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.41, 140.76, 137.78, 133.49, 132.97, 128.41, 127.05, 79.04, 68.24, 33.70, 26.30.

3-chloro-2,4-bis(tetrahydrofuran-2-yl)benzaldehyde (3-Cl-*2,4-disubstituted*-**4e**)

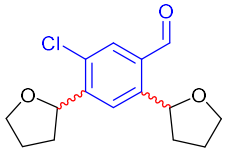


3-Cl-2R-4R *2,4-disubstituted*-**4e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.56 (s, 1H), 7.67 (d, *J* =

8.1 Hz, 1H), 7.59 – 7.52 (m, 1H), 5.47 (dd, *J* = 9.5, 6.7 Hz, 1H), 5.24 (t, *J* = 6.9 Hz, 1H), 4.21 – 4.09 (m, 2H), 4.00 – 3.87 (m, 2H), 2.64 – 2.49 (m, 2H), 2.26 – 2.07 (m, 2H), 2.10 – 1.77 (m, 3H), 1.72 – 1.64 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.25, 146.91, 140.99, 136.26, 129.98, 126.82, 125.24, 79.16, 78.02, 69.28, 68.22, 33.58, 33.13, 26.31, 25.77.

3-Cl-2S-4R *2,4-disubstituted*-**4e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.56 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 5.47 (t, *J* = 8.12 Hz, 1H), 5.24 (t, *J* = 6.9 Hz, 1H), 4.21 – 4.10 (m, 2H), 4.02 – 3.85 (m, 2H), 2.63 – 2.49 (m, 3H), 2.20 – 2.09 (m, 2H), 2.06 – 1.79 (m, 4H), 1.74 – 1.63 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.22, 146.88, 140.98, 136.29, 129.97, 126.81, 125.23, 79.16, 78.00, 69.25, 68.20, 33.57, 33.12, 26.29, 25.76.

5-chloro-2,4-bis(tetrahydrofuran-2-yl)benzaldehyde (5-Cl-*2,4-disubstituted*-**4e**)

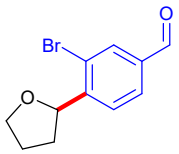


5-Cl-2S-4R *2,4-disubstituted*-**4e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 7.88 (s, 1H), 7.76 (s, 1H), 5.60 (t, *J* = 7.1 Hz, 1H), 5.21 (t, *J* = 7.2 Hz, 1H), 4.23 – 4.16 (m, 2H), 4.02 – 3.94 (m, 2H), 2.60 – 2.50 (m, 2H), 2.10 – 1.92 (m, 4H), 1.72 – 1.58 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.01, 147.92, 144.98, 133.68, 132.41, 130.32, 124.03, 77.87, 77.25, 69.26, 69.08, 34.54, 33.10, 25.93, 25.89.

5-Cl-2R-4R *2,4-disubstituted*-**4e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 7.82 (s, 1H), 7.77 (s, 1H), 5.54 (t, *J* = 7.1 Hz, 1H), 5.21 (t, *J* = 7.1 Hz, 1H), 4.20 – 4.13 (m, 2H), 4.04 – 3.90 (m, 2H), 2.62 – 2.46 (m, 2H), 2.11 – 1.89 (m, 4H), 1.76 – 1.59 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.01, 147.76, 144.70, 133.17, 132.70, 130.46, 124.45, 77.87, 77.75, 69.17, 68.93, 34.72, 33.12, 25.92, 25.87.

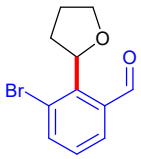
4f: *para*-**4f,** *ortho*-**4f**, 3-Cl-*2,4-disubstituted*-**4f** and 5-Cl-*2,4-disubstituted*-**4f** were synthesized via **General Procedure V-2**, affording colorless oils and white solids (25 mg, 40%, *para*-**4f**/*ortho*-**4f**/*2,4-disubstituted*-**4f** = 0.25/0.13/0.62).

3-bromo-4-(tetrahydrofuran-2-yl)benzaldehyde (*para*-**4f**)



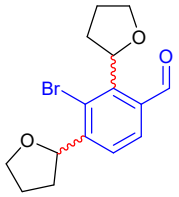
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 8.02 (d, *J* = 1.6 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 5.18 (t, *J* = 7.1 Hz, 1H), 4.23 – 4.16 (m, 1H), 4.00 (dt, *J* = 8.3, 7.0 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.11 – 1.89 (m, 2H), 1.74 – 1.61 (m, 1H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 186.67, 146.28, 132.59, 129.58, 124.88, 123.24, 117.98, 75.83, 65.48, 29.31, 21.89.

3-bromo-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4f**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.56 (d, *J* = 0.7 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.23 (dd, *J* = 16.8, 9.0 Hz, 1H), 5.37 (dd, *J* = 9.5, 6.7 Hz, 1H), 4.15 (dt, *J* = 8.7, 6.9 Hz, 1H), 3.91 (dt, *J* = 8.7, 7.2 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.20 – 2.08 (m, 2H), 1.92 – 1.78 (m, 1H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 188.26, 138.17, 134.00, 132.79, 124.81, 123.69, 118.92, 77.71, 73.43, 73.11, 72.79, 64.34, 29.67, 22.31.

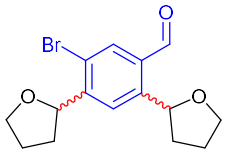
3-bromo-2,4-bis(tetrahydrofuran-2-yl)benzaldehyde (3-Br-*2,4-disubstituted*-**4f**)



3-Br-2R-4R *2,4-disubstituted*-**4e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 5.44 (dd, *J* = 9.4, 6.7 Hz, 1H), 5.22 (t, *J* = 6.9 Hz, 1H), 4.24 – 4.09 (m, 2H), 4.03 – 3.85 (m, 2H), 2.67 – 2.52 (m, 2H), 2.22 – 2.08 (m, 2H), 2.08 – 1.78 (m, 3H), 1.72 – 1.63 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.03, 148.45, 142.41, 136.60, 127.39, 125.61, 121.62, 81.87, 80.18, 69.47, 68.25, 33.42, 33.32, 26.26, 25.72.

3-Br-2S-4R *2,4-disubstituted*-**4e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 5.44 (dd, *J* = 9.3, 6.9 Hz, 1H), 5.24 (t, *J* = 7.0 Hz, 1H), 4.23 – 4.11 (m, 2H), 4.01 – 3.95 (m, 1H), 3.92 – 3.86 (m, 1H), 2.67 – 2.55 (m, 2H), 2.18 – 2.08 (m, 2H), 2.06 – 1.82 (m, 3H), 1.70 – 1.61 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.11, 148.40, 142.46, 136.61, 127.33, 125.57, 121.68, 81.93, 80.25, 69.35, 68.17, 33.43, 33.28, 26.26, 25.76.

5-bromo-2,4-bis(tetrahydrofuran-2-yl)benzaldehyde (5-Br-*2,4-disubstituted*-**4f**)

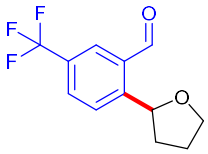


5-Br-2S-4R *2,4-disubstituted*-**4e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.10 (s, 1H), 7.93 (s, 1H), 7.85 (s, 1H), 5.59 (t, *J* = 7.1 Hz, 1H), 5.16 (t, *J* = 7.2 Hz, 1H), 4.27 – 4.13 (m, 2H), 4.05 – 3.92 (m, 2H), 2.65 – 2.48 (m, 2H), 2.06 – 1.91 (m, 4H), 1.72 – 1.54 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.89, 149.54, 145.61, 137.07, 132.72, 124.24, 119.62, 79.88, 77.27, 69.40, 69.08, 34.46, 33.20, 25.91, 25.85.

5-Br-2R-4R *2,4-disubstituted*-**4e**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 7.95 (s, 1H), 7.79 (s, 1H), 5.52 (t, *J* = 7.1 Hz, 1H), 5.16 (t, *J* = 7.1 Hz, 1H), 4.22 – 4.12 (m, 2H), 4.03 – 3.94 (m, 2H), 2.65 – 2.48 (m, 2H), 2.11 – 1.86 (m, 4H), 1.74 – 1.58 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.92, 149.41, 145.35, 136.59, 132.96, 124.60, 119.75, 79.82, 77.79, 69.33, 68.94, 34.66, 33.26, 25.90, 25.83.

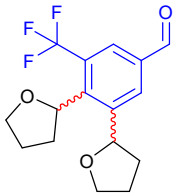
4g: *ortho*-**4g,** *3,4-disubstituted*-**4g** were synthesized via **General Procedure V-2**, affording colorless oils (26 mg, 42%, *para*-**4g**/*ortho*-**4g**/*3,4-disubstituted*-**4g** = 0.00/0.26/0.74).

4-(tetrahydrofuran-2-yl)-3-(trifluoromethyl)benzaldehyde (*ortho*-**4g**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.22 (s, 1H), 8.07 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.82 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.68 (t, *J* = 7.2 Hz, 1H), 4.22 – 4.10 (m, 1H), 4.05 – 3.95 (m, 1H), 2.66 – 2.58 (m, 1H), 2.09 – 1.92 (m, 2H), 1.67 – 1.58 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 13C NMR (101 MHz, Chloroform-d) δ 191.26, 150.30, 132.75, 130.24 (q, J = 3.6 Hz), 130.00 (q, J = 3.77 Hz), 129.74 (q, J = 6.9 Hz), 126.73, 123.60 (q, J = 272.4 Hz), 77.27, 69.21, 34.56, 25.94. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.74.

3,4-bis(tetrahydrofuran-2-yl)-5-(trifluoromethyl)benzaldehyde (*3,4-disubstituted*-**4g**)

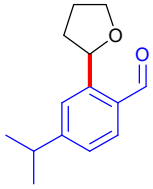


3R-4S *3,4-disubstituted*-**4g**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 8.06 (d, *J* = 10.3 Hz, 2H), 5.69 (t, *J* = 7.2 Hz, 1H), 5.30 – 5.22 (m, 1H), 4.29 – 4.14 (m, 2H), 4.06 – 3.95 (m, 2H), 2.64 – 2.56 (m, 1H), 2.49 – 2.40 (m, 1H), 2.20 – 1.85 (m, 4H), 1.75 – 1.57 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.18, 150.45, 149.21, 131.16 (q, *J* = 5.7 Hz), 125.89 (q, *J* = 31.7 Hz), 124.65, 123.83 (q, *J* = 273.9 Hz), 76.83, 76.80, 69.52, 69.24, 35.68, 34.35, 26.30, 25.93. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -58.85.

3R-4R *3,4-disubstituted*-**4g**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.21 (s, 1H), 8.05 (d, *J* = 14.0 Hz, 2H), 5.62 (t, *J* = 7.1 Hz, 1H), 5.31 – 5.23 (m, 1H), 4.27 – 4.12 (m, 2H), 4.03 – 3.97 (m, 2H), 2.64 – 2.56 (m, 1H), 2.50 – 2.42 (m, 1H), 2.13 – 1.99 (m, 3H), 2.03 – 1.87 (m, 1H), 1.74 – 1.57 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.15, 150.24, 149.14, 131.34, 130.67 (q, *J* = 5.6 Hz), 125.96 (q, *J* = 31.6 Hz), 124.86, 123.84 (q, *J* = 273.8 Hz), 77.75, 76.69, 69.43, 69.08, 35.74, 34.61, 26.24, 25.89. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -58.82.

4h: *ortho*-**4h** wsa synthesized via **General Procedure V-2**, affording colorless oil (16 mg, 34%, *para*-**4h**/*ortho*-**4h**/*2,4-disubstituted*-**4h** = 0.00/1.00/0.00).

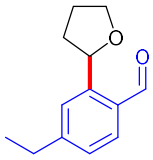
4-isopropyl-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4h**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.68 (t, *J* = 7.1 Hz, 1H), 4.23 – 4.13 (m, 1H), 3.98 (dt, *J* = 8.2, 7.1 Hz, 1H), 2.99 (hept, *J* = 6.9 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.10 – 1.87 (m, 2H), 1.66 – 1.57 (m, 1H), 1.28 (dd, *J* = 7.0, 2.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.49, 155.79, 146.47, 134.47, 130.59, 125.02, 123.99, 77.70, 69.02, 34.66, 34.49, 25.90, 23.64.

4i: *ortho*-**4i** was synthesized via **General Procedure V-2**, affording colorless oil (14 mg, 32%, *para*-**4i**/*ortho*-**4i**/*2,4-disubstituted*-**4i** = 0.00/1.00/0.00).

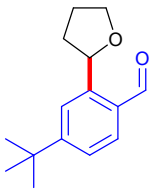
4-ethyl-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4i**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.26 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.67 (t, *J* = 7.1 Hz, 1H), 4.22 – 4.13 (m, 1H), 3.98 (dt, *J* = 8.3, 7.1 Hz, 1H), 2.78 – 2.69 (m, 2H), 2.63 – 2.54 (m, 1H), 2.08 – 1.90 (m, 2H), 1.65 – 1.57 (m, 1H), 1.27 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.49, 151.27, 146.46, 134.45, 130.45, 126.57, 125.27, 77.61, 69.03, 34.47, 29.35, 25.92, 15.17.

4j: *ortho*-**4j** was synthesized via **General Procedure V-2**, affording colorless oil (17 mg, 33%, *para*-**4j**/*ortho*-**4j**/*2,4-disubstituted*-**4j** = 0.00/1.00/0.00).

4-(tert-butyl)-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4j**)

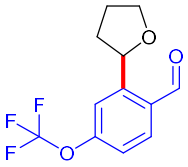


^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 7.75 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.45 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.68 (t, *J* = 7.0 Hz, 1H), 4.23 – 4.13 (m, 1H), 4.04 – 3.94 (m, 1H), 2.62 – 2.54 (m, 1H), 2.10 – 1.87 (m, 2H), 1.66 – 1.58 (m, 1H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.50, 157.91, 146.02, 134.08, 130.19, 124.10, 122.64, 77.83, 69.01, 35.46, 34.55, 31.07, 25.86.

4k: *ortho*-**4k**, *2,6-disubstituted*-**4k** was prepared according to the general procedure V-2. The

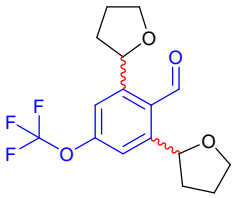
compound were synthesized via **General Procedure V-2**, affording colorless oils (31 mg, 53%, *para*-**4k**/*ortho*-**4k**/*2,6-disubstituted*-**4k** = 0.00/0.70/0.30).

2-(tetrahydrofuran-2-yl)-4-(trifluoromethoxy)benzaldehyde (*ortho*-**4k**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.14 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.29 – 7.22 (m, 1H), 5.67 (t, *J* = 7.1 Hz, 1H), 4.22 – 4.12 (m, 1H), 3.98 (dt, *J* = 8.3, 7.1 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.11 – 1.87 (m, 2H), 1.66 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.12, 153.31 (q, *J* = 1.8 Hz), 149.73, 135.86, 130.53, 120.29 (q, *J* = 259.0 Hz), 118.32, 117.78, 77.01, 69.19, 34.47, 25.86. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.35.

2,6-bis(tetrahydrofuran-2-yl)-4-(trifluoromethoxy)benzaldehyde (*2,6-disubstituted*-**4k**)

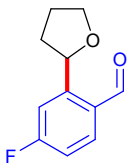


2-R-6-S *2,6-disubstituted*-**4k**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.50 (s, 1H), 7.41 (s, 2H), 5.46 (t, *J* = 7.1 Hz, 2H), 4.18 – 4.08 (m, 2H), 4.00 – 3.93 (m, 2H), 2.60 – 2.47 (m, 2H), 2.10 – 1.89 (m, 4H), 1.76 – 1.67 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.23, 152.52 (q, *J* = 1.8 Hz), 149.65, 128.03, 120.32 (q, *J* = 259.85 Hz), 116.19, 77.49, 69.08, 34.88, 25.90. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.20.

2-R-6-R *2,6-disubstituted*-**4k**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.46 (s, 1H), 7.41 (s, 2H), 5.41 (t, *J* = 7.2 Hz, 2H), 4.16 – 4.11 (m, 2H), 3.96 (dt, *J* = 8.3, 7.0 Hz, 2H), 2.57 – 2.44 (m, 2H), 2.11 – 1.90 (m, 4H), 1.76 – 1.66 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.75, 152.43 (q, *J* = 1.9 Hz), 149.58, 128.16, 120.32 (q, *J* = 258.9 Hz), 116.17, 77.56, 69.07, 35.44, 26.00. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.20.

4l: *ortho*-**4l,** *2,6-disubstituted*-**4l** were synthesized via **General Procedure V-2**, affording colorless oils (24 mg, 57%, *para*-**4l**/*ortho*-**4l**/*2,6-disubstituted*-**4l** = 0.00/0.88/0.12).

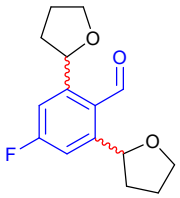
4-fluoro-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4l)**



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.09 (s, 1H), 7.83 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.45 (dd, *J* = 10.4, 2.7 Hz, 1H), 7.10 (td, *J* = 8.1, 2.6 Hz, 1H), 5.68 (t, *J* = 7.0 Hz, 1H), 4.21 – 4.11 (m, 1H), 4.02 – 3.92 (m, 1H), 2.65 – 2.56 (m, 1H), 2.10 – 1.86 (m, 2H), 1.65 – 1.56 (m, 1H). **^{13}C NMR** (101 MHz,

Chloroform-*d*) δ 191.06, 166.27 (d, *J* = 256.5 Hz), 150.60 (d, *J* = 8.6 Hz), 136.82 (d, *J* = 10.0 Hz), 128.98 (d, *J* = 2.7 Hz), 114.13 (d, *J* = 22.2 Hz), 113.32 (d, *J* = 23.9 Hz), 77.04 (d, *J* = 1.3 Hz), 69.15, 34.39, 25.85. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -102.42.

4-fluoro-2,6-bis(tetrahydrofuran-2-yl)benzaldehyde (*2,6-disubstituted*-**4l**)

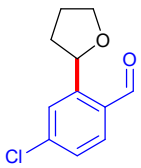


2-R-6-S *2,6-disubstituted*-**4l**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.47 (s, 1H), 7.30 (s, 1H), 7.27 (s, 1H), 5.50 (t, *J* = 7.1 Hz, 2H), 4.19 – 4.09 (m, 2H), 4.01 – 3.91 (m, 2H), 2.61 – 2.48 (m, 2H), 2.08 – 1.91 (m, 4H), 1.78 – 1.65 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.71, 165.72 (d, *J* = 254.8 Hz), 150.99 (d, *J* = 8.2 Hz), 125.95 (d, *J* = 1.9 Hz), 111.74 (d, *J* = 23.7 Hz), 77.45 (d, *J* = 0.7 Hz), 69.08, 34.81, 25.90. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -102.80.

2-R-6-R *2,6-disubstituted*-**4l**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.43 (s, 1H), 7.31 (s, 1H), 7.29 (s, 1H), 5.45 (t, *J* = 7.2 Hz, 2H), 4.19 – 4.09 (m, 2H), 4.01 – 3.91 (m, 2H), 2.58 – 2.45 (m, 2H), 2.10 – 1.90 (m, 4H), 1.75 – 1.64 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.21, 165.66 (d, *J* = 254.6 Hz), 150.94 (d, *J* = 8.4 Hz), 126.04 (d, *J* = 2.8 Hz), 111.70 (d, *J* = 23.7 Hz), 77.44 (d, *J* = 1.0 Hz), 69.08, 35.38, 25.99. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -102.98.

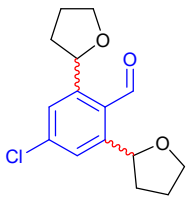
4m: *ortho*-**4m** and *2,6-disubstituted*-**4m** were synthesized via **General Procedure V-2**, affording colorless oils (25 mg, 52%, *para*-**4m**/*ortho*-**4m**/*2,6-disubstituted*-**4m** = 0.00/0.75/0.25)

4-chloro-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4m**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 7.78 – 7.71 (m, 2H), 7.41 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.65 (t, *J* = 7.1 Hz, 1H), 4.20 – 4.15 (m, 1H), 3.98 (dt, *J* = 8.2, 7.0 Hz, 1H), 2.64 – 2.55 (m, 1H), 2.10 – 1.87 (m, 2H), 1.65 – 1..56 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.45, 148.46, 140.81, 135.09, 130.80, 127.43, 126.27, 77.01, 69.18, 34.46, 25.91.

4-chloro-2,6-bis(tetrahydrofuran-2-yl)benzaldehyde (*2,6-disubstituted*-**4m)**



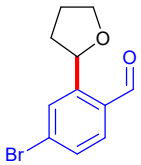
2-R-6-S *2,6-disubstituted*-**4m**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.48 (s, 1H), 7.56 (s, 2H), 5.43 (t, *J* = 7.1 Hz, 2H), 4.18 – 4.08 (m, 2H), 4.03 – 3.90 (m, 2H), 2.56 – 2.46 (m, 2H), 2.06 – 1.94

(m, 4H), 1.78 – 1.65 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.57, 148.44, 139.75, 128.29, 124.85, 77.49, 69.07, 34.84, 25.95.

2-R-6-R *2,6-disubstituted*-**4m**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.45 (s, 1H), 7.56 (s, 2H), 5.38 (t, *J* = 7.2 Hz, 2H), 4.18 – 4.09 (m, 2H), 4.01 – 3.89 (m, 2H), 2.56 – 2.43 (m, 2H), 2.07 – 1.93 (m, 4H), 1.76 – 1.64 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.10, 148.40, 139.63, 128.40, 124.83, 77.53, 69.07, 35.41, 26.05.

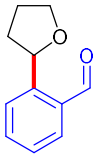
4n: *para*-**4n,** *ortho*-**4n** and *2,6-disubstituted*-**4n** were synthesized via **General Procedure V-2**, affording colorless oils (23 mg, 52%, *para*-**4n**/*ortho*-**4n**/*2,6-disubstituted*-**4n** = 0.12/0.67/0.21).

4-bromo-2-(tetrahydrofuran-2-yl)benzaldehyde (4-Br-*ortho*-**4n)**



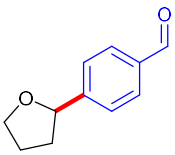
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.58 (dd, *J* = 8.1, 2.0 Hz, 1H), 5.63 (t, *J* = 7.1 Hz, 1H), 4.22 – 4.12 (m, 1H), 4.02 – 3.92 (m, 1H), 2.63 – 2.55 (m, 1H), 2.10 – 1.87 (m, 2H), 1.65 – 1.56 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.67, 148.33, 135.07, 131.17, 130.48, 129.77, 129.21, 76.95, 69.17, 34.49, 25.92.

2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4n)**



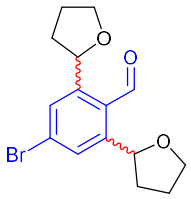
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 7.82 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.60 (td, *J* = 7.6, 1.5 Hz, 1H), 7.45 (td, *J* = 7.5, 1.3 Hz, 1H), 5.69 (t, *J* = 7.0 Hz, 1H), 4.23 – 4.12 (m, 1H), 4.03 – 3.93 (m, 1H), 2.63 – 2.54 (m, 1H), 2.10 – 1.87 (m, 2H), 1.69 – 1.59 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.89, 146.46, 134.02, 133.74, 132.52, 127.19, 125.78, 77.53, 69.07, 34.54, 25.92.

4-(tetrahydrofuran-2-yl)benzaldehyde (*para*-**4n**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 4.97 (t, *J* = 7.2 Hz, 1H), 4.17 – 4.07 (m, 1H), 4.03 – 3.91 (m, 1H), 2.46 – 2.31 (m, 1H), 2.09 – 1.95 (m, 2H), 1.84 – 1.73 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.04, 150.86, 135.46, 129.92, 126.04, 80.14, 68.97, 34.77, 25.99.

4-bromo-2,6-bis(tetrahydrofuran-2-yl)benzaldehyde (*2,6-disubstituted*-**4n**)

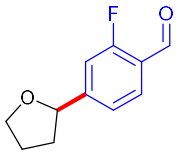


2-R-6-S *2,6-disubstituted*-**4n**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.48 (s, 1H), 7.72 (s, 1H), 5.41 (t, *J* = 7.2 Hz, 1H), 4.18 – 4.08 (m, 1H), 4.00 – 3.90 (m, 1H), 2.58 – 2.45 (m, 1H), 2.10 – 1.90 (m, 2H), 1.76 – 1.68 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.85, 148.19, 128.80, 128.62, 127.85, 77.45, 69.07, 34.88, 25.97.

2-R-6-R *2,6-disubstituted*-**4n**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.45 (s, 1H), 7.72 (s, 2H), 5.36 (t, *J* = 7.3 Hz, 2H), 4.18 – 4.08 (m, 2H), 4.00 – 3.90 (m, 2H), 2.55 – 2.42 (m, 2H), 2.10 – 1.89 (m, 4H), 1.77 – 1.63 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.37, 148.12, 128.97, 128.44, 127.84, 77.50, 69.05, 35.43, 26.06.

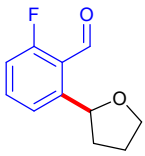
4o: *para*-**4o**, *ortho*-**4o** and *4,6-disubstituted*-**4o** were synthesized via **General Procedure V-2**, affording colorless oils (18 mg, 38%, *para*-**4o**/*ortho*-**4o**/*4,6-disubstituted*-**4o** = 0.21/0.29/0.50).

2-fluoro-4-(tetrahydrofuran-2-yl)benzaldehyde (*para*-**4o**)



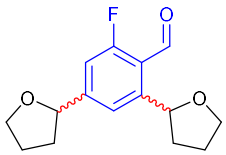
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.33 (s, 1H), 7.83 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.23 – 7.14 (m, 2H), 4.95 (t, *J* = 7.2 Hz, 1H), 4.16 – 4.06 (m, 1H), 4.02 – 3.92 (m, 1H), 2.46 – 2.33 (m, 1H), 2.07 – 1.97 (m, 2H), 1.83 – 1.72 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 186.99 (d, *J* = 6.3 Hz), 164.91 (d, *J* = 258.8 Hz), 154.04 (d, *J* = 8.1 Hz), 128.72 (d, *J* = 2.2 Hz), 122.90 (d, *J* = 8.2 Hz), 121.63 (d, *J* = 3.2 Hz), 113.26 (d, *J* = 21.6 Hz), 79.57 (d, *J* = 1.7 Hz), 69.05, 34.65, 25.90. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -121.78.

2-fluoro-6-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4o**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.51 (s, 1H), 7.61 – 7.51 (m, 2H), 7.11 – 7.03 (m, 1H), 5.61 (t, *J* = 6.9 Hz, 1H), 4.20 – 4.10 (m, 1H), 4.01 – 3.91 (m, 1H), 2.67 – 2.58 (m, 1H), 2.07 – 1.82 (m, 2H), 1.59 – 1.51 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 188.72 (d, *J* = 11.8 Hz), 166.31 (d, *J* = 257.5 Hz), 148.93, 135.66 (d, *J* = 10.4 Hz), 121.36 (d, *J* = 3.4 Hz), 120.67 (d, *J* = 5.6 Hz), 114.48 (d, *J* = 21.6 Hz), 77.68 (d, *J* = 2.4 Hz), 69.23, 34.31, 25.79. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -121.17.

2-fluoro-4,6-bis(tetrahydrofuran-2-yl)benzaldehyde(*4,6-disubstituted*-4o)

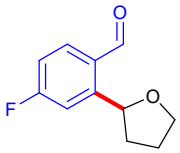


4-R-6-R *4,6-disubstituted*-**4o**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.46 (s, 1H), 7.41 (s, 1H), 7.12 (dd, *J* = 11.9, 1.6 Hz, 1H), 5.61 (t, *J* = 7.0 Hz, 1H), 4.93 (t, *J* = 7.2 Hz, 1H), 4.19 – 4.05 (m, 2H), 4.02 – 3.90 (m, 2H), 2.66 – 2.58 (m, 1H), 2.46 – 2.33 (m, 1H), 2.06 – 1.94 (m, 3H), 1.96 – 1.83 (m, 1H), 1.83 – 1.73 (m, 1H), 1.57 – 1.48 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 188.37 (d, *J* = 11.7 Hz), 166.83 (d, *J* = 257.7 Hz), 153.22 (d, *J* = 9.3 Hz), 148.78, 119.32 (d, *J* = 5.9 Hz), 118.42 (d, *J* = 3.0 Hz), 111.10 (d, *J* = 22.9 Hz), 79.90 (d, *J* = 1.7 Hz), 77.77 (d, *J* = 2.5 Hz), 69.17, 69.05, 34.58, 34.19, 25.92, 25.78. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -120.60.

4-R-6-S *4,6-disubstituted*-**4o**: **^{1}H NMR** (400 MHz, Chloroform-d) δ 10.46 (s, 1H), 7.46 (s, 1H), 7.07 (dd, J = 11.9, 1.6 Hz, 1H), 5.60 (t, J = 7.0 Hz, 1H), 4.93 (t, J = 7.2 Hz, 1H), 4.20 – 4.05 (m, 2H), 4.00 – 3.92 (m, 2H), 2.67 – 2.58 (m, 1H), 2.45 – 2.31 (m, 1H), 2.04 – 1.97 (m, 3H), 1.93 – 1.74 (m, 2H), 1.57 – 1.49 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 188.35 (d, *J* = 11.6 Hz), 166.64 (d, *J* = 257.8 Hz), 153.25 (d, *J* = 9.2 Hz), 148.82, 119.30 (d, *J* = 5.7 Hz), 117.93 (d, *J* = 2.9 Hz), 111.30 (d, *J* = 22.7 Hz), 79.81 (d, *J* = 1.8 Hz), 77.79 (d, *J* = 2.5 Hz), 69.15, 69.05, 34.66, 34.18, 25.90, 25.80. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -120.84.

4p: *ortho*-**4p** was synthesized via **General Procedure V-2**, affording colorless oil (23 mg, 41%, *para*-**4p**/*ortho*-**4p**/*2,4-disubstituted*-**4p** = 0.00/1.00/0.00).

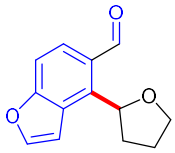
4-fluoro-2-(tetrahydrofuran-2-yl)benzaldehyde (*ortho*-**4p**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.09 (s, 1H), 7.83 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.45 (dd, *J* = 10.4, 2.7 Hz, 1H), 7.10 (td, *J* = 8.1, 2.7 Hz, 1H), 5.68 (t, *J* = 7.0 Hz, 1H), 4.21 – 4.12 (m, 2H), 3.98 (dt, *J* = 8.3, 7.1 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.10 – 1.85 (m, 2H), 1.65 – 1.56 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.10, 166.30 (d, *J* = 256.6 Hz), 150.63 (d, *J* = 8.6 Hz), 136.86 (d, *J* = 10.1 Hz), 128.96, 114.16 (d, *J* = 22.3 Hz), 113.35 (d, *J* = 23.8 Hz), 79.52 – 73.34 (m), 69.19, 34.41, 25.87. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -102.43.

4q: *ortho*-**4q** was synthesized via **General Procedure V-2**, affording colorless oil (14 mg, 30%, *para*-**4q**/*ortho*-**4q**/*2,4-disubstituted*-**4q** = 0.00/1.00/0.00).

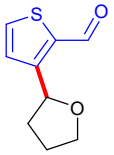
6-(tetrahydrofuran-2-yl)benzofuran-5-carbaldehyde (*ortho*-**4q**)



^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.30 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 2.3 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.20 – 7.16 (m, 1H), 5.93 (dd, *J* = 8.7, 6.8 Hz, 1H), 4.30 – 4.23 (m, 1H), 4.05 – 3.98 (m, 1H), 2.62 – 2.57 (m, 1H), 2.20 – 2.03 (m, 2H), 1.82 – 1.75 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.17, 158.28, 145.67, 140.54, 129.70, 128.44, 125.86, 110.65, 108.14, 77.97, 68.68, 34.76, 26.52.

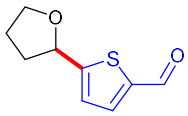
4r: *3-THF*-**4r,** *5-THF*-**4r** and *3,5-disubstituted*-**4r** were synthesized via **General Procedure V-2**, affording colorless oils (20 mg, 46%, *3-THF*-**4r,** *5-THF*-**4r** and *3,5-disubstituted*-**4r** = 0.22/0.48/0.30).

3-(tetrahydrofuran-2-yl)thiophene-2-carbaldehyde (*3-THF*-**4r**)



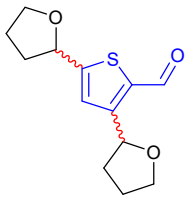
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 7.65 (d, *J* = 5.0 Hz, 1H), 7.17 (d, *J* = 5.1 Hz, 1H), 5.39 (t, *J* = 7.4 Hz, 1H), 4.11 (dt, *J* = 8.4, 6.8 Hz, 1H), 3.95 (dt, *J* = 8.3, 6.9 Hz, 1H), 2.50 – 2.42 (m, 1H), 2.12 – 2.00 (m, 2H), 1.89 – 1.79 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 182.97, 152.85, 137.75, 134.29, 128.20, 76.46, 68.81, 34.76, 26.09.

5-(tetrahydrofuran-2-yl)thiophene-2-carbaldehyde (*5-THF*-**4r**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 7.65 (d, *J* = 3.9 Hz, 1H), 7.04 (dd, *J* = 3.9, 0.9 Hz, 1H), 5.22 – 5.14 (m, 1H), 4.08 (dt, *J* = 8.3, 6.6 Hz, 1H), 3.92 (dt, *J* = 8.3, 6.8 Hz, 1H), 2.46 – 2.34 (m, 1H), 2.11 – 1.98 (m, 2H), 1.99 – 1.91 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 183.00, 159.31, 142.14, 136.76, 124.18, 76.69, 68.81, 34.85, 25.84.

3,5-bis(tetrahydrofuran-2-yl)thiophene-2-carbaldehyde (*3,5-disubstituted*-**4r)**



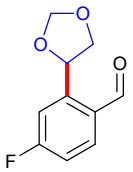
3-S-5-R *3,5-disubstituted*-**4r**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.06 (s, 1H), 7.01 (s, 1H), 5.34 (t, *J* = 7.4 Hz, 1H), 5.13 (t, *J* = 6.5 Hz, 1H), 4.14 – 4.02 (m, 2H), 3.96 – 3.88 (m, 2H), 2.50 – 2.30 (m, 2H), 2.11 – 1.97 (m, 4H), 2.00 – 1.89 (m, 1H), 1.87 – 1.78 (m, 1H). **^{13}C NMR** (101 MHz,

Chloroform-*d*) δ 182.60, 158.18, 153.09, 135.87, 124.00, 123.86, 76.79, 76.29, 68.81, 34.72, 34.64, 26.11, 25.86.

3-R-5-R *3,5-disubstituted*-**4r**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.07 (s, 1H), 7.01 (s, 1H), 5.37 – 5.29 (m, 1H), 5.17 – 5.08 (m, 1H), 4.14 – 4.02 (m, 2H), 3.96 – 3.88 (m, 2H), 2.50 – 2.31 (m, 2H), 2.12 – 1.98 (m, 4H), 1.99 – 1.89 (m, 1H), 1.87 – 1.78 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 182.68, 182.60, 158.01, 153.05, 135.92, 124.00, 123.86, 76.75, 76.40, 68.81, 68.77, 34.77, 34.68, 26.11, 25.84.

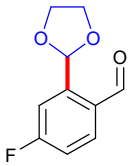
4s: *ortho*-**4s** and *2,6-disubstituted*-**4s** were synthesized via **General Procedure V-2**, affording colorless oils (14 mg, 34%, *para*-**4s**/*ortho*-**4s**/*2,6-disubstituted*-**4s** = 0.00/0.71/0.29).

2-(1,3-dioxolan-4-yl)-4-fluorobenzaldehyde (*ortho*-**4s**-1)



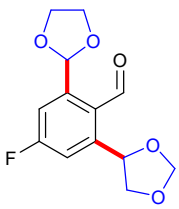
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.84 (dd, *J* = 8.4, 5.6 Hz, 1H), 7.52 (dd, *J* = 10.2, 2.6 Hz, 1H), 7.18 (td, *J* = 8.0, 2.6 Hz, 1H), 5.77 (dd, *J* = 7.3, 4.8 Hz, 1H), 5.34 (s, 1H), 5.06 (s, 1H), 4.48 (dd, *J* = 8.6, 7.3 Hz, 1H), 3.62 (dd, *J* = 8.6, 4.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.80, 166.32 (d, *J* = 257.8 Hz), 147.18 (d, *J* = 8.8 Hz), 138.32 (d, *J* = 10.0 Hz), 129.04 (d, *J* = 2.6 Hz), 114.77 (d, *J* = 22.2 Hz), 113.93 (d, *J* = 24.4 Hz), 95.96, 74.20, 71.94. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -101.39.

2-(1,3-dioxolan-2-yl)-4-fluorobenzaldehyde (*ortho*-**4s**-2)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.32 (s, 1H), 7.97 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.45 (dd, *J* = 9.5, 2.7 Hz, 1H), 7.19 (td, *J* = 8.2, 2.6 Hz, 1H), 6.44 (s, 1H), 4.20 – 3.99 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.05, 165.83 (d, *J* = 256.6 Hz), 142.89 (d, *J* = 8.2 Hz), 133.18 (d, *J* = 9.5 Hz), 130.80 (d, *J* = 3.1 Hz), 116.40 (d, *J* = 22.0 Hz), 114.20 (d, *J* = 24.1 Hz), 99.86 (d, *J* = 1.4 Hz), 65.50. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -102.69.

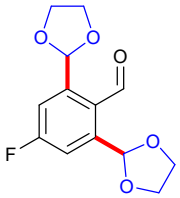
2-(1,3-dioxolan-2-yl)-6-(1,3-dioxolan-4-yl)-4-fluorobenzaldehyde (*2,6-disubstituted*-**4s**-1)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.50 (s, 1H), 7.52 (dd, *J* = 9.8, 2.8 Hz, 1H), 7.39 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.30 (s, 1H), 5.57 (dd, *J* = 7.4, 4.8 Hz, 1H), 5.34 (s, 1H), 5.04 (s, 1H), 4.47 (dd, *J*

= 8.7, 7.4 Hz, 1H), 4.16 – 4.08 (m, 4H), 3.65 (dd, *J* = 8.7, 4.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.92, 165.37 (d, *J* = 256.3 Hz), 148.08 (d, *J* = 8.5 Hz), 144.72 (d, *J* = 8.1 Hz), 127.36, 114.12 (d, *J* = 23.9 Hz), 113.13 (d, *J* = 24.1 Hz), 100.55 (d, *J* = 1.8 Hz), 95.94, 74.76, 72.40, 65.53 (d, *J* = 3.0 Hz). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -101.89.

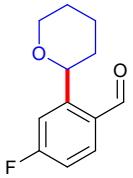
2,6-di(1,3-dioxolan-2-yl)-4-fluorobenzaldehyde (*2,6-disubstituted*-**4s**-2)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.53 (s, 1H), 7.46 (d, *J* = 9.1 Hz, 2H), 6.34 (d, *J* = 0.9 Hz, 2H), 4.11 – 4.05 (m, 8H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.51, 164.45 (d, *J* = 254.9 Hz), 143.19 (d, *J* = 7.8 Hz), 130.11 (d, *J* = 3.4 Hz), 114.61 (d, *J* = 23.6 Hz), 100.09 (d, *J* = 1.5 Hz), 65.43. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -104.10.

4t: *ortho*-**4t** were synthesized via **General Procedure V-2**, affording colorless oils (12 mg, 28%, *para*-**4t**/*ortho*-**4t**/*2,6-disubstituted*-**4t** = 0.00/1.00/0.00).

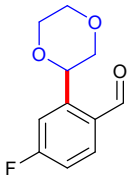
4-fluoro-2-(tetrahydro-2H-pyran-2-yl)benzaldehyde (*ortho*-**4t**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 7.83 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.44 (dd, *J* = 10.3, 2.7 Hz, 1H), 7.09 (td, *J* = 8.2, 2.6 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 4.20 – 4.11 (m, 1H), 3.72 – 3.61 (m, 1H), 1.99 – 1.89 (m, 2H), 1.87 – 1.56 (m, 3H), 1.48 – 1.34 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 191.04, 166.29 (d, *J* = 256.3 Hz), 149.52 (d, *J* = 8.8 Hz), 135.64 (d, *J* = 10.0 Hz), 128.80 (d, *J* = 2.8 Hz), 114.40 (d, *J* = 22.2 Hz), 114.02 (d, *J* = 23.5 Hz), 75.67 (d, *J* = 1.4 Hz), 68.98, 34.20, 25.78, 23.88. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -102.64.

4u: *ortho*-**4u** were synthesized via **General Procedure V-2**, affording colorless oils (11 mg, 23%, *para*-**4u**/*ortho*-**4u**/*2,6-disubstituted*-**4u** = 0.00/1.00/0.00).

2-(1,4-dioxan-2-yl)-4-fluorobenzaldehyde (*ortho*-**4u**)

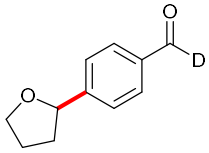


^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 7.84 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.52 (dd, *J* = 10.1, 2.6 Hz, 1H), 7.16 (td, *J* = 8.1, 2.6 Hz, 1H), 5.52 (dd, *J* = 9.5, 2.6 Hz, 1H), 4.06 – 3.88 (m, 3H),

3.88 – 3.80 (m, 1H), 3.80 – 3.67 (m, 1H), 3.27 (dd, *J* = 11.3, 9.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.89, 166.25 (d, *J* = 257.0 Hz), 143.93 (d, *J* = 9.1 Hz), 136.56 (d, *J* = 9.9 Hz), 129.29 (d, *J* = 2.9 Hz), 115.19 (d, *J* = 13.2 Hz), 114.96 (d, *J* = 15.0 Hz), 73.89(d, *J* = 1.13 Hz), 71.84, 67.15, 66.37. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -101.96.

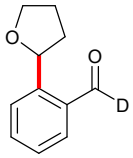
[D]**4a**: **[**D]*para*-**4a**, [D]*ortho*-**4a** and [D]*disubstituted*-**4a** were synthesized via **General Procedure V-2**, affording colorless oils (21 mg, 50%, [D]*para*-**4a**/[D]*ortho*-**4a**/[D]*disubstituted*-**4a** = 0.42/0.30/0.28).

4-(tetrahydrofuran-2-yl)benzaldehyde ([D]*para*-**4a**)



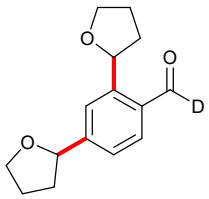
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 0.28H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 4.97 (t, *J* = 7.2 Hz, 1H), 4.17 – 4.07 (m, 1H), 4.03 – 3.93 (m, 1H), 2.46 – 2.33 (m, 1H), 2.09 – 1.97 (m, 2H), 1.83 – 1.72 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.04, 150.87, 135.46, 129.91, 126.04, 80.14, 68.96, 34.77, 25.99.

2-(tetrahydrofuran-2-yl)benzaldehyde ([D]*ortho*-**4a**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.18 (s, 0.16H), δ 7.82 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.59 (td, *J* = 7.6, 1.5 Hz, 1H), 7.44 (td, *J* = 7.5, 1.3 Hz, 1H), 5.68 (t, *J* = 7.0 Hz, 1H), 4.22 – 4.12 (m, 1H), 4.03 – 3.93 (m, 1H), 2.65 – 2.52 (m, 1H), 2.10 – 1.89 (m, 2H), 1.67 – 1.59 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.86, 146.46, 134.01, 133.62, 132.47, 127.18, 125.78, 77.54, 69.05, 34.54, 25.92.

2,4-bis(tetrahydrofuran-2-yl)benzaldehyde ([D]2,4-*disubstituted*-**4a**)



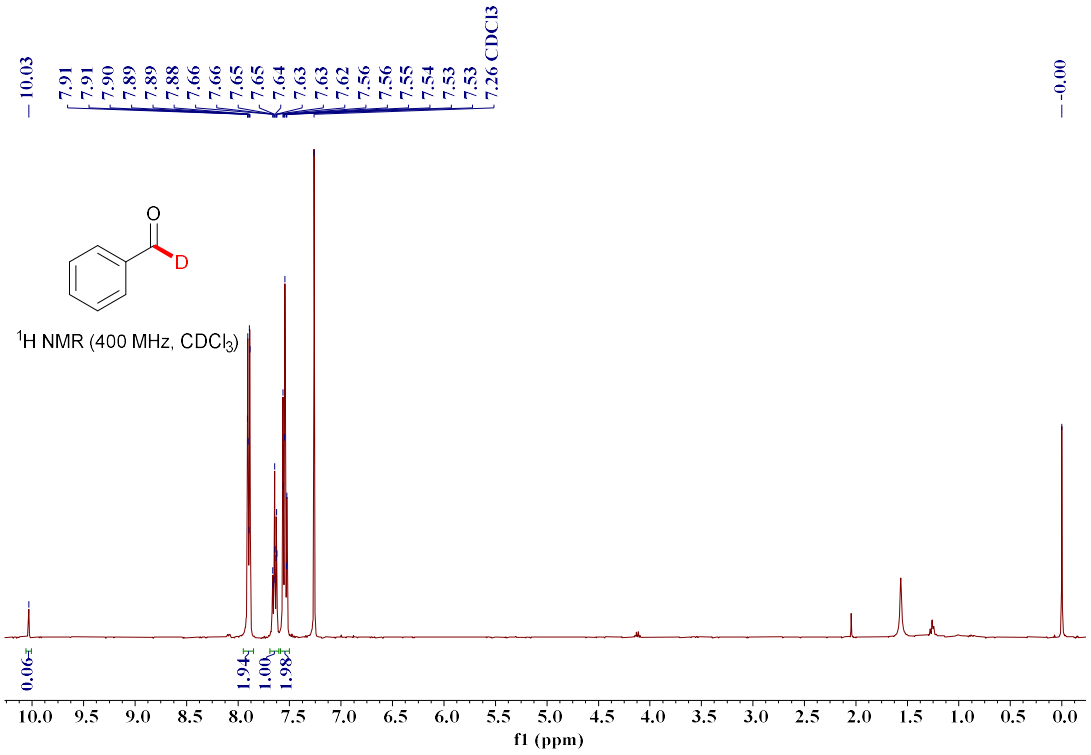
^{1}H NMR (400 MHz, Chloroform-*d*)) δ 10.14 (d, *J* = 1.2 Hz, 0.24H), 7.81 – 7.75 (m, 1H), 7.68 (s, 1H), 7.62 (s, 0H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.38 (m, 1H), 5.66 (t, *J* = 7.1 Hz, 1H), 4.96 (td, *J* = 7.2, 3.5 Hz, 1H), 4.21 – 4.08 (m, 2H), 4.00 – 3.93 (m, 3H), 2.62 – 2.53 (m, 1H), 2.43 – 2.32 (m, 2H), 2.07 – 1.89 (m, 6H), 1.83 – 1.74 (m, 1H), 1.66 – 1.57 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.40, 150.38, 150.29, 146.52, 146.41, 134.15, 134.01, 131.50, 131.47, 124.16, 123.89, 123.15, 122.59, 80.37, 80.30, 77.66, 77.63, 68.98, 68.95, 34.76, 34.65, 34.48, 34.45, 25.99,

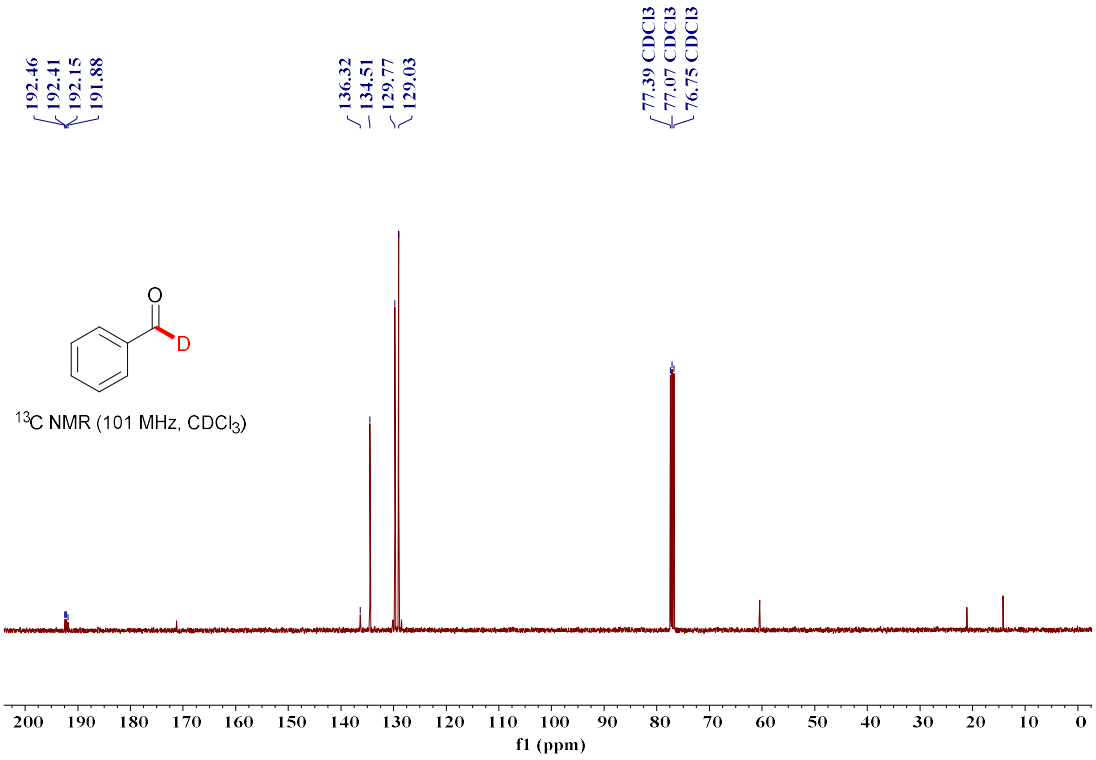
25.93, 25.91.

IX、 Copies of NMR Spectra for the Products

1. Copies of NMR Spectra of the Partial substrates

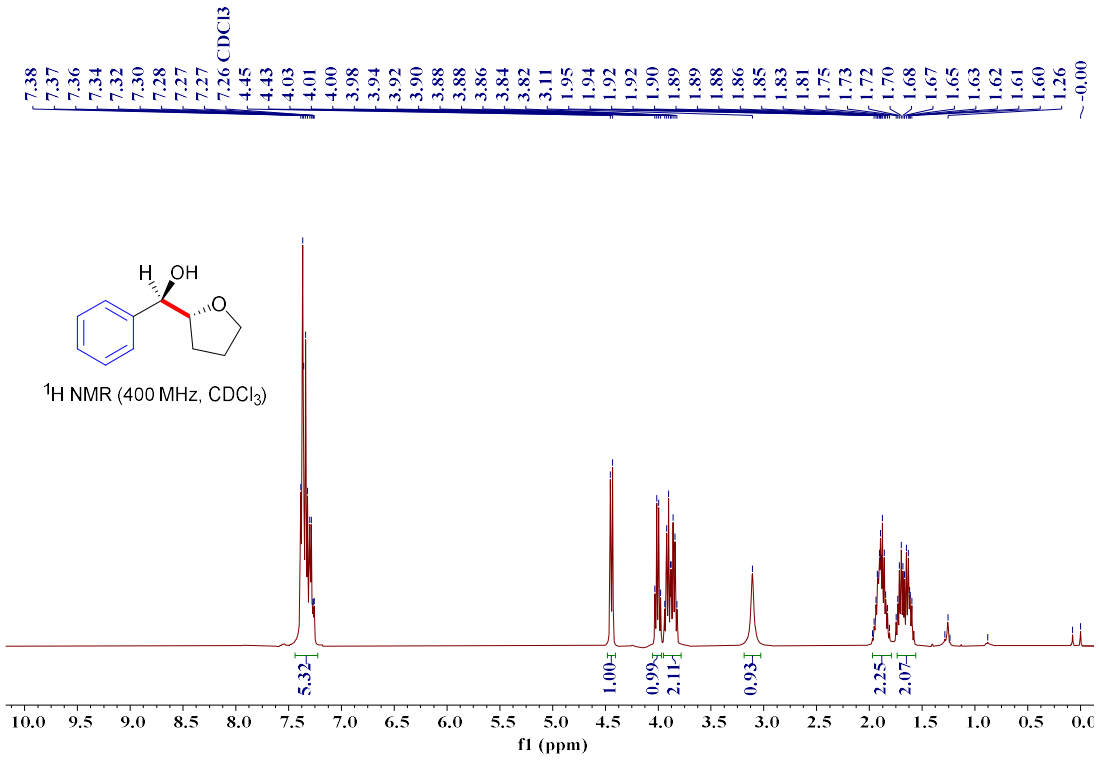
^{1}H and ^{13}C NMR spectra of compound Deuterated benzaldehyde ([D]1a)

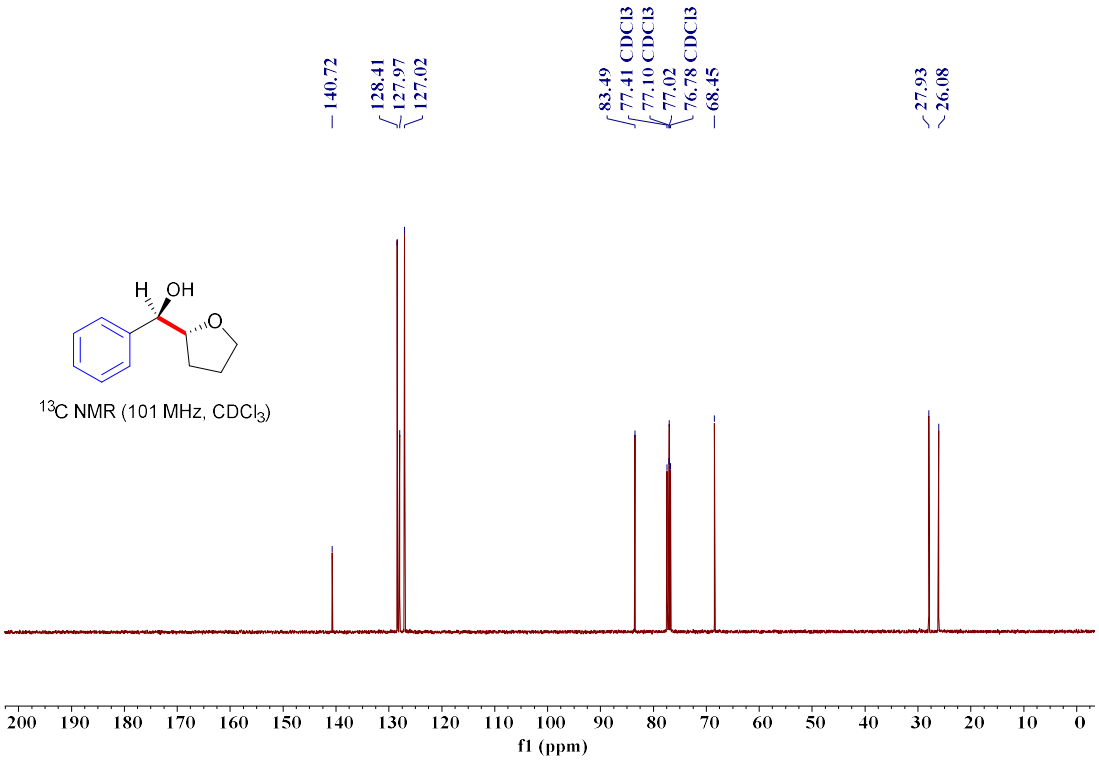




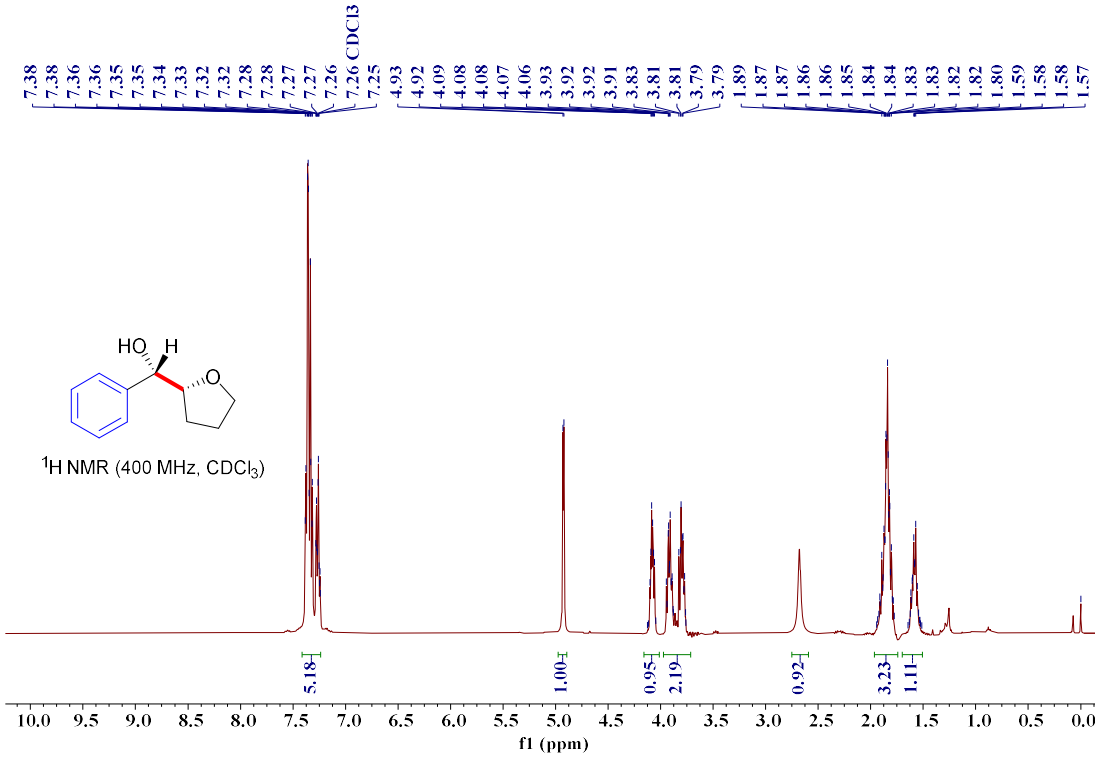
2. Copies of NMR Spectra of the α- Hydroxyarylation Products

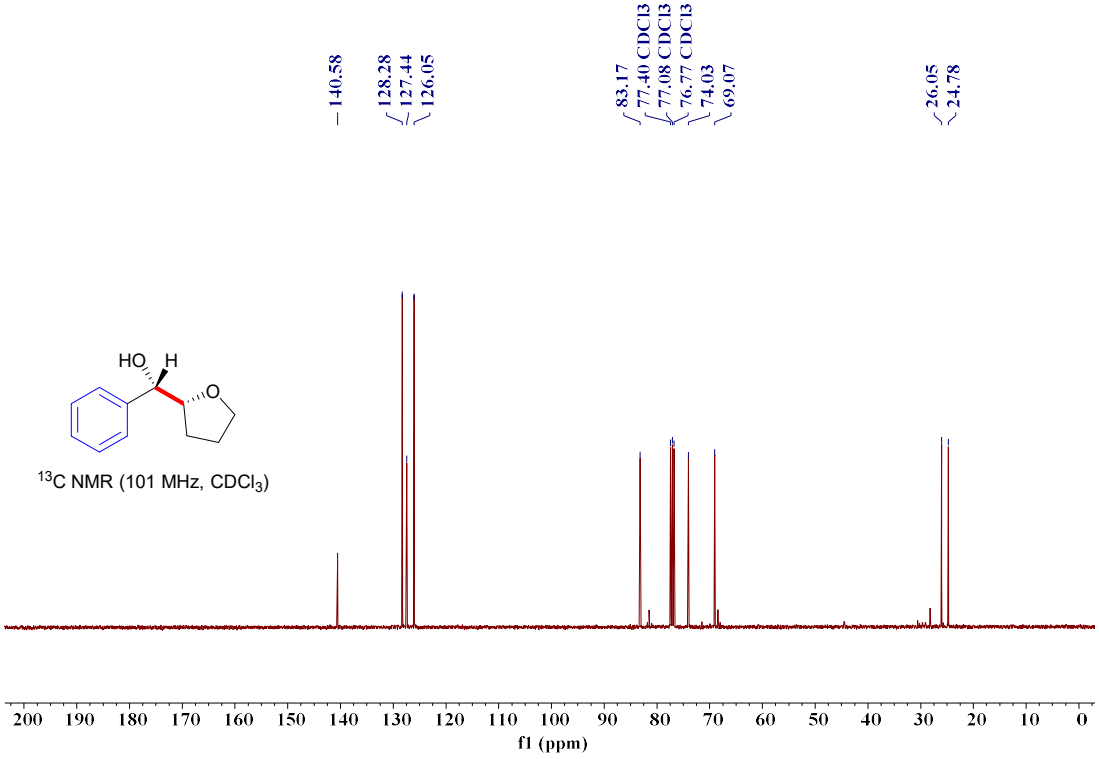
^{1}H and ^{13}C NMR spectra of compound *threo*-3a



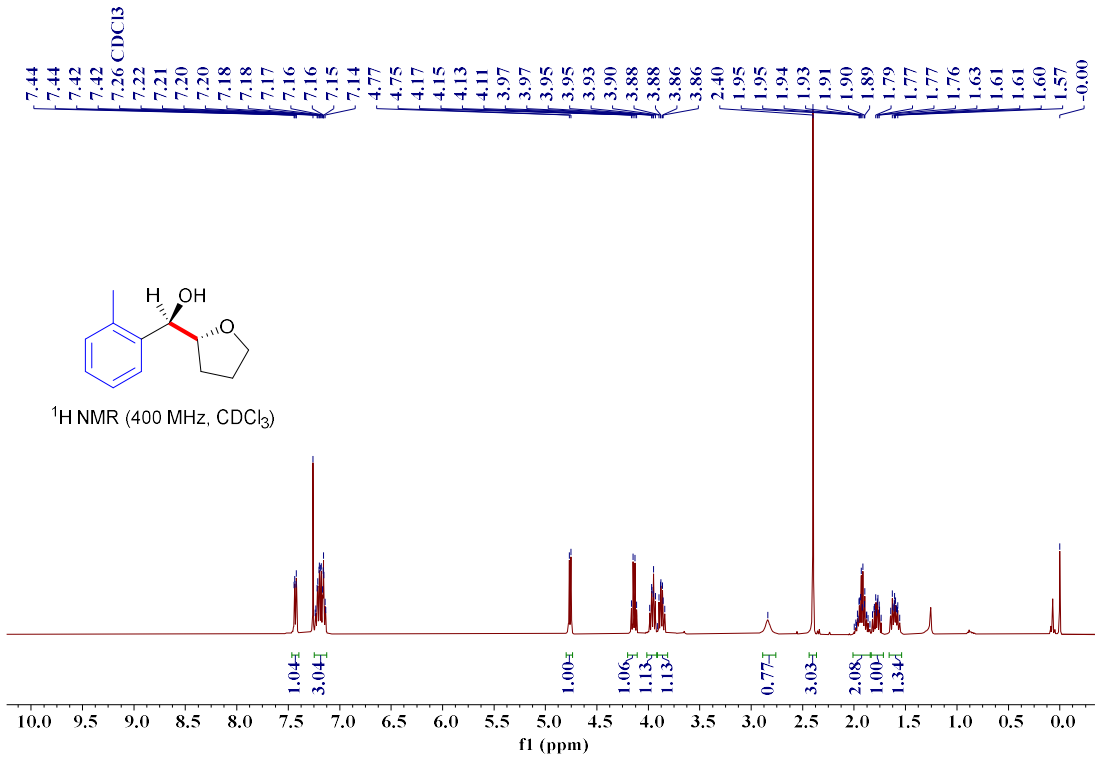


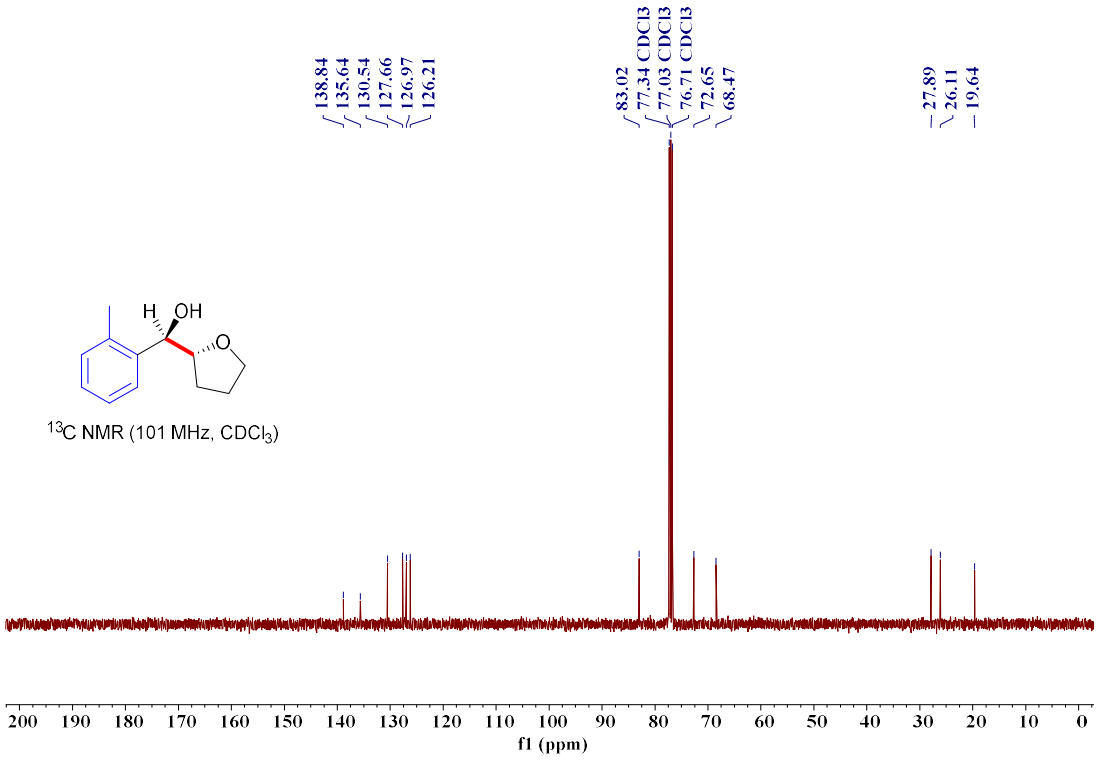
^{1}H and ^{13}C NMR spectra of compound *erythro*-3a



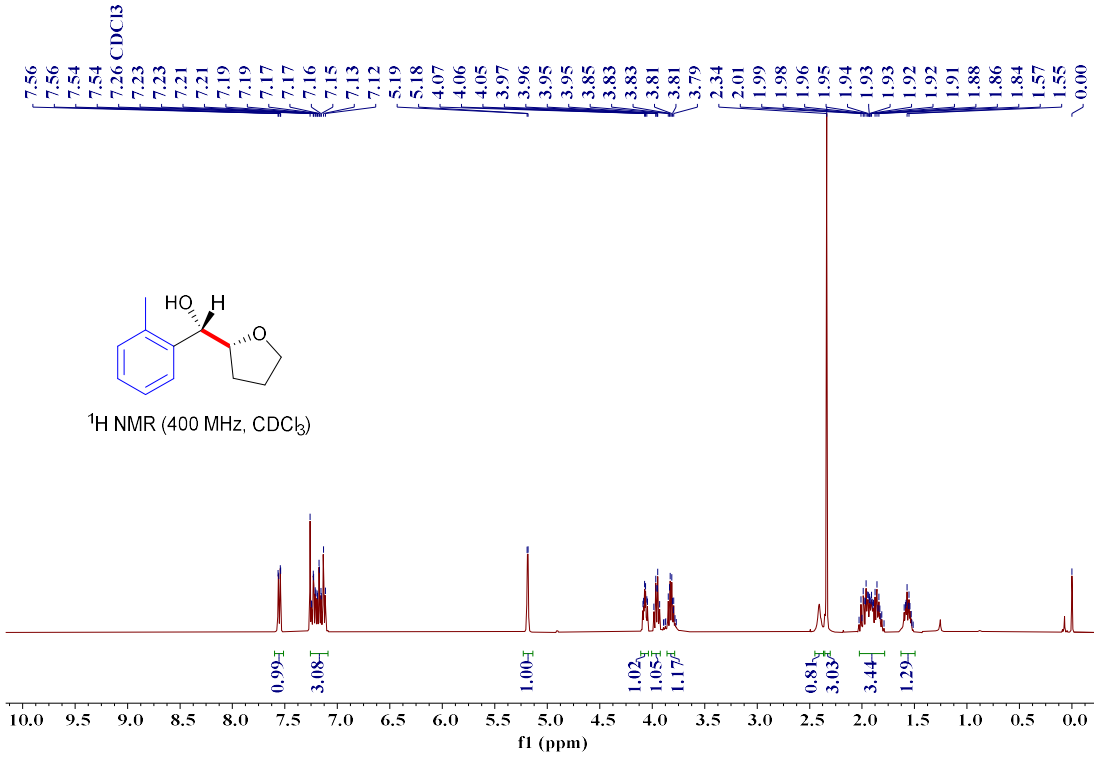


^{1}H and ^{13}C NMR spectra of compound *threo*-3b

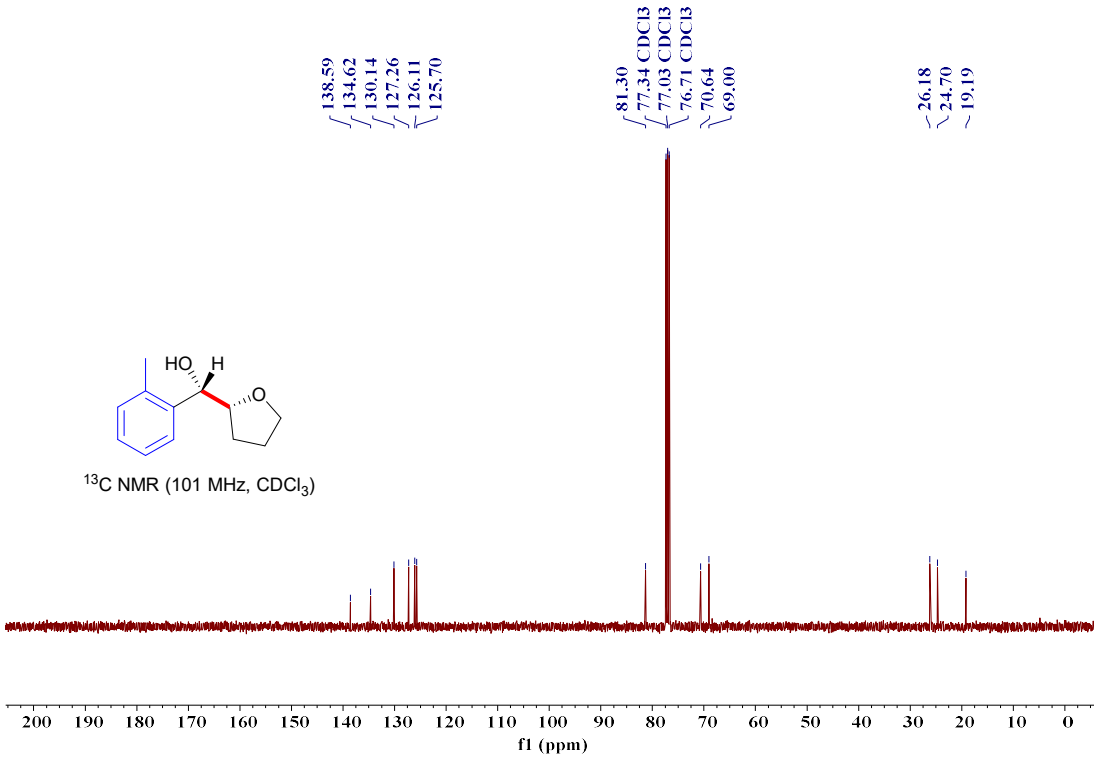




^{1}H and ^{13}C NMR spectra of compound *erythro*-3b

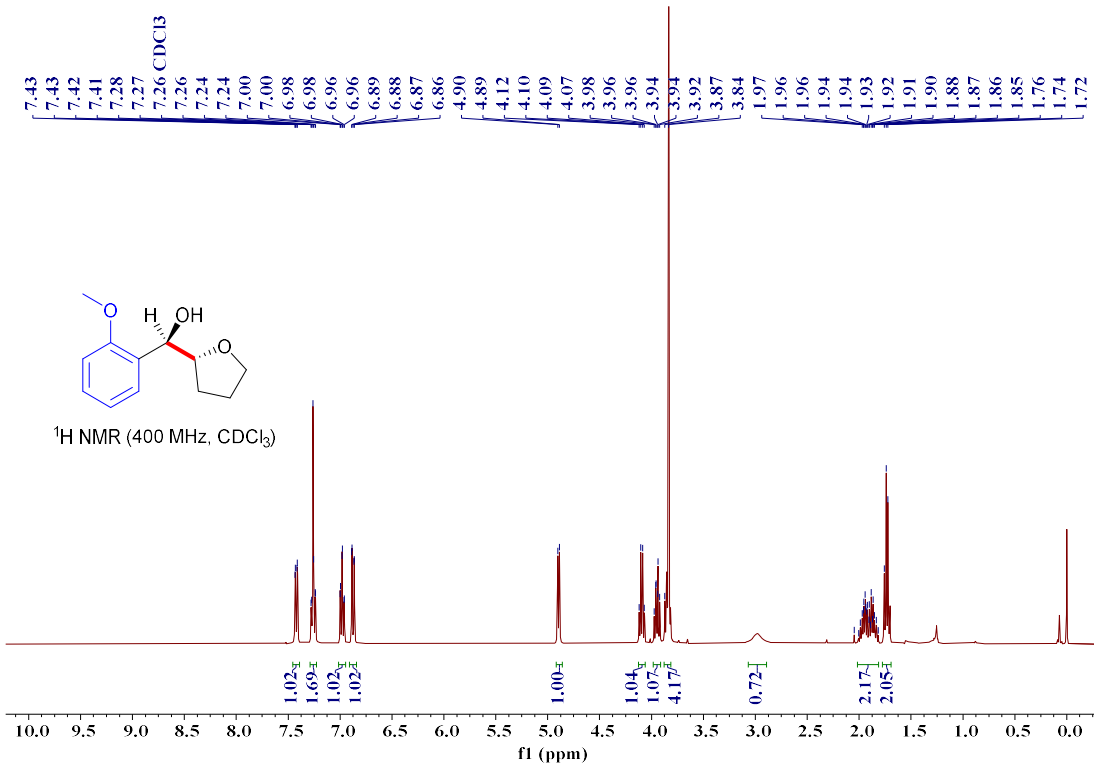


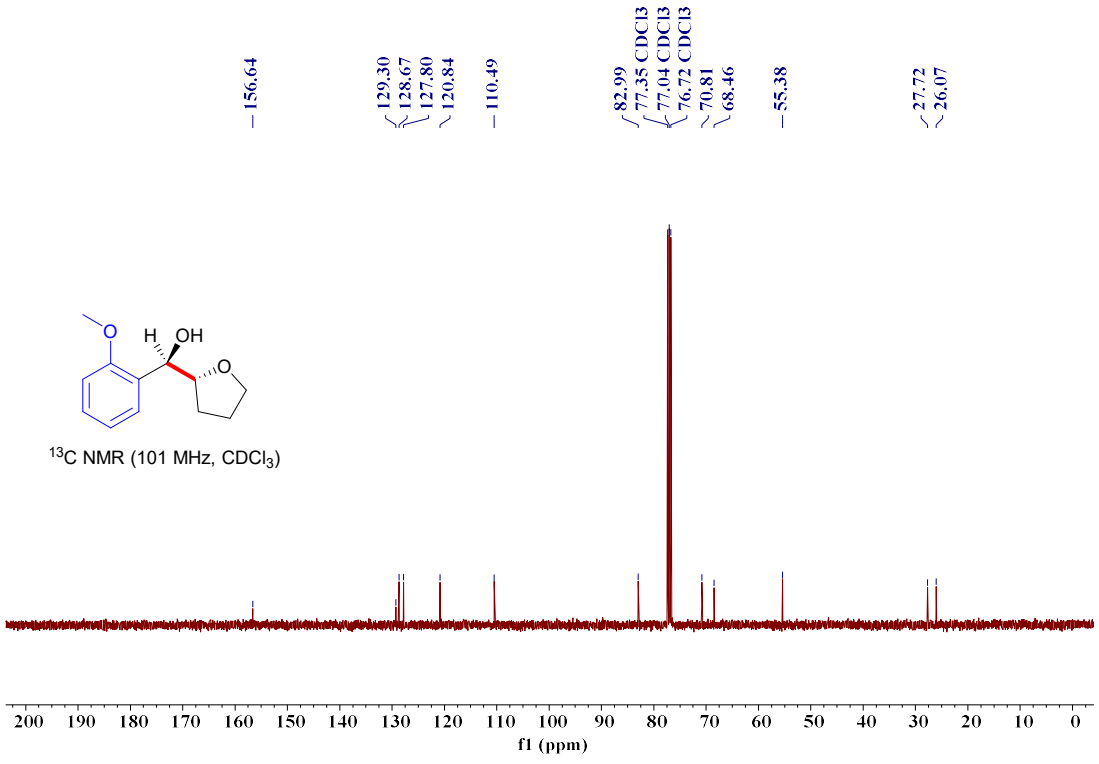
^{1}H NMR (400 MHz, $CDCl_3$)



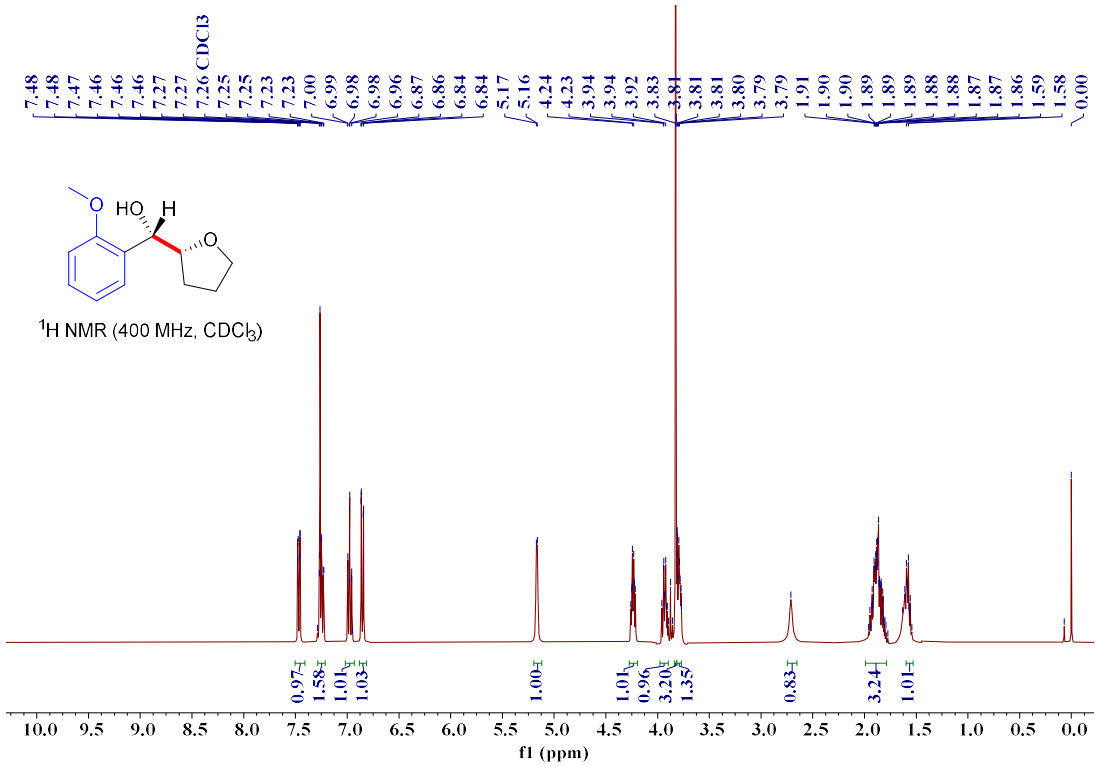
^{13}C NMR (101 MHz, $CDCl_3$)

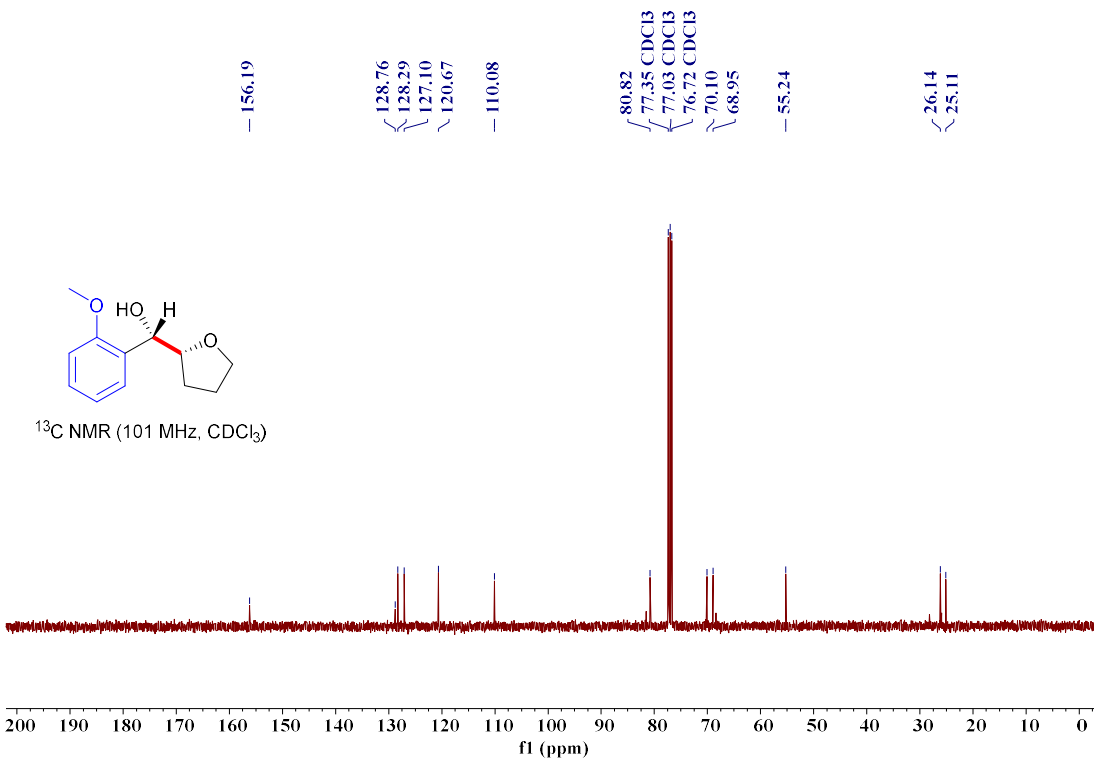
^{1}H and ^{13}C NMR spectra of compound *threo*-3c



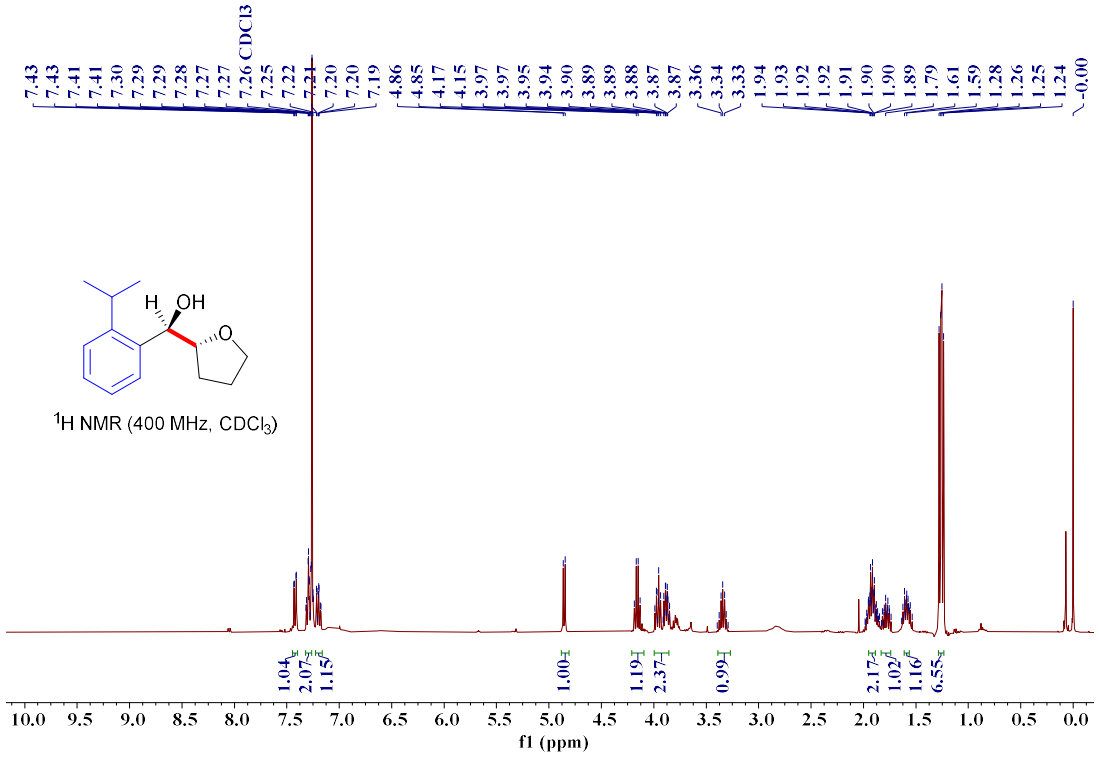


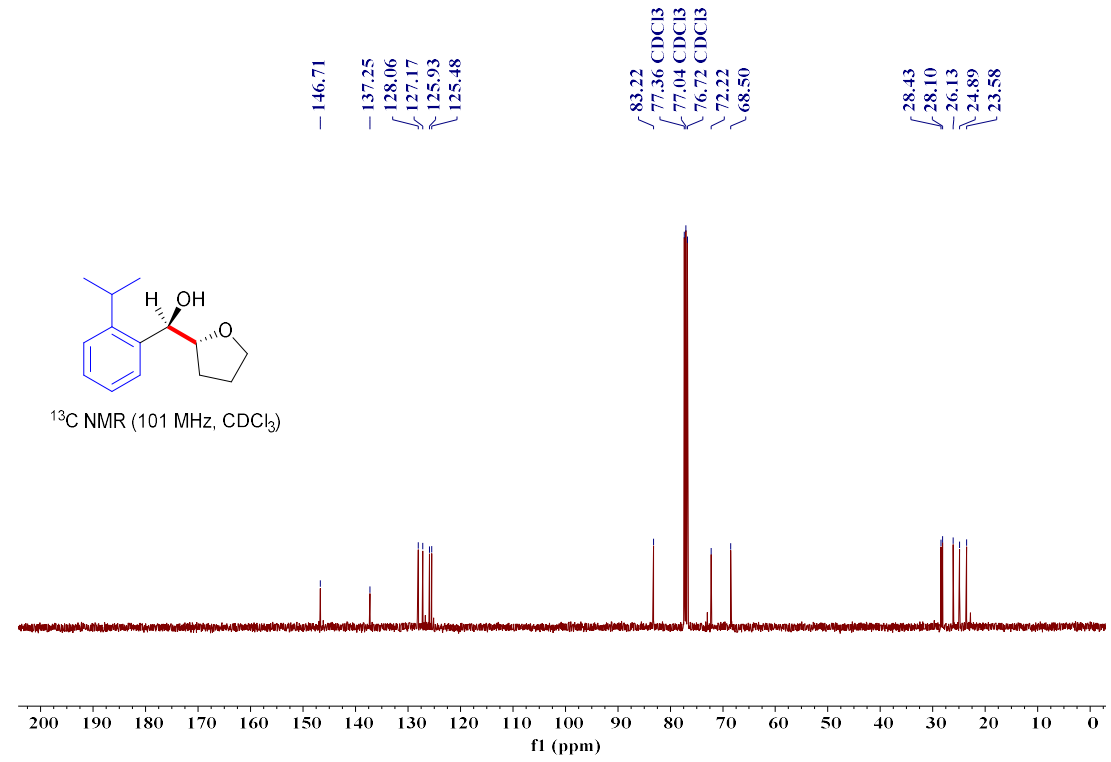
^{1}H and ^{13}C NMR spectra of compound *erythro*-3c



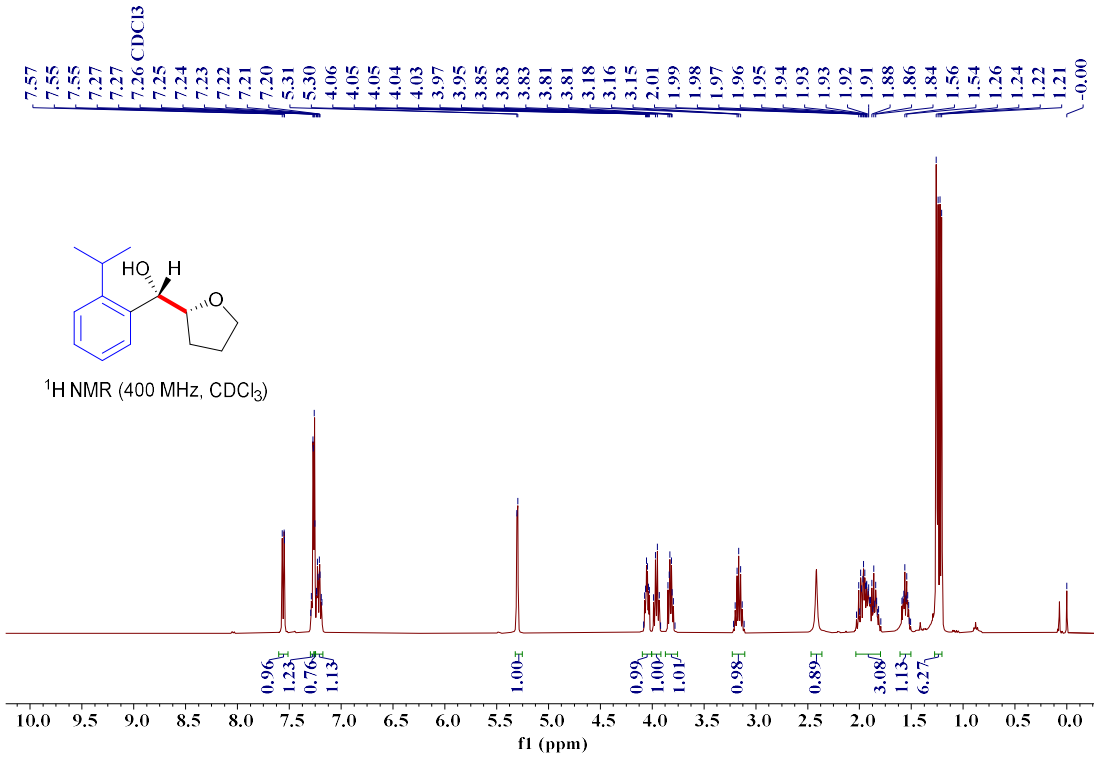


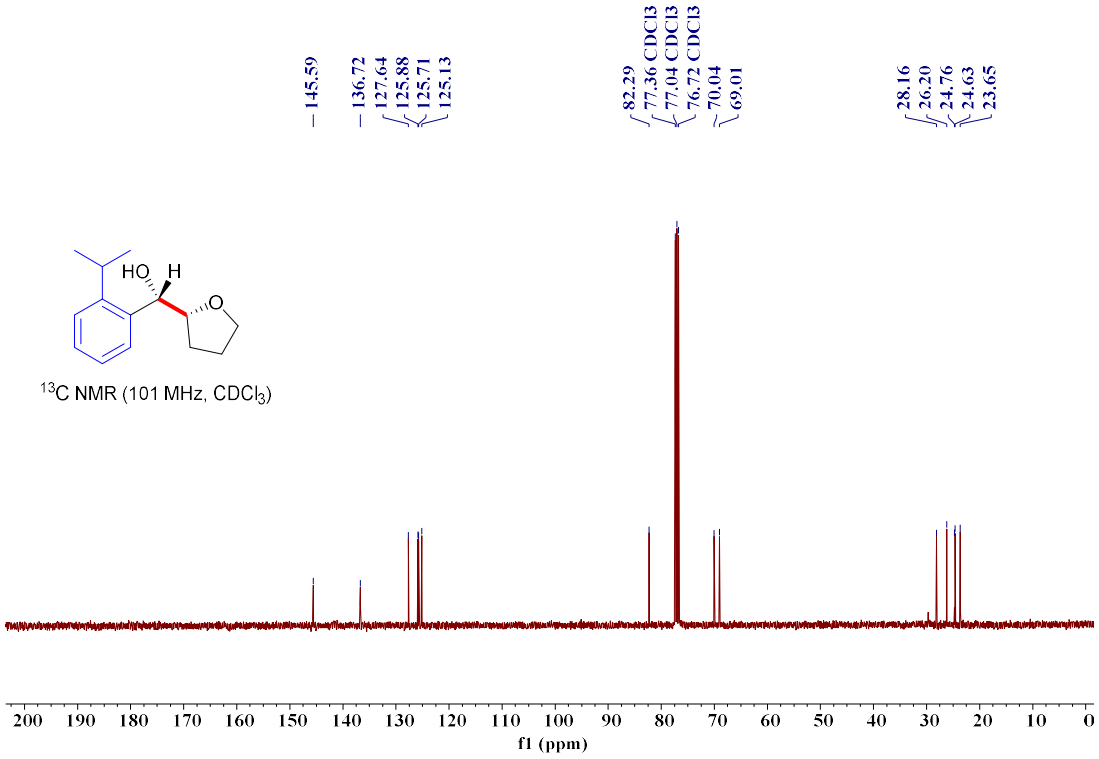
^{1}H and ^{13}C NMR spectra of compound *threo*-3d



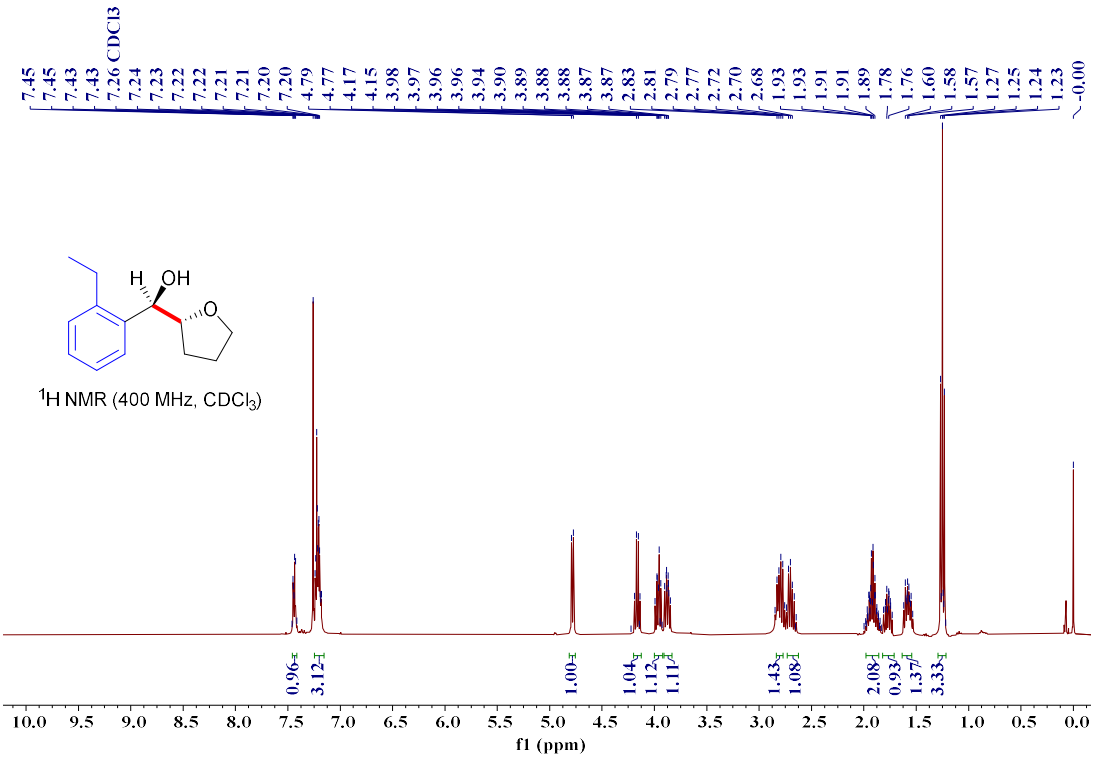


^{1}H and ^{13}C NMR spectra of compound *erythro*-3d

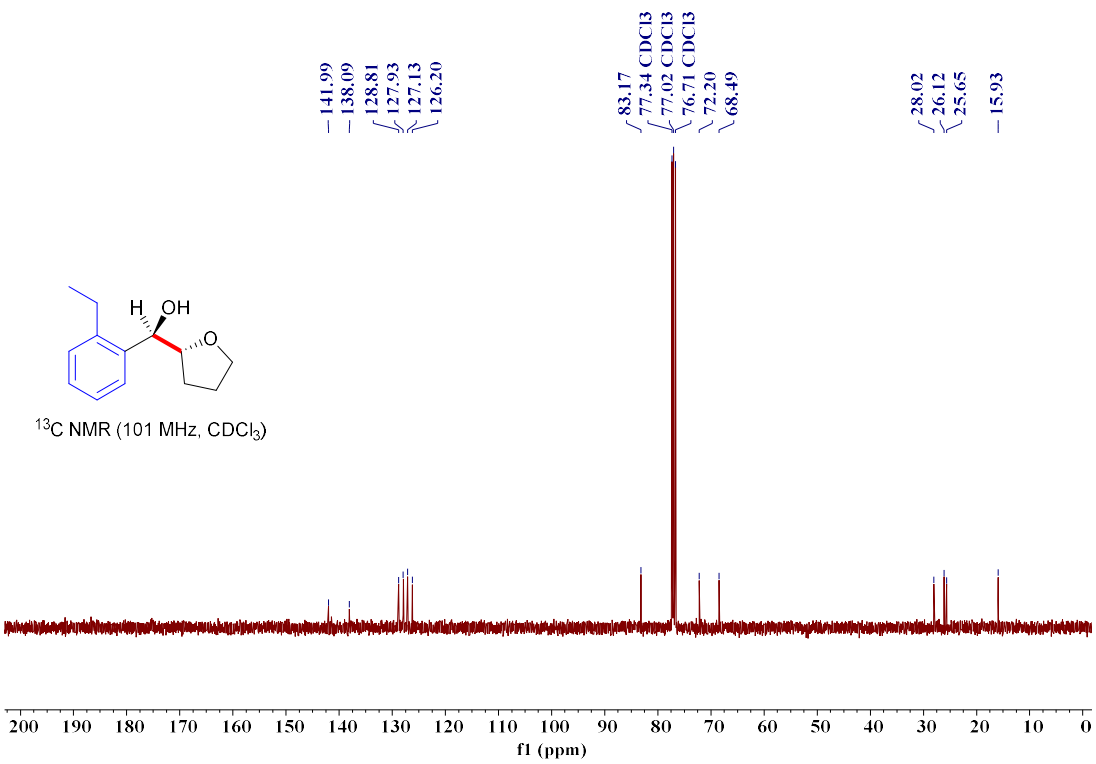




^{1}H and ^{13}C NMR spectra of compound *threo*-3e

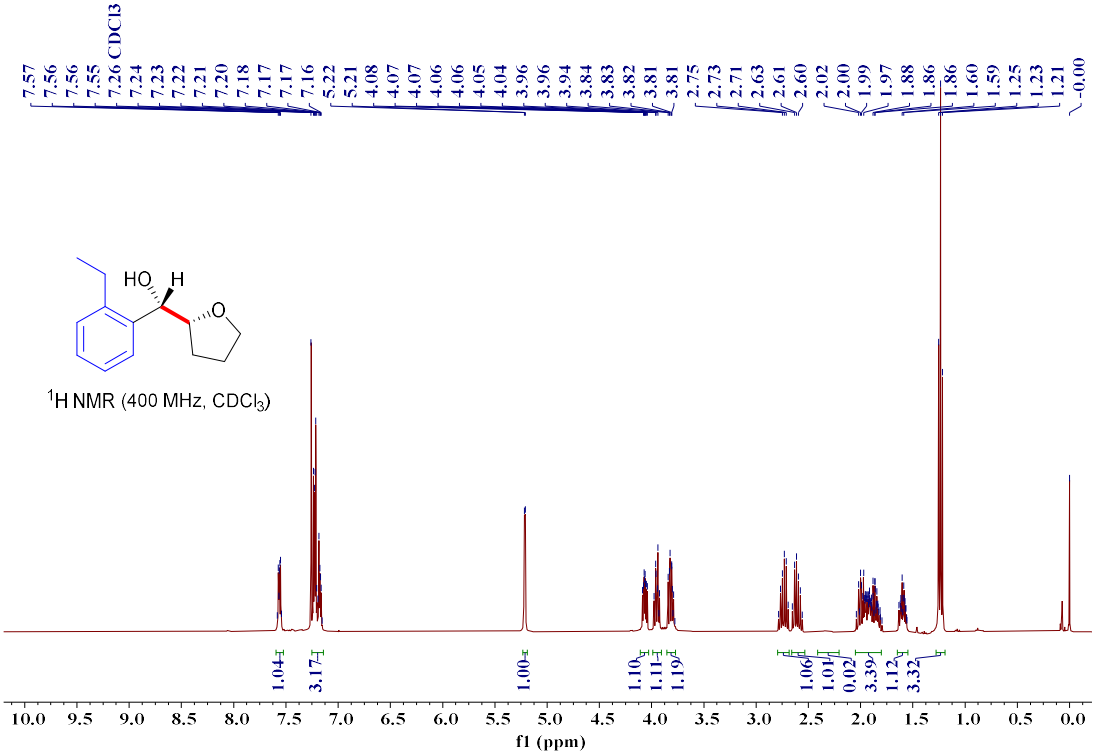


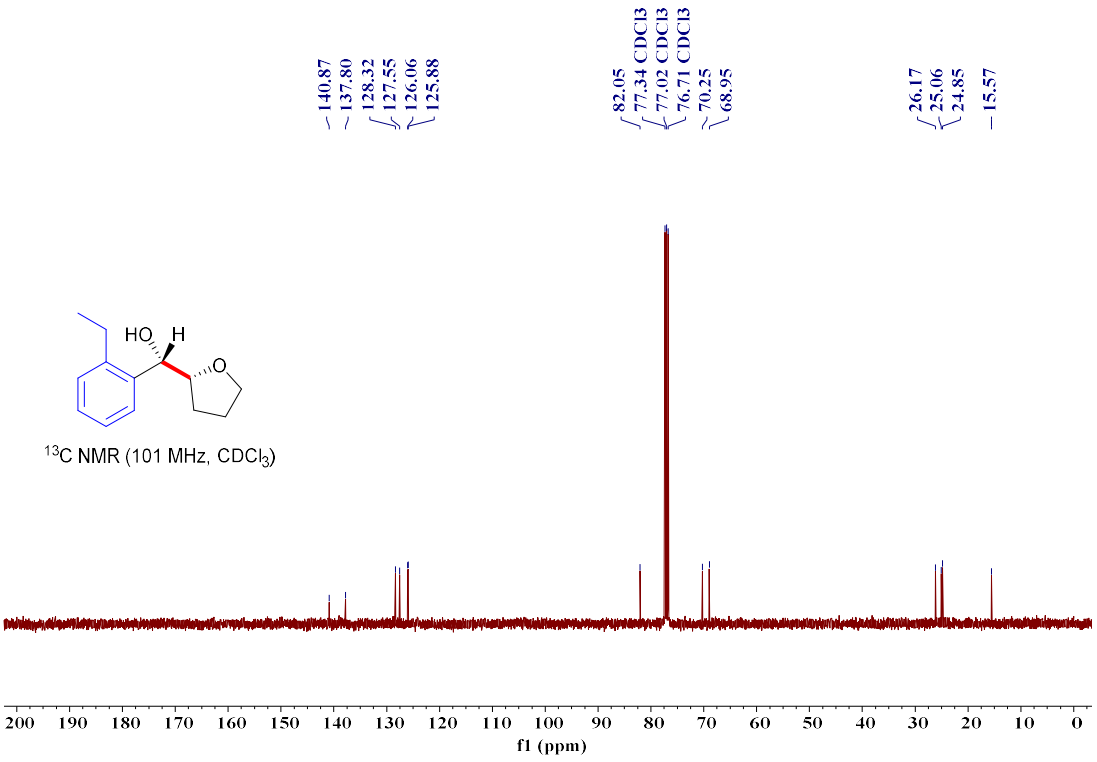
^{1}H NMR (400 MHz, $CDCl_3$)



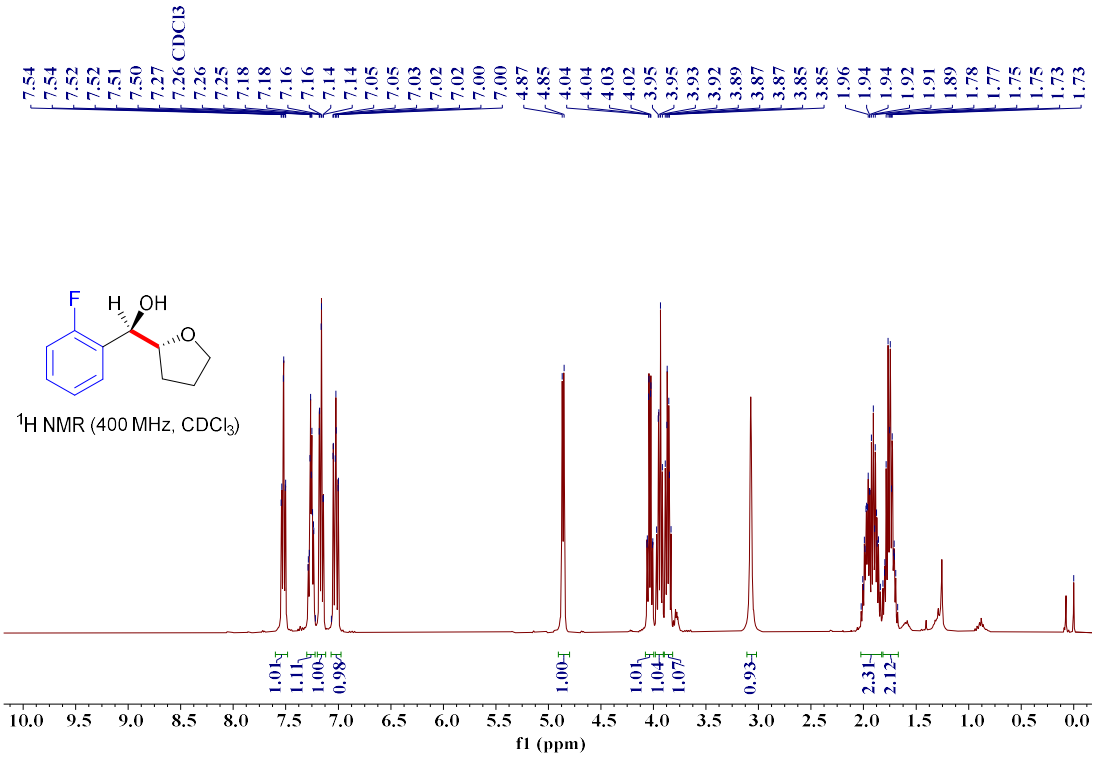
^{13}C NMR (101 MHz, $CDCl_3$)

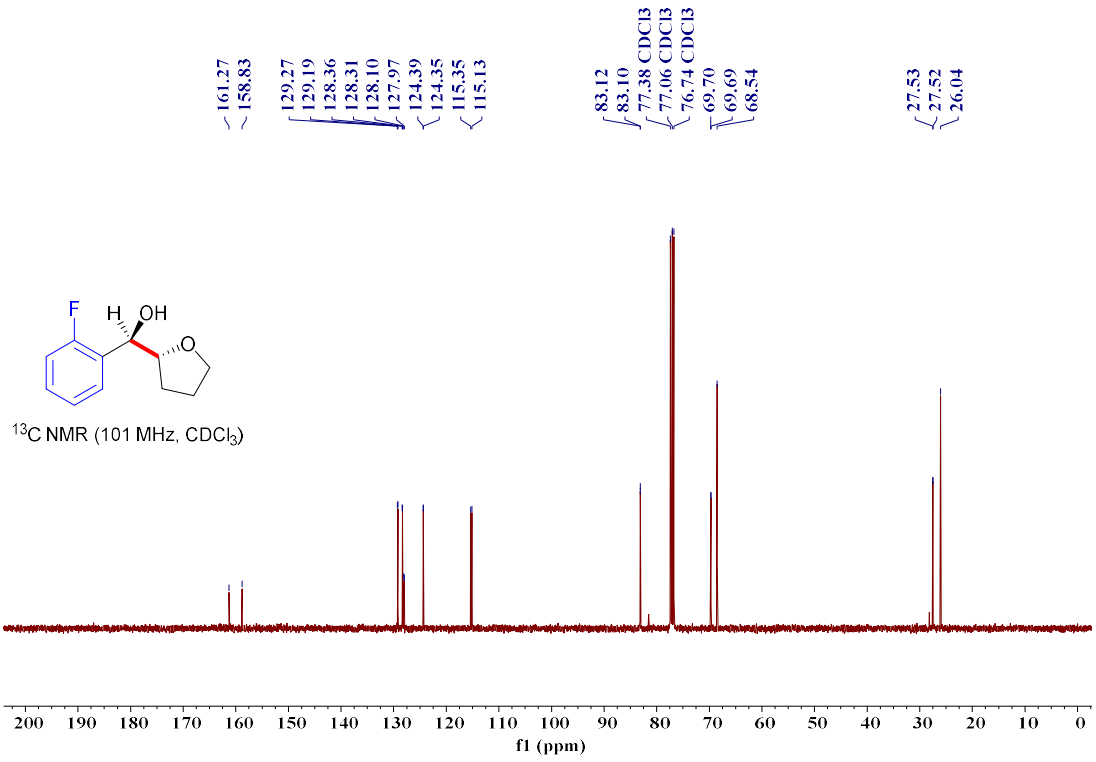
^{1}H and ^{13}C NMR spectra of compound *erythro*-3e

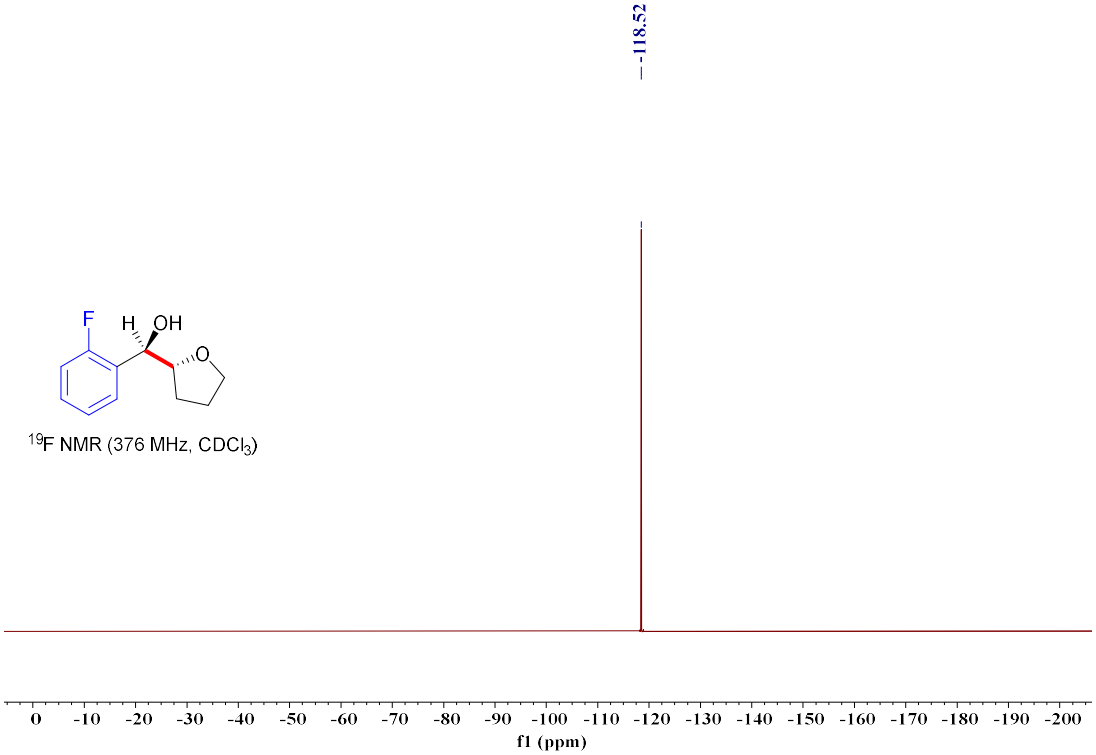




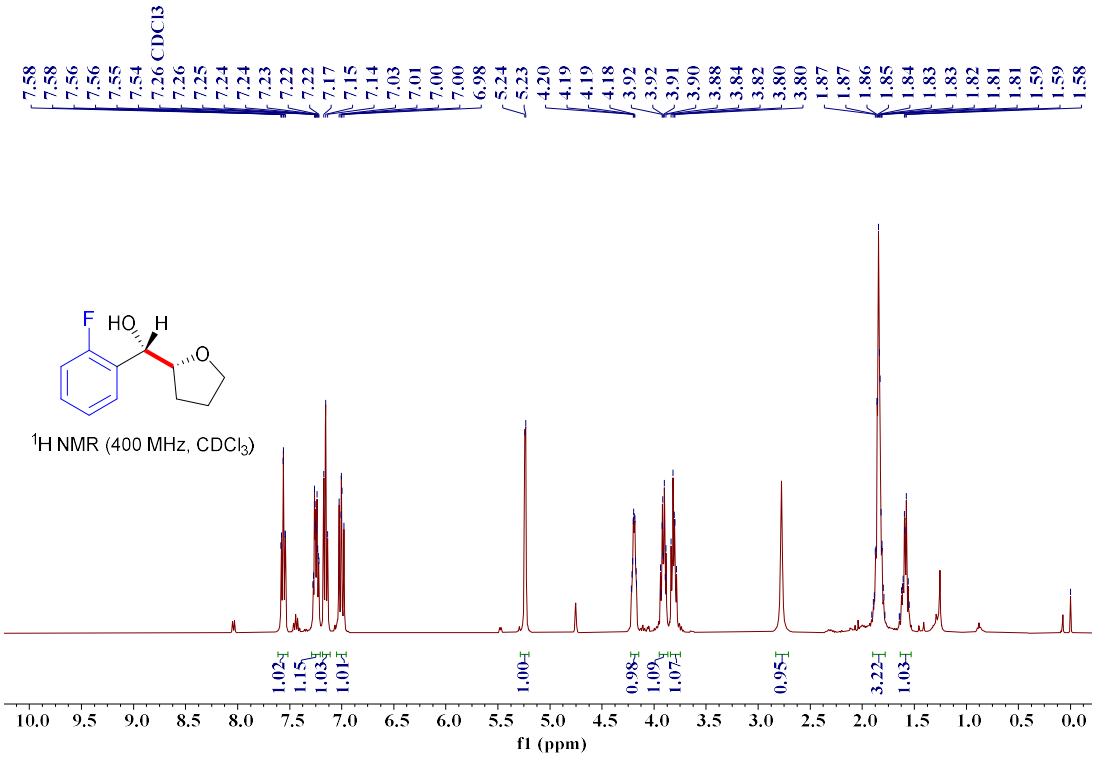
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *threo*-3f

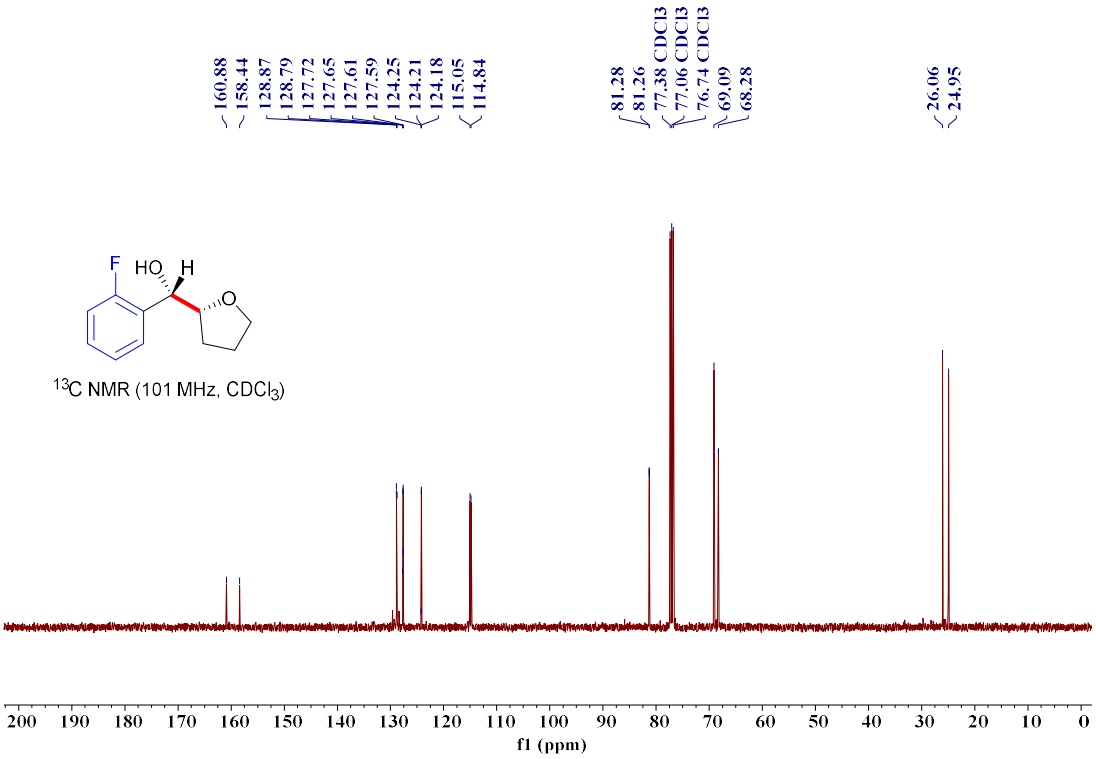




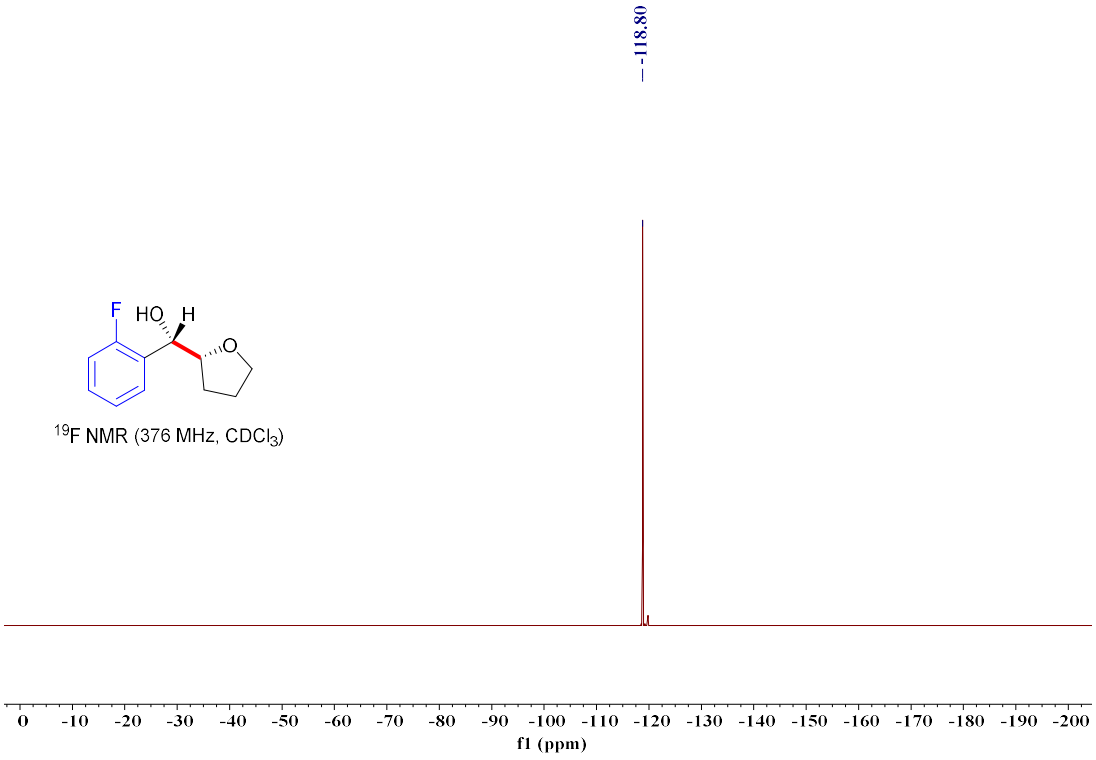


^{1}H, ^{13}C and ^{19}F NMR spectra of compound *erythro*-3f



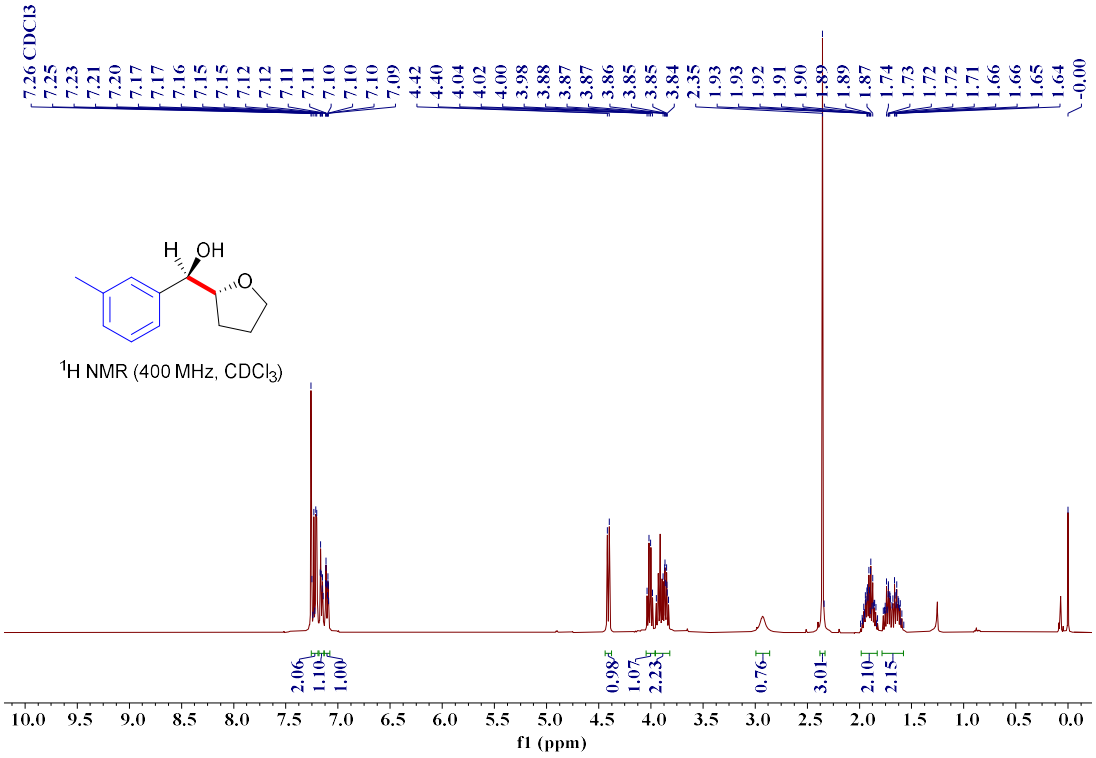


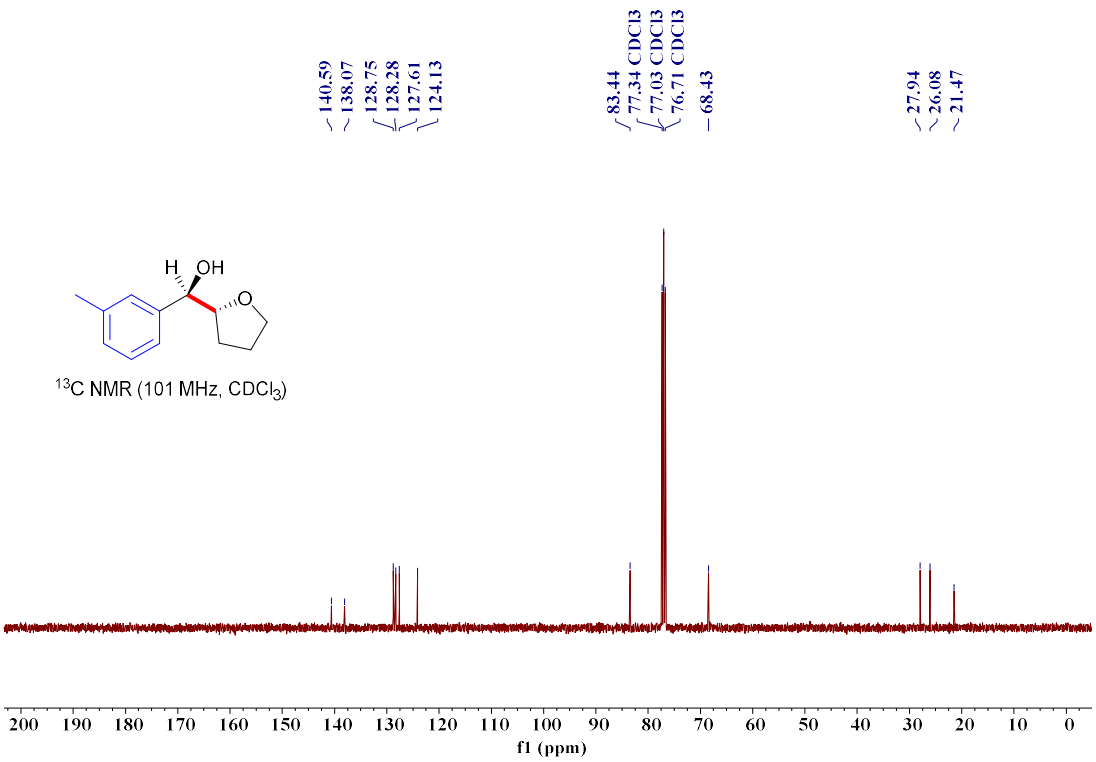
^{13}C NMR (101 MHz, $CDCl_3$)



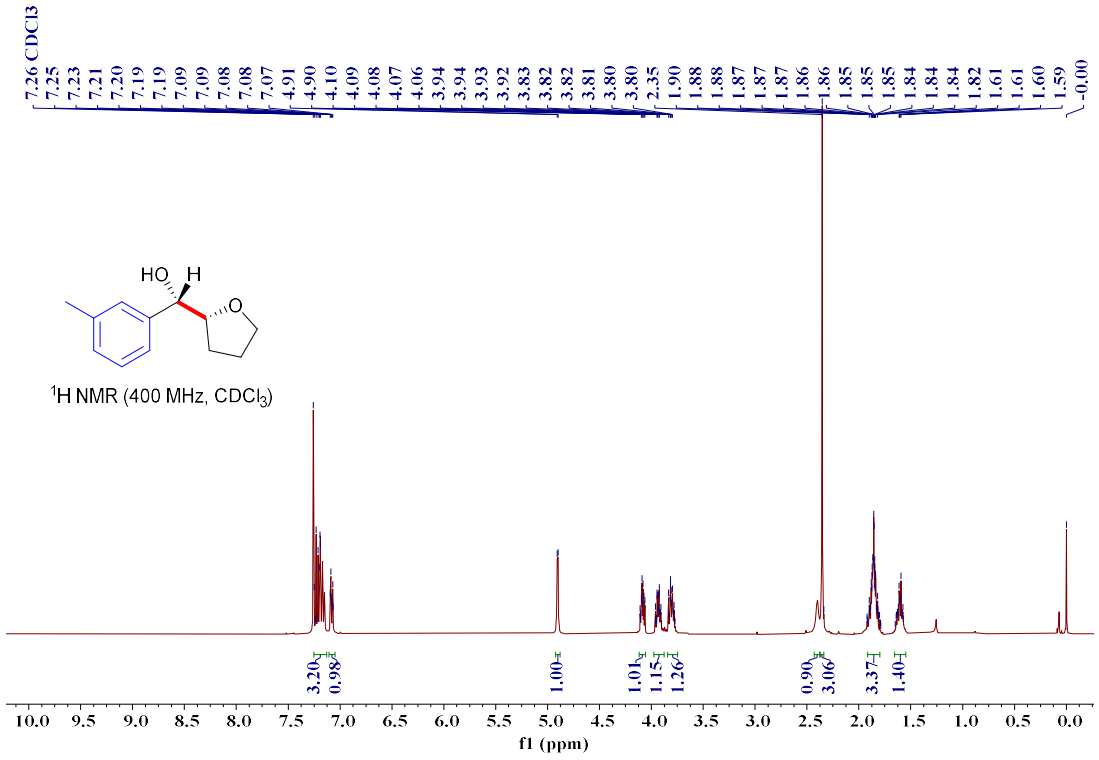
^{19}F NMR (376 MHz, $CDCl_3$)

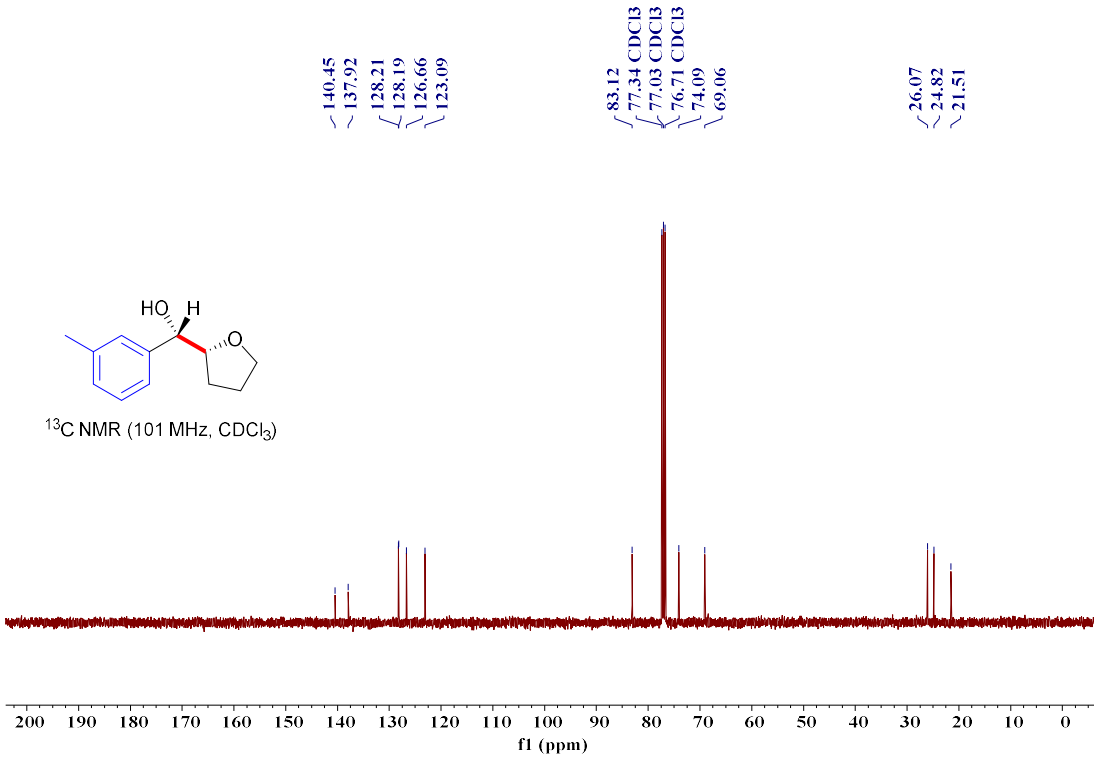
^{1}H and ^{13}C NMR spectra of compound *threo*-3g



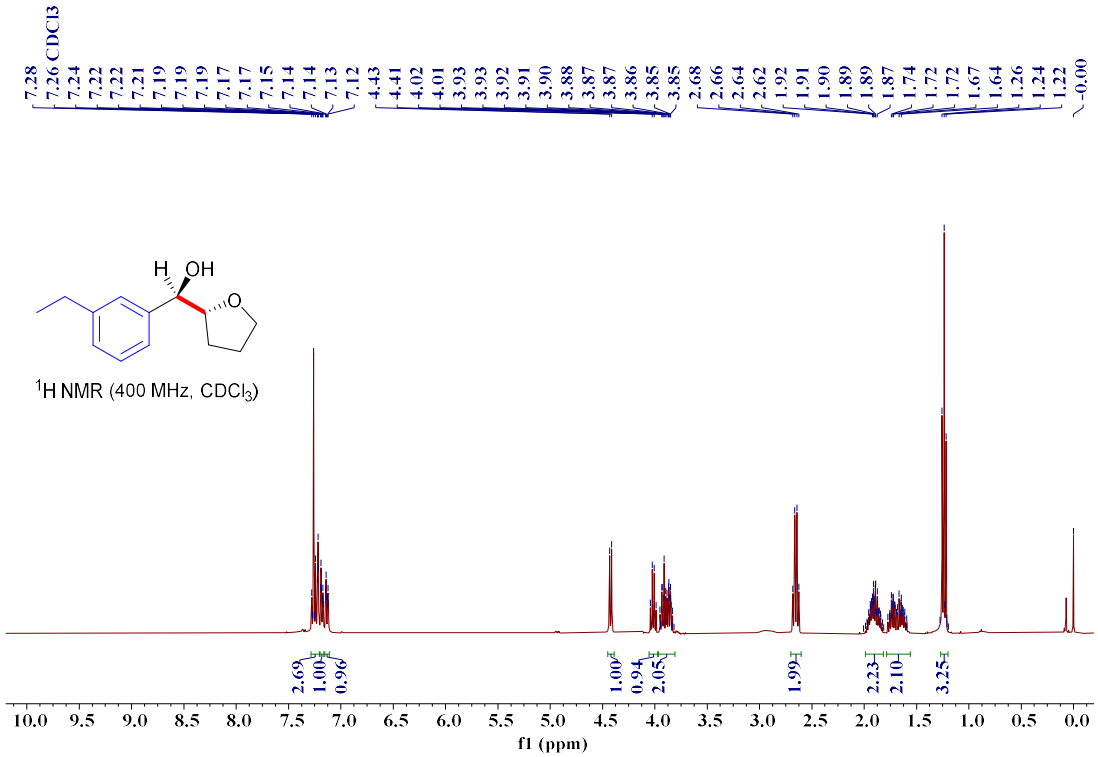


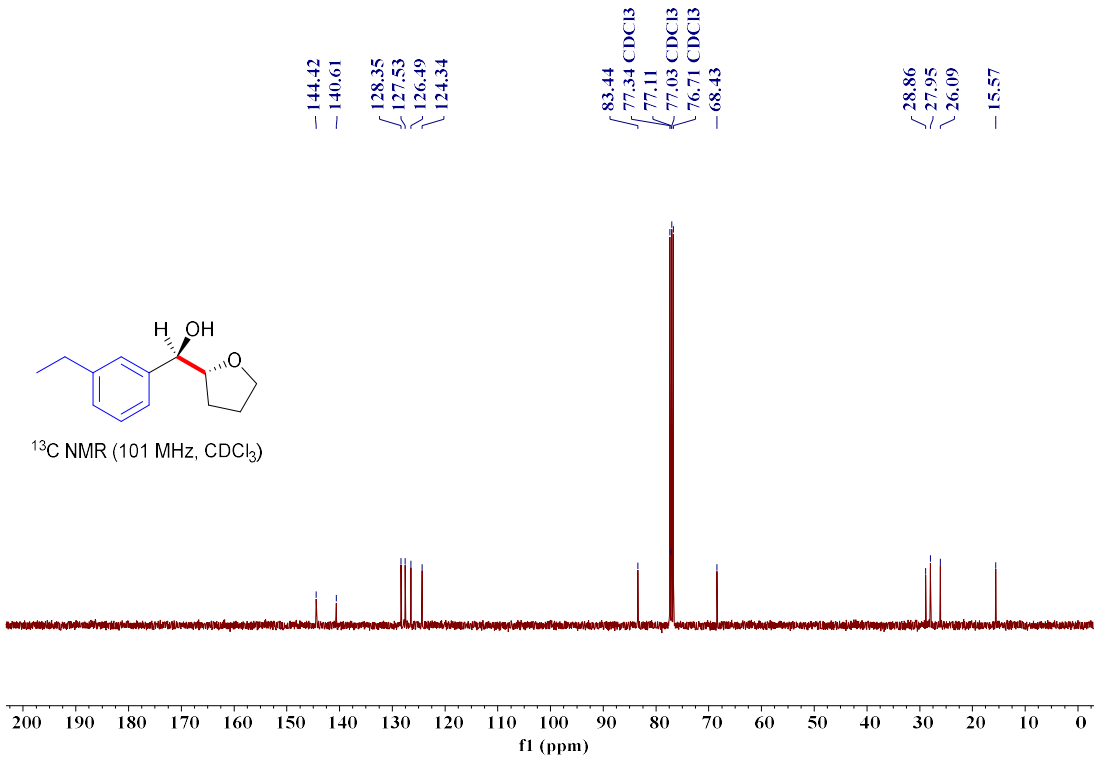
^{1}H and ^{13}C NMR spectra of compound *erythro*-3g



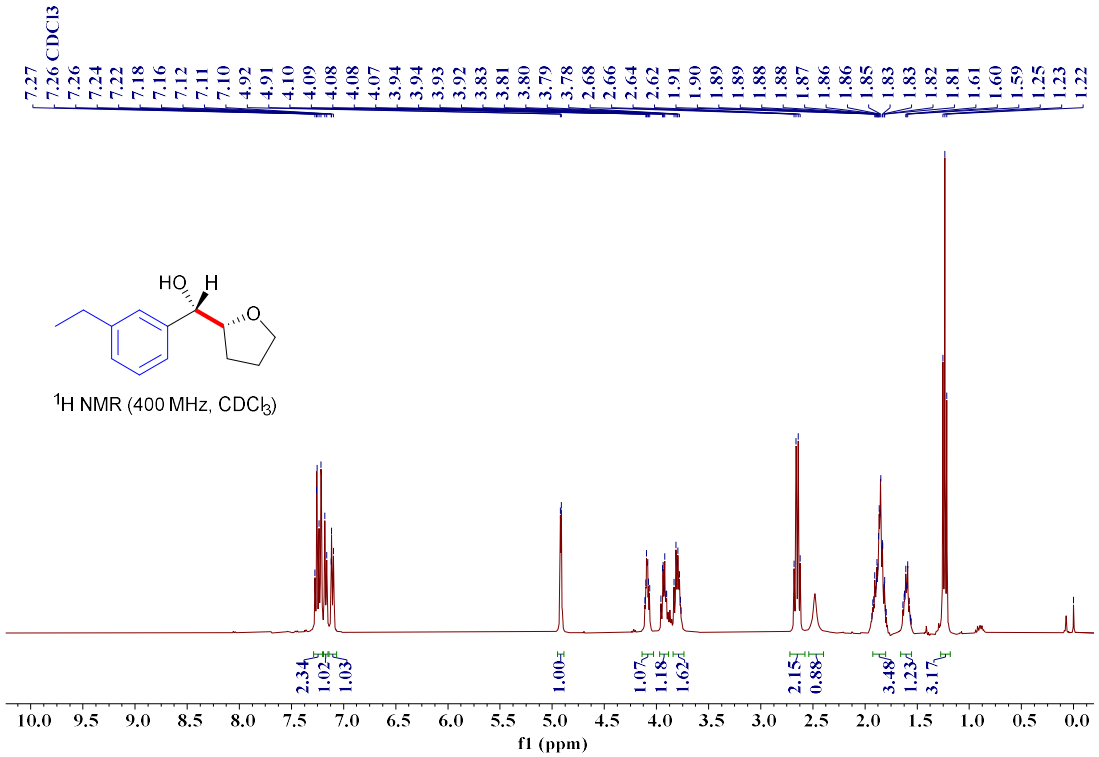


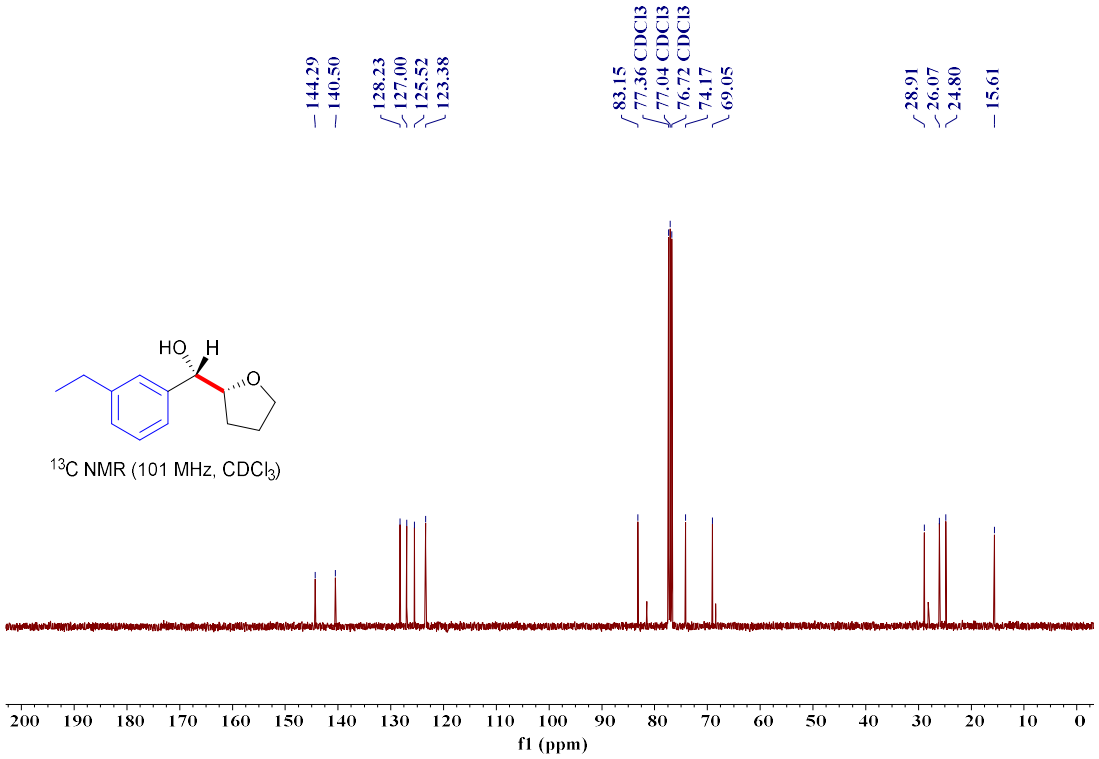
^{1}H and ^{13}C NMR spectra of compound *threo*-3h



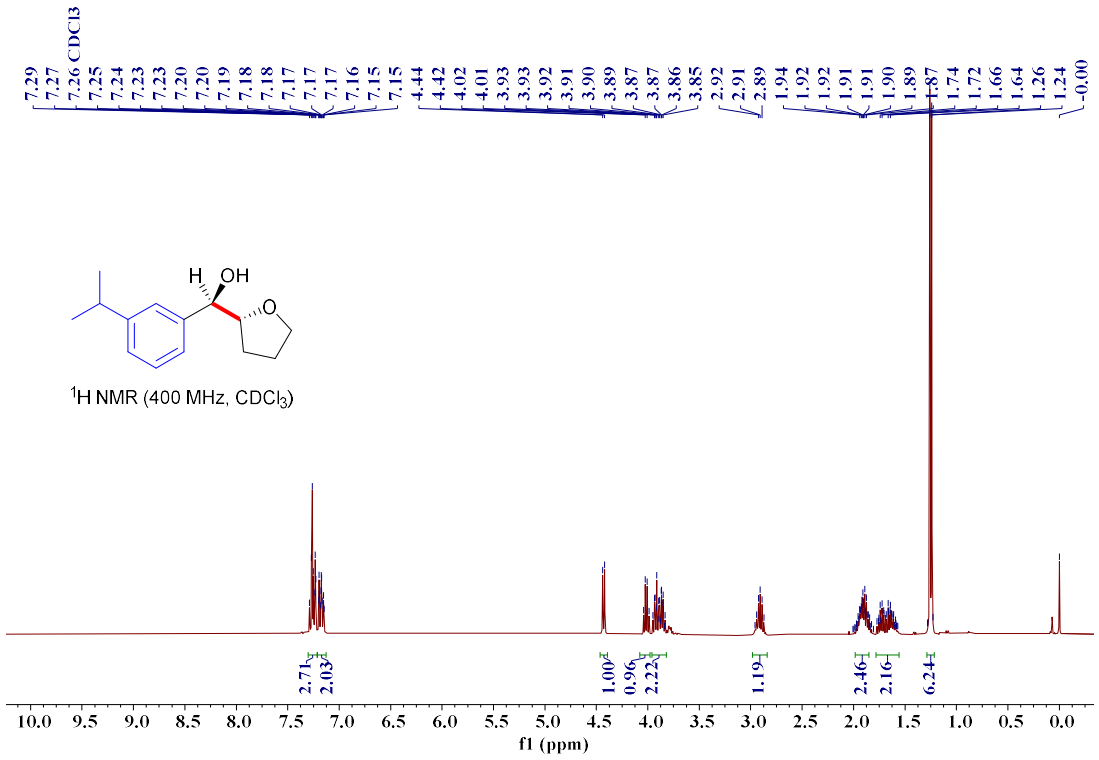


^{1}H and ^{13}C NMR spectra of compound *erythro*-3h

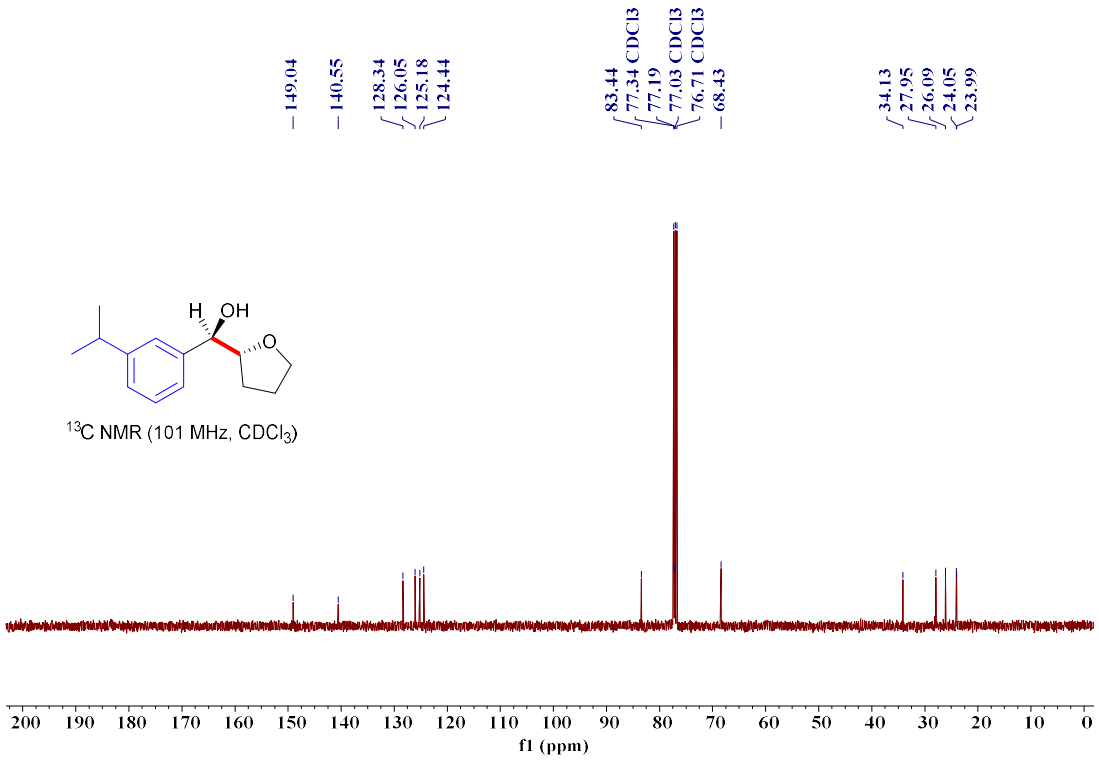




^{1}H and ^{13}C NMR spectra of compound *threo*-3i

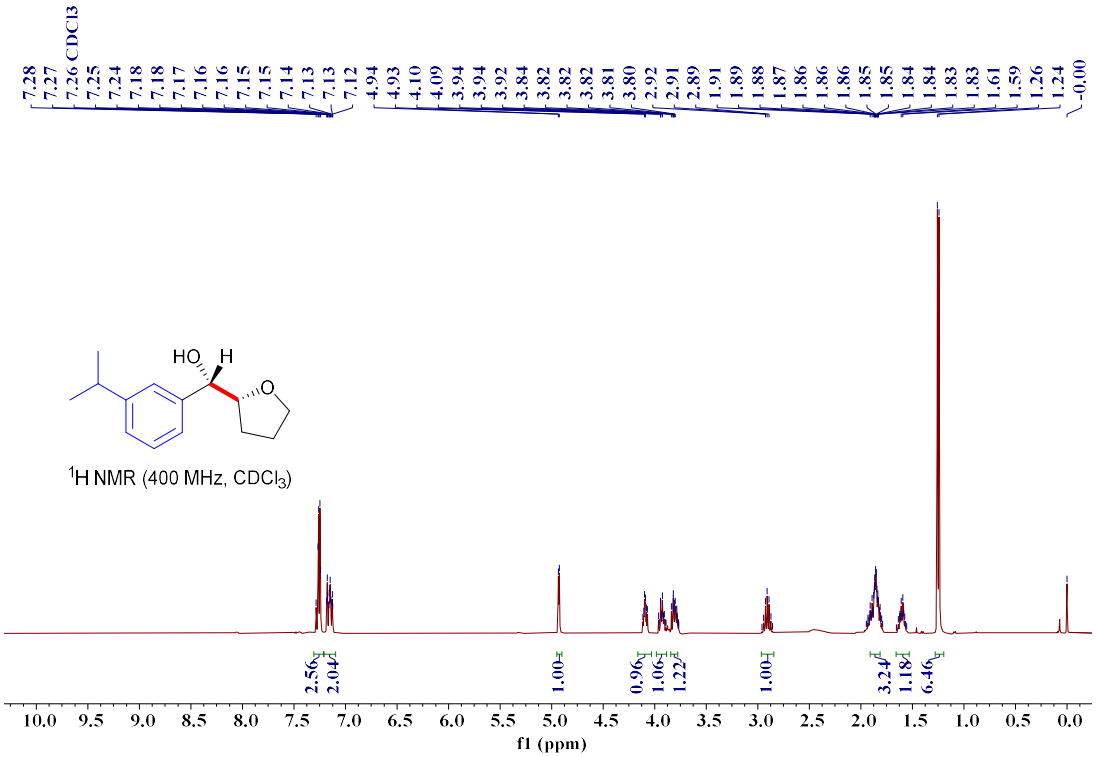


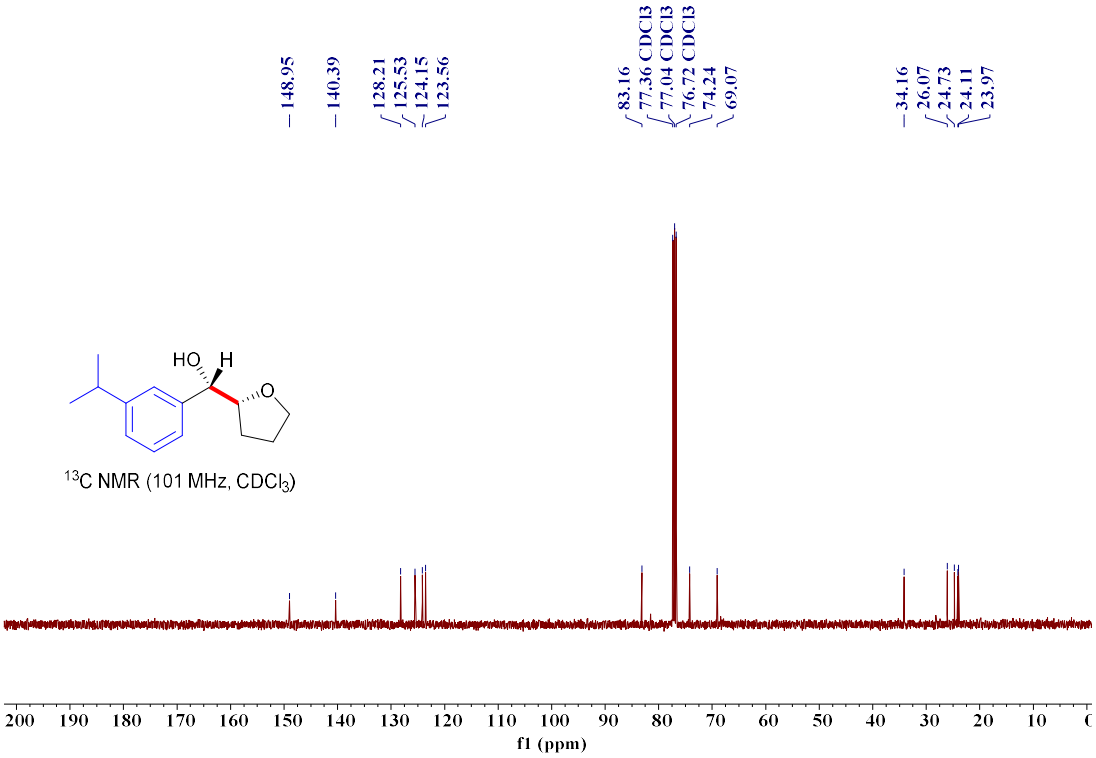
^{1}H NMR (400 MHz, $CDCl_3$)



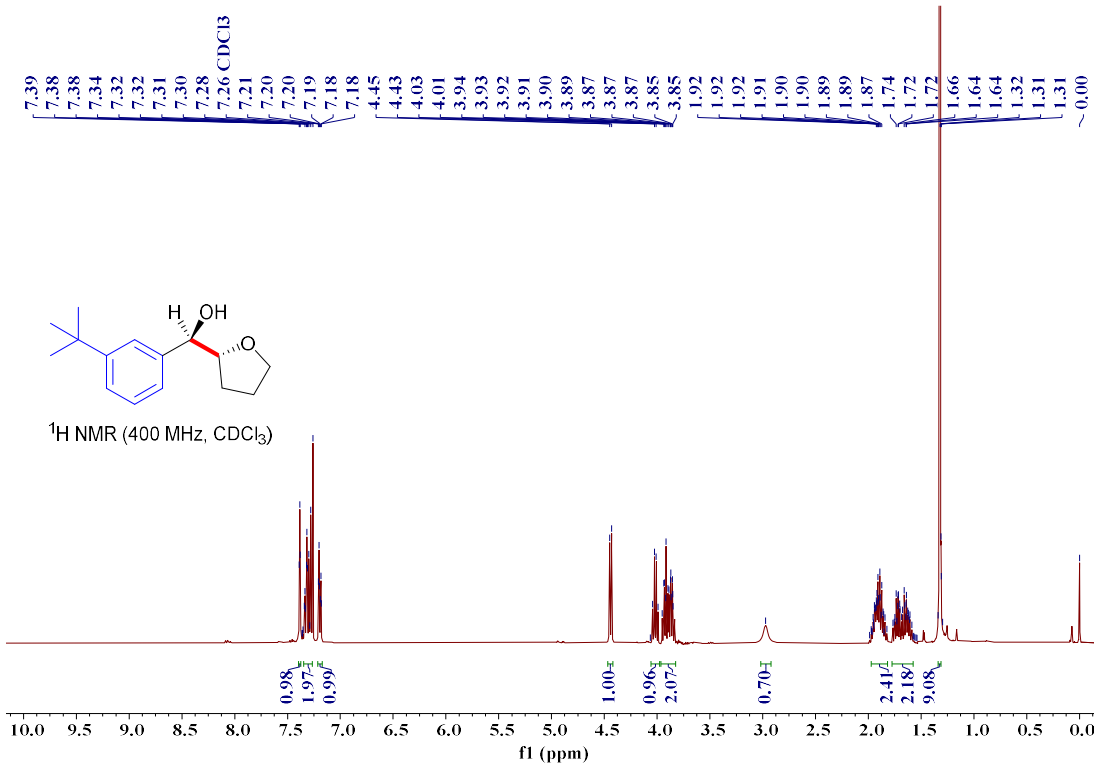
^{13}C NMR (101 MHz, $CDCl_3$)

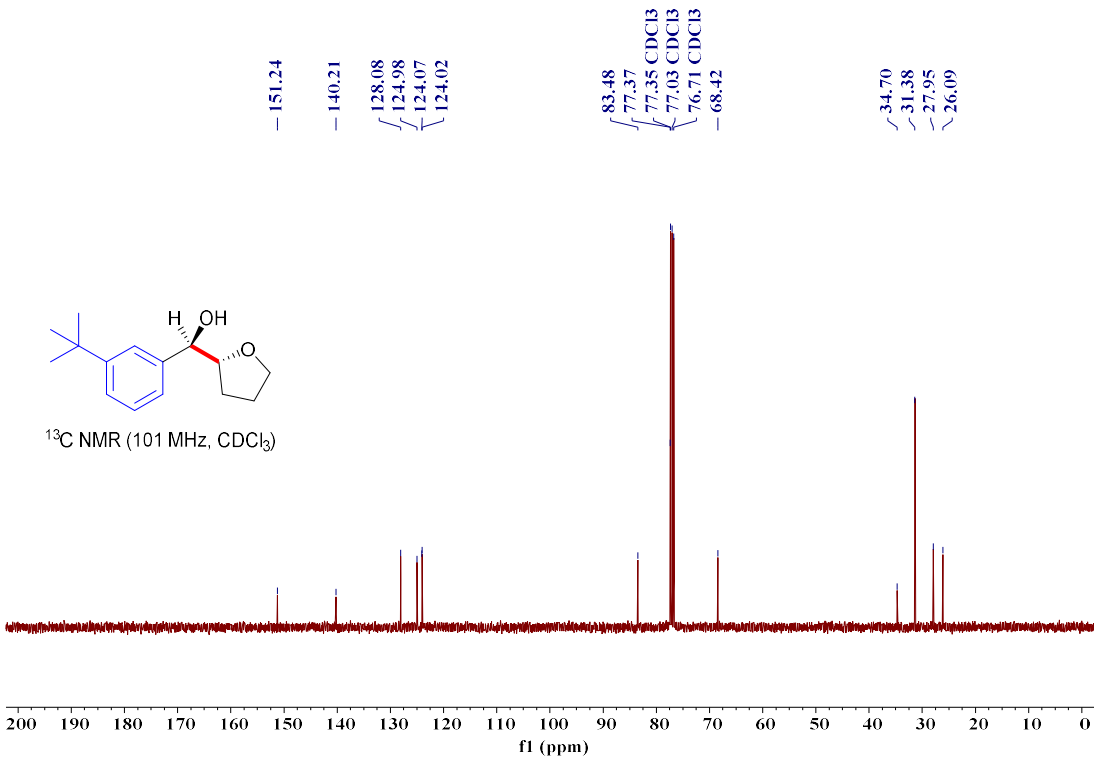
^{1}H and ^{13}C NMR spectra of compound *erythro*-3i



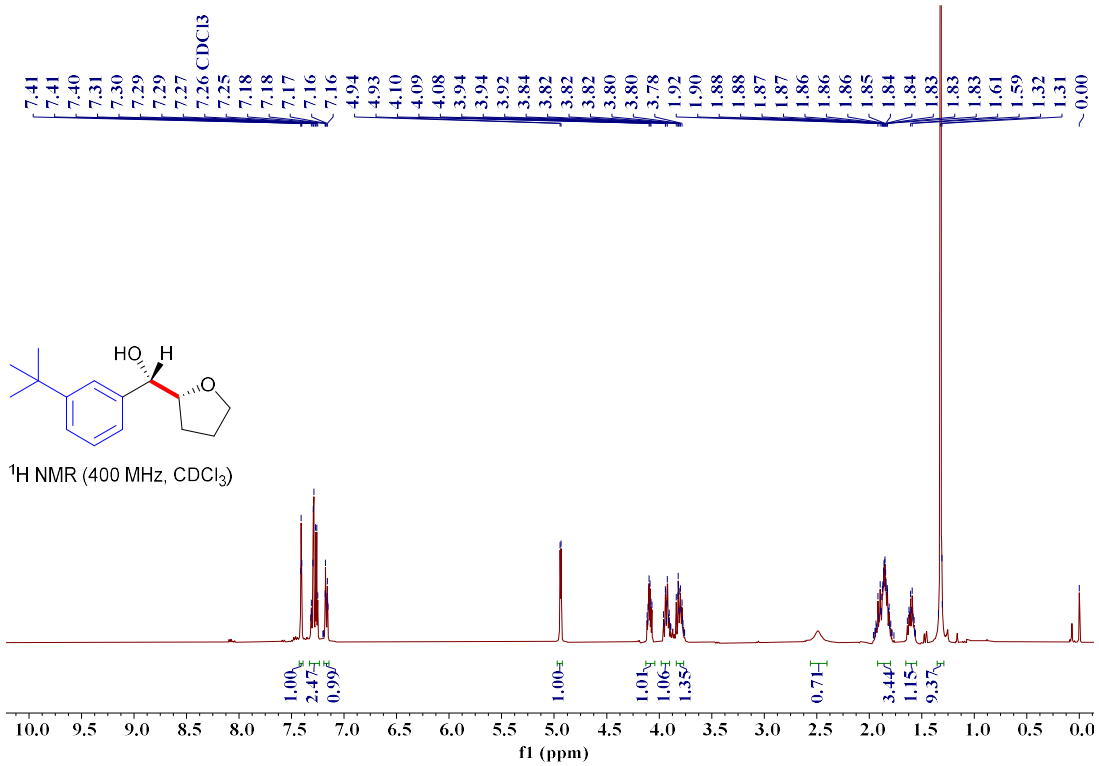


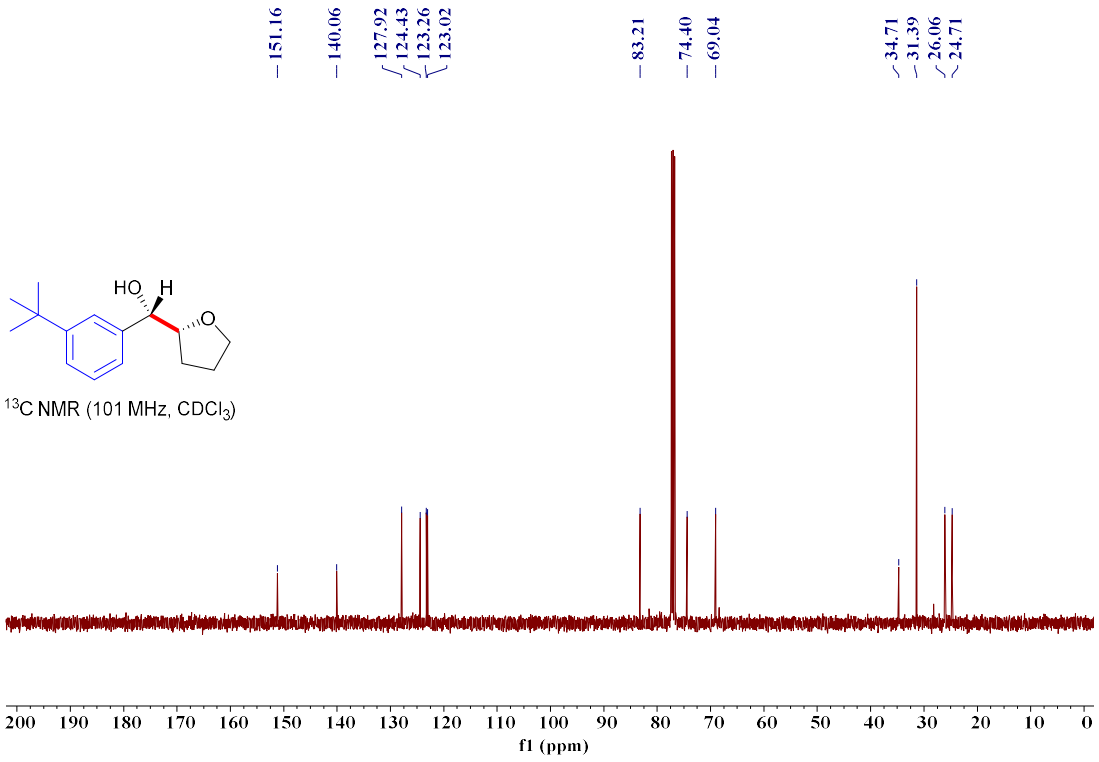
^{1}H and ^{13}C NMR spectra of compound *threo*-3j



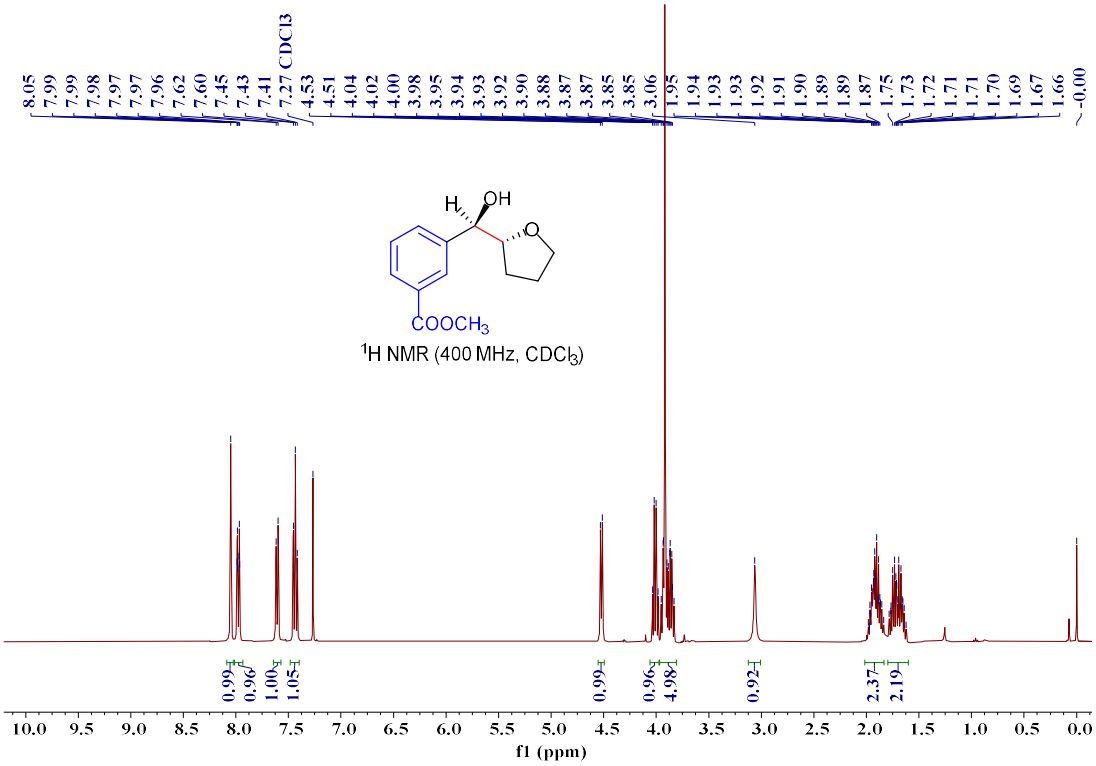


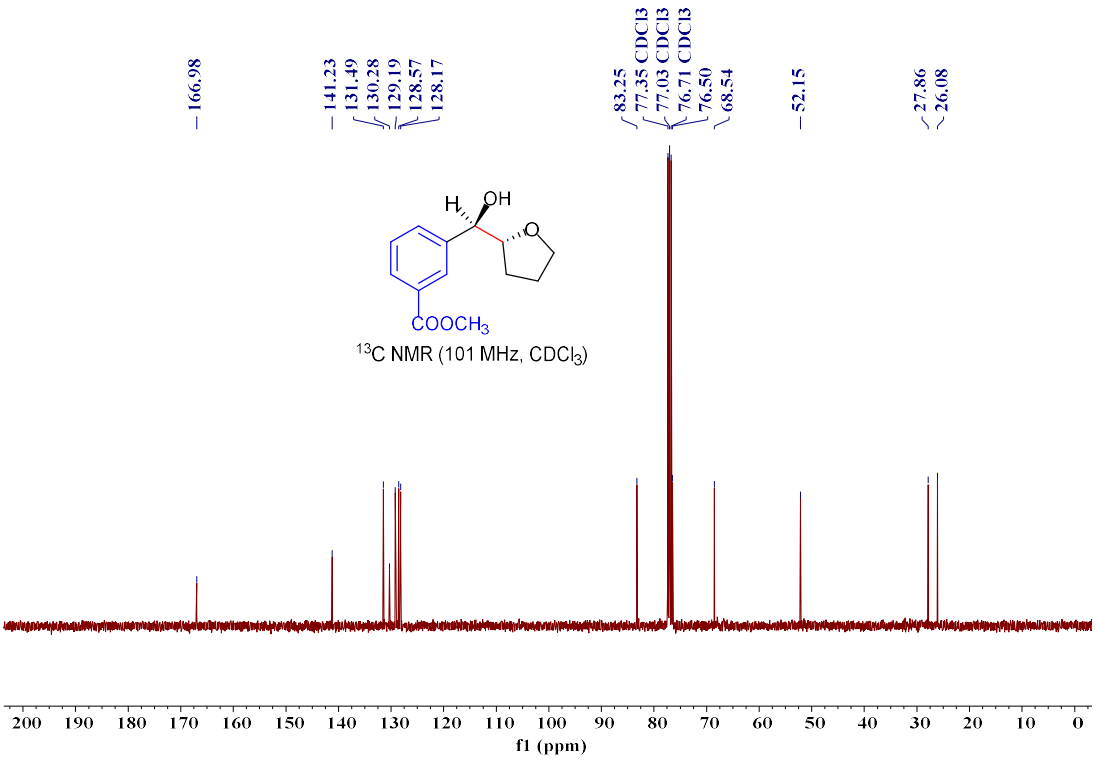
^{1}H and ^{13}C NMR spectra of compound *erythro*-3j



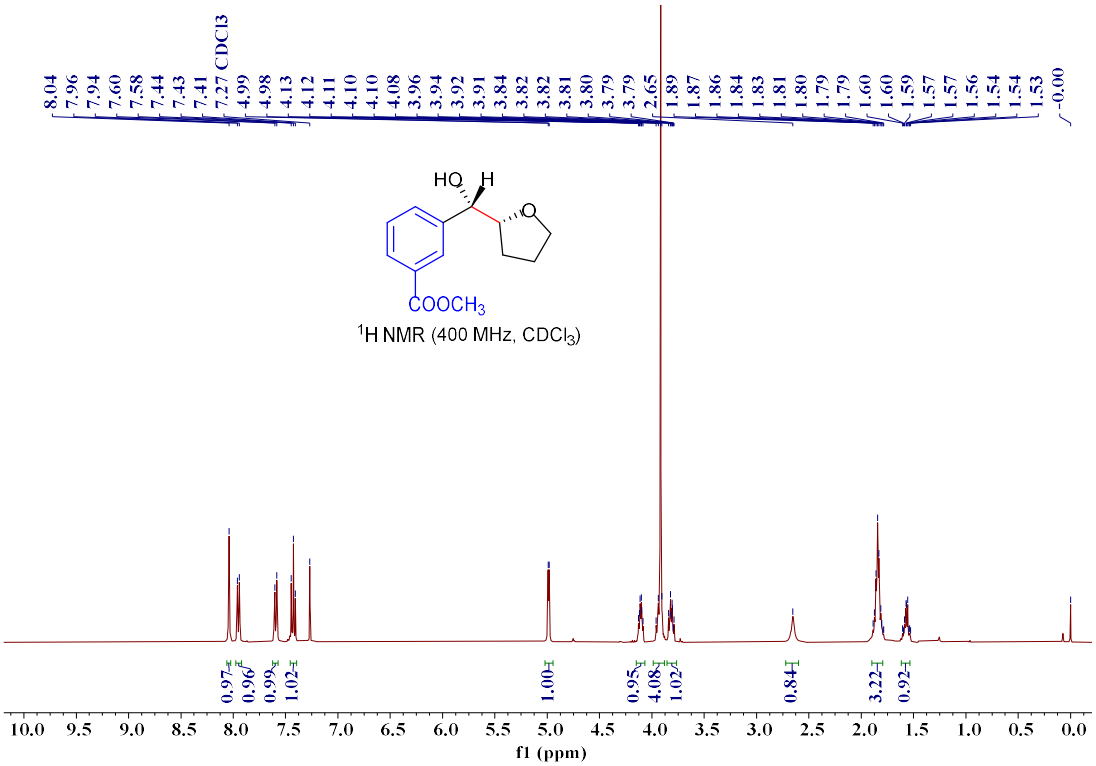


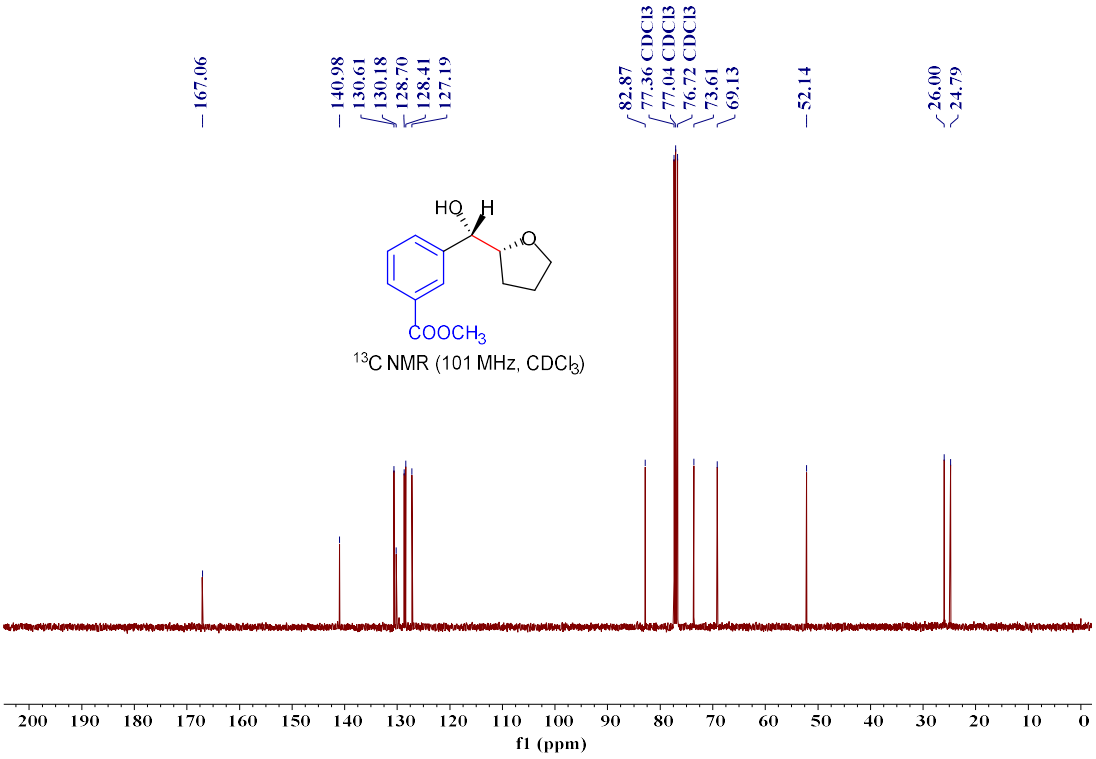
^{1}H and ^{13}C NMR spectra of compound *threo*-3k



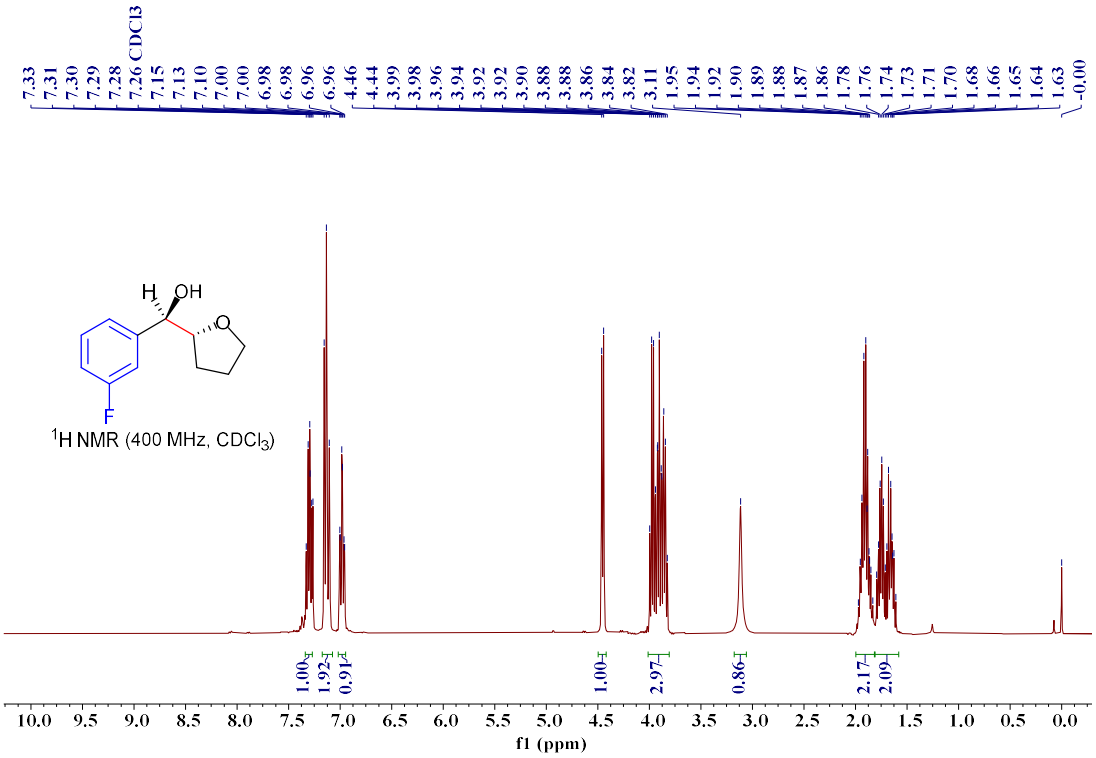


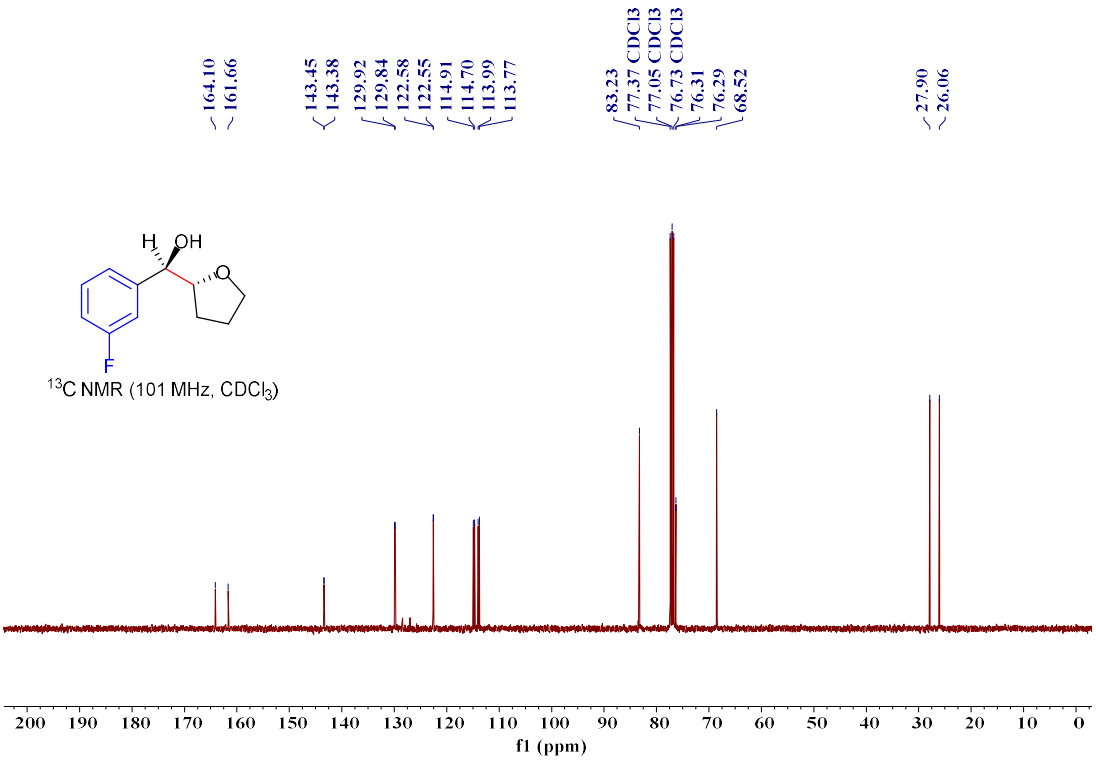
^{1}H and ^{13}C NMR spectra of compound *erythro*-3k

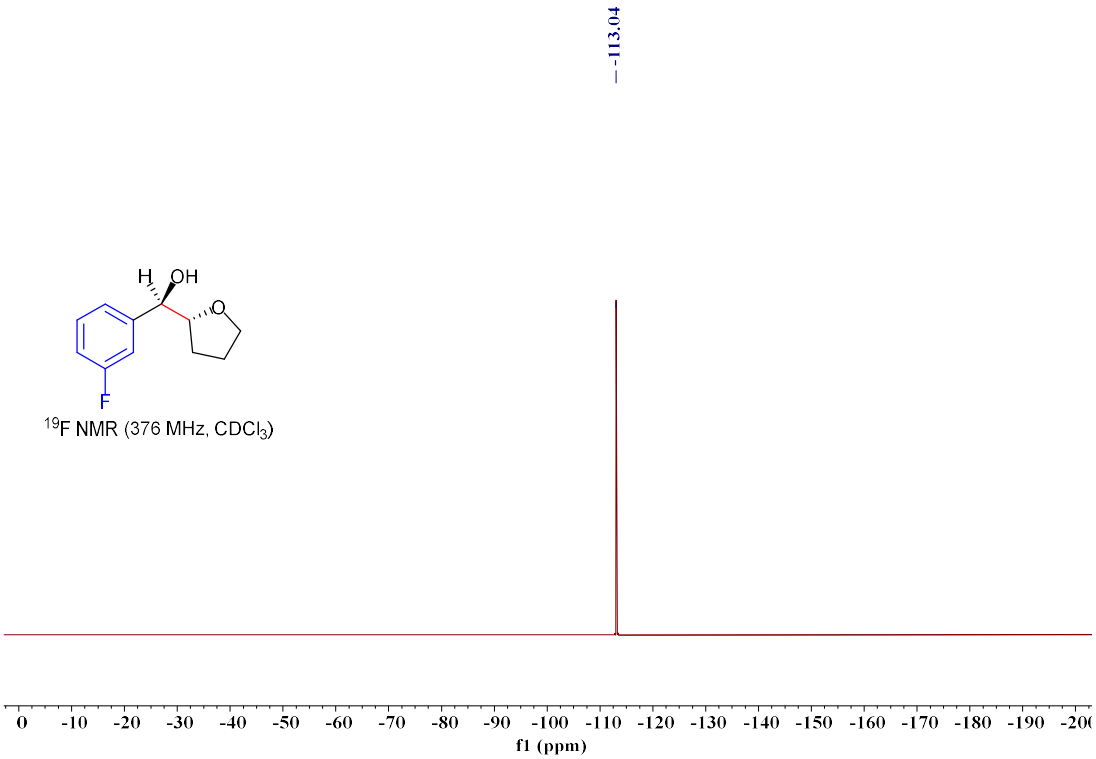




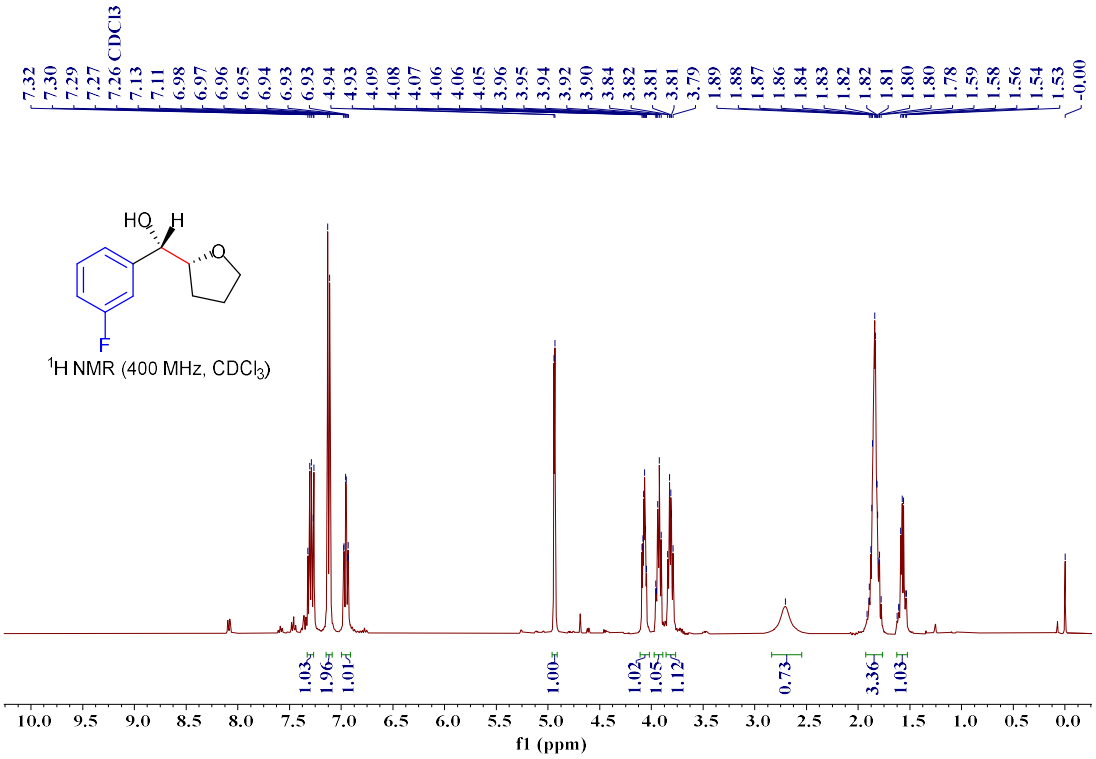
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *threo*-3l

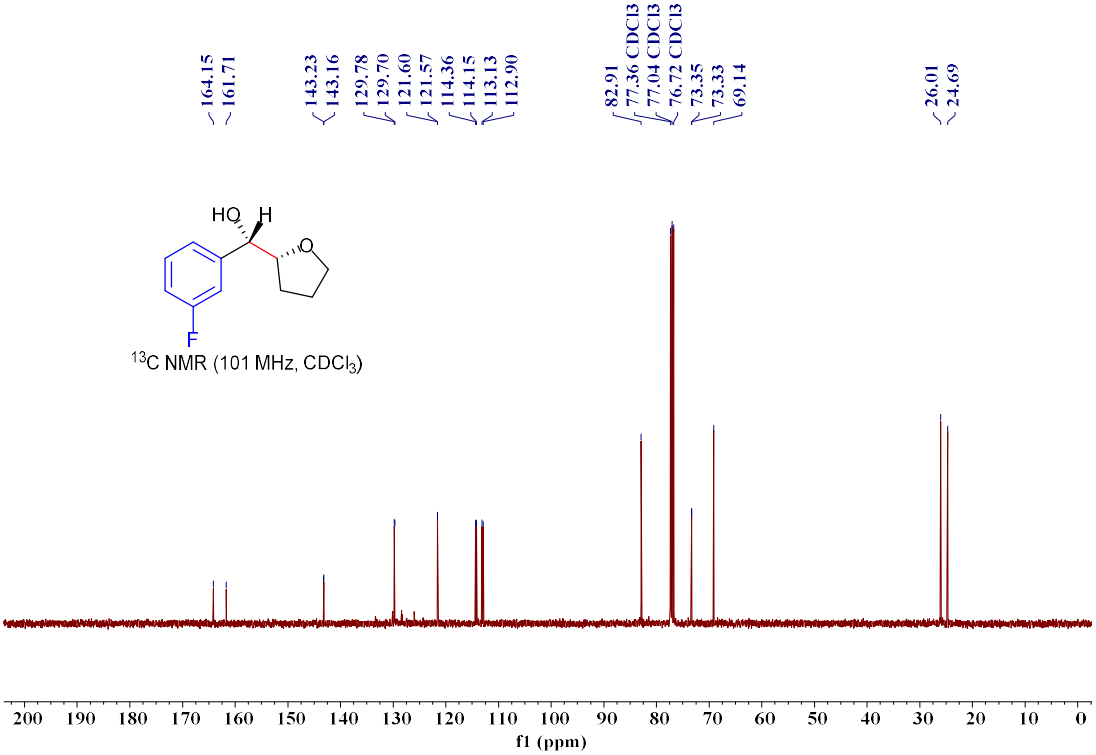


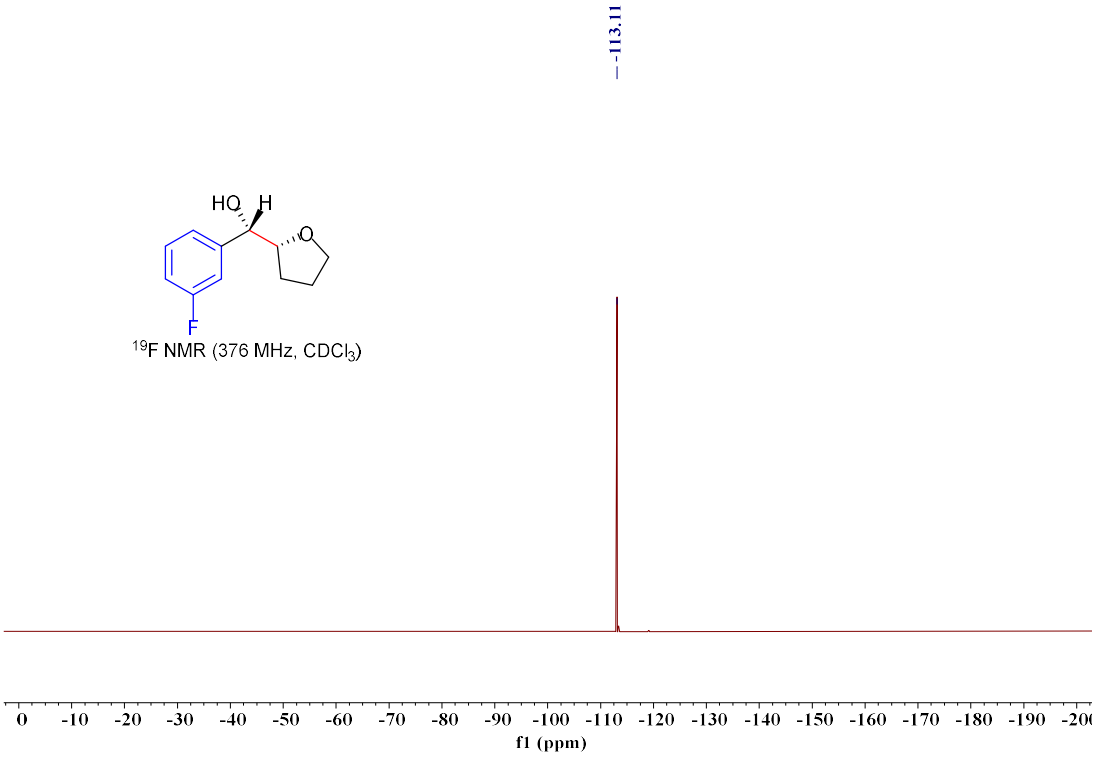




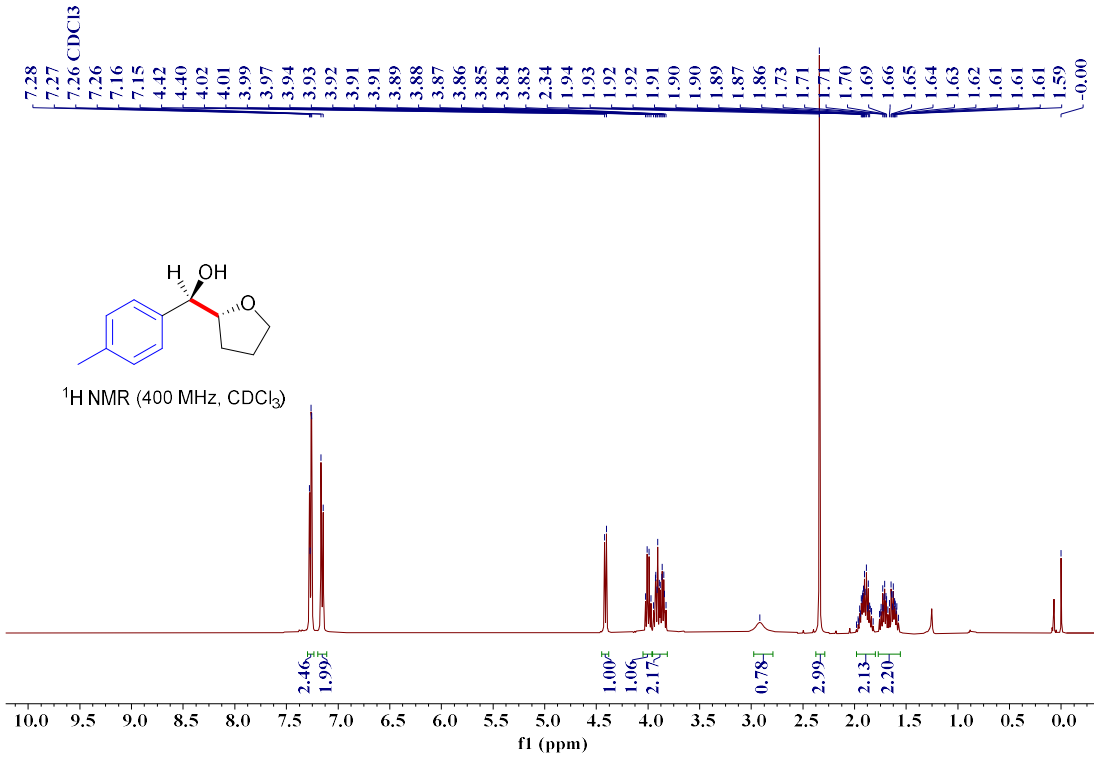
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *erythro*-3l

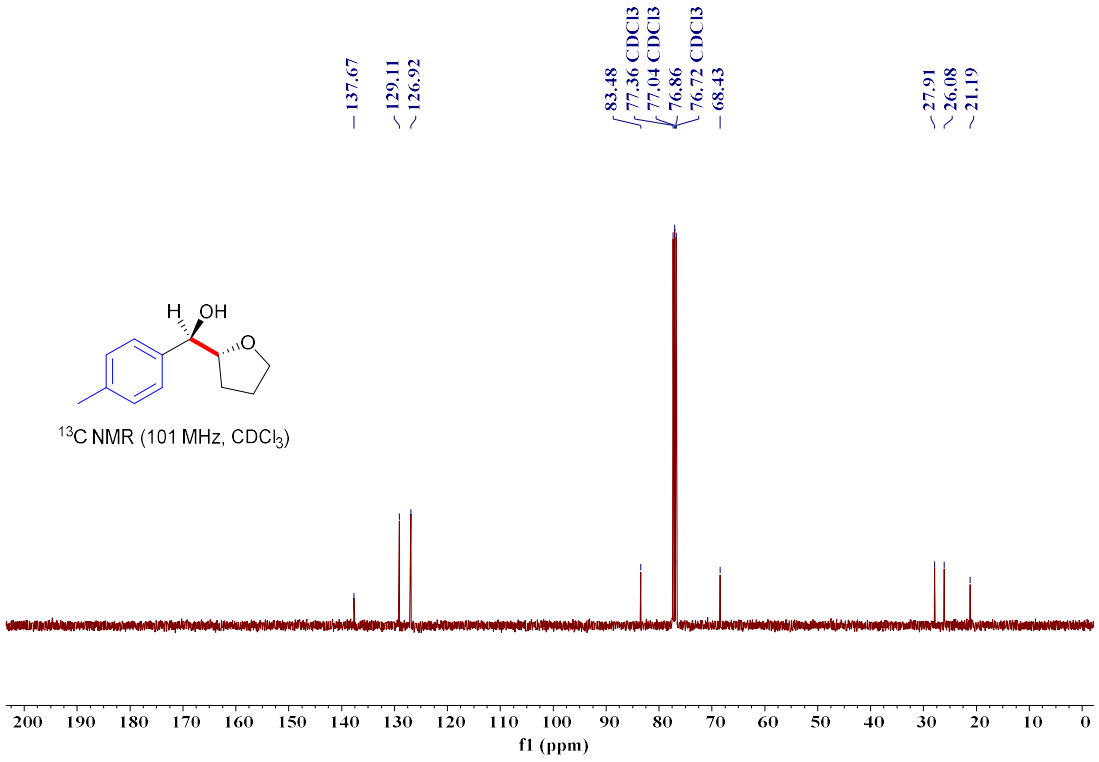



164.15
161.71
143.23
143.16
129.78
129.70
121.60
121.57
114.36
114.15
113.13
112.90
82.91
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
73.35
73.33
69.14
26.01
24.69
HO
H
O
F
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

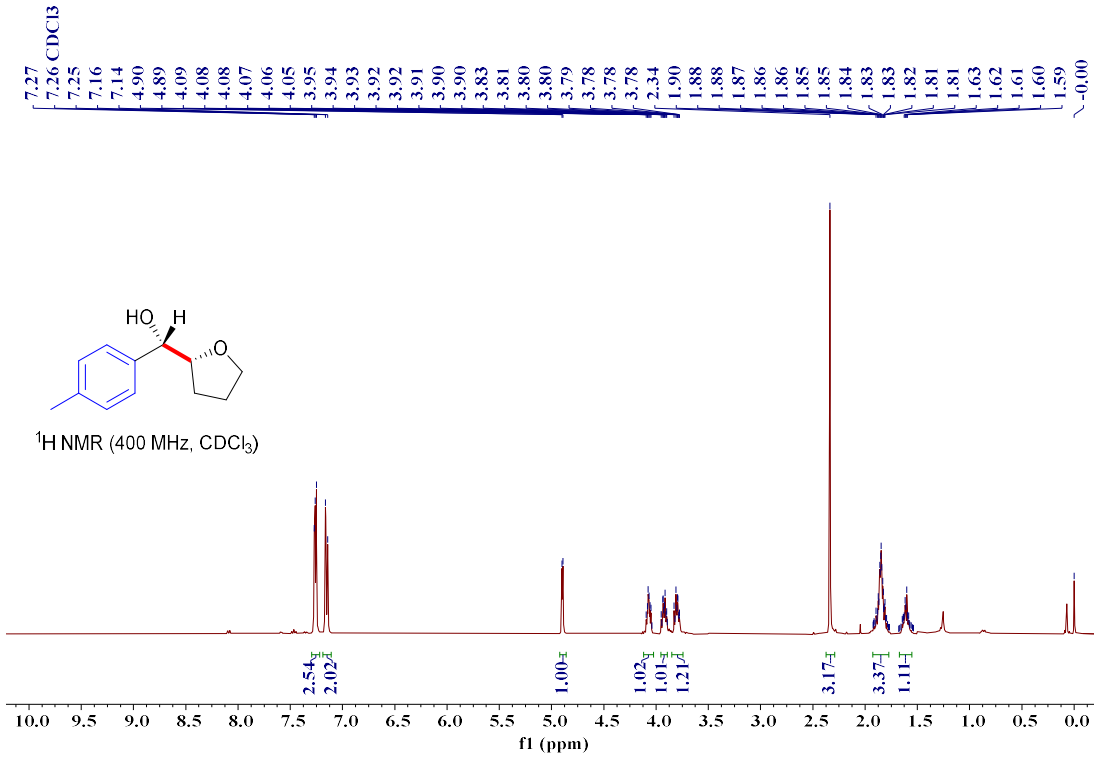

-113.11
HO
H
O
F
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

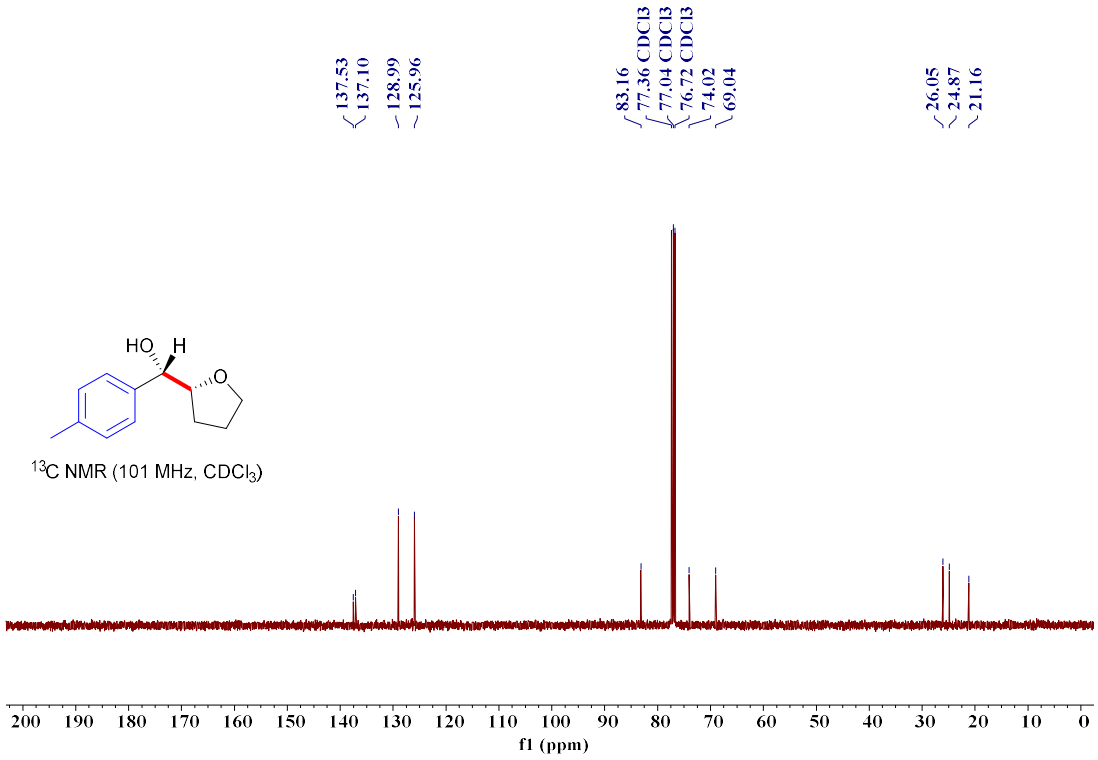
^{1}H and ^{13}C NMR spectra of compound *threo*-3m



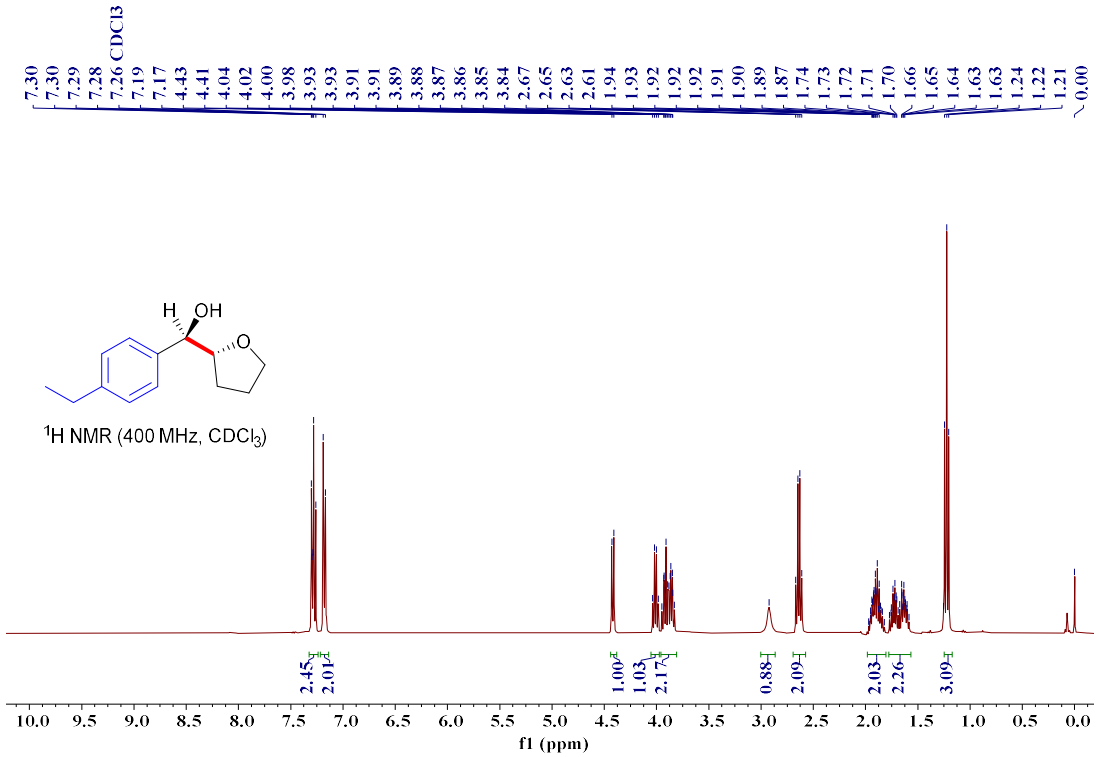


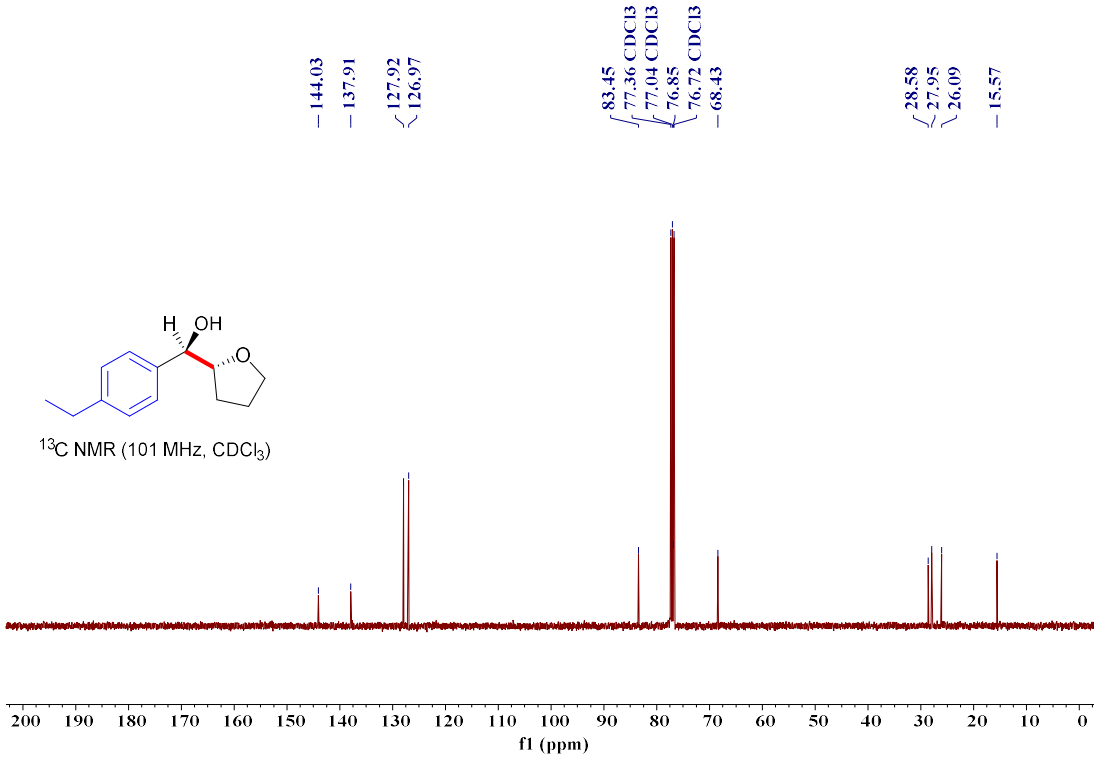
^{1}H and ^{13}C NMR spectra of compound *erythro*-3m



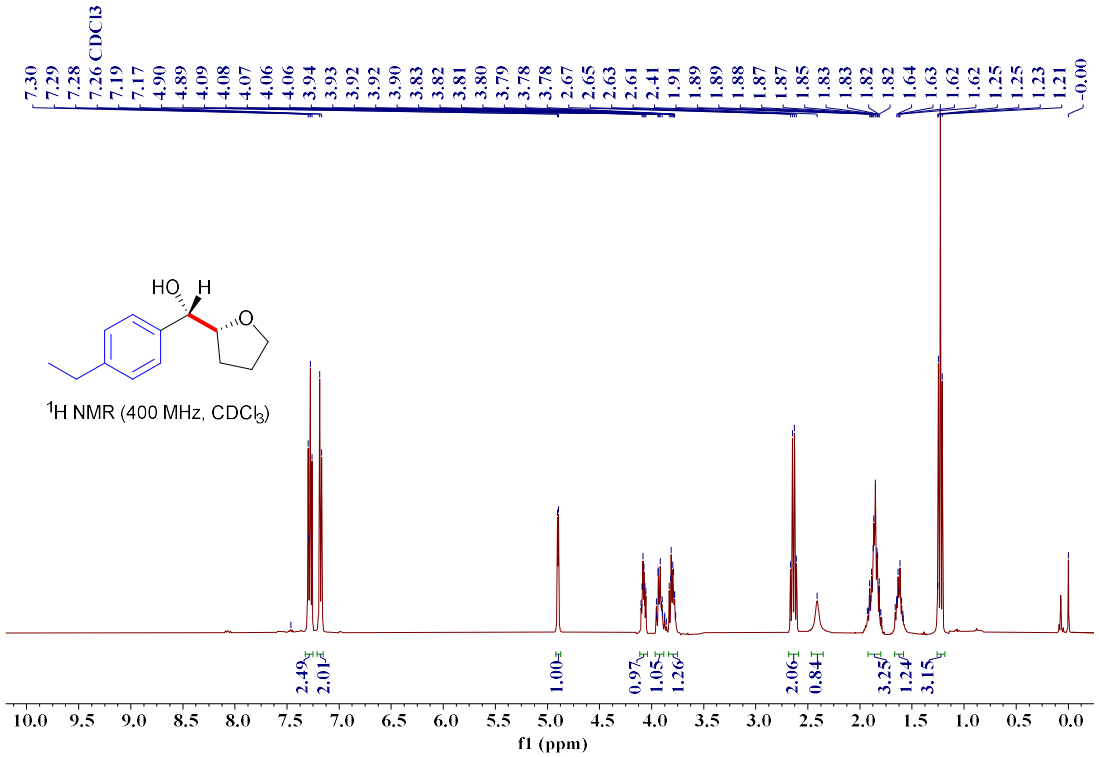


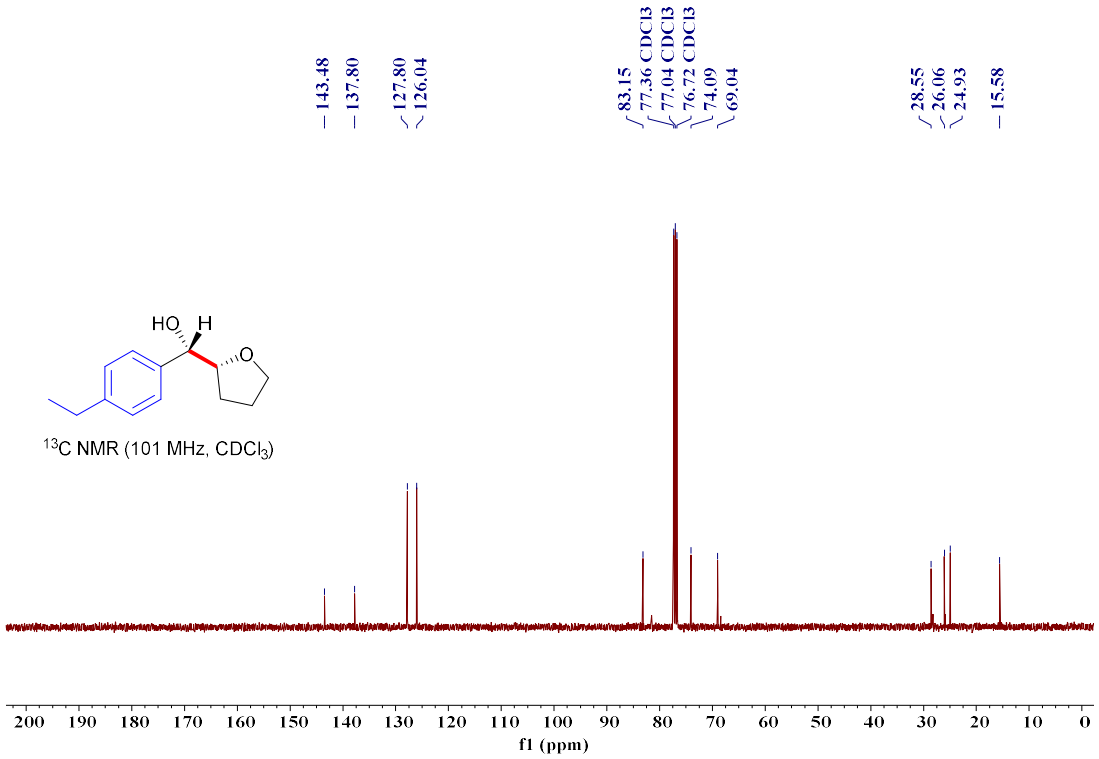
^{1}H and ^{13}C NMR spectra of compound *threo*-3n



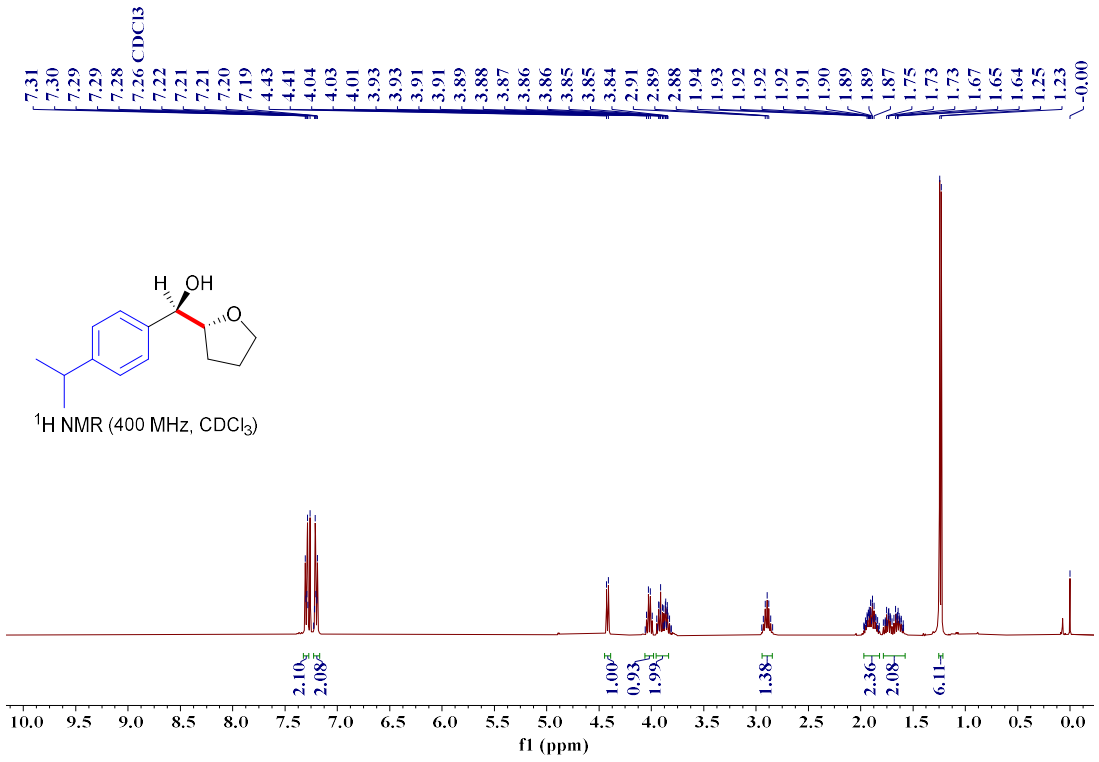


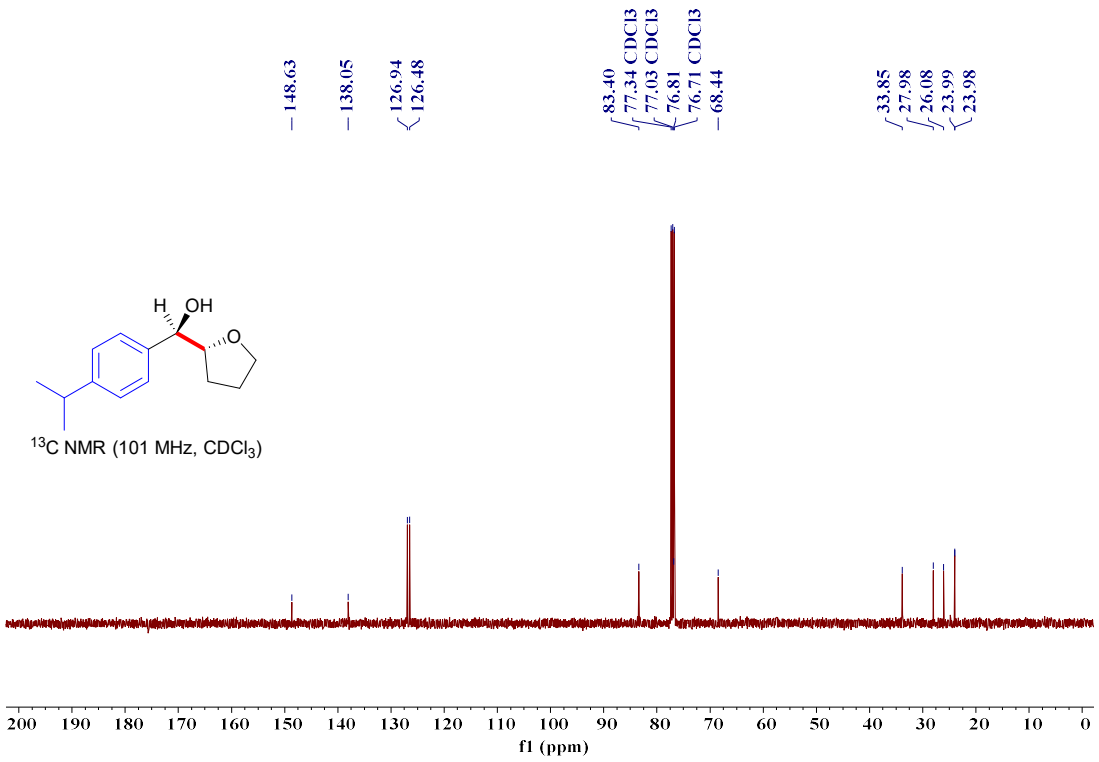
^{1}H and ^{13}C NMR spectra of compound *erythro*-3n



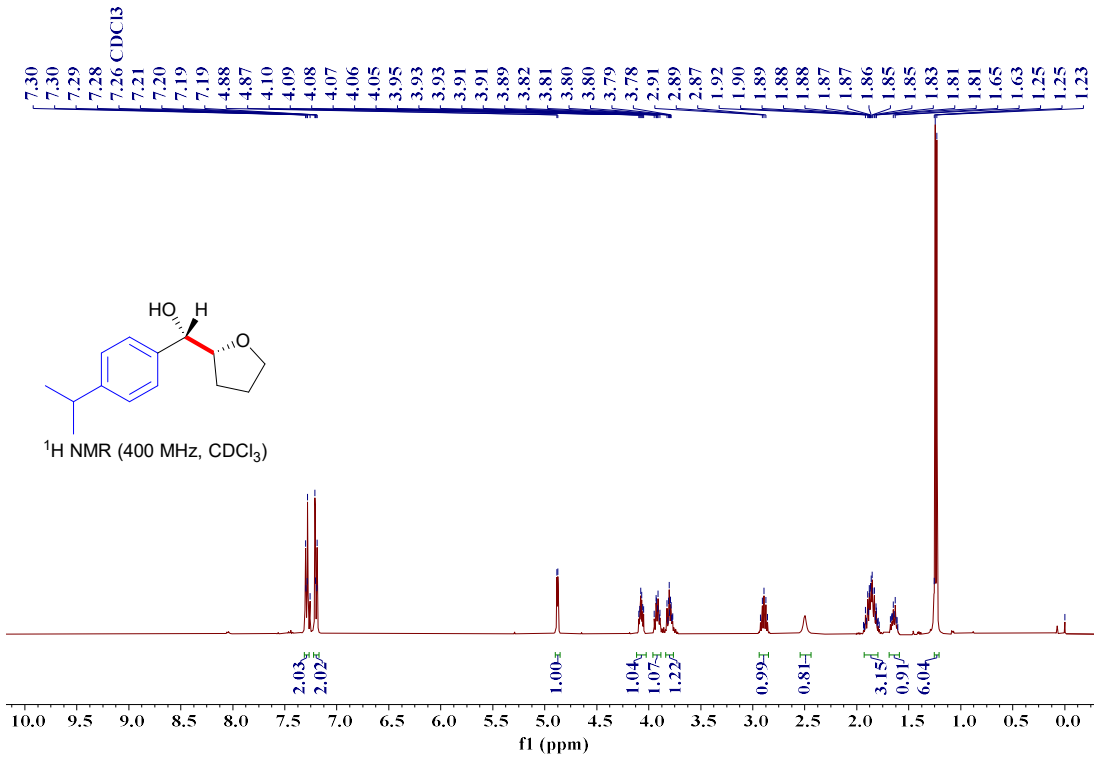


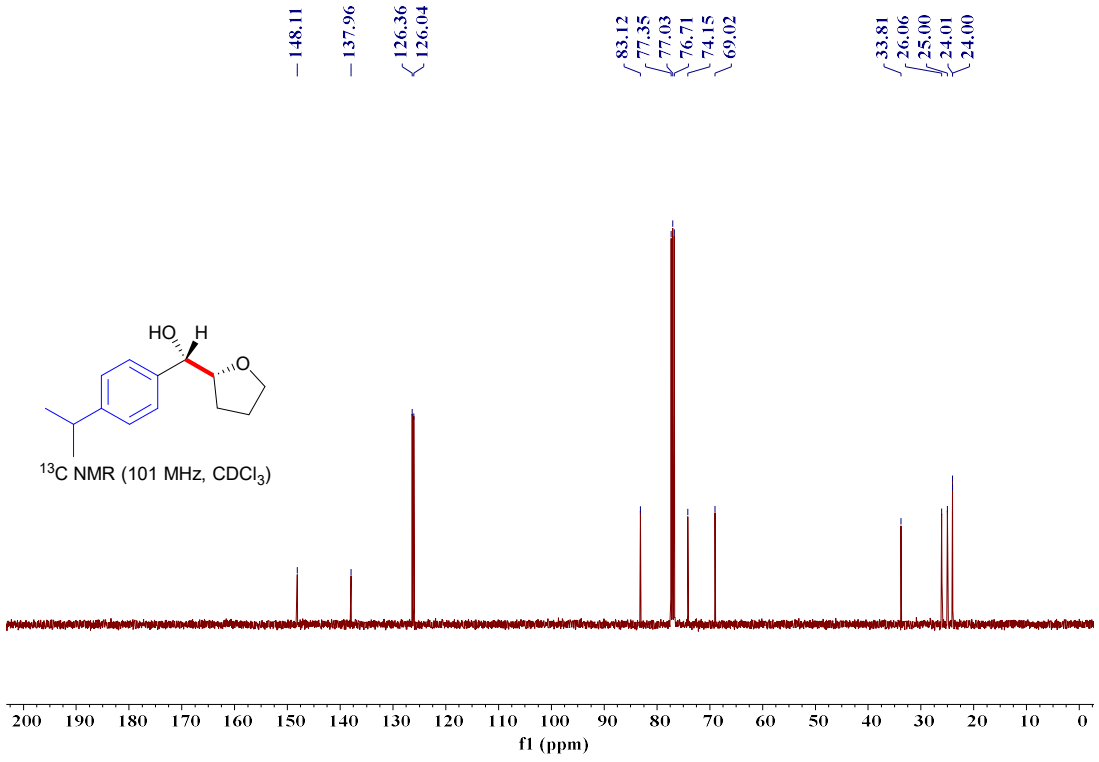
^{1}H and ^{13}C NMR spectra of compound *threo*-3o



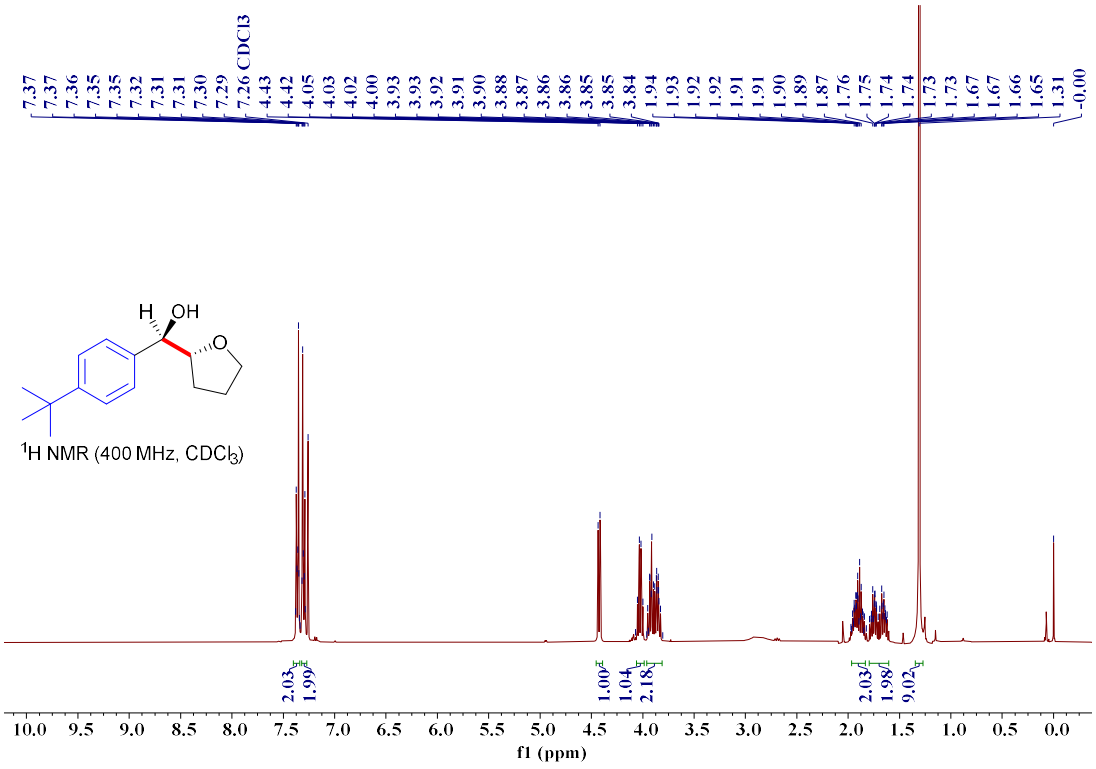


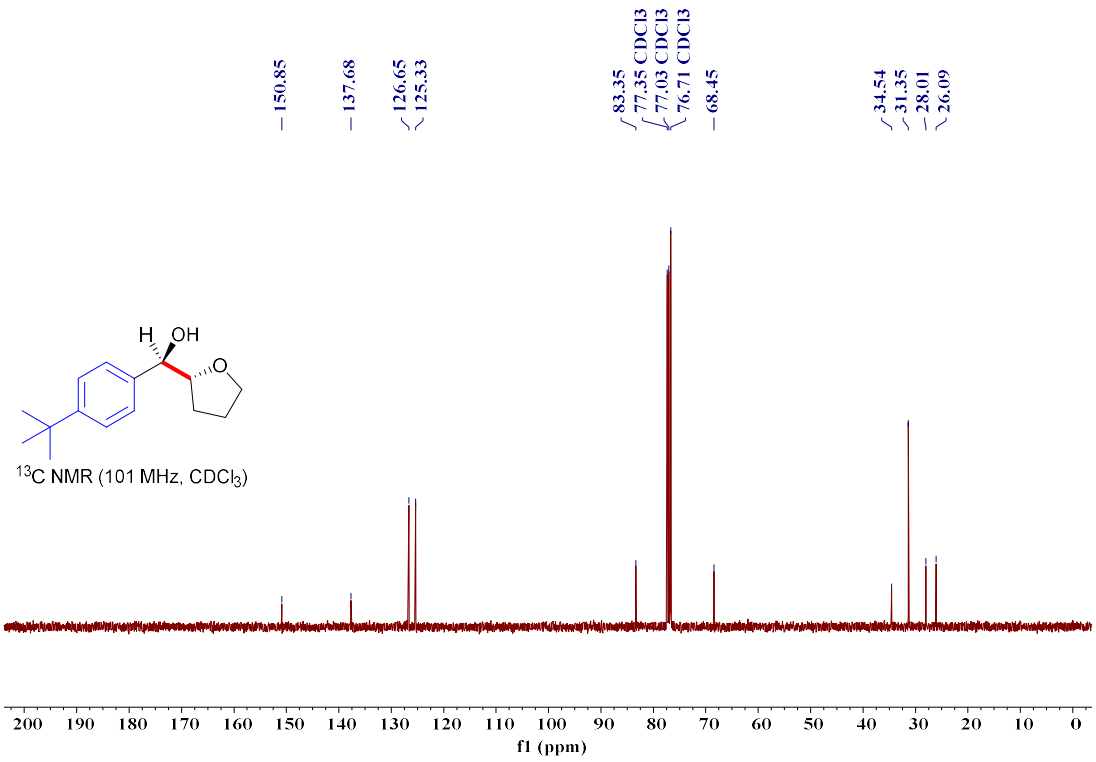
^{1}H and ^{13}C NMR spectra of compound *erythro*-3o



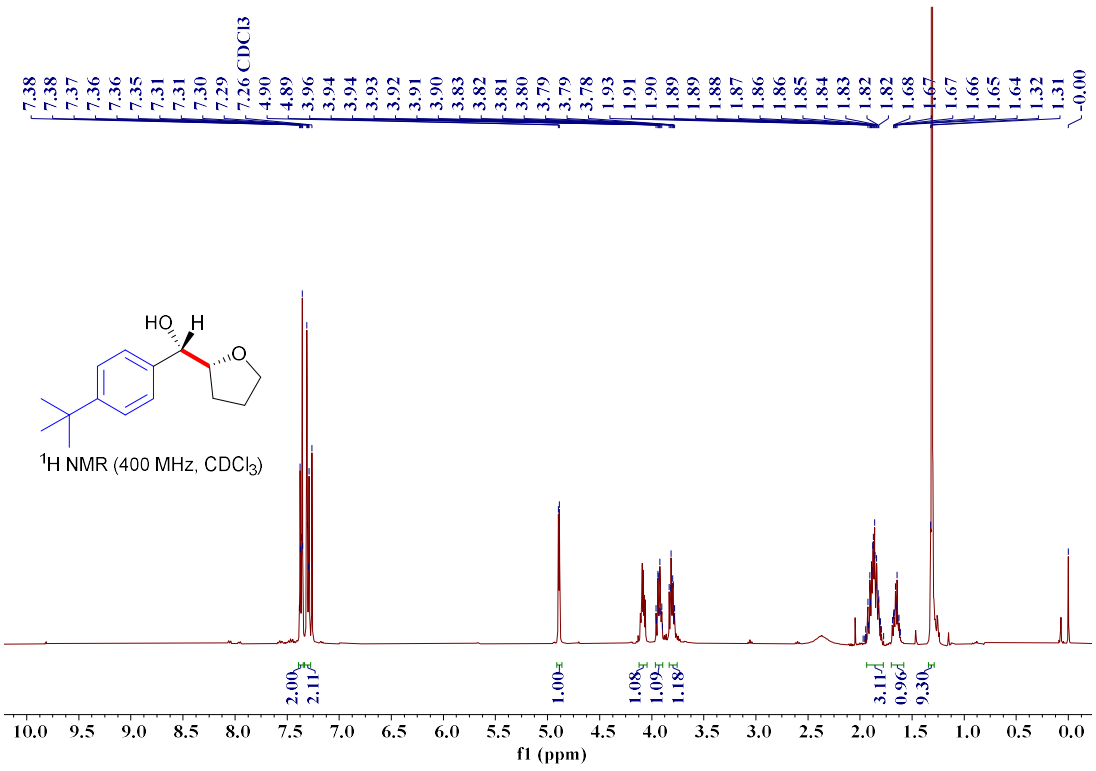


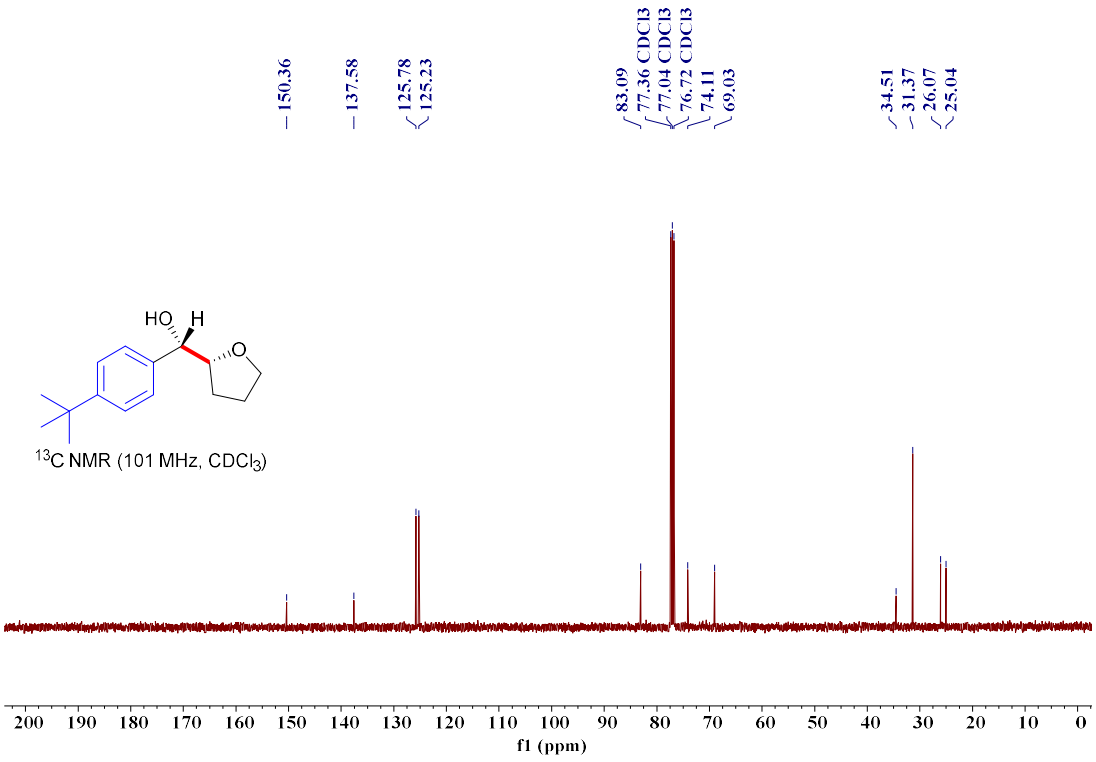
^{1}H and ^{13}C NMR spectra of compound *threo*-3p



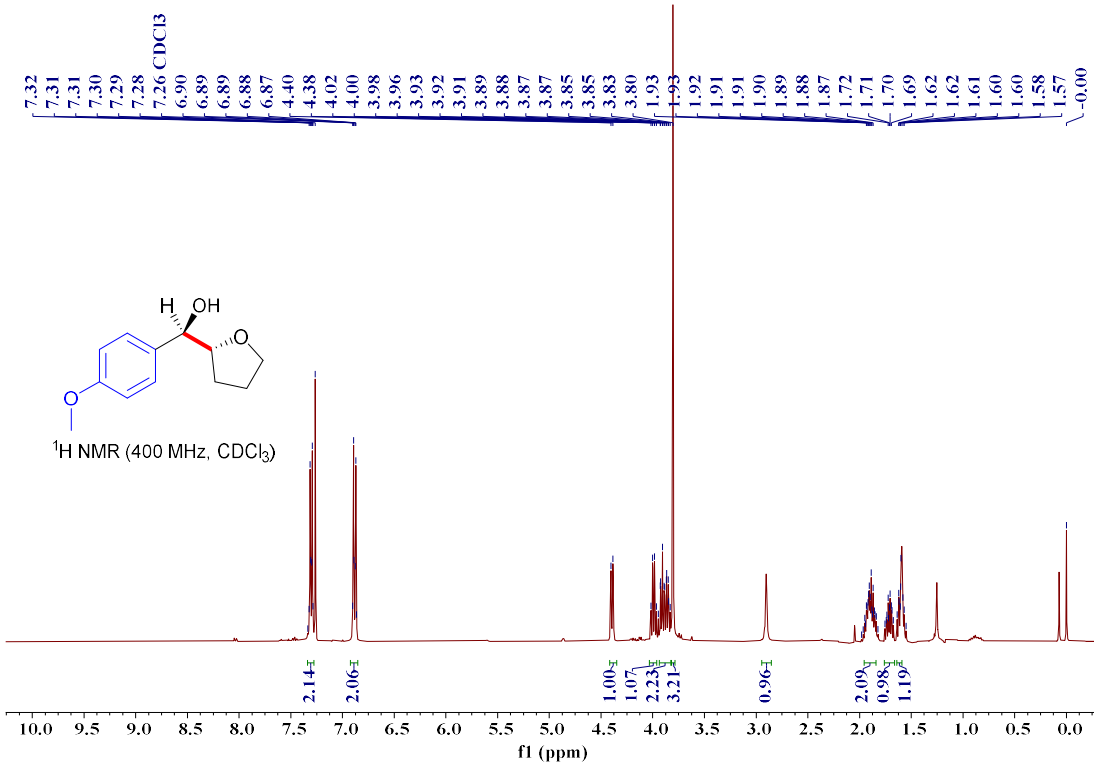


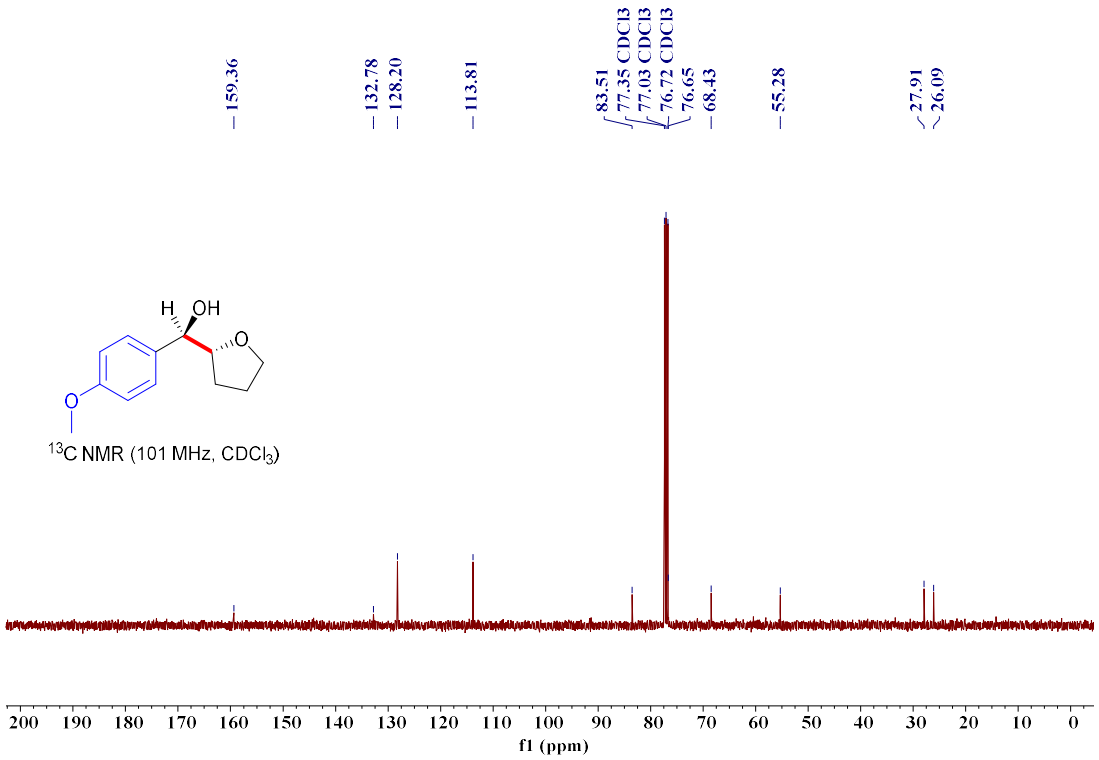
^{1}H and ^{13}C NMR spectra of compound *erythro*-3p



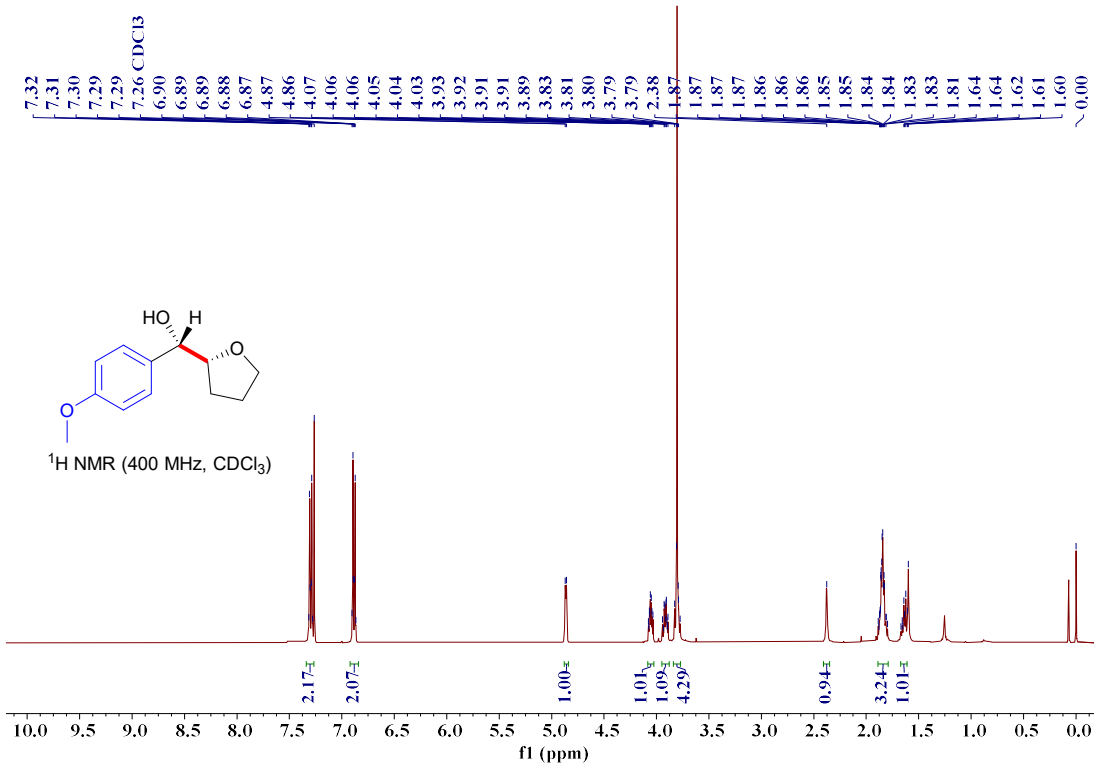


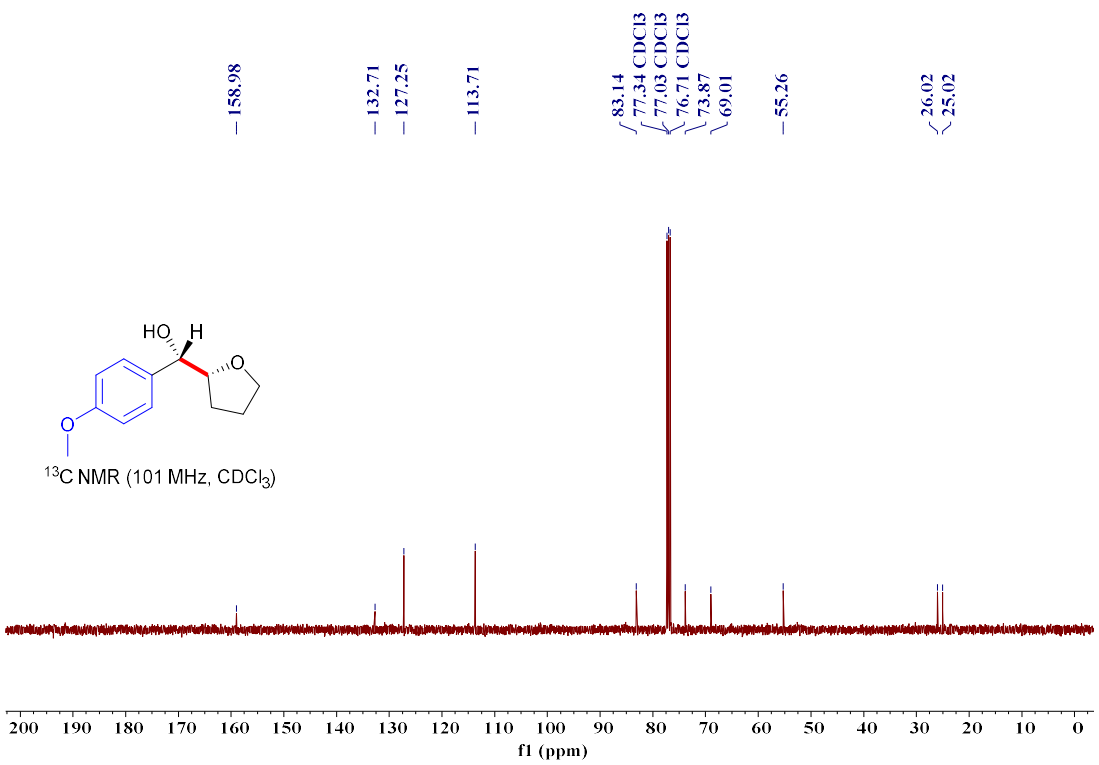
^{1}H and ^{13}C NMR spectra of compound *threo*-3q



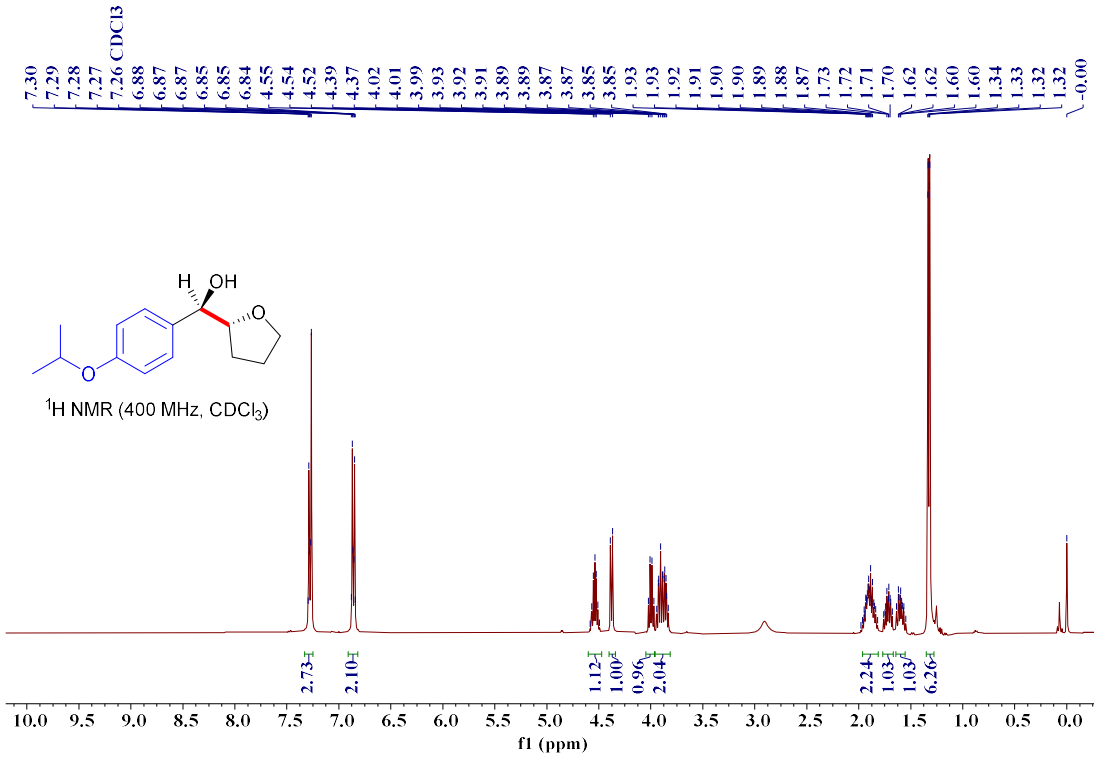


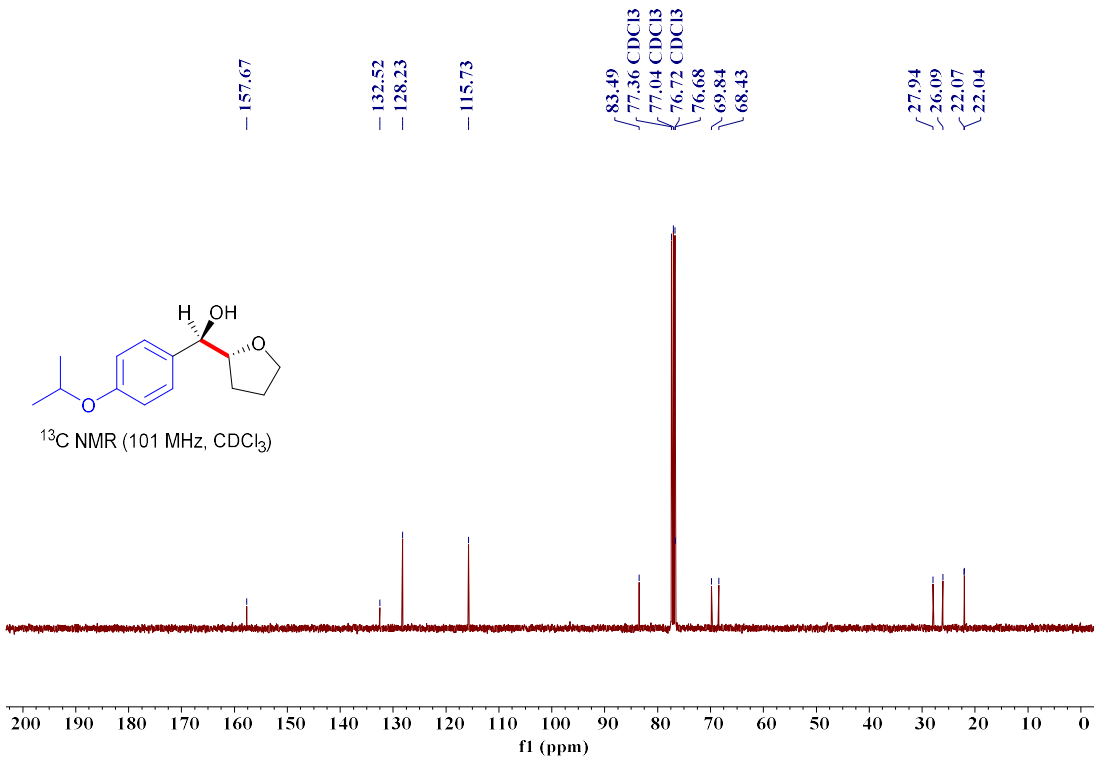
^{1}H and ^{13}C NMR spectra of compound *erythro*-3q



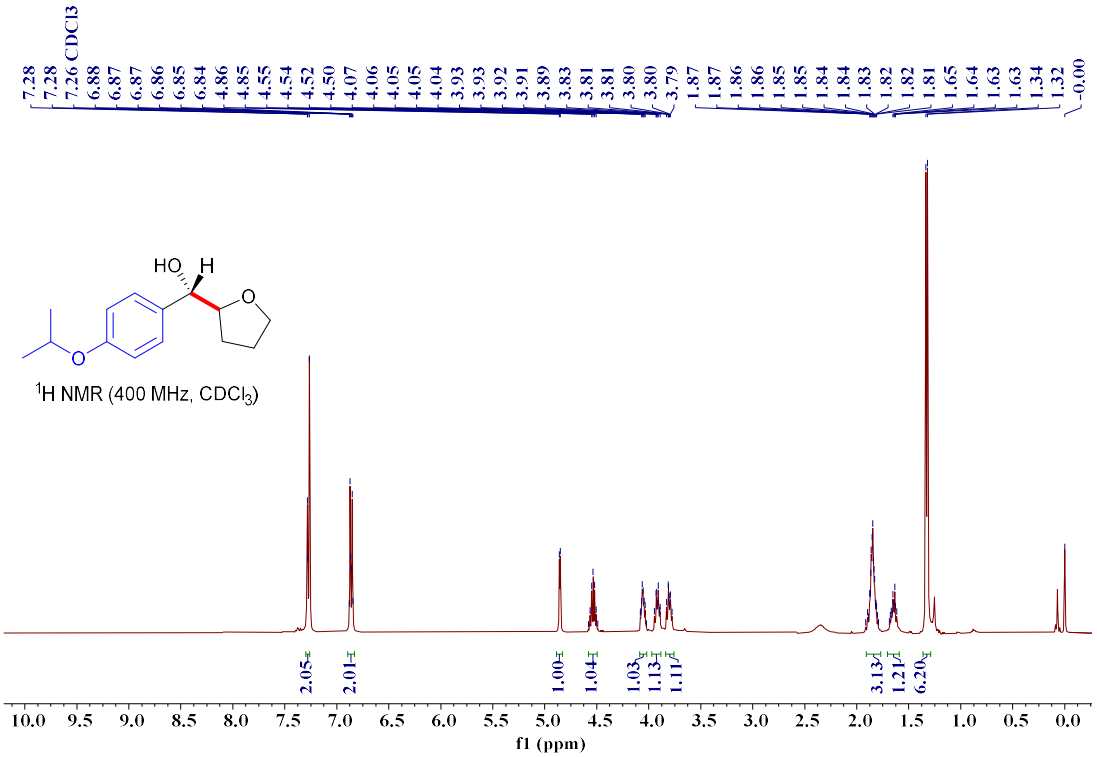


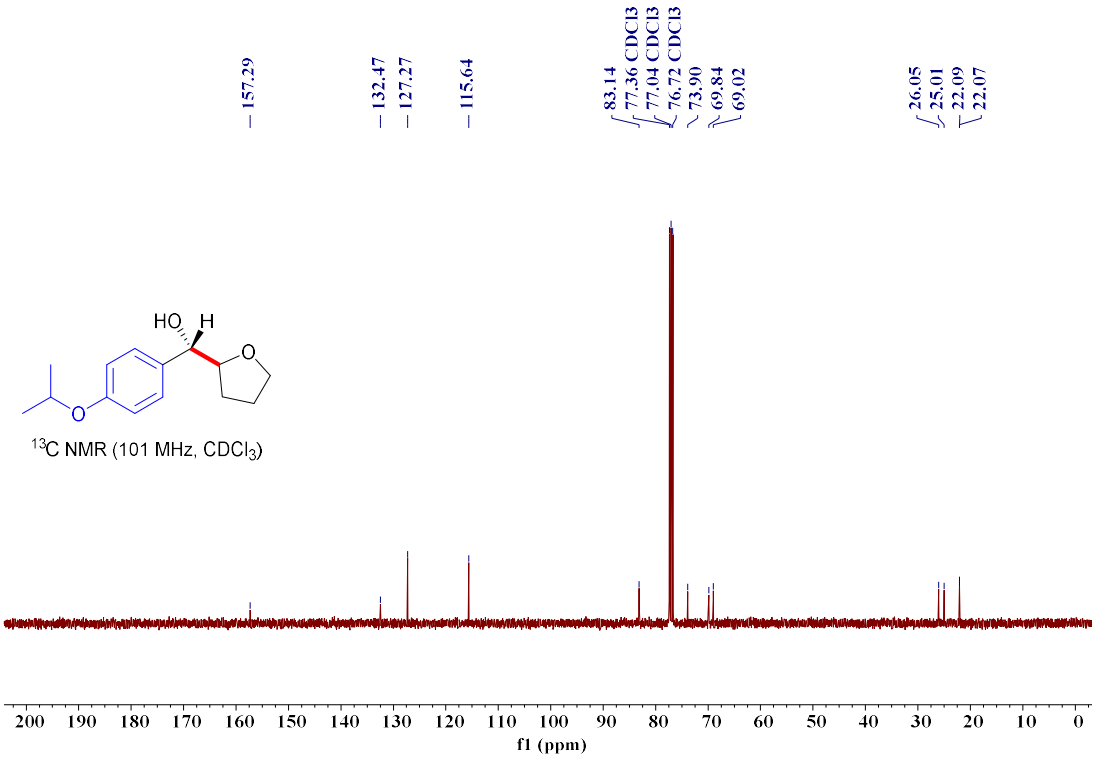
^{1}H and ^{13}C NMR spectra of compound *threo*-3r



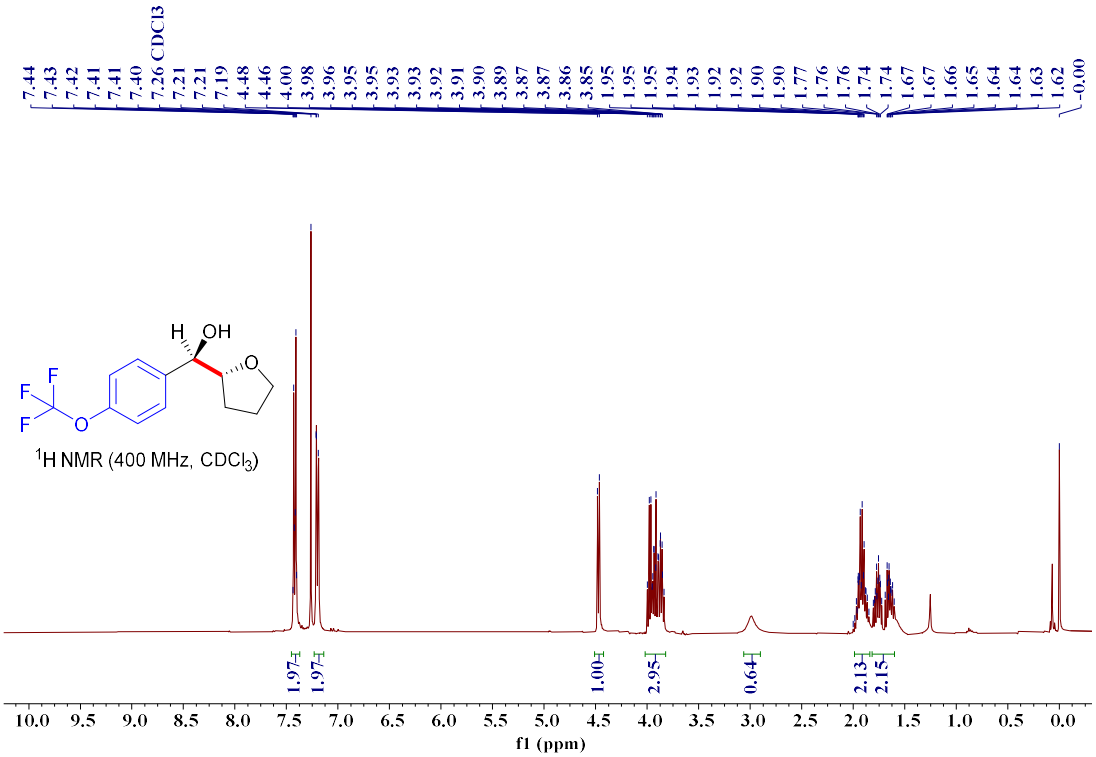


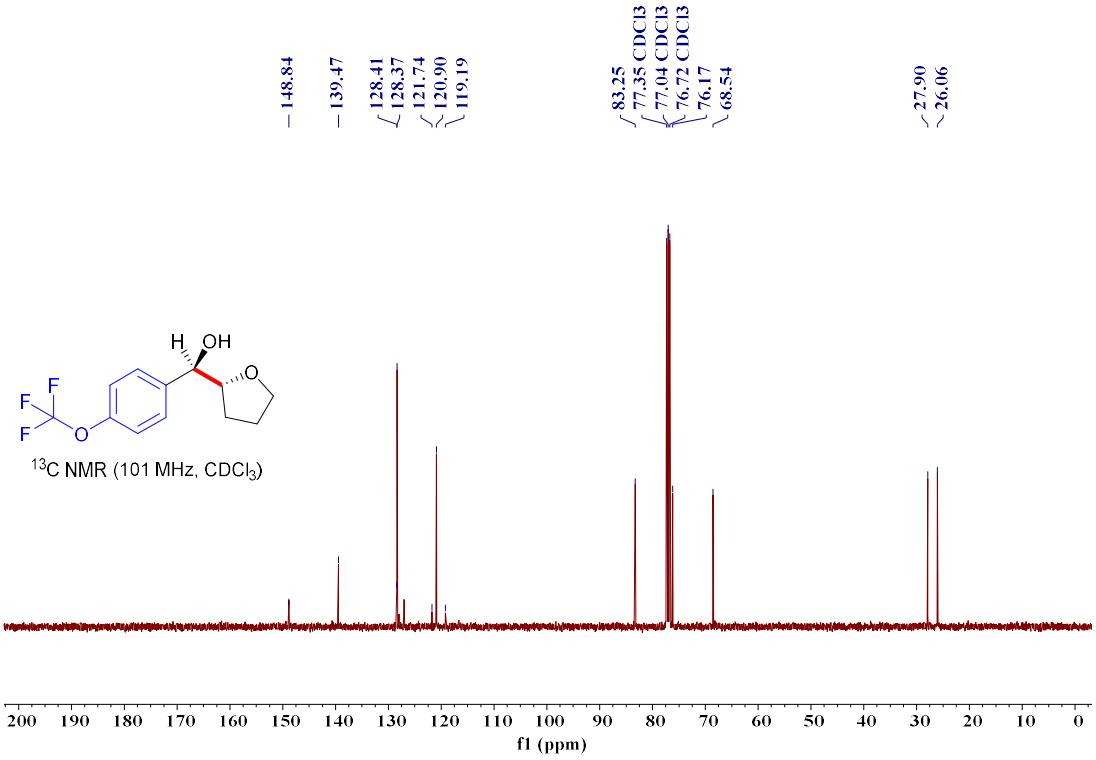
^{1}H and ^{13}C spectra of compound *erythro*-3r

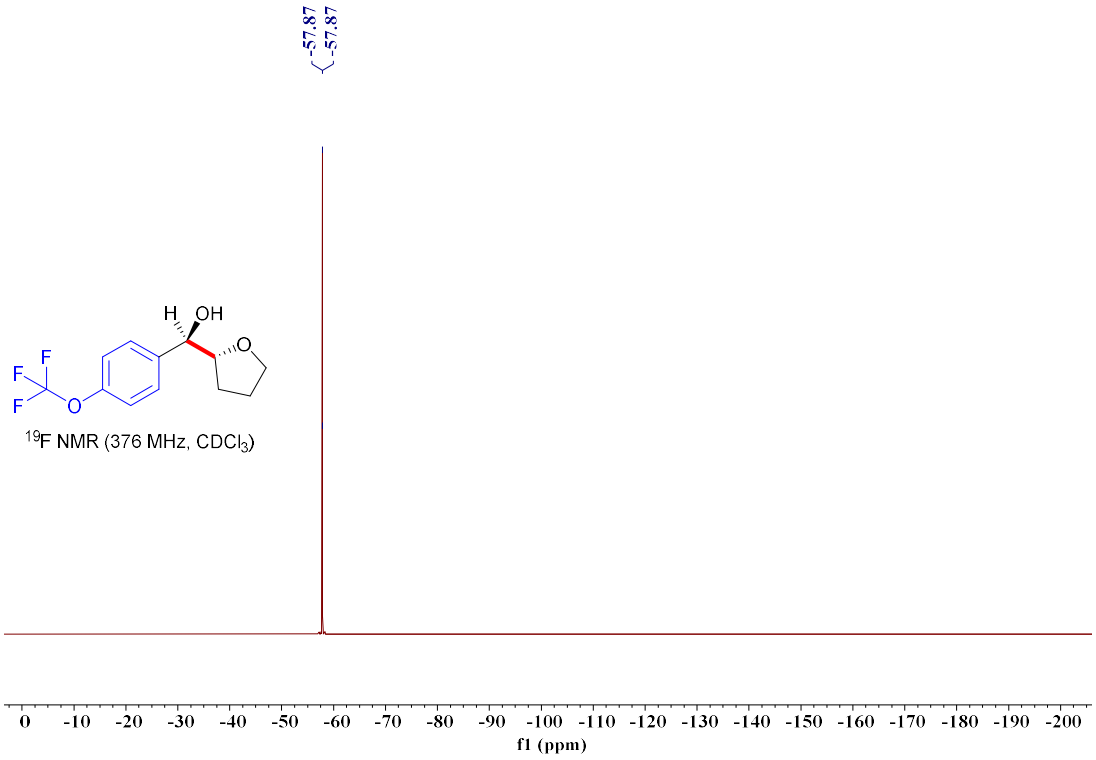




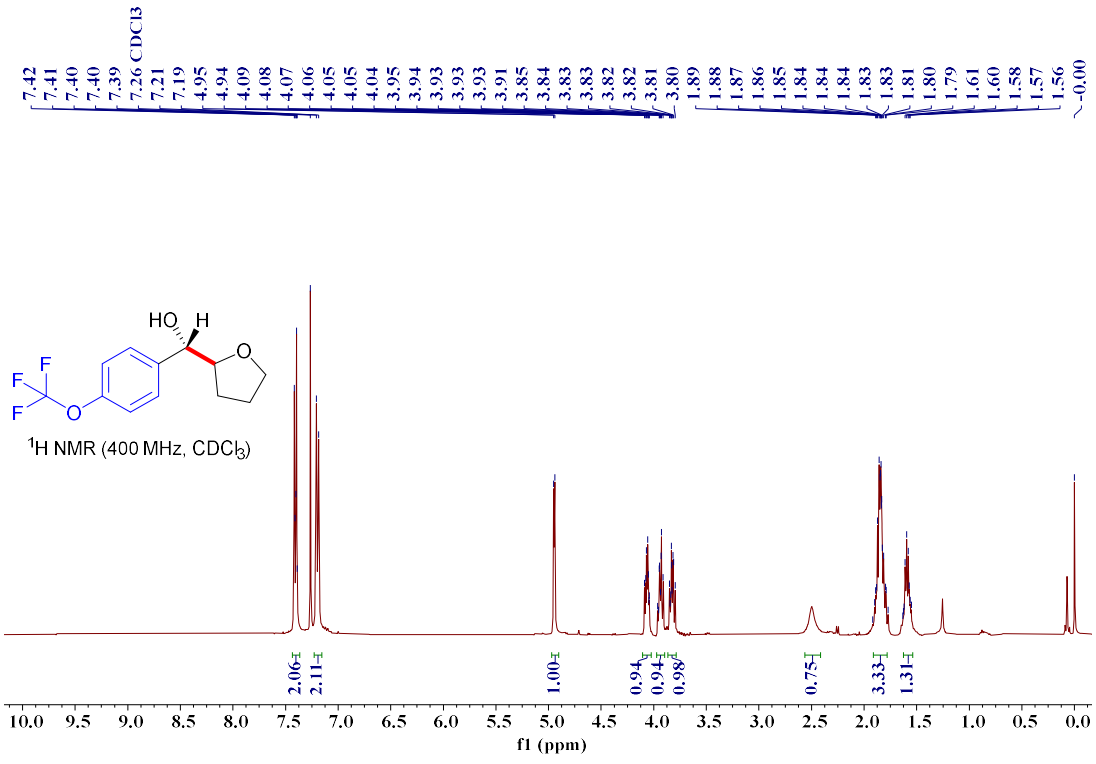
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *threo*-3s

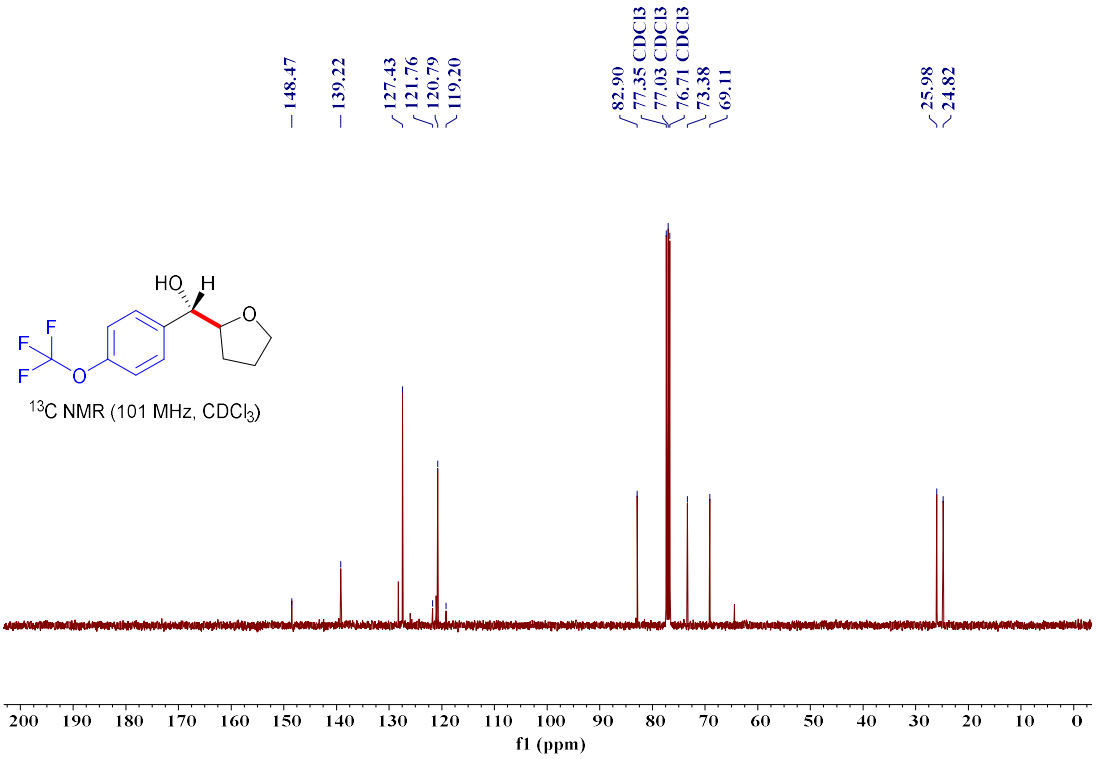


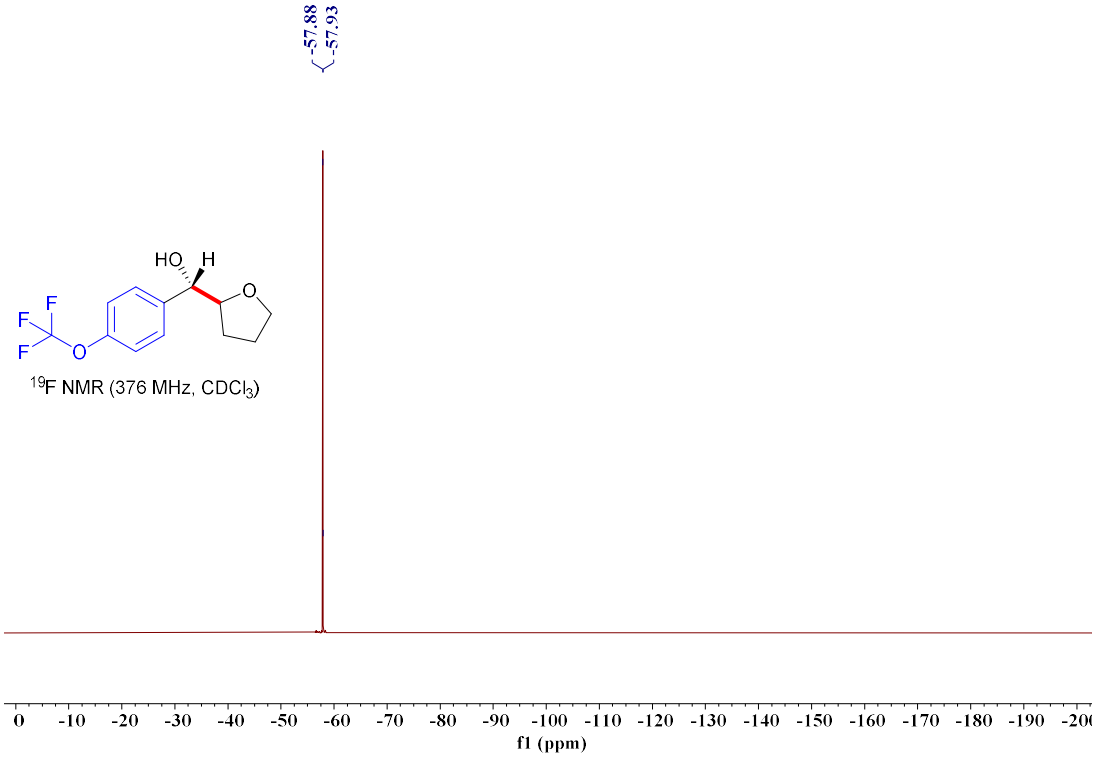




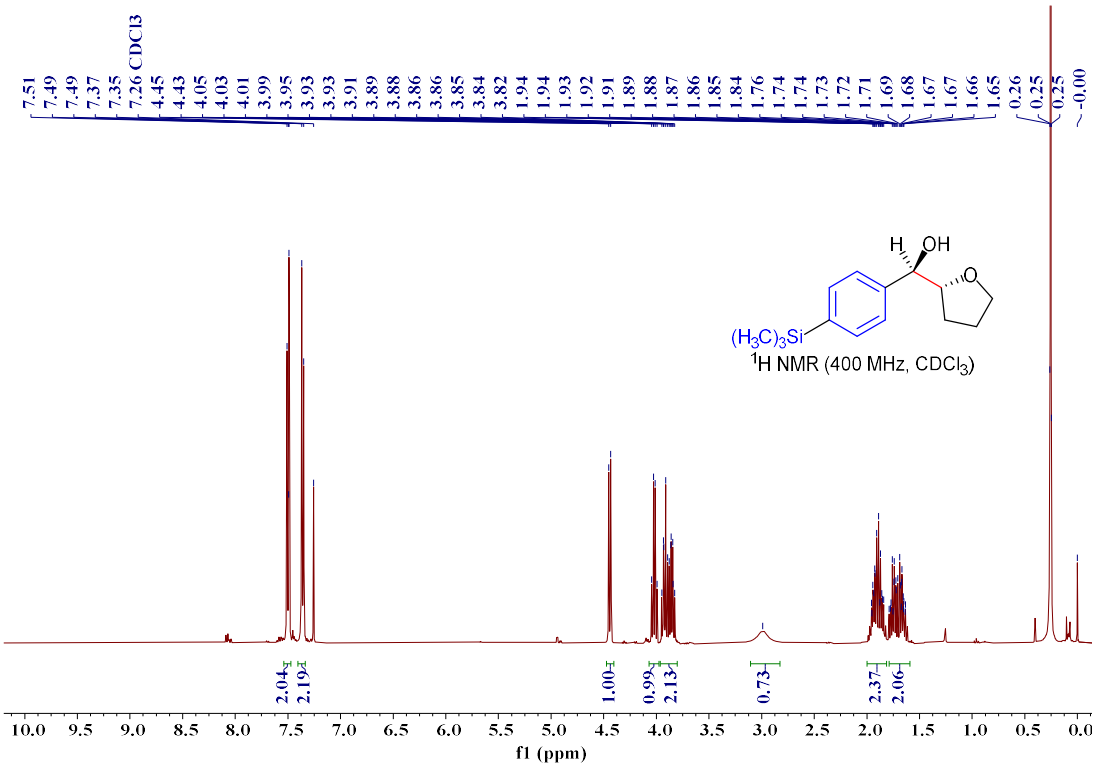
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *erythro*-3s

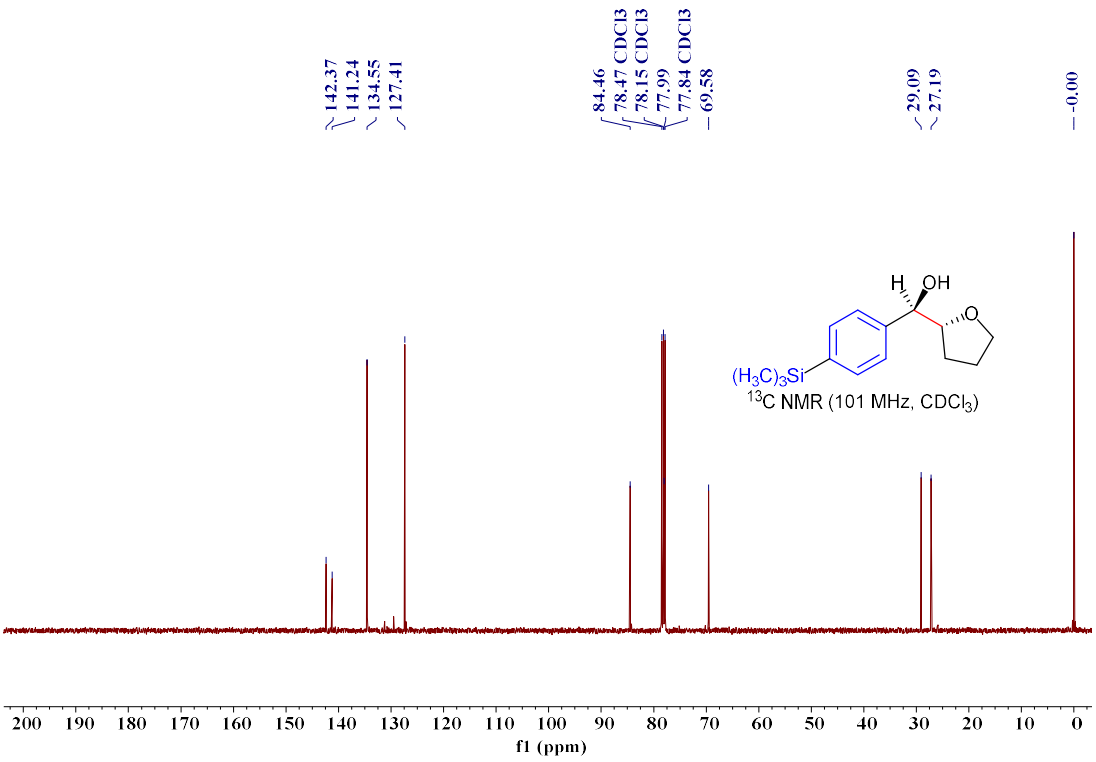



148.47
139.22
127.43
121.76
120.79
119.20
82.90
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
73.38
69.11
25.98
24.82
HO
H
O
F
F
F
O
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

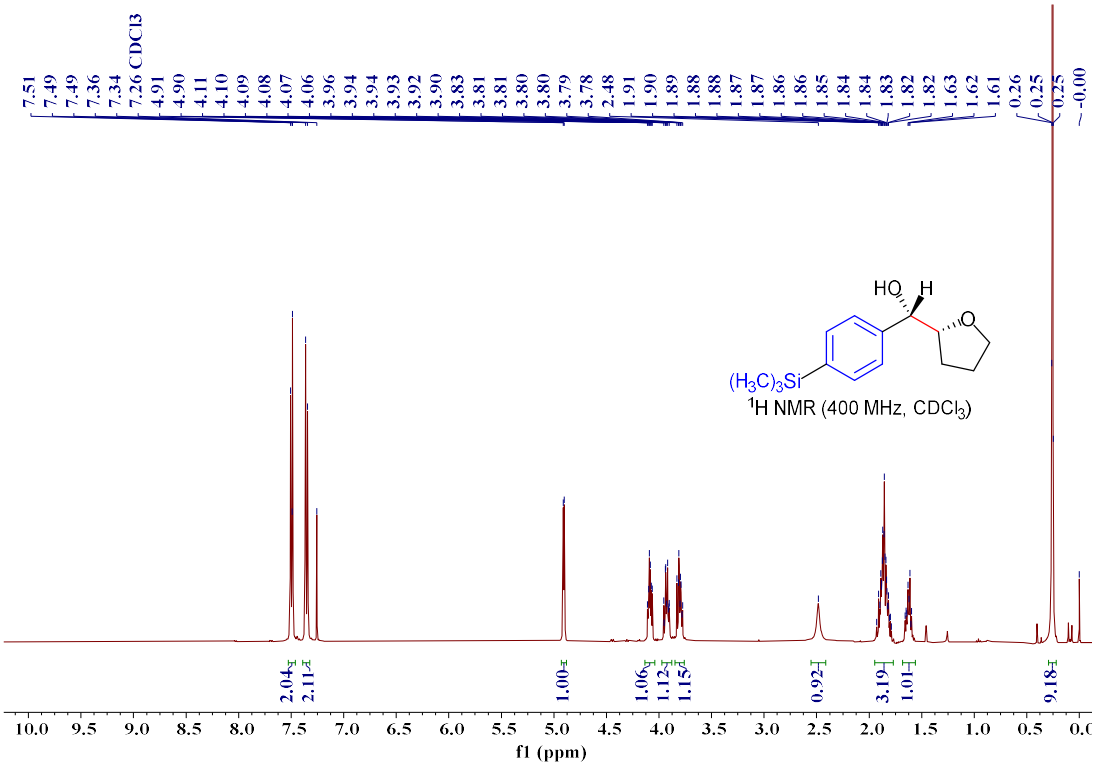

-57.88
-57.93
HO
H
O
F
F
F
O
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

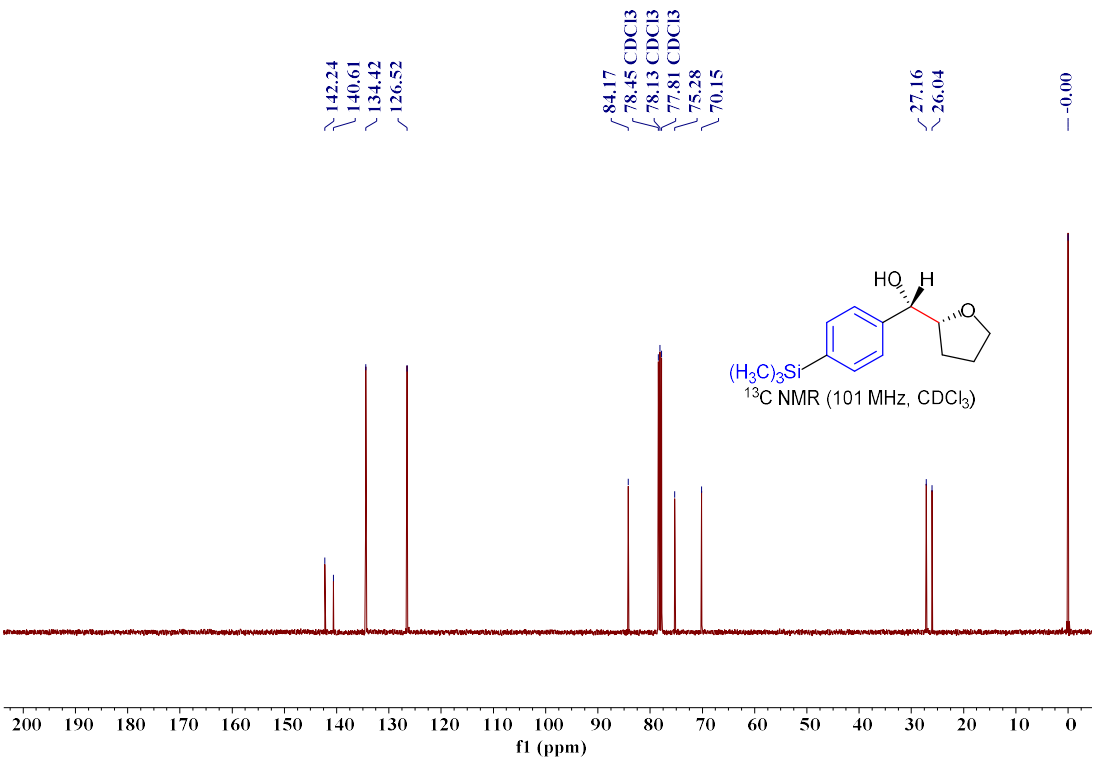
^{1}H, ^{13}C NMR spectra of compound *threo*-3t



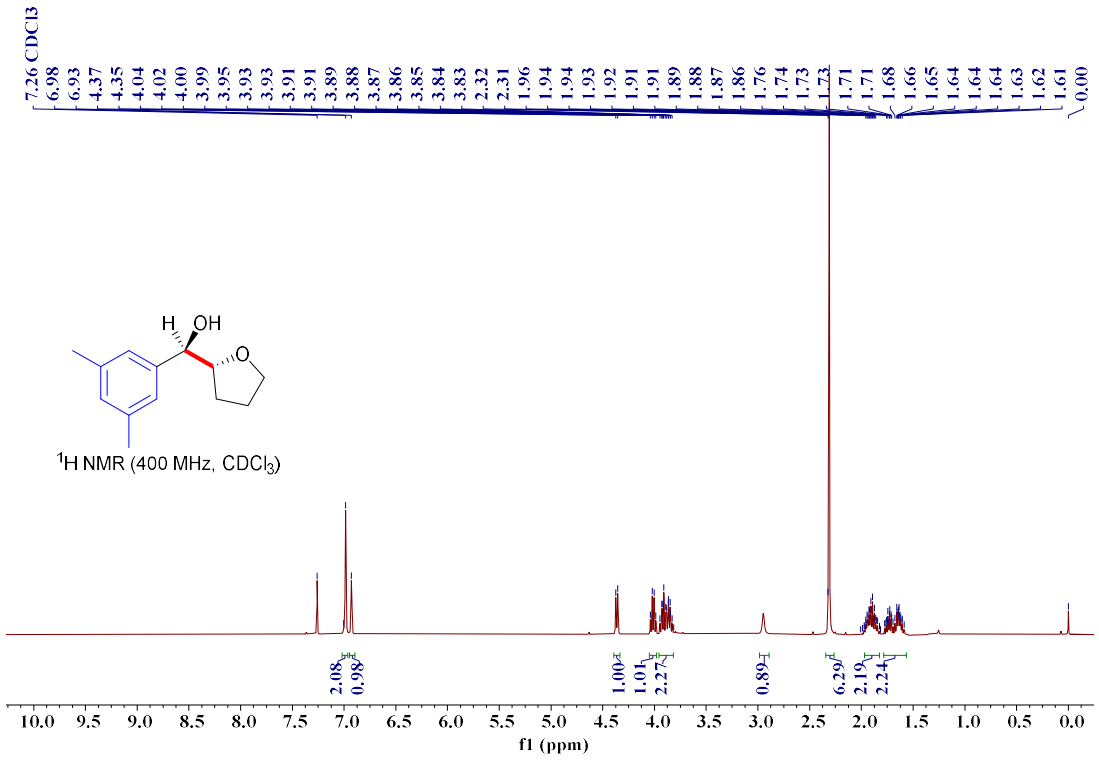


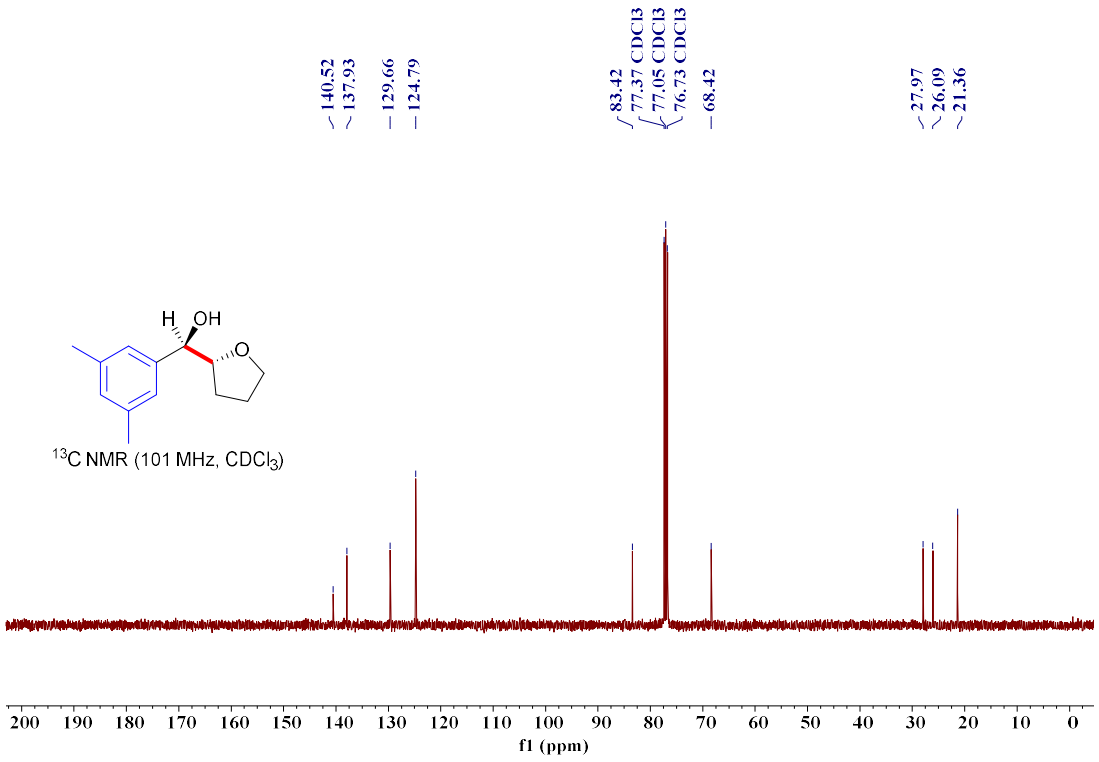
^{1}H, ^{13}C NMR spectra of compound *erythro*-3t



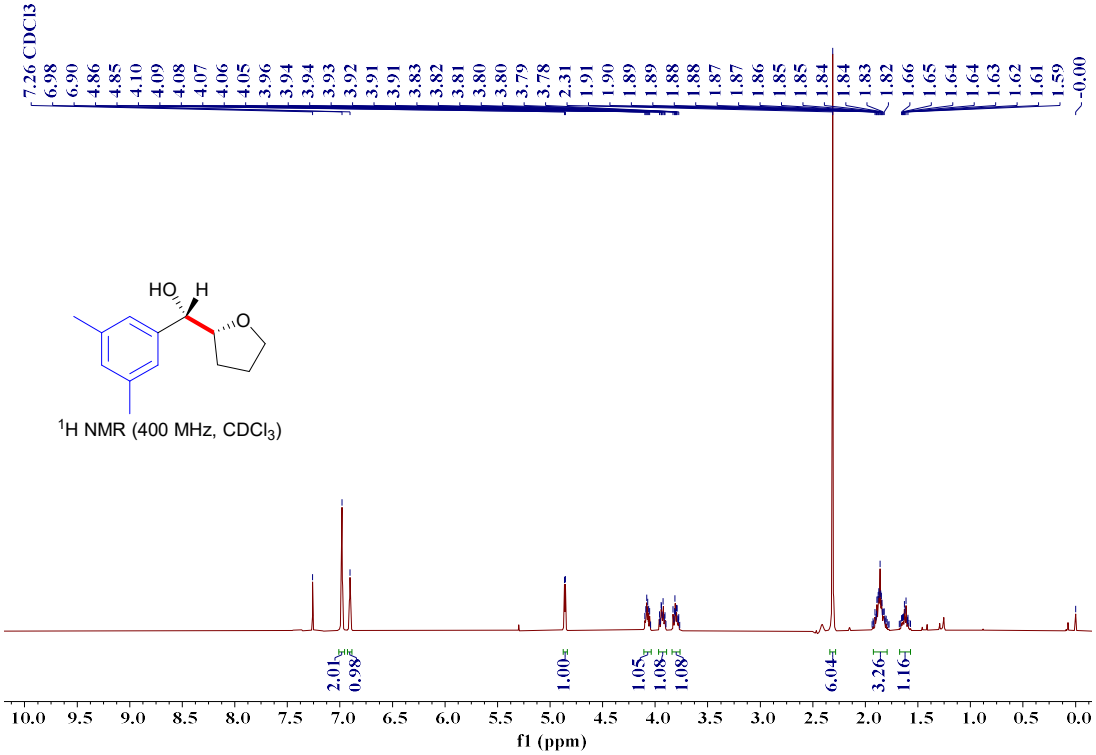


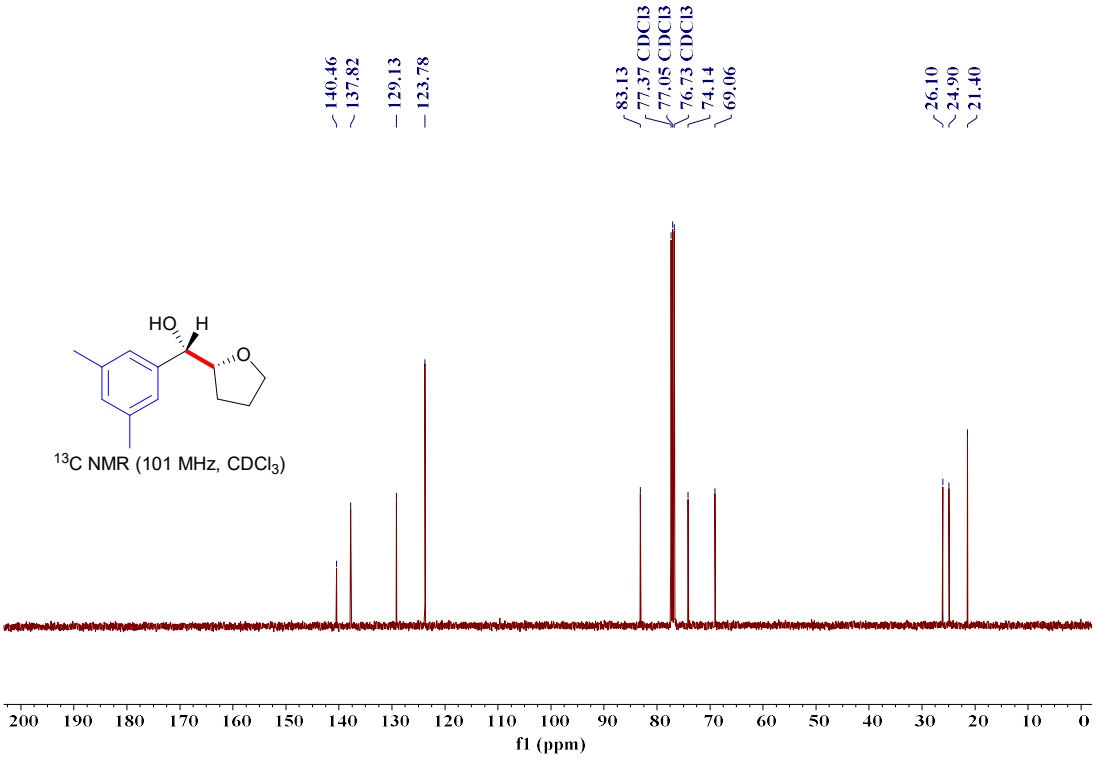
^{1}H and ^{13}C NMR spectra of compound *threo*-3u



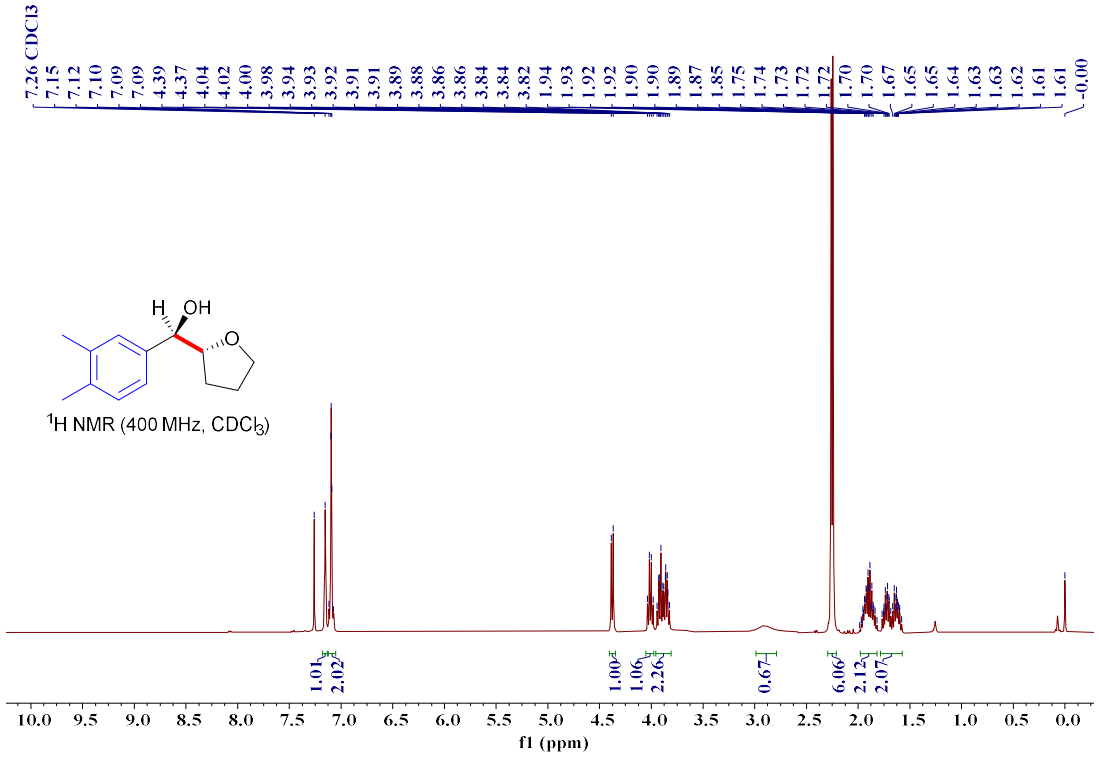


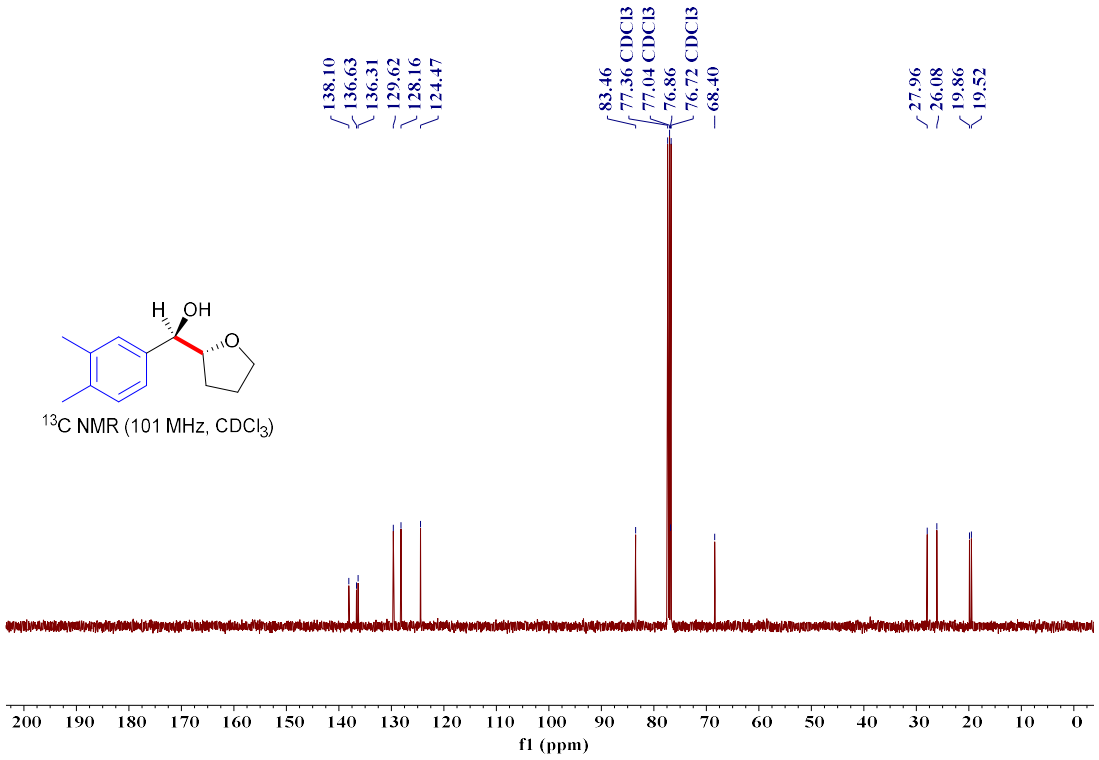
^{1}H and ^{13}C NMR spectra of compound *erythro*-3u



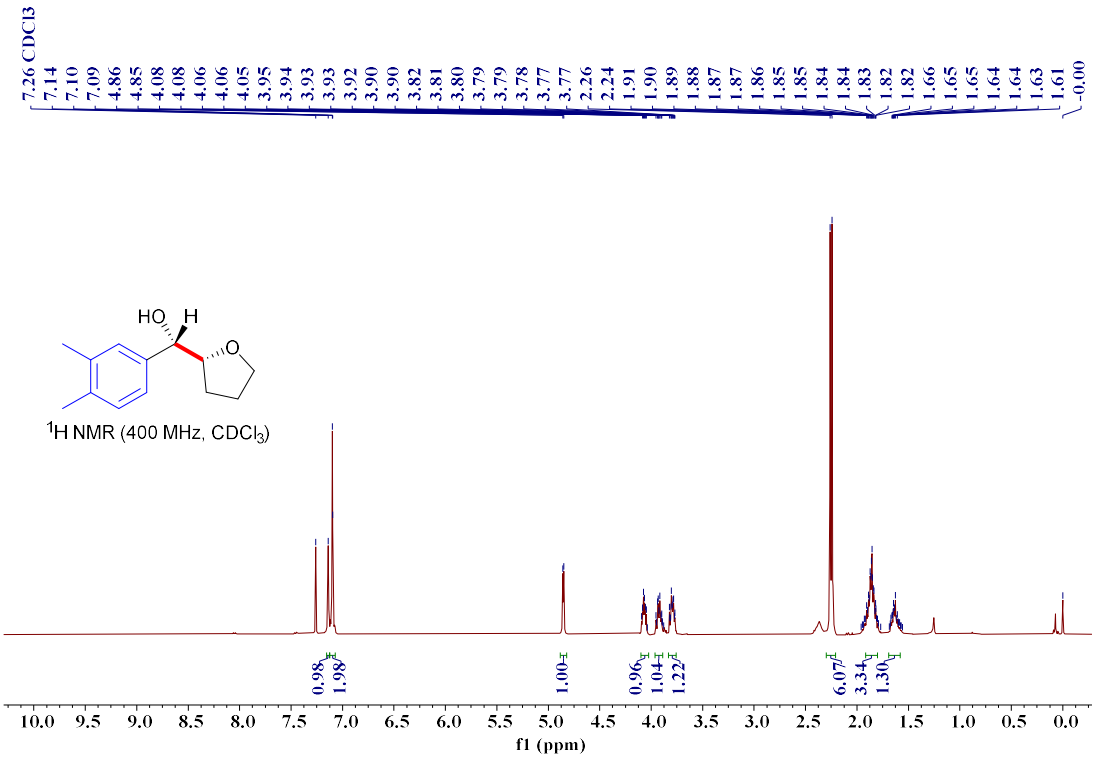


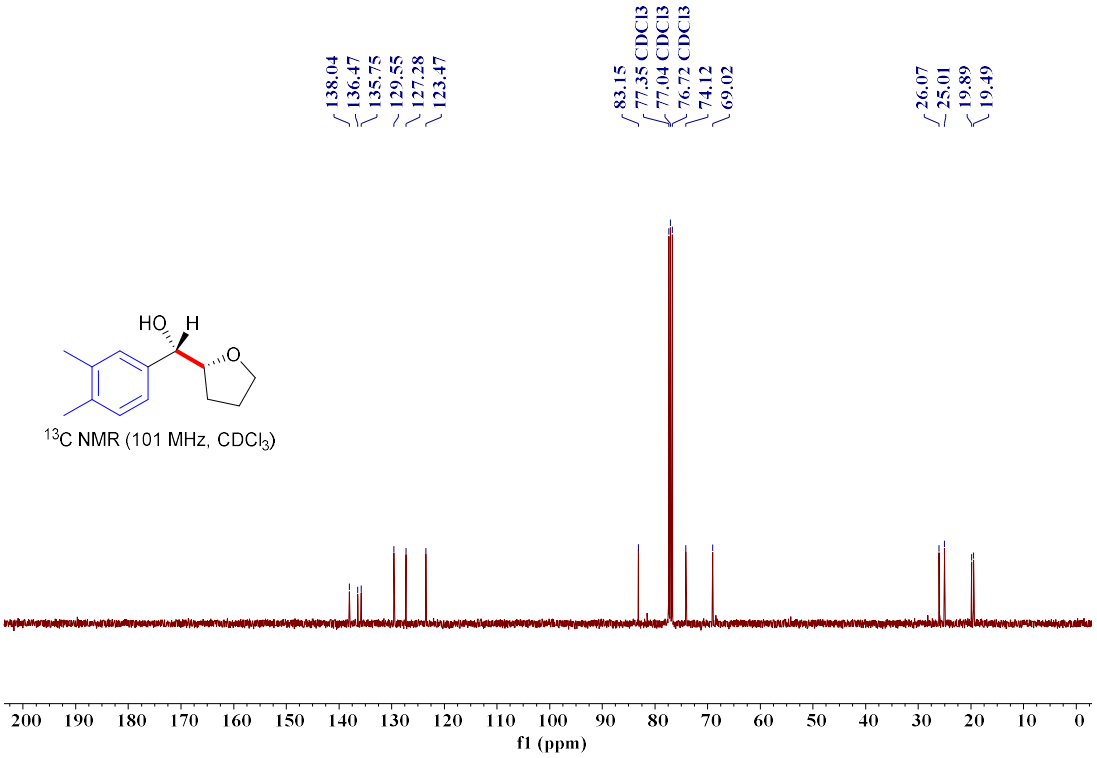
^{1}H and ^{13}C NMR spectra of compound *threo*-3v



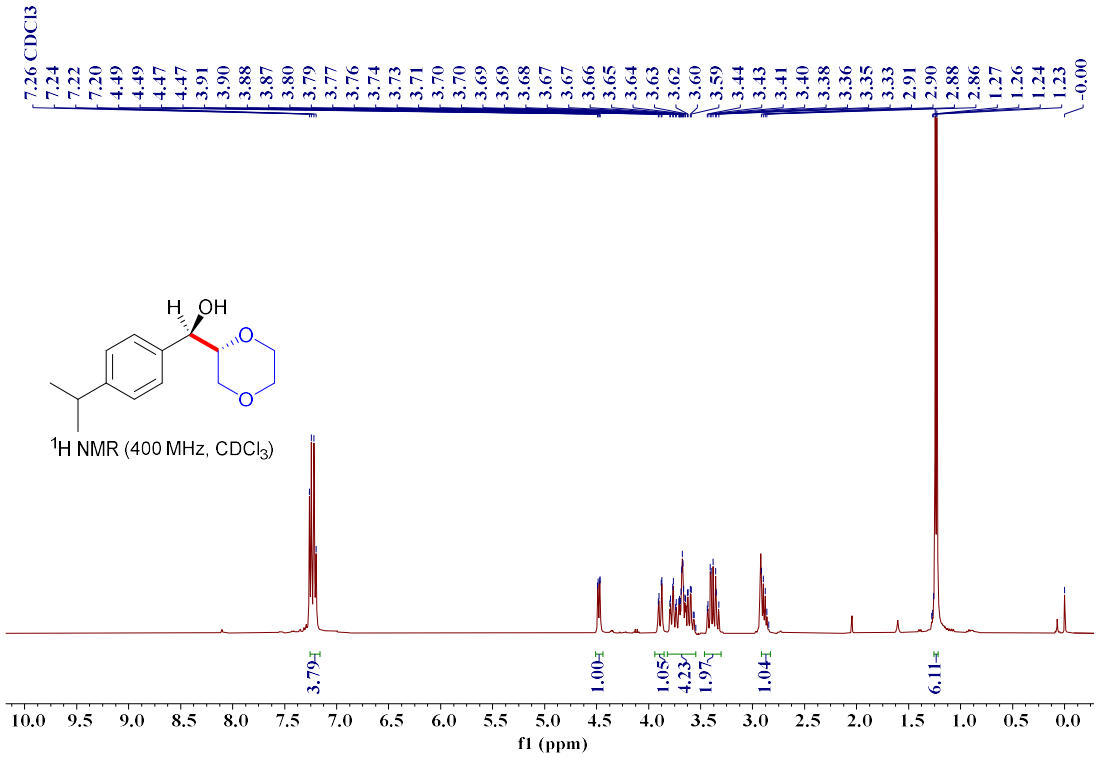


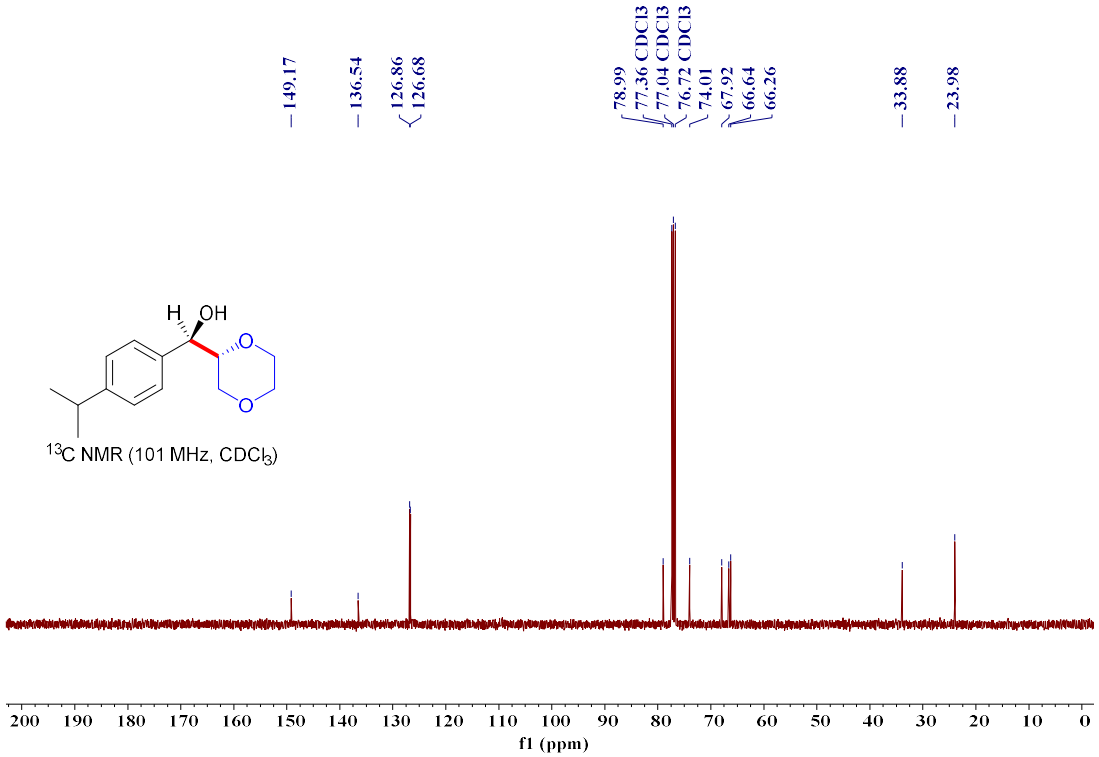
^{1}H and ^{13}C NMR spectra of compound *erythro*-3v



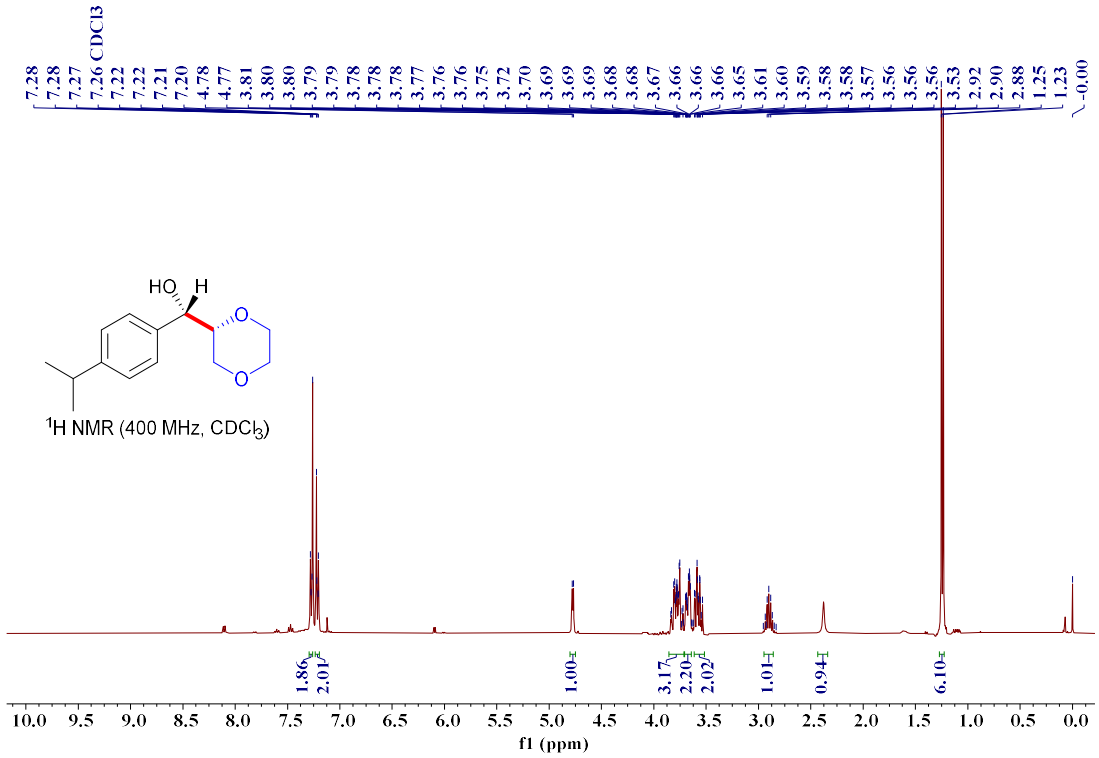


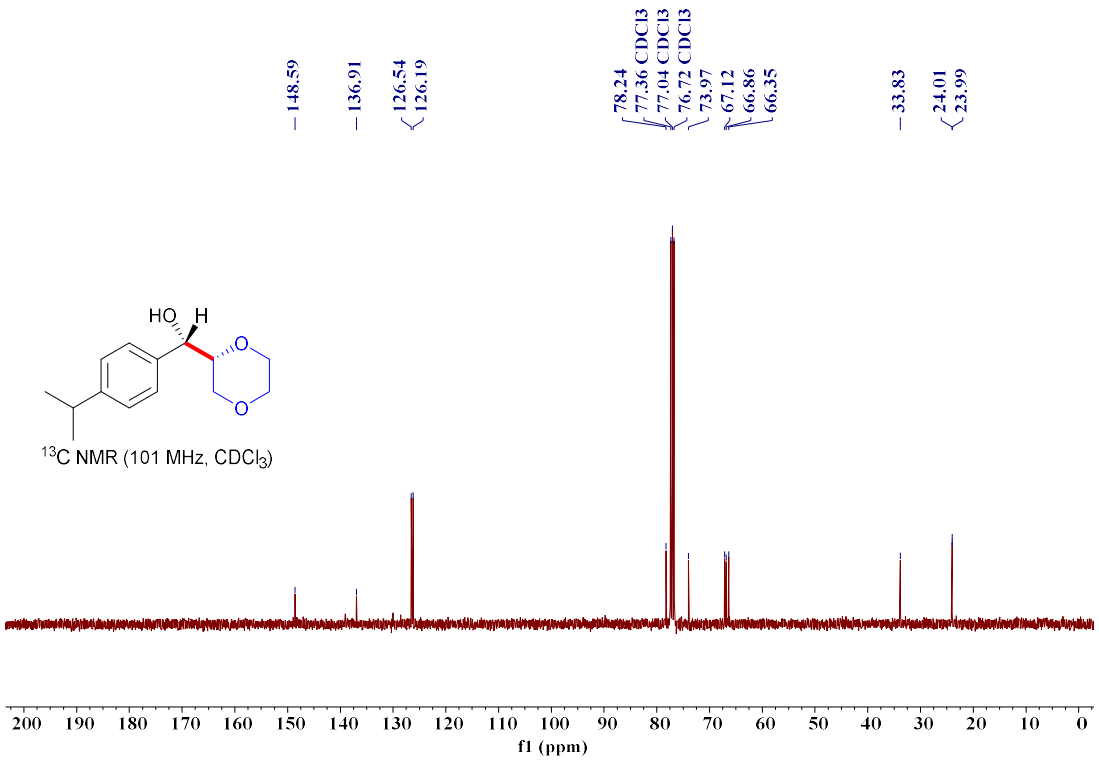
^{1}H and ^{13}C NMR spectra of compound *threo*-3w



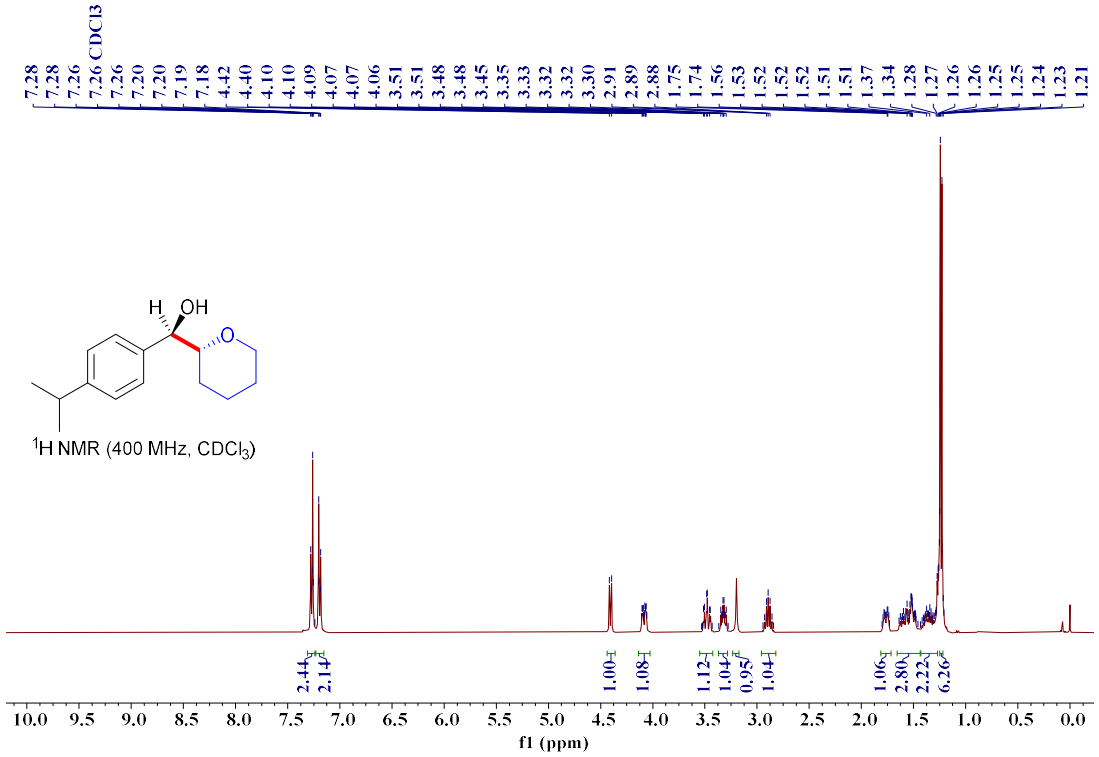


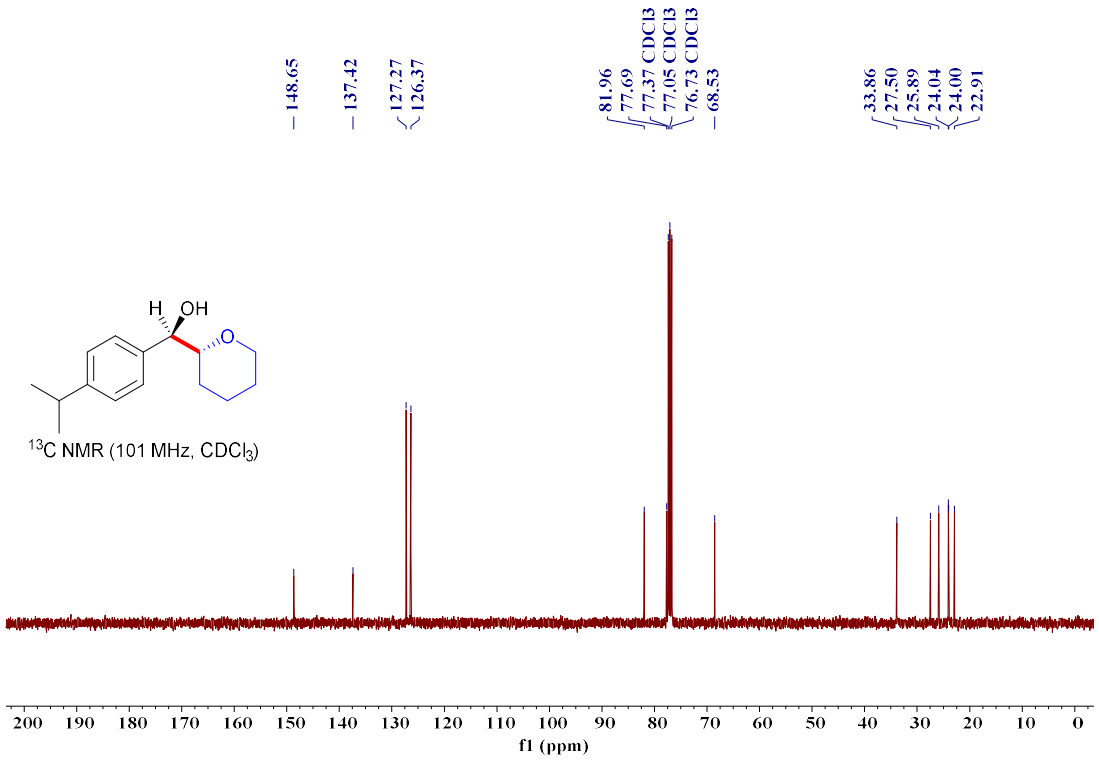
^{1}H and ^{13}C NMR spectra of compound *erythro*-3w



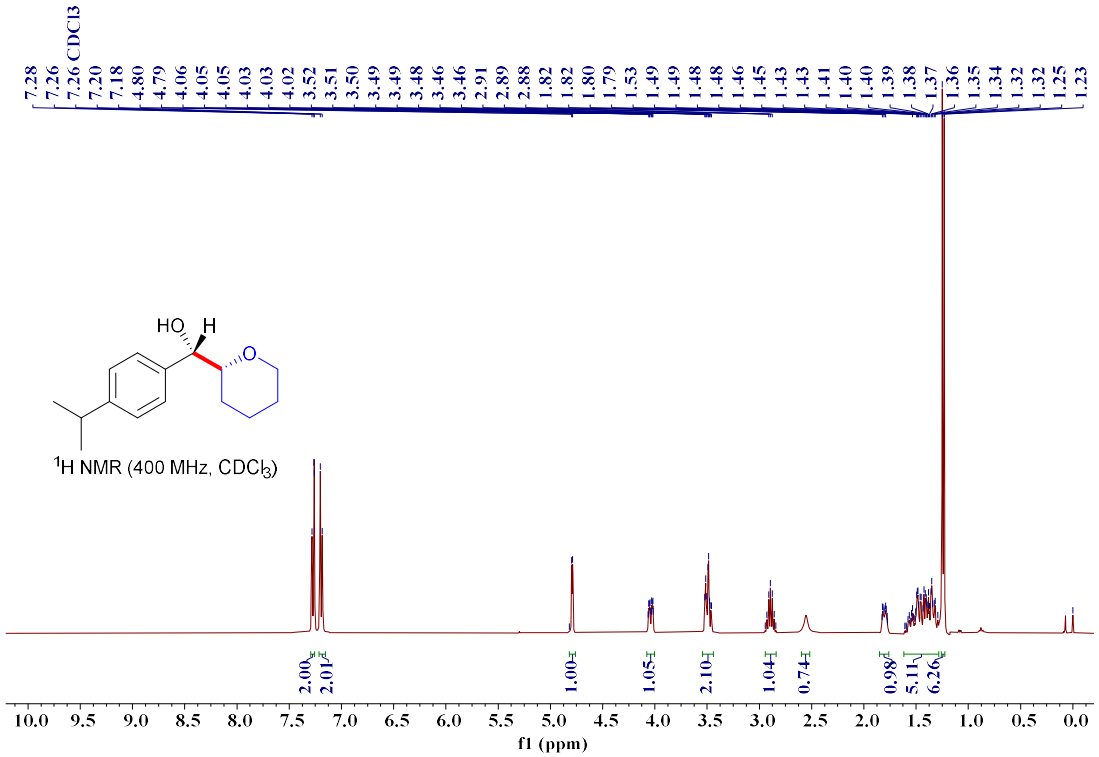


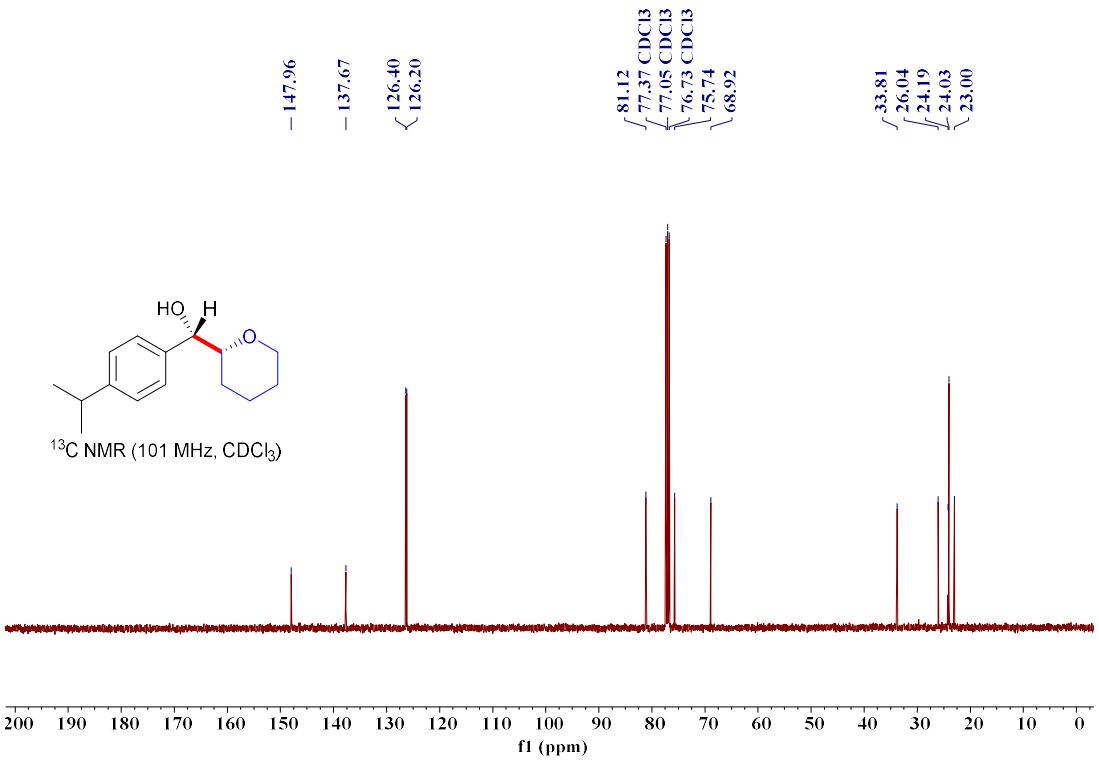
^{1}H and ^{13}C NMR spectra of compound *threo*-3x



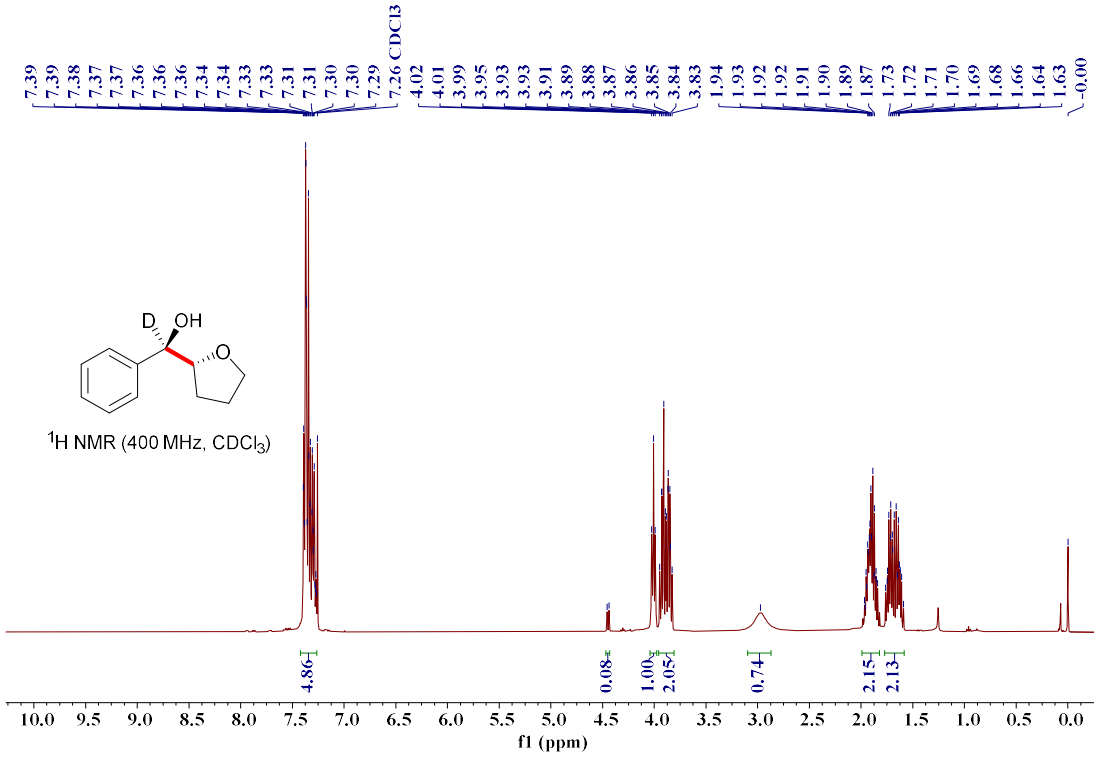


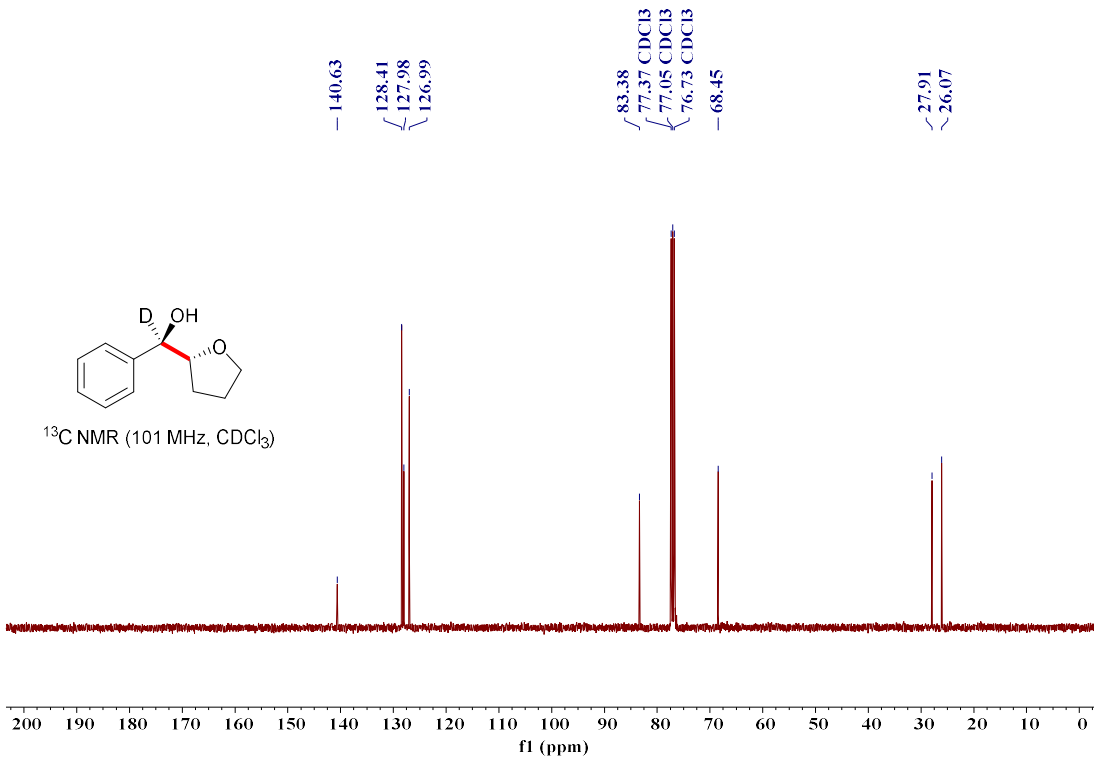
^{1}H and ^{13}C NMR spectra of compound *erythro*-3x



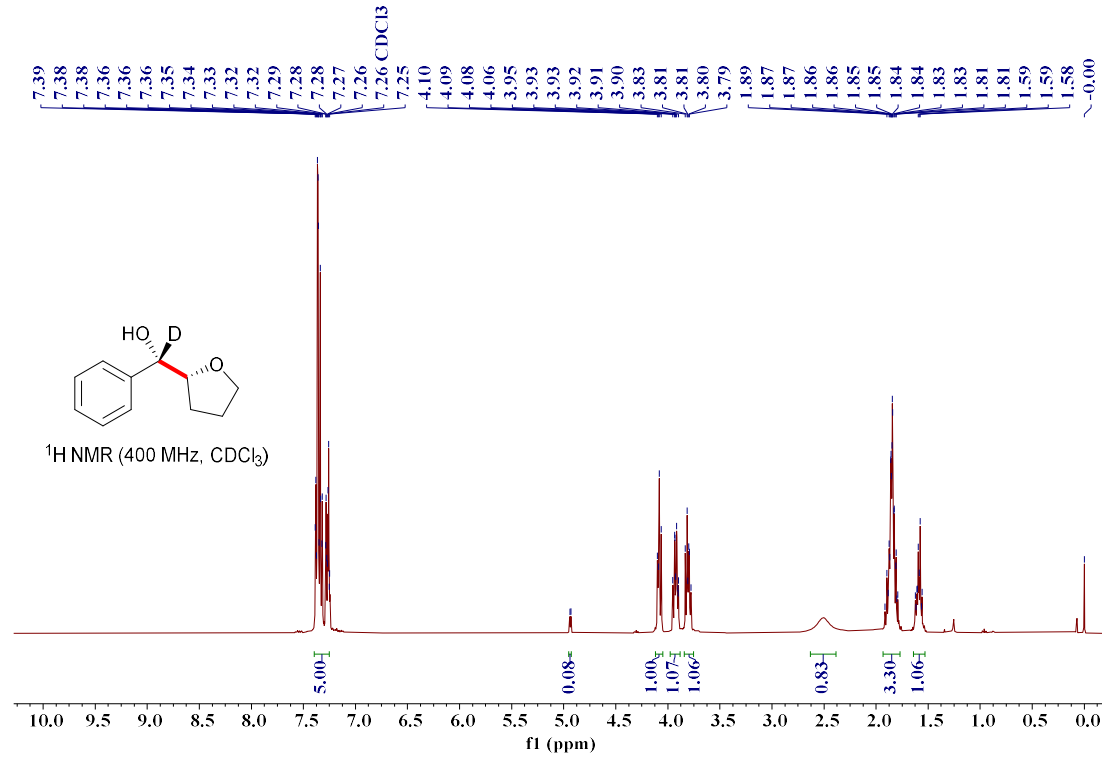


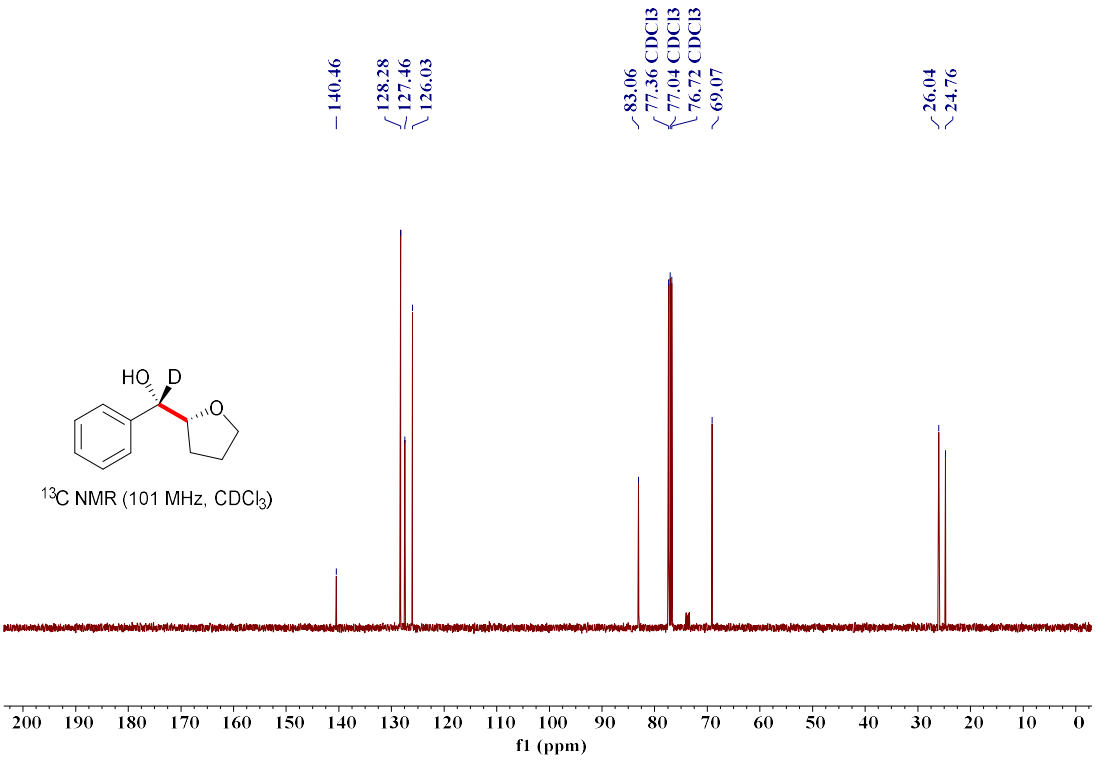
^{1}H and ^{13}C NMR spectra of compound [D]*threo*-3a





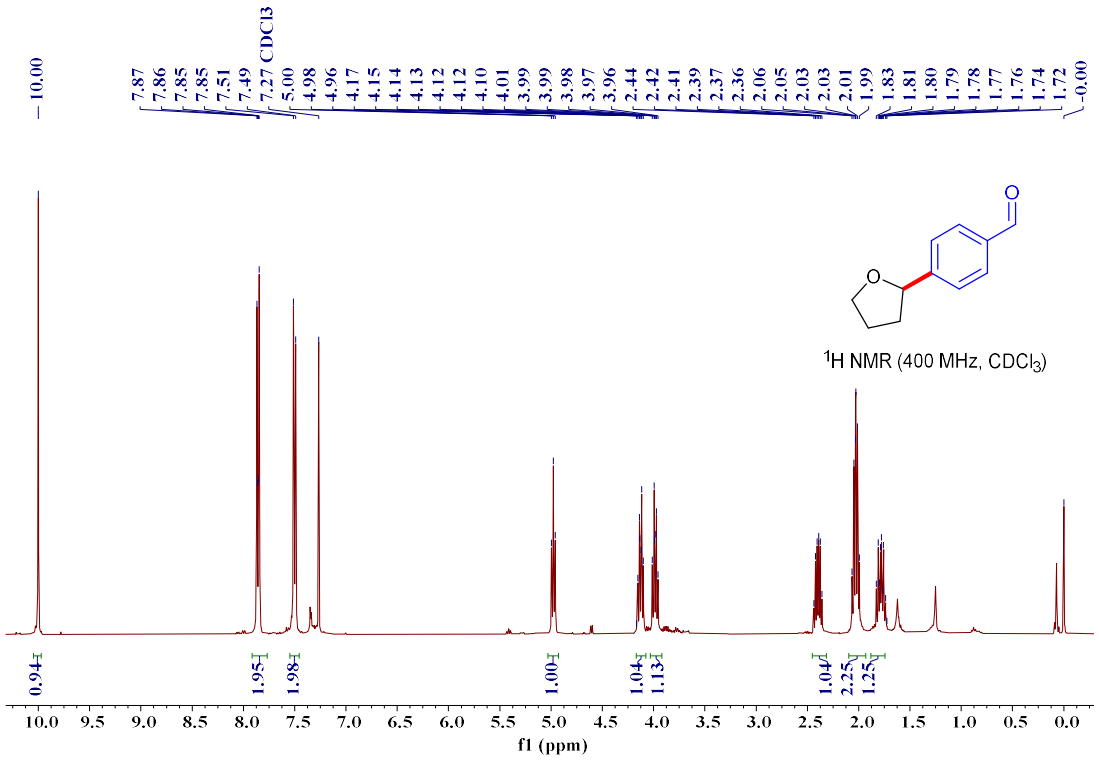
^{1}H and ^{13}C NMR spectra of compound [D]*erythro*-3a

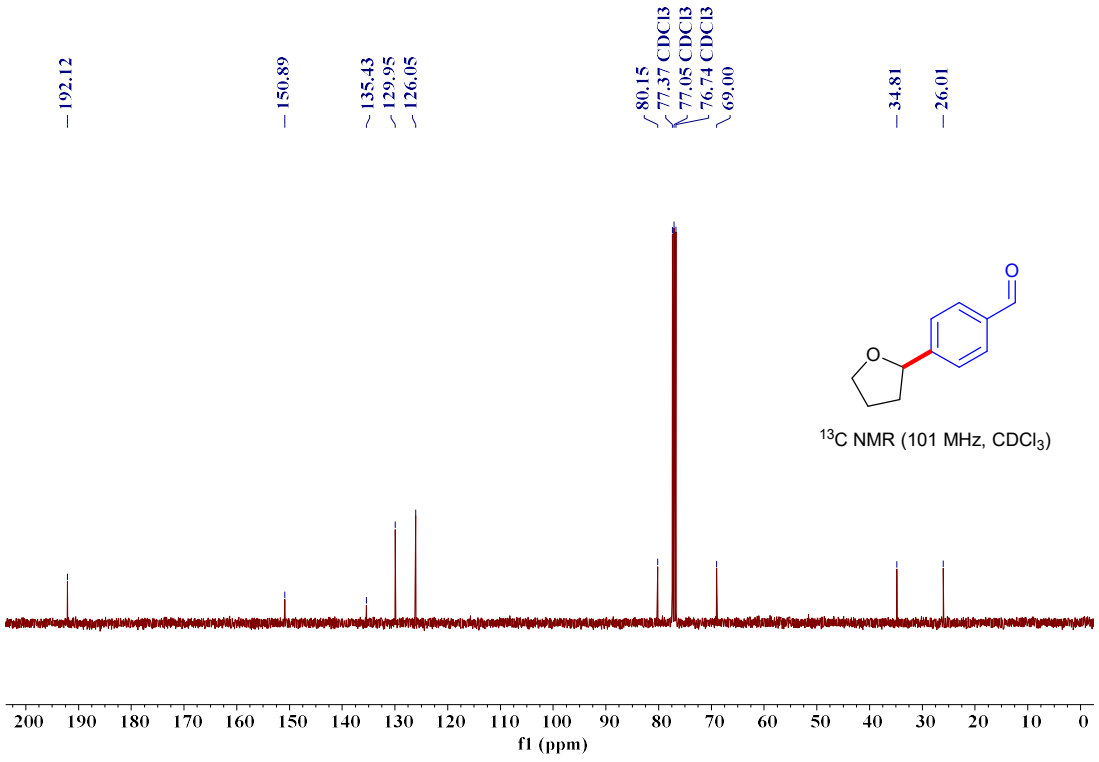




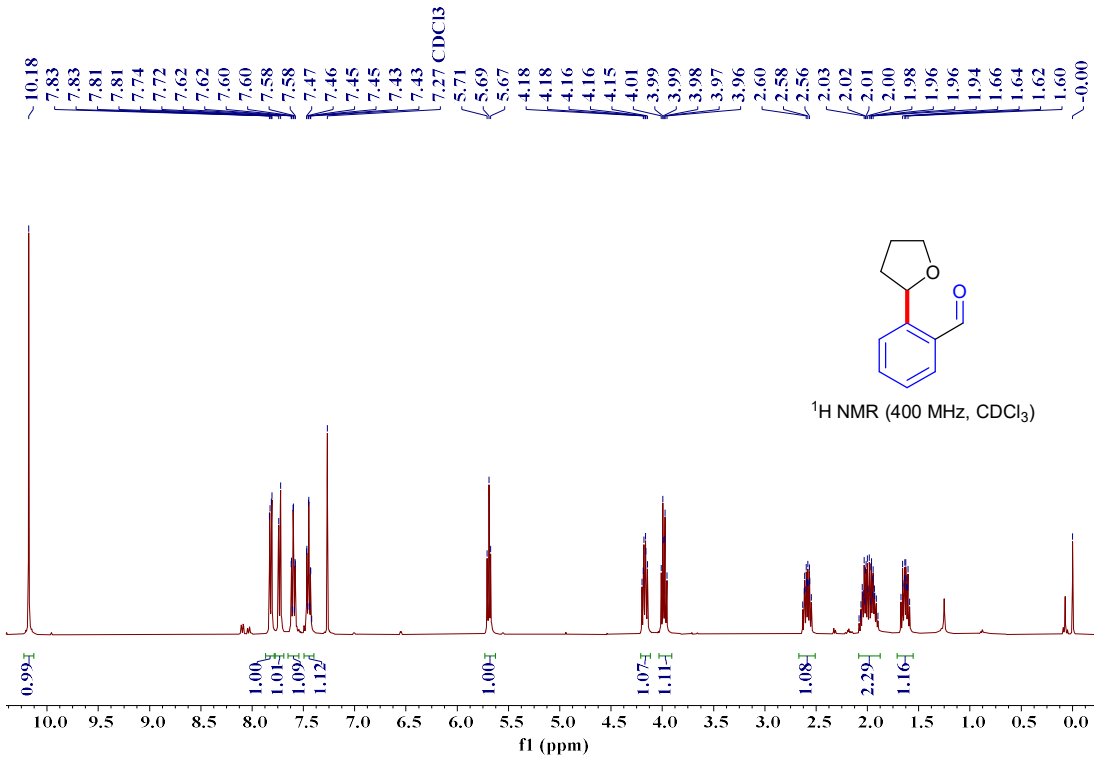
3. Copies of NMR Spectra of the Dehydrogenative Coupling Reaction Products

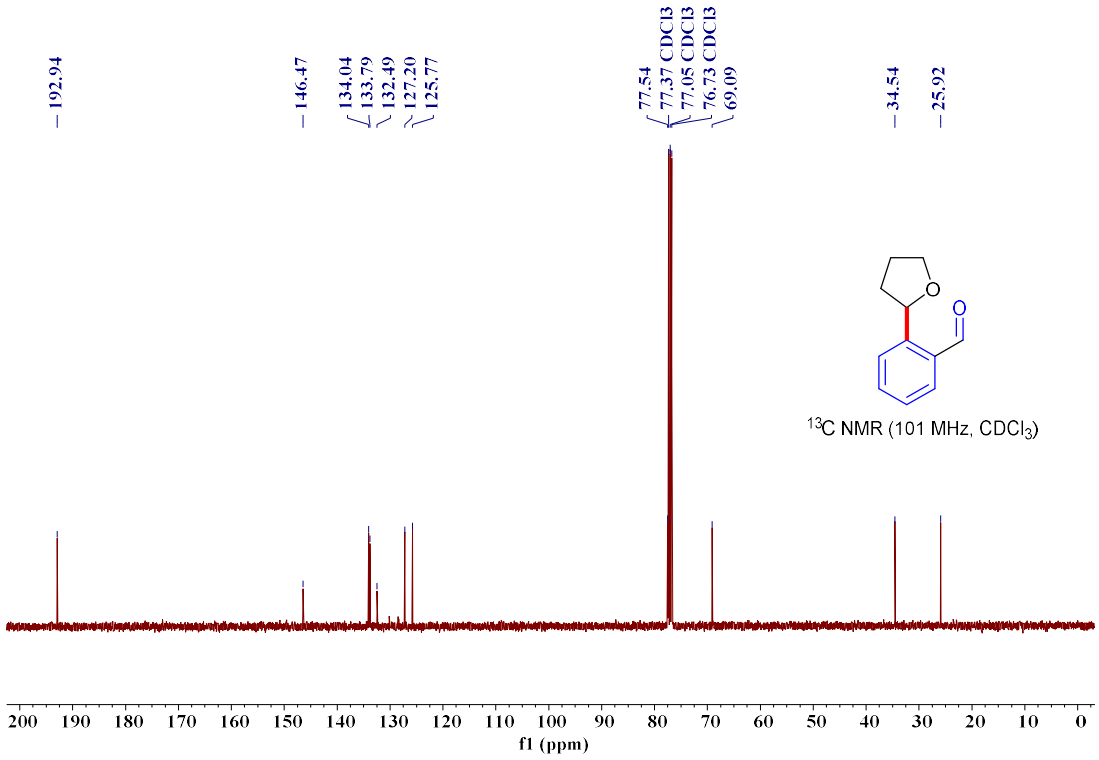
^{1}H and ^{13}C NMR spectra of compound *para*-4a



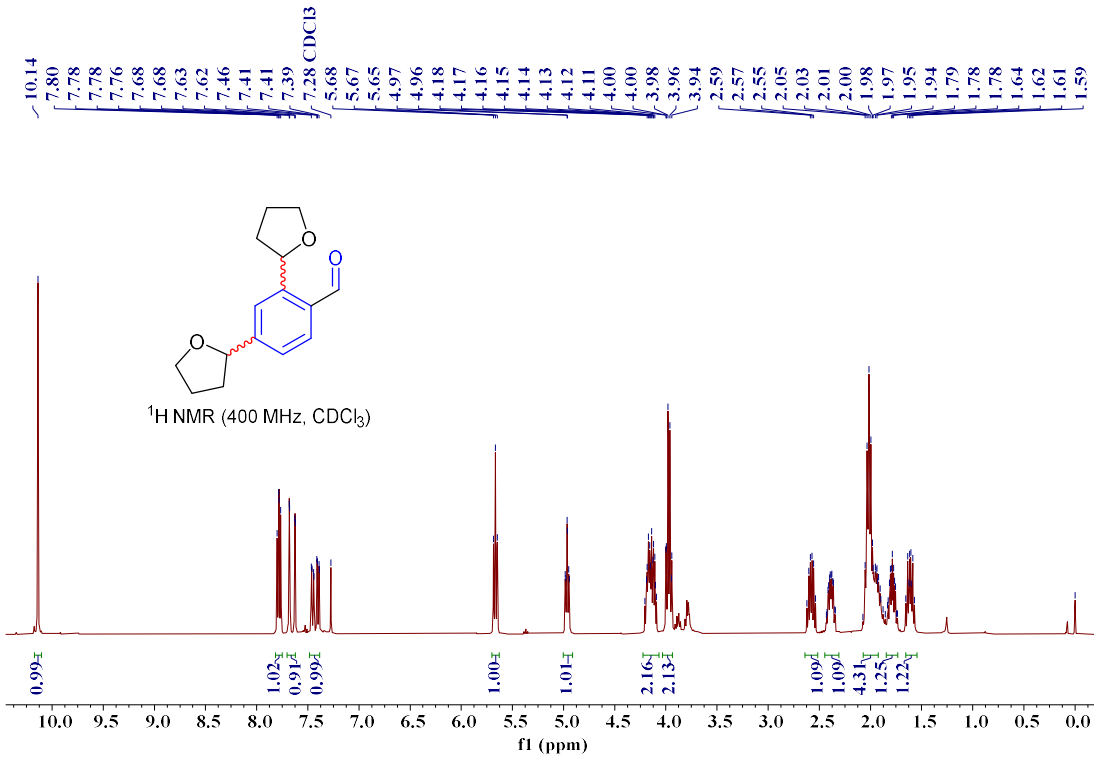


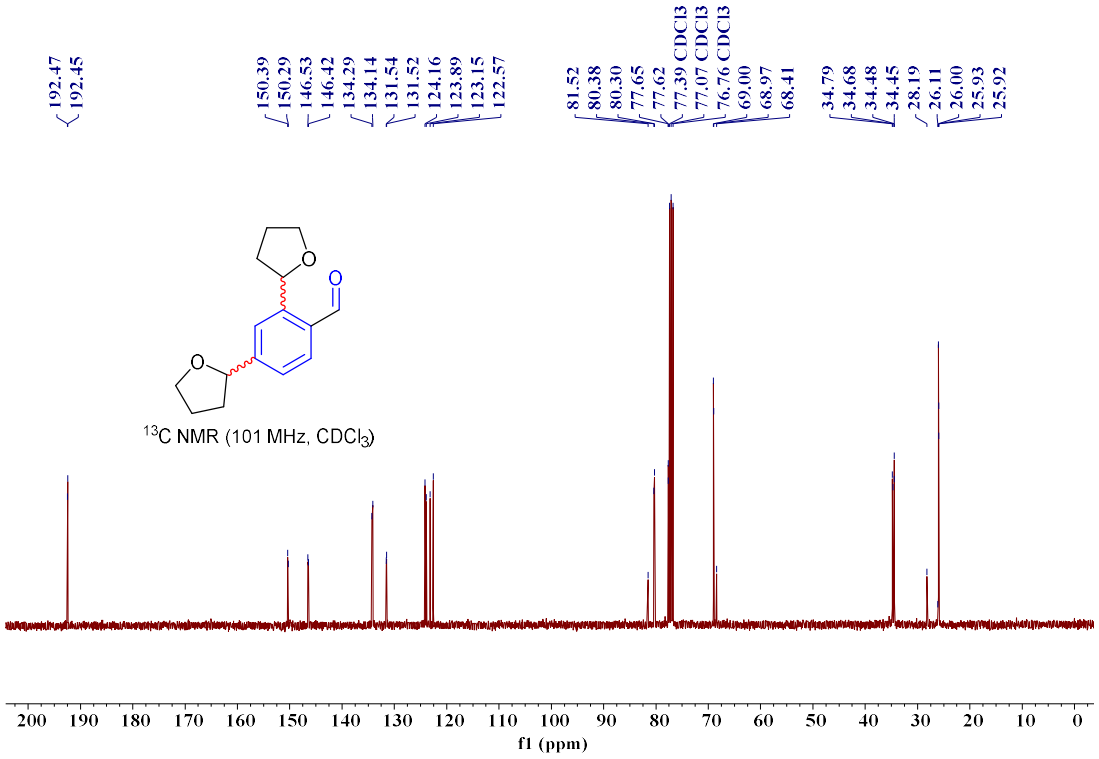
^{1}H and ^{13}C NMR spectra of compound *ortho*-4a



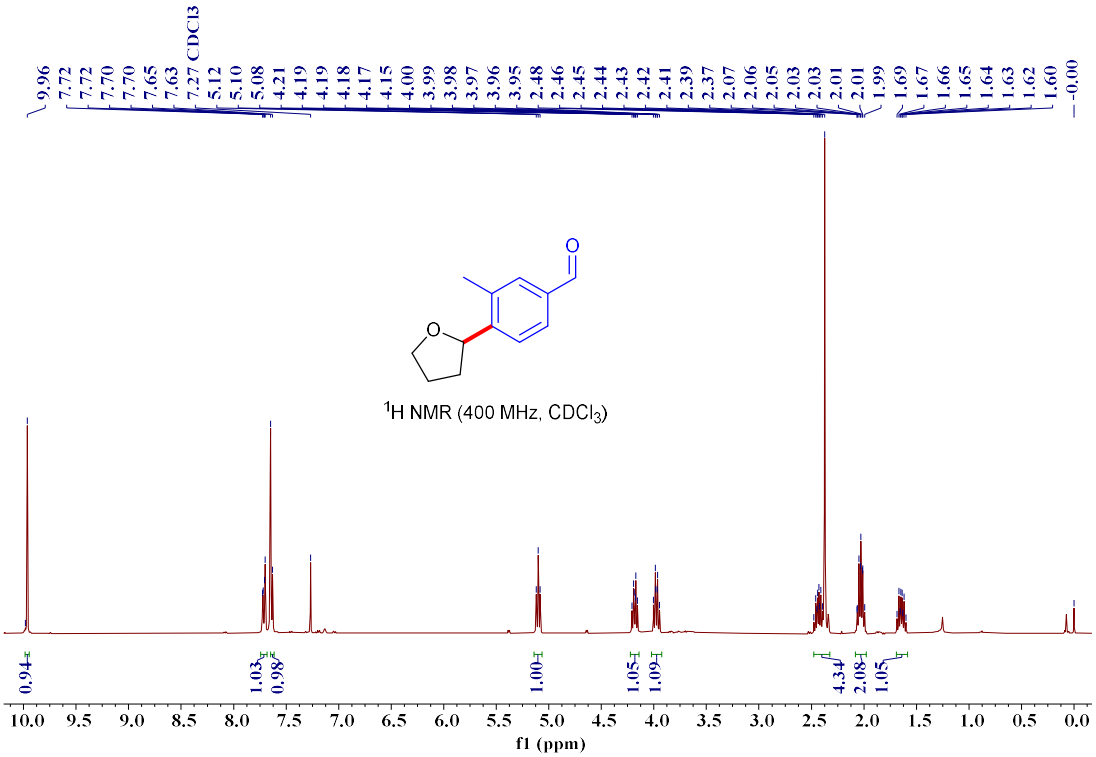


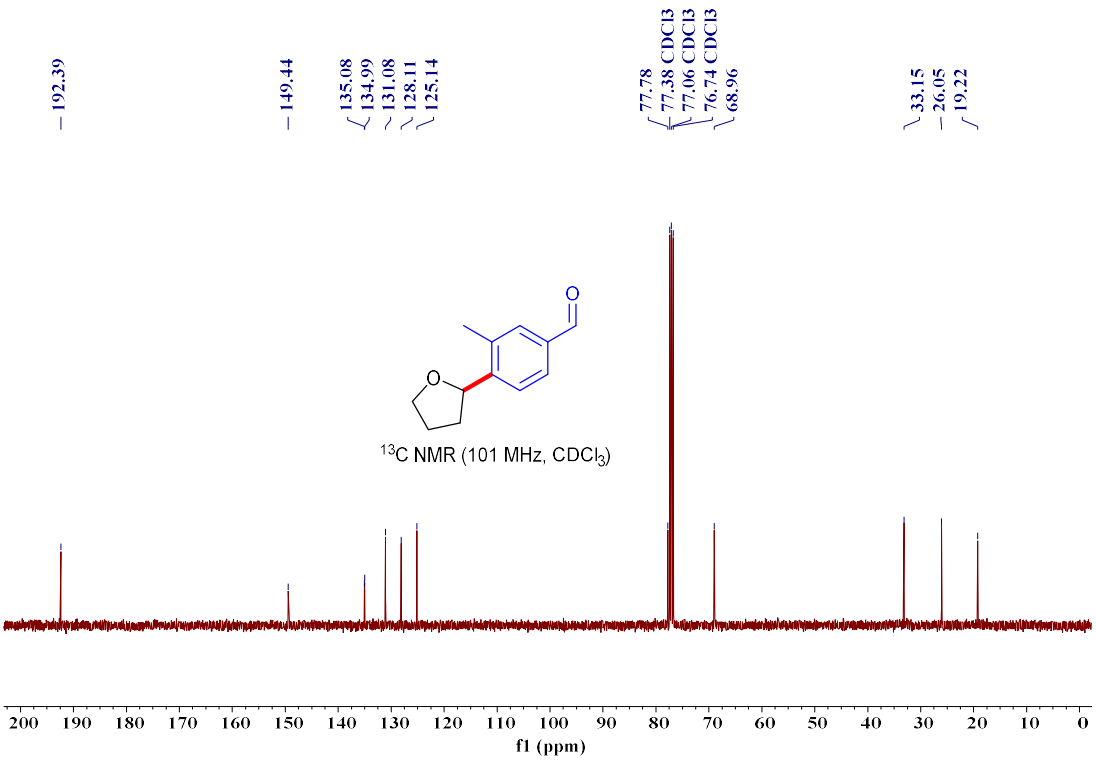
^{1}H and ^{13}C NMR spectra of compound *2,4-disubstituted*-4a



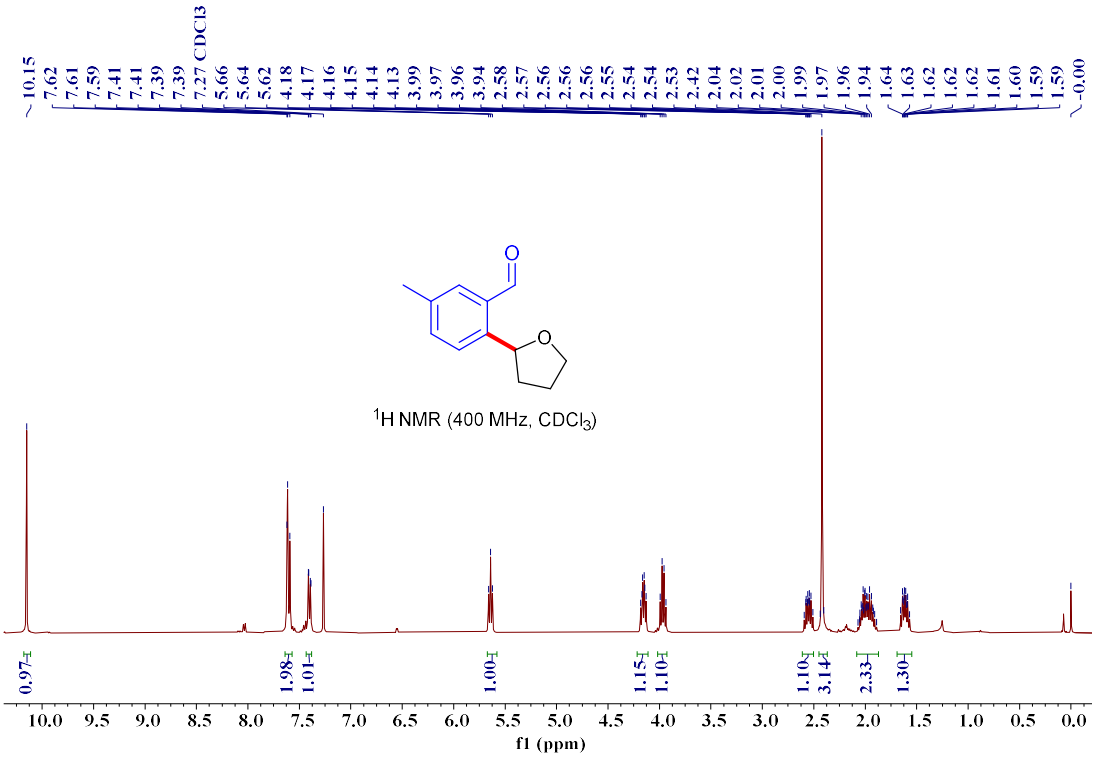


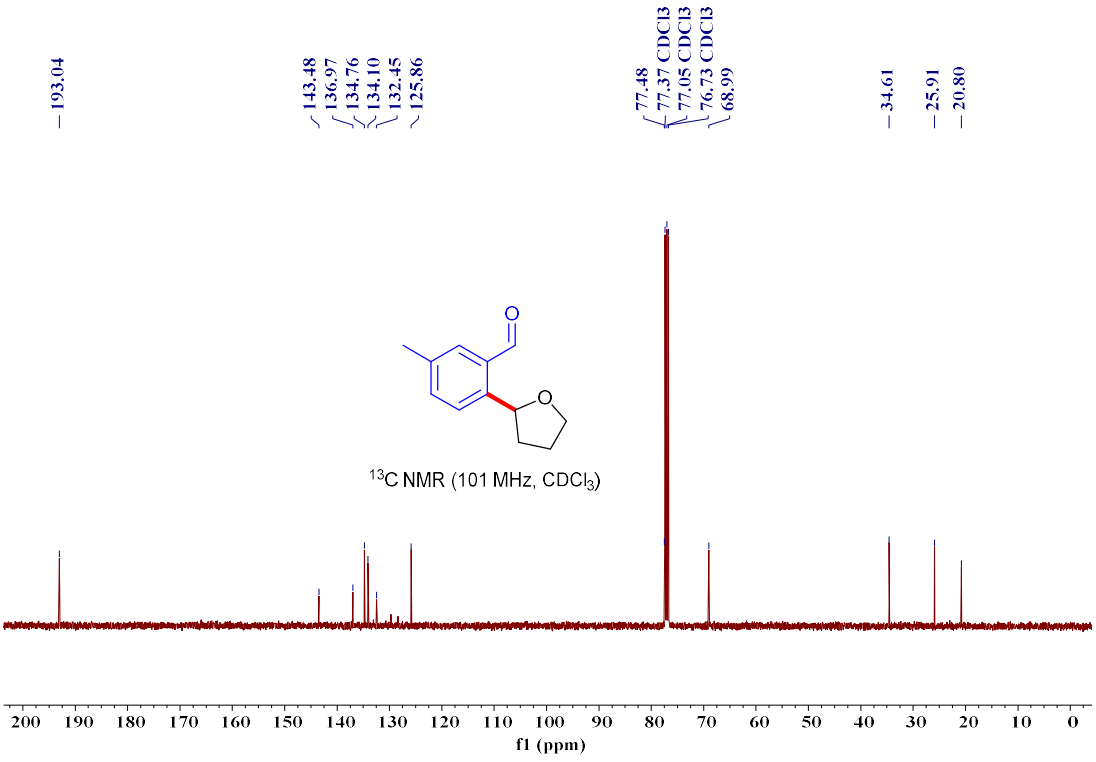
^{1}H and ^{13}C NMR spectra of compound *para*-4b



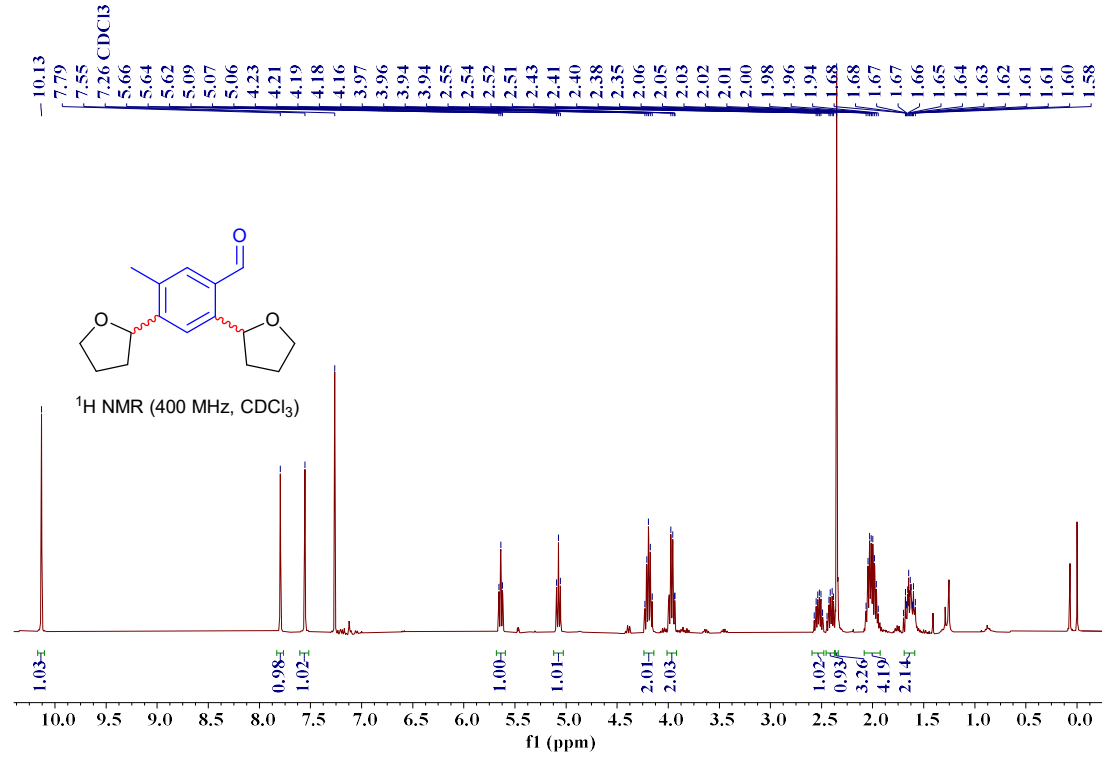


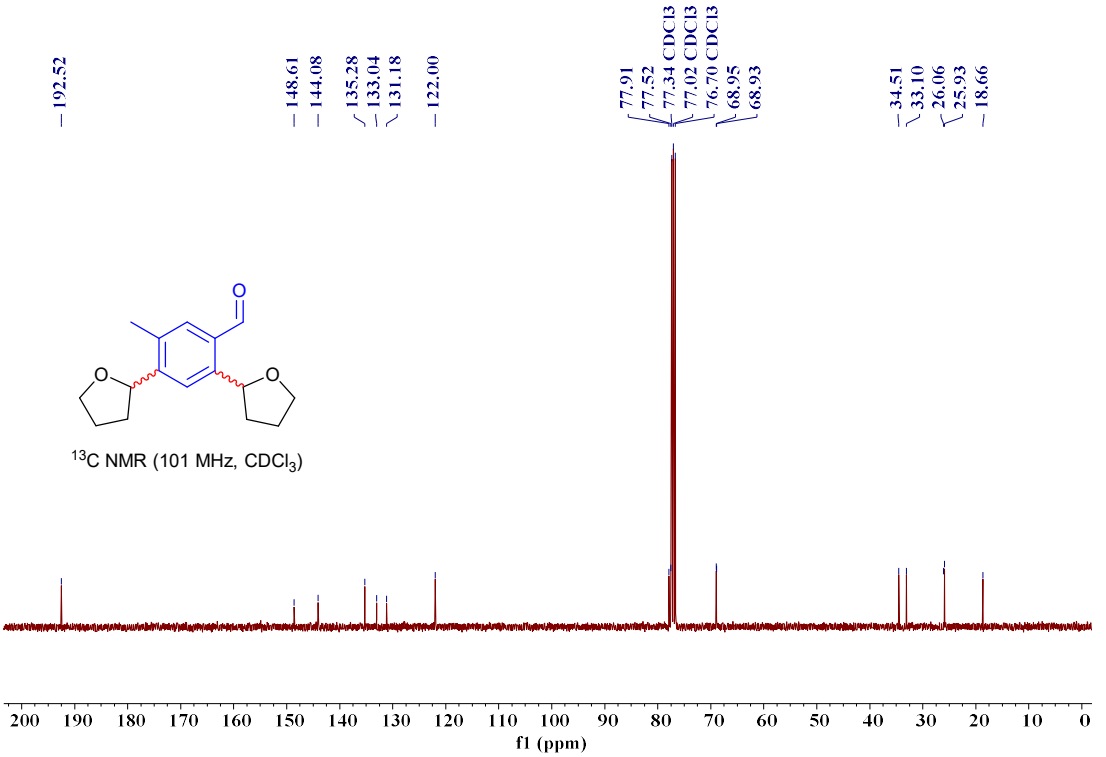
1H and 13C NMR spectra of compound *ortho*-4b



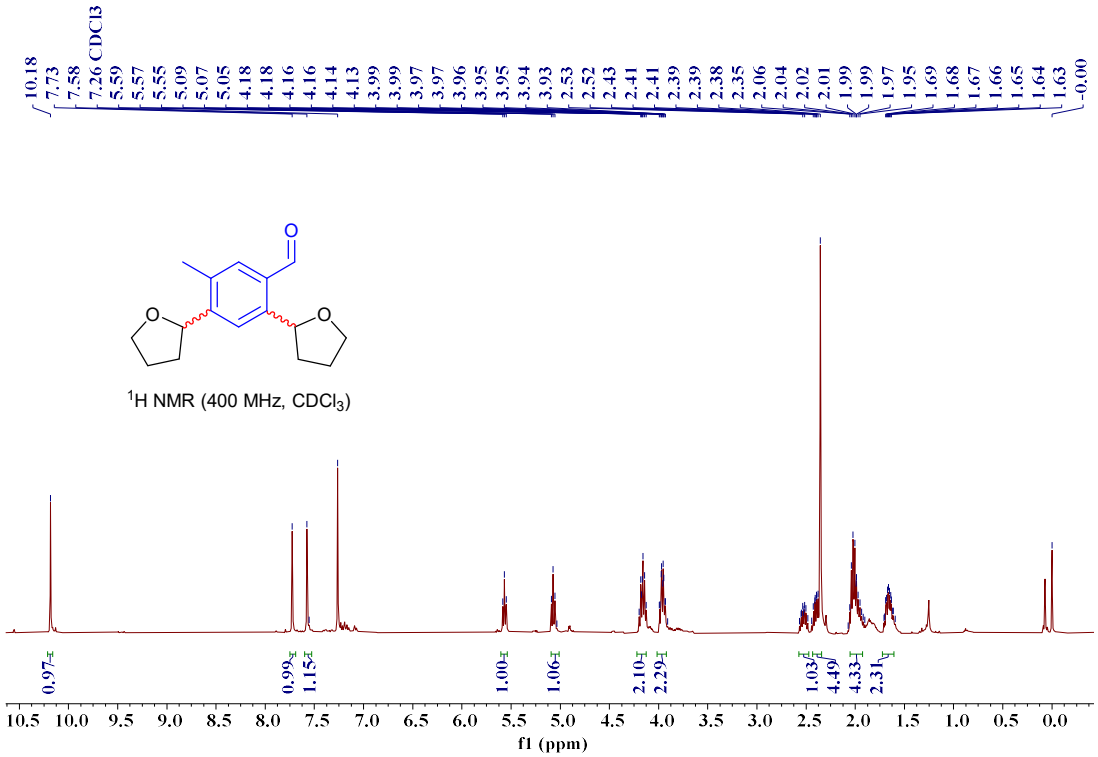


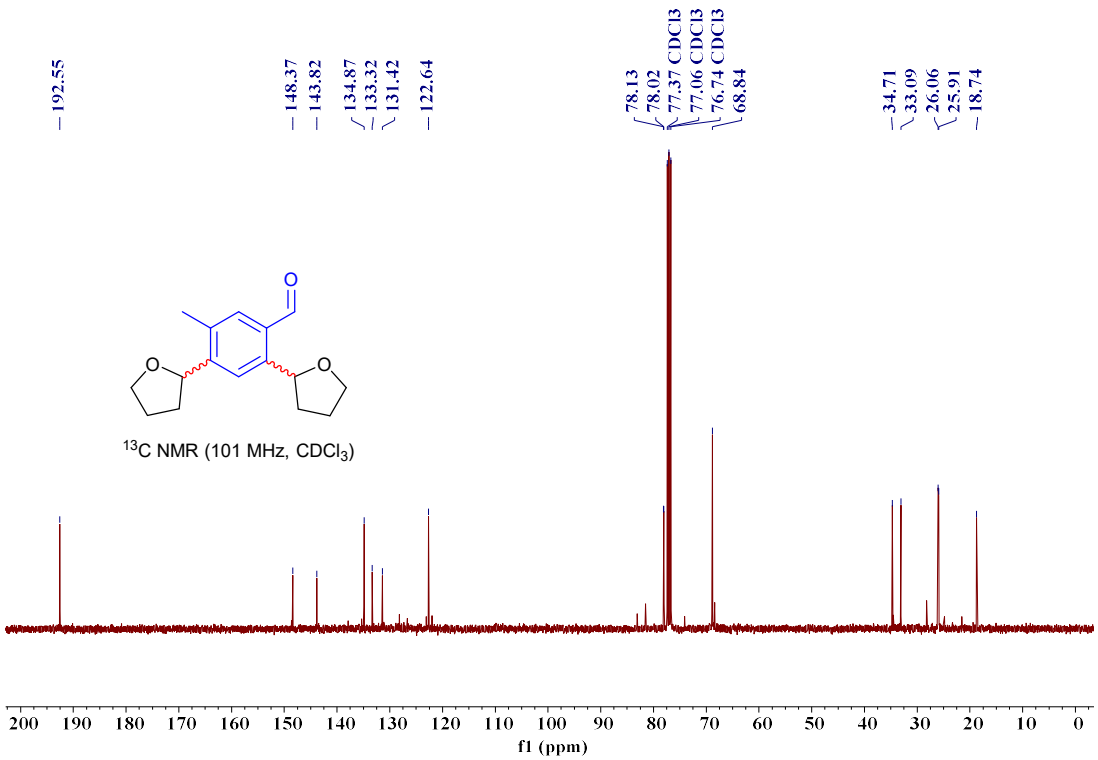
^{1}H and ^{13}C NMR spectra of compound (2-S-4-R) *2,4-disubstituted*-4b



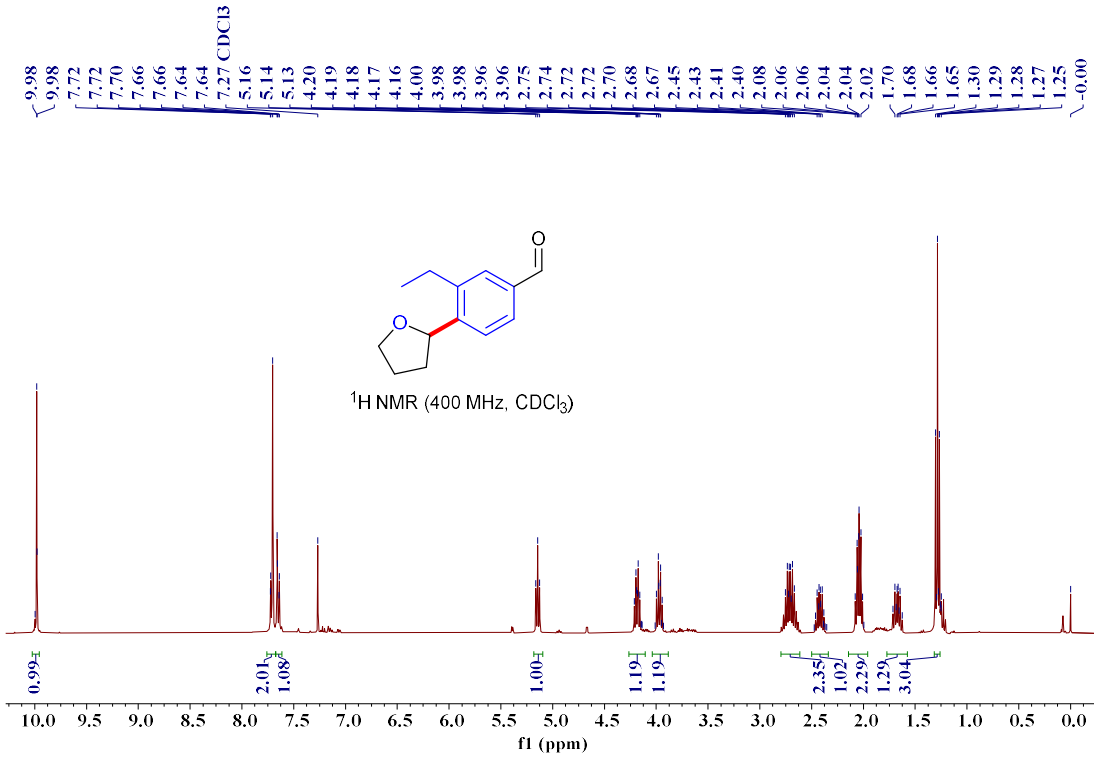


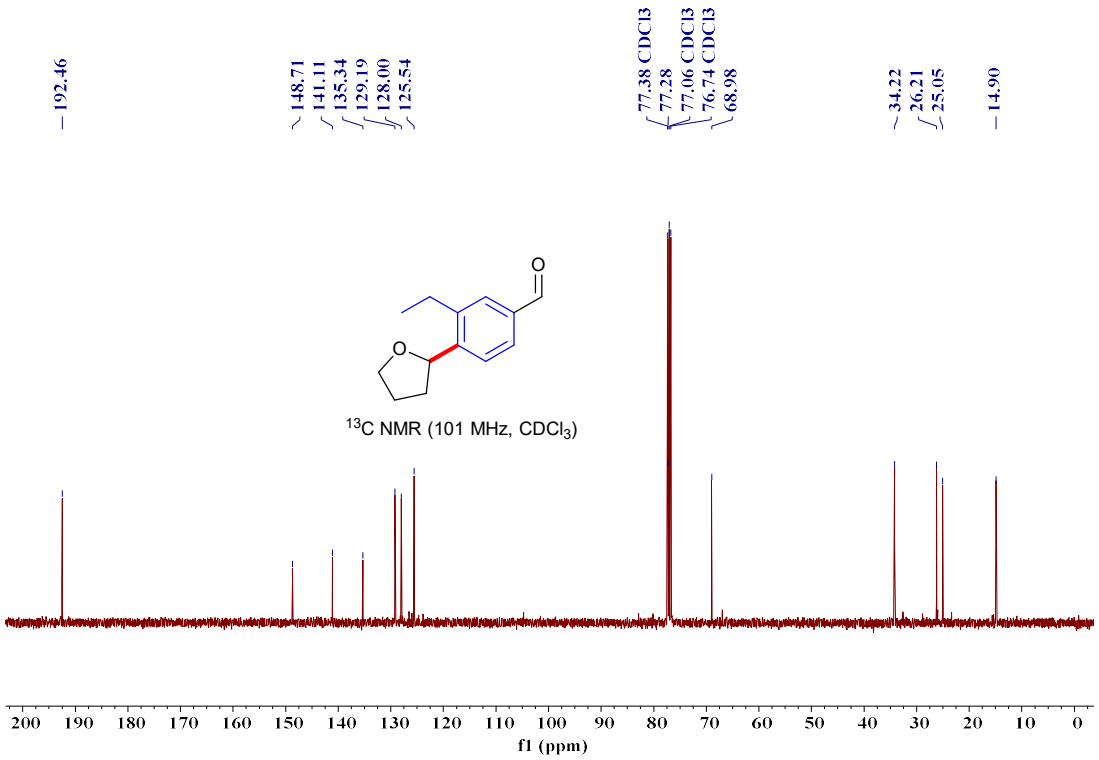
^{1}H and ^{13}C NMR spectra of compound (2-R-4-R) *2,4-disubstituted*-4b



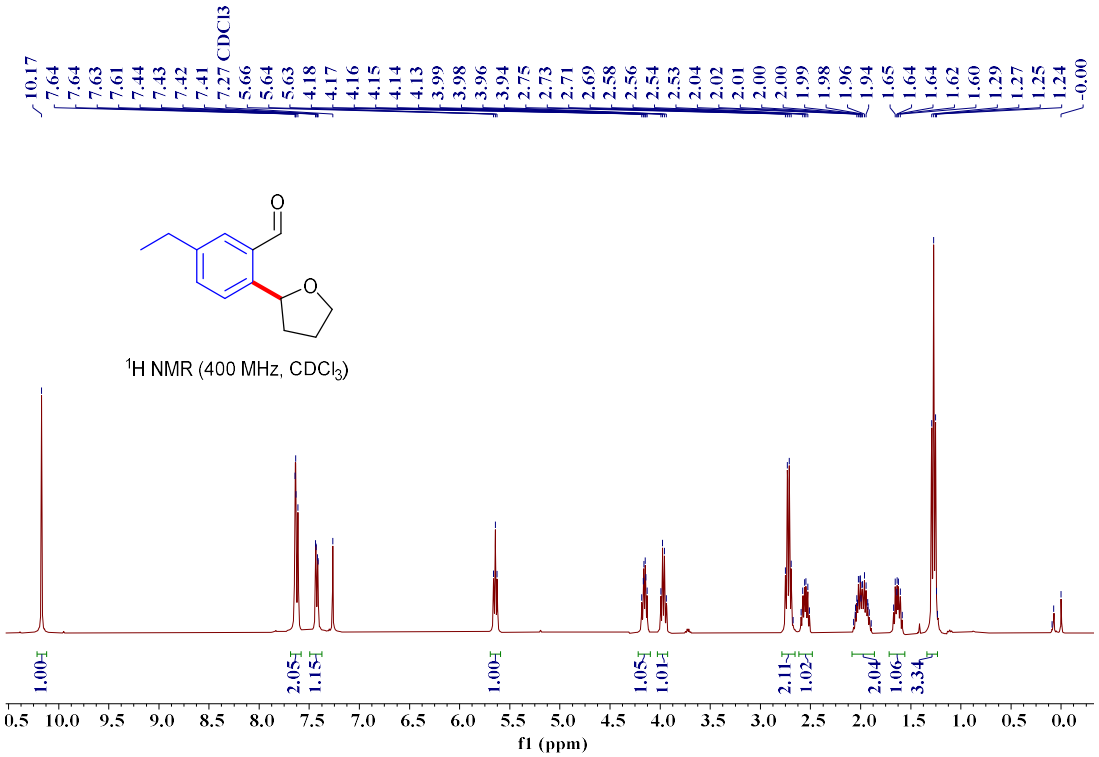


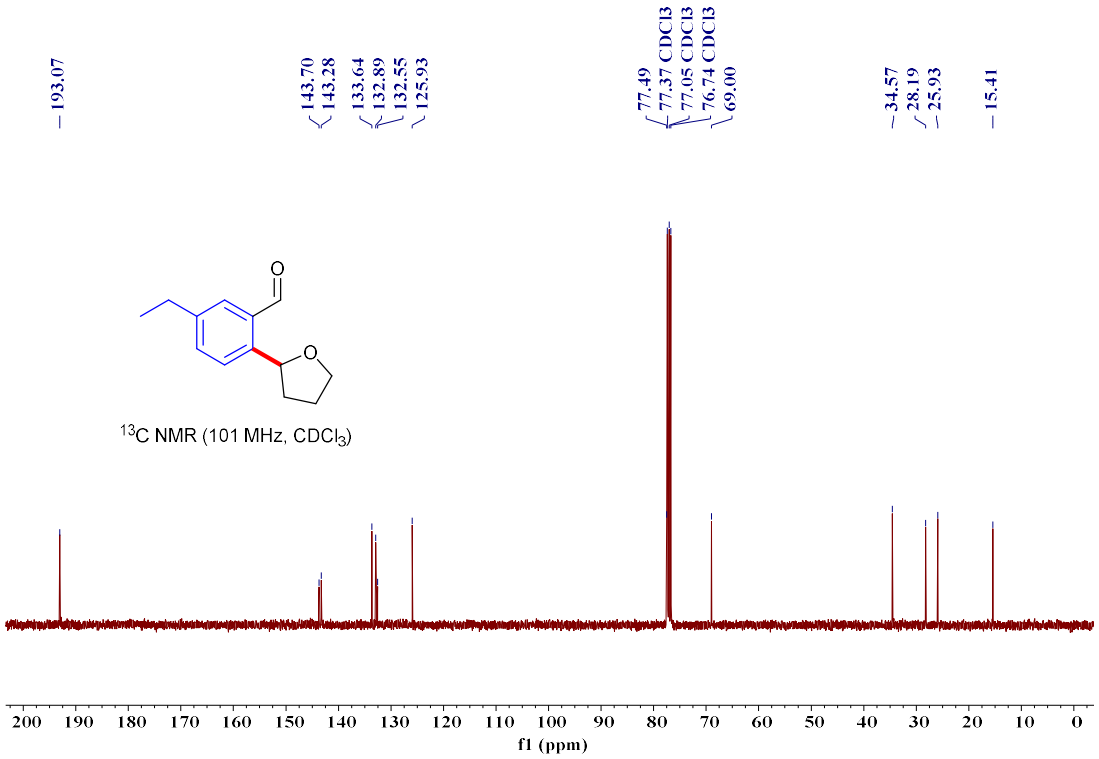
^{1}H and ^{13}C NMR spectra of compound *para*-4c



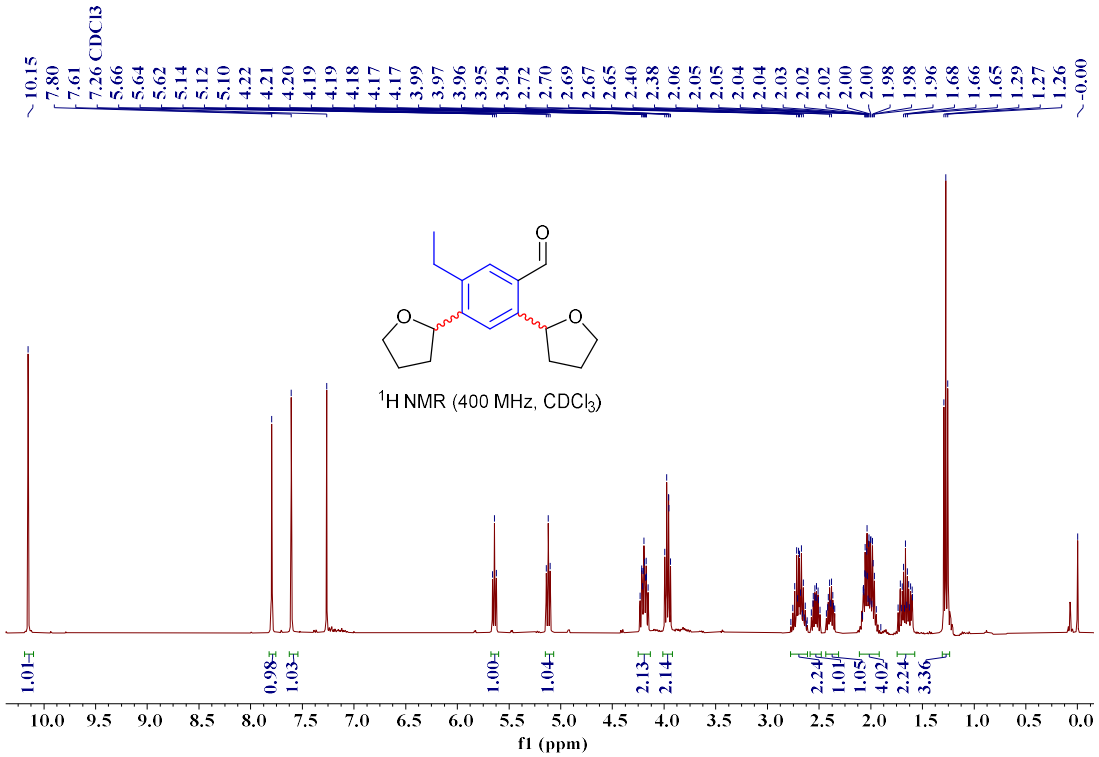


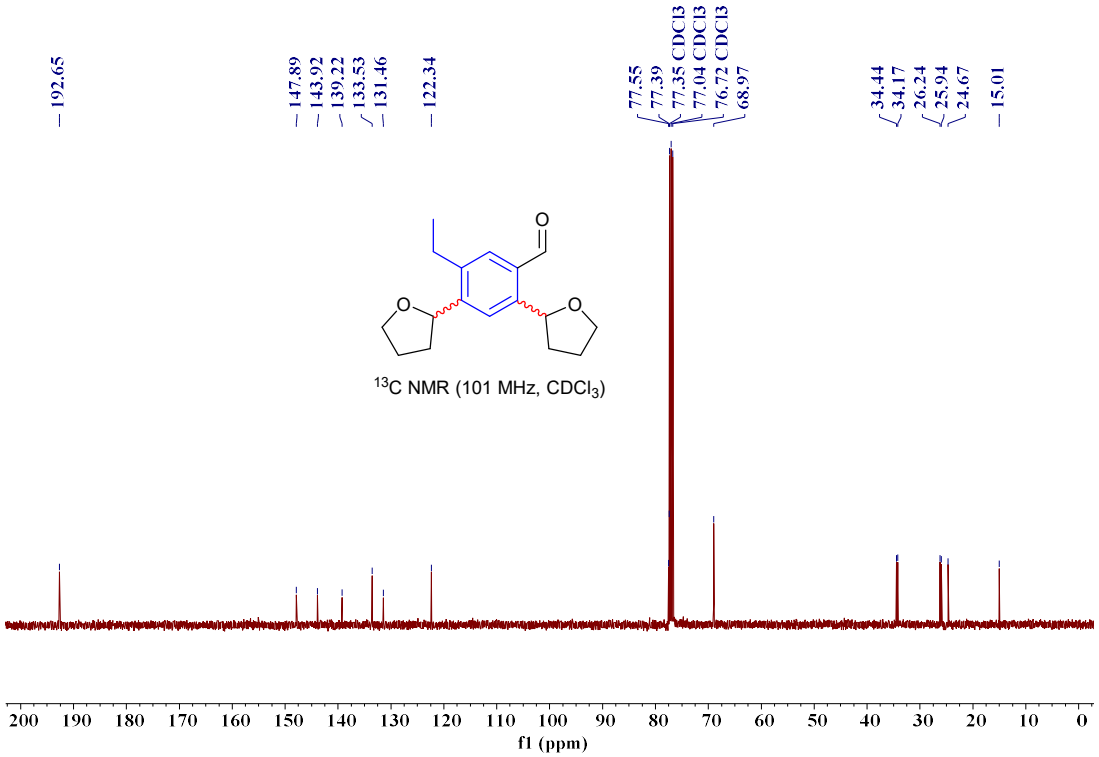
^{1}H and ^{13}C NMR spectra of compound *ortho*-4c



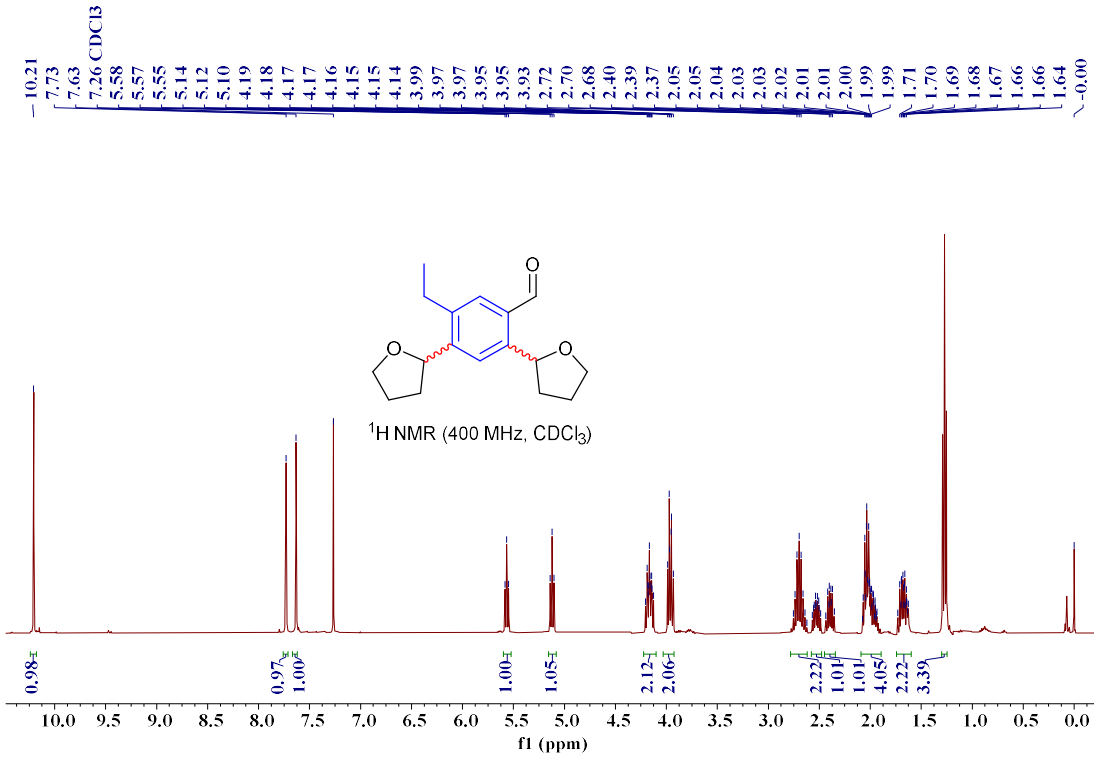


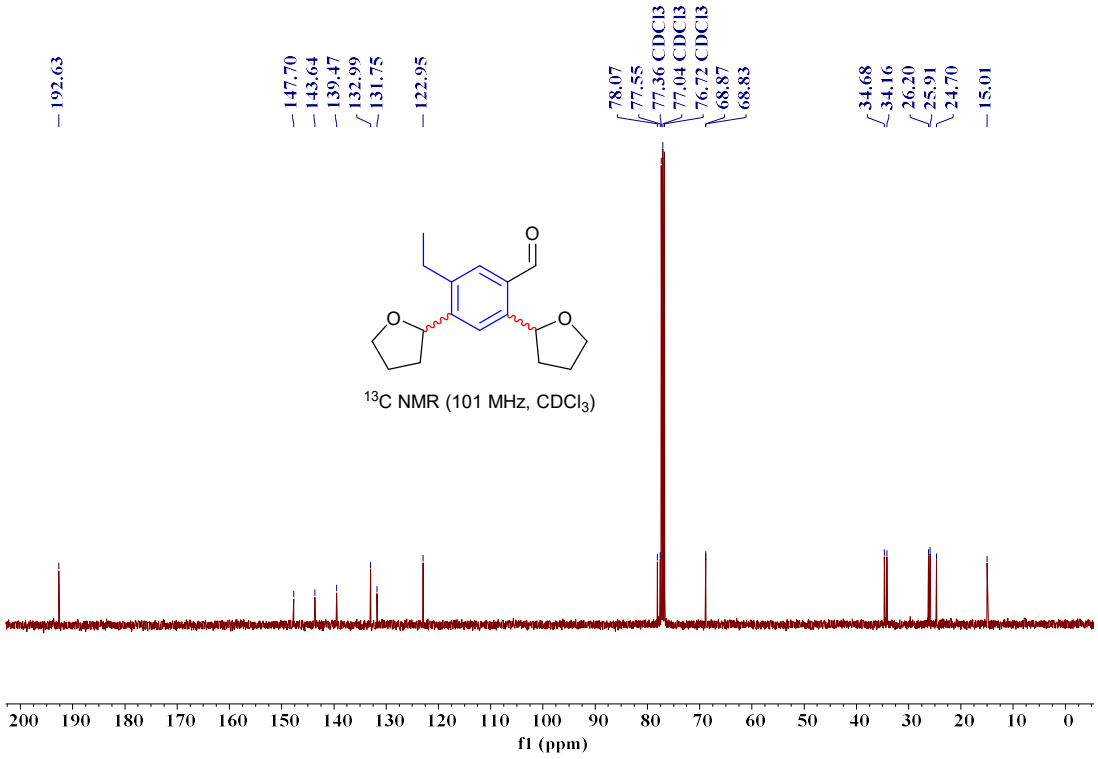
^{1}H and ^{13}C NMR spectra of compound (2-S-4-R) *2,4-disubstituted*-4c



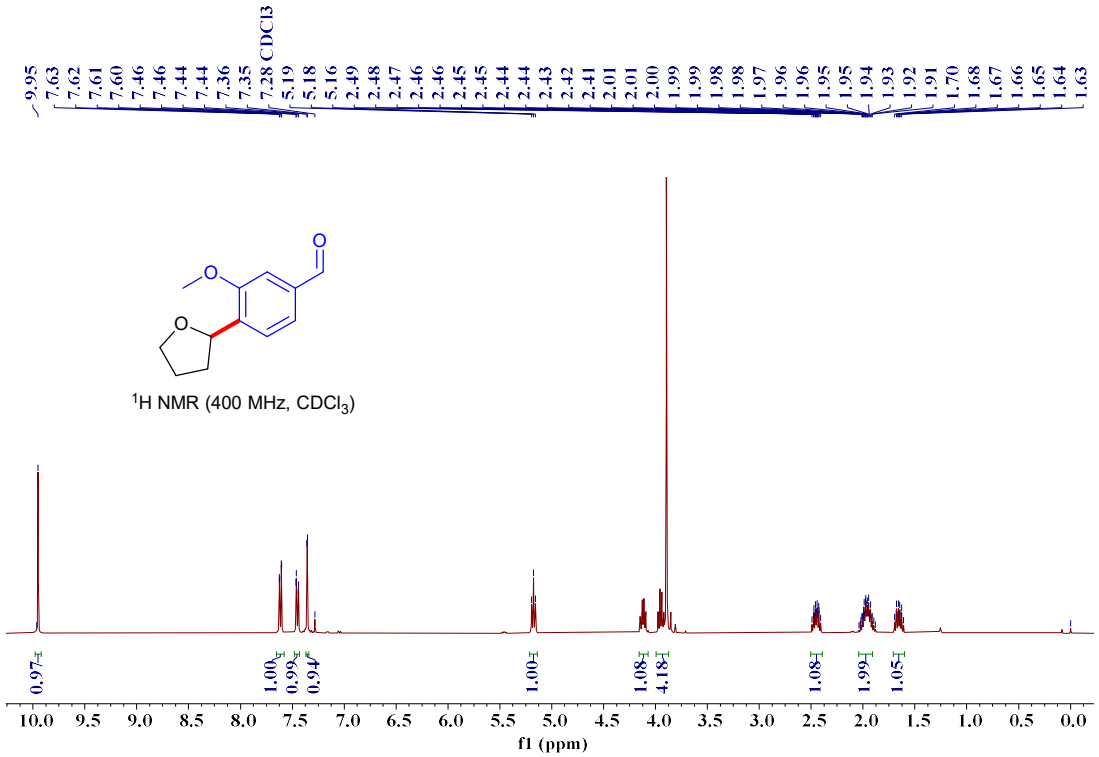


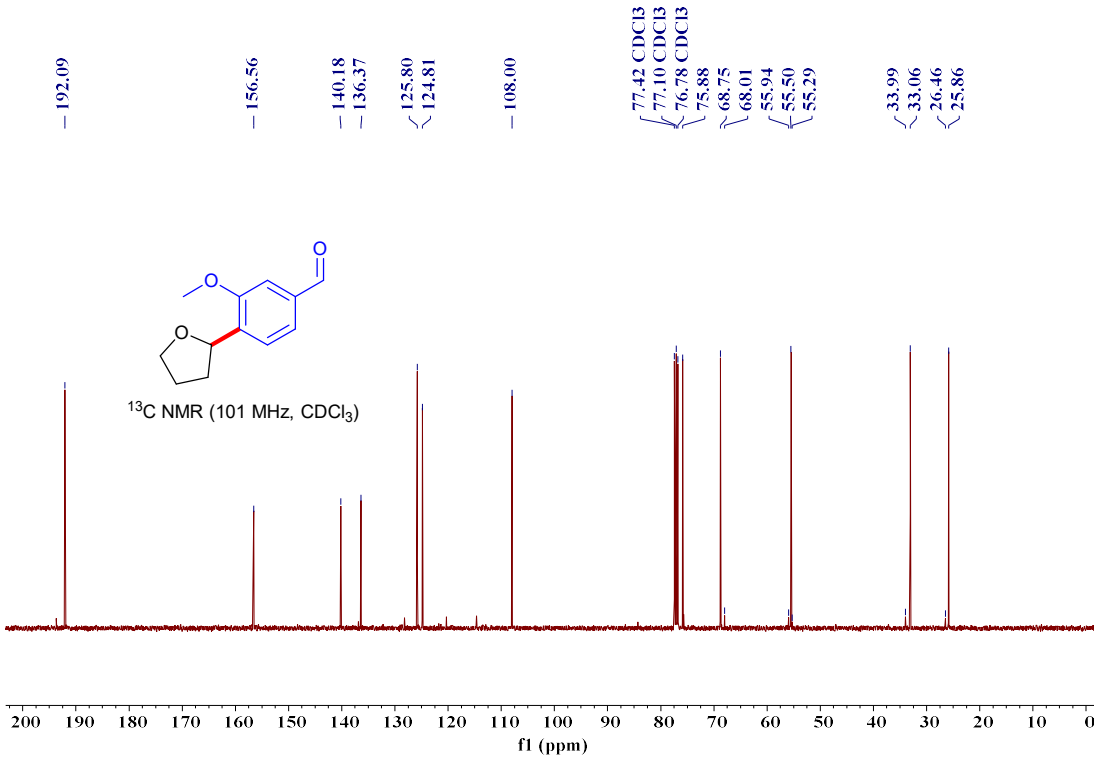
^{1}H and ^{13}C NMR spectra of compound (2-R-4-R) *2,4-disubstituted*-4c



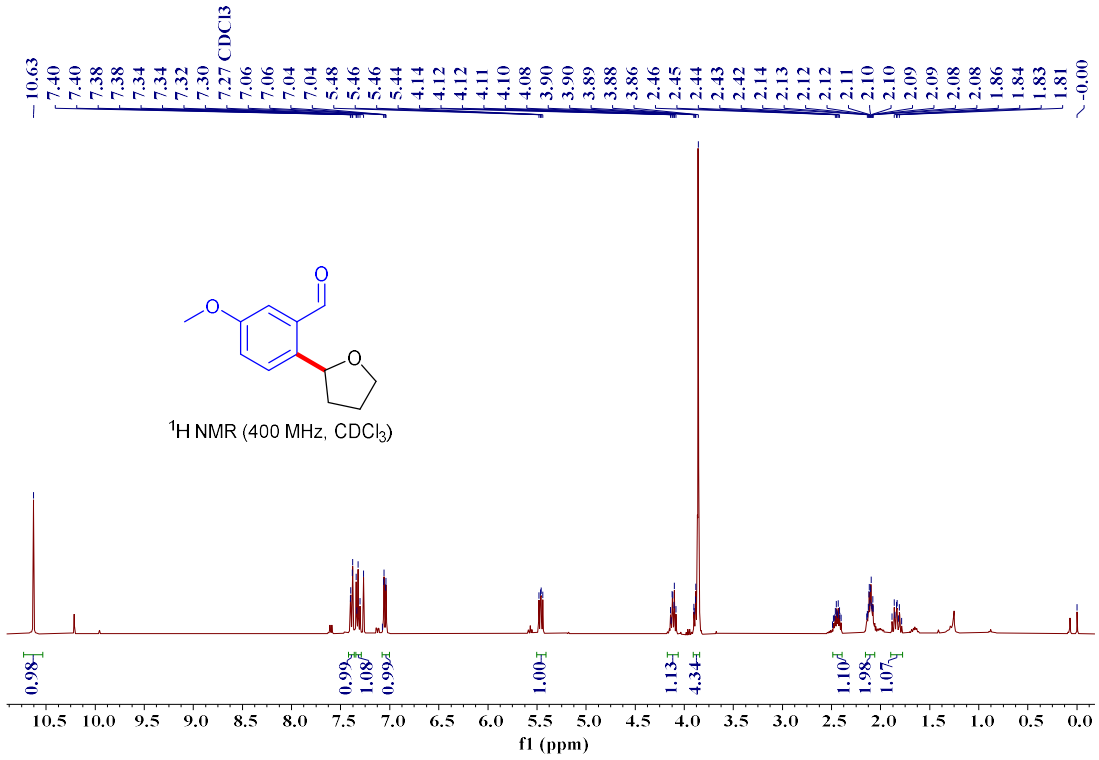


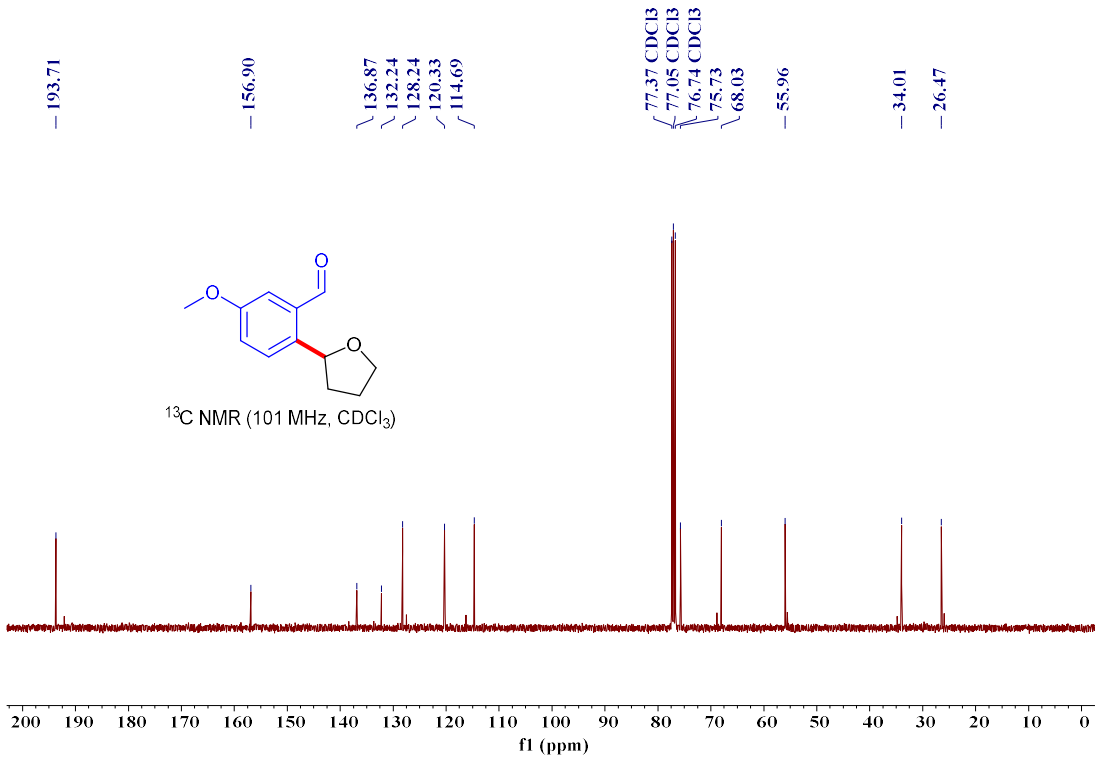
^{1}H and ^{13}C NMR spectra of compound *para*-4d



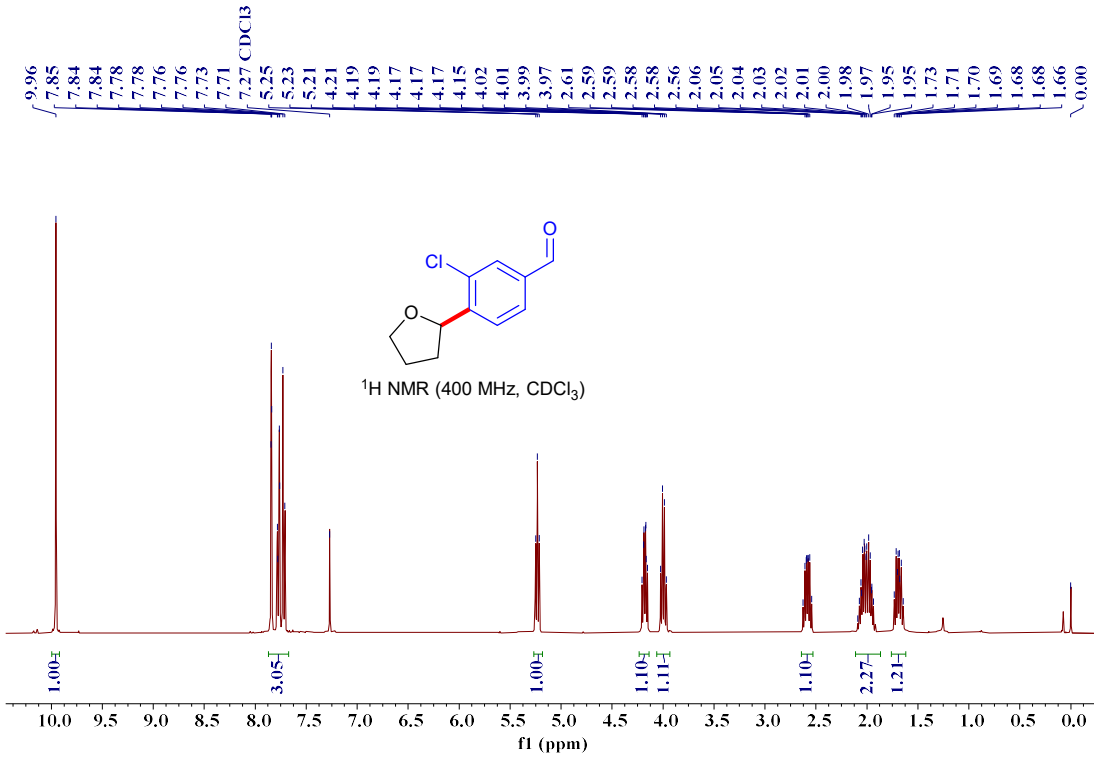


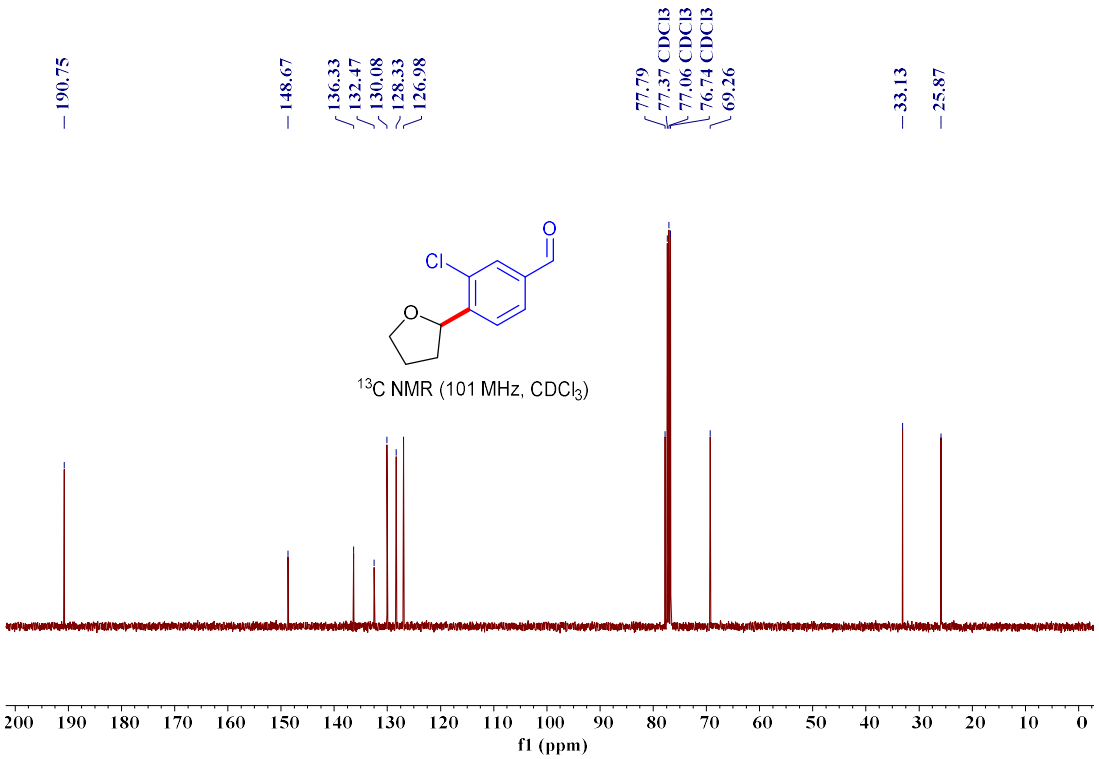
^{1}H and ^{13}C NMR spectra of compound *ortho*-4d



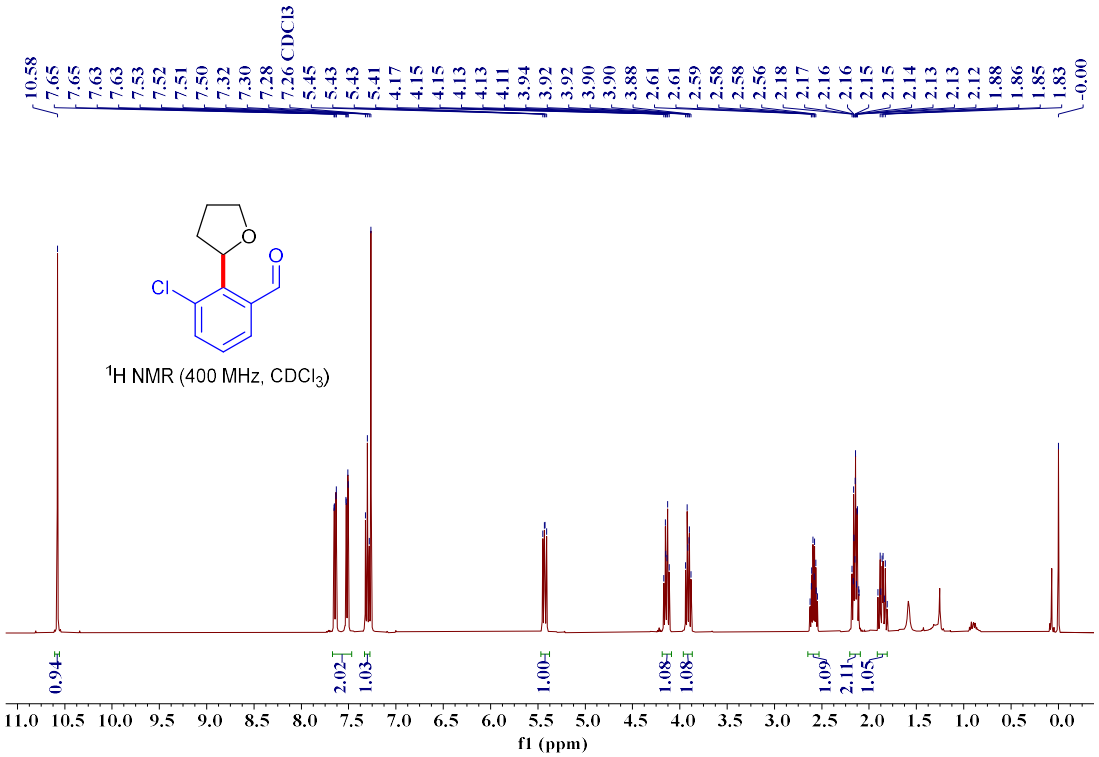


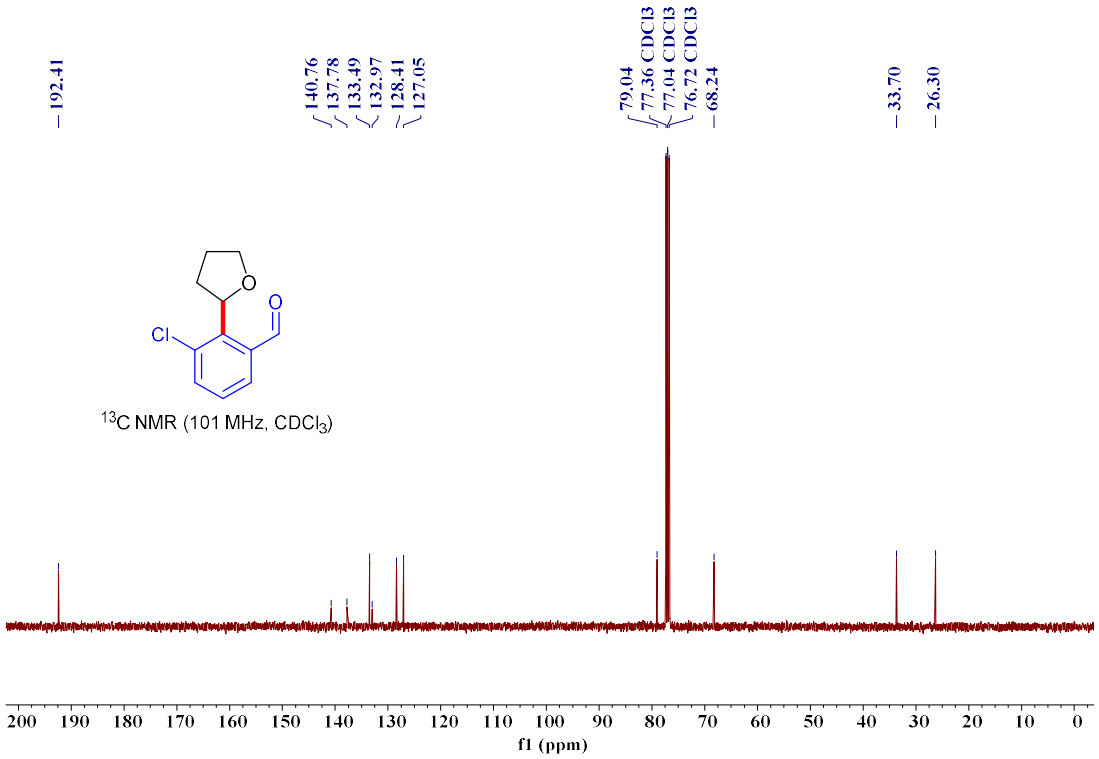
^{1}H and ^{13}C NMR spectra of compound *para*-4e



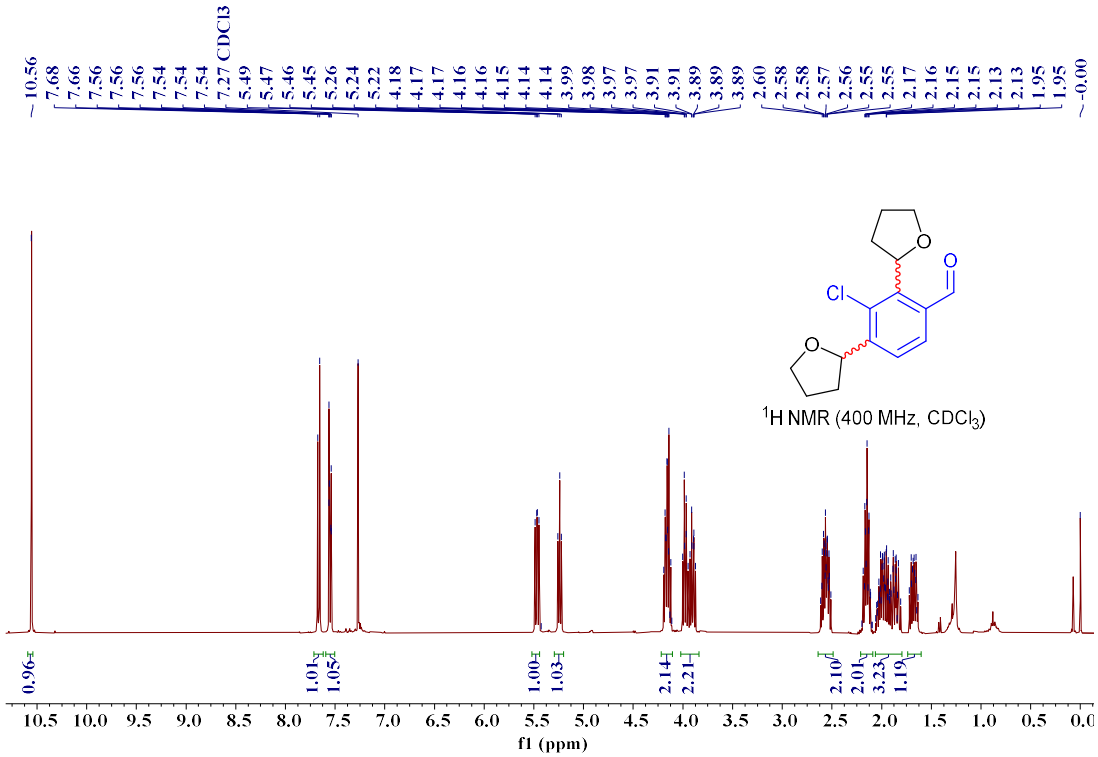


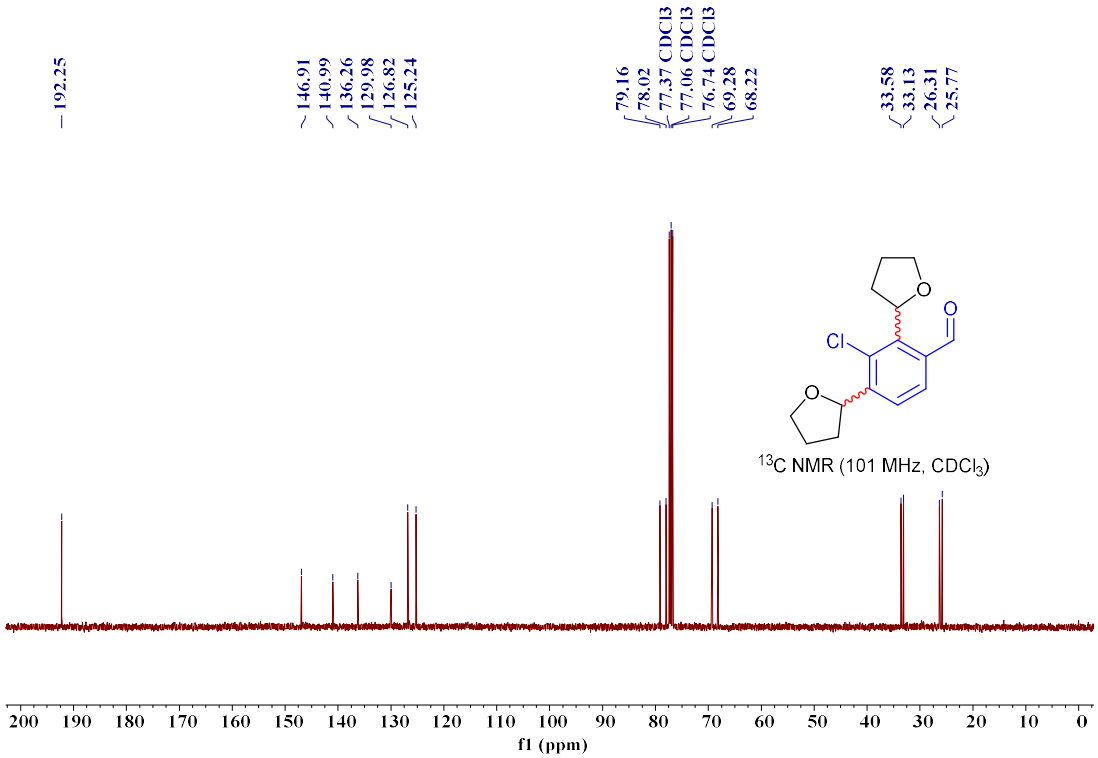
^{1}H and ^{13}C NMR spectra of compound *ortho*-4e



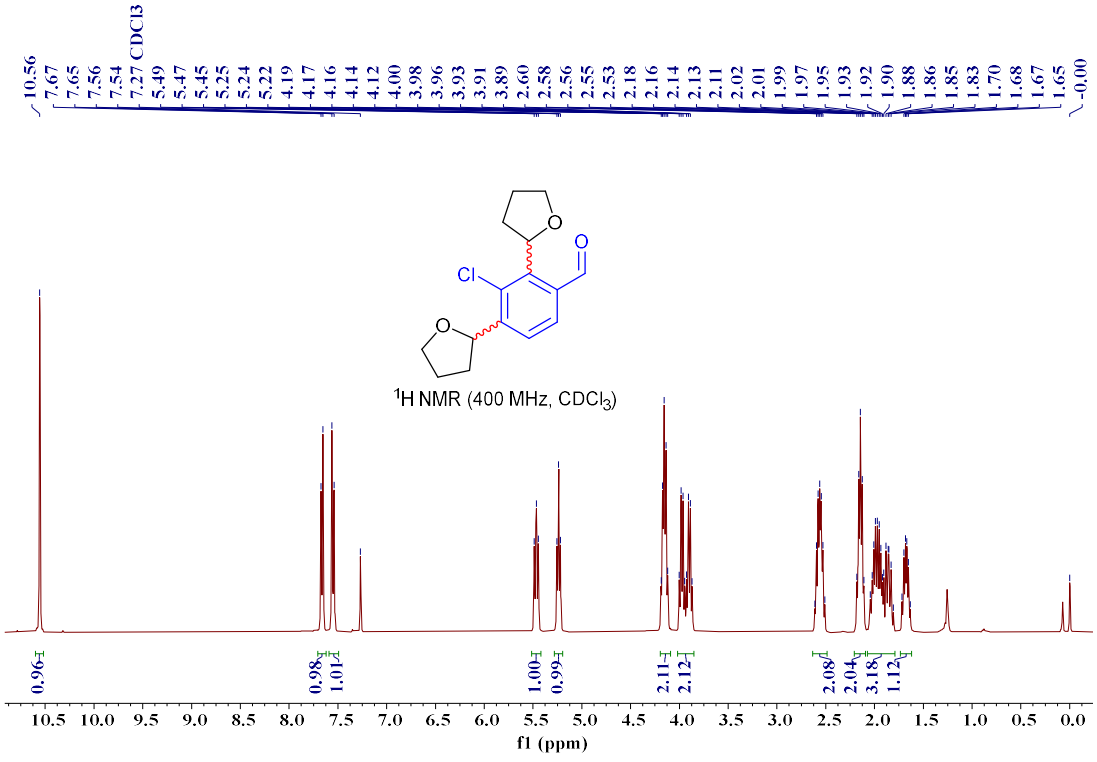


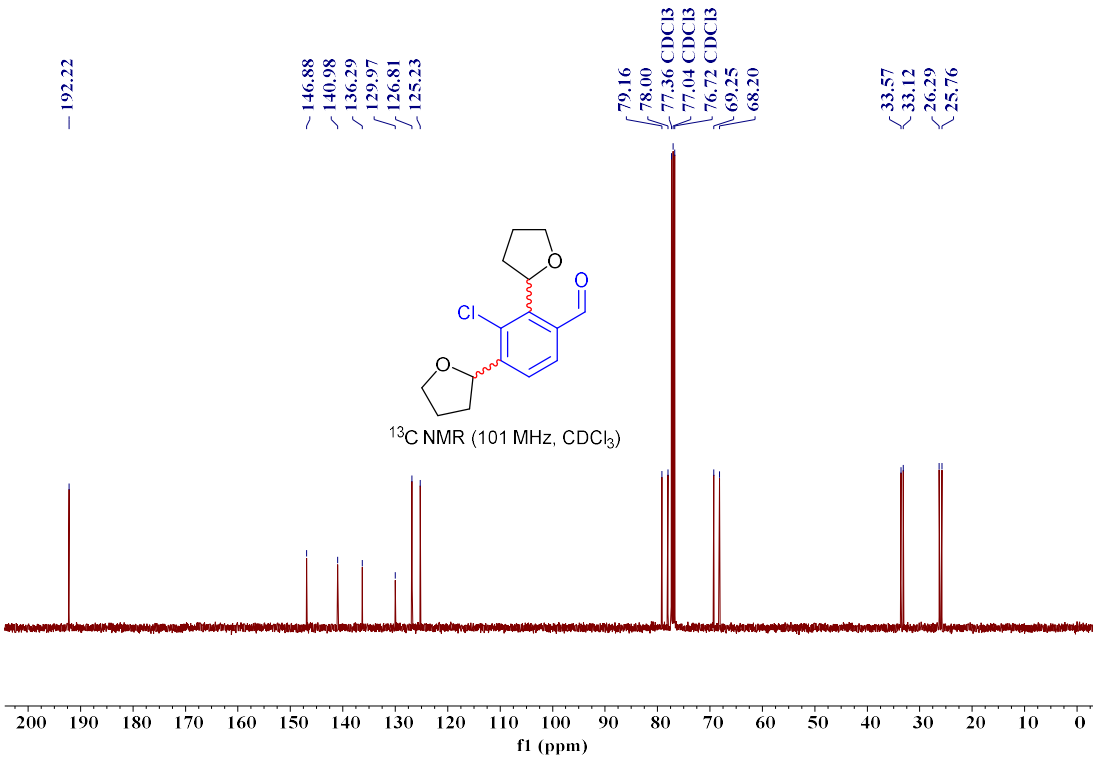
^{1}H and ^{13}C NMR spectra of compound (3-Cl-2-R-4-R) *2,4-disubstituted*-4e



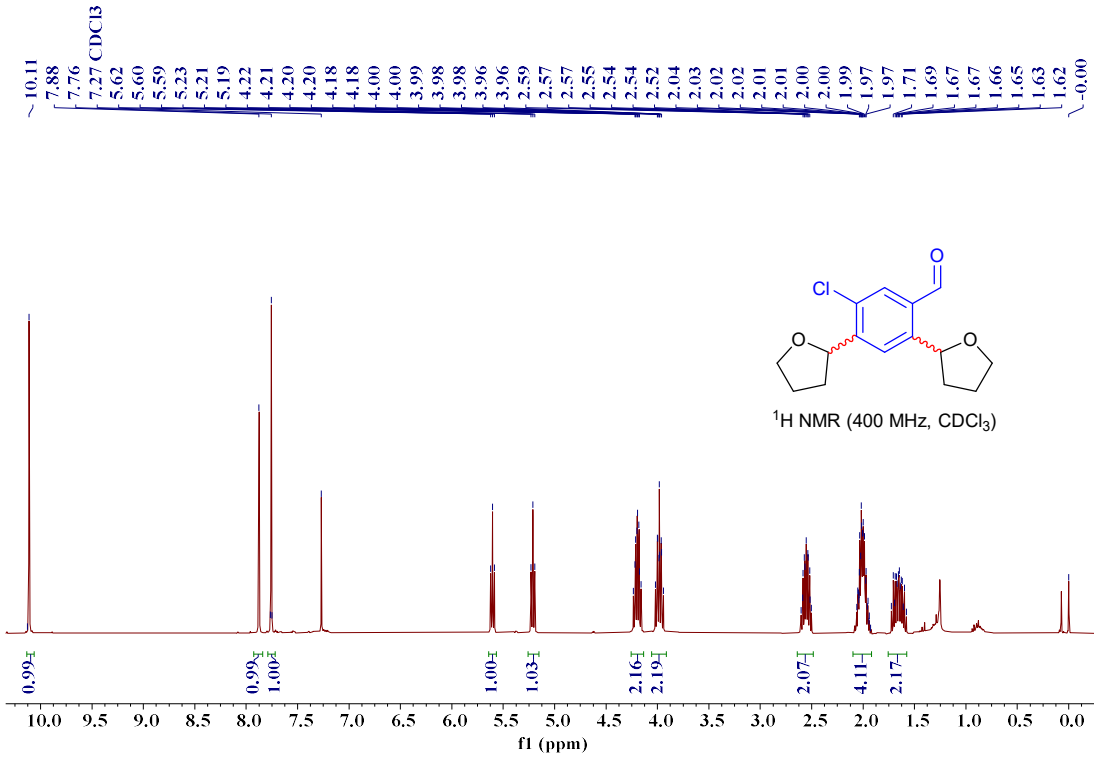


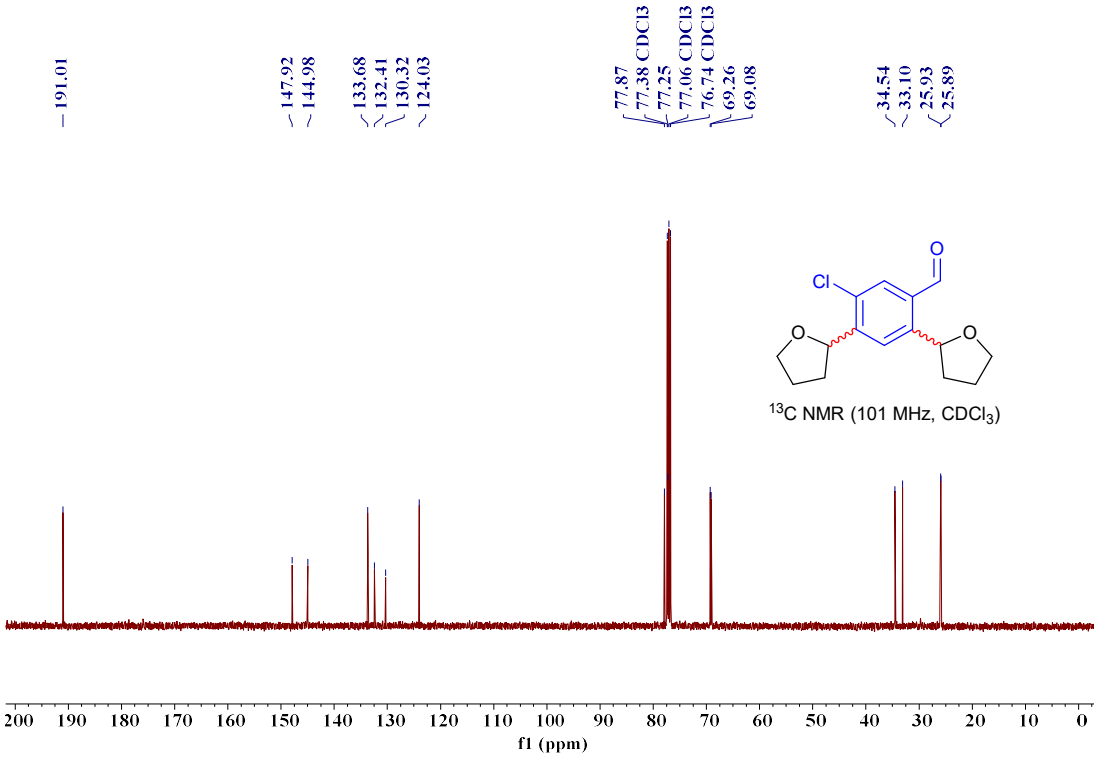
^{1}H and ^{13}C NMR spectra of compound (3-Cl-2-S-4-R) *2,4-disubstituted*-4e



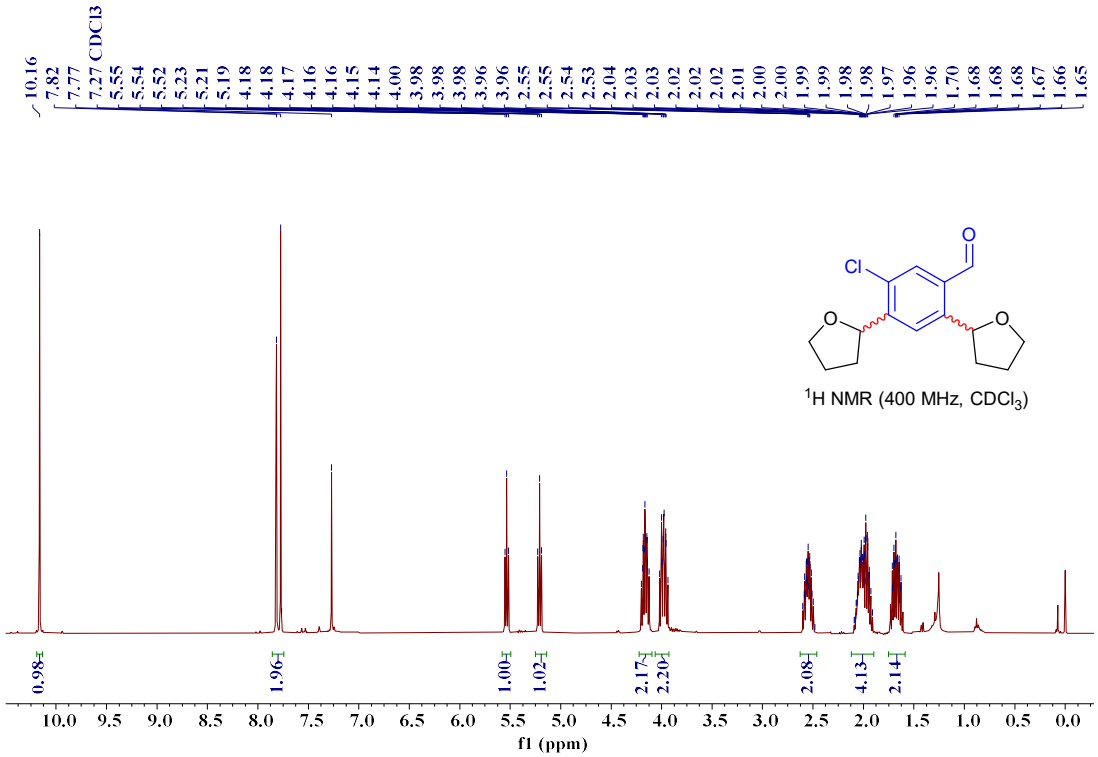


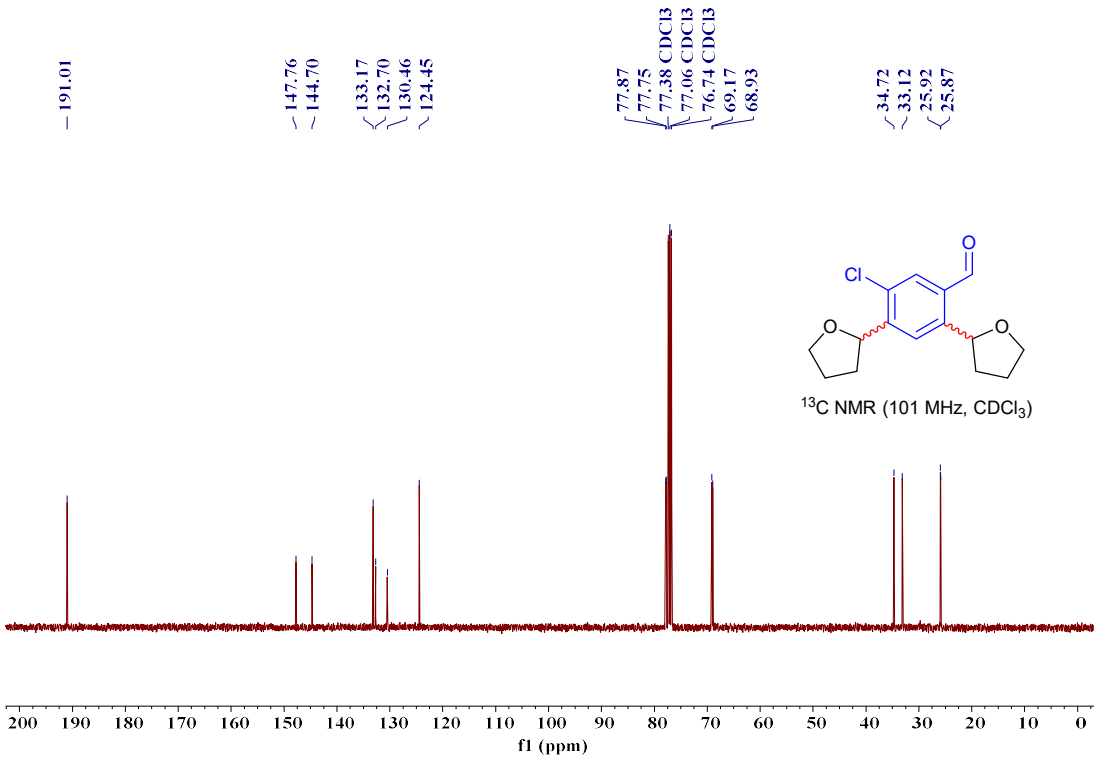
^{1}H and ^{13}C NMR spectra of compound (5-Cl-2-S-4-R) *2,4-disubstituted*-4e



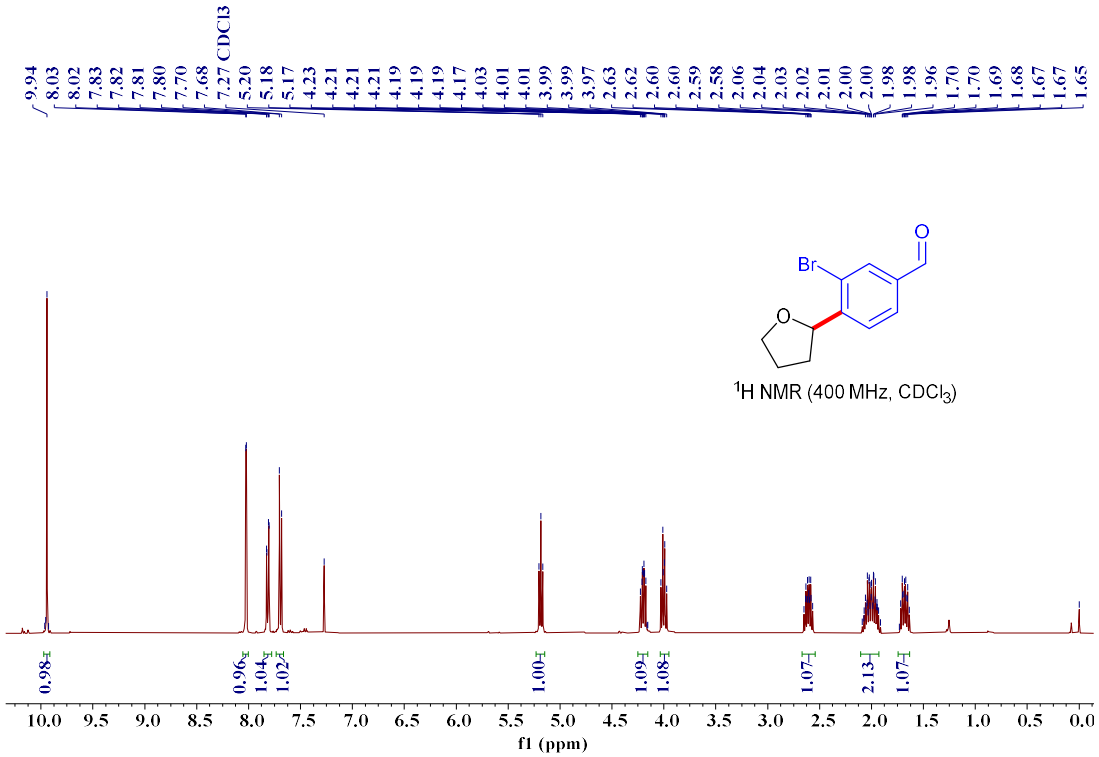


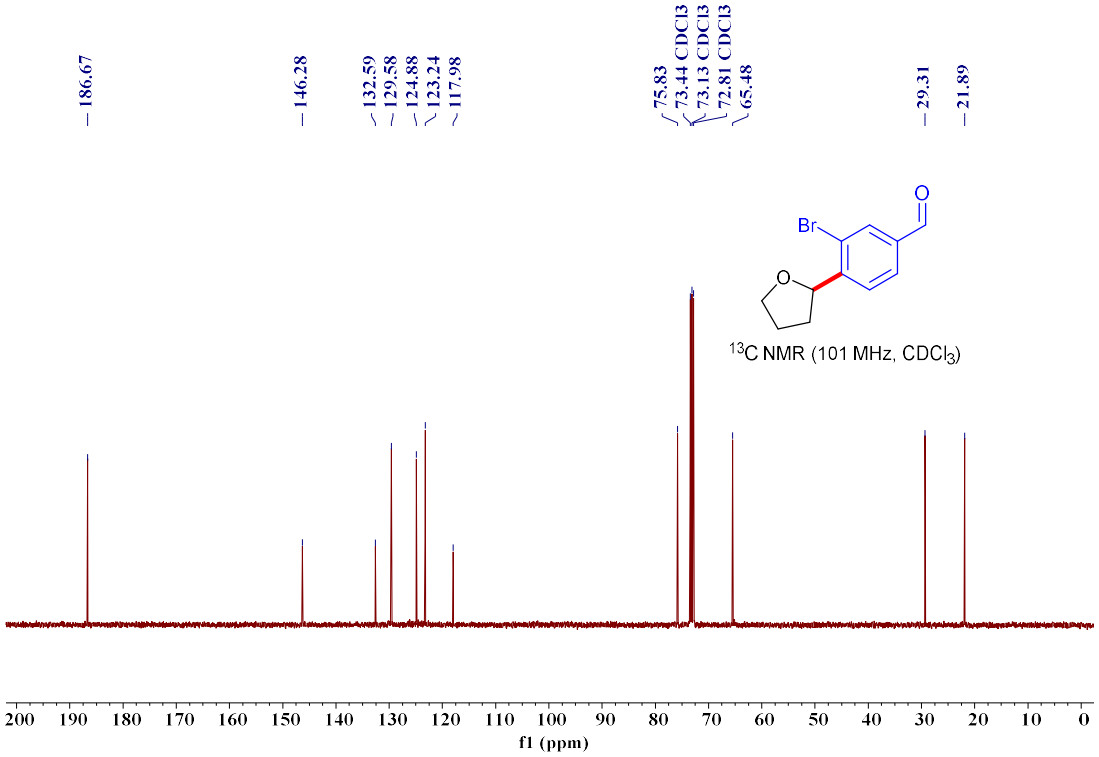
^{1}H and ^{13}C NMR spectra of compound (5-Cl-2-R-4-R) *2,4-disubstituted*-4e



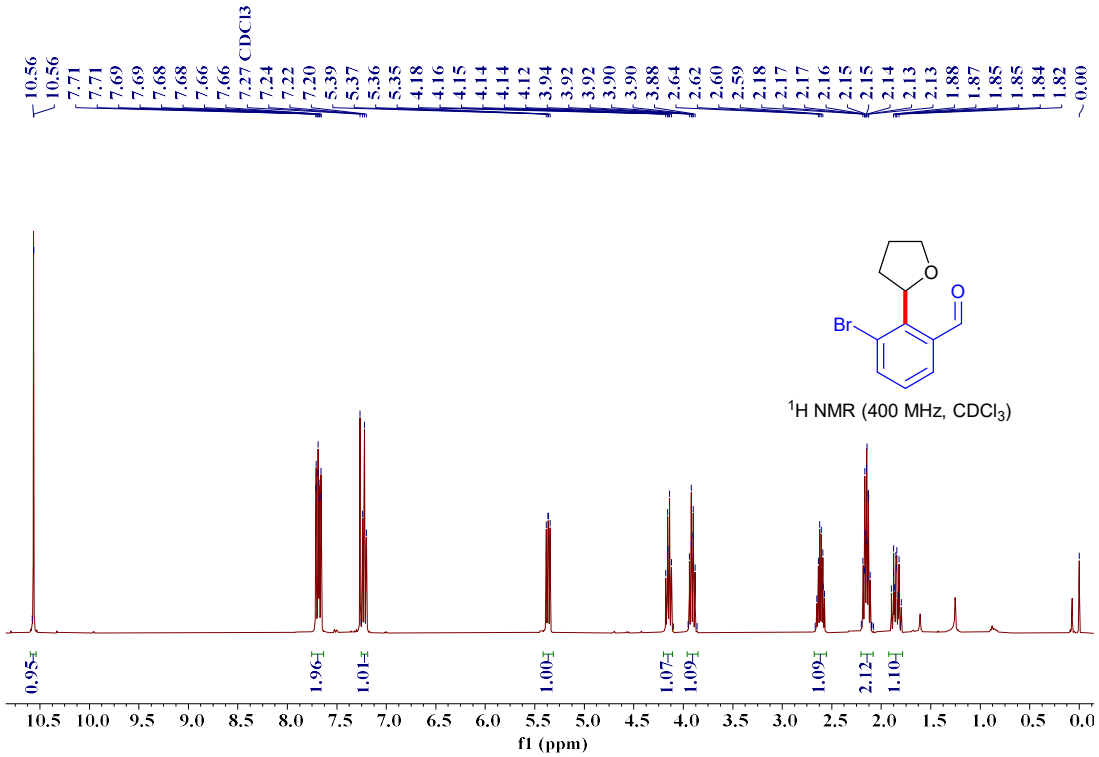


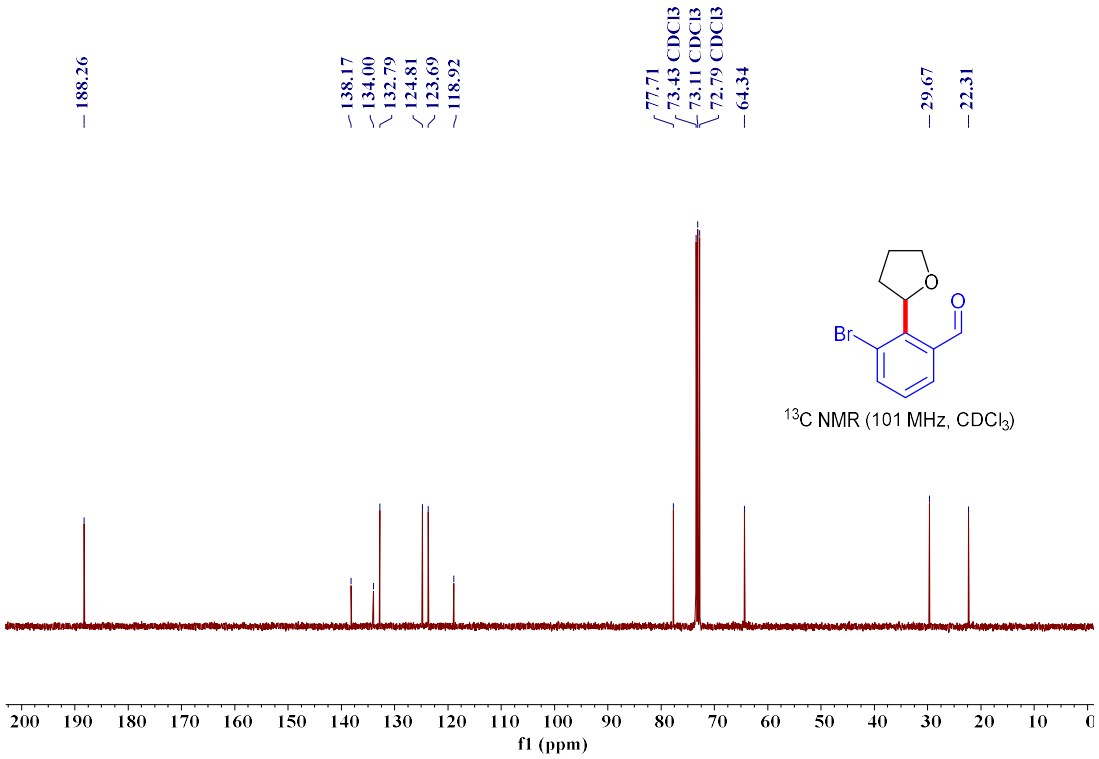
^{1}H and ^{13}C NMR spectra of compound *para*-4f



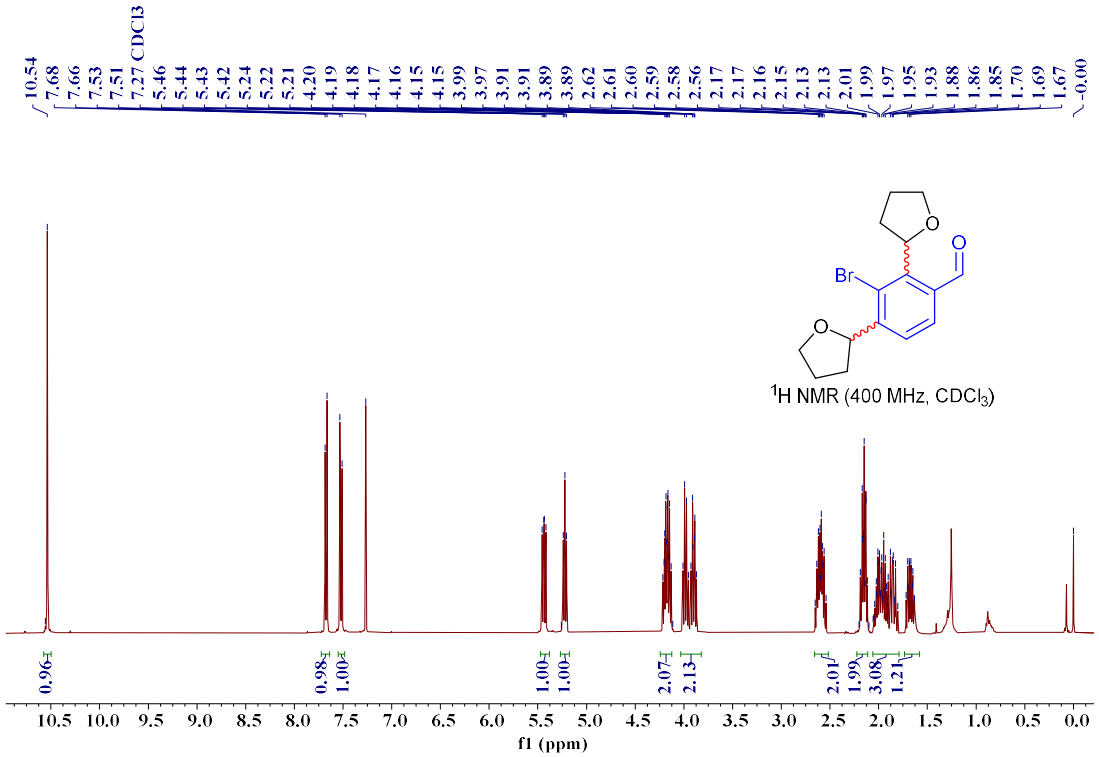


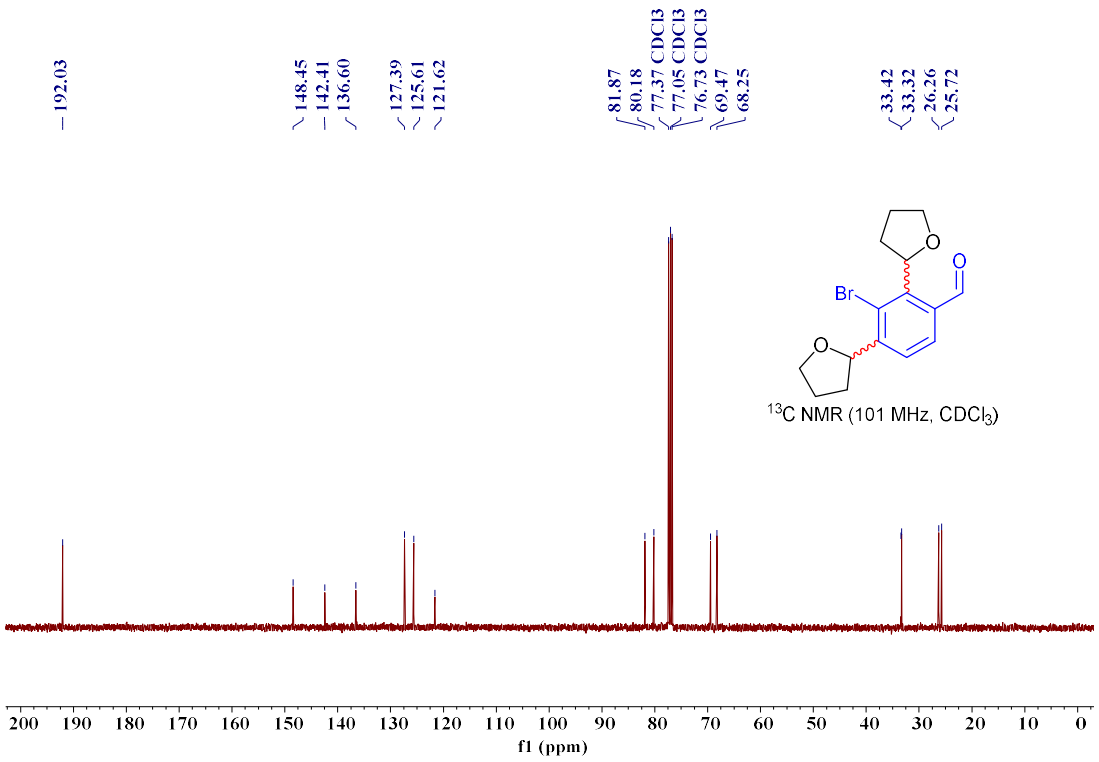
^{1}H and ^{13}C NMR spectra of compound *ortho*-4f



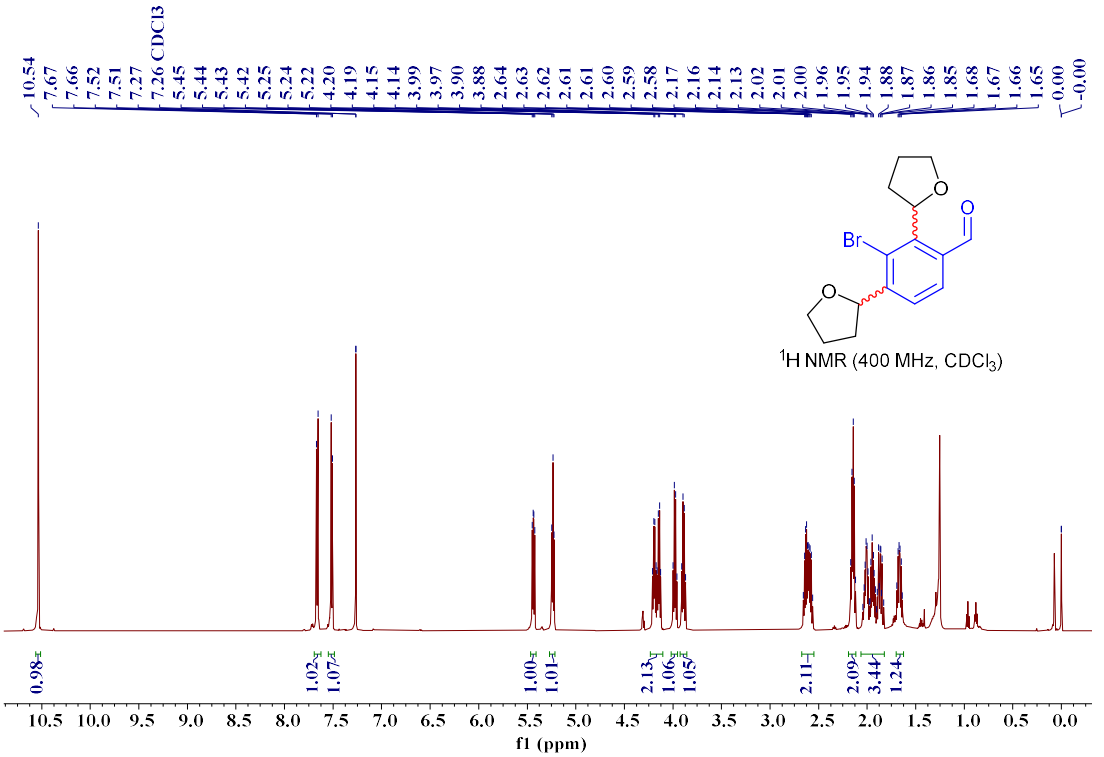


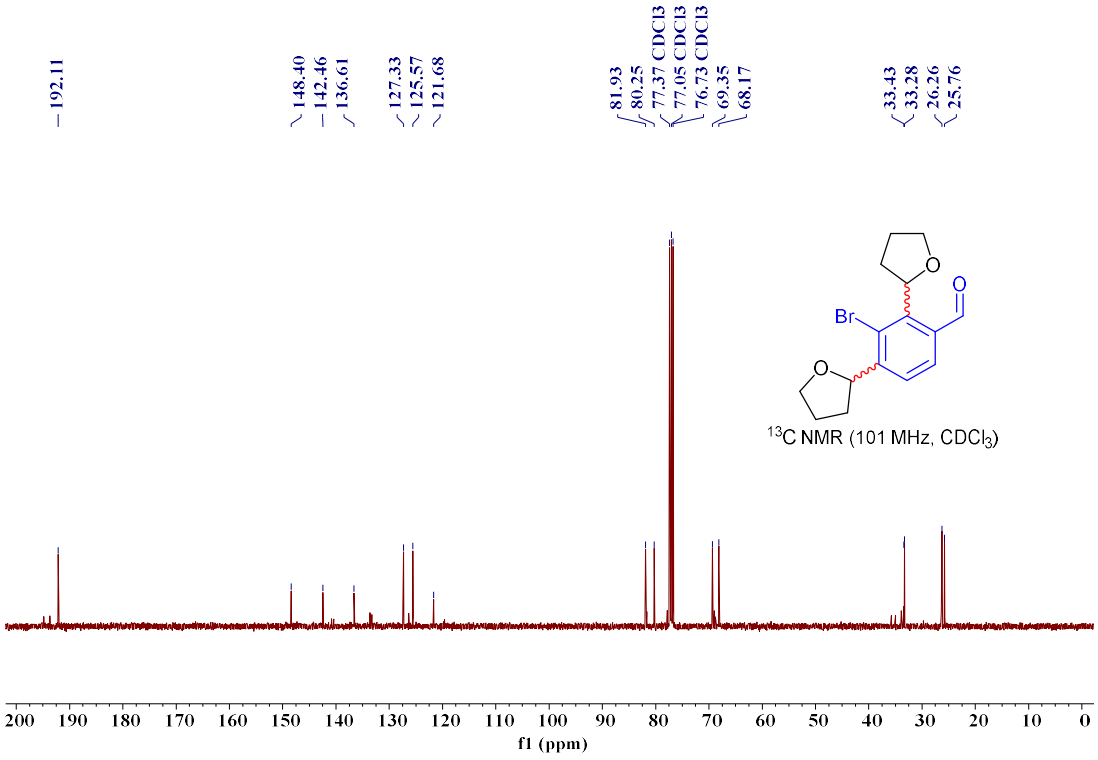
^{1}H and ^{13}C NMR spectra of compound (3-Br-2-R-4-R) *2,4-disubstituted*-4f



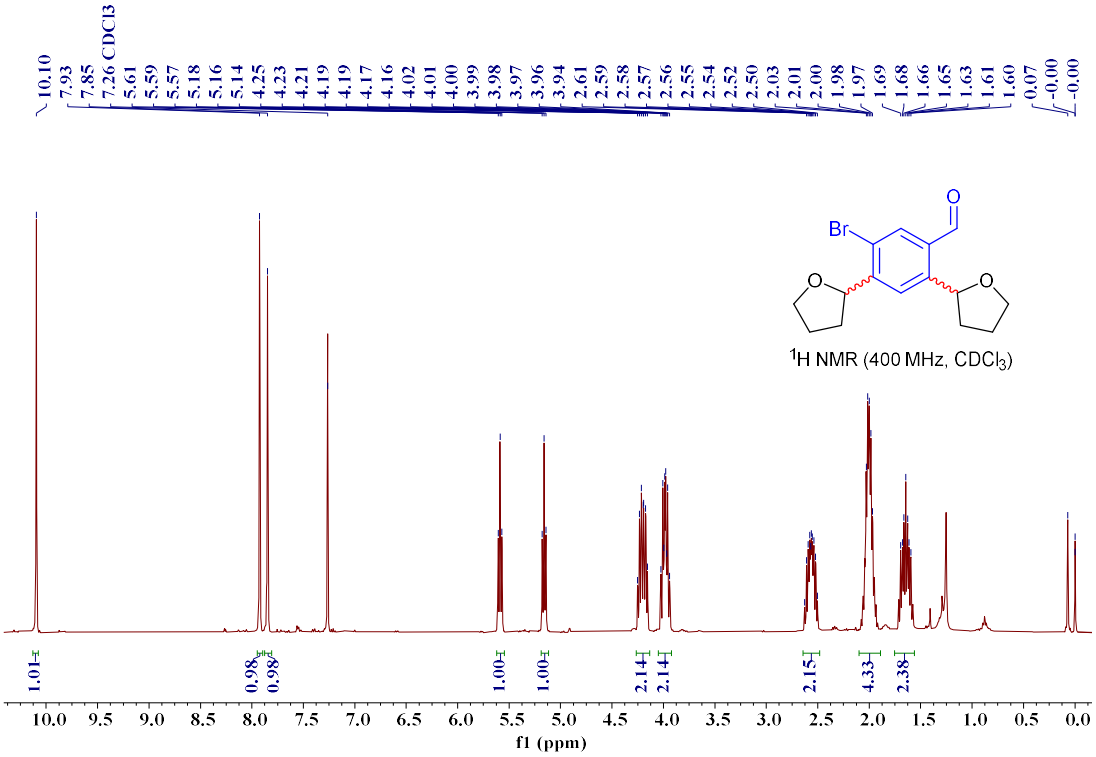


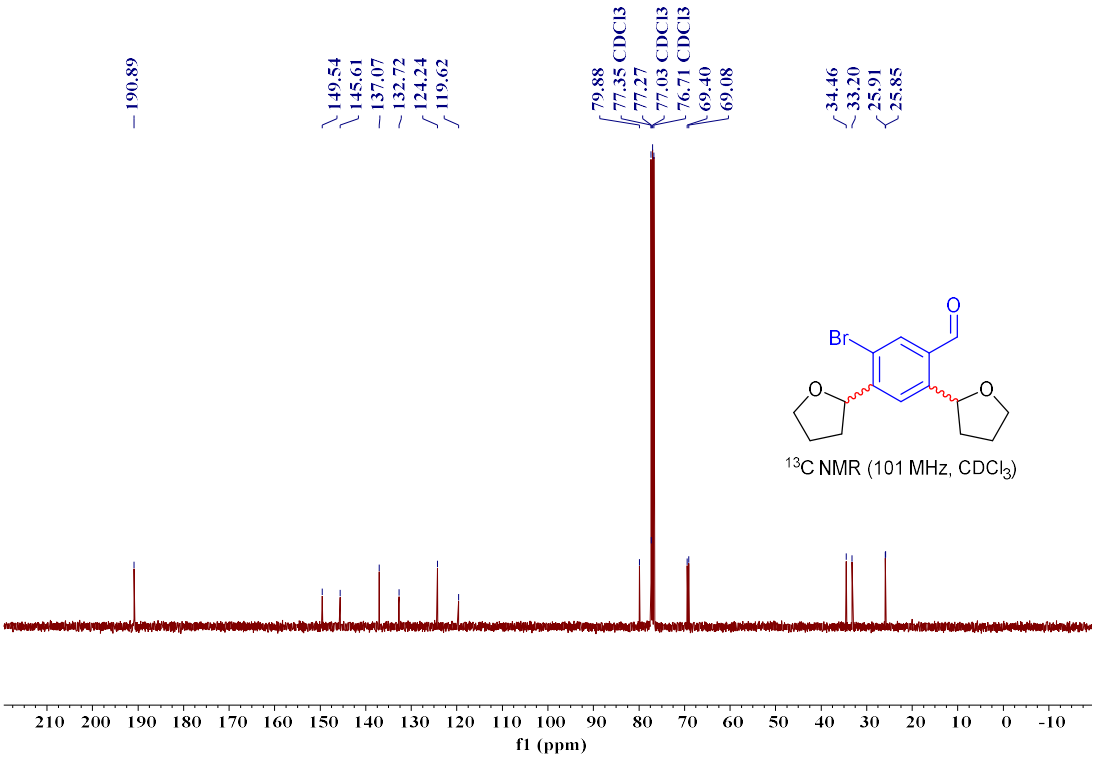
^{1}H and ^{13}C NMR spectra of compound (3-Br-2-S-4-R) *2,4-disubstituted*-4f



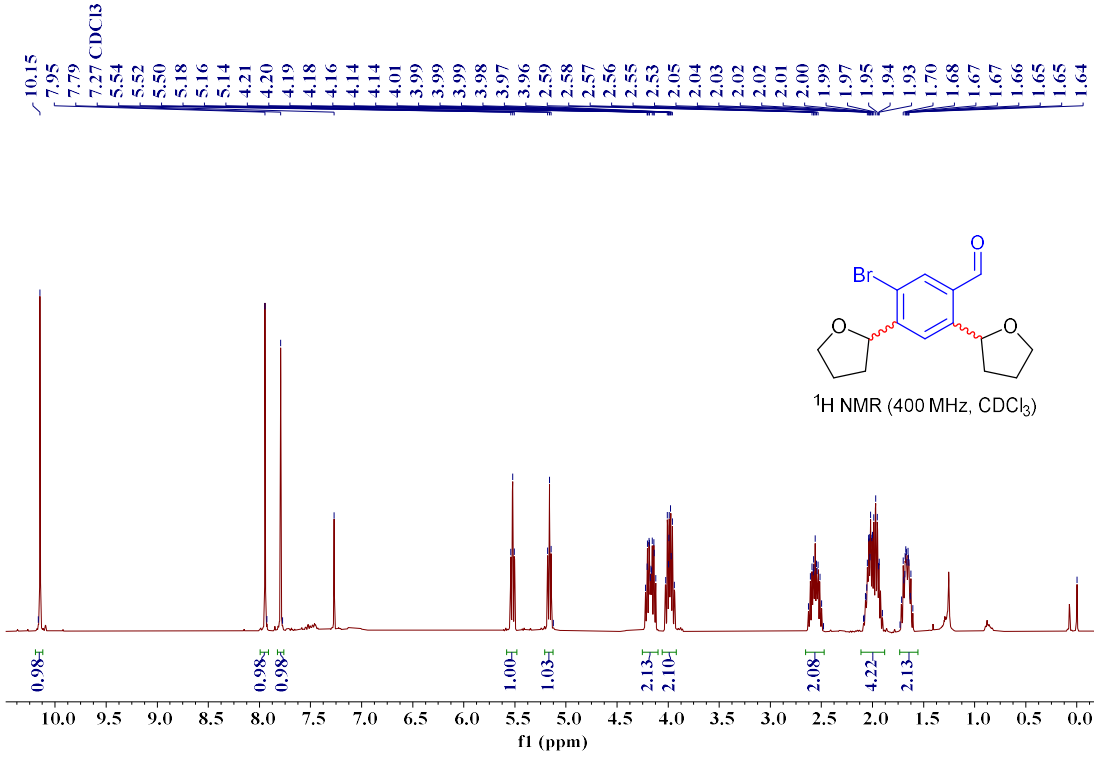


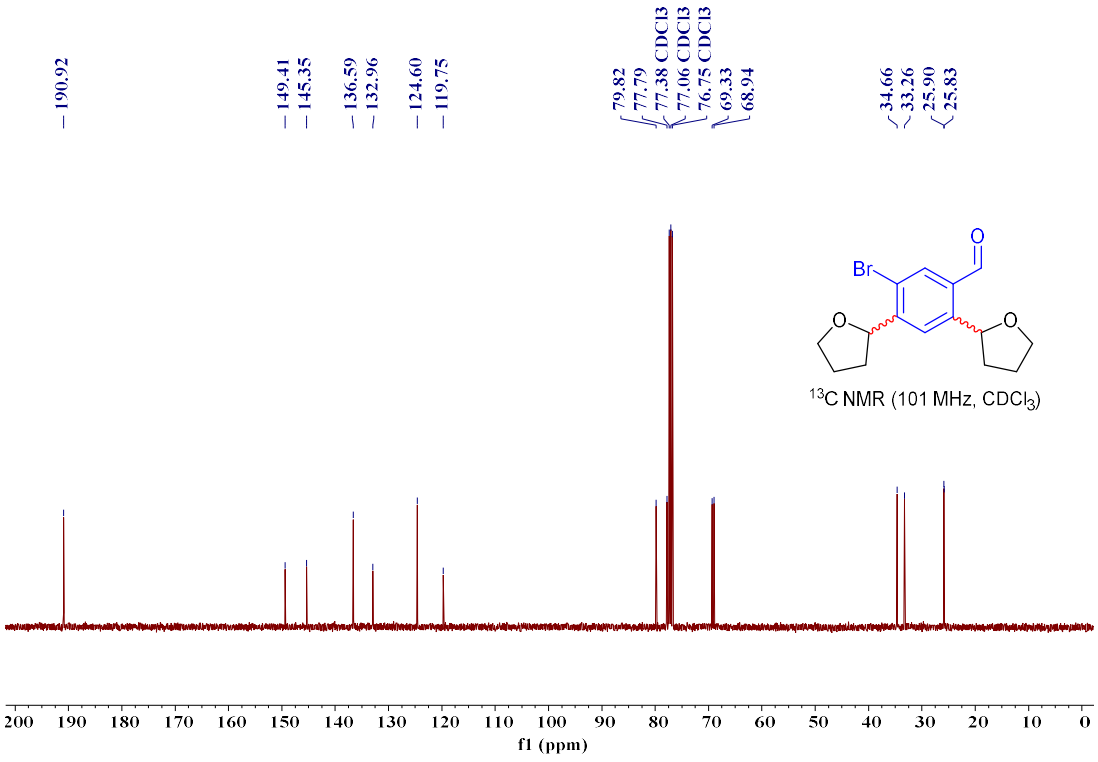
^{1}H and ^{13}C NMR spectra of compound (5-Br-2-S-4-R) *2,4-disubstituted*-4f



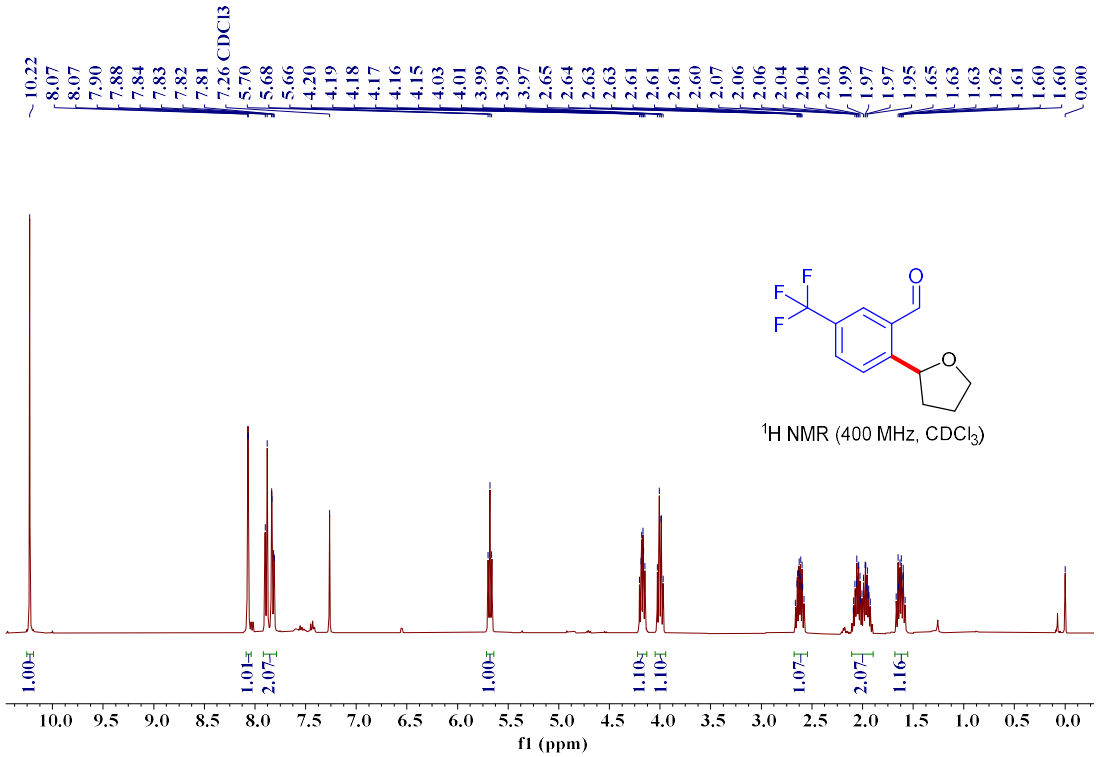


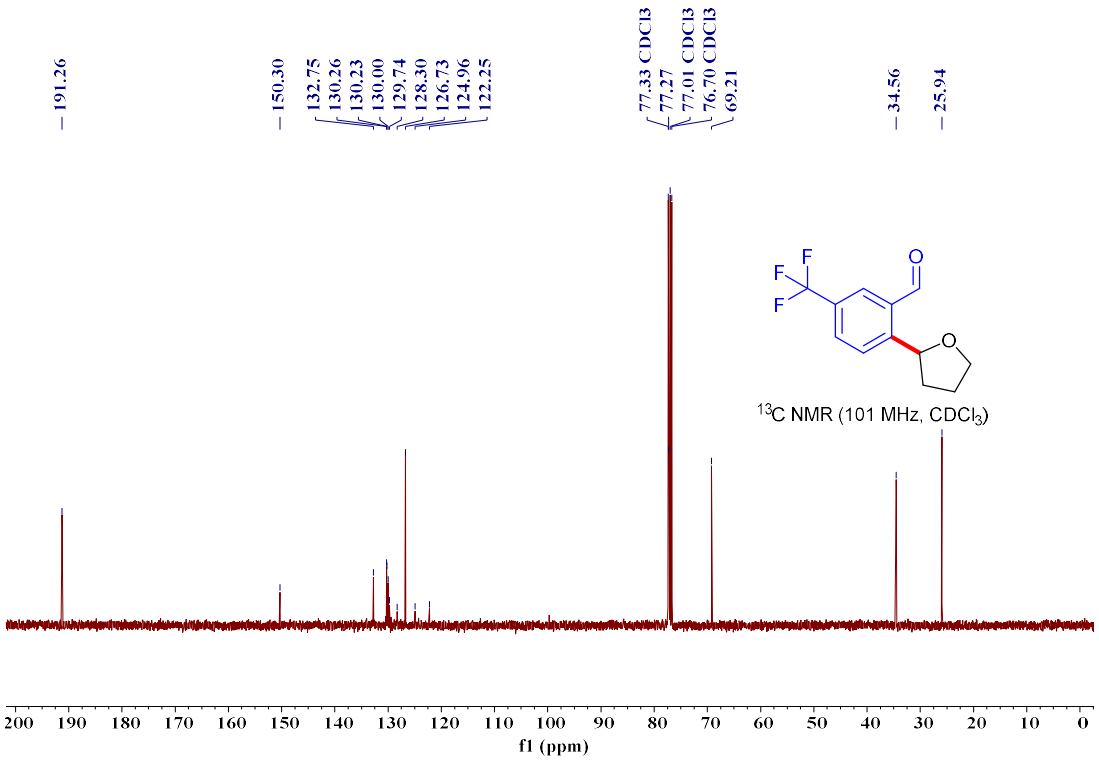
^{1}H and ^{13}C NMR spectra of compound (5-Br-2-R-4-R) *2,4-disubstituted*-4f

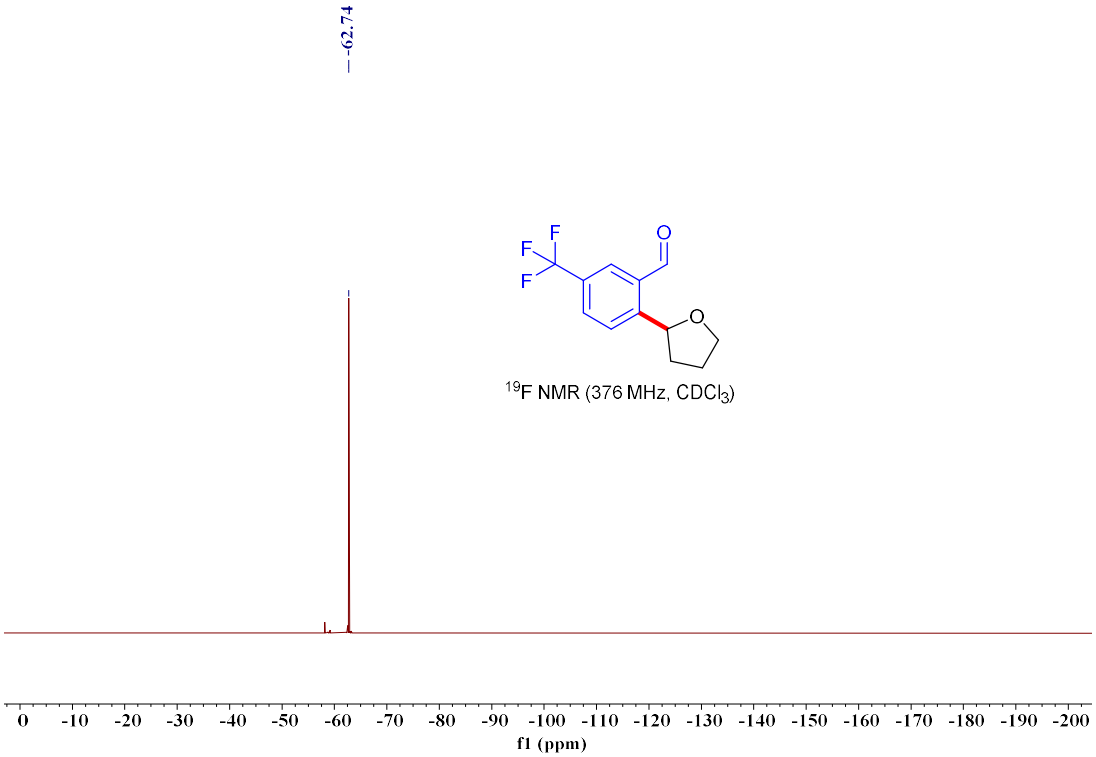




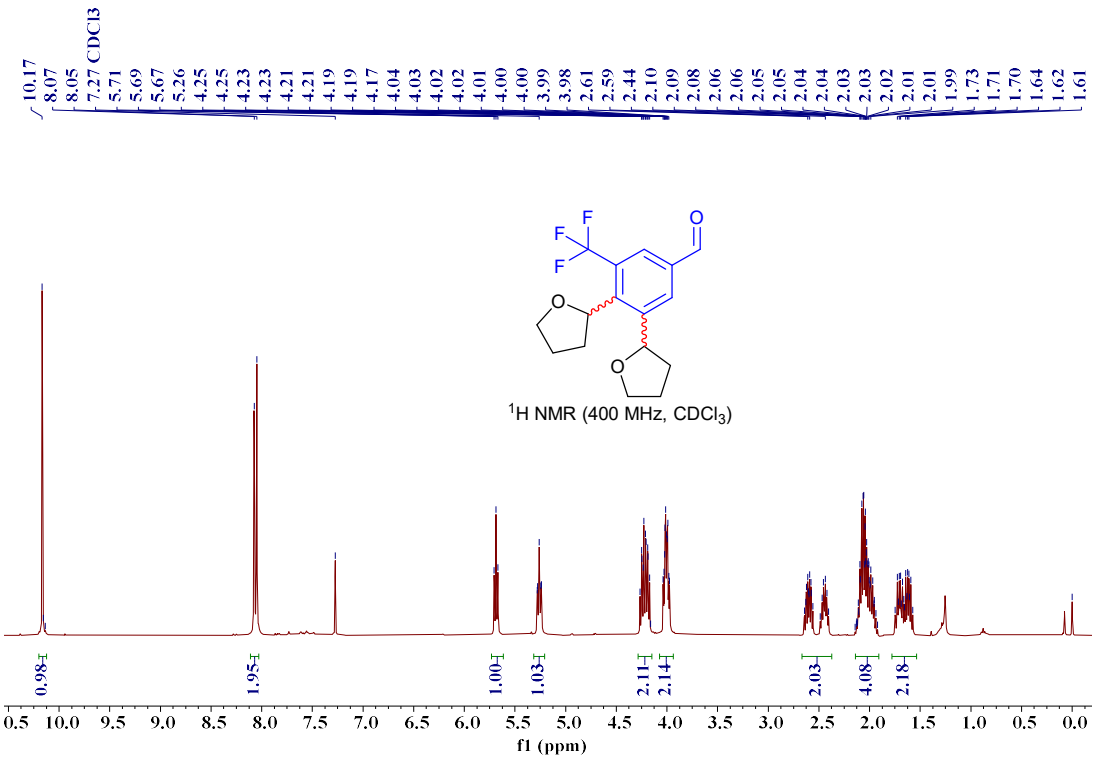
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound *ortho*-4g

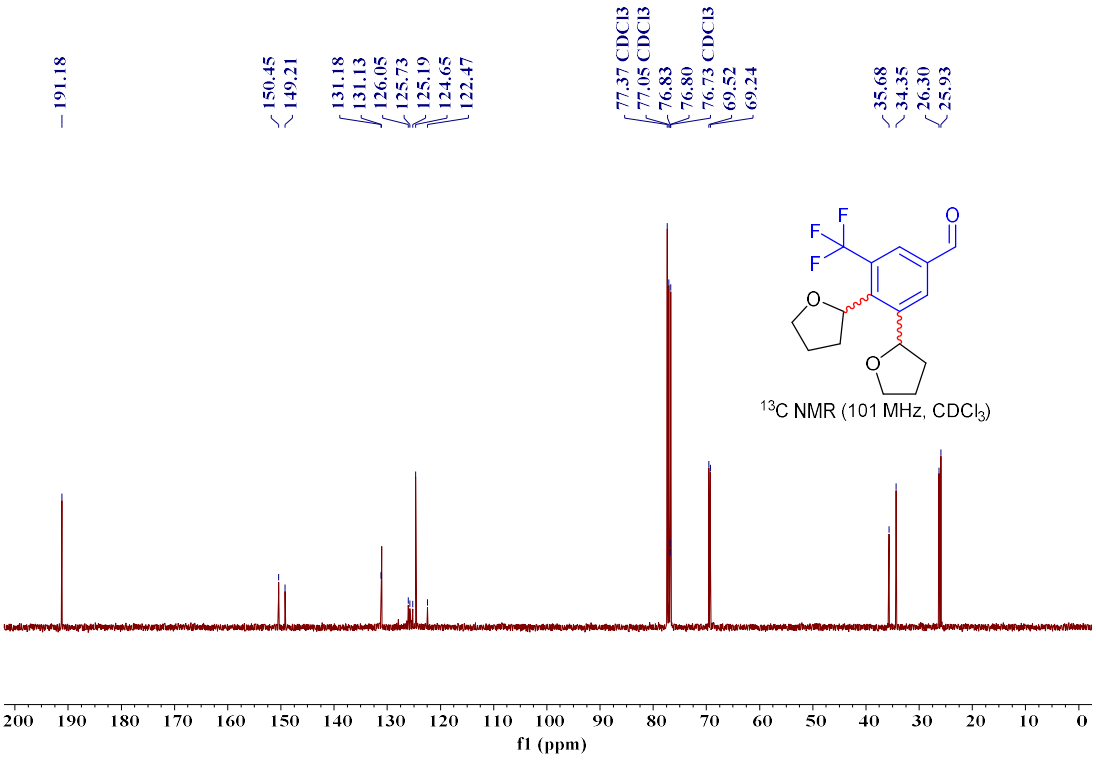


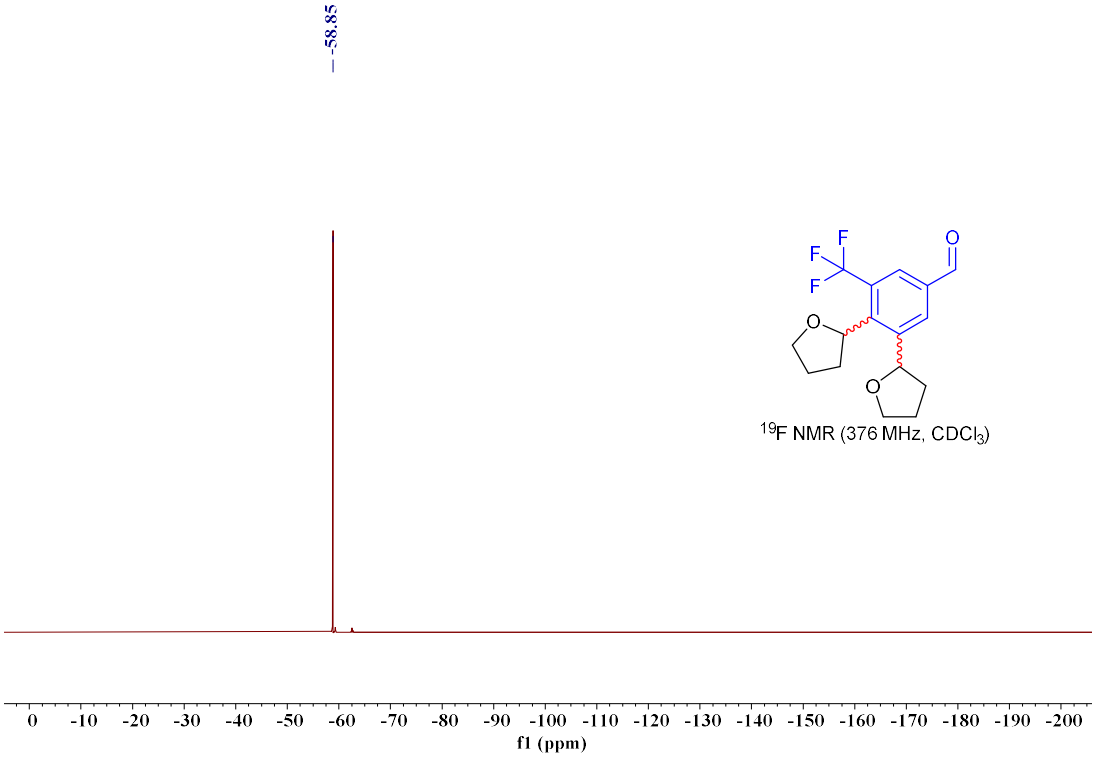




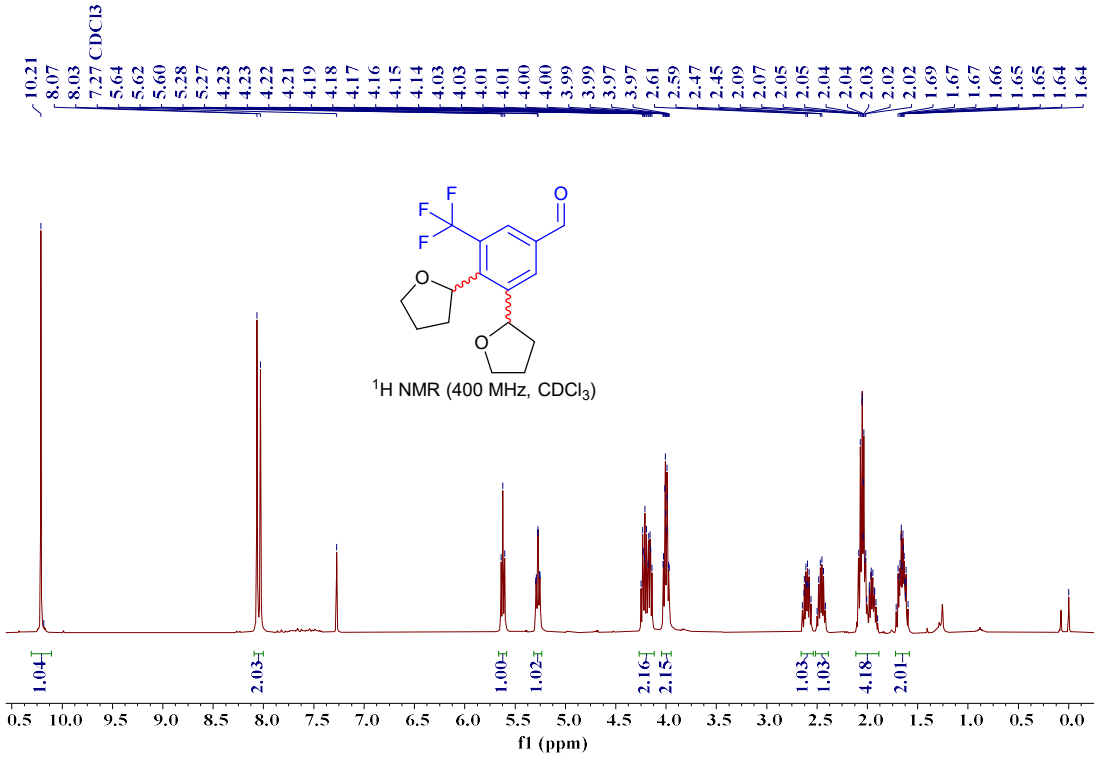
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound (3-R-4-S) *3,4-disubstituted*-4g

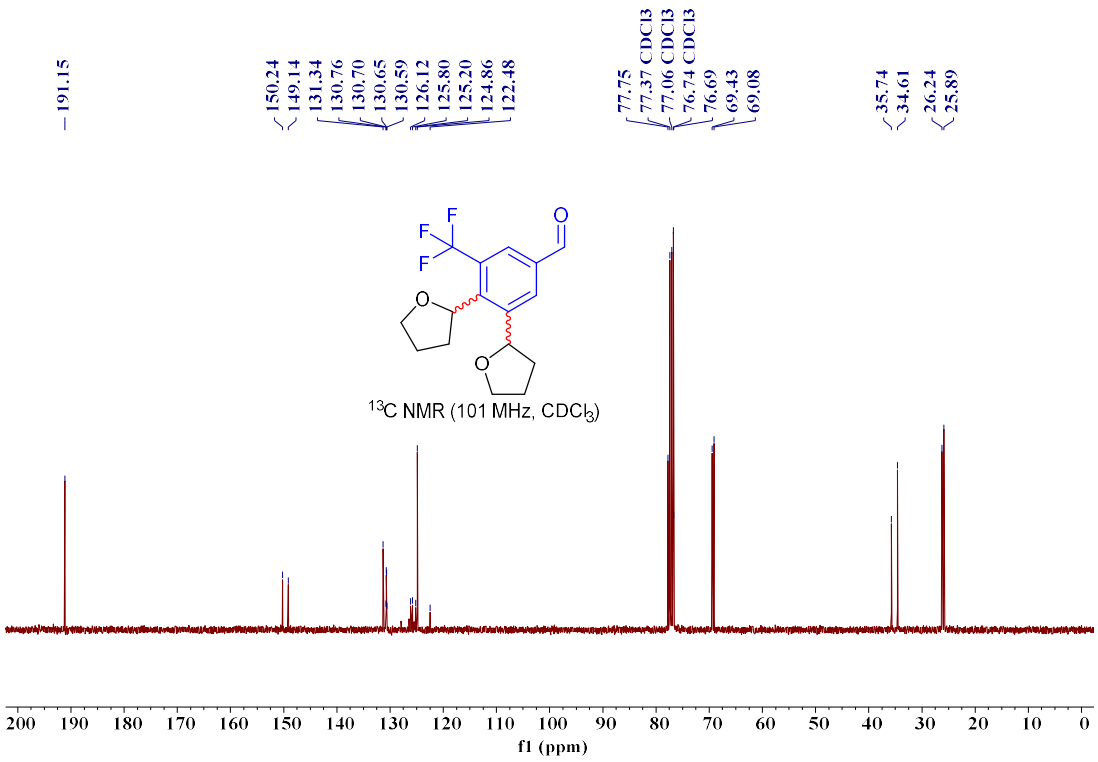


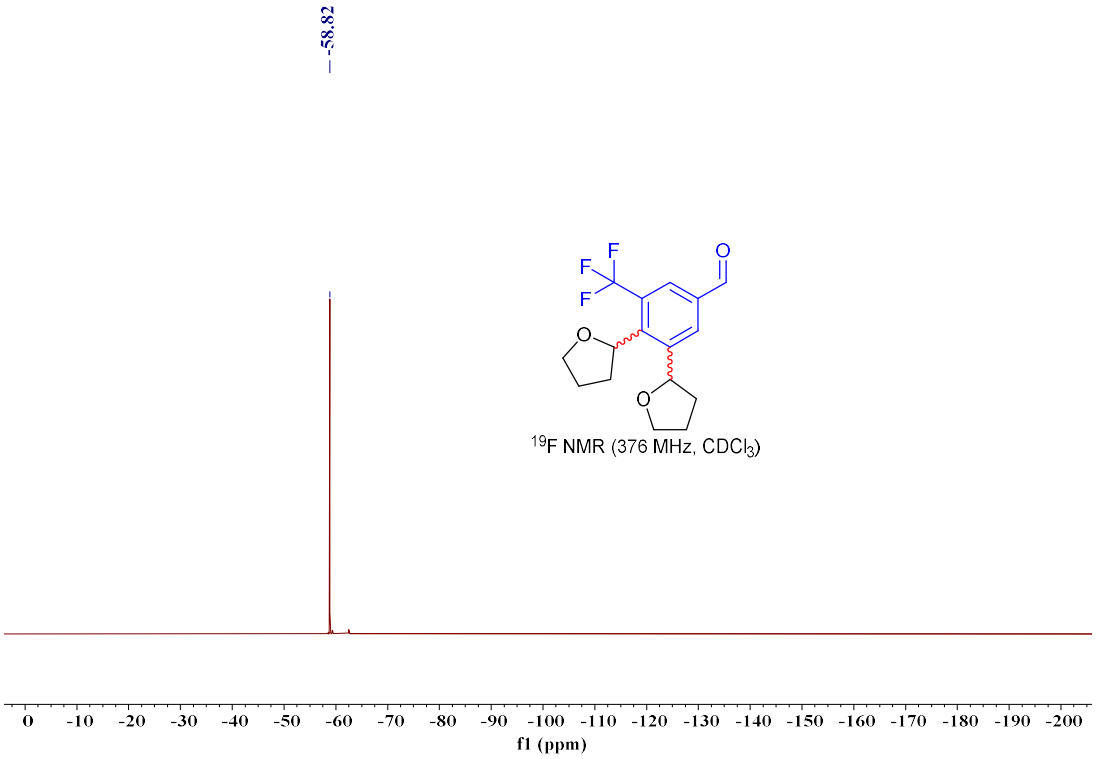

191.18
150.45
149.21
131.18
131.13
126.05
125.73
125.19
124.65
122.47
77.37 CDCl3
77.05 CDCl3
76.83
76.80
76.73 CDCl3
69.52
69.24
35.68
34.35
26.30
25.93
F
F
F
O
O
O
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-58.85
F
F
F
O
O
O
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

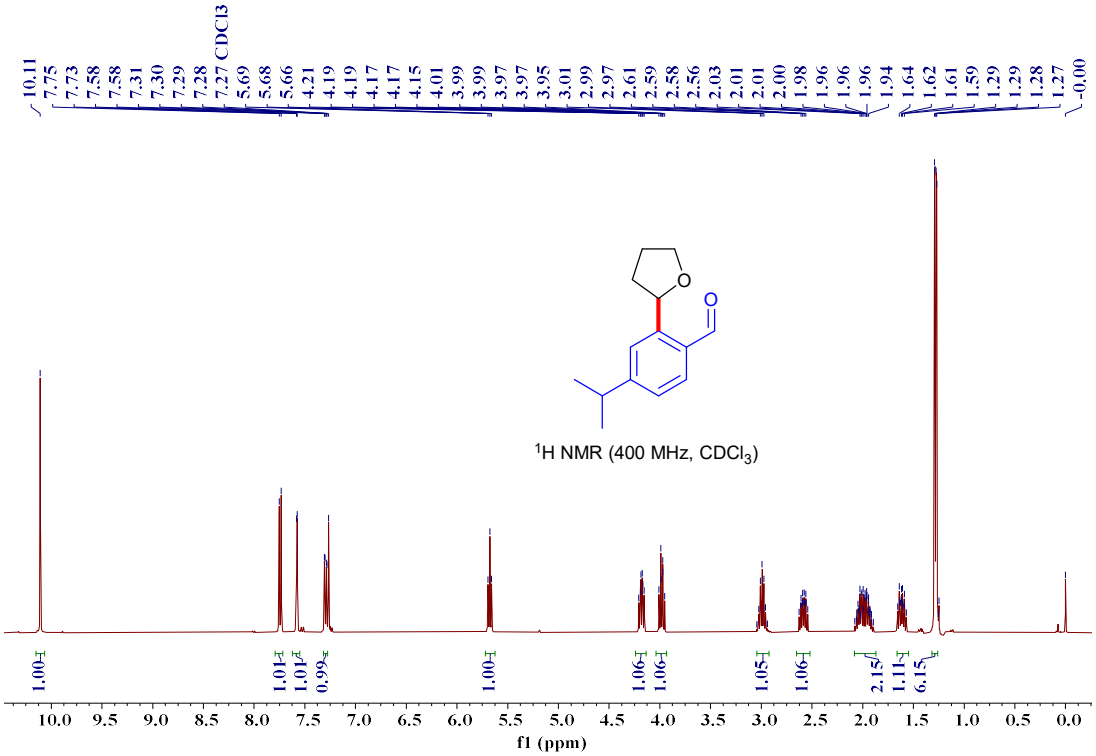
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound (3-R-4-R) *3,4-disubstituted*-4g

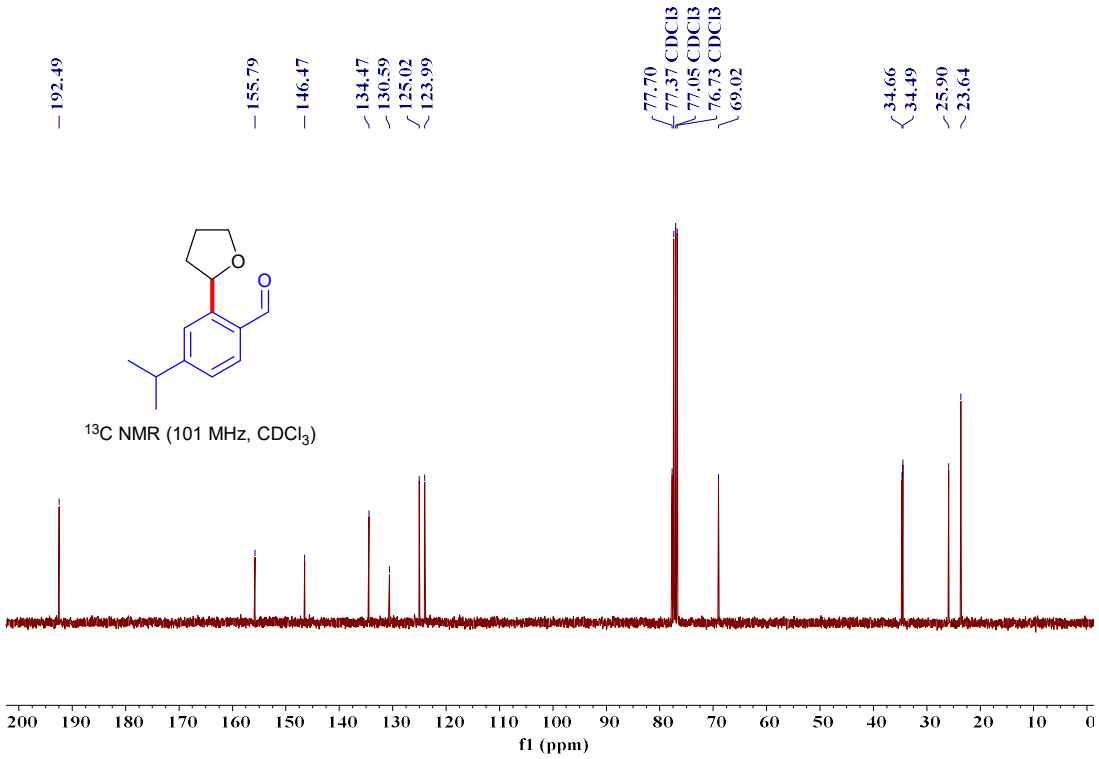




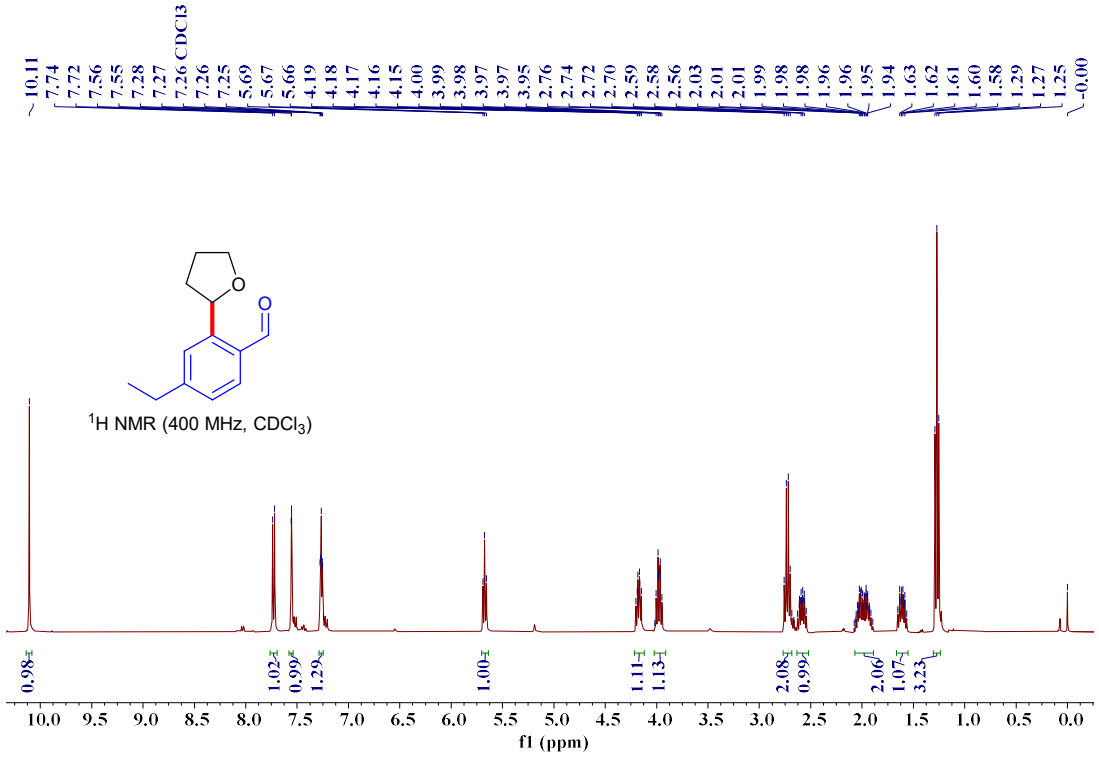


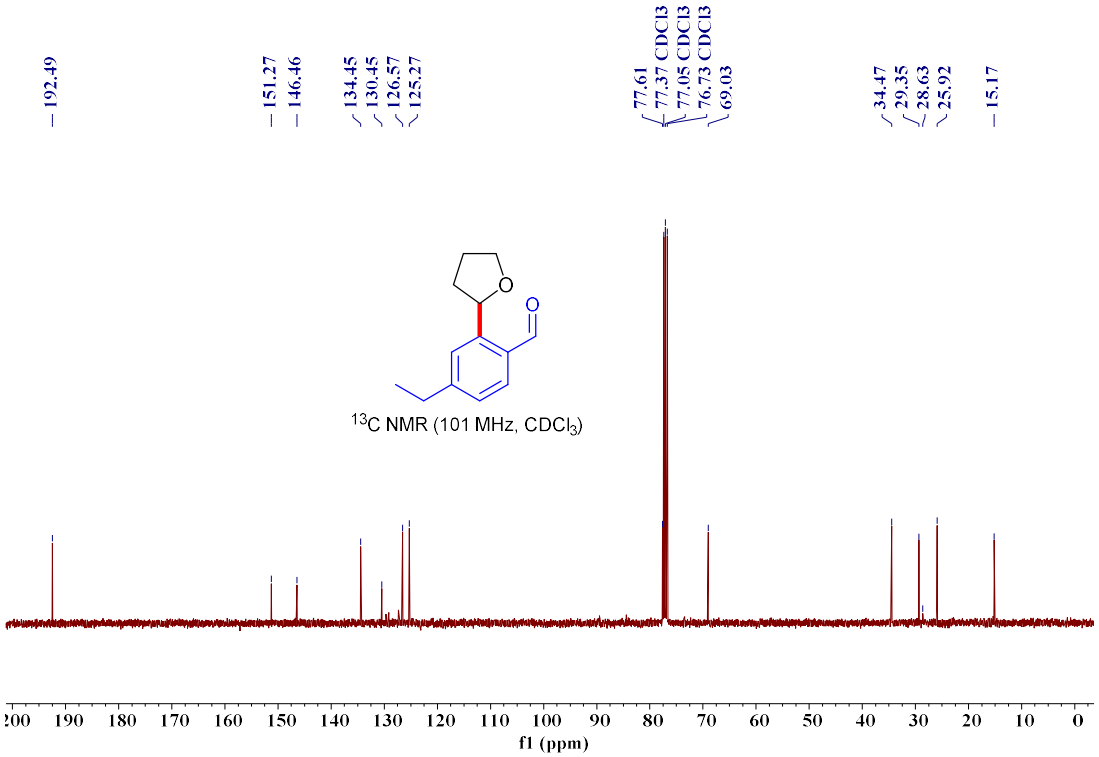
^{1}H and ^{13}C NMR spectra of compound *ortho*-4h



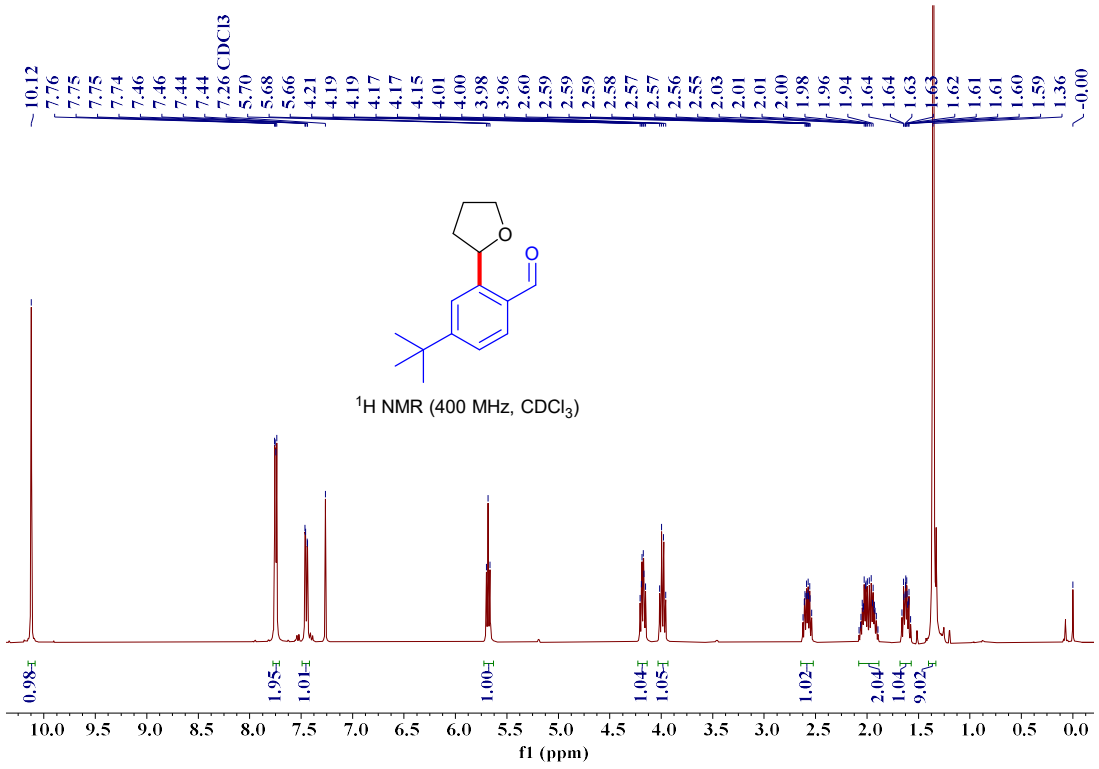


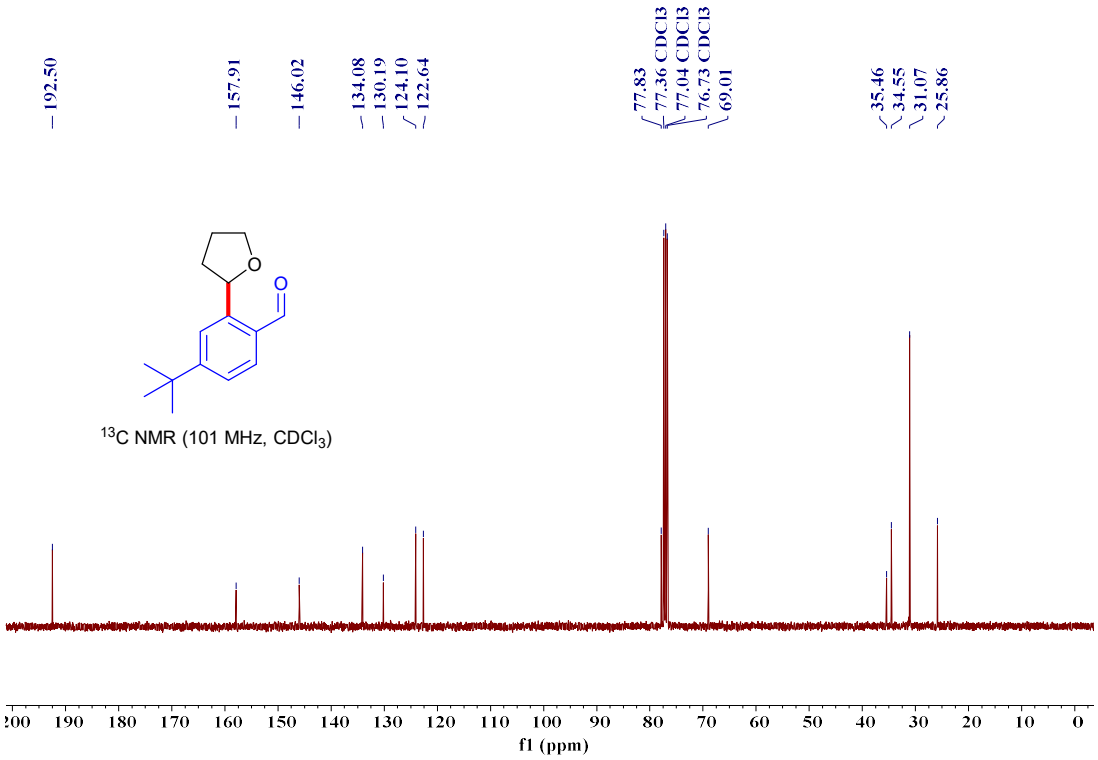
^{1}H and ^{13}C NMR spectra of compound *ortho*-4i



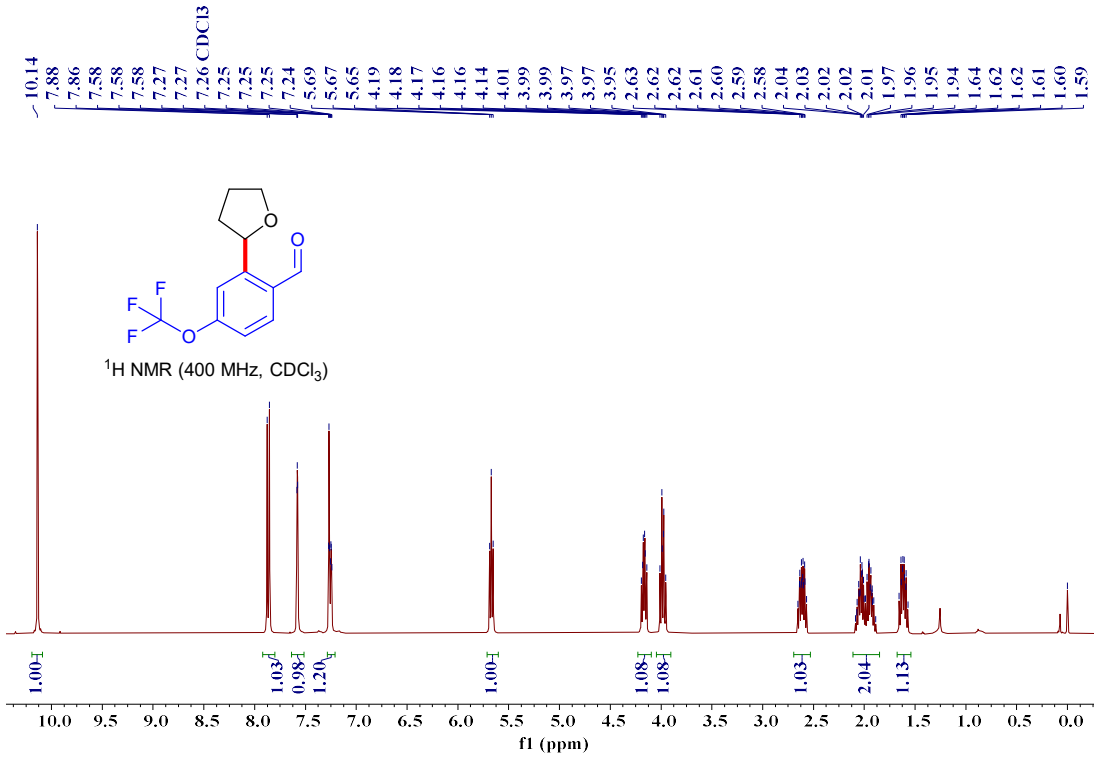


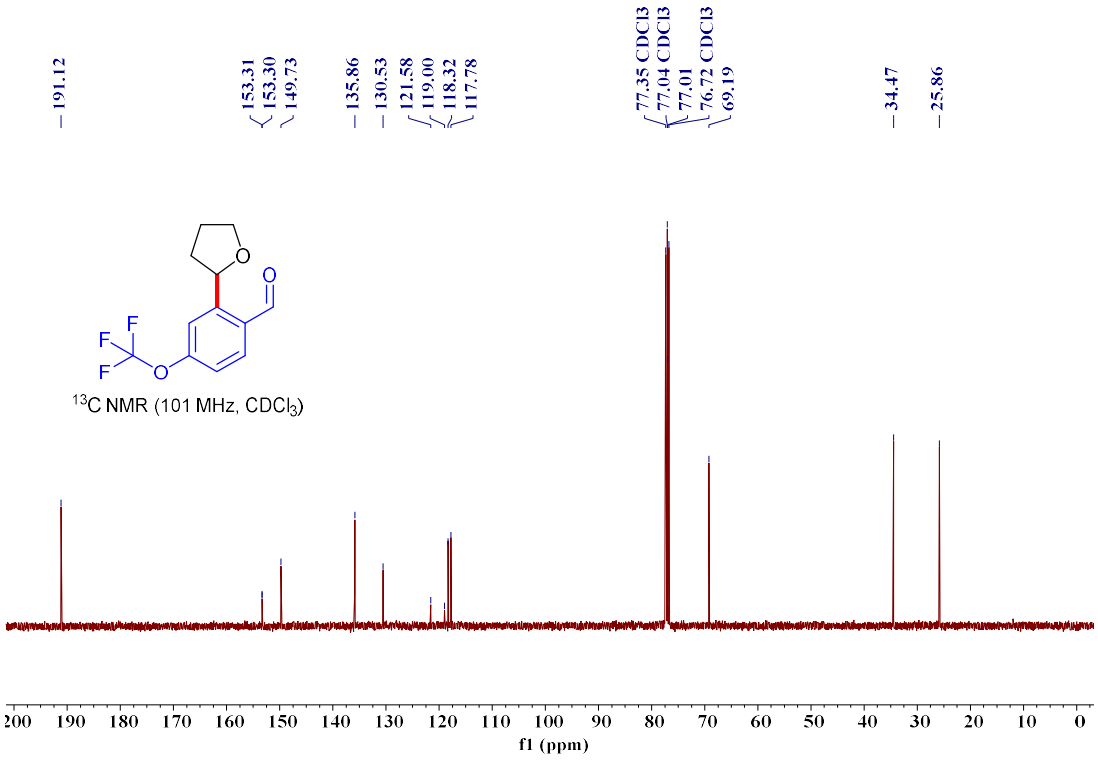
^{1}H and ^{13}C NMR spectra of compound *ortho*-4j

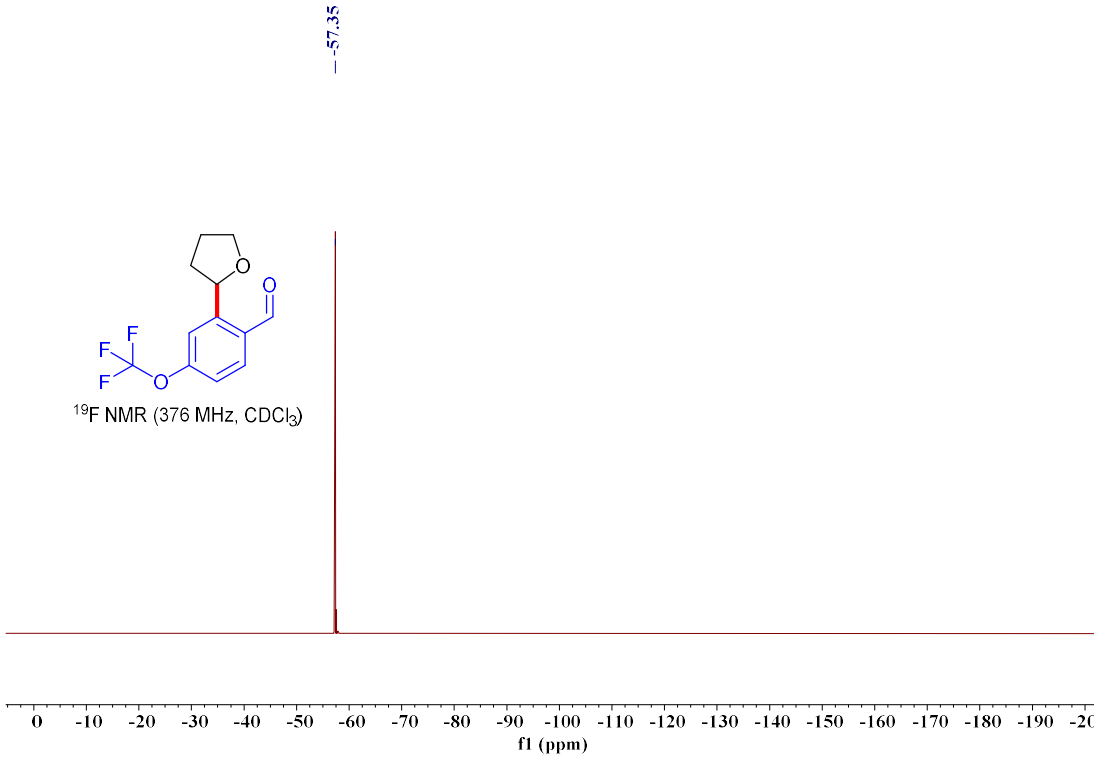




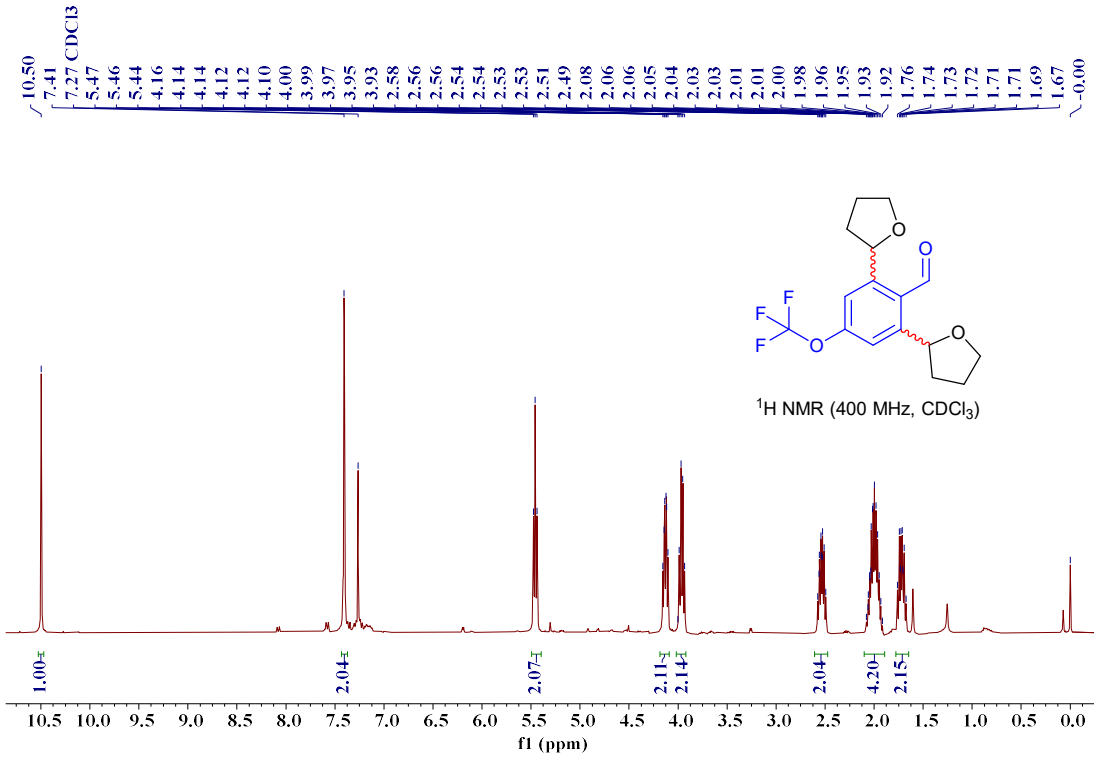
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *ortho*-4k

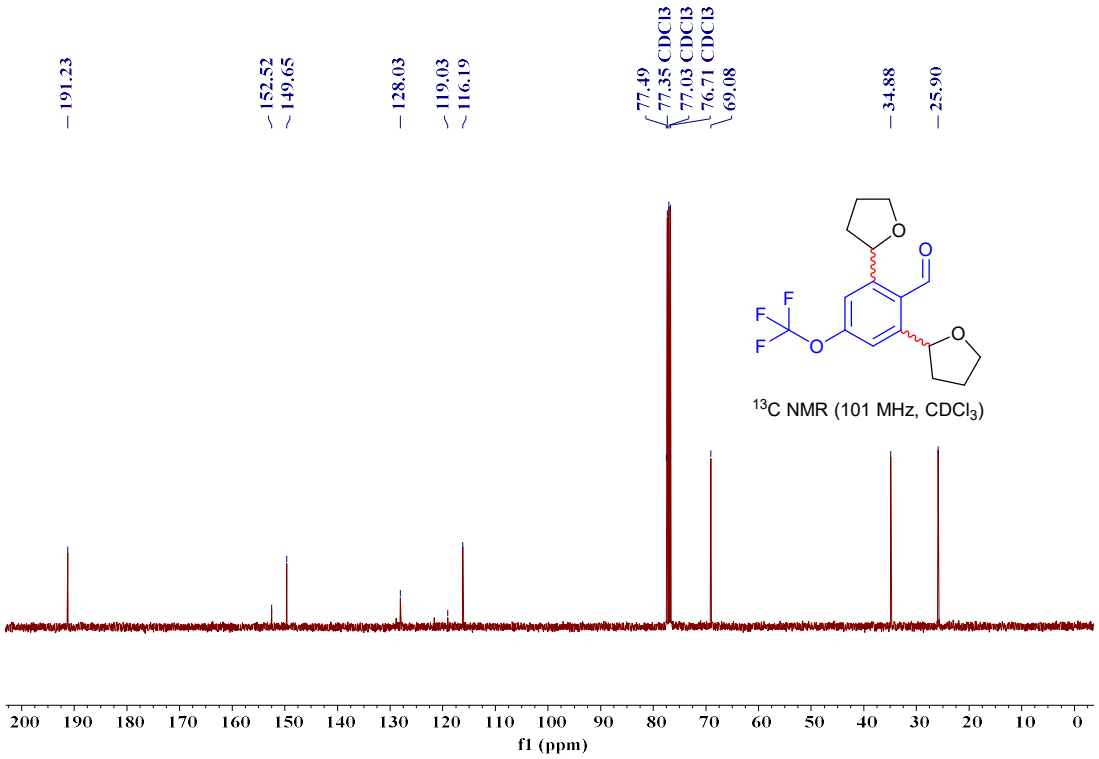


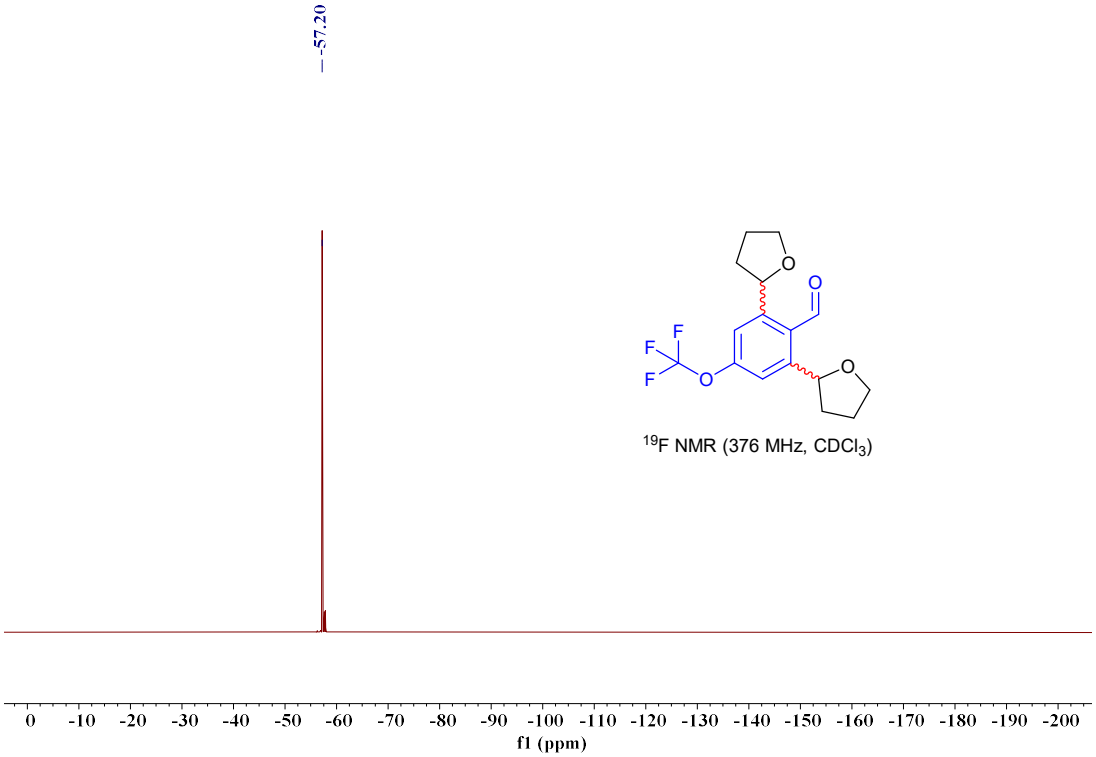

191.12
153.31
153.30
149.73
135.86
130.53
121.58
119.00
118.32
117.78
77.35 CDCl3
77.04 CDCl3
77.01
76.72 CDCl3
69.19
34.47
25.86
O
O
F
F
F
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-57.35
O
O
F
F
F
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

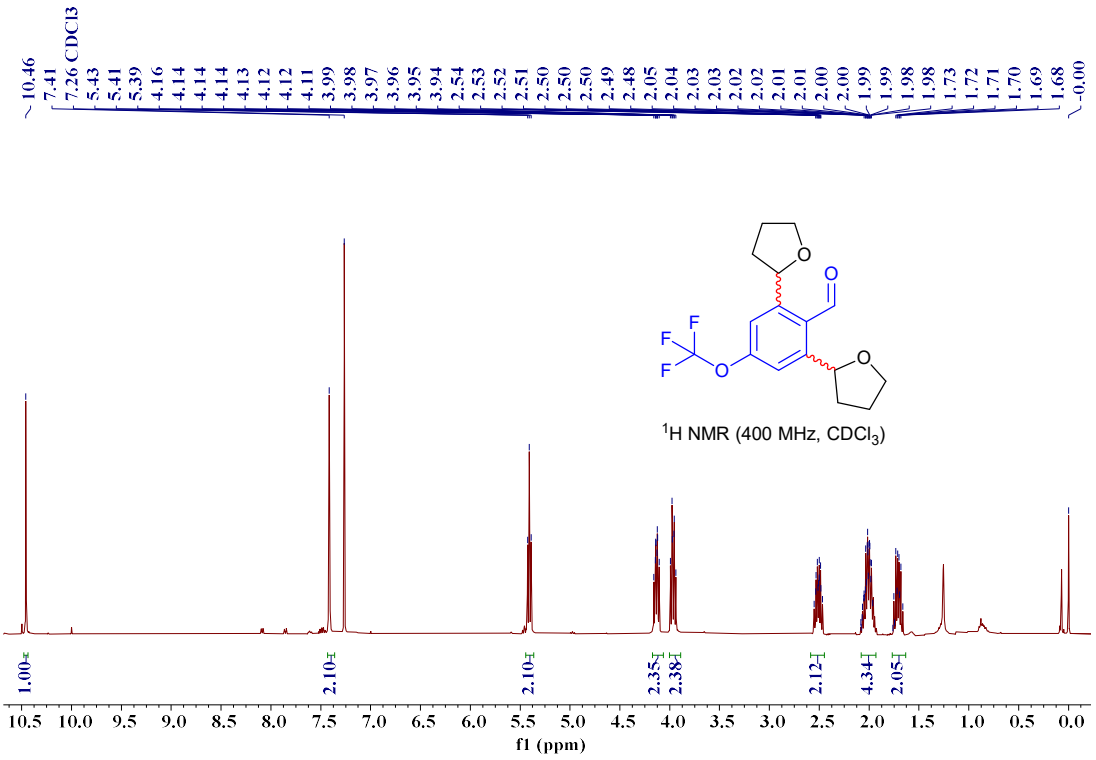
^{1}H, ^{13}C and ^{19}F NMR spectra of compound (2-R-6-S) *2,6-disubstituted*-4k

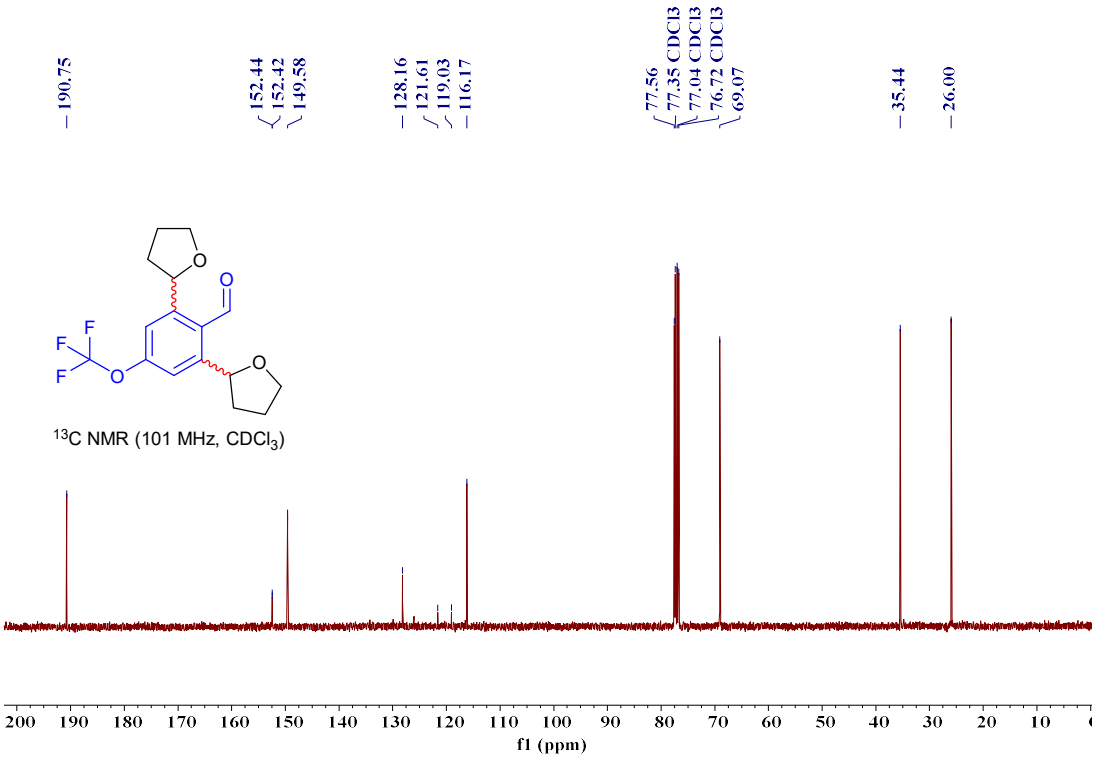


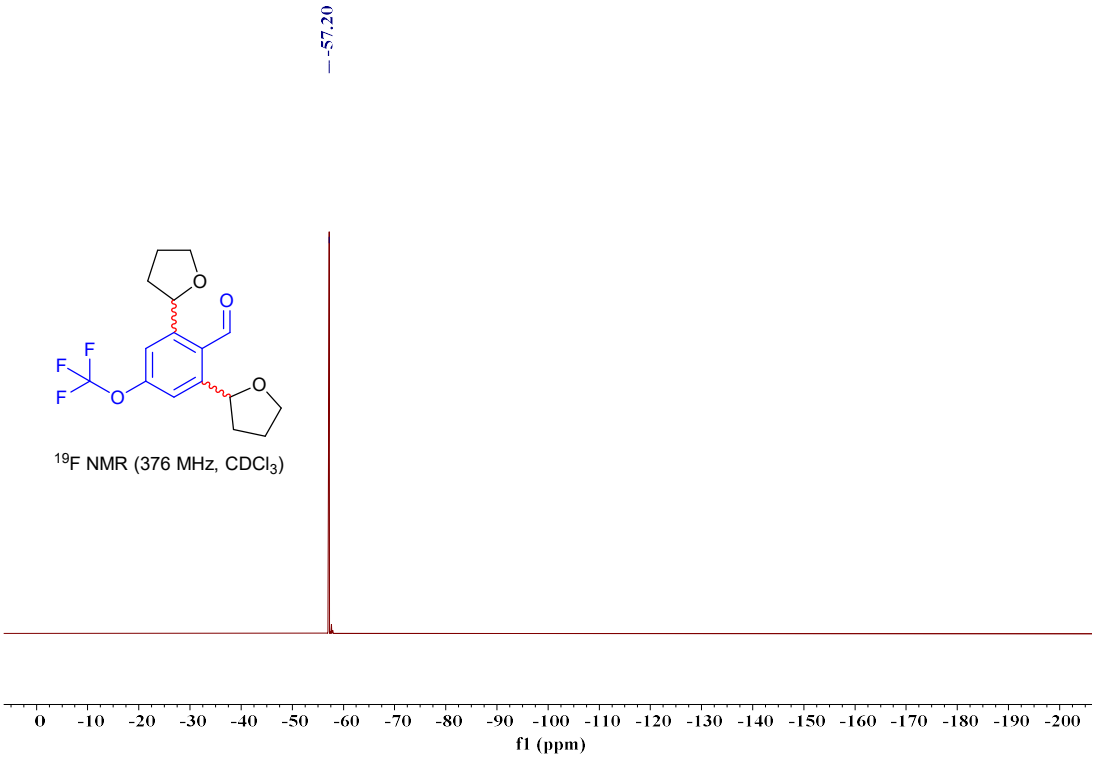




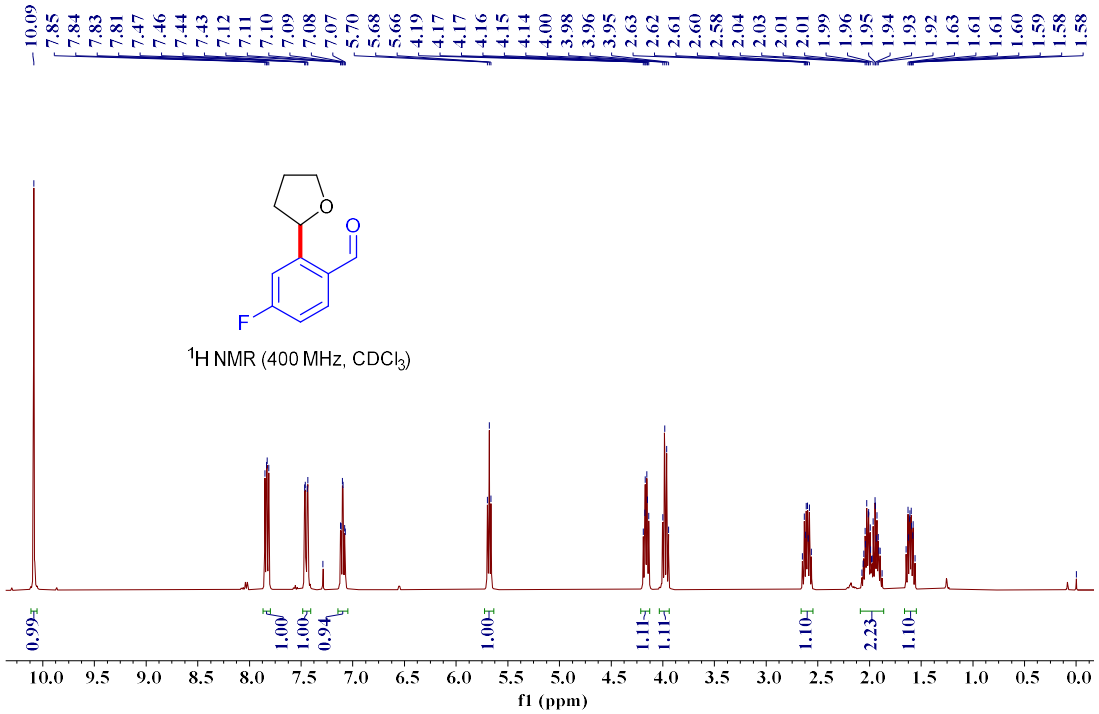
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound (2-R-6-R) *2,6-disubstituted*-4k

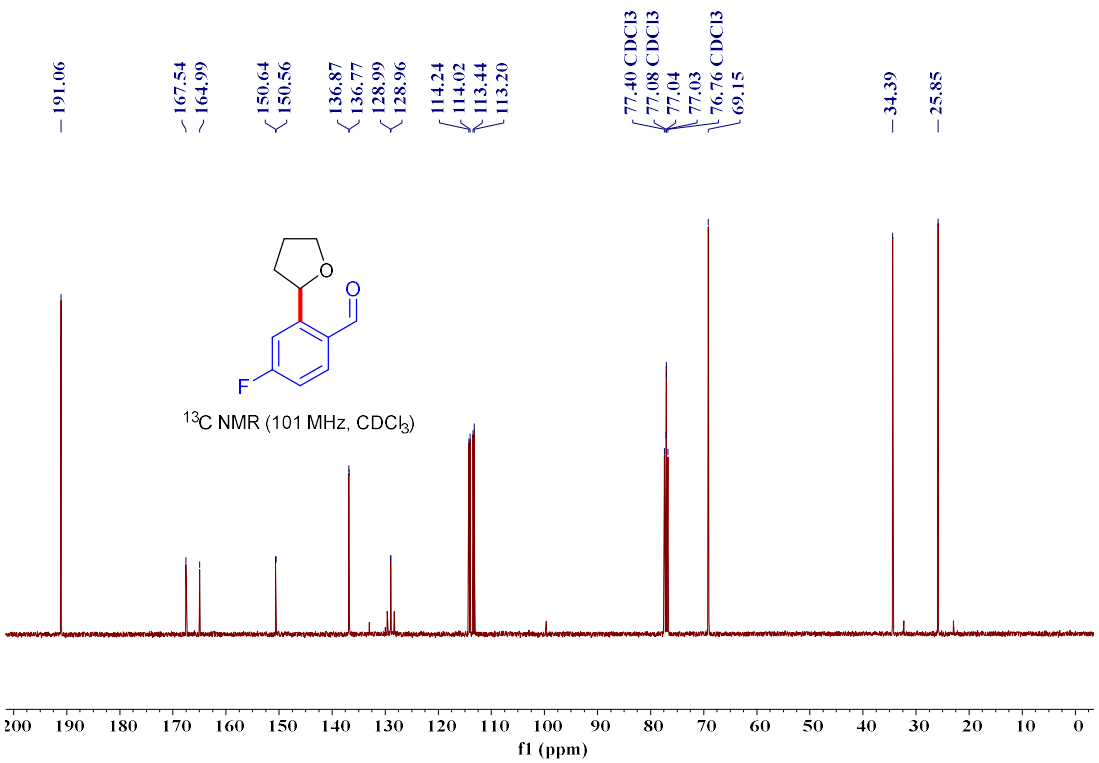


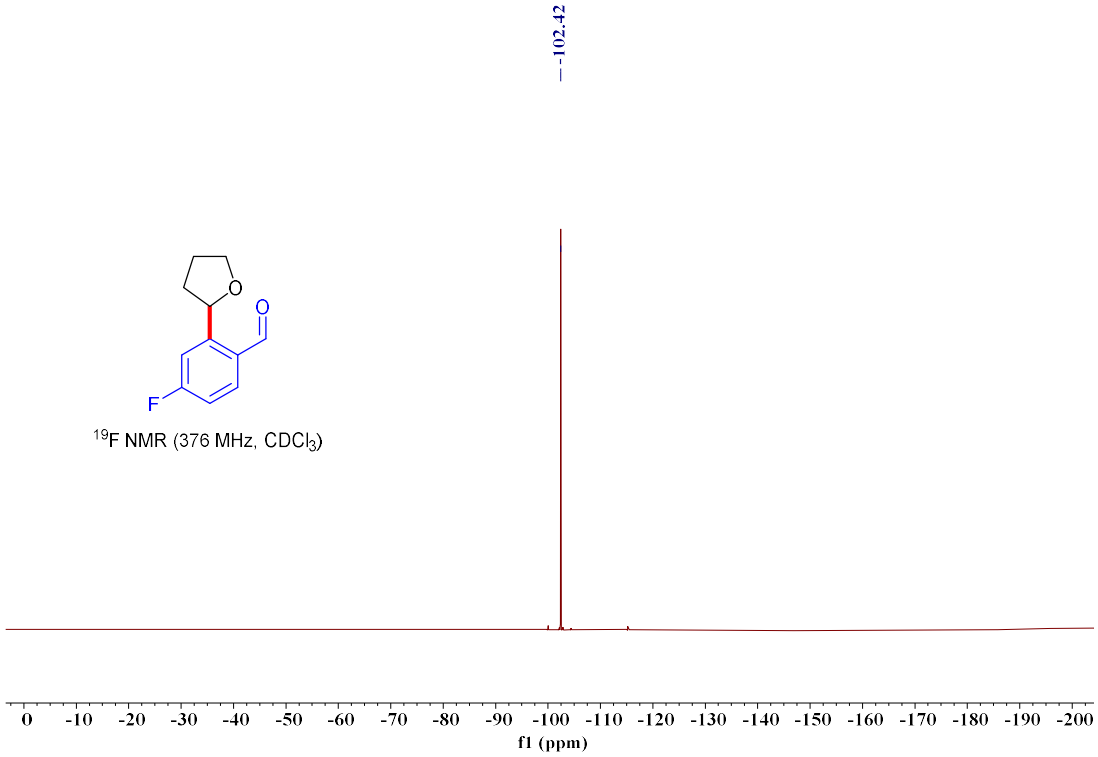

190.75
152.44
152.42
149.58
128.16
121.61
119.03
116.17
77.56
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
69.07
35.44
26.00
O
O
F
F
F
O
O
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-57.20
O
O
F
F
F
O
O
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

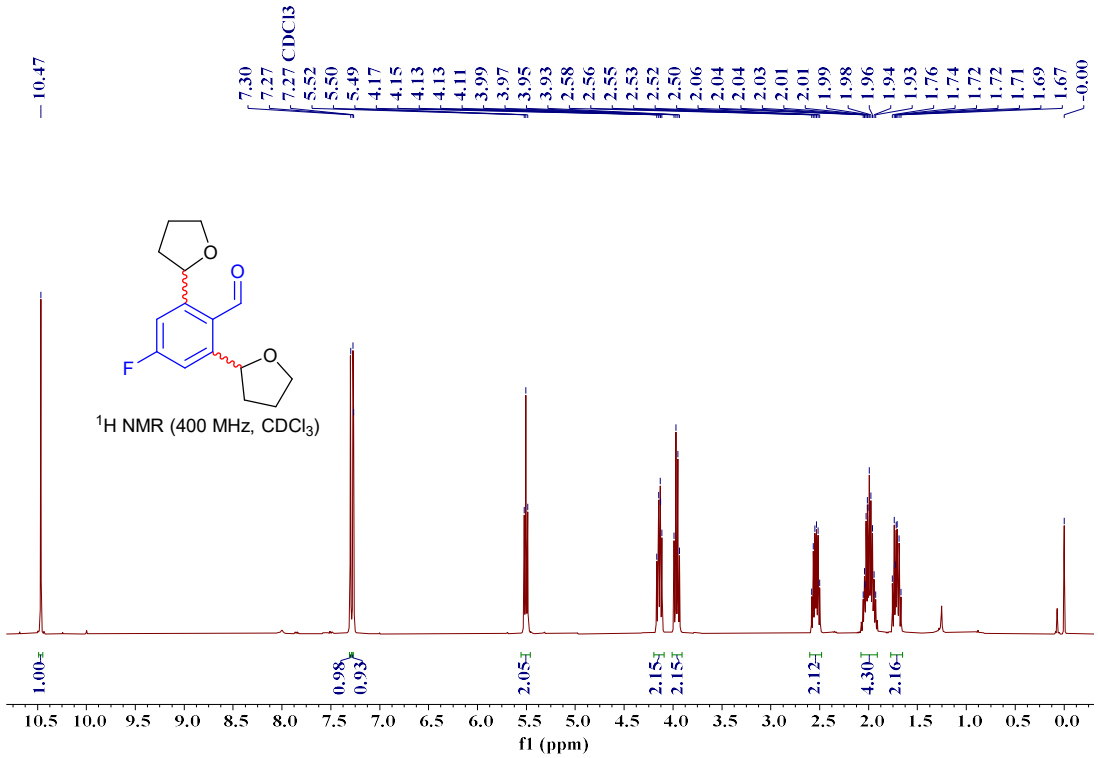
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *ortho*-4l

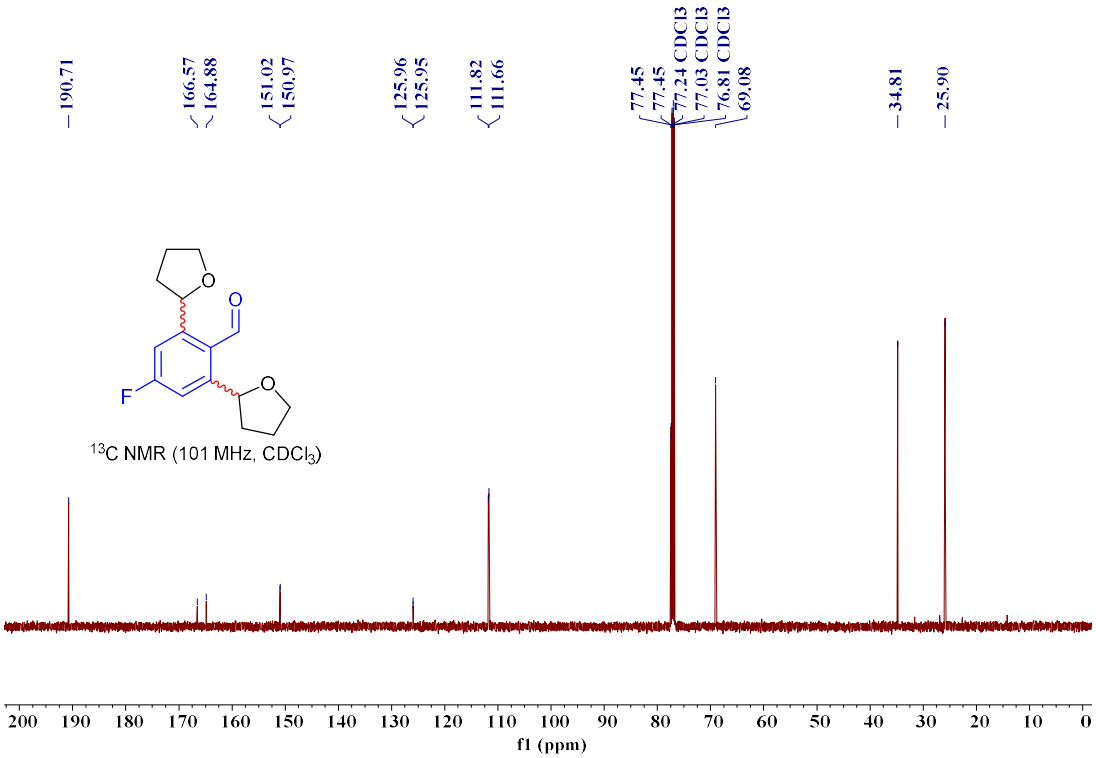


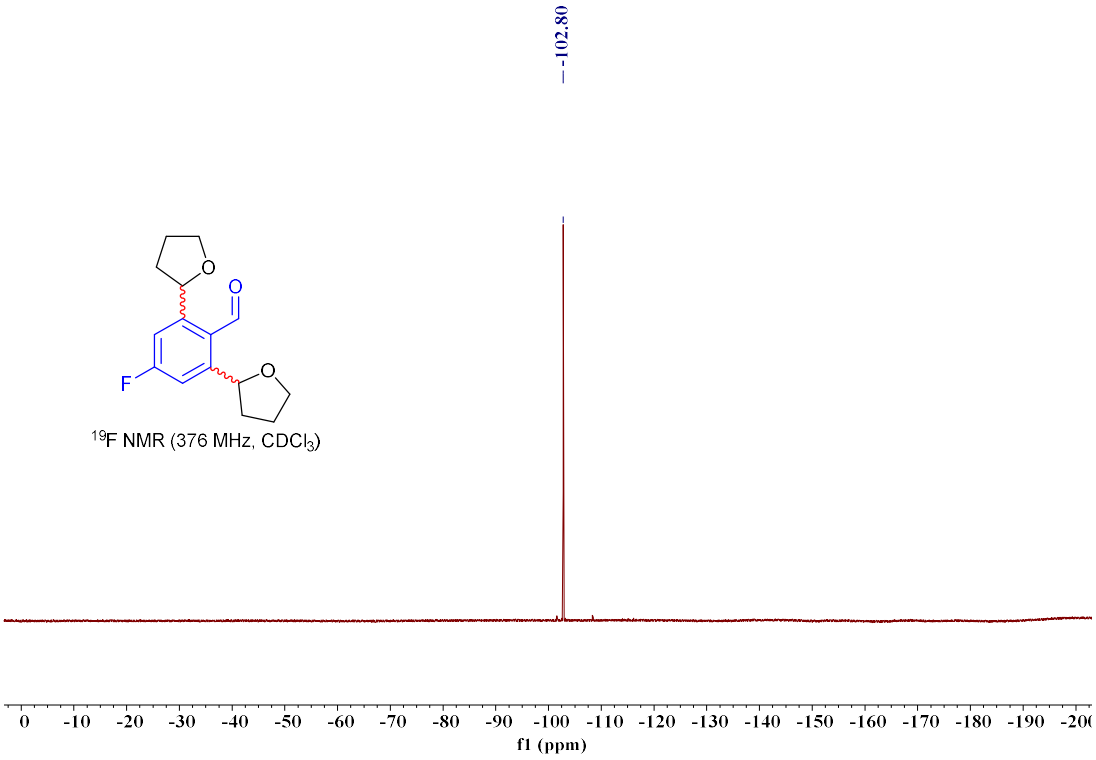




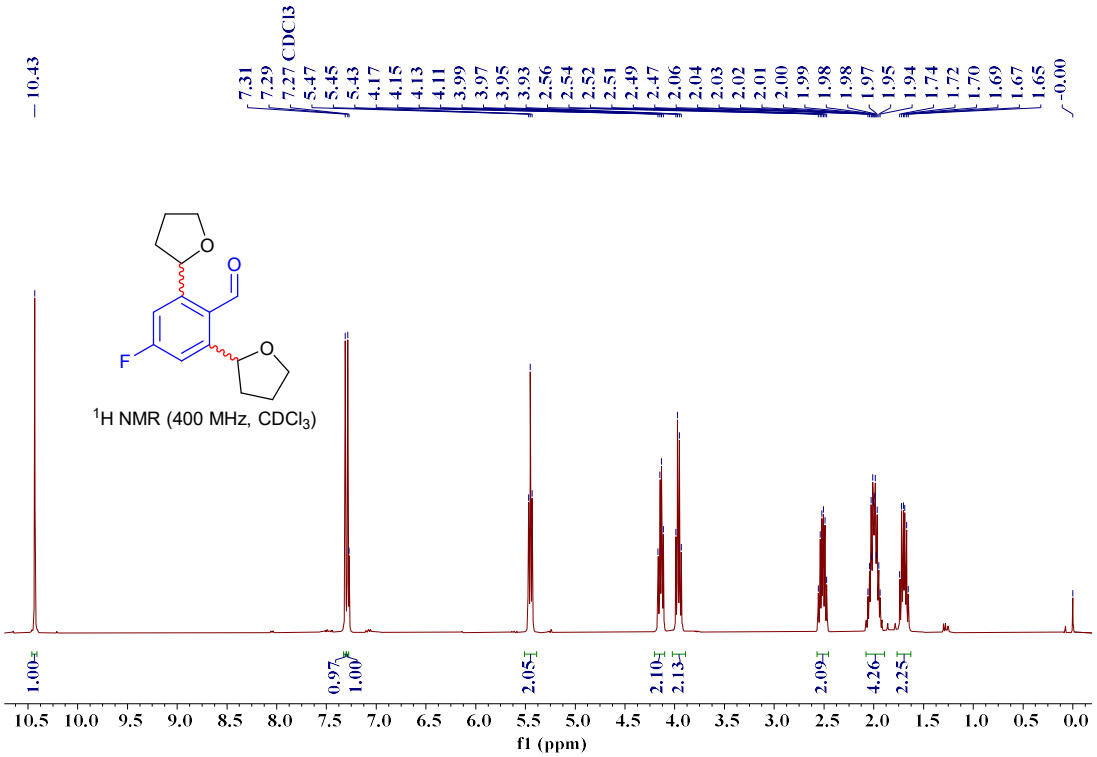
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound (2-R-6-S) *2,6-disubstituted*-4l

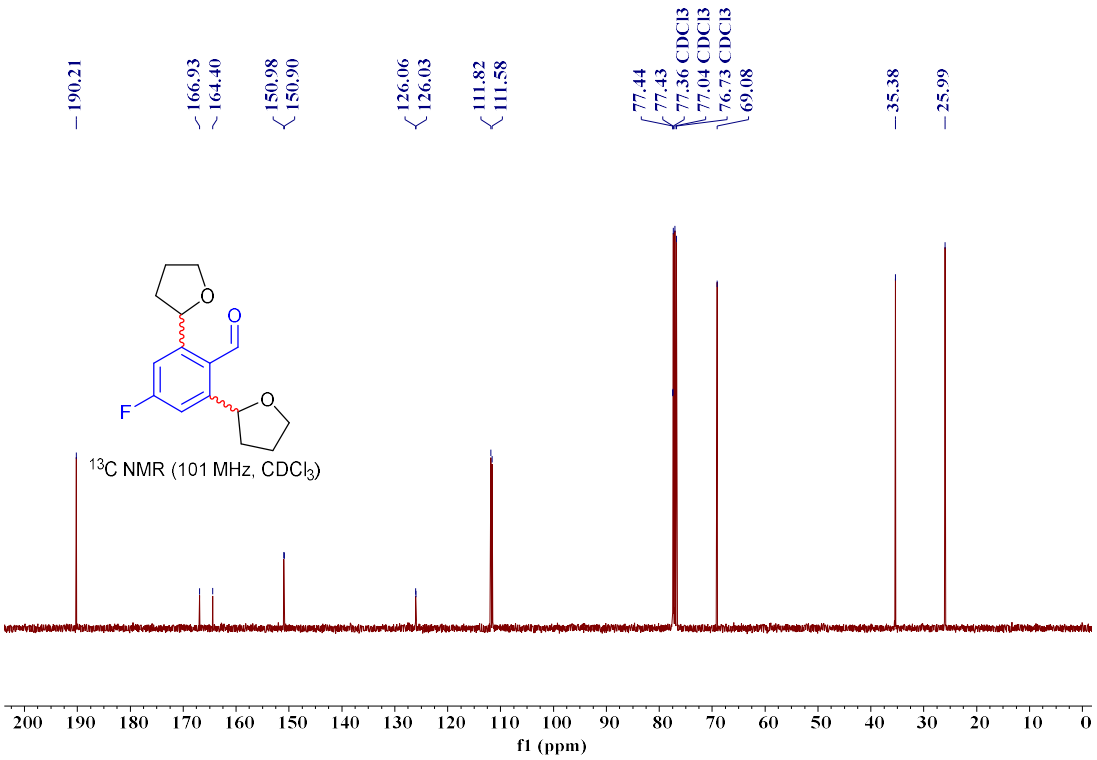


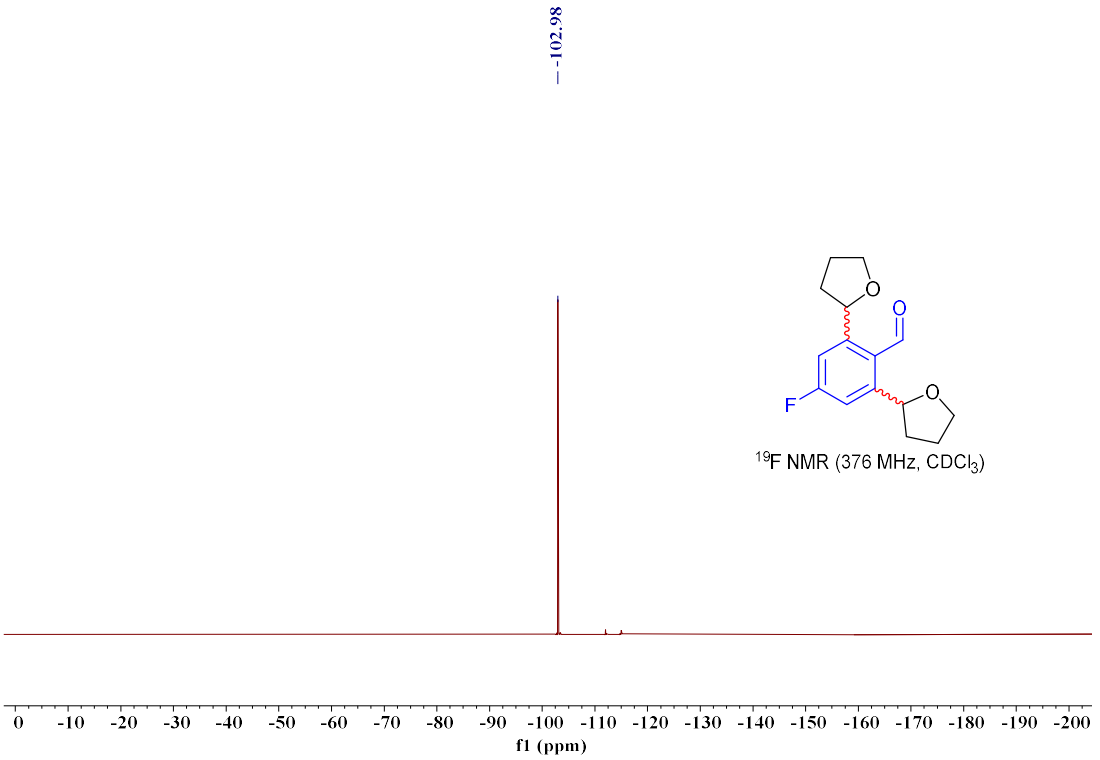

190.71
166.57
164.88
151.02
150.97
125.96
125.95
111.82
111.66
77.45
77.45
77.24 CDCl3
77.03 CDCl3
76.81 CDCl3
69.08
34.81
25.90
O
O
F
O
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-102.80
O
O
F
O
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

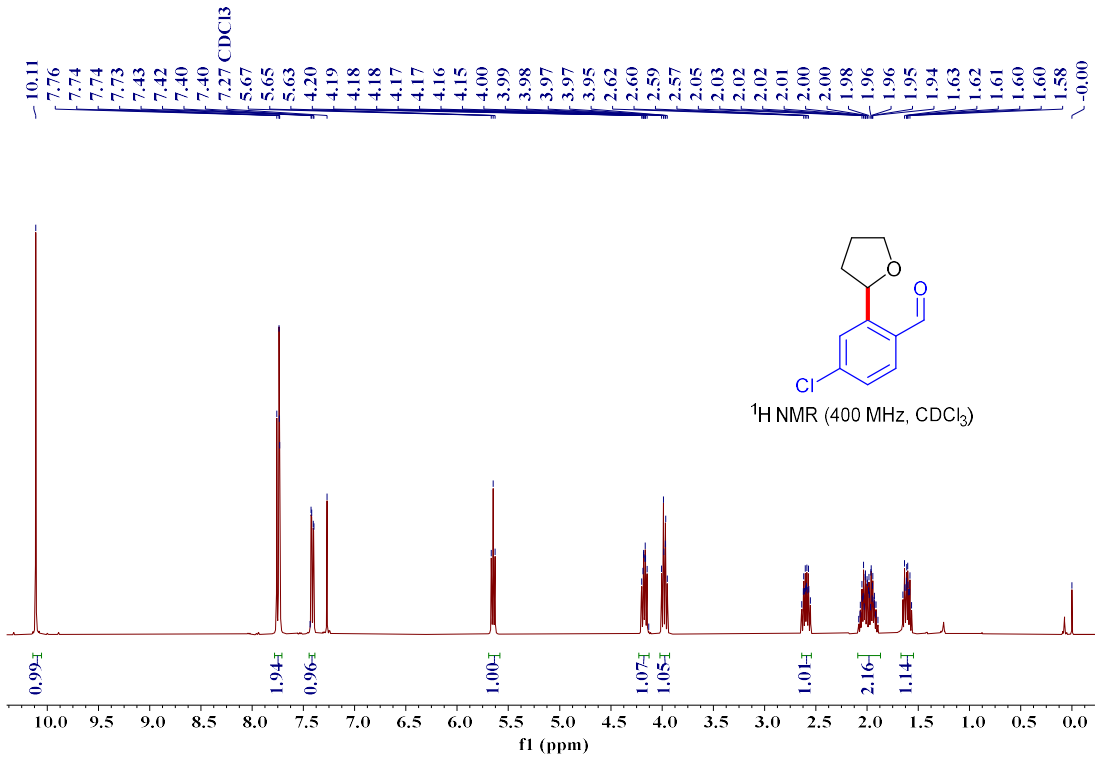
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound (2-R-6-R) *2,6-disubstituted*-4l

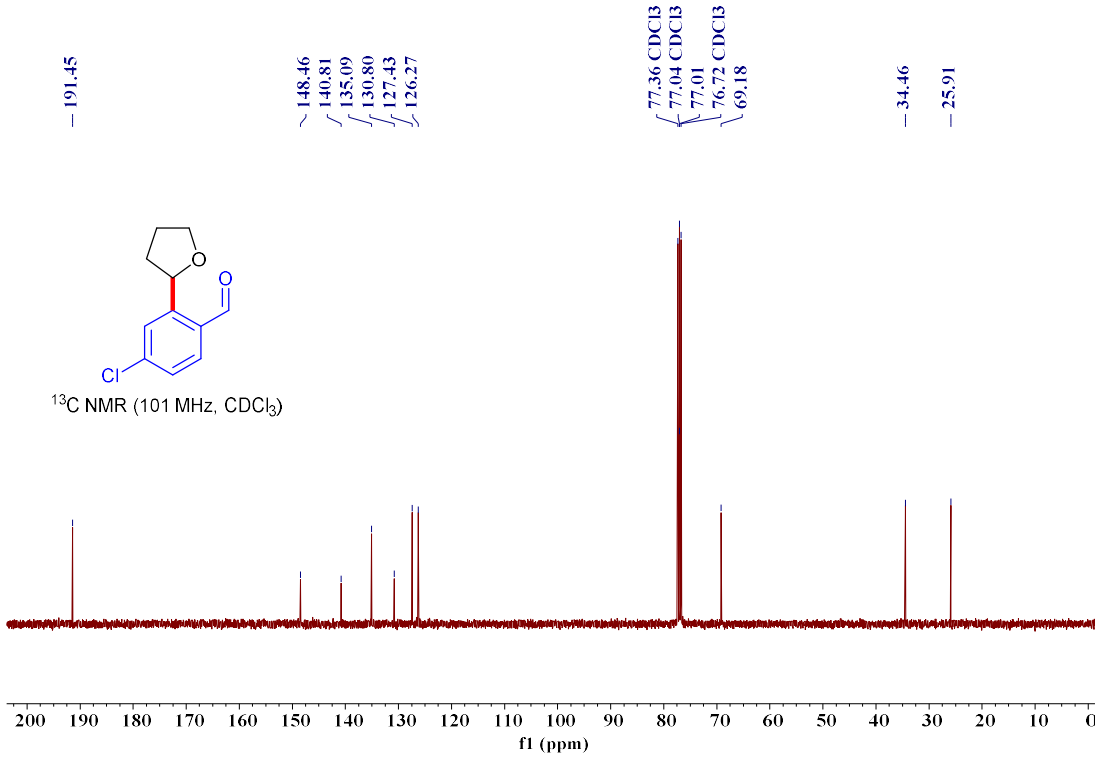




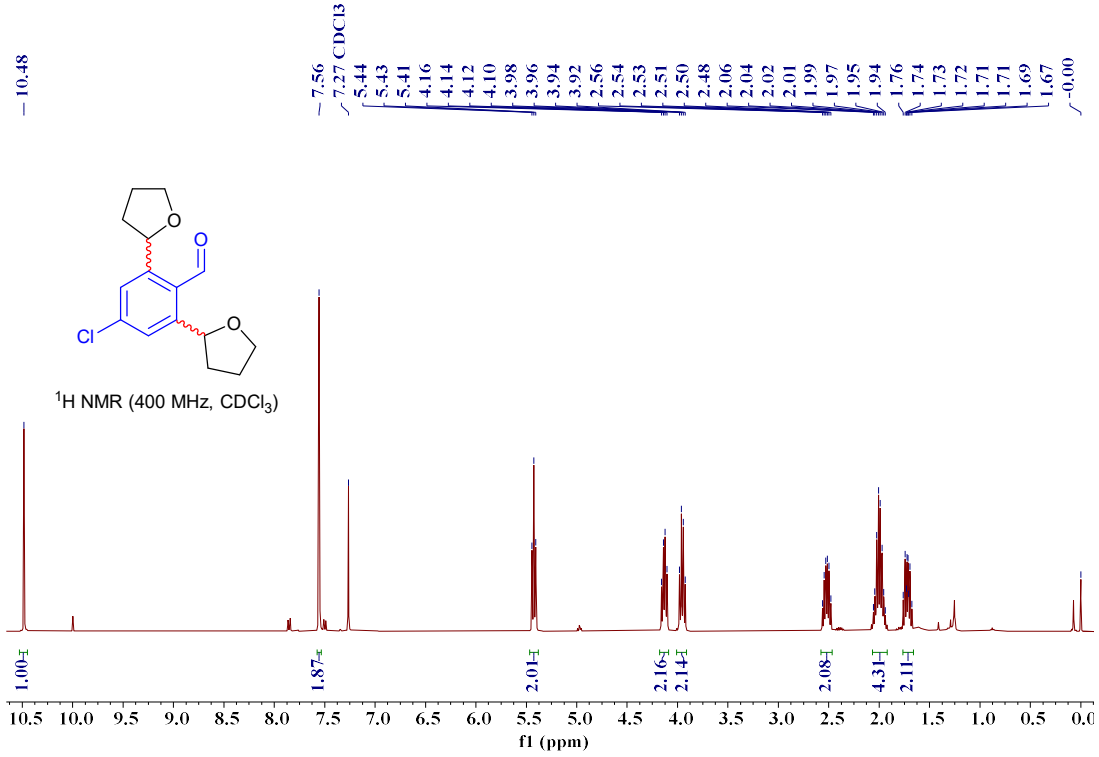


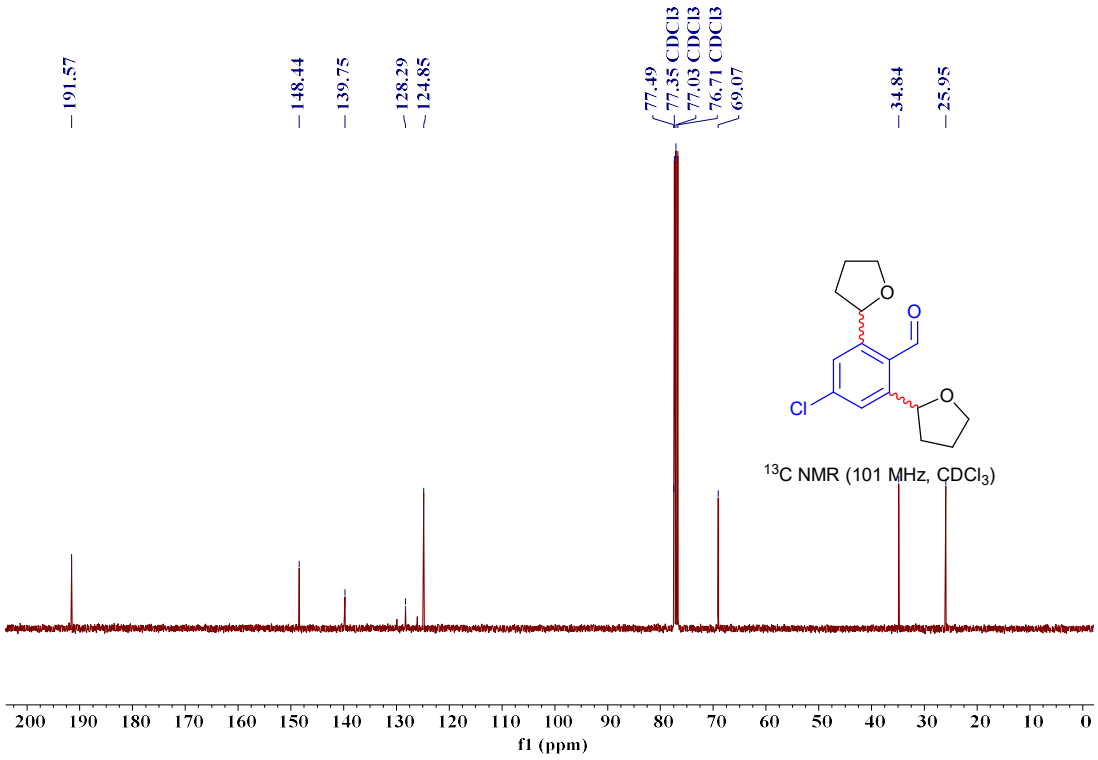
^{1}H and ^{13}C NMR spectra of compound *ortho*-4m



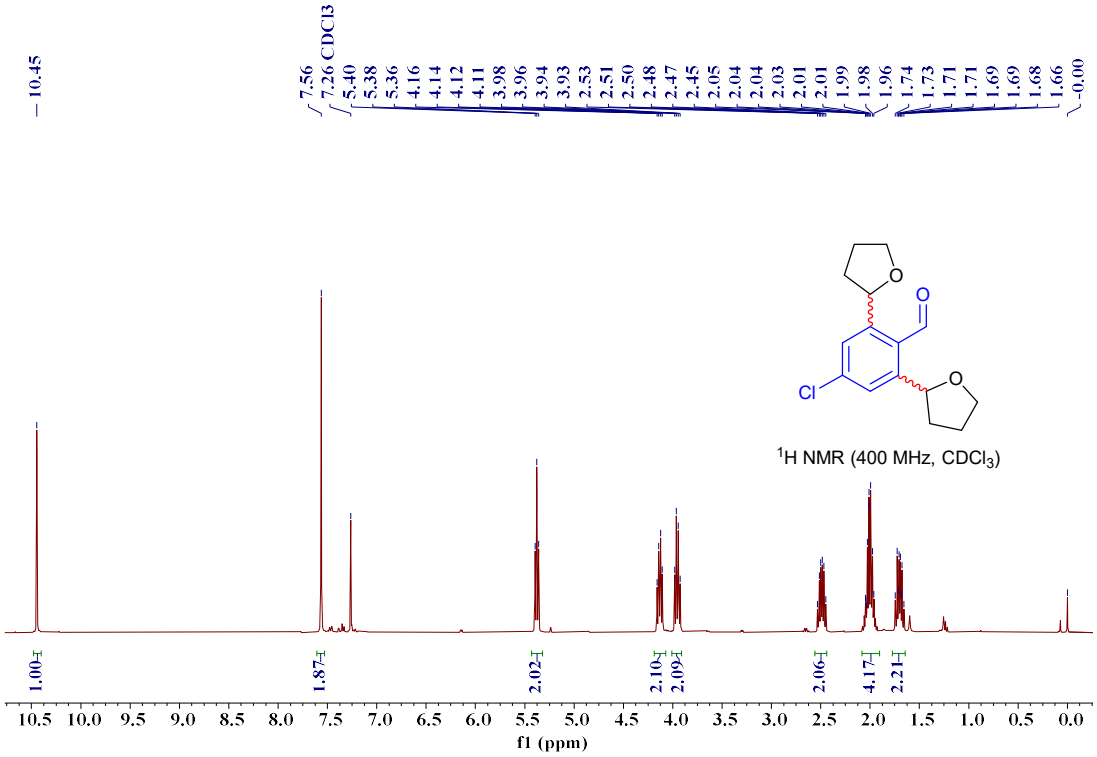


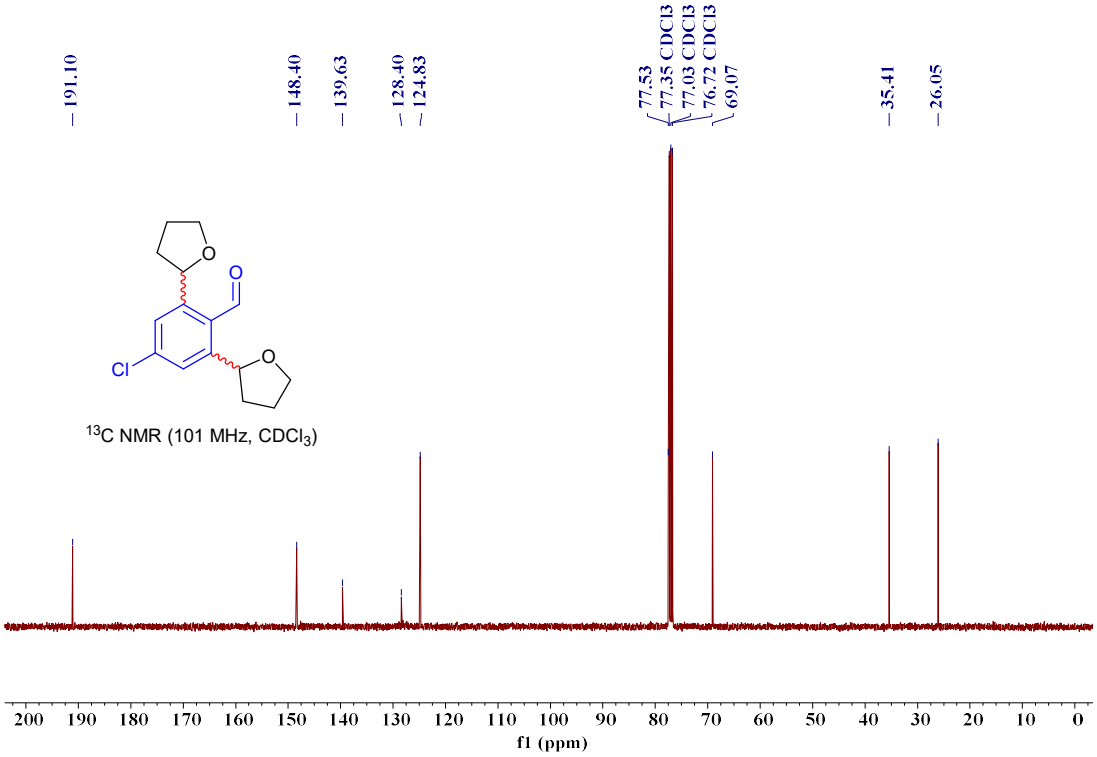
^{1}H and ^{13}C NMR spectra of compound (2-R-6-S) *2,6-disubstituted*-4m



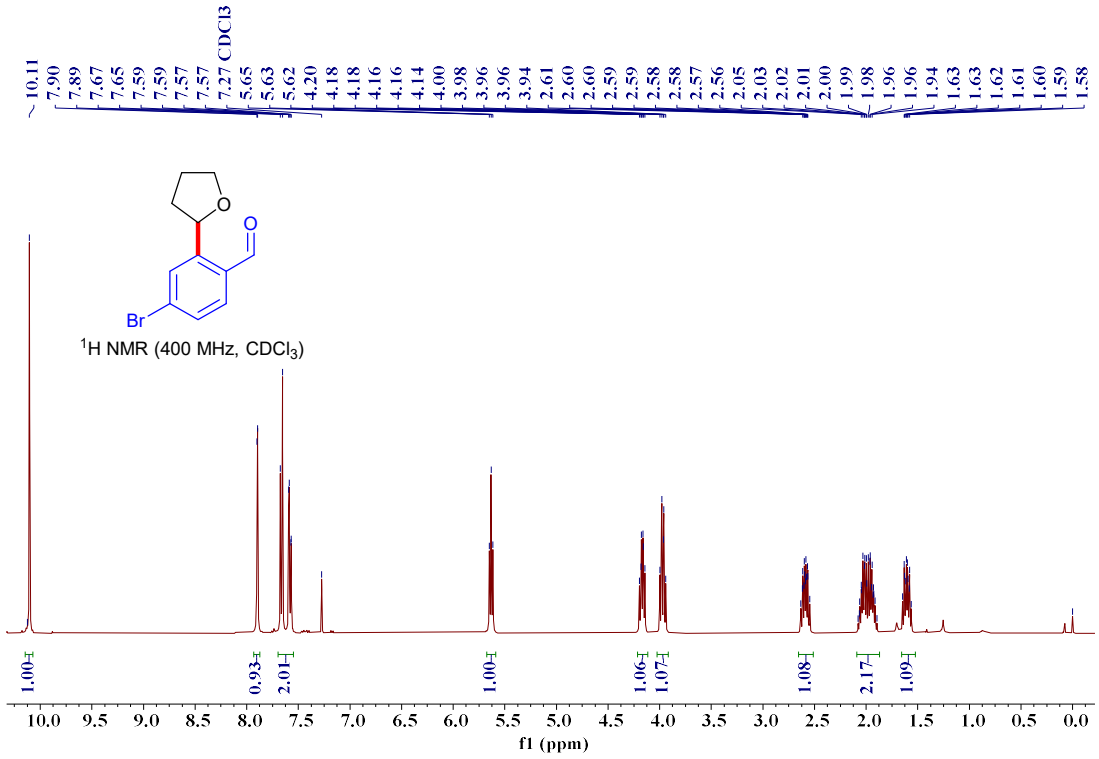


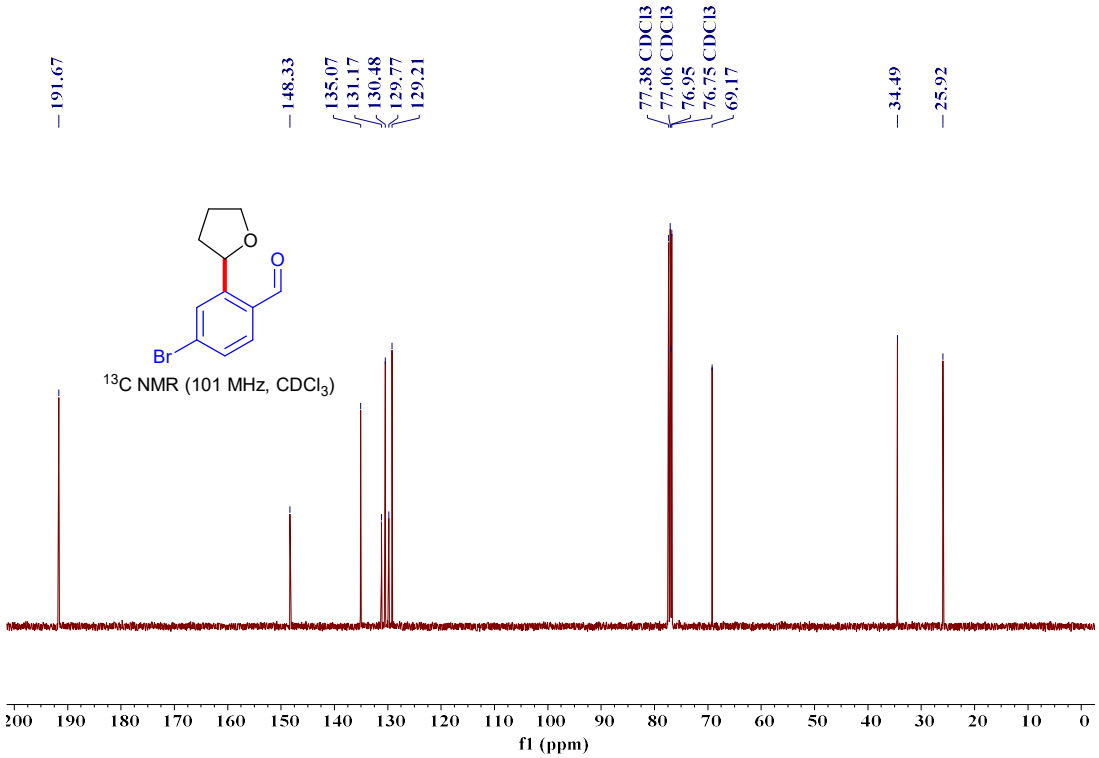
^{1}H and ^{13}C NMR spectra of compound (2-R-6-R) *2,6-disubstituted*-4m



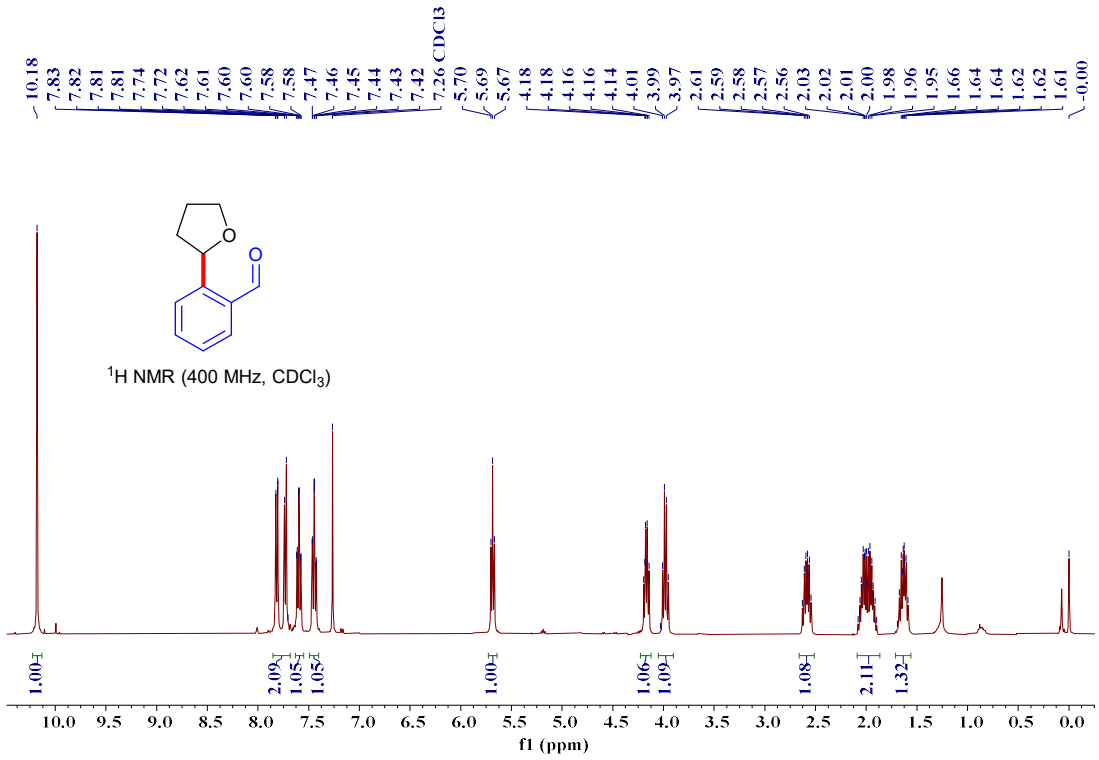


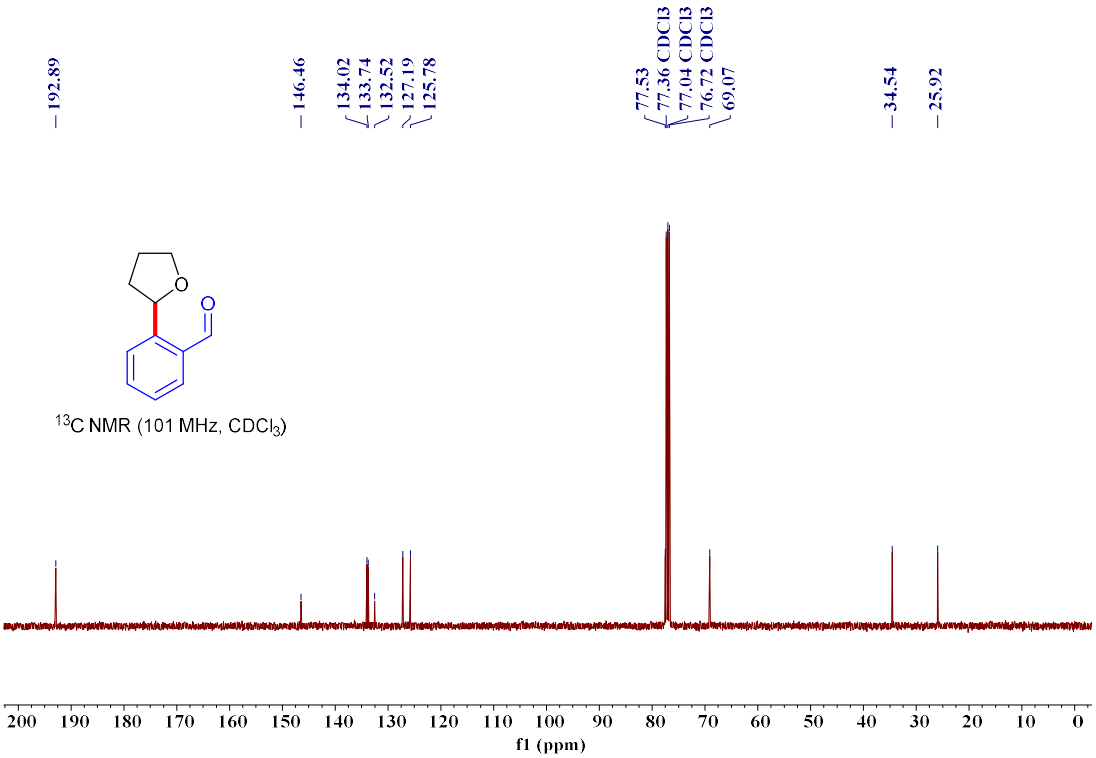
^{1}H and ^{13}C NMR spectra of compound 4Br-*ortho*-4n



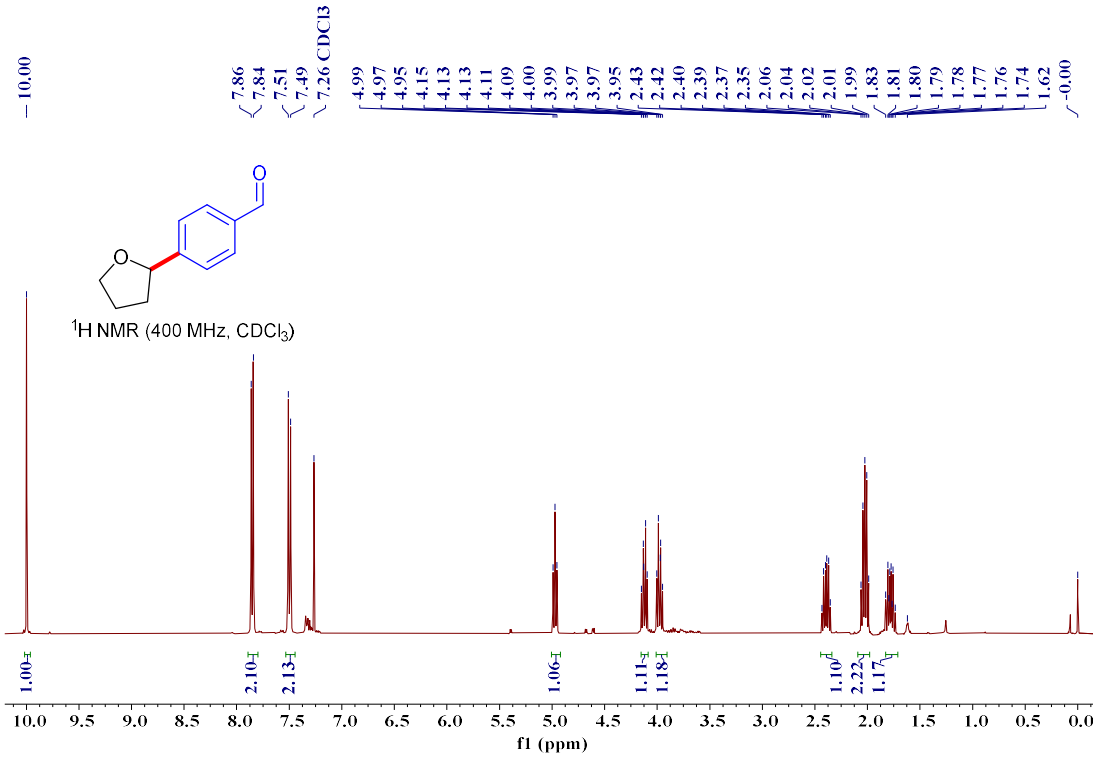


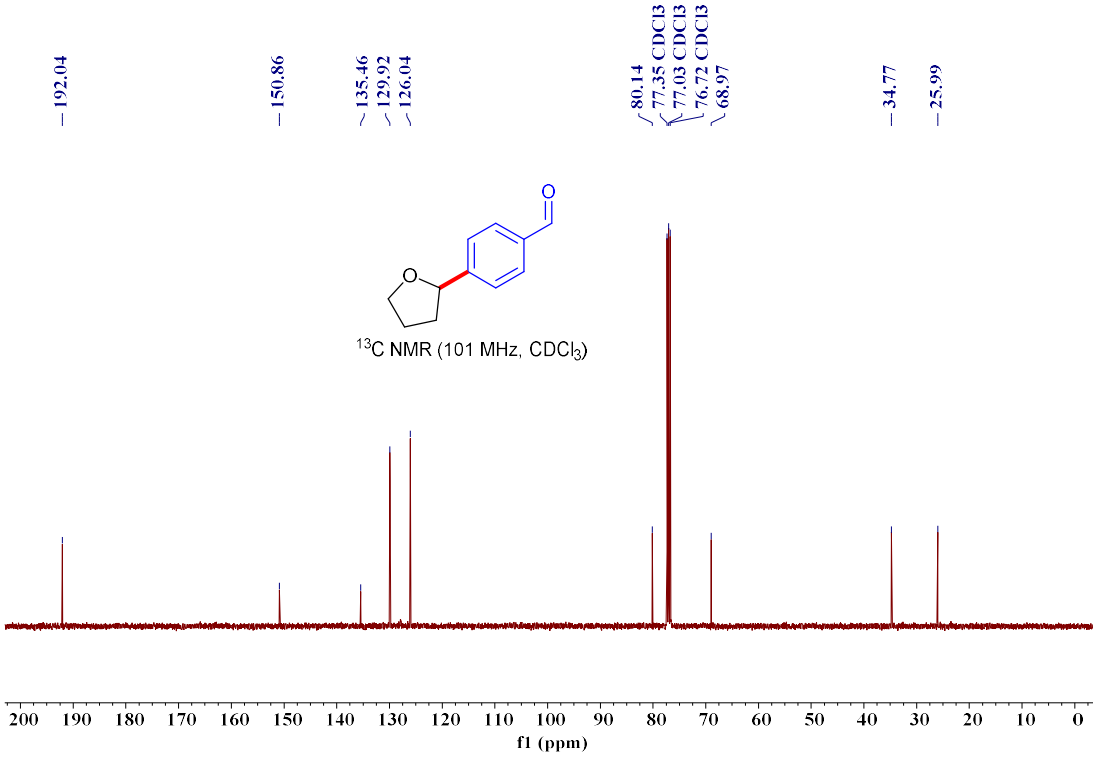
^{1}H and ^{13}C NMR spectra of compound *ortho*-4n



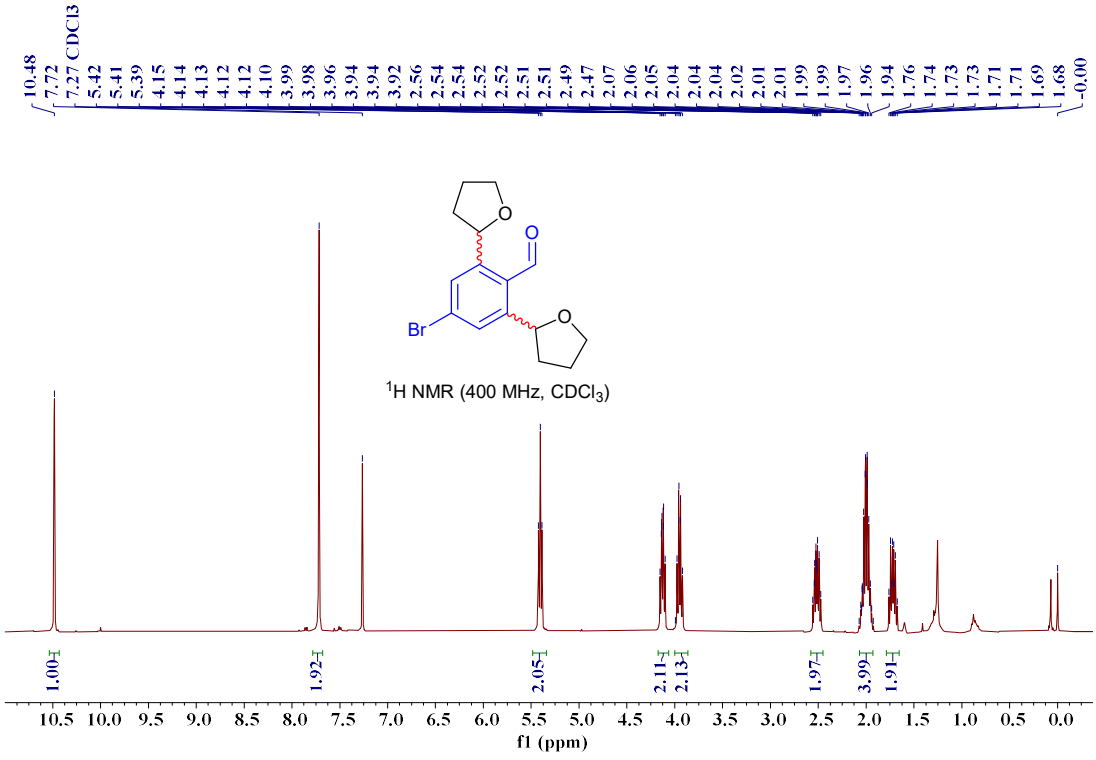


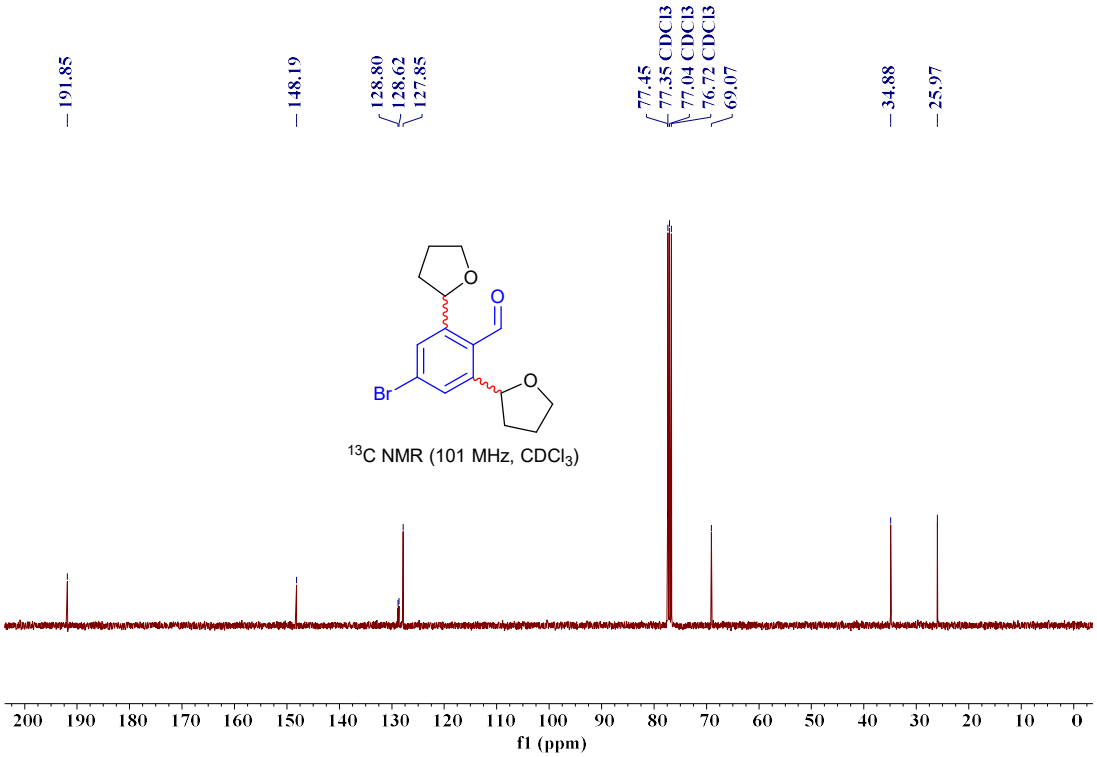
^{1}H and ^{13}C NMR spectra of compound *para*-4n



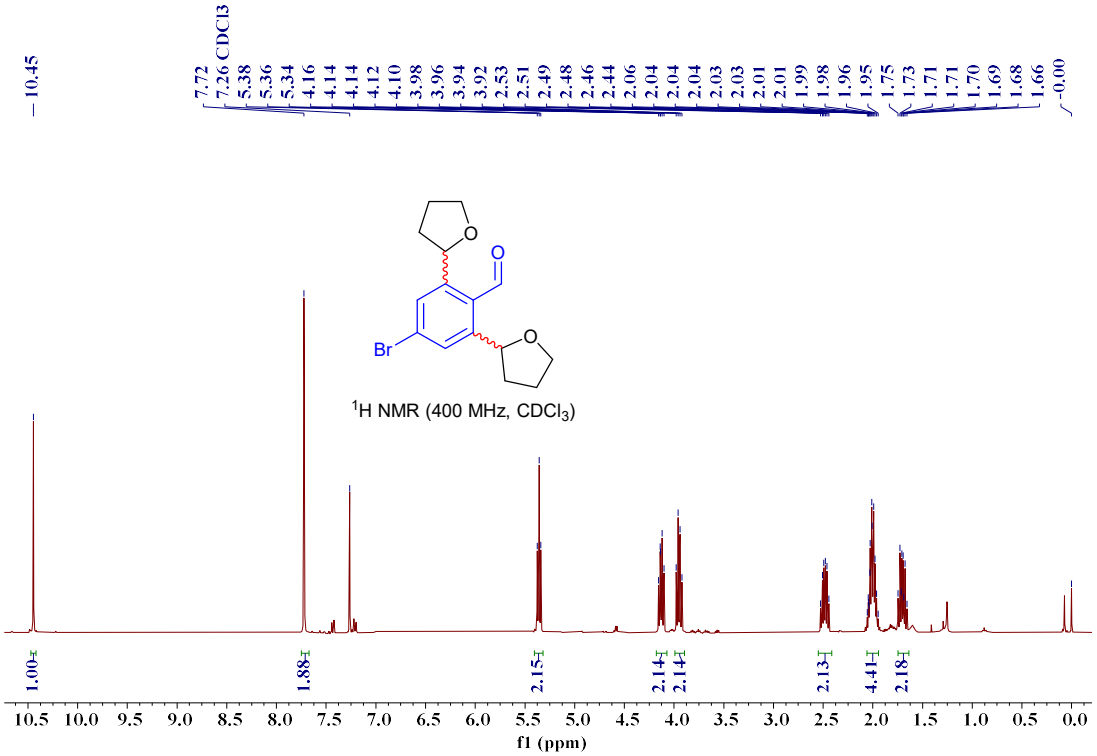


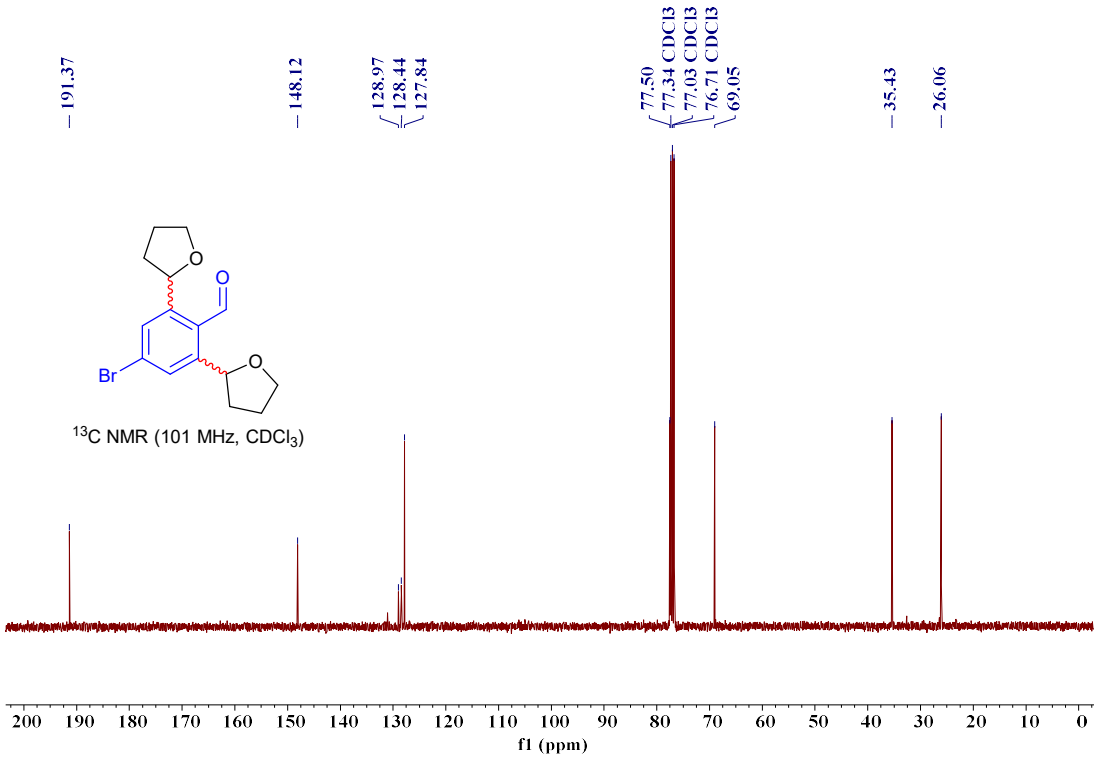
^{1}H and ^{13}C NMR spectra of compound (2-R-6-S) *2,6-disubstituted*-4n



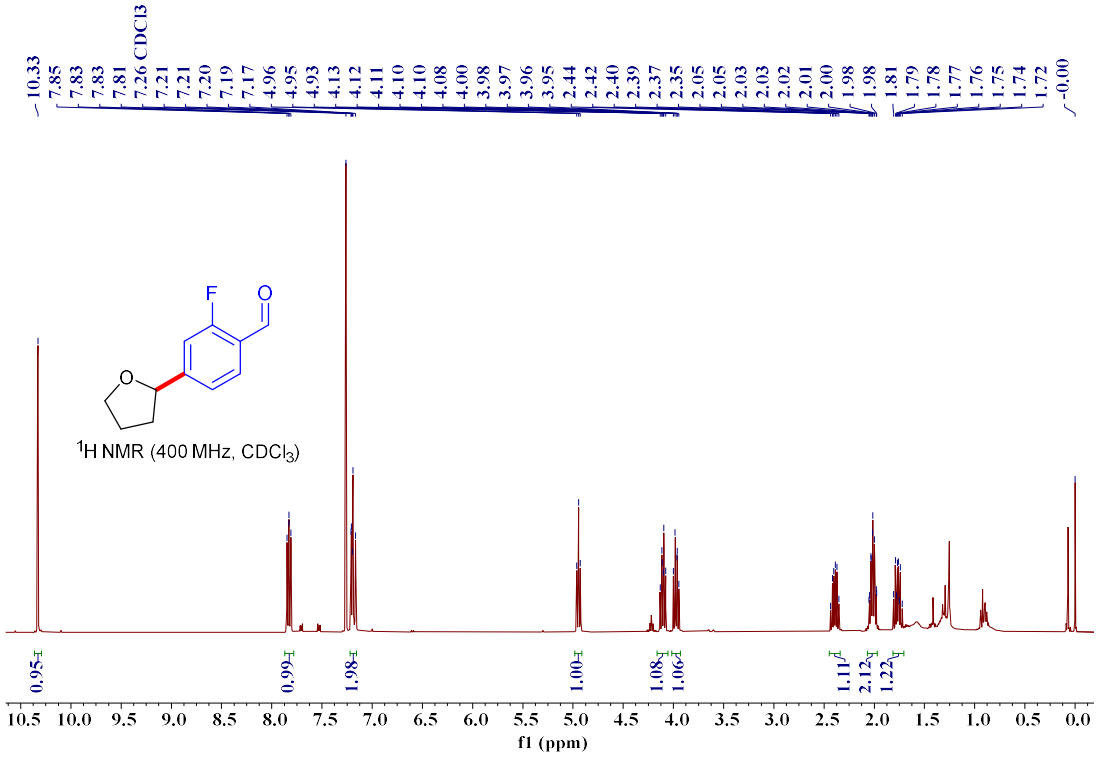


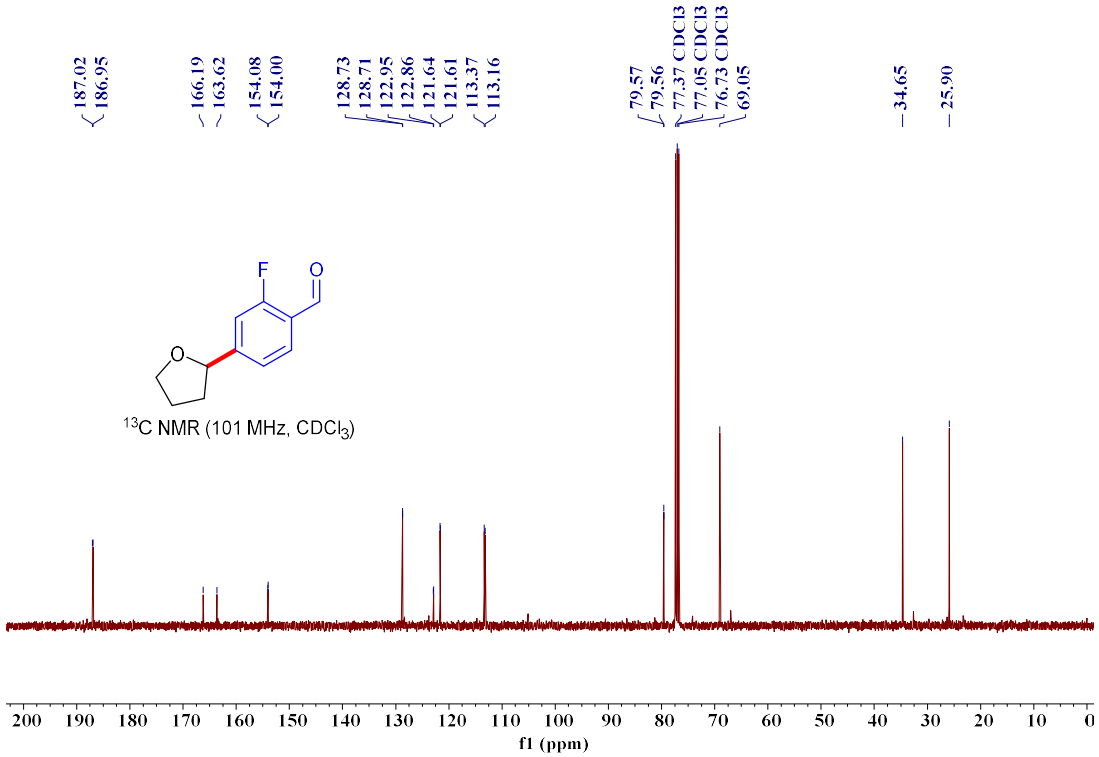
^{1}H and ^{13}C NMR spectra of compound (2-R-6-R) *2,6-disubstituted*-4n

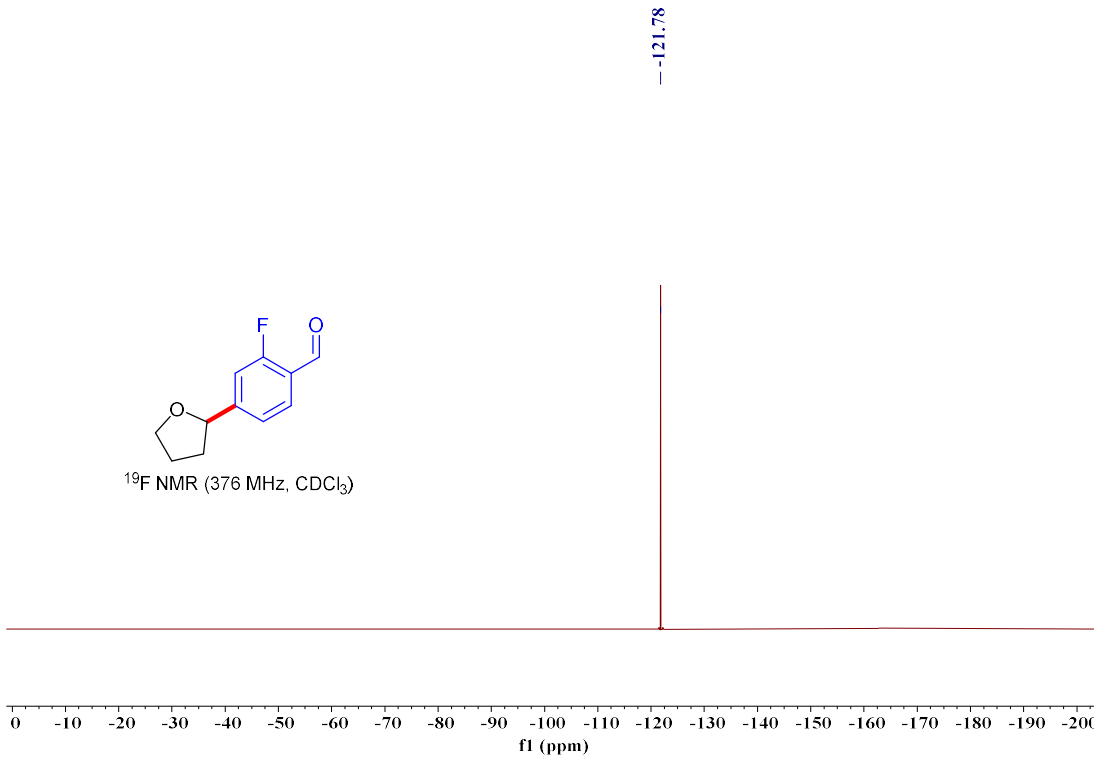




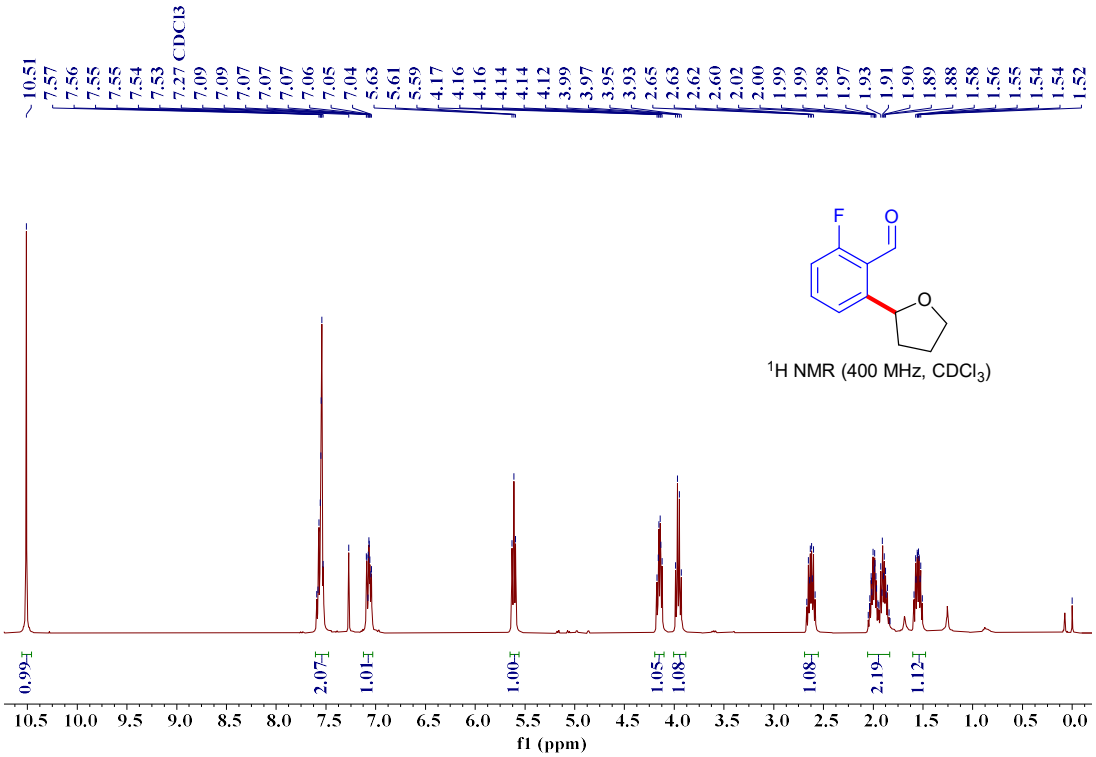
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound *para*-4o

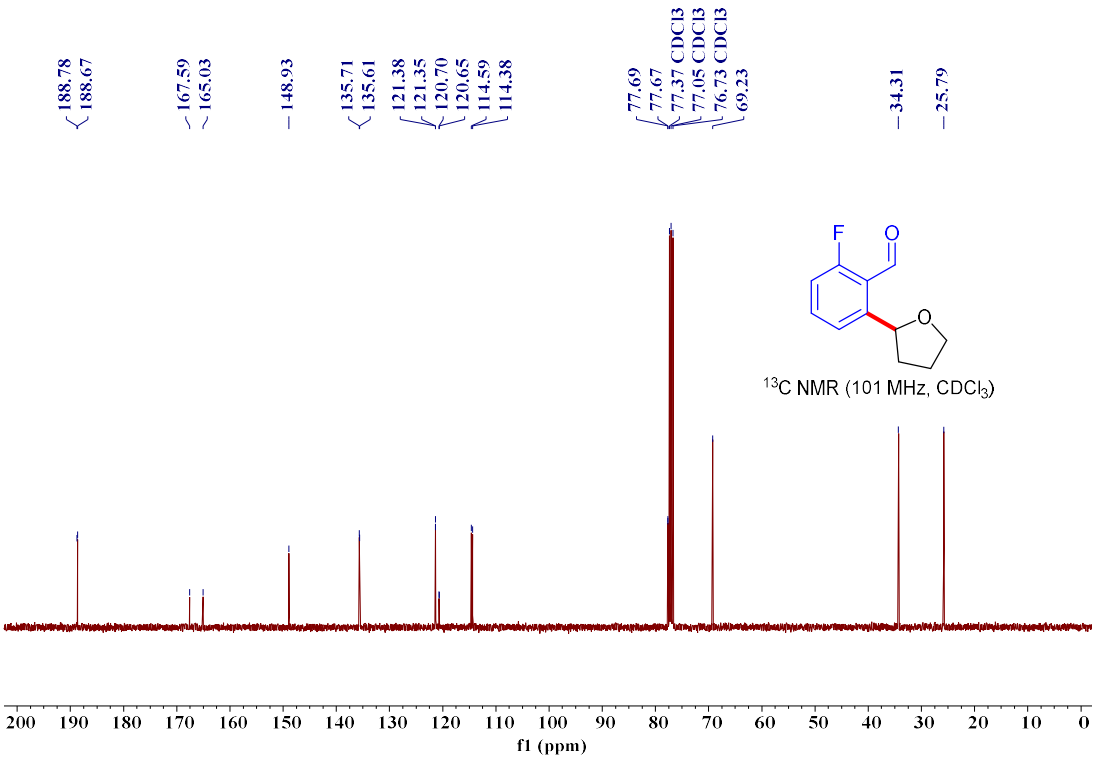


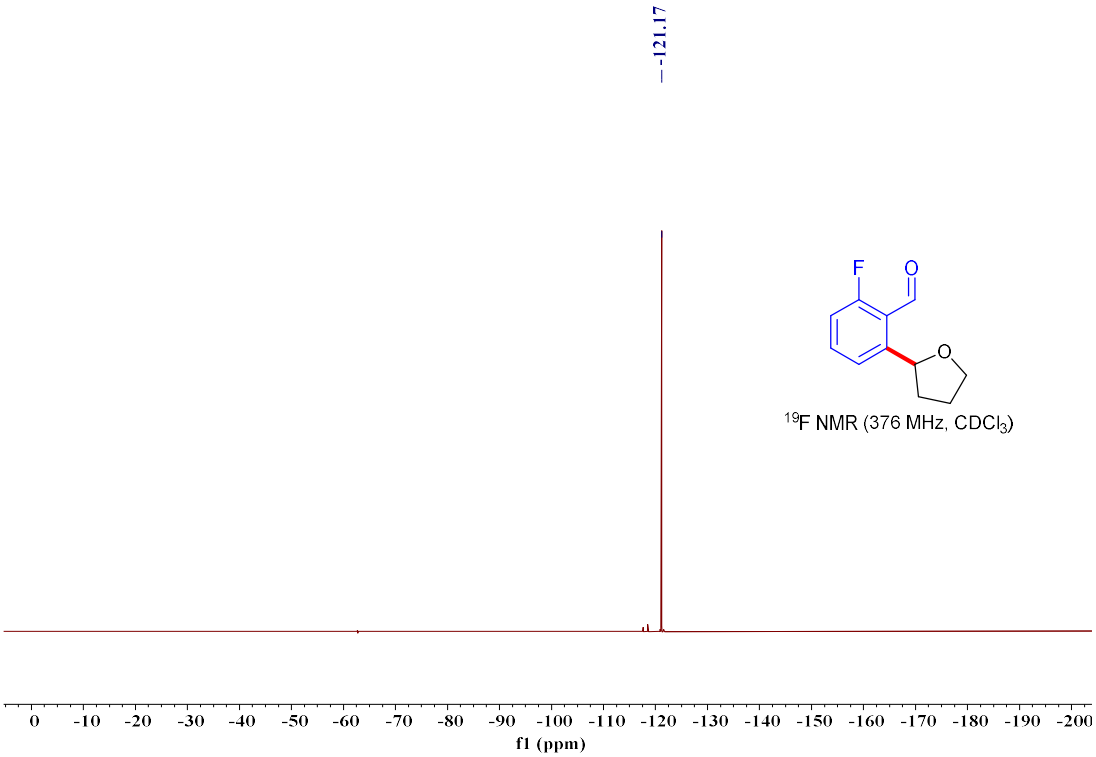

187.02
186.95
166.19
163.62
154.08
154.00
128.73
128.71
122.95
122.86
121.64
121.61
113.37
113.16
79.57
79.56
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
69.05
34.65
25.90
F
O
O
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-121.78
F
O
O
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

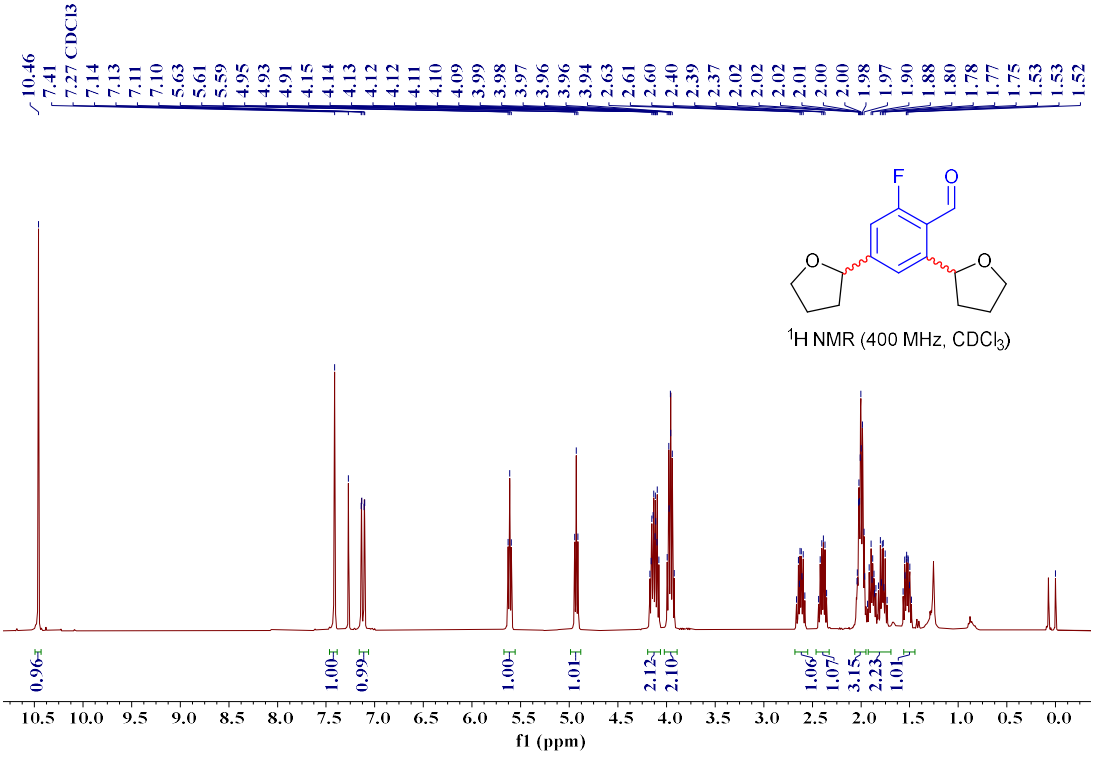
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound *ortho*-4o

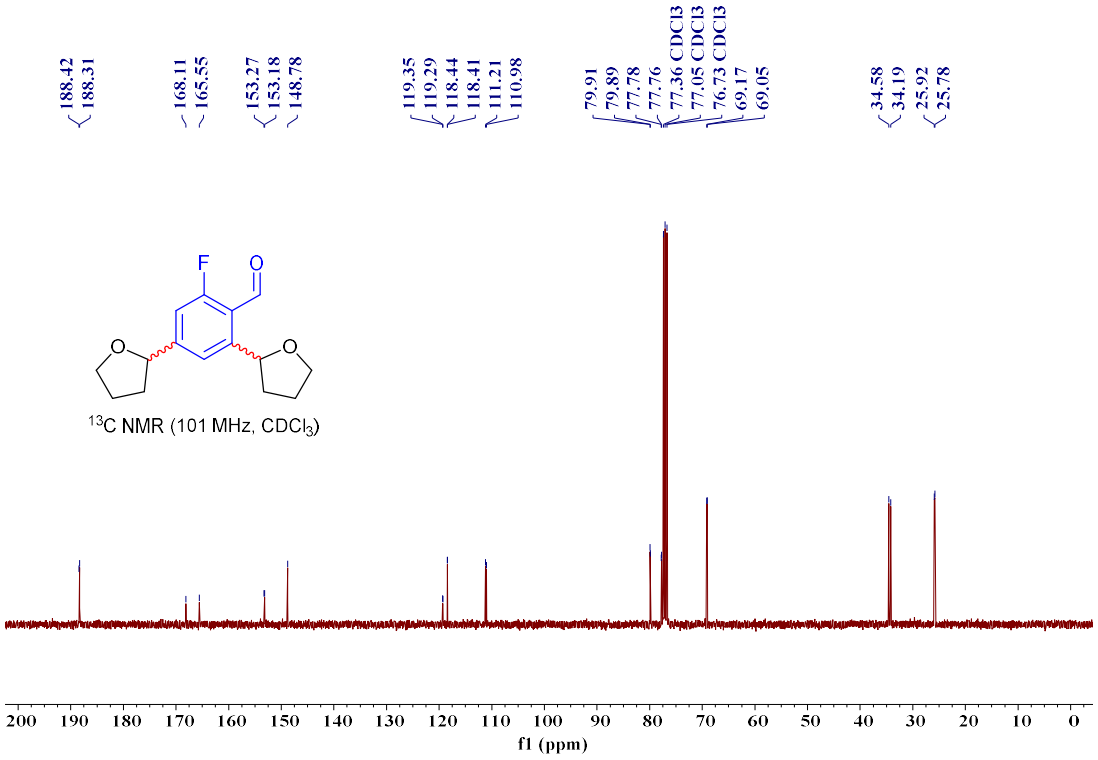


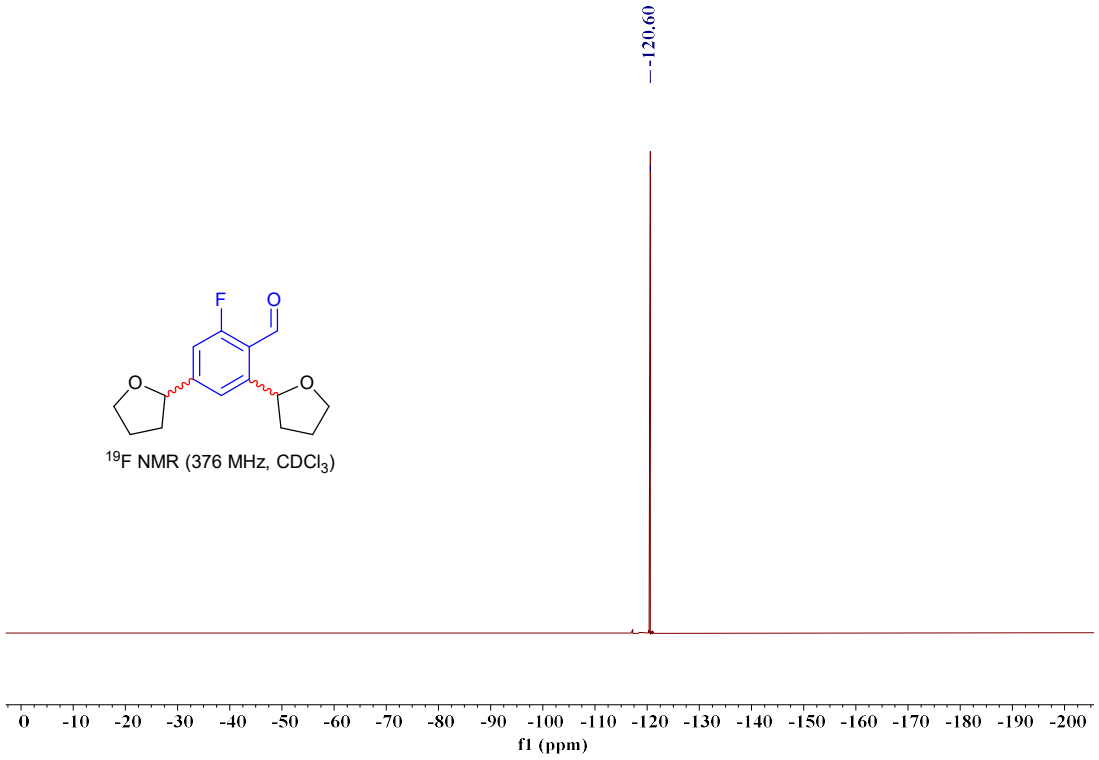




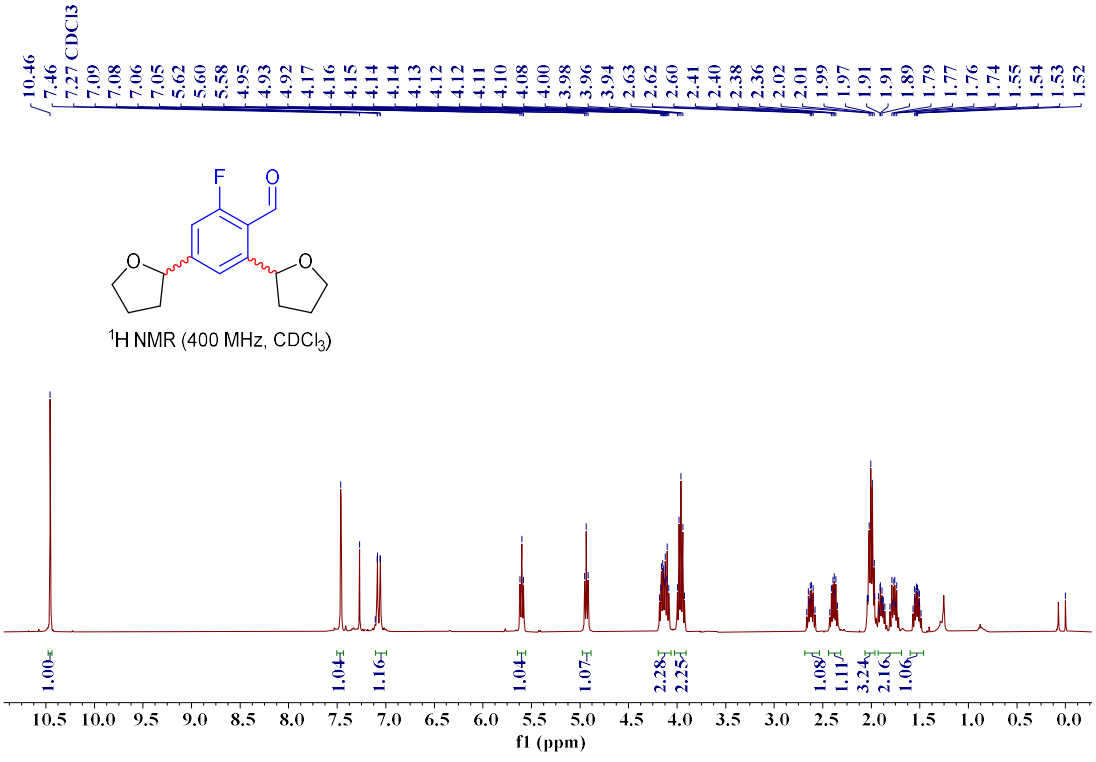
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound (4-R-6-R) *4,6-disubstituted*-4o

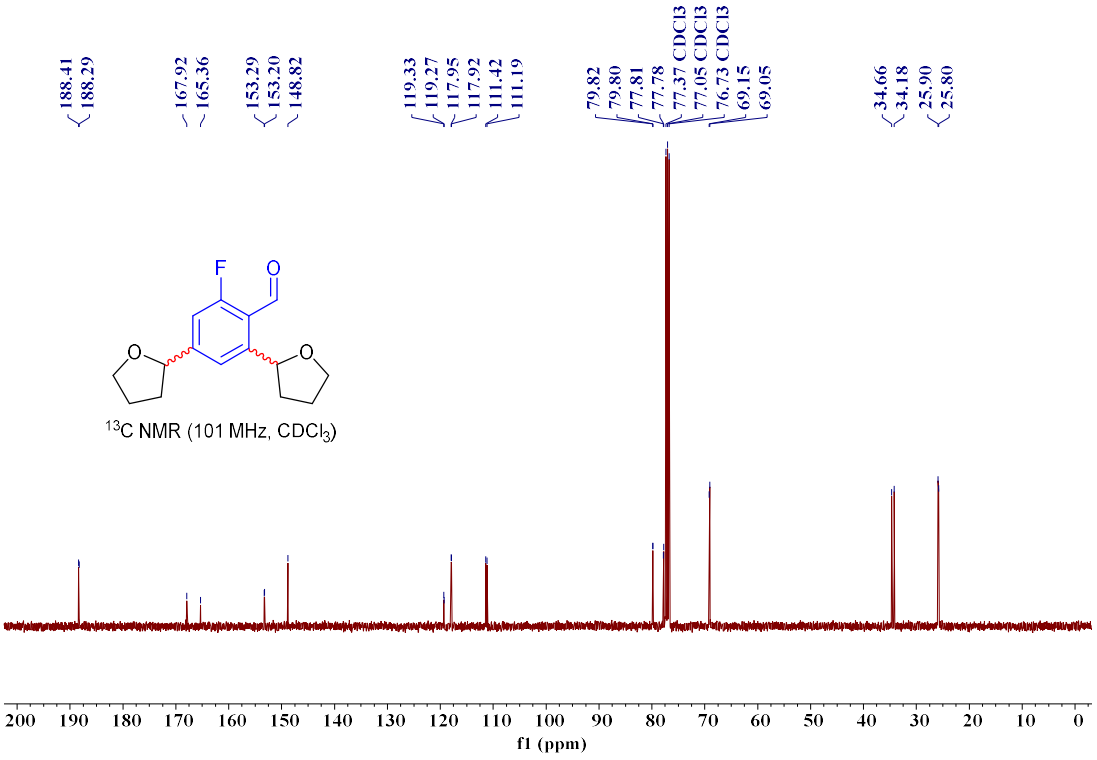


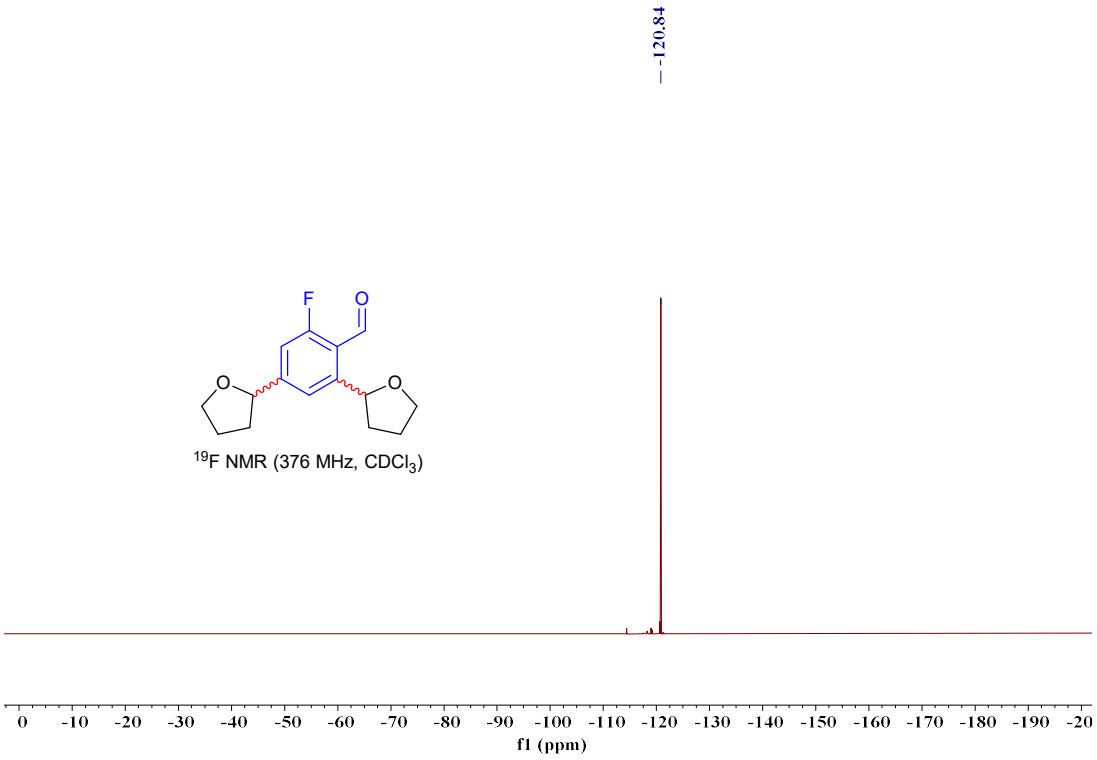

188.42
188.31
168.11
165.55
153.27
153.18
148.78
119.35
119.29
118.44
118.41
111.21
110.98
79.91
79.89
77.78
77.76
77.36 CDCl3
77.05 CDCl3
76.73 CDCl3
69.17
69.05
34.58
34.19
25.92
25.78
F
O
O
O
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-120.60
F
O
O
O
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

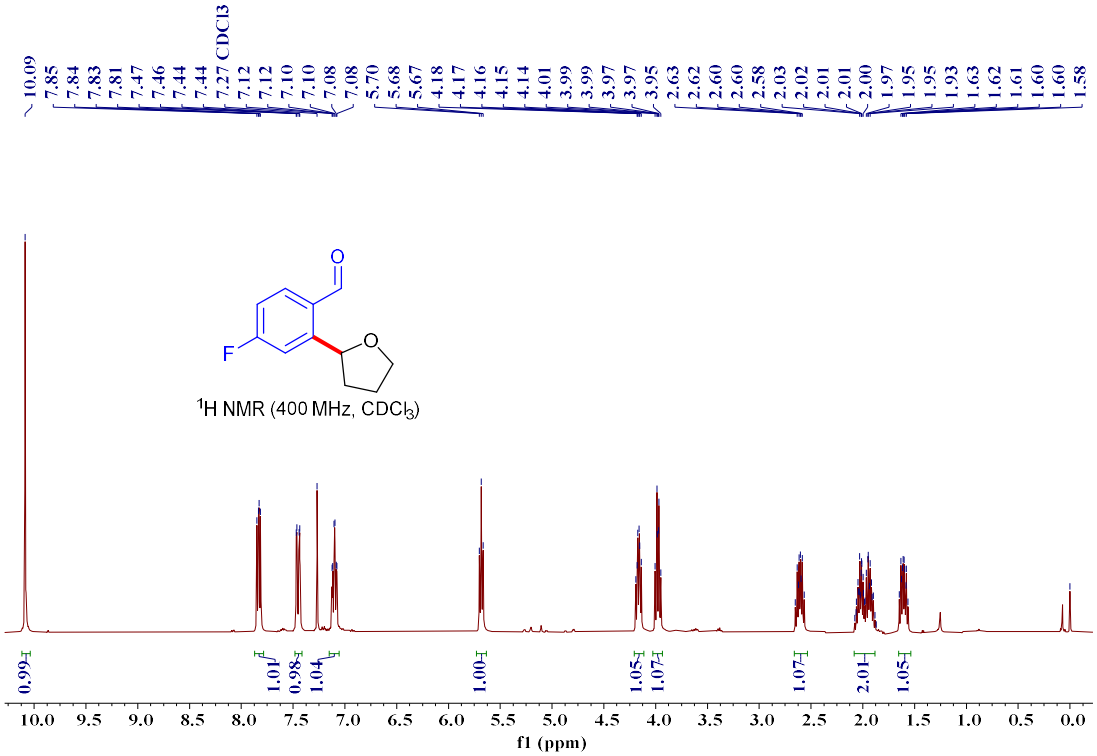
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound (4-R-6-S) *4,6-disubstituted*-4o

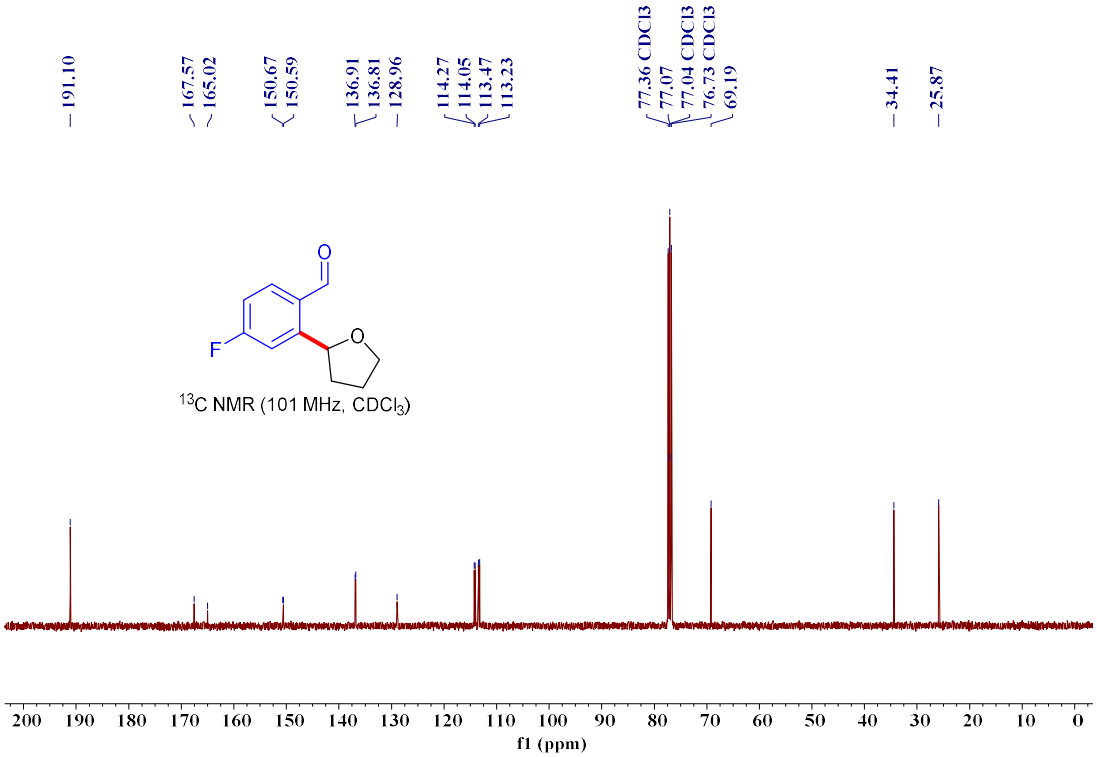


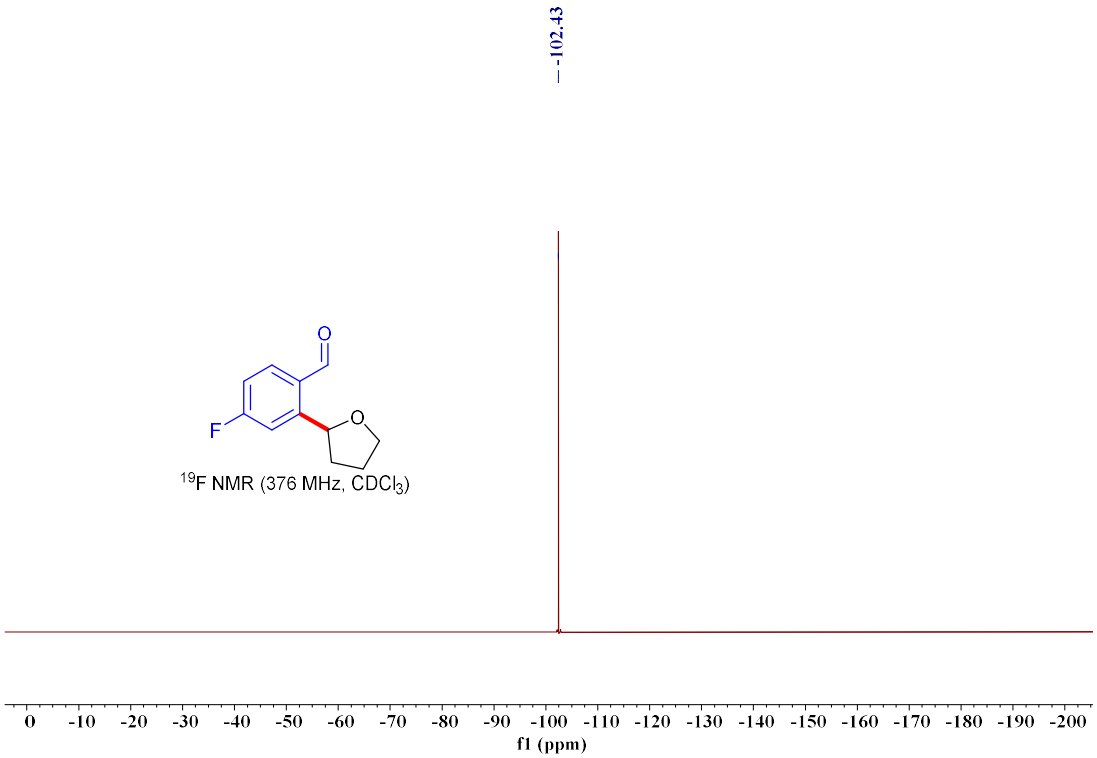




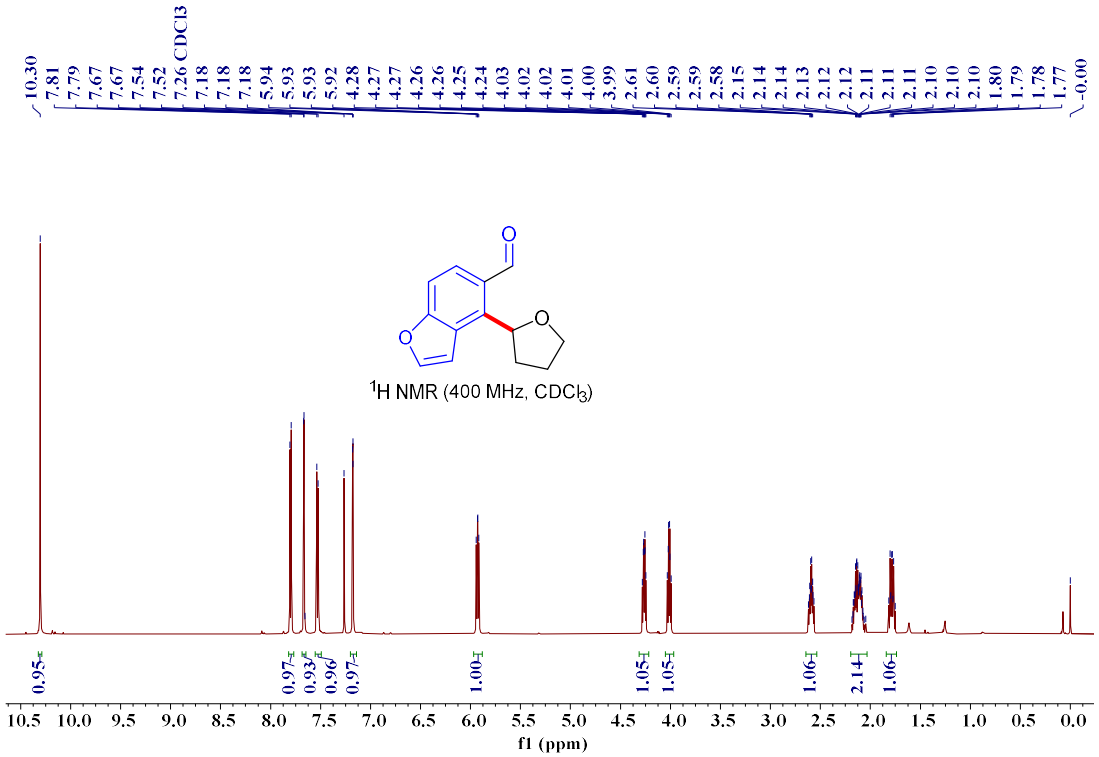
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound *ortho*-4p

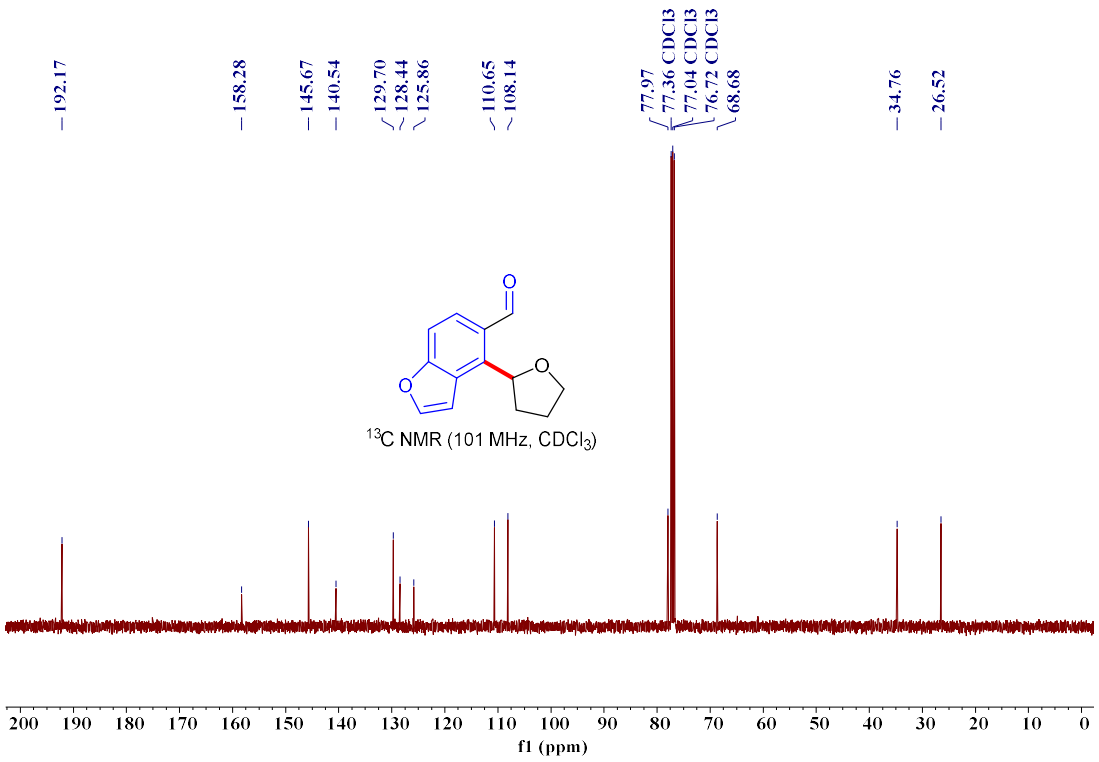



191.10
167.57
165.02
150.67
150.59
136.91
136.81
128.96
114.27
114.05
113.47
113.23
77.36 CDCl3
77.07
77.04 CDCl3
76.73 CDCl3
69.19
34.41
25.87
O
F
O
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

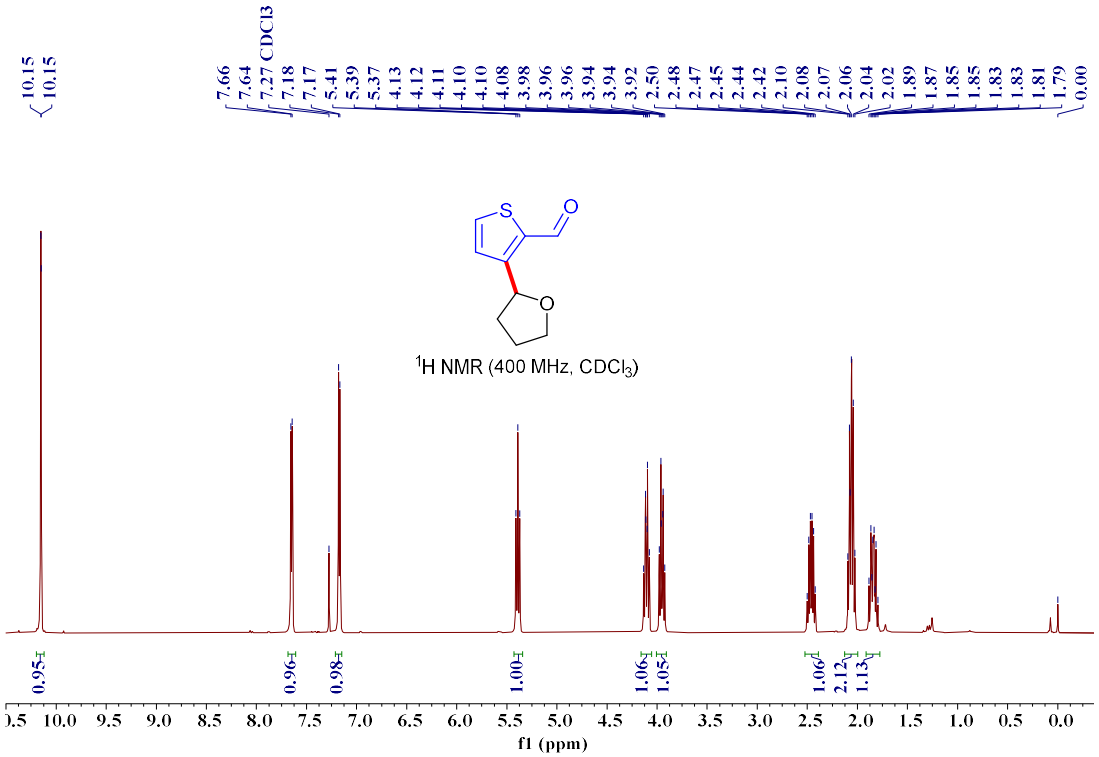

-102.43
O
F
O
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

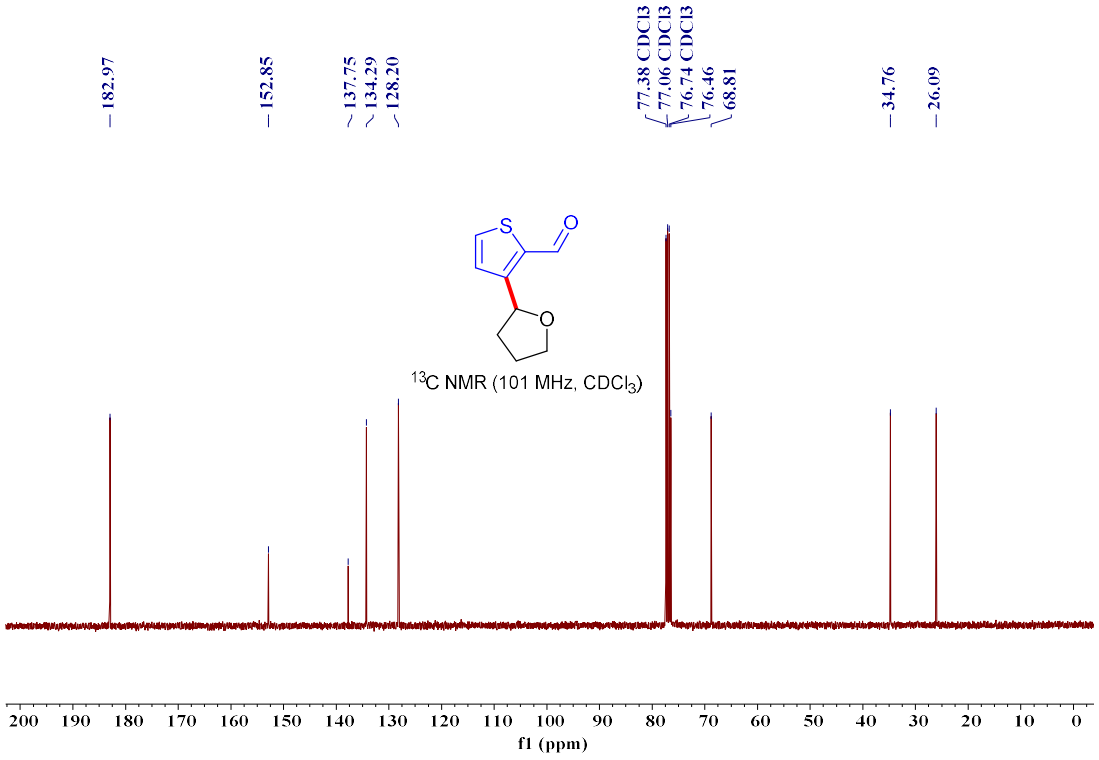
^{1}H and ^{13}C NMR spectra of compound *ortho*-4q



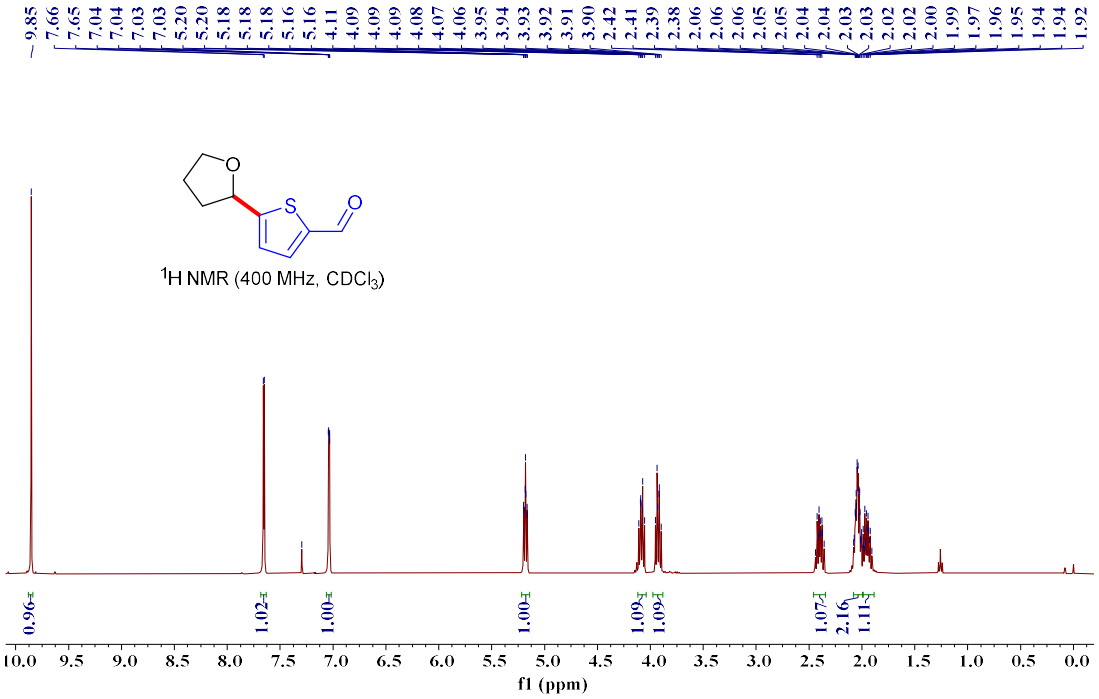


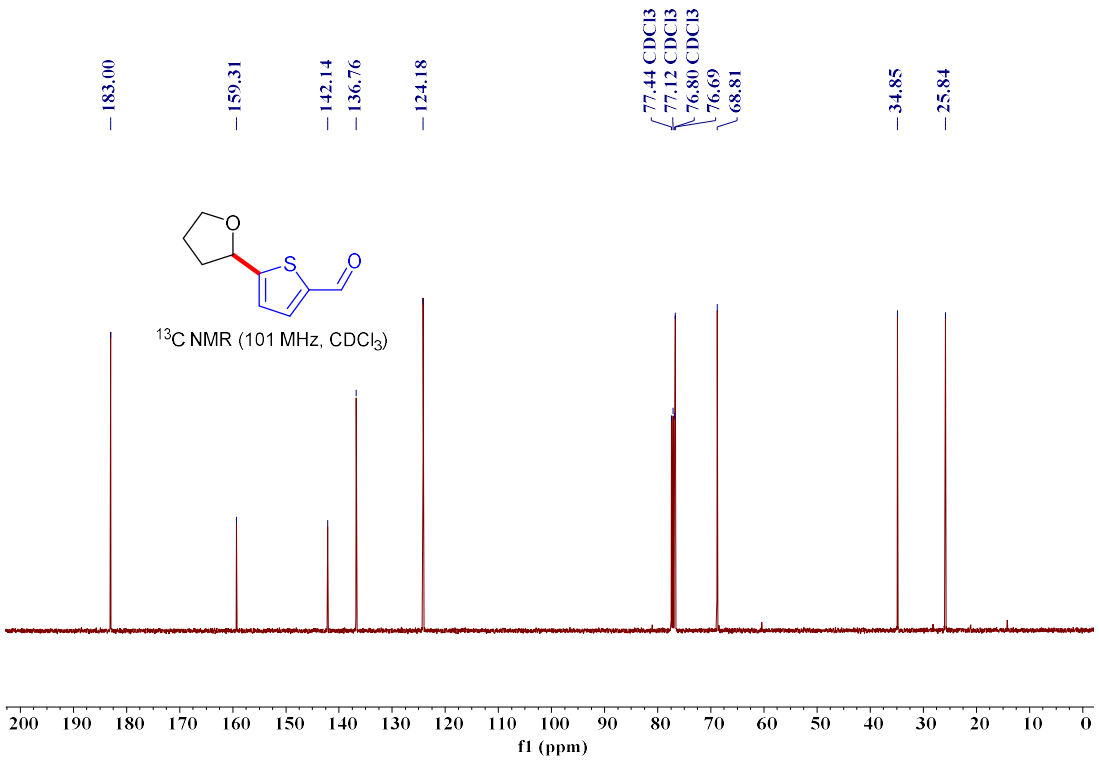
^{1}H and ^{13}C NMR spectra of compound *3-THF*-4r



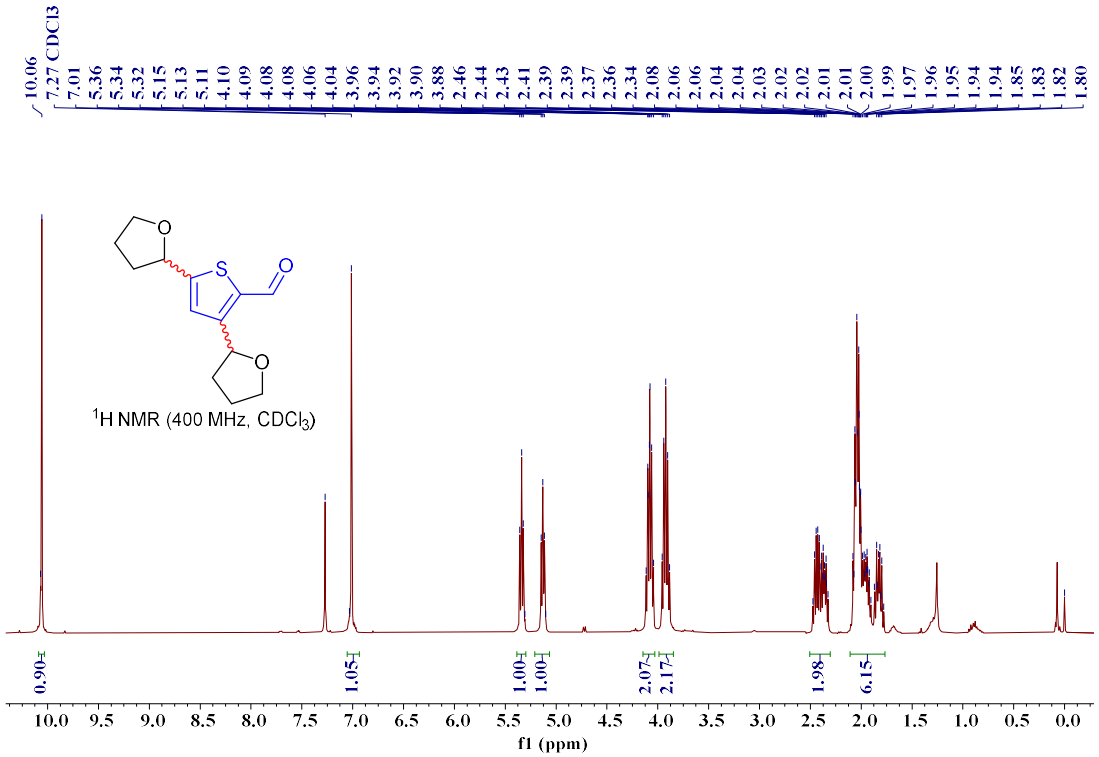


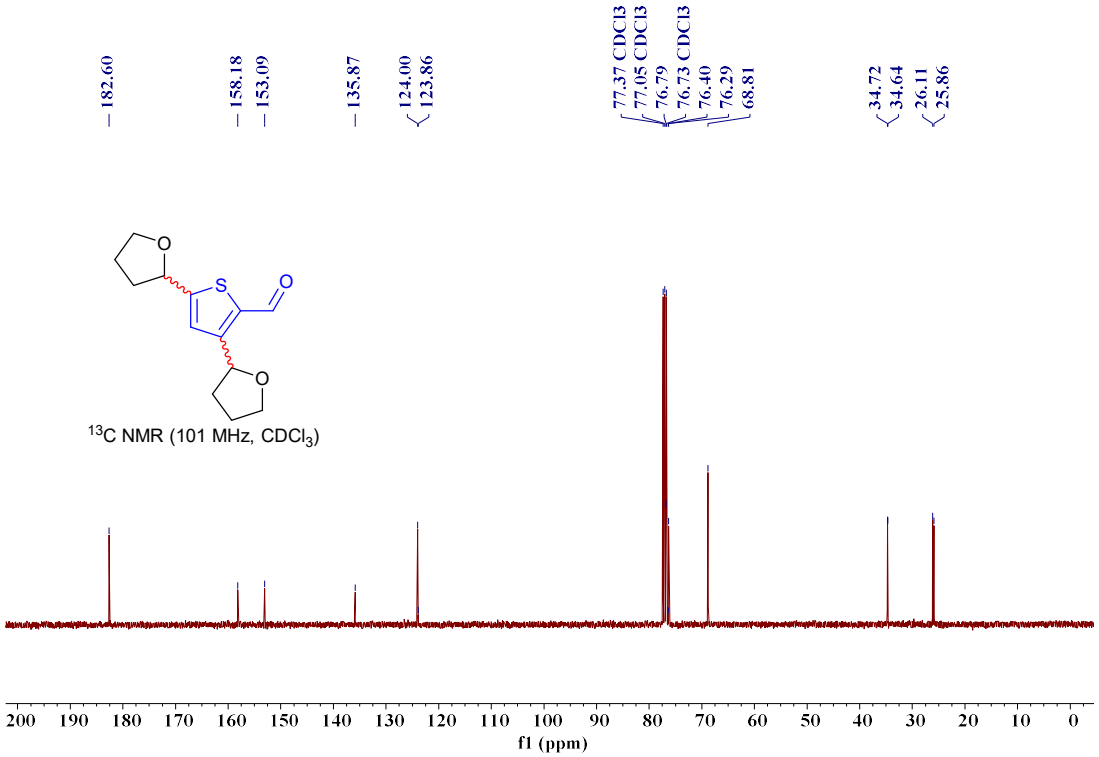
^{1}H and ^{13}C NMR spectra of compound *5-THF* -4r



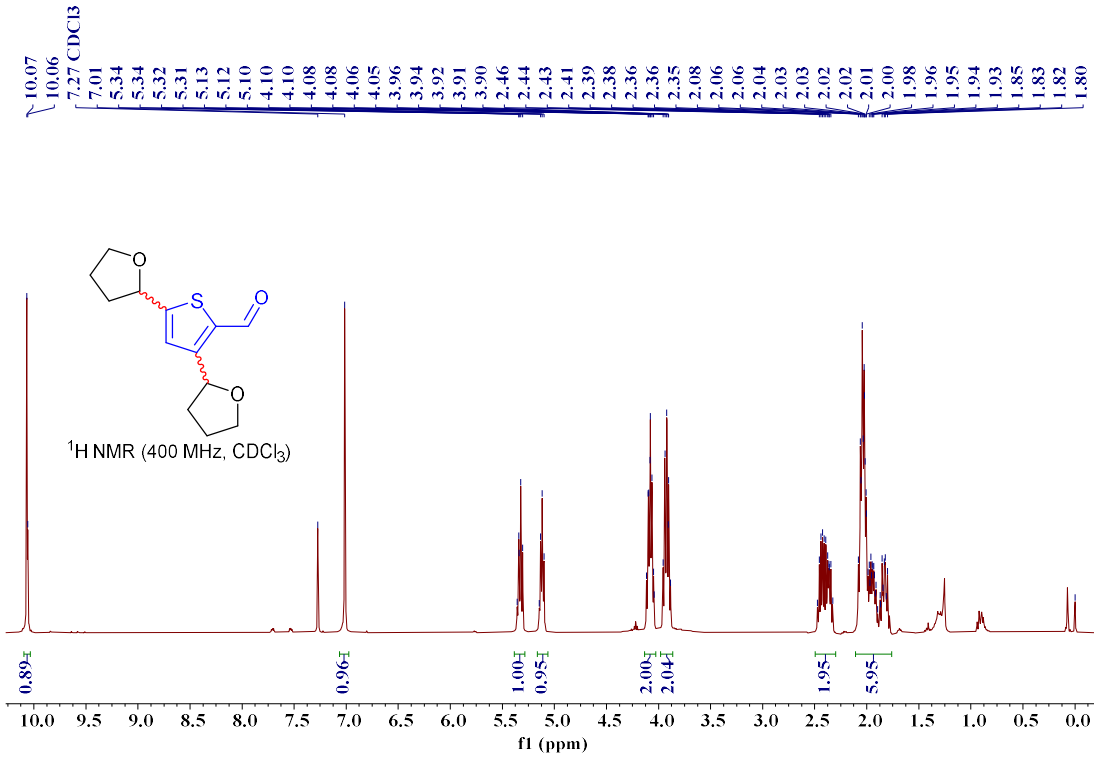


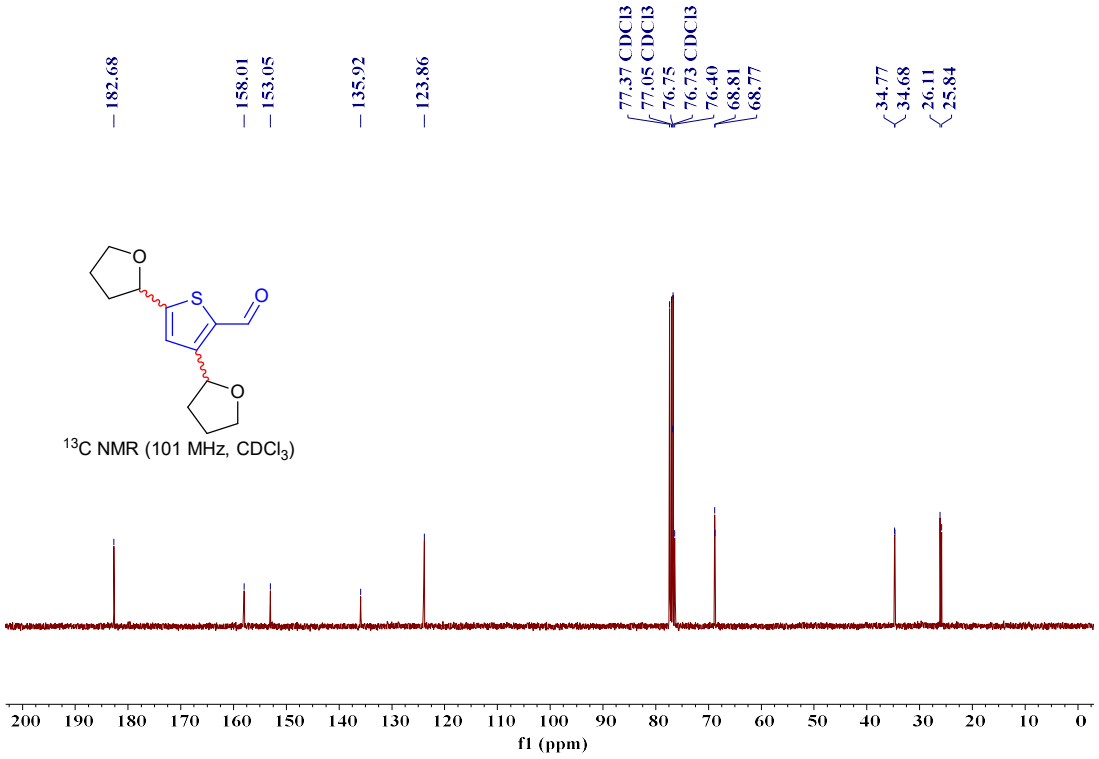
^{1}H and ^{13}C NMR spectra of compound (3-S-5-R) *3,5-disubstituted*-4r



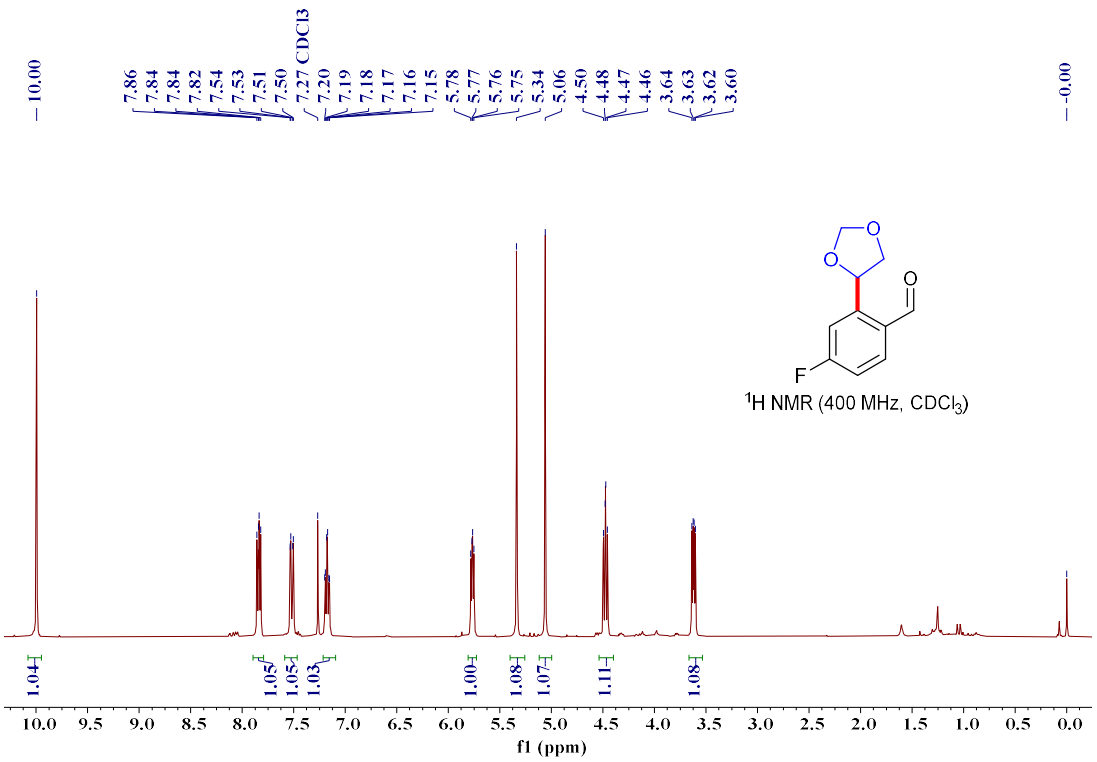


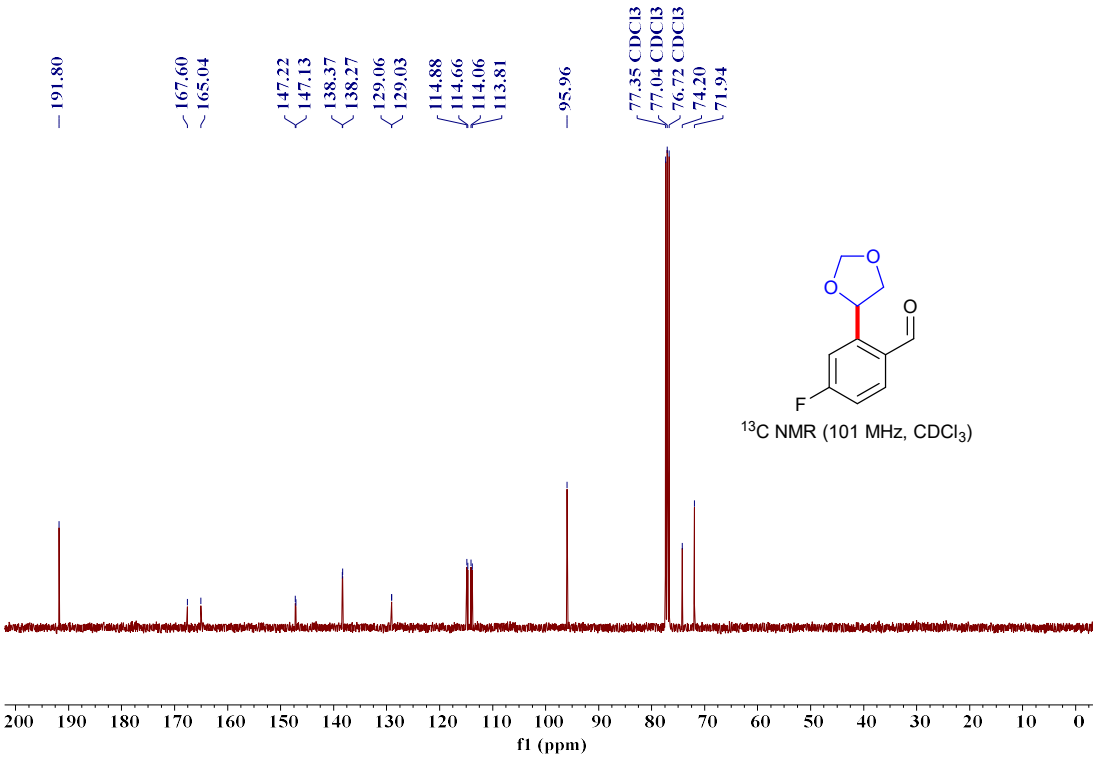
^{1}H and ^{13}C NMR spectra of compound (3-R-5-R) *3,5-disubstituted*-4r

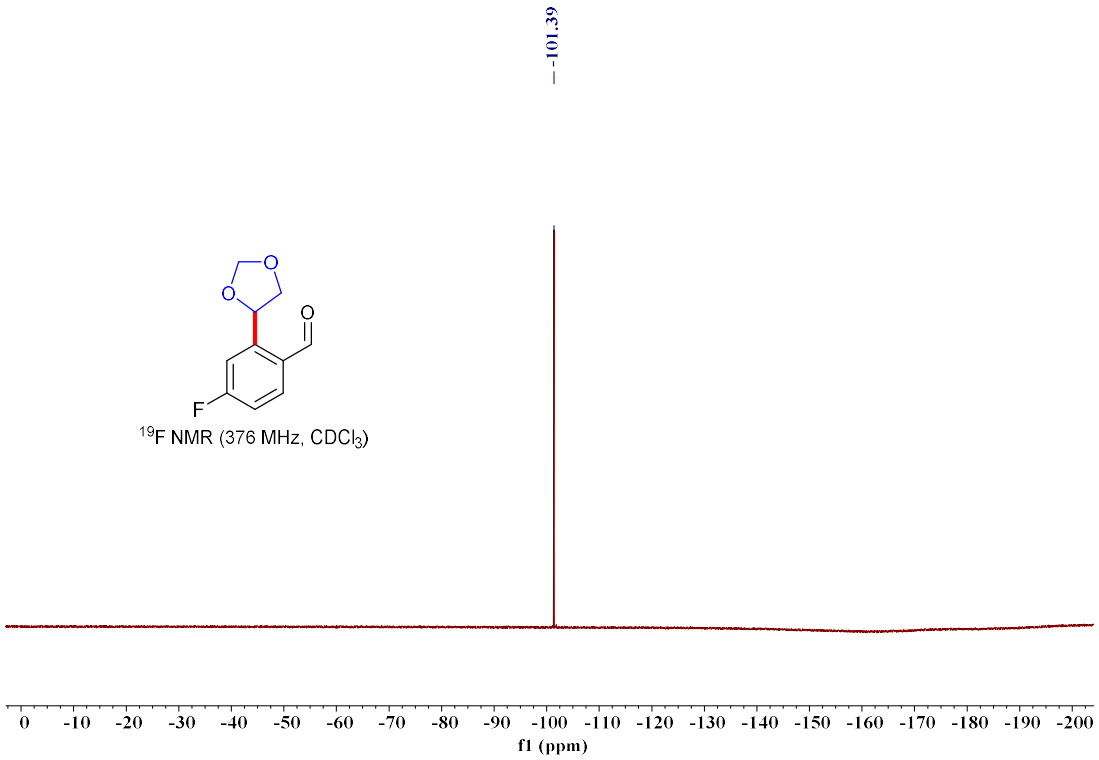




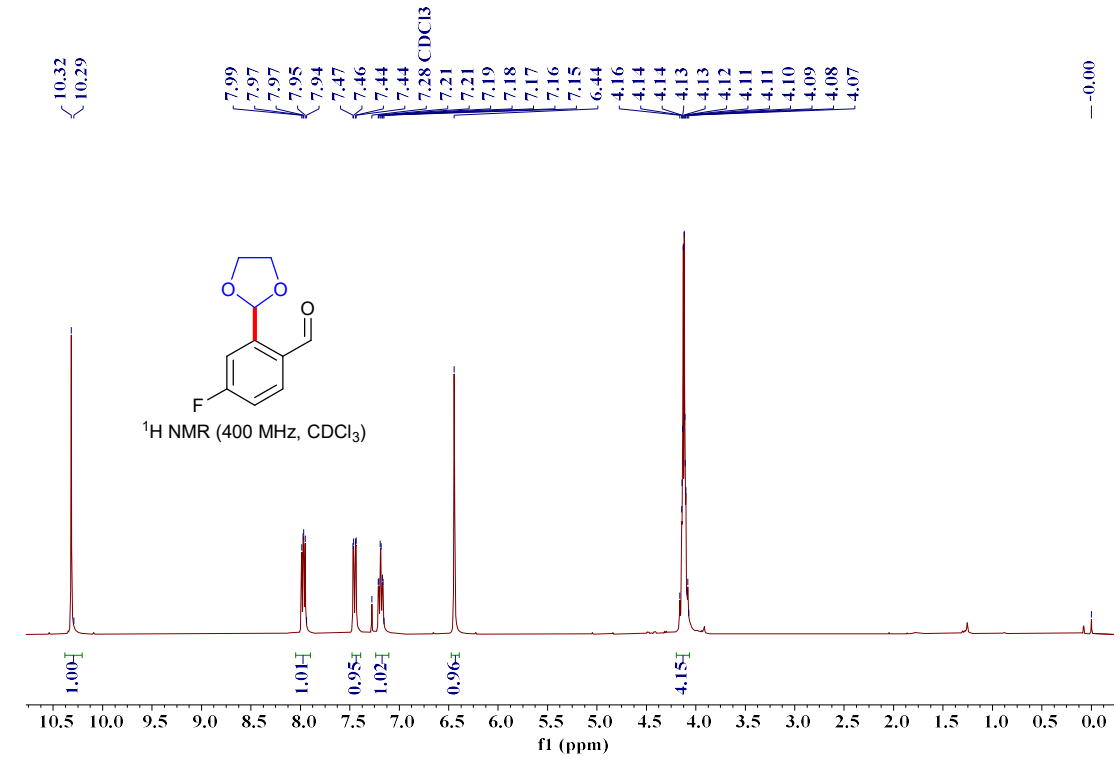
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *ortho*-4s-1

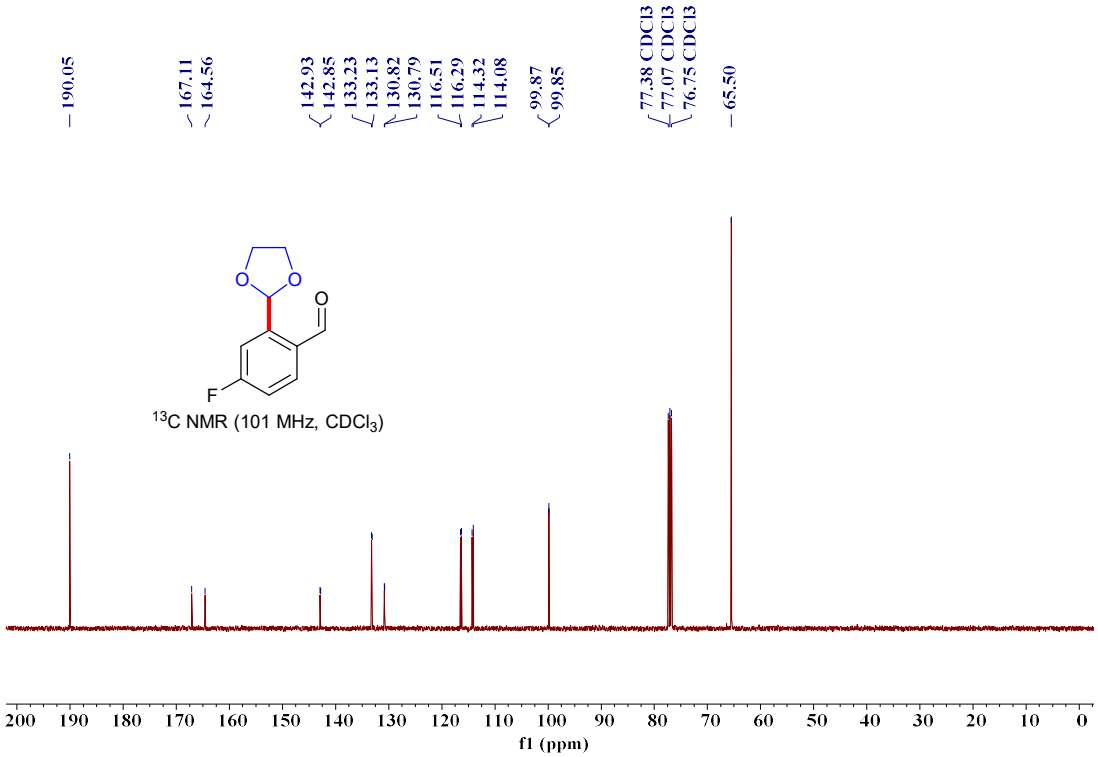


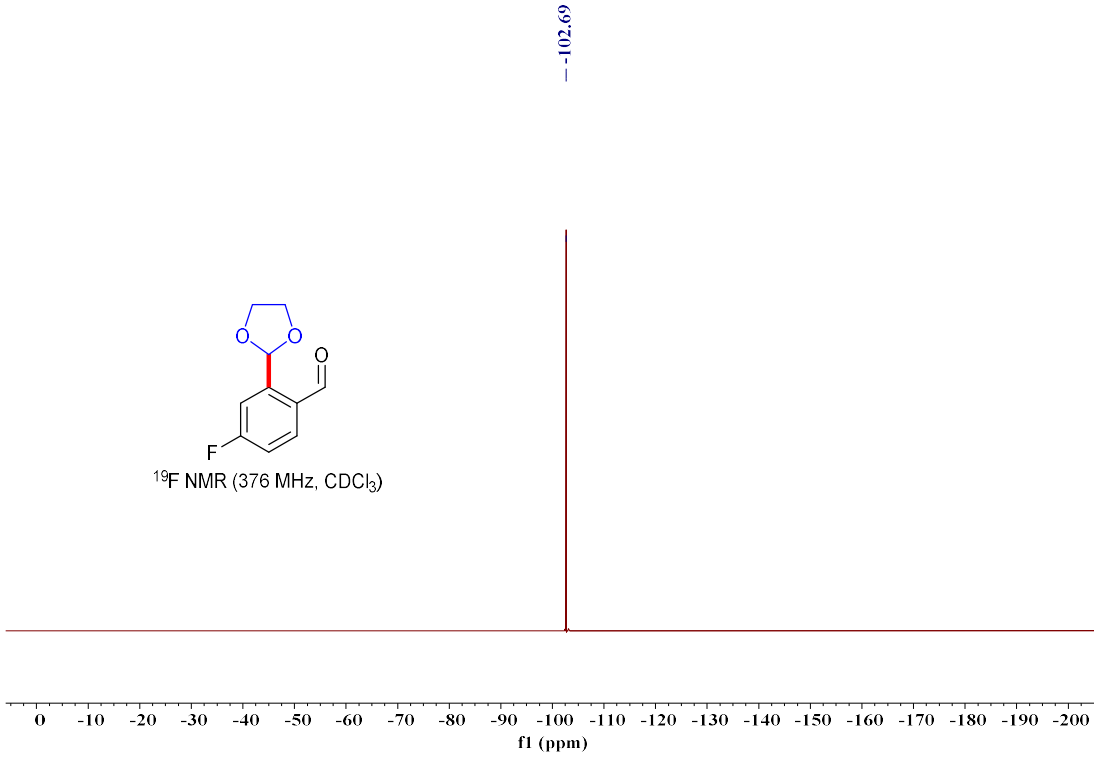




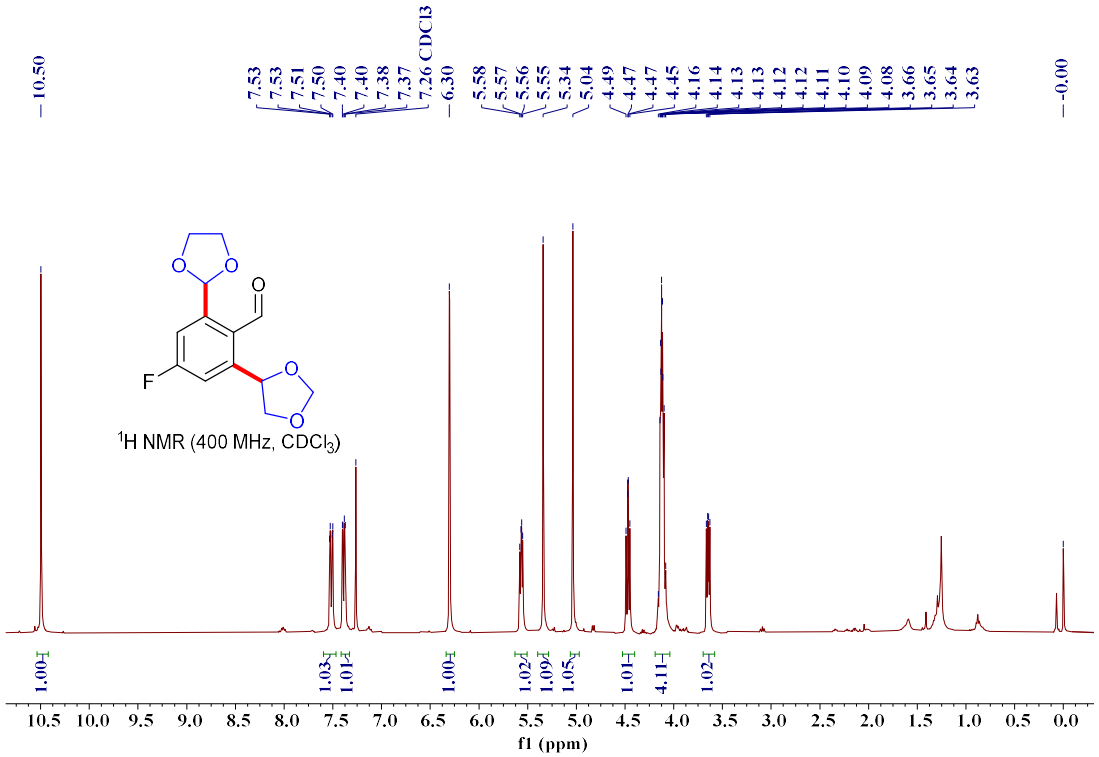
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *ortho*-4s-2

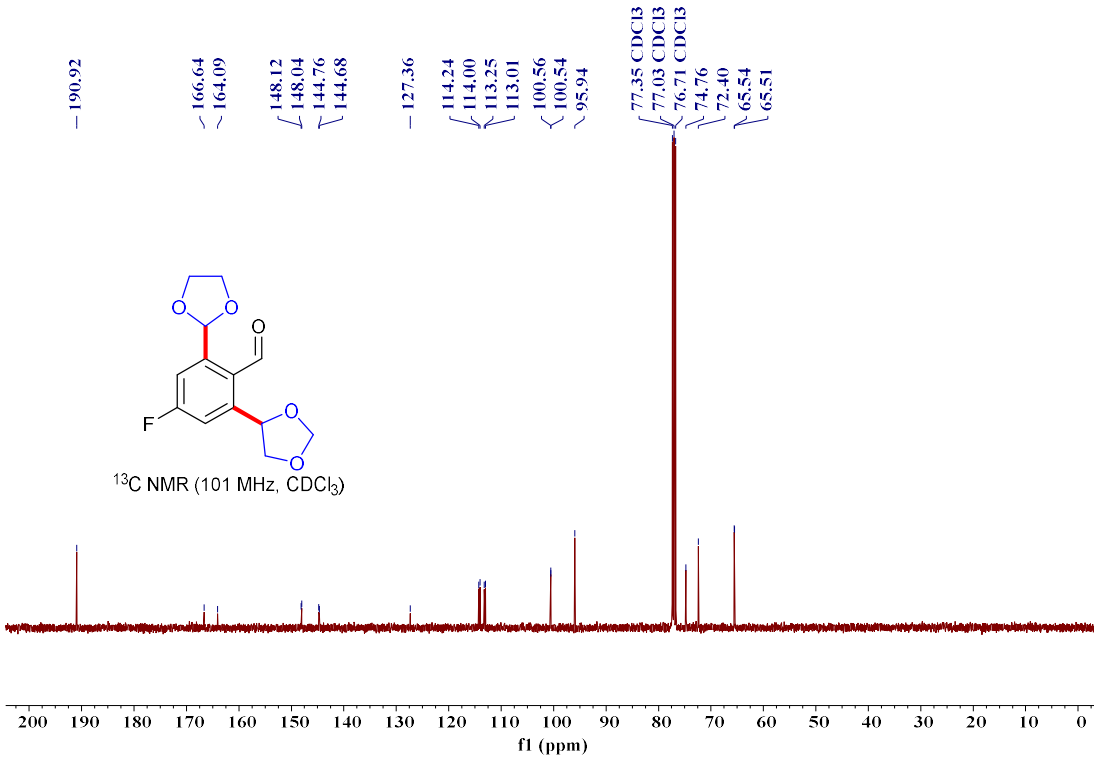


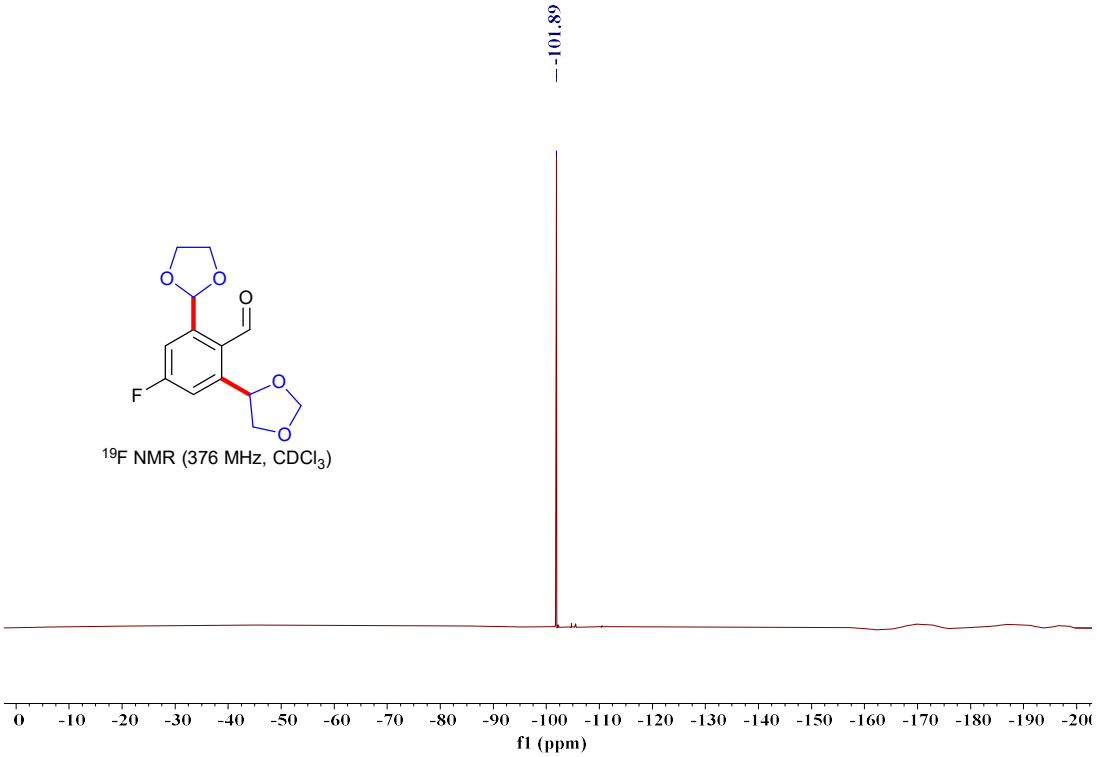

190.05
167.11
164.56
142.93
142.85
133.23
133.13
130.82
130.79
116.51
116.29
114.32
114.08
99.87
99.85
77.38 CDCl3
77.07 CDCl3
76.75 CDCl3
65.50
O
O
O
F
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-102.69
O
O
O
F
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

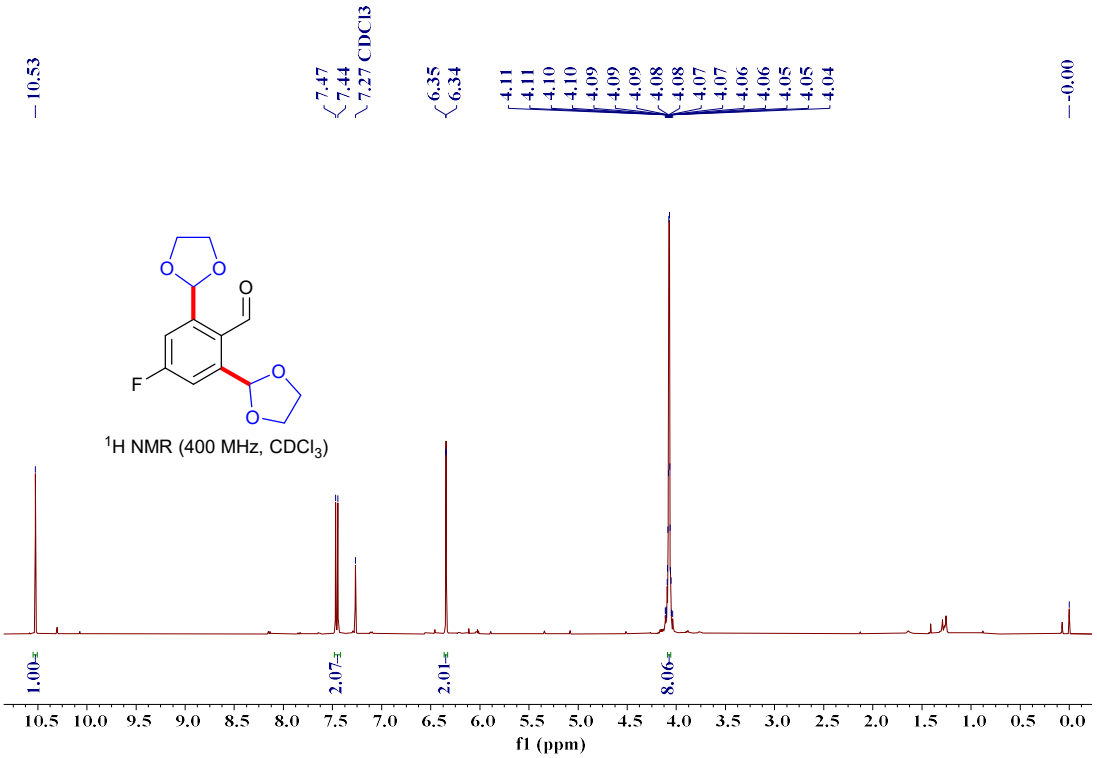
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *2,6-disubstituted*-4s-1

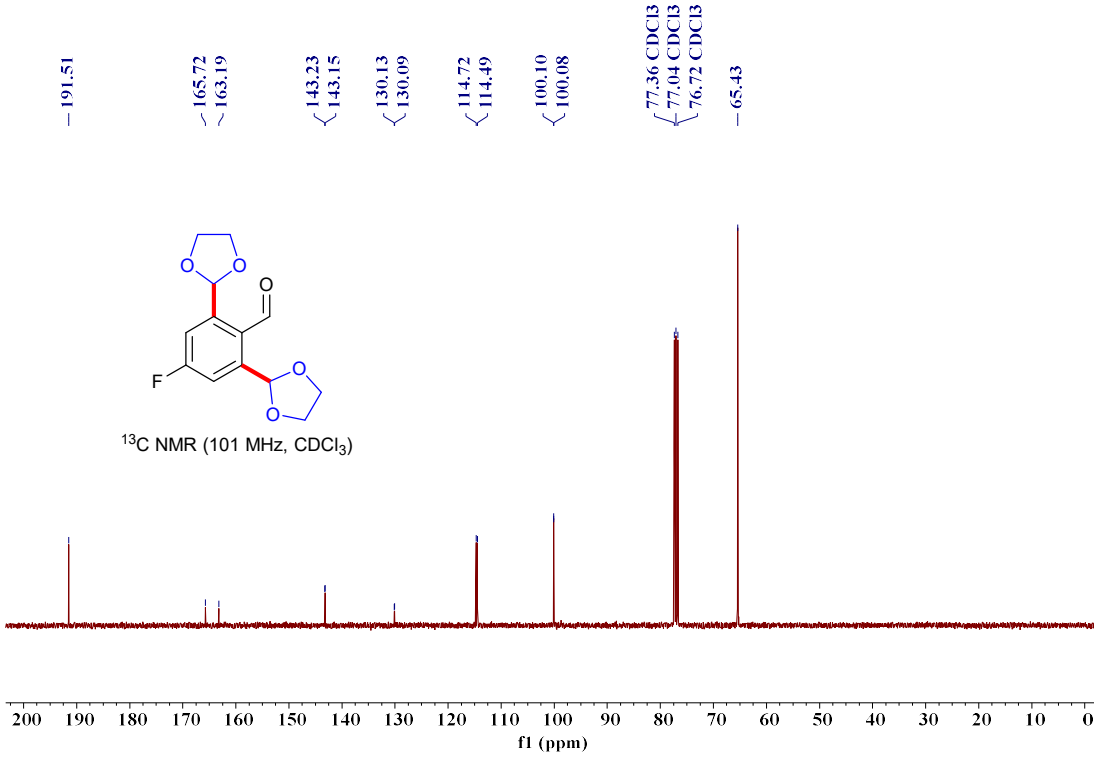




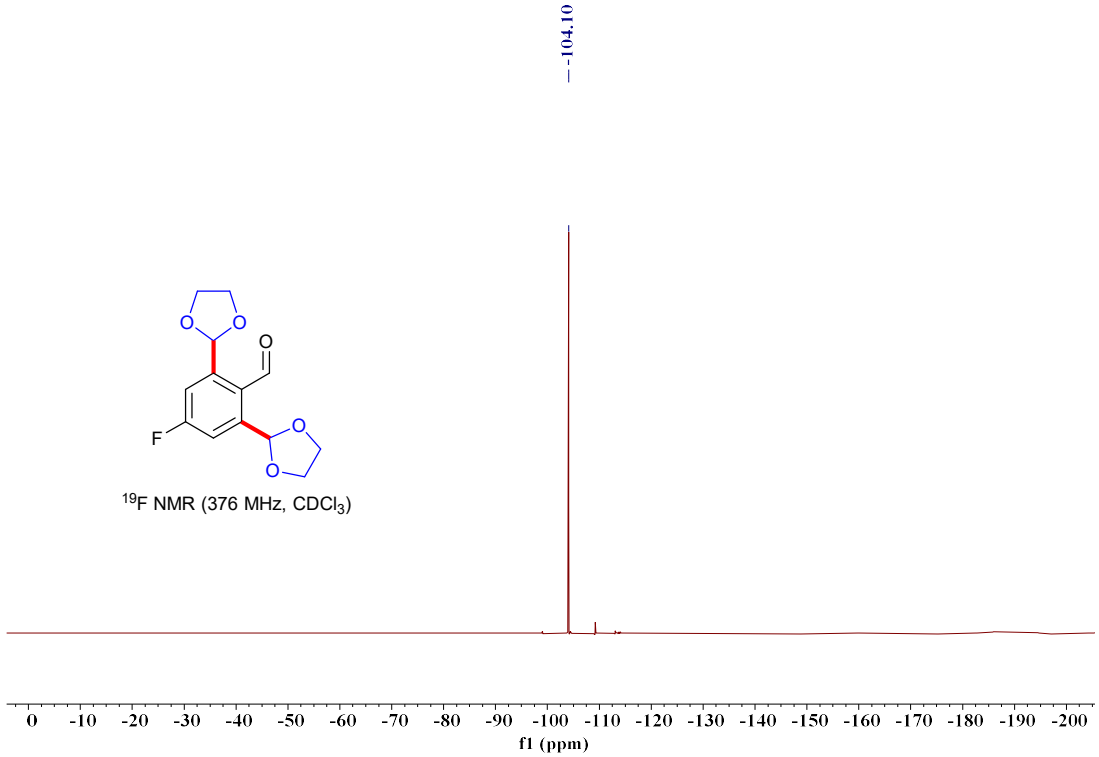


^{1}H, ^{13}C and ^{19}F NMR spectra of compound *2,6-disubstituted*-4s-2



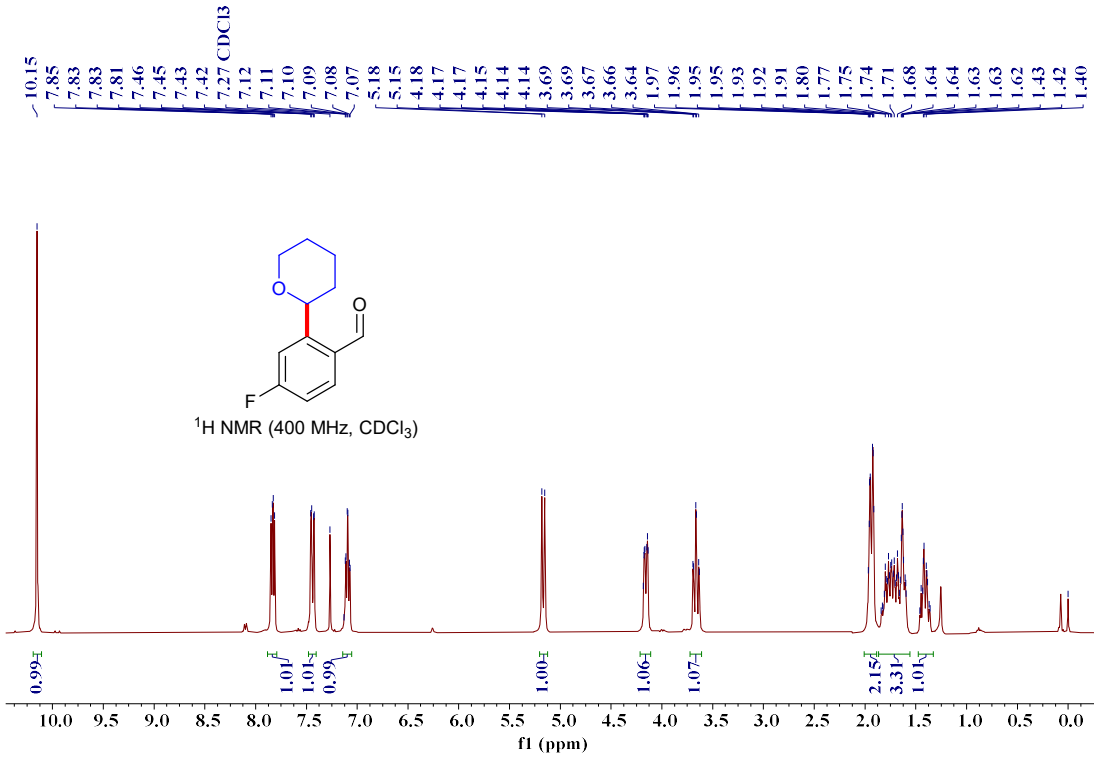


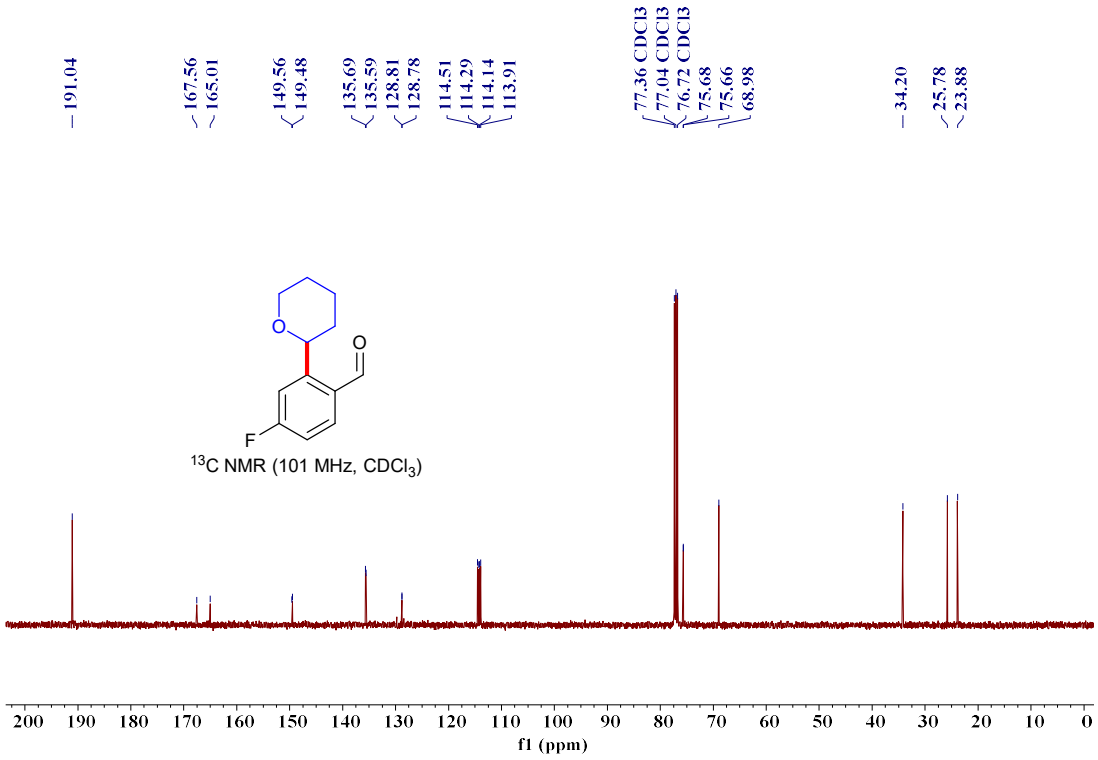
^{13}C NMR (101 MHz, $CDCl_3$)

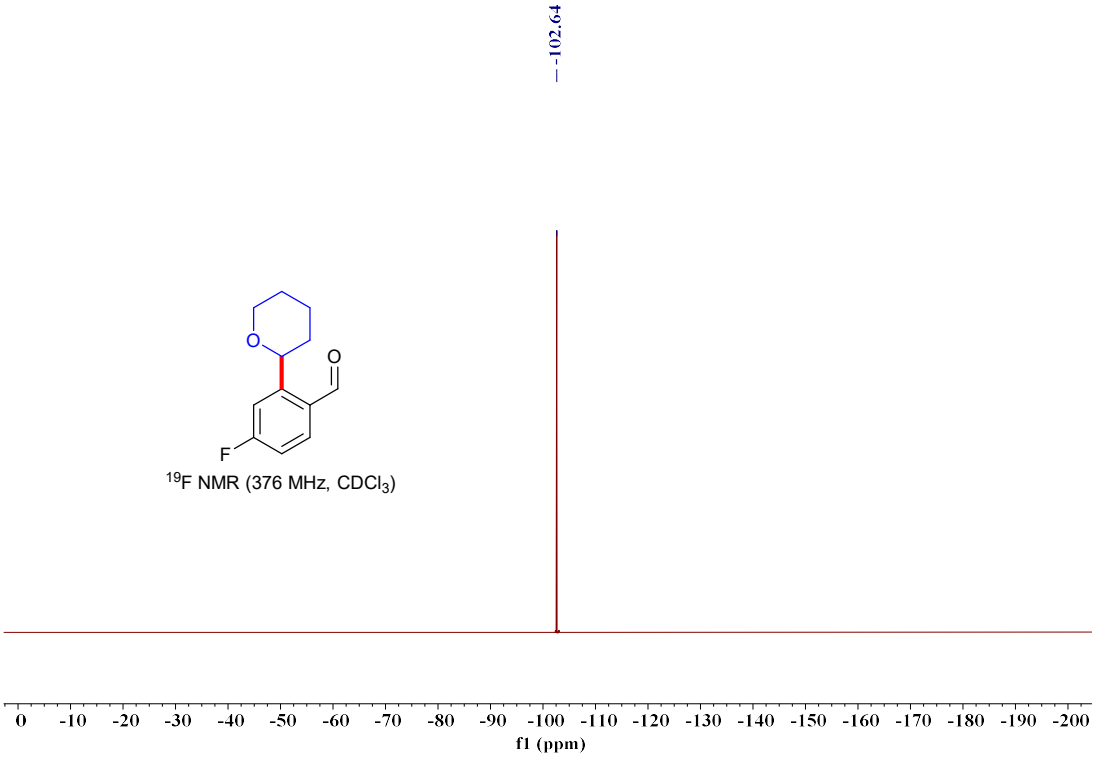


^{19}F NMR (376 MHz, $CDCl_3$)

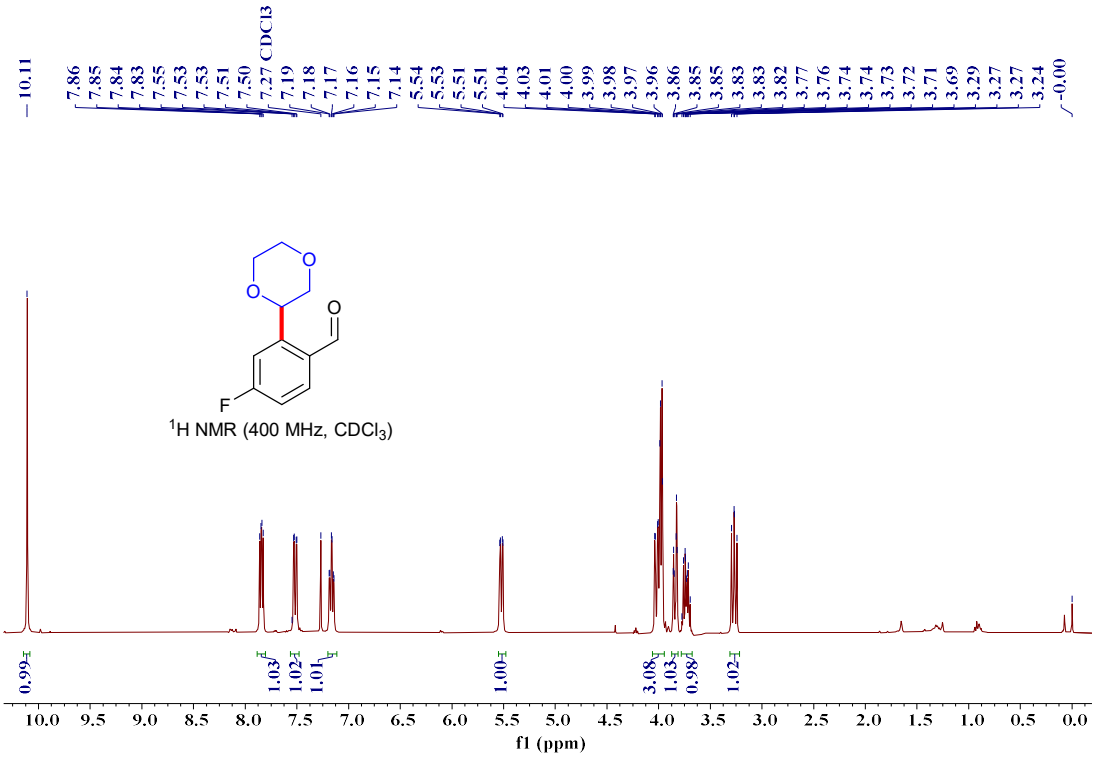
^{1}H, ^{13}C and ^{19}F NMR spectra of compound *ortho*-4t

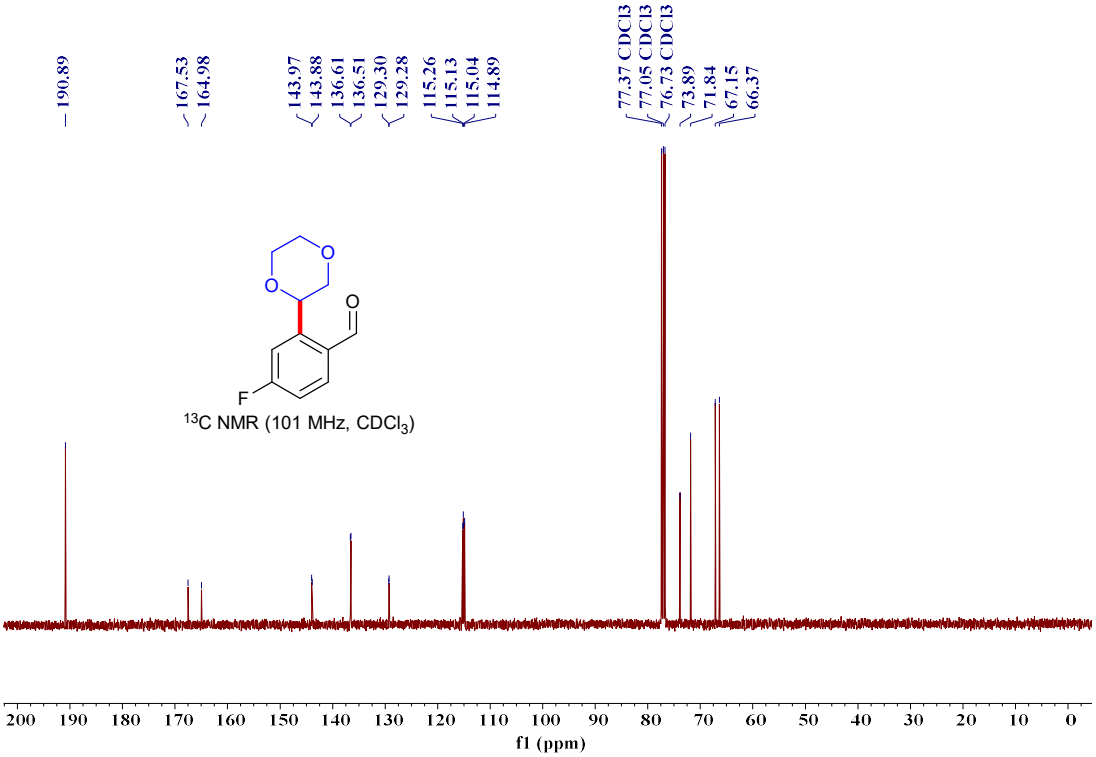


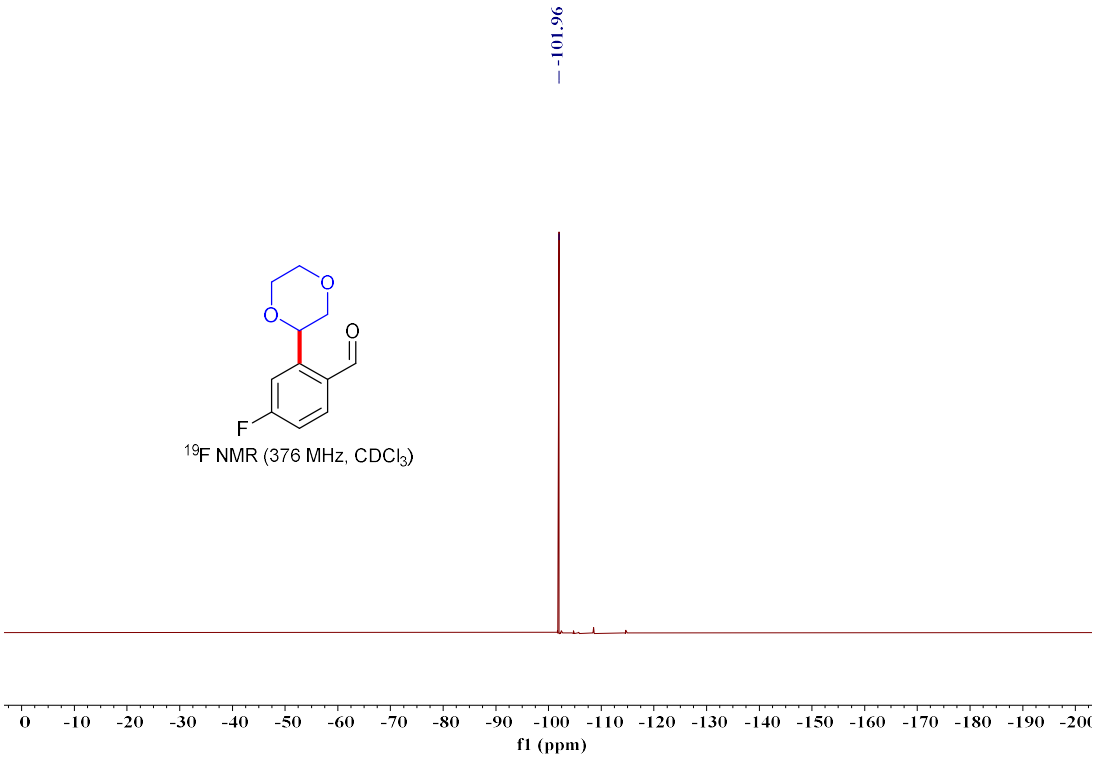




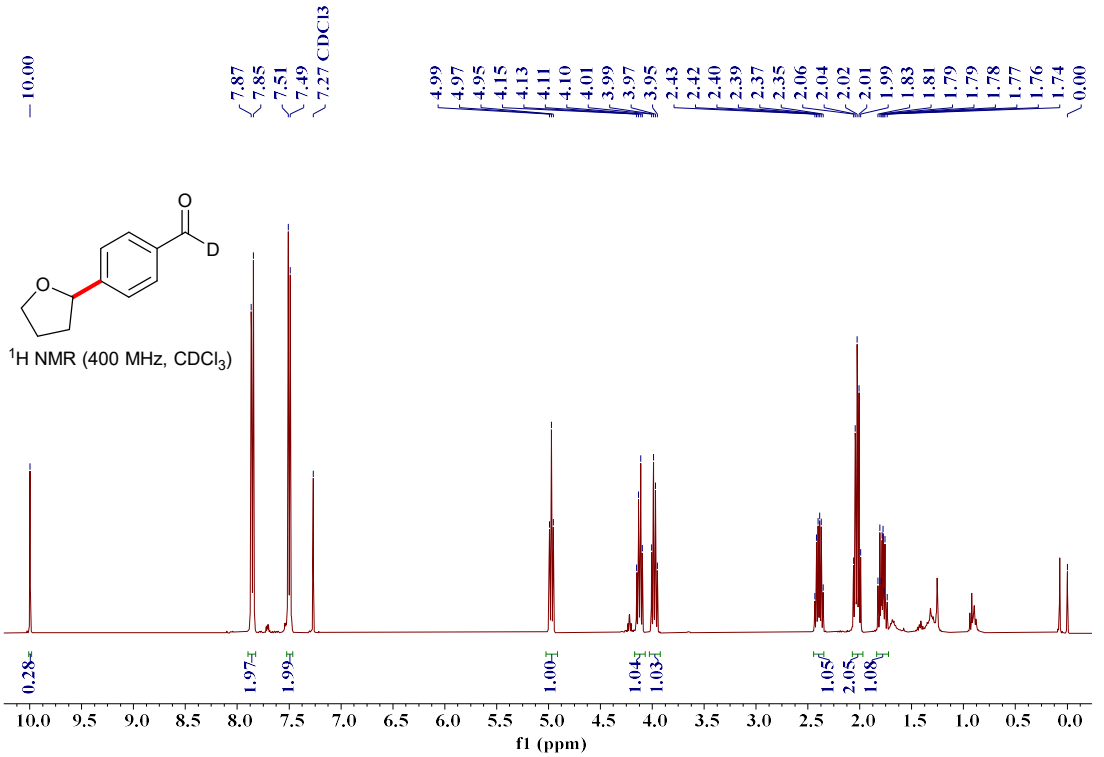
^{1}H, ^{13}C NMR and ^{19}F NMR spectra of compound *ortho*-4u

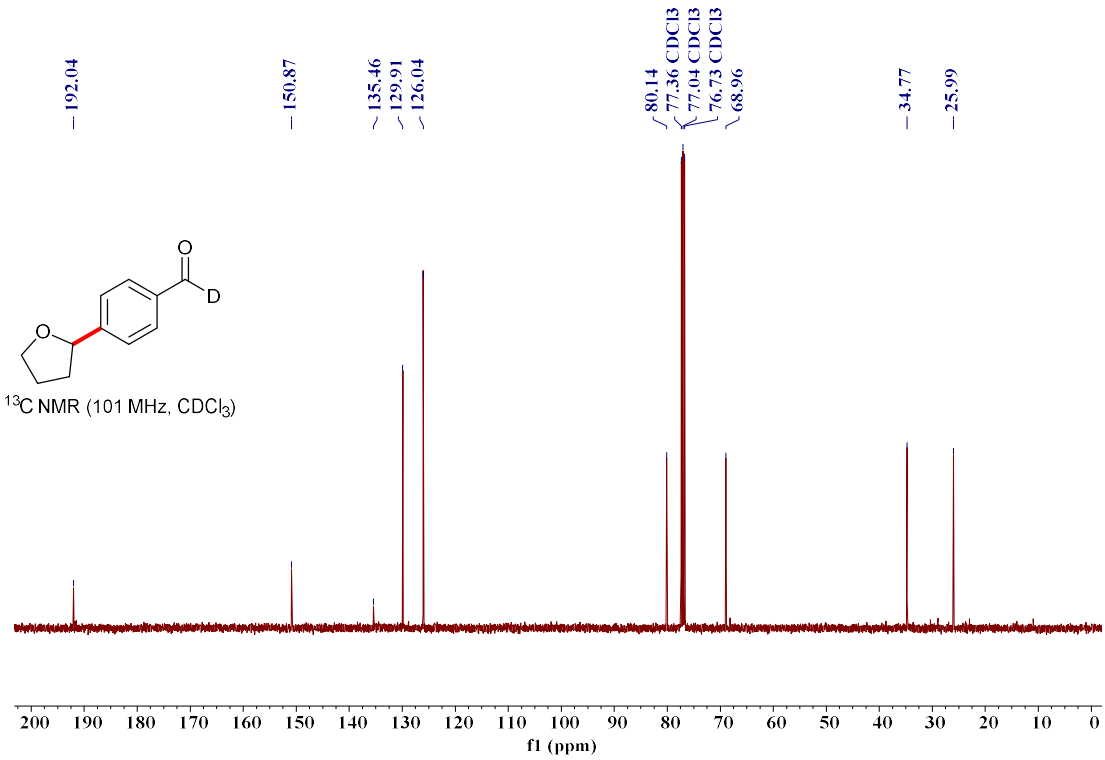



190.89
167.53
164.98
143.97
143.88
136.61
136.51
129.30
129.28
115.26
115.13
115.04
114.89
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
73.89
71.84
67.15
66.37
O
O
O
F
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

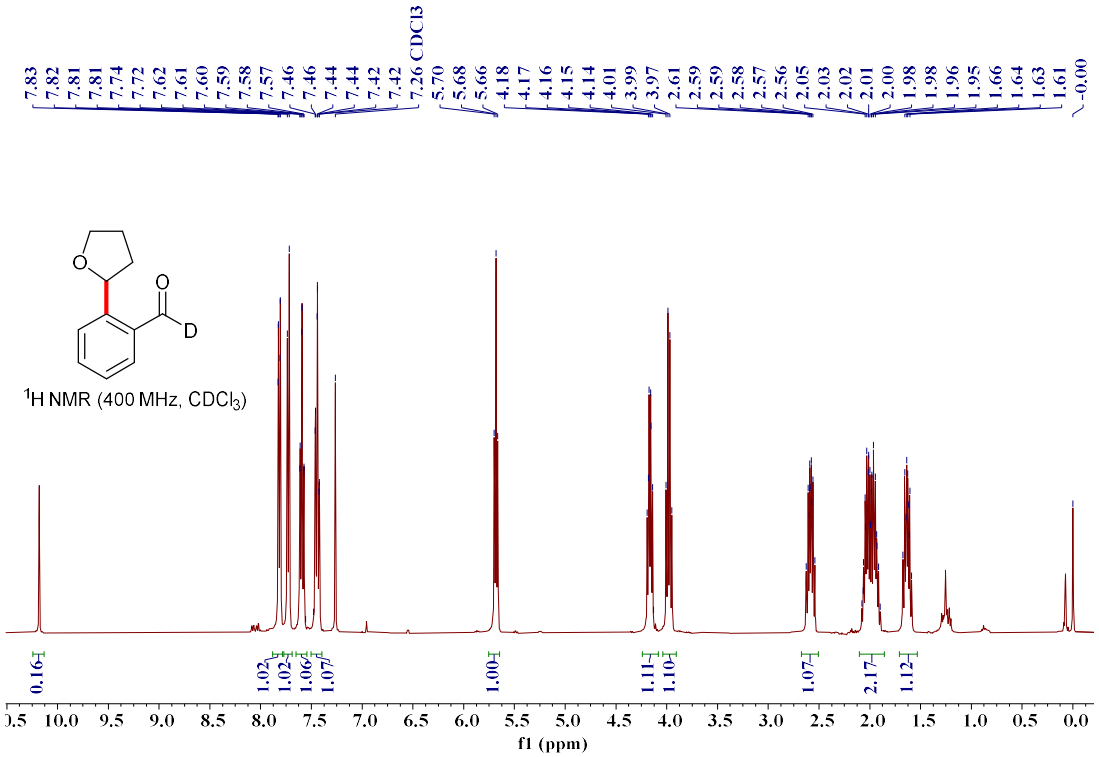

-101.96
O
O
O
F
19F NMR (376 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

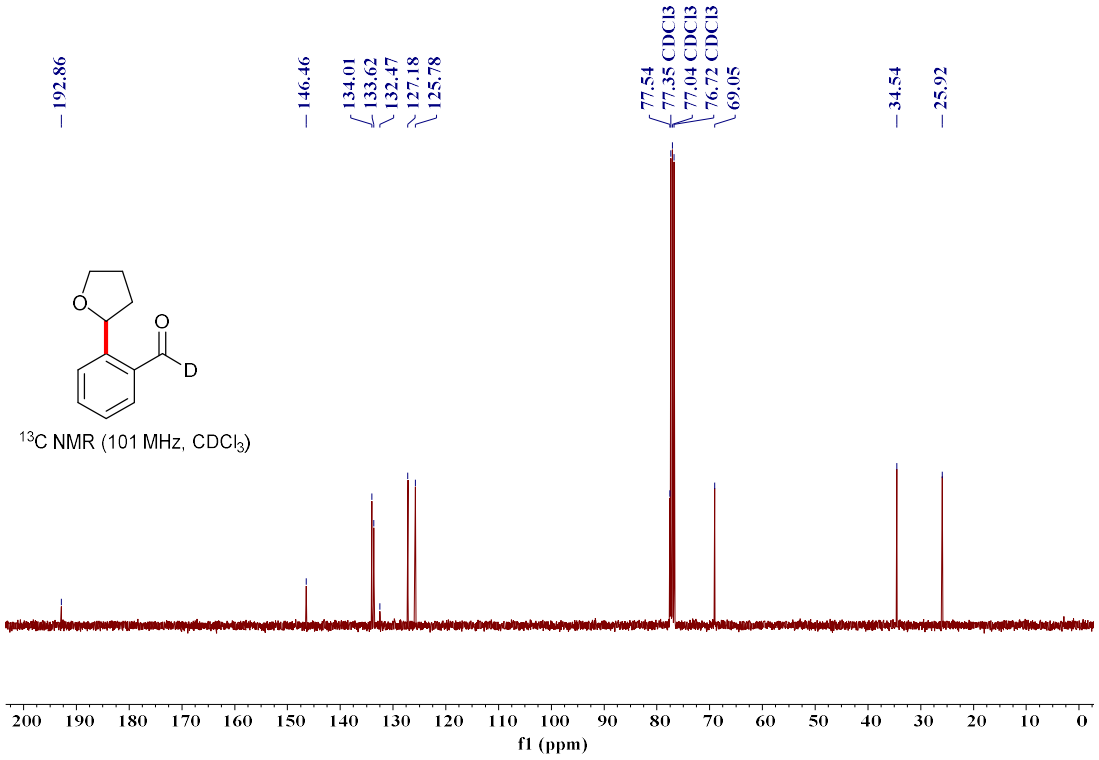
^{1}H and ^{13}C NMR spectra of compound [D]*para*-4a





^{1}H and ^{13}C NMR spectra of compound [D]*ortho*-4a





^{1}H and ^{13}C NMR spectra of compound [D]*2,4-disubsituted*-4a