Chiral Fe(II) Complex Catalyzed Enantioselective [1,3] O-to-C Rearrangement of Alkyl Vinyl Ethers and Synthesis of Chromanols and Beyond

Lifeng Wang, [a] Pengfei Zhou, [a] Qianchi Lin, [a] Shunxi Dong, [a] Xiaohua Liu,*[a] and Xiaoming Feng*[a]

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China

E-mail: liuxh@scu.edu.cn, xmfeng@scu.edu.cn

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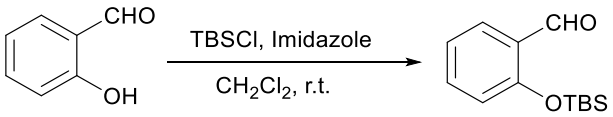
1. General information

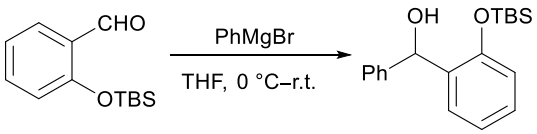
^{1}H NMR spectra were recorded on Bruker AMX-400 (400 MHz). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. $^{13}C\{^{1}H\}$ NMR spectra were collected on Bruker AMX-400 (100 MHz) with complete proton decoupling. $^{19}F\{^{1}H\}$ NMR spectra were collected on Bruker AMX-400 (376 MHz) with complete proton decoupling. Chemical shifts are reported in δ (ppm) referenced to the residual peaks of $CDCl_3$ (δ = 7.26) for ^{1}H NMR or TMS (δ = 0.00) for ^{1}H NMR and $CDCl_3$ (δ = 77.0) for $^{13}C\{^{1}H\}$ NMR. High resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C. Optical rotations were reported as follows: $[\alpha]^{T}$ (*c* g/100 mL, in solvent). IR spectra were recorded on BRUKER TENSOR II IR spectrophotometer. CD spectra were determined by Chirascan CD (DCM as the solvent) which was purchased from Applied photophysics Ltd. CH_2Cl_2 was purified by MB-SPS systeme. All other solvents were dried using standard protocol. $Fe(OTf)_2$ was purchased from Adamas Reagent, $Fe(OTf)_3$ was purchased from Alfa Reagent, PCC (Pyridinium chlorochromate) was purchased from Adamas Reagent, $[Ir(cod)Cl]_2$ was purchased from Adamas Reagent. Salicylaldehyde and Grignard reagent were commercially available. Chromatography: Qingdao Haiyangsilica gel, HG/T2354-92, H CP. The *N,N'*-dioxides were prepared according to the methods reported in the literature.[1]

2. General procedure for the synthesis of substrates



A **B**

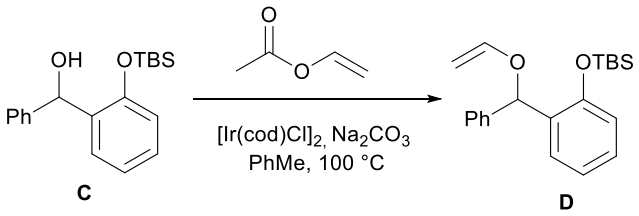
To a solution of salicylaldehyde (6.10 g, 50 mmol) and imidazole (5.10 g, 75 mmol) in CH_2Cl_2 (100 mL) was added *tert*-butyldimethylsilyl chloride (11.25 g, 75 mmol), and the reaction was stirred overnight at room temperature. Saturated NH_4Cl (200 mL) was added, the two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. the residue was purified by flash chromatography on silica gel (Pet/EtOAc = 20:1) to afford the product **B** (11.11 g, 94% yield) as a pale yellow oil.



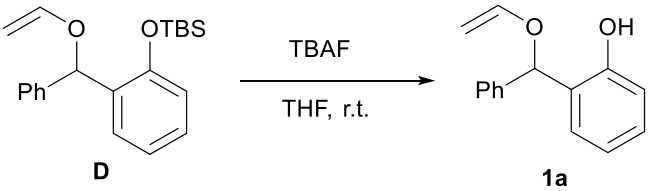
B **C**

To a solution of compound **B** (3.54 g, 15 mmol) in dry THF (20 mL) at 0 °C, solution of phenyl magnesium bromide (18.0 mL, 1M in THF) was added dropwise under N_2 atmosphere. The reaction was stirred overnight at room temperature. Saturated NH_4Cl (100 mL) was added, the two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4

and concentrated in vacuo. the residue was purified by flash chromatography on silica gel (Pet/EtOAc = 20:1) to afford the product **C** (4.0 g, 85% yield) as a colorless oil.

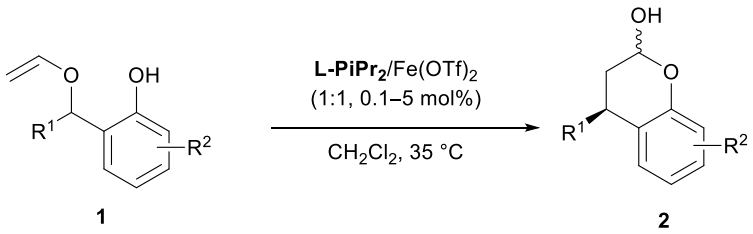


A solution of compound **C** (4.0 g, 12.73 mmol), vinyl acetate (2.19 g, 25.46 mmol), $[Ir(cod)Cl]_2$ (85 mg, 0.127 mmol) and Na_2CO_3 (0.81 g, 7.64 mmol) in toluene (30 mL) was heated at 100 °C for 6 h under N_2 atmosphere. After removing the solvent under vacuo, the residue was purified by flash chromatography on silica gel (Pet/EtOAc = 40:1) to afford the crude product of **D** (3.51 g) as a pale yellow oil. Vinyl ethers were prepared according to the literature procedure.[2]



To a solution of crude compound **D** (1.36 g) in THF (10 mL), solution of TBAF (6.0 mL, 1M in THF) was added dropwise. The reaction was stirred at room temperature for 1 h. Saturated NH_4Cl (50 mL) was added, the two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed several times with brine to remove *tert*-butyldimethylsilyl fluoride, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 20:1) to afford the product **1a** (0.86 g) as a colorless oil, the overall yield was 61% yield.

3. General procedure for the catalytic reactions



Preparation of the catalyst solution (5 x 10^{-3} M): To a 2.0 mL volumetric flask, **L-PiPr₂** (6.5 mg, 0.01 mmol), $Fe(OTf)_2$ (3.5 mg, 0.01 mmol) and CH_2Cl_2 (2.0 mL) were added.

General Procedure A:

A dry reaction tube was charged with freshly prepared **L-PiPr₂**/$Fe(OTf)_2$ catalyst solution (0.1 mol% catalyst loading; 40μL, 5 x 10^{-3} M in CH_2Cl_2), followed by the addition of CH_2Cl_2 (1.6 mL). The mixture was stirred at 35 °C for 0.5 h followed by addition of the substrate solution (0.2 mmol, 400μL; 0.5 M in CH_2Cl_2). The reaction

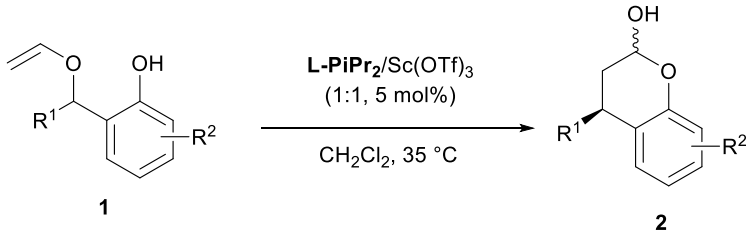
mixture was stirred at 35 °C and detected by TLC. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 10:1 – 6:1) to afford the desired products.

General Procedure B:

A dry reaction tube was charged with freshly prepared **L-PiPr$_2$**/Fe(OTf)$_2$ catalyst solution (1 mol% catalyst loading; 400μL, 5 x 10^{-3} M in CH_2Cl_2) , followed by the addition of CH_2Cl_2 (1.2 mL). The mixture was stirred at 35 °C for 0.5 h followed by addition of the substrate solution (0.2 mmol; 400μL, 0.5 M in CH_2Cl_2). The reaction mixture was stirred at 35 °C and detected by TLC. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 10:1 – 6:1) to afford the desired products.

General Procedure C:

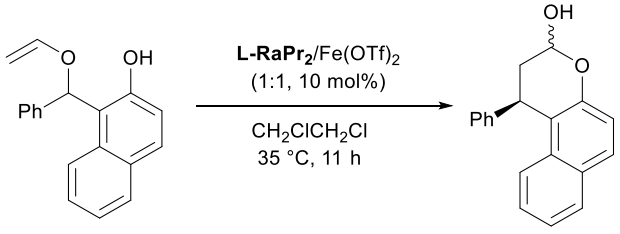
A dry reaction tube was charged with **L-PiPr$_2$** (6.5 mg, 5 mol%) and Fe(OTf)$_2$ (3.5 mg, 5 mol%) followed by the addition of CH_2Cl_2 (1.6 mL). The mixture was stirred at 35 °C for 0.5 h followed by addition of the substrate solution (0.2 mmol, 400μL; 0.5 M in CH_2Cl_2). The reaction mixture was stirred at 35 °C and detected by TLC. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 10:1 – 6:1) to afford the desired products.



1 **2**

General Procedure D:

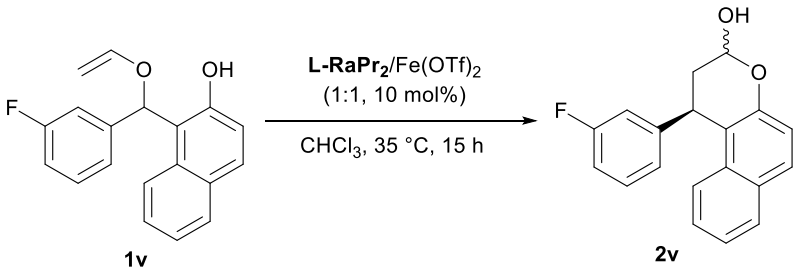
A dry reaction tube was charged with **L-PiPr$_2$** (6.5 mg, 5 mol%) and Sc(OTf)$_3$ (4.9 mg, 5 mol%) followed by the addition of CH_2Cl_2 (1.6 mL). The mixture was stirred at 35 °C for 0.5 h followed by addition of the substrate solution (0.2 mmol, 400μL; 0.5 M in CH_2Cl_2). The reaction mixture was stirred at 35 °C and detected by TLC. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 10:1 – 6:1) to afford the desired products.



1u **2u**

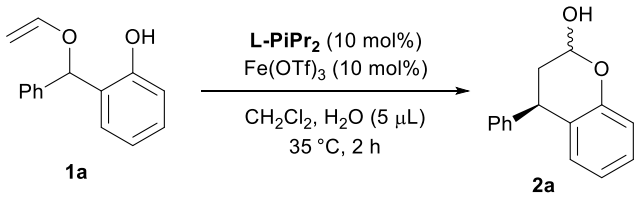
General Procedure E:

A dry reaction tube was charged with **L-RaPr$_2$** (14.0 mg, 10 mol%), Fe(OTf)$_2$ (7.0 mg, 10 mol%) and CH_2Cl_2 (1.0 mL) and the resulting solution was stirred at 35 °C for 0.5 h. After removing the solvent under vacuo, **1u** (0.2 mmol) was weighted into the tube followed by adding CH_2ClCH_2Cl (2.0 mL). The reaction mixture was stirred at 35 °C for 11 h. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 15:1 – 10:1) to afford the desired products.



General Procedure F:

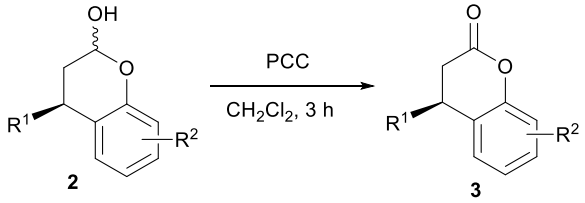
A dry reaction tube was charged with **L-RaPr$_2$** (14.0 mg, 10 mol%), $Fe(OTf)_2$ (7.0 mg, 10 mol%) and CH_2Cl_2 (1.0 mL) and the resulting solution was stirred at 35 °C for 0.5 h. After removing the solvent under vacuo, **1v** (0.2 mmol) was weighted into the tube followed by adding $CHCl_3$ (2.0 mL). The reaction mixture was stirred at 35 °C for 15 h. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 15:1 – 10:1) to afford the desired products.



General Procedure G:

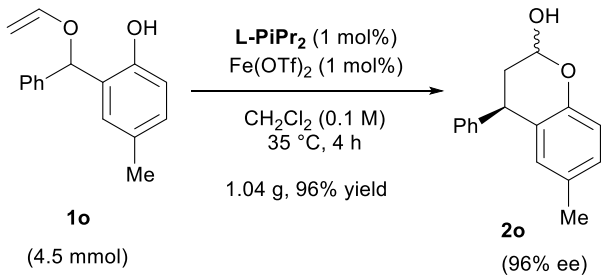
A dry reaction tube was charged with **L-PiPr$_2$** (6.5 mg, 10 mol%) and $Fe(OTf)_3$ (5.0 mg, 10 mol%) followed by the addition of CH_2Cl_2 (0.8 mL). The mixture was stirred at 35 °C for 0.5 h followed by addition of H_2O (5 μL) and then continued to stir at 35 °C for 5 minute, followed by addition of the substrate solution (0.1 mmol, 200μL; 0.5 M in CH_2Cl_2). The reaction mixture was stirred at 35 °C for 2 h. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 10:1 – 6:1) to afford the desired products.

4. General procedure for the synthesis of chromanones



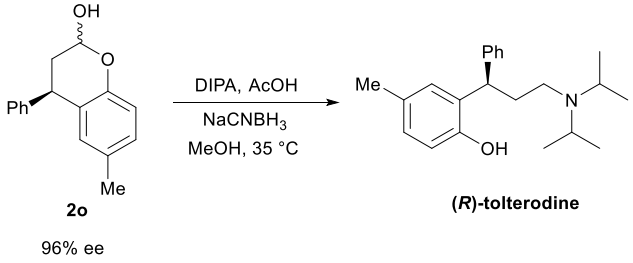
To a solution of chromanols **2** (1 equiv) in CH_2Cl_2 (0.1 M) was added PCC (3 equiv). The reaction mixture was stirred at 35 °C for 3 h. The residue was purified by flash chromatography on silica gel (Pet/EtOAc = 10:1) to afford the chromanones **3**. Isolated yield of chromanone **3** over two steps.

5. General procedure for the scale-up reaction

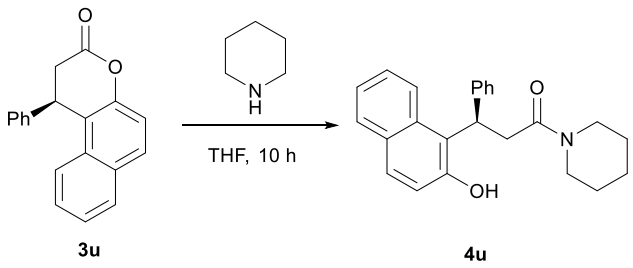


A round-bottomed flask was charged with **L-PiPr$_2$** (29.3 mg, 0.045 mmol, 1 mol%) and $Fe(OTf)_2$ (15.8 mg, 0.045 mmol, 1 mol%) followed by the addition of CH_2Cl_2 (36.0 mL). The mixture was stirred at 35 °C for 0.5 h followed by addition of the substrate solution (4.5 mmol, 9.0 mL; 0.5 M in CH_2Cl_2). The reaction mixture was stirred at 35 °C for 4 h. After removing the solvent under vacuo, the residue was purified by flash chromatography on silica gel (Pet/EtOAc = 10:1 – 6:1) to afford the desired product **2o** in 96% yield (1.04 g) with 96% ee.

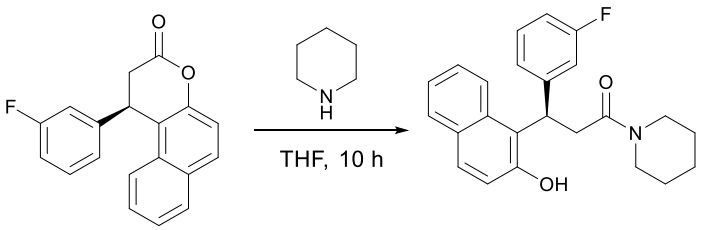
6. Synthetic transformation



A dry reaction tube was charged with chromanol **2o** (35.8 mg, 0.149 mmol), diisopropylamine (0.053 mL, 0.372 mmol), CH_3CO_2H (0.017 mL, 0.30 mmol), $NaCNBH_3$ (23.4 mg, 0.372 mmol), and dry MeOH (0.36 mL). The reaction was stirred at 35 °C under N_2 atmosphere for 70 h. After removing the solvent under vacuo, the residue was purified by flash chromatography on silica gel (Et_3N/EtOAc/Pet = 1:30:70) to afford (*R*)-tolterodine in 72% yield (35.1 mg).



To a solution of **3u** (20.2 mg, 0.074 mmol, 95% ee) in THF (3.7 mL) was added piperidine (0.4 mL, 4.05 mmol). The reaction mixture was stirred at 35 °C for 10 h. After removing the solvent under vacuo, the residue was purified by flash chromatography on silica gel (Pet/EtOAc = 4:1 – 2:1) to afford the desired product **4u** in 99% yield (26.4 mg) with 95% ee.

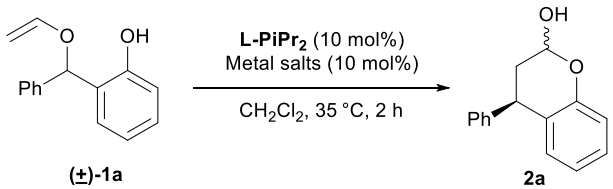


3v **4v**

To a solution of **3v** (18.5 mg, 0.063 mmol, 95% ee) in THF (3.2 mL) was added piperidine (0.34 mL, 3.48 mmol). The reaction mixture was stirred at 35 °C for 10 h. After removing the solvent under vacuo, the residue was purified by flash chromatography on silica gel (Pet/EtOAc = 4:1 – 2:1) to afford the desired product **4v** in 94% yield (22.4 mg) with 95% ee.

7. The optimization of reaction conditions

Table S1. Screening of metal salts.

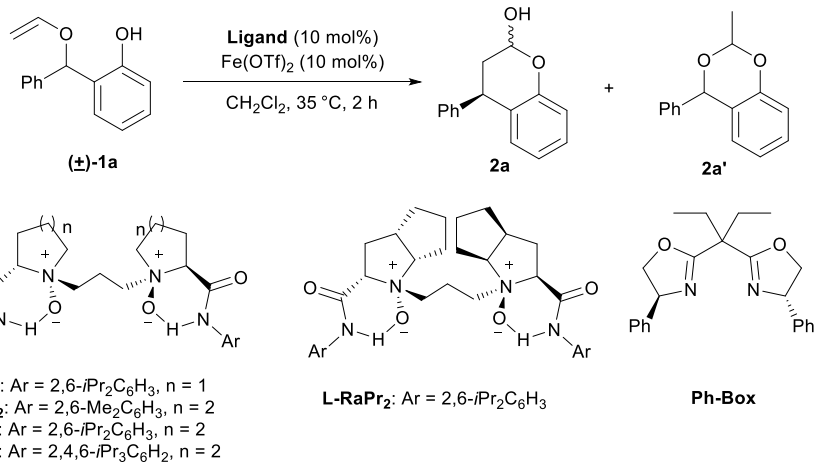


(±)-1a 2a

entry[a]	Metal salts	yield (%)[b]	ee (%)[c]
1	$Fe(OTf)_2$	93	98
2	$Sc(OTf)_3$	86	90
3	$Zn(OTf)_2$	13	69
4	$Fe(OTf)_3$	19	0

[a] Unless otherwise stated, all reactions were performed with **1a** (0.1 mmol) and **L-PiPr$_2$**/Metal salts (1/1, 10 mol%) in CH_2Cl_2 (0.1 M) at 35 °C for 2 h. [b] Isolated yields. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S2. Screening of ligands.

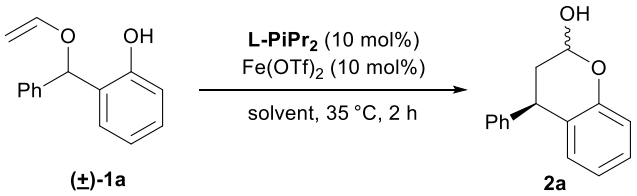


(±)-1a 2a 2a'

entry[a]	Ligand	yield (%)[b]	ee (%)[c]
1	**L-PiPr$_2$**	93	98
2	**L-RaPr$_2$**	80	94
3	**L-PrPr$_2$**	80	91
4	**L-PiMe$_2$**	86	96
5	**L-PiPr$_3$**	79	96
6	**Ph-Box**	67	0
7[d]	none	29	0

[a] Unless otherwise stated, all reactions were performed with **1a** (0.1 mmol) and **Ligand**/$Fe(OTf)_2$ (1/1, 10 mol%) in CH_2Cl_2 (0.1 M) at 35 °C for 2 h. [b] Isolated yields of **2a**. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Isolated yield of byproduct **2a′** was 63% yield.

Table S3. Screening of solvent.

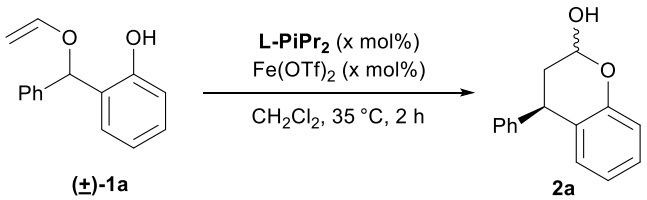


(±)-1a 2a

entry[a]	solvent	yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	93	98
2	$PhCH_3$	75	96
3	THF	90	98
4	EtOAc	87	96

[a] Unless otherwise stated, all reactions were performed with **1a** (0.1 mmol) and **L-PiPr$_2$**/$Fe(OTf)_2$ (1/1, 10 mol%) in solvent (0.1 M) at 35 °C for 2 h. [b] Isolated yields. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S4. Screening of catalyst loading.

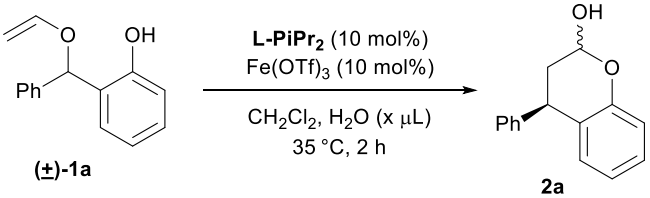


(±)-1a 2a

entry[a]	x	yield (%)[b]	ee (%)[c]
1	10	93	98
2	5	93	98
3	1	93	99
4	0.1	84	98

[a] Unless otherwise stated, all reactions were performed with **1a** (0.1 mmol) and **L-PiPr$_2$**/$Fe(OTf)_2$ (1/1, x mol%) in CH_2Cl_2 (0.1 M) at 35 °C for 2 h. [b] Isolated yields. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S5. Screening of H_2O when $Fe(OTf)_3$ as metal salt.

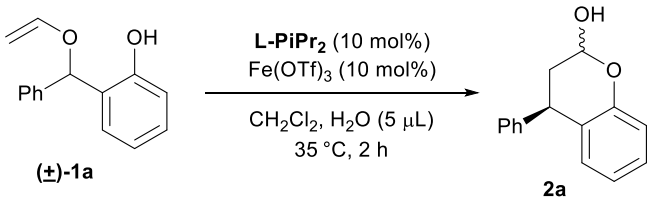


(±)-1a 2a

entry[a]	x µL	yield (%)[b]	ee (%)[c]
1	0	19	0
2	1	44	92
3	5	71	99
4	10	72	98
5[d]	0	63	98

[a] Unless otherwise stated, all reactions were performed with **1a** (0.1 mmol), **L-PiPr$_2$**/Fe(OTf)$_3$ (1/1, 10 mol%) and H_2O (x µL) in CH_2Cl_2 (0.1 M) at 35 °C for 2 h. [b] Isolated yields. [c] Determined by HPLC analysis on a chiral stationary phase. [d] 1 mol% catalyst loading.

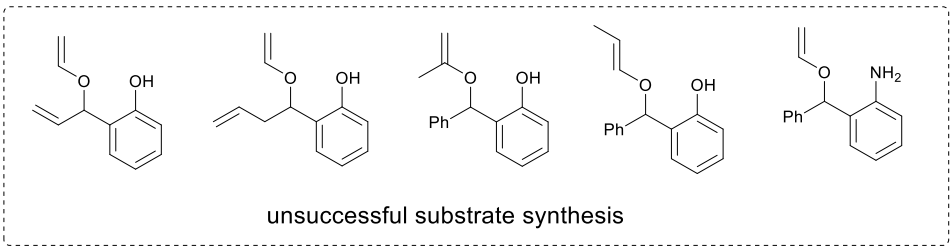
Table S6. Screening of different counteranions with Fe(III) and HOTf.



entry[a]	variation from "standard conditions"	yield (%)[b]	ee (%)[c]
1	none	71	99
2	$Fe(ClO_4)_3 \cdot xH_2O$ instead of $Fe(OTf)_3$	46	98
3	$FePO_4 \cdot xH_2O$ instead of $Fe(OTf)_3$	N.R.	-
4	$Fe(acac)_3$ instead of $Fe(OTf)_3$	0	-
5[d]	HOTf	0	-
6[e]	HOTf	N.R.	-

[a] Unless otherwise stated, all reactions were performed with **1a** (0.1 mmol), **L-PiPr$_2$**/Fe(OTf)$_3$ (1/1, 10 mol%) and H_2O (5 µL) in CH_2Cl_2 (0.1 M) at 35 °C for 2 h. [b] Isolated yields. [c] Determined by HPLC analysis on a chiral stationary phase. [d] HOTf (10 mol%) instead of H_2O (5 µL). [e] HOTf (10 mol%) instead of Fe(OTf)$_3$ (10 mol%) and H_2O (5 µL).

8. Scope limitation



9. HRMS analysis

The mixture of **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 0.01 mmol) with D_2O (50 μL) in CH_2Cl_2, and the mixture of **L-PiPr$_2$**/Fe(OTf)$_3$ (1/1, 0.01 mmol) with D_2O (50 μL) in CH_2Cl_2 were monitored by HRMS (Figure S1 and Figure S2). The signals in response to the complexes of iron salt, chiral ligand and water showed that higher peaks was found from the system of Fe(OTf)$_2$ than Fe(OTf)$_3$. It might indicate that the ferrous catalyst is a slightly sensitive to moisture than the corresponding ferric catalyst.

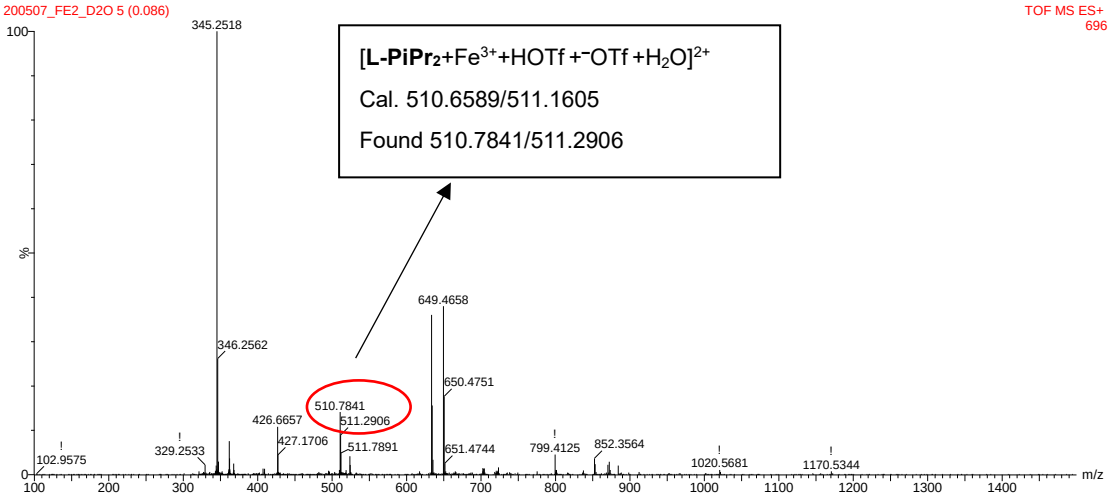


Figure S1 HRMS spectra of **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 0.01 mmol) with D_2O (50 μL)

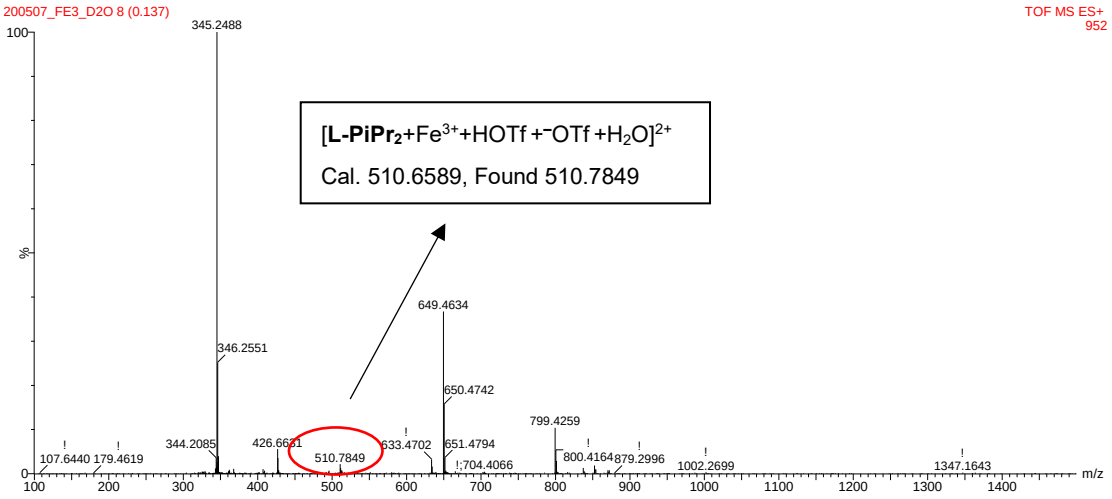
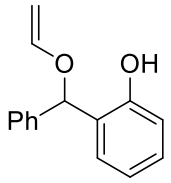


Figure S2 HRMS spectra of **L-PiPr$_2$**/Fe(OTf)$_3$ (1/1, 0.01 mmol) with D_2O (50 μL)

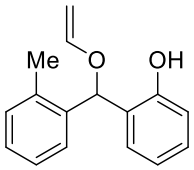
10. Spectral characterization data

2-(Phenyl(vinyloxy)methyl)phenol (1a)



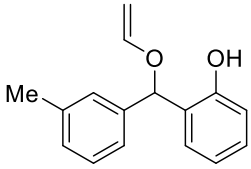
Colorless oil, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 5H), 7.20 – 7.15 (m, 1H), 7.10 – 7.05 (m, 1H), 6.92 – 6.81 (m, 2H), 6.59 (s, 1H), 6.45 (dd, *J* = 14.1, 6.6 Hz, 1H), 6.03 (s, 1H), 4.50 (dd, *J* = 14.1, 2.1 Hz, 1H), 4.16 (dd, *J* = 6.6, 2.1 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.2, 149.5, 139.2, 129.5, 128.5, 128.46, 128.1, 126.9, 125.3, 120.4, 117.0, 91.8, 82.0. IR (film): ν (cm^{-1}) 3422, 3032, 1637, 1616, 1487, 1454, 1231, 1166, 1094, 1043, 939, 835, 751, 697. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{14}O_2$+Na^+]: 249.0886, found 249.0887.

2-(*o*-tolyl(vinyloxy)methyl)phenol (1b)



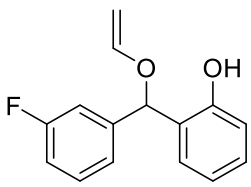
Colorless oil, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.05 (m, 5H), 6.83 – 6.71 (m, 3H), 6.57 (s, 1H), 6.34 (dd, *J* = 14.1, 6.6 Hz, 1H), 6.13 (s, 1H), 4.37 (dd, *J* = 14.1, 2.1 Hz, 1H), 4.06 (dd, *J* = 6.6, 2.1 Hz, 1H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.8, 149.6, 136.8, 136.5, 130.7, 129.6, 128.6, 128.4, 127.7, 126.1, 124.2, 120.4, 116.7, 91.6, 79.2, 19.2. IR (film): ν (cm^{-1}) 3424, 3026, 1612, 1487, 1457, 1281, 1233, 1094, 1040, 942, 818, 753. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_2$+Na^+]: 263.1043, found 263.1040.

2-(*m*-Tolyl(vinyloxy)methyl)phenol (1c)



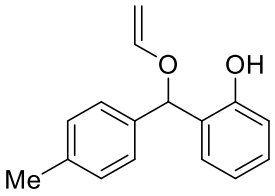
Pale yellow oil, 11% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.07 (m, 6H), 6.92 – 6.87 (m, 2H), 6.67 – 6.59 (m, 1H), 6.47 (dd, *J* = 14.0, 6.6 Hz, 1H), 6.00 (s, 1H), 4.52 (dd, *J* = 14.0, 2.1 Hz, 1H), 4.19 (dd, *J* = 6.6, 2.1 Hz, 1H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.3, 149.5, 139.1, 138.3, 129.5, 129.0, 128.5, 128.5, 127.6, 125.3, 124.0, 120.3, 117.04, 91.8, 82.4, 21.5. IR (film): ν (cm^{-1}) 3411, 2920, 1613, 1487, 1455, 1322, 1283, 1228, 1159, 1040, 943, 821, 753, 698. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_2$+Na^+]: 263.1043, found 263.1044.

2-((3-Fluorophenyl)(vinyloxy)methyl)phenol (1d)



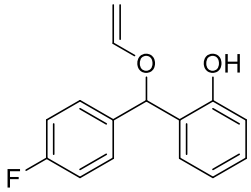
Pale yellow oil, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.12 (m, 1H), 7.10 – 7.05 (m, 1H), 7.05 – 6.95 (m, 3H), 6.88 – 6.76 (m, 2H), 6.74 – 6.69 (m, 1H), 6.39 – 6.29 (m, 2H), 5.94 (s, 1H), 4.38 (dd, *J* = 14.1, 2.2 Hz, 1H), 4.07 (dd, *J* = 6.6, 2.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 244.8 Hz), 153.9, 149.4, 142.2 (d, *J* = 6.9 Hz), 130.0 (d, *J* = 8.1 Hz), 129. 7, 128.3, 125.2, 122.4 (d, *J* = 2.9 Hz), 120.6, 116.8, 114.9 (d, *J* = 21.0 Hz), 113.8 (d, *J* = 22.4 Hz), 91.8, 80.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –112.37. IR (film): ν (cm^{-1}) 3411, 3063, 1619, 1591, 1516, 1485, 1442, 1400, 1261, 1217, 1152, 1033, 941, 815, 782, 744, 684. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}FO_2$+Na^+]: 267.0792, found 267.0798.

2-(*p*-Tolyl(vinyloxy)methyl)phenol (1e)



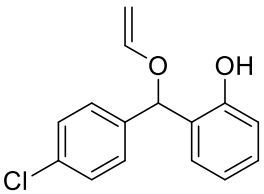
Pale yellow oil, 18% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 2H), 7.07 – 7.01 (m, 3H), 7.00 – 6.95 (m, 1H), 6.79 – 6.72 (m, 2H), 6.61 (s, 1H), 6.34 (dd, *J* = 14.1, 6.6 Hz, 1H), 5.91 (s, 1H), 4.39 (dd, *J* = 14.1, 2.1 Hz, 1H), 4.05 (dd, *J* = 6.6, 2.1 Hz, 1H), 2.20 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.2, 149.5, 137.8, 136.3, 129.3, 129.2, 128.3, 126.9, 125.5, 120.3, 116.9, 91.6, 81.8, 21.1. IR (film): ν (cm^{-1}) 3423, 3028, 1637, 1617, 1511, 1487, 1455, 1321, 1286, 1230, 1168, 1093, 1042, 942, 822, 753. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_2$+Na^+]: 263.1043, found 263.1036.

2-((4-Fluorophenyl)(vinyloxy)methyl)phenol (1f)



Pale yellow oil, 48% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 7.11 – 7.07 (m, 1H), 7.04 – 6.98 (m, 2H), 6.92 – 6.84 (m, 2H), 6.50 – 6.36 (m, 2H), 6.02 (s, 1H), 4.49 (dd, *J* = 14.1, 2.2 Hz, 1H), 4.18 (dd, *J* = 6.6, 2.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.4 Hz), 154.1, 149.4, 135.2 (d, *J* = 3.1 Hz), 129.7, 128.8 (d, *J* = 8.2 Hz), 128.3, 125.2, 120.5, 117.0, 115.4 (d, *J* = 21.5 Hz), 91.9, 81.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –113.95. IR (film): ν (cm^{-1}) 3442, 3044, 1639, 1605, 1509, 1457, 1322, 1277, 1225, 1157, 1099, 1045, 943, 832, 755. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}FO_2$+Na^+]: 267.0792, found 267.0799.

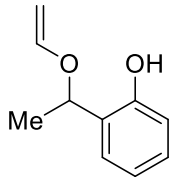
2-((4-Chlorophenyl)(vinyloxy)methyl)phenol (1g)



Pale yellow oil, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 4H), 7.06 – 7.00 (m, 2H), 6.81 – 6.75 (m, 1H), 6.72 – 6.68 (m, 1H), 6.43 (s, 1H), 6.32 (dd, *J* = 14.1, 6.6 Hz, 1H), 5.93 (s, 1H), 4.37 (dd, *J* = 14.1, 2.2 Hz, 1H), 4.06 (dd, *J* = 6.6, 2.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.7, 149.4, 138.1, 133.7, 129.5, 128.6, 128.2, 128.2, 125.3, 120.6, 116.7, 91.7, 80.2. IR (film): ν (cm^{-1}) 3426, 3041, 1639, 1618, 1489, 1456, 1403, 1322, 1284, 1230, 1166, 1090, 1045, 1013, 942, 823, 754. HRMS (FTMS+c ESI) calcd for

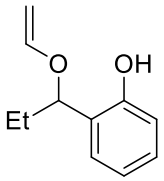
$[C_{15}H_{13}{}^{35}ClO_2+Na^+]$: 283.0496, found 283.0490; HRMS (FTMS+c ESI) calcd for $[C_{15}H_{13}{}^{37}ClO_2+Na^+]$: 285.0467, found 285.0462.

2-(1-(Vinyloxy)ethyl)phenol (1h)



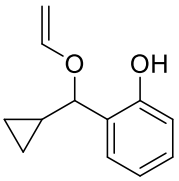
Pale yellow oil, 48% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 1H), 7.12 – 7.05 (m, 1H), 6.93 – 6.84 (m, 2H), 6.83 – 6.76 (m, 1H), 6.36 (dd, *J* = 14.1, 6.6 Hz, 1H), 5.09 (q, *J* = 6.6 Hz, 1H), 4.45 (dd, *J* = 14.1, 2.0 Hz, 1H), 4.14 (dd, *J* = 6.6, 2.1 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.1, 149.3, 129.1, 127.1, 126.7, 120.3, 116.9, 91.2, 78.0, 21.5. IR (film): ν (cm^{-1}) 3422, 2979, 1617, 1587, 1491, 1451, 1345, 1289, 1229, 1172, 1119, 1068, 1018, 961, 826, 751, 624, 568. HRMS (FTMS+c ESI) calcd for $[C_{10}H_{12}O_2+Na^+]$: 187.0730, found 187.0733.

2-(1-(Vinyloxy)propyl)phenol (1i)



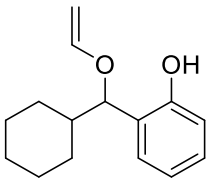
Yellow oil, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 1H), 7.09 – 6.97 (m, 1H), 6.97 – 6.82 (m, 2H), 6.81 (s, 1H), 6.37 (dd, *J* = 14.1, 6.6 Hz, 1H), 4.79 (t, *J* = 6.9 Hz, 1H), 4.44 (dd, *J* = 14.1, 2.1 Hz, 1H), 4.12 (dd, *J* = 6.6, 2.1 Hz, 1H), 2.08 – 1.95 (m, 1H), 1.93 – 1.79 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.4, 149.7, 129.1, 127.9, 125.3, 120.0, 116.9, 91.1, 83.9, 28.6, 10.1. IR (film): ν (cm^{-1}) 3432, 2931, 1618, 1491, 1455, 1350, 1228, 1172, 1082, 1039, 982, 835, 753. HRMS (FTMS+c ESI) calcd for $[C_{11}H_{14}O_2+Na^+]$: 201.0886, found 201.0888.

2-(Cyclopropyl(vinyloxy)methyl)phenol (1j)



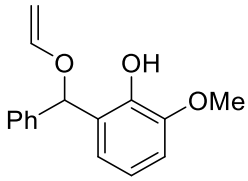
Yellow oil, 4% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 1H), 7.08 – 6.99 (m, 1H), 6.93 – 6.82 (m, 3H), 6.34 (dd, *J* = 14.0, 6.5 Hz, 1H), 4.50 – 4.28 (m, 2H), 4.09 (dd, *J* = 6.5, 2.0 Hz, 1H), 1.43 – 1.34 (m, 1H), 0.69 – 0.61 (m, 1H), 0.56 – 0.48 (m, 1H), 0.45 – 0.31 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.4, 149.4, 129.3, 128.0, 124.5, 120.0, 116.8, 91.3, 85.9, 15.6, 3.9, 2.5. IR (film): ν (cm^{-1}) 3429, 2922, 2855, 1635, 1619, 1589, 1488, 1457, 1336, 1234, 1175, 1028, 975, 828, 754. HRMS (FTMS+c ESI) calcd for $[C_{12}H_{14}O_2+Na^+]$: 213.0886, found 213.0886.

2-(Cyclohexyl(vinyloxy)methyl)phenol (1k)



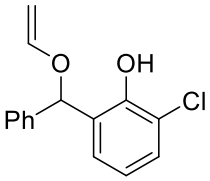
Pale yellow oil, 15% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 1H), 7.00 – 6.93 (m, 1H), 6.92 – 6.78 (m, 3H), 6.34 (dd, *J* = 14.0, 6.5 Hz, 1H), 4.52 (d, *J* = 7.9 Hz, 1H), 4.42 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.09 (dd, *J* = 6.5, 2.1 Hz, 1H), 2.10 – 2.02 (m, 1H), 1.91 – 1.81 (m, 1H), 1.81 – 1.74 (m, 1H), 1.71 – 1.58 (m, 2H), 1.43 – 1.35 (m, 1H), 1.30 – 0.87 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.7, 150.1, 129.1, 128.9, 124.0, 119.6, 117.0, 91.0, 88.0, 42.5, 29.3, 29.3, 26.2, 25.9, 25.8. IR (film): ν (cm^{-1}) 3448, 2924, 2852, 1637, 1617, 1588, 1488, 1452, 1347, 1230, 1170, 1083, 1027, 988, 941, 880, 835, 753. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{20}O_2$+Na^+]: 255.1356, found 255.1353.

2-Methoxy-6-(phenyl(vinyloxy)methyl)phenol (1l)



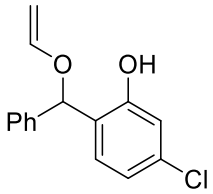
Yellow oil, 22% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.46 – 7.37 (m, 2H), 7.37 – 7.29 (m, 1H), 7.11 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.60 (dd, *J* = 14.2, 6.7 Hz, 1H), 6.43 (s, 1H), 6.06 (s, 1H), 4.51 (dd, *J* = 14.2, 1.8 Hz, 1H), 4.17 (dd, *J* = 6.7, 1.8 Hz, 1H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.4, 146.2, 142.6, 140.7, 128.2, 127.4, 126.9, 126.6, 119.8, 119.2, 109.6, 89.5, 76.2, 55.8. IR (film): ν (cm^{-1}) 3509, 3031, 1635, 1619, 1480, 1442, 1353, 1270, 1220, 1171, 1080, 1047, 1000, 827, 767, 731, 698. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_3$+Na^+]: 279.0992, found 279. 0980.

2-Chloro-6-(phenyl(vinyloxy)methyl)phenol (1m)



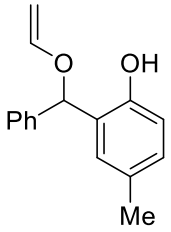
Pale yellow oil, 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 6.86 (t, *J* = 7.9 Hz, 1H), 6.45 (dd, *J* = 14.2, 6.7 Hz, 1H), 6.21 (s, 1H), 6.08 (s, 1H), 4.39 (dd, *J* = 14.2, 2.1 Hz, 1H), 4.10 (dd, *J* = 6.7, 2.1 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.1, 148.6, 139.8, 128.5, 128.5, 128.4, 127.9, 126.8, 126.4, 121.1, 120.3, 90.4, 77.7. IR (film): ν (cm^{-1}) 3511, 3032, 1618, 1452, 1322, 1242, 1165, 1130, 1051, 956, 828, 771, 733, 700, 636. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{35}ClO_2$+Na^+]: 283.0496, found 283.0497; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{37}ClO_2$+Na^+]: 285.0467, found 285.0461.

5-Chloro-2-(phenyl(vinyloxy)methyl)phenol (1n)



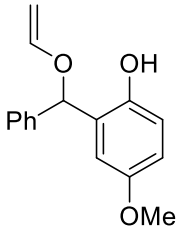
Pale yellow oil, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.80 (s, 1H), 6.43 (dd, *J* = 14.0, 6.6 Hz, 1H), 5.98 (s, 1H), 4.50 (dd, *J* = 14.0, 2.3 Hz, 1H), 4.20 (dd, *J* = 6.6, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.1, 149.2, 138.7, 134.7, 129.4, 128.7, 128.4, 126.9, 123.9, 120.6, 117.4, 92.2, 81.6. IR (film): ν (cm^{-1}) 3416, 3031, 1638, 1607, 1487, 1452, 1413, 1316, 1162, 1081, 1027, 998, 903, 841, 798, 742, 696, 638. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{35}ClO_2$+Na^+]: 283.0496, found 283.0500; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{37}ClO_2$+Na^+]: 285.0467, found 285.0461.

4-Methyl-2-(phenyl(vinyloxy)methyl)phenol (1o)



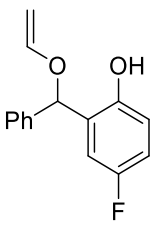
Colorless oil, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 7.04 – 6.99 (m, 1H), 6.92 – 6.87 (m, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.48 (dd, *J* = 14.0, 6.6 Hz, 1H), 6.37 (s, 1H), 5.99 (s, 1H), 4.52 (dd, *J* = 14.0, 2.1 Hz, 1H), 4.19 (dd, *J* = 6.6, 2.1 Hz, 1H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.0, 149.6, 139.3, 130.1, 129.6, 128.9, 128.6, 128.1, 126.9, 124.8, 116.9, 91.8, 82.4, 20.5. IR (film): ν (cm^{-1}) 3414, 2919, 1620, 1499, 1452, 1323, 1253, 1167, 1043, 995, 945, 814, 726, 697. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_2$+Na^+]: 263.1043, found 263.1039.

4-Methoxy-2-(phenyl(vinyloxy)methyl)phenol (1p)



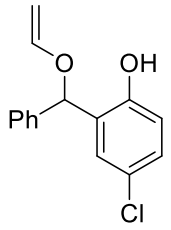
Pale yellow oil, 36% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 6.83 – 6.73 (m, 2H), 6.70 – 6.64 (m, 1H), 6.48 (dd, *J* = 14.1, 6.6 Hz, 1H), 6.11 (s, 1H), 6.00 (s, 1H), 4.51 (dd, *J* = 14.1, 2.1 Hz, 1H), 4.19 (dd, *J* = 6.6, 2.1 Hz, 1H), 3.73 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.3, 149.6, 148.0, 139.1, 128.6, 128.2, 127.0, 126.2, 117.7, 114.4, 113.9, 91.7, 81.8, 55.7. IR (film): ν (cm^{-1}) 3399, 3031, 1637, 1620, 1499, 1451, 1430, 1322, 1268, 1232, 1167, 1035, 997, 944, 816, 757, 732, 697. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_3$+Na^+]: 279.0992, found 279.0985.

4-Fluoro-2-(phenyl(vinyloxy)methyl)phenol (1q)



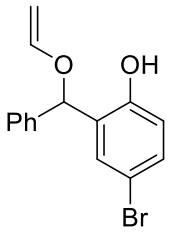
Pale yellow oil, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 6.90 – 6.79 (m, 2H), 6.79 – 6.73 (m, 1H), 6.47 – 6.25 (m, 2H), 5.99 (s, 1H), 4.48 (dd, *J* = 14.1, 2.2 Hz, 1H), 4.18 (dd, *J* = 6.6, 2.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.7 (d, *J* = 237.0 Hz), 150.0 (d, *J* = 2.1 Hz), 149.4, 138.7, 128.7, 128.4, 126.9, 126.8, 117.8 (d, *J* = 7.9 Hz), 115.7 (d, *J* = 22.9 Hz), 114.7 (d, *J* = 24.0 Hz), 91.9, 80.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –123.43. IR (film): ν (cm^{-1}) 3425, 3033,1639, 1623, 1494, 1437, 1322, 1261, 1230, 1163, 1046, 1001, 947, 816, 767, 732, 697. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}FO_2$+Na^+]: 267.0792, found 267.0789.

4-Chloro-2-(phenyl(vinyloxy)methyl)phenol (1r)



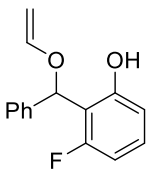
Pale yellow oil, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 7.14 – 7.06 (m, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.61 (s, 1H), 6.41 (dd, *J* = 14.1, 6.6 Hz, 1H), 5.96 (s, 1H), 4.48 (dd, *J* = 14.1, 2.3 Hz, 1H), 4.18 (dd, *J* = 6.6, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.7, 149.3, 138.6, 129.2, 128.7, 128.4, 128.0, 127.1, 126.8, 125.2, 118.3, 92.1, 81.1. IR (film): ν (cm^{-1}) 3424, 3032, 1639, 1621, 1486, 1418, 1320, 1269, 1234, 1164, 1110, 1047, 999, 886, 817, 744, 698, 649. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{35}ClO_2$+Na^+]: 283.0496, found 283.0487; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{37}ClO_2$+Na^+]: 285.0467, found 285.0460.

4-Bromo-2-(phenyl(vinyloxy)methyl)phenol (1s)



Colorless oil, 29% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 7.28 – 7.24 (m, 1H), 7.24 – 7.21 (m, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 6.64 (s, 1H), 6.42 (dd, *J* = 14.0, 6.6 Hz, 1H), 5.96 (s, 1H), 4.49 (dd, *J* = 14.0, 2.3 Hz, 1H), 4.19 (dd, *J* = 6.6, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.2, 149.2, 138.6, 132.2, 130.9, 128.7, 128.4, 127.5, 126.8, 118.8, 112.4, 92.2, 81.2. IR (film): ν (cm^{-1}) 3419, 3031, 1638, 1620, 1480, 1414, 1397, 1319, 1269, 1234, 1162, 1103, 1045, 999, 936, 814, 752, 696, 623. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{79}BrO_2$+Na^+]: 326.9991, found 326.9985; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{81}BrO_2$+Na^+]: 328.9971, found 328.9974.

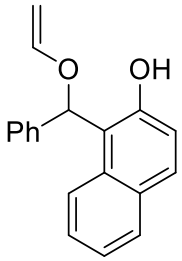
3-Fluoro-2-(phenyl(vinylox)methyl)phenol (1t)



Pale yellow oil, 44% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 3H), 7.35 – 7.23 (m, 3H), 7.17 – 7.08 (m, 1H), 6.73 – 6.66 (m, 1H), 6.66 – 6.57 (m, 1H), 6.46 (dd, *J* = 14.0, 6.6 Hz, 1H), 6.36 (s, 1H), 4.57 (dd, *J* =

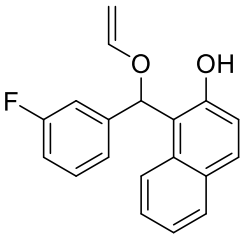
14.0, 2.5 Hz, 1H), 4.24 (dd, *J* = 6.6, 2.5 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1 (d, *J* = 243.2 Hz), 156.2 (d, *J* = 5.0 Hz), 149.0, 138.3, 130.0 (d, *J* = 10.8 Hz), 128.7, 128.4, 126.4, 113.3(d, *J* = 2.9 Hz), 113.0 (d, *J* = 16.0 Hz), 106.8 (d, *J* = 22.2 Hz), 92.3. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ –118.11. IR (film): ν (cm^{-1}) 3427, 3033, 1624, 1588, 1471, 1342, 1263, 1217, 1155, 1022, 940, 834, 781, 755, 697. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}FO_2$+Na^+]: 267.0792, found 267.0793.

1-(Phenyl(vinyloxy)methyl)naphthalen-2-ol (1u)



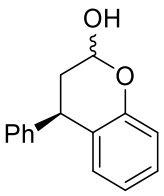
Yellow oil, 47% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.80 – 7.69 (m, 3H), 7.44 – 7.32 (m, 3H), 7.32 – 7.20 (m, 4H), 7.18 – 7.13 (m, 1H), 6.78 (s, 1H), 6.51 (dd, *J* = 14.0, 6.6 Hz, 1H), 4.52 (dd, *J* = 14.0, 2.4 Hz, 1H), 4.16 (dd, *J* = 6.6, 2.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.6, 149.3, 138.2, 131.8, 130.6, 128.9, 128.8, 128.6, 128.5, 127.3, 127.1, 123.2, 121.2, 119.5, 114.4, 92.2, 80.1. IR (film): ν (cm^{-1}) 3414, 3061, 1624, 1517, 1467, 1401, 1315, 1264, 1220, 1159, 1063, 1030, 816, 746, 701. HRMS (FTMS+c ESI) calcd for [$C_{19}H_{16}O_2$+Na^+]: 299.1043, found 299.1046.

1-((3-Fluorophenyl)(vinyloxy)methyl)naphthalen-2-ol (1v)

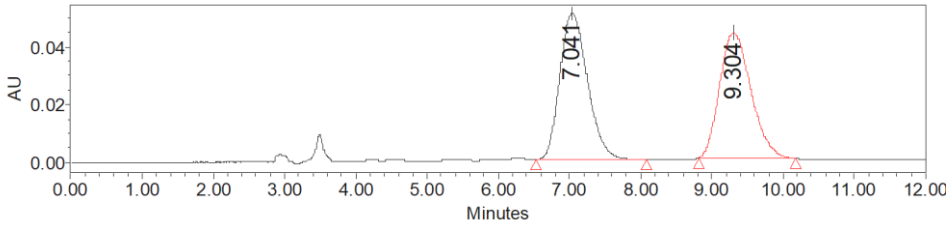


Yellow oil, 39% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.69 (m, 3H), 7.62 (s, 1H), 7.47 – 7.36 (m, 1H), 7.34 – 7.27 (m, 1H), 7.24 – 7.07 (m, 4H), 6.99 – 6.88 (m, 1H), 6.77 (s, 1H), 6.49 (dd, *J* = 14.0, 6.6 Hz, 1H), 4.52 (dd, *J* = 14.0, 2.4 Hz, 1H), 4.17 (dd, *J* = 6.6, 2.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 244.9 Hz), 153.5, 149.2, 141.1 (d, *J* = 6.9 Hz), 131.8, 130.9, 130.1 (d, *J* = 8.2 Hz), 129.0, 128.9, 127.3, 123.4, 122.7 (d, *J* = 2.9 Hz), 121.2, 119.4, 115.3 (d, *J* = 21.0 Hz), 114.3 (d, *J* = 4.8 Hz), 114.1, 92.3, 78.7. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ –112.18. IR (film): ν (cm^{-1}) 3423, 3066, 1621, 1593, 1517, 1486, 1443, 1264, 1220, 1163, 1065, 944, 819, 784, 747, 685. HRMS (FTMS+c ESI) calcd for [$C_{19}H_{15}FO_2$+Na^+]: 317.0948, found 317.0957.

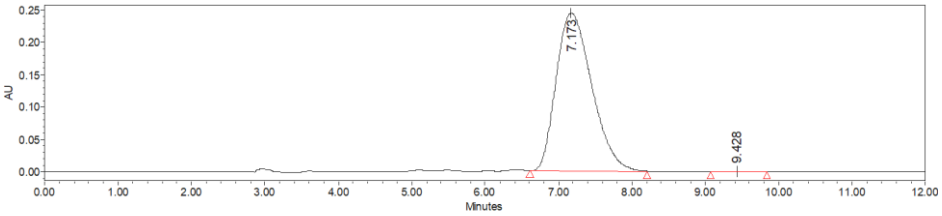
(4*R*)-4-phenylchroman-2-ol (2a)



2 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 42.0 mg, 93% yield, 3.5:1 d.r., 99% ee; $[\alpha]^{20}$ = –165.9 (*c* = 0.79 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(major)}$ = 7.17 min, $t_{R(minor)}$ = 9.43 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.06 (m, 6H), 6.94 – 6.63 (m, 3H), 5.74 – 5.59 (m, 1H), 4.33 (dd, *J* = 11.0, 5.8 Hz, 1H), 3.34 (dd, *J* = 3.8, 1.5 Hz, 1H), 2.36 – 2.2 (m, 1H), 2.20 – 2.09 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.8, 144.2, 129.6, 128.8, 128.6, 127.9, 126.7, 125.4, 121.0, 116.8, 91.3, 36.8, 36.01. IR (film): ν (cm^{-1}) 3420, 1582, 1488, 1452, 1272, 1224, 1092, 1054, 1015, 895, 754, 701. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{14}O_2$+Na^+]: 249.0886, found 249.0892.

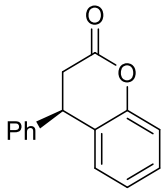


	Retention Time	Area	% Area
1	7.041	1373650	50.62
2	9.304	1340238	49.38

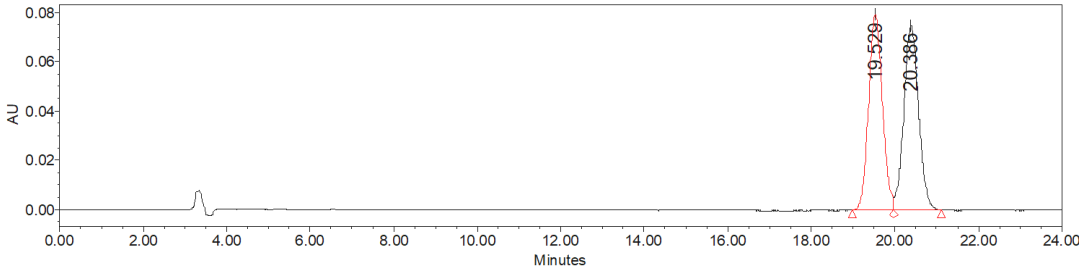


	Retention Time	Area	% Area
1	7.173	8211221	99.78
2	9.428	17706	0.22

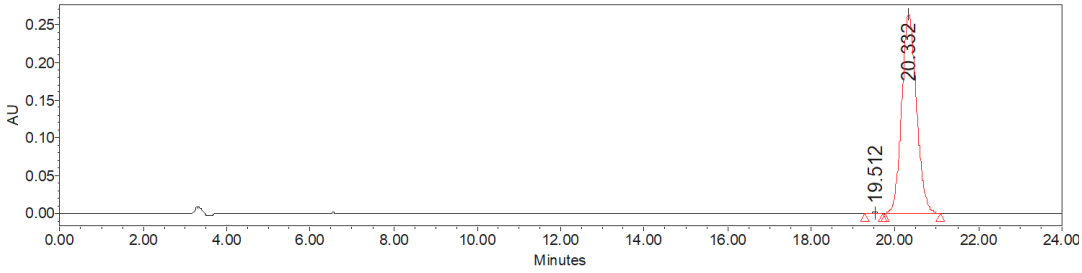
(*R*)-4-phenylchroman-2-one (3a)



White solid, Mp: 109–113 °C, 37.4 mg, 83% yield over two steps, 99% ee; $[\alpha]^{20}$ = –106.7 (*c* = 0.73 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 19.51 min, $t_{R(major)}$ = 20.33 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 4H), 7.21 – 7.01 (m, 4H), 7.01 – 6.93 (m, 1H), 4.34 (t, *J* = 6.9 Hz, 1H), 3.11 – 2.97 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.6, 151.7, 140.2, 129.1, 128.8, 128.3, 127.6, 127.5, 125.7, 124.6, 117.1, 40.6, 37.0. IR (film): ν (cm^{-1}) 1769, 1488, 1454, 1275, 1218, 1177, 1136, 920, 756, 700. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{12}O_2$+Na^+]: 247.0730, found 247.0737.

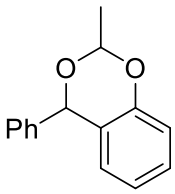


	Retention Time	Area	% Area
1	19.529	1833455	49.79
2	20.386	1849124	50.21



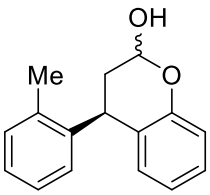
	Retention Time	Area	% Area
1	19.512	11076	0.17
2	20.332	6433799	99.83

2-methyl-4-phenyl-4H-benzo[d][1,3]dioxine (2a')



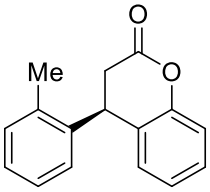
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 5H), 7.19 – 7.13 (m, 1H), 6.93 – 6.86 (m, 1H), 6.85 – 6.76 (m, 1H), 6.68 – 6.58 (m, 1H), 5.98 (s, 1H), 5.47 (q, *J* = 5.1 Hz, 1H), 1.61 (d, *J* = 5.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.1, 140.3, 128.7, 128.6, 128.6, 128.3, 127.0, 124.7, 121.0, 116.5, 97.2, 79.7, 20.9. IR (film): ν (cm^{-1}) 1585, 1485, 1459, 1406, 1352, 1238, 1123, 1094, 931, 915, 752, 698. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{14}O_2$+H^+]: 227.1067, found 227.1062.

(4*R*)-4-(o-tolyl)chroman-2-ol (2b)

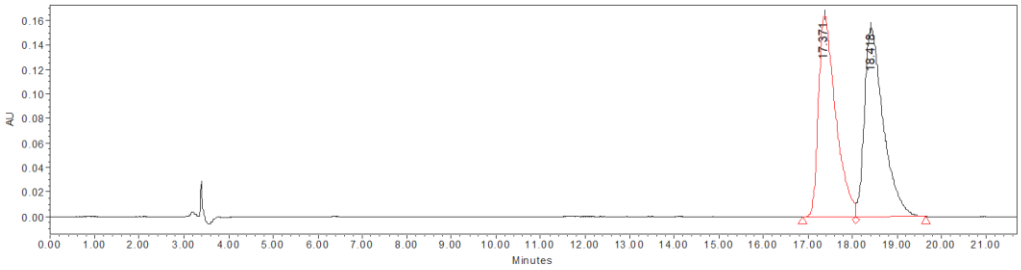


3 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 33.5 mg, 70% yield, 3.7:1 d.r.; $[\alpha]^{25}$ = –132.7 (*c* = 0.54 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.07 (m, 4H), 7.05 – 6.94 (m, 1H), 6.93 – 6.85 (m, 1H), 6. 85 – 6.76 (m, 1H), 6.76 – 6.63 (m, 1H), 5.83 – 5.62 (m, 1H), 4.60 (dd, *J* = 10.7, 5.9 Hz, 1H), 3.41 – 3.17 (m, 1H), 2.40 (s, 3H), 2.30 – 2.00 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.1, 142.2, 136.4, 130.5, 129.3, 128.7, 127.7, 126.5, 126.4, 125.5, 121.1, 116.9, 91.5, 34.6, 32.8, 19.6. IR (film): ν (cm^{-1}) 3411, 2931, 1582, 1487, 1453, 1274, 1215, 1114, 1054, 1015, 939, 898, 754. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_2$+Na$^+$]: 263.1043, found 263.1039.

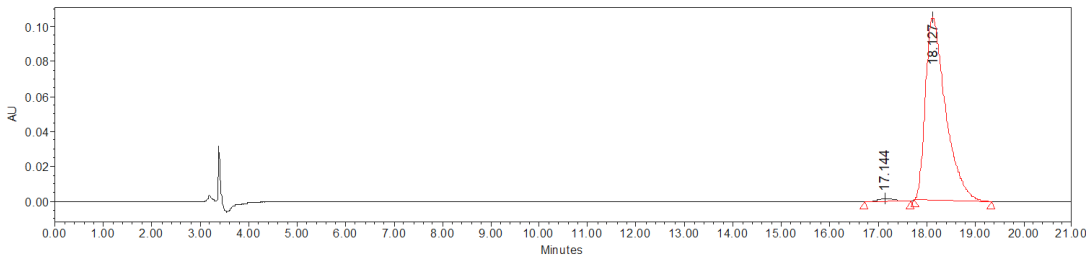
(*R*)-4-(o-tolyl)chroman-2-one (3b)



Colorless oil, 29.0 mg, 61% yield over two steps, 97% ee; $[\alpha]^{27}$ = –161.9 (*c* = 0.40 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 17.14 min, $t_{R(major)}$ = 18.13 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.11 (m, 5H), 7.10 – 7.01 (m, 1H), 6.95 – 6.87 (m, 1H), 6.87 – 6.80 (m, 1H), 4.59 (dd, *J* = 8.9, 6.0 Hz, 1H), 3.13 – 2.80 (m, 2H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.8, 152.0, 138.0, 135.9, 131.0, 128.7, 128.0, 127.5, 126.9, 126.8, 125.9, 124.7, 117.0, 36.5, 35.9, 19.5. IR (film): ν (cm^{-1}) 2922, 1770, 1609, 1587, 1487, 1454, 1279, 1215, 1175, 1143, 918, 755. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{14}O_2$+Na$^+$]: 261.0886, found 261.0882.

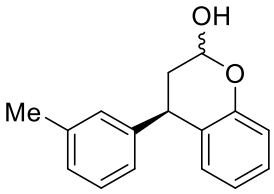


	Retention Time	Area	% Area
1	17.371	4394668	49.21
2	18.418	4535932	50.79



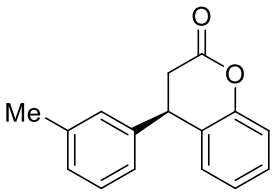
	Retention Time	Area	% Area
1	17.144	40703	1.33
2	18.127	3022177	98.67

(4*R*)-4-(*m*-tolyl)chroman-2-ol (2c)

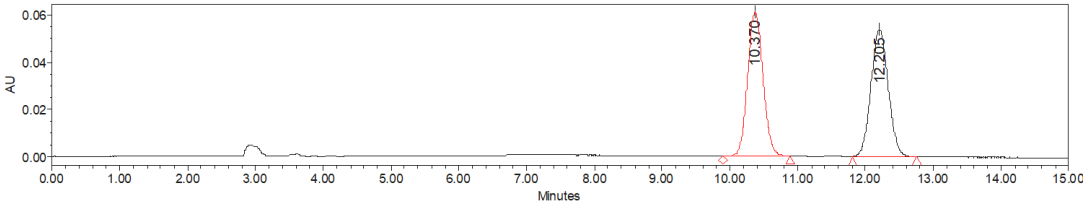


3 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 40.6 mg, 85% yield, 3.7:1 d.r.; $[\alpha]^{20}$ = –163.2 (*c* = 0.79 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 1H), 7.16 – 6.93 (m, 4H), 6.93 – 6.66 (m, 3H), 5.72 – 5.59 (m, 1H), 4.29 (dd, *J* = 11.0, 5.8 Hz, 1H), 3.39 – 3.24 (m, 1H), 2.32 (s, 3H), 2.29 – 2.23 (m, 1H), 2.21 – 2.10 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.8, 144.1, 138.2, 129.7, 129.5, 128.5, 127.8, 127.5, 125.9, 125.5, 121.0, 116.8, 91.4, 36.7, 36.1, 21.4. IR (film): ν (cm^{-1}) 3420, 2934, 1607, 1582, 1486, 1452, 1272, 1223, 1092, 1057, 1016, 913, 755. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_2$+Na$^+$]: 263.1043, found 263.1047.

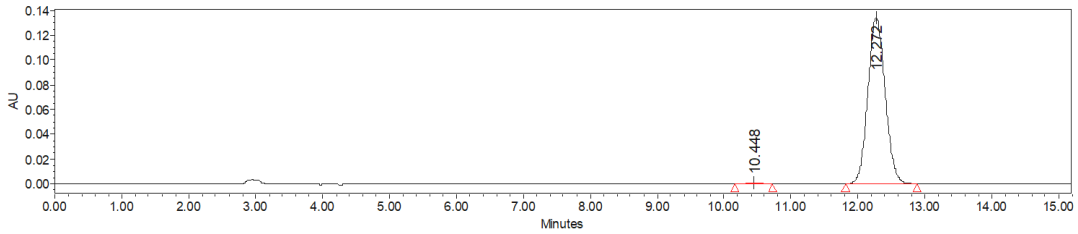
(*R*)-4-(*m*-tolyl)chroman-2-one (3c)



Colorless oil, 38.9 mg, 82% yield over two steps, 99% ee; $[\alpha]^{20}$ = –107.4 (*c* = 0.69 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 10.44 min, $t_{R(major)}$ = 12.27 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 2H), 7.17 – 7.02 (m, 3H), 7.01 – 6.88 (m, 3H), 4.30 (t, *J* = 7.0 Hz, 1H), 3.13 – 2.92 (m, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.7, 151.7, 140.2, 138.8, 129.0, 128.7, 128.4, 128.3, 128.2, 125.9, 124.6, 124.6, 117.0, 40.6, 37.0, 21.4. IR (film): ν (cm^{-1}) 2918, 1771, 1608, 1586, 1486, 1454, 1278, 1216, 1165, 1133, 920, 757, 702. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{14}O_2$+Na$^+$]: 261.0886, found 261.0882.

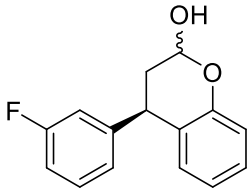


	Retention Time	Area	% Area
1	10.370	959664	50.01
2	12.205	959291	49.99



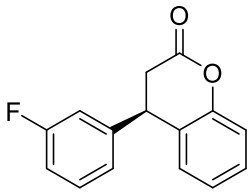
	Retention Time	Area	% Area
1	10.448	15141	0.63
2	12.272	2405694	99.37

(4*R*)-4-(3-fluorophenyl)chroman-2-ol (2d)

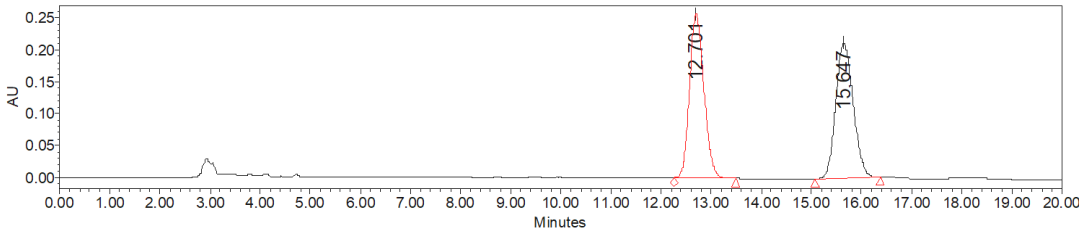


8 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 43.9 mg, 90% yield, 4:1 d.r.; $[\alpha]^{18}$ = –145.6 (*c* = 0.86 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 1H), 7.19 – 7.07 (m, 1H), 7.05 – 6.69 (m, 6H), 5.74 – 5.60 (m, 1H), 4.34 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.42 (dd, *J* = 3.6, 1.5 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.19 – 2.03 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 244.4 Hz), 151.7, 146.9 (d, *J* = 6.9 Hz), 130.1 (d, *J* = 8.2 Hz), 129.5, 128.1, 124.7, 124.5 (d, *J* = 2.6 Hz), 121.1, 117.0, 115.6 (d, *J* = 21.2 Hz), 113.7 (d, *J* = 21.0 Hz), 91.2, 36.6 (d, *J* = 1.3 Hz), 35.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –112.85. IR (film): ν (cm^{-1}) 3417, 1586, 1486, 1450, 1270, 1223, 1138, 1056, 1017, 894, 756. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}FO_2$+Na$^+$]: 267.0792, found 267.0792.

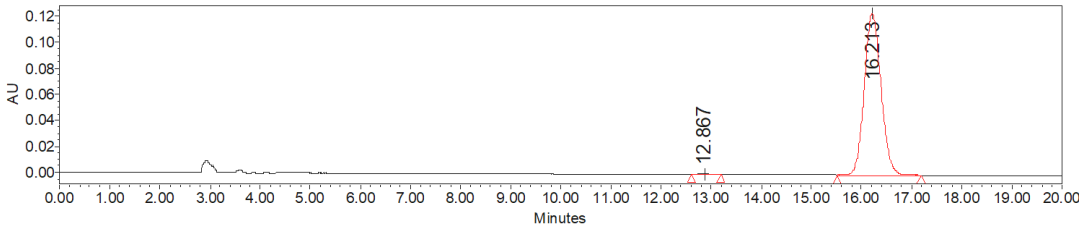
(*R*)-4-(3-fluorophenyl)chroman-2-one (3d)



Colorless oil, 40.8 mg, 84% yield over two steps, 99% ee; $[\alpha]^{19}$ = –61.8 (*c* = 0.80 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 12.87 min, $t_{R(major)}$ = 16.21 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 2H), 7.21 – 7.06 (m, 2H), 7.06 – 6.88 (m, 3H), 6.87 – 6.78 (m, 1H), 4.35 (t, *J* = 6.7 Hz, 1H), 3.16 – 2.91 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 163.1 (d, *J* = 245.7 Hz), 151.6, 142.8 (d, *J* = 6.7 Hz), 130.7 (d, *J* = 8.2 Hz), 129.1, 128.2, 124.9, 124.8, 123.2 (d, *J* = 2.8 Hz), 117.3, 114.7 (d, *J* = 7.0 Hz), 114.5 (d, *J* = 7.8 Hz), 40.4 (d, *J* = 1.7 Hz), 36.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –111.73. IR (film): ν (cm^{-1}) 1771, 1588, 1486, 1453, 1345, 1265, 1218, 1157, 919, 756. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}FO_2$+Na$^+$]: 265.0635, found 265.0638.

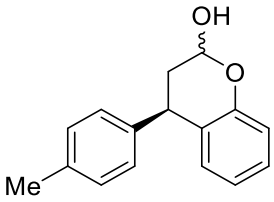


	Retention Time	Area	% Area
1	12.701	5164648	50.43
2	15.647	5076797	49.57



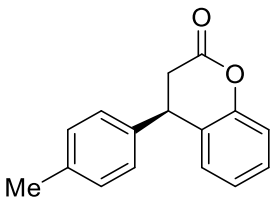
	Retention Time	Area	% Area
1	12.867	12026	0.42
2	16.213	2879313	99.58

(4*R*)-4-(*p*-tolyl)chroman-2-ol (2e)



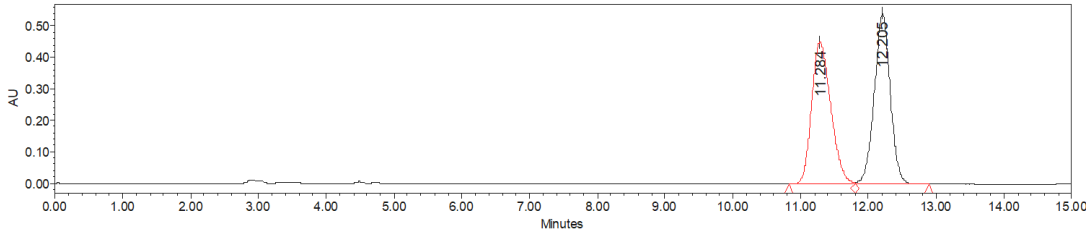
3 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 36.7 mg, 76% yield, 3.5:1 d.r.; $[\alpha]^{23}$ = –168.2 (*c* = 0.74 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.01 (m, 5H), 6.95 – 6.72 (m, 3H), 5.79 – 5.62 (m, 1H), 4.32 (dd, *J* = 11.0, 5.8 Hz, 1H), 3.43 – 3.18 (m, 1H), 2.37 (s, 3H), 2.32 – 2.23 (m, 1H), 2.22 – 2.11 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.8, 141.2, 136.3, 129.6, 129.3, 128.7, 127.8, 125.6, 121.0, 116.8, 91.4, 36.4, 36.1, 21.0. IR (film): ν (cm^{-1}) 3418, 2927, 1582, 1512, 1486, 1451, 1303, 1224, 1112, 1056, 1016, 938, 898, 815, 756. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_2$+Na^+]: 263.1043, found 263.1046.

(*R*)-4-(*p*-tolyl)chroman-2-one (3e)

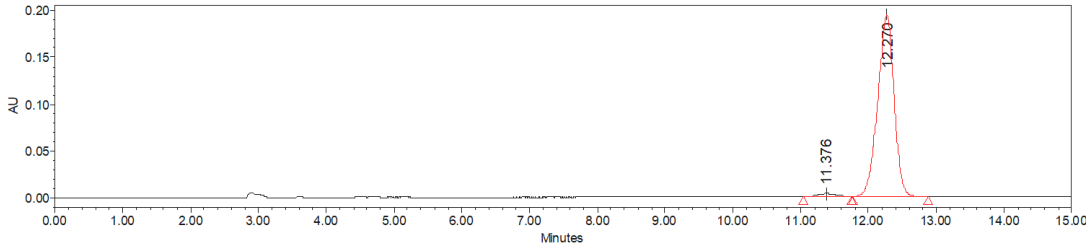


White solid, Mp: 107–111 °C, 30.9 mg, 65% yield over two steps, 96% ee; $[\alpha]^{19}$ = –96.6 (*c* = 0.39 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 11.38 min, $t_{R(major)}$

= 12.27 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.22 – 7.01 (m, 6H), 7.01 – 6.96 (m, 1H), 4.31 (t, *J* = 7.1 Hz, 1H), 3.14 – 2.87 (m, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.7, 151.7, 137.3, 137.2, 129.8, 128.7, 128.3, 127.4, 126.0, 124.6, 117.0, 40.3, 37.0, 21.0. IR (film): ν (cm^{-1}) 2921, 1769, 1513, 1486, 1454, 1279, 1218, 1177, 1136, 917, 882, 820, 759. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{14}O_2$+Na^+]: 261.0886, found 261.0881.

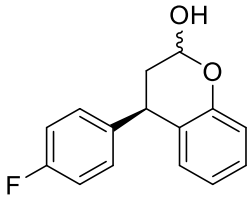


	Retention Time	Area	% Area
1	11.284	8920712	50.00
2	12.205	8919696	50.00



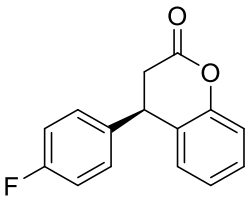
	Retention Time	Area	% Area
1	11.376	61749	1.86
2	12.270	3260516	98.14

(4*R*)-4-(4-fluorophenyl)chroman-2-ol (2f)

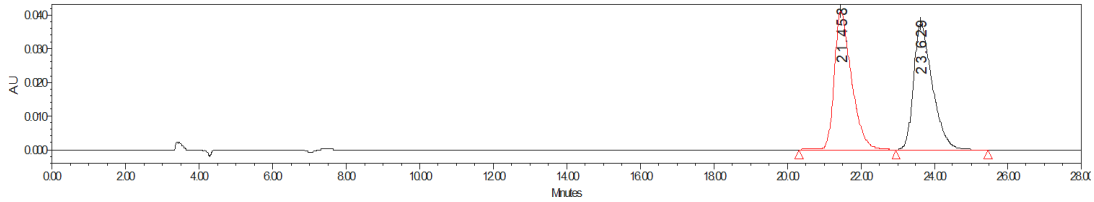


2 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 46.1 mg, 94% yield, 4:1 d.r.; $[\alpha]^{21}$ = –117.5 (*c* = 0.90 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.11 (m, 3H), 7.08 – 6.97 (m, 2H), 6.93 – 6.79 (m, 2H), 6.79 – 6.68 (m, 1H), 5.72 – 5.62 (m, 1H), 4.34 (dd, *J* = 11.3, 5.7 Hz, 1H), 3.48 (dd, *J* = 3.7, 1.7 Hz, 1H), 2.36 – 2.20 (m, 1H), 2.18 – 2.06 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7 (d, *J* = 243.4 Hz), 151.7, 139.8 (d, *J* = 3.2 Hz), 130.2 (d, *J* = 7.8 Hz), 129.4, 128.0, 125.2, 121.1, 116.9, 115.4 (d, *J* = 21.1 Hz), 91.2 (d, *J* = 2.5 Hz), 36.2, 36.0. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –116.17. IR (film): ν (cm^{-1}) 3423, 1605, 1509, 1487, 1452, 1271, 1225, 1092, 1056, 1016, 899, 834, 756. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}FO_2$+Na^+]: 267.0792, found 267.0787.

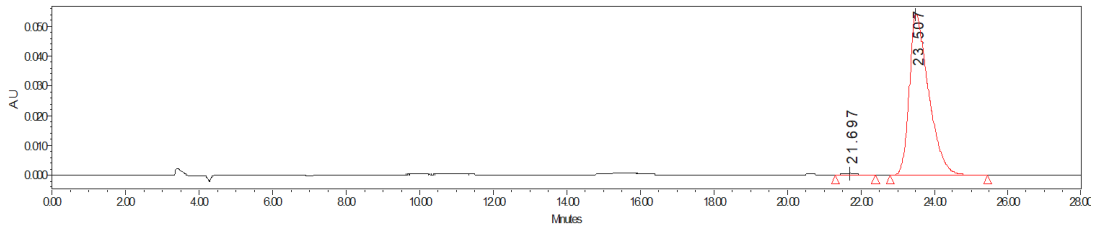
(*R*)-4-(4-fluorophenyl)chroman-2-one (3f)



Colorless oil, 39.7 mg, 82% yield over two steps, 98% ee; $[\alpha]^{22}$ = –70.3 (*c* = 0.64 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel OJH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm) $t_{R(minor)}$ = 21.70 min, $t_{R(major)}$ = 23.51 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 1H), 7.22 – 6.88 (m, 7H), 4.34 (t, *J* = 6.8 Hz, 1H), 3.16 – 2.86 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 162.1 (d, *J* = 245.1 Hz), 151.6, 136.0 (d, *J* = 3.2 Hz), 129.1 (d, *J* = 8.1 Hz), 128.9, 128.2, 125.5, 124.7, 117.2, 116.0 (d, *J* = 21.4 Hz), 40.0, 37.1. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –114.60. IR (film): ν (cm^{-1}) 1769, 1606, 1509, 1487, 1454, 1278, 1222, 1136, 918, 884, 837, 759. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}FO_2$+Na^+]: 265.0635, found 265.0633.

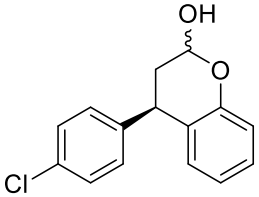


	Retention Time	Area	% Area
1	21.458	1333235	50.12
2	23.629	1326662	49.88



	Retention Time	Area	% Area
1	21.697	15721	0.79
2	23.507	1979129	99.21

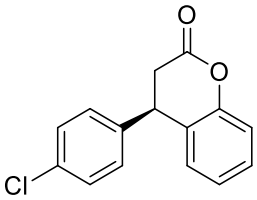
(4*R*)-4-(4-chlorophenyl)chroman-2-ol (2g)



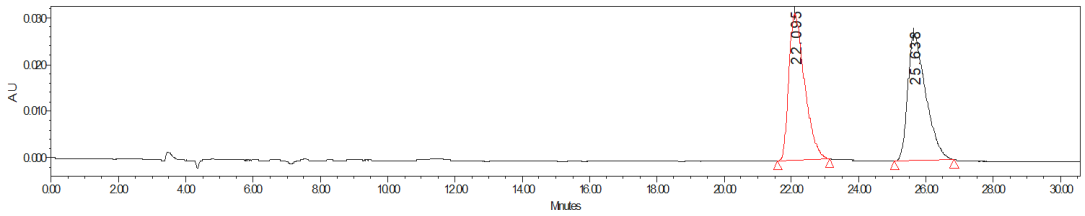
2 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 49.0 mg, 94% yield, 4:1 d.r.; $[\alpha]^{23}$ = –158.3 (*c* = 0.97 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 2H), 7.22 – 7.06 (m, 3H), 6.93 – 6.77 (m, 2H), 6.77 – 6.63 (m, 1H), 5.75 – 5.60 (m, 1H), 4.31 (dd, *J* = 11.3, 5.7 Hz, 1H), 3.49 (dd, *J* = 3.4, 1.4 Hz,

1H), 2.34 – 2.20 (m, 1H), 2.15 – 2.03 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 151.7, 142.7, 132.5, 130.1, 129.4, 128.8, 128.1, 124.9, 121.1, 117.0, 91.2, 36.2, 36.0. IR (film): ν (cm^{-1}) 3423, 1582, 1488, 1451, 1302, 1273, 1225, 1090, 1056, 1015, 939, 899, 826, 754. HRMS (FTMS+c ESI) calcd for $[C_{15}H_{13}{}^{35}ClO_2+Na^+]$: 283.0496, found 283.0490; HRMS (FTMS+c ESI) calcd for $[C_{15}H_{13}{}^{37}ClO_2+Na^+]$: 285.0467, found 285.0460.

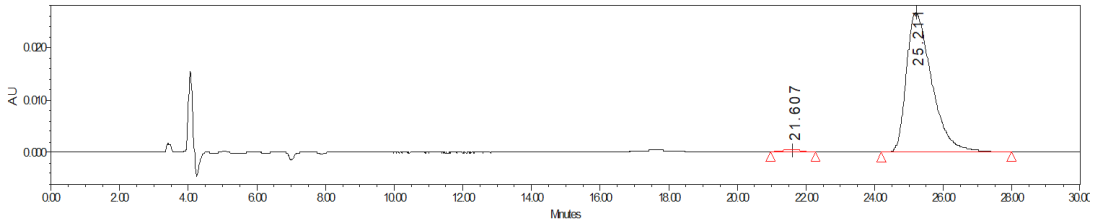
(*R*)-4-(4-chlorophenyl)chroman-2-one (3g)



White solid, Mp: 138–141 °C, 41.6 mg, 81% yield over two steps, 97% ee; $[\alpha]^{22}$ = –87.0 (*c* = 0.69 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel OJH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm) $t_{R(minor)}$ = 21.61 min, $t_{R(major)}$ = 25.21 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 3H), 7.17 – 7.05 (m, 4H), 7.02 – 6.93 (m, 1H), 4.33 (t, *J* = 6.8 Hz, 1H), 3.13 – 2.93 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 167.2, 151.6, 138.8, 133.5, 129.3, 129.0, 128.9, 128.2, 125.2, 124.7, 117.2, 40.1, 36.9. IR (film): ν (cm^{-1}) 1768, 1586, 1489, 1454, 1411, 1280, 1219, 1176, 1134, 1092, 914, 882, 830, 756. HRMS (FTMS+c ESI) calcd for $[C_{15}H_{11}{}^{35}ClO_2+Na^+]$: 281.0340, found 281.0342; HRMS (FTMS+c ESI) calcd for $[C_{15}H_{11}{}^{37}ClO_2+Na^+]$: 283.0310, found 283.0311.

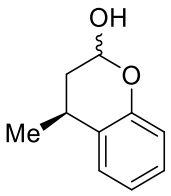


	Retention Time	Area	% Area
1	22.095	1015889	50.08
2	25.638	1012559	49.92



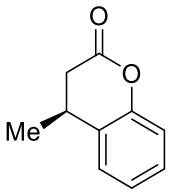
	Retention Time	Area	% Area
1	21.607	18162	1.31
2	25.211	1373331	98.69

(4*S*)-4-methylchroman-2-ol (2h)

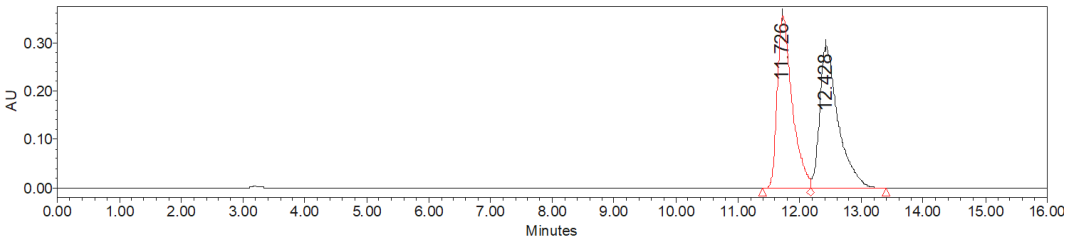


2 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 27.7 mg, 84% yield, 2.6:1 d.r.; $[\alpha]^{21}$ = –79.0 (*c* = 0.48 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 1H), 7.17 – 7.08 (m, 1H), 6.97 – 6.89 (m, 1H), 6.87 – 6.78 (m, 1H), 5.65 – 5.58 (m, 1H), 3.46 – 3.35 (m, 1H), 3.24 – 3.09 (m, 1H), 2.13 – 2.01 (m, 1H), 1.77 – 1.65 (m, 1H), 1.37 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.3, 127.4, 127.3, 127.2, 121.0, 116.8, 91.4, 35.5, 24.2, 20.4. IR (film): ν (cm^{-1}) 3413, 2960, 1581, 1488, 1450, 1219, 1131, 1099, 1039, 978, 893, 754. HRMS (FTMS+c ESI) calcd for [$C_{10}H_{12}O_2$+Na$^+$]: 187.0730, found 187.0731.

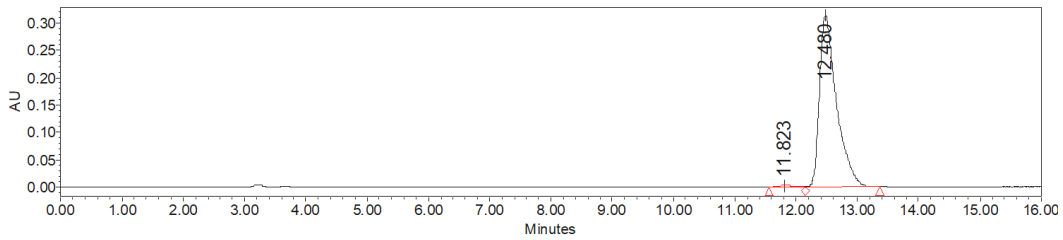
(*S*)-4-methylchroman-2-one (3h)



Colorless oil, 21.8 mg, 67% yield over two steps, 98% ee; $[\alpha]^{21}$ = –63.1 (*c* = 0.21, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 11.82 min, $t_{R(major)}$ = 12.48 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 7.09 – 7.02 (m, 1H), 7.01 – 6.95 (m, 1H), 3.18 – 3.04 (m, 1H), 2.78 (dd, *J* = 15.8, 5.5 Hz, 1H), 2.52 (dd, *J* = 15.8, 7.2 Hz, 1H), 1.27 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.3, 151.2, 128.3, 127.8, 126.5, 124.6, 117.0, 36.8, 29.5, 19.9. IR (film): ν (cm^{-1}) 2965, 1769, 1612, 1487, 1454, 1347, 1286, 1218, 1151, 1079, 909, 831, 760. HRMS (FTMS+c ESI) calcd for [$C_{10}H_{10}O_2$+Na$^+$]: 185.0573, found 185.0573.



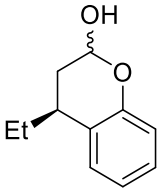
	Retention Time	Area	% Area
1	11.726	6011927	49.49
2	12.428	6134833	50.51



	Retention Time	Area	% Area

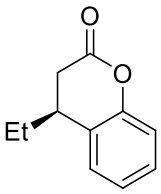
1	11.823	47223	0.78
2	12.480	6031330	99.22

(4*S*)-4-ethylchroman-2-ol (2i)

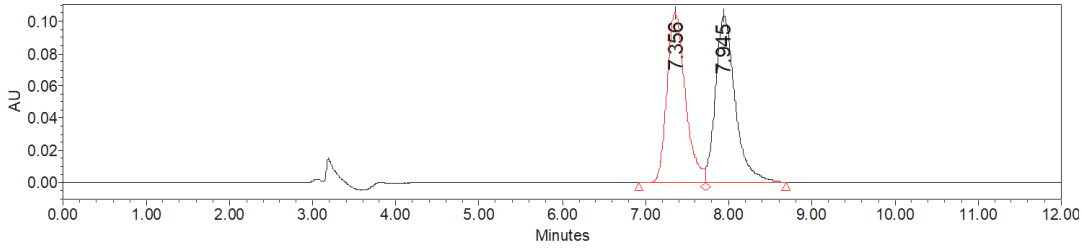


5 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 5 mol% catalyst loading); colorless oil, 32.1 mg, 90% yield, 2.7:1 d.r.; $[\alpha]^{23}$ = –57.8 (*c* = 0.61 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 1H), 7.16 – 7.05 (m, 1H), 6.97 – 6.87 (m, 1H), 6.87 – 6.73 (m, 1H), 5.70 – 5.55 (m, 1H), 3.39 (d, *J* = 4.7 Hz, 1H), 3.05 – 2.90 (m, 1H), 2.11 – 1.91 (m, 2H), 1.91 – 1.77 (m, 1H), 1.73 – 1.54 (m, 1H), 1.06 – 0.94 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.8, 127.6, 127.4, 126.0, 120.9, 116.9, 91.6, 32.0, 31.4, 27.3, 10.9. IR (film): ν (cm^{-1}) 3417, 2963, 1580, 1487, 1453, 1270, 1219, 1132, 1008, 901, 754. HRMS (FTMS+c ESI) calcd for [$C_{11}H_{14}O_2$+Na$^+$]: 201.0886, found 201.0883.

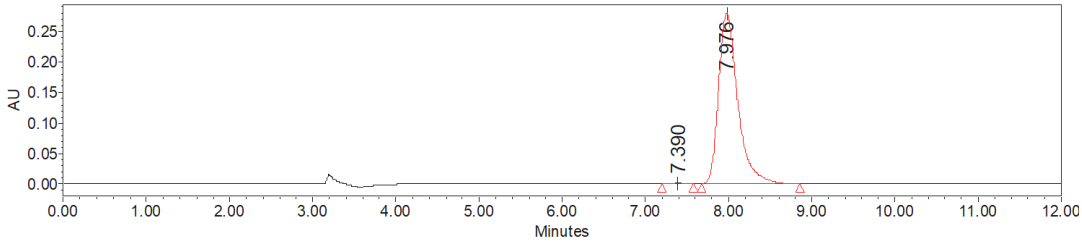
(*S*)-4-ethylchroman-2-one (3i)



Colorless oil, 28.7 mg, 82% yield over two steps, 99% ee; $[\alpha]^{21}$ = –93.0 (*c* = 0.53, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 7.39 min, $t_{R(major)}$ = 7.98 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 1H), 7.21 – 7.16 (m, 1H), 7.15 – 7.08 (m, 1H), 7. 08 – 7.01 (m, 1H), 2. 96 – 2.87 (m, 1H), 2. 87 – 2.80 (m, 1H), 2.80 – 2.72 (m, 1H), 1.72 – 1.55 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.5, 151.3, 128.2, 127.9, 126.5, 124.2, 117.0, 36.6, 34.4, 27.5, 11.1. IR (film): ν (cm^{-1}) 2967, 1769, 1613, 1486, 1456, 1267, 1217, 1151, 1116, 1091, 911, 757. HRMS (FTMS+c ESI) calcd for [$C_{11}H_{12}O_2$+Na$^+$]: 199.0730, found 199.0728.

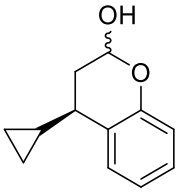


	Retention Time	Area	% Area
1	7.356	1619030	49.01
2	7.945	1684157	50.99



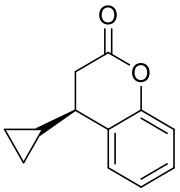
	Retention Time	Area	% Area
1	7.390	16264	0.36
2	7.976	4482590	99.64

(4*R*)-4-cyclopropylchroman-2-ol (2j)

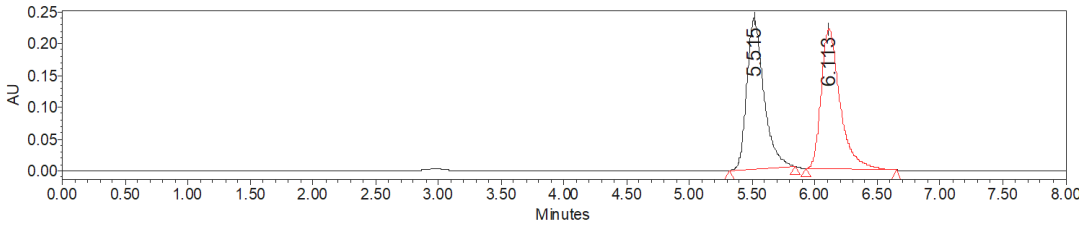


5 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 5 mol% catalyst loading); colorless oil, 29.3 mg, 77% yield, 3.0:1 d.r.; $[\alpha]^{23}$ = –284.0 (*c* = 0.48 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.56 (m, 1H), 7.11 – 7.08 (m, 1H), 7.01 – 6.89 (m, 1H), 6.88 – 6.76 (m, 1H), 5.76 – 5.60 (m, 1H), 3.37 – 3.15 (m, 1H), 2.36 – 1.99 (m, 2H), 1.96 – 1.81 (m, 1H), 0.92 – 0.76 (m, 2H), 0.62 – 0.43 (m, 2H), 0.30 – 0.15 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.3, 127.7, 127.6, 126.2, 120.8, 116.6, 91.8, 34.6, 33.6, 15.9, 6.4, 1.9. IR (film): ν (cm^{-1}) 3422, 2999, 1580, 1486, 1453, 1270, 1219, 1108, 1018, 916, 883, 754. HRMS (FTMS+c ESI) calcd for [$C_{12}H_{14}O_2$+Na$^+$]: 213.0886, found 213.0884.

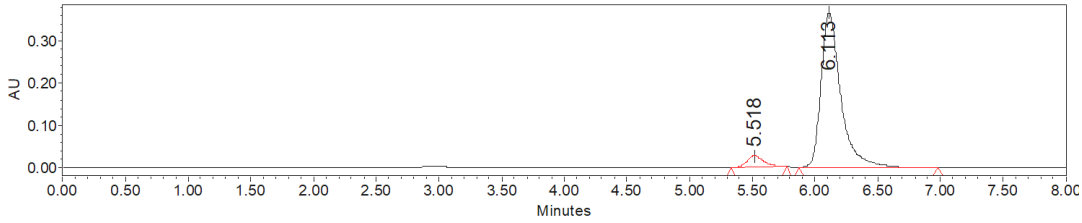
(*R*)-4-cyclopropylchroman-2-one (3j)



Colorless oil, 28.0 mg, 74% yield over two steps, 88% ee; $[\alpha]^{21}$ = –177.7 (*c* = 0.54, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 5.52 min, $t_{R(major)}$ = 6.11 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 1H), 7.09 – 7.03 (m, 1H), 6.98 – 6.88 (m, 1H), 6.87 – 6.81 (m, 1H), 2.72 – 2.64 (m, 1H), 2.59 – 2.51 (m, 1H), 2.18 (dd, *J* = 14.1, 7.2 Hz, 1H), 0.72 – 0.63 (m, 1H), 0.48 – 0.33 (m, 2H), 0.15 – 0.07 (m, 1H), 0.03 – 0.04 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.5, 151.4, 128.5, 127.5, 125.8, 124.4, 116.9, 39.2, 35.5, 15.0, 4.2, 2.7. IR (film): ν (cm^{-1}) 3000, 1769, 1612, 1586, 1485, 1455, 1274, 1216, 1154, 1023, 931, 874, 756. HRMS (FTMS+c ESI) calcd for [$C_{12}H_{12}O_2$+Na$^+$]: 211.0730, found 211.0727.

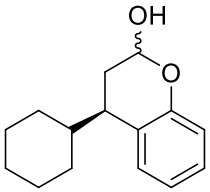


	Retention Time	Area	% Area
1	5.515	2262574	49.35
2	6.113	2322458	50.65



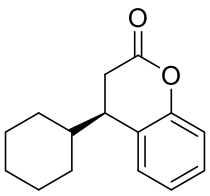
	Retention Time	Area	% Area
1	5.518	251309	5.96
2	6.113	3961834	94.04

(4*R*)-4-cyclohexylchroman-2-ol (2k)



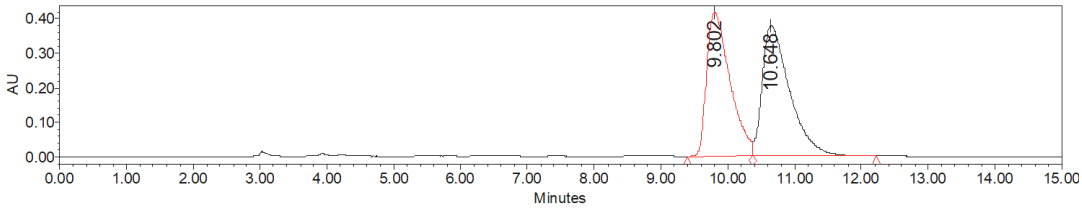
5 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 42.7 mg, 92% yield, 2.7:1 d.r.; $[\alpha]^{21}$ = –32.1 (*c* = 0.81 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.08 (m, 2H), 6.95 – 6.80 (m, 2H), 5.76 – 5.54 (m, 1H), 3.36 (d, *J* = 4.8 Hz, 1H), 2.92 – 2.84 (m, 1H), 2.16 – 1.53 (m, 8H), 1.43 – 1.07 (m, 4H), 0.97 – 0.84 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.2, 127.8, 127.2, 125.1, 120.7, 117.1, 92.0, 39.9, 35.5, 31.5, 28.7, 27.8, 26.9, 26.6, 26.6. IR (film): ν (cm^{-1}) 3409, 2924, 2851, 1581, 1487, 1450, 1220, 1187, 1125, 1051, 1013, 933, 899, 752. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{20}O_2$+Na$^+$]: 255.1356, found 255.1355.

(*R*)-4-cyclohexylchroman-2-one (3k)

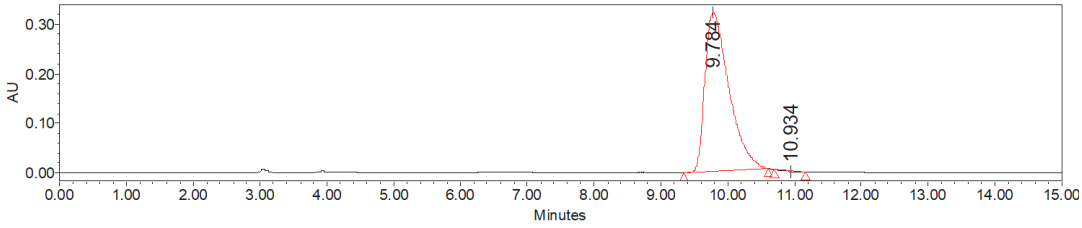


Colorless oil, 38.7 mg, 84% yield over two steps, 99% ee; $[\alpha]^{21}$ = –67.4 (*c* = 0.71, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 230 nm) $t_{R(major)}$ = 9.78 min, $t_{R(minor)}$ = 10.93 min; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.19 – 7.00 (m, 3H), 2.99 – 2.86 (m, 1H), 2.83 – 2.65 (m, 2H), 1.84 – 1.56 (m, 5H), 1.51 – 1.37 (m, 1H), 1.26 – 0.94 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.9, 151.6, 129.1, 128.1, 125.5, 123.9, 117.0, 41.7, 41.2, 32.2, 30.5, 29.5, 26.1, 26.1, 26.0. IR (film): ν (cm^{-1}) 2926, 2852, 1770, 1586, 1486, 1452, 1349, 1215, 1151, 1073, 915, 851, 759. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{18}O_2$+Na^+]: 253.1199, found 253.1196.

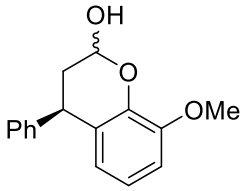


	Retention Time	Area	% Area
1	9.802	10138219	48.18
2	10.648	10905029	51.82



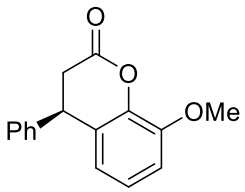
	Retention Time	Area	% Area
1	9.784	7986684	99.78
2	10.934	17768	0.22

(4*R*)-8-methoxy-4-phenylchroman-2-ol (2l)

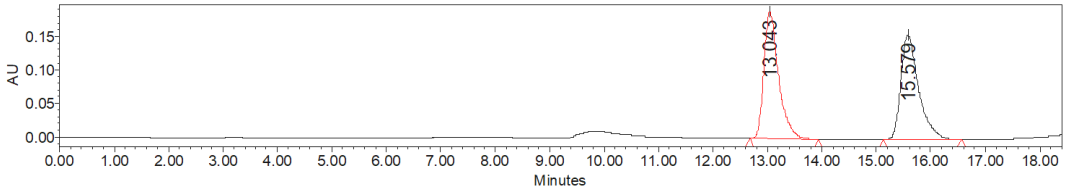


16 h, **L-PiPr$_2$**/Sc(OTf)$_3$ (1/1, 5 mol% catalyst loading); colorless oil, 49.7 mg, 97% yield, 4.9:1 d.r.; $[\alpha]^{20}$ = –137.4 (*c* = 0.45 in CH_2Cl_2, λ = 436 nm); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.14 (m, 5H), 6.84 – 6.63 (m, 2H), 6.45 – 6.23 (m, 1H), 5.88 – 5.58 (m, 1H), 4.43 – 4.11 (m, 2H), 3.86 (s, 3H), 2.51 – 2.26 (m, 1H), 2.24 – 2.08 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.1, 144.3, 141.2, 128.8, 128.5, 126.7, 126.3, 121.5, 120.1, 109.3, 91.5, 55.7, 36.6, 36.0. IR (film): ν (cm^{-1}) 3459, 1584, 1472, 1261, 1207, 1085, 1012, 956, 894, 762, 732, 700. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_3$+Na^+]: 279.0992, found 279.0997.

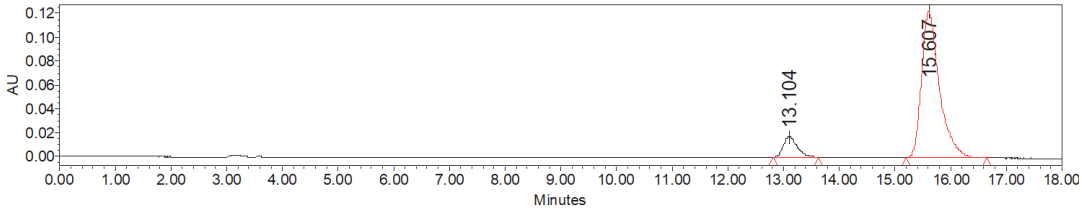
(*R*)-8-methoxy-4-phenylchroman-2-one (3l)



Colorless oil, 17.8 mg, 35% yield over two steps, 80% ee; $[\alpha]^{20}$ = –105.8 (*c* = 0.33 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, 230 nm) $t_{R\ (minor)}$ = 13.10 min, $t_{R\ (major)}$ = 15.61 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 3H), 7.21 – 7.08 (m, 2H), 7.08 – 6.97 (m, 1H), 6.95 – 6.84 (m, 1H), 6.62 – 6.46 (m, 1H), 4.34 (t, *J* = 6.6 Hz, 1H), 3.92 (s, 3H), 3.19 – 2.88 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.9, 147.8, 141.0, 140.3, 129.1, 127.6, 127.5, 126.8, 124.5, 119.7, 111.4, 56.1, 40.9, 36.8. IR (film): ν (cm^{-1}) 1767, 1589, 1481, 1275, 1180, 1138, 1091, 910, 832, 770, 730, 700. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{14}O_3$+Na$^+$]: 277.0835, found 277.0836.

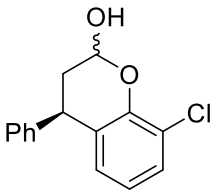


	Retention Time	Area	% Area
1	13.043	3556716	50.00
2	15.579	3557042	50.00



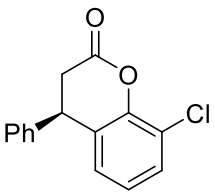
	Retention Time	Area	% Area
1	13.104	311094	10.18
2	15.607	2746126	89.82

(4*R*)-8-chloro-4-phenylchroman-2-ol (2m)

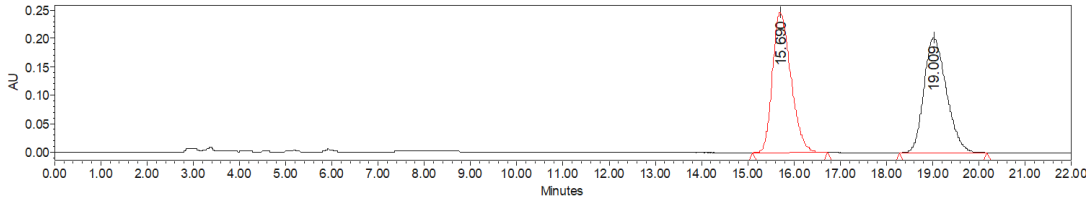


11 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 5 mol% catalyst loading); colorless oil, 51.4 mg, 99% yield, 4.9:1 d.r.; $[\alpha]^{20}$ = –217.9 (*c* = 0.85 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 7.24 – 7.11 (m, 3H), 6.77 – 6.69 (m, 1H), 6.68 – 6.56 (m, 1H), 5.89 – 5.74 (m, 1H), 4.35 (dd, *J* = 11.6, 5.8 Hz, 1H), 3.68 – 3.52 (m, 1H), 2.39 – 2.25 (m, 1H), 2.24 – 2.11 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.6, 143.6, 128.7, 128.7, 128.4, 128.1, 127.5, 126.9, 121.7, 121.0, 91.8, 36.7, 35.7. IR (film): ν (cm^{-1}) 3421, 1448, 1357, 1229, 1139, 1098, 1073, 1018, 946, 920, 889, 817, 761, 732, 700. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{35}ClO_2$+Na$^+$]: 283.0496, found 283.0499; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{37}ClO_2$+Na$^+$]: 285.0467, found 285.0466.

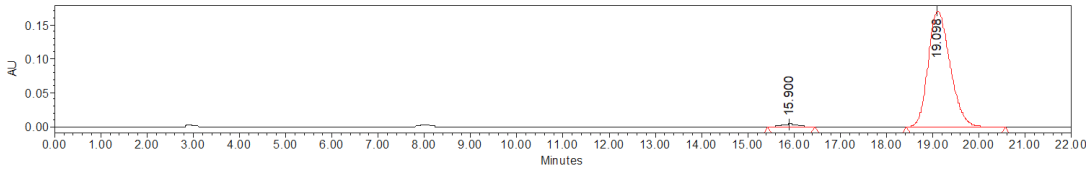
(*R*)-8-chloro-4-phenylchroman-2-one (3m)



Colorless oil, 46.9 mg, 91% yield over two steps, 96% ee; $[\alpha]^{21}$ = –210.4 (*c* = 0.82 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 240 nm) $t_{R(minor)}$ = 15.90 min, $t_{R(major)}$ = 19.10 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 4H), 7.23 – 7.13 (m, 2H), 7.06 – 6.95 (m, 1H), 6.94 – 6.82 (m, 1H), 4.37 (t, *J* = 6.9 Hz, 1H), 3.14 – 2.98 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2, 147.6, 139.6, 129.6, 129.2, 127.9, 127.7, 127.5, 126.7, 124.8, 122.1, 40.9, 36.6. IR (film): ν (cm^{-1}) 1771, 1495, 1341, 1224, 1173, 1127, 974, 908, 797, 765, 731, 699. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}{}^{35}ClO_2$+Na^+]: 281.0340, found 281.0334; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}{}^{37}ClO_2$+Na^+]: 283.0310, found 283.0300.

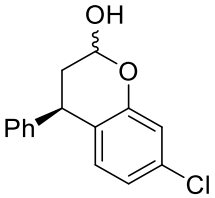


	Retention Time	Area	% Area
1	15.690	6842228	50.00
2	19.009	6843418	50.00



	Retention Time	Area	% Area
1	15.900	100907	1.78
2	19.098	5570358	98.22

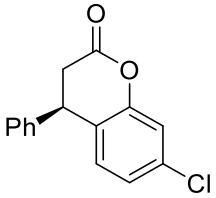
(4*R*)-7-chloro-4-phenylchroman-2-ol (2n)



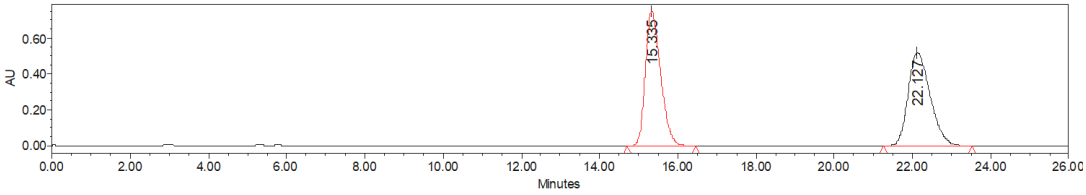
14 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 43.1 mg, 83% yield, 4.3:1 d.r.; $[\alpha]^{22}$ = –130.5 (*c* = 0.81 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.10 (m, 2H), 6.88 (d, *J* = 2.1 Hz, 1H), 6.81 – 6.73 (m, 1H), 6.72 – 6.66 (m, 1H), 5.66 (d, *J* = 2.4 Hz, 1H), 4.27 (dd, *J* = 11.4, 5.7 Hz, 1H), 3.40 (s, 1H), 2.32 – 2.20 (m, 1H), 2.19 – 2.02 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.4, 143.6, 132.8, 130.6, 128.7, 128.7, 126.9, 124.1, 121.2, 117.0, 91.5, 36.3, 35.8. IR (film): ν (cm^{-1}) 3399,

1601, 1573, 1483, 1452, 1409, 1216, 1128, 1096, 1080, 1048, 1012, 920, 858, 756, 700. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{35}ClO_2$+Na^+]: 283.0496, found 283.0500; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{37}ClO_2$+Na^+]: 285.0467, found 285.0467.

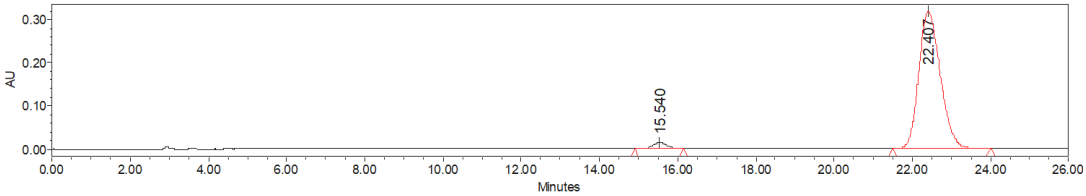
(*R*)-7-chloro-4-phenylchroman-2-one (3n)



White solid, Mp: 96–100 °C, 35.3 mg, 68% yield over two steps, 94% ee; $[\alpha]^{23}$ = –107.4 (*c* = 0.59 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 15.54 min, $t_{R(major)}$ = 22.41 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 3H), 7.20 – 7.11 (m, 3H), 7.09 – 7.10 (m, 1H), 6.95 – 6.86 (m, 1H), 4.32 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.21 – 2.97 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.8, 152.1, 139.7, 134.0, 129.3, 129.2, 127.9, 127.5, 124.8, 124.4, 117.5, 40.3, 36.7. IR (film): ν (cm^{-1}) 1777, 1606, 1579, 1485, 1453, 1409, 1221, 1179, 1132, 1078, 946, 864, 821, 757, 699. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}{}^{35}ClO_2$+Na^+]: 281.0340, found 281.0345; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}{}^{37}ClO_2$+Na^+]: 283.0310, found 283.0313.

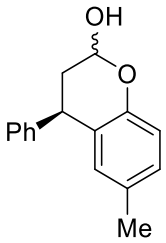


	Retention Time	Area	% Area
1	15.335	20448492	49.93
2	22.127	20506671	50.07



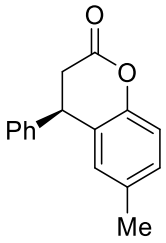
	Retention Time	Area	% Area
1	15.540	353520	2.83
2	22.407	12156271	97.17

(4*R*)-6-methyl-4-phenylchroman-2-ol (2o)

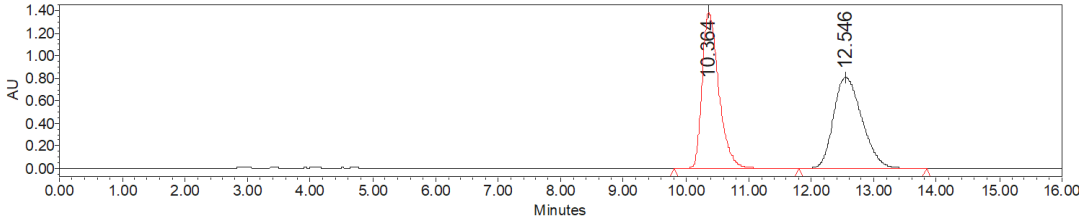


4 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 45.0 mg, 94% yield, 3.5:1 d.r.; $[\alpha]^{19}$ = –76.1 (*c* = 0.84 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.15 (m, 5H), 6.96 – 6.85 (m, 1H), 6.84 – 6.70 (m, 1H), 6.61 – 6.55 (m, 1H), 5.69 – 5.56 (m, 1H), 4.29 (dd, *J* = 10.9, 5.8 Hz, 1H), 3.52 – 3.32 (m, 1H), 2.32 – 2.21 (m, 1H), 2.19 – 2.02 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6, 144.4, 130.2, 129.8, 128.8, 128.6, 128.5, 126.6, 124.9, 116.6, 91.3, 36.9, 36.3, 20.5. IR (film): ν (cm^{-1}) 3417, 3026, 1494, 1451, 1272, 1239, 1211, 1128, 1092, 1054, 1018, 925, 893, 816, 756, 701. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_2$+Na$^+$]: 263.1043, found 263.1038.

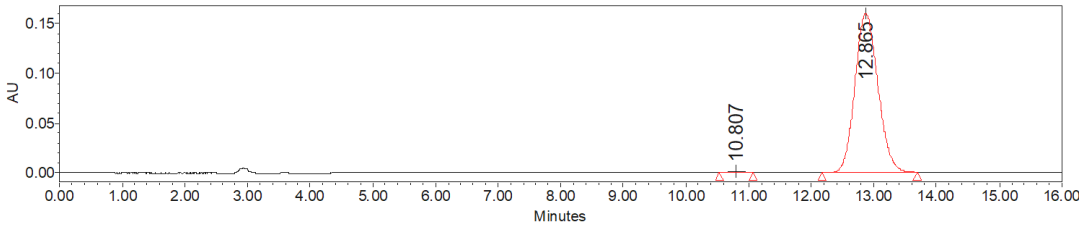
(*R*)-6-methyl-4-phenylchroman-2-one (3o)



White solid, Mp: 108–111 °C, 34.8 mg, 73% yield over two steps, 99% ee; $[\alpha]^{18}$ = –9.4 (*c* = 0.72 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 10.81 min, $t_{R(major)}$ = 12.87 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 3H), 7.21 – 7.12 (m, 2H), 7.12 – 7.05 (m, 1H), 7.05 – 6.99 (m, 1H), 6.82 – 6.74 (m, 1H), 4.29 (t, *J* = 6.7 Hz, 1H), 3.11 – 2.88 (m, 2H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.8, 149.6, 140.5, 134.3, 129.3, 129.1, 128.6, 127.6, 127.5, 125.3, 116.8, 40.7, 37.1, 20.7. IR (film): ν (cm^{-1}) 3029, 1768, 1494, 1454, 1276, 1244, 1199, 1144, 970, 927, 895, 818, 750, 700. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{14}O_2$+Na$^+$]: 261.0886, found 261.0893.

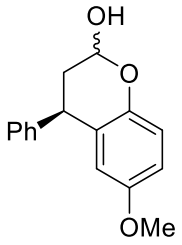


	Retention Time	Area	% Area
1	10.364	25420691	50.05
2	12.546	25370920	49.95



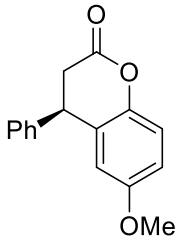
	Retention Time	Area	% Area
1	10.807	23793	0.58
2	12.865	4048689	99.42

(4*R*)-6-methoxy-4-phenylchroman-2-ol (2p)

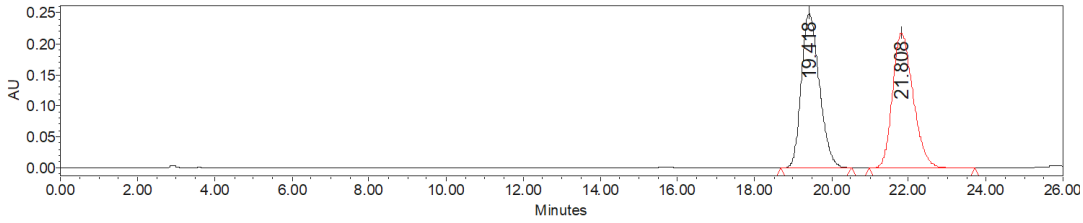


4 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 49.9 mg, 97% yield, 4.0:1 d.r.; $[\alpha]^{23}$ = –49.9 (*c* = 0.96 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.27 – 7.16 (m, 3H), 6.85 – 6.76 (m, 1H), 6.74 – 6.67 (m, 1H), 6.36 – 6.28 (m, 1H), 5.69 – 5.57 (m, 1H), 4.30 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.60 (s, 3H), 3.47 (s, 1H), 2.31 – 2.20 (m, 1H), 2.18 – 2.00 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.7, 145.8, 144.1, 128.8, 128.6, 126.7, 126.0, 117.4, 114.4, 113.8, 91.2, 55.6, 37.1, 36.2. IR (film): ν (cm^{-1}) 3421, 2936, 1491, 1453, 1422, 1273, 1151, 1092, 1039, 1014, 920, 894, 812, 761, 701. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{16}O_3$+Na$^+$]: 279.0992, found 279.0988.

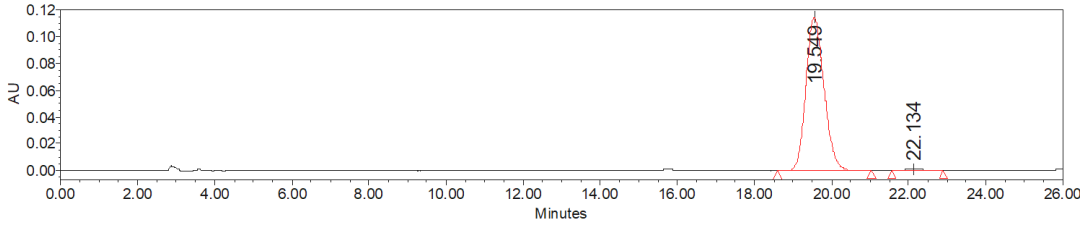
(*R*)-6-methoxy-4-phenylchroman-2-one (3p)



Colorless oil, 19.2 mg, 38% yield over two steps, 98% ee; $[\alpha]^{21}$ = +20.8 (*c* = 0.34 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(major)}$ = 19.55 min, $t_{R(minor)}$ = 22.13 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 3H), 7.20 – 7.12 (m, 2H), 7.07 (d, *J* = 8.9 Hz, 1H), 6.82 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.49 (dd, *J* = 2.9, 0.5 Hz, 1H), 4.30 (t, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.11 – 2.91 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.8, 156.3, 145.6, 140.1, 129.1, 127.7, 127.5, 126.7, 117.9, 113.7, 113.5, 55.6, 40.9, 37.0. IR (film): ν (cm^{-1}) 2920, 1758, 1490, 1454, 1426, 1274, 1193, 1137, 1033, 928, 896, 815, 767, 700. HRMS (FTMS+c ESI) calcd for [$C_{16}H_{14}O_3$+Na$^+$]: 277.0835, found 277.0836.

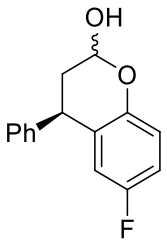


	Retention Time	Area	% Area
1	19.418	8127572	50.05
2	21.808	8109773	49.95



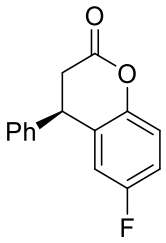
	Retention Time	Area	% Area
1	19.549	3726033	99.02
2	22.134	36904	0.98

(4*R*)-6-fluoro-4-phenylchroman-2-ol (2q)

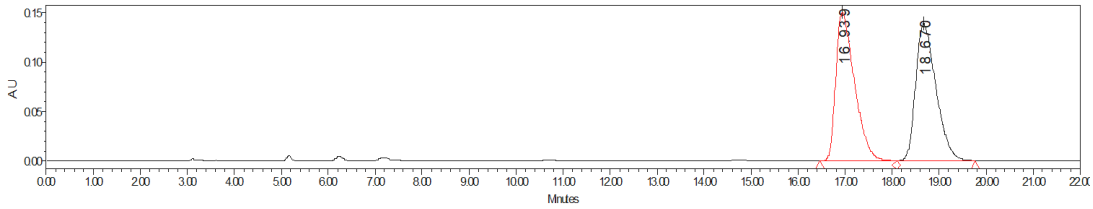


3 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 0.1 mol% catalyst loading); colorless oil, 48.4 mg, 99% yield, 4.2:1 d.r.; $[\alpha]^{24}$ = –179.1 (*c* = 0.93 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 3H), 7.25 – 7.15 (m, 2H), 6.91 – 6.72 (m, 2H), 6.52 – 6.39 (m, 1H), 5.68 (dd, *J* = 5.9, 3.1 Hz, 1H), 4.32 (dd, *J* = 11.6, 5.8 Hz, 1H), 3.43 (dd, *J* = 3.6, 1.8 Hz, 1H), 2.34 – 2.21 (m, 1H), 2.20 – 2.07 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.1 (d, *J* = 237.0 Hz), 147.7 (d, *J* = 2.0 Hz), 143.4, 128.8, 128.7, 127.0, 126.8 (d, *J* = 15.9 Hz), 117.8 (d, *J* = 7.9 Hz), 115.5 (d, *J* = 23.3 Hz), 114.6 (d, *J* = 23.1 Hz), 91.3, 36.8, 35.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –122.81. IR (film): ν (cm^{-1}) 3403, 1489, 1424, 1255, 1189, 1135, 1092, 1054, 1017, 935, 815, 757, 701. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}FO_2$+H$^+$]: 245.0972, found 245.0965.

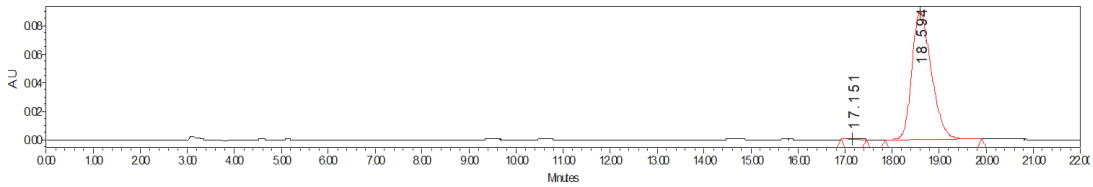
(*R*)-6-fluoro-4-phenylchroman-2-one (3q)



Colorless oil, 38.2 mg, 79% yield over two steps, 99% ee; $[\alpha]^{22}$ = –101.5 (*c* = 0.72 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm) $t_{R(minor)}$ = 17.15 min, $t_{R(major)}$ = 18.59 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 3H), 7.21 – 7.13 (m, 2H), 7.13 – 7.07 (m, 1H), 7.03 – 6.91 (m, 1H), 6.73 – 6.59 (m, 1H), 4.32 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.13 – 2.92 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.18, 159.1 (d, *J* = 242.5 Hz), 147.6 (d, *J* = 2.8 Hz), 139.38, 129.26, 127.94, 127.6 (d, *J* = 7.7 Hz), 127.51, 118.4 (d, *J* = 8.4 Hz), 115.5 (d, *J* = 23.4 Hz), 114.8 (d, *J* = 24.4 Hz), 40.67, 36.47. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –117.46. IR (film): ν (cm^{-1}) 1769, 1488, 1428, 1243, 1185, 1138, 973, 902, 820, 757, 700. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}FO_2$+H^+]: 243.0816, found 243.0816.

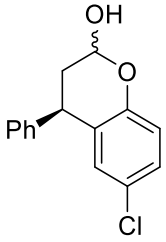


	Retention Time	Area	% Area
1	16.939	4144748	50.03
2	18.670	4139992	49.97



	Retention Time	Area	% Area
1	17.151	6784	0.26
2	18.594	2572513	99.74

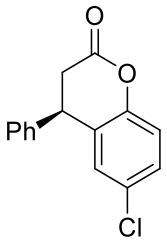
(4*R*)-6-chloro-4-phenylchroman-2-ol (2r)



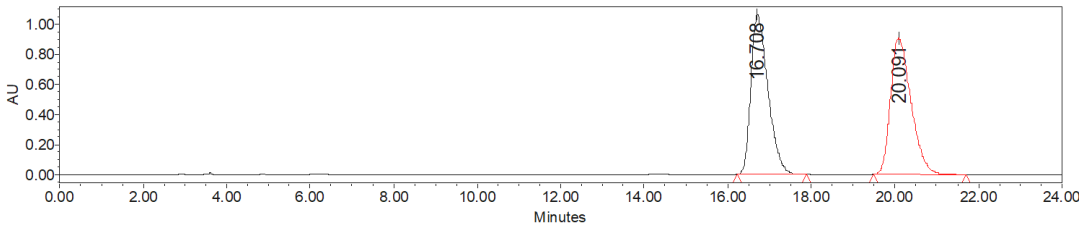
11 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 51.8 mg, 99% yield, 4.0:1 d.r.; $[\alpha]^{23}$ = –13.0 (*c* = 0.88 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 3H), 7.24 – 7.15 (m, 2H), 7.10

(dd, *J* = 8.7, 2.4 Hz, 1H), 6.85 – 6.78 (m, 1H), 6.78 – 6.67 (m, 1H), 5.72 – 5.63 (m, 1H), 4.30 (dd, *J* = 11.4, 5.7 Hz, 1H), 3.40 (d, *J* = 1.6 Hz, 1H), 2.31 – 2.24 (m, 1H), 2.20 – 2.08 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.4, 143.3, 129.1, 128.8, 128.7, 127.9, 127.1, 127.03, 125.8, 118.3, 91.3, 36.7, 35.7. IR (film): ν (cm^{-1}) 3397, 1476, 1405, 1260, 1230, 1176, 1120, 1094, 1052, 1014, 917, 896, 815, 759, 736, 699. HRMS (FTMS+c ESI) calcd for $[C_{15}H_{13}{}^{35}ClO_2+Na^+]$: 283.0496, found 283.0500; HRMS (FTMS+c ESI) calcd for $[C_{15}H_{13}{}^{37}ClO_2+Na^+]$: 285.0467, found 285.0471.

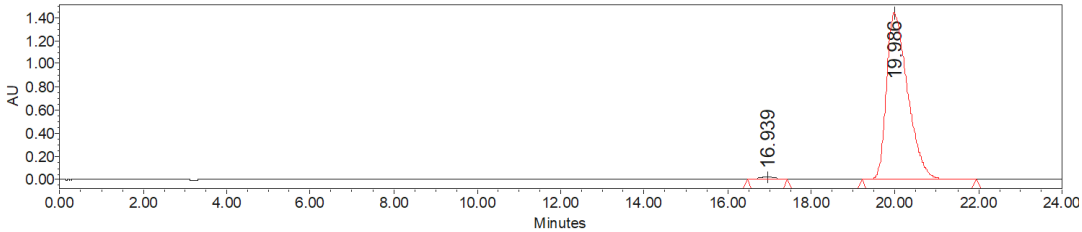
(*R*)-6-chloro-4-phenylchroman-2-one (3r)



Colorless oil, 36.9 mg, 72% yield over two steps, 98% ee; $[\alpha]^{22}$ = +52.3 (*c* = 0.63 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 16.94 min, $t_{R(major)}$ = 19.99 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 3H), 7.28 – 7.24 (m, 1H), 7.18 – 7.12 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.94 (dd, *J* = 2.5, 0.7 Hz, 1H), 4.31 (t, *J* = 7.6 Hz, 1H), 3.17 – 2.94 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 150.2, 139.4, 129.8, 129.3, 128.8, 128.1, 128.0, 127.5, 127.5, 118.5, 40.6, 36.5. IR (film): ν (cm^{-1}) 1774, 1478, 1413, 1263, 1218, 1174, 1136, 1085, 968, 924, 881, 822, 762, 699. HRMS (FTMS+c ESI) calcd for $[C_{15}H_{11}{}^{35}ClO_2+Na^+]$: 281.0340, found 281.0342; HRMS (FTMS+c ESI) calcd for $[C_{15}H_{11}{}^{37}ClO_2+Na^+]$: 283.0310, found 283.0318.

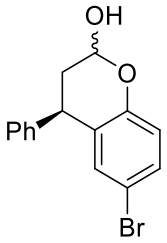


	Retention Time	Area	% Area
1	16.708	30343455	49.60
2	20.091	30833440	50.40



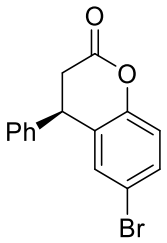
	Retention Time	Area	% Area
1	16.939	596487	1.16
2	19.986	50844763	98.84

(4*R*)-6-bromo-4-phenylchroman-2-ol (2s)

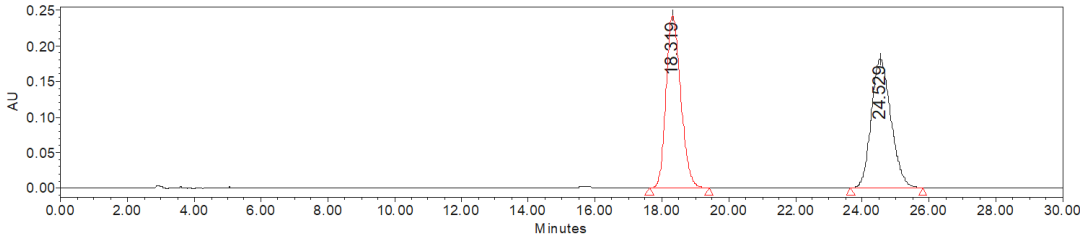


3 h, **L-PiPr$_2$**/Fe(OTf)$_2$ (1/1, 1 mol% catalyst loading); colorless oil, 58.0 mg, 95% yield, 3.9:1 d.r.; $[\alpha]^{20}$ = +61.8 (*c* = 1.08 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 3H), 7.26 – 7.16 (m, 3H), 6.93 – 6.82 (m, 1H), 6.81 – 6.72 (m, 1H), 5.67 (dd, *J* = 5.8, 3.0 Hz, 1H), 4.31 (dd, *J* = 11.3, 5.7 Hz, 1H), 3.43 (d, *J* = 2.1 Hz, 1H), 2.32 – 2.21 (m, 1H), 2.19 – 2.07 (m, 1H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.0, 143.2, 132.0, 130.8, 128.8, 128.7, 127.7, 127.0, 118.7, 113.2, 91.4, 36.7, 35.7. IR (film): ν (cm^{-1}) 3408, 1476, 1401, 1263, 1229, 1178, 1126, 1094, 1051, 1015, 918, 894, 815, 757, 701. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{79}BrO_2$+Na$^+$]: 326.9991, found 326.9996; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}{}^{81}BrO_2$+Na$^+$]: 328.9971, found 328.9976.

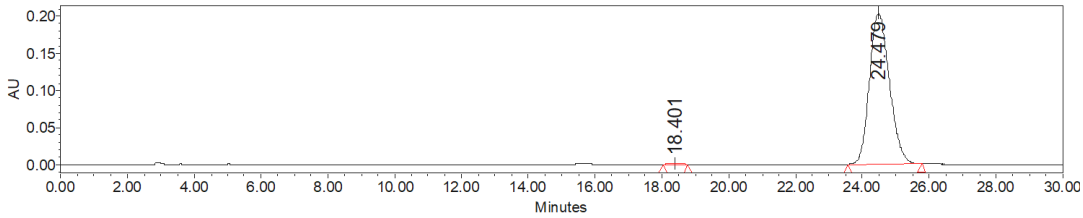
(*R*)-6-bromo-4-phenylchroman-2-one (3s)



White solid, Mp: 128–131 °C, 45.5 mg, 76% yield over two steps, 99% ee; $[\alpha]^{22}$ = +99.1 (*c* = 0.71 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 18.40 min, $t_{R(major)}$ = 24.48 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 3H), 7.34 – 7.28 (m, 1H), 7.19 – 7.12 (m, 2H), 7.10 (dd, *J* = 2.3, 0.7 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 4.31 (t, *J* = 6.8 Hz, 1H), 3.11 – 2.92 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.8, 150.7, 139.4, 131.8, 131.0, 129.3, 128.0, 127.9, 127.4, 118.9, 117.3, 40.5, 36.6. IR (film): ν (cm^{-1}) 1773, 1475, 1408, 1268, 1220, 1173, 1135, 1075, 967, 921, 882, 819, 757, 700. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}{}^{79}BrO_2$+Na$^+$]: 324.9835, found 324.9834; HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}{}^{81}BrO_2$+Na$^+$]: 326.9814, found 326.9815.

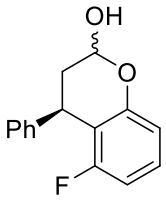


	Retention Time	Area	% Area
1	18.319	7393870	49.94
2	24.529	7410722	50.06



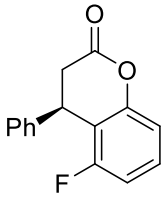
	Retention Time	Area	% Area
1	18.401	29679	0.35
2	24.479	8447951	99.65

(4*R*)-5-fluoro-4-phenylchroman-2-ol (2t)

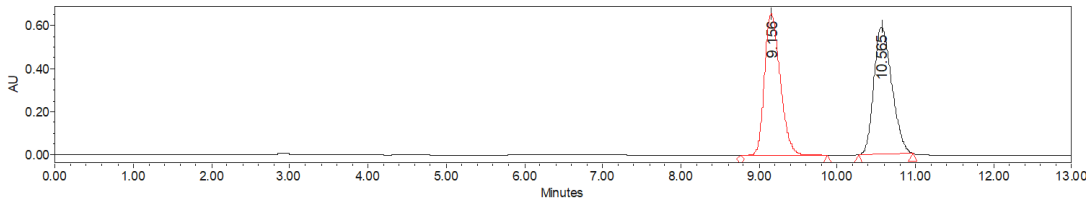


11 h, **L-PiPr$_2$**/Sc(OTf)$_3$ (1/1, 5 mol% catalyst loading); white solid, Mp: 112–116 °C, 34.0 mg, 70% yield, 4.5:1 d.r.; $[\alpha]^{18}$ = –152.6 (*c* = 0.50 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 2H), 7.25 – 7.05 (m, 4H), 6.82 – 6.68 (m, 1H), 6.68 – 6.48 (m, 1H), 5.38 (q, *J* = 5.1 Hz, 1H), 4.42 (t, *J* = 5.7 Hz, 1H), 3.52 – 3.35 (m, 1H), 2.32 – 2.02 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.0 (d, *J* = 245.6 Hz), 154.4 (d, *J* = 7.0 Hz), 144.2, 128.7, 128.6, 127.4, 126.6, 112.6 (d, *J* = 3.1 Hz), 111.9 (d, *J* = 19.7 Hz), 107.7 (d, *J* = 21.4 Hz), 91.5, 36.9, 34.5. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –113.33. IR (film): ν (cm^{-1}) 3400, 1622, 1585, 1465, 1310, 1260, 1130, 1048, 982, 884, 757, 702. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{13}FO_2$+Na$^+$]: 267.0792, found 267.0795.

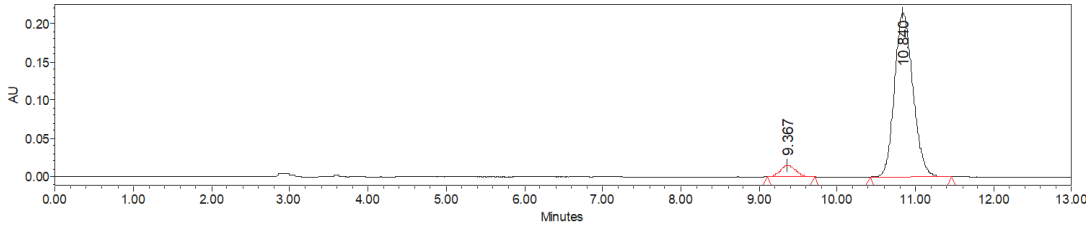
(*R*)-5-fluoro-4-phenylchroman-2-one (3t)



White solid, Mp: 108–114 °C, 30.1 mg, 62% yield over two steps, 89% ee; $[\alpha]^{20}$ = –170.8 (*c* = 0.58 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 9.37 min, $t_{R(major)}$ = 10.84 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 4H), 7.16 – 7.08 (m, 2H), 7.01 – 6.94 (m, 1H), 6.93 – 6.85 (m, 1H), 4.64 (dd, *J* = 6.1, 2.8 Hz, 1H), 3.14 – 3.00 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 159.6 (d, *J* = 246.7 Hz), 152.6 (d, *J* = 6.5 Hz), 140.0, 129.4 (d, *J* = 9.5 Hz), 129.1, 127.6, 126.6, 113.5 (d, *J* = 21.8 Hz), 113.0 (d, *J* = 3.4 Hz), 111.6 (d, *J* = 21.3 Hz), 36.3, 34.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –116.47. IR (film): ν (cm^{-1}) 1772, 1624, 1594, 1467, 1342, 1253, 1182, 1131, 1030, 966, 880, 793, 745, 698. HRMS (FTMS+c ESI) calcd for [$C_{15}H_{11}FO_2$+Na$^+$]: 265.0635, found 265.0639.

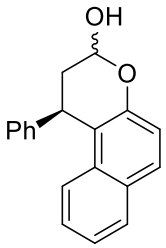


	Retention Time	Area	% Area
1	9.156	9098559	49.11
2	10.565	9429035	50.89



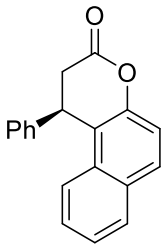
	Retention Time	Area	% Area
1	9.367	203344	5.49
2	10.840	3498607	94.51

(1*R*)-1-phenyl-2,3-dihydro-1H-benzo[*f*]chromen-3-ol (2u)

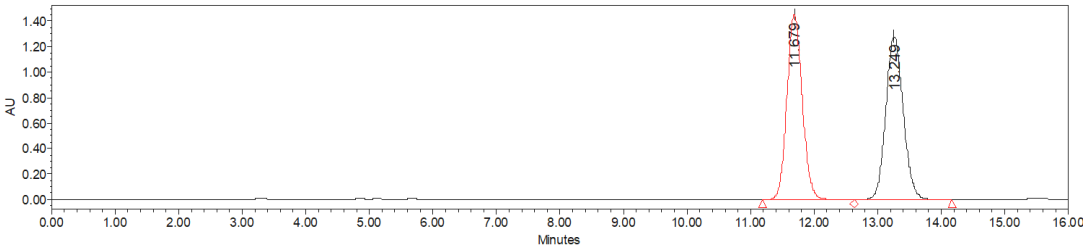


11 h, **L-RaPr$_2$**/Fe(OTf)$_2$ (1/1, 10 mol% catalyst loading) in CH_2ClCH_2Cl; white solid, Mp: 160–164 °C, 33.3 mg, 60% yield, 4.9:1 d.r.; $[\alpha]^{19}$ = –225.2 (*c* = 0.44 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.67 (m, 2H), 7.49 – 7.39 (m, 1H), 7.32 – 7.07 (m, 8H), 5.50 – 5.27 (m, 1H), 4.85 – 4.56 (m, 1H), 3.22 (d, *J* = 6.5 Hz, 1H), 2.47 – 2.17 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.8, 145.1, 132.4, 129.5, 129.4, 128.7, 128.4, 128.0, 126.5, 126.5, 123.4, 123.4, 118.7, 113.9, 91.4, 37.9, 37.7. IR (film): ν (cm^{-1}) 3386, 1622, 1598, 1454, 1398, 1344, 1230, 1121, 1063, 1020, 894, 821, 745, 698. HRMS (FTMS+c ESI) calcd for [$C_{19}H_{16}O_2$+Na$^+$]: 299.1043, found 299.1039.

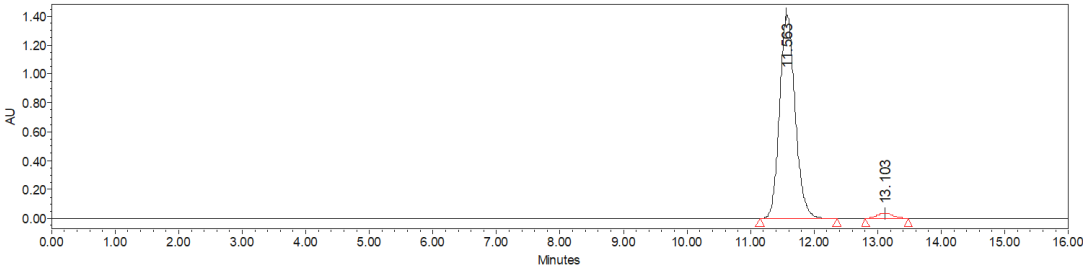
(*R*)-1-phenyl-1,2-dihydro-3H-benzo[*f*]chromen-3-one (3u)



Pale yellow solid, Mp: 150–154 °C, 32.8 mg, 60% yield over two steps, 95% ee; $[\alpha]^{20}$ = –147.9 (*c* = 0.33 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, 230 nm) $t_{R(major)}$ = 11.56 min, $t_{R(minor)}$ = 13.10 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.71 (m, 3H), 7.51 – 7.40 (m, 2H), 7.39 – 7.33 (m, 1H), 7.31 – 7.05 (m, 5H), 4.94 (dd, *J* = 6.5, 2.0 Hz, 1H), 3.31 – 3.07 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 149.7, 140.5, 131.0, 130.9, 129.9, 129.2, 128.7, 127.5, 127.4, 126.9, 125.2, 123.0, 117.5, 117.5, 37.6, 37.4. IR (film): ν (cm^{-1}) 1776, 1513, 1458, 1250, 1215, 1179, 1134, 969, 885, 816, 749, 701. HRMS (FTMS+c ESI) calcd for [$C_{19}H_{14}O_2$+Na^+]: 297.0886, found 297.0890.

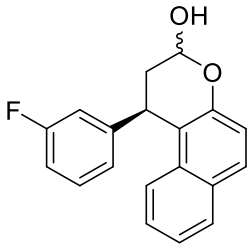


	Retention Time	Area	% Area
1	11.679	24324759	49.95
2	13.249	24374078	50.05



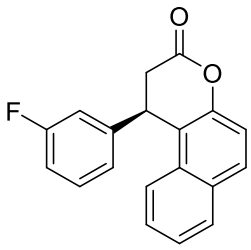
	Retention Time	Area	% Area
1	11.563	23951489	97.52
2	13.103	610085	2.48

(1*R*)-1-(3-fluorophenyl)-2,3-dihydro-1H-benzo[*f*]chromen-3-ol (2v)

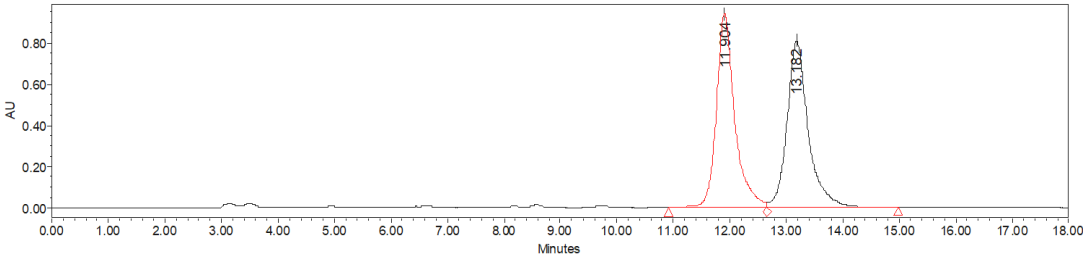


15 h, **L-RaPr$_2$**/Fe(OTf)$_2$ (1/1, 10 mol% catalyst loading) in $CHCl_3$; colorless oil, 46.2 mg, 79% yield, 6.1:1 d.r.; $[\alpha]^{18}$ = –194.7 (*c* = 0.66 in CH_2Cl_2, λ = 436 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.68 (m, 2H), 7.45 – 7.34 (m, 1H), 7.30 – 7.11 (m, 4H), 6.95 – 6.66 (m, 3H), 5.75 – 5.20 (m, 1H), 4.85 – 4.55 (m, 1H), 3.44 (d, *J* = 6.7 Hz, 1H), 2.43 – 2.22 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 244.9 Hz), 151.7, 147.8 (d, *J* = 6.5 Hz), 132.2, 130.2 (d, *J* = 8.2 Hz), 129.6, 129.5, 128.5, 126.7 (d, *J* = 2.8 Hz), 123.6, 123.5, 123.2, 118.7, 115.0 (d, *J* = 21.6 Hz), 113.5 (d, *J* = 21.0 Hz), 113.2, 91.3, 37.6, 37.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –112.57. IR (film): ν (cm^{-1}) 3403, 1618, 1591, 1483, 1442, 1265, 1229, 1130, 1057, 993, 816, 745, 700. HRMS (FTMS+c ESI) calcd for [$C_{19}H_{15}FO_2$+Na$^+$]: 317.0948, found 317.0958.

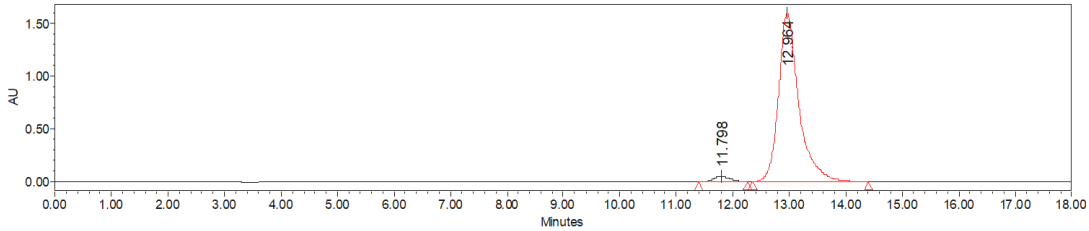
(*R*)-1-(3-fluorophenyl)-1,2-dihydro-3H-benzo[*f*]chromen-3-one (3v)



Yellow oil, 39.7 mg, 68% yield over two steps, 95% ee; $[\alpha]^{19}$ = –146.7 (*c* = 0.67 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 11.80 min, $t_{R(major)}$ = 12.96 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.82 (m, 2H), 7.81 – 7.71 (m, 1H), 7.55 – 7.39 (m, 2H), 7.39 – 7.29 (m, 1H), 7.27 – 7.19 (m, 1H), 7.04 – 6.86 (m, 2H), 6.86 – 6.69 (m, 1H), 5.04 – 4.78 (m, 1H), 3.36 – 2.96 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.7, 163.2 (d, *J* = 245.8 Hz), 149.8, 143.0 (d, *J* = 6.7 Hz), 131.08, 130.87, 130.8 (d, *J* = 2.5 Hz), 130.23, 128.82, 127.59, 125.36, 122.79, 122.6 (d, *J* = 2.9 Hz), 117.53, 116.84, 114.6 (d, *J* = 21.0 Hz), 114.1 (d, *J* = 21.9 Hz), 37.27, 37.24. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –111.67. IR (film): ν (cm^{-1}) 1773, 1589, 1486, 1444, 1252, 1217, 1158, 1123, 977, 907, 816, 784, 749. HRMS (FTMS+c ESI) calcd for [$C_{19}H_{13}FO_2$+Na$^+$]: 315.0792, found 315.0794.

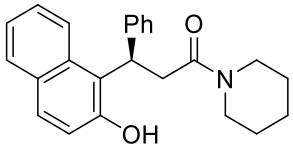


	Retention Time	Area	% Area
1	11.904	21165962	50.02
2	13.182	21151842	49.98

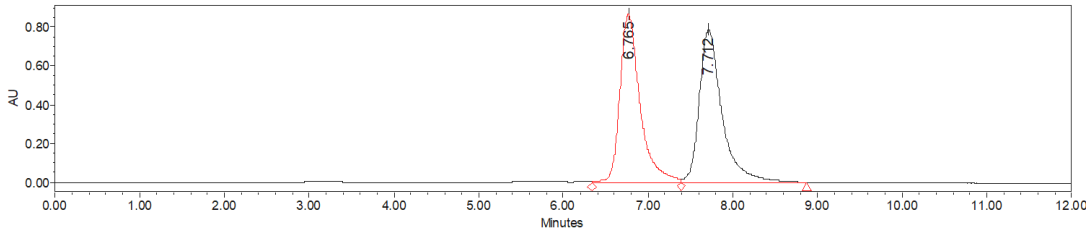


	Retention Time	Area	% Area
1	11.798	958880	2.36
2	12.964	39629076	97.64

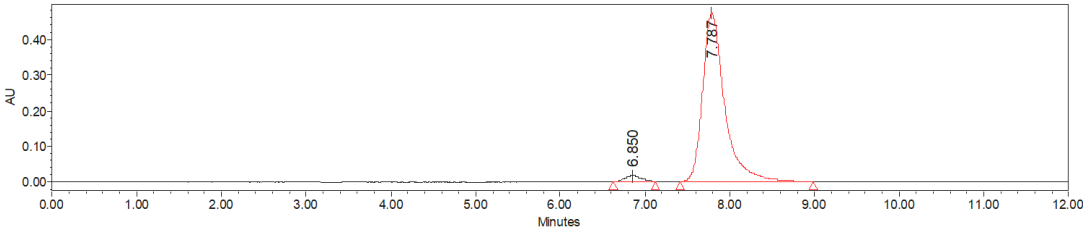
(*R*)-3-(2-hydroxynaphthalen-1-yl)-3-phenyl-1-(piperidin-1-yl)propan-1-one (4u)



White solid, Mp: 161–164 °C, 26.4 mg, 99% yield, 95% ee; $[\alpha]^{19}$ = +673.0 (*c* = 0.23 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 6.85 min, $t_{R(major)}$ = 7.79 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.76 – 7.62 (m, 2H), 7.61 – 7.46 (m, 1H), 7.31 – 7.09 (m, 8H), 5.57 (dd, *J* = 9.9, 3.7 Hz, 1H), 3.66 – 3.37 (m, 5H), 3.36 – 3.27 (m, 1H), 1.65 – 1.24 (m, 5H), 1.21 – 1.09 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 153.7, 143.3, 132.0, 130.3, 129.1, 128.9, 128.3, 127.0, 125.7, 125.4, 124.0, 122.5, 122.4, 121.0, 46.8, 43.4, 36.6, 34.9, 26.0, 25.4, 24.2. IR (film): ν (cm^{-1}) 3058, 2937, 1602, 1511, 1472, 1439, 1267, 1017, 816, 746, 700. HRMS (FTMS+c ESI) calcd for [$C_{24}H_{25}NO_2$+Na^+]: 382.1778, found 382.1769.

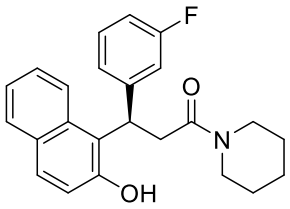


	Retention Time	Area	% Area
1	6.765	14335298	49.58
2	7.712	14579775	50.42

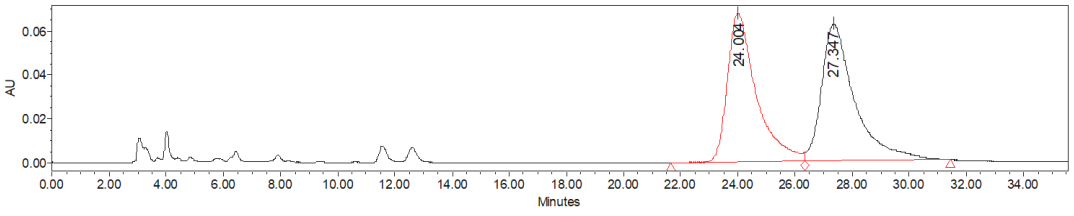


	Retention Time	Area	% Area
1	6.850	212540	2.44
2	7.787	8481699	97.56

(*R*)-3-(3-fluorophenyl)-3-(2-hydroxynaphthalen-1-yl)-1-(piperidin-1-yl)propan-1-one (4v)



White solid, Mp: 162–166 °C, 22.4 mg, 94% yield, 95% ee; $[\alpha]^{19}$ = +671.9 (*c* = 0.16 in CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 230 nm) $t_{R(minor)}$ = 24.82 min, $t_{R(major)}$ = 28.25 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.82 – 7.59 (m, 2H), 7.56 – 7.39 (m, 1H), 7.30 – 7.11 (m, 4H), 7.00 – 6.87 (m, 2H), 6.87 – 6.75 (m, 2H), 5.54 (dd, *J* = 10.2, 2.3 Hz, 1H), 3.72 – 3.09 (m, 6H), 1.69 – 1.37 (m, 4H), 1.37 – 1.27 (m, 1H), 1.23 – 1.11 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 162.9 (d, *J* = 243.5 Hz), 153.7, 146.2 (d, *J* = 6.7 Hz), 131.9, 130.4, 129.6 (d, *J* = 8.3 Hz), 129.3, 129.0, 125.6, 123.8, 122.7 (d, *J* = 2.6 Hz), 122.6, 121.8, 121.0, 114.0 (d, *J* = 22.1 Hz), 112.6 (d, *J* = 21.0 Hz), 46.8, 43.5, 36.5, 35.0, 26.1, 25.4, 24.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –113.22. IR (film): ν (cm^{-1}) 3062, 2938, 1608, 1512, 1480, 1439, 1267, 1016, 818, 742, 697. HRMS (FTMS+c ESI) calcd for [$C_{24}H_{24}FNO_2$+Na^+]: 400.1683, found 400.1678.



	Retention Time	Area	% Area
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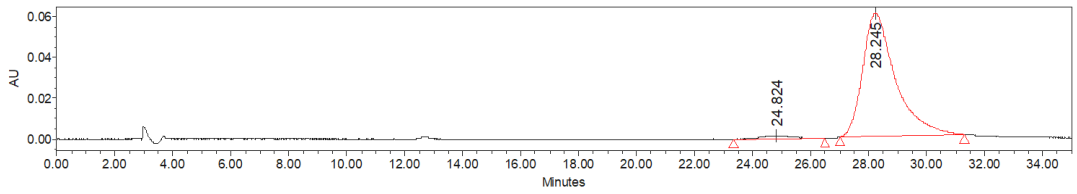
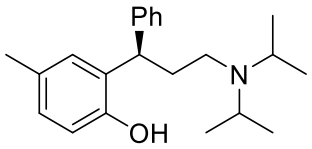
2	27.347	4995825	51.28



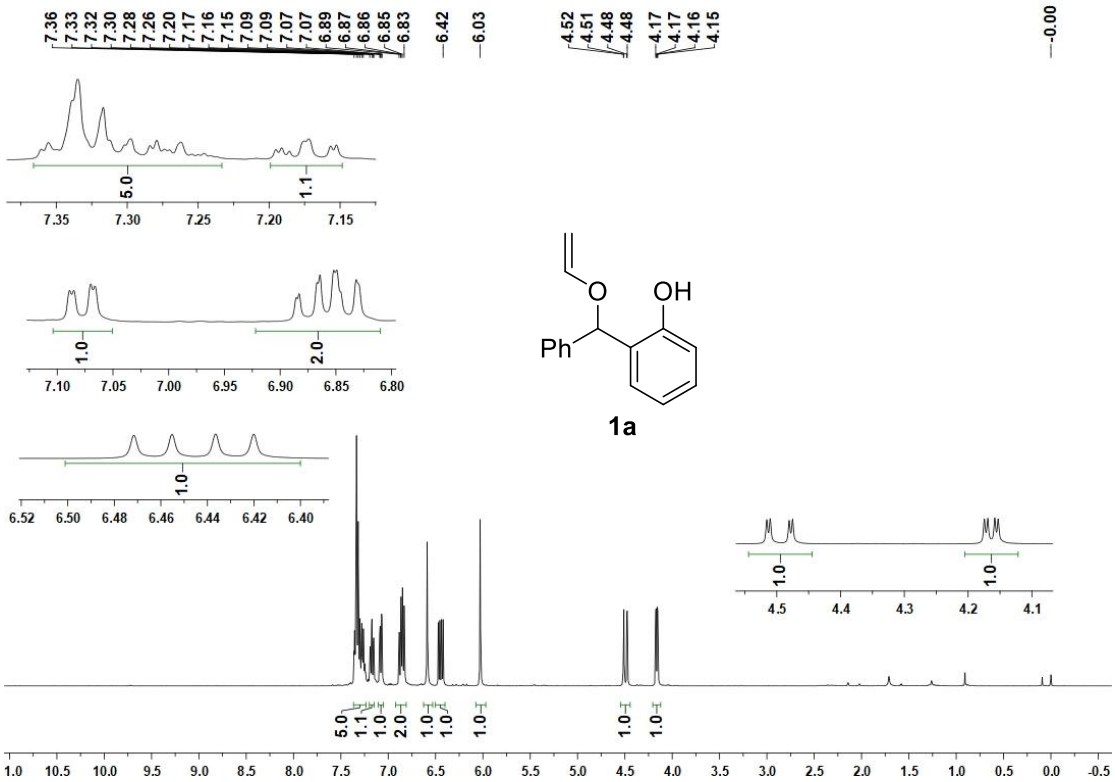
	Retention Time	Area	% Area
1	24.824	108811	2.24
2	28.245	4744373	97.76

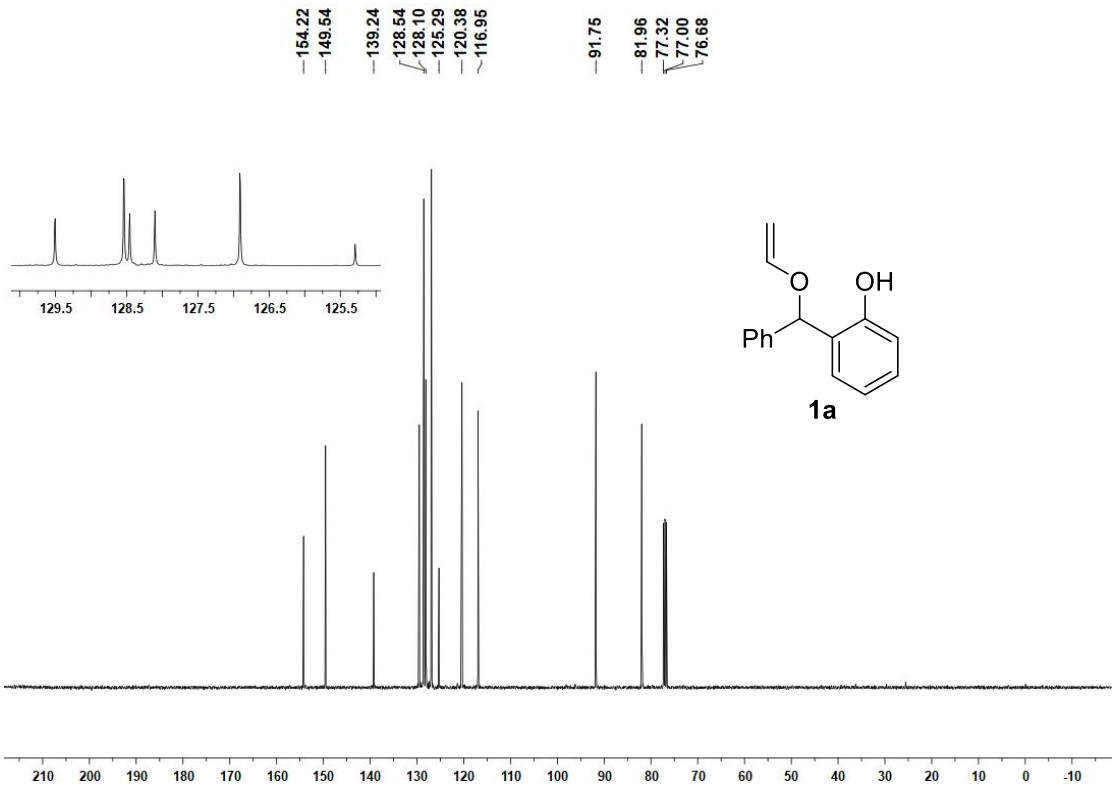
(*R*)-tolterodine

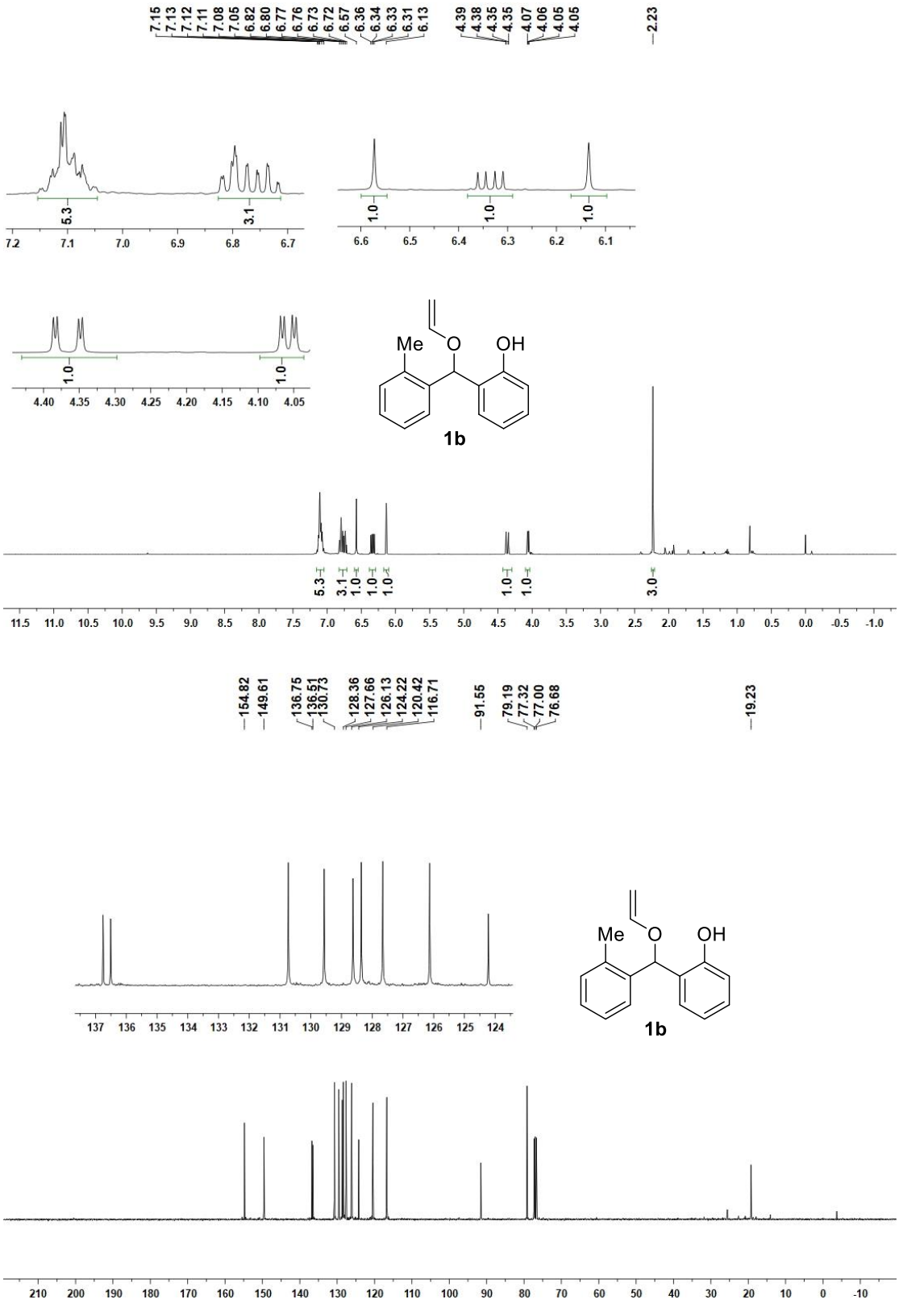


Colorless oil, 35.1 mg, 72% yield; $[\alpha]^{21}_{D}$ = +30.2 (*c* = 0.38 in CH_3OH, λ = 589 nm); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 4H), 7.25 – 7.17 (m, 1H), 6.90 – 6.75 (m, 2H), 6.63 – 6.46 (m, 1H), 4.62 – 4.40 (m, 1H), 3.36 – 3.08 (m, 2H), 2.79 – 2.67 (m, 1H), 2.45 – 2.27 (m, 2H), 2.16 – 1.98 (m, 4H), 1.14 (d, *J* = 6.7 Hz, 6H), 1.08 (d, *J* = 6.7 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.2, 144.8, 132.4, 129.3, 128.6, 128.5, 128.3, 127.7, 126.1, 118.2, 47.8, 42.0, 39.3, 33.2, 20.7, 20.0, 19.5. IR (film): ν (cm^{-1}) 2967, 1603, 1492, 1456, 1388, 1255, 1161, 1112, 1033, 815, 755, 701. HRMS (FTMS+c ESI) calcd for [$C_{22}H_{31}NO+Na^{+}$]: 348.2298, found 348.2290.

11. Copies of NMR spectra for the substrates and the products



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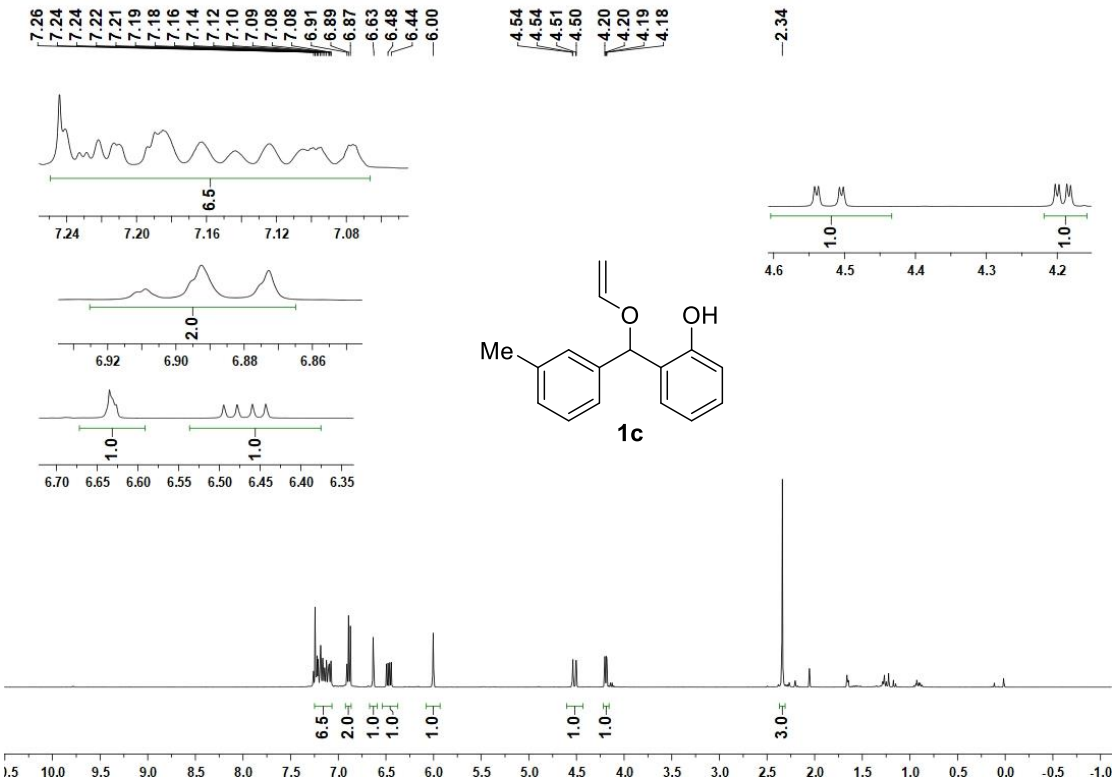
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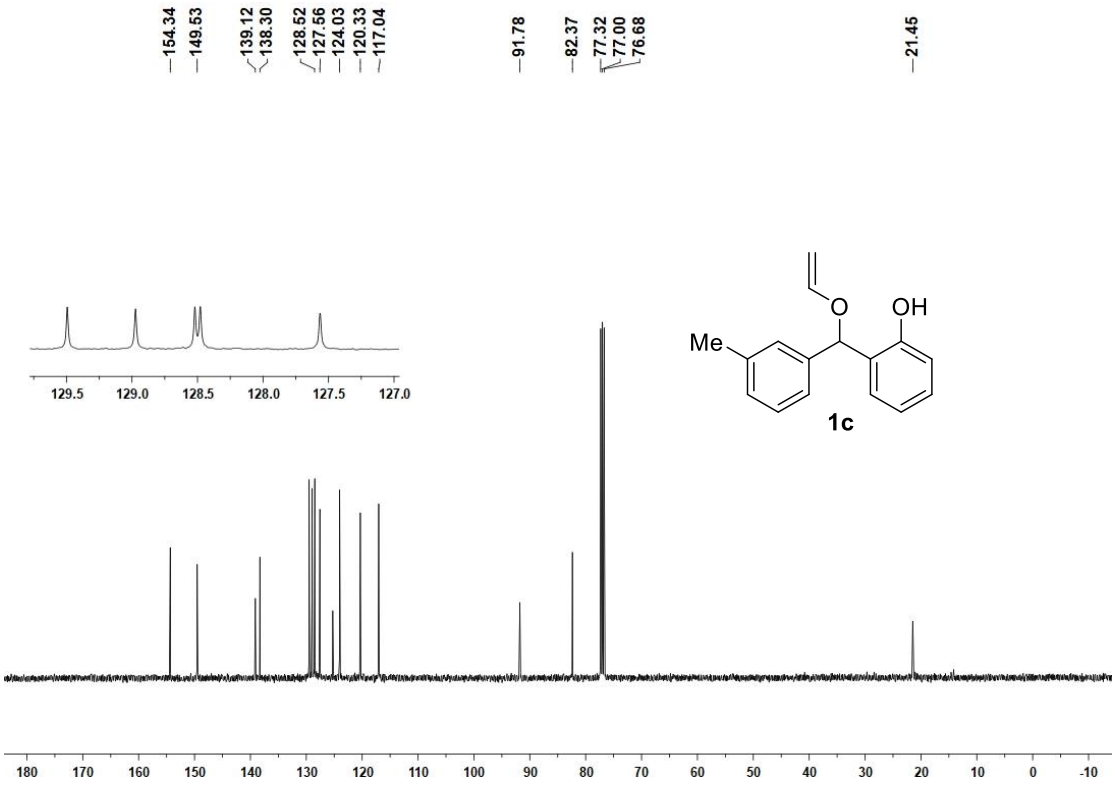
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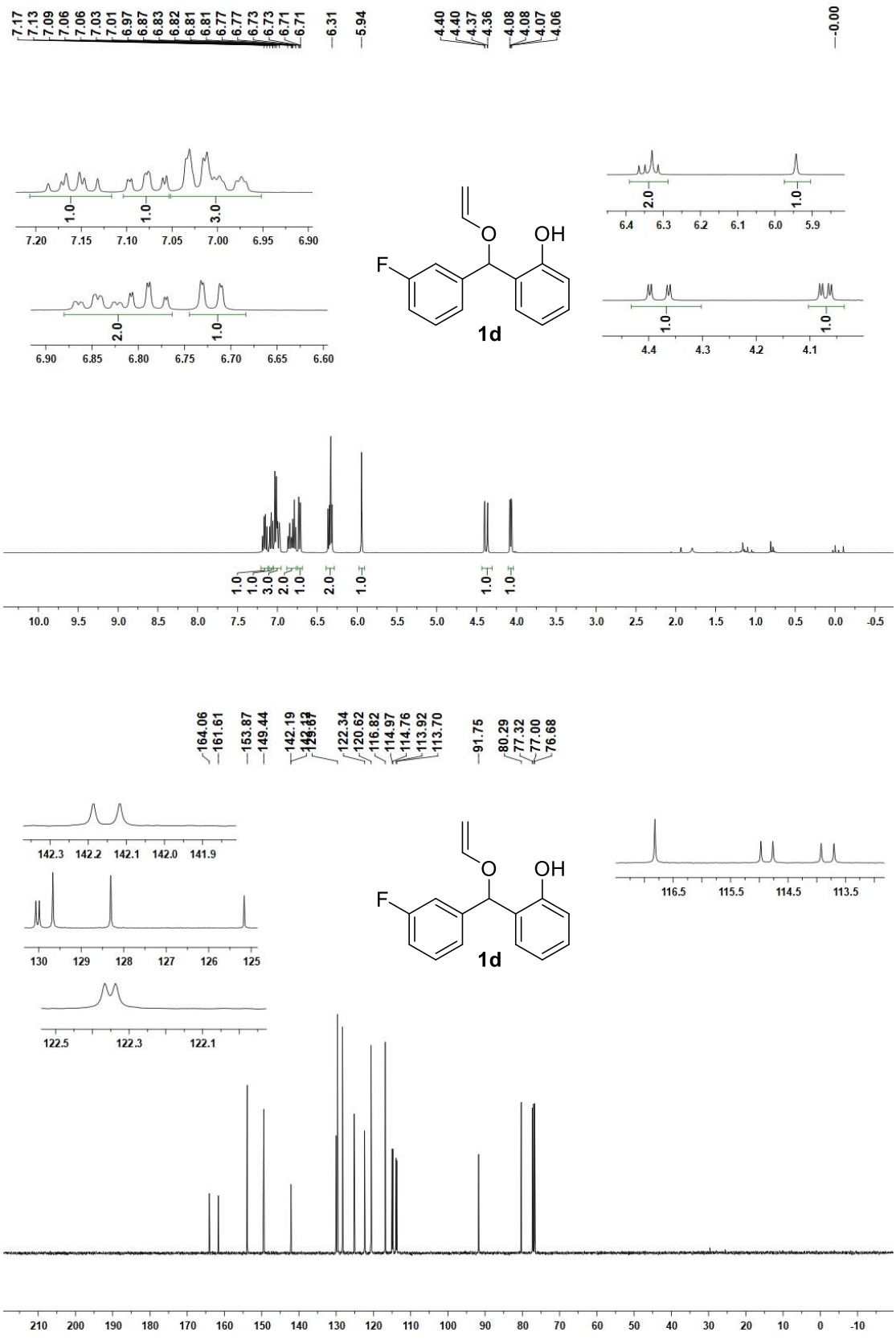
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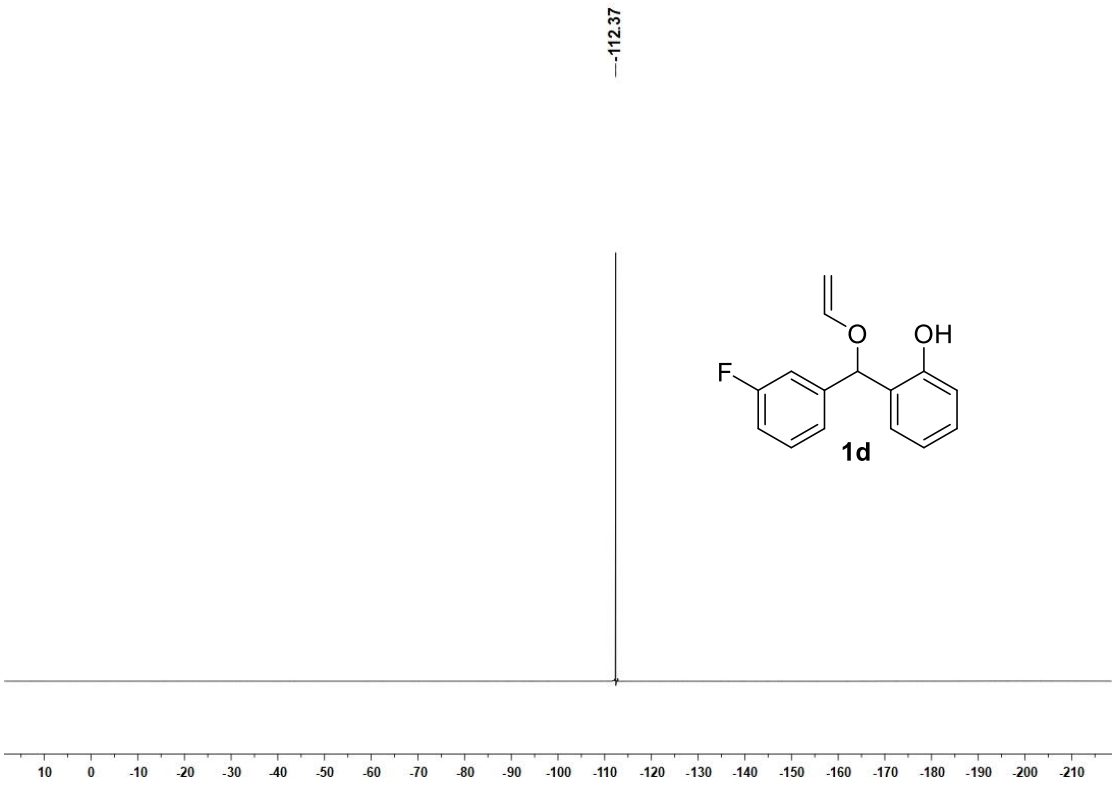
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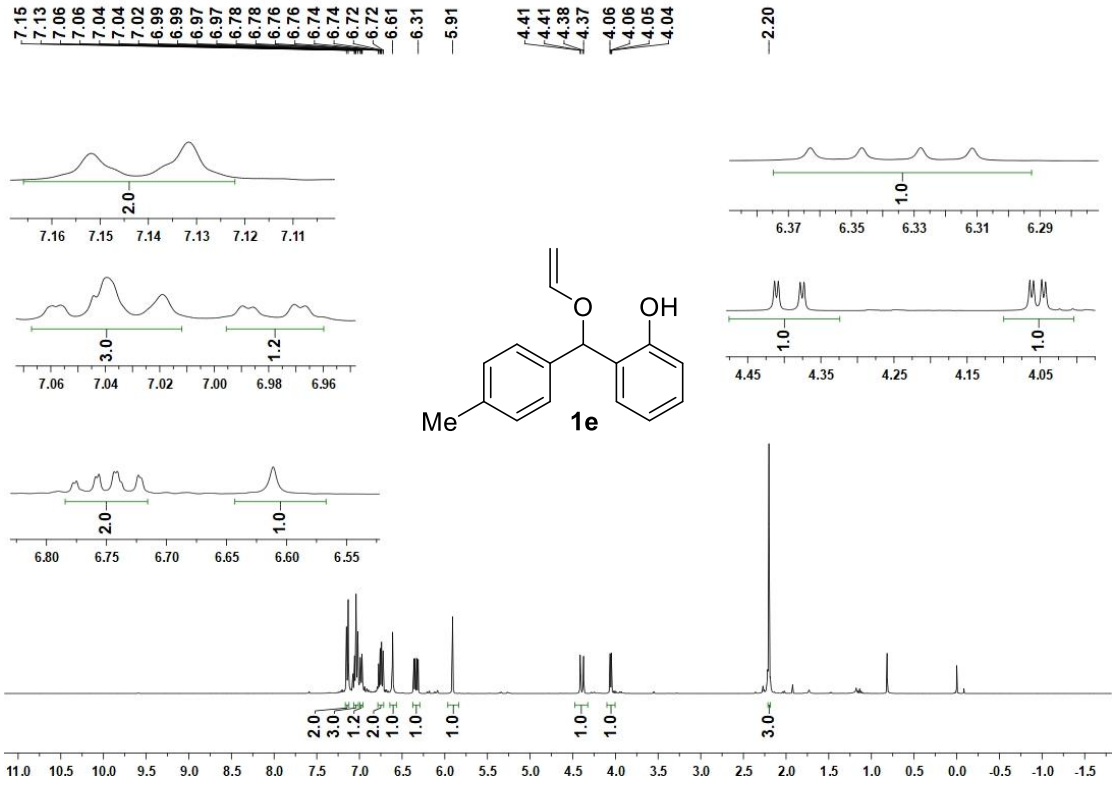
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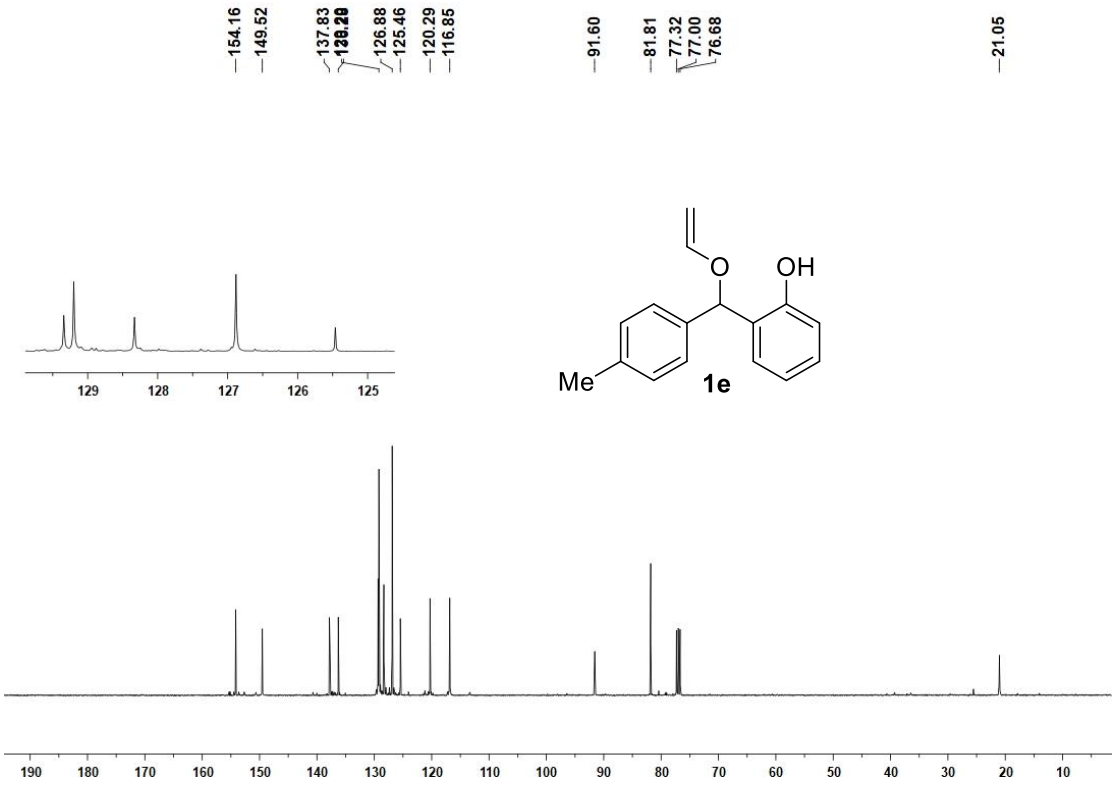
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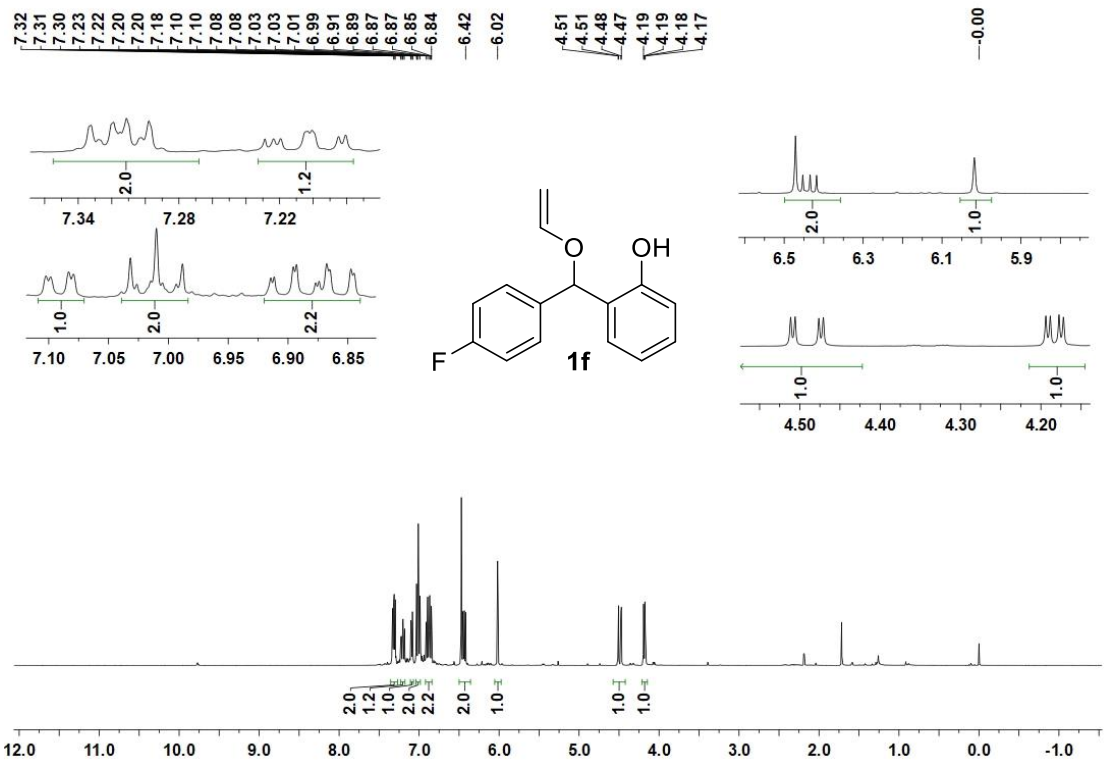
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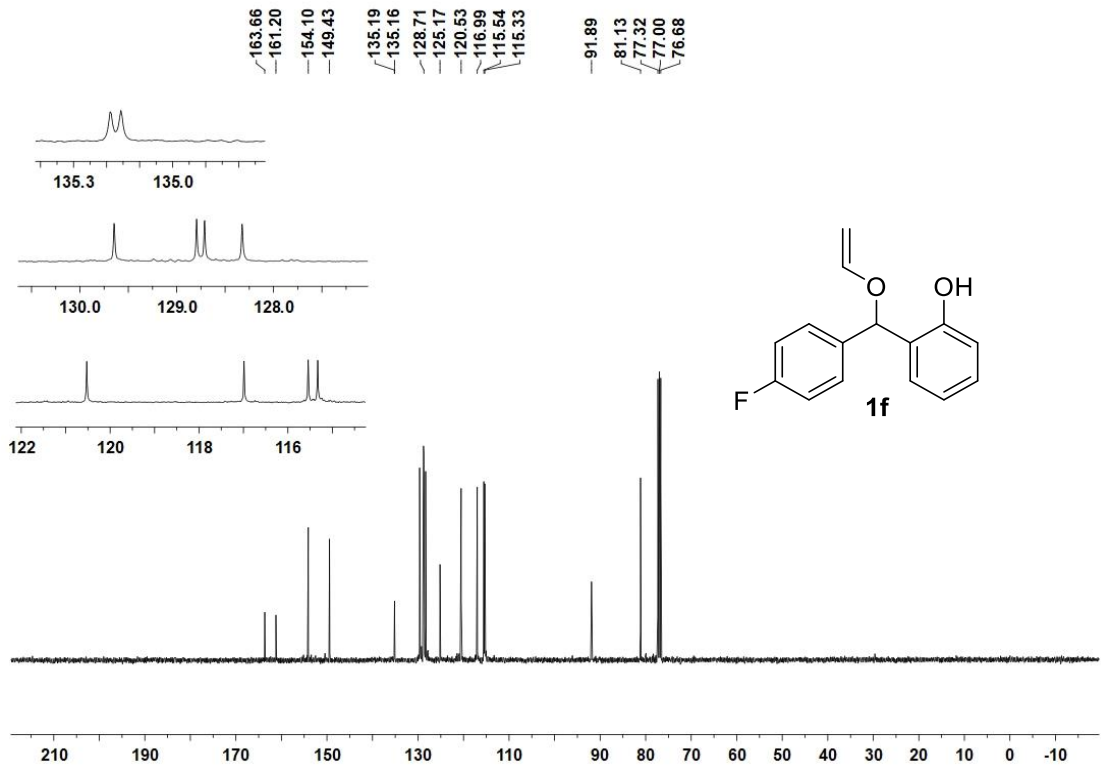
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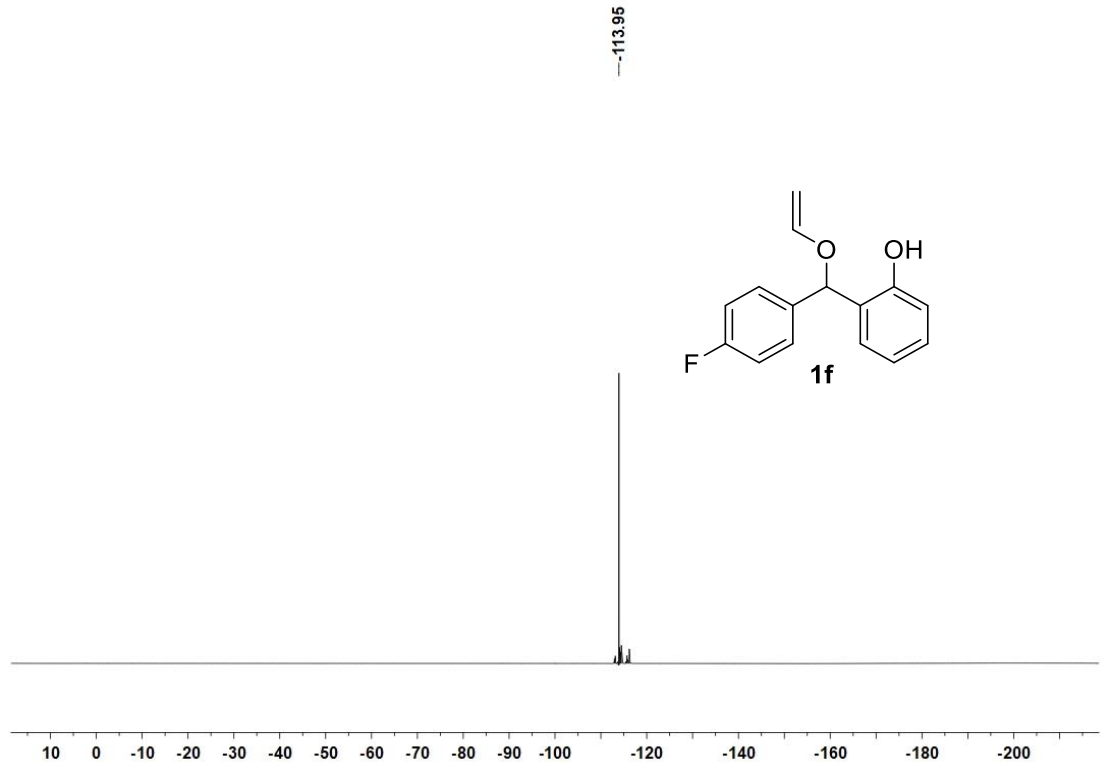
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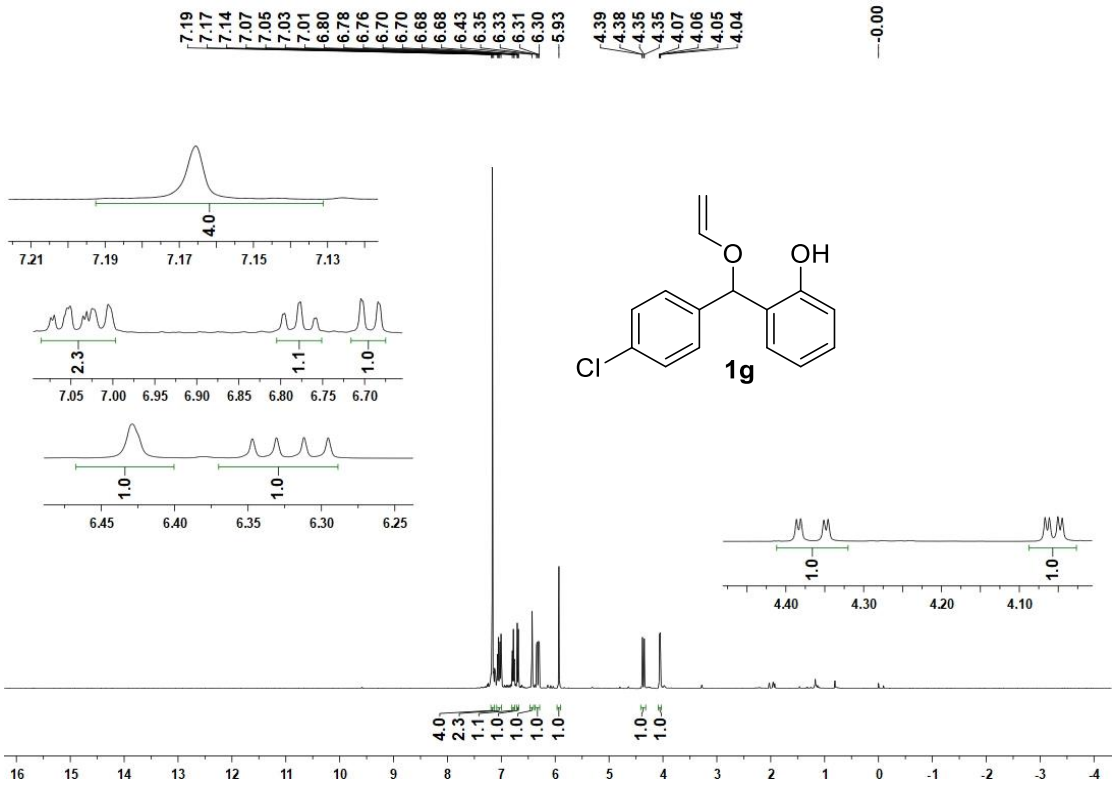
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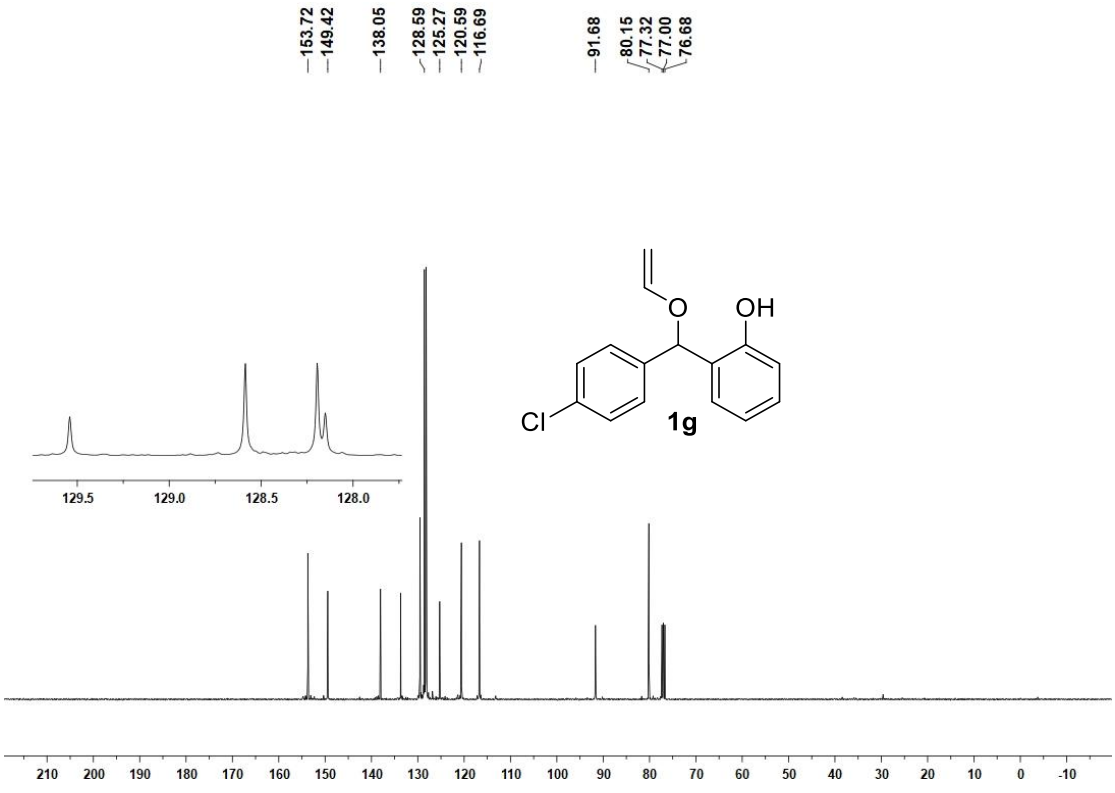
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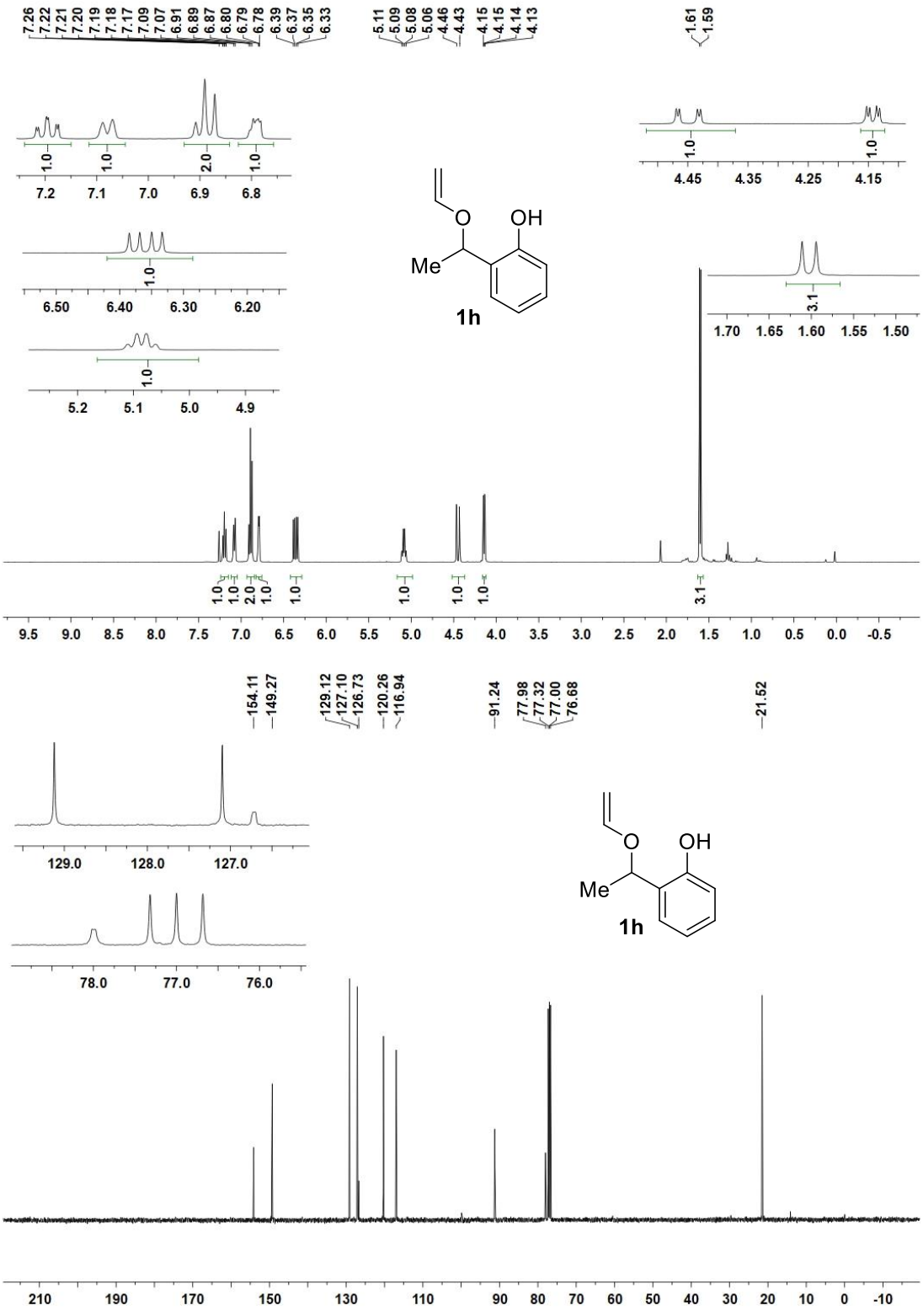
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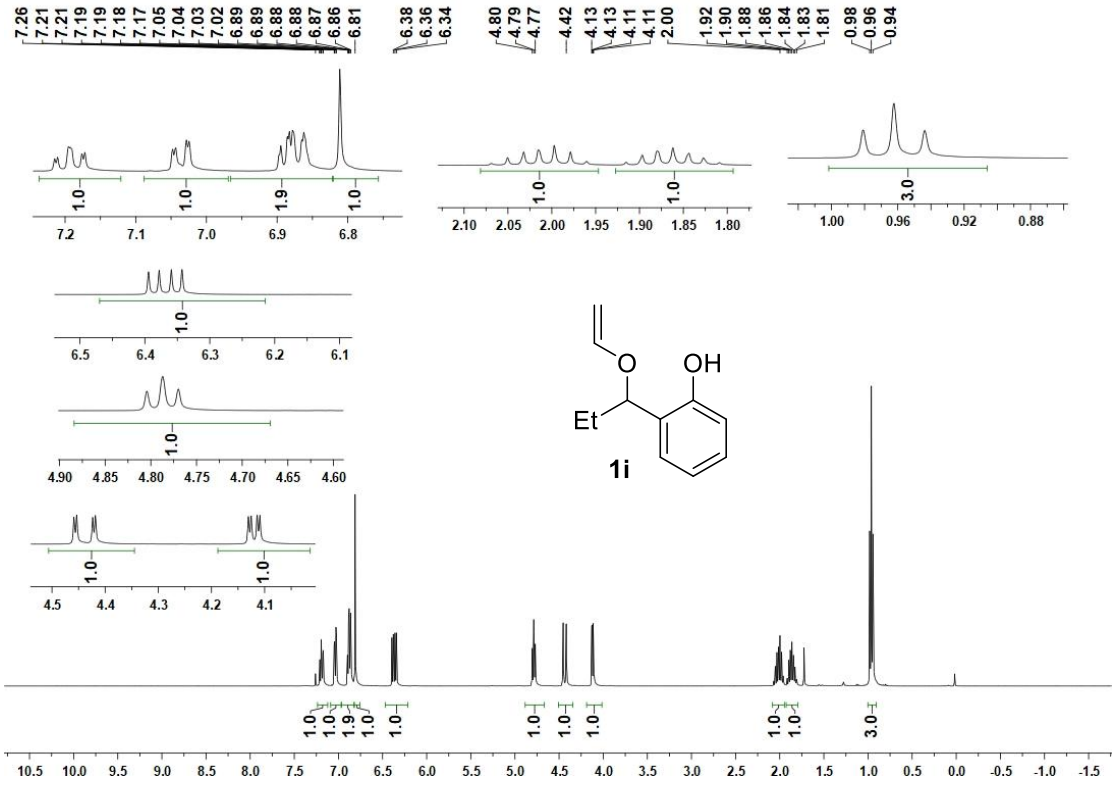
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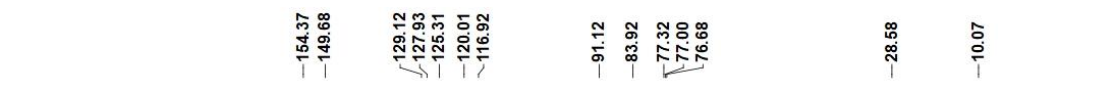
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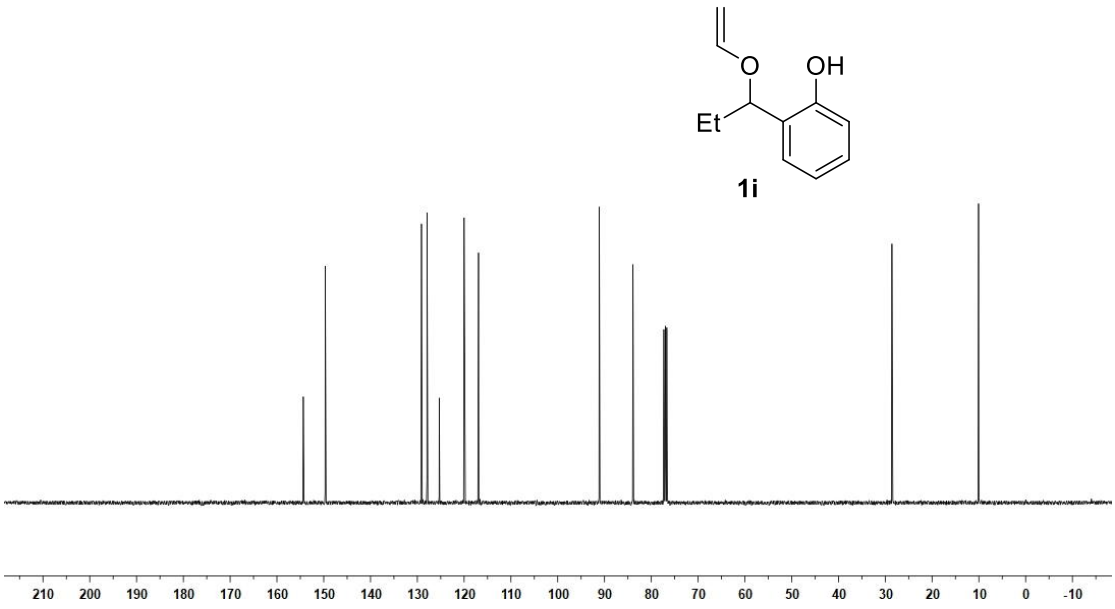
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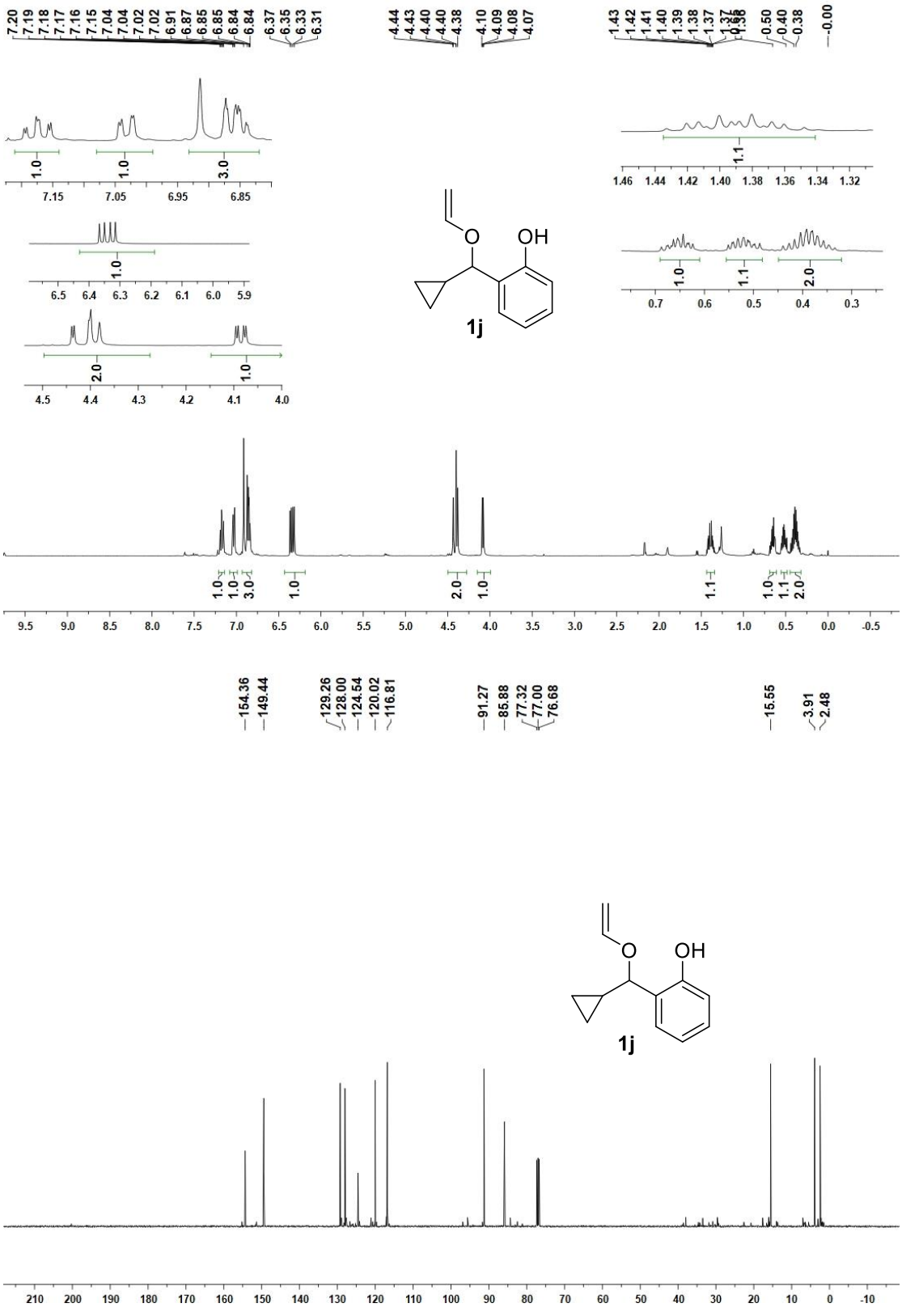
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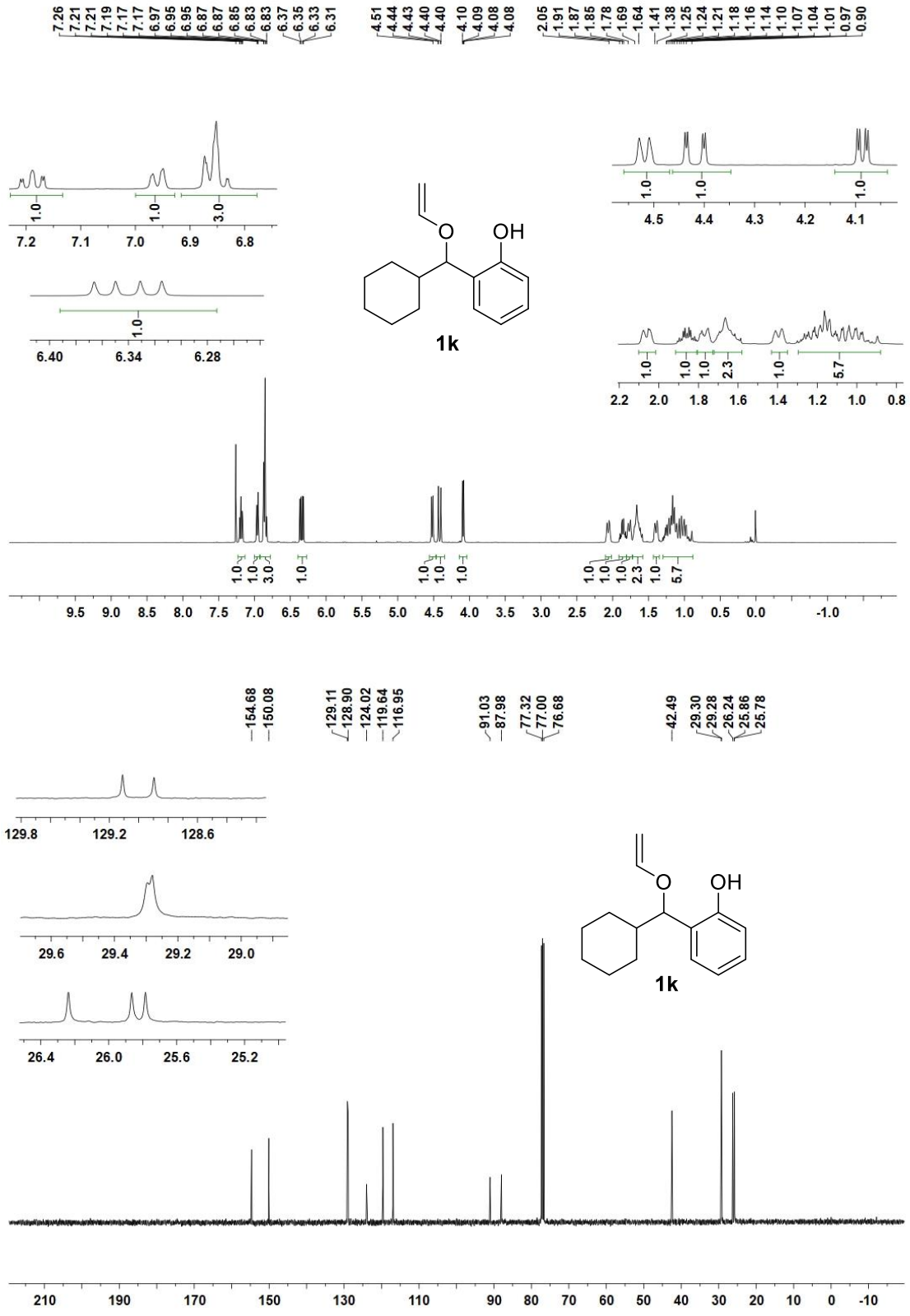
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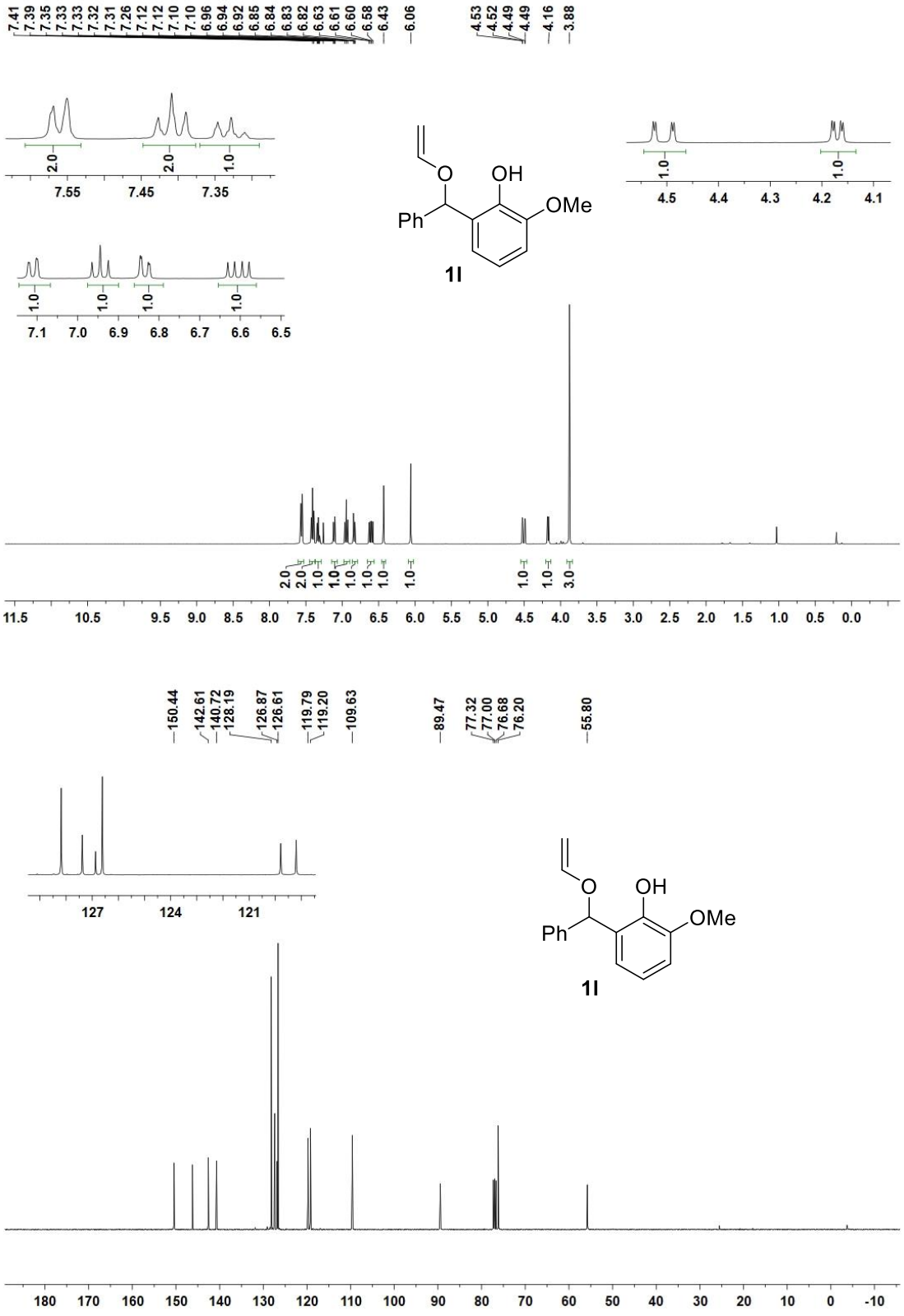
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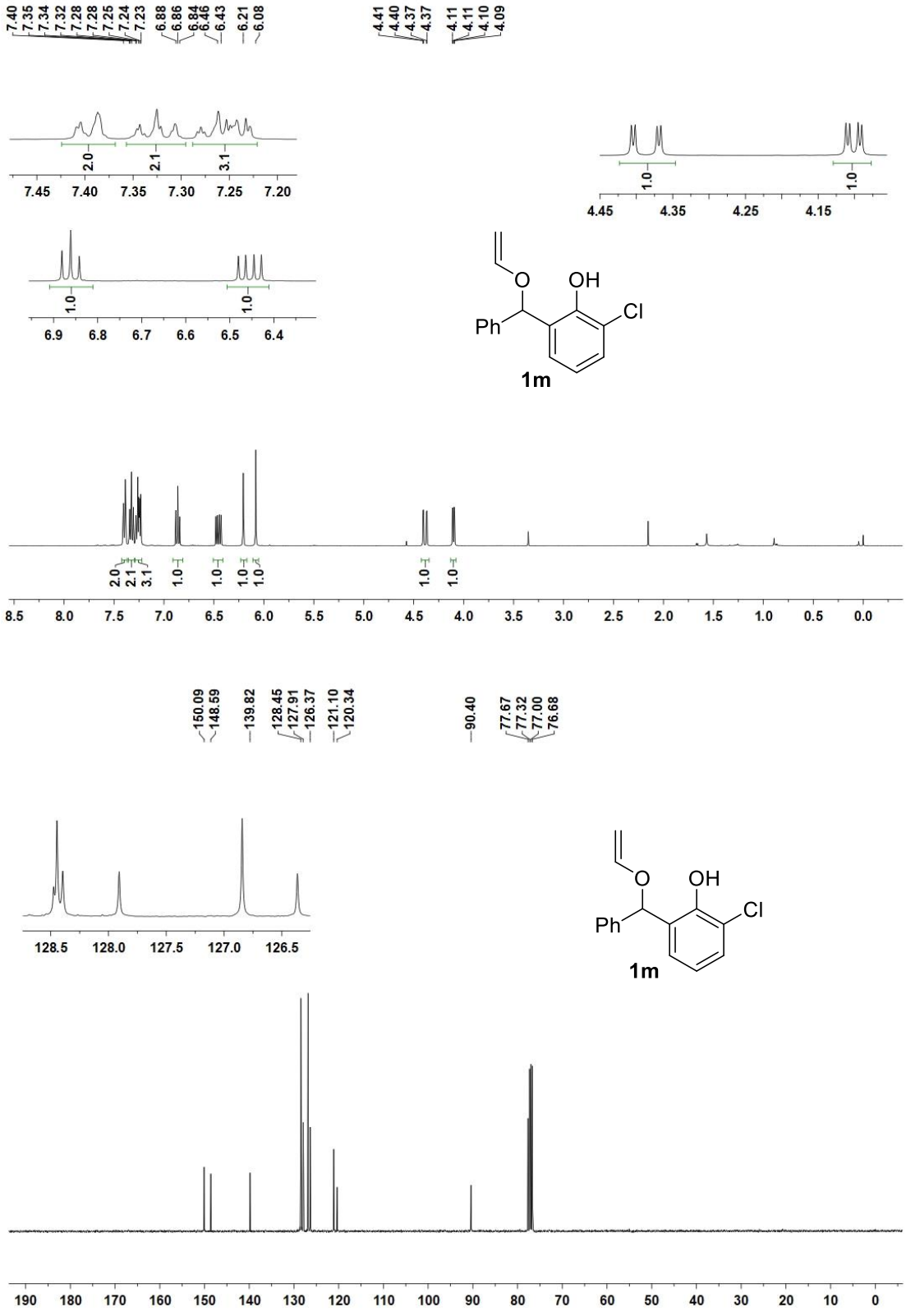
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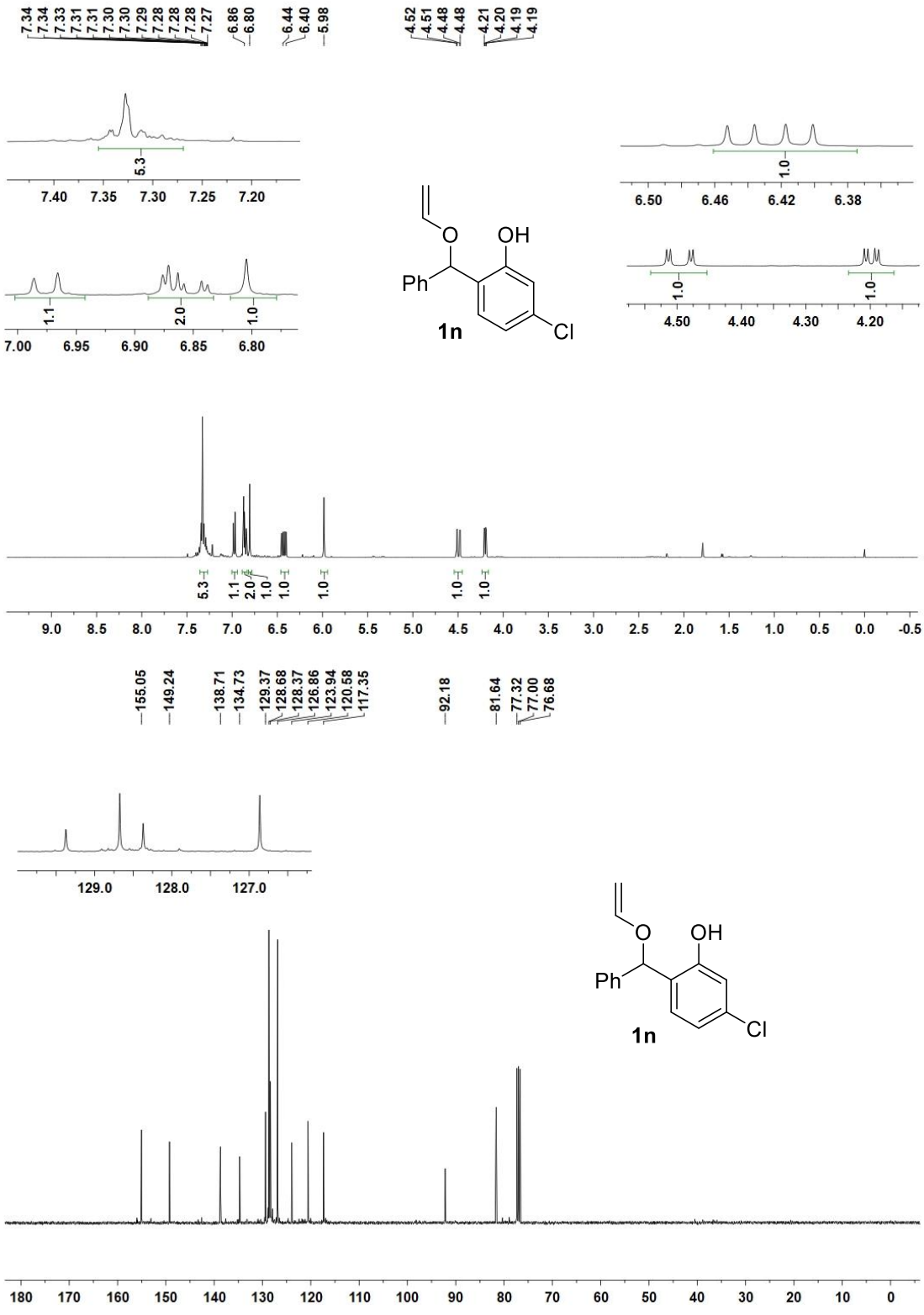
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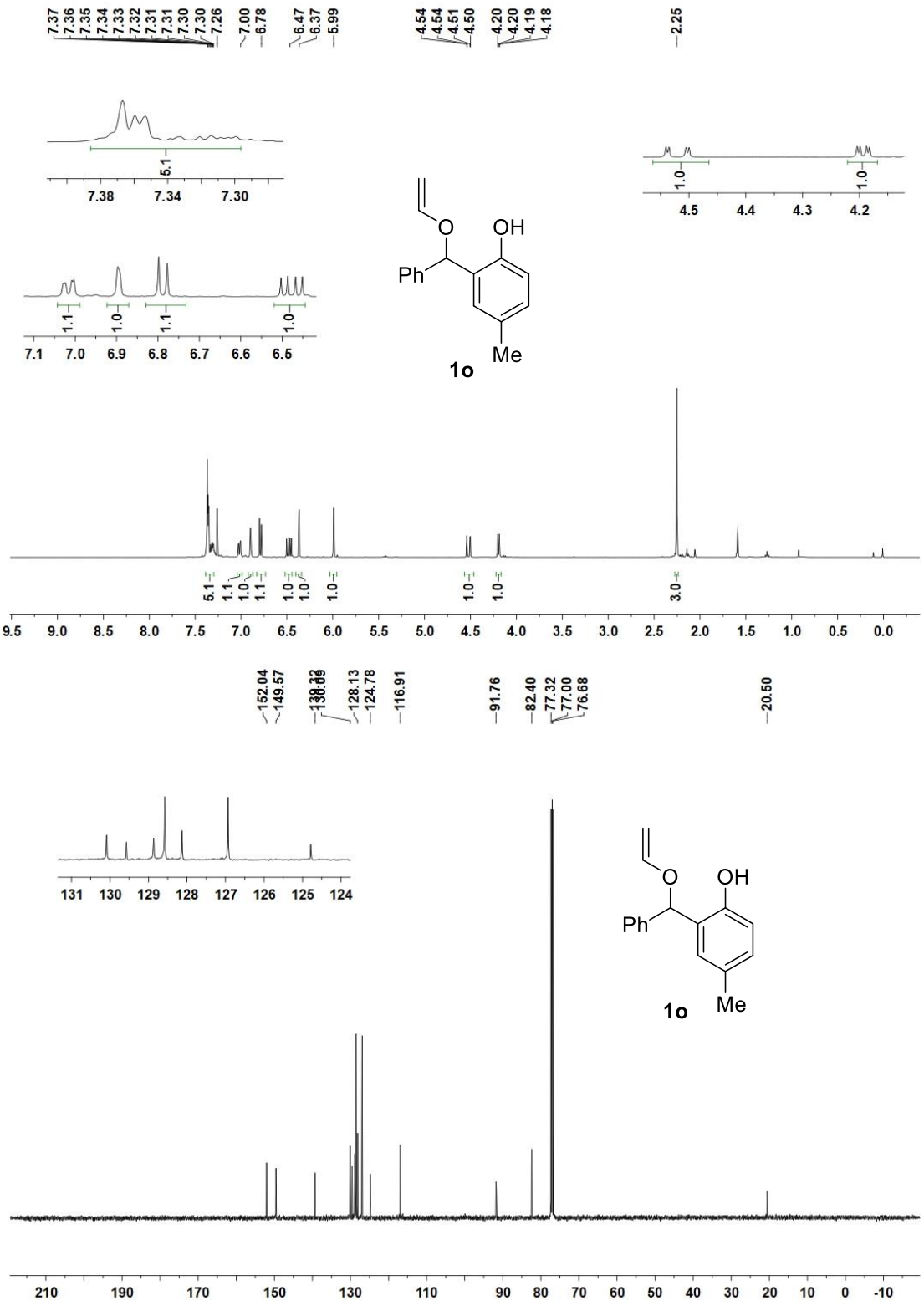
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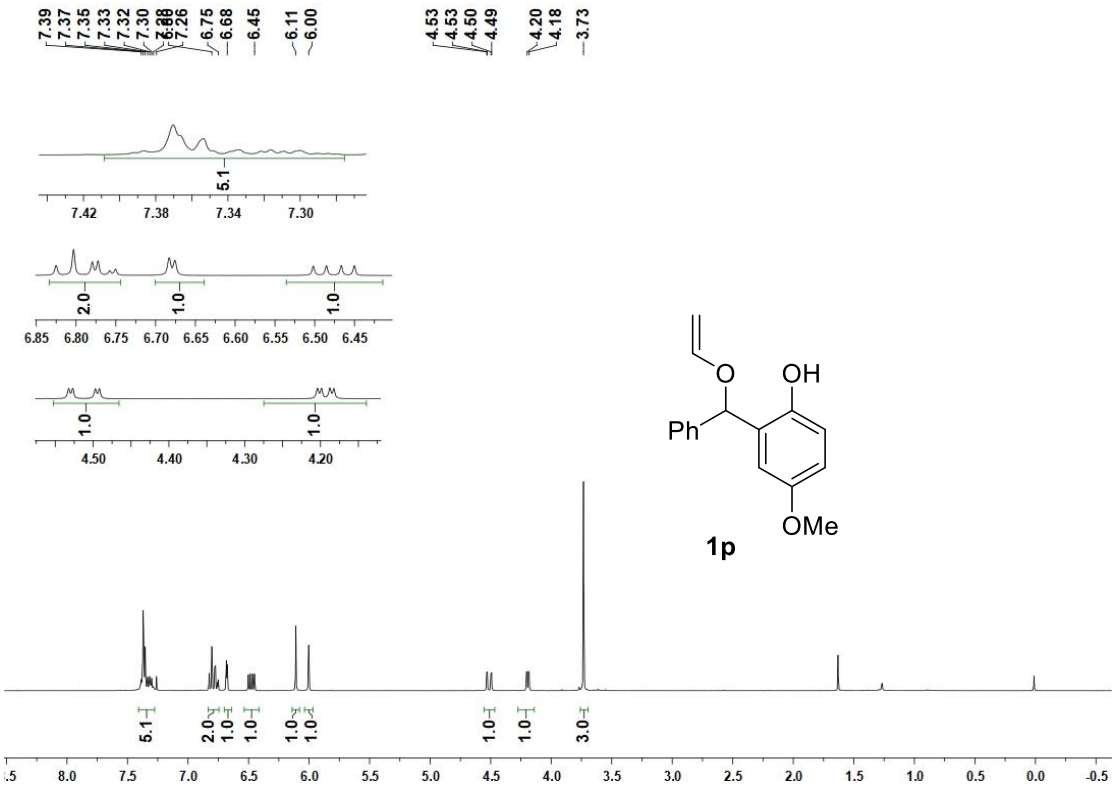
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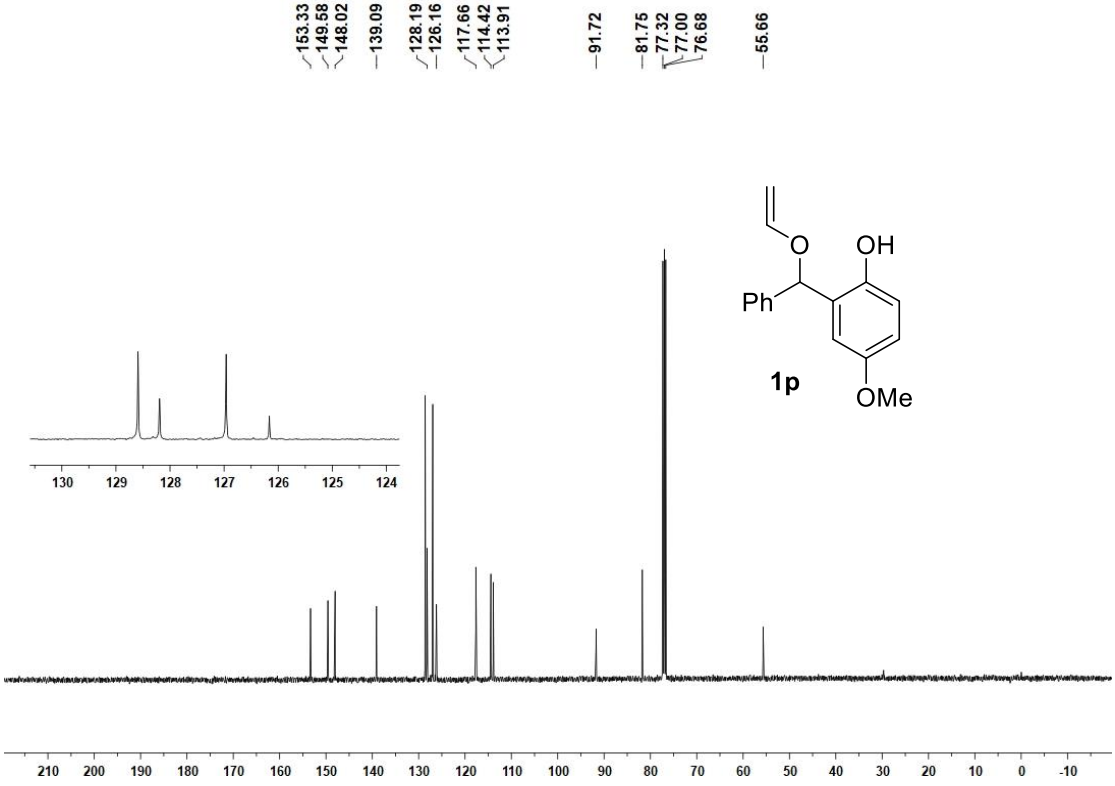
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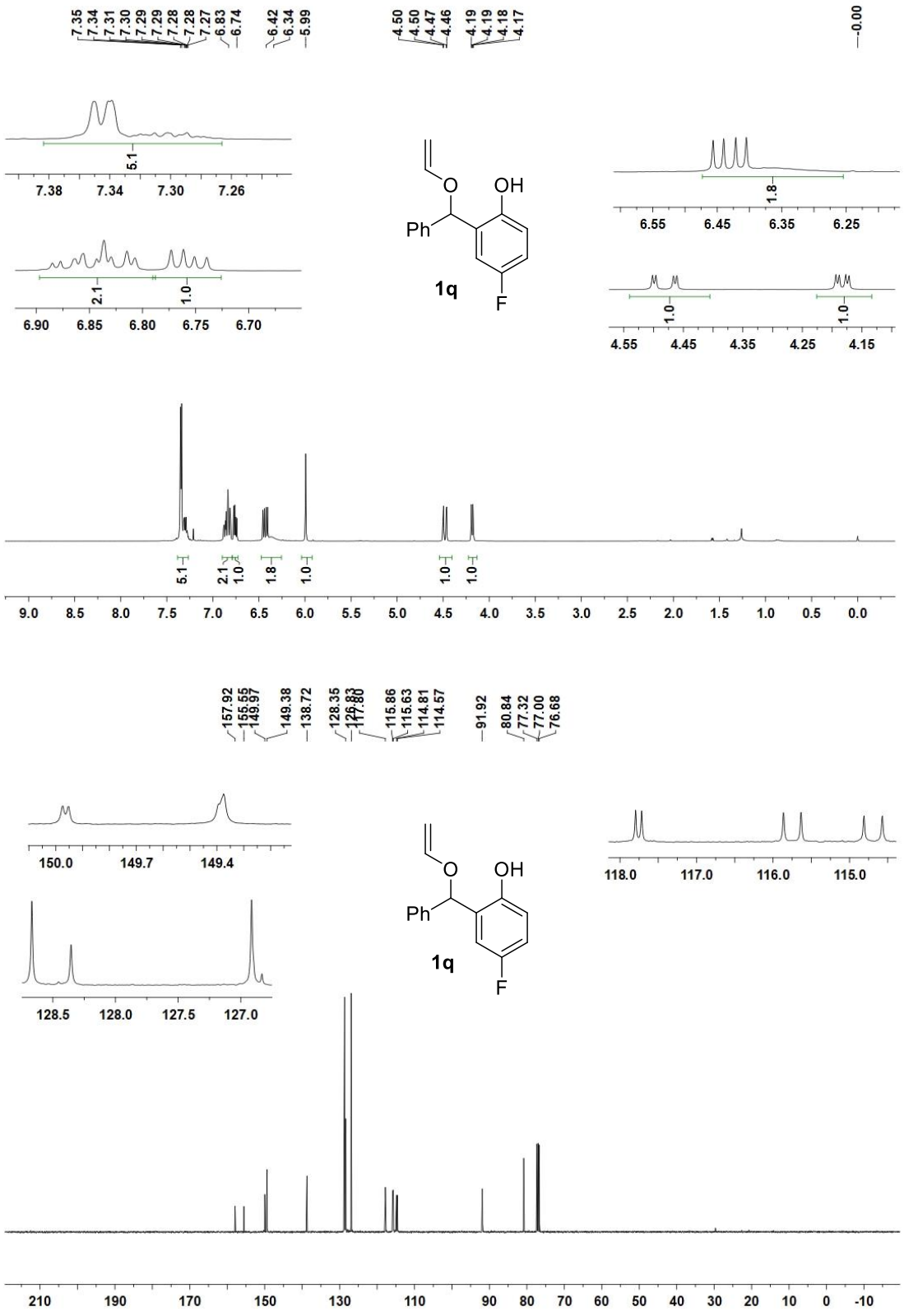
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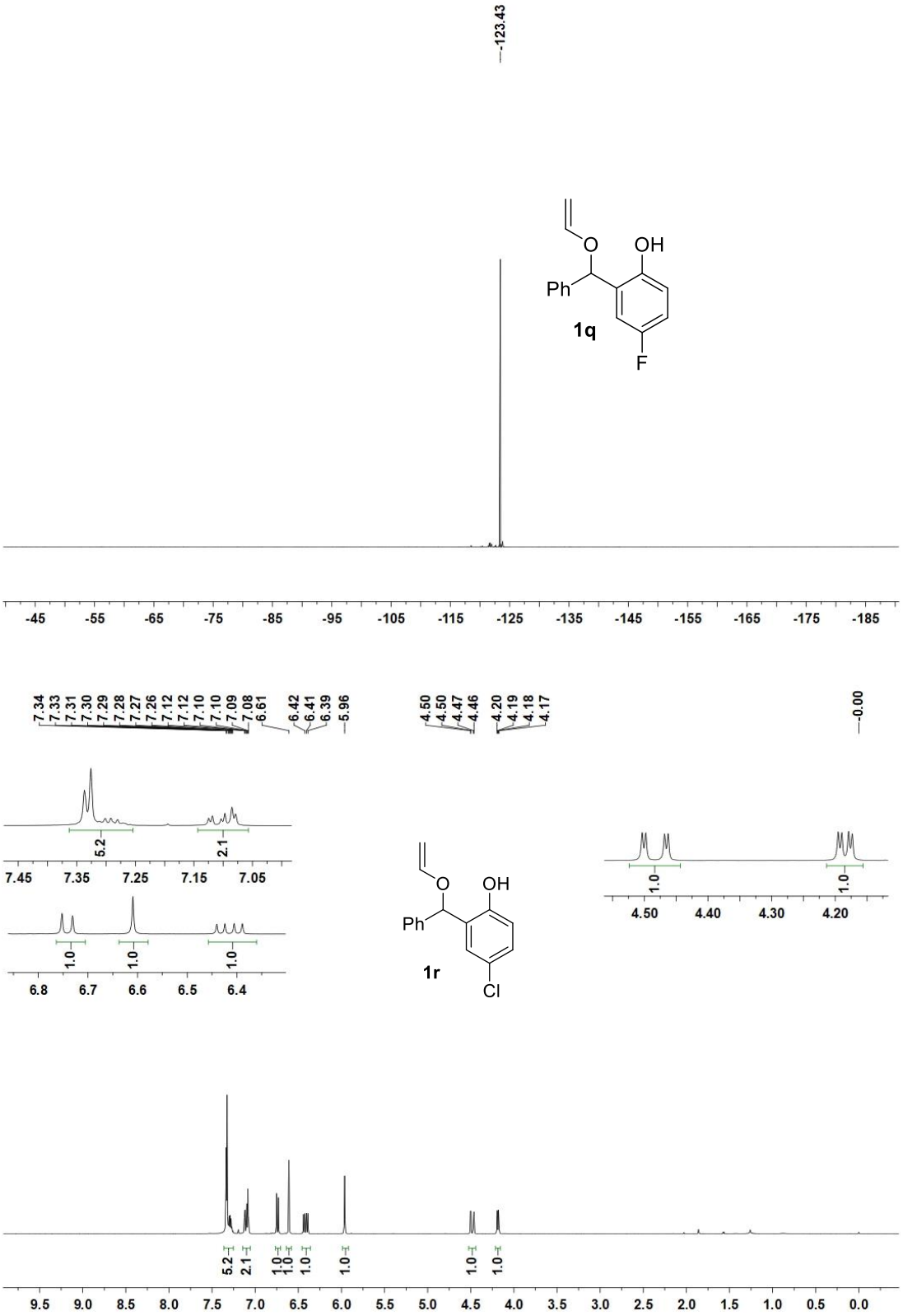
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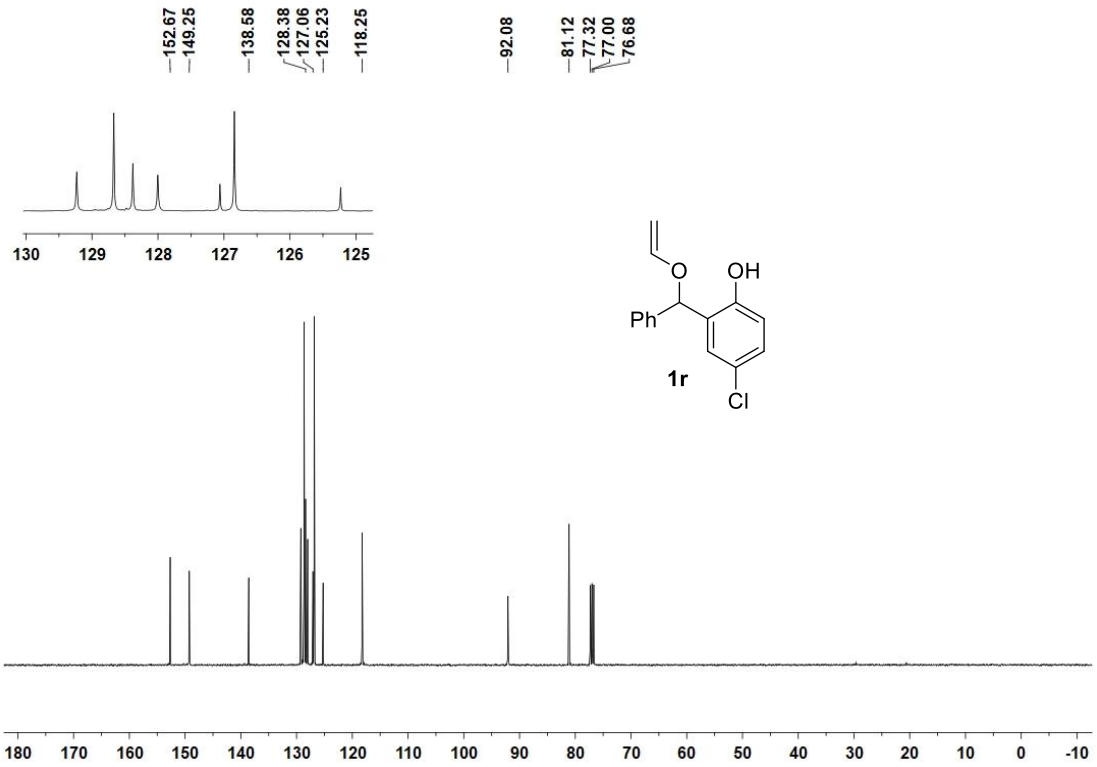
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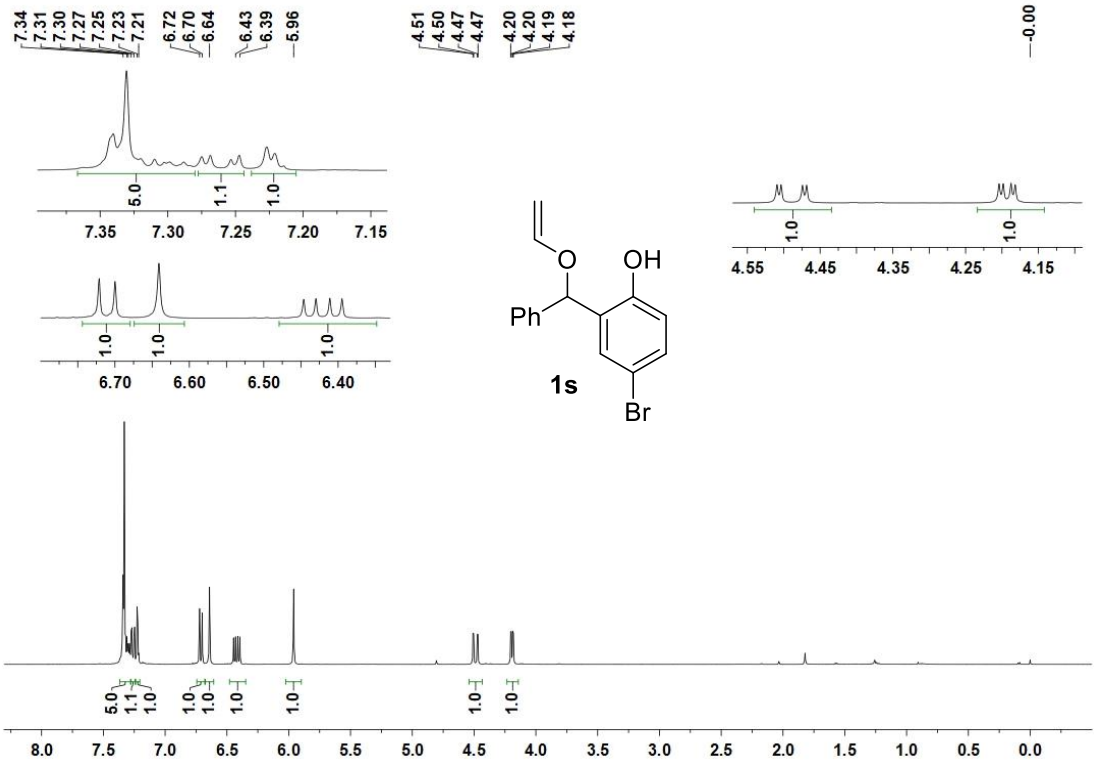
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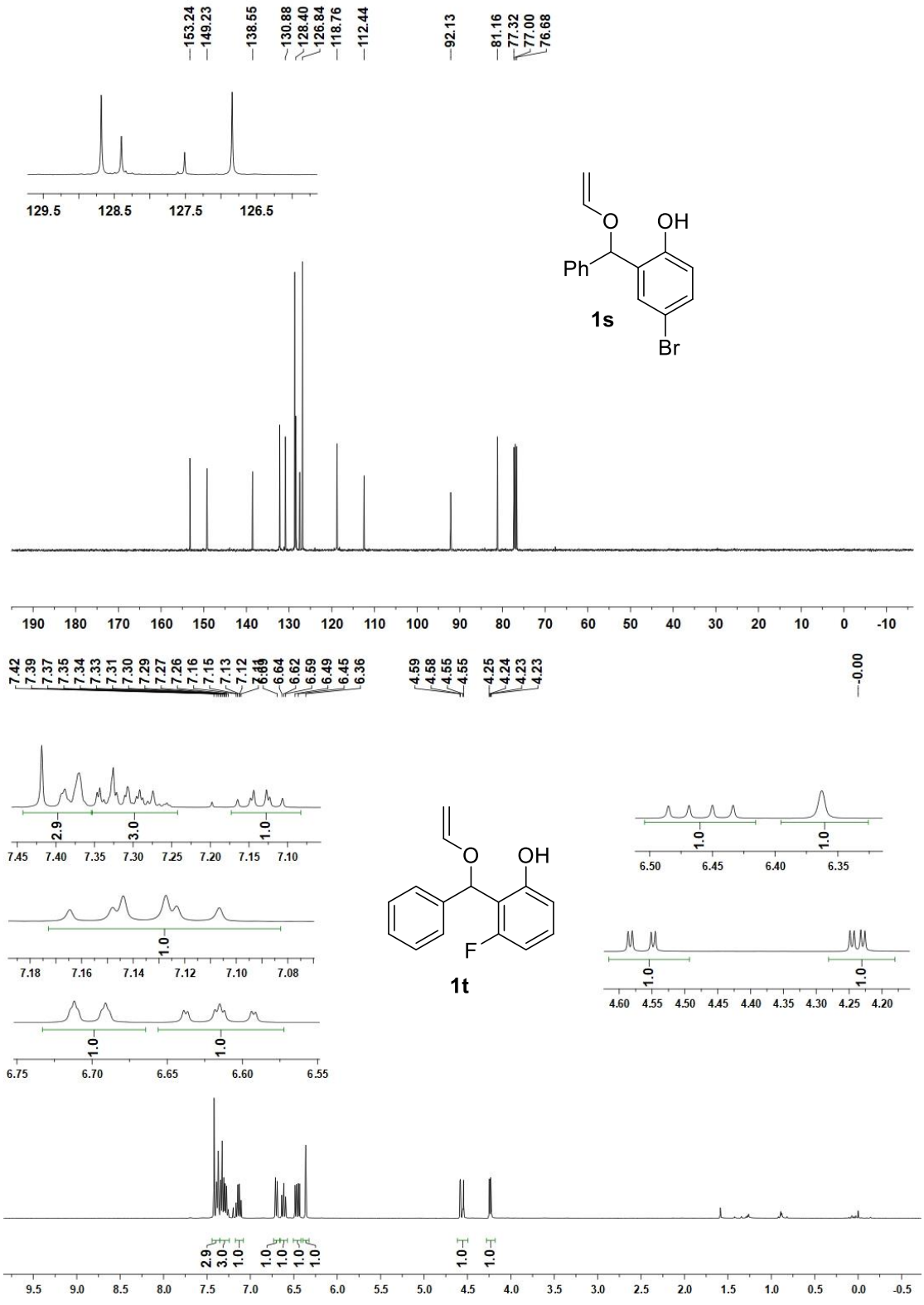
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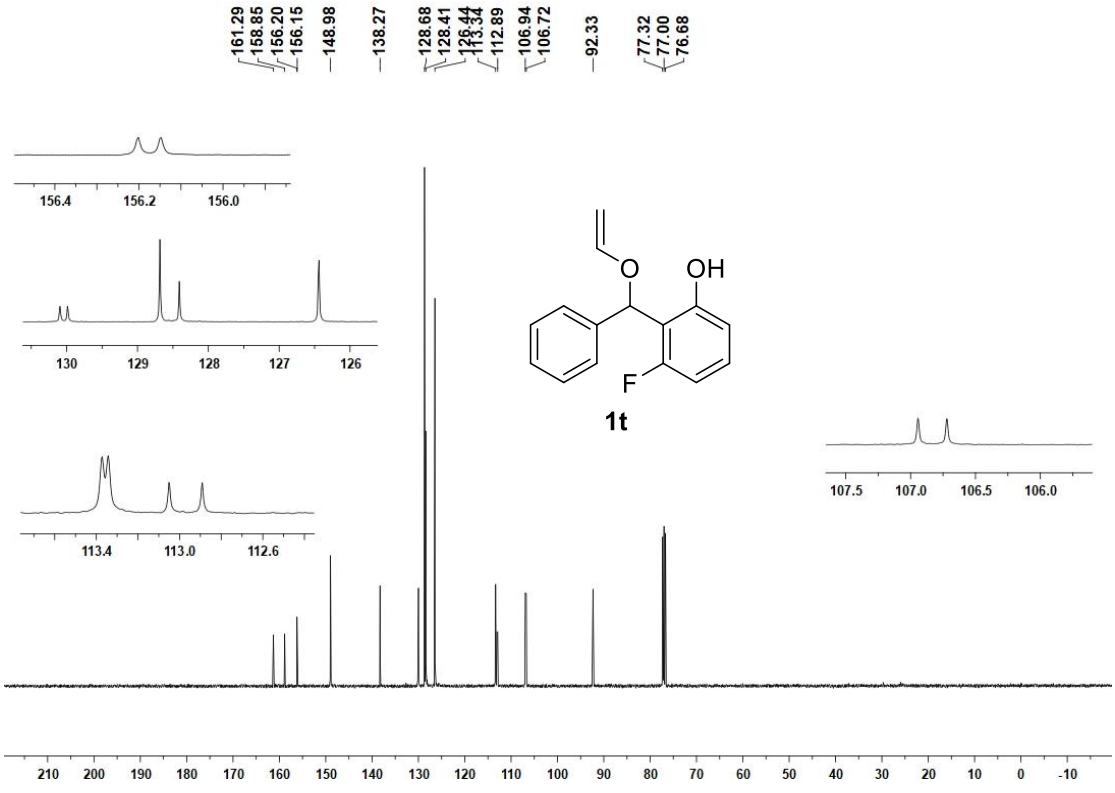
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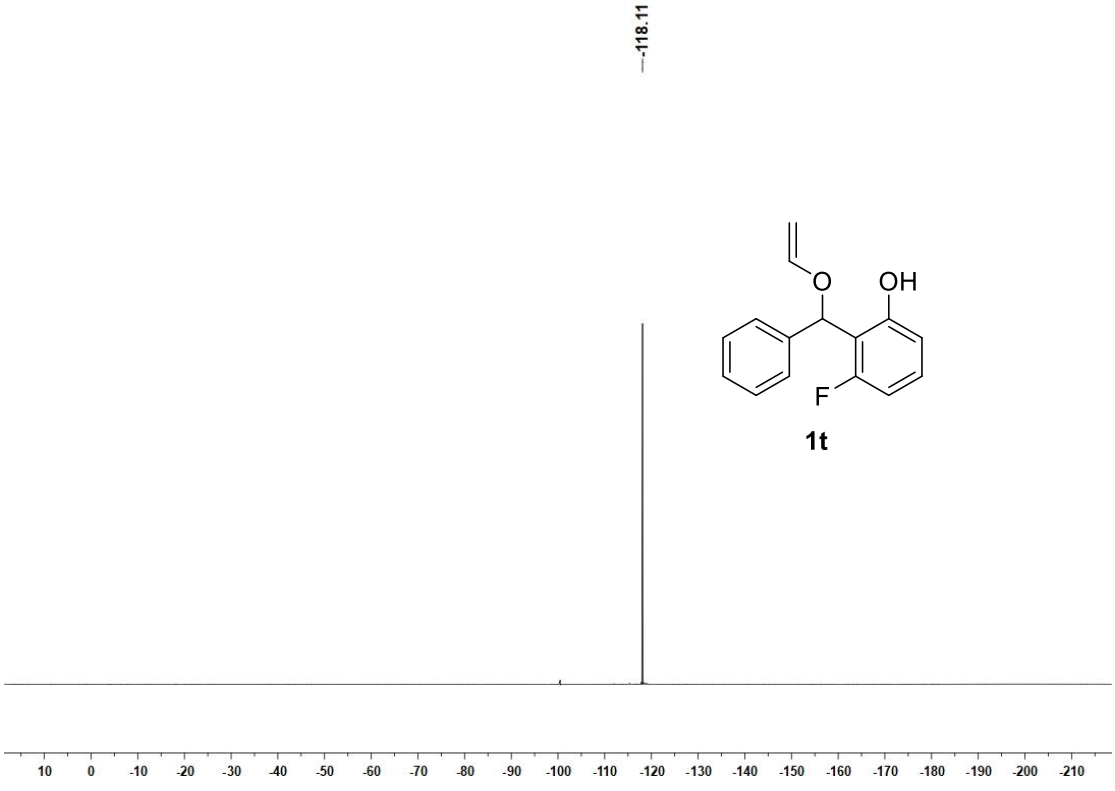
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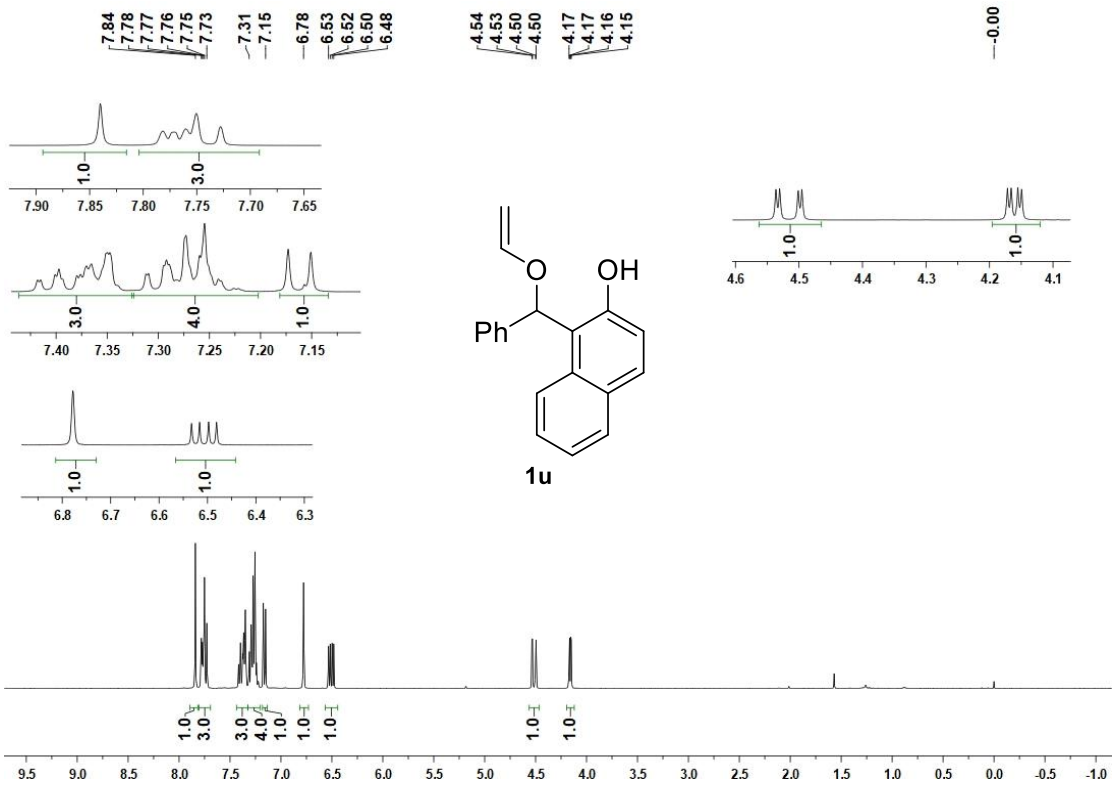
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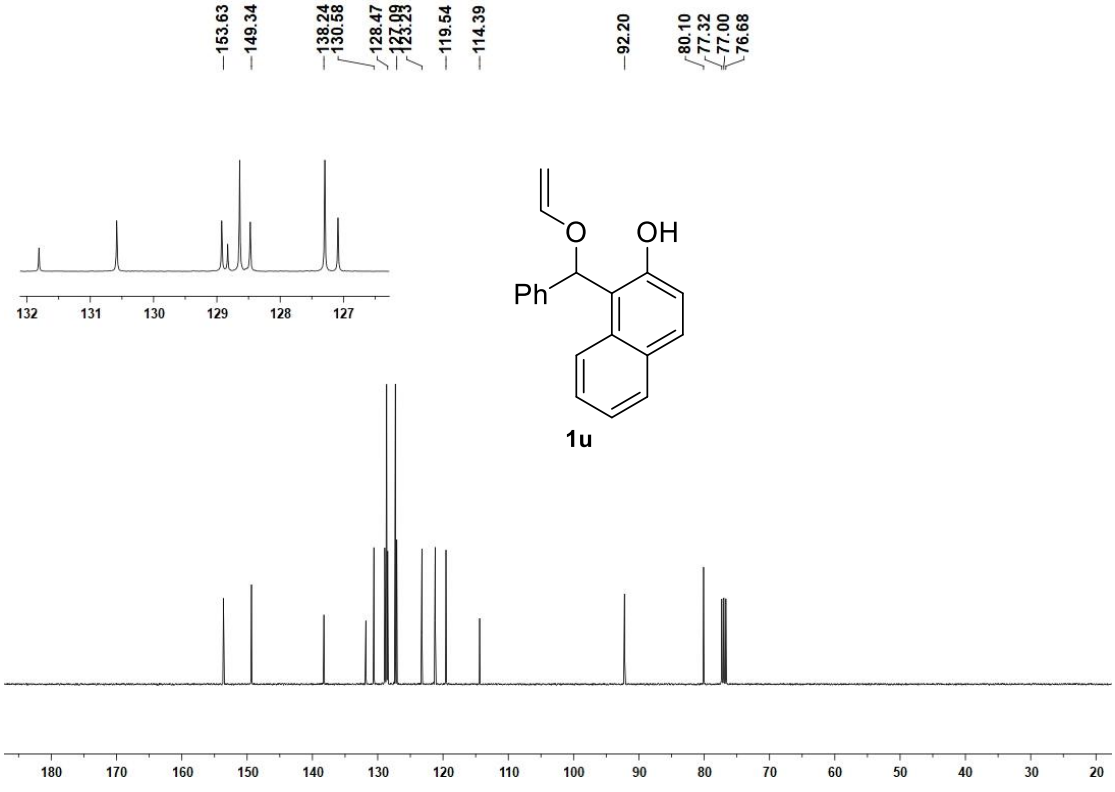
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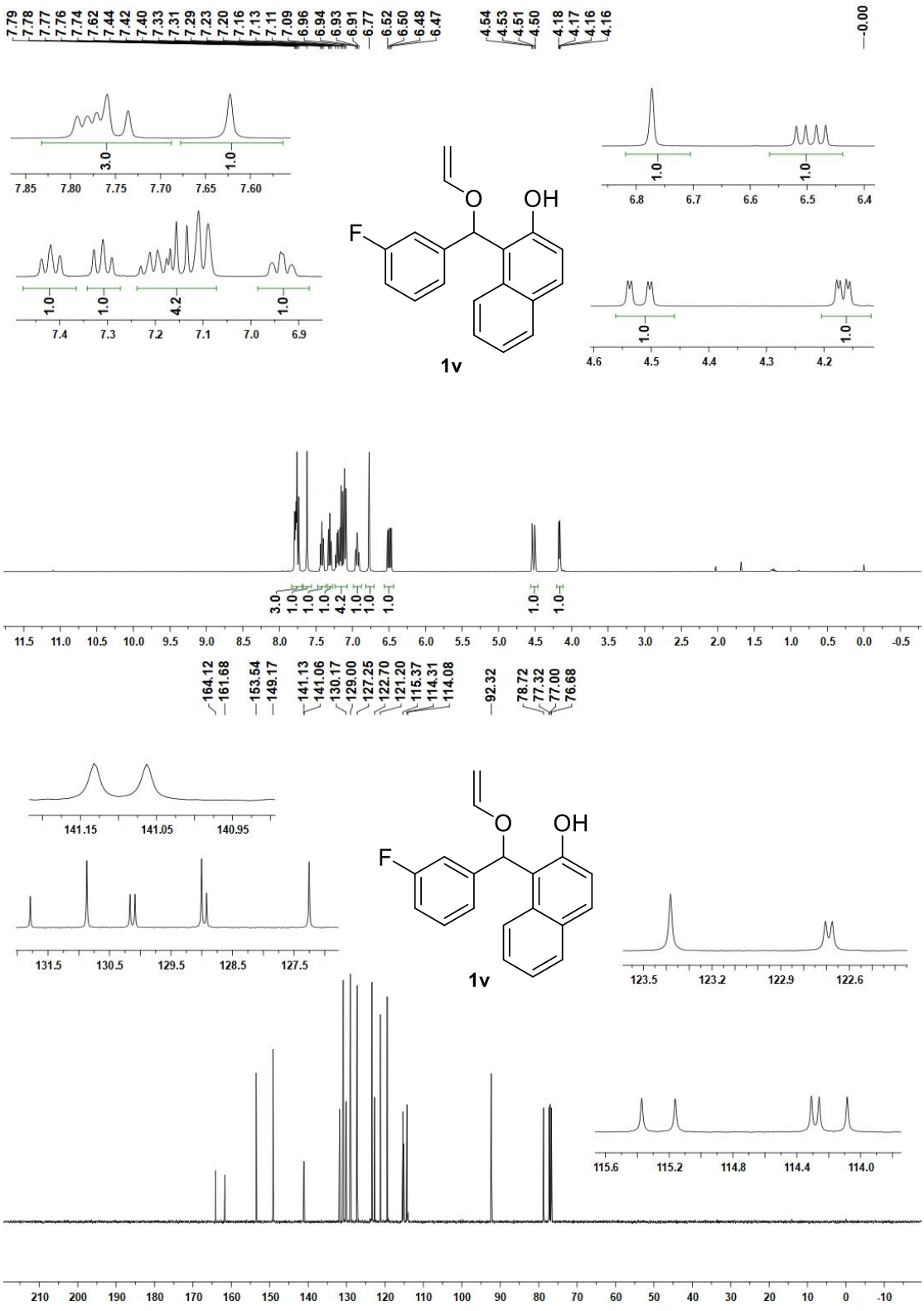
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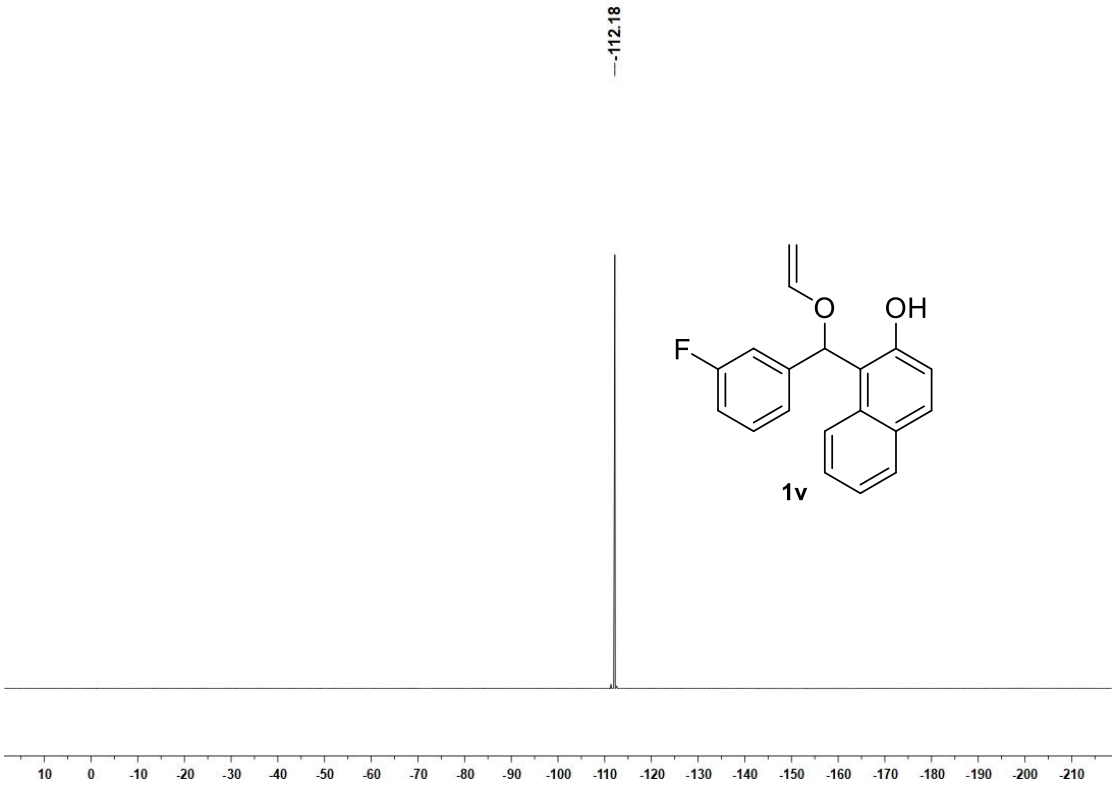
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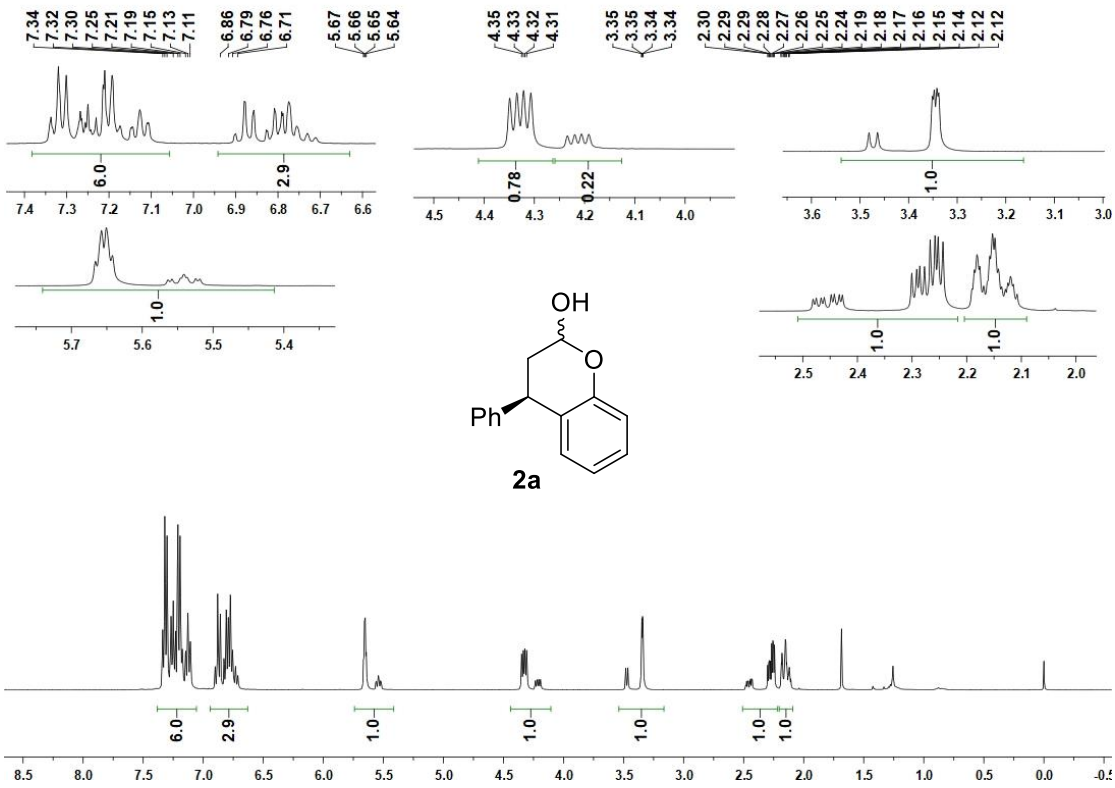
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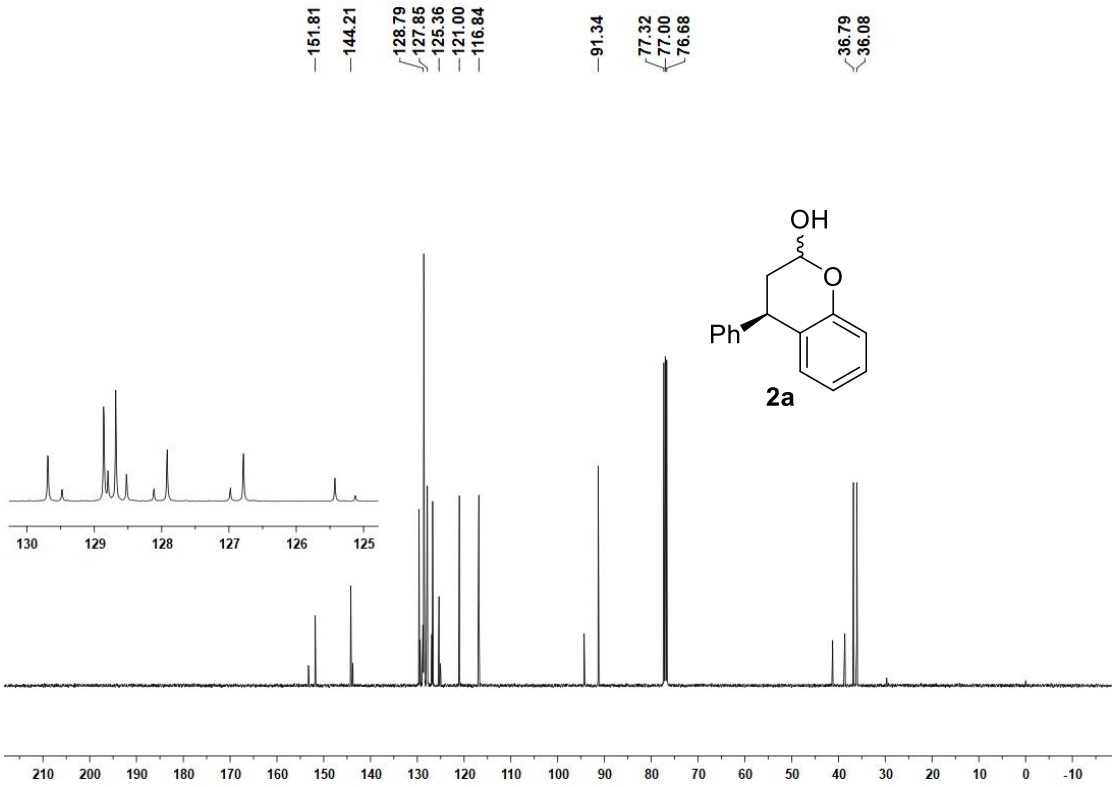
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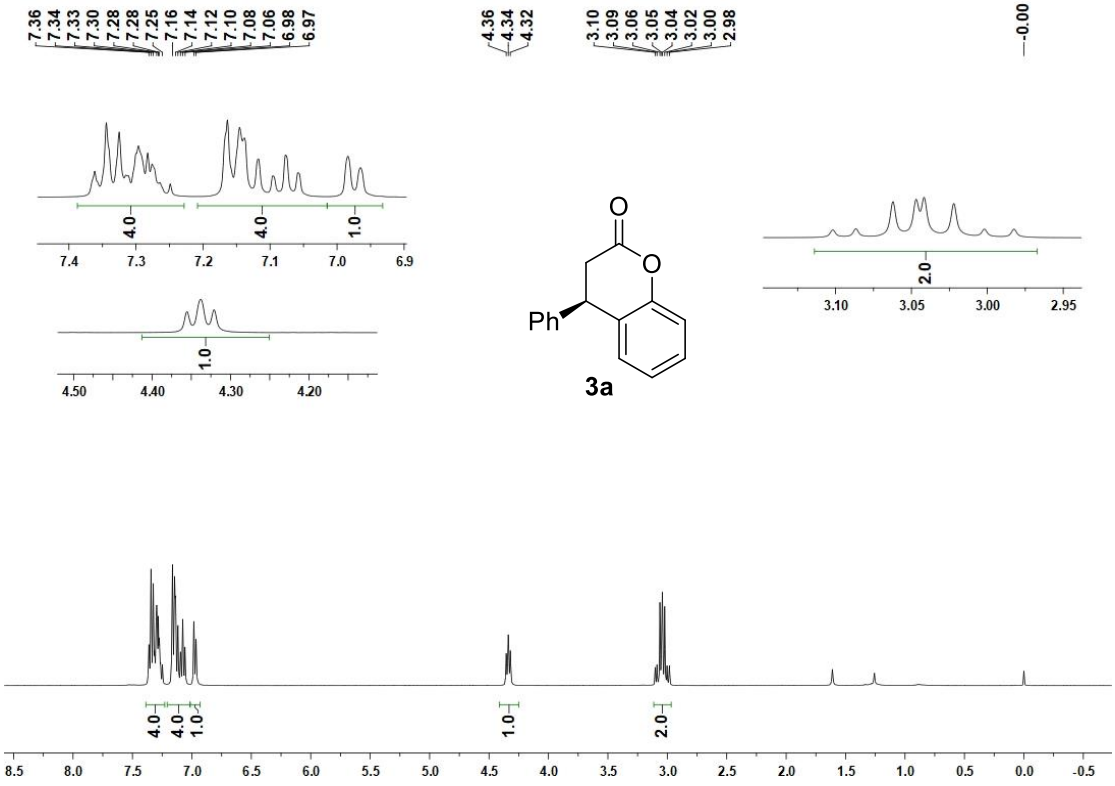
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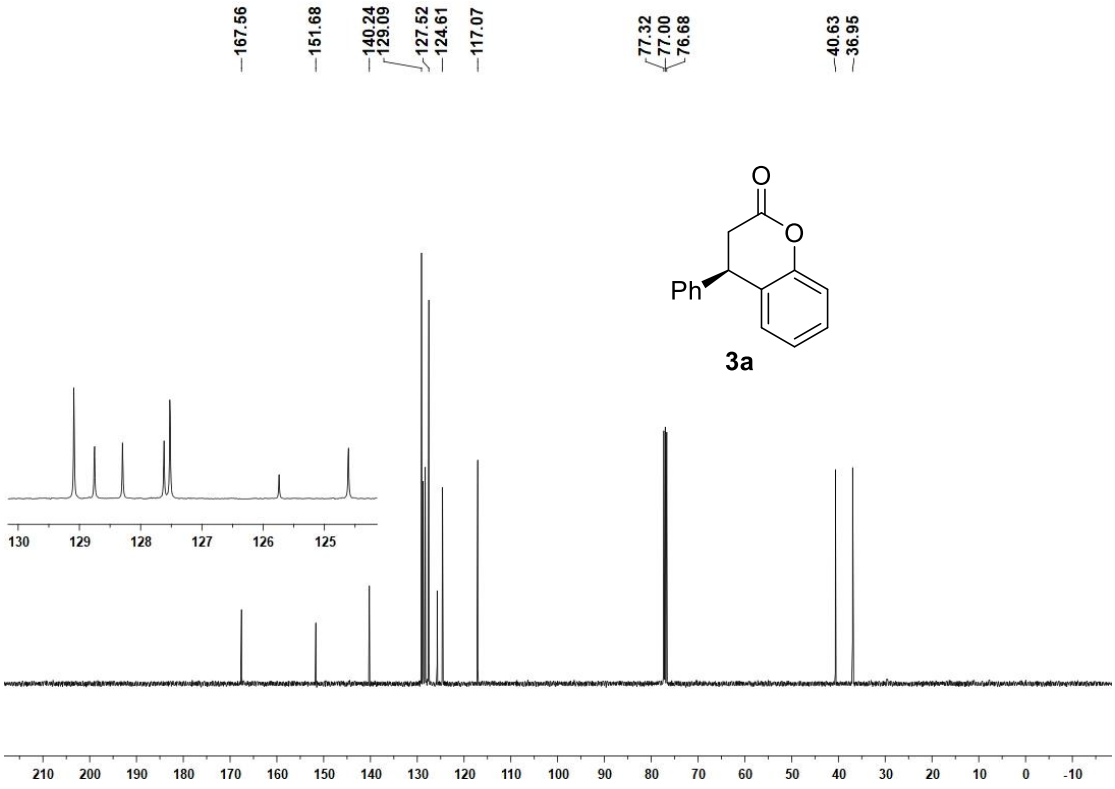
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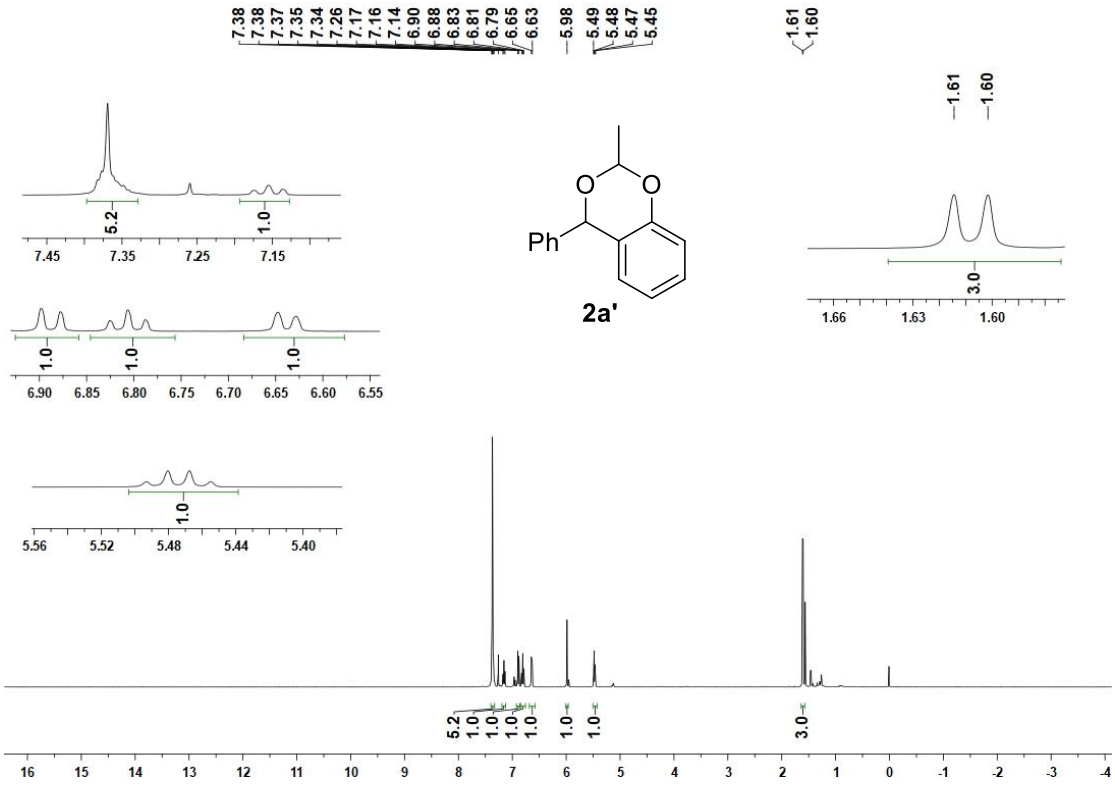
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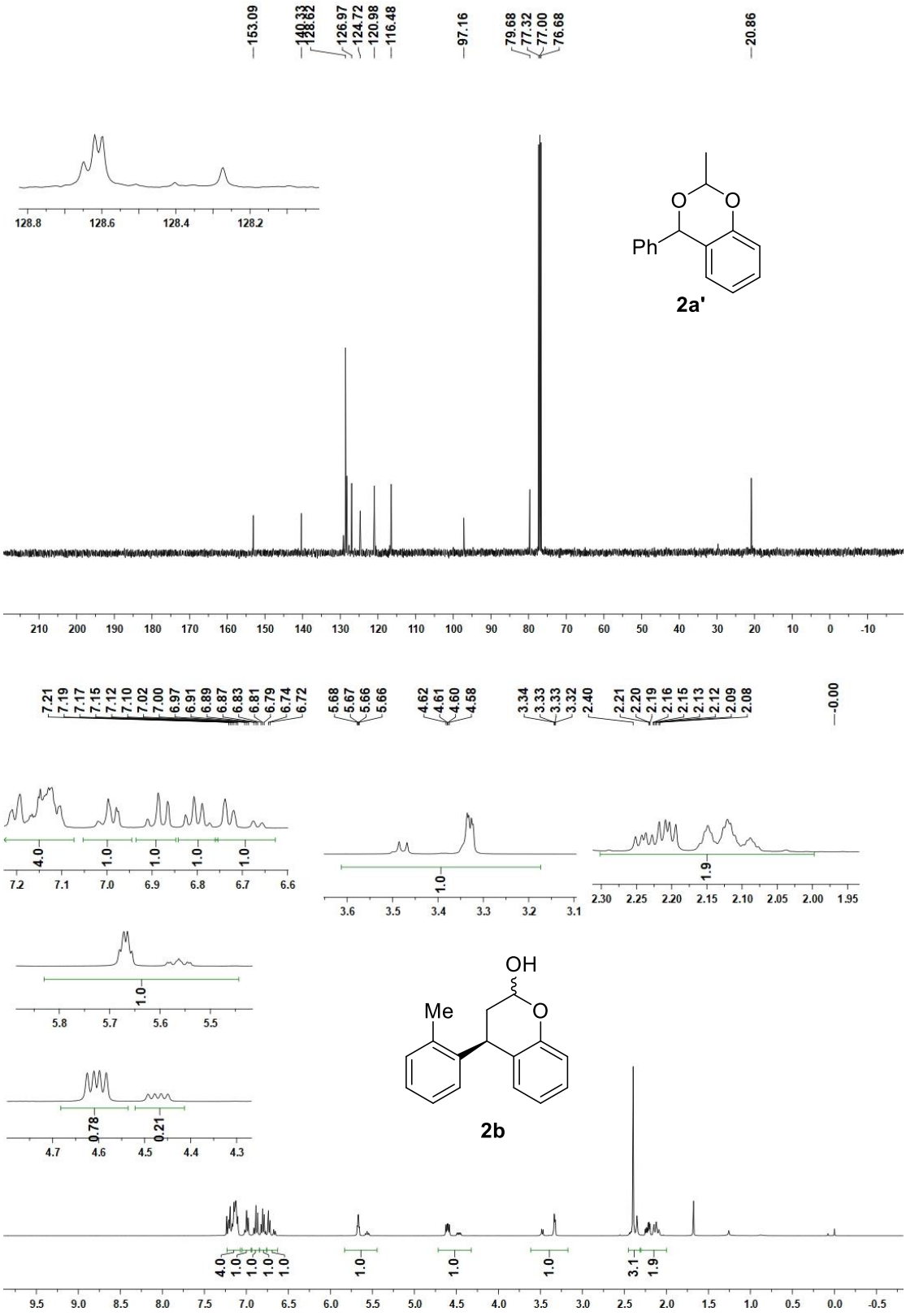
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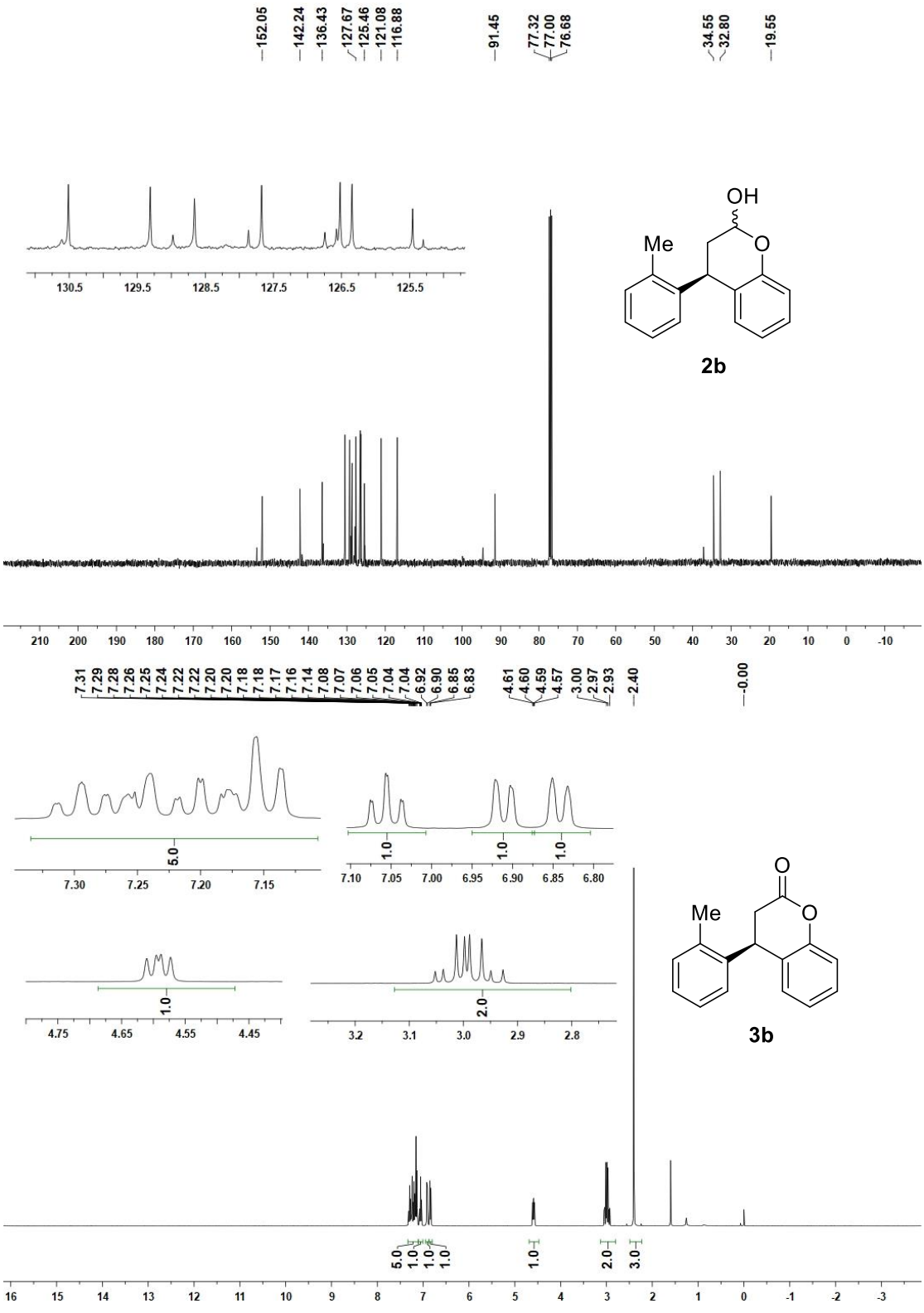
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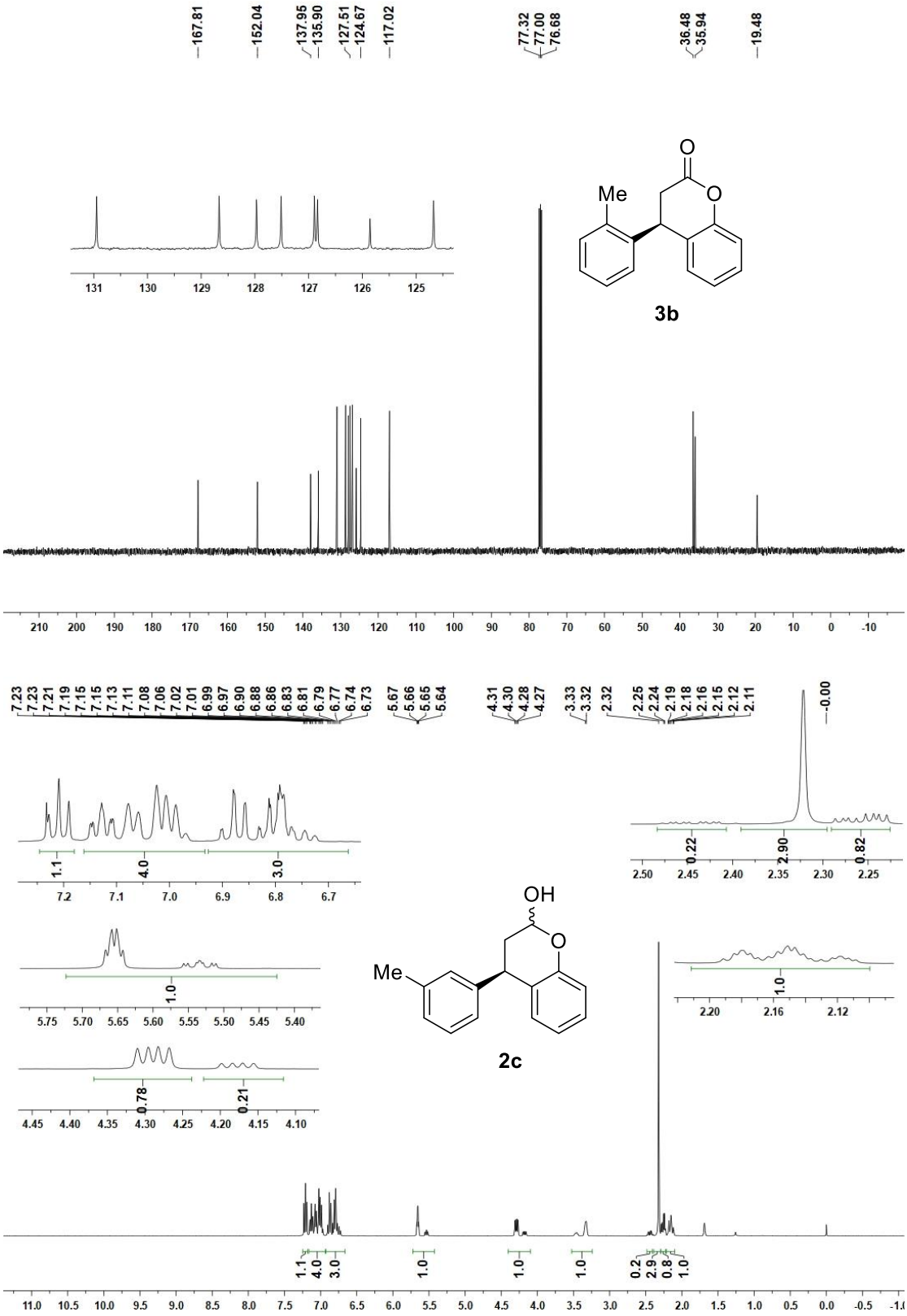
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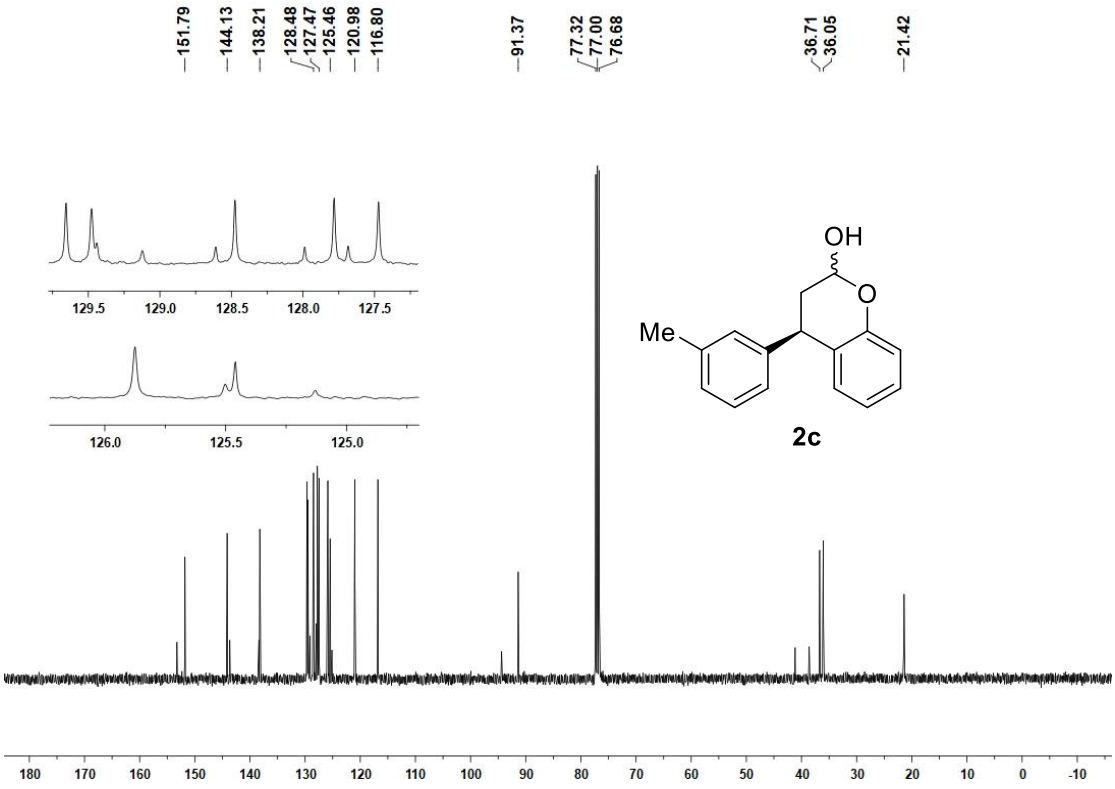
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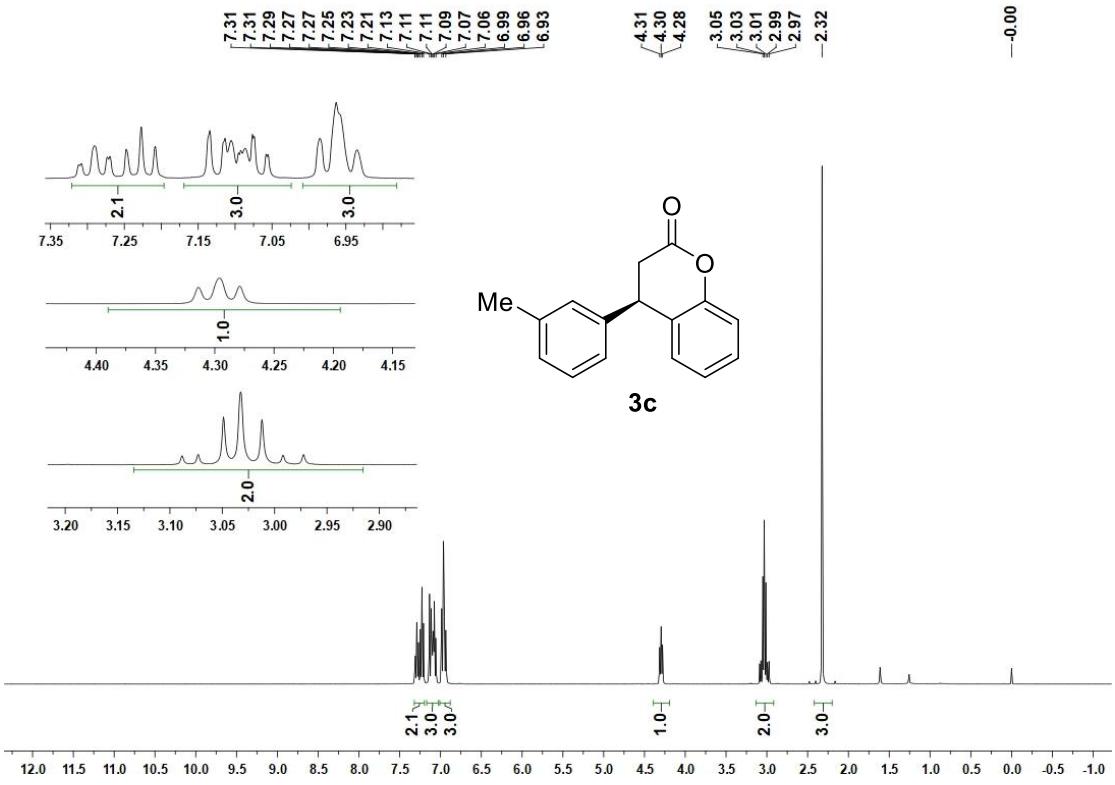
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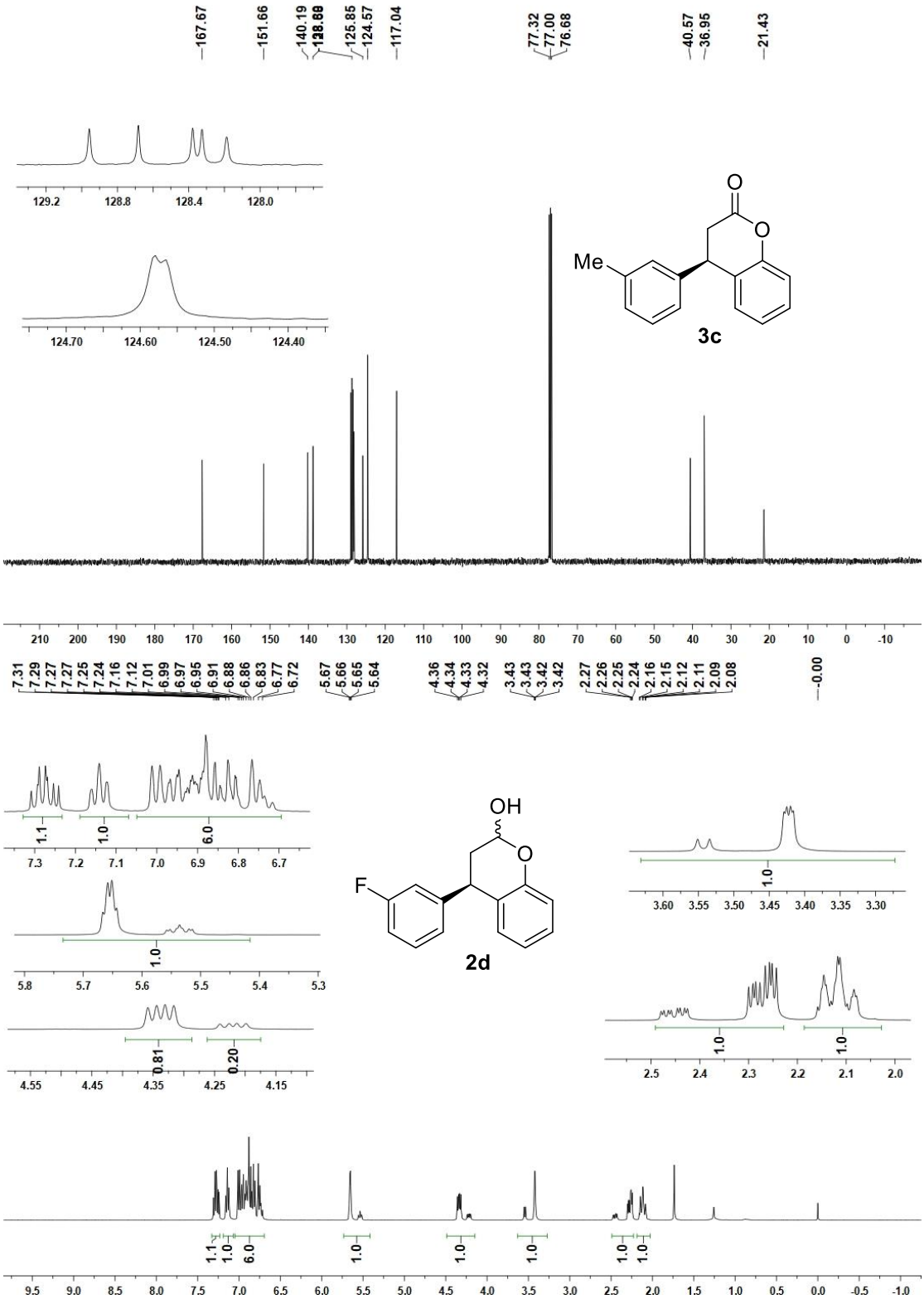
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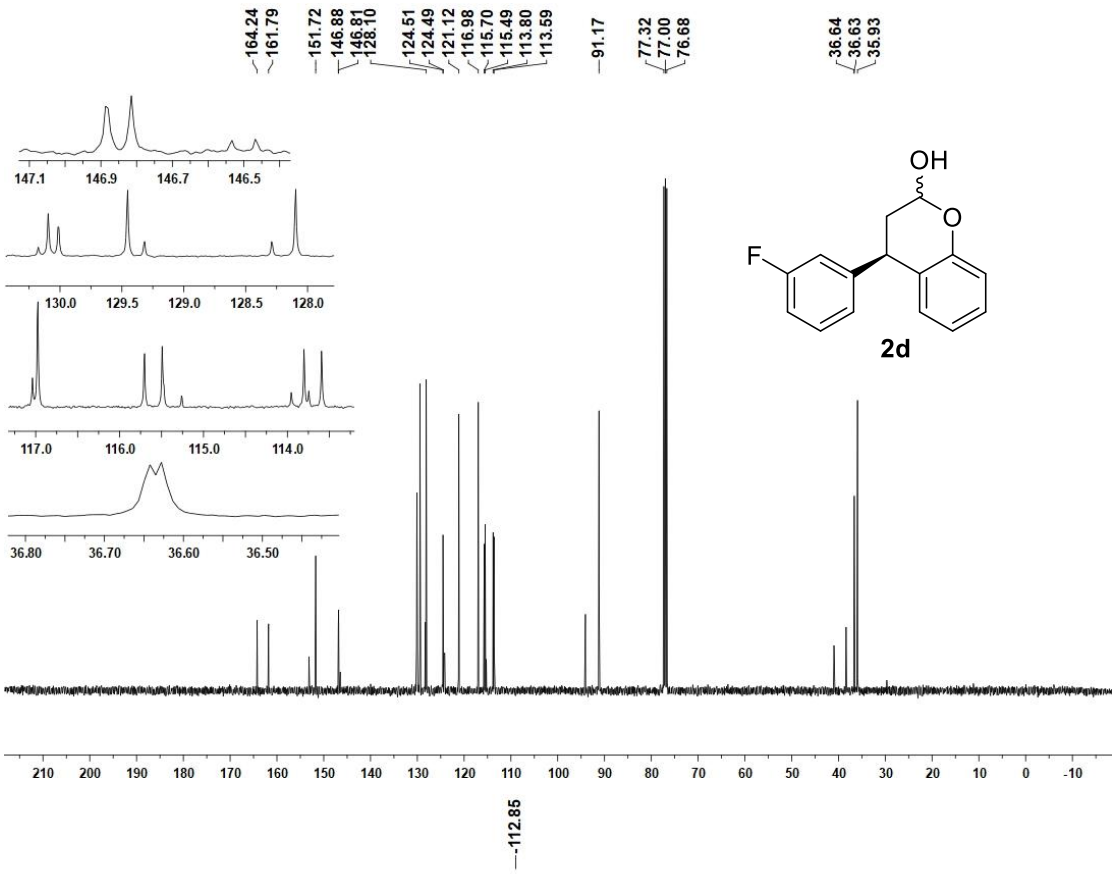
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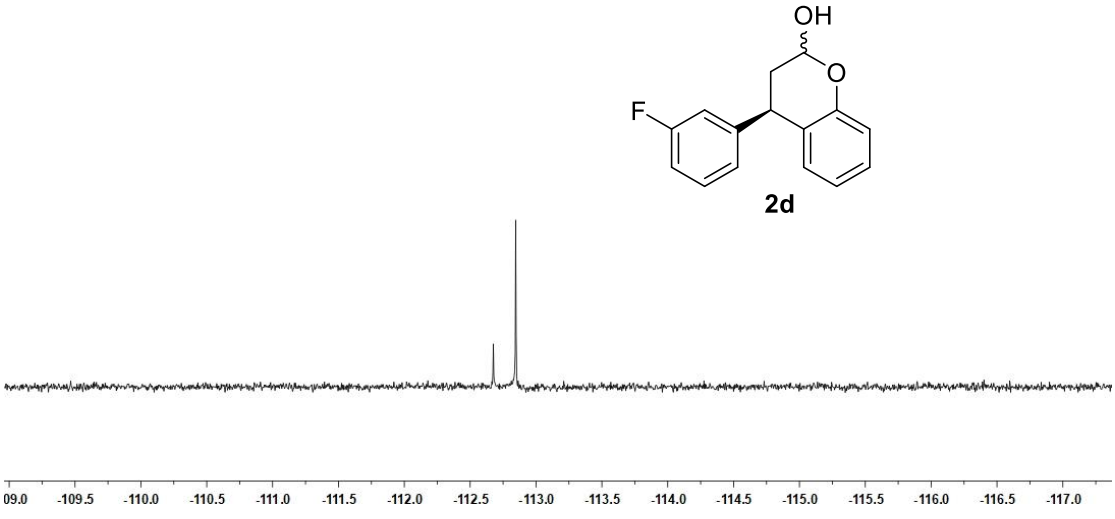
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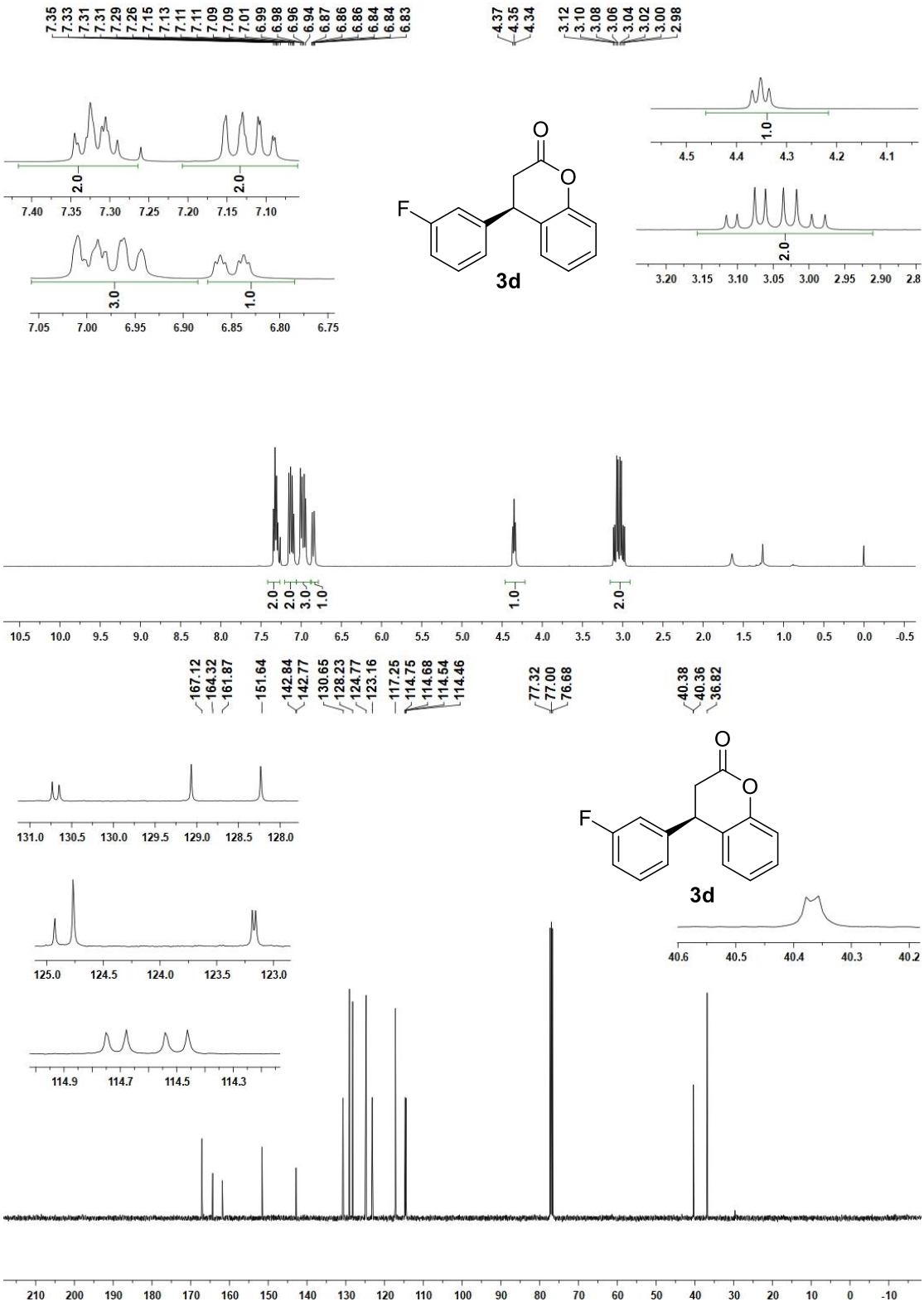
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3.12 3.10 3.08 3.06 3.04 3.02 3.00 2.98
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3.0 1.0
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2.0
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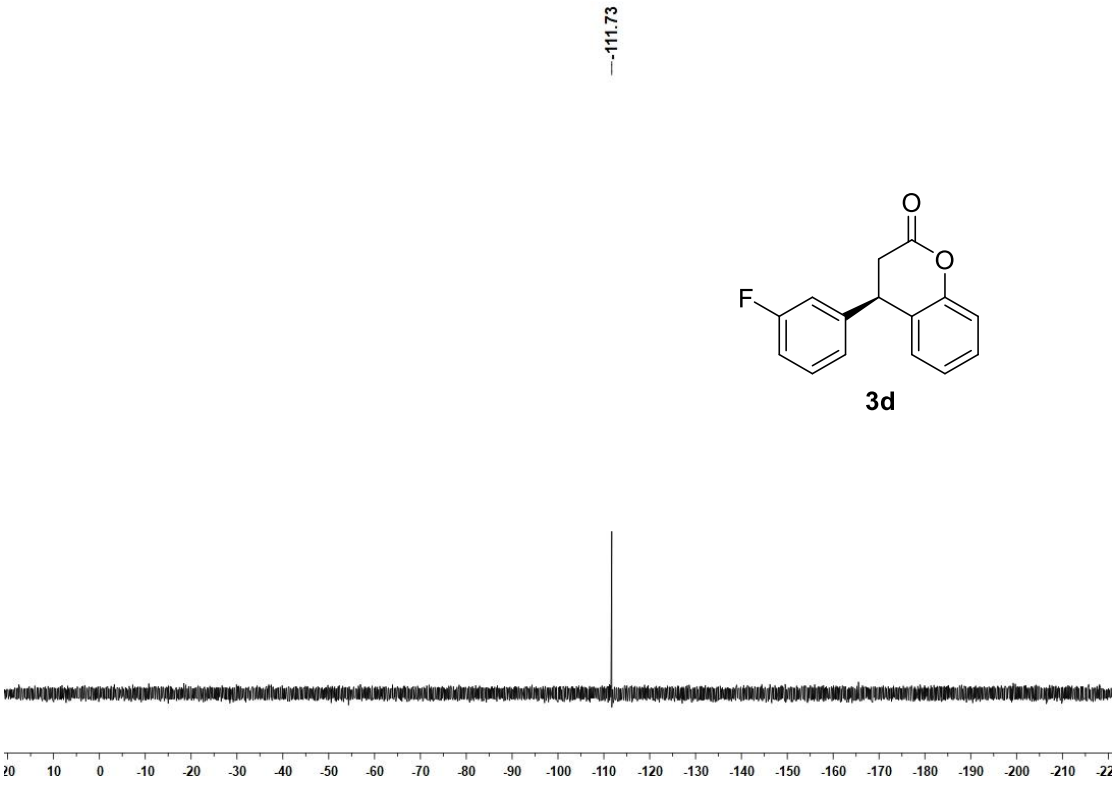
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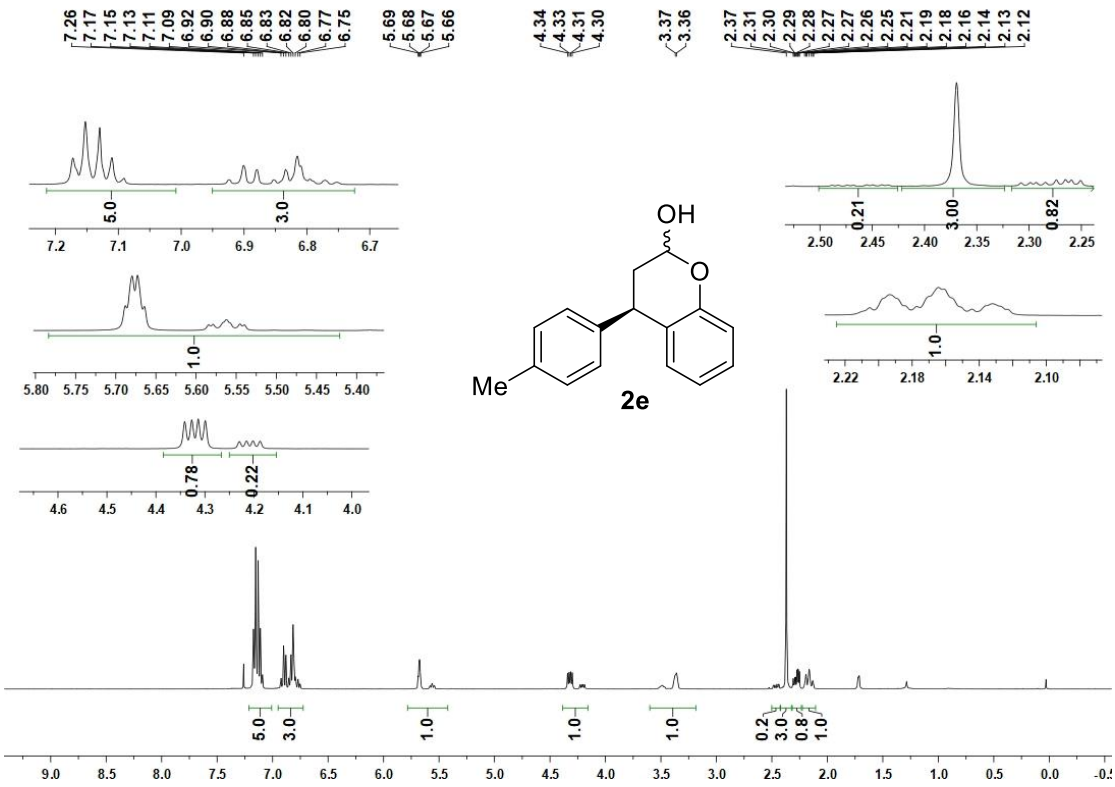
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3.37 3.36
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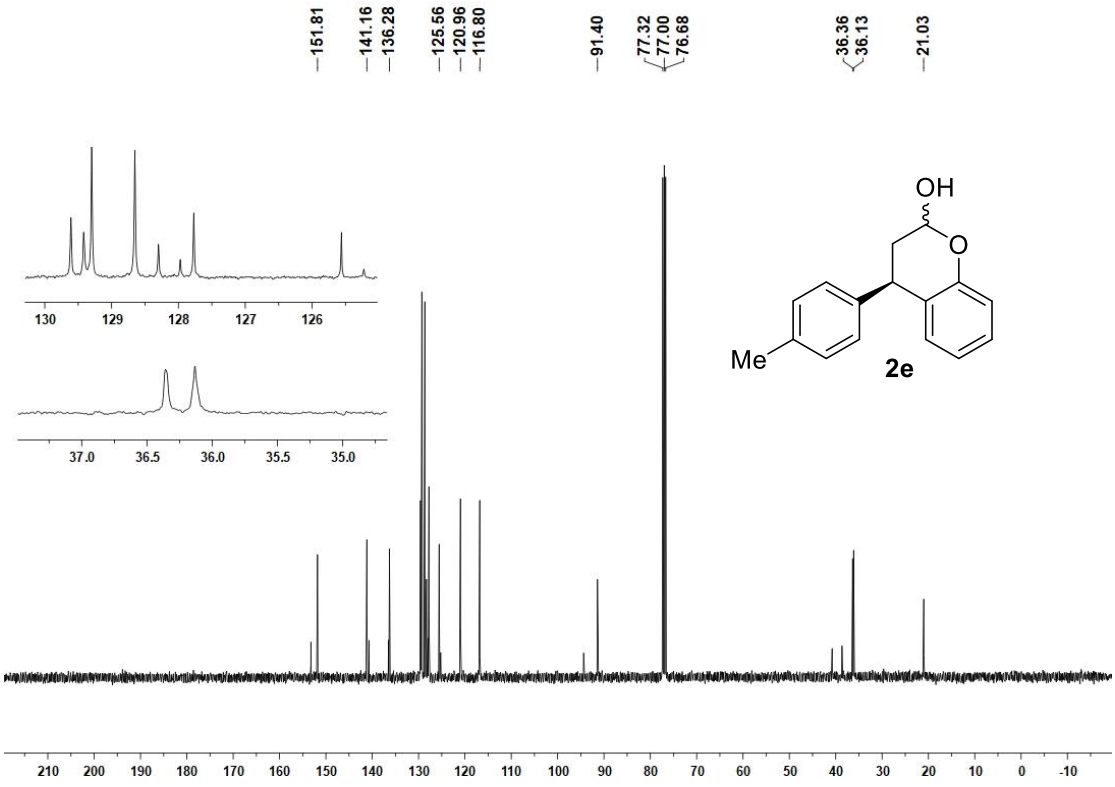
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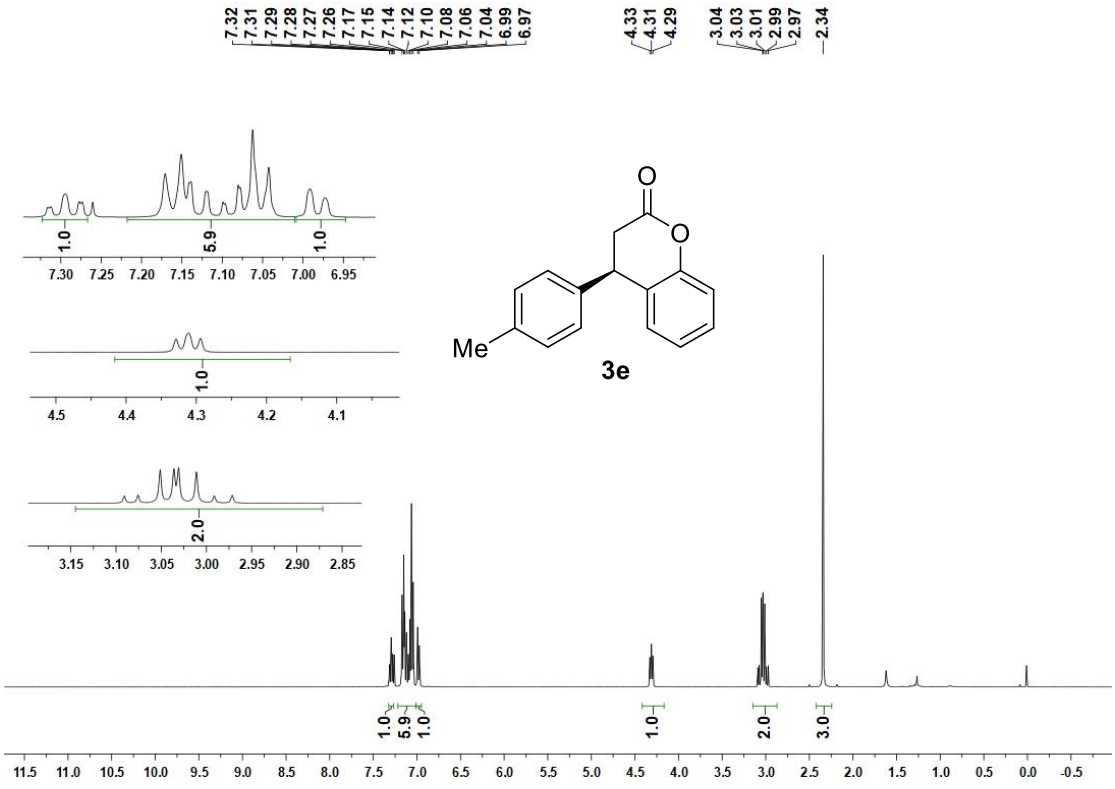
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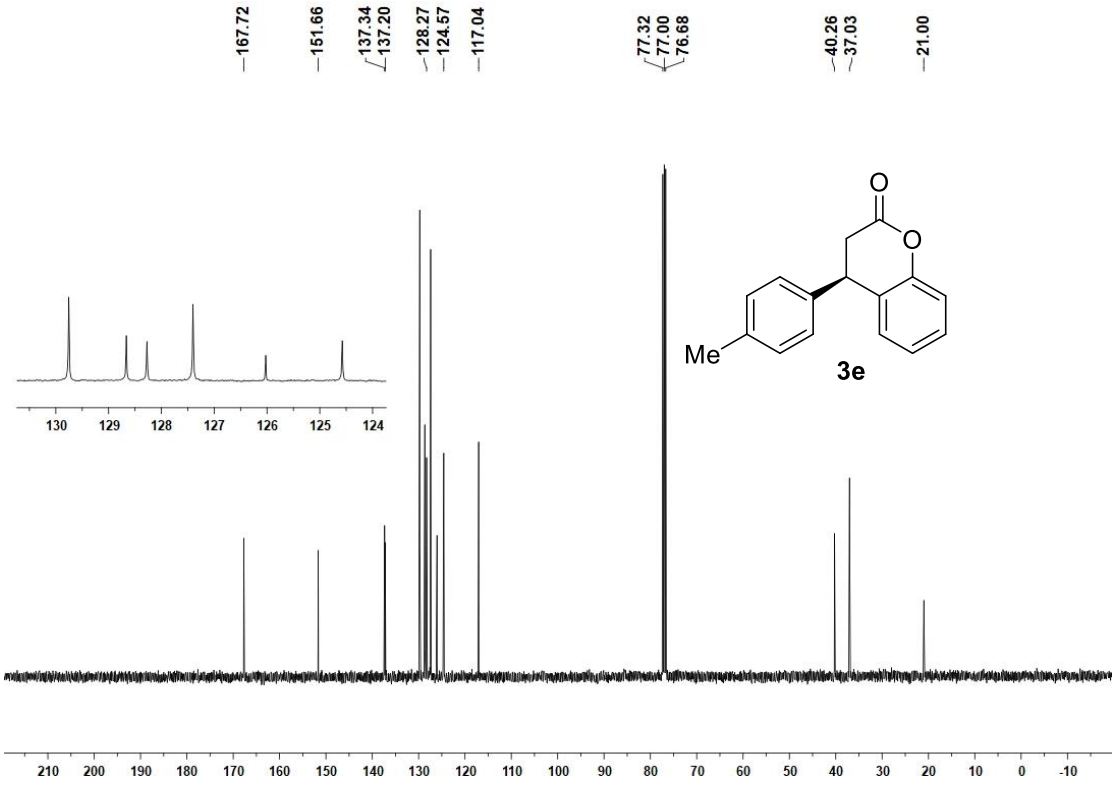
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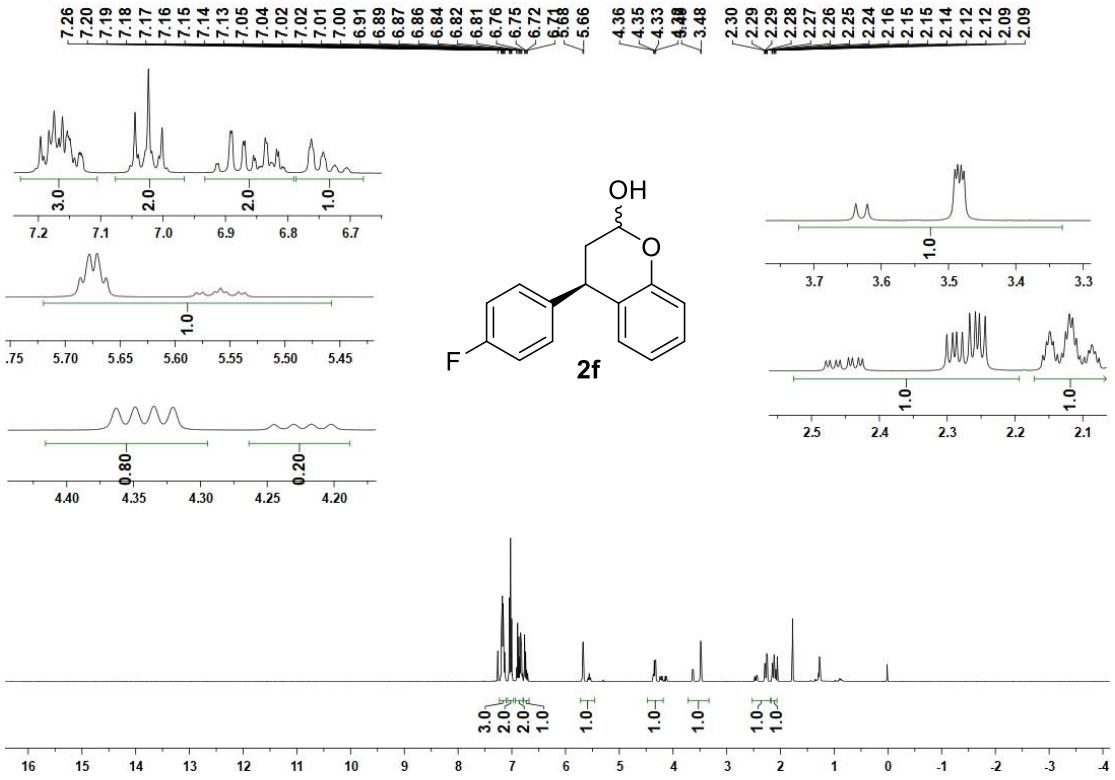
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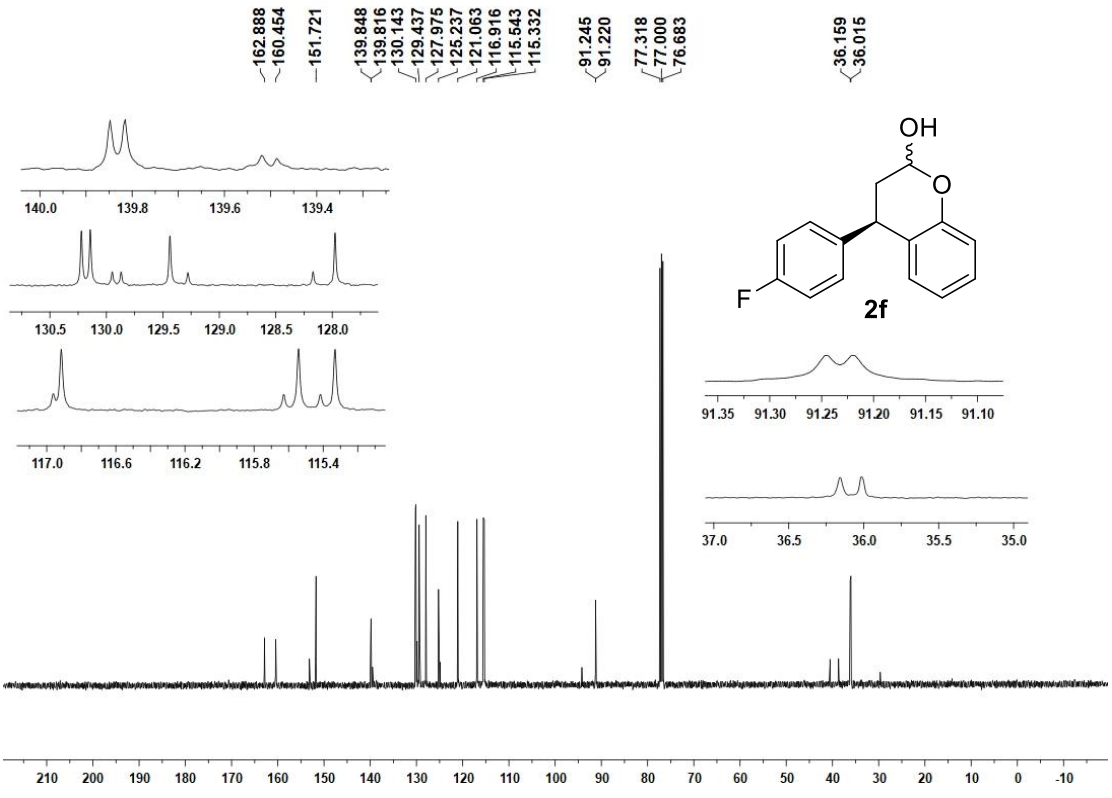
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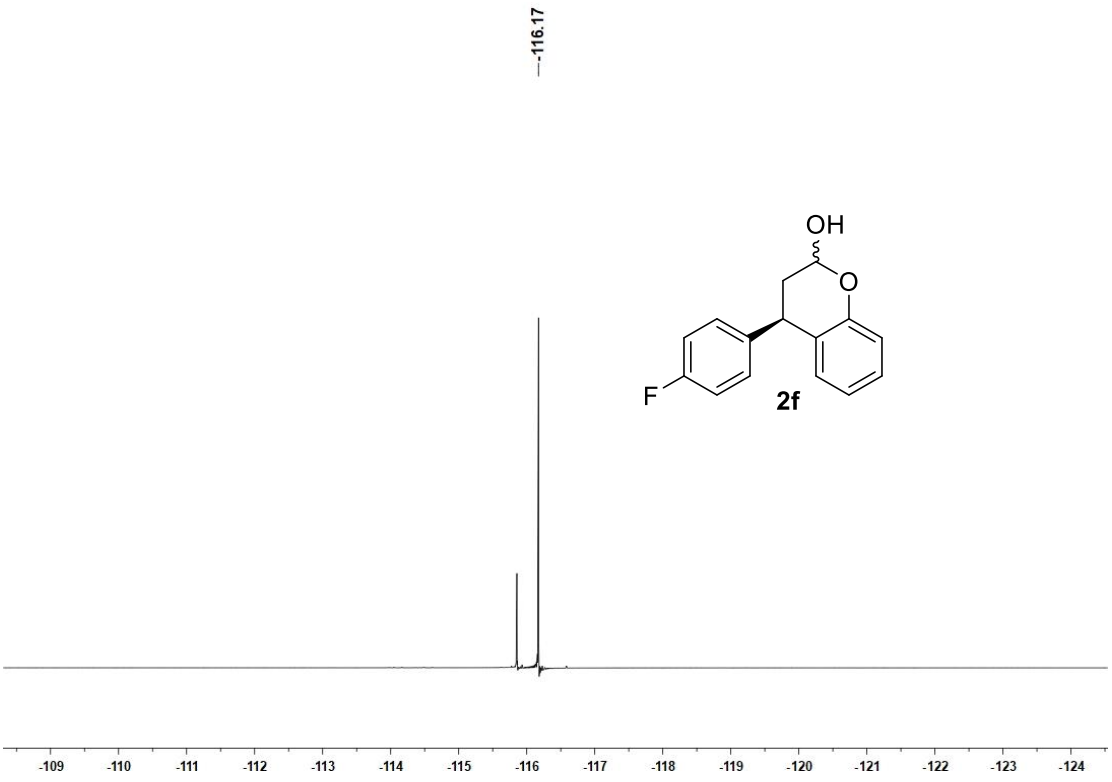
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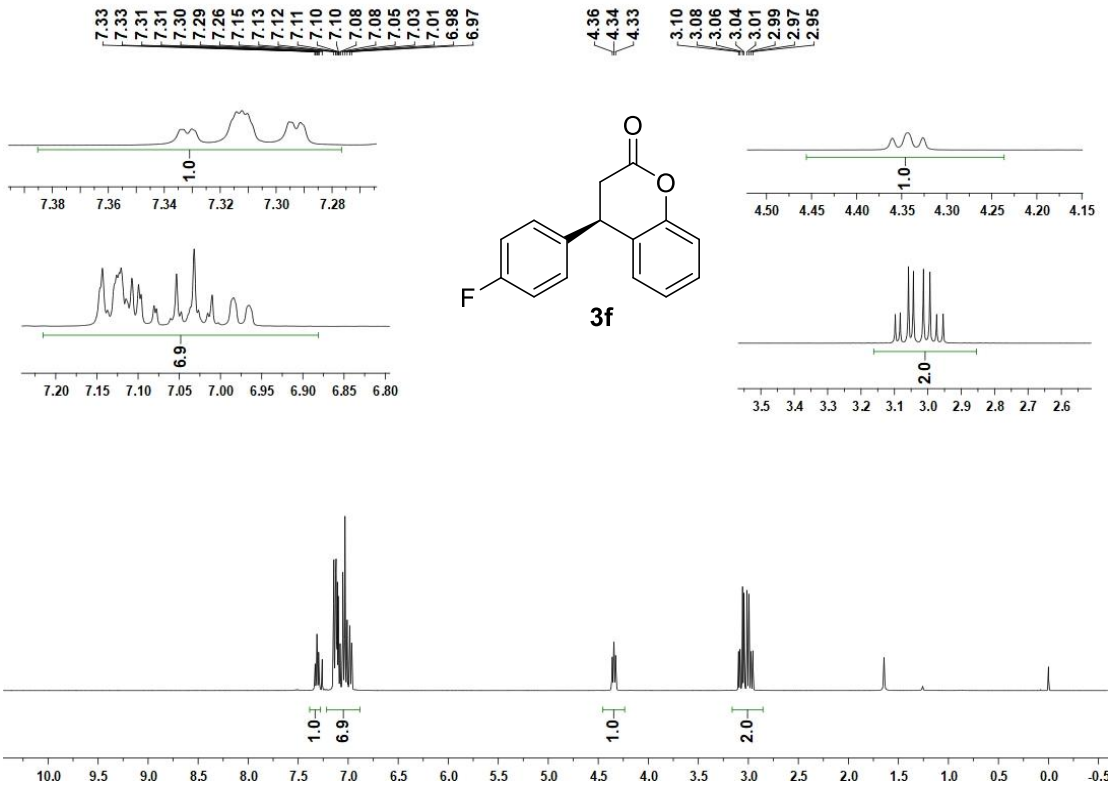
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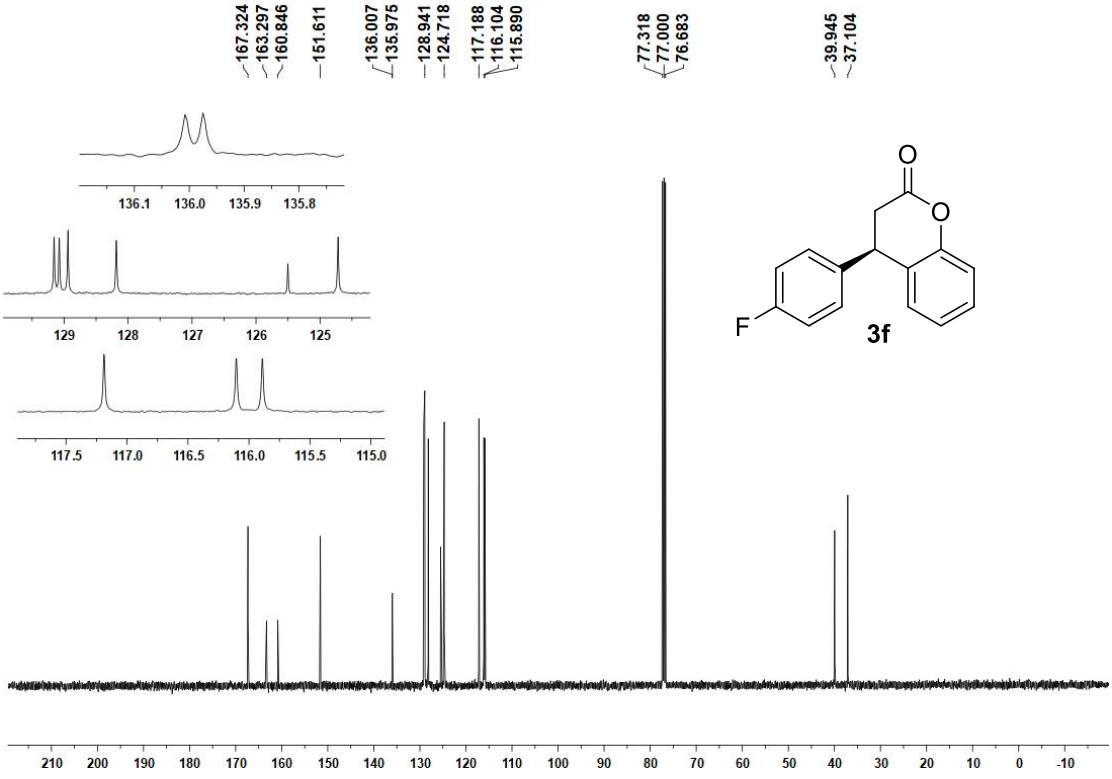
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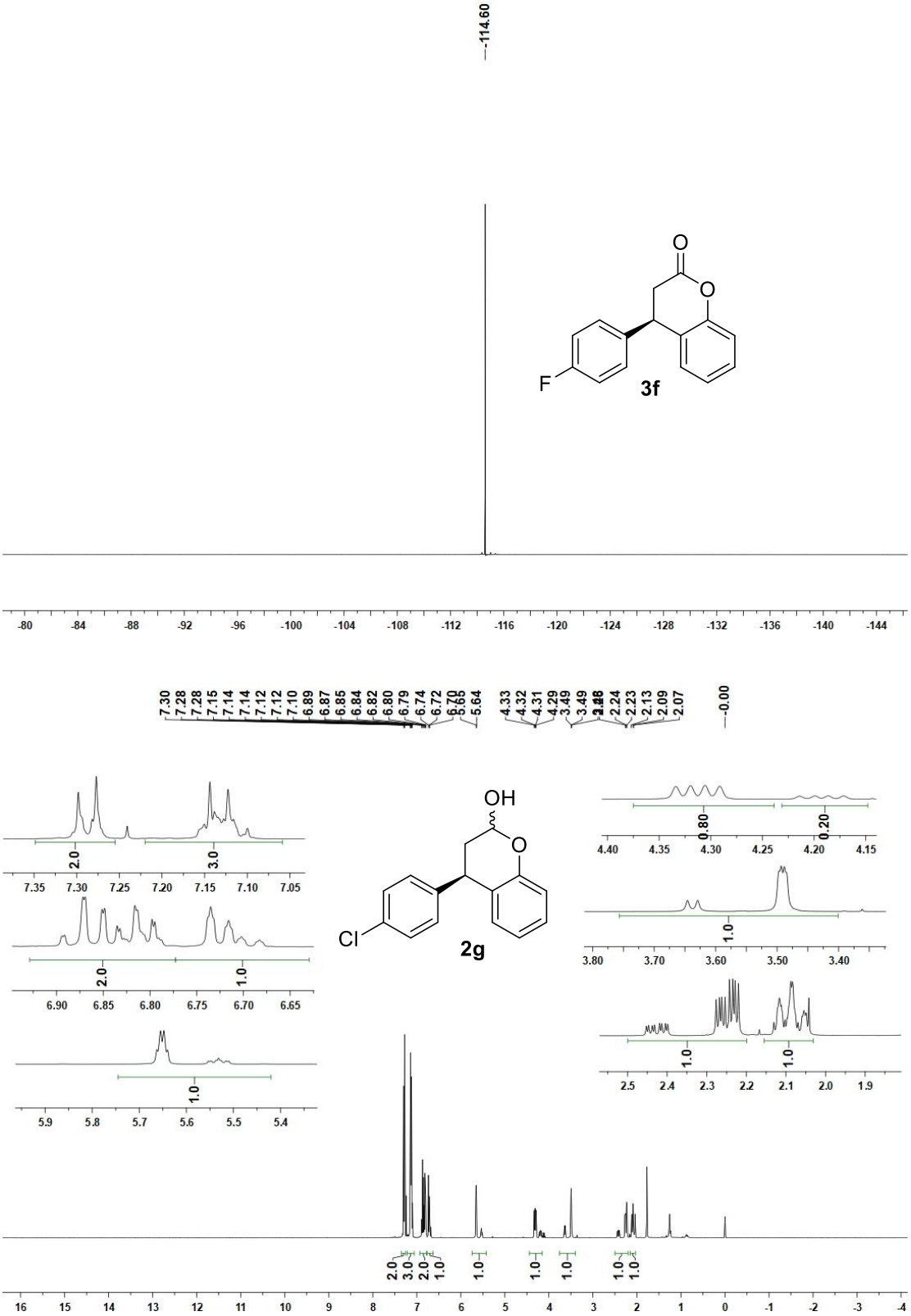
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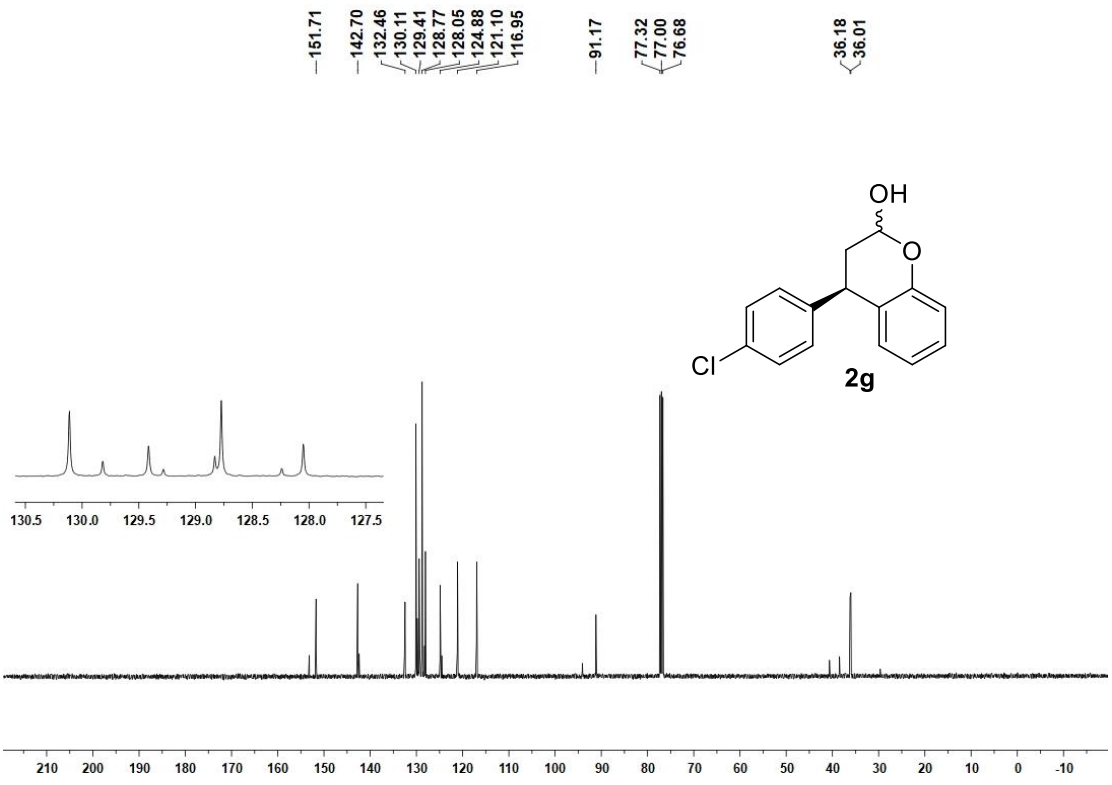
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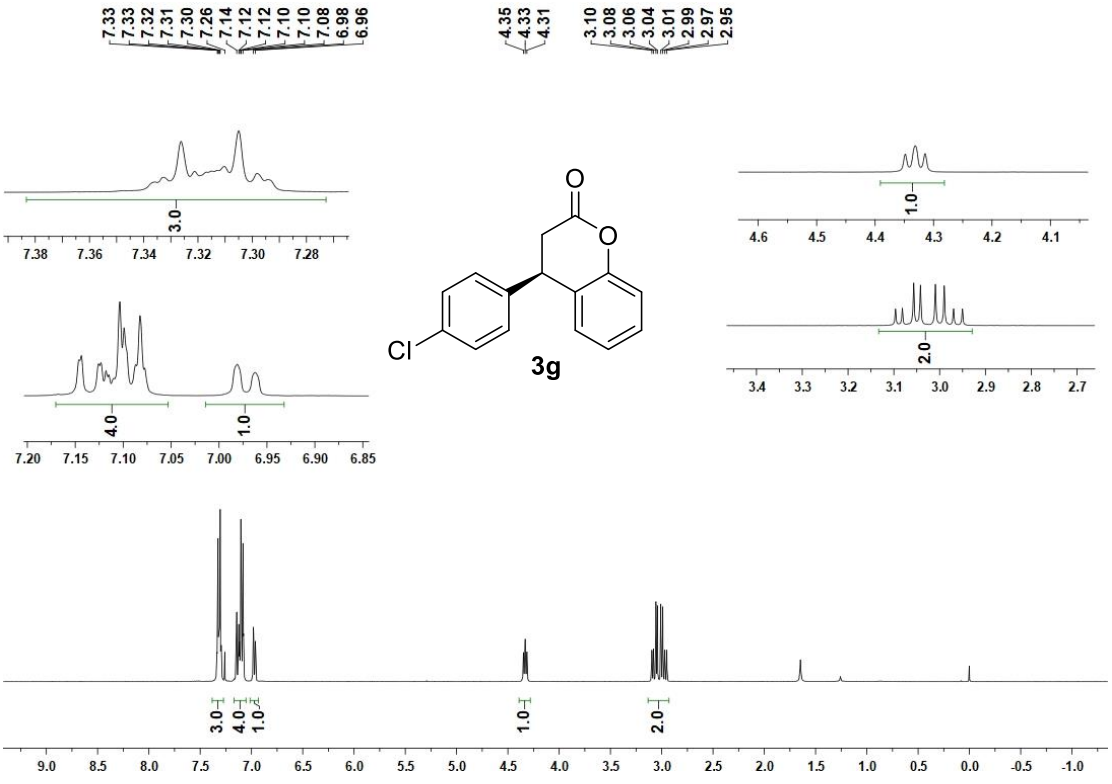
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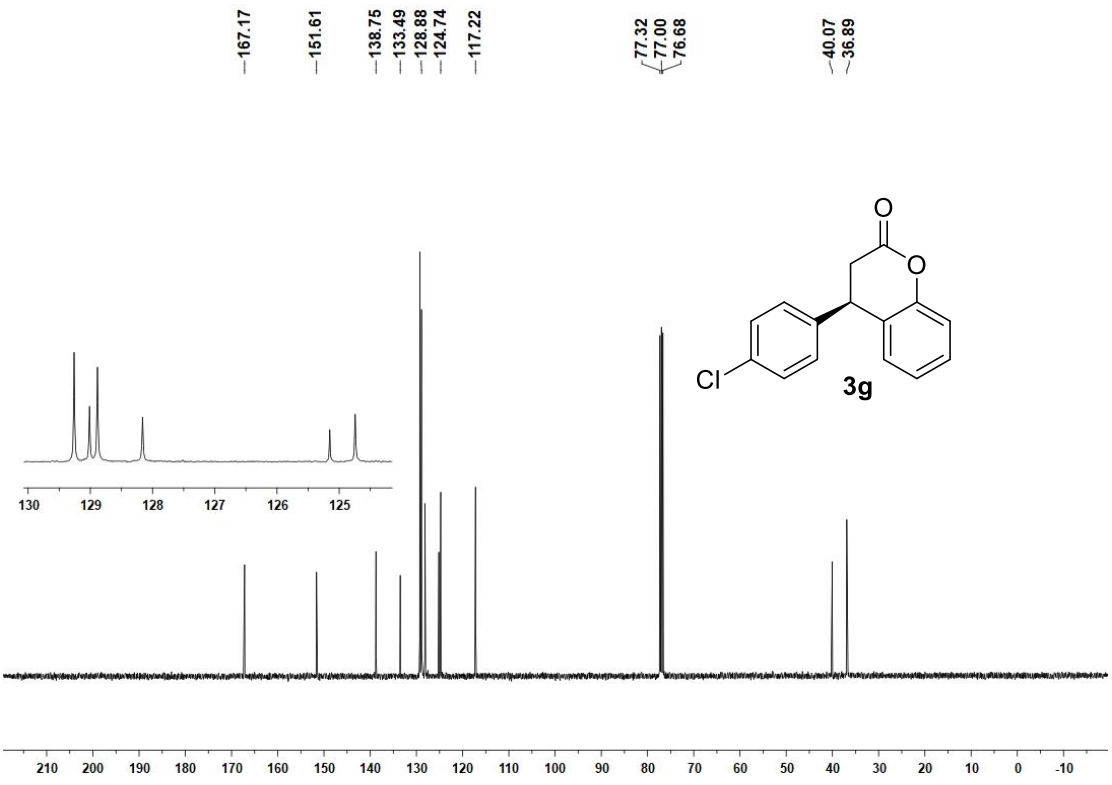
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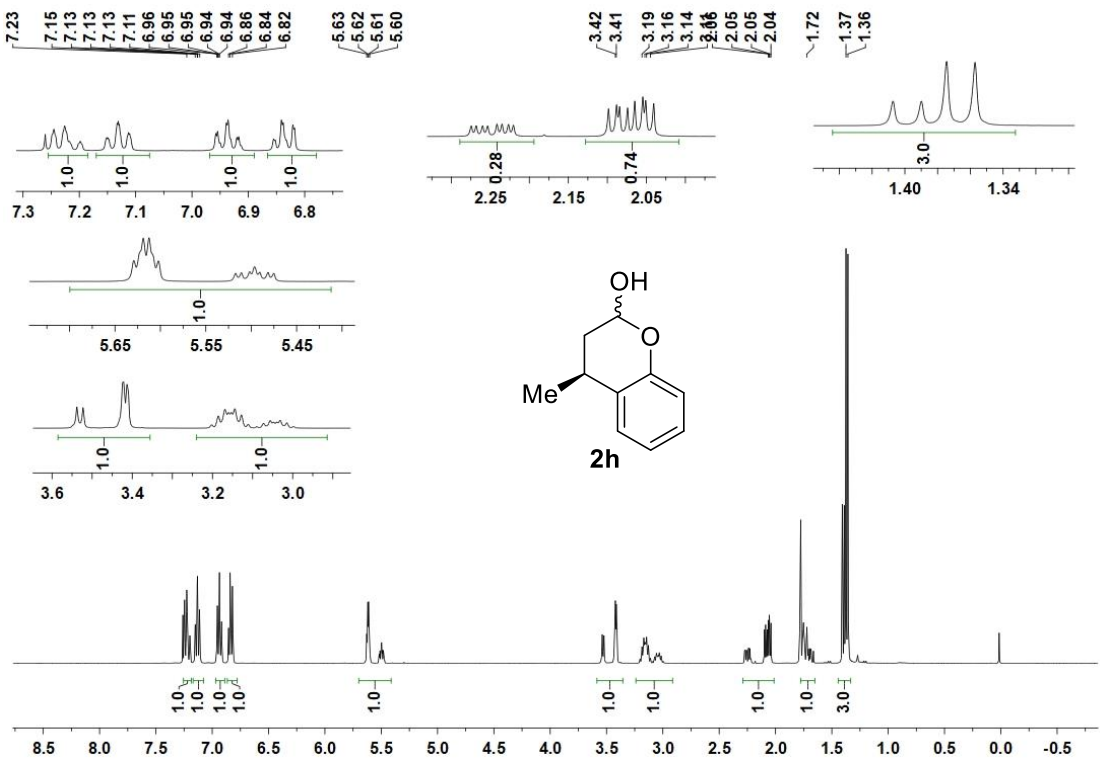
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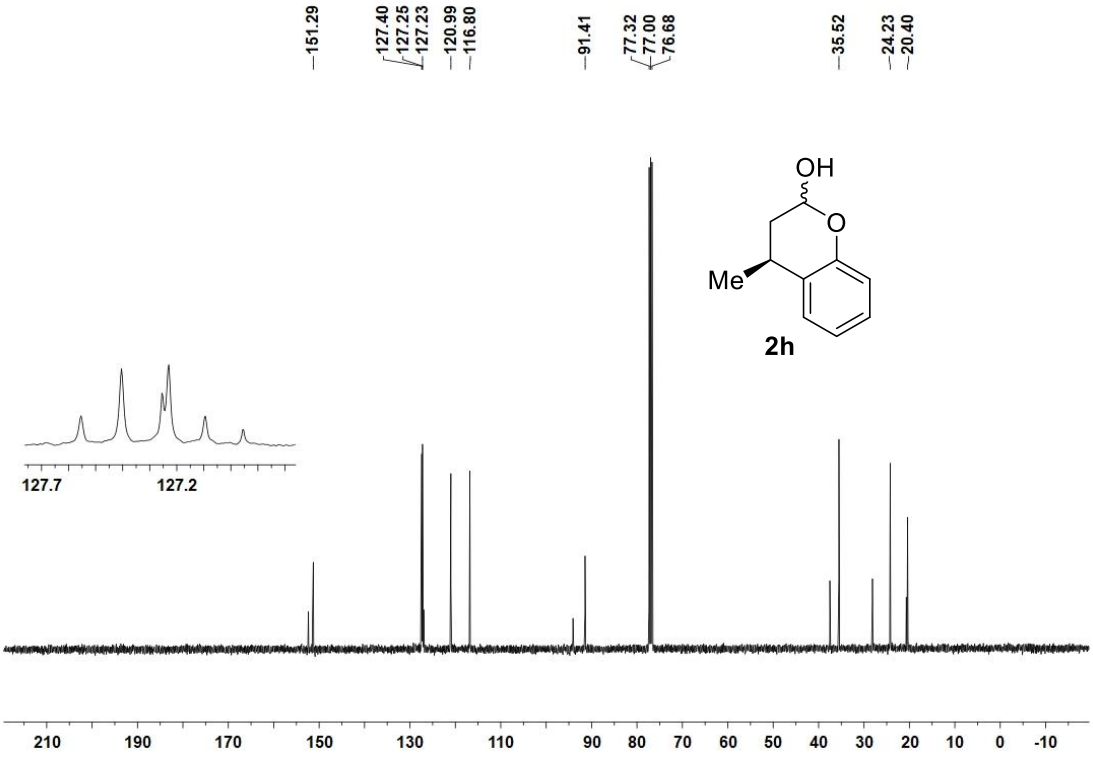
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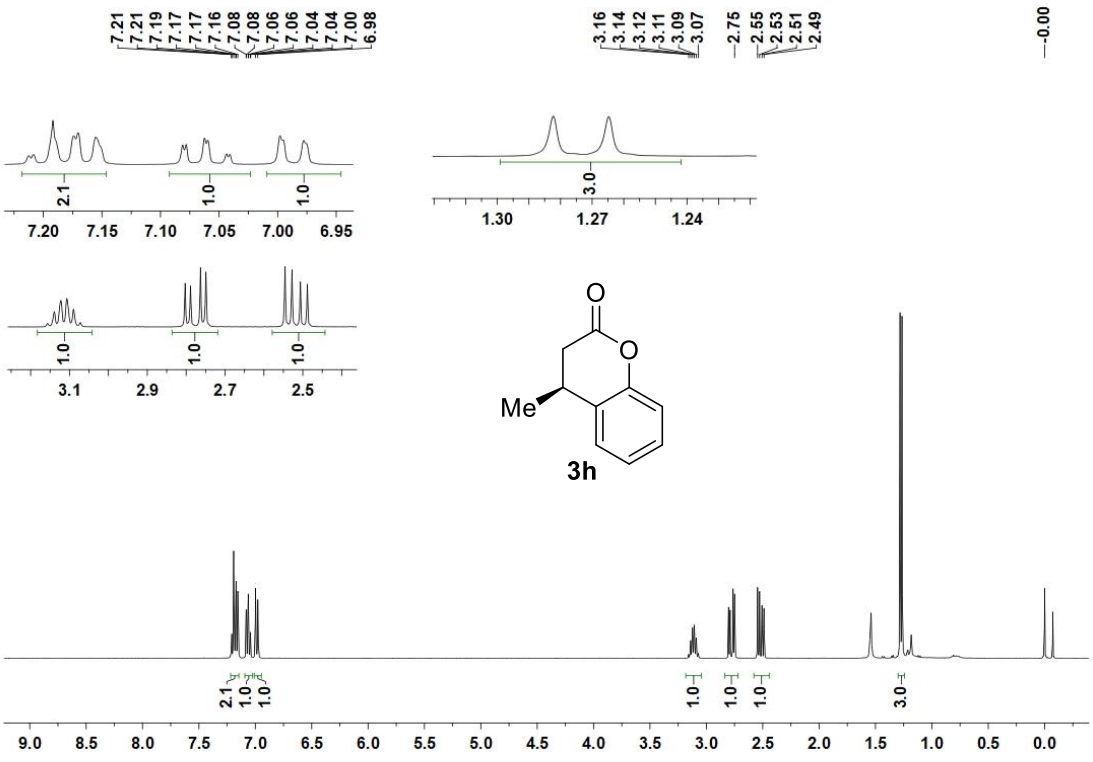
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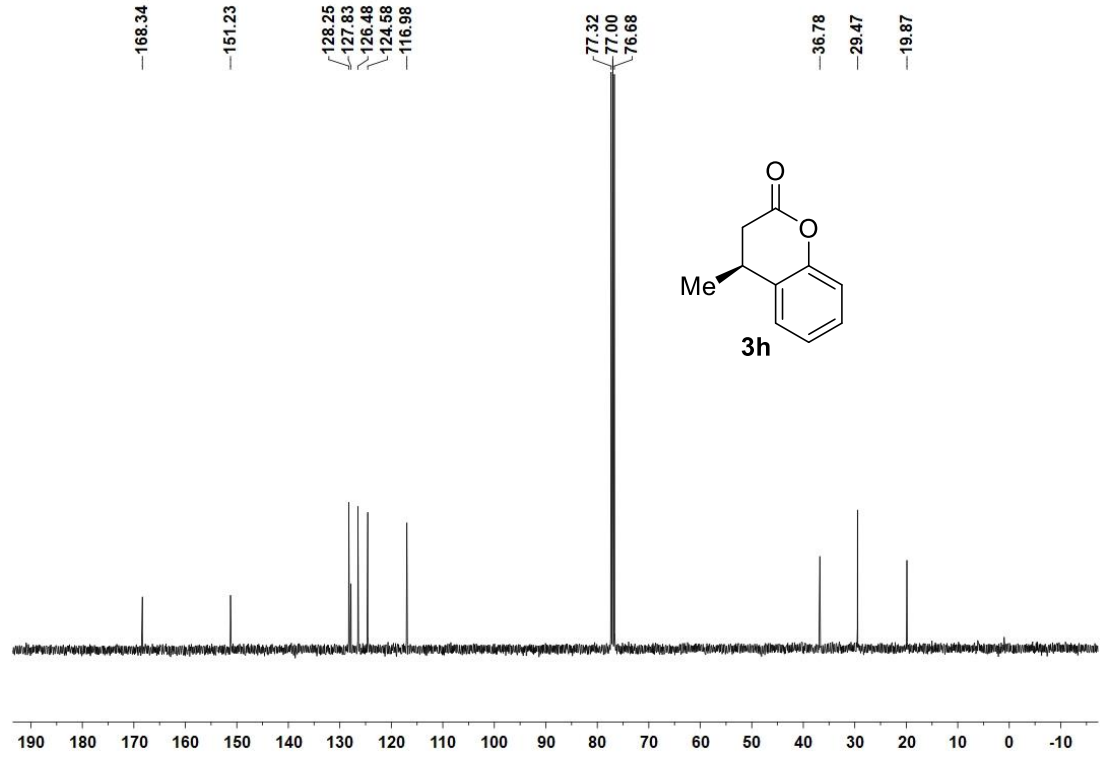
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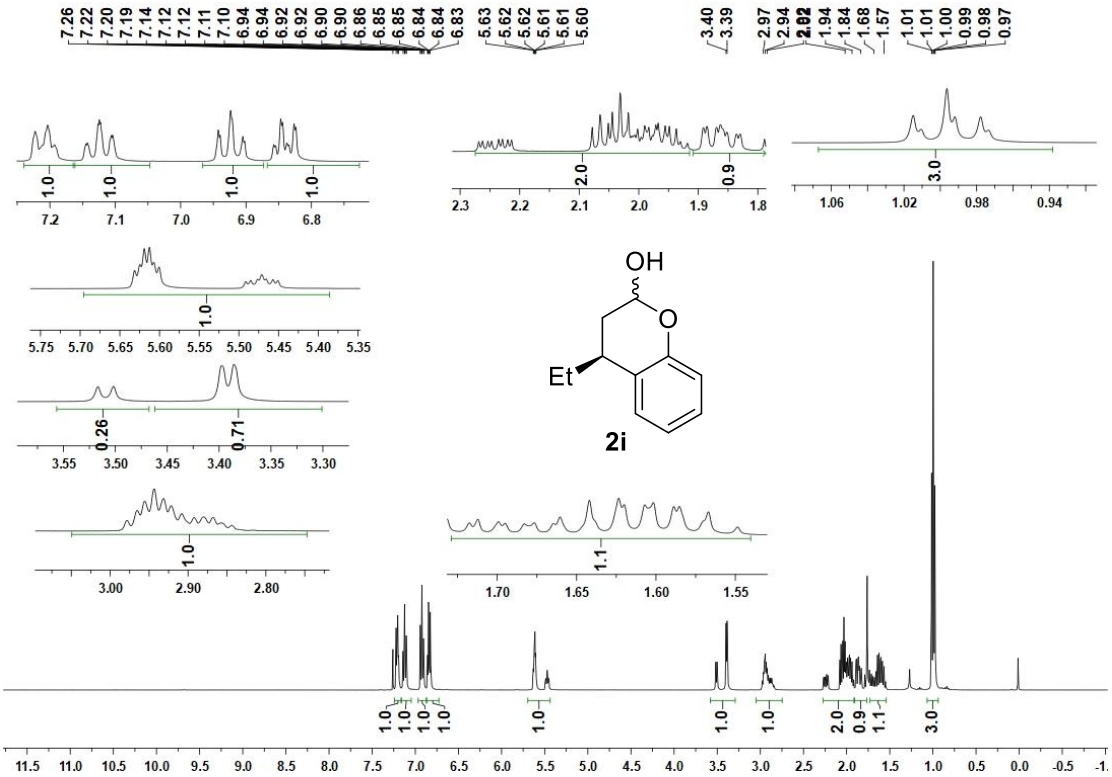
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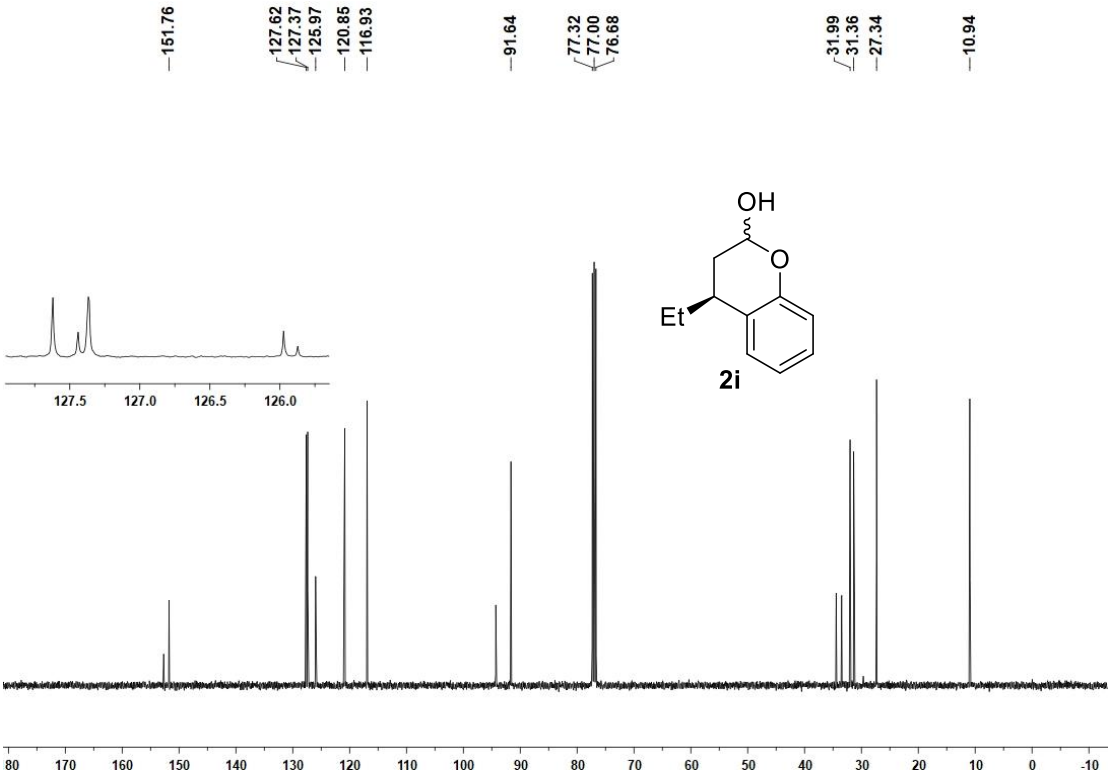
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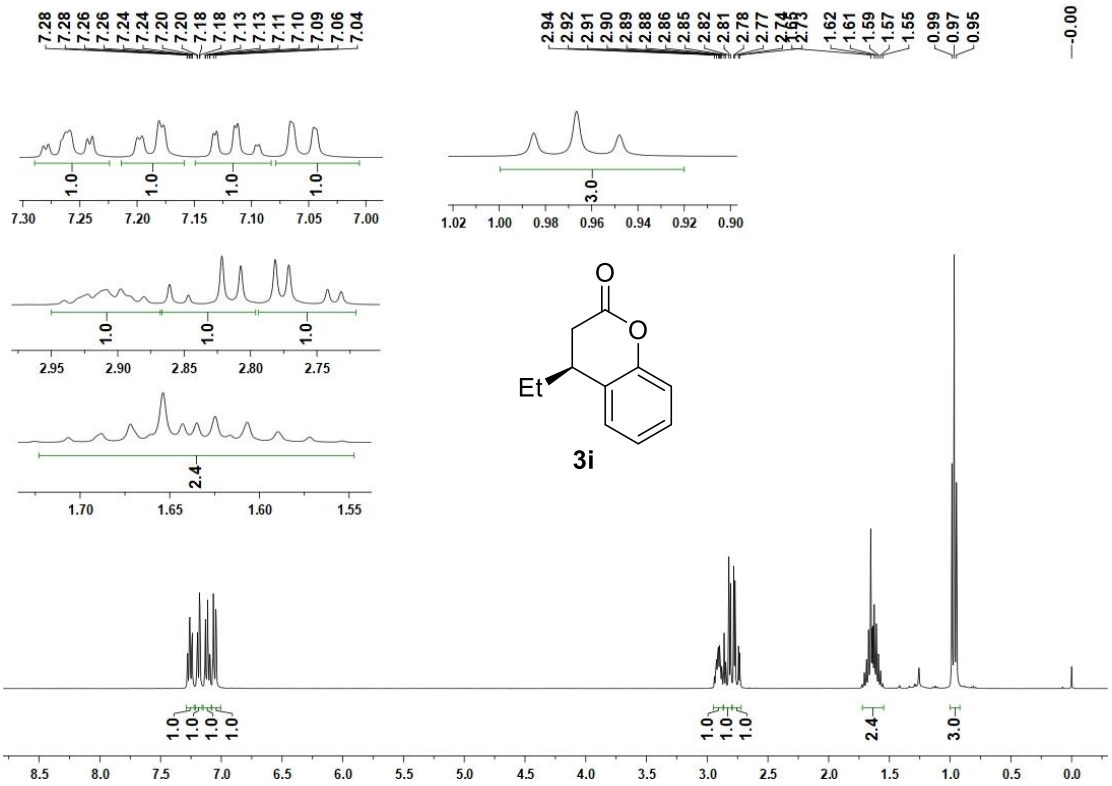
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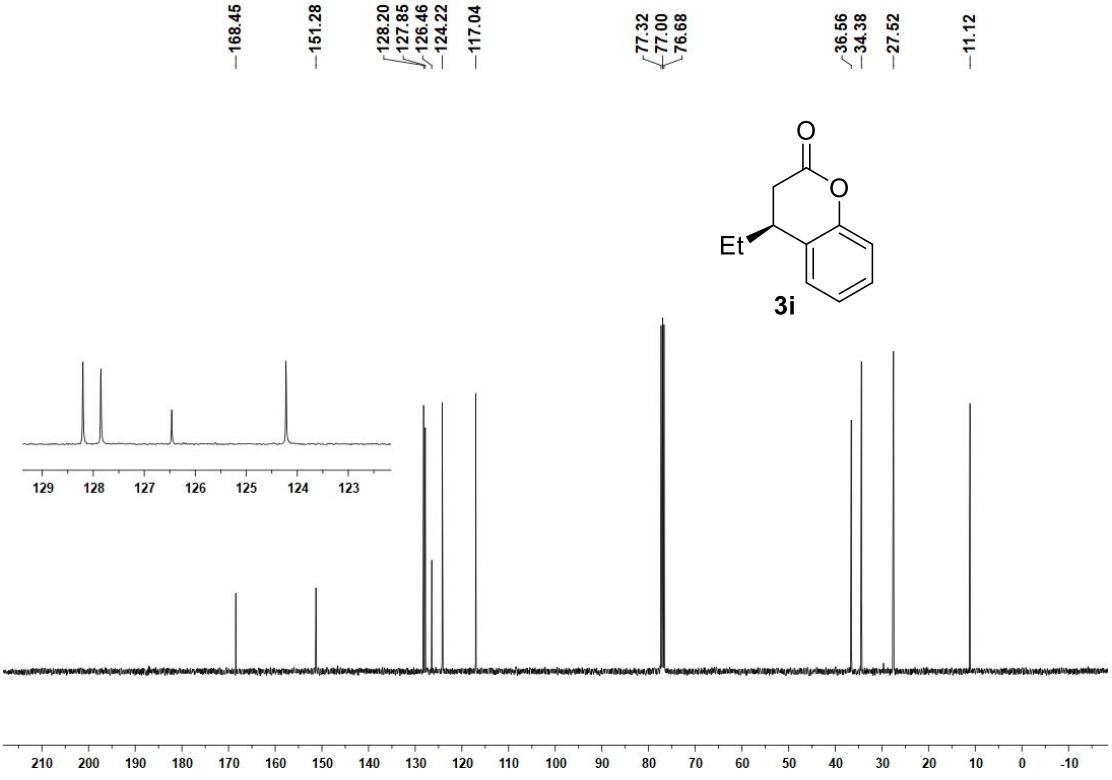
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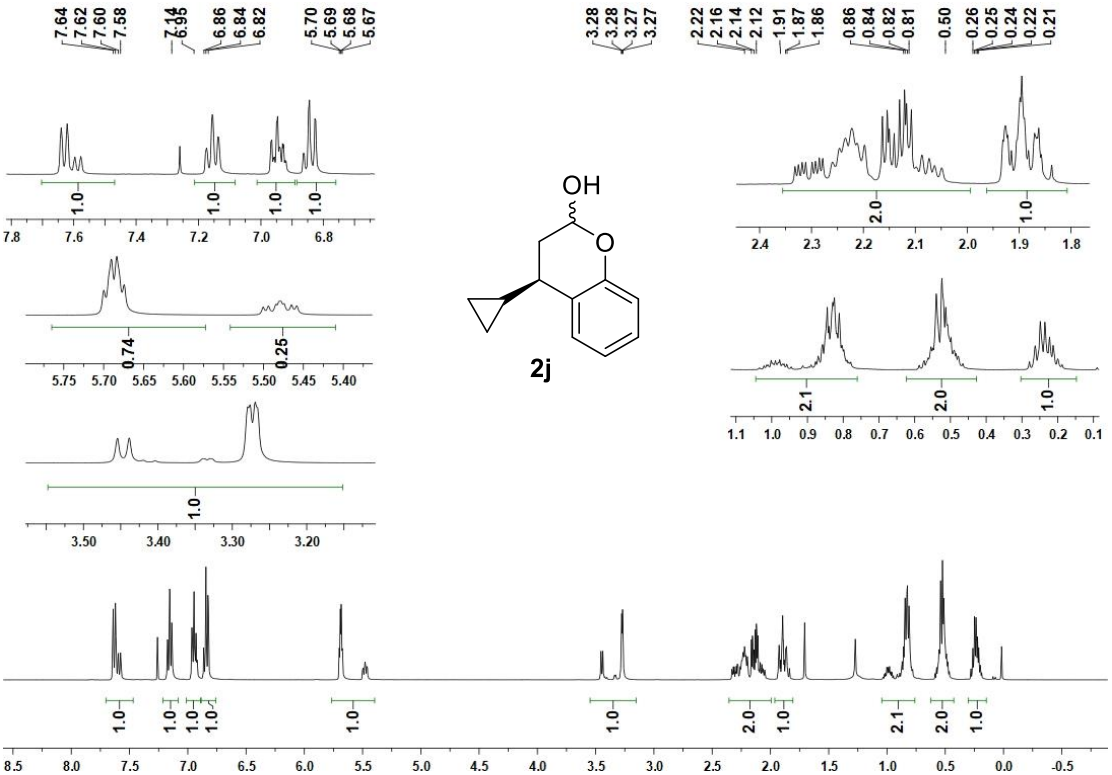
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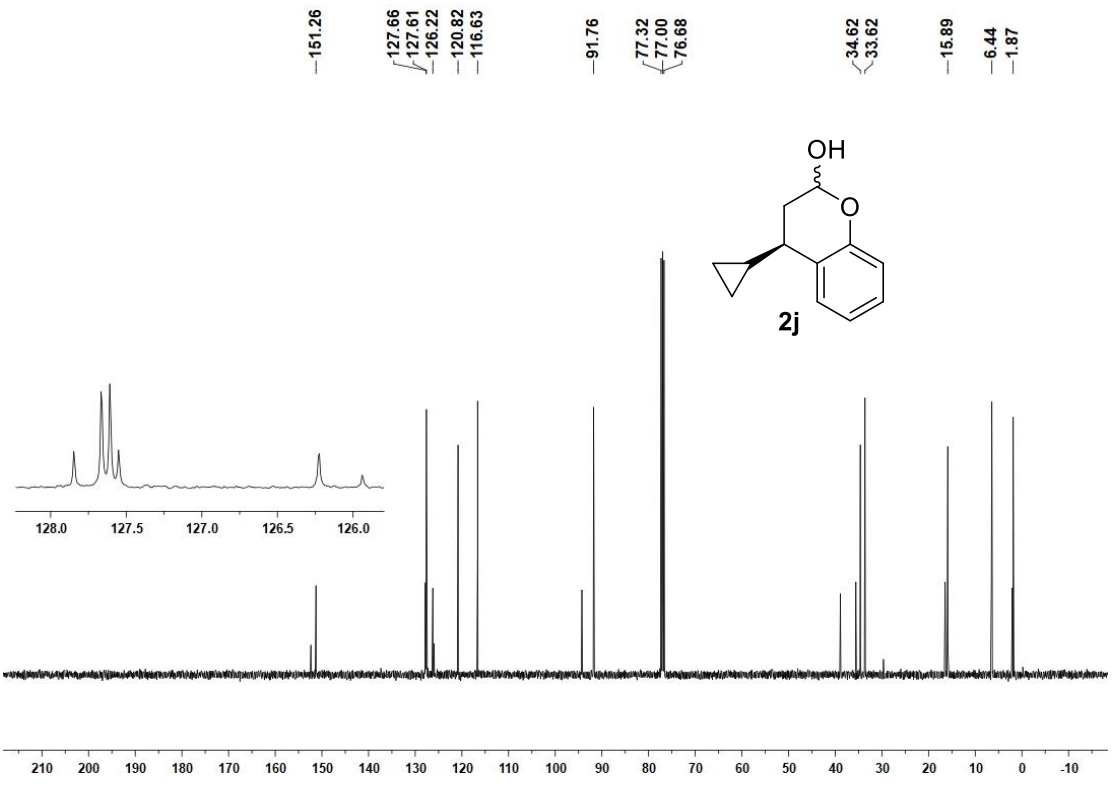
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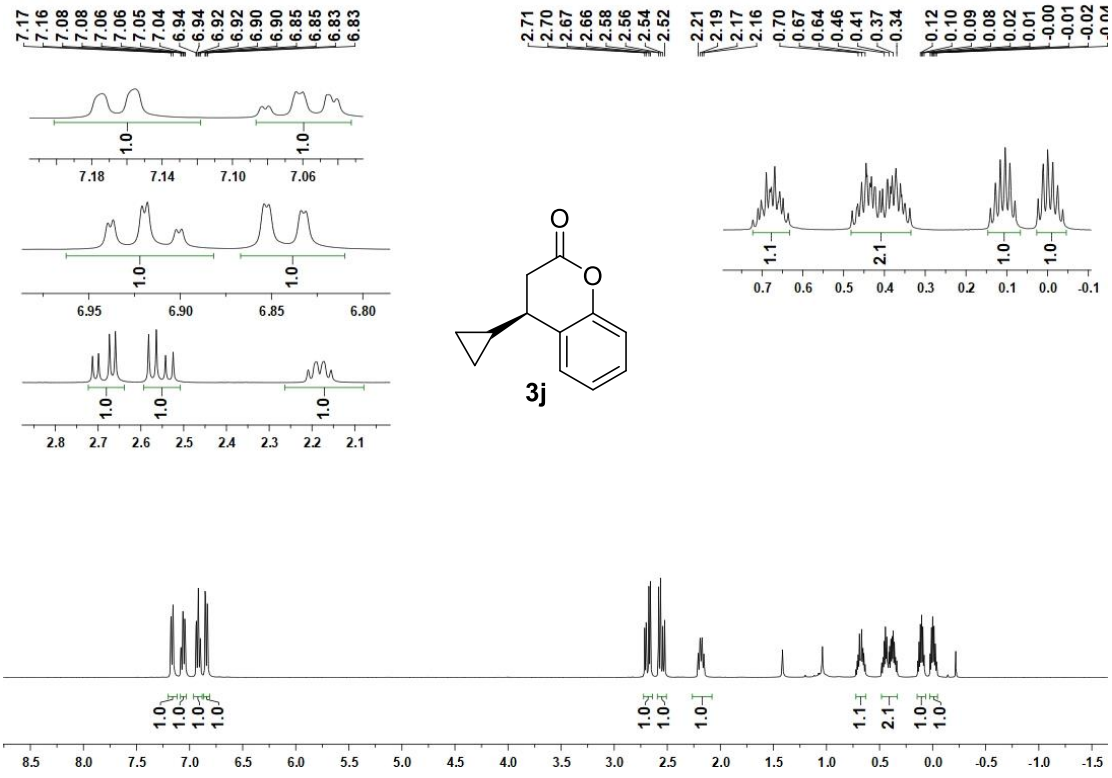
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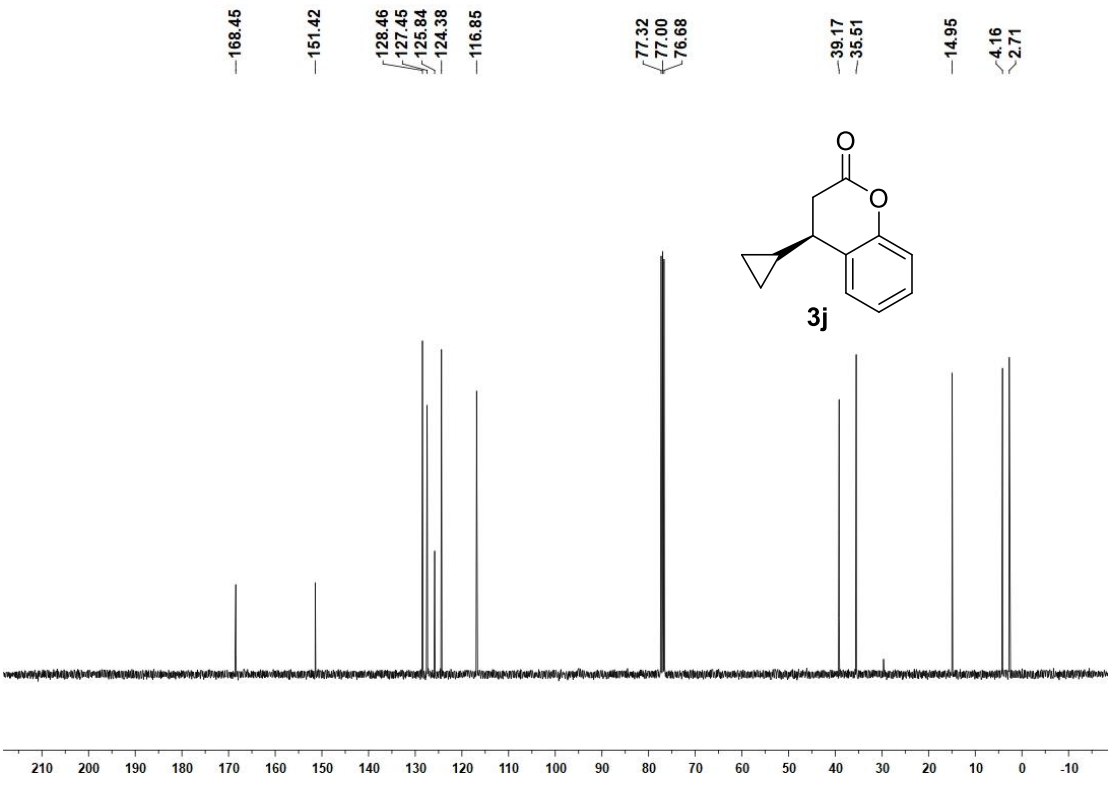
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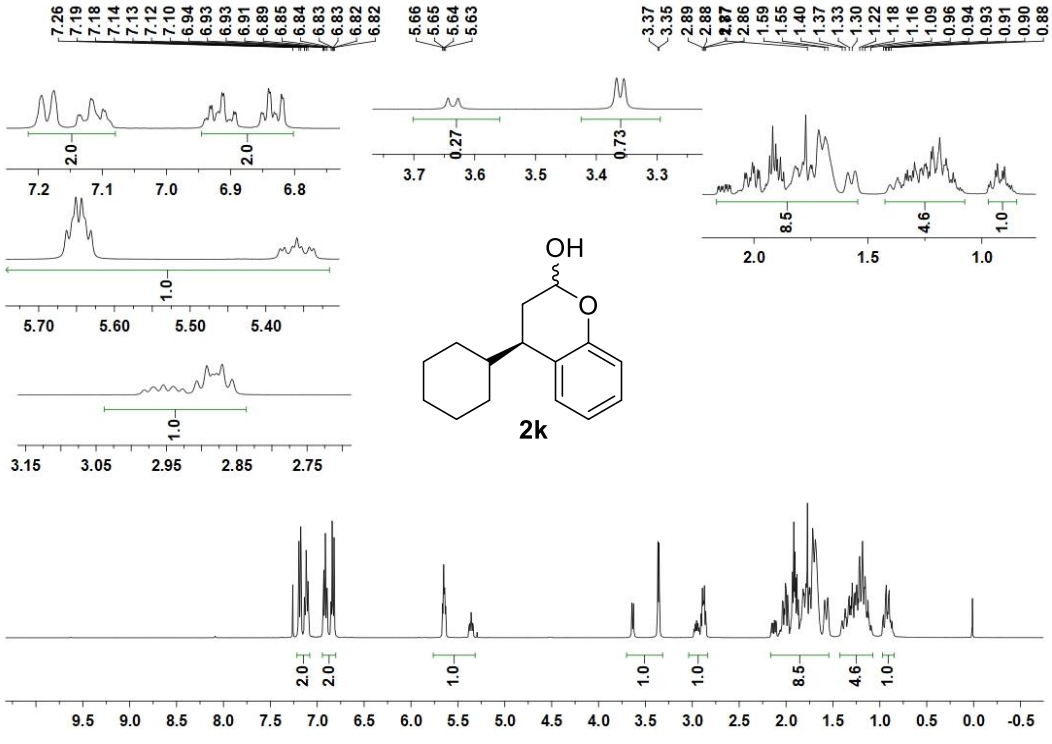
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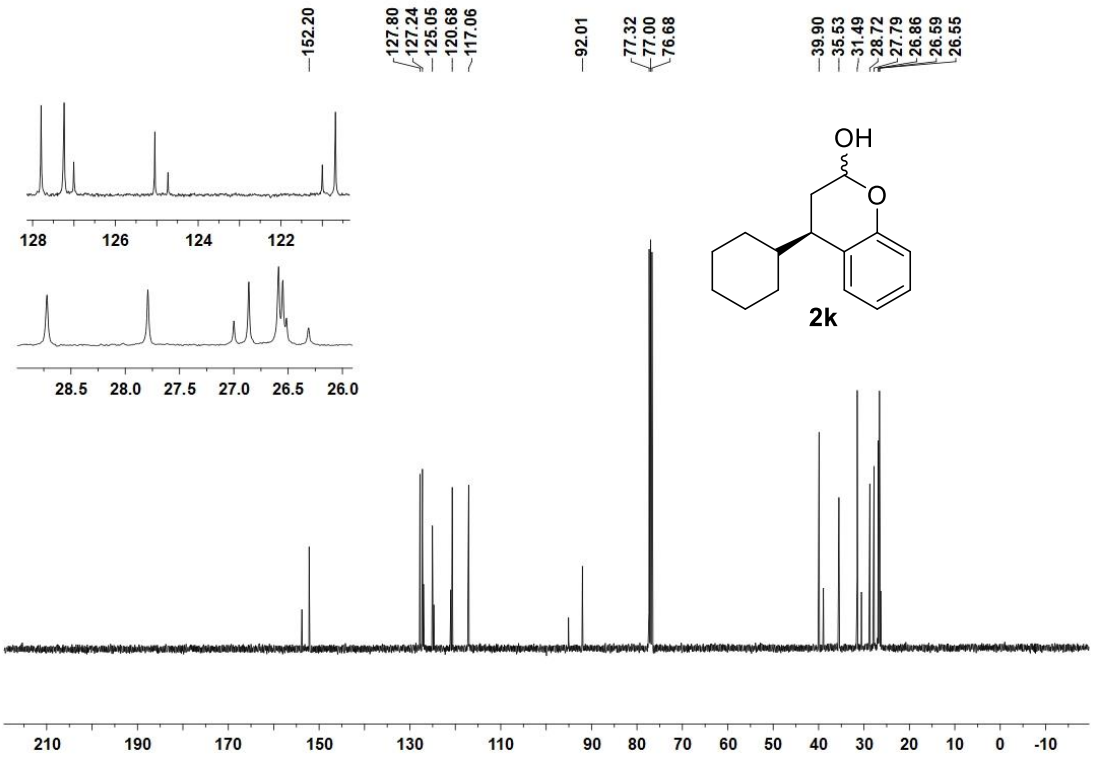
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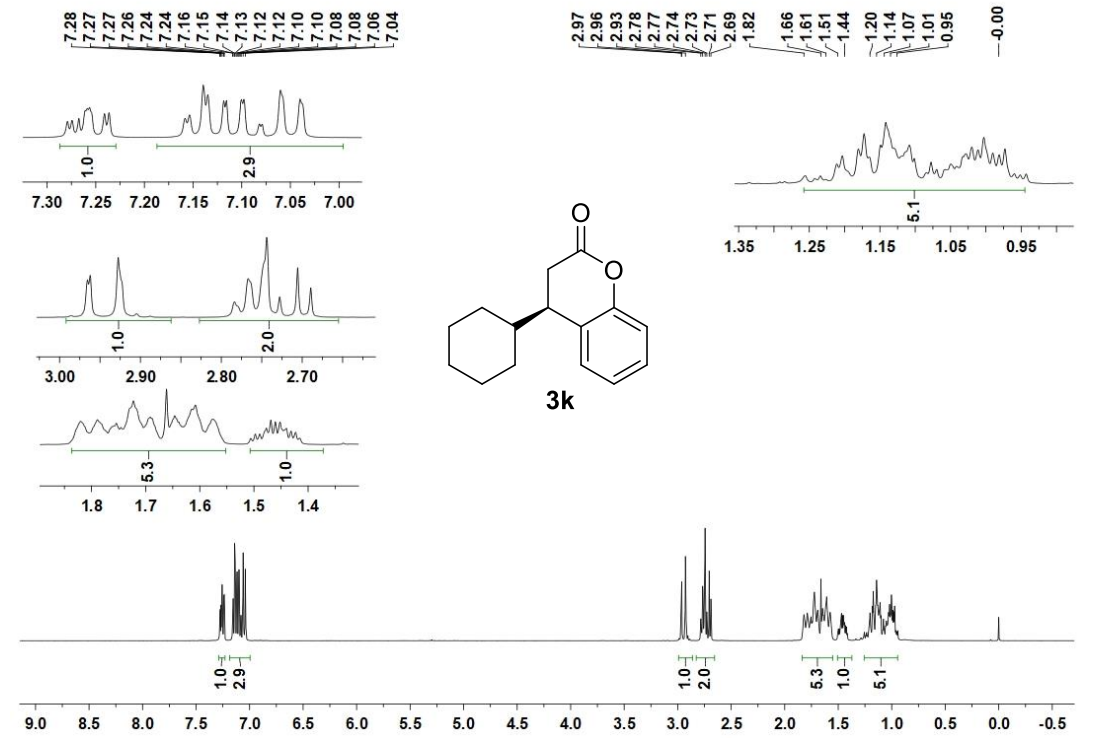
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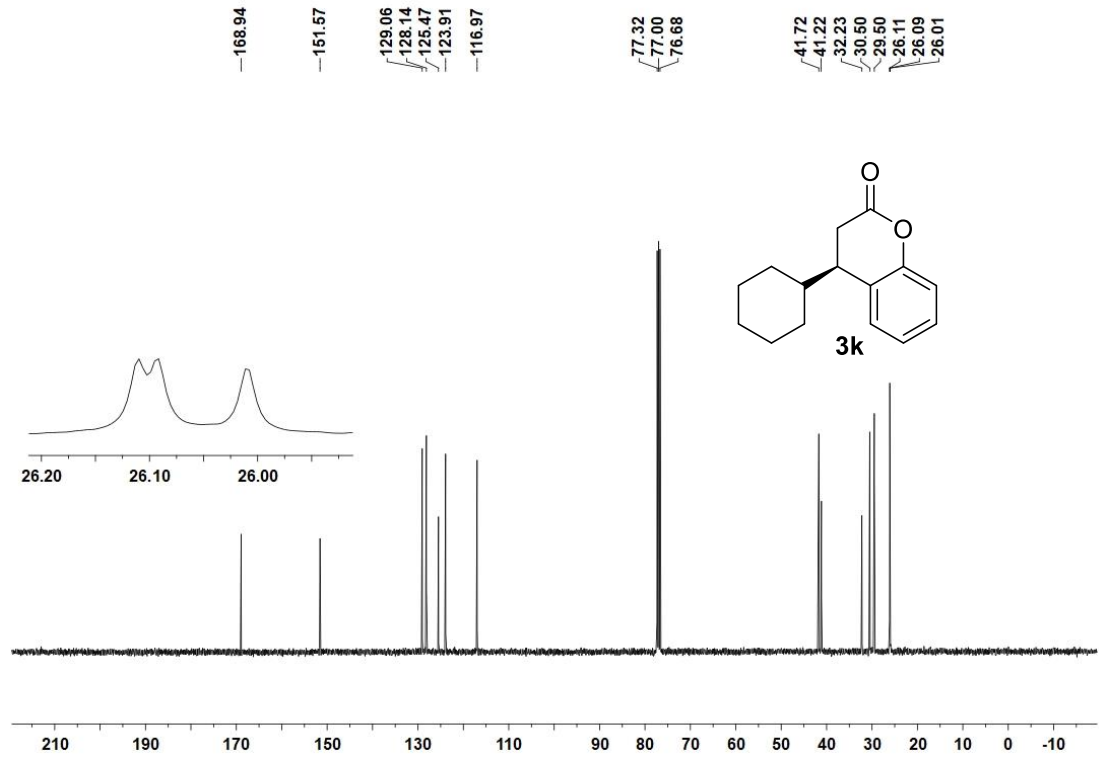
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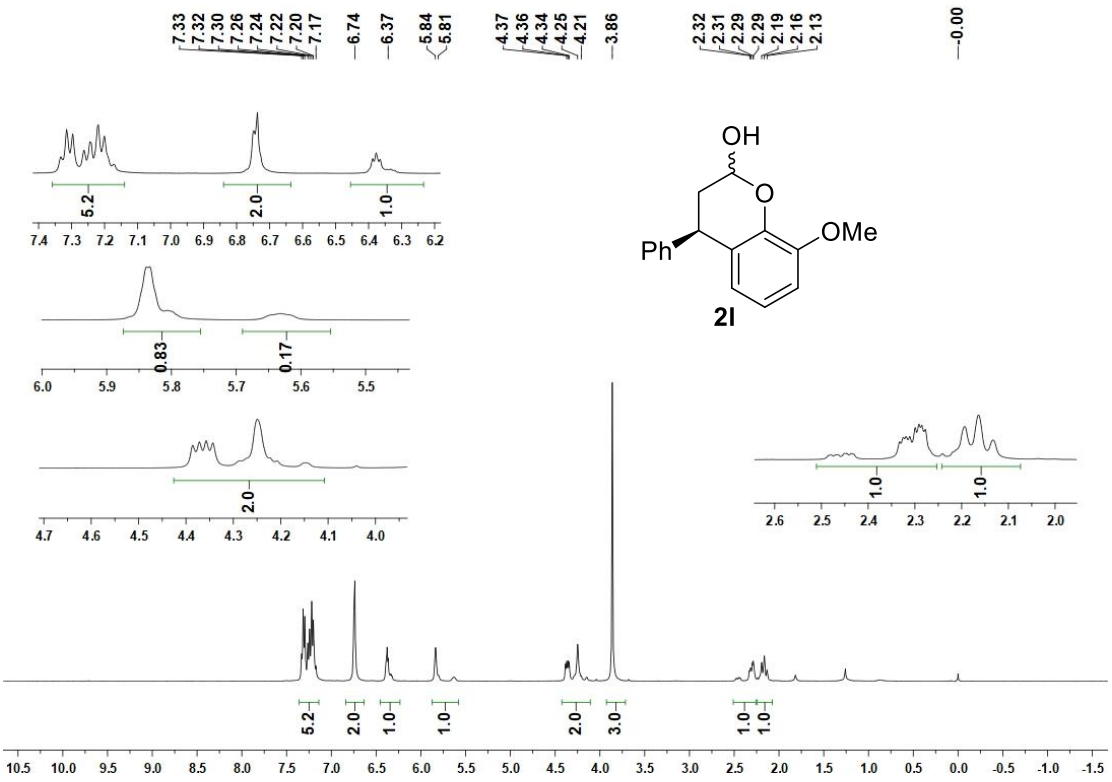
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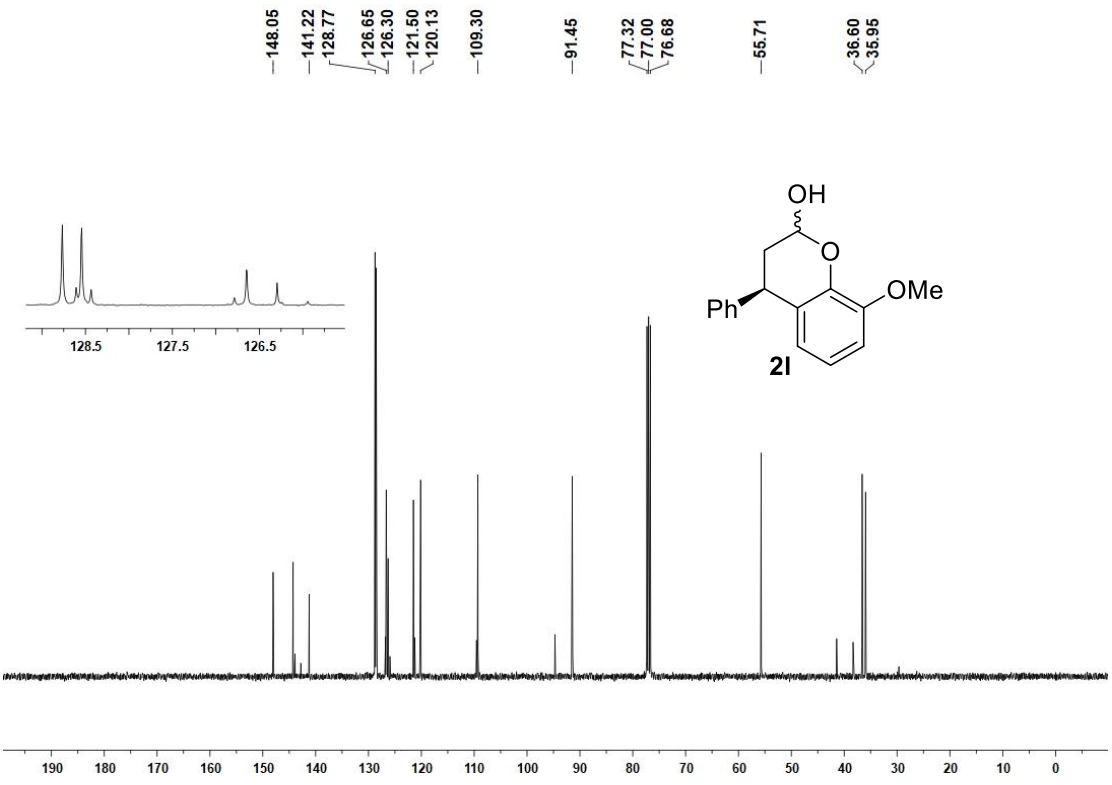
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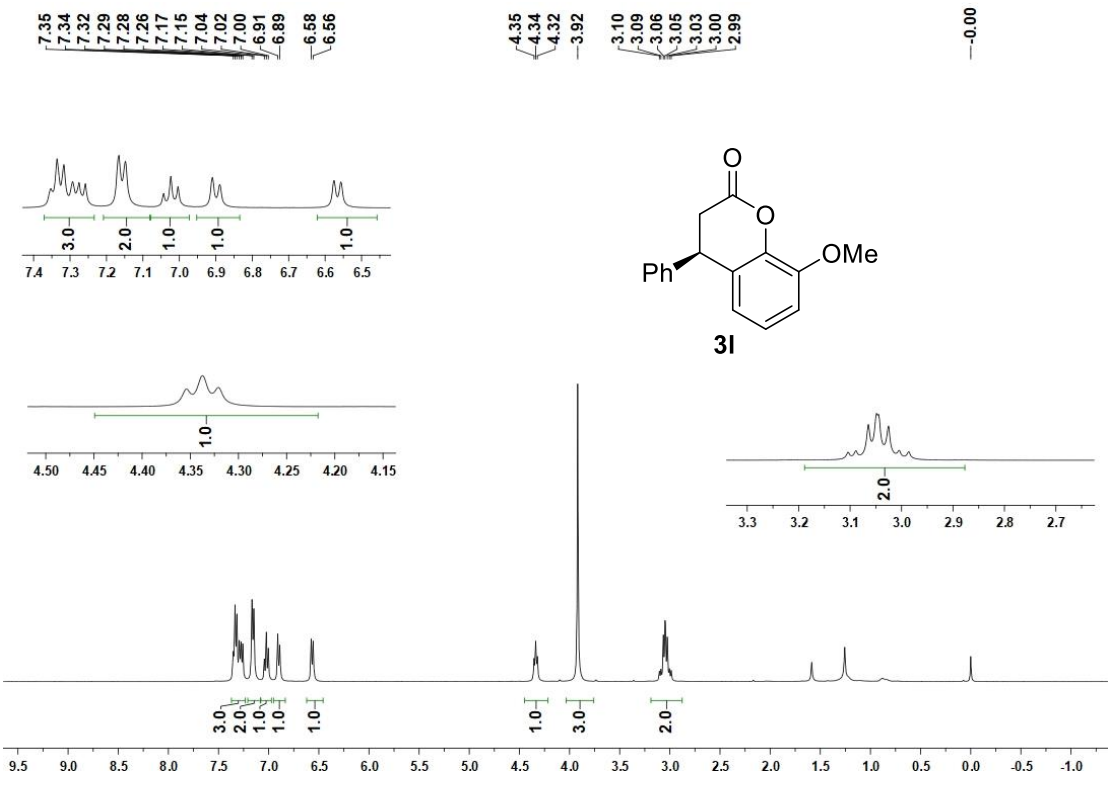
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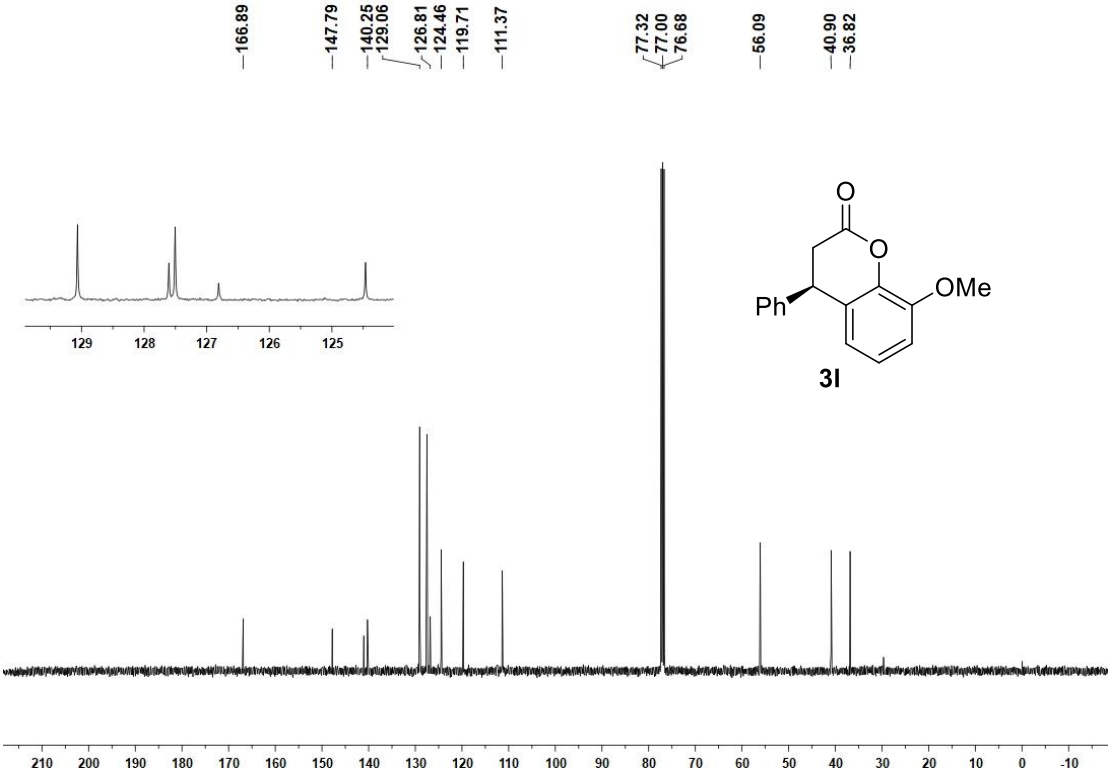
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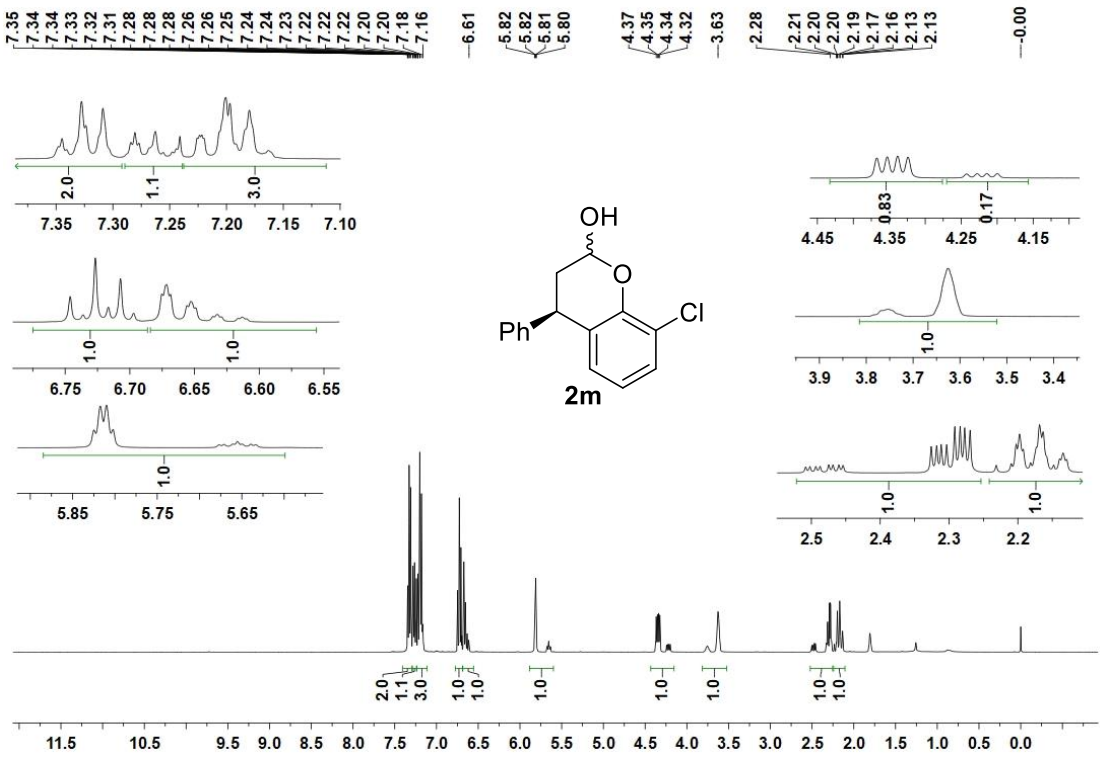
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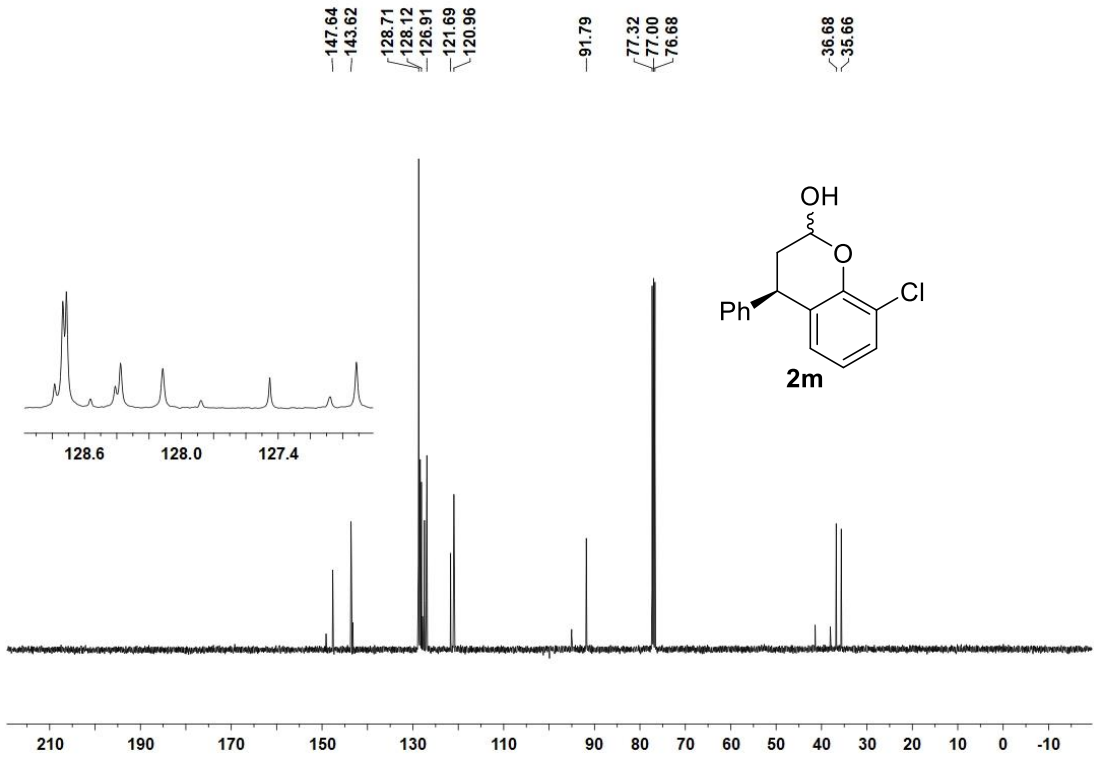
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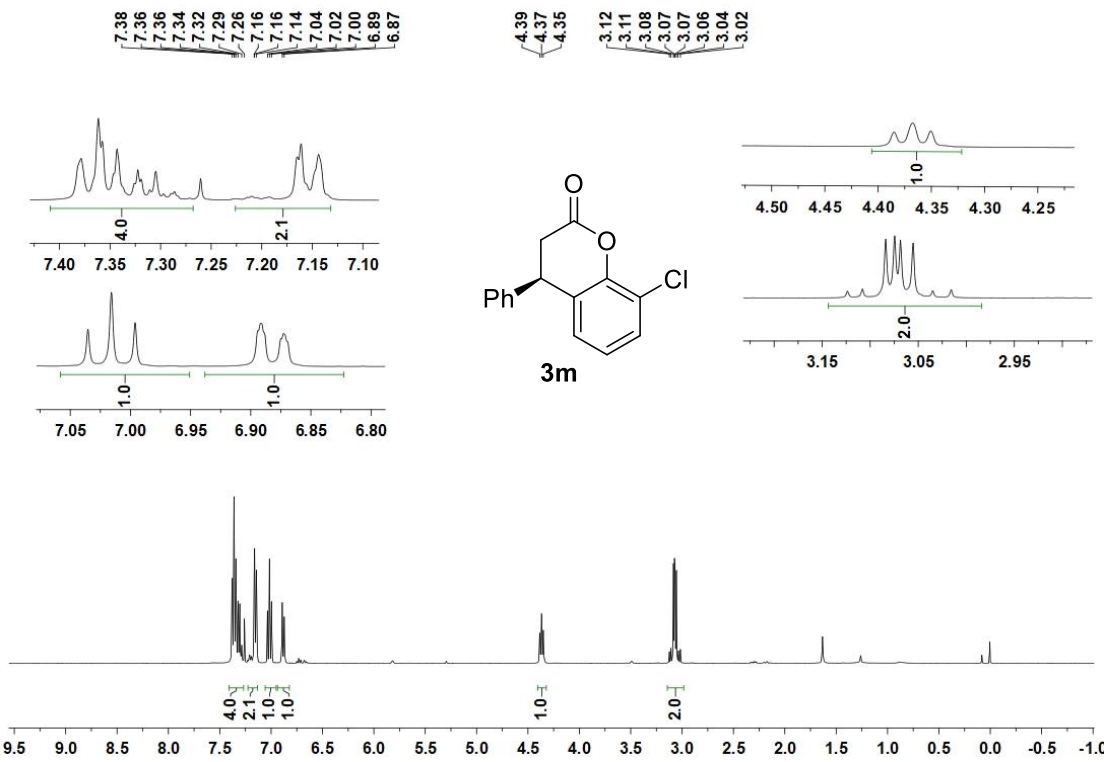
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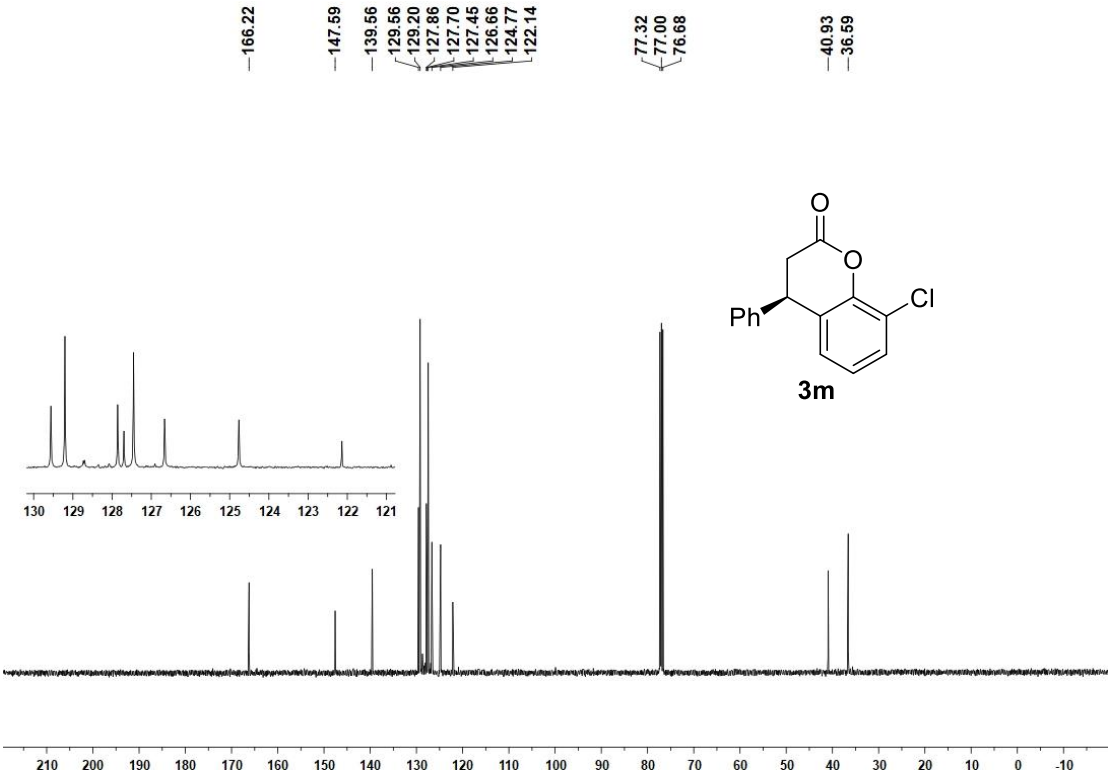
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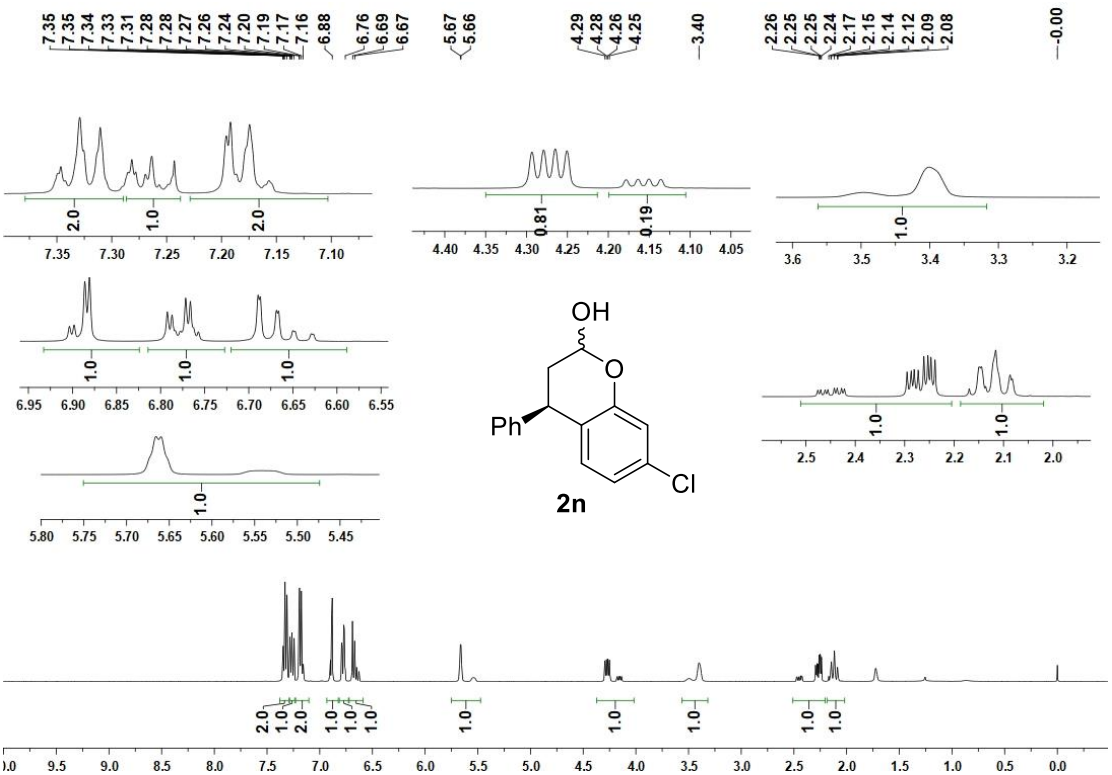
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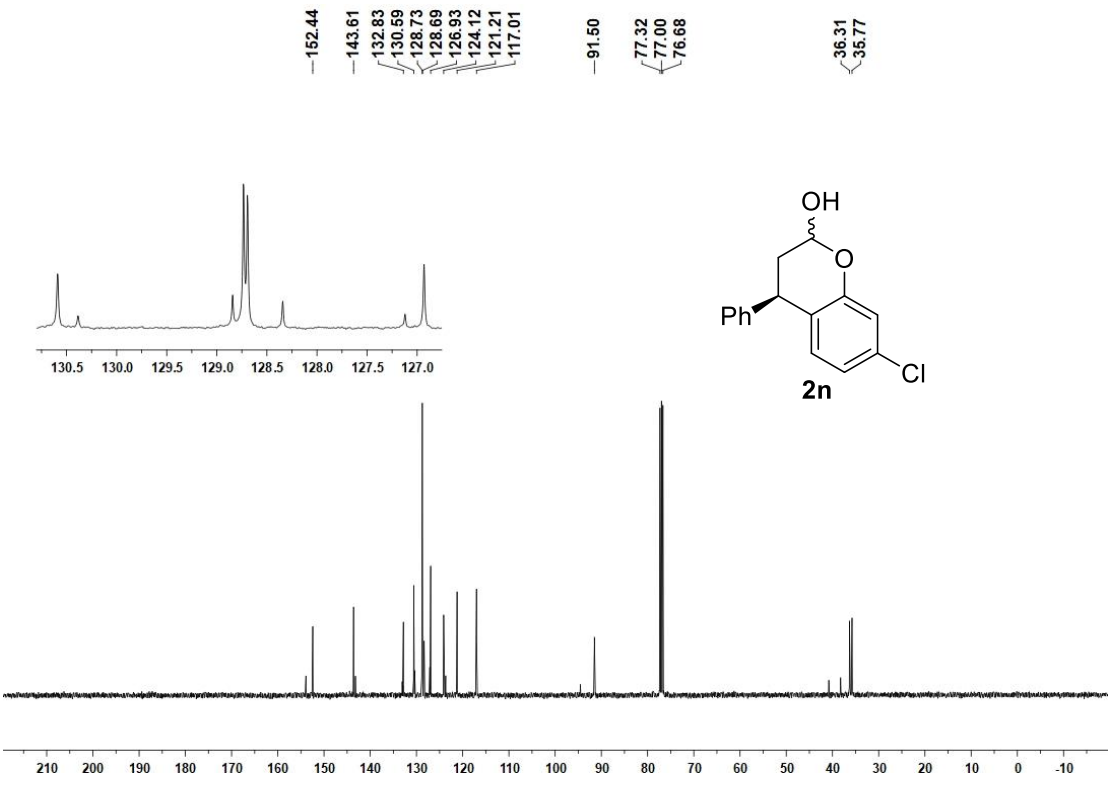
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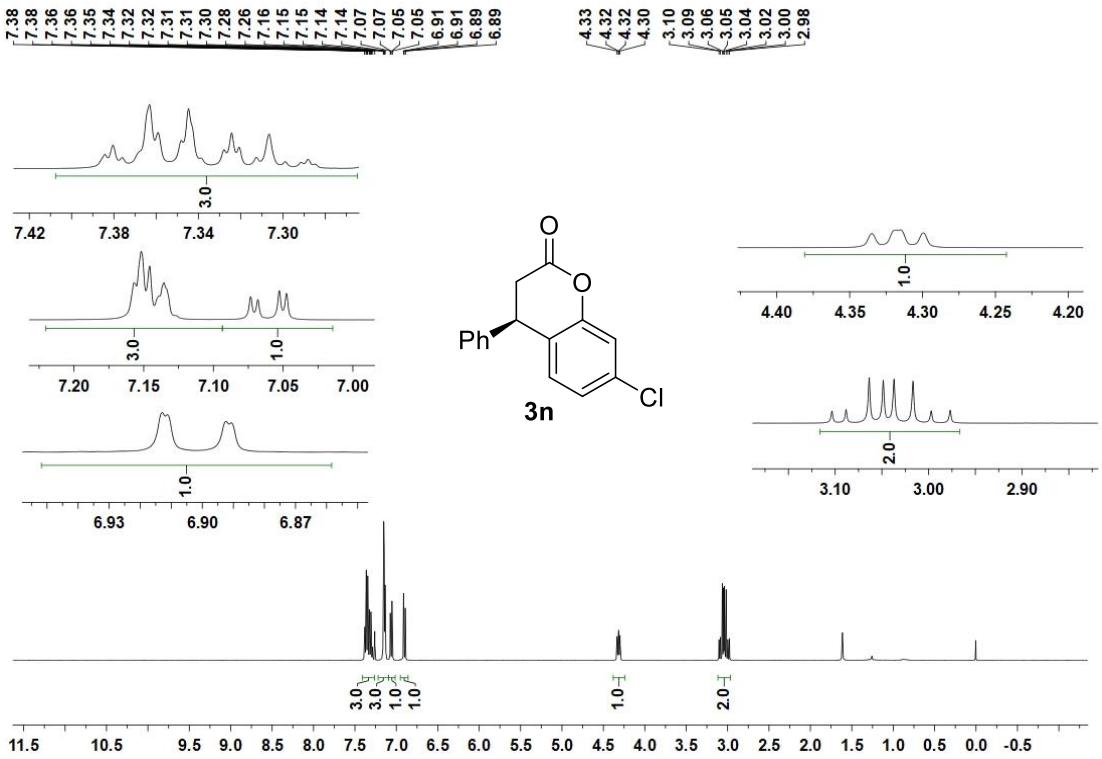
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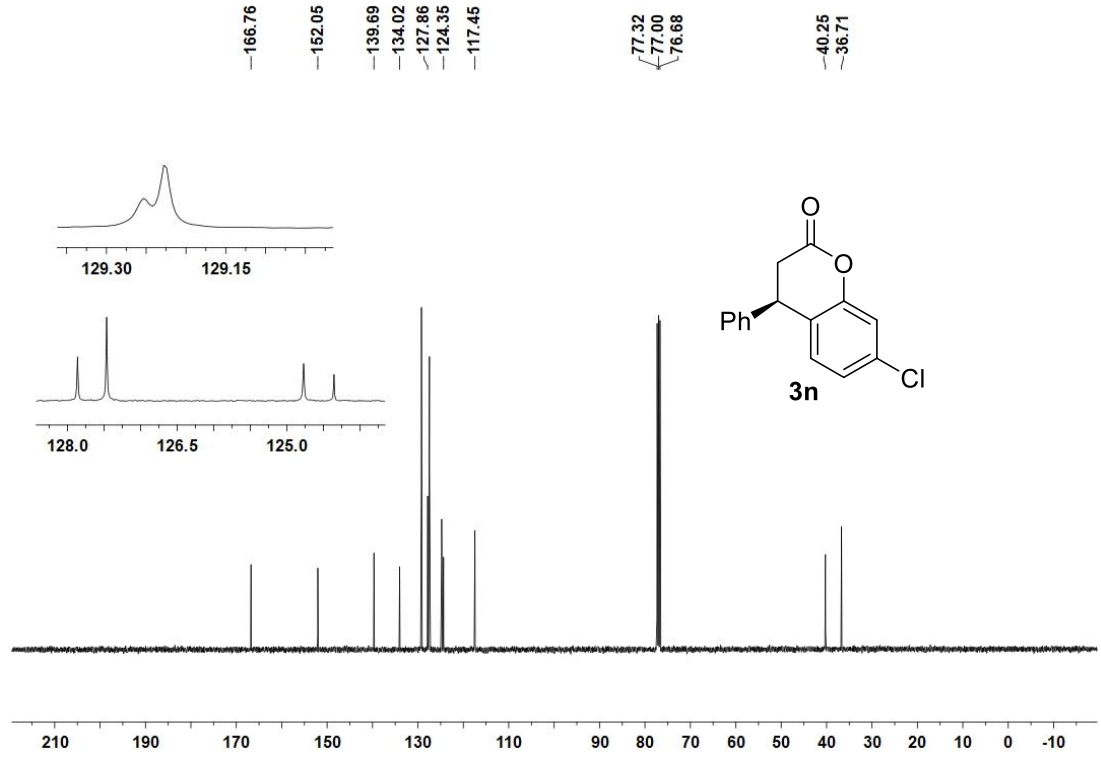
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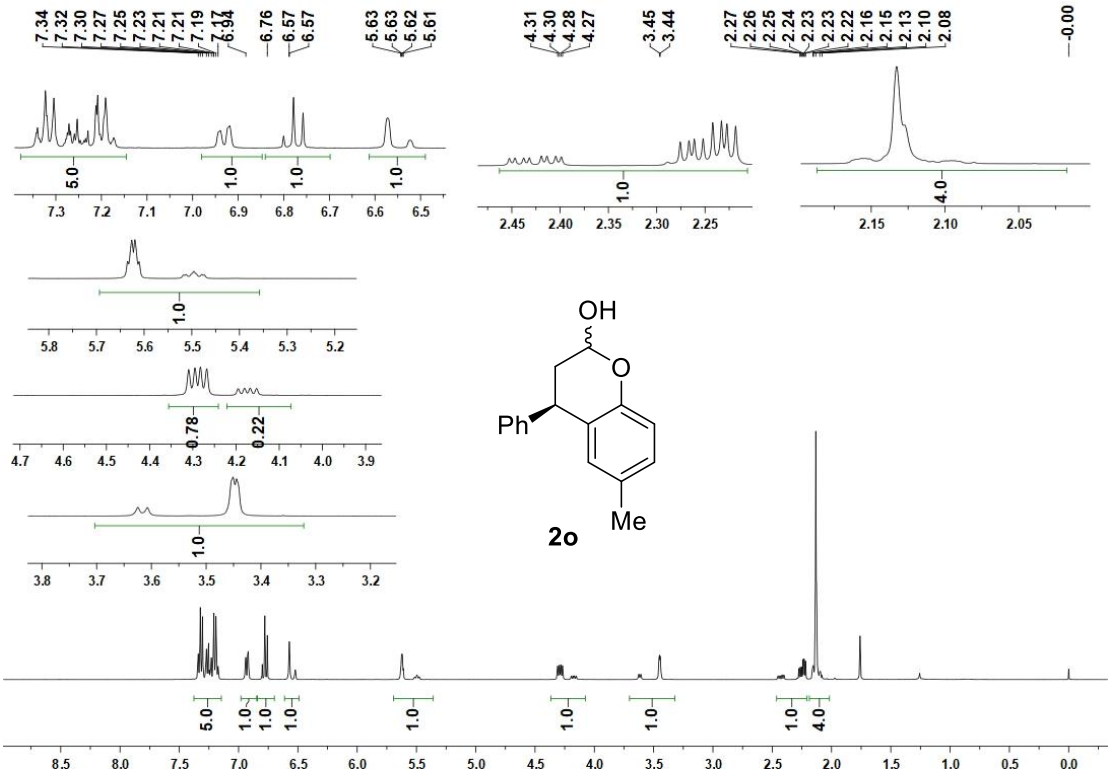
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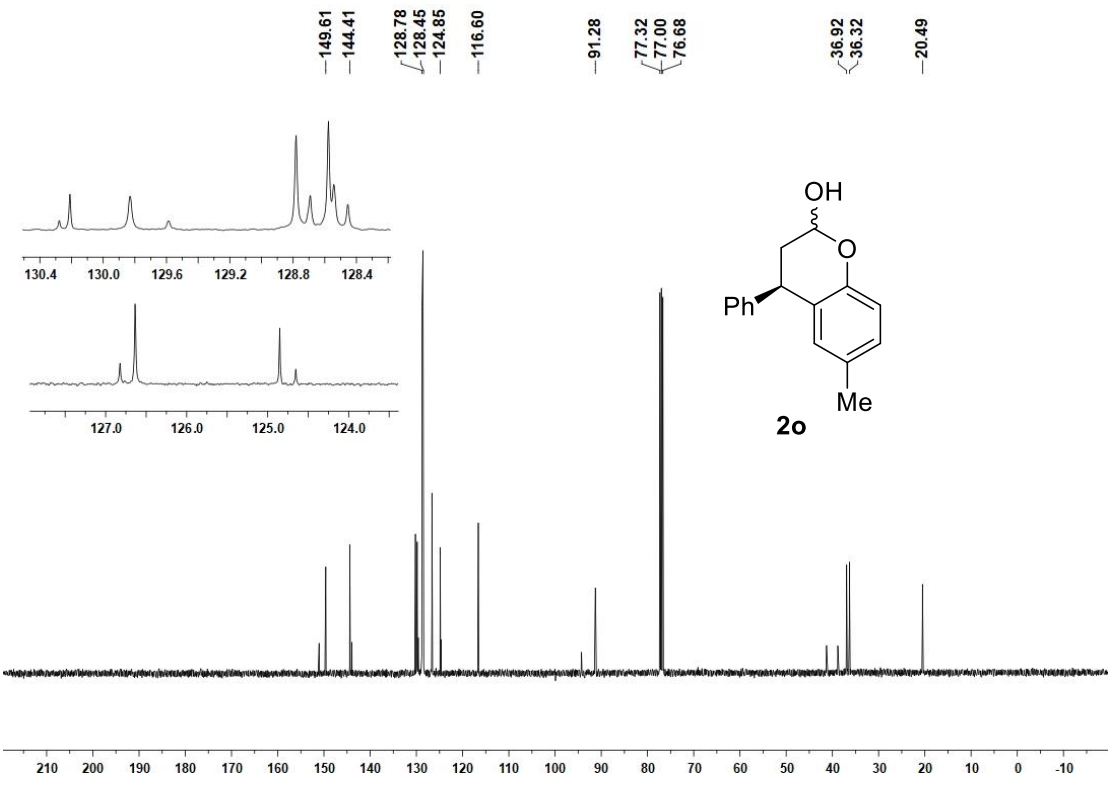
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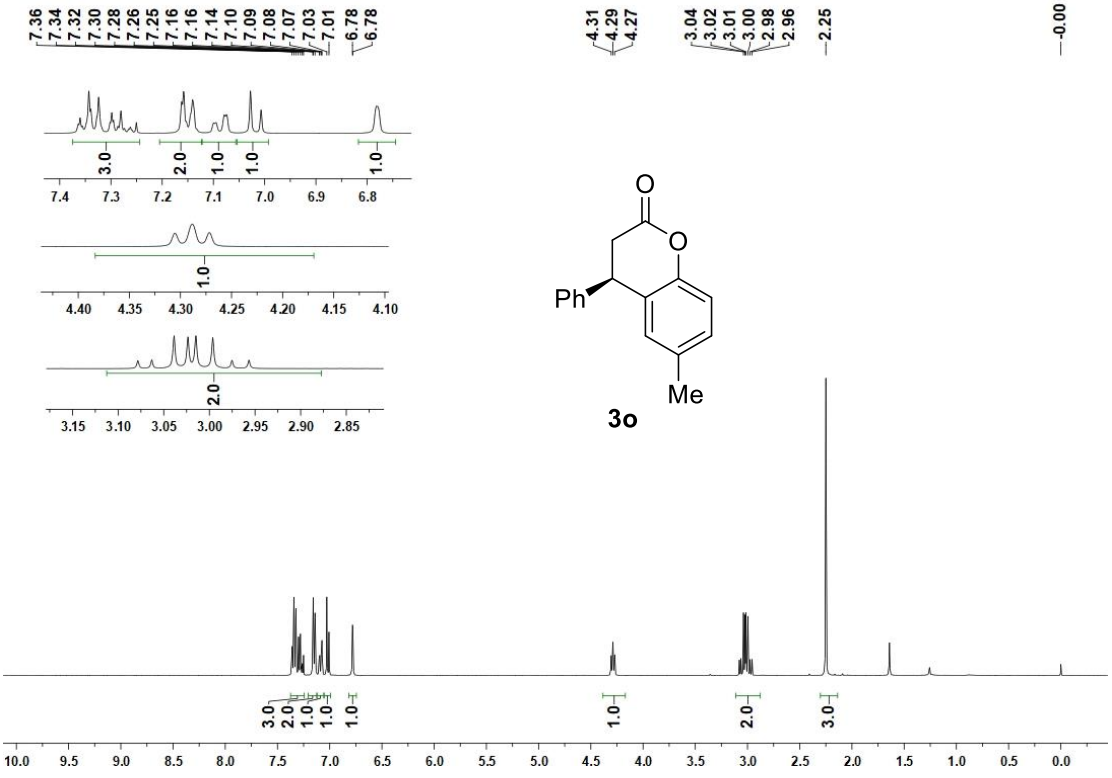
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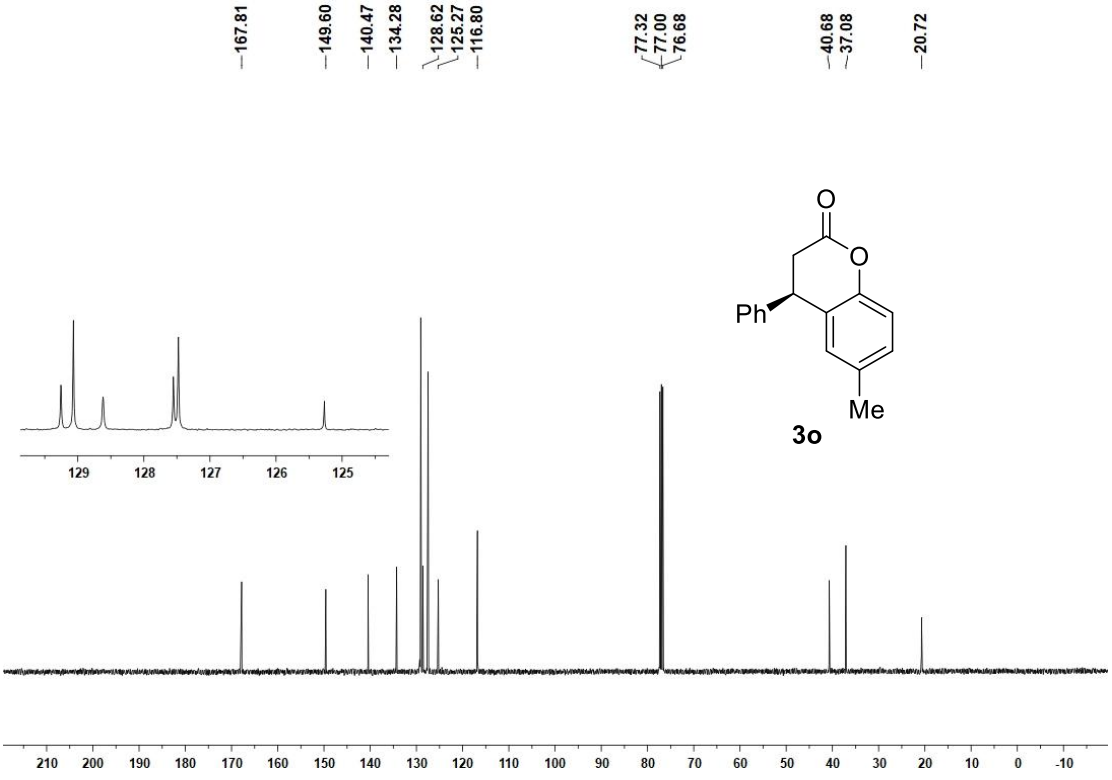
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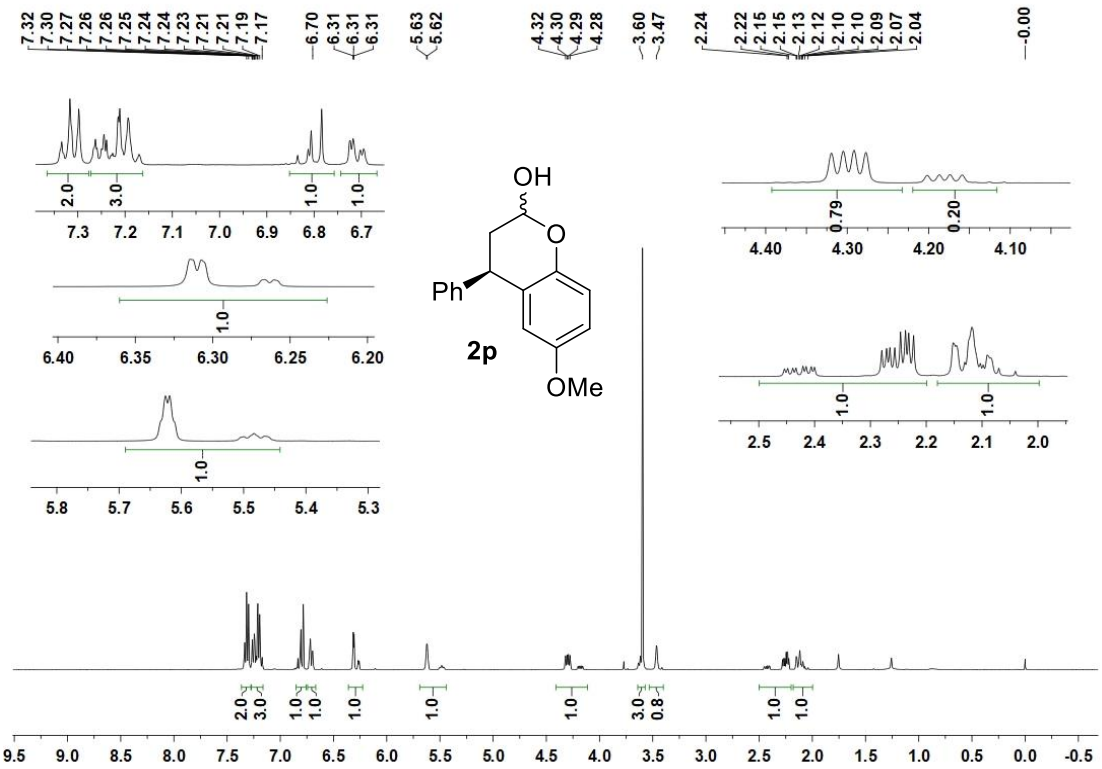
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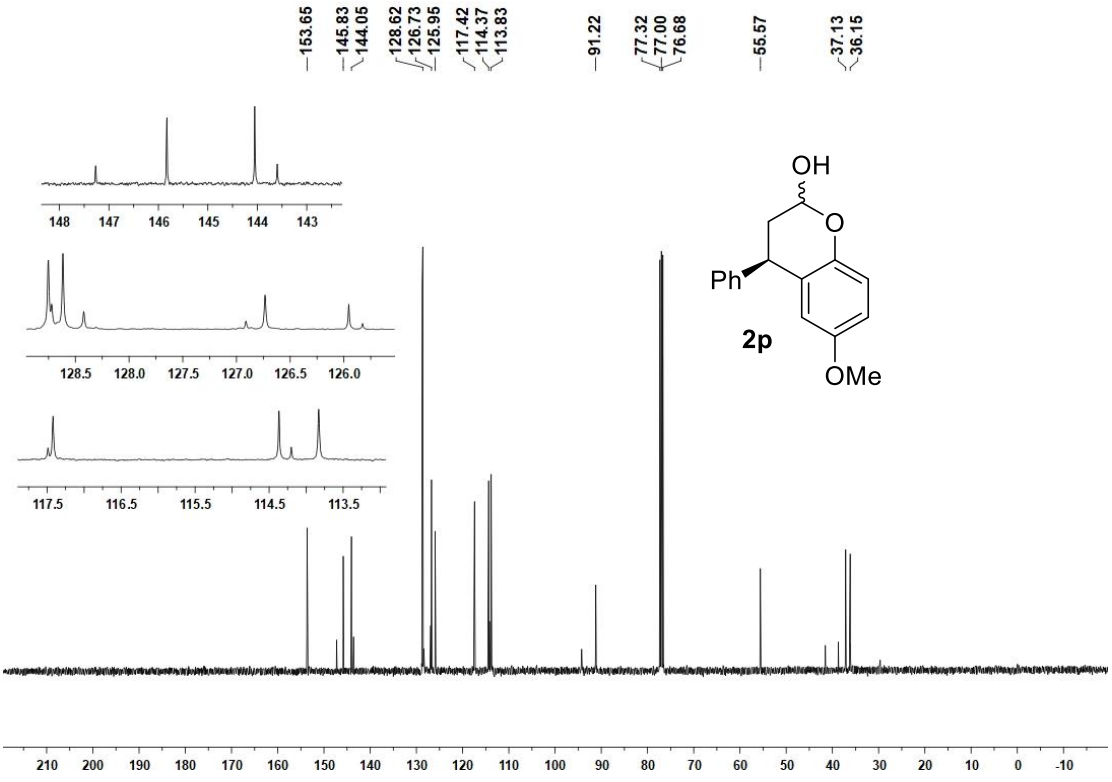
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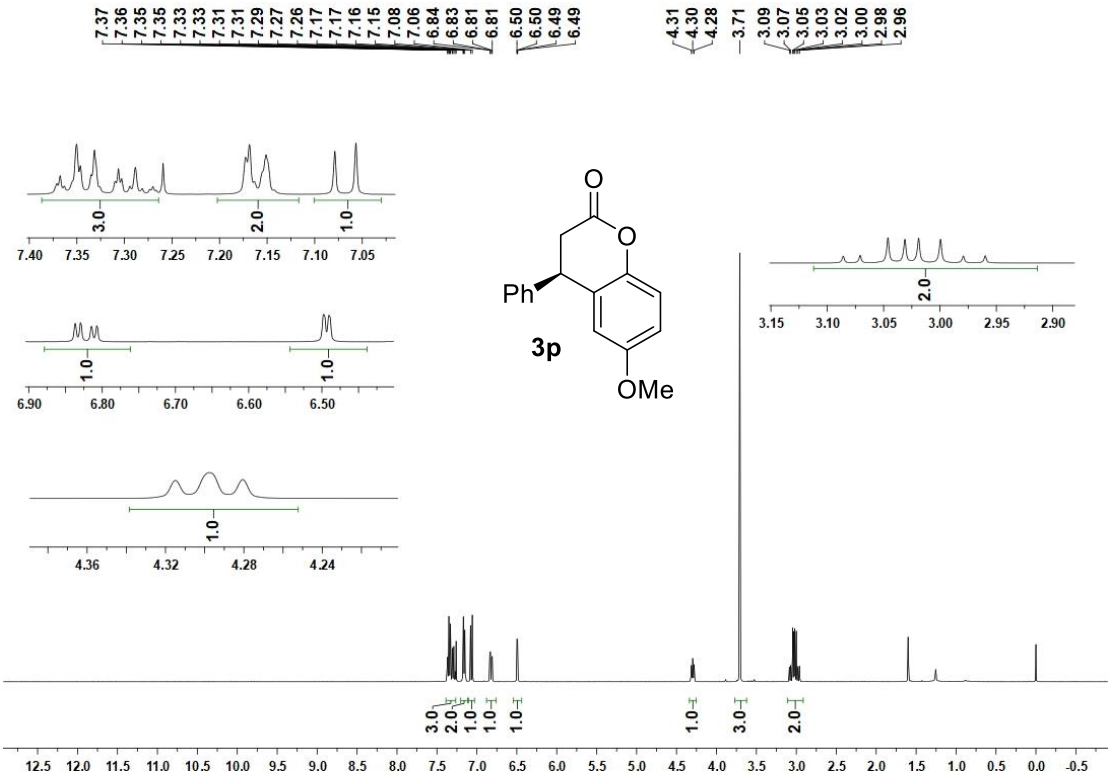
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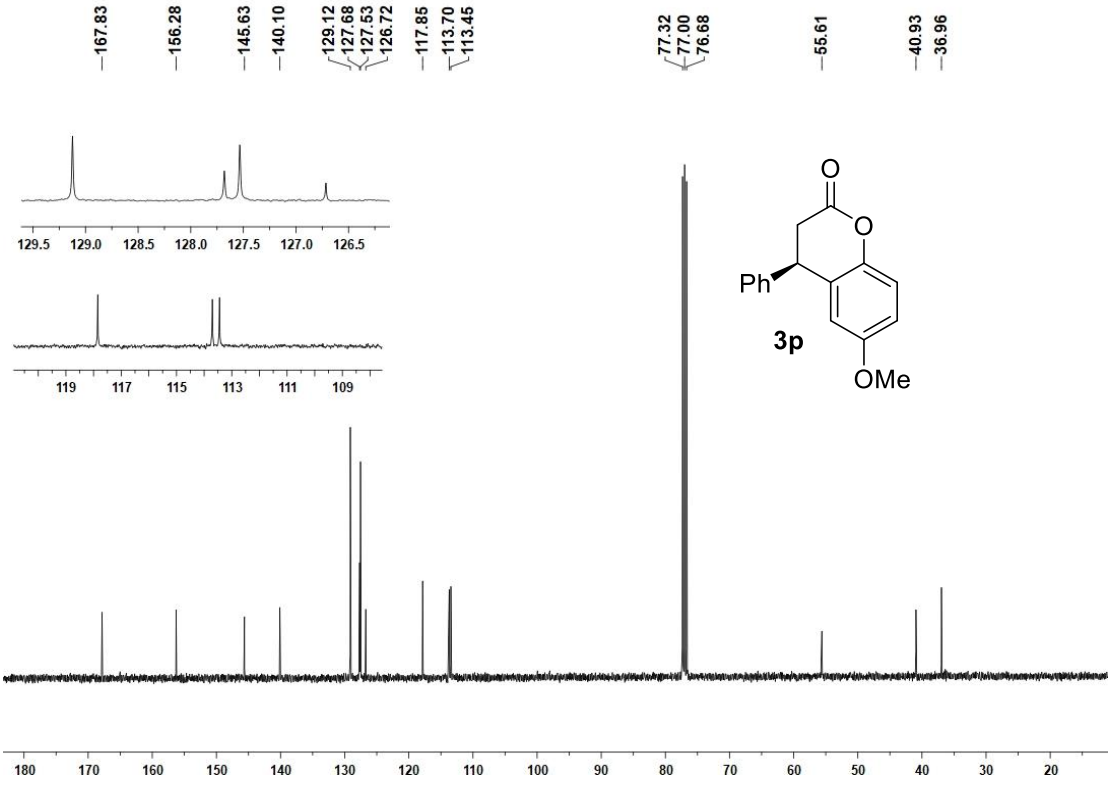
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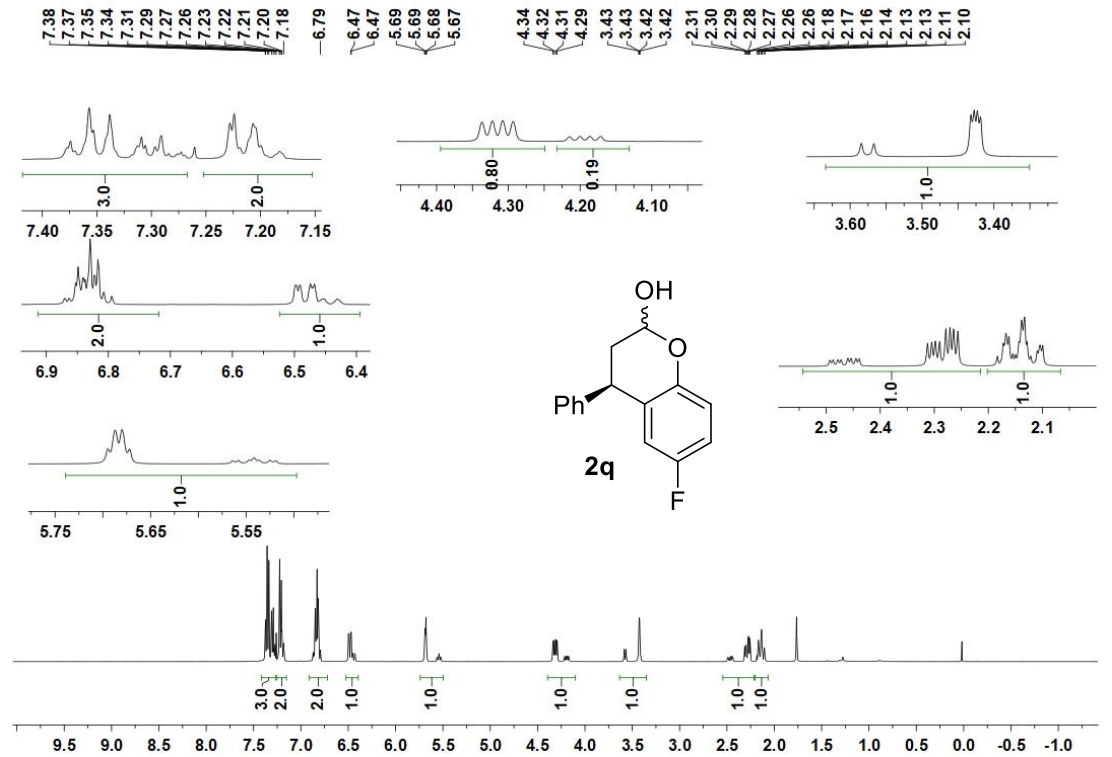
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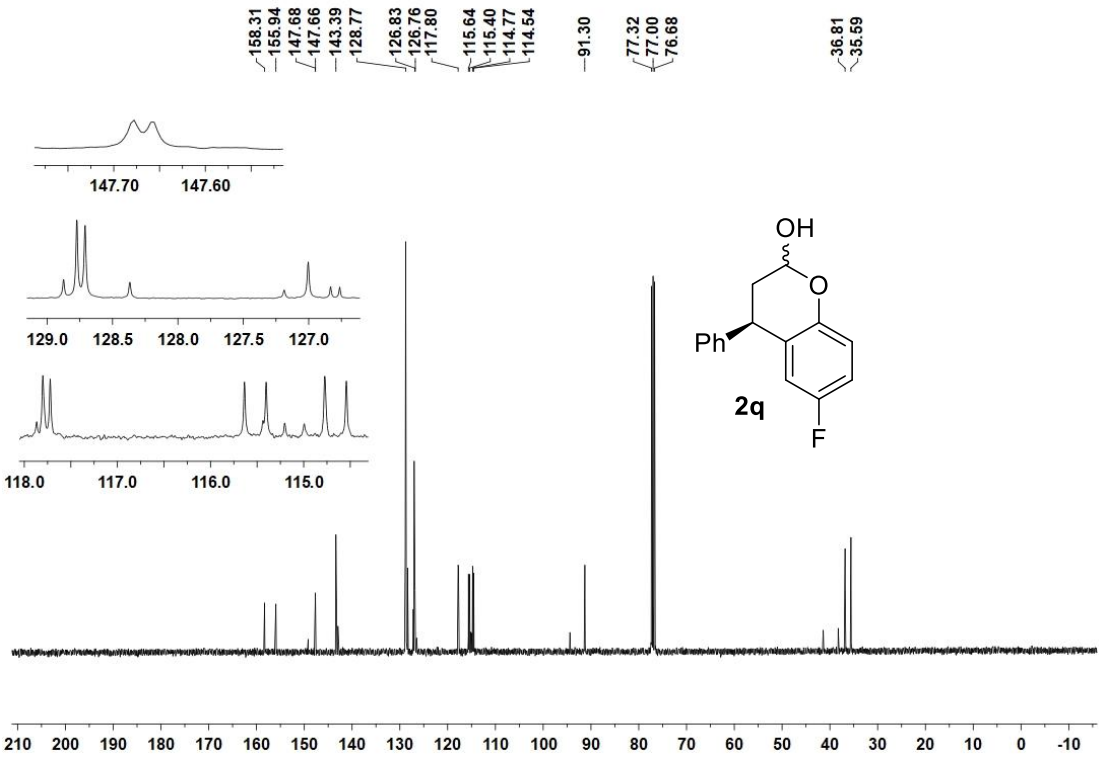
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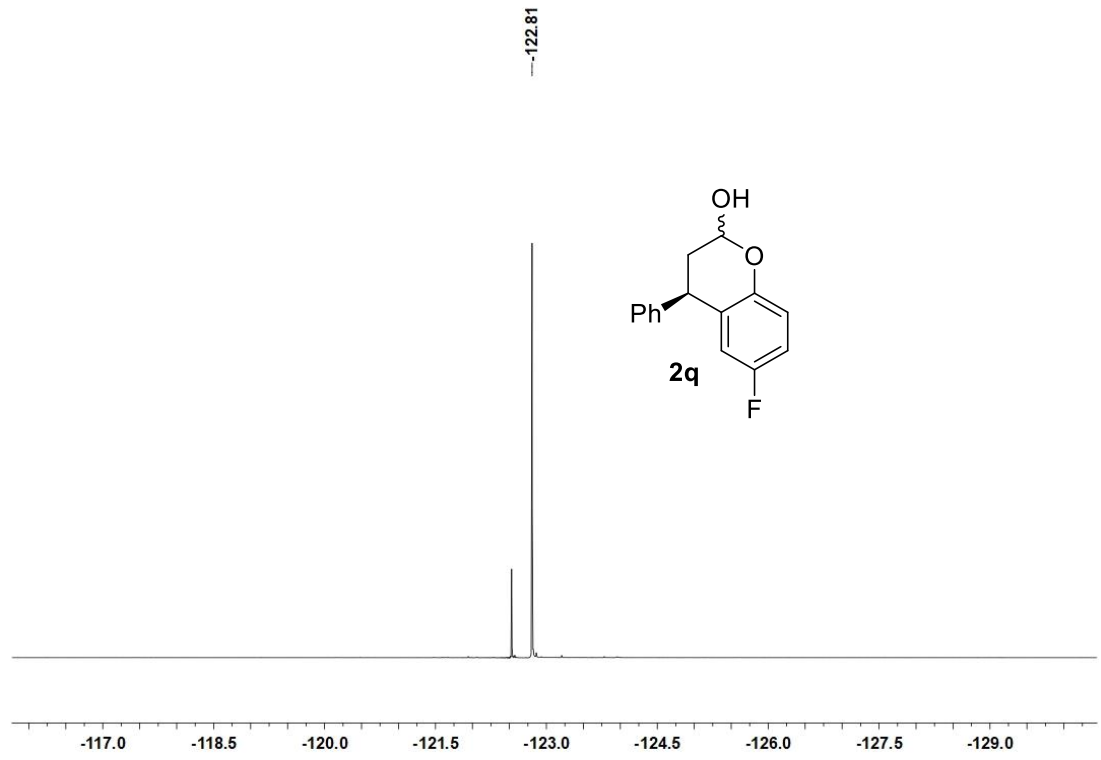
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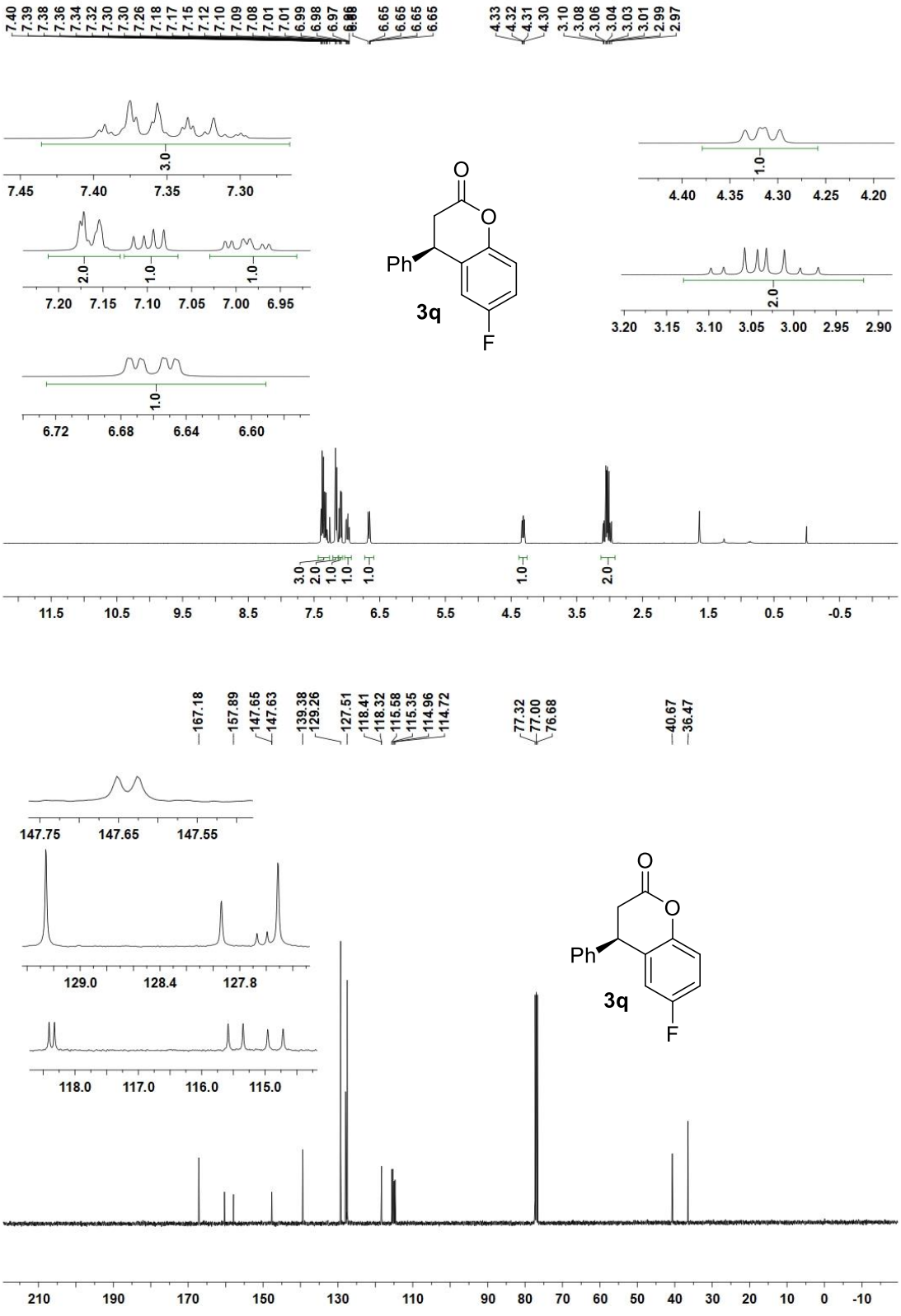
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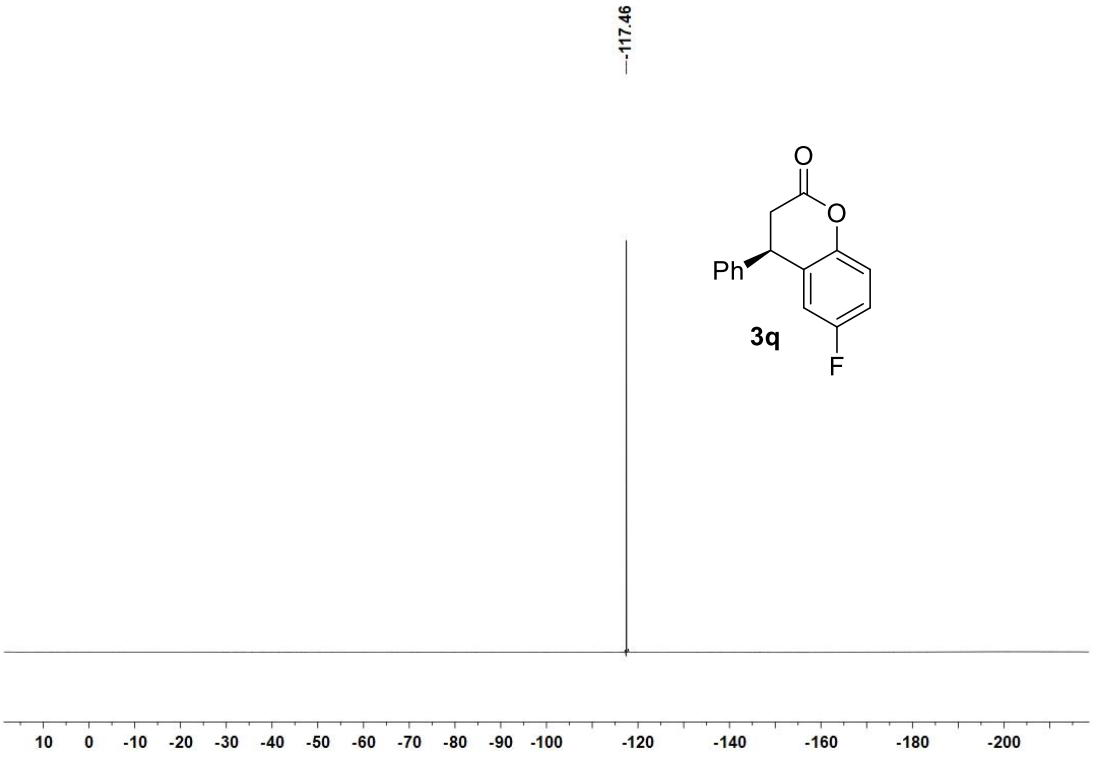
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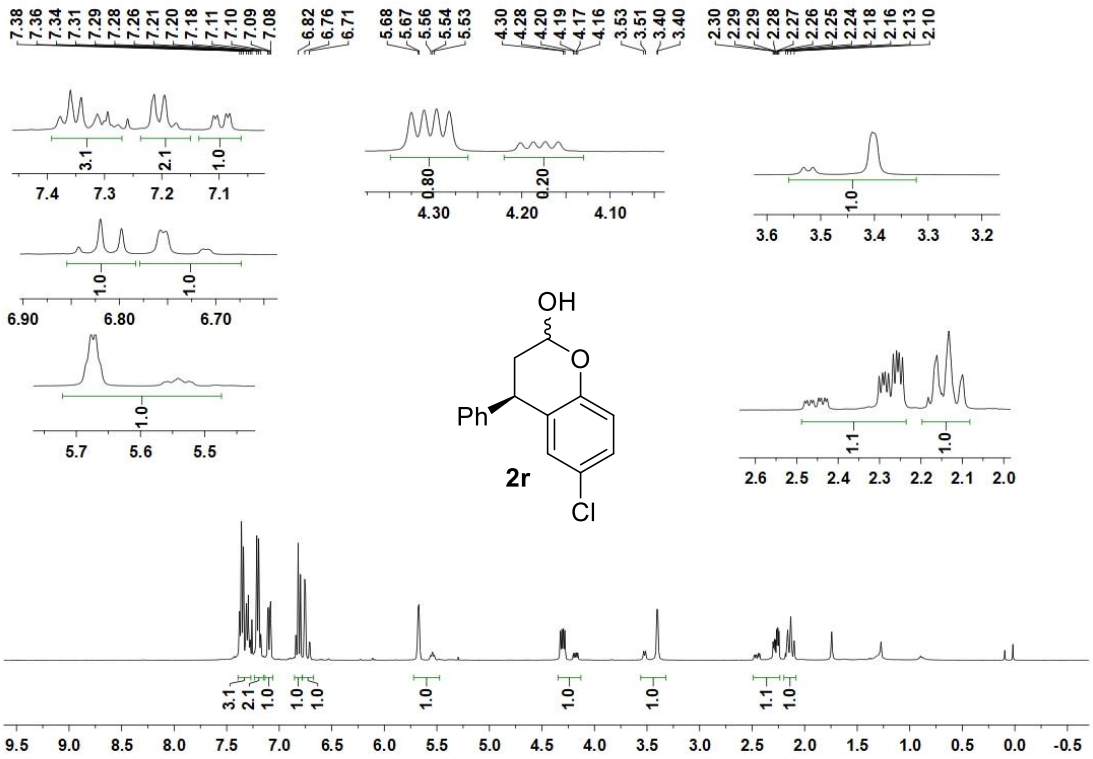
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2.30 2.29 2.29 2.28 2.27 2.26 2.25 2.24 2.18 2.16 2.13 2.10
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1.0
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Ph
2r
Cl
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2.6 2.5 2.4 2.3 2.2 2.1 2.0
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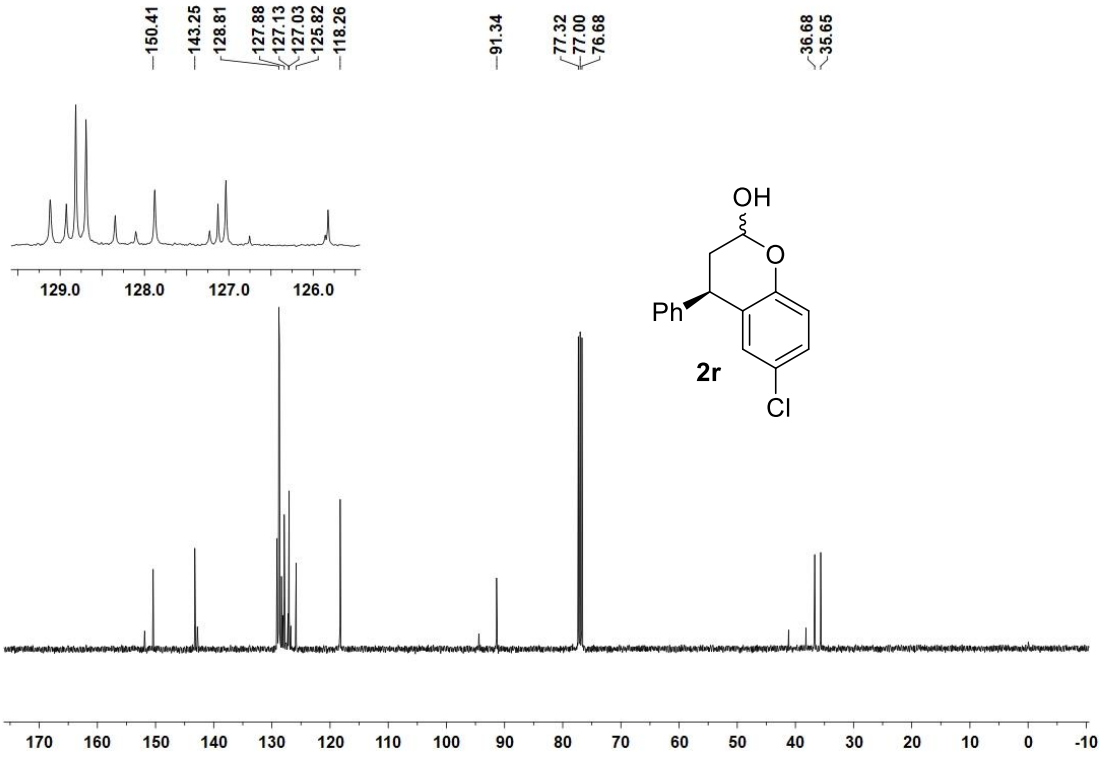
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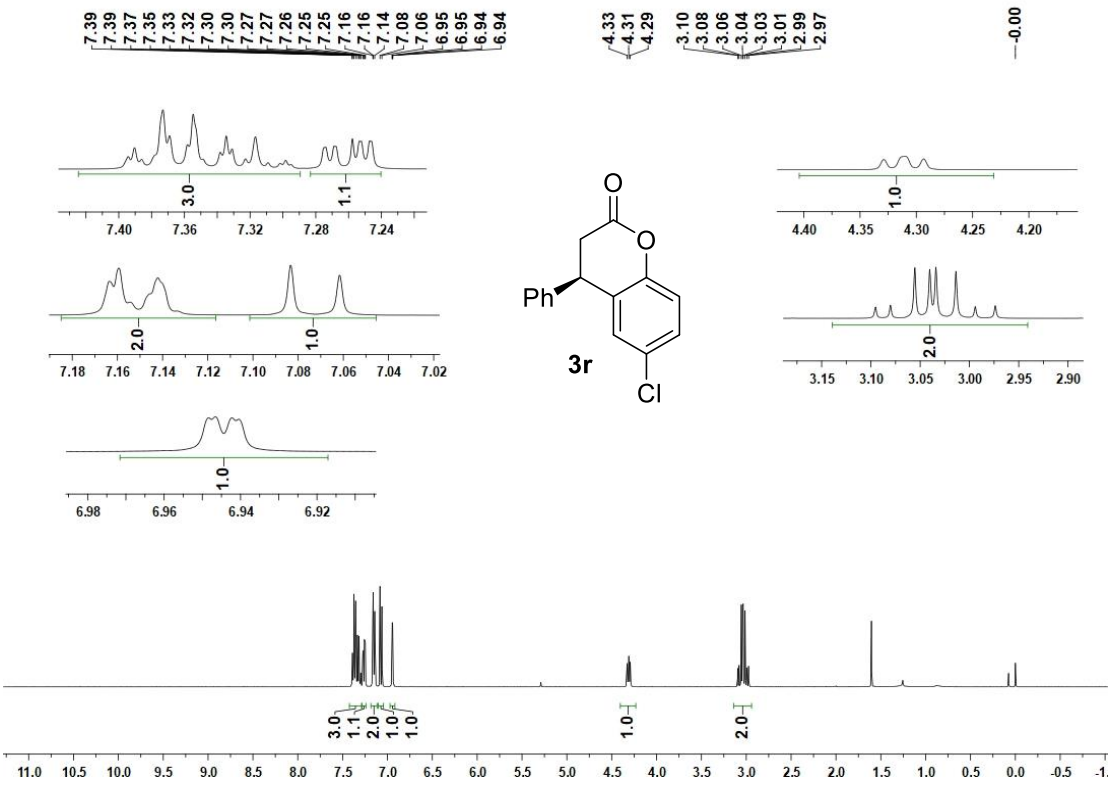
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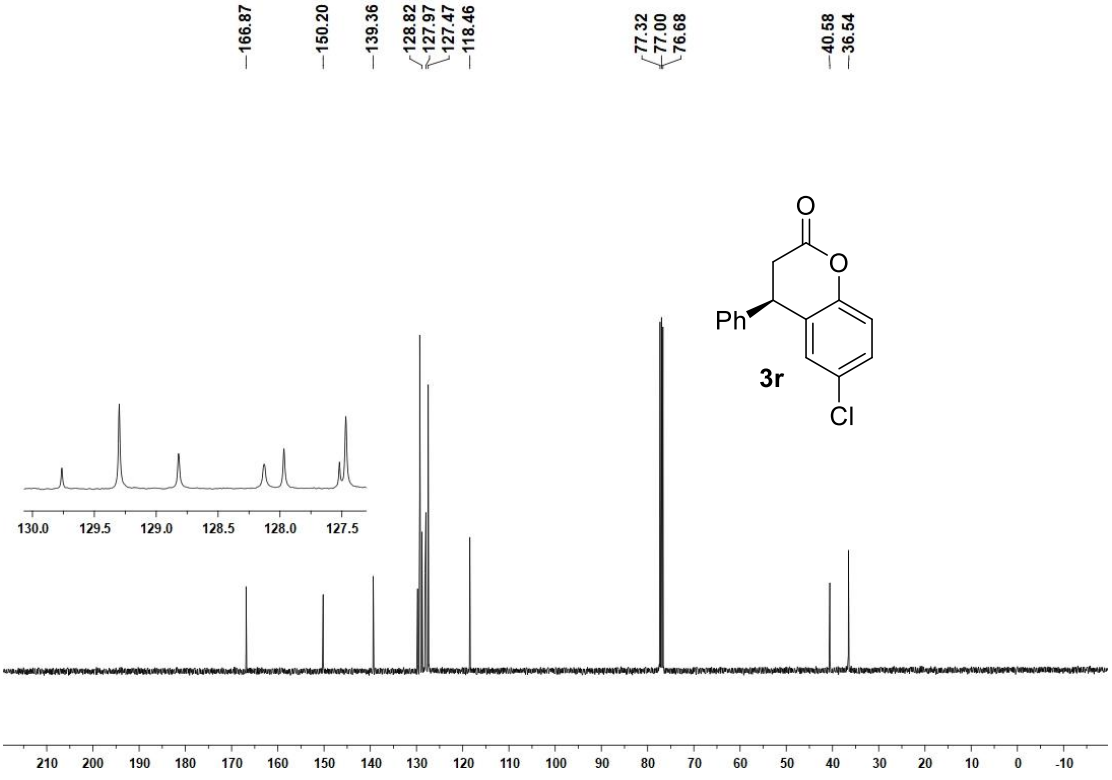
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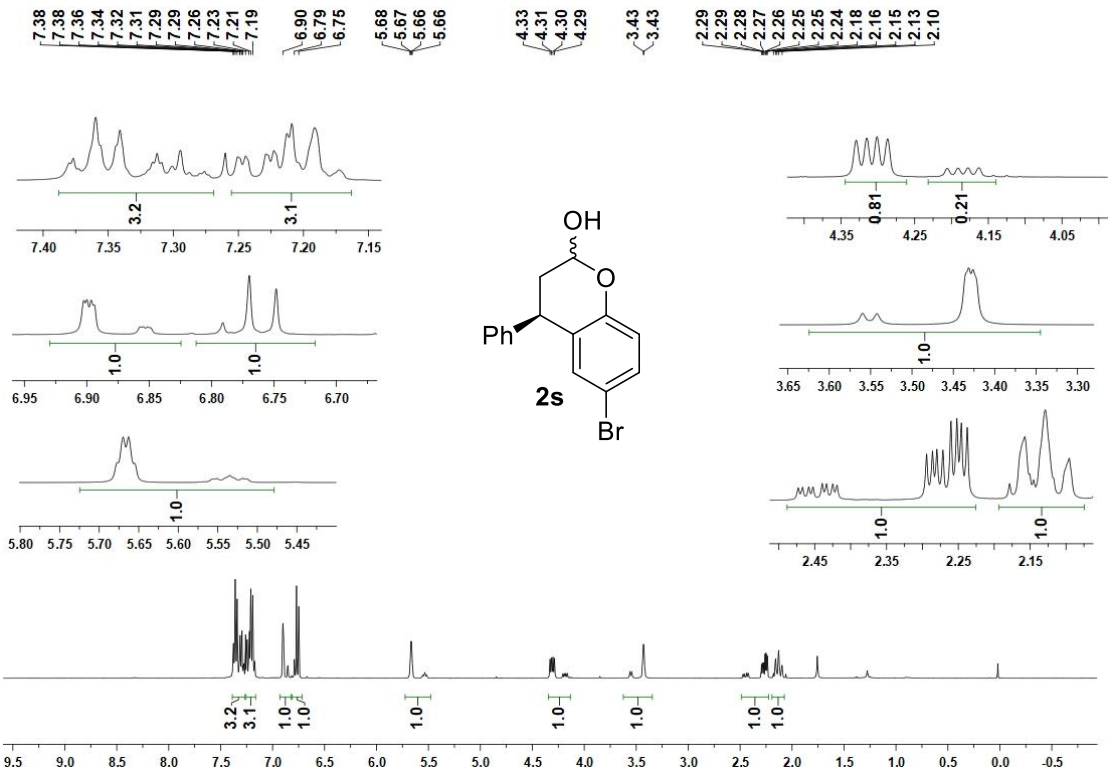
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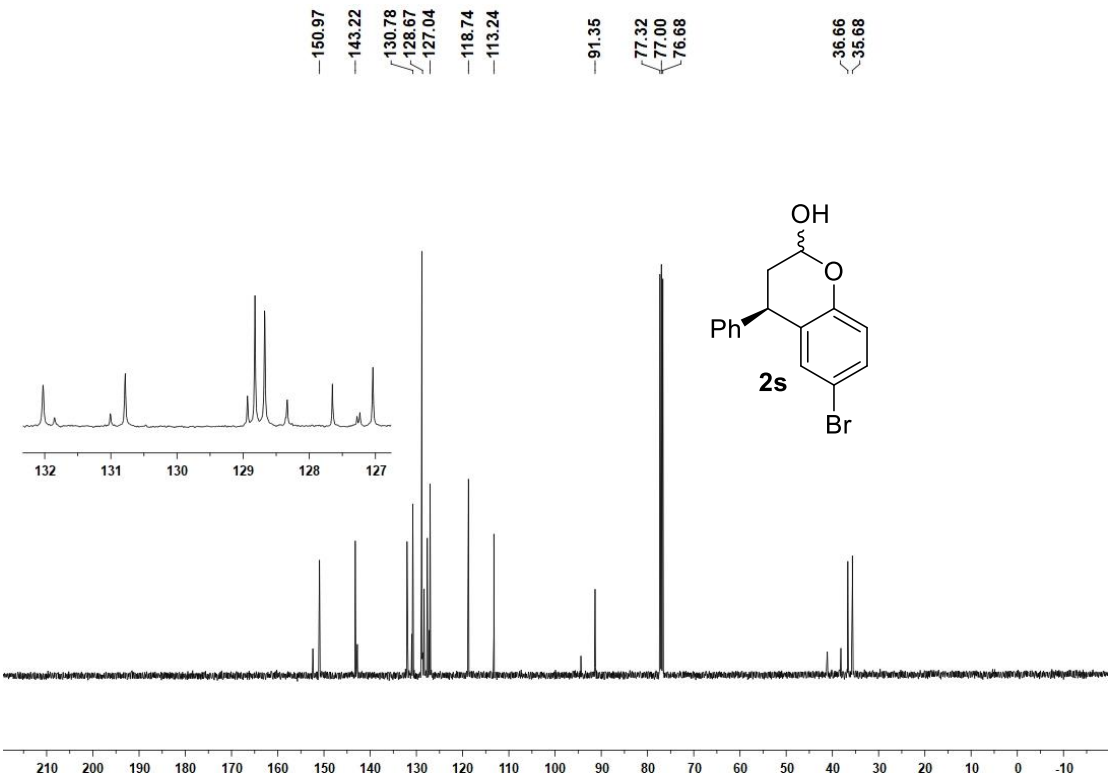
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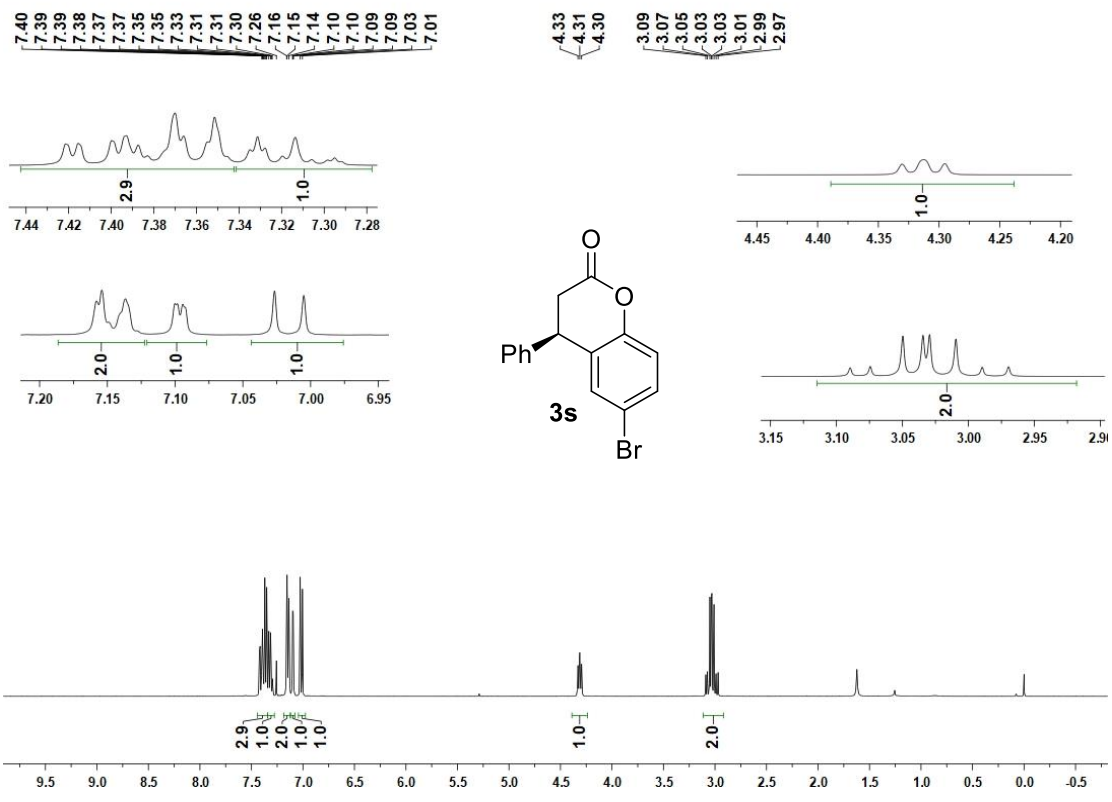
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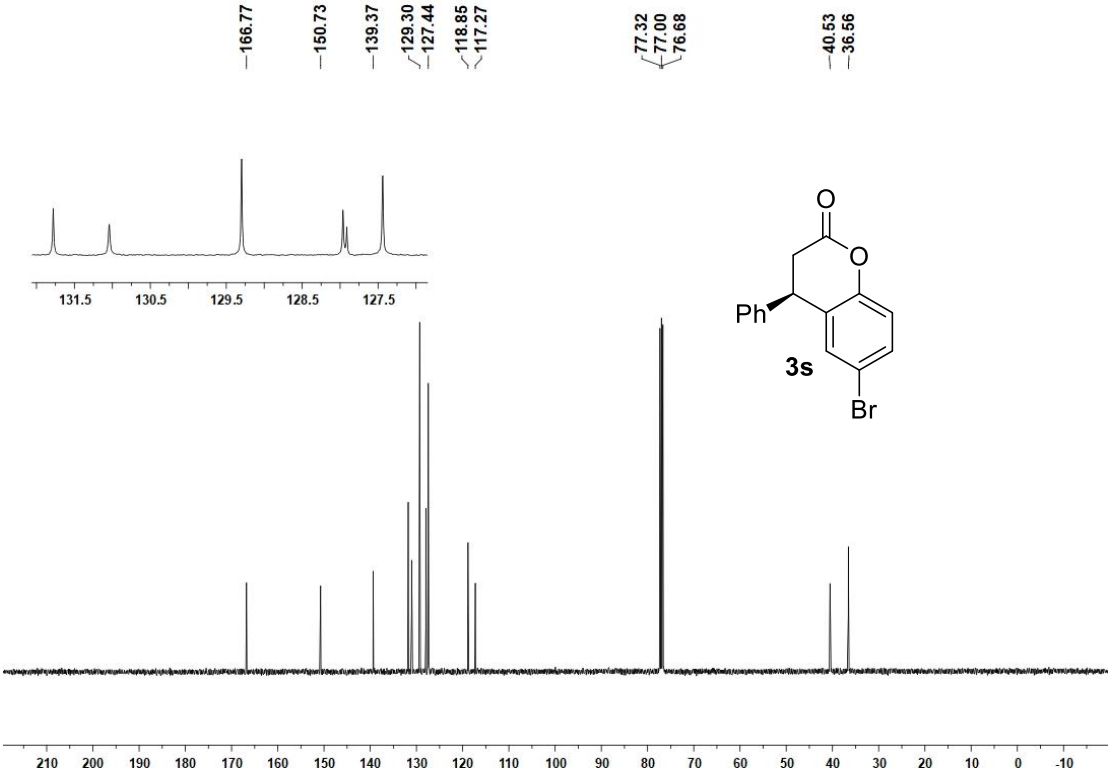
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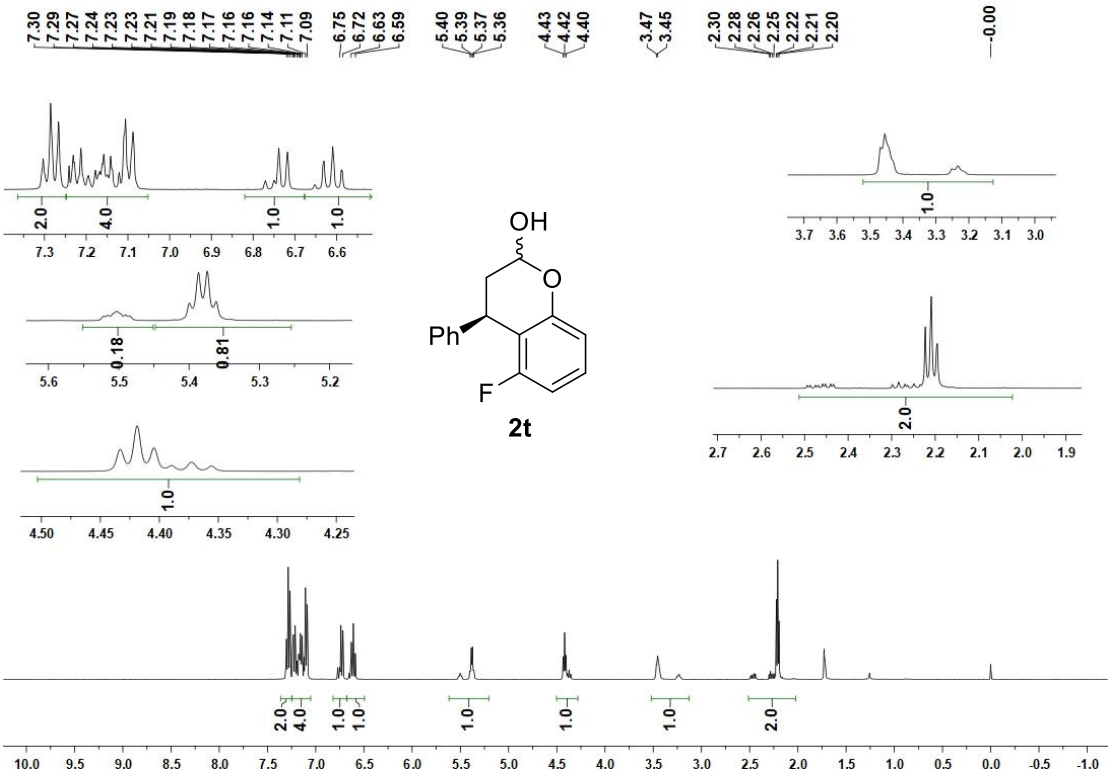
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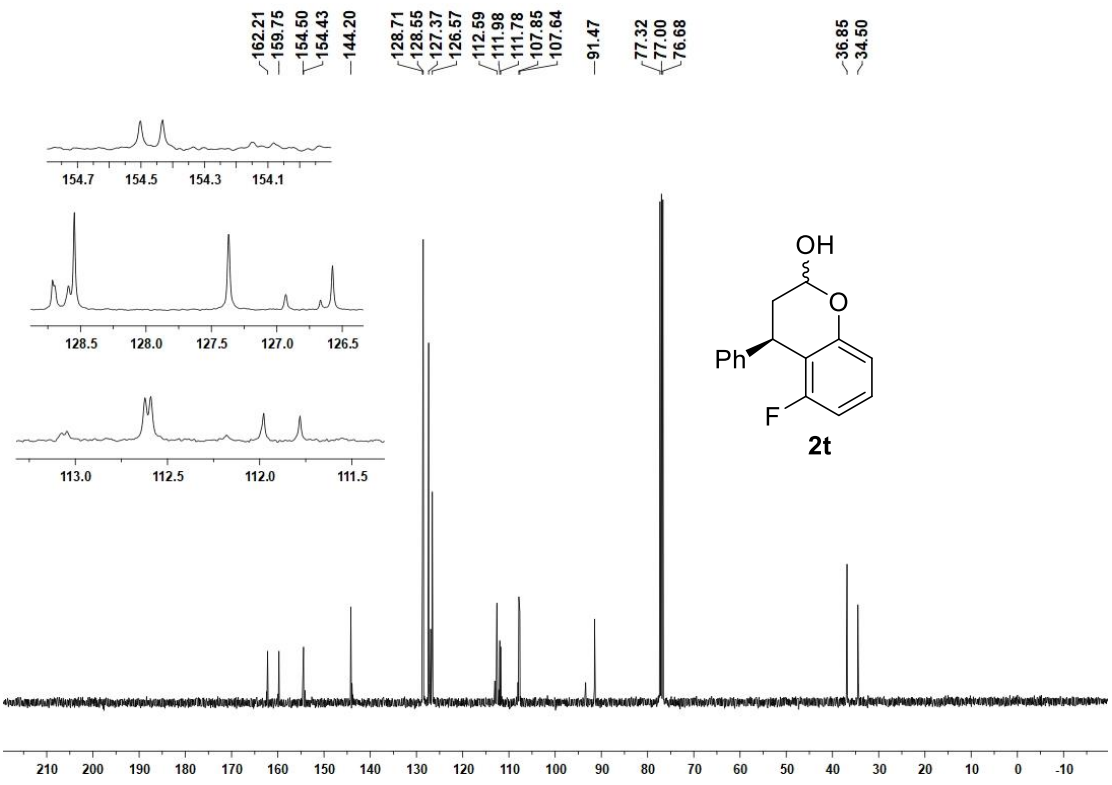
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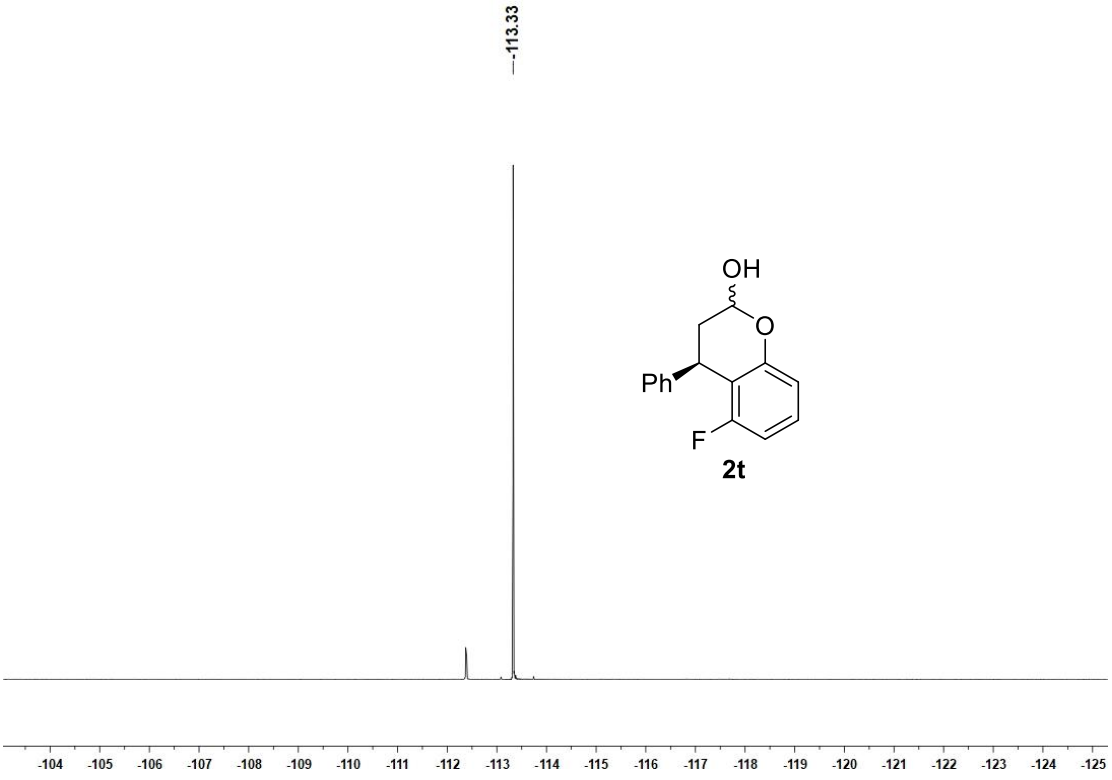
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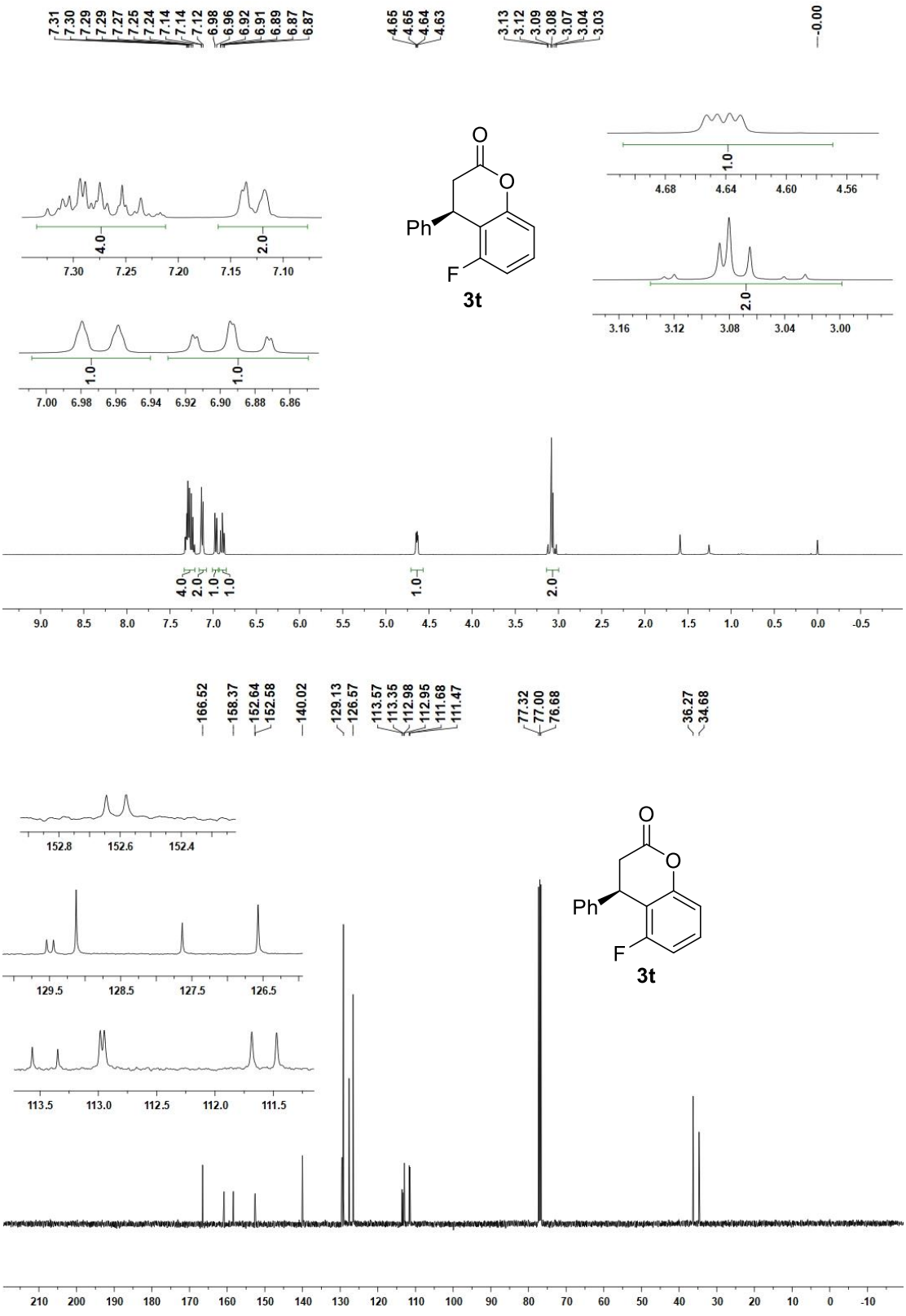
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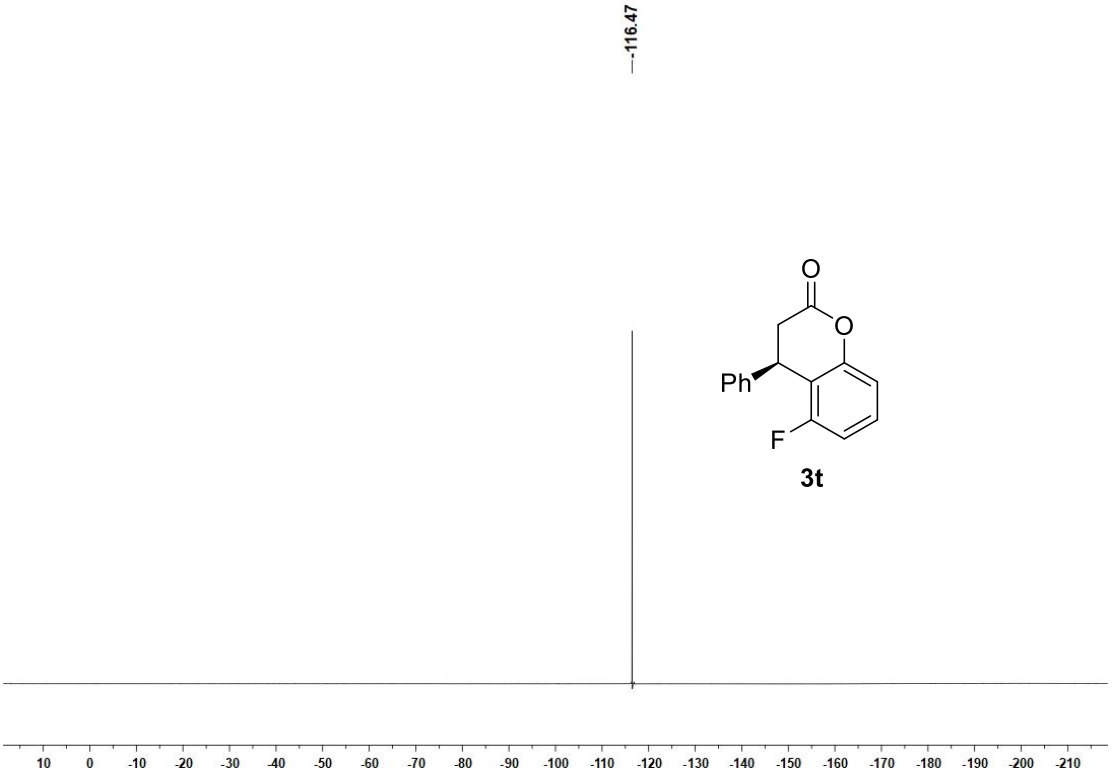
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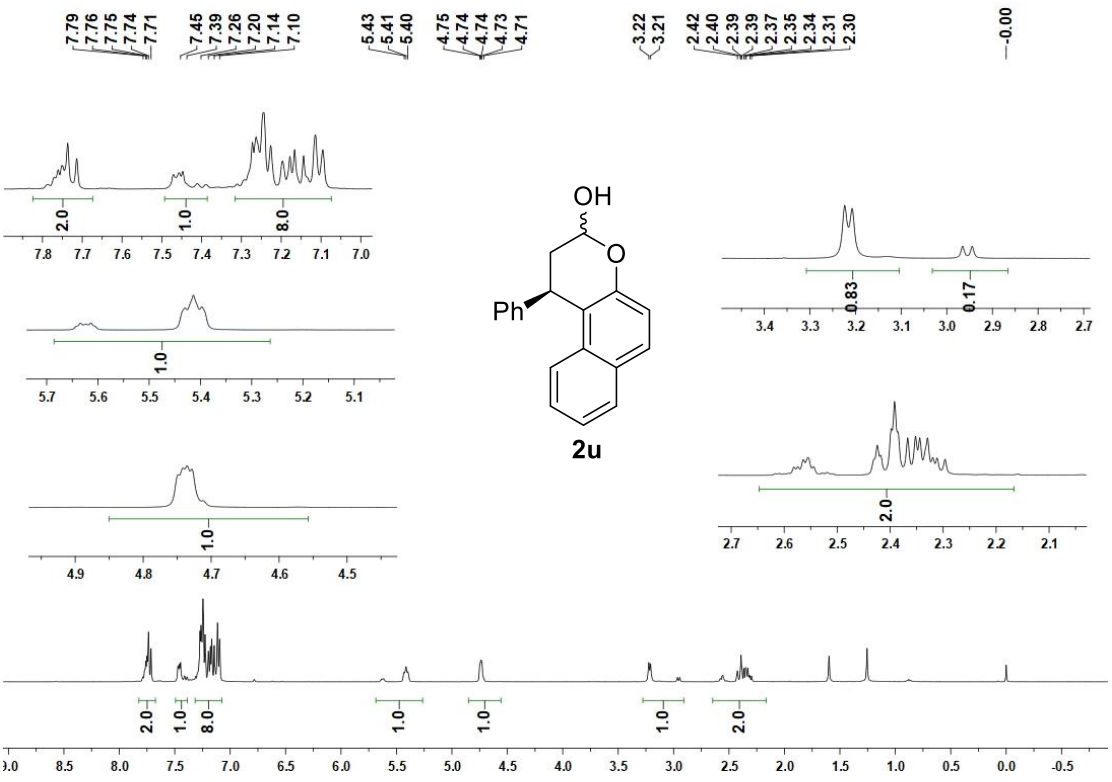
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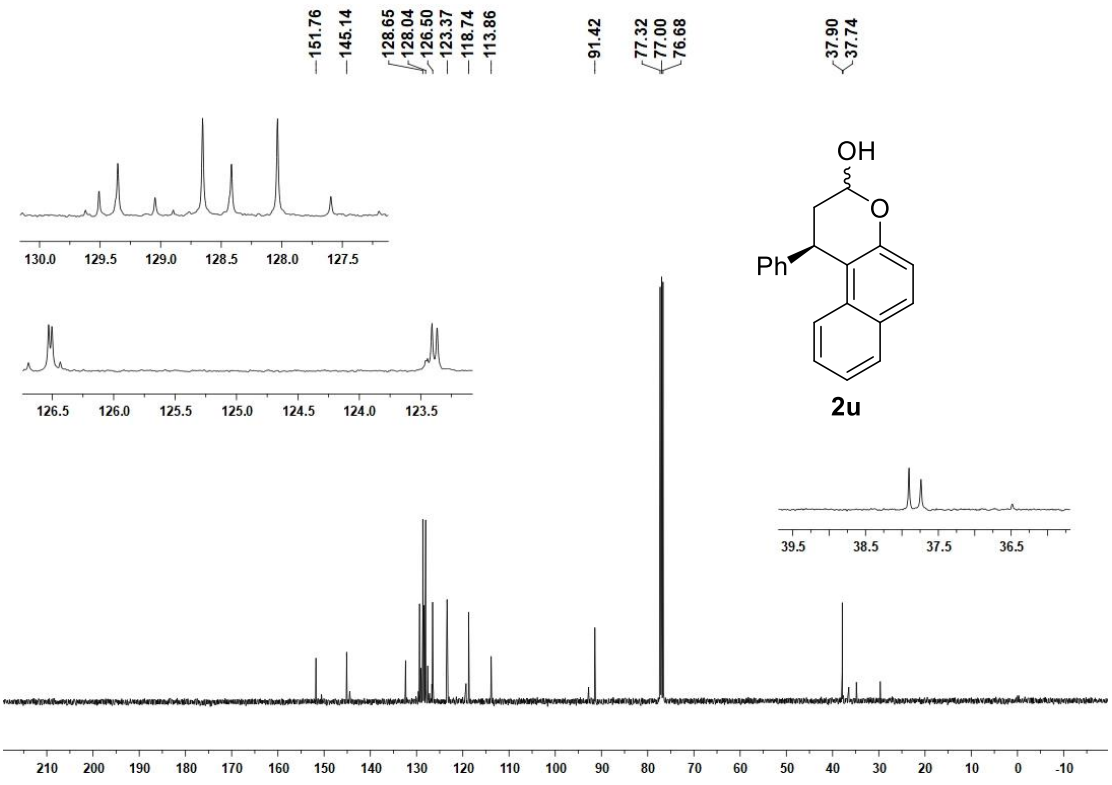
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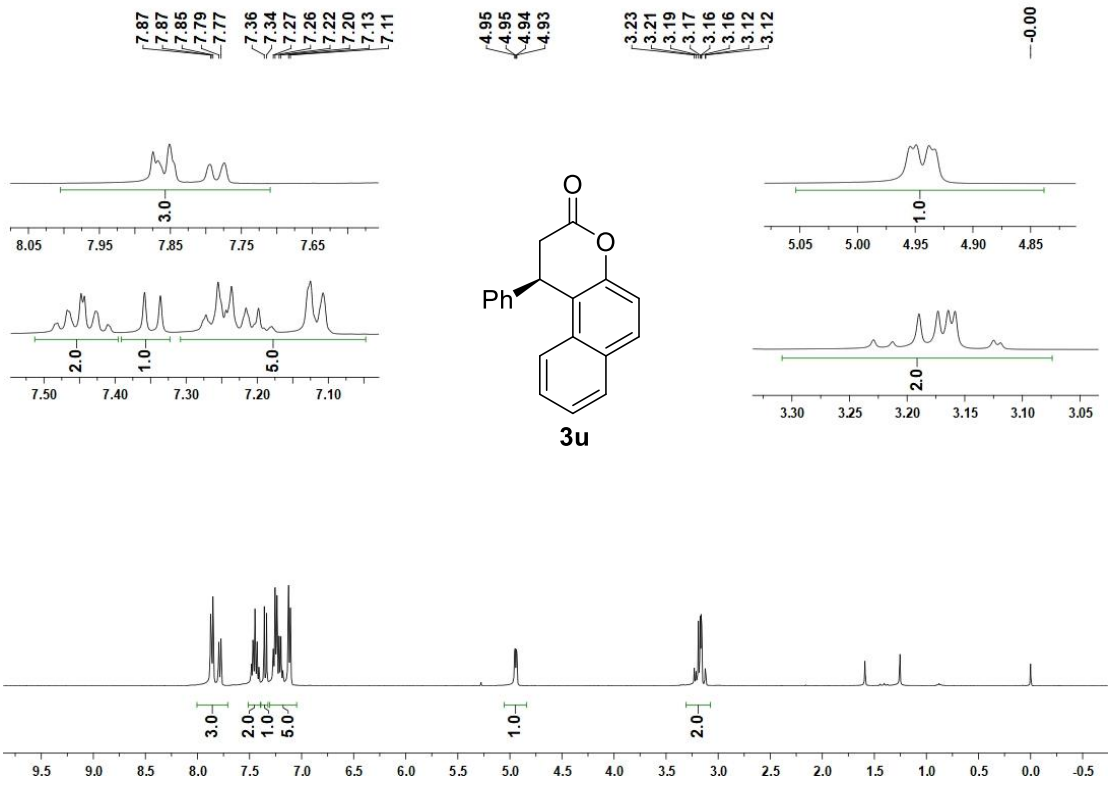
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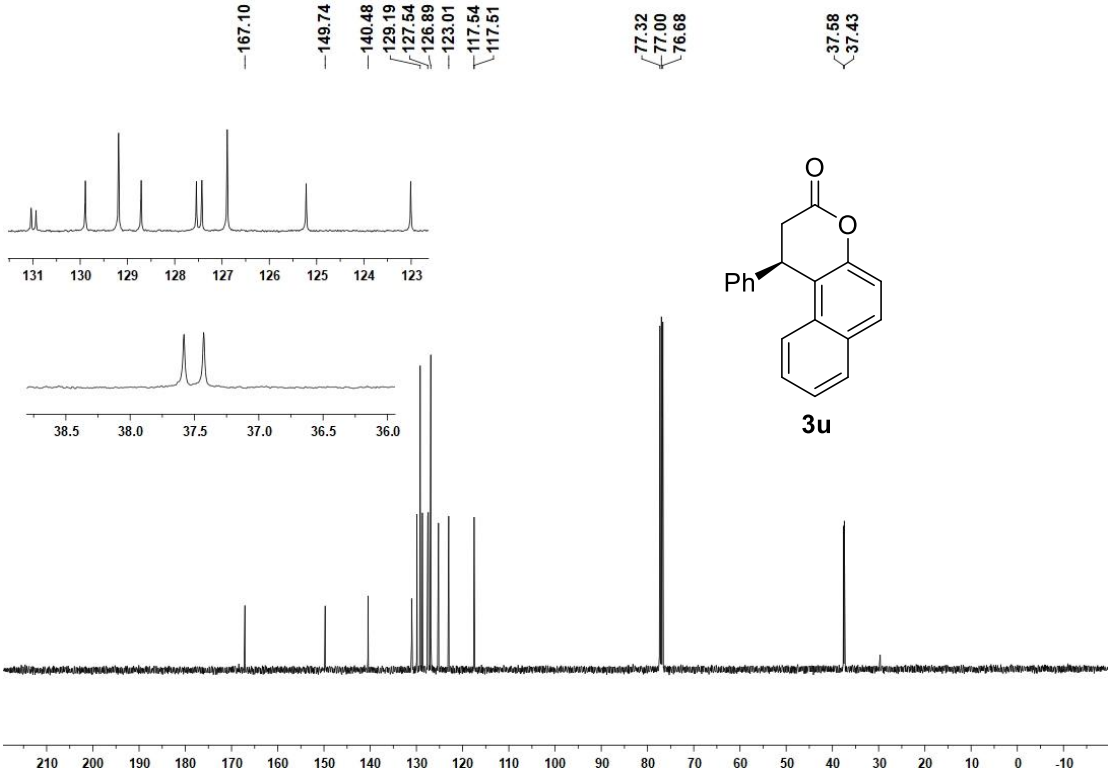
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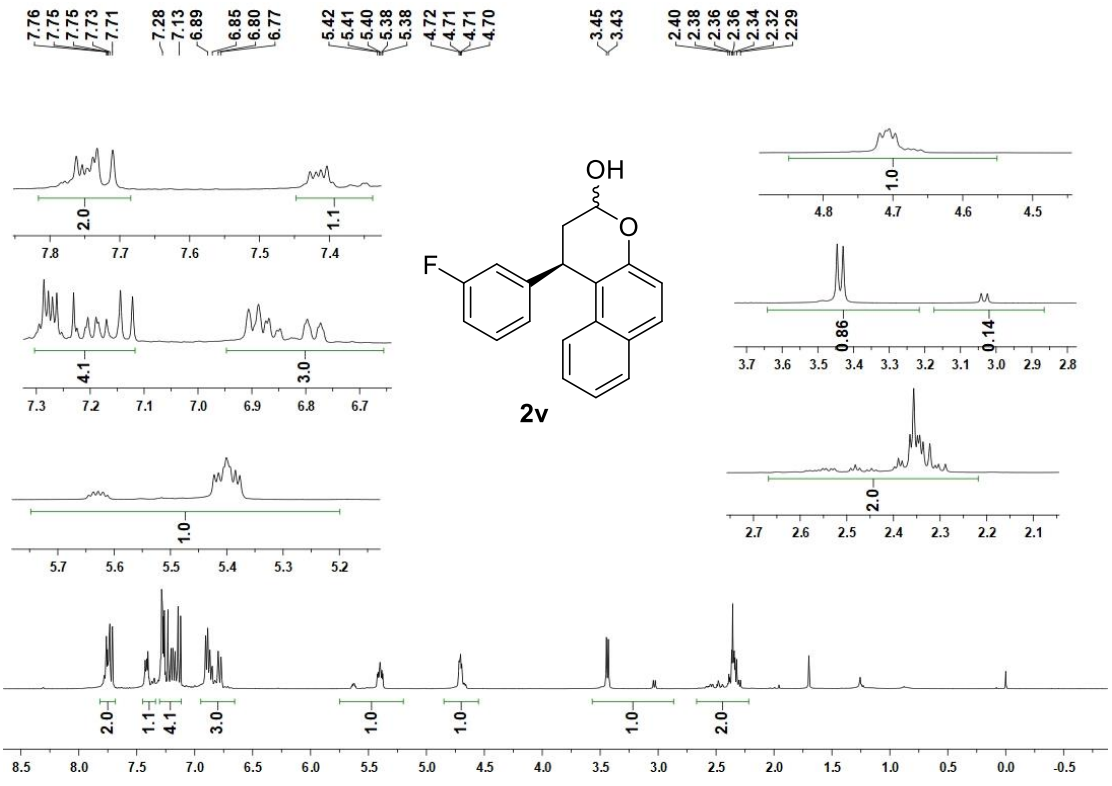
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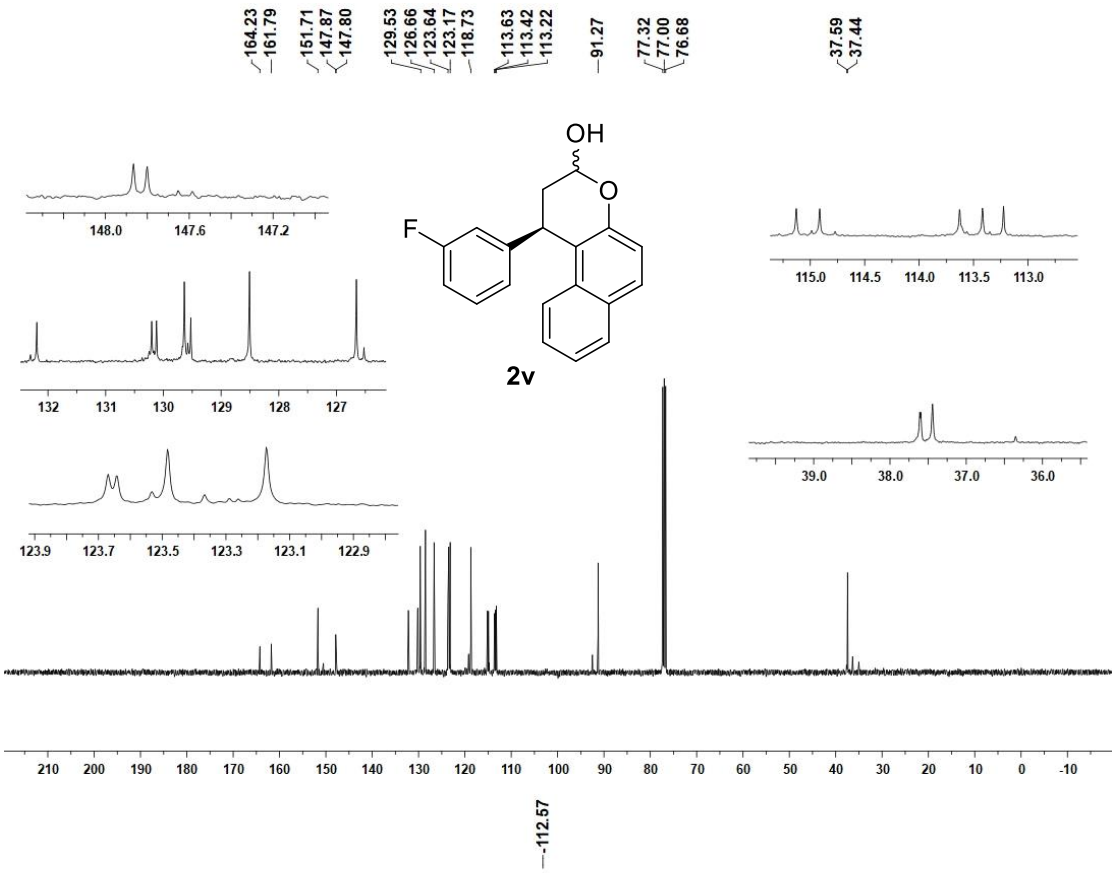
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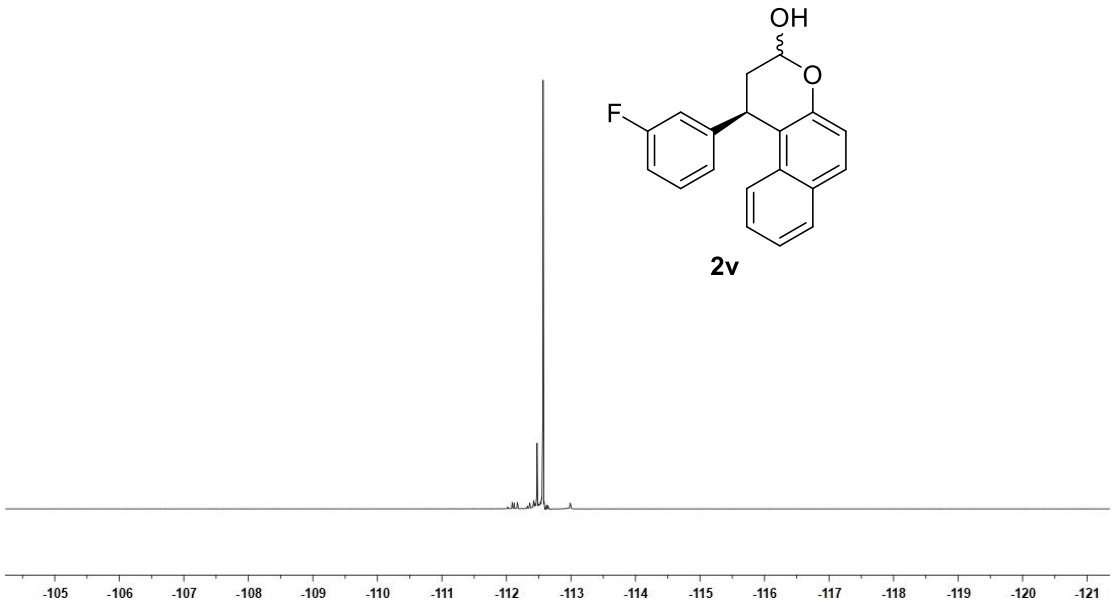
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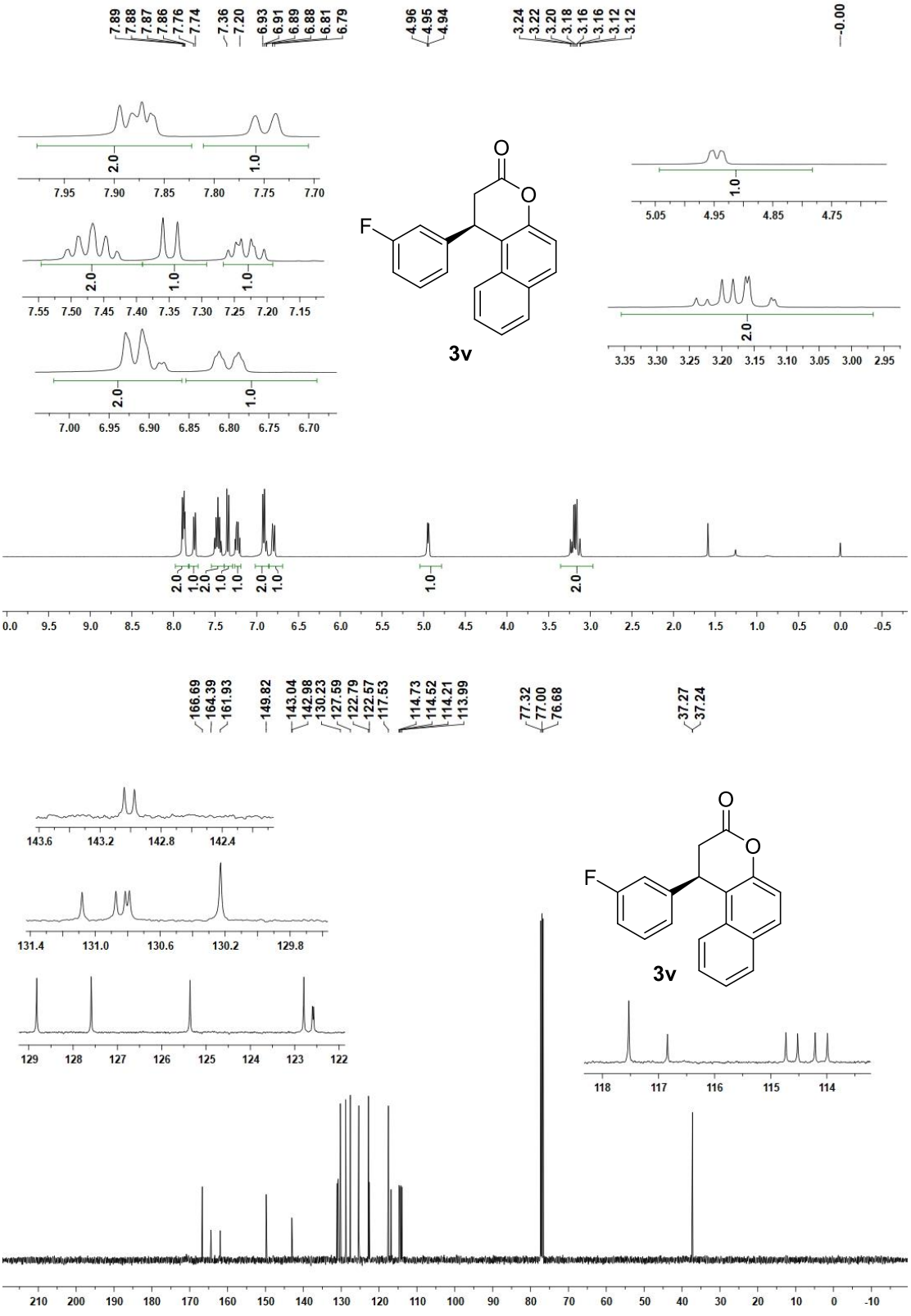
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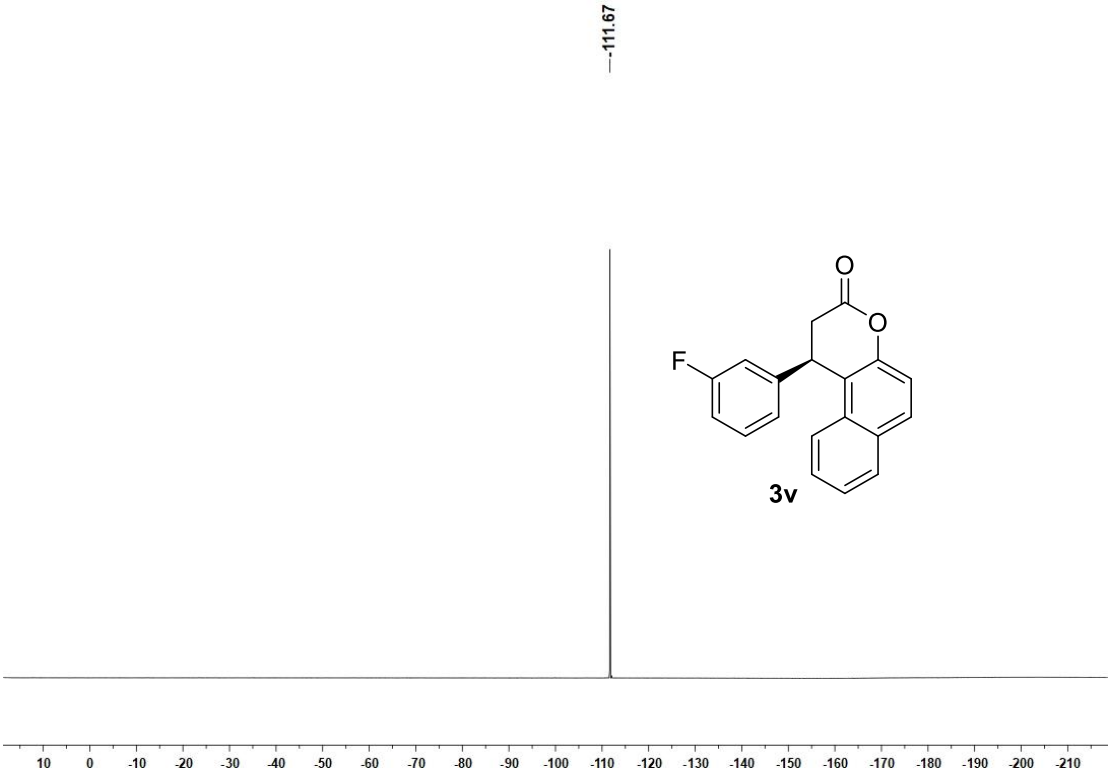
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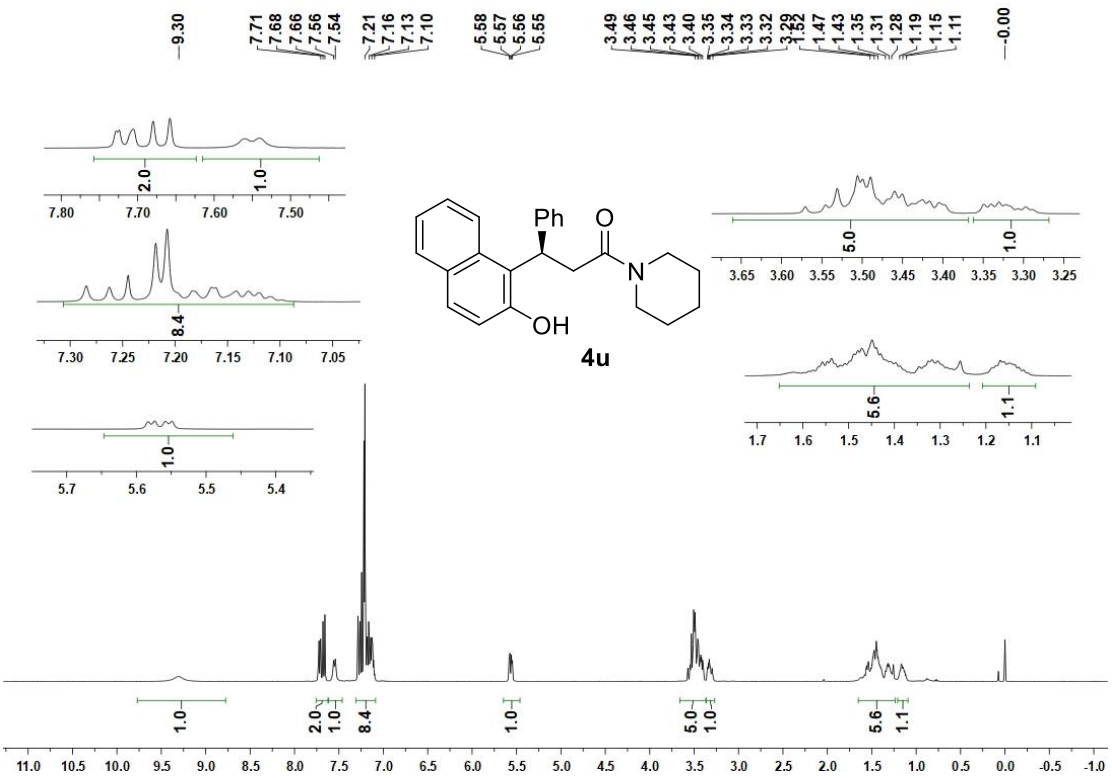
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N
OH
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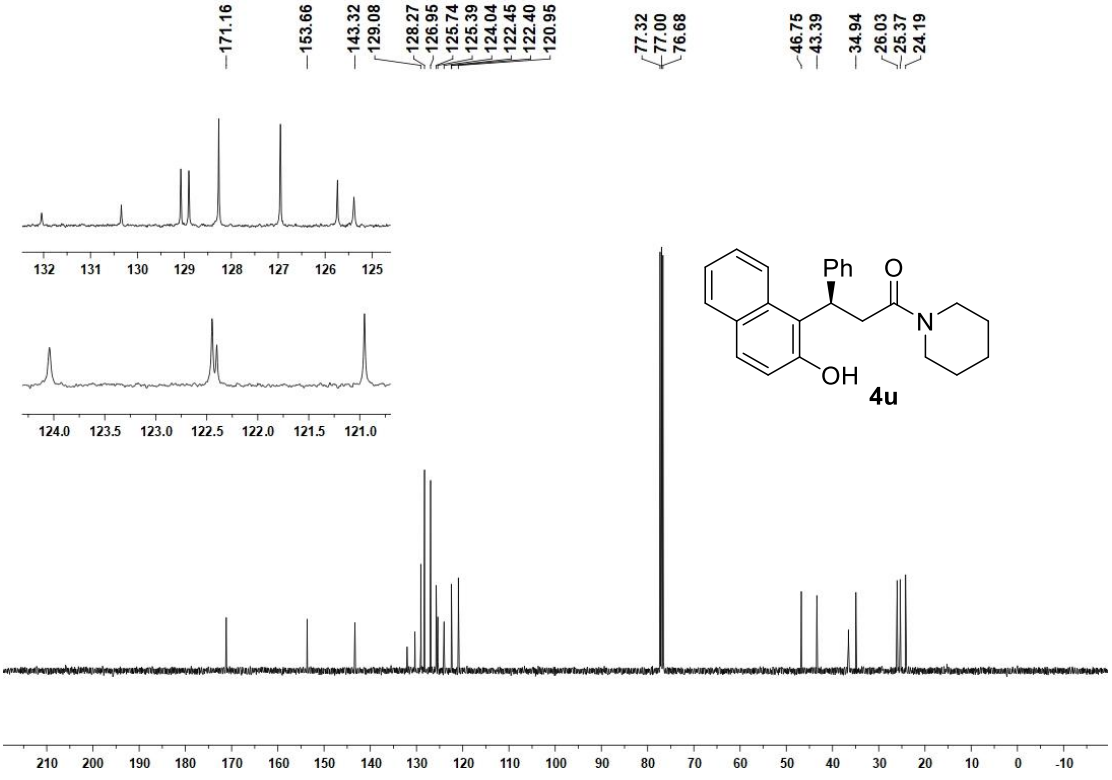
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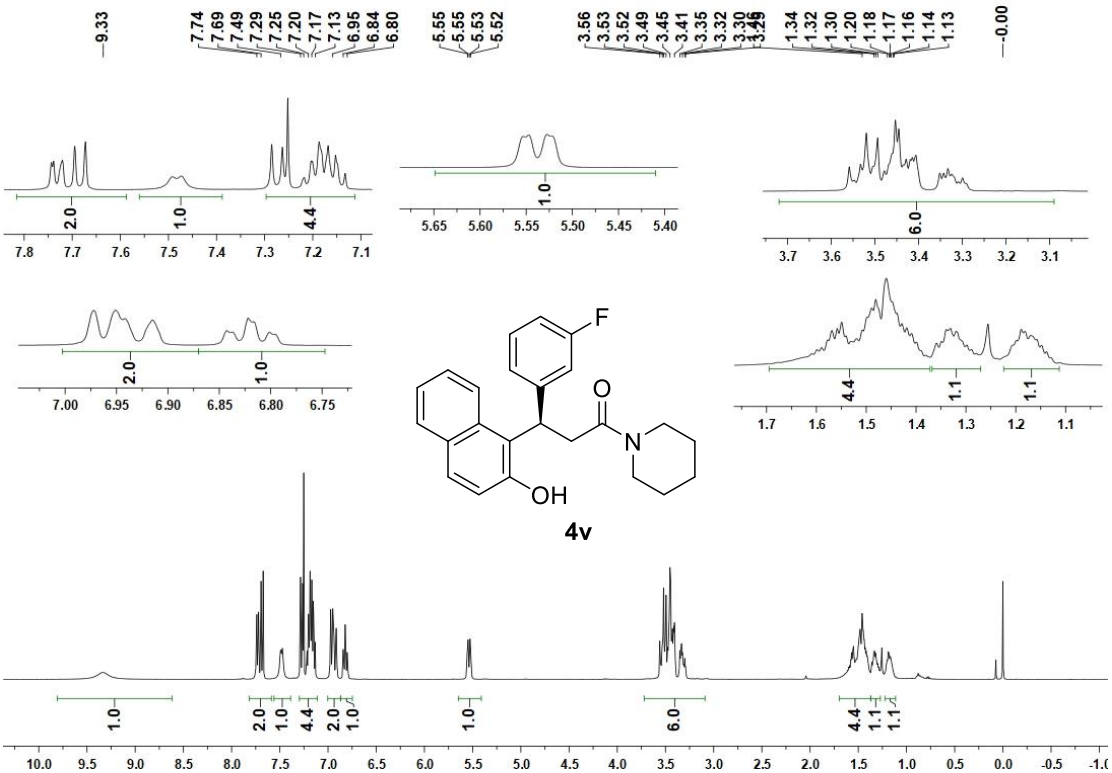
4u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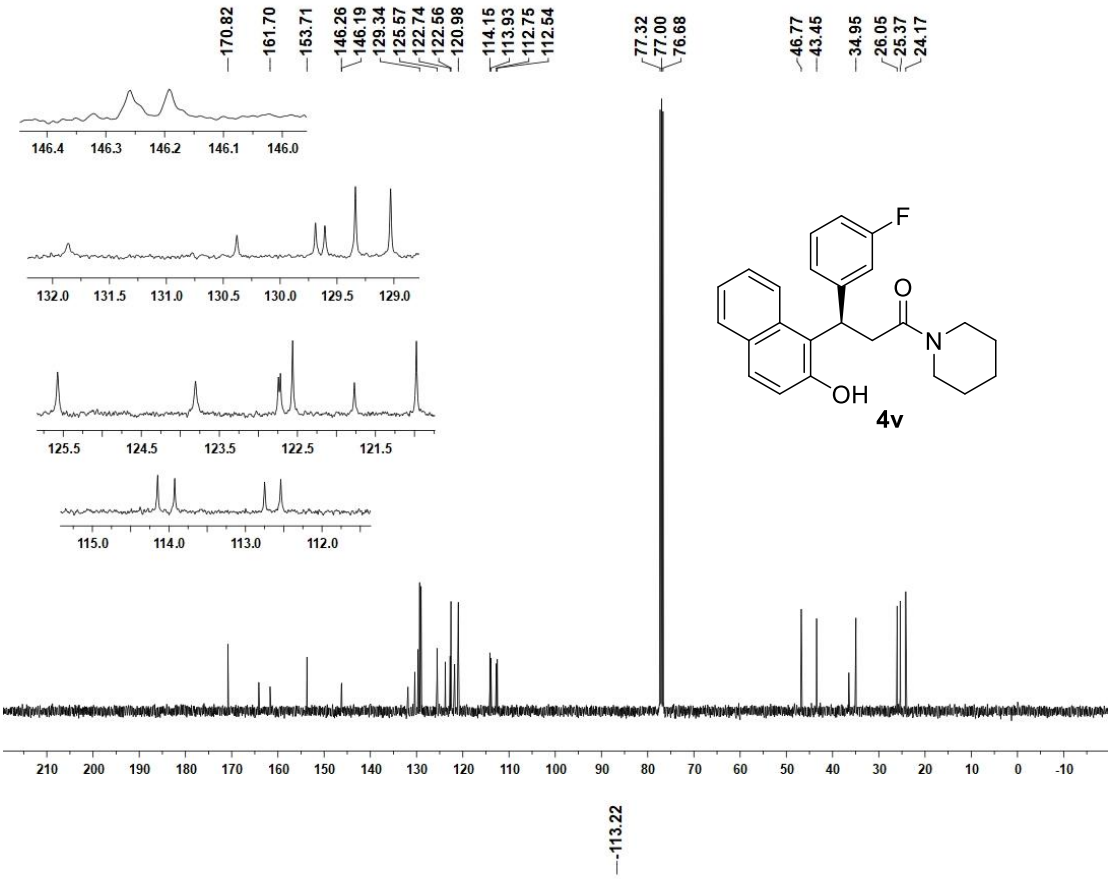
4v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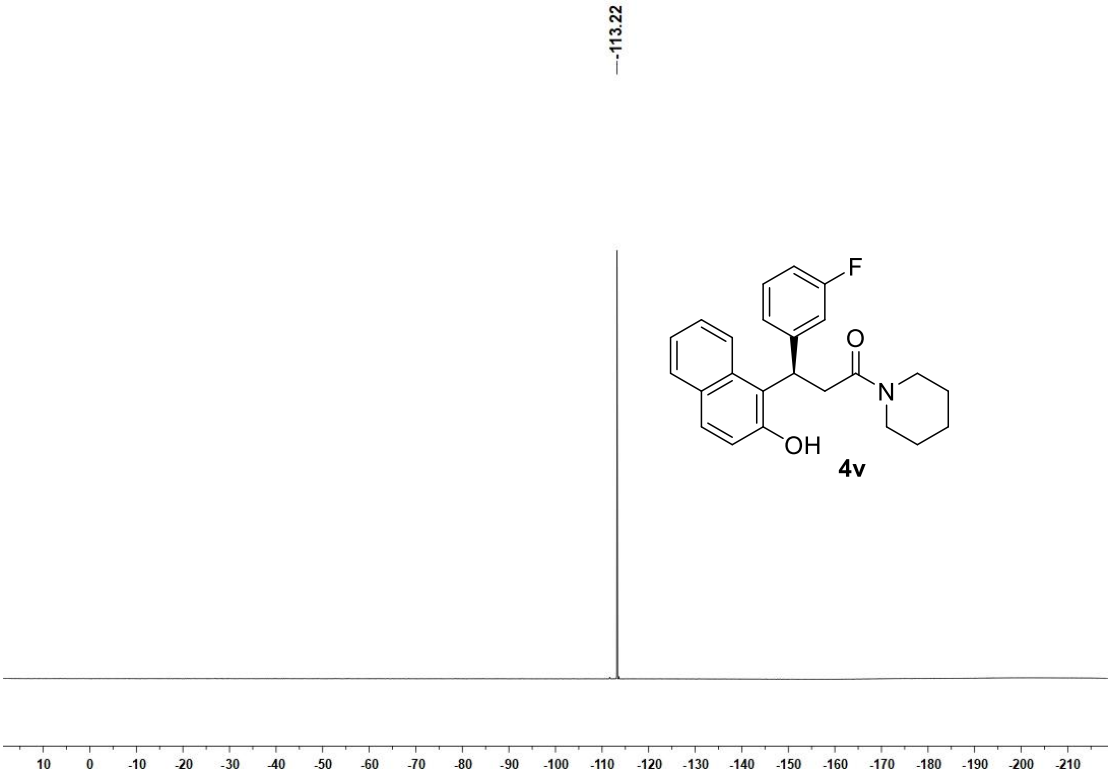
4v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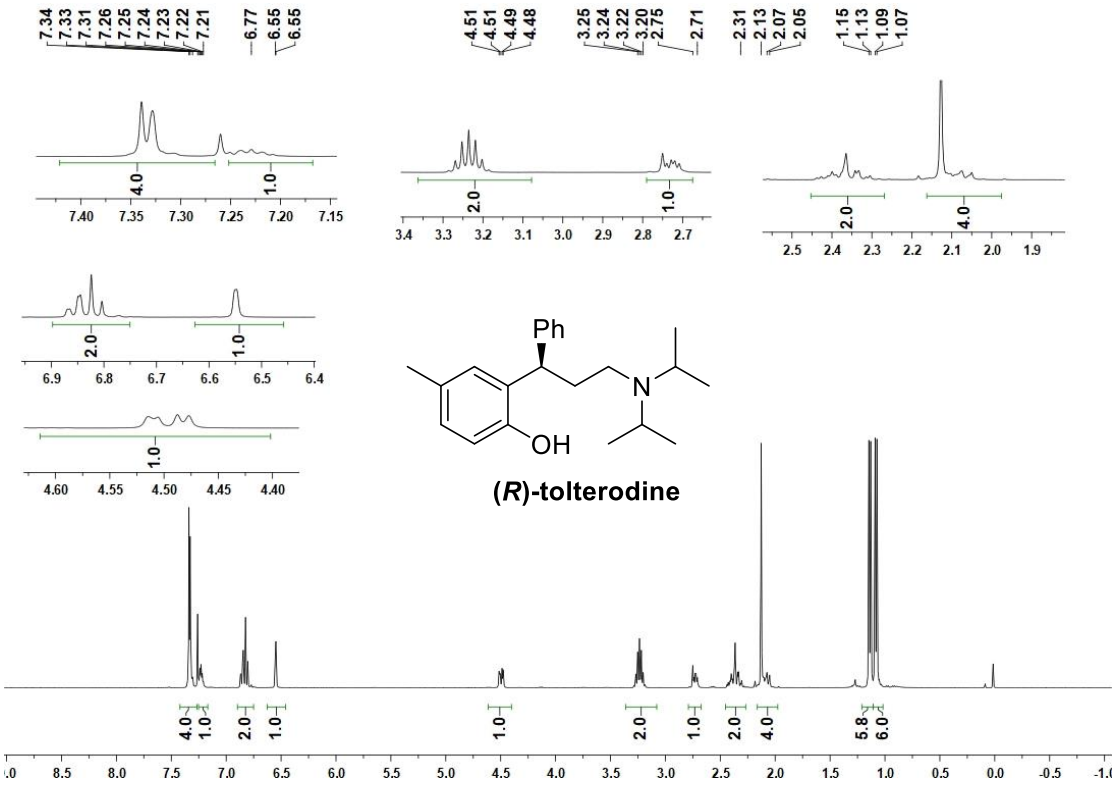
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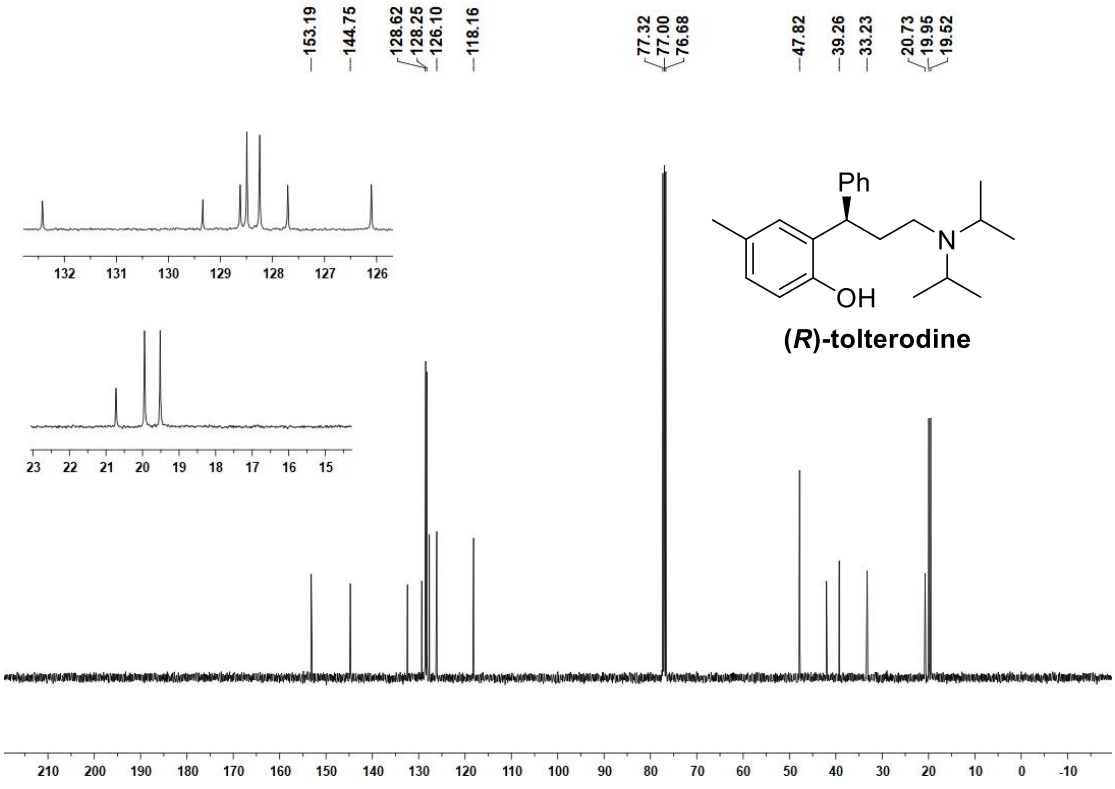
(R)-tolterodine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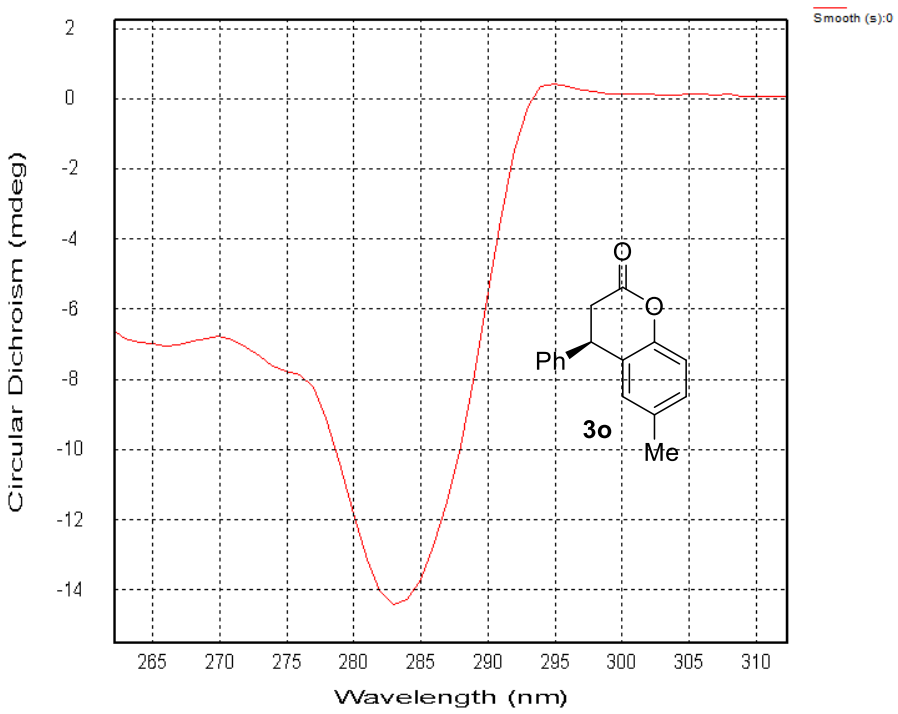
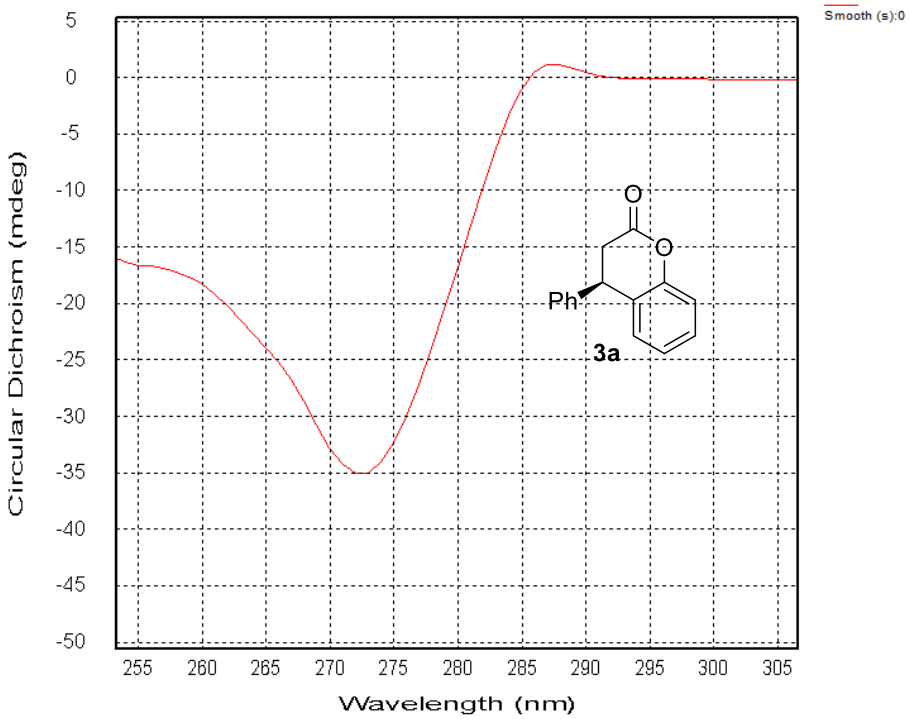
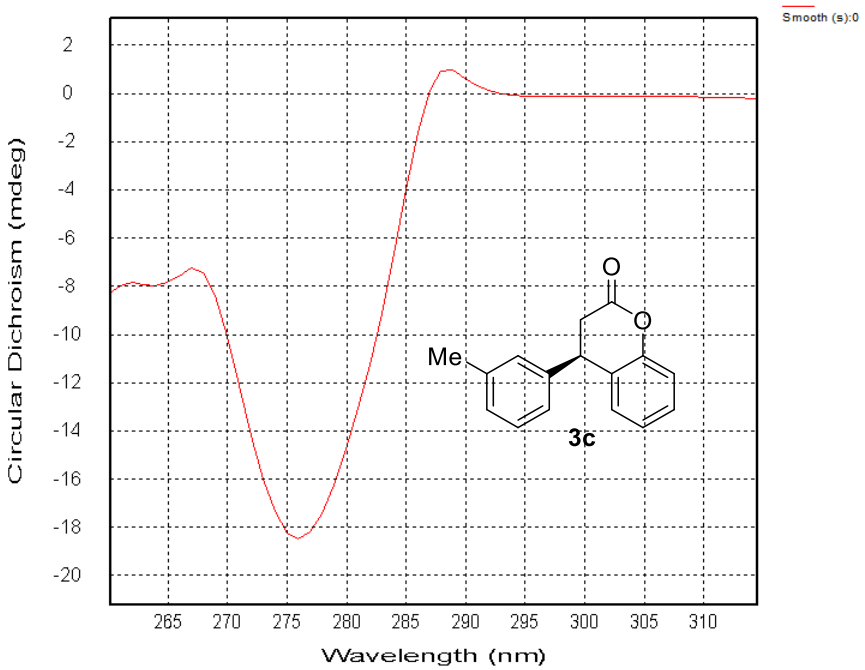
144.75
128.62
128.25
126.10
118.16
77.32
77.00
76.68
47.82
39.26
33.23
20.73
19.95
19.52
Ph
N
OH
(R)-tolterodine

12. Copies of CD spectra for in CH_2Cl_2



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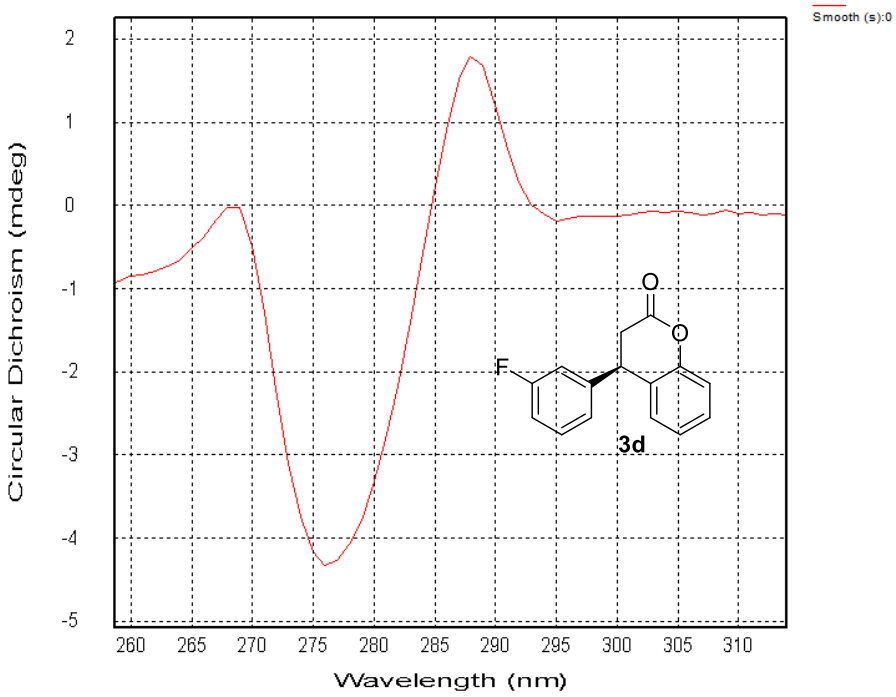
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
265
270
275
280
285
290
295
300
305
310
Wavelength (nm)
O
O
Me
3c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Circular Dichroism (mdeg)
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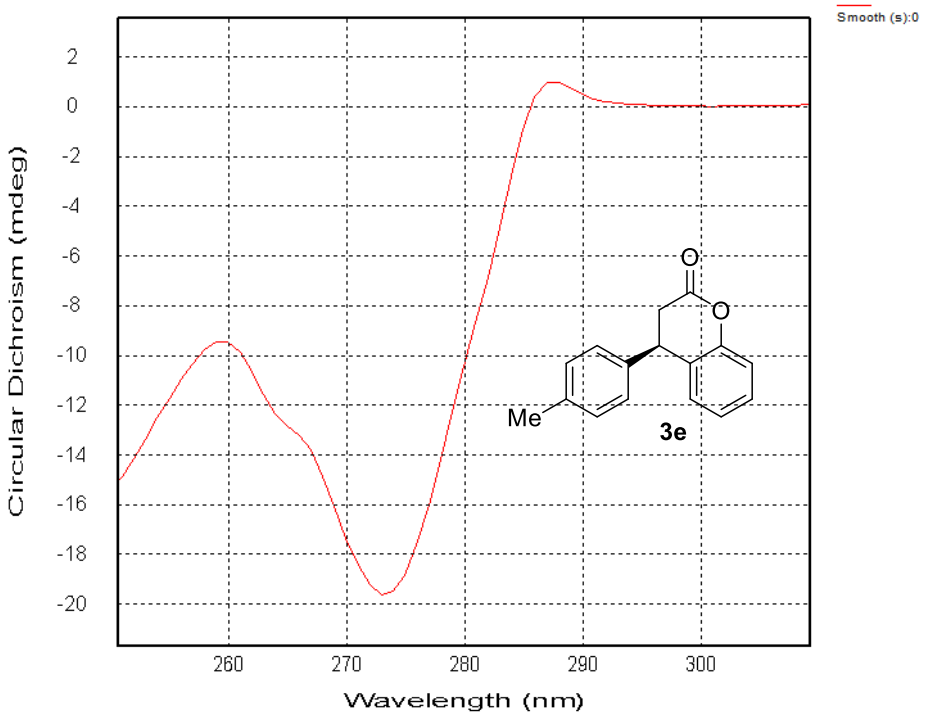
0
-1
-2
-3
-4
-5
260
265
270
275
280
285
290
295
300
305
310
Wavelength (nm)
O
O
F
3d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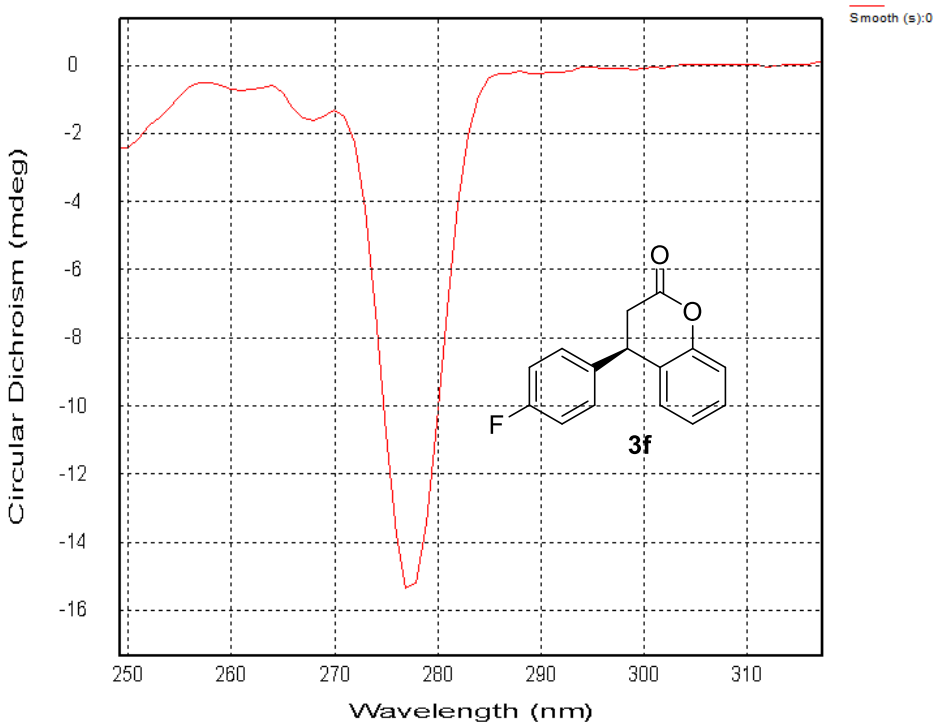
Circular Dichroism (mdeg)
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
260
270
280
290
300
Wavelength (nm)
O
O
Me
3e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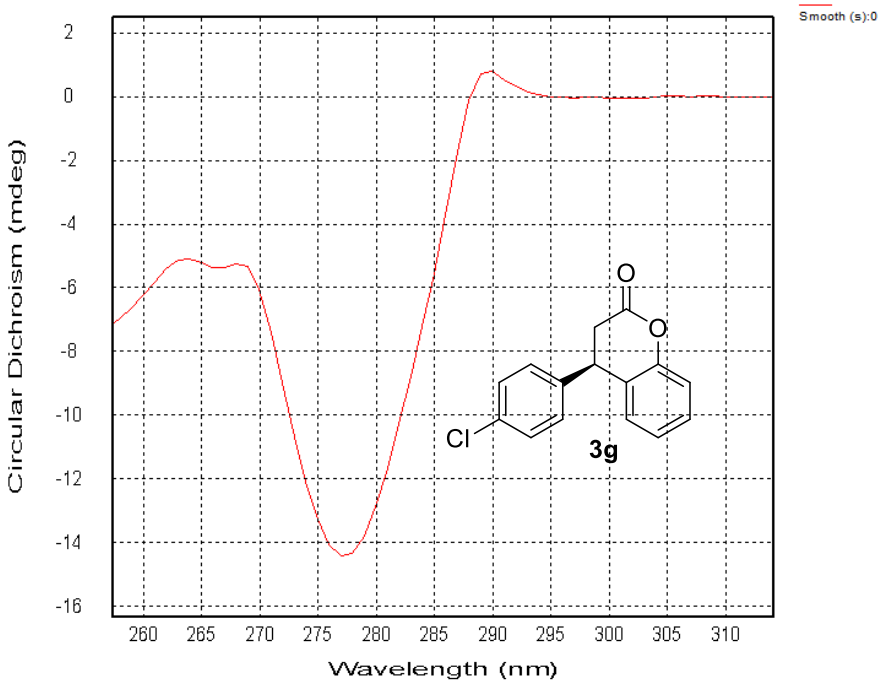
0
-2
-4
-6
-8
-10
-12
-14
-16
250
260
270
280
290
300
310
Wavelength (nm)
O
O
F
3f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Circular Dichroism (mdeg)
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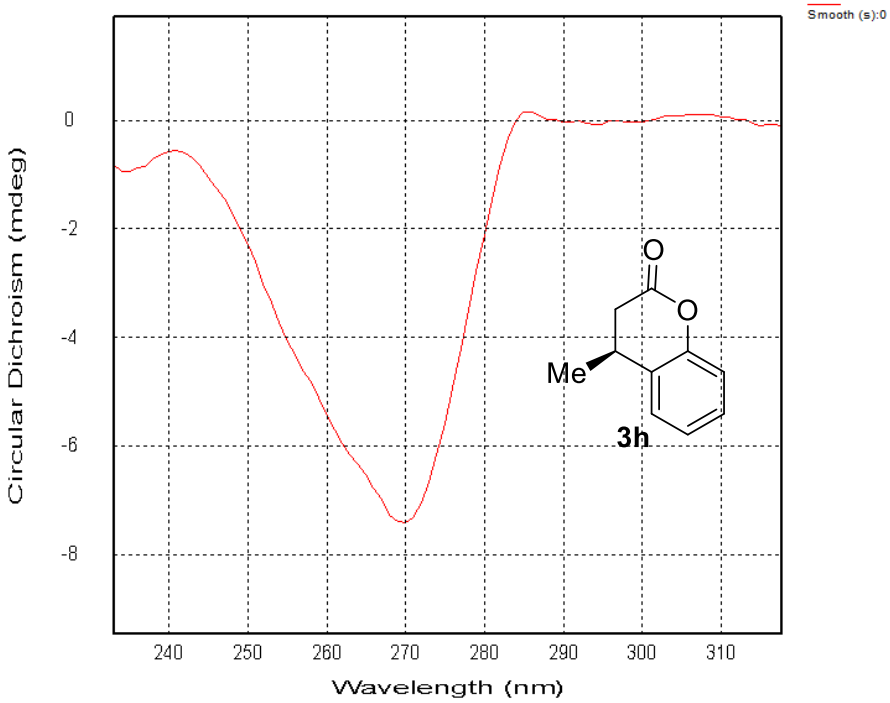
0
-2
-4
-6
-8
-10
-12
-14
-16
260
265
270
275
280
285
290
295
300
305
310
Wavelength (nm)
O
O
Cl
3g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Circular Dichroism (mdeg)
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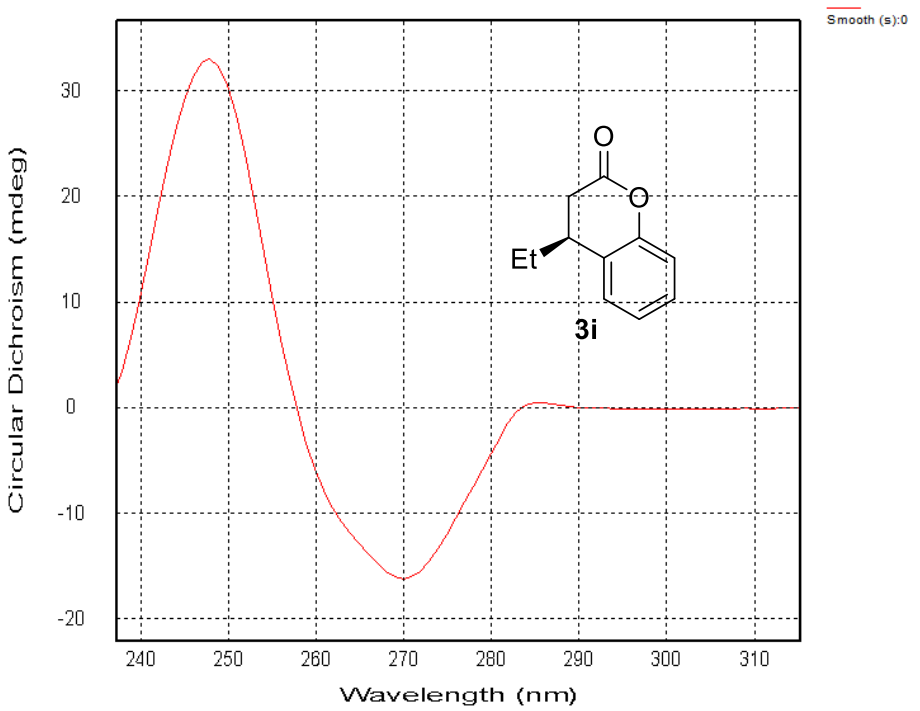
-4
-6
-8
240
250
260
270
280
290
300
310
Wavelength (nm)
O
O
Me
3h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Circular Dichroism (mdeg)
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20
10
0
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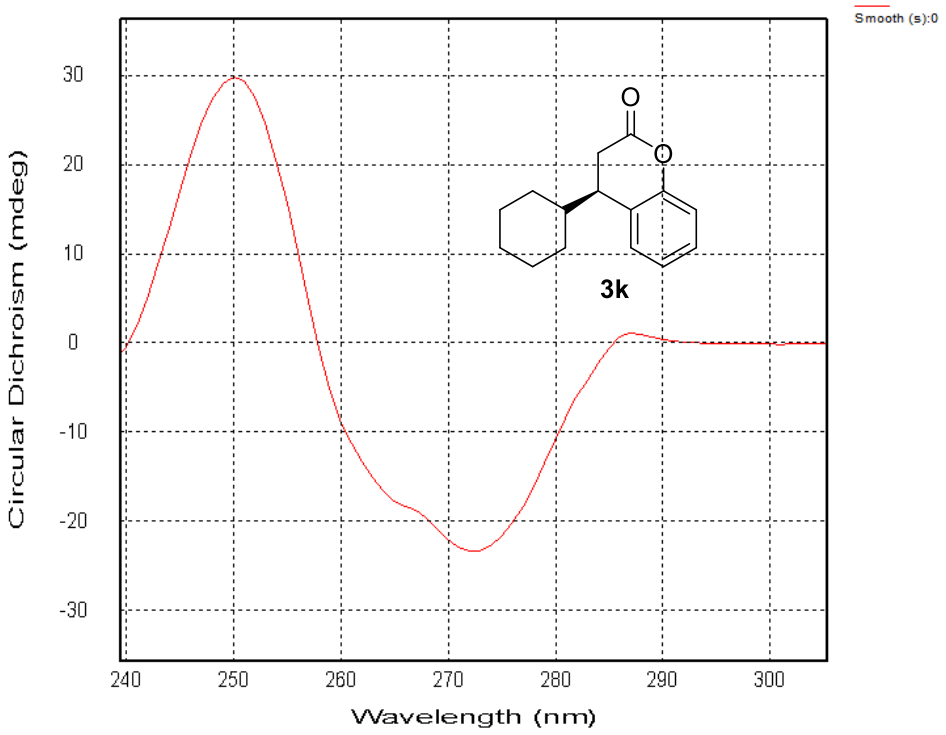
-20
240
250
260
270
280
290
300
310
Wavelength (nm)
O
O
Et
3i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Circular Dichroism (mdeg)
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20
10
0
-10
-20
-30
240
250
260
270
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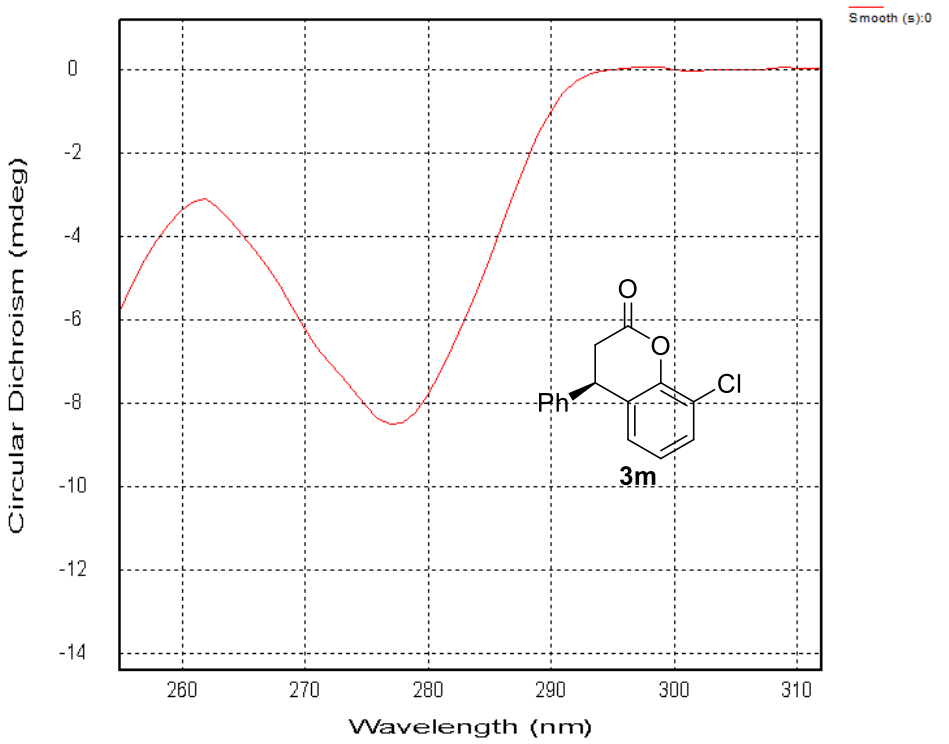
290
300
Wavelength (nm)
O
O
3k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Circular Dichroism (mdeg)
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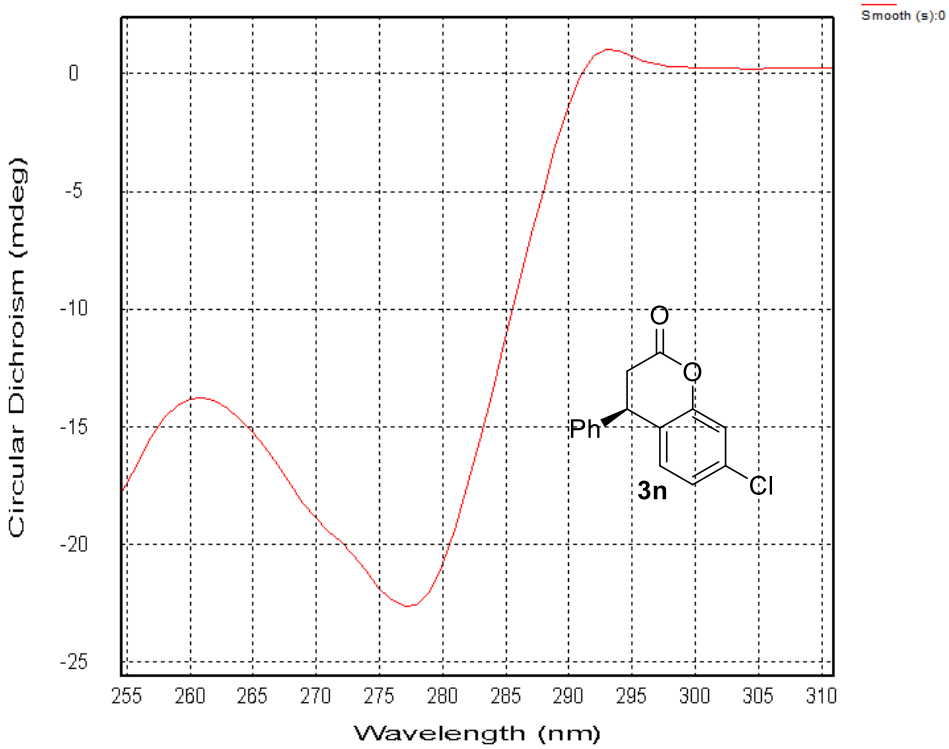
-2
-4
-6
-8
-10
-12
-14
260
270
280
290
300
310
Wavelength (nm)
O
O
Cl
Ph
3m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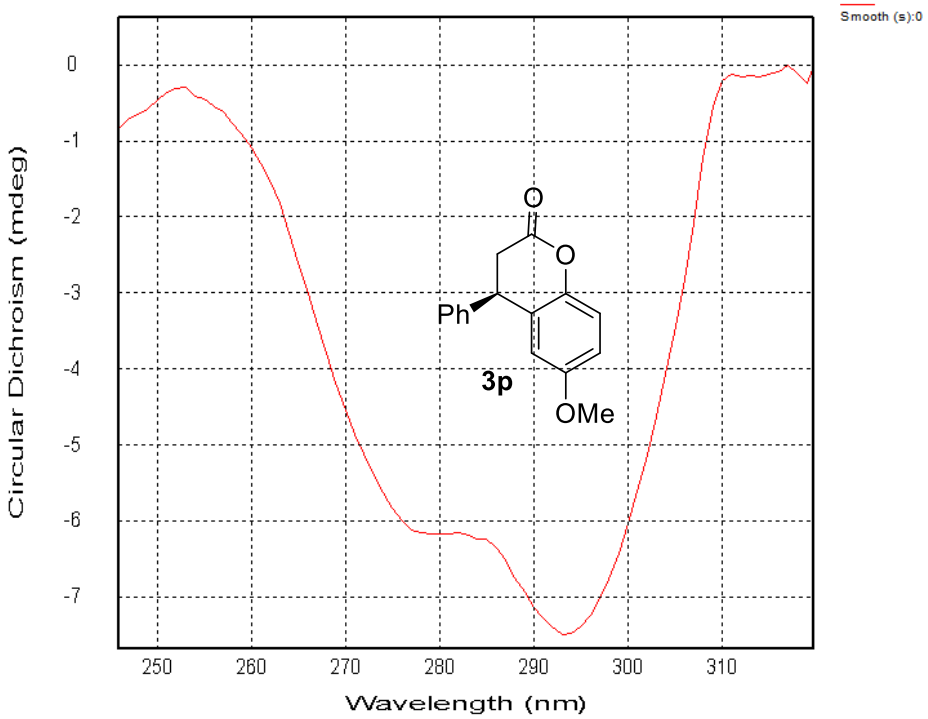
-20
-25
255
260
265
270
275
280
285
290
295
300
305
310
Wavelength (nm)
O
O
Ph
Cl
3n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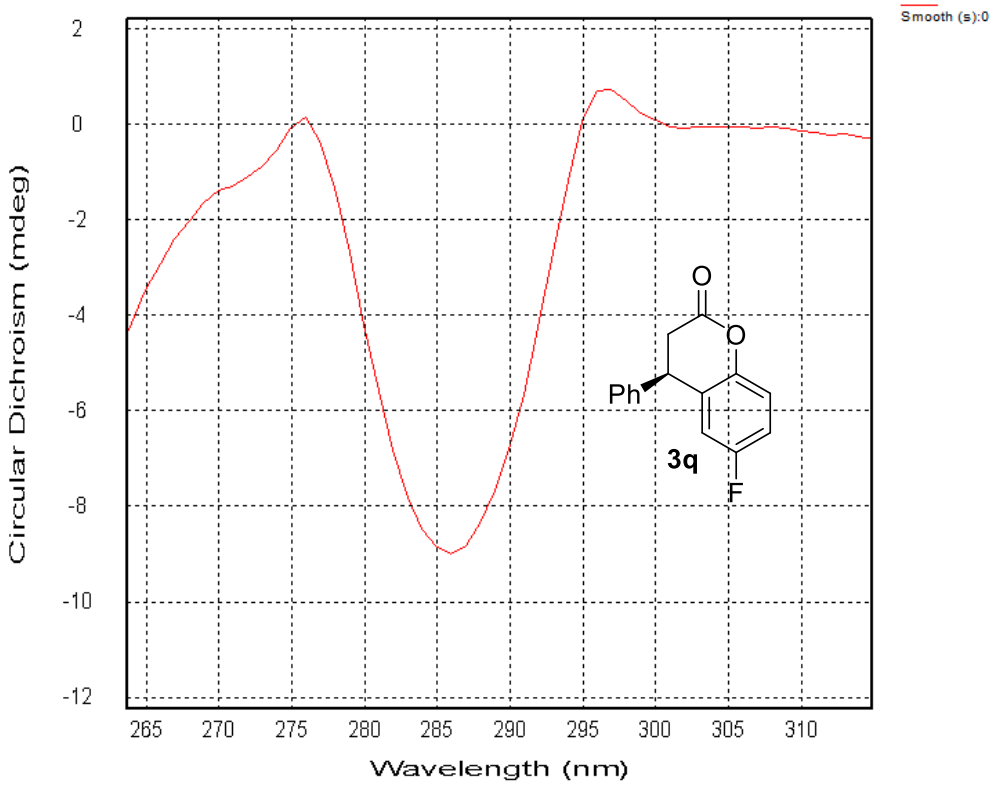
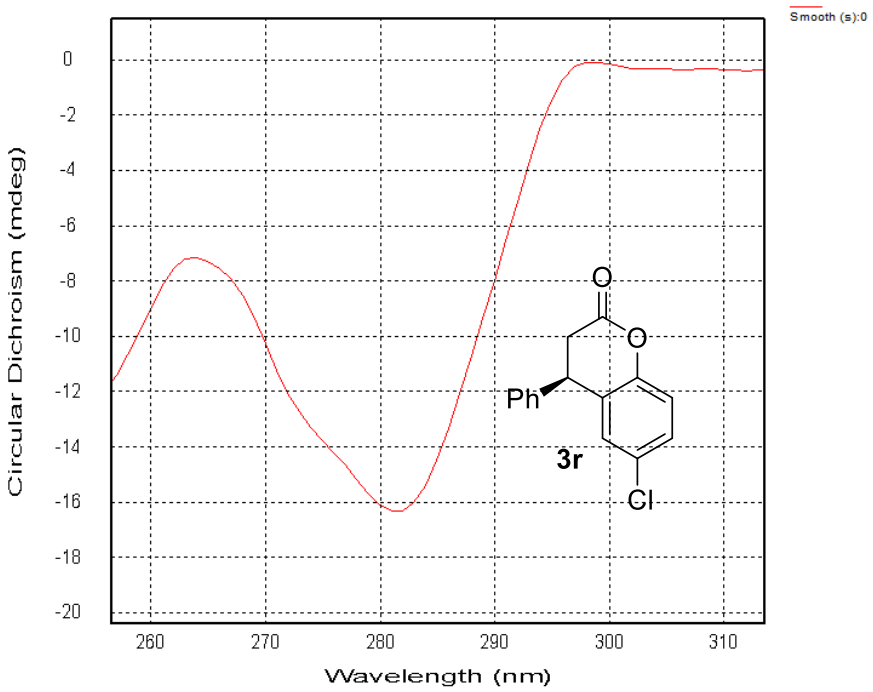
-2
-3
-4
-5
-6
-7
250
260
270
280
290
300
310
Wavelength (nm)
O
O
Ph
3p
OMe


Smooth (s):0
Circular Dichroism (mdeg)
2
0
-2
-4
-6
-8
-10
-12
265
270
275
280
285
290
295
300
305
310
Wavelength (nm)
O
O
Ph
3q
F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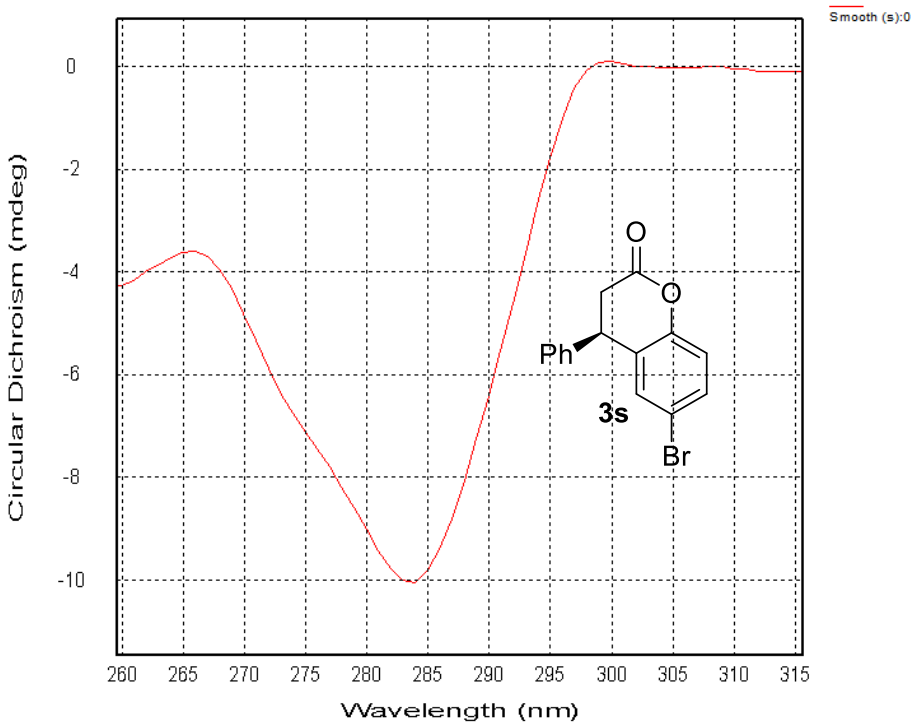
Circular Dichroism (mdeg)
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
260
270
280
290
300
310
Wavelength (nm)
O
O
Ph
3r
Cl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Circular Dichroism (mdeg)
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-4
-6
-8
-10
260
265
270
275
280
285
290
295
300
305
310
315
Wavelength (nm)
O
O
Ph
3s
Br

13. References

1 Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett*, 2005, **16**, 2445.
2 Y. Okimoto, S. Sakaguchi and Y. Ishii, *J. Am. Chem. Soc.*, 2002, **124**, 1590.