Electronic Supplementary Material (ESI) for Chemical Science.

Catalytic Enantioselective Synthesis of Tetrasubstituted Chromanones via Palladium-Catalyzed Asymmetric Conjugate Arylation Using Chiral Pyridine-Dihydroisoquinoline (PyDHIQ) Ligands

Doohyun Baek, Huijeong Ryu, Ji Yeon Ryu, Junseong Lee, Brian M. Stoltz*, and Sukwon Hong*

Table of Contents

1. General Remarks.....S2

2. Additional Screening Data and Unsuccessful Substrates.....S3

3. Ligand Synthesis and Compound Characterization.....S4

4. Experimental Procedures and Compound Characterization.....S8

5. References.....S26

6. X-Ray Analysis for Compound **6e** and **[(*S*)-3d]PdCl$_2$**.....S27

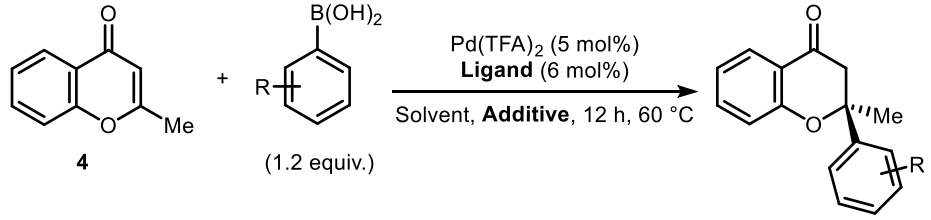
7. NMR Spectra for Compounds.....S35

1. General Remarks

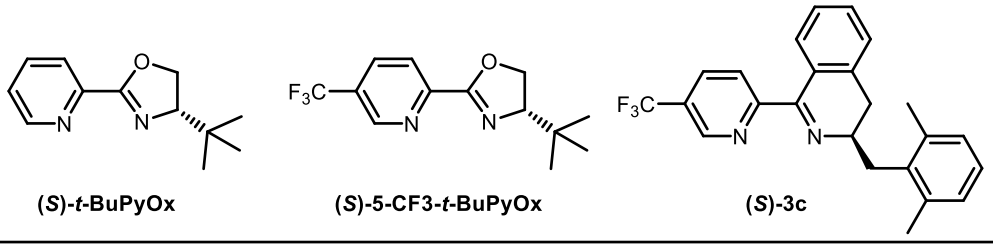
Unless otherwise specified, all reactions were performed in inert atmosphere with high purity argon (99.999%). Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and diethyl ether (Et_2O) were dried under positive pressure of high purity nitrogen (99.999%) using a J. C. Meyer Solvent Purification System prior to use. Commercially available HPLC grade water (H_2O) from fisher chemical was used. 2-substituted chromone derivatives were synthesized according to literature procedure.[1] Naphthalene was purified by sublimation and 4-dimethylaminopyiridne (DMAP) was recrystallized in toluene prior to use. All other chemicals including arylboronic acids were purchased from commercial sources (Sigma-Aldrich Co., Alfa Aesar, TCI and Acros Organics) and were used as received without further purification. Reaction temperature was controlled by IKA ETS-D5 temperature controller with IKA hotplate stirrer C-MAG HS7. Hamilton 700 series glass microliter syringes were used to measure amount of H_2O. High purity O_2 (99.995%) was used to make O_2 balloon. Racemic samples were prepared by employing 2,2'-bipyidine as a (*N,N)*-ligand. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates and visualized by UV fluorescence quenching, *p*-anisaldehyde, or iodine staining. Merck silica gel 60 (particle size 40-63 nm) was used for flash chromatography. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL spectrometer, operating at 400 MHz for ^{1}H NMR, at 101 MHz for ^{13}C NMR and at 376 MHz for ^{19}F NMR. All chemical shifts for ^{1}H and ^{13}C NMR spectroscopy were assigned to residual signals from $CDCl_3$ (^{1}H) at 7.25 ppm and (^{13}C) at 77.13 ppm. High resolution mass spectra (HRMS) were obtained using a JEOL JMS-700 MStation mass spectrometer or obtained at Korea Basic Science Institute (Daegu, South Korea). Specific Optical rotations were obtained using a JASCO P-2000 Series Polarimeter (wavelength = 589 nm). Enantiomeric ratios were determined by chiral HPLC analysis using an Agilent 1260 infinity and Daicel Chiralpak (IC or ID) columns (4.6 mm x 25 cm). Absolute configuration of compound **6e** was determined by X-ray crystallography, and all other products are assigned by analogy.

List of abbreviations: TLC – Thin-layer chromatography, NMR – Nuclear magnetic resonance, IR - Infrared, HRMS – High resolution mass, THF – Tetrahydrofuran, DCM – Dichloromethane, EA – Ethyl acetate, DMF – *N,N*-Dimethylformamide , DMAP – 4-dimethylaminopyiridine, IPA – isopropyl alcohol, EDC – 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide, HOBt – Hydroxybenzotriazole, t_R – Retention time, ee – Enantiomeric excess.

2. Additional Screening Data and Unsuccessful Substrates[a]



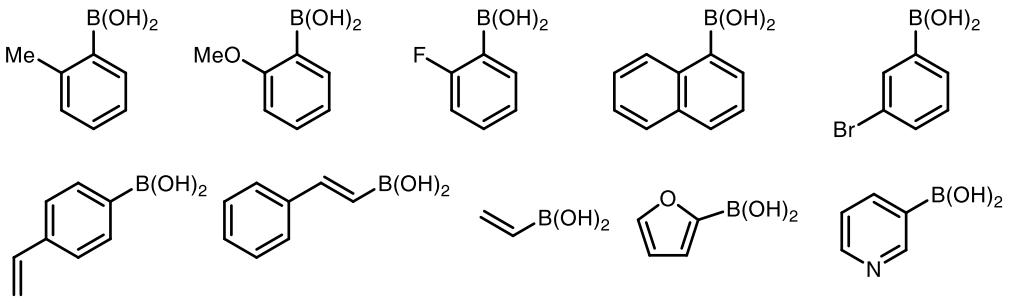
Entry	Solvent	$ArB(OH)_2$	Additive (30 mol%)	Ligand	Yield [%][b]	ee [%][c]
1	H_2O	$PhB(OH)_2$	NH_4PF_6	**(*S*)-*t*-BuPyOx**	Trace	-
2	H_2O	$PhB(OH)_2$	NH_4PF_6	**(*S*)-5-CF3-*t*-BuPyOx**	Trace	-
3	H_2O	$PhB(OH)_2$	NH_4PF_6	**(*S*)-3c**	97	95
4	H_2O/Toluene (1:1)	$PhB(OH)_2$	NH_4PF_6	**(*S*)-3c**	47	97
5	H_2O	$PhB(OH)_2$	-	**(*S*)-3c**	42	90
5	Toluene	$PhB(OH)_2$	-	**(*S*)-3c**	25	98
6	DMF	$PhB(OH)_2$	-	**(*S*)-3c**	13	98
7	1,4-dioxane	$PhB(OH)_2$	-	**(*S*)-3c**	Trace	-
8	n-BuOH	$PhB(OH)_2$	-	**(*S*)-3c**	Complicated mixture[d]	-
9	DMSO	$PhB(OH)_2$	-	**(*S*)-3c**	No reaction	-
10	H_2O	4-MePhB(OH)2	NH_4PF_6	**(*S*)-3c**	71	96
11[e]	H_2O	4-MePhB(OH)2	NH_4PF_6	**(*S*)-3c**	77	96



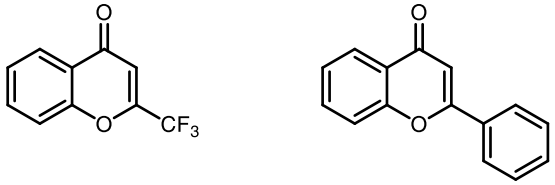
[a]Unless otherwise noted, all reactions were carried out with **4** (0.5 mmol, 1 equiv.), $ArB(OH)_2$ (0.6 mmol, 1.2 equiv.), $Pd(TFA)_2$ (0.025 mmol, 5 mol%), ligand (0.030 mmol, 6 mol%), additive (0.15 mmol, 30 mol%), H_2O (0.35 mL, 1.43 M) for 12 h.[b]Isolated yield. [c]Determined by HPLC with DAICEL chiralpak. [d]No desired product. [e]Reaction carried out in H_2O (0.7 mL, 0.71 M).

Unsuccessful Substrates

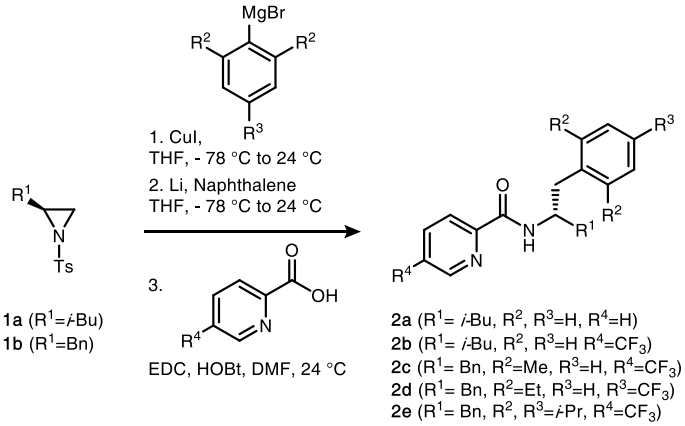
Boronic Acid Substrates



2-Substituted Chromone Substrates



3. Ligand Synthesis

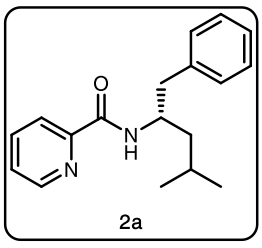


Compound **1a** and **1b** was prepared according to literature procedures.[2] To a flask charged with stir bar and CuI (2.26 mmol, 0.5 equiv.) in THF (9 mL, 0.5 M), aryl magnesium bromide (9.05 mmol, 2 equiv.) was slowly added at -78 °C and stirred for 15 min. **1a** or **1b** (4.52 mmol, 1.0 equiv.) was added to the mixture and the resulting suspension was warmed to 24 °C with vigorous stirring. Reaction was monitored by TLC (4:1 Hexanes/EtOAc), and stirred until starting material spot was disappeared. Then reaction was quenched with a saturated aqueous NH_4Cl solution (25 mL) and extracted with EtOAc (30 mL x3). The combined organic layers were dried over $MgSO_4$ and concentrated. Crude product was obtained as yellow solid. Filtered by short flash chromatography to remove dimer of Grignard reagent.

To a flask charged with glass-coated stir bar and Li (61.0 mmol, 16.0 equiv.) in THF (25 mL, 0.15 M), naphthalene (0.38 mmol, 0.10 equiv.) was added at 24 °C. When the color of solution changed to deep purple blue color, products (3.81 mmol, 1.0 equiv.) obtained from previous Grignard step were added to the suspension at -78 °C. The resulting suspension was warmed to 24 °C slowly and stirred for overnight. The solution was transferred through a cannula to another flask and quenched by saturated aqueous NH_4Cl solution (50 mL). After saturated aqueous NH_4Cl layer was discarded, 1M HCl aqueous solution was added to the solution and organic layer was discarded. Then 20% w/v NaOH aqueous solution was added to the acidic aqueous solution. When the pH of aqueous layer was 8, The aqueous layer was extracted with EtOAc and dried over $MgSO_4$. The residue was filtered and concentrated to afford chiral amines. The product used without further purification.

To a mixture of picolinic acid (2.15 mmol, 1.0 equiv.), chiral amine obtained from previous deprotection step (2.15 mmol, 1.0 equiv.), and HOBt (2.68 mmol, 1.25 equiv.) in DMF (2 mL, 0.35 M), EDC (2.68 mmol, 1.25 equiv.) was added at 0 °C and stirred for 12 h at 24 °C. The solution was quenched by water (10 mL), and extracted with EtOAc (15 mL) and dried over $MgSO_4$. The residue was filtered, concentrated and purified by flash chromatography. Compound **2a-2e** was obtained as pale yellow solid.

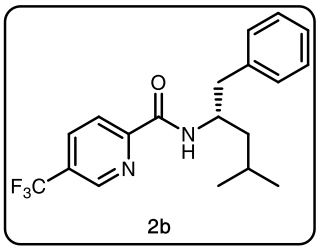
(*S*)-*N*-(4-methyl-1-phenylpentan-2-yl)picolinamide (2a)



Purified by column chromatography (4:1 Hexane/EtOAc), 66% overall yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 4.2 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 9.5 Hz, 1H), 7.76 (td, J = 7.7, 1.7 Hz, 1H), 7.34 (ddd, J = 7.5, 4.7, 1.2 Hz, 1H), 7.15-7.26 (m, 5H), 4.47 (qd, J = 10.0, 6.1 Hz, 1H), 2.88 (ddd, J = 29.6, 13.5, 6.3 Hz, 2H), 1.62-1.72 (m, 1H), 1.32-1.48 (m, 2H), 0.88 (d, J = 6.5 Hz, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.6, 149.9, 147.9, 138.1, 137.2, 129.5, 128.2, 126.2, 126.0, 122.1, 48.4, 43.2, 41.8, 24.9, 23.3, 21.9;

IR ν = 3661, 3376, 2958, 2909, 1673, 1519, 1466, 1433, 1384, 1251, 1161, 1077, 1055, 868, 819, 750, 701 cm^{-1}; HRMS (EI) calc'd for $C_{18}H_{22}N_2O$ $[M]^+$: 282.1732, found: 282.1730; $[\alpha]_D^{25}$ -4.5 (c 1.06, $CHCl_3$);

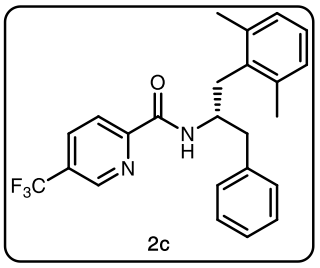
(*S*)-*N*-(4-methyl-1-phenylpentan-2-yl)-5-(trifluoromethyl)picolinamide (2b)



Purified by column chromatography (8:1 Hexane/EtOAc) , 63% overall yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 8.07 (dd, J = 8.1, 2.2 Hz, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.17-7.28 (m, 5H), 4.43-4.53 (m, 1H), 2.90 (d, J = 6.4 Hz, 2H), 1.62-1.72 (m, 1H), 1.37-1.51 (m, 2H), 0.90 (dd, J = 6.5, 1.9 Hz, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 162.3, 153.0, 145.2 (q, J = 3.8 Hz), 137.9, 134.8 (q, J = 3.8 Hz), 129.6, 128.7 (q, J = 33.7 Hz), 128.4, 126.5, 123.3 (q, J = 274.5 Hz), 122.2, 48.8, 43.4, 41.7, 25.1, 23.4, 22.0; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.39;

IR ν = 3668, 3377, 2983, 2898, 1678, 1577, 1523, 1327, 1165, 1136, 1077, 1018, 941, 870, 753, 702 cm^{-1}; HRMS (EI) calc'd for $C_{19}H_{21}F_3N_2O$ $[M]^+$: 350.1606, found: 350.1608; $[\alpha]_D^{25}$ -2.0 (c 0.55, $CHCl_3$)

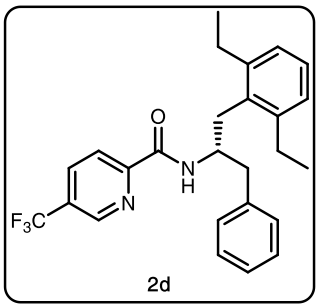
(*S*)-*N*-(1-(2,6-dimethylphenyl)-3-phenylpropan-2-yl)-5-(trifluoromethyl)picolinamide (2c)



Purified by column chromatography (10:1 Hexane/EtOAc), 67% overall yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.00-8.04 (m, 2H), 7.26-7.28 (m, 1H), 7.17-7.24 (m, 4H), 6.93-6.99 (m, 3H), 4.56-4.62 (m, 1H), 2.91-3.07 (m, 4H), 2.33 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 162.3, 152.7, 145.1 (q, J = 3.9 Hz), 138.2, 136.9, 135.1, 134.8 (q, J = 2.8 Hz), 129.3, 128.7 (q, J = 33.7 Hz),128.5, 128.5, 126.6, 126.4, 123.3 (q, J = 273.5 Hz), 122.01, 51.54, 41.19, 34.45, 20.50; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.32;

IR ν = 3673, 2985, 2911, 1605, 1562, 1470, 1391, 1321, 1162, 1128, 1078, 1016, 966, 858, 766 cm^{-1}; HRMS (EI) calc'd for $C_{24}H_{23}F_3N_2O$ $[M]^+$: 412.1762, found: 412.1764; $[\alpha]_D^{25}$ +54.4 (c 1.31, $CHCl_3$);

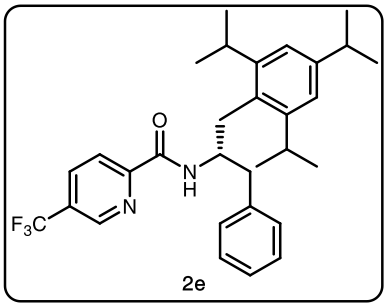
(*S*)-*N*-(1-(2,6-diethylphenyl)-3-phenylpropan-2-yl)-5-(trifluoromethyl)picolinamide (2d)



Purified by column chromatography (8:1 Hexane/EtOAc), 55% overall yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.8 Hz, 1H), 8.02 (dd, J = 8.2, 1.7 Hz, 1H), 7.30-7.34 (m, 4H), 7.21-7.26 (m, 1H), 7.15 (dd, J = 8.2, 6.7 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 4.66 (td, J = 14.9, 8.0 Hz, 1H), 3.00-3.23 (m, 4H), 2.78 (tt, J = 21.8, 7.3 Hz, 4H), 1.26 (t, J = 7.4 Hz, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 162.3, 152.7, 145.0 (q, J = 3.9 Hz), 143.0, 138.2, 134.6 (q, J = 2.9 Hz), 133.2, 129.2, 128.5 (q, J = 33.7 Hz), 128.4, 126.8, 126.5, 126.4, 123.2 (q, J = 274.4 Hz), 121.9, 52.6, 40.8, 32.8, 26.2, 15.7; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.29;

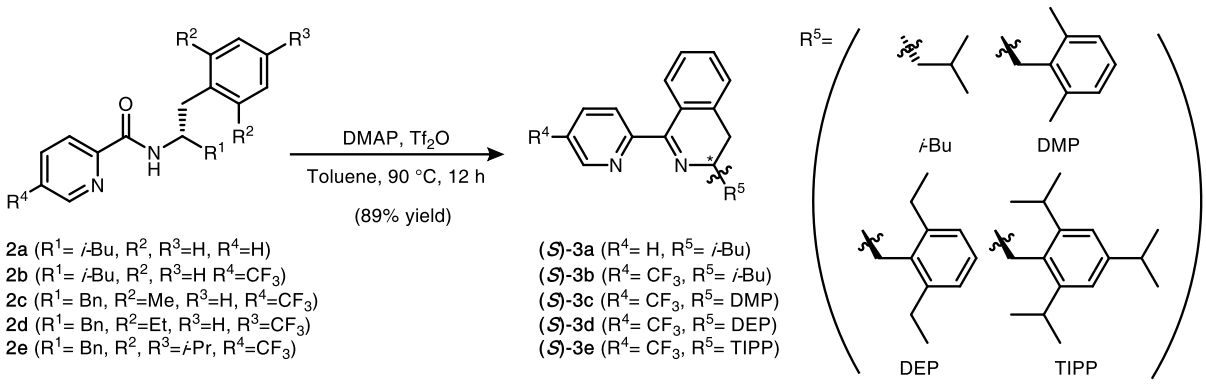
IR ν = 3385, 2963, 1681, 1579, 1520, 1455, 1327, 1166, 1136, 1076, 1018, 870, 756, 702 cm^{-1}; HRMS (EI) calc'd for $C_{26}H_{27}F_3N_2O$ $[M]^+$: 440.2075, found: 440.2078; $[\alpha]_D^{25}$ +0.5 (c 1.55, $CHCl_3$);

(*S*)-*N*-(1-phenyl-3-(2,4,6-triisopropylphenyl)propan-2-yl)-5-(trifluoromethyl) picolinamide (2e)



Purified by column chromatography (8:1 Hexane/EtOAc), 47% overall yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.21-7.33 (m, 5H), 6.98 (s, 2H), 4.52 (td, J = 14.7, 7.2 Hz, 1H), 2.97-3.24 (m, 6H), 2.81-2.92 (m, 1H), 1.18-1.29 (m, 18H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 162.5, 152.8, 147.4, 146.9, 145.0 (q, J = 3.8 Hz), 138.5, 134.7 (q, J = 2.9 Hz), 129.3, 128.9, 128.7 (q, J = 33.7 Hz), 128.5, 126.6, 123.3 (q, J = 273.5 Hz), 122.0, 121.1, 53.5, 40.9, 34.1, 31.6, 29.5, 24.5, 24.1, 24.0; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.30;

IR ν = 3407, 2960, 1678, 1606, 1575, 1510, 1473, 1326, 1165, 1141, 1076, 1018, 940, 872, 752, 705 cm^{-1}; HRMS (EI) calc'd for $C_{31}H_{37}F_3N_2O$ $[M]^+$: 510.2858, found: 510.2860; $[\alpha]_D^{25}$ +1.83 (c=2.23, $CHCl_3$);

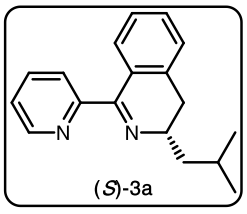


2a (R^1= *i*-Bu, R^2, R^3=H, R^4=H)
2b (R^1= *i*-Bu, R^2, R^3=H R^4=CF_3)
2c (R^1= Bn, R^2=Me, R^3=H, R^4=CF_3)
2d (R^1= Bn, R^2=Et, R^3=H, R^3=CF_3)
2e (R^1= Bn, R^2, R^3=*i*-Pr, R^4=CF_3)

(*S*)-3a (R^4= H, R^5= *i*-Bu)
(*S*)-3b (R^4= CF_3, R^5= *i*-Bu)
(*S*)-3c (R^4= CF_3, R^5= DMP)
(*S*)-3d (R^4= CF_3, R^5= DEP)
(*S*)-3e (R^4= CF_3, R^5= TIPP)

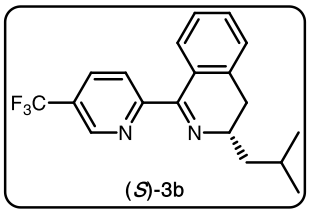
To a mixture of picolinamide **2a-2e** (1.04 mmol, 1.0 equiv.) and DMAP (3.13 mmol, 3.0 equiv.) in toluene (42 mL, 0.025 M), Tf_2O (5.22 mmol, 5.0 equiv.) was added dropwise. The mixture was heated to 90 °C in an oil bath and stirred for 12 h. The solution was cooled to 24 °C, quenched by Na_2CO_3 (50 mL), extracted with EtOAc (60 mL, x3) and dried over $MgSO_4$ successively. The residue was filtered, concentrated and purified by flash chromatography. Compound **2a-2e** was obtained as pale reddish brown oil (**3a**), or pale yellow solid (**3b**, **3c, 3d, 3e**).

(*S*)-3-isobutyl-1-(pyridin-2-yl)-3,4-dihydroisoquinoline (3a)



Purified by column chromatography (9:1 Hexane/EtOAc), 93% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 4.2 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.76 (td, J = 7.6, 1.9 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.28-7.35 (m, 2H), 7.19-7.25 (m, 2H), 3.66-3.73 (m, 1H), 2.81 (dd, J = 15.4, 5.1 Hz, 1H), 2.59 (dd, J = 15.4, 12.0 Hz, 1H), 1.98-2.08 (m, 1H), 1.77-1.84 (m, 1H), 1.44-1.50 (m, 1H), 0.97 (dd, J = 6.7, 2.1 Hz, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.6, 157.3, 148.3, 138.4, 136.8, 130.6, 128.1, 128.1, 127.5, 126.5, 123.9, 123.7, 55.3, 44.7, 31.9, 24.8, 22.8, 22.7;
IR ν = 3671, 2953, 2909, 1609, 1562, 1466, 1433, 1325, 1243, 1050, 994, 967, 900, 802, 746, 719, 689, 667 cm^{-1}; HRMS (EI) calc'd for $C_{18}H_{20}N_2$ $[M]^+$: 264.1626, found: 264.1625; $[\alpha]_D^{25}$ +136.6 (c 0.95, $CHCl_3$);

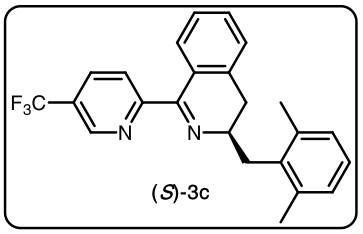
(*S*)-3-isobutyl-1-(5-(trifluoromethyl)pyridin-2-yl)-3,4-dihydroisoquinoline (3b)



Purified by column chromatography (13:1 Hexane/EtOAc), 89% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.04 (d, J = 1.5 Hz, 2H), 7.36-7.42 (m, 2H), 7.26 (t, J = 8.0 Hz, 2H), 3.73 (ddd, J = 19.7, 7.0, 5.2 Hz, 1H), 2.84 (dd, J = 15.6, 5.0 Hz, 1H), 2.61 (dd, J = 15.4, 12.4 Hz, 1H), 2.00-2.10 (m, 1H), 1.77-1.84 (m, 1H), 1.46-1.53 (m, 1H), 0.99 (q, J = 3.3 Hz, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.7, 160.7, 145.4 (q, J = 3.8 Hz), 138.5, 134.1 (q, J = 3.8 Hz), 131.1, 127.9, 127.8, 127.8, 126.7, 126.6 (q, J = 33.6 Hz), 123.9, 123.6 (q, J = 281.2 Hz), 55.8, 44.8, 32.0, 24.9, 22.8, 22.8; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.32;

IR ν = 3661, 2983, 2954, 1605, 1562, 1467, 1390, 1321, 1164, 1131, 1078, 1017, 967, 861, 746 cm^{-1}; HRMS (EI) calc'd for $C_{19}H_{19}F_3N_2$ $[M]^+$: 332.1500, found: 332.1497; $[\alpha]_D^{25}$ +122.9 (c 0.64, $CHCl_3$);

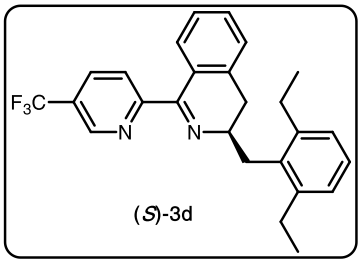
(*S*)-3-(2,6-dimethylbenzyl)-1-(5-(trifluoromethyl)pyridin-2-yl)-3,4-dihydroisoquinoline (3c)



Purified by column chromatography (13:1 Hexane/EtOAc), 81% yield. Carefully rinsed three times with distilled petroleum ether at 0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.03-8.09 (m, 2H), 7.49 (d, J = 7.8 Hz, 1H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.22-7.25 (m, 1H), 7.07-7.13 (m, 3H), 3.90-3.98 (m, 1H), 3.39 (q, J = 6.7 Hz, 1H), 3.11 (dd, J = 13.7, 8.7 Hz, 1H), 2.71-2.83 (m, 2H), 2.41 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.9, 160.4, 145.4 (q, J = 3.8 Hz), 138.4, 137.2, 136.3, 134.1 (q, J = 3.8 Hz), 131.2, 128.4, 128.0, 127.9, 127.6, 126.8, 126.6 (q, J = 33.6 Hz), 126.2, 123.8, 123.6 (q, J = 273.4 Hz), 58.2, 35.6, 31.2, 20.7; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.32;

IR ν = 3678, 2983, 2917, 1605, 1562, 1470, 1391, 1321, 1162, 1128, 1078, 966, 858, 766 cm^{-1}; HRMS (EI) calc'd for $C_{24}H_{21}F_3N_2$ $[M]^+$: 394.1657, found: 394.1656; $[\alpha]_D^{25}$ -75.5 (c 1.23, $CHCl_3$);

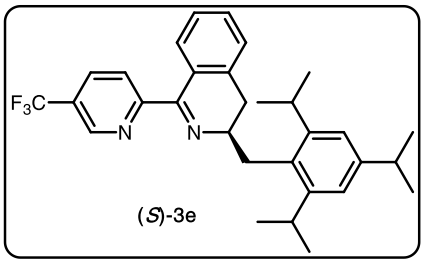
(*S*)-3-(2,6-diethylbenzyl)-1-(5-(trifluoromethyl)pyridin-2-yl)-3,4-dihydroisoquinoline (3d)



Purified by column chromatography (13:1 Hexane/EtOAc), 56% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.10 (s, 2H), 7.56 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.17-7.34 (m, 5H), 3.91-3.99 (m, 1H), 3.47-3.54 (m, 1H), 3.20 (dd, J = 14.1, 8.8 Hz, 1H), 2.79-2.89 (m, 6H), 1.29 (t, J = 7.6 Hz, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.7, 160.4, 145.3 (q, J = 4.7 Hz), 143.2, 138.4, 134.5, 133.9 (q, J = 2.8 Hz), 131.1, 128.0, 127.8, 127.6, 126.7, 126.6, 126.5 (q, J = 32.7 Hz), 126.3, 123.8, 123.5 (q, J = 273.5 Hz), 59.2, 34.1, 31.0, 26.3, 15.6; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.15;

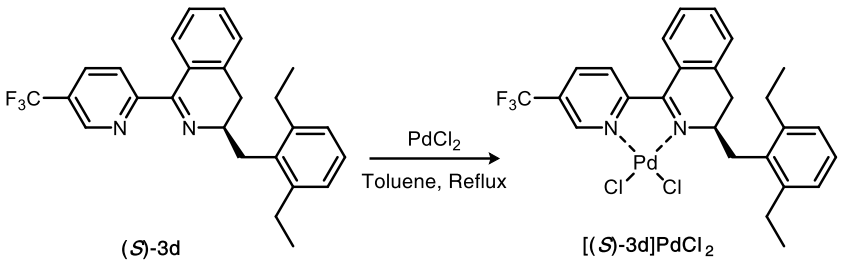
IR ν = 3597, 3065, 2961, 1605, 1562, 1456, 1391, 1320, 1163, 1129, 1078, 1016, 965, 854, 742 cm^{-1}; HRMS (EI) calc'd for $C_{26}H_{25}F_3N_2$ $[M]^+$: 422.1970, found: 422.1968; $[\alpha]_D^{25}$ -1.4 (c 0.85, $CHCl_3$);

(*S*)-1-(5-(trifluoromethyl)pyridin-2-yl)-3-(2,4,6-triisopropylbenzyl)-3,4-dihydroisoquinoline (3e)



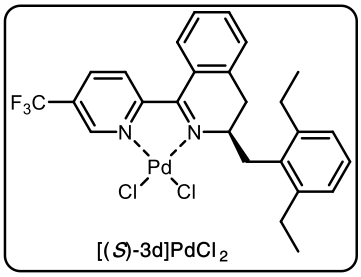
Purified by column chromatography (13:1 Hexane/EtOAc), 37% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.07 (s, 2H), 7.37-7.46 (m, 2H), 7.22-7.30 (m, 2H), 7.05 (s, 2H), 3.82-3.90 (m, 1H), 3.29-3.40 (m, 3H), 3.10 (dd, J = 14.1, 9.2 Hz, 1H), 2.72-2.95 (m, 3H), 1.19-1.30 (m, 18H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ163.9, 160.6, 147.7, 146.9, 145.5 (q, J = 3.9 Hz), 138.4, 134.0 (q, J = 2.9 Hz), 131.2, 130.1, 128.0, 127.7, 126.8 (q, J = 32.7 Hz), 126.8, 124.0, 123.6 (q, J = 273.5 Hz), 121.1, 59.8, 34.2, 32.9, 30.5, 29.5, 24.8, 24.3, 24.2; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.23;

IR ν = 3678, 2983, 2901, 1606, 1563, 1459, 1389, 1321, 1164, 1132, 1078, 1016, 966, 938, 860 cm^{-1}; HRMS (EI) calc'd for $C_{31}H_{35}F_3N_2$ $[M]^+$: 492.2752, found: 492.2750; $[\alpha]_D^{25}$ -0.9 (c 0.71, $CHCl_3$);



To a solution of **(*S*)-3d** (0.15 mmol, 1.0 equiv.) in toluene (1.5 mL, 0.1 M), $PdCl_2$ (0.15 mmol, 1.0 equiv.) was added. The mixture was stirred and refluxed for 24 h. The mixture was cooled to 24 °C, filtered, concentrated and purified with flash chromatography. Compound **[(*S*)-3d]PdCl₂** was obtained as yellow solid.

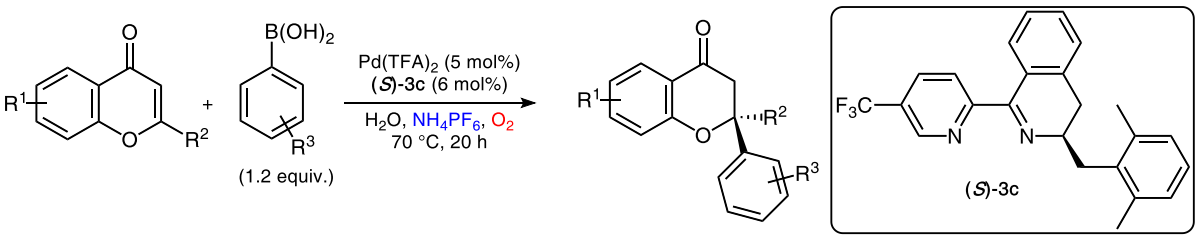
((*S*)-3-(2,6-diethylbenzyl)-1-(5-(trifluoromethyl)pyridin-2-yl)-3,4-dihydroisoquinoline) palladium(II) chloride ([(*S*)-3d]PdCl₂)



Purified by column chromatography (15:1 Hexane/EtOAc), 43% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.01-8.06 (m, 2H), 7.45 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.1 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.17-7.20 (m, 2H), 7.10 (d, J = 7.6 Hz, 2H), 3.81-3.89 (m, 1H), 3.40 (dd, J = 13.7, 6.1 Hz, 1H), 3.10 (dd, J = 13.9, 9.0 Hz, 1H), 2.67-2.81 (m, 6H), 1.20 (t, J = 7.4 Hz, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.3, 159.2, 148.9 (q, J = 3.8 Hz), 143.9, 137.5, 137.2 (q, J = 2.8 Hz), 134.5, 132.1, 130.5 (q, J = 34.7 Hz), 130.2, 128.5, 127.6 (q, 2.9 Hz), 127.1, 126.5, 125.9, 123.2, 120.5, 57.0, 29.9, 29.0, 26.3, 16.0; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.57

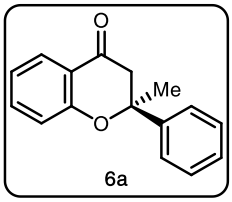
Elemental Analysis Calc'd for $C_{26}H_{25}Cl_2F_3N_2Pd$ (%): C 52.06, H 4.20, N,4.67; found C 52.44, H 4.77, N 4.47; $[\alpha]_D^{25}$ +0.01 (c 0.22, $CHCl_3$);

4. Experimental Procedures



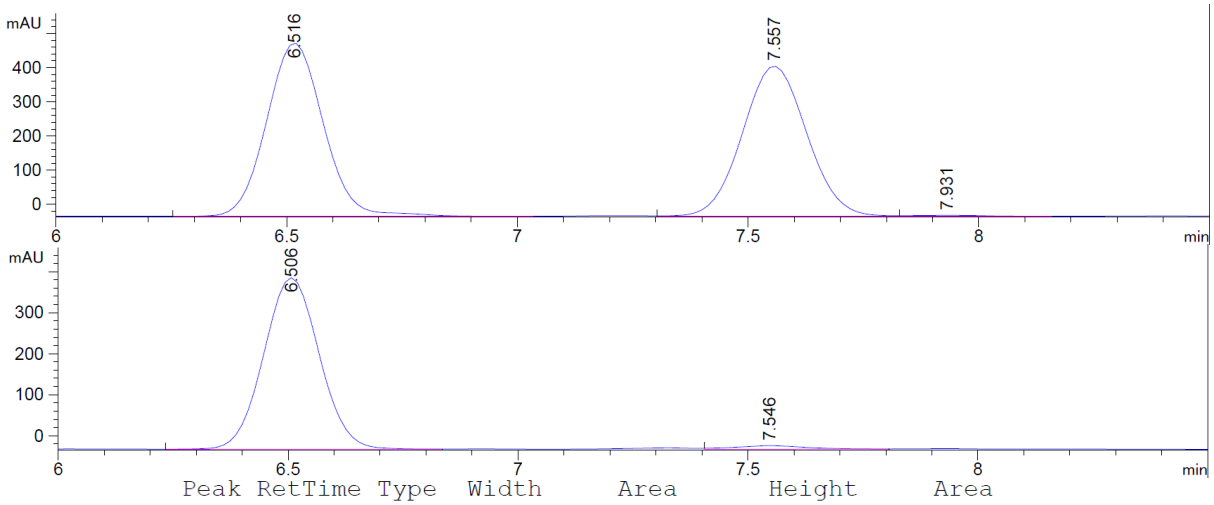
H_2O (700 µL, 0.71 M) was added through 500 µL glass microsyringes to a 4 mL screw-top septum vial charged with a stir bar, chromones (0.50 mmol), $Pd(OCOCF_3)_2$ (8.30 mg, 0.025 mmol), **(*S*)-3c** (11.8 mg, 0.03 mmol), NH_4PF_6 (24.4 mg, 0.15 mmol) and arylboronic acid (0.60 mmol). O_2 balloon was equipped to the septum of the vial. The mixture was heated to 70 °C and stirred for 20 h. The reaction was monitored by TLC (4:1 hexanes/EtOAc). To the reaction vial, EA (300 µL, x3) was added to extract products. After brief extraction, the organic layer (EA) was directly loaded on the silica gel and purified by column chromatography in each condition to afford desired products. Absolute configuration of compound **6e** was determined by X-ray crystallography, and all other products are assigned by analogy.

(*S*)-2-methyl-2-phenylchroman-4-one (6a)



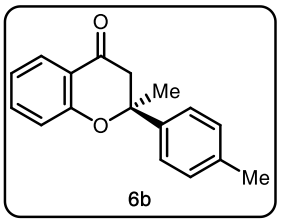
Purified by column chromatography (11:1 Hexane/EtOAc), 98% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.0, 1.5 Hz, 1H), 7.39-7.48 (m, 3H), 7.32-7.17 (3H), 7.06 (dd, J = 8.4, 0.8 Hz, 1H), 6.90-6.94 (m, 1H), 3.31 (d, J = 16.4 Hz, 1H), 3.08 (d, J = 16.4 Hz, 1H), 1.75 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.8, 160.1, 143.0, 136.3, 128.7, 127.7, 126.7, 125.3, 121.1, 121.0, 118.4, 82.5, 48.1, 30.0; The data matched with previously reported literature.[3]

IR ν = 2997, 2896, 2361, 1692, 1607, 1461, 1376, 1312, 1272, 1236, 1177, 1121, 1051, 952, 890, 765, 701 cm^{-1}; $[\alpha]_D^{25}$ +12.1 (c 0.54, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 6.1, minor = 7.55, 95% ee.



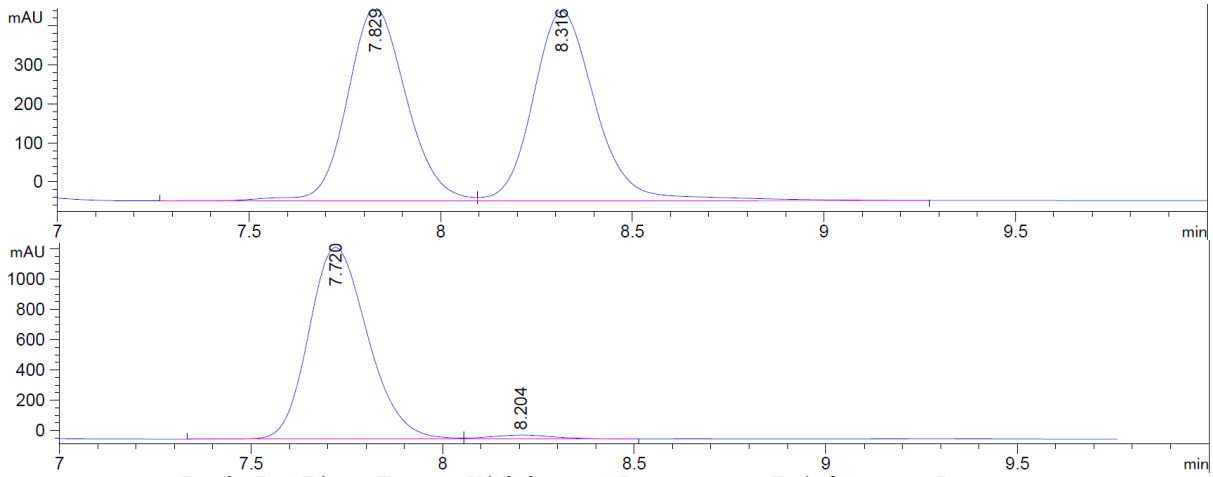
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.506	VV	0.1342	3522.37500	418.61371	97.5193
2	7.546	VV	0.1624	89.60211	8.27237	2.4807

(*S*)-2-methyl-2-(*p*-tolyl)chroman-4-one (6b)



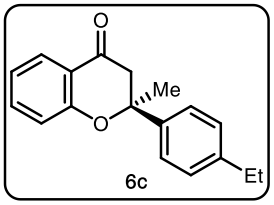
Purified by column chromatography (13:1 Hexane/EtOAc), 80% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.8, 1.6 Hz, 1H), 7.43-7.47 (m, 1H), 7.29 (dt, J = 8.4, 1.9 Hz, 2H), 7.03-7.10 (m, 3H), 6.89-6.93 (m, 1H), 3.29 (d, J = 16.5 Hz, 1H), 3.06 (d, J = 16.5 Hz, 1H), 2.27 (s, 3H), 1.74 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.9, 160.2, 140.0, 137.5, 136.2, 129.4, 126.7, 125.3, 121.2, 121.1, 118.4, 82.5, 48.2, 30.2, 21.1; The data matched with previously reported literature.[3]

IR ν = 3673, 2955, 1693, 1607, 1461, 1375, 1311, 1273, 1237, 1175, 1120, 1050, 951, 890, 818, 766 cm^{-1}; $[\alpha]_D^{25}$ +38.5 (c 0.77, $CHCl_3$); HPLC Conditions: 3% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 7.72, minor = 8.20, 96% ee.



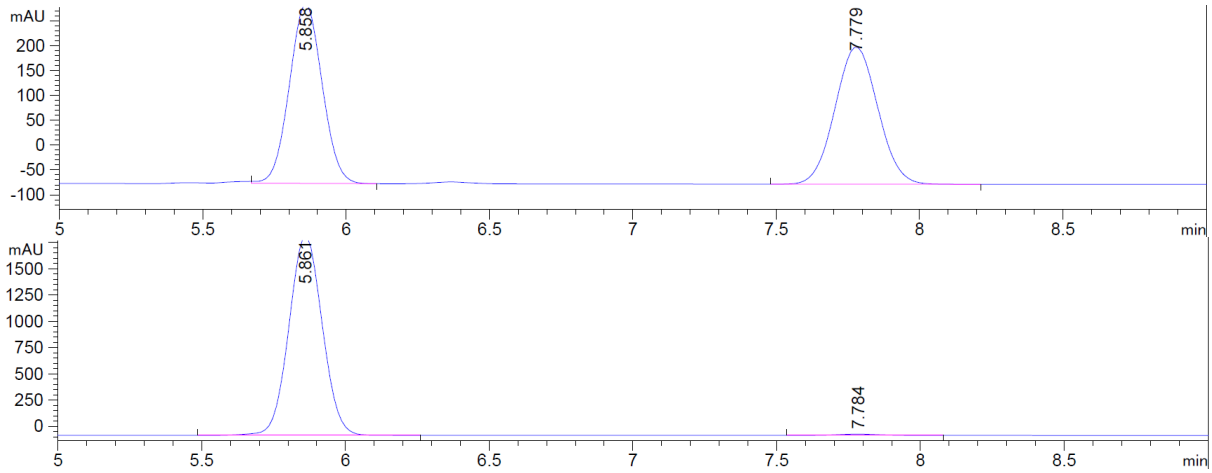
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.720	BV	0.1683	1.35149e4	1268.72705	97.8816
2	8.204	VB	0.1706	292.49518	26.12401	2.1184

(*S*)-2-(4-ethylphenyl)-2-methylchroman-4-one (6c)



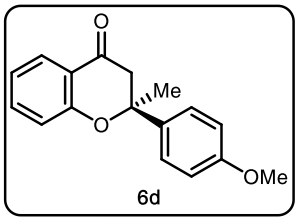
Purified by column chromatography (13:1 Hexane/EtOAc), 85% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.8, 1.7 Hz, 1H), 7.43-7.47 (m, 1H), 7.31 (dt, J = 8.4, 2.1 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.05 (dd, J = 8.4, 0.8 Hz, 1H), 6.90-6.94 (m, 1H), 3.30 (d, J = 16.4 Hz, 1H), 3.06 (d, J = 16.4 Hz, 1H), 2.57 (q, J = 7.6 Hz, 2H), 1.74 (s, 3H), 1.18 (t, J = 7.4 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.0, 160.2, 143.7, 140.2, 136.2, 128.2, 126.7, 125.3, 121.2, 121.0, 118.4, 82.5, 48.2, 30.1, 28.4, 15.3;

IR ν = 2968, 2929, 1692, 1607, 1514, 1461, 1415, 1375, 1309, 1273, 1236, 1175, 1121, 1078, 1044, 951, 890, 832, 765 cm^{-1}; HRMS (EI) calc'd for $C_{18}H_{18}O_2$ $[M]^+$: 266.1307, found: 266.1294; $[\alpha]_D^{25}$ +33.8 (c 0.89, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 5.86, minor = 7.78, 98% ee.



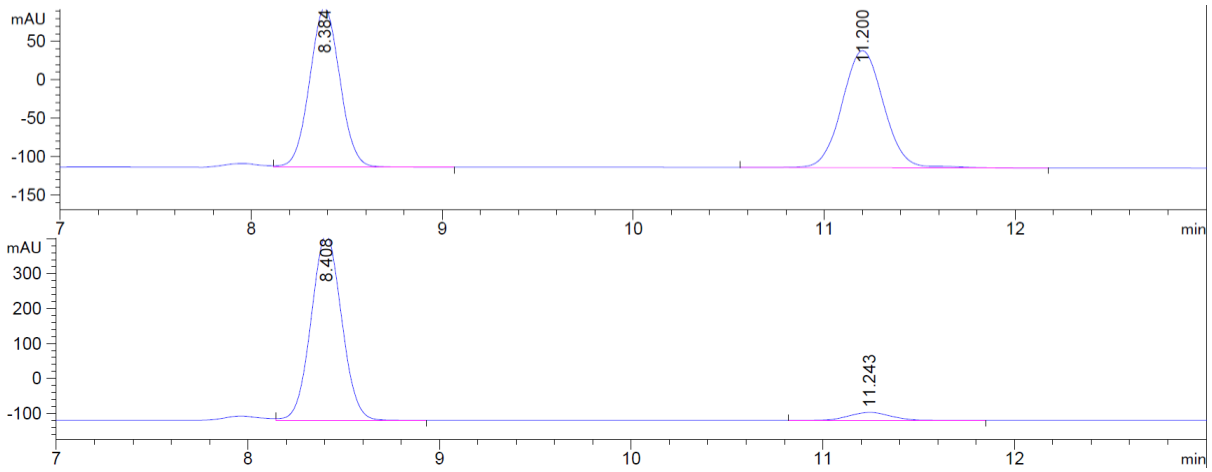
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.861	VV	0.1258	1.53032e4	1902.79700	99.1999
2	7.784	VB	0.1609	123.43153	11.91444	0.8001

(*S*)-2-(4-methoxyphenyl)-2-methylchroman-4-one (6d)



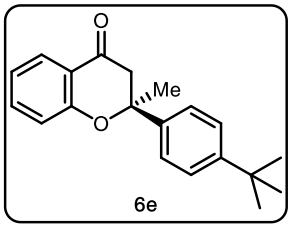
Purified by column chromatography (9:1 Hexane/EtOAc), 51% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.8, 1.8 Hz, 1H), 7.42-7.46 (m, 1H), 7.30-7.34 (m, 2H), 7.02 (d, J = 8.2 Hz, 1H), 6.89-6.93 (m, 1H), 6.78-6.82 (m, 2H), 3.73 (s, 3H), 3.28 (d, J = 16.5 Hz, 1H), 3.05 (d, J = 16.5 Hz, 1H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.0, 160.1, 159.0, 136.2, 134.9, 126.7, 121.2, 121.0, 118.4, 114.0, 82.4, 55.3, 48.1, 30.3; The data matched with previously reported literature.[3]

IR ν = 2976, 2367, 1691, 1609, 1513, 1461, 1415, 1376, 1310, 1252, 1182, 1122, 1079, 1033, 950, 890, 832, 768 cm^{-1}; $[\alpha]_D^{25}$ +42.5 (c 0.37, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 8.41, minor = 11.24, 90% ee.



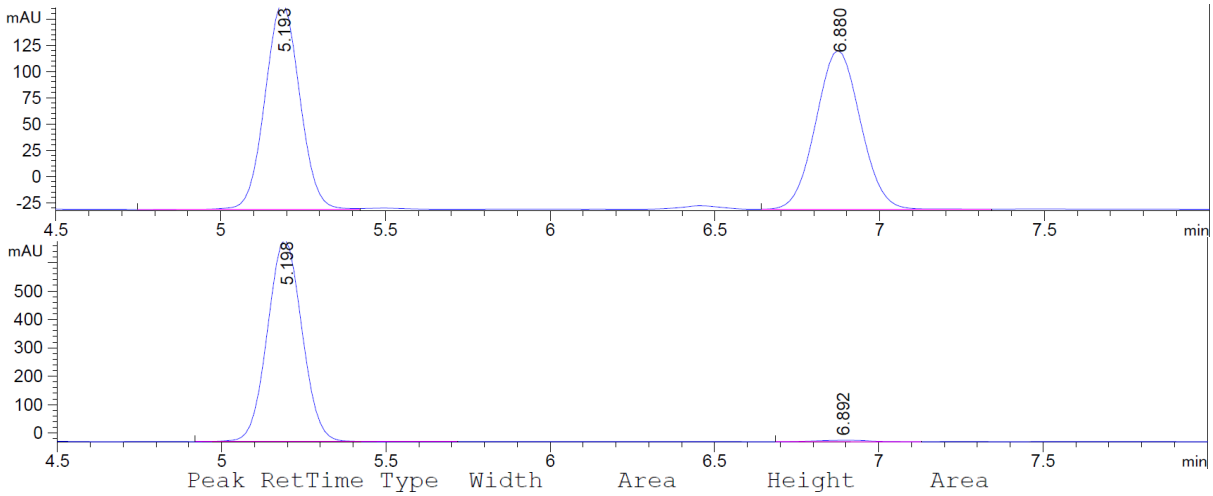
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.408	VB	0.1728	5859.71143	530.96729	94.4842
2	11.243	VB	0.2346	342.07736	22.85378	5.5158

(*S*)-2-(4-(tert-butyl)phenyl)-2-methylchroman-4-one (6e)



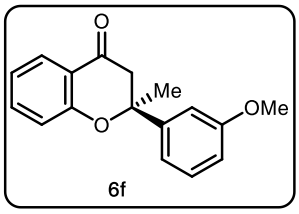
Purified by column chromatography (15:1 Hexane/EtOAc), 78% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.8, 1.8 Hz, 1H), 7.44-7.48 (m, 1H), 7.28-7.34 (m, 4H), 7.05 (dd, J = 8.2, 0.7 Hz, 1H), 6.90-6.94 (m, 1H), 3.30 (d, J = 16.5 Hz, 1H), 3.05 (d, J = 16.5 Hz, 1H), 1.74 (s, 3H), 1.26 (s, 9H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.0, 160.2, 150.6, 140.0, 136.2, 126.7, 125.6, 125.0, 121.1, 121.0, 118.5, 82.5, 48.2, 34.5, 31.3, 29.9;

IR ν = 2962, 2360, 1693, 1608, 1510, 1462, 1401, 1363, 1310, 1273, 1239, 1120, 1082, 1016, 952, 891, 835, 763 cm^{-1}; HRMS (EI) calc'd for $C_{20}H_{22}O_2$ $[M]^+$: 294.1620, found: 294.1610; $[\alpha]_D^{25}$ +27.5 (c 0.95, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 5.12, minor = 6.89, 98% ee.



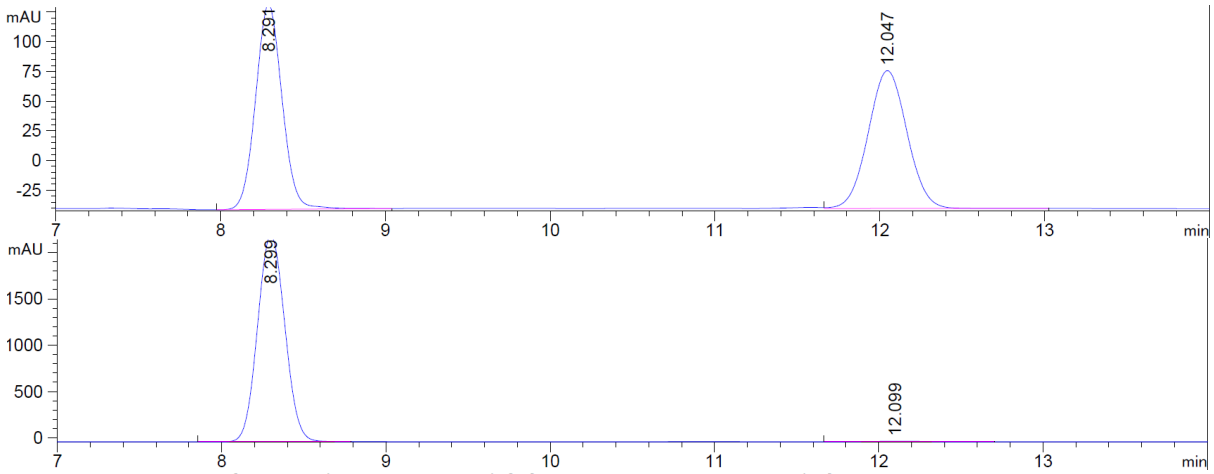
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.198	VB	0.1129	5187.58008	713.16296	99.1247
2	6.892	BB	0.1436	45.80952	4.96729	0.8753

(*S*)-2-(3-methoxyphenyl)-2-methylchroman-4-one (6f)



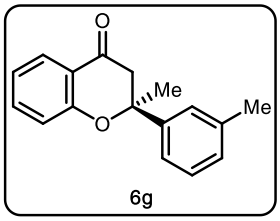
Purified by column chromatography (9:1 Hexane/EtOAc), 81% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.8, 1.7 Hz, 1H), 7.43-7.48 (m, 1H), 7.20 (t, J = 8.2 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.91-6.97 (m, 3H), 6.73-6.76 (m, 1H), 3.74 (s, 3H), 3.28 (d, J = 16.8 Hz, 1H), 3.07 (d, J = 16.4 Hz, 1H), 1.74 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.7, 160.1, 159.9, 144.8, 136.3, 129.8, 126.7, 121.2, 118.4, 117.7, 112.8, 111.6, 82.5, 55.3, 48.2, 30.0; The data matched with previously reported literature.[3]

IR ν = 3072, 2836, 1691, 1607, 1461, 1376, 1325, 1290, 1237, 1177, 1150, 1121, 1046, 952, 868, 767, 701 cm^{-1}; $[\alpha]_D^{25}$ +34.0 (c 1.00, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 8.30, minor = 12.01, 99% ee.



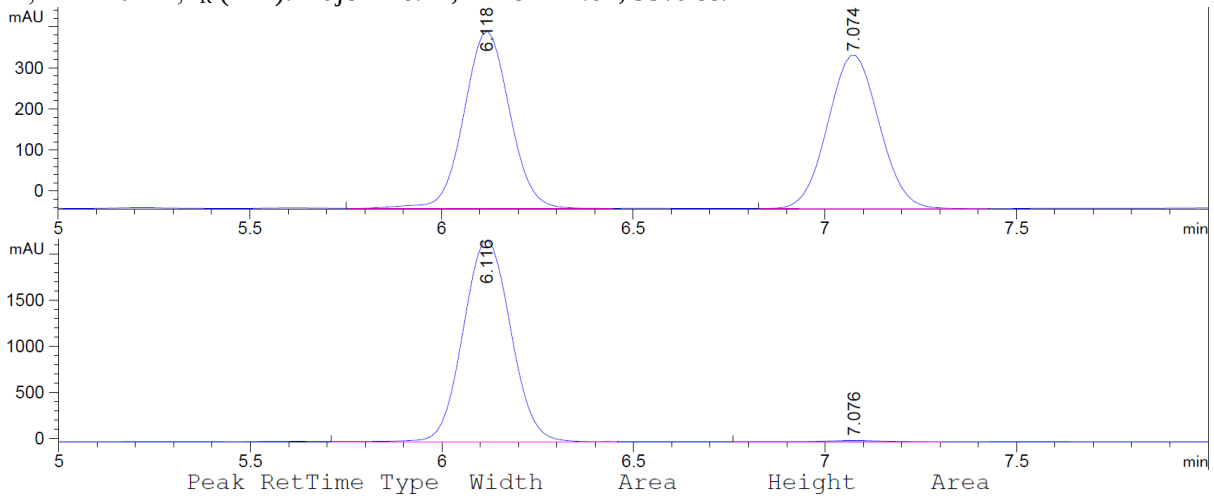
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.299	BV	0.1826	2.57069e4	2228.88428	99.5530
2	12.099	BB	0.2643	115.43274	6.72360	0.4470

(*S*)-2-methyl-2-(*m*-tolyl)chroman-4-one (6g)



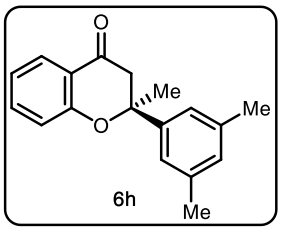
Purified by column chromatography (15:1 Hexane/EtOAc), 82% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.8, 1.7 Hz, 1H), 7.44-7.48 (m, 1H), 7.15-7.21 (m, 3H), 7.02-7.07 (m, 2H), 6.92 (td, J = 7.4, 1.0 Hz, 1H), 3.29 (d, J = 16.4 Hz, 1H), 3.06 (d, J = 16.8 Hz, 1H), 2.30 (s, 3H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.9, 160.2, 143.1, 138.3, 136.2, 128.6, 128.6, 126.7, 126.0, 122.4, 121.1, 121.1, 118.5, 82.5, 48.2, 29.9, 21.7; The data matched with previously reported literature.[3]

IR ν = 2978, 2922, 2361, 1692, 1607, 1461, 1376, 1325, 1278, 1237, 1120, 1081, 1044, 952, 896, 865, 766, 704cm^{-1}; $[\alpha]_D^{25}$ +10.4 (c 0.91, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 6.12, minor = 7.01, 99% ee.



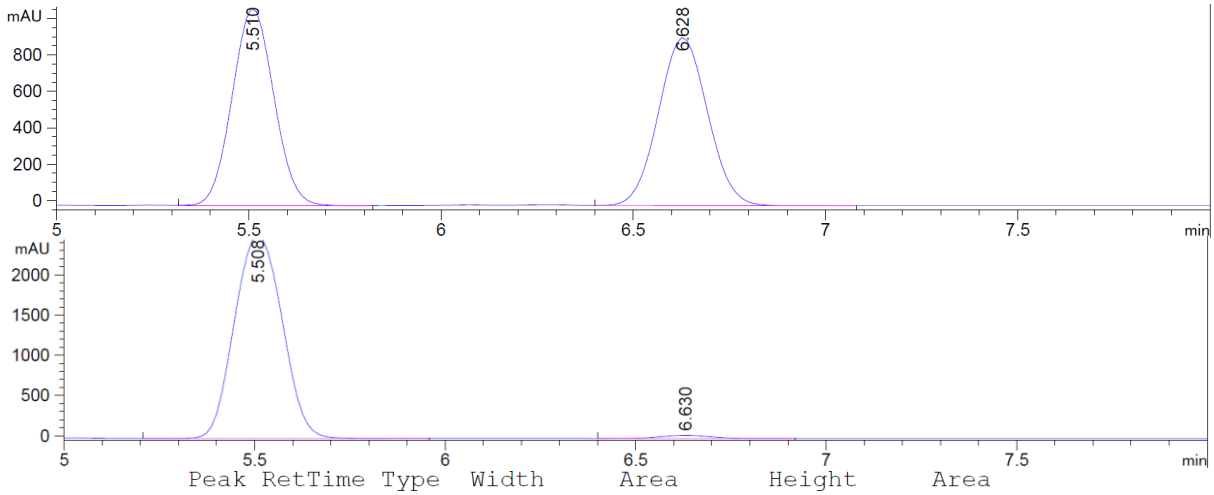
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.116	VV	0.1360	1.88089e4	2194.24487	99.3741
2	7.076	BB	0.1450	118.46085	12.67903	0.6259

(*S*)-2-(3,5-dimethylphenyl)-2-methylchroman-4-one (6h)



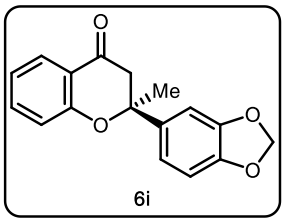
Purified by column chromatography (15:1 Hexane/EtOAc), 77% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.0, 1.6 Hz, 1H), 7.43-7.48 (m, 1H), 7.06 (dd, J = 8.2, 0.9 Hz, 1H), 7.02 (s, 2H), 6.90-6.94 (m, 1H), 6.85 (s, 1H), 3.29 (d, J = 16.5 Hz, 1H), 3.04 (d, J = 16.5 Hz, 1H), 2.26 (s, 6H), 1.72 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.9, 160.2, 143.1, 138.2, 136.2, 129.4, 126.7, 123.1, 121.1, 121.0, 118.4, 82.5, 48.2, 29.8, 21.5; The data matched with previously reported literature.[3]

IR ν = 2977, 2920, 1693, 1608, 1461, 1376, 1303, 1238, 1181, 1122, 1081, 1045, 939, 899, 851, 765, 706 cm^{-1}; $[\alpha]_D^{25}$ +8.4 (c 1.00, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 5.51, minor = 6.63, 97% ee.



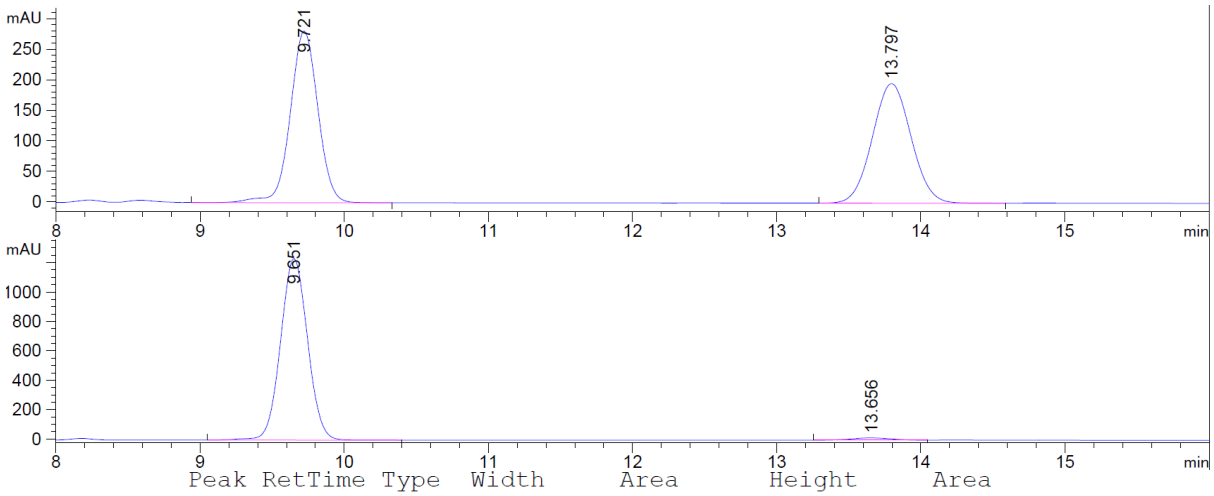
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.508	VV	0.1411	2.18728e4	2523.11133	98.4235
2	6.630	BV	0.1406	350.35849	39.08049	1.5765

(*S*)-2-(benzo[d][1,3]dioxol-5-yl)-2-methylchroman-4-one (6i)



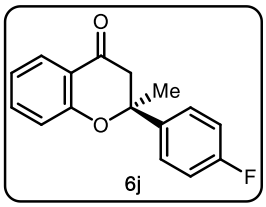
Purified by column chromatography (13:1 Hexane/EtOAc), 47% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.8, 1.7 Hz, 1H), 7.42-7.46 (m, 1H), 7.01 (dd, J = 8.4, 0.8 Hz, 1H), 6.89-6.93 (m, 2H), 6.81 (dd, J = 8.4, 1.9 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 5.87 (dd, J = 4.6, 1.5 Hz, 2H), 3.24 (d, J = 16.4 Hz, 1H), 3.04 (d, J = 16.8 Hz, 1H), 1.71 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.7, 159.9, 148.1, 147.1, 136.9, 136.2, 126.6, 121.2, 118.9, 118.4, 108.1, 106.2, 101.2, 82.4, 48.1, 30.4; The data matched with previously reported literature.[3]

IR ν = 2978, 2900, 2373, 1689, 1608, 1488, 1461, 1325, 1236, 1119, 1039, 935, 881, 812, 768 cm^{-1}; $[\alpha]_D^{25}$ +67.2 (c 0.50, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 9.65, minor = 13.66, 96% ee.



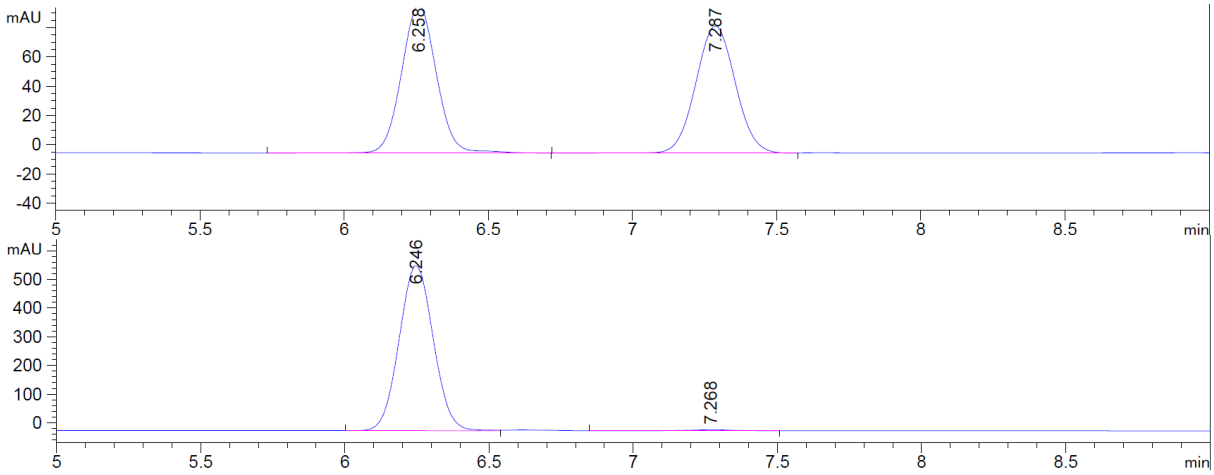
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.651	VB	0.2040	1.60979e4	1235.74329	98.2036
2	13.656	BV	0.2913	294.47656	15.95588	1.7964

(*S*)-2-(4-fluorophenyl)-2-methylchroman-4-one (6j)



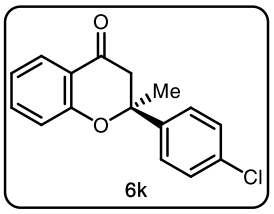
Purified by column chromatography (15:1 Hexane/EtOAc), 80% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.8, 1.8 Hz, 1H), 7.46 (ddd, J = 8.6, 6.9, 1.5 Hz, 1H), 7.35-7.40 (m, 2H), 7.03 (dd, J = 8.2, 0.7 Hz, 1H), 6.91-6.99 (m, 3H), 3.27 (d, J = 16.5 Hz, 1H), 3.07 (d, J = 16.5 Hz, 1H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.6, 162.2 (d, J = 248.4 Hz), 159.9, 138.9 (d, J = 2.9 Hz), 136.4, 127.2 (d, J = 8.7 Hz), 126.7, 121.3, 121.1, 118.4, 115.6 (d, J = 21.2 Hz), 82.2, 48.2, 30.2; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -114.50; The data matched with previously reported literature.[3]

IR ν = 3665, 2963, 1691, 1606, 1461, 1416, 1308, 1271, 1233, 1163, 1121, 1051, 1015, 952, 892, 837, 767 cm^{-1}; $[\alpha]_D^{25}$ +15.4 (c 0.93, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 6.25, minor = 7.27, 98% ee.



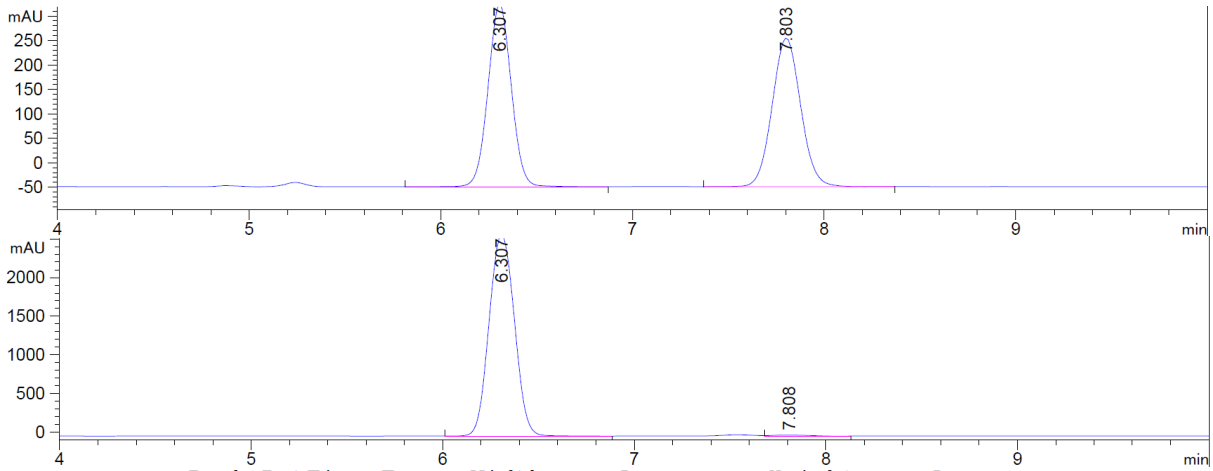
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.246	BV	0.1278	4744.93604	577.59821	99.1438
2	7.268	BB	0.1549	40.97900	4.02200	0.8562

(*S*)-2-(4-chlorophenyl)-2-methylchroman-4-one (6k)



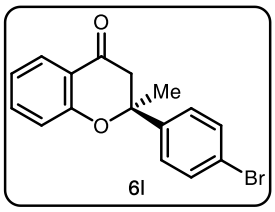
Purified by column chromatography (15:1 Hexane/EtOAc), 86% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.8, 1.6 Hz, 1H), 7.44-7.48 (m, 1H), 7.34 (dt, J = 9.1, 2.4 Hz, 2H), 7.23-7.27 (m, 2H), 7.04 (dd, J = 8.5, 0.7 Hz, 1H), 6.92-6.96 (m, 1H), 3.25 (d, J = 16.5 Hz, 1H), 3.07 (d, J = 16.5 Hz, 1H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.4, 159.8, 141.7, 136.4, 133.7, 128.9, 126.8, 126.8, 121.4, 121.1, 118.4, 82.2, 48.0, 30.1; The data matched with previously reported literature.[3]

IR ν = 3671, 2959, 1693, 1607, 1461, 1400, 1308, 1270, 1236, 1175, 1121, 1096, 1013, 953, 891, 829, 765, 740 cm^{-1}; $[\alpha]_D^{25}$ +22.7 (c 0.94, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 6.31, minor = 7.81, 99% ee.



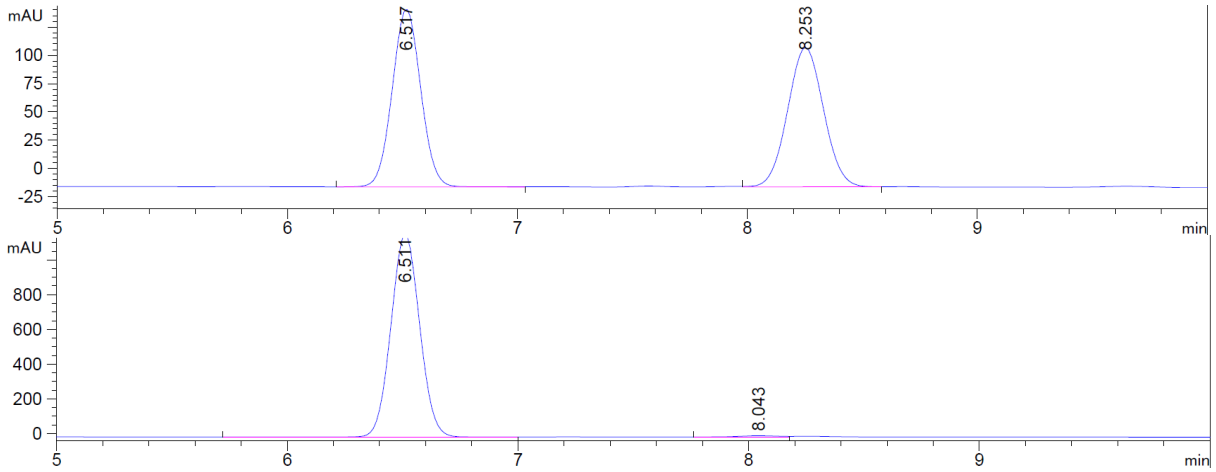
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.307	VB	0.1508	2.38716e4	2606.55151	99.3559
2	7.808	VB	0.1606	154.74690	14.49076	0.6441

(*S*)-2-(4-bromophenyl)-2-methylchroman-4-one (6l)



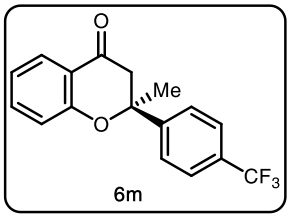
Purified by column chromatography (15:1 Hexane/EtOAc), 80% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.8, 1.7 Hz, 1H), 7.39-7.48 (m, 3H), 7.25-7.29 (m, 2H), 7.04 (dd, J = 8.4, 0.8 Hz, 1H), 6.94 (td, J = 7.5, 1.0 Hz, 1H), 3.25 (d, J = 16.4 Hz, 1H), 3.07 (d, J = 16.4 Hz, 1H), 1.72 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.4, 159.8, 142.2, 136.4, 131.9, 127.2, 126.8, 121.9, 121.4, 121.1, 118.4, 82.2, 48.0, 30.0; The data matched with previously reported literature.[3]

IR ν = 2984, 2903, 1693, 1607, 1461, 1309, 1271, 1235, 1121, 1080, 1009, 953, 891, 825, 770 cm^{-1}; $[\alpha]_D^{25}$ +19.1 (c 0.40, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 6.51, minor = 8.04, 98% ee.



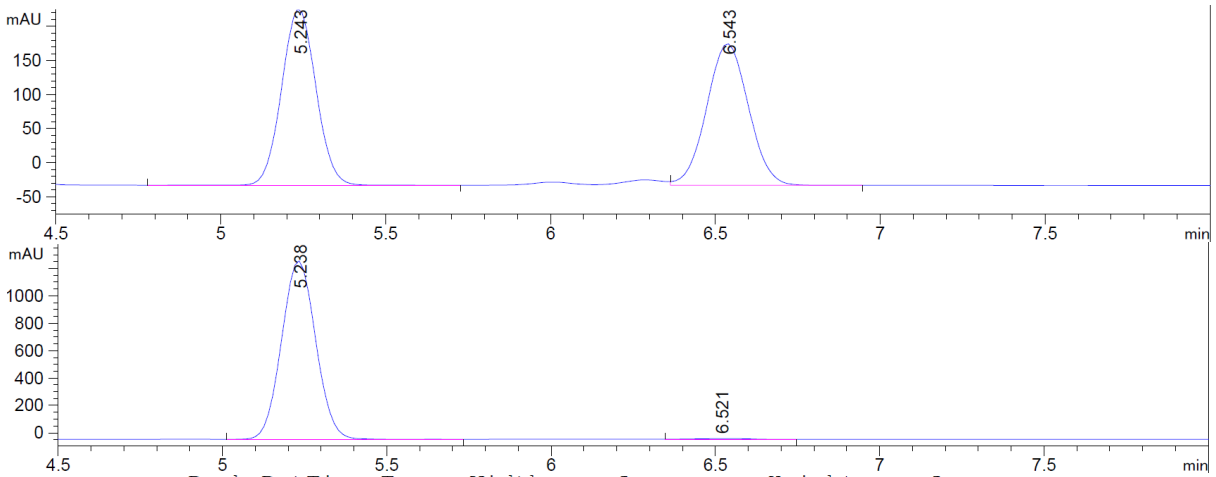
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.511	BV	0.1364	1.00791e4	1170.91785	99.1682
2	8.043	BV	0.1783	84.54333	7.13010	0.8318

(*S*)-2-methyl-2-(4-(trifluoromethyl)phenyl)chroman-4-one (6m)



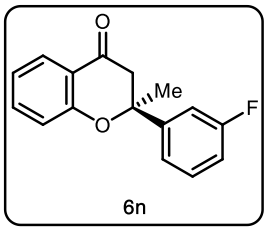
Purified by column chromatography (13:1 Hexane/EtOAc), 31% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.8, 1.7 Hz, 1H), 7.46-7.57 (m, 5H), 7.07 (d, J = 9.2 Hz, 1H), 6.94-6.98 (m, 1H), 3.29 (d, J = 16.4 Hz, 1H), 3.12 (d, J = 16.4 Hz, 1H), 1.75 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.2, 159.8, 147.2, 136.6, 130.1 (q, J = 32.7 Hz) 126.8, 125.8 (q, J = 3.8 Hz), 124.0 (q, J = 273.5 Hz), 121.6, 121.1, 118.4, 82.2, 48.0, 29.9; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.55; The data matched with previously reported literature.[3]

IR ν = 3669, 2963, 1693, 1607, 1462, 1410, 1326, 1236, 1168, 1122, 1080, 1016, 954, 893, 844, 766 cm^{-1}; $[\alpha]_D^{25}$ -8.3 (c 0.36, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 5.24, minor = 6.52, 99% ee.



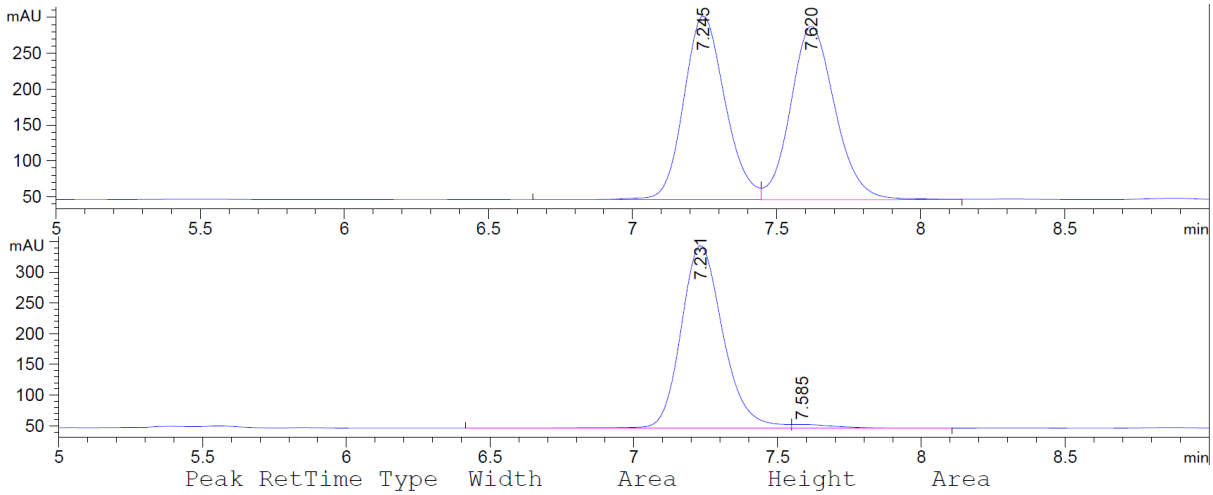
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.238	VB	0.1121	9395.54590	1304.03687	99.4564
2	6.521	VB	0.1439	51.35479	5.55069	0.5436

(*S*)-2-(3-fluorophenyl)-2-methylchroman-4-one (6n)



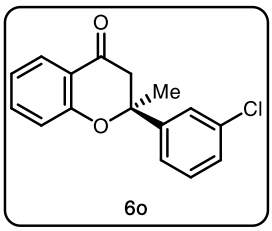
Purified by column chromatography (16:1 Hexane/EtOAc), 60% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.8, 1.7 Hz, 1H), 7.46-7.50 (m, 1H), 7.23-7.29 (m, 1H), 7.12-7.16 (m, 2H), 7.06 (dd, J = 8.4, 0.8 Hz, 1H), 6.89-6.97 (m, 2H), 3.25 (d, J = 16.8 Hz, 1H), 3.08 (d, J = 16.4 Hz, 1H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.4, 163.1 (d, J = 247.5 Hz), 159.8, 146.0 (d, J = 6.8 Hz), 136.5, 130.4 (d, J = 8.7 Hz), 126.8, 121.4, 121.1, 120.9 (d, J = 2.9 Hz), 118.4, 114.9 (d, J = 21.2 Hz), 112.7 (d, J = 23.1 Hz), 82.1, 48.1, 29.9; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -111.81;

IR ν = 2971, 1692, 1609, 1461, 1377, 1326, 1274, 1235, 1121, 1045, 954, 910, 879, 766, 700 cm^{-1}; HRMS (EI) calc'd for $C_{16}H_{13}FO_2$ $[M]^+$: 256.0900, found: 256.0894; $[\alpha]_D^{25}$ -3.5 (c 0.46, $CHCl_3$); HPLC Conditions: 8% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 7.23, minor = 7.59, 96% ee.



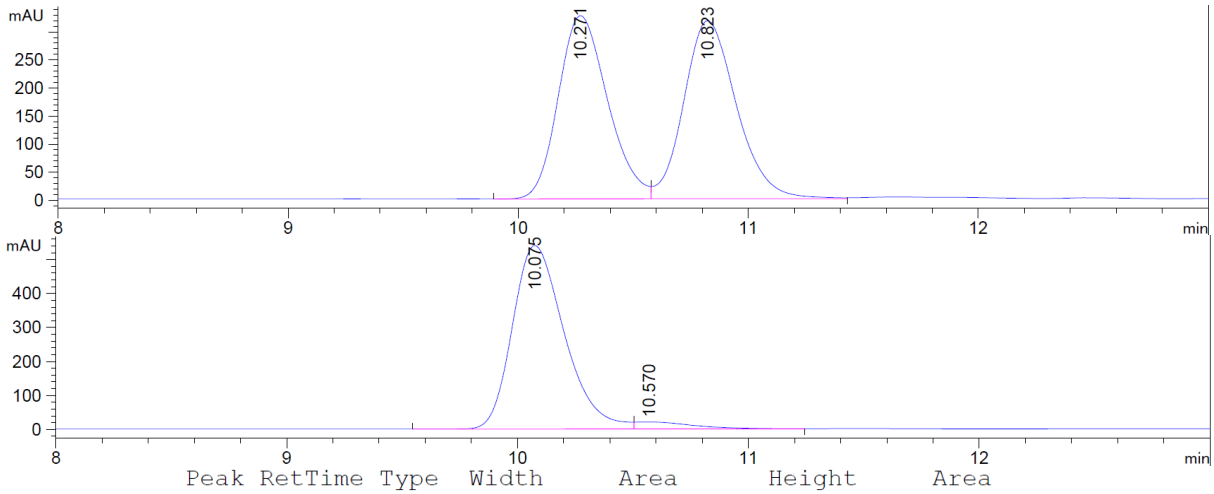
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.231	BV	0.1543	3023.58887	298.25348	97.7919
2	7.585	VV	0.1633	68.27254	6.06447	2.2081

(*S*)-2-(3-chlorophenyl)-2-methylchroman-4-one (6o)



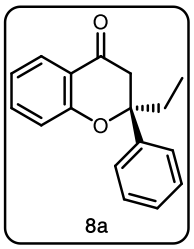
Purified by column chromatography (16:1 Hexane/EtOAc), 55% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.9, 1.7 Hz, 1H), 7.46-7.50 (m, 1H), 7.42 (t, J = 1.8 Hz, 1H), 7.18-7.28 (m, 3H), 7.06 (dd, J = 8.4, 0.6 Hz, 1H), 6.93-6.97 (m, 1H), 3.24 (d, J = 16.5 Hz, 1H), 3.07 (d, J = 16.5 Hz, 1H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.2, 159.8, 145.4, 136.5, 134.9, 130.0, 128.1, 126.8, 125.7, 123.4, 121.4, 121.0, 118.5, 82.1, 48.1, 29.7; The data matched with previously reported literature.[3]

IR ν = 3675, 2977, 1692, 1607, 1461, 1418, 1377, 1325, 1235, 1165, 1122, 1079, 1047, 954, 893, 765, 698 cm^{-1}; $[\alpha]_D^{25}$ +8.6 (c 0.89, $CHCl_3$); HPLC Conditions: 1% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 10.08, minor = 10.57, 92% ee.



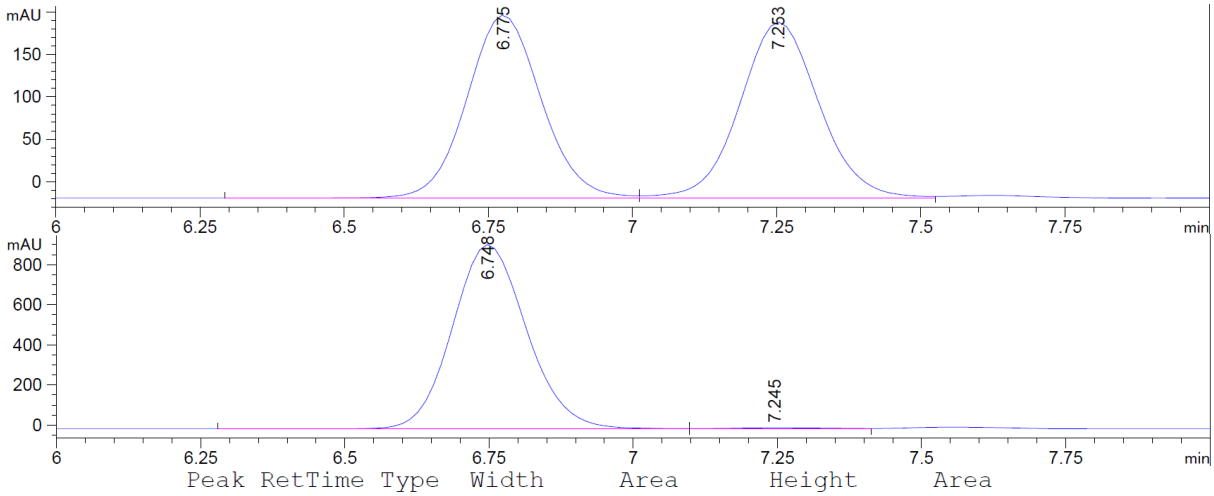
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.075	BV	0.2387	8466.64258	540.78540	95.8823
2	10.570	VV	0.2572	363.60144	20.67586	4.1177

(*S*)-2-ethyl-2-phenylchroman-4-one (8a)



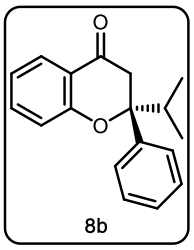
Purified by column chromatography (15:1 Hexane/EtOAc), 93% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.0, 1.5 Hz, 1H), 7.43-7.47 (m, 1H), 7.33-7.36 (m, 2H), 7.25-7.30 (m, 2H), 7.17-7.21 (m, 1H), 7.07 (dd, J = 8.4, 0.8 Hz, 1H), 6.88-6.92 (m, 1H), 3.26 (d, J = 16.4 Hz, 1H), 3.10 (d, J = 16.4 Hz, 1H), 1.97-2.13 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.9, 160.1, 141.3, 136.2, 128.5, 127.6, 126.6, 126.0, 121.4, 121.0, 118.4, 85.2, 46.2, 35.3, 8.0; The data matched with previously reported literature.[3]

IR ν = 2971, 1692, 1608, 1461, 1306, 1232, 1121, 1153, 1121, 1079, 1028, 957, 887, 760, 701 cm^{-1}; $[\alpha]_D^{25}$ +7.0 (c 1.01, $CHCl_3$); HPLC Conditions: 5% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 6.75, minor = 7.25, 98% ee.



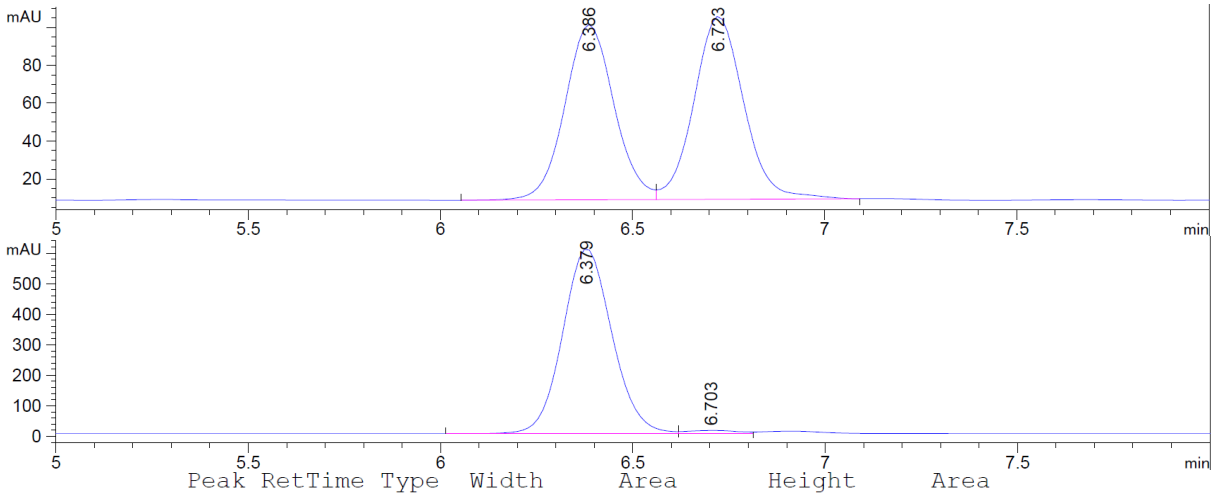
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.748	BV	0.1406	8241.70898	919.13916	99.1969
2	7.245	VV	0.2068	66.72200	5.03014	0.8031

(*R*)-2-isopropyl-2-phenylchroman-4-one (8b)



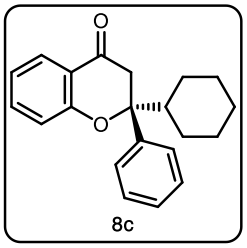
Purified by column chromatography (15:1 Hexane/EtOAc), 47% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.8, 1.7 Hz, 1H), 7.39-7.44 (m, 1H), 7.14-7.30 (m, 5H), 7.04 (dd, J = 8.4, 1.1 Hz, 1H), 6.83-6.87 (m, 1H), 3.28 (d, J = 16.4 Hz, 1H), 3.14 (d, J = 16.4 Hz, 1H), 2.21-2.31 (m, 1H), 1.04 (d, J = 6.9 Hz, 3H), 0.86 (d, J = 6.9 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.4, 160.3, 140.0, 136.1, 128.2, 127.7, 127.1, 126.5, 121.6, 120.9, 118.4, 87.6, 42.4, 39.0, 17.5, 17.0; The data matched with previously reported literature.[3]

IR ν = 2975, 1692, 1608, 1461, 1306, 1233, 1118, 1030, 980, 898, 841, 760, 703 cm^{-1}; $[\alpha]_D^{25}$ +71.1 (c 0.42, $CHCl_3$); HPLC Conditions: 5% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 6.38, minor = 6.70, 97% ee.



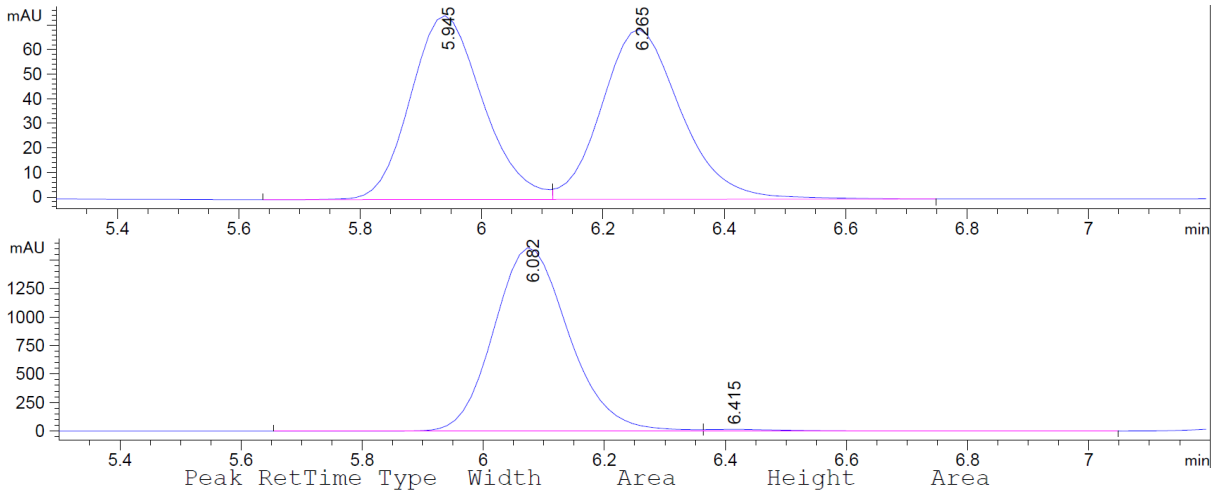
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.379	BV	0.1359	5397.03906	606.00732	98.2915
2	6.703	VV	0.1330	93.81014	10.42589	1.7085

(*R*)-2-cyclohexyl-2-phenylchroman-4-one (8c)



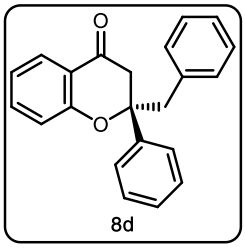
Purified by column chromatography (15:1 Hexane/EtOAc), 48% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.8, 1.7 Hz, 1H), 7.39-7.43 (m, 1H), 7.13-7.29 (m, 5H), 7.03 (dd, J = 8.4, 0.8 Hz, 1H), 6.82-6.86 (m, 1H), 3.28 (d, J = 16.4 Hz, 1H), 3.16 (d, J = 16.4 Hz, 1H), 0.89-1.98 (m, 12H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.5, 160.3, 140.3, 136.0, 128.2, 127.6, 127.1, 126.5, 121.6, 120.8, 118.3, 87.5, 49.1, 42.9, 27.6, 27.0, 26.5, 26.5, 26.4; The data matched with previously reported literature.[3]

IR ν = 3665, 2972, 2928, 1692, 1609, 1461, 1407, 1307, 1228, 1056, 902, 879, 842, 819, 760, 705 cm^{-1}; $[\alpha]_D^{25}$ +43.5 (c 0.53, $CHCl_3$); HPLC Conditions: 1% MeOH/ Hexanes, 0.9 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 6.08, minor = 6.41, 98% ee.



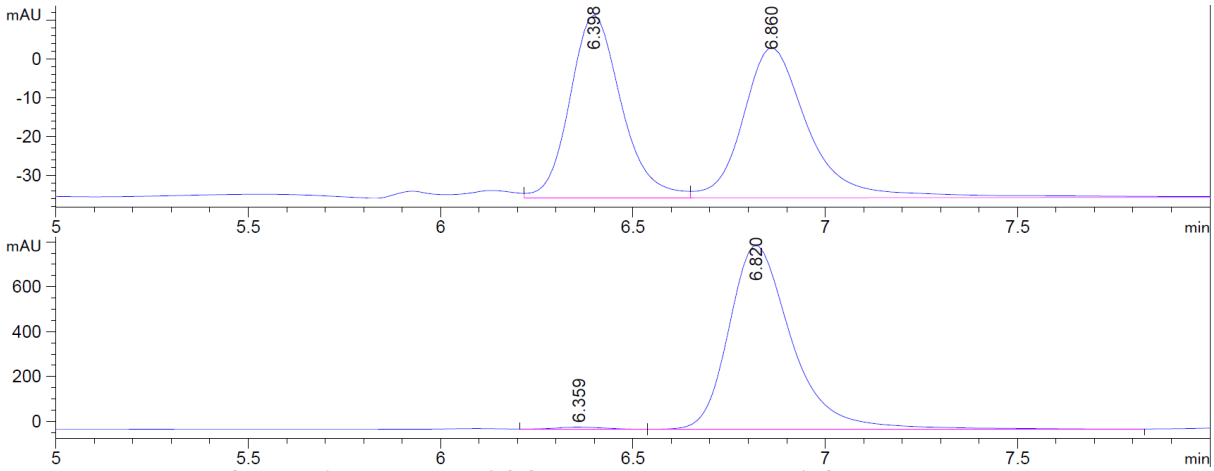
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.082	BV	0.1363	1.38396e4	1610.42395	98.8650
2	6.415	VV	0.1566	158.88559	14.41769	1.1350

(*S*)-2-benzyl-2-phenylchroman-4-one (8d)



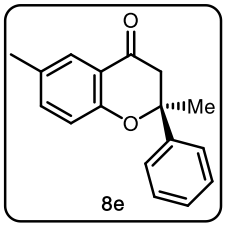
Purified by column chromatography (13:1 Hexane/EtOAc), 52% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.6, 1.5 Hz, 1H), 7.45 (ddd, J = 8.8, 6.9, 1.5 Hz, 1H), 7.17-7.28 (m, 8H), 7.09 (dd, J = 8.4, 0.8 Hz, 1H), 6.97-7.02 (m, 2H), 6.89 (td, J = 7.5, 0.9 Hz, 1H), 3.36 (d, J = 13.7 Hz, 1H), 3.24 (d, J = 16.4 Hz, 1H), 3.17 (d, J = 13.7 Hz, 1H), 3.08 (d, J = 16.4 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.8, 160.0, 141.2, 136.2, 135.3, 130.9, 128.5, 128.1, 127.9, 127.0, 126.6, 126.3, 121.5, 121.2, 118.5, 84.9, 49.7, 45.3;

IR ν = 3061, 3031, 2922, 2851, 1692, 1605, 1462, 1307, 1231, 1122, 1031, 996, 911, 768, 701 cm^{-1}; HRMS (FAB) calc'd for $C_{22}H_{18}O_2$ $[M+1]^+$: 315.1380, found: 315.1397; $[\alpha]_D^{25}$ +36.5 (c 0.20, $CHCl_3$); HPLC Conditions: 3% MeOH/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 6.82, minor = 6.36, 98% ee.



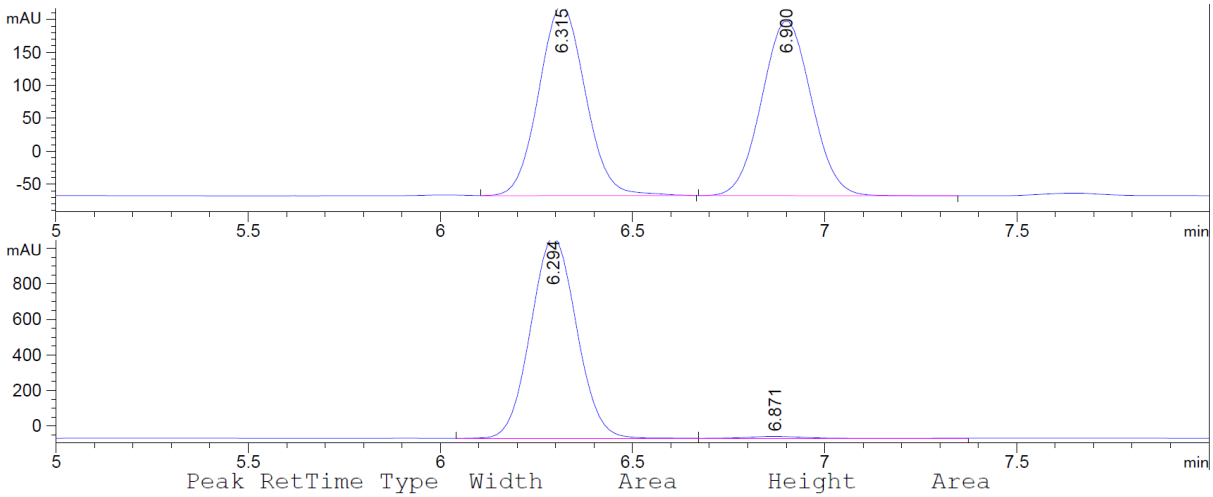
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.359	VV	0.1480	95.60377	9.96174	1.0058
2	6.820	VV	0.1737	9410.04590	821.19696	98.9942

(*S*)-2,6-dimethyl-2-phenylchroman-4-one (8e)



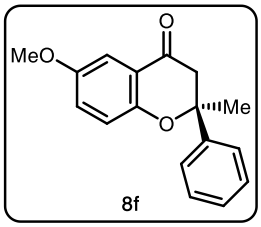
Purified by column chromatography (13:1 Hexane/EtOAc), 89% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 1.9 Hz, 1H), 7.39-7.42 (m, 2H), 7.25-7.30 (m, 3H), 7.18-7.22 (m, 1H), 6.96 (d, J = 8.4 Hz, 1H), 3.29 (d, J = 16.8 Hz, 1H), 3.06 (d, J = 16.4 Hz, 1H), 2.22 (s, 3H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.0, 158.1, 143.1, 137.3, 130.5, 128.6, 127.7, 126.3, 125.3, 120.7, 118.2, 82.3, 48.1, 30.1, 20.4;

IR ν = 3663, 2975, 1689, 1618, 1488, 1423, 1292, 1236, 1193, 1132, 953, 825, 762, 701 cm^{-1}; HRMS (EI) calc'd for $C_{17}H_{16}O_2$ $[M+1]^+$: 252.1150, found: 252.1150; $[\alpha]_D^{25}$ +24.8 (c 0.99, $CHCl_3$); HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 6.29, minor = 6.87, 98% ee.



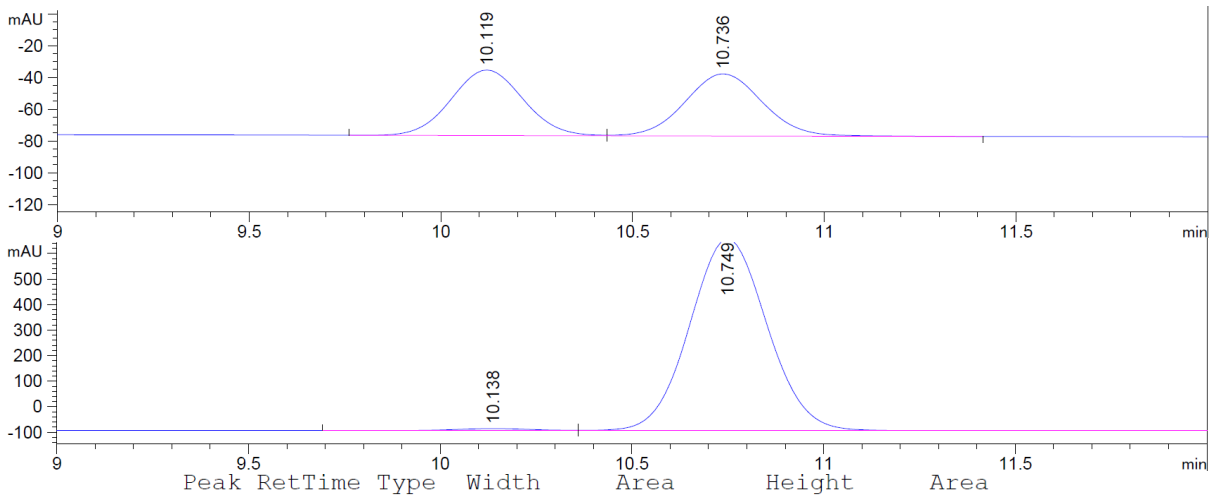
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.294	BV	0.1323	9368.90332	1135.57849	98.9476
2	6.871	VB	0.1441	99.65145	10.75034	1.0524

(*S*)-6-methoxy-2-methyl-2-phenylchroman-4-one (8f)



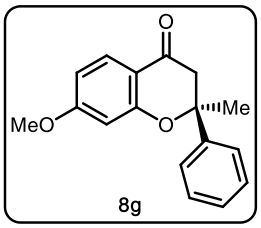
Purified by column chromatography (10:1 Hexane/EtOAc), 88% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.40 (m, 2H), 7.17-7.30 (m, 4H), 7.06 (dd, J = 9.0, 3.2 Hz, 1H), 6.98 (d, J = 9.2 Hz, 1H), 3.71 (s, 3H), 3.30 (d, J = 16.4 Hz, 1H), 3.07 (d, J = 16.4 Hz, 1H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.8, 154.7, 153.8, 143.1, 128.6, 127.7, 125.4, 125.3, 120.9, 119.7, 107.1, 82.4, 55.7, 47.9, 30.2; The data matched with previously reported literature.[3]

IR ν = 3669, 2965, 1688, 1619, 1487, 1431, 1284, 1220, 1174, 1123, 1072, 1032, 955, 878, 829, 766, 01 cm^{-1}; $[\alpha]_D^{25}$ +39.5 (c 1.09, $CHCl_3$); HPLC Conditions: 5% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ = 220 nm, t_R (min): major = 10.75, minor = 10.14, 98% ee.



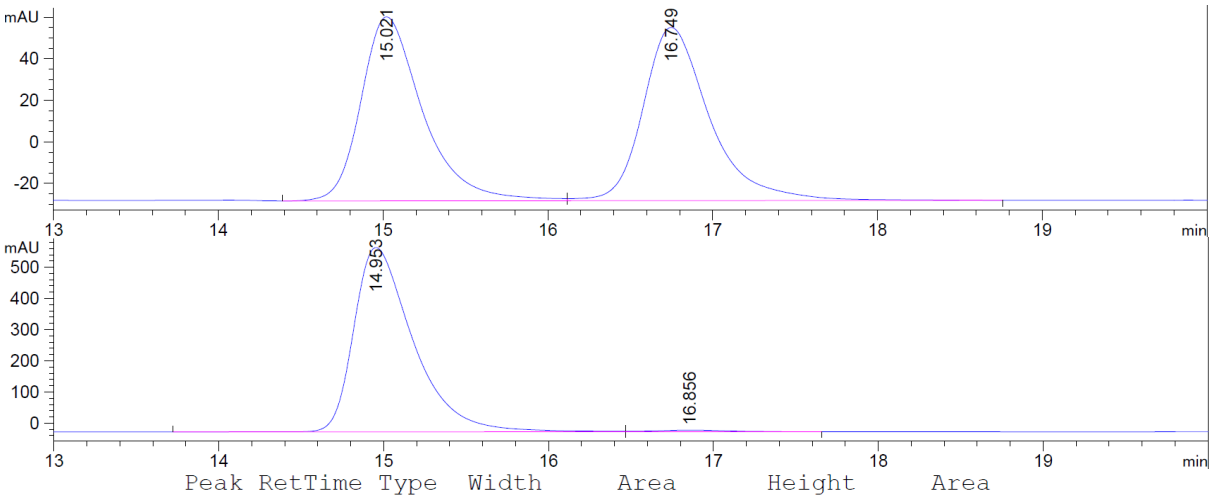
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.138	BV	0.2066	94.76254	7.15093	0.8939
2	10.749	VB	0.2193	1.05060e4	750.62079	99.1061

(*S*)-7-methoxy-2-methyl-2-phenylchroman-4-one (8g)



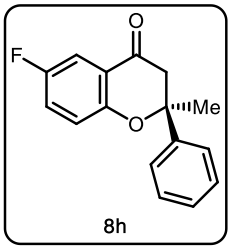
Purified by column chromatography (10:1 Hexane/EtOAc), 92% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.8 Hz, 1H), 7.40 (dt, J = 7.9, 1.9 Hz, 2H), 7.25-7.30 (m, 2H), 7.18-7.23 (m, 1H), 6.52-6.45 (2H), 3.81 (s, 3H), 3.24 (d, J = 16.8 Hz, 1H), 3.02 (d, J = 16.8 Hz, 1H), 1.73 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 190.3, 166.3, 162.0, 143.2, 128.6, 128.4, 127.7, 125.1, 115.0, 109.4, 101.5, 82.9, 55.6, 47.8, 29.9;

IR ν = 3676, 2977, 2896, 1681, 1607, 1495, 1439, 1311, 1264, 1204, 1159, 1136, 1020, 980, 943, 839, 762, 702 cm^{-1}; HRMS (EI) calc'd for $C_{17}H_{16}O_3$ $[M]^+$: 268.1099, found: 268.1094; $[\alpha]_D^{25}$ -95.4 (c 0.99, $CHCl_3$); HPLC Conditions: 5% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 14.95, minor = 16.86, 98% ee.



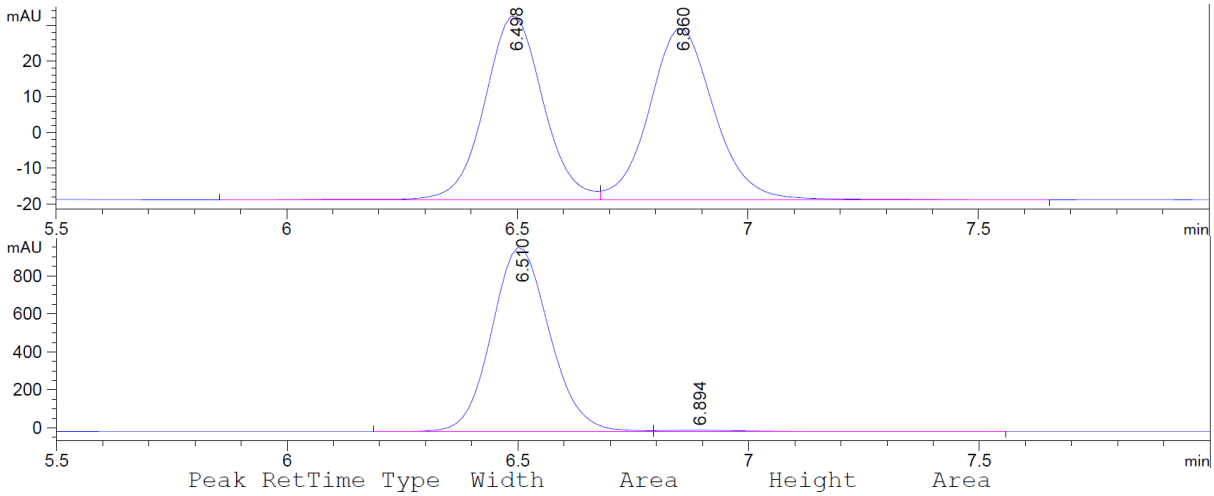
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.953	BV	0.3763	1.48200e4	591.54187	98.8146
2	16.856	VB	0.4703	177.78194	5.66182	1.1854

(*S*)-6-fluoro-2-methyl-2-phenylchroman-4-one (8h)



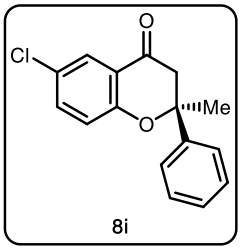
Purified by column chromatography (13:1 Hexane/EtOAc), 74% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.41 (m, 3H), 7.14-7.31 (m, 4H), 7.02 (q, J = 4.5 Hz, 1H), 3.32 (d, J = 16.8 Hz, 1H), 3.07 (d, J = 16.4 Hz, 1H), 1.74 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.0, 157.0 (d, J = 243.7 Hz), 156.3 (d, J = 1.9 Hz), 142.6, 128.8, 127.9, 125.3, 123.7 (d, J = 24.0 Hz), 121.5 (d, J = 6.8 Hz), 120.0 (d, J = 7.8 Hz), 111.8 (d, J = 23.1 Hz), 82.8, 47.7, 30.1; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -121.77;

IR ν = 2982, 2901, 1694, 1620, 1481, 1436, 1378, 1309, 1266, 1170, 1117, 1067, 955, 879, 828, 765, 701 cm^{-1}; HRMS (EI) calc'd for $C_{16}H_{13}FO_2$ $[M]^+$: 256.0900, found: 256.0901; $[\alpha]_D^{25}$ +14.5 (c 1.00, $CHCl_3$); HPLC Conditions: 5% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 6.51, minor = 6.89, 98% ee.



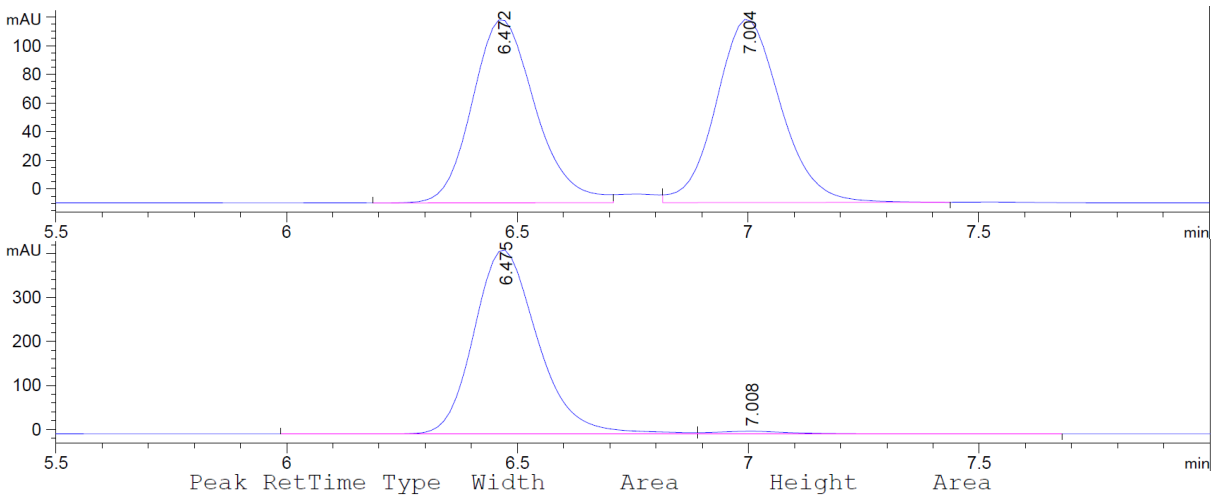
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.510	BV	0.1338	8470.74609	970.72095	98.8320
2	6.894	VB	0.2066	100.10647	7.36196	1.1680

(*S*)-6-chloro-2-methyl-2-phenylchroman-4-one (8i)



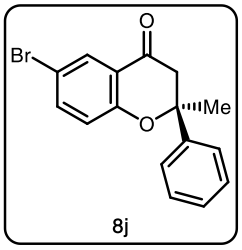
Purified by column chromatography (13:1 Hexane/EtOAc), 90% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 2.7 Hz, 1H), 7.35-7.39 (m, 3H), 7.20-7.31 (m, 3H), 7.01 (d, J = 8.8 Hz, 1H), 3.32 (d, J = 16.8 Hz, 1H), 3.07 (d, J = 16.4 Hz, 1H), 1.75 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 190.6, 158.5, 142.5, 136.0, 128.8, 128.0, 126.6, 126.1, 125.3, 121.9, 120.2, 83.0, 47.7, 30.1;

IR ν = 3675, 2976, 2901, 1696, 1603, 1469, 1422, 1267, 1229, 1177, 1131, 1068, 954, 897, 826, 763, 701 cm^{-1}; HRMS (EI) calc'd for $C_{16}H_{13}ClO_2$ $[M]^+$: 272.0604, found: 272.0604; $[\alpha]_D^{25}$ +37.7 (c 0.93, $CHCl_3$); HPLC Conditions: 5% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 6.48, minor = 7.01, 96% ee.



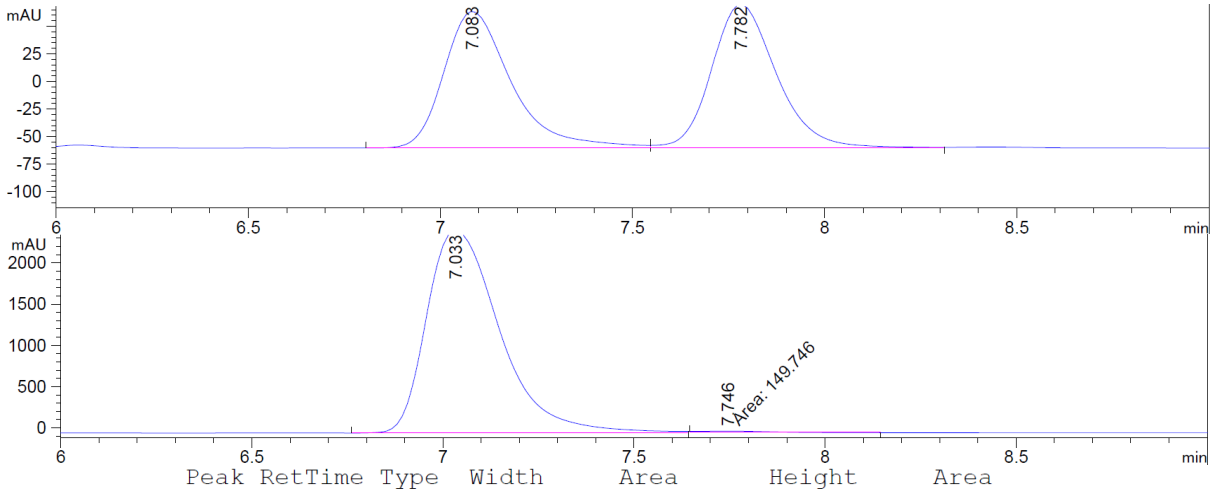
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.475	BV	0.1441	4028.67773	419.24066	98.0113
2	7.008	VB	0.1901	81.74281	6.19049	1.9887

(*S*)-6-bromo-2-methyl-2-phenylchroman-4-one (8j)



Purified by column chromatography (13:1 Hexane/EtOAc), 64% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 2.7 Hz, 1H), 7.52 (dd, J = 8.8, 2.3 Hz, 1H), 7.35-7.38 (m, 2H), 7.26-7.31 (m, 2H), 7.20-7.25 (m, 1H), 6.95 (d, J = 8.8 Hz, 1H), 3.31 (d, J = 16.8 Hz, 1H), 3.07 (d, J = 16.4 Hz, 1H), 1.74 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 190.5, 159.0, 142.4, 138.8, 129.2, 128.8, 128.0, 125.3, 122.4, 120.5, 113.8, 83.0, 47.7, 30.2;

IR ν = 3673, 2975, 2901, 1696, 1598, 1467, 1416, 1266, 1230, 1176, 1133, 1079, 1045, 954, 897, 825, 762, 700 cm^{-1}; HRMS (EI) calc'd for $C_{16}H_{13}BrO_2$ $[M]^+$: 316.0099, found: 316.0092; $[\alpha]_D^{25}$ +33.3 (c 0.63, $CHCl_3$); HPLC Conditions: 5% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak ID column, λ = 220 nm, t_R (min): major = 7.03, minor = 7.75, 99% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.033	BV	0.2073	3.26682e4	2454.45483	99.5437
2	7.746	MM	0.1763	149.74600	14.16015	0.4563

5. References

1. D. Zhao, B. Beiring, F. Glorius, *Angew. Chem. Int. Ed.* 2013, **52**, 8454.
2. J. L. Vicario, D. Badia, L. Carrillo, *Arkivoc*, 2007, 304.
3. A. L. Gerten, L. M. Stanley, *Tetrahedron Lett.* 2016, **57**, 5460.

6. X-Ray Analysis for Compound 6e and [(*S*)-3d]$PdCl_2$

An X-Ray quality single crystal of compound **6e** was obtained by slow recrystallization from hexane solution (76 mg/700 μL) at 25 ℃. Weak argon blowing helps to make seed in the solution. An X-ray quality single crystal of **[(*S*)-3d]$PdCl_2$** was obtained by following recrystallization method. To a solution of **[(*S*)-3d]$PdCl_2$** (50 mg) in DCM (0.1 mL), diethyl ether (10 mL) was added slowly to make bilayer system. Reflection data for **6e** and **[(*S*)-3d]$PdCl_2$** were collected on a Bruker APEX-II CCD-based diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å).

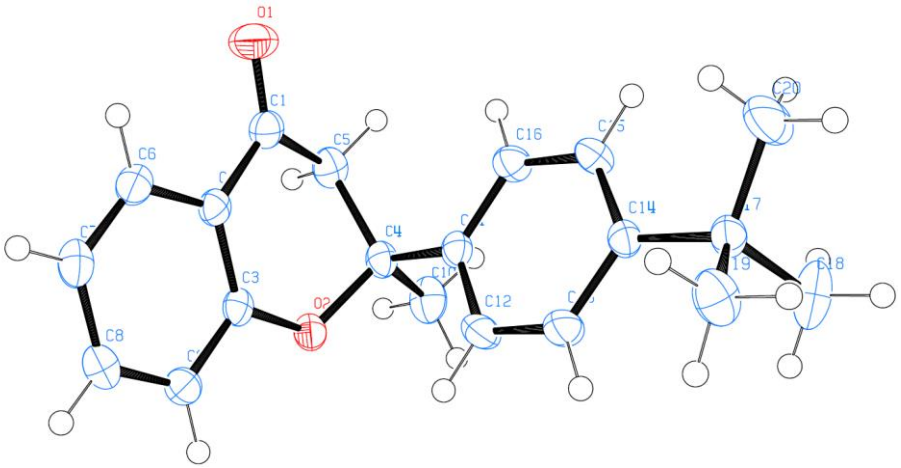


Figure S1. X-Ray Coordinate of Compound 6e

Table S1. X-Ray Crystal Data and Structure Refinement for Compound 6e

Identification code	**6e**	
CCDC number	1954885	
Empirical formula	C20 H22 O2	
Formula weight	294. 37	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system Triclinic	Monoclinic	
Space group	C2	
Unit cell dimensions	a=23.2747(4) Å	α = 90°
	b=6.77810(10) Å	β = 91.9349(17)°
	c=10.2443(2) Å	γ = 90°
Volume	1615.20(5) $Å^3$	
Z	4	
Density (calculated)	1.211 mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	632	
Theta range for data collection	2.61° to 25.42°	
Index ranges	-28≤h≤28, -8≤k≤8, -12≤l≤12	
Reflections collected	12536	
Independent reflections	2965 [R(int)=0.0180]	
Completeness to theta =	99.4%	
Data / restraints / parameters	2965/1/203	
Goodness-of-fit on F^2	1.043	
Final R indices [I > 2σ((I)]	R1 = 0.0306, wR2 = 0.0793[2880]	
R indices (all data)	R1 =0.0315, wR2 = 0.0802	
Absolute structure parameter	0.0(2)	
Largest diff. peak and hole	0.147 and -0.182 e·$Å^{-3}$	

Table S2. Bond lengths[Å] and angles[°] for compound 6e

O1-C1	1.216(2)
O2-C3	1.367(2)
O2-C4	1.457(2)
C1-C2	1.475(3)
C1-C5	1.506(3)
C2-C3	1.400(2)
C2-C6	1.401(3)
C3-C9	1.389(3)
C4-C10	1.524(2)
C4-C5	1.526(3)
C4-C11	1.530(2)
C6-C7	1.377(3)
C7-C8	1.393(3)
C8-C9	1.386(3)
C11-C16	1.386(2)
C11-C12	1.387(3)
C12-C13	1.388(3)
C13-C14	1.390(3)
C14-C15	1.387(3)
C14-C17	1.538(2)
C15-C16	1.389(3)
C17-C20	1.519(3)
C17-C19	1.530(3)
C17-C18	1.537(3)
C3-O2-C4	116.87(12)
O1-C1-C2	123.18(18)
O1-C1-C5	122.50(18)
C2-C1-C5	114.26(16)
C3-C2-C6	118.66(17)
C3-C2-C1	119.77(16)
C6-C2-C1	121.46(16)
O2-C3-C9	116.42(15)

O2-C3-C2	122.90(16)
C9-C3-C2	120.66(16)
O2-C4-C10	103.81(14)
O2-C4-C5	108.49(13)
C10-C4-C5	111.36(16)
O2-C4-C11	109.21(14)
C10-C4-C11	109.83(14)
C5-C4-C11	113.65(14)
C1-C5-C4	111.86(16)
C7-C6-C2	121.02(17)
C6-C7-C8	119.38(17)
C9-C8-C7	120.88(18)
C8-C9-C3	119.38(16)
C16-C11-C12	117.40(16)
C16-C11-C4	121.96(16)
C12-C11-C4	120.39(16)
C11-C12-C13	120.96(18)
C12-C13-C14	122.04(19)
C15-C14-C13	116.52(17)
C15-C14-C17	122.14(15)
C13-C14-C17	121.21(17)
C14-C15-C16	121.74(16)
C11-C16-C15	121.31(17)
C20-C17-C19	108.34(18)
C20-C17-C18	109.30(18)
C19-C17-C18	108.22(17)
C20-C17-C14	112.37(16)
C19-C17-C14	111.19(15)
C18-C17-C14	107.32(15)

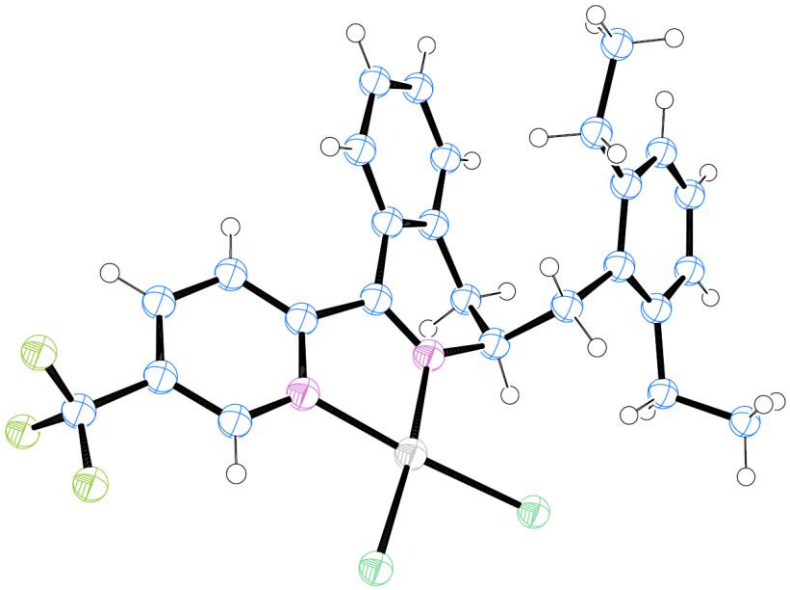


Figure S2. X-Ray Coordinate of [(*S*)-3d]$PdCl_2$

Table S3. X-ray crystal data and structure refinement for [(*S*)-3d]$PdCl_2$

Identification code	**[(S)-3d]$PdCl_2$**	
CCDC number	1843946	
Empirical formula	C27 H27 Cl4 F3 N2 Pd	
Formula weight	684.71	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system Triclinic	Orthohombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a=7.3222(2) Å	α = 90°
	b=16.3645(5) Å	β = 90°
	c=22.9119(6) Å	γ = 90°
Volume	2745.40(13) $Å^3$	
Z	4	
Density (calculated)	1.657 mg/m^3	
Absorption coefficient	1.104 mm^{-1}	
F(000)	1272	
Theta range for data collection	2.17° to 19.77°	
Index ranges	-8≤h≤8, -19≤k≤19, -27≤l≤27	
Reflections collected	37246	
Independent reflections	5004 [R(int)=0.0716]	
Completeness to theta =	99.7%	
Data / restraints / parameters	5004/0/336	
Goodness-of-fit on F^2	0.996	
Final R indices [I > 2σ((I)]	R1 = 0.0441, wR2 = 0.0932[3907]	
R indices (all data)	R1 =0.0676, wR2 = 0.1018	
Absolute structure parameter	-0.04(2)	
Largest diff. peak and hole	0.689 and -0.472 e·$Å^{-3}$	

Table S4. Bond lengths[Å] and angles[°] for [(*S*)-3d]$PdCl_2$

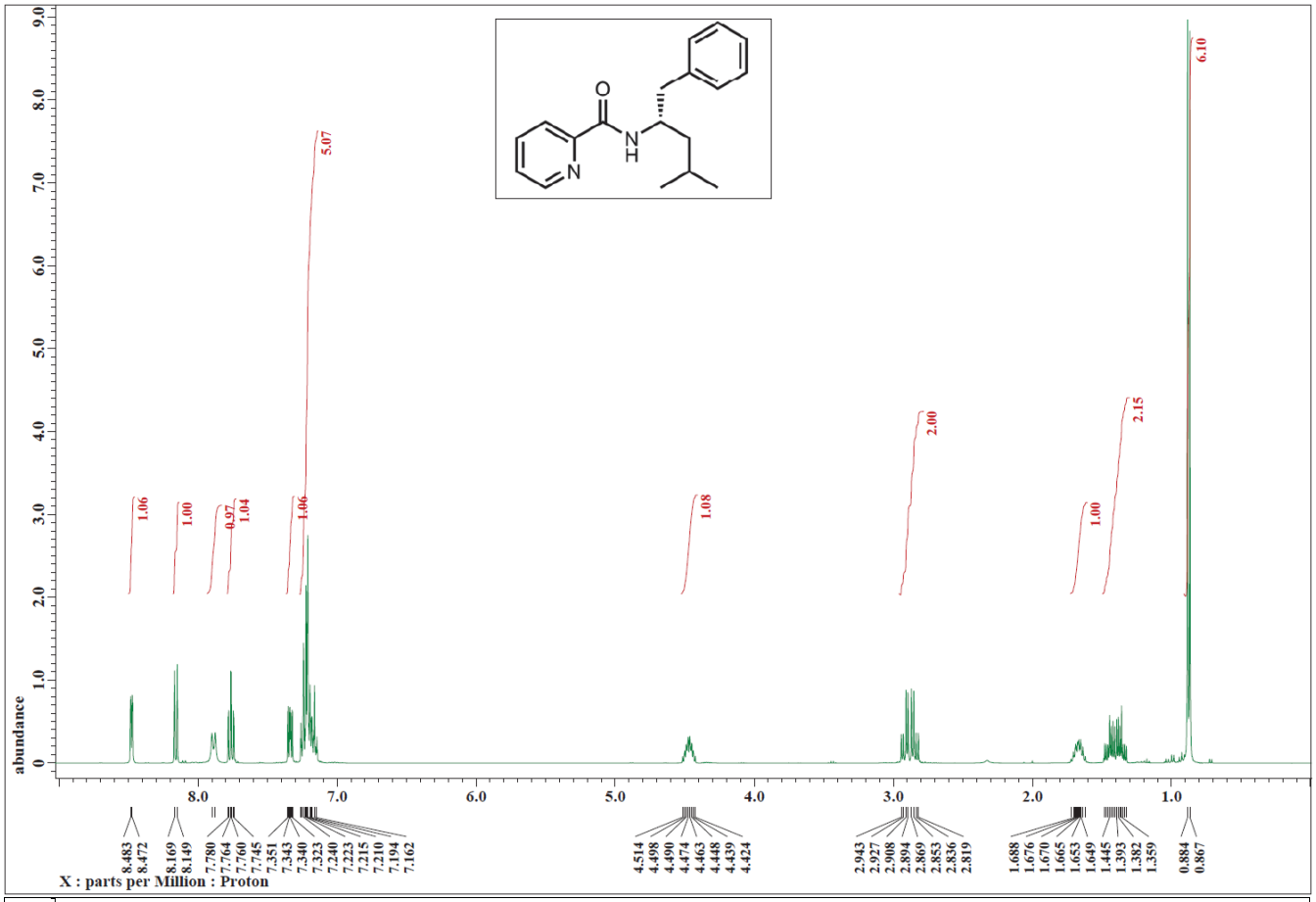
Pd1-N2	2.017(5)
Pd1-N1	2.024(6)
Pd1-Cl2	2.2800(18)
Pd1-Cl1	2.2870(17)
N1-C5	1.313(9)
N1-C1	1.361(8)
N2-C7	1.301(9)
N2-C11	1.479(9)
C12-C13	1.387(10)
C12-C8	1.398(10)
C15-C9	1.381(9)
C15-C14	1.395(10)
C14-C13	1.394(10)
C7-C1	1.474(9)
C7-C8	1.475(9)
C8-C9	1.403(10)
C9-C10	1.492(10)
C1-C2	1.379(10)
C11-C10	1.515(10)
C11-C16	1.562(10)
C17-C22	1.385(11)
C17-C18	1.418(11)
C17-C16	1.524(9)
C22-C21	1.410(10)
C22-C25	1.503(11)
C21-C20	1.371(12)
C19-C20	1.360(12)
C19-C18	1.398(11)
C18-C23	1.518(11)
C4-C5	1.373(10)
C4-C3	1.375(10)
C4-C6	1.498(10)

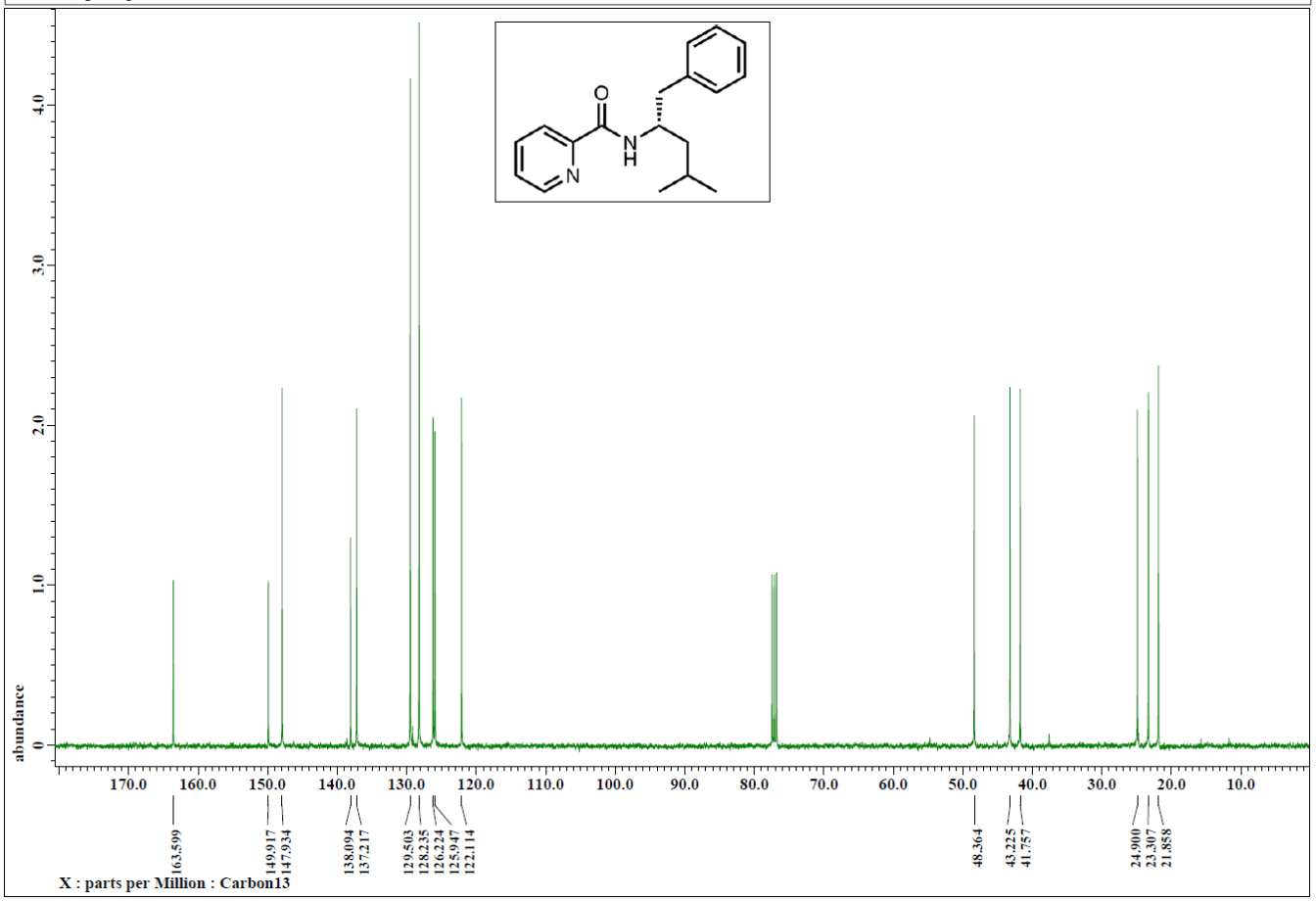
C3-C2	1.384(10)
C26-C25	1.527(11)
C24-C23	1.515(11)
C6-F1	1.334(10)
C6-F3	1.335(8)
C6-F2	1.342(10)
Cl3-C27	1.723(13)
Cl4-C27	1.765(12)
N2-Pd1-N1	80.1(2)
N2-Pd1-Cl2	95.34(17)
N1-Pd1-Cl2	175.41(18)
N2-Pd1-Cl1	174.39(16)
N1-Pd1-Cl1	94.30(16)
Cl2-Pd1-Cl1	90.27(8)
C5-N1-C1	119.0(6)
C5-N1-Pd1	127.2(5)
C1-N1-Pd1	113.7(5)
C7-N2-C11	118.2(5)
C7-N2-Pd1	115.3(5)
C11-N2-Pd1	126.5(4)
C13-C12-C8	119.9(7)
C9-C15-C14	121.2(7)
C13-C14-C15	119.4(7)
N2-C7-C1	115.5(6)
N2-C7-C8	121.9(6)
C1-C7-C8	122.6(6)
C12-C8-C9	120.2(6)
C12-C8-C7	122.9(7)
C9-C8-C7	116.6(6)
C15-C9-C8	118.9(7)
C15-C9-C10	124.7(7)
C8-C9-C10	116.3(6)
C12-C13-C14	120.1(7)

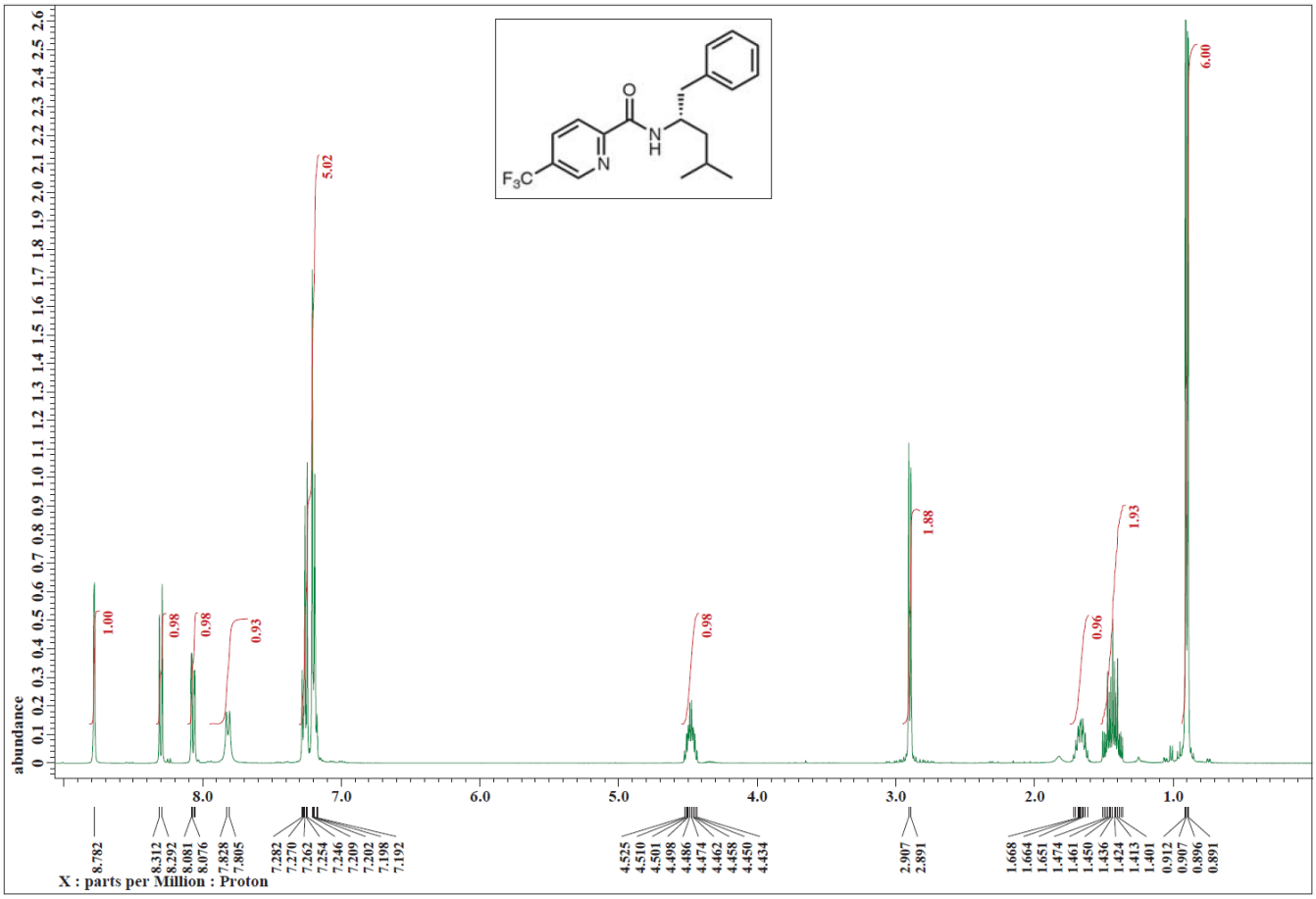
N1-C1-C2	120.9(6)
N1-C1-C7	114.4(6)
C2-C1-C7	124.4(6)
N2-C11-C10	109.8(6)
N2-C11-C16	109.5(6)
C10-C11-C16	114.7(6)
C9-C10-C11	109.8(6)
C22-C17-C18	119.4(7)
C22-C17-C16	121.2(7)
C18-C17-C16	119.4(7)
C17-C16-C11	111.9(6)
C17-C22-C21	119.3(8)
C17-C22-C25	123.3(7)
C21-C22-C25	117.4(8)
C20-C21-C22	121.3(8)
C20-C19-C18	122.7(9)
C19-C18-C17	118.0(7)
C19-C18-C23	121.4(8)
C17-C18-C23	120.6(7)
C19-C20-C21	118.8(9)
C5-C4-C3	119.1(7)
C5-C4-C6	121.6(6)
C3-C4-C6	119.3(7)
C4-C3-C2	118.8(7)
C1-C2-C3	119.2(7)
N1-C5-C4	122.9(7)
C24-C23-C18	116.8(8)
C22-C25-C26	112.6(7)
F1-C6-F3	107.0(7)
F1-C6-F2	106.8(6)
F3-C6-F2	105.9(7)
F1-C6-C4	111.8(7)
F3-C6-C4	112.5(7)

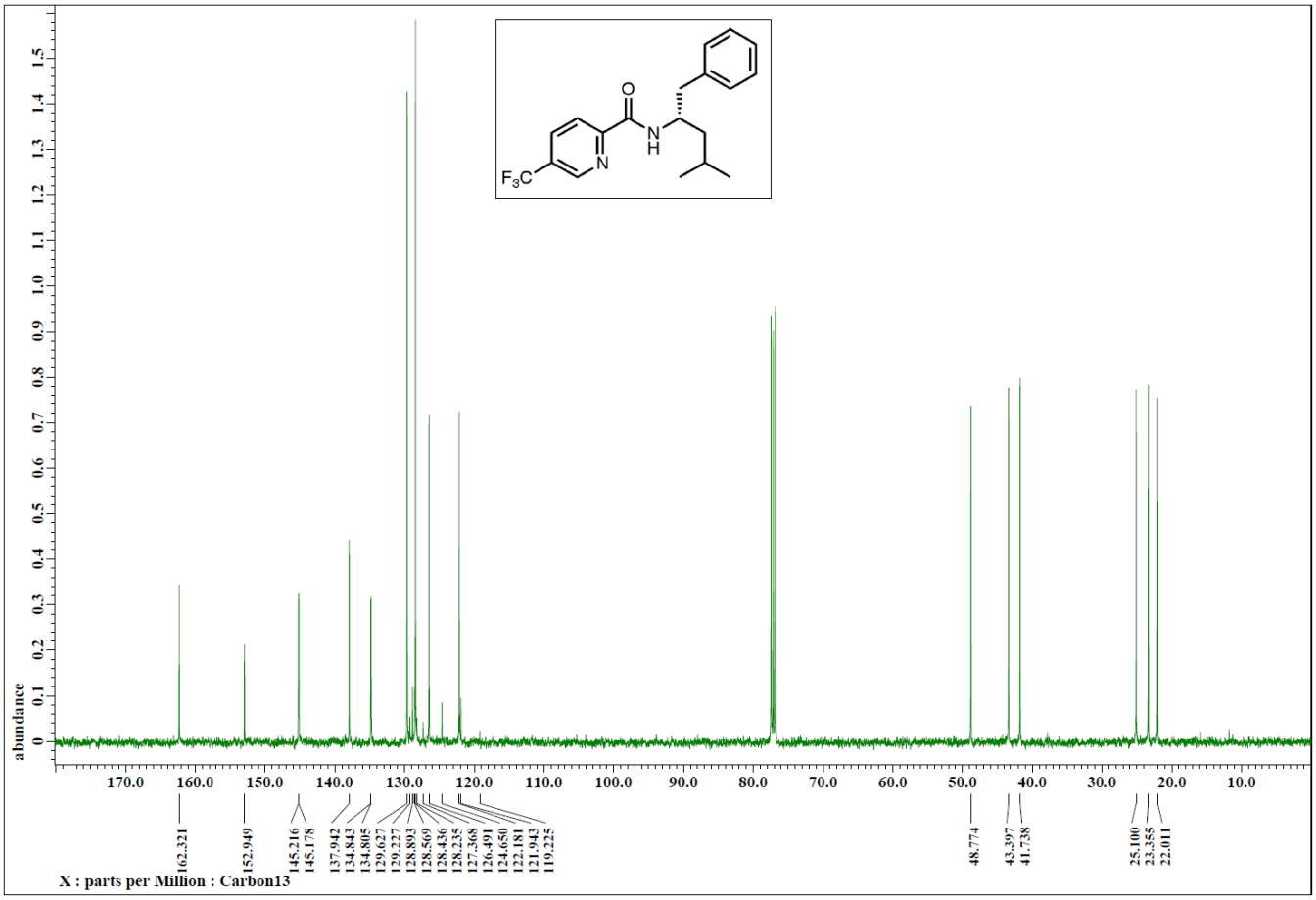
F2-C6-C4	112.4(7)
Cl3-C27-Cl4	112.4(5)

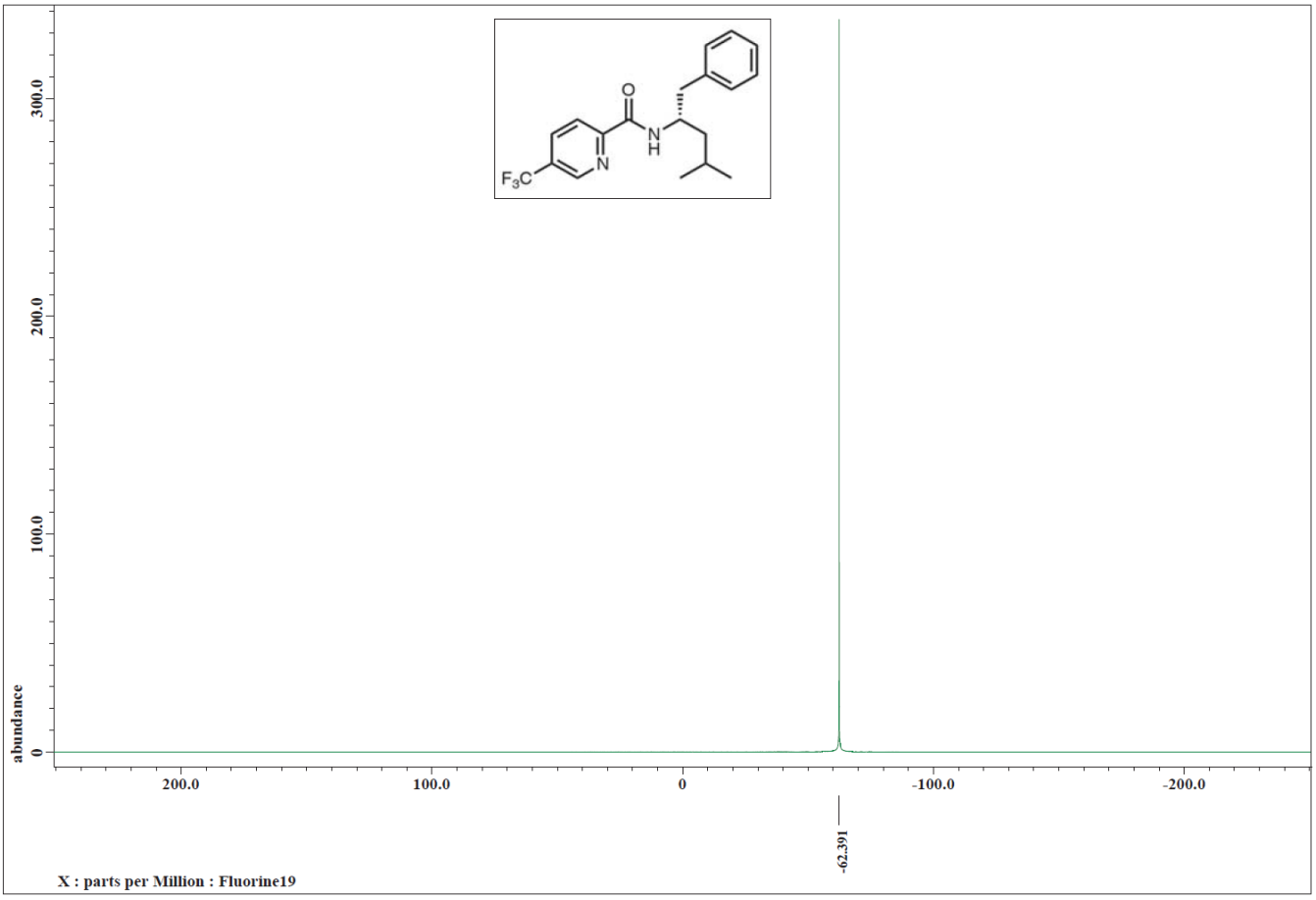
7. NMR Spectra for Compounds

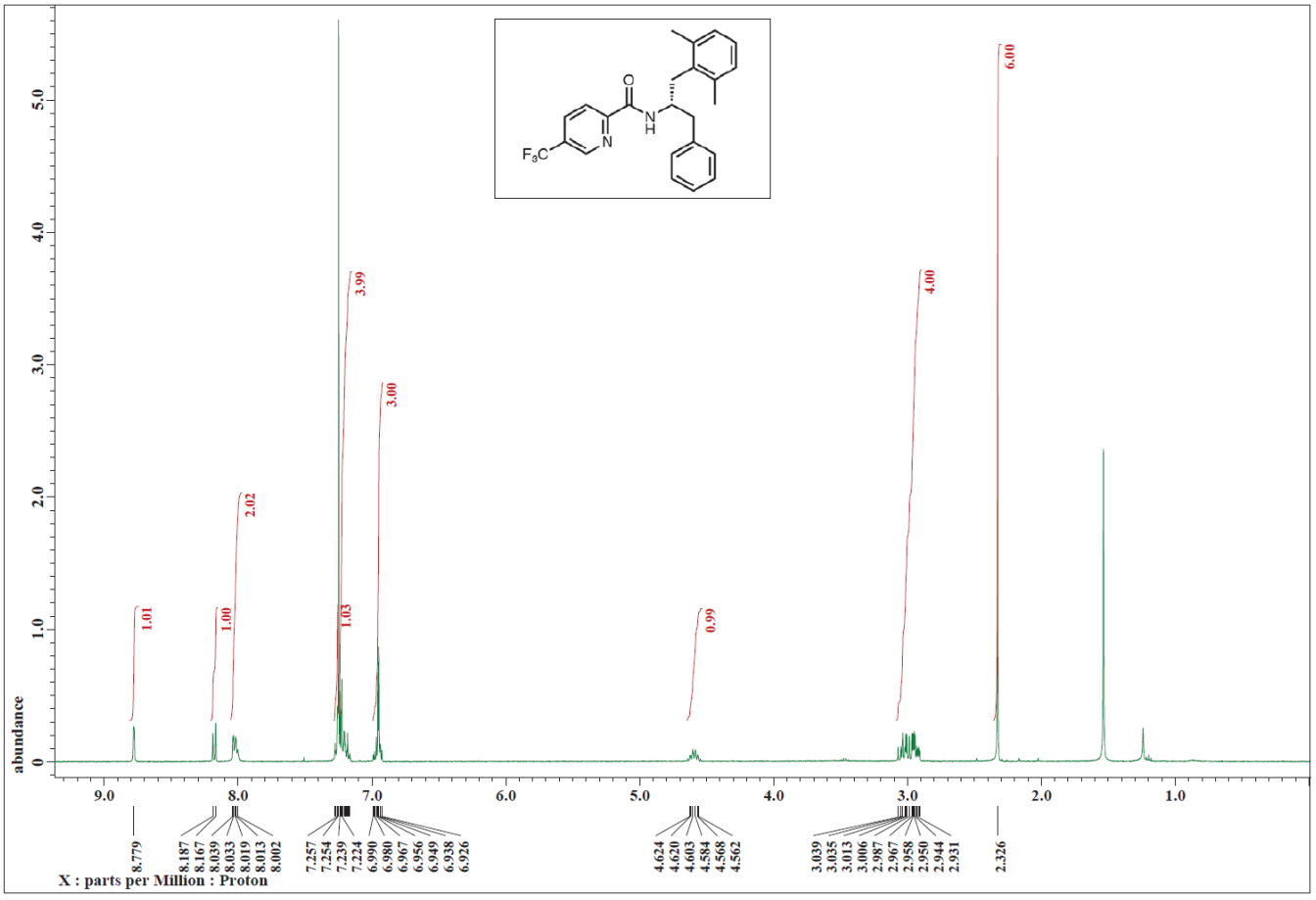


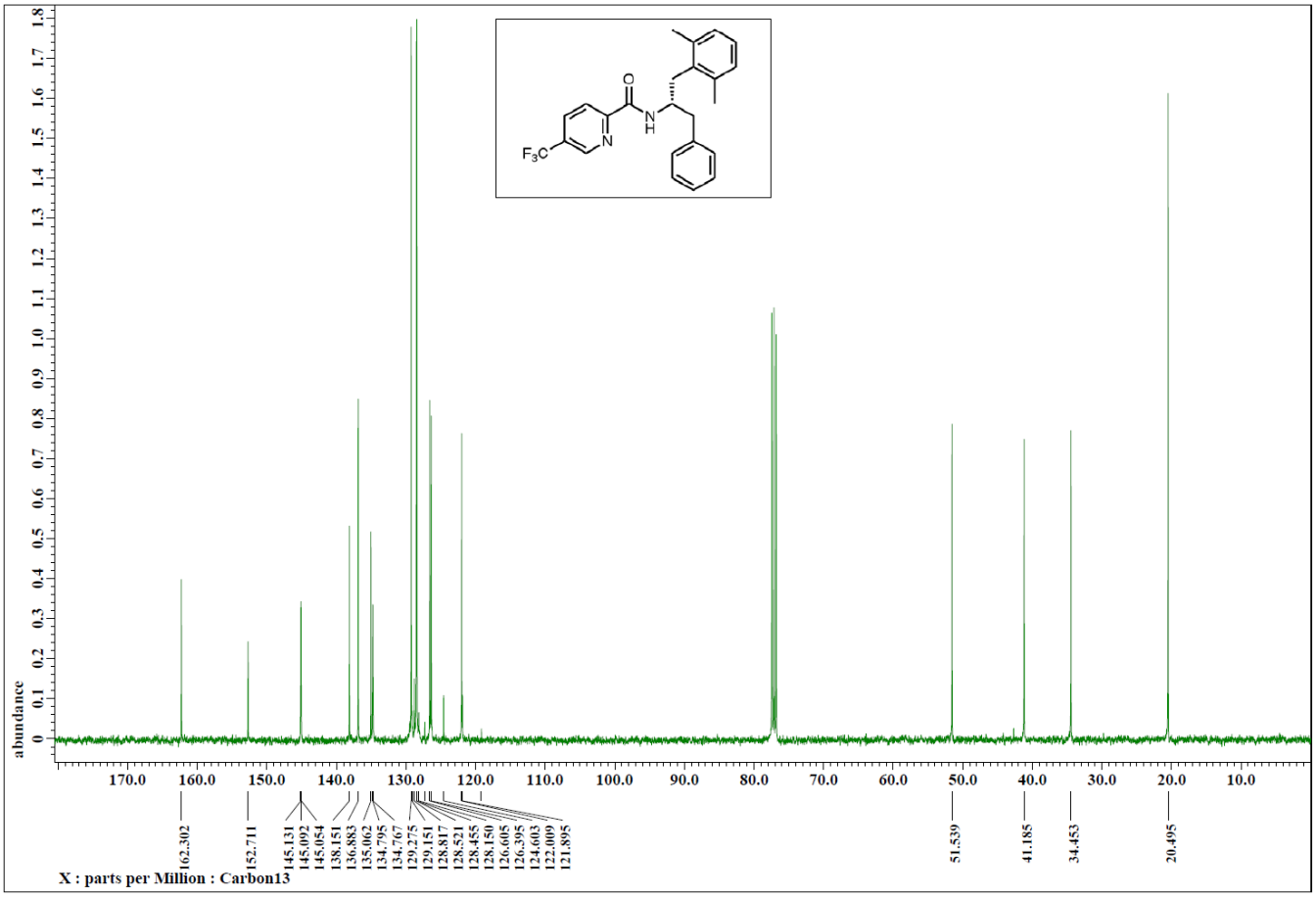


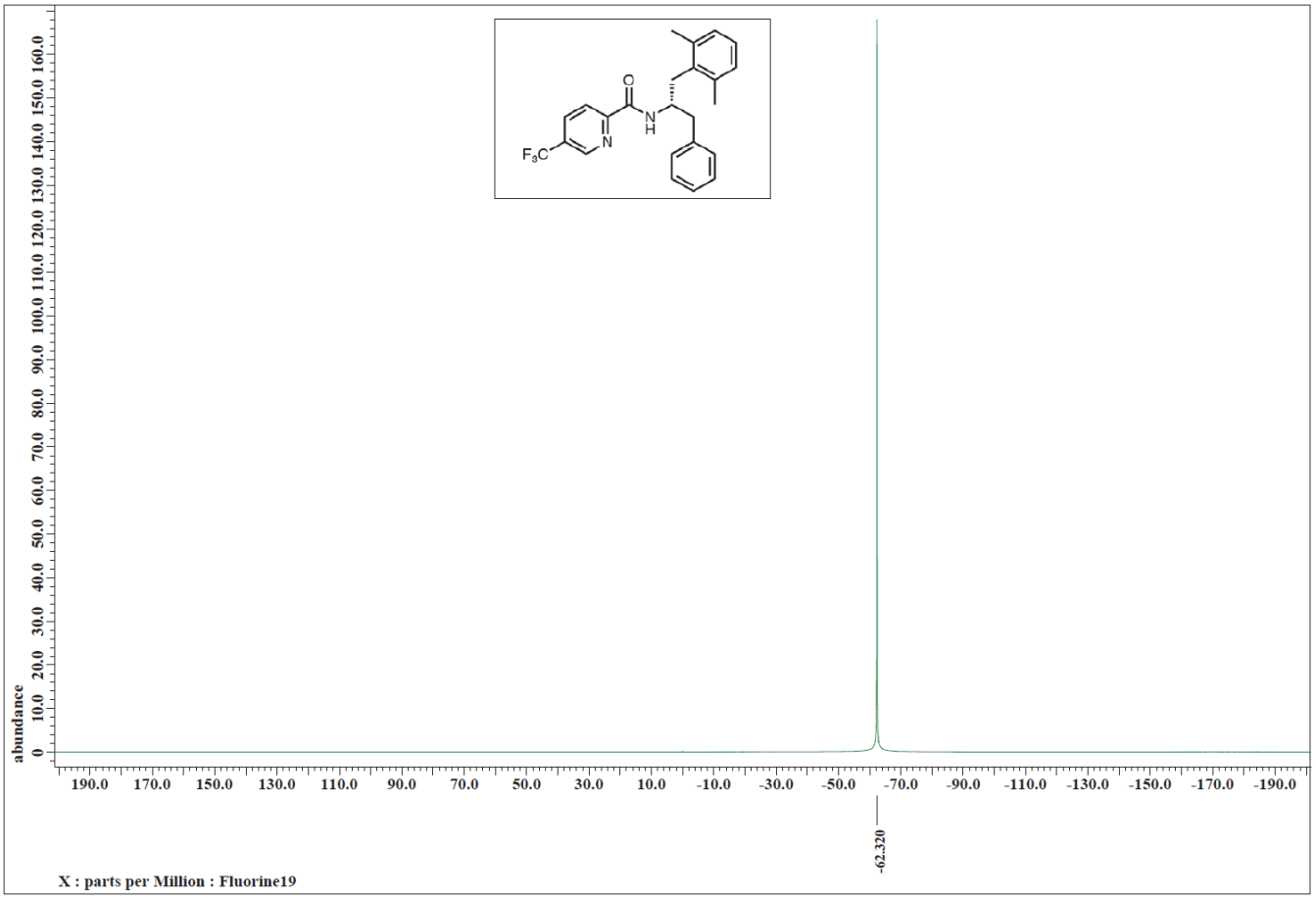

abundance
X : parts per Million : Proton
8.782
8.312
8.292
8.081
8.076
7.828
7.805
7.282
7.270
7.262
7.254
7.246
7.209
7.202
7.198
7.192
4.525
4.510
4.501
4.498
4.486
4.474
4.462
4.458
4.450
4.434
2.907
2.891
1.668
1.664
1.651
1.474
1.461
1.450
1.436
1.424
1.413
1.401
0.912
0.907
0.896
0.891
1.00
0.98
0.98
0.93
5.02
0.98
1.88
0.96
1.93
6.00

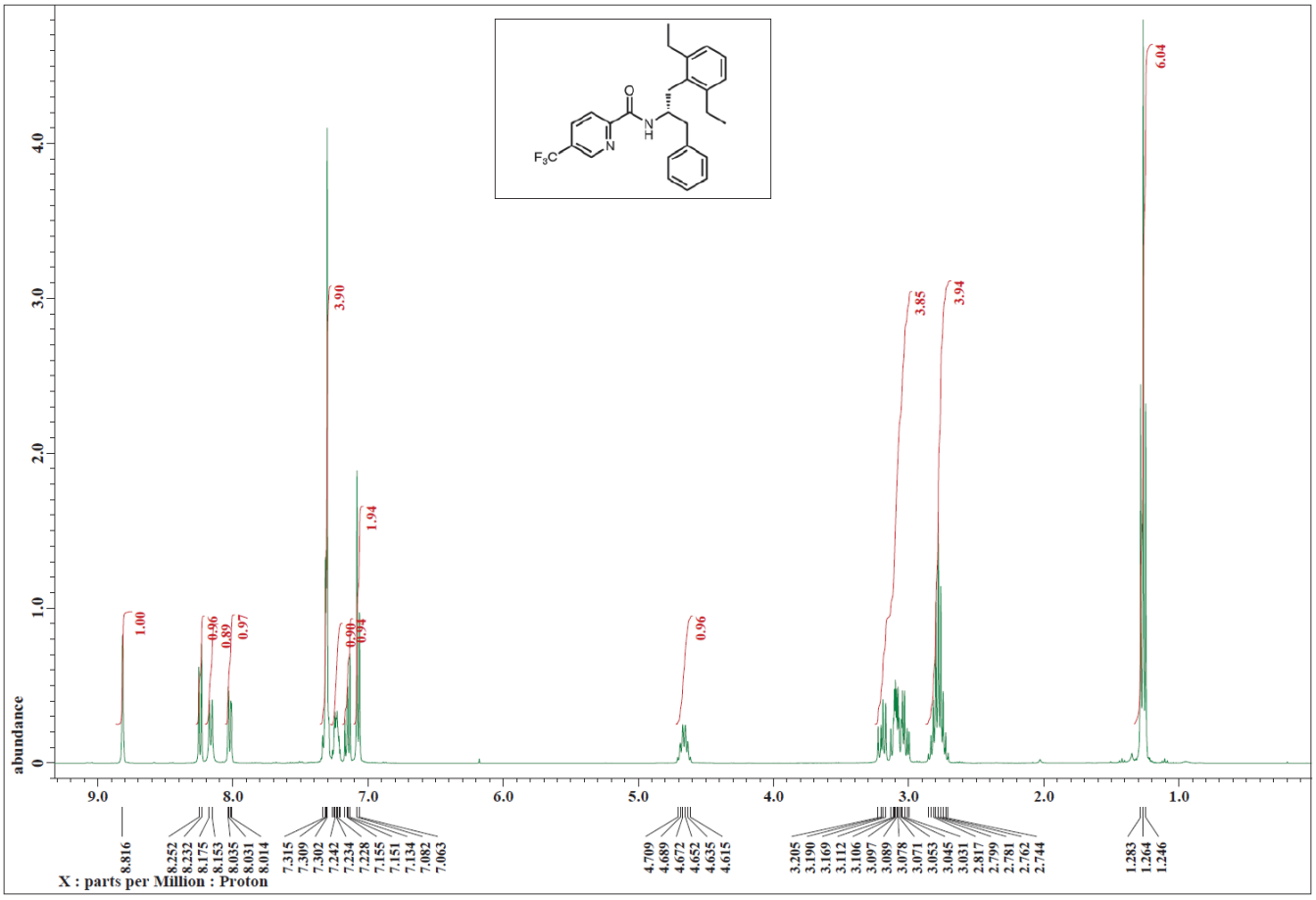

abundance
X : parts per Million : Carbon13
162.321
152.949
145.216
145.178
137.942
134.843
134.805
129.627
129.227
128.893
128.569
128.436
128.235
127.368
126.491
124.650
122.181
121.943
119.225
48.774
43.397
41.738
25.100
23.355
22.011

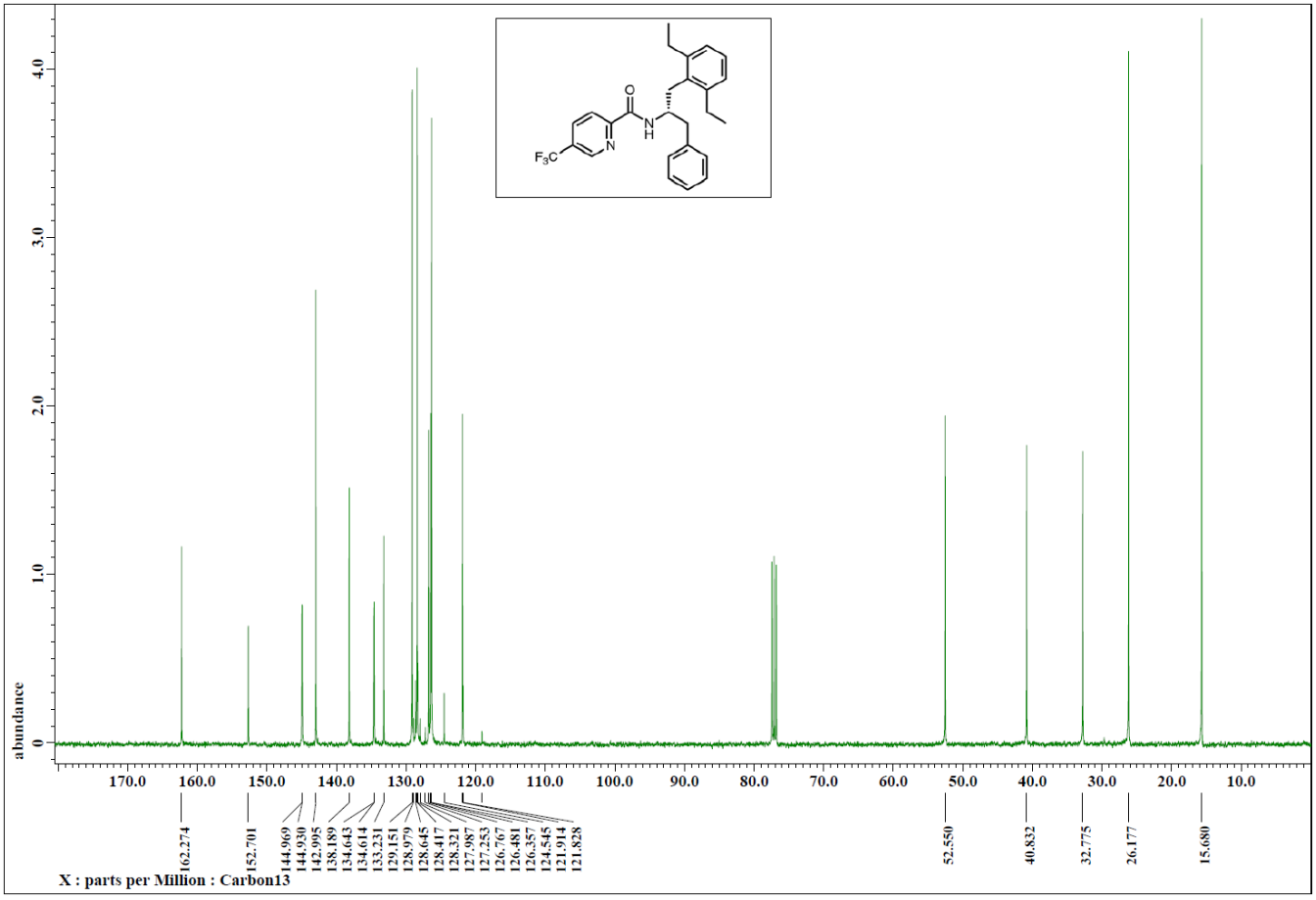

abundance
300.0
200.0
100.0
0
200.0
100.0
0
-100.0
-200.0
-62.391
X : parts per Million : Fluorine19

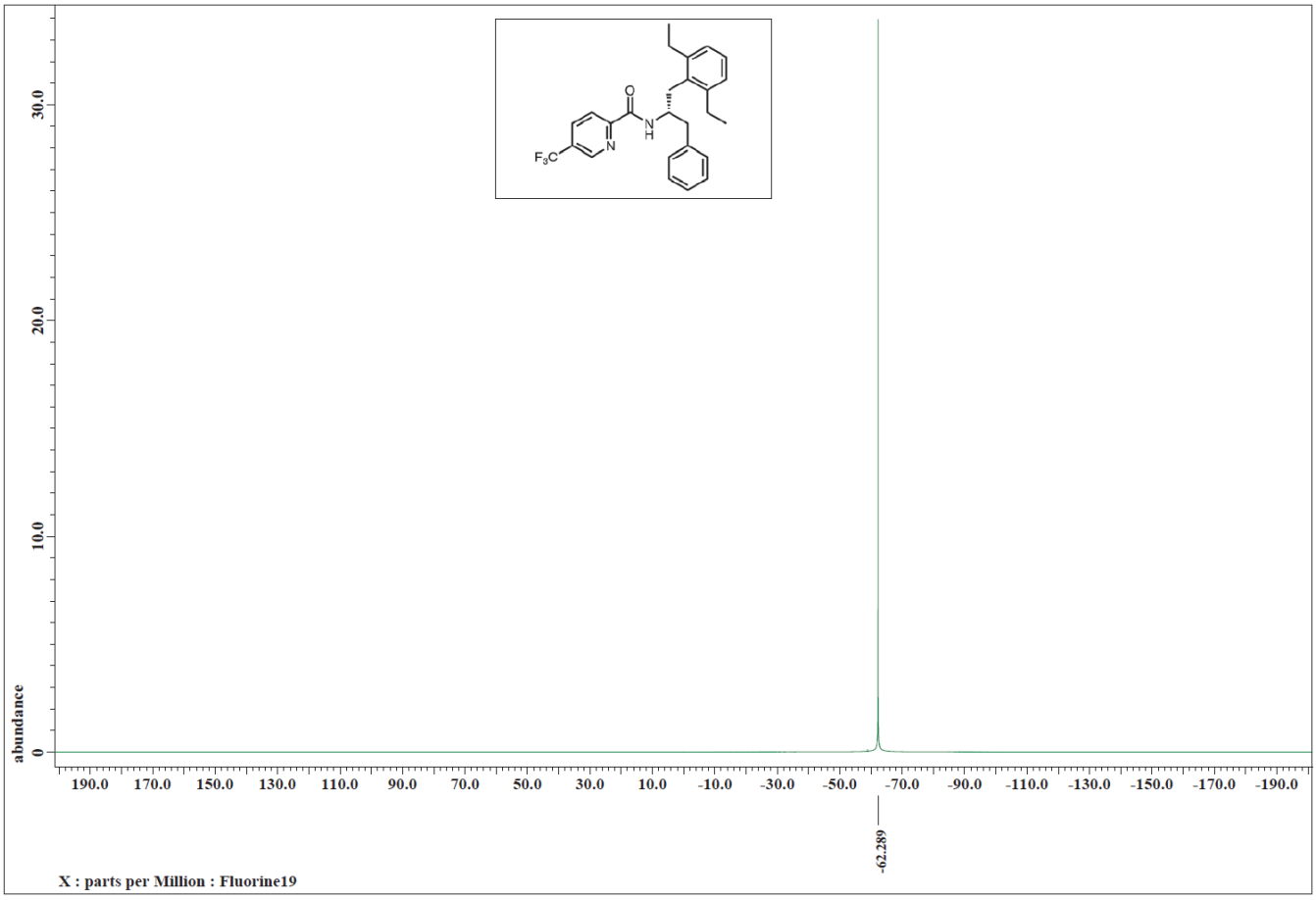

abundance
5.0
4.0
3.0
2.0
1.0
0
1.01
1.00
2.02
3.99
3.00
1.03
0.99
4.00
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
8.779
8.187
8.167
8.039
8.033
8.019
8.013
8.002
7.257
7.254
7.239
7.224
6.990
6.980
6.967
6.956
6.949
6.938
6.926
4.624
4.620
4.603
4.584
4.568
4.562
3.039
3.035
3.013
3.006
2.987
2.967
2.958
2.950
2.944
2.931
2.326
X : parts per Million : Proton

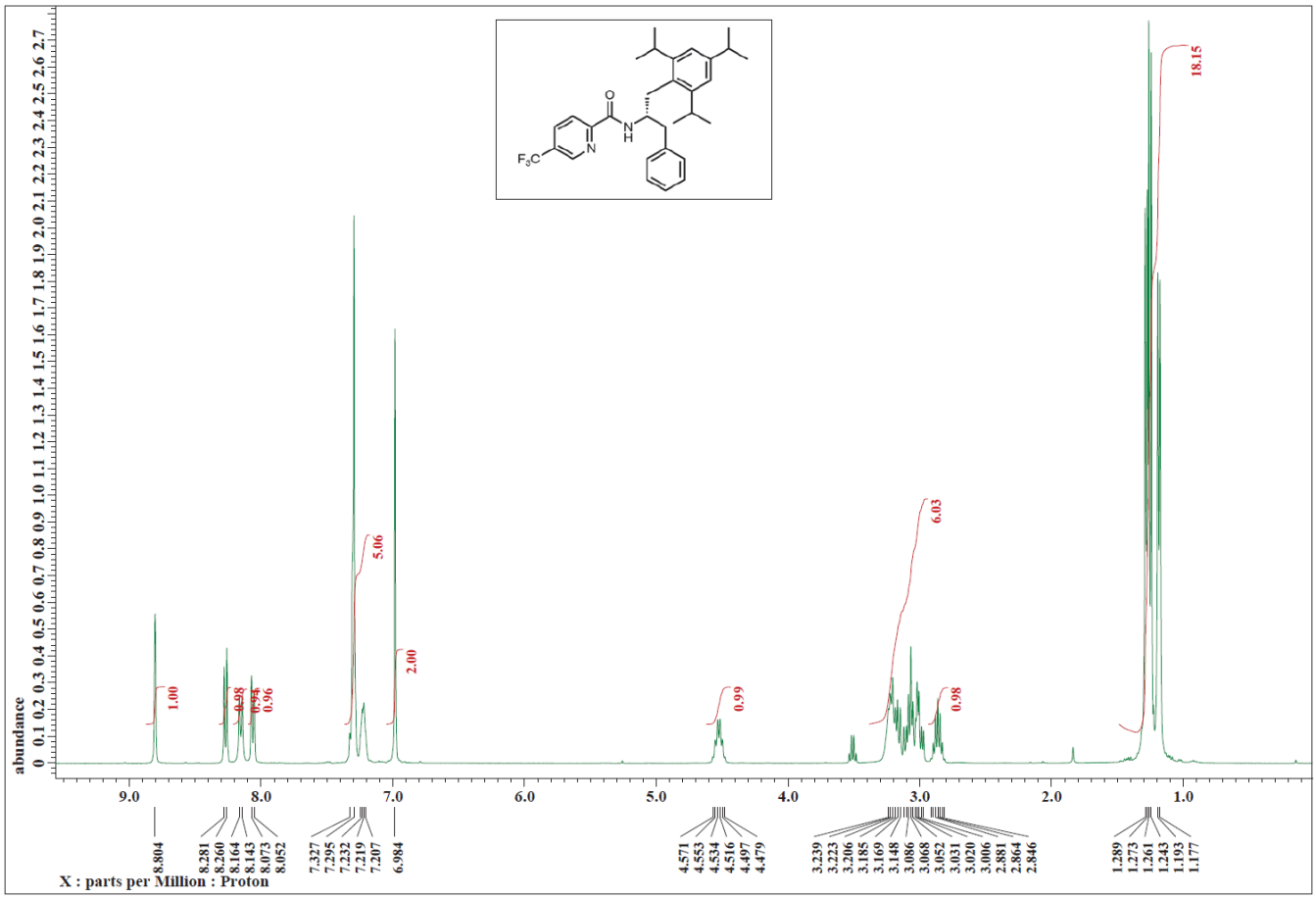

abundance
X : parts per Million : Carbon13
162.302
152.711
145.131
145.092
145.054
138.151
136.883
135.062
134.795
134.767
129.275
129.151
128.817
128.521
128.455
128.150
126.605
126.395
124.603
122.009
121.895
51.539
41.185
34.453
20.495

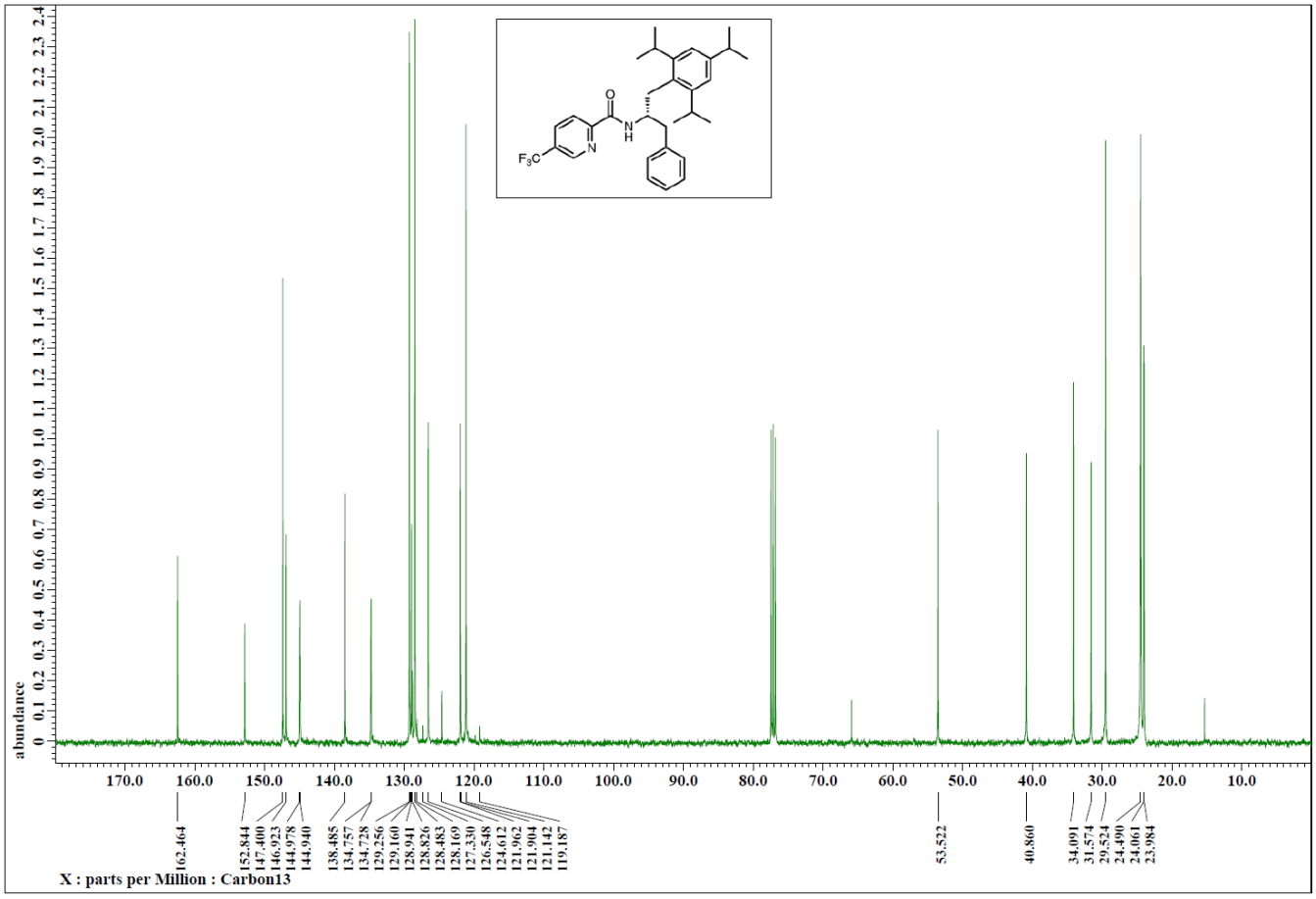

abundance
X : parts per Million : Fluorine19
-62.320

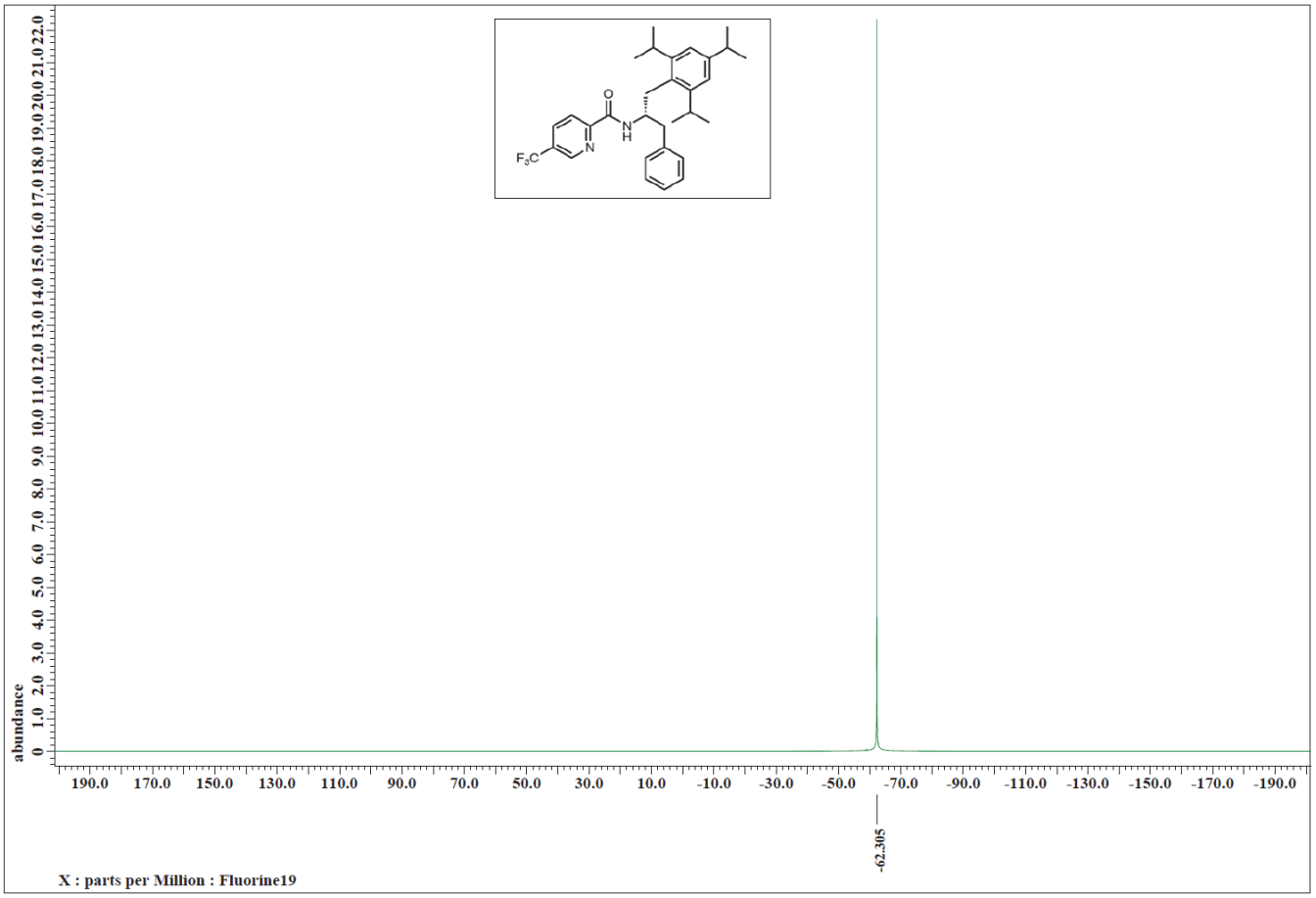

abundance
X : parts per Million : Proton
1.00
0.96
0.89
0.97
3.90
1.94
0.90
0.94
0.96
3.85
3.94
6.04
8.816
8.252
8.232
8.175
8.153
8.035
8.031
8.014
7.315
7.309
7.302
7.242
7.234
7.228
7.155
7.151
7.134
7.082
7.063
4.709
4.689
4.672
4.652
4.635
4.615
3.205
3.190
3.169
3.112
3.106
3.097
3.089
3.078
3.071
3.053
3.045
3.031
2.817
2.799
2.781
2.762
2.744
1.283
1.264
1.246

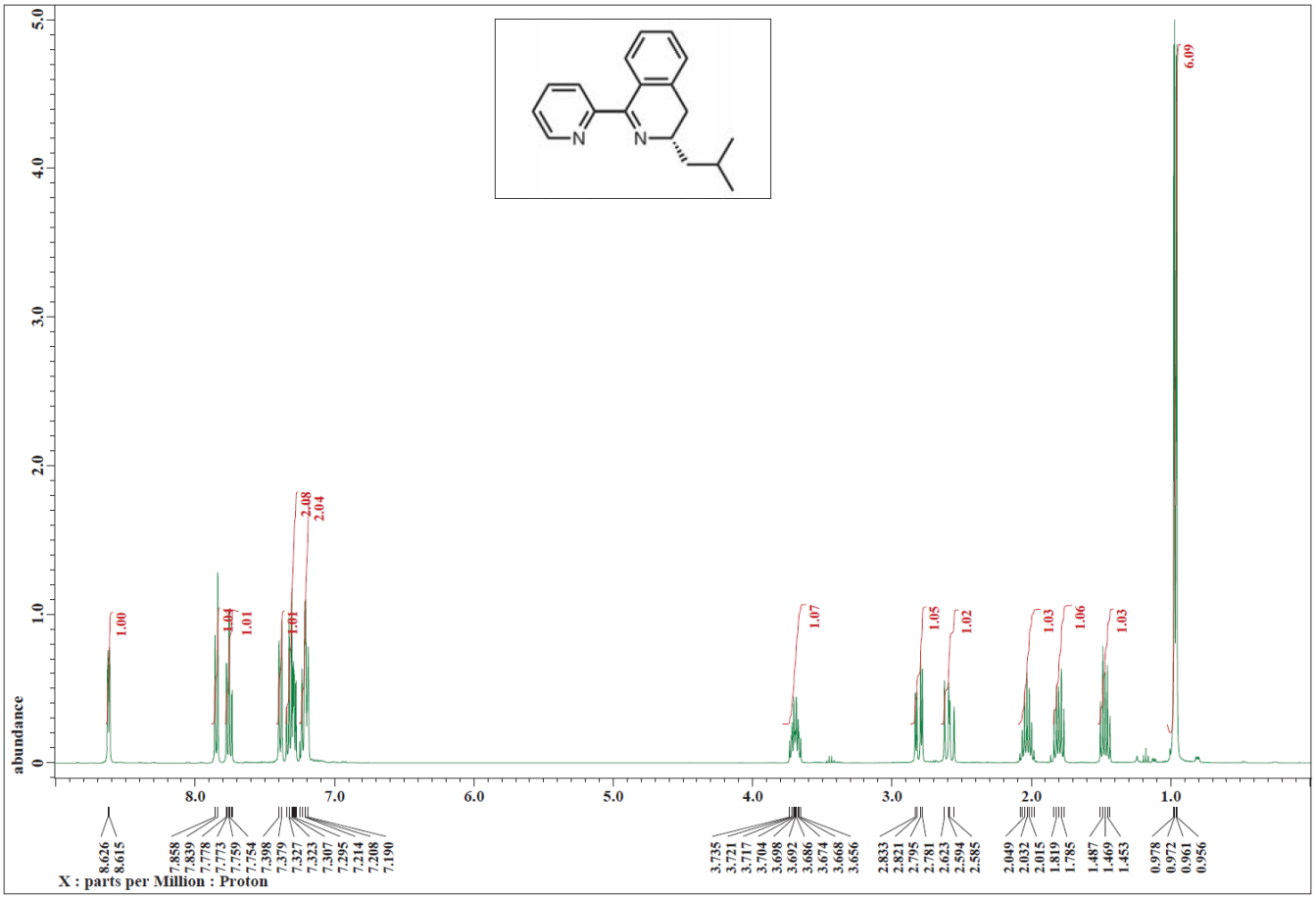

abundance
X : parts per Million : Carbon13
162.274
152.701
144.969
144.930
142.995
138.189
134.643
134.614
133.231
129.151
128.979
128.645
128.417
128.321
127.987
127.253
126.767
126.481
126.357
124.545
121.914
121.828
52.550
40.832
32.775
26.177
15.680

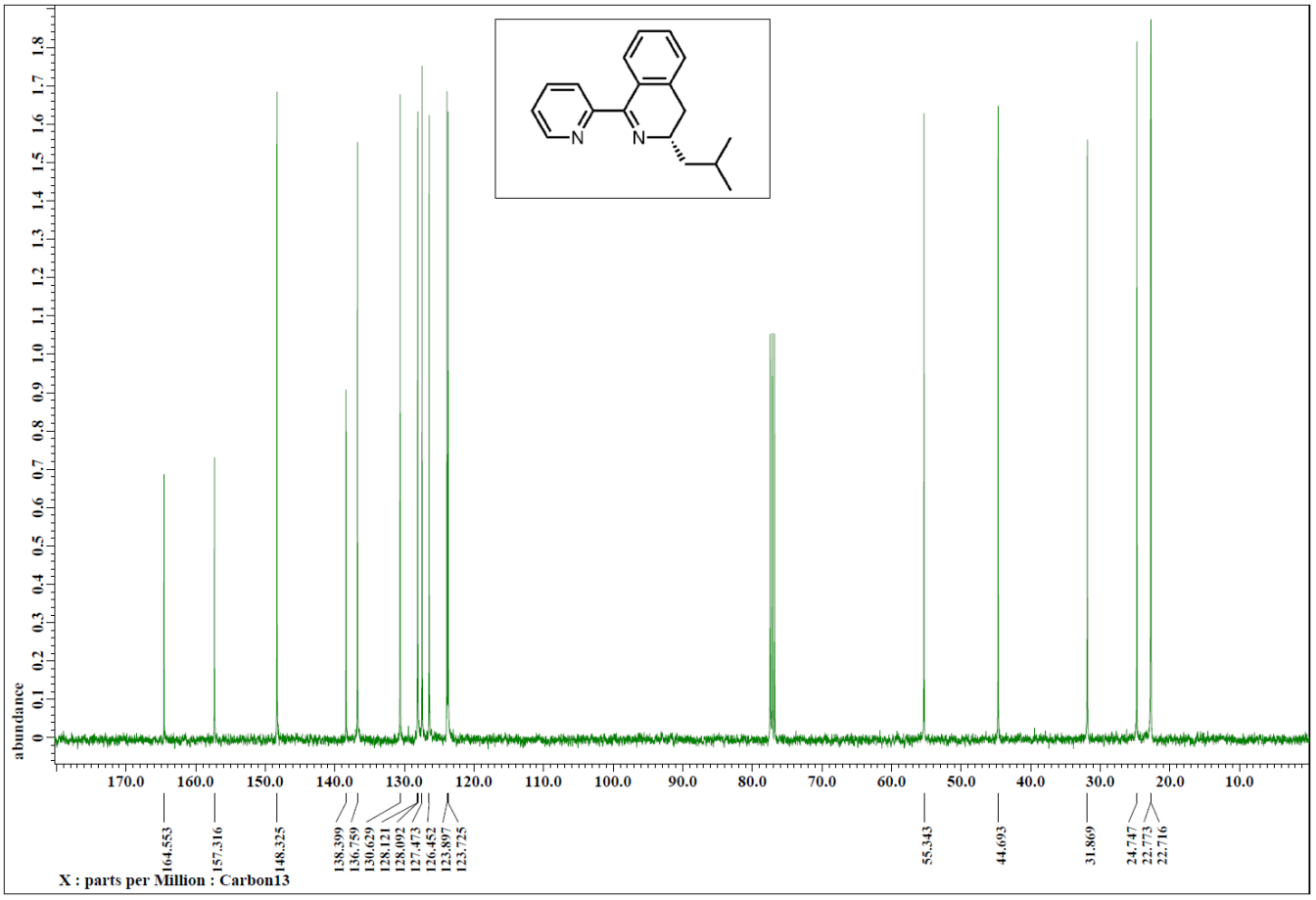

abundance
30.0
20.0
10.0
0
190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0
-62.289
X : parts per Million : Fluorine19

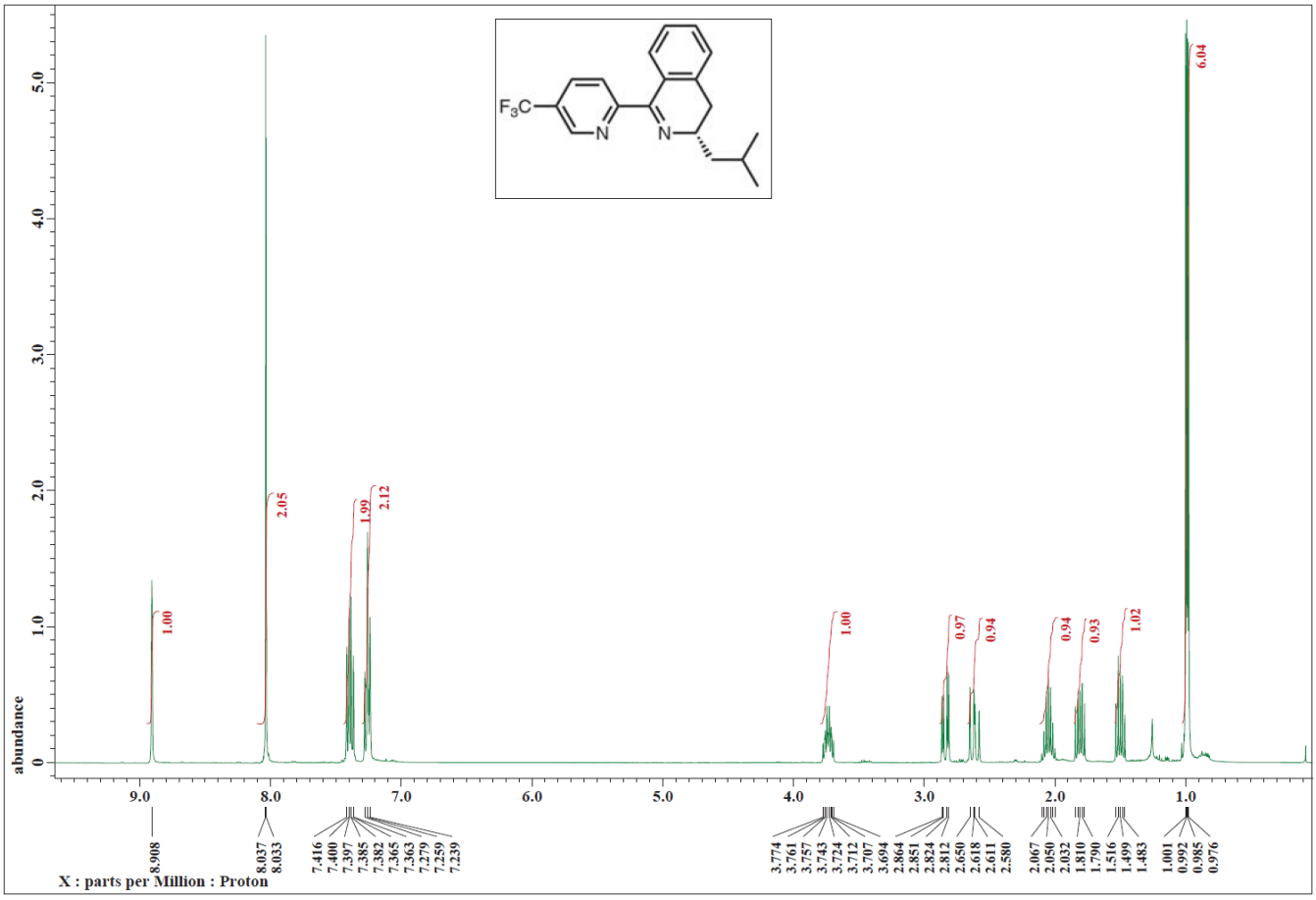

abundance
1.00
0.38
0.94
0.96
5.06
2.00
0.99
6.03
0.98
18.15
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
8.804
8.281 8.260 8.164 8.143 8.073 8.052
7.327 7.295 7.232 7.219 7.207
6.984
4.571 4.553 4.534 4.516 4.497 4.479
3.239 3.223 3.206 3.185 3.169 3.148 3.086 3.068 3.052 3.031 3.020 3.006 2.881 2.864 2.846
1.289 1.273 1.261 1.243 1.193 1.177
X : parts per Million : Proton

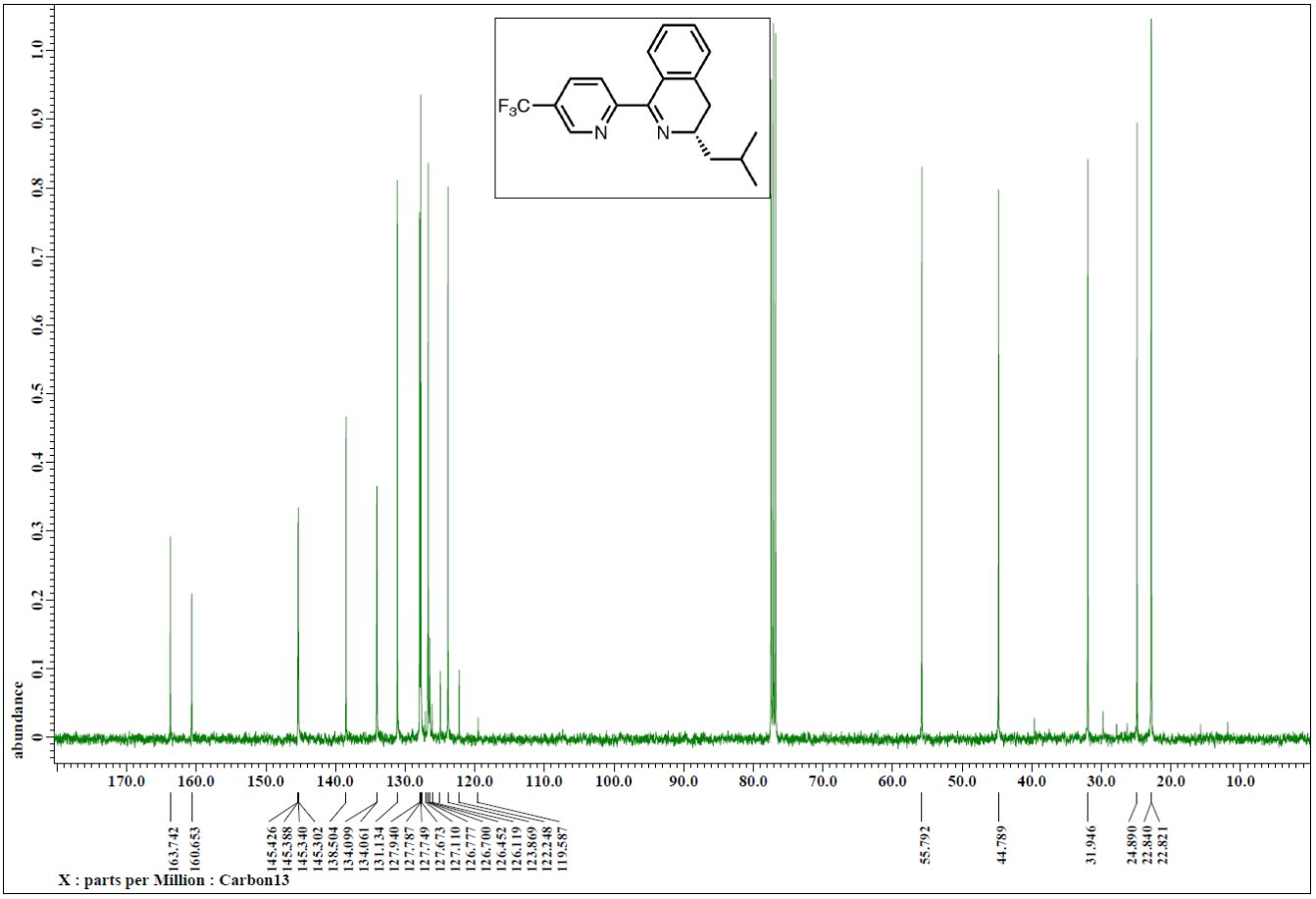

abundance
X : parts per Million : Carbon13
162.464
152.844
147.400
146.923
144.978
144.940
138.485
134.757
134.728
129.256
129.160
128.941
128.826
128.483
128.169
127.330
126.548
124.612
121.962
121.904
121.142
119.187
53.522
40.860
34.091
31.574
29.524
24.490
24.061
23.984

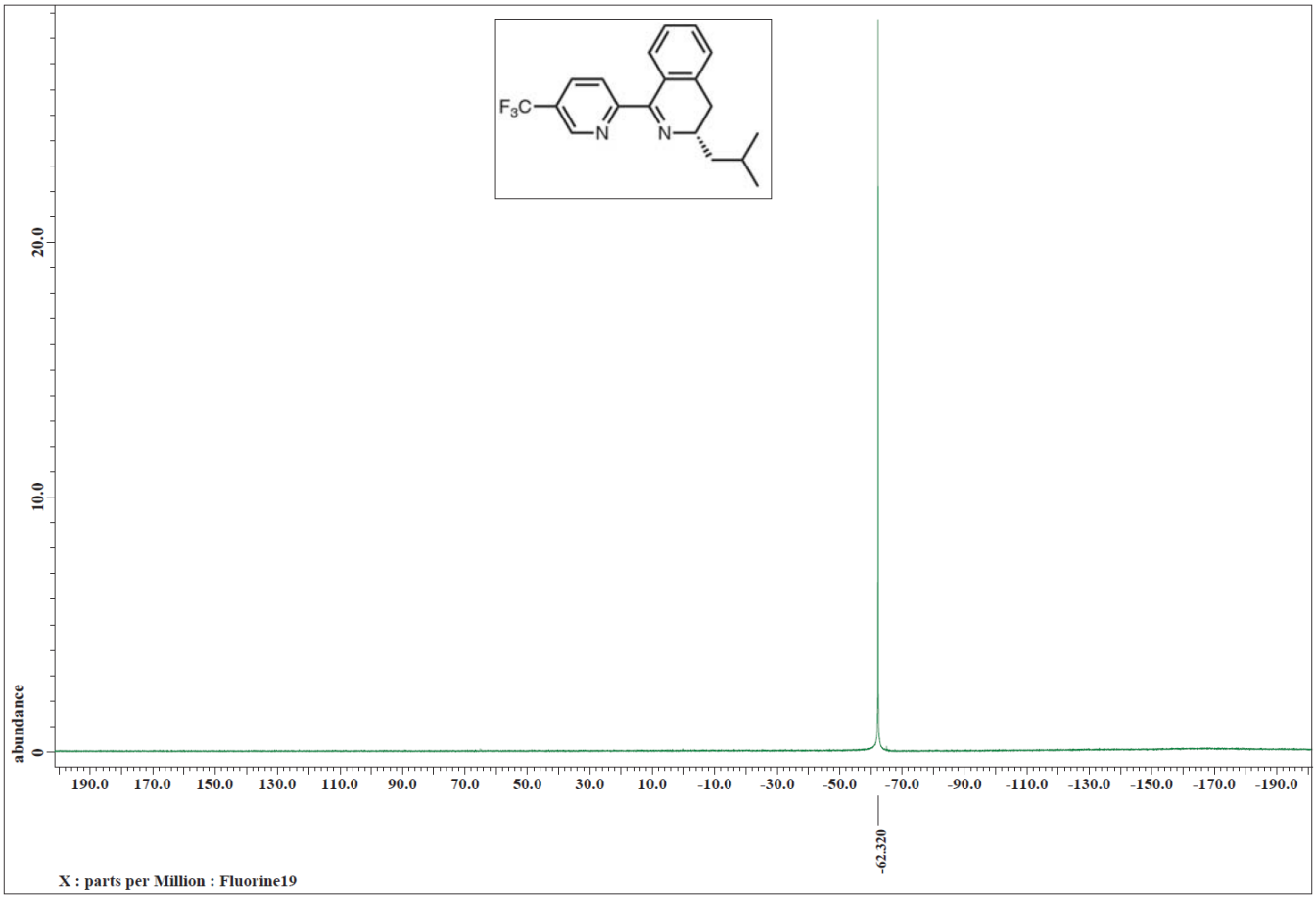

abundance
X : parts per Million : Fluorine19
-62.305

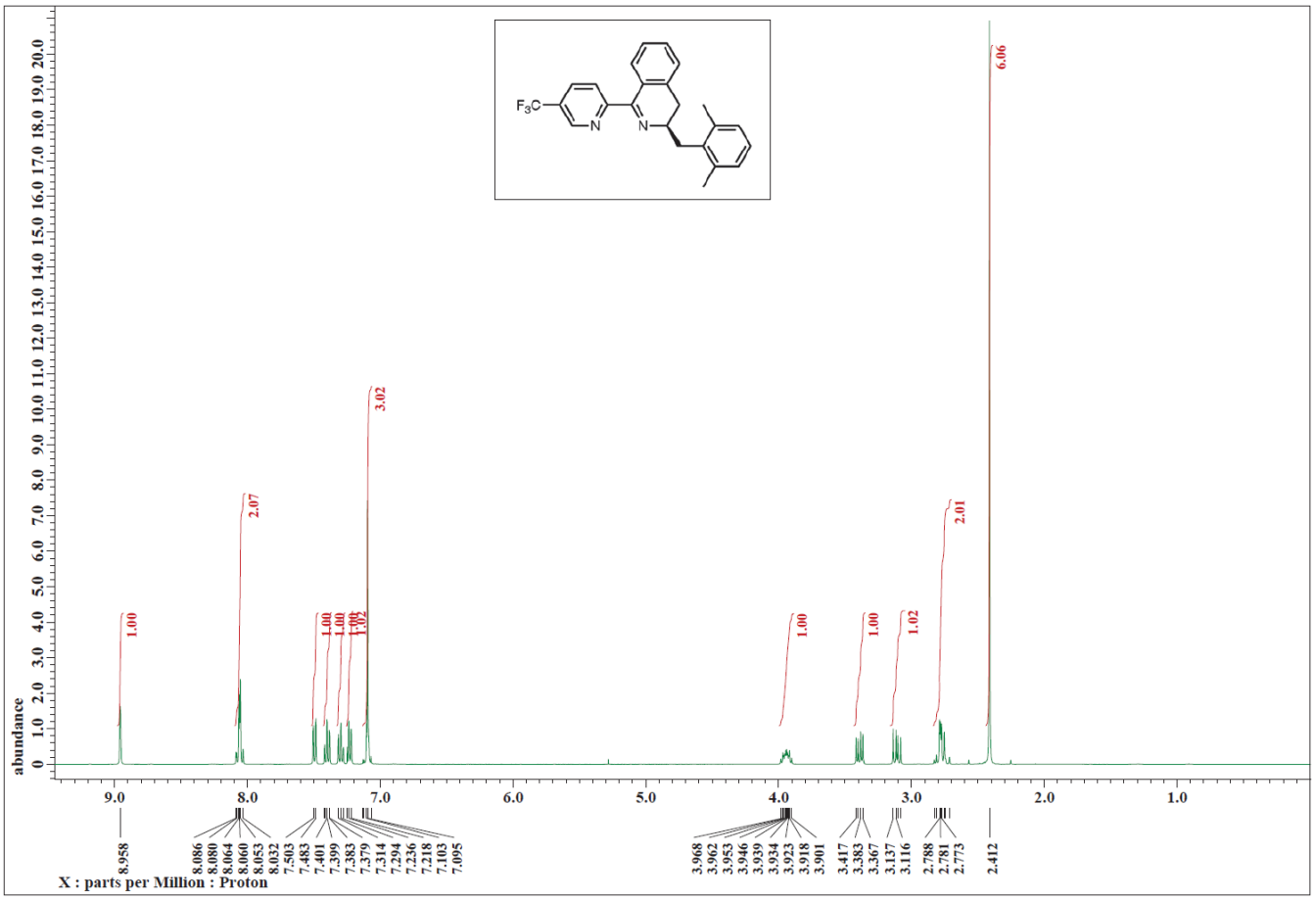

abundance
X : parts per Million : Proton
1.00
1.04
1.01
1.01
2.08
2.04
1.07
1.05
1.02
1.03
1.06
1.03
6.09
8.626
8.615
7.858
7.839
7.778
7.773
7.759
7.754
7.398
7.379
7.327
7.323
7.307
7.295
7.214
7.208
7.190
3.735
3.721
3.717
3.704
3.698
3.692
3.686
3.674
3.668
3.656
2.833
2.821
2.795
2.781
2.623
2.594
2.585
2.049
2.032
2.015
1.819
1.785
1.487
1.469
1.453
0.978
0.972
0.961
0.956

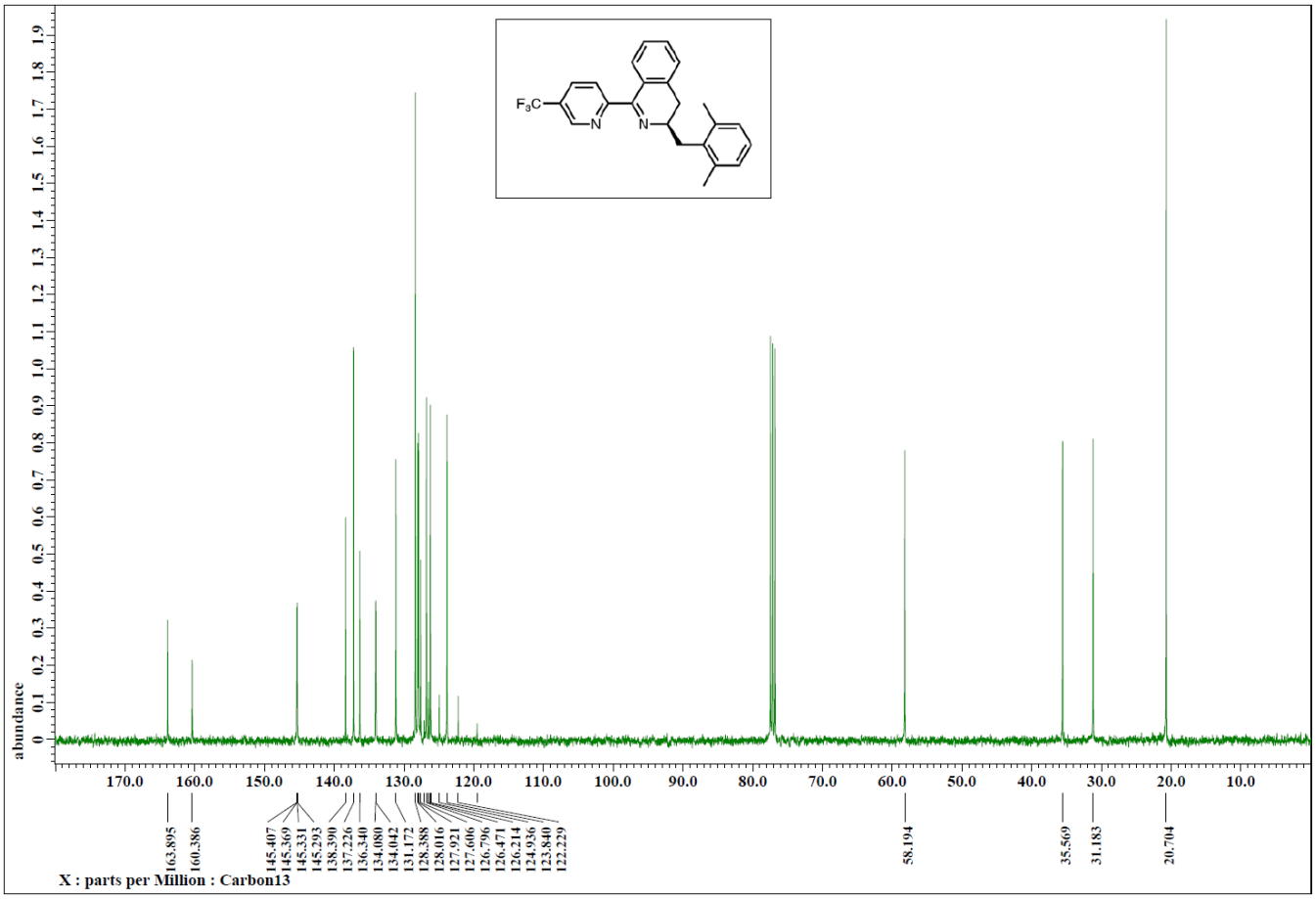

abundance
X : parts per Million : Carbon13
164.553
157.316
148.325
138.399
136.759
130.629
128.121
128.092
127.473
126.452
123.897
123.725
55.343
44.693
31.869
24.747
22.773
22.716

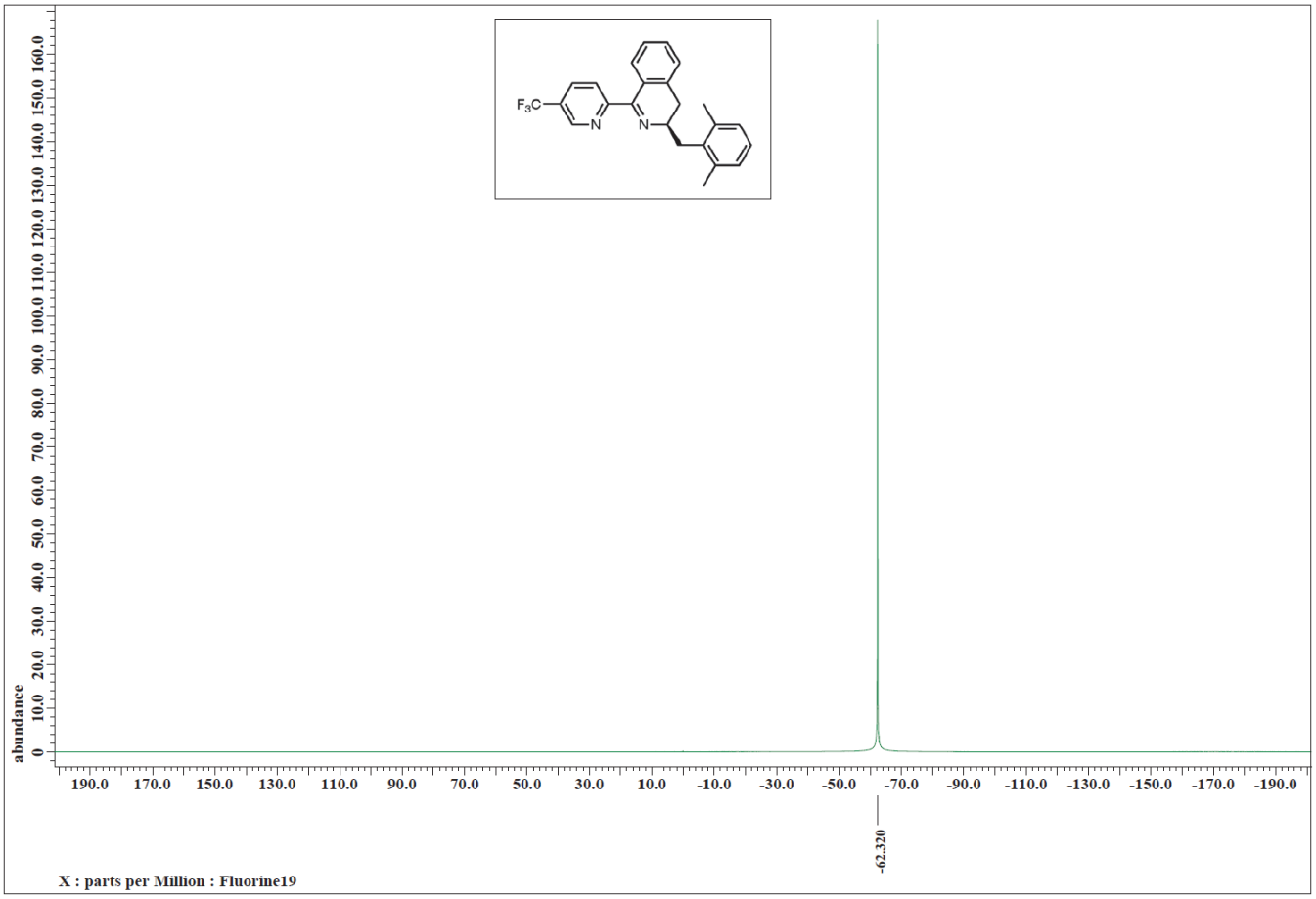

abundance
X : parts per Million : Proton
8.908
8.037
8.033
7.416
7.400
7.397
7.385
7.382
7.365
7.363
7.279
7.259
7.239
3.774
3.761
3.757
3.743
3.724
3.712
3.707
3.694
2.864
2.851
2.824
2.812
2.650
2.618
2.611
2.580
2.067
2.050
2.032
1.810
1.790
1.516
1.499
1.483
1.001
0.992
0.985
0.976

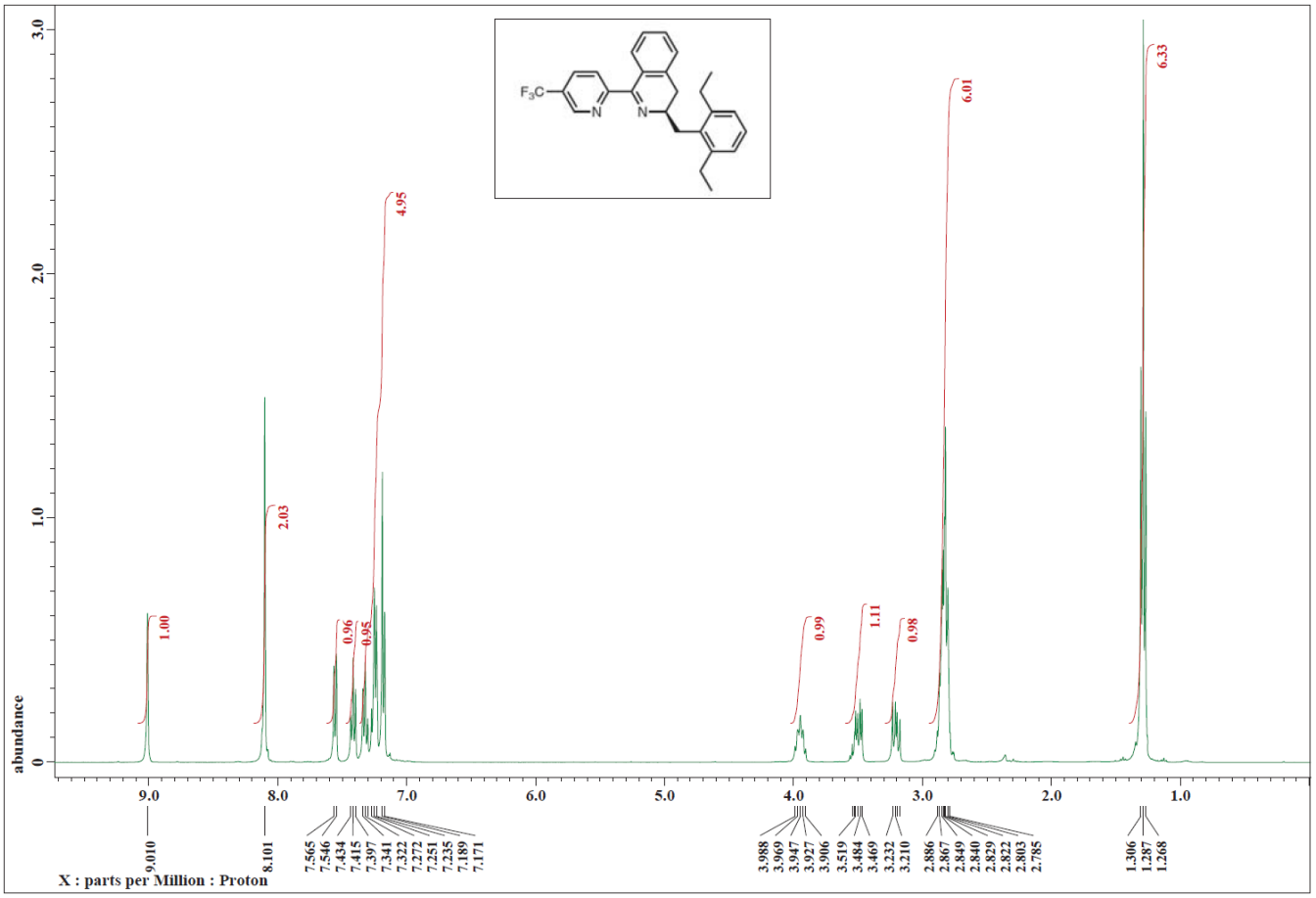

abundance
X : parts per Million : Carbon13
163.742
160.653
145.426
145.388
145.340
145.302
138.504
134.099
134.061
131.134
127.940
127.787
127.749
127.673
127.110
126.777
126.700
126.452
126.119
123.869
122.248
119.587
55.792
44.789
31.946
24.890
22.840
22.821

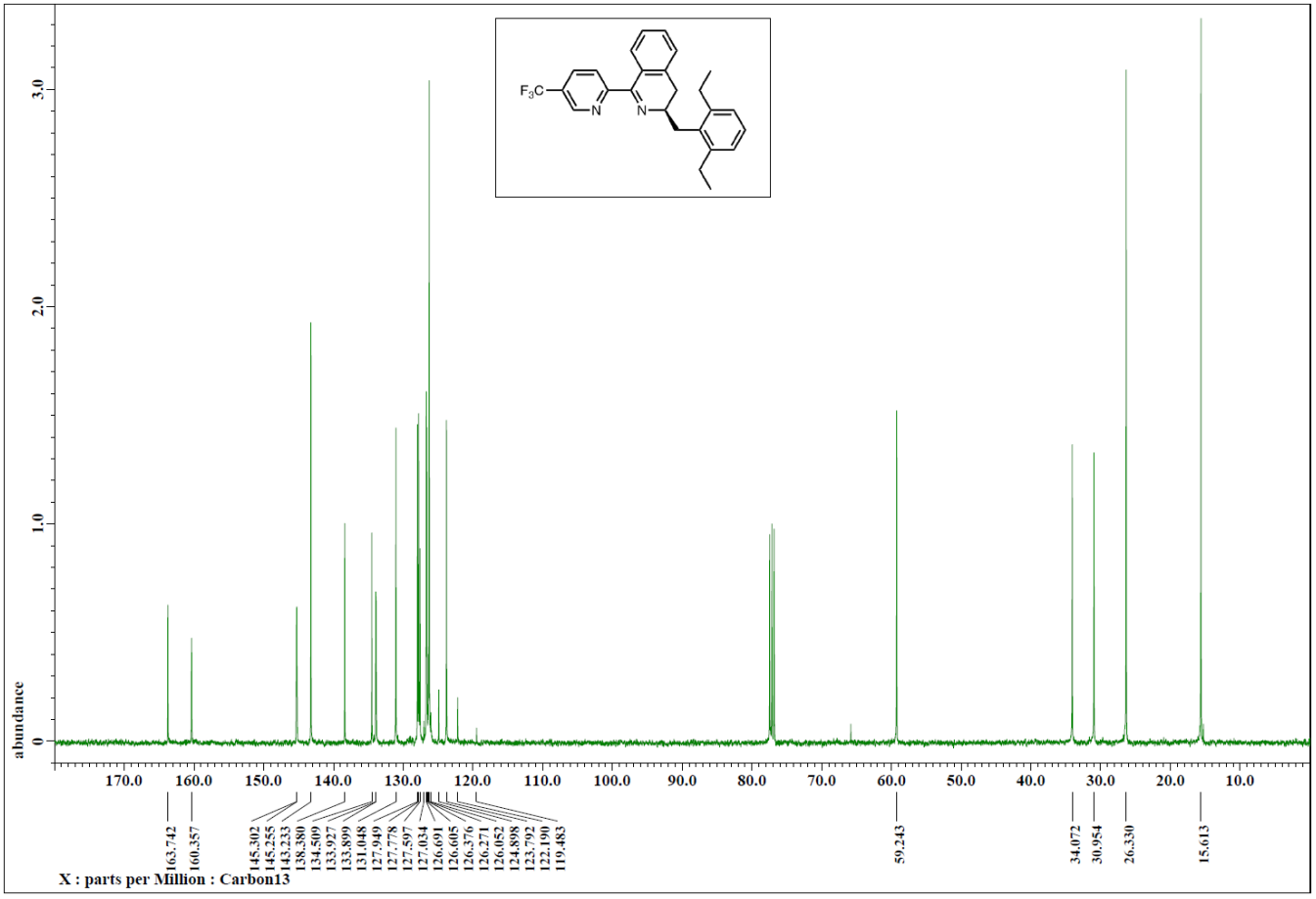

F3C
N
N
abundance
20.0
10.0
0
190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0
-62.320
X : parts per Million : Fluorine19

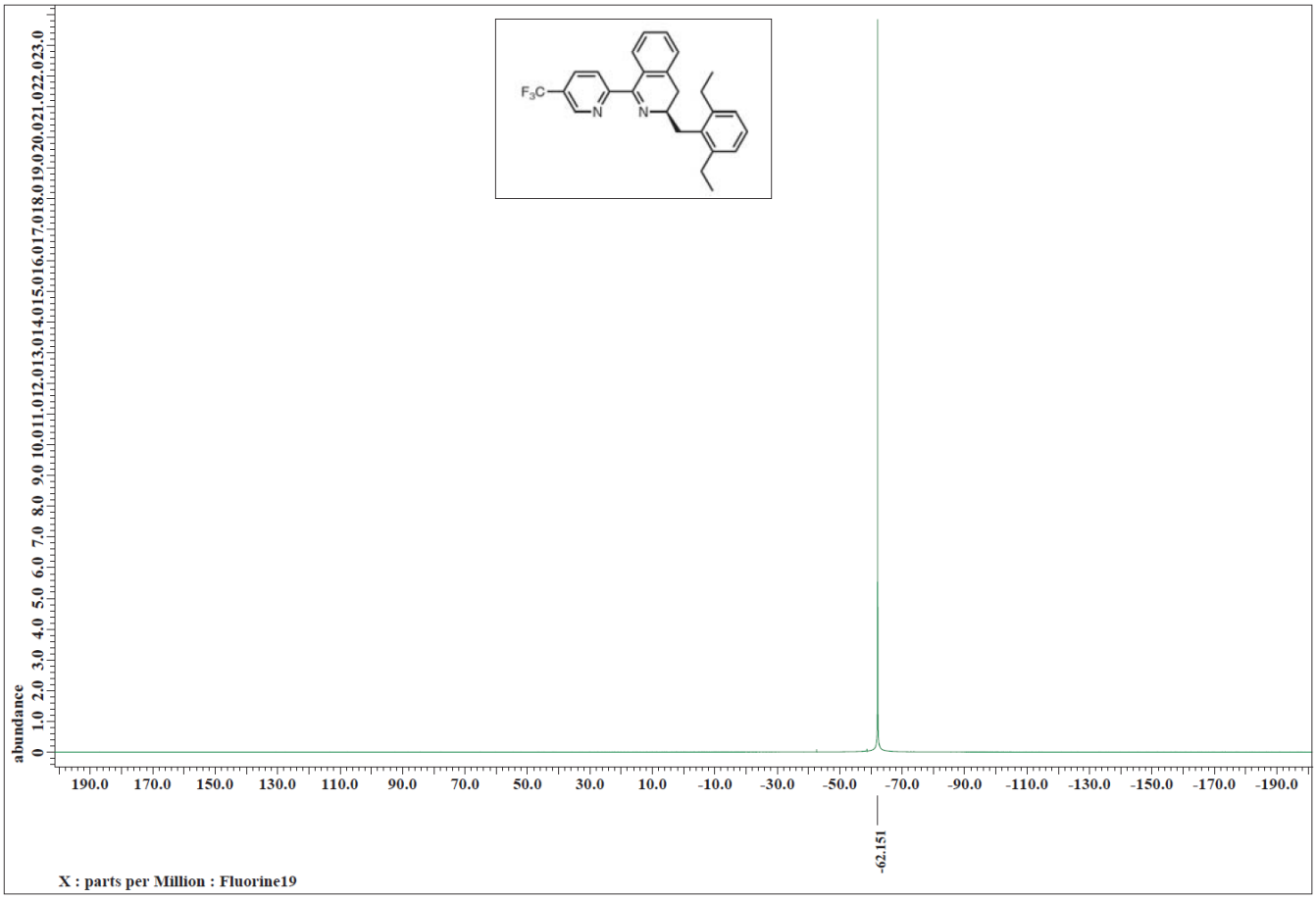

F3C
N
N
abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0
1.00
2.07
1.00
1.00
1.00
1.02
3.02
1.00
1.00
1.02
2.01
6.06
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
8.958
8.086 8.080 8.064 8.060 8.053 8.032
7.503 7.483 7.401 7.399 7.383 7.379 7.314 7.294 7.236 7.218 7.103 7.095
3.968 3.962 3.953 3.946 3.939 3.934 3.923 3.918 3.901
3.417 3.383 3.367
3.137 3.116
2.788 2.781 2.773
2.412
X : parts per Million : Proton

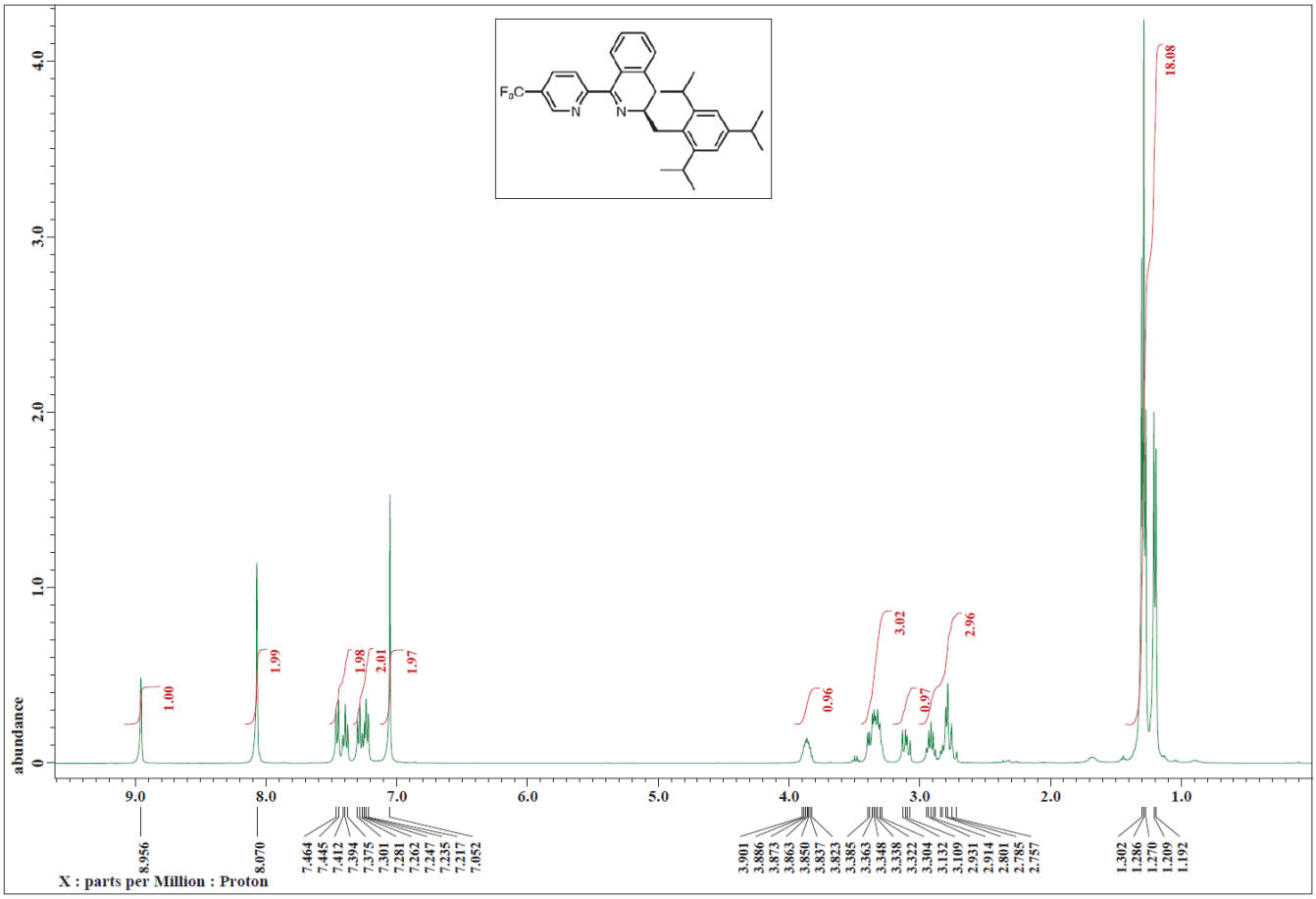

abundance
X : parts per Million : Carbon13
163.895
160.386
145.407
145.369
145.331
145.293
138.390
137.226
136.340
134.080
134.042
131.172
128.388
128.016
127.921
127.606
126.796
126.471
126.214
124.936
123.840
122.229
58.194
35.569
31.183
20.704

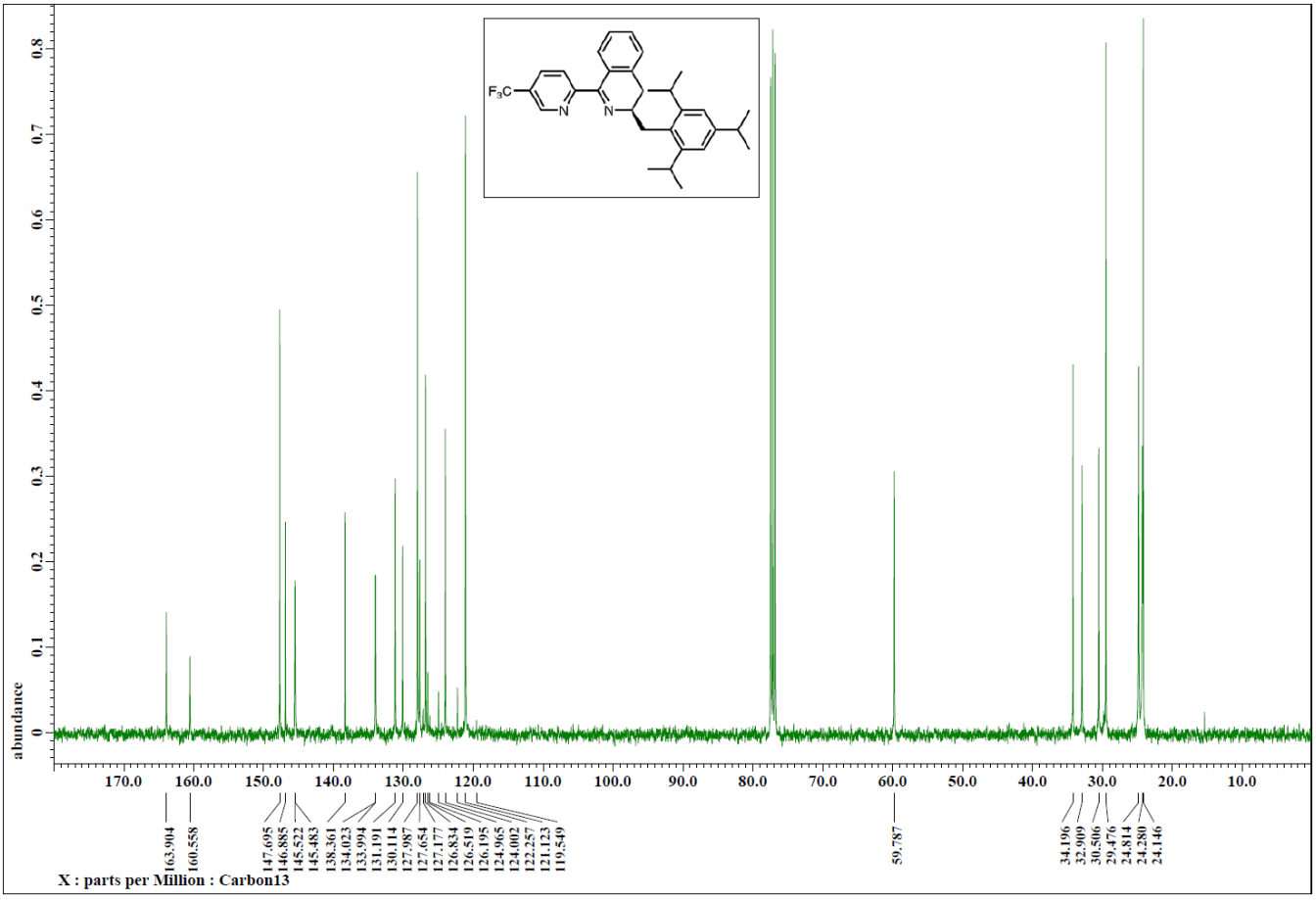

abundance
X : parts per Million : Fluorine19
-62.320

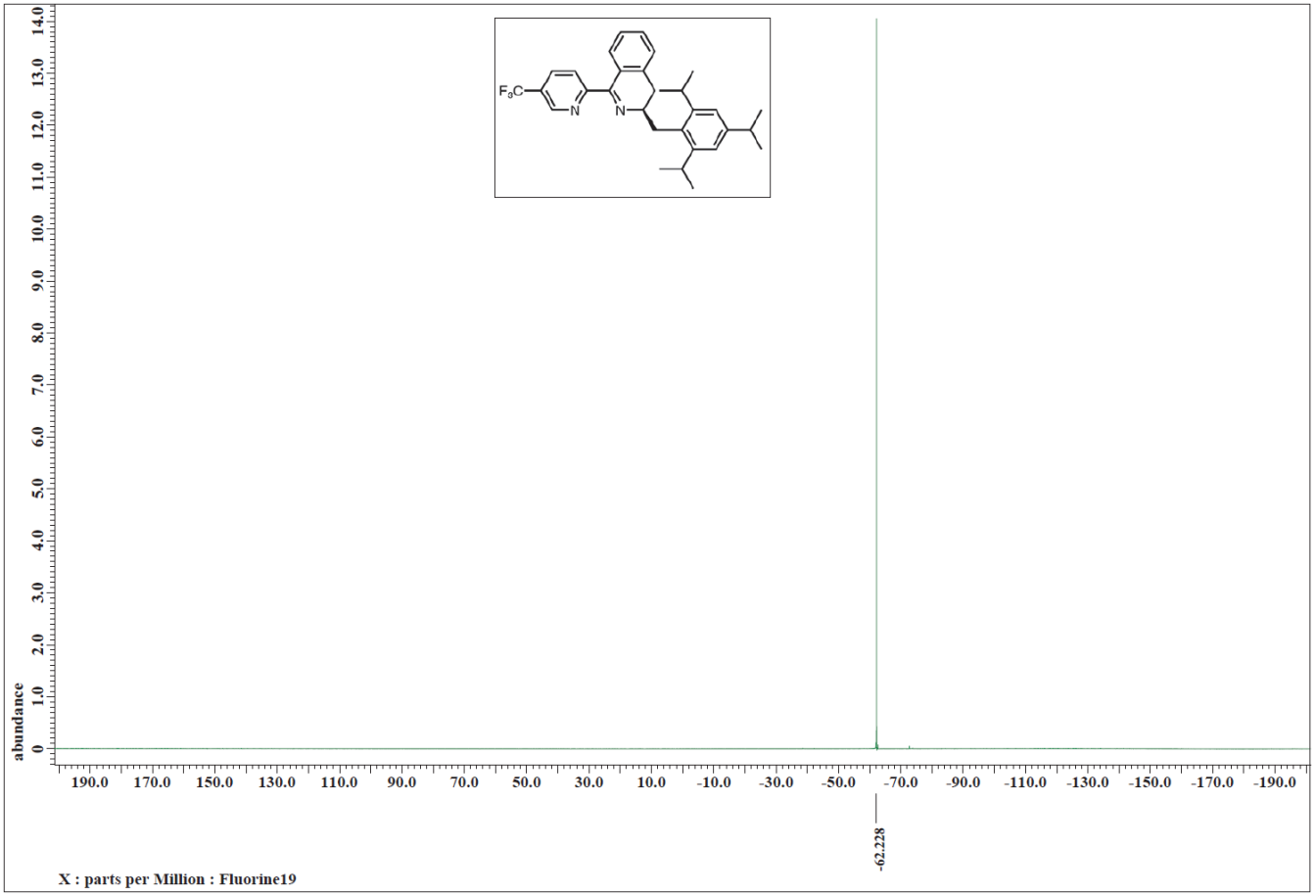

abundance
X : parts per Million : Proton
1.00
2.03
0.96
0.95
4.95
0.99
1.11
0.98
6.01
6.33
9.010
8.101
7.565
7.546
7.434
7.415
7.397
7.341
7.322
7.272
7.251
7.235
7.189
7.171
3.988
3.969
3.947
3.927
3.906
3.519
3.484
3.469
3.232
3.210
2.886
2.867
2.849
2.840
2.829
2.822
2.803
2.785
1.306
1.287
1.268

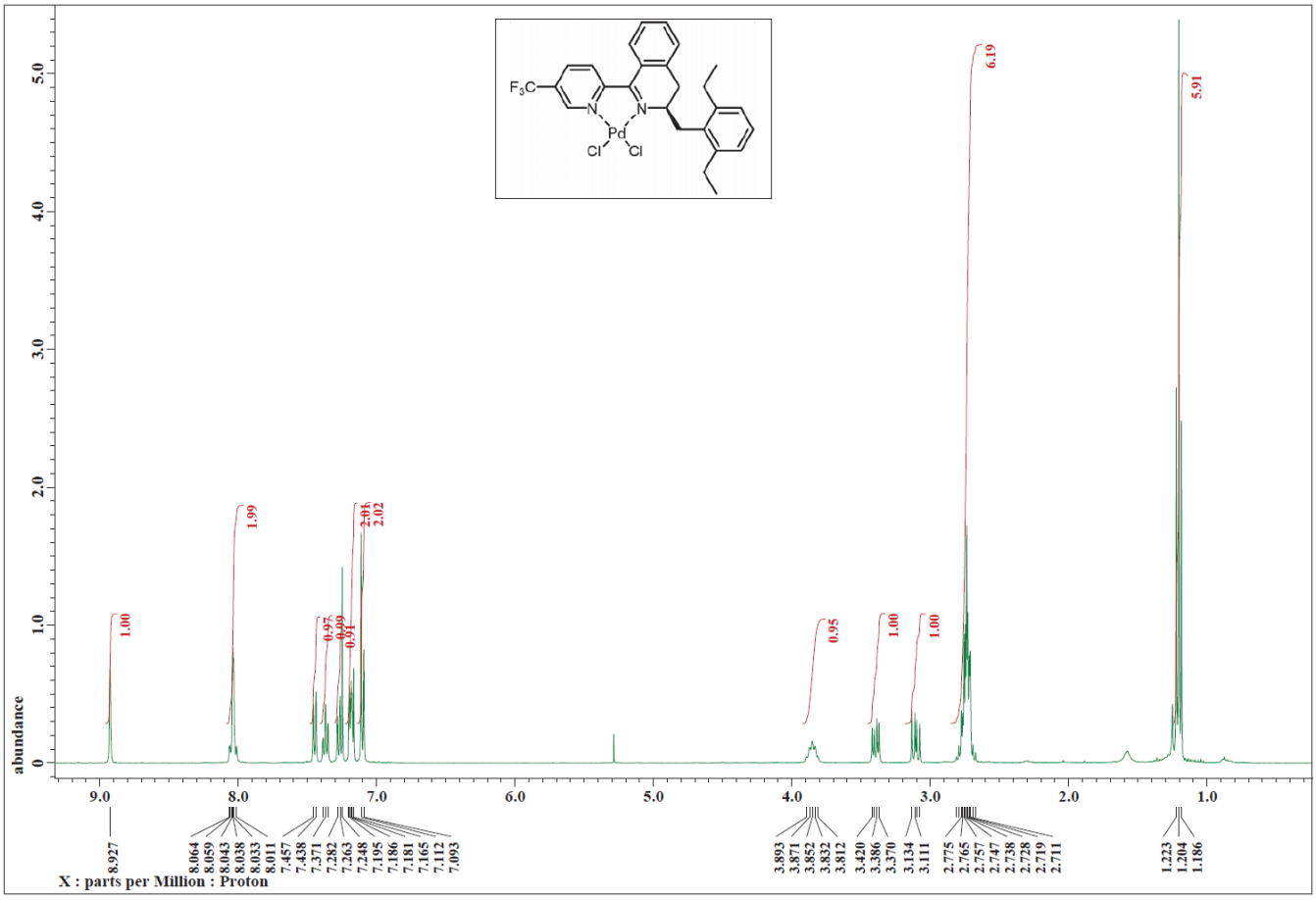

abundance
X : parts per Million : Carbon13
163.742
160.357
145.302
145.255
143.233
138.380
134.509
133.927
133.899
131.048
127.949
127.778
127.597
127.034
126.691
126.605
126.376
126.271
126.052
124.898
123.792
122.190
119.483
59.243
34.072
30.954
26.330
15.613

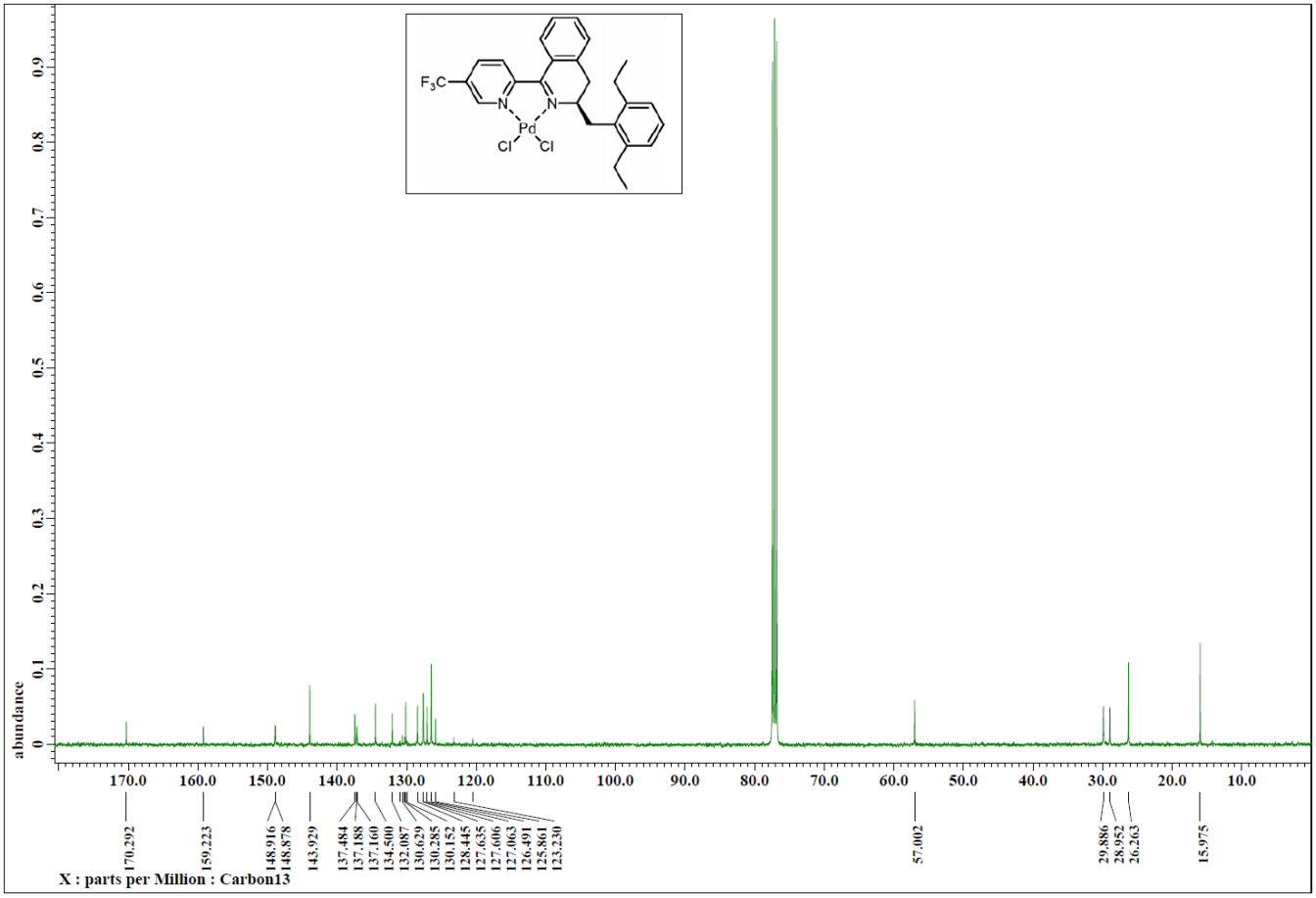

abundance
X : parts per Million : Fluorine19
-62.151

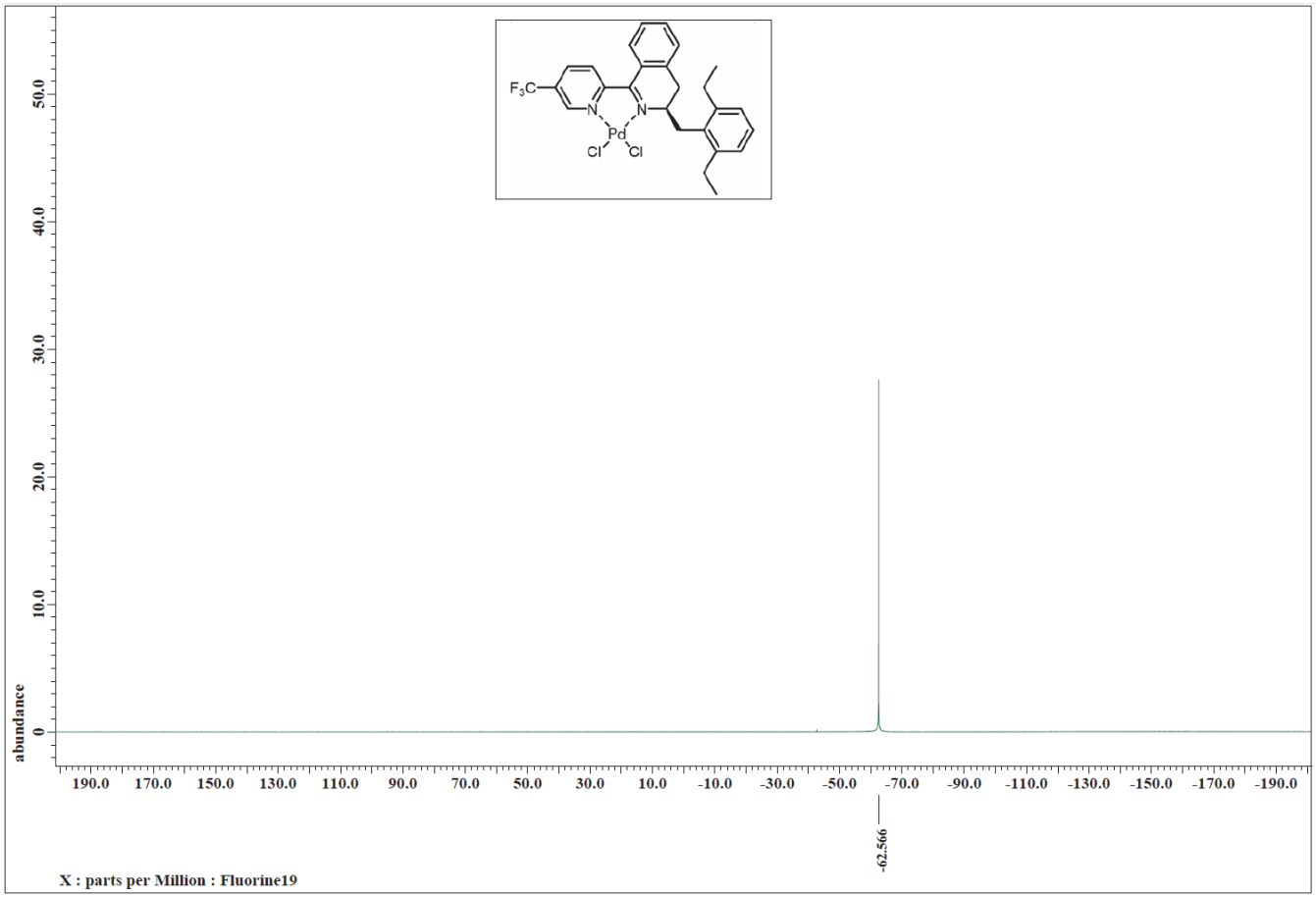

abundance
X : parts per Million : Proton
1.00
1.99
1.98
2.01
1.97
0.96
3.02
0.97
2.96
18.08

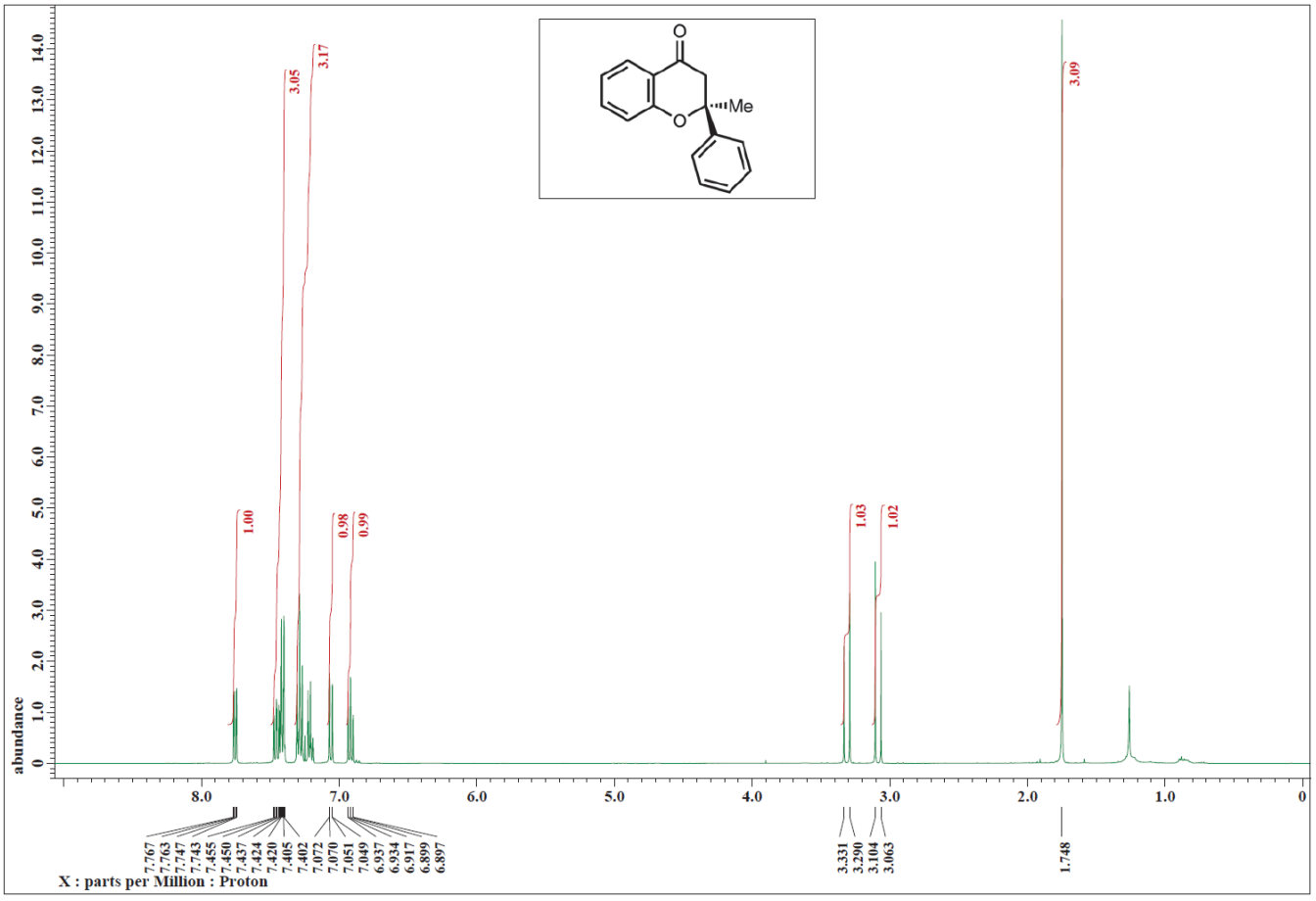

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
163.904
160.558
147.695
146.885
145.522
145.483
138.361
134.023
133.994
131.191
130.114
127.987
127.654
127.177
126.834
126.519
126.195
124.965
124.002
122.257
121.123
119.549
59.787
34.196
32.909
30.506
29.476
24.814
24.280
24.146
X : parts per Million : Carbon13

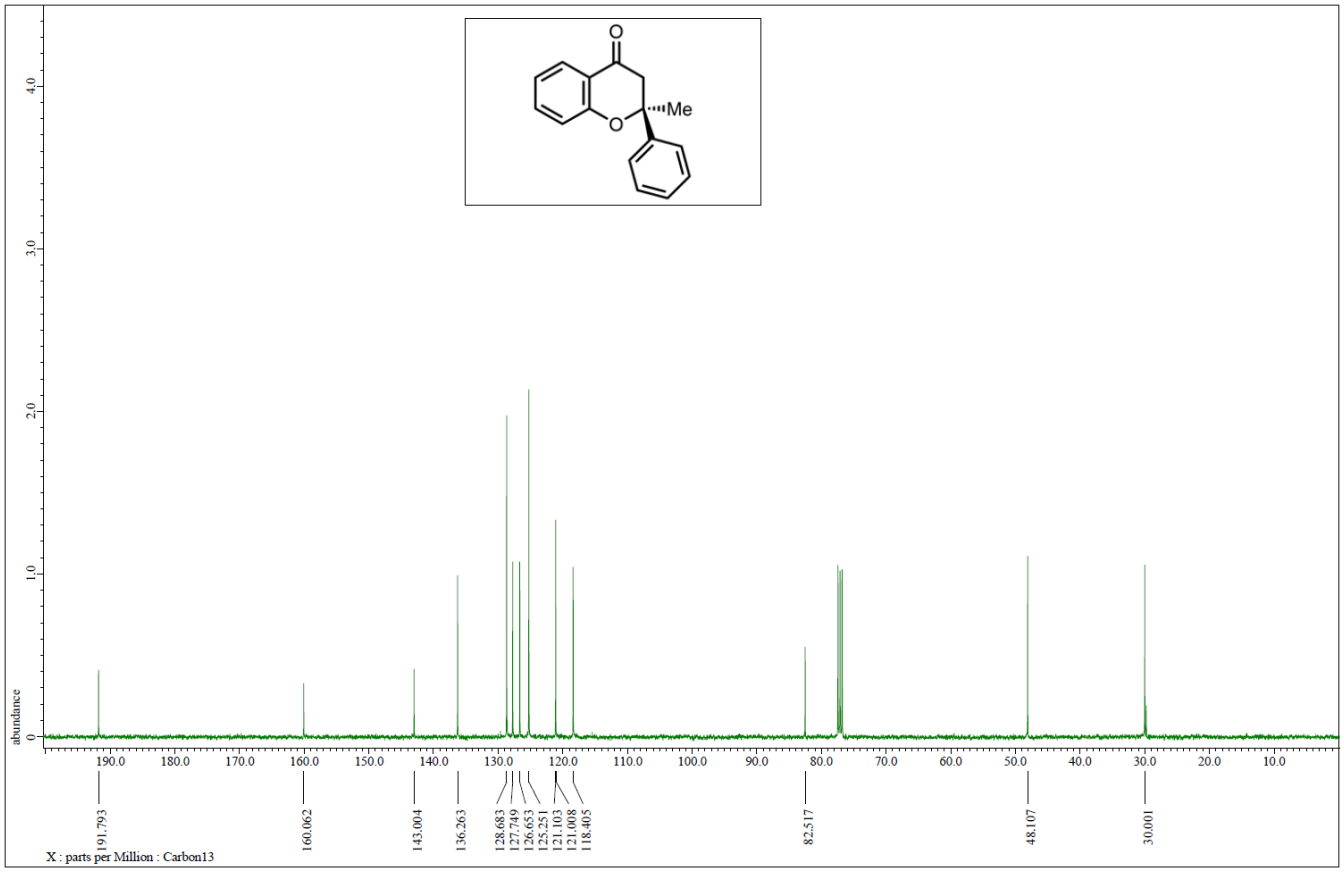

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
-110.0
-130.0
-150.0
-170.0
-190.0
-62.228
X : parts per Million : Fluorine19

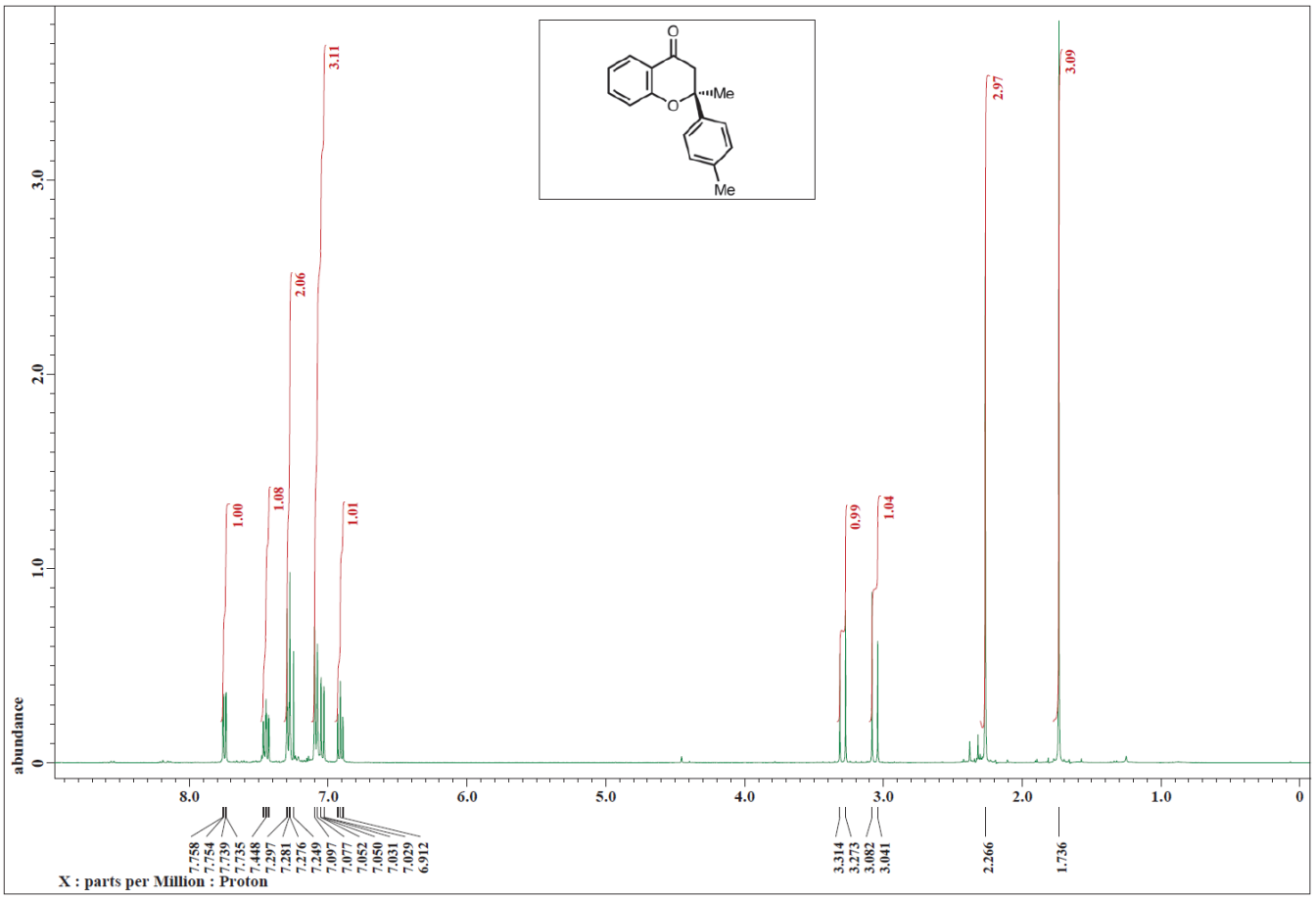

F3C
N
N
Pd
Cl
Cl
abundance
X : parts per Million : Proton
8.927
8.064
8.059
8.043
8.038
8.033
8.011
7.457
7.438
7.371
7.282
7.263
7.248
7.195
7.186
7.181
7.165
7.112
7.093
3.893
3.871
3.852
3.832
3.812
3.420
3.386
3.370
3.134
3.111
2.775
2.765
2.757
2.747
2.738
2.728
2.719
2.711
1.223
1.204
1.186

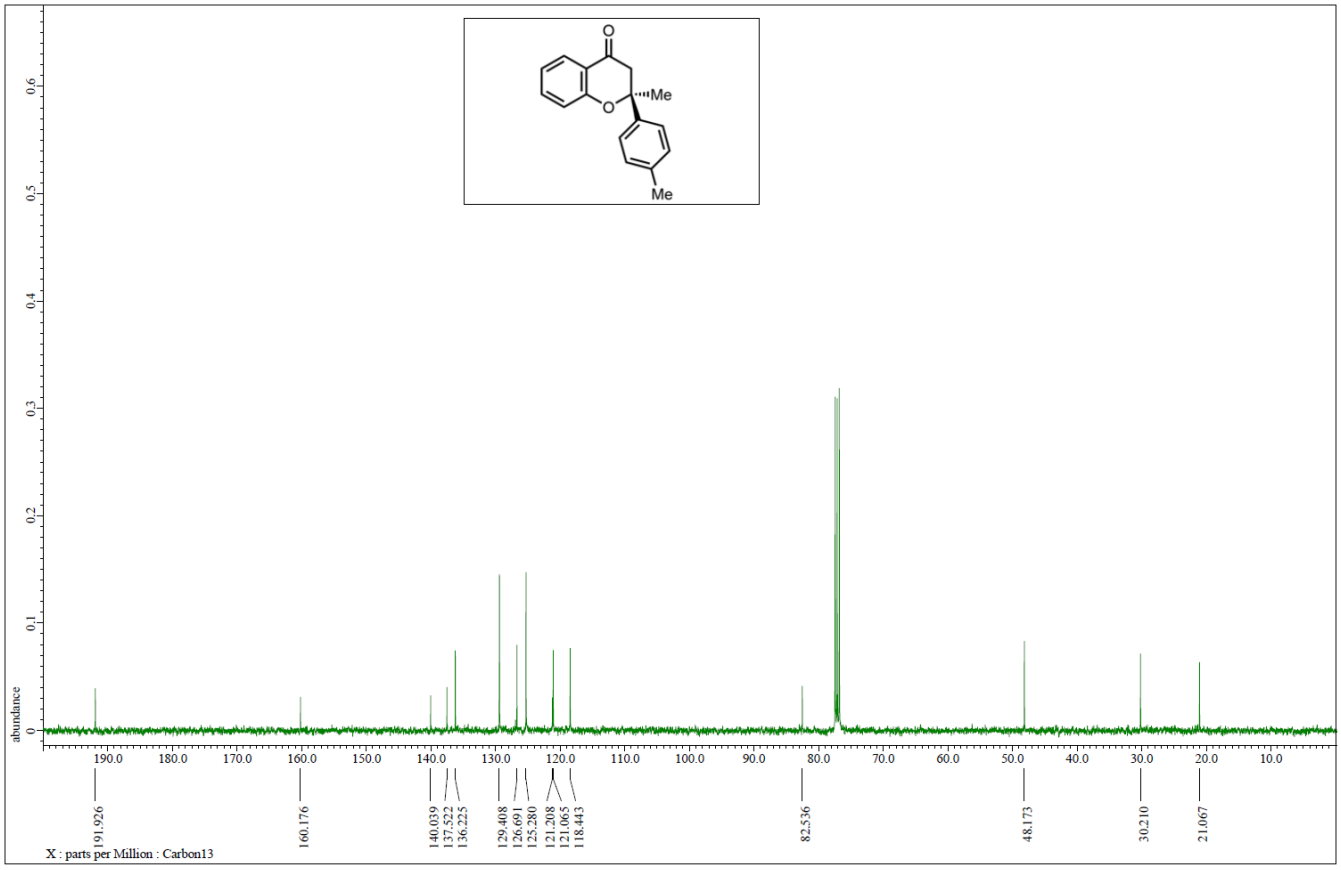

F3C
N
N
Pd
Cl
Cl
abundance
X : parts per Million : Carbon13
170.292
159.223
148.916
148.878
143.929
137.484
137.188
137.160
134.500
132.087
130.629
130.285
130.152
128.445
127.635
127.606
127.063
126.491
125.861
123.230
57.002
29.886
28.952
26.263
15.975

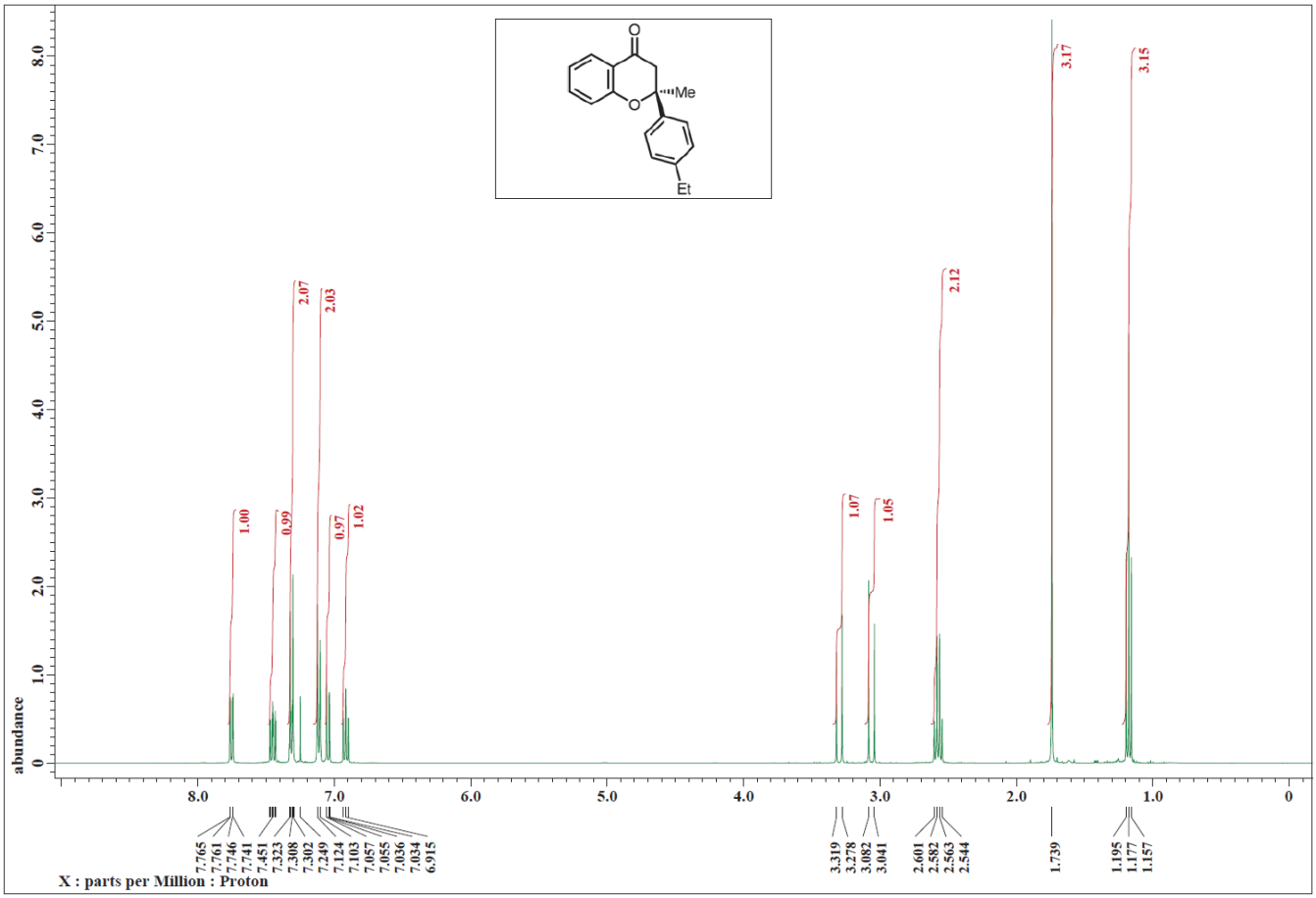

F3C
N
N
Pd
Cl
Cl
abundance
50.0
40.0
30.0
20.0
10.0
0
190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0
-62.566
X : parts per Million : Fluorine19

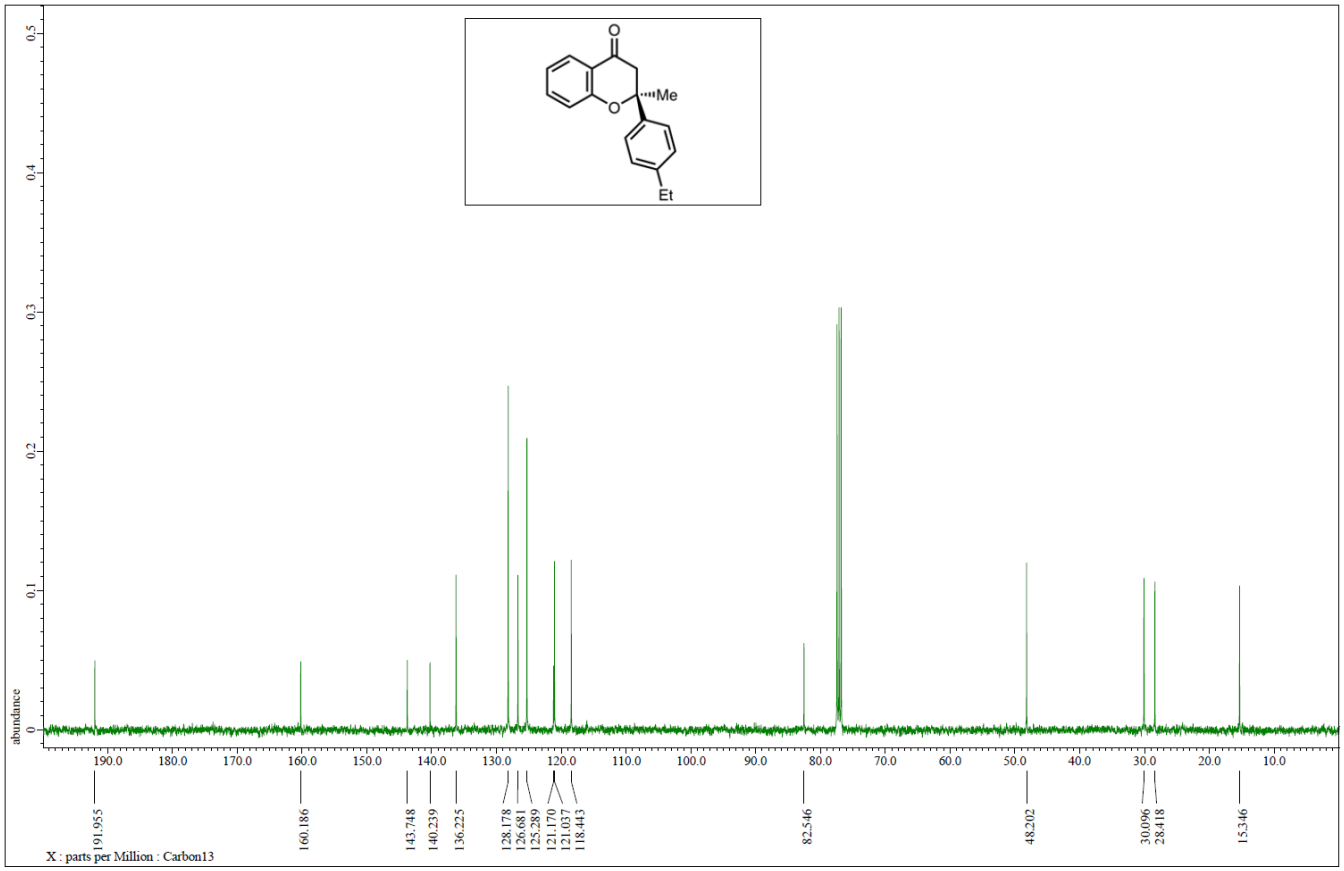

O
O
Me
abundance
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.17
3.05
3.09
1.00
0.98
0.99
1.03
1.02
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.767 7.763 7.747 7.743 7.455 7.450 7.437 7.424 7.420 7.405 7.402 7.072 7.070 7.051 7.049 6.937 6.934 6.917 6.899 6.897
3.331 3.290 3.104 3.063
1.748
X : parts per Million : Proton

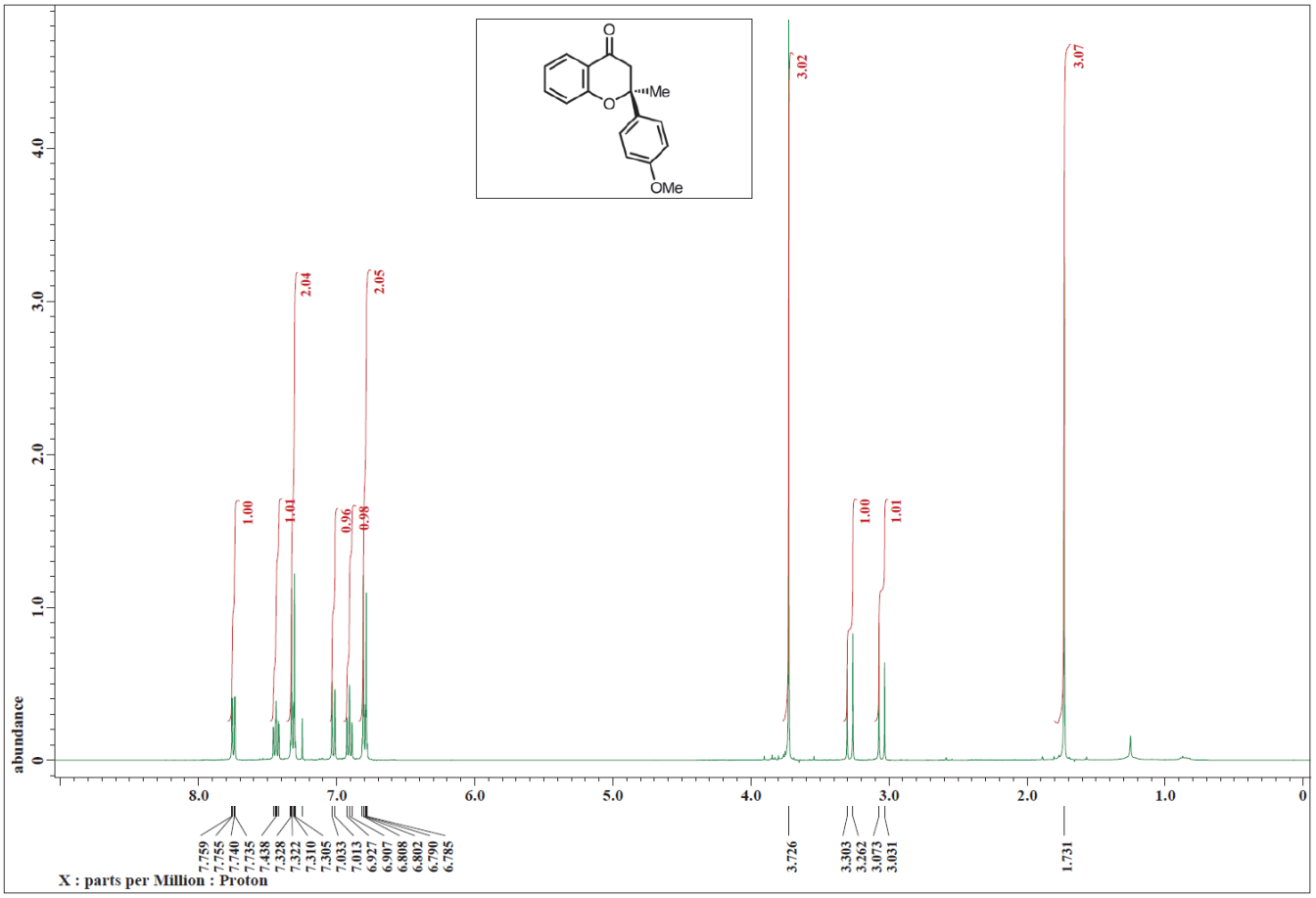

Me
abundance
191.793
160.062
143.004
136.263
128.683
127.749
126.653
125.251
121.103
121.008
118.405
82.517
48.107
30.001
X : parts per Million : Carbon13

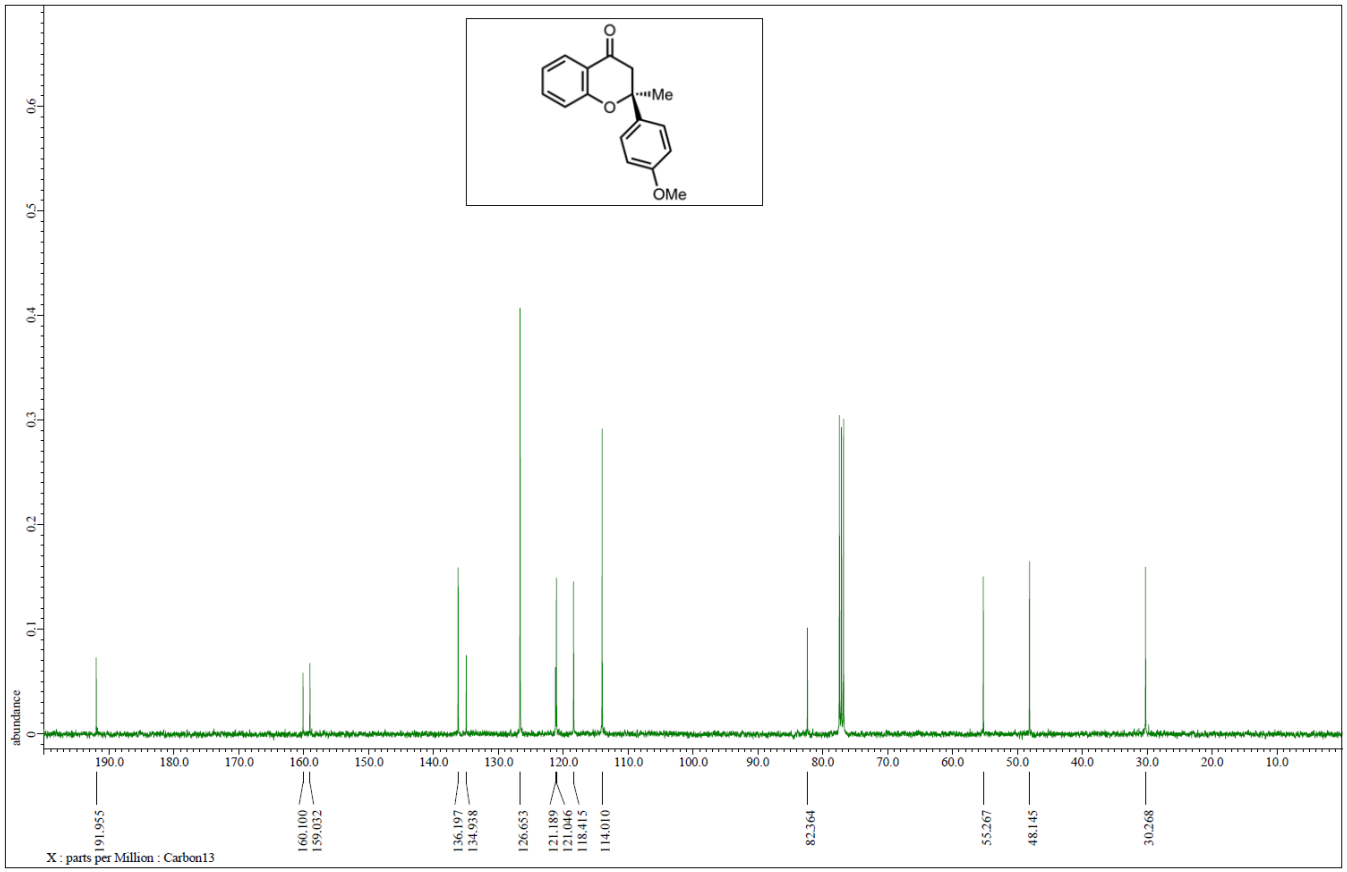

Me
Me
abundance
3.11
2.06
1.08
1.00
1.01
0.99
1.04
2.97
3.09
7.758
7.754
7.739
7.735
7.448
7.297
7.281
7.276
7.249
7.097
7.077
7.052
7.050
7.031
7.029
6.912
3.314
3.273
3.082
3.041
2.266
1.736
X : parts per Million : Proton

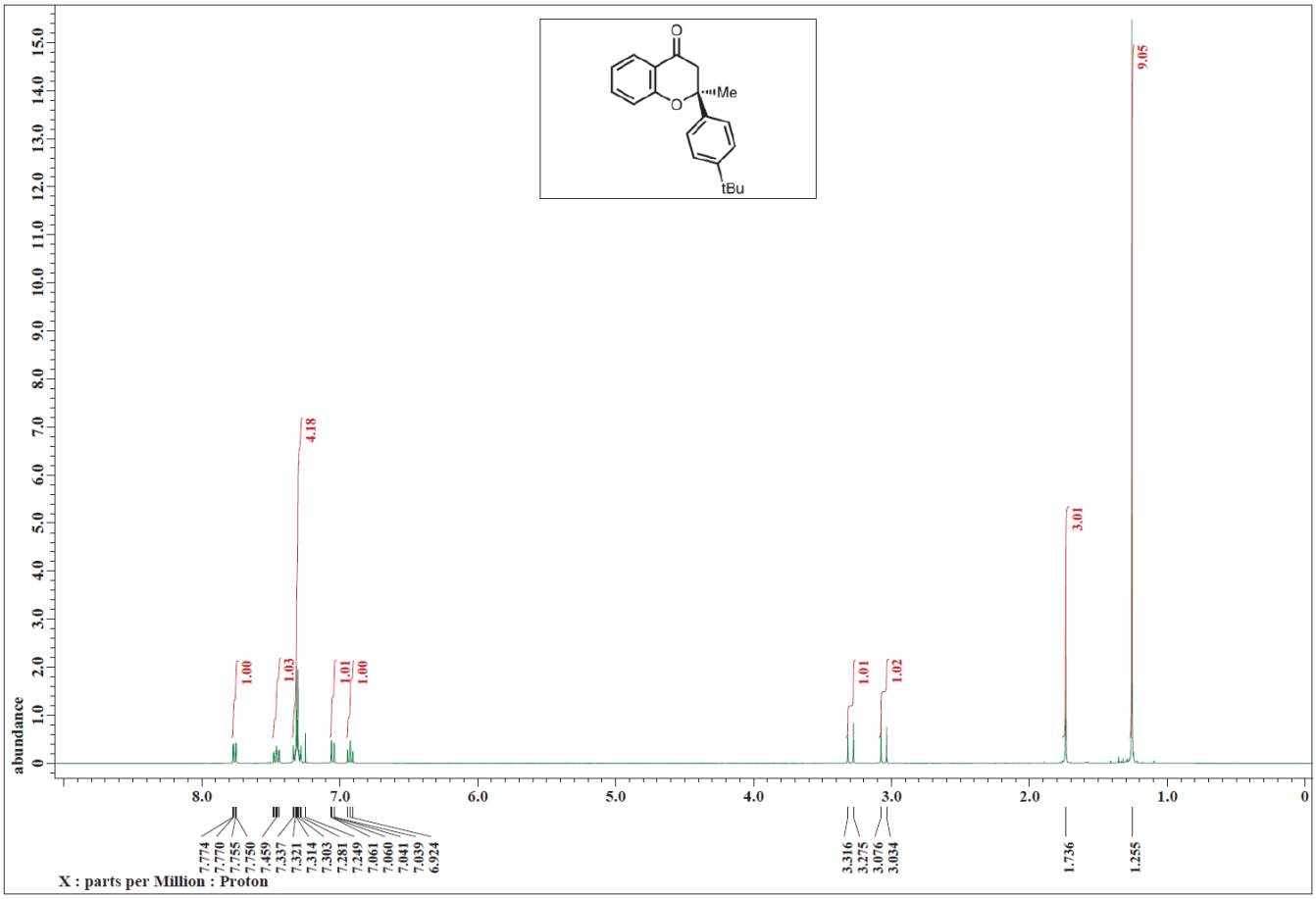

O
Me
O
Me
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
191.926
160.176
140.039
137.522
136.225
129.408
126.691
125.280
121.208
121.065
118.443
82.536
48.173
30.210
21.067
X : parts per Million : Carbon13

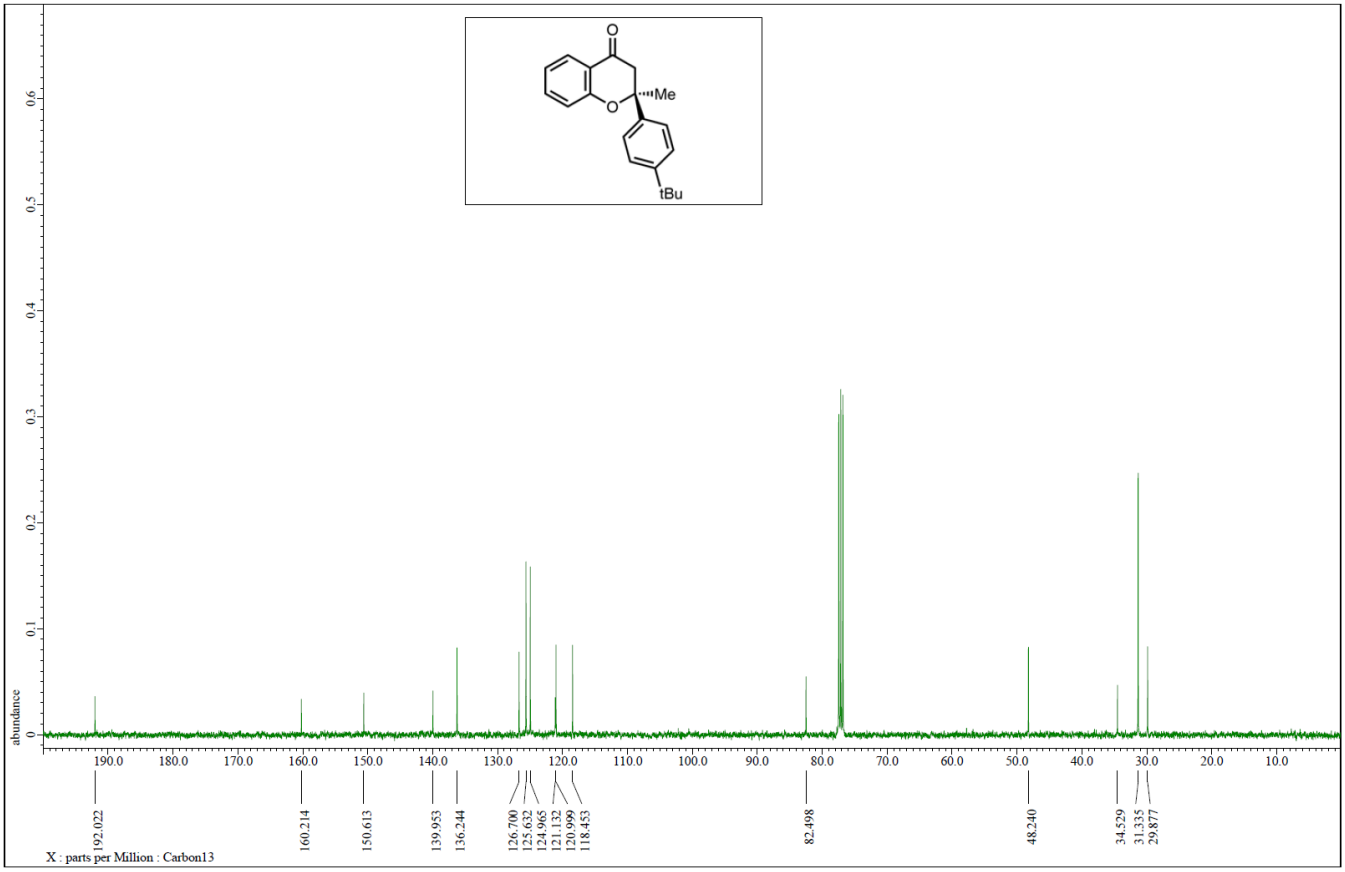

O
Me
O
Et
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
1.00
0.99
2.07
2.03
0.97
1.02
1.07
1.05
2.12
3.17
3.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.765
7.761
7.746
7.741
7.451
7.323
7.308
7.302
7.249
7.124
7.103
7.057
7.055
7.036
7.034
6.915
3.319
3.278
3.082
3.041
2.601
2.582
2.563
2.544
1.739
1.195
1.177
1.157
X : parts per Million : Proton

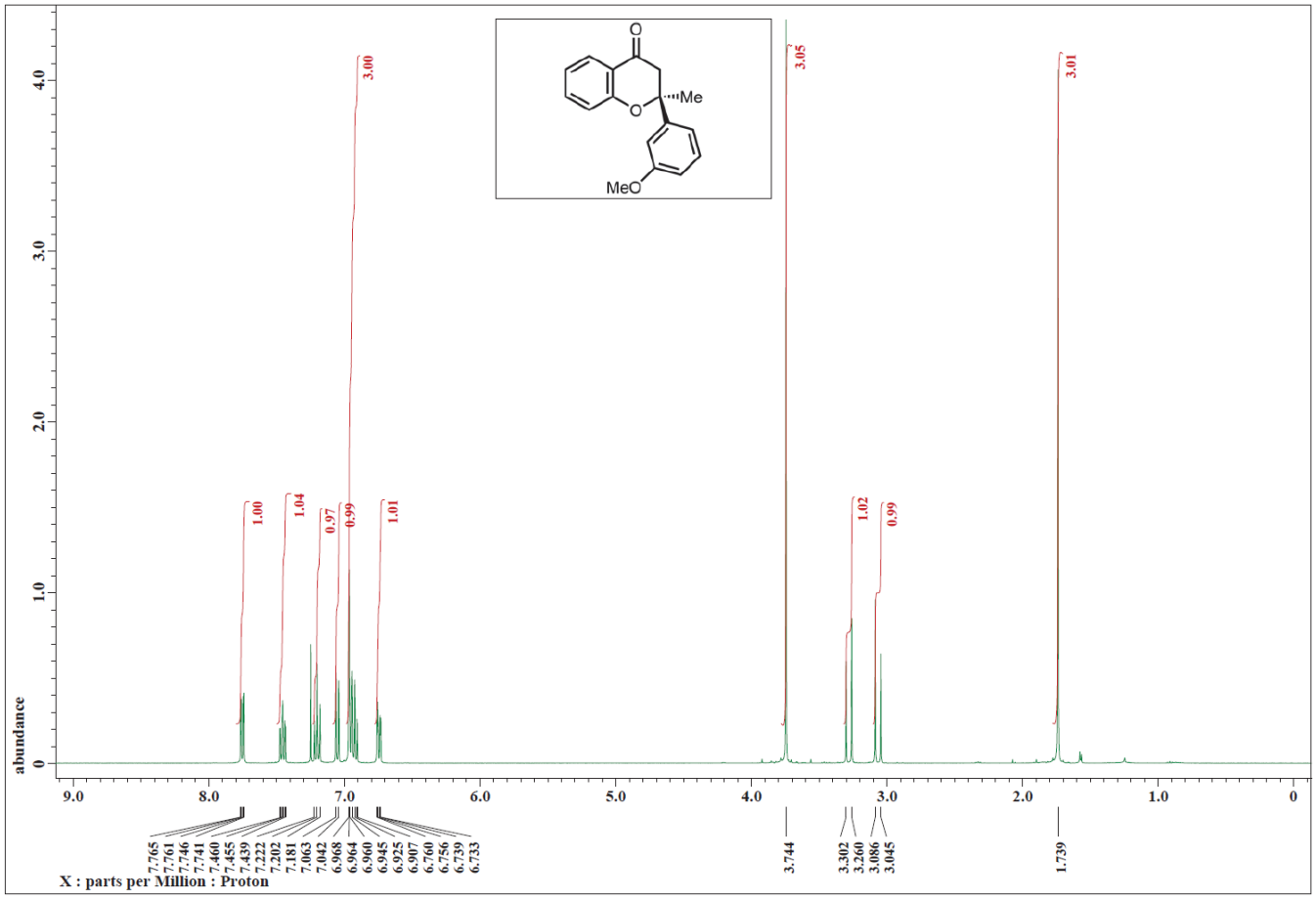

Me
Et
abundance
X : parts per Million : Carbon13
191.955
160.186
143.748
140.239
136.225
128.178
126.681
125.289
121.170
121.037
118.443
82.546
48.202
30.096
28.418
15.346

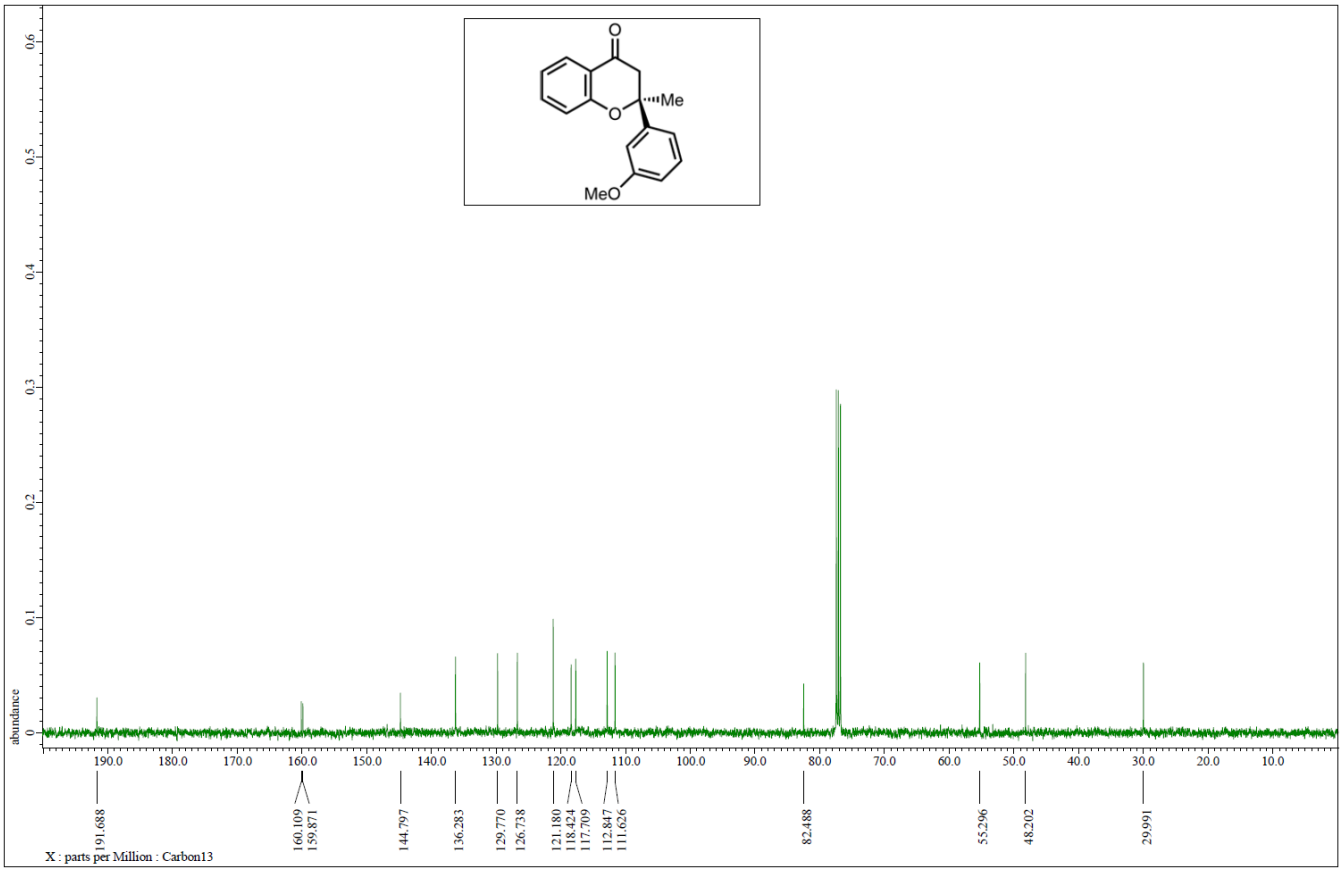

Me
OMe
abundance
X : parts per Million : Proton
1.00
1.01
2.04
0.96
0.98
2.05
3.02
1.00
1.01
3.07
7.759
7.755
7.740
7.735
7.438
7.328
7.322
7.310
7.305
7.033
7.013
6.927
6.907
6.808
6.802
6.790
6.785
3.726
3.303
3.262
3.073
3.031
1.731

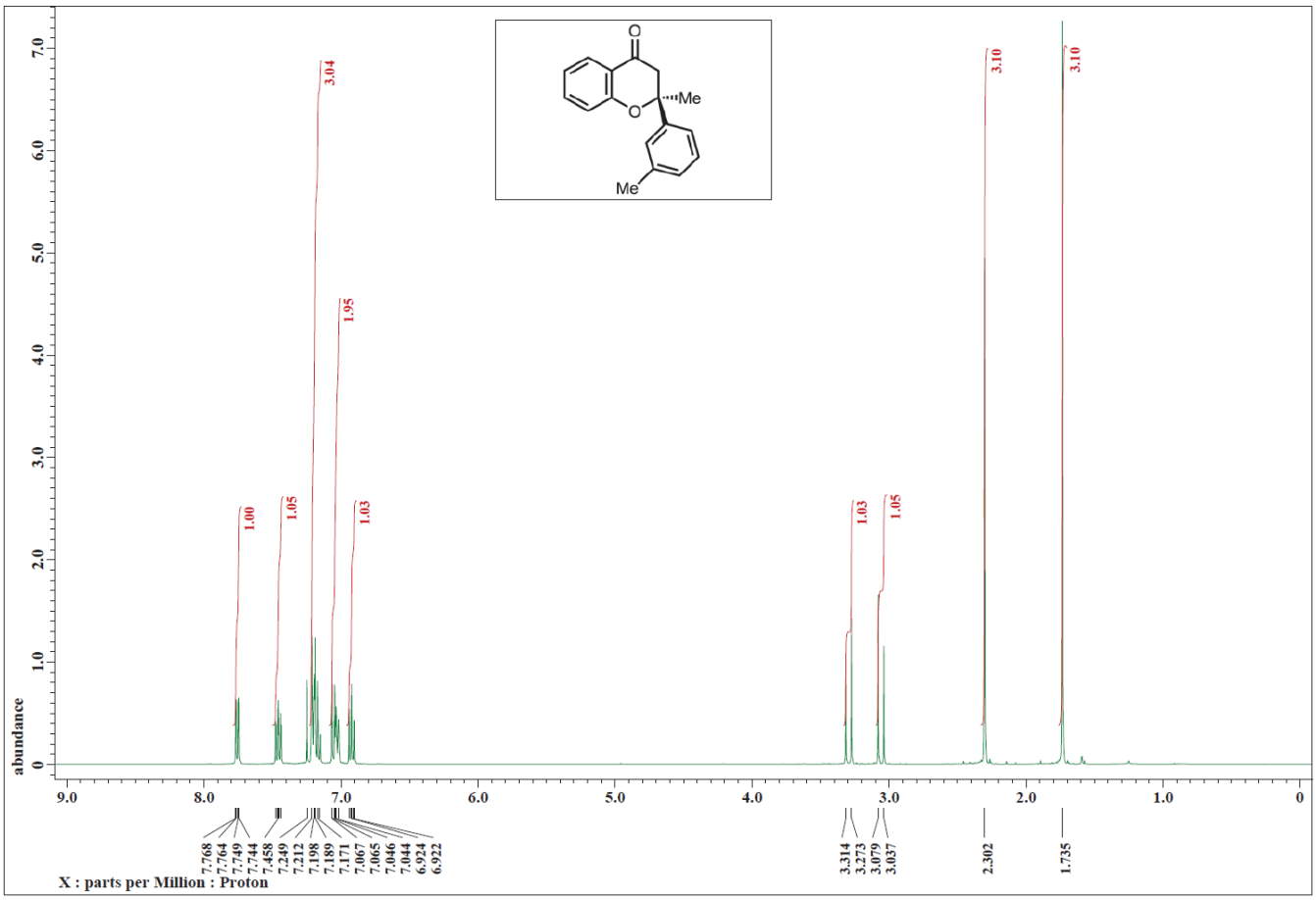

O
Me
O
OMe
abundance
191.955
160.100
159.052
136.197
134.938
126.653
121.189
121.046
118.415
114.010
82.364
55.267
48.145
30.268
X : parts per Million : Carbon13

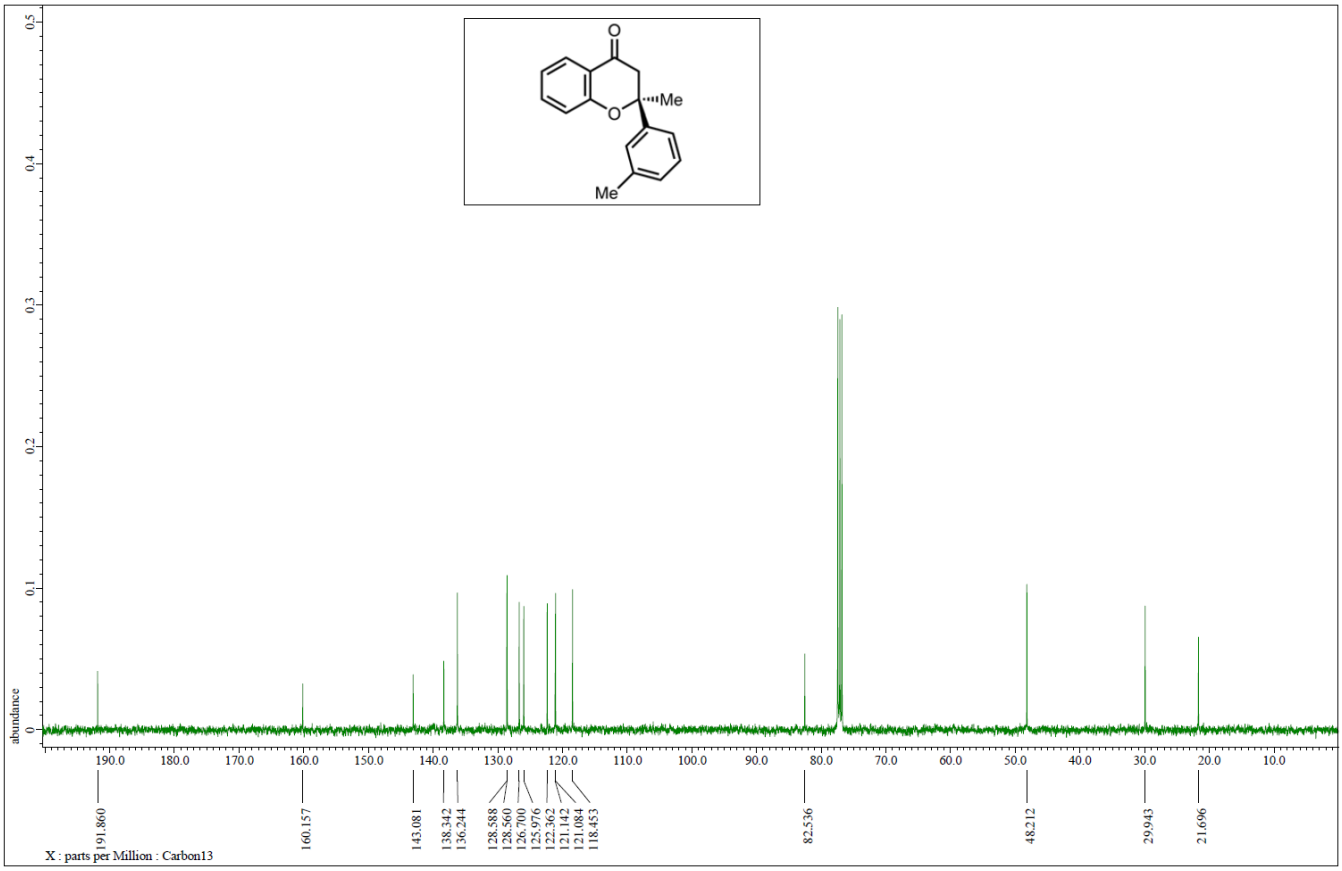

O
Me
O
tBu
abundance
4.18
9.05
3.01
1.00
1.03
1.01
1.00
1.01
1.02
7.774
7.770
7.755
7.750
7.459
7.337
7.321
7.314
7.303
7.281
7.249
7.061
7.060
7.041
7.039
6.924
3.316
3.275
3.076
3.034
1.736
1.255
X : parts per Million : Proton

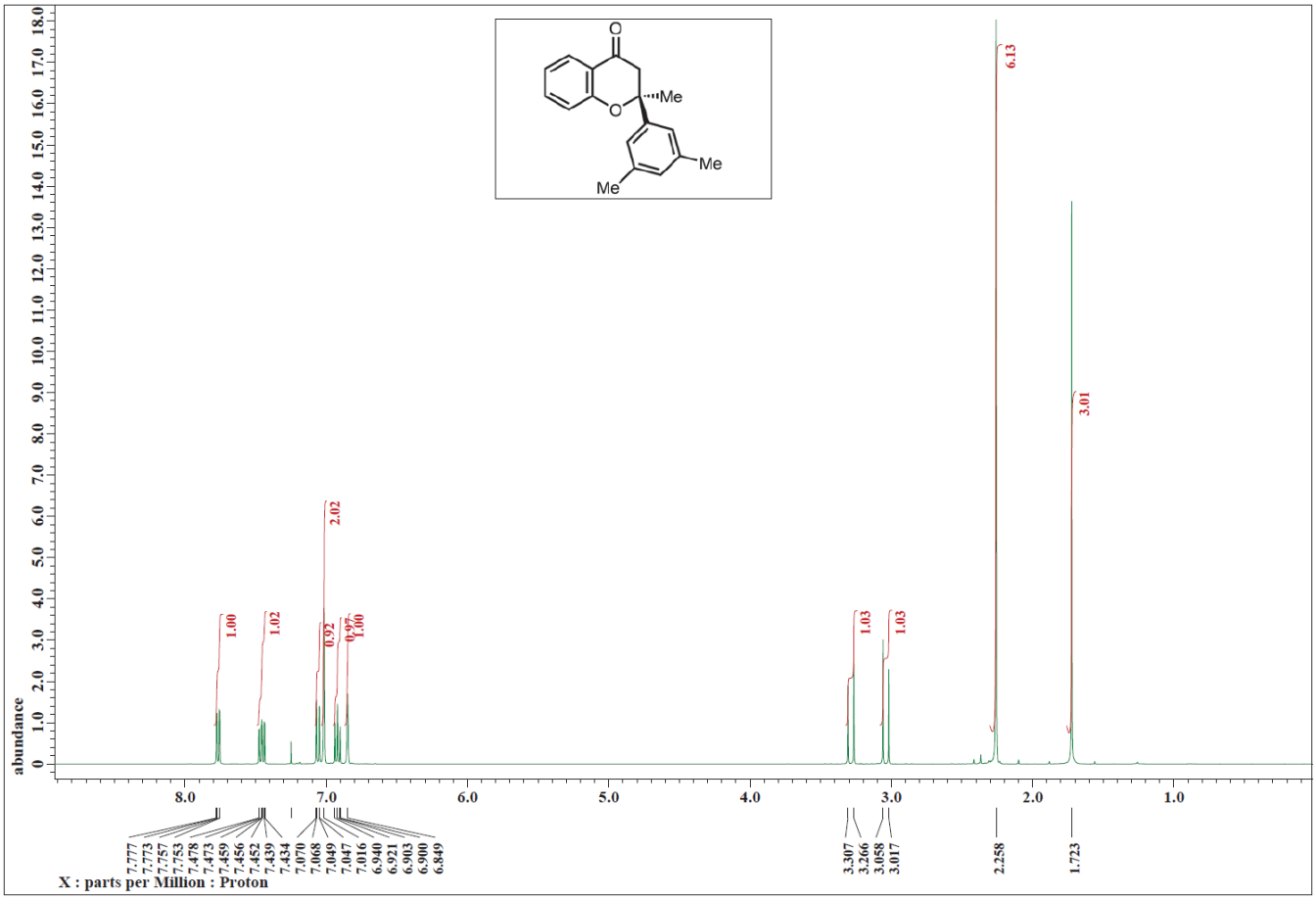

O
Me
tBu
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
192.022
160.214
150.613
139.953
136.244
126.700
125.632
124.965
121.132
120.999
118.453
82.498
48.240
34.529
31.335
29.877
X : parts per Million : Carbon13

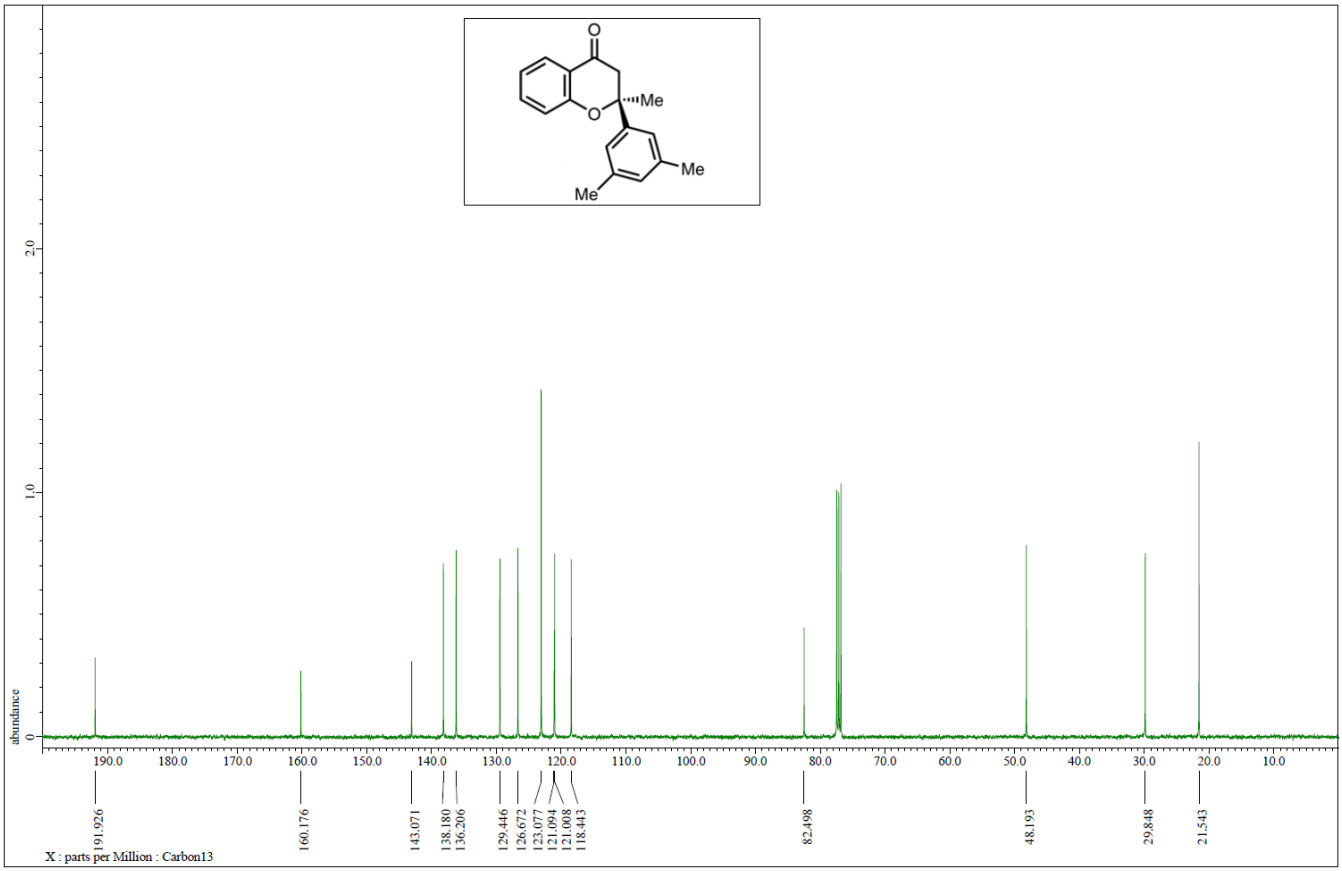

O
Me
MeO
abundance
0
1.0
2.0
3.0
4.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.00
1.00
1.04
0.97
0.99
1.01
3.05
1.02
0.99
3.01
7.765
7.761
7.746
7.741
7.460
7.455
7.439
7.222
7.202
7.181
7.063
7.042
6.968
6.964
6.960
6.945
6.925
6.907
6.760
6.756
6.739
6.733
3.744
3.302
3.260
3.086
3.045
1.739
X : parts per Million : Proton

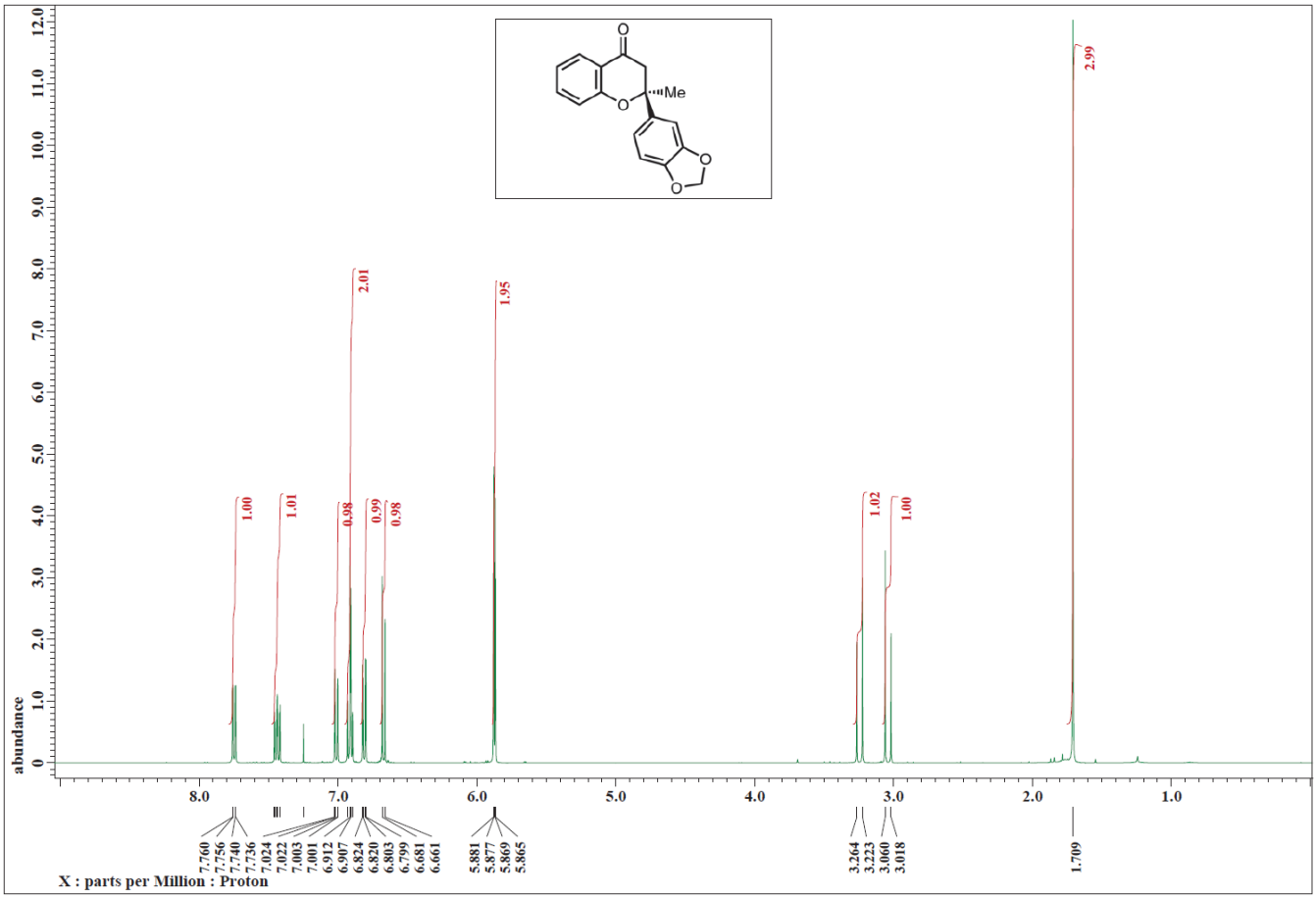

O
Me
O
MeO
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
191.688
160.109
159.871
144.797
136.283
129.770
126.738
121.180
118.424
117.709
112.847
111.626
82.488
55.296
48.202
29.991
X : parts per Million : Carbon13

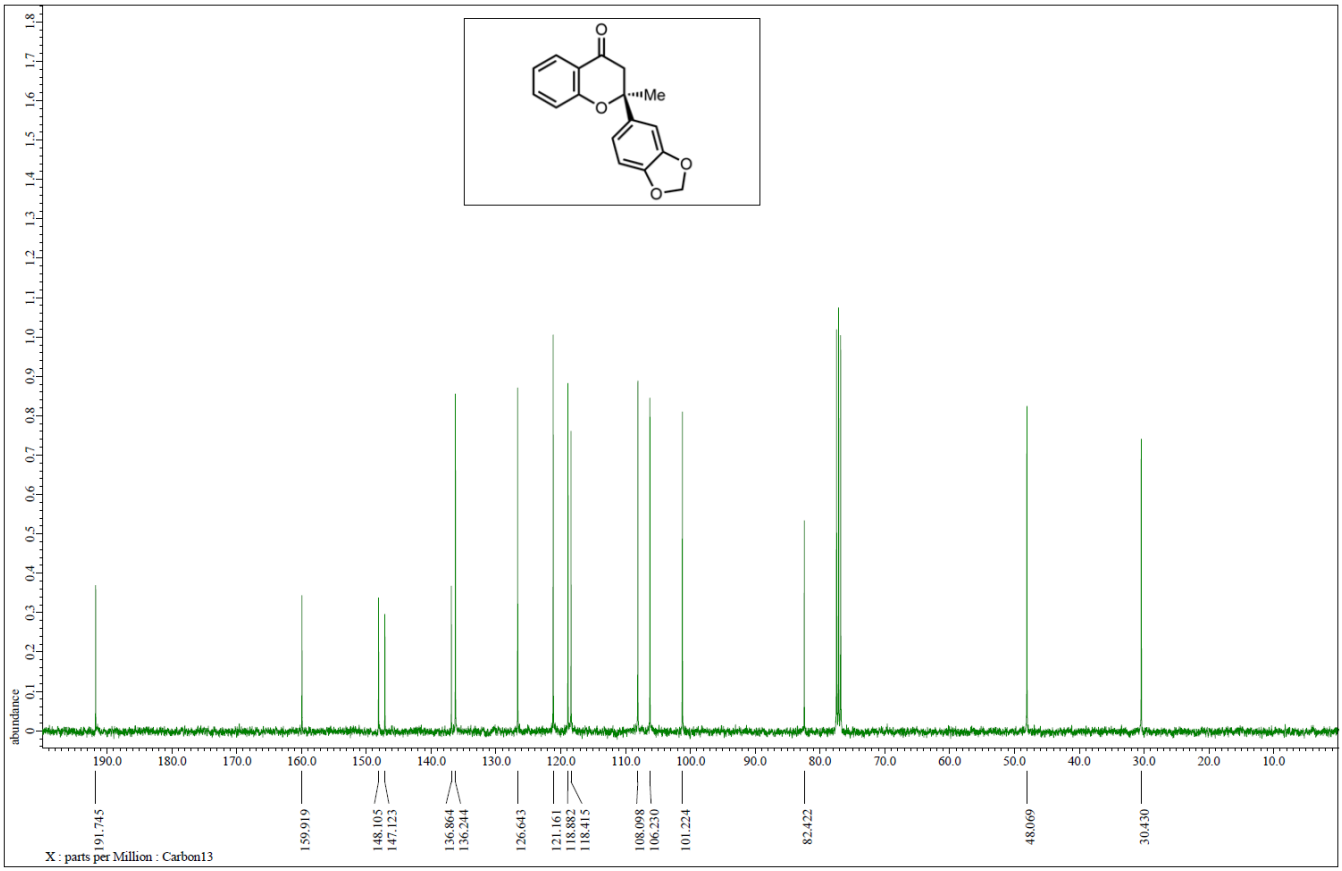

O
Me
Me
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
1.00
1.05
3.04
1.95
1.03
1.03
1.05
3.10
3.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.768
7.764
7.749
7.744
7.458
7.249
7.212
7.198
7.189
7.171
7.067
7.065
7.046
7.044
6.924
6.922
3.314
3.273
3.079
3.037
2.302
1.735
X : parts per Million : Proton

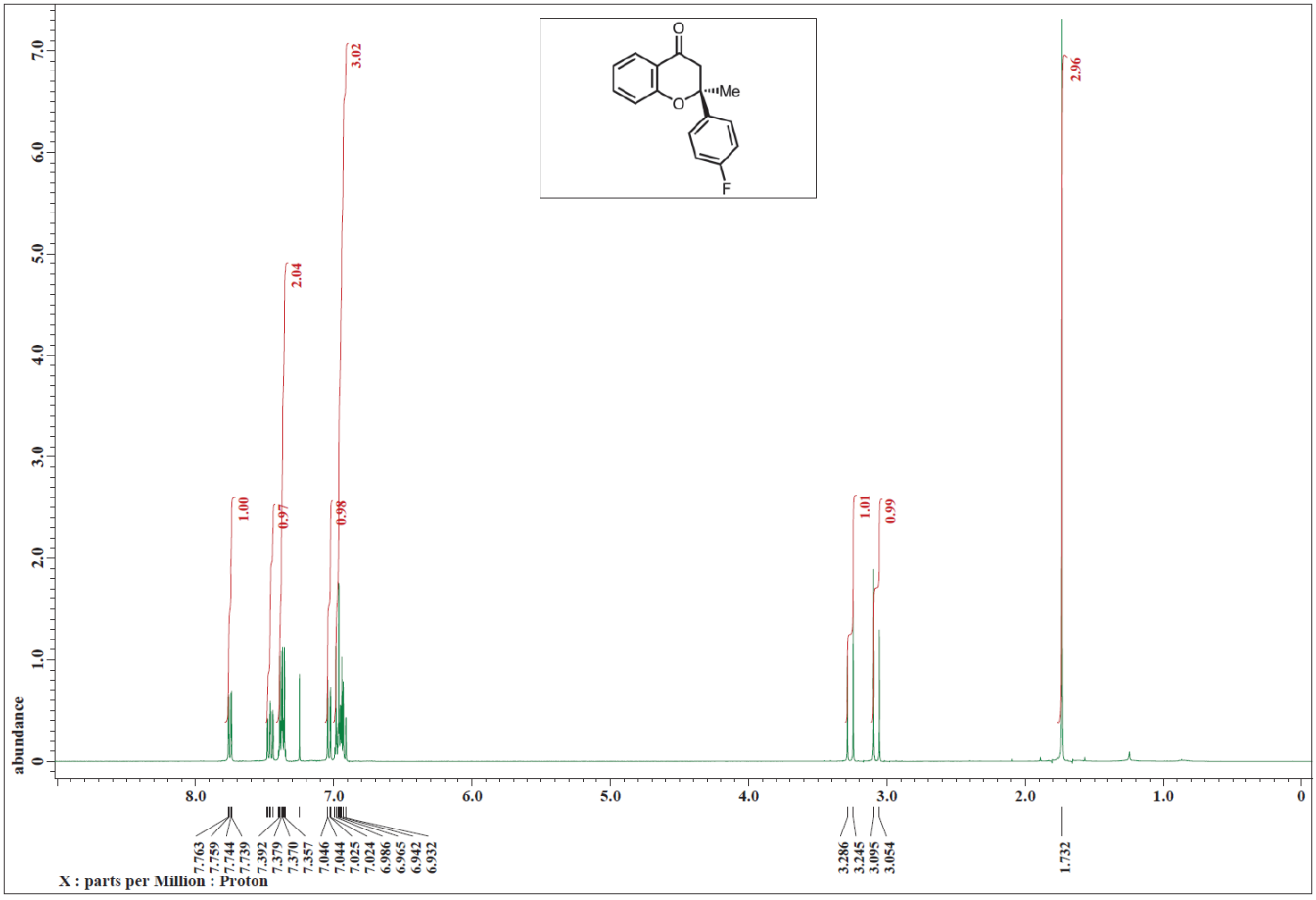

O
Me
O
Me
abundance
0
0.1
0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
191.860
160.157
143.081
138.342
136.244
128.588
128.560
126.700
125.976
122.362
121.142
121.084
118.453
82.536
48.212
29.943
21.696
X : parts per Million : Carbon13

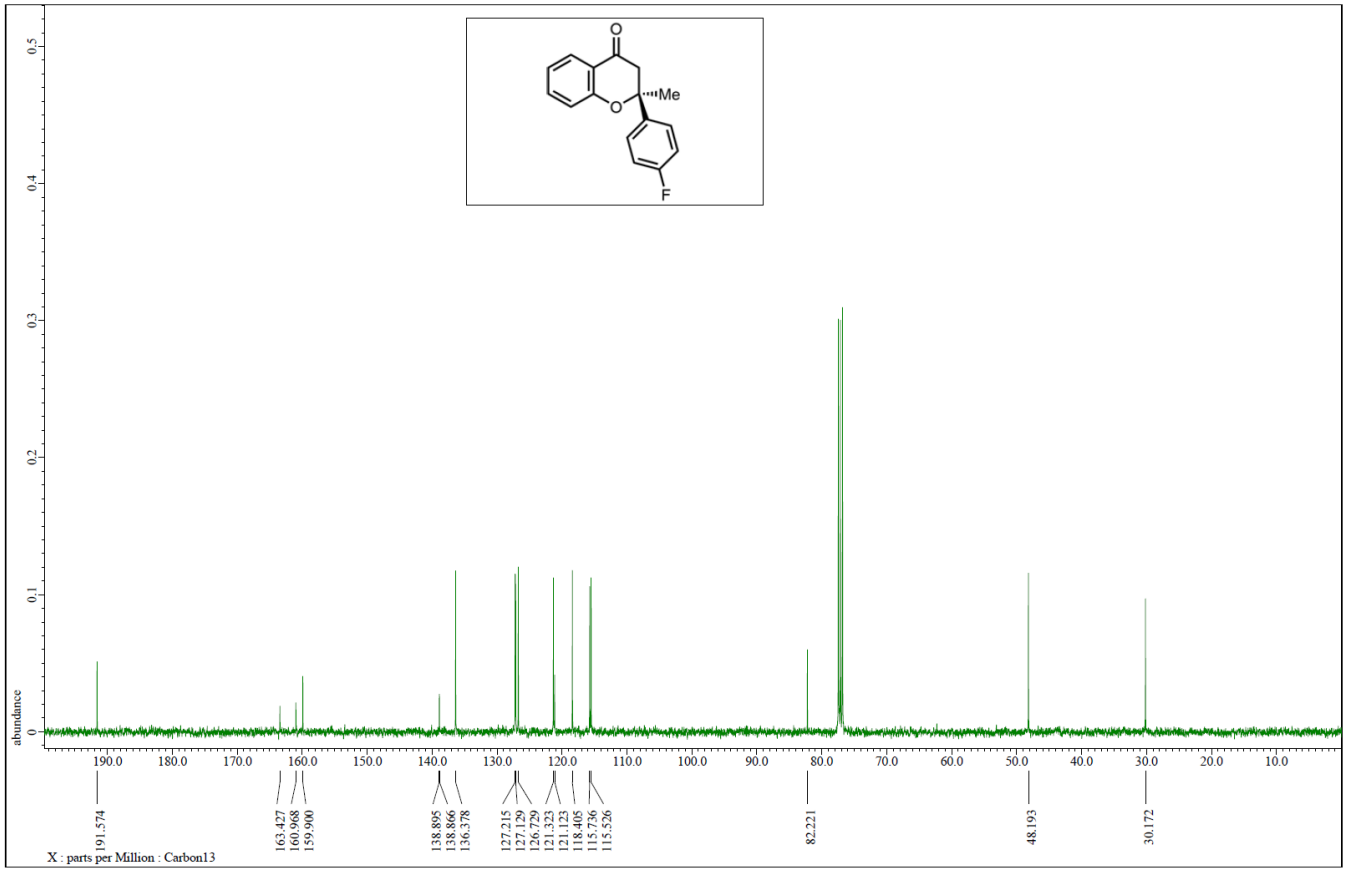

O
Me
Me
Me
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
1.00
1.02
2.02
0.92
0.97
1.00
1.03
1.03
6.13
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.777
7.773
7.757
7.753
7.478
7.473
7.459
7.456
7.452
7.439
7.434
7.070
7.068
7.049
7.047
7.016
6.940
6.921
6.903
6.900
6.849
3.307
3.266
3.058
3.017
2.258
1.723
X : parts per Million : Proton

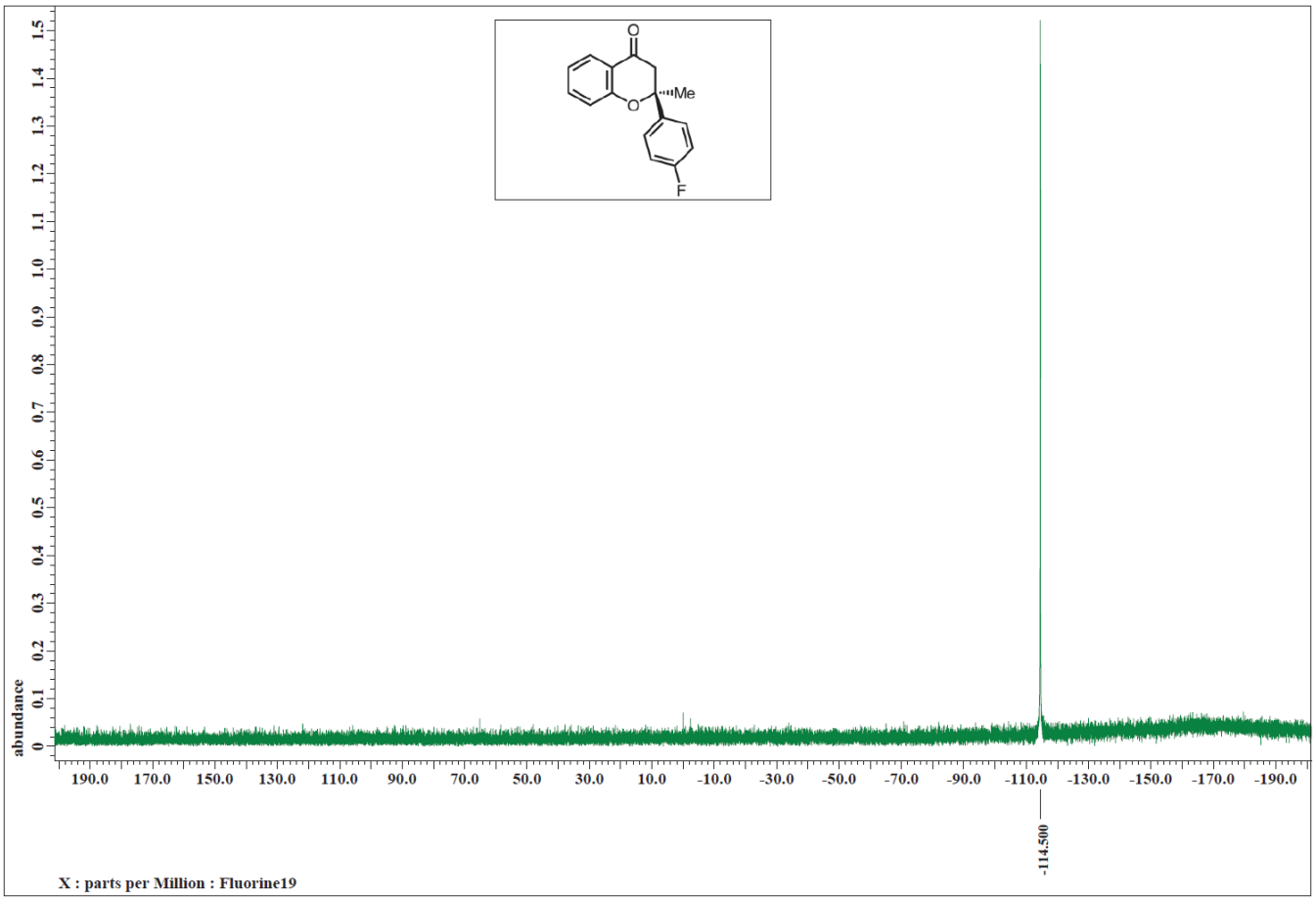

Me
Me
Me
abundance
X : parts per Million : Carbon13
191.926
160.176
143.071
138.180
136.206
129.446
126.672
123.077
121.094
121.008
118.443
82.498
48.193
29.848
21.543

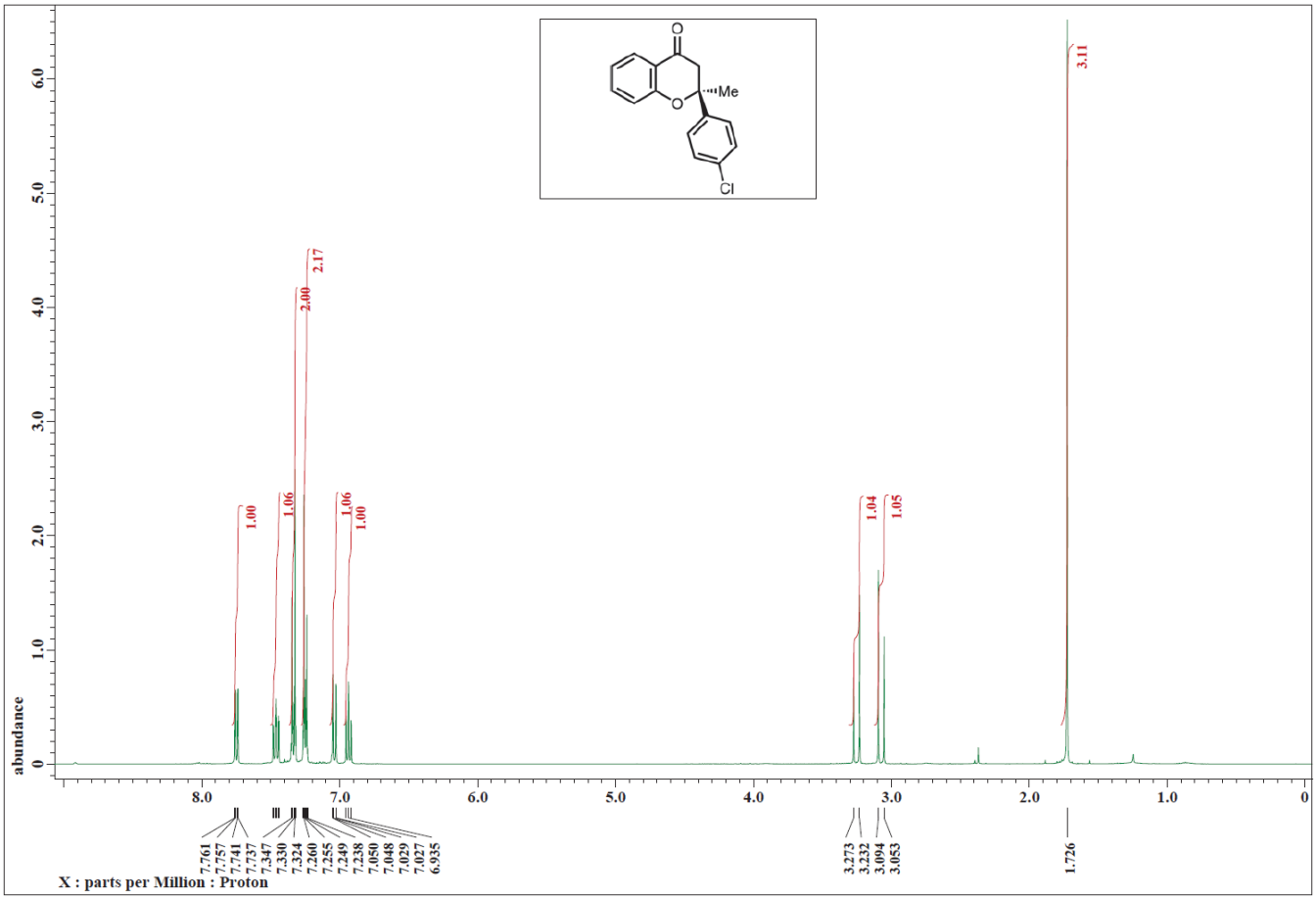

Me
abundance
X : parts per Million : Proton
1.00
1.01
0.98
2.01
0.99
0.98
1.95
1.02
1.00
2.99
7.760
7.756
7.740
7.736
7.024
7.022
7.003
7.001
6.912
6.907
6.824
6.820
6.803
6.799
6.681
6.661
5.881
5.877
5.869
5.865
3.264
3.223
3.060
3.018
1.709

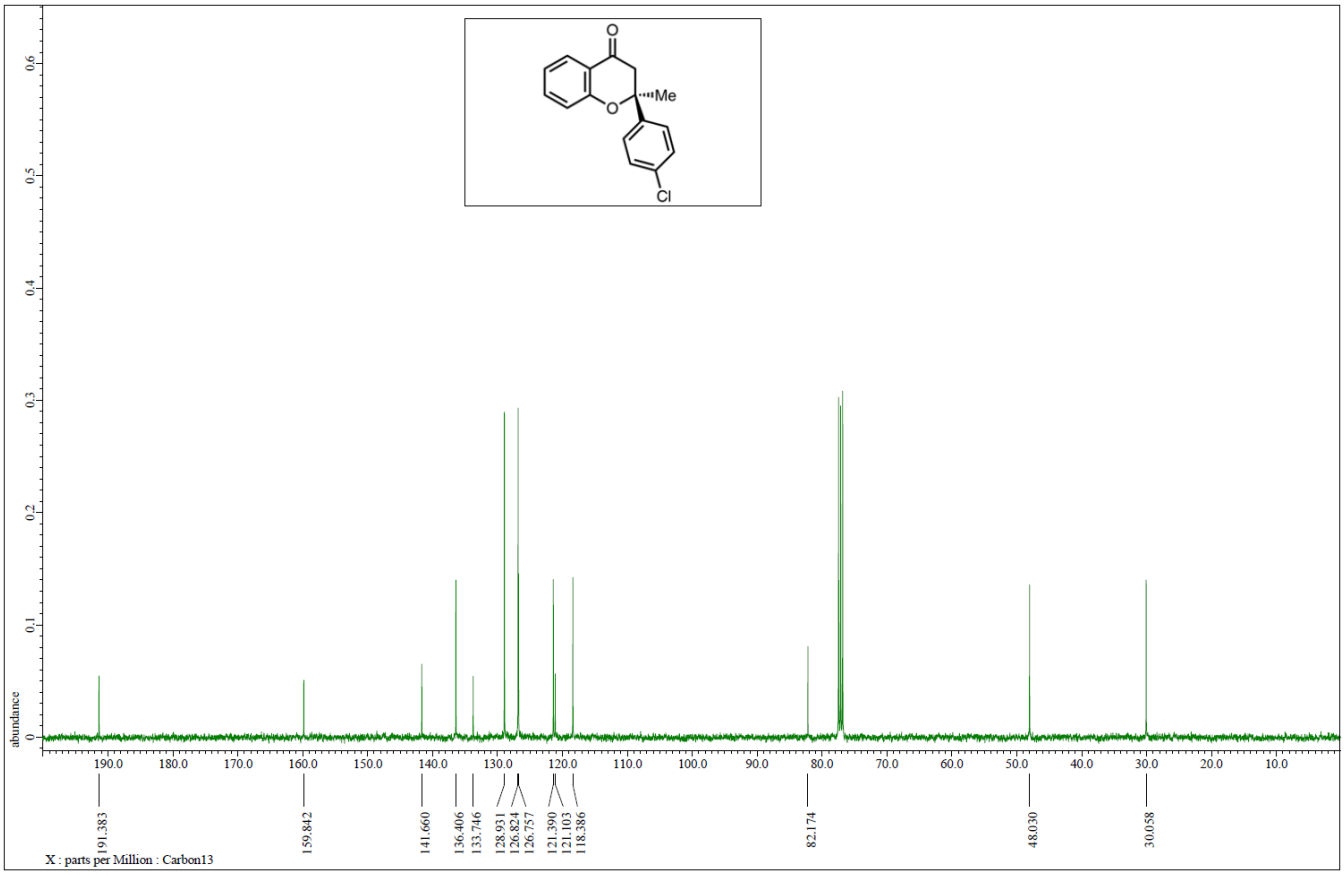

Me
O
O
O
abundance
X : parts per Million : Carbon13
191.745
159.919
148.105
147.123
136.864
136.244
126.643
121.161
118.882
118.415
108.098
106.230
101.224
82.422
48.069
30.430

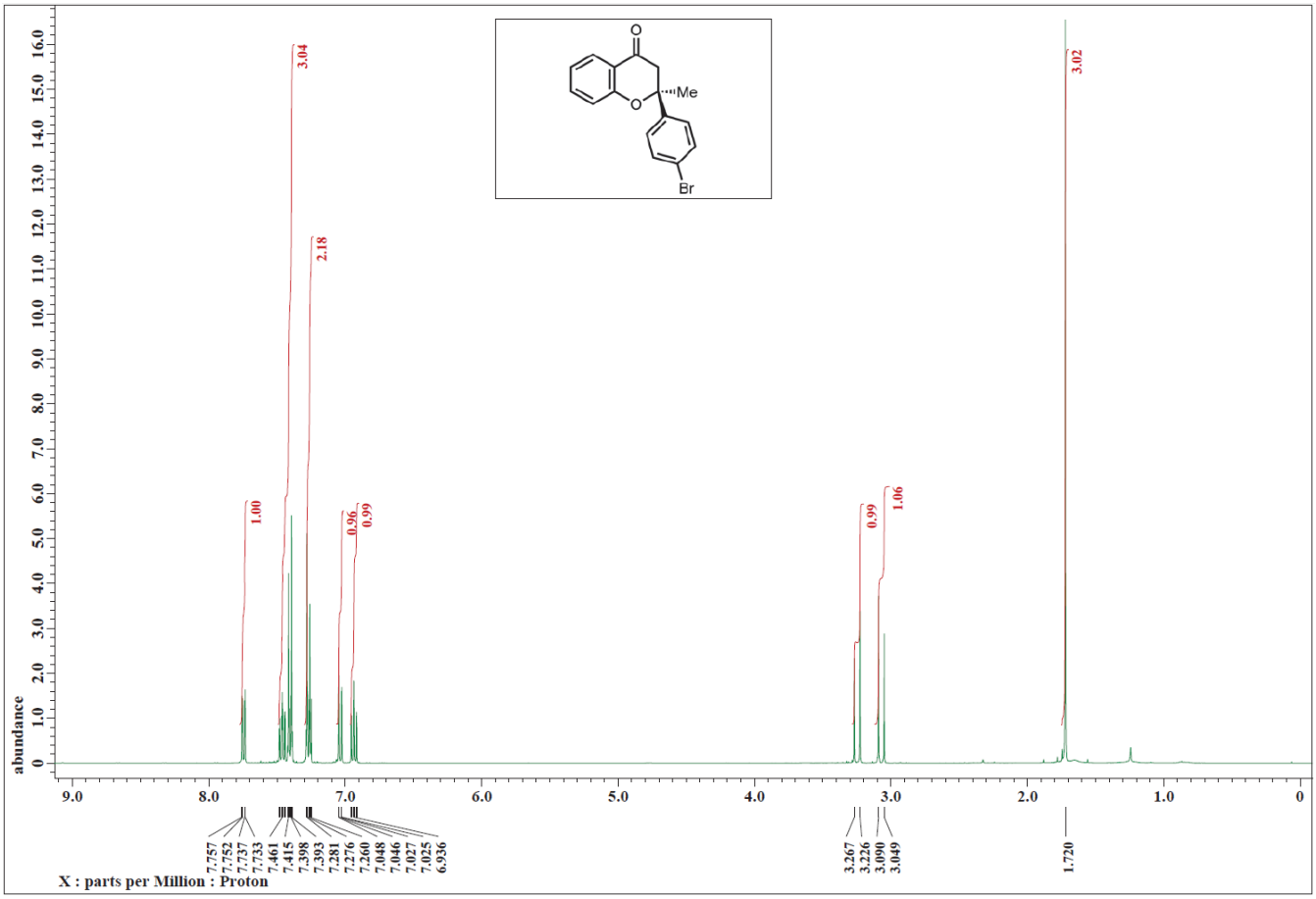

Me
O
O
F
abundance
X : parts per Million : Proton
1.00
0.97
2.04
0.98
3.02
1.01
0.99
2.96
7.763
7.759
7.744
7.739
7.392
7.379
7.370
7.357
7.046
7.044
7.025
7.024
6.986
6.965
6.942
6.932
3.286
3.245
3.095
3.054
1.732

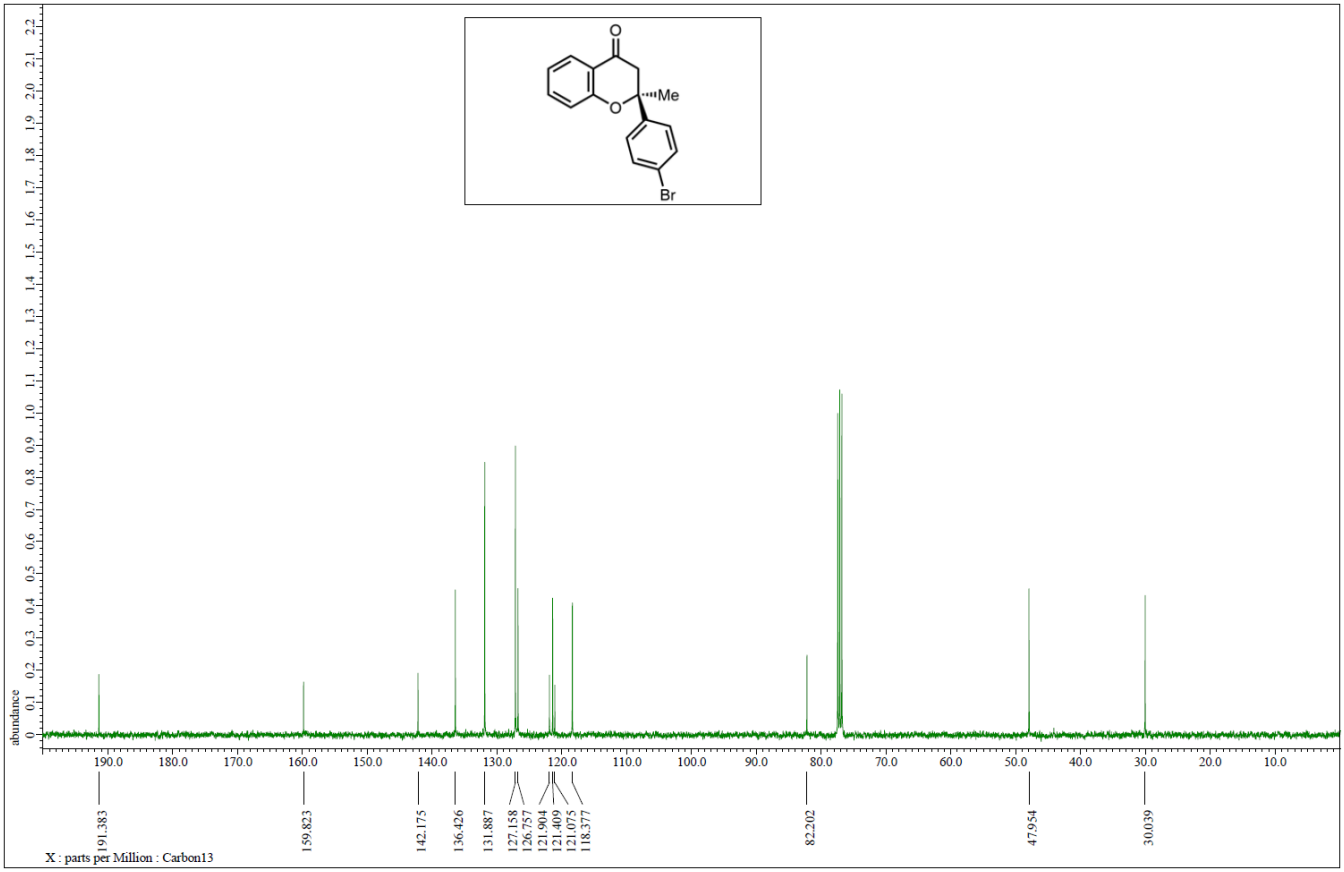

O
Me
O
F
abundance
0
0.1
0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
191.574
163.427
160.968
159.900
138.895
138.866
136.378
127.215
127.129
126.729
121.323
121.123
118.405
115.736
115.526
82.221
48.193
30.172
X : parts per Million : Carbon13

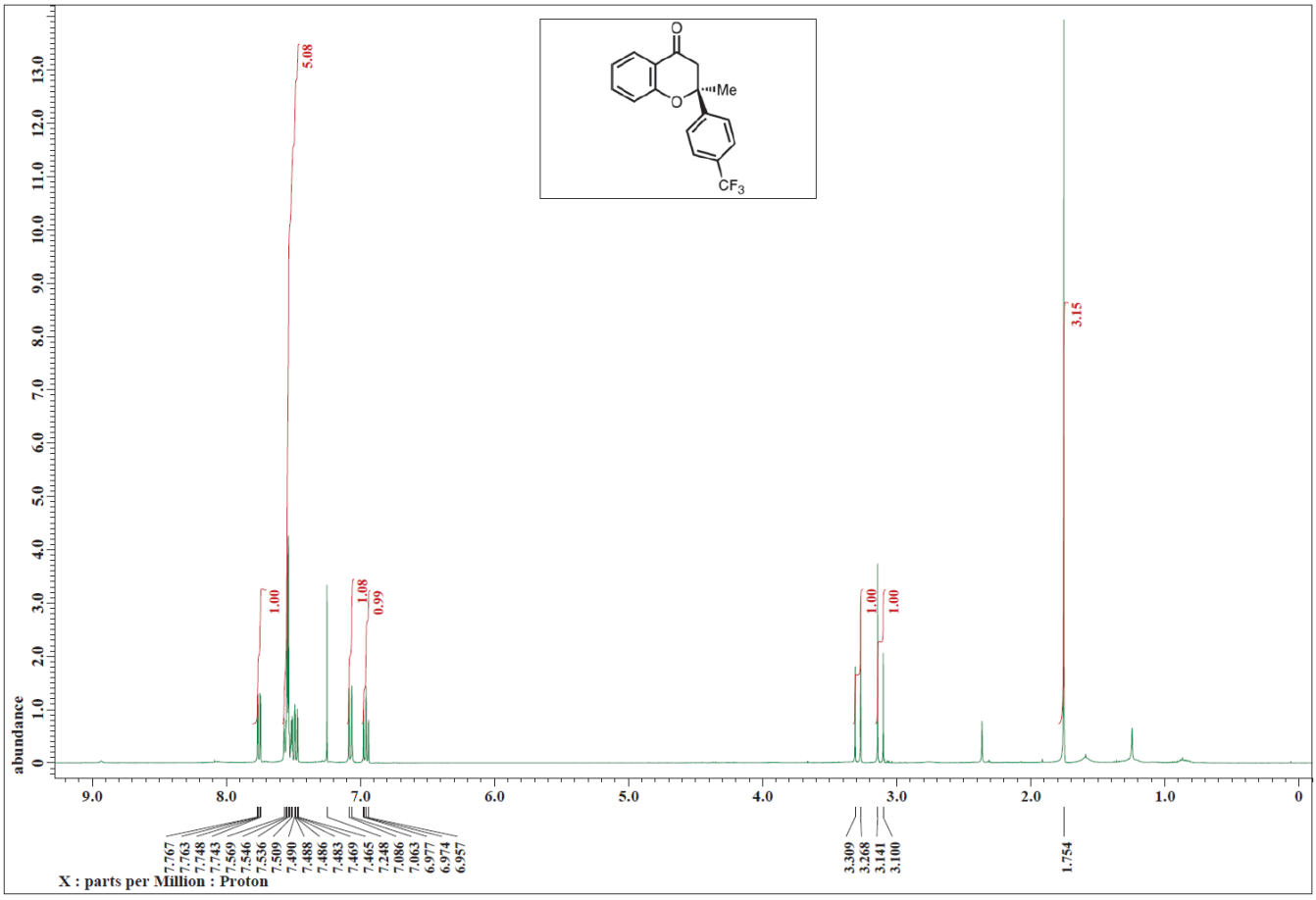

O
Me
O
F
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
-110.0
-130.0
-150.0
-170.0
-190.0
-114.500
X : parts per Million : Fluorine19

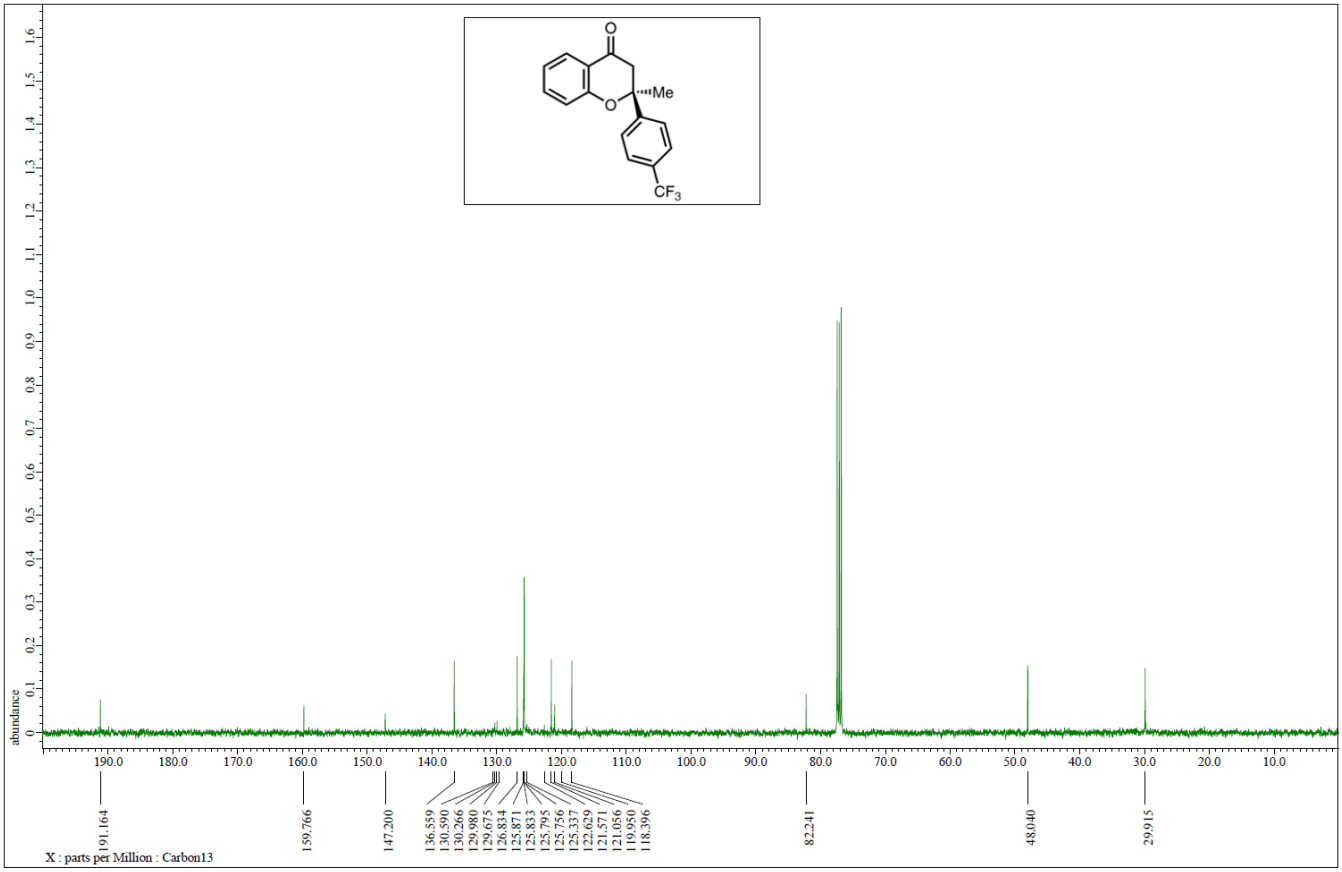

O
Me
O
Cl
3.11
2.17
2.00
1.06
1.06
1.00
1.00
1.04
1.05
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.761
7.757
7.741
7.737
7.347
7.330
7.324
7.260
7.255
7.249
7.238
7.050
7.048
7.029
7.027
6.935
3.273
3.232
3.094
3.053
1.726
X : parts per Million : Proton

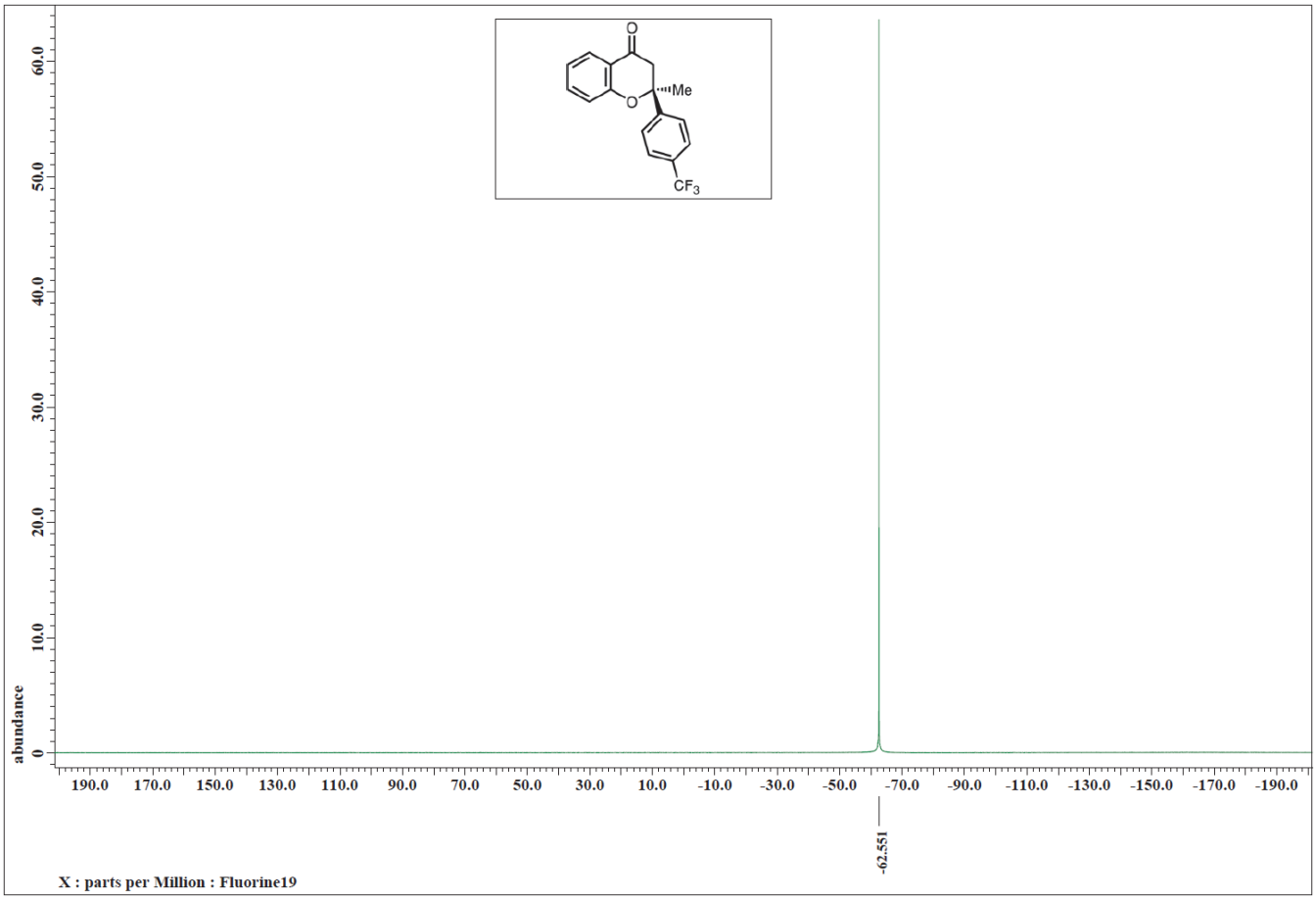

O
Me
O
Cl
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
191.383
159.842
141.660
136.406
133.746
128.931
126.824
126.757
121.390
121.103
118.386
82.174
48.030
30.058
X : parts per Million : Carbon13

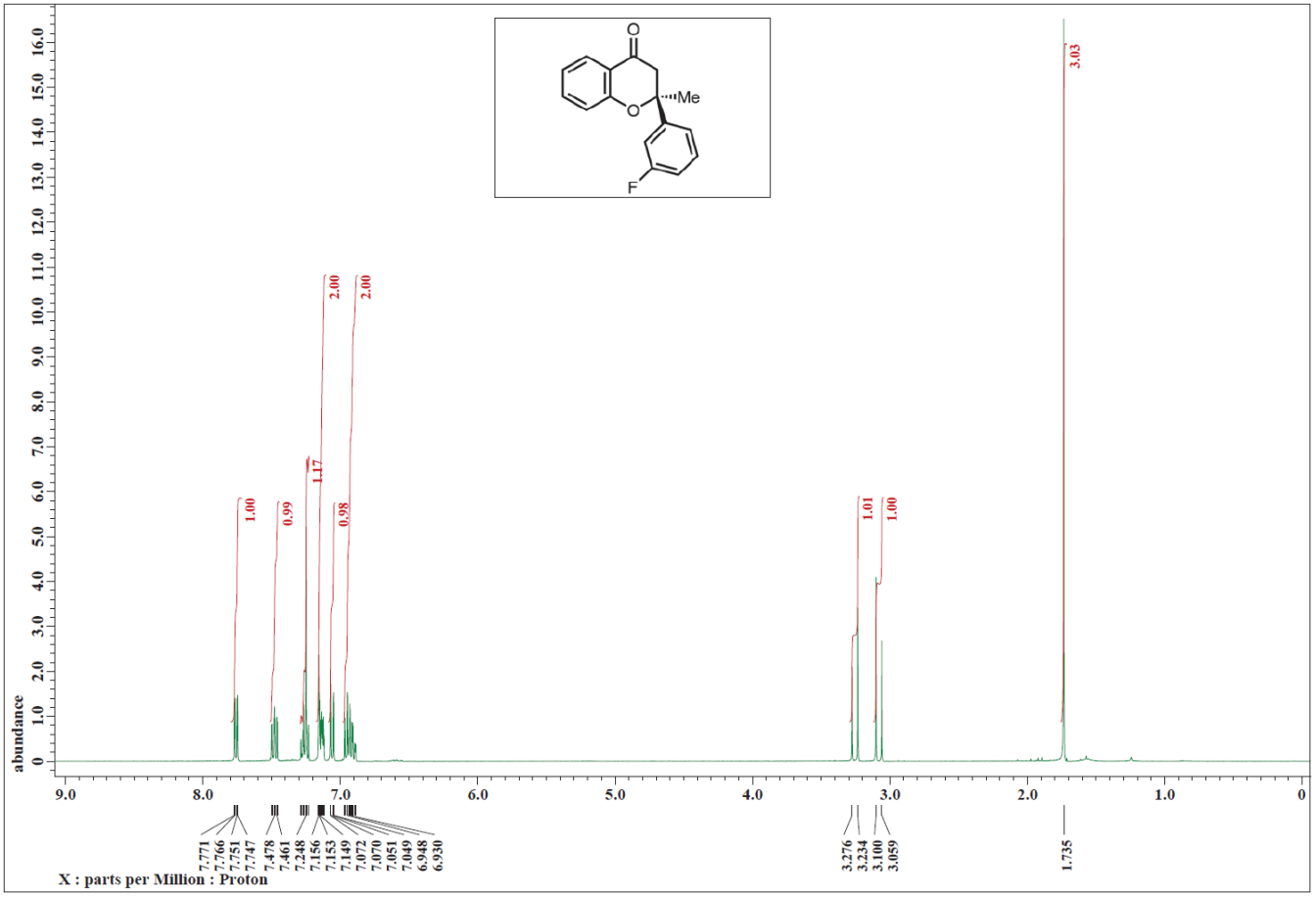

O
Me
O
Br
3.04
2.18
3.02
1.00
0.96
0.99
0.99
1.06
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.757
7.752
7.737
7.733
7.461
7.415
7.398
7.393
7.281
7.276
7.260
7.048
7.046
7.027
7.025
6.936
3.267
3.226
3.090
3.049
1.720
X : parts per Million : Proton

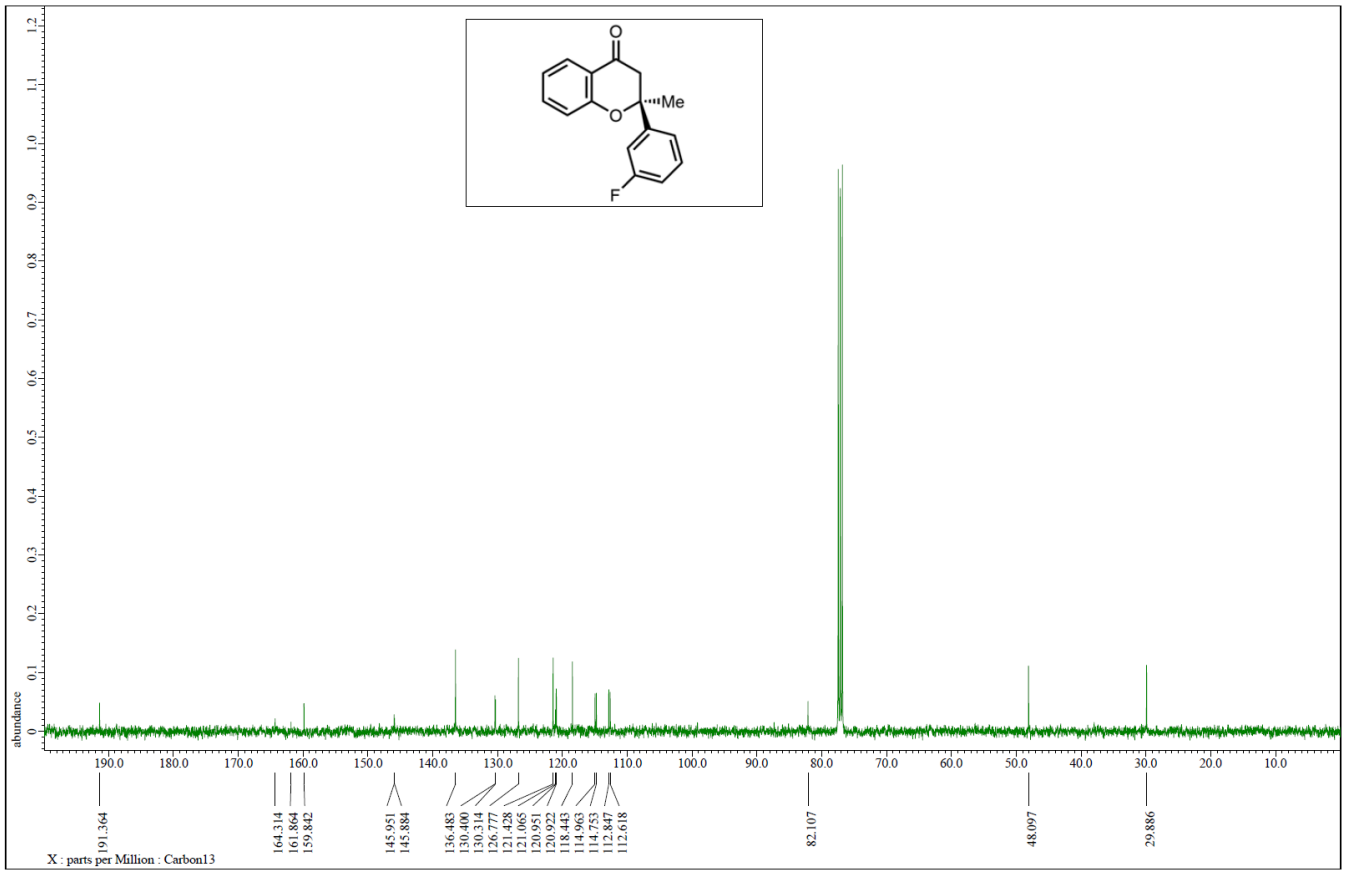

O
Me
O
Br
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
191.383
159.823
142.175
136.426
131.887
127.158
126.757
121.904
121.409
121.075
118.377
82.202
47.954
30.039
X : parts per Million : Carbon13

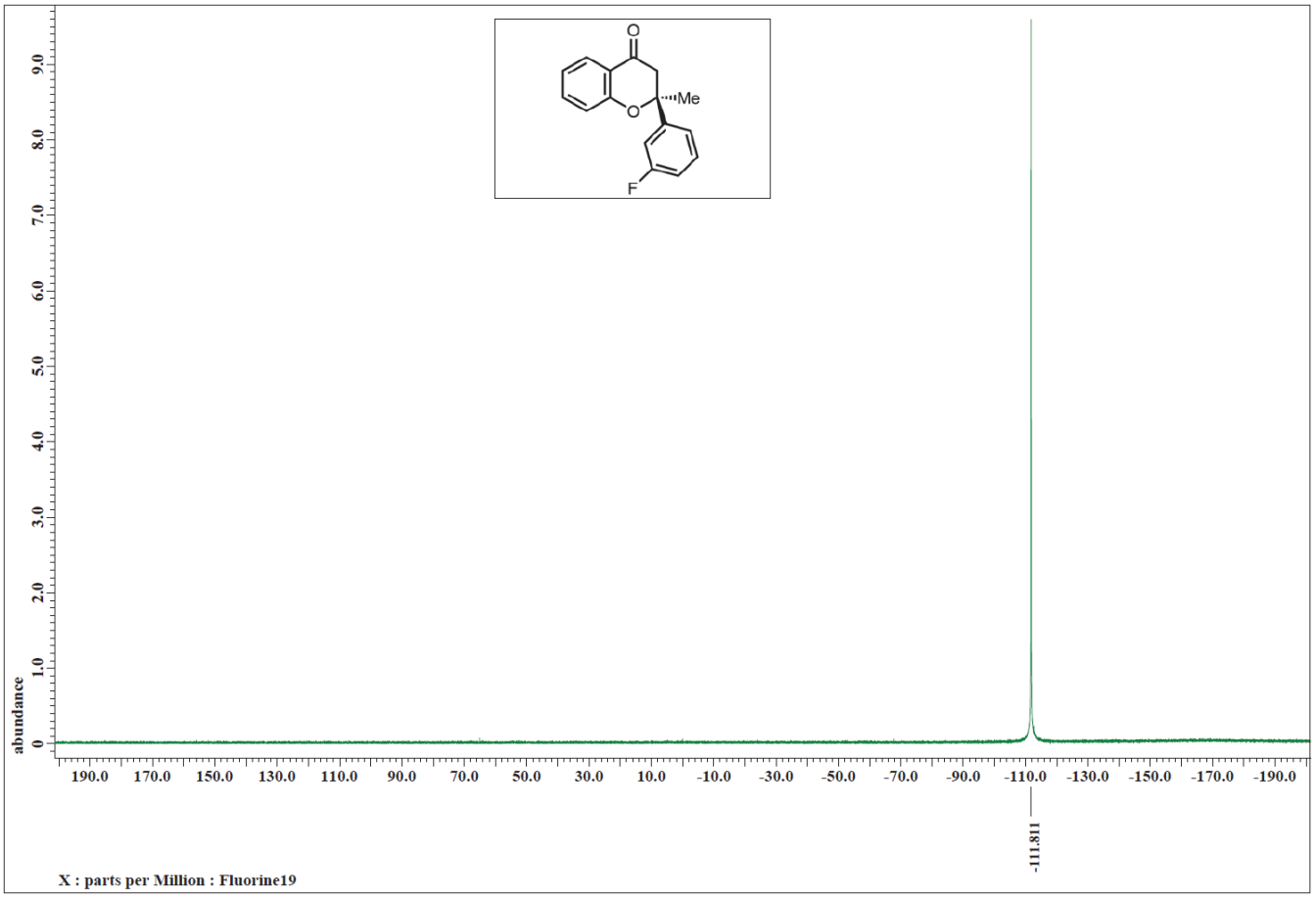

abundance
X : parts per Million : Proton
5.08
1.00
1.08
0.99
1.00
1.00
3.15
7.767
7.763
7.748
7.743
7.569
7.546
7.536
7.509
7.490
7.488
7.486
7.483
7.469
7.465
7.248
7.086
7.063
6.977
6.974
6.957
3.309
3.268
3.141
3.100
1.754
Me
CF3

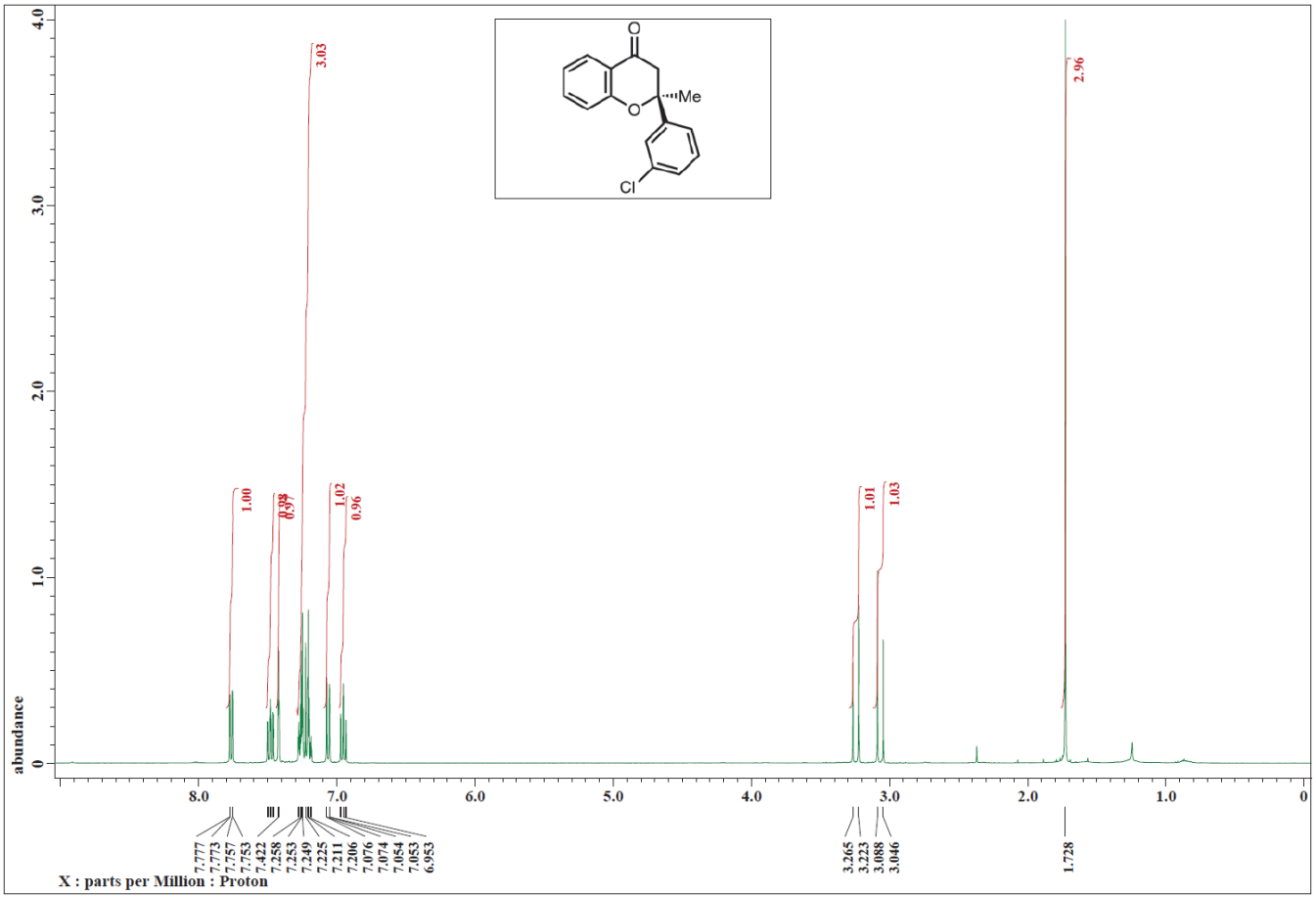

abundance
X : parts per Million : Carbon13
191.164
159.766
147.200
136.559
130.590
130.266
129.980
129.675
126.834
125.871
125.833
125.795
125.756
125.133
122.629
121.571
121.056
119.950
118.396
82.241
48.040
29.915
Me
CF3

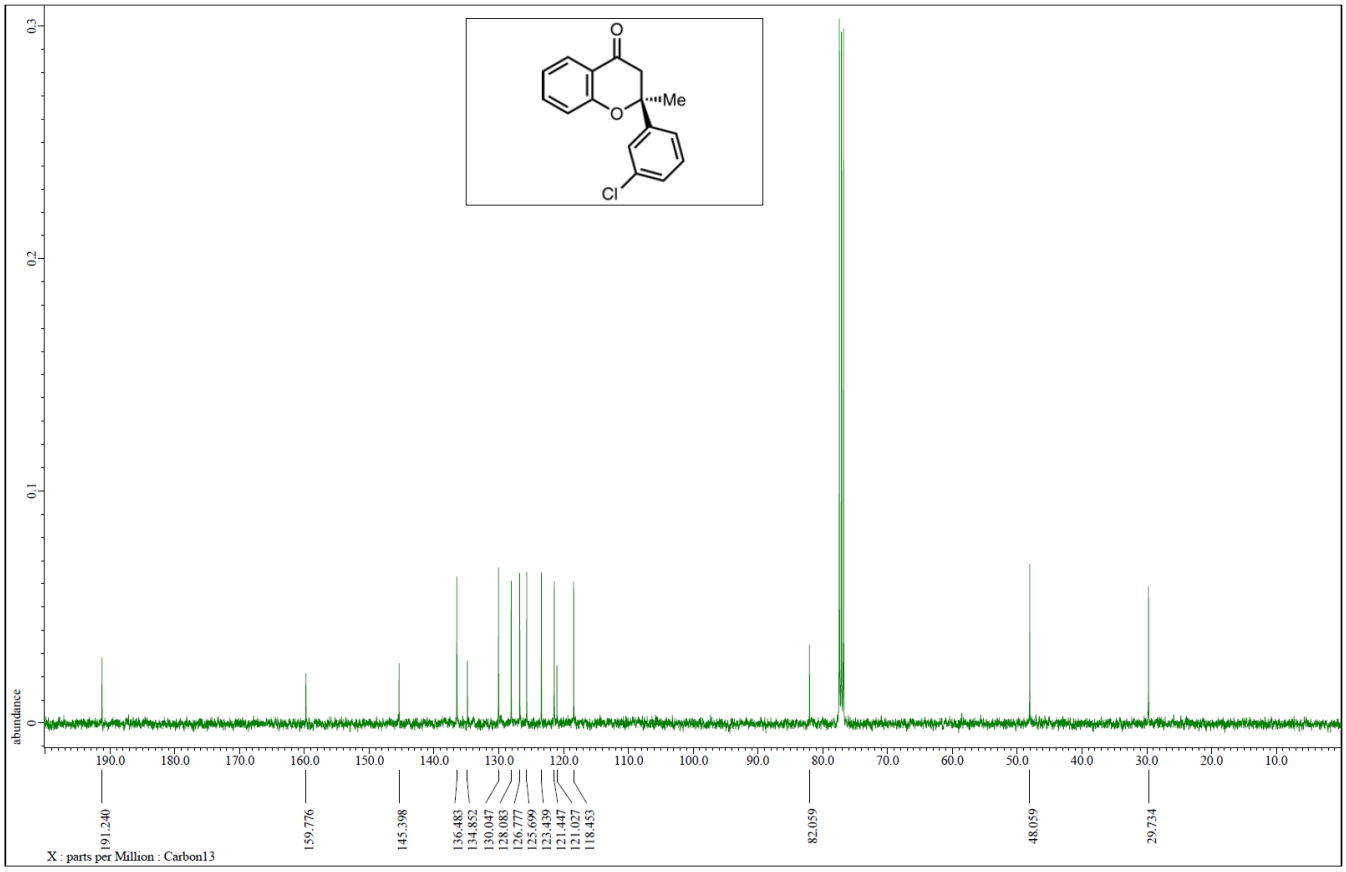

O
Me
O
CF3
abundance
60.0
50.0
40.0
30.0
20.0
10.0
0
190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0
-62.551
X : parts per Million : Fluorine19

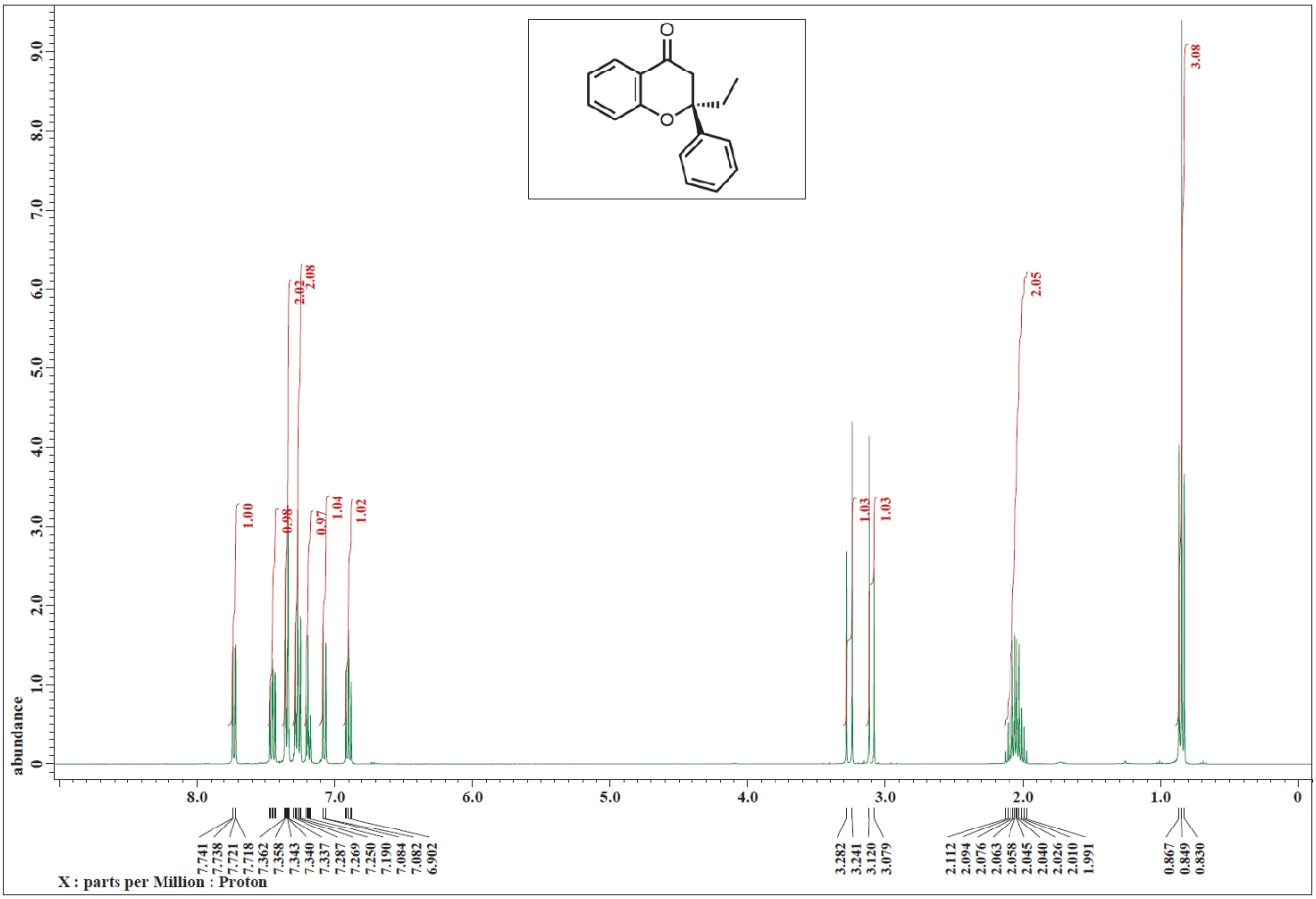

O
Me
O
F
abundance
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
1.00
0.99
1.17
2.00
0.98
2.00
1.01
1.00
3.03
7.771
7.766
7.751
7.747
7.478
7.461
7.248
7.156
7.153
7.149
7.072
7.070
7.051
7.049
6.948
6.930
3.276
3.234
3.100
3.059
1.735
X : parts per Million : Proton

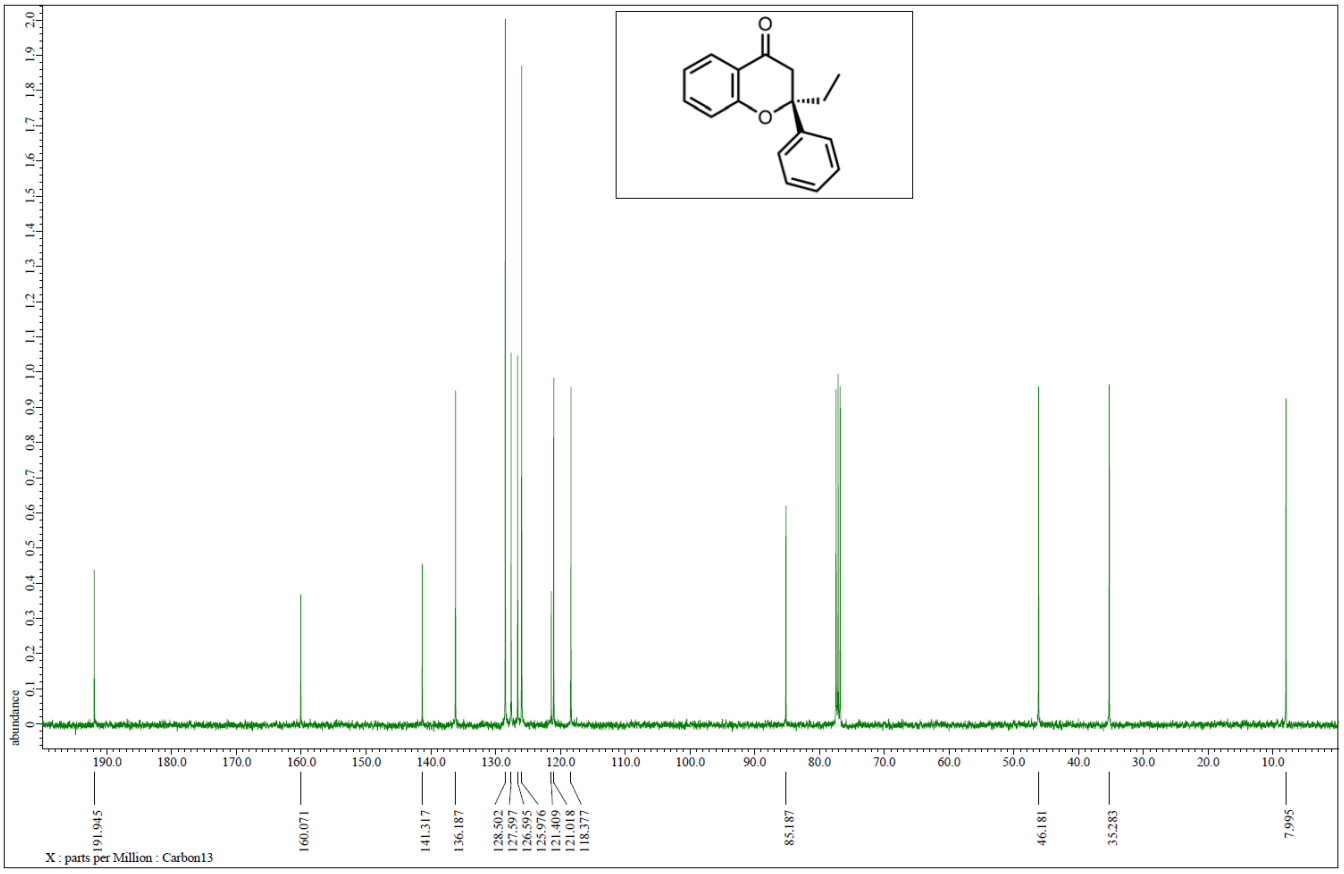

O
Me
O
F
abundance
191.364
164.314
161.864
159.842
145.951
145.884
136.483
130.400
130.314
126.777
121.428
121.065
120.951
120.922
118.443
114.963
114.753
112.847
112.618
82.107
48.097
29.886
X : parts per Million : Carbon13

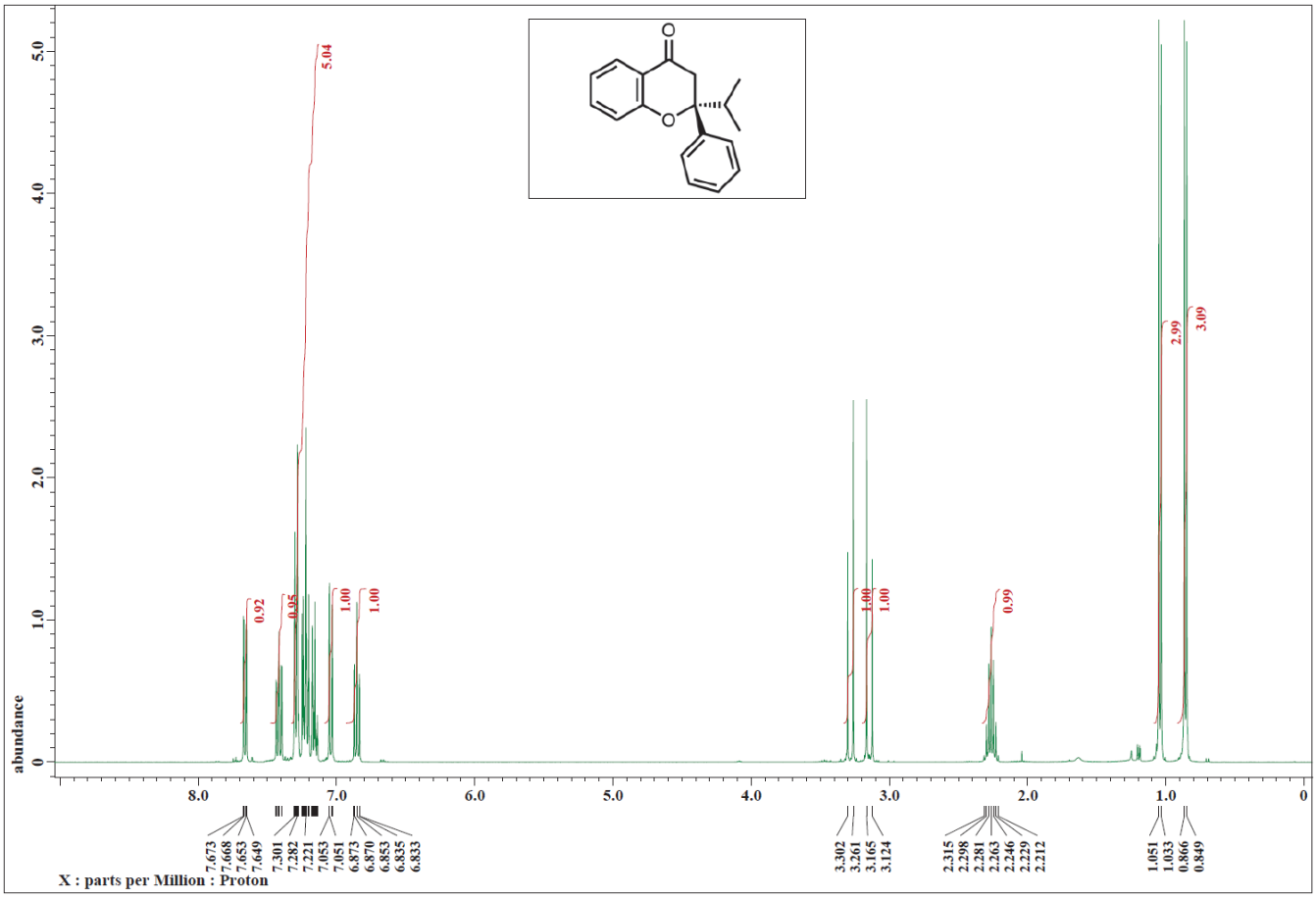

O
Me
O
F
abundance
-111.811
X : parts per Million : Fluorine19

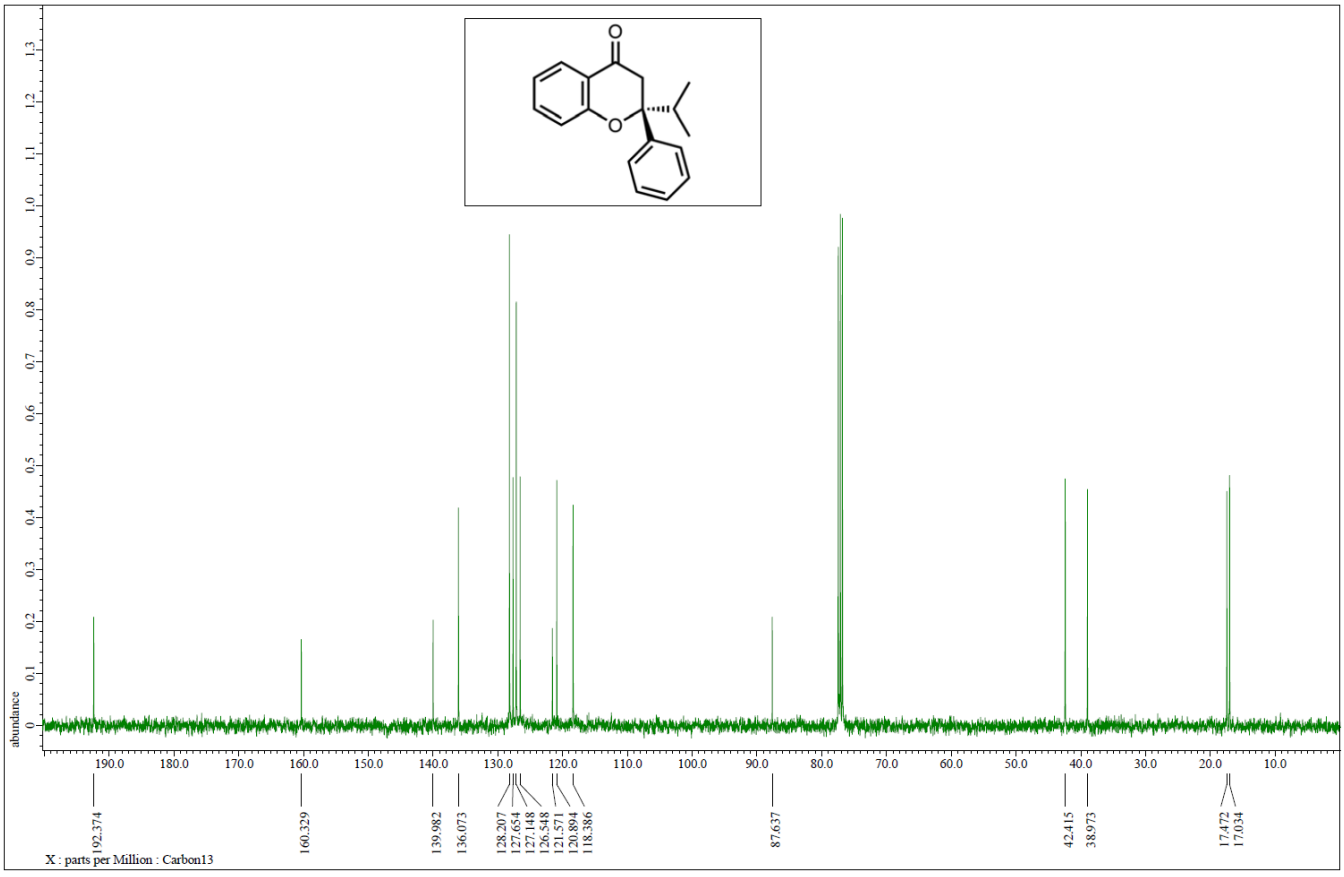

O
Me
O
Cl
abundance
4.0
3.0
2.0
1.0
0
3.03
2.96
1.00
1.02
0.96
1.01
1.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.777
7.773
7.757
7.753
7.422
7.258
7.253
7.249
7.225
7.211
7.206
7.076
7.074
7.054
7.053
6.953
3.265
3.223
3.088
3.046
1.728
X : parts per Million : Proton

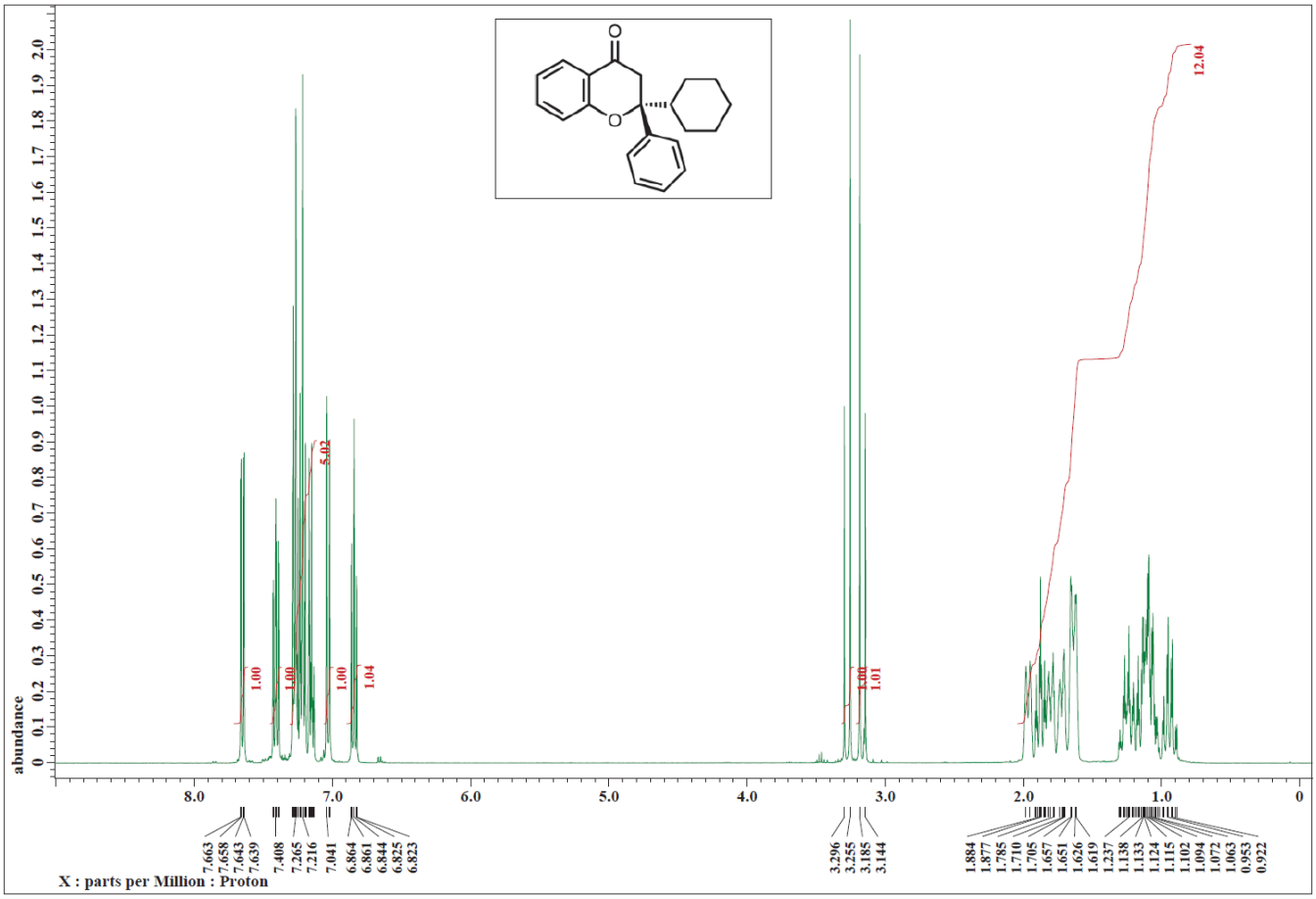

O
Me
O
Cl
abundance
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
191.240
159.776
145.398
136.483
134.852
130.047
128.083
126.777
125.699
123.439
121.447
121.027
118.453
82.059
48.059
29.734
X : parts per Million : Carbon13

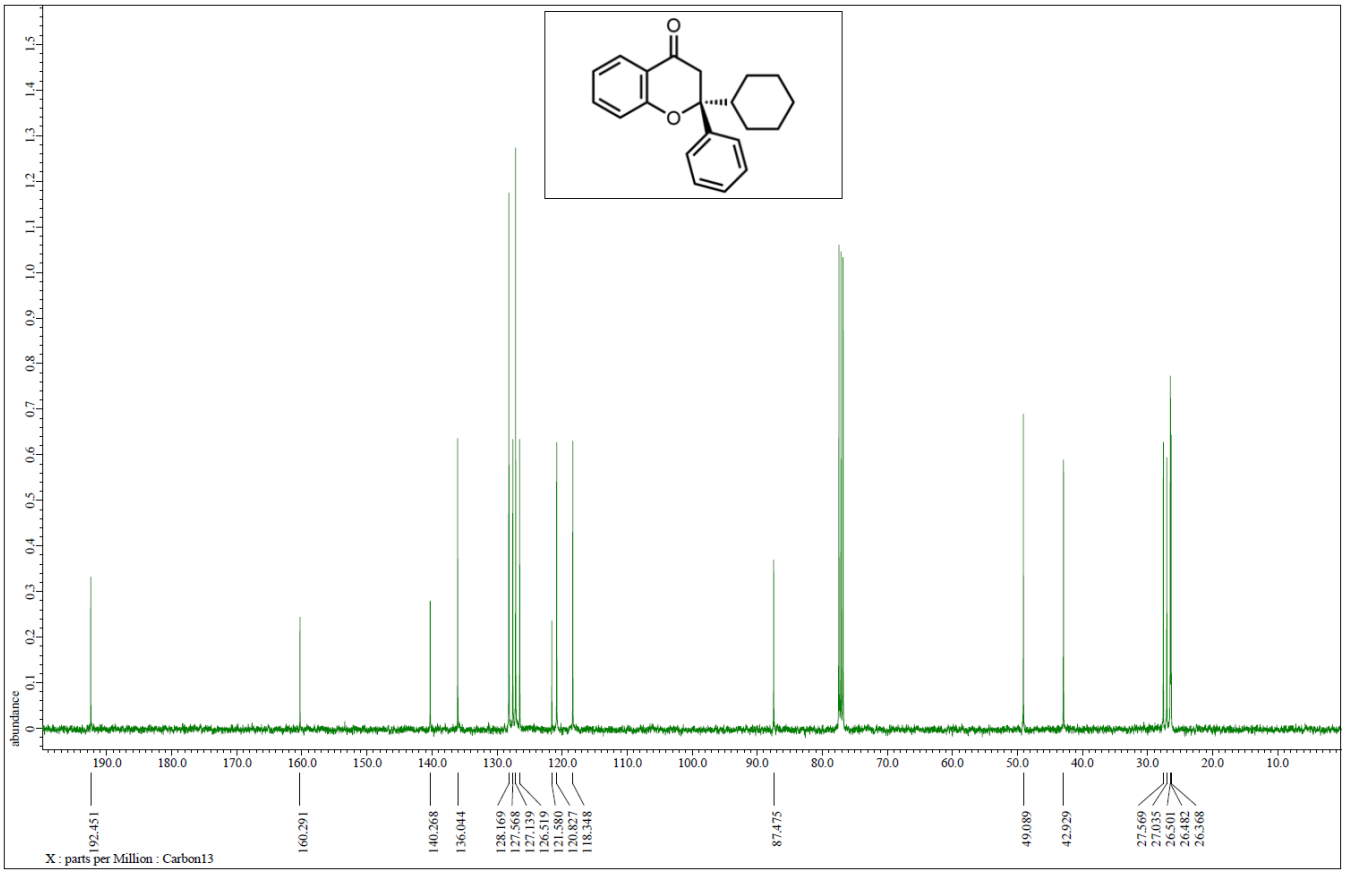

abundance
X : parts per Million : Proton
7.741
7.738
7.721
7.718
7.362
7.358
7.343
7.340
7.337
7.287
7.269
7.250
7.190
7.084
7.082
6.902
3.282
3.241
3.120
3.079
2.112
2.094
2.076
2.063
2.058
2.045
2.040
2.026
2.010
1.991
0.867
0.849
0.830
1.00
0.98
2.02
2.08
0.97
1.04
1.02
1.03
1.03
2.05
3.08

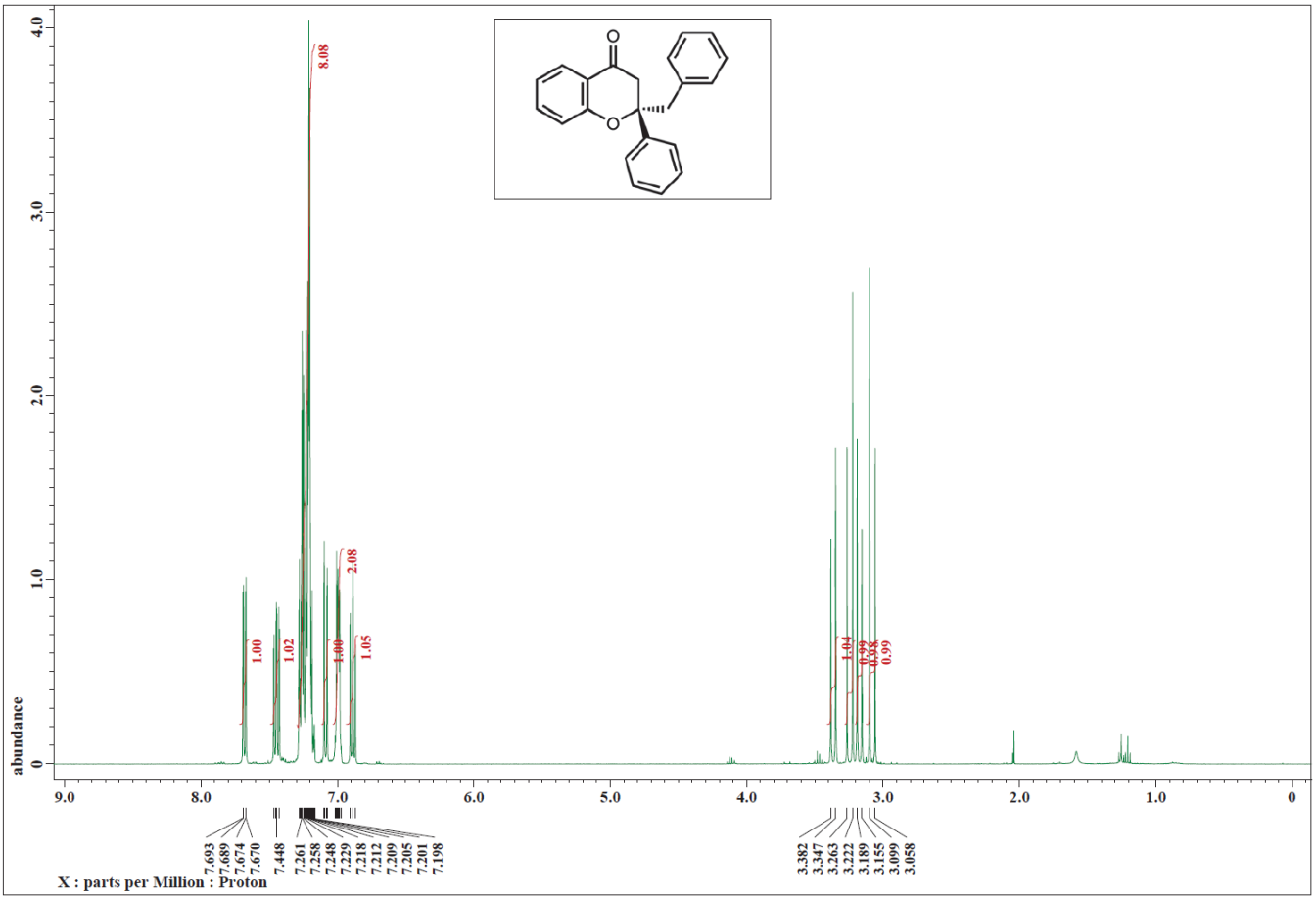

abundance
X : parts per Million : Carbon13
191.945
160.071
141.317
136.187
128.502
127.597
126.595
125.976
121.409
121.018
118.377
85.187
46.181
35.283
7.995

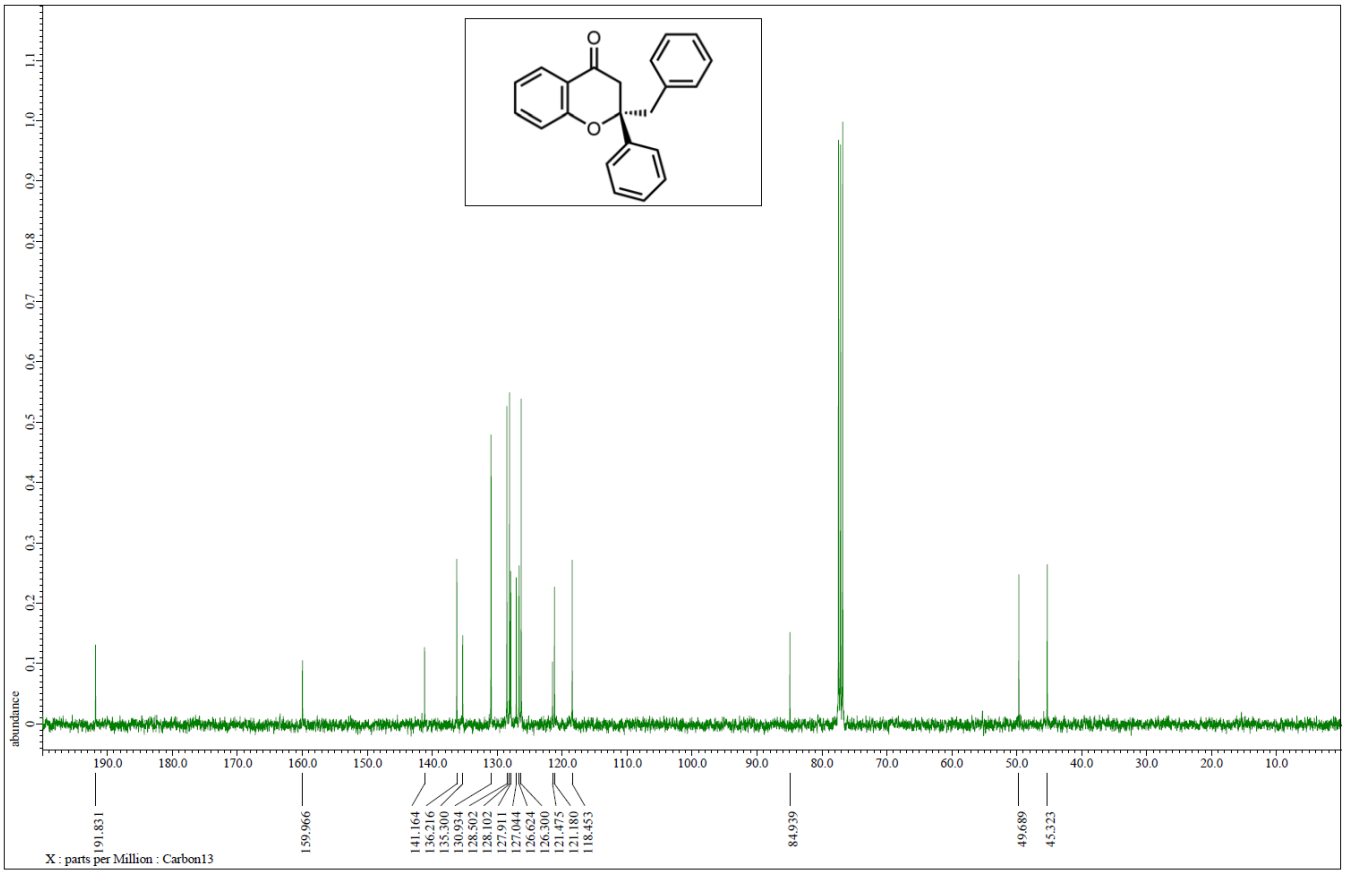

abundance
X : parts per Million : Proton
5.04
0.92
0.95
1.00
1.00
1.00
1.00
0.99
2.99
3.09
7.673
7.668
7.653
7.649
7.301
7.282
7.221
7.053
7.051
6.873
6.870
6.853
6.835
6.833
3.302
3.261
3.165
3.124
2.315
2.298
2.281
2.263
2.246
2.229
2.212
1.051
1.033
0.866
0.849

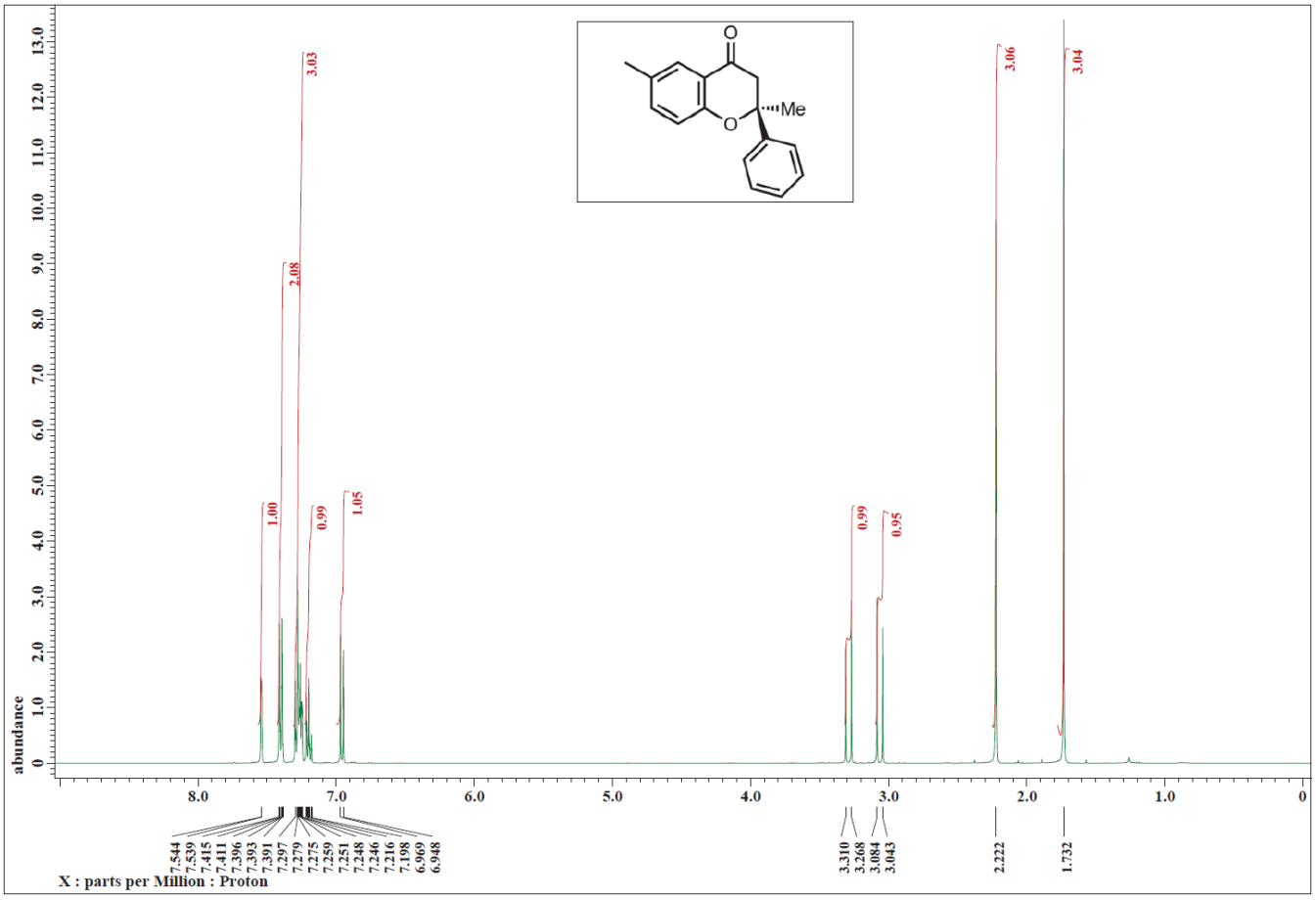

abundance
X : parts per Million : Carbon13
192.374
160.329
139.982
136.073
128.207
127.654
127.148
126.548
121.571
120.894
118.386
87.637
42.415
38.973
17.472
17.034

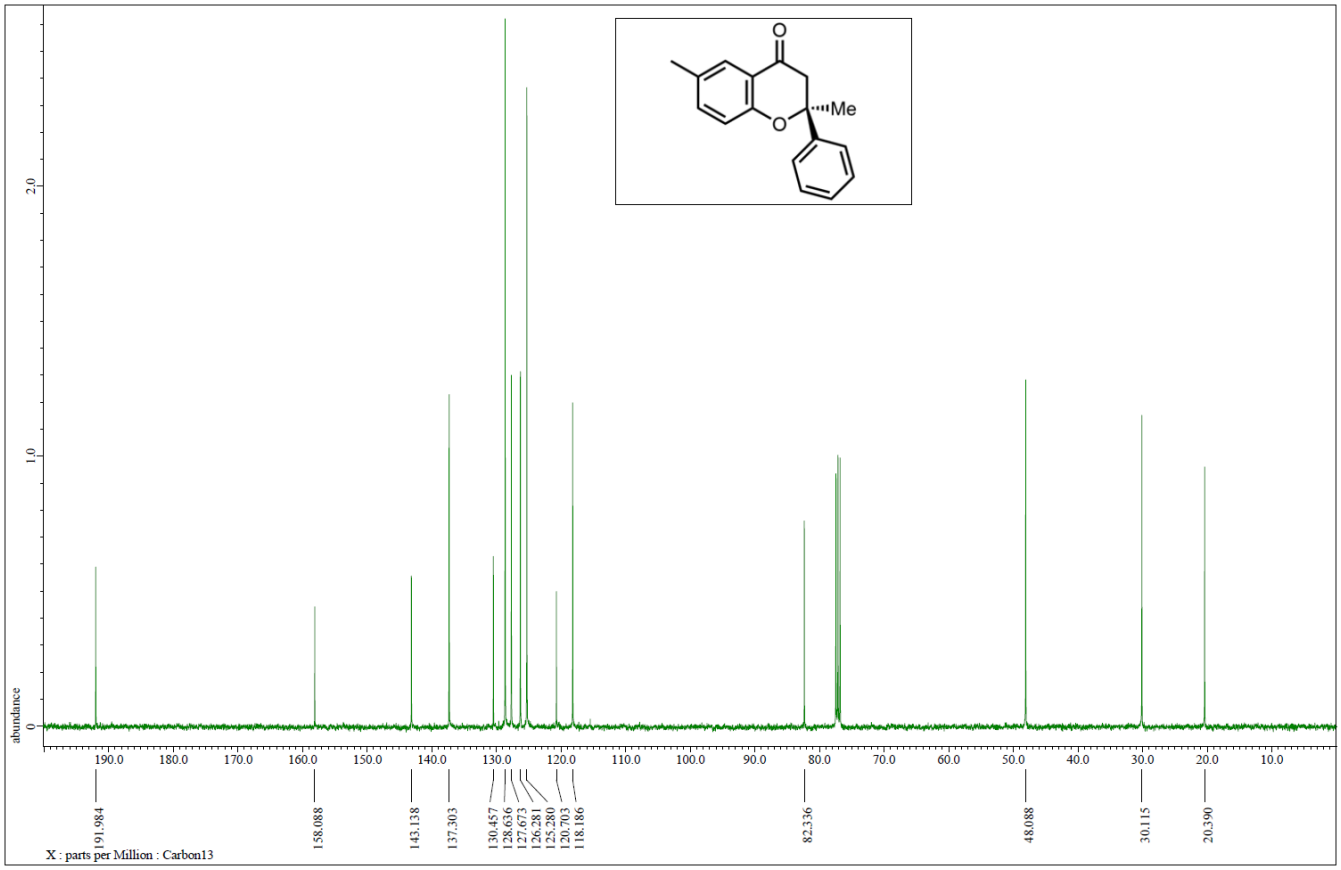

abundance
X : parts per Million : Proton
7.663
7.658
7.643
7.639
7.408
7.265
7.216
7.041
6.864
6.861
6.844
6.825
6.823
3.296
3.255
3.185
3.144
1.884
1.877
1.785
1.710
1.705
1.657
1.651
1.626
1.619
1.237
1.138
1.133
1.124
1.115
1.102
1.094
1.072
1.063
0.953
0.922
1.00
1.00
5.02
1.00
1.04
1.00
1.01
12.04

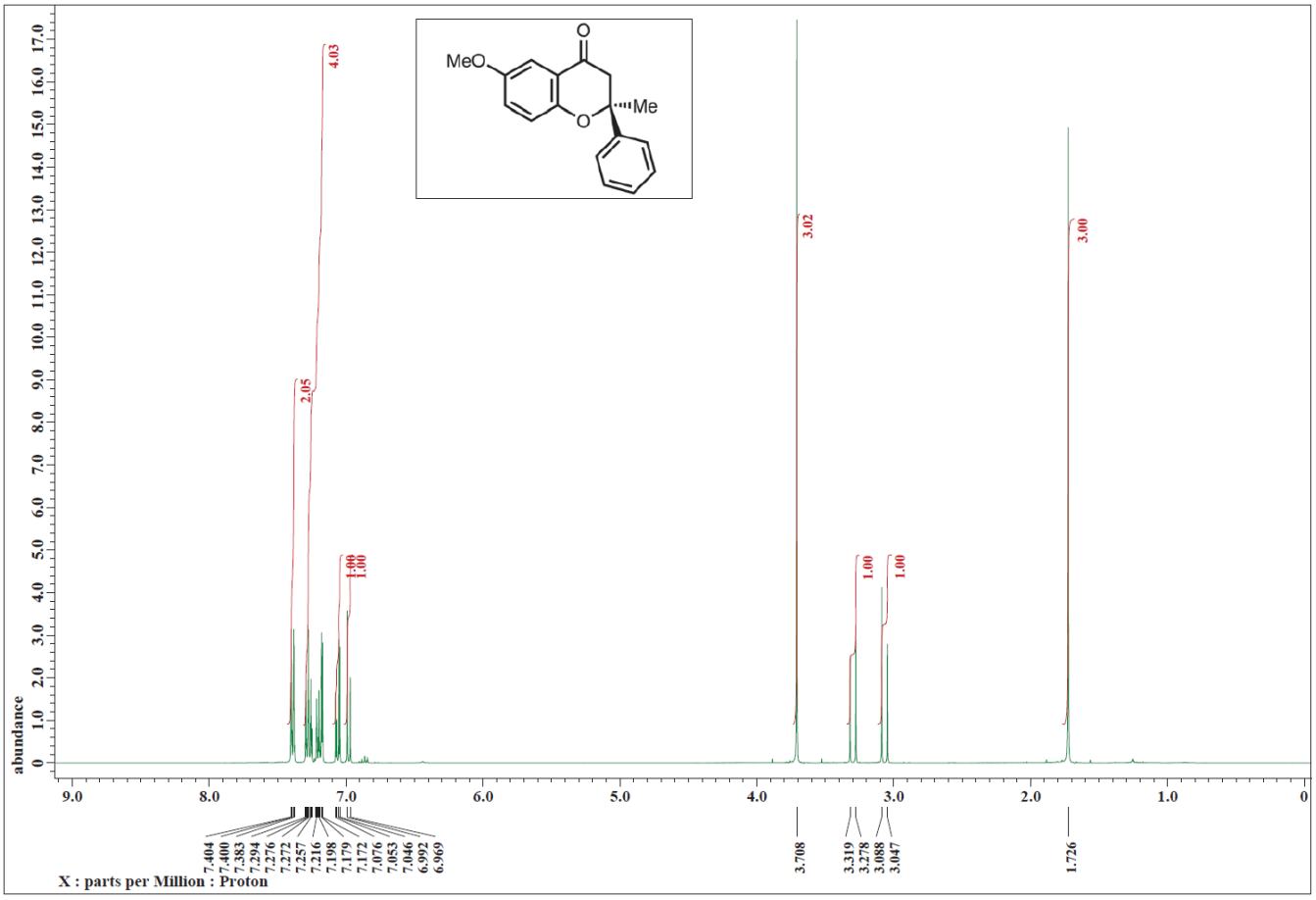

abundance
X : parts per Million : Carbon13
192.451
160.291
140.268
136.044
128.169
127.568
127.139
126.519
121.580
120.827
118.348
87.475
49.089
42.929
27.569
27.035
26.501
26.482
26.368

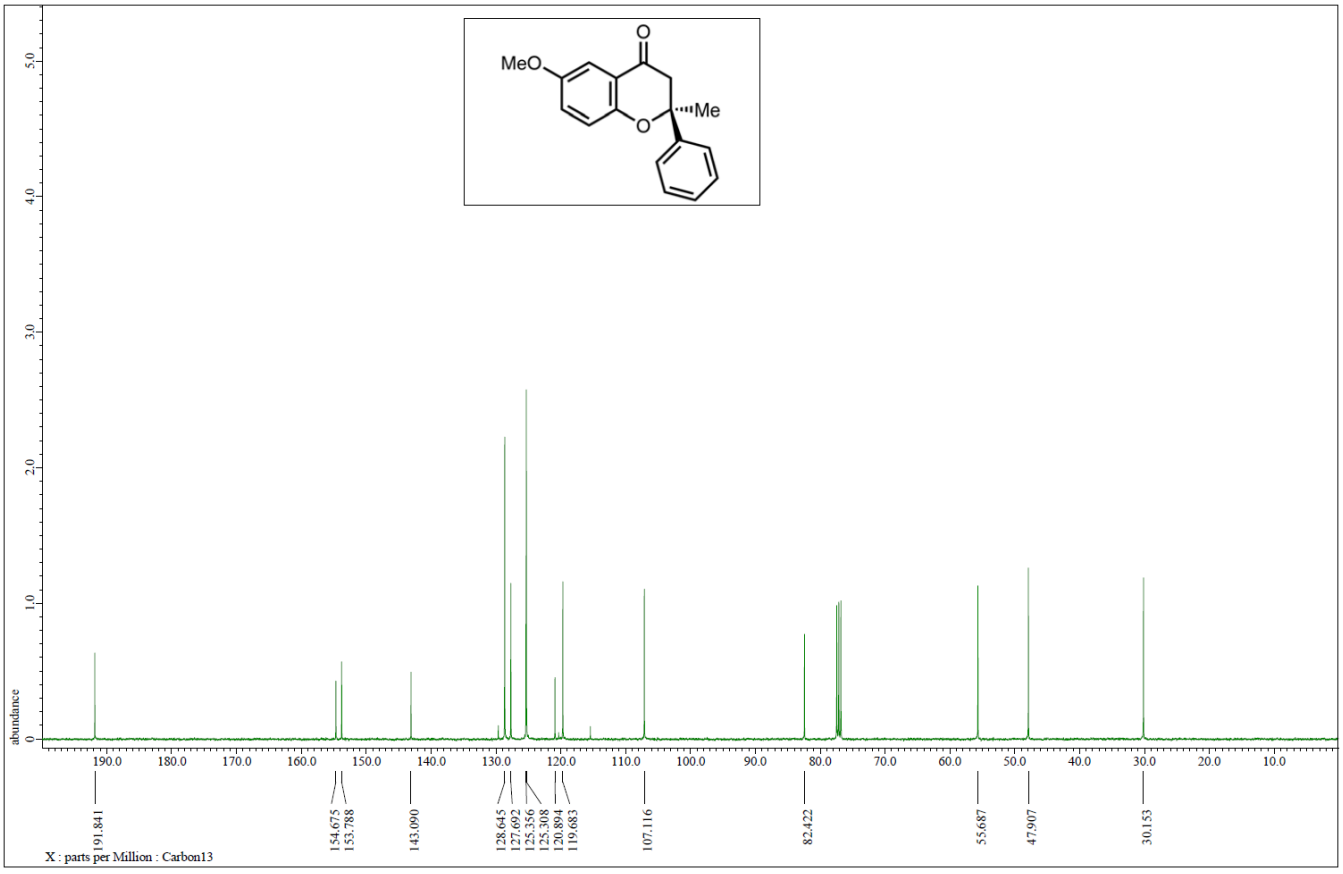

abundance
X : parts per Million : Proton
8.08
1.00
1.02
2.08
1.00
1.05
1.04
0.99
0.98
0.99
7.693
7.689
7.674
7.670
7.448
7.261
7.258
7.248
7.229
7.218
7.212
7.209
7.205
7.201
7.198
3.382
3.347
3.263
3.222
3.189
3.155
3.099
3.058

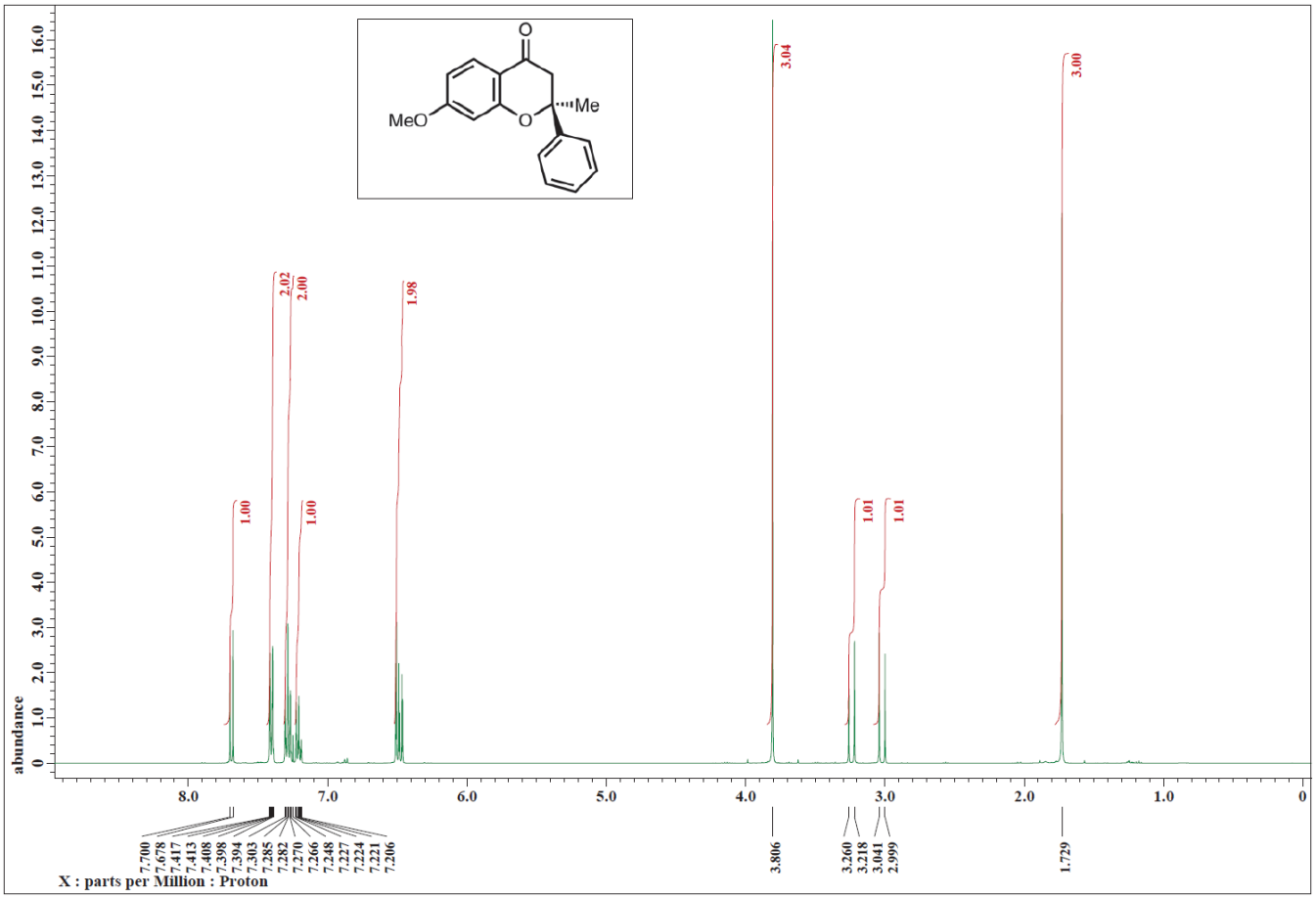

abundance
X : parts per Million : Carbon13
191.831
159.966
141.164
136.216
135.300
130.934
128.502
128.102
127.911
127.044
126.624
126.300
121.475
121.180
118.453
84.939
49.689
45.323

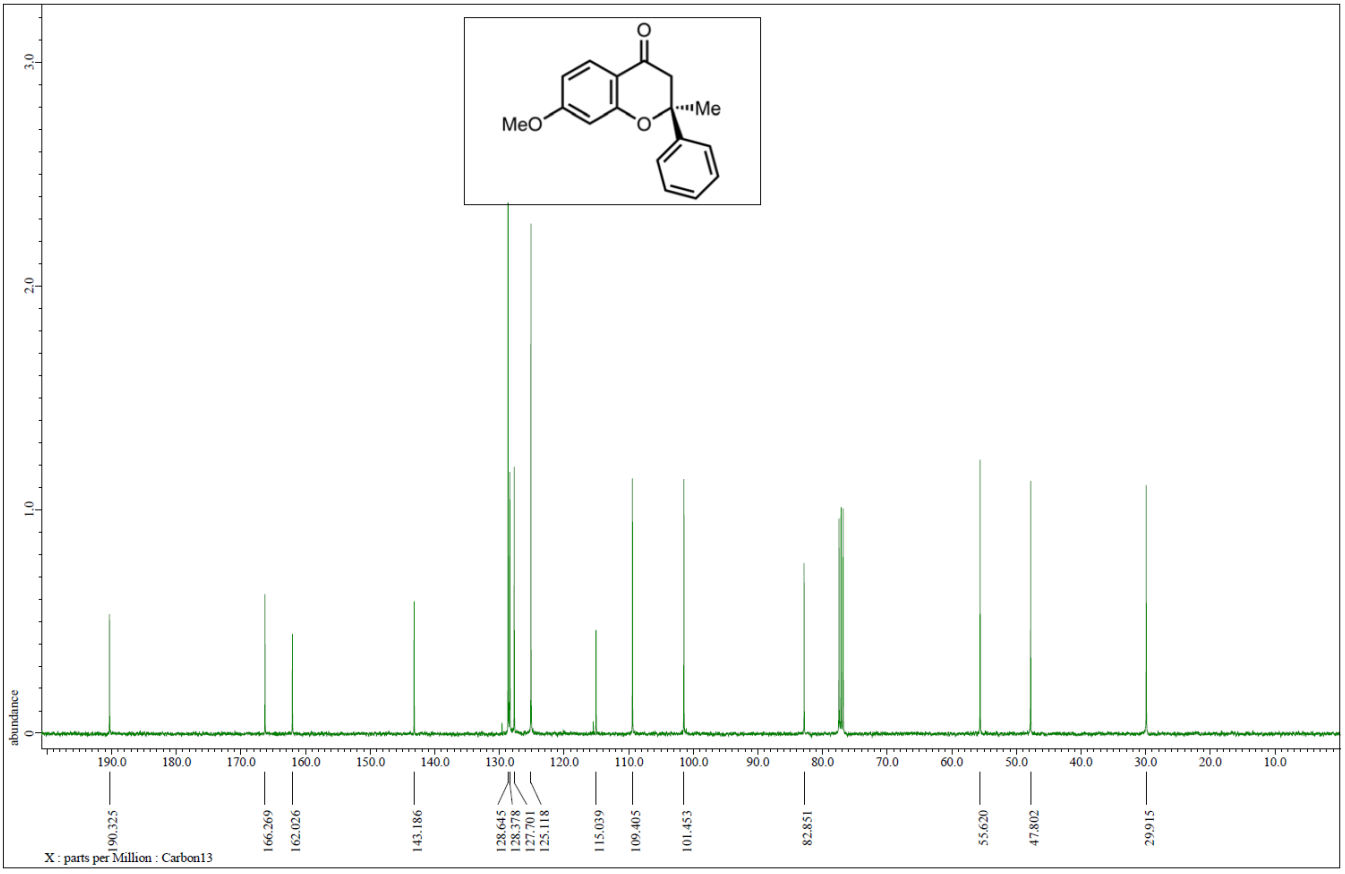

abundance
X : parts per Million : Proton
Me
O
3.03
2.08
1.00
0.99
1.05
3.06
3.04
0.99
0.95
7.544
7.539
7.415
7.411
7.396
7.393
7.391
7.297
7.279
7.275
7.259
7.251
7.248
7.246
7.216
7.198
6.969
6.948
3.310
3.268
3.084
3.043
2.222
1.732

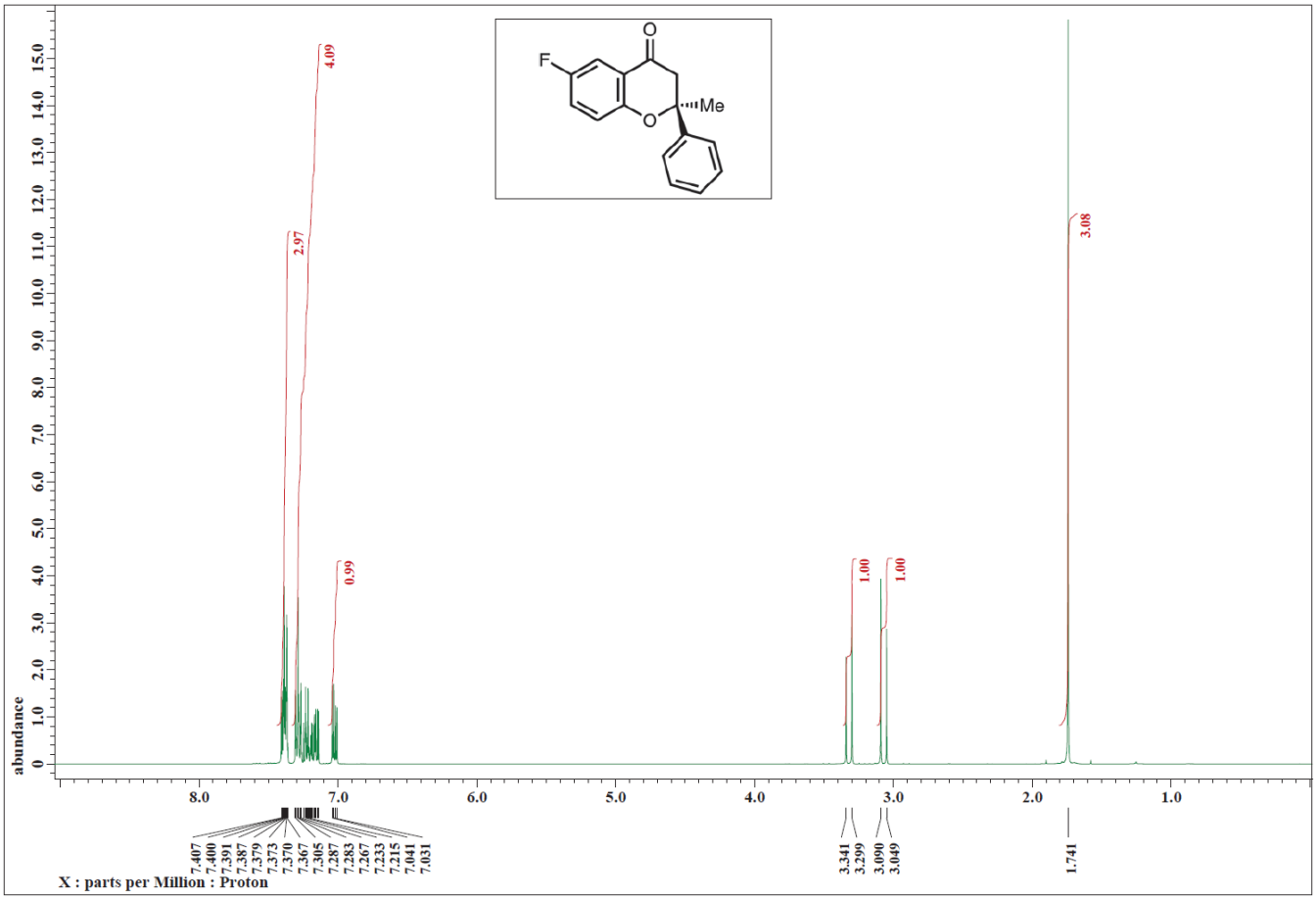

abundance
X : parts per Million : Carbon13
Me
O
191.984
158.088
143.138
137.303
130.457
128.636
127.673
126.281
125.280
120.703
118.186
82.336
48.088
30.115
20.390

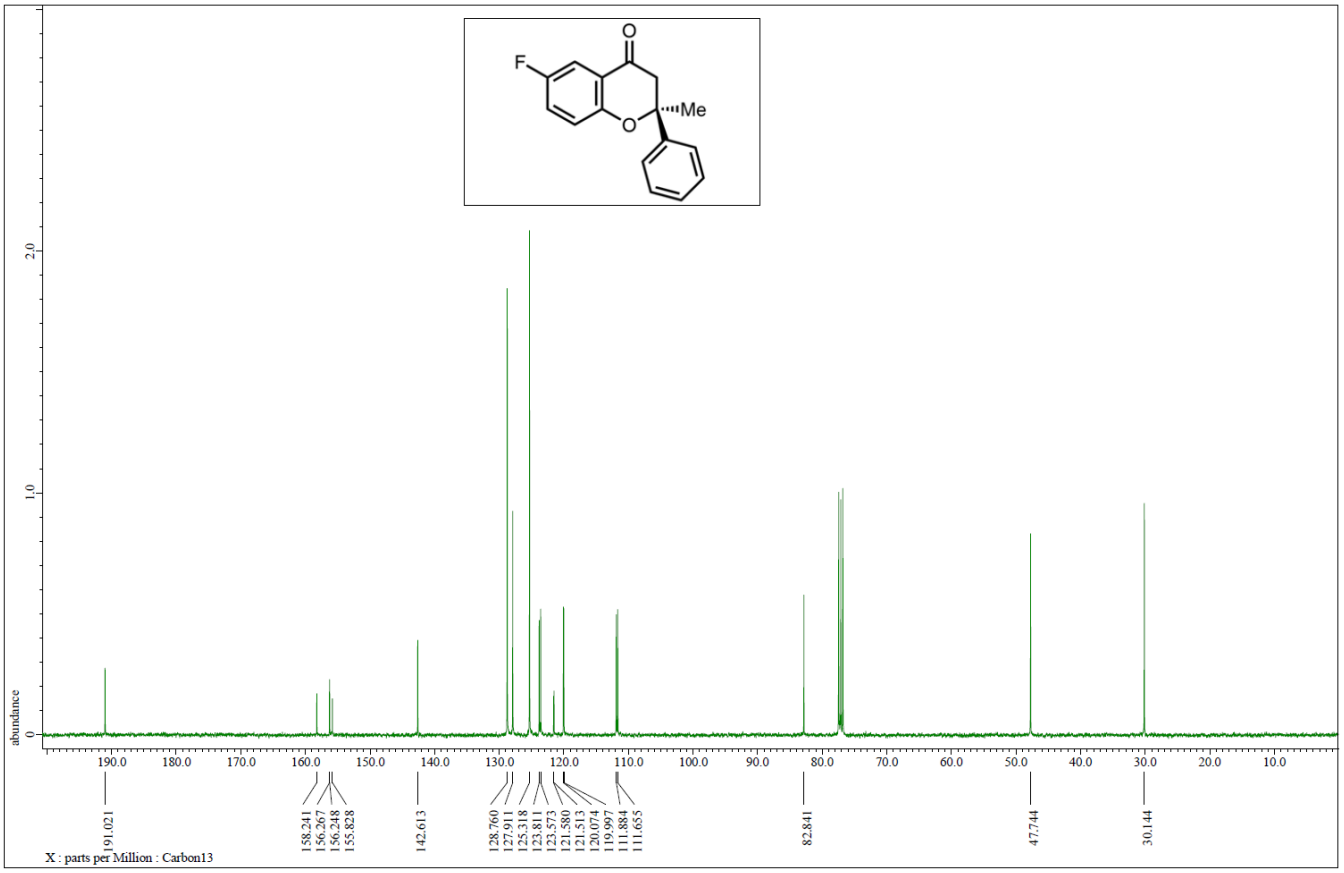

MeO
Me
O
4.03
2.05
1.00
1.00
3.02
1.00
1.00
3.00
abundance
X : parts per Million : Proton
7.404
7.400
7.383
7.294
7.276
7.272
7.257
7.216
7.198
7.179
7.172
7.076
7.053
7.046
6.992
6.969
3.708
3.319
3.278
3.088
3.047
1.726

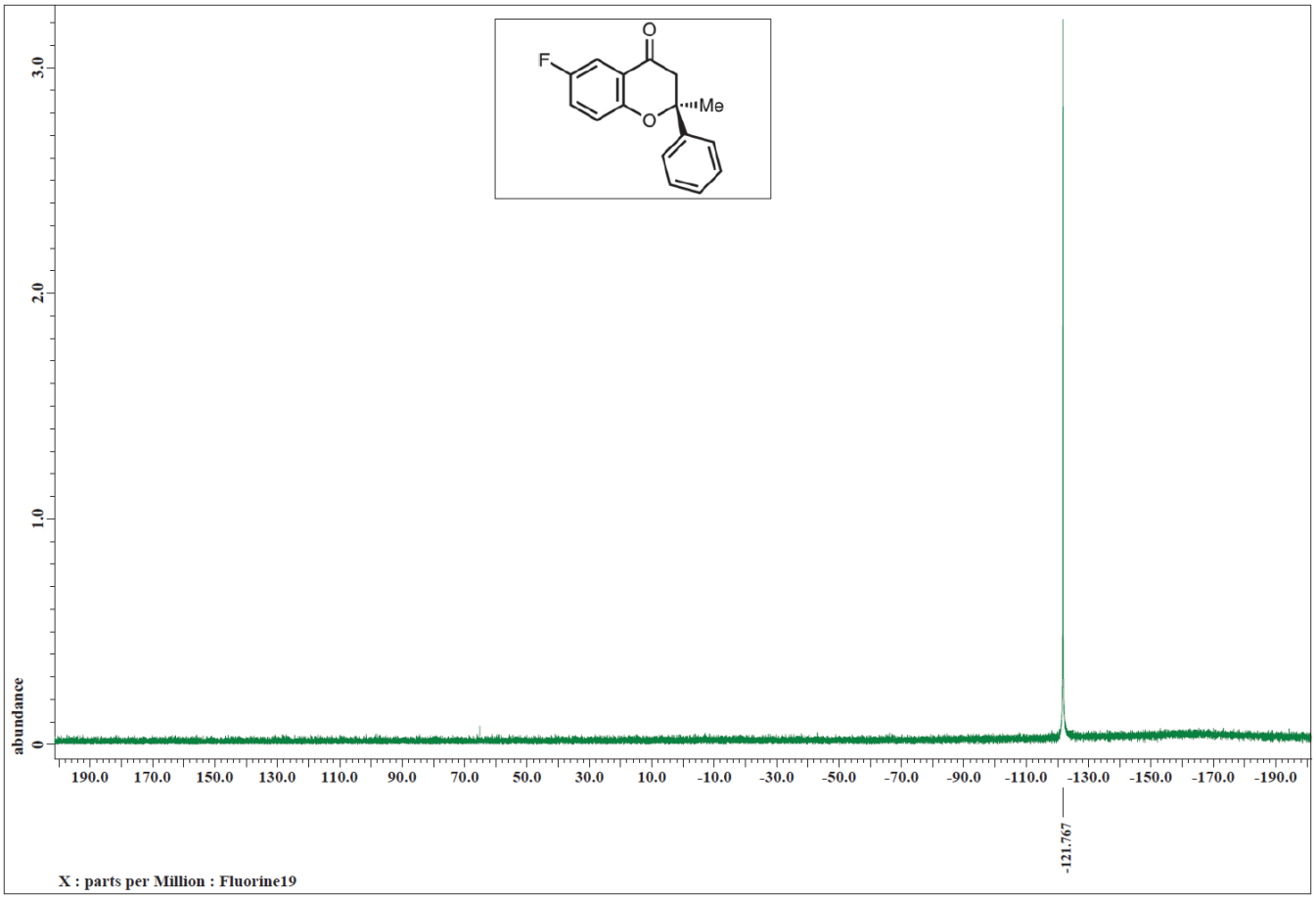

MeO
Me
O
abundance
X : parts per Million : Carbon13
191.841
154.675
153.788
143.090
128.645
127.692
125.356
125.308
120.894
119.683
107.116
82.422
55.687
47.907
30.153

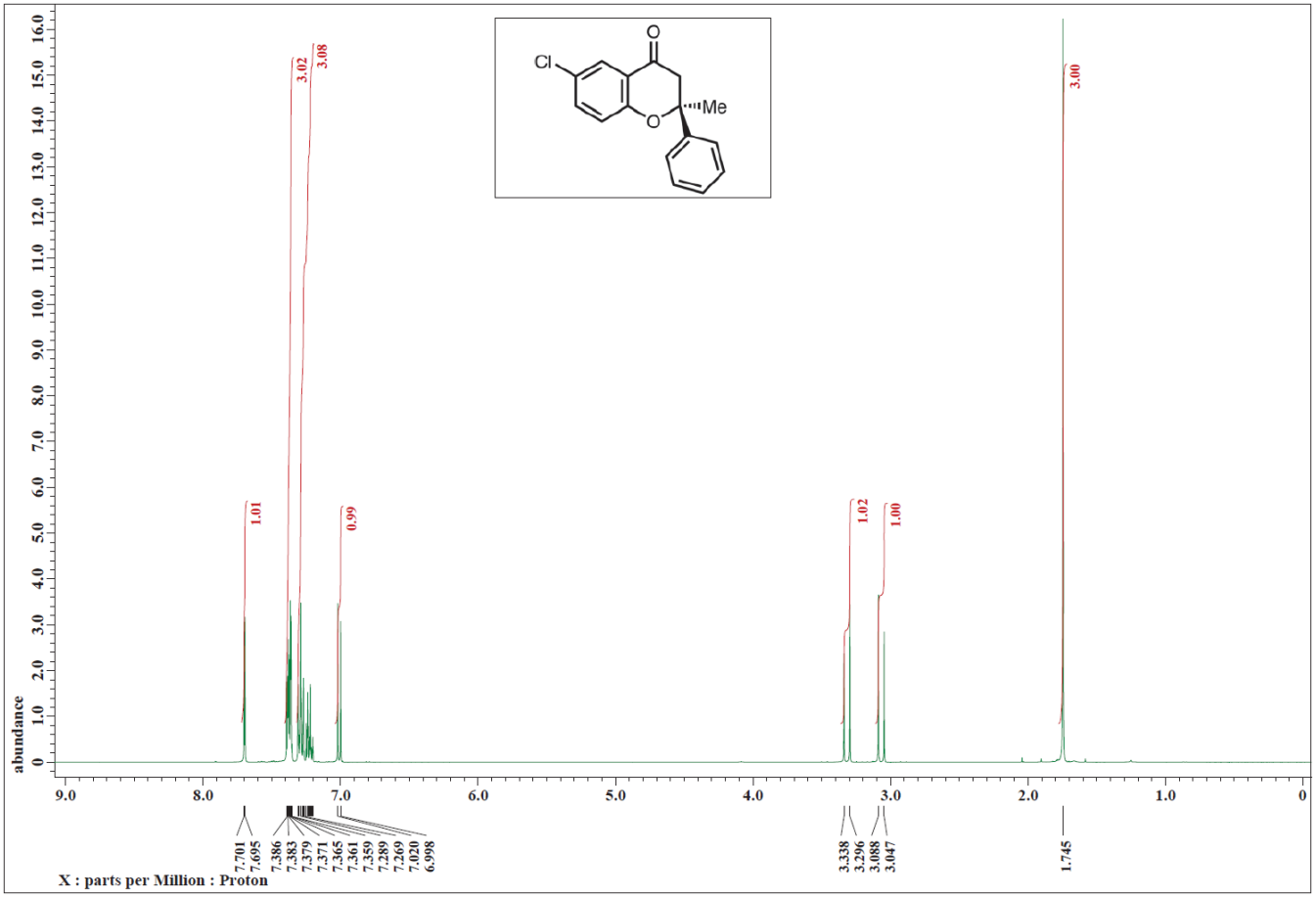

MeO
Me
O
abundance
X : parts per Million : Proton
7.700
7.678
7.417
7.413
7.408
7.398
7.394
7.303
7.285
7.282
7.270
7.266
7.248
7.227
7.224
7.221
7.206
3.806
3.260
3.218
3.041
2.999
1.729
1.00
2.02
2.00
1.00
1.98
3.04
1.01
1.01
3.00

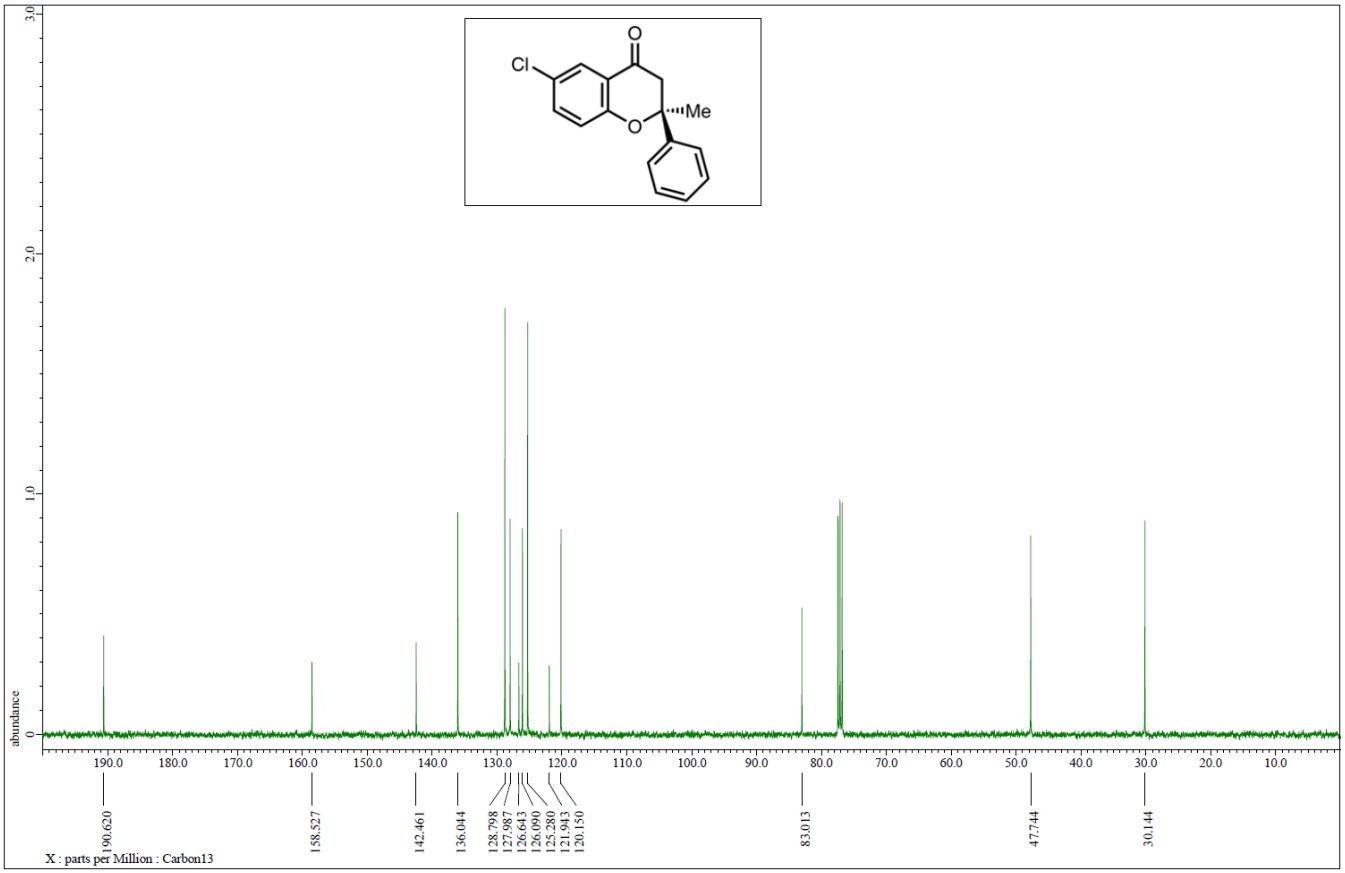

MeO
Me
O
abundance
X : parts per Million : Carbon13
190.325
166.269
162.026
143.186
128.645
128.378
127.701
125.118
115.039
109.405
101.453
82.851
55.620
47.802
29.915

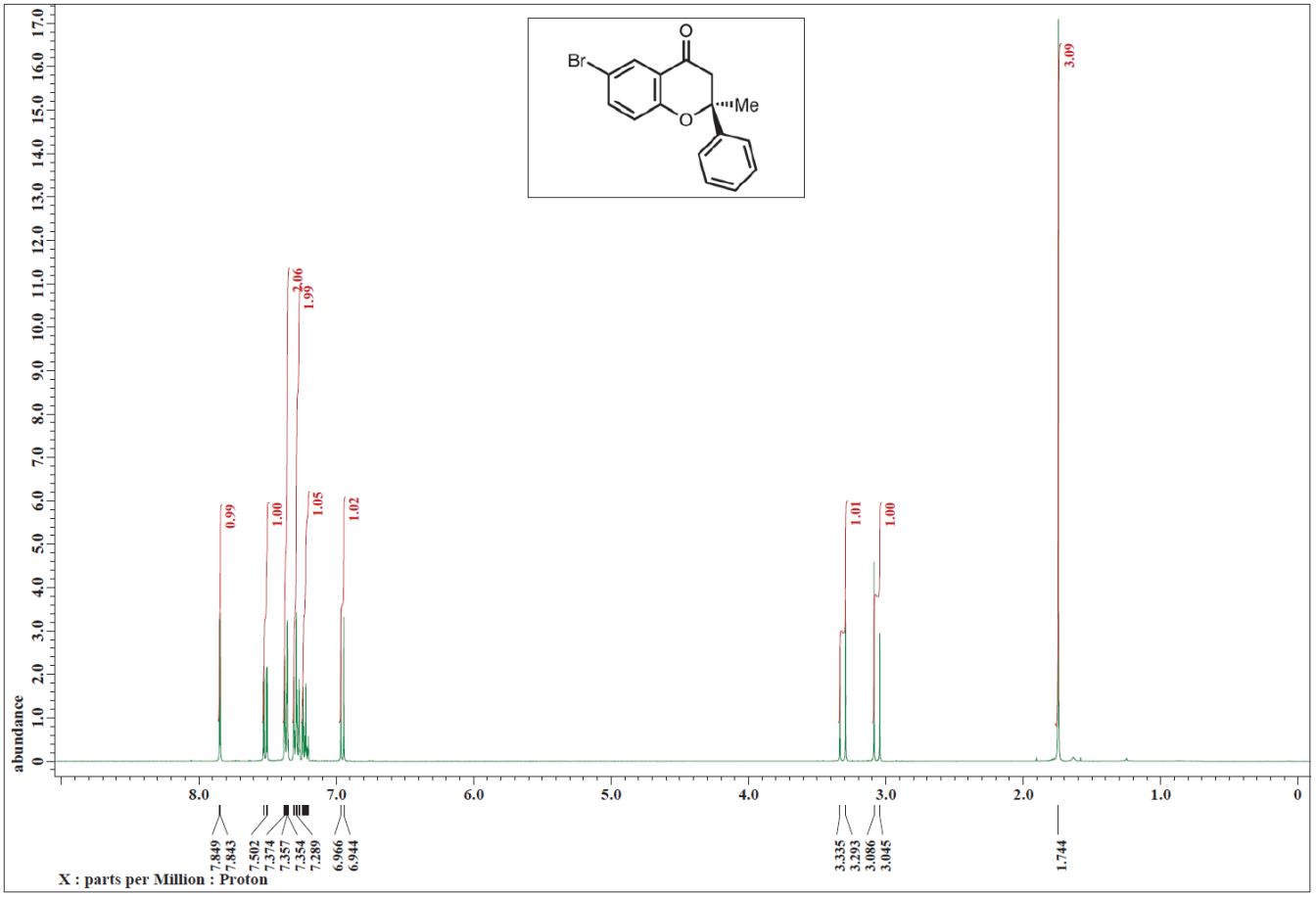

F
O
Me
O
4.09
2.97
0.99
1.00
1.00
3.08
abundance
X : parts per Million : Proton
7.407
7.400
7.391
7.387
7.379
7.373
7.370
7.367
7.305
7.287
7.283
7.267
7.233
7.215
7.041
7.031
3.341
3.299
3.090
3.049
1.741

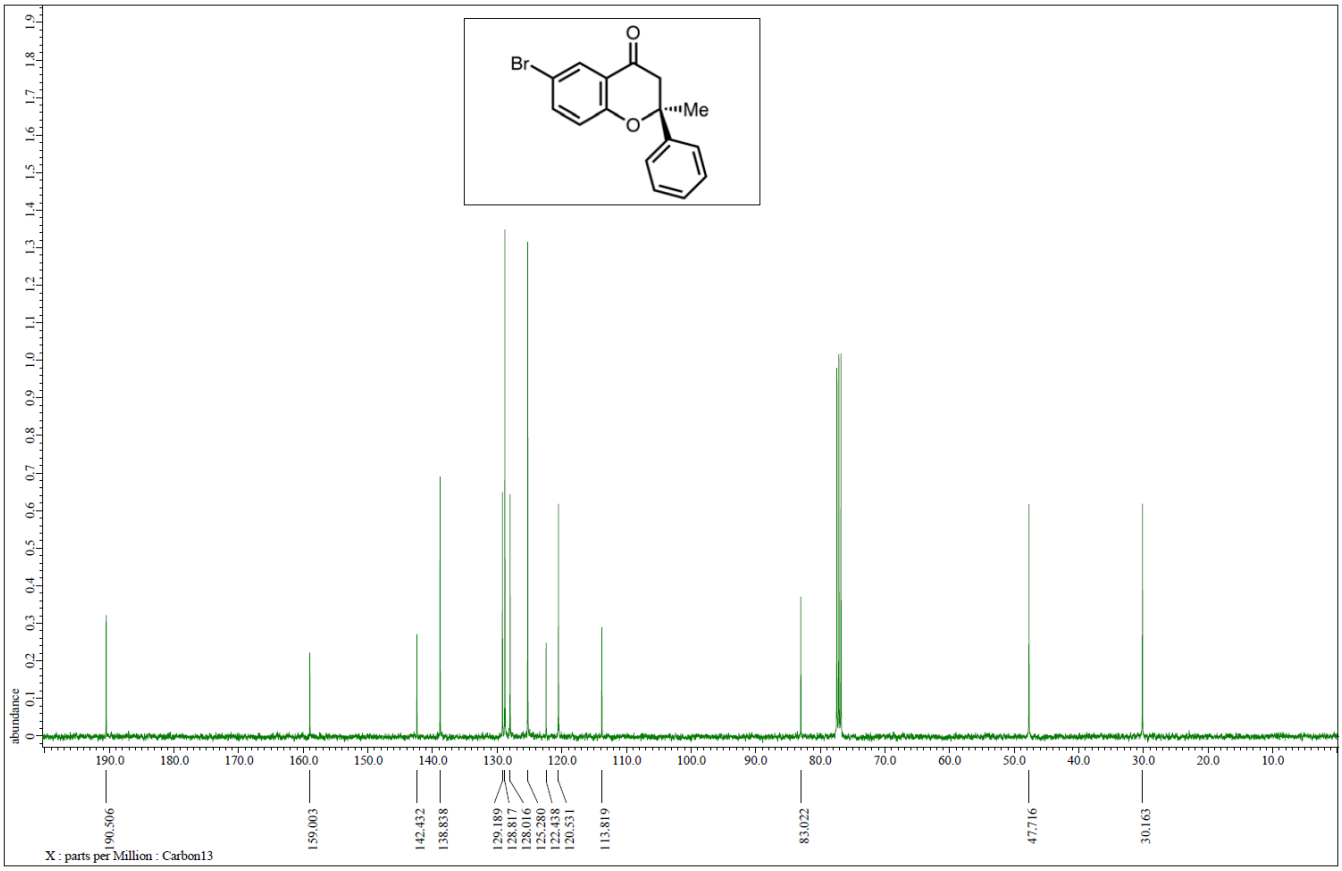

F
O
Me
O
abundance
X : parts per Million : Carbon13
191.021
158.241
156.267
156.248
155.828
142.613
128.760
127.911
125.318
123.811
123.573
121.580
121.513
120.074
119.997
111.884
111.655
82.841
47.744
30.144


F
O
O
Me
abundance
3.0
2.0
1.0
0
190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0
-121.767
X : parts per Million : Fluorine19


Cl
O
O
Me
abundance
16.0 15.0 14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
3.08
3.02
3.00
1.01
0.99
1.02
1.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.701 7.695 7.386 7.383 7.379 7.371 7.365 7.361 7.359 7.289 7.269 7.020 6.998
3.338 3.296 3.088 3.047
1.745
X : parts per Million : Proton


Cl
O
Me
O
abundance
190.620
158.527
142.461
136.044
128.798
127.987
126.643
126.690
125.280
121.943
120.150
83.013
47.744
30.144
X : parts per Million : Carbon13


Br
O
Me
O
abundance
0.99
1.00
2.06
1.99
1.05
1.02
1.01
1.00
3.09
7.849
7.843
7.502
7.374
7.357
7.354
7.289
6.966
6.944
3.335
3.293
3.086
3.045
1.744
X : parts per Million : Proton


Br
O
O
Me
abundance
190.506
159.003
142.432
138.838
129.189
128.817
128.016
125.280
122.438
120.531
113.819
83.022
47.716
30.163
X : parts per Million : Carbon13