Dynamic Kinetic Resolution of Biaryl Atropisomers by Chiral Dialkylaminopyridine Catalysts

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Supporting Information

1. General

All solvents were dried and degassed by standard methods and stored under nitrogen. Flash chromatography was performed using EM Science silica gel 60 (230-400 mesh) or on an ISCO Combiflash. ^{1}H NMR spectra were recorded on Varian Unity/Inova-400 NB (400 MHz) spectrometer or Bruker Ascend^{TM} 400 (400 MHz for ^{1}H) spectrometer. ^{13}C NMR spectra were recorded on Varian Unity/Inova-400 NB (100 MHz) spectrometer or Bruker Ascend^{TM} 400 (100 MHz for ^{13}H) spectrometer. HPLC analyses were carried out with Waters 515 HPLC pumps and a 2487 dual wavelength absorbance detector connected to a PC with Empower workstation. Rotations were recorded on a JASCO-DIP-370 polarimeter. High-resolution mass spectra were obtained at a Waters ACQUITY UPLC with ESI Positive Mode.

2. HPLC Analysis of Substrate

HPLC analysis (Figure S1) of biaryl *rac*-**1a** suggested that at higher temperature, the lesser resolution occurred. At room temperature, two clear peaks were assigned to two enantiomers of *rac*-**1a**. When raising the temperature, two peaks were getting close and started overlapping at 55 °C. Finally a single peak was observed at 80 °C.

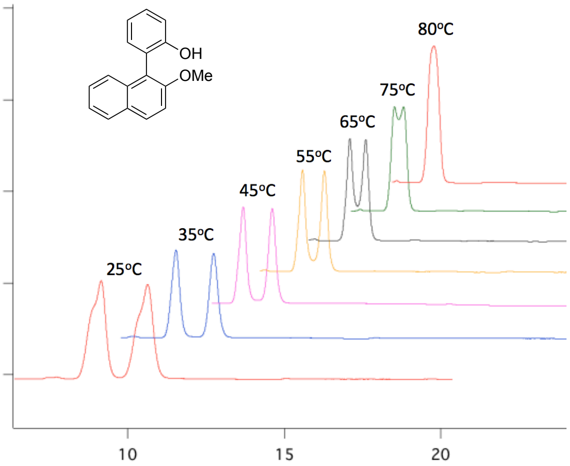


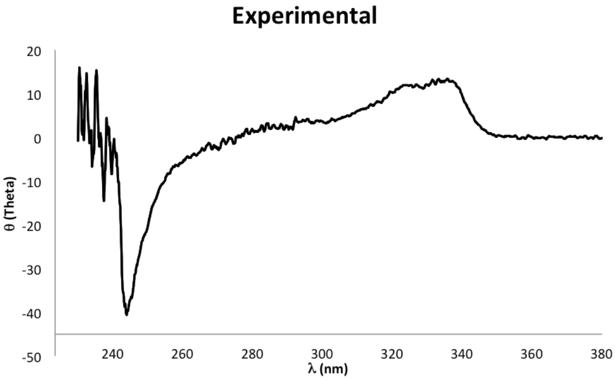
Figure S1. HPLC Analysis of Substrate

3. The Absolute Configuration Discussion

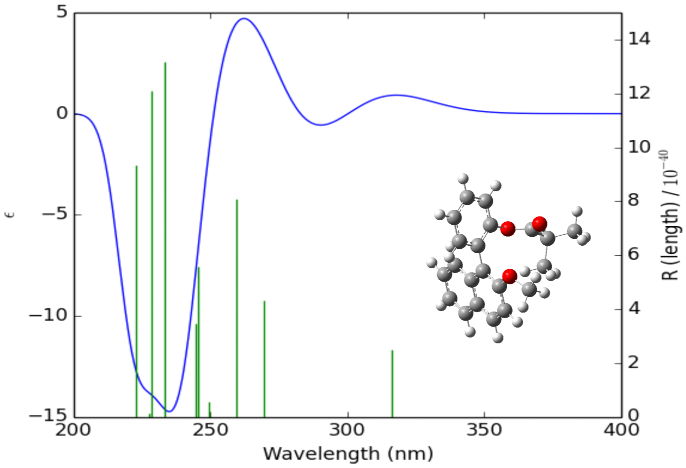
Electronic circular dichroism (ECD or CD) is a powerful spectroscopic method for solving stereochemical problems of chiral molecules.[1] By using quantum chemical calculations of time-dependent density functional theory (TD-DFT), ECD has become a rapid and reliable way to establish the absolute configuration of chiral compounds.[2] In this study, we employed ECD spectra and TD-DFT calculation to assign the absolute configuration of **2a**.

The ECD spectra of **2a** in methanol at a concentration of 0.8-0.9 mg/mL were recorded in a 1mm path length quartz cuvette using a Jasco J-815 CD spectrometer (Jasco Inc., Japan).

The ECD spectra were calculated by the TD-DFT method, which has been proven to be reliable in predicting ECD spectra and assigning the absolute configuration of organic molecules. Calculations of the ECD spectra of 3D structure of *S*-**2a** (Figure S2) were carried out using the TD-M06/6-31+G** level with Gaussian 09.[3] Electronic excitation energies (nm) and rotational strengths (Δε) were calculated for structures A. In order to cover the 200-400 nm range, 19 transitions were calculated. As shown in Figure S2, the simulated spectra is in good agreement with the experimental spectral data, and the *S* configuration could be reliably assigned to compound **2a**. The remaining configurations of acylated products were assumed by analogy.



Experimental CD spectra of **2a**

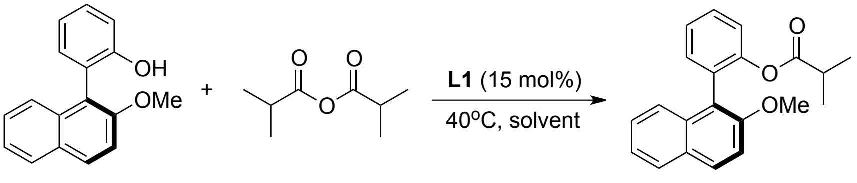


Simulated CD spectra of *S*-**2a**

Figure S2. TD-DFT Simulated Spectrum Calculated using B3LYP Method (M06/6-31+G(d,p)optimization, the first 19 excited states were calculated.)

5. Experimental Details and Characterization

Solvents evaluation



rac-**1a** **2a**

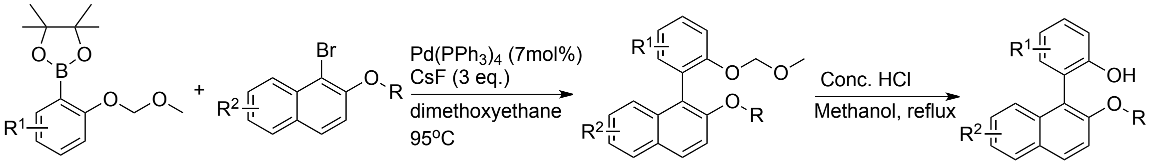
entry	Solvents	Time	Yield%[a]	e.r.[b]
1	CH_2Cl_2	48h	95	87:13
2	THF	3d	64	71:29
3	$ClCH_2CH_2Cl$	40h	92	86:14
4	Toluene	40h	95	84:16
5	$CHCl_3$	48h	95	87:12
6	DMF	3d	60	72:28
7	EtOAc	24h	87	81:19

[a] Conditions: racemic biaryl substrate *rac*-**1** (1 equiv.) and anhydride (1.2 equiv.) in the presence of catalyst **L1** (15 mol%), Solvent (2 ml), at 40 °C;
[b] Determined by chiral HPLC analysis.

Table S1. Evaluation of Solvents

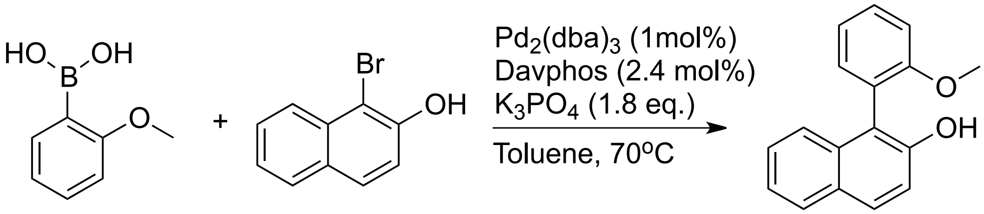
General procedure for the preparation of biaryl compounds

Condition A[4] (*rac*-**1a**, *rac*-**1b**, *rac*-**1c**, *rac*-**1d**, *rac*-**1f**, *rac*-**1g**, *rac*-**1h**, *rac*-**1i**, *rac*-**1j**, *rac*-**1k**, *rac*-**1l**):

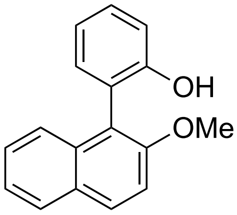


Under an atmosphere of argon, degassed dimethoxyethane solution was added to a mixture of 1-bromo-2-methoxynaphthalene (1 equiv.), 2-[2-(methoxymethoxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.1 equiv.), CsF (3 equiv.) and $Pd(PPh_3)_4$ (7 mol%). After being stirred overnight at 95 °C, the resulting suspension was filtered through a pad of celite and washed with ethyl acetate. After evaporation *in vacuo*, the residue was purified by flash chromatography on silica gel eluting with ethyl acetate/hexane (5/95) to yield MOM protected product (60-80 %yield). Concentrated HCl was added to a solution of MOM protected compound in methanol. The reaction mixture was stirred overnight under reflux. After removal of the solvent, flash column chromatography with ethyl acetate/hexane (5/95) gave the desired product. (70-90 %yield).

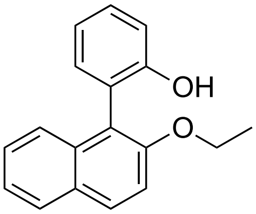
Condition B[5] (*rac*-**1e**) :



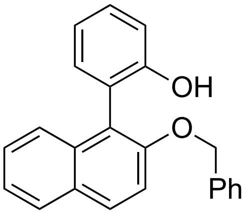
Under an atmosphere of argon, degassed toluene solution was added to a mixture of 1-bromo-2-naphthol (1 equiv.), 2-methoxyphenylboronic acid (1.5 equiv.), 2-dicyclohexylphosphino-2'-(N,N'-dimethylamino)biphenyl (Davephos) (2.4 mol%), $Pd_2(dba)_3$ (1 mol%) and K_3PO_4 (1.8 eq.). After being stirred overnight at 70 °C, the resulting suspension was filtered through a pad of celite and washed with ethyl acetate. After evaporation *in vacuo*, the residue was purified by flash chromatography on silica gel eluting with ethyl acetate/hexane (5/95) to yield product. (50-60 %yield).



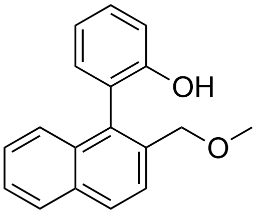
rac-**1a**. Condition A. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.92 (s, 3H), 4.97 (s, 1H), 7.1 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (dd, *J* = 8, 1.2 Hz, 1H), 7.25 (dd, *J* = 7.6, 2 Hz, 1H), 7.38-7.44 (m, 4H), 7.51-7.54 (m, 1H), 7.87-7.89 (m, 1H), 7.99 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.8, 113.5, 116.0, 118.5, 120.5, 122.4, 124.1, 125.0, 127.1, 126.6, 126.8, 128.1, 129.4, 129.4, 130.5, 132.1, 133.7, 153.8, 154.5; ESI-HRMS: *m/z* calcd. for $(C_{17}H_{14}O_2Na)^+$ 273.0886; found 273.0894.



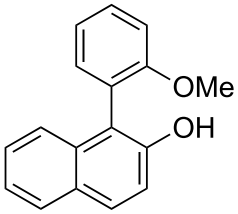
rac-**1b**. Condition A. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.3 (t, *J* = 7.2 Hz, 3H), 4.1-4.2 (m, 2H), 5.18 (s, 1H), 7.08 (td, *J* = 7.2, 1.2 Hz, 1H), 7.14 (dd, *J* = 8, 1.2 Hz, 1H), 7.26 (dd, *J* = 7.2, 2 Hz, 1H), 7.37-7.42 (m, 4H), 7.56-7.59 (m, 1H), 7.85-7.87 (m, 1H), 7.93 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15, 65.7, 115.4, 116.2, 119.9, 120.4, 122.7, 124.2, 125.2, 126.9, 128.1, 129.3, 129.7, 130.3, 132.3, 133.8, 153.7, 153.9; ESI-HRMS *m/z* calcd. for $(C_{18}H_{17}O_2)^+$ 265.1229; found 265.1232.



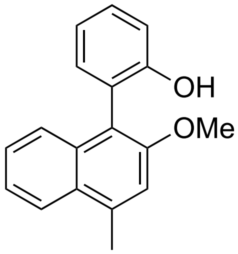
rac-**1c**. Condition A. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.96 (s, 1H), 5.12-5.19 (m, 2H), 7.07 (td, *J* = 7.2, 1.2 Hz, 1H), 7.13 (dd, *J* = 8, 1.2 Hz, 1H), 7.2-7.25 (m, 3H), 7.25-7.31 (m, 3H), 7.37-7.42 (m, 4H), 7.51-7.55 (m, 1H), 7.82-7.86 (m, 1H), 7.9 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 71.8, 116, 120.2, 120.5, 122.5, 124.4, 125.1, 127.04, 127.05, 127.8, 128.1, 128.5, 129.4, 129.8, 130.4, 132.1, 133.7, 136.8, 153.6, 153.8; ESI-HRMS *m/z* calcd. for $(C_{23}H_{18}O_2Na)^+$ 349.1205; found 349.1207.



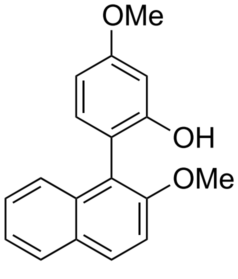
rac-**1d**. Condition A. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.33 (s, 3H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 5.44 (s, 1H), 7.05-7.14 (m, 3H), 7.38-7.45 (m, 3H), 7.48-7.52 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.9 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 58.6, 73.3, 116.8, 120.7, 124.9, 126.2, 126.3, 126.61, 126.64, 128, 128.9, 129.7, 131.4, 132.9, 133, 133.5, 134.8, 153.9; ESI-HRMS *m/z* calcd. for $(C_{18}H_{16}O_2Na)^+$ 287.1048; found 287.1055.



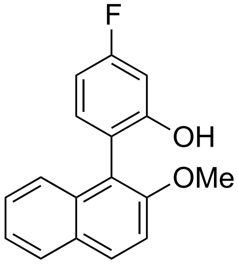
rac-**1e**. Condition B. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.78 (s, 3H), 5.32 (s, 1H), 7.15-7.21 (m, 2H), 7.29-7.4 (m, 5H), 7.51-7.55 (m, 1H), 7.83-7.85 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 55.8, 111.9, 117.7, 117.8, 121.5, 122.5, 123.2, 124.8, 126.3, 128, 129.1, 129.5, 130.2, 133.4, 133.5, 150.6, 157.8; ESI-HRMS *m/z* calcd. for $(C_{17}H_{15}O_2)^+$ 251.1072; found 251.1077.



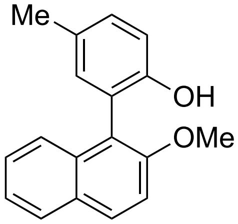
rac-**1f**. Condition A. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.26 (s, 3H), 4.06 (s, 3H), 4.65 (s, 1H), 6.81 (s, 1H), 7.03-7.14 (m, 3H), 7.35-7.44 (m, 4H), 8.27-8.3 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 21.1, 55.8, 106.9, 115.4, 120.8, 122.2, 123.1, 124.7, 124.9, 125.3, 125.4, 127.4, 129.5, 131.7, 134.1, 136.4, 153.7, 155.8; ESI-HRMS *m/z* calcd. for $(C_{18}H_{17}O_2)^+$ 265.1229; found 265.1223.



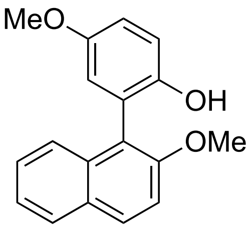
rac-**1g**. Condition A. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.87 (s, 3H), 3.9 (s, 3H), 5.01 (s, 1H), 6.67 (td, *J* = 8.4, 2.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.35-7.42 (m, 3H), 7.52-7.55 (m, 1H), 7.83-7.86 (m, 1H), 7.94 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 55.5, 57, 101.6, 107.1, 113.7, 114.8, 118.6, 124.2, 125.3, 127.2, 128.2, 129.7, 130.5, 132.8, 134.3, 154.8, 154.9, 160.9; ESI-HRMS *m/z* calcd. for $(C_{18}H_{17}O_3)^+$ 281.1178; found 281.1183.



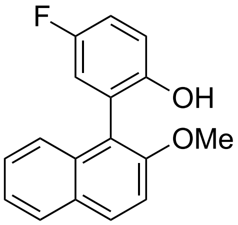
rac-**1h**. Condition A. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.9 (s, 3H), 5.09 (s, 1H), 6.8 (td, *J* = 8.4, 2.8 Hz, 1H), 6.84 (dd, *J* = 10, 2.4 Hz, 1H), 7.16 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.37-7.44 (m, 3H), 7.46-7.49 (m, 1H), 7.85-7.87 (m, 1H), 7.97 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 56.7, 103.6 (d, *J* = 25 Hz), 107.7 (d, *J* = 22 Hz), 113.4, 117.4, 118.3 (d, *J* = 4 Hz), 124.2, 124.7, 127.3, 128.2, 129.4, 130.8, 132.9 (d, *J* = 9 Hz), 133.8, 154.7, 155 (d, *J* = 12 Hz), 163.4 (d, *J* = 244 Hz); ^{19}F NMR (CDCl$_3$, 376 MHz) δ -112.7; ESI-HRMS *m/z* calcd. for $(C_{17}H_{14}FO_2)^+$ 269.0978; found 269.0976.



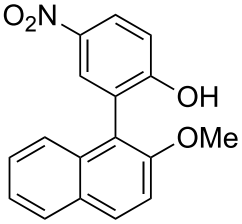
rac-**1i**. Condition A. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.35 (s, 3H), 3.91 (s, 3H), 4.8 (s, 1H), 7-7.03 (m, 2H), 7.17 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.36-7.42 (m, 3H), 7.51-7.53 (m, 1H), 7.84-7.86 (m, 1H), 7.95 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 20.6, 56.8, 113.4, 115.8, 118.7, 122.1, 124, 125.1, 127, 128, 129.4, 129.6, 130, 130.4, 132.4, 133.8, 151.6, 154.4; ESI-HRMS *m/z* calcd. for $(C_{18}H_{17}O_2)^+$ 265.1229; found 265.1231.



rac-**1j**. Condition A. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.78 (s, 3H), 3.91 (s, 3H), 4.72 (s, 1H), 6.79 (d, *J* = 3.2 Hz, 1H), 6.95 (dd, *J* = 8.8, 3.2 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 7.37-7.43 (m, 3H), 7.55-7.57 (m, 1H), 7.84-7.87 (m, 1H), 7.95 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 55.8, 56.8, 113.5, 115.1, 116.81, 116.84, 118.7, 123.1, 124.1, 125, 127.1, 128.1, 129.4, 130.5, 133.6, 147.9, 153.4, 154.3; ESI-HRMS *m/z* calcd. for $(C_{18}H_{17}O_3)^+$ 281.1178; found 281.1181.



rac-**1k**. Condition A. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.91 (s, 3H), 4.82 (s, 1H), 6.95 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.02-7.1 (m, 2H), 7.37-7.44 (m, 3H), 7.48-7.51 (m, 1H), 7.85-7.87 (m, 1H), 7.97 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 56.8, 113.3, 115.8 (d, *J* = 23 Hz), 116.9 (d, *J* = 8 Hz), 117.5, 118.2 (d, *J* = 23 Hz), 123.5 (d, *J* = 8 Hz), 124.2, 124.6, 127.4, 128.2, 129.4, 130.9, 133.3, 149.9 (d, *J* = 3 Hz), 154.4, 156.8 (d, *J* = 236 Hz); ^{19}F NMR (CDCl$_3$, 376 MHz) δ -124.5; ESI-HRMS *m/z* calcd. for $(C_{17}H_{14}FO_2)^+$ 269.0978; found 269.0976.

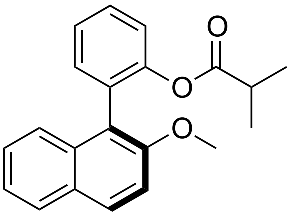


rac-**1l**. Condition A. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.91 (s, 3H), 5.57 (s, 1H), 7.17 (d, *J* = 9.2 Hz, 1H), 7.36-7.46 (m, 4H), 7.87-7.9 (m, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 2.8 Hz, 1H), 8.28 (dd, *J* = 9.2, 2.8 Hz, 1H); ^{13}C

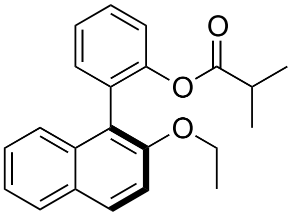
NMR ($CDCl_3$, 100 MHz) δ 56.6, 113, 115.1, 116.3, 123.1, 123.9, 124.5, 125.6, 127.9, 128.4, 128.5, 129.3, 131.8, 133.1, 141.6, 154.9, 159.5; ESI-HRMS *m/z* calcd. for $(C_{17}H_{14}NO_4)^+$ 296.0923; found 296.0926.

General procedure for dynamic kinetic resolution of biaryl compounds

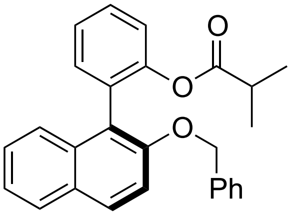
To a mixture of racemic biaryl compounds (0.05 mmol), catalyst (15 mol%), Proton sponge (0.06 mmol) and Molecular sieves 13X (Aldrich), 2 ml dry $CHCl_3$ was added. Under 40 °C, isobutyric anhydride (0.06 mmol) was added. After stirring for indicated time in Scheme 2, the reaction mixture was purified by column chromatography (hexane/ethyl acetate = 95/5) to afford the corresponding ester. The optical purity of the obtained product was determined by chiral HPLC.



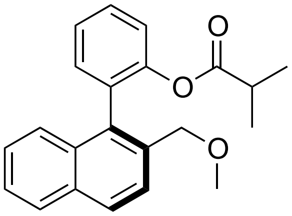
2a (90:10 er) HPLC (UV 220 nm, Chiralpak AD-3, *i*-PrOH/Hexane = 3/97, 0.5 mL/min), t_1 (minor) = 12.8 min, t_2 (major) = 14.8 min. $[\alpha]_D^{22}$ 12.1 (*c* 0.66, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.66 (d, *J* = 6.8 Hz, 3H), 0.7 (d, *J* = 6.8 Hz, 3H), 2.3 (m, 1H), 3.86 (s, 3H), 7.28-7.31 (m, 1H), 7.34-7.43 (m, 6H), 7.48-7.52 (m, 1H), 7.81-7.83 (m, 1H), 7.9 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.2, 18.3, 33.8, 56.7, 113.4, 120.4, 122.8, 123.6, 125.2, 125.7, 126.4, 127.6, 128.6, 128.8, 129.4, 129.5, 132.5, 133.4, 149.3, 154.2, 174.7; ESI-HRMS: *m/z* calcd. for $(C_{21}H_{20}O_3Na)^+$ 343.1305; found 343.1302.



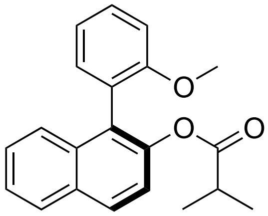
2b (89:11 er) HPLC (UV 220 nm, Chiralpak AD-3, *i*-PrOH/Hexane = 1/99, 0.5 mL/min), t_1 (minor) = 14.7 min, t_2 (major) = 20 min. $[\alpha]_D{}^{23}$ 19.1 (*c* 0.69, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.63 (d, *J* = 6.8 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H), 1.24 (t, *J* = 6.8 Hz, 3H), 2.27 (m, *J* = 6.8 Hz, 1H), 4.04-4.12 (m, 2H), 7.27 (d, *J* = 8 Hz, 1H), 7.3-7.42 (m, 6H), 7.45-7.49 (m, 1H), 7.78-7.8 (m, 1H), 7.85 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15, 18.2, 33.8, 65.4, 115.3, 121.3, 122.7, 123.6, 125.3, 125.5, 126.3, 127.6, 128.4, 129, 129.4, 129.5, 132.6, 133.5, 149.3, 153.6, 174.7; ESI-HRMS *m/z* calcd. for $(C_{22}H_{22}O_3Na)^+$ 357.1467; found 357.1460.



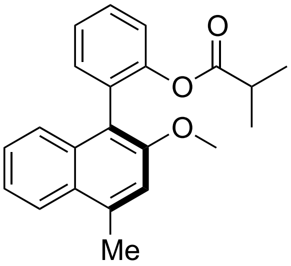
2c (84:16 er) HPLC (UV 220 nm, Chiralpak AD-3, *i*-PrOH/Hexane = 1/99, 0.5 mL/min), t_1 (minor) = 30.4 min, t_2 (major) = 40.3 min. $[\alpha]_D{}^{22}$ 9.5 (*c* 0.71, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.55 (d, *J* = 7.2 Hz, 3H), 0.63 (d, *J* = 7.2 Hz, 3H), 2.24 (m, *J* = 7.2 Hz, 1H), 5.1 (s, 2H), 7.2-7.34 (m, 9H), 7.35-7.38 (m, 2H), 7.4-7.43 (m, 1H), 7.45-7.5 (m, 1H), 7.75-7.78 (s, 1H), 7.8 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.3, 34, 71.7, 115.9, 121.9, 123, 124, 125.6, 125.9, 126.6, 127.1, 127.7, 127.8, 128.5, 128.8, 129.3, 129.6, 129.7, 132.8, 133.6, 137.7, 149.5, 153.5, 175; ESI-HRMS *m/z* calcd. for $(C_{27}H_{24}O_3Na)^+$ 419.1623; found 419.1633.



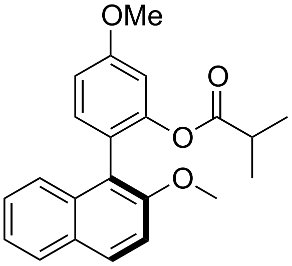
2d (56:44 er) HPLC (UV 220 nm, Chiralpak OD-3, *i*-PrOH/Hexane = 1/99, 0.5 mL/min), t_1 (major) = 13.4 min, t_2 (minor) = 16.1 min. $[\alpha]_D{}^{22}$ -6.7 (*c* 0.6, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.51 (d, *J* = 7.2 Hz, 3H), 0.55 (d, *J* = 6.8 Hz, 3H), 2.2 (m, *J* = 7.2, 6.8 Hz, 1H), 3.3 (s, 3H), 4.32 (s, 2H), 7.25 (dd, *J* = 8, 1.2 Hz, 1H), 7.33-7.39 (m, 4H), 7.42-7.46 (m, 1H), 7.5-7.54 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18, 18.1, 33.7, 58.3, 72.3, 122.9, 125.5, 125.6, 125.9, 126.1, 126.3, 127.7, 128.2, 129.1, 131.3, 131.9, 132.4, 132.7, 133, 134.5, 149.1, 174.9; ESI-HRMS *m/z* calcd. for $(C_{22}H_{22}O_3)^+$ 357.1467; found 357.1472.



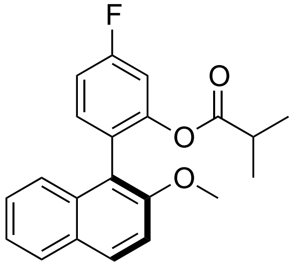
2e (61:39 er) HPLC (UV 220 nm, Chiralpak AD-H, *i*-PrOH/Hexane = 0.5/0.995, 0.5 mL/min), t_1 (minor) = 22.3 min, t_2 (major) = 29.1 min. $[\alpha]_D{}^{25}$ 5.5 (*c* 0.71, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.94 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 2.53 (m, *J* = 6.8 Hz, 1H), 3.68 (s, 3H), 7.02-7.07 (m, 2H), 7.16-7.19 (m, 1H), 7.3 (d, *J* = 8.8 Hz, 1H), 7.35-7.49 (m, 4H), 7.87-7.9 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.7, 18.8, 34.2, 55.9, 111.2, 120.6, 121.8, 124.1, 125.5, 126.2, 126.4, 127.7, 128.2, 129, 129.6, 131.9, 132.2, 133.6, 146.1, 157.8; ESI-HRMS *m/z* calcd. for $(C_{21}H_{20}O_3Na)^+$ 343.1310; found 343.1315.



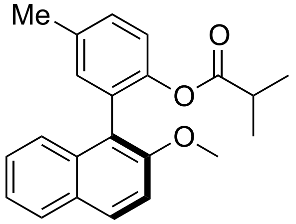
2f (63:37 er) HPLC (UV 220 nm, Whelk-(R,R), *i*-PrOH/Hexane = 1/99, 0.5 mL/min), t_1 (major) = 18.2 min, t_2 (minor) = 20.6 min. $[\alpha]_D^{22}$ -7.4 (*c* 0.69, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.58 (d, *J* = 6.8 Hz, 3H), 0.61 (d, *J* = 6.8 Hz, 3H), 2.22 (s, 3H), 2.23 (m, *J* = 6.8 Hz, 1H), 4.03 (s, 3H), 6.73 (s, 1H), 7.23 (dd, *J* = 8, 1.2 Hz, 1H), 7.27-7.3 (m, 2H), 7.32-7.4 (m, 3H), 7.47 (td, *J* = 7.6, 2 Hz, 1H), 8.21-8.23 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.1, 18.2, 21, 33.8, 55.5, 106.4, 121.5, 122.9, 123.9, 124.1, 125.5, 125.6, 126, 126.5, 128.5, 132.4, 132.8, 133.6, 134.4, 149.5, 154.9, 175; ESI-HRMS *m/z* calcd. for $(C_{22}H_{22}O_3Na)^+$ 357.1467; found 357.1477.



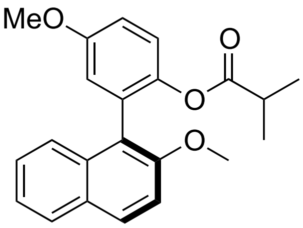
2g (86:14 er) HPLC (UV 220 nm, Chiralpak AD-3, *i*-PrOH/Hexane = 4/96, 0.5 mL/min), t_1 (minor) = 16.7 min, t_2 (major) = 20.7 min. $[\alpha]_D^{23}$ 4.7 (*c* 0.8, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.63 (d, *J* = 6.8 Hz, 3H), 0.66 (d, *J* = 6.8 Hz, 3H), 2.26 (m, *J* = 6.8 Hz, 1H), 3.84 (s, 3H), 3.89 (s, 3H), 6.83 (d, *J* = 2.8 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.29-7.36 (m, 3H), 7.42-7.44 (m, 1H), 7.77-7.79 (m, 1H), 7.86 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.21, 18.24, 33.8, 55.5, 56.7, 108.4, 111.9, 113.5, 120.2, 121.3, 123.5, 125.3, 126.4, 127.6, 128.9, 129.3, 132.8, 133.8, 150, 154.5, 159.8, 174.6; ESI-HRMS *m/z* calcd. for $(C_{22}H_{22}O_4Na)^+$ 373.1416; found 371.1423.



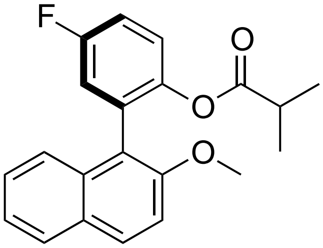
2h (83:17 er) HPLC (UV 220 nm, Chiralpak AD-3, *i*-PrOH/Hexane = 1/99, 0.5 mL/min), t_1 (minor) = 15.8 min, t_2 (major) = 23.2 min. $[\alpha]_D^{23}$ 8.7 (*c* 0.76, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.63 (d, *J* = 6.8 Hz, 3H), 0.67 (d, *J* = 7.2 Hz, 3H), 2.27 (m, *J* = 7.2, 6.8 Hz, 1H), 3.84 (s, 3H), 7.05 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.1 (td, *J* = 8.4, 2.4 Hz, 1H), 7.31-7.38 (m, 5H), 7.78-7.81 (m, 1H), 7.89 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.15, 18.17, 33.8, 56.6, 110.8 (d, *J* = 24 Hz), 112.9 (d, *J* = 21 Hz), 113.3, 119.3, 123.6, 124.9, 125.3 (d, *J* = 3 Hz), 126.6, 127.8, 128.8, 129.8, 133.2 (d, *J* = 9 Hz), 133.5, 149.9 (d, *J* = 11 Hz), 154.3, 162.2 (d, *J* = 246 Hz), 174.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -112.8; ESI-HRMS *m/z* calcd. for $(C_{21}H_{19}FO_3Na)^+$ 361.1216; found 361.1207.



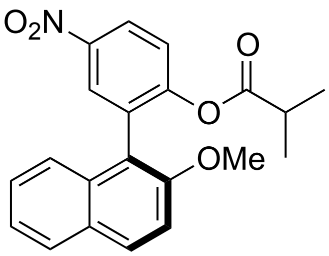
2i (89:11 er) HPLC (UV 220 nm, Whelk (R, R), *i*-PrOH/Hexane = 1/99, 0.5 mL/min), t_1 (major) = 22.9 min, t_2 (minor) = 26.6 min. $[\alpha]_D^{23}$ 36.2 (*c* 0.69, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.63 (d, *J* = 7.2 Hz, 3H), 0.67 (d, *J* = 6.8 Hz, 3H), 2.28 (m, *J* = 7.2, 6.8 Hz, 1H), 2.42 (s, 3H), 3.85 (s, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.17-7.18 (m, 1H), 7.26-7.37 (m, 4H), 7.41-7.44 (m, 1H), 7.78-7.81 (m, 1H), 7.87 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.26, 18.28, 21, 33.8, 56.7, 113.4, 120.5, 122.4, 123.5, 125.3, 126.4, 127.6, 128.9, 129, 129.3, 129.4, 132.9, 133.5, 135.2, 147, 154.2, 174.9; ESI-HRMS *m/z* calcd. for $(C_{22}H_{22}O_3Na)^+$ 357.1467; found 357.1475.



2j (87:13 er) HPLC (UV 220 nm, Chiralpak IA, *i*-PrOH/Hexane = 1/99, 0.5 mL/min), t_1 (minor) = 20.5 min, t_2 (major) = 27.7 min. $[\alpha]_D^{23}$ 28.3 (*c* 0.84, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.61 (d, *J* = 6.8 Hz, 3H), 0.65 (d, *J* = 6.8 Hz, 3H), 2.25 (m, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 3.85 (s, 3H), 6.9 (d, *J* = 2.8 Hz, 1H), 7 (dd, *J* = 8.8, 3.2 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.3-7.37 (m, 3H), 7.42-7.45 (m, 1H), 7.78-7.8 (m, 1H), 7.87 (d, *J* = 9.2Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.2, 18.3, 33.8, 55.6, 56.8, 113.4, 114, 117.3, 120.3, 123.4, 123.6, 125.2, 126.5, 127.6, 128.8, 129.6, 130.2, 133.3, 142.9, 154.1, 157, 175.1; ESI-HRMS *m/z* calcd. for $(C_{22}H_{22}O_4Na)^+$ 373.1416; found 373.1414.



2k (87:13 er) HPLC (UV 220 nm, Chiralpak IA, *i*-PrOH/Hexane = 1/99, 0.4 mL/min), t_1 (minor) = 16.6 min, t_2 (major) = 22.5 min. $[\alpha]_D^{22}$ -0.4 (*c* 0.83, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.61 (d, *J* = 6.8 Hz, 3H), 0.65 (d, *J* = 6.8 Hz, 3H), 2.25 (m, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 7.09 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.13-7.23 (m, 2H), 7.31-7.4 (m, 4H), 7.79 (dd, *J* = 6.8, 1.6 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.16, 18.19, 33.7, 56.7, 113.2, 115.2 (d, *J* = 23 Hz), 119.07 (d, *J* = 17 Hz), 119.2, 123.7, 124 (d, *J* = 9 Hz), 124.8, 126.7, 127.8, 128.8, 130, 131.2 (d, *J* = 8 Hz), 133.1, 145.2 (d, *J* = 2 Hz), 154.1, 160 (d, *J* = 243 Hz), 174.8; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -117.6; ESI-HRMS *m/z* calcd. for $(C_{21}H_{19}FO_3Na)^+$ 361.1216; found 361.1215.



2l (51:49 er) HPLC (UV 220 nm, Chiralpak AD-H, *i*-PrOH/Hexane = 5/95, 0.5 mL/min), t_1 (major) = 28.2 min, t_2 (minor) = 36 min. $[\alpha]_D^{23}$ 2.5 (*c* 0.9, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.66 (d, *J* = 7.2 Hz, 3H), 0.69 (d, *J* = 6.8 Hz, 3H), 2.3 (m, *J* = 7.2, 6.8 Hz, 1H), 3.85 (s, 3H), 7.27-7.3 (m, 1H), 7.33-7.4 (m, 3H), 7.44 (d, *J* = 9.2 Hz, 1H), 7.81-7.84 (m, 1H), 7.94 (d, *J* = 9.2 Hz, 1H), 8.29 (d, *J* = 2.8 Hz, 1H), 8.35 (dd, *J* = 8.8, 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.08, 18.1, 33.9, 56.5, 112.9, 117.6, 123.8, 123.9, 124, 124.2, 127.1, 128, 128.4, 128.7, 130.6, 131.1, 132.8, 145.4, 154.2, 154.4, 174; ESI-HRMS *m/z* calcd. for $(C_{21}H_{19}NO_5Na)^+$ 388.1161; found 388.1164.

5. Crystal Structure of Catalyst L1

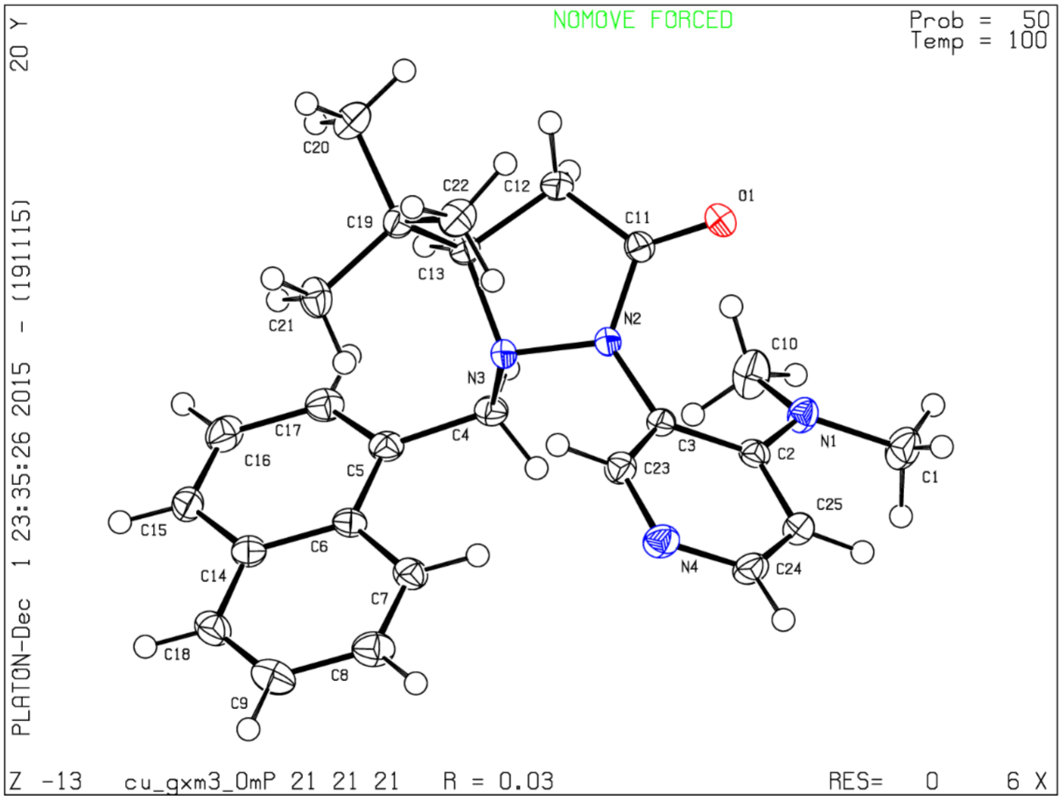


Figure S3. Crystal Structure of Catalyst **L1**

X-ray Structure determination: Single crystal X-ray diffraction data of **L1** was collected on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100K during data collection. Cu radiation was used for the sample. Using Olex2,[6] the structure was solved with the ShelXS[7] structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimization. Basic information pertaining to crystal parameters and structure refinement is summarized in Table S2.

Identification code	cu_gxm3_0m
Empirical formula	$C_{25}H_{30}N_4O$
Formula weight	402.53

Temperature	100K
Crystal system	orthorhombic
space group	$P2_12_12_1$
a/Å	11.2926(3)
b/Å	12.7919(3)
c/Å	15.5672(4)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	2248.74(10)
Z	4
d_{calcd}, g.cm^{-3}	1.189
μ, mm^{-1}	0.580
F(000)	864.0
Crystal size/mm^3	0.25 × 0.23 × 0.2
Radiation	CuKa (l = 1.54178)
2Θ range for data collection	8.948 to 133.288
Index ranges	$-12 \leq h \leq 13$, $-15 \leq k \leq 11$, $-18 \leq l \leq 18$
Reflections collected	15267
Independent reflections	3960 [R_{int} = 0.0252, R_{sigma} = 0.0209]
Data/restraints/parameters	3960/0/276
GOOF on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0279, wR_2 = 0.0693
Final R indexes [all data]	R_1 = 0.0292, wR_2 = 0.0702
Largest diff. peak/hole/e Å^{-3}	0.15/-0.16
Flack parameter	0.00(8)

Table S2. Crystal Data and Structure Refinement

6. References

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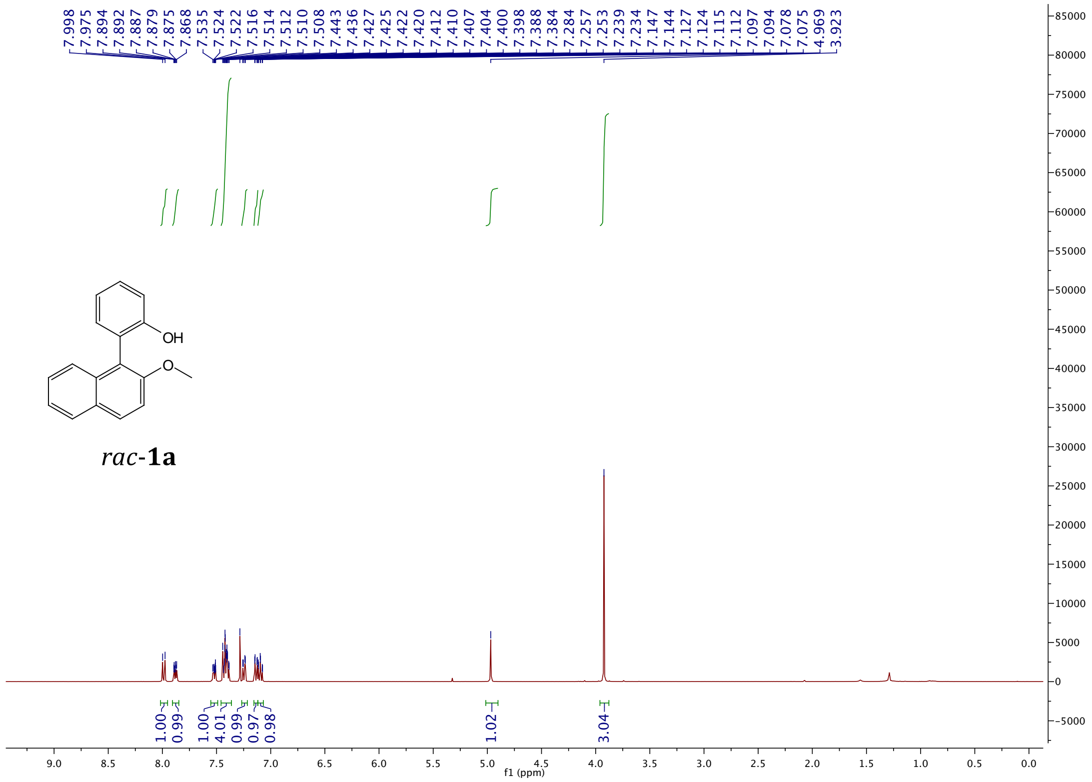
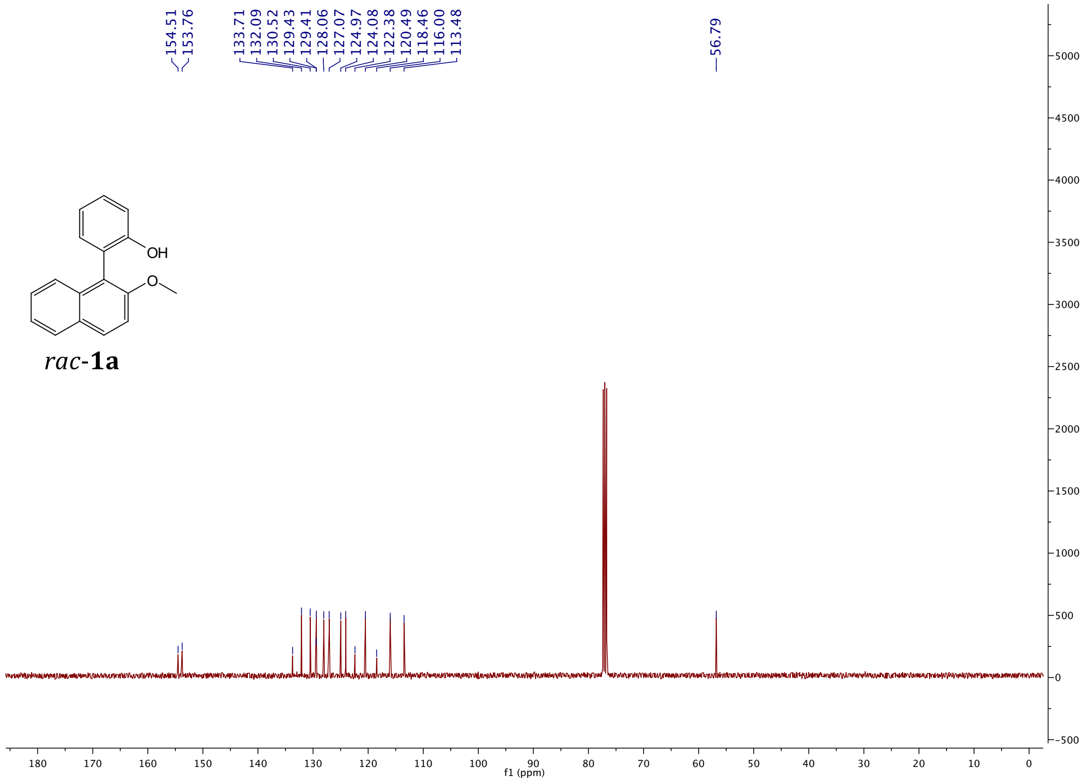
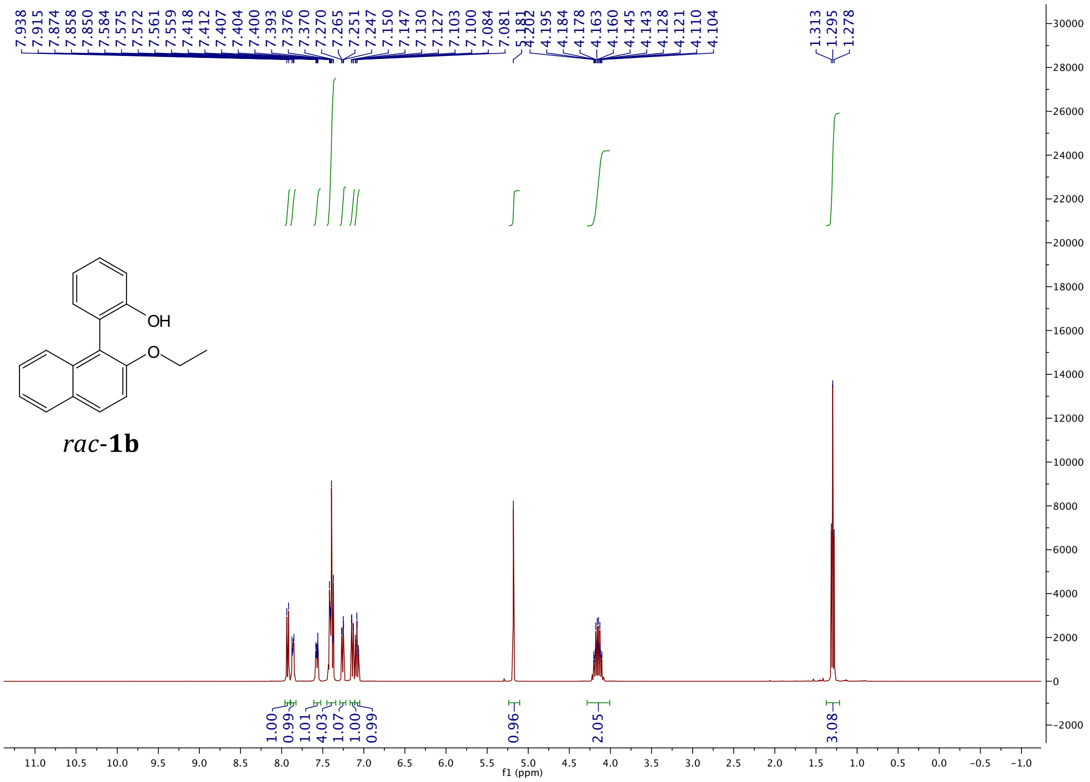
7. NMR Spectra and HPLC Spectra



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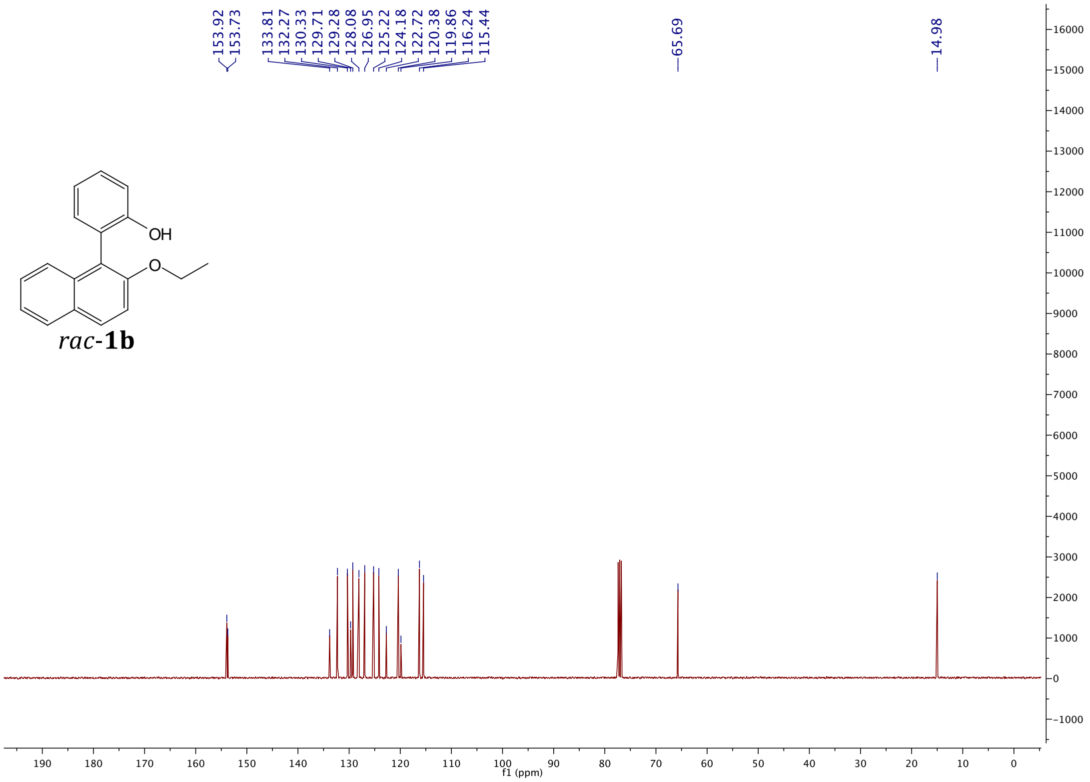
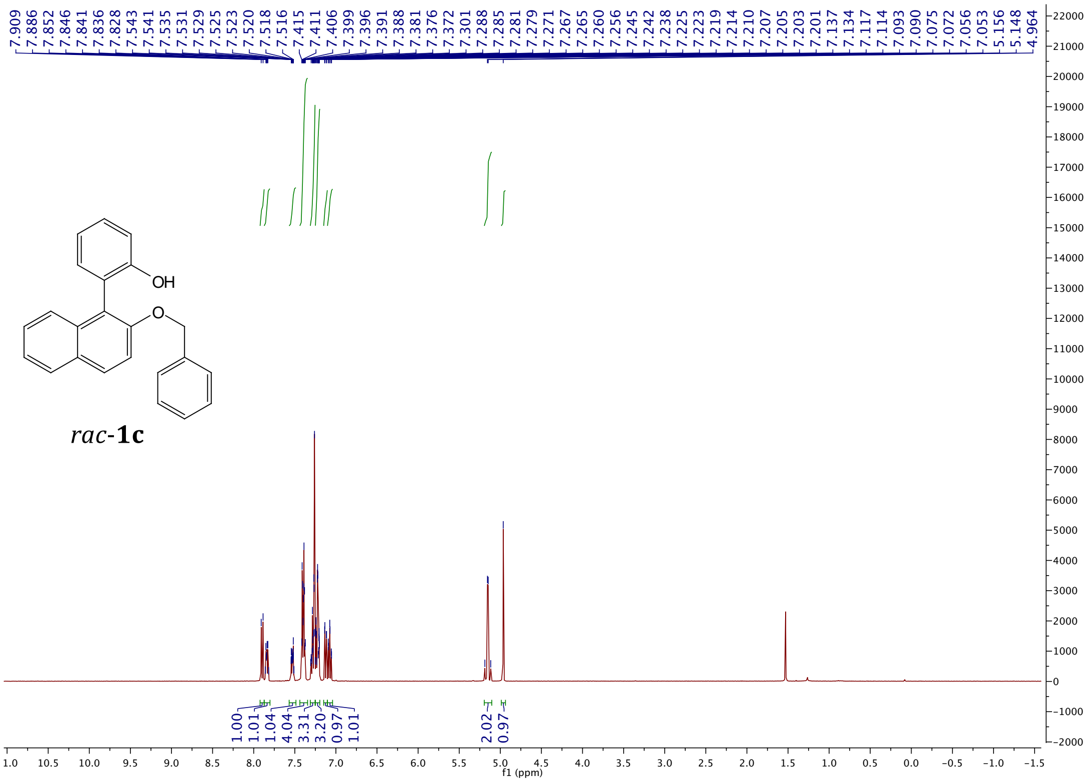
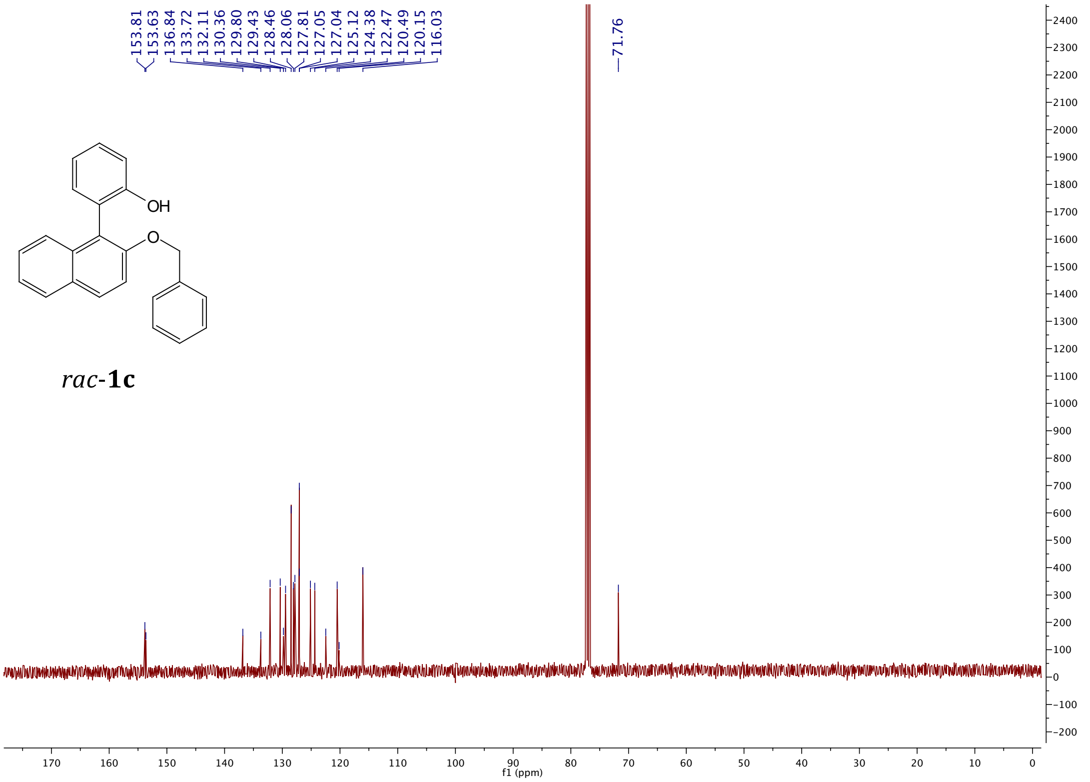
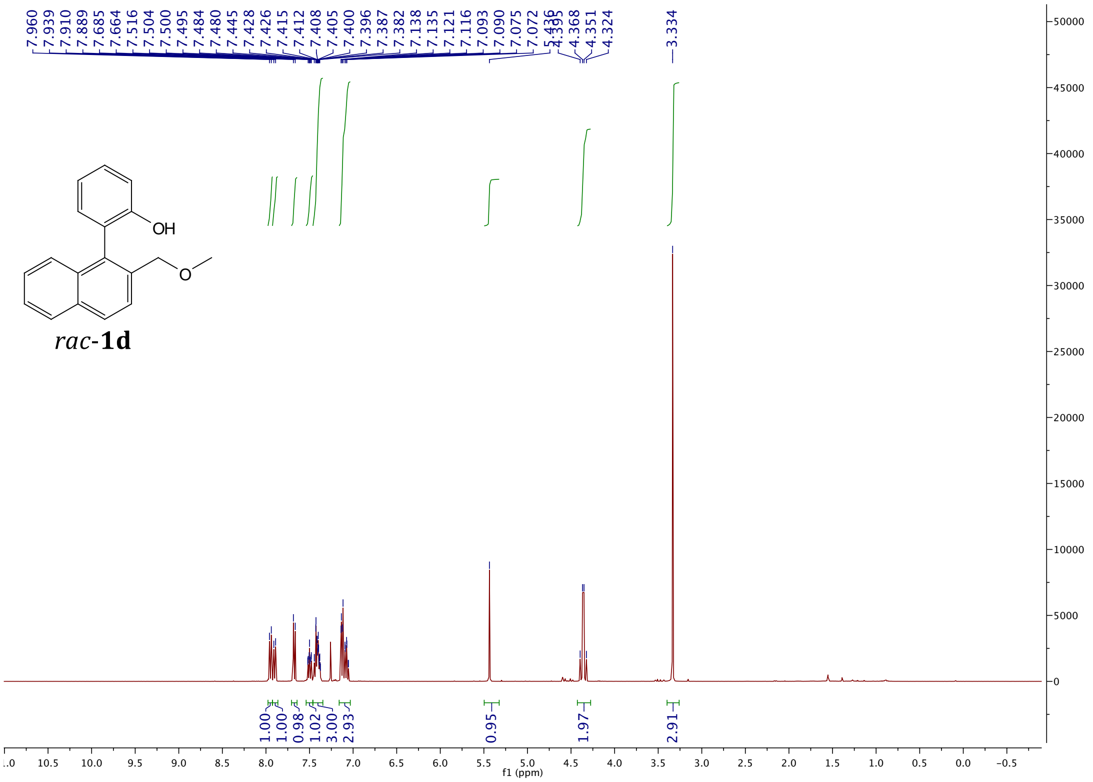
-1.0
f1 (ppm)

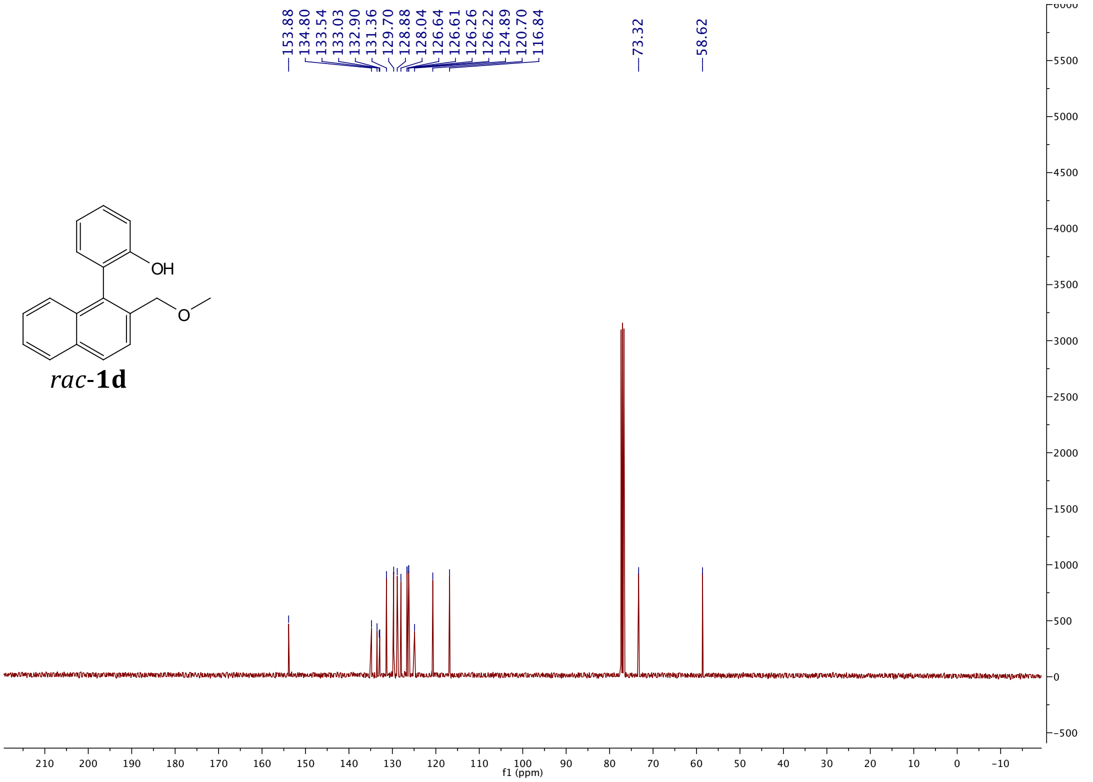

153.92
153.73
133.81
132.27
130.33
129.71
129.28
128.08
126.95
125.22
124.18
122.72
120.38
119.86
116.24
115.44
65.69
14.98
OH
O
rac-**1b**
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.909
7.886
7.852
7.846
7.841
7.836
7.828
7.543
7.541
7.535
7.531
7.529
7.525
7.523
7.520
7.518
7.516
7.415
7.411
7.406
7.399
7.396
7.391
7.388
7.381
7.376
7.372
7.301
7.288
7.285
7.281
7.279
7.271
7.267
7.265
7.260
7.256
7.245
7.242
7.238
7.225
7.223
7.219
7.214
7.210
7.207
7.205
7.203
7.201
7.137
7.134
7.117
7.114
7.093
7.090
7.075
7.072
7.056
7.053
5.156
5.148
4.964
OH
O
rac-1c
1.00
1.01
1.04
4.04
3.31
3.20
0.97
1.01
2.02
0.97
f1 (ppm)

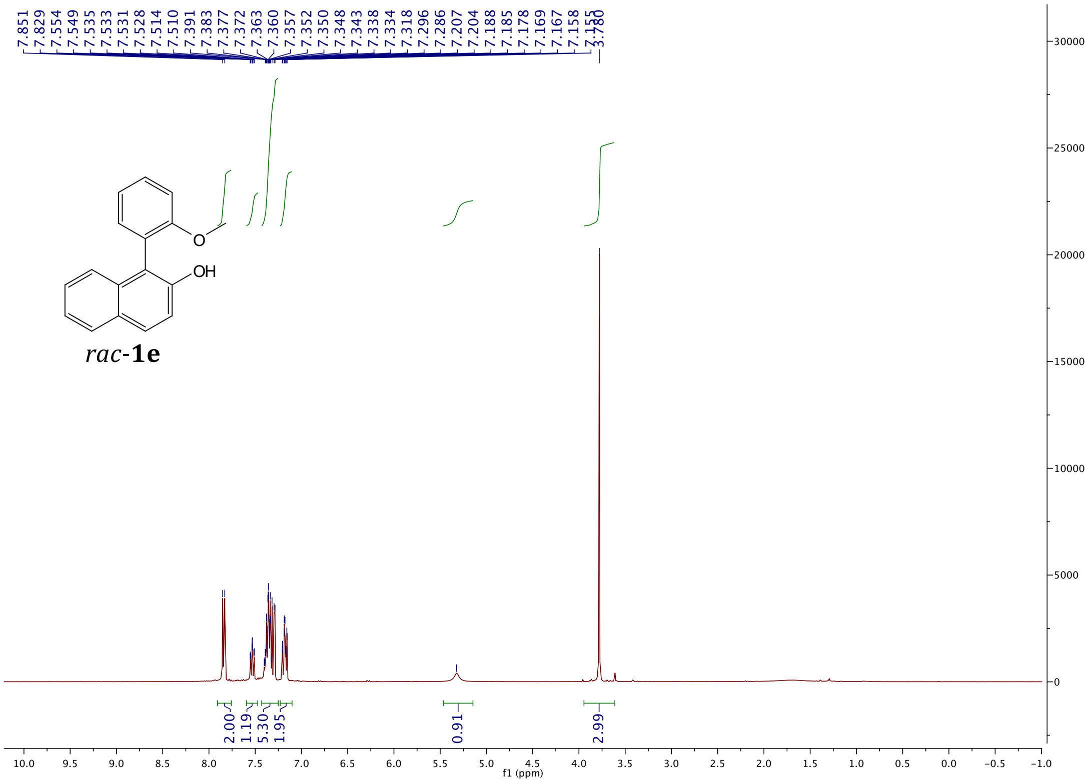

153.81
153.63
136.84
133.72
132.11
130.36
129.80
129.43
128.46
128.06
127.81
127.05
127.04
125.12
124.38
122.47
120.49
120.15
116.03
71.76
OH
O
rac-1c
f1 (ppm)


7.960
7.939
7.910
7.889
7.685
7.664
7.516
7.504
7.500
7.495
7.484
7.480
7.445
7.428
7.426
7.415
7.412
7.408
7.405
7.400
7.396
7.387
7.382
7.138
7.135
7.121
7.116
7.093
7.090
7.075
7.072
5.436
4.395
4.368
4.351
4.324
3.334
OH
O
1.00
1.00
0.98
1.02
3.00
2.93
0.95
1.97
2.91
f1 (ppm)

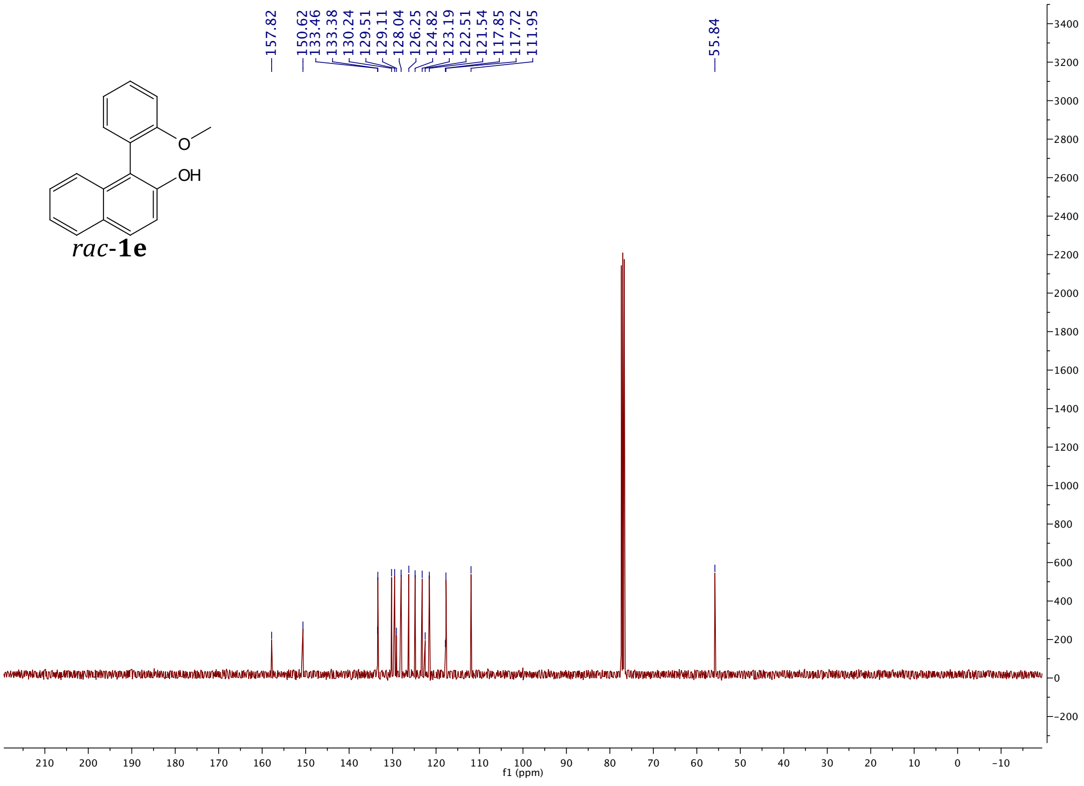
rac-**1d**


153.88
134.80
133.54
133.03
132.90
131.36
129.70
128.88
128.04
126.64
126.61
126.26
126.22
124.89
120.70
116.84
73.32
58.62
OH
O
f1 (ppm)

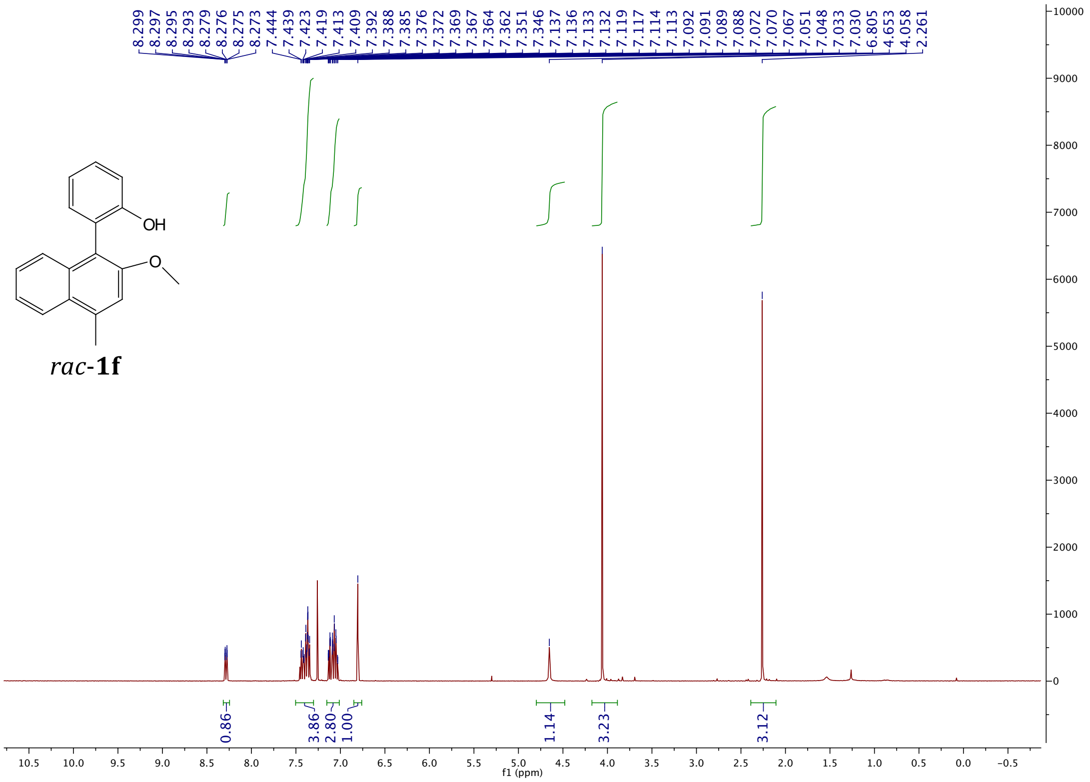
rac-**1d**

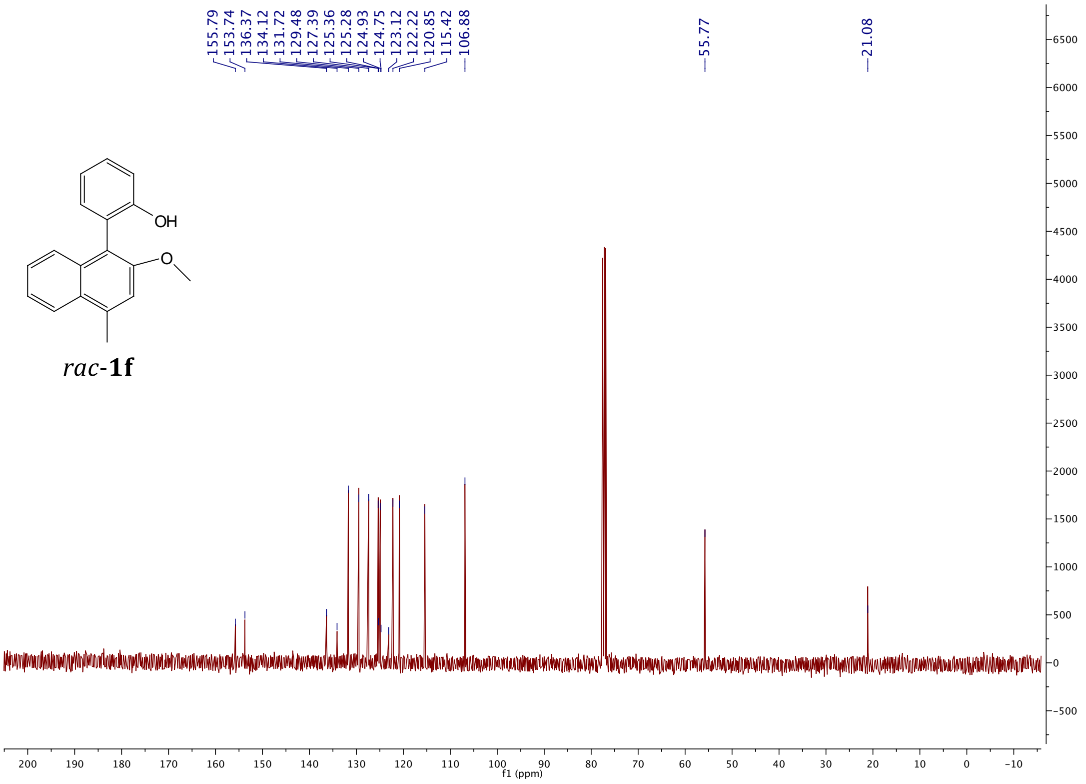

7.851
7.829
7.554
7.549
7.535
7.533
7.531
7.528
7.514
7.510
7.391
7.383
7.377
7.372
7.363
7.360
7.357
7.352
7.350
7.348
7.343
7.338
7.334
7.318
7.296
7.286
7.207
7.204
7.188
7.185
7.178
7.169
7.167
7.158
7.155
3.780
O
OH
2.00
1.19
5.30
1.95
0.91
2.99
30000
25000
20000
15000
10000
5000
0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

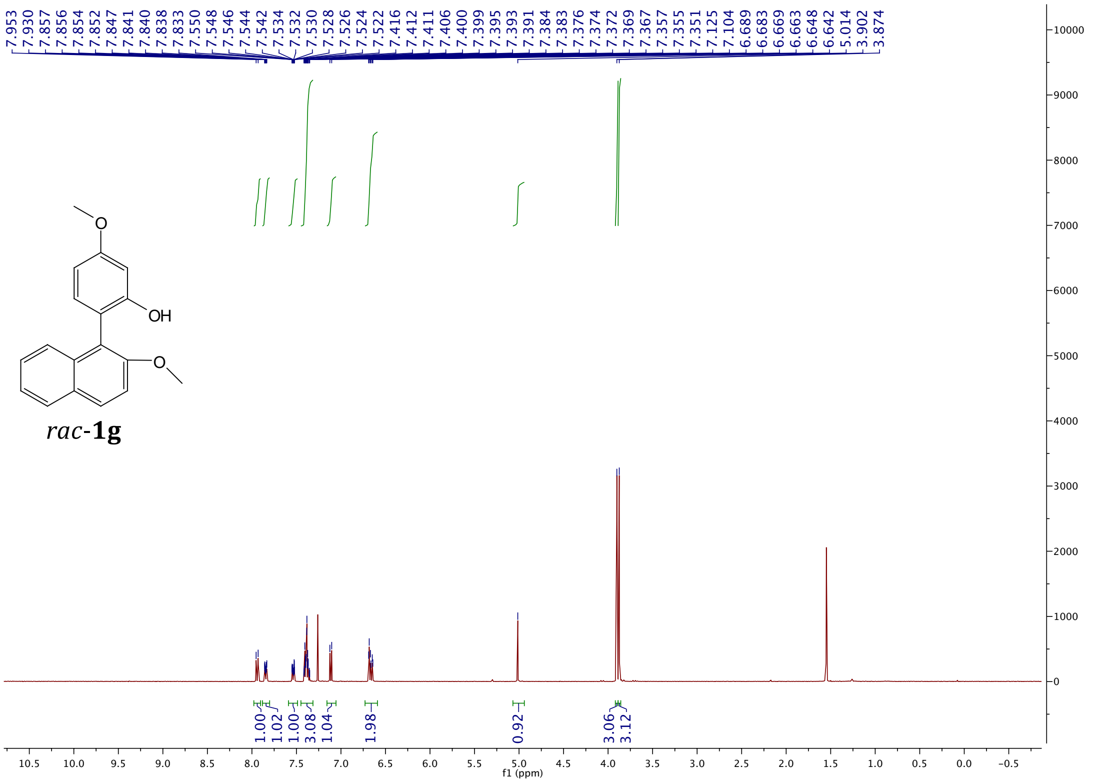
rac-**1e**

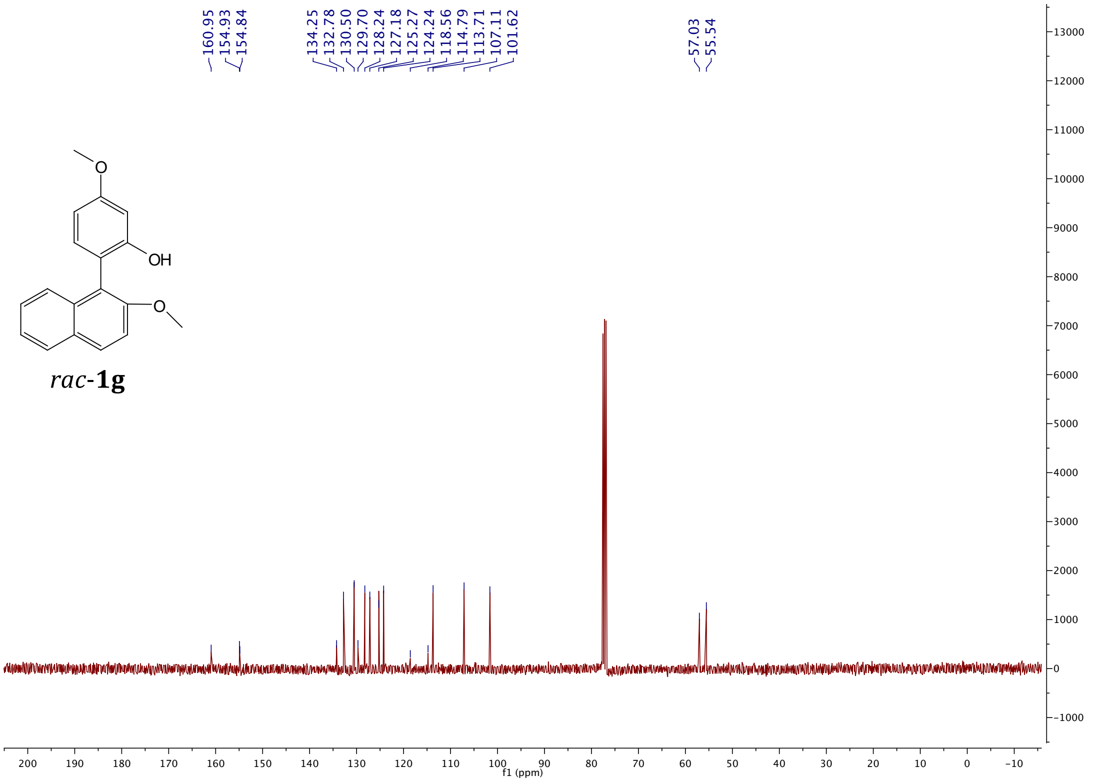

157.82
150.62
133.46
133.38
130.24
129.51
129.11
128.04
126.25
124.82
123.19
122.51
121.54
117.85
117.72
111.95
55.84
O
OH
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

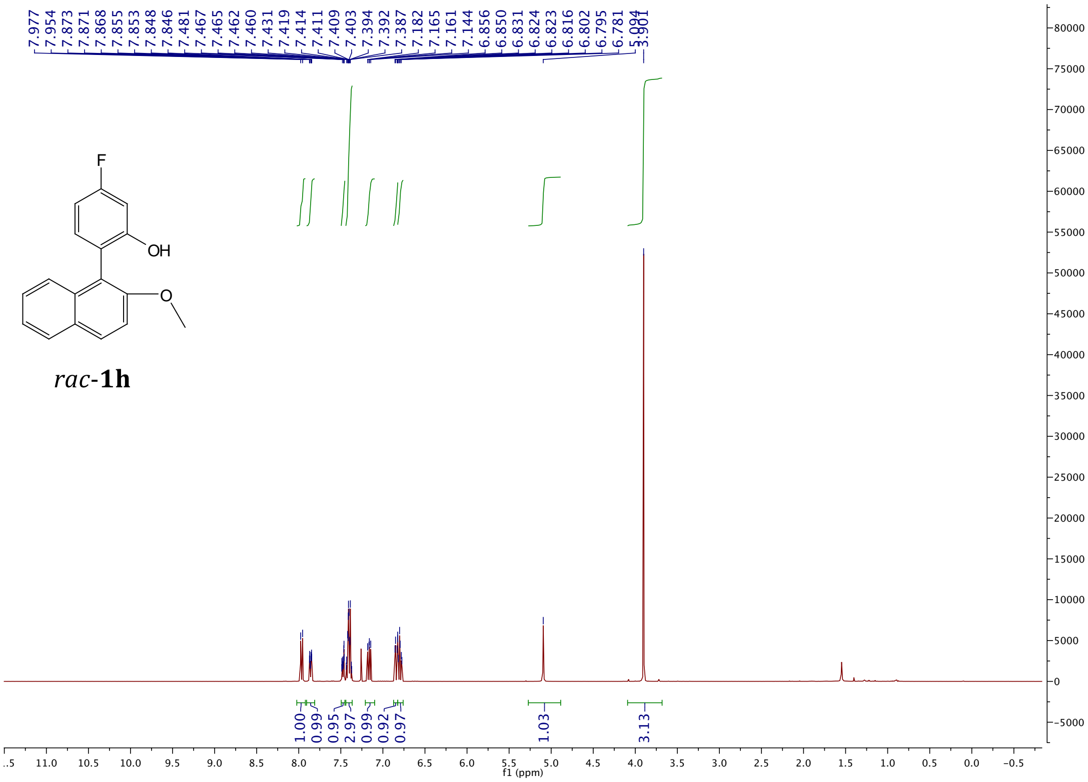
rac-**1e**


8.299
8.297
8.295
8.293
8.279
8.276
8.275
8.273
7.444
7.439
7.423
7.419
7.413
7.409
7.392
7.388
7.385
7.376
7.372
7.369
7.367
7.364
7.362
7.351
7.346
7.137
7.136
7.133
7.132
7.119
7.117
7.114
7.113
7.092
7.091
7.089
7.088
7.072
7.070
7.067
7.051
7.048
7.033
7.030
6.805
4.653
4.058
2.261
OH
O
rac-**1f**
0.86
3.86
2.80
1.00
1.14
3.23
3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0

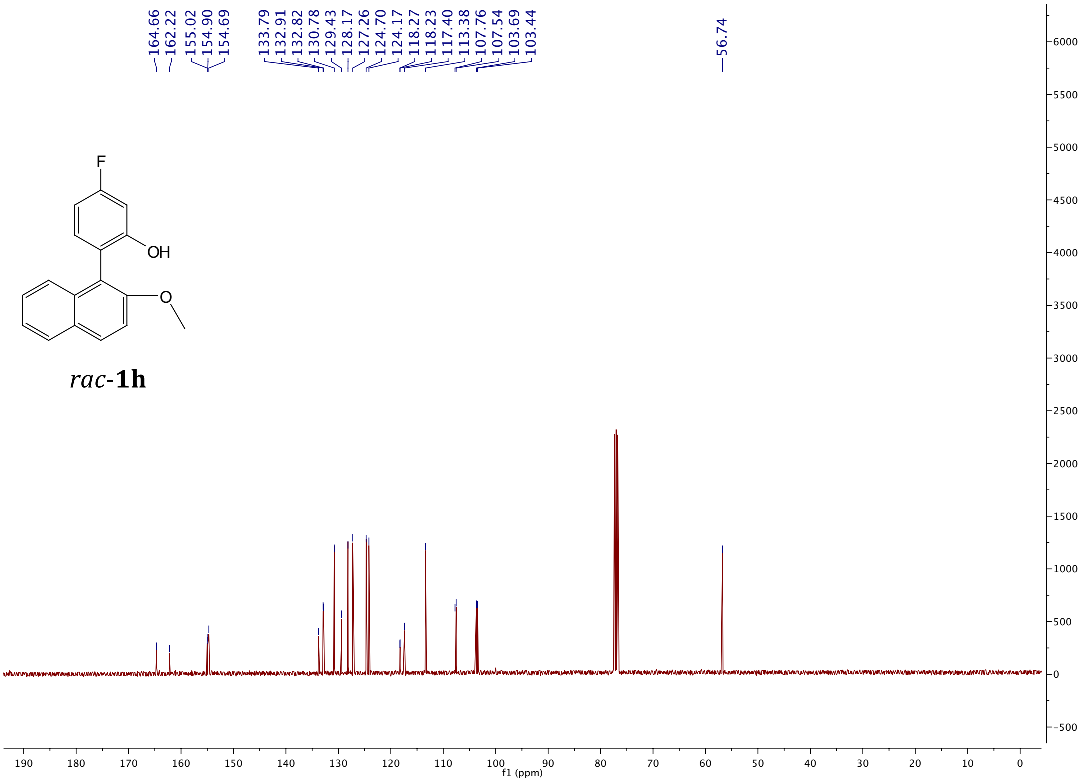

155.79
153.74
136.37
134.12
131.72
129.48
127.39
125.36
125.28
124.93
124.75
123.12
122.22
120.85
115.42
106.88
55.77
21.08
OH
O
rac-**1f**
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


7.953
7.930
7.857
7.856
7.854
7.852
7.847
7.841
7.840
7.838
7.833
7.550
7.548
7.546
7.544
7.542
7.534
7.532
7.530
7.528
7.526
7.524
7.522
7.416
7.412
7.411
7.406
7.400
7.399
7.395
7.393
7.391
7.384
7.383
7.376
7.374
7.372
7.369
7.367
7.357
7.355
7.351
7.125
7.104
6.689
6.683
6.669
6.663
6.648
6.642
5.014
3.902
3.874
O
OH
O
rac-1g
1.00
1.02
1.00
3.08
1.04
1.98
0.92
3.06
3.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

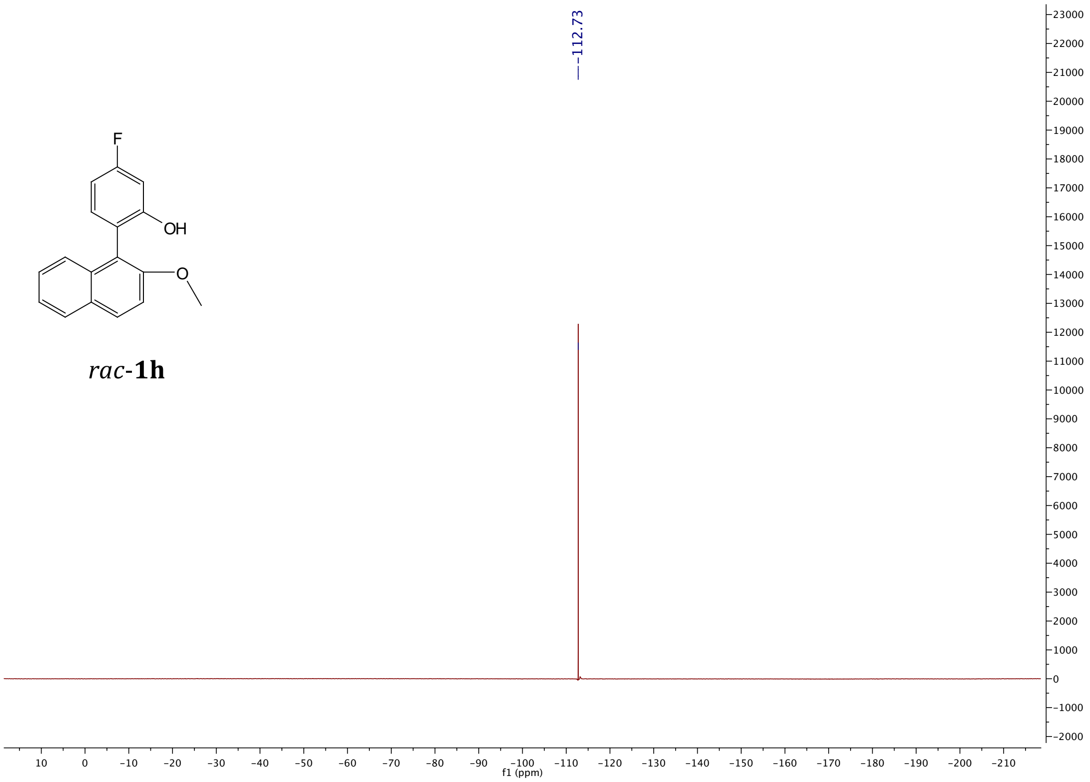

160.95
154.93
154.84
134.25
132.78
130.50
129.70
128.24
127.18
125.27
124.24
118.56
114.79
113.71
107.11
101.62
57.03
55.54
O
OH
O
rac-1g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


rac-**1h**

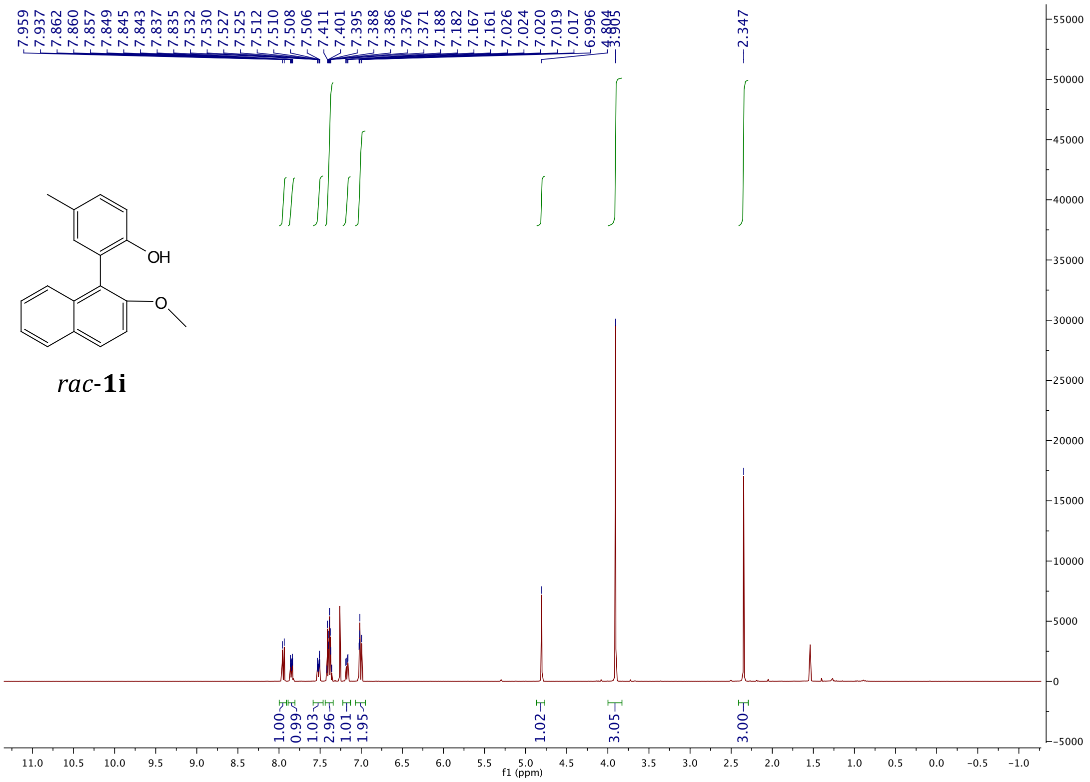
7.977
7.954
7.873
7.871
7.868
7.855
7.853
7.848
7.846
7.481
7.467
7.465
7.462
7.460
7.431
7.419
7.414
7.411
7.409
7.403
7.394
7.392
7.387
7.182
7.165
7.161
7.144
6.856
6.850
6.831
6.824
6.823
6.816
6.802
6.795
6.781
5.094
3.901
F
OH
O
1.00
0.99
0.95
2.97
0.99
0.92
0.97
1.03
3.13
f1 (ppm)


rac-**1h**

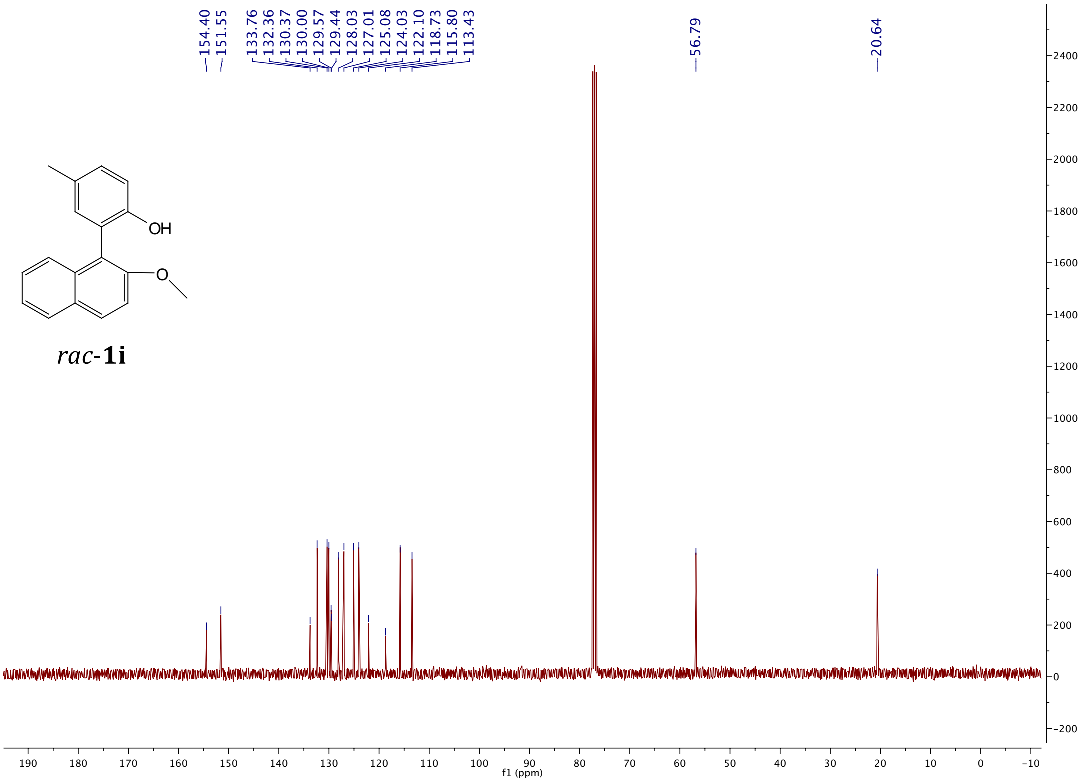
164.66
162.22
155.02
154.90
154.69
133.79
132.91
132.82
130.78
129.43
128.17
127.26
124.70
124.17
118.27
118.23
117.40
113.38
107.76
107.54
103.69
103.44
56.74
F
OH
O
f1 (ppm)


F
OH
O
−112.73
f1 (ppm)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
23000 22000 21000 20000 19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000 −2000

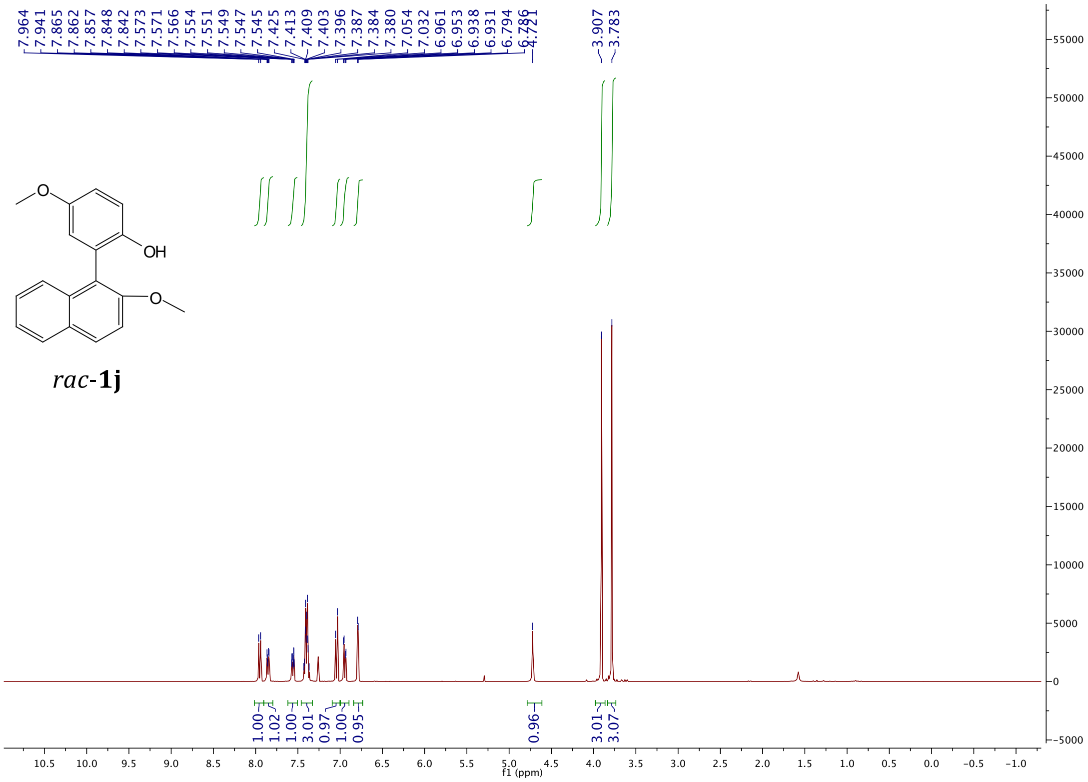
rac-**1h**


OH
O
7.959 7.937 7.862 7.860 7.857 7.849 7.845 7.843 7.837 7.835 7.532 7.530 7.527 7.525 7.512 7.510 7.508 7.506 7.411 7.401 7.395 7.388 7.386 7.376 7.371 7.188 7.182 7.167 7.161 7.026 7.024 7.020 7.019 7.017 6.996 4.804 3.905
2.347
1.00 0.99 1.03 2.96 1.01 1.95
1.02
3.05
3.00
f1 (ppm)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 −5000

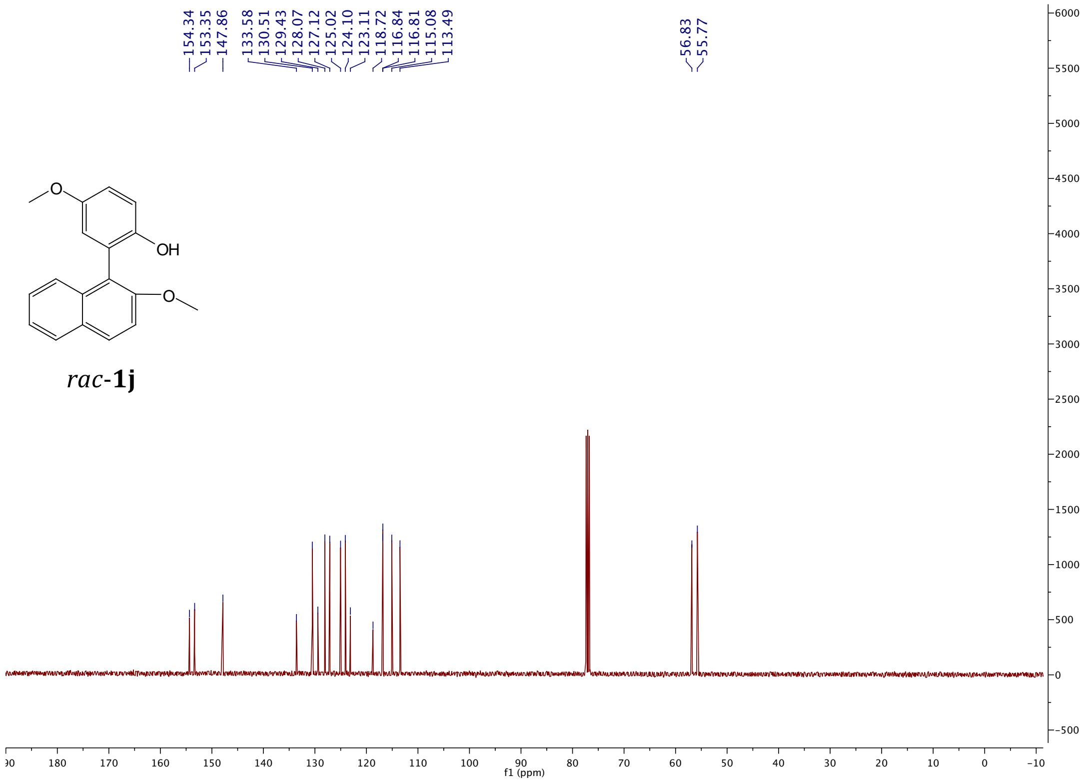
rac-**1i**


154.40
151.55
133.76
132.36
130.37
130.00
129.57
129.44
128.03
127.01
125.08
124.03
122.10
118.73
115.80
113.43
56.79
20.64
OH
O
f1 (ppm)

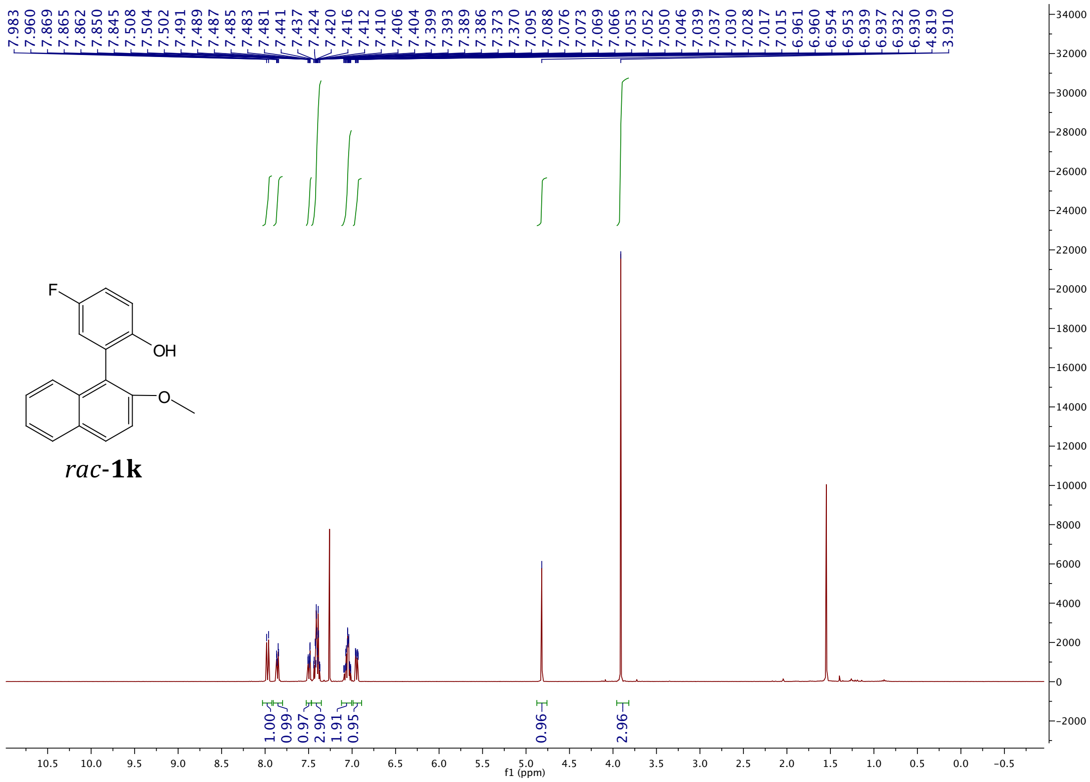
rac-**1i**


7.964
7.941
7.865
7.862
7.857
7.848
7.842
7.573
7.571
7.566
7.554
7.551
7.549
7.547
7.545
7.425
7.413
7.409
7.403
7.396
7.387
7.384
7.380
7.054
7.032
6.961
6.953
6.938
6.931
6.794
6.786
4.721
3.907
3.783
1.00
1.02
1.00
3.01
0.97
1.00
0.95
0.96
3.01
3.07
O
OH
O
f1 (ppm)

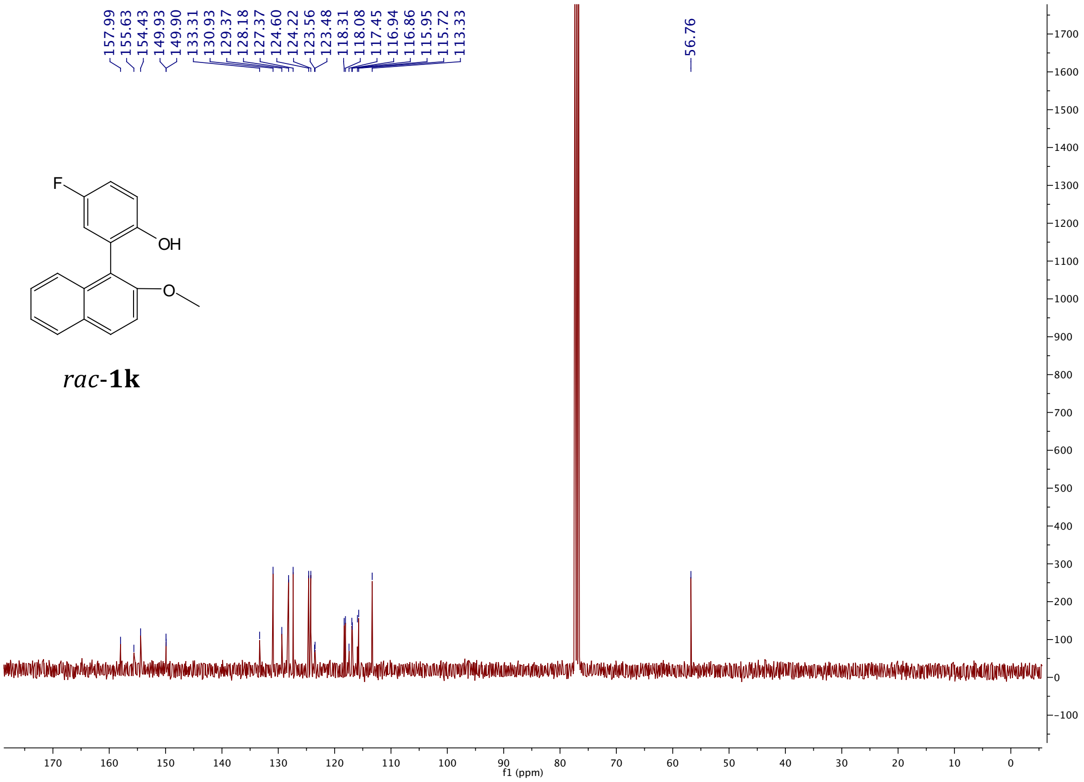
rac-**1j**


154.34
153.35
147.86
133.58
130.51
129.43
128.07
127.12
125.02
124.10
123.11
118.72
116.84
116.81
115.08
113.49
56.83
55.77
O
OH
O
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500

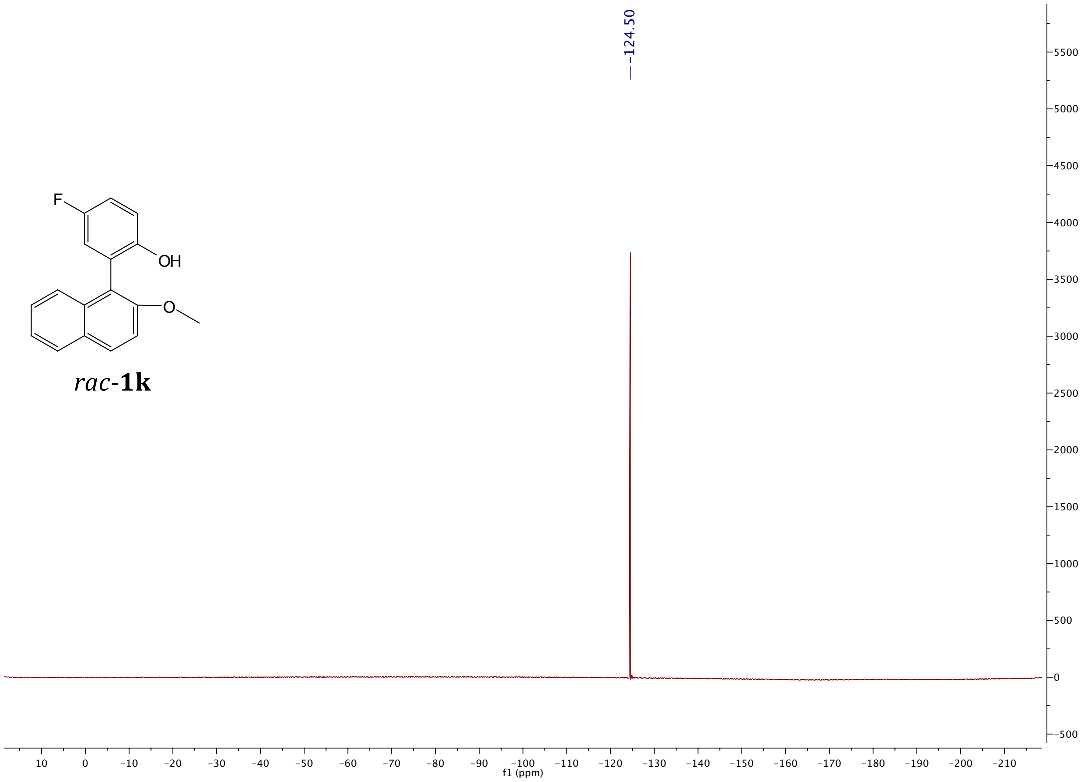
rac-**1j**


7.983
7.960
7.869
7.865
7.862
7.850
7.845
7.508
7.504
7.502
7.491
7.489
7.487
7.485
7.483
7.481
7.441
7.437
7.424
7.420
7.416
7.412
7.410
7.406
7.404
7.399
7.393
7.389
7.386
7.373
7.370
7.095
7.088
7.076
7.073
7.069
7.066
7.053
7.052
7.050
7.046
7.039
7.037
7.030
7.028
7.017
7.015
6.961
6.960
6.954
6.953
6.939
6.937
6.932
6.930
4.819
3.910
F
OH
O
1.00
0.99
0.97
2.90
1.91
0.95
0.96
2.96
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
34000 32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 −2000

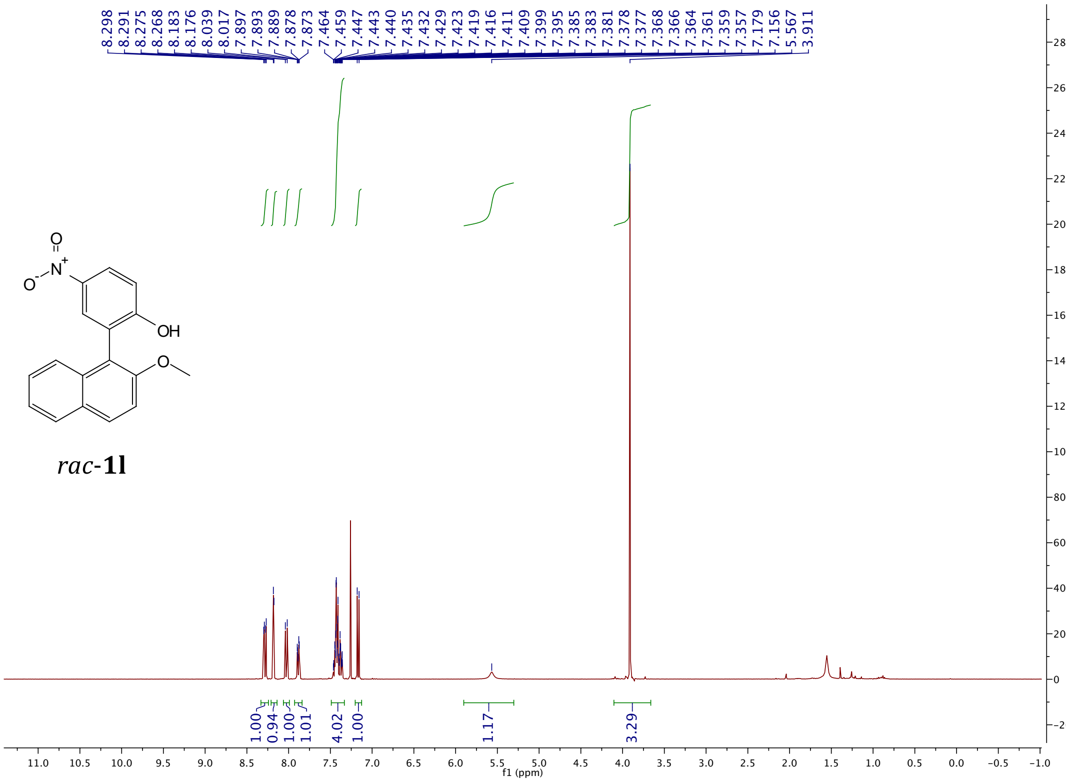
rac-**1k**

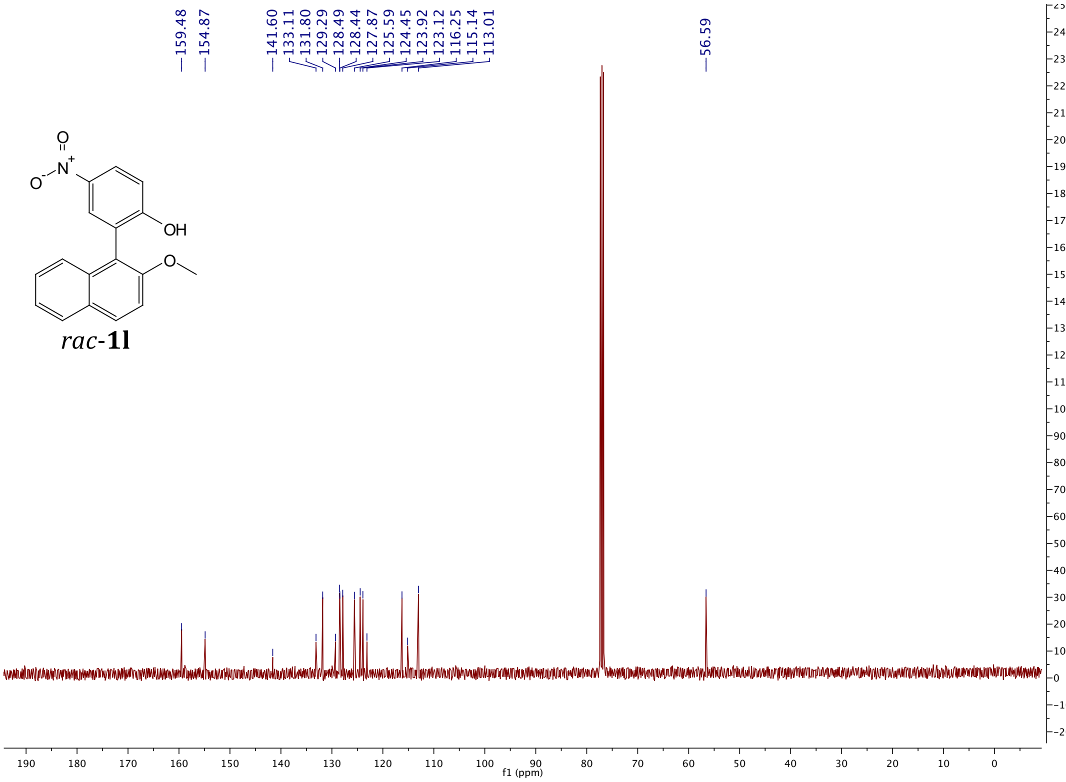

157.99
155.63
154.43
149.93
149.90
133.31
130.93
129.37
128.18
127.37
124.60
124.22
123.56
123.48
118.31
118.08
117.45
116.94
116.86
115.95
115.72
113.33
56.76
F
OH
O
f1 (ppm)

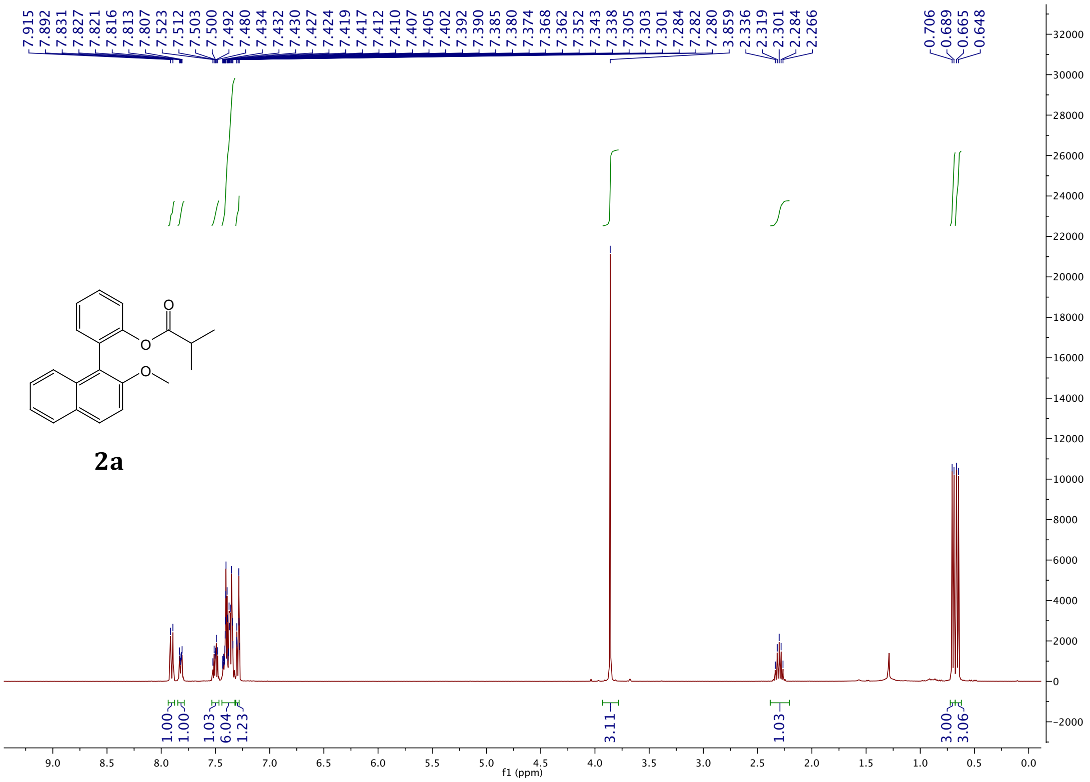
rac-**1k**

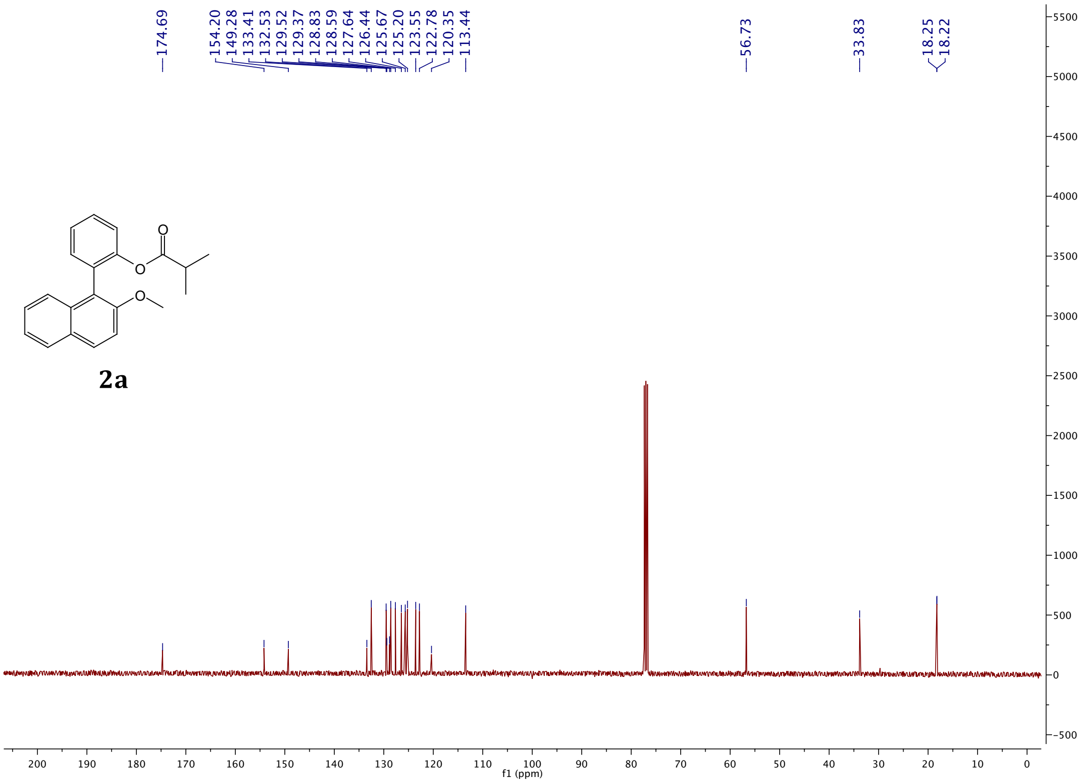

-124.50
F
OH
O
f1 (ppm)

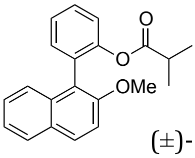
rac-**1k**


8.298
8.291
8.275
8.268
8.183
8.176
8.039
8.017
7.897
7.893
7.889
7.878
7.873
7.464
7.459
7.447
7.443
7.440
7.435
7.432
7.429
7.423
7.419
7.416
7.411
7.409
7.399
7.395
7.385
7.383
7.381
7.378
7.377
7.368
7.366
7.364
7.361
7.359
7.357
7.179
7.156
5.567
3.911
O
N+
O-
OH
O
rac-1l
1.00
0.94
1.00
1.01
4.02
1.00
1.17
3.29
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000


159.48
154.87
141.60
133.11
131.80
129.29
128.49
128.44
127.87
125.59
124.45
123.92
123.12
116.25
115.14
113.01
56.59
O
N+
O-
OH
O
rac-1l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
2300 2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200


7.915
7.892
7.831
7.827
7.821
7.816
7.813
7.807
7.523
7.512
7.503
7.500
7.492
7.480
7.434
7.432
7.430
7.427
7.424
7.419
7.417
7.412
7.410
7.407
7.405
7.402
7.392
7.390
7.385
7.380
7.374
7.368
7.362
7.352
7.343
7.338
7.305
7.303
7.301
7.284
7.282
7.280
3.859
2.336
2.319
2.301
2.284
2.266
0.706
0.689
0.665
0.648
1.00
1.00
1.03
6.04
1.23
3.11
1.03
3.00
3.06
O
O
O
2a
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

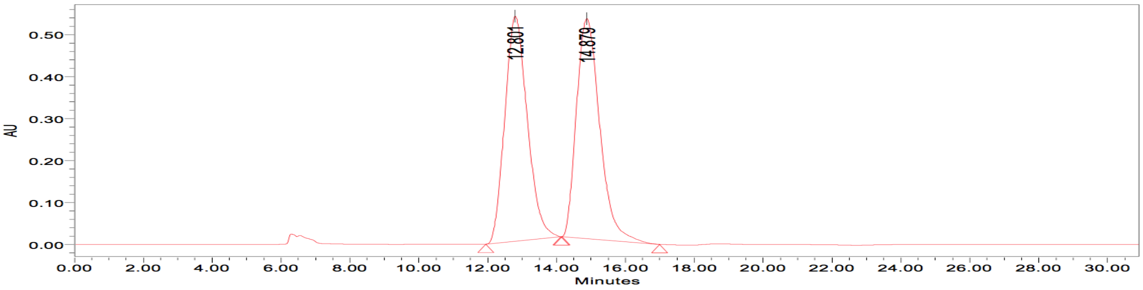

174.69
154.20
149.28
133.41
132.53
129.52
129.37
128.83
128.59
127.64
126.44
125.67
125.20
123.55
122.78
120.35
113.44
56.73
33.83
18.25
18.22
O
O
O
2a
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

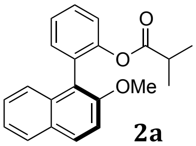


(±)-**2a**

Peak Results

	Name	RT	Area	% Area
1		12.801	24397583	49.75
2		14.879	24643322	50.25

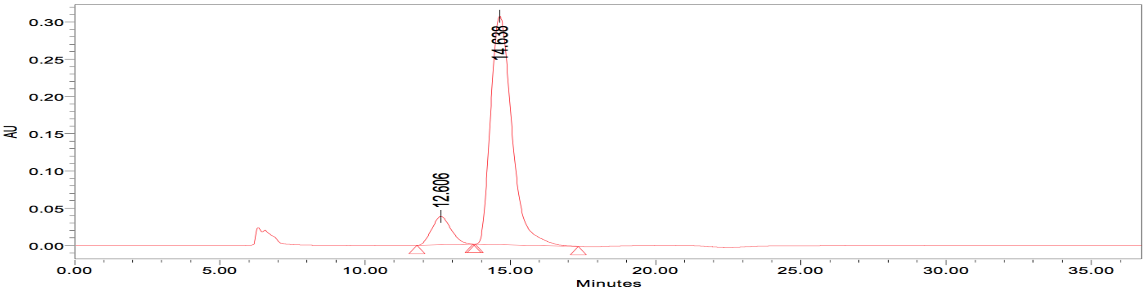


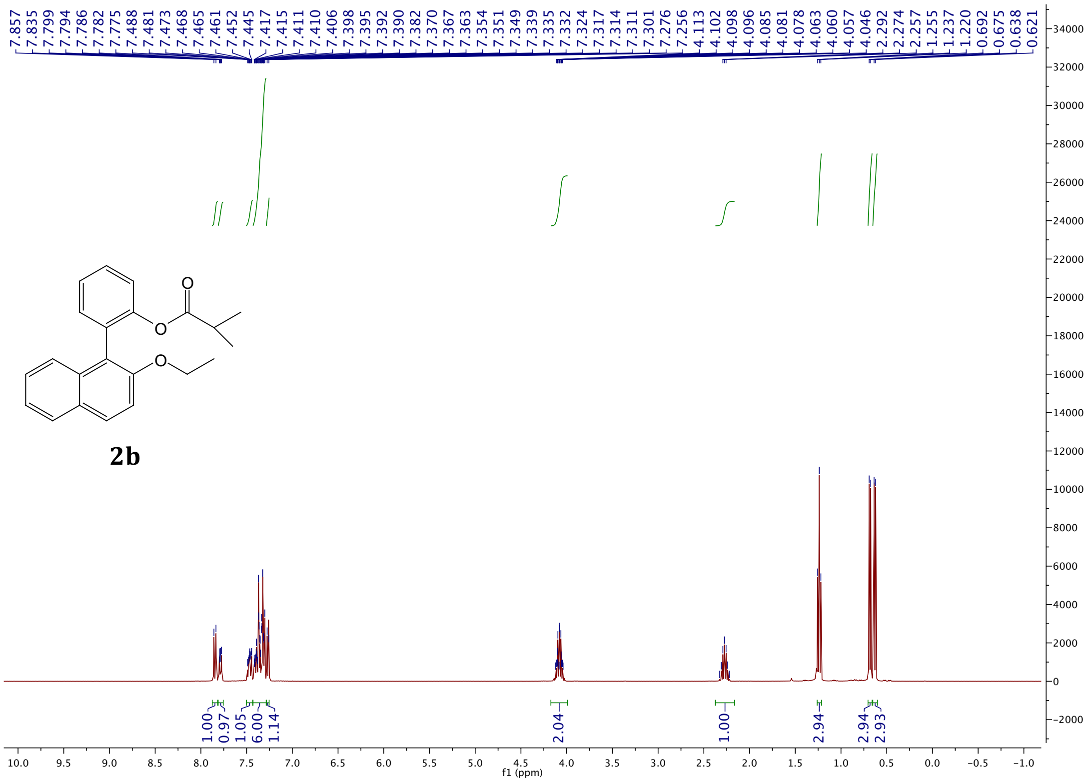


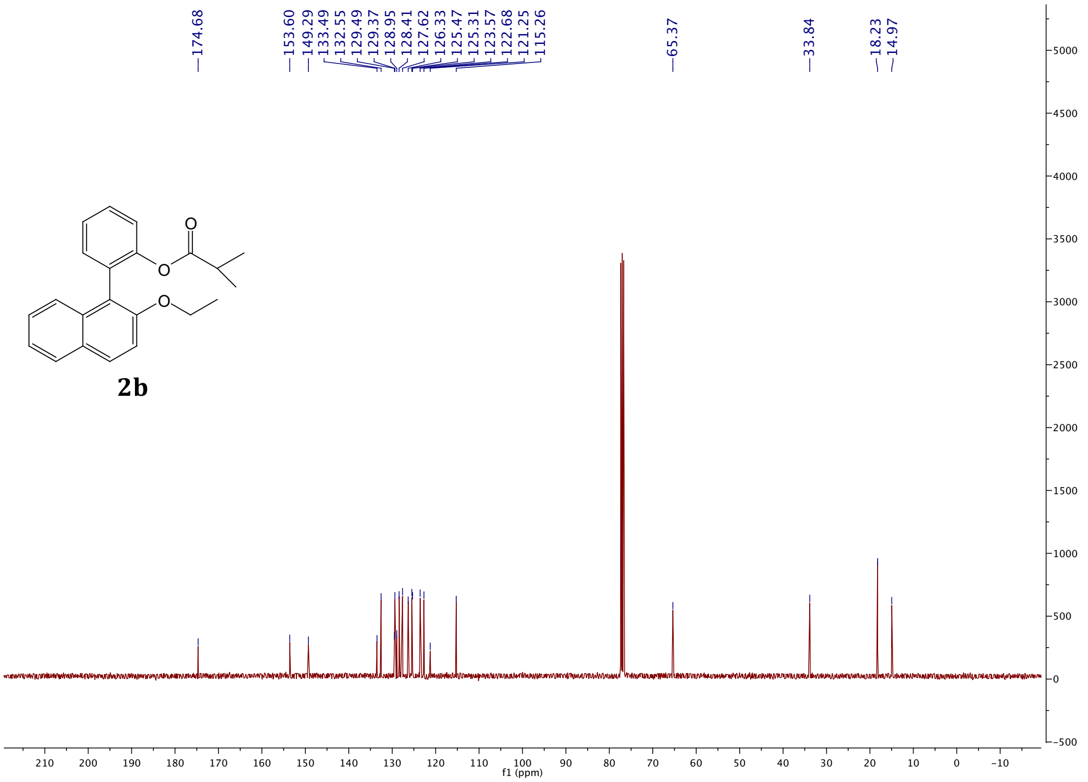
2a

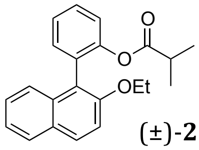
Peak Results

	Name	RT	Area	% Area
1		12.606	1748733	10.07
2		14.638	15620691	89.93




2b
7.857
7.835
7.799
7.794
7.786
7.782
7.775
7.488
7.481
7.473
7.468
7.465
7.461
7.452
7.445
7.417
7.415
7.411
7.410
7.406
7.398
7.395
7.392
7.390
7.382
7.370
7.367
7.363
7.354
7.351
7.349
7.339
7.335
7.332
7.324
7.317
7.314
7.311
7.301
7.276
7.256
4.113
4.102
4.098
4.096
4.085
4.081
4.078
4.063
4.060
4.057
4.046
2.292
2.274
2.257
1.255
1.237
1.220
0.692
0.675
0.638
0.621
O
O
O
1.00
0.97
1.05
6.00
1.14
2.04
1.00
2.94
2.94
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000

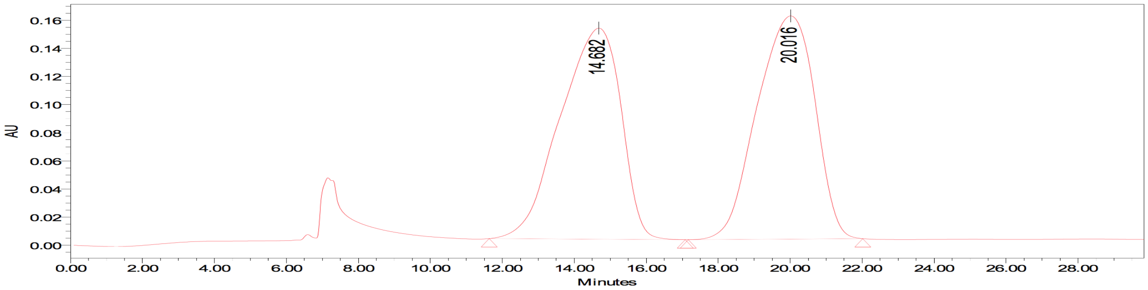

2b
174.68
153.60
149.29
133.49
132.55
129.49
129.37
128.95
128.41
127.62
126.33
125.47
125.31
123.57
122.68
121.25
115.26
65.37
33.84
18.23
14.97
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500

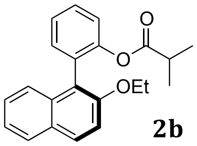


(±)-**2b**

Peak Results

	Name	RT	Area	% Area
1		14.682	17635873	49.81
2		20.016	17772846	50.19

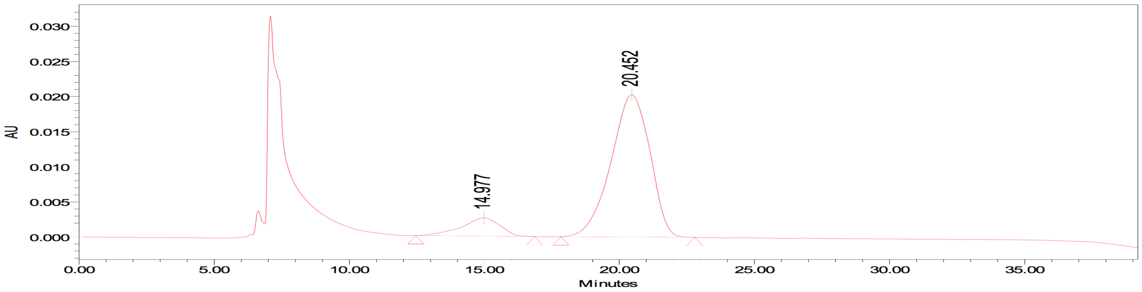


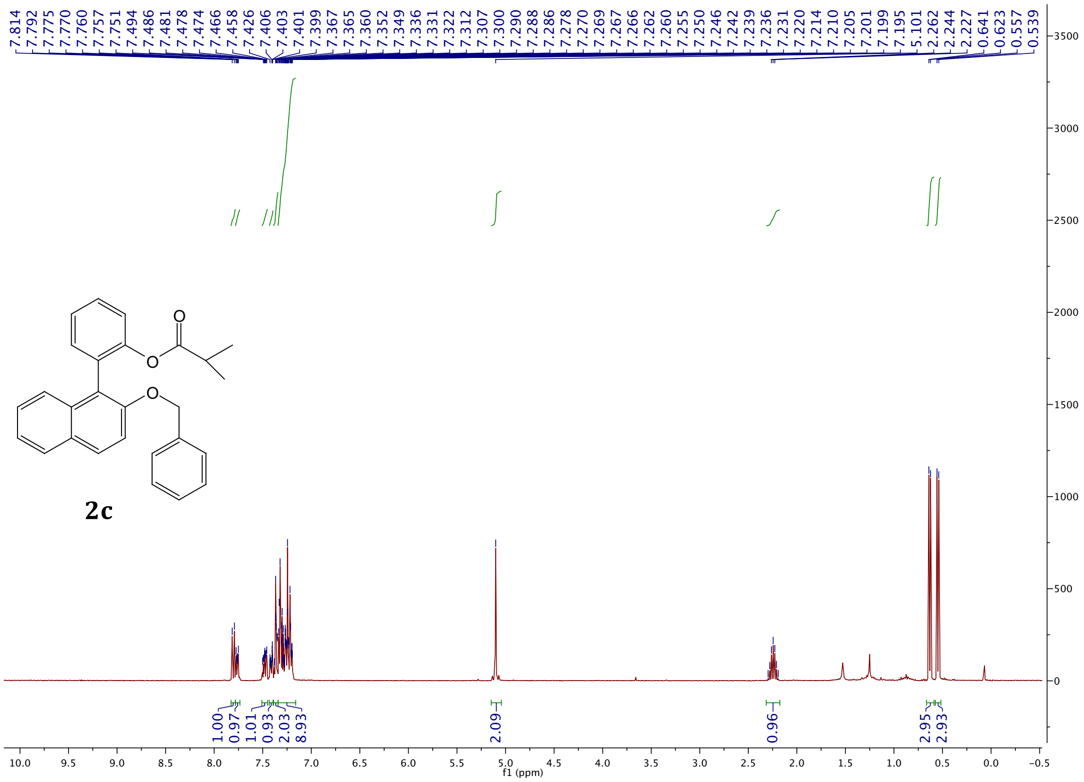


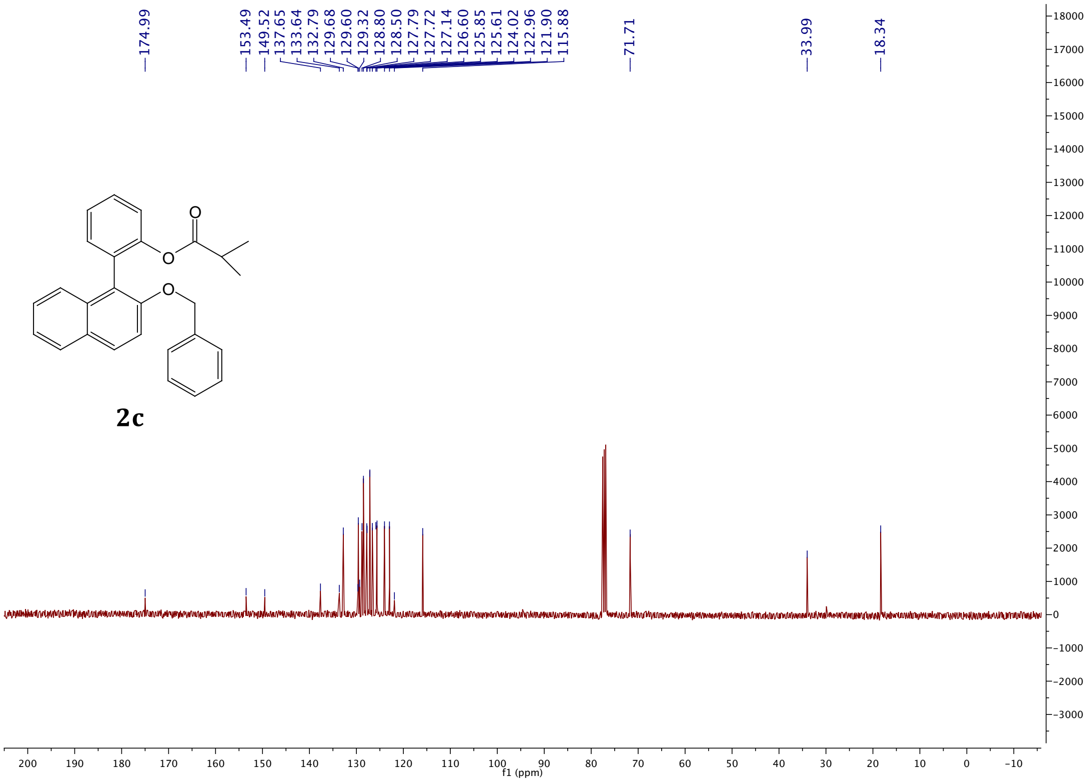
2b

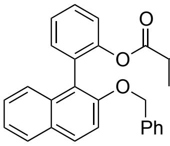
Peak Results

	Name	RT	Area	% Area
1		14.977	257054	11.23
2		20.452	2032657	88.77




7.814
7.792
7.775
7.770
7.760
7.757
7.751
7.494
7.486
7.481
7.478
7.474
7.466
7.458
7.426
7.406
7.403
7.401
7.399
7.367
7.365
7.360
7.352
7.349
7.336
7.331
7.322
7.312
7.307
7.300
7.290
7.288
7.286
7.278
7.270
7.269
7.267
7.266
7.262
7.260
7.255
7.250
7.246
7.242
7.239
7.236
7.231
7.220
7.214
7.210
7.205
7.201
7.199
7.195
5.101
2.262
2.244
2.227
0.641
0.623
0.557
0.539
1.00
0.97
1.01
0.93
2.03
8.93
2.09
0.96
2.95
2.93
O
O
O
2c
f1 (ppm)

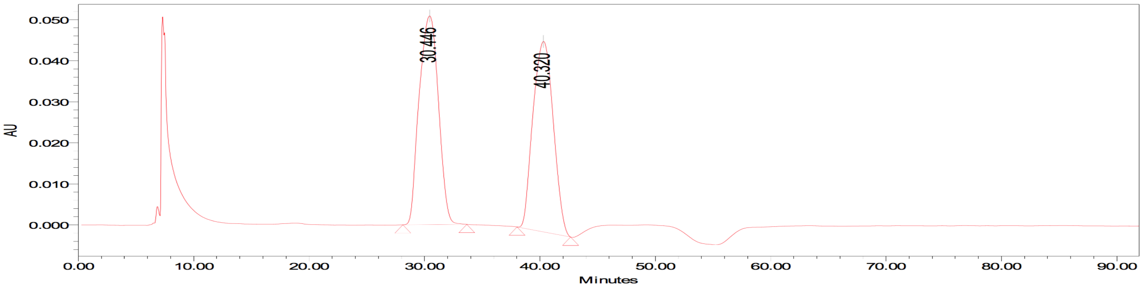

174.99
153.49
149.52
137.65
133.64
132.79
129.68
129.60
129.32
128.80
128.50
127.79
127.72
127.14
126.60
125.85
125.61
124.02
122.96
121.90
115.88
71.71
33.99
18.34
O
O
O
2c
f1 (ppm)

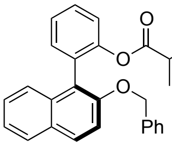


(±)-**2c**

Peak Results

	Name	RT	Area	% Area
1		30.446	5898895	50.93
2		40.320	5683874	49.07

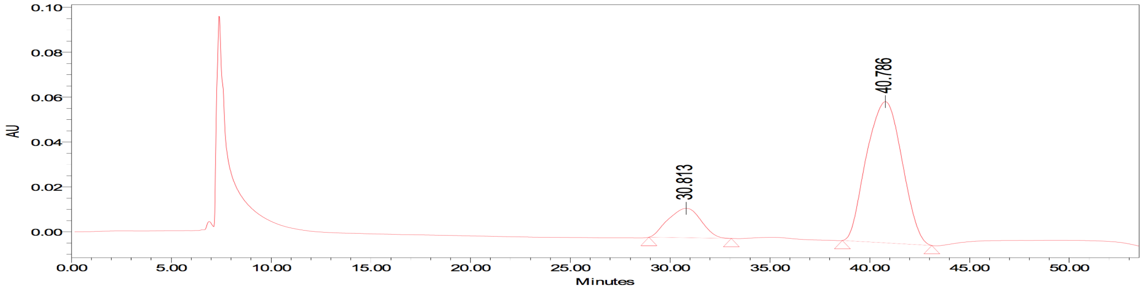


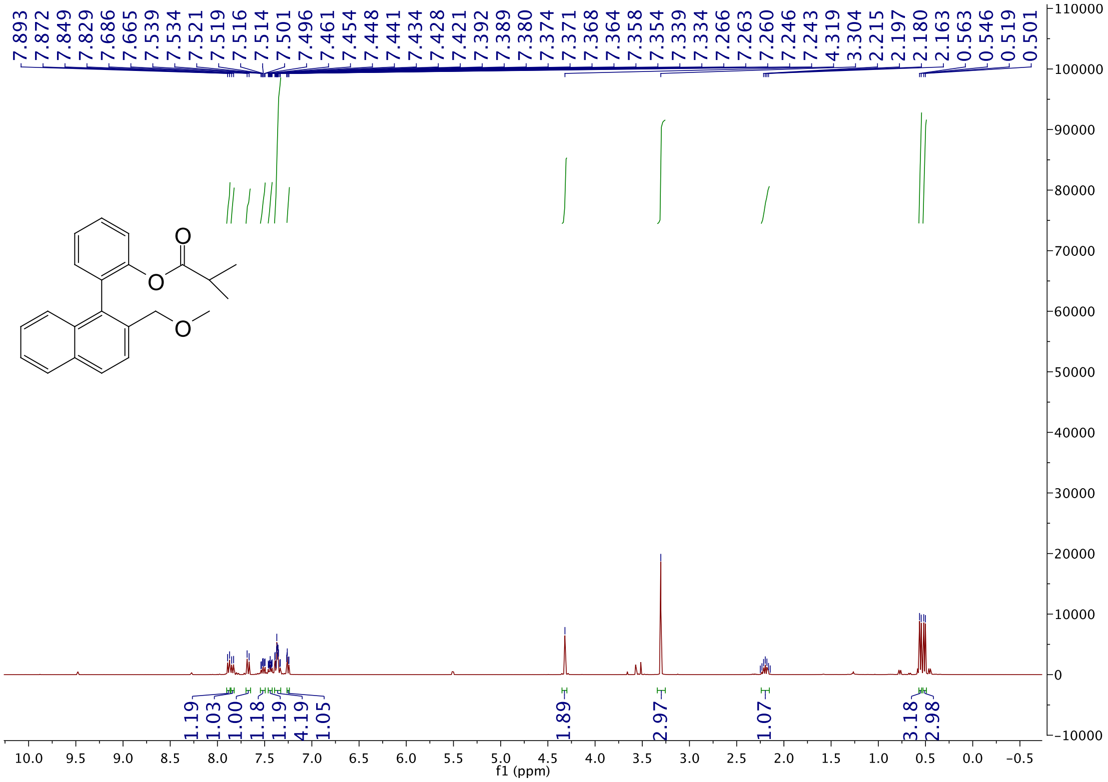


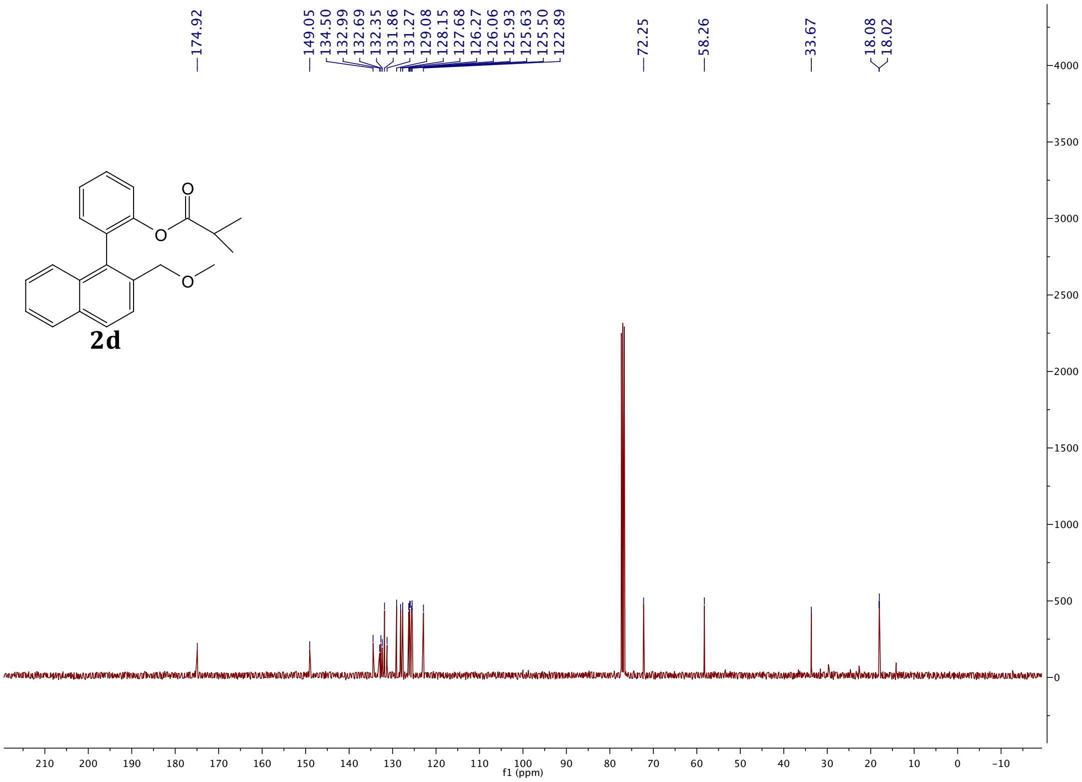
2c

Peak Results

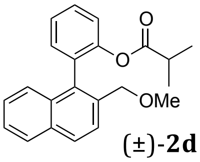
	Name	RT	Area	% Area
1		30.813	1504654	16.16
2		40.786	7803629	83.84




7.893
7.872
7.849
7.829
7.686
7.665
7.539
7.534
7.521
7.519
7.516
7.514
7.501
7.496
7.461
7.454
7.448
7.441
7.434
7.428
7.421
7.392
7.389
7.380
7.374
7.371
7.368
7.364
7.358
7.354
7.339
7.334
7.266
7.263
7.260
7.246
7.243
4.319
3.304
2.215
2.197
2.180
2.163
0.563
0.546
0.519
0.501
1.19
1.03
1.00
1.18
1.19
4.19
1.05
1.89
2.97
1.07
3.18
2.98
O
O
O
f1 (ppm)


174.92
149.05
134.50
132.99
132.69
132.35
131.86
131.27
129.08
128.15
127.68
126.27
126.06
125.93
125.63
125.50
122.89
72.25
58.26
33.67
18.08
18.02
O
O
O
f1 (ppm)

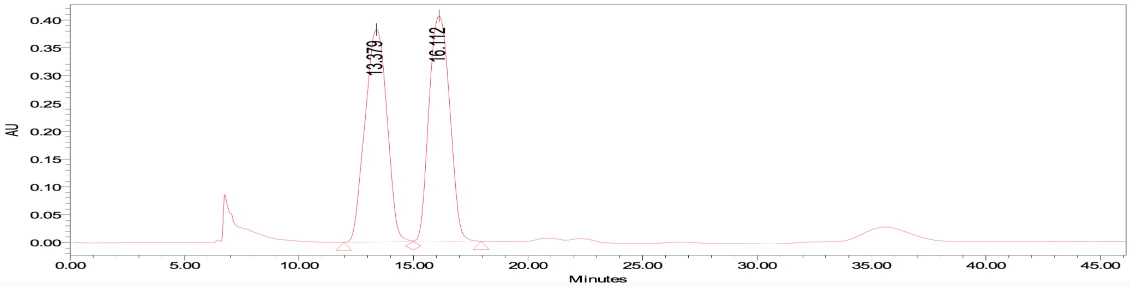
2d

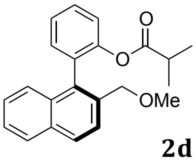


(±)-**2d**

Peak Results

	Name	RT	Area	% Area
1		13.379	25559144	50.02
2		16.112	25539133	49.98

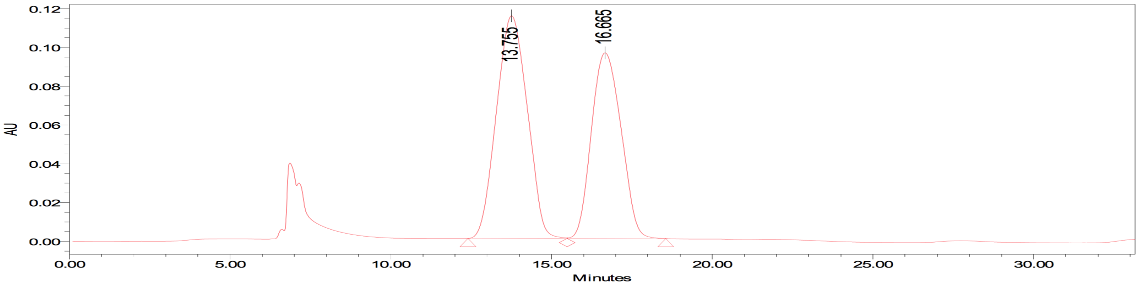


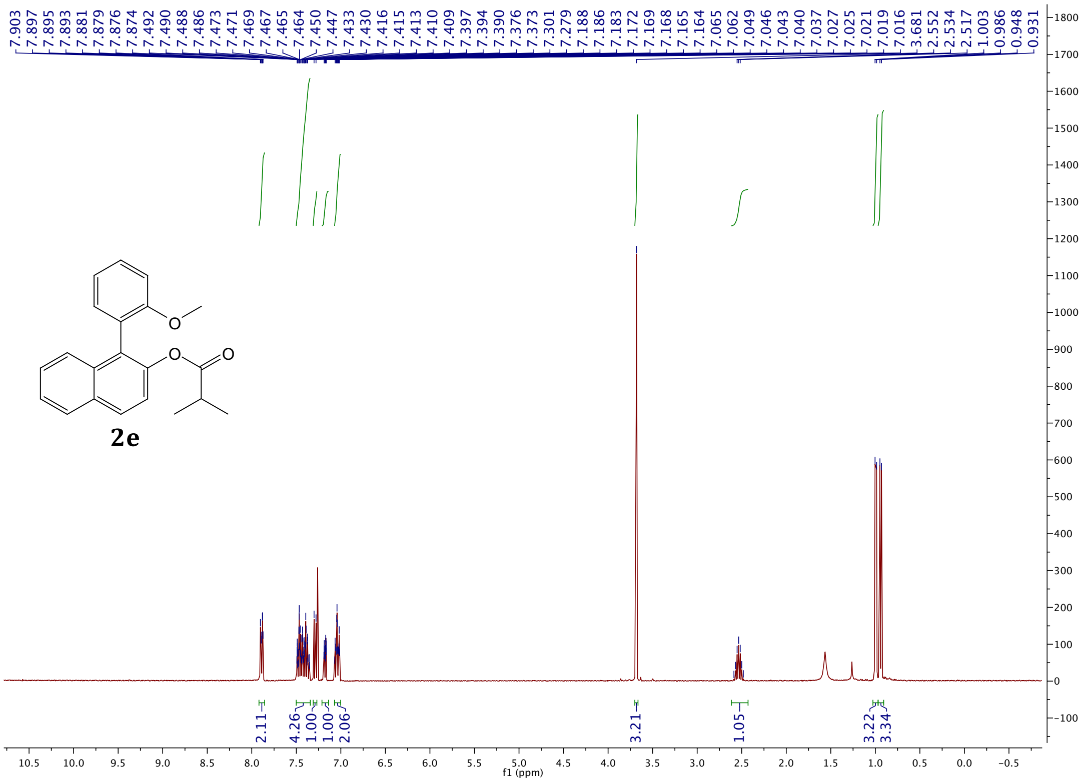


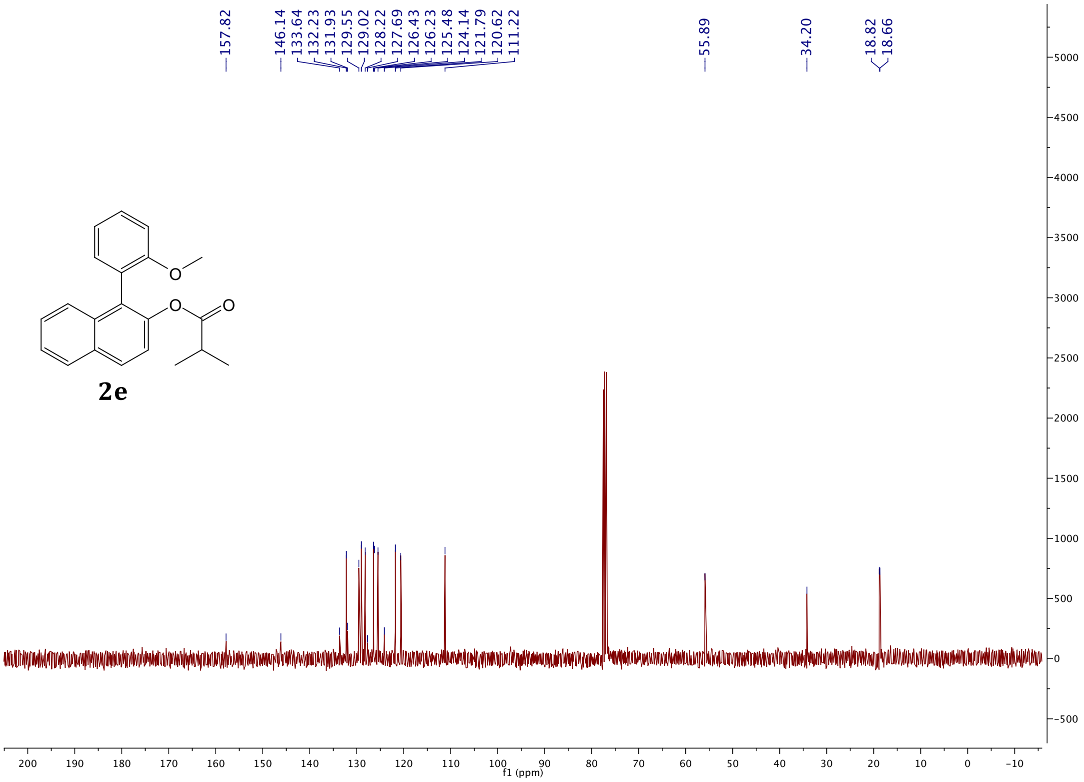
2d

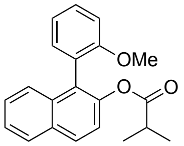
Peak Results

	Name	RT	Area	% Area
1		13.755	7666183	55.53
2		16.665	6139517	44.47




7.903
7.897
7.895
7.893
7.881
7.879
7.876
7.874
7.492
7.490
7.488
7.486
7.473
7.471
7.469
7.467
7.465
7.464
7.450
7.447
7.433
7.430
7.416
7.415
7.413
7.410
7.409
7.397
7.394
7.390
7.376
7.373
7.301
7.279
7.188
7.186
7.183
7.172
7.169
7.168
7.165
7.164
7.065
7.062
7.049
7.046
7.043
7.040
7.037
7.027
7.025
7.021
7.019
7.016
3.681
2.552
2.534
2.517
1.003
0.986
0.948
0.931
O
O
O
2e
2.11
4.26
1.00
1.00
2.06
3.21
1.05
3.22
3.34
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

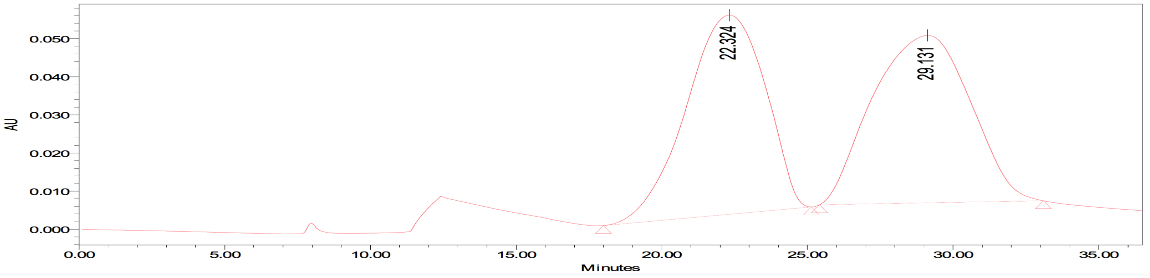

157.82
146.14
133.64
132.23
131.93
129.55
129.02
128.22
127.69
126.43
126.23
125.48
124.14
121.79
120.62
111.22
55.89
34.20
18.82
18.66
O
O
O
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

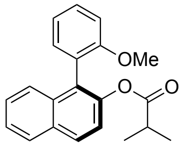


(±)-**2e**

Peak Results

	Name	RT	Area	% Area
1		22.324	9863570	49.03
2		29.131	10255166	50.97

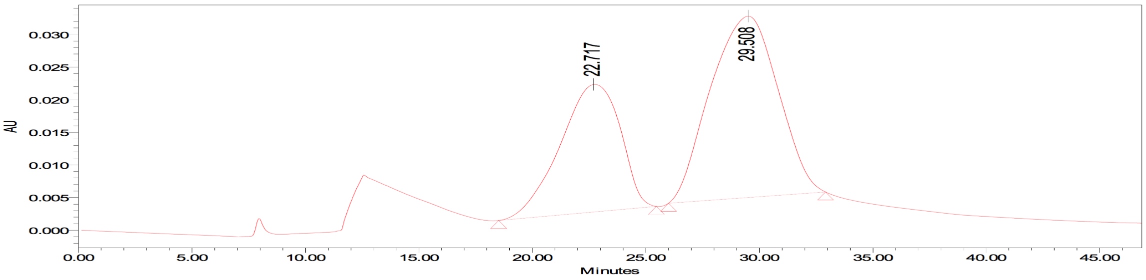


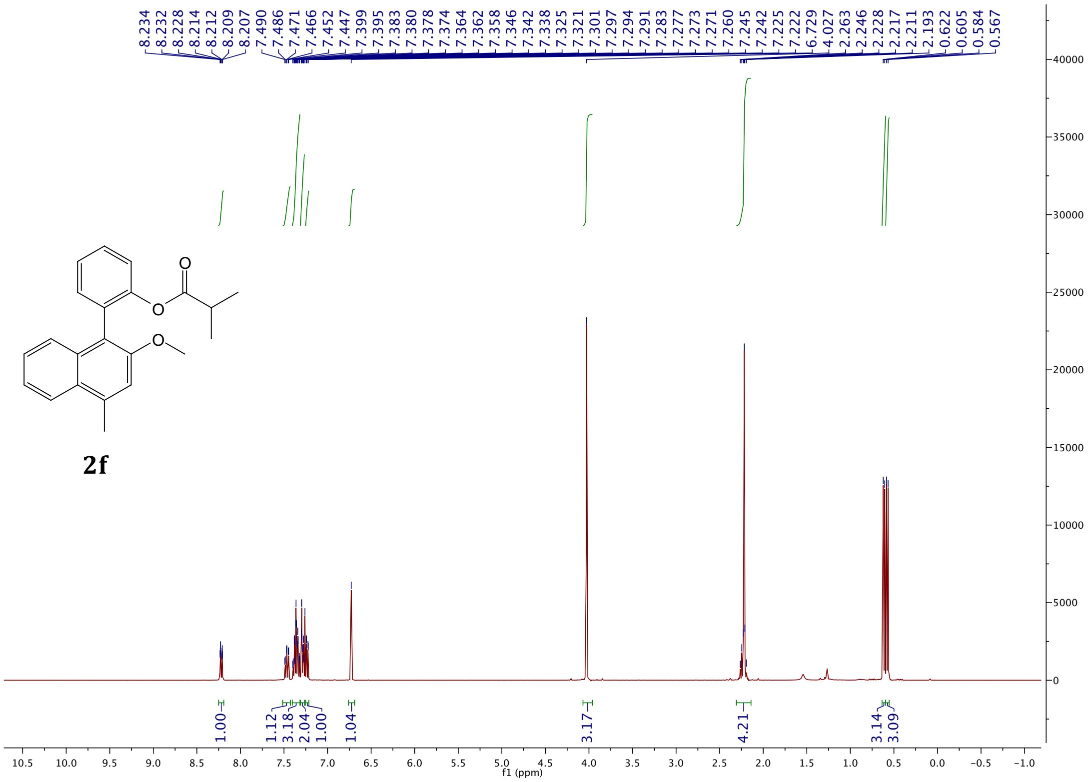


2e

Peak Results

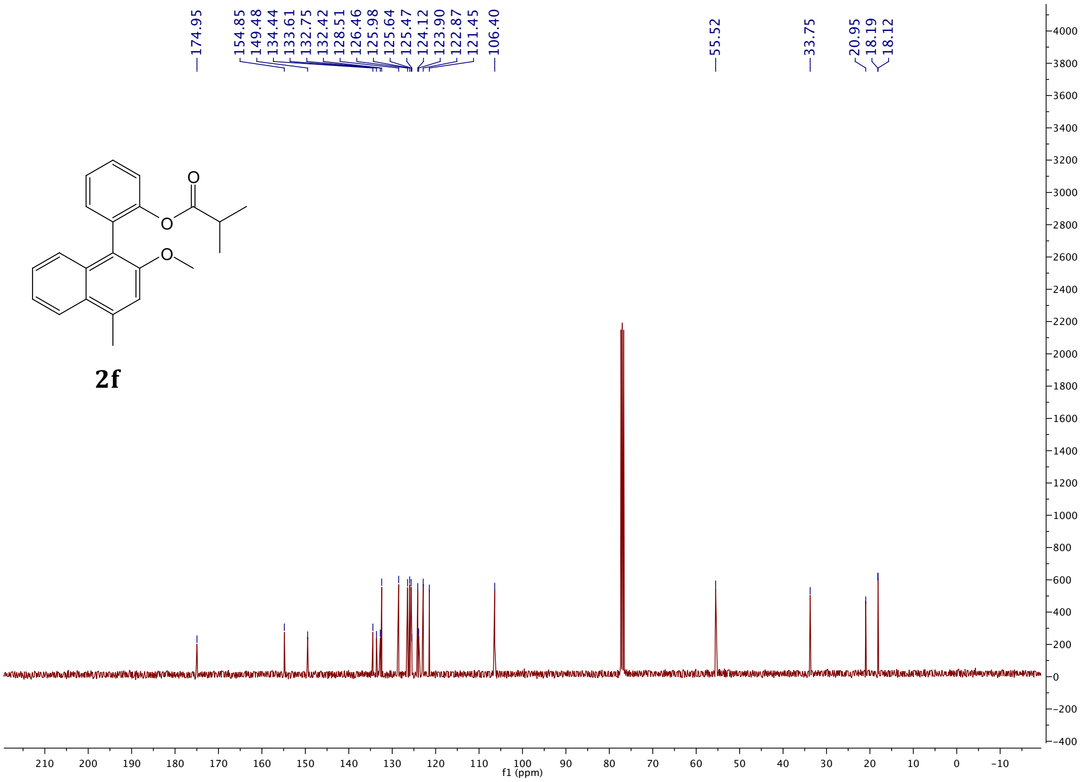
	Name	RT	Area	% Area
1		22.717	3606674	38.52
2		29.508	5757523	61.48





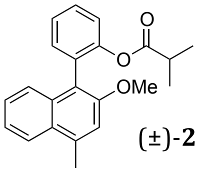
2f

8.234
8.232
8.228
8.214
8.212
8.209
8.207
7.490
7.486
7.471
7.466
7.452
7.447
7.399
7.395
7.383
7.380
7.378
7.374
7.364
7.362
7.358
7.346
7.342
7.338
7.325
7.321
7.301
7.297
7.294
7.291
7.283
7.277
7.273
7.271
7.260
7.245
7.242
7.225
7.222
6.729
4.027
2.263
2.246
2.228
2.217
2.211
2.193
0.622
0.605
0.584
0.567
1.00
1.12
3.18
2.04
1.00
1.04
3.17
4.21
3.14
3.09
O
O
O
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
40000 35000 30000 25000 20000 15000 10000 5000 0



2f

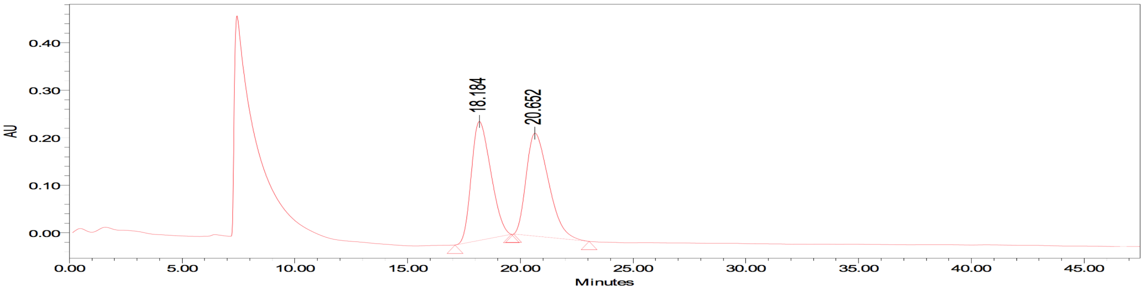
174.95
154.85
149.48
134.44
133.61
132.75
132.42
128.51
126.46
125.98
125.64
125.47
124.12
123.90
122.87
121.45
106.40
55.52
33.75
20.95
18.19
18.12
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200 -400

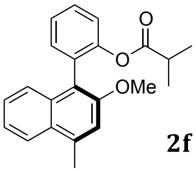


(±)-**2f**

Peak Results

	Name	RT	Area	% Area
1		18.184	14995998	50.00
2		20.652	14994195	50.00

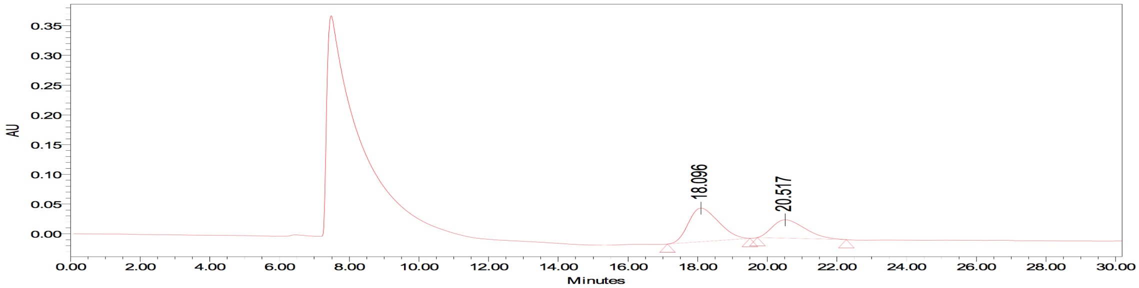


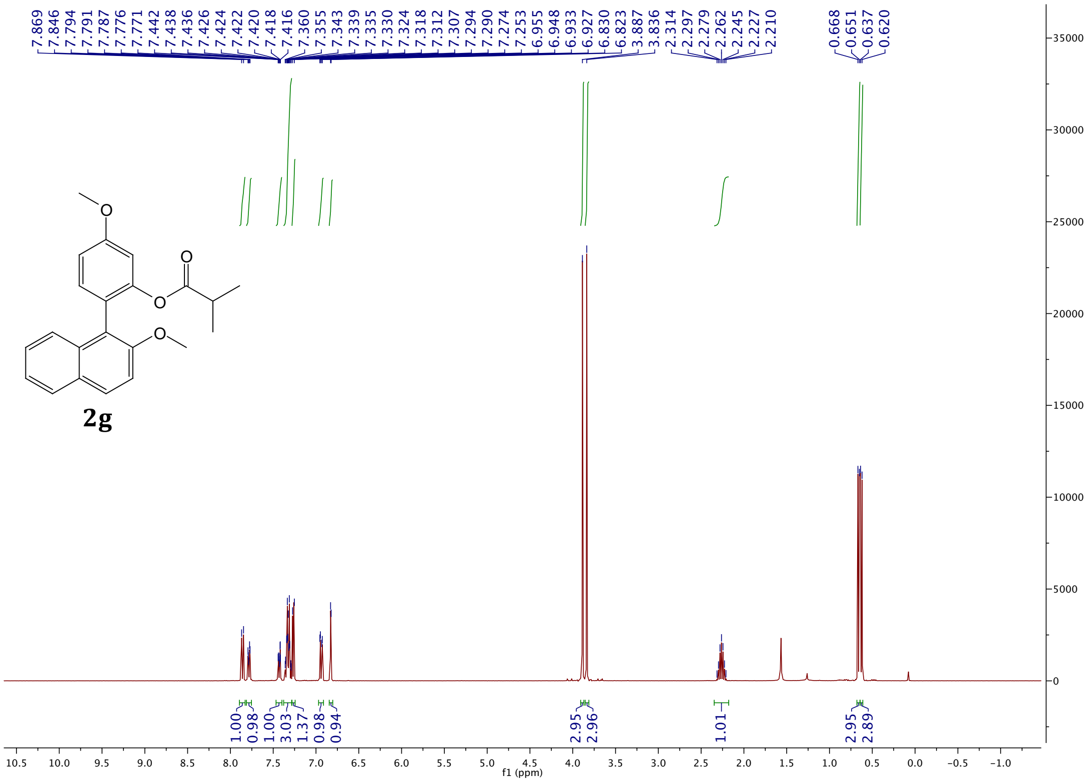


2f

Peak Results

	Name	RT	Area	% Area
1		18.096	3396142	62.68
2		20.517	2022368	37.32




7.869
7.846
7.794
7.791
7.787
7.776
7.771
7.442
7.438
7.436
7.426
7.424
7.422
7.420
7.418
7.416
7.360
7.355
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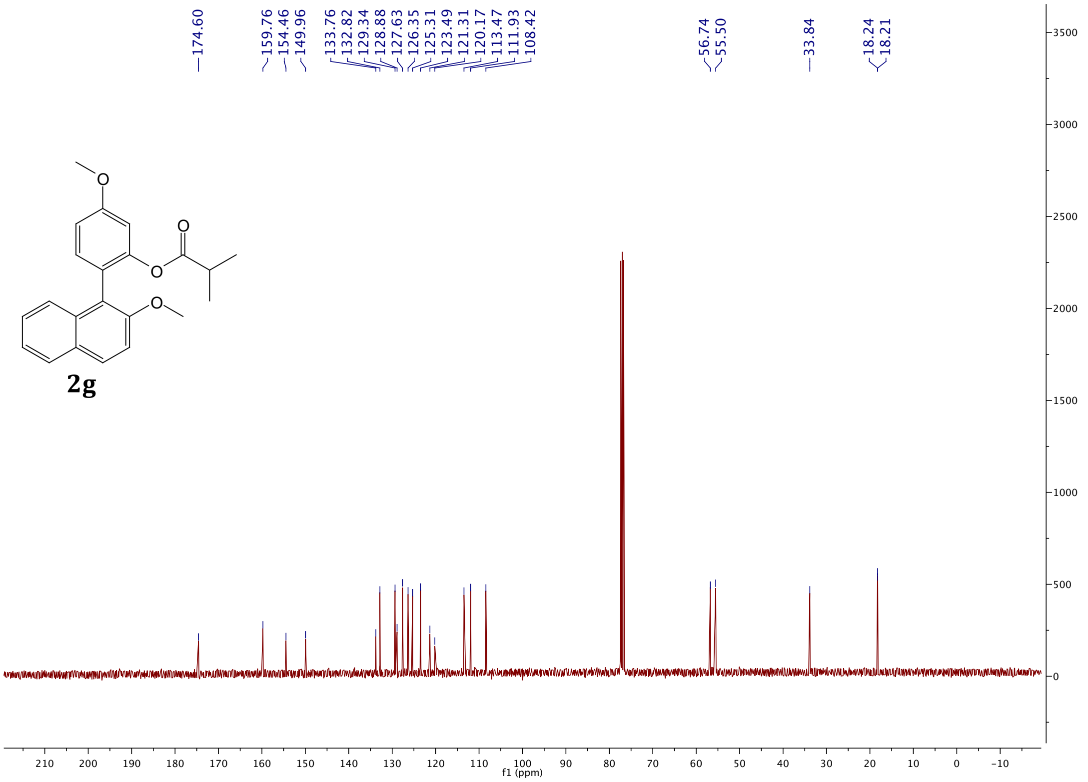
7.339
7.335
7.330
7.324
7.318
7.312
7.307
7.294
7.290
7.274
7.253
6.955
6.948
6.933
6.927
6.830
6.823
3.887
3.836
2.314
2.297
2.279
2.262
2.245
2.227
2.210
0.668
0.651
0.637
0.620
1.00
0.98
1.00
3.03
1.37
0.98
0.94
2.95
2.96
1.01
2.95
2.89
35000
30000
25000
20000
15000
10000
5000
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
O
O
O
O

2g


174.60
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132.82
129.34
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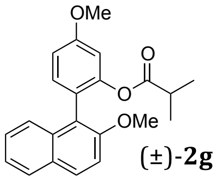
127.63
126.35
125.31
123.49
121.31
120.17
113.47
111.93
108.42
56.74
55.50
33.84
18.24
18.21
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
O
O
O
O

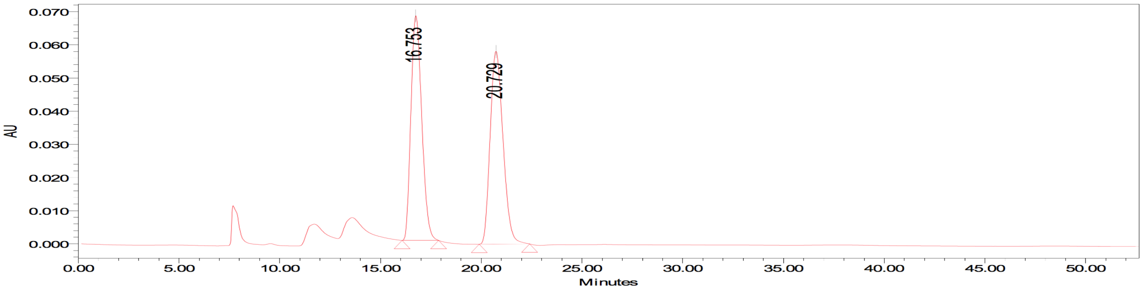
2g

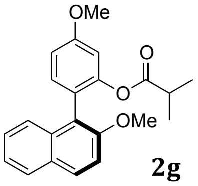


(±)-**2g**

Peak Results

	Name	RT	Area	% Area
1		16.753	2527467	49.52
2		20.729	2575984	50.48

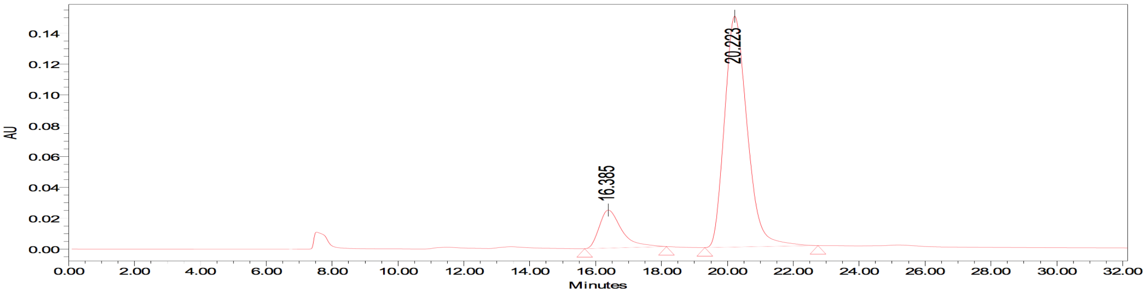


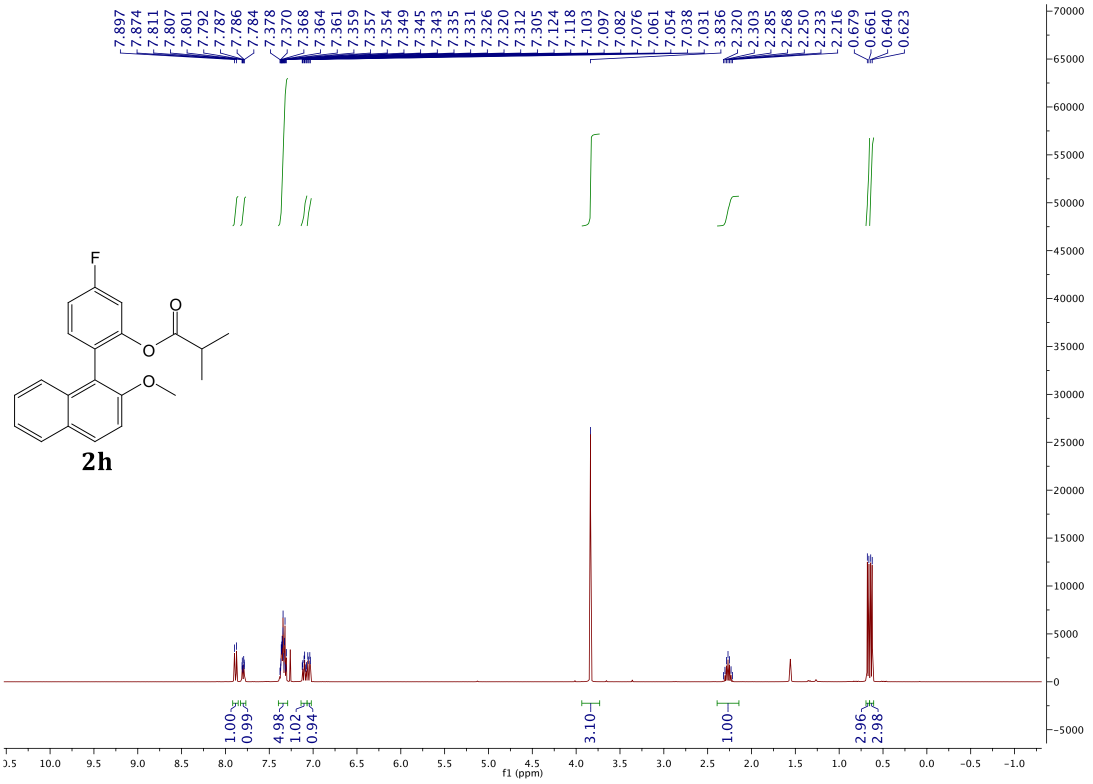


2g

Peak Results

	Name	RT	Area	% Area
1		16.385	1162804	13.97
2		20.223	7159484	86.03

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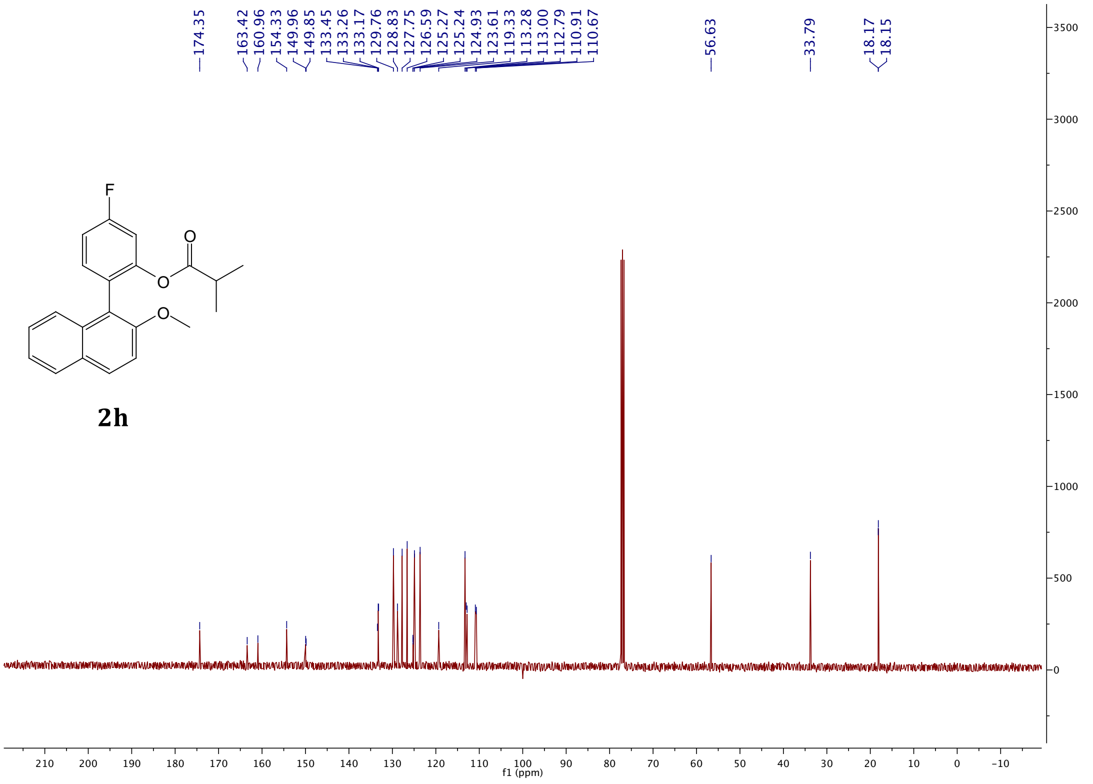
7.368
7.364
7.361
7.359
7.357
7.354
7.349
7.345
7.343
7.335
7.331
7.326
7.320
7.312
7.305
7.124
7.118
7.103
7.097
7.082
7.076
7.061
7.054
7.038
7.031
3.836
2.320
2.303
2.285
2.268
2.250
2.233
2.216
0.679
0.661
0.640
0.623
F
O
O
O
2h
1.00
0.99
4.98
1.02
0.94
3.10
1.00
2.96
2.98
f1 (ppm)


174.35
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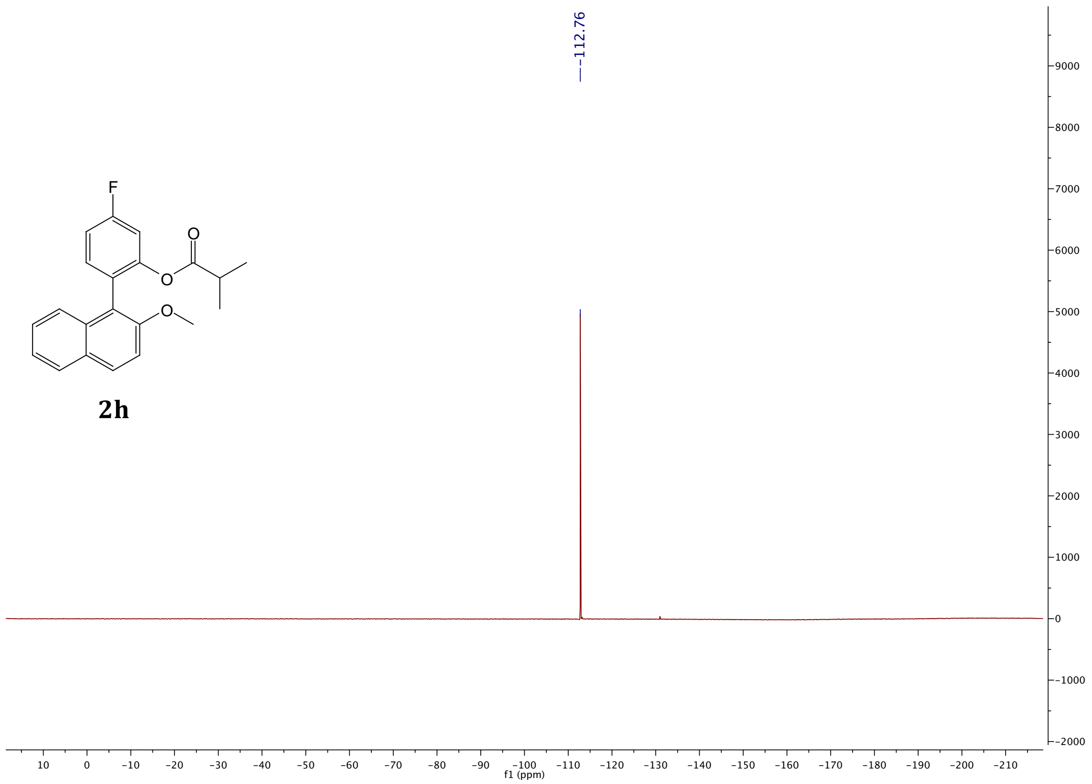
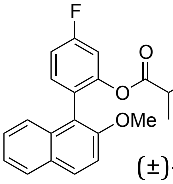
154.33
149.96
149.85
133.45
133.26
133.17
129.76
128.83
127.75
126.59
125.27
125.24
124.93
123.61
119.33
113.28
113.00
112.79
110.91
110.67
56.63
33.79
18.17
18.15
F
O
O
O
2h
f1 (ppm)

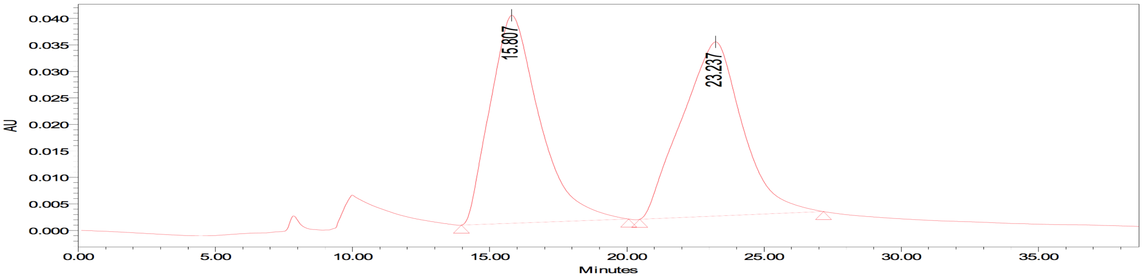


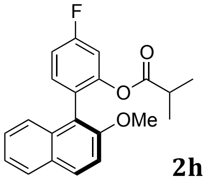


(±)-**2h**

Peak Results

	Name	RT	Area	% Area
1		15.807	4921792	49.29
2		23.237	5062646	50.71

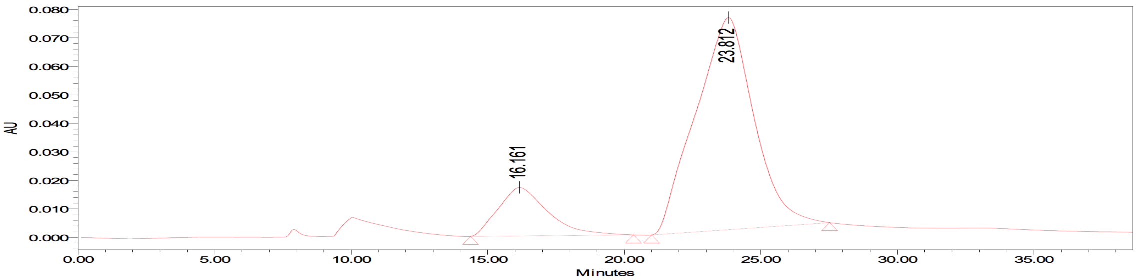


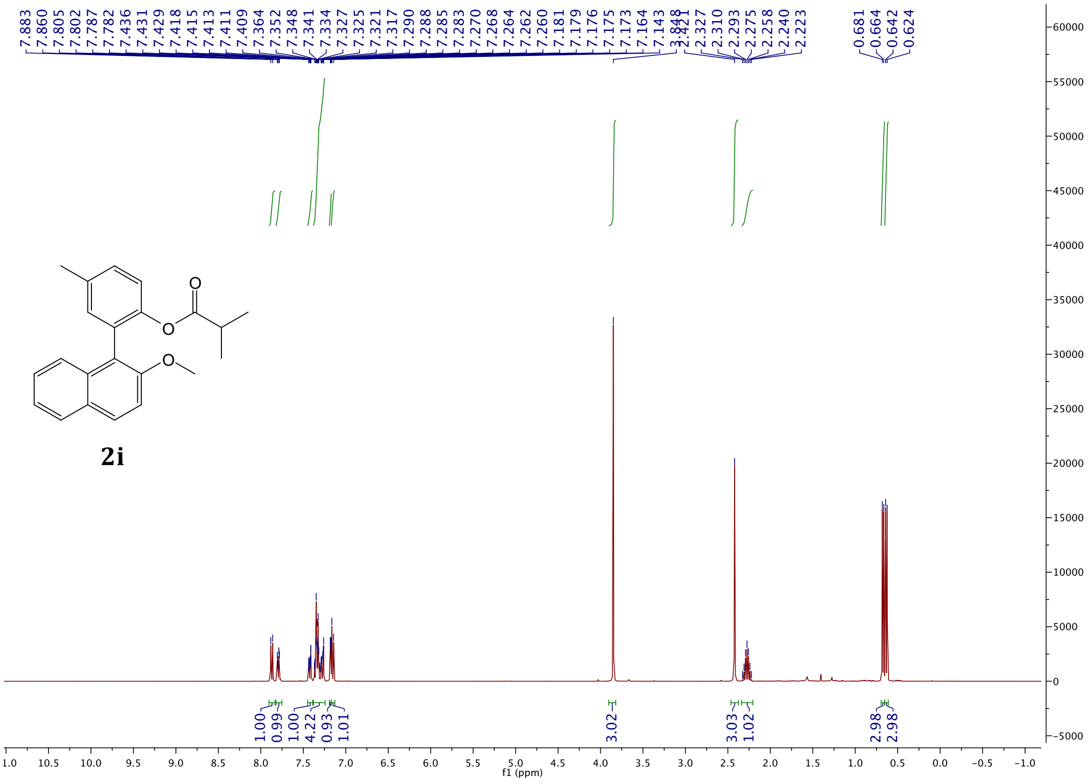


2h

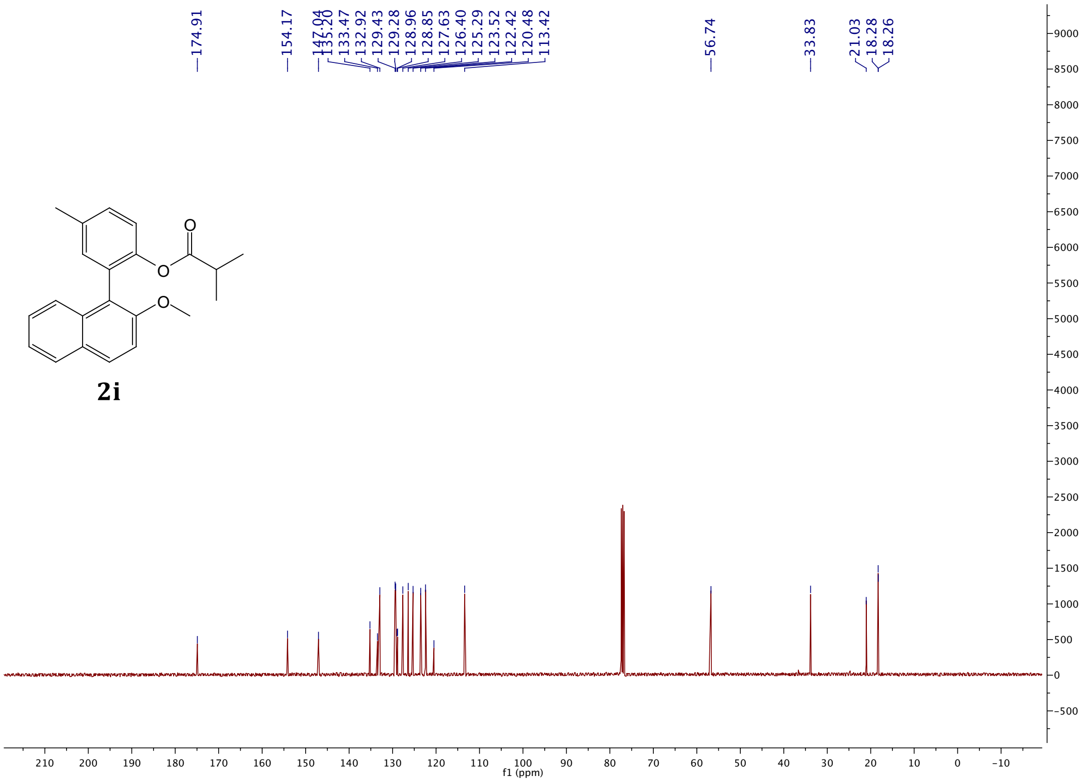
Peak Results

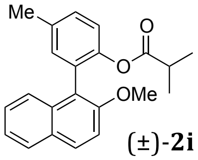
	Name	RT	Area	% Area
1		16.161	2137703	16.24
2		23.812	11029349	83.76





2i

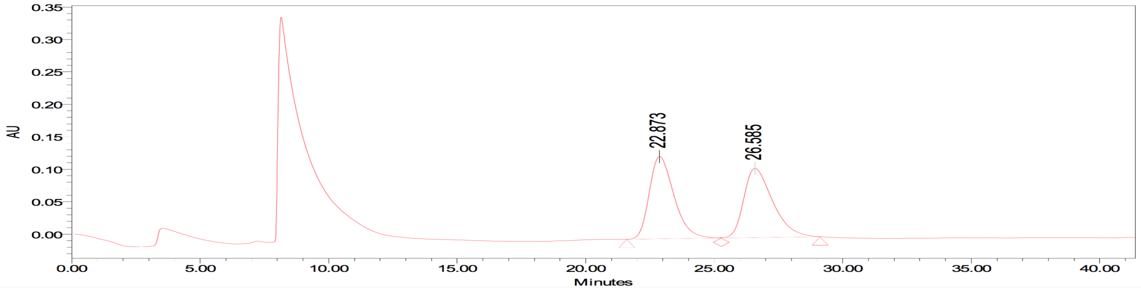


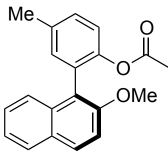


(±)-**2i**

Peak Results

	Name	RT	Area	% Area
1		22.873	8471344	50.37
2		26.585	8347833	49.63

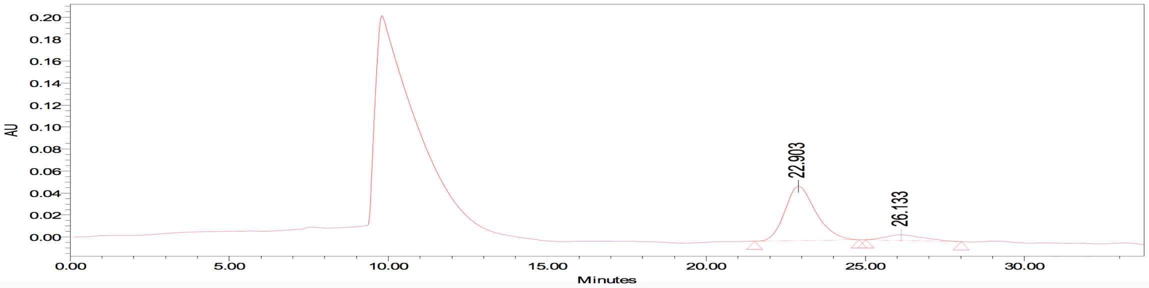


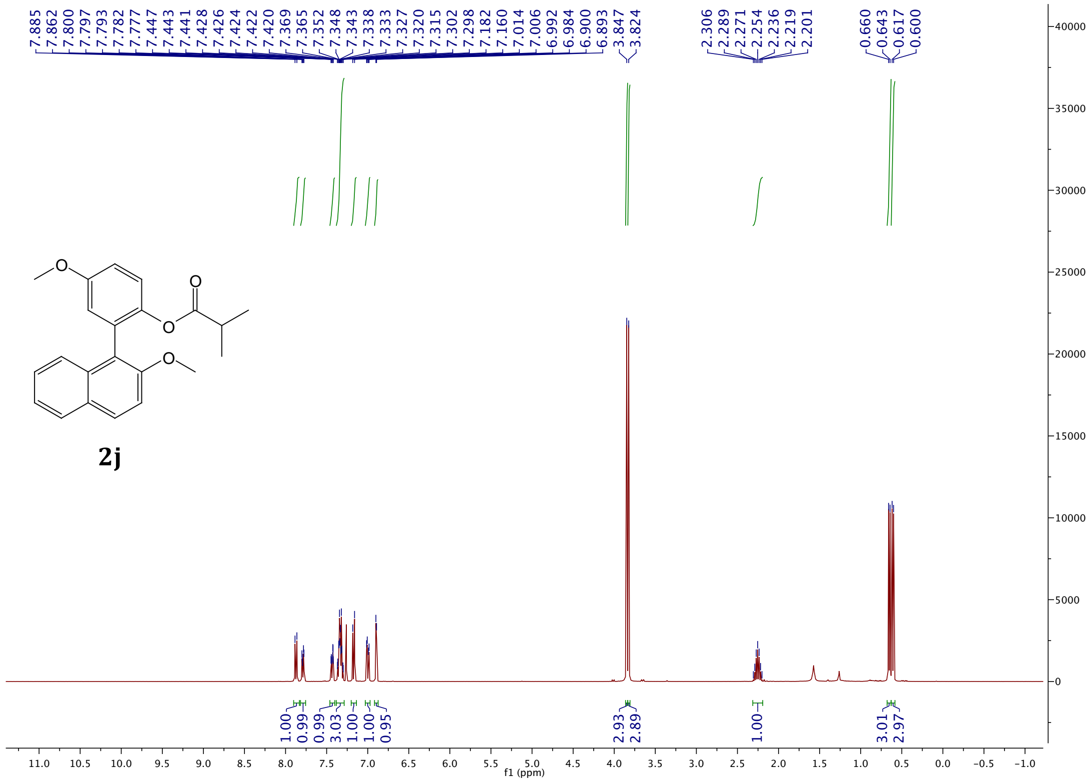


2i

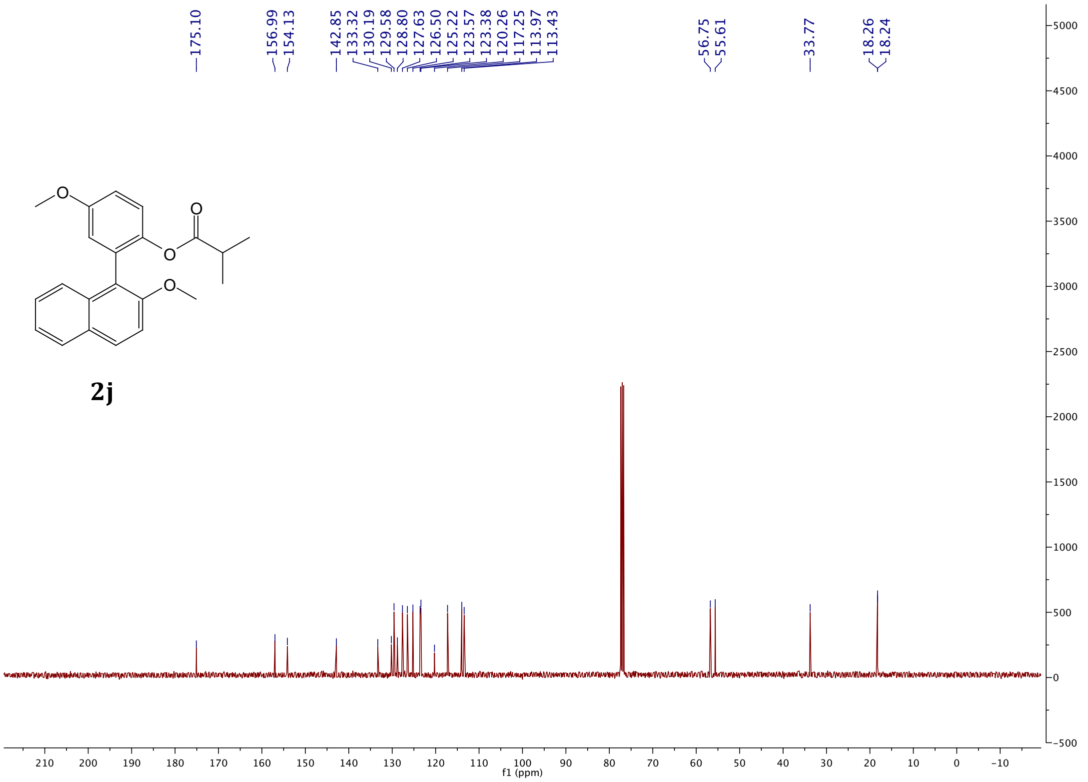
Peak Results

	Name	RT	Area	% Area
1		22.903	3339259	88.85
2		26.133	419018	11.15

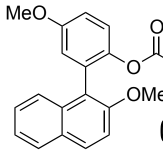




2j



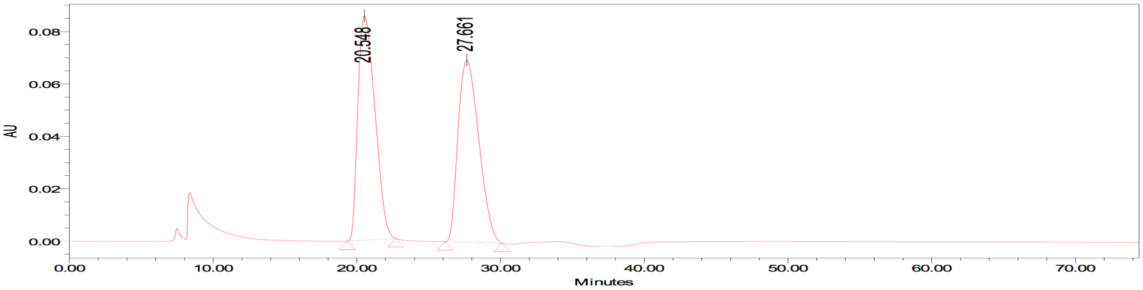
2j

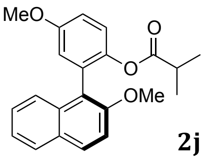


(±)-**2j**

Peak Results

	Name	RT	Area	% Area
1		20.548	7073645	50.33
2		27.661	6981117	49.67

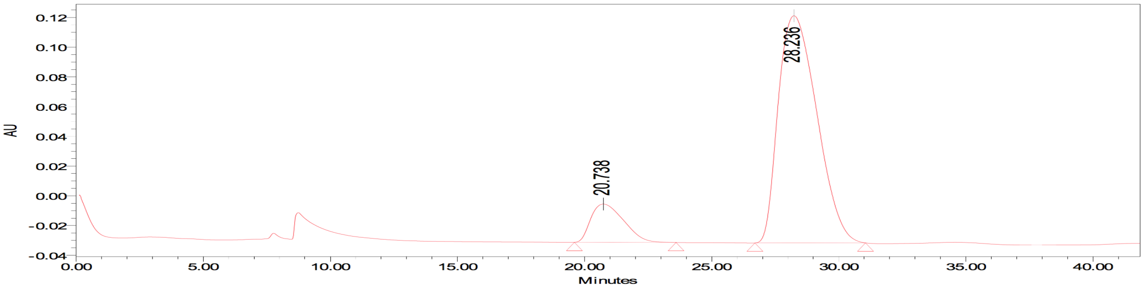


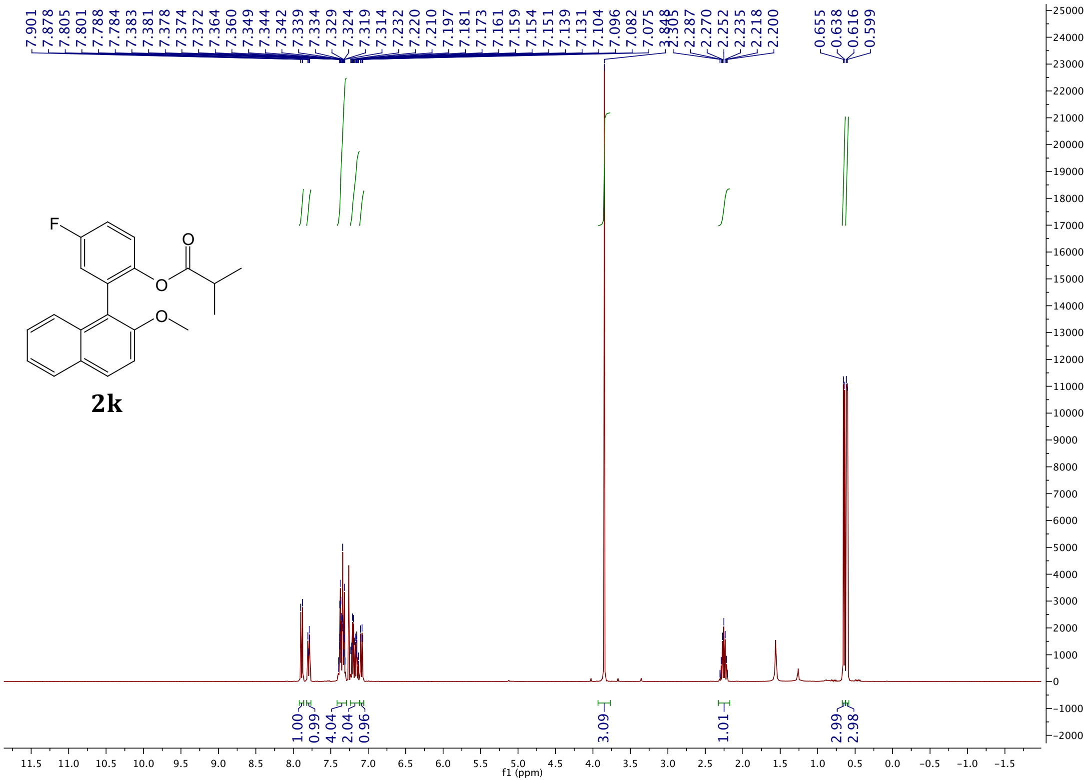


2j

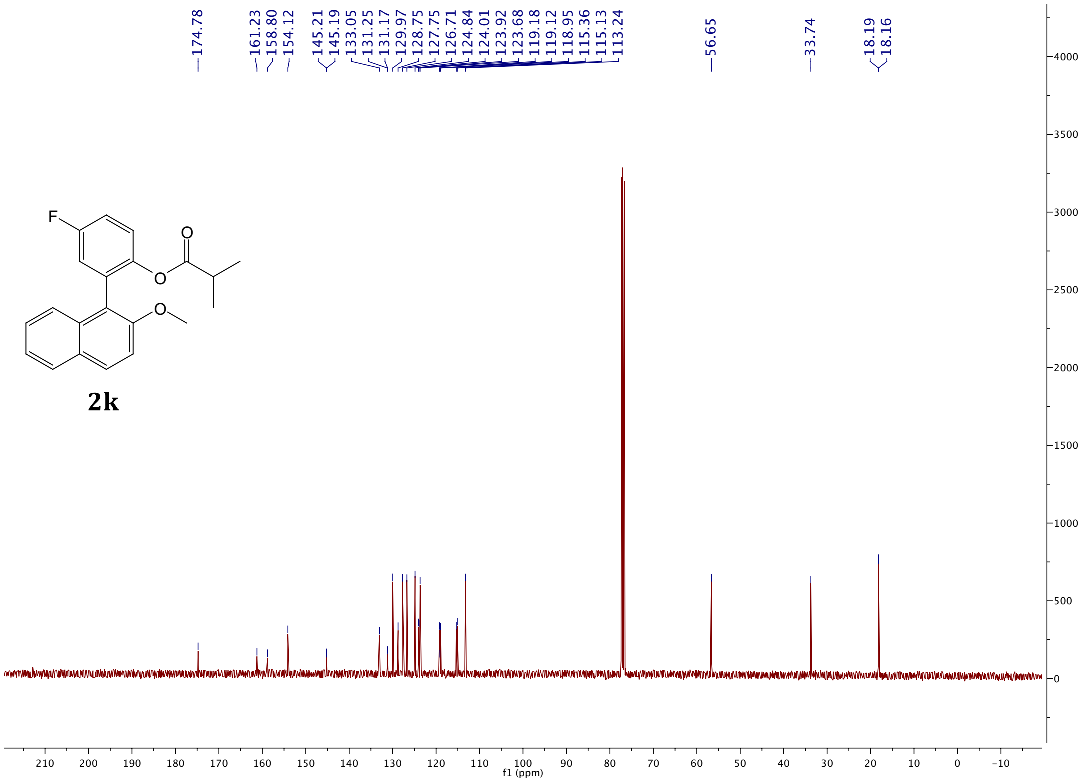
Peak Results

	Name	RT	Area	% Area
1		20.738	2311685	12.53
2		28.236	16135349	87.47

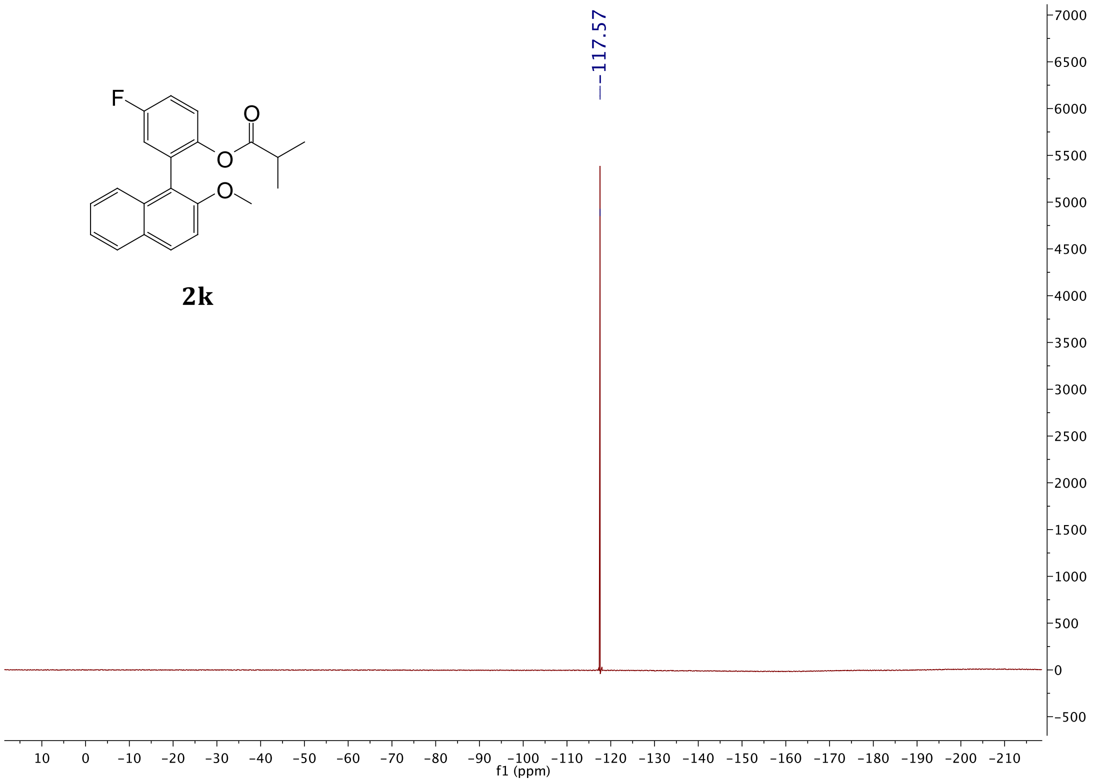




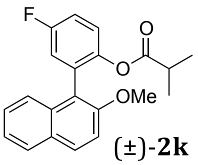
2k


2k

174.78
161.23
158.80
154.12
145.21
145.19
133.05
131.25
131.17
129.97
128.75
127.75
126.71
124.84
124.01
123.92
123.68
119.18
119.12
118.95
115.36
115.13
113.24
56.65
33.74
18.19
18.16
F
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
4000 3500 3000 2500 2000 1500 1000 500 0


2k

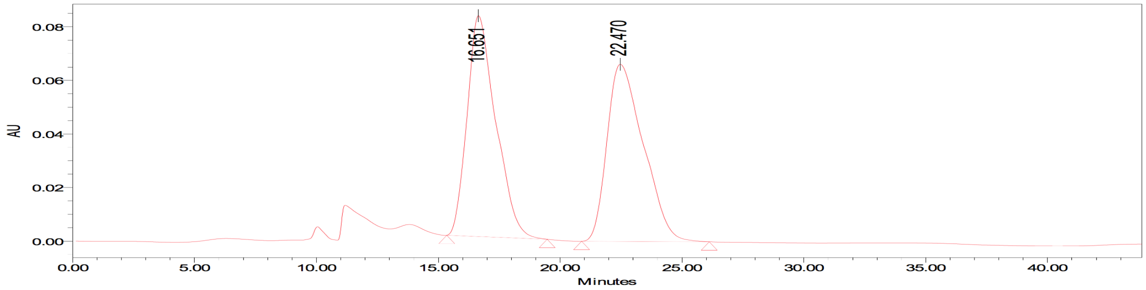
−117.57
F
O
O
O
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)
7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500

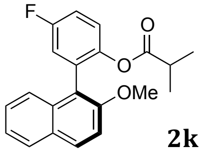


(±)-**2k**

Peak Results

	Name	RT	Area	% Area
1		16.651	6728401	49.53
2		22.470	6856503	50.47

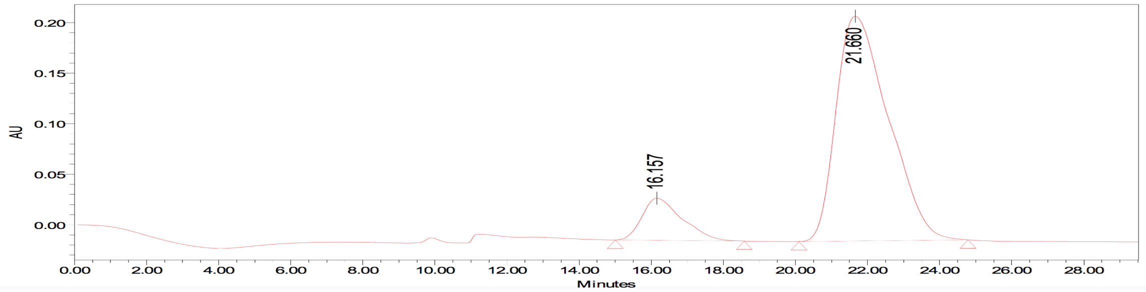


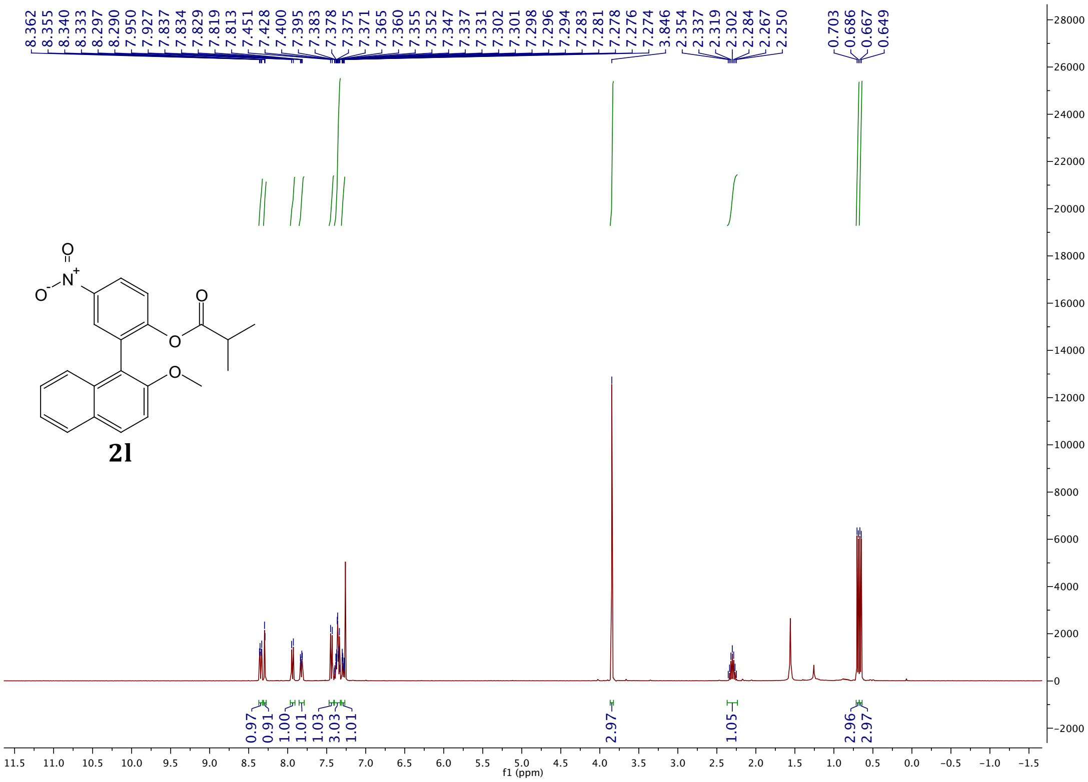


2k

Peak Results

	Name	RT	Area	% Area
1		16.157	3214880	12.54
2		21.660	22424792	87.46

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8.333
8.297
8.290
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7.927
7.837
7.834
7.829
7.819
7.813
7.451
7.428
7.400
7.395
7.383
7.378
7.375
7.371
7.365
7.360
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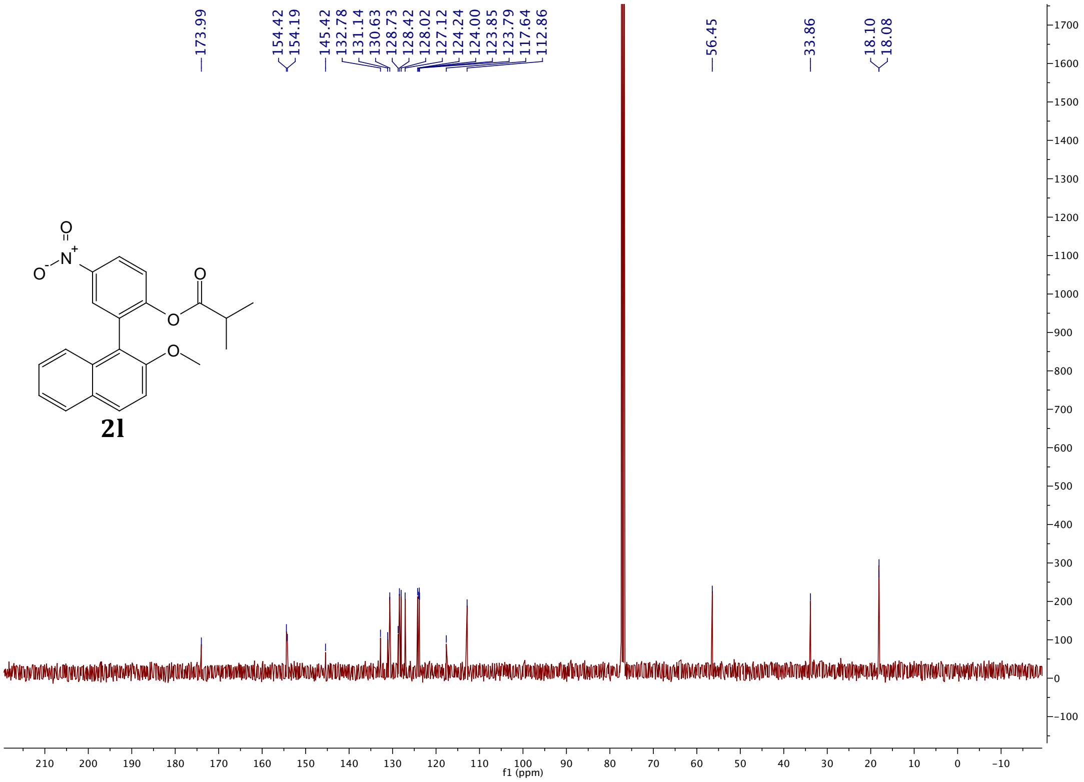
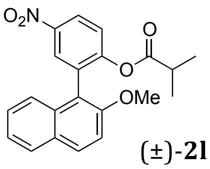
7.278
7.276
7.274
3.846
2.354
2.337
2.319
2.302
2.284
2.267
2.250
0.703
0.686
0.667
0.649
0.97
0.91
1.00
1.01
1.03
3.03
1.01
2.97
1.05
2.96
2.97
2l
f1 (ppm)

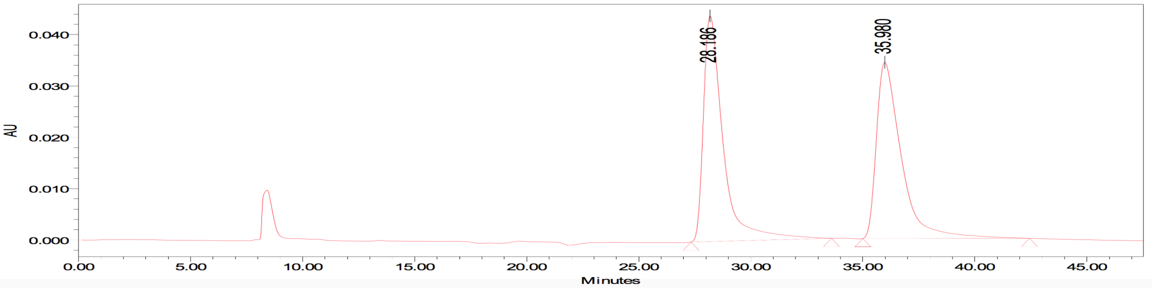

173.99
154.42
154.19
145.42
132.78
131.14
130.63
128.73
128.42
128.02
127.12
124.24
124.00
123.85
123.79
117.64
112.86
56.45
33.86
18.10
18.08
2l
f1 (ppm)

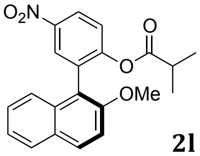


(±)-**2l**

Peak Results

	Name	RT	Area	% Area
1		28.186	2692341	50.44
2		35.980	2645486	49.56





2l

Peak Results

	Name	RT	Area	% Area
1		28.535	6849044	51.21
2		36.624	6525749	48.79