

Enantioselective Copper-Catalyzed Methylboration of Alkenes

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Supporting Information

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1. General

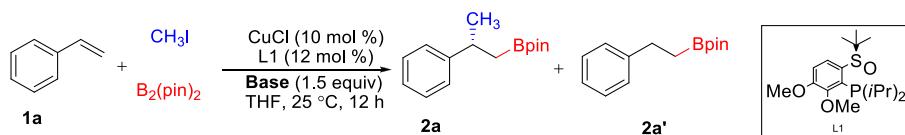
All commercial available reagents were used directly without further purification. Solvents used in catalytic reactions were dried and distilled in appropriate method. Solvent employed for column chromatography were purchased in technical grade quality without distillation before use. All catalytic reactions were operated in glovebox. NMR spectra were obtained on a Bruker 400 spectrometer in CDCl_3 , operating at 400 MHz for ^1H NMR, 101 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR and 128 MHz for ^{11}B NMR. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, t = triplet and m = multiplet. Optical rotation was recorded on PE polarimeter 341. Enantiomical excess were measured by chiral HPLC analysis on Chiralcel OD-H, AD-H, OJ-H, AS-H chiral column (Daicel Chemical Industries, LTD). Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Bruke P-SIMS-Gly FT-ICR mass spectrometer.

2. Preparation of Substrates

All commercially available reagents were used as received without further purification. **1w**¹, **3g**², **3h**², was synthesized according to literature.

3. Optimization of Enantioselective Methylboration of Alkenes

Table S1. Screening of Base^a



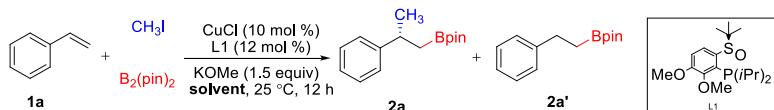
entry	base	yield(%) ^b (2a / 2a')	er ^c
1	KOH	90:10	94:6
2	KO'Bu	88:12	93.5:6.5
3	NaO'Bu	92:8	92:8

4	LiO'Bu	98:trace	92.5:7.5
5	KOMe	96:trace	94.5:5.5
6	NaOMe	65:3	83:17

^aConditions: **1a** (0.2 mmol), CH₃I (0.3 mmol), B₂(pin)₂ (0.3 mmol), CuCl (10 mol %), **L1** (12 mol %), **Base** (0.3 mmol), THF (1.5 mL) at 25 °C for 12 h. ^bDetermined by ¹H NMR spectroscopy.

^cDetermined by chiral HPLC analysis.

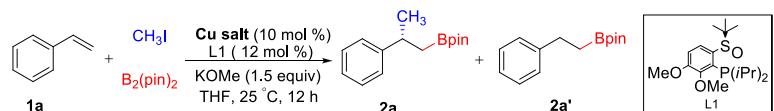
Table S2. Screening of Solvent^a



entry	solvent	yield(%) ^b (2a/2a')	er ^c
1	THF	96:trace	94.5:5.5
2	2-MeTHF	83:15	85:15
3	Dioxane	88:10	87:13
4	MTBE	50:50	83:17
5	Toluene	60:40	75:25
6	DMF	Trace:15	n.d.

^aConditions: **1a** (0.2 mmol), CH₃I (0.3 mmol), B₂(pin)₂ (0.3 mmol), CuCl (10 mol %), **L1** (12 mol %), KOMe (0.3 mmol), **Solvent** (1.5 mL) at 25 °C for 12 h. ^bDetermined by ¹H NMR spectroscopy. ^cDetermined by chiral HPLC analysis.

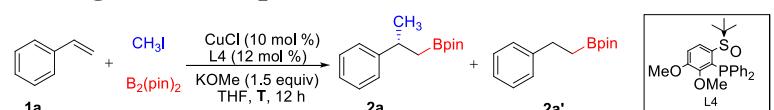
Table S3. Screening of Copper Salts^a



entry	copper salt	yield(%) ^b (2a/2a')	er ^c
1	CuCl	97:trace	94.5:5.5
2	CuBr	96:trace	94:6
3	CuI	97:trace	92.5:7.5
4	CuOAc	68:30	93.5:6.5
5	Cu(OAc) ₂	86:8	93:7

^aConditions: **1a** (0.2 mmol), CH₃I (0.3 mmol), B₂(pin)₂ (0.3 mmol), **Copper Salt** (10 mol %), **L1** (12 mol %), KOMe (0.3 mmol), THF (1.5 mL) at 25 °C for 12 h. ^bDetermined by ¹H NMR spectroscopy. ^cDetermined by chiral HPLC analysis.

Table S4. Screening of the Temperature^a

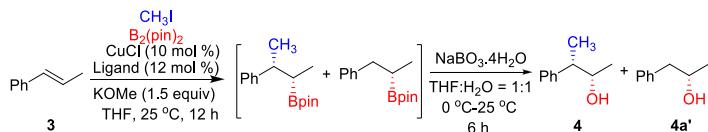


entry	temp	yield(%) ^b (2a/2a')	er ^c
1	45 °C	96:trace	94.5:5.5
2	25 °C	97:trace	97:3
3	10 °C	96:trace	95:5

4	0 °C	80:2	95:5
5	-10 °C	64:3	95.5:4.5

^aConditions: **1a** (0.2 mmol), CH₃I (0.3 mmol), B₂(pin)₂ (0.3 mmol), CuCl (10 mol %), **L4** (12 mol %), KOMe (0.3 mmol), THF (1.5 mL) at the appropriate temperature for 12 h. ^bDetermined by ¹H NMR spectroscopy. ^cDetermined by chiral HPLC analysis.

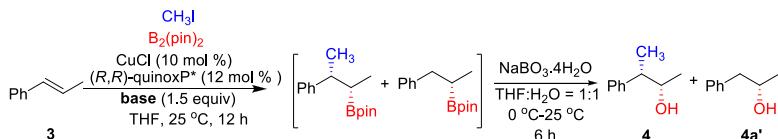
Table S5. Screening of ligands in the internal olefinsystem^a



entry	ligand	yield(%) ^b (4/4a')	er ^c
1	L4	n.r.	n.d.
2	(<i>S,S</i>)-Me-DUPHOS	85:15	86:14
3	(<i>S,S</i>)- <i>i</i> Pr-DUPHOS	30:40	70:30
4	(<i>R,R</i>)-quinoxP*	82:18	95:5

^aConditions: **3** (0.2 mmol), CH₃I (0.3 mmol), B₂(pin)₂ (0.3 mmol), CuCl (10 mol %), **Ligand** (12 mol %), KOMe (0.3 mmol), THF (1.5 mL) at 25 °C for 12 h. ^bDetermined by ¹H NMR spectroscopy. ^cDetermined by chiral HPLC analysis.

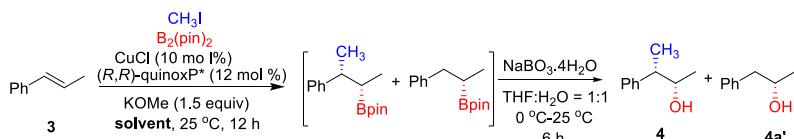
Table S6. Screening of Bases in the internal olefinsystem^a



entry	base	yield(%) ^b (4/4a')	er ^c
1	LiOMe	30:20	91:9
2	NaOMe	57:19	92:8
3	KOMe	83:17	95:5
4	KO'Bu	80:19	89:11

^aConditions: **3** (0.2 mmol), CH₃I (0.3 mmol), B₂(pin)₂ (0.3 mmol), CuCl (10 mol %), (*R,R*)-quinoxP* (12 mol %), **Base** (0.3 mmol), THF (1.5 mL) at 25 °C for 12 h. ^bDetermined by ¹H NMR spectroscopy. ^cDetermined by chiral HPLC analysis.

Table S7. Screening of Solvent in the internal olefinsystem^a

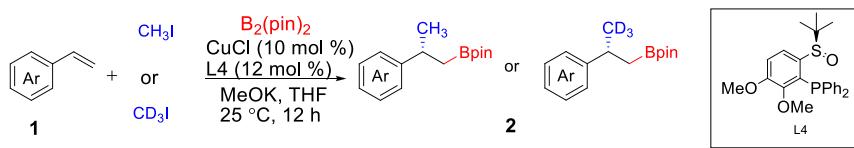


entry	solvent	yield(%) ^b (4/4a')	er ^c
1	THF	82:18	95:5
2	2-MeTHF	74:23	92.5:7.5
3	Toluene	76:24	92.5:7.5
4	Dioxane	81:18	93.5:6.5

^aConditions: **3** (0.2 mmol), CH₃I (0.3 mmol), B₂(pin)₂ (0.3 mmol), CuCl (10 mol %), (*R,R*)-quinoxP* (12 mol %), MeOK (0.3 mmol), solvent (1.5 mL) at 25 °C for 12 h. ^bDetermined by ¹H NMR spectroscopy. ^cDetermined by chiral HPLC analysis.

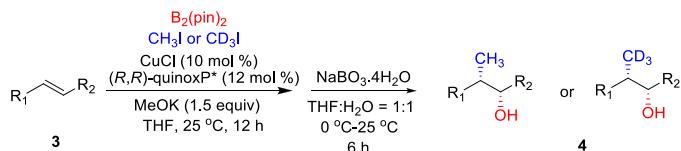
4. Copper-Catalyzed Enantioselective Methylboration of Alkenes

4.1 Procedure A for the transformation of vinylarenes:



In the glovebox, to a dry vial with a magnetic stir bar was added CuCl (10 mol %, 0.02 mmol, 1.9 mg), **L4**(12 mol %, 0.024 mmol, 10.2 mg) and 1mL THF, then the mixture was stirred 30 minutes at room temperature. To the mixture was added B₂(pin)₂ (76.3 mg, 0.3 mmol), styrene (0.2 mmol), CH₃I or CD₃I (0.3 mmol) and MeOK (0.3 mmol, 21 mg) successively (Note: MeOK must be added at last). After that, 0.5 mL of THF was added along the vial's wall to keep all reagents into the reaction solution. The vial was sealed with a rubber stopper, removed from the glovebox and stirred at room temperature for 12 hours. The reaction mixture was filtrated a celite pad, the solvent was removed under vacuo, and the residue was purified by column chromatography on silica gel to give the product **3**, the er was determined by chiral HPLC.

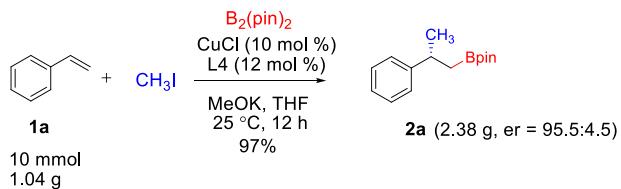
4.2 Procedure B for the transformation of β -substituted styrenes or aliphatic olefins:



In the glovebox, to a dry vial with magnetic stir bar was added CuCl (10 mol %, 0.02 mmol, 1.9 mg), (*R,R*)-quinoxP* (12 mol %, 0.024 mmol, 8.1 mg) and 1 mL THF,

then the mixture was stirred 30 minutes at room temperature. To the mixture was added $B_2(pin)_2$ (76.3 mg, 0.3 mmol), alkenes **3** (0.2mmol), CH_3I or CD_3I (0.3 mmol) and MeOK (0.3 mmol, 21 mg) successively (Note: MeOK must be added at last). After that, 0.5 mL THF was added along the vial's wall to keep all reacts into the reaction solution. The vial was sealed with a rubber stopper, removed from the glovebox and stirred at room temperature for 12 hours. The reaction mixture was filtrated a celite pad, the solvent was removed under vacuo, and the residue was roughly purified by a flash column chromatography on silica gel to give methylboration product mixed with sidehydroboration adduct. Considering that the corresponding alcohol derivatives can be separated, the methylboration product was characterized after oxidized to the alcohol. The mixture was dissolved in THF (2.0 mL) at 0 °C, then the aqueous solution of $NaBO_3 \cdot 4H_2O$ (123.2 mg, 0.8 mmol) in 2 mL water was added dropwise. After addition, the reaction mixture was stirred for 6 hours at room temperature. After both methyl- and hydroboration adducts were consumed, sat. $Na_2S_2O_3$ solution was added to quench the reaction. The mixture was extracted with EtOAc (3×10 mL) and the combined organic phase was dried over Na_2SO_4 . After evaporating the solvent under vacuo, the residue was purified by flash column chromatography on silica gel with EtOAc: Petroleum ether (1:3) to give the product**4**.

4.3 The procedure for Scaled-up Reaction

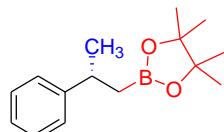


In the glovebox, to a 100 mL Schlenkflask with magnetic stir bar was added $CuCl$ (10 mol %, 1 mmol, 95 mg), **L4**(12 mol %, 2.4 mmol, 510 mg) and 30 mL THF, then the mixture was stirred 60 minutes at room temperature. To the mixture was added $B_2(pin)_2$ (3.82 g, 15 mmol), **1a** (10 mmol), CH_3I (15 mmol, 2.13 g) and MeOK (15

mmol, 1.05 g) successively (Note: MeOKwas added slowly to prevent the vigorously exothermic reaction).25 mL THF was then added. The flask was sealed with rubber stopper, removed from the glovebox and stirred at room temperature for 24 hours. The reaction mixture was filtrated through a celite pad, the solvent was removed under vacuo, and the residue was purified by column chromatography on silica gel with EtOAc: Petroleum ether (40: 1)to give the product **2a** (2.38 g, 97% yield, er = 95.5:4.5) as a colorless oil.

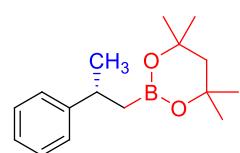
5. The Characterization Data for products

(R)-4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (**2a**)



colorless oil (46.2 mg, 94% yield). er = 97:3, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, λ = 220 nm, retention time: 14.74 min (major) and 18.00 min (minor)]; ^1H NMR (400 MHz, CDCl₃) δ 7.32–7.21 (m, 4H), 7.21–7.16 (m, 1H), 3.12–3.02 (m, 1H), 1.31 (d, J = 3.5 Hz, 3H), 1.21–1.18 (m, 14H). ^{13}C NMR (100 MHz, CDCl₃) δ 149.23, 128.19, 126.64, 125.69, 82.99, 35.83, 24.94, 24.79, 24.71. ^{11}B NMR (128 MHz, CDCl₃) δ 33.54. Optical Rotation: $[\alpha]_D^{22}$ -19.2 (c = 0.255, CH₂Cl₂).[Lit., +19.7945 (c 0.56 in CH₂Cl₂), (*S*)-isomer]³, confirmed as a (*R*)-isomer.HRMS-ESI (*m/z*): Calcd for C₁₅H₂₃BO₂, [M+H]: 247.1863; found: 247.1844.

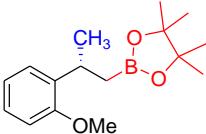
(R)-4,4,6,6-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborinane (**2A**)



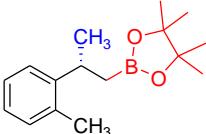
Colorless oil (46.8 mg, 90% yield). er = 95:5 [Daicel Chiralpak OJ-H, *n*-hexane/*i*-propanol = 98:2, 0.5 mL/min, λ = 220 nm, retention time: 7.79 min (major) and 8.22 min (minor)]; ^1H NMR (400 MHz, CDCl₃) δ 7.31–7.28 (m, 4H), 7.19–7.14 (m, 1H), 3.08–2.99 (m, 1H), 1.73 (s, 2H), 1.29–1.26 (m, 15H), 1.08 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl₃) δ 149.90, 128.01, 126.87, 125.38, 70.23, 48.73, 36.09, 31.71, 31.69, 25.03. ^{11}B NMR (128 MHz, CDCl₃) δ 29.44. Optical Rotation: $[\alpha]_D^{25}$ -5.56 (c = 0.4, CHCl₃).

HRMS-ESI (*m/z*): Calcd for C₁₆H₂₅BO₂, [M+Na]: 283.1845; found: 283.1836.

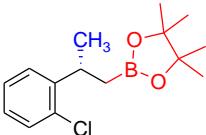
(R)-2-(2-methoxyphenyl)propyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)

 colorless oil (49.6 mg, 90% yield). er = 93.5:6.5, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 500:1, 1.0 mL/min, λ = 220 nm, retention time: 4.51 min (major) and 5.14 min (minor)]; ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.13 (m, 2H), 6.94–6.83 (m, 2H), 3.84 (s, 3H), 3.53–3.44(m, 1H), 1.27 (d, *J* = 3.4 Hz, 3H), 1.21–1.15 (m, 14H). ¹³C NMR (100 MHz, CDCl₃) δ 156.76, 137.45, 126.58, 126.43, 120.46, 110.37, 82.85, 55.33, 28.49, 24.79, 24.67, 23.42.Optical Rotation: $[\alpha]_D^{22}$ -5.33 (c = 0.60, CHCl₃).HRMS-ESI (*m/z*): Calcd for C₁₆H₂₅BO₃, [M+Na]: 299.1789; found: 299.1787.

(R)-4,4,5,5-tetramethyl-2-(2-o-tolylpropyl)-1,3,2-dioxaborolane (2c)

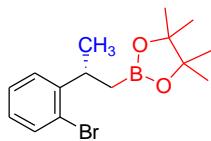
 colorless oil (49.4 mg, 95% yield). er = 97:3, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, λ = 220 nm, retention time: 17.63 min (major) and 26.97 min (minor)]; ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.15 (m, 1H), 7.10 (t, *J* = 8.1 Hz, 1H), 7.06–7.04 (m, 2H), 3.33–3.27(m, 1H), 2.39 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.17–1.15 (m, 14H). ¹³C NMR (100 MHz, CDCl₃) δ 147.20, 134.96, 129.97, 126.09, 125.35, 82.91, 30.68, 24.70, 24.61, 19.52.Optical Rotation: $[\alpha]_D^{22}$ -4.00 (c = 0.45, CHCl₃). HRMS-ESI (*m/z*): Calcd for C₁₆H₂₅BO₂, [M+Na]: 283.1840; found: 283.1850.

(R)-2-(2-chlorophenyl)propyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)

 colorless oil (49.3 mg, 88% yield). er = 95:5, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 98:2, 0.7 mL/min, λ = 220 nm, retention time: 5.33 min (major) and 5.74 min (minor)]; ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.31 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 3.62–3.53(m, 1H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.22–1.12 (m, 14H). ¹³C NMR (100 MHz, CDCl₃) δ 146.14, 133.33, 129.31, 127.07, 126.83, 126.73, 82.03, 31.63, 24.71, 24.65, 23.45.Optical Rotation: $[\alpha]_D^{22}$ -4.00 (c = 0.50, CHCl₃).HRMS-ESI (*m/z*): Calcd

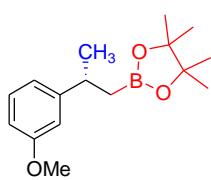
for $C_{15}H_{22}BClO_2$, [M+Na]: 303.1294; found: 303.1303.

(R)-2-(2-(2-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)



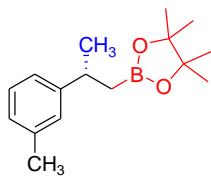
colorless oil (55.9 mg, 86% yield). er = 92.5:7.5, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.7 mL/min, λ = 220 nm, retention time: 5.52 min (major) and 6.16 min (minor)]; 1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.9 Hz, 1H), 7.32–7.25 (m, 2H), 7.04–7.00 (m, 1H), 3.58–3.49 (m, 1H), 1.27 (d, J = 6.8 Hz, 3H), 1.23–1.11 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.76, 132.65, 127.51, 127.16, 127.11, 124.23, 82.04, 34.39, 24.70, 24.66, 23.62. Optical Rotation: $[\alpha]_D^{22}$ +1.39 (c = 0.645, $CHCl_3$). HRMS-ESI (*m/z*): Calcd for $C_{15}H_{22}BBrO_2$, [M+Na]: 347.0788; found: 347.0789.

(R)-2-(2-(3-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)



colorless oil (49.6 mg, 90% yield). er = 97:3, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, λ = 220 nm, retention time: 20.13 min (major) and 22.64 min (minor)]; 1H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 7.8 Hz, 1H), 6.87–6.82 (m, 2H), 6.73–6.71 (m, 1H), 3.81 (s, 3H), 3.07–2.98 (m, 1H), 1.29 (d, J = 6.8 Hz, 3H), 1.20 (s, 12H), 1.18–1.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.52, 151.04, 129.12, 112.44, 110.98, 83.00, 55.09, 35.86, 24.79, 24.73, 24.70. Optical Rotation: $[\alpha]_D^{22}$ -15.00 (c = 0.32, $CHCl_3$). HRMS-ESI (*m/z*): Calcd for $C_{16}H_{25}BO_3$, [M+Na]: 299.1789; found: 299.1796.

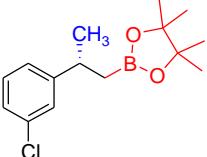
(R)-4,4,5,5-tetramethyl-2-(2-m-tolylpropyl)-1,3,2-dioxaborolane (2g)



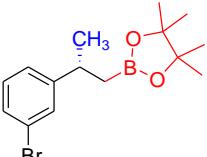
colorless oil (47.8 mg, 92% yield). er = 97.5:2.5, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, λ = 220 nm, retention time: 13.29 min (major) and 15.44 min (minor)]; 1H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 7.4 Hz, 1H), 7.07–6.97 (m, 3H), 3.06–2.97 (m, 1H), 2.34 (s, 3H), 1.29 (d, J = 6.8 Hz, 3H), 1.19–1.15 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.20, 137.54, 128.08, 127.48, 126.38, 123.59, 82.96, 35.69, 24.77, 24.69, 21.47. Optical Rotation: $[\alpha]_D^{22}$ -4.22 (c = 0.45, $CHCl_3$). HRMS-ESI (*m/z*): Calcd for

$C_{16}H_{25}BO_2$, [M+Na]: 283.1840; found: 283.1844.

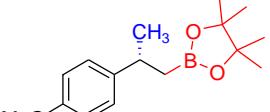
(R)-2-(2-(3-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)

 colorless oil (48.7 mg, 87% yield). er = 82:18, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation)[Daicel Chiralpak OJ-H, *n*-hexane/*i*-propanol = 95:5, 0.5 mL/min, λ = 220 nm, retention time: 18.60 min (major) and 19.55 min (minor)]; 1H NMR (400 MHz, $CDCl_3$) δ 7.24–7.12 (m, 4H), 3.07–2.98(m, 1H), 1.28 (d, J = 7.2 Hz, 3H), 1.17 (s, 12H), 1.14 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.25, 133.85, 129.47, 127.02, 125.81, 124.84, 83.07, 35.63, 24.75, 24.71, 21.60. Optical Rotation: $[\alpha]_D^{22}$ -14.91 (c = 0.61, $CHCl_3$). HRMS-ESI (*m/z*): Calcd for $C_{15}H_{22}BClO_2$, [M+Na]: 303.1294; found: 303.1297.

(R)-2-(2-(3-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)

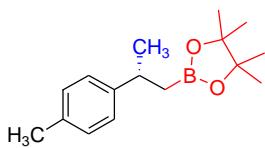
 colorless oil (55.2 mg, 85% yield). er = 77:23, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation)[Daicel Chiralpak OJ-H, *n*-hexane/*i*-propanol = 95:5, 0.5 mL/min, λ = 220 nm, retention time: 20.12 min (major) and 21.08 min (minor)]; 1H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, J = 2.0 Hz, 1H), 7.29–7.27 (m, 1H), 7.19–7.11 (m, 2H), 3.06–2.97(m, 1H), 1.28 (d, J = 6.8 Hz, 3H), 1.17 (s, 12H), 1.14 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.55, 129.98, 129.82, 128.76, 125.29, 122.23, 83.07, 35.63, 24.78, 24.73, 21.61. Optical Rotation: $[\alpha]_D^{22}$ -12.02 (c = 0.715, $CHCl_3$). HRMS-ESI (*m/z*): Calcd for $C_{15}H_{22}BBrO_2$, [M+Na]: 347.0788; found: 347.0790.

(R)-2-(2-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)

 colorless oil (49.1 mg, 89% yield). er = 94:6, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, λ = 220 nm, retention time: 36.67 min (major) and 39.54 min (minor)]; 1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.06–2.97(m, 1H), 1.27 (d, J = 6.8 Hz, 3H), 1.18 (s, 12H), 1.16–1.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.60, 141.48, 127.47, 113.55, 82.96, 55.25, 34.98,

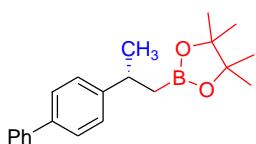
25.13, 24.77, 21.71. Optical Rotation: $[\alpha]_D^{22}$ -14.50 ($c = 0.60$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{16}\text{H}_{25}\text{BO}_3$, [M+Na]: 299.1789; found: 299.1785.

(R)-4,4,5,5-tetramethyl-2-(2-p-tolylpropyl)-1,3,2-dioxaborolane (2k)



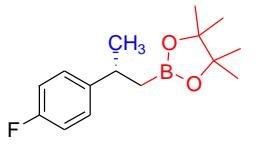
colorless oil (46.8 mg, 90% yield). er = 95:5, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation)[Daicel Chiraldak AS-H, *n*-hexane/*i*-propanol = 98:2, 0.5 mL/min, $\lambda = 220$ nm, retention time: 22.27 min (major) and 23.20 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.16-7.09(m, 4H), 3.07-2.98(m, 1H), 2.32 (s, 3H), 1.28 (d, $J = 6.8$ Hz, 3H), 1.20 (s, 12H), 1.17-1.14 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.31, 135.01, 128.84, 126.45, 82.98, 35.33, 24.88, 24.79, 24.70, 20.96. Optical Rotation: $[\alpha]_D^{22}$ -17.93 ($c = 0.485$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{16}\text{H}_{25}\text{BO}_2$, [M+Na]: 283.1840; found: 283.1845.

(R)-2-(2-(biphenyl-4-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)



white solid (56.1 mg, 87% yield), m.p.=70°C. er = 96:4, [Daicel Chiraldak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, $\lambda = 220$ nm, retention time: 22.00 min (major) and 24.30 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.54(m, 4H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.37-7.33(m, 3H), 3.18-3.09(m, 1H), 1.36 (d, $J = 6.8$ Hz, 3H), 1.25-1.23 (m, 2H), 1.21 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.42, 141.30, 138.64, 128.69, 127.08, 127.01, 126.95, 126.91, 83.05, 35.50, 24.87, 24.81, 24.73. Optical Rotation: $[\alpha]_D^{22}$ -37.20 ($c = 0.25$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{21}\text{H}_{27}\text{BO}_2$, [M+Na]: 345.1996; found: 345.2001.

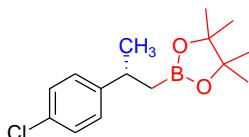
(R)-2-(2-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m)



colorless oil (48.1 mg, 91% yield). er = 97:3, [Daicel Chiraldak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, $\lambda = 220$ nm, retention time: 23.03 min (major) and 24.14 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.19(m, 2H), 6.98-6.94(m, 2H), 3.09-3.01(m, 1H),

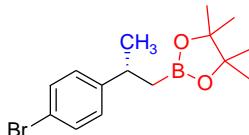
1.27 (d, $J = 6.8$ Hz, 3H), 1.17 (s, 12H), 1.15 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.09 (d, $J = 241.3$ Hz), 144.80 (d, $J = 3.0$ Hz), 127.95 (d, $J = 7.6$ Hz), 114.76 (d, $J = 20.8$ Hz), 83.02, 35.15, 25.12, 24.73, 24.69. ^{19}F NMR (376 MHz, CDCl_3) δ -118.20. Optical Rotation: $[\alpha]_D^{22}$ -12.08 ($c = 0.695$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{15}\text{H}_{22}\text{BFO}_2$, [M+Na]: 287.1589; found: 287.1588.

(R)-2-(2-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)



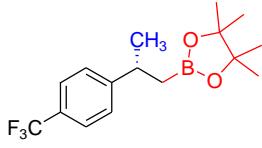
white solid (48.2 mg, 86% yield), m.p. = 32 °C. er = 96:4, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation)[Daicel Chiraldak AD-H, n -hexane/*i*-propanol = 98:2, 1.0 mL/min, $\lambda = 220$ nm, retention time: 18.29 min (minor) and 20.01 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.17(m, 4H), 3.07-2.98(m, 1H), 1.27 (d, $J = 6.8$ Hz, 3H), 1.18 (s, 12H), 1.14 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.67, 131.19, 128.22, 128.03, 83.08, 35.26, 24.85, 24.75, 24.70. Optical Rotation: $[\alpha]_D^{22}$ -26.41 ($c = 0.265$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{15}\text{H}_{22}\text{BClO}_2$, [M+Na]: 303.1294; found: 303.1298.

(R)-2-(2-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)



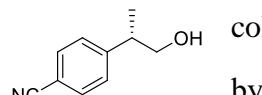
white solid (55.2 mg, 85% yield), m.p.= 52 °C. er = 96:4, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation)[Daicel Chiraldak AD-H, n -hexane/*i*-propanol = 98: 2, 1.0 mL/min, $\lambda = 220$ nm, retention time: 19.95 min (minor) and 21.86 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 3.06-2.97(m, 1H), 1.26 (d, $J = 6.8$ Hz, 3H), 1.18 (s, 12H), 1.14 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.21, 131.18, 128.47, 119.22, 83.08, 35.32, 24.76, 24.71. Optical Rotation: $[\alpha]_D^{22}$ -29.45 ($c = 0.55$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{15}\text{H}_{22}\text{BBrO}_2$, [M+Na]: 347.0788; found: 347.0789.

(R)-4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)propyl)-1,3,2-dioxaborolane (2p)



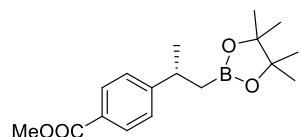
colorless oil (54.6 mg, 87% yield). er = 63:37, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation)[Daicel Chiraldpak AD-H, *n*-hexane/*i*-propanol = 95: 5, 0.5 mL/min, λ = 220 nm, retention time: 16.70 min (minor) and 18.51 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 3.16-3.07(m, 1H), 1.30 (d, J = 7.2 Hz, 3H), 1.19-1.18 (m, 14H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.28, 128.01 (q, J = 31.3 Hz), 126.99, 125.13 (q, J = 3.7 Hz), 83.15, 35.74, 24.73, 24.66, 24.62. ^{19}F NMR (376 MHz, CDCl_3) δ -62.24. Optical Rotation: $[\alpha]_D^{22}$ -4.00 (c = 0.50, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{16}\text{H}_{22}\text{BF}_3\text{O}_2$, [M+Na]: 337.1563; found: 337.1562.

4-(1-hydroxypropan-2-yl)benzonitrile (2q)



colorless oil (17.9 mg, 56% yield).(The products were characterized by an oxidation procedure to convert Bpin to hydroxyl group, because the targeted methylboration product and the hydroboration by-product can not be separated by chromatography). er = 50:50, [Daicel ChiraldpakAS-H, *n*-hexane/*i*-propanol = 95:5, 1.0 mL/min, λ = 220 nm, retention time: 32.08 min and 33.95 min]; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 3.79–3.73 (m, 2H), 3.09–3.00 (m, 1H), 1.49–1.46 (m, 1H), 1.31(d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.68, 132.38, 128.37, 118.96, 110.44, 68.05, 42.56, 17.31.

(*R*)-methyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzoate (2r)

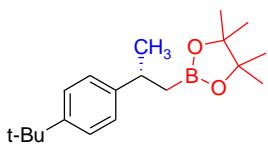


Colorless oil (41.3 mg, 68% yield).er = 95.5:4.5, [Daicel Chiraldpak OD-H, *n*-hexane/*i*-propanol = 98:2, 1.0 mL/min, λ = 220 nm, retention time: 4.81 min (major) and 5.49 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 3.90 (s, 3H), 3.15–3.05 (m, 1H), 1.29 (d, J = 6.8 Hz, 3H), 1.18–1.16 (m, 14H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.25, 154.73, 129.63, 127.64, 126.71, 83.10, 51.93, 35.90, 24.74, 24.70, 24.64. Optical Rotation: $[\alpha]_D^{25}$ -1.00 (c = 1.4, CHCl_3).HRMS-ESI

(*m/z*): Calcd for C₁₇H₂₅BO₄, [M+Na]:327.1744; found: 327.1745.

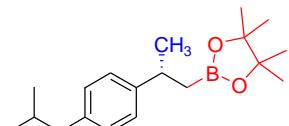
(R)-2-(2-(4-tert-butylphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s)

(2s)



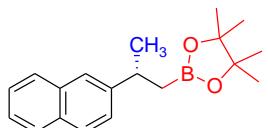
white solid (56.1 mg, 93% yield), m.p. = 36 °C. er = 98:2, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation)[Daicel Chiraldak OJ-H, *n*-hexane/*i*-propanol = 98:2, 0.7 mL/min, λ = 220 nm, retention time: 16.59 min (minor) and 17.70 min (major)]; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 3.09-3.01(m, 1H), 1.33 (s, 9H), 1.31 (d, J = 6.8 Hz, 3H), 1.19-1.15 (m, 14H). ¹³C NMR (100 MHz, CDCl₃) δ 148.36, 146.13, 126.25, 125.00, 82.94, 35.26, 34.30, 31.44, 24.81, 24.78, 24.65. Optical Rotation: $[\alpha]_D^{22}$ -23.68 (c = 0.38, CHCl₃). HRMS-ESI (*m/z*): Calcd for C₁₉H₃₁BO₂, [M+Na]: 325.2309; found: 325.2318.

(R)-2-(2-(4-isobutylphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t)



colorless oil (54.4 mg, 90% yield). er = 96:4, [Daicel Chiraldak OZ-H, *n*-hexane/*i*-propanol = 90:10, 1.0 mL/min, λ = 220 nm, retention time: 4.20 min (minor) and 5.86 min (major)]; ¹H NMR (400 MHz, CDCl₃) δ 7.16(d, J = 8.1 Hz, 2H), 7.06(d, J = 8.1 Hz, 2H), 3.03 (sext, J = 7.2 Hz, 1H), 2.45 (d, J = 7.4 Hz, 2H), 1.90-1.79 (m, 1H), 1.29 (d, J = 6.8 Hz, 3H), 1.18-1.15 (m, 14H), 0.91 (d, J = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 146.38, 138.88, 128.88, 126.32, 82.93, 45.05, 35.44, 30.25, 25.05, 24.75, 24.68, 22.37, 22.34. Optical Rotation: $[\alpha]_D^{22}$ -23.03 (c = 0.165, CHCl₃). HRMS-ESI (*m/z*): Calcd for C₁₉H₃₁BO₂, [M+H]: 303.2489; found: 303.2496.

(R)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane (2u)

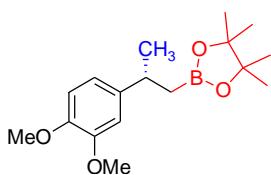


white solid (53.8 mg, 91% yield), m.p. = 56 °C. er = 97.5:2.5, [Daicel Chiraldak AD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, λ = 220 nm, retention time: 18.71 min (major) and

20.68 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.79(m, 3H), 7.71(s, 1H), 7.49-7.41(m, 3H), 3.27(sext, $J = 7.2$ Hz, 1H), 1.42 (d, $J = 7.2$ Hz, 3H), 1.32-1.28 (m, 2H), 1.19(s, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.74, 133.64, 132.13, 127.77, 127.61, 127.55, 125.88, 125.70, 124.95, 124.43, 83.04, 35.91, 24.79, 24.74. Optical Rotation: $[\alpha]_D^{22}$ -30.53 ($c = 0.465$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{19}\text{H}_{25}\text{BO}_2$, [M+Na]: 319.1840; found: 319.1833.

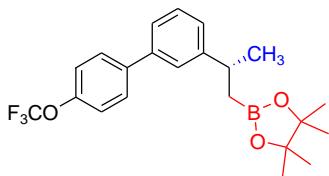
(R)-2-(2-(3,4-dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(2v)



colorless oil (53.8 mg, 88% yield). er = 94:6, [Daicel Chiralpak AD-H, n -hexane/*i*-propanol = 98:2, 1.0 mL/min, $\lambda = 220$ nm, retention time: 6.21 min (major) and 7.38 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 6.79(s, 3H), 3.88(s, 3H), 3.85(s, 3H), 3.00 (sext, $J = 7.2$ Hz, 1H), 1.27 (d, $J = 6.8$ Hz, 3H), 1.17 (s, 12H), 1.45 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.60, 146.96, 142.11, 118.21, 111.13, 110.21, 82.98, 55.92, 55.75, 45.05, 35.44, 25.12, 25.02, 24.79, 24.72. Optical Rotation: $[\alpha]_D^{22}$ -25.78 ($c = 0.19$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{17}\text{H}_{27}\text{BO}_4$, [M+Na]: 329.1895; found: 329.1894.

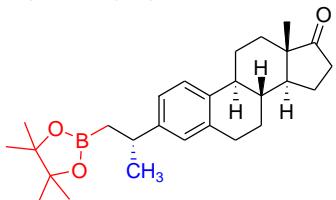
(R)-4,4,5,5-tetramethyl-2-(2-(4'-(trifluoromethoxy)biphenyl-3-yl)propyl)-1,3,2-di oxaborolane (2w)



colorless oil (73.1 mg, 90% yield). er = 92:8, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation) [Daicel Chiralpak OJ-H, n -hexane/*i*-propanol = 95:5, 0.5 mL/min, $\lambda = 220$ nm, retention time: 8.79 min (minor) and 9.20 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.61(m, 2H), 7.47(s, 1H), 7.38-7.37(m, 2H), 7.31-7.27(m, 2H), 3.15 (sext, $J = 7.2$ Hz, 1H), 1.36 (d, $J = 7.0$ Hz, 3H), 1.26-1.23(m, 2H), 1.19 (s, 6H), 1.18 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.92, 148.52, 140.42, 139.65, 128.78, 128.45, 126.07, 125.66, 124.53, 121.16, 83.05, 35.93, 24.93, 24.74, 24.68. ^{19}F NMR (376 MHz, CDCl_3) δ -57.79. Optical Rotation: $[\alpha]_D^{22}$ -18.23 ($c = 0.17$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{22}\text{H}_{26}\text{BF}_3\text{O}_3$,

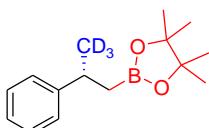
[M+Na]: 429.1819; found: 429.1817.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((*R*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (2x)



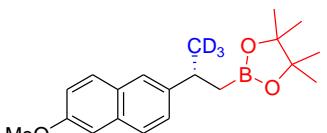
white solid (80.2 mg, 95% yield), m.p. = 116 °C. dr = 97.5:2.5, (Measured by chiral HPLC analysis with the corresponding alcohol obtained after oxidation) [Daicel Chiraldpak OJ-H, *n*-hexane/*i*-propanol = 90:10, 0.5 mL/min, λ = 220 nm, retention time: 31.20 min (minor) and 33.25 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.22(d, J = 8.0 Hz, 1H), 7.06(d, J = 8.0 Hz, 1H), 7.00 (s, 1H), 3.01 (sext, J = 7.2 Hz, 1H), 2.91-2.89 (m, 2H), 2.56-2.41 (m, 2H), 2.32-2.27 (m, 1H), 2.16-1.96 (m, 4H), 1.70-1.42 (m, 6H), 1.29 (d, J = 7.2 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 1.16-1.13 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.87, 136.96, 136.05, 127.13, 125.21, 124.12, 123.95, 83.01, 50.53, 48.05, 44.35, 38.28, 35.90, 35.16, 31.63, 29.52, 26.65, 25.75, 24.68, 24.71, 24.45, 24.43, 21.61, 13.88. Optical Rotation: $[\alpha]_D^{22} +71.00$ (c = 0.20, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{27}\text{H}_{39}\text{BO}_3$, [M+H]: 423.3065; found: 423.3073.

(*R*)-4,4,5,5-tetramethyl-2-(1,1,1-d₃-2-phenylpropyl)-1,3,2-dioxaborolane (2a-D)



colorless oil (47.3 mg, 95% yield). er = 95:5, [Daicel Chiraldpak OD-H, *n*-hexane/*i*-propanol = 500:1, 0.4 mL/min, λ = 220 nm, retention time: 12.76 min (major) and 14.41 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.27 (m, 4H), 7.21–7.16 (m, 1H), 3.07 (t, J = 8.0 Hz, 1H), 1.22-1.18 (m, 14H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.22, 128.20, 126.66, 125.70, 82.97, 35.62, 24.81, 24.73. Optical Rotation: $[\alpha]_D^{22} -17.55$ (c = 0.49, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{15}\text{H}_{20}\text{D}_3\text{BO}_2$, [M+Na]: 272.1877; found: 272.1873.

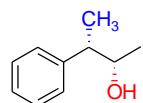
(*R*)-1,1,1-d₃-2-(2-(6-methoxynaphthalen-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (2y-D)



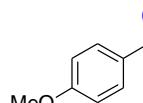
white solid (59.1 mg, 90% yield), m.p. = 58 °C. er = 93.5:6.5,

[Daicel Chiralpak AD-H, *n*-hexane/*i*-propanol = 98: 2, 1.0 mL/min, λ = 254 nm, retention time: 41.26 min (minor) and 45.72 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.73–7.70 (m, 2H), 7.65 (s, 1H), 7.45–7.42 (m, 1H), 7.18–7.14 (m, 2H), 3.93 (s, 1H), 3.23 (*t*, J = 8.0 Hz, 1H), 1.33–1.26 (m, 2H), 1.19 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.11, 144.46, 133.13, 129.13, 129.11, 126.73, 126.38, 124.37, 118.51, 83.02, 55.22, 35.53, 24.82, 24.78. Optical Rotation: $[\alpha]_D^{22}$ -34.75 (c = 0.40, CHCl_3). HRMS-ESI (*m/z*): Calcd for $\text{C}_{20}\text{H}_{24}\text{D}_3\text{BO}_3$, [M+H]: 330.2320; found: 330.2319.

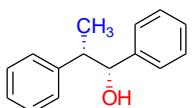
(2*S*,3*S*)-3-phenylbutan-2-ol (4a)

 colorless oil (21.1 mg, 70% yield). dr >99:1, er = 95:5, [Daicel ChiralpakAD-H, *n*-hexane/*i*-propanol = 98:2, 1.0 mL/min, λ = 220 nm, retention time: 12.04 min (minor) and 14.08 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.36–7.33(m, 2H), 7.27–7.23(m, 2H), 3.94–3.87(m, 1H), 2.80–2.73(m, 1H), 1.65(br, 1H), 1.37 (*d*, J = 7.2 Hz, 3H), 1.12 (*d*, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.31, 128.45, 127.88, 126.46, 72.38, 47.21, 21.08, 16.08. The spectral data of the product were identical with the reported in the literature⁴.Optical Rotation: $[\alpha]_D^{22}$ -0.85 (c = 1.05, EtOH), [Lit., -0.1 (c = 0.9 in EtOH), (2*S*,3*S*)-isomer]⁴, confirmed as a (2*S*,3*S*)-isomer. HRMS-ESI (*m/z*): Calcd for $\text{C}_{10}\text{H}_{14}\text{O}$, [M+H]: 151.1117; found: 151.1121.

(2*S*,3*S*)-3-(4-methoxyphenyl)butan-2-ol (4b)

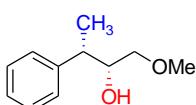
 white solid (24.5 mg, 68% yield), m.p. = 78 °C. dr >99:1, er = 93.5:6.5, [Daicel Chiralpak OC-H, *n*-hexane/*i*-propanol = 90:10, 0.5 mL/min, λ = 220 nm, retention time: 14.08 min (minor) and 14.90 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.17–7.13 (m, 2H), 6.90–6.86 (m, 2H), 3.89–3.84 (m, 1H), 3.82 (s, 3.82), 2.76–2.69 (m, 1H), 1.55 (br, 1H), 1.32 (*d*, J = 7.0 Hz, 3H), 1.10 (*d*, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.16, 136.23, 128.75, 113.80, 72.46, 55.25, 46.22, 20.91, 16.14.Optical Rotation: $[\alpha]_D^{22}$ +2.71 (c = 0.185, CHCl_3). HRMS-ESI (*m/z*): Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$, [M+H]: 181.1223; found: 181.1228.

(1*R*,2*S*)-1,2-diphenylpropan-1-ol (4c)



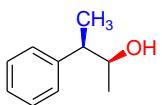
white solid (23.7 mg, 56% yield), m.p. = 57 °C. dr >99:1, er = 99:1, [Daicel Chiraldak OD-H, *n*-hexane/*i*-propanol = 90:10, 0.5 mL/min, λ = 220 nm, retention time: 14.79 min (minor) and 15.96 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.17 (m, 10H), 4.85 (dd, J = 2.8 Hz, 2.8 Hz, 1H), 3.17-3.11 (m, 1H), 1.89 (br, 1H), 1.34 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.58, 142.91, 128.28, 128.14, 128.02, 127.26, 126.50, 126.35, 78.75, 47.24, 14.98. Optical Rotation: $[\alpha]_D^{22}+45.16$ (c = 0.155, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{15}\text{H}_{16}\text{O}$, [M+H]: 213.1273; found: 213.1275.

(2*R*,3*S*)-1-methoxy-3-phenylbutan-2-ol (4d)



colorless oil (28.8 mg, 80% yield). dr >99:1, er = 92:8, [Daicel Chiraldak OD-H, *n*-hexane/*i*-propanol = 90:10, 0.5 mL/min, λ = 220 nm, retention time: 9.69 min (minor) and 10.37 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.31(m, 2H), 7.26-7.22(m, 3H), 3.88-3.82(m, 1H), 3.31 (s, 3H), 3.25-3.22(m, 1H), 3.16-3.12(m, 1H), 2.87-2.80(m, 1H), 2.72(br, 1H), 1.41 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.04, 128.53, 127.62, 126.54, 75.26, 74.76, 58.92, 43.06, 17.73. Optical Rotation: $[\alpha]_D^{22}+14.8$ (c = 0.25, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$, [M+H]: 181.1223; found: 181.1225.

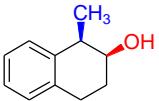
(2*S*,3*R*)-3-phenylbutan-2-ol (4e)



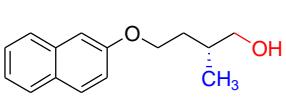
colorless oil (8.4 mg, 28% yield). dr >99:1, er = 99:1, [Daicel Chiraldak OJ-H, *n*-hexane/*i*-propanol = 95:5, 0.5 mL/min, λ = 220 nm, retention time: 23.46 min (major) and 26.86 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.34(m, 2H), 7.28-7.22(m, 3H), 3.91-3.84(m, 1H), 2.74-2.66(m, 1H), 1.29 (d, J = 7.0 Hz, 3H), 1.25 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.58, 128.66, 128.06, 126.46, 72.38, 47.21, 21.08, 16.08. The spectral data of the product were identical with the reported in the literature⁴. Optical Rotation: $[\alpha]_D^{22}+11.86$ (c = 1.5, EtOH), [Lit., +19.55 (c = 1.4 in EtOH), (2*S*,3*R*)-isomer]⁴, confirmed as a

(2S,3R)-isomer.HRMS-ESI (*m/z*): Calcd for C₁₀H₁₄O, [M+H]: 151.1117; found: 151.1118.

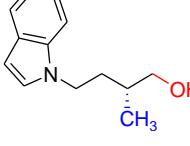
(1*R*,2*S*)-1-methyl-1,2,3,4-tetrahydronaphthalen-2-ol (4f)

 white solid (22.7 mg, 70% yield), m.p. = 89° C. dr >99:1, er = 98:2, [Daicel Chiralpak OD-H, *n*-hexane/*i*-propanol = 95:5, 1.0 mL/min, λ = 220 nm, retention time: 8.51 min (minor) and 9.18 min (major)]; ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.13 (m, 4H), 4.19-4.14 (m, 1H), 3.11-2.98 (m, 2H), 2.93-2.85 (m, 1H), 2.06-1.91 (m, 3H), 1.35 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.36, 135.21, 128.85, 128.65, 126.04, 126.01, 70.21, 38.54, 27.31, 27.20, 16.62. Optical Rotation: [α]_D²²-53.78 (c = 0.225, CHCl₃). HRMS-ESI (*m/z*): Calcd for C₁₁H₁₄O, [M+H]: 163.1117; found: 163.1118.

(*R*)-2-methyl-4-(naphthalen-2-yloxy)butan-1-ol (4g)

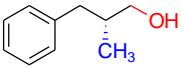
 white solid (35.9 mg, 78% yield), m.p. = 45 °C. er = 92:8, [Daicel Chiralpak OJ-H, *n*-hexane/*i*-propanol = 90:10, 1.0 mL/min, λ = 254 nm, retention time: 30.05 min (major) and 36.93 min (minor)]; ¹H NMR (400 MHz, CDCl₃) δ 7.81-7.74 (m, 3H), 7.49-7.35 (m, 2H), 7.18-7.16 (m, 2H), 4.25-4.14 (m, 2H), 3.61 (d, *J* = 5.4 Hz, 2H), 2.06-1.96 (m, 2H), 1.85 (br, 1H), 1.79-1.75 (m, 1H), 1.06 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.78, 134.58, 129.43, 129.00, 127.67, 126.74, 126.39, 123.63, 118.88, 106.71, 68.02, 66.17, 33.36, 32.81, 16.86. Optical Rotation: [α]_D²²-3.57 (c = 0.28, CHCl₃). HRMS-ESI (*m/z*): Calcd for C₁₅H₁₈O₂, [M+H]: 231.1385; found: 231.1387.

(*R*)-4-(1H-indol-1-yl)-2-methylbutan-1-ol (4h)

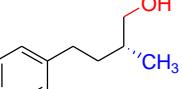
 yellow oil (30.5 mg, 75% yield). er = 90:10, [Daicel Chiralpak OJ-H, *n*-hexane/*i*-propanol = 95:5, 1.0 mL/min, λ = 254 nm, retention time: 43.08 min (minor) and 44.02 min (major)]; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.31-7.27 (m, 1H), 7.21-7.16 (m, 2H), 6.57 (d, *J* = 3.0 Hz, 1H), 4.21-4.20 (m, 2H), 3.47-3.45 (m, 2H),

2.08-2.02 (m, 1H), 1.81 (br, 1H), 1.68-1.65 (m, 2H), 1.04 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.95, 128.64, 127.72, 121.48, 121.07, 119.32, 109.44, 101.12, 67.85, 44.31, 33.69, 33.37, 16.52. Optical Rotation: $[\alpha]_D^{22} +11.33$ ($c = 0.30$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$, [M+H]: 204.1382; found: 204.1385.

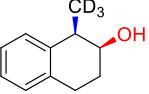
(R)-2-methyl-3-phenylpropan-1-ol (4i)

 colorless oil (21.1 mg, 70% yield). er = 88:12, [Daicel Chiralpak OJ-H, *n*-hexane/*i*-propanol = 98:2, 1.0 mL/min, $\lambda = 220$ nm, retention time: 14.51 min (major) and 15.69 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.29 (m, 2H), 7.24-7.19 (m, 2H), 3.57 (dd, $J = 10.5, 5.8$ Hz, 1H), 3.51 (dd, $J = 10.5, 5.8$ Hz, 1H), 2.79 (dd, $J = 13.4, 6.3$ Hz, 1H), 2.46 (dd, $J = 13.4, 6.3$ Hz, 1H), 2.02-1.94 (m, 1H), 1.44 (br, 1H), 0.95 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.64, 129.17, 128.29, 125.91, 67.68, 39.72, 37.82, 16.49. Optical Rotation: $[\alpha]_D^{22} +2.22$ ($c = 0.36$, CHCl_3), [Lit., -3.0 ($c = 0.67$ in CHCl_3), (*S*)-isomer]⁵, confirmed as a (*R*)-isomer. HRMS-ESI (m/z): Calcd for $\text{C}_{10}\text{H}_{14}\text{O}$, [M+H]: 151.1117; found: 151.1123.

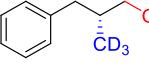
(R)-2-methyl-4-phenylbutan-1-ol (4j)

 colorless oil (22.3 mg, 68% yield). er = 89:11, [Daicel Chiralpak AS-H, *n*-hexane/*i*-propanol = 95:5, 0.5 mL/min, $\lambda = 220$ nm, retention time: 12.80 min (minor) and 13.47 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.32 (m, 2H), 7.26-7.22 (m, 3H), 3.56 (dd, $J = 11.2, 6.0$ Hz, 1H), 3.49 (dd, $J = 11.2, 6.0$ Hz, 1H), 2.80-2.73 (m, 1H), 2.69-2.61 (m, 1H), 2.18 (br, 1H), 1.86-1.77 (m, 1H), 1.71 (sext, $J = 6.0$ Hz, 1H), 1.53-1.44 (m, 1H), 1.04 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.70, 128.42, 128.39, 125.77, 67.07, 35.37, 35.06, 33.35, 16.58. Optical Rotation: $[\alpha]_D^{22} +9.09$ ($c = 0.55$, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$, [M+H]: 165.1273; found: 165.1280.

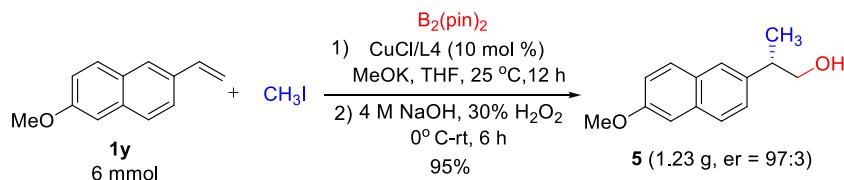
(1*R*,2*S*)-1-d₃-methyl-1,2,3,4-tetrahydronaphthalen-2-ol (4f-D)


 white solid(25.2 mg, 76% yield), m.p. = 90 °C. dr >99:1, er = 98:2, [Daicel Chiraldpak OD-H, *n*-hexane/*i*-propanol = 95:5, 1.0 mL/min, λ = 220 nm, retention time: 9.08 min (minor) and 9.75 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.12 (m, 4H), 4.19-4.14 (m, 1H), 3.06-2.97 (m, 2H), 2.92-2.86 (m, 1H), 2.04-1.94 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.27, 135.19, 128.78, 128.62, 126.01, 125.99, 70.22, 38.30, 27.38, 27.12. Optical Rotation: $[\alpha]_D^{22}$ -53.48 (c = 0.215, CHCl_3). HRMS-ESI (*m/z*): Calcd for $\text{C}_{11}\text{H}_{11}\text{D}_3\text{O}$, [M+H]: 166.1308; found: 166.1306.

(*R*)-2-d3-methyl-3-phenylpropan-1-ol (4i-D)

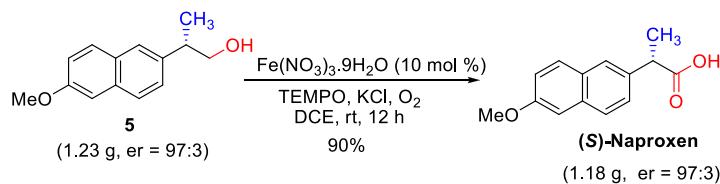

 colorless oil (21.5 mg, 70% yield). er = 87:13, [Daicel Chiraldpak OJ-H, *n*-hexane/*i*-propanol = 98:2, 1.0 mL/min, λ = 220 nm, retention time: 17.20 min (major) and 18.77 min (minor)]; ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.29 (m, 2H), 7.24-7.20 (m, 3H), 3.56 (dd, J = 10.5, 5.8 Hz, 1H), 3.50 (dd, J = 10.5, 5.8 Hz, 1H), 2.79 (dd, J = 13.4, 6.3 Hz, 1H), 2.46 (dd, J = 13.4, 6.3 Hz, 1H), 2.00-1.93 (m, 1H), 1.59 (br, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.67, 129.16, 128.28, 125.89, 67.64, 39.66, 37.58. Optical Rotation: $[\alpha]_D^{22}$ +1.95 (c = 0.41, CHCl_3). HRMS-ESI (*m/z*): Calcd for $\text{C}_{10}\text{H}_{11}\text{D}_3\text{O}$, [M+H]: 154.1308; found: 154.1309.

6. Synthesis of (*S*)-Naproxen



Preparation of (*S*)-2-(6-methoxynaphthalen-2-yl)propan-1-ol (5). In the glovebox, to a 100 mL Schlenk flask with magnetic stir bar was added CuCl (10 mol %, 57 mg, 0.6 mmol), **L4** (12 mol %, 306 mg, 0.72 mmol) and 25 mL THF. The mixture was stirred 60 minutes at room temperature. To the mixture was added $\text{B}_2(\text{pin})_2$ (2.29 g, 9 mmol), 2-Methoxy-6-vinyl-naphthalene **1y** (1.1 g, 6 mmol), CH_3I (1.27 g, 9 mmol), and MeOK (9 mmol, 0.63 g) successively (Note: MeOK was added

slowly to prevent the vigorously exothermic reaction), finally diluted by 15 mL THF. The flask was sealed with rubber stopper, removed from the glovebox and stirred at room temperature for 24 hours. The reaction mixture was filtrated through a celite pad and the solvent was removed under vacuo. The residue was dissolved in THF (30 mL) at 0 °C, then 4 M of aqueous NaOH (18 mL) and 30% H₂O₂ (6 mL) was added slowly. After addition, the reaction mixture was stirred for 6 hours at room temperature. After the reaction was completed, sat. Na₂S₂O₃ solution (15 ml) was added to quench the reaction. The mixture was extracted with EtOAc (3×60 mL) and the combined organic phase was dried over Na₂SO₄. After evaporating solvent under vacuo, the residue was purified by column chromatography on silica gel with EtOAc:Petroleum ether (1:3) to obtain the product **5** as a white solid (1.23 g, 95% yield), m.p. = 87 °C. er = 97:3, [Daicel Chiraldak AD-H, *n*-hexane/*i*-propanol = 98:2, 1.0 mL/min, λ = 254 nm, retention time: 39.91 min (minor) and 44.21 min (major)]; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 5.8 Hz, 1H), 7.73 (d, *J* = 6.2 Hz, 1H), 7.63 (s, 1H), 7.74 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.19-7.13 (m, 2H), 3.95 (s, 3H), 3.79 (d, *J* = 4.6 Hz, 2H), 3.15-3.06 (m, 1H), 1.52 (br, 1H), 1.38 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.45, 138.71, 133.56, 129.13, 129.06, 127.23, 126.31, 125.92, 118.93, 105.62, 68.64, 54.33, 42.38, 17.67. Optical Rotation: [α]_D²²-8.23 (*c* = 0.255, CHCl₃). HRMS-ESI (*m/z*): Calcd for C₁₄H₁₆O₂, [M+H]: 217.1223; found: 217.1231.

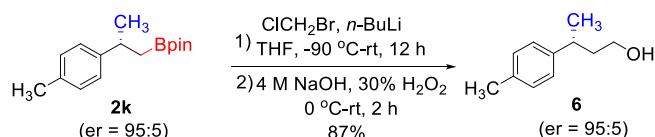


Preparation of (*S*)-2-(6-Methoxy-naphthalen-2-yl)-propionic acid

(S)-Naproxen. To a 50mL Schlenk flask were added $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.23 g, 0.57 mmol), DCE (17 mL), TEMPO (89 mg, 0.57 mmol), KCl (42.5 mg, 0.57 mmol), and **5** (1.23 g, 5.7 mmol) sequentially. After evacuated and filled in the pure O_2 for three times with a balloon, the reaction was stirred at 25 °C for 24 h. The crude reaction mixture was filtrated through a celite, the combined organic phase was evaporated

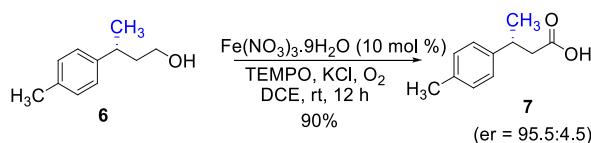
under vacuo and the residue was purified by column chromatography on silica gel with EtOAc:Petroleum ether (1:1.5) to obtain the product (*S*)-**Naproxen** as a white solid (1.18 g, 90% yield), m.p. = 142 °C. er = 97/3, [Daicel Chiraldak AD-H, *n*-hexane/*i*-propanol = 95:5, 0.5 mL/min, λ = 220 nm, retention time: 54.08 min (minor) and 57.43 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.71 (m, 3H), 7.42 (dd, J = 8.4, 1.6 Hz, 1H), 7.16 – 7.13 (m, 2H), 3.94 (s, 3H), 3.90 (q, J = 7.2 Hz, 1H), 1.62 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 180.87, 157.72, 134.88, 133.84, 129.33, 128.91, 127.26, 126.22, 126.18, 119.07, 105.59, 55.33, 45.30, 18.15. Optical Rotation: $[\alpha]_D^{22} +59.02$ (c = 0.205, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3$, [M+H]: 231.1015; found: 231.1013.

7. Formal Synthesis of (*R*)-*ar*-Turmerone and 8-Deoxyanisatin

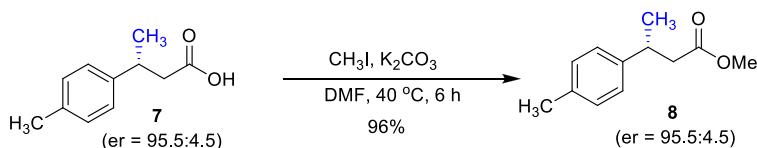


Preparation of (*R*)-3-*p*-tolylbutan-1-ol (6). To the dried Schlenk tube with magnetic stir bar was added **2k** (130 mg, 0.5 mmol, er = 95:5). After evacuated and filled in Ar for three times, ClCH_2Br (193.5 mg, 1.5 mmol) and dried THF (1.5 mL) were added. The solution was cooled to -90 °C and added BuLi (0.6 mL, 2.5 M) very slowly. The reaction was warmed to room temperature and stirred for overnight. Quenched by saturated aq. NH_4Cl , the mixture was extracted with EtOAc (3x15 mL). The organic phase was combined and washed with saturated aq. NaCl and dried over Na_2SO_4 . After the removal of solvent, the residue was dissolved in 5 mL THF and cooled to 0 °C. The aq. NaOH (5 mL, 4 M) was added and the aq. H_2O_2 (2 mL, 30% w) was added dropwise. The mixture was stirred at room temperature for 2 hours and quenched by saturated aq. $\text{Na}_2\text{S}_2\text{O}_3$ at 0 °C. Then the mixture was extracted with EtOAc(3x15 mL), the organic phase was combined and dried over Na_2SO_4 . After the removal of solvent, the residue was purified by flash column chromatography with

Petroether:Acetate(4:1) as the eluent to get **6** as a colorless oil (71.3 mg, 87% yield). er = 95:5, [Daicel Chiralpak OJ-H, *n*-hexane/*i*-propanol = 98:2, 1.0 mL/min, λ = 254 nm, the environment temperature of chiral column is 40 °C, retention time: 19.22 min (minor) and 20.28 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.19-7.13 (m, 4H), 3.63-3.53 (m, 2H), 2.89 (sext, J = 7.2 Hz, 1H), 2.38 (s, 3H), 1.90-1.85 (m, 2H), 1.78 (br, 1H), 1.31 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.87, 135.58, 129.21, 126.86, 67.21, 41.03, 36.07, 22.58, 21.04. Optical Rotation: $[\alpha]_D^{22}$ -24.09 (c = 0.22, CHCl_3). HRMS-ESI (*m/z*): Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$, [M+H]: 165.1273; found: 165.1278.



Preparation of (*R*)-3-p-tolylbutanoic acid (7). To a tube with magnetic stir bar was added **6** (71.3 mg, 0.435 mmol), Fe(NO₃)₃·9H₂O (17.6 mg, 0.0435 mmol), DCE (1.5 mL), TEMPO (6.8 mg, 0.0435 mmol), KCl (3.2 mg, 0.0435 mmol) sequentially. After evacuated and filled in the pure O₂ with a balloon for three times, the reaction was stirred at 25 °C for 12 h. The crude reaction mixture was filtrated through a celite, the combined organic phase was evaporated under vacuo and purified by column chromatography on silica gel with EtOAc:Petroleum ether (1:2) to obtain the product (**R**)-3-p-tolylbutanoic acid (**7**) as a white solid (69.6 mg, 90% yield), m.p. = 128 °C. er = 95.5:4.5, [Daicel Chiraldak AD-H, *n*-hexane/*i*-propanol = 95:5, 0.2 mL/min, λ = 220 nm, retention time: 36.03 min (minor) and 40.28 min (major)]; ¹H NMR (400 MHz, CDCl₃) δ 7.16 (s, 4H), 3.29 (sext, *J* = 7.2 Hz, 1H), 2.70 (dd, *J* = 15.4 Hz, 6.8 Hz, 1H), 2.61 (dd, *J* = 15.4 Hz, 6.8 Hz, 1H), 2.37 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 179.00, 142.48, 136.04, 129.28, 126.61, 42.74, 35.77, 21.99, 21.04. Optical Rotation: [α]_D²²-44.0 (c = 0.15, CHCl₃). HRMS-ESI (*m/z*): Calcd for C₁₁H₁₄O₂, [M+H]: 179.1066; found: 179.1069.



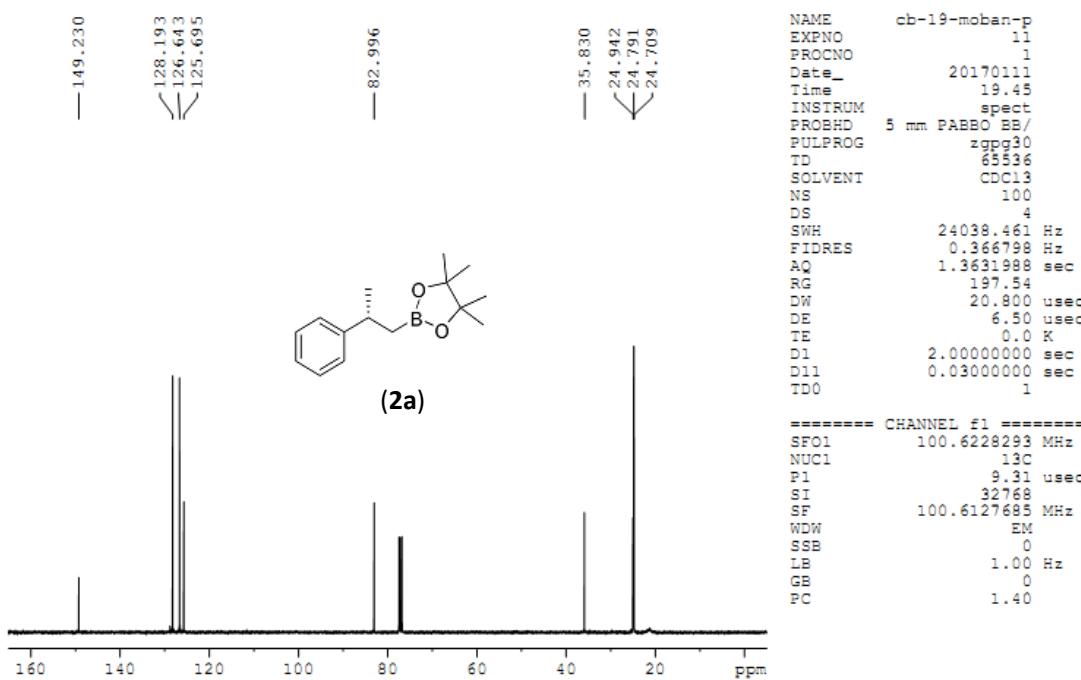
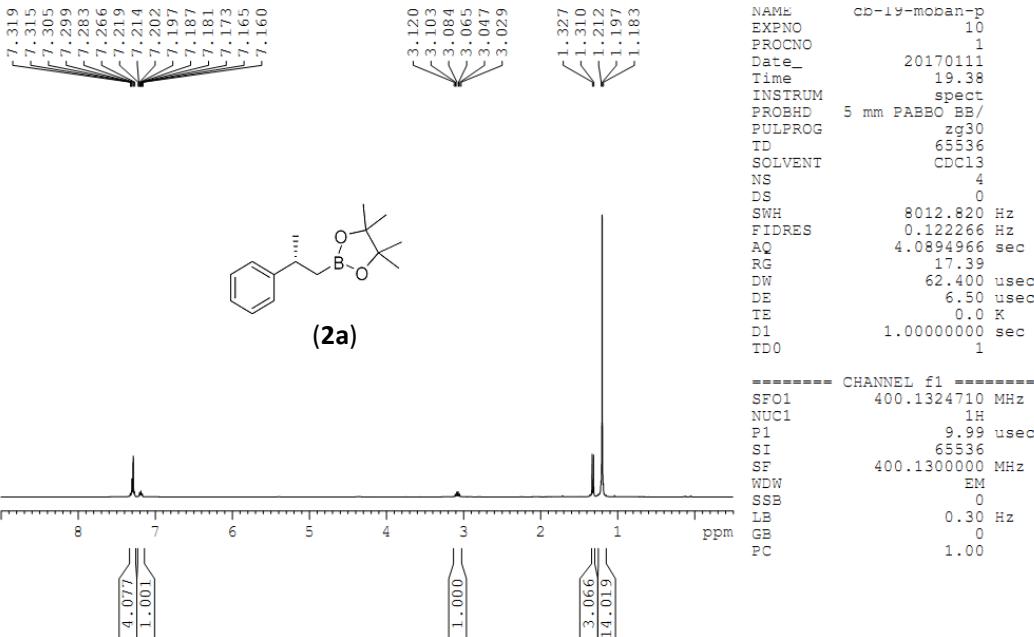
Preparation of (*R*)-methyl 3-p-tolylbutanoate (8). To a tube with magnetic stir bar was added **7** (0.2 mmol, 35.6 mg) and K_2CO_3 (0.4 mmol, 55.2 mg). After evacuated and filled in Ar for three times, DMF (1 mL) and CH_3I (0.4 mmol, 56.4 mg) were added and the mixture was stirred at 40 °C for 6 h. The reaction was quenched by addition of 3 mL H_2O and extracted with EtOAc(3x5 mL). The organic phase was combined and dried over Na_2SO_4 . After the removal of solvent, the residue was purified by flash column chromatography with petroether:Acetate(10:1) as the eluent to get colorless oil **8** (36.8 mg, 90% yield), er = 95.5:4.5, [Daicel Chiralpak AD-H, *n*-hexane/*i*-propanol = 500:1, 0.5 mL/min, λ = 254 nm, retention time: 19.21 min (minor) and 20.28 min (major)]; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (s, 4H), 3.66 (s, 3H), 3.28 (m, 1H), 2.64 (dd, J = 15.1 Hz, 6.9 Hz, 1H), 2.56 (dd, J = 15.1 Hz, 6.9 Hz, 1H), 2.35 (s, 3H), 1.32 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.94, 142.73, 135.89, 129.21, 126.58, 51.48, 42.84, 36.04, 21.88, 21.00. Optical Rotation: $[\alpha]_D^{22}$ -31.05 (c = 0.95, CHCl_3). HRMS-ESI (m/z): Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$, $[\text{M}+\text{Na}]$: 215.1048; found: 215.1052.

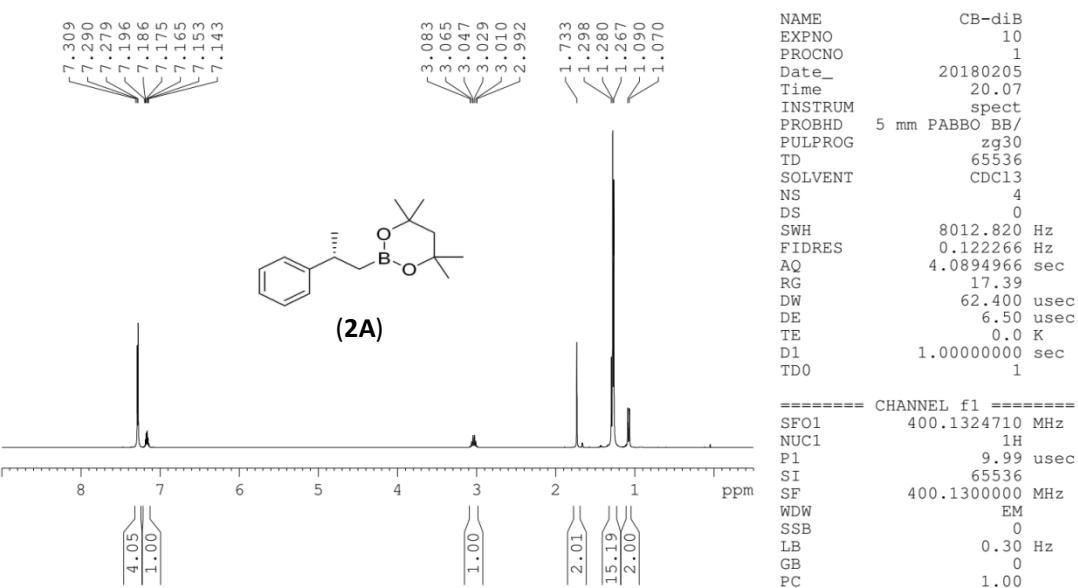
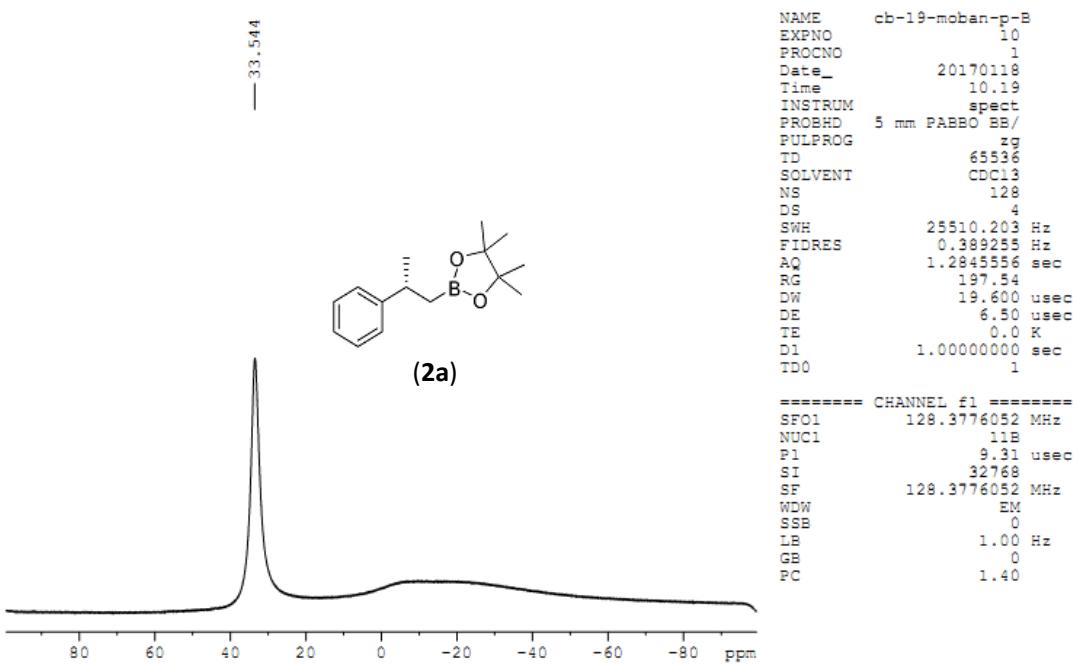
8. References

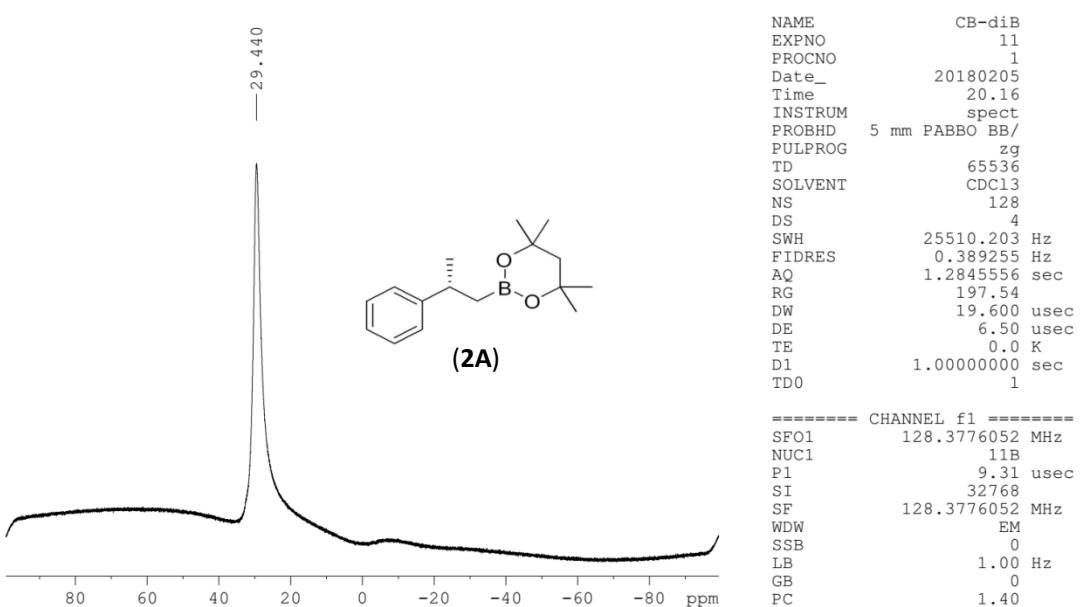
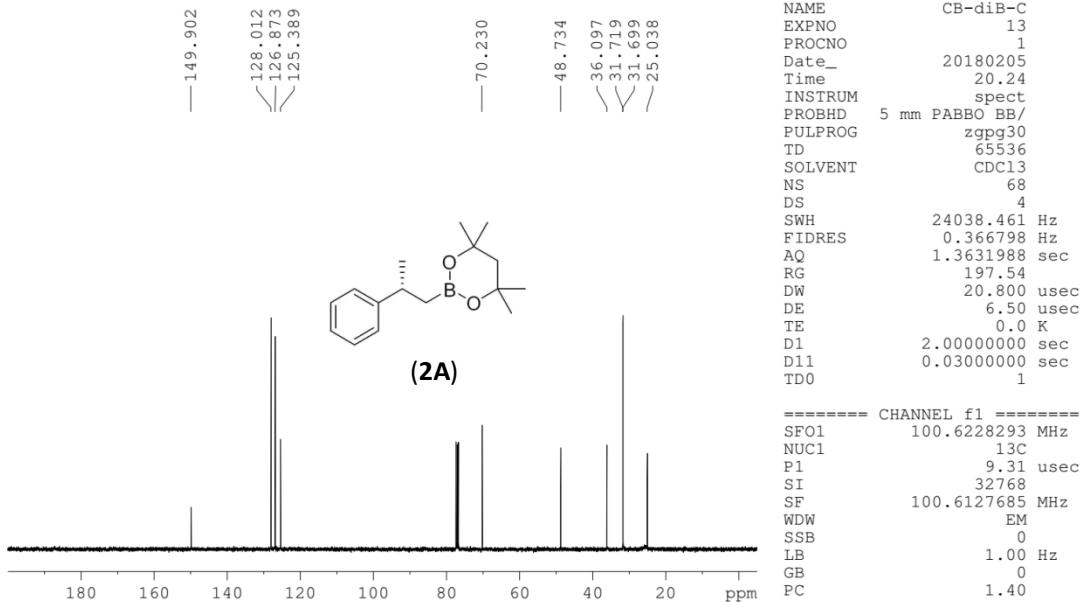
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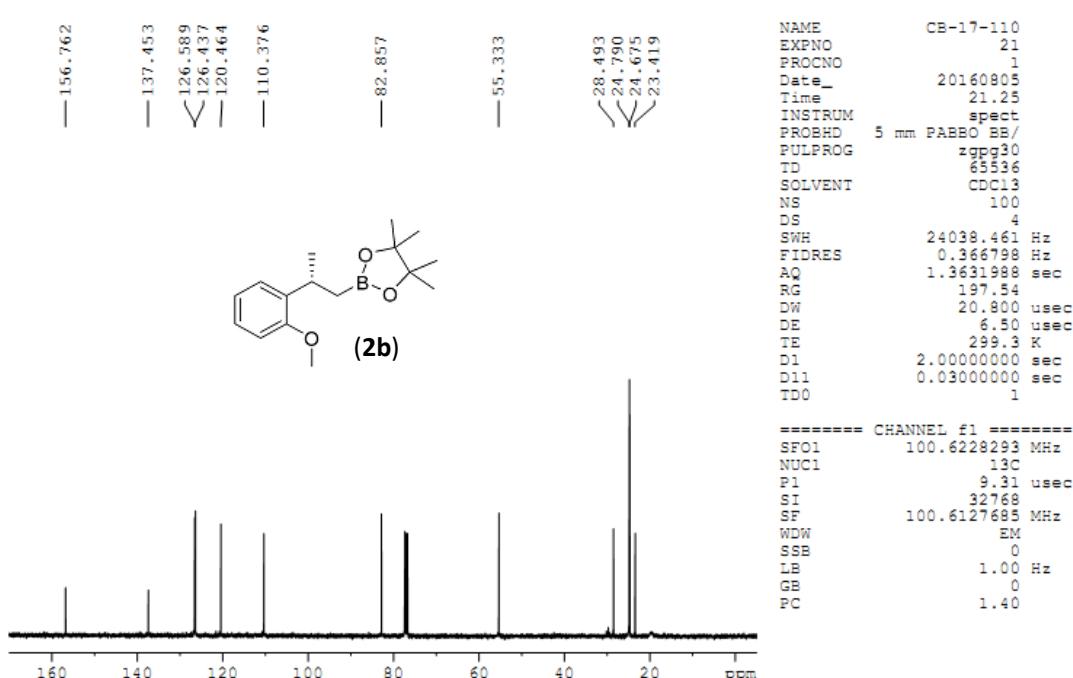
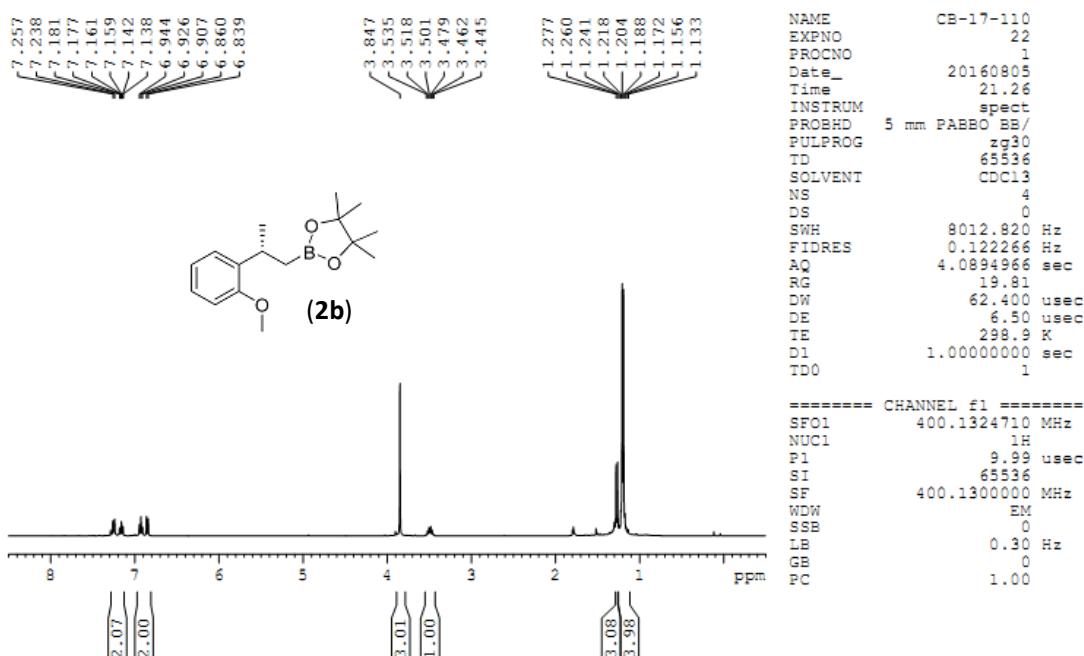
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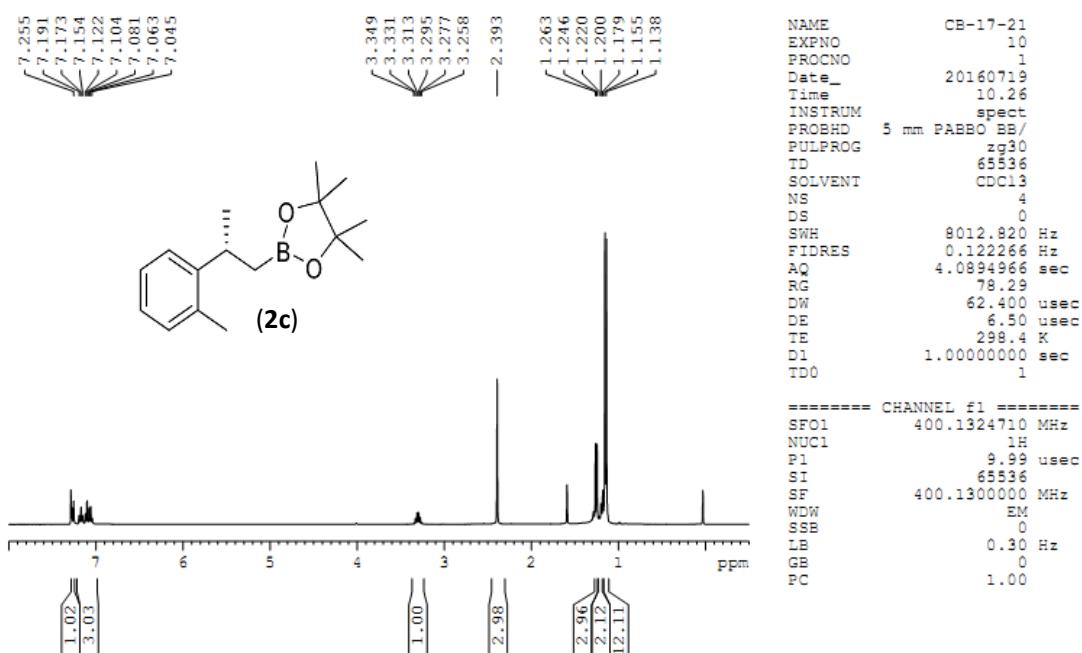
NMR

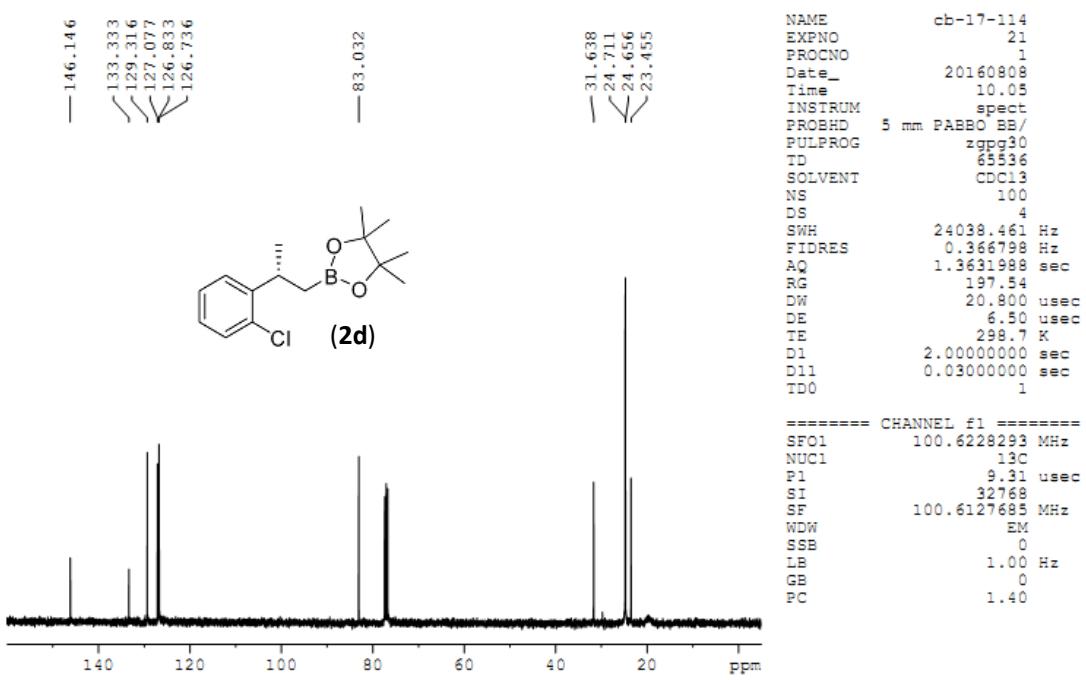
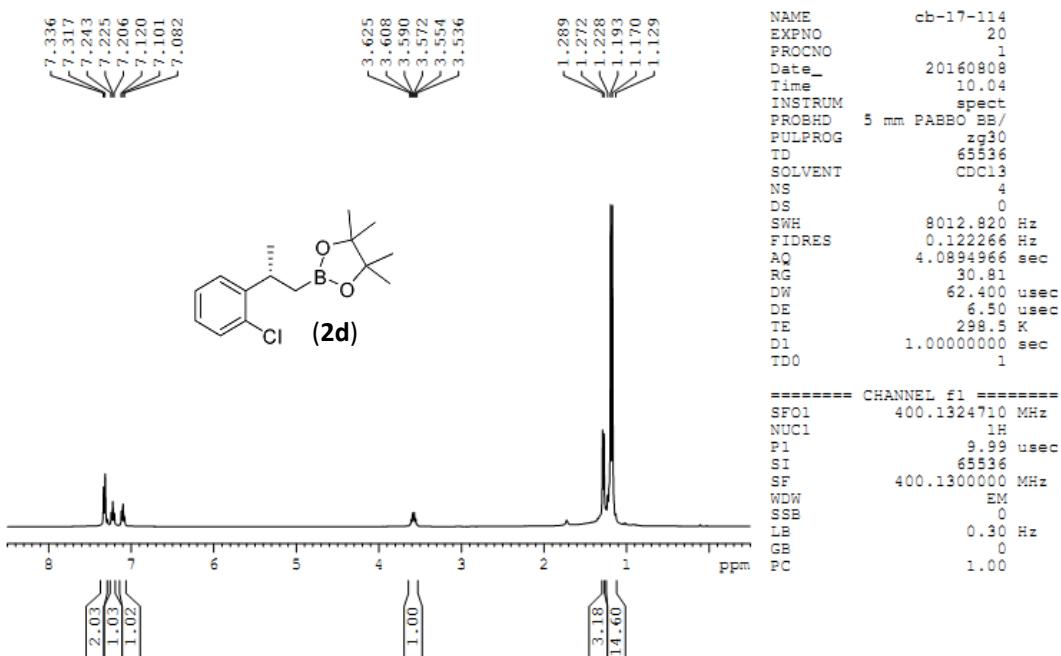


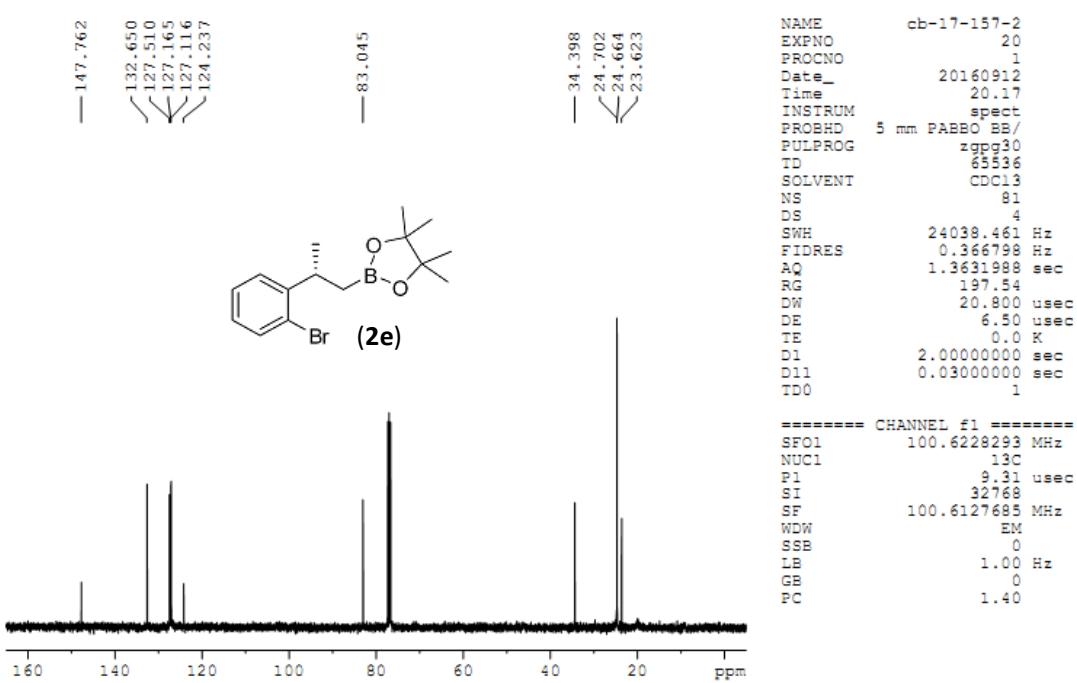
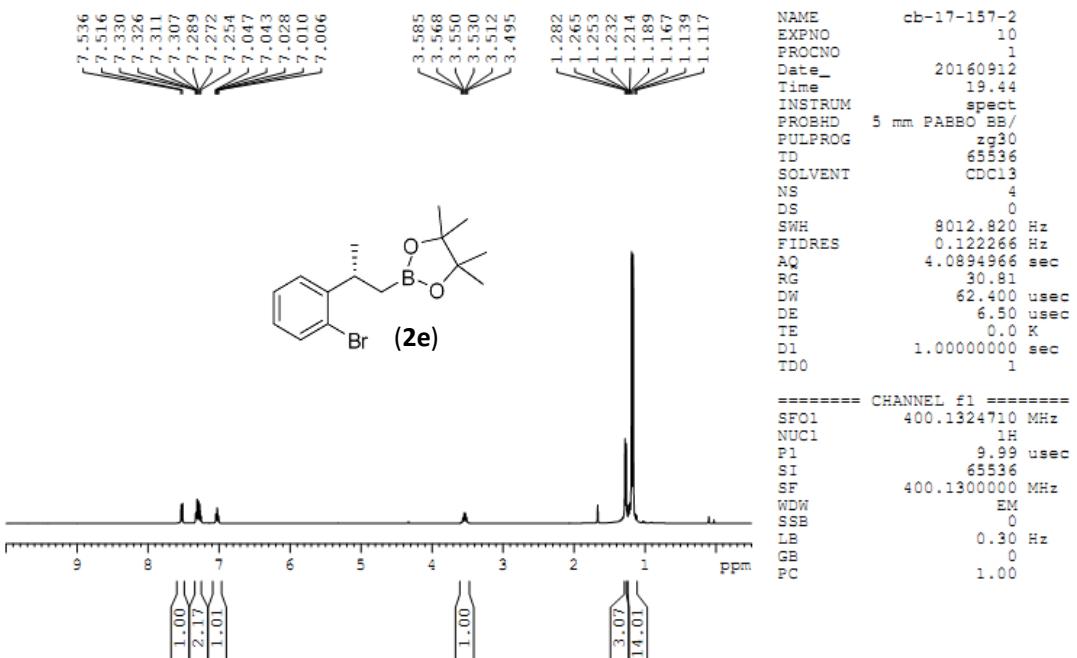


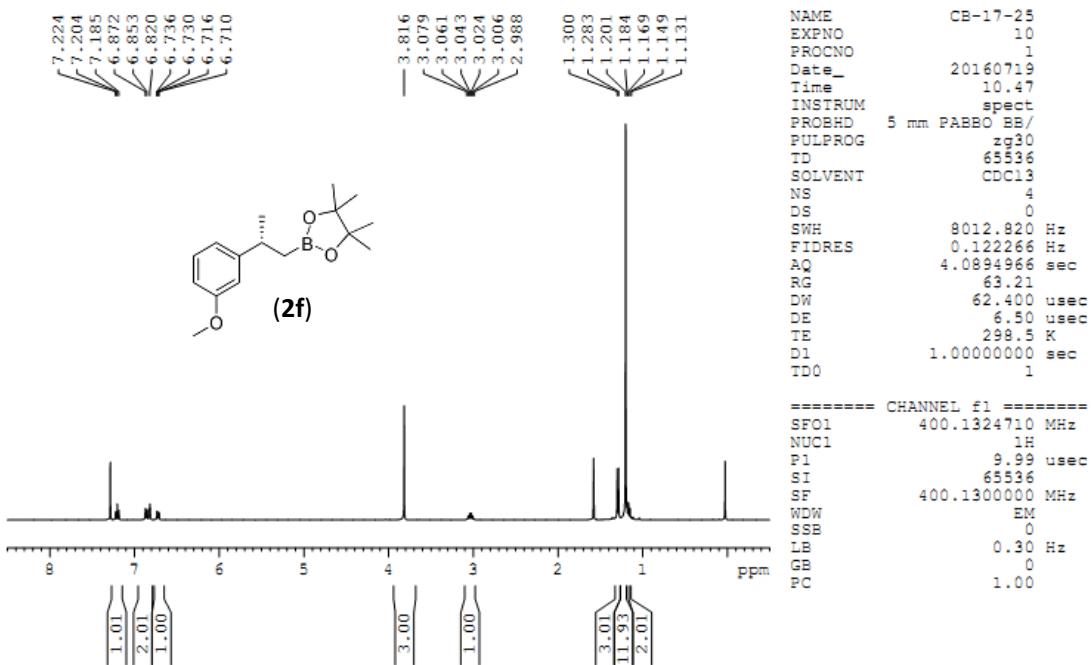


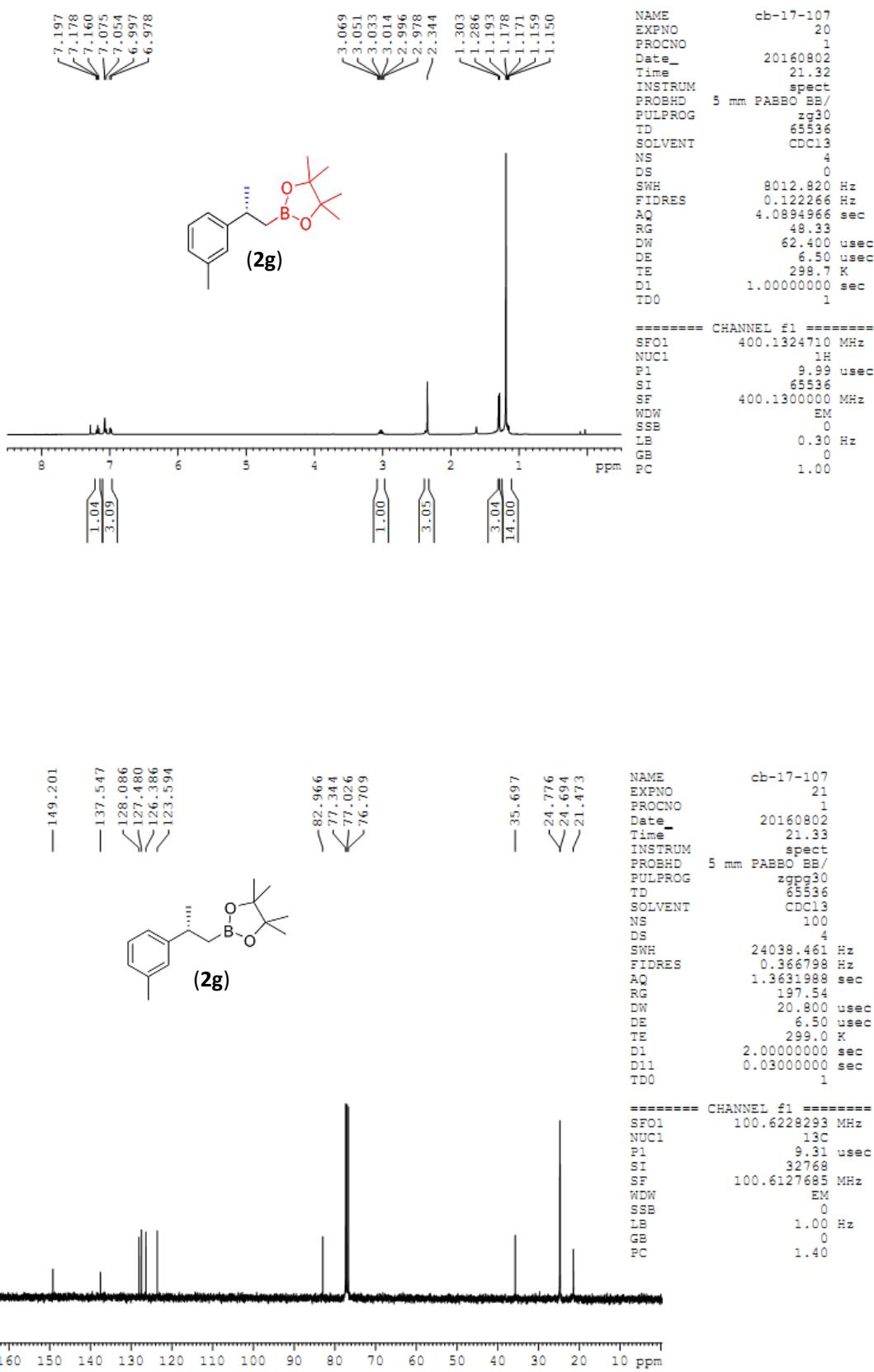


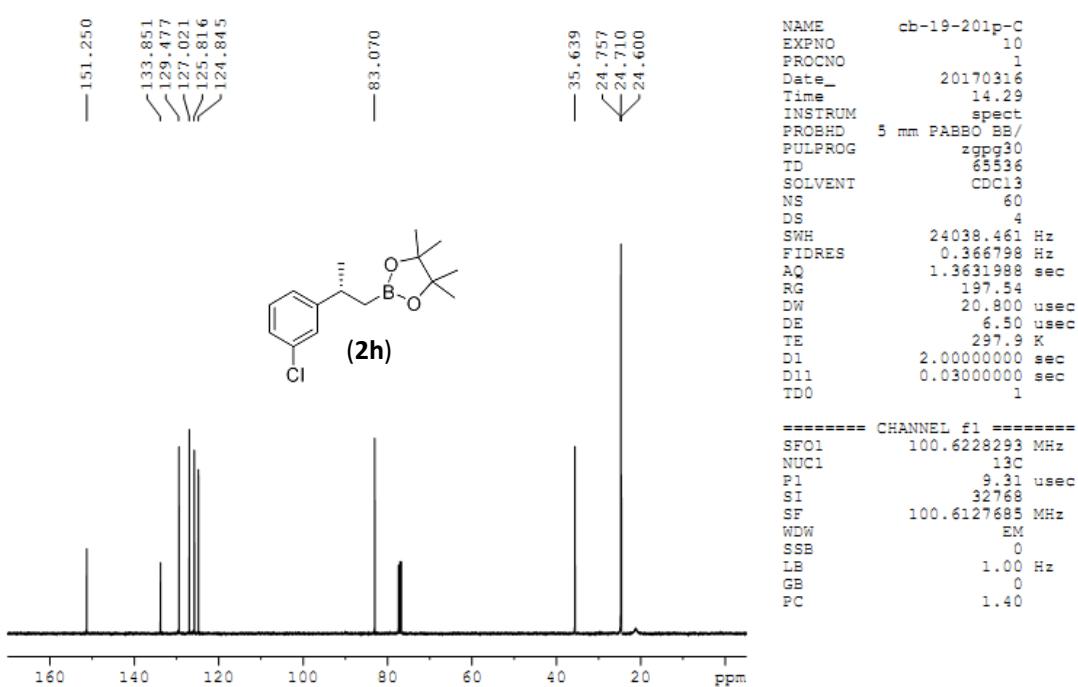
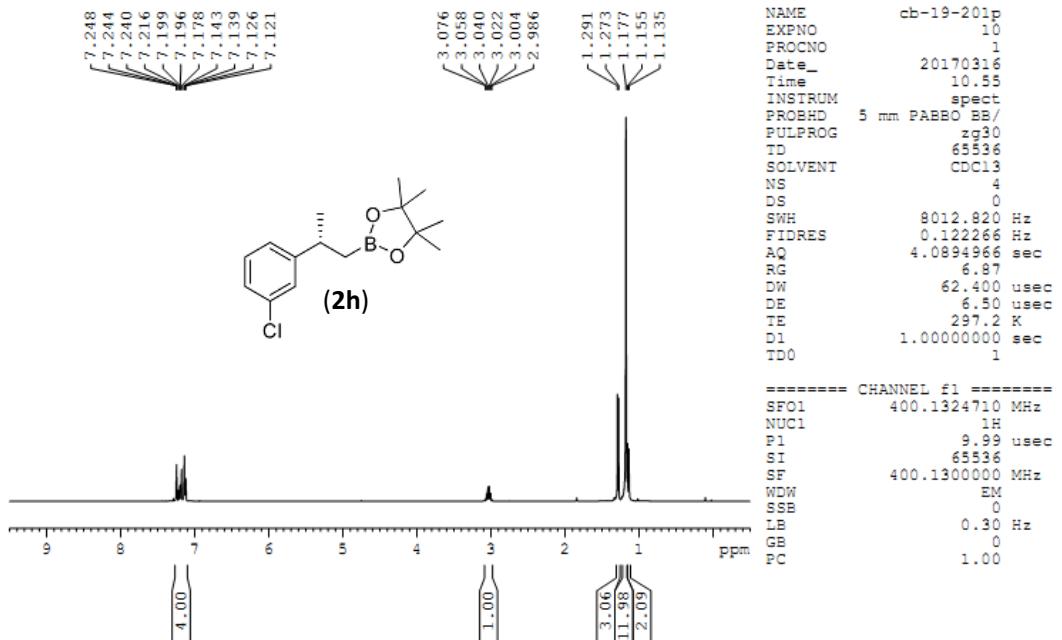


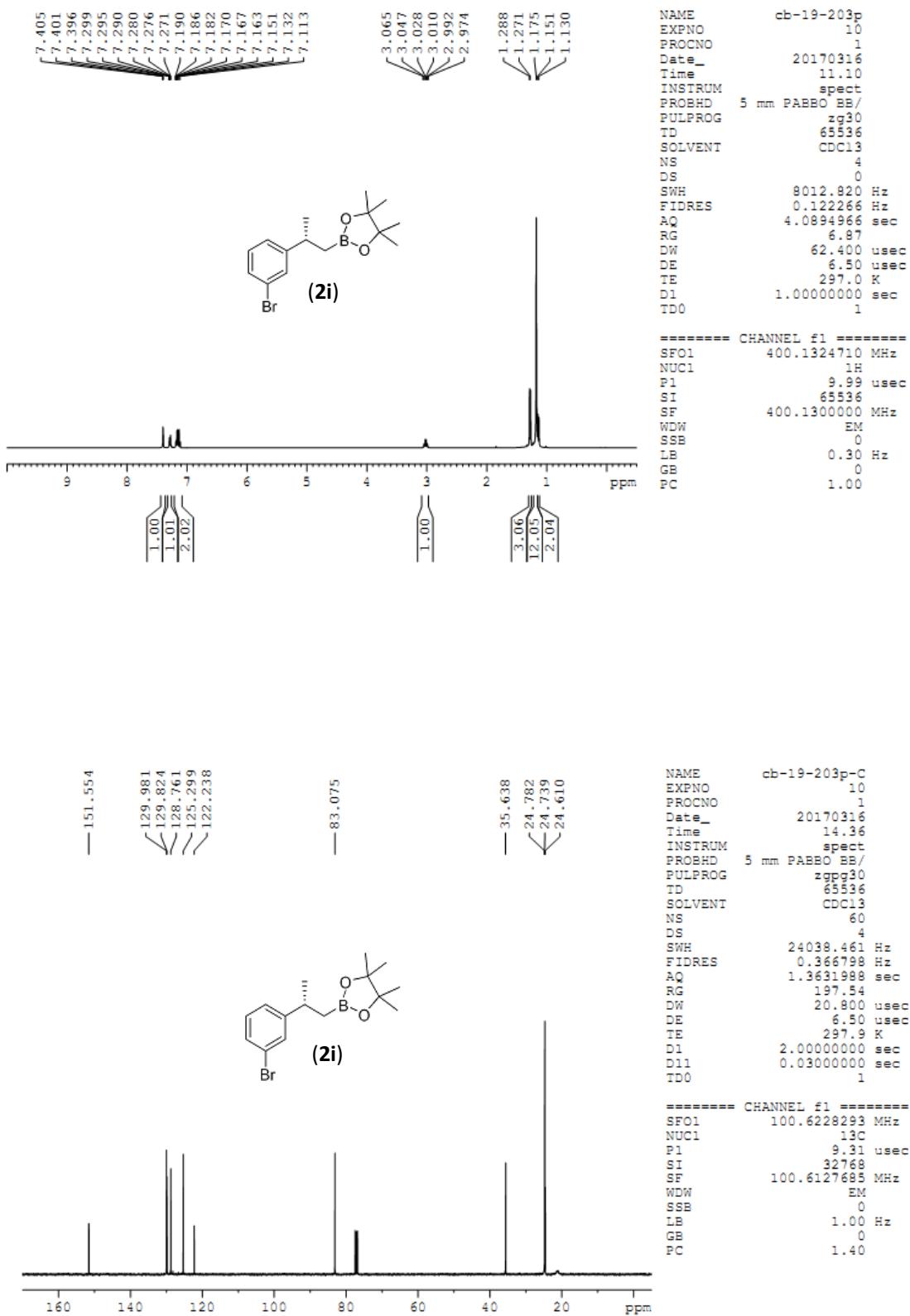


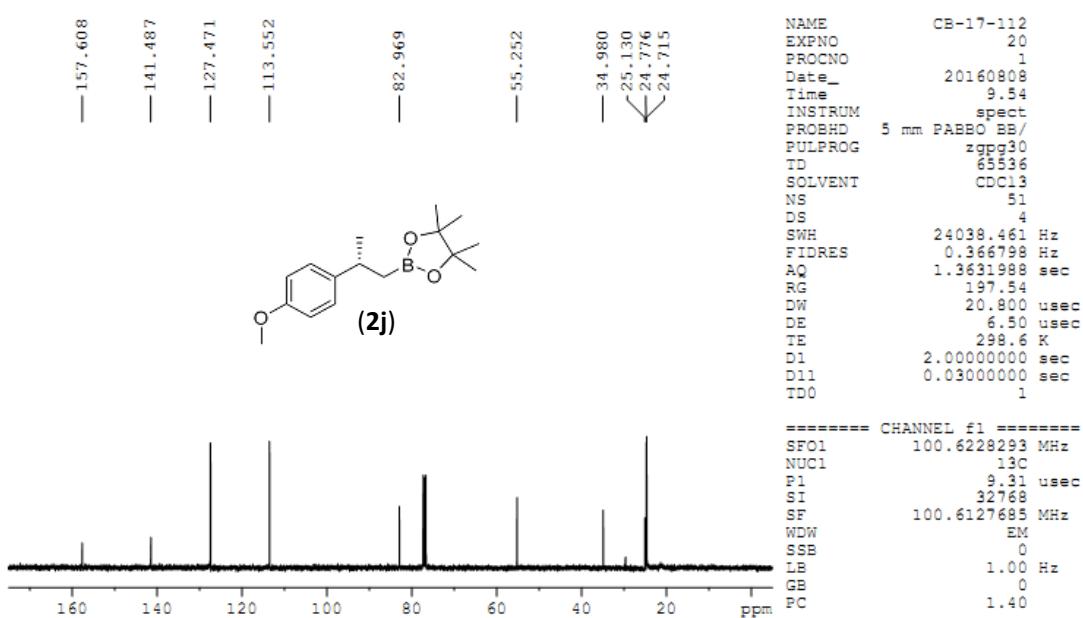
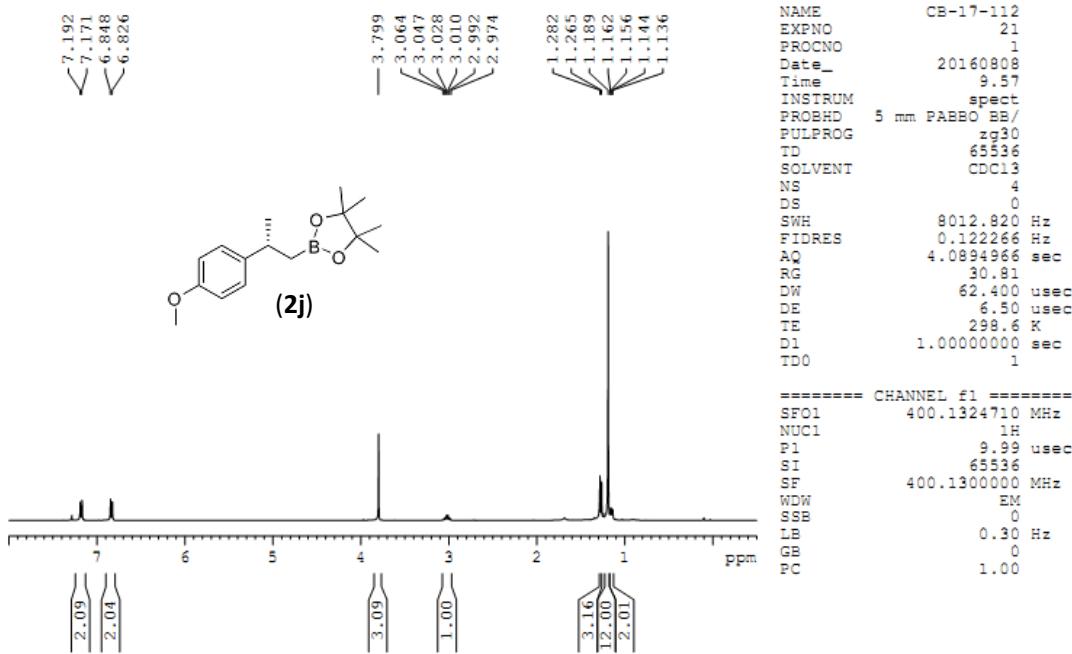


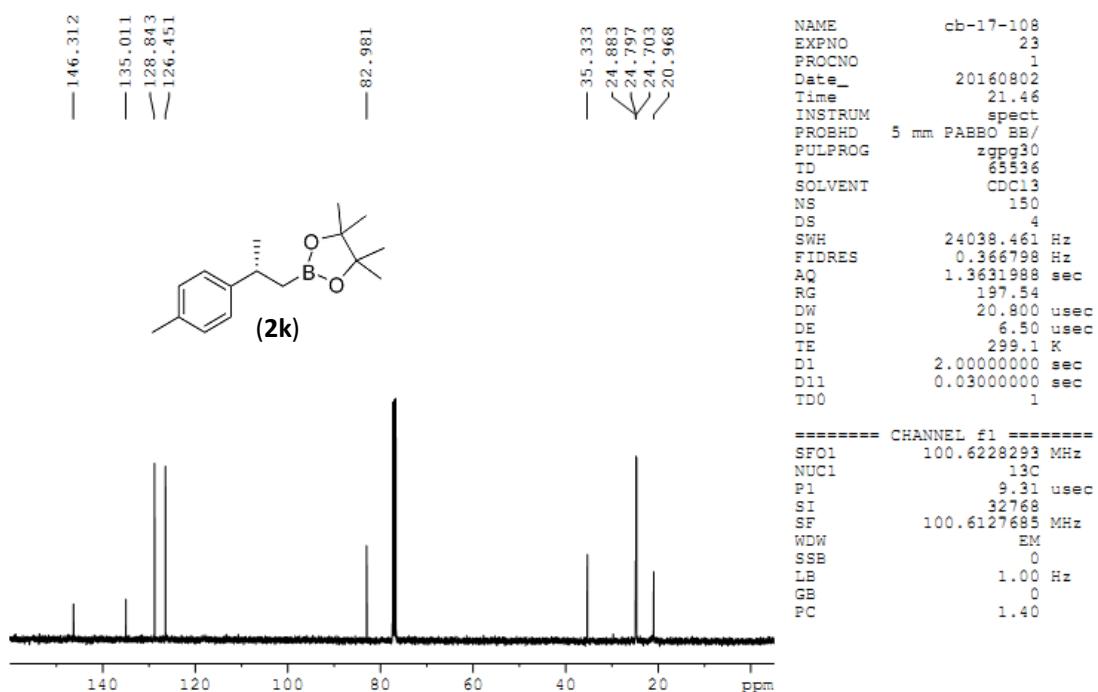
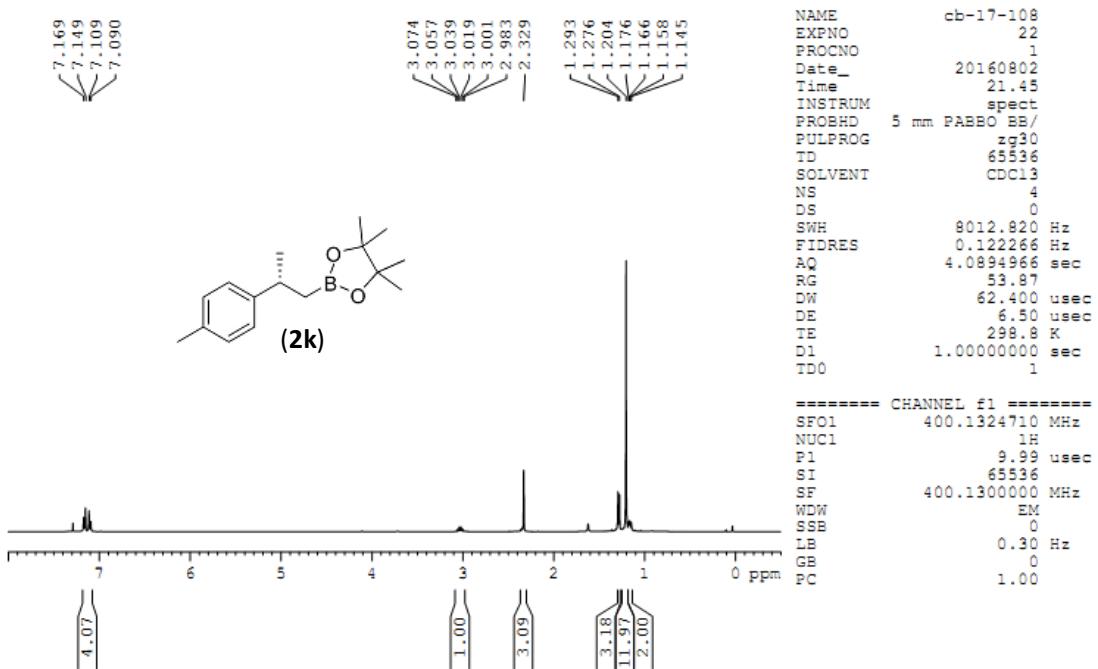


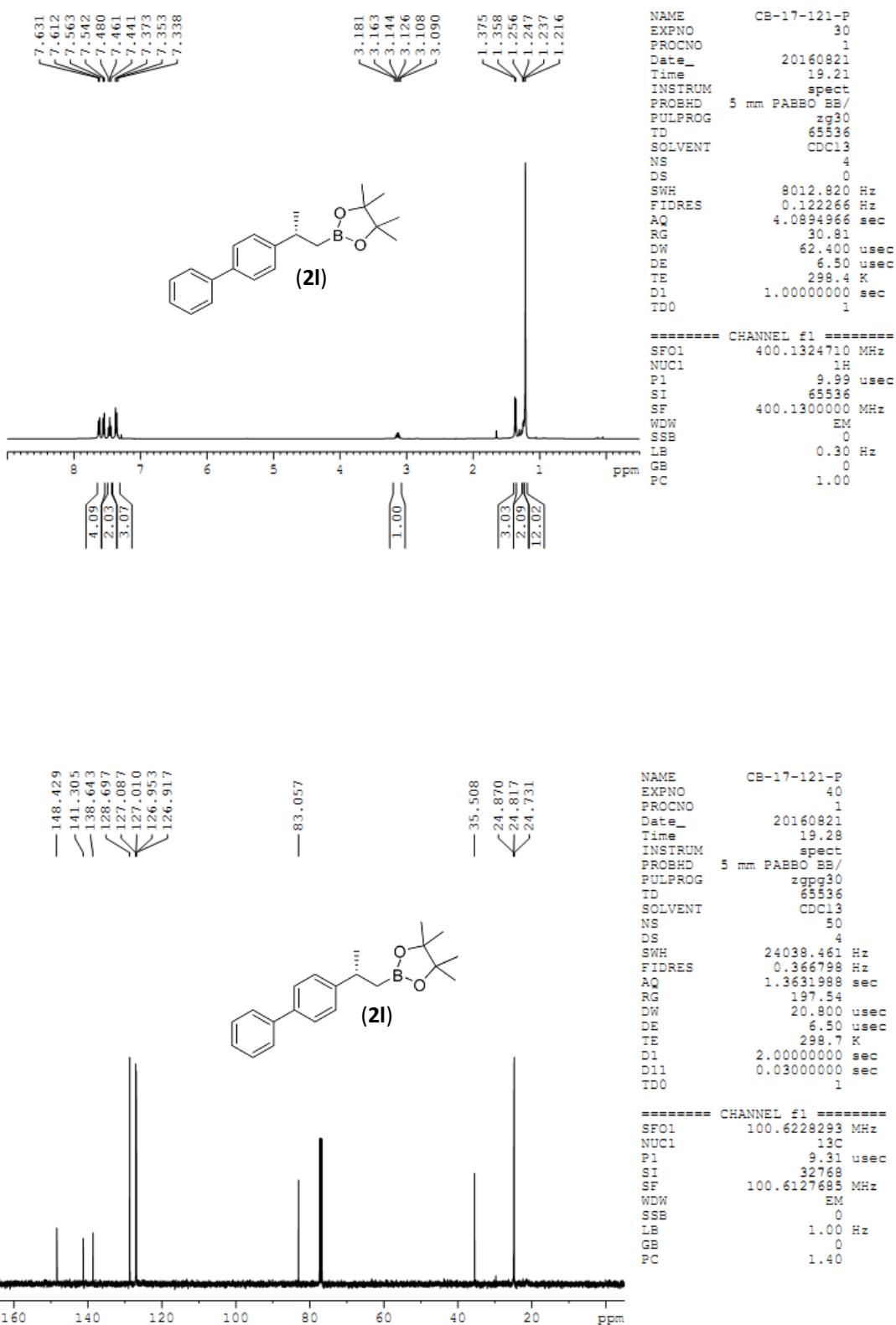


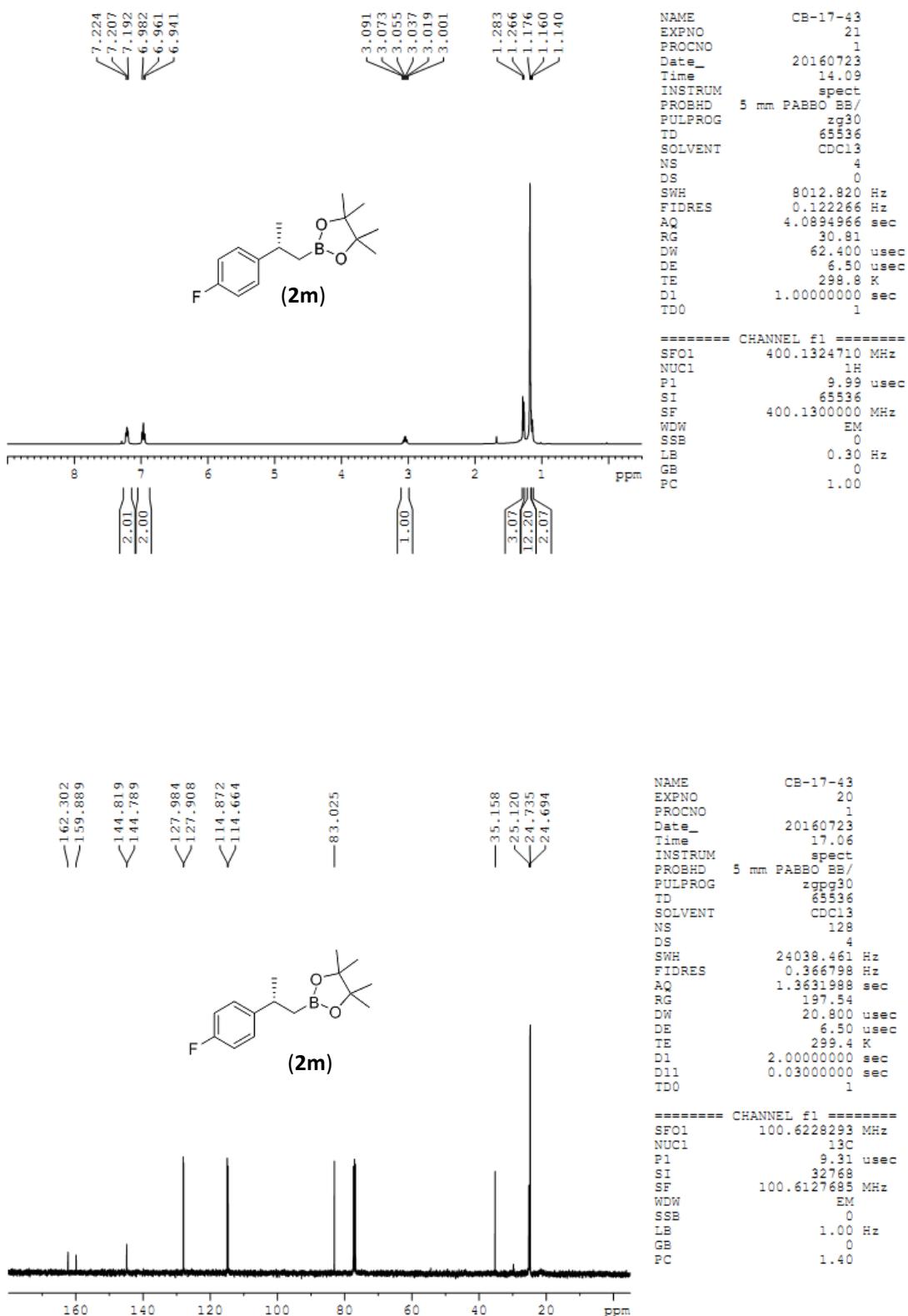


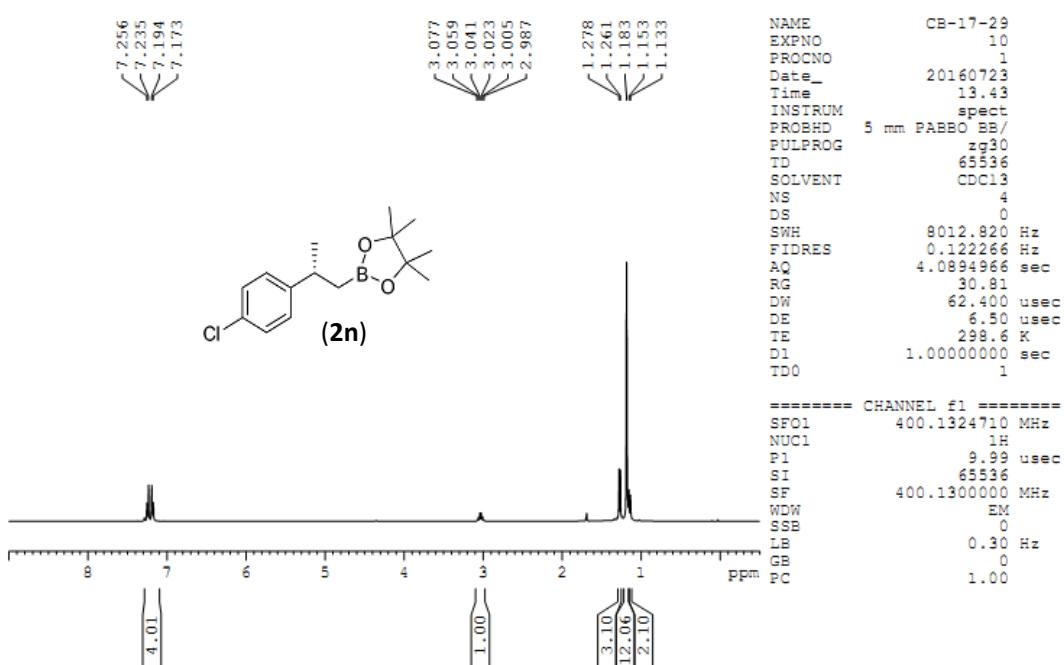
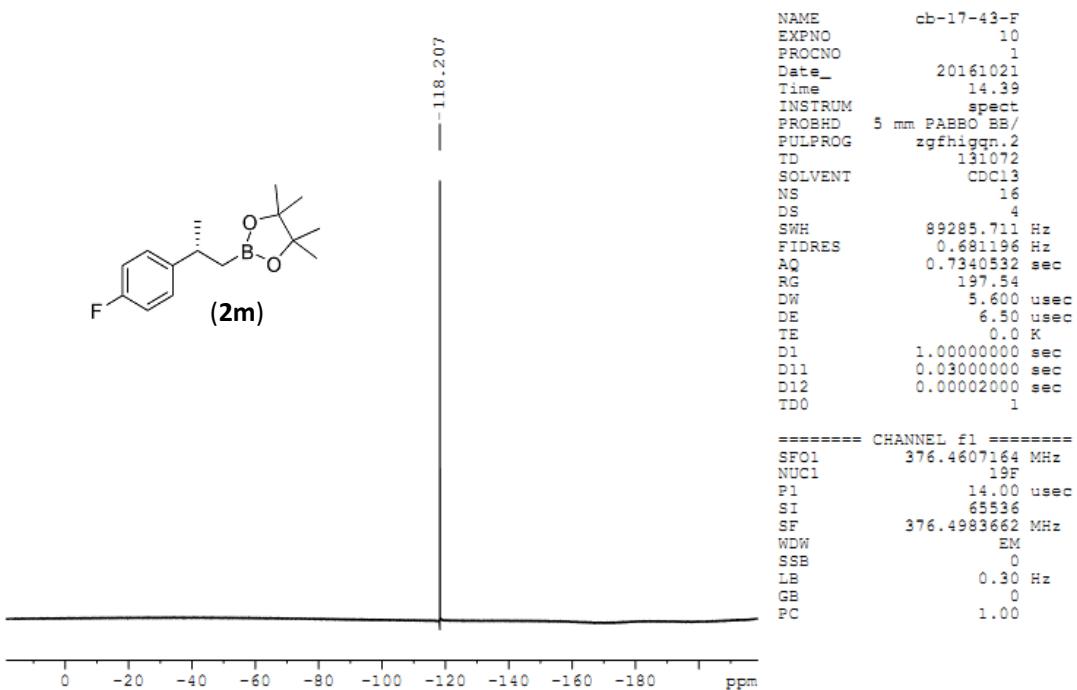


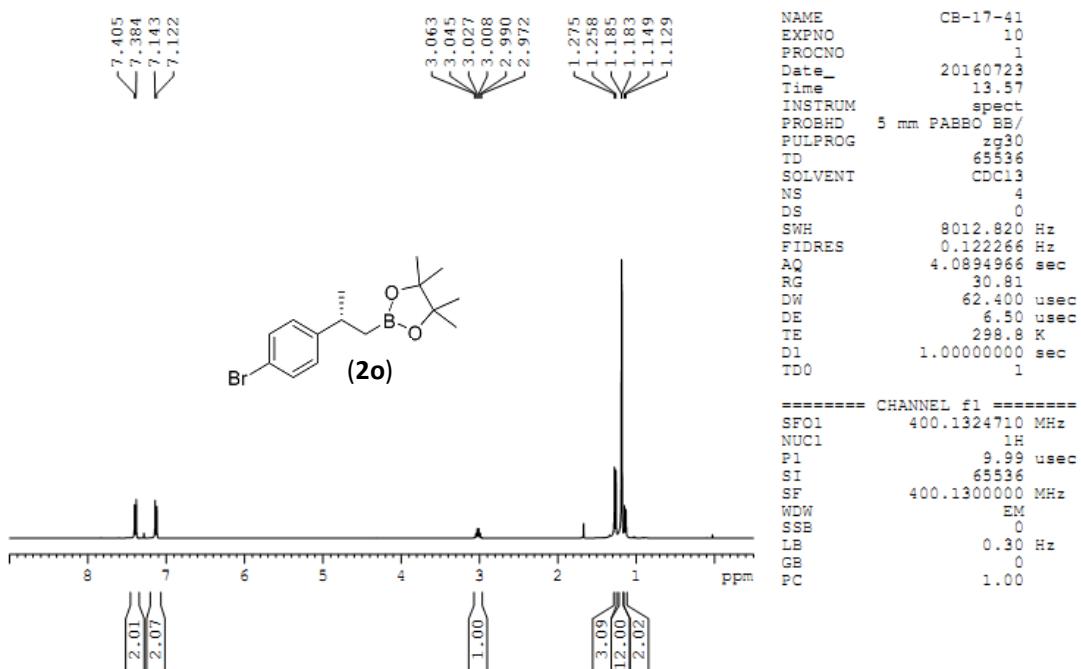
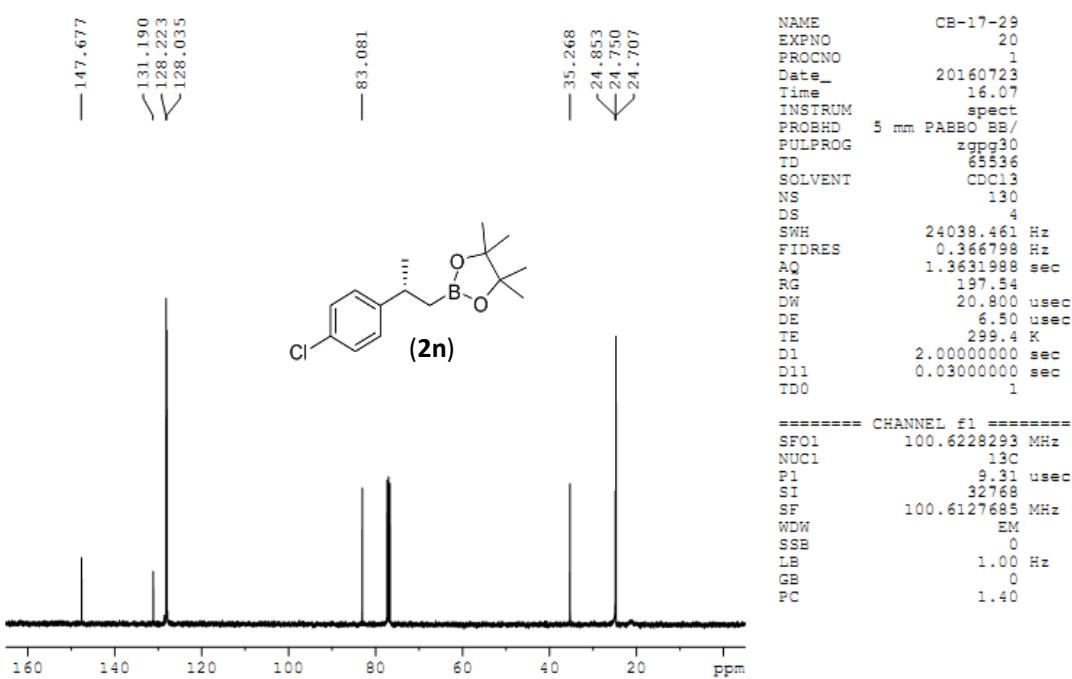


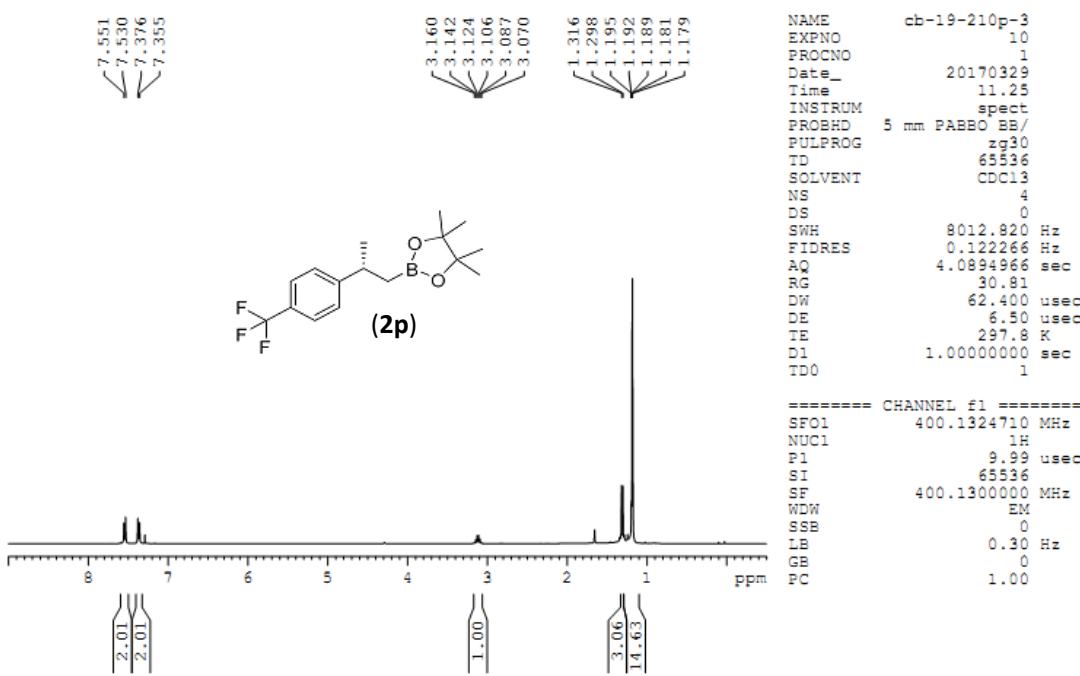
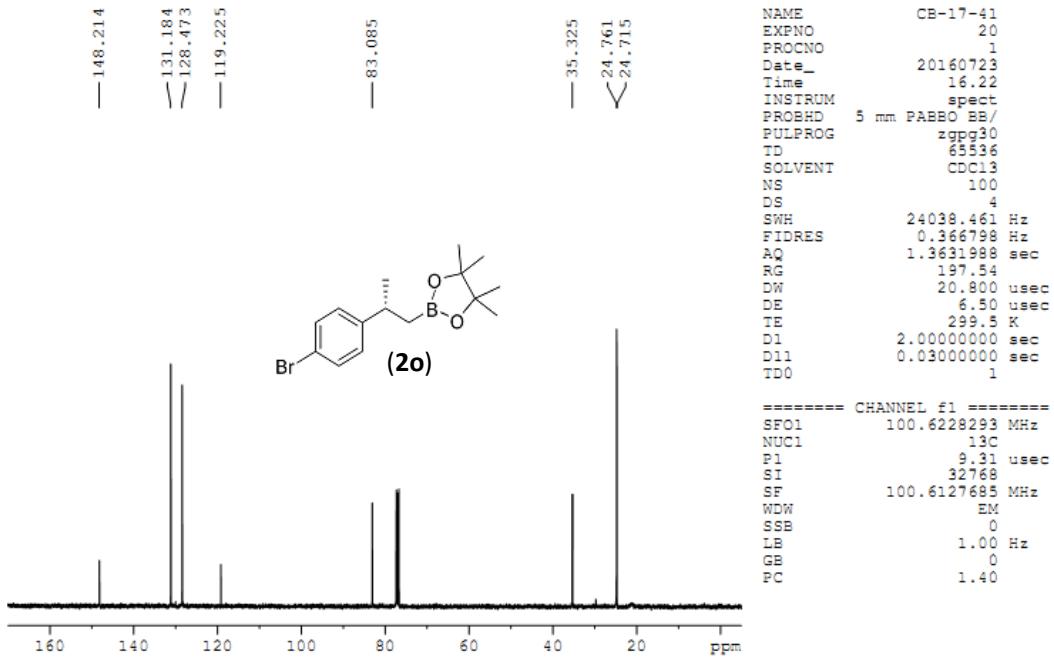


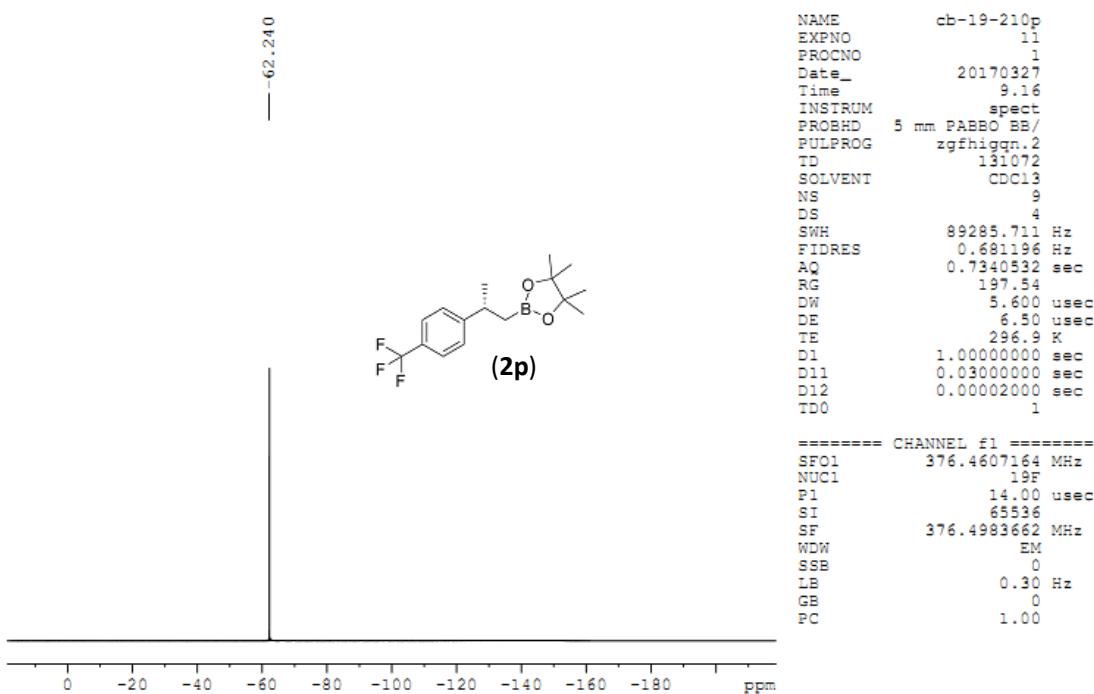
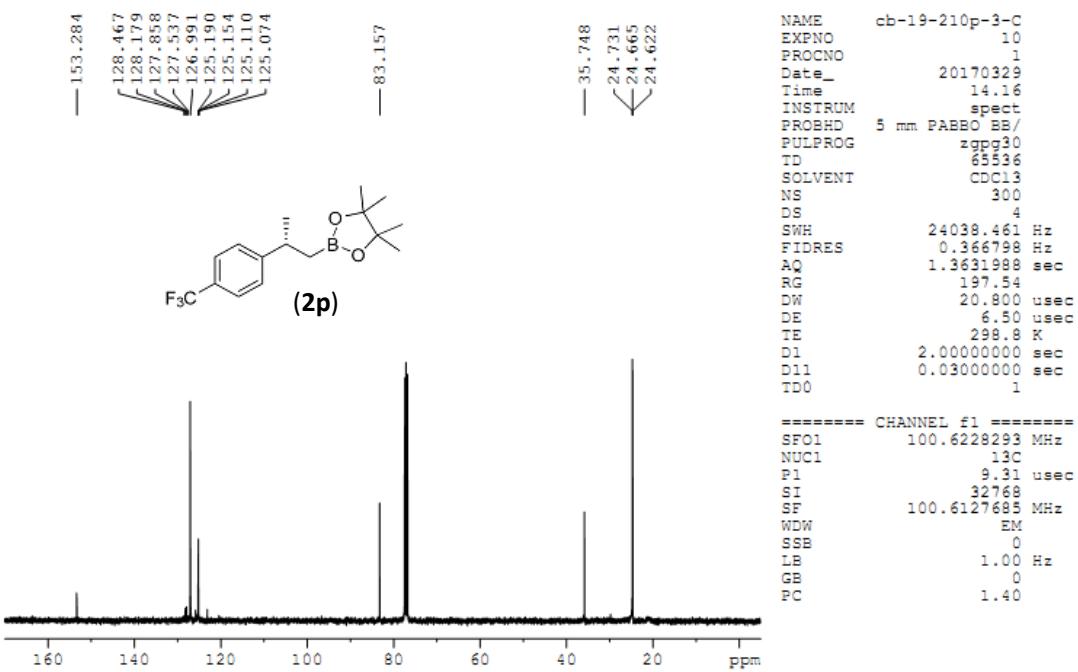


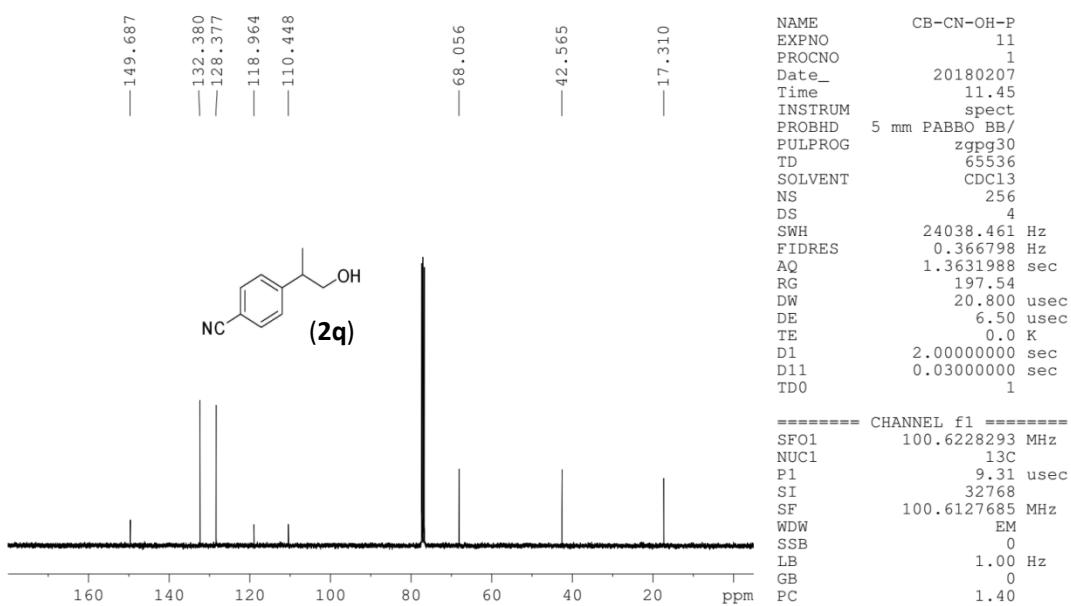
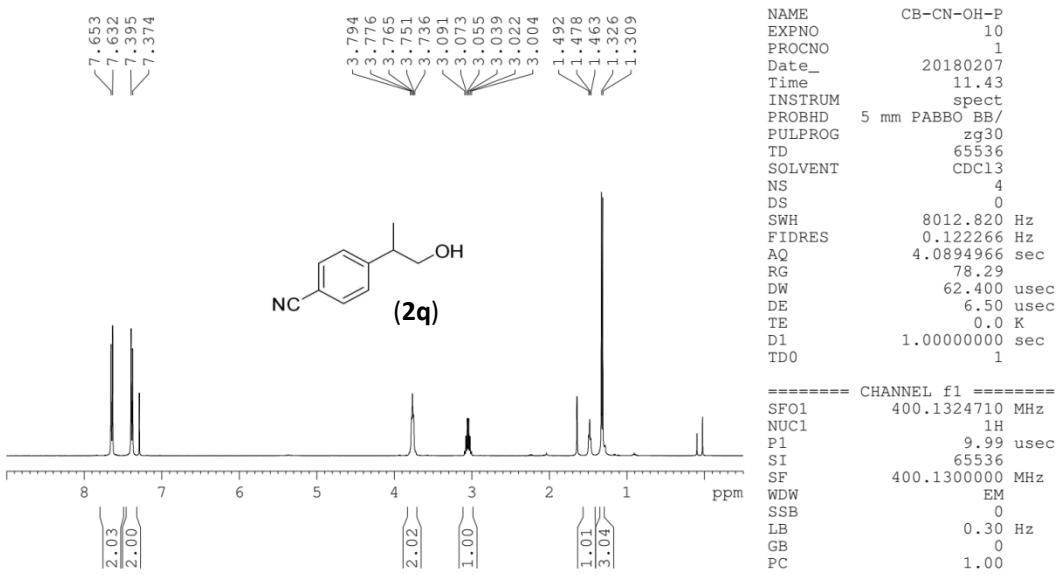


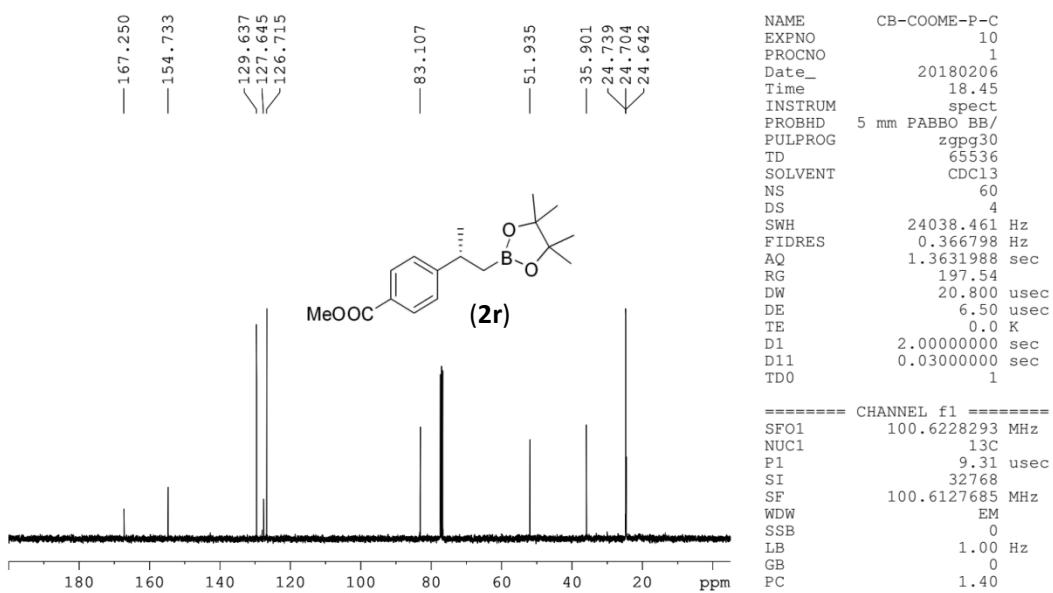
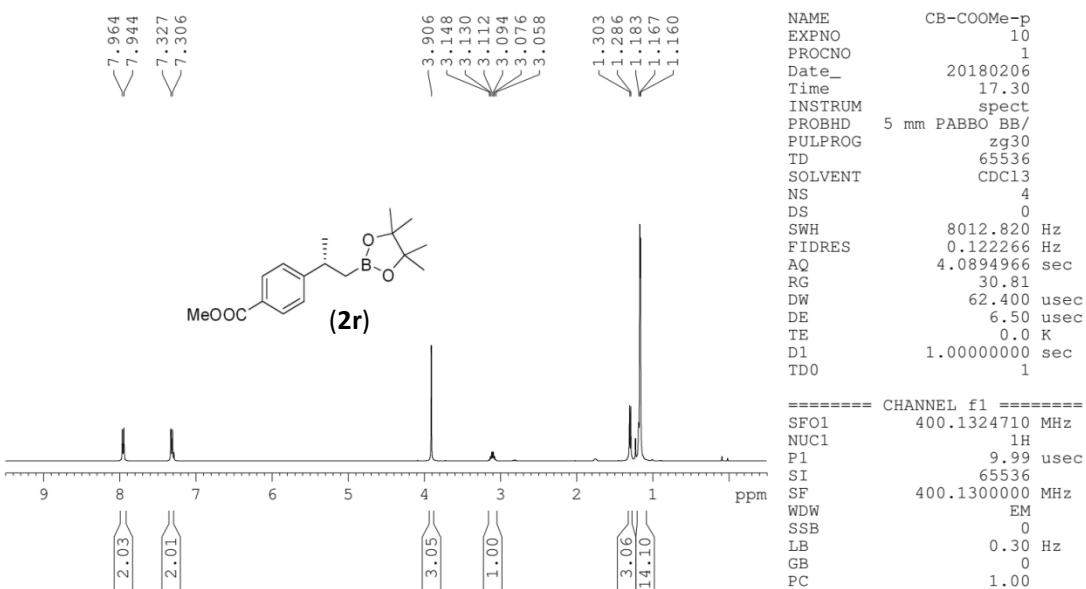


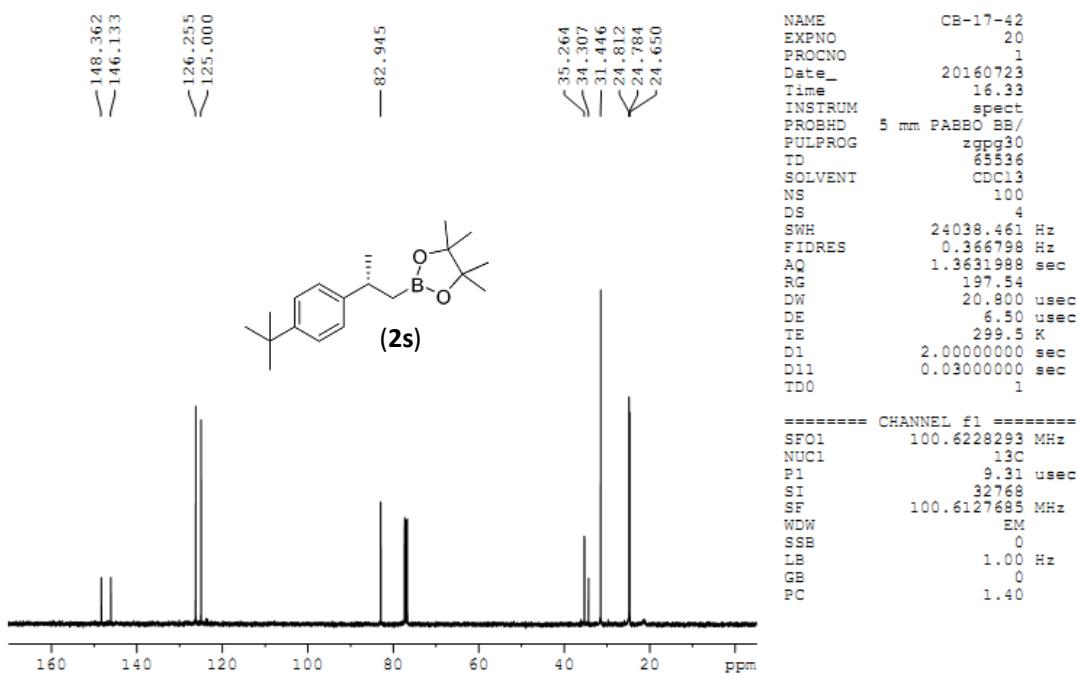
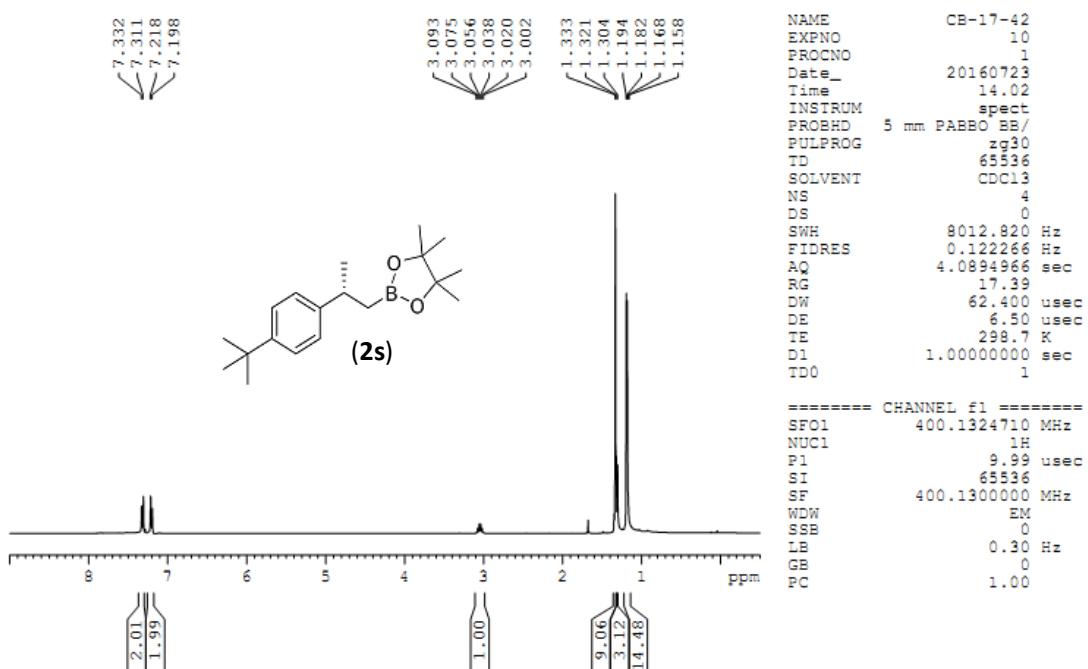


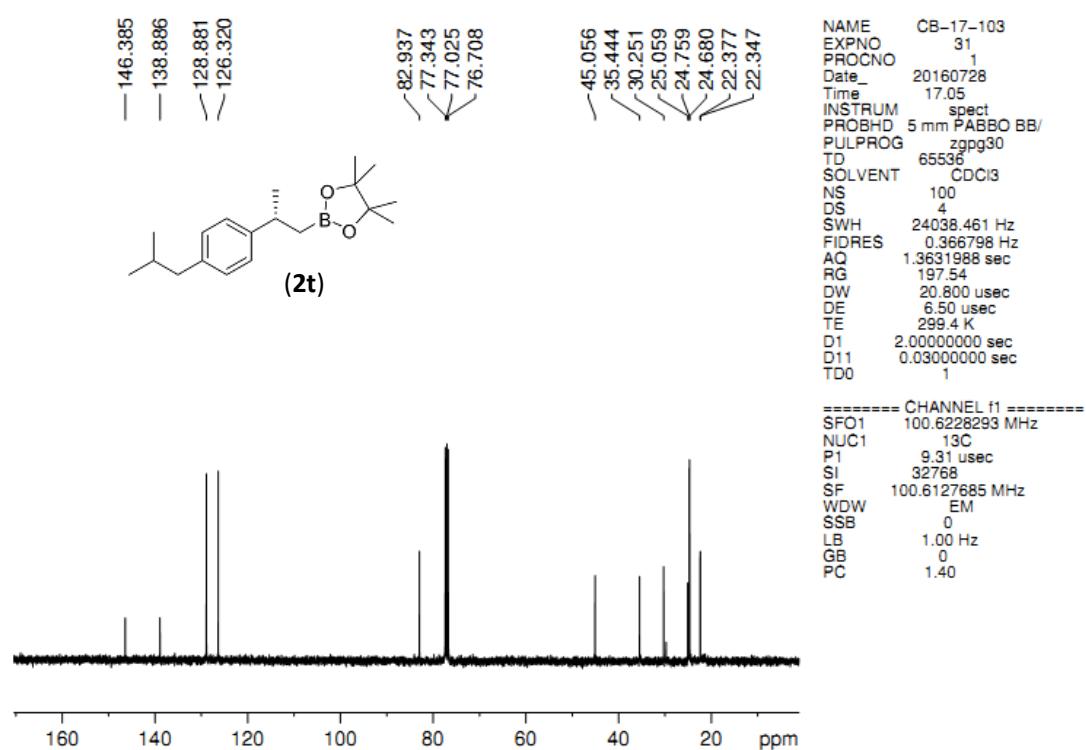
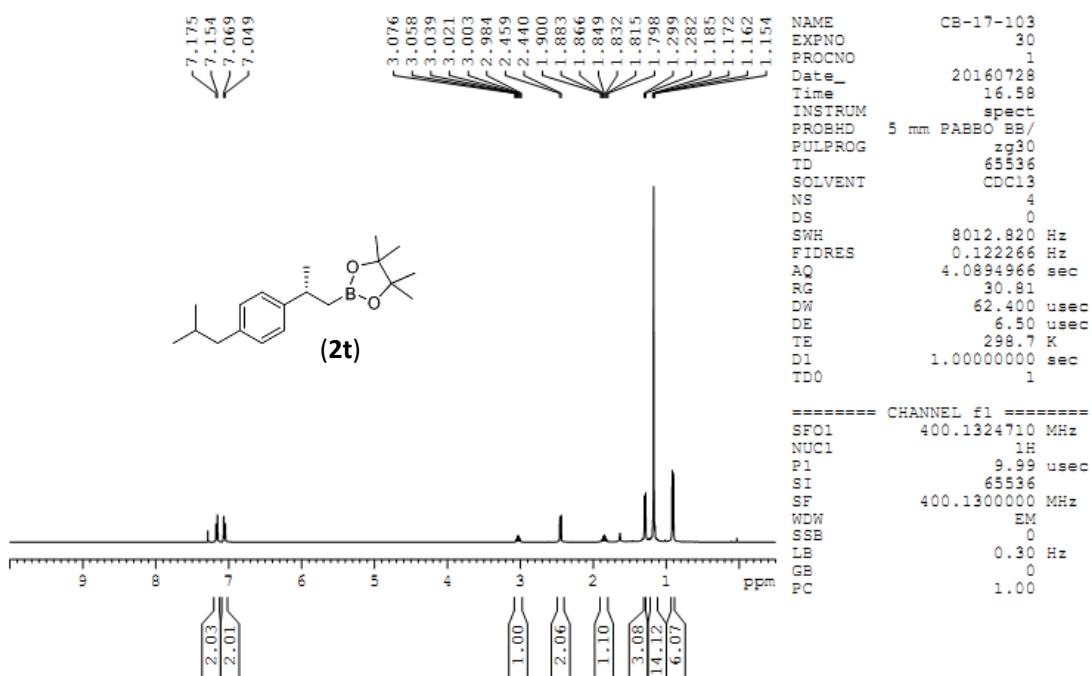


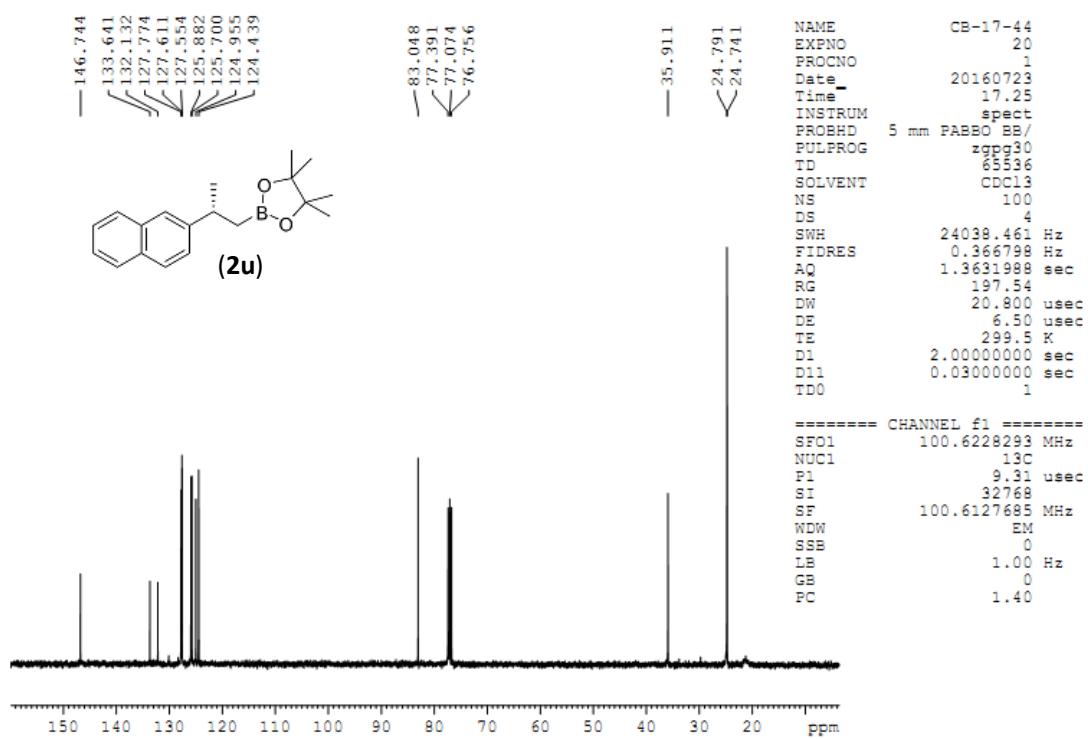
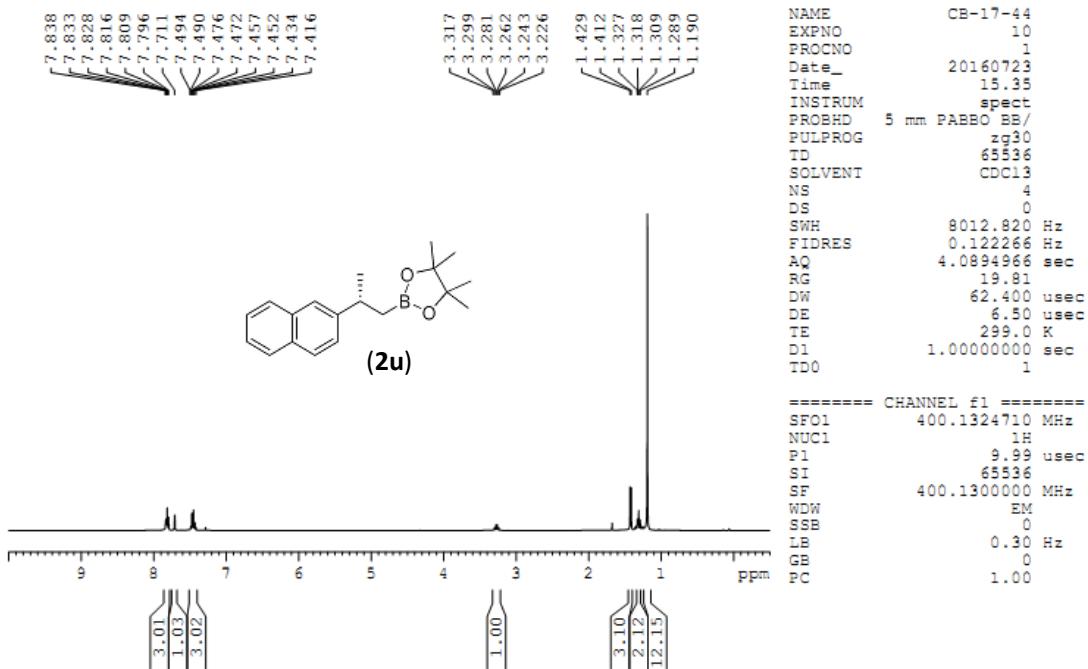


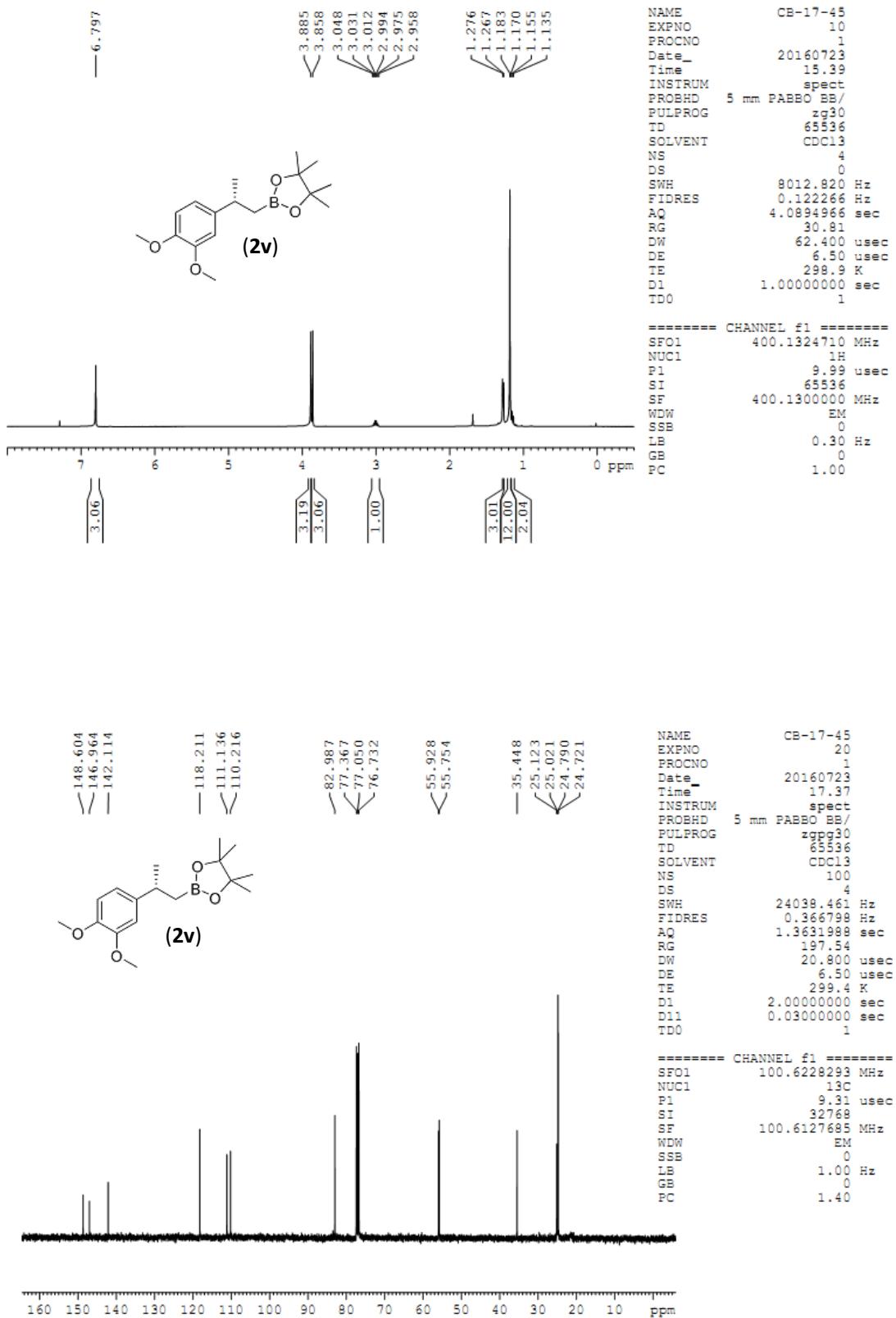


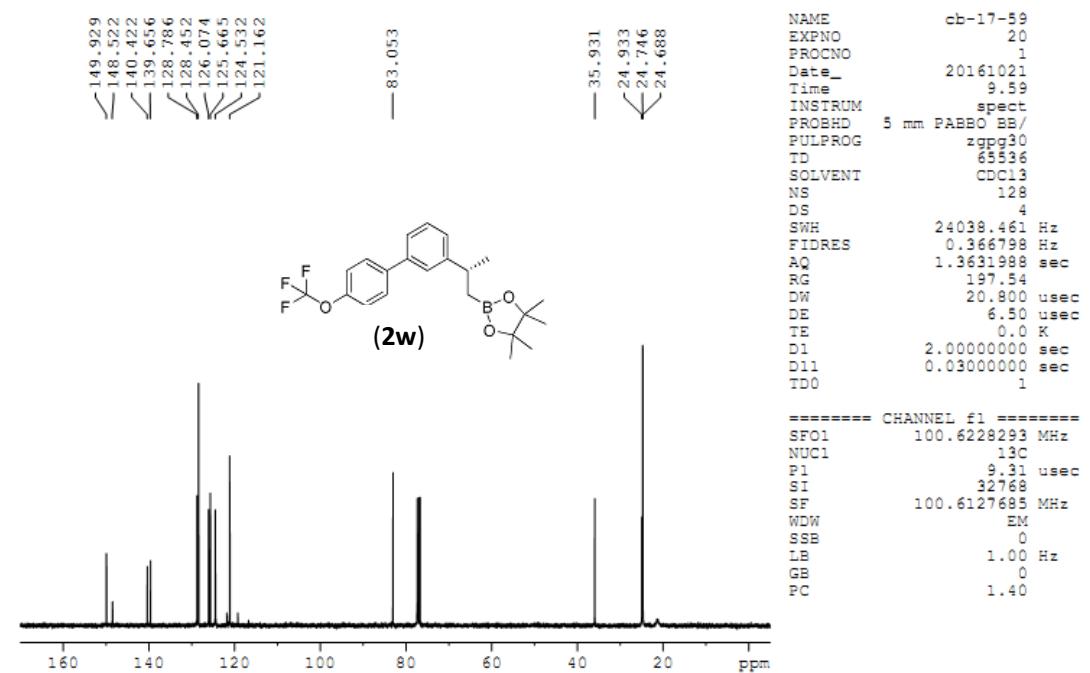
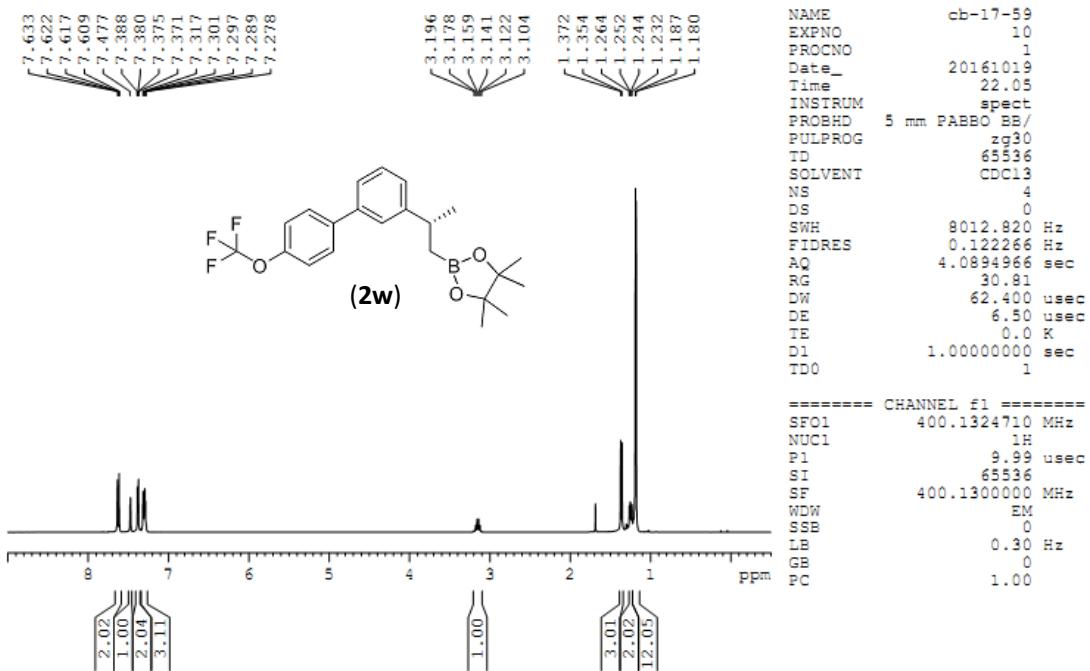


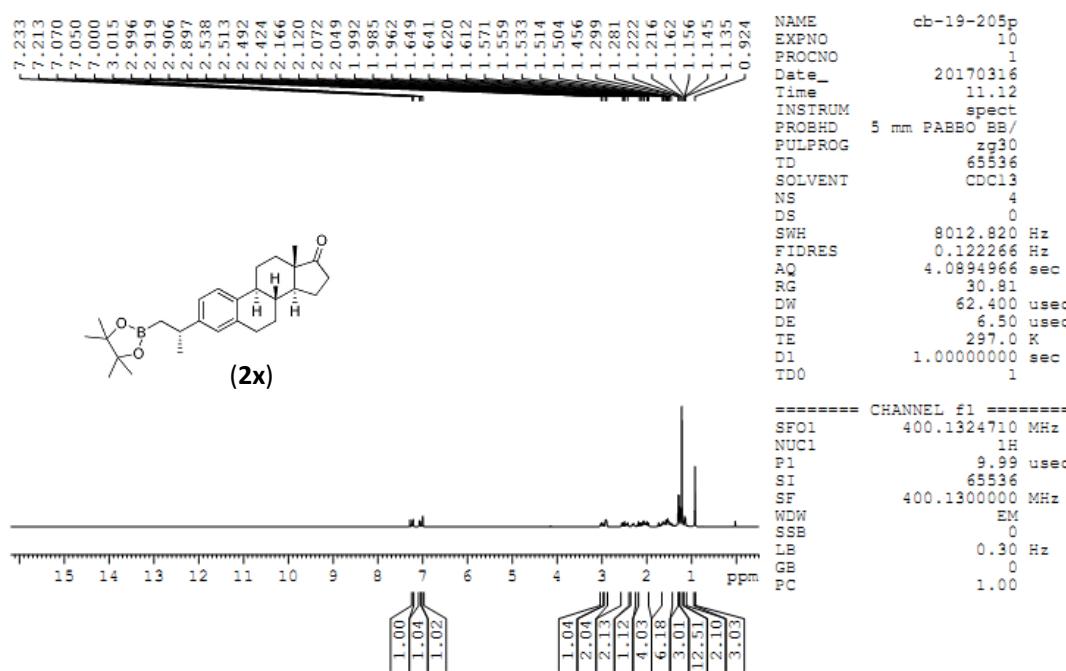
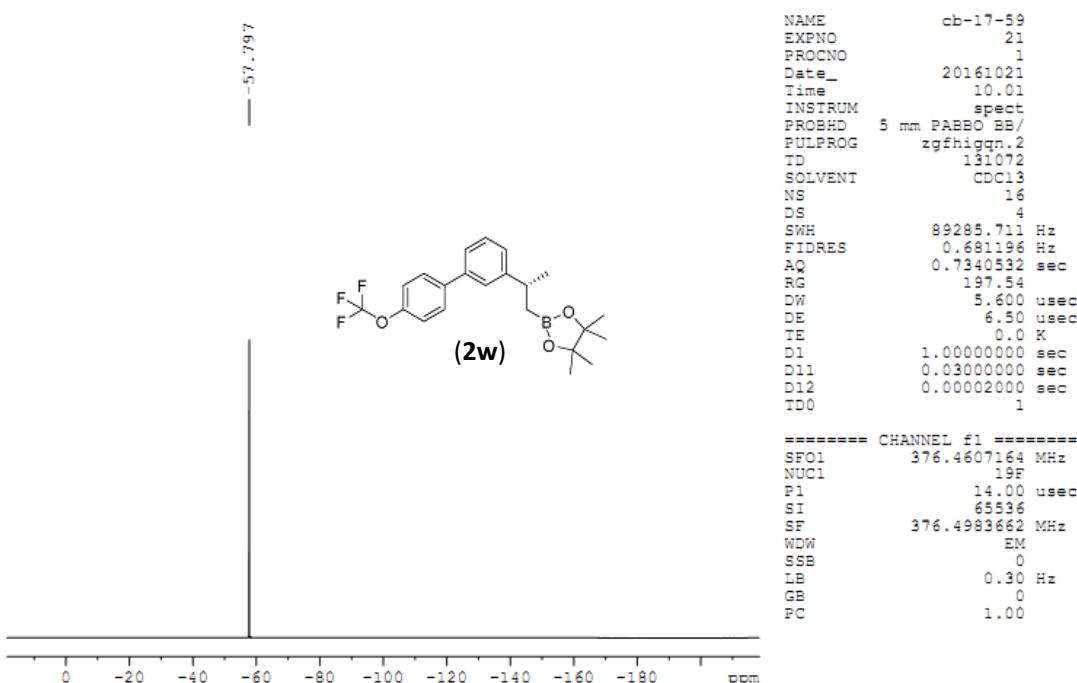


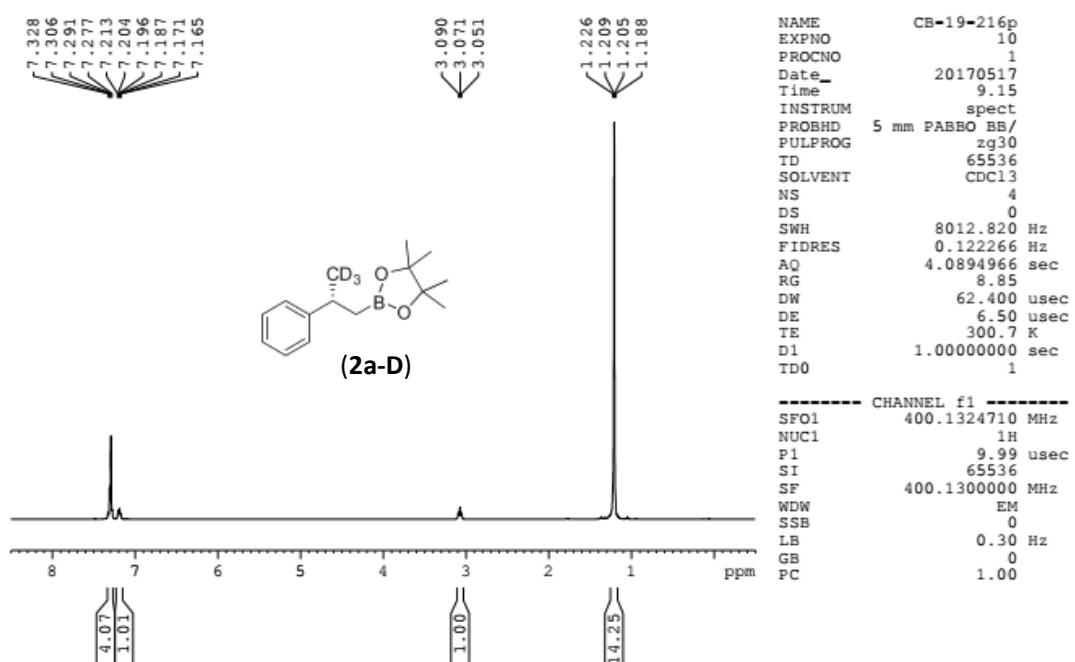
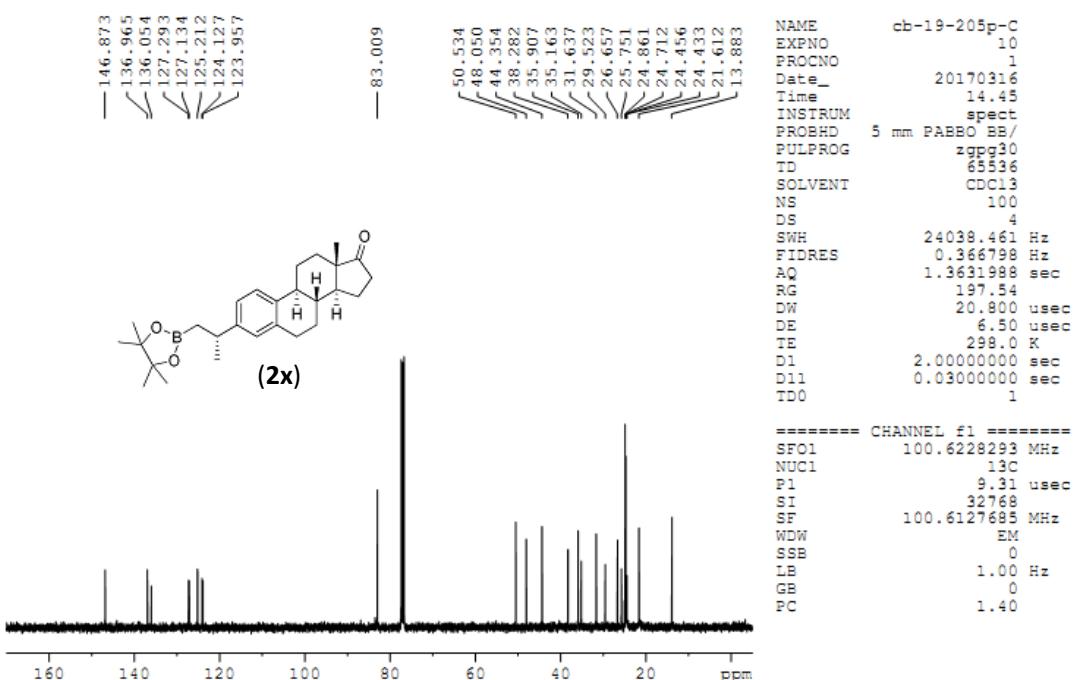


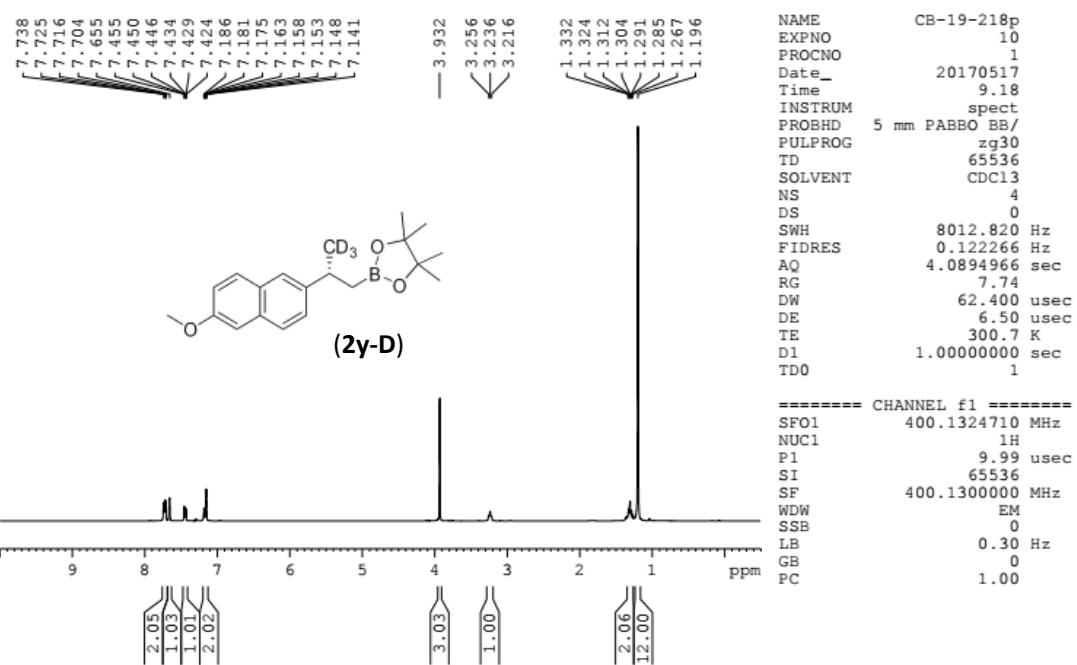
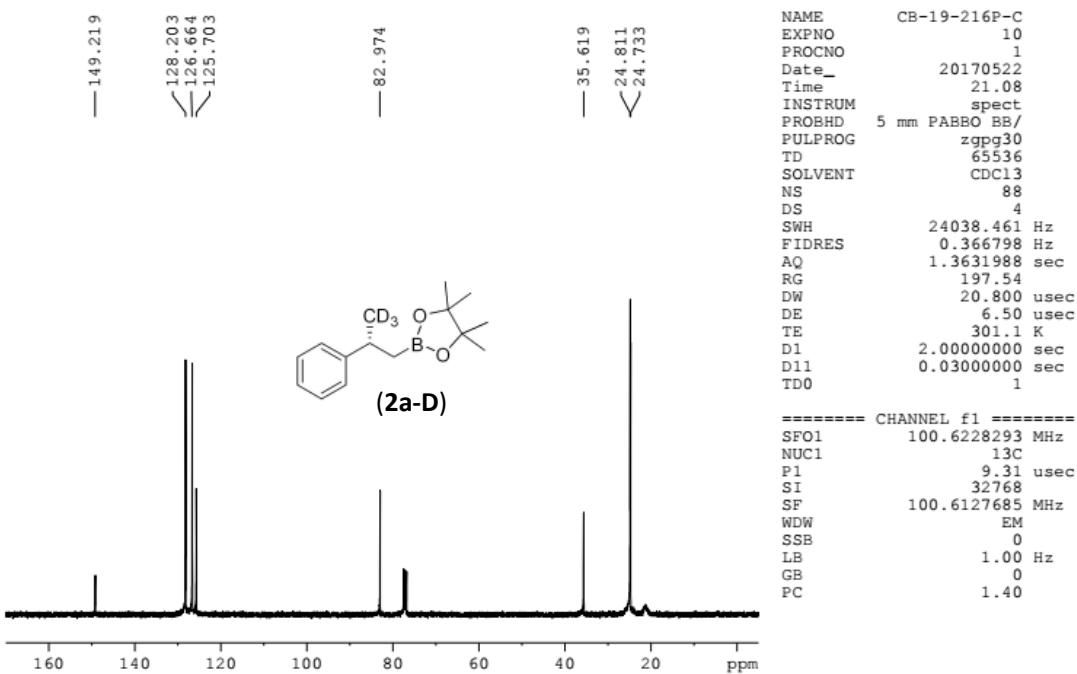


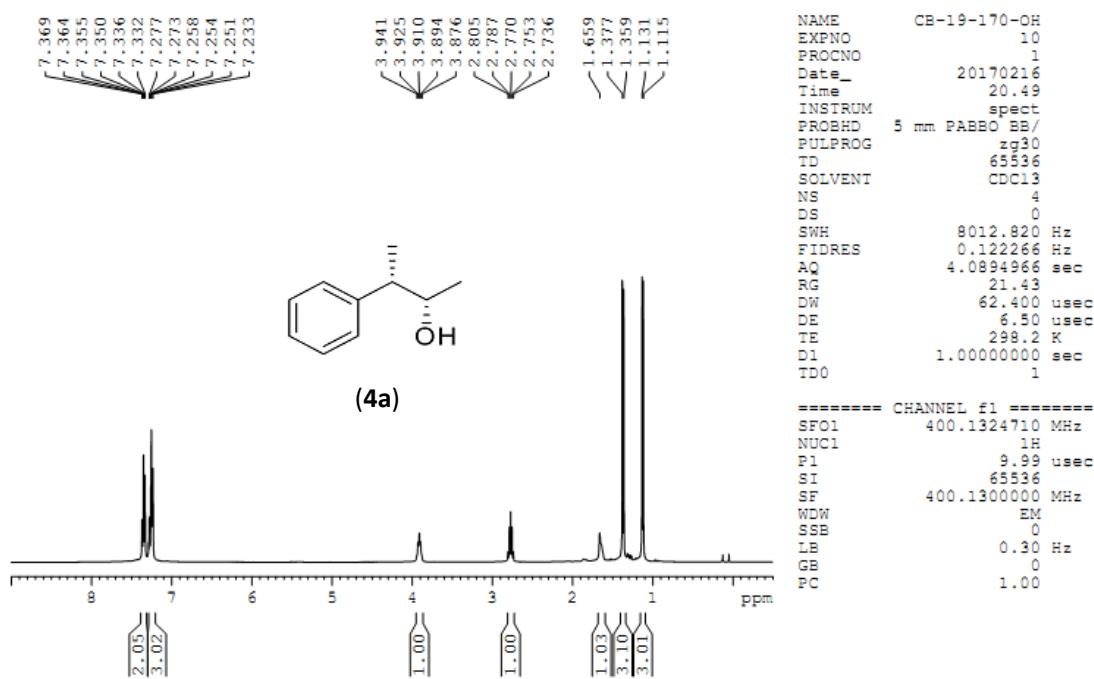
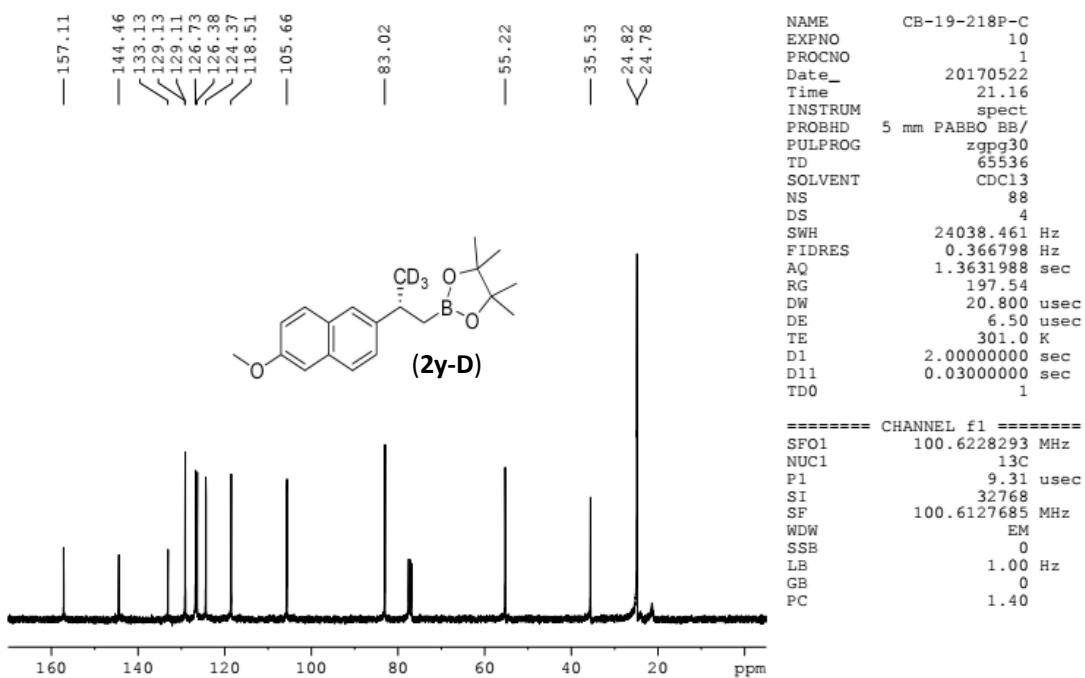


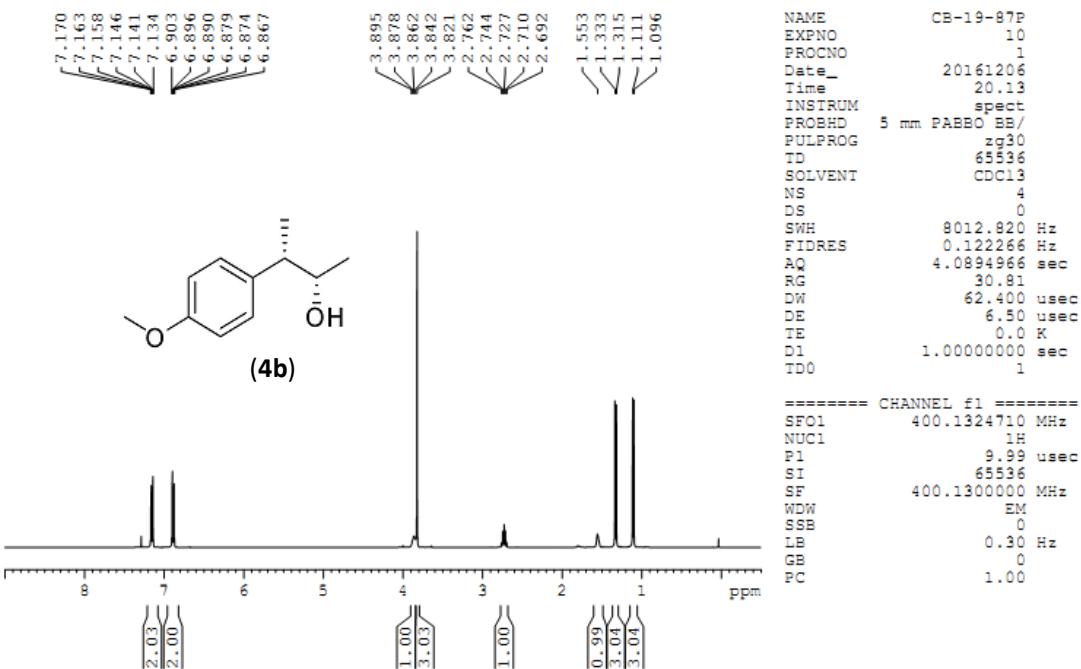
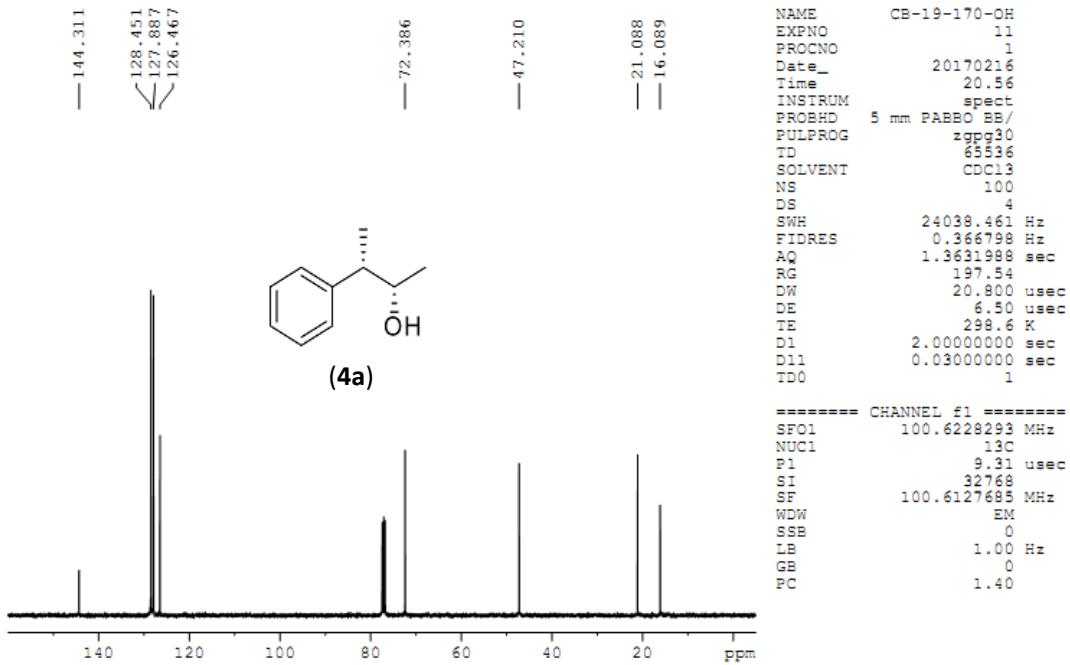


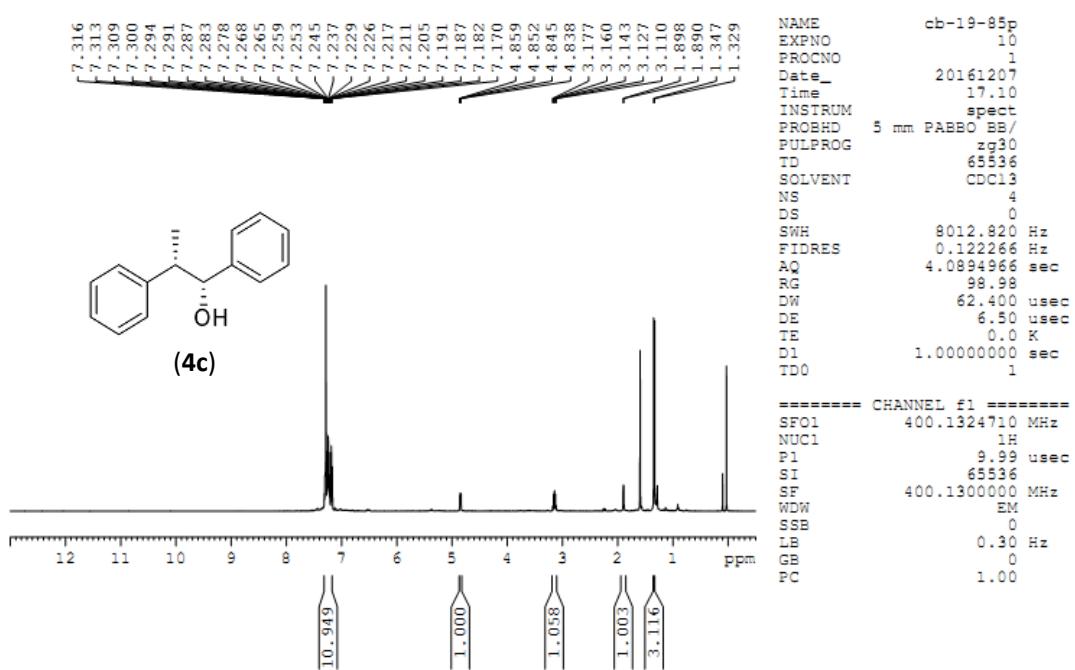
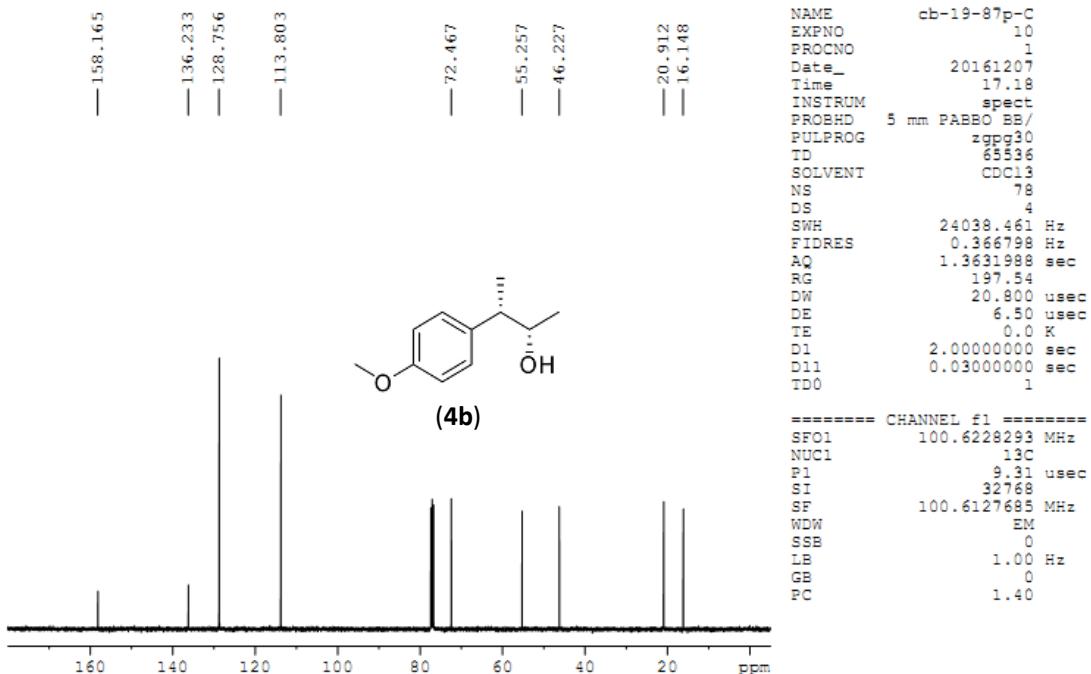


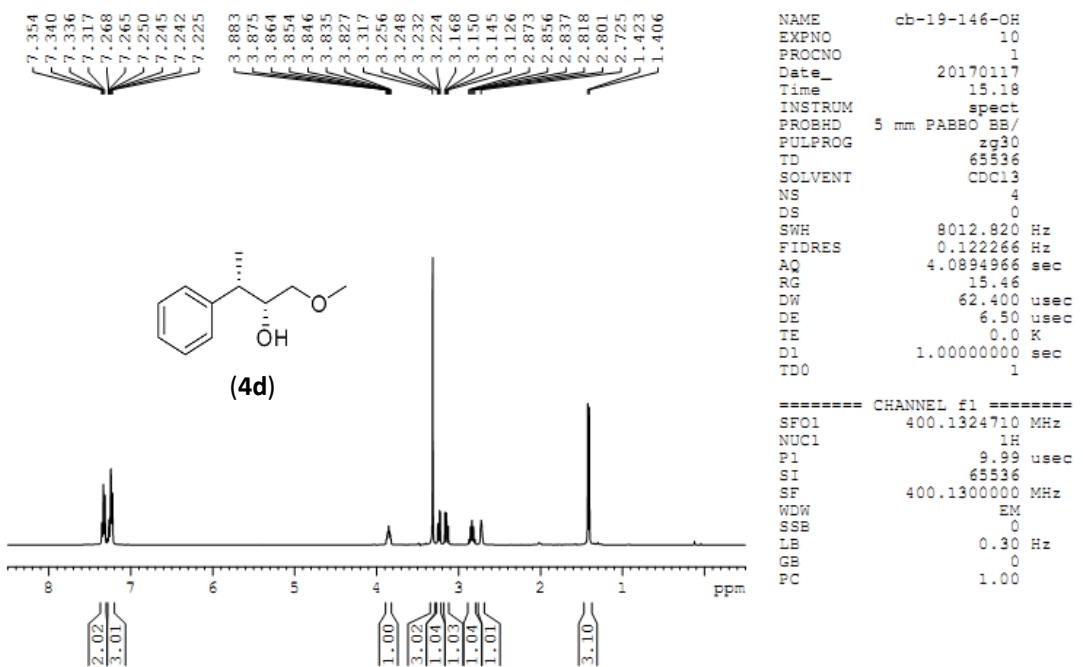
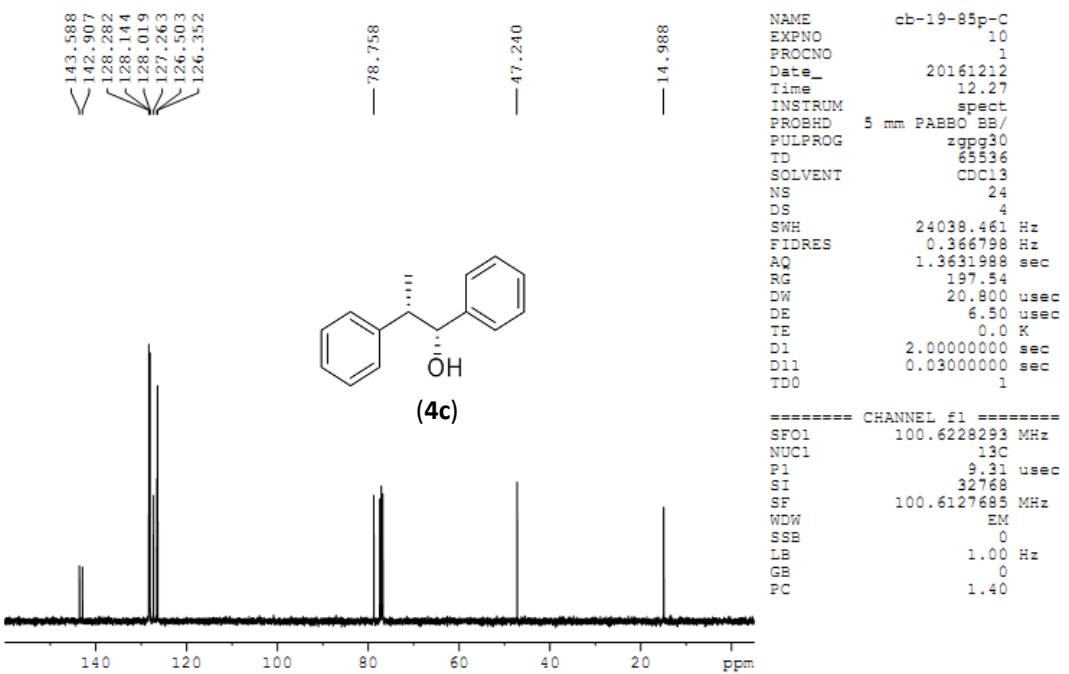


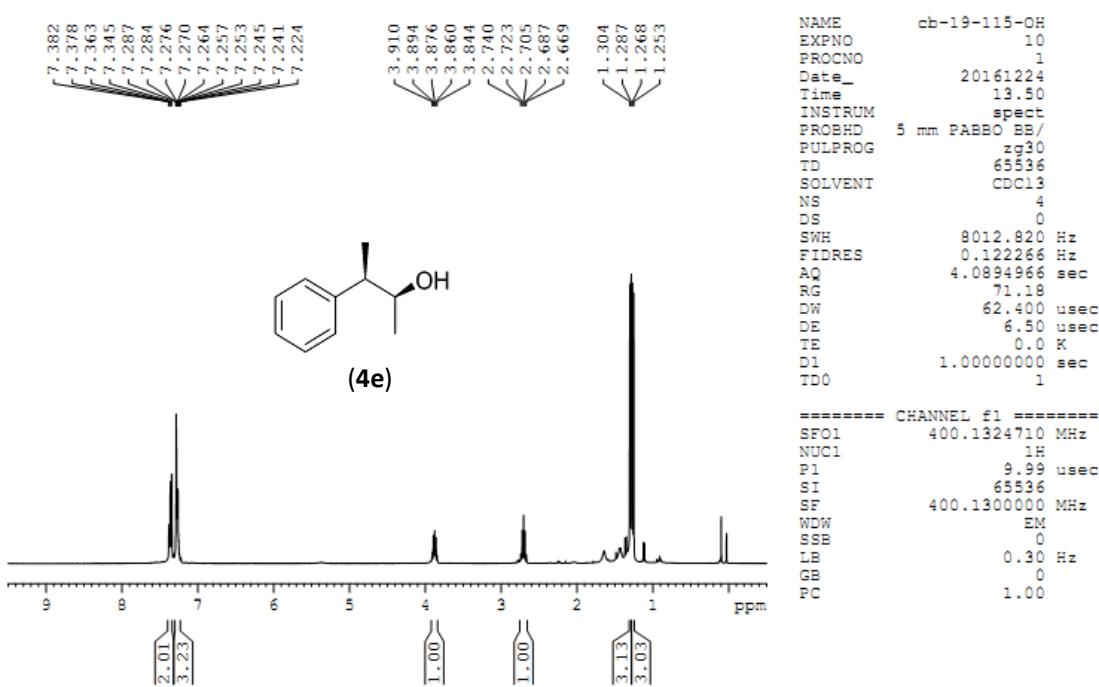
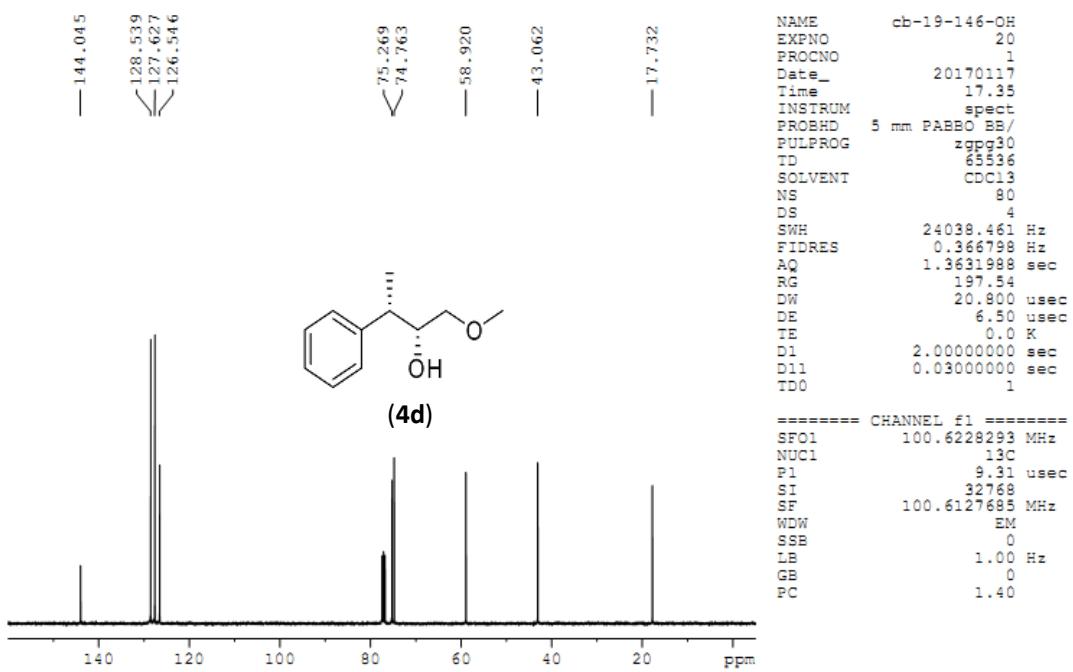


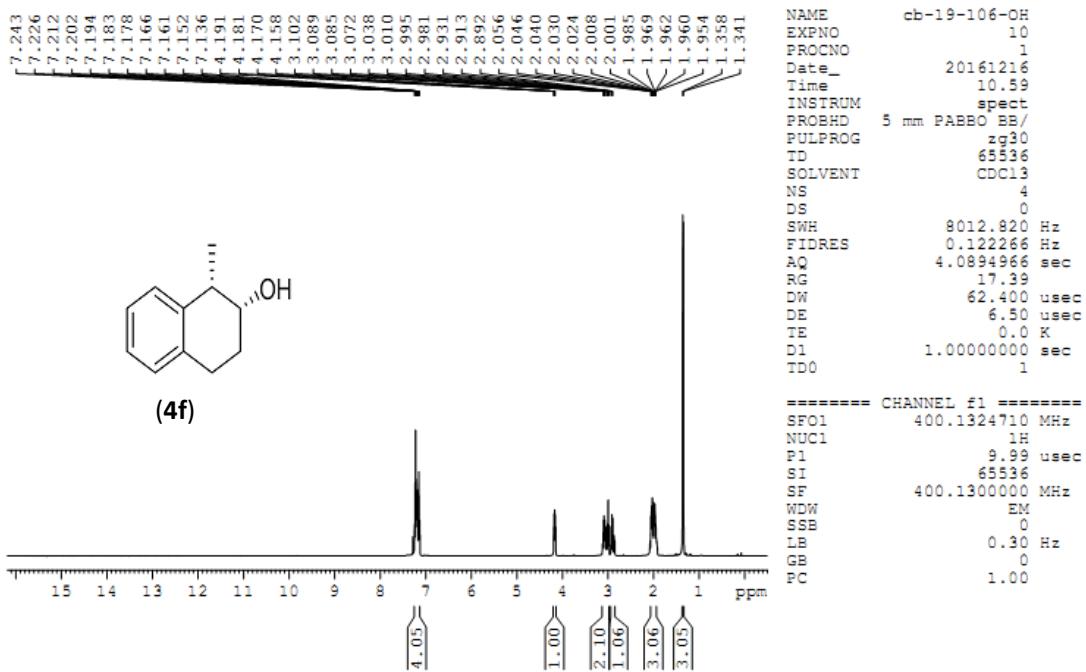
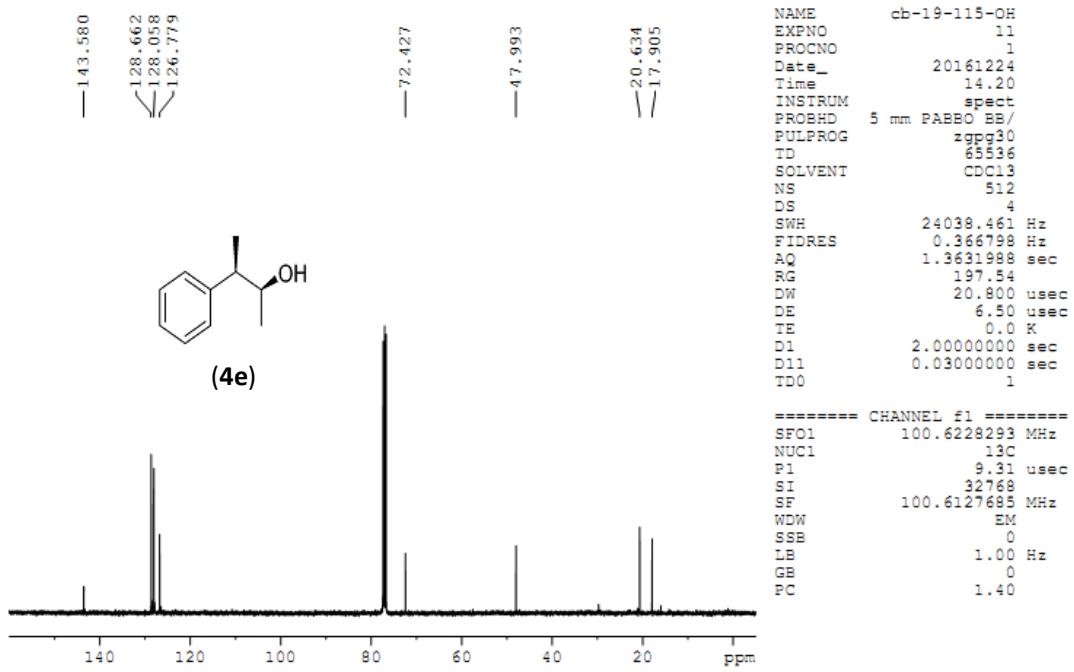


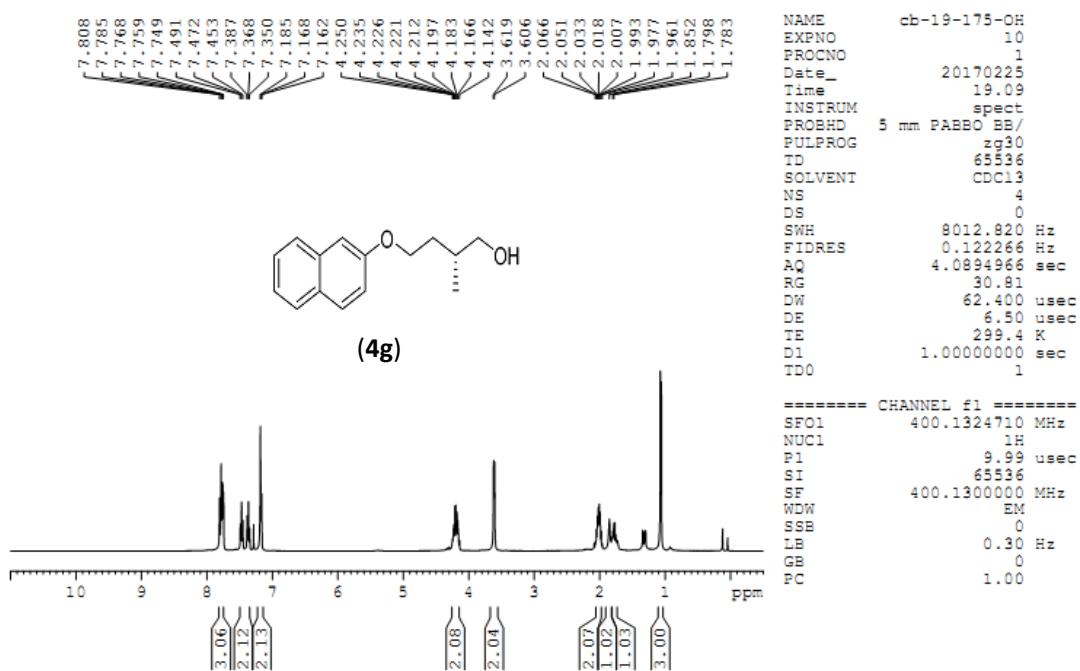
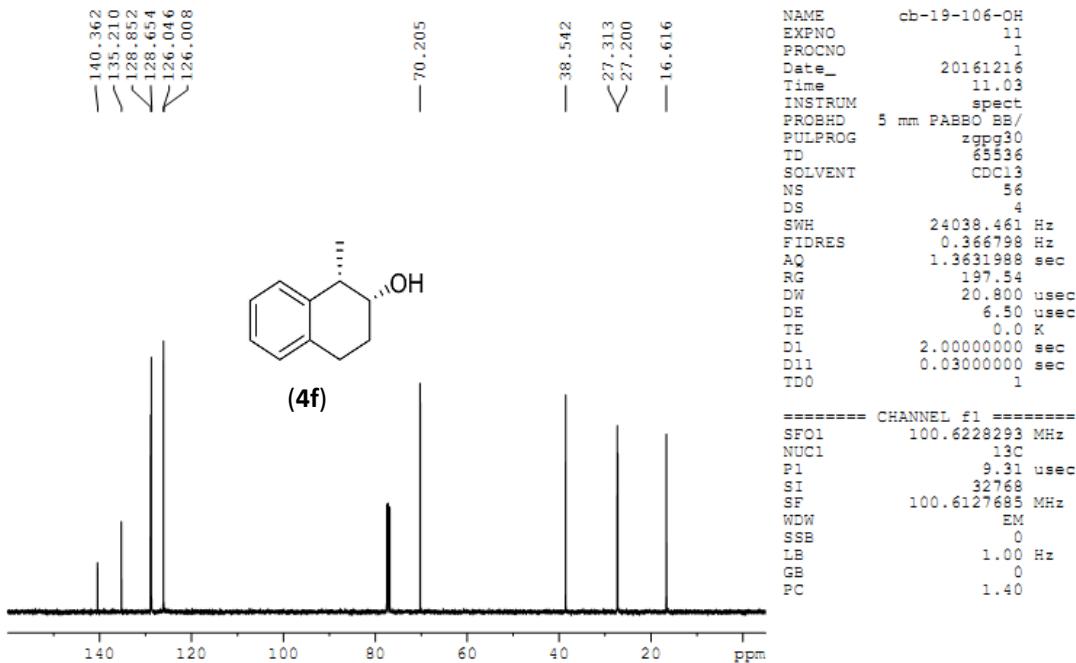


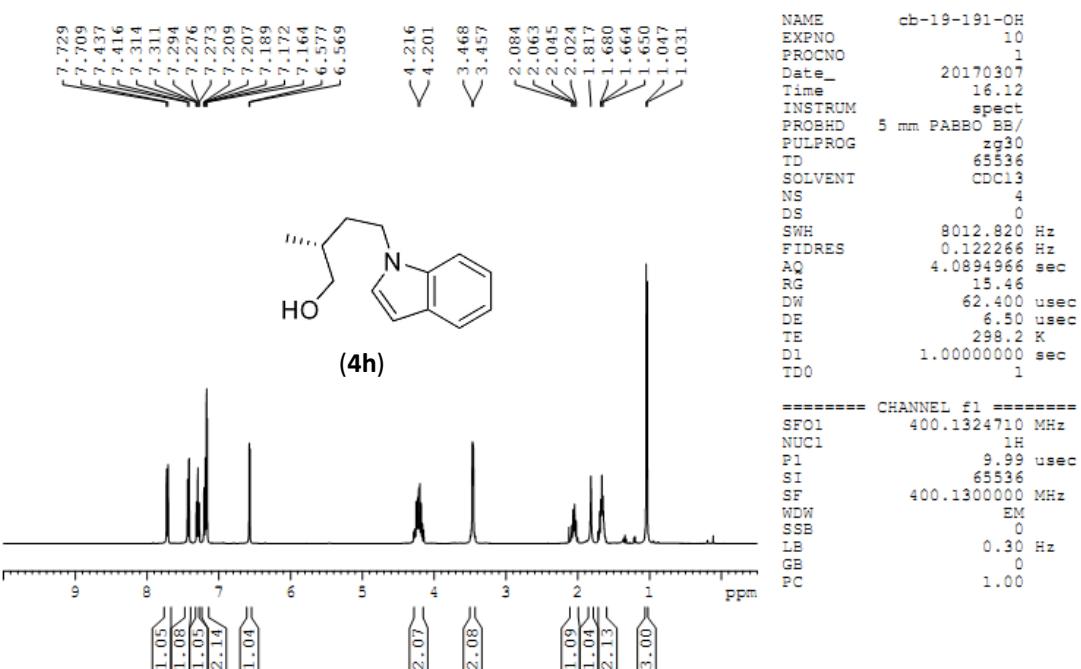
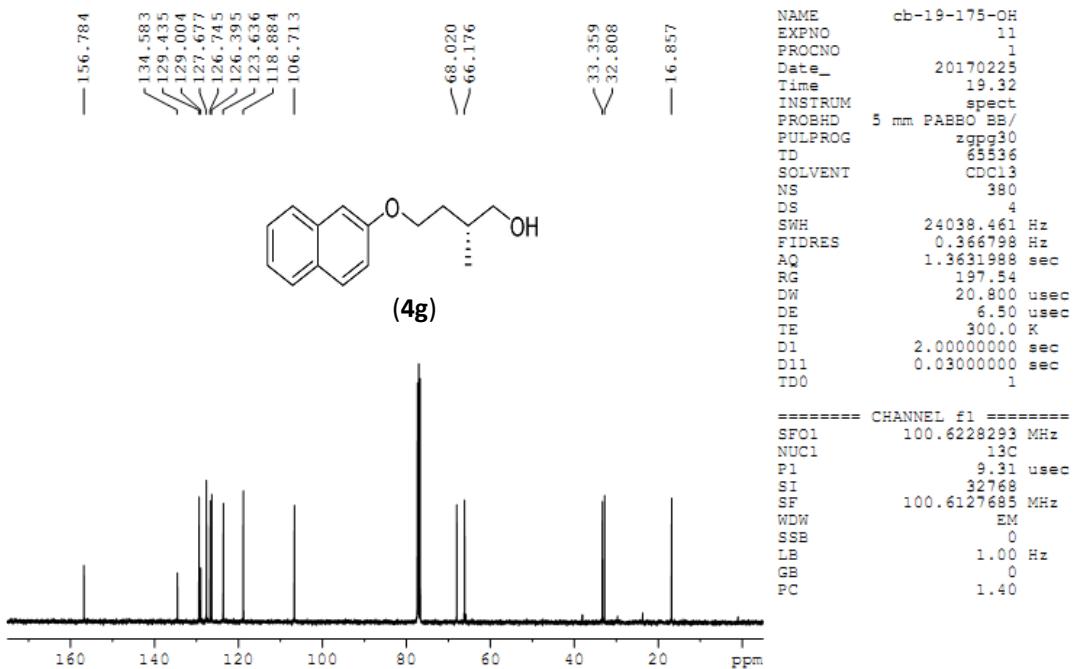


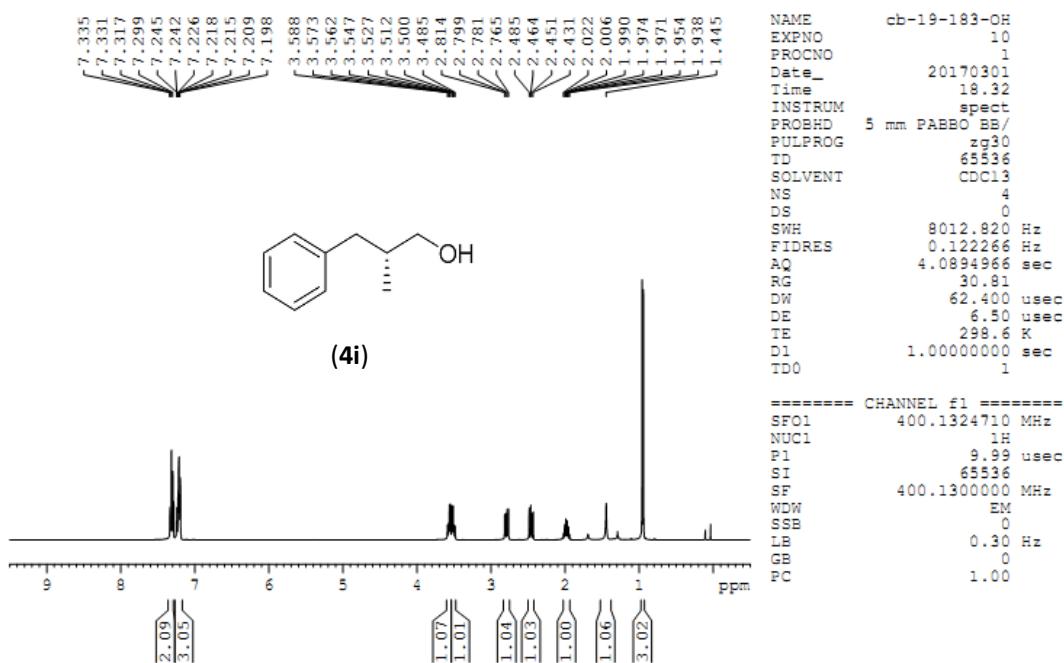
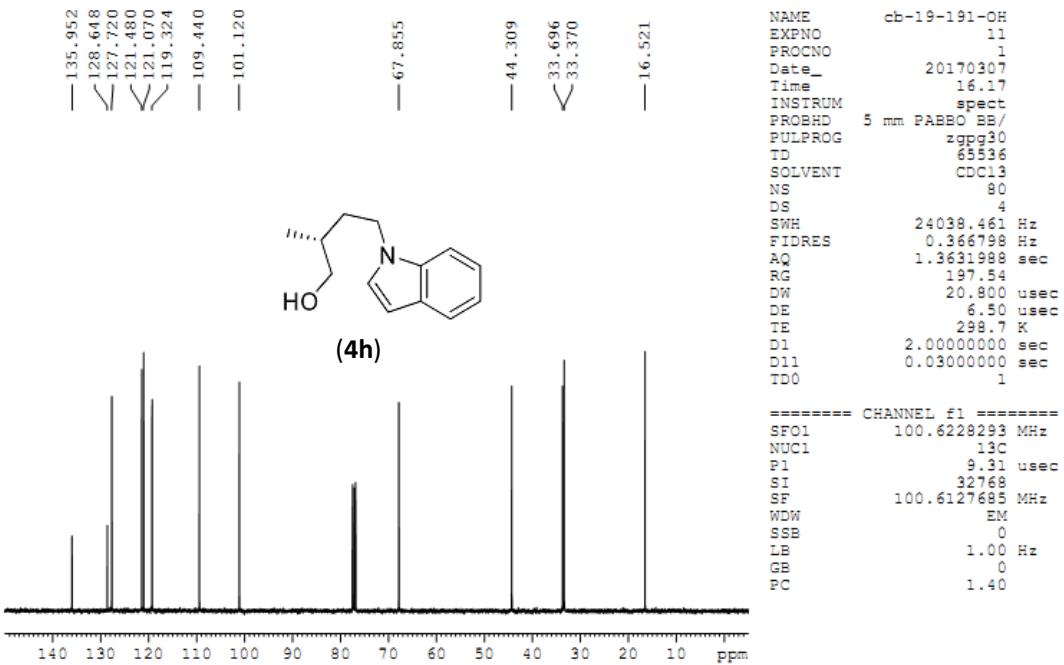


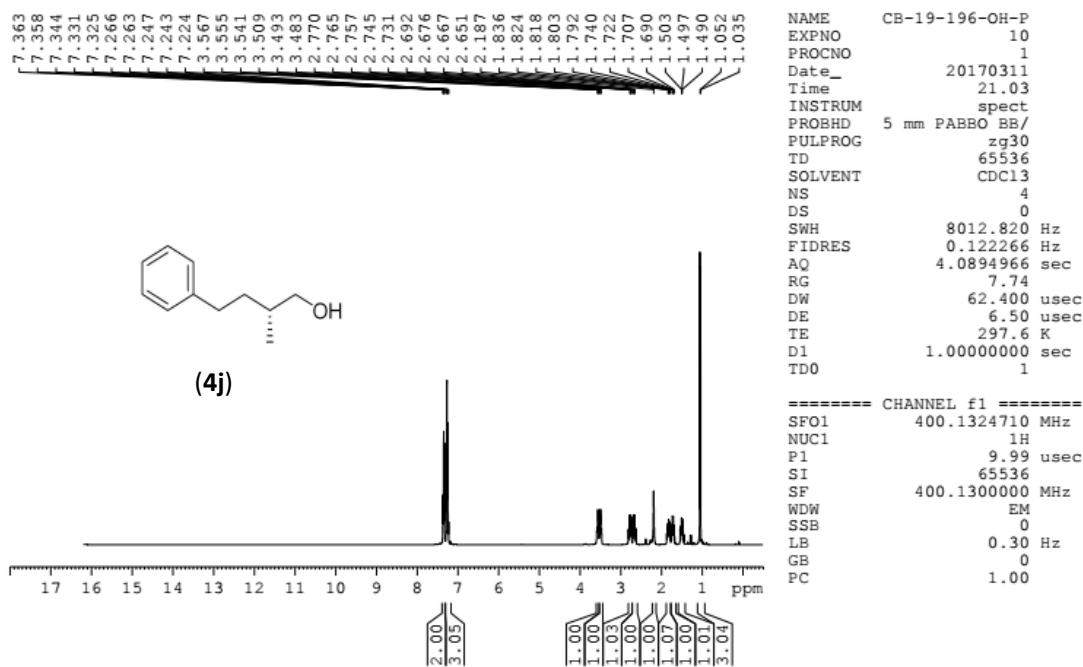
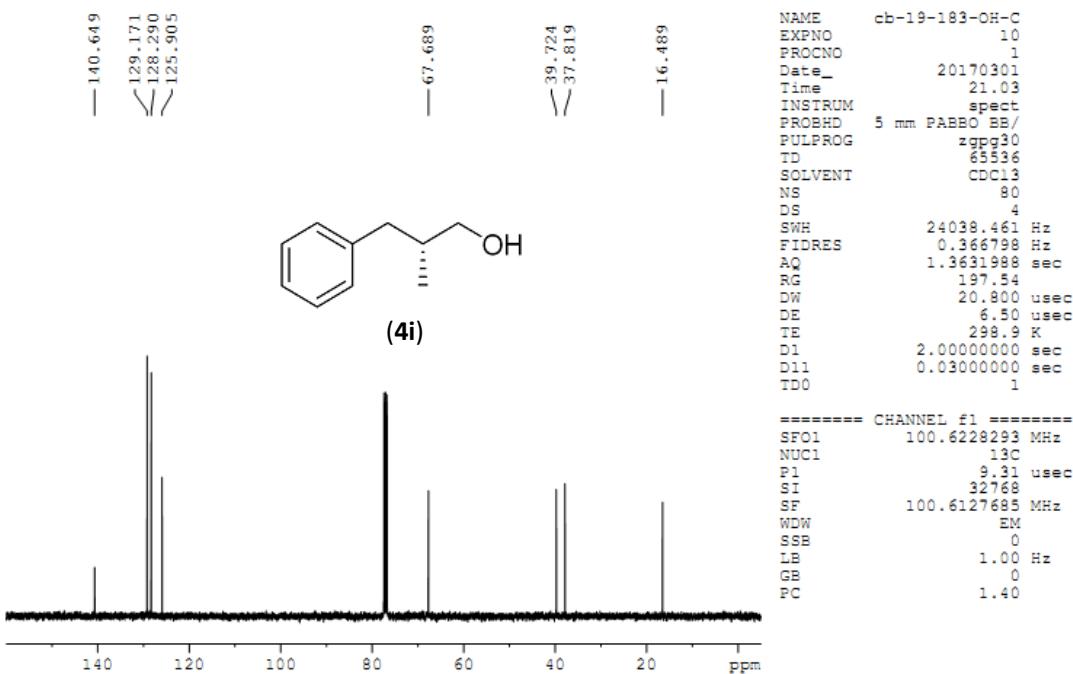


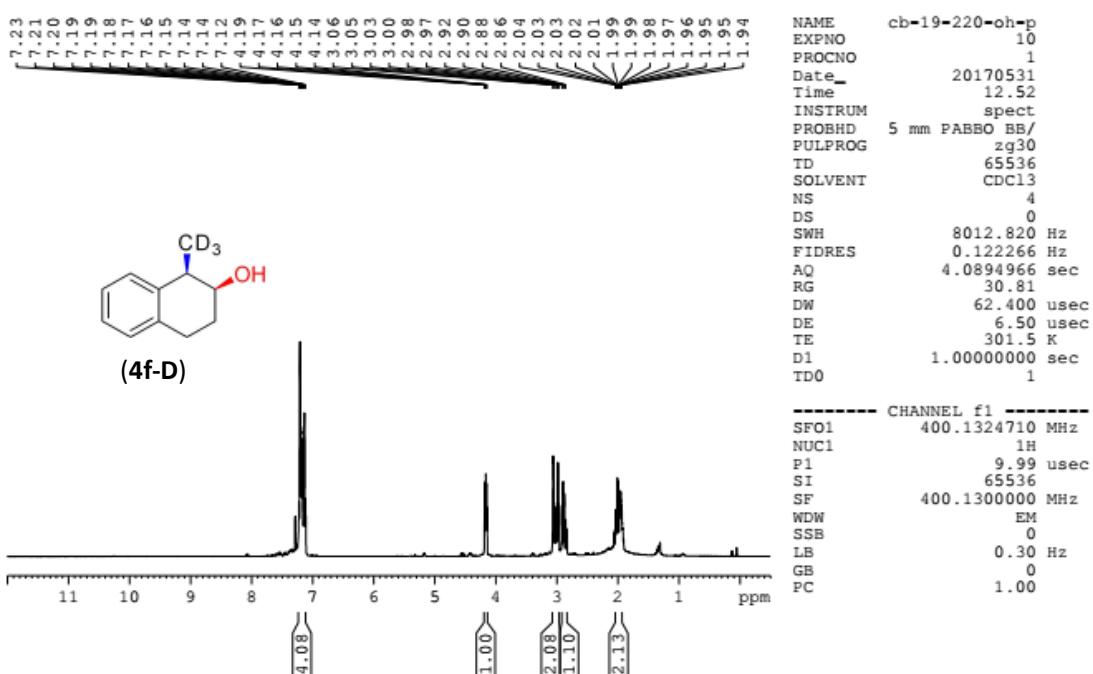
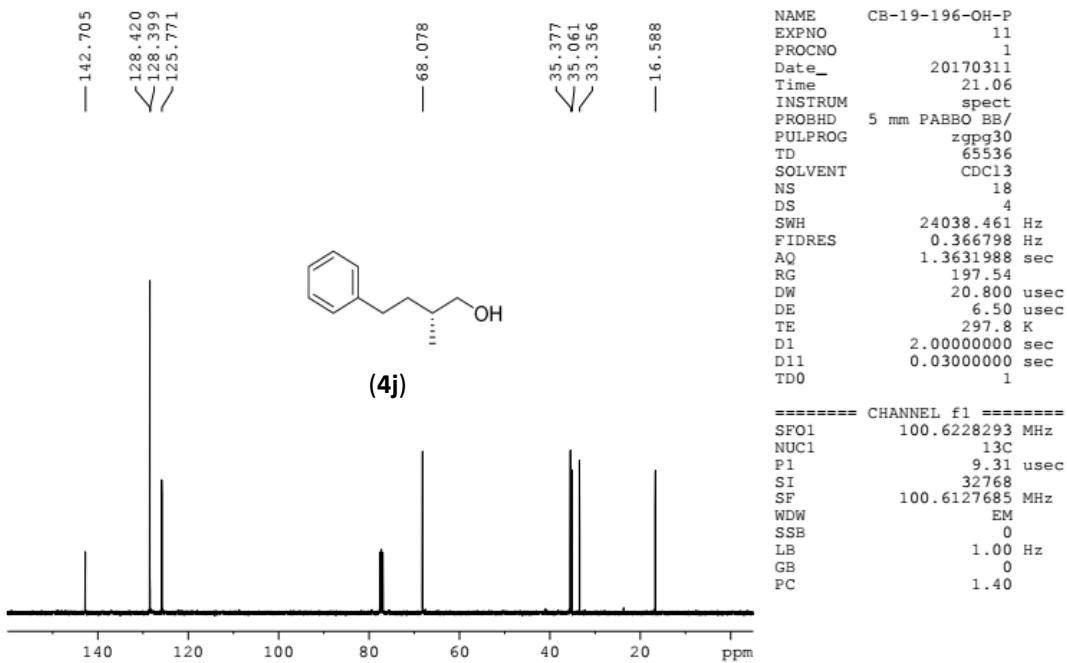


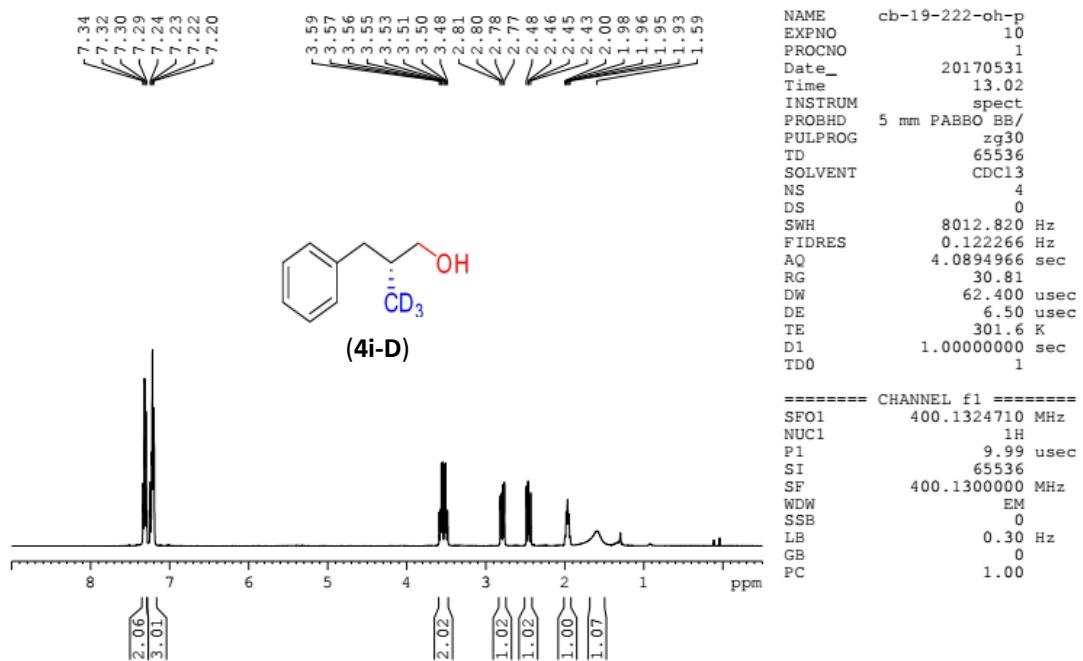
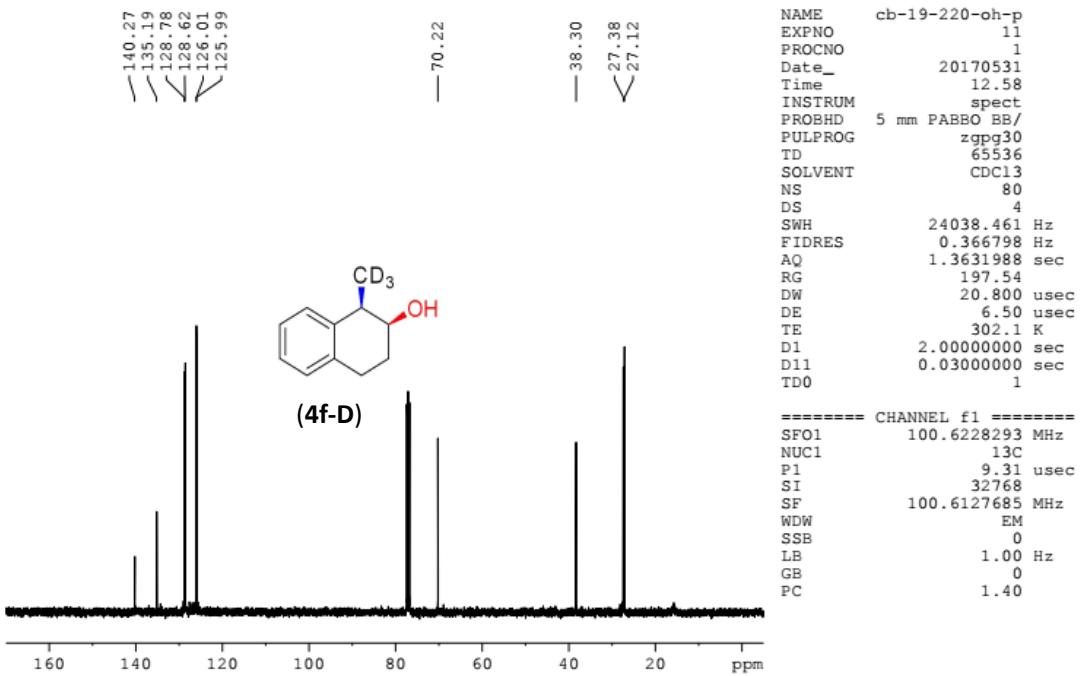


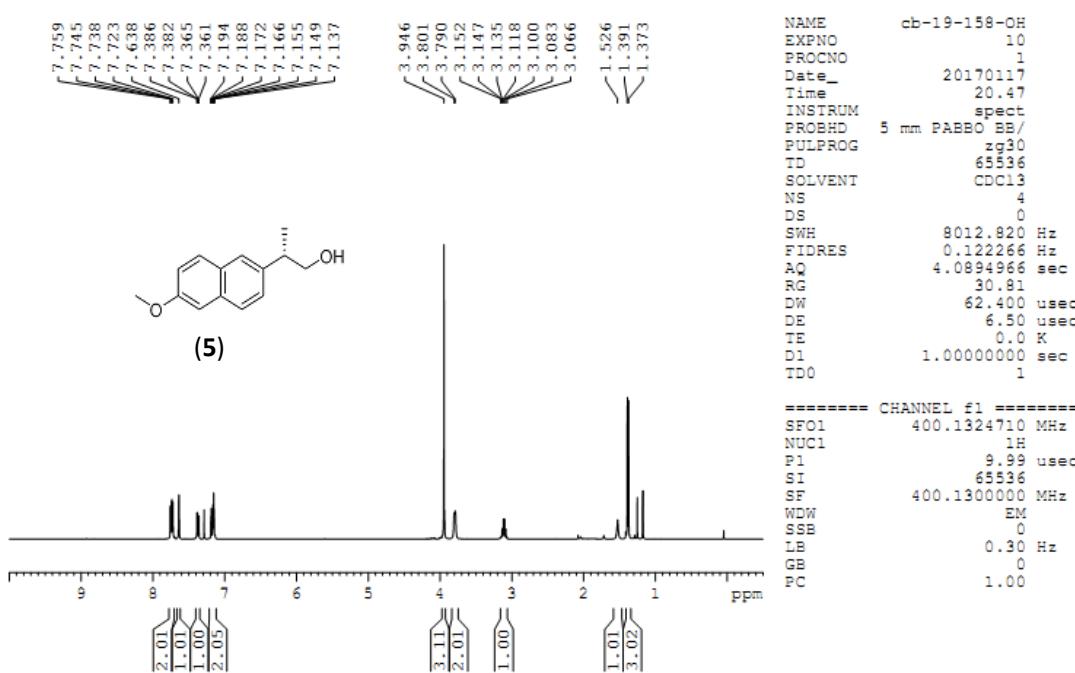
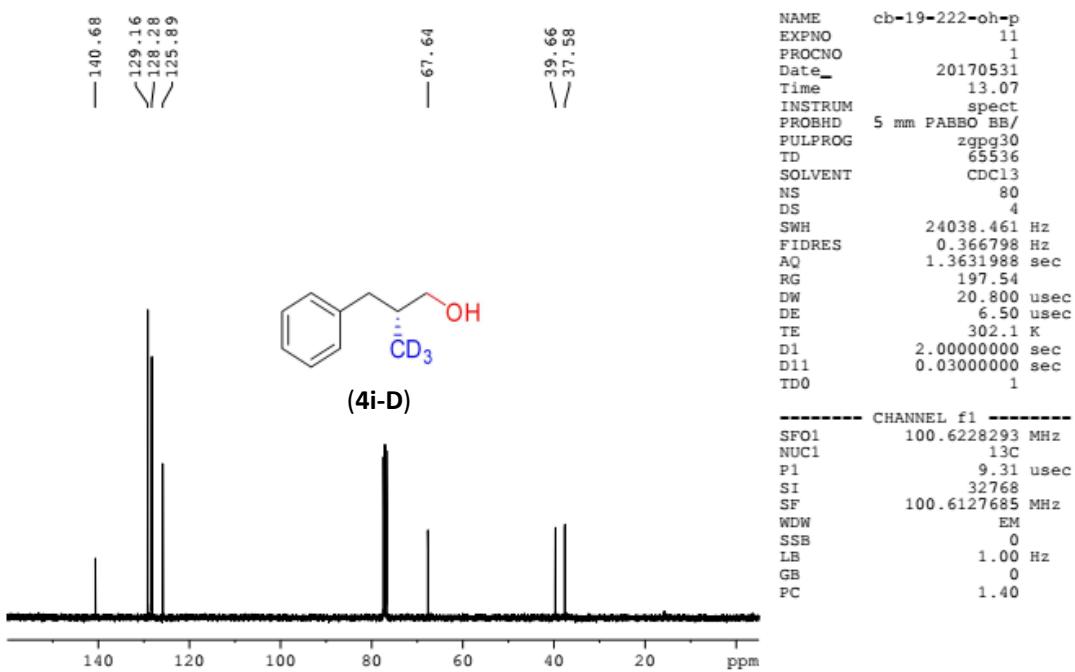


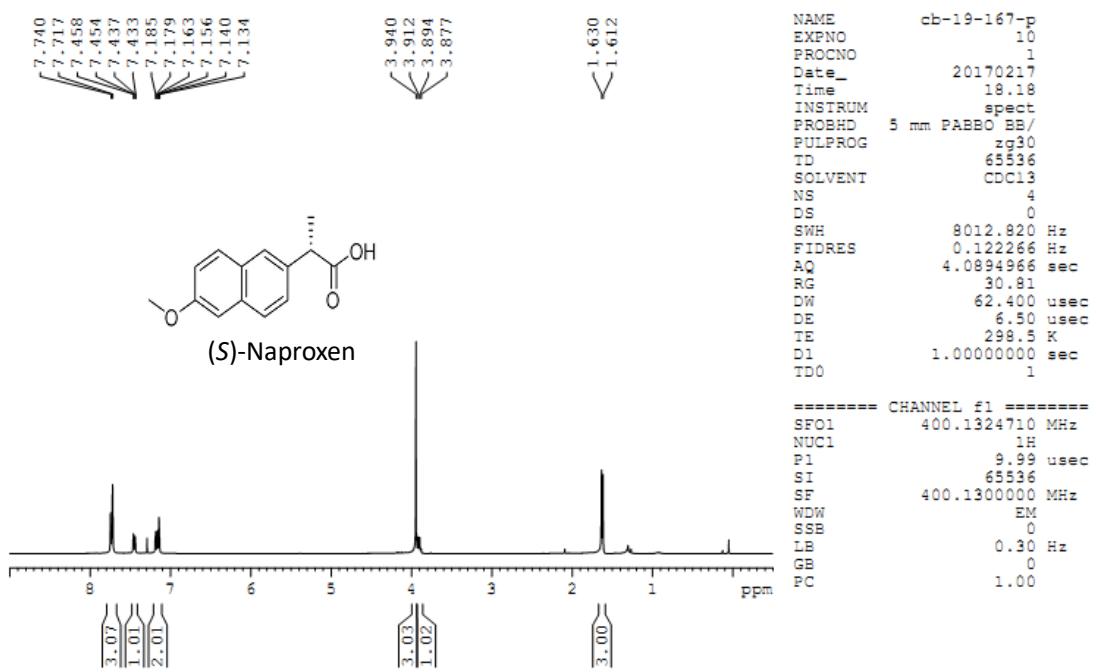
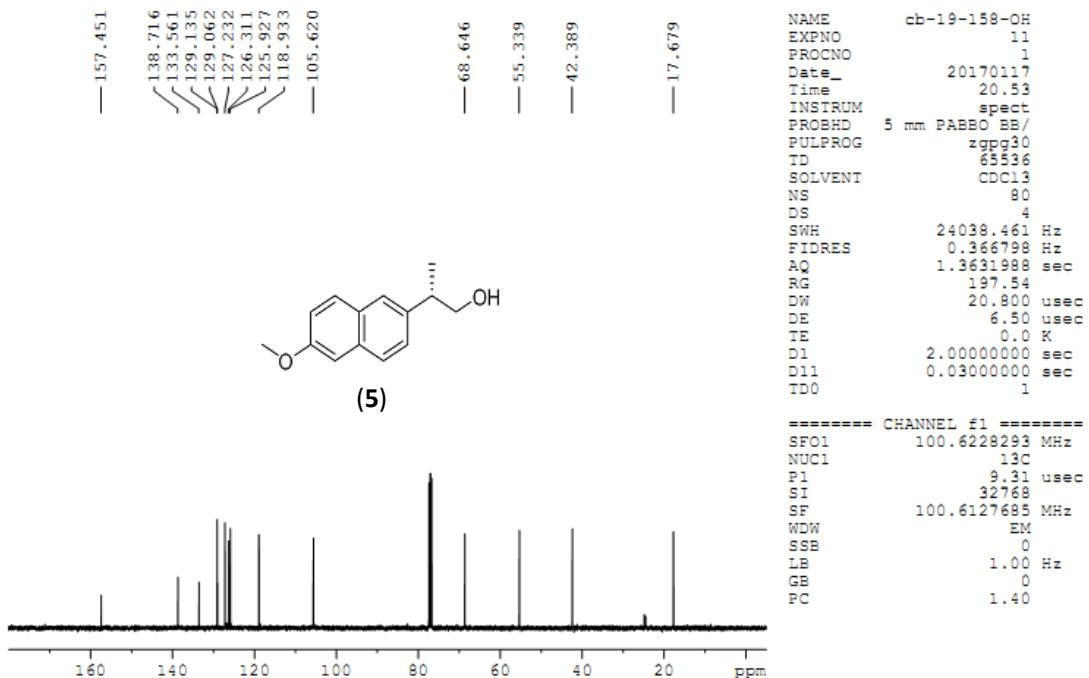


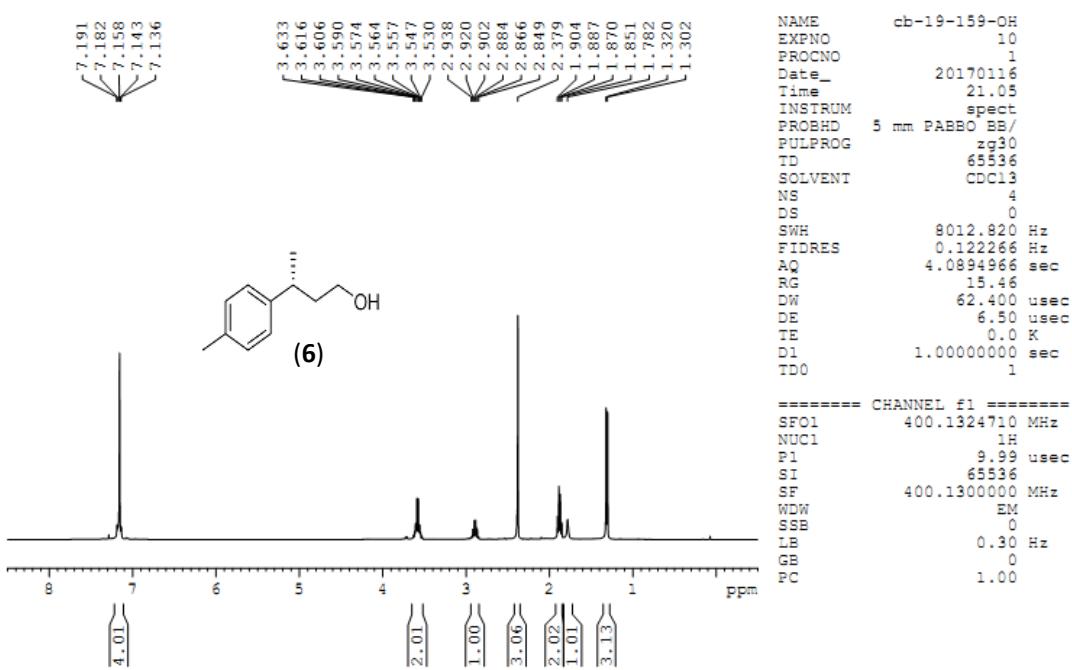
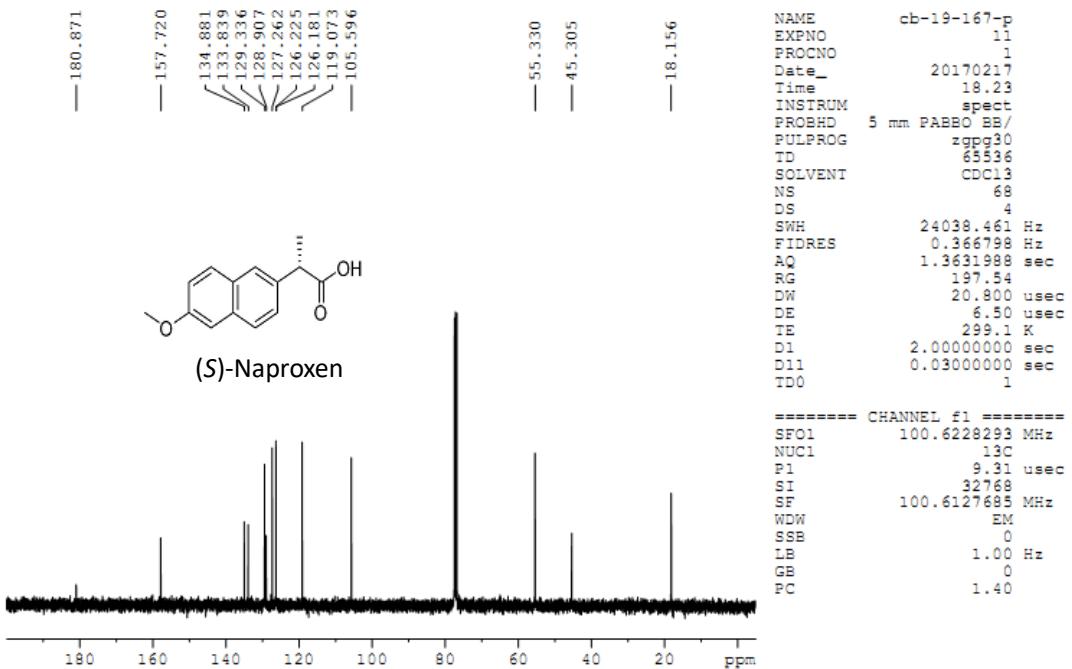


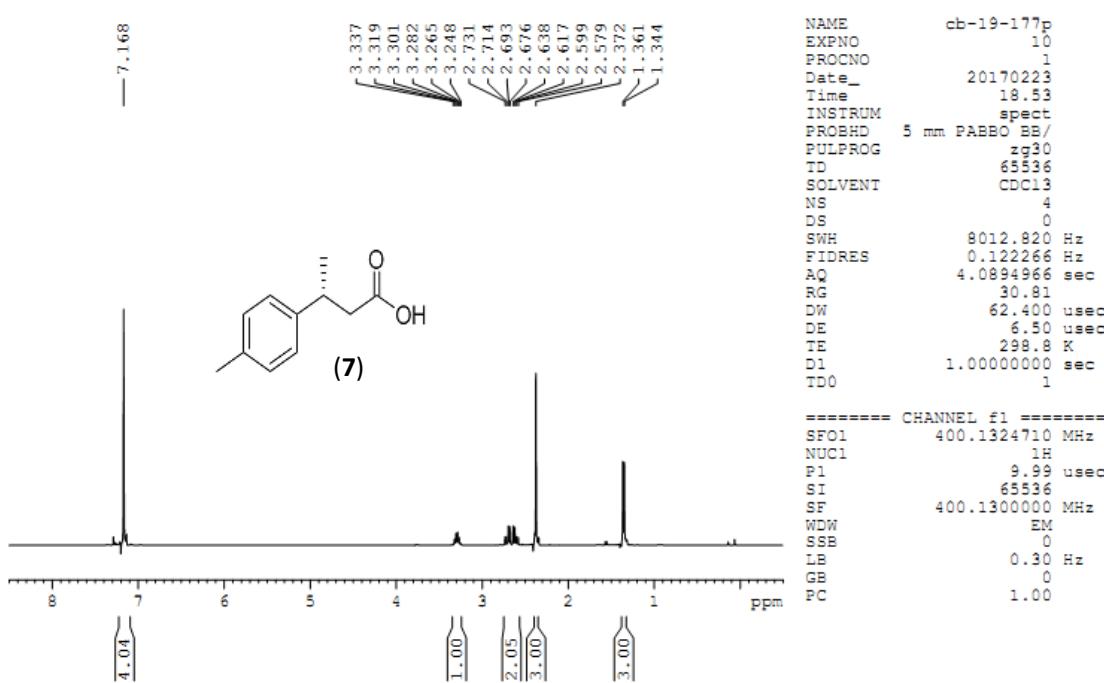
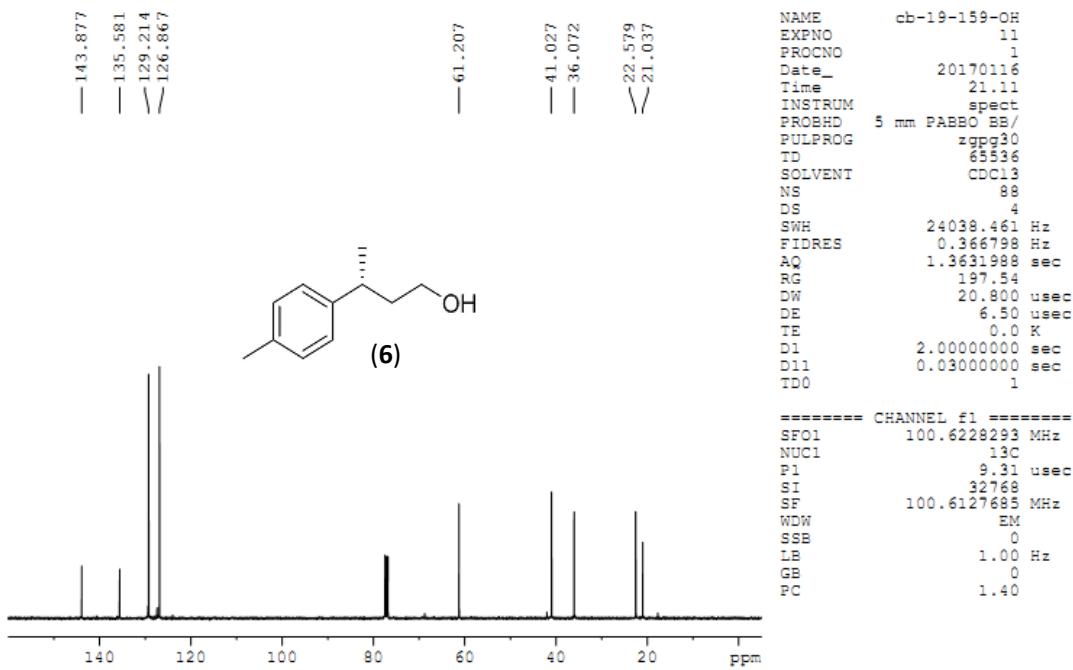


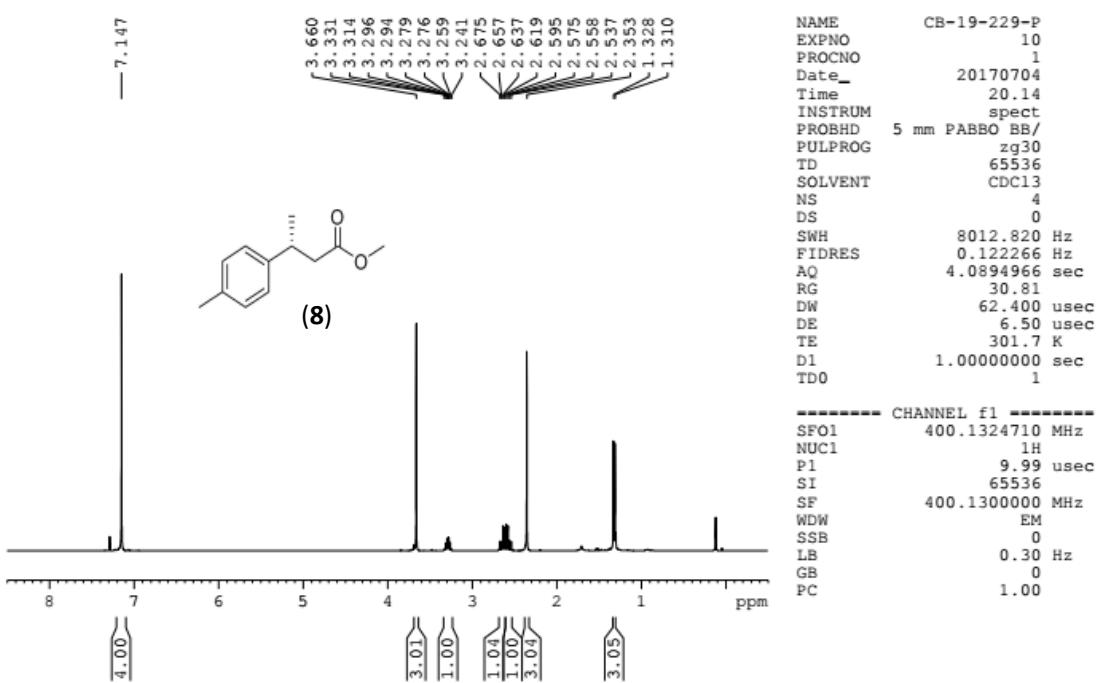
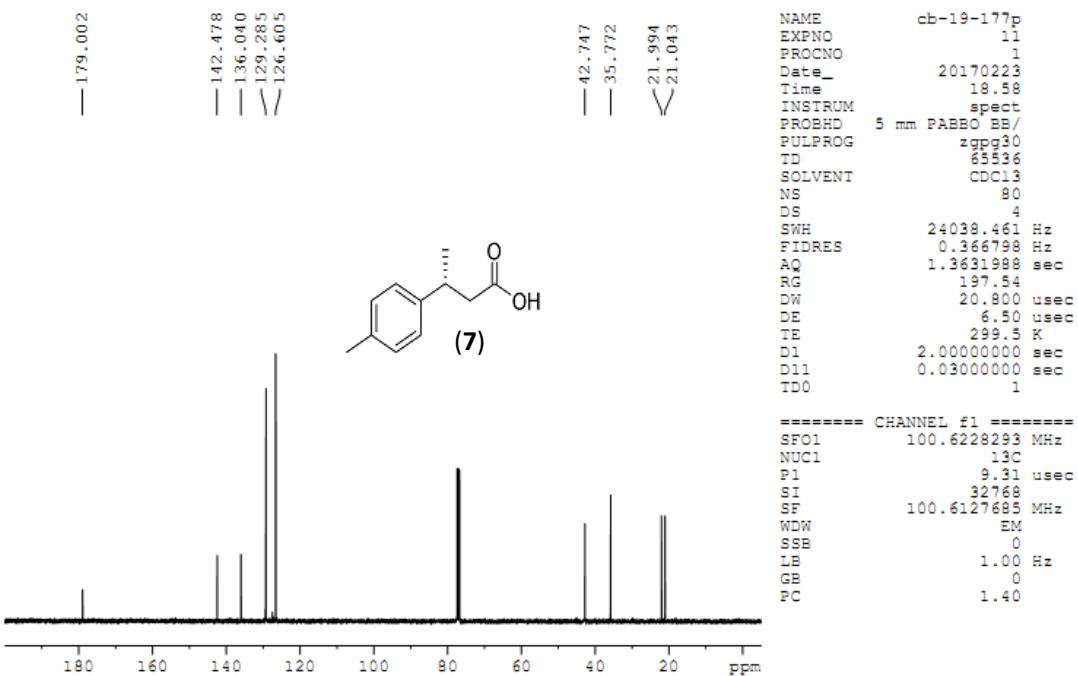


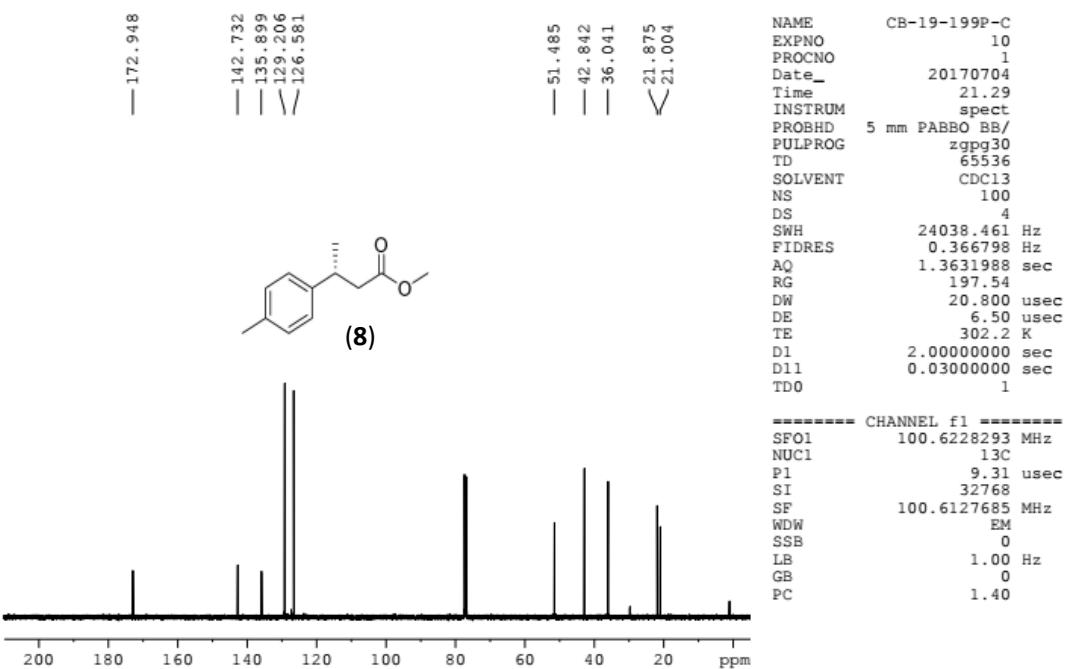




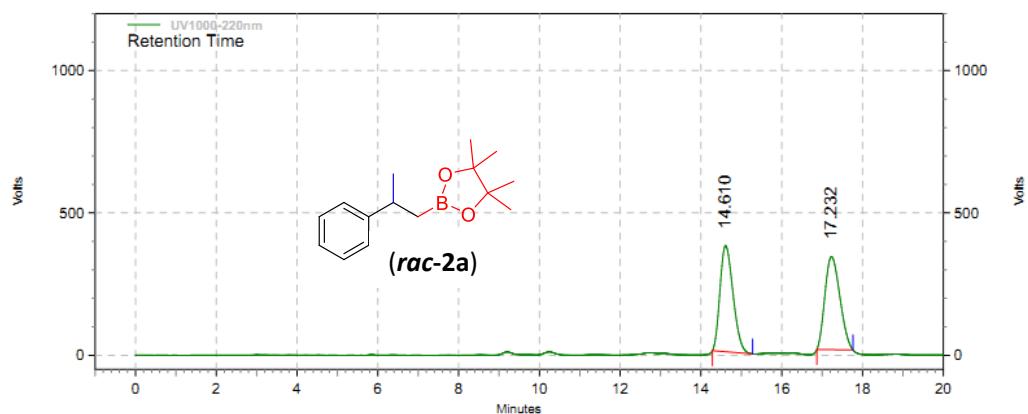






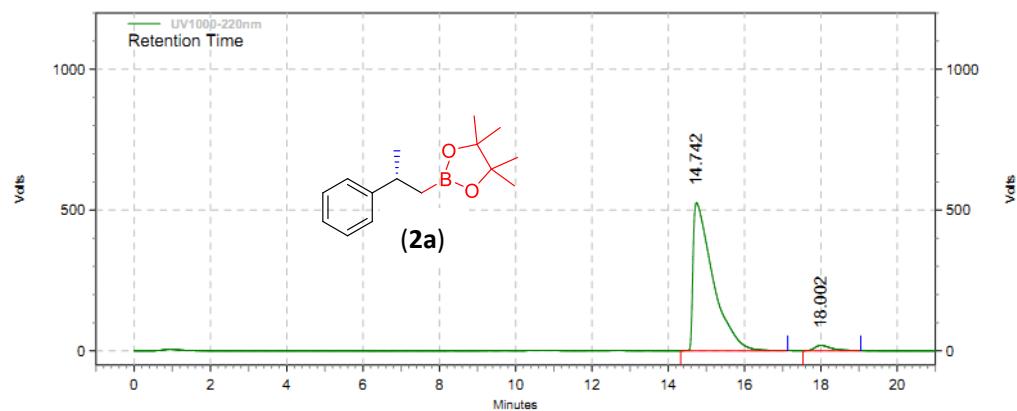


HPLC



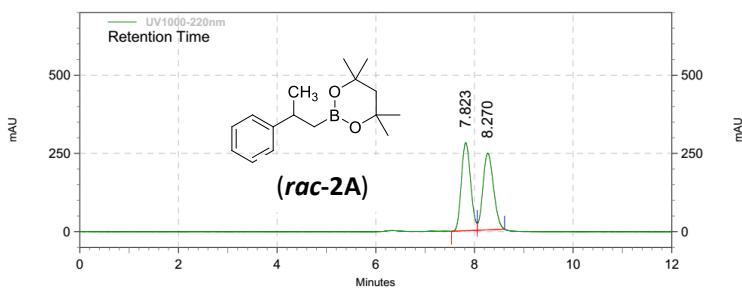
UV1000-220nm
Results

Retention Time	Area	Area %	Height	Height %
14.610	8385510	49.98	372936	53.31
17.232	8391552	50.02	326621	46.69
Totals	16777062	100.00	699557	100.00



UV1000-220nm
Results

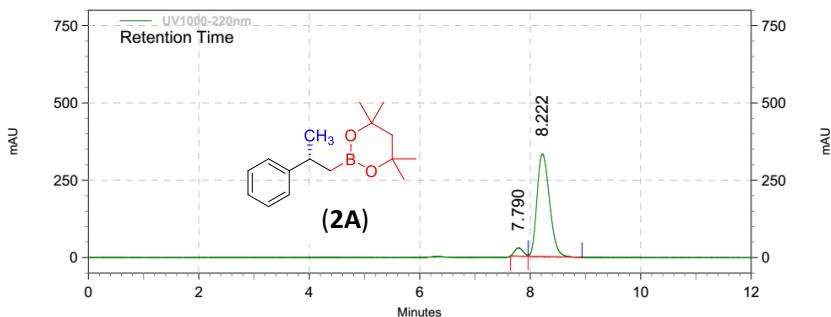
Retention Time	Area	Area %	Height	Height %
14.742	18992727	97.08	525174	96.50
18.002	570797	2.92	19036	3.50
Totals	19563524	100.00	544210	100.00



UV1000-220nm

Results

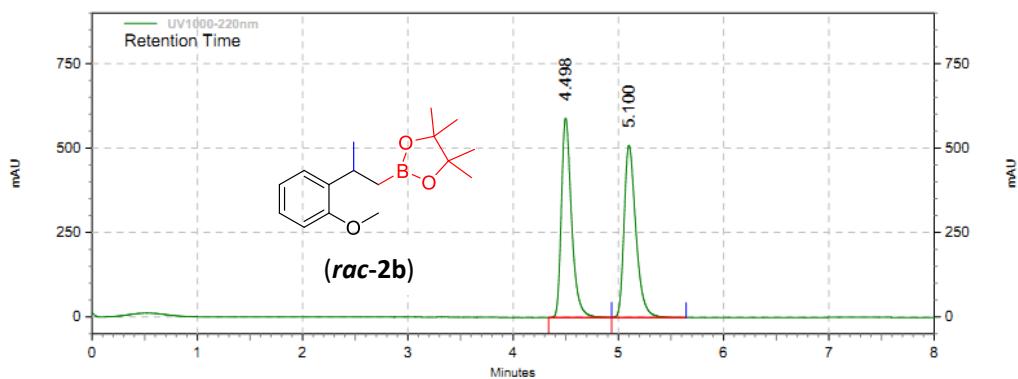
Retention Time	Area	Area %	Height	Height %
7.823	3655872	50.03	280995	53.44
8.270	3651052	49.97	244811	46.56
Totals	7306924	100.00	525806	100.00



UV1000-220nm

Results

Retention Time	Area	Area %	Height	Height %
7.790	281249	5.10	26497	7.39
8.222	5233258	94.90	331869	92.61
Totals	5514507	100.00	358366	100.00

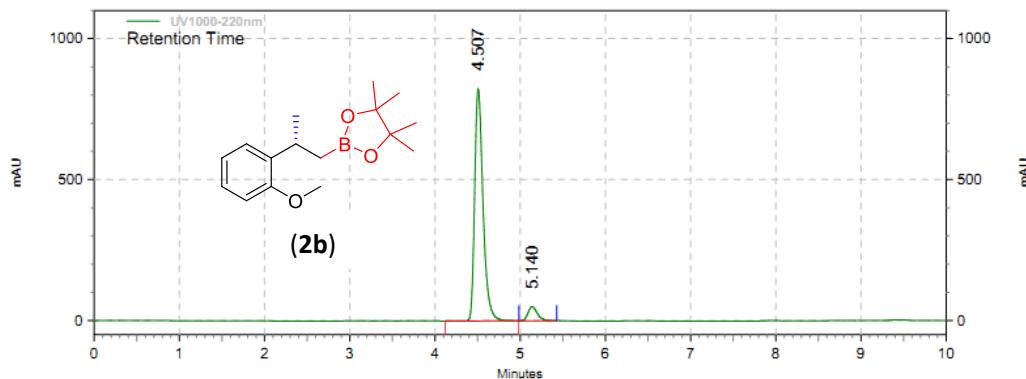


UV1000-220nm

Results

Retention Time	Area	Area %	Height	Height %
4.498	3979942	50.02	590787	53.66
5.100	3976328	49.98	510236	46.34

Totals	7956270	100.00	1101023	100.00
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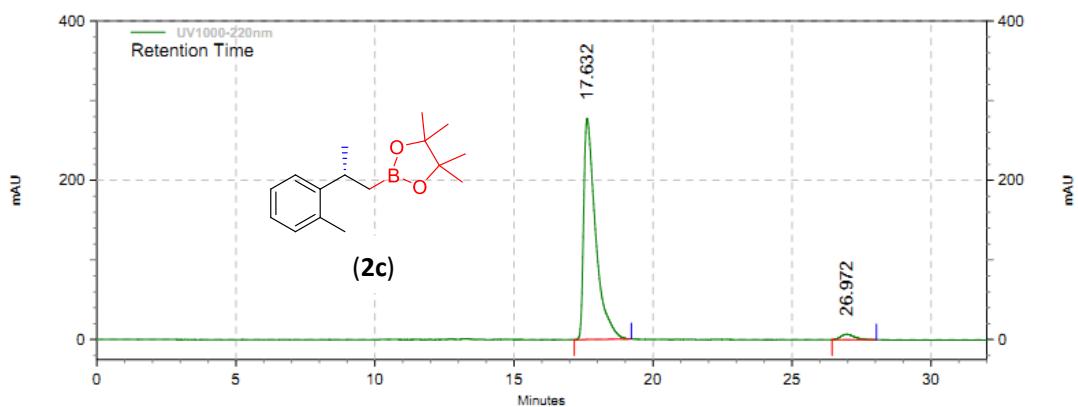
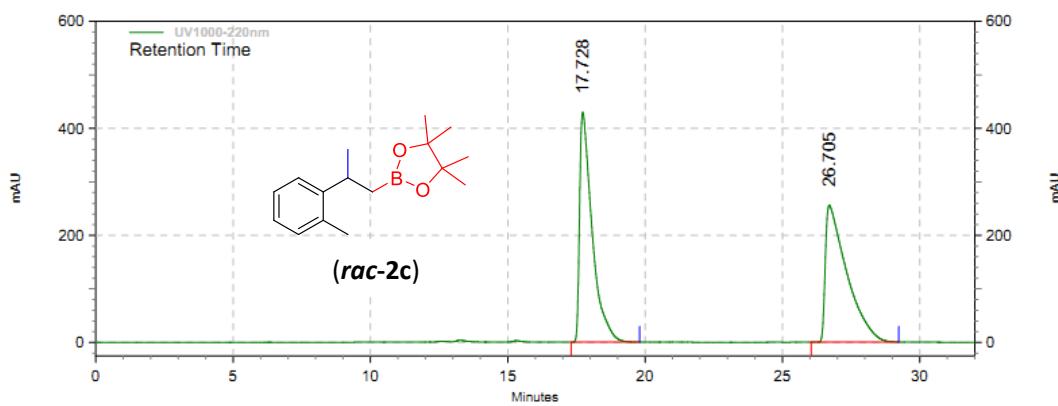


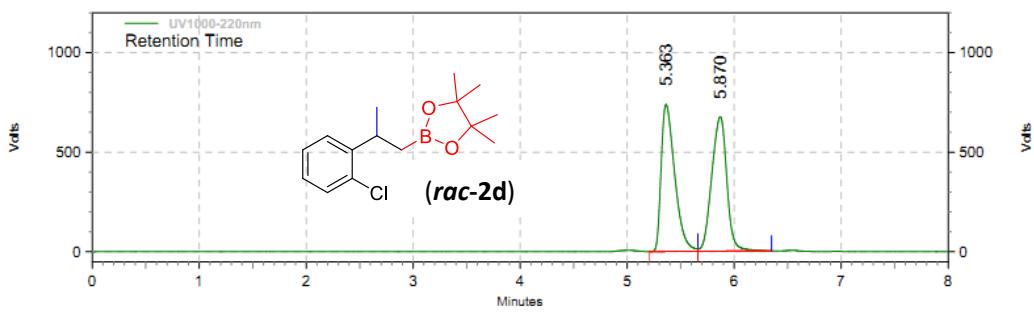
UV1000-220nm

Results

Retention Time	Area	Area %	Height	Height %
4.507	5639752	93.55	824274	94.21
5.140	389099	6.45	50615	5.79

Totals	6028851	100.00	874889	100.00
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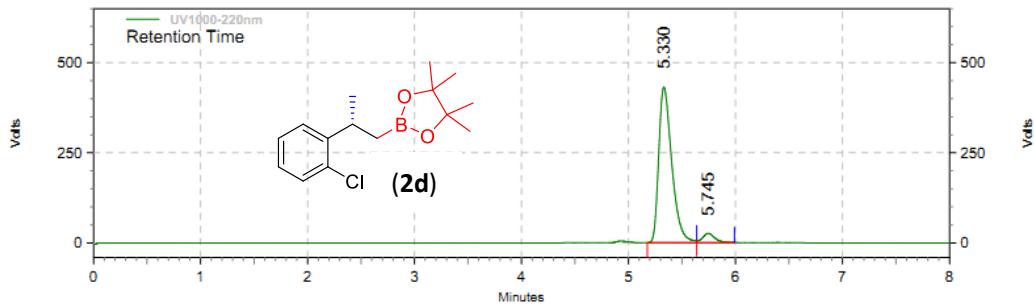




UV1000-220nm

Results

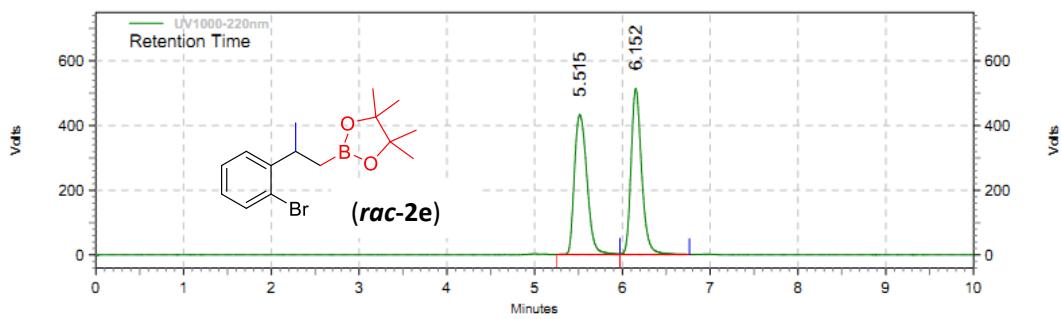
Retention Time	Area	Area %	Height	Height %
5.363	6513047	49.62	737694	52.24
5.870	6613475	50.38	674503	47.76
Totals	13126522	100.00	1412197	100.00



UV1000-220nm

Results

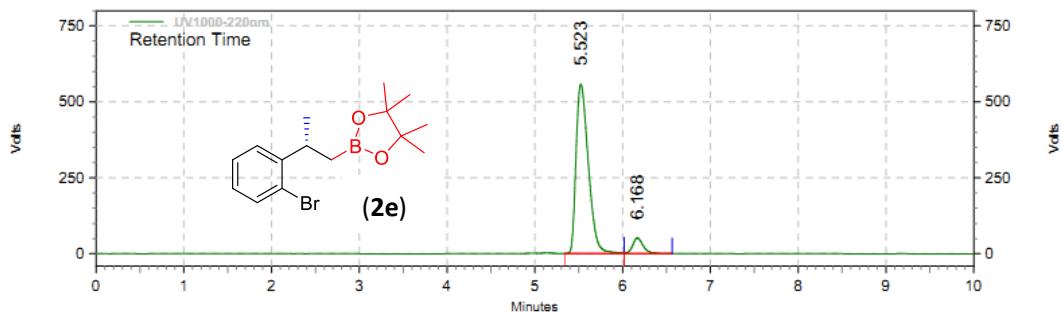
Retention Time	Area	Area %	Height	Height %
5.330	3658603	94.75	431341	94.41
5.745	202800	5.25	25536	5.59
Totals	3861403	100.00	456877	100.00



UV1000-220nm

Results

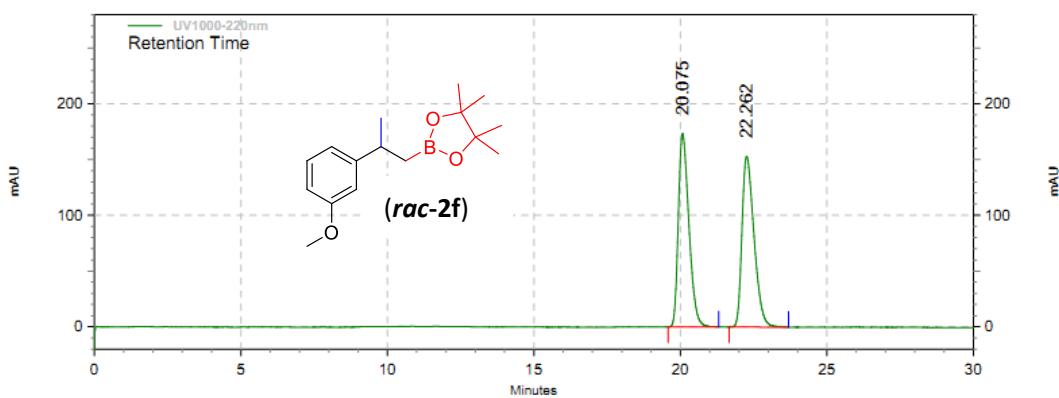
Retention Time	Area	Area %	Height	Height %
5.515	4299249	50.03	432027	45.75
6.152	4293775	49.97	512396	54.25
Totals	8593024	100.00	944423	100.00



UV1000-220nm

Results

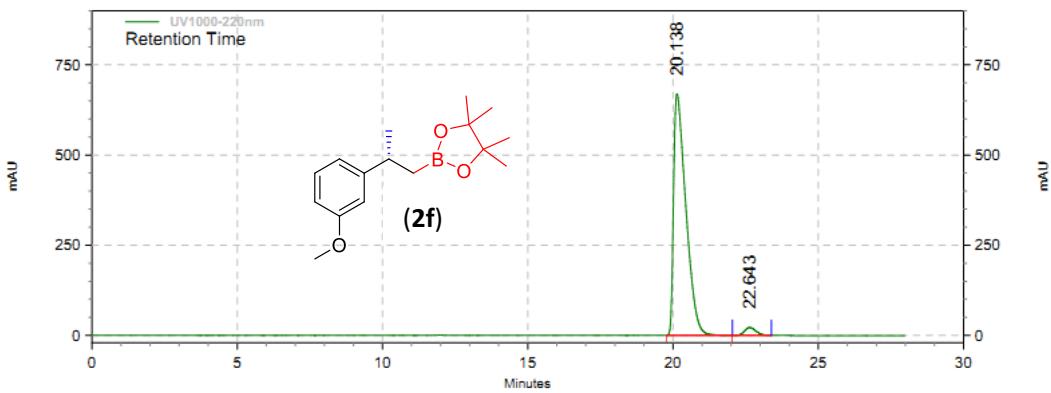
Retention Time	Area	Area %	Height	Height %
5.523	5420434	92.69	556963	91.57
6.168	427524	7.31	51278	8.43
Totals	5847958	100.00	608241	100.00



UV1000-220nm

Results

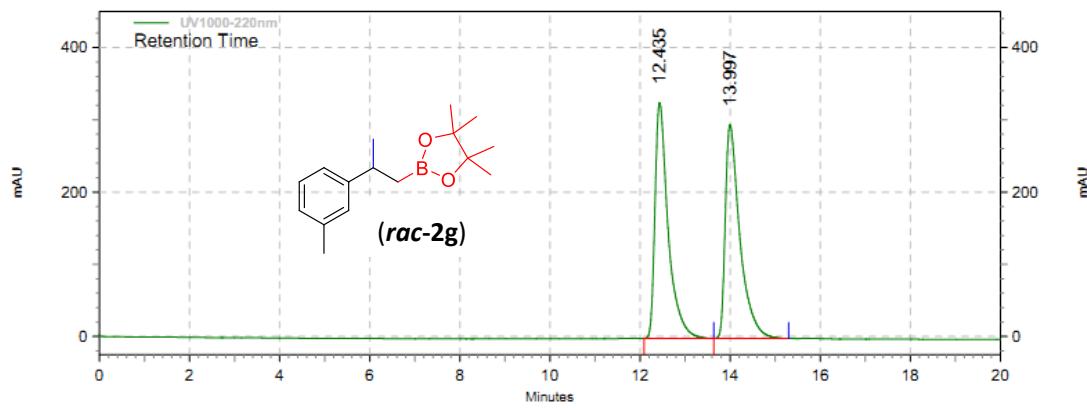
Retention Time	Area	Area %	Height	Height %
20.075	4353476	49.83	173409	53.10
22.262	4383500	50.17	153159	46.90
Totals	8736976	100.00	326568	100.00



UV1000-220nm

Results

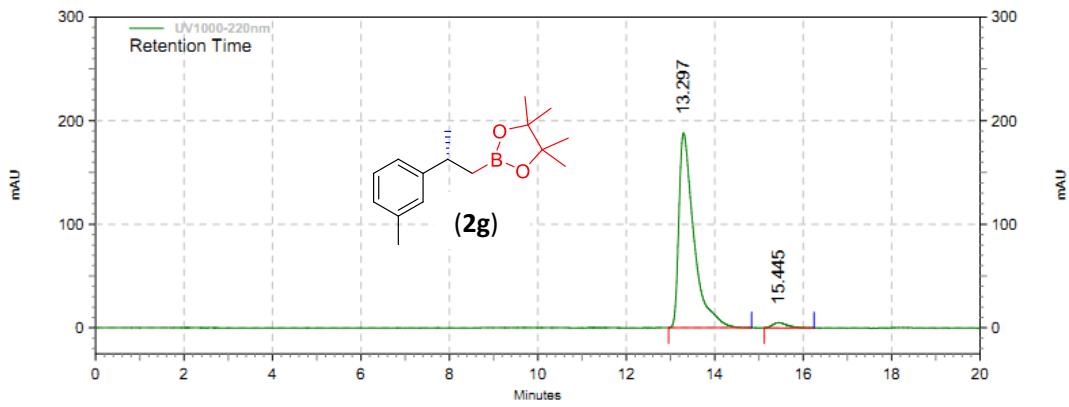
Retention Time	Area	Area %	Height	Height %
20.138	19713748	96.99	669960	96.82
22.643	611737	3.01	22026	3.18
Totals	20325485	100.00	691986	100.00



UV1000-220nm

Results

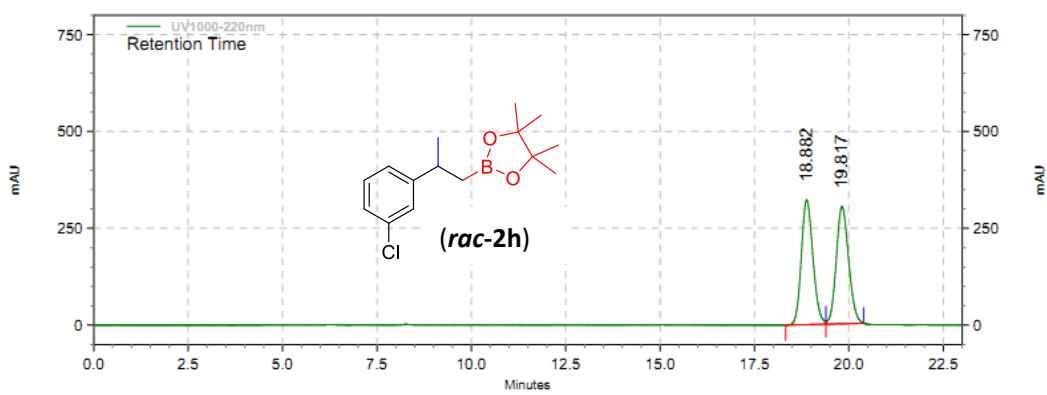
Retention Time	Area	Area %	Height	Height %
12.435	6619991	49.84	326466	52.45
13.997	6663677	50.16	296011	47.55
Totals	13283668	100.00	622477	100.00



UV1000-220nm

Results

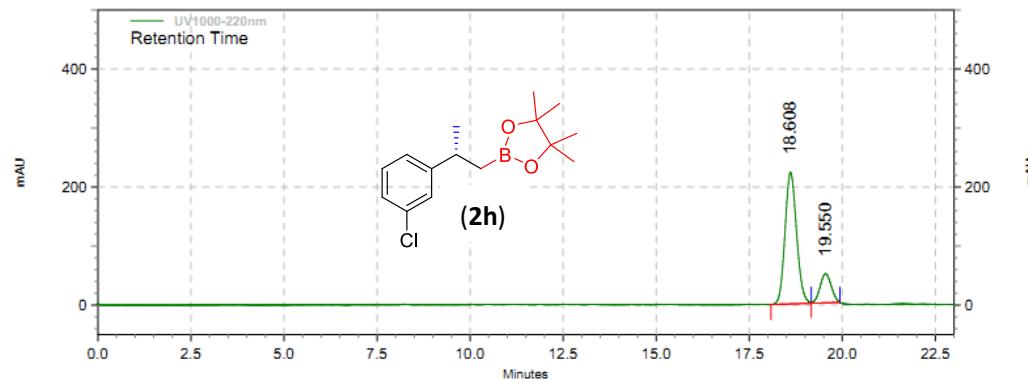
Retention Time	Area	Area %	Height	Height %
13.297	4439258	97.41	187915	97.39
15.445	118145	2.59	5041	2.61
Totals	4557403	100.00	192956	100.00



UV1000-220nm

Results

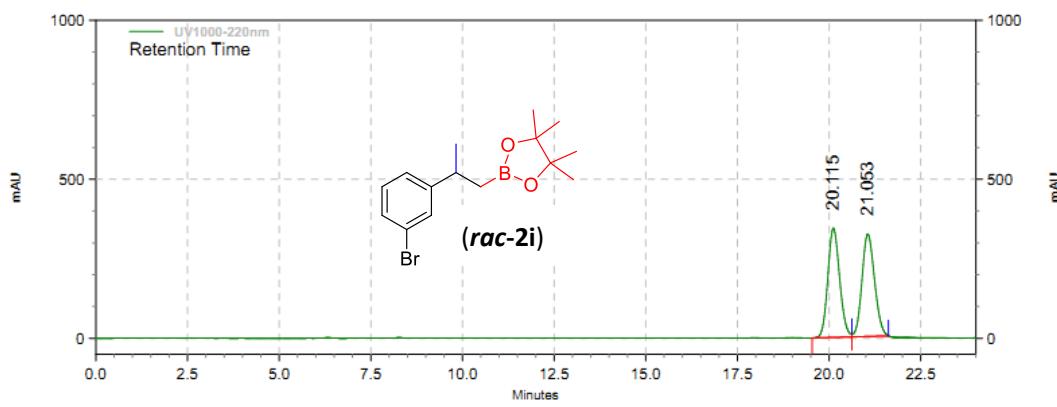
Retention Time	Area	Area %	Height	Height %
18.882	6862882	49.93	321453	51.52
19.817	6882652	50.07	302438	48.48
Totals	13745534	100.00	623891	100.00



UV1000-220nm

Results

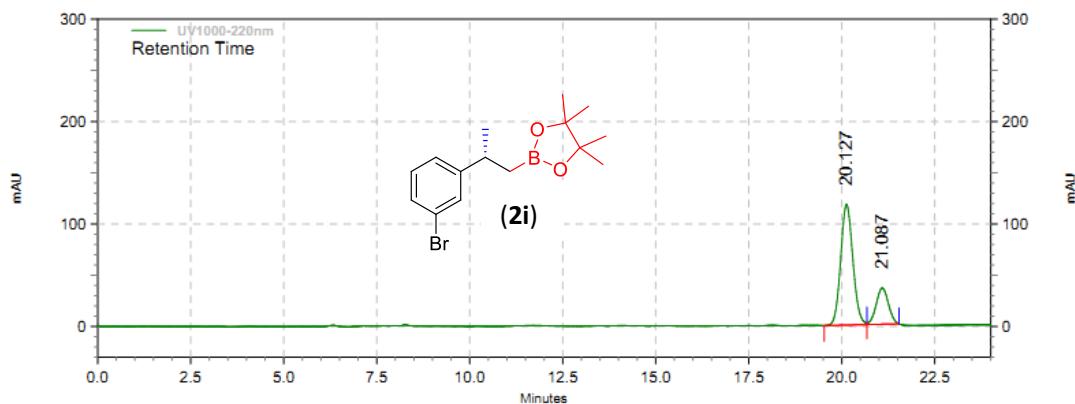
Retention Time	Area	Area %	Height	Height %
18.608	4791635	82.30	223087	81.92
19.550	1030709	17.70	49230	18.08
Totals	5822344	100.00	272317	100.00



UV1000-220nm

Results

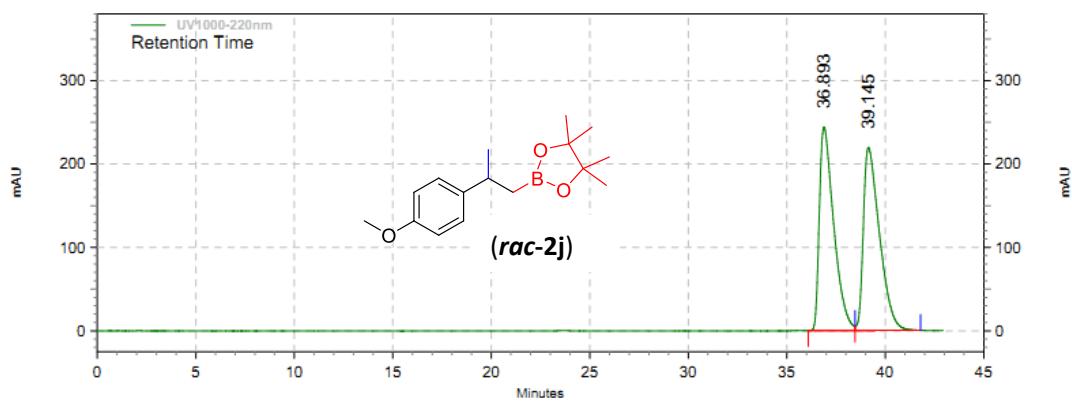
Retention Time	Area	Area %	Height	Height %
20.115	7668416	50.00	343502	51.60
21.053	7667939	50.00	322190	48.40
Totals	15336355	100.00	665692	100.00



UV1000-220nm

Results

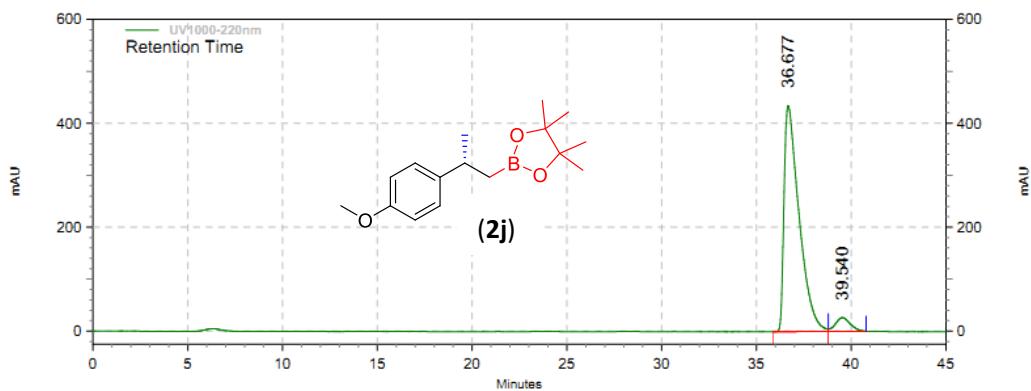
Retention Time	Area	Area %	Height	Height %
20.127	2679172	76.82	117721	76.93
21.087	808272	23.18	35303	23.07
Totals	3487444	100.00	153024	100.00



UV1000-220nm

Results

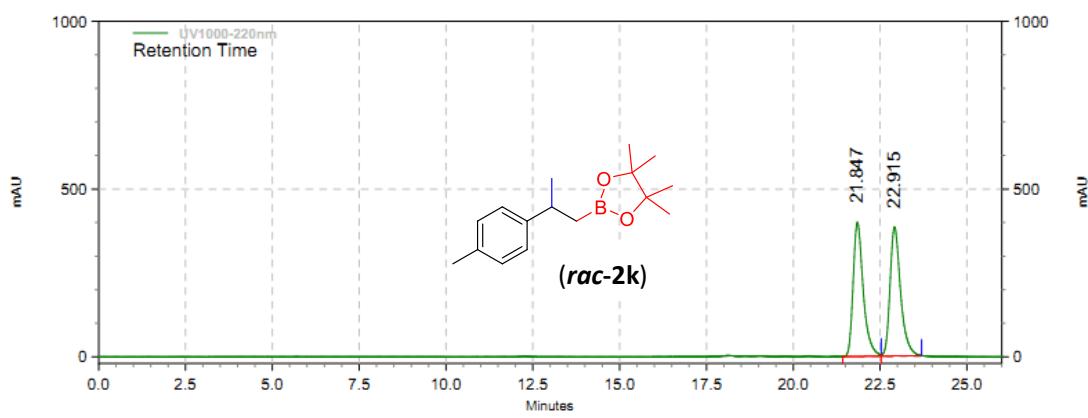
Retention Time	Area	Area %	Height	Height %
36.893	12405261	49.81	244160	52.66
39.145	12501299	50.19	219512	47.34
Totals	24906560	100.00	463672	100.00



UV1000-220nm

Results

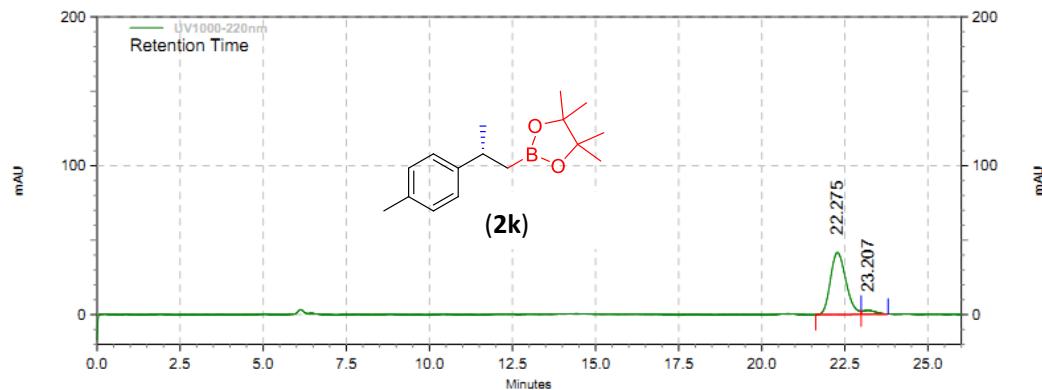
Retention Time	Area	Area %	Height	Height %
36.677	23966279	94.34	435002	94.28
39.540	1437904	5.66	26394	5.72
Totals	25404183	100.00	461396	100.00



UV1000-220nm

Results

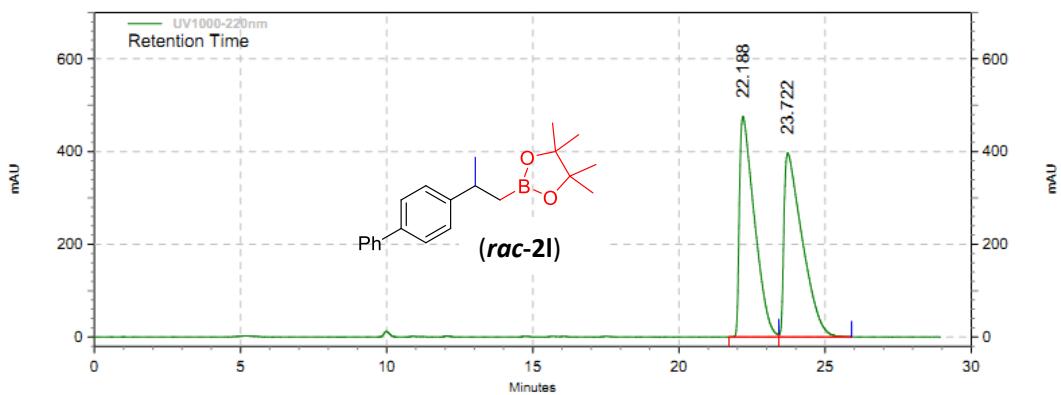
Retention Time	Area	Area %	Height	Height %
21.847	8091601	49.85	399680	50.94
22.915	8140409	50.15	384890	49.06
Totals	16232010	100.00	784570	100.00



UV1000-220nm

Results

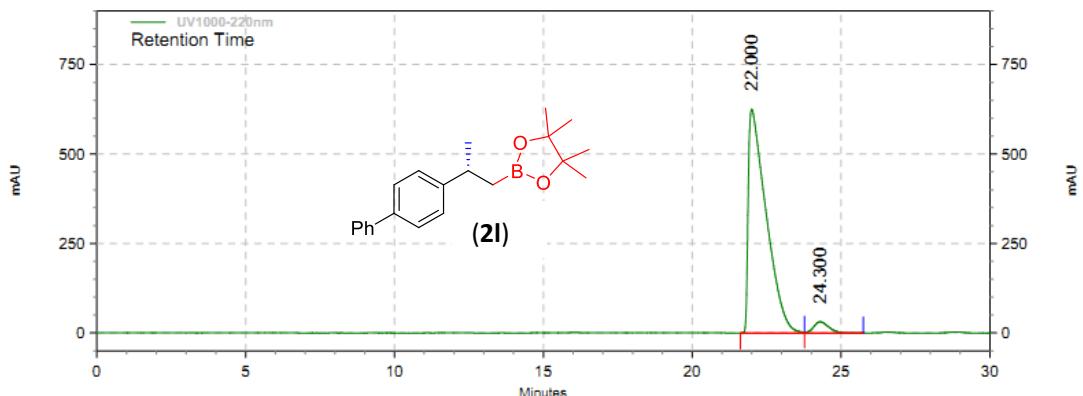
Retention Time	Area	Area %	Height	Height %
22.275	1347045	94.90	41662	94.12
23.207	72464	5.10	2604	5.88
Totals	1419509	100.00	44266	100.00



UV1000-220nm

Results

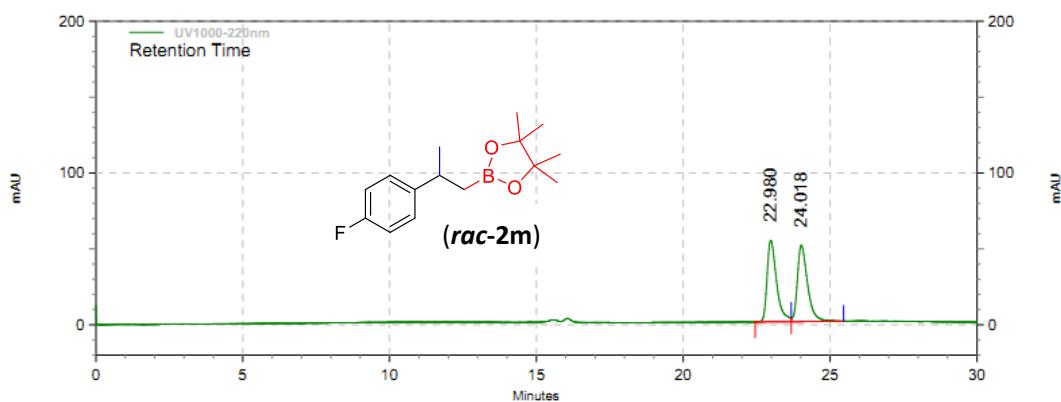
Retention Time	Area	Area %	Height	Height %
22.188	16977696	49.54	475504	54.51
23.722	17292475	50.46	396887	45.49
Totals	34270171	100.00	872391	100.00



UV1000-220nm

Results

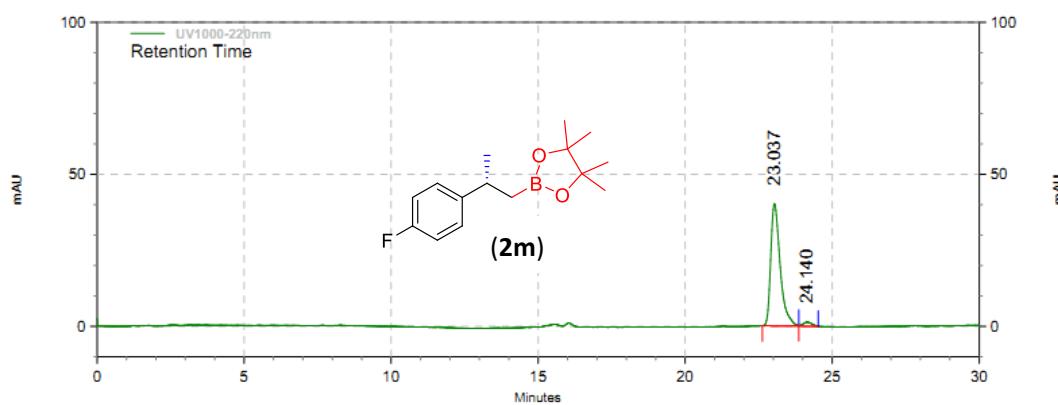
Retention Time	Area	Area %	Height	Height %
22.000	26219499	95.96	625606	95.23
24.300	1104451	4.04	31345	4.77
Totals	27323950	100.00	656951	100.00



UV1000-220nm

Results

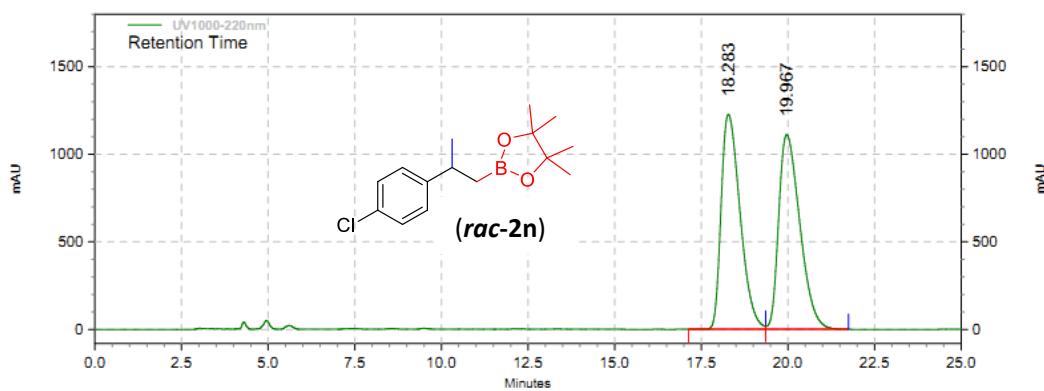
Retention Time	Area	Area %	Height	Height %
22.980	1209098	49.91	53665	51.59
24.018	1213337	50.09	50350	48.41
Totals	2422435	100.00	104015	100.00



UV1000-220nm

Results

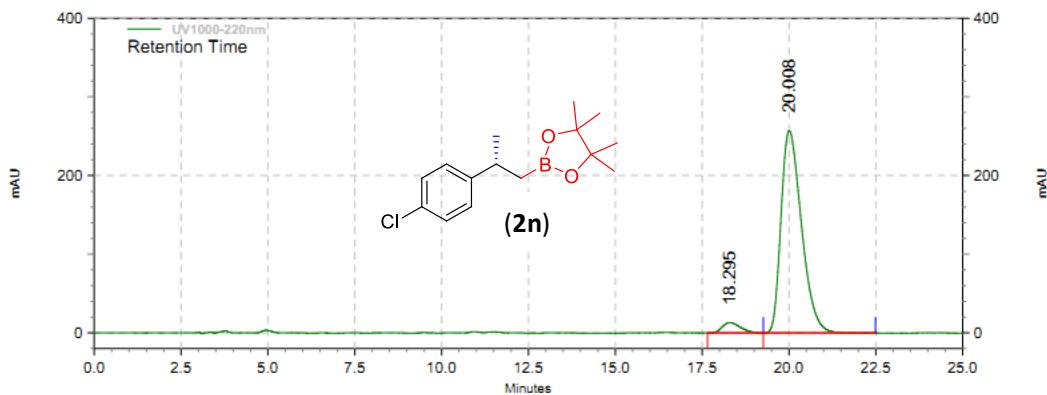
Retention Time	Area	Area %	Height	Height %
23.037	896676	97.05	40220	96.83
24.140	27243	2.95	1318	3.17
Totals	923919	100.00	41538	100.00



UV1000-220nm

Results

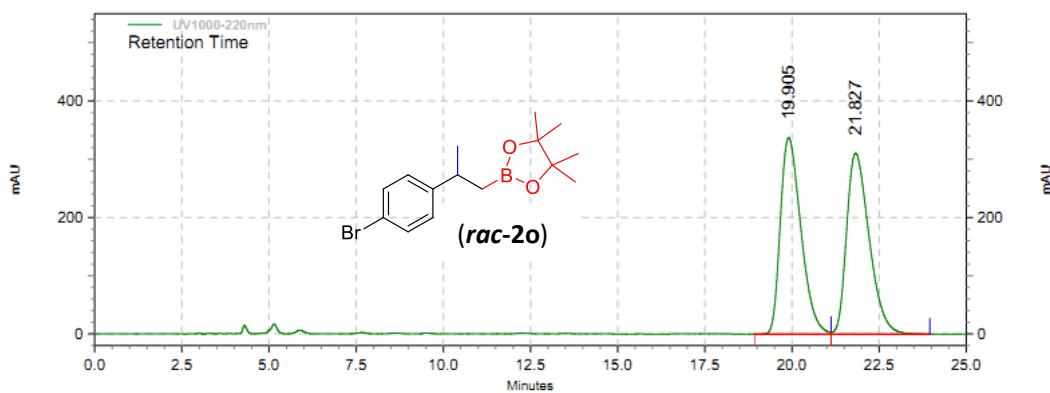
Retention Time	Area	Area %	Height	Height %
18.283	46669024	49.69	1227262	52.47
19.967	47250751	50.31	1111605	47.53
<hr/>				
Totals	93919775	100.00	2338867	100.00



UV1000-220nm

Results

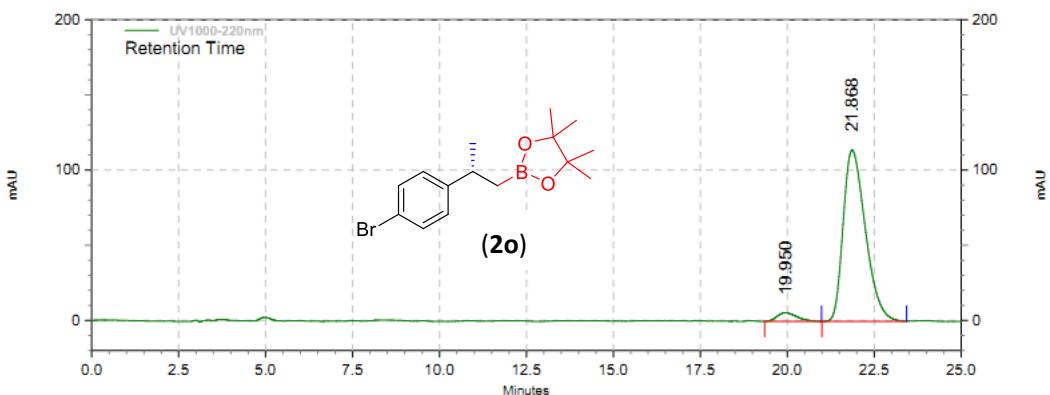
Retention Time	Area	Area %	Height	Height %
18.295	481334	4.36	13136	4.86
20.008	10557360	95.64	257290	95.14
<hr/>				
Totals	11038694	100.00	270426	100.00

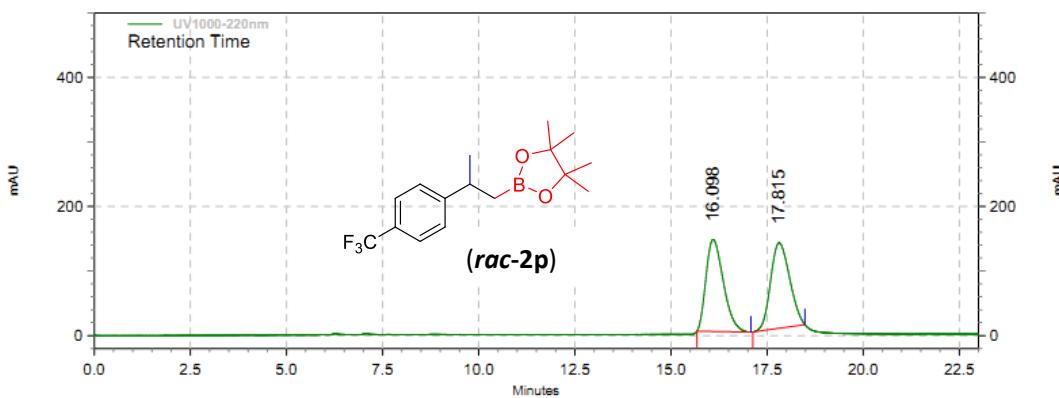


UV1000-220nm

Results

Retention Time	Area	Area %	Height	Height %
19.905	13820832	49.69	337284	52.03
21.827	13993144	50.31	310953	47.97
Totals	27813976	100.00	648237	100.00

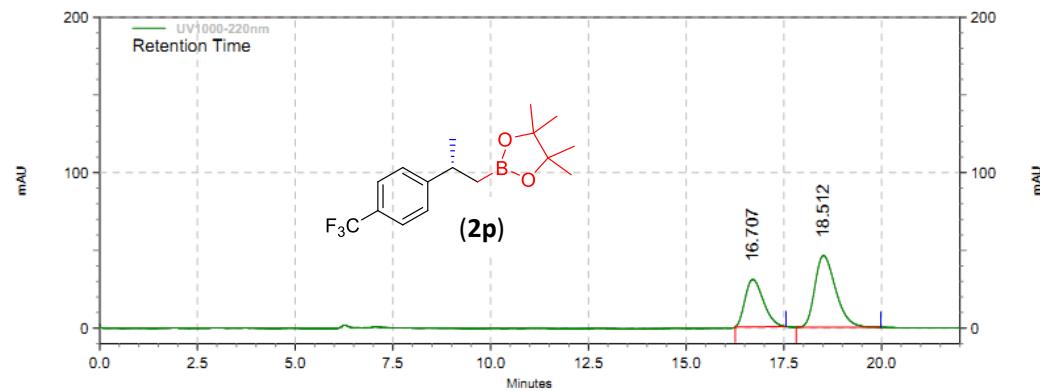




UV1000-220nm

Results

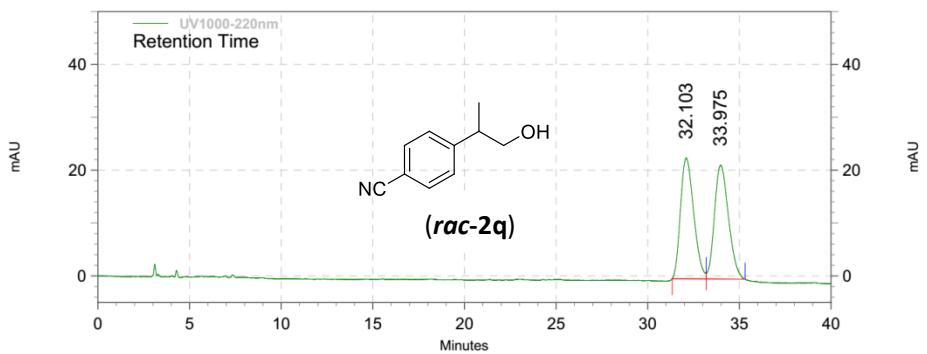
Retention Time	Area	Area %	Height	Height %
16.098	4494000	49.66	142485	51.84
17.815	4555343	50.34	132392	48.16
Totals	9049343	100.00	274877	100.00



UV1000-220nm

Results

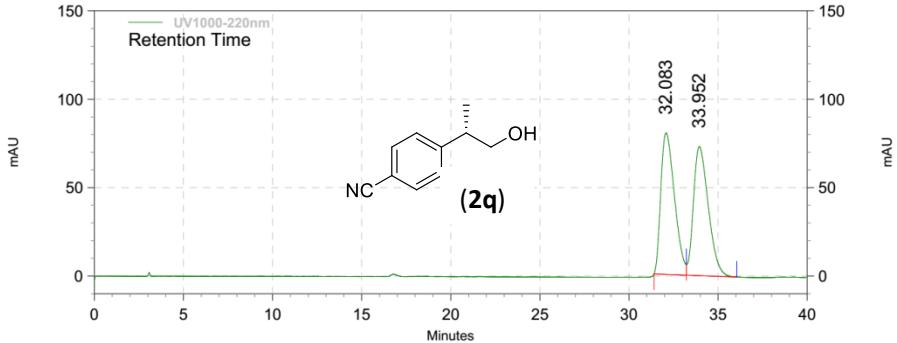
Retention Time	Area	Area %	Height	Height %
16.707	993747	36.77	30516	39.78
18.512	1708571	63.23	46198	60.22
Totals	2702318	100.00	76714	100.00



UV1000-220nm

Results

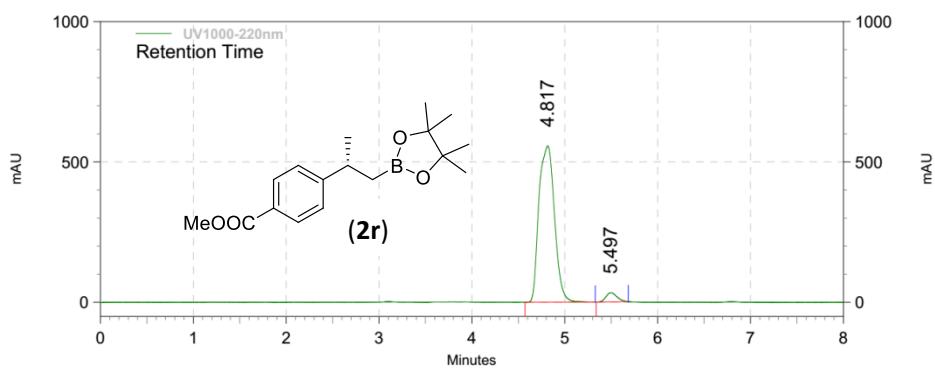
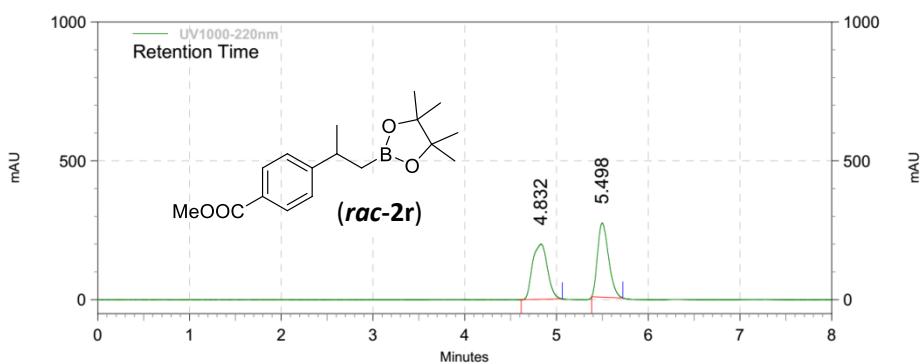
Retention Time	Area	Area %	Height	Height %
32.103	1143488	49.96	22837	51.48
33.975	1145441	50.04	21527	48.52
Totals	2288929	100.00	44364	100.00

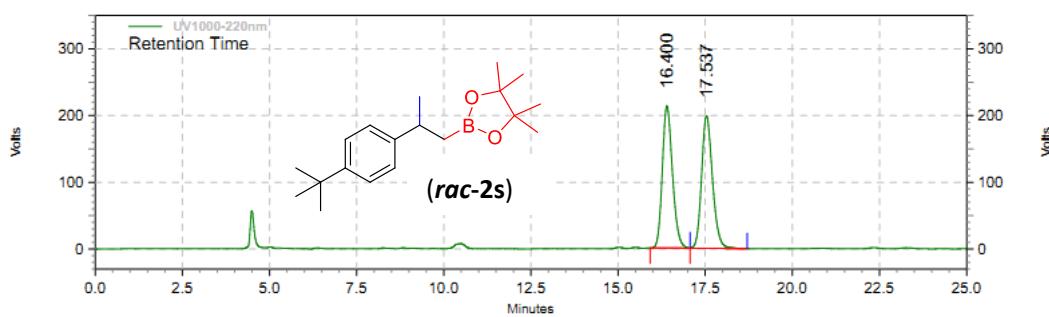


UV1000-220nm

Results

Retention Time	Area	Area %	Height	Height %
32.083	4265891	50.12	79992	52.29
33.952	4245668	49.88	72978	47.71
Totals	8511559	100.00	152970	100.00

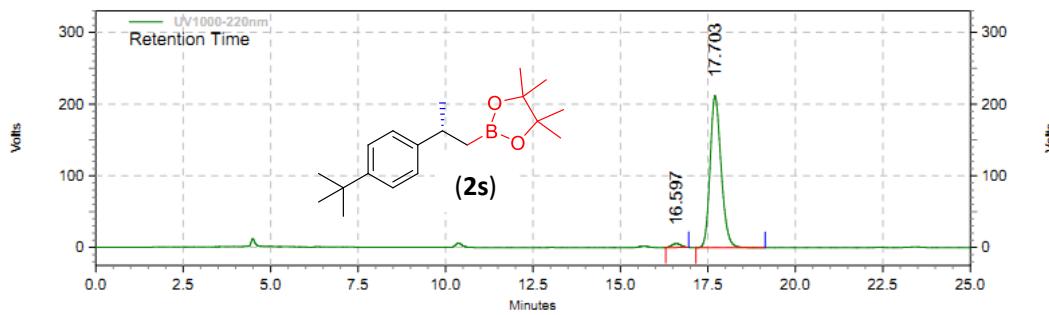




UV1000-220nm

Results

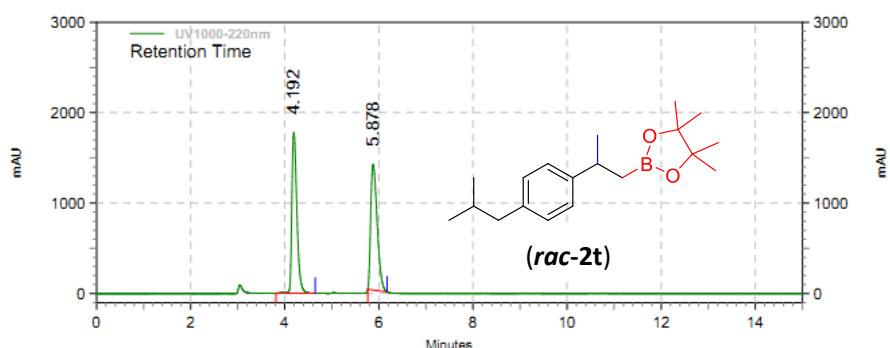
Retention Time	Area	Area %	Height	Height %
16.400	4307064	49.79	213181	51.72
17.537	4343597	50.21	199012	48.28
Totals	8650661	100.00	412193	100.00



UV1000-220nm

Results

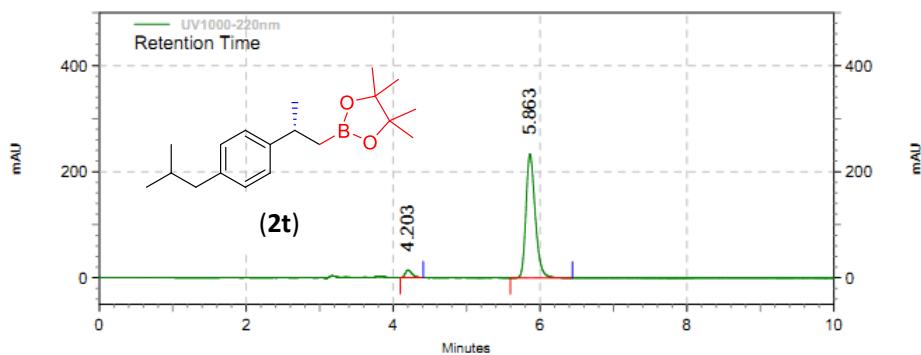
Retention Time	Area	Area %	Height	Height %
16.597	99245	2.08	5432	2.50
17.703	4664860	97.92	211975	97.50
Totals	4764105	100.00	217407	100.00



UV1000-220nm

Results

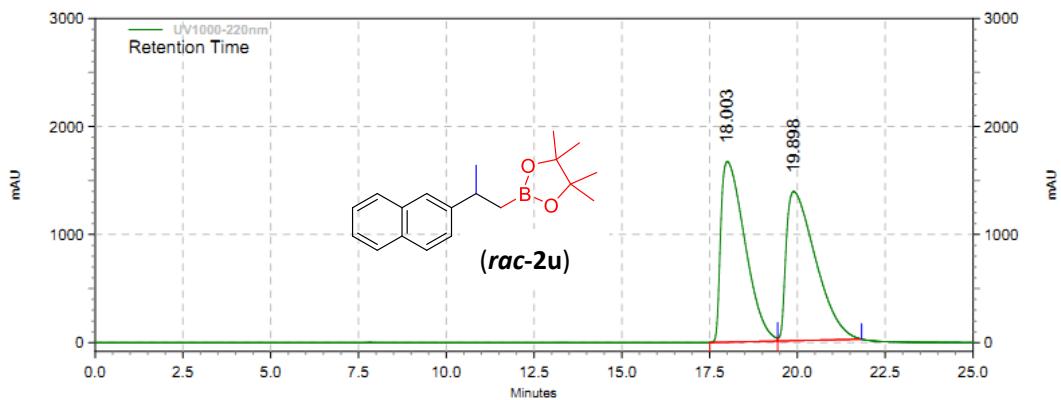
Retention Time	Area	Area %	Height	Height %
4.192	13175467	49.92	1777894	56.10
5.878	13215887	50.08	1391167	43.90
Totals	26391354	100.00	3169061	100.00



UV1000-220nm

Results

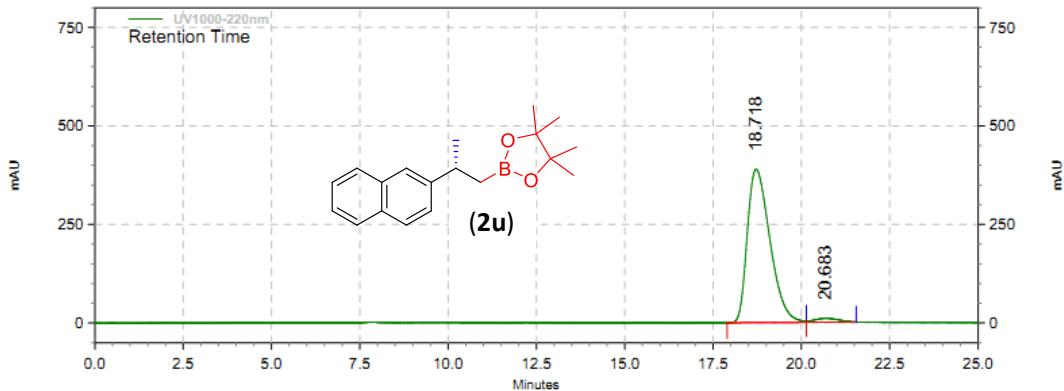
Retention Time	Area	Area %	Height	Height %
4.203	92205	4.32	14295	5.77
5.863	2041705	95.68	233459	94.23
Totals	2133910	100.00	247754	100.00



UV1000-220nm

Results

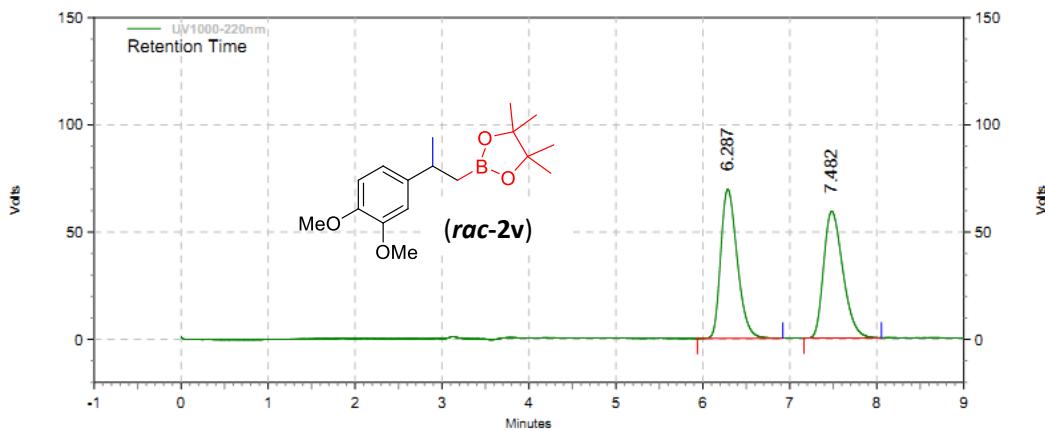
Retention Time	Area	Area %	Height	Height %
18.003	79965494	49.83	1670678	54.76
19.898	80520172	50.17	1380142	45.24
Totals	160485666	100.00	3050820	100.00



UV1000-220nm

Results

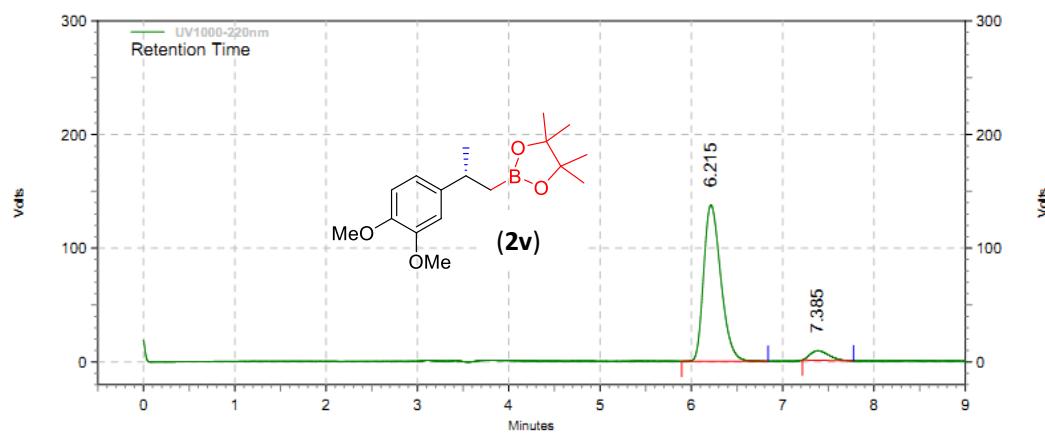
Retention Time	Area	Area %	Height	Height %
18.718	17335309	97.45	389107	97.59
20.683	452827	2.55	9629	2.41
Totals	17788136	100.00	398736	100.00



UV1000-220nm

Results

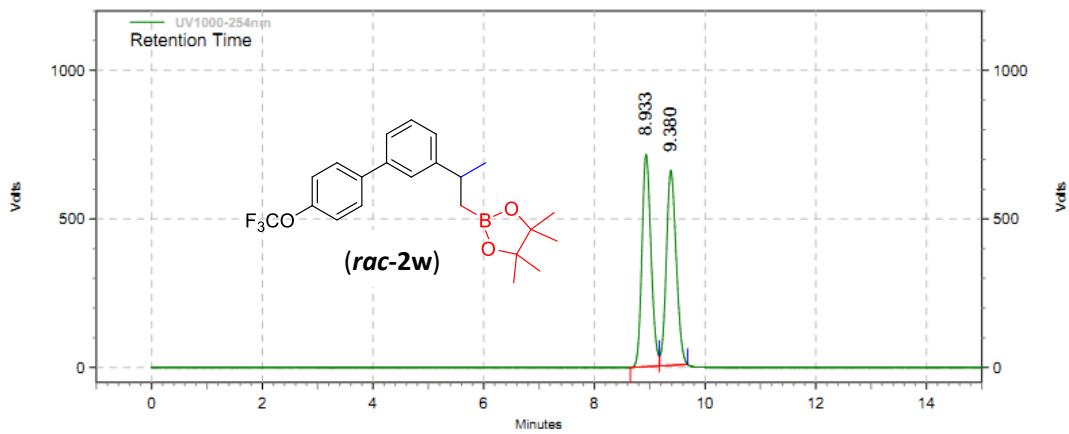
Retention Time	Area	Area %	Height	Height %
6.287	918831	50.27	69491	54.04
7.482	908836	49.73	59112	45.96
Totals	1827667	100.00	128603	100.00



UV1000-220nm

Results

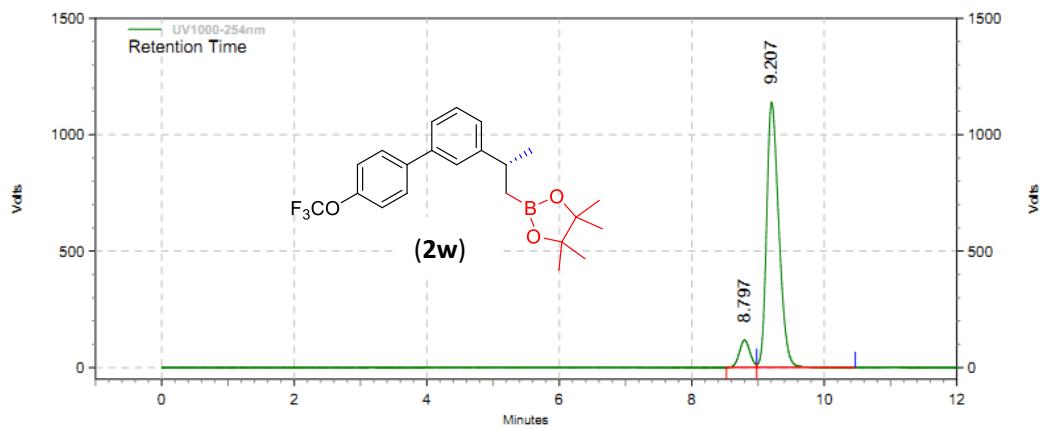
Retention Time	Area	Area %	Height	Height %
6.215	1793684	93.76	137576	94.25
7.385	119373	6.24	8393	5.75
Totals	1913057	100.00	145969	100.00



UV1000-254nm

Results

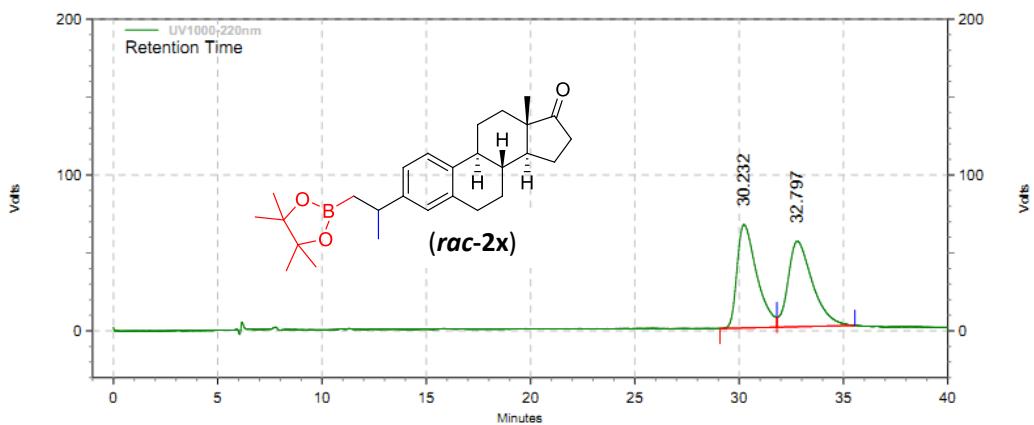
Retention Time	Area	Area %	Height	Height %
8.933	8137736	49.98	713445	52.15
9.380	8143242	50.02	654553	47.85
Totals	16280978	100.00	1367998	100.00



UV1000-254nm

Results

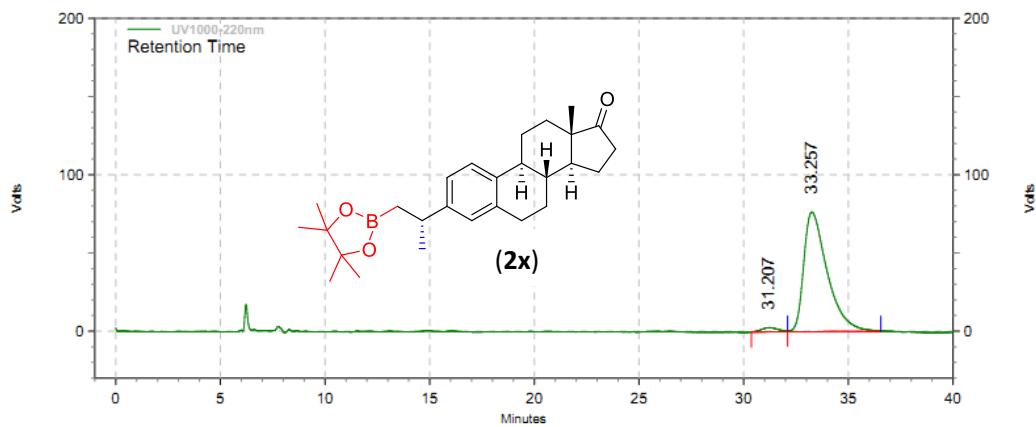
Retention Time	Area	Area %	Height	Height %
8.797	1313131	8.26	117261	9.34
9.207	14581061	91.74	1138655	90.66
Totals	15894192	100.00	1255916	100.00



UV1000-220nm

Results

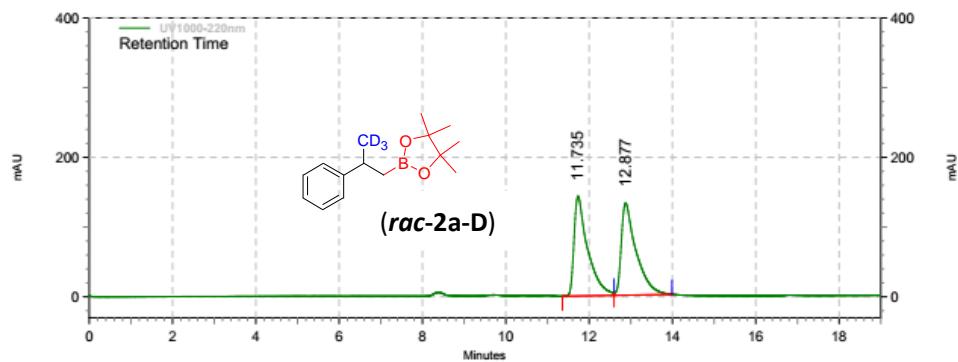
Retention Time	Area	Area %	Height	Height %
30.232	4369288	49.45	66250	54.70
32.797	4467271	50.55	54861	45.30
Totals	8836559	100.00	121111	100.00



UV1000-220nm

Results

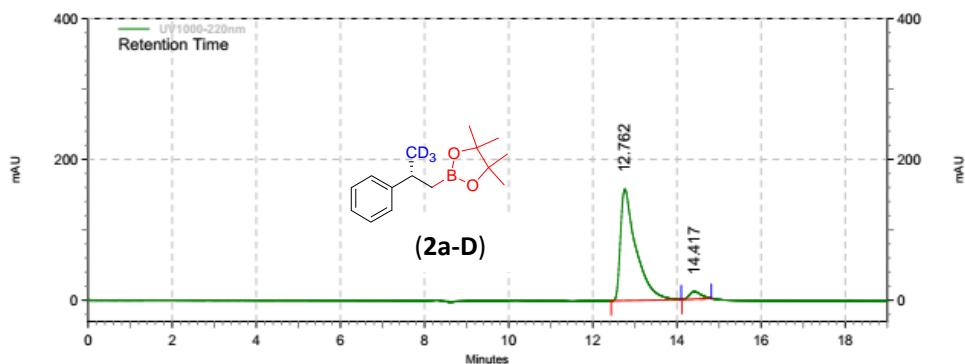
Retention Time	Area	Area %	Height	Height %
31.207	152135	2.49	2769	3.49
33.257	5967384	97.51	76524	96.51
Totals	6119519	100.00	79293	100.00



UV1000-220nm

Results

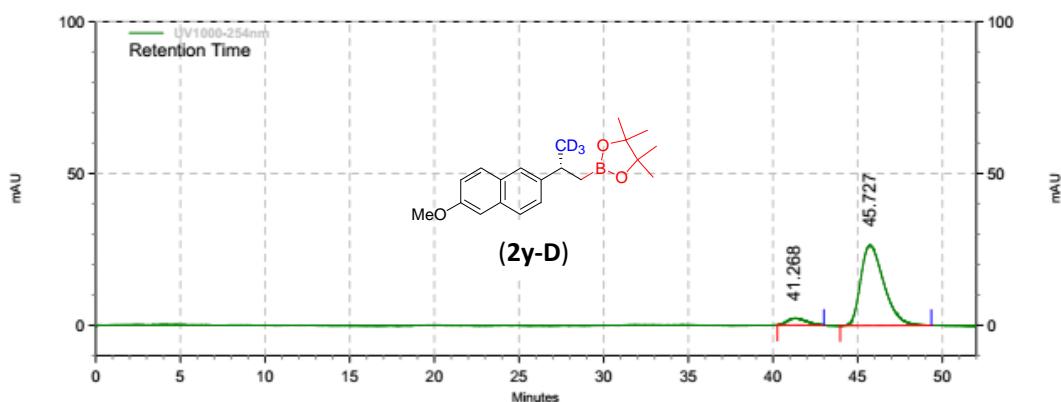
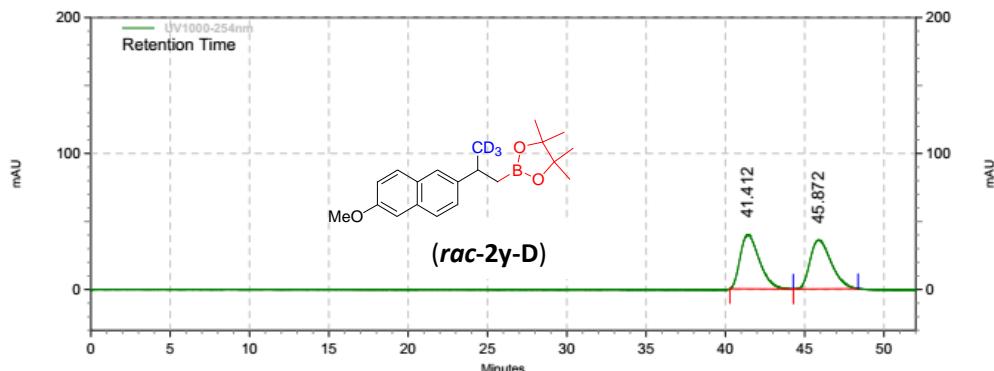
Retention Time	Area	Area %	Height	Height %
11.735	3256694	49.92	143190	52.05
12.877	3267661	50.08	131933	47.95
Totals	6524355	100.00	275123	100.00

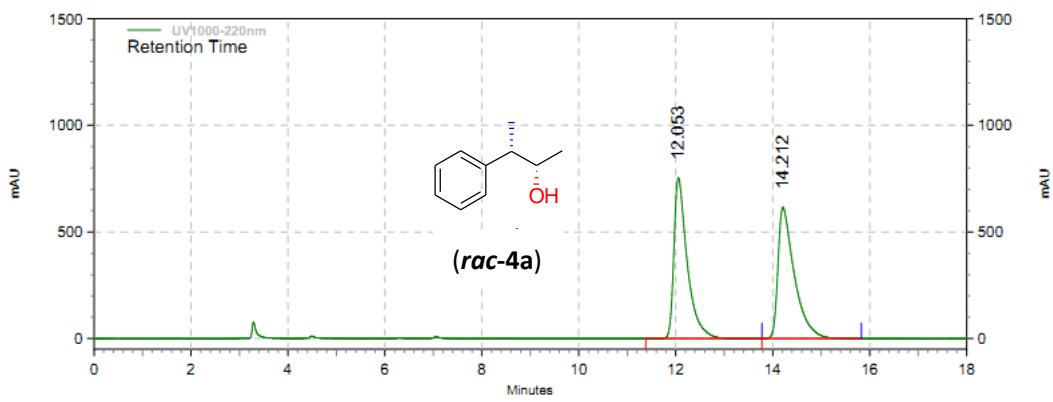


UV1000-220nm

Results

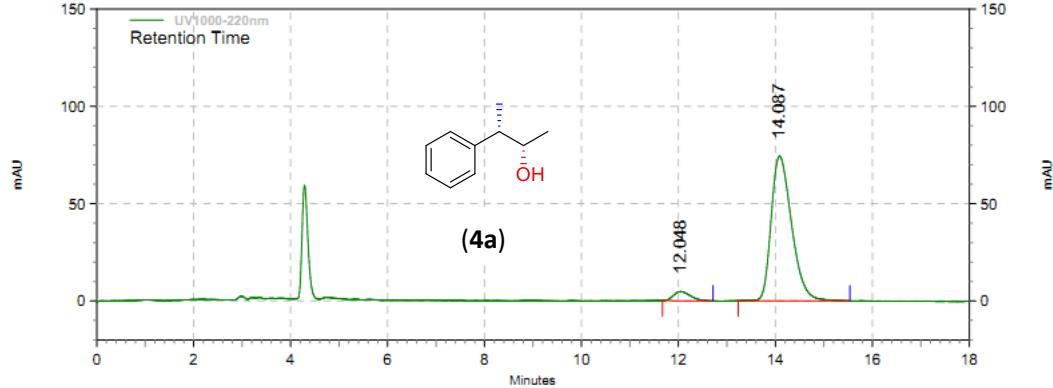
Retention Time	Area	Area %	Height	Height %
12.762	4057592	95.32	158126	93.74
14.417	199331	4.68	10563	6.26
Totals	4256923	100.00	168689	100.00





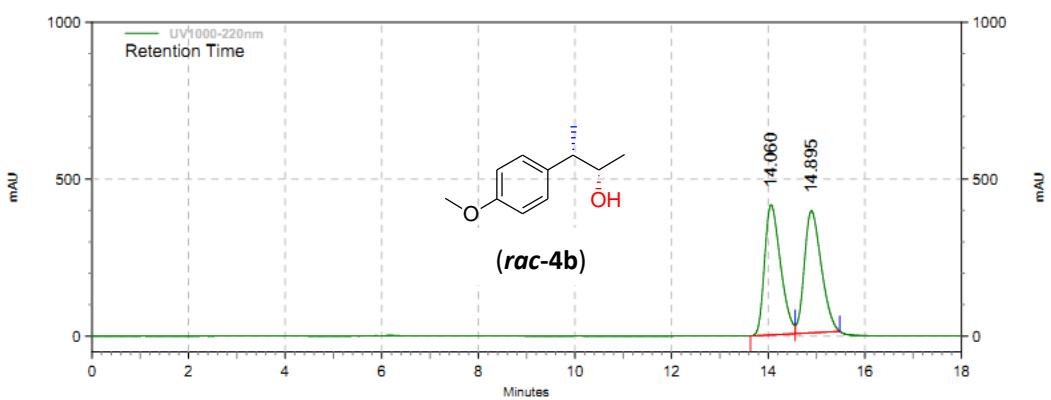
UV1000-220nm
Results

Retention Time	Area	Area %	Height	Height %
12.053	14452208	50.01	754183	55.06
14.212	14448952	49.99	615599	44.94
Totals	28901160	100.00	1369782	100.00



UV1000-220nm
Results

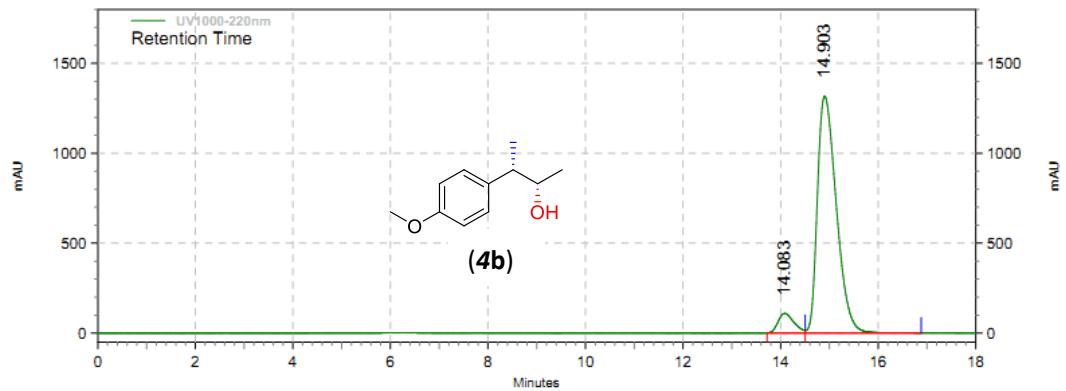
Retention Time	Area	Area %	Height	Height %
12.048	115137	5.01	4742	5.99
14.087	2184005	94.99	74362	94.01
Totals	2299142	100.00	79104	100.00



UV1000-220nm

Results

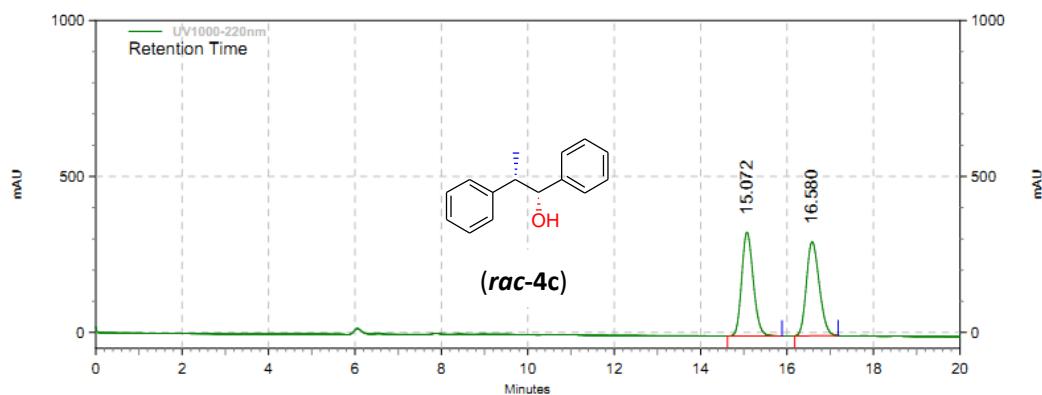
Retention Time	Area	Area %	Height	Height %
14.060	9519757	50.06	414393	51.57
14.895	9498811	49.94	389085	48.43
Totals	19018568	100.00	803478	100.00



UV1000-220nm

Results

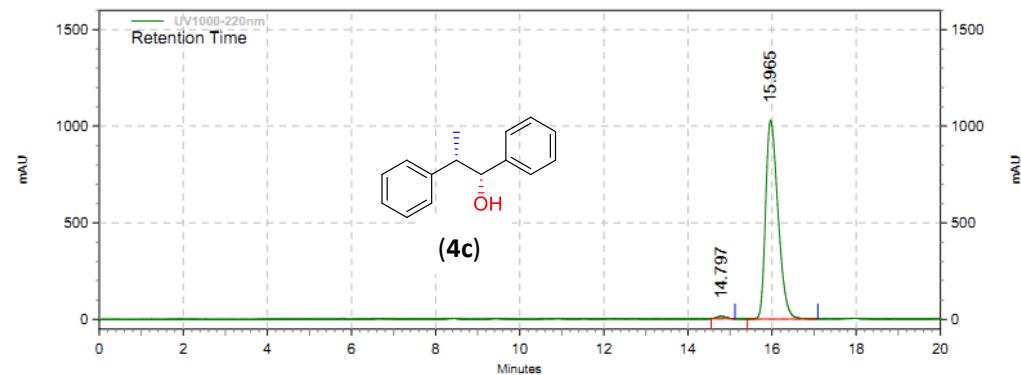
Retention Time	Area	Area %	Height	Height %
14.083	2462807	6.49	108677	7.62
14.903	35467423	93.51	1318163	92.38
Totals	37930230	100.00	1426840	100.00



UV1000-220nm

Results

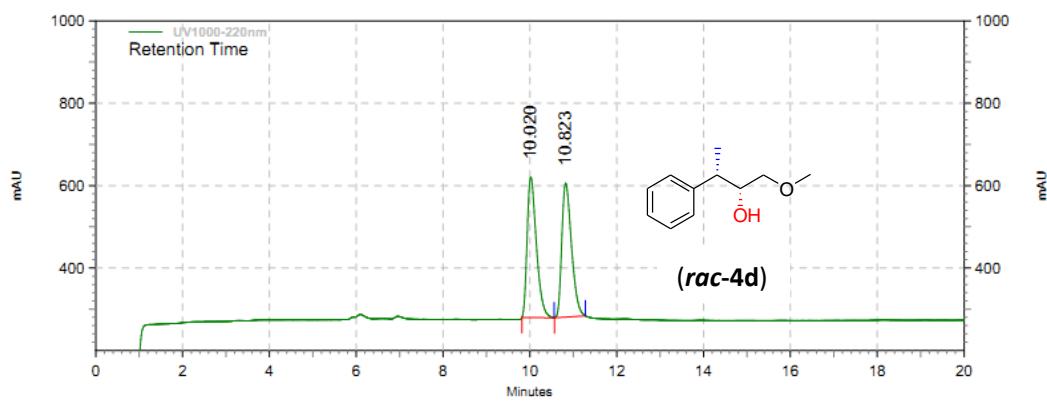
Retention Time	Area	Area %	Height	Height %
15.072	6191568	49.82	332512	52.43
16.580	6236920	50.18	301727	47.57
Totals	12428488	100.00	634239	100.00



UV1000-220nm

Results

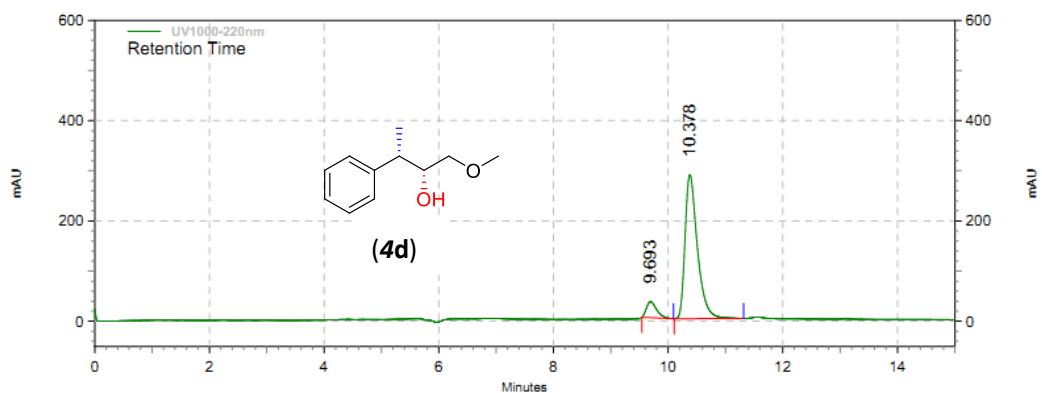
Retention Time	Area	Area %	Height	Height %
14.797	212870	1.00	13155	1.26
15.965	21080327	99.00	1027894	98.74
Totals	21293197	100.00	1041049	100.00



UV1000-220nm

Results

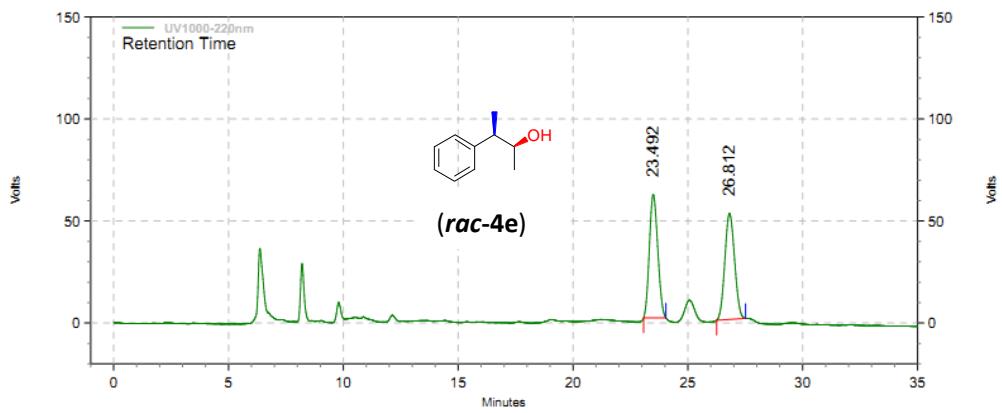
Retention Time	Area	Area %	Height	Height %
10.020	5046521	50.05	341314	51.21
10.823	5035656	49.95	325140	48.79
Totals	10082177	100.00	666454	100.00



UV1000-220nm

Results

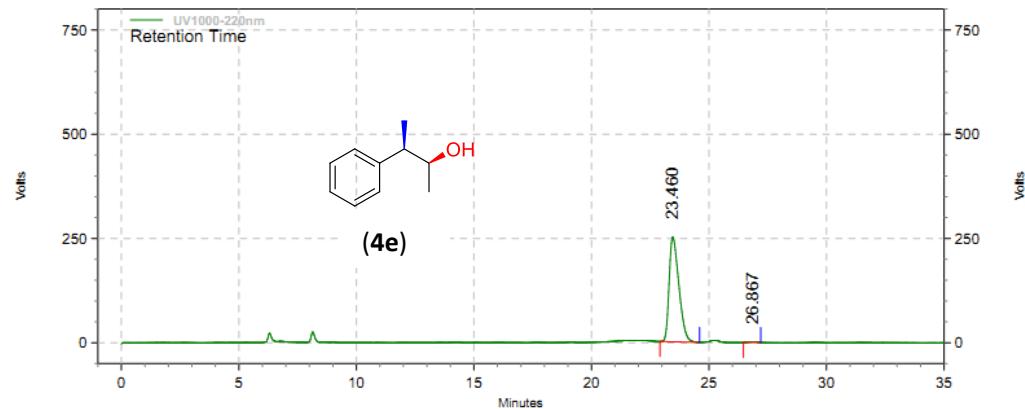
Retention Time	Area	Area %	Height	Height %
9.693	393449	8.40	31816	9.98
10.378	4291315	91.60	287045	90.02
Totals	4684764	100.00	318861	100.00

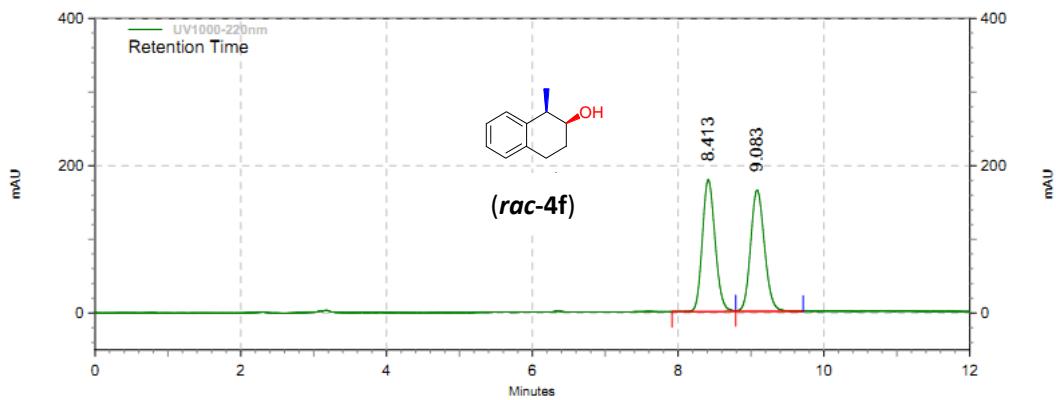


UV1000-220nm

Results

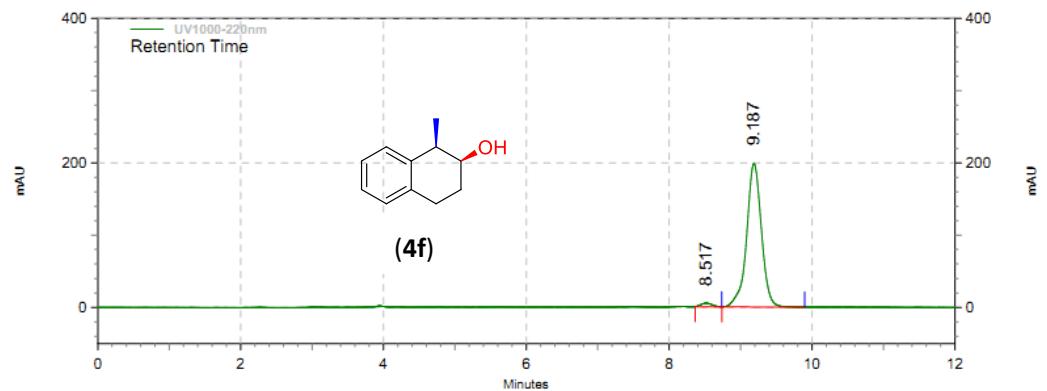
Retention Time	Area	Area %	Height	Height %
23.492	1535228	50.15	60468	53.78
26.812	1525743	49.85	51965	46.22
Totals	3060971	100.00	112433	100.00





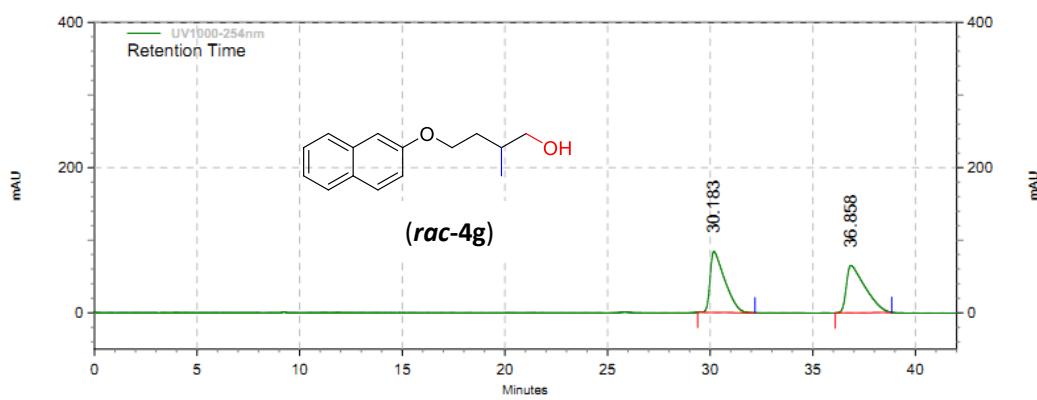
UV1000-220nm Results

Retention Time	Area	Area %	Height	Height %
8.413	2179208	49.91	178920	52.03
9.083	2186990	50.09	164933	47.97
Totals	4366198	100.00	343853	100.00



UV1000-220nm Results

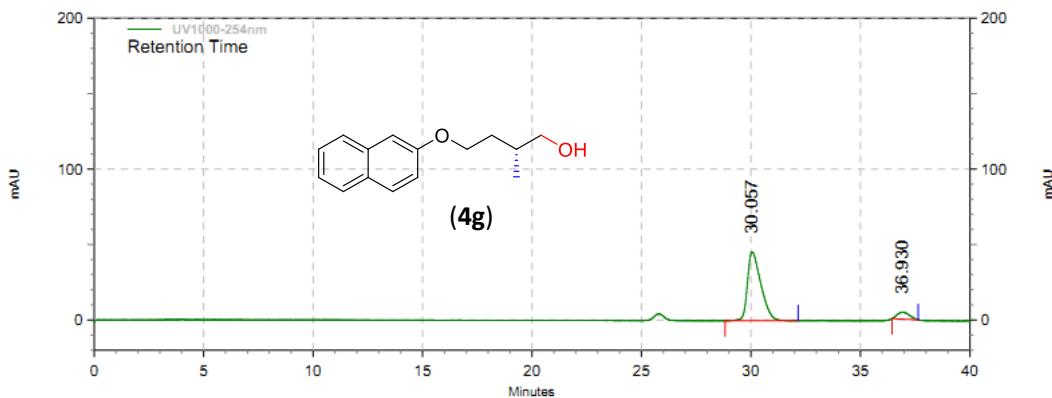
Retention Time	Area	Area %	Height	Height %
8.517	52315	1.80	4904	2.41
9.187	2858486	98.20	198397	97.59
Totals	2910801	100.00	203301	100.00

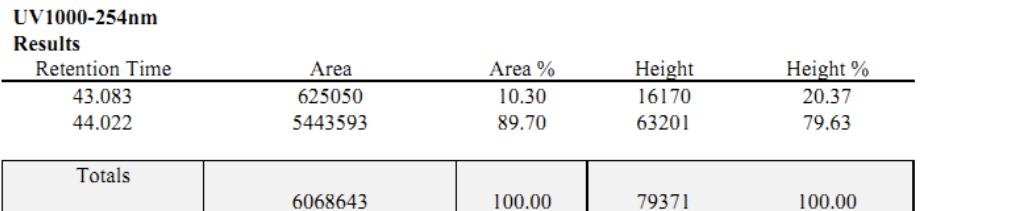
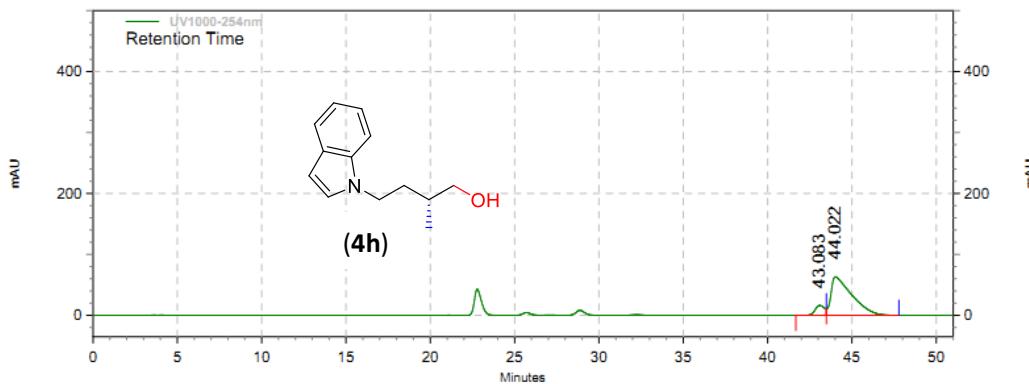
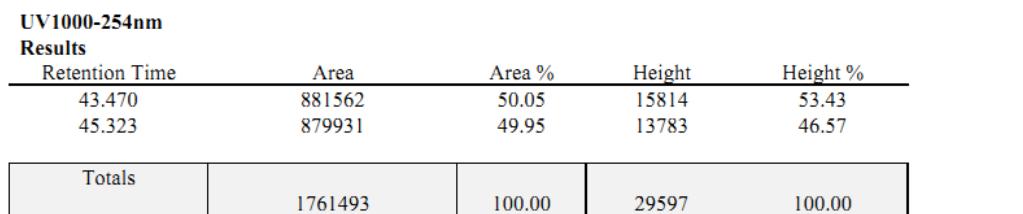
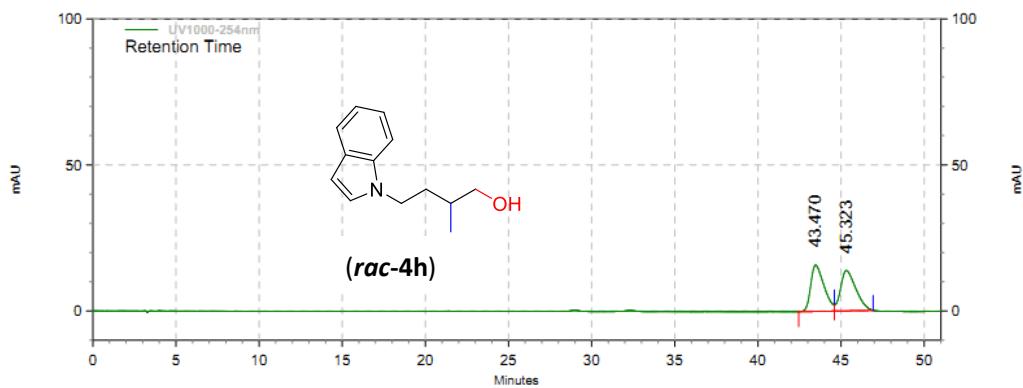


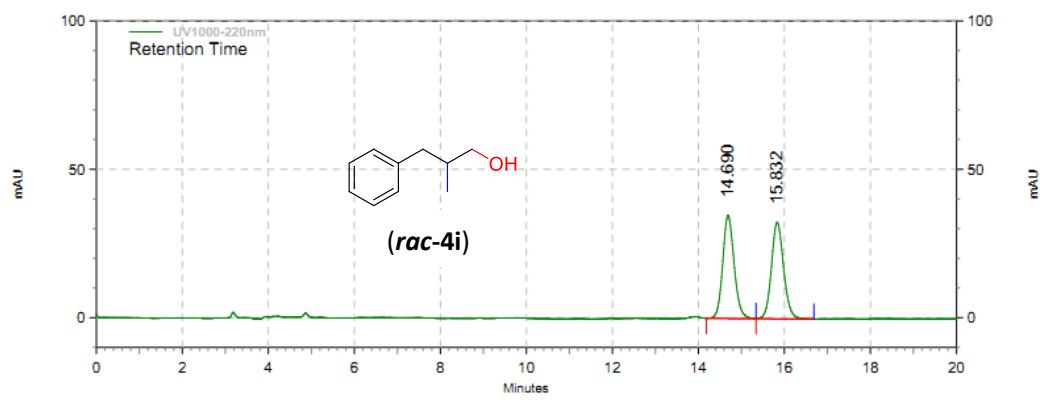
UV1000-254nm

Results

Retention Time	Area	Area %	Height	Height %
30.183	4176599	50.15	83959	56.26
36.858	4151475	49.85	65277	43.74
Totals	8328074	100.00	149236	100.00



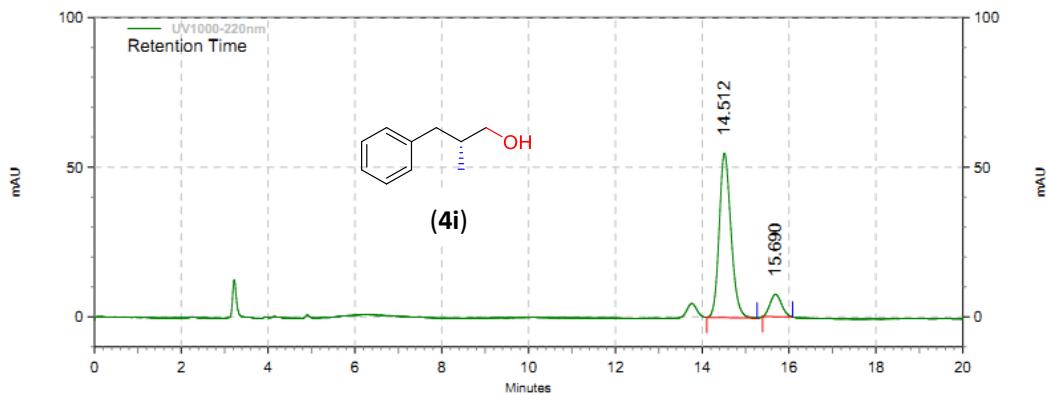




UV1000-220nm

Results

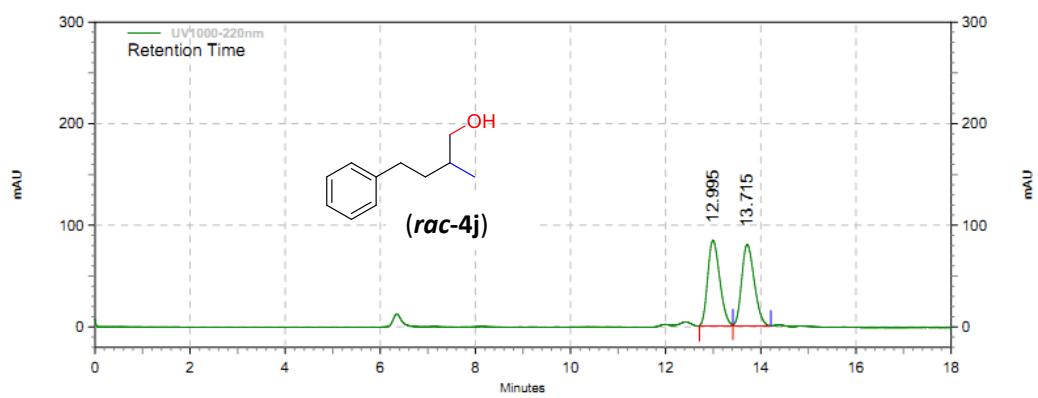
Retention Time	Area	Area %	Height	Height %
14.690	640077	49.95	34781	51.66
15.832	641377	50.05	32541	48.34
Totals	1281454	100.00	67322	100.00



UV1000-220nm

Results

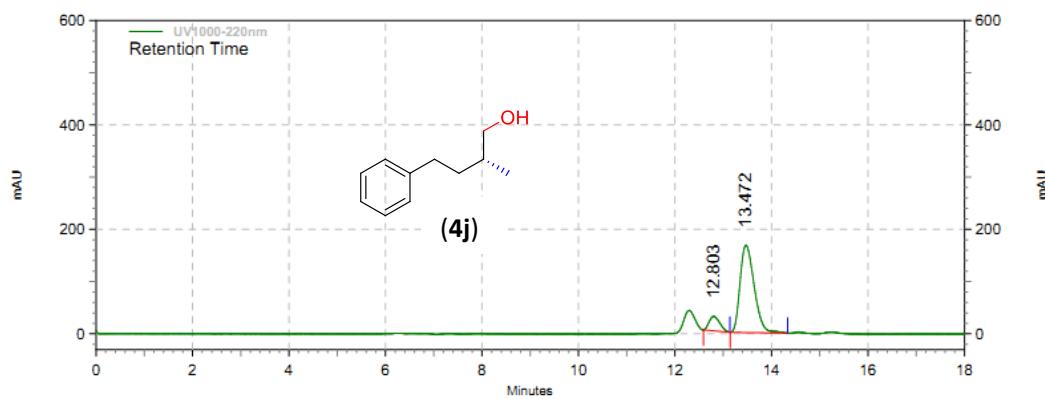
Retention Time	Area	Area %	Height	Height %
14.512	1035401	88.19	54979	87.98
15.690	138709	11.81	7511	12.02
Totals	1174110	100.00	62490	100.00



UV1000-220nm

Results

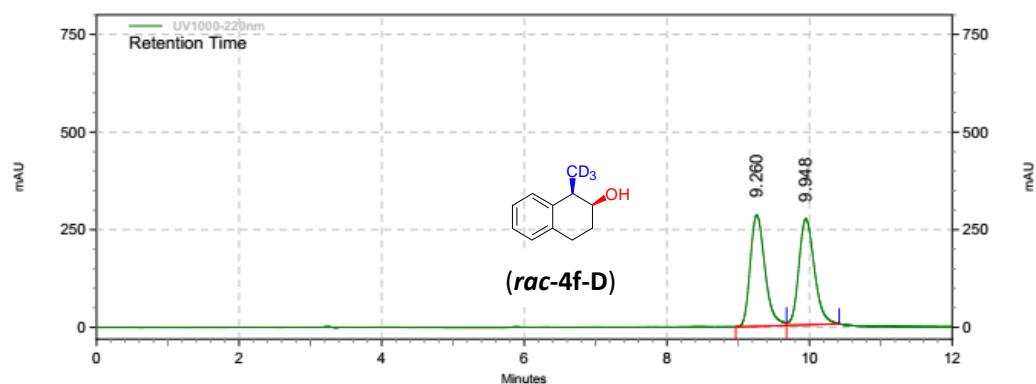
Retention Time	Area	Area %	Height	Height %
12.995	1476038	50.12	84210	51.24
13.715	1469121	49.88	80146	48.76
Totals	2945159	100.00	164356	100.00



UV1000-220nm

Results

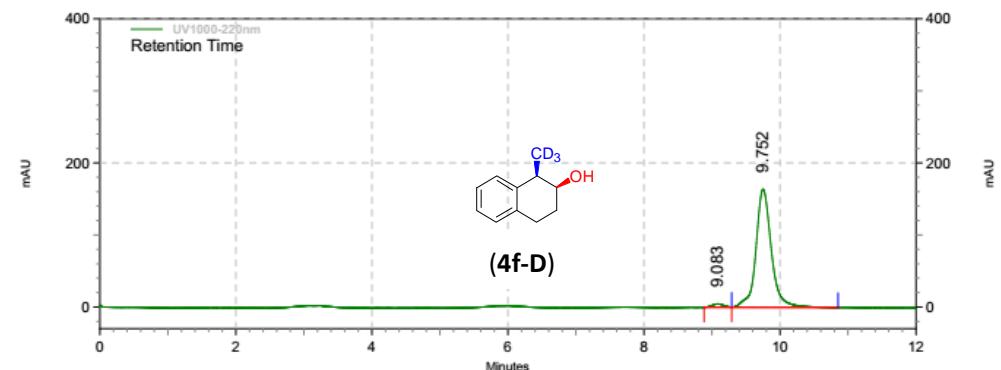
Retention Time	Area	Area %	Height	Height %
12.803	427186	11.16	27781	14.24
13.472	3399415	88.84	167289	85.76
Totals	3826601	100.00	195070	100.00



UV1000-220nm

Results

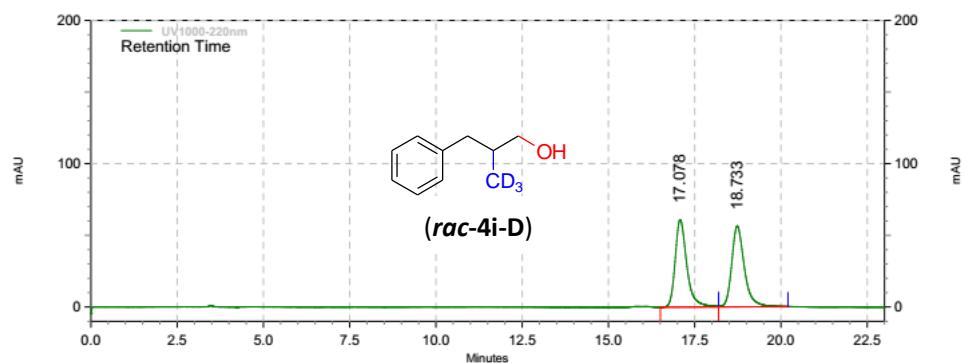
Retention Time	Area	Area %	Height	Height %
9.260	4094735	49.90	285369	51.29
9.948	4111902	50.10	271043	48.71
Totals	8206637	100.00	556412	100.00



UV1000-220nm

Results

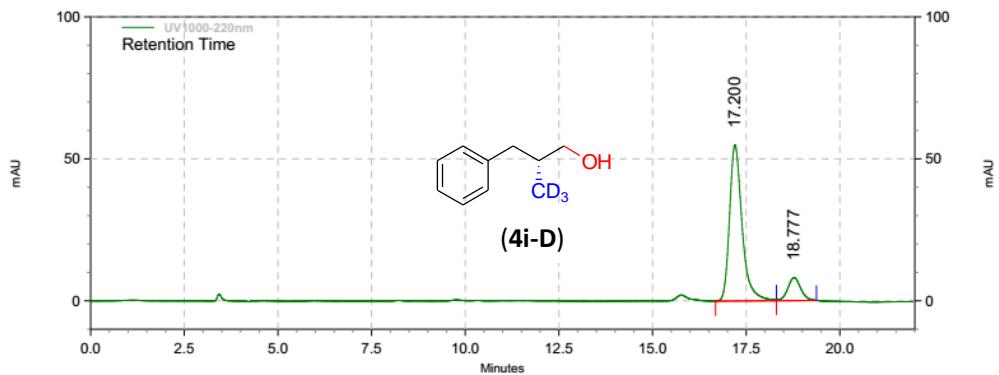
Retention Time	Area	Area %	Height	Height %
9.083	56549	2.14	4736	2.81
9.752	2584084	97.86	163986	97.19
Totals	2640633	100.00	168722	100.00



UV1000-220nm

Results

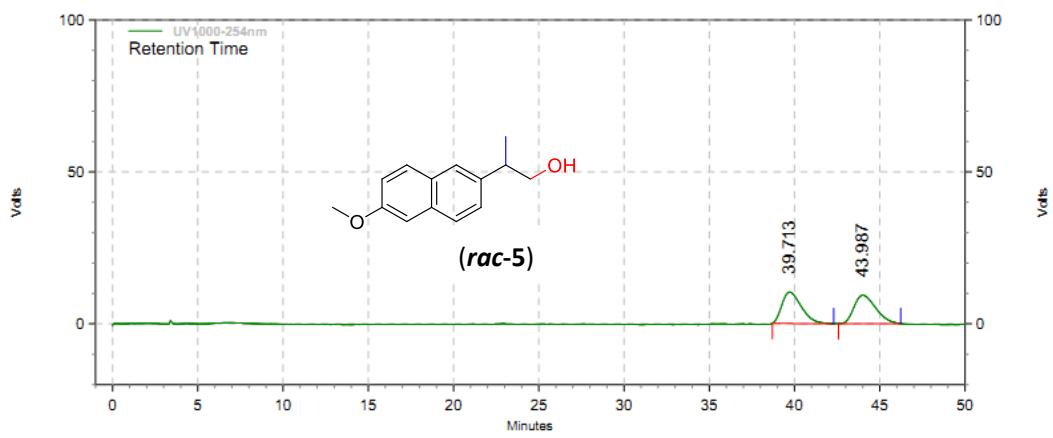
Retention Time	Area	Area %	Height	Height %
17.078	1436981	49.93	61135	52.01
18.733	1440886	50.07	56407	47.99
Totals	2877867	100.00	117542	100.00



UV1000-220nm

Results

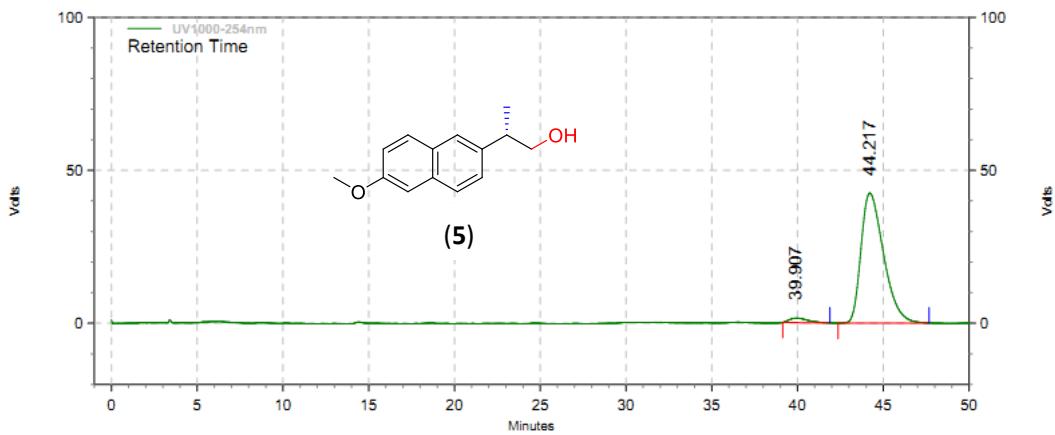
Retention Time	Area	Area %	Height	Height %
17.200	1284779	86.91	55037	87.17
18.777	193548	13.09	8098	12.83
Totals	1478327	100.00	63135	100.00



UV1000-254nm

Results

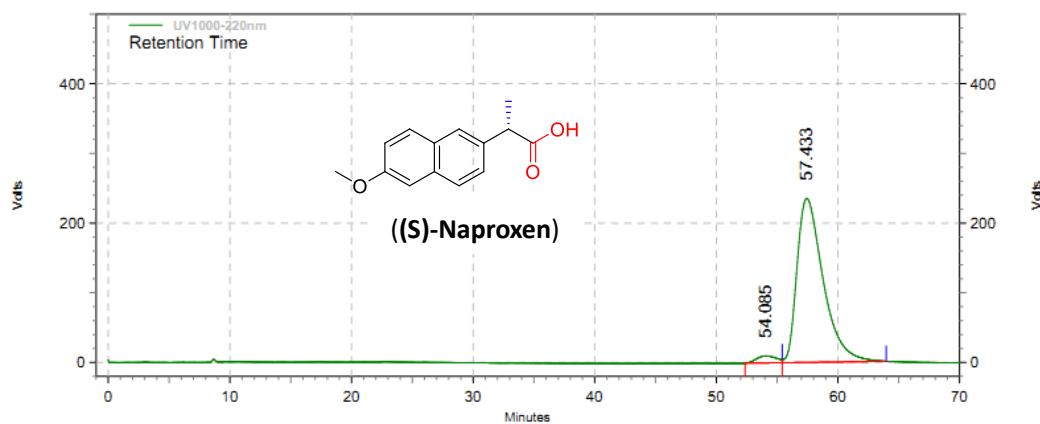
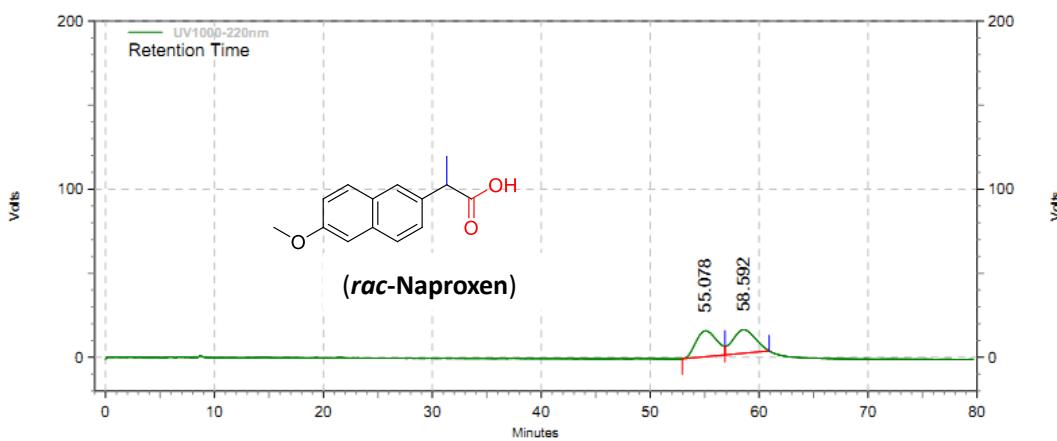
Results	Retention Time	Area	Area %	Height	Height %
	39.713	822679	49.82	10342	52.51
	43.987	828576	50.18	9354	47.49
	Totals	1651255	100.00	19696	100.00

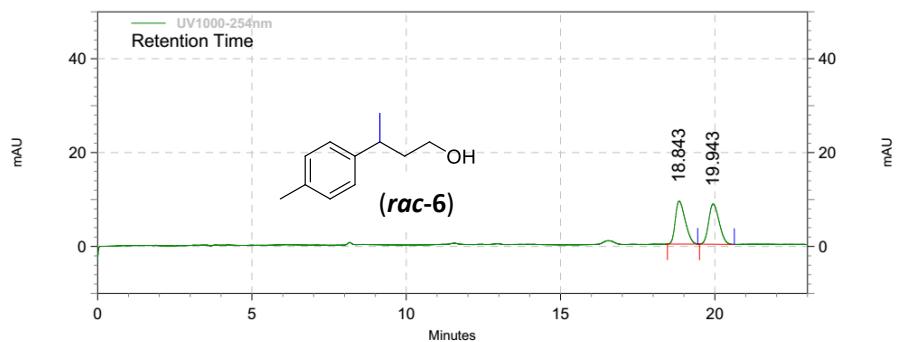


UV1000-254nm

Results

Retention Time	Area	Area %	Height	Height %
39.907	109835	2.75	1449	3.30
44.217	3888296	97.25	42524	96.70
Totals	3998131	100.00	43973	100.00



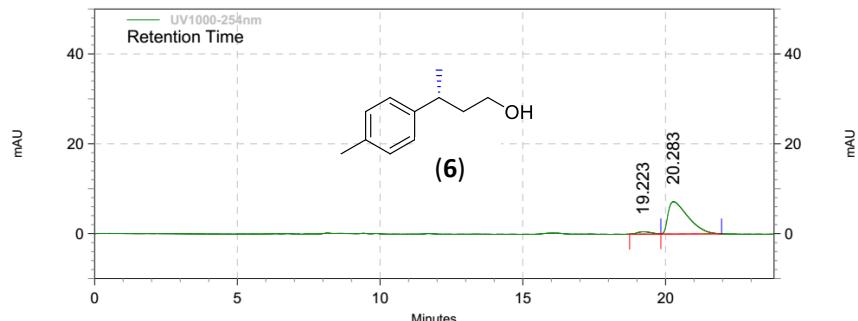


UV1000-254nm

Results

Retention Time	Area	Area %	Height	Height %
18.843	203212	50.01	9180	51.63
19.943	203092	49.99	8600	48.37

Totals	406304	100.00	17780	100.00
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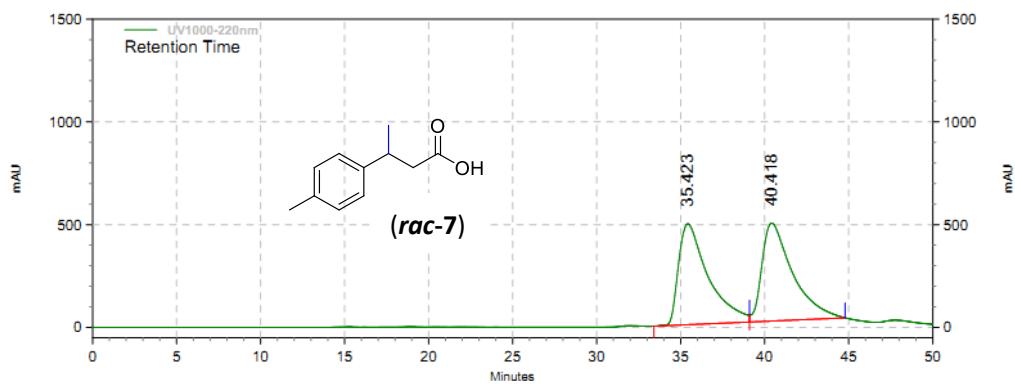


UV1000-254nm

Results

Retention Time	Area	Area %	Height	Height %
19.223	17946	4.88	529	6.85
20.283	349873	95.12	7196	93.15

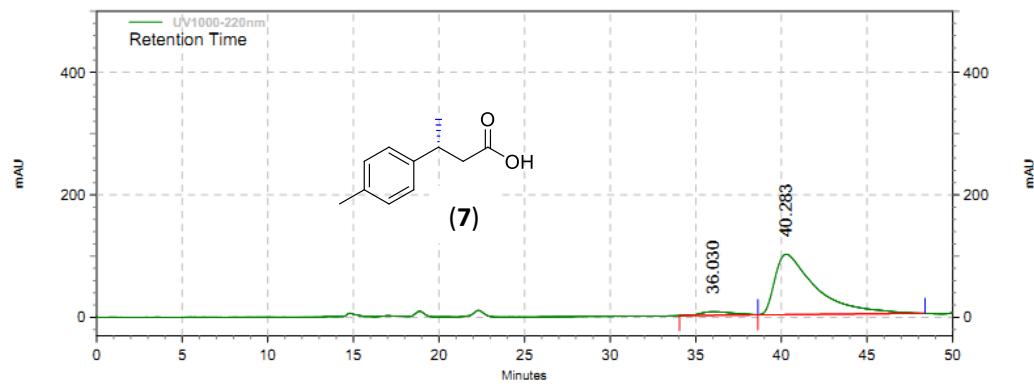
Totals	367819	100.00	7725	100.00
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UV1000-220nm

Results

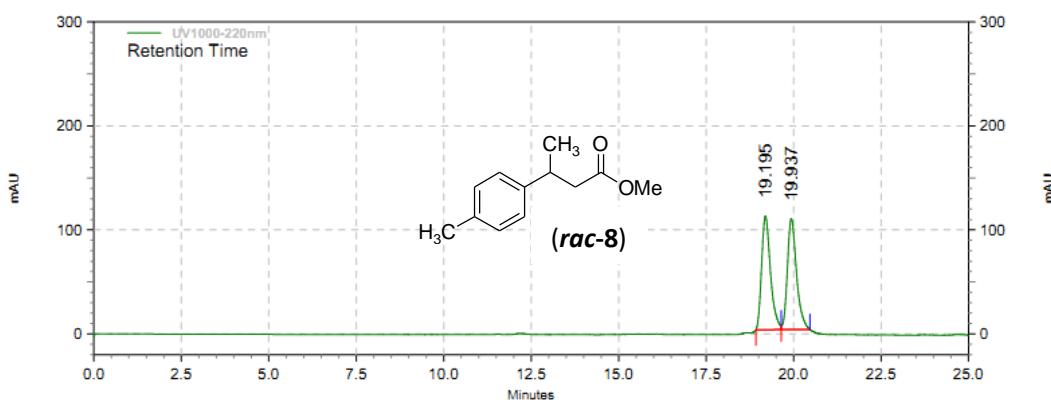
Retention Time	Area	Area %	Height	Height %
35.423	60291281	49.86	490744	50.73
40.418	60630393	50.14	476557	49.27
Totals	120921674	100.00	967301	100.00



UV1000-220nm

Results

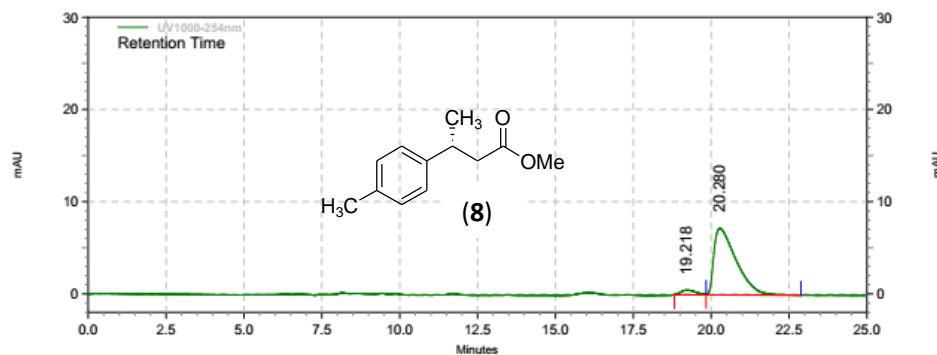
Retention Time	Area	Area %	Height	Height %
36.030	757884	4.43	5773	5.54
40.283	16339049	95.57	98471	94.46
Totals	17096933	100.00	104244	100.00



UV1000-220nm

Results

Retention Time	Area	Area %	Height	Height %
19.195	1924987	49.72	109216	50.58
19.937	1946508	50.28	106714	49.42
Totals	3871495	100.00	215930	100.00



UV1000-254nm

Results

Retention Time	Area	Area %	Height	Height %
19.218	17033	4.56	512	6.63
20.280	356734	95.44	7216	93.37
Totals	373767	100.00	7728	100.00